UNIVERSITÀ DEGLI STUDI DI PARMA

Dottorato di ricerca in Scienze Chimiche

Ciclo XXVII (2012–2014)

Palladium/norbornene catalysis for selective aromatic functionalization via C–H activation

Coordinatore:

Chiar.mo Prof. Roberto Cammi

Tutor:

Chiar.ma Prof. Marta Catellani

Dottorando:

Marco Fontana

2015

Abstract

The subject of this PhD thesis is the study of new processes in homogeneous catalysis for the synthesis of selectively substituted compounds containing the biaryl unit. The methodology, discovered in our laboratory, utilizes simple and readily available starting materials to form complex molecular structures under mild conditions. It takes advantage of the catalytic system based on palladium and norbornene. The metal, the strained olefin and an aryl halide work in a cooperative way to build up an arylnorbornylmetallacycle through C–H activation.

This key intermediate is able to drive selective transformations on either the aryl or the norbornyl side of the palladacycle. A biaryl unit can be formed by oxidative addition of a second aryl halide on the palladacycle and subsequent Csp^2–Csp^2 coupling by reductive elimination. The removal of norbornene from the organometallic complex affords a biarylpalladium species. which can close the catalytic cycle in several ways, each leading to different synthetic pathways. In the course of my PhD work various termination steps have been studied. Intermolecular couplings have been obtained by C–heteroatom reductive elimination and condensed cyclic structures have been achieved by nucleophilic attack of the biarylpalladium intermediate to a carbonyl group present in the same biaryl fragment. Moreover, a different type of reactivity, that leads to the functionalization of the norbornyl side of the palladacycle with retention of the norbornyl moiety in the final organic product, has been studied. A straightforward and general methodology has thus been developed for the synthesis of dibenzoazepine derivatives.

In all cases, target compounds can be of interest for the fine chemicals and pharmaceutical industry.

Contents

List of Figures

List of Schemes

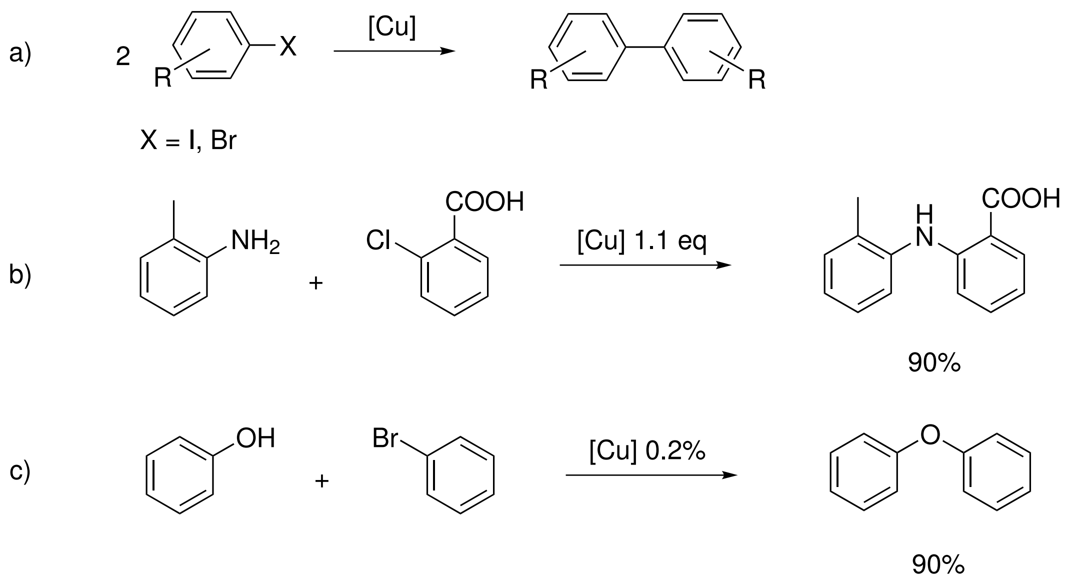
List of Tables

Chapter 1

Carbon-halogen bond formation by transition metal catalysis

1.1 Ullmann coupling and the role of organic halides in organometallic chemistry

Since the discovery of the organometallic catalysis organic halides had been important compounds used as building block for the synthesis of complex molecules. The process known as Ullmann coupling (1901) use aryl halides as versatile substrates in a copper catalyzed reaction. The first type of Ullmann process refers to the reaction of an aryl iodide or bromide in the presence of copper metal, oxide or its salts, to afford the corresponding symmetric biaryl (Scheme 1.1, equation a)[1]. With a modified version of the process the arylation of various nucleophiles, such as aryl amines or phenols, can also be achieved[2,3] (Scheme 1.1, equation b and c). The process requires harsh conditions (T $>$ 200 °C) and activated substrates, and in many cases a high catalyst load. The reaction lost its synthetic importance with the advent of palladium catalysis, which allows to achieve similar results using mild conditions and a low amount of catalyst. Only in recent times due to the discovery of appropriate ligands, copper catalyzed coupling of aryl halides with nucleophiles has returned to be an attractive process.



Scheme 1.1 Copper-catalyzed coupling of aryl halides with nucleophiles (Ullmann coupling).

Nowadays, palladium catalysis remain the preferred choice in the synthesis of fine chemicals due to its versatility and organic halides continue to be important substrates in the several catalytic processes developed in the second half of the last century.

In the recent years the possibility to achieve the formation of C–X bonds by metal catalysis was developed, thus reverting the role of organic halides in organometallic chemistry, from substrates to products. In the following sections some processes involving the formation of a C–X bonds by metal catalysis are discussed.

1.2 Finkelstein reaction

The Finkelstein reaction is a halogen metathesis reaction where the halide present in an organic molecule exchanges with another halide acting as nucleophile[4].

$$R{-}X + X'^{-} \rightleftharpoons R{-}X' + X^{-}$$

The process is synthetically useful for the preparation of alkyl iodides from the corresponding bromides or chlorides using NaI as source of I-. In this case, the equilibrium is shifted towards the products by taking advantage of the lower solubility of NaBr or NaCl in acetone, compared to NaI.
The reaction follows the SN2 mechanism and works well with primary alkyl halides. Aryl and tertiary alkyl halides are less reactive and need a catalyst to achieve the halogen exchange[5].

1.3 Copper catalyzed halogen exchange

The first example of metal mediated halogen exchange in aryl substrates was reported in the 1960s. Various processes were developed using copper halide salts as reagents, or as catalysts together with inorganic halides. The reaction requires high temperature and is strongly influenced by the nature of the solvent, usually a polar one. The reactivity of the substrate follows the order ArI $>$ ArBr $>$ ArCl, while the opposite reactivity is observed for the inorganic halide acting as nucleophile; thus, the process is not useful for the synthesis of the more expensive aryl iodides. Moreover, the presence of side reactions like dehalogenation and Ullmann coupling lowers the yields at high conversions[6].
Later on, a slightly modified version of the process referring to the conversion of polycyclic aromatic bromides to the corresponding iodides was achieved with KI in the presence of CuI as catalyst in HMPA (hexamethylphosphoric triamide). However, a large excess of the iodide salt and harsh conditions are required to obtain high yields[7]. Vinyl bromides can be converted in similar conditions as well[8]. In a more general process, conversion of bromobenzene to iodobenzene was accomplished using CuI supported on activated alumina as reagent[9]. The kinetic of the reaction is slow and several hours are needed in a solventless system at 150°C. Bulky substituents, especially in the ortho position, are detrimental to the reaction

because of the presence of the heterogeneous support.

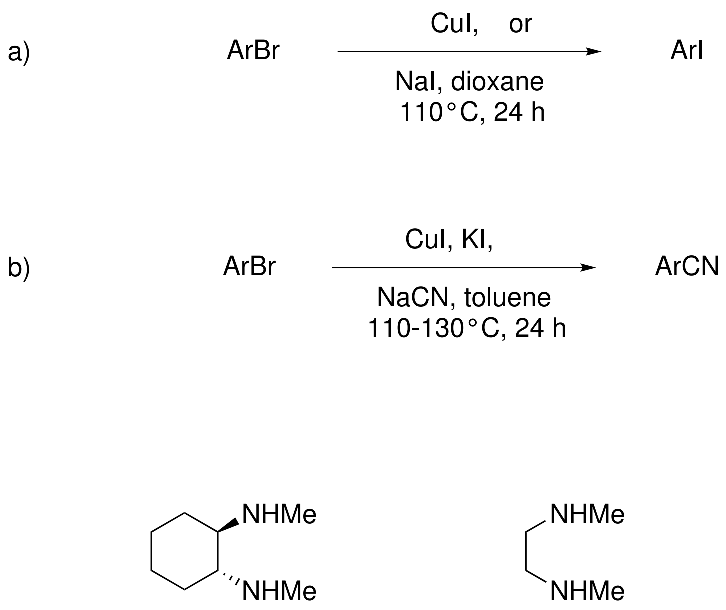
1.4 Recent development in copper catalyzed halogen exchange reaction

As reported above, copper catalyzed halogen exchange reactions are affected by major issues. Harsh conditions, formation of byproducts and the need for a large amount of metal salts, are just a few problems that prevented the process to be exploited for synthetic purposes.

However, in the last decade, Buchwald and Klapars discovered that the reaction kinetic can be substantially increased by using 1,2-diamine ligands. Bromine-iodine exchange reaction is preferably carried out in dioxane, at 110°C, with a 5% CuI load and a ligand/catalyst ratio of 2. Twice of the stoichiometric amount of NaI is required for the reaction to go to completion. Both **1** and **2** in Scheme 1.2 are effective ligands for the reaction.

While these simple ligands strongly affect the reaction rate, making possible to reach the complete conversion in 24 h, the position of the thermodynamic equilibrium is determined by other factors. The process is under thermodynamic control and the solubility of salts plays a crucial role in product distribution as it occurs in the alkyl Finkelstein reaction. The solubility of the formed NaBr is very low in dioxane while NaI remains soluble and available, thus shifting the equilibrium toward the formation of the aryl iodide. The reaction can be also carried out in apolar solvent such as *m*-xylene, but a 5–60% of diglyme is needed to increase NaI solubility to maintain a minimal concentration of the iodide salt. It should be noted that if I- concentration is too high the reaction is inhibited, probably by the formation of unreactive copper species[10].

The same authors in a different work, showed the possibility to combine the exchange reaction with a sequential nucleophilic substitution. For example, it is well known that the copper mediated cyanation is remarkably slower with aryl bromides than iodides. However, in the presence of a catalytic amount of KI, the reaction of the aryl bromide to cyanide becomes fast due to the previous conversion of the bromide into the more reactive iodide. which is transformed into the benzonitrile derivative as soon as it is formed[11].



1 **2**

Scheme 1.2 Halogen exchange reaction (a) and halogen exchange followed by cyanation (b).

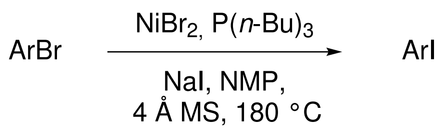
1.5 Nickel catalyzed Finkelstein reaction

Nickel compounds are known to catalyze a variety of reactions of aryl halides and nucleophiles. During their studies on nickel catalyzed amination, Cramer and Coulson observed the formation of chlorobenzene from bromobenzene. They found that the reaction could be carried out using LiCl as reagent in ethanol at 210°C in the presence of a small amount (about 1%) of $NiCl_2$[12].

A major contribution to the nickel catalyzed bromide-iodide exchange came from

Takagi and coworkers. They performed an intensive screening of ligands and conditions in order to optimize the process, showing that polar aprotic solvents (HMPA) and high temperature are required. The reaction, however, can proceed without any ligand when the Ni(0) catalyst is formed in situ from $NiCl_2$and zinc powder. The amount of the latter must be kept to a minimum in order to avoid the formation of biaryls. Preformed nickel(0) species can be used but they are usually less reactive[13].

In a recent study (2012), $NiBr_2$ in combination with $P(n\text{-Bu})_3$ was used as catalyst for the conversion of various aryl and heteroaryl bromides to the corresponding iodides by NaI in moderate to good yields (Scheme 1.3). Several examples are provided with yields ranging from 60 to 90%[14].



Scheme 1.3 Nickel-catalyzed aromatic Finkelstein reaction.

1.6 Carbon-halogen bond formation by palladium catalysis

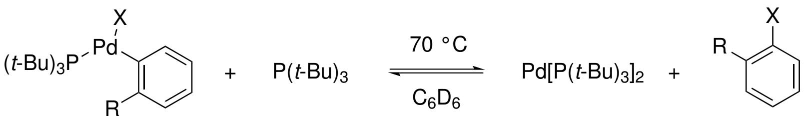
The oxidative addition of organic halides to palladium(0) is the starting step in many catalytic processes. Its microscopical reverse, the reductive elimination, has been extensively exploited in C–C, C–N and C–O bond formation. However, the above step is not commonly observed in the case of carbon-halogen coupling. No direct halogen exchange reaction has been reported so far in the literature, and only recently a few palladium catalyzed processes involving carbon-halogen bond formation have been developed.

Roy and Hartwig, in 2001, were the first researchers to investigate this reaction; they published a mechanistic study that shed light on thermodynamic and kinetic aspects of the reductive elimination of aryl halides from Pd(II) complexes[15].

While is generally accepted that reductive elimination is favored by electron-deficient ligands, the authors experimentally obtained the reductive elimination of aryl halides from palladium complexes containing a strong donating ligand such as $P(t\text{-Bu})_3$, which , however, also possesses a high steric hindrance (cone angle > 180°).
The tri-coordinated complex **3** shown in the equation of Table 1.1 readily undergoes reductive elimination of the aryl halide **4** upon heating at 70 °C in C_6D_6 in the presence of an excess of $P(t\text{-Bu})_3$. In the process, palladium is reduced to the oxidation state zero and a new C–X bond is formed[16].
Usually the equilibrium of the reductive elimination step is completely shifted towards the left, irrespectively of the halogen atom involved. The bulkiness of the ligand $P(t\text{-Bu})_3$, however, influences both the kinetic and the thermodynamic of the process so severely that the reaction can proceed toward the right, to reach an equilibrium. The measured equilibrium constants appear proportional to the carbon-halide bond strength. Thus, due to the strength of the carbon-chloride bond, the reductive elimination of aryl chlorides is thermodynamically favored over that of the other halides.

The kinetic of the reaction, however, follows the opposite order and reductive elimination is faster for iodides than for chlorides. As shown in Table 1.1, the yield of ArBr is higher than that of ArCl in spite of the lower value of Keq. A high energy transition state is responsible for the lower rate of reductive elimination of aryl chlorides from palladium species and the same applies to the reverse pathway, the oxidative addition. For aryl iodides and bromides this mechanism is by far more accessible in both directions because of their greater polarizability, hence the yield of the reductive elimination product (**4**) is higher. However, the reductive elimination of aryl iodides, although kinetically favored over that of bromides, is actually penalized by the adverse equilibrium and lower yields are obtained. Besides the steric effect of the ligand, the relative stability of the species involved

Table 1.1 Hartwig stoichoimetric experiments on reductive elimination of aryl halides.



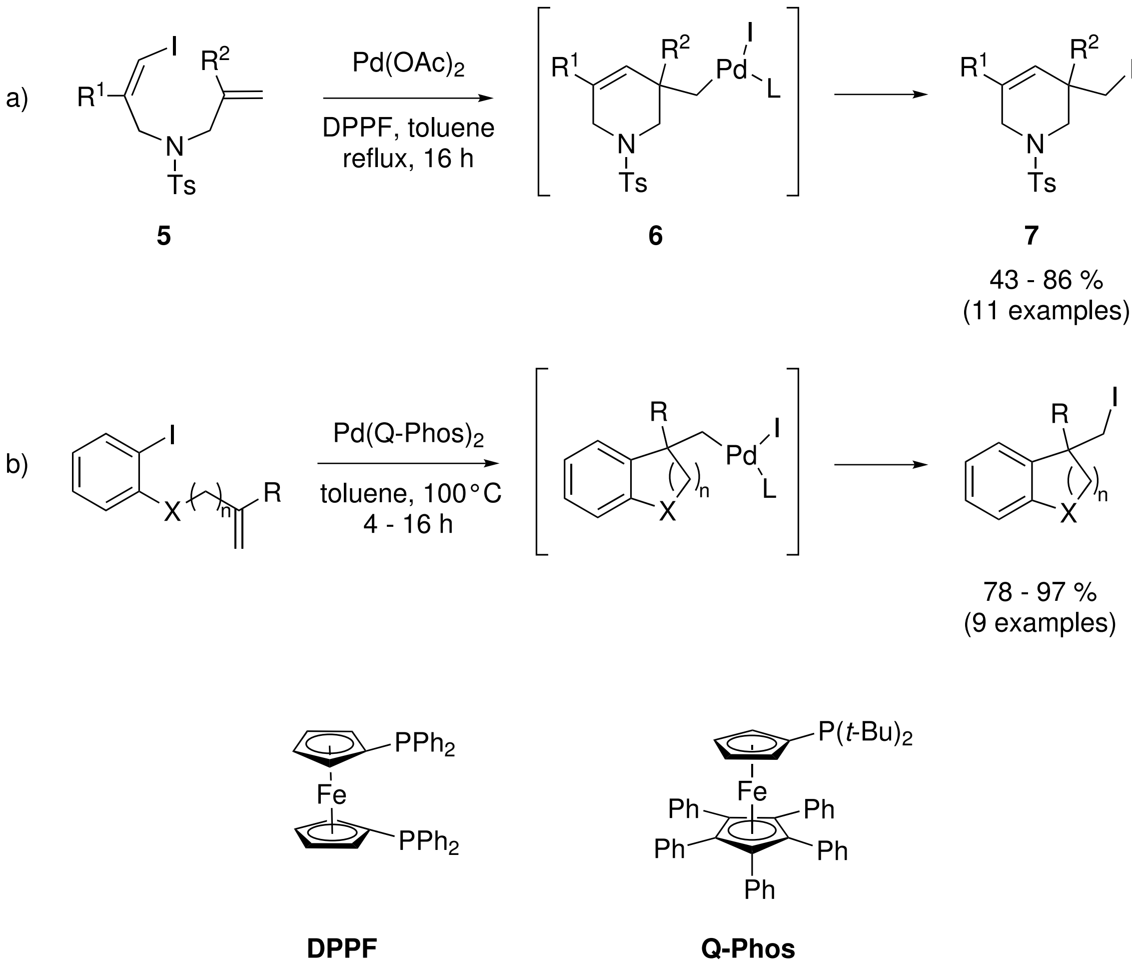
3 **4**

R	X	Yield (%)	K_{eq}
Me	Cl	76	$1.09 \cdot 10^{3}$
Me	Br	98	3.27
Me	I	79	$1.79 \cdot 10^{-1}$
H	Br	68	1.34
H	I	60	$5.10 \cdot 10^{-2}$

Reaction conditions: starting complex 10 mM, 20 equiv P(t-Bu)$_3$, 70 °C, C_6D_6. Values of K_{eq} referred to 1 M standard conditions.

and the rate of the reaction are strongly influenced by the nature of the substrate as well. The last two entries of Table 1.1 show that in the absence of a substituent in the ortho position a lower yield and a lower value of the equilibrium constant are obtained. Recently Tong[17] and Lautens[18] independently achieved the C–I bond formation as terminating step in palladium catalyzed reactions. In both cases key to the success is the use of a palladium species with sterically encumbered phosphine ligands, such as DPPF (1,1'-bis(diphenylphosfino)ferrocene) and Q-Phos, respectively. Under such conditions, and in the absence of any other concurrent process, the reductive elimination can be easily achieved.

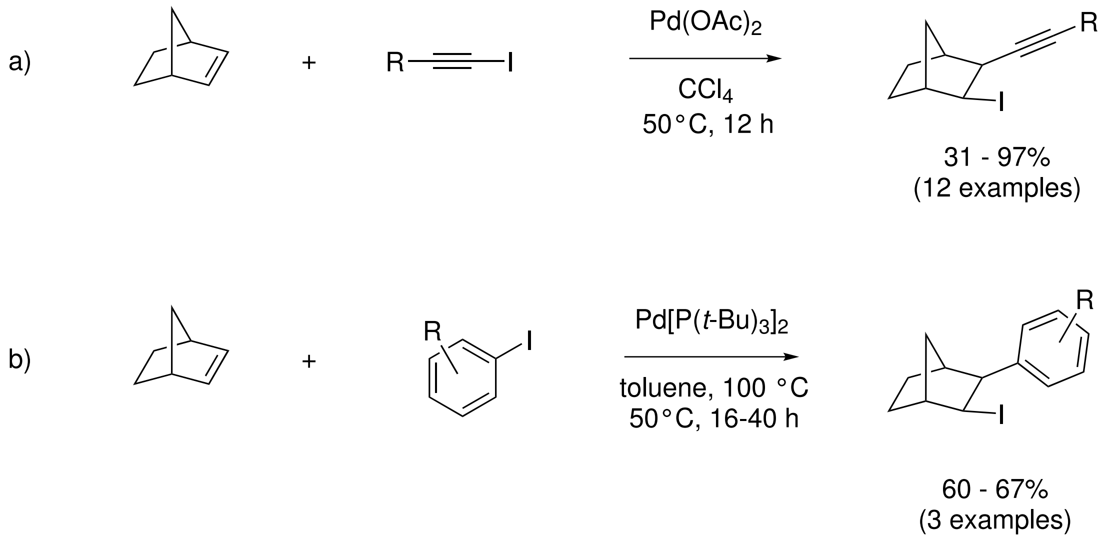
In Tong's group paper, (Scheme 1.4, equation a) the catalytic reaction starts with the oxidative addition of the vinyl iodide **5** to palladium(0). The resulting arylpalladium(II) species can readily inserts into the double bond to form (**6**). The cyclic intermediate obtained (**6**) does not possess any β-hydrogen to readily eliminate. Instead, the high steric hindrance of the ligands, forces the *cis* coordinated iodide close to the α-carbon favoring the C–I bond formation by reductive elimination.



Scheme 1.4 Two example of intramolecular formation of a new C–I bond by Tong (a) and Lautens (b) groups.

The final compound **7** which contains a new C–C and a new C–I bond, is obtained with an atom economy of 100%. The same mechanism applies to Lautens reaction (Scheme 1.4, equation b). Thus, the intermediacy of a complex where an alternative termination step is precluded appears to be a prerequisite for the carbon–iodide bond formation. The Lautens group has demonstrated that the reaction can also take place starting from an analogous aryl bromide in the presence of KI as iodide source[19].

Palladium catalyzed carboiodination can be also obtained in substrates, such as norbornene or its derivatives, that cannot undergo an easy syn β-H elimination for geometrical reasons. In Scheme 1.5 two examples from Tong and Lautens groups are reported[18,20].



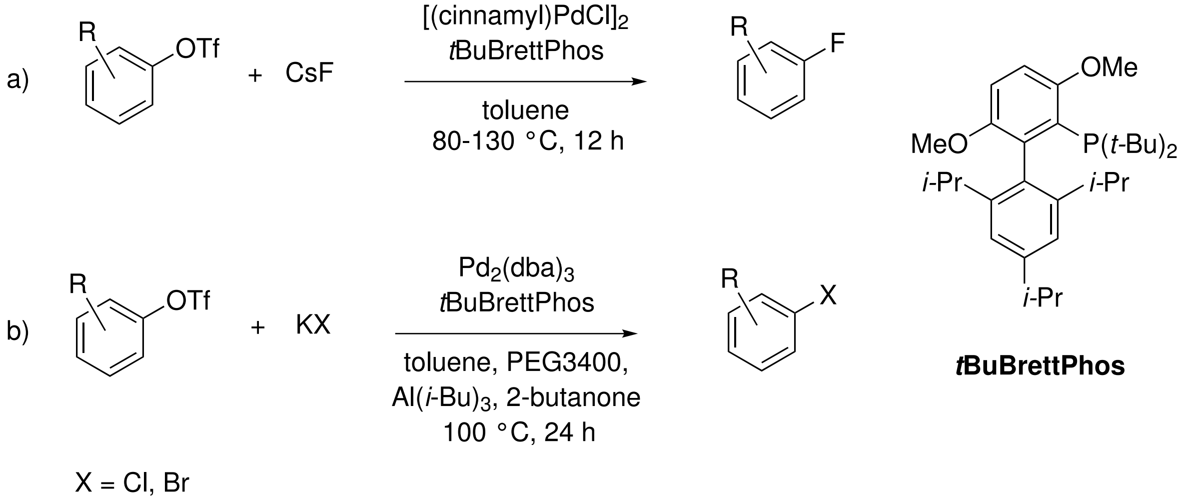
Scheme 1.5 The intermolecular carboiodination of norbornene obtained by Tong (a) and Lautens (b).

These studies confirm that C–I reductive elimination is a possible terminating step for palladium catalyzed processes, although thermodynamic and kinetic requirements limit its application to specific cases: very bulky ligands and suitable substrates are needed for the transformation to occur at an appreciable rate.

On the contrary, the C–X bond formation when the halogen anion is chloride or fluoride is still a challenging process, for the reasons explained above.

Buchwald *et al.* have recently developed a new catalytic methodology that, for the first time, leads to C–F reductive elimination from Pd(II) complexes[21].

When an aryl triflate reacts with CsF in the presence of $[(\text{cinnamyl})PdCl]_2$ and tBuBrettPhos as ligand in toluene, the corresponding aryl fluoride is obtained in good yield (57–83%). The reaction is tolerant to various functional groups but very sensitive to water. Also in this case a ligand with a high steric hindrance is needed to achieve the coupling reaction.



Scheme 1.6 Conversion of aromatic triflates to bromides and chlorides by palladium catalysis.

The same ligand (tBuBrettPhos) can be utilized for the conversion of aryl triflates to bromides and chlorides; in this case the coupling partner is a potassium salt of the desired halogen[22]. The reaction proceeds under similar conditions but the addition of as phase-transfer catalyst, such as PEG, is needed to increase solubility and nucleophilicity of the halide anion in toluene. However, in this case, the authors surprisingly have found that the reaction is inhibited by the triflate released as byproduct, despite the low coordinating character of this anion. The addition of a Lewis acid, Al(i-Bu)$_3$ is beneficial to the reaction due to sequestration of the triflate, but 2-butanone have to be added to suppress the formation of the coupling product i-Bu-Ar.

1.7 References

(1) Ullmann, F.; Bielecki, J. *Chem. Ber.* **1901**, *34*, 2174–2185.

(2) Ullmann, F. *Chem. Ber.* **1903**, *36*, 2382–2384.

(3) Ullmann, F.; Sponagel, P. *Chem. Ber.* **1905**, *38*, 2211–2212.

(4) Finkelstein, H. *Chem. Ber.* **1910**, *43*, 1528–1532.

(5) Smith, M. B.; March, J., *Marchs Advanced Organic Chemistry*; John Wiley & Sons, Inc.: 2006, pp 574–575.

(6) a) Bacon, R. G. R.; Hill, H. A. O. *J. Chem. Soc.* **1964**, 1097–1107; b) Bacon, R. G. R.; Hill, H. A. O. *J. Chem. Soc.* **1964**, 1108–1112.

(7) Suzuki, H.; Kondo, A.; Inouye, M.; Ogawa, T. *Synthesis* **1986**, 121–122.

(8) Suzuki, H.; Aihara, M.; Yamamoto, H.; Takamoto, Y.; Ogawa, T. *Synthesis* **1988**, 236–238.

(9) Clark, J. H.; Jones, C. W. *J. Chem. Soc., Chem. Commun.* **1987**, 1409–1410.

(10) Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14844–14845.

(11) Zanon, J.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 2890–2891.

(12) Cramer, R.; Coulson, D. R. *J. Org. Chem.* **1975**, *40*, 2267–2273.

(13) Takagi, K.; Hayama, N.; Inokawa, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3691–3695.

(14) Cant, A. A.; Bhalla, R.; Pimlott, S. L.; Sutherland, A. *Chem. Commun.* **2012**, *48*, 3993–3995.

(15) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 1232–1233.

(16) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 13944–13945.

(17) Liu, H.; Li, C.; Qiu, D.; Tong, X. *J. Am. Chem. Soc.* **2011**, *133*, 6187–6193.

(18) Newman, S. G.; Lautens, M. *J. Am. Chem. Soc.* **2011**, *133*, 1778–1780.

(19) Newman, S. G.; Howell, J. K.; Nicolaus, N.; Lautens, M. *J. Am. Chem. Soc.* **2011**, *133*, 14916–14919.

(20) Liu, H.; Chen, C.; Wang, L.; Tong, X. *Org. Lett.* **2011**, *13*, 5072–5075.

(21) Watson, D. A.; Su, M.; Teverovskiy, G.; Zhang, Y.; García-Fortanet, J.; Kinzel, T.; Buchwald, S. L. *Science* **2009**, *325*, 1661–1664.

(22) Shen, X.; Hyde, A. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 14076–14078.

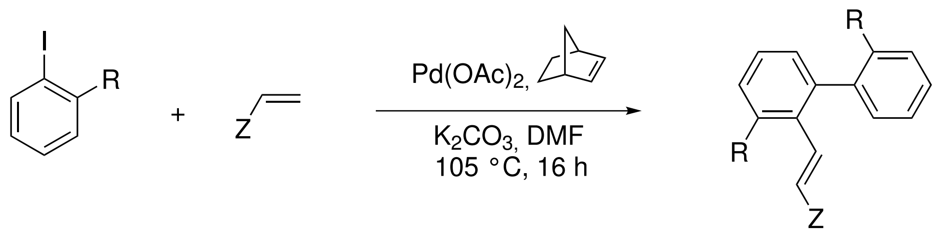
Chapter 2

Combined Pd/norbornene catalysis: from *ortho*-substituted aryl iodides and bromides to *o*-iodobiaryls.

2.1 Previous studies of the palladium norbornene catalytic system

The main subject of my thesis project is the study of new synthetic methodologies based on the palladium-norbornene catalytic system developed in our laboratory[1]. The metal and the strained olefin, together with an aryl halide, act in a concerted way to form a five-membered arylnorbornyl palladacyle. This species controls the subsequent steps and allows the construction of a great variety of complex molecules starting from simple building blocks in a sequential catalytic cycle.

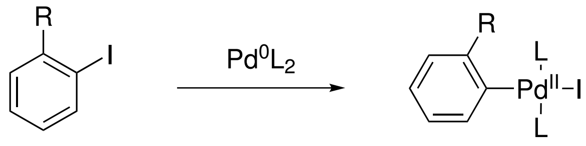
Scheme 2.1 above illustrates the reaction of two molecules of an *ortho*-substituted aryl iodide with an olefin in the presence of palladium and norbornene as catalyst, K_2CO_3 as base in DMF at 105 °C leading to the formation of biaryls vinylated at the *ortho* position. In the *one-pot* process two new C–C bonds are selectively formed[2]. The presence of a substituent in the *ortho* position of the starting aryl



Scheme 2.1 Molar ratio of the reagents: ArI:olefin:K_2CO_3:norbornene:$Pd(OAc)_2$/40: 24: 40: 12: 1; 105 °C, 16 h, DMF as solvent, under N_2; 0.0045 mmol $Pd(OAc)_2$/ml DMF.

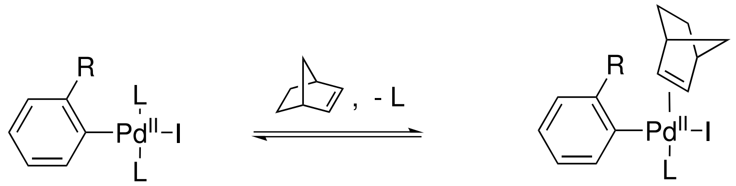
iodide is essential for the success of the reaction. On the basis of previous works, the reaction pathway is proposed to proceed through several fundamental steps which are summarized here.

The catalytic cycle starts with the oxidative addition of the *ortho*-substituted aryl iodide to palladium(0), formed in situ, to afford the well known arylpalladium(II) iodide complex **I**. L indicates a stabilizing ligand, such as phosphine or nitrogen ligand, or any coordinating species present in the reaction mixture.



I

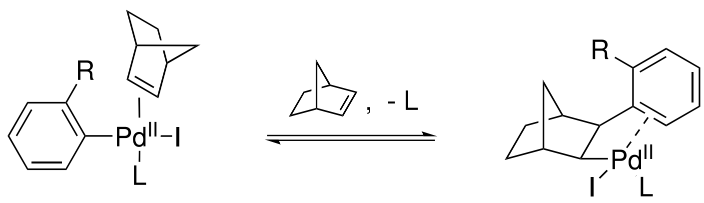
In the subsequent step a ligand is exchanged with a norbornene molecule: the electron-rich, strained olefin readily coordinates to the electron-demanding Pd(II) species giving **II**.



I **II**

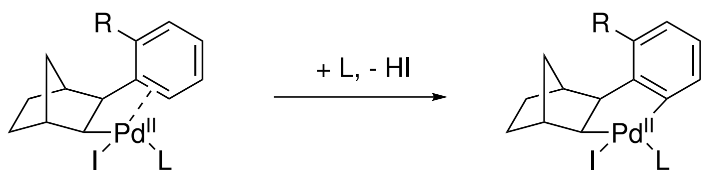
The norbornene insertion into the Pd–aryl bond occurs stereoselectively to form intermediate **III**, a species containing both the metal and the aryl group on the same side of the methylene bridge (*cis,exo* geometry). As revealed by ^{1}H NMR and confirmed by X-ray crystallography carried out on species of this type, palladium is coordinated to the aromatic ring through an η^2 interaction[3,4].

Due to the absence of any *syn* β-hydrogen the alkylpalladium complex **III** is stable towards β-H elimination; this result is to be ascribed to the rigidity of the system which prevents the possibility to attain the right geometry for β-hydrogen elimination[5].



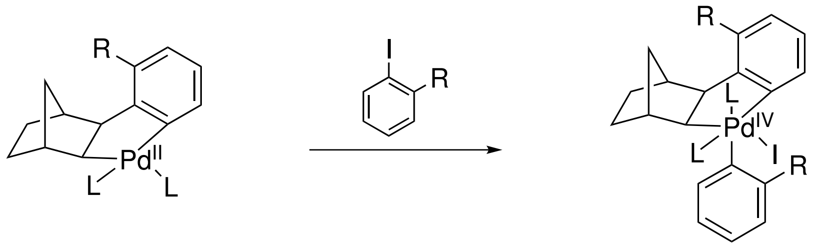
II **III**

The presence of the η^2 coordination favors the activation of the adjacent C–H bond and the attack of palladium onto the aromatic ring by base-assisted electrophilic aromatic substitution. The resulting palladacycle **IV** has been isolated using nitrogen containing stabilizing ligands, such as phenanthroline, and characterized by X-ray diffraction analysis[6].



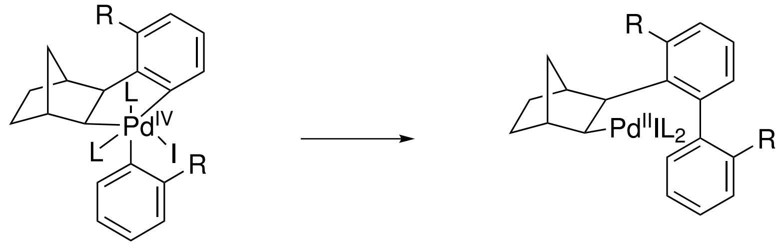
III **IV**

This palladacycle **IV** is reactive towards oxidative addition and readily reacts with another molecule of aryl iodide to form the Pd(IV) species **V**. Although complexes of Pd(IV) obtained by oxidative addition of an aryl iodide to the arylnorbornylpalladium(II) species (**IV**) had not been previously isolated we proposed their intermediacy by analogy to what was reported in the case of the oxidative addition of alkyl halides. More recently, Pd(IV) complexes resulting from oxidative addition of aryl halides to Pd(II) species have been isolated and fully characterized by X-ray crystallography by Vicente group[7]. A recent work published by our and Malacria's groups confirms the possible intermediacy of a palladium in the +4 oxidation state using DFT calculations[8].



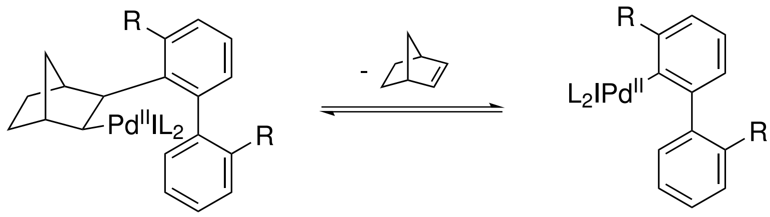
IV **V**

The Pd(IV) complex **V** readily undergoes reductive elimination of the two aryl groups, thus forming the biaryl unit. This step occurs selectively between the two palladium-coordinated aromatic carbons, yielding the biarylnorbornylpalladium(II) iodide **VI**. As previously stated for intermediate **III**, a Heck-type termination is forbidden in this intermediate as well, and the palladium species found a different way to proceed further.



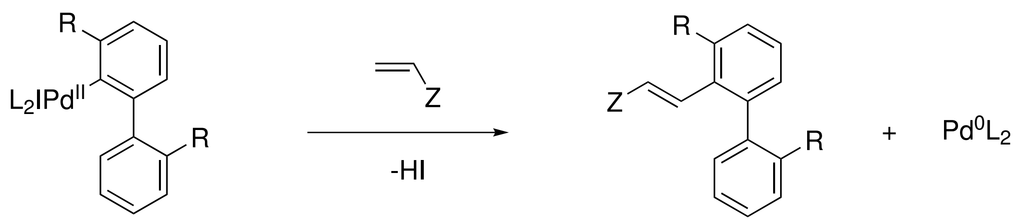
V **VI**

The increased steric hindrance due to the presence of the two *ortho* substituents favors the deinsertion reaction of norbornene leading to the biarylpalladium iodide complex **VII**. Thus, the liberated strained olefin becomes available for a new catalytic cycle.



VI **VII**

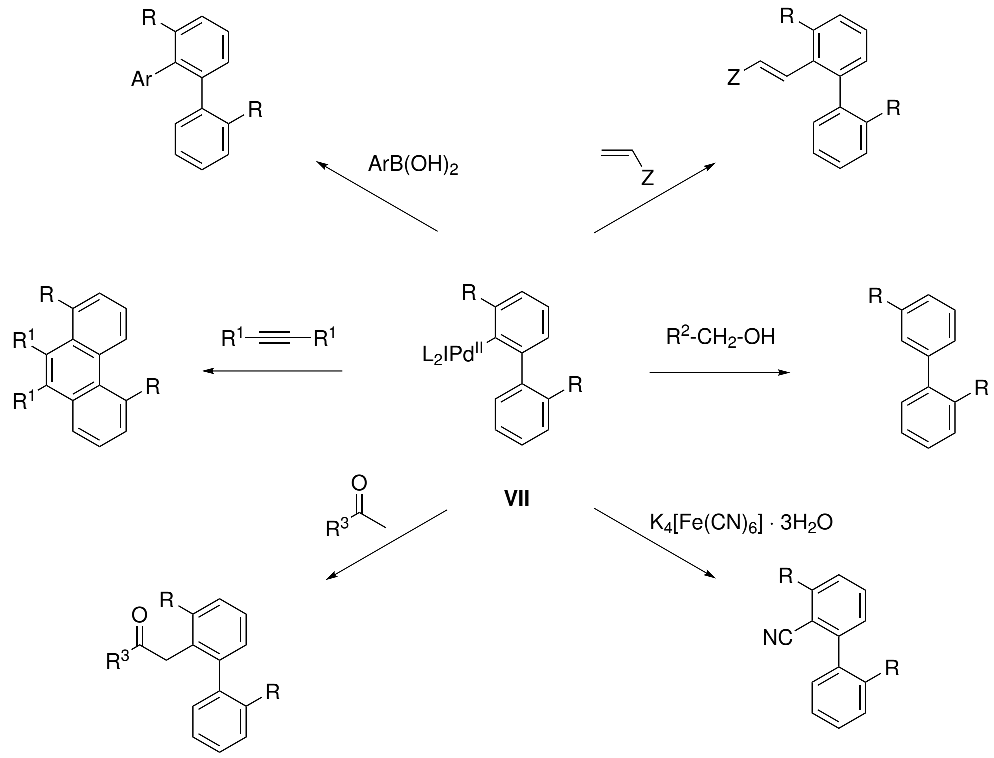
This intermediate (**VII**) can terminate the cycle reacting with the terminal olefin according to the Heck coupling to give the desired product and regenerate Pd(0). It is worth noting that the reaction takes place in the presence of two olefins and that the olefin insertion is controlled by steric effects. Norbornene selectively inserts into the monosubstituted arylpalladium bond of **I** while only the terminal olefin is able to react with the 2,6-disubstituted arylpalladium species **VII**.



VII

2.1.1 Other termination strategies

The general mechanism reported above shows the termination of the catalytic cycle by the Heck coupling. However, the biaryl iodide **VII** is able to react in various ways which are typical of arylpalladium species and the catalytic cycle can thus be terminated by reactions with compounds other than olefins. Several biaryl derivatives become available by replacing the third component of the reaction, *i.e.* the olefin, with other appropriate compounds. Some successful possibilities are shown in Scheme 2.2.



Scheme 2.2 Several compounds are able to react with intermediate **VII**.

Terphenyl derivatives can be obtained by Suzuki coupling when an arylboronic acid is used in place of the olefin[9]. Phenantrenes are formed by insertion of an internal alkyne in the Pd–C(aryl) bond followed by cyclization[10]. The reaction with ketones forms biarylketones through arylation at the α-carbon[11]. The coupling with the cyanide anion was obtained catalytically by Lautens group[12].

Another possible termination step can occur by intermolecular hydride transfer: when the palladium species **VII** reacts with an alcohol, acting as reducing agent, a biaryl product is formed and the alcohol is oxidized to a carbonylic compound[13]. The biaryl thus obtained is formed by two units of the starting aryl iodide bonded in a non-symmetrical way.

This species is also commonly found as byproduct in reactions carried out with poorly reactive terminating reagents, in this situation hydrogenolysis from hydrogen-donor species present in the reaction media becomes a competitive pathway.

2.1.2 Norbornene as catalyst

Norbornene is a rigid and strained bicyclic olefin which is used, in combination with palladium, to accomplish the sequential catalytic cycle. Its role is that of a scaffold that covalently bonds the metal and the substrate allowing them to react in an unique way. In this process norbornene behaves like an organic catalyst, it works in substoichiometric amounts and is retrieved unaltered at the end of the cycle. This is possible because this olefin possesses distinctive properties due to its particular geometry: the bridging methylene group binds the cyclohexenyl unit in a rigid, strained system. The main consequence of the rigidity of the molecule is the absence of any internal rotations of the methylene groups; for this reason intermediate **III** and **VI** are stable towards β-H elimination since no hydrogens are allowed to reach the position *syn* to palladium, required for hydrogen elimination. Because of the constrained geometry the orbitals forming the double bond are poorly overlapped. The partial release of this strain, by η^2 binding to the transition metal, makes norbornene very reactive towards palladium coordination as in intermediate **II**. This step is in competition with the coordination of the olefin present as terminating agent and in some cases the possible Heck product between the starting aryl iodide and the terminal olefin is obtained. Small amounts of this byproduct can be formed when the reactivity of the two olefins is not well matched. By a delicate tuning of the amount of norbornene and reaction conditions, the formation of byproducts can be kept under control. Depending on the nature of the substrates used as terminating agent a catalytic amount or an excess of norbornene can be required to avoid concurrent reactions.

Another particular feature of this strained olefin is its ability to deinsert from intermediate **VI**, with the cleavage of a carbon-carbon bond. The mechanism is the same of norbornene insertion in complex **III**, but here the increased steric hindrance drives the equilibrium reaction towards the deinsertion product. However, if this step is slow some biaryl byproducts containing the norbornane unit are formed.

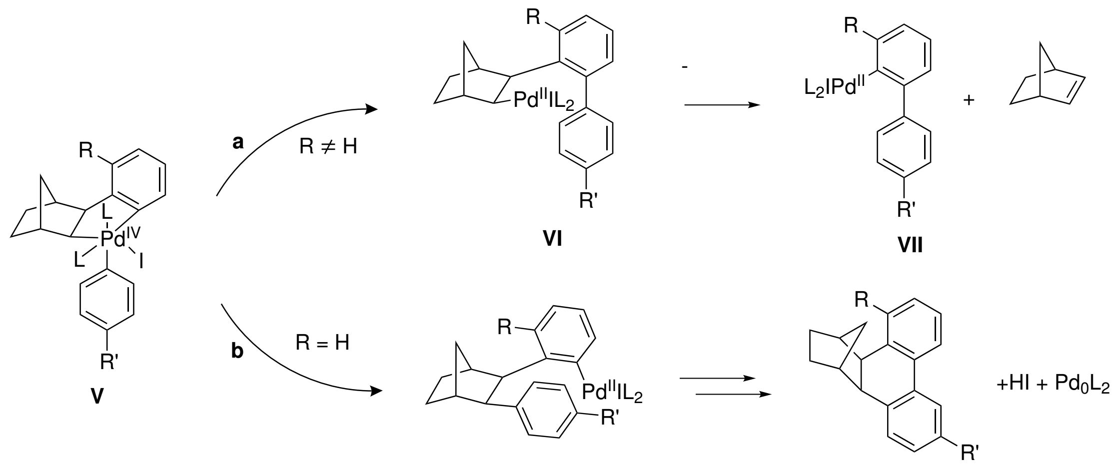
2.1.3 Regioselectivity of the C–C coupling

The previously reported examples showed the reactions of *ortho*-substituted aryl iodides. The substituent at the *ortho* position of the aryl iodide influences the reactivity of the resulting palladacycle. As previously shown an *ortho* substituent in the starting aryl iodide is required to ensure the aryl–aryl coupling. In the absence of a substituent in *ortho* position a different regioselectivity of the C–C coupling is observed.

In stoichiometric experiments palladacycle **IV**, formed *in situ* from its open precursor **III**, reacts at room temperature with a *para*-substituted aryl iodide to form **V**. This Pd(IV) intermediate can now undertake two different routes, depending on the presence of an *ortho* substituent, as illustrated in Scheme 2.3. If $R \neq H$ (path a) a reductive elimination occurs between the two aromatic carbons with formation of the biaryl unit **VI**. In the case of $R = H$ the reductive elimination occurs selectively between the norbornyl and the aromatic carbon, as shown in Scheme 2.3 (path b), leading to an arylpalladium complex. The latter forms a methanotriphenylene derivative by intramolecular aromatic substitution. This compound is a regioisomer of the previously reported analogous byproduct that forms from the reaction of intermediate **VI** and norbornene.

2.1.4 Synthesis of unsymmetrical biaryls with different aryl rings

The process described above gives rise to a non-symmetrical biaryl unit starting from two equivalents of the same aryl iodide. Therefore, the resulting biaryl is formed by two rings with the same substituent in different positions. This fact



Scheme 2.3 If a substituent is present on the aryl iodide at the *ortho* position (R $\neq$ H) the carbon(sp^2)–carbon(sp^2) coupling is obtained (path a). If R = H the C–C bond formation occur selectively at the alkyl carbon of the palladacycle (path b).

greatly limits the synthetic scope of the process.

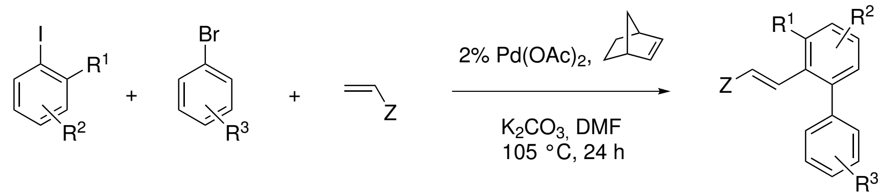
However, the reaction of two different aryl halides is not an easy task because, it can lead to the formation of four possible biaryl products.

In order to overcome this issue the reaction can be carried out using two aryl halides to obtain products formed by two aromatic rings with different substituents[14,15].

The aryl halides enter the catalytic cycle through oxidative addition to palladium intermediates. The first oxidative addition occurs to a Pd(0) species while the second one takes place onto the palladacyle **IV**, with the metal in the oxidation state II. The two species, due to electronic and steric reasons, have quite different reactivity to discriminate between two distinct aryl halides.

Attempts to carry out the reaction using aryl iodides with different steric hindrance generated by the *ortho* group were unsuccessful and a mixture of products was obtained. However when the reaction was carried out using an electron-rich aryl iodide and an electron-poor aryl bromide, a single product was retrieved.

We observed that aryl bromides selectively react with intermediate **IV**, a Pd(II) species, while aryl iodides are more prone to react with the metal in the oxidation state 0. Therefore the mixed aryl-aryl coupling can be obtained selectively starting from a mixture of the two halides. Scheme 2.4 below shows a three component reaction successfully achieved in a sequential, selective way.

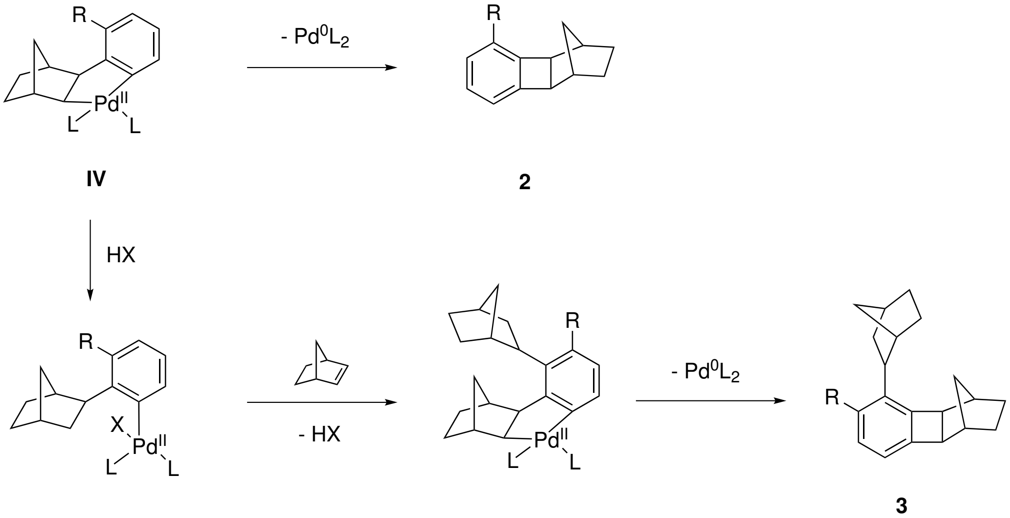


Scheme 2.4 Palladium/norbornene catalytic reaction of an aryl iodide with an aryl bromide in the presence of an olefin, K_2CO_3 as base in DMF at 105 °C.

The requirement of a substituent in the *ortho* position is limited to the first halide entering the cycle, in this case the aryl iodide. The latter forms palladacycle **IV** containing an *ortho* substituent, which determines the selective reductive elimination by aryl–aryl coupling in palladacycle **V**, as described in the previous section.

2.1.5 Formation of byproducts in palladium/norbornene catalyzed reactions

Various byproducts are formed from the intermediates of this complex catalytic cycle. Palladacycle **IV** originates methanobiphenylene **2** by reductive elimination, the yield of this compound rises when the aryl halide is poorly reactive towards the oxidative addition to Pd(II). Hydrogenolysis of intermediate **IV** and subsequent insertion of a second norbornene molecule leads to compound **3**, as shown in the Scheme. Product **3** is particularly abundant when water or other hydrogen donor species, such as bicarbonate, are present in the reaction medium.
Other byproducts are formed from intermediate **VII**. As previously illustrated this biarylpalladium iodide complex readily reacts with a variety of terminating agents (Scheme 2.2). The reaction of **VII** with hydrogen donor species lead to non-symmetric biaryls, such as **4** (Scheme 2.6). In other cases norbornene itself can behave as terminating agent, even though intermediate **VI** is stable



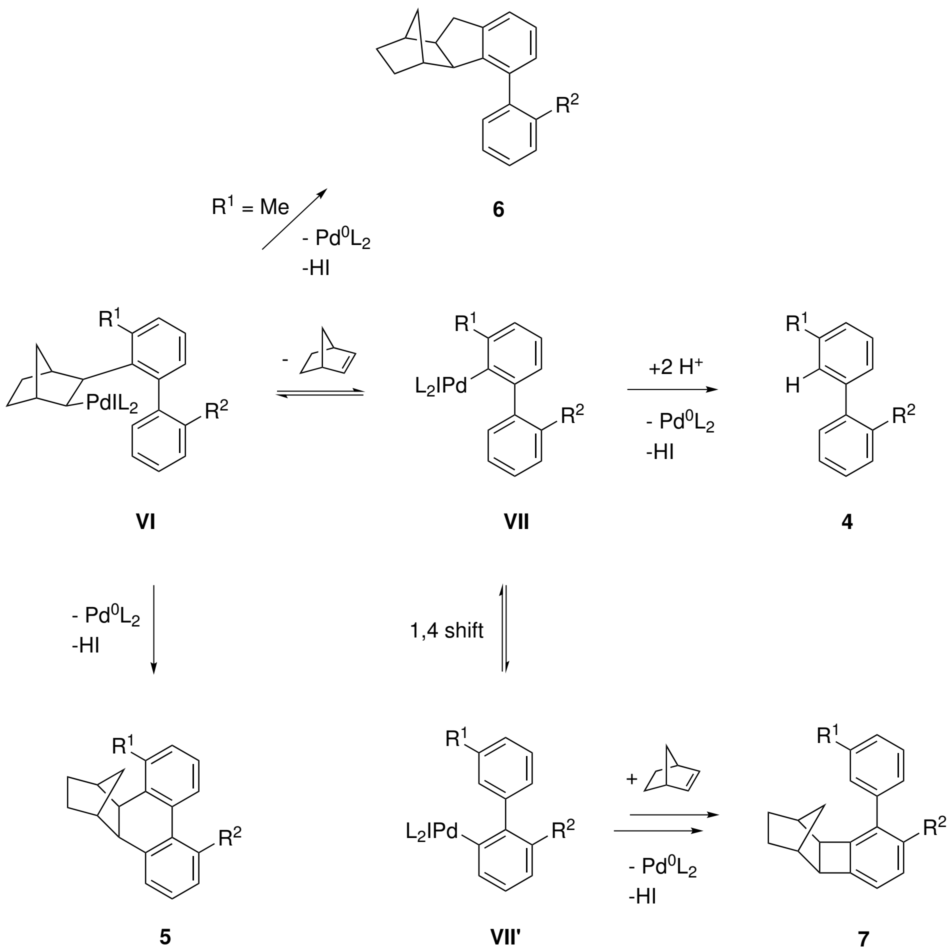
Scheme 2.5 Formation of biphenylenes by reaction of norbornene with intermediate **IV**.

towards β-H elimination other terminating routes are possible, like the formation of methanotriphenylene **5** by aryl-norbornyl coupling, previously described.

Two other byproducts are commonly formed by reaction of intermediate **VII** with norbornene. Compound **6** is often obtained when R^1 = Me by activation of a benzylic C–H bond while compound **7** is likely formed by palladium 1,4 biphenyl shift according the mechanism reported by Larock[16]. To avoid the formation of these byproducts the concentrations of norbornene and hydrogen donor species must be kept as low as possible.

2.2 Catalytic synthesis of selectively substituted o-iodobiaryls from aryl iodides

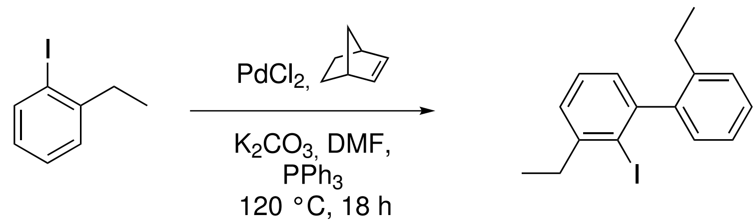
In the introduction section the reactivity of the biarylpalladium halide **VII** with various compounds, able to terminate the catalytic cycle, was discussed. In the course of our studies we observed that, in the absence of a fast termination step, a biaryl compound containing a C–I bond was unexpectedly formed.



Scheme 2.6 Intermediate **VII** can react with norbornene to form compound **5**, **6** and **7**. These type of termination are not particularly fast and if hydrogen-donor species are present the biarylic compound **4** is formed.

The equation shows the reaction of *o*-iodoethylbenzene in the presence of $PdCl_2$, PPh_3 and norbornene, and K_2CO_3 as a base in DMF at 120°C. The product reported above was obtained only in ca. 5% yield. Its structure, initially proposed on the basis of MS fragmentation, was confirmed after isolation and characterization. Together with the *o*-biaryl derivative a major amount of compounds containing the norbornyl unit was obtained (Figure 2.1).

Aryl iodides are versatile and very reactive building blocks often used in organic and organometallic chemistry. Direct iodination of biaryl derivatives is usually



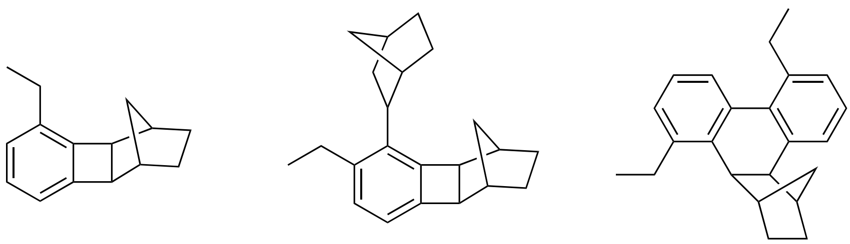
8b

Scheme 2.7 Reaction of *ortho*-iodoethylbenzene in the presence of the catalytic system palladium norbornene, Cs_2CO_3, KI and *p*-TCPP, in toluene at 120 °C.

carried out by the Sandmeyer reaction of the corresponding aniline because any other methods lack selectivity, especially when the target position is a sterically hindered *ortho* carbon.

Thus, the catalytic synthesis of *ortho*-biaryl iodides from simple starting materials is an attractive goal. In our case simple aryl iodides as starting reagents are used and their reactive functionality (the halide ion) is retained in the final product. This allows for further functionalization of the biaryl structure.

The synthesis of organic iodides by palladium catalysis has been reported in the literature only recently[17] and is still a relatively unknown process worth to be studied. Due to the rising interest in this kind of reactions, both for synthetic and theoretical purposes, we decided to further investigate this process and carry out and carry out an optimization work.

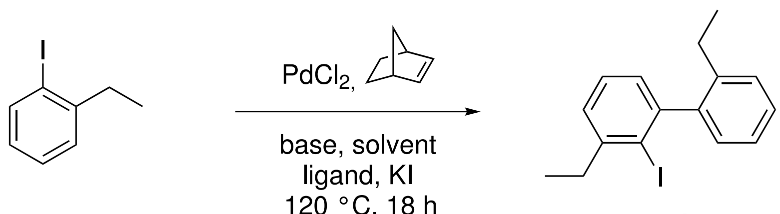


2b **3b** **5b**

Fig. 2.1 Byproducts formed in the catalytic synthesis of *o*-biaryl iodides from aryl iodides.

An extensive screening of conditions was performed using *o*-iodoethylbenzene as model substrate because of its better performance in preliminary experiments compared to other aryl iodides.

Table 2.1 Screening of solvent, base, ligand and KI for the iodination reaction of an *o*-iodoethylbenzene.[a]



8b

Entry	Solvent	Base	Ligand	KI	Conversion (%)[b]	Yield **8b** (%)[c]
1	DMF	K_2CO_3	PPh_3	0	45	5
2	DMF/toluene	K_2CO_3	PPh_3	0	46	12
3	DMF/toluene	K_2CO_3	*p*-TCPP	0	38	20
4	DMF/toluene	Cs_2CO_3	PPh_3	0	44	traces
5	toluene	K_2CO_3	PPh_3	0	5	traces
6	toluene	Cs_2CO_3	PPh_3	0	50	21
7	toluene	Cs_2CO_3	*p*-TCPP	0	52	28
8	anisole	Cs_2CO_3	*p*-TCPP	0	55	22
9	toluene	Cs_2CO_3	*m*-TCPP	0	45	28
10	toluene	Cs_2CO_3	*p*-TFPP	0	39	24
11	toluene	Cs_2CO_3	*p*-TMPP	0	45	23
12	toluene	Cs_2CO_3	DPPE	0	5	traces
13	toluene	Cs_2CO_3	*p*-TCPP	5	50	30
14	toluene	Cs_2CO_3	*p*-TCPP	10	55	37
15	toluene	Cs_2CO_3	*p*-TCPP	20	48	24

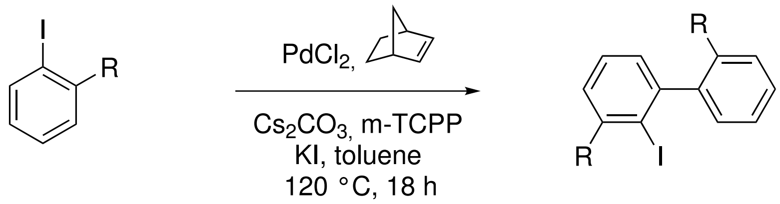
[a] Reaction of *o*-iodoethylbenzene in the presence of $PdCl_2$, a ligand, norbornene and a base in the following molar ratio 40:1:2:10:45 in toluene at 120 °C, [Pd] = 4.5×10^{-3} mmol/ml, t = 18 h; [b] determined by GC using internal standard; [c] determined by ^1H NMR using internal standard.

As previously anticipated and reported in Table 2.1 (entry 1), the product was initially obtained in low yield in DMF as solvent with K_2CO_3 as a base. Under these conditions the main byproducts are compounds **2** and **3** in *ca.* 20 and 3%

yield, respectively. The yield of norbornane-containing byproducts accounts for the total norbornene put into reaction, thus explaining the limited conversion (45%). Increasing the amount of norbornene improves the conversion without favoring the formation of the desired product, a number of byproducts retaining the norbornyl structure are formed instead. A high norbornene concentration favors, for example, the formation of **5** usually found in traces.
We have found that the use of a 1:1 solution of DMF and toluene was beneficial to the yield of the reaction which increases to 12% while maintaining a similar conversion and byproduct distribution (Table 2.1, entry 2). The use of tris(p-chlorophenyl)phosphine (*p*-TCPP) further improved the yield to 20% (entry 3). Low conversion of the starting material and only traces of the desired product were obtained using toluene as solvent (entry 5). However, when the reaction was carried out in toluene in the presence of Cs_2CO_3 as a base, the yield of **8b** increased to 21% using $PdCl_2/PPh_3$ and to 28% with $PdCl_2$/*p*-TCPP (entries 6, 7).
A further screening of the ligand (entries 6–12) shows only low variations of yield and conversion. Electron donating and electron withdrawing monodentate phosphines behave in a similar way and gave results comparable to that of PPh_3, while bidentate ligands, such as DPPE, gave only 5% conversion and traces of the product, if any. However, we observed that *p*-TCPP led to slightly better results. Furthermore, we investigated the effect of an iodide salt on yield and conversion. In the presence of NBu_4I the expected iodinated product has never obtained, even in detectable traces. However, when KI was used a considerable increase of yield and selectivity was observed (entries 13–15). A low amount of KI (10:1 molar ratio to palladium) is sufficient to ensure better a yield.

In Table 2.2 are summarized the results obtained by the reaction of simple aryl iodides under the optimized conditions. Although the selectivities are good, still a lot of work is needed to improve conversion and yield. The best yield (36%) was obtained starting from *o*-iodoethylbenzene while other substrates gave lower

Table 2.2 Palladium-catalyzed synthesis of biaryl iodides from aryl iodides.[a]



Entry	R	Product	Conversion (%)	Yield[b] (%)
1	Me	**8a**	48	22
2	Et	**8b**	55	36
3	*i*-Pr	**8c**	52	22
4	*s*-Bu	**8d**	46	20

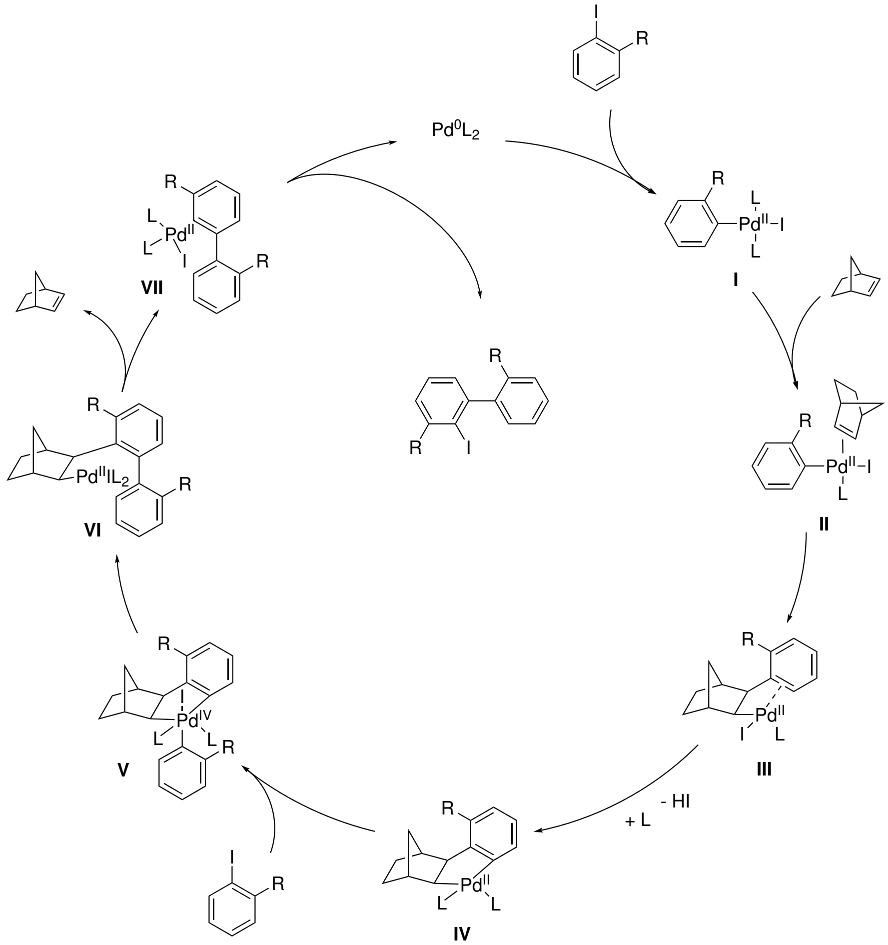
[a] Reaction of an *ortho*-substituted aryl iodide in the presence of $PdCl_2$, *p*-TCPP, norbornene, Cs_2CO_3 in the following molar ratio: 40:1:2:10:45 in toluene at 120 °C, [Pd] = 4.5×10^{-3} mmol/ml, t = 18 h; [b] determined by NMR.

results. The two-carbon alkyl chain avoids activation of benzylic hydrogens leading to the formation of compounds of type **6** which occurs when *o*-iodotoluene is used as starting material.

2.2.1 Reactivity of the system

The catalytic cycle (Scheme 2.8) leading to the formation of *o*-iodobiaryls is similar to the general one presented for the synthesis of *ortho*-vinylated biaryl at the *ortho* position, it differs only for the last step that, in this case, leads to the formation of a C–I bond. Intermediate **VII** is postulated as a square planar Pd(II) complex with the iodide close to the biaryl in *cis* geometry. The coupling of the biaryl group with the iodide anion leads to the *ortho*-biaryl iodide via reductive elimination. In the literature a few examples of C–I reductive elimination by palladium catalysis have been recently reported[17], but this is the first time that this step is achieved, catalytically, on an aromatic carbon.

When an aryl halide undergoes oxidative addition to a palladium(0) species, both



Scheme 2.8 Biaryl iodides synthesis from *o*-substituted aryl-iodides.

oxidation state and coordination number of the metal are raised by two units. The resulting square planar complex is usually obtained in its *cis* geometry, with the iodide close to the aryl group; the first formed *cis* species readily isomerizes to the more stable *trans* complex.

The reductive elimination is considered as the microscopic reverse of the oxidative addition. In the reductive elimination process the intramolecular coupling between the iodide anion and the organic group occurs when the two units are in a *cis* configuration. This is consistent with oxidative addition step which leads to *cis* isomer as the first formed species.

Bulky ligands are usually employed to allow the complex to assume the appropriate configuration and to force the two groups close to each other, thus favoring the coupling.

The reaction involves two equivalents of an aryl iodide with liberation of a stoichiometric amount of iodide anion in the solution. Only one equivalent of the anion is incorporated in the final product, the other one is released in solution its concentration increases along with the conversion. However, only a low amount of inorganic iodide is present at the beginning of the reaction making the termination step more difficult. To reduce this issue KI is added to ensure the presence of a sufficient amount of I^- from the beginning; however, the reaction slows down when an excess of this salt is present in solution. A decreased yield is observed when more than half of the stoichiometric amount of KI is added and, as anticipated, the desired product is not obtained adding NBu_4I.

As expected, the addition of KBr does not yield the corresponding biaryl bromide, not even in detectable traces[18].

We had experimentally found that norbornene in 10:1 molar ratio to palladium gives the best results. This is likely due to the fact that the resulting biaryl iodide is reactive towards the oxidative addition to Pd(0) and the subsequent norbornene insertion leading to the biarylnorbornylpalladium iodide **VI**. Complex **VI** cannot lead to the formation of the five-membered palladacycle –because of the lack of C–H bonds in the *ortho* position– but can react according to the pathways previously discussed and reported in Scheme 2.6.

We noted that the strength of the base plays an important role in the formation of byproduct **5**. If Cs_2CO_3 is used in a DMF/toluene solution (Table 2.1, entry 4), a higher yield of norbornane-containing byproducts (such as methanotriphenylene **5**) are obtained, compared to K_2CO_3 in the same solvent mixture (entry 2). We have found that Cs_2CO_3 in toluene gave the best selectivity, with a relatively low formation of norbornane-containing biaryls (entry 6).

All other bases examined afforded lower yields in toluene; K_2CO_3 gave low or no conversion and PhOK increased the yield of byproducts. Carboxylate bases, such as cesium pivalate and potassium acetate, did not lead to the formation of the desired *o*-biaryl iodide, as well.

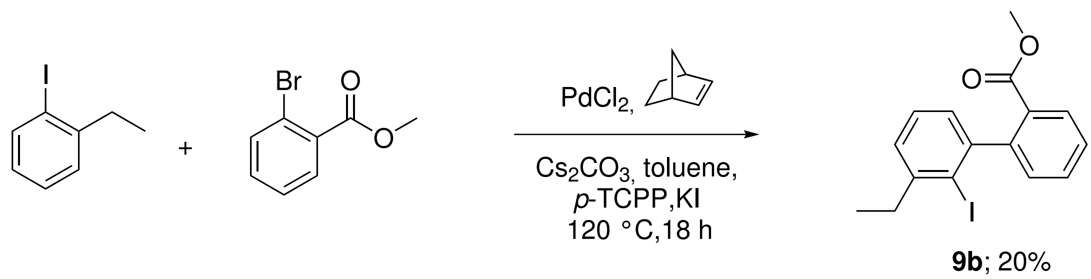
The palladium species that starts the catalytic cycle is in the oxidation state 0, however, the palladium can be introduced as a Pd(II) salt that undergoes reduction under the reaction conditions. Water, phosphines, amines and other impurities present in the reaction medium can behave as reducing agents bringing the metal to the lower oxidation state[19].

The use of PdI_2 in place of $PdCl_2$ as catalyst precursor gave similar results while a lower yield was obtained with palladium acetate .

2.3 *ortho*-Biaryl iodides from aryl iodides and aryl bromides

The reaction illustrated in the previous section yields a biaryl iodide from two equivalents of an aryl iodide, thus the resulting product contains the same substituents in the *meta* and *ortho* positions of the two rings, respectively.

We attempted to carry out the iodination reaction using two different aryl halides, namely an iodide and a bromide. The reaction of *o*-iodoethylbenzene with methyl *o*-bromobenzoate in the presence of the palladium/norbornene catalytic system under the previously reported conditions (Table 2.2) gives the corresponding biaryl iodide in 20% yield, as shown in the following equation.

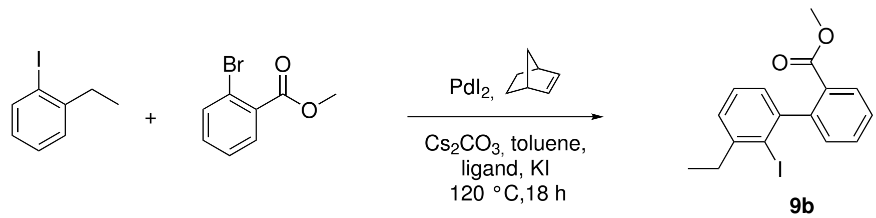


Scheme 2.9 Biaryl iodide synthesis from an *o*-substituted aryl iodide.

After 18 h we observed the formation of Pd black, the analysis of the crude reaction after the work up shows only a 40% conversion of the aryl bromide. A fluorenone and a biaryl derivative without the iodide functionality were also obtained, each in *ca.* 10% yield.

This modest result was encouraging though, considering the complexity of the reaction. A new screening of conditions is carried out in order to improve yield and conversion.

Table 2.3 Effect of ligand and KI on the reaction of *o*-iodoethylbenzene and methyl *o*-bromobenzoate.[a]



9b

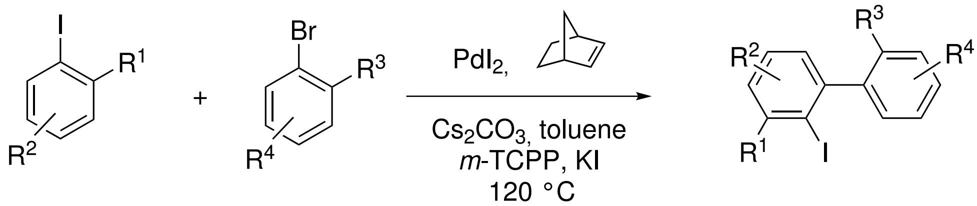
Entry	KI (equiv)	Ligand (equiv)	Conversion (%)[b]	Yield **9b** (%)[c]
1	10	*p*-TCPP (2)	45	20[d]
2	10	*p*-TCPP (2)	42	24
3	10	PPh_3 (2)	35	11
4	10	*m*-TCPP (2)	40	28
5	10	*p*-TFPP (2)	40	8
6	10	*p*-TMPP (2)	46	20
7	10	DPPE (1)	5	–
8	10	*m*-TCPP (3)	80	59
9	15	*m*-TCPP(3)	87	65
10	20	*m*-TCPP (3)	82	44
11	15	*m*-TCPP (4)	84	35

[a] Reaction of *o*-iodoethylbenzene and methyl *o*-bromobenzoate with PdI_2, norbornene and a base in the following molar ratio: 20:20:1/10/45; in toluene at 120 °C; [Pd] = 4.5×10^{-3} mmol/ml; t = 18 h. [b] determined with GC using internal standard. [c] determined by NMR using internal standard. [d] $PdCl_2$ was used.

Since PdI_2 as catalyst precursor behaves slightly better than $PdCl_2$, it has been

used in the optimization work. The ligand screening revealed that *m*-TCPP is the phosphine of choice. A good yield (59%) was reached when the ligand was used in 3:1 to palladium (entry 8). Other monodentante phosphine ligands (entries 5, 6) gave lower results and chelating ligands, such as DPPE, greatly reduced the conversion (entry 7).
Increasing the amount of KI to 15 equivalent to palladium a further improvement was obtained (65% yield).

Table 2.4 Synthesis of biaryl iodides from *ortho*-substituted aryl iodides and bromides.[a]



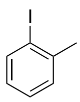
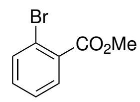
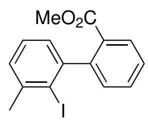
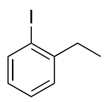
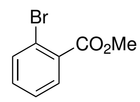
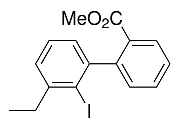
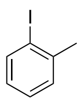
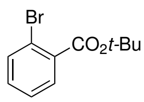
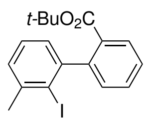
Entry	ArI	ArBr	Time (h)	Conversion (%)[b]	Product	Yield (%)[b]
1			18	80	 **9a**	50 (43)
2			18	87	 **9b**	65 (57)
3			42	92	 **9c**[c]	71 (60)

Table 2.4: continued on next page

Table 2.4: continued from previous page

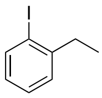
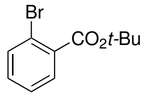
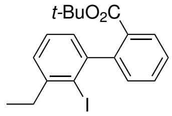
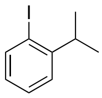
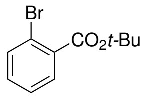
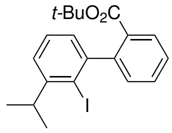
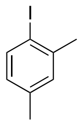
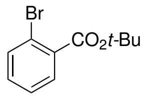
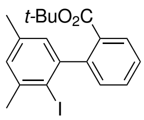
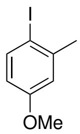
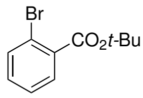
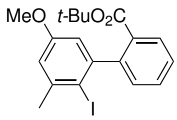
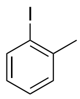
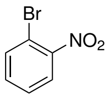
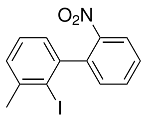
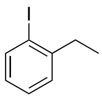
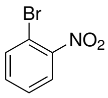
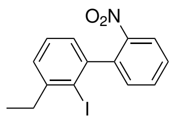
Entry	ArI	ArBr	Time (h)	Conversion (%)[b]	Product	Yield (%)[b]
4			42	93	 **9d**	69 (62)
5			42	91	 **9e**	68 (62)
6			42	95	 **9f**	77 (68)
7			42	99	 **9g**	71 (66)
8			65	88	 **9h**[c]	65 (53)
9			65	90	 **9i**	73 (62)

Table 2.4: continued on next page

Table 2.4: continued from previous page

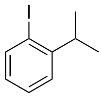
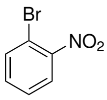
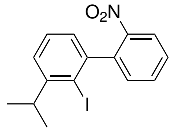
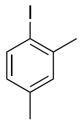
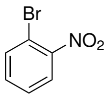
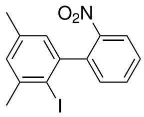
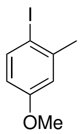
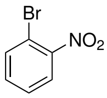
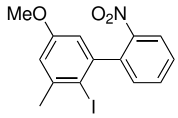
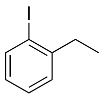
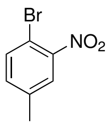
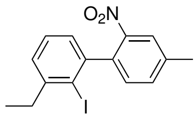
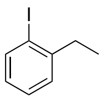
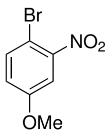
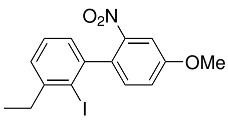
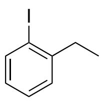
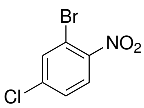
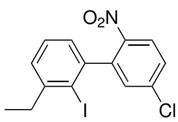
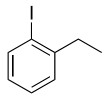
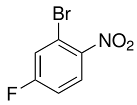
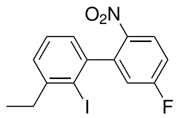
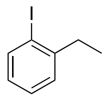
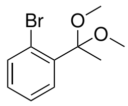
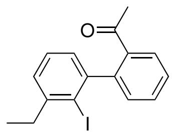
Entry	ArI	ArBr	Time (h)	Conversion (%)[b]	Product	Yield (%)[b]
10			65	96	 **9j**	71 (61)
11			65	89	 **9k**	66 (61)
12			65	94	 **9l**	61 (54)
13			65	95	 **9m**	62 (50)
14			24	92	 **9n**	61 (54)
15			65	88	 **9o**	64 (55)

Table 2.4: continued on next page

Table 2.4: continued from previous page

Entry	ArI	ArBr	Time (h)	Conversion (%)[b]	Product	Yield (%)[b]
16			65	96	 **9p**	57 (48)
17			24	60	 **9q**[d]	45 (40)

[a] Reaction of an *ortho*-substituted aryl iodide and an *ortho*-substituted aryl bromides in the presence of PdI_2, *m*-TCPP, norbornene and KI in the following molar ratio: 1:3:10:15:20:20 in toluene at 120 °C, [Pd] = 2.2×10^{-3} mmol/ml; [b] determined by NMR, isolated yield in parenthesis. [c] 4 equivalents of ligands were used. [d] Recovered as ketone.

Under the optimized conditions we studied the scope of the reaction by causing several aryl iodides and bromides to react (Table 2.4).

Compounds **9a** and **9b** were obtained by reaction of *o*-iodotoluene and *o*-iodoethylbenzene with methyl *o*-bromobenzoate. Despite a high conversion the yield was moderate due to the presence of byproducts. Better yields were obtained when the ester methyl group was replaced by a *t*-butyl one (**9c-g**). Reaction of *o*-bromonitrobenzene with various aryl iodides also afforded the corresponding biaryl iodides in good yields (**9h-m**). *o*-Bromonitrobenzene derivatives, with both electron withdrawing and electron donor substituents, can also be utilized and lead to results comparable to those of the unsubstituted substrate (**9n-p**).

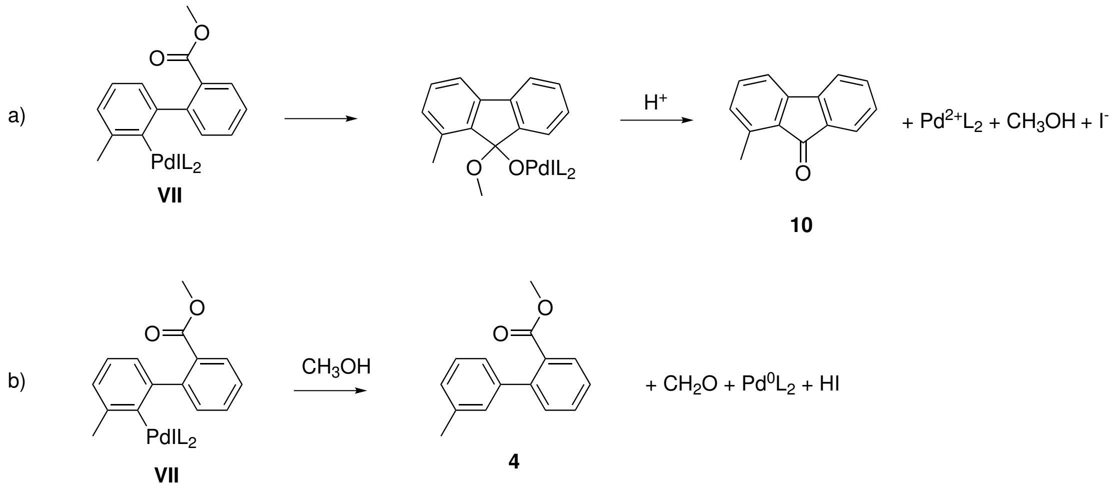
The reaction of *o*-iodotoluene and *o*-bromoacetophenone dimethyl acetale leads to the formation of the corresponding product in 45% yield. The carbonyl group of this product was deprotected after isolation by flash column chromatography,

thus the corresponding ketone **9q** is recovered. The major byproduct obtained was methanobiphenylene **2**, which removes norbornene from the reaction mixture, and greatly reduced the conversion of the substrates.
The reactivity of **o**-bromoacetophenone dimethyl acetale, compared to other electron-poor aryl bromides, confirms the fact that electronic factors affects only in part the reactivity of the aryl bromide and that coordinating factors can be complementary to the activation of the ring by the use of electron-withdrawing substituents.

2.3.1 Formations of byproducts

As already pointed out, the biaryls **9** bear a iodide functionality still reactive towards oxidative addition to palladium(0). Therefore the biarylpalladium iodide intermediate (**VII**) can also be formed by oxidative addition of the biaryl iodide to palladium(0). The biarylpalladium complex **VII** is able to react again with norbornene forming the byproducts illustrated in Scheme 2.6, in the introduction. In addition to intermolecular terminations involving norbornene, the arylpalladium complex **VII** can also react intramolecularly, in the presence of appropriate functional groups, with formation of cyclic compounds. For example, the biarylpalladium iodide intermediate **VII** obtained by an *ortho*-substituted aryl iodide and methyl *o*-bromobenzoate readily reacted to form a fluorenone derivative together with a biaryl derivative not containing the iodide functionality. Scheme 2.10 depicts a possible reaction pathway for the concomitant formation of both compounds.

Biarylpalladium intermediate **VII** forms the fluorenone derivative by intramolecular cyclization. In complex **VII**, a nucleophilic substitution to the *ortho*-carbomethoxy group in proximity to the palladium atom takes place. The resulting hemiacetal-like intermediate, in the presence of a hydrogen donor, rapidly rearranges to 9-ethylfluorenone (**10**) together with palladium in the +2 oxidation state. More-

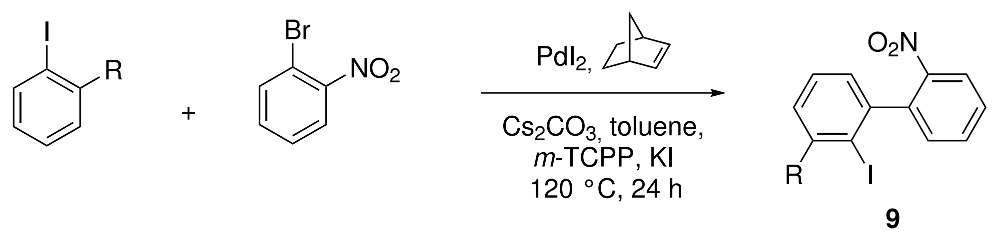


Scheme 2.10 Formation of byproducts in the catalytic reaction of *o*-iodotoluene and methyl *o*-bromobenzoate.

over, methanol, obtained as a consequence of the fluorenone formation, readily reacts with a molecule of the biarylpalladium(II) species (**VII**) to deliver the corresponding biaryl derivative and formaldehyde, and liberate palladium(0). As a consequence, the formation of these byproducts, both in *ca.* 10% yield, reduces the yield of the desired *ortho*-biaryl iodide **9a** of *ca.* 20%. This reaction proceeds according to a pathway reported by Lautens group some years ago[LautensFluo2009].
The final *o*-biaryl iodide **9** is still able to oxidatively add to palladium(0) with formation of intermediate **VII**, which in its turn proceeds, as previously described, to fluorenone **10** and biaryl **4**.
To avoid the loss of product by the formation of these compounds the reaction time has to be carefully controlled, in order to avoid the oxidative addition of the biaryl iodide **9** to palladium(0) species. We also found that compounds **4** and **10** are not formed using *t*-butyl *o*-bromobenzoate in place of the corresponding methyl ester. The bulky *t*-butyl group, as expected, avoided cyclization to fluorenone by nucleophilic attack and the consequent formation of free methanol.
When the reaction of *o*-iodoethylbenzene is carried out with **t**-butyl **o**-bromobenzoate the desired biaryl iodide was obtained with a 69% yield (Table 2.4, entry 4).

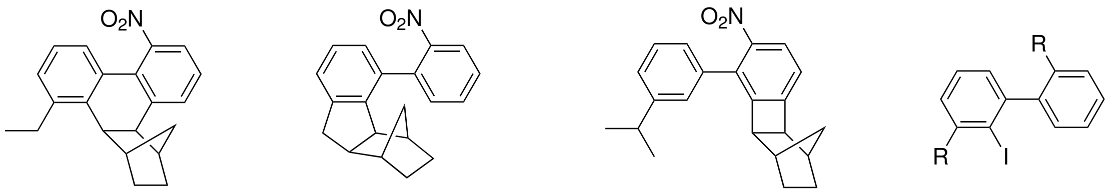
Methanobiphenylene **2**, obtained from palladacycle **IV** by reductive elimination (Scheme 2.5), was the main byproduct (8%) together with small amounts of biaryl derivative (< 5% by GC). Despite the steric hindrance, the *t*-butoxy group present on the aryl bromide does not interfere with the oxidative addition step to palladacyle **IV**, thus limiting the formation of compound **2** to 8%. This fact, together with the good stability of the final biaryl iodide **9**, allows the reaction to reach a high yield.

Among the studied aryl bromides we found that *o*-bromonitrobenzene derivatives delivered the desired products with good yields. The presence of a non-reactive group in the *ortho* position of the starting aryl bromide avoids intramolecular reactions. Nevertheless, the reaction carried out using *o*-bromonitrobenzene and its derivatives leads to byproducts formation, derived from norbornene insertion into the Pd–C bond of intermediate **VII**.



Scheme 2.11 Catalytic reaction of an *ortho* substituted aryl iodide and *o*-bromonitrobenzene.

For example the reaction of intermediate **VII** with norbornene leads to compounds **5**, **6** and **7** by the mechanism already explained in Scheme 2.6. The biaryl derivative **4** is also obtained in *ca.* 10% yield. The major byproducts formed by the reaction of aryl iodides with *o*-bromonitrobenzene are shown in Figure 2.2. The formation of these compounds containing the norbornyl structure depends on the *ortho* substituent of the initial aryl iodide. With R = Me compound **7** is obtained by C–H activation of the benzylic methyl group. While when R = Et and R = *i*-Pr the major byproducts formed are **5** and **6**, respectively. In each cases the yield of these norbornane-containing compounds is *ca.* 10–12%.



5i **6l** **7j** **8**

Fig. 2.2 Byproducts formed in the catalytic reaction of *ortho* substituted aryl iodides and *o*-bromonitrobenzene.

In addition to these byproducts each substrate leads to the formation of the corresponding compound **2**, in 10–15% yield. Moreover the biaryl iodide **8** formed by two units of the starting aryl iodide is always found, at least in traces.
Compounds **4**, **5**, **6** and **7** result from undesired reactions of intermediate **VII**. This biaryl palladium intermediate is formed both by norbornene deinsertion from **VI** and by oxidative addition of **9** to palladium(0). At the end of the reaction when the concentration of the starting aryl iodide is low the oxidative addition of **9** to palladium(0) becomes competitive. As a consequence, a prolonged reaction time increases the amount of these byproducts, therefore the conversion is kept around 90% in order to avoid these side reactions.

2.3.2 Effect of ligands

A variety of phosphine ligands have been examined. Although the formation of the product can be achieved with various arylphosphines *m*-TCPP performs better when added in 3:1 molar ratio to palladium. Other electron-poor phosphines, such as *p*-TFPP (tris(4-fluorophenyl)phosphine), do not behave equally well, and poor results were obtained using the strongly electron-donating *p*-TMPP (tris(4-methoxyphenyl)phosphine). Both steric and electronic effects appear to be at work. The great steric hindrance and the low nucleophilicity of *m*-TCPP allow a better performance even in a solvent with a large coordination inertness, such as toluene[20]. At the opposite, almost no conversion was obtained in the presence of a chelating ligand, such as DPPE.

The reaction carried out with *o*-bromonitrobenzene and an aryl iodide containing a small *ortho* group, such as *o*-iodotoluene, did not lead to the desired biaryl iodide in satisfactory yield in the presence of *m*-TCPP in 3:1 molar ratio to palladium (Table 2.5, entry 2). Increasing the ligand amount up to 4:1 molar ratio to palladium the expected compound **9h** was formed in 65% yield.

On the contrary when a bulky substituent is present in the *ortho* position of the starting aryl iodide the yield decreases in the presence of a 4:1 molar ratio of the ligand *m*-TCPP (entry 5). Steric molecular features of the substrates are an important factor influencing yield and selectivity. The steric hindrance generated by the substituents is not always sufficient to allow the final reductive elimination and should be compensated by the amount of the phosphine added.

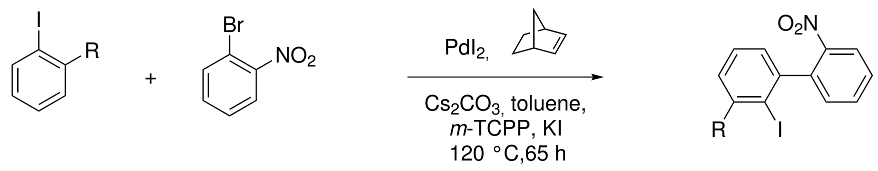
The reaction of *o*-iodotoluene with *t*-butyl *o*-bromobenzoate behaves in a similar way to the one with *o*-bromonitrobenzene as partner and gave the best yield when 4 equivalents of ligand were used (Table 2.6, entry 3). On the contrary *o*-iodoethylbenzene gave similar results irrespectively of the amount of ligand.

Therefore the bulkiness of the substituents of both the aryl halides involved in the process strongly affects the formation of the biaryl iodide. The steric effect plays a critical role in the biarylpalladium iodide species **VII** from which the organic product **9** is formed by reductive elimination of the biaryl moiety and the *cis* iodide.

2.3.3 Screening of substrates

As reported in Table 2.4, the best yields were obtained with *o*-bromobenzoic acid esters and *o*-bromonitrobenzene derivatives. However, the desired biaryl iodides were not obtained by reaction of an *ortho*-substituted aryl iodide with methyl

Table 2.5 Effect of ligand amount on the catalytic reaction of *o*-iodotoluene and *o*-iodoisopropylbenzene with *o*-bromonitrobenzene.[a]



Entry	R	Ligand (equiv)	Conversion (%)[b]	Yield (%)[b]
1	Me	2	41	18
2	Me	3	45	34
3	Me	4	88	65
4	*i*-Pr	3	96	71
5	*i*-Pr	4	87	53

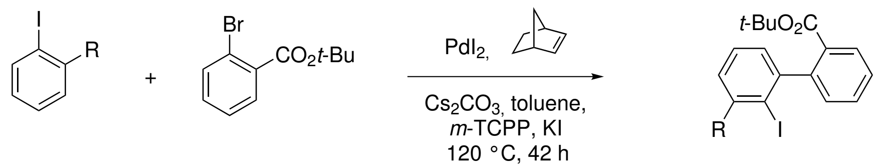
[a] Reaction of an *ortho*-substituted aryl iodide and *o*-bromonitrobenzene in the presence of PdI_2, KI, norbornene, Cs_2CO_3 as a base in the following molar ratio: 1/15/10/45/20/20. $[Pd] = 2.2 \times 10^{-3}$ mmol/ml. [b] Determined by NMR using internal standard, conversion calculated on ArBr.

p-bromobenzoate or *p*-bromonitrobenzene, not containing the functional group in adjacent position to the bromide.

When *o*-iodoethylbenzene reacted with *p*-bromonitrobenzene, under the general conditions reported in Table, only the methanobiphenylene **2** from the aryl iodide, was isolated in 24% yield. The reaction of *o*-iodoethylbenzene was also carried out with methyl *p*-bromobenzoate, *p*-chlorobromobenzene and the corresponding *meta*-substituted compounds with analogous results (Scheme 2.12).

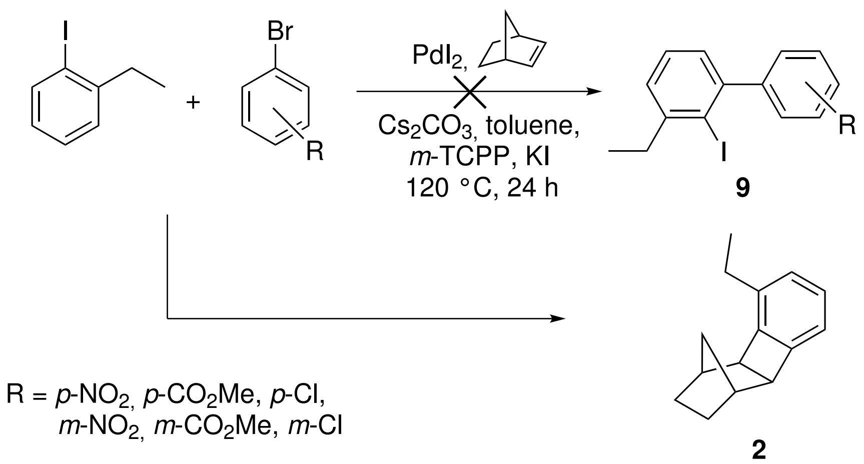
The formation of compound **2** is usually observed when the aryl bromide is poorly reactive towards the Pd(II)/Pd(IV) oxidative addition. However, *p*-bromobenzoate and *p*-bromonitrobenzene are known to be very reactive compounds towards the oxidative addition to palladium(II) and this behavior was unexpected. Since the lack of an *ortho* substituent on the aryl bromide would determine a minor steric hindrance around the metal group of complex **VII**, we have supposed that the

Table 2.6 Effect of ligand amount on the catalytic reaction of *o*-iodotoluene and *o*-iodoethylbenzene with *t*-butyl *o*-bromobenzoate.[a]



Entry	R	Ligand (equiv)	Conversion (%)[a]	Yield (%)[a]
1		2	39	27
2	Me	3	91	64
3		4	92	71
4		2	96	65
5	Et	3	91	68
6		4	93	69

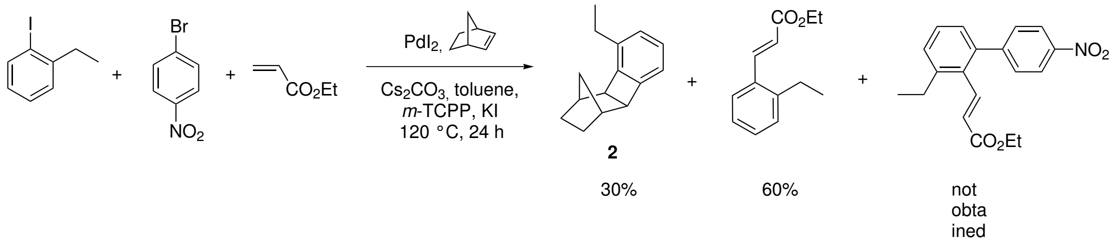
[a] Reaction of an *ortho*-substituted aryl iodide and *t*-butyl *o*-bromobenzoate in the presence of PdI_2, KI, norbornene, Cs_2CO_3 as a base in the following molar ratio: 1/15/10/45/20/20. [Pd] = 2.2×10^{-3} mmol/ml. [b] Determined by NMR using internal standard, conversion calculated on ArBr.



Scheme 2.12 Methyl *p*-bromobenzoate, *o*-bromonitrobenzene, *p*-chlorobromobenzene and their *meta*-substituted analogue does not afford the corresponding *o*-biaryl iodide.

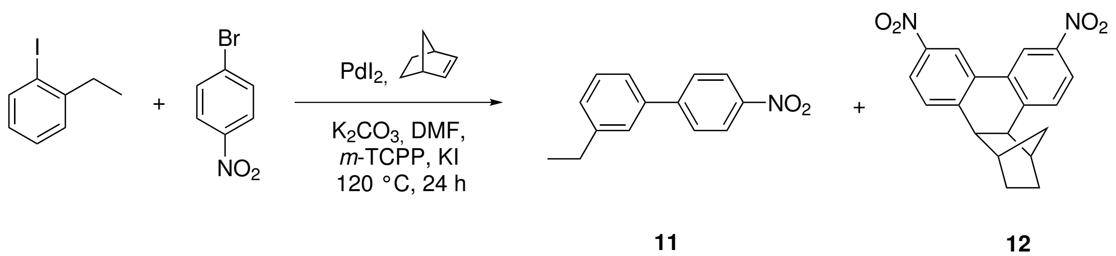
reduced bulkiness caused a slower rate of reductive elimination, as observed by Hartwig in stoichiometric experiments[18]. If this were the case the biarylpalladium iodide complex **VII** could be trapped by a very reactive terminating agent such as an olefin.

The reaction of *o*-iodoethylbenzene and *p*-bromonitrobenzene carried out in the presence of ethyl acrylate was unsuccessful in obtaining the biarylated olefin, the Heck product between the starting aryl iodide and the olefin is formed in *ca.* 60% yield, together with 30% of compound **2**. The aryl bromide was recovered unaltered almost quantitatively (Scheme 2.13, >90%).



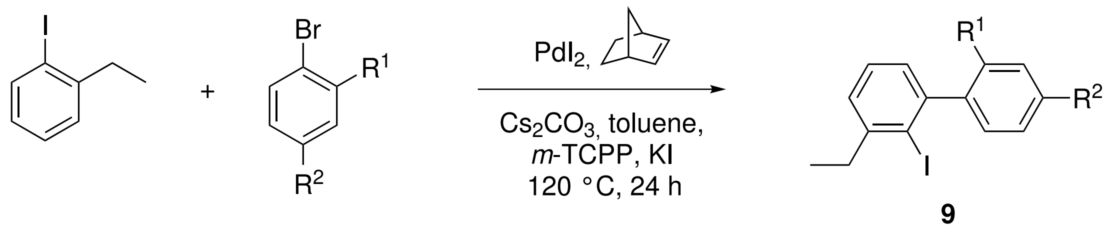
Scheme 2.13 Reaction of *o*-iodoethylbenzene and *p*-bromonitrobenzene in the presence of ethyl acrylate does not afford the corresponding biarylated olefin.

When the same reaction was carried out in DMF with K_2CO_3 as a base the desired biarylated olefin was obtained in high yield, as described in the introduction section. Therefore we attributed the particular inertness of *p*-substituted aryl bromides to the solvent effect. However, the desired biaryl iodide was not obtained in an experiment carried out in DMF, either, as shown in Scheme 2.14.



Scheme 2.14 Reaction of *o*-iodoethylbenzene and *p*-bromonitrobenzene in DMF.

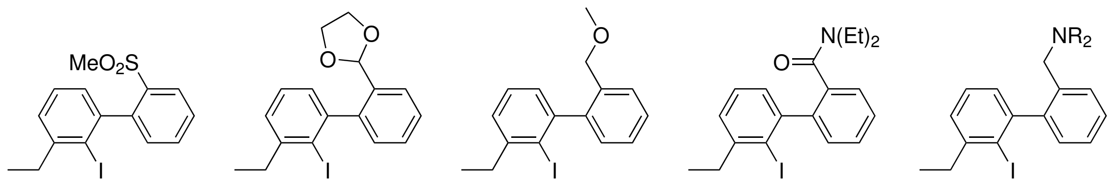
The reaction carried out replacing toluene with DMF and Cs_2CO_3 with K_2CO_3 gave a 22% yield of the biaryl derivative **11** and a 14% yield of the methanotriphenylene compound **12**. The formation of compounds of type **12** under these conditions has been previously reported by our research group and others.
Since *p*-bromonitrobenzene was not reactive under our reaction condition we tried to investigate the effect of the addition of an *ortho* methyl group to this compound. Two parallel experiments were carried out using 2-methyl-4-nitrobromonzene (R^1 = Me, R^2 = NO_2) and 2-nitro-4-methylbromobenzene (R^1 = NO_2, R^2 = Me) under the general reaction conditions. The desired biaryl iodide is obtained only with the substrate bearing the nitro group at the *ortho* position.



R^1 = NO_2, R^2 = Me: **9m**, yield = 62%
R^1 = Me, R^2 = NO_2: no product

Scheme 2.15 Comparison of the reactivity of 2-methyl-4-nitrobromonzene (R^1 = Me, R^2 = NO_2) and 2-nitro-4-methylbromobenzene (R^1 = NO_2, R^2 = Me)

In order to investigate the substrate scope of the reaction we carried out a screening of several aryl bromides. We focused our attention on electron-poor aryl bromides bearing a functional group with a low coordinating character at the *ortho* position. Some results are summarized in Figure 2.3. When the reaction of *o*-iodoethylbenzene is carried out with *o*-bromomethylsulfone under the general conditions, only a 20% yield of the desired product **9r** is obtained. The reaction of 2-(2-bromophenyl)-1,3-dioxolane and 2-bromobenzyl methyl ether as aryl bromides gave poor results (**9s**, **9t**). The first reagent gave a high yield of the hydrogenolysis product while the latter shows a low tendency to undergo the Pd(II)/Pd(IV) oxidative addition, therefore an high yield of methanobiphenylene **2** is obtained. The reaction with *N,N*-diethyl-2-bromobenzamide was also unsuccessful and a very low amount of product **9u** is obtained. Other nitrogen containing compounds, such as *N,N*-disubstituted benzylamines (Figure 2.3, **9w**, R = Et and R = $(CH_2)_4$) gave no product at all.



9r 20% | **9s** < 10% | **9t** traces | **9u** traces | **9w** traces

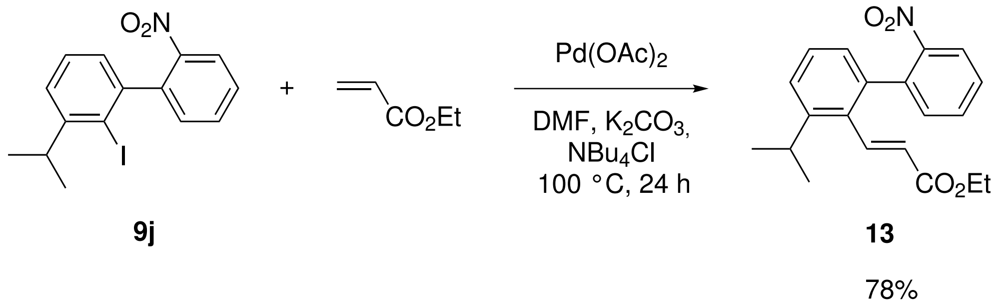
Fig. 2.3 Poorly reactive aryl bromides.

2.3.4 Reactivity of the *o*-biaryl iodides

Finally we have checked the reactivity of the products obtained in this catalytic process. A Heck reaction was carried out using 2-iodo-3-isopropyl-2'-nitro-1,1'-biphenyl and ethyl acrylate, in the presence of $Pd(OAc)_2$ as catalyst, K_2CO_3 as a base and NBu_4Cl in DMF at 100°C, following a known procedure[16]. The vinylation of the biaryl compound, under the reported conditions,leads to a 78% yield with a 92% conversion is obtained after 24 h (Scheme 2.16).

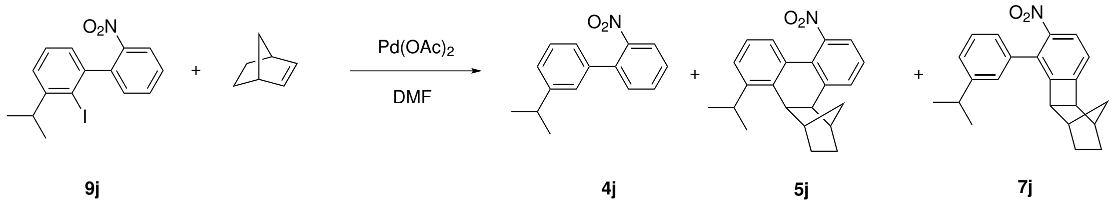
In further experiment we carried out the reaction of the same *o*-iodobiaryl derivative with norbornene. As previously discussed, the expected Heck product is not obtained with norbornene. As shown in the Scheme, this reaction leads to the formation of compounds of type **4**, **5** and **7**, in a 1:1:1 molar ratio. This reaction requires harsh conditions, a four-time excess of the olefin and a long reaction time to go to completion.

These organic compounds derive from the intermediates that we have encountered in the catalytic pathway leading to the *o*-biaryl iodide. By oxidative addition



Scheme 2.16 The Heck reaction of compound **9j** and ethyl acrilate afford the corresponding biarylated olefin in high yield.

of product **9j** to a palladium(0) species intermediate **VII** is obtained. From **VII**, hydrogenolysis of the Pd–C bond leads to the organic compound **4j**, while norbornene insertion forms complex **VI**. The latter can cyclize to compounds **5j** and **7j**, in accordance with the mechanism previously reported (Scheme 2.17).



Scheme 2.17 Reaction of compound **9j** and norbornene leads to the byproducts obtained by its synthesis.

2.4 Conclusions

In conclusions we have developed a palladium/norbornene catalyzed process for the synthesis of *ortho*-biaryl iodides from simple and readily available starting materials. The reaction occurs in relatively mild conditions and leads to the formation of one C–C and a C–I bonds in *one-pot*. *ortho*-Substituted aryl iodides and bromides are the preferred substrates for the reaction and afford the corresponding *o*-biaryl iodides in moderate to good yields. The reaction can be also carried out using only an *ortho*-substituted aryl iodide as substrate, but in this case lower yields are obtained. The formation of the C–I bond is supposed to occur by reductive elimination from a palladium(II) species. In the literature only few palladium catalyzed processes which leads to the formation of a C–I bond are known but, to the best of our knowledge, this is the first example of catalytic $C_{(aryl)}$–I bond formation.

We had been able to accomplish this challenging goal by combining the appropriate molecular features of the organometallic intermediates involved in the catalytic cycle and the steric and electronic effect of *m*-TCPP ligand.

The reactivity of the final product towards oxidative addition is reduced by the increased steric hindrance around the iodide. However, when the concentration of the *o*-biaryl iodide increases, its oxidative addition becomes competitive to that of the starting aryl iodide, leading to formation of byproducts containing the norbornyl fragment.

The results obtained are satisfactory in the light of the complexity of the reaction mechanism however there is still space for improvements.

2.5 Experimental

2.5.1 Instrumentation

All reactions were carried out under N_2 in a Schlenk-type tube. Most reagents were purchased from common suppliers and usually employed without further purification. *o*-Iodoethylbenzene[21] and *o*-iodoisopropylbenzene[22] were prepared by Sandmeyer reaction from the corresponding anilines. 2-Bromo-5-methyl-nitrobenzene, 2-bromo-4-chloro-nitrobenzene and 2-bromo-4-fluoronitrobenzene are synthesized by oxidation of the corresponding aniline[23]. **o**-Bromoacetophenone was converted into the corresponding dimethyl acetale according to the literature[24].

Gaschromatographic analysis were performed with a Agilent Technologies 7820A GC System using a 30 m SE-30 capillary column. Flash column chromatography is

conducted using Merck Kiesegel 60 as stationary phase and thin layer chromatography using Merck 60F254 plates. A mixture of *n*-hexane/EtOAc in the reported ratios is used as eluent.
Electron impact mass spectra (m/z, relative intensity (%)) were determined with an Agilent Technologies 6890N GC system and 5973 Mass selective detector working at 70 eV ionization energy. High resolution mass analyses were performed using a Thermo Scientific LTQ ORBITRAP XL mass spectrometer.
Uncorrected melting points were determined with an Electrothermal apparatus. ^{1}H and^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE 400 spectrometer at 400 and 100 MHz, respectively and on a Bruker AVANCE 300 spectrometer at 300 and 75.4 MHz, respectively, using the solvent peak as internal reference.
IR spectra were recorded on a Nicolet FT-IR 5700 spectrophotometer (Thermo Electron Corporation).

2.5.2 Preparations of starting materials

Palladium iodide To a 500 ml round bottom flask containing a suspension of $PdCl_2$ (1g, 5.7 mmol) in 200 ml distilled H_2O, 75 ml of conc. HCl are added. The mixture is stirred at room temperature until complete dissolution of the solid. The solution is then heated at 80 °C and a solution of KI (2g, 12.0 mmol) in 30 ml of distilled H_2O is added. The black precipitate is collected by suction filtration, washed with distilled H_2O and dried at 80 °C under vacuum. Yield 1.86 g (91%).

2.5.3 Procedures for palladium/norbornene catalyzed reactions

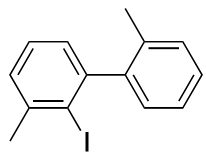
General procedure for the synthesis of biaryl iodides from aryl iodides
Cesium carbonate (165 mg, 0.50 mmol) is heated at 110 °C under vacuum in a Schlenk type tube for 1.5 h. After cooling to room temperature the tube is filled with nitrogen and evacuated three times. A toluene solution (3.7 ml) of the aryl iodide (0.45 mmol) and norbornene (10.6 mg, 0.11 mmol) is added to the

flask, followed by $PdCl_2$ (2.0 mg, 0.0113 mmol), tris(4-chlorophenyl)phosphine (8.3 mg, 0.022 mmol) and KI (18.8 mg, 0.11 mmol) as solids. The reaction flask is transferred into an oil bath at 120°C until the end of the reported reaction time. After cooling the mixture is diluted with ethyl acetate (30 ml) transferred to a separatory funnel and washed twice with water (25 ml). The resulting solution is dried over$Na_2SO_4$and the solvent was removed under vacuum. The crude mixture is separated by flash column chromatography on silica gel using *n*-hexane eluent.

General procedure for the synthesis of biaryl iodides from aryl iodides and bromides
Cesium carbonate (120 mg, 0.37 mmol) is heated at 110 °C under vacuum in a Schlenk type tube for 1.5 h. After cooling to room temperature the tube is filled with nitrogen and evacuated three times. A toluene solution (3.7 ml) of the aryl iodide (0.17 mmol), the aryl bromide (0.16 mmol) and norbornene (7.8 mg, 0.0830 mmol) is added to the flask, followed by $PdCl_2$ (3.0 mg, 0.0083 mmol), tris(3-chlorophenyl)phosphine (9.1 mg, 0.0249 mmol) and KI (20.8 mg, 0.1253 mmol) as solids. The reaction mixture is stirred under N_2 at r.t. for 10 minutes and transferred into an oil bath at 120°C until the end of the reported reaction time. After cooling the mixture is diluted with ethyl acetate (30 ml) transferred to a separatory funnel and washed twice with water (25 ml). The resulting solution is dried over$Na_2SO_4$and the solvent was removed under vacuum. The crude mixture is separated by flash column chromatography on silica gel using the reported eluent.

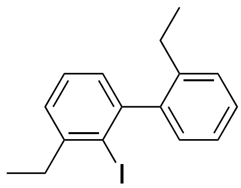
2.5.4 Characterizations

2-Iodo-2',3-dimethyl-1,1'-biphenyl (**8a**)



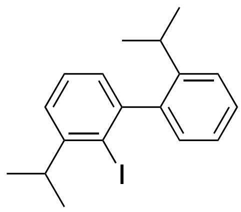
MS (EI, 70 eV): *m/z* 308 (M^+, 100), 181 (40), 178 (15), 165 (65).

2',3-Diethyl-2-iodo-1,1'-biphenyl (**8b**)



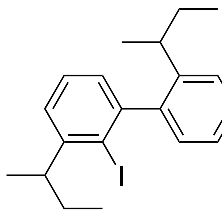
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.39–7.36 (1H, m), 7.35–7.30 (1H, m), 7.29 (1H, t, J = 7.6 Hz), 7.29–7.25 (1H, m), 7.20 (1H, dd, J = 7.6, 1.8 Hz), 7.06–7.02 (2H, m), 2.85 (2H, q, J = 7.6 Hz), 2.48–2.77 (2H, m), 1.27 (3H, t, J = 7.6 Hz), 1.09 (3H, t, J = 7.6 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 147.5, 147.2, 145.3, 141.4, 129.5, 128.1, 127.9, 127.7, 127.3, 126.8, 125.4, 107.0, 35.5, 26.2, 14.8, 14.7. MS (EI, 70 eV): *m/z* 336 (M^+, 60), 209 (23), 181 (100), 179 (54), 165 (71).

2-Iodo-2',3-di-i-propyl-1,1'-biphenyl (**8c**)



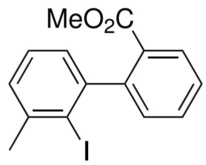
MS (EI, 70 eV): *m/z* 364 (M^+, 23), 237 (10), 195 (100), 179 (30), 165 (18), 152 (5).

2',3-Di-sec-butyl-2-iodo-1,1'-biphenyl (**8d**)



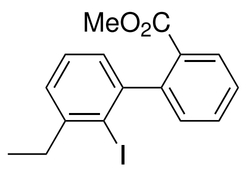
MS (EI, 70 eV): *m/z* 392 (M^+, 16), 209 (100), 180 (24), 179 (42), 165 (18).

2-Iodo-2'-methoxycarbonyl-3-methyl-1,1'-biphenyl (**9a**)



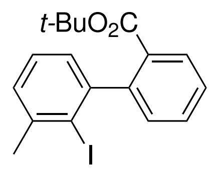
Yellow solid, yield 43%,eluent *n*-hexane/EtOAc 96:4. ^{1}H NMR (400.13 MHz,$CDCl_3$): δ 8.04 (1H, ddd, J = 7.8, 1.0, 0.4 Hz), 7.57 (1H, td, J = 7.5, 1.4 Hz), 7.47 (1H, ddd, J = 7.8, 7.6, 1.3 Hz), 7.26 (1H, t, J = 7.8 Hz), 7.21–7.19 (2H, m), 6.99 (1H, ddd, J = 7.2, 1.9, 0.5 Hz), 3.66 (3H, s), 2.53 (3H, s). ^{13}C NMR (100.62 MHz,$CDCl_3$): δ 167.1, 147.8, 146.9, 141.8, 132.0, 131.2, 130.3, 129.8, 128.3, 127.9, 127.5, 126.2, 105.9, 52.1, 29.8. MS (EI, 70 eV): *m/z* 225 (100), 210 (45), 181 (18), 165 (22). IR (neat, cm^{-1}): ν 2947, 1718, 1430, 1264, 1091, 1065, 1009, 788, 775, 706, 669.

2-Iodo-3-ethyl–2'-methoxycarbonyl -1,1'-biphenyl (**9b**)



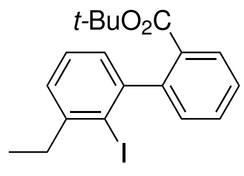
White solid, isolated yield 57%, eluent *n*-hexane/EtOAc 96:4, m.p. (*n*-hexane): 72 °C. ^{1}H NMR (400.13 MHz,$CDCl_3$): δ 8.03 (1H, ddd, J = 7.8, 1.4, 0.4 Hz), 7.57 (1H, td, J = 7.5, 1.5 Hz), 7.47 (1H, ddd, J = 7.8, 7.5, 1.4 Hz), 7.30 (1H, t, J = 7.5 Hz), 7.23–7.17 (2H, m), 7.00 (1H, dd, J = 7.4, 1.7 Hz), 3.64 (3H, s), 2.85 (2H, q, J = 7.5 Hz), 1.26 (3H, t, J = 7.5 Hz). ^{13}C NMR (100.62 MHz,$CDCl_3$): δ 167.0, 147.9, 146.9, 146.7, 131.8, 131.1, 130.1, 129.8, 127.8, 127.6, 126.8, 126.3, 105.2, 52.0, 35.4, 14.7. MS (EI, 70 eV): m/z 239 (100), 209 (32), 165 (10), 152 (12). IR (neat, cm^{-1}): ν 2968, 1721, 1575, 1264, 1093, 1007, 802, 762, 706, 668.

*2-Iodo-3-methyl-2'-*t*-butoxycarbonyl-1,1'-biphenyl* (**9c**)



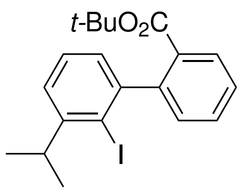
Pale yellow oil, eluent *n*-hexane/EtOAc 98:2, yield 60%. ^{1}H NMR (400.13 MHz,$CDCl_3$): δ 7.97 (1H, d, J = 7.7 Hz), 7.52 (1H, t, J = 7.4 Hz), 7.45 (1H, t, J = 7.5 Hz), 7.26–7.18 (2H, m), 7.15 (1H, d, J = 7.7 Hz), 6.98 (1H, d, J = 7.1 Hz), 2.53 (3H, s), 1.19 (9H, s). ^{13}C NMR (100.62 MHz,$CDCl_3$): δ 166.5, 148.4, 145.7, 141.6, 132.0, 131.1, 130.8, 130.1, 127.9, 127.7, 127.3, 126.4, 106.5, 80.9, 29.7, 27.6. MS (EI, 70 eV): m/z 211 (100), 194 (12), 165 (26).

*2-Iodo-3-ethyl-2'-*t*-butoxycarbonyl-1,1'-biphenyl* (**9d**)



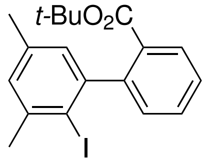
White solid, eluent *n*-hexane/EtOAc 97:3, yield 57%, m.p. (*n*-hexane): 67 °C. ^{1}H NMR (400.13 MHz,$CDCl_3$): δ 7.98 (1H, dd, J = 7.7, 1.4 Hz), 7.52 (1H, td, J = 7.4, 1.5 Hz), 7.45 (1H, td, J = 7.6, 1.4 Hz), 7.28 (1H, t, J = 7.5 Hz), 7.19 (1H, dd, J = 7.6, 1.7 Hz), 7.15 (1H, dd, J = 7.45, 1.3 Hz), 7.00 (1H, dd, J = 7.4, 1.7 Hz), 2.85 (2H, q, J = 7.5 Hz), 1.26 (3H, t, J = 7.5 Hz), 1.19 (9H, s). ^{13}C NMR (100.62 MHz,$CDCl_3$): δ 166.6, 148.6, 146.7, 145.9, 132.0, 131.1, 130.9, 130.1, 127.7, 127.6, 126.7, 126.6, 105.7, 80.9, 35.4, 27.6, 14.8. MS (EI, 70 eV): *m/z* 225 (100), 209 (10), 178 (8), 165 (10), 152 (10).

*2-Iodo-3-*i*-propyl-2'-*t*-butoxycarbonyl-1,1'-biphenyl* (**9e**)



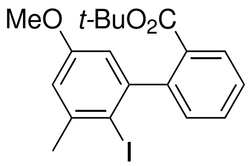
Colorless oil, eluent *n*-hexane/EtOAc 97:3, yield 62%. ^{1}HNMR (400.13 MHz,$CDCl_3$): δ 7.98 (1H, dd, J = 7.7, 1.3Hz), 7.52 (1H, td, J = 7.4, 1.5 Hz), 7.45 (1H, td, J = 7.6, 1.4 Hz), 7.31 (1H, t, J = 7.5 Hz), 7.20 (1H, dd, J = 7.8, 1.6 Hz), 7.16 (1H, dd, J = 7.5, 1.2Hz), 7.01 (1H, dd, J = 7.3, 1.7 Hz), 3.37 (1H, heptet, J = 6.8 Hz), 1.28 (3H, d, J = 6.8 Hz), 1.27 (3H, d, J = 6.8 Hz), 1.17 (9H, s). ^{13}CNMR (100.62 MHz,$CDCl_3$): δ 166.7, 150.6, 148.5, 146.2, 132.0, 131.1, 130.9, 130.1, 127.7, 126.9, 124.1, 106.5, 80.9, 38.9, 27.6, 23.4, 23.3. MS (EI, 70 eV): *m/z* 239 (100), 223 (15), 197 (10), 178 (17), 165 (10), 152 (10).

*2-Iodo-3,5-dimethyl-2'-*t*-butoxycarbonyl-1,1'-biphenyl* (**9f**)



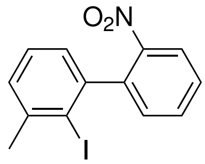
Colorless oil, eluent *n*-hexane/EtOAc 97:3, yield 68 ^{1}HNMR (400.13 MHz,$CDCl_3$): δ 7.94 (1H, d, J = 7.7, 1.3 Hz), 7.51 (1H, td, J = 7.5, 1.4 Hz), 7.44 (1H, td, J = 7.6, 1.0 Hz), 7.16 (1H, dd, J = 7.6, 1.0 Hz), 7.04 (1H, s), 6.83 (1H, s), 2.48 (3H, s), 2.28 (3H, s), 1.20 (9H, s). ^{13}CNMR (100.62 MHz,$CDCl_3$): δ 166.8, 148.1, 145.7, 141.4, 137.2, 132.2, 131.1, 130.9, 130.0, 129.0, 127.7, 127.5, 102.4, 80.9, 29.6, 27.7, 20.8. MS (EI, 70 eV): m/z 225 (100), 208 (10), 165 (16).

*2-Iodo-5-methoxy-3-methyl-2'-*t*-butoxycarbonyl-1,1'-biphenyl* (**9g**)



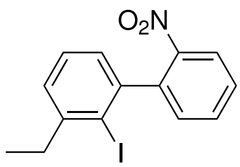
White solid, eluent *n*-hexane/EtOAc 96:4, yield 66%, m.p. (*n*-hexane): 89 °C. ^{1}HNMR (400.13 MHz,$CDCl_3$): δ 7.96 (1H, dd, J = 7.6, 1.2 Hz), 7.52 (1H, td, J = 7.4, 1.5 Hz), 7.45 (1H, ddd, J = 7.7, 7.5, 1.4 Hz), 7.16 (1H, dd, J = 7.6, 1.1 Hz), 6.82 (1H, d, J = 3.0 Hz), 6.60 (1H, d, J = 3.0 Hz), 3.76 (3H, s), 2.49 (3H, s), 1.22 (9H, s). ^{13}CNMR (100.62 MHz,$CDCl_3$): δ 166.7, 159.1, 149.0, 145.6, 142.6, 132.1, 131.2, 130.8, 130.1, 127.9, 114.6, 112.1, 95.4, 81.0, 55.5, 29.8, 27.7. MS (EI, 70 eV): m/z 241 (100), 224 (8), 152 (18). IR (neat, cm^{-1}): ν 2970, 1717, 1579, 1529, 1077, 1049, 848, 759, 709.

2-Iodo-3-methyl-2'-nitro-1,1'-biphenyl (**9h**)



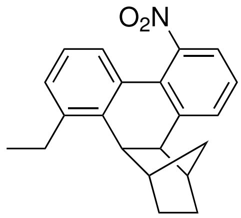
Yellow solid, eluent *n*-hexane/EtOAc 95:5, isolated yield 53%, m.p. (*n*-hexane): 101–103 °C. ^{1}HNMR (300.11 MHz,$CDCl_3$): δ 8.10 (1H, dd, J = 8.2, 1.1 Hz), 7.67 (1H, td, J = 7.5, 1.4 Hz), 7.58 (1H, td, J = 8.2, 1.4 Hz), 7.32–7.24 (3H, m), 7.01 (1H, dd, J = 7.0, 1.7 Hz), 2.53 (3H, s). ^{13}CNMR (100.62 MHz,$CDCl_3$): δ 148.0, 144.2, 142.4, 140.2, 133.0, 132.4, 129.0, 128.9, 127.8, 126.0, 124.4, 105.1, 29.6. MS (EI, 70 eV): m/z 212 (100), 181 (22), 165 (27), 152 (14). IR (KBr, cm^{-1}): ν 2982, 1518, 1354, 787, 750.

2-Iodo-3-ethyl-2'-nitro-1,1'-biphenyl (**9i**)



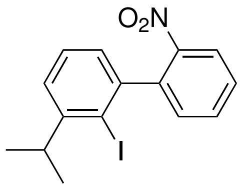
Pale yellow solid, eluent *n*-hexane/EtOAc 95:5, yield 62%, m.p. (*n*-hexane) 80 °C. ^{1}HNMR (400.13 MHz,$CDCl_3$): δ 8.10 (1H, dd, J = 8.2, 1.1 Hz), 7.67 (1H, td, J = 7.5, 1.3 Hz), 7.57 (1H, ddd, J = 8.2, 7.5, 1.5 Hz), 7.33 (1H, t, J = 7.6 Hz), 7.31 (1H, dd, J = 7.6, 1.3 Hz), 7.24 (1H, dd, J = 7.7, 1.7 Hz), 7.01 (1H, dd, J = 7.4, 1.7 Hz), 2.84 (2H, q, J = 7.5 Hz), 1.26 (3H, t , J = 7.5 Hz). ^{13}CNMR (100.62 MHz,$CDCl_3$): δ 148.0, 147.4, 144.4, 140.4, 133.0, 132.5, 128.8, 128.1, 127.6, 126.2, 124.4, 104.5, 35.3, 14.6. MS (EI, 70 eV): m/z 226 (100), 181 (20), 180 (12), 165 (20), 154 (11). IR (KBr, cm^{-1}): ν 2965, 1521, 1343, 791.

5-Ethyl-9-nitro-1,2,3,4,4a,12b-hexahydro-1,4-methanotriphenylene (**5i**)



m.p. (n-hexane): 121 °C. ^{1}HNMR (400.13 MHz,$CDCl_3$): δ 7.43 (1H, d, J = 7.8 Hz), 7.37 (1H, d, J = 7.6 Hz), 7.21 (1H, t, J = 7.8 Hz), 7.19 (1H, t, J = 4.6 Hz), 7.10 (2H, d, J = 4.6 Hz), 3.35 (1H, d, J = 9.6 Hz), 3.11 (1H, d, J = 9.5 Hz), 2.67 (2H, m, J = 7.5 Hz), 2.37 (1H, s), 2.25 (1H, d, J = 4.4 Hz), 1.85–1.61 (4H, m), 1.42 (1H, d, J = 10.4 Hz), 1.28 (3H, t, J = 7.5 Hz), 1.10 (1H, d, J = 10.4 Hz). ^{13}CNMR (100.62 MHz,$CDCl_3$): δ 149.3, 142.9, 142.4, 134.0, 132.0, 129.2, 128.2, 127.5, 126.9, 126.7, 124.6, 122.8, 48.6, 47.4, 46.8, 42.9, 33.5, 31.8, 28.7, 25.2, 14.6. MS (EI, 70 eV): m/z 319 (M^+, 100), 181 (26), 165 (24), 152 (24). IR (neat, cm^{-1}): ν 2966, 1522, 1352, 738.

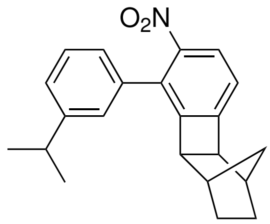
*2-Iodo-3-*i*-propyl-2'-nitro-1,1'-biphenyl* (**9j**)



Pale yellow solid, eluent n-hexane/EtOAc 95:5, isolated yield 61%, m.p. (n-hexane): 68°C. ^{1}HNMR (400.13 MHz,$CDCl_3$): δ 8.10 (1H, dd, J = 8.2, 1.0 Hz), 7.67 (1H, td, J = 7.5, 1.2 Hz), 7.56 (1H, ddd, J = 8.2, 7.5, 1.4 Hz), 7.35 (1H, t, J = 7.5 Hz), 7.31 (1H, dd, J = 7.6, 1.2 Hz), 7.25 (1H, dd, J = 7.8, 1.6 Hz), 7.02 (1H, dd, J = 7.3, 1.6 Hz), 3.35 (1H, hept, J = 6.8 Hz), 1.29 (3H, d, J = 6.8 Hz), 1.27 (3H, d, J = 6.8 Hz); ^{13}CNMR (100.62 MHz,$CDCl_3$): δ 151.3, 148.0, 144.4, 140.8, 133.0, 132.5, 128.8, 128.2, 126.4, 125.0, 124.3, 105.3, 38.9, 23.3, 23.2. MS (EI, 70 eV): m/z

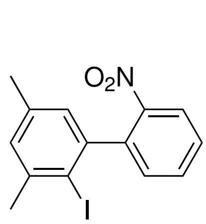
240 (100), 212 (55), 194 (32), 165 (30), 152 (28). IR (KBr, cm^{-1}): ν 2959, 1518, 1350, 791.

5-(3-isopropylphenyl)-6-nitro-1,2,3,4,4a,8b-hexahydro-1,4-methanobiphenylene (**7j**)



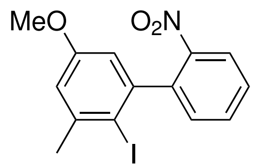
^{1}HNMR (400.13 MHz,$CDCl_3$): δ 7.87 (1H, d, J = 7.8 Hz), 7.33 (1H, t, J = 7.6 Hz), 7.22 (1H, d, J = 7.6 Hz), 7.15 (1H, s), 7.11 (1H, d, J = 7.6 Hz), 7.05 (1H, d, J = 7.7 Hz), 3.20 (2H, s), 2.94 (1H, heptet, J = 6.9 Hz), 2.35 (1H, d, J = 3.7 Hz), 2.14 (1H, d, J = 3.9 Hz), 1.70–1.51 (4H, m), 1.28 (3H, s), 1.26 (3H, s), 1.03 (1H, d, J = 10.4 Hz), 0.94 (1H, d, J = 10.4 Hz). ^{13}CNMR (100.62 MHz,$CDCl_3$): δ 151.5, 149.0, 148.3, 146.5, 134.1, 131.4, 128.4, 126.2, 126.1, 125.3, 124.6, 121.4, 49.8, 49.4, 36.6, 36.5, 34.0, 31.9, 27.7, 27.5, 24.0, 23.9. MS (EI, 70 eV): m/z 333 (M^+, 100), 292 (25), 274 (42), 250 (35), 215 (66), 202 (72), 189 (25).

2-Iodo-3,5-dimethyl-2'-nitro-1,1'-biphenyl (**9k**)



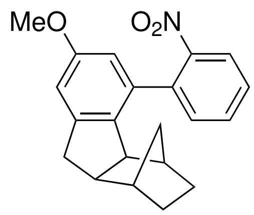
Yellow solid, eluent n-hexane/EtOAc 95:5, isolated yield 61%,m.p. (n-hexane): 119 °C. ^{1}HNMR (300.11 MHz,$CDCl_3$): δ 8.09 (1H, dd, J = 8.2, 1.2 Hz), 7.67 (1H, td, J = 7.5, 1.3 Hz), 7.55 (1H, ddd, J = 8.1, 7.5, 1.5 Hz), 7.29 (1H, dd, J = 7.6, 1.4 Hz), 7.08 (1H, d, J = 1.4 Hz), 6.83 (1H, d, J = 1.4 Hz), 2.48 (3H, s), 2.29 (3H, s). ^{13}CNMR (100.62 MHz,$CDCl_3$): δ 148.2, 144.1, 142.1, 140.4, 137.8, 133.0, 132.6, 130.2, 128.9, 127.0, 124.4, 101.1, 29.4, 20.9. MS (EI, 70 eV): m/z 226 (100), 198 (28), 183 (20), 165 (24). IR (neat, cm^{-1}): ν 1519, 1348, 1007, 867, 789, 751, 720, 700.

2-Iodo-5-methoxy-3-methyl-2'-nitro-1,1'-biphenyl (**9l**)



White solid, eluent n-hexane/EtOAc 90:10, isolated yield 61%, m.p. (n-hexane): 126–128 °C. ^{1}HNMR (400.13 MHz,$CDCl_3$): δ 8.09 (1H, d, J = 8.1 Hz), 7.67 (1H, t, J = 7.4 Hz), 7.56 (1H, t, J = 7.4 Hz), 7.30 (1H, d, J = 7.4 Hz), 6.85 (1H, d, 2.7 Hz), 6.60 (1H, d, 2.7 Hz), 3.78 (3H, s), 2.49 (3H, s). ^{13}CNMR (100.62 MHz,$CDCl_3$): δ 159.3, 148.0, 144.8, 143.2, 140.0, 133.0, 132.3, 128.9, 124.4, 115.0, 112.2, 93.8, 55.4, 29.6. IR (KBr, cm^{-1}): ν 2962, 1522, 1349, 756.

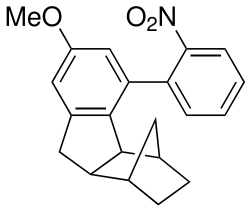
7-methoxy-5-(2-nitrophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (**9l**)



^{1}H NMR (400.13 MHz, DMSO-d^6): δ 8.02 (1H, d, J = 7.9 Hz), 7.76 (1H, t, J = 7.2 Hz), 7.64 (1H, t, J = 7.6 Hz), 7.58–7.46 (1H, m), 6,74 (1H, d, J = 1.7 Hz), 6.49 (1H, broad s.), 3.70 (3H, s), 3.27–3.10 (1H, m), 2.53 (1H, d), 2.50 (3H, s), 1.98 (1H, s), 1.4–0.7 (6H, m). MS (EI, 70 eV): m/z 242 (100), 227 (20), 214 (45), 199

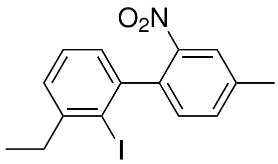
(38), 170 (35), 152 (72), 141 (35), 115 (52).

7-Methoxy-5-(2-nitrophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (**6l**)



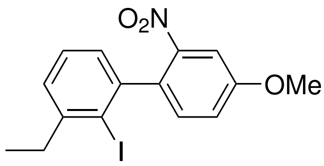
^{1}H NMR (400.13 MHz, DMSO-d_6): 8.02 (1H, d, J = 7.9 Hz), 7.76 (1H, t, J = 7.2 Hz), 7.64 (1H, t, J = 7.6 Hz), 7.58–7.46 (1H, m), 6,74 (1H, d, J = 1.7 Hz), 6.49 (1H, broad s.), 3.70 (3H, s), 3.27–3.10 (1H, m), 2.53 (1H, d), 2.50 (3H, s), 1.98 (1H, s), 1.4–0.7 (6H, m).

3-Ethyl-2-iodo-4'-methyl-2'nitro-1,1'-biphenyl (**9m**)



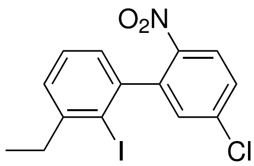
Pale yellow oil, eluent n-hexane/EtOAc 97:3, isolated yield 50%. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.91 (1H, s further split), 7.48 (1H, d further split, J = 7.8 Hz), 7.31 (1H, t, J = 7.6 Hz), 7.22 (1H, dd, J = 7.6, 1.7 Hz), 7.18 (1H, d, J = 7.8 Hz) 7.00 (1H, dd, J = 7.4, 1.7 Hz), 2.83 (2H, q, J = 7.5 Hz), 2.51 (3H, s), 1.26 (3H, t, J = 7.5 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 148.0, 147.4, 144.6, 139.5, 137.8, 133.9, 132.3, 128.2, 127.6, 126.5, 124.8, 105.0, 35.4, 21.2, 14.7. MS (EI, 70 eV): m/z 240 (100), 195 (24), 178 (18), 165 (16). MS (EI, 70 eV): m/z 240 (100), 195 (24), 178 (18), 165 (16).

3-Ethyl-2-iodo-4'methoxy-2'-nitro-1,1'-biphenyl (**9n**)



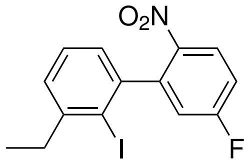
White solid, isolated yield 54%, eluent *n*-hexane/EtOAc 95:5. ^{1}H NMR (300.11 MHz, $CDCl_3$): δ 7.60 (1H, dd, J = 1.7, 0.8 Hz), 7.31 (1H, t, J = 7.5 Hz), 7.21 (1H, dd, J = 7.4, 1.7 Hz), 7.20 (1H, s), 7.00 (1H, dd, J = 7.4, 1.7 Hz), 3.94 (3H, s), 2.83 (2H, J = 7.5 Hz), 1.25 (3H, t, J = 7.5 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 159.5, 148.5, 147.3, 144.3, 133.2, 133.0, 128.1, 127.5, 126.6, 119.5, 108.9, 105.5, 55.9, 35.5, 14.6.

3-Ethyl-5'-chloro-2-iodo-2'-nitro-1,1'-biphenyl (**9o**)



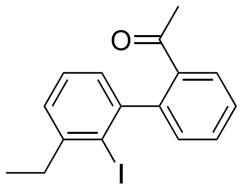
Yellow to orange oil, isolated yield 55%, eluent *n*-hexane/EtOAc 97:3. ^{1}H NMR (300.11 MHz, $CDCl_3$): δ 8.08 (1H, d, J = 8.8 Hz), 7.53 (1H, dd, J = 8,8, 2.3 Hz), 7.34 (1H, t, J = 7.6 Hz), 7.31 (1H, d, J = 2.5 Hz), 7.24 (1H, dd, J = 7.7, 1.7 Hz), 7.00 (1H, dd, J = 7.4, 1.8 Hz), 2.83 (2H, q, J = 7.5 Hz), 1.25 (3H, t, J = 7.5 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 147.5, 146.3, 143.2, 142.0, 139.2, 132.4, 128.9, 128.2, 128.0, 126.1, 125.9, 103.9, 35.2, 14.5.

3-Ethyl-5'-fluoro-2-iodo-2'-nitro-1,1'-biphenyl (**9p**)



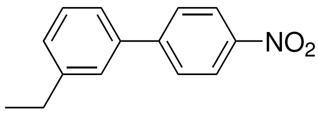
Yellow oil, isolated yield 48%, eluent *n*-hexane/EtOAc 97:3. ^{1}H NMR (300.11 MHz, $CDCl_3$): δ 8.18 (1H, dd, J = 9.1, 5.1 Hz), 7.34 (1H, t, J = 7.6 Hz), 7.28–7.21 (2H, m), 7.05 – 6.98 (2H, m), 2.84 (2H, q, J = 7.5 Hz), 1.26 (3H, t, J = 7.5 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 165.6, 163.1, 147.5, 143.48, 128.3 (d, 1J = 319.8 Hz), 128.2, 127.9, 127.3 (d, 3J = 9.9 Hz), 125.9, 119.4 (d, J = 23.4 Hz), 115.8 (d, 2J = 22.9 Hz), 103.7, 35.2, 14.5.

3-Ethyl-2-iodo-2'-acetyl-1,1'-biphenyl (**9q**)



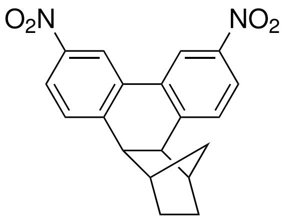
White solid, isolated yield 40%, eluent *n*-hexane/EtOAc 97:3. ^{1}H NMR (300.11 MHz, $CDCl_3$): δ 7.75 (1H, dd, J = 7.6, 1 Hz), 7.54 (1H, td, J = 7.5, 1.5 Hz), 7.47 (1H, td, J = 7.5, 1.5 Hz), 7.31 (1H, t, J = 7.5 Hz), 7.22 (2H, d, J = 7.5 Hz), 7.03 (1H, dd, J = 7.4, 1.7 Hz), 2.85 (2H, q, J = 7.5 Hz), 2.13 (3H, s), 1.26 (3H, t, J = 7.5 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 201.4, 147.5, 147.1, 144.6, 138.9, 131.2, 131.0, 128.4, 128.0, 127.9, 127.4, 127.3, 105.6, 35.4, 29.5, 14.6. MS (EI, 70 eV): m/z 223 (100), 208 (22), 165 (8).

3-Ethyl-4'-nitro-1,1'-biphenyl (**11**)



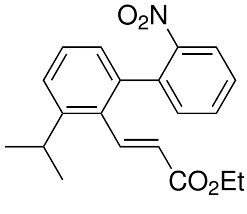
^{1}H NMR (300.1 MHz, $CDCl_3$): δ 8.28 (2H, d, J = 9.0 Hz), 7.74 (2H, d, J = 9.0 Hz), 7.46–7.40 (3H, m), 7.28 (1H, d, 6.8 Hz), 2.75 (2H, q, J = 7.6 Hz), 1.30 (3H, t, J = 7.6 Hz). MS (EI, 70 eV): m/z 227 (M^+, 100), 212 (81), 166 (32), 165 (50), 152 (32).

7,10-Dinitro-1,2,3,4,4a,12b-hexahydro-1,4-methanotriphenylene (**12**)



^{1}H NMR (400.13 MHz, $CDCl_3$): δ 9.66 (2H, d, J = 2.1 Hz), 8.51 (2H, dd, J = 8.8, 2.1 Hz), 8.20 (2H, d, J = 8.8 Hz), 4.12 (2H, s), 2.19 (2H, d, J = 7.3 Hz), 2.02 (1H, d, J = 8.9 Hz), 1.84 (1H, d, J = 8.8 Hz), 1.26–1.23 (4H, m). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 145.8, 131.5, 129.4, 125.8, 121.7, 120.1, 49.5, 42.4, 26.8.

Ethyl (E)-3-(3-isopropyl-2'-nitro-[1,1'-biphenyl]-2-yl)acrylate (**13**)



^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.94 (1H, dd, J = 8.2, 1.2 Hz), 7.70 (1H, d, J = 16.2 Hz), 7.58 (1H, td, J = 7.6, 1.3 Hz), 7.47 (1H, td, J = 7.8, 1.4 Hz), 7.39–7.29 (3H, m), 7.01 (1H, dd, J = 7.2, 1.5 Hz), 7.62 (1H, d, J = 16.2 Hz), 4.12 (2H, q, J

= 7.1 Hz), 3.21 (1H, heptet, J = 6.9 Hz), 1.29–1.20 (9H, m). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 166.0, 149.1, 147.6, 142.2, 137.0, 136.7, 132.7, 132.6, 132.4, 128.7, 128.3, 126.5, 125.6, 125.3, 124.3, 60,4, 30.0, 23.8, 23.7, 14.2. MS (EI, 70 eV): *m/z* 339 (M^+, 10), 322 (22), 296 (60), 268 (68), 248 (49), 233 (100), 217 (55), 202 (68), 189 (36), 178 (42), 165 (32).

2.6 References

(1) Catellani, M.; Motti, E.; Della Ca', N. *Acc. Chem. Res.* **2008**, *41*, 1512–1522.

(2) Motti, E.; Ippomei, G.; Deledda, S.; Catellani, M. *Synthesis* **2003**, 2671–2678.

(3) Liu, C. H.; Li, C. S.; Cheng, C. H. *Organometallics* **1994**, *13*, 18–20.

(4) Catellani, M.; Mealli, C.; Motti, E.; Paoli, P.; Perez-Carreño, E.; Pregosin, P. S. *J. Am. Chem. Soc.* **2002**, *124*, 4336–4346.

(5) Sicher, J. *Angew. Chem. Int. Ed. in English* **1972**, *11*, 200–214.

(6) Della Ca', N.; Catellani, M.; Massera, C.; Motti, E.

(7) Vicente, J.; Arcas, A.; Juliá-Hernández, F.; Bautista, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 6896–6899.

(8) Maestri, G.; Motti, E.; Della Ca', N.; Malacria, M.; Derat, E.; Catellani, M. *J. Am. Chem. Soc.* **2011**, *133*, 8574–8585.

(9) Catellani, M.; Motti, E. *New J. Chem.* **1998**, *22*, 759–761.

(10) Catellani, M.; Motti, E.; Baratta, S. *Org. Lett.* **2001**, *3*, 3611–3614.

(11) Maestri, G.; Della Ca', N.; Catellani, M. *Chem. Commun.* **2009**, 4892–4894.

(12) Mariampillai, B.; Alliot, J.; Li, M.; Lautens, M. *J. Am. Chem. Soc.* **2007**, *129*, 15372–15379.

(13) Deledda, S.; Motti, E.; Catellani, M. *Canadian Journal of Chemistry* **2005**, *83*, 741–747.

(14) Faccini, F.; Motti, E.; Catellani, M. *J. Am. Chem. Soc.* **2004**, *126*, 78–79.

(15) Sui, X.; Zhu, R.; Li, G.; Ma, X.; Gu, Z. *J. Am. Chem. Soc.* **2013**, *135*, 9318–9321.

(16) Campo, M. A.; Larock, R. C. *J. Am. Chem. Soc.* **2002**, *124*, 14326–14327.

(17) a) Newman, S. G.; Lautens, M. *J. Am. Chem. Soc.* **2010**, *132*, PMID: 20681622, 11416–11417; b) Newman, S. G.; Lautens, M. *J. Am. Chem. Soc.* **2011**, *133*, PMID: 21265523, 1778–1780; c) Newman, S. G.; Howell, J. K.; Nicolaus, N.; Lautens, M. *J. Am. Chem. Soc.* **2011**, *133*, PMID: 21894960, 14916–14919.

(18) a) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, PMID: 11456679, 1232–1233; b) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, PMID: 14611215, 13944–13945; c) Roy, A. H.; Hartwig, J. F. *Organometallics* **2004**, *23*, 1533–1541.

(19) a) Amatore, C.; Carre, E.; Jutand, A.; M'Barki, M. A. *Organometallics* **1995**, *14*, 1818–1826; b) Amatore, C.; Carre, E.; Jutand, A.; M'Barki, M. A.; Meyer, G. *Organometallics* **1995**, *14*, 5605–5614.

(20) Tolman, C. A. *Chemical Reviews* **1977**, *77*, 313–348.

(21) Weygand, F.; Weber, H.; Maekawa, E.; Eberhardt, G. *Chem. Ber.* **1956**, *89*, 1994–1999.

(22) Della Ca', N.; Sassi, G.; Catellani, M. *Adv. Synth. Catal.* **2008**, *350*, 2179–2182.

(23) Morrison, M. D.; Hanthorn, J. J.; Pratt, D. A. *Org. Lett.* **2009**, *11*, 1051–1054.

(24) Wang, S.; Morrow, G. W.; Swenton, J. S. *J. Org. Chem.* **1989**, *54*, 5364–5371.

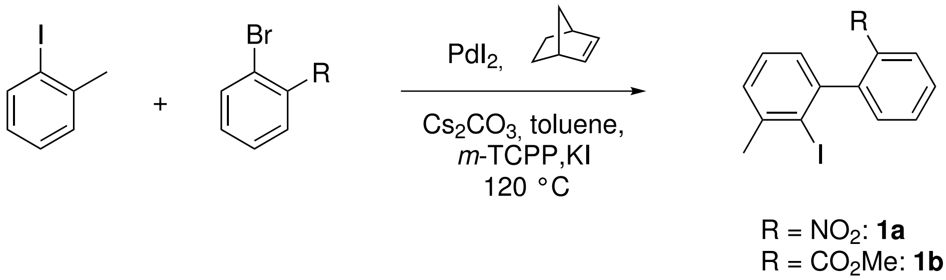
Chapter 3

Combined Pd/norbornene catalysis: from *ortho*-substituted aryl iodides and bromides to *o*-iodobiaryls. A DFT study

3.1 Introduction

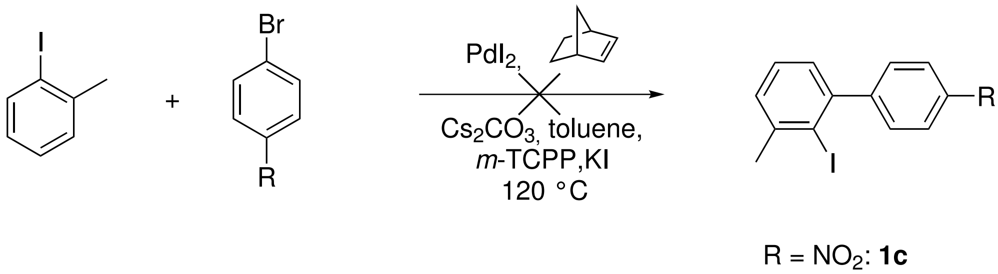
We have recently discovered a new catalytic methodology for the direct synthesis of *o*-iodobiaryls from *ortho*-substituted aryl iodides and bromides. The process takes advantage of the palladium/norbornene system to build up a biarylpalladium complex which readily forms the C–I bond and restores palladium in its initial oxidation state by reductive elimination. As reported in chapter 2, which describes the new synthetic methodology, the formation of a carbon–halogen bond by palladium catalysis has only recently been investigated and is still widely unknown[1,2]. The main aim of the work reported in this chapter was to investigate mechanistic details of the process involved in the carbon–iodide bond formation by DFT calculations and herein the results of our research are presented.

The synthesis of selectively substitute *o*-iodobiaryls **1a** and **1b** is shown in Scheme 3.1. It takes place by the reaction of an *ortho*-substituted aryl iodide, here represented



Scheme 3.1 Catalytic synthesis of *o*-iodobiaryls from *ortho*-substituted aryl iodides and bromides.

by *o*-iodotoluene and an aryl bromide bearing an *ortho* electron-withdrawing group in the presence of PdI_2 and norbornene as catalyst, tris(3-chlorophenyl)phosphine (*m*-TCPP) as ligand, Cs_2CO_3 as a base and KI, in toluene at 120 °C.



Scheme 3.2 *o*-Iodotoluene and *p*-bromonitrobenzene (**1c**, R = NO_2) do not afford the desired *o*-iodobiaryl.

The results greatly depend on the nature of the aryl bromide, electron-poor ones, such as *o*-bromonitrobenzene (**1a**, R = NO_2) and methyl *o*-bromobenzoate (**1b**, R = CO_2Me) are the most suitable. The reaction appears to be very specific. No conversion of the starting bromide was observed replacing *o*-bromonitrobenzene with the *para* isomer (Scheme 3.2). While the presence of a substituent in the *ortho* position of the aryl bromide appears to be crucial for the formation of the product, no evidence of the role played by the *ortho* substituent was known. Thus, as anticipated theoretical calculations were performed to disclose the still unclear steps of the process and to find out how the *ortho* substituent affects the reactivity of the system.

Initially we focused on the calculation of energies for intermediates and transition states of the reactions of *o*-iodotoluene with: a) *o*-bromonitrobenzene (path a) and b) methyl *o*-bromobenzoate (path b). The reaction of *p*-bromonitrobenzene (path c) was taken as a model for substrates not leading to the desired *o*-iodobiaryls. Pathways a and c were then reoptimized to take into account the solvent effect (toluene) using the PCM method (path a* and c*).

The role played by *m*-TCPP, the ligand that allows to achieve the best results, was also investigated. The entire reaction pathway of *o*-bromonitrobenzene in the presence of *m*-TCPP as ligand (path a) has also been modelled using PPh_3 as ligand (path d). To roman numerals indicating intermediates and transition states in the text, schemes and figures of this chapter the corresponding letter indicating the pathway is appended; the entire reaction schemes for every pathway are summarized in section 3.9.

Structures of reagents, products, intermediates and transition states in XYZ format, together with the related energies are reported in Appendix A

3.2 Computational details

3.2.1 Computational methods

All calculations were performed with the GAUSSIAN 09 package[3] using the default threshold values for SCF convergence and geometry optimization.

To maintain calculations feasible and low computational costs, we applied the ONIOM methodology[4] in two layers. The first ONIOM layer (high) included the organic substrate, the metal and phosphor atoms, while the aryl groups of the phosphines were included in the low layer. For an example of subdivision of the two layers see Figure 3.1. Both ONIOM layers were treated with the M06 hybrid functional by Zhao and Truhlar[5] which is expected to give good results with transition metal complexes. Calculations on the low layer, consisting of the aryl rings of the phosphine ligands, were performed at the 3-21G level for all but chlorine, bromine, iodine and palladium atoms where the LANL2DZ[6] basis set was used in order to reduce the global amount of basis functions by means of pseudopotentials.

In the high layer for C, H, N, O and P atoms the double-ζ Pople basis set 6-31G* was used, whereas for palladium and bromine atoms the standard LANL2DZ/ECP approach was applied. Because of the main role played by the iodine atom in the reaction particular care was taken in the choice of the basis functions. Thus we employed a small-core pseudopotential (Stuttgart-Dresden-Bonn) with SDB-cc-pVTZ basis functions for outer shells[7]. This is a correlation-consistent, triple-ζ quality basis set which is known to give good results for the iodine atom in combination with standard Pople basis sets[8].

Transition states and stable minima were then reoptimized to take account of the solvent effect using integral equation formalism polarizable continuum model (IEF-PCM)[9].

Frequency calculations to compute thermodynamic quantities were performed on all optimized structures at the same level of theory and the obtained energies are summarized in the Tables at the end of this chapter. The energy values were related to 298 K for the calculations in the gas phase and to 383 K for IEF-PCM in toluene, and were unscaled.

The thermal contribution to enthalpy as outputted by Gaussian already includes zero point energy (ZPE) and is calculated with the formula:

$$H_{\mathrm{corr}} = \mathrm{ZPE} + E_{\mathrm{th}} + k_{\mathrm{B}}T$$

where E_{th} is the thermal contribution to energy (not shown in Tables) $E_{\mathrm{th}} = E_{\mathrm{trans}} + E_{\mathrm{rot}} + E_{\mathrm{vib}}$. Contribution to Gibbs free energy is calculated using entropy and corrected enthalpy:

$$G_{\text{corr}} = H_{\text{corr}} - TS_{\text{tot}}$$

where S_{tot} is the total entropy due to all molecular vibrations. The value E_{el} is the total electronic energy and does not include ZPE. For better readability total electronic energy, total enthalpy and total Gibbs free energy values converted in $kcal/mol$ are supplied.

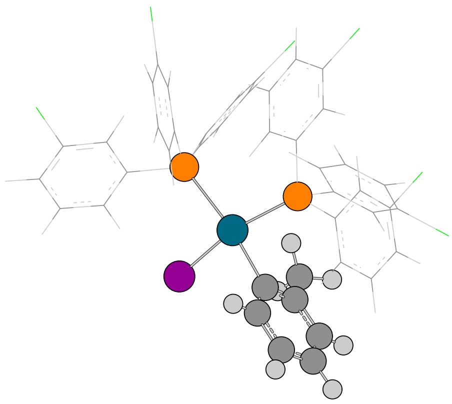


Fig. 3.1 ONIOM layers are shown in intermediate *cis*-IIIa. Phosphines aryl groups are included in the low layer to save computational time.

3.2.2 How transition states and stable minima were found

Some intermediates had been previously isolated by the use of appropriate stabilizing ligands and fully characterized by X-ray crystallography[10]. Other structures were known by previous DFT studies on the system[11]. Initial guesses of some transition states and stable intermediates were proposed on the basis of these previously reported data.

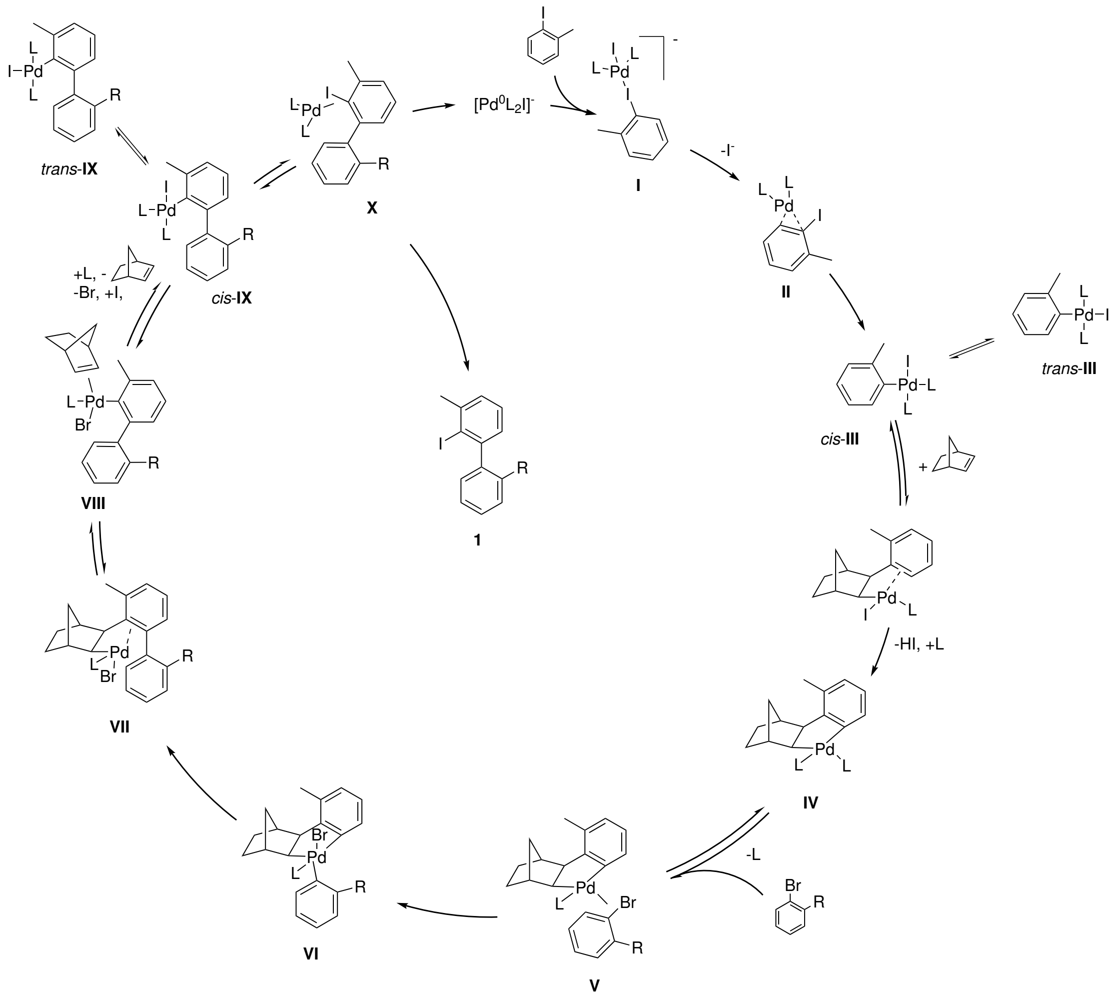
Transition states were found through a linear scan, keeping fixed the reaction coordinate and optimizing every other degree of freedom. The candidate structure was then reoptimized with the Berny algorithm and checked for a single negative frequency.

For each TS the corresponding pre-reactive complex had to be identified; to correctly calculate the energy barrier we looked for the first stable structure before the

TS along the Fukui's intrinsic reaction coordinate. This allowed a fair comparison of the same type of intermediate bearing different substituents and/or the same substituent in different positions.

3.2.3 Modelling of ligands

Usually, when it comes to DFT calculations, a simpler ligand replace the actual one. For example, PH_3 usually replaces PPh_3 and PMe_3 is used in place of higher alkyl phosphines. The assumption that these simplified ligands perform equally well in DFT calculations has been the subject of many debates[12,13].
The ligand used in the process under study is tris(3-chlorophenyl)phosphine (*m*-TCPP). In order to take into account both the steric and electronic properties of the phosphine ligand we decided to maintain its entire structure, using the ONIOM methodology to reduce computational costs.
Due to the high number of degrees of freedom of the phosphine rings calculations on intermediates containing the entire ligand structure can be inaccurate. In order to minimize errors, we tried as much as possible to preserve phosphine elicity through the reaction path, and in particular in the calculations of the TSs and their pre-reactive adducts. When two phosphines were present as ligands in the same compound they were modelled with opposite elicity; this was inherited from the starting linear complex $Pd(m\text{-TCPP})_2$ which belongs to the S_6 point group. The rotation of a phosphine aryl group by 180° can give errors in the 1 $kcal/mol$ range.



Scheme 3.3 A possible catalytic cycle for the synthesis of *o*-iodobiaryls, exemplified by the reaction of *o*-iodotoluene and aryl bromides.

3.3 The proposed reaction pathway

The catalytic cycle of Scheme 3.3 shows the reaction of *o*-iodotoluene with an *ortho* substituted aryl bromide under the previously reported conditions.

The palladium species that starts the cycle is likely a tri-coordinated anionic palladium(0) complex. Palladium in the oxidation state 0 is rarely found as PdL_2 as still reported in some textbooks, more likely an anionic trigonal planar complex, with the general formula $[PdXL_2]^-$, is formed when an anion is included in the coordination sphere[14]. In our computational study it was assumed that the palladium(0) species that undergoes the oxidative addition is the trigonal planar complex $[PdI(m\text{TCPP})_2]^-$, formed by association of an iodide ion to a neutral species of the type PdL_2. The cycle starts with the coordination of the aryl iodide to the anionic palladium complex $[PdI(m\text{TCPP})_2]^-$ to form adduct **I**. To achieve the oxidative addition this complex has to rearrange to the η^2 complex **II**. After oxidative addition of the coordinated aryl iodide, the resulting intermediate *cis*-**III** isomerizes to the more stable *trans*-**III** complex. Coordination and subsequent insertion of norbornene into the arylpalladium bond leads to the *cis*,*exo* *o*-tolylnorbornylpalladium complex containing a weak interaction between the palladium atom and one double bond of the tolyl ring, which favors palladacycle **IV** formation by aromatic substitution. Intermediate steps going from **III** to **IV** has not been computed in this work.

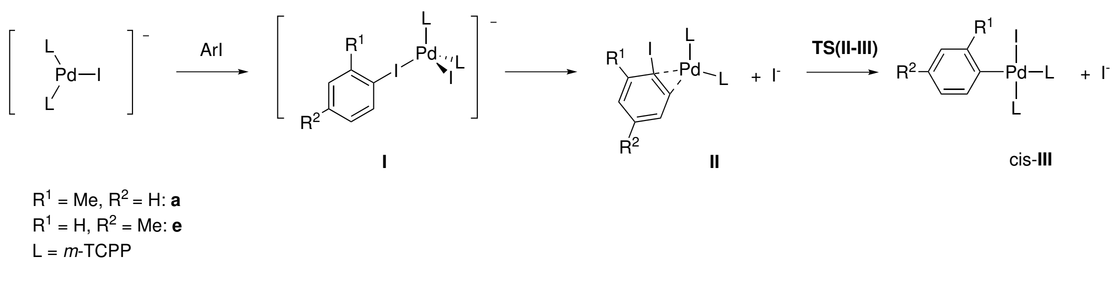
Coordination of the aryl bromide to the palladacycle **IV** by ligand exchange, affords **V**. The coordinated aryl bromide oxidatively adds to the palladium(II) metallacycle to yield the palladium(IV) complex **VI**. This species forms the C(aryl)–C(aryl) bond by reductive elimination, which occurs by selective migration of the *ortho*-substituted aryl group onto the aromatic carbon of the palladacycle **VI**, as previously described[15] and in agreement with formerly reported theoretical calculations[16]. Likely due to steric hindrance norbornene deinserts from intermediate **VII** by an equilibrium process to form the biarylpalladium species **VIII** containing a coordinated norbornene molecule. The formation of this species is thermodynamically disfavored and the low barrier of the reverse step indicates that norbornene insertion, leading back to complex **VII** through **TS(VII-VIII)**, is the favored process. However, by intervention of the phosphine ligand the more stable intermediate **IX** is formed, the equilibrium is shifted to the right and the reaction allowed to proceed.

In the step going from **VIII** to **IX** norbornene is replaced by *m*-TCPP and the bromide anion by the iodide one; the study of the mechanism of ligand exchanges was not taken into account in this work. The biarylpalladium iodide **IX** undergoes a reductive elimination reaction to form adduct **X** from which product **1** and the palladium in the oxidation state 0 are released.

3.4 Pd(0) → Pd(II) oxidative addition

3.4.1 Energy profile for the oxidative addition step of *o*- and *p*-iodotoluene to palladium(0)

The complexity of the system under study, that comprises the entire structure of every intermediate and transition state, almost reached the limit of basis functions for DFT. Calculations on such large molecular system had been possible applying the ONIOM methodology and using mixed basis sets on both ONIOM layers. In order to verify the reliability of our computational methodologies we carried out calculations on the oxidative addition of *o*- (path **a**) and *p*-iodotoluene (path **e**) to palladium(0) species.

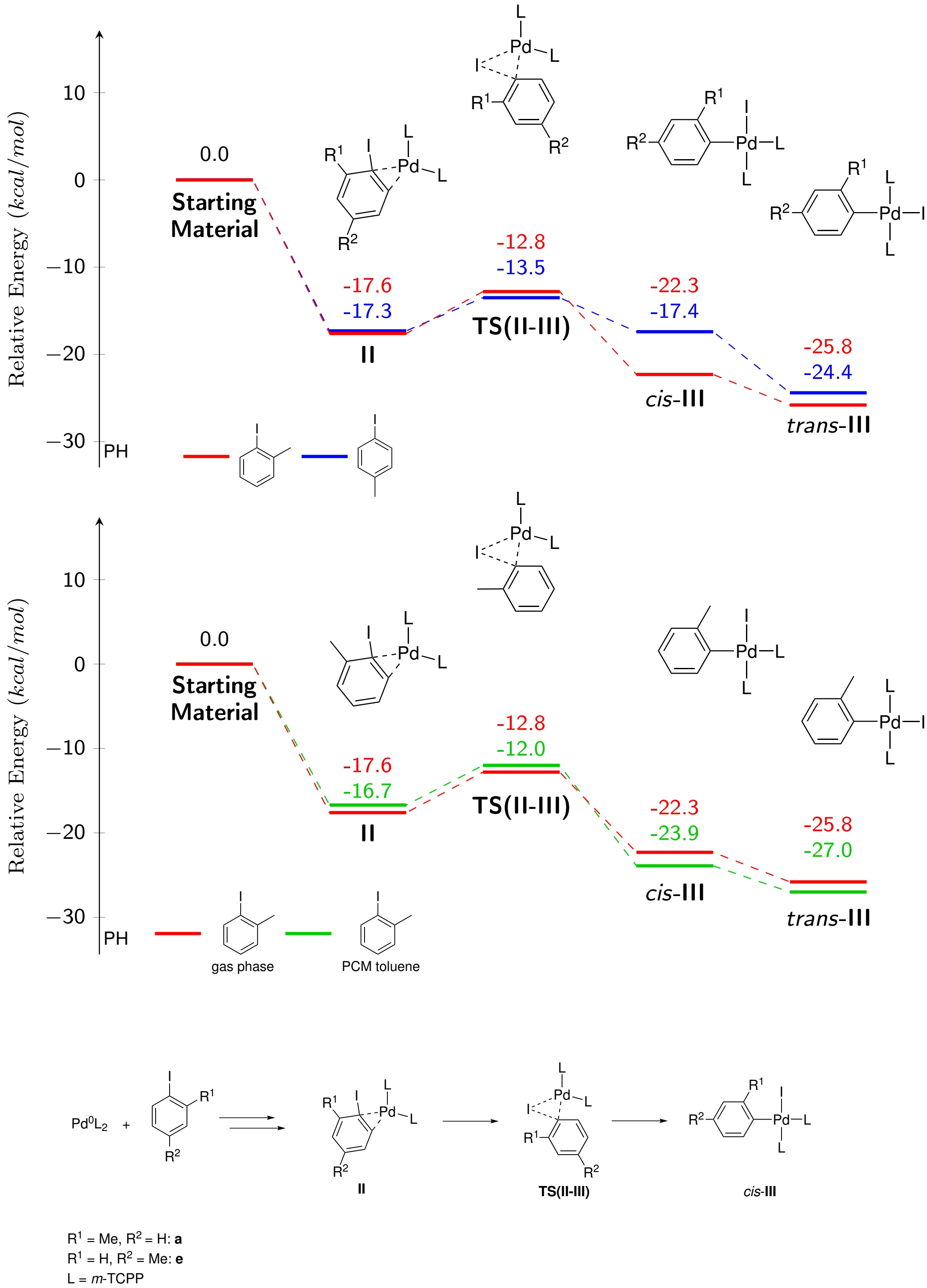


Scheme 3.4 Mechanism for the oxidative addition of an *o*- and *p*-iodotoluene to the anionic palladium(0) species $[Pd(m\mathrm{TCPP})_2I]^-$. The structure of the TS is omitted this scheme.

Scheme 3.4 shows intermediates involved in the Pd(0)–Pd(II) oxidative addition of *o*- and *p*-iodotoluene. The aryl iodide coordinates to the starting trigonal palladium

anionic complex forming intermediate **I**. The species **Ia** and **Ie** are Pd(0) complexes with the aryl iodide bonded to the metal through the halide. The rearrangement of the intermediate **I** to complex **II**, leading to the formation of a neutral species and an anionic iodide, involves more than one step[17] not analyzed in details in this work. The pre-reactive complex **II** undergoes oxidative addition, through **TS(II-III)**, to form intermediate *cis*-**III**.
As shown in Scheme 3.5, the barrier for the cleavage of the C–I bond is 4.8 *kcal/mol* and 3.8 *kcal/mol* for *o*- and *p*-iodotoluene, respectively.
The intermediate *cis*-**III**, resulting from oxidative addition, was found in a square planar geometry with the tolyl ring perpendicular to the plane of the complex for both substrates. PCM calculations in toluene were performed in order to determine the energy of intermediates taking into account the effect of the solvent. The barrier to reach the corresponding transition state is only slightly influenced by the inclusion of the solvent effect in the calculation and the energy gap is similar to those observed for the gas-phase (4.7 *kcal/mol* for *o*-iodotoluene).
The calculated energy values are comparable to those found in the literature (within 1 *kcal/mol*) for the oxidative addition of aryl iodides. Structures of intermediates and transition states are also acceptable, and show slight differences reasonably explained by the steric effect of the ligands.

It is worth noting that the catalytic cycle leads to the formation of a biaryl iodide, still reactive towards the oxidative addition to palladium(0) species. When its concentration increases it can compete with *o*-iodotoluene. Thus, the oxidative addition step of *o*-iodotoluene and structures **1a**, **1b** and **1c** was modelled and the data are presented in Scheme 3.6.
The pre-reactive complex of *ortho*-disubstituted aryl iodides was very different from the one found for *o*-iodotoluene, therefore the comparison between the corresponding reaction pathways should be done with extreme caution.
In complex **Xa-c**, because of the relevant steric hindrance, palladium does not



Scheme 3.5 Energy profiles for the oxidative addition of *o*- and *p*-iodotoluene (top) and comparison of gas phase and solvent corrected calculations for *o*-iodotoluene (bottom). All values in ΔE.

interact with the aromatic system of the substrates (**1a-c**) which are coordinated through the iodide instead. Pd–I bonding distances are 2.89, 2.88 and 2.85 Å, respectively. These complexes resemble the pre-reactive adducts for the oxidative addition of alkyl halides to palladium species, where the metal interacts with the substrate only through the halogen atom.

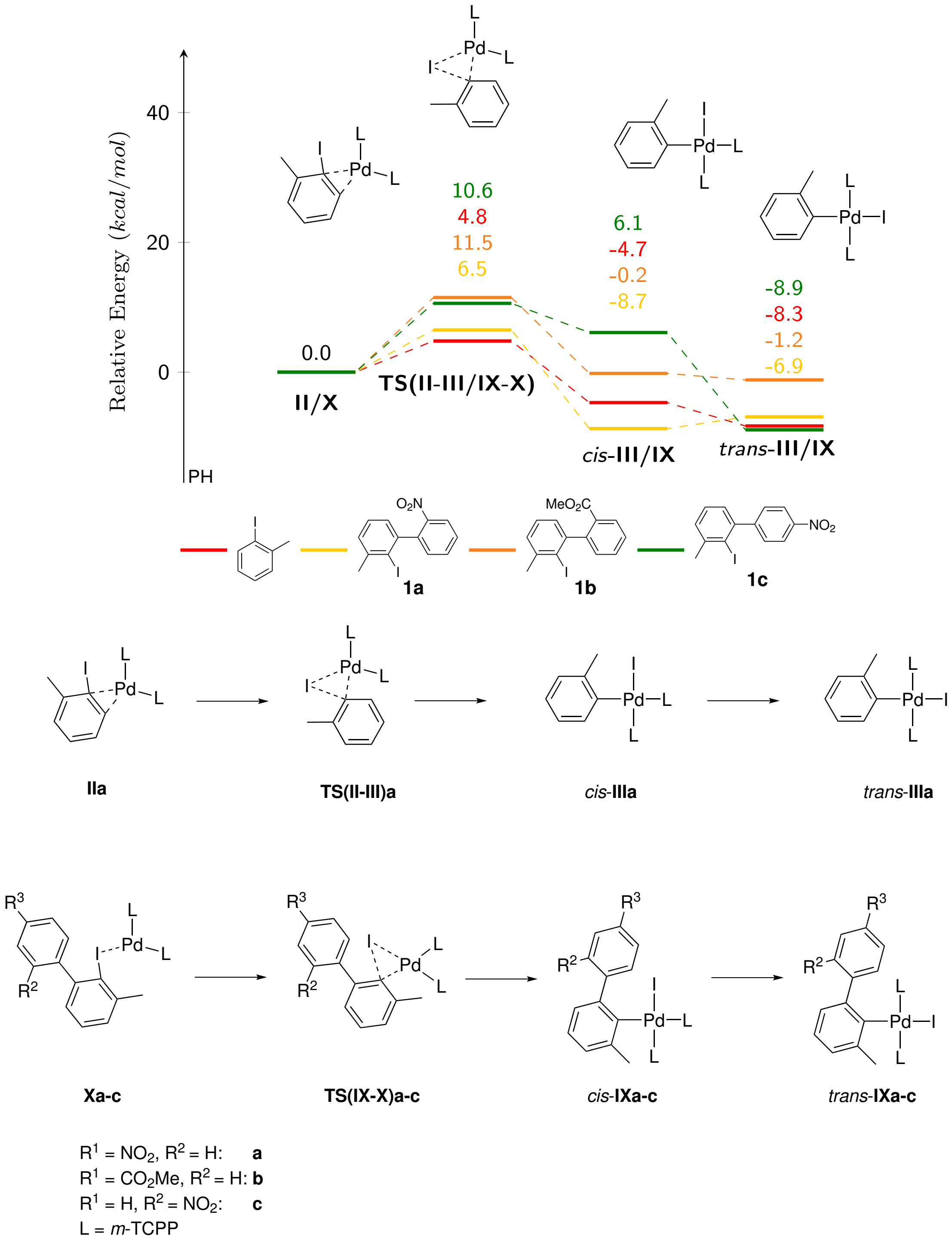
The barrier for the oxidative addition of product **1a** (6.3 *kcal/mol*) is lower than those of **1b** (11.5 *kcal/mol*) and **1c** (10.6 *kcal/mol*) and comparable to that of *o*-iodotoluene (4.8 *kcal/mol*). These energy values, however, refer to the barrier for the cleavage of the C–X bond, which is only a part of the more complex oxidative addition mechanism as described in detail by Goossen[18], therefore only qualitative conclusions can be drawn.

3.4.2 Palladium(0) species involved in the oxidative addition step

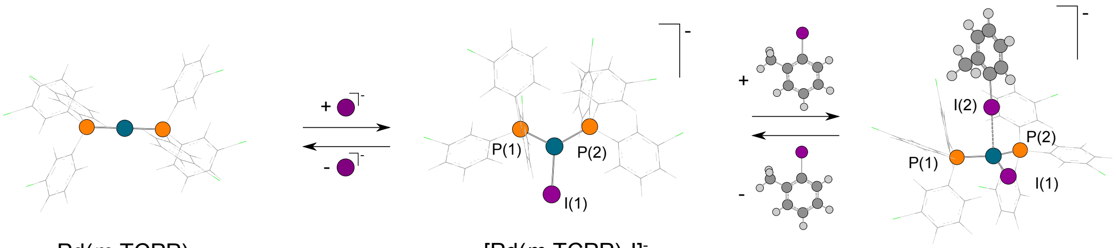
As previously anticipated the palladium species that starts the catalytic cycle by oxidative addition is most likely an anionic palladium(0) complex $[PdXL_2]^-$, a species proposed many years ago by Amatore and Jutand[19]. In our case, due to the presence of KI as additive in the reaction mixture, we postulated the complex $[PdI(m\text{TCPP})_2]^-$ to initiate the cycle (Figure 3.2). According to our calculations, the formation of this species from $Pd(m\text{TCPP})_2$ and I^- is thermodynamically favored and occurs with an energy gain (ΔE_{el}) of -23.0 *kcal/mol*. This value is in agreement with those reported by Goossen[18] for the formation of the anionic palladium complex $[Pd(OAc)(PPh_3)_2]^-$ (-21.8 *kcal/mol*), while the value for the corresponding complex with PMe_3 ($[Pd(OAc)(PMe_3)_2]^-$) is only -9.9 *kcal/mol*.

As expected, palladium-phosphine complexes have a great affinity for the iodide ligand whatever is the metal oxidation state[20].

The reaction starts when the palladium complex $[PdI(m\text{TCPP})_2]^-$ approaches the aromatic compound (Scheme 3.7); at first a tetrahedral intermediate where the organic substrate coordinates to the metal through the halide is formed. In this



Scheme 3.6 Pd(0)–Pd(II) oxidative addition of *o*-iodotoluene, and structures **1a**, **1b** and **1c** (ΔE_{el}).



Pd(*m*-TCPP)$_2$ | [Pd(*m*-TCPP)$_2$I]$^-$ | **Ia**

Pd - P(1)	2.33 Å
P(1) - Pd - P(2)	180.0 °

Pd - I(1)	2.77 Å
Pd - P(1)	2.30 Å
Pd - P(2)	2.31 Å
P(1) - Pd - P(2)	118.3 °

Pd - I(1)	2.75 Å
Pd - I(2)	3.20 Å
Pd - P(1)	2.30 Å
Pd - P(2)	2.32 Å
P(1) - Pd - P(2)	120.8 °

Fig. 3.2 Addition of I$^-$ to the palladium(0) center provides -23.0 *kcal/mol*. The subsequent coordination of *o*-iodotoluene, leading to intermediate **Ia**, occurs with an energy gain of -10.4 *kcal/mol*.

intermediate the C–X bond of the aryl iodide is linear with the palladium atom (C–I–Pd angle is *ca.* 180 °). The formation of this key intermediate, suggested by Goossen[17] and by other groups, is not in agreement with the mechanism proposed by Amatore and Jutand[19]. They noted that upon addition of a stoichometric amount of iodobenzene to a solution of $[Pd(OAc)(PPh_3)_2]^-$ neither free acetate nor free aryl iodide was detected after few seconds. To explain this behavior Amatore and Jutand hypothesized a fast oxidative addition leading to a penta-coordinate palladium(II) complex, which slowly releases I$^-$ in solution to form a neutral species, the well known square planar arylpalladium(II) complex. Any evidence of the presence in solution of the above-mentioned penta-coordinate palladium complex (Scheme 3.7, eq. a) has never been provided. Goossen[17,18] proposed a mechanism explaining the above experimental data without involving the five-coordinate intermediate: the formation of the linear adduct between the anionic palladium(0) complex and the aryl iodide may explain the absence of OAc$^-$ and iodobenzene in solution (Scheme 3.7, eq. b); the subsequent oxidative addition step allows the acetate anion release.

In our case (Scheme 3.7, eq. c), the species resulting from the coordination of *p*-iodotoluene to the trigonal complex $[PdI(mTCPP)_2]^-$ shows a tetrahedral geometry in place of the square planar one reported by Goossen. Any attempt to obtain a square planar complex converged to the tetrahedral one. These differences can likely be attributed to steric effects because the square planar isomer easily converges when the ligand is replaced by PH_3 (Figure 3.3).

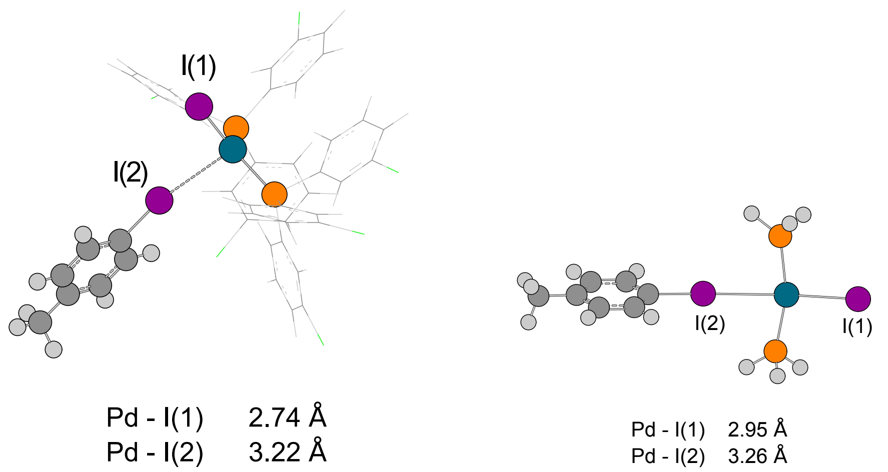
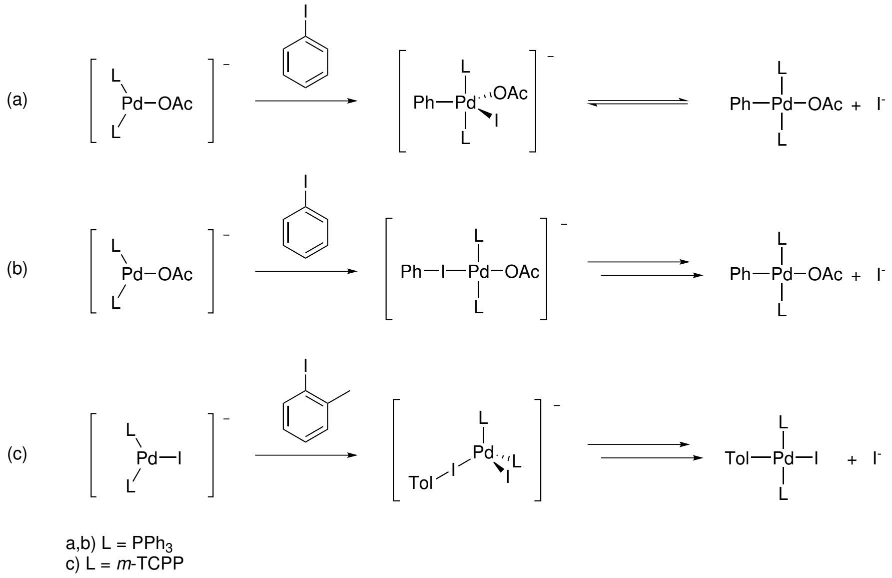


Fig. 3.3 Intermediate **Ie** (left) and **IeH** (right).

The energy gain (ΔE_{el}) for the coordination of *o*-iodotoluene to $[PdI(mTCPP)_2]^-$ is -10.4 *kcal/mol*. Goossen *et al.* found quite different energies involved in the process: for the coordination of phenyl iodide to $[Pd(OAc)(PMe_3)_2]^-$ they obtained a difference of -20.3 *kcal/mol* while -13.6 *kcal/mol* were calculated for phenyl bromide[18].

3.4.3 Pre-reactive complex

As the oxidative addition step requires the cleavage of the C–I bond by the metal, complex **I** has to rearrange moving the palladium atom closer to the *ipso* carbon up to the formation of the pre-reactive adduct **II** (Figure 3.4). The several steps connecting these intermediates, extensively studied by Goossen and coworkers[18],



Scheme 3.7 Oxidative addition of aryl iodides to palladium(0) species. (a) Mechanism proposed by Amatore and Jutand; (b) DFT mechanism reported by Goossen ; (c) mechanism found in this work. The first step is always *fast* and the second *slow*.

are omitted in this work. As previously pointed out the early steps of the oxidative addition involve anionic complexes, but the anion (OAc^- in Goossen work) is removed from the coordination sphere and remains in the structure as a remote ligand in the last steps of the mechanism, including the pre-reactive adduct. The pre reactive complex identified by Goossen is an η^2 square planar complex with the metal bonding the C1 and the C6 carbons of the aryl iodide. This intermediate is considered to be the correct pre-reactive adduct for the oxidative addition of aryl halides to palladium(0) species[14,21].

In the case of the oxidative addition of *o*-iodotoluene, we found an analogous structure (**IIa**) optimizing the first stable structure prior to the TS along the Fukui's intrinsic reaction coordinate. Since in our modelling the **TS(II-III)** does not bear an iodide anion ligand, this intermediate is not anionic; any attempt to remodel the structure of compound **IIa** with an additional iodide ligand, failed.

Intermediate **IIa** is an η^2 complex with palladium bonding the C1 and the C6 carbons; Pd–C1 distance is 2.44 Å while Pd–C6 is 2.64 Å. These elongated bonds

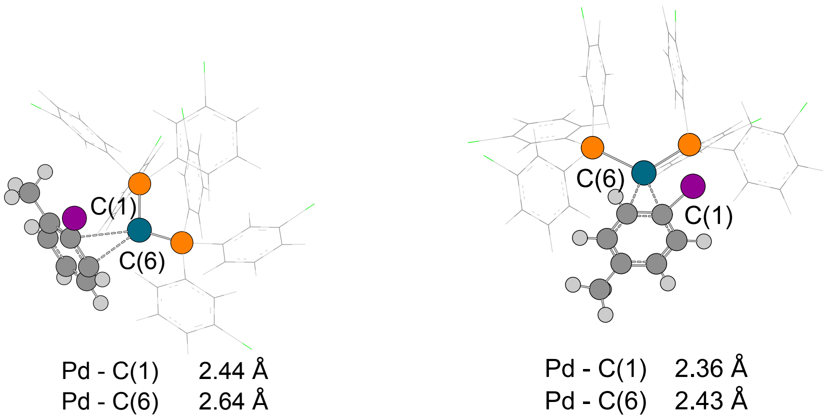


Fig. 3.4 Pre-reactive complex **IIa** (left) and pre-reactive complex **IIe** (right).

can be explained by the steric effect of the *ortho* methyl group. The C1–C6 bond of the substrate lies on the P–Pd–P plane, therefore the geometry of this complex resembles to a square planar one.

In the case of *p*-iodotoluene the analogous η^2 complex shows a Pd–C1 distance of 2.36 Å while Pd–C6 is 2.43 Å, 10% longer than the values reported by Goossen for the coordination of phenyl iodide[18].

In *ortho*-disubstituted aryl iodides, the type of products obtained in the process, the η^2 intermediate could not be found due to the increased steric hindrance; we were able, however, to find a complex with the palladium ligated to the iodine atom.

We attributed the difficulty to identify a well defined pre reactive adduct to the complexity of the system which includes the entire phosphine structures. In this case weak interactions (steric) of the ligands with the substrate dominate over the formation of a coordination bond between the metal and the aromatic ring of the biaryl system. Moreover, the interaction of the *ortho* group (NO_2 or CO_2Me) with the metal could lead to discrepancy between intermediates **Xa-b** and **Xc** (Scheme 3.6).

3.4.4 Oxidative addition/reductive elimination transition states

In the past years some mechanisms for the oxidative addition of aryl halides to transition metals were proposed, the most accepted ones are the SN_{Ar} mechanism and the concerted insertion of the metal into the C–X bond. The mechanism involving a concerted insertion of the metal was investigated in this work.
Our calculations show that palladium, η^2-coordinated to the aryl iodide in complex **II** (Figure 3.4, Scheme 3.6), moves towards the *ipso* carbon and the iodine atom; the insertion of the metal into the C–I bond occurs in a concerted fashion: as soon as the C–I bond is cleaved, a Pd–I and a Pd–C bonds are formed. Every component of the transition state is determining for the kinetic of this step. The three-center transition state involved in the mechanism (Figure 3.5) explains the dominant role of the halide ion without ignoring the importance of the nucleophilic character of the metal[22,23].
TS(II-III) leads to the square planar complex *cis*-**III** which rearranges to the more stable *trans*-**III** complex. As oxidative addition and reductive elimination steps are supposed to occur through the same intermediates and transition states, we already calculated the structural data and energetics for the oxidative addition of products (**1a-c**); these data are shown in Figure 3.5. TSs structures present already a square planar geometry and lead, as expected, to the *cis* oxidative addition of the aryl iodide. Any attempt to model a *trans* transition state failed.

3.5 Pd(II) → Pd(IV) oxidative addition

3.5.1 Comparison of oxidative addition reaction pathways

The five-membered palladacycle **IV** (Scheme 3.8) is a key intermediate of the process and its oxidative addition to the aryl bromide affords the palladium(IV) complex (**VI**). On the basis of our theoretical calculations the intermediate **VI** possesses an octahedral geometry when the aryl bromide bears an *ortho* group able

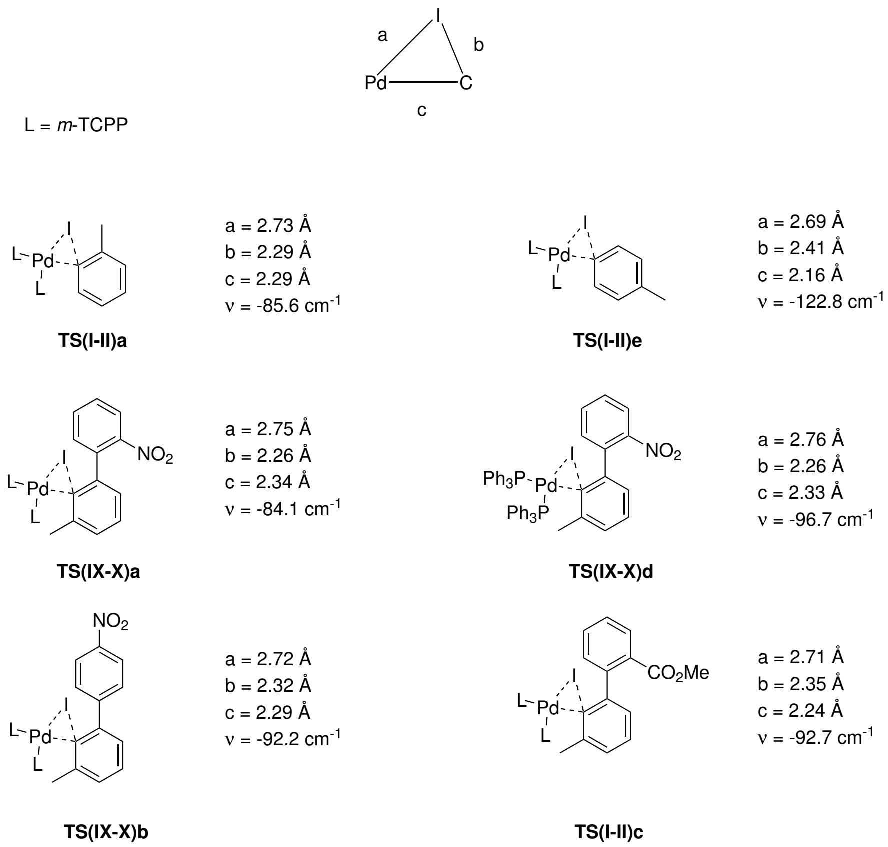


Fig. 3.5 Oxidative additions/reductive eliminations TSs

to coordinate to the metal, while a trigonal bipyramidal geometry results in the case of *p*-substituted substrates[11]. Anionic species, observed for the Pd(0) → Pd(II) oxidative addition, may be also involved in the Pd(II) → Pd(IV) oxidative addition but our first approach to this problem has considered only neutral structures for the steps going from **IV** to **X**.

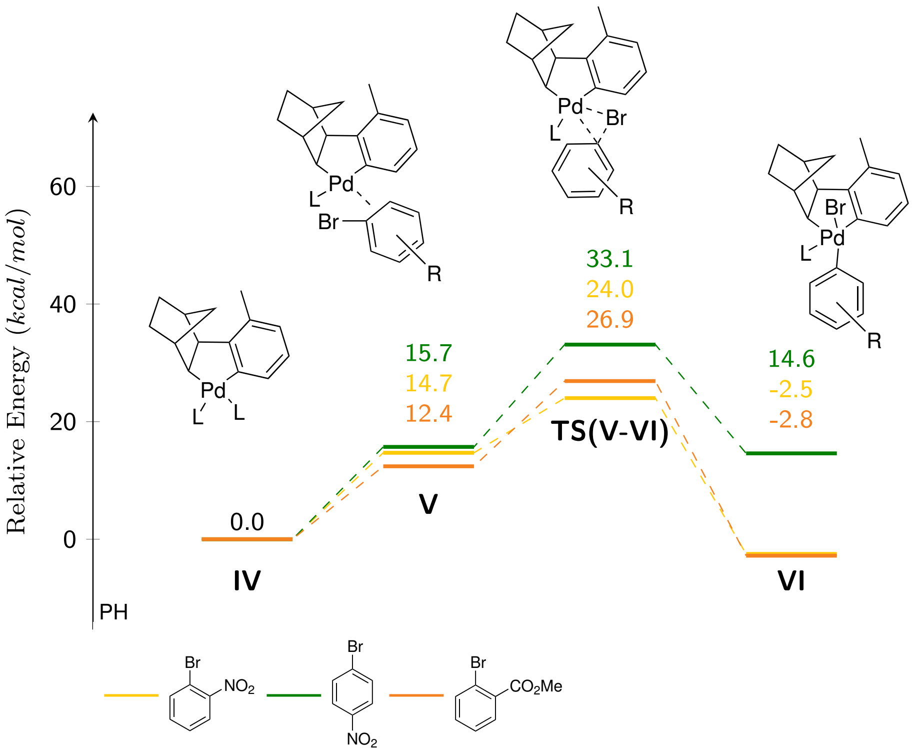
The reaction of the arylpalladium complex **III** and norbornene forms palladacycle **IV** through a series of steps not taken into consideration in this study. Compound **IV** is a very reactive arylnorbornylpalladium(II) complex, which readily undergoes oxidative addition of aryl halides to afford the palladium(IV) species **VI**. Under our experimental conditions we noticed that only aryl bromides bearing a coordinating *ortho* substituent leads, through a sequential series of steps, to the desired biaryl iodide. In a control experiment carried out with *p*-bromonitrobenzene the expected *o*-iodobiaryl (**1c**, Scheme 3.2) was not obtained .

Scheme 3.8 shows the pathways for the Pd(II) → Pd(IV) oxidative addition for *ortho*-bromonitrobenzene (**a**), methyl *o*-bromobenzoate (**b**) and *p*-bromonitrobenzene (**c**).

The aryl bromide coordinates to palladacycle **IV** by exchange of a phosphine ligand, forming adduct **V**. The geometry of complex **V** depends on the nature of the substrate and is very different in the case of *p*- and *o*-bromonitrobenzene. Intermediate **V** undergoes oxidative addition through transition state **TS(V-VI)** forming compound **VI**, a Pd(IV) complex. The energy barrier of this step for *p*-bromonitrobenzene is slightly higher than that for other substrates, 17.4 *kcal/mol* compared to 14.5 *kcal/mol* of *o*-bromonitrobenzene and 9.4 *kcal/mol* of methyl *o*-bromobenzoate. These small differences in the energy barriers may not be conclusive, however, different intermediates are involved in the oxidative addition of *ortho*-substitued aryl bromides. In our computational study the *ortho* group actively participates to the reaction mechanism allowing this step to occur through different geometries.

3.5.2 Pre-reactive complex for the Pd(II) → Pd(IV) oxidative addition

The pre-reactive complex for the Pd(II) → Pd(IV) oxidative addition is very different from the one seen for the Pd(0) → Pd(II) oxidative addition. Intermediate **Va** shown in Figure 3.6 is a square planar complex in which *o*-bromonitrobenzene coordinates the metal with an oxygen atom belonging to the nitro group. A very similar structure is obtained for methyl *o*-bromobenzoate, which coordinates to the metal with the carbonyl oxygen of the *ortho* substituent. Due to the lack of a coordinating *ortho* group, the corresponding intermediate **Vc** shows a quite different geometry, *p*-bromonitrobenzene approaches to the palladium(II) complex with long range interactions (Pd–C1 3.72 Å, Pd–C6 3.32 Å).



Scheme 3.8 Pd(II)-Pd(IV) oxidative addition pathway for different aryl bromides (ΔE_{el}).

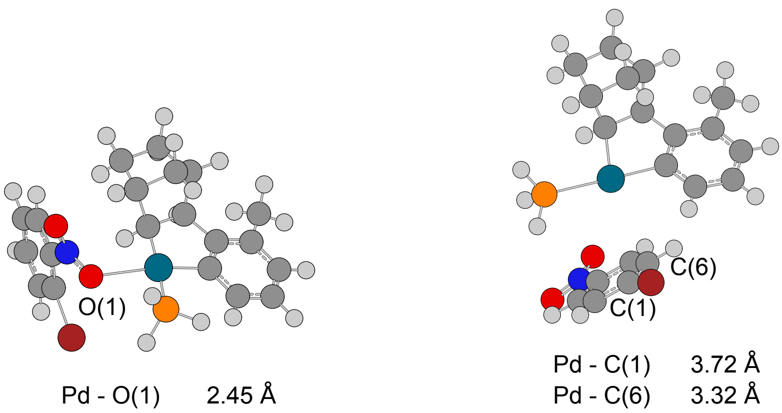


Fig. 3.6 Intermediate **Va** (left) and **Vc** (right), pre-reactive adducts for the Pd(II) → Pd(IV) oxidative addition. The phosphine ligand (*m*-TCPP) was fully calculated but is represented here as PH_3 for clarity.

3.5.3 Transition states for the Pd(II) → Pd(IV) oxidative addition

Like in the case of Pd(0) → Pd(II) oxidative addition, a three-center transition state was calculated for the oxidative addition step of aryl bromides to the palladium(II) metallacycle **IV** (Scheme 3.8). Three aryl bromides have been subjects of our study, the main differences between them, as we pointed out in the discussion of the pre-reactive complex **V**, is the participation of the *ortho* group to the oxidative addition step through coordination to the metal.

In the structure of **TS(V-VI)a** and **TS(V-VI)b** the *ortho* nitro and the *ortho* methoxycarbonyl groups maintain the coordination to the metal during the entire oxidative addition process leading to the formation of the octahedral complexes **VIa** and **VIb**. Instead, intermediate **VIc**, due to the absence of a coordinating *ortho* group, is a trigonal bipyramidal complex. In Figure 3.7 the two structures of **TS(V-VI)a** and **TS(V-VI)c** are shown; the geometry of the TS is greatly altered by the coordination of the *ortho* group to the metal, Pd–Br and Pd–C1 distances are longer for *o*-bromonitrobenzene than those for the corresponding *para* isomer.

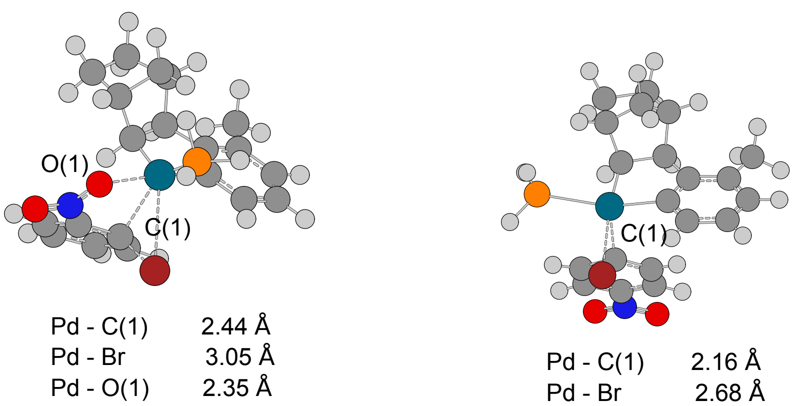


Fig. 3.7 **TS(V-VI)a** (left) and **TS(V-VI)b** (right) for the Pd(II) → Pd(IV) oxidative addition. The phosphine ligand (*m*-TCPP) was fully calculated but is represented here as PH_3 for clarity.

3.6 Carbon–iodide reductive elimination

3.6.1 Reductive elimination pathway

The reductive elimination from palladium complex **IX** (Scheme 3.9) leading to the formation of a C–I bond is the fundamental step of the present process. Reductive elimination takes place when two groups are in mutually *cis* positions, however, palladium(II) complexes cannot readily undergo reductive elimination of organic halides[1]. While the C–C reductive elimination reaction readily occurs once the implicated groups are in *cis*-coordinated, this condition is not sufficient for the C–I reductive elimination to occur.

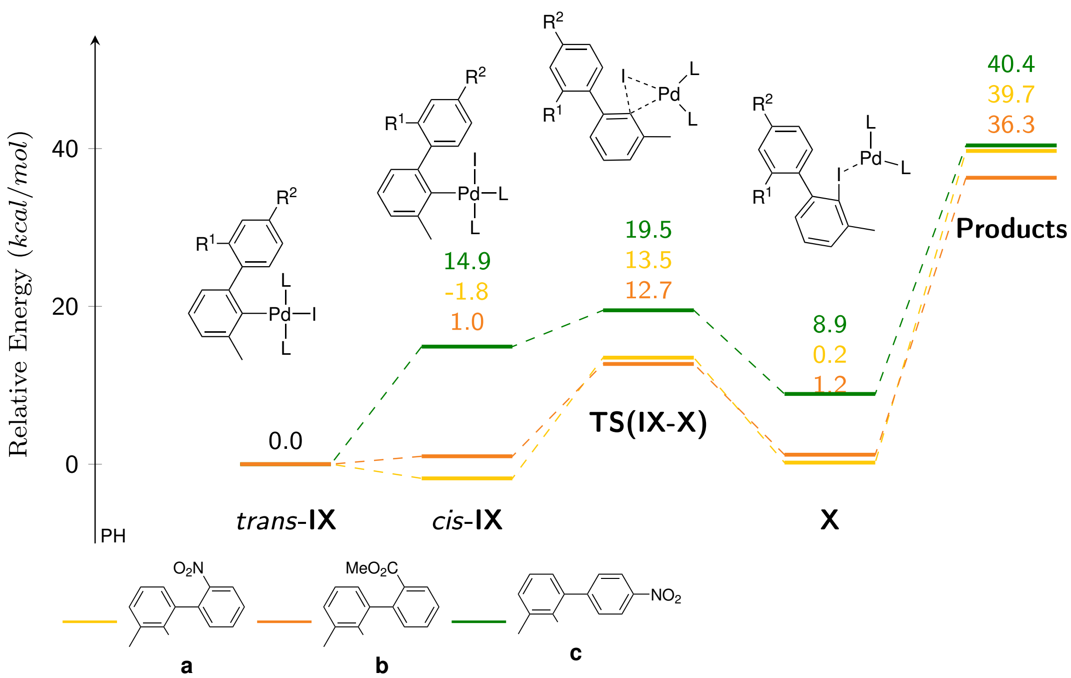
Bulky phosphine ligands are usually employed to force the coordinated iodide close to the organic unit in order to achieve the C–I bond formation[24]. Here, a phosphine ligand with a moderate steric hindrance was used, but the formation of the C–I bond was made possible by the steric effect provided by molecular features of the coordinated biaryl unit.

Scheme 3.9 shows the reductive elimination pathway starting from structures *trans*-**IXa**, *trans*-**IXb** and *trans*-**IXc** derived from the three substrates *o*-bromonitrobenzene (**a**), methyl *o*-bromobenzoate (**b**) and *p*-bromonitrobenzene (**c**), respectively. Intermediate *trans*-**IX** rearranges to the corresponding *cis* isomer, where the iodide is close to the biaryl group and thus in appropriate position for coupling. Reductive elimination can now occur through **TS(IX-X)** to form adduct **X**, which liberates the substrate and palladium in the oxidation state 0.

As previously anticipated, the reductive elimination can be obtained when particular conditions are met, the bulkiness of the ligand and the nature of the substrates involved can severely alter the kinetic of the process making it possible.

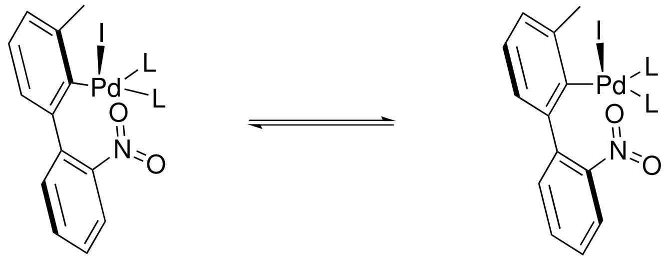
As shown in Scheme 3.9 intermediate **IX**, resulting from a ligand exchange on complex **VIII**, can be found in *cis* or *trans* configuration; the mechanism for the isomerization step was not investigated, however, is it possible that an equilibrium exists between the two conformations. Likely due to the presence of the *ortho* group, the energy gap for the *trans–cis* isomerization is negative for *o*-bromonitrobenzene (-1.8 $kcal/mol$) and is very low for methyl *o*-bromobenzoate (1.0 $kcal/mol$). On the contrary for *p*-bromonitrobenzene 14.9 $kcal/mol$ are required to reach the *cis* isomer.

The barrier to **TS(IX-X)c** is, however, only 4.6 $kcal/mol$, much lower that the *o*-bromonitrobenzene (15.3 $kcal/mol$) and methyl *o*-bromobenzoate (11.7 $kcal/mol$). Despite this low barrier, the *o*-iodobiaryl expected from the reaction of *o*-iodotoluene and *p*-bromonitrobenzene was not isolated. It is still not clear if this substrate can undergo the Pd(II)–Pd(IV) oxidative addition, as discussed in the previous section, however, the importance of the steric hindrance in the *cis–trans* isomerization step is clearly remarked by these results.



Scheme 3.9 Pd(II)-Pd(0) reductive elimination pathways for differents biaryl groups (ΔE).

The last intermediate of the catalytic cycle, *cis*-**IX**, exists in two stable conformations:



cis-**IXa** *cis*-**IXa'**

The interconvertion between the two forms would be easily achieved either by rotation along the biphenyl bond or by loss of a ligand followed by reintroduction of the same on the opposite side.

In structure *cis*-**IXa** the nitro group is closer to the palladium atom and to the bulky phosphine ligands. This conformation and the related transition state are high in energy but the barrier for the reductive elimination is only 15.2 *kcal/mol*, considerably lower than the one obtained for the conformation *cis*-**IXa'** (20.9 *kcal/mol*).

3.7 The effect of ligands

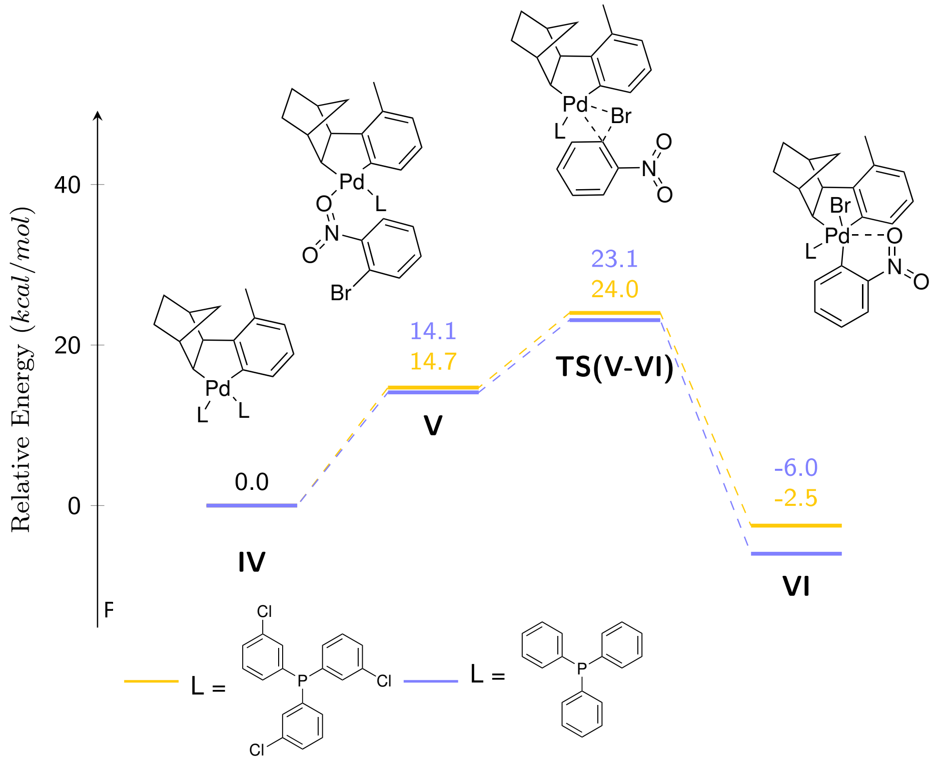
As previously pointed out *m*-TCPP was the ligand experimentally employed and fully included in the calculations reported in this chapter. To evaluate the effect of ligands the pathway of the reaction of *o*-iodotoluene and *o*-bromonitrobenzene (path a) was recalculated using PPh_3 (path d).

Scheme 3.10 shows the steps involved in the Pd(II)–Pd(IV) oxidative addition reaction. Very little differences in energy of intermediate **V** and **TS(V-VI)** were

found (< 1 *kcal/mol*) between the two ligands, while the Pd(IV) complex with PPh_3 (**VId**) is 3.5 *kcal/mol* more stable than the corresponding intermediate with *m*-TCPP (**VIa**). These energy values are likely to be ascribed to both the different steric and electronic properties of the two phosphines.
Scheme 3.11 shows the pathway for the C–I reductive elimination from complex **IX** to **X** with the two ligands. In this case a distinctive behavior between the two phosphines was observed. The energy barrier for the reductive elimination from *cis*-**IX** to **TS(IX-X)** is 18.9 *kcal/mol* for PPh_3 while only 15.3 *kcal/mol* are needed when the ligand is *m*-TCPP. On analysing the reverse pathway (oxidative addition from **X** to *cis*-**IX** through **TS(IX-X)**) it was noted that the barrier was almost the same (6.4 *kcal/mol* for *m*-TCPP, 7.3 *kcal/mol* for PPh_3); the oxidative addition was not influenced by the ligand as the reductive elimination. These results confirmed our experimental findings that the ligand *m*-TCPP behaves well. We can conclude that steric and electronic properties of the ligand *m*-TCPP favor the reductive elimination without penalizing too much the Pd(II)–Pd(IV) oxidative addition reaction.

3.8 Conclusions

The catalytic reaction of *ortho* substituted aryl iodides and bromides leading to the formation of *o*-iodobiaryls was simulated using quantum mechanics computational tools. Due to the complex mechanism, it was not possible to investigate every aspect of the process, however, some important information fully consistent with the experimental data was collected.
With the aid of the ONIOM methodology we managed to model a complex molecular system that comprised the entire structure of the ligands used in the experimental process. The reliability of our methods was verified by replicating previously reported data on the oxidative addition of aryl iodides to palladium(0) species. We

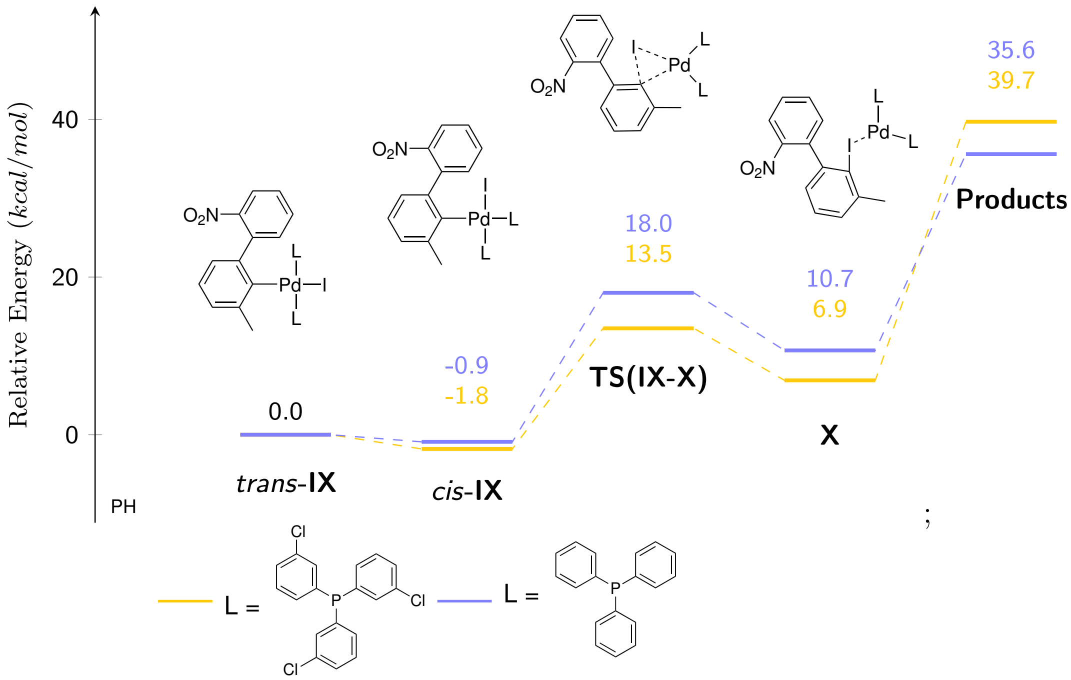


Scheme 3.10 Pd(II)-Pd(IV) oxidative addition pathways with different ligands (ΔE).

found that geometrical and energetic parameters of the oxidative addition of *o*- and *p*-iodotoluenene to palladium(0) species were comparable to those found in the literature (Scheme 3.5).

Entire pathways for the reactions of *o*-iodotoluene and *o*-bromonitrobenzene, methyl *o*-bromobenzoate or *p*-bromonitrobenzene were modelled. We focused our attention on some key steps of the process, the Pd(II)–Pd(IV) oxidative addition of the aryl bromide to the palladacycle **IV** (Scheme 3.8) and the final C–I reductive elimination (**IX**–**X**, Scheme 3.9) leading to the desired *o*-iodobiaryl derivative.

Our computational analysis on the Pd(II)–Pd(IV) oxidative addition provided some evidence of the key role played by coordinating groups, such as the $-NO_2$ and $-CO_2Me$ ones present at the *ortho* position of the bromoarene ring. They actively participate to the reaction mechanism by coordinating to the metal. A



Scheme 3.11 Ligand effect on Pd(II)→ Pd(0) reductive elimination (ΔE).

higher barrier was calculated when no substituent was present at the *ortho* position, however, an extensive study on the coordination equilibria which are certainly involved in the process is needed to better understand how the step occurs.

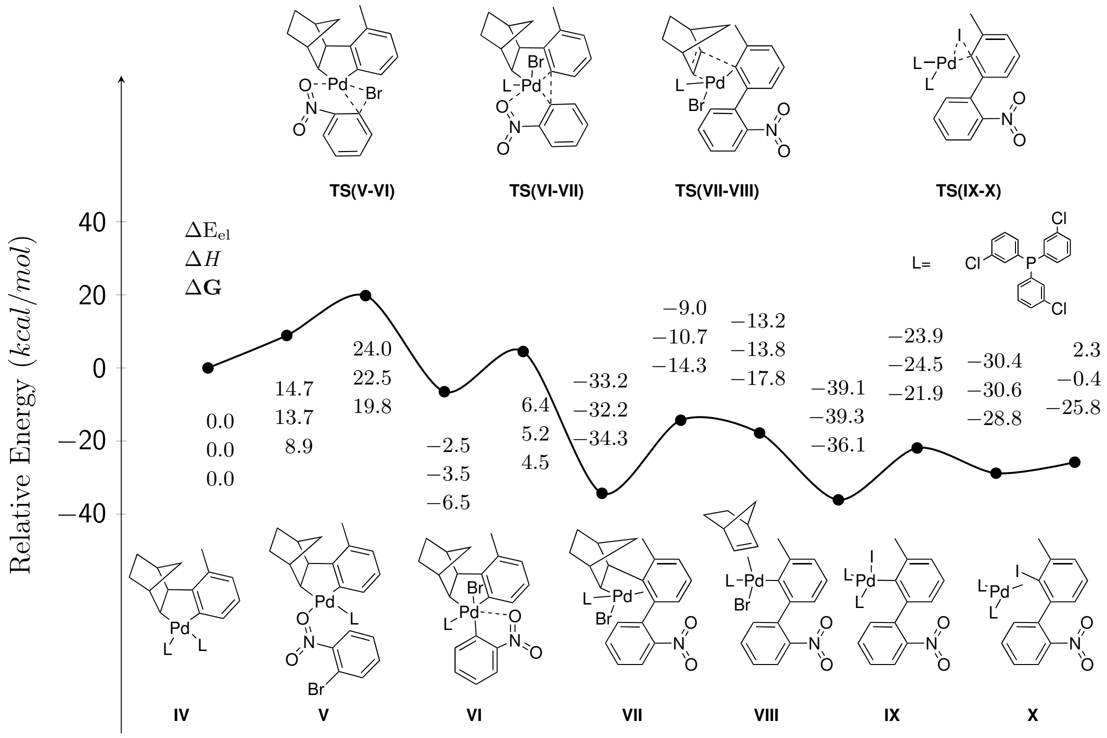
The C–I reductive elimination step leading to the *o*-iodobiaryl from intermediate **IX** was modelled as an intramolecular process where the the palladium-coordinated iodide migrates to the palladium-coordinated biaryl group. The energy barrier for this step seems possible for all the substrates taken into consideration in this study; intermediates **IXa** and **IXb** requires an activation energy of 15.3 and 11.7 *kcal/mol*, respectively, while for the reductive elimination from complex **IXc** only 4.6 *kcal/mol* are needed (Scheme 3.9). We found, however, that the *cis* isomer of intermediate **IXa** is favored over the *trans* form and the analogous complex **IXb** shows only a slightly lower energy for the *trans* isomer. On the contrary, the *trans*-*cis* equilibrium for intermediate **IXc** is almost completely shifted towards the unreactive *trans* isomer (Scheme 3.9).

Since it is not clear whether *p*-bromonitrobenzene can undergo the steps from **IVc** to **Xc**, the data collected for these steps are only hypothesis of the mechanism, however, a clear indication that the steric hindrance plays a crucial role in the reductive elimination is attained.
The reaction pathway for *o*-bromonitrobenzene in which PPh_3 is used as ligand, (path d) shows very little difference in energies compared to the one calculated for *m*-TCPP in all steps but the last. No significative differences are found for the Pd(II)$\rightarrow$ Pd(IV) oxidative addition between the two ligands (Scheme 3.10) while a lower energy barrier for the reductive elimination (steps *cis*-**IXd**–**Xd**) is obtained when the ligand is *m*-TCPP (Scheme 3.11). We can therefore assume that the use of *m*-TCPP as ligand has some advantages over the use of the more common PPh_3, in particular, it favors the reductive elimination step without interfering with oxidative addition processes that occur in this complex catalytic cycle.

I want to thank Prof. Roberto Cammi for the support that made possible the realization of this chapter.

3.9 Reaction Schemes

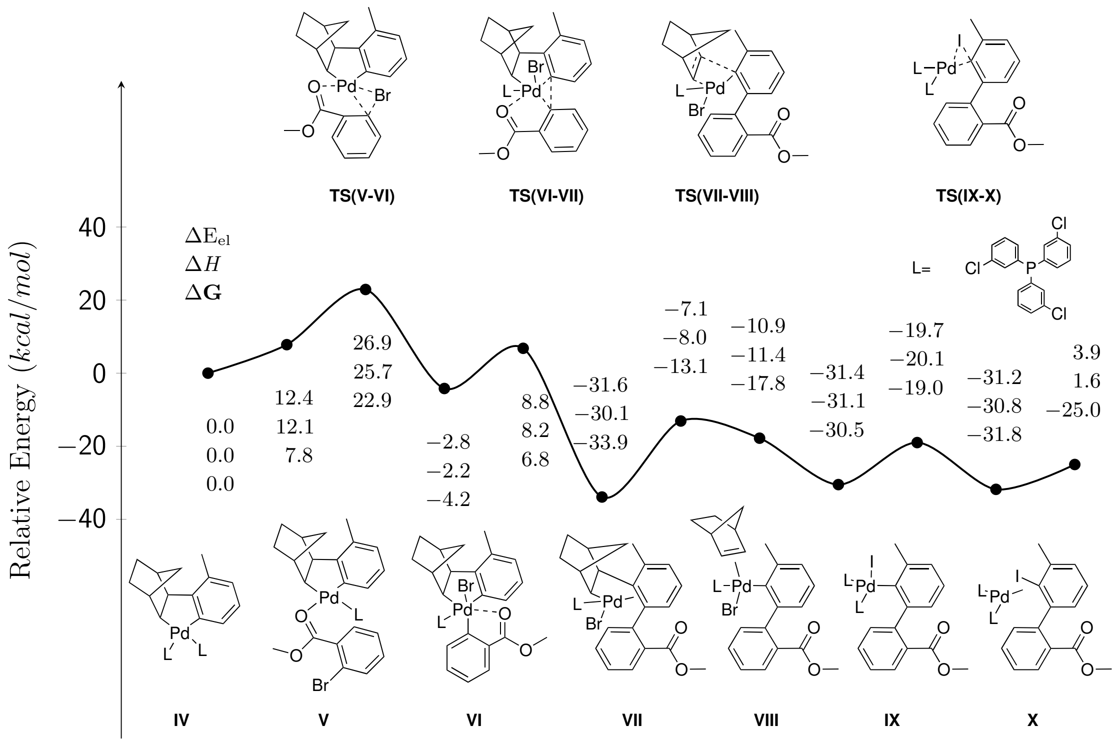
3.9.1 Scheme a



Relative Energies (*kcal/mol*)

	ΔE_{el}	ΔH_{298}	ΔG_{298}
IVa	0.0	0.0	0.0
Va	14.7	13.7	8.9
TS(V-VI)a	24.0	22.5	19.8
VIa	−2.5	−3.5	−6.5
TS(VI-VII)a	6.4	5.2	4.5
VIIa	−33.2	−32.2	−34.3
TS(VII-VIII)a	−9.0	−10.7	−14.3
VIIIa	−13.2	−13.8	−17.8
IXa	−39.1	−39.3	−36.1
TS(IX-X)a	−23.9	−24.5	−21.9
Xa	−30.4	−30.6	−28.8
Products	2.3	−0.4	−25.8

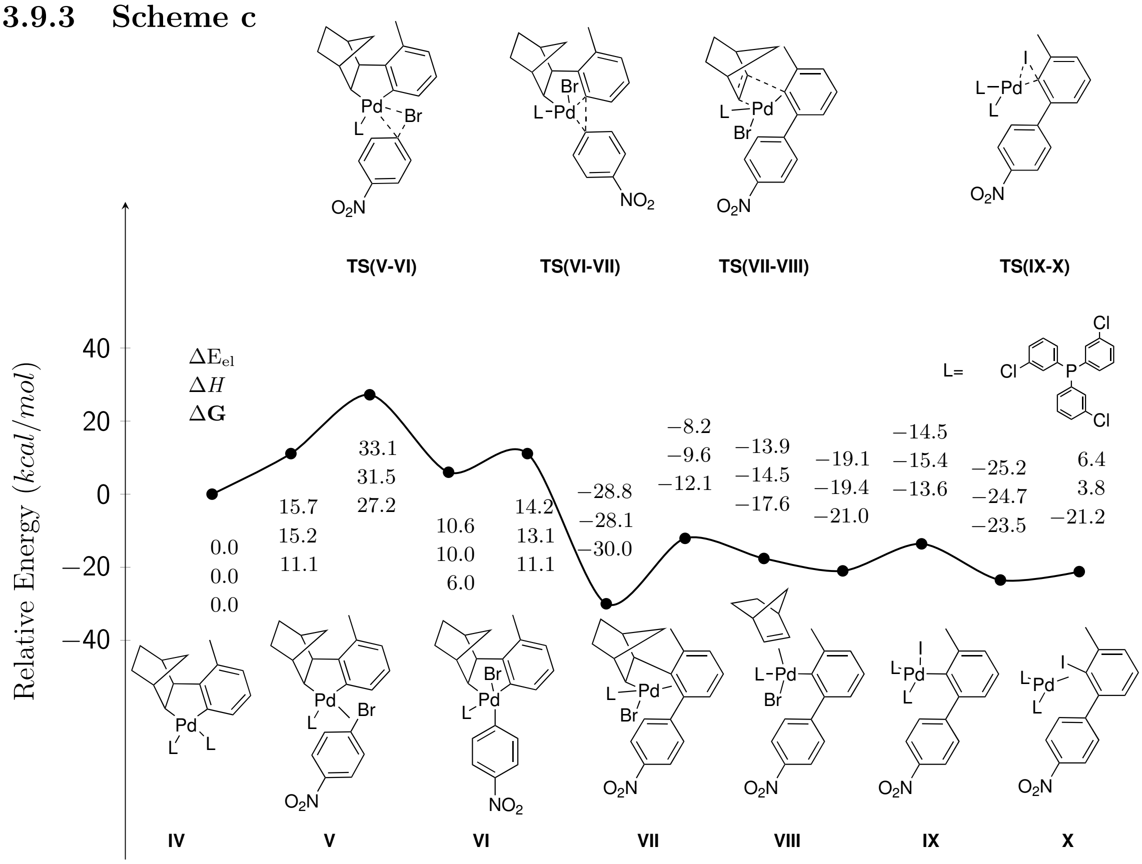
3.9.2 Scheme b



Relative Energies (*kcal/mol*)

	ΔE_{el}	ΔH_{298}	ΔG_{298}
IVb	0.0	0.0	0.0
Vb	12.4	12.1	7.8
TS(V-VI)b	26.9	25.7	22.9
VIb	−2.8	−2.2	−4.2
TS(VI-VII)b	8.8	8.2	6.8
VIIb	−31.6	−30.1	−33.9
TS(VII-VIII)b	−7.1	−8.0	−13.1
VIIIb	−10.9	−11.4	−17.8
IXb	−31.4	−31.1	−30.5
TS(IX-X)b	−19.7	−20.1	−19.0
Xb	−31.2	−30.8	−31.8
Products	3.9	1.6	−25.0

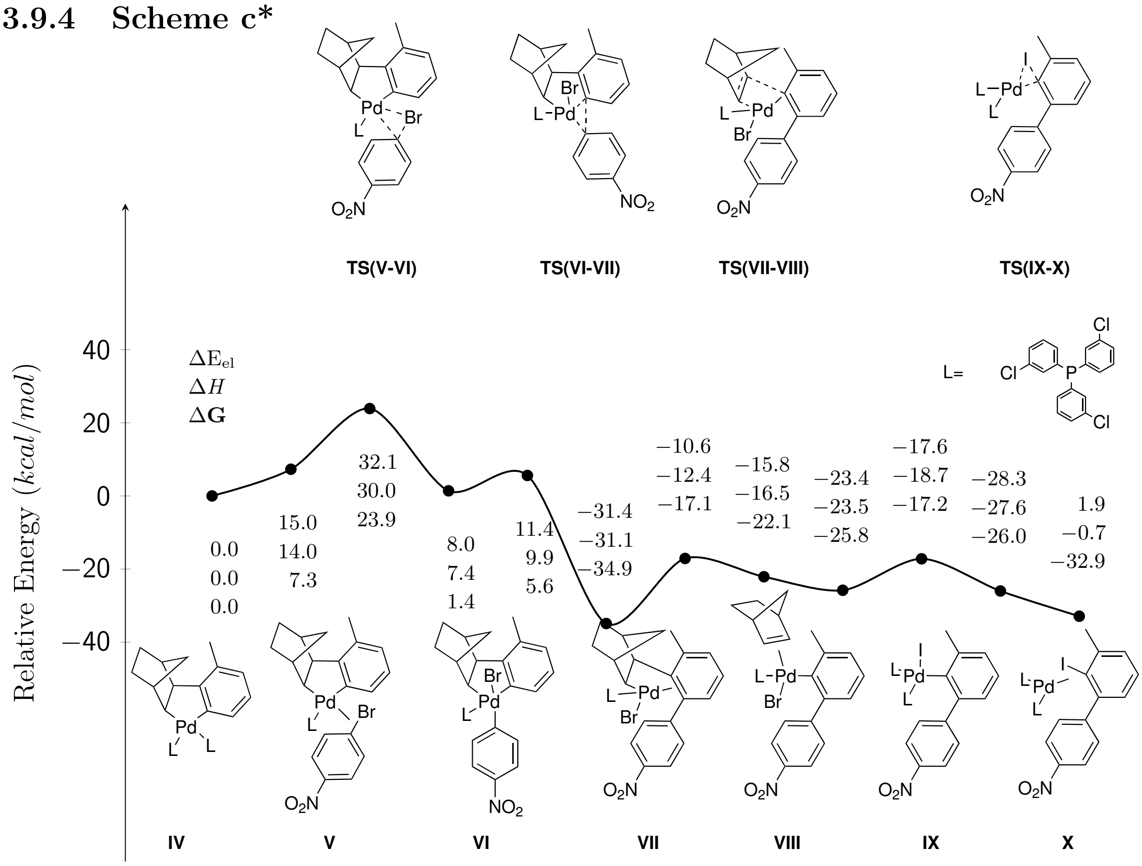
3.9.3 Scheme c



Relative Energies (*kcal/mol*)

	ΔE_{el}	ΔH_{298}	ΔG_{298}
IVc	0.0	0.0	0.0
Vc	15.7	15.2	11.1
TS(V-VI)c	33.1	31.5	27.2
VIc	10.6	10.0	6.0
TS(VI-VII)c	14.2	13.1	11.1
VIIc	−28.8	−28.1	−30.0
TS(VII-VIII)c	−8.2	−9.6	−12.1
VIIIc	−13.9	−14.5	−17.6
IXc	−19.1	−19.4	−21.0
TS(IX-X)c	−14.5	−15.4	−13.6
Xc	−25.2	−24.7	−23.5
Products	6.4	3.8	−21.2

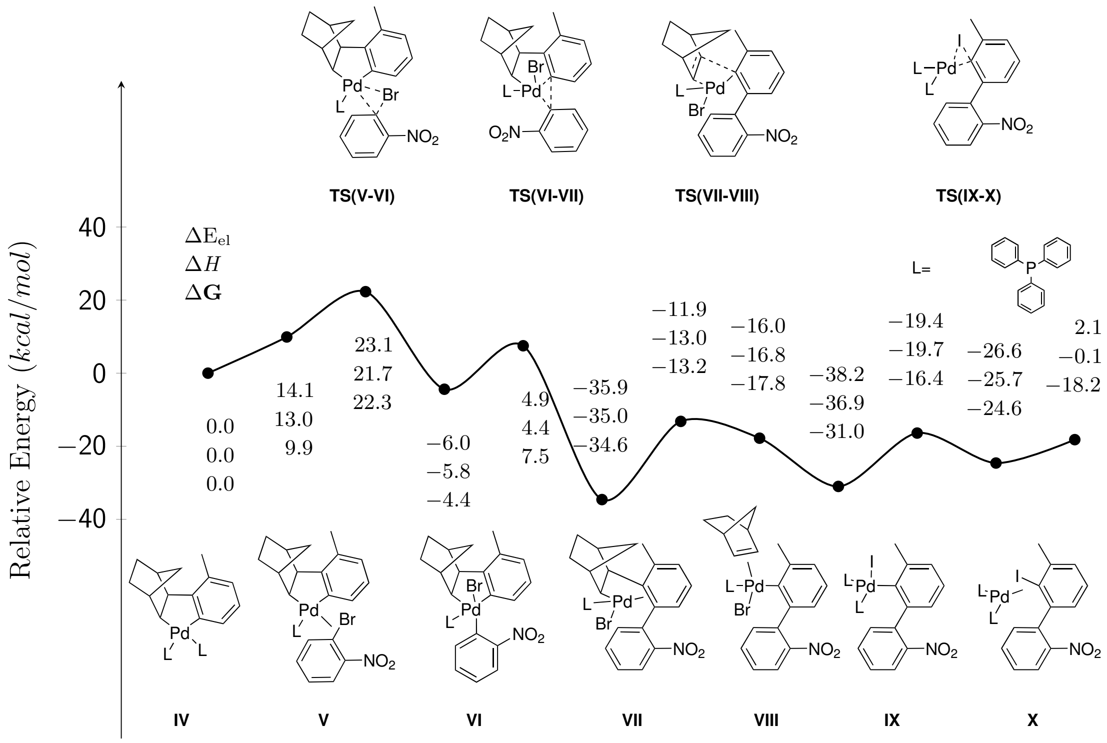
3.9.4 Scheme c*



Relative Energies (*kcal/mol*)

	ΔE_{el}	ΔH_{383}	ΔG_{383}
IVc*	0.0	0.0	0.0
Vc*	15.0	14.0	7.3
TS(V-VI)c*	32.1	30.0	23.9
VIc*	8.0	7.4	1.4
TS(VI-VII)c*	11.4	9.9	5.6
VIIc*	−31.4	−31.1	−34.9
TS(VII-VIII)c*	−10.6	−12.4	−17.1
VIIIc*	−15.8	−16.5	−22.1
IXc*	−23.4	−23.5	−25.8
TS(IX-X)c*	−17.6	−18.7	−17.2
Xc*	−28.3	−27.6	−26.0
Products	1.9	−0.7	−32.9

3.9.5 Scheme d



Relative Energies (*kcal/mol*)

	ΔE_{el}	ΔH_{298}	ΔG_{298}
IVd	0.0	0.0	0.0
Vd	14.1	13.0	9.9
TS(V-VI)d	23.1	21.7	22.3
VId	−6.0	−5.8	−4.4
TS(VI-VII)d	4.9	4.4	7.5
VIId	−35.9	−35.0	−34.6
TS(VII-VIII)d	−11.9	−13.0	−13.2
VIIId	−16.0	−16.8	−17.8
IXd	−38.2	−36.9	−31.0
TS(IX-X)d	−19.4	−19.7	−16.4
Xd	−26.6	−25.7	−24.6
Products	2.1	−0.1	−18.2

3.10 References

(1) a) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, PMID: 11456679, 1232–1233; b) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, PMID: 14611215, 13944–13945; c) Roy, A. H.; Hartwig, J. F. *Organometallics* **2004**, *23*, 1533–1541.

(2) Newman, S. G.; Lautens, M. *J. Am. Chem. Soc.* **2010**, *132*, 11416–11417.

(3) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09 Revision D.01.

(4) a) Dapprich, S.; Komáromi, I.; Byun, K.; Morokuma, K.; Frisch, M. J. *J. Mol. Str. Theochem.* **1999**, *461–462*, 1–21; b) Vreven, T.; Morokuma, K.; Farkas, Ö.; Schlegel, H. B.; Frisch, M. J. *J. Comput. Chem.* **2003**, *24*, 760–769.

(5) Zhao, Y.; Truhlar, D. English *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(6) a) Dunning Thom.H., J.; Hay, P. English In *Methods of Electronic Structure Theory*, Schaefer HenryF., I., Ed.; Modern Theoretical Chemistry, Vol. 3;

Springer US: 1977, pp 1–27; b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270–283; c) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284–298; d) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299–310.

(7) Martin, J. M.; Sundermann, A. *J. Chem. Phys.* **2001**, *114*, 3408–3420.

(8) Marten, J.; Seichter, W.; Weber, E.; Bohme, U. *Cryst. Eng. Comm.* **2008**, *10*, 541–547.

(9) a) Miertuš, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117–129; b) Miertuš, S.; Tomasi, J. *Chem. Phys.* **1982**, *65*, 239–245; c) Pascual-ahuir, J. L.; Silla, E.; Tuñon, I. *J. Comput. Chem.* **1994**, *15*, 1127–1138; d) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Letters* **1996**, *255*, 327–335; e) Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210–3221; f) Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032–3041; g) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151–5158; h) Mennucci, B.; Cancès, E.; Tomasi, J. *J. Phys. Chem. B* **1997**, *101*, 10506–10517; i) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995–2001; j) Cossi, M.; Barone, V.; Mennucci, B.; Tomasi, J. *Chem. Phys. Letters* **1998**, *286*, 253–260; k) Barone, V.; Cossi, M.; Tomasi, J. *J. Comput. Chem.* **1998**, *19*, 404–417; l) Cammi, R.; Mennucci, B.; Tomasi, J. *J. Phys. Chem. A* **1999**, *103*, 9100–9108; m) Cossi, M.; Barone, V.; Robb, M. A. *J. Chem. Phys.* **1999**, *111*, 5295–5302; n) Tomasi, J.; Mennucci, B.; Cancès, E. *J. Mol. Str. Theochem.* **1999**, *464*, 211–226; o) Cossi, M.; Barone, V. *J. Chem. Phys.* **2000**, *112*, 2427–2435; p) Cossi, M.; Barone, V. *J. Chem. Phys.* **2001**, *115*, 4708–4717; q) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Chem. Phys.* **2001**, *114*, 5691–5701; r) Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. *J. Chem. Phys.* **2002**, *117*, 43–54; s) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669–681.

(10) a) Bocelli, G.; Catellani, M.; Ghelli, S. *J. Organomet. Chem.* **1993**, *458*, C12–C15; b) Catellani, M.; Mealli, C.; Motti, E.; Paoli, P.; Perez-Carreño, E.; Pregosin, P. S. *J. Am. Chem. Soc.* **2002**, *124*, PMID: 11960463, 4336–4346; c) Della Ca', N.; Catellani, M.; Massera, C.; Motti, E., manuscript submitted.

(11) Maestri, G.; Motti, E.; Della Ca', N.; Malacria, M.; Derat, E.; Catellani, M. *J. Am. Chem. Soc.* **2011**, *133*, 8574–8585.

(12) a) Jacobsen, H.; Berke, H. *Chem. Eur. J.* **1997**, *3*, 881–886; b) González-Blanco, Ò.; Branchadell, V. *Organometallics* **1997**, *16*, 5556–5562; c) Sieffert, N.; Bühl, M. *Inorg. Chem.* **2009**, *48*, 4622–4624.

(13) Ananikov, V. P.; Szilagyi, R.; Morokuma, K.; Musaev, D. G. *Organometallics* **2005**, *24*, 1938–1946.

(14) Kozuch, S.; Amatore, C.; Jutand, A.; Shaik, S. *Organometallics* **2005**, *24*, 2319–2330.

(15) Catellani, M.; Motti, E.; Della Ca', N. *Acc. Chem. Res.* **2008**, *41*, 1512–1522.

(16) Della Ca', N.; Maestri, G.; Malacria, M.; Derat, E.; Catellani, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 12257–12261.

(17) a) Goossen, L. J.; Koley, D.; Hermann, H. L.; Thiel, W. *J. Am. Chem. Soc.* **2005**, *127*, PMID: 16076218, 11102–11114; b) Goossen, L. J.; Koley, D.; Hermann, H. L.; Thiel, W. *Organometallics* **2006**, *25*, 54–67.

(18) Goossen, L. J.; Koley, D.; Hermann, H. L.; Thiel, W. *Organometallics* **2005**, *24*, 2398–2410.

(19) Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314–321.

(20) a) Fagnou, K.; Lautens, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 26–47; b) Maitlis, P. M.; Haynes, A.; James, B. R.; Catellani, M.; Chiusoli, G. P. *Dalton Trans.* **2004**, 3409–3419.

(21) Ahlquist, M.; Norrby, P.-O. *Organometallics* **2007**, *26*, 550–553.

(22) Semmelhack, M.; Ryono, L. *Tetrahedron Lett.* **1973**, *14*, 2967–2970.

(23) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434–442.

(24) Newman, S. G.; Lautens, M. *J. Am. Chem. Soc.* **2011**, *133*, 1778–1780.

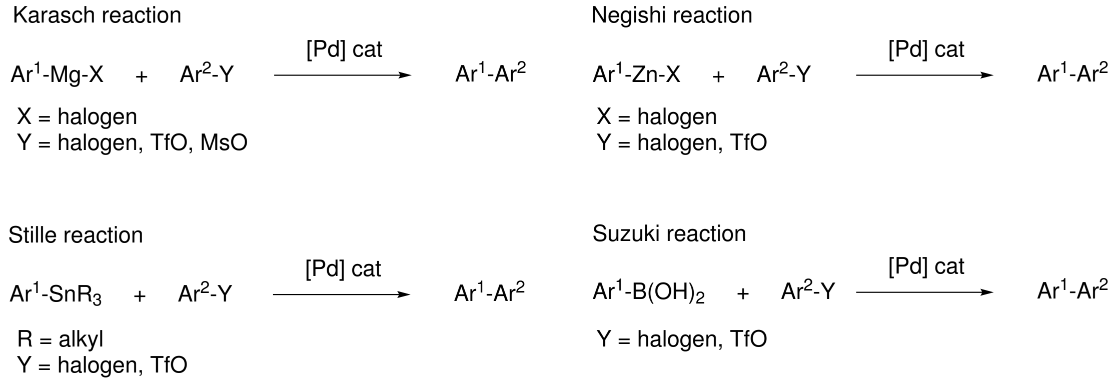
Chapter 4

Fluorenyl alcohols synthesis by dual palladium catalysis

4.1 Introduction

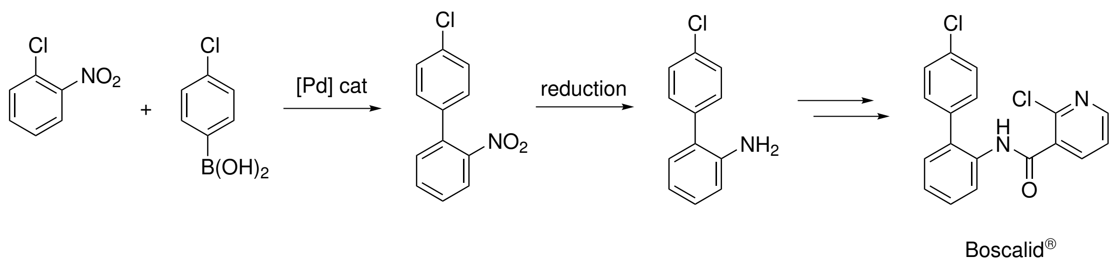
The biaryl unit is frequently found in a large number of biologically active and pharmaceutically important compounds. While many methods based on the use of transition metal catalysis are available for the synthesis of the biaryl moiety, the achievement of straightforward synthesis of complex biaryl systems is still an important target. The most common procedures are the palladium-catalyzed couplings including the Karasch, Stille, Negishi and Suzuki reactions (Scheme 4.1).

Among these processes the Suzuki reaction is the most used, in particular in the fine chemicals and pharmaceuticals industry. According to the Suzuki protocol, a biaryl is readily obtained by reaction of an aryl halide and an arylboronic acid in the presence of a palladium catalyst, often $Pd(PPh_3)_4$, and a base. In some cases the palladium species can be substituted by the nickel one. The mild conditions, the high tolerance towards functional groups, the readily available starting materials and their low toxicity compared to organozinc and organostannanes utilized in the Negishi and Stille reactions, make possible its application on a large scale.



Scheme 4.1 Aryl–aryl coupling reactions by palladium catalysis.

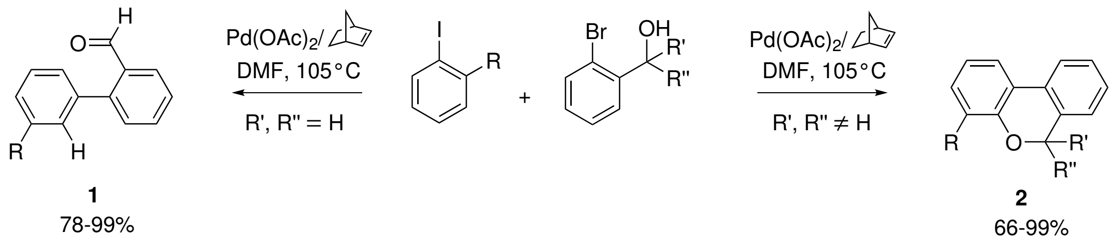
An example of industrial application is shown in Scheme 4.2 which reports the manufacture of the fungicide Boscalid by BASF; the first step, leading to 4-chloro-2'-nitro-1,1'-biphenyl is achieved by Suzuki coupling[1].



Scheme 4.2 Industrial synthesis of Boscalid by BASF.

Our research group has worked out a versatile methodology based on the palladium/norbornene catalytic system for the one-pot synthesis of selectively functionalized biaryls[2], also condensed with other rings. More recently, the reactivity of *o*-bromobenzyl alcohols in combination with *ortho*-substituted aryl iodides has been explored in a palladium/norbornene catalytic reaction. *o*-Bromobenzyl alcohols are versatile reagents that, depending on whether the hydroxyl group is primary, secondary or tertiary, allow various termination steps of the catalytic cycle to occur, leading to different products such as dibenzopyrans and *o*-biarylcarbaldehydes

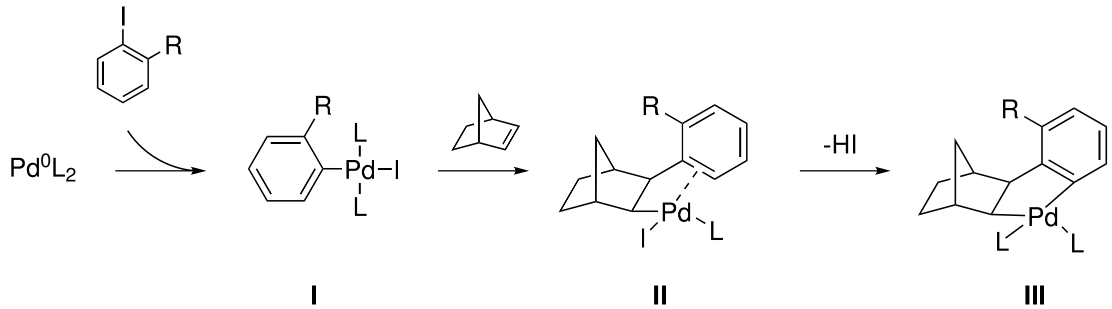
(Scheme 4.3)[3].



Scheme 4.3 *o*-Biarylcarbaldehydes and dibenzopyrans synthesis by palladium/norbornene catalysis.

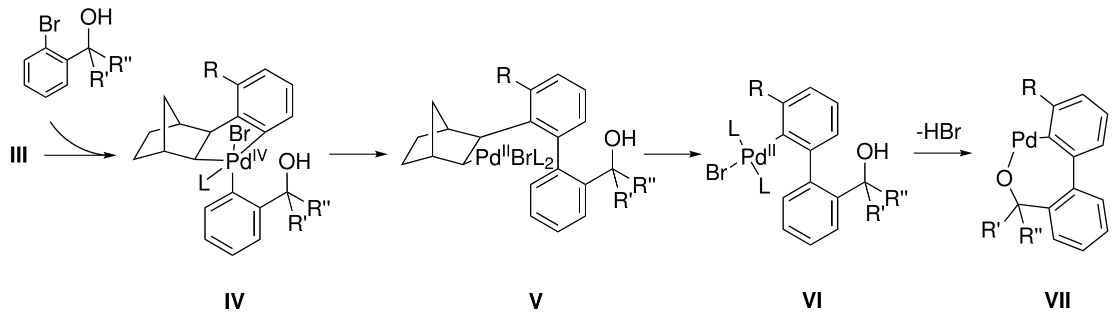
The selectivity of the process is thus uniquely driven by the nature of the *o*-bromobenzyl alcohol; tertiary alcohols (R′, R″ ≠ H) lead to dibenzopyrans while primary alcohols (R′, R″ = H) selectively forms *o*-biarylcarbaldehydes. In both cases a high yield of the desired product is achieved.

As previously proposed[3], the reaction is likely to proceed according to the pathway reported in Scheme 4.4 and 4.5. An *ortho* substituted aryl halide reacts with a palladium(0) species to form **I**; norbornene coordination is then followed by insertion into the arylpalladium bond affording **II**. Cyclization of complex **II** by electrophilic aromatic substitution gives palladacycle **III** containing the norbornyl unit.



Scheme 4.4 Proposed pathway from the oxidative addition of the *ortho*-substituted aryl iodide to palladacycle **III**.

Palladacycle **III** undergoes oxidative addition by the *o*-bromobenzyl alcohol leading to a Pd(IV) complex (**IV**), which reductively eliminates to the norbornylpalladium(II) bromide species **V**, containing the biaryl unit. Deinsertion of norbornene affords the complex **VI**, which cyclizes to the seven-membered oxapalladacycle **VII**.



Scheme 4.5 Proposed pathway from palladacycle **III** to the oxapalladacycle **VII**.

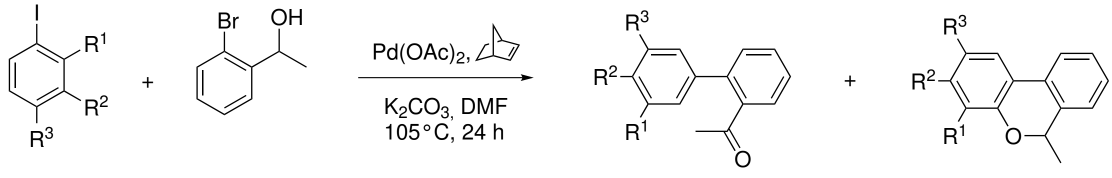
From intermediate **VII** (R′, R″ = H), an *o*-biarylcarbaldehyde (**1**) is obtained through an intramolecular hydrogen transfer, while in the presence of substituents (R′, R″ ≠ H), a dibenzopyran (**2**) is formed via C–O reductive elimination. The intermediacy of the oxapalladacycle **VII** is proposed on the basis of the data reported in the literature[4].

When a secondary *o*-bromobenzyl alcohol (R′ = H, R″ ≠ H), such as 1-(2-bromophenyl)ethanol, is used as coupling partner, the formation of the dibenzopyran derivative is always accompanied by the carbonyl compound. In Table 4.1 some examples of the reaction of an *ortho*-substituted aryl iodide with 1-(2-bromophenyl)ethanol are reported. The results show that the reaction is affected not only by the nature of the alcohol but also by the substituents present in the aryl iodide.

4.2 Results and discussion

In the attempt to find appropriate conditions to make the reaction selective we used $Pd(OAc)_2/PPh_3$ as catalyst and toluene as solvent in place of DMF. Under these different conditions a new product was isolated. Scheme 4.6 shows the reaction of

Table 4.1 Reaction of an *ortho*-substituted aryl iodide and 1-(2-bromophenyl)ethanol.[a]



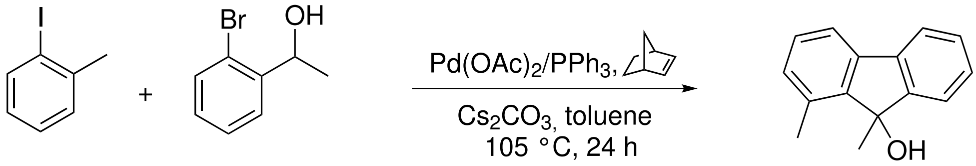
1 2

Entry	R^1	R^2	R^3	**1** (yield %)[b]	**2** (yield %)[b]
1[c]	Me	H	H	43	37
2[c]	Me	H	OMe	78	8
3	Me	OMe	OMe	85	9
4	-(CH=CH)$_2$-		H	24	49
5	-(CH=CH)$_2$-		OMe	80	16

[a] Reaction conditions: molar ratio of ArI, 1-(2-bromophenyl)ethanol, $Pd(OAc)_2$, norbornene, and K_2CO_3 20:20:1:20:50; in DMF at 105 °C, under N_2; t = 24 h; [Pd] = 2.2×10^{-3} mmol/ml. [b] Isolated yield. [c] Molar ratio of norbornene to Pd = 10:1.

o-iodotoluene and 1-(2-bromophenyl)ethanol leading to the corresponding fluorenyl alcohol.

The reaction was carried out in toluene at 105 °C in the presence of $Pd(OAc)_2/PPh_3$ as catalyst, with Cs_2CO_3 as a base and norbornene. Compound **3a** was obtained as the major product in very low yield (10%) together with equimolar amounts of the *o*-biarylketone **1a** and the dibenzopyran **2a** (equation of Table 4.1). Conversion of



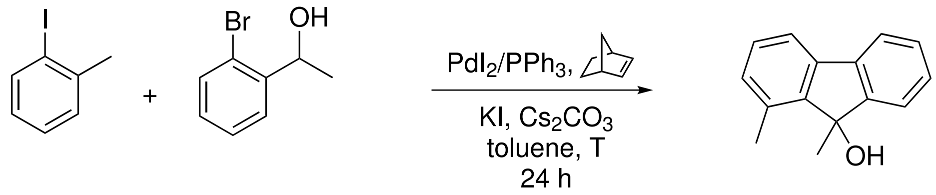
3a

Scheme 4.6 The catalytic reaction of *o*-iodotoluene and 1-(2-bromobenzyl)ethanol leads to the formation of fluorenyl alcohols when carried out in toluene.

both the aryl halides was around 50%.

Fluorenyl alcohols are compounds with interesting biological and spectroscopic properties[5,6], therefore we decided to further investigate this transformation and examined a series of reaction parameters. Some significant results are show in Table 4.2.

Table 4.2 Optimization of the reaction conditions.[a]

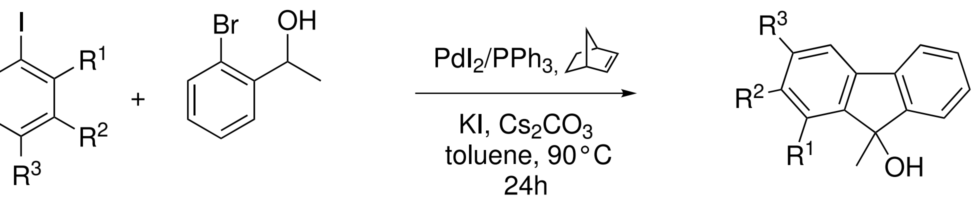


Entry	Pd cat (5 mol %)	PPh_3 (mol %)	KI (equiv[c])	T(°C)	Yield (%)
1	$Pd(OAc)_2$	10	—	90	10
2	PdI_2	10	—	90	67
3	PdI_2	10	5	90	76
4	PdI_2	10	10	90	68
5	PdI_2	—	5	90	0
6	PdI_2	15	5	90	49
7	PdI_2	10	5	120	68
8	PdI_2	10	5	105	75
9	PdI_2	10	5	80	70
10	$PdCl_2$	10	5	120	65

[a] Reaction of *o*-iodotoluene and 1-(2-bromophenyl)ethanol in toluene with a Pd salt, PPh_3, norbornene, Cs_2CO_3 and KI in the following molar ratio: 20:20:1:20:50:5; [Pd] = 2.2×10^{-3} mmol/ml; t = 24 h. [b] Determined by NMR analysis. [c] Equivalents to palladium.

Surprisingly PdI_2 in place of $Pd(OAc)_2$ gave 67% of compound **3a** (Table 4.2, entry 2). The addition of an additive such as KI was beneficial to the reaction. The amount of this salt was verified and the best results were obtained with 5 equivalents with respect to the palladium salt (entries 3, 4). No conversion was obtained in the absence of a ligand (entry 5), and PPh_3 proved to be the best one. The amount of the phosphine is critical to the outcome of the reaction and the best results were obtained with 10 mol% of PPh_3 (*cf.* entries 3 and 5). An increase of PPh_3 to 15 mol% is detrimental and reduces the yield to 49% (entry 6). The screening of the temperature revealed that the reaction, initially carried out at 105 °C (entry 8), occurs at 90 °C without penalizing yield and conversion (entry 3). Higher or lower temperatures reduce the yield (entry 7, 9). The use of $PdCl_2$ as catalyst gave results comparable to those obtained in the presence of PdI_2. The best yield (76%, entry 2) was obtained in the presence of PdI_2 (5 mol%), PPh_3 (10 mol%), norbornene (20 eq to palladium) and KI (5 eq to palladium) in toluene at 90 °C for 24 h.

Table 4.3 Synthesis of fluorenyl alcohols.[a]



3

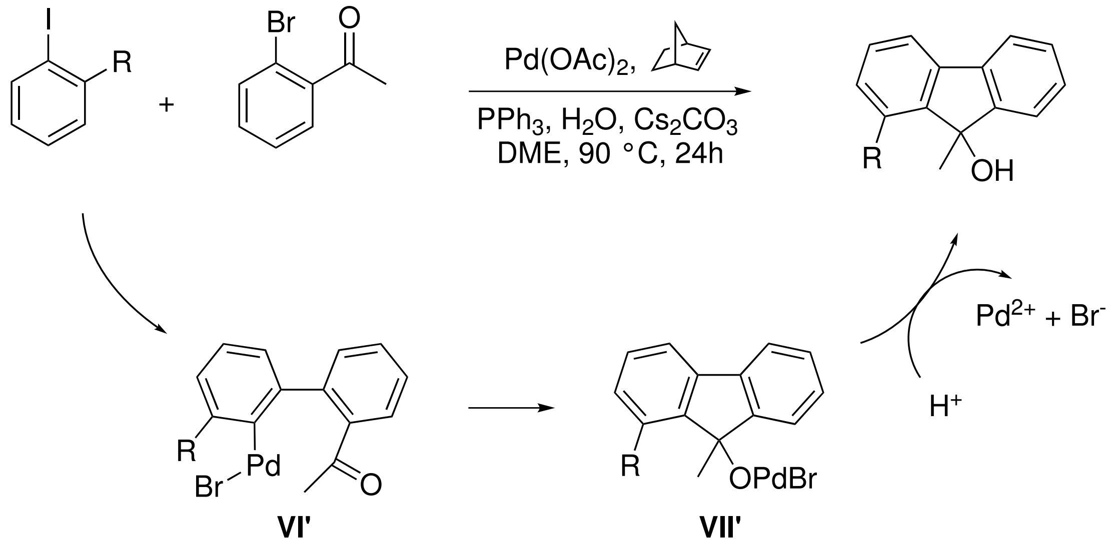
Entry	R^1	R^2	R^3	Product	Yield (%)[b]
1	Me	H	H	**3a**	76
2	Et	H	H	**3b**	71
3	*i*Pr	H	H	**3c**	49
4	-(CH=CH)$_2$-		H	**3d**	79
5	Me	H	Me	**3e**	71
6	OMe	H	H	**3f**	57

[a] Reaction of an *ortho*-substituted aryl iodide and 1-(2-bromophenyl)ethanol in toluene with PdI_2, PPh_3, norbornene, Cs_2CO_3 and KI in the following molar ratio: 20:20:1:2:20:50:5M [Pd] = 2.2×10^{-3} mmol/ml; t = 24 h. [b] Determined by NMR analysis.

Under these conditions a number of substrates were converted to the corresponding fluorenyl alcohols. Table 4.3 reports some results of the reaction of *ortho*-substituted aryl iodides and 1-(2-bromophenyl)ethanol. Good yields were obtained with *o*-

iodotoluene, *o*-iodoethylbenzene and 2,4-dimethyliodobenzene (Table 4.3, entries 1, 2 and 5), while low yields were achieved with *o*-iodoisopropylbenzene (entry 3) and *o*-iodoanisole (entry 6). 1-Iodonaftalene as starting aryl iodide gave the best result (entry 4, 79%).

The synthesis of fluorenyl alcohols starting from an *ortho*-substituted aryl iodide and *o*-bromoacetophenone in the presence of the palladium/norbornene catalytic system was recently published by Lautens *et al.* (Scheme 4.7)[7].

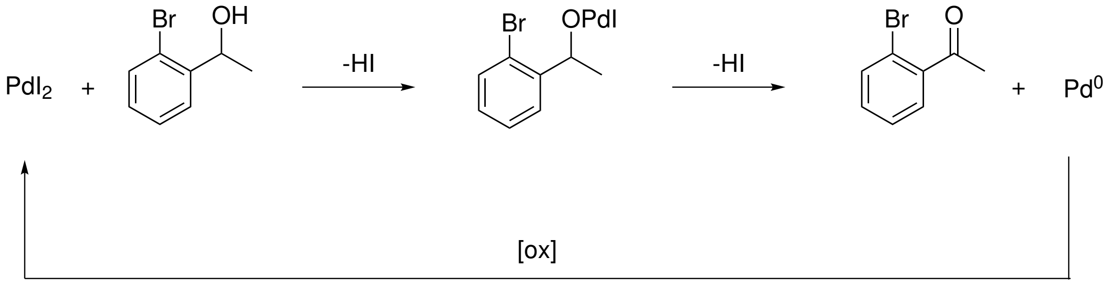


Scheme 4.7 Synthesis of fluorenyl alcohol by Pd/norbornene catalysis reported by Lautens group[7].

The reaction of an *ortho*-substituted aryl iodide and *o*-bromoacetophenone (Scheme 4.7) follows the general mechanism reported in the introduction for the synthesis of dibenzopyrans and *o*-biarylketones until the formation of a complex of type **VI** (Scheme 4.5). In the complex of type **VI**, involved in Lautens reaction, the palladium atom is in appropriate position for a nucleophilic attack to the *ortho* carbonyl group. The resulting palladium alcoholate, which does not bear any β-hydrogen to eliminate readily, undergoes hydrogenolysis to the fluorenyl alcohol with release of the metal in the oxidation state +2.

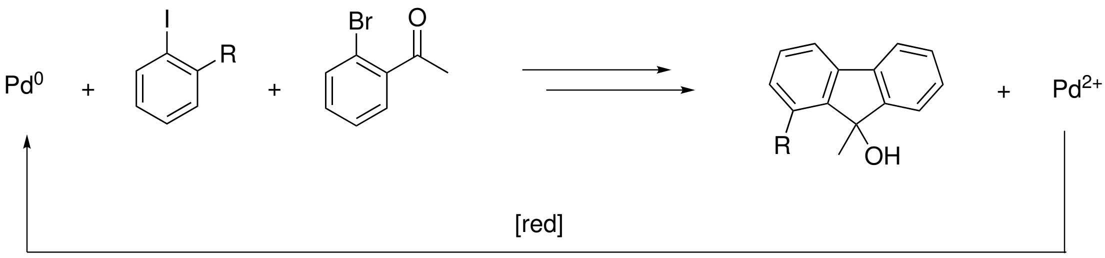
Also in our case, the synthesis of fluorenyl alcohols involves *o*-bromoacetophenone, which is formed *in situ* by palladium(II)-mediated oxidation of the secondary *o*-bromobenzy alcohol.

As exemplified in Scheme 4.8 the presence of the base favors the deprotonation of the alcohol which easily coordinates to the palladium in the oxidation state +2 and then oxidizes to ketone with palladium reduction. Thus *o*-bromoacetophenone is formed in a stoichiometric amount and is present in solution in very low concentration.



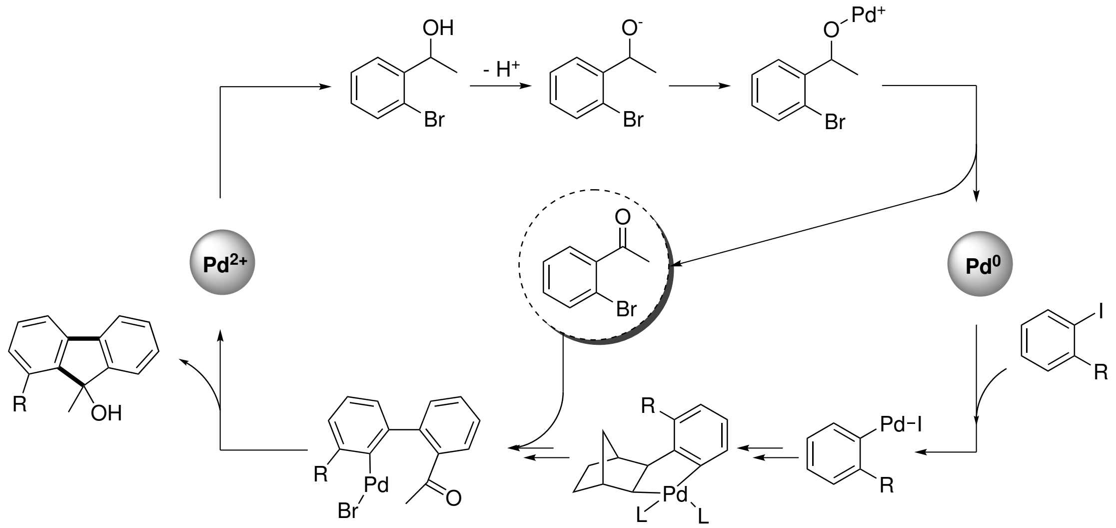
Scheme 4.8 Palladium-mediated oxidation of 1-(2-bromophenyl)ethanol. An oxidant makes the process catalytic.

The palladium(0) species resulting from the redox process is now ready to start the palladium/norbornene cycle (Scheme 4.9) by the oxidative addition of the aryl iodide, leading after a few steps to the palladacycle **III**, as reported in the Scheme 4.4 of the introduction.



Scheme 4.9 Synthesis of a fluorenyl alcohol. A reducting agent makes the process catalytic.

Palladacycle **III** selectively reacts with *o*-bromoacetophenone in spite of the concentration much lower than that of the *o*-bromobenzyl alcohol. The electron-withdrawing character of the carbonyl substituent favors the oxidative addition step. At the end of the process Pd(II) is released in solution and another benzyl alcohol molecule can be oxidized to *o*-bromoacetophenone (Scheme 4.10).



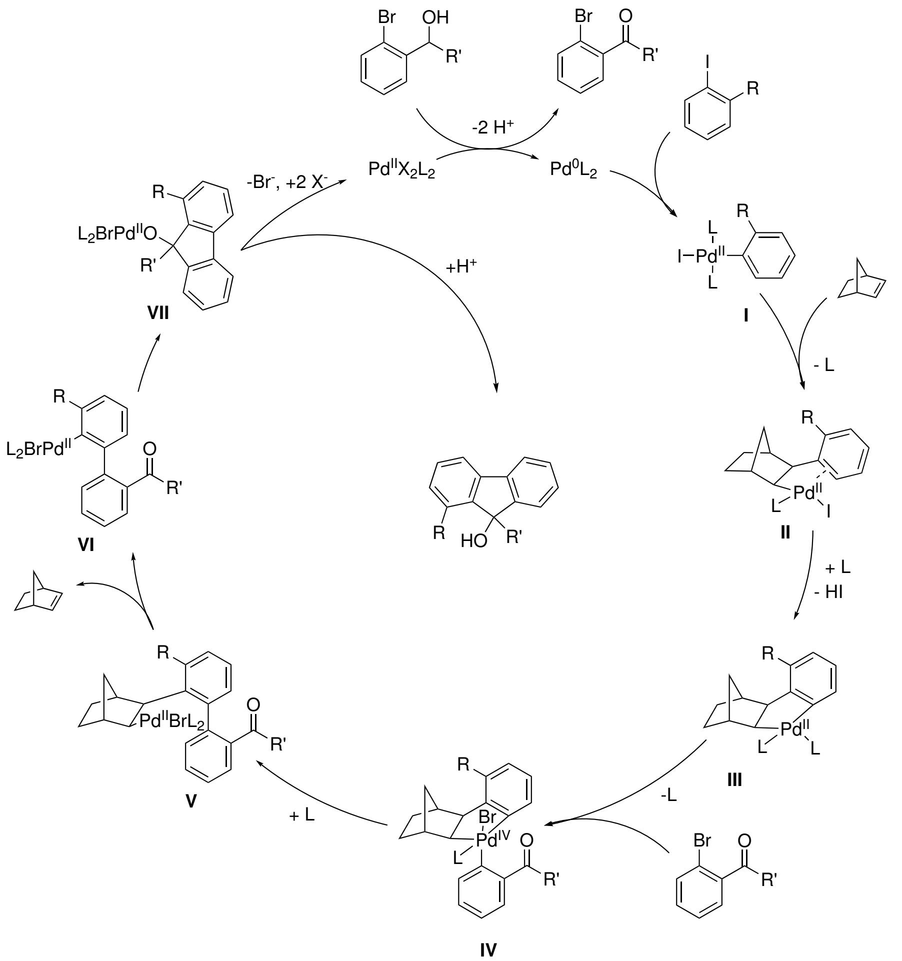
Scheme 4.10 Fluorenyl alcohol synthesis from an *ortho*-substituted aryl iodide and 1-(2-bromophenyl)ethanol.

Thus, this complex catalytic cycle consists of two complementary processes: the former (upper part of Scheme 4.10) starts from a Pd(II) species and leads to the formation of Pd(0) involving the OH group of the *o*-bromobenzyl alcohol; the latter starts with the oxidative addition of the Pd(0) species by the aryl iodide, and ends up with the release of the metal in the oxidation state +2 (lower part of Scheme 4.10). The combination of the two stoichiometric reactions makes the entire process catalytic. Moreover, *o*-bromoacetophenone, coming from the first redox, becomes substrate for the subsequent palladium-mediated synthesis of the fluorenyl alcohol.

Transition metals have been previously utilized in processes that require more than one concomitant catalytic transformation[8–11]. We succeeded, however, to efficiently synchronize two reactions and combine them in a single process where the "spent" catalyst at the end of a reaction is regenerated by the other one, and vice versa.

Our dual catalysis relies on the fact that the two processes occur sequentially as two independent stoichiometric reactions; they entwine each other by sharing stable intermediates and not transient species that can undergo side reactions. The delicate balance between the two processes has been achieved using a single catalyst, in a one-pot reaction.

Scheme 4.11 shows the proposed catalytic cycle. It starts with the *o*-acetophenone and Pd(0) formation according to the previously described redox process (Scheme 4.8). The aryl iodide now oxidatively adds to the metal forming the arylpalladium iodide **I**. Norbornene readily coordinates and inserts into the arylpalladium bond of **I** affording intermediate **II**; complex **II** contains the metal and the aryl ring on the same side of the methylene bridge of the norbornyl ring. This *cis, exo* geometry allows a weak interaction through an η^2 coordination between the palladium atom and a double bond of the aromatic ring, in a sort of pre-organization favoring ring closure, to afford the alkylarylpalladacycle **III**. The resulting metallacycle undergoes oxidative addition by the *in situ* formed *o*-bromoacetophenone, giving the Pd(IV) complex **IV**. A C–C coupling by reductive elimination readily occurs to generate intermediate **V**, containing the biaryl unit. This intermediate, due to the steric hindrance around the metal center, undergoes a C–C cleavage with norbornene deinsertion yielding complex **VI**. As previously anticipated, palladium is in proper position to attack the *ortho* carbonyl substituent. The resulting intermediate **VII** undergoes hydrolysis to afford the organic product and liberate palladium in the oxidation state +2. By oxidation of a new alcohol molecule, *o*-bromoacetophenone is formed and palladium is reduced to the oxidation state 0, ready to start a new catalytic cycle.



Scheme 4.11 Proposed catalytic cycle for the synthesis of fluorenyl alcohols.

4.3 Conclusions

In conclusion we have reported a new palladium-catalyzed synthesis of fluorenyl alcohols starting from *ortho*-substituted aryl iodides and 1-(2-bromophenyl)ethanol. The catalytic cycle is constituted by two entwined complementary stoichiometric reactions: a) oxidation of an *o*-bromobenzyl alcohol to the corresponding ketone by Pd(II) with liberation of Pd(0); b) Pd(0)-mediated reaction of an aryl iodide and the *in situ* formed ketone, to give the corresponding fluorenyl alcohol and release Pd(II). The combination of the two stoichiometric processes makes catalytic the entire transformation.

4.4 Experimental

4.4.1 General Remarks

All reactions were carried out under N_2 in a Schlenk-type tube. Most reagents were purchased from common suppliers and usually employed without further purification. *o*-Iodoethylbenzene[12] and *o*-iodoisopropylbenzene[13] were prepared by Sandmeyer reaction from the corresponding anilines, 1-(2-bromophenyl)ethanol was prepared by reduction of *o*-bromoacetophenone[14]. Gas chromatographic analyses were performed with a Agilent Technologies 7820A GC System using a 30 m SE-30 capillary column.

Flash column chromatography was carried out using Merck Kiesegel 60 as stationary phase and thin layer chromatography using Merck 60F254 plates. A mixture of *n*-hexane/EtOAc is used as eluent.

Electron impact mass spectra (m/z, relative intensity (%)) were determined with an Agilent Technologies 6890N GC system and 5973 Mass selective detector working at 70 eV ionization energy.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE 400 spectrometer at 400 and 100 MHz, respectively, using the solvent peak as internal reference.

4.4.2 General procedure for the catalytic synthesis of fluorenyl alcohols

General procedure for the synthesis of fluorenyl alcohols from ortho-*substituted aryl iodides and 1-(2-bromophenyl)ethanol*

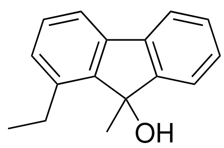
Cesium carbonate (120 mg, 0.37 mmol) is heated at 110 °C under vacuum in a Schlenk type tube for 1.5 h. After cooling to room temperature the tube is filled with nitrogen, evacuated and back-filled with nitrogen, three times. A toluene

solution (3.7 ml) of the aryl iodide (0.17 mmol), 1-(2-bromophenyl)ethanol (0.16 mmol) and norbornene (7.8 mg, 0.0830 mmol) is added to the flask, followed by PdI_2 (3.0 mg, 0.0083 mmol), PPh_3 (4.4 mg, 0.0249 mmol) and KI (6.9 mg, 0.04 mmol) as solids. The reaction flask is stirred under nitrogen at r.t. for 10 minutes and heated into an oil bath at 90 °C for 24 h.
After cooling the mixture is diluted with ethyl acetate (30 ml), transferred to a separatory funnel and washed twice with water (25 ml). The resulting solution is dried over Na_2SO_4 and the solvent was removed under vacuum. The crude mixture is separated by flash column chromatography on silica gel using a mixture of *n*-hexane/EtOAc.

4.4.3 Characterizations

Compounds prepared by the reported procedure are already known and their characterization is available in the literature[7].

1-Ethyl-9-methyl-9H-fluoren-9-ol (**3b**)



White solid, yield 71%, eluent *n*-hexane/EtOAc 95:5.
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.58 (1H, d, J = 7.6 Hz), 7.50 (1H, d, J = 7.6 Hz), 7.45 (2H, dd, J = 7.5 Hz, 0.9 Hz), 7.34 (1H, td, J = 7.4, 1.4 Hz), 7.31 (1H, t, J = 7.4 Hz), 7.29 (1H, td, J = 7.4, 1.4 Hz), 7.15 (1H, d, J = 7.6 Hz), 3.01 (2H, qd, J = 7.6, 1.9 Hz), 2.03 (1H, broad s), 1.79 (3H, s), 1.32 (3H, t, J = 7.6 Hz).
^{13}C NMR (100.62 MHz, $CDCl_3$): δ 150.6, 145.9, 141.9, 140.0, 138.5, 129.0, 128.8,

128.6, 127.9, 122.9, 119.8, 117.4, 81.1, 25.9, 23.8, 15.8.

4.5 References

(1) Rouhi, A. M. *C&N News* **2004**, *82*, 49–58.

(2) Catellani, M.; Motti, E.; Della Ca', N. *Acc. Chem. Res.* **2008**, *41*, 1512–1522.

(3) Motti, E.; Ca', N. D.; Xu, D.; Piersimoni, A.; Bedogni, E.; Zhou, Z.-M.; Catellani, M. *Org. Lett.* **2012**, *14*, 5792–5795.

(4) a) Alsters, P. L.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; Van Koten, G. *Organometallics* **1993**, *12*, 1639–1647; b) Palucki, M.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 10333–10334; c) Fernández-Rivas, C.; Cárdenas, D. J.; Martín-Matute, B.; Monge, Á.; Gutiérrez-Puebla, E.; Echavarren, A. M. *Organometallics* **2001**, *20*, 2998–3006; d) Terao, Y.; Wakui, H.; Nomoto, M.; Satoh, T.; Miura, M.; Nomura, M. *J. Org. Chem.* **2003**, *68*, PMID: 12816483, 5236–5243.

(5) Wan, P.; Krogh, E. *J. Am. Chem. Soc.* **1989**, *111*, 4887–4895.

(6) Ting, P. C.; Lee, J. F.; Albanese, M. M.; Tom, W. C.; Solomon, D. M.; Aslanian, R.; Shih, N.-Y.; West, R. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 2643–2646.

(7) Zhao, Y.-B.; Mariampillai, B.; Candito, D. A.; Laleu, B.; Li, M.; Lautens, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 1849–1852.

(8) Trost, B. M.; Luan, X. *J. Am. Chem. Soc.* **2011**, *133*, 1706–1709.

(9) Ajamian, A.; Gleason, J. L. *Angew. Chem. Int. Ed.* **2004**, *43*, 3754–3760.

(10) Gabriele, B.; Mancuso, R.; Salerno, G.; Veltri, L. *Chem. Commun.* **2005**, 271–273.

(11) Batt, F.; Gozzi, C.; Fache, F. *Chem. Commun.* **2008**, 5830–5832.

(12) Weygand, F.; Weber, H.; Maekawa, E.; Eberhardt, G. *Chem. Ber.* **1956**, *89*, 1994–1999.

(13) Della Ca', N.; Sassi, G.; Catellani, M. *Adv. Synth. Catal.* **2008**, *350*, 2179–2182.

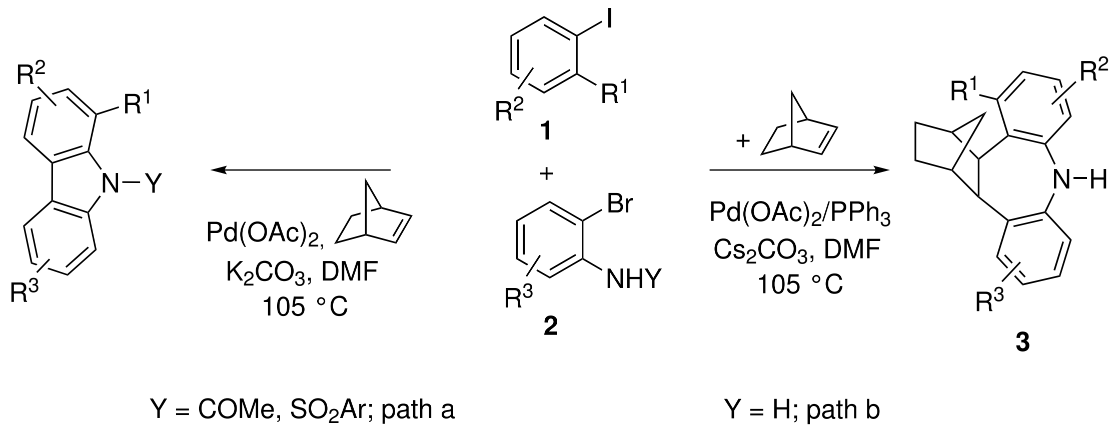
(14) Studer, A.; Bossart, M.; Vasella, T. *Org. Lett.* **2000**, *2*, 985–988.

Chapter 5

A straightforward and general Pd-catalyzed synthesis of dibenzoazepine derivatives from aryl iodides or bromides, *o*-bromoanilines and norbornene or norbornadiene

5.1 Introduction

A Pd/norbornene-catalyzed sequential reaction of *o*-substituted aryl iodides and protected *o*-bromoanilines leading to the formation of five-membered condensed heterocycles such as carbazoles (Scheme 5.1, path a; R^1 = alkyl, Y = acetyl, arenesulfonyl) has been previously reported[1]. This reaction is based on our general methodology which allows the selective synthesis of unsymmetrical biaryl structures starting from *ortho*-substituted aryl iodides and aryl bromides under the combined Pd/norbornene catalysis[2]. The *ortho* substituent in the aryl iodide is required to promote aryl–aryl rather than aryl–norbornyl coupling[2,3]. The final step, leading to liberation of Pd(0) for a new catalytic cycle, is offered by C–N coupling[4] to form the five-membered carbazole ring. To our surprise, using *ortho*-substituted or unsubstituted aryl iodides with unprotected *o*-bromoanilines under similar conditions and adding a triarylphosphine as ligand, the unexpected formation of the dibenzoazepine instead of the carbazole ring was observed (Scheme 5.1, path b)[5]. The different role played by norbornene in these reactions is noteworthy: while,



Scheme 5.1 Pd-catalyzed reactions of *o*-substituted aryl iodides and *o*-bromoanilines: norbornene catalysis to carbazoles (path a) *vs* norbornene incorporation to dihydrodibenzoazepine derivatives (path b).

in combination with Pd, it acts as organic catalyst in the synthesis of carbazoles, it is incorporated instead in the dihydrodibenzoazepine structures. The construction of the tricyclic compound **3** thus represents a deviation from the *"ortho"* effect which states that, in Pd/norbornene catalysis the presence of an ortho-substituent in the aryl iodide, favors the Csp^2-Csp^2 bond formation rather than the Csp^2-Csp^3 one. The deviation from the general rule is ascribed to the chelating effect of the NH_2 group to Pd[6], which is sufficiently high to offset the ortho effect. The proposal is based on detailed mechanistic analyses by DFT calculations[5,7].

Dihydrodibenzoazepines and dibenzoazepines are two classes of pharmaceutically interesting compounds with antidepressant and antiepileptic properties[8]. Figure 5.1 shows some active ingredients of the most popular antidepressant drugs available in pharmacies and drug stores. Recently, the dibenzoazepine structure has been inserted in organic electroluminescent materials[9]. Moreover, phosphoranes of dibenzo[*b*,*f*]azepine molecules, as alkene-bearing structures, are promising as chiral phosphine-alkene ligands[10].

Given their importance in the pharmaceutical industry, various synthetic methods of these compounds have been reported in the literature[11]. Nevertheless, the development of selective and efficient methods for the synthesis of these tricyclic compounds still represents an important target.

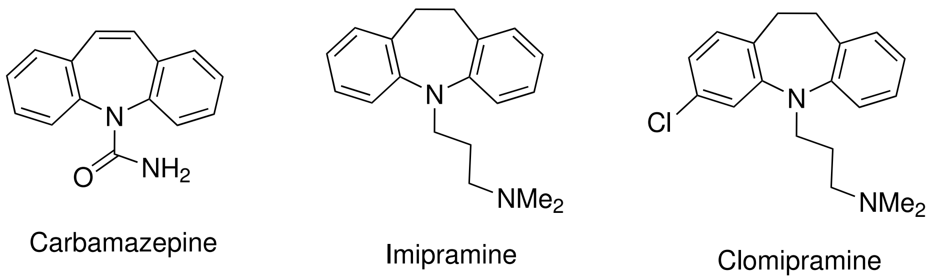


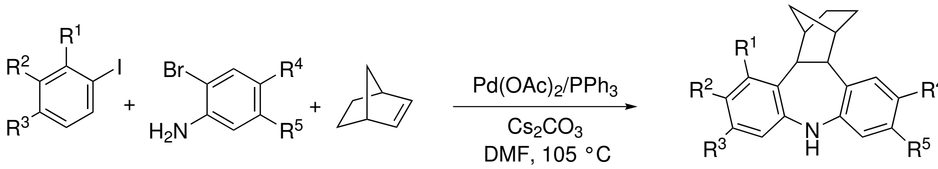
Fig. 5.1 Active ingredients of well-known antidepressant drugs.

A preliminary communication in this field has been published[5] and herein we report the results of our studies focused to the development of a new protocol which complements the previous one and leads to a general and straightforward synthesis of dihydrodibenzoazepine and dibenzoazepine derivatives with a wide substrate scope.

5.2 Results and discussion

Our initial studies were carried out under the conditions previously optimized, with an aryl iodide (**1**; 1.1 equiv), an *o*-bromoaniline (**2**; 1.0 equiv), norbornene (1.2 equiv), $Pd(OAc)_2$ (5 mol%) and PPh_3 (12.5 mol%) as catalyst, Cs_2CO_3 (2.25 equiv) as a base, in DMF as solvent, at 105 °C under nitrogen for the time required for Pd black precipitation (6–24 h). The expected dihydrodibenzoazepine derivatives were obtained in satisfactory to good yields in a one-pot reaction under mild conditions starting from commercially available or readily prepared reagents. The substrate scope of the reaction was further investigated with norbornene as model using a number of aryl iodides and bromides bearing a variety of substituents which can be present in the different positions of the aryl ring. Some new results are reported in Table 5.1. As expected on the basis of our previous knowledge also *ortho*-unsubstituted aryl iodides could react with *o*-bromoaniline to afford the desired dibenzoazepine derivative **3** (Table 5.1, entry 7). Thus, this three-component transformation involving norbornene incorporation in the final product, performs well even in the absence of a substituent in the ortho position of the initial aryl iodide. Satisfactory to good yields can be obtained when *o*-bromoaniline reacts with aryl iodides bearing an alkyl or alkoxy group in *ortho* position (entries 1–4). The substituent effect is not easily rationalized in the presence of two substituents in the aryl iodide (entries 5, 6). 2-Bromo-4-chloroaniline (entry 7) gives a 75% yield of the expected compound **3g** when combined with 4-iodoanisole in spite of the presence of the methoxy group in *p*- position. Indeed, under the reaction conditions a *para*-substituent in the aryl iodide can promote side reactions.[12] *o*-Bromo-*N*-methylaniline as well as *N*-acetylated or *N*-sulphonylated ones do not lead to compound **3**. The former is not reactive and the latter gives carbazole derivatives (Scheme 5.1)[1].

Table 5.1 Direct synthesis of dihydrodibenzoazepine derivatives: *cis,exo*-1,2,4,4a,13b,-hexahydro-1,4-methano-9*H*-tribenzo[*b,f*]azepines.[a]



1 **2** **3**

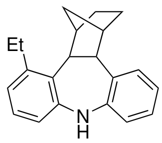
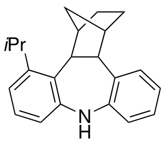
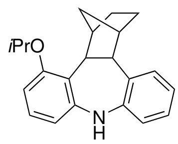
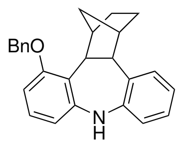
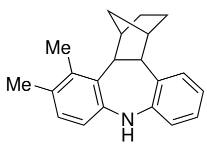
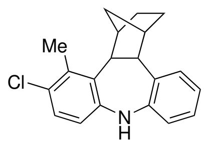
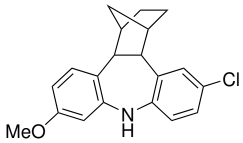
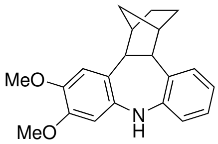
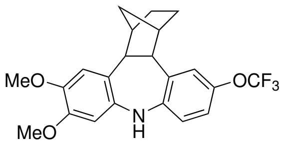
Entry	R^1	R^2	R^3	R^4	R^5	Time (h)	Product	Yield **3** (%)[b]
1	Et	H	H	H	H	22	 **3a**	80
2	*i*-Pr	H	H	H	H	60	 **3b**	55
3	O*i*-Pr	H	H	H	H	22	 **3c**	83
4	OBn	H	H	H	H	20	 **3d**	76
5	Me	Me	H	H	H	22	 **3e**	54
6	Me	Cl	H	H	H	21	 **3f**	65

Table 5.1: continued on next page

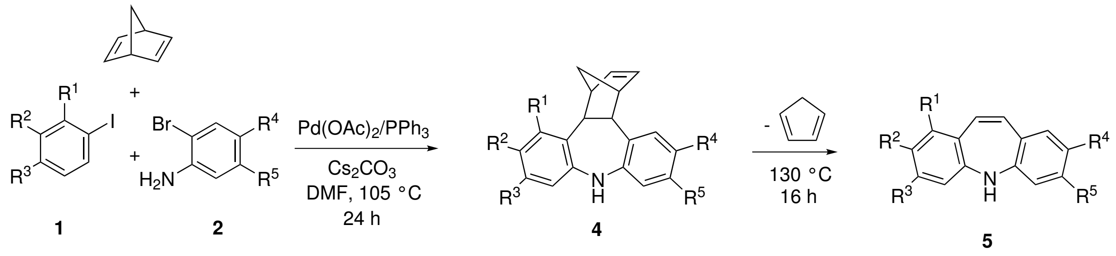
Table 5.1: continued from previous page

Entry	R^1	R^2	R^3	R^4	R^5	Time (h)	Product	Yield **3** (%)[b]
7	H	H	OMe	Cl	H	21	 **3g**	75
8	H	OMe	OMe	H	H	42	 **3h**	51
9	H	OMe	OMe	OCF_3	H	24	 **3i**	44

[a] Reaction conditions: **1** (1.1 equiv), **2** (1.0 equiv), norbornene (1.2 equiv), $Pd(OAc)_2$ (5 mol%), PPh_3 (12.5%), Cs_2CO_3 (2.25 equiv) in DMF at 105 °C under N_2, for the time needed for palladium black precipitation; 2.2×10^{-3} mmol $Pd(OAc)_2$/mL DMF. The reaction was carried out on a 0.5 mmol scale. [b] Isolated yield on the charged amount of the *o*-bromoaniline.

The use of norbornadiene in place of norbornene leads to similar results (Table 5.2, compound **4**). However, compound **4** undergoes a retro Diels-Alder reaction which easily occurs at 130 °C leading to dibenzoazepine **5** in a *one-pot* fashion. It is worth noting that compound **5** is also formed under the reaction conditions at 105 °C. Yields are usually lower than those of the corresponding dihydrodibenzoazepines **3** and a higher ratio of the strained olefin to palladium is needed to compensate depletion of the highly reactive norbornadiene. Data in Table 5.2 are from reference 5 and are reported for the sake of completeness.

Table 5.2 Straightforward synthesis of 5*H*-dibenzo[*b*,*f*]azepines.[a]



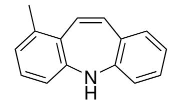
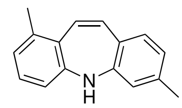
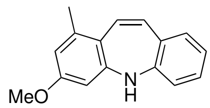
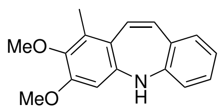
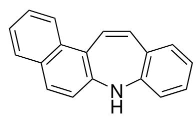
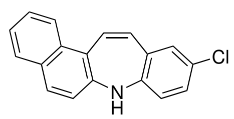
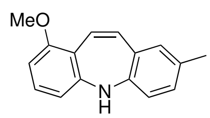
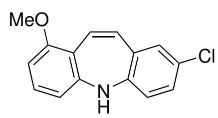
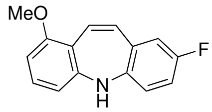
Entry	R^1	R^2	R^3	R^4	R^5	Product	Yield **5** (%)[b]
1	Me	H	H	H	H		61
2	Me	H	H	H	Me		66
3	Me	H	OMe	H	H		72
4	Me	OMe	OMe	H	H		72
5	-(CH=CH)$_2$-		H	H	H		70
6	-(CH=CH)$_2$-		H	Cl	H		50
7[c]	OMe	H	H	Me	H		65
8[c]	OMe	H	H	Cl	H		74

Table 5.2: continue in the next page

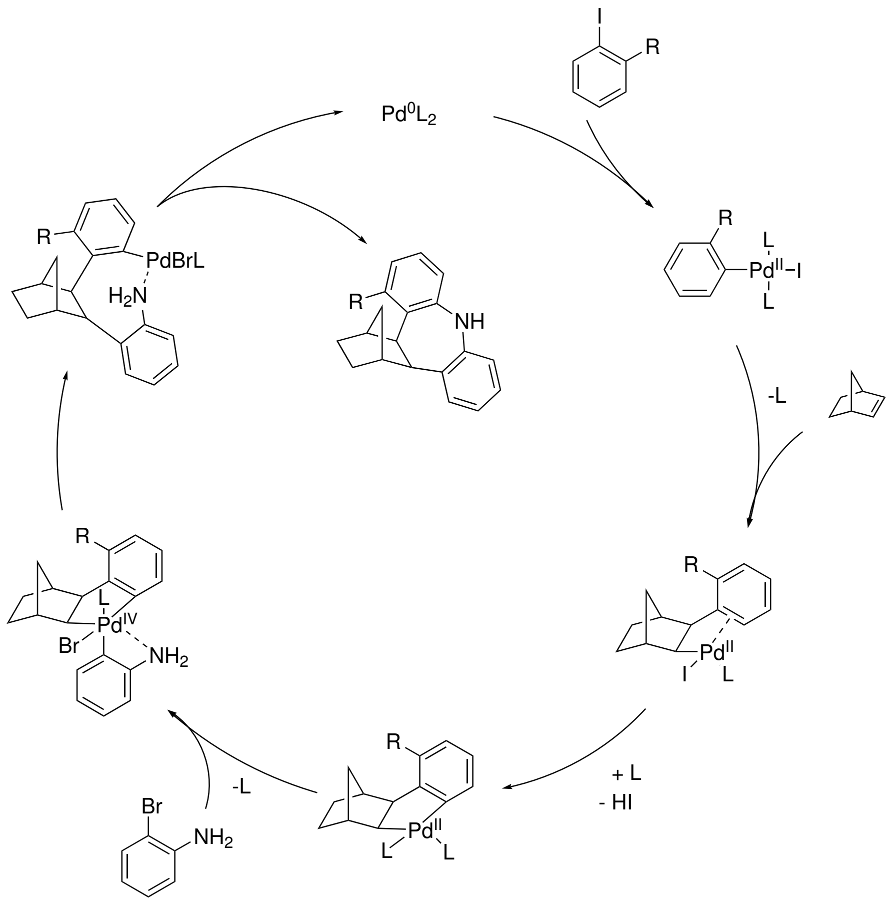
Table 5.2: continued from the previous page.

Entry	R^1	R^2	R^3	R^4	R^5	Product	Yield **5** (%)[b]
9[c]	OMe	H	H	F	H		66

[a] Reaction condition as in Table 5.1 using norbornadiene (2 equiv) in place of norbornene at 105 °C for 24 h and then at 130 °C for additional 16 h. [b] Isolated yield on the charged amount of the *o*-bromoaniline. [c] K_2CO_3 as a base.

A possible reaction pathway for the formation of dihydrodibenzoazepine and dibenzoazepine derivatives[5] is illustrated in Scheme 5.2 for an ortho substituted aryl iodide, *o*-bromoaniline and norbornene. Oxidative addition of the *ortho*-substituted aryl iodide to Pd^0L_2 formed *in situ*, yields the arylpalladium intermediate **I** which, by stereoselective insertion of norbornene affords the *cis,exo*-arylnorbornylpalladium(II) complex **II**.[13] This species, stable towards β-hydrogen elimination, readily undergoes ring closure to form the arylnorbornylpalladacycle **III**[14] by intramolecular aromatic substitution. Reaction of *o*-bromoaniline with the carbopalladacycle **III** generates the Pd(IV)[15] intermediate **IV** which delivers **V** by reductive elimination involving a Csp^2–Csp^3 bond formation. The aromatic to aliphatic C–C bond formation is favored by chelation of the NH_2 group to palladium[6]. The final C–N coupling[4] leads to the seven-membered organic compound **3** and palladium(0).

A straightforward synthesis of a great variety of dihydrodibenzoazepine and dibenzoazepine derivatives has thus been achieved starting from simple and readily available reagents. The reaction performs well with *o*-bromoanilines bearing either electron-donating or electron-withdrawing substituents in combination with aryl iodides containing electron-donating groups, while poor results are generally ob-

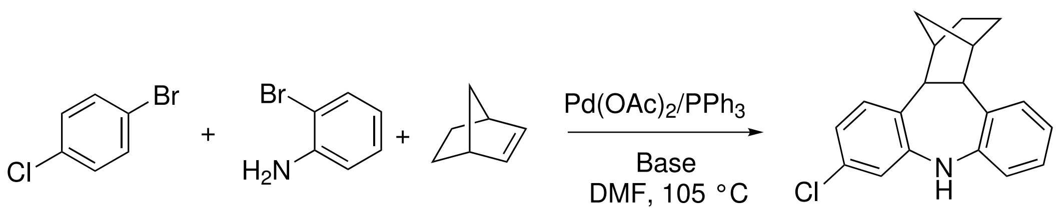


Scheme 5.2 Proposed catalytic cycle for the synthesis of dibenzoazepine derivatives.

tained in the presence of electron-withdrawing substituents in the aryl iodide. In fact an essential issue for the success of palladium-catalyzed reactions involving the formation of arylnorbornylpalladacycles, is the ability of an electron-rich aryl iodide to selectively react with Pd(0) and of an aryl bromide, activated by a chelating group or an electron-withdrawing substituent, to oxidatively add to palladium(II). In accordance with what stated above, the reaction of *p*-chloroiodobenzene (**1**; $R^3 =$ Cl) with *o*-bromoaniline and norbornene carried out under the standard conditions for 24 h gave only a 4% yield of the expected dihydrodibenzoazepine **3**. Similar results were obtained starting from other aryl iodides bearing electron-withdrawing substituents such as methyl *p*-iodobenzoate and *p*-trifluoromethyliodobenzene.

In the attempt to overcome the limitation of the aryl iodide, which should not bear electron-withdrawing substituents, we replace the C–I bond with the C–Br one and examined the behavior of an aryl bromide bearing an electron-withdrawing substituent. Table 5.3 reports the results obtained using 1-bromo-4-chlorobenzene as model substrate in place of the corresponding iodide, in the reaction with *o*-bromoaniline and norbornene.

Table 5.3 Screening of the reaction conditions of the palladium-catalyzed reaction of 1-bromo-4-chlorobenzene, *o*-bromoaniline and norbornene.[a]



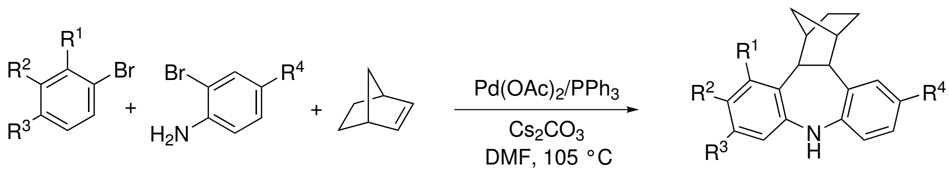
Entry	Base	Additive (equiv)	Time (h)	Yield **3** (%)[b]
1	K_2CO_3	—	24	21
2	KOAc	—	24	—
3	K_3PO_4	—	24	4
4	Cs_2CO_3	—	24	22
5	Cs_2CO_3	KI (0.25)	24	37
6	Cs_2CO_3	NBu_4I (0.25)	24	23
7	Cs_2CO_3	KI (0.5)	24	52
8	Cs_2CO_3	KI (0.5)	40	69[c]

[a] Reaction conditions: 6 (1.1 equiv), 2 (1.0 equiv), norbornene (1.2 equiv), $Pd(OAc)_2$ (5 mol%), PPh_3 (12.5 mol%), base (2.25 equiv), in DMF at 105 °C under N_2. 2.2×10^{-3} mmol $Pd(OAc)_2$/mL DMF. The reaction was carried out on a 0.5 mmol scale. [b] Determined by ^1H NMR of the reaction crude. [c] Isolated yield.

A number of palladium salts was examined and $Pd(OAc)_2$ was the best catalyst. All other palladium salts and complexes employed gave comparable or lower yields. A triarylphoshine as ligand was essential for the reaction to occur and PPh_3 in 2.5:1 molar ratio to $Pd(OAc)_2$, proved to be the ligand of choice. Among the bases tested

under the standard conditions, K_2CO_3 and Cs_2CO_3 afforded comparable yields (21 and 22%, respectively) in 24 h (Table 5.3, entries 1 and 4). AcOK gave no product (entry 3). Only a 4% yield was estimated when K_3PO_4 was used. To our delight the addition of 0.5 equiv of KI to the reaction mixture caused a significant increase of the yield up to 52% after 24 h (entry 7). Product **3** was isolated in 69% yield after 40 h (entry 8). The positive effect of KI was less significant if its relative amount was decreased (entry 5) or increased. A worse outcome was obtained using NBu_4I in place of KI (entry 6).
Under the reaction conditions of entry 8 (Table 5.3) we studied the scope of this three component process by causing to react a large number of aryl bromides containing electron-withdrawing substituent in *ortho*, *meta* or *para* positions with substituted or un-substituted *o*-bromoanilines and norbornene. The results are reported in Table 5.4.

Table 5.4 One-pot Pd-catalyzed synthesis of dihydrodibenzoazepine derivatives **3** from electron-poor aryl bromides, *o*-bromoanilines and norbornene.[a]



1 **2** **3**

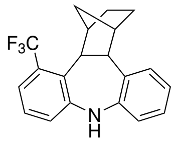
Entry	R^1	R^2	R^3	R^4	Time (h)	Product	Yield **3** (%)[b]
1	CF_3	H	H	H	24	 **3j**	64 (5)

Table 5.4: continued on next page

Table 5.4: continued from previous page

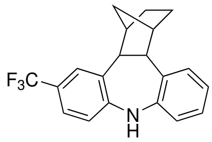
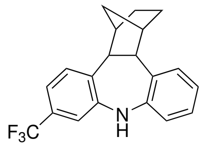
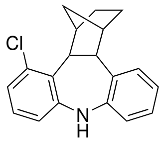
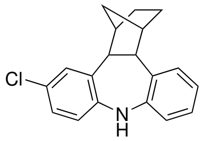
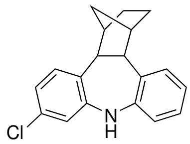
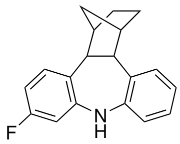
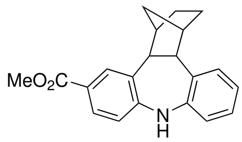
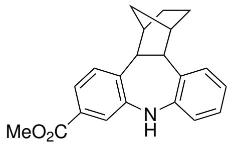
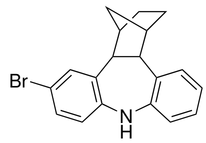
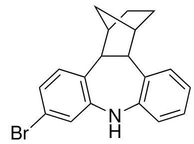
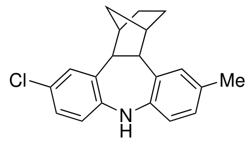
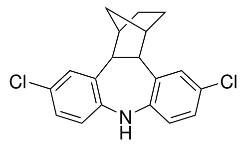
Entry	R^1	R^2	R^3	R^4	Time (h)	Product	Yield **3** (%)[b]
2	H	CF_3	H	H	64	 **3k**	80
3	H	H	CF_3	H	24	 **3l**	67
4	Cl	H	H	H	20	 **3m**	52 (32)
5	H	Cl	H	H	40	 **3n**	90
6	H	H	Cl	H	40	 **3o**	69
7	H	H	F	H	40	 **3p**	59
8	H	CO_2Me	H	H	90	 **3q**	74
9	H	H	CO_2Me	H	42	 **3r**	65

Table 5.4: continued on next page

Table 5.4: continued from previous page

Entry	R^1	R^2	R^3	R^4	Time (h)	Product	Yield **3** (%)[b]
10	H	Br	H	H	40	 **3s**	54
11	H	H	Br	H	40	 **3t**	56
12	H	Cl	H	Me	48	 **3u**	87
13	H	Cl	H	Cl	48	 **3v**	62

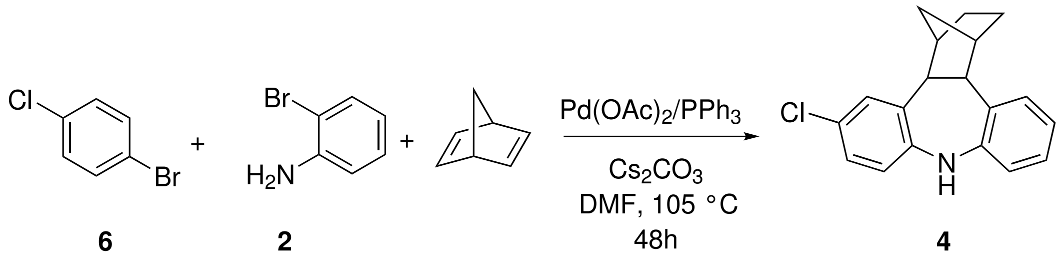
[a] Reaction conditions: **6** (1.1 equiv), **2** (1.0 equiv), norbornene (1.2 equiv), $Pd(OAc)_2$ (5 mol%), PPh_3 (12.5%), Cs_2CO_3 (2.25 equiv), KI (0.5 equiv), in DMF at 105 °C under N_2. 2.2×10^{-3} mmol $Pd(OAc)_2$/mL DMF. The reaction was carried out on a 0.5 mmol scale. [b] Isolated yield. In parentheses the yield of **3** in the absence of KI.

The effect of KI was marked using 1-bromo-2-(trifluoromethyl)benzene which, in combination with *o*-bromoaniline and norbornene, gave compound **3j** in 64% isolated yield while in the absence of KI only a low amount (*ca.* 5%) was determined by ^{1}H NMR of the crude reaction (Table 5.4, entry 1). A still important difference (*ca.* 30%) was detected when the less activated 1-bromo-2-chlorobenzene was used (entry 4). A variety of electron-withdrawing substituents are well tolerated under the new reaction conditions and the resulting dihydrodibenzoazepine derivatives can be easily further functionalized. Substituents in meta position in the starting aryl bromide, allowed to reach higher yields of the corresponding products **3** (entries

2, 5 and 8). *o*-Bromoanilines bearing either an electron-donating or an electron-withdrawing group nicely reacted with 1-bromo-3-chlorobenzene and norbornene affording the corresponding tricyclic compounds in 87 and 62% yield, respectively (entries 12, 13).

Since most commercially available antidepressant drugs contain 5H-dibenzoazepines as active ingredients, our efforts have then been addressed to the optimization of the synthesis of these compounds, which can be obtained employing norbornadiene in place of norbornene following the same methodology. 1-Bromo-4-chlorobenzene was used as model substrate in combination with *o*-bromoaniline and norbornadiene.

Table 5.5 Screening of the reaction conditions for the palladium-catalyzed reaction of 1-bromo-4-chlorobenzene, *o*-bromoaniline and norbornadiene.[a]



Entry	Norbornadiene (equiv)	KI (equiv)	Conv. **6** (%)	Conv. **2** (%)	Yield **4** (%)[b]
1	4	—	70	61	38
2	6	—	94	80	20
3	4	0.25	60	55	39
4	4	0.5	99	95	65[c]
5	4	1	45	40	31

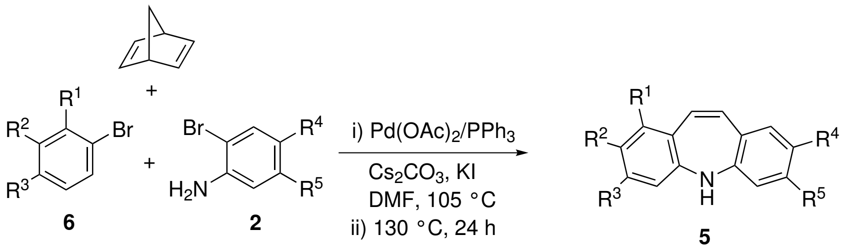
[a] Reaction conditions: **6** (1.1 equiv), **2** (1.0 equiv), norbornadiene (4 equiv), $Pd(OAc)_2$ (10 mol%), PPh_3 (25 mol%), Cs_2CO_3 (2.25 equiv), in DMF at 105 °C under N_2 for 48h. 2.2×10^{-3} mmol $Pd(OAc)_2$/mL DMF. The reaction was carried out on a 0.5 mmol scale. [b] Determined by ^{1}H NMR of the reaction crude. [c] Isolated yield.

The three components of reaction were allowed to react under the general conditions at the standard temperature of 105 °C. After 48 h the reaction was stopped to prevent the retro-Diels-Alder cleavage and obtain compound **4**, the precursor of the dibenzoazepine **5**, for an easier analysis of the sample. The most significant results are reported in Table 5.5.

A 10 mol% of $Pd(OAc)_2$ was used. The optimal amount of norbornadiene was found to be 4 equivalents with respect to *o*-bromoaniline. A further increase of norbornadiene caused a decrease of the yield of compound **4** (Table 5.5, entries 1 and 2). As for norbornene, 0.5 equivalents of KI proved to be optimal and allowed to achieve a 65% yield of compound **4** with almost complete conversion of both starting materials (entries 3–5).

The substrate scope of the reaction was then investigated under the best conditions reported above. A wide variety of electron-poor aryl bromides was allowed to react with substituted or un-substituted *o*-bromoanilines and norbornadiene at 105 °C for 46–90 h and then at 130 °C for further 24 h to afford compounds **5**. The results are reported in Table 5.6.

Table 5.6 One-pot Pd-catalyzed synthesis of 5*H*-dibenzoazepines **5**.[a]



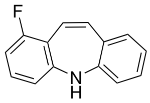
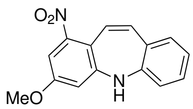
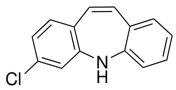
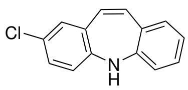
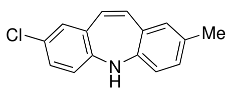
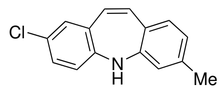
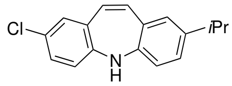
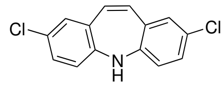
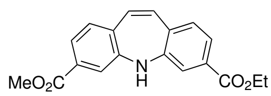
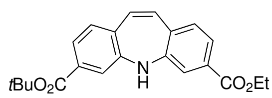
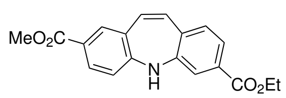
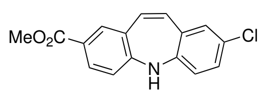
Entry	R^1	R^2	R^3	R^4	R^5	Time (h)	Product	Yield **3** (%)[b]
1	F	H	H	H	H	90	 **5a**	65
2	NO_2	H	OMe	H	H	90	 **5b**	60
3	H	H	Cl	H	H	46	 **5c**	65
4	H	Cl	H	H	H	90	 **5d**	67
5	H	Cl	H	Me	H	50	 **5e**	68

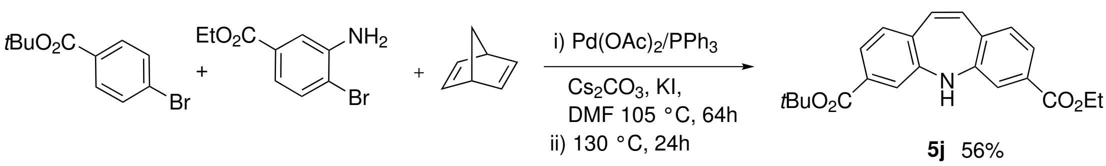
Table 5.6: continued on next page

Table 5.6: continued from previous page

Entry	R^1	R^2	R^3	R^4	R^5	Time (h)	Product	Yield **3** (%)[b]
6	H	Cl	H	H	Me	48	 **5f**	72
7	H	Cl	H	*i*-Pr	H	66	 **5g**	74
8	H	Cl	H	Cl	H	68	 **5h**	47
9	H	H	CO_2Me	H	CO_2Et	64	 **5i**	50
10	H	H	CO_2tBu	H	CO_2Et	64	 **5j**	56
11	H	CO_2Me	H	H	CO_2Et	46	 **5k**	72
12	H	CO_2Me	H	Cl	H	46	 **5l**	82

[a] Reaction conditions: **6** (1.1 equiv), **2** (1.0 equiv), norbornadiene (4 equiv), $Pd(OAc)_2$ (10 mol%), PPh_3 (25%), Cs_2CO_3 (2.25 equiv), KI (0.5 equiv), in DMF at 105 °C under N_2 for the time showed in table and at 130 °C for 24 h. 2.2×10^{-3} mmol $Pd(OAc)_2$/ml DMF. The reaction was carried out on a 0.5 mmol scale. [b] Isolated yield.

Aryl bromides bearing electron-withdrawing groups readily reacted with electron-rich and electron-poor *o*-bromoanilines. F and NO_2 functional groups can be well tolerated providing satisfactory yields of compounds **5a** and **5b** (Table 5.6 entries 1, 2). 1-Bromo-4-chlorobenzene in combination with *o*-bromoaniline and norbornadiene gave the corresponding dibenzoazepine **5c**, which is the most direct precursor of the commercial Clomipramine ® (entry 3). Satisfactory to good results were obtained starting from 1-bromo-3-chlorobenzene and the unsubstituted *o*-bromoaniline or electron-rich *o*-bromoanilines (entries 4–7), while a yield of 47% was obtained with 2-bromo-4-chloroaniline. It is worth noting that in the absence of KI compounds **5i**–**5l** (entries 9–12) have not been obtained even in detectable traces. Compounds **5j** (entry 10), which has been recently prepared through 8 steps[16], can now be obtained in one-pot reaction from commercially available or readily prepared starting materials (Scheme 5.3).



Scheme 5.3 One-pot synthesis of a biologically active dibenzoazepine precursor.

5.3 Conclusions

In conclusion we have developed a general and straightforward methodology for the *one-pot* catalytic synthesis of dihydrodibenzoazepine and dibenzoazepine derivatives starting from simple commercially available reagents, namely aryl iodides or bromides, norbornene or norbornadiene and *o*-bromoanilines. A Pd catalyst controls the complex series of steps leading to the azepine ring selectively through two C–C and one C–N bond formation. The synthesis can be readily achieved starting not only from aryl iodides bearing electron-donating substituents, as previously reported, but also from aryl bromides activated by electron-withdrawing substituents in *ortho*, *meta* or *para* position.

5.4 Experimental

5.4.1 General Remarks

The Pd-catalyzed reactions were carried out under nitrogen using standard Schlenk techniques. DMF was dried and stored over 4 Å molecular sieves under nitrogen. Gas chromatography analyses were performed with an Agilent Technology 7820A instrument using a 30 m SE-30 capillary column. Flash column chromatography was carried out on Merck Kieselgel 60 and TLC on Merck 60F254 plates. Mass spectra (EI) were obtained with a Hewlett Packard instrument working at 70 eV ionization energy. Unless otherwise indicated NMR spectra were recorded in deuterated chloroform, using the solvent as internal reference (7.26 and 77.00 ppm, respectively for ^{1}H and ^{13}C), on Bruker AVANCE 300 and 400 spectrometers. IR spectra were run on a Nicolet FT-IR 5700 spectrophotometer and a Diamond Smart Orbit accessory. Melting points were determined with an Electrothermal apparatus and are uncorrected. Elemental analyses were performed with a Carlo Erba EA 1108-Elemental Analyzer.

5.4.2 Experimental procedures

*General procedure for the palladium-catalyzed synthesis of cis,exo-1,2,3,4,4a,13b-hexahydro-1,4-methano-9Htribenzo[*b,f*]azepines* (**3**)
A Schlenk-type flask, equipped with a magnetic stirring bar, was charged, under nitrogen, with Cs_2CO_3, dried at 110 °C for 2 h (326 mg, 1.0 mmol), PPh_3 (14 mg, 0.055 mmol) and $Pd(OAc)_2$ (5 mg, 0.022 mmol) in DMF (5 mL). After 10 minutes under stirring, a DMF solution (5 mL) of the aryl bromide 6 (0.48 mmol),

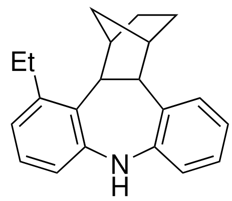
the *o*-bromoaniline 2 (0.44 mmol) and norbornene (50 mg, 0.53 mmol) was added, and finally KI was introduced (36 mg, 0.22 mmol). The resulting mixture was stirred in an oil bath at 105 °C for the time needed for Pd black formation. After cooling to room temperature, the mixture was diluted with EtOAc (30 mL) and washed with a saturated solution of NaCl (3 × 25 mL). The organic layer was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the products were isolated by flash column chromatography on silica gel using mixtures of *n*-hexane-EtOAc as eluent.

*General procedure for the palladium-catalyzed synthesis of 5*H*-dibenz[*b,f*]azepine* (**5**)

A Schlenk-type flask, equipped with a magnetic stirring bar, was charged under nitrogen with Cs_2CO_3 (326 mg, 1.0 mmol), PPh_3 (29 mg, 0.11 mmol) and $Pd(OAc)_2$ (10 mg, 0.044 mmol) in DMF (5 mL). After 10 minutes under stirring, a DMF solution (5 mL) of the aryl bromide 6 (0.48 mmol), the 2-bromoaniline 2 (0.44 mmol) and norbornadiene (162 mg, 1.76 mmol) was added, and finally KI was introduced (36 mg, 0.22 mmol). The resulting mixture was stirred in an oil bath at 90–105 °C for 24–72 h and then at 130 °C for additional 24 h. After cooling to room temperature, the mixture was diluted with EtOAc (30 mL) and extracted three times with a saturated solution of NaCl (25 mL). The organic layer was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the products were isolated by flash column chromatography on silica gel using mixtures of *n*-hexane-EtOAc as eluent.

5.4.3 Characterizations

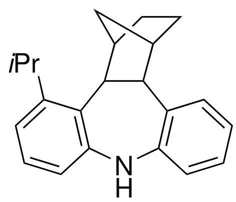
cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-5-ethyl-9H-tribenzo[b,f]azepine (**3a**)



Yield: 80% (102 mg); white solid; m.p. (*n*-hexane): 96–97 °C. Eluent: *n*-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.29 (1H, dd, J = 7.6, 1.2 Hz), 7.15 (1H, td, J = 7.6, 1.6 Hz), 7.09 (1H, t, J = 8.0 Hz), 7.00 (1H, td, J = 7.2, 1.6 Hz), 6.96 (1H, dd, J = 7.6, 1.2 Hz), 6.87 (1H, dd, J = 8.0, 1.2 Hz), 6.76 (1H, dd, J = 7.6, 1.2 Hz), 5.10 (1H, br s), 3.53 (1H, d, J = 9.6 Hz), 3.25 (1H, d, J = 9.6 Hz), 2.99 (1H, d further split, J = 9.6 Hz), 2.91 (1H, sextet, J = 7.6 Hz), 2.79 (1H, sextet, J = 7.6 Hz), 2.45 (1H, br s), 2.36 (1H, br s), 1.77–1.64 (4H, m), 1.38 (3H, d, J = 7.6 Hz), 1.27 (1H, d further split, J = 9.6 Hz); ^{13}C NMR (100 MHz): δ 144.8, 144.5, 144.4, 133.9, 132.2, 131.9, 126.5, 126.0, 123.0, 121.8, 119.6, 118.4, 53.2, 50.1, 48.5, 45.6, 38.2, 31.2, 30.7, 27.5, 15.5; IR (KBr, cm^{-1}): ν 3363, 2941, 2873, 1575, 1494, 1466, 1448, 1313, 769, 745; MS: m/z 289 (M+, 78), 222 (82), 208 (100), 204 (25), 193 (31). Anal. Calcd. for $C_{21}H_{23}N$: C, 87.15; H, 8.01; N, 4.84. Found: C, 87.41; H, 8.08.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-5-isopropyl-9H-tribenzo[b,f]azepine (**3b**)

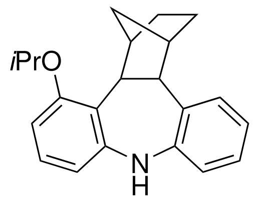


Yield: 55% (73 mg); white solid; m.p. (*n*-hexane): 127–128 °C. Eluent: *n*-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.16 (1H, br d, J = 7.6 Hz), 7.06–6.98 (2H, m), 6.94 (1H, br d, J = 7.6 Hz), 6.88 (1H, br t, J = 7.6 Hz), 6.77 (1H, br d, J = 7.6 Hz), 6.65 (1H, br d, J = 7.6 Hz), 4.98 (1H, br s), 3.50 (1H, d, J = 9.6 Hz), 3.35 (1H, heptet, J = 6.8 Hz), 3.12 (1H, d, J = 9.6 Hz), 2.86 (1H, d further split, J = 9.6 Hz), 2.31 (1H, br s), 2.21 (1H, br s), 1.68–1.50 (4H, m), 1.30 (3H, d, J = 6.8 Hz), 1.22 (3H, d, J = 6.8 Hz), 1.14 (1H, d further split, J = 9.6 Hz); ^{13}C NMR (100 MHz): δ 149.0, 144.8, 144.7, 134.0, 132.2, 131.5, 126.6, 126.1, 121.9, 119.65, 119.61, 118.1, 53.3, 50.1, 48.7, 45.1, 38.3, 31.1, 30.8, 29.4, 24.6, 23.7; IR (KBr, cm^{-1}): ν 3362, 3056, 3030, 2951, 2919, 1579, 1496, 1473, 1448, 1314, 785, 746; MS: m/z 303 (M+, 84), 236 (80), 222 (100), 206 (35), 204 (26).

Anal. Calcd. for $C_{22}H_{25}N$: C, 87.08; H, 8.30; N, 4.62. Found: C, 87.24; H, 8.36.

1,2,3,4,4a,13b-Hexahydro-1,4-methano-5-isopropoxy-9H-tribenzo[b,f]azepine (**3c**)

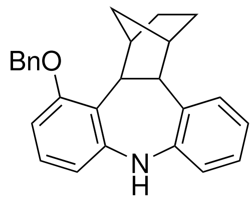


Yield: 83% (116 mg); white solid; m.p. (*n*-hexane): 158–159 °C. Eluent: *n*-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.27 (1H, d further split, J = 7.6 Hz), 7.12 (1H, td, J = 7.6, 1.6 Hz), 7.04 (1H, t, J = 8.0 Hz), 6.97 (1H, td, J = 7.6, 1.0 Hz), 6.83 (1H, d further split, J = 8.0 Hz), 6.60 (1H, d, J = 8.0 Hz), 6.47 (1H, d, J = 8.0 Hz), 5.17 (1H, br s), 4.63 (1H, heptet, J = 6.0 Hz), 3.88 (1H, d, J = 9.6 Hz), 3.19 (1H, d, J = 9.6 Hz), 2.70 (1H, d further split, J = 9.6 Hz), 2.38 (1H, br s), 2.30 (1H, br s), 1.70–1.61 (4H, m), 1.47 (3H, d, J = 6.0 Hz), 1.44 (3H, d, J = 6.0 Hz), 1.19 (1H, d further split, J = 9.6 Hz); ^{13}C NMR (100 MHz): δ 156.8, 145.2, 144.0, 133.8, 132.5, 126.4, 126.0, 123.8, 121.6, 119.6, 112.2, 106.5, 70.1, 52.7, 49.8, 48.6, 42.4, 37.9, 31.2, 30.2, 22.3; IR (KBr, cm^{-1}): ν 3373, 2970, 2953, 2864, 1584, 1492, 1467, 1449, 1240,

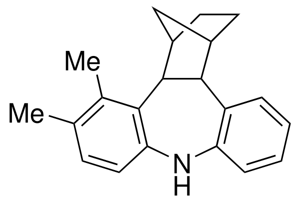
1121, 1050, 743; MS: m/z 319 (M+, 100), 276 (12), 252 (54), 238 (65), 210 (36), 196 (72), 180 (25), 167 (13).
Anal. Calcd. for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.39; H, 7.78.

1,2,3,4,4a,13b-Hexahydro-1,4-methano-5-benzyloxy-9H-tribenzo[b,f]azepine (**3d**)



Yield: 76% (123 mg); white solid; m.p. (*n*-hexane): 171–172 °C. Eluent: *n*-hexane/EtOAc 98:2.
^{1}H NMR (400 MHz): δ 7.50 (2H, d further split, J = 7.6 Hz), 7.43 (2H, t further split, J = 7.6 Hz), 7.39–7.33 (1H, m), 7.17 (1H, d further split, J = 7.5 Hz), 7.04 (1H, td, J = 7.5, 1.5 Hz), 6.99 (1H, t, J = 8.0 Hz), 6.88 (1H, t further split, J = 7.4 Hz), 6.77 (1H, br d, J = 7.8 Hz), 6.59 (1H, br d, J = 8.0 Hz), 6.46 (1H, br d, J = 7.9 Hz), 5.14, 5.12 (2H, 2 partly overlapping signals: d, J = 11.8 Hz and br s), 5.04 (1H, d, J = 11.8 Hz), 3.86 (1H, d, J = 9.6 Hz), 3.10 (1H, d, J = 9.6 Hz), 2.62 (1H, d further split, J = 10.0 Hz), 2.30, 2.28 (2H, 2 br s), 1.65–1.49 (4H, m), 1.12 (1H, d further split, J = 10.0 Hz); ^{13}C NMR (100 MHz): δ 157.8, 145.1, 144.0, 137.5, 133.8, 132.6, 128.4, 127.6, 127.0, 126.5, 126.2, 123.2, 121.8, 119.6, 113.1, 105.4, 70.3, 52.7, 49.6, 48.8, 42.7, 38.1, 31.4, 30.0; IR (KBr, cm^{-1}): ν 3368, 2948, 2866, 1584, 1496, 1470, 1445, 1244, 1100, 747; MS: m/z 367 (M+, 100), 300 (18), 286 (68), 276 (16), 220 (14), 209 (27), 195 (51), 180 (63), 167 (21), 152 (15), 91 (87), 65 (14).
Anal. Calcd. for $C_{26}H_{25}NO$: C, 84.98; H, 6.86; N, 3.81. Found: C, 85.21; H, 6.88.

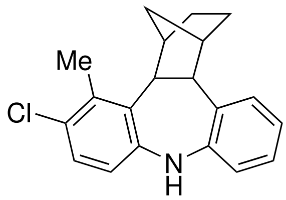
cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-5,6-dimethyl-9H-tribenzo[b,f]azepine (**3e**)



Yield: 54% (69 mg); white solid; m.p. (*n*-hexane): 119–120 °C. Eluent: *n*-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.18 (1H, dd, J = 7.6, 1.2 Hz), 7.06 (1H, td, J = 7.6, 1.6 Hz), 6.90, 6.88 (2H, 2 partly overlapping signals: td, J = 7.6, 1.6 Hz and d, J = 8.0 Hz), 6.79 (1H, dd, J = 7.6, 1.2 Hz), 6.61 (1H, d, J = 8.0 Hz), 4.93 (1H, br s), 3.49 (1H, d, J = 9.6 Hz), 3.14 (1H, d, J = 9.6 Hz), 2.85 (1H, d further split, J = 9.6 Hz), 2.34 (1H, br s), 2.33 (3H, s), 2.28 (3H, s), 2.27 (1H, br s), 1.69–1.54 (4H, m), 1.18 (1H, d further split, J = 9.6 Hz); ^{13}C NMR (100 MHz): δ 144.8, 142.6, 136.7, 133.8, 132.8, 132.1, 130.4, 127.7, 126.6, 121.8, 119.4, 117.7, 53.3, 49.5, 48.2, 46.9, 38.4, 31.5, 30.5, 21.1, 16.6; IR (KBr, cm^{-1}): ν 3365, 2948, 2869, 1571, 1476, 1455, 1446, 1310, 809, 753; MS: m/z 289 (M+, 58), 222 (68), 208 (100), 204 (22). Anal. Calcd. for $C_{21}H_{23}N$: C, 87.15; H, 8.01; N, 4.84. Found: C, 87.35; H, 8.10.

1,2,3,4,4a,13b-Hexahydro-1,4-methano-5-methyl-6-chloro-9H-tribenzo[b,f]azepine (**3f**)

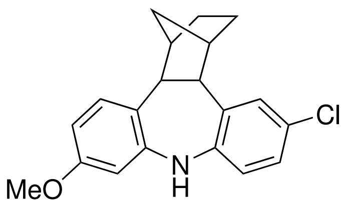


Yield: 65% (88 mg); white solid; m.p. (*n*-hexane): 155–156 °C. Eluent: *n*-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.16 (1H, d further split, J = 7.6 Hz), 7.04, 7.03 (2H, 2 partly overlapping signals: td, J = 7.5, 1.6 Hz and d, J = 8.2 Hz), 6.89 (1H, br t, J = 7.2 Hz), 6.76 (1H, br d, J = 7.6 Hz), 6.59 (1H, br d, J = 8.2 Hz), 4.95 (1H, br s), 3.42 (1H, d, J = 9.6 Hz), 3.10 (1H, d, J = 9.6 Hz), 2.72 (1H, dq, J = 9.6, 1.9 Hz), 2.45 (3H, s), 2.29 (1H, br s), 2.21 (1H, br s), 1.67–1.50 (4H, m), 1.14 (1H, dq, J = 9.6, 1.5 Hz); ^{13}C NMR (100 MHz): δ 144.0, 143.1, 135.9, 134.5, 133.6, 132.2, 128.3, 126.76, 126.73, 122.2, 119.6, 119.2, 53.1, 49.5, 48.3, 47.7, 38.4, 31.4, 30.5, 17.7; IR (KBr, cm^{-1}): ν 3369, 2949, 2868, 1573, 1493, 1462, 1315, 817, 748; MS: m/z 311 (M+, 15), 309 (40), 242 (57), 230 (33), 228 (100), 204 (34), 191 (15), 178 (10), 67 (16).

Anal. Calcd. for $C_{20}H_{20}ClN$: C, 77.53; H, 6.51; Cl, 11.44; N, 4.52. Found: C, 77.68; H, 6.47.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-12-chloro-7-methoxy-9H-tribenzo[b,f]azepine (**3g**)



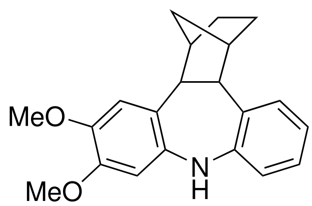
Yield: 75% (107 mg); white solid; m.p. (n-hexane): 148.5–149.0 °C. Eluent: n-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.18 (1H, d, J = 2.4 Hz), 7.11 (1H, d, J = 8.4 Hz), 6.98 (1H, dd, J = 8.4, 2.4 Hz), 6.68 (1H, d, J = 8.0 Hz), 6.51 (1H, dd, J = 8.4, 2.8 Hz), 6.34 (1H, d, J = 2.8 Hz), 5.04 (1H, br s), 3.78 (3H, s), 3.08 (1H, d, J = 9.2 Hz), 3.03 (1H, d, J = 9.2 Hz), 2.56 (1H, d further split, J = 9.6 Hz), 2.31 (1H, br s), 2.27 (1H, br s), 1.61–1.45 (4H, m), 1.10 (1H, d further split, J = 9.6 Hz); ^{13}C NMR (100 MHz): δ 158.2, 144.8, 143.0, 135.3, 133.5, 132.0, 126.4, 126.2, 125.8, 121.1, 107.6, 105.3, 55.2, 52.8, 52.0, 49.20, 49.15, 37.1, 30.6, 30.4; IR (KBr, cm^{-1}):

ν 3368, 2952, 2915, 2868, 1615, 1466, 1264, 1230, 1217, 1113, 1041, 832, 810; MS: m/z 327 (M+, 33), 325 (88), 260 (36), 258 (100), 246 (24), 244 (68), 214 (32), 201 (15), 178 (15).

Anal. Calcd. for $C_{20}H_{20}ClNO$: C, 73.72; H, 6.19; Cl, 10.88; N, 4.30. Found: C, 74.04; H, 6.13.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-6,7-dimethoxy-9H-tribenzo[b,f]azepine (**3h**)

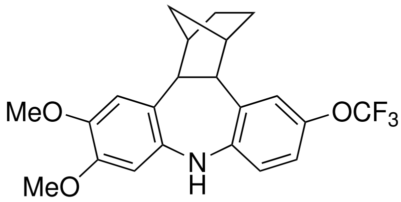


Yield: 51% (72 mg); white solid; m.p. (*n*-hexane): 159.5–159.9 °C. Eluent: *n*-hexane/EtOAc 95:5.

^{1}H NMR (400 MHz): δ 7.22 (1H, dd, J = 7.6, 1.4 Hz), 7.06 (1H, td, J = 7.6, 1.6 Hz), 6.91 (1H, td, J = 7.2, 0.8 Hz), 6.82 (1H, dd, J = 7.6, 0.8 Hz), 6.74 (1H, s), 6.38 (1H, s), 4.99 (1H, br s), 3.87 (3H, s), 3.85 (3H, s), 3.15 (1H, d, J = 9.2 Hz), 3.07 (1H, d, J = 9.2 Hz), 2.71 (1H, d, J = 9.6 Hz), 2.36 (1H, br s), 2.32 (1H, br s), 1.67–1.50 (4H, m), 1.14 (1H, d, J = 9.6 Hz); ^{13}C NMR (100 MHz): δ 147.2, 145.0, 143.8, 138.0, 133.4, 132.6, 126.4, 125.0, 121.7, 119.6, 116.0, 104.2, 56.3, 55.8, 53.1, 52.6, 49.2 (X2), 37.2, 30.8, 30.5; IR (KBr, cm^{-1}): ν 3371, 2947, 2915, 2869, 1607, 1586, 1527, 1477, 1264, 1233, 849, 753; MS: m/z 321 (M+, 100), 306 (28), 254 (72), 240 (55), 238 (24), 210 (39), 196 (18), 180 (19), 167 (38), 67 (21).

Anal. Calcd. for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.25; H, 7.28.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-6,7-dimethoxy-12-trifluoromethoxy-9H-tribenzo[b,f]azepine (**3i**)

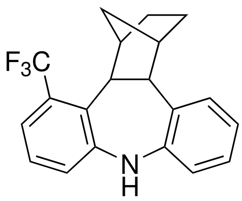


Yield: 44% (78 mg); pale yellow solid; Eluent: Hexane/EtOAc 95:5.

^{1}H NMR (400 MHz): δ 7.03 (1H, d, J = 1.6 Hz), 6.87 (1H, dd, J = 8.4, 1.6 Hz), 6.76 (1H, d, J = 8.4 Hz), 6.69 (1H, s), 6.34 (1H, s), 4.97 (1H, br s), 3.83 (6H, s), 3.06 (1H, d, J = 9.2 Hz), 3.01 (1H, d, J = 9.2 Hz), 2.61 (1H, d, J = 9.6 Hz), 2.31 (1H, br s), 2.29 (1H, br s), 1.64–1.45 (4H, m), 1.10 (1H, d, J = 9.6 Hz); ^{13}C NMR (100 MHz): δ 147.4, 144.1, 143.8, 143.4, 137.5, 134.9, 125.0, 124.9, 120.5, 120.5 (q, JC,F = 254.7 Hz), 119.0, 116.0, 104.3, 56.4, 55.9, 53.2, 52.3, 49.2, 49.0, 37.2, 30.7, 30.4; MS: m/z 405 (M+, 100), 390 (25), 338 (72), 324 (52), 294 (38), 280 (16), 251 (24), 168 (23), 154 (13), 67 (18).

Anal. Calcd. for $C_{22}H_{22}F_3NO_3$: C, 65.18; H, 5.47; F, 14.06; N, 3.45. Found: C, 65.34; H, 5.42.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-5-trifluoromethyl-9H-tribenzo[b,f]azepine (**3j**)

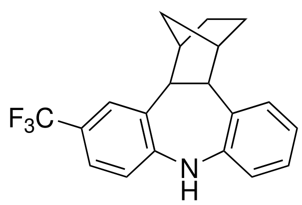


Yield: 64% (93 mg); white solid; m.p. (n-hexane): 136–137 °C. Eluent: n-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.31 (1H, d, further split, J = 7.6 Hz), 7.21 (1H, d further split, J = 7.6 Hz), 7.10, 7.06 (2H, 2 partly overlapping signals: t, J = 8.0 Hz and t, J = 7.2 Hz), 6.98 (1H, d further split, J = 7.6 Hz), 6.93 (1H, t further split, J = 7.2 Hz), 6.79 (1H, d further split, J = 8.0 Hz), 5.10 (1H, br s), 3.51 (1H, d, J = 9.4 Hz), 3.18 (1H, d, J = 9.4 Hz), 2.87 (1H, d, J = 9.8 Hz), 2.33 (1H, br s), 2.27 (1H, br s), 1.66–1.43 (4H, m), 1.14 (1H, d further split, J = 9.8 Hz); ^{13}C NMR (100 MHz): δ 146.4, 143.6, 134.2, 132.5, 130.6 (q, JC,F = 27.2 Hz), 126.8, 126.2, 124.7 (q, JC,F = 272.9 Hz), 124.4, 122.9 (q, JC,F = 4.4 Hz), 122.5, 120.5 (q, JC,F = 6.7 Hz), 119.9, 53.2, 50.8, 48.9, 45.6, 38.4, 31.2, 29.8; IR (ATR diamond, cm^{-1}): ν 3363, 2954, 2873, 1494, 1308, 1184, 1090, 961, 745; MS: m/z 329 (M+, 52), 262 (50), 248 (100).

Anal. Calcd. for $C_{20}H_{18}F_3N$: C, 72.93; H, 5.51; F, 17.30; N, 4.25. Found: C, 72.79; H, 5.47.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-6-trifluoromethyl-9H-tribenzo[b,f]azepine (**3k**)



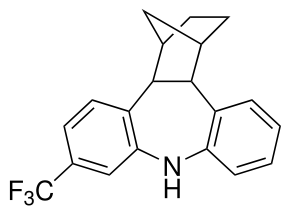
Yield: 80% (116 mg); white solid; m.p. (*n*-hexane): 135–136 °C. Eluent: *n*-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.49 (1H, s), 7.31 (1H, d further split, J = 8.2 Hz), 7.26 (1H, d, J = 7.5 Hz), 7.11 (1H, td, J = 7.6, 1.2 Hz), 6.97 (1H, t further split, J = 7.5 Hz), 6.85 (1H, d, J = 8.2 Hz), 6.82 (1H, d, J = 7.8 Hz), 5.32 (1H, br s), 3.24–3.15 (2H, m), 2.58 (1H, d further split, J = 9.8 Hz), 2.35, 2.33 (2H, 2 partly overlapping signals: 2 br s), 1.67–1.52 (4H, m), 1.15 (1H, d further split, J = 9.8

Hz); ^{13}C NMR (100 MHz): δ 147.2, 143.2, 133.6, 133.4, 132.8, 129.7 (q, JC,F = 3.7 Hz), 126.8, 124.5 (q, JC,F = 269.6 Hz), 123.6 (q, JC,F = 3.6 Hz), 123.5 (q, JC,F = 32.2 Hz), 122.4, 120.05, 120.01, 53.3, 52.7, 49.8, 49.5, 37.4, 30.62, 30.57; IR (ATR diamond, cm^{-1}): ν 3367, 2958, 2873, 1585, 1483, 1336, 1254, 1104, 1085, 758; MS: m/z 329 (M+, 89), 262 (81), 248 (100).

Anal. Calcd. for $C_{20}H_{18}F_3N$: C, 72.93; H, 5.51; F, 17.30; N, 4.25. Found: C, 73.22; H, 5.43.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-7-trifluoromethyl-9H-tribenzo[b,f]azepine (**3l**)



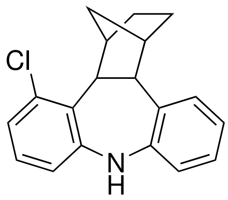
Yield: 67% (97 mg); white solid; m.p. (*n*-hexane): 130–131 °C. Eluent: *n*-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.34 (1H, d, J = 8.0 Hz), 7.28 (1H, dd, J = 7.6, 1.6 Hz), 7.19 (1H, dd, J = 8.0, 0.8 Hz), 7.13, 7.10 (2H, 2 partly overlapping signals: td, J = 7.6, 1.6 Hz and br s), 6.99 (1H, td, J = 7.6, 1.2 Hz), 6.85 (1H, dd, J = 8.0, 1.2 Hz), 5.25 (1H, br s), 3.29–3.18 (2H, m), 2.67 (1H, d further split, J = 9.6 Hz), 2.40, 2.37 (2H, 2 partly overlapping signals: 2 br s), 1.70–1.57 (4H, m), 1.19 (1H, d further split, J = 9.6 Hz); ^{13}C NMR (100 MHz): δ 144.7, 143.7, 137.5, 133.5, 133.2, 132.7, 128.8 (q, JC,F = 32.1 Hz), 126.9, 124.1 (q, JC,F = 270.3 Hz), 122.5, 120.1, 118.3 (q, JC,F = 3.7 Hz), 116.7 (q, JC,F = 3.6 Hz), 53.1, 52.7, 49.6, 49.4, 37.5, 30.68, 30.67; IR (ATR diamond, cm^{-1}): ν 3363, 2944, 2871, 1517, 1473, 1159, 1083, 829, 752; MS: m/z 329 (M+, 97), 262 (96), 248 (100).

Anal. Calcd. for $C_{20}H_{18}F_3N$: C, 72.93; H, 5.51; F, 17.30; N, 4.25. Found: C, 73.14;

H, 5.58.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-5-chloro-9H-tribenzo[b,f]azepine (**3m**)

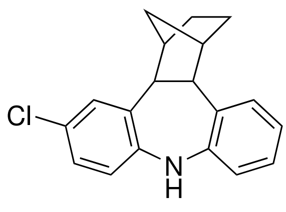


Yield: 52% (67 mg); white solid; m.p. (*n*-hexane): 124–125 °C. Eluent: *n*-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.24 (1H, d, J = 7.6 Hz), 7.14–7.06 (2H, m), 6.97 (2H, t, J = 7.6 Hz), 6.81 (1H, d, J = 8.0 Hz), 6.72 (1H, d, J = 7.6 Hz), 5.16 (1H, br s), 3.86 (1H, d, J = 9.6 Hz), 3.19 (1H, d, J = 9.6 Hz), 2.68 (1H, d further split, J = 9.6 Hz), 2.36 (2H, br s), 1.74–1.55 (4H, m), 1.20 (1H, d further split, J = 9.6 Hz); ^{13}C NMR (100 MHz): δ 145.7, 143.7, 136.7, 133.7, 132.6, 131.8, 126.8, 126.6, 123.5, 122.4, 119.8, 118.9, 52.7, 49.8, 48.5, 47.6, 38.3, 31.4, 30.2; IR (ATR diamond, cm^{-1}): ν 3366, 2953, 2866, 1488, 1441, 1295, 1252, 926, 764; MS: m/z 297 (M+, 22), 295 (61), 230 (22), 228 (58), 216 (36), 214 (100), 191 (10).

Anal. Calcd. for $C_{19}H_{18}ClN$: C, 77.15; H, 6.13; Cl, 11.98; N, 4.74. Found: C, 77.32; H, 6.09.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-6-chloro-9H-tribenzo[b,f]azepine (**3n**)

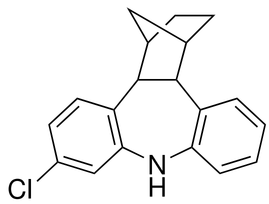


Yield: 90% (117 mg); white solid; m.p. (*n*-hexane): 196–197 °C. Eluent: *n*-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.24–7.17 (2H, m), 7.07 (1H, t further split, J = 7.5 Hz), 6.99 (1H, dd, J = 8.3, 2.3 Hz), 6.92 (1H, t further split, J = 7.2 Hz), 6.78 (1H, d, J = 7.8 Hz), 6.72 (1H, d, J = 8.4 Hz), 5.07 (1H, br s), 3.14 (1H, d, J = 9.4 Hz), 3.07 (1H, d, J = 9.4 Hz), 2.60 (1H, d, J = 9.7 Hz), 2.33 (2H, br s), 1.65–1.46 (4H, m), 1.12 (1H, d, J = 9.7 Hz); ^{13}C NMR (100 MHz): δ 144.1, 143.2, 135.4, 133.4, 132.6, 132.0, 126.7, 126.5, 126.3, 122.2, 121.1, 119.9, 52.9, 52.8, 49.31, 49.26, 37.4, 30.7, 30.6; IR (ATR diamond, cm^{-1}): ν 3368, 2918, 2849, 1580, 1472, 1306, 1129, 954, 895, 745; MS: m/z 297 (M+, 35), 295 (99), 230 (36), 228 (100), 216 (36), 214 (99), 191 (15), 179 (10).

Anal. Calcd. for $C_{19}H_{18}ClN$: C, 77.15; H, 6.13; Cl, 11.98; N, 4.74. Found: C, 77.25; H, 6.08.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-7-chloro-9H-tribenzo[b,f]azepine (**3o**)

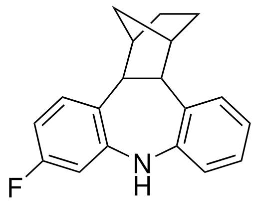


Yield: 69% (90 mg); white solid; m.p. (*n*-hexane): 177–178 °C. Eluent: n-exane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.23 (1H, d, J = 7.6 Hz), 7.14 (1H, d, J = 8.0 Hz), 7.09 (1H, t, J = 7.5 Hz), 6.95 (1H, t, J = 7.5 Hz), 6.88 (1H, d, J = 8.0 Hz), 6.83 (1H, s), 6.80 (1H, d, J = 7.6 Hz), 5.09 (1H, br s), 3.14 (2H, m), 2.61 (1H, d, J = 9.6 Hz), 2.34, 2.30 (2H, 2 partly overlapping signals: 2 br s), 1.68–1.50 (4H, m), 1.14 (1H, d J = 9.6 Hz); ^{13}C NMR (100 MHz): δ 145.4, 143.8, 133.8, 133.6, 132.7, 132.2, 131.3, 126.7, 122.3, 121.8, 120.0, 119.7, 52.8, 52.6, 49.5, 49.3, 37.4, 30.7, 30.6; IR

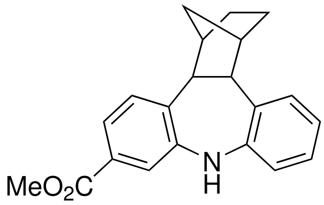
(ATR diamond, cm^{-1}): ν 3359, 2945, 2866, 1577, 1473, 1306, 1244, 746; MS: m/z 297 (M+, 32), 295 (87), 230 (36), 228 (100), 216 (36), 214 (99), 191 (15).
Anal. Calcd. for $C_{19}H_{18}ClN$: C, 77.15; H, 6.13; Cl, 11.98; N, 4.74. Found: C, 77.40; H, 6.22.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-7-fluoro-9H-tribenzo[b,f]azepine (**3p**)



Yield: 59% (72 mg); white solid; m.p. (*n*-hexane): 175–176 °C. Eluent: n-exane/EtOAc 98:2.
^{1}H NMR (400 MHz, DMSO-d6): δ 7.40 (1H, br s), 7.16–7.09 (2H, m), 7.08–6.98 (2H, m), 6.91 (1H, dd, J = 10.8, 2.7 Hz), 6.81 (1H, td, J = 7.6, 1.7 Hz), 6.59 (1H, td, J = 8.3, 2.7 Hz), 3.10–3.00 (2H, m), 2.44 (1H, d, J = 9.4 Hz), 2.10, 2.07 (2H, 2 partly overlapping signals: 2 br s), 1.49–1.36 (4H, m), 0.97 (1H, d J = 9.4 Hz); ^{13}C NMR (100 MHz, DMSO-d6): δ 160.8 (d, JC,F = 240.0 Hz), 146.9 (d, JC,F = 9.4 Hz), 144.9, 134.1 (d, JC,F = 9.1 Hz), 133.3, 132.7, 129.4 (d, JC,F = 2.8 Hz), 126.8, 121.6, 120.4, 107.6 (d, JC,F = 20.1 Hz), 106.4 (d, JC,F = 21.9 Hz), 52.5, 52.0, 49.9, 49.8, 37.2, 30.4, 30.3; IR (ATR diamond, cm^{-1}): ν 3368, 2956, 1608, 1473, 1184, 986, 752; MS: m/z 279 (M+, 97), 212 (90), 198 (100), 183 (8).
Anal. Calcd. for $C_{19}H_{18}FN$: C, 81.69; H, 6.49; F, 6.80; N, 5.01. Found: C, 81.51; H, 6.57.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-7-carbomethoxy-9H-tribenzo[b,f]azepine (**3r**)

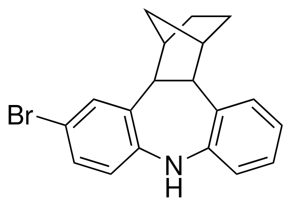


Yield: 65% (91 mg); white solid; m.p. (*n*-hexane): 170–171 °C. Eluent: *n*-hexane/EtOAc 95:5.

^{1}H NMR (400 MHz): δ 7.56–7.51 (2H, m), 7.26 (1H, d, J = 7.6 Hz), 7.21 (1H, dd, J = 8.0, 1.2 Hz), 7.07 (1H, td, J = 7.2, 1.6 Hz), 6.92 (1H, td, J = 7.6, 1.2 Hz), 6.82 (1H, dd, J = 7.6, 1.2 Hz), 5.28 (1H, br s), 3.20 (1H, d, J = 9.6 Hz), 3.15 (1H, d, J = 9.6 Hz), 2.63 (1H, d further split, J = 9.8 Hz), 2.34, 2.32 (2H, 2 partly overlapping singlets), 1.63–1.49 (4H, m), 1.13 (1H, d further split, J = 9.8 Hz); ^{13}C NMR (100 MHz): δ 166.8, 144.5, 144.0, 139.0, 133.4, 132.7, 132.6, 128.3, 126.8, 122.7, 122.2, 121.1, 120.0, 53.2, 52.8, 52.0, 49.6, 49.3, 37.5, 30.5; IR (ATR diamond, cm^{-1}): ν 3356, 2949, 2864, 1696, 1584, 1484, 1368, 1241, 1034, 755; MS: m/z 319 (M+, 100), 252 (88), 251 (22), 239 (15), 238 (86), 192 (19).

Anal. Calcd. for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39; O, 10.02. Found: C, 78.09; H, 6.56.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-6-bromo-9H-tribenzo[b,f]azepine (**3s**)

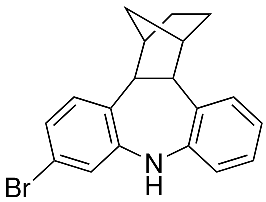


Yield: 54% (81 mg); white solid; m.p. (*n*-hexane): 193–194 °C. Eluent: *n*-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.34 (1H, s), 7.20 (1H, d, J = 7.6 Hz), 7.13 (1H, d further split, J = 8.2 Hz), 7.06 (1H, t, J = 7.5 Hz), 6.92 (1H, t, J = 7.5 Hz), 6.78 (1H, d, J = 7.6 Hz), 6.67 (1H, d, J = 8.2 Hz), 5.08 (1H, br s), 3.13 (1H, d, J = 9.6 Hz), 3.07 (1H, d, J = 9.6 Hz), 2.59 (1H, d, J = 9.8 Hz), 2.34, 2.32 (2H, 2 partly overlapping singlets), 1.65–1.45 (4H, m), 1.12 (1H, d, J = 9.8 Hz); ^{13}C NMR (100 MHz): δ 144.0, 143.7, 135.8, 134.9, 133.4, 132.6, 129.2, 126.7, 122.2, 121.5, 119.9, 114.0, 52.9, 52.8, 49.4, 49.3, 37.4 ,30.7, 30.6; IR (ATR diamond, cm^{-1}): ν 3367, 2964, 2866, 1577, 1473, 1303, 1248, 1127, 814, 745; MS: m/z 341 (M+, 100), 339 (98), 276 (75), 274 (77), 260 (80), 258 (78), 191 (25).

Anal. Calcd. for $C_{19}H_{18}BrN$: C, 67.07; H, 5.33; Br, 23.48; N, 4.12. Found: C, 67.25 ;H, 5.26.

cis,ex*o-1,2,3,4,4a,13b-Hexahydro-1,4-methano-7-bromo-9H-tribenzo[b,f]azepine* (**3t**)



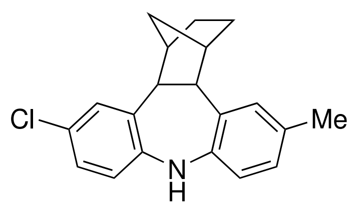
Yield: 56% (84 mg); white solid; m.p. (nhexane): 199–200 °C. Eluent: *n*-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.20 (1H, dd, J = 7.6, 1.2 Hz), 7.09–7.04 (2H, m), 7.00 (1H, dd, J = 8.0, 2.0 Hz), 6.97 (1H, d, J = 2.0 Hz), 6.92 (1H, td, J = 7.6, 1.2 Hz), 6.78 (1H, dd, J = 8.0, 0.8 Hz), 5.07 (1H, br s), 3.15–3.05 (2H, m), 2.58 (1H, d further split, J = 9.6 Hz), 2.31, 2.28 (2H, 2 partly overlapping singlets), 1.63–1.46 (4H, m), 1.11 (1H, d, J = 9.6 Hz); ^{13}C NMR (100 MHz): δ 145.7, 143.7, 134.0, 133.6, 132.7, 132.6, 126.7, 124.7, 122.5, 122.3, 120.0, 119.1, 52.7, 52.6, 49.4, 49.3, 37.3, 30.7, 30.6; IR (ATR diamond, cm^{-1}): ν 3354, 2943, 2867, 1575, 1471, 1255, 1116, 915, 747; MS: m/z 341 (M+, 96), 339 (95), 298 (10), 274 (98), 272 (100), 261 (95), 259 (94), 191 (30), 179 (25), 165 (17).

Anal. Calcd. for $C_{19}H_{18}BrN$: C, 67.07; H, 5.33; Br, 23.48; N, 4.12. Found: C, 66.83

;H, 5.28.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-6-chloro-12-methyl-9H-tribenzo[b,f]azepine (**3u**)

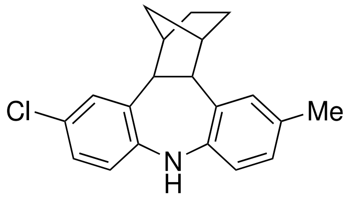


Yield: 87% (118 mg); white solid; m.p. (*n*-hexane): 228–229 °C. Eluent: *n*-hexane/EtOAc 98:2.

^{1}H NMR (400 MHz, DMSO-d6): δ 7.21 (1H, s), 7.18 (2H, s further split), 7.05–6.99 (2H, m), 6.94 (1H, d, J = 1.5 Hz), 6.91 (1H, d, J = 8.0 Hz), 6.80 (1H, dd, J = 8.0, 1.5 Hz), 3.04 (1H, d, J = 9.3 Hz), 2.98 (1H, d, J = 9.3 Hz), 2.45 (1H, d, J = 9.4 Hz), 2.17 (3H, s), 2.11 (2H, s), 1.50–1.35 (4H, m), 0.98 (1H, d, J = 9.4 Hz); ^{13}C NMR (100 MHz, DMSO-d6): δ 145.0, 142.7, 135.3, 133.0, 132.9, 131.7, 130.1, 127.4, 126.4, 124.4, 121.9, 120.4, 52.3, 49.8, 49.7, 37.3, 30.4, 30.3, 20.6; IR (ATR diamond, cm^{-1}): ν 3365, 2957, 1458, 1254, 819, 649; MS: m/z 311 (M+, 36), 309 (100), 244 (33), 242 (94), 229 (15), 230 (29), 228 (83), 204 (10).

Anal. Calcd. for $C_{20}H_{20}ClN$: C, 77.53; H, 6.51; Cl, 11.44; N, 4.52. Found: C, 77.41; H, 6.57.

cis,exo-1,2,3,4,4a,13b-Hexahydro-1,4-methano-6,12-dichloro-9H-tribenzo[b,f]azepine (**3v**)

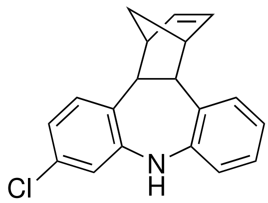


Yield: 62% (90 mg); white solid; m.p. (*n*-hexane): 232–233 °C. Eluent: n-exane/EtOAc 98:2.

^{1}H NMR (400 MHz, DMSO-d6): δ 7.49 (1H, s), 7.20 (2H, s), 7.04 (4H, s), 3.03 (2H, s), 2.37 (1H, d, J = 9.5 Hz), 2.10 (2H, s), 1.48–1.43 (4H, m), 0.98 (1H, d, J = 9.5 Hz); ^{13}C NMR (100 MHz, DMSO-d6): δ 144.0, 135.1, 131.8, 126.6, 124.9, 122.1, 51.9, 49.9, 37.3, 30.2; IR (ATR diamond, cm^{-1}): ν 3373, 2949, 1476, 1255, 1129, 818, 635; MS: m/z 331 (M+, 65), 329 (100), 264 (65), 262 (97), 250 (62), 248 (94), 227 (13), 213 (12), 190 (17).

Anal. Calcd. for $C_{19}H_{17}Cl_2N$: C, 69.10; H, 5.19; Cl, 21.47; N, 4.24. Found: C, 69.33; H, 5.17.

cis,exo-1,4,4a,13b-Tetrahydro-1,4-methano-7-chloro-9H-tribenzo[b,f]azepine (**4**)

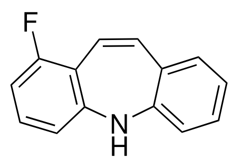


Yield: 60% (77 mg); white solid; m.p. (*n*-hexane): 185–186 °C. Eluent: n-exane/EtOAc 98:2.

^{1}H NMR (400 MHz): δ 7.24 (1H, br d, J = 7.6 Hz), 7.15 (1H, d, J = 8.4 Hz), 7.07 (1H, br t, J = 7.6 Hz), 6.93 (1H, br t, J = 7.6 Hz), 6.87 (1H, dd, J = 8.0, 2.0 Hz), 6.81 (1H, d, J = 2.0 Hz), 6.78 (1H, br d, J = 7.6 Hz), 6.43–6.37 (2H, m), 5.18 (1H, br s), 3.04–2.96 (2H, m), 2.88 (1H, br s), 2.84 (1H, br s), 2.72 (1H, br d, J = 8.8

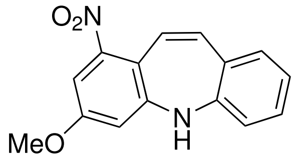
Hz), 1.31 (1H, br d, $J = 8.8$ Hz); ^{13}C NMR (100 MHz): δ 144.4, 142.8, 139.3, 139.0, 134.2, 133.1, 132.2, 131.5, 130.9, 126.7, 122.4, 121.8, 120.0, 119.6, 55.5, 55.4, 46.6, 46.5, 46.4; MS: m/z 229 ((M-66)+, 46), 227 ((M-66)+, 100), 191 (28), 165 (19).
Anal. Calcd. for $C_{19}H_{16}ClN$: C, 77.68; H, 5.49; Cl, 12.07; N, 4.77. Found: C, 77.29; H, 5.44.

1-Fluoro-5H-dibenzo[b,f]azepine (**5a**)



Yield: 65% (60 mg); yellow solid; m.p. (n-hexane): 113–114 °C. Eluent: n-hexane/EtOAc 95:5.
^{1}H NMR (400 MHz): δ 7.08 (1H, ddd, J = 8.0, 6.8, 2.4 Hz), 7.01 (1H, dt, J = 8.0, 6.0 Hz), 6.95–6.86 (2H, m), 6.59, 6.58 (2H, 2 overlapping signals: dd, J = 12.0, 1.2 Hz and ddd, J = 9.6, 8.4, 1.2 Hz), 6.53 (1H, d further split, J = 7.6 Hz), 6.45 (1H, d, J = 12.0 Hz), 6.32 (1H, d further split, J = 8.0 Hz), 5.06 (1H, br s); ^{13}C NMR (100 MHz): δ 160.7 (d, JC,F = 246.8 Hz), 151.0 (d, JC,F = 5.3 Hz), 148.0, 133.1 (d, JC,F = 1.7 Hz), 130.6, 130.1 (d, JC,F = 10.7 Hz), 129.8, 129.6, 123.8 (d, JC,F = 8.0 Hz), 123.4, 119.6, 118.0 (d, JC,F = 14.5 Hz), 114.8 (d, JC,F = 2.7 Hz), 109.7 (d, JC,F = 22.8 Hz); IR (ATR diamond, cm-1): ν 3365, 2976, 1616, 1437, 1224, 1019, 722; MS: m/z 211 (M+, 100), 183 (14).
Anal. Calcd. for $C_{14}H_{10}FN$: C, 79.60; H, 4.77; F, 8.99; N, 6.63. Found: C, 79.72; H, 4.72.

1-Nitro-3-methoxy-5H-dibenzo[b,f]azepine (**5b**)

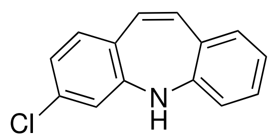


Yield: 60% (71 mg); red solid; m.p. (n-hexane): 126–127 °C. Eluent: n-exane/EtOAc 70:30.

^{1}H NMR (400 MHz): δ 7.13 (1H, td, J = 6.8, 2.0 Hz), 7.30–6.95 (2H, m), 6.90 (1H, d, J = 2.8 Hz), 6.62 (1H, d, J = 7.6 Hz), 6.58 (1H, d, J = 12.0 Hz), 6.49 (1H, d, J = 12.0 Hz), 6.39 (1H, d, J = 2.8 Hz), 5.22 (1H, br s), 3.82 (3H, s); ^{13}C NMR (100 MHz): δ 160.1, 153.4, 150.6, 147.5, 133.0, 130.4, 129.9, 129.6, 126.1, 124.1, 119.8, 116.9, 109.9, 103.4, 55.8; IR (ATR diamond, cm-1): ν 3371, 2918, 1526, 1147, 1051, 748; MS: m/z 268 (M+, 31), 239 (14), 209 (100), 178 (23).

Anal. Calcd. for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.51; N, 10.44. Found: C, 67.25; H, 4.46.

3-Chloro-5H-dibenzo[b,f]azepine (**5c**)



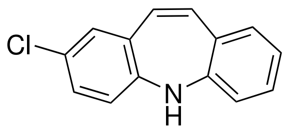
Yield: 65% (65 mg); yellow solid; m.p. (n-hexane): 168–169 °C. Eluent: n-hexane/EtOAc 90:10.

^{1}H NMR (300 MHz): δ 7.10–7.03 (1H, m), 6.90–6.75 (4H, m), 6.53 (1H, s), 6.49 (1H, d, J = 8.0 Hz), 6.31 (1H, d, J = 11.6 Hz), 6.24 (1H, d, J = 11.6 Hz), 4.95 (1H, br s); ^{13}C NMR (100 MHz, DMSO-d6): δ 151.3, 148.9, 134.3, 132.8, 132.3, 131.3, 131.1, 130.3, 129.3, 128.4, 122.8, 121.8, 119.6, 118.8; IR (ATR diamond, cm-1): ν 3365, 3055, 2977, 1610, 1464, 1247, 1120, 782; MS: m/z 229 (M+, 32), 227 (100), 191 (23), 165 (16).

Anal. Calcd. for $C_{14}H_{10}ClN$: C, 73.85; H, 4.43; Cl, 15.57; N, 6.15. Found: C, 74.03;

H, 4.49.

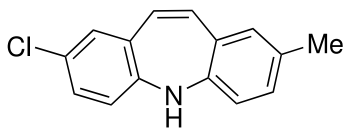
2-Chloro-5H-dibenzo[b,f]azepine (**5d**)



Yield: 67% (67 mg); yellow solid; m.p. (n-hexane): 166–167 °C. Eluent: n-hexane/EtOAc 90:10.

^{1}H NMR (300 MHz): δ 7.04 (1H, ddd, J = 7.8, 6.0, 3.0 Hz), 6.96 (1H, dd, J = 8.1, 2.7 Hz), 6.87–6.80 (3H, m), 6.47 (1H, d further split, J = 8.1 Hz), 6.41 (1H, d, J = 8.1 Hz), 6.34 (1H, d, J = 11.7 Hz), 6.20 (1H, d, J = 11.7 Hz), 4.90 (1H, br s); ^{13}C NMR (100 MHz): δ 148.1, 146.9, 133.4, 131.4, 130.8, 129.9, 129.8, 129.4, 128.9, 128.0, 123.3, 120.4, 119.4; IR (ATR diamond, cm-1): ν 3366, 3057, 2976, 1608, 1464, 1247, 1122, 892, 784; MS: m/z 229 (M+, 34), 227 (100), 191 (23), 165 (15). Anal. Calcd. for $C_{14}H_{10}ClN$: C, 73.85; H, 4.43; Cl, 15.57; N, 6.15. Found: C, 74.08; H, 4.39.

2-Chloro-8-methyl-5H-dibenzo[b,f]azepine (**5e**)

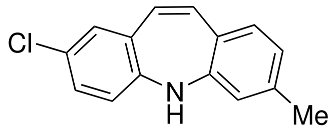


Yield: 68% (73 mg); yellow solid; m.p. (n-hexane): 193–194 °C. Eluent: n-hexane/EtOAc 90:10.

^{1}H NMR (300 MHz): δ 6.96 (1H, dd, J = 8.4, 2.4 Hz), 6.85, 6.82 (2H, 2 partly overlapping signals: dd, J = 7.8, 1.5 Hz and d, J = 2.4 Hz), 6.68 (1H, d, J = 1.5 Hz), 6.41, 6.39 (2H, 2 partly overlapping signals: d, J = 8.4 Hz and d, J = 7.8 Hz), 6.32 (1H, d, J = 11.7 Hz), 6.21 (1H, d, J = 11.7 Hz), 4.85 (1H, br s), 2.18 (3H, s);

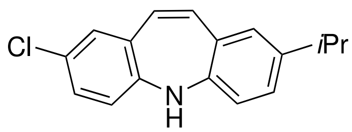
^{13}C NMR (100 MHz): δ 147.2, 145.4, 133.4, 132.6, 131.3, 131.2, 130.7, 130.2, 129.9, 129.2, 128.8, 127.8, 120.2, 119.3, 20.3; IR (ATR diamond, cm-1): ν 3355, 3025, 2918, 1472, 1253, 1157, 1124, 814, 736; MS: m/z 243 (M+, 35), 241 (100), 204 (13). Anal. Calcd. for $C_{15}H_{12}ClN$: C, 74.54; H, 5.00; Cl, 14.67; N, 5.79. Found: C, 74.73; H, 5.08.

2-Chloro-7-methyl-5H-dibenzo[b,f]azepine (5f)



Yield: 72% (76 mg); yellow solid; Eluent: n-hexane/EtOAc 95:5.
^{1}H NMR (400 MHz, DMSO-d6): δ 6.97, 6.97 (2H, 2 overlapping signals: dd, J = 8.4, 2.4 Hz and s), 6.78 (1H, d, J = 2.4 Hz), 6.63 (1H, d, J = 7.6), 6.58 (1H, d, J = 8.4 Hz), 6.51 (1H, d further split, J = 7.6 Hz), 6.41 (1H, br s), 6.06 (1H, d, J = 12.0 Hz), 5.95 (1H, d, J = 12.0 Hz), 2.10 (3H, s); ^{13}C NMR (100 MHz, DMSO-d6): δ 149.4, 148.6, 140.0, 133.8, 131.5, 131.2, 130.0, 129.9, 129.2, 126.4, 125.9, 123.1, 120.8, 120.2, 21.0.
Anal. Calcd. for $C_{15}H_{12}ClN$: C, 74.54; H, 5.00; Cl, 14.67; N, 5.79. Found: C, 74.69; H, 5.04.

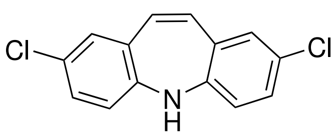
2-Chloro-8-isopropyl-5H-dibenzo[b,f]azepine (**5g**)



Yield: 74% (87 mg); pale orange solid; m.p. (n-hexane): 170–171 °C. Eluent: n-exane/EtOAc 97:3.
^{1}H NMR (300 MHz): δ 6.98 (1H, dd, J = 8.4, 2.4 Hz), 6.95 (1H, dd, J = 8.0, 2.0

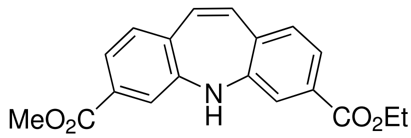
Hz), 6.85 (1H, d, J = 2.4 Hz), 6.77 (1H, d, J = 2.4 Hz), 6.46, 6.43 (2H, 2 partly overlapping signals: d, J = 8.0 Hz and d, J = 8.4 Hz), 6.39 (1H, d, J = 11.6 Hz), 6.25 (1H, d, J = 11.6 Hz), 4.91 (1H, br s), 2.79 (1H, heptet, J = 6.8 Hz), 1.21 (6H, d, J = 6.8 Hz); ^{13}C NMR (100 MHz): δ 147.2, 145.7, 143.9, 133.6, 131.4, 130.6, 129.8, 129.2, 128.8, 128.7, 127.8, 127.6, 120.3, 119.4, 33.1, 23.9; IR (ATR diamond, cm-1): ν 3360, 2958, 1502, 1463, 1256, 1122, 896, 785; MS: m/z 271 (M+, 25), 269 (71), 256 (34), 254 (100), 219 (18), 191 (8).
Anal. Calcd. for $C_{17}H_{16}ClN$: C, 75.69; H, 5.98; Cl, 13.14; N, 5.19. Found: C, 75.89; H, 5.94.

2,8-Dichloro-5H-dibenzo[b,f]azepine (**5h**)



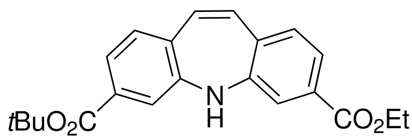
Yield: 47% (54 mg); pale orange solid; m.p. (n-hexane): 151–152 °C. Eluent: n-exane/EtOAc 90:10.
^{1}H NMR (300 MHz): δ 6.98 (2H, dd, J = 8.4, 2.4 Hz), 6.81 (2H, d, J = 2.4 Hz), 6.39 (2H, d, J = 8.4 Hz), 6.22 (2H, s), 4.87 (1H, br s); ^{13}C NMR (100 MHz): δ 146.6, 132.1, 131.0, 130.1, 129.2, 128.3, 120.4; IR (ATR diamond, cm-1): ν 3352, 2958, 1466, 1378, 1259, 1243, 1127, 788; MS: m/z 263 (M+, 70), 262 (20), 261 (100), 226 (13), 207 (10), 190 (22).
Anal. Calcd. for $C_{14}H_{9}Cl_{2}N$: C, 64.15; H, 3.46; Cl, 27.05; N, 4.33. Found: C, 63.97; H, 3.51.

3-Carbomethoxy-7-carboethoxy-5H-dibenzo[b,f]azepine (**5i**)



Yield: 50% (71 mg); red solid; m.p. (n-hexane): 164–165 °C. Eluent: n-exane/EtOAc 90:10. ^{1}H NMR (300 MHz): δ 7.47, 7.46 (2H, 2 overlapping signals: 2 dd, J = 7.8, 1.5 Hz), 7.23, 7.22 (2H, 2 overlapping signals: 2 d, J = 1.5 Hz), 6.87 (2H, d, J = 7.8 Hz), 6.34 (2H, s), 5.45 (1H, br s), 4.33 (2H, q, J = 7.2 Hz), 3.87 (3H, s), 1.36 (3H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz): δ 166.6, 166.1, 148.4, 148.3, 134.1, 134.0, 133.4, 133.2, 131.7, 131.2, 130.7, 130.6, 124.4, 120.4, 120.3, 61.1, 52.2, 14.3; IR (ATR diamond, cm-1): ν 3354, 2945, 2918, 2863, 1723, 1710, 1467, 1433, 1381, 1118, 1025, 1098, 746; MS: m/z 323 (M+, 100), 295 (65), 236 (21), 190 (15). Anal. Calcd. for $C_{19}H_{17}NO_4$: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.47; H, 5.27.

3-Carbo-tert-Butoxy-7-carboethoxy-5H-dibenzo[b,f]azepine (**5j**)

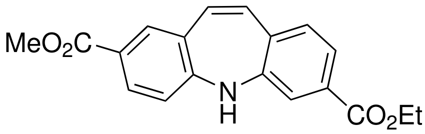


Yield: 56% (90 mg); brown solid; m.p. (n-hexane): 132–133 °C. Eluent: n-exane/EtOAc 95:5.

^{1}H NMR (400 MHz): δ 7.49 (1H, d further split, J = 8.0 Hz), 7.44 (1H, d further split, J = 8.0 Hz), 7.27 (1H, s further split), 7.18 (1H, s further split), 6.89, 6.87 (2H, 2 partly overlapping signals: d further split, J = 8.0 Hz and d further split, J = 8.0 Hz), 6.39–6.33 (2H, m), 5.48 (1H, br s), 4.36 (2H, q, J = 6.8 Hz), 1.58 (9H, s), 1.38 (3H, t, J = 6.8 Hz); ^{13}C NMR (100 MHz): δ 166.1, 165.1, 148.4, 148.2, 134.1, 133.6, 133.4, 133.2, 133.0, 131.5, 130.6, 130.5, 124.33, 124.30, 120.3, 120.2, 81.2, 61.1, 28.2, 14.3; IR (ATR diamond, cm-1): ν 3362, 2976, 1711, 1701, 1382, 1275, 1101, 751; MS: m/z 388.1514 (M+ Na+).

Anal. Calcd. for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83. Found: C, 72.06; H, 6.25.

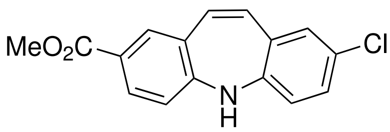
2-Carbomethoxy-7-carboethoxy-5H-dibenzo[b,f]azepine (**5k**)



Yield: 72% (102 mg); red solid; m.p. (n-hexane): 154–155 °C. Eluent: n-hexane/EtOAc 90:10.

^{1}H NMR (300 MHz): δ 7.65 (1H, dd, J = 8.0, 2.0 Hz), 7.47–7.41 (2H, m), 7.10 (1H, d, J = 1.6 Hz), 6.80 (1H, d, J = 8.0 Hz), 6.43 (1H, d, J = 8.0 Hz), 6.19 (1H, d, J = 12.0 Hz), 6.12 (1H, d, J = 12.0 Hz), 5.42 (1H, br s), 4.34 (2H, q, J = 7.2 Hz), 3.86 (3H, s), 1.38 (3H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz): δ 166.3, 166.0, 152.8, 147.0, 133.8, 133.7, 132.8, 131.7, 131.5, 131.4, 130.8, 128.4, 124.5, 124.4, 120.1, 118.8, 61.1, 51.9, 14.3; IR (ATR diamond, cm-1): ν 3358, 2984, 1700, 1600, 1479, 1289, 1196, 1127, 1103, 1017, 767, 737; MS: m/z 323 (M+, 100), 295 (74), 236 (25), 190 (18). Anal. Calcd. for $C_{19}H_{17}NO_4$: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.32; H, 5.35.

2-Carbomethoxy-8-chloro 5H-dibenzo[b,f]azepine (**5l**)



Yield: 82% (102 mg); yellow solid; m.p. (n-hexane): 186–187 °C. Eluent: n-exane/EtOAc 90:10.

^{1}H NMR (300 MHz): δ 7.65 (1H, dd, J = 8.4, 2.0 Hz), 7.45 (1H, d, J = 2.0 Hz), 6.94 (1H, dd, J = 8.4, 2.4 Hz), 6.75 (1H, d, J = 2.4 Hz), 6.39 (1H, d, J = 8.0 Hz), 6.33 (1H, d, J = 8.0 Hz), 6.16 (1H, d, J = 12.0 Hz), 6.06 (1H, d, J = 12.0 Hz), 5.12

(1H, br s), 3.86 (3H, s); ^{13}C NMR (100 MHz): δ 166.3, 152.6, 145.4, 132.8, 132.7, 131.5, 131.2, 130.7, 130.4, 129.2, 128.4, 128.3, 124.6, 120.3, 118.8, 51.9; IR (ATR diamond, cm-1): ν 3361, 2945, 1695, 1475, 1428, 1296, 1118, 752, 690; MS: m/z 285 (M+, 100), 254 (16), 226 (29), 190 (17), 95 (10).
Anal. Calcd. for $C_{16}H_{12}ClNO_2$: C, 67.26; H, 4.23; Cl, 12.41; N, 4.90. Found: C, 67.12; H, 4.30.

5.5 References

(1) a) Della Ca', N.; Sassi, G.; Catellani, M. *Adv. Synth. Catal.* **2008**, *350*, 2179–2182; b) Catellani, M.; Motti, E.; Della Ca', N. *Top. Catal.* **2010**, *53*, 991–996.

(2) a) Faccini, F.; Motti, E.; Catellani, M. *J. Am. Chem. Soc.* **2004**, *126*, PMID: 14709068, 78–79; b) Tsuji, J., *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*; Wiley: 2004; c) Catellani, M.; Motti, E.; Della Ca', N. *Acc. Chem. Res.* **2008**, *41*, PMID: 18680317, 1512–1522; d) Martins, A.; Mariampillai, B.; Lautens, M. In *CH Activation*; Springer: 2010, pp 1–33; e) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174–238; f) Lautens, M.; Alberico, D.; Bressy, C.; Fang, Y.-Q.; Mariampillai, B.; Wilhelm, T. *Pure Appl. Chem.* **2006**, *78*, 351–361; g) Sehnal, P.; Taylor, R. J.; Fairlamb, I. J. *Chem. Rev.* **2010**, *110*, 824–889; h) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.* **2010**, *39*, 712–733; i) Muñiz, K. *Angew. Chem. Int. Ed.* **2009**, *48*, 9412–9423; j) Johnson, J. B.; Rovis, T. *Angew. Chem. Int. Ed.* **2008**, *47*, 840–871.

(3) a) Catellani, M.; Motti, E. *New J. Chem.* **1998**, *22*, 759–761; b) Catellani, M.; Motti, E.; Baratta, S. *Org. Lett.* **2001**, *3*, 3611–3614; c) Catellani, M.; Mealli, C.; Motti, E.; Paoli, P.; Perez-Carreño, E.; Pregosin, P. S. *J. Am.*

Chem. Soc. **2002**, *124*, PMID: 11960463, 4336–4346; d) Maestri, G.; Motti, E.; Della Ca', N.; Malacria, M.; Derat, E.; Catellani, M. *J. Am. Chem. Soc.* **2011**, *133*, PMID: 21563760, 8574–8585.

(4) a) Surry, D. S.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2008**, *47*, 6338–6361; b) Hartwig, J. F. *Acc. Chem. Res.* **2008**, *41*, 1534–1544.

(5) Della Ca', N.; Maestri, G.; Malacria, M.; Derat, E.; Catellani, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 12257–12261.

(6) a) Solé, D.; Vallverdú, L.; Solans, X.; Font-Bardia, M.; Bonjoch, J. *Organometallics* **2004**, *23*, 1438–1447; b) Vicente, J.; Abad, J.-A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chemistry-A European Journal* **1999**, *5*, 3066–3075.

(7) Larraufie, M.-H.; Maestri, G.; Beaume, A.; Derat, É.; Ollivier, C.; Fensterbank, L.; Courillon, C.; Lacôte, E.; Catellani, M.; Malacria, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 12253–12256.

(8) a) Hirschfeld, R. M. A.; Kasper, S. *Int. J. Neuropsychopharmacol.* **Dec. 2004**, *7*, 507–522; b) Gomez-Arguelles, J.; Dorado, R.; Sepulveda, J.; Herrera, A.; Arrojo, F. G.; Aragón, E.; Huete, C. R.; Terrón, C.; Anciones, B. *J. Clin. Neurosci.* **2008**, *15*, 516–519.

(9) Yoon, S.; Kim, S.; Kim, B.; Kwon, H.; Cho, Y. Novel organic electroluminescent compounds and organic electroluminescent device using the same., May 2010.

(10) a) Defieber, C.; Grützmacher, H.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2008**, *47*, 4482–4502; b) Drinkel, E.; Briceno, A.; Dorta, R.; Dorta, R. *Organometallics* **2010**, *29*, 2503–2514.

(11) a) Singh, H.; Gupta, N.; Kumar, P.; Dubey, S. K.; Sharma, P. K. *Org. Process Res. Dev.* **2009**, *13*, 870–874; b) Kricka, L.; Ledwith, A. *Chemical Reviews* **1974**, *74*, 101–123; c) Arnold, L. A.; Luo, W.; Guy, R. K. *Org. Lett.* **2004**,

6, PMID: 15330669, 3005–3007; d) Tsvelikhovsky, D.; Buchwald, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 14048–14051; e) Thansandote, P.; Chong, E.; Feldmann, K.-O.; Lautens, M. *J. Org. Chem.* **2010**, *75*, 3495–3498.

(12) a) Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem.* **1985**, *286*, c13–c16; b) Catellani, M.; Motti, E.; Paterlini, L.; Bocelli, G.; Righi, L. *J. Organomet. Chem.* **1999**, *580*, 191–196; c) Albrecht, K.; Reiser, O.; Weber, M.; Knieriem, B.; de Meijere, A. *Tetrahedron* **1994**, *50*, 383–401.

(13) a) Horino, H.; Arai, M.; Inoue, N. *Tetrahedron Lett.* **1974**, *15*, 647–650; b) Li, C.-S.; Cheng, C.-H.; Liao, F.-L.; Wang, S.-L. *J. Chem. Soc., Chem. Commun.* **1991**, 710–712; c) Portnoy, M.; Ben-David, Y.; Rousso, I.; Milstein, D. *Organometallics* **1994**, *13*, 3465–3479.

(14) a) Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem.* **1988**, *346*, C27–C30; b) Liu, C. H.; Li, C. S.; Cheng, C. H. *Organometallics* **1994**, *13*, 18–20; c) Beletskaya, I. P.; Cheprakov, A. V. *J. Organomet. Chem.* **2004**, *689*, 4055–4082.

(15) a) Canty, A. J. *Acc. Chem. Res.* **1992**, *25*, 83–90; b) Catellani, M.; Fagnola, M. C. *Angew. Chem. Int. Ed. in English* **1995**, *33*, 2421–2422; c) Lyons, T. W.; Sanford, M. S. *Chemical Reviews* **2010**, *110*, 1147–1169; d) Amatore, C.; Catellani, M.; Deledda, S.; Jutand, A.; Motti, E. *Organometallics* **2008**, *27*, 4549–4554; e) Vicente, J.; Arcas, A.; Juliá-Hernández, F.; Bautista, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 6896–6899.

(16) Christensen, H.; Schjøth-Eskesen, C.; Jensen, M.; Sinning, S.; Jensen, H. H. *Chem. Eur. J.* **2011**, *17*, 10618–10627.

Appendix A

Supplementary data

A.1 Comprehensive Tables of Energies

A.1.1 Reagents

	E_{el} (*Hartrees*)	ZPE + $\Delta H_{0\rightarrow T}$ (*Hartrees*)	ZPE + $\Delta G_{0\rightarrow T}$ (*Hartrees*)	E_{el} (*kcal/mol*)	H_T (*kcal/mol*)	G_T (*kcal/mol*)
Br^-	-13.202844	0.002360	-0.016176	-8284.90	-8283.42	-8295.05
Br^-*	-13.267506	0.003032	-0.021538	-8325.48	-8323.58	-8339.00
m-TCPP	-1075.115589	0.267868	0.196606	-674644.71	-674476.62	-674521.34
m-TCPP*	-1075.120137	0.278442	0.171911	-674647.56	-674472.84	-674539.69
$Pd(PPh_3)_2$	-2191.125815	0.590774	0.481819	-1374951.17	-1374580.45	-1374648.82
Pd(*m*-TCPP)$_2$	-2277.062366	0.539799	0.403821	-1428877.13	-1428538.40	-1428623.73
Pd(*m*-TCPP)$_2$*	-2277.071262	0.563781	0.362107	-1428882.71	-1428528.93	-1428655.49
p-iodotoluene	-282.135748	0.125886	0.083132	-177042.72	-176963.73	-176990.55
o-bromonitrobenzene	-448.983152	0.102333	0.058018	-281740.97	-281676.75	-281704.56
o-bromonitrobenzene*	-448.986932	0.107104	0.044714	-281743.34	-281676.13	-281715.28
norbornene	-272.508516	0.159194	0.124535	-171001.55	-170901.65	-170923.40
norbornene*	-272.508945	0.162955	0.114063	-171001.82	-170899.56	-170930.24
p-bromonitrobenzene	-448.995821	0.102384	0.058275	-281748.92	-281684.67	-281712.35
p-bromonitrobenzene*	-448.999085	0.107187	0.045087	-281750.97	-281683.71	-281722.67
[Pd(*m*-TCPP)$_2$I]$^-$	-2288.613484	0.542102	0.408527	-1436125.56	-1435785.38	-1435869.20
[Pd(*m*-TCPP)$_2$I]$^-$*	-2288.650025	0.565677	0.372558	-1436148.49	-1435793.52	-1435914.70
o-bromomethylbenzoate	-472.336225	0.143783	0.098005	-296395.23	-296305.01	-296333.73
I^-	-11.476223	0.002360	-0.016848	-7201.43	-7199.95	-7212.01
I^-*	-11.534871	0.003032	-0.022402	-7238.24	-7236.33	-7252.29
PPh_3	-1032.148595	0.292563	0.231275	-647682.53	-647498.95	-647537.41
o-iodotoluene	-282.136509	0.125909	0.083489	-177043.20	-176964.19	-176990.81
o-iodotoluene*	-282.137874	0.130321	0.070298	-177044.05	-176962.28	-176999.94

A.1.2 Products

	E_{el} (*Hartrees*)	ZPE + $\Delta H_{0\rightarrow T}$ (*Hartrees*)	ZPE + $\Delta G_{0\rightarrow T}$ (*Hartrees*)	E_{el} (*kcal/mol*)	H_T (*kcal/mol*)	G_T (*kcal/mol*)
1a	-717.409220	0.216630	0.155661	-450180.74	-450044.81	-450083.06
1a*	-717.413552	0.225312	0.138016	-450183.46	-450042.08	-450096.85
1c	-717.415322	0.216908	0.156727	-450184.57	-450048.46	-450086.22
1c*	-717.419267	0.225515	0.138368	-450187.05	-450045.53	-450100.22
1b	-740.759707	0.258699	0.194381	-464833.38	-464671.05	-464711.41

A.1.3 Intermediates

	E_{el} (*Hartrees*)	ZPE + $\Delta H_{0\rightarrow T}$ (*Hartrees*)	ZPE + $\Delta G_{0\rightarrow T}$ (*Hartrees*)	E_{el} (*kcal/mol*)	H_T (*kcal/mol*)	G_T (*kcal/mol*)
IaH	-1106.661597	0.191520	0.115574	-694440.11	-694319.93	-694367.59
IIa	-2559.226870	0.667954	0.522596	-1605937.89	-1605518.75	-1605609.96
trans-**IIIa**	-2559.240039	0.667754	0.520537	-1605946.16	-1605527.14	-1605619.52
cis-**IIIa**	-2559.234383	0.669432	0.526680	-1605942.61	-1605522.53	-1605612.11
IVa	-2819.727244	0.817637	0.671449	-1769404.22	-1768891.15	-1768982.88
Va	-2193.571310	0.650475	0.523515	-1376485.74	-1376077.56	-1376157.23
VIa	-2193.598837	0.650510	0.526508	-1376503.01	-1376094.81	-1376172.62
VIIa	-2193.647741	0.653727	0.531108	-1376533.70	-1376123.48	-1376200.43
VIIIa	-2193.615805	0.651087	0.525594	-1376513.66	-1376105.10	-1376183.85
cis-**IXa**	-2994.537585	0.760477	0.609063	-1879099.29	-1878622.08	-1878717.09
trans-**IXa**	-2994.534779	0.760708	0.605186	-1879097.52	-1878620.17	-1878717.76
Xa	-2994.523712	0.760530	0.606785	-1879090.58	-1878613.34	-1878709.82
IIa*	-2559.235817	0.696788	0.477308	-1605943.51	-1605506.27	-1605643.99
trans-**IIIa**	-2559.252130	0.696607	0.476629	-1605953.74	-1605516.62	-1605654.66
cis-**IIIa***	-2559.247246	0.697860	0.484226	-1605950.68	-1605512.77	-1605646.82
IVa*	-2819.736010	0.849104	0.625719	-1769409.72	-1768876.90	-1769017.08
Va*	-2193.580225	0.675626	0.483019	-1376491.33	-1376067.37	-1376188.23
VIa*	-2193.609617	0.675840	0.487036	-1376509.78	-1376085.68	-1376204.16
VIIa*	-2193.659940	0.678736	0.492501	-1376541.36	-1376115.44	-1376232.31
VIIIa*	-2193.626887	0.676562	0.486271	-1376520.61	-1376096.07	-1376215.47
cis-**IXa***	-2994.548185	0.793578	0.561409	-1879105.94	-1878607.96	-1878753.65
Xa*	-2994.534499	0.793168	0.558135	-1879097.35	-1878599.63	-1878747.11
Vb	-2216.928167	0.693099	0.565620	-1391142.38	-1390707.45	-1390787.45
VIb	-2216.952359	0.694465	0.570619	-1391157.56	-1390721.77	-1390799.49
VIIb	-2216.998149	0.695932	0.569064	-1391186.29	-1390749.59	-1390829.20
VIIIb	-2216.965273	0.692814	0.561958	-1391165.66	-1390730.91	-1390813.03
cis-**IXb**	-3017.878367	0.802774	0.645690	-1893745.84	-1893242.09	-1893340.66
trans-**IXb**	-3017.879916	0.802972	0.643641	-1893746.81	-1893242.94	-1893342.92
Xb	-3017.877986	0.802704	0.643301	-1893745.60	-1893241.89	-1893341.92
Vc	-2193.582475	0.651343	0.525832	-1376492.75	-1376084.02	-1376162.78

Table A.3: continue in the next page

Table A.3: continued from the previous page

	E_{el} (*Hartrees*)	ZPE + $\Delta H_{0\rightarrow T}$ (*Hartrees*)	ZPE + $\Delta G_{0\rightarrow T}$ (*Hartrees*)	E_{el} (*kcal/mol*)	H_T (*kcal/mol*)	G_T (*kcal/mol*)
VIc	-2193.590621	0.651296	0.525837	-1376497.86	-1376089.16	-1376167.89
VIIc	-2193.653295	0.653156	0.531162	-1376537.19	-1376127.32	-1376203.88
VIIIc	-2193.629694	0.651196	0.527238	-1376522.38	-1376113.74	-1376191.53
cis-**IXc**	-2994.518341	0.760370	0.601481	-1879087.21	-1878610.07	-1878709.77
trans-**IXc**	-2994.542130	0.759901	0.602671	-1879102.14	-1878625.29	-1878723.96
Xc	-2994.528013	0.761509	0.607145	-1879093.28	-1878615.42	-1878712.29
Vc*	-2193.591023	0.676219	0.486598	-1376498.11	-1376073.78	-1376192.76
VIc*	-2193.602139	0.676780	0.488265	-1376505.08	-1376080.40	-1376198.69
VIIc*	-2193.664965	0.678351	0.493218	-1376544.51	-1376118.84	-1376235.01
VIIIc*	-2193.640077	0.676707	0.488817	-1376528.89	-1376104.25	-1376222.15
cis-**IXc***	-2994.530828	0.793244	0.552154	-1879095.05	-1878597.28	-1878748.56
Xc*	-2994.538592	0.794466	0.559539	-1879099.92	-1878601.38	-1878748.80
IVd	-2733.790392	0.867855	0.737129	-1715478.07	-1714933.49	-1715015.52
Vd	-2150.602519	0.675970	0.557267	-1349522.44	-1349098.26	-1349172.75
VId	-2150.634510	0.677990	0.566405	-1349542.51	-1349117.07	-1349187.09
VIId	-2150.682112	0.678963	0.565965	-1349572.38	-1349146.33	-1349217.23
VIIId	-2150.650470	0.676355	0.561044	-1349552.53	-1349128.11	-1349200.47
trans-**IXd**	-2908.597870	0.812371	0.677071	-1825171.34	-1824661.57	-1824746.47
cis-**IXd**	-2908.599245	0.813081	0.681338	-1825172.20	-1824661.99	-1824744.66
Xd	-2908.580851	0.812451	0.673222	-1825160.66	-1824650.84	-1824738.21
IIe	-2559.225669	0.696595	0.476336	-1605937.14	-1605500.02	-1605638.24
trans-**IIIe**	-2559.236993	0.668269	0.519670	-1605944.25	-1605524.90	-1605618.15
cis-**IIIe**	-2559.233475	0.668393	0.525420	-1605942.04	-1605522.62	-1605612.33

A.1.4 TSs

	E_{el} (*Hartrees*)	ZPE + $\Delta H_{0\rightarrow T}$ (*Hartrees*)	ZPE + $\Delta G_{0\rightarrow T}$ (*Hartrees*)	E_{el} (*kcal/mol*)	H_T (*kcal/mol*)	G_T (*kcal/mol*)
I-IIa	-2559.219214	0.668695	0.528597	-1605933.09	-1605513.48	-1605601.39
V-VIa	-2193.556577	0.649808	0.526182	-1376476.49	-1376068.73	-1376146.31
VI-VIIa	-2193.584629	0.650183	0.529894	-1376494.10	-1376086.10	-1376161.58
VII-VIIIa	-2193.609148	0.649437	0.524357	-1376509.48	-1376101.96	-1376180.44
IX-Xa	-2994.513323	0.759755	0.607458	-1879084.06	-1878607.31	-1878702.88
I-IIa*	-2559.228266	0.668431	0.528781	-1605938.77	-1605519.32	-1605606.96
V-VIa*	-2193.551254	0.673784	0.488746	-1376473.15	-1376050.35	-1376166.46
VI-VIIa*	-2193.597192	0.675394	0.491721	-1376501.98	-1376078.16	-1376193.42
VII-VIIIa*	-2193.621117	0.674655	0.485862	-1376516.99	-1376093.64	-1376212.11
IX-Xa*	-2994.523237	0.792461	0.559932	-1879090.28	-1878593.01	-1878738.92
V-VIb	-2216.905033	0.691734	0.566480	-1391127.86	-1390693.79	-1390772.39
VI-VIIb	-2216.933859	0.692598	0.569645	-1391145.95	-1390711.34	-1390788.49
VII-VIIIb	-2216.959243	0.692160	0.563331	-1391161.88	-1390727.54	-1390808.38
IX-Xb	-3017.859724	0.801527	0.645394	-1893734.14	-1893231.17	-1893329.15

Table A.4: continue in the next page

Table A.4: continued from the previous page

	E_{el} (*Hartrees*)	ZPE + $\Delta H_{0\to T}$ (*Hartrees*)	ZPE + $\Delta G_{0\to T}$ (*Hartrees*)	E_{el} (*kcal/mol*)	H_T (*kcal/mol*)	G_T (*kcal/mol*)
V-VIc	-2193.554728	0.649606	0.523815	-1376475.33	-1376067.70	-1376146.64
VI-VIIc	-2193.584834	0.650348	0.528122	-1376494.23	-1376086.13	-1376162.82
VII-VIIIc	-2193.620464	0.649892	0.526897	-1376516.58	-1376108.77	-1376185.95
IX-Xc	-2994.511074	0.759425	0.605955	-1879082.65	-1878606.10	-1878702.41
V-VIc*	-2193.563869	0.674656	0.485833	-1376481.07	-1376057.72	-1376176.20
VI-VIIc*	-2193.596725	0.675375	0.489664	-1376501.69	-1376077.88	-1376194.42
VII-VIIIc*	-2193.631839	0.675013	0.488566	-1376523.72	-1376100.15	-1376217.14
IX-Xc*	-2994.521559	0.791659	0.556535	-1879089.23	-1878592.46	-1878740.00
V-VId	-2150.588094	0.675383	0.562601	-1349513.38	-1349089.58	-1349160.35
VI-VIId	-2150.617063	0.676756	0.567962	-1349531.56	-1349106.89	-1349175.16
VII-VIIId	-2150.643924	0.675908	0.561838	-1349548.42	-1349124.28	-1349195.86
IX-Xd	-2908.569258	0.810418	0.674562	-1825153.39	-1824644.84	-1824730.09
II-IIIe	-2559.219631	0.667685	0.526063	-1605933.35	-1605514.37	-1605603.24

A.2 XYZ structures

A.2.1 Reagents

Br^-

1

Br 0. 0. 0.

Br^-*

1

Br 0. 0. 0.

m-TCPP

34

P -0.0000000007 -0.0000000004 2.1299082037
C -0.8014799801 -1.427025796 1.2459158126
C -0.8351006018 1.4076149202 1.2459158126
C 1.6365805799 0.0194108746 1.2459158126
C 2.6353075378 -0.8304410847 1.7314652072
C 3.8708727721 -0.9005222066 1.0956679537
C 4.128720341 -0.1125442291 -0.025289914
C 3.1274870217 0.7265472627 -0.4834568678
C 1.8842604802 0.8082032526 0.1218876258
C -2.0368368453 -1.8670227334 1.7314652072
C -2.7153114943 -2.9020130534 1.0956679537
C -2.1618263326 -3.5193045872 -0.025289914
C -0.9345351249 -3.0717568434 -0.4834568678
C -0.2422056926 -2.0359190708 0.1218876258
C -1.6420547897 1.2277158169 0.1218876258
C -2.1929518988 2.3452095794 -0.4834568678
C -1.9668940105 3.631848815 -0.025289914
C -1.1555612799 3.8025352587 1.0956679537
C -0.5984706946 2.6974638169 1.7314652072
Cl 3.4552549517 1.7593390167 -1.9414248089
Cl -3.2512597596 2.1126690564 -1.9414248089
Cl -0.2039951943 -3.8720080743 -1.9414248089
H 2.4387350066 -1.4404536878 2.6110750515
H 4.6416836234 -1.5664524559 1.4728348373
H 5.0874651418 -0.1475565129 -0.5321904491
H 1.1223989485 1.4719634944 -0.2770264006
H -2.4668369906 -1.3917796262 2.6110750515
H -3.677429433 -3.2365897075 1.4728348373
H -2.6715202603 -4.3320957985 -0.5321904491
H 0.7135583047 -1.708007751 -0.2770264006
H -1.8359572552 0.2360442553 -0.2770264006
H -2.4159448836 4.4796523101 -0.5321904491
H -0.9642541925 4.8030421621 1.4728348373
H 0.0281019819 2.8322333127 2.6110750515

m-TCPP*

```
34

P 0.005568541 -0.0023918761 2.1067706601
C 0.5671245108 -1.5353694325 1.2148494869
C -1.6102953427 0.2804852422 1.2285587454
C 1.0560750892 1.2617426981 1.2326718746
C 2.3307884187 1.4996566313 1.7553696388
C 3.1886433282 2.4040924114 1.1368167009
C 2.7791549584 3.0896152523 -0.0061137677
C 1.5119845929 2.8378040266 -0.502988866
C 0.6387917642 1.9378932347 0.084898474
C 0.096739191 -2.7613437181 1.6963379548
C 0.4388886517 -3.9484915418 1.0560444219
C 1.2680956231 -3.9265920112 -0.0647292145
C 1.7278180841 -2.701790282 -0.5162510786
C 1.39530209 -1.5026024936 0.0914593632
C -2.0269788816 -0.4859954674 0.1395983065
C -3.2446581592 -0.1891430547 -0.4487872866
C -4.0604540174 0.8387434657 -0.0097436228
C -3.6315207766 1.6046091169 1.073961976
C -2.4174937934 1.3239595964 1.6928317739
Cl 0.9720586787 3.7244420139 -1.999320699
Cl -3.793929928 -1.1917450383 -1.8666676597
Cl 2.81449616 -2.6702212552 -1.977374873
H 2.6505437811 0.971750329 2.6517928648
H 4.1791098702 2.5838003138 1.5445563216
H 3.4306777332 3.8033531297 -0.4986509159
H -0.3442719582 1.7620558097 -0.3435075276
H -0.5444491984 -2.7823207484 2.5753309805
H 0.0665213105 -4.8980722122 1.4294262463
H 1.5523832448 -4.8414849437 -0.5739787035
H 1.769465748 -0.5623402063 -0.3040466742
H -1.4142339794 -1.2969133627 -0.242029882
H -5.0079607774 1.0360465138 -0.4997483077
H -4.2538030596 2.4180547487 1.4349390786
H -2.090179513 1.9187155412 2.5434490701
```

$Pd(PPh_3)_2$

```
69

Pd 0. -0.0000000005 0.
P 0.0069543785 -0.0136475861 2.3167282203
C -1.352687021 0.921228648 3.1615530783
C 1.4911134802 0.7035680128 3.1638706755
C -0.1091043978 -1.6580314671 3.1609460594
C -0.8984680484 -2.6396176352 2.557090728
C -1.0591986689 -3.8809456482 3.1650858835
C -0.4241084586 -4.1496156235 4.3762344263
C 0.3716204909 -3.1760405133 4.9759849683
C 0.5308798937 -1.9314001938 4.3704771304
C -1.738921227 2.1387804436 2.5950725859
C -2.7177119417 2.9162158395 3.2058726487
C -3.3245778254 2.4746423536 4.3805115053
C -2.9500874032 1.2561850148 4.9410023906
C -1.9644285992 0.4791364234 4.3344346435
C 1.3992989307 1.4951357507 4.3085761974
C 2.5572978974 1.9742202234 4.9193573173
C 3.8073322101 1.6638302891 4.390553562
C 3.9013915695 0.8758645142 3.2443376138
C 2.7467412915 0.4017624296 2.6296373922
H -1.3754013881 -2.422897341 1.6014563531
H -1.6746243551 -4.6409529084 2.6907509594
H -0.5437341423 -5.1204927288 4.849750232
H 1.1532826284 -1.169468972 4.8355959839
H -1.2699939262 2.465147274 1.6670439145
H -3.0122446812 3.8635992534 2.7619369158
H -4.0929160493 3.0787444571 4.8558183275
H -1.6680551191 -0.4705654541 4.7744094019
H 0.4226338209 1.7358914527 4.7230389106
H 4.70858428 2.0394994182 4.8681785816
H 4.8752355622 0.6365952899 2.8249723066
H 2.8092540195 -0.2013198925 1.7242909613
P -0.0069543785 0.0136475852 -2.3167282203
C -1.4911134802 -0.7035680138 -3.1638706755
C 0.1091043978 1.6580314661 -3.1609460594
C 1.352687021 -0.9212286489 -3.1615530783
C 1.7389212269 -2.1387804446 -2.5950725859
C 2.7177119417 -2.9162158405 -3.2058726487
C 3.3245778254 -2.4746423546 -4.3805115053
C 2.9500874031 -1.2561850158 -4.9410023906
C 1.9644285992 -0.4791364244 -4.3344346435
C -2.7467412915 -0.4017624305 -2.6296373922
C -3.9013915696 -0.8758645152 -3.2443376138
C -3.8073322101 -1.6638302901 -4.390553562
C -2.5572978975 -1.9742202244 -4.9193573173
C -1.3992989307 -1.4951357517 -4.3085761974
C -0.5308798937 1.9314001928 -4.3704771304
C -0.3716204909 3.1760405123 -4.9759849683
C 0.4241084586 4.1496156225 -4.3762344263
C 1.0591986689 3.8809456472 -3.1650858835
C 0.8984680484 2.6396176342 -2.557090728
H 1.2699939262 -2.465147275 -1.6670439145
H 3.0122446812 -3.8635992544 -2.7619369158
H 4.0929160492 -3.078744458 -4.8558183275
H 1.668055119 0.4705654531 -4.7744094019
H -2.8092540196 0.2013198916 -1.7242909613
H -4.8752355622 -0.6365952908 -2.8249723066
H -4.7085842801 -2.0394994192 -4.8681785816
H -0.4226338209 -1.7358914537 -4.7230389106
H -1.1532826284 1.169468971 -4.8355959839
H 0.5437341423 5.1204927278 -4.849750232
H 1.6746243551 4.6409529074 -2.6907509594
H 1.3754013881 2.42289734 -1.6014563531
H -3.4270154331 0.9070562375 5.8533425196
```

H	2.4805328361	2.5931845573	5.809516951
H	0.8730815395	-3.3871253997	5.9172289157
H	3.4270154331	-0.9070562385	-5.8533425196
H	-0.8730815396	3.3871253987	-5.9172289157
H	-2.4805328361	-2.5931845583	-5.809516951

Pd(m-TCPP)$_2$

69

Pd	-0.0000000008	-0.000000001	-0.0000000011
P	-0.0147864615	0.0051621771	2.3139961986
C	-1.5341219637	0.6496289064	3.1556144086
C	1.3065198536	0.9890022966	3.1612165962
C	0.1731103164	-1.6299134705	3.1659015954
C	-0.5731792761	-2.7024991636	2.6689214922
C	-0.5072694723	-3.9466586593	3.2871842567
C	0.3149609874	-4.1366780644	4.3975038321
C	1.0525923001	-3.0620984381	4.863022579
C	0.9992288954	-1.8080135892	4.2755015999
C	-2.1940024897	1.7332421581	2.5717237854
C	-3.3174681486	2.2803031325	3.1849617386
C	-3.7985736611	1.7424430781	4.3773637066
C	-3.1319052222	0.6623106968	4.9314003323
C	-2.0069813976	0.1027497139	4.34956373
C	1.0734788706	1.6981102744	4.339722878
C	2.1332460759	2.3723755789	4.9236581818
C	3.4090316462	2.3649925201	4.385857727
C	3.6305349536	1.6518182304	3.2085465711
C	2.5837521605	0.9719259167	2.5942834976
Cl	2.1373614128	-3.3052364496	6.2984579269
Cl	1.8368176584	3.2966666806	6.457690009
Cl	-3.7587471035	-0.0482422526	6.4800808269
H	-1.2012258053	-2.5548660264	1.7916893371
H	-1.0919983076	-4.7778859675	2.903684913
H	0.3846883478	-5.1012338379	4.8895720934
H	1.5910351046	-0.9897227205	4.6767052117
H	-1.8251984971	2.1372840955	1.630196547
H	-3.829223241	3.1249917856	2.7326280208
H	-4.6766316648	2.1507662832	4.8673857911
H	-1.5069814848	-0.7409756807	4.8179858093
H	0.0885180679	1.7209983822	4.7979060864
H	4.2096776154	2.9085184978	4.8759034074
H	4.6240231588	1.6361822201	2.769467258
H	2.7456720287	0.4263237069	1.6655911515
P	0.0147864599	-0.005162179	-2.3139962009
C	-1.3065198552	-0.9890022986	-3.1612165984
C	-0.1731103181	1.6299134685	-3.1659015977
C	1.5341219621	-0.6496289084	-3.1556144109
C	2.1940024881	-1.7332421601	-2.5717237876
C	3.3174681469	-2.2803031345	-3.1849617408
C	3.7985736594	-1.7424430801	-4.3773637089
C	3.1319052206	-0.6623106988	-4.9314003346
C	2.0069813959	-0.1027497159	-4.3495637322
C	-2.5837521621	-0.9719259187	-2.5942834999
C	-3.6305349553	-1.6518182324	-3.2085465734
C	-3.4090316479	-2.3649925221	-4.3858577293
C	-2.1332460775	-2.3723755809	-4.9236581841
C	-1.0734788722	-1.6981102764	-4.3397228803
C	-0.999228897	1.8080135872	-4.2755016022
C	-1.0525923017	3.0620984361	-4.8630225812
C	-0.3149609891	4.1366780624	-4.3975038344
C	0.5072694707	3.9466586573	-3.287184259
C	0.5731792744	2.7024991616	-2.6689214945
Cl	3.7587471019	0.0482422506	-6.4800808292
Cl	-2.1373614145	3.3052364476	-6.2984579292
Cl	-1.83681766	-3.2966666826	-6.4576900113
H	1.8251984955	-2.1372840975	-1.6301965493
H	3.8292232393	-3.1249917876	-2.7326280231
H	4.6766316632	-2.1507662852	-4.8673857934
H	1.5069814832	0.7409756787	-4.8179858116
H	-2.7456720304	-0.4263237089	-1.6655911537
H	-4.6240231604	-1.6361822221	-2.7694672603
H	-4.2096776171	-2.9085184998	-4.8759034096
H	-0.0885180695	-1.7209983842	-4.7979060887
H	-1.5910351063	0.9897227185	-4.676705214
H	-0.3846883494	5.1012338359	-4.8895720957
H	1.091998306	4.7778859655	-2.9036849153
H	1.2012258037	2.5548660244	-1.7916893394

Pd(m-TCPP)$_2$*

69

Pd	-0.0000000008	-0.000000001	-0.0000000011
P	-0.0156233615	0.0058338167	2.3137844796
C	-1.5348941583	0.6507462939	3.155880285
C	1.3065253875	0.9896992124	3.1601319812
C	0.1717093775	-1.6298880553	3.1651849682
C	-0.5749226202	-2.7025412052	2.6682844733
C	-0.5091513686	-3.9474417323	3.2856484496
C	0.3131967216	-4.1382900051	4.3963338756
C	1.0492393646	-3.0625058135	4.8607195028
C	0.9978468861	-1.8077845597	4.2750891983
C	-2.1944409345	1.7361562136	2.574374334
C	-3.3186994059	2.2821819538	3.1876625575
C	-3.8009650566	1.7419173159	4.3790606292
C	-3.1327130349	0.6613964822	4.9296178507
C	-2.0077868673	0.1013781104	4.3489771733
C	1.0734214733	1.698271052	4.339259561
C	2.1343027307	2.3727193568	4.92025335
C	3.4099127711	2.3686884616	4.3827642171
C	3.6306937051	1.655284702	3.2048953238
C	2.5835642524	0.9739761327	2.5922360626

Cl 2.1354839818 -3.3051925657 6.3005008822
Cl 1.8370259772 3.2977275912 6.4587645562
Cl -3.7601599319 -0.0536554098 6.4809216096
H -1.205177428 -2.5557708992 1.7925283488
H -1.0938357527 -4.7784178868 2.9020552593
H 0.3816162778 -5.1038028129 4.8865933308
H 1.588849144 -0.9893436287 4.6770343928
H -1.825307499 2.1450093497 1.6350993395
H -3.8302511237 3.1276615469 2.7370156809
H -4.6796481399 2.1503817126 4.8677252729
H -1.507212215 -0.742378541 4.816553112
H 0.0890930799 1.7192550319 4.7987936975
H 4.211696311 2.9128356974 4.8701335319
H 4.6235979593 1.6407356872 2.7649519375
H 2.747323547 0.4275592713 1.6643614257
P 0.0156233598 -0.0058338187 -2.3137844819
C -1.3065253891 -0.9896992143 -3.1601319835
C -0.1717093791 1.6298880533 -3.1651849705
C 1.5348941567 -0.6507462959 -3.1558802873
C 2.1944409329 -1.7361562156 -2.5743743363
C 3.3186994042 -2.2821819558 -3.1876625598
C 3.800965055 -1.7419173179 -4.3790606315
C 3.1327130333 -0.6613964842 -4.929617853
C 2.0077868657 -0.1013781124 -4.3489771756
C -2.583564254 -0.9739761346 -2.5922360649
C -3.6306937067 -1.655284704 -3.2048953261
C -3.4099127727 -2.3686884635 -4.3827642194
C -2.1343027323 -2.3727193588 -4.9202533523
C -1.073421475 -1.698271054 -4.3392595632
C -0.9978468878 1.8077845577 -4.2750892006
C -1.0492393662 3.0625058115 -4.8607195051
C -0.3131967232 4.1382900031 -4.3963338778
C 0.509151367 3.9474417303 -3.2856484519
C 0.5749226185 2.7025412032 -2.6682844756
Cl 3.7601599303 0.0536554078 -6.4809216119
Cl -2.1354839835 3.3051925637 -6.3005008845
Cl -1.8370259789 -3.2977275931 -6.4587645585
H 1.8253074974 -2.1450093517 -1.6350993418
H 3.830251122 -3.1276615489 -2.7370156832
H 4.6796481382 -2.1503817146 -4.8677252752
H 1.5072122134 0.7423785391 -4.8165531143
H -2.7473235486 -0.4275592733 -1.664361428
H -4.6235979609 -1.6407356892 -2.7649519397
H -4.2116963126 -2.9128356994 -4.8701335342
H -0.0890930816 -1.7192550339 -4.7987936997
H -1.5888491456 0.9893436267 -4.6770343951
H -0.3816162795 5.1038028109 -4.8865933331
H 1.0938357511 4.7784178848 -2.9020552616
H 1.2051774264 2.5557708972 -1.7925283511

p-iodotoluene

15

C -1.1604853683 0.6506859787 0.0372289601
C 0.2357569373 0.6723171422 0.0553196006
C 0.9409963915 1.8700124266 0.0661512401
C 0.2389470738 3.071699553 0.0562205668
C -1.1516459237 3.0804979853 0.0341612483
C -1.8378241927 1.8706496332 0.02363192
H 0.7850552494 -0.2700617353 0.0592080048
H 2.0289077701 1.8672413942 0.0780075128
H -1.69732041 4.0216343976 0.0210646683
H -2.9282437019 1.8764360125 0.0024830395
I 1.2935597144 4.8949226653 0.0658729807
C -1.9083584723 -0.6488158609 0.0535652291
H -1.3928017132 -1.4183222664 -0.5347491826
H -2.0088405131 -1.039501994 1.076115624
H -2.9212587613 -0.5358188619 -0.3517210226

o-bromonitrobenzene

14

C 2.6615773205 -1.2681397023 0.0573241958
C 2.2711448274 0.0606721991 0.0293995855
C 1.6940648965 -2.2676945777 0.0243830305
C 0.3455260076 -1.937869429 -0.0354991306
C -0.0542162816 -0.6052460847 -0.0374569356
C 0.9195254534 0.392882462 -0.0028174202
H 2.9957097749 0.8705295074 0.0361547932
H 3.7181991752 -1.5215606033 0.0983242799
H 1.9860737266 -3.3157757129 0.0362940549
H -0.4121223326 -2.716153207 -0.0852358854
Br -1.9580222304 -0.2721406464 -0.1946568762
N 0.6126135627 1.832610927 0.0147005806
O 1.4189511288 2.5652851388 -0.5357637967
O -0.3912750291 2.1954697291 0.5955295244

o-bromonitrobenzene*

14

C 2.6618858711 -1.2680734797 0.0569164938
C 2.2729973757 0.0613224804 0.0295352743
C 1.6937391438 -2.2670140741 0.0239983595
C 0.3443823625 -1.9375684008 -0.0352733395
C -0.0534387213 -0.6052823658 -0.0364734417
C 0.9208844715 0.3932173496 -0.0025345174
H 3.0002609435 0.8684871495 0.0417707308
H 3.7180235519 -1.5221100905 0.0986129902
H 1.9853018538 -3.31491076 0.0354677618
H -0.4116684947 -2.7171739173 -0.0854136723
Br -1.9593277578 -0.2703760055 -0.1972566536
N 0.612623488 1.8292836153 0.014463902

O 1.4105249864 2.5667559453 -0.5437474955
O -0.3884390745 2.1963125536 0.6006136078

norbornene

17

C -3.8326186292 4.0862291136 1.0305697592
C -2.3498816865 3.6391700084 1.0463040901
C -3.9626051022 4.8052155875 -0.3422542765
C -1.8174826061 4.1584618646 -0.3194821159
C -3.8041799662 3.7286165227 -1.3935053105
C -2.5240430816 3.3426647354 -1.3799220182
C -2.5876352863 5.48136135 -0.4301509625
H -4.8438770543 5.4488552546 -0.433181036
H -0.7257396644 4.2072431914 -0.3894664608
H -2.4229378726 5.9939726368 -1.3857845266
H -2.3881645214 6.1722706946 0.4024184212
H -4.6231104902 3.2774685471 -1.9490713103
H -2.0802818891 2.510807968 -1.9220712575
H -4.0466029653 4.7846169553 1.8510721562
H -4.5339677006 3.2478951522 1.119916696
H -2.2306505343 2.5534210127 1.1443413999
H -1.8015609498 4.1076994051 1.8749067521

norbornene*

17

C -3.8326576402 4.0862880813 1.0301679856
C -2.3497989465 3.639212964 1.0459132278
C -3.9627311407 4.8054583296 -0.3425735103
C -1.8172373529 4.1585871056 -0.3197989396
C -3.8044595413 3.7285174512 -1.3937000008
C -2.5238792362 3.3424115996 -1.3800992116
C -2.5875734025 5.4815727667 -0.4295751353
H -4.8441275997 5.4489058881 -0.4332956968
H -0.7255008192 4.2071321627 -0.3895829215
H -2.4225246609 5.9953619648 -1.3846956381
H -2.3883374588 6.1717185441 0.4036067017
H -4.6237976356 3.2765233729 -1.9482733259
H -2.0802760567 2.5096265583 -1.9212560926
H -4.04639815 4.7849971717 1.8503903776
H -4.5342747691 3.2480662622 1.119361052
H -2.2302543037 2.5534138652 1.143827165
H -1.8015112859 4.1081759118 1.8742239629

p-bromonitrobenzene

14

C -0.2750437296 1.2176142818 0.0000692407
C 1.1125897295 1.2165373389 -0.0000208998
C -0.9468363132 0.0000012038 0.00011373
C -0.275045254 -1.2176127108 0.0000695435
C 1.1125881985 -1.2165374969 -0.0000205786
C 1.7823187241 -0.0000004912 -0.000067377
H -0.8293002519 2.1527635551 0.0001052153
H 1.6819473834 2.1416368704 -0.0000588161
H -0.8293029342 -2.1527613013 0.0001058173
H 1.6819446894 -2.1416377477 -0.0000582221
N 3.2505814702 -0.000001505 -0.0001638447
O 3.8120554413 -1.0829410568 0.0002425101
O 3.8120568506 1.08293736 0.0002435791
Br -2.890624004 0.0000023855 0.0002401024

p-bromonitrobenzene*

14

C 0.2679518954 1.218684737 0.0000611028
C -1.1195545563 1.2177438649 0.0000851207
C 0.9378547213 0.0000000639 0.0000421863
C 0.2679519022 -1.2186846131 0.0000611028
C -1.1195545494 -1.2177437487 0.0000851207
C -1.7882197941 0.0000000562 0.0000941142
H 0.82080058 2.1544440057 0.000047107
H -1.6853463148 2.1446540387 0.0000921772
H 0.8208005921 -2.1544438786 0.000047107
H -1.6853463027 -2.1446539257 0.0000921772
N -3.2538906695 0.0000000521 0.0001005238
O -3.8202228936 -1.0814679856 0.0000843691
O -3.8202228997 1.0814680866 0.0000843691
Br 2.8833333207 0.0000000693 -0.0000475782

[Pd(*m*-TCPP)$_2$I]$^-$

70

Pd -0.5042972099 -0.5286929405 -0.02360397
P -1.2553322721 0.4404149215 1.9403498041
C -2.899418575 1.3030766328 2.0254226868
C -0.0989151156 1.8638668099 2.2879823781
C -1.1720302944 -0.3802991386 3.611594061
C -0.912734706 -1.7500611622 3.6359192238
C -0.7782091629 -2.415968714 4.8543126103
C -0.8935595283 -1.7184874089 6.0531379385
C -1.1377500148 -0.3544268748 6.0002490683
C -1.2731321347 0.3345312094 4.8108872438
C -3.1892275239 2.2103742695 0.9951245786
C -4.4283200081 2.833924584 0.923278584
C -5.4163569726 2.5419436734 1.8667613022
C -5.114794422 1.6312109903 2.8628679659
C -3.8822811937 1.0078754433 2.9727432192

C -0.5122617041 3.178330138 2.5057835388
C 0.4559483318 4.1571867994 2.6512706475
C 1.8117183741 3.8918171591 2.6092190423
C 2.2138169934 2.5688330364 2.4113160176
C 1.269167606 1.5625333748 2.2458852904
Cl -1.2679192609 0.5650772013 7.5756836673
Cl -0.0830827311 5.8945621723 2.857702606
Cl -6.4049394524 1.2357017258 4.0953034455
H -0.7839108773 -2.2819683603 2.6930854692
H -0.5687121362 -3.4817483363 4.8688537157
H -0.7856493568 -2.2165246573 7.0114295066
H -1.4463393642 1.4082614459 4.8113250002
H -2.4345073116 2.4213706874 0.2408238168
H -4.6308708161 3.5466475788 0.1264311414
H -6.3953005633 3.0078331912 1.8258387424
H -3.6895824981 0.3075484226 3.7804401259
H -1.5659777834 3.4421604817 2.5261861654
H 2.5335620019 4.6938832842 2.7228076716
H 3.2731475011 2.3298949985 2.3713622928
H 1.5821809099 0.5368467779 2.0443538692
P -0.9087045255 0.5654271977 -2.0045442017
C -2.5264436227 0.2901748576 -2.8825534614
C -1.0208741234 2.4125841394 -1.7483905069
C 0.2924356271 0.5296067908 -3.4254482477
C 1.1465974199 -0.5721475224 -3.4980464164
C 2.0734005825 -0.6712380886 -4.5345057031
C 2.1616944574 0.3306792194 -5.4980077827
C 1.3131529838 1.421355475 -5.3922968404
C 0.3834576773 1.5513520776 -4.3771969323
C -3.6581908957 0.131724559 -2.0716459141
C -4.9092723504 -0.0764062348 -2.6413066377
C -5.0479721832 -0.1560722657 -4.0275632481
C -3.9128142703 -0.0140325527 -4.8052429189
C -2.6559932199 0.2137330879 -4.2702892513
C -2.1430121416 3.1713784067 -2.0917367935
C -2.1946402571 4.4927777443 -1.676992925
C -1.1844402464 5.100443815 -0.9554040308
C -0.0495980941 4.3442028237 -0.6542260297
C 0.0299128789 3.0124466419 -1.0421758917
Cl 1.4387167202 2.7436449702 -6.649562966
Cl -3.6894896482 5.4733939401 -2.0760372967
Cl -4.0841236151 -0.1294658309 -6.6200826703
H 1.0967979059 -1.3353565803 -2.7191586602
H 2.7403024145 -1.5272981424 -4.5841917307
H 2.8797965794 0.275103313 -6.3100462717
H -0.2592129011 2.4276277595 -4.323423498
H -3.5433273671 0.159678946 -0.9880871285
H -5.7832301833 -0.1908053358 -2.0057509393
H -6.0127770829 -0.3314560645 -4.4922262442
H -1.7933402375 0.3267985137 -4.9207132718
H -2.9729916998 2.7314001181 -2.6388971146
H -1.2796625697 6.1300658454 -0.6271498165
H 0.756690844 4.7941497786 -0.0812803506
H 0.8925718837 2.4103715212 -0.7585767215
I 1.4514406216 -2.4629664703 0.2659472871

[Pd(*m*-TCPP)$_2$I]$^{-*}$

70

Pd -0.4064526896 -0.5480365828 0.0001858447
P -1.1551738976 0.4712380873 1.9473549924
C -2.8370125926 1.265671342 1.9569807604
C -0.0836604436 1.9461231889 2.3370242519
C -1.1348003144 -0.3477084316 3.6199772741
C -1.0307215597 -1.7380401756 3.6535199546
C -0.9732011334 -2.4093593472 4.8747089442
C -1.0083127557 -1.6960171316 6.0700641722
C -1.1035345613 -0.3141727073 6.0077224808
C -1.1655924231 0.3802659128 4.8148633355
C -3.1426973126 2.1133930899 0.8828006579
C -4.4037824886 2.6842329949 0.762789117
C -5.3948790246 2.4024563183 1.7060888703
C -5.0721346944 1.5567793327 2.7512402423
C -3.8196949889 0.9844859256 2.9076424472
C -0.5792269773 3.2333552383 2.5499247507
C 0.3260635133 4.2630390756 2.7414445428
C 1.6960416039 4.0758937615 2.7512085601
C 2.1802093959 2.7809669226 2.5515603675
C 1.2995442328 1.7261265876 2.3390388538
Cl -1.1357451505 0.6251563379 7.5766403122
Cl -0.3195182144 5.9639257443 2.9343032541
Cl -6.3578473712 1.18088138 3.9952710187
H -0.9691914372 -2.2871810003 2.7146016003
H -0.8875173428 -3.4918190878 4.8968881396
H -0.9538945456 -2.1994845311 7.0298416909
H -1.233477133 1.4657401535 4.8095864422
H -2.3861473549 2.3232690843 0.1304284711
H -4.6214437171 3.3479198292 -0.0711877157
H -6.3892539177 2.8295717257 1.627968931
H -3.6143814413 0.3364624025 3.7539328934
H -1.6470843425 3.4351243966 2.5304814159
H 2.3687790405 4.9143419035 2.901136511
H 3.2520001042 2.6036281409 2.5511334291
H 1.681260351 0.723599601 2.1461351774
P -0.7978799175 0.5429786778 -2.0030732095
C -2.4502005123 0.2573276072 -2.811408657
C -0.9178184011 2.3886750504 -1.7493984912
C 0.3270681623 0.5024045439 -3.4856754032
C 1.0494087556 -0.6739222399 -3.69900805
C 1.8930901624 -0.78946327 -4.8014728927
C 2.0353348925 0.2727222184 -5.6927876945
C 1.3217408526 1.4337825844 -5.4471636887
C 0.4720673379 1.5803142544 -4.3652413487
C -3.5229271664 -0.026113439 -1.9590604183

C -4.8056881951 -0.1950272176 -2.4710143179
C -5.0318337501 -0.1029529189 -3.8443580464
C -3.9508945934 0.1637404142 -4.6663932661
C -2.6653161582 0.3504532721 -4.187745169
C -2.0352893125 3.1428115333 -2.1178319946
C -2.1069270058 4.4598416772 -1.6936394469
C -1.1211607905 5.068525278 -0.9396821899
C 0.0114509569 4.3177628142 -0.6155524219
C 0.1090488474 2.989290926 -1.0111364693
Cl 1.5199906099 2.835227071 -6.6054799071
Cl -3.6033584372 5.4252616339 -2.1184330704
Cl -4.2386569564 0.2848745551 -6.4674142374
H 0.9602339435 -1.4901256112 -2.9822042418
H 2.4551690399 -1.7048767293 -4.9623994369
H 2.6937548272 0.2042066056 -6.5528366347
H -0.0703245634 2.5102636117 -4.2092186025
H -3.3392892332 -0.120166909 -0.8890992291
H -5.6345735195 -0.4087388124 -1.8022723472
H -6.0224709102 -0.2413284934 -4.2650413253
H -1.8496769219 0.5697991086 -4.8706613323
H -2.8480534628 2.7037467494 -2.6910230589
H -1.230113263 6.0940054913 -0.6031266009
H 0.8013663691 4.7684989306 -0.0210916392
H 0.9673008368 2.3898984017 -0.7088688791
I 1.2888951512 -2.7451209818 0.2228290667

o-bromomethylbenzoate

18

C 0.021556896 0.0004076731 -0.0149043436
C 0.0226316464 -0.0000659061 1.3765380019
C 1.2216848584 0.0004578333 -0.7397900385
C 2.4178595853 0.0000048199 -0.0052505223
C 2.4272706397 -0.0004530701 1.3796543791
C 1.222825556 -0.0004839179 2.0741485399
Br -1.7510387419 0.0008897094 -0.8271633933
H -0.925776024 -0.0001038103 1.9078667356
C 1.2897533166 0.0010272348 -2.2298287936
H 3.3547869074 0.0000309523 -0.5539503297
H 3.3739751934 -0.00078416 1.9155383375
H 1.2104234638 -0.0008460965 3.1625366919
O 0.353886562 0.0019102728 -2.9901067931
O 2.5692408081 0.0002137011 -2.6587837905
C 2.7194310374 0.0006031762 -4.0723784835
H 2.2537455593 -0.8882588407 -4.5121060957
H 3.7955356621 0.0000191411 -4.2580826873
H 2.2548126709 0.8903181074 -4.5115099975

I^-

1

I 0. 0. 0.

I^-*

1

I 0. 0. 0.

PPh_3

34

P 0.0000000407 0.0000000505 2.0770745166
C 1.0014388045 -1.2965446743 1.1959741769
C -1.62356001 -0.2189989968 1.1959741769
C 0.6221213277 1.5155438227 1.1959741769
C 1.8028926317 2.0897466096 1.6775326394
C 2.3573167458 3.1981883723 1.045534902
C 1.727089517 3.750216645 -0.0683065987
C 0.547267788 3.1869247736 -0.5473120699
C -0.0030270739 2.0701208023 0.0795587151
C 0.9083273529 -2.6062240131 1.6775326394
C 1.591054021 -3.6405902618 1.045534902
C 2.3842381431 -3.3708116078 -0.0683065987
C 2.4863239372 -2.0674100829 -0.5473120699
C 1.794290758 -1.0324387673 0.0795587151
C -1.7912635619 -1.0376818835 0.0795587151
C -3.0335916031 -1.1195145392 -0.5473120699
C -4.111327538 -0.3794048857 -0.0683065987
C -3.9483706446 0.442402041 1.045534902
C -2.7112198624 0.516477555 1.6775326394
H 2.2885441794 1.6580419251 2.5516463731
H 3.2780374684 3.6345522295 1.4242810035
H 2.1547507343 4.6196680374 -0.5607850167
H -0.919825201 1.6260399167 -0.3013990458
H 0.2916343554 -2.8109582486 2.5516463731
H 1.5085958453 -4.6561397259 1.4242810035
H 2.9233745277 -4.1759027824 -0.5607850167
H 1.8681044933 -0.0164278563 -0.3013990458
H -0.9482791701 -1.6096119089 -0.3013990458
H -5.0781251398 -0.4437651035 -0.5607850167
H -4.7866331915 1.0215876479 1.4242810035
H -2.5801784126 1.152916475 2.5516463731
H -3.1581798838 -1.7613375776 -1.4156615951
H 3.1044531335 -1.8543951798 -1.4156615951
H 0.0537268724 3.6157329089 -1.4156615951

o-iodotoluene

15

C	0.005814158	-0.0001209721	0.0077622218
C	-0.0050625197	0.0001274899	1.3975278798
C	1.2164543326	-0.0004593684	-0.674072587
C	2.4435522731	-0.0005636456	-0.0039232284
C	2.4000922046	-0.0003080665	1.395659068
C	1.1971339396	0.0000385802	2.0965249695
H	-0.9300204534	-0.0000499709	-0.54809918
H	-0.9456961321	0.0003999517	1.9454652644
H	1.2232118015	-0.0006598818	-1.7645522951
C	3.7237100029	-0.0009316717	-0.7789778519
I	4.1880789967	-0.0004310561	2.520757196
H	1.2016859976	0.0002238419	3.1845530875
H	3.5275111049	-0.0010504521	-1.8574176418
H	4.3367075739	-0.8816154214	-0.5442429484
H	4.3370694677	0.879562641	-0.5444849922

o-iodotoluene*

15

C	3.279868137	-0.3887641176	0.000000557
C	2.5156762369	-1.5500450991	-0.0000004958
C	2.6538330064	0.8520812846	0.0000000817
C	1.2609401245	0.9784549821	-0.0000014704
C	0.5186385335	-0.2093318366	-0.0000001371
C	1.1276903859	-1.461781875	0.0000008616
H	4.3666030756	-0.4478864087	0.0000005612
H	2.9922982668	-2.5285892397	-0.000002503
H	3.2555015709	1.7613212149	0.0000001528
C	0.6298570659	2.3355759402	-0.0000005087
I	-1.5949550993	-0.1497633392	0.0000038748
H	0.5193204238	-2.3638290062	0.0000023731
H	1.3935782788	3.1215731092	-0.0000366996
H	-0.0094410371	2.4828704911	0.8810677476
H	-0.0095039695	2.4828439	-0.8810263462

A.2.2 Products

1a

27

C	-0.0093456246	0.3163430733	-0.0005772813
C	0.0127479187	0.1456765066	1.3761140368
C	1.2072960352	-0.0685063138	2.070252007
C	2.3904013874	-0.1051619415	1.3218379568
C	2.3901230538	0.0534903088	-0.0675225634
C	1.1772262664	0.2762873196	-0.719694849
C	3.634483254	0.0905226021	-0.8807378197
H	1.1772854278	0.4117872978	-1.8009039151
H	-0.9539357808	0.4820935708	-0.5150506886
H	-0.9179885436	0.1745699911	1.9426615543
C	1.1813953141	-0.2544539784	3.5555062427
H	0.1566102523	-0.184626744	3.9382140758
H	1.7878624059	0.5027609717	4.070704367
H	1.5847119143	-1.2342259953	3.8447024485
I	4.2329584936	-0.466647281	2.2879413459
C	4.2426315313	1.3337972456	-1.0744779931
C	4.2113119071	-1.0032428996	-1.5360706635
C	5.3416885222	-0.8763419559	-2.336785078
C	5.9337239382	0.3667745204	-2.4938453362
C	5.3792587727	1.4750944703	-1.860575497
H	5.7373320817	-1.7642462516	-2.8206379391
H	6.8239897612	0.4688370153	-3.1104882731
H	5.8317041914	2.4576258071	-1.9811524933
H	3.8018194633	2.1995288821	-0.5815937849
N	3.6513310945	-2.3580529609	-1.3980734595
O	2.8706189985	-2.5639672394	-0.4856338141
O	4.0138615237	-3.1976371627	-2.2077936021

1a*

27

C	1.4400945297	3.1081152522	-0.6499642401
C	2.5833939335	2.366697056	-0.3866807396
C	2.5298819586	0.9858273263	-0.1735664518
C	1.2719701698	0.372060619	-0.2359706727
C	0.1067458486	1.0995085622	-0.4990382383
C	0.2063222245	2.4749694117	-0.713072034
C	-1.2276663166	0.4636495666	-0.6587783599
H	-0.6993010496	3.0421263565	-0.9263325674
H	1.5106524316	4.1820590964	-0.8106407696
H	3.5532766783	2.8615761715	-0.3397212851
C	3.7901075988	0.2290676671	0.1102229422
H	4.6556126366	0.9012841615	0.1071063554
H	3.9684324028	-0.5557765612	-0.6373723493
H	3.7509021744	-0.2675800247	1.0888464151
I	1.1004199326	-1.6989865285	0.1458664963
C	-1.5702473517	-0.0127390994	-1.9270948302
C	-2.2088377598	0.3723746743	0.3354915782
C	-3.4658139201	-0.1729841422	0.0917203671
C	-3.7676981034	-0.6569860426	-1.1712980079
C	-2.8155596537	-0.5732649083	-2.1834310214
H	-4.1843261789	-0.2145387421	0.9046090303
H	-4.744171822	-1.0952468472	-1.3639657197
H	-3.04325959	-0.9438627792	-3.1808859528
H	-0.827039104	0.0622401794	-2.7198724824
N	-1.9484457791	0.838274464	1.7038854157
O	-0.7887701681	0.9812080493	2.0528700475
O	-2.9167517229	1.0459890613	2.4208760745

1c

27

C 0.0070418364 -3.7186153713 0.1911872252
C -1.329056759 -3.5570498192 0.8124597597
C -1.4388821421 -2.9657339088 2.0750572806
C -2.6726227339 -2.8456898577 2.6986238141
C -3.7952817975 -3.3334598799 2.0449966545
C -3.7199892375 -3.9356881008 0.794852657
C -2.4811485799 -4.0438064649 0.1837252288
C 0.9298446202 -4.5404717676 0.8471284061
C 2.1914026379 -4.7596324604 0.3153416692
C 2.5469199129 -4.153389333 -0.8813026117
C 1.6679640064 -3.3091283501 -1.5650814053
C 0.3980140227 -3.1012550997 -1.0060063013
C 2.1101709032 -2.6635036191 -2.8418358418
H -2.7794976298 -2.3824367851 3.6750790911
H -4.6246618249 -4.3133147619 0.3275327079
H 0.6288173652 -5.0212203615 1.7774160112
H 2.897242619 -5.4074750599 0.831458309
H 3.5363878666 -4.3254020225 -1.3046042724
H 3.1293740206 -2.9725098874 -3.1004869966
H 1.4512579817 -2.9297061399 -3.6794009629
H 2.0961645758 -1.5677691641 -2.7680070021
I -0.9150253057 -1.7396193675 -1.9556091382
H -2.3976528868 -4.5228192083 -0.7906952029
N -5.103785014 -3.2166241968 2.6998701353
O -6.0753508877 -3.6464774696 2.0995072584
O -5.1374910046 -2.6981538145 3.804295162
H -0.5426812849 -2.5859068884 2.563632395

1c*

27

C 0.0076729782 -3.7168795594 0.1931446332
C -1.3285524102 -3.5560105748 0.8140936837
C -1.4389262765 -2.9658380888 2.0774595755
C -2.673012454 -2.8463643779 2.7000070557
C -3.7956331807 -3.3336757137 2.0443389938
C -3.7193781434 -3.9354795607 0.7931975043
C -2.4800194873 -4.0428257542 0.183506959
C 0.9306283777 -4.5384199718 0.8494391045
C 2.1915519803 -4.7586235941 0.3157789691
C 2.5460239236 -4.1538468072 -0.8821743949
C 1.6669225286 -3.3089800134 -1.5659168605
C 0.3980450007 -3.1004302948 -1.004779873
C 2.1086344005 -2.6650561509 -2.8437257824
H -2.7765708242 -2.3833127039 3.6766933428
H -4.62100855 -4.3146942993 0.3218154346
H 0.6315401297 -5.0180331674 1.7808388957
H 2.8977280739 -5.4060379487 0.831726595
H 3.5347760024 -4.3271326598 -1.306305261
H 3.1261644909 -2.9775897326 -3.1039205786
H 1.4475268125 -2.929970416 -3.6799700315
H 2.0991527033 -1.5692665993 -2.7699881056
I -0.9153986767 -1.7354744608 -1.9518738175
H -2.3963014489 -4.5224802387 -0.7904322527
N -5.101826414 -3.2174868466 2.6966807881
O -6.0774116294 -3.6420997297 2.0965391549
O -5.1409931638 -2.7036818631 3.8044539872
H -0.5438594635 -2.5871680326 2.5685063106

1b

31

C 1.5207447207 3.0881692024 -0.7983908165
C 2.6404787709 2.3315183213 -0.4809364107
C 2.5447896499 0.9666981608 -0.1986607011
C 1.2703633033 0.3860708441 -0.2468671402
C 0.1263010901 1.1284390849 -0.5558249965
C 0.2718578271 2.4874116724 -0.8413719597
C -1.2245175793 0.5193725308 -0.6898757852
H -0.6174345335 3.0671297021 -1.0872153322
H 1.6230720374 4.1499992255 -1.0150397246
H 3.6234647334 2.8016643292 -0.447587441
C 3.7803311057 0.1902993229 0.1373476757
H 4.6647694279 0.8373565592 0.1073750156
H 3.9421767689 -0.6398942949 -0.5639630513
H 3.7180453477 -0.2526801349 1.1407003341
I 1.0547738252 -1.6730296548 0.1846158034
C -1.5870136186 0.0686732999 -1.9606036133
C -2.1529626285 0.3983413926 0.3605920094
C -3.4034963578 -0.1774401299 0.1108760046
C -3.7446371153 -0.6252463921 -1.1566532529
C -2.8316422521 -0.5002668834 -2.1983008026
H -4.1098694751 -0.2680481334 0.9316022692
H -4.7222956946 -1.0707147663 -1.3302022264
H -3.0875437412 -0.8467997861 -3.1981705223
H -0.8623287713 0.1629701147 -2.7689492106
O -0.7780213958 1.4106795025 2.0528281328
O -2.8092119312 0.6364675056 2.6034648761
C -2.5493037968 1.069445613 3.9316943253
H -2.3659040225 2.1493812693 3.9588431603
H -3.4420735133 0.818817564 4.5086930016
H -1.671854363 0.5573260058 4.3417367013
C -1.8108394286 0.8718335129 1.7282879276

A.2.3 Intermediates

IaH

25

Pd	1.78425553	-0.0020518868	-0.0635339722
I	4.3919288998	0.0556497199	1.0897107119
I	-1.4422890972	0.024918013	-0.5472123351
C	-3.6057000354	0.048595883	-0.7310713583
C	-4.2128530957	0.2335504885	-1.9701214045
C	-4.4083099995	-0.1169782807	0.3974020694
C	-5.6018687106	0.2522917895	-2.076668533
H	-3.5977109921	0.3677184525	-2.8605501883
C	-5.7937846861	-0.0967158515	0.2830341761
C	-6.4142806137	0.0863817221	-0.9554233496
H	-6.0664674817	0.4010529359	-3.0540403345
H	-6.412155758	-0.2240954089	1.1748790542
H	-3.9446740384	-0.2595631772	1.373975163
C	-7.911027637	0.091651671	-1.0681635879
H	-8.3359186242	-0.9099923797	-0.9066103477
H	-8.3709635838	0.7548741865	-0.3222115203
H	-8.2376231967	0.4291201921	-2.0602741329
P	1.5593336026	2.2887061502	-0.4166692996
H	1.6463106138	3.1111601632	0.7366584535
H	2.6276401923	2.9188824964	-1.1056972252
H	0.5327333188	3.0662159864	-1.0383753365
P	1.4328399648	-2.299125355	-0.1213522582
H	0.4519112376	-3.0858911531	-0.8007073825
H	2.5350799932	-3.1026211592	-0.5141387183
H	1.2422980071	-2.9413146681	1.1308270665

IIa

84

C	-0.9213476025	-3.7699653605	1.1459098546
C	-0.2001531228	-4.2442802768	2.2413473426
C	1.1695160945	-4.5131194657	2.1701606278
C	1.8631157668	-4.2771676037	0.9950810831
C	1.1831811029	-3.7735548589	-0.1204990915
C	-0.2005056179	-3.5337746021	-0.047386519
Pd	0.5613890879	-1.2389130689	0.259259193
H	-0.7401747118	-4.4290390103	3.1705344878
H	2.9343431617	-4.4626641588	0.9238529997
P	2.7656174035	-0.4976386171	0.1524500987
C	3.8056903746	-1.3458290308	-1.1265614948
C	3.0700201299	1.2940815537	-0.2252176518
C	3.7724158784	-0.7052593285	1.6934685883
C	3.2712080654	-1.5601997628	2.6775708235
C	3.9850420057	-1.7656559964	3.8569494457
C	5.1968818509	-1.1122112638	4.0653651143
C	5.6698394071	-0.2606816413	3.0780211464
C	4.9857633705	-0.039475975	1.895900063
C	3.2468876292	-1.4847142357	-2.4044198916
C	3.9384658069	-2.158629212	-3.4051134956
C	5.1825957109	-2.7303839329	-3.1369024927
C	5.7014770678	-2.6031650932	-1.8608574747
C	5.0456403479	-1.9194372945	-0.8490092743
C	3.5136938133	1.7326113401	-1.471809642
C	3.6264149217	3.0962973202	-1.6912272977
C	3.3504851163	4.0398084259	-0.7201551071
C	2.9009738179	3.5919034698	0.521878562
C	2.7450797281	2.2322325928	0.7620289505
Cl	7.2445695597	0.6006192167	3.354589368
Cl	4.1307018578	3.6698767681	-3.342233525
Cl	7.3071457696	-3.367922665	-1.4911599937
H	2.3203352818	-2.0648975416	2.5080651373
H	3.5957034047	-2.4343976397	4.6198333369
H	5.7668176588	-1.2548027614	4.9776406074
H	5.3845435719	0.6422357637	1.1483072222
H	2.2564230902	-1.0725910878	-2.5995265765
H	3.5062104226	-2.2553536774	-4.3970804243
H	5.7322173696	-3.2713858903	-3.8999781762
H	5.4970549762	-1.8392354456	0.1355865918
H	3.7611983167	1.031639881	-2.2633492262
H	3.4573475261	5.0973973497	-0.9356142424
H	2.6571142989	4.3137535244	1.2963369874
H	2.3639578622	1.8964448795	1.7245936751
P	-1.023996264	0.4805282212	0.2637123259
C	-0.4517264791	1.5949156368	-1.1129152028
C	-0.9653144752	1.5950210006	1.7453349582
C	-2.8596875747	0.4648954987	-0.0475254364
C	-3.424000709	0.8864590769	-1.2505975569
C	-4.7903275909	0.7378705525	-1.4306754406
C	-5.6199102991	0.2030611761	-0.4624076799
C	-5.04807833	-0.2066175073	0.7427533609
C	-3.6788402639	-0.0845392258	0.9468848736
C	-0.222464219	0.9902986121	-2.3563672322
C	0.2257076301	1.7432146666	-3.4363869265
C	0.4615728299	3.1096618899	-3.2894196394
C	0.2324572031	3.6820672783	-2.052367946
C	-0.2140168121	2.9589434301	-0.9571192414
C	-0.0282846156	1.3114930253	2.7406278241
C	0.0750893484	2.1300307255	3.863868253
C	-0.7596493085	3.2363827364	4.0027436179
C	-1.69207166	3.490972867	3.0090008405
C	-1.8222956027	2.690773615	1.8875416389
Cl	0.5371213755	5.4629969664	-1.8534288237
H	-6.6852518806	0.1071465057	-0.6442960876
H	-0.4003969247	-0.0791812343	-2.4692180006
H	0.3940050568	1.270392478	-4.4002963292
H	0.8196919384	3.7165454408	-4.1144485974
H	-0.3628202701	3.4542969641	-0.0020305731
H	0.6113471847	0.4346596692	2.6242012784

H	-0.6961696011	3.8867288464	4.8690787363
H	-2.5772475109	2.9148513085	1.1374177197
H	-3.2362131252	-0.4104839372	1.8876839732
H	-2.8142781312	1.3241416648	-2.0360002166
Cl	-2.782495186	4.9320773785	3.1839975737
Cl	-5.521120585	1.2666548997	-3.0092572155
H	0.8019648439	1.9045231515	4.639319803
H	-5.681025291	-0.6249036368	1.5207237162
H	1.7070195122	-3.6529415926	-1.0673289663
I	-1.2153926063	-3.2067316536	-1.8863077802
H	1.6888330381	-4.9090378599	3.0421403666
C	-2.3982481394	-3.5553967261	1.2403065206
H	-2.9491414071	-4.3110559125	0.6615931247
H	-2.7355302103	-3.6190810479	2.2817419966
H	-2.69305612	-2.5752723653	0.84045933

trans-**IIIa**

84

C	0.2781456882	2.9678944047	-0.3417436347
C	0.3006448936	4.2308491096	-0.9316170116
C	0.2050556029	4.3472856945	-2.3143877231
C	0.0986191639	3.2017862219	-3.0974786995
C	0.0826130721	1.9257209255	-2.5220993159
C	0.1710357289	1.821865512	-1.1261608826
C	-0.0473375995	0.7082095978	-3.3927914013
Pd	0.1451423741	-0.0368703503	-0.2513101323
H	0.3957804807	5.1189336347	-0.3079856381
H	0.219287764	5.3294501421	-2.7852808915
H	0.0252318057	3.2902363722	-4.1834426505
H	-0.9813262322	0.1598428092	-3.1911284334
H	-0.0437833775	0.9720156512	-4.4581626873
H	0.7739849168	-0.00461142	-3.2207725345
P	-2.2094210002	0.1128683096	-0.017177631
C	-3.2099964083	-0.8701348496	-1.2226601843
C	-2.7476454401	-0.5091583323	1.633956686
C	-3.097023025	1.7398797581	-0.0891690334
C	-2.9254742195	2.5440893588	-1.2186192759
C	-3.590236504	3.7603898672	-1.317506782
C	-4.4412551773	4.1834438647	-0.2979583402
C	-4.6043872417	3.3640735665	0.8047989625
C	-3.9516595616	2.148793787	0.9357516797
C	-2.6196710135	-1.9285978163	-1.9149965362
C	-3.3765293693	-2.6844697452	-2.8076439151
C	-4.7206946361	-2.389317793	-3.0169752006
C	-5.2823470074	-1.3303028628	-2.3213257812
C	-4.5581335772	-0.5598595137	-1.4296214227
C	-3.7092790643	-1.5047946304	1.7706078783
C	-4.0224860389	-1.9415746055	3.0481157637
C	-3.4209147873	-1.4242177255	4.1808253289
C	-2.4654347299	-0.4195590262	4.0290356106
C	-2.1242871008	0.0331891248	2.7610821538
Cl	-5.7196721766	3.9010636846	2.1335165903
Cl	-5.2684096428	-3.2449339851	3.2400867128
Cl	-7.0322145765	-0.9388218412	-2.5931610478
H	-2.2441274441	2.2363692902	-2.0069997826
H	-3.4366381095	4.3877007707	-2.1906874844
H	-4.9677599836	5.1303025855	-0.3566991292
H	-4.1081324329	1.5361870317	1.8183485004
H	-1.573352269	-2.1713184493	-1.7381306769
H	-2.9175997571	-3.5118778377	-3.3407253032
H	-5.3259320471	-2.9688733306	-3.7062700555
H	-5.0340087496	0.2656261437	-0.9064883585
H	-4.1943410334	-1.9458684076	0.9048488587
H	-3.6915448801	-1.801035764	5.1615787192
H	-1.9840165278	-0.0000310618	4.907464043
H	-1.3649982413	0.8059501276	2.6381871393
P	2.5076213719	0.0022462847	-0.281858111
C	3.3854636773	-1.0035318777	-1.5617050097
C	3.2937327064	-0.5248179648	1.3048617629
C	3.2637634903	1.6779176803	-0.4955131137
C	3.2479408484	2.288355714	-1.7532209931
C	3.6749713354	3.603112317	-1.8949351849
C	4.1118515301	4.3264283331	-0.7860957903
C	4.118058705	3.6992037305	0.4462997881
C	3.7084222297	2.3873835801	0.619190178
C	2.7984971663	-2.1814031436	-2.0283630463
C	3.4653990018	-2.9684181582	-2.9645310776
C	4.7161323392	-2.5885542651	-3.4439019911
C	5.2773832278	-1.4156595525	-2.9665156269
C	4.6421385605	-0.6116517838	-2.0367388533
C	4.5808325242	-1.0589200928	1.3228990623
C	5.1464572419	-1.3718184351	2.547324715
C	4.4838116949	-1.1708137936	3.7458371268
C	3.1968115258	-0.6371851843	3.7138141776
C	2.5988368328	-0.320142505	2.4979306784
Cl	4.6882341943	4.6301772431	1.8981203494
Cl	6.8198425616	-2.0707634082	2.5765555602
Cl	6.9047766454	-0.9079895392	-3.5873187293
H	4.4393640296	5.3569498607	-0.8777134949
H	1.8273889317	-2.4907498129	-1.6446264469
H	3.0088993042	-3.8870098865	-3.3212885064
H	5.2487675269	-3.1900149184	-4.1734360119
H	5.1130777055	0.3069978639	-1.6966036513
H	5.1331076239	-1.237173739	0.404753678
H	4.9620611191	-1.4329277944	4.6840109436
H	2.6550725711	-0.4850877305	4.6425293766
H	1.5804198245	0.0643795836	2.4677251333
I	0.0984037281	-2.5844150635	0.7575884536
H	3.6479174414	4.0784640365	-2.8710746516
H	3.7331874582	1.9320616885	1.6053782775
H	2.87760351	1.7472323443	-2.6211206206
H	0.3579194265	2.882780001	0.7449580197

cis-**IIIa**

84

C	-1.760530336	-3.2292751759	-2.2200198109
C	-2.8912063736	-3.9564230654	-2.5896999096
C	-3.8180102034	-4.3204055938	-1.6172677902
C	-3.5774948116	-4.0029486944	-0.2852401774
C	-2.429035745	-3.3061605976	0.114490159
C	-1.5560921865	-2.8695401931	-0.8877820045
C	-2.1448180664	-3.1301197559	1.5753743924
Pd	0.024517889	-1.574799073	-0.5962952346
H	-3.0490660834	-4.2198582684	-3.6350345862
H	-4.7172153734	-4.8701085723	-1.8918775065
H	-4.2861642174	-4.31708285	0.48318444
H	-3.0687622337	-3.0569721378	2.1644333013
H	-1.5723128401	-3.9927746341	1.9464794783
H	-1.537830886	-2.2406272015	1.7735624379
P	-1.5928446856	0.2423126061	-0.5041960722
C	-2.3994577211	0.1462312561	1.1606722589
C	-1.0067672753	2.0014524533	-0.5223454806
C	-3.0891823384	0.4505951782	-1.5945573717
C	-3.756579381	-0.6736738398	-2.0832957438
C	-4.9344903691	-0.5280867951	-2.8121821227
C	-5.4578142958	0.736510549	-3.0646851114
C	-4.7747995882	1.8371894172	-2.573544079
C	-3.6047453296	1.7271018373	-1.8439646971
C	-1.5876624007	0.2609960868	2.2945568708
C	-2.1455074864	0.1693576731	3.5634211401
C	-3.511691224	-0.0685822541	3.7147771347
C	-4.288312455	-0.1940748219	2.5767257609
C	-3.7660009677	-0.0836396737	1.2974591814
C	-1.3763471624	2.9336836232	0.4506733325
C	-0.9970365643	4.2551950934	0.2764210649
C	-0.2479292068	4.6789838184	-0.8096964755
C	0.1093535677	3.7419895039	-1.7770093314
C	-0.2772684619	2.4127548454	-1.6388173999
Cl	-5.4474601117	3.4938998848	-2.8903262745
Cl	-1.536615425	5.4855838853	1.4915574158
Cl	-6.0654048376	-0.5125004586	2.7651337928
H	-3.3553676698	-1.6615687058	-1.9083527437
H	-5.4427362213	-1.4145276243	-3.1820426896
H	-6.3752614588	0.8696782497	-3.628760131
H	-3.1134655558	2.6211478592	-1.4737905746
H	-0.5205830123	0.4350197564	2.1855150998
H	-1.5124105693	0.2769465045	4.4399604039
H	-3.9648402931	-0.1526635733	4.6967651511
H	-4.4107568096	-0.185806686	0.4291279846
H	-1.9608066629	2.6447086505	1.3196827725
H	0.0342413265	5.7226209342	-0.9022899376
H	0.6830312602	4.0528037703	-2.6447473192
H	-0.0184354434	1.6913045251	-2.4096756988
P	2.1358178866	-0.2930178293	-0.2767524635
C	2.0445756413	0.3220121318	1.462156635
C	2.6363273739	1.152262429	-1.3300722168
C	3.7979495453	-1.1169126307	-0.3535282387
C	4.8293717848	-0.7661822557	0.5171518048
C	6.0705875732	-1.3530551629	0.3372497302
C	6.3265100906	-2.2585456255	-0.677864659
C	5.2920957657	-2.5860011043	-1.5511795044
C	4.0307368955	-2.0208800364	-1.3903271931
C	2.2772816331	-0.6074037158	2.4859887162
C	2.0447957985	-0.2606919724	3.8123464999
C	1.555626893	1.0041204702	4.1365323681
C	1.3068258559	1.8958171888	3.1078173589
C	1.5417903862	1.5878465677	1.7756345168
C	2.4095170461	1.0179592072	-2.7026485218
C	2.8487413739	1.998570745	-3.5872332097
C	3.5104839875	3.1282352721	-3.107639617
C	3.7321396591	3.2336236889	-1.7444740555
C	3.3249090903	2.2626745525	-0.8438201136
Cl	0.5631622514	3.4973172509	3.5021540846
H	7.3133351496	-2.6978707073	-0.7801220363
H	2.6259659921	-1.6089151146	2.2424118414
H	2.2344197241	-0.9839084285	4.6002113829
H	1.3603816713	1.2886616486	5.1656512626
H	1.2955369406	2.3165392027	1.006120088
H	1.8834193856	0.1391835995	-3.0768576568
H	3.8586199053	3.9066019769	-3.7791438448
H	3.550643107	2.3756869955	0.2132458555
I	1.2421611315	-3.8803666022	-0.0990734827
H	3.2199189956	-2.3009731831	-2.0586337338
H	4.6754123481	-0.0545446461	1.3236004307
Cl	4.5972196109	4.6970311004	-1.113384265
Cl	7.4156240034	-0.9130751898	1.4759238397
H	2.6789663798	1.8885388594	-4.6546382519
H	5.4693029918	-3.2984305924	-2.3512564326
H	-1.047314572	-2.9200258058	-2.985125218

IVa

99

C	0.1575447156	4.3174722539	-0.818590086
C	0.6308389385	3.0420989586	-1.1752699687
C	0.6037677475	5.4623196649	-1.5025997803
C	1.5219466957	5.3084941075	-2.5420854618
C	1.9805768566	4.0497463446	-2.9157790197
C	1.5339341525	2.9178233615	-2.2374303349
C	0.0772664039	6.8275322283	-1.1650510153
H	1.8693516908	6.1940384513	-3.0769110859
H	2.6864803979	3.9493220259	-3.7404338073
H	1.8950263172	1.9327406152	-2.5462140533
H	-1.0143754866	6.8827550852	-1.2908717147

H	0.5226264296	7.5941538207	-1.8112389636
H	0.2829264877	7.1129494812	-0.1240413863
C	-0.8541655525	4.3598901195	0.2761895682
C	-1.3558255512	2.92388999	0.6077277277
H	-1.6987957628	5.0107068148	-0.0165552245
C	-0.3137630582	4.8453391786	1.6498089637
H	-2.4147186354	2.7747770527	0.353897549
C	-1.0965242711	2.7948579957	2.1132238554
C	-1.5195299369	5.1404628872	2.5505000624
C	-2.0878195355	3.7272900131	2.8450720822
H	-2.2488466468	5.8023022502	2.0632107185
H	-1.1993349493	5.6347317256	3.4779789195
H	-3.1173462508	3.5984000286	2.4802815307
H	-2.0949882001	3.5167756724	3.9243521338
C	0.2205228122	3.5579823045	2.2837227489
H	-1.1121349936	1.7655367641	2.5002562497
H	1.0611022438	3.1056687564	1.7396604617
H	0.506955083	3.6965463132	3.3364339856
H	0.4036315306	5.6724775645	1.5732075653
Pd	-0.1917865328	1.4014080906	-0.2678108378
P	1.8067533059	-0.0286995674	-0.2034017242
P	-1.9914040864	-0.2295282948	-0.1522414126
C	3.3026099162	0.7579432667	0.5740435888
C	2.5454564575	-0.9143346739	-1.6522345734
C	1.5259827938	-1.3961576646	1.0238914235
C	-2.6128384317	-1.11107101	1.3574721715
C	-3.5595053461	0.5021128786	-0.8195055691
C	-1.7270368457	-1.5664028636	-1.4154839371
C	3.675417315	2.0459966445	0.1799783646
C	4.062346152	0.0749022627	1.5287099608
C	3.8504297868	-1.4139255841	-1.6373433332
C	1.7423874669	-1.0855177481	-2.7821167696
C	0.774640383	-1.0640923052	2.1562393752
C	1.9767409411	-2.7054167035	0.846316692
C	-3.0838332764	-0.3010585505	2.4000653475
C	-2.5158149697	-2.4889785898	1.5414727725
C	-4.7993657027	-0.0804102003	-0.5542976278
C	-3.4681065992	1.6020207392	-1.6770374492
C	-0.738837134	-2.5327576964	-1.1891553475
C	-2.370446046	-1.5206869843	-2.6547975487
C	4.8097375115	2.6411165582	0.725791426
C	5.1854896437	0.6945099108	2.0492173969
H	3.7846040995	-0.9189938918	1.8673654172
C	4.3045739469	-2.1010508896	-2.748715563
H	4.5001891434	-1.2653916906	-0.777890849
C	2.2285068997	-1.781278294	-3.8864851194
C	0.4367375356	-2.0402401036	3.0868556449
C	1.6337902672	-3.654936295	1.7983938241
C	-3.4509656004	-0.8657562574	3.6163476268
C	-2.8677247874	-3.019186185	2.7724438848
H	-2.1690208793	-3.1462927913	0.7496991123
C	-5.9243398929	0.4625483441	-1.1503593355
C	-4.6174327407	2.1183507944	-2.2706329385
C	-0.420556098	-3.4160961772	-2.2038387571
C	-2.0266453232	-2.4246238891	-3.6584293892
C	5.5795246998	1.9657978122	1.669720036
Cl	6.1780301241	-0.196966277	3.2832095459
C	3.5194039094	-2.3011798094	-3.8737810935
Cl	5.99548605	-2.7606523408	-2.7371407367
C	0.8595444768	-3.3568096817	2.9072508008
Cl	2.2160493778	-5.3571764324	1.5770947633
C	-3.3346751627	-2.2417514243	3.8169323862
Cl	-2.6872740924	-4.8069683942	3.0279044931
C	-5.8622221499	1.5503708939	-2.0061981315
Cl	-7.5415384067	-0.2872064066	-0.8051885015
C	-1.040877595	-3.3836382892	-3.4416795044
H	0.5925566373	-4.1362048009	3.6130365266
H	-0.7554432049	-4.0900767556	-4.2142747749
H	-3.1355551202	-0.7724899112	-2.8415250158
H	-0.196480658	-2.5802304739	-0.2496322364
H	-3.8276656363	-0.2359137312	4.4171266765
H	5.0938821772	3.6428147135	0.4170268457
H	6.4635666139	2.4172836095	2.1080134486
H	3.0746330526	2.5852268202	-0.5481683541
H	0.4328774173	-0.0374216698	2.2925291794
H	-0.174201238	-1.7838426991	3.9481068666
H	2.560075411	-2.9922266688	-0.025696317
H	1.5949013475	-1.9251471818	-4.7575350914
H	3.916281812	-2.8498835741	-4.7218027918
H	0.7350428822	-0.6713578353	-2.7929160223
H	-4.8860017049	-0.9431462895	0.1004630762
H	-4.5465868639	2.9714115043	-2.9393786531
H	-6.7686246114	1.9428902863	-2.4552606756
H	-2.4923312828	2.0496134212	-1.8701166839
H	-3.1705148131	0.7752913251	2.2518271533
H	-3.6047316614	-2.700636699	4.7625181097
H	-2.5312237729	-2.3803367749	-4.6195058245
Cl	0.9037750401	-4.6207096841	-1.9226676677

Va

79

C	3.744622666	-3.8312072873	-0.4760719869
C	2.598036121	-3.1627053992	-0.8939497355
C	2.6850713637	-2.3313320412	-2.018744963
C	3.8883739043	-2.1891752526	-2.7120208998
C	5.0228092049	-2.8495121442	-2.2749076805
C	4.9480742422	-3.668310852	-1.1517214568
Pd	0.9571154868	0.5364130939	-0.1073694402
Br	0.9860534524	-3.5084194286	0.1127016427
H	5.9628860273	-2.7200854467	-2.8055517779
C	3.0223689591	0.6802404297	-0.299672828
C	3.7018292477	1.6676216882	0.6852685722
C	4.2026927662	2.7911693724	-0.259669858

C	5.4271162316	2.2560496285	-1.0119417927
C	4.8151502797	1.1847486491	-1.9531879846
C	3.2989947107	1.296598646	-1.6728277252
C	3.1536190581	2.7931210531	-1.3748343658
C	2.7184389794	2.07839741	1.7262404929
C	1.3946576375	1.6396455397	1.529479973
C	0.4247621307	1.9187454823	2.4931980747
C	0.7604374734	2.649649935	3.6306196781
C	2.0648388173	3.0929432152	3.8141084456
C	3.0587307436	2.811683186	2.8764166524
C	4.4664364216	3.2770308564	3.1158489502
P	-1.4807267257	0.4339524555	-0.2479962234
H	-0.0025052982	2.8693809599	4.3777309012
H	2.3264300167	3.6595128713	4.709470183
H	4.581161413	1.1994844825	1.1661088378
H	3.4085557338	-0.3496796875	-0.2018967867
H	2.6755237519	0.910486239	-2.4952967497
H	4.370735881	3.7525913776	0.2417561228
H	2.1462259023	3.0647117604	-1.0344475118
H	3.4381982725	3.4348838655	-2.221579283
H	5.036485447	1.4036743172	-3.0084700262
H	5.1911455497	0.1721277529	-1.7427271805
H	6.1851016533	1.845163728	-0.3302208726
H	5.907401134	3.057552869	-1.5903006526
H	4.5944381184	3.6330960689	4.1458373513
H	5.1995238028	2.4754456001	2.9456165714
H	4.7495287532	4.1036212744	2.44829929
H	-0.6024880285	1.5794139443	2.366008387
H	3.9101852974	-1.5322787384	-3.5775877341
H	5.8324757605	-4.1929267898	-0.7960332558
C	-2.5520960837	1.5205578394	0.8019786586
C	-2.2764410731	2.8918248193	0.793077879
C	-3.5956502839	1.022178734	1.5796101466
C	-3.043105711	3.7621059589	1.5589074094
H	-1.442041553	3.2684814776	0.2036608488
C	-4.3382680694	1.9145021554	2.3372313757
H	-3.8278712174	-0.0388953362	1.5991712428
C	-4.0871182791	3.2747413194	2.3457983741
H	-2.824976329	4.8261265975	1.5550807074
H	-4.691819968	3.9384222892	2.9552065963
Cl	-5.696178083	1.2645045115	3.3541358649
C	-2.1062626965	-1.2469867855	0.1992454529
C	-1.6677358046	-1.7847093824	1.4153236716
C	-2.9201785082	-1.9969778704	-0.6458167081
C	-2.0628602701	-3.0634498952	1.7957863326
H	-1.0016966355	-1.1992582533	2.049956287
C	-3.2777319374	-3.2764852013	-0.2500172308
H	-3.2662497064	-1.5954940011	-1.5944132049
C	-2.8718623875	-3.8273730121	0.9528441034
H	-1.7358595898	-3.4760299467	2.7465799624
H	-3.1824966284	-4.830533421	1.2261539521
Cl	-4.3274504066	-4.2680528408	-1.3515703894
C	-2.2738850804	0.7202779166	-1.9055671333
C	-1.563882486	0.4441295897	-3.0783559524
C	-3.5794533661	1.2147876197	-1.9821772724
C	-2.1575162765	0.6708833492	-4.3185011609
H	-0.5623722257	0.0277378941	-3.0294703866
C	-4.1385587375	1.4270561541	-3.2293528128
H	-4.1497712451	1.4341598594	-1.084035759
C	-3.454106582	1.1708482374	-4.4051247706
H	-1.6027653718	0.4576725584	-5.2276924529
H	-3.927132394	1.3568556968	-5.3637502086
Cl	-5.8350392674	2.0709822605	-3.3271036341
N	1.5759646043	-1.528303836	-2.5119045017
O	1.619722415	-1.1162137677	-3.6578897973
O	0.6545528767	-1.2717898765	-1.735780671
H	3.6837129975	-4.4843860966	0.3908868259

VIa

79

C	-0.8039353672	4.3983017002	0.9840646837
C	-0.2274524552	3.3538087312	0.2591671762
C	-0.1801187709	5.6583979181	0.9579435962
C	1.0088023884	5.8006187997	0.2402153338
C	1.5874899539	4.7313155977	-0.4328909998
C	0.9620760027	3.4864067865	-0.438311515
C	-0.7605969904	6.8529411978	1.6607148711
C	-2.0539907752	4.0926916486	1.7545162053
C	-2.421015198	2.5867288335	1.629847019
C	-1.8869419583	4.2372170434	3.2901581297
C	-2.2590573258	2.0371734768	3.0421949289
C	-3.2624296408	4.0517810903	3.9454500937
C	-3.5134769106	2.5286408193	3.7995139903
C	-1.179404225	2.9323774329	3.6501307828
Pd	-1.2611100606	1.6102996648	0.1908078729
P	-2.6087398247	-0.6002981581	0.0772591253
C	-2.7665224384	-1.5837621027	1.636764539
C	-4.3738384714	-0.6473315436	-0.4940042468
C	-1.8273148648	-1.7695439145	-1.1251645865
C	-3.5744037449	-1.0519846047	2.6477299095
C	-2.1002630386	-2.7892732402	1.8372919319
C	-5.1823913621	-1.7487934271	-0.1888926496
C	-4.8796371898	0.3886629154	-1.2783665525
C	-0.4747471546	-2.1016727609	-0.9740838554
C	-2.5499551114	-2.2608508827	-2.2139275558
C	-3.7020145843	-1.7157344306	3.8619191351
C	-2.2491411618	-3.4298264613	3.0572129508
C	-6.4744479879	-1.7770611496	-0.6785664367
C	-6.1859484416	0.3295849552	-1.7619229492
C	0.1373433022	-2.9473752809	-1.893337897
C	-1.9036084535	-3.0858948506	-3.1187390392
C	-3.0302435591	-2.9185580176	4.0780784833
Cl	-1.3918486722	-5.0063336127	3.3202232043

C -6.9979156219 -0.7594895791 -1.4625880089
Cl -7.5293966899 -3.199422397 -0.2851827015
C -0.5760767921 -3.4480556308 -2.9817808789
H 1.1851862162 -3.2059380969 -1.7730963402
Br 0.4500121487 0.3669952087 1.7203551276
C -2.252806559 2.5099033279 -1.3631023057
C -3.3102155692 3.4199913775 -1.3308245197
C -1.8403351103 2.0970390673 -2.634813894
C -3.93392239 3.8483764156 -2.4994809498
C -2.4537846839 2.5021033734 -3.8206315614
C -3.5189281688 3.3815643888 -3.7475196696
N -0.7053184839 1.187083637 -2.7565124549
O -0.1548136502 0.8011377788 -1.7121268662
O -0.3283753647 0.8464168602 -3.8573297396
H 1.4893474649 6.7795767106 0.2135420884
H 2.5259265461 4.8670489234 -0.9689848836
H 1.4012449208 2.640948232 -0.9656910226
H -1.8575208276 6.8240520003 1.7002898592
H -0.469158336 7.7796121127 1.150575287
H -0.4048209052 6.9361925292 2.6979130474
H -2.8856487757 4.7344275373 1.411933031
H -3.4208699756 2.393872707 1.2090616492
H -1.3757105228 5.1616327359 3.5793687081
H -2.0878858963 0.9598020679 3.1092713969
H -4.0385675726 4.6610180133 3.4606473853
H -3.2321113795 4.348496726 5.0019203183
H -3.5608500722 2.0335963472 4.7799209779
H -4.4508788525 2.2961824646 3.2731682826
H -1.0771150031 2.7836336127 4.7336931297
H -0.1984681276 2.8050737265 3.1787480101
H -4.1111581675 -0.1194716119 2.4791946873
H -1.4762886474 -3.2241615342 1.0622417698
H -4.8051347456 -2.5707895167 0.4134943766
H -4.2588024057 1.2473617536 -1.5066730097
H 0.1026065481 -1.6759331281 -0.1532064969
H -3.5961250961 -2.0099770469 -2.3580077887
H -4.3271293831 -1.3000092726 4.6472413163
H -6.5712242818 1.1403598561 -2.3739546759
Cl -2.8439134981 -3.7085169656 -4.5434257263
H -3.1141986412 -3.4498736663 5.019931458
H -8.017532026 -0.8241940303 -1.8287818826
H -0.1078758601 -4.0973754532 -3.7143044707
H -3.6809725899 3.7901403479 -0.3762466761
H -4.7600729072 4.5556290902 -2.4346897114
H -2.0811666737 2.1219947958 -4.7682793908
H -4.015949499 3.7129900301 -4.6562719605

VIIa

79

C 5.0564602135 0.096441493 1.3333705786
C 3.851616411 -0.5382055319 1.0076653285
C 2.9480048917 -0.7468898096 2.0579349421
C 3.1950224475 -0.2604776691 3.3356921285
C 4.37275419 0.429728838 3.6108616202
C 5.3177822966 0.5874274185 2.6102432502
Pd 0.6526639749 -0.6114402901 -0.6855584744
P -1.5302613955 -0.1106504515 -0.2373156984
C 1.154000326 1.2626644723 -1.4304098489
C 2.6668450475 1.0125990691 -1.5950224283
C 3.2662987925 2.0851607019 -0.6624844426
C 3.0840844089 3.4283254808 -1.3967502887
C 1.555756191 3.6747773737 -1.3243904196
C 1.055795765 2.4660641064 -0.5056287657
C 2.2272752361 2.2484946164 0.4533070778
C 2.9095852646 -0.5045479977 -1.4160009814
C 3.5209456269 -1.1575592829 -0.3088033438
C 3.8016245192 -2.5222176892 -0.3608721858
C 3.5007177641 -3.279177405 -1.4809735907
C 2.9052368952 -2.6690796717 -2.5705634706
C 2.6137320921 -1.3054729345 -2.5661640503
C 2.1100191935 -0.7100000862 -3.8530869087
Br 0.2825390781 -3.0015333297 0.3900271718
O 7.2448077581 0.5353507715 0.7610931254
O 5.8678807376 0.0728756278 -0.8373668197
N 6.1357705142 0.2466633904 0.3417023082
C -1.9072598945 -0.2185747587 1.5650962807
C -3.0321529218 -0.8871252444 2.0397928982
C -1.0073252594 0.3731849503 2.4577062638
C -3.2418989606 -0.930189346 3.4087487874
C -1.2532230526 0.3245304109 3.8251899507
C -2.3807032459 -0.3349192356 4.3133885391
Cl -4.7030668022 -1.7993696955 4.0378366996
C -2.8591219118 -1.0952790717 -1.0622509708
C -4.1460938868 -0.5506698332 -1.1542324155
C -2.5928252531 -2.3592334871 -1.5874332131
C -5.1364842911 -1.2962499646 -1.7657694456
C -3.6143669246 -3.0824923614 -2.2017037455
C -4.898459055 -2.5546240552 -2.2962032109
Cl -6.8058036174 -0.5939542741 -1.8883018976
C -2.0755697602 1.6081552373 -0.6629397251
C -2.3653905559 2.556405436 0.3163769962
C -2.0576831251 1.9772055773 -2.0114981088
C -2.5998361116 3.8640508821 -0.0789560493
C -2.303299742 3.2950589586 -2.3779427159
C -2.5667998833 4.2590000167 -1.4041118782
Cl -2.9381725298 5.1085537702 1.1976238615
H 2.0317546487 -1.3042112783 1.8439624092
H 2.4604930468 -0.4305660679 4.121322795
H 4.5681612701 0.820335943 4.6072108457
H 6.2706817513 1.0744556998 2.7951840574
H 0.5862622524 1.3862141329 -2.3627988838
H 3.0030111326 1.243474577 -2.6179487349
H 4.3012232056 1.9062815615 -0.3657727712

H	3.4708315319	3.3990973288	-2.4238334197
H	3.6349749325	4.2175449818	-0.8682915067
H	1.0741049999	3.7254522091	-2.311316289
H	1.3171703715	4.612087196	-0.8025023947
H	0.0696046605	2.6279940096	-0.0611229434
H	2.4309339155	3.125763014	1.0839434392
H	2.1103081313	1.3704363322	1.0987974078
H	4.2462479005	-2.9947492475	0.5139709461
H	3.7183412772	-4.3449603473	-1.4945189785
H	2.667373815	-3.2527746637	-3.4591637477
H	1.240062401	-0.0567392465	-3.730843647
H	1.8281323778	-1.5047479512	-4.5527089519
H	2.8962579362	-0.1126721661	-4.3397227406
H	-3.7275613411	-1.3748366749	1.3632450192
H	-0.1123382371	0.8667005062	2.0785008935
H	-0.5649543392	0.7966880275	4.5203235082
H	-2.5842322443	-0.3904012789	5.3776925723
H	-4.3713260544	0.437001689	-0.7603267028
H	-1.5960761482	-2.7855533572	-1.4891587547
H	-3.4070334398	-4.0688986902	-2.6058365793
H	-5.7028662496	-3.1068764819	-2.7712016179
H	-2.3843723763	2.2906209354	1.3690960137
H	-1.8451141965	1.2282382742	-2.7728716222
H	-2.2871500192	3.5817539768	-3.4253052979
H	-2.7469243685	5.2949789343	-1.6707710382

VIIIa

79

C	4.7298803175	0.5249291229	1.5242042575
C	3.7163731155	-0.3661534765	1.1313213404
C	2.6417373641	-0.4963628157	2.0216438376
C	2.5620836846	0.2448838116	3.1944859787
C	3.572101529	1.1392279075	3.5365158158
C	4.6731556363	1.2614527992	2.7039689078
Pd	0.853738398	-0.4916717256	-0.7742626351
P	-1.5223001979	-0.0330697536	-0.2955577355
C	0.7935688184	1.4967152047	-1.8534020454
C	2.1213711253	1.1113469261	-1.9349798795
C	2.9132928233	2.1111301864	-1.1297893542
C	2.8583891917	3.394342108	-2.0096908023
C	1.3765073292	3.8344642293	-1.9045670777
C	0.7570158693	2.7425588185	-0.9922447943
C	1.9219142821	2.4929914951	-0.0283908321
C	2.754136967	-1.3278659407	-1.0143141829
C	3.7877409325	-1.2252612447	-0.076486401
C	4.9406087993	-2.0066008797	-0.2550808477
C	5.078822162	-2.8349509193	-1.3530672528
C	4.0603510977	-2.8917258107	-2.2968743618
C	2.8878008598	-2.1512660381	-2.1412761559
C	1.7875288198	-2.3057938618	-3.151932922
Br	0.3112206734	-2.7645923009	0.3292088608
O	6.980661487	0.9403244462	1.3054330014
O	5.8197467286	0.7900653625	-0.5104643438
N	5.9329111078	0.7612677472	0.7051374767
C	-1.7736198756	-0.0600365435	1.5329424168
C	-2.6602963056	-0.9357579618	2.1545445858
C	-0.9810581584	0.7993661386	2.3026886879
C	-2.7603561973	-0.9035646696	3.5359985152
C	-1.1109327513	0.8152640206	3.6878156801
C	-2.009302347	-0.0437697924	4.3186241874
Cl	-3.922727666	-2.0308705492	4.3491436778
C	-2.8190321351	-1.1630776274	-0.9831482227
C	-4.1719033442	-0.8632160255	-0.7797854266
C	-2.4573873794	-2.2760585406	-1.741031369
C	-5.1243009241	-1.7032163541	-1.3260586099
C	-3.4422409135	-3.0972713318	-2.2879386836
C	-4.7887063738	-2.8175707186	-2.0790218316
Cl	-6.8790509749	-1.3290321174	-1.0550317272
C	-2.3121912234	1.5868761796	-0.7661516731
C	-2.6262772907	2.5745756769	0.1662658089
C	-2.5066993995	1.8345156006	-2.1299052753
C	-3.0923893119	3.7968438139	-0.2919244032
C	-2.972446477	3.0713404079	-2.5599195051
C	-3.261333889	4.075445815	-1.6358772526
Cl	-3.4849889142	5.0855032734	0.9241941129
H	1.8694121071	-1.2303967326	1.7955027483
H	1.7100189802	0.0955021359	3.855716233
H	3.5194632337	1.7190679345	4.4556140322
H	5.5010387714	1.9223337862	2.9466973357
H	0.0530940524	1.3088022119	-2.6315161177
H	2.5636408393	0.5558160339	-2.7581289731
H	3.9184854354	1.7978991361	-0.8413564328
H	3.1797306094	3.2024253034	-3.0410384027
H	3.534783104	4.1528604428	-1.5956015549
H	0.8677422717	3.8935950013	-2.8757739619
H	1.2800730424	4.8177813702	-1.4260727332
H	-0.2148487882	3.006553378	-0.5654520783
H	2.2236752336	3.3999009947	0.5137488298
H	1.7471558238	1.6809631292	0.6929038007
H	5.7331180948	-1.9564029034	0.4931750876
H	5.9790752506	-3.4337228557	-1.4766704472
H	4.1608110811	-3.5389435125	-3.1695387093
H	0.9597709175	-2.8933817101	-2.7291156834
H	2.1442956431	-2.8262049561	-4.0500792055
H	1.3650975816	-1.3401889987	-3.4693772724
H	-3.2546842227	-1.6387011822	1.5785398886
H	-0.2582937985	1.4561113674	1.8175596479
H	-0.5094055251	1.497582092	4.2825295887
H	-2.1205763278	-0.0505817621	5.3976920624
H	-4.4778689461	0.0099124338	-0.2087954267
H	-1.4070375233	-2.519118581	-1.8770181481
H	-3.1574447202	-3.9664039276	-2.8733160032
H	-5.5682643625	-3.4499889975	-2.490890131

H	-2.5029169353	2.4054759801	1.2318384448
H	-2.30098901	1.0508900908	-2.8578530183
H	-3.1172280133	3.2596453275	-3.6198114586
H	-3.6200909692	5.0490628779	-1.9528504871

cis-**IXa**

96

C	0.8975550887	3.7098066444	-0.3704481877
C	1.9794692718	3.2771099937	0.5573138089
C	1.8141127552	2.6661247378	1.8039582023
C	2.8816676091	2.1987816964	2.5705817745
C	4.1731633956	2.3667292272	2.09904928
C	4.3789842939	2.9981537421	0.8731057991
C	3.2987797958	3.4376209302	0.1192290641
C	0.6387488229	5.0789708272	-0.4760232239
C	-0.2245282026	5.5520125187	-1.4525096696
C	-0.7862835561	4.6553734877	-2.3520780436
C	-0.5473884166	3.2782373244	-2.2688116689
C	0.2627106106	2.7994124412	-1.2268525604
C	-1.2153011127	2.3831164279	-3.2685008957
Pd	0.6339669376	0.809064462	-0.74846786
H	2.6838013195	1.7353349033	3.5346337437
H	5.017732414	2.0097770595	2.6842685649
H	5.3896707645	3.1266227333	0.4921370016
H	1.1329993285	5.7642949921	0.213311814
H	-0.4295931288	6.6180007492	-1.5359200225
H	-1.4316059243	5.0207473971	-3.1526369347
H	-2.1634866487	1.9745147103	-2.8857080045
H	-1.4503110555	2.9370883242	-4.1859876669
H	-0.5771755413	1.5331611238	-3.5385299401
P	-1.6199991487	0.4510621648	0.1140873821
C	-2.6021417965	-0.1110976724	-1.3598523896
C	-1.98067977	-0.9418847243	1.2887453572
C	-2.7303496429	1.775979515	0.7934991188
C	-2.6762833371	3.0479978756	0.2205845183
C	-3.5189595029	4.0554783838	0.6757694813
C	-4.4290639874	3.8066426829	1.7000245914
C	-4.473359147	2.5335009466	2.2411839495
C	-3.645550376	1.5094866747	1.8141860011
C	-1.9597292033	-0.7689639154	-2.4098224707
C	-2.6969829335	-1.2431931866	-3.4918585252
C	-4.0744304804	-1.050342401	-3.5422181396
C	-4.6870710404	-0.3808255806	-2.49479844
C	-3.9838909432	0.091714259	-1.4008763882
C	-2.6436063586	-2.0992228723	0.869762012
C	-2.8770166411	-3.0985613563	1.8020960144
C	-2.5115439518	-2.9810856654	3.1312290295
C	-1.8791011579	-1.8111701647	3.542557014
C	-1.5977963038	-0.8017644844	2.6276583724
Cl	-5.6705540198	2.1869681045	3.5635349966
Cl	-3.7291663808	-4.6112696406	1.27405208
Cl	-6.4814337128	-0.1195992567	-2.5576799781
H	-1.9755585923	3.253220147	-0.5788956588
H	-3.4561462021	5.0438623676	0.229494748
H	-5.0926461245	4.5808995628	2.0709880056
H	-3.7119135297	0.5283857252	2.2730311395
H	-0.8780420924	-0.8926569675	-2.3962982975
H	-2.1924734156	-1.7664886238	-4.2995912745
H	-4.6654869505	-1.4115143749	-4.3774352662
H	-4.5016011541	0.6099359463	-0.5978286433
H	-2.9935833623	-2.221326156	-0.1525734464
H	-2.7319828234	-3.7810499519	3.8306205047
H	-1.5987927782	-1.6871664661	4.5849324583
H	-1.0977622636	0.1060820813	2.9628090274
P	1.534473725	-1.4240550694	-0.2010638737
C	0.9399033633	-2.6164511633	-1.4808436149
C	1.2467805329	-2.252000162	1.4340568798
C	3.3732740881	-1.6958410974	-0.2149907281
C	3.890130207	-2.9722140972	-0.4443292176
C	5.2619878735	-3.1941567921	-0.3853765158
C	6.1270593245	-2.144065957	-0.0917906938
C	5.5880672127	-0.8914829862	0.1439310752
C	4.2270809752	-0.6347831669	0.0931839753
C	1.6075723094	-2.6784998246	-2.7096105807
C	1.0641059248	-3.4034571511	-3.7658246097
C	-0.1534917857	-4.0631229957	-3.6172412715
C	-0.8020268647	-3.9782722135	-2.3973014089
C	-0.2856561949	-3.2717533367	-1.3236653466
C	1.3755835836	-1.4201948407	2.5493112575
C	1.3435771208	-1.9951782178	3.8052237157
C	1.1569763403	-3.3524661934	4.002377157
C	0.9955528693	-4.1657369807	2.8835391549
C	1.0527037028	-3.6224304383	1.6013057484
Cl	6.7490370839	0.4640672841	0.5011432366
Cl	1.4861129985	-0.913848922	5.2594139316
Cl	-2.4307682297	-4.7512486734	-2.2282185546
H	7.2010711558	-2.2913850999	-0.0486140609
H	2.5405602823	-2.1395750614	-2.8520619273
H	1.5874049879	-3.4447431213	-4.7167483198
H	-0.5973922906	-4.6241499748	-4.4333195368
H	-0.8501321431	-3.2058304073	-0.3951807416
H	1.4457779804	-0.3380564872	2.4453441256
H	1.1278378309	-3.7608804766	5.0076448116
H	0.8361358129	-5.2325598657	3.0118926999
H	0.9504687888	-4.2737870458	0.7371145881
I	2.4884857431	1.1101902725	-2.6434389724
H	3.4587632425	3.8936749771	-0.8564536551
O	0.3023529983	1.5765899415	3.1452193384
N	0.4842022485	2.5380037291	2.3979588823
O	-0.3484898307	3.3890569306	2.160421261
H	5.6616352819	-4.1873464959	-0.569211422
H	3.845803228	0.3695439052	0.2708325581
H	3.2214701462	-3.7962661676	-0.6793475001

trans-**IXa**

96

C	-0.0028794794	-2.4997380781	0.508231036
C	-0.8489163532	-2.497944471	1.738269326
C	-0.7720396549	-1.6989795916	2.8898041329
C	-1.7365681554	-1.7119927101	3.8978825269
C	-2.8230090271	-2.5644228528	3.8053687194
C	-2.9161054103	-3.4077823503	2.7039481296
C	-1.9613148667	-3.355588795	1.6999239344
C	0.2932682805	-3.7765441586	0.0000747048
C	0.7703011214	-3.948968121	-1.2884018228
C	0.9156765602	-2.8368337211	-2.1060619277
C	0.6877913475	-1.5460246353	-1.6158940066
C	0.2845801253	-1.3621119381	-0.2769865189
C	0.9127748869	-0.3971848647	-2.5617502579
Pd	0.2334066471	0.58506174	0.4319555865
H	-1.5972671455	-1.0648834617	4.7602280513
H	-3.5760946851	-2.5829803343	4.5895861864
H	-3.7609372628	-4.0862907947	2.6045527729
H	0.1217455753	-4.646570791	0.6340645489
H	0.9905225167	-4.9473275834	-1.6631637108
H	1.2358257532	-2.9574420927	-3.1424880179
H	1.9221598202	0.026287995	-2.4609986996
H	0.8073062757	-0.7252300464	-3.6042121424
H	0.2080220463	0.4290131954	-2.3986589987
P	2.6643818865	0.6587349504	0.6424734999
C	3.3696002092	1.336145315	-0.9408293538
C	3.4182401457	1.7858305305	1.8995709179
C	3.7099398208	-0.8591343823	0.8841840504
C	3.5032793581	-1.9787500088	0.0740160742
C	4.2800906865	-3.1193871091	0.2455994124
C	5.2619734493	-3.164074441	1.2327523189
C	5.4416513929	-2.0450923833	2.0263506666
C	4.6908628991	-0.8917217547	1.8761561409
C	2.8340100407	2.518700855	-1.4638996517
C	3.300283498	3.0199650687	-2.6742462456
C	4.2985301322	2.3483268247	-3.3799018367
C	4.8208136556	1.189912078	-2.8341794885
C	4.3864638422	0.6700560339	-1.6260398304
C	4.4602007439	2.6399860243	1.5408844164
C	5.0337093561	3.4271411482	2.5250584777
C	4.6149645838	3.3940985034	3.8428349515
C	3.5765291048	2.5298766757	4.1855016656
C	2.9739498326	1.727775269	3.2222404251
Cl	6.7114533335	-2.0909306714	3.3253225696
Cl	6.3944322727	4.5399133271	2.0644438556
Cl	6.1282275343	0.3075163638	-3.7357553072
H	2.7301146242	-1.9663999243	-0.687317371
H	4.1109256566	-3.9842933666	-0.3898656802
H	5.8736288688	-4.0472494928	1.3856165478

H	4.8642406699	-0.0399355951	2.5263230378
H	2.0552774461	3.0495142558	-0.9166919008
H	2.8848193979	3.9398100606	-3.0753445607
H	4.6662540217	2.7202599672	-4.3301890961
H	4.8230531137	-0.2446366023	-1.2371222621
H	4.8211531225	2.6957866717	0.5183328153
H	5.0889047936	4.0305924915	4.5830087522
H	3.2282418281	2.490174953	5.213418294
H	2.1555315682	1.0687729035	3.4973429015
P	-2.0607289969	0.7010647769	0.0087049412
C	-2.4227628482	1.5791317322	-1.5812150096
C	-3.1098550718	1.549845842	1.2677282464
C	-3.0633372833	-0.841635774	-0.2482454732
C	-2.748023025	-1.6922417031	-1.3141431971
C	-3.4985530721	-2.8419244417	-1.5329922326
C	-4.5677762798	-3.158305535	-0.6921131146
C	-4.8474499928	-2.3072647936	0.3607741019
C	-4.1165994467	-1.1570664752	0.6085707907
C	-3.6104296563	1.3431699308	-2.281238991
C	-3.8597522428	2.0118429156	-3.4772364704
C	-2.9215325825	2.9004820403	-3.9973198137
C	-1.7477541513	3.1056680434	-3.2927139538
C	-1.480244195	2.4739490479	-2.0917539208
C	-4.1994496064	2.3297781449	0.8851117137
C	-5.0078764576	2.8602516348	1.8764596841
C	-4.7719602227	2.6455863098	3.2229676442
C	-3.6707632738	1.8736364075	3.5896968739
C	-2.8340216275	1.33206187	2.6193494731
Cl	-6.2122758858	-2.7307387627	1.4867127224
Cl	-6.4359961806	3.8698236019	1.3894296461
Cl	-0.5023635301	4.231150855	-3.9795182256
H	-5.1689955671	-4.0472648532	-0.8539408675
H	-4.3363985182	0.6305498122	-1.8975240763
H	-4.7864427929	1.8336995889	-4.0151822442
H	-3.094823586	3.4196254964	-4.934218701
H	-0.558423113	2.680115438	-1.5509059022
H	-4.4138550665	2.5324882969	-0.1602381277
H	-5.4293751107	3.0817908268	3.9674693622
H	-3.4552677143	1.7104468999	4.6417405678
H	-1.951026581	0.7723070194	2.9191180909
I	0.1126348569	3.1645839555	1.3051013381
H	-2.1035906293	-3.9612680416	0.8075460424
O	0.1956413589	0.1752794716	3.8047992685
N	0.3871797981	-0.8590867647	3.1712397647
O	1.4842626518	-1.2416289232	2.8003515286
H	-3.2550041738	-3.4986355498	-2.3631728587
H	-4.3537119575	-0.5286096851	1.462641015
H	-1.9131596814	-1.4589849334	-1.9711743955

Xa

96

C -1.582165144 -4.0045543729 -0.8231344947
C -0.123720864 -3.9085741709 -1.1064182193
C 0.5062351558 -2.9998627628 -1.9755413823
C 1.8913800678 -2.9851613156 -2.1480060113
C 2.6865958797 -3.8785259721 -1.4505000761
C 2.0894774311 -4.7978727333 -0.5936336656
C 0.7117563217 -4.8032893875 -0.4281394711
C -2.4128543095 -4.6430488519 -1.7482443746
C -3.7681849872 -4.7855532601 -1.5034677642
C -4.3181683098 -4.271341007 -0.3345087959
C -3.5302132421 -3.6315501174 0.6234919908
C -2.150880662 -3.5389997584 0.370610675
C -4.1721222193 -3.0269815216 1.8325796883
Pd 0.2108586307 -0.7135566029 0.0027664096
H 2.3313506517 -2.2661769019 -2.8337565238
H 3.7680343063 -3.8530621311 -1.5724196833
H 2.7023664072 -5.5118975894 -0.0459591602
H -1.9773564836 -5.0011017613 -2.6800486389
H -4.4033213288 -5.2852955605 -2.2323965334
H -5.3891214046 -4.3586652652 -0.1503300671
H -5.2603998384 -3.1513904365 1.8053591507
H -3.8021935711 -3.4711680048 2.7668249651
H -3.9613450584 -1.9493730096 1.8934753915
P -1.6580717217 0.6851474569 -0.3040757393
C -2.377241472 0.9101675521 1.3965020298
C -1.1428105597 2.413648685 -0.7290159298
C -3.2171811681 0.4591785872 -1.2757398413
C -3.7180908299 -0.8419100067 -1.3750710647
C -4.913204913 -1.0788073917 -2.0463302147
C -5.607103703 -0.0254839163 -2.639769131
C -5.0823157725 1.2521116258 -2.5348762136
C -3.9029147974 1.5222378776 -1.862143768
C -1.5001020488 1.2416257231 2.4364773313
C -1.9495396532 1.2837994008 3.7498960333
C -3.2730189929 0.9582446067 4.0535810762
C -4.1167357959 0.6262260877 3.0100088344
C -3.709151954 0.6145157356 1.6848271532
C -1.6765005722 3.5478301229 -0.1141289377
C -1.1312882565 4.7831088 -0.4251969375
C -0.0625959759 4.9334194388 -1.293680319
C 0.45783474 3.7957492204 -1.9103038356
C -0.0894757072 2.545843952 -1.6381306031
Cl -5.9848529648 2.6321060572 -3.3018801023
Cl -1.8255779266 6.2623010999 0.3686121534
Cl -5.8379480775 0.1607847419 3.3866443685
H -3.1683910902 -1.6695476591 -0.9305096768
H -5.2963966853 -2.0928051254 -2.1181783083
H -6.5343789735 -0.1913636501 -3.1786409463
H -3.5279110661 2.5399468946 -1.7979131903
H -0.4538430022 1.446967971 2.2197815408
H -1.2609614504 1.5590672727 4.5448206113
H -3.6375772335 0.9597853422 5.0754637772
H -4.4137092274 0.3600702224 0.8974577378
H -2.4824407236 3.4718468656 0.6116795168
H 0.3575150654 5.9172584321 -1.4755493701
H 1.312992769 3.8748896436 -2.5789181449
H 0.3217460742 1.6529200317 -2.1043318578
P 2.3903014172 0.0293041973 0.136803418
C 2.4831641953 1.117064558 1.6421386539
C 3.0885504024 1.1483936244 -1.1671439487
C 3.8235166302 -1.1235585851 0.4133623692
C 3.5809561939 -2.2675223533 1.1799141955
C 4.5964014587 -3.1895896763 1.4126078433
C 5.8580706978 -3.0008355789 0.8491803825
C 6.0679667518 -1.8736930645 0.0724998697
C 5.0832138127 -0.9250414037 -0.1522735204
C 3.1506434149 0.7375515996 2.8058602095
C 3.0280030318 1.5025325393 3.9658483343
C 2.2344981301 2.6462057504 3.9786351667
C 1.5920032887 3.0117865042 2.8048658462
C 1.7049595637 2.2836319307 1.6359573906
C 3.9174292129 2.2283420143 -0.8547192966
C 4.367562102 3.0380081338 -1.8835462887
C 4.0310124016 2.8151266892 -3.2090022595
C 3.2076699589 1.7310234224 -3.510895827
C 2.7351699872 0.9010471748 -2.4960157994
Cl 7.7057813414 -1.6221811929 -0.6733577665
Cl 5.4289563986 4.4547936009 -1.4776517512
Cl 0.5075898498 4.4653002867 2.8123377948
H 6.6610276859 -3.7136767487 1.0059531347
H 3.7627555387 -0.1607270443 2.8113706838
H 3.5519875596 1.2035463291 4.8696074176
H 2.1161018248 3.2453667321 4.8754563643
H 1.1776683754 2.6083485107 0.7393324977
H 4.1984302107 2.4407524002 0.1735956937
H 4.4028776025 3.47676802 -3.9851677306
H 2.924742974 1.5424925256 -4.5428070825
H 2.0532316469 0.0835208628 -2.730630785
I -0.9210158294 -2.6395899879 1.8431102049
H 0.2456935814 -5.5159730643 0.2518365709
O 0.3682348246 -1.1577207434 -3.376958847
O -1.462926611 -2.1847056154 -2.8971861968
H 4.404715992 -4.0709484984 2.0191655451
H 5.2971705806 -0.0497903022 -0.7589073318
H 2.5769596484 -2.4447747699 1.5669082427
N -0.2592676095 -2.0370199809 -2.8004298392

IIa*

84

C -0.5792798981 -3.8813157671 1.8428661542
C 0.3278327544 -3.9849203512 2.8973580892
C 1.7079917899 -3.8758710597 2.7046729851

C 2.2148564032 -3.6240582972 1.4406887262
C 1.3374043014 -3.4839417873 0.3582857452
C -0.0474123629 -3.6225096664 0.5586497517
Pd 0.0680544471 -1.1791012033 0.5216384921
H -0.0649832383 -4.1806779279 3.895536112
H 3.2861930812 -3.5196140235 1.2724878751
P 1.963602044 0.0998724034 0.0943289125
C 3.0937238246 -0.5985310492 -1.1992935126
C 1.7193195547 1.8410106747 -0.5025590791
C 3.1118403388 0.3814446464 1.5205301538
C 2.9470683813 -0.4255109472 2.6484848702
C 3.7858160655 -0.2703157137 3.7511449127
C 4.7892252588 0.6957295205 3.7377196982
C 4.9271935314 1.4892093331 2.6089409463
C 4.1116522607 1.3598210089 1.4993503358
C 2.4974411374 -1.0477618295 -2.385532778
C 3.2674174245 -1.6388840289 -3.3815217368
C 4.6390699053 -1.8186678558 -3.1961393405
C 5.1985801353 -1.3901139522 -2.006169731
C 4.4625800576 -0.7794607174 -1.0033590507
C 1.9246822471 2.2159543804 -1.8296982633
C 1.6343055386 3.5197004642 -2.1978846095
C 1.1837116758 4.4742659302 -1.3064624331
C 0.9748631845 4.0872545748 0.0175244903
C 1.2233432872 2.7780617299 0.4119772336
Cl 6.2359507752 2.7544482499 2.5891493786
Cl 1.8297010407 3.9911392583 -3.9481050083
Cl 6.9821528692 -1.6430817754 -1.7388027856
H 2.1595840693 -1.1787817677 2.6523840079
H 3.6580635078 -0.9008986969 4.6265617354
H 5.4507282279 0.8339391374 4.5866149059
H 4.2469247606 2.0077136925 0.636518799
H 1.4197455973 -0.9431779841 -2.5130928965
H 2.80236131 -1.9760905711 -4.303386694
H 5.2538275079 -2.2893873167 -3.956031993
H 4.9499623136 -0.4536757786 -0.0891777126
H 2.2942638213 1.5096557665 -2.5671936754
H 0.9777390475 5.4857815137 -1.6390995469
H 0.6035673411 4.812041162 0.7364931945
H 1.0288255442 2.4812362915 1.4410027305
P -1.9313144356 0.0299685522 0.502472563
C -1.8011824912 1.0623074937 -1.0410052378
C -2.0886111825 1.3066093351 1.8392384279
C -3.7055238852 -0.5267520866 0.391619387
C -4.4527271483 -0.4364913682 -0.7823005242
C -5.7300908437 -0.9738585757 -0.7956880609
C -6.3029661826 -1.5827253173 0.3051311353
C -5.5509772666 -1.6586172515 1.4789101421
C -4.2611794812 -1.1422538586 1.5205598385
C -1.5110285775 0.3801450184 -2.2304814294
C -1.378043442 1.0730536259 -3.4291785974
C -1.5226694748 2.4600639157 -3.4573097921
C -1.8035004673 3.1091282833 -2.2700859161
C -1.9421100558 2.448769853 -1.0595815491
C -1.0454321438 1.4230041073 2.7598066538
C -1.1012020946 2.3802803343 3.7712627613
C -2.2023799257 3.2280307281 3.8725021401
C -3.2312521849 3.084385032 2.9552555074
C -3.2080700367 2.1380824063 1.9463386059
Cl -1.9952468556 4.920230356 -2.2993544911
H -7.3074908804 -1.9891156927 0.2514314977
H -1.3922317422 -0.7031318722 -2.2090394252
H -1.1616240835 0.5373498302 -4.3494332562
H -1.417225147 3.0228623827 -4.3789414424
H -2.1473811661 3.0096976827 -0.1524968348
H -0.1935684206 0.7456668662 2.6758643881
H -2.2645414249 3.9801621326 4.6520885923
H -4.0438559106 2.0480866698 1.2563898391
H -3.6776628438 -1.2094810797 2.4382449699
H -4.0510623436 0.043083222 -1.6704336869
Cl -4.6729474053 4.1880648094 3.0807687109
Cl -6.6962847834 -0.8752297177 -2.3384260154
H -0.2904768332 2.4656002151 4.4892102092
H -5.9802775046 -2.1278338446 2.3598229855
H 1.7318608902 -3.356404367 -0.648530364
I -1.2508566268 -3.8344827844 -1.1815425407
H 2.3825714687 -3.989632093 3.5522906881
C -2.0445283259 -4.0668158055 2.0767335662
H -2.4003446819 -5.0155046459 1.6492908615
H -2.2699046636 -4.0771092867 3.1495812976
H -2.6346992605 -3.2673998752 1.6074990058

trans-**IIIa**

84

C 0.2980861831 2.9223113967 -0.2815005465
C 0.3317155156 4.2115302191 -0.8112789153
C 0.2172392248 4.3942785991 -2.1857160083
C 0.0829913235 3.2895553595 -3.0213981683
C 0.0593242102 1.9872055242 -2.508716925
C 0.1621339777 1.8193536756 -1.1207581473
C -0.0872961967 0.8135493502 -3.4356433985
Pd 0.1477125536 -0.0708137143 -0.3336425969
H 0.4505716147 5.0679804643 -0.148592306
H 0.2397321076 5.3974057023 -2.6094011349
H -0.0031722551 3.4318395452 -4.1005597785
H -1.0022960038 0.2365597832 -3.2259287422
H -0.1312755003 1.1331475904 -4.484510553
H 0.7530174709 0.1089102635 -3.3351426651
P -2.2019809476 0.0641977218 -0.0510475603
C -3.2332101374 -0.9205294923 -1.2268555969
C -2.6830521794 -0.5545618815 1.6191871281
C -3.0942242555 1.6898701556 -0.0959203096
C -2.9474534348 2.4995107963 -1.2251519935

C	-3.6046341215	3.7216654648	-1.3006748236
C	-4.4292891683	4.1436378163	-0.2583260176
C	-4.5706447497	3.316024445	0.840863043
C	-3.9211567445	2.0972248717	0.9521979571
C	-2.6448968974	-1.9293965197	-1.9909955631
C	-3.4226319593	-2.683656307	-2.8675883201
C	-4.7871368877	-2.4355031716	-2.9887593673
C	-5.3448732866	-1.4230957949	-2.2240456476
C	-4.6013646071	-0.6540923013	-1.3477033214
C	-3.6347864241	-1.5539470494	1.7942642606
C	-3.9047116561	-1.9792278446	3.0850141464
C	-3.2721663519	-1.4504096959	4.195309469
C	-2.3236376828	-0.4448746469	4.0039425425
C	-2.0245110851	-0.0019558981	2.7217400975
Cl	-5.6592531469	3.8470624257	2.199314783
Cl	-5.1405159798	-3.2906346485	3.321789782
Cl	-7.1246605547	-1.0909216115	-2.382418069
H	-2.2903857645	2.1921013548	-2.0335239073
H	-3.4674041266	4.3545702327	-2.1725411128
H	-4.9505192758	5.0942410663	-0.3004556623
H	-4.0583481611	1.4809788272	1.8355645247
H	-1.5815576655	-2.1359484334	-1.884805705
H	-2.9652212038	-3.4729186572	-3.4566857254
H	-5.4076935603	-3.0161759099	-3.6633045575
H	-5.0759875446	0.1354962163	-0.7704810603
H	-4.1462770343	-2.0029242023	0.9479527528
H	-3.5095355281	-1.8174846835	5.1881177705
H	-1.8146869382	-0.0175936862	4.8627337978
H	-1.2698975673	0.7699719216	2.5672059805
P	2.5039883399	0.0254228351	-0.3440753851
C	3.4333443131	-0.9858230622	-1.5768334318
C	3.2043796651	-0.4680549466	1.2908922727
C	3.2671392786	1.6987695776	-0.5782876017
C	3.2456777449	2.2777057844	-1.8504763595
C	3.6894383999	3.5819748498	-2.0298240321
C	4.1588331009	4.3236024713	-0.9455685468
C	4.1781616943	3.7215740982	0.2987139428
C	3.746532681	2.4231797762	0.5114892402
C	2.8054346248	-2.0546508113	-2.2168232601
C	3.5124735924	-2.8318634926	-3.1325091303
C	4.8458838567	-2.5486895255	-3.4146132197
C	5.4449666813	-1.4784390556	-2.7694520471
C	4.7712499539	-0.6845615104	-1.8595456798
C	4.3454835847	-1.2574812126	1.3982297942
C	4.8178507926	-1.5564679163	2.6658949604
C	4.2029757685	-1.1058812038	3.8200611729
C	3.0563642188	-0.3214006757	3.6981797504
C	2.5528465624	-0.0096967285	2.4402455955
Cl	4.7976416588	4.6726149864	1.7225150606
Cl	6.3098076133	-2.5828472459	2.8155575237
Cl	7.1834556706	-1.0994229864	-3.1380167162
H	4.500948147	5.3460699656	-1.0689946818
H	1.7675813131	-2.2876087596	-1.986370501
H	3.0236044114	-3.6657216351	-3.6269202879
H	5.4109579419	-3.1455770015	-4.1229671465
H	5.2734122074	0.1534624033	-1.3829578116
H	4.8568466275	-1.6381595282	0.5189792604
H	4.6050939048	-1.366469669	4.793663509
H	2.5518384946	0.0346150784	4.591514581
H	1.6437267801	0.5842855404	2.3434349933
I	0.1794956196	-2.668524157	0.580501944
H	3.6575301629	4.0350620378	-3.0163436114
H	3.7805339674	1.9891040354	1.5066511863
H	2.8638231155	1.7176401937	-2.7012888994
H	0.3981400327	2.781172461	0.7984631532

cis-IIIa*

84

C	-1.7813058535	-3.2051841524	-2.0671856207
C	-2.8459498563	-4.0399294231	-2.4001615692
C	-3.6445235985	-4.5669822067	-1.3898750202
C	-3.3499279546	-4.2800352602	-0.0613682226
C	-2.261971482	-3.4713584263	0.299701153
C	-1.5049105561	-2.9067945724	-0.73333292
C	-1.9341134633	-3.2890345213	1.7514576264
Pd	0.0475333915	-1.5714601917	-0.502078969
H	-3.0562035271	-4.2600788534	-3.4461093974
H	-4.4916884524	-5.2063447997	-1.6341527007
H	-3.9652767602	-4.7043514868	0.7341722683
H	-2.8319760087	-3.3685917285	2.3790011374
H	-1.2228125163	-4.0609230345	2.0792375977
H	-1.4655661147	-2.3197112161	1.9490142222
P	-1.6848287952	0.1029016968	-0.3515059611
C	-2.4027949506	0.0113551795	1.3561810963
C	-1.265992703	1.9060758228	-0.4402305589
C	-3.1976584171	0.086117952	-1.4362875714
C	-4.0133022246	-1.0507558072	-1.4796572594
C	-5.1464988888	-1.068056379	-2.2868813669
C	-5.4807551658	0.0379497505	-3.0647369832
C	-4.6592701637	1.1491337686	-3.0029958352
C	-3.5287893523	1.2040654862	-2.2067416363
C	-1.5126245313	0.1028661688	2.4318920359
C	-1.9840477651	0.0323048817	3.7370467828
C	-3.3440525448	-0.1561387153	3.9850147016
C	-4.2004065018	-0.245946953	2.9032987916
C	-3.7652664023	-0.1532709847	1.5906643164
C	-1.7659356697	2.8191876994	0.4913294636
C	-1.4877518813	4.163007956	0.3085066383
C	-0.715434298	4.6320297272	-0.7421799586
C	-0.2281165568	3.7130625796	-1.6689597823
C	-0.5121850918	2.3571905302	-1.5245137816
Cl	-5.0876474812	2.6090302891	-4.0021197676
Cl	-2.1836183088	5.3654259072	1.4778084873

Cl -5.9754745856 -0.495112609 3.2103460726
H -3.7767404693 -1.9204869435 -0.8760352992
H -5.7701637382 -1.9569515158 -2.3116126344
H -6.3591147302 0.037649567 -3.7014472278
H -2.92267377 2.1036665731 -2.1877589057
H -0.4499121601 0.2372756638 2.2477224506
H -1.2909479518 0.1148182074 4.5692138745
H -3.7272653773 -0.2266126342 4.9974394718
H -4.4770636849 -0.2131052782 0.7734760951
H -2.3669566301 2.491344434 1.3341656519
H -0.5082262203 5.6928020482 -0.8387942856
H 0.3812134892 4.0545024359 -2.5008636609
H -0.1502041456 1.649058768 -2.2647658599
P 2.1044692881 -0.1868382463 -0.3054908914
C 2.0504490467 0.4648920727 1.4209861289
C 2.4640427334 1.2619408713 -1.408380209
C 3.8082690032 -0.9127108007 -0.4546168608
C 4.8595423902 -0.4962363812 0.3620047021
C 6.1225176279 -1.008956927 0.1175794143
C 6.384577285 -1.8983978572 -0.9096014869
C 5.3284938303 -2.2901365958 -1.7294767397
C 4.0446212781 -1.8036046068 -1.5026307673
C 2.4302802923 -0.3982661292 2.4574516919
C 2.2359053954 -0.0280176099 3.7843216591
C 1.6375585407 1.1920270964 4.0961735238
C 1.2387145332 2.0120994051 3.0548787988
C 1.4303384599 1.6819614544 1.7221953186
C 2.1964278859 1.0842411397 -2.7688947543
C 2.5135421328 2.0845977121 -3.6833474375
C 3.0928723205 3.2756126251 -3.2456314773
C 3.3563985074 3.4206561751 -1.893991295
C 3.0720375309 2.4347065311 -0.9632356523
Cl 0.3501727887 3.5424548917 3.4466064682
H 7.3894410777 -2.2766276569 -1.0651105783
H 2.8646655848 -1.3688036706 2.2276679942
H 2.5406741085 -0.6982327918 4.5825165597
H 1.4693981411 1.4905668176 5.1259465592
H 1.0604809367 2.3448303556 0.9424798757
H 1.7283120469 0.1610030083 -3.1113638576
H 3.3408044026 4.0700632388 -3.9421246113
H 3.3221642276 2.5857804431 0.083572269
I 1.4187064959 -3.8226166973 -0.0788764957
H 3.2221769028 -2.1316932821 -2.133632148
H 4.7059825994 0.2078328037 1.1750417363
Cl 4.1072554057 4.9702425293 -1.3139789363
Cl 7.4965739333 -0.4858260839 1.1910161504
H 2.3081264532 1.9447029757 -4.7406180772
H 5.5086424404 -2.9889969967 -2.5407564092
H -1.1695822064 -2.7763602134 -2.8626493447

IVa*

99

C 0.1653118464 4.3255143383 -0.8315747867
C 0.6428099726 3.0483467965 -1.1792138823
C 0.6161664962 5.4693079429 -1.5150645322
C 1.544396511 5.3138025756 -2.5460130849
C 2.008655552 4.0541840335 -2.9110895181
C 1.5567750807 2.9238109132 -2.2327787086
C 0.084617189 6.834966868 -1.1867347595
H 1.8954284378 6.1982359904 -3.0804339049
H 2.7233314128 3.9520856205 -3.72807198
H 1.9240695008 1.9386772517 -2.5344266152
H -1.0058968011 6.8878301807 -1.3227323805
H 0.5351455259 7.6001368874 -1.8310234742
H 0.2798958777 7.1232781549 -0.1445728348
C -0.8556859035 4.3717542187 0.2547261464
C -1.3562505833 2.9366539339 0.5911847893
H -1.699273577 5.0188944334 -0.0486608182
C -0.3256046138 4.8662994879 1.62894111
H -2.4140635191 2.7845060262 0.335391689
C -1.1007838405 2.8140358306 2.0978925335
C -1.5375600972 5.1591560785 2.5222809686
C -2.0993411899 3.7444826509 2.8220882687
H -2.2680637052 5.8140030454 2.0273521367
H -1.224274134 5.6601919066 3.4484579917
H -3.1268489782 3.6073751446 2.455005651
H -2.1078838937 3.5389110336 3.9021913333
C 0.2117968593 3.5840470777 2.2707012808
H -1.1125976581 1.78623099 2.4882297958
H 1.0563202862 3.13272993 1.7316058005
H 0.4927317131 3.7283163204 3.3241094058
H 0.387572975 5.6971980011 1.5525454431
Pd -0.1914467273 1.4104057395 -0.2733071591
P 1.8007340391 -0.0335119213 -0.1943575072
P -1.9921196071 -0.2234197133 -0.1544013915
C 3.2989759992 0.7467283601 0.5877033565
C 2.5407812457 -0.9184023273 -1.6441733824
C 1.5183169521 -1.4023168986 1.0314193596
C -2.5964726391 -1.1161907976 1.3553375221
C -3.5726404146 0.4965238857 -0.8063007529
C -1.7226817837 -1.5510968292 -1.425753595
C 3.6747394486 2.0365208687 0.2016698183
C 4.0577120871 0.0573111829 1.5389818139
C 3.8411096826 -1.4306833692 -1.6232725832
C 1.7436658507 -1.0769688555 -2.7804258867
C 0.7778907947 -1.0705161822 2.1711238881
C 1.9624167519 -2.7128031179 0.8458528551
C -3.0590227677 -0.313670874 2.4075810637
C -2.5025520868 -2.4961247832 1.526982409
C -4.8053864757 -0.0938826946 -0.5247451581
C -3.5003238883 1.5954339023 -1.6668194268
C -0.7397946548 -2.5232376943 -1.2010809956
C -2.3585119718 -1.4933873394 -2.6686286884
C 4.8098353214 2.6280000887 0.7504258908

C	5.1811364761	0.6741462133	2.0616313348
H	3.7793825955	-0.9385110914	1.8713866435
C	4.2936988941	-2.1159680205	-2.7360953643
H	4.4865209188	-1.2946455087	-0.7585356893
C	2.2303128333	-1.7704053875	-3.8863154536
C	0.4461788346	-2.0474968592	3.1032822144
C	1.6231872547	-3.6619460845	1.7988766346
C	-3.4192639202	-0.8865589185	3.6221772324
C	-2.8477356369	-3.0331622904	2.7565959088
H	-2.1655590154	-3.148400242	0.7268968011
C	-5.939717118	0.4431347872	-1.1079090326
C	-4.6597373939	2.1049010789	-2.2467349663
C	-0.4233867136	-3.4011551058	-2.2206613285
C	-2.0138479092	-2.3914249883	-3.6773623677
C	5.579085972	1.9465260311	1.6910153486
Cl	6.1740047	-0.2281615664	3.2934837461
C	3.5168345603	-2.3021855695	-3.8689577589
Cl	5.9813430261	-2.7949909394	-2.7149153994
C	0.8623083808	-3.3655586672	2.9168289924
Cl	2.1984485518	-5.3696650854	1.5662102593
C	-3.3046667685	-2.2646109654	3.8115646987
Cl	-2.6736541707	-4.8273526584	2.9953157282
C	-5.8980113705	1.5302677583	-1.9653795128
Cl	-7.5511678494	-0.3188110591	-0.7424055632
C	-1.0348073702	-3.3583245576	-3.4621265227
H	0.6003754841	-4.1439993923	3.6256273322
H	-0.7497674119	-4.0591311007	-4.2398086541
H	-3.1182259709	-0.7399451578	-2.8555990709
H	-0.2024342929	-2.5802808398	-0.2593349234
H	-3.7887513764	-0.2626039376	4.4306473437
H	5.0960186781	3.6308643248	0.4477155108
H	6.4633937696	2.3959071949	2.1307576366
H	3.0754836503	2.5804413546	-0.5240615987
H	0.4406442577	-0.0434406995	2.3144023499
H	-0.1545140722	-1.791859856	3.9716637283
H	2.5397824414	-2.9972624365	-0.0308490988
H	1.6013270474	-1.9037752713	-4.7622229039
H	3.9126134916	-2.8486166979	-4.7189199301
H	0.7389130724	-0.6567417088	-2.7959934848
H	-4.8786509912	-0.9567513596	0.1313971368
H	-4.6025860957	2.9565123271	-2.9183173895
H	-6.8114835762	1.9179372051	-2.4039626712
H	-2.5307664499	2.0477987147	-1.8765492578
H	-3.1467056167	0.7638537144	2.2690584993
H	-3.5685975068	-2.7282967298	4.7564368445
H	-2.5114033945	-2.3367015958	-4.641318249
Cl	0.8950712036	-4.6173896492	-1.9374902479

Va*

79

C	-4.1591349884	-3.1268480753	-1.6562203212
C	-2.9800946144	-2.8333328211	-0.9799572692
C	-3.0308612729	-2.6683713159	0.4115018578
C	-4.2352313835	-2.8112791355	1.104128541
C	-5.4024789156	-3.0890069807	0.4152011168
C	-5.3616193304	-3.2422019254	-0.9678008397
Pd	-1.0408485429	0.641668193	0.1600424886
Br	-1.3747846013	-2.7436318042	-2.0551773205
H	-6.3411765061	-3.1804953018	0.9555302703
C	-3.0946537181	0.8253148992	0.4180154582
C	-3.6756898851	2.2204579639	0.0671504493
C	-4.1348493845	2.7494271434	1.4513535201
C	-5.4138943441	1.9967188656	1.8372082172
C	-4.9010053241	0.5578422268	2.1100639965
C	-3.3728965741	0.6877470093	1.9164024918
C	-3.1236754507	2.1167388866	2.4113746916
C	-2.632332659	3.0282813289	-0.6250893568
C	-1.3454835379	2.4560046888	-0.6790722651
C	-0.326159249	3.1196356278	-1.3647678687
C	-0.57543708	4.3487216698	-1.9723868891
C	-1.8441826064	4.9135981026	-1.9072266997
C	-2.8867026294	4.2655964043	-1.2432662482
C	-4.2547739594	4.8849245238	-1.2156477128
P	1.3813143343	0.2849627915	0.2064724252
H	0.226043213	4.8634851618	-2.5029009702
H	-2.0389286567	5.8724096236	-2.3909749418
H	-4.5662984633	2.1239299451	-0.5814887672
H	-3.5448514152	0.0131619523	-0.1796409922
H	-2.80185005	-0.1030157144	2.4285997827
H	-4.2258340935	3.8418148899	1.5027620254
H	-2.090828046	2.4515117237	2.2503280283
H	-3.3947643724	2.2645140995	3.4670444964
H	-5.1397193497	0.2335286385	3.1337253739
H	-5.3333055898	-0.1840945164	1.4223349692
H	-6.1736265738	2.0379590109	1.0439851135
H	-5.8606294355	2.4319476031	2.7419350724
H	-4.32236351	5.7232551175	-1.9203452561
H	-5.0390623378	4.161001905	-1.4795305691
H	-4.5140292592	5.2743847224	-0.2207311893
H	0.6733033471	2.6909862106	-1.4266273053
H	-4.2321042871	-2.6744653168	2.1822005348
H	-6.2717356838	-3.4601646615	-1.5222866299
C	2.5684842446	1.6568069921	-0.1702749975
C	2.4146465598	2.8510871742	0.5423599535
C	3.5811630751	1.5352365744	-1.1198453667
C	3.2704713876	3.9205854469	0.3065742076
H	1.6073510794	2.9456959449	1.2668193371
C	4.4141382054	2.6220134888	-1.3353401912
H	3.7201933998	0.6161434776	-1.6818856427
C	4.2852792087	3.8139068898	-0.6459269826
H	3.1474921176	4.8480636942	0.8579972499
H	4.9580912136	4.6412709151	-0.8467070052
Cl	5.7364789824	2.4620111547	-2.5766151627

C	1.8990605869	-1.0033642009	-1.0140772608
C	1.4684874078	-0.8392663306	-2.336123583
C	2.6245081392	-2.1351839825	-0.6491037907
C	1.7811461982	-1.795572486	-3.2973349835
H	0.8739700448	0.0348344918	-2.6027649705
C	2.9014101942	-3.0792279985	-1.6252116406
H	2.9639740655	-2.2801154944	0.3728796467
C	2.500739637	-2.9379007179	-2.9419310408
H	1.4585337766	-1.662333926	-4.3263126443
H	2.7446813014	-3.6996237749	-3.6751425577
Cl	3.8399368685	-4.5667354853	-1.1561180456
C	2.1305442193	-0.3508806692	1.7859806475
C	1.3607525004	-1.1145682839	2.6692625779
C	3.4651269476	-0.0668348801	2.0919980521
C	1.9232651854	-1.5810670167	3.8561328557
H	0.3348263247	-1.3718172096	2.4232038457
C	3.9902966559	-0.5471605683	3.2776187594
H	4.0826327127	0.5198875776	1.4179409017
C	3.248777986	-1.2959211628	4.1750849823
H	1.3229221425	-2.1718653727	4.5417711871
H	3.6968945414	-1.6489939989	5.0979693637
Cl	5.7285189754	-0.1750627821	3.6739420525
N	-1.8807484408	-2.2948381354	1.2175213818
O	-1.9170190666	-2.499425723	2.4189006645
O	-0.9257329289	-1.7537500957	0.6565929067
H	-4.1277496627	-3.2653668867	-2.7338572163

VIa*

79

C	-0.8073402977	4.4036092274	0.9895497413
C	-0.2300143825	3.3692116808	0.2502671563
C	-0.18886666	5.667004593	0.9750868009
C	0.9949807074	5.8233753803	0.2510877341
C	1.5727107629	4.7655744717	-0.4413003851
C	0.9523487967	3.5178297499	-0.4572205814
C	-0.7695508801	6.8499977694	1.6967923432
C	-2.0562350951	4.0899623488	1.7586710422
C	-2.4334902718	2.5895032199	1.6142826725
C	-1.8869910517	4.2147565162	3.296833249
C	-2.2947843028	2.0244235676	3.0203141598
C	-3.265657145	4.0471700232	3.9477930502
C	-3.5502316086	2.5340132082	3.7683709331
C	-1.2048116715	2.893795408	3.6469350766
Pd	-1.2487309909	1.6153377719	0.1897660467
P	-2.6014533747	-0.5955490147	0.0750388316
C	-2.7502937231	-1.5773766142	1.6371238313
C	-4.369289121	-0.6322726032	-0.4871511378
C	-1.8347710944	-1.7723033915	-1.1303461681
C	-3.5789950451	-1.0629663314	2.6405980904
C	-2.0555557401	-2.7657050057	1.8474363396
C	-5.1790437744	-1.7326365042	-0.1800590229
C	-4.8759792959	0.4064332127	-1.2677189009
C	-0.4830892197	-2.1120113598	-0.990020813
C	-2.5703791898	-2.2676091177	-2.2088016052
C	-3.6982572241	-1.7244103873	3.8573005609
C	-2.1970997422	-3.4024159439	3.0698212992
C	-6.4732397999	-1.7540970052	-0.6635620352
C	-6.1854307302	0.3527738007	-1.7441422972
C	0.1162422163	-2.9702119706	-1.9064429311
C	-1.9359358387	-3.1044986706	-3.1107840352
C	-2.9971162424	-2.9087866207	4.0842885117
Cl	-1.3000084748	-4.9592817837	3.3452040886
C	-6.9997476304	-0.7343638061	-1.4421476132
Cl	-7.5308587378	-3.1780311365	-0.2665855777
C	-0.6101062778	-3.4759353804	-2.9844830222
H	1.1626455857	-3.2367941583	-1.7925376216
Br	0.4944398079	0.3682341961	1.7153331418
C	-2.2285494162	2.5085628321	-1.3709316574
C	-3.2785294343	3.4261875587	-1.3455537492
C	-1.8173010576	2.0793332365	-2.6390175066
C	-3.9013424688	3.8456399102	-2.518596196
C	-2.4318189066	2.4765035392	-3.8276827339
C	-3.4918966776	3.3623397643	-3.7620793863
N	-0.6845752415	1.1708527832	-2.7535886531
O	-0.1286660249	0.7963320351	-1.7073407253
O	-0.3082963985	0.8163957167	-3.8514635124
H	1.4710866197	6.8046140632	0.2333812331
H	2.5052800159	4.9125675189	-0.984602228
H	1.390637298	2.6837101449	-1.0033289795
H	-1.8657792633	6.8149314488	1.7454723662
H	-0.4860898709	7.7840597745	1.1959764022
H	-0.4048446375	6.9212586994	2.7316107953
H	-2.8853493387	4.7394870232	1.4258115166
H	-3.4256080186	2.4029042954	1.1753885922
H	-1.3584891495	5.1261187857	3.5958383407
H	-2.1584795535	0.9410937725	3.0797134757
H	-4.027638615	4.6845054289	3.4775142616
H	-3.2262673126	4.3184460496	5.0107012158
H	-3.6246547645	2.019776494	4.7369268169
H	-4.4832872839	2.3353114135	3.2218151041
H	-1.11396098	2.7329093288	4.7296501496
H	-0.2224508764	2.7572075962	3.1812508153
H	-4.1418399224	-0.1474894402	2.4648656799
H	-1.4188923732	-3.190926006	1.077507175
H	-4.800674318	-2.5576077549	0.4173843677
H	-4.2547953178	1.2644128333	-1.4989245791
H	0.1043459652	-1.6857507215	-0.177116418
H	-3.6160140146	-2.0104624685	-2.3452382844
H	-4.3394135195	-1.3218269057	4.6361573005
H	-6.5725775951	1.1653996255	-2.3521249366
Cl	-2.8971060693	-3.7372088297	-4.521797213
H	-3.0756002669	-3.4364684579	5.0285240696
H	-8.0215326649	-0.7928812161	-1.8031689594

H	-0.1516021182	-4.1359922572	-3.7134843041
H	-3.6451277525	3.8120436813	-0.3961275082
H	-4.7225253835	4.558556276	-2.4594531302
H	-2.0644047103	2.0869625438	-4.7732986229
H	-3.9889818249	3.6861405443	-4.6731613476

VIIa*

79

C	5.0738662811	0.1003861683	1.3315864166
C	3.864886427	-0.5304407195	1.0106899371
C	2.9612436353	-0.7235807158	2.0630216138
C	3.209058439	-0.2247552679	3.3362185628
C	4.3903089844	0.4621497171	3.6050325511
C	5.3372991	0.6033341643	2.6038348467
Pd	0.6431322125	-0.6234363082	-0.6683478338
P	-1.541107269	-0.0923166796	-0.237043493
C	1.1439633077	1.2441976591	-1.4244150511
C	2.6544827905	0.9923811791	-1.5923559598
C	3.2587991159	2.0718073421	-0.6700889508
C	3.0768319409	3.4085931408	-1.415204984
C	1.5483908167	3.6539951108	-1.3444392758
C	1.0490166201	2.4544732324	-0.5097255843
C	2.2235549003	2.2470919214	0.4474455443
C	2.9081400557	-0.5227268649	-1.4069127923
C	3.5355483455	-1.1614857648	-0.3005491755
C	3.844751362	-2.5202595193	-0.3509540511
C	3.5515359926	-3.2854857232	-1.4681679827
C	2.9366905913	-2.6896419249	-2.5554942102
C	2.6206087941	-1.3309581805	-2.5535452489
C	2.1002763415	-0.7485546989	-3.8398192864
Br	0.2696637519	-3.0313947676	0.4168364932
O	7.2695683351	0.4973833651	0.7563033951
O	5.8817290295	0.0727578453	-0.8408173085
N	6.1516419526	0.233910058	0.3403401163
C	-1.922464628	-0.2149708235	1.5640956432
C	-3.048034784	-0.8881885089	2.0318278635
C	-1.0211203929	0.3648719371	2.4633304924
C	-3.2543301267	-0.945955549	3.4005377692
C	-1.2650470694	0.3007946568	3.8307301823
C	-2.393033474	-0.3632205761	4.3128122404
Cl	-4.7183255412	-1.8252812152	4.020551751
C	-2.8669404074	-1.072311701	-1.071385912
C	-4.1579801916	-0.5353250088	-1.1518579955
C	-2.5932998936	-2.3258899927	-1.6171635247
C	-5.1429188868	-1.2813465383	-1.7711102331
C	-3.6103277181	-3.049242832	-2.2388817806
C	-4.8993932802	-2.5302775521	-2.3206168366
Cl	-6.8209722407	-0.5886470594	-1.8782178115
C	-2.0826430809	1.6284958347	-0.6541689918
C	-2.3719070453	2.5699462275	0.3322148905
C	-2.0683924836	2.0044940574	-2.0009069802
C	-2.6095803733	3.8782772894	-0.0573192032
C	-2.3174262849	3.3241960719	-2.3595556027
C	-2.5806123438	4.2824810484	-1.3796399801
Cl	-2.9499308686	5.1162842925	1.2300917443
H	2.042058963	-1.2777350908	1.8550996228
H	2.4726435239	-0.3805954821	4.1226894087
H	4.5862017177	0.8634809557	4.5966800989
H	6.290646276	1.089711131	2.7872531981
H	0.5700655921	1.3538671674	-2.354458927
H	2.9813865792	1.2172983774	-2.619506056
H	4.2940348472	1.8926456226	-0.3742682002
H	3.4625881916	3.3711195687	-2.4423240611
H	3.62680376	4.2020397504	-0.8923344738
H	1.0679472154	3.6930908604	-2.332103207
H	1.3091812838	4.5963354941	-0.8324049293
H	0.0641064012	2.6224831803	-0.0650144854
H	2.4288170872	3.1320251306	1.0664799698
H	2.1082383988	1.3774954232	1.1042001263
H	4.3091227417	-2.9809098779	0.5201200132
H	3.7942487138	-4.3459058574	-1.4831899881
H	2.7071752008	-3.2795206467	-3.4421591853
H	1.2219719578	-0.106983295	-3.7157839504
H	1.826029102	-1.5503520973	-4.5341779668
H	2.8750271636	-0.1423172413	-4.3335487906
H	-3.7455185208	-1.3660447319	1.3505323242
H	-0.1258660136	0.8622109553	2.0900408138
H	-0.5753583028	0.7628797445	4.5307843237
H	-2.5932659776	-0.4302336287	5.377004113
H	-4.3888853415	0.4450690767	-0.7432826098
H	-1.5920527812	-2.7435875141	-1.533337857
H	-3.3970594782	-4.0269347886	-2.6603197891
H	-5.6997343976	-3.0832502632	-2.8013311551
H	-2.3889438985	2.2980945966	1.3833214462
H	-1.856703597	1.2617390435	-2.7684086672
H	-2.3036857718	3.6169728403	-3.4050082413
H	-2.7630173757	5.319120769	-1.641882932

VIIIa*

79

C	4.7405267109	0.5321344256	1.5141369348
C	3.7253478194	-0.3617594989	1.1295166077
C	2.6550096335	-0.4873032221	2.0249487524
C	2.5797250017	0.25842594	3.1954243814
C	3.5905173374	1.1550820998	3.5290093614
C	4.6874043937	1.2752620709	2.6907904242
Pd	0.8501903503	-0.5005324429	-0.7504759362
P	-1.5242564975	-0.0230960018	-0.2799317806
C	0.7879146128	1.4813471934	-1.8404483367
C	2.1169284759	1.0977558887	-1.9248471052

C	2.910307875	2.1085566414	-1.135927322
C	2.8477999214	3.3791529187	-2.0339797068
C	1.3653429942	3.8162886855	-1.9280578189
C	0.7537964083	2.737155183	-0.9944223588
C	1.9251054131	2.5056584272	-0.0343440773
C	2.7500049185	-1.330348708	-1.0058348141
C	3.7886699727	-1.2295680275	-0.0726969532
C	4.9348406669	-2.0217372154	-0.2489941355
C	5.0640398785	-2.8566042435	-1.3437286275
C	4.043193715	-2.908560392	-2.2860933878
C	2.876385173	-2.1583709747	-2.131040542
C	1.7743200865	-2.3087239854	-3.1407354349
Br	0.3120678652	-2.7885531686	0.3543769884
O	6.9868612807	0.9707547148	1.2822497809
O	5.8282571166	0.7630774509	-0.5269682544
N	5.9382173095	0.7641469665	0.689732687
C	-1.7845364599	-0.0580692827	1.5473214062
C	-2.6858974408	-0.9236814372	2.162642698
C	-0.9854322714	0.7902804521	2.3229155792
C	-2.7888237916	-0.8922668823	3.5438391362
C	-1.1191112766	0.8039517439	3.7077750184
C	-2.0302536679	-0.0460533447	4.3333135296
Cl	-3.9733401833	-2.0071648603	4.3514370162
C	-2.8063191068	-1.1566822137	-0.986941229
C	-4.1639972266	-0.8814121668	-0.7807236137
C	-2.4260001271	-2.245096857	-1.7710487601
C	-5.0996443582	-1.7258828803	-1.3483009532
C	-3.3955389211	-3.0700594072	-2.3393728871
C	-4.7472065847	-2.8178296437	-2.125565169
Cl	-6.863983599	-1.3840922741	-1.0719458372
C	-2.3137367084	1.5963911589	-0.7485901457
C	-2.6250866451	2.5812068338	0.1880126936
C	-2.5119190573	1.8467396299	-2.1113496698
C	-3.0927375327	3.803373928	-0.2680087139
C	-2.9779092857	3.0851703943	-2.5373955953
C	-3.2647172978	4.0874175841	-1.6102189378
Cl	-3.4876207334	5.0895506009	0.9554920651
H	1.8817913981	-1.2217782225	1.8040338672
H	1.7301864617	0.1141299461	3.8607757742
H	3.5402829089	1.7402241862	4.4445256526
H	5.5109438229	1.9437491036	2.9264275802
H	0.0481000613	1.2841927513	-2.6168713347
H	2.5535642897	0.5396883234	-2.7491471094
H	3.9177831424	1.802490234	-0.8478076898
H	3.1648985784	3.1739053247	-3.063939246
H	3.5231312013	4.1448241465	-1.6318136936
H	0.8520884311	3.8579003572	-2.8976411639
H	1.268601183	4.8060854344	-1.4637401088
H	-0.2156058521	3.0064108687	-0.5656638187
H	2.2285274238	3.4224446964	0.4893680055
H	1.7558108744	1.7070618474	0.702539857
H	5.7291582848	-1.9758098522	0.4976707358
H	5.9585651824	-3.4643298858	-1.4657557837
H	4.1374827416	-3.5595618948	-3.1566228362
H	0.9495905952	-2.9035306702	-2.7219647272
H	2.1310573132	-2.8205162247	-4.0436406462
H	1.3469720852	-1.3423734955	-3.4482438836
H	-3.28870942	-1.6162168314	1.5825965867
H	-0.2560726193	1.4433303306	1.8428072223
H	-0.512304113	1.4771280441	4.3071141909
H	-2.1433749395	-0.0534838074	5.4120311803
H	-4.4855364387	-0.024654242	-0.193687551
H	-1.37154834	-2.4629897384	-1.9172043489
H	-3.096269988	-3.9188898111	-2.9465537746
H	-5.5143081952	-3.4542254933	-2.5541212618
H	-2.4991253914	2.409926993	1.2528142616
H	-2.3091978064	1.0664578979	-2.8434085182
H	-3.1239050973	3.276473287	-3.5962955373
H	-3.6233339366	5.0613235953	-1.9263058376

cis-**IXa***

96

C	0.8907392861	3.7066714873	-0.363392844
C	1.9726070875	3.2783461609	0.5671867018
C	1.8087951295	2.6676798545	1.8149506641
C	2.8777368771	2.2060535453	2.5832904955
C	4.1691490132	2.3801406967	2.1138818775
C	4.3735846263	3.0135367275	0.8887360364
C	3.2919802503	3.4470297035	0.1328523152
C	0.6290403819	5.0753693075	-0.4714938279
C	-0.232902745	5.5458591658	-1.4509327289
C	-0.7905943232	4.6473970212	-2.3513840001
C	-0.5486741868	3.2704948847	-2.2660404175
C	0.2600539258	2.79473335	-1.2217758218
C	-1.212180776	2.3734373792	-3.2675074273
Pd	0.6422330813	0.8065775687	-0.7481300965
H	2.6823814737	1.7449785828	3.5486700942
H	5.0139465118	2.0293807544	2.7022132507
H	5.3840564039	3.1512887804	0.5106541216
H	1.1213152537	5.7631466405	0.2168707795
H	-0.4407357748	6.6111761163	-1.534961983
H	-1.4356787549	5.010728438	-3.1529942706
H	-2.1696185758	1.9784175002	-2.8937946036
H	-1.4290750535	2.9220753589	-4.1926140474
H	-0.5808712308	1.5133096777	-3.5203560746
P	-1.6159138499	0.4482689163	0.0990075038
C	-2.5977845993	-0.1029462111	-1.37865933
C	-1.9890125497	-0.9483729598	1.2656994889
C	-2.7254388529	1.7701205957	0.7875230947
C	-2.6848736056	3.0429933925	0.2144456704
C	-3.5274706014	4.0465624752	0.678656022
C	-4.4245920082	3.7938129323	1.7141231867
C	-4.454790513	2.5201261744	2.2539564617

C	-3.6282039987	1.4988954297	1.8183648932
C	-1.960938962	-0.7968362866	-2.408704486
C	-2.6962717528	-1.2684317533	-3.4931380311
C	-4.0669298481	-1.0356194504	-3.5668483928
C	-4.6724047031	-0.3335338868	-2.537172037
C	-3.9729669594	0.1363293492	-1.4398021648
C	-2.7148579827	-2.0691779048	0.8515671582
C	-2.9820947355	-3.0597608224	1.7837095575
C	-2.581364017	-2.9730042554	3.1050256496
C	-1.880705654	-1.8399567277	3.5100753186
C	-1.574064413	-0.8360066909	2.5971153544
Cl	-5.6387258512	2.1663674177	3.5910924143
Cl	-3.9412718591	-4.516219389	1.2700584028
Cl	-6.4615786703	-0.0251600837	-2.6281376692
H	-1.9940889634	3.2519118522	-0.5928846109
H	-3.4779222799	5.0352156559	0.2314313719
H	-5.0871727398	4.5660334812	2.0909483158
H	-3.6874750238	0.5166205716	2.2754011163
H	-0.8846439964	-0.9549364001	-2.3770165026
H	-2.1966492781	-1.8193605547	-4.28538533
H	-4.6551044988	-1.3924557105	-4.4058289545
H	-4.4869421657	0.6770445599	-0.6495052707
H	-3.0903385204	-2.1584041639	-0.1650007268
H	-2.8240029717	-3.7656748198	3.8051281649
H	-1.5769451069	-1.7385592667	4.5481231427
H	-1.0388361029	0.0517752395	2.9306709822
P	1.5439598403	-1.4284370909	-0.1951493891
C	0.9380518563	-2.6258702959	-1.4653768699
C	1.2718241372	-2.251126029	1.4449654036
C	3.3831616149	-1.6940290605	-0.2215935681
C	3.906257809	-2.9646167639	-0.4692236057
C	5.2798007518	-3.1798290089	-0.4176654123
C	6.1407881166	-2.1288440061	-0.1135522403
C	5.5944840327	-0.8829189399	0.1403007383
C	4.2322464561	-0.6323404657	0.0985217039
C	1.5930699327	-2.6920773245	-2.7009243383
C	1.0417453694	-3.4225909568	-3.7493955066
C	-0.1724051108	-4.0861595798	-3.586518326
C	-0.8064784132	-3.9971672067	-2.3597924145
C	-0.2844010954	-3.2836905289	-1.2939761794
C	1.3920221399	-1.4161791768	2.5590506551
C	1.3728666056	-1.9926988888	3.8147388515
C	1.2123082822	-3.3529174388	4.0141859438
C	1.067834669	-4.1704590198	2.8956061161
C	1.1059926344	-3.6253497869	1.6134593098
Cl	6.7472978988	0.4788308996	0.5105036815
Cl	1.5052932438	-0.9083803991	5.2711916562
Cl	-2.4302524022	-4.7810875845	-2.1632523597
H	7.2154579417	-2.2728402061	-0.0765685553
H	2.5256525272	-2.1557533159	-2.8552688348
H	1.5560757755	-3.4671654466	-4.7048012226
H	-0.620892226	-4.651490562	-4.3969097161
H	-0.8452083713	-3.2160361347	-0.3636517831
H	1.4483524775	-0.3333964843	2.4543113525
H	1.1944638929	-3.7633505713	5.0188107496
H	0.9352888411	-5.2406245845	3.0249910033
H	1.0155569641	-4.2797958702	0.7503659083
I	2.5029317477	1.1133201634	-2.6443197701
H	3.4528359056	3.9077233562	-0.8404171458
O	0.2989942952	1.5802192591	3.162069298
N	0.4805178153	2.5369597486	2.4088169782
O	-0.3573133091	3.3828396976	2.1658858874
H	5.6842941304	-4.168059773	-0.6157879981
H	3.8468784046	0.3673526743	0.2931395784
H	3.2427158922	-3.7900767187	-0.7132244336

Xa*

96

C	-1.5783838041	-4.009231224	-0.8281236932
C	-0.1203672819	-3.9137995234	-1.1132249944
C	0.5088750972	-3.0039400547	-1.9825492791
C	1.8939954601	-2.9896517264	-2.1582253993
C	2.6895141676	-3.8842497686	-1.4627174382
C	2.0934571928	-4.8047140288	-0.6059699918
C	0.7156491361	-4.8102082781	-0.4383489266
C	-2.4101851821	-4.6479927701	-1.7522819113
C	-3.7658638255	-4.7886876252	-1.5067007853
C	-4.3148428795	-4.273830183	-0.337285348
C	-3.5251430011	-3.6351163601	0.6204053499
C	-2.1461921642	-3.5426382819	0.3656633254
C	-4.1656071427	-3.0334178143	1.8319550056
Pd	0.2071050606	-0.7138645673	0.0012646606
H	2.334502738	-2.2726849673	-2.8455872138
H	3.7705138375	-3.8603817761	-1.5875369127
H	2.7064185231	-5.5198423634	-0.0602503451
H	-1.9753081244	-5.0097302021	-2.6829995287
H	-4.4020367173	-5.2879116992	-2.2348524564
H	-5.3857306073	-4.360437278	-0.1531457259
H	-5.2528880511	-3.1666701563	1.8085246122
H	-3.7888316723	-3.4754095201	2.7644872013
H	-3.9616253492	-1.9540385372	1.8912293699
P	-1.6536658248	0.6888953508	-0.2979552462
C	-2.3721601177	0.9201176619	1.4025129999
C	-1.141285312	2.4175302384	-0.7305884583
C	-3.21617951	0.4614328878	-1.2660731408
C	-3.7171475035	-0.8403175153	-1.3621960954
C	-4.9139685297	-1.0799113653	-2.0302320874
C	-5.6103606344	-0.0283066515	-2.6250231211
C	-5.0842389986	1.2486077535	-2.5223109501
C	-3.9041968185	1.5231320298	-1.8529930125
C	-1.4960583436	1.2615813443	2.4404342479
C	-1.9439197326	1.3067788451	3.7545477817
C	-3.2661488885	0.9772448828	4.0616198521

C -4.1079305012 0.6384269843 3.0190359108
C -3.7026255718 0.6199672215 1.6934970919
C -1.6778543686 3.5540449211 -0.1221278168
C -1.1328981923 4.7873275948 -0.4401792958
C -0.0643046372 4.9377790533 -1.3081954938
C 0.458534514 3.7970823641 -1.918078487
C -0.0867370423 2.5477139881 -1.6388832596
Cl -5.9906166818 2.63065746 -3.2919539859
Cl -1.8303988646 6.2721118977 0.3505251301
Cl -5.8320926773 0.1728816141 3.3981591537
H -3.166217471 -1.667149333 -0.9170385952
H -5.2985182335 -2.0935926214 -2.098363027
H -6.538567356 -0.1978896938 -3.1611221904
H -3.5305882697 2.5414334976 -1.7902662786
H -0.4512521624 1.4725167489 2.2218831687
H -1.2563507407 1.5860437845 4.5488374032
H -3.6275612547 0.9818999158 5.0845999278
H -4.4067581832 0.3577984076 0.9084374023
H -2.4854383993 3.480533382 0.6020739222
H 0.3550796792 5.9206937531 -1.496474909
H 1.3137434339 3.8749298072 -2.5867152261
H 0.3289295569 1.6535292828 -2.0988317861
P 2.3905306122 0.0246533217 0.1328722664
C 2.4734657788 1.1121137622 1.6401405617
C 3.0903725182 1.146870804 -1.1677549623
C 3.8238727815 -1.1260389783 0.4142868022
C 3.5796071424 -2.2739429219 1.174315652
C 4.5947215679 -3.1966935653 1.4068367567
C 5.8590908976 -3.0036417239 0.8504342371
C 6.0693561511 -1.8712691812 0.0822421813
C 5.0861374853 -0.9220973202 -0.1443125007
C 3.122055543 0.7238811172 2.8119442708
C 2.9929752225 1.4871722133 3.9725183801
C 2.2116330018 2.6399048485 3.9782826271
C 1.5886393573 3.012000314 2.7966547507
C 1.7058706782 2.2858482707 1.627147047
C 3.918915316 2.2262861769 -0.8515335578
C 4.3678143379 3.0375349893 -1.8791676118
C 4.0334252157 2.8203354349 -3.2056902507
C 3.2115690767 1.7355109787 -3.5108077576
C 2.7393133117 0.9027163751 -2.4979493498
Cl 7.7141591297 -1.6121711118 -0.6565514894
Cl 5.4307722364 4.4566930533 -1.4667136588
Cl 0.5163804837 4.4795534629 2.7930710894
H 6.6601865285 -3.7185447968 1.0067138518
H 3.7248347041 -0.1805588102 2.8245912824
H 3.5018229584 1.1805962382 4.8821168493
H 2.0888326049 3.2368430024 4.8758912742
H 1.1892326673 2.615614233 0.7262598663
H 4.2008725137 2.4345949385 0.1773005162
H 4.4031218172 3.4839622288 -3.9810443404
H 2.9307804036 1.5500206184 -4.5436764209
H 2.0608965019 0.083163865 -2.7359712421
I -0.9118273733 -2.6479387897 1.8382268659
H 0.2517467613 -5.5251741178 0.2404911023
O 0.3693884305 -1.1614372055 -3.3839963951
O -1.4628431166 -2.1762195996 -2.8898328915
H 4.4011809736 -4.0822868077 2.0060656004
H 5.301633581 -0.0437631382 -0.7458014624
H 2.5752358802 -2.4547475833 1.5585508558
N -0.2564734539 -2.0389833829 -2.8008168997

Vb

83

C -4.1318810586 -2.4937620509 -2.11039051
C -4.1122320563 -3.0026884317 0.6242798781
C -5.3138501396 -3.0116268554 -0.0701706892
C -5.3218293637 -2.7504032456 -1.4364304115
Pd -1.1173329519 0.5771060839 -0.0326244462
Br -1.2967612671 -2.1783755531 -2.40129773
H -6.2425403982 -3.2208833812 0.4562233971
C -3.1300930833 0.7275709551 0.4660840024
C -3.7158292252 2.1568360518 0.3057415183
C -4.0220966126 2.5613121735 1.7725051126
C -5.2809430825 1.8025781393 2.2076483278
C -4.7870602505 0.3339991207 2.2904959698
C -3.2813633501 0.450039925 1.9644460762
C -2.9442410132 1.8186928742 2.5678603092
C -2.7446849279 3.0159348876 -0.4307300262
C -1.4834357007 2.4417258413 -0.6853871491
C -0.5512159764 3.1488351927 -1.4491345358
C -0.8568634746 4.4177827993 -1.933882838
C -2.0979676665 4.9840234362 -1.6664856171
C -3.0574578966 4.2948070619 -0.9239307614
C -4.4090759399 4.9084776917 -0.6963585163
P 1.3206462043 0.3030498338 -0.0529858868
H -0.1249296089 4.9632868162 -2.5301820741
H -2.340221934 5.9747042829 -2.0550750611
H -4.6728719512 2.1294640869 -0.2490766791
H -3.6503005254 -0.017199682 -0.1583490909
H -2.6958089936 -0.405658587 2.3360194961
H -4.0719125714 3.6452952202 1.9351501744
H -1.9245457973 2.1546636368 2.3371137018
H -3.1124798677 1.8728366825 3.6540503968
H -4.9415166883 -0.0829371816 3.2970368505
H -5.3023350135 -0.329149269 1.5801977478
H -6.1102986561 1.93671369 1.4990823491
H -5.6288253008 2.1567433421 3.1882556542
H -4.5185034307 5.8434796804 -1.2602851239
H -5.2204375503 4.2345096794 -1.0087012426
H -4.5910830148 5.1427517643 0.3621995687
H 0.4215260019 2.7126531781 -1.6776505151
H -4.0923305409 -3.1962866424 1.6954905102

H	-6.2587746166	-2.7541255505	-1.9900923142
C	2.6121238798	1.5780844494	-0.4399094258
C	2.3880589949	2.8627522288	0.0664879026
C	3.7801971296	1.3028834665	-1.1513246815
C	3.3283843371	3.8668765599	-0.1360692133
H	1.4660563044	3.0762455106	0.6049977274
C	4.696574327	2.3249805595	-1.3373287479
H	3.9762800635	0.3139212023	-1.556485726
C	4.4996997131	3.6029762591	-0.8454238298
H	3.1497412308	4.8646978591	0.2540305234
H	5.2439360516	4.3741023673	-1.0143584657
Cl	6.224230555	1.9656902035	-2.2554247426
C	1.9002079374	-1.1642191842	-1.0147230136
C	1.8956193632	-1.0889171028	-2.4127191124
C	2.1457928879	-2.3868513721	-0.3928190988
C	2.1744147548	-2.2178207033	-3.1765644142
H	1.6572565862	-0.1447265431	-2.9017770638
C	2.3884967485	-3.4999191562	-1.1781618374
H	2.1398174511	-2.4677110766	0.6900205119
C	2.4225195558	-3.4456812282	-2.559487547
H	2.1844512491	-2.1525281624	-4.2608546642
H	2.6229705143	-4.3390610079	-3.1409892565
Cl	2.6481510074	-5.0953496914	-0.3441085326
C	1.8698115238	-0.106987255	1.6770325546
C	0.932369688	-0.0571216595	2.7092853796
C	3.2041496011	-0.4110471667	1.9635641683
C	1.3199517467	-0.3199372369	4.0231226105
H	-0.1000080616	0.1990320116	2.4768358875
C	3.5573066285	-0.6809552824	3.2730649764
H	3.9579291182	-0.4342005252	1.1806073698
C	2.6424071607	-0.6421359472	4.314118314
H	0.5903382605	-0.2643892185	4.8266199607
H	2.9647798188	-0.8488043269	5.3294458632
Cl	5.2871535454	-1.0876163577	3.6478641677
O	-1.5312727153	-3.5987679379	1.6350871393
O	-0.8969033369	-1.6545106038	0.7415036332
H	-4.1261195206	-2.3115112618	-3.1823382492
C	-0.3803431596	-3.5387080841	2.4832025712
H	-0.3522733305	-2.5939813424	3.0375707397
H	-0.4692103687	-4.3887216586	3.1610152639
H	0.5317468429	-3.6284635325	1.8825588275
C	-1.6786743034	-2.5890927907	0.7859442563
C	-2.9110711573	-2.7099127167	-0.0287216188
C	-2.9371195725	-2.4720806423	-1.4049931902

VIb

83

C	-4.2494840428	0.0399219811	0.272134553
C	-3.3719963988	-0.4482330393	-0.6973929988
C	-5.6204550248	-0.2466875119	0.1455054217
C	-6.0511023408	-0.9746232248	-0.9649625334
C	-5.1625382978	-1.4060264285	-1.9431533571
C	-3.7991754237	-1.1518767683	-1.8117931807
C	-6.6248285848	0.188259866	1.1745751426
C	-3.652874386	0.8519861509	1.3822335134
C	-2.1238827604	1.0375267043	1.1592249114
C	-4.1362367523	2.3260399605	1.4067798263
C	-1.9535240972	2.534601224	0.925655729
C	-3.5749889386	2.9964304792	2.6680384191
C	-2.0731944761	3.1731683149	2.3281464204
C	-3.2859730406	2.9516973886	0.3020420013
Pd	-1.394800485	-0.1616095323	-0.3892235142
P	1.1574843637	0.1394789142	0.0118641998
C	1.7815811554	1.8794638896	0.0615654934
C	1.9784032813	-0.5683178728	1.52058535
C	2.1671839011	-0.6537414764	-1.3275547266
C	1.34712699	2.6844243499	1.1202828116
C	2.6150331445	2.410965516	-0.9188492306
C	3.0181986274	0.0966914185	2.1752448751
C	1.572093884	-1.8288509218	1.9696891701
C	1.8891341969	-0.3372859999	-2.6634243792
C	3.1636255795	-1.5830708478	-1.0229045919
C	1.7352929937	4.0168438614	1.1940510855
C	2.9855523595	3.7425969212	-0.8194606638
C	3.6056865936	-0.5094218737	3.2723890431
C	2.1862437856	-2.4145555841	3.0725204656
C	2.6296691643	-0.9265818191	-3.683660161
C	3.8652704109	-2.1679779411	-2.0645357996
C	2.5614251686	4.5613507424	0.2117867083
Cl	4.0697571011	4.4395737658	-2.0962038
C	3.2118430689	-1.7511338403	3.7421570961
Cl	4.9512991218	0.3602611071	4.1270727146
C	3.6294642091	-1.8547355559	-3.3913901619
H	2.4213832515	-0.6685713483	-4.7182387392
Br	-1.1940509709	1.6259257886	-2.3124236576
C	-1.5263896099	-1.8519180681	0.7802295587
C	-1.9321522976	-1.9668403201	2.1061692514
C	-1.0555455619	-3.0143499024	0.134244663
C	-1.8568604683	-3.1867952632	2.7753725257
C	-0.976944347	-4.2393503598	0.8096257082
C	-1.3766305034	-4.3266602271	2.133603846
O	-0.6537676225	-1.8333091775	-1.8854793341
O	-0.0607785405	-3.9864568856	-1.7709747578
H	-7.1130945331	-1.2056977315	-1.0593742265
H	-5.5305884858	-1.9546869586	-2.8095198497
H	-3.0883087967	-1.4837874439	-2.5668994621
H	-6.2022142059	0.205602768	2.1878430718
H	-7.4864991071	-0.4909816616	1.1837487193
H	-7.014952546	1.1963055572	0.9721812002
H	-3.8593133783	0.3810910728	2.3601395928
H	-1.4967920266	0.6689989391	1.9849109317
H	-5.2216270384	2.4245921375	1.2970649738
H	-1.0469381316	2.819257174	0.3853311594

H	-3.7383200174	2.3868185153	3.568319509
H	-4.0597864448	3.9659307305	2.8420342994
H	-1.7956526933	4.23532648	2.2659856658
H	-1.4101231047	2.7072733209	3.0718775582
H	-3.3950519759	4.0434518455	0.2443724592
H	-3.4533802113	2.524072046	-0.6929775907
H	0.7087340289	2.2635721036	1.8950994375
H	2.966245231	1.8053402993	-1.7484481115
H	3.367075322	1.0678139933	1.8379036973
H	0.7831924982	-2.360303522	1.4485158399
H	1.0843027684	0.359412155	-2.9007650227
H	3.3939934612	-1.8451088164	0.0052919165
H	1.3921890966	4.6380561398	2.0165506789
H	1.8586932646	-3.3931396014	3.4119672178
Cl	5.1511625539	-3.389325125	-1.6693535974
H	2.86963184	5.6010610022	0.2462986141
H	3.6997545972	-2.1877043198	4.60773606
H	4.212644791	-2.3247206626	-4.1768454183
H	-2.3037705369	-1.100396377	2.6502476754
H	-2.17681783	-3.2449139044	3.815353466
H	-0.5965434811	-5.111747814	0.2817171451
H	-1.3225237364	-5.2762319166	2.6622428041
C	-0.5866349685	-2.8844184091	-1.2523516313
C	0.4597427666	-3.8651198372	-3.0972236295
H	0.8769402459	-4.8440218764	-3.3394283964
H	-0.3402208206	-3.6027918078	-3.7974933588
H	1.2367813043	-3.0944064685	-3.1355818652

VIIb

83

C	5.0446481084	0.0073106984	1.2993830005
C	3.8021588561	-0.5945487938	1.0273652456
C	2.8970443079	-0.7641414575	2.0805982204
C	3.1686248846	-0.263901993	3.3483430975
C	4.3699244619	0.3932490398	3.5960824696
C	5.308224607	0.5052965502	2.5810751666
Pd	0.6058777916	-0.6238769142	-0.6782753775
P	-1.5665097734	-0.075275151	-0.2347217166
C	1.1455997381	1.2326715907	-1.4401253582
C	2.6534278861	0.9518671675	-1.5983727763
C	3.2710429419	2.0214754013	-0.6755624037
C	3.1147481599	3.3606906649	-1.4229898896
C	1.5911233253	3.6371642105	-1.3547826827
C	1.0679165825	2.445746516	-0.5260548289
C	2.2333508276	2.2133764098	0.4366661846
C	2.8619462541	-0.5678406722	-1.4007261666
C	3.4490970499	-1.2217879949	-0.2807592291
C	3.6984818384	-2.5937261393	-0.3219169078
C	3.3886536186	-3.3546497254	-1.43605892
C	2.8143419175	-2.7420941055	-2.5363219064
C	2.55444264	-1.3729187981	-2.5460723639
C	2.072083132	-0.7785254525	-3.841785033
Br	0.1698381021	-2.9976816779	0.4095071942
O	7.2988622936	0.3814895186	0.7584720725
O	5.9092967048	-0.0597911044	-0.9443773263
C	-1.9459917117	-0.1698273754	1.5679911155
C	-3.0768919178	-0.8250359981	2.046757693
C	-1.0373594066	0.4140977775	2.4568433519
C	-3.2833998501	-0.8626487607	3.4162797355
C	-1.2803810802	0.3714404073	3.8250145797
C	-2.4139025406	-0.2744513637	4.317445479
Cl	-4.7513434775	-1.7178107151	4.0510307872
C	-2.9179378387	-1.0342755177	-1.0559666072
C	-4.1947597862	-0.4660479229	-1.1459667414
C	-2.6768210287	-2.304089064	-1.5792516931
C	-5.2004452225	-1.1949389504	-1.7526793954
C	-3.7132712375	-3.0100406286	-2.1883000013
C	-4.9877912862	-2.4590541469	-2.2800507952
Cl	-6.857832718	-0.4628389165	-1.8729537845
C	-2.0808535922	1.6530304086	-0.6641262817
C	-2.3579062641	2.6072836733	0.3130656084
C	-2.0531715723	2.0202788	-2.0131034181
C	-2.5707279074	3.9178382325	-0.0845009379
C	-2.2764822779	3.3414786339	-2.381683795
C	-2.5279384606	4.3107629915	-1.409908589
Cl	-2.8932772941	5.1695643893	1.1898523541
H	1.9639862822	-1.2992502748	1.8842019512
H	2.4371231663	-0.3977753071	4.1443306671
H	4.5876508489	0.7942558016	4.5842706814
H	6.2684791912	0.9770231608	2.772922875
H	0.5817040322	1.356943939	-2.3748156814
H	2.9981493489	1.1645650403	-2.6223513861
H	4.2997666016	1.8212798328	-0.3722935202
H	3.5011286227	3.3143902429	-2.4498337937
H	3.6791243504	4.1453723715	-0.9015575844
H	1.10961178	3.6880469207	-2.3421743849
H	1.370382119	4.5836568337	-0.8413918485
H	0.0844333357	2.6298450054	-0.084264686
H	2.4525590284	3.0907190462	1.0621597167
H	2.1000722296	1.341270099	1.0866047145
H	4.1273869072	-3.066653701	0.5606470568
H	3.5813676528	-4.4255107067	-1.4378709787
H	2.568858868	-3.3288938024	-3.4209847067
H	1.2179722522	-0.1025432761	-3.7312988752
H	1.7737416913	-1.573534792	-4.5345068218
H	2.8751901228	-0.2059467684	-4.3308480563
H	-3.7782082368	-1.307736958	1.372877176
H	-0.1374675876	0.895534358	2.0740698934
H	-0.5847478749	0.8370383286	4.517091115
H	-2.6152760891	-0.3253917059	5.3823708664
H	-4.4003806971	0.5265853338	-0.7537565733
H	-1.6879147786	-2.7486380088	-1.4827606101
H	-3.5252515091	-4.0011657695	-2.5903019197

H	-5.8040560446	-2.9976280027	-2.7504223559
H	-2.3837898384	2.3429850895	1.3660520695
H	-1.850238632	1.267009561	-2.7728286014
H	-2.2521560157	3.6266990187	-3.4293643988
H	-2.6910445474	5.3491626054	-1.6783456217
C	8.345057232	0.4859496102	-0.199021246
H	8.1232142947	1.2675835258	-0.9338762034
H	9.2449573174	0.7362120741	0.3665682313
H	8.4775168487	-0.4635423059	-0.7289611194
C	6.0876319418	0.0980555985	0.2438287098

VIIIb

83

C	4.7525186502	0.5451159244	1.4446846532
C	3.7052781989	-0.3396096277	1.113163263
C	2.6365106811	-0.4453765749	2.0113967468
C	2.5820441848	0.3227827214	3.1690162776
C	3.6077660533	1.2107586193	3.4732109829
C	4.6979274471	1.3008728394	2.6193956252
Pd	0.8297850387	-0.5302991278	-0.7590116008
P	-1.5348066583	-0.0528708156	-0.2573428276
C	0.7611327819	1.4304217168	-1.8914314065
C	2.0734335108	1.0181919093	-2.0454931816
C	2.934301002	2.0206193773	-1.3213629686
C	2.8406038802	3.2834595844	-2.2285022889
C	1.3767225129	3.7547551565	-2.0401573837
C	0.7997784898	2.6972499769	-1.0618201225
C	2.0197205866	2.4481695969	-0.1699818309
C	2.7297027022	-1.3627148791	-1.0096637792
C	3.7699190269	-1.2189725939	-0.0822159027
C	4.9387876918	-1.9745558775	-0.2694061782
C	5.086381395	-2.8151676136	-1.3583104842
C	4.0555135839	-2.9174821026	-2.2833099726
C	2.864957785	-2.2070120797	-2.1195806126
C	1.7511165869	-2.4252576477	-3.1038880392
Br	0.3066512516	-2.7930008981	0.377835112
O	7.0751776283	0.7414680471	1.2732782604
O	5.9179033081	0.912181519	-0.639458483
C	-1.8178554407	-0.1375070527	1.5655410738
C	-2.8131123539	-0.9297391868	2.1320990804
C	-0.965307187	0.6123176122	2.382925693
C	-2.9501724777	-0.9292397348	3.5108602515
C	-1.1370919874	0.6018567339	3.7635703328
C	-2.1389587423	-0.1760837683	4.3410183742
Cl	-4.2487037428	-1.9502835683	4.2589291678
C	-2.8417699337	-1.1393616611	-0.994383163
C	-4.1887442685	-0.7733257273	-0.8779966107
C	-2.4919847015	-2.29664888	-1.6898645659
C	-5.1484974191	-1.5887209634	-1.4476112726
C	-3.4836845899	-3.0939482174	-2.2594776966
C	-4.8253597793	-2.7455738489	-2.1396053
Cl	-6.8949984664	-1.1193650728	-1.2922811981
C	-2.2937375896	1.5984768437	-0.6661527942
C	-2.5465412056	2.5646305769	0.3063466174
C	-2.5219288185	1.8972760721	-2.0146335073
C	-2.9909164356	3.8141445779	-0.0971153108
C	-2.9613693108	3.1613199112	-2.3898064792
C	-3.192713278	4.1422782744	-1.4252396636
Cl	-3.3161312823	5.0672580796	1.1752116742
H	1.8531614071	-1.1757108631	1.8129457197
H	1.7401688887	0.1963824079	3.8489561632
H	3.5748150495	1.8100066144	4.3813809126
H	5.5243904409	1.9687761584	2.85454738
H	-0.0244293824	1.2381205042	-2.6224052568
H	2.4490121019	0.4219873982	-2.8736444789
H	3.952407373	1.699268114	-1.0880186932
H	3.0919291123	3.0636007296	-3.2737991013
H	3.5544755527	4.0387486592	-1.8757370868
H	0.8085692618	3.799949331	-2.9789499498
H	1.3297075361	4.7514899562	-1.5824069133
H	-0.1382639582	2.98721596	-0.5787514694
H	2.3719189336	3.3592359239	0.3333044267
H	1.8755717807	1.6531928071	0.5744127222
H	5.7359042541	-1.8973451392	0.472587243
H	6.000487892	-3.3924316935	-1.4854170889
H	4.1588809924	-3.5779716248	-3.1459480358
H	1.0072092782	-3.1197092593	-2.6865603601
H	2.1272683095	-2.859132775	-4.0396054509
H	1.2137620043	-1.4974509247	-3.3518548434
H	-3.4650556324	-1.5423760445	1.5167000867
H	-0.1626576644	1.2018384878	1.9393699801
H	-0.486625828	1.1991194572	4.3966597568
H	-2.2832845763	-0.2028282318	5.4158638105
H	-4.483020397	0.1348075243	-0.357944847
H	-1.4474385792	-2.5875583544	-1.7606605742
H	-3.2086295404	-3.9973852347	-2.7958534431
H	-5.6094856127	-3.356461575	-2.5750005433
H	-2.3961591057	2.3552031844	1.3613545368
H	-2.3664772433	1.1313968674	-2.7730048572
H	-3.1320167608	3.3889196036	-3.4380906974
H	-3.5322579386	5.1357128532	-1.6995628218
C	5.9341679144	0.7430679738	0.5592978292
C	8.2580328506	0.9486847965	0.5089177112
H	8.221485905	1.9113649579	-0.0127176536
H	9.0837261164	0.930039789	1.2229603311
H	8.3761212652	0.1538387801	-0.2359402944

cis-IXb

100

C	-1.0936012296	-3.5095884757	-0.3285511382

C	-2.2250588205	-2.9612479584	0.4845200277
C	-2.1773163983	-2.5059727423	1.816459597
C	-3.3620854684	-2.1386221147	2.4751606887
C	-4.5883070979	-2.2081308347	1.835830209
C	-4.6457323664	-2.6666859259	0.5220101794
C	-3.4808730538	-3.0405562054	-0.1332565268
C	-0.8846131566	-4.8910917676	-0.2594826008
C	-0.0494753394	-5.5230239665	-1.1712107668
C	0.5445658387	-4.7774127667	-2.1811614548
C	0.3794160779	-3.3880048762	-2.2590247717
C	-0.4058619858	-2.7545551876	-1.2879123201
C	1.1069144059	-2.6255751033	-3.323640464
Pd	-0.6101002161	-0.7375634605	-0.9225450378
H	-3.3050613343	-1.7945149289	3.5050875238
H	-5.4943965092	-1.9092129905	2.3598269122
H	-5.6015721164	-2.7412205425	0.0046048437
H	-1.4177713919	-5.4687563191	0.497317545
H	0.1045117959	-6.5997855042	-1.1185822353
H	1.1705488481	-5.2698834019	-2.9270924928
H	1.9563477695	-2.0627115071	-2.9080939883
H	1.5054643483	-3.301144424	-4.0905501794
H	0.448879943	-1.895481686	-3.8133363979
P	1.6938155591	-0.5284573243	-0.1128987705
C	2.6411167848	0.1211967957	-1.5786676461
C	2.1023525956	0.7742708956	1.1462338548
C	2.8227166351	-1.8704216368	0.5107836505
C	2.6409104677	-3.1757155208	0.0569916348
C	3.4708773481	-4.1974127571	0.506671156
C	4.491905799	-3.930662862	1.4155944375
C	4.6543181927	-2.6262264416	1.8496722286
C	3.8438118314	-1.5880852076	1.4239208092
C	1.9422833906	0.7155740251	-2.6327685317
C	2.6304650014	1.2546548125	-3.7165708938
C	4.0199391364	1.2030201958	-3.762508502
C	4.6922416923	0.5984018527	-2.713068026
C	4.0371449154	0.0511507993	-1.6238518456
C	2.8617420698	1.9083338397	0.8500266315
C	3.1533529459	2.7918894048	1.8815391728
C	2.7574602903	2.5688900373	3.187967234
C	2.0180282919	1.4232740539	3.4724423109
C	1.67781264	0.5379238174	2.4574700247
Cl	5.9779791482	-2.2610239923	3.0430420913
Cl	4.1175668861	4.2835656954	1.525633786
Cl	6.5044379365	0.511810664	-2.777142245
H	1.844981999	-3.397505331	-0.640775491
H	3.3092740314	-5.2111115174	0.1501442592
H	5.1455111976	-4.7154482762	1.7826086572
H	4.0024179254	-0.5842821081	1.8071626645
H	0.8524972947	0.7345411346	-2.6251634151
H	2.0775801666	1.7103665495	-4.5333413906
H	4.575390812	1.6196716817	-4.5961563681
H	4.6059601664	-0.4207643548	-0.8266365583
H	3.240968826	2.0916266035	-0.1543391554
H	3.0154429881	3.2836900119	3.9623697842
H	1.701376889	1.232342374	4.4943358359
H	1.1222242793	-0.3731330382	2.6699332262
P	-1.4005153012	1.4718528135	-0.2507898902
C	-0.7558006644	2.7952734354	-1.3575687803
C	-1.0983722167	2.0146973624	1.5004650051
C	-3.2285351131	1.7776741417	-0.2062287568
C	-3.7161685659	3.0854414664	-0.1489271448
C	-5.0795266869	3.2747222488	-0.0146226602
C	-5.9714312063	2.2184641093	0.0846758192
C	-5.4685097797	0.9216301092	0.0500189223
C	-4.1010423815	0.6969553106	-0.0986756333
C	-1.4740179207	3.1421948188	-2.5065387629
C	-0.8928767796	3.9611974743	-3.4710405314
C	0.4111785784	4.4253828457	-3.3147344711
C	1.1083732132	4.0521430539	-2.1784497807
C	0.5563634566	3.250633561	-1.1960969699
C	-1.5185466638	1.1026864651	2.4756775627
C	-1.4396595761	1.4311155701	3.8229654555
C	-0.909021695	2.6615302974	4.213048007
C	-0.4831841495	3.5356828328	3.2295246601
C	-0.5811035053	3.2500180744	1.876233871
Cl	2.8409044052	4.5535067531	-2.0054930735
H	-7.0343383996	2.4114924498	0.1880225908
H	-2.4767862308	2.7528187784	-2.6611330659
H	-1.4565987966	4.2309560071	-4.3592146105
H	0.8824040526	5.0536386514	-4.0637941428
H	1.1587612196	2.9557103619	-0.3406325633
H	-1.9381692052	0.1444544707	2.1685049519
H	-0.8303705469	2.9380870761	5.2596597158
H	-0.2657829525	3.9865083691	1.1423041021
I	-2.3287835157	-0.8029975143	-2.9632494455
H	-3.5240016469	-3.4025132274	-1.1597111337
O	-1.0717144957	-2.2761646924	3.8694089316
O	0.2072996284	-2.3251178348	2.0212333896
H	-3.7255685263	-0.3221353625	-0.1451545581
H	-3.0484376848	3.9417693068	-0.2040343773
H	-1.7919999571	0.7291382855	4.5746383808
H	-6.1465927377	0.0764627154	0.1310131391
Cl	-5.7223420559	4.9722174203	0.0507176735
Cl	0.243114984	5.1237670443	3.7272295842
C	-0.8904602531	-2.3718491183	2.5388505267
C	0.0981140778	-2.0818214171	4.6550549502
H	0.3774785411	-1.0195206234	4.6532091268
H	-0.1609195014	-2.3894530415	5.6705164899
H	0.934087888	-2.6727800152	4.2688011634

trans-**IXb**

100

C	-0.5713687506	2.7716623171	1.020431129

C -1.361304292 3.0992692273 -0.2141550933
C -0.9003904315 3.2508179849 -1.5397827919
C -1.7802602176 3.6270141277 -2.5620055956
C -3.1242624591 3.8514680454 -2.3045614296
C -3.5887413706 3.743899076 -0.9985001649
C -2.7123075778 3.394208799 0.0219780193
C -0.458942996 3.821325243 1.9437515091
C -0.0044285678 3.6008541625 3.2370775808
C 0.2907667529 2.3062744034 3.639326886
C 0.2122902813 1.2366856739 2.7385187761
C -0.1759510555 1.4768004213 1.4085282798
C 0.5716053987 -0.1361786164 3.2406025729
Pd -0.1352881911 -0.0539520475 0.0301454638
H -1.3853627445 3.7504540221 -3.5678672966
H -3.7985703398 4.1291346041 -3.1125869875
H -4.6361047997 3.9331714707 -0.7631485037
H -0.7653824759 4.8225021837 1.6376091545
H 0.0743737468 4.4305164982 3.938059152
H 0.6019829039 2.1075811607 4.667026266
H 1.6379000307 -0.3688138247 3.0938860012
H 0.3737131357 -0.2256417128 4.3174702514
H 0.0144587 -0.9283427757 2.72195947
P 2.29993924 0.0482118406 -0.0945778371
C 3.0051664628 -1.2279231581 1.058383565
C 3.1092273484 -0.4267094477 -1.6914512731
C 3.3140427756 1.5457679443 0.3397574971
C 3.069126743 2.2323554518 1.5297782391
C 3.7651059928 3.3999937743 1.8265736827
C 4.7036261445 3.9099042773 0.9325461702
C 4.9167862308 3.2187395073 -0.2474849012
C 4.2505914242 2.048952685 -0.564483595
C 2.4793760073 -2.5244858207 1.0138351026
C 2.9192859403 -3.4876244538 1.9152877817
C 3.8872123098 -3.1734625726 2.8691748528
C 4.4058658824 -1.8914036801 2.8789154032
C 3.9926773248 -0.910534718 1.9920941064
C 4.2916784961 -1.1659911102 -1.6868606467
C 4.9030931193 -1.442263363 -2.8989664228
C 4.3840782864 -1.0168638242 -4.1089949816
C 3.1981420295 -0.2842807456 -4.10043928
C 2.5598646853 0.0078192537 -2.8991079762
Cl 6.1004636665 3.8938500358 -1.4563338736
Cl 6.4499269098 -2.3929163945 -2.8932207735
Cl 5.6738667877 -1.4652025801 4.1091918089
H 2.3003151796 1.8841820359 2.2100420748
H 3.5581584455 3.9256951933 2.7546765866
H 5.2496470016 4.824141513 1.1402331708
H 4.441819547 1.5550376212 -1.5118298718
H 1.7285553138 -2.7805542502 0.2650095276
H 2.5026337305 -4.4898671479 1.8804309803
H 4.2334296448 -3.9101436654 3.5863756563
H 4.422338156 0.0857397218 2.0407202945
H 4.7359207513 -1.5168246694 -0.759112161
H 4.8923737893 -1.2594155179 -5.0366197328
H 2.7625206648 0.0440620999 -5.0400303722
H 1.6249449008 0.5589096147 -2.8960365925
P -2.3896979163 -0.5369013842 0.4392230165
C -2.629892733 -2.126288283 1.3598373729
C -3.447499498 -0.6908947243 -1.0651919721
C -3.4479724825 0.5730139541 1.4906880473
C -3.022850103 0.8732322027 2.7876834746
C -3.7496165714 1.7577521501 3.5768698608
C -4.9157551271 2.345529472 3.0856004956
C -5.3253432668 2.0152181213 1.8063832403
C -4.6214651263 1.1404416677 0.9957800086
C -3.8481136256 -2.4022417958 1.9900406426
C -4.0240479877 -3.6032906697 2.6714542826
C -2.9855769571 -4.5302196434 2.7466858921
C -1.785631934 -4.2253212586 2.1282336195
C -1.5838344011 -3.0458380166 1.4346397757
C -4.3180521045 -1.7621419167 -1.2473517361
C -5.0879724896 -1.793383325 -2.3981005543
C -5.0271433422 -0.8039337662 -3.3632343369
C -4.1453407114 0.2586472146 -3.1701887497
C -3.3476958834 0.3123239957 -2.0330761663
Cl -6.8220771648 2.8032637908 1.1358315012
Cl -6.2143059384 -3.1943013153 -2.6553738022
Cl -0.4246703765 -5.4244976 2.2143867138
H -5.4910213009 3.0460339715 3.682205433
H -4.6577395804 -1.6772996112 1.9469936016
H -4.9737163741 -3.8209682016 3.1516262156
H -3.1053688763 -5.4704237246 3.2749954793
H -0.637242987 -2.8478700115 0.9383493585
H -4.3864692933 -2.5665627554 -0.5208326861
H -5.6490141069 -0.8686286249 -4.2497884203
H -4.0690653757 1.0400200128 -3.9212037445
H -2.6361070424 1.1263286669 -1.9098226204
I -0.2348713468 -1.9999842546 -1.8985166769
H -3.0834827385 3.3344827009 1.0434965796
O 0.9203507089 3.7583696153 -2.9443129801
O 1.2922288098 2.3765384233 -1.2262158359
H -3.4004758396 2.0032778136 4.5755952903
H -4.9633795812 0.9366245229 -0.0142812383
H -2.1127045615 0.4287729029 3.1782958856
C 2.3199159817 3.6907912055 -3.2257543292
H 2.8993211915 4.0021681116 -2.348978849
H 2.6214542439 2.6711131342 -3.4961575847
H 2.4879606996 4.3725556744 -4.0611592797
C 0.527977597 3.0662664728 -1.8671924434

Xb

100

C 0.2549192821 -4.3325911161 0.6005826376

C	-1.1393566764	-4.0394745072	1.0357870237
C	-1.4773214867	-3.0769452331	2.0123219945
C	-2.8248880119	-2.8570703554	2.3247392732
C	-3.8318124498	-3.5874629936	1.710966439
C	-3.5019094702	-4.5457534342	0.7583044376
C	-2.1696408835	-4.7567147545	0.4236502657
C	1.0528309439	-5.1660437465	1.3886220901
C	2.3534135341	-5.4640053127	1.0158511901
C	2.886176812	-4.9102793406	-0.1425807843
C	2.128588969	-4.0801428941	-0.9713561532
C	0.7995636377	-3.834085502	-0.5907057338
C	2.7536723802	-3.4662979988	-2.1855084886
Pd	-0.4405050153	-0.6316713713	0.1876855053
H	-3.0766592452	-2.1084598764	3.072619413
H	-4.8718125227	-3.4028955201	1.9736502239
H	-4.2809067226	-5.1334159537	0.2745650061
H	0.6394861409	-5.5530809305	2.3186949268
H	2.9626037971	-6.1157560292	1.6397433907
H	3.9196798533	-5.1167134315	-0.4217990539
H	3.8283210655	-3.680801904	-2.2257475441
H	2.2982057314	-3.83752757	-3.11434329
H	2.6378442536	-2.3738684841	-2.1873707381
P	1.721586866	0.1879900835	0.470231525
C	2.5977935302	0.266278012	-1.168727445
C	1.7063577967	1.9885392942	0.9300197983
C	3.0860757925	-0.4652158565	1.5371878399
C	3.2691688839	-1.8515146212	1.5569532233
C	4.2932260009	-2.4071732952	2.3164527421
C	5.1299435314	-1.591344144	3.0773318565
C	4.9186279467	-0.2232868077	3.04890767
C	3.9173172674	0.3625604746	2.2927168812
C	1.8758565036	0.7630299195	-2.2615516572
C	2.4436915689	0.7741024499	-3.5292259695
C	3.7268726709	0.2631267166	-3.7326667159
C	4.4152031908	-0.2281241826	-2.6387136164
C	3.8887205446	-0.2268323401	-1.3568206477
C	2.6010744117	2.9117318141	0.3850964189
C	2.4530822412	4.2486619656	0.7170995835
C	1.4463338633	4.7059665084	1.5518807089
C	0.5662356585	3.775874402	2.1033299989
C	0.7015019518	2.4244641205	1.797769242
Cl	6.0091574052	0.8505195397	4.0332372642
Cl	3.603538826	5.4562118616	0.0002779936
Cl	6.0690124929	-0.9449769488	-2.8945764195
H	2.6053740661	-2.496197518	0.9839135306
H	4.4326692966	-3.4844584843	2.3284889563
H	5.9273273069	-2.0082442743	3.6840928758
H	3.7946727224	1.4419523417	2.2887697399
H	0.8628774813	1.1369732271	-2.1183846368
H	1.8818504936	1.1743144634	-4.3692203665
H	4.1784904163	0.2425912158	-4.7187701342
H	4.4653154485	-0.6276495199	-0.5280207425
H	3.3835738996	2.5988387949	-0.3026957828
H	1.350454842	5.7667651095	1.758632812
H	-0.2395196264	4.106468981	2.7545939428
H	-0.0070164794	1.7012658226	2.1971072396
P	-2.3165335956	0.7233917064	0.0403181443
C	-1.9397359137	1.737282452	-1.4703265911
C	-2.6702463843	1.9990965169	1.3415016012
C	-4.0404265163	0.1411724615	-0.3458600239
C	-4.2236675643	-1.2227057581	-0.5754054342
C	-5.4905720816	-1.7176215814	-0.8838945541
C	-6.5796555272	-0.8554448759	-0.9645332362
C	-6.3722608342	0.4963031241	-0.729916544
C	-5.1290944448	1.0149089508	-0.4196136249
C	-2.4945117511	1.3838000116	-2.7028641466
C	-2.0414536731	1.9814994765	-3.876710025
C	-1.026378526	2.9348397818	-3.8388358125
C	-0.490935238	3.2707447403	-2.6052259059
C	-0.9209429994	2.6995131706	-1.4211251352
C	-2.9631416354	3.3360376925	1.0685919775
C	-3.1657175313	4.1987534684	2.134270791
C	-3.0907357317	3.786346422	3.4540124559
C	-2.7984893068	2.4470732897	3.7151903148
C	-2.58511157	1.5574361064	2.6663904219
Cl	-7.7933801042	1.6241750943	-0.8397654673
Cl	-3.5301687759	5.9441716	1.7886632395
Cl	0.8907829731	4.4431991864	-2.5398382562
H	-7.5745035225	-1.2197793283	-1.199501828
H	-3.2815878192	0.6337214358	-2.7449589468
H	-2.480102169	1.7023451343	-4.830819449
H	-0.6561501261	3.4068886851	-4.7434112685
H	-0.4350216161	2.9755266988	-0.4859456365
H	-3.0065894545	3.7080879965	0.0474588562
H	-3.2544370898	4.4965899025	4.258330119
H	-2.7345613542	2.1042114232	4.7448703109
H	-2.3093557812	0.5197236245	2.8610984162
I	-0.4069928571	-2.64692719	-1.8686102019
H	-1.9064527077	-5.4960130936	-0.3329941413
O	-0.913059595	-1.2608888649	3.4240027937
O	0.7254531865	-2.6950774236	2.8894441674
H	-5.63157864	-2.781527085	-1.0559798133
H	-5.0111961686	2.0797605387	-0.2354989003
H	-3.3741324998	-1.9001711065	-0.4947680434
C	-0.426348839	-2.3437257955	2.7763952405
C	0.0598418513	-0.5434415525	4.178801821
H	0.4391891709	-1.1594317686	5.0011425306
H	0.9049578518	-0.2522310334	3.5430934725
H	-0.4501558183	0.3422698999	4.5680325717

Vc

79

C	-1.3961552584	-2.7444141095	2.012254886

C	-0.0322144037	-2.7549750428	2.2828463939
C	0.9145739884	-3.1366669164	1.3378230802
C	0.4800100313	-3.5196669372	0.0758625686
C	-0.8830573343	-3.5198600929	-0.1894375031
C	-1.8300041669	-3.1400737341	0.7547612449
Br	0.5812607495	-2.1924244164	4.0408127452
Pd	1.5551352795	0.0517284385	0.4182313339
P	-0.6870418219	0.9043755595	0.0879360148
C	3.4365257191	-0.7024396256	0.5894671926
C	4.3169353882	-0.575230866	-0.4999269765
C	5.5486077406	-1.2515769374	-0.5074468015
C	5.9001056153	-2.0097160477	0.6109807303
C	5.0697277872	-2.0813620159	1.7241375152
C	3.8383216569	-1.4284746091	1.7137620559
C	6.4854463578	-1.184284124	-1.6794975114
C	3.8646551648	0.3470901847	-1.5847128133
C	2.4492644843	0.9009365222	-1.2527744614
C	2.6649521833	2.4050025396	-1.0907846887
C	2.8670773811	2.9698050476	-2.5144804752
C	4.2690376635	2.4362478722	-2.9068356559
C	4.7013601841	1.6513646215	-1.661062322
C	4.0876695138	2.4879833761	-0.5365765637
H	5.3782535078	-2.6553667548	2.5980178333
H	6.8510217333	-2.545293826	0.6074491702
H	3.8661937007	-0.1547577312	-2.5693093677
H	1.6941843138	0.6547001031	-2.0176351585
H	1.8872508032	2.9287098335	-0.5245506373
H	5.782047787	1.4779762476	-1.5960467968
H	4.1944615531	2.0364158146	0.4574256495
H	4.4730755847	3.5171859925	-0.5110336931
H	2.8462235052	4.0692827141	-2.4883522317
H	2.078893792	2.6463036041	-3.2100982567
H	4.2472790335	1.803099313	-3.8048537189
H	4.9646687073	3.2618664886	-3.1082504198
H	3.1907750196	-1.4949738386	2.5926694516
H	1.1891524357	-3.8009762127	-0.6975379597
H	-2.8857490983	-3.1396114459	0.4939682109
H	7.1691254094	-2.0426021905	-1.6842379033
H	5.9486384766	-1.1776559411	-2.6379444244
H	7.1091565674	-0.2784605574	-1.6614907589
C	-1.5879920244	0.3308416503	-1.4205066193
C	-2.700886058	1.0230231735	-1.9112554002
C	-1.1612755613	-0.8386141951	-2.0480016651
C	-3.3606466543	0.5120288358	-3.0135719072
C	-1.8558545425	-1.338917712	-3.1503880193
C	-2.9654636564	-0.6593252557	-3.6422189779
Cl	-4.7995604134	1.4103543922	-3.6580416051
H	-3.5202773257	-1.0316375287	-4.4970983254
C	-0.9355403756	2.7411904004	-0.044252551
C	-1.493061321	3.4901941164	0.990162861
C	-0.4857434261	3.382660982	-1.2038683107
C	-1.5713000976	4.8662823162	0.8446342971
H	-1.8658070778	3.017669053	1.8940237187
C	-0.5813829228	4.7642205507	-1.3229211622
C	-1.1263105236	5.523798214	-0.2878714434
Cl	-2.2879800518	5.8394876649	2.1993294457
C	-1.8734291349	0.4801193603	1.4461140237
C	-3.1401411263	-0.0454787128	1.19451456
C	-1.4363456165	0.646339635	2.7643836426
C	-3.9395458871	-0.3902594736	2.2707431773
C	-2.2749694635	0.3206626799	3.8272537861
C	-3.5416102872	-0.2097027975	3.5856571403
Cl	-5.5556364467	-1.146874391	1.9420159886
H	-4.2037642304	-0.4844138916	4.4004241713
H	-2.1097638453	-2.4057402396	2.7597982797
N	-1.3376981751	-3.8657581996	-1.5350071859
O	-2.5334992	-4.0076145037	-1.7173795283
O	-0.48834274	-3.9385649753	-2.4155247047
H	-3.0433971158	1.9422743482	-1.4435159418
H	-0.2863298086	-1.3663797247	-1.6693690745
H	-1.5374538781	-2.2761305183	-3.5986733297
H	-0.2317161344	5.2569416737	-2.2256314562
H	-1.2054640432	6.6034951883	-0.3601441307
H	-0.0652835781	2.7970842986	-2.0188502216
H	-3.4908438874	-0.2021001243	0.1784015577
H	-0.4303534473	1.0178570636	2.9613254515
H	-1.934858411	0.4576514397	4.8496322863
H	1.9779284785	-3.1231194529	1.5669224237

VIc

79

C	1.43932758	2.4259867819	-0.495034678
C	1.7283246945	1.2706724615	0.2370149793
C	2.2328739616	1.3702314512	1.5311340251
C	2.3939131624	2.6196844676	2.1186360911
C	2.059563549	3.7543762227	1.3915204248
C	1.5909383	3.679625897	0.0852892206
Pd	1.2262839544	-0.3478477491	-0.8906837938
P	-1.2584773005	-0.0486350168	-0.4158386372
C	1.5170054051	-1.5366416054	0.8094824237
C	3.007308039	-1.9198998188	0.9681463265
C	2.9480820162	-3.4661139983	0.7916008149
C	2.264002922	-4.0588832859	2.0280812081
C	0.7948827114	-3.6032524048	1.8621001719
C	0.8121706633	-2.8452143236	0.5066795101
C	1.8663383897	-3.6316497838	-0.2773631636
C	3.8720683034	-1.2512338182	-0.057840792
C	3.2422897193	-0.504638573	-1.057107174
C	3.9505725337	0.1350657549	-2.0639794561
C	5.3373889725	0.0191797328	-2.0710687085
C	5.983463381	-0.7126764518	-1.0804280092
C	5.2744776944	-1.3617607973	-0.0694938826
C	6.0197654053	-2.1390329267	0.9772256043

Br	0.7677767677	-0.8634803568	-3.4121412145
H	5.9174681943	0.512050274	-2.8501068605
H	7.0719556958	-0.7802371388	-1.0829784859
H	3.3600860551	-1.6795524673	1.9866865874
H	1.0622340306	-0.9698947094	1.6310380701
H	-0.1860611102	-2.7574927163	0.0614050805
H	3.9248877896	-3.9046688868	0.559189906
H	2.122486603	-3.1848056601	-1.2470404108
H	1.5806087306	-4.6806004417	-0.4322630382
H	0.1038210055	-4.4543053719	1.7948525074
H	0.4419207618	-2.9674319595	2.6850832011
H	2.7175373087	-3.7052509537	2.9639628543
H	2.3405468137	-5.1539467667	2.0235932752
H	7.0644440848	-1.8102072313	1.0346205667
H	5.5798229097	-2.0249509699	1.9773693585
H	6.0349177675	-3.2168876662	0.7596466166
H	3.4343685792	0.7060691938	-2.8342858703
H	2.4938874482	0.4857453238	2.1077704844
H	1.3564114209	4.591652019	-0.4565167691
H	2.7768993337	2.727037291	3.1300667168
C	-2.5398017036	-1.2750755343	-0.9475949235
C	-3.8705818396	-1.1010552293	-0.5506882502
C	-2.1852640461	-2.3533823897	-1.7584084603
C	-4.8085779143	-2.030046094	-0.9580289436
H	-4.1727696455	-0.2580312046	0.065234074
C	-3.15745351	-3.2723611881	-2.1550141853
H	-1.1598465556	-2.4611372386	-2.108262778
C	-4.4795502684	-3.1188311894	-1.7521326951
Cl	-6.5329383148	-1.8128269283	-0.4401927776
H	-2.8816296666	-4.1078282297	-2.7913504911
H	-5.2475116682	-3.8243007577	-2.0518732293
C	-2.0261571939	1.5299531325	-0.9940944295
C	-2.8068270053	2.3377220721	-0.1675925438
C	-1.8366305166	1.8691786791	-2.3378459076
C	-3.3763083974	3.4786427095	-0.7083148485
H	-2.9698298045	2.0932812552	0.8782173551
C	-2.4281624887	3.0199390213	-2.8504624645
H	-1.2306978726	1.2278116869	-2.9796250151
C	-3.2041809637	3.8400568876	-2.0329937885
Cl	-4.3874812258	4.5337555207	0.3672026308
H	-2.2866656588	3.2815117737	-3.8950545086
H	-3.6687135963	4.7424781746	-2.4160870051
C	-1.4533603226	-0.028172427	1.4213599449
C	-1.8905977992	-1.1760384906	2.0874644398
C	-0.9544275118	1.0529927555	2.1591387167
C	-1.8051570464	-1.2179627097	3.4686700512
H	-2.2863128948	-2.0279996875	1.5409133809
C	-0.8900608369	0.983190417	3.5474975146
H	-0.6019398114	1.9474140962	1.6512144884
C	-1.3119325208	-0.1635750193	4.2183427001
Cl	-2.3509712027	-2.7242043344	4.3212656913
H	-0.498729437	1.8258118954	4.1111605832
H	-1.2627499247	-0.2366080533	5.299808521
N	2.2171151787	5.0707477504	2.0170135678
O	1.9507354592	6.0516441557	1.3418825775
O	2.6009981568	5.1018949228	3.1758251168
H	1.0830361225	2.3565317779	-1.5247941899

VIIc

79

C	4.5785826278	0.2250171053	1.4921352995
C	3.5403585565	-0.599503194	1.0476387898
C	2.5390864942	-0.9798291727	1.9520835424
C	2.4966183767	-0.4398872763	3.227623796
C	3.4778559634	0.4682936591	3.5989995072
C	4.5481546943	0.7762163884	2.7666601497
Pd	0.6622453502	-0.6646495725	-0.900000347
P	-1.449783737	-0.0757381896	-0.2706099459
C	1.2120146035	1.2237785327	-1.5734210055
C	2.7259228818	0.9644747979	-1.7022010006
C	3.3215776603	2.0581908625	-0.7924081616
C	3.1713511013	3.3807662047	-1.5692448453
C	1.6420437937	3.6356216728	-1.5454339222
C	1.1127830634	2.4620890158	-0.6940552305
C	2.2611627047	2.2660720684	0.2942727608
C	3.0096895038	-0.5446900213	-1.5003512315
C	3.4862690298	-1.1927740492	-0.321224638
C	3.8466812655	-2.5409453799	-0.3643244835
C	3.731750195	-3.2875043632	-1.5247420629
C	3.2315572851	-2.6883271827	-2.6677708845
C	2.8756441202	-1.3414420515	-2.6802667622
C	2.4361120003	-0.758805765	-3.9961909425
Br	0.2447769713	-3.1500024608	-0.1277195487
C	-1.597111332	-0.1767907814	1.5681447872
C	-2.5885664141	-0.9374647978	2.1836877935
C	-0.6455016853	0.4967195679	2.342419708
C	-2.6184803375	-0.9795426829	3.5686832605
C	-0.6998643114	0.4362795567	3.7320752921
C	-1.6998806545	-0.308209995	4.3573023814
Cl	-3.9096208819	-1.9636882674	4.375392206
C	-2.910051505	-0.9939069505	-0.9337937165
C	-4.188086255	-0.4631357068	-0.7150553638
C	-2.754043559	-2.1735577883	-1.6585345916
C	-5.2797614587	-1.1450608521	-1.2176224473
C	-3.8766263277	-2.8306619582	-2.1616776609
C	-5.1519955112	-2.3211124886	-1.9412893102
Cl	-6.9399572697	-0.475109401	-0.9213825802
C	-1.9945364669	1.6584057545	-0.6359015976
C	-2.2655544316	2.5797696779	0.3736958509
C	-2.035346604	2.052699767	-1.9763978261
C	-2.5382155639	3.8905608798	0.0146828368
C	-2.3140220337	3.373885647	-2.3056899428
C	-2.5587788121	4.3123144743	-1.302587929

Cl	-2.8615748486	5.1009179227	1.3255767361
H	1.7691949701	-1.686622627	1.6335110575
H	1.7062971788	-0.7103228547	3.9210553648
H	5.324469217	1.4506412731	3.1168191916
H	0.6703618313	1.3270537419	-2.5258149437
H	3.0638060656	1.1811736012	-2.7264831097
H	4.3474431059	1.8692252103	-0.4620130073
H	3.5847227927	3.3206670594	-2.5849920571
H	3.711507089	4.1819994383	-1.0477956227
H	1.1875143711	3.6508517362	-2.5460385307
H	1.3951527155	4.5930271409	-1.0662833323
H	0.1248406626	2.6548406548	-0.2706121846
H	2.4590361678	3.1577094256	0.9062131064
H	2.1177532325	1.4077037003	0.957547729
H	4.1892901294	-3.0129007523	0.5556262831
H	4.0050935238	-4.340505937	-1.5267664658
H	3.1144761053	-3.270733596	-3.5809503577
H	1.5444009067	-0.1268772942	-3.9193266513
H	2.2093666186	-1.5608361047	-4.7074619902
H	3.2306297968	-0.1425187894	-4.4444540606
H	-3.3151506121	-1.4960878665	1.6013410968
H	0.1537516618	1.0570818473	1.8593507831
H	0.0586171266	0.9371684881	4.3308377632
H	-1.7563277174	-0.3751180278	5.4388491122
H	-4.3294059241	0.4629616629	-0.1631480424
H	-1.7603805002	-2.5936088561	-1.7974633581
H	-3.7549545271	-3.7530055215	-2.721851957
H	-6.0355026935	-2.8241092092	-2.3210204006
H	-2.2409710827	2.2905433722	1.4206173399
H	-1.8380753086	1.3234238672	-2.7609036127
H	-2.3405892635	3.6832982764	-3.3466505784
H	-2.769196551	5.3496234901	-1.5409366924
N	3.3716499781	1.1279448785	4.9021797045
O	4.3519801646	1.716928386	5.3240180604
O	2.2950894988	1.0631093981	5.4819236649
H	5.4083325578	0.4541077904	0.8251945286

VIIIc

79

C	-4.728577004	0.9228248897	-0.3341085836
C	-3.7671491919	0.10077011	-0.9426470734
C	-2.7841600608	0.7014380303	-1.7405445302
C	-2.7159242296	2.0797390393	-1.8699085401
C	-3.6366642722	2.8667332759	-1.190091398
C	-4.6668216393	2.3036555926	-0.4431716665
Pd	-0.875413027	-1.2886371995	0.1349248281
P	1.3933467889	-0.3207734053	0.2125191808
C	-0.8363260633	-0.9319887478	2.4006737642
C	-2.1009531957	-1.4250274078	2.1411792297
C	-3.0705097954	-0.3138508964	2.4586790489
C	-3.0342402629	-0.2338784944	4.0120638063
C	-1.6173962734	0.3222232108	4.3025749675
C	-1.0126735927	0.4916053756	2.882121216
C	-2.2545257917	0.9320745116	2.1016283236
C	-2.7191175345	-2.1348901906	-0.3522462702
C	-3.8175452109	-1.3698359035	-0.7697487212
C	-5.0330279614	-2.0191161892	-1.0401524672
C	-5.1446650568	-3.3950544922	-0.928058611
C	-4.0372874649	-4.1406478755	-0.5419257468
C	-2.8156060722	-3.5290103972	-0.2510507688
C	-1.6385129335	-4.3799713743	0.1307852462
Br	-0.2848136687	-1.8461703799	-2.3051617608
C	1.4669536361	1.1002064195	-0.9605399981
C	2.4018755734	1.1785704623	-1.9907281109
C	0.4892776298	2.0918640757	-0.8242745159
C	2.348306172	2.2689999946	-2.8435918229
C	0.4616695429	3.1796763743	-1.6928051694
C	1.4027354617	3.2725096746	-2.7173472933
Cl	3.5564768658	2.3742034893	-4.192177524
C	2.8297687445	-1.4069660546	-0.208462917
C	4.1315710831	-0.8995981178	-0.1125364953
C	2.6246871087	-2.7436537813	-0.5480142516
C	5.191791305	-1.7443321911	-0.3832185238
C	3.7154882516	-3.5727160016	-0.8060283748
C	5.012209664	-3.0749876228	-0.7286428835
Cl	6.8804987051	-1.0925961348	-0.2665685655
C	2.0757112716	0.4287876643	1.7737327415
C	2.149114666	1.8064645556	1.9730790237
C	2.4303338925	-0.4420479124	2.8100247271
C	2.5446228697	2.2778883948	3.2155268009
C	2.8220849274	0.0595120462	4.0456806692
C	2.8745824371	1.4363911676	4.2624495673
Cl	2.6189292161	4.0707529872	3.4771851643
H	-2.0714029426	0.0762138395	-2.2750298969
H	-1.9563886402	2.5395566198	-2.4948193787
H	-5.3868139759	2.9500261618	0.0509883387
H	0.0109352206	-1.5487379432	2.6991117096
H	-2.3844778093	-2.473353913	2.1916421186
H	-4.0717843803	-0.4110942474	2.0285514699
H	-3.2202726498	-1.2079764511	4.481742919
H	-3.8141421674	0.4526610671	4.3655530979
H	-1.0085461983	-0.341796379	4.9300029839
H	-1.6627445203	1.2961306064	4.8064685908
H	-0.1253777238	1.1296711717	2.8395409605
H	-2.6988767093	1.8563993447	2.4953277808
H	-2.0857119611	1.0391411032	1.0209693471
H	-5.8839630185	-1.4224072208	-1.3710269812
H	-6.089604096	-3.8879642102	-1.1497166277
H	-4.1130070566	-5.226312516	-0.4627456204
H	-0.9203186952	-4.432767808	-0.7002568851
H	-1.9484258073	-5.4034589	0.3779473106
H	-1.0896726969	-3.9721711042	0.9938959991
H	3.1481916742	0.4035575338	-2.1378782027

H -0.2697380891 2.0062276904 -0.0465850949
H -0.3197265772 3.9310257061 -1.5969113528
H 1.3932452065 4.1037739811 -3.4142134093
H 4.3142316402 0.1325948792 0.1761138757
H 1.6119297593 -3.1294823987 -0.632279229
H 3.5539718794 -4.6126937471 -1.0737962649
H 5.8724150101 -3.7057215214 -0.928296754
H 1.8957554343 2.506055763 1.1816356079
H 2.4106927793 -1.5180751305 2.643567187
H 3.0970333671 -0.6203155953 4.8469338573
H 3.1762478838 1.8465508678 5.2205450235
N -3.5186119289 4.3221135672 -1.2566487887
O -2.496781932 4.7931584619 -1.7426166208
O -4.4388048707 4.9890900007 -0.8140475027
H -5.5181619179 0.466305149 0.2629397102

cis-**IXc**

96

C -1.1530812503 -3.593912828 -0.5639570985
C -2.0347869713 -3.1171284793 0.5294450222
C -1.5218213763 -2.4883507845 1.6713803671
C -2.3700611743 -1.9497230224 2.6292036303
C -3.7427125622 -2.0441591645 2.4234437881
C -4.2841132705 -2.697203002 1.3224292552
C -3.4207199722 -3.2454244198 0.3873735755
C -1.0614290089 -4.9634866408 -0.832382493
C -0.3216639823 -5.4131552948 -1.9169828367
C 0.2972194983 -4.4902121285 -2.7523846691
C 0.2185035122 -3.1129299591 -2.5148508439
C -0.4906411962 -2.675972457 -1.3882219157
C 0.9474955998 -2.1671476834 -3.4190320517
Pd -0.6575509659 -0.711218335 -0.7686947832
H -1.9946085456 -1.4495242854 3.518230028
H -5.3623071181 -2.7543529829 1.2035921925
H -1.5845434732 -5.6669875516 -0.1834401729
H -0.2484105629 -6.4786385999 -2.1281592355
H 0.8599693576 -4.8355948453 -3.6210208708
H 1.8830461941 -1.8125432477 -2.9584630446
H 1.212491133 -2.6502750301 -4.3674452366
H 0.3443869506 -1.276625984 -3.639735424
P 1.6159024736 -0.6990906697 0.0287941346
C 2.680040061 0.0435661721 -1.294920806
C 2.0369935631 0.40761906 1.450925676
C 2.6146214748 -2.1912235196 0.5228889159
C 2.4227548552 -3.4001767039 -0.1496863052
C 3.1939096854 -4.513589363 0.1730768216
C 4.1703709635 -4.4355478018 1.1614281256
C 4.3553449308 -3.2224731487 1.8040786467
C 3.6034367039 -2.0989276959 1.5101093296
C 2.1323906245 1.0450938919 -2.1001461595
C 2.9170698911 1.6641689141 -3.0694039751
C 4.2418125398 1.2749514642 -3.2554758996
C 4.755957759 0.2712947914 -2.4511622989
C 4.0069838036 -0.3519625795 -1.4669113556
C 2.7745194797 1.5774672595 1.2741360107
C 3.0893088411 2.3329249048 2.3943587506
C 2.7251921406 1.9538574739 3.6750185558
C 1.9639595897 0.7958413262 3.8362300654
C 1.6016343994 0.0382113578 2.7286541174
Cl 5.6360169063 -3.0985547852 3.084131917
Cl 3.9688128976 3.8976291018 2.1652388055
Cl 6.4761311129 -0.2476812048 -2.6939056598
H 1.6792233938 -3.4727996571 -0.9324623005
H 3.0248565067 -5.447898395 -0.3549291608
H 4.7790280338 -5.2935249557 1.4278337755
H 3.7916631236 -1.171624113 2.0415988161
H 1.0920917027 1.3373546008 -1.9761053882
H 2.4885813896 2.4520370301 -3.6825652548
H 4.8657484801 1.7412491095 -4.0108095342
H 4.4494754945 -1.1307587353 -0.8523571698
H 3.0867136885 1.9068062192 0.2859067936
H 3.016256041 2.5596367596 4.5274358747
H 1.6488689391 0.4943697654 4.8306909312
H 1.0008471154 -0.8601609851 2.8595120065
P -1.4952218551 1.6408818486 -0.104614099
C -0.8123243037 2.8256396605 -1.3661616852
C -1.4352541151 2.7245646634 1.4167952953
C -3.330708203 1.6433460927 -0.3064749284
C -4.0133997505 0.7216219773 0.4887211763
C -5.4008354137 0.6701837542 0.4744376813
C -6.1170147519 1.5318176479 -0.356755987
C -5.4151874311 2.436843459 -1.1341247965
C -4.0309385328 2.5264834122 -1.1201208377
C -1.1018976368 2.6543800302 -2.7258867744
C -0.4630855456 3.4422028605 -3.6805852854
C 0.4930204198 4.3829572211 -3.3003401151
C 0.7811992068 4.5144797794 -1.9524512648
C 0.1415940236 3.77042411 -0.9765480961
C -2.5589297962 3.4630999278 1.8037625894
C -2.45022639 4.3280764526 2.8777320025
C -1.2707852264 4.5035699048 3.5811137126
C -0.1592031575 3.7637695261 3.1926751162
C -0.2445327283 2.8687938896 2.1285031946
Cl -6.3416853346 3.5745528102 -2.2054031527
Cl -3.9100064194 5.2815840571 3.3784789862
Cl 2.0663374613 5.6889742947 -1.4431736904
H -7.2010627357 1.5071449519 -0.3936400576
H -1.8098219065 1.890179627 -3.0416244416
H -0.7059593079 3.3167545642 -4.7321733812
H 1.0045953474 5.0000617955 -4.0324853128
H 0.3892111287 3.9264006916 0.0702620017
H -3.5026088001 3.3752691318 1.2764309943
H -1.2267104597 5.2014159199 4.4104091383

H	0.7819231186	3.8832683194	3.7216115442
H	0.6266193206	2.2975196368	1.838312003
I	-2.661645685	-0.9029844557	-2.5409505532
H	-3.8163159279	-3.7345928943	-0.5015474484
H	-5.9139823593	-0.0352045821	1.1245530156
H	-3.5214615001	3.2664068689	-1.7313462539
H	-3.4544992483	0.0264026166	1.1123746988
N	-4.646873613	-1.3979247199	3.3765189945
O	-5.8274414147	-1.3027162861	3.0639471408
O	-4.1724191331	-0.9889522163	4.4221818871
H	-0.4405328745	-2.4412688819	1.8030274945

trans-**IXc**

96

C	0.5540983876	-2.5211108819	1.4750567545
C	1.0689245099	-2.9654234249	0.1594140277
C	0.3835683932	-2.7277704494	-1.0423224777
C	0.9557561045	-3.0439203824	-2.2662865057
C	2.2076032163	-3.6500795472	-2.2785698086
C	2.8854471333	-3.9655705089	-1.1089212829
C	2.3102477403	-3.6148660421	0.1034721089
C	0.5373997558	-3.4541821272	2.5225115313
C	0.1460472563	-3.0773962308	3.797255231
C	-0.1992637097	-1.7521473408	4.0403531686
C	-0.1851935963	-0.7965249374	3.0183312999
C	0.1732265754	-1.189801763	1.7146124427
C	-0.5478385387	0.6248589367	3.3488394443
Pd	0.1579531219	0.2267097273	0.2045960197
H	0.4477319024	-2.8365349838	-3.2050587847
H	3.8601978806	-4.4433026936	-1.1630713245
H	0.8235359369	-4.486262025	2.3170110311
H	0.121825387	-3.8083840225	4.6039061742
H	-0.4912949681	-1.4430611997	5.0455231476
H	-1.4329566012	0.9675687867	2.7965314188
H	-0.762557255	0.7426617137	4.4184904582
H	0.2644967828	1.3231997099	3.0959923959
P	-2.1922577769	-0.0709578704	-0.1075344075
C	-3.1320740836	1.0893324851	0.9895542946
C	-2.9053047396	0.2530379456	-1.7767760291
C	-2.9539405651	-1.7265842887	0.2479555184
C	-2.7743658454	-2.3230525157	1.501722017
C	-3.3046909602	-3.5831680909	1.7577554323
C	-4.0093603138	-4.2682649805	0.7701169007
C	-4.1705489983	-3.6610216129	-0.4623390656
C	-3.662933225	-2.4045555353	-0.7469527991
C	-2.7542827845	2.4373861477	0.9828620296
C	-3.3654450891	3.3326470668	1.8535510212
C	-4.3550465358	2.8959635936	2.7344887294
C	-4.7229753674	1.5626072395	2.7044981953
C	-4.1374574305	0.644803945	1.8467041202
C	-4.1885645732	0.7847234791	-1.8952910024
C	-4.7251220636	0.9292172493	-3.1635350882
C	-4.035287638	0.5644541955	-4.3071001366
C	-2.7529289308	0.0352833514	-4.1737131241
C	-2.1840268294	-0.1167054211	-2.9130095299
Cl	-5.0805406044	-4.5423870451	-1.760946217
Cl	-6.3924101812	1.6224713327	-3.3297358456
Cl	-6.0192721243	0.9829125857	3.8346879291
H	-2.204709045	-1.8127769895	2.2733234929
H	-3.1562280638	-4.0390121918	2.7324190953
H	-4.4220059172	-5.2551600446	0.9512216249
H	-3.8195633874	-1.9656024376	-1.7273125143
H	-1.9737127675	2.7798499568	0.3030805479
H	-3.0617323376	4.3757848561	1.8562744422
H	-4.8338329592	3.5786975558	3.4287160906
H	-4.45052628	-0.3951080265	1.8615101025
H	-4.7615464656	1.0748526716	-1.0190066088
H	-4.4899541715	0.6984998328	-5.2830978011
H	-2.1919827658	-0.2427594945	-5.0608081705
H	-1.1688239066	-0.4963171856	-2.8154651611
P	2.4532501784	0.6032479839	0.5104187659
C	2.8733291722	2.1709909878	1.3899823363
C	3.3761883722	0.6142559292	-1.0849957132
C	3.4551595458	-0.6116200019	1.4901554331
C	3.1577411835	-0.7925257291	2.8436309725
C	3.8360543778	-1.7518127619	3.5860346999
C	4.8178266966	-2.5419421207	2.9872715502
C	5.0976878227	-2.337102988	1.6482747756
C	4.4407758411	-1.3878070333	0.8826927437
C	4.1694474194	2.4050149362	1.8605376964
C	4.4595352973	3.5870901495	2.5367592689
C	3.4598872831	4.5300013598	2.7705853936
C	2.1803581362	4.263133448	2.314712711
C	1.86564807	3.1075655724	1.623320308
C	4.3764369143	1.5349531942	-1.3808540915
C	5.0204795697	1.4243309951	-2.6036191583
C	4.7085648908	0.4447202784	-3.5309849196
C	3.6965778317	-0.4653620462	-3.2255099565
C	3.0311174932	-0.373948084	-2.009155803
Cl	6.330520394	-3.3995064339	0.839489937
Cl	6.3259929644	2.621290379	-3.0045085993
Cl	0.8617429967	5.4668817313	2.6373296407
H	5.3513814043	-3.3023630031	3.5483312892
H	4.9476938944	1.6601423704	1.7072706023
H	5.468531321	3.7754841941	2.8921186319
H	3.6686030599	5.4525855453	3.302250141
H	0.8544587638	2.9392705318	1.2593187008
H	4.6406153864	2.3322872692	-0.6925045322
H	5.2402023009	0.3998802712	-4.4755943264
H	3.4092773595	-1.2380714465	-3.9359359014
H	2.2218517494	-1.0637413472	-1.787075919
I	0.2280678446	2.2388864396	-1.6453868864
H	2.8542807377	-3.7961911146	1.0302986692

H	3.5898513435	-1.8988083202	4.6337755399
H	4.6730376235	-1.276832367	-0.1728006004
H	2.382111578	-0.1947843251	3.3154882697
H	-0.617538706	-2.3001284556	-1.010980859
N	2.8582641824	-3.9170861042	-3.5600431273
O	3.7556848033	-4.7404059126	-3.5821455114
O	2.4668381149	-3.2815006044	-4.5325908656

Xc

96

C	-0.7437567889	-3.3372028571	1.2963464211
C	-2.1894824995	-3.0260445955	1.1913612026
C	-2.6718699117	-1.8062402404	1.6819089463
C	-4.0312301373	-1.5254088207	1.696628401
C	-4.9067290523	-2.4871929394	1.2117203785
C	-4.4622593169	-3.699883474	0.699245881
C	-3.102491819	-3.9654842185	0.697622199
C	-0.1715003771	-3.3000224448	2.5748483959
C	1.1788097034	-3.5558445555	2.7633081906
C	1.9807172433	-3.8608504214	1.6722104901
C	1.457776165	-3.9274197982	0.3768550323
C	0.0913408548	-3.649447693	0.2119801425
C	2.3551586434	-4.2887858574	-0.7629551333
Pd	-0.4473175141	-0.757580947	-1.4678715077
H	-4.4174496534	-0.577911327	2.0641835003
H	-5.1845486869	-4.4231601151	0.3316325694
H	-0.8172251054	-3.0759419171	3.4242867057
H	1.6091973606	-3.5153943428	3.7622663836
H	3.0430718434	-4.0608944995	1.8144897001
H	3.3851599532	-4.432968993	-0.4175244497
H	2.0230686329	-5.2124129787	-1.2571385415
H	2.3712445485	-3.5007222335	-1.5272109558
P	1.654996255	0.0697617386	-0.9011324771
C	3.2211915721	-0.8973030088	-1.1130702865
C	2.0563887949	1.6844806456	-1.7349191311
C	1.7488463969	0.5527420408	0.8881007385
C	1.0673029742	-0.2482962935	1.8078790298
C	1.0446889988	0.0965499348	3.1570103743
C	1.6934325687	1.2493553413	3.5990551743
C	2.3698014716	2.0213327933	2.6680580678
C	2.4206369412	1.6958308875	1.3232608443
C	3.5414943171	-1.357734454	-2.3980422198
C	4.6696693431	-2.1449797581	-2.6032236421
C	5.4593816574	-2.5372366404	-1.5216693006
C	5.0896230133	-2.1152825221	-0.2571693184
C	4.0015988048	-1.2902612064	-0.0255874577
C	3.1265906828	1.8607150332	-2.6104887551
C	3.2384804831	3.0671825095	-3.284311737
C	2.3500141865	4.1118620597	-3.1093254594
C	1.2955051183	3.9364171047	-2.2130596351
C	1.1468717821	2.7314788905	-1.5373574032
Cl	3.2132346629	3.5265728653	3.2354509026
Cl	4.6092029403	3.271987831	-4.4607886695
Cl	6.0506170822	-2.7017251695	1.1735439152
H	0.5480682993	-1.1418423188	1.4631381977
H	0.5169056104	-0.5317928717	3.870535041
H	1.6798857951	1.5428805049	4.6439644922
H	2.9606957727	2.3286690425	0.624809597
H	2.8929734706	-1.1057514871	-3.2370151507
H	4.9271152268	-2.4777451011	-3.6049400796
H	6.3293335355	-3.1712750955	-1.6569735722
H	3.7615553519	-0.9692452866	0.9845796865
H	3.8613906621	1.0782285109	-2.7739727023
H	2.470760684	5.0342396369	-3.66719491
H	0.5793473288	4.739144845	-2.0506536711
H	0.3085201661	2.5929336765	-0.8613133583
P	-2.2301161597	0.714473995	-1.6849748442
C	-2.2882644969	1.565108855	-3.3336600898
C	-2.0185707209	2.1930675604	-0.5711710474
C	-4.0173413385	0.3149056605	-1.4075732126
C	-4.4641441999	-0.9379990661	-1.8337250368
C	-5.7901942092	-1.3112575409	-1.6388320298
C	-6.6764829485	-0.447170332	-0.9964824496
C	-6.2080704102	0.7861605373	-0.57793154
C	-4.8979817896	1.1920997319	-0.7729665728
C	-3.4690104741	2.001763315	-3.9342026235
C	-3.4227897994	2.6676441143	-5.1588872088
C	-2.2035221527	2.9058076268	-5.7887400778
C	-1.0447446824	2.4611808398	-5.1714245789
C	-1.0587371457	1.7915347849	-3.9630605556
C	-2.1345272871	3.5053904551	-1.0331186359
C	-1.798276594	4.5397292525	-0.1740879231
C	-1.3637779696	4.3287383693	1.1226455516
C	-1.2723864929	3.0151571379	1.5830468322
C	-1.5932203773	1.9568532436	0.7399644473
Cl	-7.3481164977	1.9042122674	0.284524147
Cl	-1.8897689925	6.2471740339	-0.7950915115
Cl	0.5541439405	2.7588795282	-5.980697413
H	-7.6949238678	-0.751229195	-0.7790764472
H	-4.4239195991	1.8257681435	-3.4443860024
H	-4.3422527365	3.006788892	-5.6275774718
H	-2.1514476053	3.4226560556	-6.7413394775
H	-0.1300264023	1.4495194549	-3.5088284692
H	-2.4443042248	3.7193186697	-2.0530782714
H	-1.0904957201	5.1688004799	1.7525323027
H	-0.9230433648	2.8209542341	2.5932259808
H	-1.458232455	0.9315827318	1.0785043723
I	-0.6790594147	-3.5855045403	-1.7653928701
H	-2.7409499064	-4.9276681753	0.3380701376
H	-6.1355745165	-2.2954359666	-1.9424381059
H	-4.5694954525	2.1684160347	-0.4267337821
H	-3.7560108353	-1.6322758472	-2.2855556248
N	-6.3455670725	-2.2216161609	1.2402521957

O	-7.0713944635	-2.976514594	0.6080406299
O	-6.733405716	-1.2498004974	1.8650642756
H	-1.9644866156	-1.072211949	2.0697731642

Vc*

79

C	-1.4039544716	-2.7489676111	2.0067418425
C	-0.0406114215	-2.7790693502	2.2780920725
C	0.9019126446	-3.1804307906	1.3369067726
C	0.4641661385	-3.5612043858	0.0759169477
C	-0.8987571412	-3.5386099324	-0.1918430717
C	-1.8416511003	-3.1419292096	0.7496973454
Br	0.5801987435	-2.2127468452	4.0325337241
Pd	1.5631652617	0.0597783748	0.4323183491
P	-0.6796401845	0.9127317716	0.0901350902
C	3.4413088176	-0.7073771209	0.5974139103
C	4.3233267326	-0.5672751724	-0.490102936
C	5.556038479	-1.2428073158	-0.5056694635
C	5.9078193893	-2.0156541123	0.6031681331
C	5.0744989161	-2.105664553	1.7132750461
C	3.8422752138	-1.4535009854	1.7096058943
C	6.4931913323	-1.1604102308	-1.6766887465
C	3.8682536763	0.3579445277	-1.5715427895
C	2.447007228	0.9011911448	-1.2446216967
C	2.6522331192	2.408142886	-1.0911003372
C	2.8584167643	2.9669569107	-2.5165884611
C	4.2679945095	2.4449567732	-2.8968222643
C	4.6975136278	1.6670868193	-1.6458119399
C	4.0710005122	2.5042473012	-0.5288685799
H	5.3806705589	-2.6946394093	2.5781205824
H	6.8595523973	-2.5498557853	0.5933597569
H	3.8762481911	-0.1421002379	-2.5569786598
H	1.6977186587	0.6472725419	-2.0124376193
H	1.8677415573	2.930943192	-0.5333856495
H	5.7789997319	1.5013617098	-1.5733486944
H	4.1756037689	2.0574951925	0.4678535558
H	4.4490815808	3.5362066962	-0.5056660341
H	2.8265019912	4.0661580828	-2.4968521039
H	2.0775446018	2.6313314865	-3.2143546456
H	4.258855883	1.8089718493	-3.7930235109
H	4.9578845129	3.2763548392	-3.0941788621
H	3.1909441297	-1.5395902125	2.5841931578
H	1.1701980243	-3.8609128732	-0.6931273922
H	-2.897006984	-3.1251663866	0.4889612456
H	7.1824874514	-2.0141609972	-1.687808681
H	5.9565135265	-1.1487983794	-2.6351584946
H	7.1105734918	-0.250578343	-1.6510748043
C	-1.5794016024	0.3306921443	-1.4168616384
C	-2.6917656407	1.0214032504	-1.9113008088
C	-1.1527869651	-0.8411979829	-2.040633659
C	-3.3479783176	0.5068107442	-3.0137380546
C	-1.8439929998	-1.3426720784	-3.1444923385
C	-2.9525866737	-0.6643279493	-3.641620395
Cl	-4.7883254507	1.4064330186	-3.6635075945
H	-3.5025721848	-1.0382021539	-4.4988784558
C	-0.9337307902	2.7482444069	-0.0509904322
C	-1.4844366445	3.5000904344	0.9854505337
C	-0.4950955641	3.3856337214	-1.217123255
C	-1.5674404828	4.8747077382	0.8313406808
H	-1.8465159778	3.0303199022	1.8950808276
C	-0.5968164186	4.7663164118	-1.3433220405
C	-1.1358690636	5.5296870935	-0.3074635978
Cl	-2.2758444359	5.8554808004	2.1905140959
C	-1.8625259937	0.4877876311	1.4508564015
C	-3.1342310755	-0.0271358847	1.2008057267
C	-1.4204745797	0.6473259914	2.7683274644
C	-3.9321022141	-0.3667633917	2.2793643276
C	-2.2583787623	0.3249195416	3.8330169912
C	-3.5302437085	-0.1948112309	3.5939591178
Cl	-5.5608251538	-1.1045139433	1.9511755873
H	-4.1905541253	-0.4665934007	4.4110671213
H	-2.1138673451	-2.3999864364	2.7529648862
N	-1.3555701781	-3.8817485204	-1.5354916581
O	-2.5534303183	-4.0077936912	-1.7217305438
O	-0.5076534377	-3.9715514273	-2.4163274369
H	-3.035524611	1.9413438249	-1.4459961662
H	-0.2790513566	-1.3691748395	-1.6596817256
H	-1.5238945662	-2.2786864984	-3.5936996802
H	-0.2573640241	5.2558161084	-2.2514545545
H	-1.2186706909	6.6086064224	-0.3864342037
H	-0.0785816635	2.7983853955	-2.0329657704
H	-3.4889948396	-0.17879007	0.1854824214
H	-0.4126695066	1.0139713944	2.9645143168
H	-1.9153492546	0.4579264102	4.854773819
H	1.9645434819	-3.1828791072	1.5685559307

VIc*

79

C	1.4347488913	2.4352189232	-0.5013033251
C	1.7285166208	1.276417337	0.2238631725
C	2.2395589645	1.3694325475	1.5163643759
C	2.4038231028	2.6157831901	2.1088296393
C	2.0668004499	3.7542991986	1.3877745679
C	1.5902975755	3.6858779807	0.0834778106
Pd	1.2245379184	-0.3430592522	-0.9008117316
P	-1.2600547452	-0.0455242928	-0.4169089989
C	1.5147219448	-1.5378468334	0.8009168433
C	3.0044943801	-1.9186184955	0.96380505
C	2.9465708709	-3.4663464164	0.7984865898
C	2.2615509806	-4.0482737424	2.0393699222

C	0.7934842221	-3.5923797	1.8685954174
C	0.8107485637	-2.8472710798	0.5048034182
C	1.8658249151	-3.6420949079	-0.269620896
C	3.8699423827	-1.2524572921	-0.0630131494
C	3.2422393111	-0.4968028593	-1.0569031925
C	3.952883867	0.1523375747	-2.0566383414
C	5.3396032421	0.0313786268	-2.0666337786
C	5.9832528405	-0.7125207108	-1.0828589811
C	5.2724556192	-1.3670206436	-0.0760834906
C	6.0160772396	-2.152776347	0.9653200785
Br	0.7716747029	-0.8663455334	-3.4525043659
H	5.9210888194	0.5302829142	-2.8407990951
H	7.0714314258	-0.7841680838	-1.0866080449
H	3.354405389	-1.6699866948	1.9810604334
H	1.0585675604	-0.9631096975	1.6158807796
H	-0.188044339	-2.763657014	0.0605298343
H	3.9234736554	-3.9066069484	0.5709171735
H	2.1253808453	-3.2073884664	-1.2439292227
H	1.5793923272	-4.6921816885	-0.4134271989
H	0.1010259795	-4.4424288974	1.8062781571
H	0.4414645617	-2.9477359534	2.685030321
H	2.7150559631	-3.6868898553	2.9720348557
H	2.3365618566	-5.1432349667	2.0424316494
H	7.0602077593	-1.8234186616	1.027363426
H	5.5728204491	-2.0482456727	1.9648675818
H	6.0322872317	-3.2281664502	0.7368355068
H	3.4388017722	0.7371080272	-2.8183028621
H	2.5044352125	0.48351204	2.0886341802
H	1.3521152881	4.5979939956	-0.4561382292
H	2.7915311018	2.7138939648	3.1191294019
C	-2.5376360682	-1.2751920306	-0.949588411
C	-3.8743180337	-1.0896173393	-0.5780947142
C	-2.1726935096	-2.3721620472	-1.7304136233
C	-4.806071366	-2.0250342412	-0.9843267882
H	-4.1840257173	-0.2349501669	0.0176406101
C	-3.1396523916	-3.297514132	-2.125055426
H	-1.1406951151	-2.49419677	-2.0538823989
C	-4.4689175199	-3.1312938612	-1.7499871174
Cl	-6.5422877111	-1.7911023974	-0.5013369711
H	-2.8556174209	-4.1485913842	-2.736434425
H	-5.2323034481	-3.841548997	-2.0498347121
C	-2.0303748679	1.5340026751	-0.9892028355
C	-2.8123835953	2.3373890719	-0.159139445
C	-1.8408196805	1.8797856728	-2.3313189466
C	-3.3823322057	3.4786874071	-0.6980591807
H	-2.9757170247	2.0883087165	0.8854965123
C	-2.4337024684	3.0312276434	-2.8410413718
H	-1.2332458473	1.2430166848	-2.9755670499
C	-3.2118556224	3.8471593159	-2.0207659422
Cl	-4.3974994595	4.5306717428	0.3833253802
H	-2.2920337957	3.2975939907	-3.8841865228
H	-3.6769784361	4.7497655039	-2.4024672131
C	-1.4526916452	-0.0309280787	1.4204668621
C	-1.8975047546	-1.1780756457	2.0827783245
C	-0.9508624433	1.0469100798	2.1610282465
C	-1.8154372287	-1.2200916892	3.4640906591
H	-2.295492408	-2.0275682013	1.5339876644
C	-0.8889273064	0.9749844199	3.549380251
H	-0.5961042103	1.9419598951	1.6559535995
C	-1.3180933528	-0.1709175735	4.217810325
Cl	-2.3737032003	-2.7266104656	4.3146439929
H	-0.4948266839	1.8143388281	4.115655895
H	-1.2701286389	-0.2443609121	5.2992057087
N	2.2301581094	5.0652380375	2.0157496273
O	1.9554028256	6.0526257859	1.3512621938
O	2.6291302112	5.0967640917	3.1705304555
H	1.0711353116	2.3736522069	-1.528593496

VIIc*

79

C	4.5917318125	0.2209056656	1.4934135798
C	3.5505847308	-0.6017532645	1.0520409077
C	2.5491748857	-0.9776014877	1.9580159293
C	2.5084901213	-0.4365330002	3.2326775544
C	3.4936078055	0.4692238741	3.6012966011
C	4.5639974644	0.7739427509	2.767009227
Pd	0.6550666554	-0.6731444974	-0.8917001372
P	-1.4599204145	-0.0585331855	-0.2753285517
C	1.2051646144	1.2122968309	-1.5670947904
C	2.7174912138	0.9532518361	-1.6945435269
C	3.3134175458	2.0461841614	-0.7837089244
C	3.1625598465	3.3689551392	-1.5594946933
C	1.6329142091	3.6208107659	-1.5385431757
C	1.1040660616	2.4475328346	-0.6850631237
C	2.2528483504	2.252547386	0.3031186268
C	3.0037628459	-0.5554309901	-1.4919386798
C	3.4938832541	-1.1978123335	-0.315332389
C	3.8715663697	-2.5410796444	-0.3595008521
C	3.7570220211	-3.2892734949	-1.5196460805
C	3.2414903342	-2.6969609028	-2.6596267088
C	2.8717467718	-1.353048586	-2.6713233191
C	2.4259948581	-0.7745061536	-3.9869055077
Br	0.2236923174	-3.1791765005	-0.1061149807
C	-1.6026706995	-0.1645043897	1.5638901937
C	-2.5805613858	-0.9402632159	2.1830686633
C	-0.6542648447	0.517331864	2.3349956938
C	-2.5963280048	-0.9892291276	3.5679445797
C	-0.6948038283	0.4473827833	3.7244936389
C	-1.6796019903	-0.3136760219	4.3546194112
Cl	-3.8761159903	-1.9894702923	4.3817899786
C	-2.9192452668	-0.9789191886	-0.9371632616
C	-4.200630404	-0.4649727761	-0.699591744
C	-2.7568468656	-2.1413566056	-1.6877980728

C -5.2869750187 -1.1491740678 -1.2101361967
C -3.8751025597 -2.8013709758 -2.1966915924
C -5.1544559264 -2.3094238339 -1.9574112539
Cl -6.9551280096 -0.4985258426 -0.8937348957
C -2.0043321502 1.6744233653 -0.6422398624
C -2.2846854365 2.5957205674 0.3653718994
C -2.0381801657 2.0663877113 -1.983770258
C -2.5583038185 3.9042027753 0.0001416745
C -2.3185547591 3.3863494681 -2.3172805464
C -2.5721765368 4.3257959437 -1.3170185514
Cl -2.8953067253 5.1185669331 1.3093890466
H 1.7767082258 -1.6814270184 1.6405582228
H 1.7181534745 -0.704670092 3.9269385297
H 5.3430717437 1.4479227088 3.1113156664
H 0.6593992323 1.3093704316 -2.5173194197
H 3.0534773565 1.1693971824 -2.7193175455
H 4.3394437936 1.8564849173 -0.4544907252
H 3.57761432 3.3104271811 -2.5744397678
H 3.6996810068 4.1702634002 -1.03532437
H 1.1803213687 3.6332248364 -2.5398930308
H 1.3827855571 4.5775764808 -1.0600363396
H 0.1156935316 2.6406231501 -0.2629348641
H 2.4491589359 3.1450365341 0.9141173513
H 2.1098330499 1.3946118214 0.9674885816
H 4.2304937667 -3.0074963755 0.5571267361
H 4.0466823595 -4.3379609555 -1.5244864063
H 3.12885114 -3.2804363664 -3.5726426655
H 1.5306858593 -0.1477496342 -3.9109727985
H 2.2048668678 -1.5784538464 -4.6975659689
H 3.216893719 -0.1539623028 -4.435396006
H -3.3077339564 -1.5014801252 1.6038347246
H 0.1281077026 1.0971907681 1.84829779
H 0.0611022452 0.9557613786 4.3198691597
H -1.7254687468 -0.3866382776 5.4362640391
H -4.3472848561 0.449020013 -0.1294333756
H -1.7596672902 -2.5440834577 -1.8477192514
H -3.7487945271 -3.710089494 -2.7774274825
H -6.033922367 -2.8150187517 -2.3427896544
H -2.2678535287 2.3085997139 1.4129627952
H -1.8340251264 1.3384727815 -2.7675588589
H -2.3387006998 3.6941555226 -3.3586397353
H -2.7832428699 5.3618351023 -1.5597834748
N 3.389994022 1.1283436992 4.9019170772
O 4.3709984552 1.7168420656 5.3266285129
O 2.3146633993 1.0675935724 5.4858175345
H 5.4210310768 0.4482113683 0.8257540406

VIIIc*

79

C -4.7338853964 0.9257284052 -0.3060193769
C -3.7925575697 0.0374690943 -0.849731938
C -2.8244396465 0.5445234865 -1.7269964605
C -2.748996988 1.9009371588 -1.999071816
C -3.6481806623 2.7616460185 -1.381595551
C -4.6641286023 2.287437749 -0.5564582288
Pd -0.8814276835 -1.2688620204 0.2825191422
P 1.3984004118 -0.3245259384 0.2246924711
C -0.7880407625 -0.6935518289 2.5014301877
C -2.0664466765 -1.1889662516 2.3221370929
C -3.012169841 -0.0374551648 2.5530889788
C -2.9331292425 0.1884736509 4.0907979141
C -1.5023476704 0.7476273544 4.2911867305
C -0.9332612618 0.7723354058 2.8460014252
C -2.1893802476 1.1555822762 2.058447238
C -2.7449211555 -2.1369533701 -0.0630909293
C -3.8484568389 -1.4080232665 -0.5297844771
C -5.0738160235 -2.0706129926 -0.7096434377
C -5.1907280461 -3.4284540838 -0.4611770513
C -4.0791843985 -4.1416017931 -0.0269506075
C -2.8479098085 -3.5137907122 0.1780316014
C -1.6693967098 -4.3316126059 0.6233280169
Br -0.3543532026 -2.0749695095 -2.1158098127
C 1.4574073261 0.9663973015 -1.092441681
C 2.3731825167 0.9328228448 -2.1426263382
C 0.4882451298 1.9744417787 -1.0401420432
C 2.3061463731 1.9308676448 -3.100750459
C 0.4484104926 2.9674160854 -2.0152179809
C 1.3687321632 2.9488130284 -3.0628196228
Cl 3.4912001013 1.8887305254 -4.4785841015
C 2.809735498 -1.4690168571 -0.1181848034
C 4.1195905575 -0.9731254801 -0.1132987356
C 2.5793214837 -2.8315175978 -0.3061044344
C 5.1593494051 -1.8590579353 -0.3237960458
C 3.6516534051 -3.7002620057 -0.5048240226
C 4.9562780804 -3.2162317641 -0.5196963583
Cl 6.8615546389 -1.2215580679 -0.3279710448
C 2.1262524579 0.5754721626 1.6811766737
C 2.2223007455 1.9654947686 1.7280944448
C 2.4955434693 -0.1848918595 2.7962521542
C 2.6567656518 2.5589996502 2.9028860806
C 2.9254123403 0.4401617103 3.9611718889
C 3.0025361837 1.8316756693 4.0270012057
Cl 2.764432567 4.3721553523 2.9658315129
H -2.1285762084 -0.1387143908 -2.2098644554
H -2.0023416742 2.2859758119 -2.6867252644
H -5.3674342901 2.9852016636 -0.1109258159
H 0.0544169045 -1.2950499877 2.8420899399
H -2.3609090766 -2.2222418645 2.487305203
H -4.0264596154 -0.1596127095 2.1618426401
H -3.119189229 -0.7340447372 4.654812329
H -3.69461005 0.9174979863 4.3953684339
H -0.8858918979 0.1367893097 4.9633768826
H -1.5218760201 1.7659899369 4.6993894458

H	-0.039695149	1.3901133639	2.7208437315
H	-2.6105566718	2.119751585	2.3737541244
H	-2.0469074134	1.1573089218	0.968684566
H	-5.928980478	-1.5023695218	-1.0774905322
H	-6.1431872666	-3.9331377452	-0.6131152587
H	-4.1598511613	-5.2134207827	0.1608836516
H	-0.9612203976	-4.4688624547	-0.2066330077
H	-1.9809800858	-5.3249348438	0.9704978038
H	-1.1079123198	-3.8471939173	1.4369971313
H	3.1145940088	0.1433044086	-2.2221107325
H	-0.2528812954	1.9766813036	-0.2410299995
H	-0.3257852599	3.7313442066	-1.980536524
H	1.3481598792	3.7044952354	-3.840728681
H	4.3227425023	0.0809000405	0.0598489336
H	1.5605961425	-3.2109401336	-0.3152569895
H	3.47087538	-4.7607058935	-0.6524742578
H	5.8013424263	-3.878890821	-0.6755763571
H	1.9572360707	2.5801379371	0.8727981205
H	2.4561363382	-1.2719303229	2.7501280063
H	3.2095700499	-0.1536990307	4.8247485971
H	3.3339920553	2.3356682072	4.9287900736
N	-3.5211858083	4.1982376621	-1.600562615
O	-2.509276867	4.6103584108	-2.1577103063
O	-4.4242474167	4.9203617314	-1.2082045402
H	-5.5122156697	0.5414964179	0.3529943219

cis-**IXc***

96

C	-1.1518390111	-3.5934293412	-0.5585518238
C	-2.0376344922	-3.1176979117	0.5320012373
C	-1.5295866789	-2.4917032594	1.6778495386
C	-2.3818334511	-1.9576667998	2.6344221971
C	-3.7541114732	-2.0534783656	2.4223130225
C	-4.2910522601	-2.7046084477	1.3171121622
C	-3.4230881742	-3.2488012159	0.3842669489
C	-1.0629966451	-4.9628779956	-0.8298920199
C	-0.320663032	-5.4118680984	-1.9132796388
C	0.302038489	-4.4887272381	-2.7457452935
C	0.2259353952	-3.1113579677	-2.505552556
C	-0.4841916489	-2.676091756	-1.3791181735
C	0.958386239	-2.1661269199	-3.4080077415
Pd	-0.6607386422	-0.7124733183	-0.7660345849
H	-2.0062253663	-1.4615901826	3.5255301196
H	-5.3683808212	-2.7671281756	1.1936497495
H	-1.590035189	-5.6666854354	-0.1845942496
H	-0.2475779478	-6.4770878197	-2.1251680433
H	0.8674857075	-4.8339018549	-3.6125757216
H	1.8998969882	-1.8234498355	-2.9507648069
H	1.2130597756	-2.645757772	-4.3609014848
H	0.3627126914	-1.2681381575	-3.6182168203
P	1.6142919351	-0.6981974055	0.0334397199
C	2.6721194102	0.0387207211	-1.2988218503
C	2.0340706424	0.4137001603	1.4520435699
C	2.6166379641	-2.188205653	0.5270593969
C	2.43227826	-3.3979297421	-0.1466732253
C	3.2097758259	-4.5076325127	0.1738141335
C	4.1858651752	-4.4256208119	1.162874444
C	4.3617917222	-3.2116696125	1.8055409921
C	3.6050757394	-2.0909072406	1.5142259871
C	2.131652777	1.0571650016	-2.0880891082
C	2.9078826093	1.6601769131	-3.0740528237
C	4.2183488922	1.2393477373	-3.2928446433
C	4.7245765507	0.2224534121	-2.5010932959
C	3.9855254821	-0.3868853072	-1.5008969774
C	2.7746599123	1.5808788926	1.269067983
C	3.0940171557	2.3369048086	2.3871969146
C	2.7317852308	1.9653926109	3.6702631636
C	1.9673701262	0.8098096189	3.8364411139
C	1.6009654909	0.0489479017	2.7319647217
Cl	5.6442357905	-3.081272721	3.0883549331
Cl	3.9867543187	3.8971735112	2.1511739681
Cl	6.4288342236	-0.3392809265	-2.7860778367
H	1.6898036721	-3.4741661876	-0.9299148279
H	3.0488832352	-5.442357784	-0.3558294315
H	4.7985983789	-5.2814014732	1.4266982381
H	3.7889040098	-1.1628539015	2.0455933972
H	1.1026807994	1.3768104602	-1.9404544517
H	2.4853468155	2.4594481733	-3.6765020382
H	4.8333543839	1.6923496465	-4.0633306049
H	4.423269201	-1.1777989993	-0.8986554518
H	3.0854477538	1.9057881353	0.2791878925
H	3.0250140521	2.5722740911	4.5210889651
H	1.6536228276	0.5127204998	4.8323965644
H	0.9982014255	-0.8466499806	2.8697669675
P	-1.4876749228	1.6477894302	-0.1005624244
C	-0.805114063	2.838291843	-1.3561810802
C	-1.435029317	2.7286223179	1.4230960274
C	-3.3236908502	1.6462859411	-0.3069846943
C	-4.0069456745	0.7249199312	0.4887113913
C	-5.3941826297	0.6661010826	0.4664097854
C	-6.1108273961	1.5210765042	-0.3721886426
C	-5.4069601736	2.425958307	-1.1473818167
C	-4.0235353008	2.5232373244	-1.1280758784
C	-1.0813886018	2.6639409711	-2.7182304381
C	-0.4408432189	3.4553215528	-3.6687966268
C	0.503492005	4.4054390254	-3.2812747712
C	0.7755532464	4.5409447229	-1.9308355526
C	0.1368228083	3.7918102914	-0.9584344754
C	-2.5567020355	3.4779044286	1.796267511
C	-2.4510689975	4.339825718	2.8725629439
C	-1.2803050181	4.5042173833	3.5925641423
C	-0.1709740713	3.7541510441	3.216144607
C	-0.2515272094	2.8621206373	2.1487775739

Cl	-6.3344589307	3.5597851655	-2.2285429965
Cl	-3.9123046018	5.3073670794	3.3575551813
Cl	2.0404685713	5.7369750351	-1.4082946804
H	-7.1944434496	1.489201745	-0.4143108332
H	-1.781921318	1.8956804937	-3.0399928206
H	-0.6713386957	3.3259810984	-4.7224382776
H	1.0165032118	5.0233514668	-4.0114303051
H	0.3765137693	3.9477148055	0.0900883098
H	-3.4940463665	3.4000623778	1.2562273225
H	-1.2382175331	5.19918039	4.4242526551
H	0.7634369892	3.8626403348	3.7587992782
H	0.6185704872	2.2846738441	1.8679563772
I	-2.667930978	-0.9001572864	-2.5491030657
H	-3.8157988686	-3.7409067936	-0.5041955812
H	-5.9085230304	-0.0402132379	1.1145899946
H	-3.5135256808	3.2623858486	-1.7397574379
H	-3.4482182226	0.0359258571	1.1199563719
N	-4.6622332628	-1.4171238822	3.3737865498
O	-5.8415498627	-1.3122395385	3.0560021676
O	-4.1985634404	-1.0208854679	4.4304694902
H	-0.4496117189	-2.4449963296	1.8160706917

Xc*

96

C	-0.7441945376	-3.3327145952	1.2960256236
C	-2.1905264276	-3.0258862545	1.1876352686
C	-2.6782145897	-1.8091914632	1.6815682914
C	-4.038024488	-1.5316953578	1.6913195412
C	-4.9093875708	-2.4945941341	1.1992048858
C	-4.4595114572	-3.7046430461	0.6836520395
C	-3.0991222518	-3.9660429385	0.686126498
C	-0.1740142588	-3.2878844619	2.5753393053
C	1.1766203413	-3.5407084558	2.766783617
C	1.9803090111	-3.8503129565	1.6780990598
C	1.4593413814	-3.9243665822	0.3821795113
C	0.0928497248	-3.6489017006	0.2140576044
C	2.3588765855	-4.2905405349	-0.7544885936
Pd	-0.4487831721	-0.7592582714	-1.4623546493
H	-4.4246910768	-0.5850075437	2.0600885986
H	-5.1755687372	-4.4314086028	0.311340148
H	-0.8197290781	-3.0589054053	3.4232602755
H	1.6050219876	-3.4940189201	3.7661603508
H	3.0426162602	-4.0486537219	1.8228825691
H	3.3876053824	-4.4360115471	-0.4058195924
H	2.0267810177	-5.2150438693	-1.2468706682
H	2.3786128395	-3.5042045505	-1.5204475188
P	1.6567012088	0.0618426403	-0.8948068727
C	3.2243095683	-0.901458022	-1.1112346379
C	2.047207666	1.6778047475	-1.7336976274
C	1.7537190083	0.5506254956	0.8924524752
C	1.0619042894	-0.2391025675	1.8139477573
C	1.0387214966	0.1104850742	3.1621354651
C	1.6989882285	1.2579211292	3.601738789
C	2.386732346	2.0163017003	2.6682641365
C	2.4388059245	1.6873062621	1.3248116143
C	3.5377799567	-1.3705581229	-2.3947444102
C	4.6665946491	-2.1568693489	-2.6014002986
C	5.4643813712	-2.5390273623	-1.5219472484
C	5.1002112197	-2.1078462968	-0.2591273938
C	4.011096441	-1.2855086652	-0.0248423156
C	3.0919452818	1.8471513271	-2.6416846778
C	3.1870390786	3.0518001193	-3.3204955834
C	2.3125725618	4.1037010819	-3.1211595982
C	1.283005832	3.9332278745	-2.1950882031
C	1.1476800737	2.7294256788	-1.514552444
Cl	3.2531784063	3.5145335038	3.2331842637
Cl	4.5115691648	3.2417341376	-4.5571630306
Cl	6.0760485991	-2.6783624395	1.1720375472
H	0.5341685141	-1.1282254611	1.4711819585
H	0.5012978049	-0.5083286384	3.8766834061
H	1.6838038913	1.5548002892	4.645541817
H	2.9907268664	2.3096538833	0.6262139268
H	2.8829578379	-1.1299528323	-3.2320674422
H	4.9175793351	-2.4982027229	-3.6016405268
H	6.3339378586	-3.1729411627	-1.6597555624
H	3.7740282665	-0.9608011063	0.9847995502
H	3.8161760879	1.059705794	-2.8271847933
H	2.419118089	5.0244338535	-3.684529695
H	0.5743060307	4.7387980623	-2.0160091452
H	0.3240691891	2.595199391	-0.8197236396
P	-2.222162732	0.7203362882	-1.6802769759
C	-2.2746449839	1.5739390275	-3.3285326155
C	-2.0162998801	2.1968350534	-0.5622541381
C	-4.0115785361	0.320269957	-1.410796306
C	-4.4562548984	-0.9326402087	-1.8396066602
C	-5.7822756625	-1.308421154	-1.6486133273
C	-6.6714679185	-0.4460825816	-1.007361131
C	-6.2032675151	0.7860160113	-0.5862811416
C	-4.8941826371	1.1957216715	-0.7760859624
C	-3.45151976	2.0238678709	-3.9273431544
C	-3.4015303762	2.687601613	-5.1532203174
C	-2.1811227234	2.9108198561	-5.7874994529
C	-1.0274574591	2.4530343135	-5.1709687178
C	-1.0439952537	1.7857841253	-3.9614616858
C	-2.1320841636	3.5103743531	-1.0213289382
C	-1.801613364	4.5412332956	-0.1561262946
C	-1.3706472604	4.3287285703	1.1412533303
C	-1.2791031757	3.0133732933	1.5978555119
C	-1.5967686104	1.9574827625	0.7504196525
Cl	-7.3499860758	1.9037427807	0.2783404131
Cl	-1.8993279918	6.2541623116	-0.7709832718
Cl	0.5768695322	2.7300863903	-5.9855469145
H	-7.6908057969	-0.7511951276	-0.7960075668

H -4.4077088041 1.8608782229 -3.4355831392
H -4.3180201924 3.0369449106 -5.6198315782
H -2.1275743617 3.4256119832 -6.7410640746
H -0.1185043375 1.4323637169 -3.5096361212
H -2.4389856111 3.7272048933 -2.041474183
H -1.1014392602 5.1662037152 1.7762611369
H -0.9356581416 2.8178572318 2.6096456526
H -1.4664643181 0.9318641291 1.0892416775
I -0.6741821244 -3.5922727557 -1.7655006824
H -2.7349534022 -4.9264770923 0.3250832306
H -6.1252438695 -2.2926232616 -1.9548120515
H -4.5673915523 2.1719554574 -0.428154443
H -3.7475020976 -1.6259256624 -2.2918902363
N -6.3467477413 -2.2351553796 1.2268303734
O -7.0731997161 -2.989956986 0.5939406128
O -6.7431543954 -1.267078973 1.8546741141
H -1.9759565914 -1.0756554563 2.0787968891

IVd

99

C -3.331881 -1.661173 0.754263
C -1.928616 -1.777839 0.845802
C -4.171253 -2.537685 1.465773
C -3.592306 -3.527213 2.261975
C -2.211902 -3.651385 2.361743
C -1.383799 -2.779288 1.659193
C -5.668196 -2.423068 1.407502
H -4.241947 -4.201025 2.823744
H -1.777765 -4.421757 2.999595
H -0.30133 -2.877445 1.770212
H -6.007579 -1.380981 1.488163
H -6.137582 -2.990559 2.22127
H -6.079189 -2.811394 0.464377
C -3.848718 -0.552306 -0.104845
C -2.675376 0.341412 -0.598099
H -4.59128 0.048194 0.453175
C -4.474839 -1.023711 -1.441742
H -2.807904 1.392326 -0.305896
C -2.709804 0.177787 -2.127247
C -5.121373 0.190245 -2.127657
C -3.904074 1.001466 -2.646598
H -5.747432 0.765805 -1.431268
H -5.766761 -0.127321 -2.958149
H -3.886245 2.035783 -2.274254
H -3.897714 1.046383 -3.745959
C -3.234966 -1.247285 -2.310772
H -1.763994 0.400839 -2.643274
H -2.553355 -2.014506 -1.921504
H -3.482427 -1.480004 -3.356934
H -5.147965 -1.884073 -1.337212
Pd -0.776962 -0.288279 0.023628
P 1.332094 -1.488008 -0.228633
P 0.057519 1.99565 0.203939
C 1.187474 -2.940888 -1.374899
C 2.35683 -2.180412 1.146681
C 2.58621 -0.481166 -1.150212
C 1.503904 2.055338 1.369038
C 0.495006 3.210157 -1.12508
C -1.177279 2.973413 1.196
C 0.070064 -3.774798 -1.277797
C 2.184031 -3.228231 -2.311875
C 3.004946 -3.412791 1.056897
C 2.47772 -1.409606 2.307429
C 2.103219 0.370793 -2.147199
C 3.948977 -0.500325 -0.857885
C 2.821196 2.009511 0.900735
C 1.266503 2.019094 2.746761
C 1.488701 4.183482 -1.008504
C -0.249106 3.12708 -2.305502
C -2.068347 2.277044 2.019937
C -1.200258 4.36733 1.175944
C -0.040204 -4.890925 -2.103555
C 2.068138 -4.344565 -3.136526
H 3.050453 -2.57597 -2.396901
C 3.780879 -3.868221 2.120913
H 2.900546 -4.015828 0.157825
C 3.259129 -1.866534 3.364324
C 2.967454 1.228207 -2.821087
C 4.81898 0.342928 -1.548069
C 3.882004 1.952015 1.801438
C 2.330224 1.953641 3.642916
H 0.24548 2.049198 3.120377
C 1.752236 5.043852 -2.0726
C 0.012162 3.988502 -3.36671
C -2.959212 2.975184 2.830682
C -2.101053 5.062493 1.979897
C 0.956108 -5.176977 -3.033493
C 3.910379 -3.095298 3.272133
C 4.328802 1.216738 -2.517353
C 3.641012 1.92662 3.172171
C 1.020387 4.944044 -3.253522
C -2.97719 4.368188 2.810349
H 5.006997 1.889062 -3.036096
H -3.67813 4.912307 3.437938
H -0.517493 4.912444 0.528442
H -2.067811 1.185336 2.008629
H 4.901482 1.920526 1.425311
H -0.911053 -5.535597 -2.019813
H 0.865059 -6.04592 -3.679881
H -0.712222 -3.550997 -0.554868
H 1.036697 0.379867 -2.372859
H 2.571395 1.918333 -3.562394
H 4.324442 -1.15831 -0.076599

H 3.351739 -1.266041 4.265315
H 4.513887 -3.454449 4.101624
H 1.959098 -0.453689 2.38547
H 2.063388 4.264015 -0.088981
H -0.572178 3.914433 -4.28001
H 1.230081 5.615159 -4.082184
H -1.038231 2.380161 -2.390187
H 3.024779 2.012471 -0.166595
H 4.471542 1.880249 3.871743
H -2.117102 6.149002 1.957307
H 2.530569 5.796447 -1.977253
H 2.132456 1.930218 4.711688
H 5.881518 0.3274 -1.318392
H -3.64669 2.428425 3.470818
H 4.281877 -4.8303 2.051658
H 2.846413 -4.561228 -3.863737

Vd

79

C -4.1090537938 -3.3056778356 -1.5053862841
C -2.9368703449 -2.8911015861 -0.8788789144
C -2.9659363063 -2.6709327307 0.5054947514
C -4.1384599042 -2.8689188823 1.2367496109
C -5.2976520865 -3.2677787912 0.5958326576
C -5.2794898701 -3.4841907063 -0.7793025789
Pd -0.9914077456 0.7741516694 0.2654636277
Br -1.3799931213 -2.7063250864 -2.0087971253
H -6.2128331892 -3.4017102267 1.1672697006
C -3.0605024515 0.8731589953 0.3982891227
C -3.6812299295 2.2346795676 -0.0107436656
C -4.2627863706 2.7516939566 1.3312526443
C -5.5329740342 1.9463558704 1.6299503811
C -4.9803854553 0.5316320513 1.9478934482
C -3.4488761074 0.7289812573 1.8714120884
C -3.2999262926 2.170147249 2.3699427401
C -2.6302039132 3.0870521424 -0.6336017935
C -1.3152975793 2.5843029905 -0.5751241121
C -0.2759624077 3.2987883638 -1.1729730367
C -0.5400902339 4.5065358911 -1.8149237588
C -1.8388682148 4.9974022787 -1.8742028408
C -2.8977326852 4.2993602194 -1.2924488058
C -4.296476651 4.8361728454 -1.4042044663
P 1.425616532 0.3753476155 0.2822036589
H 0.2764630376 5.0620305816 -2.2770436486
H -2.0443354343 5.9367186312 -2.3907829006
H -4.5180615835 2.0941890284 -0.7209525759
H -3.422742445 0.0379412447 -0.2272180672
H -2.8823749274 -0.0311923854 2.4321742432
H -4.4026813586 3.8393052747 1.3663215569
H -2.2731813243 2.5474298759 2.2822330229
H -3.6560130909 2.3133204459 3.4009450159
H -5.2866376793 0.1961352585 2.9503309521
H -5.3247224608 -0.2271793226 1.2290380763
H -6.2376276533 1.9508169312 0.7863303467
H -6.0610807014 2.3650629863 2.4982463064
H -4.3355333892 5.689181876 -2.0935052496
H -4.9984740592 4.0760328684 -1.7766783834
H -4.6945729655 5.1794712436 -0.4384485808
H 0.7474791669 2.9290437032 -1.1397507501
H -4.1171535327 -2.6747471046 2.3056189012
H -6.1847326711 -3.7963999201 -1.2962113187
C 2.6619027597 1.6931331577 -0.119377031
C 2.5730020211 2.8896253516 0.599524041
C 3.6614887453 1.5342914904 -1.0778488414
C 3.4791734959 3.9160711579 0.3620940887
H 1.7736527788 3.0184291375 1.328808237
C 4.5670506501 2.5676458288 -1.3169173196
H 3.7322192037 0.6053246418 -1.6388576901
C 4.4780010084 3.7561057946 -0.5984533278
H 3.4018258167 4.8455192581 0.919651651
H 5.1827478225 4.5613009218 -0.7881885084
C 1.8103386326 -0.9097673732 -0.9934522563
C 1.3413862888 -0.6797706247 -2.2919091548
C 2.4626783033 -2.1033990517 -0.6948116391
C 1.5393636455 -1.6334978798 -3.2855128918
H 0.7972080503 0.2397074008 -2.511810973
C 2.6489314074 -3.0638012324 -1.6889906783
H 2.819887281 -2.2846790784 0.3162871259
C 2.1921802146 -2.8303431209 -2.9829745961
H 1.1784028007 -1.4475500803 -4.2943423524
H 2.3393250017 -3.5798041785 -3.7561817678
C 2.201167906 -0.342388665 1.809759359
C 1.4206275933 -1.0843457161 2.7023264188
C 3.5636441551 -0.1663739521 2.0672138136
C 2.005248075 -1.6419017932 3.8374598011
H 0.3656363662 -1.2562252909 2.5078518808
C 4.1419760032 -0.7274005487 3.2022445124
H 4.1723046599 0.4134101907 1.3773016281
C 3.362540917 -1.4642855397 4.0908066154
H 1.3920753004 -2.2168181643 4.5264092519
H 3.8134253504 -1.8990317014 4.9791925234
N -1.8198520949 -2.1883197522 1.264022854
O -1.832399968 -2.3123184014 2.478303841
O -0.9040717674 -1.6493128641 0.6457701728
H -4.0931512537 -3.486281144 -2.577339934
H 5.2026616877 -0.5856781152 3.3930761056
H 5.3436537 2.4406016499 -2.0665996045
H 3.1533331298 -3.9965426185 -1.4498803319

VId

79

C	-4.1820209368	0.0460209168	0.2794342436
C	-3.3355042592	-0.5059341528	-0.6834705236
C	-5.5608952667	-0.2191291329	0.2015934793
C	-6.0332868776	-0.9909520074	-0.8610293259
C	-5.1777368521	-1.4860862299	-1.8378680777
C	-3.8068251776	-1.2537044538	-1.7512639571
C	-6.5323078885	0.2850418696	1.2312633122
C	-3.5502537437	0.910157318	1.3282895136
C	-2.0238218729	1.0610380559	1.0759339398
C	-4.0187259915	2.3887260719	1.2583131574
C	-1.8331093062	2.537190952	0.7595282078
C	-3.4519378922	3.1334373507	2.4723056325
C	-1.9458965847	3.2494348227	2.1299741272
C	-3.1619478429	2.934916552	0.1163678355
Pd	-1.3364517977	-0.2602813745	-0.4000416788
P	1.1931366546	0.0410727634	-0.0058692579
C	1.7204246631	1.803294845	0.1318508968
C	1.9310337255	-0.7463627238	1.5053023013
C	2.334361143	-0.6078742614	-1.3131380007
C	1.376500191	2.5411000321	1.2691592031
C	2.3680634109	2.4347283674	-0.9288762357
C	2.8235931628	-0.0992258533	2.3621305604
C	1.5997556322	-2.0829665985	1.7442982315
C	1.8682810801	-0.821821559	-2.611341387
C	3.6755258741	-0.8533881766	-1.0033178201
C	1.6939364715	3.8929504669	1.3511011932
C	2.6778507613	3.7903385732	-0.847584064
C	3.3591321637	-0.7785904679	3.4552054331
C	2.1294591422	-2.7572626569	2.838210152
C	2.746398747	-1.2764559152	-3.5945077822
C	4.5457969041	-1.3070087069	-1.9888402354
C	2.3447629606	4.5196795942	0.2902326063
C	3.0091554939	-2.1041331356	3.699009514
C	4.0808543035	-1.520012574	-3.2858234462
H	2.3787868124	-1.4404241784	-4.6036647644
Br	-1.1130099676	1.3806540666	-2.416191032
C	-1.5260489855	-1.8709078369	0.854702333
C	-1.7895831521	-1.8953882958	2.223522102
C	-1.2943885072	-3.116067743	0.2578716414
C	-1.7927142448	-3.0872791319	2.9418551197
C	-1.2951082613	-4.3268042655	0.9525878001
C	-1.5441871613	-4.3082605419	2.3126907371
N	-0.9532480597	-3.1755312098	-1.1567929997
O	-0.7959748109	-2.104359142	-1.7654321819
O	-0.8206744215	-4.2551798431	-1.6958641854
H	-7.1016208355	-1.2046098527	-0.9187789048
H	-5.5753302726	-2.0689712948	-2.6679521952
H	-3.1277402755	-1.6425190032	-2.508468572
H	-6.0756960116	0.3801772043	2.2251644214
H	-7.388413238	-0.3957232995	1.3199351638
H	-6.9372019133	1.2733094232	0.9690320168
H	-3.7433337286	0.5018427434	2.3367862203
H	-1.3868260349	0.7248451615	1.9071448228
H	-5.1030165053	2.488195472	1.1392729485
H	-0.9185319045	2.7819153465	0.213185564
H	-3.6368026307	2.594278135	3.412581669
H	-3.9145123689	4.1243307496	2.5711920559
H	-1.6343501574	4.2969083622	2.0133245631
H	-1.2972241693	2.8048937898	2.8986142966
H	-3.2567301048	4.0226476336	-0.0062103195
H	-3.3378487296	2.4508281688	-0.8510901553
H	0.855019929	2.0588114912	2.0946218958
H	2.6206674577	1.8677606494	-1.8209934025
H	3.1025408363	0.9351021911	2.1762303249
H	0.9145038934	-2.5957110387	1.0742359716
H	0.8278949643	-0.626864277	-2.8576081094
H	4.0372769688	-0.6942899345	0.0102955083
H	1.4231897767	4.4586015032	2.2391742256
H	1.8447021132	-3.7913104469	3.0163825932
H	2.5848425409	5.5778516883	0.3481537487
H	3.4241954167	-2.6282979435	4.5557640349
H	4.7613052448	-1.8759958772	-4.0547740833
H	-1.9767086204	-0.9676886799	2.7627201366
H	-1.9871144221	-3.0624090159	4.0133780617
H	-1.0951640113	-5.2482425594	0.4120311676
H	-1.5475748284	-5.2352264144	2.8816693109
H	3.1765515283	4.2775370004	-1.6805928739
H	4.0545627529	-0.2682761101	4.1165727103
H	5.5876813847	-1.4962665255	-1.7439888947

VIId

79

C	4.9540707749	0.1318156564	1.37728883
C	3.7657148911	-0.5151151005	1.0150858268
C	2.821549551	-0.7100786587	2.0327461015
C	3.0149828805	-0.2006172873	3.3103807796
C	4.1775328366	0.501265437	3.6194874497
C	5.1604798098	0.6473876472	2.6547173464
Pd	0.6198090215	-0.6047344537	-0.7408825796
P	-1.540205775	-0.0563661483	-0.2410692392
C	1.1409461146	1.2566715227	-1.5040792224
C	2.657161678	0.9980284912	-1.6375798855
C	3.2474713059	2.08337441	-0.7127587398
C	3.1012065608	3.4121812964	-1.4795759503
C	1.5726093924	3.668036521	-1.4639673718
C	1.0370544266	2.4909147383	-0.62175771
C	2.1818892649	2.2872465856	0.3715591244
C	2.9025933103	-0.5151114429	-1.4363316217
C	3.4818781785	-1.1527058906	-0.3042552882
C	3.7607771833	-2.5185427694	-0.3292943102
C	3.4923520163	-3.2897142231	-1.4476036289
C	2.9286345614	-2.6936181924	-2.5616725188

C	2.6363551579	-1.3307831181	-2.5818247699
C	2.1472779906	-0.7520012171	-3.881551149
Br	0.236024427	-3.0106561305	0.2871805246
O	7.156628824	0.5996946517	0.8862437586
O	5.8626296826	0.0552707914	-0.754377005
N	6.0728083358	0.2730153877	0.4288084012
C	-1.8432802144	-0.1755192786	1.5722590832
C	-2.892238061	-0.9262724998	2.0955627934
C	-0.9512334879	0.4734873241	2.4327983646
C	-3.0667617061	-1.0065406914	3.4758779248
C	-1.1376746936	0.4023039065	3.8088947249
C	-2.1972216033	-0.3383856645	4.3318440655
C	-2.8944498325	-1.0261780266	-1.0333769103
C	-4.2027852625	-0.530593113	-0.9862788338
C	-2.6264797873	-2.226219864	-1.6892611521
C	-5.2372872181	-1.2431169374	-1.5824069709
C	-3.6661236934	-2.9302642669	-2.2955618271
C	-4.9676781723	-2.4420831377	-2.2413623662
C	-2.0873384148	1.664257297	-0.6503202105
C	-2.4040274432	2.6048923393	0.3273676694
C	-2.0745405245	2.0403263835	-1.9973414305
C	-2.6718471371	3.9240461582	-0.0368841009
C	-2.3396041294	3.3559531648	-2.3570584341
C	-2.6254429872	4.3039570522	-1.3742145533
H	1.9168670781	-1.2764470311	1.7942397169
H	2.2510431563	-0.363223563	4.0688274583
H	4.3322605754	0.9097506751	4.6159161003
H	6.1021592206	1.1443374899	2.8678784929
H	0.5929113175	1.3571979389	-2.4515472597
H	3.0076550121	1.2156864242	-2.6590124957
H	4.2722390117	1.8991494029	-0.3849804238
H	3.5221073585	3.3588095629	-2.4924058615
H	3.6398717682	4.208084669	-0.9480690798
H	1.1283238893	3.6839427903	-2.4686479165
H	1.3215569674	4.625841867	-0.9869469261
H	0.0418376104	2.6752194188	-0.2082497654
H	2.3801518512	3.17883878	0.9842327104
H	2.03411438	1.4288534009	1.0364985159
H	4.1774181806	-2.9799858229	0.5651433711
H	3.7066615009	-4.3562395026	-1.4402034792
H	2.7130110814	-3.2898351778	-3.4477097044
H	1.2604333269	-0.1190214844	-3.7736633092
H	1.8936625954	-1.5556951825	-4.5818738502
H	2.9271763706	-0.1382004723	-4.3575265562
H	-3.5621359467	-1.4608903767	1.4271018237
H	-0.1060722381	1.0292209426	2.0244536416
H	-0.4508077006	0.9182253092	4.4752496389
H	-2.336530333	-0.4016915983	5.4074819733
H	-4.4077717102	0.4127924413	-0.4833812436
H	-1.6117955358	-2.6195747079	-1.6980436549
H	-3.453463883	-3.8658544086	-2.805400881
H	-5.776094727	-2.9954332957	-2.7122129
H	-2.4228108964	2.3148276285	1.3750589153
H	-1.8474360601	1.2982496315	-2.7624024886
H	-2.3200545709	3.6454825265	-3.4044413649
H	-2.8196055088	5.335510786	-1.6548006824
H	-3.8803296717	-1.6020407414	3.8806946706
H	-6.2532461796	-0.8600857082	-1.5387330657
H	-2.9112215634	4.656123458	0.7298662807

VIIId

79

C	4.6371879595	0.5635268362	1.5974374034
C	3.6471687985	-0.3392911407	1.1734452942
C	2.5272565678	-0.4459171817	2.0101394851
C	2.3839209283	0.3251331948	3.1571871142
C	3.3758867722	1.2265030814	3.531544053
C	4.5194370755	1.3277975038	2.7553603076
Pd	0.8463683053	-0.5455373896	-0.8031280377
P	-1.5177206279	-0.0487309654	-0.3222865469
C	0.792554624	1.408144008	-1.9534696245
C	2.1179383932	1.010342607	-2.0103604617
C	2.9114484135	2.0370860779	-1.2409447315
C	2.8711262629	3.2843223861	-2.1709898247
C	1.3923689181	3.7390804219	-2.0923675886
C	0.7574106621	2.6879233554	-1.1438975065
C	1.9136412251	2.4676106322	-0.1620018231
C	2.7627652614	-1.3722662808	-0.9717613865
C	3.7738191385	-1.2225064615	-0.0130457715
C	4.950609425	-1.9765626665	-0.1482443612
C	5.1360529541	-2.8260523159	-1.2230107708
C	4.1379028013	-2.9371926675	-2.1838071013
C	2.9428931886	-2.2263828842	-2.0696472374
C	1.8617510886	-2.4496447228	-3.0884575046
Br	0.3011879103	-2.8154334424	0.3061923343
O	6.8976452789	0.9658181631	1.4870239182
O	5.8270973371	0.809932639	-0.3826776797
N	5.8792373943	0.7880853095	0.8369874869
C	-1.7216901212	-0.0091072104	1.5111582046
C	-2.5225819407	-0.9220460286	2.1944058549
C	-0.9746015494	0.931348562	2.2294437893
C	-2.6073391559	-0.8693606923	3.5838344405
C	-1.0806125611	0.9964708234	3.6157313051
C	-1.8988961599	0.0954398536	4.2946328426
C	-2.8315650937	-1.190362655	-0.9463486624
C	-4.1748055862	-0.921591559	-0.6598645418
C	-2.5011514051	-2.2626937866	-1.7724264348
C	-5.1740522304	-1.7382754686	-1.1769486053
C	-3.5064294201	-3.0716080892	-2.3001285827
C	-4.8397135729	-2.8140651342	-1.998825872
C	-2.3023185094	1.5520492431	-0.8574784263
C	-2.6365454617	2.5826946696	0.0193496011
C	-2.4894239181	1.7326717496	-2.2326954702

C -3.1125084874 3.7966061435 -0.4767808386
C -2.9567264978 2.9450069722 -2.7253238659
C -3.2587948999 3.9854073372 -1.8467836514
H 1.7644726698 -1.1818304203 1.7603386481
H 1.4874156072 0.2008588104 3.7626529193
H 3.273631868 1.8308558793 4.4305857341
H 5.3321185847 1.9972687496 3.023929364
H 0.0535177058 1.1917743533 -2.7247416763
H 2.561336115 0.4244505058 -2.8116814374
H 3.9130675138 1.7322462462 -0.9307123084
H 3.195355207 3.0471928828 -3.1921805397
H 3.5514232596 4.0546755515 -1.7857746311
H 0.8900794041 3.7668865735 -3.0682786125
H 1.3024795659 4.7404942674 -1.6513275783
H -0.2187040535 2.9733433837 -0.7399522711
H 2.2186300291 3.3913790304 0.3497042437
H 1.7258692013 1.6844382296 0.5862366717
H 5.7255374479 -1.8871797156 0.6145759406
H 6.05572774 -3.4009114304 -1.313486054
H 4.2733668675 -3.6045042742 -3.0366127427
H 1.0782573337 -3.1014121219 -2.6737125627
H 2.2590396643 -2.9304076582 -3.9919694135
H 1.3674470288 -1.5140183031 -3.3911153943
H -3.0695749365 -1.6811856029 1.6415652317
H -0.3031743966 1.6119609132 1.704776636
H -0.5157328524 1.7457505849 4.1656608231
H -1.9749271527 0.1383903971 5.3777138899
H -4.4372632104 -0.0666852655 -0.0393976599
H -1.4573806754 -2.4761623094 -1.9864884224
H -3.2424211635 -3.9072981091 -2.9424218083
H -5.6217975501 -3.4492227544 -2.4060532005
H -2.5186763031 2.4448428406 1.0910008622
H -2.2749422923 0.9147092681 -2.9206145168
H -3.0912655748 3.0786633912 -3.7952416831
H -3.6186250587 4.9354354954 -2.2324852656
H -3.226416999 -1.5893261937 4.1117910629
H -6.2155879376 -1.5305199303 -0.9465356521
H -3.3676039723 4.5956168171 0.2144182081

trans-**IXd**

96

C -0.6248920953 2.8724819168 1.0245616207
C -1.4194267195 3.1653499726 -0.2071817651
C -1.0345713425 3.138893593 -1.5570399209
C -1.9119234225 3.4289403818 -2.6020258746
C -3.223122019 3.7776710769 -2.3266377907
C -3.6457056671 3.8155496387 -1.0023925186
C -2.7601965487 3.5146178486 0.0236797977
C -0.5529230656 3.9197568388 1.9528650724
C -0.0758276549 3.7028409649 3.2369227289
C 0.2735801905 2.4145418611 3.6188226511
C 0.228064765 1.351947278 2.7088085073
C -0.1729737533 1.5891893014 1.3806646052
C 0.6318154921 -0.0133417976 3.1909850391
Pd -0.0795504636 0.1175308296 -0.0588527271
H -1.5364250125 3.3872848501 -3.6201390013
H -3.9072414744 4.0120890206 -3.1394193615
H -4.6764629357 4.0674891587 -0.7580532628
H -0.8966117022 4.9117917006 1.6570746504
H -0.0175030528 4.5263880578 3.9469780376
H 0.6039305909 2.2177116725 4.64057456
H 1.6861821297 -0.2343918889 2.9711214592
H 0.5046020244 -0.0984478675 4.2786787152
H 0.0474591787 -0.8134364965 2.7153915683
P 2.3660540322 0.2048160567 -0.1932261763
C 2.9461069419 -1.1313882217 0.9644101065
C 3.1988587671 -0.2530886192 -1.7768590139
C 3.4475887704 1.6141400371 0.3584142176
C 3.0561597534 2.4165087627 1.43120089
C 3.8849927542 3.4398688233 1.8786292782
C 5.1104189074 3.6704029026 1.2581425275
C 5.5050996405 2.8683691157 0.1909257057
C 4.6771763568 1.8430324753 -0.2612471611
C 2.3486798846 -2.3944288763 0.8944782146
C 2.6799934834 -3.3777613046 1.8196043229
C 3.6140264977 -3.1114118295 2.8199938196
C 4.2328514345 -1.8661908235 2.8733005569
C 3.9034671365 -0.8776016688 1.9472253235
C 4.0412680622 -1.3591602119 -1.8635423663
C 4.6678237208 -1.6615159336 -3.0711459188
C 4.4570402456 -0.857902678 -4.1868187498
C 3.6214564417 0.2537280475 -4.0936172821
C 2.9897860057 0.5589371056 -2.8933125849
H 2.1062283002 2.2401551529 1.9203786021
H 3.560871225 4.0601920708 2.7105149247
H 5.7567747717 4.4727693161 1.6041468386
H 4.9866931461 1.2236253504 -1.0984249874
H 1.6252179266 -2.6026803352 0.1057117634
H 2.2084584245 -4.3557649601 1.7582316253
H 3.8635580351 -3.8765660766 3.5502543711
H 4.3778733854 0.0990428139 2.0014292695
H 4.2047448041 -1.9892365447 -0.9935975306
H 4.9412687492 -1.0980006413 -5.1298382702
H 3.4492652668 0.8822993098 -4.9630647132
H 2.3240314363 1.416671032 -2.8364441001
P -2.3320720582 -0.4437914609 0.381334812
C -2.4576640183 -2.0312196885 1.3272780726
C -3.4189651132 -0.6788712721 -1.0910186892
C -3.4443006778 0.6370945037 1.4115563831
C -3.0308320379 1.0084973544 2.6946503205
C -3.83171221 1.8306417007 3.4796692307
C -5.0623059909 2.2758651077 2.9965854597
C -5.4893294862 1.887242801 1.7299227923

C	-4.6825237682	1.0720031936	0.9367532093
C	-3.5662486135	-2.2942561608	2.1384898083
C	-3.6461545111	-3.493077245	2.8414830888
C	-2.6190993042	-4.4299405757	2.7482290537
C	-1.5128464123	-4.1687958729	1.9446421682
C	-1.4330715451	-2.9745230151	1.2338719561
C	-4.3247013048	-1.7321082802	-1.1765279617
C	-5.1941353157	-1.8086214757	-2.2637513469
C	-5.1581521589	-0.8352680602	-3.2581224152
C	-4.2431527676	0.2133187191	-3.1733810117
C	-3.3686718258	0.2889026368	-2.096068112
H	-5.6886434559	2.916719863	3.611513197
H	-4.363180621	-1.5592018585	2.2242277223
H	-4.5105645095	-3.6928669203	3.469219584
H	-2.6816409126	-5.3617684109	3.3039967814
H	-0.5795818138	-2.7738092788	0.5902667411
H	-4.3529128576	-2.4917732144	-0.3991782078
H	-5.8369789702	-0.8974795491	-4.1043799591
H	-4.1982823841	0.9674450227	-3.9551273686
H	-2.6434970162	1.098388094	-2.0436686646
I	-0.0964126423	-1.6527843334	-2.1334608572
H	-3.1140326847	3.5151491052	1.0535851787
O	0.527542824	2.5120071976	-3.1256535173
N	0.3428134209	2.8501736177	-1.9646391004
O	1.2337652415	2.9761845385	-1.1407976045
H	-3.4939630384	2.122314161	4.4706434479
H	-5.015346891	0.7795391767	-0.0559231203
H	-2.076403632	0.6609045938	3.0790935619
H	-5.898088553	-2.6336702923	-2.3334526248
H	-0.7075358249	-4.8944443625	1.8666417227
H	-6.4549787758	2.2164606558	1.3536580588
H	5.318548251	-2.529592396	-3.1369255067
H	6.4608873458	3.0399697965	-0.2973664806
H	4.9734218204	-1.6576405653	3.6411227938

cis-**IXd**

96

C	0.5724203902	-3.9610811538	0.3257853887
C	-0.4948141654	-3.7351409049	1.3449147703
C	-0.3766281725	-3.0282261605	2.5461000657
C	-1.4441234183	-2.8333520908	3.4201282196
C	-2.6832270628	-3.3704847365	3.1121925302
C	-2.8386484616	-4.0895128766	1.9280558082
C	-1.7638340019	-4.2616857855	1.0661142659
C	1.301449901	-5.1517025797	0.3918423749
C	2.1680317146	-5.4914516017	-0.6359630991
C	2.2695615923	-4.658293356	-1.7434362422
C	1.5581972571	-3.4557513716	-1.8316139931
C	0.7320491758	-3.085851308	-0.7570646135
C	1.7482709754	-2.6036683117	-3.0520958501
Pd	-0.3377559143	-1.322141859	-0.5238506988
H	-1.2794310737	-2.2730055944	4.3366816334
H	-3.5204530597	-3.2293137226	3.7924185097
H	-3.8079477995	-4.511732624	1.6663265552
H	1.1726097456	-5.8067868075	1.2541600789
H	2.7392845026	-6.4174235498	-0.5895175888
H	2.9165389082	-4.939907653	-2.5765880899
H	2.5624582077	-1.8756662423	-2.9198599698
H	2.0030546438	-3.2245958985	-3.9207378836
H	0.8419640513	-2.0351461509	-3.2909617246
P	1.6807326495	-0.1290595347	0.0686620695
C	2.3616722291	0.3737299942	-1.5797890123
C	1.6153234004	1.5300539706	0.8970132642
C	3.1335287236	-0.9274115359	0.900222783
C	3.6118940915	-2.1353974372	0.3809209498
C	4.6879005253	-2.7787340427	0.9784916773
C	5.2958499817	-2.2260333373	2.1029376406
C	4.8250658257	-1.0234824141	2.6205196153
C	3.7482039704	-0.3726222784	2.022465454
C	1.4644958842	0.8306282099	-2.5493246654
C	1.9336224115	1.2596145752	-3.7858862374
C	3.2982464089	1.2174890303	-4.0668631758
C	4.1929938425	0.7656946414	-3.0995413545
C	3.7281428002	0.3520628286	-1.8522389304
C	1.9421630763	2.7018398295	0.2114315332
C	1.8548185708	3.9362674816	0.8524807506
C	1.4332296194	4.0106562935	2.1768085113
C	1.1202086749	2.8427050895	2.8690987965
C	1.2155610662	1.6074049634	2.2357257696
H	3.1250947402	-2.588173546	-0.4751453704
H	5.0313556422	-3.7250195823	0.5682628747
H	6.1309307546	-2.7339813039	2.5781664928
H	3.394007612	0.5675319385	2.4334661365
H	0.3952789167	0.8559487779	-2.3445984518
H	1.2249473733	1.6231595296	-4.5263431016
H	3.6651301478	1.5399727795	-5.0378054778
H	4.4251184208	0.0012124746	-1.0950646278
H	2.2543705265	2.6581277018	-0.8278415038
H	1.3549647004	4.9748086656	2.6723841423
H	0.7846614052	2.8885415655	3.9018705981
H	0.9977268727	0.6970598911	2.788538833
P	-1.9330186853	0.4805473898	-0.111079948
C	-1.6779870245	1.8682957199	-1.2911830352
C	-2.0046187721	1.2319035542	1.5764695902
C	-3.7343097169	0.0795080041	-0.2283282616
C	-4.1488279617	-1.0797594531	0.429720076
C	-5.4960507093	-1.4124593773	0.4682637446
C	-6.4344043965	-0.5922274964	-0.1575583843
C	-6.0196891846	0.5620591203	-0.8150422548
C	-4.6676415577	0.9035963806	-0.8481969089
C	-1.9576176116	1.6330803751	-2.6451761855
C	-1.628563324	2.5900565756	-3.5991916421
C	-1.0009244614	3.7758592625	-3.2148389449

C -0.7072864528 4.0015555199 -1.8740628639
C -1.0468554822 3.0524511695 -0.9108975706
C -2.6292137941 2.4517241203 1.8448201247
C -2.7263646786 2.9081743571 3.1556830307
C -2.2276926356 2.1374524629 4.2064080911
C -1.6311717379 0.9085434251 3.9419595031
C -1.5196761041 0.45965343 2.6282056499
H -7.4881449581 -0.8567270672 -0.1359438001
H -2.4129537998 0.6900682669 -2.9490677969
H -1.85367299 2.4059993997 -4.6466567697
H -0.736384353 4.5178794165 -3.9635525241
H -0.8054485619 3.2294101887 0.1348248297
H -3.0489322874 3.0427654582 1.033379143
H -2.3090121915 2.4963321126 5.2293588822
H -1.2194863706 0.3053916504 4.7477809769
H -1.0161946002 -0.4828793467 2.4266452203
I -2.0441847143 -2.5062150112 -2.2192854919
H -1.8944994644 -4.7906296935 0.1235073047
O 0.8751961526 -1.3686534715 3.5416925777
N 0.9073129835 -2.4499798137 2.9527431649
O 1.918856806 -3.0766731833 2.7177112254
H -5.8138072687 -2.3190452983 0.9778661014
H -4.3440267034 1.8050876838 -1.3644365779
H -3.4098000662 -1.7271673334 0.9002875179
H -6.7487699109 1.2013230752 -1.3061928333
H -0.2074765511 4.9180036862 -1.5698662826
H 2.1172331624 4.8411169243 0.30973779
H 5.2583265739 0.7368495627 -3.313341609
H -3.2045291143 3.8625172786 3.3603076428
H 5.2950726278 -0.5847975154 3.4967951674

Xd

96

C -1.6410810177 -4.1450396303 -1.0499894044
C -0.1561417869 -4.1729332624 -1.0924064164
C 0.6424448609 -3.331343079 -1.8806077403
C 2.0346628925 -3.3835637774 -1.8445065558
C 2.664855828 -4.2800662595 -0.9984580115
C 1.8987297177 -5.1432807561 -0.2208291787
C 0.5130667709 -5.0929970114 -0.2795557131
C -2.3669963366 -4.7203505022 -2.0948563172
C -3.7520614866 -4.6803361928 -2.095691353
C -4.4254499862 -4.0554344852 -1.0532203957
C -3.7423241666 -3.4812105577 0.0212409484
C -2.341441013 -3.5664320004 0.0162697232
C -4.508445767 -2.771584787 1.0938890658
Pd 0.0955603851 -0.7175044985 0.0492724677
H 2.6098155464 -2.7010326642 -2.4652091695
H 3.7505867006 -4.2855870365 -0.9278831359
H 2.3873062225 -5.8514864487 0.4465401956
H -1.8236711782 -5.1742007417 -2.923516026
H -4.3098290573 -5.1271223805 -2.916549792
H -5.5148104035 -4.0051138974 -1.06157049
H -5.5801045178 -2.7647978581 0.8622392125
H -4.3721911657 -3.2415168591 2.0775169473
H -4.1802664737 -1.7261512038 1.1960160949
P -1.6376776549 0.8488438567 -0.2514936217
C -2.4321095303 1.1546397648 1.403260751
C -0.9504166943 2.5312590213 -0.633484893
C -3.152488312 0.7707858533 -1.3103829441
C -3.6805626543 -0.4961725471 -1.5672913691
C -4.8815374513 -0.6245675262 -2.2585924835
C -5.5479995232 0.5114284701 -2.7137678394
C -5.0112695214 1.7762197807 -2.4770958702
C -3.8159434287 1.9073353427 -1.7737601732
C -1.5833504726 1.2888541312 2.5104625419
C -2.1118697427 1.4476461972 3.785688436
C -3.4945826647 1.4563551641 3.9738757453
C -4.3412370299 1.3169892536 2.8787331714
C -3.8137512742 1.1721622634 1.59451901
C -1.2937972108 3.6830090258 0.0770168283
C -0.6249895685 4.8813452048 -0.1742830635
C 0.390044136 4.9329742969 -1.127509515
C 0.72735979 3.7880013175 -1.8491425998
C 0.0550265416 2.5954303645 -1.6032028371
H -3.149459628 -1.3842585488 -1.2288093651
H -5.2843625739 -1.6158910503 -2.4523372777
H -6.4820460862 0.4120987308 -3.2610249207
H -3.3988424472 2.8928861847 -1.5748261552
H -0.5034716926 1.2528931407 2.3677711456
H -1.4414338391 1.5571606361 4.6347581554
H -3.9081256051 1.5687483738 4.972977387
H -4.479969967 1.0721063437 0.7401283528
H -2.0669947364 3.6357645679 0.8414422362
H 0.9236735835 5.8636344011 -1.3019076014
H 1.5359346451 3.8083173181 -2.5768994198
H 0.345247326 1.6877232526 -2.1300983428
P 2.3240437161 -0.1479553919 0.2365983578
C 2.5243667597 1.0433360437 1.6508428722
C 3.0851516658 0.8351014574 -1.1398176699
C 3.6739973379 -1.3730396441 0.6076349858
C 3.3649840117 -2.3978118672 1.5078493854
C 4.3150307289 -3.3587155114 1.8360074133
C 5.5731670236 -3.3275558155 1.2335385824
C 5.8761511308 -2.3257359876 0.3142733879
C 4.9321723663 -1.3445240672 0.0080964668
C 3.3220404904 0.7827560387 2.7632931609
C 3.3469681141 1.6798408822 3.8319897987
C 2.5826595754 2.8419337257 3.79086759
C 1.794991994 3.1134988829 2.6717417781
C 1.76405384 2.220685686 1.6065849175
C 3.982839073 1.877336301 -0.8984666422
C 4.4790943047 2.6349376851 -1.9566015718

C	4.0820841324	2.3545438953	-3.2629399552
C	3.1968444678	1.3065239137	-3.5098022809
C	2.6985528103	0.5490099319	-2.4513222011
H	6.3144443279	-4.0838826284	1.4791350397
H	3.9205868367	-0.1244811227	2.801159544
H	3.9695954556	1.4671230721	4.6974355939
H	2.6013854618	3.5371346468	4.6261958009
H	1.1407881069	2.4307717595	0.7381199317
H	4.2801446082	2.1050738257	0.123333168
H	4.4644527132	2.9509693098	-4.0877849805
H	2.8832430681	1.0809373219	-4.5258091331
H	1.9847719435	-0.2510210073	-2.6507001177
I	-1.2624151645	-2.7545563555	1.6458675201
H	-0.0879650327	-5.7615129197	0.3365495201
O	0.7975484507	-1.8142102087	-3.6139001604
O	-1.1442980291	-2.1068218983	-2.7251641358
H	4.0699445886	-4.1436232853	2.5480063099
H	5.1768474587	-0.5529980033	-0.6965362649
H	2.3613684221	-2.4433134126	1.934498848
N	0.0479420586	-2.3397805202	-2.8009165631
H	-0.8907253565	5.7748819783	0.3858744221
H	1.1953026989	4.0197565657	2.6276939759
H	-5.5267860006	2.6625330503	-2.8387146834
H	-5.4194918338	1.3248770123	3.0189313584
H	5.1706525474	3.4502603288	-1.7598411169
H	6.8543078468	-2.2997439939	-0.1599929971

IIe

84

C	-1.1669003333	-3.4927623196	1.3579844642
C	-0.4730624533	-3.9642358814	2.4534269992
C	0.8949394144	-4.3055178034	2.3715101417
C	1.540643696	-4.1518511576	1.1585529459
C	0.8729292256	-3.6372990126	0.0278571173
C	-0.4943602855	-3.3059406518	0.1284590863
Pd	0.6130938509	-1.2308036482	0.2851776923
H	-0.9962397274	-4.0913684516	3.4023920993
H	2.5959890102	-4.4147306635	1.0622827659
P	2.8316753442	-0.4974107139	0.1472250845
C	3.8367707495	-1.3196238279	-1.1770465818
C	3.1383419755	1.2944145057	-0.2291431454
C	3.8904887369	-0.7199777159	1.6536003079
C	3.4690613275	-1.6429975876	2.6143259514
C	4.2350885679	-1.8579861186	3.7588949315
C	5.4168741675	-1.1489780973	3.9580454077
C	5.8076179741	-0.2294751493	2.9968950486
C	5.0709738042	0.0039831954	1.8492762539
C	3.1910369455	-1.5643693009	-2.3955379863
C	3.8714024675	-2.1824414334	-3.4398062204
C	5.19617885	-2.5851208329	-3.2725943423
C	5.8078189701	-2.3460121642	-2.0542803129
C	5.1609320753	-1.718649256	-1.0018581355
C	3.5545053621	1.7258526251	-1.4879307416
C	3.6932588898	3.0870881824	-1.7067994103
C	3.4595292227	4.0340241935	-0.7283875478
C	3.0324020688	3.5939137011	0.5237854503
C	2.8605514606	2.237020191	0.7686869339
Cl	7.3371280033	0.7109685499	3.2649406552
Cl	4.1775089029	3.6606767885	-3.3638605928
Cl	7.5292471586	-2.8757816506	-1.8233543737
H	2.5380790797	-2.1893528399	2.4607864752
H	3.9092884218	-2.57594794	4.5061891093
H	6.0240389316	-1.2995924591	4.8448680645
H	5.4007467161	0.7446225376	1.124609071
H	2.1460458828	-1.2729602097	-2.5106770659
H	3.3703687934	-2.365409745	-4.3862810923
H	5.7411251479	-3.0803352734	-4.0696444858
H	5.6823000442	-1.5487691855	-0.0642323479
H	3.7660987934	1.0187541797	-2.2852830573
H	3.5895978766	5.0886713783	-0.9438681384
H	2.8260240007	4.3200764875	1.3052861599
H	2.5191423837	1.9074214309	1.7476776774
P	-0.9083895349	0.5566339297	0.2625808433
C	-0.3812796038	1.6811061664	-1.1148523627
C	-0.9597839662	1.6843148463	1.7298400754
C	-2.7224027079	0.3603618072	-0.0743996992
C	-3.3286523648	0.7908381279	-1.2523325567
C	-4.6618987979	0.4750515418	-1.4617537273
C	-5.4153692884	-0.2373272717	-0.5469428868
C	-4.8015299388	-0.649807123	0.6368860063
C	-3.4638894746	-0.3578034481	0.8704732114
C	-0.1465128884	1.0849060517	-2.3619778493
C	0.3199579141	1.8451247555	-3.4287123055
C	0.5662200137	3.2086040323	-3.2664328521
C	0.3291847381	3.7719485895	-2.0265744896
C	-0.1396836606	3.0425629256	-0.9449018936
C	-0.0278921683	1.4815881502	2.7497887441
C	-0.0319435258	2.2988665263	3.8787942793
C	-0.9744326071	3.3167694141	4.0023134202
C	-1.899517855	3.4905258661	2.9841458707
C	-1.9170364236	2.6967452895	1.8510340101
Cl	0.6518378163	5.5468527344	-1.8002883991
H	-6.4562269162	-0.4636836645	-0.7520396559
H	-0.3218308235	0.0155197593	-2.4843466144
H	0.5018083944	1.3798791821	-4.3936120738
H	0.9551632272	3.8140335659	-4.078598773
H	-0.2925839918	3.5295600634	0.0137392281
H	0.6877255384	0.6631506415	2.6585066619
H	-1.0013841374	3.9592432179	4.8764745464
H	-2.6648720664	2.8571711149	1.0773725906
H	-2.9803173504	-0.6928832216	1.7877817008
H	-2.7739357795	1.3523406715	-1.9989565404
Cl	-3.1453045458	4.7993699063	3.1581458093

Cl -5.4521341341 1.031976552 -3.0017919014
H 0.6906647586 2.1369286285 4.6737095658
H -5.3770840176 -1.2045168573 1.3727532977
H -2.230041062 -3.265640017 1.4261287717
H 1.3678823363 -3.6565505328 -0.9417799393
C 1.620870067 -4.8123288506 3.5807716891
H 2.6851785128 -4.9765053807 3.3690101266
H 1.5479538686 -4.1021913408 4.4179715868
H 1.201941117 -5.7627910861 3.9392872624
I -1.6296764953 -3.0525194595 -1.6484393342

trans-**IIIe**

84

C -0.2755390494 2.8309393198 -0.5336326734
C -0.276413358 4.1726514203 -0.1701651839
C -0.0000097098 4.5652303885 1.1431581707
C 0.2949443338 3.5724440539 2.07688871
C 0.2875877381 2.2204992274 1.7208053615
C -0.0066468264 1.8393377816 0.4124466684
Pd -0.0950124415 -0.1446897943 -0.0997524277
H -0.5138713437 4.9329151352 -0.9169204746
H 0.5282933341 3.8570006686 3.1049905583
P 2.2785862764 -0.0473685265 -0.2130529743
C 2.9391689477 -0.2238937529 1.5061949294
C 3.2028246177 -1.3701945321 -1.1118929208
C 3.1590017695 1.4519594839 -0.871089427
C 2.9587493499 2.7080688187 -0.2857334216
C 3.6038151889 3.8286242764 -0.7983158598
C 4.4462118997 3.7193527908 -1.9027693606
C 4.6266163916 2.4685482838 -2.4654995722
C 4.0080282676 1.3318695492 -1.9741528032
C 2.4050532358 -1.2492221306 2.2935630667
C 2.8688016797 -1.442231026 3.590778122
C 3.8604613563 -0.6141845996 4.1154999712
C 4.3744528836 0.3889636283 3.3129868742
C 3.9406463101 0.6024722975 2.0142030538
C 4.4026854345 -1.8636877613 -0.6001985058
C 5.1055568303 -2.7907971021 -1.3508053786
C 4.6630013037 -3.2404153499 -2.5827954021
C 3.462612911 -2.7391704261 -3.0819658759
C 2.7289890297 -1.8113971957 -2.3483821818
Cl 5.7149575449 2.304701162 -3.9095822476
Cl 6.668420044 -3.4370707809 -0.6916950753
Cl 5.6720779497 1.4647825859 3.9854860344
H 2.2958668561 2.8142440968 0.5669604752
H 3.4382774014 4.7979517449 -0.3362920518
H 4.950454268 4.5848236964 -2.320069397
H 4.1873045123 0.3713992127 -2.4461685552
H 1.6333315356 -1.9006492917 1.8835256996
H 2.458517092 -2.2419514989 4.2004841624
H 4.2295050488 -0.7469263521 5.1271040835
H 4.3758584137 1.3969314639 1.415011133
H 4.7894290303 -1.5300542781 0.3587909457
H 5.2437208209 -3.9701069669 -3.137528736
H 3.0920140616 -3.087284174 -4.0413279344
H 1.7818127165 -1.4401779329 -2.7321554854
P -2.450255433 -0.0076730701 0.0533072143
C -3.3241114744 -0.8732051719 1.4315176043
C -3.2654628447 -0.6270350636 -1.4832964427
C -3.1647384475 1.6981048519 0.2056080602
C -2.9787599567 2.381938632 1.4105601027
C -3.3784899686 3.7065738702 1.5302253883
C -3.9688282289 4.3644918325 0.4510036436
C -4.1570483472 3.6596486717 -0.7238822
C -3.7732049805 2.3362374966 -0.8735915428
C -2.6836031586 -1.8738213173 2.1608553907
C -3.3624719463 -2.5318593216 3.1849962683
C -4.6785186242 -2.1968451515 3.4878772396
C -5.2914274982 -1.1926000104 2.7546564475
C -4.6443536256 -0.5181272619 1.7359566231
C -4.3765058053 -1.465338996 -1.4496733381
C -4.9194356174 -1.885356548 -2.6534777979
C -4.4001649393 -1.5066632387 -3.8783448779
C -3.2819485154 -0.6741256845 -3.8986296361
C -2.70989012 -0.2432011659 -2.7074447683
Cl -4.9250148493 4.5055591105 -2.137119739
Cl -6.3614931399 -2.984165596 -2.6209168354
Cl -7.0036909463 -0.7433986951 3.1495799232
H -4.2783594631 5.4024457723 0.5225863811
H -1.6612226551 -2.1516993269 1.9154681934
H -2.8633528221 -3.3153371189 3.7472899442
H -5.2232257134 -2.7025576876 4.2783830791
H -5.1543662925 0.2725350269 1.1913065669
H -4.8072394021 -1.798973195 -0.5103042644
H -4.852977927 -1.864863353 -4.796983202
H -2.8510770095 -0.376276188 -4.8498984792
H -1.8157409167 0.3790903361 -2.7231934477
I -0.2990702779 -2.8097916307 -0.6407061806
H -3.2144470327 4.2402969183 2.4623943078
H -3.9382025024 1.8213884287 -1.8158835148
H -2.4907687348 1.8863280277 2.2463306466
H -0.5018017789 2.5624989213 -1.5675028176
H 0.5245588228 1.4707162944 2.4780632241
C -0.076442116 6.0105475989 1.5356971791
H 0.3746089907 6.1905102831 2.519284199
H 0.426904587 6.6608748706 0.8079672979
H -1.1236461559 6.3447054548 1.5870373053

cis-**IIIe**

84

C -1.704375902 -3.5896902308 -1.8760982822
C -2.8403064706 -4.383906788 -2.0306467774
C -3.7540863765 -4.5488741051 -0.9875410387
C -3.47821959 -3.9248024245 0.2307431638
C -2.3345812388 -3.1473846672 0.4029549302
C -1.4707499072 -2.9339986151 -0.6669519185
Pd 0.0745637124 -1.5775846207 -0.5814311375
H -3.0209750423 -4.8832360033 -2.9847109099
H -4.1700398358 -4.0473673966 1.0670302306
P -1.6269655659 0.1573625103 -0.5181127366
C -2.3852411698 -0.0378876647 1.158222551
C -1.1922249052 1.9602995304 -0.5295238937
C -3.131586547 0.2213374437 -1.6061782568
C -3.5924948227 -0.938841353 -2.228748679
C -4.7624899878 -0.9086811265 -2.9838768365
C -5.4770002907 0.2760223975 -3.133452574
C -4.9942380265 1.4162798396 -2.5112398533
C -3.8402126382 1.4190126319 -1.7492117064
C -1.5602387766 0.1002829724 2.279519028
C -2.066549388 -0.1495672713 3.5499588738
C -3.387299947 -0.5677575318 3.7117058174
C -4.1769930843 -0.7065749482 2.5837514043
C -3.7107687955 -0.4393635388 1.3071573925
C -1.6050396885 2.845075233 0.4706084694
C -1.3037788197 4.1907392247 0.3259091915
C -0.5857105657 4.6829179459 -0.7520095642
C -0.1856704147 3.7932543582 -1.7464174906
C -0.5026996626 2.4423453233 -1.6430443257
Cl -5.9134748552 2.9706244137 -2.7029305459
Cl -1.8832031677 5.3613961195 1.5812814112
Cl -5.8860025118 -1.2876220706 2.7793293784
H -3.0445731633 -1.8668046262 -2.1217184672
H -5.1163972909 -1.821437903 -3.4556980017
H -6.3891528528 0.3188084568 -3.7198866048
H -3.5021539718 2.3370370298 -1.277723496
H -0.5244052638 0.4091103333 2.1644616067
H -1.424322561 -0.029059592 4.4179631687
H -3.793724462 -0.7869207044 4.6932969837
H -4.3569261957 -0.5823154127 0.4459620469
H -2.1532566183 2.4992813329 1.3430055727
H -0.3550056797 5.7413388819 -0.8151540675
H 0.3850423683 4.1521358942 -2.5985018372
H -0.2047948326 1.7560618358 -2.4311611117
P 2.109812771 -0.1994440989 -0.340026547
C 2.0227991563 0.4234381302 1.395114142
C 2.4590922795 1.2581576287 -1.4343149141
C 3.8256984981 -0.8939265329 -0.4574058808
C 4.848254067 -0.4391165856 0.3741797944
C 6.1326592643 -0.906965577 0.1547603287
C 6.4372588594 -1.7988347397 -0.8588968305
C 5.4071329141 -2.2388401303 -1.6867193644
C 4.104364397 -1.7912850973 -1.4880303274
C 2.2975117999 -0.4965225518 2.4167524527
C 2.067330525 -0.1550067551 3.7448772277
C 1.5351583725 1.0918180361 4.0717603643
C 1.2493279093 1.9741027886 3.0452054899
C 1.4858001365 1.6731333334 1.7119021982
C 2.1816194536 1.0717723003 -2.7918074676
C 2.4912392011 2.0649476103 -3.7162590256
C 3.0678008965 3.2606531357 -3.2909237564
C 3.3423946156 3.4174491741 -1.9422051309
C 3.0708460172 2.4346668586 -1.0044114827
Cl 0.4652083631 3.5542317258 3.4428476251
H 7.4573483119 -2.1416547006 -0.9962411768
H 2.6666795178 -1.4895449015 2.1685815989
H 2.288800423 -0.869545514 4.5321534283
H 1.3378107395 1.3701777955 5.1022302514
H 1.2258059394 2.3993575451 0.9460357205
H 1.7103719621 0.1451049685 -3.1206568854
H 3.3099592318 4.0522569779 -3.992865217
H 3.33719889 2.5935820952 0.0373533442
I 1.4120804809 -3.782268123 0.0361735658
H 3.3024233411 -2.1524060353 -2.1272078528
H 4.6540560775 0.2621650244 1.1812660567
Cl 4.0884400853 4.9732593486 -1.3843218445
Cl 7.4688469131 -0.3160976943 1.2338952847
H 2.2804563362 1.9151120868 -4.7715155077
H 5.6221679313 -2.9442070106 -2.4837649659
H -1.0128998966 -3.4722748932 -2.7115458422
H -2.1391578651 -2.6918375475 1.3738282425
C -4.9738422119 -5.4066478109 -1.1523367303
H -5.2481920666 -5.5217745606 -2.2085977125
H -4.8110588324 -6.4159786553 -0.7484613763
H -5.8381089095 -4.9858498228 -0.622248485

A.2.4 TSs

I-IIa

84

C -1.4181814557 -3.7083405539 -1.8433364656
C -2.6621299262 -4.122940821 -2.3140530327
C -3.75916627 -4.1327487433 -1.4594704366
C -3.6001768194 -3.7459514382 -0.1289489701
C -2.3650994113 -3.3572416849 0.3884555767
C -1.2788364726 -3.2867995231 -0.5123479028
C -2.219497095 -3.0623598448 1.8468598762
Pd -0.1612354532 -1.2963392923 -0.6366791253
H -2.7652528307 -4.437115201 -3.3525401074
H -4.7369922725 -4.448362385 -1.81918357
H -4.4586198451 -3.753541109 0.5457698285
H -3.2002146652 -2.996798254 2.333061617

H	-1.6437277668	-3.8560264324	2.346784031
H	-1.6886423078	-2.1177571133	2.0276529506
P	-2.0069365913	0.3019425571	-0.520916747
C	-2.849894408	0.1947018173	1.1225552066
C	-1.6300643212	2.1153391962	-0.6397071501
C	-3.4560391553	0.219348149	-1.676292145
C	-3.6338749365	-0.9452166468	-2.4194405833
C	-4.7267648902	-1.0683720263	-3.2761156034
C	-5.6398591003	-0.0266722073	-3.4034939834
C	-5.4361445552	1.1251586007	-2.6573344829
C	-4.3653413988	1.2745094529	-1.7957388089
C	-2.1292998628	0.5512891673	2.2690386475
C	-2.6875220353	0.3754059913	3.5285623393
C	-3.9495453493	-0.20643648	3.6650260814
C	-4.625118648	-0.5786628167	2.5167424189
C	-4.1162597101	-0.3745163082	1.2446221363
C	-2.185504538	3.0826672845	0.2005908145
C	-1.8454156059	4.4099067639	-0.0081635745
C	-0.9532078908	4.8083822169	-0.9903149874
C	-0.4067629138	3.8356815007	-1.8258285534
C	-0.7545847557	2.4989644167	-1.6579864623
Cl	-6.6281238422	2.4874470043	-2.8159205982
Cl	-2.595036811	5.6783915828	1.0503834699
Cl	-6.2314361428	-1.4163609746	2.6785265743
H	-2.9253183582	-1.7625005181	-2.325650344
H	-4.8636713862	-1.9821063244	-3.8484958711
H	-6.494338125	-0.0997630941	-4.0684488981
H	-4.2404646953	2.1935202249	-1.2291388654
H	-1.1286349286	0.9651774274	2.1768245567
H	-2.1308204669	0.6781988178	4.4117485804
H	-4.3926872663	-0.3755040255	4.6407372722
H	-4.6875030953	-0.6714827873	0.3690781334
H	-2.8618145463	2.8107436307	1.0073315704
H	-0.6959168842	5.8567011752	-1.0990081488
H	0.3000681737	4.1170893105	-2.6024617979
H	-0.3317634901	1.7411127513	-2.3134399803
P	1.8496939403	0.0952744611	-0.5683426868
C	1.7124869512	0.7420445385	1.163829757
C	2.3764063133	1.5748219492	-1.5672720426
C	3.5075439824	-0.7476948462	-0.5699215732
C	4.5941224382	-0.2697298672	0.1653532243
C	5.8117991715	-0.9134959275	0.038915559
C	5.9952742594	-2.0065675305	-0.7934442706
C	4.9078167477	-2.4707269788	-1.5273216831
C	3.6667375945	-1.8468957941	-1.41406412
C	2.0772869718	-0.0999149437	2.2217205958
C	1.8121958204	0.2647946822	3.5373489403
C	1.1731099439	1.4697603347	3.819416169
C	0.8079205057	2.2820946221	2.7590715663
C	1.0541992914	1.9485567503	1.4359248061
C	2.1757988101	1.4929501228	-2.9477273813
C	2.5794653238	2.5328239793	-3.7805526394
C	3.1880630156	3.6658972914	-3.2421781371
C	3.3866260021	3.7193251934	-1.8723775369
C	3.0007789012	2.6966542257	-1.0217459635
Cl	-0.0932486904	3.8117822279	3.1215982738
H	6.967992306	-2.482820911	-0.8613546308
H	2.5617755302	-1.0511832868	2.014748452
H	2.1022714913	-0.3943584054	4.3504780066
H	0.9588468891	1.7732194453	4.8391429683
H	0.7059003709	2.6038650901	0.6391914965
H	1.6906271959	0.6111032065	-3.366485234
H	3.5072202116	4.4892807528	-3.8726977056
H	3.1739865649	2.7875989873	0.0470215035
I	0.8107773192	-3.6455698455	0.3606382023
H	2.8112964659	-2.2203677441	-1.9739619312
H	4.4998899779	0.5857552417	0.8285641233
Cl	4.1788428504	5.1893874645	-1.1618169769
Cl	7.2280027796	-0.2953537136	0.9940095031
H	2.4228973777	2.4662567311	-4.8536211255
H	5.028285356	-3.3281114689	-2.1832543608
H	-0.5507813376	-3.7151188679	-2.5019660239

V-VIa

79

C	4.4643301242	-0.8045517902	-0.0884399839
C	3.2736067643	-1.3821860884	-0.5655198657
C	3.2154596369	-1.7267602446	-1.9340333746
C	4.3044362539	-1.5278757407	-2.7884946046
C	5.4524136263	-0.9368334706	-2.3022673242
C	5.5106509945	-0.5508922189	-0.9527936487
Pd	1.2844718148	0.0269537669	-0.4102955549
Br	2.3568360618	-2.5715259366	0.7764798794
H	6.2968943909	-0.758773029	-2.9631516074
C	2.2519728068	1.4835106785	-1.55909443
C	2.6263338722	2.7602344166	-0.7623099553
C	1.694424384	3.8300164529	-1.396023822
C	2.2719660707	4.1837624412	-2.7705474473
C	2.0323814776	2.8871426947	-3.5864608183
C	1.2567568649	1.9825397138	-2.5988282095
C	0.4592358462	3.0163118191	-1.7974569321
C	2.441559607	2.5175379672	0.6966686772
C	1.8354010706	1.2994094609	1.0405611123
C	1.6721463796	0.9409417427	2.378486899
C	2.0953427551	1.8159497511	3.3769984817
C	2.6876664178	3.028400035	3.0384809452
C	2.874455946	3.3965304789	1.7048463049
C	3.5410542648	4.699868492	1.3709883833
P	-1.1807582105	-0.5893901457	0.2504187556
H	1.967846384	1.5446701466	4.4249191377
H	3.0275083322	3.7041218356	3.8248872935
H	3.6765024411	3.0444653147	-0.9618853598
H	3.1183903641	0.9633564401	-1.992623377

H	0.6799272188	1.1937147316	-3.0975176899
H	1.5095547236	4.6948147998	-0.7465356647
H	-0.0840304938	2.579028605	-0.9488165395
H	-0.251982723	3.5885152079	-2.4112060182
H	1.4273759984	3.0826902367	-4.4825544347
H	2.9664889743	2.4160672141	-3.9232932771
H	3.332197606	4.4679977104	-2.7163330079
H	1.729219668	5.0312351609	-3.2110605806
H	4.0033396449	5.1457200961	2.2603901761
H	4.3264007022	4.5771752753	0.611438649
H	2.8319635205	5.4369231585	0.968020617
H	1.2057655862	-0.007727147	2.6489926201
H	4.1946074461	-1.8040757286	-3.8347862347
H	6.4106625534	-0.0767645681	-0.5649992698
C	-1.8762407693	0.0238713906	1.8504651999
C	-1.4692080218	1.2900398505	2.292598662
C	-2.7042845116	-0.7586558905	2.6576061902
C	-1.9047446945	1.7767668751	3.5204562384
H	-0.7910382517	1.8861581831	1.68511678
C	-3.1136722569	-0.2480517229	3.878102239
H	-3.028669018	-1.7465531144	2.3439534943
C	-2.7366953763	1.0045738031	4.3293710023
H	-1.5789067241	2.7563817823	3.8583882736
H	-3.0794689115	1.3640682358	5.2941081821
Cl	-4.1853868132	-1.2680400664	4.9327689034
C	-2.1105086193	-2.1701968788	-0.0252380558
C	-1.3975660911	-3.3626519015	-0.1352954979
C	-3.502453416	-2.16970559	-0.1746322872
C	-2.0700166047	-4.5610377115	-0.3734149683
H	-0.3135229978	-3.3502669899	-0.0510643405
C	-4.1419266282	-3.3730405649	-0.4042309964
H	-4.0730181979	-1.2459634319	-0.1155660297
C	-3.4547925724	-4.5737715358	-0.506306584
H	-1.5128615387	-5.488875264	-0.4639211063
H	-3.9961354014	-5.4953239878	-0.6939944307
Cl	-5.9480800266	-3.3844365014	-0.589207982
C	-2.0623622363	0.4723278774	-0.9989911548
C	-1.8494100666	0.1577299187	-2.3466607015
C	-2.8704272641	1.5533108705	-0.6521916582
C	-2.4356102932	0.9311159032	-3.3419583144
H	-1.207607019	-0.6821289587	-2.6106515635
C	-3.4309940385	2.3094935905	-1.669758316
H	-3.0562146247	1.8110063833	0.3872065161
C	-3.2327548151	2.0263254873	-3.0087460901
H	-2.2698831638	0.686141025	-4.3875180525
H	-3.691927539	2.6454916691	-3.772476659
Cl	-4.4706850939	3.7328466172	-1.2263684167
N	1.9709349438	-2.1001203779	-2.5423915748
O	1.9641519708	-2.8355210963	-3.5114860178
O	0.9270919113	-1.5895680278	-2.0738207938
H	4.5388416643	-0.5618080168	0.9697405113

VI-VIIa

79

C	-0.2887298824	1.0884044402	-0.8154754224
C	-0.0223153163	-0.0790900668	-0.0555031926
C	-0.5040177842	-1.271491355	-0.6320120581
C	-1.2048132114	-1.2877862718	-1.8246538536
C	-1.4736685841	-0.1070830762	-2.5259042254
C	-1.0104880655	1.0867978851	-2.0122732697
Pd	1.6524638554	0.2069087857	1.1542581634
P	3.6043601868	0.1790679641	-0.3906497388
C	1.8381389067	-1.8486606212	1.424007152
C	0.6030988451	-2.4236392822	2.1670820261
C	1.2762674652	-3.073814287	3.4132748968
C	2.0002124294	-4.3357195067	2.9285105575
C	3.1809362643	-3.7588567968	2.1091666433
C	3.0225690483	-2.2264322683	2.2915573676
C	2.4455537468	-2.1379176541	3.704907518
C	-0.4378104442	-1.3752214037	2.463456465
C	-0.3014054488	-0.0965548256	1.8755743183
C	-1.1318963374	0.9598353919	2.2551246351
C	-2.171555173	0.7260048919	3.1409359362
C	-2.3922425956	-0.5588933795	3.6202710824
C	-1.5370627222	-1.6171632956	3.3031871997
C	-1.8622955223	-2.9764429071	3.8597681629
Br	2.8567494047	1.3946974344	3.2508508356
H	-2.0312725129	-0.1250327694	-3.4588996854
H	-2.8252060806	1.5440423134	3.4380739135
H	-3.2468480635	-0.7557758045	4.2685227478
H	0.1501327798	-3.2347588253	1.5661543729
H	1.9291303243	-2.1799999004	0.3813964386
H	3.9435861575	-1.6675204952	2.0907443567
H	0.5892162259	-3.2462911907	4.245760318
H	2.1564598508	-1.1195128135	3.9892856343
H	3.1278015289	-2.5440673221	4.4642103208
H	4.1504514001	-4.0781481257	2.5142181173
H	3.1614518253	-4.0567560924	1.0510326969
H	1.3492779022	-4.9975771093	2.3396730444
H	2.3631716365	-4.9178030423	3.7857782686
H	-2.9507804098	-3.1047469394	3.9179025961
H	-1.4649870439	-3.7952428988	3.247497846
H	-1.4745394233	-3.1125197652	4.8791164126
H	-0.9700914484	1.9615163191	1.8647925233
H	-0.3386716687	-2.2165478211	-0.1223037776
H	-1.1692578273	2.0340953918	-2.5205399524
O	-0.1430585088	3.38730526	-0.9396012429
H	-1.5523990017	-2.2428964586	-2.2169210809
O	1.0544583831	2.384156797	0.5456340969
N	0.2313447264	2.3696500314	-0.3889060661
C	5.401223787	0.1785381042	0.0455846257
C	6.3578094563	0.0556001073	-0.9702691007
C	5.7975327464	0.3541660432	1.3706460122
C	7.6939955126	0.0835388908	-0.6213349845

H 6.0698145616 -0.055451844 -2.0127459968
C 7.157254171 0.383445291 1.6861457386
H 5.0486569078 0.5001317348 2.1510446599
C 8.1172398289 0.2417849143 0.6905058156
Cl 8.9423575903 -0.0878126385 -1.9283053746
H 7.4662672749 0.524700574 2.7176144491
H 9.1777437336 0.2607276203 0.9201141701
C 3.5499089683 1.5874841591 -1.5861396358
C 3.5784687414 1.4238262466 -2.9708022984
C 3.5062041486 2.8686030798 -1.025833481
C 3.5423781532 2.5567427885 -3.7669689247
H 3.6269825348 0.438621728 -3.4262237226
C 3.4713448772 3.9847129954 -1.8551677362
H 3.4901920928 2.9889434644 0.0560515183
C 3.4848697104 3.8352164792 -3.2415536173
Cl 3.5788634261 2.3495667169 -5.5718791564
H 3.4266035625 4.9794640453 -1.4220247587
H 3.4537434497 4.6956279211 -3.9015987128
C 3.4281764914 -1.3376345151 -1.4267454079
C 4.2577642625 -2.4391356021 -1.1992753884
C 2.3197171912 -1.4665991383 -2.2737622865
C 3.964946691 -3.6347022296 -1.8323847796
H 5.1139592874 -2.3715618619 -0.5336267062
C 2.0662662281 -2.6771446384 -2.9120081417
H 1.6396504517 -0.6295406512 -2.4215379641
C 2.8899871661 -3.7795500847 -2.6927120349
Cl 5.0234100949 -5.0712570195 -1.5021183642
H 1.2139235116 -2.7669827399 -3.5797943527
H 2.6998548914 -4.7327398754 -3.1750489714

VII-VIIIa

79

C 4.8215899597 0.0329441731 1.5853790193
C 3.7244760338 -0.658179936 1.0440965157
C 2.6237323734 -0.8248294862 1.8949591008
C 2.595323558 -0.2847361782 3.1752771047
C 3.6836813565 0.431298413 3.6639233876
C 4.8107543317 0.5708833909 2.8695292239
Pd 0.7298123832 -0.4486322865 -0.8041446675
P -1.5238805019 0.02983945 -0.2610579832
C 1.0366369232 1.471668824 -1.6506021216
C 2.381232581 1.0101147491 -1.7734279238
C 3.2040046407 1.9299771295 -0.9044372463
C 3.2067578001 3.2574244027 -1.7167086031
C 1.7562268211 3.7796015358 -1.569821865
C 1.0847042812 2.6727626057 -0.7232679617
C 2.2313494113 2.3006741385 0.2189977762
C 2.737168526 -1.0906001812 -1.2718315748
C 3.7121837437 -1.3195841048 -0.2873148137
C 4.6817841126 -2.3067754633 -0.5085783526
C 4.704252037 -3.0376845707 -1.6821055611
C 3.7467261017 -2.7908477263 -2.6583248132
C 2.7599563297 -1.8260783365 -2.4733068209
C 1.7074428975 -1.6649748155 -3.5326369996
Br 0.2338322264 -2.8998397528 0.0102015418
O 7.1013724584 0.3235881726 1.4685113366
O 6.0007583235 0.367671306 -0.3890739688
N 6.0665292549 0.252219021 0.8254946072
C -1.8136776558 -0.1829623139 1.5490398248
C -2.8605009126 -0.9556392097 2.0450423588
C -0.9176880275 0.435965607 2.4274956233
C -3.003370624 -1.0671222626 3.4189457344
C -1.0957986574 0.316155096 3.8020104161
C -2.1486320998 -0.4432263868 4.3102385211
Cl -4.3677357165 -2.0625278672 4.0762789264
C -2.9117902127 -0.8841693323 -1.073003075
C -4.2146749936 -0.3830139715 -0.9605074329
C -2.6696665202 -2.0434770458 -1.8091024022
C -5.2425313947 -1.0655451829 -1.583007707
C -3.7286635581 -2.7053283139 -2.4298165264
C -5.0280033484 -2.2195744971 -2.3207572583
Cl -6.9313997164 -0.4170515378 -1.4366679475
C -2.1085742489 1.7712927337 -0.5466379773
C -2.329719953 2.668804125 0.4962179547
C -2.2289750325 2.2022310664 -1.8727505072
C -2.6384473149 3.9844043844 0.1847619189
C -2.5387898637 3.5274565035 -2.1539839222
C -2.7382985843 4.439461932 -1.1170913552
Cl -2.9152131446 5.1539682432 1.5444746786
H 1.7847346762 -1.425618291 1.5425410823
H 1.7168801254 -0.450507607 3.7974075829
H 3.669855708 0.8579113172 4.664669129
H 5.6953798876 1.0925870252 3.2238842523
H 0.3801010799 1.5001727059 -2.5257085247
H 2.7850544677 0.7064724734 -2.7365457625
H 4.2002575722 1.5699460625 -0.6428856787
H 3.5088468134 3.104650042 -2.7608390854
H 3.9322136677 3.9492952296 -1.2705572548
H 1.2476670943 3.928020969 -2.5319271623
H 1.7251451209 4.7369628988 -1.0328190582
H 0.130705401 2.9625198511 -0.2719381339
H 2.5876960435 3.1533151979 0.8130397461
H 2.0006237113 1.4645804286 0.8905928698
H 5.417933192 -2.5038292972 0.2714173977
H 5.4643910838 -3.8007164976 -1.837190203
H 3.7500613286 -3.3683238981 -3.5835740939
H 0.7775426517 -2.1694318574 -3.231114008
H 2.0324321226 -2.1103708231 -4.4814021853
H 1.4500836834 -0.6144039515 -3.7284872501
H -3.5479257434 -1.4675641124 1.3784552478
H -0.0774147172 1.0090418191 2.0345808914
H -0.4133201526 0.8148500593 4.4849049879
H -2.2997491573 -0.5534270475 5.3788917243

H	-4.4233594114	0.5253899435	-0.4009540619
H	-1.6599809453	-2.4442462444	-1.8661203236
H	-3.5390881493	-3.6110379132	-2.9983598748
H	-5.8621530512	-2.7240517343	-2.7977874021
H	-2.255392223	2.3574834134	1.5342236971
H	-2.0833201137	1.4943109322	-2.6872570104
H	-2.6296316949	3.8586016811	-3.1844631403
H	-2.9751224564	5.4793279813	-1.3174305771

IX-Xa

96

C	-1.2048235943	-3.51101376	0.7709589384
C	-2.5805862964	-3.2628531328	1.2815336548
C	-3.0666909596	-2.1277021833	1.9462762225
C	-4.4132835344	-1.9525989177	2.2522159611
C	-5.3201182998	-2.9495381841	1.93026834
C	-4.8685233213	-4.1106344551	1.3125016367
C	-3.5240752273	-4.2545087221	0.9926276374
C	-0.4340613572	-4.4891595382	1.4091526505
C	0.757063024	-4.9324933325	0.8547838647
C	1.1691677362	-4.4322259118	-0.3796299003
C	0.427239833	-3.4760455622	-1.0675120886
C	-0.7306002505	-2.9564967025	-0.4389751159
C	0.8425046071	-3.0504294709	-2.4405190743
Pd	-0.5326613008	-0.6307987914	-0.2439906086
H	-4.7303049922	-1.0422103115	2.7538921927
H	-6.3731096249	-2.8187132092	2.1676026485
H	-5.5690349095	-4.9046445476	1.0613592342
H	-0.7986206314	-4.904335154	2.3497231821
H	1.3563378733	-5.6814002675	1.3691497042
H	2.0884271538	-4.8005781336	-0.8384468837
H	1.8491599567	-3.4144530869	-2.6781214473
H	0.1465197149	-3.4508340344	-3.1932873251
H	0.8395483044	-1.9572691793	-2.5531519589
P	1.7909058096	-0.3377007119	0.3634375859
C	2.9138360349	-0.7556962755	-1.046177697
C	2.2891033366	1.3951953147	0.8012263245
C	2.6180527645	-1.2407836776	1.7580314653
C	1.9344526201	-2.2841256921	2.3770003729
C	2.5392105565	-2.998722736	3.4106584207
C	3.8195119273	-2.6679721054	3.8403279714
C	4.4741680796	-1.6158793333	3.2156830277
C	3.9048937536	-0.8930823309	2.184812198
C	2.8228871309	-0.0132596708	-2.2304077856
C	3.5494031587	-0.3919249053	-3.3526152923
C	4.3395928925	-1.542185156	-3.3283621737
C	4.390062814	-2.2722262838	-2.1548131908
C	3.7116769999	-1.8992592287	-1.0065653919
C	3.3540236983	2.0826181621	0.21571326
C	3.6279375889	3.3686373172	0.6559457927
C	2.8846561565	3.9954917317	1.6418538541
C	1.8300772489	3.2956956813	2.2265916618
C	1.5339084371	2.0022037465	1.8096706748
Cl	6.1450605273	-1.1728391062	3.7796712906
Cl	5.0295819651	4.2647332042	-0.073754534
Cl	5.3594072464	-3.8120831552	-2.1217630232
H	0.9259004133	-2.5367038452	2.0685017492
H	2.0015841013	-3.8158718583	3.8849779814
H	4.3053352198	-3.2090428683	4.6456003783
H	4.4521371316	-0.0759621743	1.7211354053
H	2.1784780602	0.8608105698	-2.2819608258
H	3.4899157476	0.2041987858	-4.2592529629
H	4.8970391494	-1.8666538127	-4.2007506751
H	3.7943448518	-2.4968327558	-0.1032032501
H	3.9581343964	1.6298409128	-0.5665890901
H	3.130636453	5.0060739747	1.9511647221
H	1.2350125049	3.76461908	3.0057194816
H	0.7142474697	1.4497186139	2.269438832
P	-1.4465144153	1.6174245792	-0.5331165124
C	-0.5148399754	2.0519301379	-2.078053434
C	-1.3854534505	3.1873857974	0.4648520863
C	-3.2288444823	1.7409668111	-1.0485711025
C	-3.6785016167	2.510367692	-2.120965836
C	-5.0389968032	2.5732049013	-2.4145065522
C	-5.9608631907	1.8800144147	-1.6332586118
C	-5.4884296789	1.1399507588	-0.5624278144
C	-4.1450522602	1.0488065748	-0.2494414912
C	-0.8652436544	1.4368968403	-3.2875442784
C	-0.0611004139	1.5814037353	-4.4129797193
C	1.1126884004	2.3301692624	-4.3510530985
C	1.4535699645	2.9114278798	-3.1415858606
C	0.6725287536	2.7899239202	-2.0024590081
C	-1.5638043159	3.0416196147	1.8430789312
C	-1.5435590626	4.1760458465	2.6331413936
C	-1.3521210196	5.4456259208	2.1151924098
C	-1.1959282374	5.5798356847	0.7371474001
C	-1.2216995513	4.457861946	-0.087611986
Cl	-6.693113282	0.2442814538	0.4685702548
Cl	-1.7223441647	3.987123844	4.4334683895
Cl	3.0341067814	3.7914187312	-3.0198040921
H	-7.0241297567	1.9169771156	-1.8466182405
H	-1.7640838641	0.8279798977	-3.3434290477
H	-0.3443894488	1.10188619	-5.3460078941
H	1.7558822662	2.4507525858	-5.2168486938
H	1.0023867153	3.2388652927	-1.0673881757
H	-1.7169062934	2.0570848558	2.2821375116
H	-1.330606715	6.3079130838	2.7734997852
H	-1.057164289	6.5678381466	0.3071562686
H	-1.1060607612	4.5767110902	-1.1619842574
I	-2.3167718045	-2.0595639285	-1.7771452656
H	-3.179868301	-5.1428049438	0.4637590249
O	-2.6272461218	0.0685501352	2.4777570083
N	-2.1653968164	-1.0670937761	2.3873231792

O -1.0117922356 -1.3562649265 2.653495237
H -5.388570171 3.1700361673 -3.2524312575
H -3.8084581308 0.4730598972 0.6126813782
H -2.9670587474 3.0594939475 -2.7329860515

I-IIa*

84

C -1.3877033019 -3.663093807 -1.9013143581
C -2.6611766294 -3.9463606539 -2.3908476183
C -3.7585565513 -3.9010312216 -1.5374818541
C -3.5724397055 -3.5907908906 -0.1902473659
C -2.3105459582 -3.3341886159 0.344894442
C -1.2187334726 -3.3171650723 -0.5519589532
C -2.1464280267 -3.1175804797 1.8151401422
Pd 0.0429495991 -1.402938396 -0.5979280774
H -2.7872644449 -4.1998330477 -3.4431316875
H -4.7583815551 -4.1121757418 -1.9126640166
H -4.4314335702 -3.55413039 0.4828613687
H -3.1203934759 -2.9932201818 2.3034199543
H -1.63998989 -3.9768087841 2.280520057
H -1.5411115638 -2.2280236775 2.0369391043
P -1.6709447254 0.3238358551 -0.3967672241
C -2.5186552375 0.2126195008 1.2439306007
C -1.1550539318 2.106715286 -0.4404045057
C -3.1216014974 0.4034763684 -1.5514614914
C -3.3778672035 -0.7044288516 -2.356085341
C -4.4702189991 -0.7046214401 -3.222685125
C -5.3062558089 0.4051457508 -3.298276918
C -5.025139771 1.496626978 -2.4894222203
C -3.9534642589 1.5257259911 -1.616931365
C -1.7692584161 0.4566927041 2.401574415
C -2.3360379938 0.2674217996 3.6554930812
C -3.6411758715 -0.2163715092 3.7731685028
C -4.3461234269 -0.4771390333 2.6122426607
C -3.8268225186 -0.2575678922 1.3471265357
C -1.6315088774 3.0772620825 0.4437407543
C -1.1870293737 4.3804789648 0.2886397078
C -0.267692353 4.7518641125 -0.6784321241
C 0.2001382236 3.7751893565 -1.5566942106
C -0.2525026753 2.4641689756 -1.4447534438
Cl -6.1190676495 2.9502287427 -2.5782312092
Cl -1.8337932539 5.6590964827 1.4085435981
Cl -6.0194062046 -1.1868877784 2.7442573439
H -2.7304497077 -1.574609804 -2.303370964
H -4.6682108588 -1.5742374397 -3.843733057
H -6.1576561581 0.4269666792 -3.9707948945
H -3.7680047641 2.4018158898 -1.0009891025
H -0.7386069134 0.7928858433 2.3221051104
H -1.7547370118 0.4807896021 4.5487912345
H -4.0920138219 -0.3946401717 4.7436632316
H -4.4222639361 -0.4666809367 0.4623753366
H -2.3268565999 2.825156123 1.2405809018
H 0.0721012176 5.7799845075 -0.7448016769
H 0.9279190211 4.0331153577 -2.3220349793
H 0.1093626923 1.7048196461 -2.1340562689
P 2.1587224966 -0.1867878848 -0.4788032723
C 2.079396318 0.3888297005 1.2816908012
C 2.8000190266 1.2905336656 -1.4118508411
C 3.7427518628 -1.159096024 -0.5413829774
C 4.861492636 -0.8380448703 0.2302204513
C 6.0230156315 -1.5645533325 0.0378820283
C 6.1241302873 -2.5874086261 -0.8912712784
C 5.0040128856 -2.8950769947 -1.6588490478
C 3.8168534697 -2.1870833046 -1.4823791973
C 2.3772016825 -0.5239601706 2.3012133297
C 2.1431575731 -0.1970465394 3.6328764751
C 1.6023720083 1.0418462698 3.9699072531
C 1.3037120873 1.924371644 2.9457940289
C 1.5195025584 1.6313461903 1.6081909822
C 2.5811103138 1.2971168351 -2.791950053
C 3.0665446581 2.3398236865 -3.5767300953
C 3.776835917 3.3868330915 -2.989978981
C 3.9913055282 3.3496058297 -1.6222767816
C 3.5262475136 2.323202827 -0.8175745086
Cl 0.5302231561 3.5091697025 3.378367908
H 7.0560189101 -3.1304587707 -1.0100487031
H 2.7861667553 -1.5005389198 2.0533120653
H 2.3805236759 -0.9113501696 4.4157322881
H 1.4133693815 1.3144871681 5.0030836252
H 1.2250056304 2.3460316241 0.8412266048
H 2.0179685649 0.483885006 -3.2500004175
H 4.1590785789 4.2105536263 -3.5837394502
H 3.7184929766 2.341634057 0.2516702697
I 0.829900241 -3.8676753475 0.2985964585
H 2.9379827477 -2.4354191437 -2.0745651623
H 4.8354084046 -0.0412835464 0.9683720887
Cl 4.9210380585 4.7074412948 -0.84690138
Cl 7.4858689427 -1.1459025743 1.0380387327
H 2.8944294064 2.343391434 -4.649223928
H 5.0579443098 -3.6944939384 -2.3919118702
H -0.5217799832 -3.7132912783 -2.560116477

V-VIa*

79

C 2.9345829362 -1.899231936 -1.4815261098
C 1.7129765866 -1.9025470552 -0.7984266468
C 0.574778347 -2.3223729579 -1.4997931355
C 0.6325851795 -2.5924520934 -2.8609676426
C 1.8352347992 -2.4763942801 -3.5557665633
C 2.9799067503 -2.1354011558 -2.8581098957

Pd	1.2231173035	-0.2818590929	0.5203729325
Br	1.3207843586	-2.8386895114	1.4298593786
H	1.8864801916	-2.6838185241	-4.6215967452
C	1.5806616731	1.3414479801	-0.7522222867
C	3.0713495599	1.7907659078	-0.7751215161
C	2.9252941729	3.3299510841	-0.6752618795
C	2.2526653912	3.8448638129	-1.9574115645
C	0.7720540132	3.4229647043	-1.7775180121
C	0.8050928	2.6312136733	-0.4569453239
C	1.7997742607	3.4631963286	0.354769918
C	3.7912011645	1.2006818256	0.395787823
C	3.0568024495	0.2991168626	1.1789066964
C	3.5524261214	-0.2037151693	2.3790673784
C	4.8309970187	0.1720579877	2.7815240021
C	5.6062093143	0.9871551313	1.9637947563
C	5.110846447	1.5112509579	0.7688753842
C	6.0077033192	2.3483929913	-0.0972191986
P	-1.3351164621	-0.145980448	0.2073898587
H	5.2419466903	-0.2168201293	3.7127024376
H	6.6322118216	1.2213953414	2.251832594
H	3.5543816237	1.5054975581	-1.7273856515
H	1.2555198062	0.8792750388	-1.6987464861
H	-0.191797223	2.4986138179	-0.0211713102
H	3.8613828715	3.8425197492	-0.430515271
H	2.0523103841	3.0336351713	1.3337416742
H	1.4650750307	4.5005412656	0.4930567574
H	0.1177661387	4.3000521302	-1.6698907181
H	0.3751286114	2.8222162198	-2.6071066465
H	2.7123607146	3.4125053854	-2.8570993582
H	2.3480886652	4.9356312746	-2.0371086167
H	7.0596690228	2.0979251543	0.0880051702
H	5.808559325	2.1829050462	-1.1643511683
H	5.8974318464	3.4257766067	0.0925996954
H	2.9797886142	-0.9191394107	2.9667043519
H	-0.2759757959	-2.914170349	-3.3693808172
H	-0.3628203571	-2.4595131395	-0.9680864691
H	3.9447667343	-2.0529885213	-3.3522877885
O	5.0553928816	-1.0225520911	-1.5018702214
C	-2.0795480275	0.7174196053	1.6626150626
C	-1.2519576477	1.470507622	2.4983008912
C	-3.4481236736	0.6211221237	1.935737149
C	-1.7866325636	2.1317468831	3.6027210236
H	-0.1828659743	1.5398527998	2.2965311225
C	-3.9479437056	1.2893820695	3.0386774753
H	-4.1076199637	0.0336541145	1.3016843874
C	-3.1477569863	2.0438520979	3.8819445206
H	-1.1402603675	2.7130699557	4.2529953311
H	-3.5793454087	2.5488613756	4.7398661842
Cl	-5.7248798303	1.1698334207	3.3979266072
C	-2.4226107026	-1.644933484	0.0838894065
C	-2.3923792609	-2.5587688089	1.1435681021
C	-3.1986025857	-1.9068179349	-1.0455038538
C	-3.1415278126	-3.728150674	1.0753941052
H	-1.7806312995	-2.3549708879	2.0197486023
C	-3.923563488	-3.0866681992	-1.0847294676
H	-3.2415676924	-1.206226179	-1.8746186573
C	-3.9159892108	-4.0055379242	-0.0509613105
H	-3.1189666663	-4.4365796969	1.897812516
H	-4.4984214404	-4.9180644935	-0.1223792844
Cl	-4.9284990968	-3.4382167162	-2.5600851429
C	-1.9276593903	0.8714829699	-1.2244634796
C	-1.4654688169	0.5368661415	-2.5030750306
C	-2.761066587	1.9770250799	-1.0526789214
C	-1.8559878133	1.2893927474	-3.607084247
H	-0.7897570905	-0.3071493438	-2.6339475017
C	-3.1163623141	2.7151575536	-2.1692907948
H	-3.1215931283	2.2641511726	-0.0690444607
C	-2.6886233062	2.3955691637	-3.4457267564
H	-1.5025097185	1.0239203049	-4.5992355584
H	-2.9936417797	2.9992698096	-4.2937091923
Cl	-4.1889564127	4.1657506598	-1.9507766792
N	4.2280342203	-1.6459229455	-0.8481342936
O	4.4193524394	-2.107304525	0.2598613801

VI-VIIa*

79

C	-0.2914636455	1.1009547508	-0.8145542818
C	-0.0230961003	-0.0687903701	-0.0600012281
C	-0.5143839814	-1.2592989392	-0.6270248924
C	-1.225673648	-1.2732629576	-1.8147767294
C	-1.4938605016	-0.092062534	-2.5147029849
C	-1.022242768	1.1007729153	-2.0067474364
Pd	1.6437638497	0.2113758253	1.1546780934
P	3.5923773054	0.1798134041	-0.3940567935
C	1.8272319694	-1.8487398792	1.4099532547
C	0.6021532114	-2.4236249175	2.1670259703
C	1.2897451081	-3.0713974789	3.4068151336
C	2.012817178	-4.3313564208	2.9165217766
C	3.1825835934	-3.752132293	2.0839619926
C	3.0217747356	-2.2192394439	2.2655423792
C	2.4588458835	-2.1314094512	3.6847446305
C	-0.4339891778	-1.3748674017	2.4767544669
C	-0.2979961336	-0.0929651445	1.899162765
C	-1.1330069326	0.9604239828	2.2742661343
C	-2.1742901402	0.7207830534	3.1577342639
C	-2.3896753824	-0.5656206757	3.6366450096
C	-1.5319165867	-1.621568845	3.3178981378
C	-1.8505097652	-2.9827398329	3.8726371072
Br	2.8332727638	1.4490335157	3.2781135097
H	-2.0579894093	-0.1088503004	-3.4434997953
H	-2.8331850303	1.5352306173	3.452945968
H	-3.2439768374	-0.7655979951	4.2841193529
H	0.141280585	-3.2337736768	1.5718529761

H	1.9092471638	-2.1755203501	0.3655293334
H	3.9406189047	-1.6599140986	2.0546677528
H	0.611217762	-3.244284265	4.2460664274
H	2.1661296843	-1.1143991303	3.9696030641
H	3.1504589987	-2.533072793	4.437698223
H	4.1579035558	-4.0653768796	2.4793482403
H	3.1520854185	-4.0504486773	1.0264499925
H	1.3573724713	-4.9950564634	2.3354437958
H	2.3870047854	-4.9102219315	3.7708994116
H	-2.9379575645	-3.1128493028	3.9404932708
H	-1.4563698165	-3.7986418213	3.2546223657
H	-1.4533282845	-3.1197010933	4.8880939761
H	-0.9771087568	1.9624986716	1.8824596603
H	-0.3510577615	-2.2045888106	-0.1174074625
H	-1.1832101317	2.0463145188	-2.5171737807
O	-0.1339952125	3.399055389	-0.9418957698
H	-1.5823914006	-2.2262716588	-2.2028698433
O	1.050657249	2.394266611	0.5504600085
N	0.2315931146	2.3790848673	-0.388256705
C	5.3856267654	0.1787574462	0.0562430791
C	6.3504033081	0.0907425056	-0.9552914386
C	5.7709172632	0.3113209121	1.3895281582
C	7.6827255838	0.1142706603	-0.5922513553
H	6.0695506789	0.0095029417	-2.0024475936
C	7.1274041732	0.3369513229	1.7187633505
H	5.0152232261	0.425990713	2.1674733954
C	8.0965599507	0.2337970586	0.7265576863
Cl	8.9451801556	-0.0113814532	-1.8955768611
H	7.4284656013	0.4445770214	2.7563984687
H	9.1545154311	0.2520240668	0.9672701565
C	3.5483730602	1.58024365	-1.5999218964
C	3.585839891	1.4035486793	-2.9830938609
C	3.5091138919	2.8669155606	-1.0525643249
C	3.5644602161	2.5308091192	-3.7875304511
H	3.6306627751	0.414027947	-3.4292297022
C	3.4900396116	3.9768008293	-1.8910205555
H	3.487758549	2.9975698764	0.0276242065
C	3.5134846995	3.815113391	-3.2762250668
Cl	3.6118724264	2.3068258908	-5.5933615382
H	3.4521918137	4.9757389292	-1.4673111226
H	3.4954780995	4.6709520924	-3.9426602336
C	3.4233351895	-1.3409148816	-1.425483993
C	4.2650870575	-2.4340314192	-1.2035926471
C	2.3142247655	-1.4775661845	-2.2704357947
C	3.9804091783	-3.629448767	-1.8405316234
H	5.1212436531	-2.3612208861	-0.5385808952
C	2.0687216847	-2.6889296727	-2.9103466058
H	1.6278661206	-0.6455754933	-2.4179860301
C	2.9037889042	-3.7844740955	-2.6963768781
Cl	5.0577241578	-5.0574385647	-1.5174659566
H	1.2145412194	-2.7859751312	-3.5744451706
H	2.718281896	-4.7376377535	-3.1804394572

VII-VIIIa*

79

C	4.8570857967	0.0481789014	1.5617555666
C	3.7471775423	-0.6433946133	1.0466984399
C	2.6570708496	-0.786117433	1.9150533558
C	2.6511317496	-0.2263455649	3.187343229
C	3.7518712148	0.4885413803	3.6492280334
C	4.8686382983	0.6073784562	2.8373449858
Pd	0.731125619	-0.4526062331	-0.7680232471
P	-1.5287600859	0.0476427312	-0.2449287382
C	1.0260025947	1.4596280726	-1.6429616083
C	2.3700820646	1.0021014286	-1.7727016057
C	3.1975240124	1.9304496742	-0.9188904045
C	3.1904768641	3.2492604889	-1.7461196781
C	1.7394454019	3.767970972	-1.5943952268
C	1.0782333949	2.6698338191	-0.7279795294
C	2.2333477697	2.3110061064	0.2083559525
C	2.7258555735	-1.1067048744	-1.2475435728
C	3.7128201852	-1.3270007443	-0.2729633463
C	4.6733480075	-2.3243228101	-0.4922297148
C	4.676667208	-3.0710882581	-1.656540484
C	3.7103645167	-2.8287519929	-2.6258654959
C	2.7323389527	-1.8539352009	-2.4423056084
C	1.6730265969	-1.6948083136	-3.4955245485
Br	0.2279580778	-2.9094285679	0.0896605999
O	7.1376721865	0.3173134985	1.4042535467
O	6.0092988559	0.3452175337	-0.4348243089
N	6.0895856369	0.2455124681	0.7806647369
C	-1.8430189843	-0.185624211	1.5589056538
C	-2.9075290618	-0.9471233323	2.035179645
C	-0.9423611205	0.4025078452	2.4537106538
C	-3.0583047712	-1.0783488545	3.4062963706
C	-1.1284253783	0.2605046452	3.8249337086
C	-2.1976037176	-0.4890292496	4.3146163929
Cl	-4.4485893026	-2.0616924203	4.0388337058
C	-2.8944150288	-0.8676687742	-1.0903016415
C	-4.2067584572	-0.3904717584	-0.9838180248
C	-2.6234187363	-2.0064159247	-1.8485180163
C	-5.2130867338	-1.080236233	-1.6327036243
C	-3.6618629738	-2.6744387696	-2.4965542272
C	-4.9714766871	-2.2145718103	-2.3918095769
Cl	-6.918656673	-0.4649728997	-1.4922610054
C	-2.1121281816	1.7894729621	-0.5221578451
C	-2.3284564741	2.6789371221	0.5288681977
C	-2.2355624389	2.2297076323	-1.8450507223
C	-2.6369862091	3.9960956953	0.2258434605
C	-2.5444963221	3.5576253991	-2.1157496288
C	-2.7405159755	4.4624651144	-1.0714903509
Cl	-2.9095041995	5.1574865176	1.59842353
H	1.8083398791	-1.3836539903	1.5816507916

H 1.7824753663 -0.3734462784 3.8272401082
H 3.754383634 0.931777194 4.6424838854
H 5.7584565014 1.1323169655 3.1728367197
H 0.3609524605 1.4727543723 -2.5116795135
H 2.7648920193 0.680935589 -2.73379897
H 4.1969219714 1.5761687203 -0.6613235903
H 3.4854234867 3.085652483 -2.7904471145
H 3.9161459518 3.9477239344 -1.3111157553
H 1.2237209977 3.9021493687 -2.5545726985
H 1.7094332588 4.7310344322 -1.0681417817
H 0.1279251669 2.9615221766 -0.2707369239
H 2.5922896293 3.1706446313 0.7902024573
H 2.0069063702 1.4820759828 0.8897874537
H 5.4175684229 -2.5165743087 0.2813748973
H 5.4290833825 -3.8420365161 -1.8101486323
H 3.7009115904 -3.4157112637 -3.5450488683
H 0.7471395002 -2.2064660384 -3.1936850626
H 1.9960857626 -2.1338673304 -4.4477503379
H 1.4081340053 -0.6451238882 -3.6836363952
H -3.6020721954 -1.4336067702 1.3569132546
H -0.0911374301 0.9695169228 2.0761224184
H -0.4402268055 0.7320008591 4.5208432441
H -2.3529587064 -0.6163874514 5.3807536318
H -4.437087303 0.503306448 -0.4093972083
H -1.6056842693 -2.3848985031 -1.9074327432
H -3.450236231 -3.5631678242 -3.0835734226
H -5.789618414 -2.7246118813 -2.8898629442
H -2.251384352 2.3598726472 1.5642214174
H -2.0928077182 1.5298097498 -2.6667653664
H -2.6364947787 3.8967802361 -3.1432868726
H -2.9763086107 5.5036867109 -1.2656280623

IX-Xa*

96

C -1.1856173409 -3.5276077773 0.662868438
C -2.564997824 -3.3028105478 1.1746627521
C -3.0612132618 -2.1908671643 1.8711365218
C -4.4099475851 -2.0345254694 2.1794396225
C -5.3085983177 -3.0285264138 1.8265214002
C -4.8471430099 -4.1672088589 1.1747141925
C -3.5007766671 -4.2916442169 0.8532285399
C -0.4161812553 -4.5257791561 1.2715165803
C 0.7791692866 -4.9478577769 0.7090840827
C 1.1961639856 -4.4058629969 -0.5060151692
C 0.4556312874 -3.4280220722 -1.1648990455
C -0.7052909433 -2.930304624 -0.5244273398
C 0.8751484177 -2.9591751541 -2.5226618469
Pd -0.5331644659 -0.6229298589 -0.2693259715
H -4.7352973345 -1.1442323962 2.7108456596
H -6.3623465308 -2.9151844019 2.0689669451
H -5.5408060329 -4.9591038347 0.8998992468
H -0.7847637475 -4.9744872546 2.1948212155
H 1.3763647707 -5.713184203 1.2010505219
H 2.1183953881 -4.7569169605 -0.9724951632
H 1.8858889455 -3.3086133162 -2.764817174
H 0.1868765207 -3.3436292478 -3.2907287122
H 0.8637917496 -1.8634696773 -2.6041653326
P 1.7877825062 -0.3310979566 0.3633248228
C 2.9259576401 -0.709316193 -1.0457799735
C 2.2832132037 1.3904310378 0.8493749329
C 2.6064931678 -1.2672913934 1.7418644426
C 1.9257795117 -2.3353975264 2.3211575543
C 2.5248740214 -3.077205884 3.3392028398
C 3.7975948578 -2.7489969066 3.7943219968
C 4.4474888553 -1.6722841053 3.208470553
C 3.8857487932 -0.921936915 2.1935820862
C 2.8406023165 0.0632190687 -2.2110533239
C 3.5809911437 -0.2789538582 -3.3361075289
C 4.3822749993 -1.4223054227 -3.3338615026
C 4.4272736018 -2.1805451972 -2.1783890003
C 3.7335525778 -1.8466264163 -1.0274208361
C 3.3586437795 2.0892927723 0.2968912019
C 3.6310872181 3.3603266251 0.7786740026
C 2.8791124067 3.9649336028 1.7714369415
C 1.81199045 3.2542533872 2.3200201078
C 1.516274072 1.9743276012 1.8626608744
Cl 6.1120776187 -1.230625845 3.8056409786
Cl 5.0518931626 4.2697055286 0.0936816506
Cl 5.4167324076 -3.7117924935 -2.1733501501
H 0.922723488 -2.5871281231 1.9943255731
H 1.9903830178 -3.9140426466 3.7813959481
H 4.2775085142 -3.3119285103 4.5880232229
H 4.4314488489 -0.0874163545 1.760029325
H 2.1896004737 0.9334303667 -2.244932037
H 3.5248373888 0.3385350229 -4.2284567118
H 4.9503405715 -1.7172473556 -4.2098248187
H 3.8120714906 -2.4681443026 -0.1400460565
H 3.9702969069 1.6564260291 -0.4907666878
H 3.1242062445 4.9649720505 2.1139034445
H 1.2081036911 3.7050116583 3.1028910455
H 0.6857588363 1.4152008071 2.2936056271
P -1.4466821889 1.6357012489 -0.4975938814
C -0.5091658469 2.1166819156 -2.0248066204
C -1.3987671643 3.1768996721 0.5456302247
C -3.2278630593 1.7663278069 -1.0142102369
C -3.6770989181 2.5694940533 -2.0620133272
C -5.0369097124 2.6361629515 -2.3589800284
C -5.9590378496 1.9127493547 -1.6051737655
C -5.4859784708 1.1401526863 -0.5579502522
C -4.1437047521 1.0439110446 -0.241468161
C -0.8528462625 1.5382298012 -3.2540861954
C -0.0410953492 1.7134381789 -4.3699592815
C 1.1337784722 2.4582964313 -4.2791721684

C 1.46431424 3.0049349626 -3.0512542874
C 0.6777209035 2.8521036421 -1.9201116691
C -1.5914608553 2.9904655894 1.9173636603
C -1.5858768225 4.1025325675 2.7384278098
C -1.3948545574 5.387928595 2.2614369401
C -1.2242772541 5.5619897421 0.8891142944
C -1.2355965033 4.4638119145 0.0319957669
Cl -6.6896456234 0.2014223503 0.4394964171
Cl -1.7902484756 3.859420575 4.5332307728
Cl 3.0460279907 3.8846000684 -2.8933299092
H -7.0212039143 1.9526899202 -1.8233786556
H -1.7528948077 0.9339604423 -3.3353329681
H -0.3188184329 1.2620646249 -5.3183466532
H 1.7825692016 2.5999161907 -5.1374158791
H 1.0009303513 3.2746284881 -0.9706069558
H -1.7436726315 1.9928855999 2.3260384344
H -1.3844368304 6.2321703128 2.9428688065
H -1.0861925654 6.5625617424 0.4894694849
H -1.1104837689 4.6157243133 -1.0370691414
I -2.2995654054 -2.0073933631 -1.8526998449
H -3.1504160132 -5.162479764 0.3000822306
O -2.6335951644 -0.0088178421 2.4681541275
N -2.1685778167 -1.1408396596 2.3491227069
O -1.0152809006 -1.4322216396 2.6175403107
H -5.3858624709 3.2588258463 -3.1779182486
H -3.8088689498 0.4411960696 0.6029873568
H -2.9673396407 3.1431237926 -2.6529657224

V-VIb

83

C 4.0757075769 1.5765366279 -1.6171349646
C 2.8809007265 1.9876428704 -1.0045410857
C 2.9332411316 2.8817238151 0.0955170579
C 4.1778476668 3.343913311 0.5494651986
C 5.3508642274 2.9110917991 -0.0395481983
C 5.2874027905 2.006958214 -1.1106076736
Pd 1.3906135731 0.368812094 -0.2831244935
Br 1.3551150004 2.3535314196 -2.4175056677
H 6.3122199097 3.2635828501 0.3263820164
C 2.8398067881 -0.4528767693 0.9948745284
C 3.367387237 -1.8398372677 0.5329287739
C 2.8820300963 -2.7732761669 1.6762758016
C 3.7759811377 -2.516957043 2.8940385333
C 3.3590609998 -1.0884091019 3.3291024835
C 2.2112094502 -0.7378198113 2.3528747053
C 1.5752017072 -2.1116190206 2.12459127
C 2.8389390032 -2.156418607 -0.8256175555
C 1.9326006678 -1.2281894561 -1.3607382924
C 1.3845364411 -1.4128901743 -2.629136546
C 1.7378992412 -2.5404564913 -3.3666842503
C 2.6424934981 -3.4593485161 -2.8446685658
C 3.2078732349 -3.2847194569 -1.5801936
C 4.1983776169 -4.2860394211 -1.0593791062
P -1.2882298195 0.0664577952 -0.1240006197
H 1.3085903849 -2.6978961527 -4.3560256773
H 2.9301651786 -4.3313817584 -3.4342688777
H 4.4735105202 -1.8487528809 0.5153445873
H 3.6132236314 0.3286083417 1.0258157595
H 1.5470849961 0.049184986 2.7309964715
H 2.8096212025 -3.8284937183 1.3854627756
H 0.7951496124 -2.1021304731 1.3526959672
H 1.1568345816 -2.5554475506 3.0400365243
H 2.9955483391 -1.0758698552 4.3662624767
H 4.1842309363 -0.3654313724 3.265978896
H 4.8445151285 -2.5979617029 2.6501901375
H 3.5662782203 -3.2470176179 3.687713676
H 4.5659397938 -4.932115118 -1.8662859521
H 5.0687260798 -3.7995467604 -0.5969459283
H 3.7631614302 -4.9417231032 -0.2915842654
H 0.6731822724 -0.6941040375 -3.038343289
H 4.1987671041 4.0198567447 1.4029828169
H 6.2072307668 1.6561520333 -1.5769303659
C -2.116025163 -1.2670584526 -1.1054855313
C -1.3882906852 -2.4490401035 -1.2994873324
C -3.3785167295 -1.1275908496 -1.6831387747
C -1.9286512713 -3.4895266245 -2.047340622
H -0.386211782 -2.5475451283 -0.884586372
C -3.8860118879 -2.1799768568 -2.4273000706
H -3.9589256383 -0.2183281734 -1.5598356198
C -3.1928446919 -3.3618818802 -2.6208551294
H -1.3546700266 -4.3993610298 -2.1982759318
H -3.6281371076 -4.1589616965 -3.2142643972
Cl -5.5286196666 -1.9989198553 -3.1835591377
C -2.532366987 1.4436296522 -0.1243472112
C -2.1706900452 2.6589843271 -0.7062885909
C -3.785078031 1.3047772023 0.4839659579
C -3.0650291262 3.7285845295 -0.7087496222
H -1.18159015 2.7662393278 -1.1477217742
C -4.6523065996 2.3815945003 0.4622245419
H -4.0742480829 0.375788156 0.9706441657
C -4.3211164521 3.5940451887 -0.1240875196
H -2.7845703977 4.6714854581 -1.169966693
H -5.0333591179 4.4126887207 -0.1182414814
Cl -6.2863597919 2.2077028676 1.2357803603
C -1.5663932619 -0.5418796118 1.6119671602
C -1.1362155935 0.2936469775 2.6493767056
C -2.149065015 -1.7740472804 1.9014440579
C -1.287428368 -0.1068850121 3.9718651509
H -0.6645857636 1.2452017537 2.4052021911
C -2.278065117 -2.1461024246 3.2303080601
H -2.4901105419 -2.4359815382 1.1099623622
C -1.8623455864 -1.3414252145 4.2756501095
H -0.9534130889 0.5397816247 4.7790007266

H -1.9847700717 -1.6706658707 5.3023021908
Cl -3.0318477153 -3.7548049562 3.6146062274
O 1.6626437993 4.2743947476 1.5146561234
O 0.8212547282 2.2717887607 0.9644514193
H 4.0297499479 0.9179757029 -2.4822961765
C 1.7207961014 3.1138783878 0.8698517224
C 0.5181768635 4.4668427245 2.345040863
H -0.4021182254 4.4192160322 1.751719213
H 0.478449323 3.7000933588 3.127165546
H 0.6361419346 5.4569420613 2.7883526506

VI-VIIb

83

C 1.4001222629 2.5071413263 1.3733538039
C 1.9173630451 1.184793065 1.2652001942
C 2.281067799 0.5630797219 2.4705207922
C 2.1822482672 1.2118352608 3.6916105095
C 1.7153745987 2.5236794285 3.7755613503
C 1.3224622119 3.1594565006 2.6117335823
Pd 1.1935350078 0.3004575274 -0.5160747589
P -1.2207705892 -0.1111116443 -0.2556634613
C 1.6617284419 -1.5743367416 0.2603730758
C 3.1994071934 -1.7234785605 0.4183285495
C 3.4882713921 -2.9393661018 -0.5133372226
C 2.9862413554 -4.1909723415 0.2135634751
C 1.4492316559 -4.0061511029 0.1785158091
C 1.2637699544 -2.7114089453 -0.657592537
C 2.4486220465 -2.7902886084 -1.6214607846
C 3.9452641069 -0.4594325397 0.0798645665
C 3.2062710414 0.7248906548 -0.135067715
C 3.8284152576 1.8777229537 -0.6171298355
C 5.2028539658 1.8907133602 -0.7933750816
C 5.9512614227 0.7679443464 -0.4610619507
C 5.3442825285 -0.4148012132 -0.0322264069
C 6.2310330004 -1.5784731256 0.3184282109
Br 1.0815049951 0.1325987698 -3.2553982609
H 1.6539953793 3.0343437037 4.7341257311
H 5.6949549052 2.7877403917 -1.1655817607
H 7.0386686166 0.7986653581 -0.5398874602
H 3.4421214339 -2.0288510149 1.4536646844
H 1.1037746381 -1.5575527368 1.2074861029
H 0.2619679613 -2.6260398657 -1.0909873477
H 4.5273314587 -3.0009109335 -0.8471648082
H 2.5644635103 -1.8919969396 -2.2384084768
H 2.406312311 -3.6726702975 -2.2749991298
H 0.9515610352 -4.8425529214 -0.3300371877
H 1.0019423763 -3.9289360312 1.180047807
H 3.3878234444 -4.2798489809 1.2331320386
H 3.2861337745 -5.0945455322 -0.3336826791
H 7.1665968268 -1.2156832806 0.7632416269
H 5.7667284651 -2.266085791 1.036392483
H 6.5105453026 -2.17030096 -0.5647163047
H 3.2390615978 2.7613669904 -0.8503625822
H 2.676049424 -0.4484599541 2.4651750892
H 0.9223781456 4.1706411467 2.6386865113
O 0.4989200031 4.4322370643 0.3561676902
H 2.4824661899 0.6807006884 4.59437614
O 0.693011815 2.5860344864 -0.8919051556
C -2.3042752763 -1.2924325331 -1.1841768767
C -3.6009641861 -1.548882123 -0.7219437231
C -1.858396549 -1.854443996 -2.379974071
C -4.406353184 -2.3963273871 -1.4578959778
H -3.9779967476 -1.0939857052 0.1907828616
C -2.700227837 -2.7037631964 -3.0997244603
H -0.8694369828 -1.6011250539 -2.7653776014
C -3.9811371034 -2.9875620322 -2.6382715305
Cl -6.0880934205 -2.7396792902 -0.8644265467
H -2.3543854386 -3.1404563342 -4.0319450351
H -4.6462827551 -3.6481850376 -3.184913866
C -2.219238467 1.4271841394 -0.4972440201
C -3.0949724163 1.9384786718 0.458226077
C -2.1126592226 2.0278625095 -1.7572434809
C -3.8513656903 3.0519920485 0.1270939995
H -3.2013311498 1.4771102463 1.4364500212
C -2.9046723703 3.129703374 -2.063468335
H -1.400549911 1.636707533 -2.4864410898
C -3.784839733 3.655439319 -1.1161123055
Cl -4.9922988464 3.7277770166 1.3701685543
H -2.8369342916 3.587212524 -3.0467850261
H -4.4085986008 4.5151031442 -1.338706446
C -1.4592209278 -0.6137350359 1.5022687893
C -1.6875790774 -1.9577879243 1.8143621694
C -1.149712775 0.2907334538 2.5250696595
C -1.6203185116 -2.3531538659 3.1388642028
H -1.9026452176 -2.6872960058 1.038264232
C -1.1080631723 -0.1355670341 3.848988192
H -0.8991263887 1.3223584768 2.2857428806
C -1.3463874945 -1.470515314 4.1696452362
Cl -1.8779221661 -4.1070553388 3.5315827158
H -0.8638258375 0.5751537686 4.6335642629
H -1.307082913 -1.8219991428 5.1953265068
C 0.8486870102 3.1613494407 0.1818300677
C -0.1575239765 5.0483084583 -0.7538462836
H -1.0715149825 4.498718418 -1.0030413965
H -0.3917557689 6.0640868094 -0.4308946523
H 0.5009998025 5.0610914177 -1.6285066204

VII-VIIIb

83

C 4.7588752975 0.4898170527 1.5202169993

C 3.6870071445 -0.3437920866 1.1324591709
C 2.5892364311 -0.4411487033 1.9952728764
C 2.5221169668 0.2952051069 3.1725858487
C 3.56326833 1.1450129928 3.5276003846
C 4.6806593132 1.2238624924 2.7095241091
Pd 0.7104946701 -0.5859536046 -0.7294911069
P -1.5598068911 -0.1006119855 -0.2629070372
C 0.9463623211 1.1710096801 -1.8939331401
C 2.3010315087 0.7326502231 -1.96544221
C 3.1123517915 1.8102274253 -1.2903020041
C 3.0527749581 2.9781715997 -2.3176156879
C 1.5898624271 3.478437339 -2.2225037782
C 0.9725043431 2.5130104662 -1.1842361399
C 2.1494472333 2.3385823944 -0.2225005228
C 2.7433227621 -1.2241243184 -1.0806506817
C 3.720644049 -1.219386642 -0.0711190119
C 4.7419525988 -2.1778617008 -0.1228730458
C 4.8146537996 -3.0996264602 -1.1512416991
C 3.8510475548 -3.0833890529 -2.1521096188
C 2.8106723367 -2.1581000449 -2.1328813629
C 1.7504112322 -2.2498474423 -3.1923822819
Br 0.2796177385 -2.8954339184 0.4577741952
O 7.0493446021 0.9805190949 1.4124488346
O 6.0235056488 0.5449921861 -0.5316270527
C -1.8650508108 -0.056945369 1.5564407971
C -2.8996641422 -0.7749093049 2.1503101974
C -0.9911933369 0.7008929126 2.3435169211
C -3.0534103654 -0.6932911642 3.5249394808
C -1.180662218 0.7738212708 3.7197692204
C -2.2214121469 0.0704673514 4.3241695134
Cl -4.4017125291 -1.6191644147 4.3076285257
C -2.9086951049 -1.1687354147 -0.9426075746
C -4.2294713386 -0.7038907145 -0.9132865952
C -2.6175572676 -2.4117340275 -1.5033815603
C -5.224776404 -1.5046388647 -1.44068889
C -3.6446756041 -3.1928575193 -2.0323700018
C -4.9611885579 -2.7434384506 -2.0046287699
Cl -6.9377461874 -0.9044258799 -1.4019884777
C -2.2010911862 1.5607722808 -0.8000916588
C -2.456704861 2.5914025818 0.1022427109
C -2.3356317816 1.7902651564 -2.1742683005
C -2.8142779718 3.83544107 -0.3952148902
C -2.6922825019 3.0488835254 -2.6433517934
C -2.9283549342 4.0935530436 -1.7487934003
Cl -3.1455804046 5.1751671845 0.7839251705
H 1.7892750515 -1.139605662 1.7484947266
H 1.6540848938 0.1790536478 3.8208389588
H 3.5202451662 1.7258338841 4.4472757947
H 5.5156026784 1.8638333224 2.9843988823
H 0.2757086876 1.0315376272 -2.747487715
H 2.693118381 0.2673389286 -2.8668296406
H 4.1249608452 1.5261715391 -0.9980319221
H 3.3353796304 2.6568643222 -3.3285765732
H 3.7651953402 3.7570773172 -2.0173987474
H 1.0571535585 3.4484871476 -3.1826657911
H 1.5413267699 4.5118795998 -1.8541046191
H 0.018812675 2.8457512478 -0.7617232738
H 2.4890227375 3.2884918957 0.2129588935
H 1.9579598188 1.6203823921 0.5831726904
H 5.4782177984 -2.1973991686 0.6811720297
H 5.6163031898 -3.8355967466 -1.171376458
H 3.8902772532 -3.8140771663 -2.9611084359
H 0.871307286 -2.7861412432 -2.8053567964
H 2.1145688213 -2.7992006082 -4.0700137466
H 1.3952983728 -1.2671684318 -3.5337864275
H -3.5689983136 -1.3922135116 1.5587034809
H -0.1568998333 1.2274197895 1.8786761705
H -0.5127136762 1.376563746 4.3292218877
H -2.3790455461 0.1083763685 5.396879111
H -4.4763865672 0.2667501684 -0.4905650193
H -1.593829708 -2.7801637044 -1.4934440754
H -3.4164524803 -4.1631449118 -2.4635017005
H -5.7711672526 -3.3406001694 -2.4111509172
H -2.3736563147 2.4361068532 1.1740966833
H -2.1661587402 0.9765149353 -2.877671164
H -2.7931682335 3.2237753785 -3.7105505156
H -3.2043439125 5.0836815892 -2.0967918279
C 5.9711538646 0.6561927314 0.6740507083
C 8.2402028787 1.204493006 0.6674369329
H 8.1066636063 2.0302435579 -0.0403209305
H 9.0107418604 1.4497693959 1.4010832043
H 8.5186354 0.3068902654 0.1048669305

IX-Xb

100

C 0.0222860434 -3.8028746323 0.6509010034
C -1.3885428521 -3.731872468 1.1368899619
C -1.8419208561 -2.9815510696 2.2448057802
C -3.175964677 -3.0976257283 2.6601405322
C -4.0615398826 -3.9436695034 2.0114341376
C -3.6184306724 -4.6926275251 0.9264277388
C -2.2998660136 -4.5837422554 0.5031183017
C 0.8963003167 -4.6072516994 1.3950186818
C 2.1847757698 -4.8636530064 0.9577003858
C 2.6233043648 -4.3119118001 -0.2445037597
C 1.8048405894 -3.4936714895 -1.0169950346
C 0.501531877 -3.2125254331 -0.538501539
C 2.314717959 -2.9747851121 -2.3254871703
Pd -0.1853990782 -1.0944356072 -0.278519586
H -3.5128837363 -2.5123609922 3.5111327055
H -5.0910723388 -4.0197094544 2.3558968709
H -4.2948623984 -5.3755512549 0.4141680167
H 0.5307697421 -5.0404647772 2.3271958236

H 2.8451980686 -5.5030967117 1.5412577686
H 3.6350722802 -4.5128156074 -0.5979551323
H 3.4018127337 -3.100522816 -2.3996717004
H 1.8539017261 -3.5155593551 -3.1654641455
H 2.0861886756 -1.9118361055 -2.4695207361
P 1.9283035321 0.0262415703 0.2331537627
C 2.8949569142 0.3011426687 -1.3245978051
C 1.7024304101 1.7529702077 0.8709598202
C 3.2540479879 -0.5269297684 1.4092580109
C 3.1940655495 -1.8142815553 1.9374618643
C 4.1883045481 -2.2584875988 2.808067393
C 5.2394850204 -1.4203790727 3.165197009
C 5.2692762502 -0.1381631969 2.6368324822
C 4.2991174887 0.3319097345 1.7722263738
C 2.2078846557 0.8150988485 -2.4325232184
C 2.8472627869 0.9362772559 -3.6601515183
C 4.1689173979 0.5138971086 -3.8102643368
C 4.8216379086 -0.000750537 -2.7048543777
C 4.221098853 -0.107968793 -1.4605775233
C 2.2468269132 2.8917147317 0.2766008964
C 1.9875207332 4.1231750163 0.8614024018
C 1.2015882234 4.2625008782 1.9930480967
C 0.66863216 3.1146055337 2.5797340465
C 0.9181814475 1.8663001447 2.0232976605
Cl 6.6413792737 0.9611175508 3.10268686
Cl 2.7257008606 5.6109933784 0.1305153262
Cl 6.5353622007 -0.5783191058 -2.8917000005
H 2.3678201091 -2.4675581753 1.6855518604
H 4.1385565316 -3.2658145233 3.2134337595
H 6.0205524742 -1.7464203624 3.8444809267
H 4.3551586654 1.3477618347 1.3876913304
H 1.163000081 1.1083767933 -2.3388117244
H 2.3102013853 1.3515482322 -4.5087994805
H 4.6789461823 0.5797246371 -4.7655765154
H 4.7736064973 -0.5145418603 -0.6187240898
H 2.8541489412 2.8261391935 -0.6235535944
H 1.0173839711 5.2467147599 2.4098566722
H 0.0360402838 3.2041865079 3.4593121086
H 0.511711218 0.9584874561 2.4714544244
P -1.9669600391 0.5483311229 -0.1782016386
C -1.7007509755 1.5585896519 -1.7051574121
C -2.2969142032 1.8015556095 1.1570689573
C -3.7310998246 0.0054495599 -0.4157556544
C -4.045719699 -1.3501488289 -0.3656100286
C -5.3672647053 -1.7670689585 -0.5318346781
C -6.3776751465 -0.836459011 -0.7446609073
C -6.0403744302 0.5088972643 -0.778984208
C -4.7426507872 0.9520928831 -0.6164042844
C -2.3631440249 1.230007337 -2.8913875969
C -2.0131945597 1.8524638051 -4.0863881912
C -1.0012391376 2.8091999735 -4.1166368329
C -0.3575819751 3.118909337 -2.9303098181
C -0.6773016737 2.5131603624 -1.7272823654
C -2.3395505511 3.1801114453 0.9570384087
C -2.6025030573 3.9998739652 2.0429446296
C -2.8501180316 3.505865189 3.3110805244
C -2.8199216259 2.1229858491 3.4973836968
C -2.5343388655 1.2757172181 2.4318818402
Cl -7.3594021845 1.7324329474 -1.0389455313
Cl -2.6119492397 5.7982459722 1.7891391004
Cl 1.0044634765 4.3153602069 -2.9608599039
H -7.4106337216 -1.1410501304 -0.8781256812
H -3.1469223935 0.477518459 -2.8827697554
H -2.5302223669 1.58936722 -5.0050088344
H -0.7153185782 3.3028003291 -5.0398765664
H -0.1108163529 2.7561419643 -0.8304061361
H -2.1669125934 3.6196919435 -0.0209697409
H -3.0650237847 4.1838994624 4.1306200442
H -3.0255287552 1.70986275 4.4816605703
H -2.5009661477 0.197171696 2.5925948298
I -1.0157201288 -2.7408235031 -2.2662418436
H -1.9457022548 -5.1836594463 -0.3343091203
O -1.5736156179 -1.4511414761 4.0115112509
O 0.2111599951 -1.8002194191 2.7019985136
H -5.6079353949 -2.8257713847 -0.4980509964
H -4.5219139309 2.0162290185 -0.6433281611
H -3.260473594 -2.0842093758 -0.2045109181
C -0.9447204638 -2.0444895744 2.9709080078
C -0.7649499956 -0.5799759873 4.7950965284
H 0.1725822827 -1.0693505075 5.076339889
H -0.5345199988 0.3366563739 4.2372129293
H -1.3567120402 -0.337835403 5.6809042781

V-VIc

79

C 2.9745435602 -2.1105705794 -0.9350100248
C 1.635703579 -1.9501121998 -0.5689521309
C 0.5930944916 -2.389583164 -1.3913215294
C 0.8898607822 -2.8618446645 -2.6618298604
C 2.2191466925 -2.9391003497 -3.0601327868
C 3.2598857136 -2.5901390746 -2.2036787323
Pd 1.1235115599 -0.1696210596 0.5403061509
Br 1.080160701 -2.5994801003 1.6812344448
C 1.4360572947 1.424954483 -0.7764650379
C 2.9262663407 1.8456496392 -0.9109833688
C 2.8431920065 3.3794244932 -0.706200473
C 2.1227087665 3.9909935321 -1.9160218043
C 0.6471583352 3.567988887 -1.7008673129
C 0.7165441787 2.7270616844 -0.4103937325
C 1.7771085053 3.4891316847 0.3873994183
C 3.7527955424 1.1542691343 0.1221403043
C 3.0723076314 0.2768716325 0.9814654641
C 3.7357937339 -0.3508047152 2.0338844181

C 5.1027456536 -0.1353803201 2.1992213891
C 5.7943338504 0.6777777801 1.3095407988
C 5.1384726755 1.3389119488 0.2695170881
C 5.9282548918 2.2156659542 -0.6600605528
P -1.4084523372 -0.0702611234 0.2372348136
H 5.6334403322 -0.627711785 3.0137243203
H 6.8714502799 0.8112381972 1.4215248279
H 3.3019955464 1.6233319005 -1.9263811654
H 1.0305180273 0.9745237379 -1.6953515293
H -0.2637394522 2.6107887956 0.0664470726
H 3.810997048 3.8421369118 -0.4810641233
H 2.0669110359 2.9972331997 1.3264013444
H 1.4857180877 4.5273443593 0.5988235258
H -0.0008017459 4.4422111567 -1.5433516958
H 0.2222886675 2.9997369527 -2.5405900726
H 2.5382032126 3.6248282135 -2.8651218313
H 2.2246313162 5.0842575874 -1.9189814731
H 6.9731273684 1.8845183559 -0.7119759097
H 5.5236426839 2.2112688865 -1.6806533474
H 5.9420871091 3.2637218521 -0.3270328865
H 3.2113827405 -1.0320134753 2.7008323705
H 0.1057526584 -3.1990305372 -3.335055787
H -0.4337406238 -2.3989709134 -1.0322146373
H 4.2869134011 -2.6926157712 -2.5432653523
C -2.1449694336 0.8412657316 1.6667507505
C -1.3004419909 1.574843142 2.5025464576
C -3.5199155431 0.8045785471 1.917715766
C -1.8276839504 2.2871158377 3.5780217468
H -0.2257831528 1.5831433336 2.317381155
C -4.0140143971 1.5195350616 2.9939559742
H -4.1908542426 0.2261843022 1.2869188646
C -3.1965014296 2.264655668 3.830023911
H -1.1693978088 2.8562271057 4.2280648467
H -3.6255613957 2.8093362542 4.6646563321
Cl -5.7950672553 1.4742329866 3.3269479153
C -2.5161677539 -1.5577160708 0.1549502306
C -2.5166212646 -2.432346637 1.247622557
C -3.2966837903 -1.8415337625 -0.9664991305
C -3.2943167583 -3.5844563679 1.2167833361
H -1.9055042487 -2.2136697013 2.1200592991
C -4.0501900444 -3.00470783 -0.9705876969
H -3.3235109984 -1.1730846372 -1.8217416126
C -4.0685730529 -3.8843428267 0.096956758
H -3.2934267612 -4.2606496327 2.0662782755
H -4.6742305272 -4.7835462509 0.0536932037
Cl -5.0497381352 -3.3857994699 -2.4361039197
C -1.9808783182 0.9082801168 -1.2270208968
C -1.5307464153 0.514864384 -2.4937415641
C -2.7740110798 2.0478813037 -1.0951258074
C -1.8893702151 1.246607376 -3.6219459642
H -0.8906706818 -0.3605010242 -2.5992996758
C -3.0971938909 2.7667638832 -2.2345152242
H -3.1276401136 2.3788044377 -0.1227018426
C -2.6777431662 2.3895792761 -3.4981576094
H -1.5460603025 0.9337046709 -4.6038901764
H -2.9560593216 2.9783445036 -4.3659782553
Cl -4.0995758907 4.2676203534 -2.0620401058
N 2.5299830686 -3.4256965177 -4.399578221
O 3.708118708 -3.5235112457 -4.7085643752
O 1.590924685 -3.7005482942 -5.1327487644
H 3.7781625066 -1.8354051549 -0.2575082316

VI-VIIc

79

C 1.4438765858 2.7958321134 0.5328462854
C 1.8221889267 1.5003729569 0.9111150414
C 2.0927068548 1.218349223 2.253116541
C 1.9416404219 2.2058594798 3.2154303698
C 1.5242485625 3.4731521305 2.8267483928
C 1.2765425535 3.7829410242 1.4946387628
Pd 1.2224209798 0.1984738493 -0.5779050944
P -1.2286210407 0.0131435039 -0.242587165
C 1.5689533575 -1.3993628192 0.7256166847
C 3.0922368289 -1.620907952 0.894084818
C 3.2887917005 -2.9906876379 0.1735151709
C 2.6866260031 -4.0789885169 1.0685239983
C 1.1684402146 -3.7999186067 0.9756389318
C 1.0887260085 -2.6249642096 -0.0338166085
C 2.2694037594 -2.9233708258 -0.9627051154
C 3.9181893006 -0.5316732225 0.2717044542
C 3.2580513107 0.5136679543 -0.3914827066
C 3.9557454013 1.5070444023 -1.074482601
C 5.3426672895 1.4691386636 -1.0747427264
C 6.011039733 0.4664315322 -0.3782774774
C 5.3243217888 -0.547525168 0.2900400591
C 6.1113223683 -1.6004059761 1.0186770678
Br 0.9838598693 1.0903770238 -3.0556321329
H 5.9066487346 2.2363949531 -1.6024938264
H 7.1012258609 0.4680849129 -0.3450747045
H 3.350910552 -1.7376063505 1.9618713169
H 1.0042291851 -1.1896686453 1.642566419
H 0.1029504091 -2.5366031846 -0.5055320706
H 4.3256133895 -3.1751948771 -0.1248470486
H 2.4681229699 -2.1312257277 -1.6988820769
H 2.1627478305 -3.8790466647 -1.4931601415
H 0.6130805007 -4.663494881 0.5851880942
H 0.7163418373 -3.538007663 1.9415856301
H 3.0700102691 -4.0302869253 2.096953477
H 2.9306900468 -5.0747912887 0.6762217988
H 7.0656694431 -1.1893326373 1.3703399611
H 5.5790848177 -1.9980160933 1.8922492252
H 6.3532077253 -2.4571584272 0.3734205338
H 3.4225168482 2.2950890918 -1.6026881998

H	2.4135697241	0.2282846869	2.5673855095
H	0.9575144166	4.7858299673	1.2246776772
H	2.1397814408	2.0074460593	4.2653213217
C	-2.2841711171	-1.0679828864	-1.3041326578
C	-3.6116416376	-1.3386446142	-0.9566582745
C	-1.7535123746	-1.5611876229	-2.4972081676
C	-4.3664867	-2.1269894581	-1.8046714603
H	-4.0529114114	-0.9419816879	-0.0459673503
C	-2.5454713474	-2.3441360705	-3.3365018838
H	-0.7318970096	-1.3100952034	-2.7821813109
C	-3.8607925132	-2.6380433183	-2.9910554659
Cl	-6.0827025978	-2.4990630669	-1.3520883796
H	-2.1362911464	-2.7224128624	-4.2684832708
H	-4.4902010156	-3.2479429555	-3.6309728444
C	-2.1949572652	1.5923452296	-0.2534869055
C	-3.1503045926	1.8777067479	0.7247957798
C	-1.9865597123	2.4792295753	-1.312816983
C	-3.8696216938	3.0553545247	0.6201151743
H	-3.3288825903	1.2063041995	1.5595588846
C	-2.7311271131	3.6532479709	-1.3895202673
H	-1.241940158	2.2494236241	-2.0760333127
C	-3.6810661364	3.9537213822	-0.4160794234
Cl	-5.1063448273	3.4351320914	1.8936429002
H	-2.5699470413	4.3409175465	-2.2146865686
H	-4.2656663429	4.8668196711	-0.4588615229
C	-1.4806785296	-0.6229134917	1.4731324137
C	-1.8267418792	-1.9535605895	1.7138703094
C	-1.0869694559	0.1971364365	2.5396216137
C	-1.7658378154	-2.4314220985	3.0129138522
H	-2.1247994535	-2.6153303852	0.9049639538
C	-1.0497338468	-0.3086593051	3.8344190864
H	-0.7879994255	1.2278954752	2.3564892975
C	-1.3872915951	-1.6394638698	4.082773346
Cl	-2.1697104071	-4.175400104	3.311493298
H	-0.7463898217	0.333649816	4.6567398339
H	-1.3555525535	-2.0524420317	5.0854630014
N	1.3484181065	4.5072089534	3.846505486
O	1.0128636545	5.6193399534	3.4718473894
O	1.5450322052	4.1912994554	5.0104764482
H	1.2639923815	3.0318637405	-0.5156838655

VII-VIIIc

79

C	-4.8462801153	0.7903378511	-0.1044464105
C	-3.824971738	0.0270597045	-0.6893138305
C	-2.8570608431	0.6795608239	-1.4633326345
C	-2.8526125679	2.0619348235	-1.575181845
C	-3.8193765782	2.7938397475	-0.8998794091
C	-4.8428705663	2.174597725	-0.1893550343
Pd	-0.7257866115	-1.341109958	0.0877569626
P	1.4303341753	-0.3648523595	0.0806643681
C	-0.8810966409	-1.1813056759	2.1910197936
C	-2.1999703314	-1.6847305605	1.9506136327
C	-3.1311384839	-0.6040189733	2.4495365215
C	-2.9866964544	-0.6911602676	3.9942882308
C	-1.5692709186	-0.1242222312	4.2583236538
C	-1.0576703618	0.1832456216	2.8321106156
C	-2.3430081896	0.6789026132	2.1682630361
C	-2.7237556351	-2.1867831006	-0.0339998867
C	-3.8049897508	-1.4512396329	-0.5602246214
C	-4.9118958253	-2.1383565889	-1.0747865242
C	-4.9391309529	-3.5233573685	-1.1129519422
C	-3.842429405	-4.2402593415	-0.6509529651
C	-2.7324681415	-3.5937830724	-0.1108164869
C	-1.5510901035	-4.4141036855	0.3161008768
Br	-0.4202089574	-1.8462363677	-2.464204977
C	1.4157969282	1.1837683198	-0.9228526736
C	2.3706544177	1.451144031	-1.9004801186
C	0.3752004965	2.089402328	-0.6902407786
C	2.2720082305	2.6402330944	-2.6054218592
C	0.3016133383	3.2776538486	-1.41133544
C	1.2617379664	3.5602826728	-2.3821972916
Cl	3.5149871017	3.0017614035	-3.8750151987
C	2.9178598334	-1.3086347276	-0.4826901676
C	4.1913490692	-0.7815913963	-0.2328307034
C	2.7830536227	-2.5422733611	-1.1175842057
C	5.2968357735	-1.5013065419	-0.6446169303
C	3.9194188286	-3.2486332021	-1.5099111552
C	5.189419832	-2.7297179757	-1.2781000182
Cl	6.9476340738	-0.8116035357	-0.3415871637
C	2.0584708231	0.2400797652	1.7224736377
C	2.1122439141	1.5950455579	2.0445016787
C	2.3814877586	-0.7196304179	2.6880450035
C	2.4586210889	1.955564039	3.3378471319
C	2.7263933767	-0.3278979456	3.9762269299
C	2.759093184	1.0250176511	4.3155899856
Cl	2.5012736333	3.7173139671	3.7669965411
H	-2.1074265669	0.0935293112	-1.9948663215
H	-2.1052333391	2.5647366361	-2.1814932627
H	-5.6032299943	2.7813109241	0.2944930364
H	-0.100473819	-1.8462894425	2.5734989519
H	-2.4373840119	-2.7182397528	2.1942136327
H	-4.1626842961	-0.6654735751	2.0916493596
H	-3.1185527442	-1.715573706	4.3666312618
H	-3.7609682727	-0.0733658354	4.4666412425
H	-0.9133339063	-0.8254746272	4.7910155283
H	-1.6102469983	0.7991561218	4.8510403131
H	-0.1829461349	0.8390361839	2.79283042
H	-2.775139959	1.5550508758	2.6709739407
H	-2.2279724248	0.8965416599	1.100324983
H	-5.7394270277	-1.5604198343	-1.4872564046
H	-5.8036916662	-4.0432016486	-1.5215365422
H	-3.8394634014	-5.329159367	-0.7099839365

H -0.7464922465 -4.323120373 -0.4286329059
H -1.8124992714 -5.4761937772 0.4018349589
H -1.1267874928 -4.0934228557 1.2789917136
H 3.170719849 0.7491120255 -2.1162609603
H -0.391272948 1.8577375395 0.049668852
H -0.5253971858 3.9657885677 -1.2449936416
H 1.2188840246 4.4752515756 -2.963723299
H 4.3187681183 0.1699956482 0.2768807328
H 1.7908166522 -2.9326041212 -1.3328442597
H 3.8130295028 -4.2076097513 -2.0081464957
H 6.0827850094 -3.2658346497 -1.5813711434
H 1.8743757896 2.3580259367 1.308693525
H 2.3647140098 -1.777083878 2.4272606171
H 2.9764387277 -1.0744196071 4.7247271234
H 3.0205136493 1.3494662672 5.3172912539
N -3.7589761712 4.2553650325 -0.9358889116
O -2.7414211512 4.7742037046 -1.3786991757
O -4.7186550204 4.875538858 -0.5104584784
H -5.6342375766 0.2876066329 0.4567859642

IX-Xc

96

C 0.2420376968 -3.8361348223 0.3654142637
C -1.1009573798 -3.7048902577 0.9904131508
C -1.2602261821 -2.985716082 2.1836541491
C -2.5064505482 -2.8708996864 2.7838165325
C -3.5948651262 -3.4865725301 2.1763985346
C -3.4644458726 -4.2402809467 1.0164859146
C -2.2106519741 -4.3539056694 0.4361770648
C 1.1710512833 -4.6661711275 1.0047749864
C 2.4518178434 -4.8296571765 0.4965058431
C 2.8145610413 -4.1582875361 -0.6682570712
C 1.924048633 -3.33191984 -1.3514165799
C 0.6383719138 -3.1321962412 -0.794148211
C 2.3384087988 -2.7253055791 -2.6537269641
Pd -0.0705019823 -0.9983014348 -0.3495869055
H -2.6518057194 -2.3126706766 3.704806995
H -4.3345983426 -4.7323769837 0.5907298933
H 0.8634738736 -5.1848036253 1.9142855591
H 3.1657000731 -5.4796271659 0.9991249662
H 3.8186831903 -4.2804732719 -1.0780678063
H 3.4240150215 -2.7974722584 -2.7894757107
H 1.8541086014 -3.2471754881 -3.4926391701
H 2.0589165494 -1.6676339845 -2.7290817573
P 1.9784976245 0.0298951649 0.4187264147
C 3.2463848906 0.0223951176 -0.9280080413
C 1.9247853607 1.8229576956 0.8990530777
C 2.964132257 -0.6406031282 1.8370121849
C 2.7523426375 -1.9643450964 2.2168824456
C 3.5094517079 -2.5290562041 3.2414973478
C 4.4708236766 -1.7700515396 3.9018955209
C 4.6559797769 -0.4516932685 3.511307064
C 3.9276381701 0.1325059169 2.4911296649
C 2.9549899804 0.704834978 -2.1153903245
C 3.8515740794 0.6786737821 -3.1766518693
C 5.0226717546 -0.0754975833 -3.087477429
C 5.2652451008 -0.7748082479 -1.9186547983
C 4.414075587 -0.7310865283 -0.8263685028
C 2.7204816064 2.814601342 0.3206102358
C 2.5511345763 4.1253258673 0.7403775535
C 1.622858978 4.4884685087 1.7017359921
C 0.8556792968 3.487169386 2.2936228134
C 1.0054723873 2.1630592301 1.895714764
Cl 5.9114599315 0.5393500389 4.3712021549
Cl 3.6080504824 5.4161379959 0.0281540361
Cl 6.7514041162 -1.8162302738 -1.8149137189
H 2.0085590229 -2.5655552529 1.7033160663
H 3.3491516113 -3.5668244219 3.522733145
H 5.0708506291 -2.1878972343 4.7034717258
H 4.1071934447 1.1663623278 2.2081848558
H 2.0147482615 1.2452993128 -2.2111705111
H 3.6344945924 1.2375261753 -4.0825346224
H 5.7266846845 -0.1254593217 -3.9113413869
H 4.6534689894 -1.2820428569 0.078490371
H 3.4499251289 2.5795498569 -0.4493300024
H 1.5073211333 5.5291992279 1.9853428788
H 0.1184734787 3.7445835941 3.048660213
H 0.3901618824 1.3882444771 2.3509116723
P -1.8030273727 0.7221993899 -0.3114503829
C -1.3873646517 1.7283288162 -1.8056869751
C -2.1113891854 1.9903510814 1.0127459287
C -3.5850408289 0.2626975435 -0.5498504173
C -3.9900464974 -1.0049634516 -0.1340566734
C -5.3426091412 -1.3456197078 -0.1292275997
C -6.2922364112 -0.431587403 -0.5767540553
C -5.8632278624 0.8160911409 -1.0042087585
C -4.5337612552 1.1943362945 -0.9811723588
C -2.0344778842 1.5105708872 -3.0234672111
C -1.5827882927 2.139374506 -4.1817763233
C -0.4729870838 2.9769967483 -4.1420447381
C 0.1644456587 3.1675533933 -2.9257316748
C -0.2648936463 2.5694578404 -1.7538123255
C -2.1433851579 3.3643360362 0.788916778
C -2.385411142 4.2027835809 1.864977205
C -2.6252162446 3.7307373366 3.143488968
C -2.6083612701 2.3505975561 3.3531361267
C -2.3422389531 1.4863550241 2.2967336644
Cl -7.0989164045 2.0128740266 -1.5905444086
Cl -2.3407218515 5.99708955 1.5903409599
Cl 1.6465177938 4.2170585924 -2.8894783399
H -7.349529204 -0.6749283691 -0.5830415507
H -2.8913164969 0.8435024716 -3.0701546996
H -2.0964190559 1.9709430526 -5.1240742774

H	-0.1033925868	3.4711989257	-5.0347914433
H	0.2770384009	2.7347299049	-0.8209678193
H	-1.9604013918	3.7845934704	-0.1958699418
H	-2.8182887123	4.4235125958	3.9562770105
H	-2.800878042	1.9567534232	4.3471349035
H	-2.3133842347	0.4079972394	2.4597527808
I	-0.9896690057	-2.5830846381	-2.3563113801
H	-2.0831661579	-4.9475255099	-0.4672425225
H	-5.6605638617	-2.3106905043	0.2585139896
H	-4.2455633813	2.2001875711	-1.2763556504
H	-3.2480358457	-1.7264333812	0.2003538392
N	-4.9243143212	-3.321105487	2.765935031
O	-5.8872528133	-3.6899189971	2.1046232761
O	-4.995491441	-2.8214495596	3.8752369442
H	-0.3949812845	-2.4955507248	2.6315065036

V-VIc*

79

C	2.9884036047	-2.1081098451	-0.9418382728
C	1.6443615567	-1.9490310423	-0.5868390739
C	0.6126686001	-2.3540796969	-1.4426654666
C	0.9258091633	-2.7766615555	-2.725773268
C	2.2609744436	-2.8462827434	-3.1092232885
C	3.2911773259	-2.5385777005	-2.2222076288
Pd	1.1192330632	-0.1874420558	0.5457713031
Br	1.0939290645	-2.6709727357	1.6195552894
C	1.4452087511	1.3944842206	-0.7852576714
C	2.938118604	1.8050576195	-0.9197821698
C	2.8603995387	3.3416592129	-0.735485368
C	2.1417990106	3.9384143475	-1.9543520217
C	0.6639554832	3.5280476547	-1.7308750149
C	0.7310248804	2.7018357299	-0.4307179979
C	1.7948229409	3.4700016158	0.3567225206
C	3.7567078472	1.1218106591	0.1255115625
C	3.0684581338	0.2525424455	0.986797869
C	3.7211225164	-0.3662512862	2.0510689869
C	5.0874801617	-0.1514592715	2.2268399986
C	5.7876149234	0.6524747604	1.3349364734
C	5.1415817869	1.3051368386	0.2826587927
C	5.941390322	2.1718405359	-0.6478111447
P	-1.4181116194	-0.0643539084	0.2612506379
H	5.6106818425	-0.6364725165	3.0505776835
H	6.8639269133	0.7854252626	1.4547122692
H	3.3162773238	1.567650069	-1.930716115
H	1.0398345684	0.9336307373	-1.6989415919
H	-0.2499059798	2.5944340148	0.0467768919
H	3.8299570517	3.8040118937	-0.5176178905
H	2.0814929298	2.9902901894	1.302973701
H	1.5069863085	4.5118969102	0.5536179369
H	0.0234642992	4.4086494192	-1.5790616997
H	0.2305199748	2.9534093345	-2.5619384576
H	2.5538625838	3.5539036926	-2.8975955666
H	2.2503466873	5.0307383447	-1.974329872
H	6.9851860074	1.8360928977	-0.6895021953
H	5.5436589008	2.1620569623	-1.6709847757
H	5.9569214108	3.2218800785	-0.3215196517
H	3.1892278557	-1.0397883474	2.7206096744
H	0.1466848664	-3.0783708465	-3.4208679575
H	-0.4212242383	-2.3702572995	-1.1037635288
H	4.3240717915	-2.6345566779	-2.5448440901
C	-2.1656137313	0.8563114304	1.6806453964
C	-1.3411111259	1.6208936417	2.5086156382
C	-3.5413240241	0.796613207	1.92583123
C	-1.8879586819	2.3378056689	3.5717489605
H	-0.2664163334	1.6555634337	2.3320950697
C	-4.0529836695	1.5167665331	2.9898759051
H	-4.1978406305	0.1985011052	1.2984474849
C	-3.2570902452	2.2907204875	3.819888565
H	-1.2445586395	2.9305392998	4.2152237755
H	-3.6983857829	2.8393587895	4.6453925814
Cl	-5.8384702105	1.4393887248	3.3137672494
C	-2.5185695679	-1.5571954524	0.1924813379
C	-2.5096763009	-2.4232185923	1.2919728417
C	-3.3073598308	-1.850073006	-0.920746511
C	-3.2859095116	-3.5767023254	1.2775238778
H	-1.8953701604	-2.195166473	2.1598497508
C	-4.0581068481	-3.0148031918	-0.9074687131
H	-3.3423835112	-1.1877674884	-1.7805001523
C	-4.0684764125	-3.887086702	0.1657217737
H	-3.2791171274	-4.2453133041	2.1328351635
H	-4.6729039936	-4.7876187585	0.1364452346
Cl	-5.0714967039	-3.4091480818	-2.3650714498
C	-1.9922526774	0.9059077593	-1.2085906104
C	-1.5541266096	0.5042607698	-2.4767217718
C	-2.7780442507	2.0510132876	-1.0761371273
C	-1.9164588274	1.2322109803	-3.6063499732
H	-0.9205070736	-0.3750490089	-2.5846004575
C	-3.1048053903	2.7640788393	-2.2177171691
H	-3.1232730834	2.3879615884	-0.1029283661
C	-2.6979045431	2.3803396064	-3.4831644387
H	-1.5822979825	0.912570795	-4.5890201239
H	-2.9782316278	2.9647337678	-4.3531576718
Cl	-4.1023709379	4.272816364	-2.0439708809
N	2.5873723494	-3.2794028716	-4.4577033591
O	3.7696869075	-3.3668302689	-4.7611544007
O	1.6601371917	-3.5279163703	-5.2177228621
H	3.7841558779	-1.8651181222	-0.2431867088

VI-VIIc*

79

C 1.7649592293 2.3635607953 -0.7640143443
C 2.015752975 1.231505838 0.023406342
C 2.3671385877 1.3827871506 1.3680327517
C 2.4216959145 2.6475176076 1.9345064345
C 2.1274783016 3.7557710903 1.148068605
C 1.8020774045 3.6301949827 -0.1981907753
Pd 1.1489365059 -0.400010691 -0.8994277182
P -1.2738794058 -0.1154787053 -0.3983113525
C 1.4238023185 -1.5005403747 0.8603380576
C 2.9194320599 -1.8563087537 1.0368280755
C 2.8955961979 -3.4050043134 0.8469049774
C 2.2480069445 -4.0152194113 2.0941433807
C 0.7708712541 -3.5775140616 1.9631004391
C 0.743058594 -2.8326906019 0.6012034127
C 1.799288017 -3.6013962307 -0.1987975677
C 3.8065992998 -1.1716117845 0.037504073
C 3.2163458159 -0.3287839972 -0.9163983571
C 3.9627813901 0.2775224068 -1.9242073559
C 5.331309393 0.0513076225 -1.9702646169
C 5.9368656569 -0.7454010776 -1.0025784288
C 5.1983311821 -1.3730064747 0.0013901209
C 5.9197142124 -2.2169720612 1.0141028125
Br 0.7982454616 -0.3750969903 -3.546738311
H 5.9325966896 0.5157251447 -2.7500011182
H 7.0185787942 -0.8830507259 -1.0178827881
H 3.2516037225 -1.626144573 2.0646883903
H 0.9650413592 -0.9094068377 1.6626269154
H -0.2627685069 -2.778197119 0.1682723694
H 3.8754578027 -3.8234955221 0.5971069115
H 2.0295177752 -3.1610836365 -1.1793328171
H 1.5362994541 -4.657810775 -0.3417658457
H 0.0867261123 -4.4358544364 1.9265852651
H 0.4368174578 -2.9328357072 2.7868510719
H 2.7191697893 -3.662610763 3.0216364619
H 2.3393526471 -5.1087759863 2.0749260036
H 6.941077286 -1.8453010205 1.1619400872
H 5.4221894614 -2.2224338018 1.9921632801
H 6.0064463531 -3.2643227888 0.6915519015
H 3.4824779119 0.9164083783 -2.6627892386
H 2.5923420562 0.5233405959 1.9943151347
H 1.5829996445 4.5154050009 -0.7884386865
H 2.6853829036 2.7829593438 2.9796729406
C -2.5450573657 -1.3245988666 -0.9748782353
C -3.8606070205 -1.2623670639 -0.5035688097
C -2.1859905309 -2.2679633455 -1.9388157874
C -4.7766138728 -2.1728804922 -0.9951553262
H -4.167522291 -0.5208384288 0.2293935954
C -3.1382351528 -3.1650347364 -2.4218402163
H -1.168483387 -2.2855977627 -2.3280533862
C -4.4457756834 -3.1263127193 -1.9466321847
Cl -6.4829524449 -2.1127644303 -0.3729094381
H -2.8617572212 -3.895454721 -3.1759919778
H -5.1979350979 -3.8189651249 -2.3098563527
C -2.0423100114 1.4909835869 -0.9059435568
C -2.862864205 2.2220160275 -0.0434409763
C -1.8263544036 1.933333761 -2.2137417907
C -3.4402300717 3.387026639 -0.5170112592
H -3.0444997502 1.9016709687 0.9782310733
C -2.427169936 3.1083747834 -2.6576908251
H -1.1879080928 1.3569669013 -2.8840413019
C -3.2415697868 3.8514975146 -1.8055951592
Cl -4.5030500744 4.3477193821 0.6043406976
H -2.2603049504 3.4500029799 -3.6749659378
H -3.7124538135 4.7715971086 -2.1355901285
C -1.4405968773 -0.1008358528 1.4405958418
C -1.9220529704 -1.2108054977 2.1367456184
C -0.858922632 0.9634378921 2.1432106016
C -1.804416323 -1.2281284904 3.5169558416
H -2.3677339189 -2.0548588835 1.6171188696
C -0.7667784776 0.9195051108 3.5301228746
H -0.4589582235 1.8216785382 1.6057222845
C -1.2388987664 -0.1889634174 4.2343501889
Cl -2.3926386639 -2.695719872 4.4141254047
H -0.3164244167 1.748388152 4.0690970407
H -1.1667677259 -0.2418122719 5.3154105373
N 2.1686705261 5.0846346697 1.7502183019
O 1.9291372848 6.043675432 1.0318316378
O 2.4378160237 5.1628161279 2.9407929551
H 1.5243443002 2.2570346663 -1.8214426093

VII-VIIIc*

79

C -4.7950350357 0.9746501933 -0.286309476
C -3.789626333 0.1372749045 -0.7924229885
C -2.7835446028 0.6996258607 -1.5884535045
C -2.7276149767 2.0685806994 -1.8002650936
C -3.6822670446 2.8794633712 -1.2011438187
C -4.7407782872 2.3480022321 -0.4700759924
Pd -0.7576192149 -1.2702354792 0.1424043071
P 1.4341519447 -0.3705307998 0.1319676618
C -0.9431045276 -0.9563166235 2.2277196589
C -2.2763683383 -1.4237959891 2.0021946739
C -3.1723259052 -0.2741652919 2.3981836527
C -3.057482758 -0.254391356 3.9482186099
C -1.6225263216 0.2725379513 4.1982315799
C -1.0751377991 0.457533947 2.7634534052
C -2.3287746261 0.9535117771 2.0415643841
C -2.7758728591 -2.058295764 0.0375427759
C -3.8239263979 -1.3274099387 -0.5576850819
C -4.9485303661 -2.0117903669 -1.0373793495
C -5.0246639648 -3.3942291976 -0.9723569655
C -3.9610925882 -4.112097493 -0.4386768448
C -2.83561145 -3.4660378527 0.0705898561

C	-1.6973612884	-4.2944549366	0.5904140529
Br	-0.3912146289	-1.9702427169	-2.3766521841
C	1.4953617357	1.0858323982	-0.9999559179
C	2.4617839597	1.2299366125	-1.9926069978
C	0.4913842657	2.0489542821	-0.8518230167
C	2.4113256756	2.3589313664	-2.7944817019
C	0.4670128653	3.1737011732	-1.6713035245
C	1.4400547923	3.3356353162	-2.6571864599
Cl	3.6744227173	2.5627350017	-4.0847667937
C	2.8833954829	-1.4270552949	-0.3131867129
C	4.1781263765	-0.9215461477	-0.143411209
C	2.6943175047	-2.735060087	-0.7571901731
C	5.2487404364	-1.7404284564	-0.4481794492
C	3.7970173739	-3.5390217066	-1.0431873028
C	5.0889544359	-3.0433645161	-0.8940803655
Cl	6.9313698843	-1.0833177473	-0.2429181735
C	2.0636597047	0.3439010506	1.7276219365
C	2.172481421	1.7176321995	1.9377822873
C	2.3365786966	-0.5465144197	2.7718537464
C	2.5231650002	2.1652862696	3.2019862865
C	2.6864337133	-0.0658627741	4.0283729369
C	2.7747034548	1.3079315155	4.2569911147
Cl	2.6400422178	3.9569115594	3.4867128245
H	-2.0438977464	0.0523479929	-2.0587000441
H	-1.9517908867	2.4994160508	-2.4256315938
H	-5.4891588036	3.0106333007	-0.0448742469
H	-0.1954651141	-1.6231854007	2.667895221
H	-2.5592426646	-2.4279765713	2.3101001146
H	-4.1994671564	-0.3223079945	2.0263904359
H	-3.238277293	-1.2425538481	4.3906019181
H	-3.8131869841	0.4278240838	4.3572291991
H	-1.0057257571	-0.4149341351	4.7918237946
H	-1.6349735065	1.2373549207	4.7218002469
H	-0.1741170445	1.0741435413	2.694999365
H	-2.7332497012	1.8788130332	2.4738508545
H	-2.1877343776	1.0909603917	0.9633318222
H	-5.7506021697	-1.4382178007	-1.5026937175
H	-5.9020803907	-3.9130909856	-1.3537241415
H	-3.9986098029	-5.2015863673	-0.4124965421
H	-0.8686627439	-4.2920751511	-0.1329850441
H	-2.0023721613	-5.3365155311	0.7465240342
H	-1.2879716566	-3.9189286766	1.5396670517
H	3.2325695481	0.4804207888	-2.1458525074
H	-0.2855890413	1.9118194484	-0.0993691638
H	-0.3322314768	3.9054533076	-1.5683182533
H	1.4347031313	4.1996394904	-3.3133951684
H	4.3469903957	0.0871289371	0.2259005195
H	1.6851901412	-3.1132779465	-0.9024240621
H	3.6494422046	-4.5572179269	-1.390727247
H	5.9562825328	-3.6563715422	-1.1162255756
H	1.974789439	2.4276671328	1.1399127252
H	2.2763601679	-1.6203337816	2.6004099171
H	2.8957160075	-0.7584319022	4.8383575585
H	3.0402977436	1.7002432651	5.2328851845
N	-3.5694154436	4.3286091314	-1.3422960634
O	-2.5266940611	4.782205034	-1.8002398604
O	-4.5134046772	5.0148311542	-0.9847220642
H	-5.6110059958	0.542154831	0.2925736799

IX-Xc*

96

C	0.0670165616	-3.8199928633	0.2351120315
C	-1.2644240365	-3.6620358199	0.8785192684
C	-1.3832275186	-2.9910911314	2.1044288237
C	-2.6176255535	-2.8531603983	2.723078267
C	-3.7355971781	-3.3991575468	2.1013825647
C	-3.6468956256	-4.1050260142	0.9071400271
C	-2.4044941451	-4.2411763636	0.3079612661
C	0.9684782819	-4.7093088233	0.8335224096
C	2.2371066601	-4.9039131245	0.3056655889
C	2.6159453406	-4.2040215212	-0.8370298909
C	1.752854894	-3.3174108465	-1.4791259225
C	0.4816327751	-3.0886734048	-0.9008457062
C	2.1797339837	-2.6787380448	-2.7620697961
Pd	-0.1332614159	-0.947193142	-0.3674481458
H	-2.7285135003	-2.3272240705	3.6673923431
H	-4.5377853264	-4.5467849107	0.469474153
H	0.6503541273	-5.2487334405	1.7269663536
H	2.9290531171	-5.5988732477	0.7775506193
H	3.6108987866	-4.349667296	-1.2612543127
H	3.2603149489	-2.7892704768	-2.9111273429
H	1.6684727886	-3.149103416	-3.6153242687
H	1.9422163474	-1.6086765483	-2.7944086633
P	1.9657474007	-0.0357737823	0.4182846805
C	3.2157044117	-0.0360491578	-0.9455504463
C	1.9906185006	1.7363072183	0.9750901714
C	2.943356696	-0.803306941	1.7929681824
C	2.6778102392	-2.1293320392	2.1284274458
C	3.4252670296	-2.7667491083	3.1172603907
C	4.4319974843	-2.0775917219	3.7873709481
C	4.6687545199	-0.7554605224	3.44066523
C	3.9523234317	-0.0991489089	2.4569839314
C	2.9349897682	0.7031429285	-2.1011025904
C	3.8142600329	0.6844587512	-3.1770588009
C	4.9575684276	-0.1158229531	-3.1351560654
C	5.188132668	-0.8671372872	-1.996937588
C	4.3549660113	-0.8367308413	-0.8907234587
C	2.820756536	2.7188859806	0.4301789315
C	2.7084401441	4.0147279594	0.9099638898
C	1.8064064808	4.3752383912	1.8964447504
C	1.0043078893	3.3805281241	2.453062524
C	1.0962184852	2.070043874	1.9965174586
Cl	5.9851830608	0.1479979022	4.3150379505

```
Cl 3.8156432628 5.2936615097 0.2429626688
Cl 6.6390981492 -1.9671206268 -1.9537887703
H 1.8978102106 -2.6765987605 1.6083683281
H 3.2224730037 -3.8057472203 3.3637934229
H 5.0249013101 -2.5537314781 4.561211991
H 4.1751675056 0.935012567 2.2080469892
H 2.014815568 1.2819351068 -2.161361194
H 3.6056733063 1.2836754769 -4.0586875162
H 5.6458306571 -0.1596162757 -3.9724968566
H 4.5846567289 -1.4325872251 -0.0122453481
H 3.5331157009 2.4874009339 -0.3566040219
H 1.7358239717 5.4059289218 2.2277044096
H 0.2864589349 3.6350495642 3.2274792056
H 0.4544083972 1.3020616364 2.4259544951
P -1.790911221 0.8389560532 -0.238614586
C -1.349045339 1.8889909927 -1.6949114321
C -2.0349014499 2.0611679163 1.1408660684
C -3.592755615 0.4610767644 -0.4762734416
C -4.045061622 -0.8046900515 -0.1052789909
C -5.4098737914 -1.0926290256 -0.102091729
C -6.3269182751 -0.1257916076 -0.5057261137
C -5.8498404805 1.118948937 -0.8877152214
C -4.5069296335 1.4454582258 -0.8636000168
C -2.0097541909 1.7436466434 -2.9164036609
C -1.5415820143 2.4012070039 -4.0522668511
C -0.4018315841 3.1966823461 -3.9868975596
C 0.2461732609 3.3152805346 -2.7673454241
C -0.1966092775 2.6867546316 -1.6167864713
C -2.0254141909 3.4434340451 0.9702475993
C -2.2205585419 4.2443946053 2.0833735842
C -2.4521781701 3.7323613732 3.3476387582
C -2.4774641828 2.3448409058 3.5029821783
C -2.2597240862 1.5146354799 2.4084736783
Cl -7.0443217618 2.3879105065 -1.4171702987
Cl -2.1251606309 6.0494231489 1.8750729116
Cl 1.7664048588 4.3122732318 -2.6974582062
H -7.3926804239 -0.3287334324 -0.5128294069
H -2.8909118578 1.11124913 -2.9858922234
H -2.0654735172 2.2891541435 -4.9971104219
H -0.0201571997 3.7110052369 -4.8629657954
H 0.3553736539 2.7953569736 -0.6815981806
H -1.8472488238 3.8956356183 -0.0010718969
H -2.6054365229 4.3967888156 4.1918583095
H -2.6622591084 1.9190176757 4.4849399139
H -2.2618886805 0.4305731866 2.5314401549
I -1.137283169 -2.4114434341 -2.4253433801
H -2.3107919079 -4.8011133323 -0.6205895127
H -5.7625835147 -2.0594536269 0.2492431841
H -4.1809926914 2.4492211671 -1.1247280789
H -3.3299876264 -1.5670134839 0.195682137
N -5.0484567039 -3.2140476703 2.7144744037
O -6.0356459378 -3.5050470821 2.0483531246
O -5.0919948281 -2.775705423 3.8520685274
H -0.4955734389 -2.5567146682 2.5652933613
```

V-VId

```
79

C 3.1944814998 1.7445374228 -1.6064646704
C 2.0205336234 2.1406339063 -0.9437213791
C 2.1542844506 2.9051868699 0.2337951642
C 3.4083588067 3.2906920835 0.7157716201
C 4.5494548275 2.8750121347 0.0591084142
C 4.4316257504 2.0731723297 -1.0872972664
Pd 0.6000689466 0.2820245668 -0.0373415981
Br 0.4679086871 2.4808381867 -2.1637510887
H 5.5293470674 3.1554520539 0.4370792869
C 2.2321089598 -0.3565608348 1.1095132985
C 2.8603544163 -1.6866712625 0.6169195852
C 2.4984538379 -2.6664807711 1.7684061536
C 3.4174536139 -2.3441993983 2.9516350342
C 2.9050762042 -0.9567235685 3.4164828343
C 1.6908687572 -0.698530552 2.4934110616
C 1.1608676321 -2.118975922 2.2775643788
C 2.3126216495 -2.0339101597 -0.7252242541
C 1.2565883062 -1.2293846561 -1.182656303
C 0.7075881381 -1.4343475031 -2.4481303853
C 1.2000190306 -2.4604110324 -3.2513867107
C 2.2419360243 -3.2631646043 -2.7976579217
C 2.8158889398 -3.0622431321 -1.5413226318
C 3.9678532513 -3.9163754128 -1.0967475317
P -1.9601976414 -0.121751096 -0.0480344421
H 0.7672064381 -2.6314513386 -4.2370779958
H 2.6316304997 -4.0583233774 -3.4354752243
H 3.9620187461 -1.6008652394 0.5592342556
H 2.9368808971 0.4874597307 1.115639452
H 0.9814055984 0.0320641098 2.9014631676
H 2.5014500313 -3.7219795681 1.4677276259
H 0.3487708448 -2.1647342647 1.5402277427
H 0.8206780563 -2.6033554672 3.2047113196
H 2.5904123526 -0.9769160805 4.469277959
H 3.6651051411 -0.1683863823 3.3210827952
H 4.4786240408 -2.3373987411 2.6653220171
H 3.2992326271 -3.0936172752 3.7465765093
H 4.3160124639 -4.5636554072 -1.9113586832
H 4.8221511378 -3.3079258853 -0.7659378514
H 3.7051172076 -4.567052619 -0.2506505072
H -0.1143132741 -0.8116651461 -2.8047976672
H 3.4485875133 3.8743109586 1.6326135033
H 5.3273996012 1.7322765583 -1.6035686845
C -2.6445677457 -1.4540334425 -1.1307184009
C -1.917693144 -2.6481640111 -1.2311102198
C -3.7865550035 -1.2787471275 -1.9138914827
C -2.3438320039 -3.6575951228 -2.0868633353
```

H -1.0053270987 -2.7803957053 -0.6516191683
C -4.2080628921 -2.291690538 -2.7732377241
H -4.3498211423 -0.3511915755 -1.8501663722
C -3.4908156106 -3.4814772588 -2.8589211181
H -1.7649463713 -4.574030654 -2.1644836728
H -3.8189538749 -4.2678624744 -3.5335528169
C -3.3124207386 1.142263071 -0.0111395711
C -3.0190254205 2.4524258142 -0.3862234954
C -4.5959198905 0.822443822 0.4451984053
C -4.008001899 3.4342829882 -0.3335077239
H -2.0092797357 2.7074290093 -0.7025232261
C -5.5826543863 1.8008620785 0.4902293872
H -4.8144808568 -0.1935630004 0.7695524347
C -5.2891947557 3.1075316765 0.0979151449
H -3.7729579206 4.4547762176 -0.6234399187
H -6.0603540356 3.8720476887 0.1397131119
C -2.1861361315 -0.8282545464 1.6601496018
C -1.8566151097 0.0142676409 2.7282418907
C -2.6260010338 -2.1255505825 1.9115035804
C -1.9521291599 -0.4489518722 4.0353393712
H -1.5118469358 1.0285757899 2.528683353
C -2.7144509586 -2.5877336352 3.2247054707
H -2.8892655626 -2.7808232213 1.0844456119
C -2.3750661769 -1.7542619317 4.2858263242
H -1.6926744743 0.2094730274 4.8606006832
H -2.4428950281 -2.1173793068 5.3079810072
N 1.0266644818 3.1430791721 1.0930757465
O 0.9905705999 4.1528606289 1.7722894429
O 0.1478499274 2.2557845126 1.1529620047
H 3.1074308448 1.1773194566 -2.5311591805
H -3.052375368 -3.6032556423 3.4152746992
H -6.5796456345 1.5494470097 0.8429044804
H -5.0982174563 -2.1466881689 -3.3797537077

VI-VIId

79

C 0.7120494349 2.8886451626 0.4152915263
C 1.304945866 1.6317405213 0.701219409
C 1.7905106443 1.5053430494 2.0197571459
C 1.7263274015 2.5379740209 2.9369665433
C 1.1678335199 3.7763922999 2.5990116973
C 0.6557486364 3.9450217114 1.3297465845
Pd 0.5398877632 0.1642006062 -0.5599869641
P -1.7739901995 -0.2253632174 0.1992665736
C 1.2158819799 -1.3265213238 0.7245351932
C 2.7664290491 -1.3144012449 0.8021062171
C 3.1054601072 -2.7605913212 0.3277129974
C 2.7249018065 -3.709183707 1.471013527
C 1.1769810045 -3.6476631415 1.4610012012
C 0.8652845208 -2.7242104569 0.2543877724
C 2.0150080243 -3.0586150403 -0.6967331347
C 3.3883724188 -0.2024565165 -0.0035848218
C 2.5516954148 0.7989804445 -0.5457263819
C 3.0580066125 1.7528896177 -1.4305641601
C 4.4163041851 1.7788401604 -1.7043900669
C 5.2634089862 0.8758683425 -1.0742343454
C 4.7721261049 -0.1223193011 -0.2294689646
C 5.7651708622 -1.0430114645 0.4260890863
Br 0.3415468936 -0.911167768 -3.0295649052
H 1.129015367 4.5876949646 3.3217456664
H 4.817735351 2.5213828458 -2.3917987198
H 6.3397289057 0.935853063 -1.2406820369
H 3.0868177286 -1.2237932294 1.8573371309
H 0.7156726621 -1.0404673688 1.6583831847
H -0.1557422535 -2.840932061 -0.1255526737
H 4.1323230637 -2.8790730208 -0.0280039947
H 2.0390318877 -2.4200187424 -1.5870864955
H 2.0112438848 -4.1122157738 -1.0088953288
H 0.7332844364 -4.6374787359 1.2882246266
H 0.7524311528 -3.2606724404 2.3983946562
H 3.1621037236 -3.4081640555 2.4339403827
H 3.0806637181 -4.7255790026 1.256053679
H 6.6899145935 -0.4956663876 0.6499148803
H 5.3947568774 -1.4662796236 1.3680950402
H 6.0460665818 -1.885293382 -0.2217033931
H 2.3956820232 2.4735402743 -1.9043106445
H 2.2456898689 0.5699209977 2.3333321507
H 0.1859494855 4.8727848656 1.0141654358
O -0.321076306 4.2359718346 -1.1473810058
H 2.1233743919 2.3764736192 3.9385751078
O -0.0423961222 2.1565768831 -1.6403691615
N 0.0732582233 3.121152202 -0.8621642948
C -2.9274873173 -1.5500948352 -0.3709130442
C -4.2126386803 -1.6209973794 0.179825141
C -2.5449624201 -2.4399916552 -1.3733096382
C -5.0999518659 -2.5979778455 -0.2535430359
H -4.5162778573 -0.9090003502 0.9450523579
C -3.4439135054 -3.4158806019 -1.8078192086
H -1.5637485435 -2.3487856291 -1.8409379194
C -4.713227181 -3.4990104986 -1.2471405762
H -3.1468690942 -4.1032160038 -2.5949647597
H -5.4107273188 -4.2593627732 -1.5886664865
C -2.7901451153 1.2854758262 -0.1111507033
C -3.4555922989 2.001499961 0.8822727994
C -2.8735919915 1.6917038768 -1.4475718771
C -4.1916021796 3.1357005956 0.5414075287
H -3.4033158188 1.677995838 1.9191697155
C -3.6065485666 2.8247761135 -1.7793011449
H -2.353896167 1.1285699095 -2.2221653034
C -4.2621150819 3.5499699946 -0.7851924517
H -3.6591369621 3.1453411966 -2.8155450371
H -4.8284598649 4.4393494136 -1.0475307697
C -1.7479173024 -0.4517150706 2.0310164247

C -2.0172139578 -1.7017404495 2.5945700232
C -1.26418566 0.5791165891 2.8477129405
C -1.8236417416 -1.9131859088 3.958100143
H -2.3833322138 -2.5098909215 1.9655450274
C -1.0792983829 0.364597541 4.2101069014
H -1.0153771138 1.5498120553 2.4225994117
C -1.3584079042 -0.8809937539 4.7685082848
H -0.7057763048 1.1738474539 4.8327995
H -1.2107221785 -1.0465919997 5.83209058
H -4.7102697191 3.6950895816 1.3156529294
H -2.0394512065 -2.8883036515 4.3868660127
H -6.0969757666 -2.652530778 0.1756543131

VII-VIIId

79

C 4.3234627058 0.5643765674 1.2608943019
C 3.1929516017 -0.2192960616 0.9749984454
C 2.1782911401 -0.2047478383 1.9414320851
C 2.2640400129 0.5787400659 3.08641453
C 3.3851521244 1.3688369311 3.3204793434
C 4.4289794937 1.34394922 2.4097055396
Pd 0.0355301452 -0.4623502071 -0.5834143586
P -2.1611945818 0.0956795103 0.103066657
C 0.1757093946 1.236844746 -1.8429281844
C 1.5231583472 0.7845022141 -1.9850019613
C 2.3786736554 1.8884208284 -1.4091971969
C 2.2633153718 3.0083662479 -2.4822718787
C 0.8118909825 3.5238640568 -2.3188893515
C 0.2534202955 2.6109274044 -1.202745314
C 1.4870038907 2.4702502094 -0.3077043903
C 2.0180785554 -1.1431674753 -1.1013685341
C 3.0833138105 -1.1424021844 -0.1852374093
C 4.0661214913 -2.1366901053 -0.2843144363
C 4.0169186877 -3.0972046776 -1.2778377829
C 2.971689323 -3.0777431597 -2.1927732173
C 1.968511921 -2.1150731193 -2.1208752634
C 0.8212176873 -2.2065654721 -3.0858634933
Br -0.2589636832 -2.7074360864 0.7543827126
O 6.576211754 0.8135775273 0.8666965568
O 5.294696104 0.5377133664 -0.8496460978
N 5.4825761835 0.6362358209 0.353457869
C -2.1979675648 0.287957495 1.93698475
C -3.0270942937 -0.4882234441 2.7428995398
C -1.3042213392 1.1912648314 2.522548611
C -2.9839119757 -0.342441086 4.1277845189
C -1.2780957142 1.3478621603 3.9048595667
C -2.1182992731 0.5789223861 4.708960652
C -3.5834158417 -1.0142364174 -0.2952002184
C -4.8876234256 -0.5842593362 -0.02290725
C -3.3728088172 -2.252323886 -0.8983549541
C -5.9686778011 -1.3997650568 -0.3369406
C -4.4605002993 -3.0621434146 -1.2218678273
C -5.7550958554 -2.6398801655 -0.9383934323
C -2.8628939839 1.7025391557 -0.5097878278
C -3.077978386 2.8101632947 0.3074782326
C -3.111071833 1.8004149903 -1.8834362736
C -3.5056005043 4.0161500562 -0.2493058349
C -3.5311970171 3.0037218418 -2.4365251757
C -3.7196288213 4.118897771 -1.6196961889
H 1.3155073877 -0.8560374924 1.796885376
H 1.4468691841 0.5480602526 3.8055005488
H 3.4583596997 1.9843116193 4.2147020218
H 5.3354476071 1.9218454189 2.5658072554
H -0.5566329117 1.0634681135 -2.6372576476
H 1.8539187055 0.2974482377 -2.89959947
H 3.4068438496 1.6149322776 -1.1652697469
H 2.4789384118 2.6361040806 -3.492278469
H 2.9983750102 3.7940685897 -2.2662727977
H 0.219770285 3.4569460123 -3.2413066113
H 0.7928957637 4.5729366255 -1.9943514068
H -0.6737440058 2.9690690061 -0.7429040836
H 1.8581446976 3.4355076932 0.0641166993
H 1.3381904865 1.7885636803 0.5381875659
H 4.8709782801 -2.1557366951 0.4514331616
H 4.7886625466 -3.8620526984 -1.3390636858
H 2.915266206 -3.8370206047 -2.9738939895
H -0.0376192833 -2.7027427119 -2.6107158699
H 1.0956188113 -2.7964326716 -3.9700196385
H 0.468230607 -1.2258456798 -3.4335853991
H -3.695906611 -1.2143971674 2.2887872149
H -0.625986749 1.7705056781 1.8948380488
H -0.5964462435 2.0655750267 4.3550582681
H -2.0899910431 0.692196847 5.7891765808
H -5.0536633717 0.3897847176 0.4335336546
H -2.35774427 -2.594108187 -1.0840450463
H -4.2896309405 -4.0285987592 -1.6877287904
H -6.6009140519 -3.2758914049 -1.1853351218
H -2.9043124513 2.7376211777 1.3782850823
H -2.9778229471 0.9262774759 -2.5201821892
H -3.71565288 3.0734379994 -3.5053090299
H -4.0414986884 5.0618543305 -2.0529473035
H -6.9795673777 -1.0658653821 -0.1185284785
H -3.668291389 4.876928568 0.3939134477
H -3.6256119918 -0.956746479 4.7529313903

IX-Xd

96

C 1.110404845 -3.293287353 -0.3699134037
C 2.475118199 -3.0520217654 -0.9158789462
C 2.9194079328 -2.0279818715 -1.7659487042

C 4.258444995 -1.887663321 -2.1305890105
C 5.1958505825 -2.7975071565 -1.6731596918
C 4.7864711221 -3.8449023265 -0.8532882265
C 3.4532523415 -3.9586026167 -0.4854621625
C 0.4100442865 -4.4054303323 -0.8495652733
C -0.7588089591 -4.8305835663 -0.2362776037
C -1.2046216746 -4.1803462761 0.9135406187
C -0.5278795313 -3.0881302284 1.4483718807
C 0.5868998404 -2.583343096 0.7343451235
C -0.9729602958 -2.4862521029 2.7433504651
Pd 0.2080841544 -0.357431776 0.1462735043
H 4.5374805486 -1.0664199879 -2.7844448857
H 6.2390771545 -2.6937352768 -1.9632443907
H 5.5100408585 -4.5708813893 -0.4870585271
H 0.8107702377 -4.9404356899 -1.7117028201
H -1.3096072452 -5.6807889241 -0.634365161
H -2.1041219427 -4.5285168417 1.4239335408
H -1.9191306582 -2.9267014433 3.0776087394
H -0.2169181064 -2.6521544568 3.5257603254
H -1.1206115875 -1.4004275321 2.6640748763
P -2.1801353255 -0.3575516211 -0.3595729702
C -3.2361590224 -0.626095876 1.1343807356
C -2.8308637276 1.2505282525 -1.0258703664
C -2.9558923638 -1.518404127 -1.5805025866
C -2.1789220713 -2.543631317 -2.1140481873
C -2.738523367 -3.4449988038 -3.0192731492
C -4.0699030737 -3.3164077329 -3.3994750892
C -4.8466918502 -2.2801970489 -2.8780314085
C -4.2911231424 -1.3815846418 -1.974458851
C -3.1351303518 0.2954798255 2.1848121371
C -3.8160527261 0.0768146356 3.3758474377
C -4.585312316 -1.076397105 3.5410621663
C -4.676274199 -2.0010448526 2.5049746116
C -4.0065188855 -1.7769225844 1.3017843243
C -3.9383678752 1.9294862928 -0.5172776192
C -4.3268705507 3.147294209 -1.0738713243
C -3.6112254249 3.6908841349 -2.1386482104
C -2.5125683764 3.0078596719 -2.658406138
C -2.1263428933 1.7907810693 -2.1052434712
H -1.1356699052 -2.6350576205 -1.8277198923
H -2.1251049924 -4.2462955825 -3.4252387217
H -4.5065603783 -4.017478803 -4.1060984102
H -4.8949312161 -0.5719246748 -1.5685090511
H -2.5221131885 1.1870245566 2.0690175666
H -3.7355816589 0.8050480255 4.1793013349
H -5.1116689024 -1.2515038117 4.4759527531
H -4.0857277041 -2.4958335751 0.4897554891
H -4.4885551452 1.5158111865 0.3247023262
H -3.9081602277 4.6456555965 -2.5648338022
H -1.9444784104 3.4293388767 -3.4834299963
H -1.2647930096 1.2533068937 -2.5020815513
P 0.8936915062 1.9926792366 0.0653644707
C -0.1579468464 2.6849252388 1.4272552988
C 0.8035376985 3.2725716335 -1.2791891489
C 2.6306126328 2.3466319637 0.6157448123
C 2.9736528678 3.2933353867 1.5797604204
C 4.3130605597 3.5094122905 1.8989587244
C 5.3124962007 2.7884082514 1.2504900664
C 4.9721518319 1.8553638917 0.2729870794
C 3.635843159 1.6336549319 -0.0430130393
C 0.1262719591 2.3287280595 2.7535016908
C -0.7400348939 2.6867856178 3.7815689689
C -1.9096801155 3.3919498703 3.4992482252
C -2.2116626284 3.7234427965 2.1814254193
C -1.3441450501 3.3710912571 1.1485869821
C 1.0078585541 2.8331839495 -2.5894224525
C 0.9915430547 3.7477876591 -3.6408910444
C 0.7687620378 5.0992587132 -3.3894587997
C 0.5871056217 5.5411343648 -2.07994872
C 0.6160076301 4.6319897068 -1.025881971
H 6.356069566 2.9550048378 1.504739279
H 1.0250338768 1.7583225964 2.9797231048
H -0.50438872 2.4074385078 4.805245487
H -2.5882004193 3.6698378112 4.3020726514
H -1.6094749615 3.6142771837 0.1225693319
H 1.2027002193 1.7786525909 -2.7844066131
H 0.7500207579 5.811644174 -4.2104338759
H 0.4345862898 6.5985441405 -1.8784561297
H 0.4876991434 4.9827412878 -0.0036029481
I 2.0960790163 -1.3594048302 1.8907707121
H 3.137702799 -4.7569193976 0.1853717851
O 2.4856450682 -0.0149568195 -2.7981772935
N 1.9992862076 -1.0478484342 -2.3362374647
O 0.7994254588 -1.2825497762 -2.3234040083
H 4.5756767933 4.2467138313 2.653438177
H 3.3646763735 0.9219832272 -0.8229197225
H 2.1964824541 3.8622269484 2.0856939369
H -5.1903151488 3.6730113684 -0.6726708296
H -3.1350652409 4.2468774417 1.9446635564
H 1.156599484 3.4016519432 -4.6583083667
H 5.7470150458 1.2925056765 -0.2414622804
H -5.8858259817 -2.1737556189 -3.1793220917
H -5.2765046775 -2.8993246279 2.628263267

II-IIIe

84

C -1.246682941 -3.6251133372 -1.4020365012
C -2.3933102071 -4.0026074985 -2.106461589
C -3.6651491746 -3.8323814974 -1.5649286748
C -3.7677241965 -3.2859619415 -0.2758309713
C -2.6463716534 -2.9024012239 0.4394644549
C -1.3783786147 -3.0123340014 -0.1507839567
Pd 0.0232485226 -1.3671445072 -0.239678013

H	-2.2869459225	-4.4510664546	-3.0959540159
H	-4.7548695047	-3.1462989125	0.1713459274
P	-1.6318158635	0.4417097463	-0.323632822
C	-2.7055250863	0.2312310296	1.1696715175
C	-1.1752634346	2.2357076767	-0.2019083162
C	-2.8874302858	0.500690964	-1.6821901249
C	-3.0882197872	-0.6559251178	-2.4366009839
C	-4.0633128274	-0.6803408302	-3.4316413451
C	-4.8286267353	0.4531921554	-3.6932440594
C	-4.5981852672	1.5947006452	-2.9399273533
C	-3.6478125823	1.6460809253	-1.935856217
C	-2.0746815025	0.1334176503	2.4162474704
C	-2.8216979844	-0.1340714318	3.5582490138
C	-4.1985468944	-0.3414689346	3.4660126163
C	-4.7935276733	-0.2571171074	2.2196141962
C	-4.0820016146	0.0384905024	1.0683180267
C	-1.5973847395	3.0566335619	0.8456956792
C	-1.1832963458	4.3792977752	0.856556666
C	-0.3618455235	4.913134563	-0.120926897
C	0.0496541712	4.0865925802	-1.1655962002
C	-0.3531988951	2.7559976297	-1.2077529784
Cl	-5.5793871686	3.0826097568	-3.2923892754
Cl	-1.7514027391	5.4600772133	2.1988874481
Cl	-6.5770636439	-0.5780697762	2.0785120889
H	-2.49019238	-1.5433876307	-2.2460966588
H	-4.2215938888	-1.5895619759	-4.0067565898
H	-5.5881960255	0.4575158022	-4.4680643832
H	-3.5031714258	2.556671852	-1.3600572034
H	-0.9926932603	0.2429068458	2.4900882808
H	-2.3309590752	-0.1990489077	4.5248639414
H	-4.7950033161	-0.5718205517	4.3424464681
H	-4.5882223542	0.0887368578	0.1081862415
H	-2.2282382952	2.6745004021	1.6433207203
H	-0.0516019073	5.9513204688	-0.067759732
H	0.6973151983	4.482988319	-1.9426907879
H	-0.0142249157	2.1122744232	-2.0182097204
P	2.180121876	-0.294755116	-0.3197181571
C	2.446901191	0.3200595846	1.403855881
C	2.5962214764	1.17480085	-1.3732750065
C	3.6905728031	-1.3264761483	-0.6238600519

C	4.9724204146	-0.7699009519	-0.5653449572
C	6.0595257112	-1.5909690833	-0.7984332241
C	5.9247285325	-2.9387398258	-1.0977782519
C	4.6447314083	-3.4796988271	-1.1662749263
C	3.529550442	-2.6769579194	-0.9295589569
C	3.2948379048	-0.3405644033	2.2919470081
C	3.3284322208	0.0328327427	3.6345751155
C	2.5090178692	1.0543314494	4.1047226208
C	1.6650499866	1.688409404	3.2054637573
C	1.615416879	1.3503642827	1.8660071472
C	2.3094180568	1.0582356227	-2.7369125738
C	2.5691618166	2.1159178229	-3.6014010777
C	3.1038061549	3.3078090111	-3.1107507957
C	3.3719120329	3.4002429865	-1.7560788153
C	3.1384729752	2.3580520381	-0.8738676931
Cl	0.5511771869	2.9843341327	3.816724221
H	6.8055070355	-3.547773904	-1.2730896293
H	3.9245051775	-1.1526223105	1.938121672
H	3.9925830826	-0.4819003885	4.3228594358
H	2.5154048917	1.3493943089	5.1487230333
H	0.9344678662	1.8711538457	1.1932595701
H	1.8653798674	0.1375223081	-3.114614636
H	3.3023272141	4.1491770263	-3.7667452285
H	3.3489688888	2.4797959025	0.1853018224
I	0.3931998262	-3.4479874201	1.42826998
H	2.5267828075	-3.0992924403	-0.9715429525
H	5.1207418813	0.2836504422	-0.3415928304
Cl	4.0035435655	4.9704663335	-1.0993926747
Cl	7.7280955179	-0.8801737214	-0.7086521042
H	2.349637078	2.0227905263	-4.6612032209
H	4.5181131798	-4.5328628335	-1.4000264399
H	-0.2589694256	-3.8007916295	-1.8292702488
H	-2.7513835823	-2.4824549556	1.4389515857
C	-4.8991370741	-4.2190626838	-2.3228022613
H	-5.4434319491	-5.0333447576	-1.8246337766
H	-5.5984443217	-3.3742145136	-2.4022251625
H	-4.659637155	-4.5569181155	-3.3389748044