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Catalytic oxidative carbonylation of amino moieties to ureas, oxamides, 2-oxazolidinones, and benzoxazolones

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Recyclable Catalytic Oxidative Carbonylation of Amines, β-Amino alcohols, and 2-Aminophenols to Ureas, Oxamides, 2-Oxazolidinones, and Benzoxazolones

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Abstract: The direct syntheses of ureas, oxamides, 2-oxazolidinones, and benzoxazolones by oxidative carbonylation of amines, β-amino alcohols, and 2-aminophenols allows obtaining high value added molecules, with a large number of important applications in several fields, starting from very simple building blocks. In this work, we have found that it is possible to carry out these transformations using the PdI_2/KI catalytic system in an ionic liquid (IL), such as $BmimBF_4$, as the solvent, and that the solvent-catalyst system can be recycled several times with only a slight loss of activity, while the product can be easily recovered by crystallization.

Introduction

Ureas, oxamides, 2-oxazolidinones, and benzoxazolones are between the most important carbonyl derivatives.[1-11] The classical approaches to these molecules are based on the use of toxic reactants, such as phosgene and its derivatives, or oxalyl chloride and its derivatives.[12] Recently, the possibility to directly synthesize these important compounds by catalytic oxidative carbonylation of amines or β-amino alcohols has been extensively explored.[13] In fact, this approach may allow obtaining the target molecules in a multicomponent fashion starting from very simple and largely available building blocks (the organic substrate, CO, and an external oxidant). Moreover, when the oxidant corresponds to molecular oxygen, the process becomes particularly attractive from a sustainable perspective, since the coproduct formed is water and the atom economy is particularly high. Several methods have thus appeared in the literature for realizing these processes with oxygen as reoxidant.[14, 15] Unfortunately, most of the proposed methods have been proposed under potentially explosive conditions, with CO/O_2 mixtures in volume ratios very close to, or even within, the flammability range for this kind of mixture.[14c] Moreover, to the best of our knowledge, no oxidative carbonylation method reported so far has allowed the general synthesis of ureas, oxamides, 2-oxazolidinones, and benzoxazolones with recycling of the catalytic system and of the reaction medium, which would clearly increase the attractiveness of the process and its sustainability.[16]

Some years ago we found that a very simple catalytic system, consisting of PdI_2 in conjunction with an excess of KI, is an excellent catalyst for performing the oxidative carbonylation of primary amines to 1,2-symmetrically disubtituted ureas (or of a mixture of a primary and a secondary amine to trisubstituted ureas)[17] as well as of β-amino alcohols bearing a primary amino group to the corresponding oxazolidinones.[18] Reactions were carried out in 1,2-dimethoxyethane (DME) as the solvent, under non-explosive conditions (typically, 100 °C under 60 atm of a $CO/air/CO_2$ mixture or 20 atm of a CO/air mixture). The use of an excess of CO_2 in the reaction mixture caused in several cases a significant improvement in the product yield and selectivity. Later on, we also found that, employing the same type of catalytic system, it was possible to carry out the oxidative carbonylation of primary amines to the corresponding ureas in carbon dioxide medium.[19]

We have now found that by using a suitable ionic liquid (IL),[20] such as $BmimBF_4$, as the reaction medium, in the presence of the PdI_2/KI catalytic system, it is possible not only to convert primary aromatic amines to 1,3-aryl ureas, β-amino alcohols to 2-oxazolidinones, and 2-aminophenols to benzoxazolones (through an oxidative *mono* carbonylation process), but also

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Table 1. Synthesis of 1,3-diaryl ureas **2a-e** by recyclable PdI$_2$/KI-catalyzed oxidative carbonylation of primary anilines **1a-e** in BmimBF$_4$[a]

$$2\ ArNH_2 + CO + (1/2)\ O_2 \xrightarrow[\substack{BmimBF_4 \\ -H_2O}]{PdI_2/KI} ArHN-\overset{\overset{O}{\|}}{C}-NHAr$$

1 → **2**

Entry	Aryl amine 1	Urea 2	Yield of 2 [%][b]					
			Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
1	PhNH$_2$ **1a**	PhHN-C(=O)-NHPh **2a**	94	87	85	80	77	75
2	Me-C$_6$H$_4$-NH$_2$ **1b**	Me-…-C(=O)-…-Me **2b**	87	81	80	77	75	75
3	i-Pr-C$_6$H$_4$-NH$_2$ **1c**	i-Pr-…-C(=O)-…-i-Pr **2c**	92	87	87	85	86	85
4	MeO-C$_6$H$_4$-NH$_2$ **1d**	MeO-…-C(=O)-…-OMe **2d**	88	80	78	77	75	75
5	Cl-C$_6$H$_4$-NH$_2$ **1e**	Cl-…-C(=O)-…-Cl **2e**	91	80	80	78	77	76

[a] All reactions were carried out at 100 °C for 24 h in BmimBF$_4$ (0.5 mmol of **1** at start per mL of BmimBF$_4$, 1 mmol scale based on **1**) using a **1**:KI:PdI$_2$ molar ratio of 100:10:1, under 20 atm (at 25 °C) of a 4:1 mixture of CO-air. Substrate conversion was quantitative. [b] Isolated yield from **1**. Run 1 corresponds to the 1st experiment, the next runs to recycles. See text for details.

secondary amines to tetrasubstituted oxamides (through an oxidative *double* carbonylation process). Moreover, primary aliphatic amines can be selectively converted into either 1,3-dialkyl ureas or *N,N'*-dialkyloxalamides depending on reaction conditions. In all cases, the process is carried out under conditions that allow an efficient recovery and recycling of the solvent-catalyst system.

Results and Discussion

Initial experiments were carried out with aniline **1a** as the substrate, using 1 mol % of PdI$_2$ in conjunction with 10 mol % of KI, at 100 °C under 20 atm of a 4:1 mixture of CO-air, in BmimF$_4$ as the solvent (0.5 mmol of **1a** per mL of solvent). After 24 h, substrate conversion was quantitative, and extraction with Et$_2$O followed by repeated crystallization from cold Et$_2$O allowed the isolation of pure 1,3-diphenylurea **2a** in almost quantitative yield (94%, Table 1, entry 1, run 1). The ether used for extraction and

purification could be easily recovered and reused for other experiments. We then verified the recyclability of the catalyst-ionic liquid system by adding fresh aniline to the recovered ionic liquid phase and repeating the carbonylation procedure under the same conditions reported above, but without adding fresh catalyst. After 24 h, **1a** conversion was still quantitative, and **2a** was recovered in 87% yield (Table 1, entry 1, run 2). The recycling process was repeated for additional 4 times, with formation of **2a** in yields ranging from 75 to 85% (Table 1, entry 1, runs 3-6). These results therefore confirmed the possibility to use an ionic liquid medium in the PdI$_2$/KI-catalyzed direct oxidative carbonylation of amines to ureas and to recycle the catalyst several times with only a slight loss of activity.

The method was then extended to other primary aromatic amines **1b-e**, and the results obtained are shown in Table 1, entries 2-5. As can be seen from Table 1, excellent results in terms of product yield and catalyst recycling were obtained with
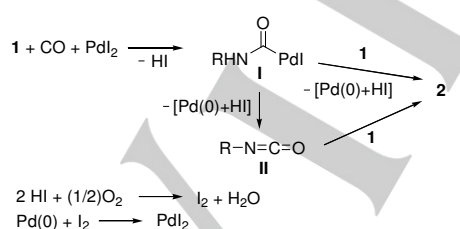
Table 2. PdI$_2$/KI-catalyzed oxidative carbonylation of primary amines **1f-h** in BmimBF$_4$ leading to 1,3-dialkylureas **2f-h** and/or *N,N'*-dialkyloxalamides **3f-g** [a]

$$RNH_2 + CO + O_2 \xrightarrow[\text{BmimBF}_4]{\text{PdI}_2/\text{KI}} \underset{\textbf{2}}{RHN\overset{O}{\underset{}{\|}}NHR} + \underset{\textbf{3}}{RHN\overset{O}{\underset{O}{\|}}NHR}$$

Entry	Alkylamine **1**	Dialkylurea **2**	Yield of **2** [%][b]	Oxamide **3**	Yield of **3** [%][b]
1	BuNH$_2$ **1f**	BuHN⌃(O)⌃NHBu **2f**	40	BuHN⌃(O)(O)⌃NHBu **3f**	44
2	*t*-BuNH$_2$ **1g**	*t*-Bu–NH(O)NH–*t*-Bu **2g**	98 (94-94-93-92-92)		
3	BnNH$_2$ **1h**	BnHN⌃(O)⌃NHBn **2h**	47	BnHN⌃(O)(O)⌃NHBn **3h**	45
4[c]	**1f**	**2f**	83 (81-80-78-77-77)		
5[d]	**1h**	**2h**	90 (89-89-88-88-87)		
6[e]	**1f**			**3f**	82 (80-81-79-80-81)
7[e]	**1h**			**3h**	86 (85-85-84-83-84)

[a] Unless otherwise noted, all reactions were carried out at 100 °C for 24 h in BmimBF$_4$ (0.5 mmol of **1** at start per mL of BmimBF$_4$, 1 mmol scale based on **1**) using a **1**:KI:PdI$_2$ molar ratio of 100:10:1, under 20 atm (at 25 °C) of a 4:1 mixture of CO-air. Substrate conversion was quantitative. [b] Isolated yields from **1**. Figures in parentheses refer to recycles. [c] The reaction was carried out with a **1f**:KI:PdI$_2$ molar ratio of 200:10:1 and a substrate concentration of 1 mmol of **1f** per mL of BmimBF$_4$. [d] The reaction was carried out with a **1h**:KI:PdI$_2$ molar ratio of 500:10:1 and a substrate concentration of 1 mmol of **1h** per mL of BmimBF$_4$. [e] The reaction was carried out at 80 °C under 40 atm (at 25 °C) of a 4:1 mixture of CO-air.

all the amines tested, bearing electron-donating (Table 1, entries 2-4) as well as electron-withdrawing (Table 1, entry 5) groups.

Mechanistically, the reaction may start with the formation of a carbamoylpalladium iodide intermediate **I**, from the reaction between PdI$_2$, the primary amine **1**, and CO (Scheme 1; anionic iodide ligands are omitted for clarity).[14c, 17-19]
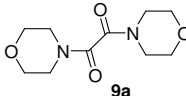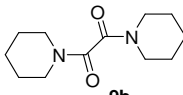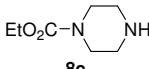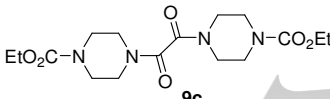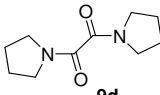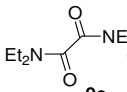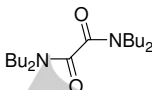

Scheme 1. Possible mechanistic pathways for the PdI$_2$-catalyzed oxidative monocarbonylation of primary amines **1a-h** to ureas **2a-h**. Both carbamoylpalladium complex **I** and isocyanate intermediate **II** may lead to the final product.

Either the direct nucleophilic displacement by the amine, or the formation of an isocyanate intermediate **II** (by formal β-

elimination of HI from the I-Pd-(CO)NHR moiety) followed by addition of **1** to **II**, may then occur, leading to the formation of the final urea product **2** and Pd(0).The latter is eventually reoxidized back to PdI$_2$, according to the mechanism we demonstrated several years ago,[21] involving oxidation of HI (formally deriving from the carbonylation process) to I$_2$ followed by oxidative addition of I$_2$ to Pd(0).

When butylamine **1f** was subjected to the same carbonylation conditions as those reported in Table 1, a mixture of 1,3-dibutylurea **2f** and *N,N'*-dibutyloxalamide **3f** was obtained, as confirmed by GC-MS analysis (total yield: 84%; **3f**/**2f** molar ratio = 1.1, Table 2, entry 1). The formation of **3f**, ensuing from a double carbonylation process, is clearly due to the higher nucleophilicity of **1f** as compared to anilines **1a-e**, which allows for the formation of a *bis*-carbamoylpalladium complex Pd(CONHR)$_2$ **III** (from the reaction between PdI$_2$ and 2 mol of RNH$_2$ and CO, with formal elimination of 2 HI; Scheme 2, R = alkyl, R' = H). The latter, according to the literature,[14] is the key intermediate in the formation of the oxamide product, obtained by reductive elimination (Scheme 2). Accordingly, a less nucleophilic, sterically hindered primary aliphatic amine, such as *tert*-butylamine **1g**, selectively led to the urea derivative in practically quantitative yield (Table 2, entry 2), while

Table 3. Synthesis of 2-oxazolidinones **5** and benzoxazolones **7** by recyclable PdI$_2$/KI-catalyzed oxidative carbonylation of β-amino alcohols **4** and 2-aminophenols **6**, respectively, in BmimBF$_4$[a]

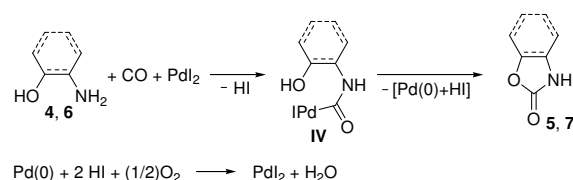| Entry	β-Aminoalcohol **4** or 2-aminophenol **6**	2-Oxazolidinone **5** or benzoxazolone **7**	Yield of **5** or **7** [%][b]					
			Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
1	**4a**	**5a**	94	88	86	85	83	84
2	**4b**	**5b**	80	75	74	72	73	72
3	**6a**	**7a**	98	93	90	88	85	85
4[c]	**6a**	**7a**	95	94	90	88	88	89
5	**6b**	**7b**	92	90	88	86	85	86
6	**6c**	**7c**	90	87	85	83	84	84

[a] Unless otherwise noted, all reactions were carried out at 100 °C in BmimBF$_4$ (0.5 mmol of **5** at start per mL of BmimBF$_4$, 1 mmol scale based on **5**) using a **5**:KI:PdI$_2$ molar ratio of 100:10:1, under 20 atm (at 25 °C) of a 4:1 mixture of CO-air. Substrate conversion was quantitative. [b] Isolated yield from **5**. Run 1 corresponds to the 1st experiment, the next runs to recycles. [c] The reaction was carried out with a **5a**:KI:PdI$_2$ molar ratio of 500:10:1.

benzylamine **1h** behaved similarly to butylamine **1f** (Table 2, entry 3).

Scheme 2. Formation of oxamides by PdI$_2$-catalyzed oxidative double carbonylation of amines through the formation of *bis*-carbamoylpalladium complex **III**.

Very interestingly, both for BuNH$_2$ **1f** and BnNH$_2$ **1h**, it has been possible to work out suitable reaction conditions able to selectively promote the formation of either the urea or the oxamide derivative. In particular, when the carbonylation reaction of **1f** was carried out with a higher substrate concentration (1 mmol per mL of BmimBF$_4$) with a catalyst loading of 0.5%, urea **2f** was the only product formed in 83% yield (Table 2, entry 4). Under similar conditions, and with a catalyst loading as low as 0.2%, benzylamine **1h** was converted into dibenzylurea **2h** in 90% yield (Table 2, entry 5). On the other hand, oxamides **3f** and **3h** were selectively formed when the reactions were conducted at 80 °C under a total pressure of 40 atm (entries 6 and 7 of Table 2). As shown in Table 2, entries 2 and 4-7, the recyclability of the catalyst was successfully verified also in these experiments.

In the case of β-amino alcohols **4** as starting materials, an intramolecular nucleophilic attack may take place at level of the

Table 4. Synthesis of tetrasubstituted oxamides **9** by recyclable PdI$_2$/KI-catalyzed oxidative carbonylation of secondary amines **8** in BmimBF$_4$[a]

$$2\ R_2NH + 2\ CO + (1/2)\ O_2 \xrightarrow[-H_2O]{\substack{PdI_2/KI \\ BmimBF_4}} R_2N\text{-C(O)-C(O)-}NR_2$$
8 → **9**

Entry	Dialkyl amine **8**	Oxamide **9**	Yields of **9** [%][b]					
			Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
1	**8a** (morpholine, O-ring-NH)	**9a**	85	86	85	85	85	87
2[c]	**8a**	**9a**	85	83	83	90	81	81
3	**8b** (piperidine, NH)	**9b**	91	90	92	91	90	91
4	EtO$_2$C-N-ring-NH **8c**	EtO$_2$C-piperazine...CO$_2$Et **9c**	97	95	96	94	94	92
5	**8d** (pyrrolidine, NH)	**9d**	90	90	91	90	89	91
6	Et$_2$NH **8e**	Et$_2$N-C(O)-C(O)-NEt$_2$ **9e**	92	90	87	85	85	86
7	Bu$_2$NH **8f**	Bu$_2$N-C(O)-C(O)-NBu$_2$ **9f**	89	86	84	83	83	82

[a] Unless otherwise noted, all reactions were carried out at 100 °C in BmimBF$_4$ (0.5 mmol of **8** at start per mL of BmimBF$_4$, 1 mmol scale based on **8**) using a **8**:KI:PdI$_2$ molar ratio of 100:10:1, under 20 atm (at 25 °C) of a 4:1 mixture of CO-air. Substrate conversion was quantitative. [b] Isolated yield from **8**. Run 1 corresponds to the 1st experiment, the next runs to recycles. [c] The reaction was carried out with a **8a**:KI:PdI$_2$ molar ratio of 500:10:1.

β-hydroxycarbamoylpalladium complex **IV**, with formation of particularly important products, 2-oxazolidinones (Scheme 3).

Accordingly, the reactivity of 2-aminopropan-1-ol **4a** and (R)-2-amino-2-phenylethanol **4b** was tested under our reaction conditions. Excellent yields in the corresponding 4-methyloxazolidin-2-one **5a** and (R)-4-phenyloxazolidin-2-one **5b** were obtained (Table 3, entries 1 and 2). Again, 2-oxazolidinones were recovered by simple crystallization, while the ionic liquid-catalyst system could be successfully recycled several times.

Scheme 3. Formation of 2-oxazolidinones **5** and benzoxazolones **7** by PdI$_2$-catalyzed oxidative monocarbonylation of β-amino alcohols **4** or 2-aminophenols **6**, respectively, by intramolecular trapping of the β-hydroxycarbamoylpalladium complex **IV**.

Pd(0) + 2 HI + (1/2)O$_2$ ⟶ PdI$_2$ + H$_2$O

Extension to 2-aminophenols **6a,b** to give the corresponding benzoxazolones **7a,b** was also successful (Table 3, entries 3-5), and the possibility to lower the catalyst loading to 0.2 mol% verified (Table 3, entry 4). A pyridine ring was compatible with the reactions conditions, 2-aminopyridin-3-ol **6c** being converted into oxazolo[4,5-*b*]pyridin-2(3*H*)-one **7c** in 90% yield in the first experiment, and in 84-87% yield in the recycles (Table 3, entry 6).

In sharp contrast to our previously reported method,[17] involving the use of DME as the solvent, which did not work with secondary amines **8**, this class of compounds was smoothly converted into tetrasubstituted oxamides **9** under the conditions reported in the present work, through the intermediate formation of the corresponding *bis*-carbamoylpalladium complex Pd(CONRR')₂ **III** (Scheme 2, R, R' = alkyl). Thus, the reaction of morpholine **8a**, carried out in BmimBF₄ under the same conditions reported in Table 1, entry 1, run 1, led to the formation of 1,2-dimorpholinoethane-1,2-dione **9a** in 85% isolated yield, after extraction of the reaction mixture with Et₂O (Table 4, entry 1).[22] Also in this case, the ethereal solvent used for crystallization could be recovered and reused, while the IL phase, still containing the active catalyst, could be recycled several times using a fresh amount of substrate **8a** in each run, without appreciable loss of activity (Table 4, entry 1, runs 2-6). The oxidative double carbonylation reaction leading to **9a** worked nicely even when the catalyst loading was lowered to 0.2% (Table 4, entry 2). Under the same conditions employed for morpholine **8a**, other cyclic and acyclic secondary amines **8b-f** were efficiently converted into the corresponding oxamides **9b-f** in high yields and excellent recyclability of the catalyst-IL system (Table 4, entries 2-7).

Conclusions

In conclusion, we have reported the first general recyclable Pd-catalyzed oxidative carbonylation of primary amines, β-amino alcohols, 2-aminophenols, and secondary amines to give 1,3-disubstituted ureas, 2-oxazolidinones, benzoxazolones, and oxamides, in high yields and selectivity. Carbonylations were carried out in an ionic liquid, such as BmimBF₄, as the reaction medium, under non-explosive conditions (100 °C and 20 atm of a 4:1 mixture of CO-air), using a particularly simple and robust catalytic system, consisting of PdI₂ in conjunction with KI. While primary aromatic amines selectively led to 1,3-aryl ureas, tetrasubstituted oxamides were formed from secondary amines. On the other hand, primary aliphatic amines could be selectively converted into either 1,3-dialkyl ureas or *N,N*-dialkyloxalamides depending on reaction conditions. Oxazolidinones and benzoxazolones were obtained from β-amino alcohols and 2-aminophenols, respectively. All products were easily recovered by simple extraction with Et₂O from the reaction mixture followed by crystallization. The ethereal solvent was recovered and reused, while the IL phase, still containing the active catalyst dissolved in it, could be recycled several times without appreciable loss of activity.

Experimental Section

All solvents and chemicals were purchased from Sigma-Aldrich, were reagent grade and used without further purification. All reactions were analyzed by TLC on silica gel 60 F254 (Merck), or by GLC, using a Shimadzu GC-2010 gas chromatograph using capillary columns with polymethylsilicone+5% phenylsilicone as the stationary phase (HP-5). Column chromatography was performed on silica gel 60 (Merck, 70–230 mesh). Evaporation refers to the removal of solvent under reduced pressure.

Melting points are uncorrected. ¹H and ¹³C NMR spectra were recorded at 25 °C on a Bruker DPX Avance 300 Spectrometer at 300 and 75 MHz, respectively, with Me₄Si as internal standard. IR spectra were recorded on a JASCO FT-IR 4200 spectrometer. GC–MS spectra were recorded on a Shimadzu QP-2010 GC-MS apparatus at 70 eV ionization voltage. The electrospray ionization mass spectra were acquired by direct infusion on MSD Sciex Applied Biosystem API 4000 Q-Trap mass spectrometer equipped with a turbo ion spray ionization source. The spectra in the positive ion mode were obtained at ionspray voltage 5500 V, curtain gas 20 psi, temperature 25 °C, ion source gas 12 psi, collision gas thickness (CAD) medium; entrance potential (EP) between 6 and 10 eV; declustering potential (DP) between 70 and 85 eV; entrance collision energy (CE) between 15 and 30 eV and exit collision energy (CXP) between 8 and 10 eV. Microanalyses were carried out with a Thermo-Fischer Elemental Analyzer Flash 2000.

All starting materials (amines **1a-h** and **8a-8f**, β-amino alcohols **4a-b**, 2-aminophenols **6a-c**) were commercially available (Sigma–Aldrich) and were used as received.

Characterization data for all products are given in the Supporting Information.

Recyclable synthesis of 1,3-disubstituted ureas 2a–h (Tables 1 and 2)

The general procedure for the recyclable catalyzed oxidative carbonylation of primary amines **1a-h** is as follows: A 100 mL stainless steel autoclave was charged in air with PdI₂ (4.0 mg, 1.11×10⁻² mmol), KI (18.4 mg, 1.11×10⁻¹ mmol), and a solution of **1** [**1a**, 103 mg (1.11 mmol, Table 1, entry 1); **1b**, 120 mg (1.12 mmol, Table 1, entry 5); **1c**, 150 mg (1.11 mmol, Table 1, entry 3); **1d**, 137mg (1.11 mmol, Table 1, entry 4); **1e**, 142 mg (1.11 mmol, Table 1, entry 5); **1f**, 162 mg (2.22 mmol, Table 2, entry 4); **1g**, 81 mg (1.11 mmol, Table 2, entry 2); **1h**, 595 mg (5.55 mmol Table 2, entry 5)] in BmimBF₄ (for **1a-g**: 2.2 mL; for **1h**: 5.5 mL); see Tables 1, 2. The autoclave was sealed and, with stirring of the mixture, pressurized with CO (16 atm) and air (4 atm). After stirring at 100 °C for 24 h, the autoclave was cooled, degassed, and opened. The crude reaction mixture was transferred to a round-bottom flask, and Et₂O (for **1a**, **1c-h**: 5 mL; for **1b**: 10 mL) was added. The mixture was stirred for 15 min, and the ethereal phase was decanted. Part of the urea product was thus extracted in Et₂O, while some part remained in the IL phase as a white solid in suspension. To recover the product suspended in the IL phase, CH₂Cl₂ (for **1a**, **1c-h**: 3 mL; for **1b**: 8 mL) was added to the IL phase, followed by stirring for 5 min. Excess of CH₂Cl₂ was evaporated, the distilled CH₂Cl₂ recovered in order to be reused again, and the IL residue re-extracted with Et₂O (for **1a**, **1c-h**: 5 mL; for **1b**: 10 mL). The extraction process was repeated for additional five times. The collected ethereal phases were evaporated to remove about the 80% of the solvent, and the distilled Et₂O recovered in order to be reused again. The residual ethereal solution was kept at 0 °C for 15 h. Crystals of the pure urea product separated, and were collected by decantation (1st

crop). The decanted solution was evaporated to remove about the 50% of the solvent, and the distilled Et_2O recovered in order to be reused again. The residual ethereal solution was kept at 0 °C for 15 h. Additional crystals of the pure urea product separated were collected by decantation (2nd crop). The collected crystals (1st crop + 2nd crop) were eventually dried in vacuo. 1,3-Diphenylurea (**2a**): 111 mg yield (94% from **1a**; Table 1, entry 1, run 1); 1,3-di-*p*-tolylurea (**2b**): 116 mg yield (87% from **1b**; Table 1, entry 2, run 1); 1,3-*bis*-(4-isopropylphenyl)urea (**2c**): 151 mg yield (92% from **1c**; Table 1, entry 3, run 1); 1,3-*bis*-(4-methoxyphenyl)urea (**2d**): 133 mg yield (88% from **1d**; Table 1, entry 4, run 1); 1,3-*bis*-(4-chlorophenyl)urea (**2e**): 142 mg yield (91% from **1e**; Table 1, entry 5, run 1); 1,3-dibutylurea (**2f**): 159 mg yield (83% from **1f**; Table 2, entry 4, run 1); 1,3-di-*tert*-butylurea (**2g**): 94 mg yield (98% from **1g**; Table 2, entry 2, run 1); 1,3-dibenzylurea (**2h**): 600 mg yield (90% from **1h**; Table 2, entry 5, run 1).

Recycling Procedure: The IL residue obtained as described above, still containing the catalytic system dissolved in it, was dried in vacuo for 15 h, in order to remove traces of Et_2O, CH_2Cl_2, and moisture. The dried IL residue was then used as such for the next recycle. Thus, it was transferred into the 100 mL stainless steel autoclave, the amine substrate was added, and then the same procedure described above was followed.

Recyclable synthesis of disubstituted oxamides 3f and 3h (Table 2)

The general procedure for the recyclable catalyzed oxidative carbonylation of primary aliphatic amines **1f** and **1h** is as follows: A 100 mL stainless steel autoclave was charged in air with PdI_2 (4.0 mg, 1.11×10^{-2} mmol), KI (18.4 mg, 1.11×10^{-1} mmol), and a solution of **1** [(1.11 mmol); **1f**, 81 mg (Table 2, entry 6); **1h**, 119 mg (Table 2, entry 7)] in $BmimBF_4$ (2.2 mL); see Table 2. The autoclave was sealed and, with stirring of the mixture, pressurized with CO (32 atm) and air (8 atm). After stirring at 80 °C for 24 h, the autoclave was cooled, degassed, and opened. The crude reaction mixture was transferred to a round-bottom flask, and Et_2O (5 mL) was added. The mixture was stirred for 15 min, the ethereal phase was decanted, and the IL residue was re-extracted with Et_2O (5 × 5 mL). the collected ethereal phases were evaporated to remove about the 80% of the solvent, and the distilled Et_2O recovered in order to be reused again. The residual ethereal solution was kept at 0 °C for 15 h. Crystals of the pure product separated, and were collected by decantation (1st crop). The decanted solution was evaporated to remove about the 50% of the solvent, and the distilled Et_2O recovered in order to be reused again. The residual ethereal solution was kept at 0 °C for 15 h. Additional crystals of the pure product separated, and were collected by decantation (2nd crop). The collected crystals (1st crop + 2nd crop) were eventually dried in vacuo. *N,N'*-Dibutyloxalamide (**3f**): 91 mg yield (82% from **1f**; Table 2, entry 6, run 1); *N,N'*-dibenzyloxalamide (**3h**): 128 mg yield (86% from **1h**; Table 2, entry 7, run 1).

Recycling Procedure: The IL residue obtained as described above, still containing the catalytic system dissolved in it, was dried in vacuo for 15 h, in order to remove traces of Et_2O, CH_2Cl_2, and moisture. The dried IL residue was then used as such for the next recycle. Thus, it was transferred into the 100 mL stainless steel autoclave, the amine substrate was added, and then the same procedure described above was followed.

Recyclable synthesis of 2-oxazolidinones 5a and 5b and benzoxazolones 7a-c (Table 3)

The general procedure for the recyclable catalyzed oxidative carbonylation of β-amino alcohols **4a** and **4b** and 2-aminophenols **6a-c** is

as follows. A 100 mL stainless steel autoclave was charged in air with PdI_2 (4.0 mg, 1.11×10^{-2} mmol), KI (18.4 mg, 1.11×10^{-1} mmol), and a solution of **4** [1.11 mmol; **4a**, 83 mg (Table 3, entry 1); **4b**, 152 mg (Table 3, entry 2)] or **6** [1.11 mmol; **6a**, 121 mg (Table 3, entry 3); **6b**, 137 mg (Table 3, entry 5); **6c**, 122 mg (Table 2, entry 6)] in $BmimBF_4$ (2.2 mL); see Table 3. The autoclave was sealed and, with stirring of the mixture, pressurized with CO (16 atm) and air (4 atm). After stirring at 100 °C for 24 h, the autoclave was cooled, degassed, and opened. The crude reaction mixture was transferred to a round-bottomed flask, and Et_2O (5 mL) was added. The mixture was stirred for 15 min, and the ethereal phase was decanted, and the IL residue was re-extracted with Et_2O (5 × 5 mL).

In the case of the reaction of **4a**, the collected ethereal phases were evaporated, and the residue purified by column chromatography on silica gel using 95:5 hexane/AcOEt to give pure 4-methyloxazolidin-2-one **5a** (105 mg yield; 94% from **4a**; Table 3, entry 1, run 1).

In the case of the reactions of **4b** and **6a-c**, the collected ethereal phases were evaporated to remove about the 80% of the solvent, and the distilled Et_2O recovered in order to be reused again. The residual ethereal solution was kept at 0 °C for 15 h. Crystals of the pure product separated, and were collected by decantation (1st crop). The decanted solution was evaporated to remove about the 50% of the solvent, and the distilled Et_2O recovered in order to be reused again. The residual ethereal solution was kept at 0 °C for 15 h. Additional crystals of the pure product separated, and were collected by decantation (2nd crop). The collected crystals (1st crop + 2nd crop) were eventually dried in vacuo. (*R*)-4-Phenyloxazolidin-2-one (**5b**): 144 mg yield (80% from **4b**; Table 3, entry 2, run 1); benzo[*d*]oxazol-2(3*H*)-one (**7a**): 147 mg yield (98% from **6a**; Table 3, entry 3, run 1); 6-methylbenzo[*d*]oxazol-2(3*H*)-one (**7b**): 153 mg yield (92% from **6b**; Table 3, entry 5, run 1); oxazolo[4,5-*b*]pyridin-2(3*H*)-one (**7c**): 136 mg yield (90% from **6c**; Table 3, entry 6, run 1).

With 2-aminophenol **6a**, the oxidative carbonylation reaction was also carried out using only 0.2 mol % of catalyst (Table 3, entry 4). The general procedure described above was followed, starting from 606 mg of **6a** (5.55 mmol) in 11.1 mL of $BmimBF_4$. The reaction mixture was then extracted with 6 × 10 mL of Et_2O, and the product separated by crystallization as described above (yield: 710 mg, 95% from **6a**; Table 3, entry 4, run 1).

Recycling Procedure: The IL residue obtained as described above, still containing the catalytic system dissolved in it, was dried in vacuo for 15 h, in order to remove traces of Et_2O and moisture. The dried IL residue was then used as such for the next recycle. Thus, it was transferred into the 100 mL stainless steel autoclave, the substrate was added, and then the same procedure described above was followed.

Recyclable synthesis of tetrasubstituted oxamides 9a-f (Table 4)

The general procedure for the recyclable catalyzed oxidative carbonylation of secondary amines **8a-f** is as follows. A 100 mL stainless steel autoclave was charged in air with PdI_2 (4.0 mg, 1.11×10^{-2} mmol), KI (18.4 mg, 1.11×10^{-1} mmol), and a solution of **8** [1.11 mmol; **8a**, 97 mg (Table 4, entry 1); **8b**, 95 mg (Table 4, entry 3); **8c**, 176 mg (Table 4, entry 4); **8d**, 75 mg (Table 4, entry 5); **8e**, 81 mg (Table 4, entry 6), **8f**, 112 mg (Table 4, entry 7)] in $BmimBF_4$ (2.2 mL); see Table 4. The autoclave was sealed and, with stirring of the mixture, pressurized with CO (16 atm) and air (4 atm). After stirring at 100 °C for 24 h, the autoclave was cooled, degassed, and opened. The crude reaction

mixture was transferred to a round-bottom flask, and Et$_2$O (5 mL) was added. The mixture was stirred for 15 min, the ethereal phase was decanted, and the IL residue was re-extracted with Et$_2$O (5 × 5 mL).

In the case of the reactions of **8a-e**, the collected ethereal phases were evaporated to remove about the 80% of the solvent, and the distilled Et$_2$O recovered in order to be reused again. The residual ethereal solution was kept at 0 °C for 15 h. Crystals of the pure product separated, and were collected by decantation (1st crop). The decanted solution was evaporated to remove about the 50% of the solvent, and the distilled Et$_2$O recovered in order to be reused again. The residual ethereal solution was kept at 0 °C for 15 h. Additional crystals of the pure product separated, and were collected by decantation (2nd crop). The collected crystals (1st crop + 2nd crop) were eventually dried in vacuo. 1,2-Dimorpholinoethane-1,2-dione (**9a**): 108 mg yield (85% from **8a**; Table 4, entry 1, run 1); 1,2-di(piperidin-1-yl)ethane-1,2-dione (**9b**): 113 mg yield (91% from **8b**; Table 4, entry 3, run 1); 1,2-di-(4-ethoxycarbonyl)piperazinoethane-1,2-dione (**9c**): 200 mg yield (97% from **8c**; Table 4, entry 4, run 1); 1,2-di(pyrrolidin-1-yl)ethane-1,2-dione (**9d**): 98 mg yield (90% from **8d**; Table 4, entry 5, run 1); tetraethyloxalamide (**9e**): 102 mg yield (92% from **8e**; Table 4, entry 6, run 1).

In the case of the reaction of **8f**, the collected ethereal phases were evaporated, and the residue purified by column chromatography on silica gel using 8:2 hexane/AcOEt to give pure tetraisopropyloxalamide **9f** (Yield: 154 mg; 89% from **8f**; Table 4, entry 7, run 1).

With morpholine **8a**, the oxidative carbonylation reaction was also carried out using only 0.2 mol % of catalyst (Table 4, entry 2). The general procedure described above was followed, starting from 484 mg of **8a** (5.55 mmol) in 11.1 mL of BmimBF$_4$. The reaction mixture was then extracted with 6 × 10 mL of Et$_2$O, and the product separated by crystallization as described above. (Yield: 540 mg; 85% from **8a**; Table 4, entry 2, run 1).

Recycling Procedure: The IL residue obtained as described above, still containing the catalytic system dissolved in it, was dried in vacuo for 15 h, in order to remove traces of Et$_2$O and moisture. The dried IL residue was then used as such for the next recycle. Thus, it was transferred into the 100 mL stainless steel autoclave, the substrate was added, and then the same procedure described above was followed.

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[22] Following a referee's suggestion, in order to verify the effect of the ionic liquid on the reactivity of secondary amines, we carried out some experiments in DME-BmimBF$_4$ mixtures with different *v/v* ratios (*a*: 95/5; *b*: 75/25; *c*: 50/50; *d*: 25/75; and *e*: 5/95) using morpholine **8a** as substrate, under the same conditions reported in Table 4, entry 1, run 1. A consistent trend was found, the yield in the corresponding oxamide **9a** increasing with the augment of the relative amount of the IL: 18% (mixture *a*); 28% (*b*); 34% (*c*); 48% (*d*); and 65% (*e*). From these data, we may conclude that the IL does not participate as a catalyst for the process; rather, its high dielectric constant may be responsible for the co-(activation) of the substrate and/or the Pd catalyst.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

The first general recyclable catalytic oxidative carbonylation of amines, b-amino alcohols and 2-aminophenols to ureas, oxamides, oxazolidinones, and benzoxazolones is reported.
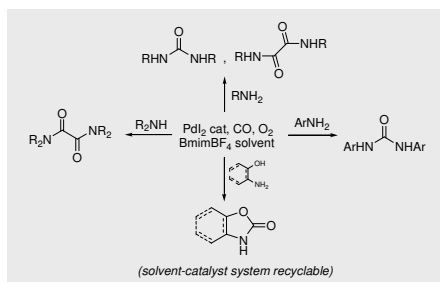
(solvent-catalyst system recyclable)

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Recyclable Catalytic Oxidative Carbonylation of Amines, β-Amino alcohols, and 2-Aminophenols to Ureas, Oxamides, 2-Oxazolidinones, and Benzoxazolones