

Supporting Information for

Intra- and Intermolecular Cooperativity in the Catalytic Activity of Phosphodiester Cleavage by Self-Assembled Systems Based on Guanidinylated Calix[4]arenes.

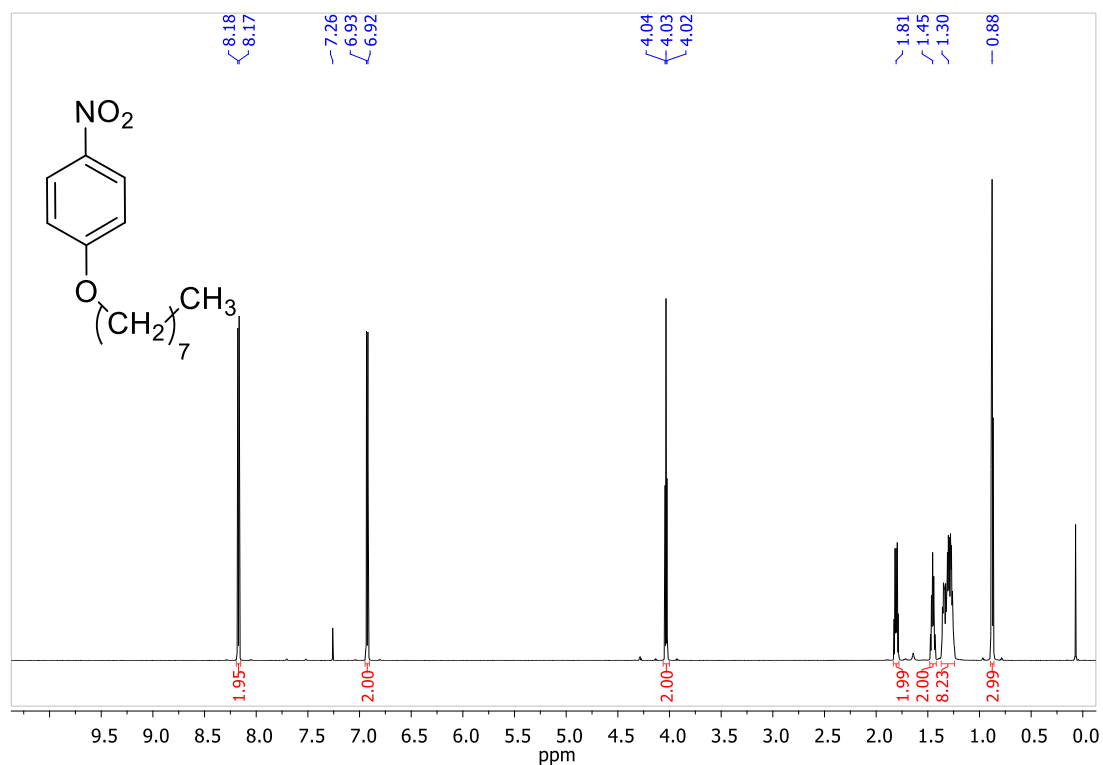
Daniele Lisi,^{a,‡} Carlo Alberto Vezzoni,^{b,‡} Alessandro Casnati,^b Francesco Sansone,^{b,*} Riccardo Salvio,^{a,c*}

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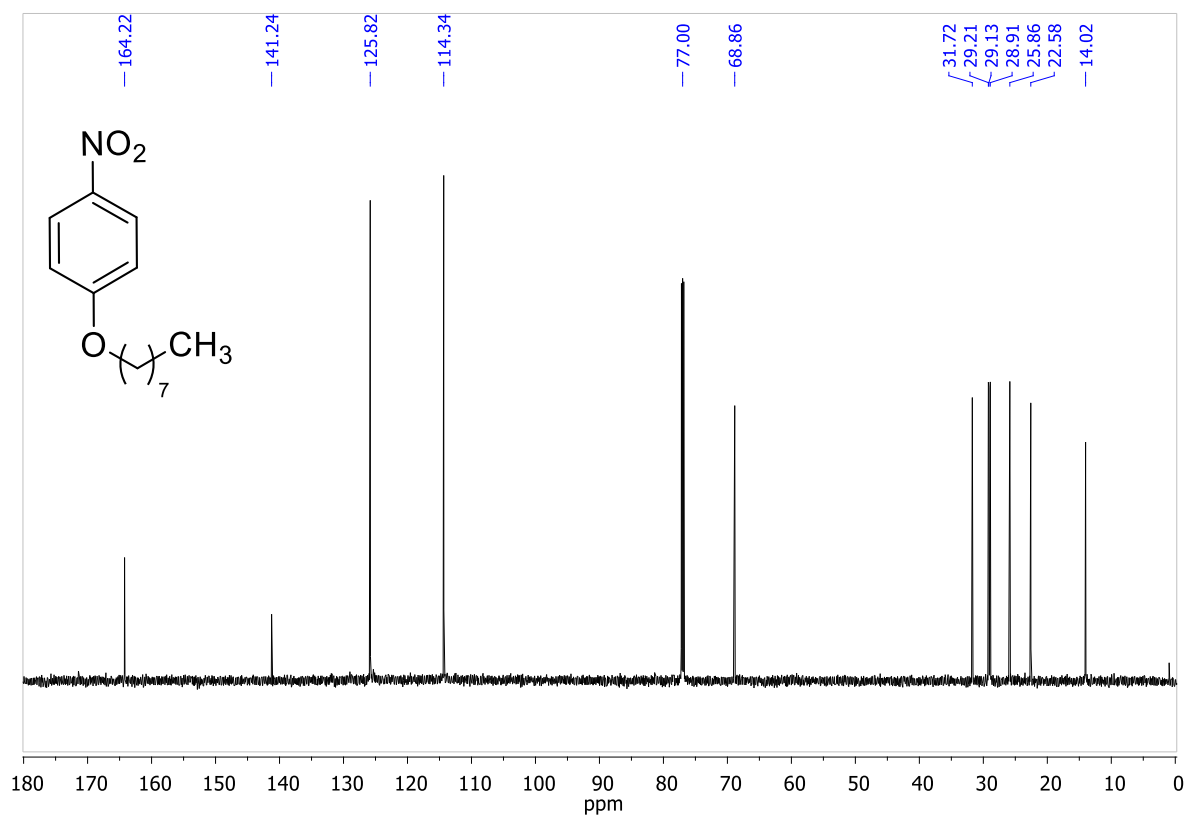
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S.1 ^1H NMR and ^{13}C NMR of compounds

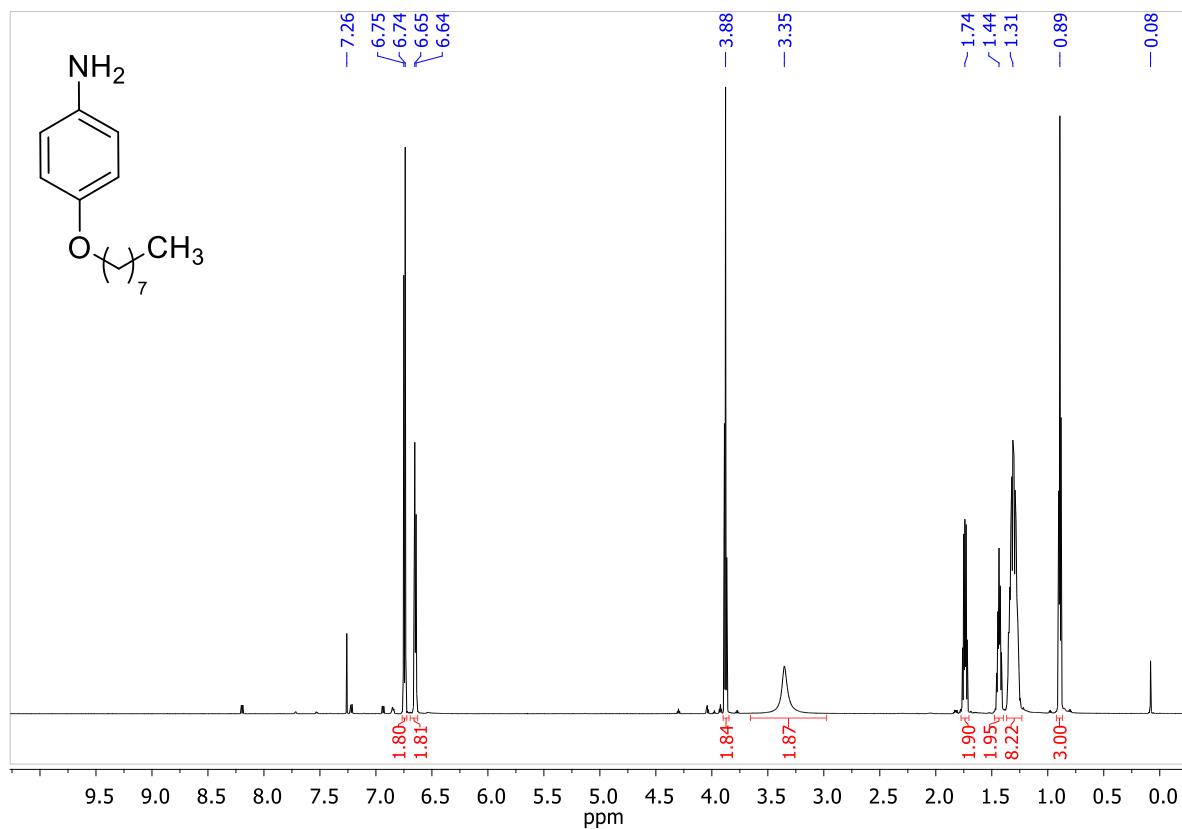
^1H NMR (700MHz, CDCl_3)



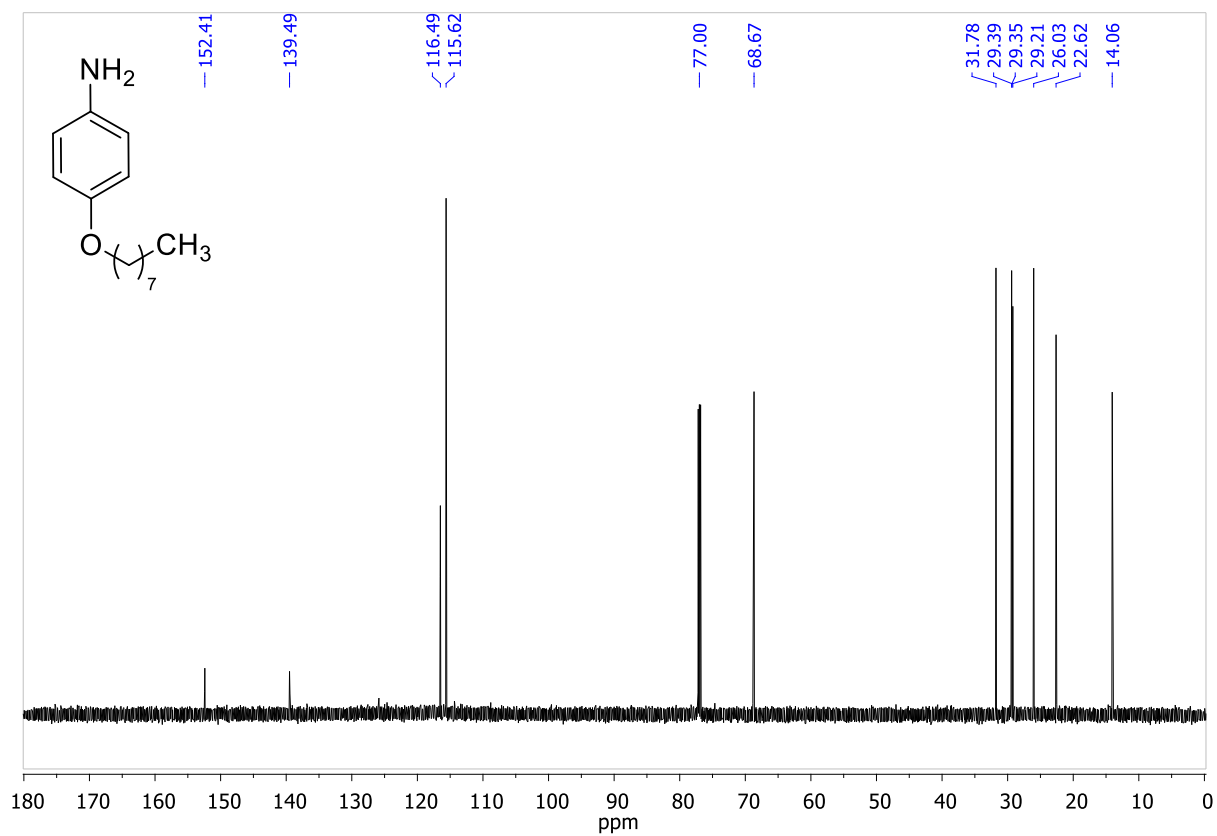
^{13}C NMR (175 MHz, CDCl_3)



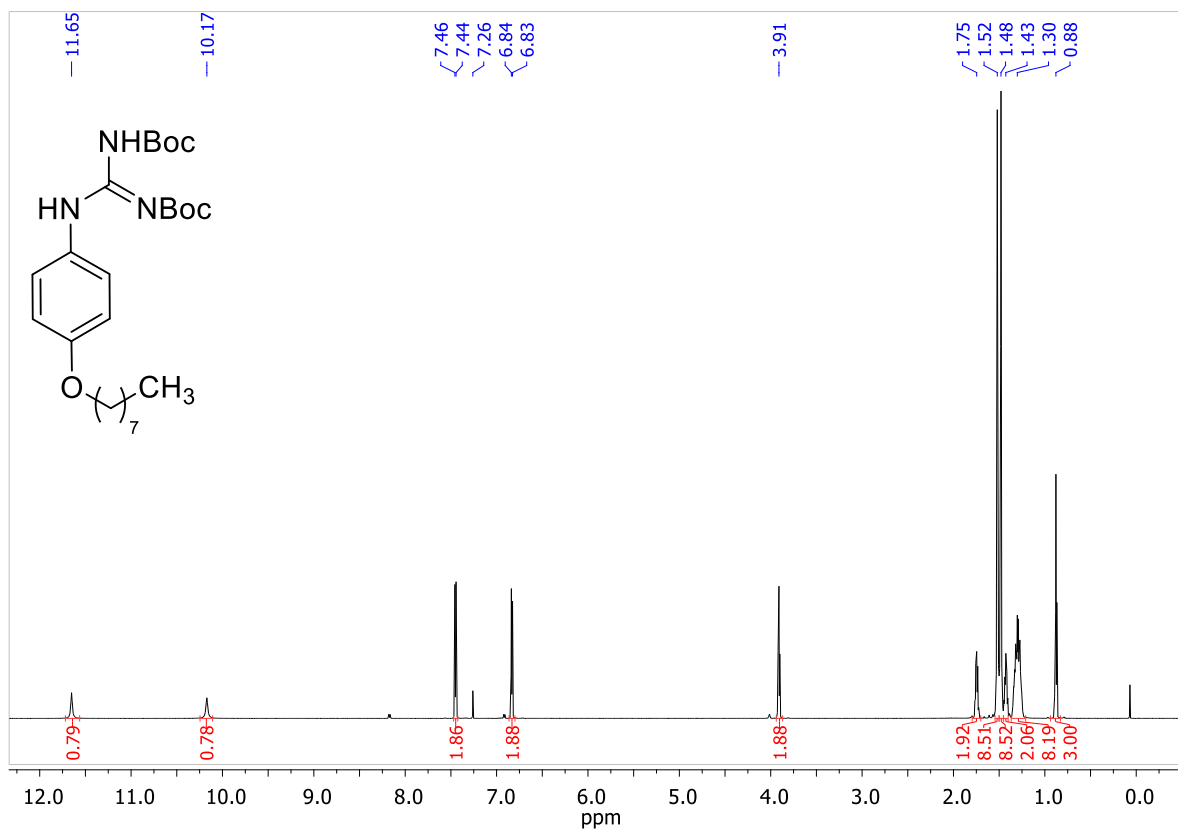
¹H NMR (700MHz, CDCl₃)



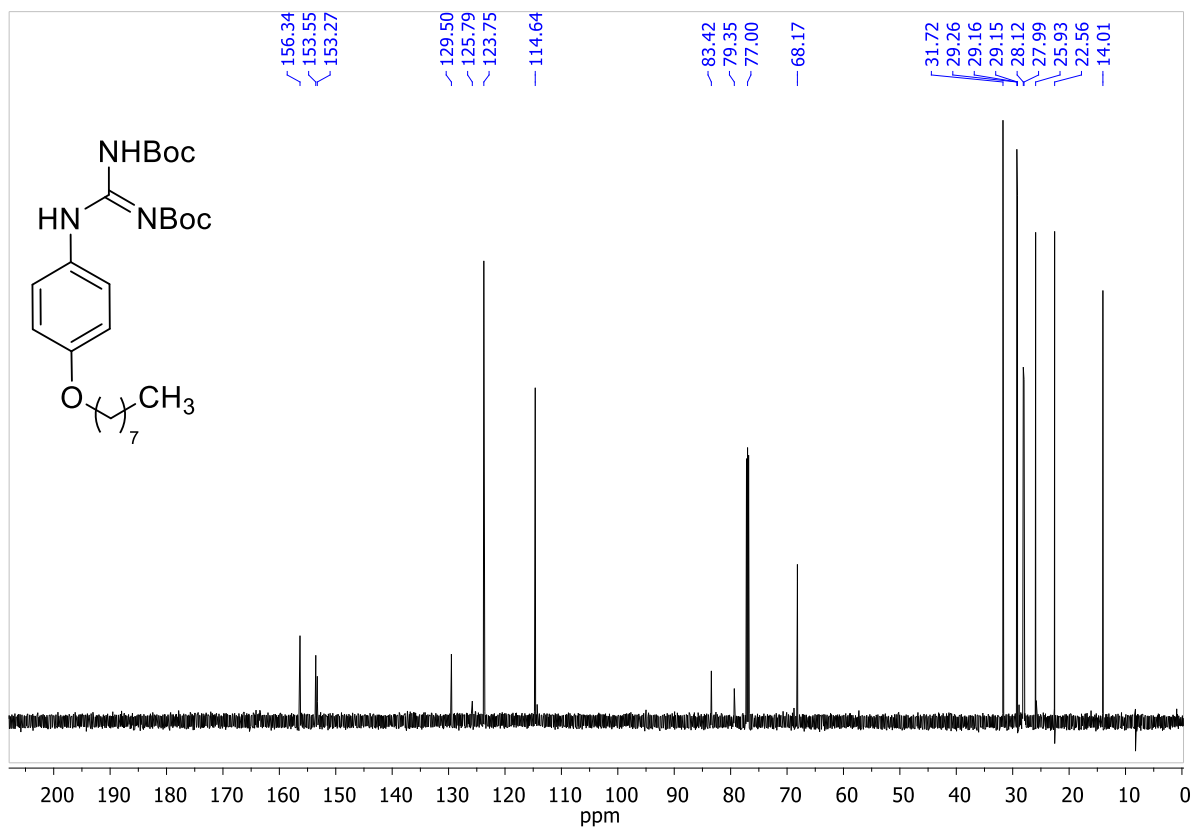
¹³C NMR (175 MHz, CDCl₃)



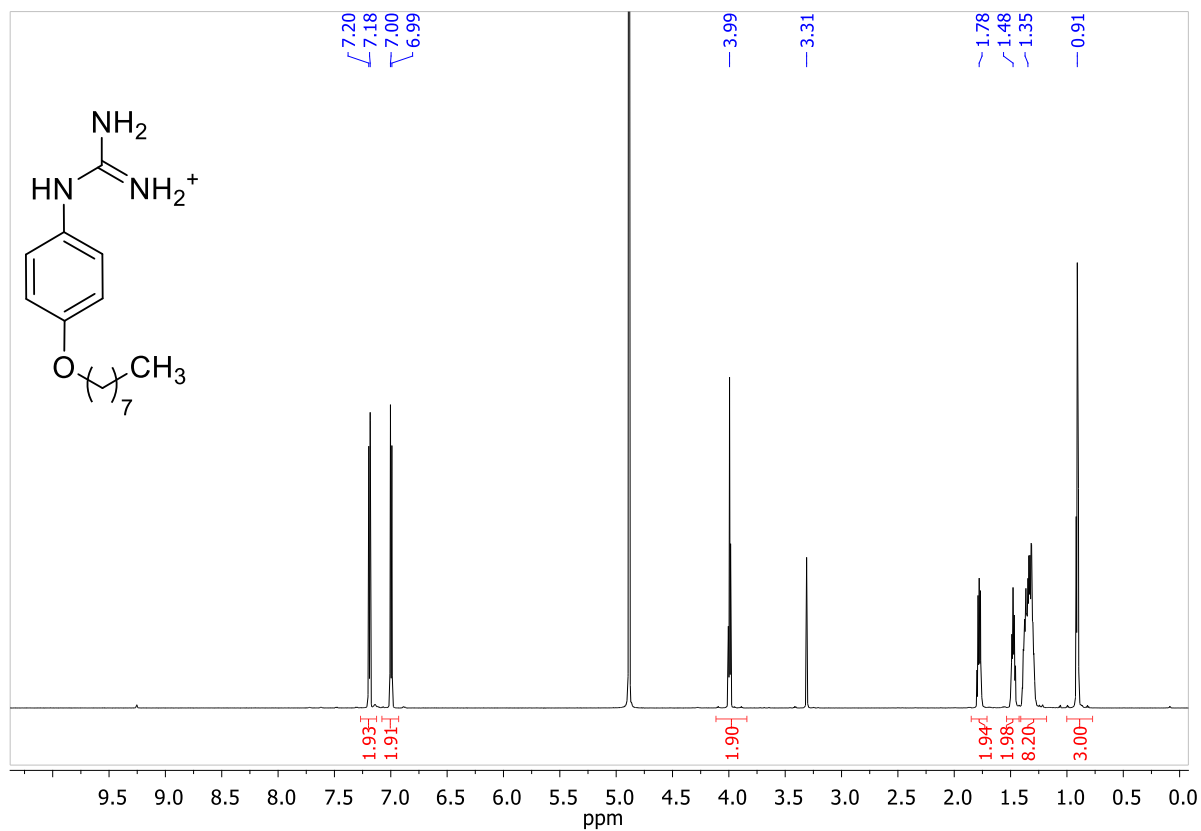
^1H NMR (700MHz, CDCl_3)



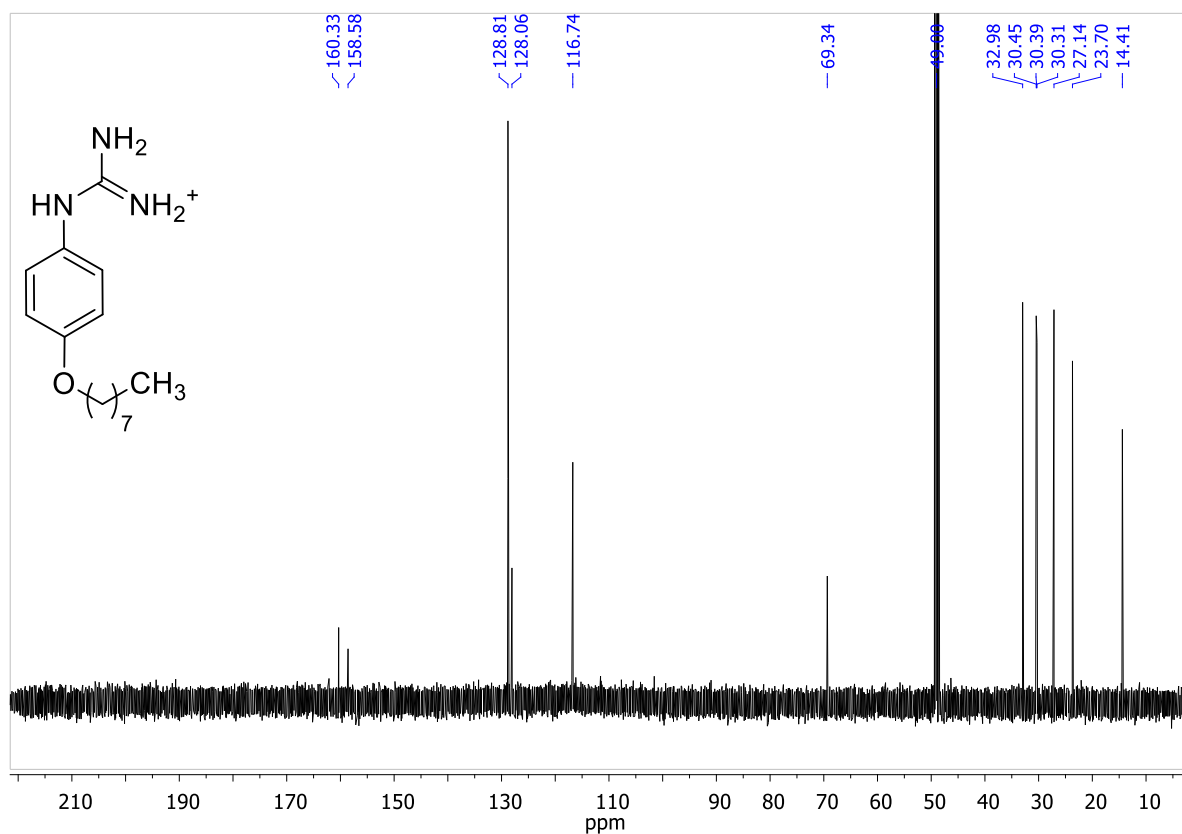
^{13}C NMR (175 MHz, CDCl_3)



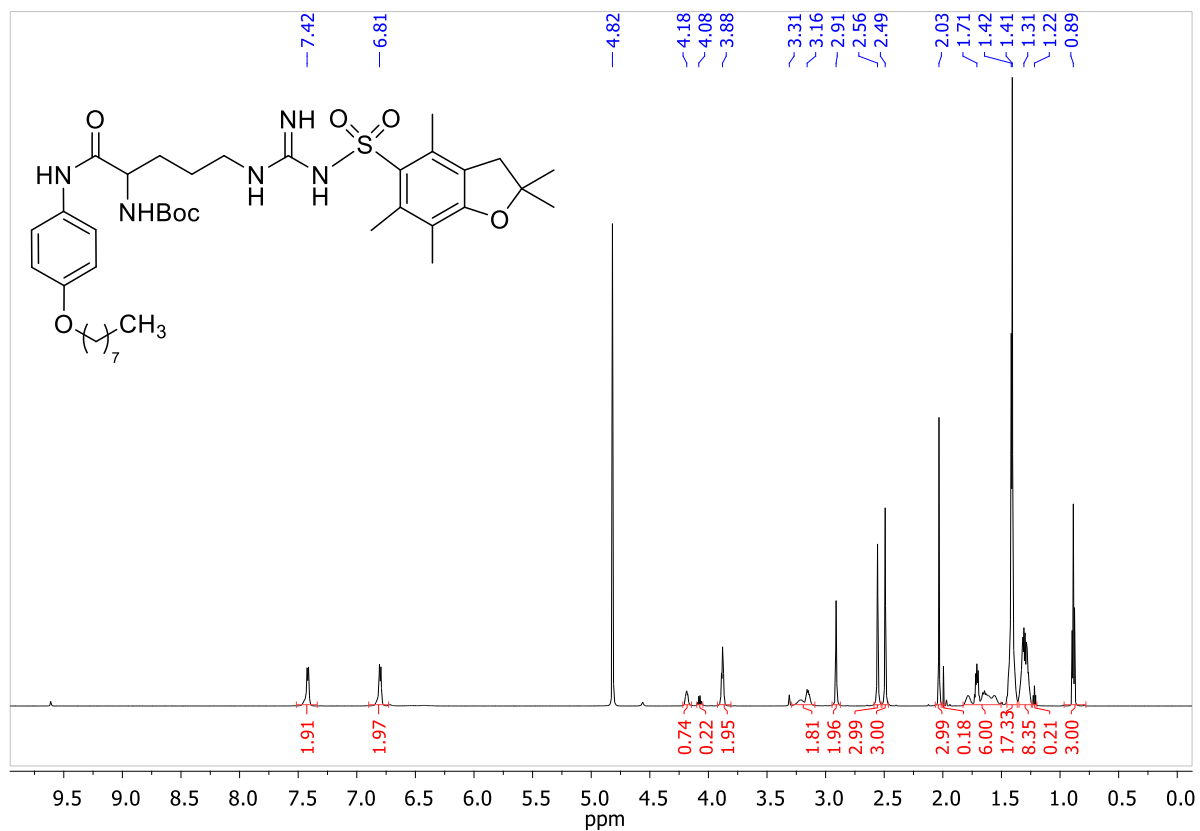
^1H NMR (700 MHz, CD_3OD)



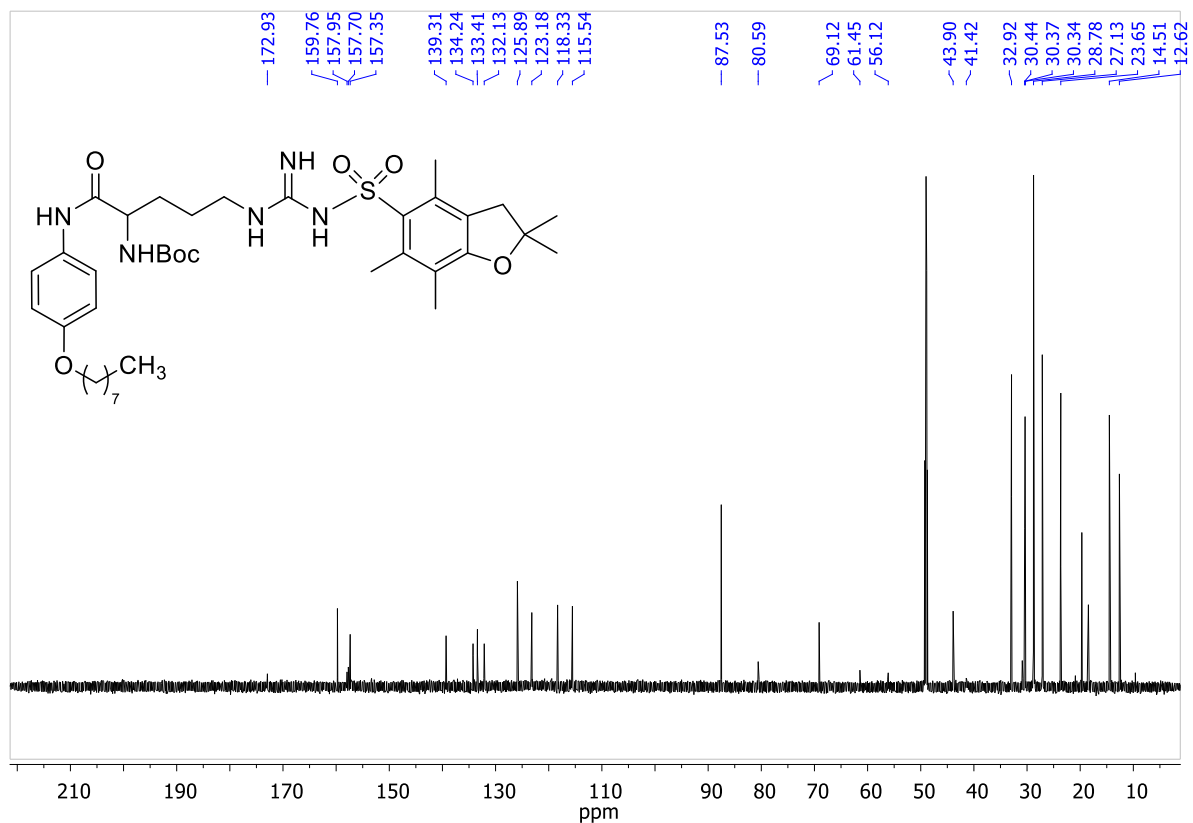
^{13}C NMR (175 MHz, CD_3OD)



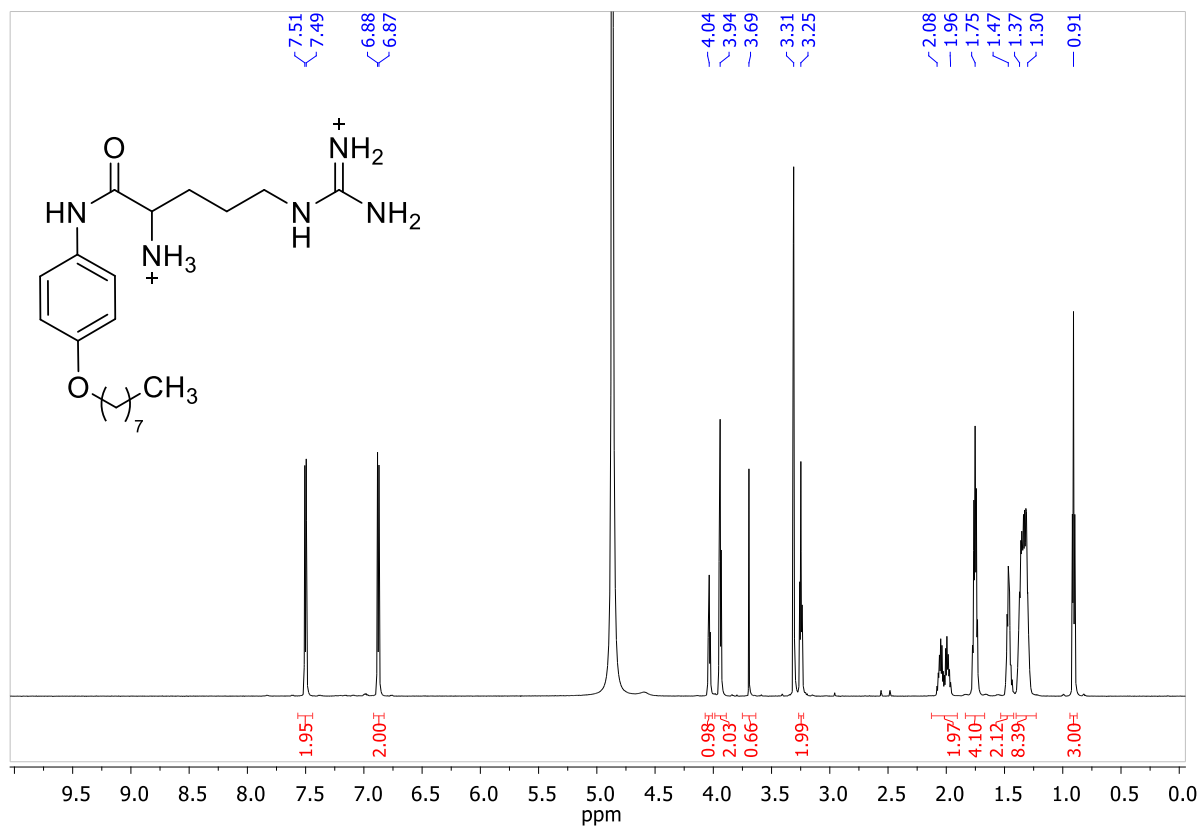
^1H NMR (700 MHz, CD_3OD)



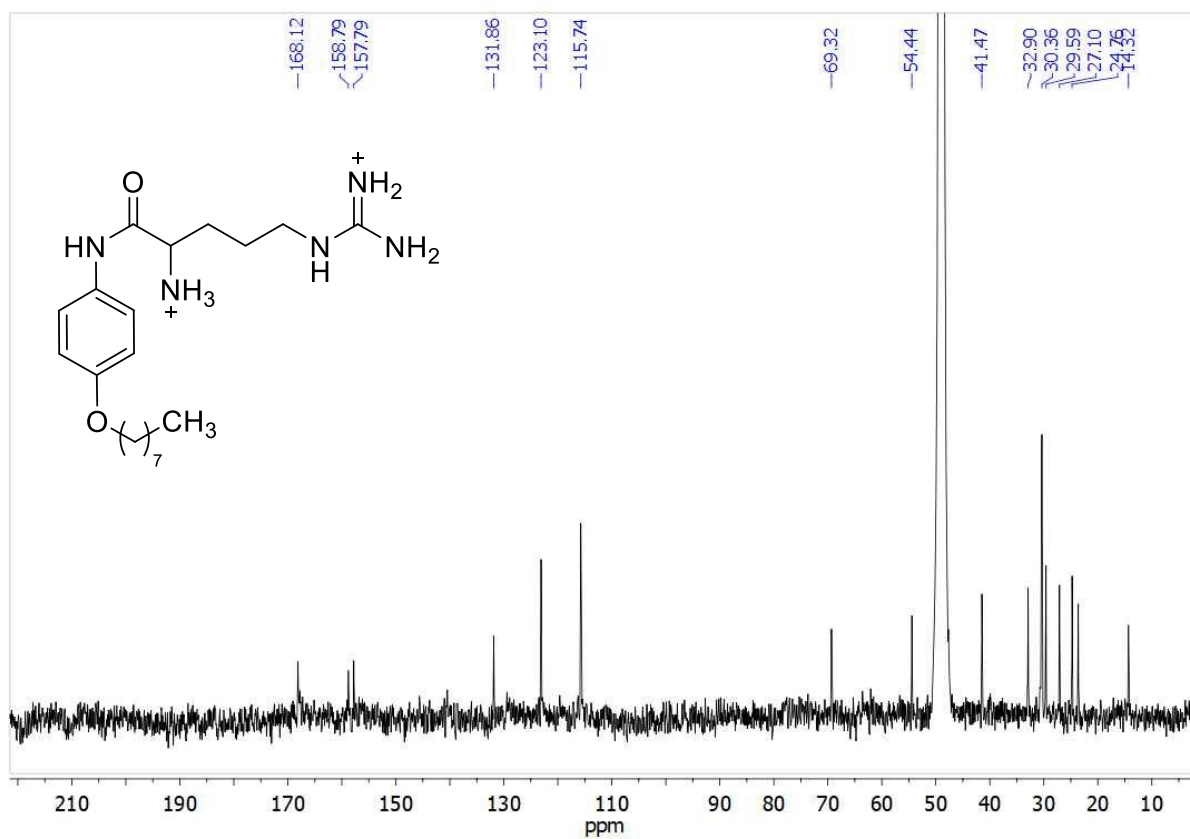
^{13}C NMR (175 MHz, CD_3OD)



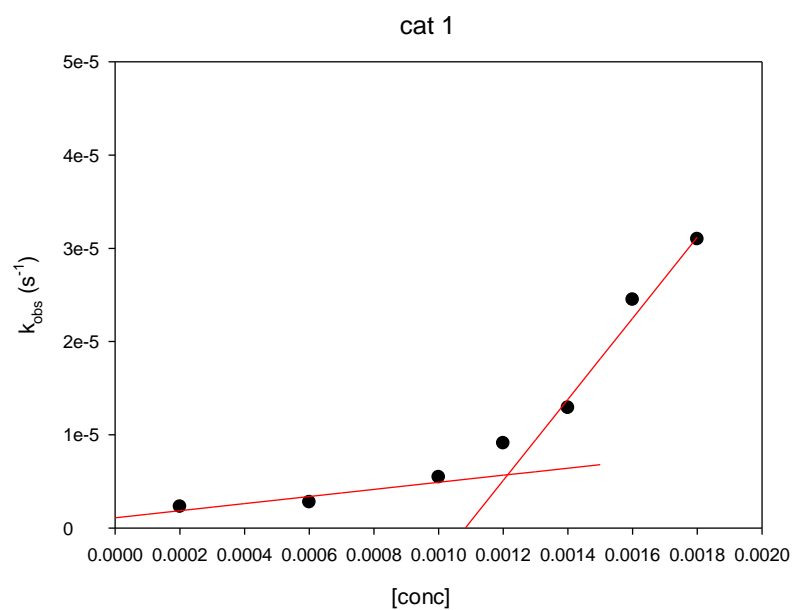
^1H NMR (700 MHz, CD_3OD)



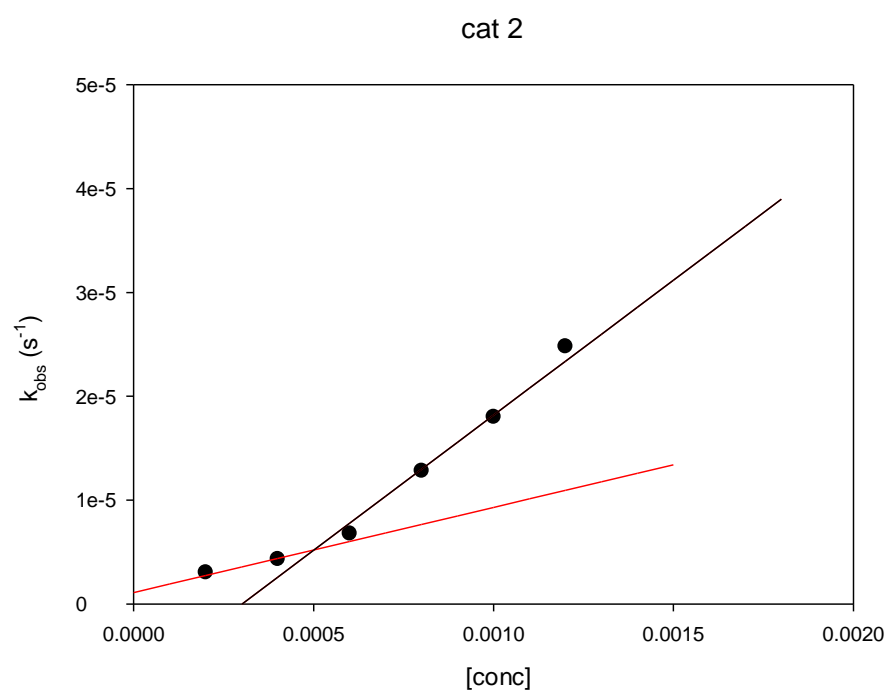
^{13}C NMR (175 MHz, CD_3OD)



S.2 Kinetic Data and Elaborations

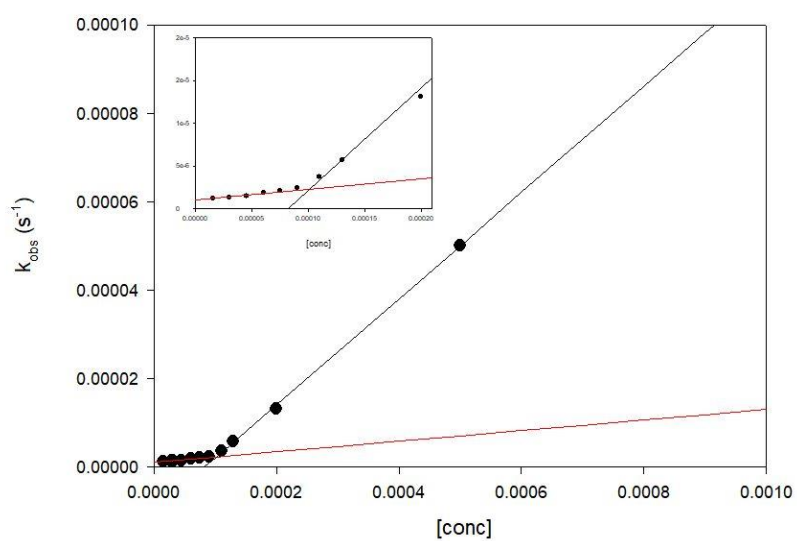


Conc (M)	kobs (s-1)
2.0000e-4	2.3000e-6
6.0000e-4	2.7800e-6
1.0000e-3	5.4600e-6
1.2000e-3	9.1000e-6
1.4000e-3	1.2900e-5
1.6000e-3	2.4500e-5
1.8000e-3	3.1000e-5



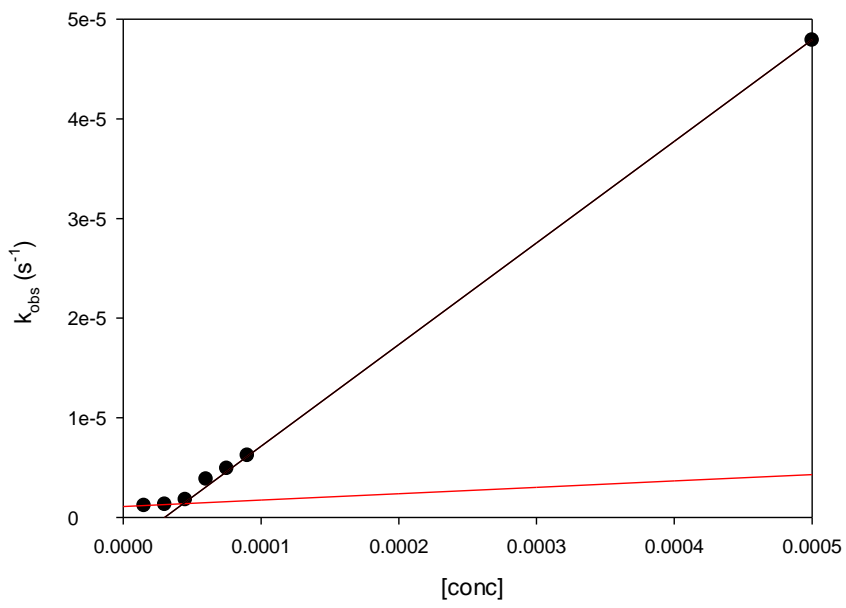
Conc. (M^{-1})	k_{obs} (s^{-1})
2.0000e-4	3.0436e-6
4.0000e-4	4.3244e-6
6.0000e-4	6.7808e-6
8.0000e-4	1.2827e-5
1.0000e-3	1.8018e-5
1.2000e-3	2.4813e-5

Cat 3



Conc. (M^{-1})	k_{obs} (s^{-1})
1.5000e-5	1.2270e-6
3.0000e-5	1.3740e-6
4.5000e-5	1.4910e-6
6.0000e-5	1.9048e-6
7.5000e-5	2.1350e-6
9.0000e-5	2.4220e-6
1.1000e-4	3.7400e-6
1.3000e-4	5.7400e-6
5.0000e-4	5.0140e-5
2.0000e-4	1.3100e-5

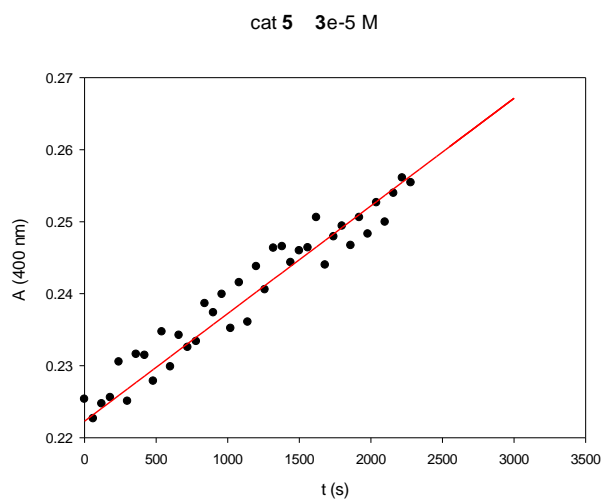
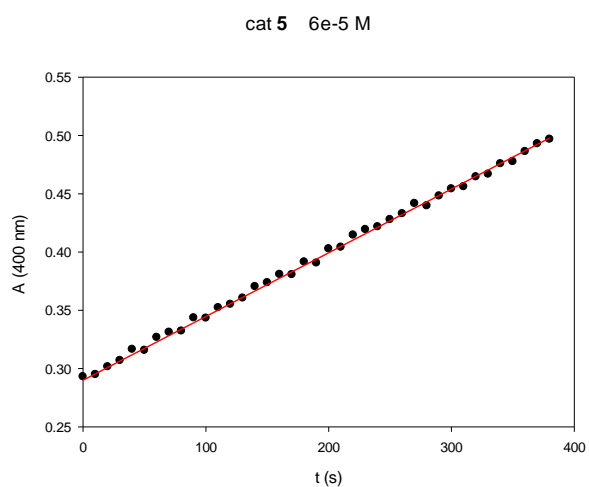
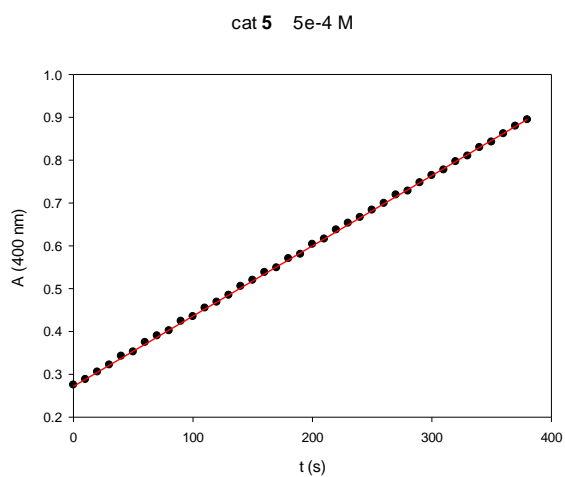
cat 4



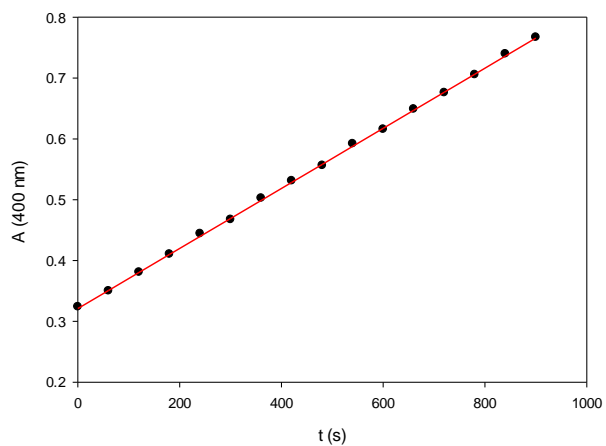
1.5000e-5	1.1960e-6
3.0000e-5	1.3220e-6
4.5000e-5	1.7880e-6
6.0000e-5	3.8505e-6
7.5000e-5	4.9170e-6
9.0000e-5	6.2350e-6
5.0000e-4	4.7900e-5

S.3 Raw Kinetic Data

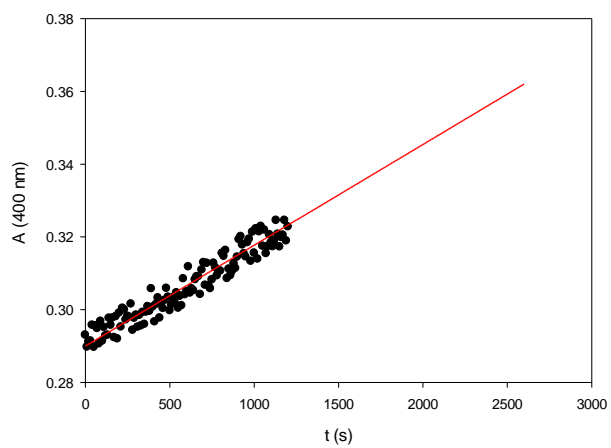
In this section are reported the raw kinetic data of the experiments for the cleavage of HPNP. To convert the Absorbance value into concentration the following value of molar extinction coefficient was use: $\epsilon=18230 \text{ M}^{-1} \text{ cm}^{-1}$.



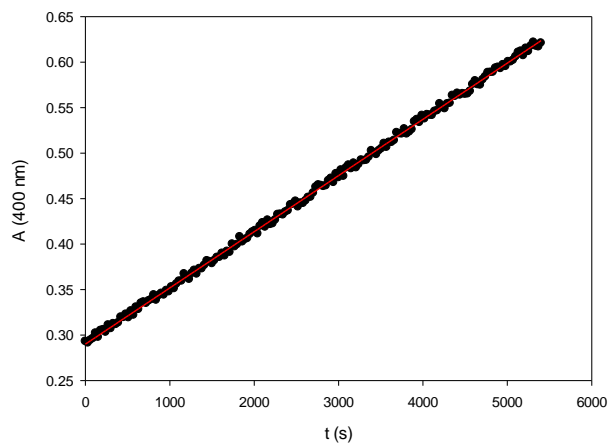
cat 5 2e-4 M



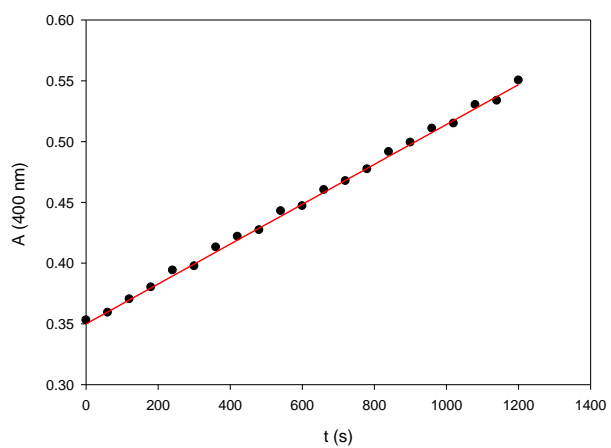
cat 2 4e-4 M



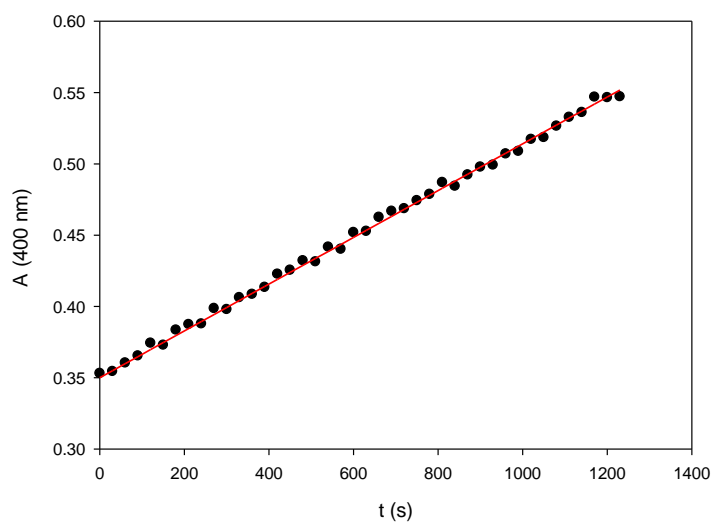
cat 2 6e-4 M



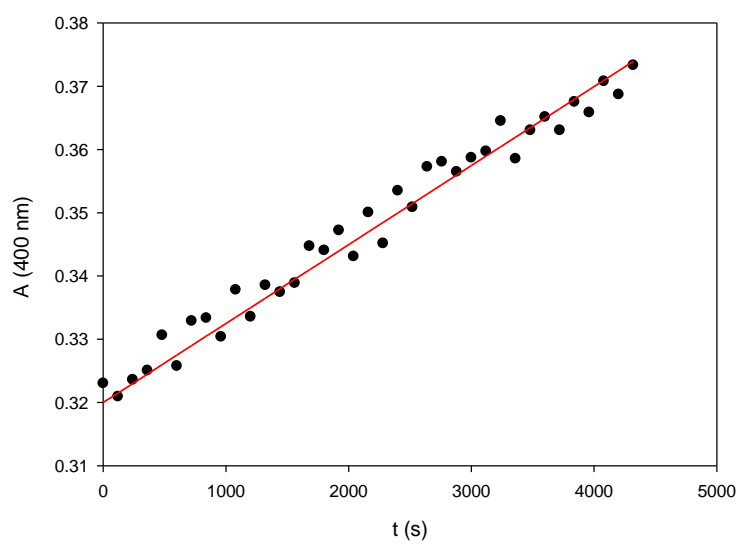
cat 2 1e-3 M



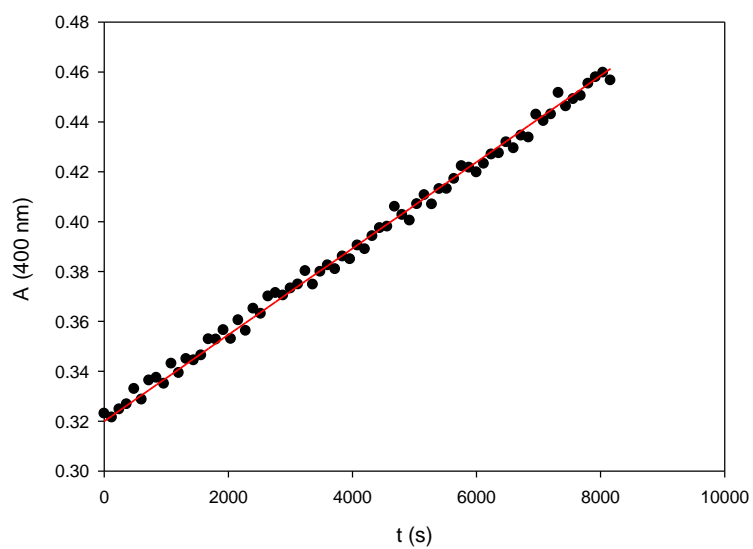
cat 2 1.2e-3 M



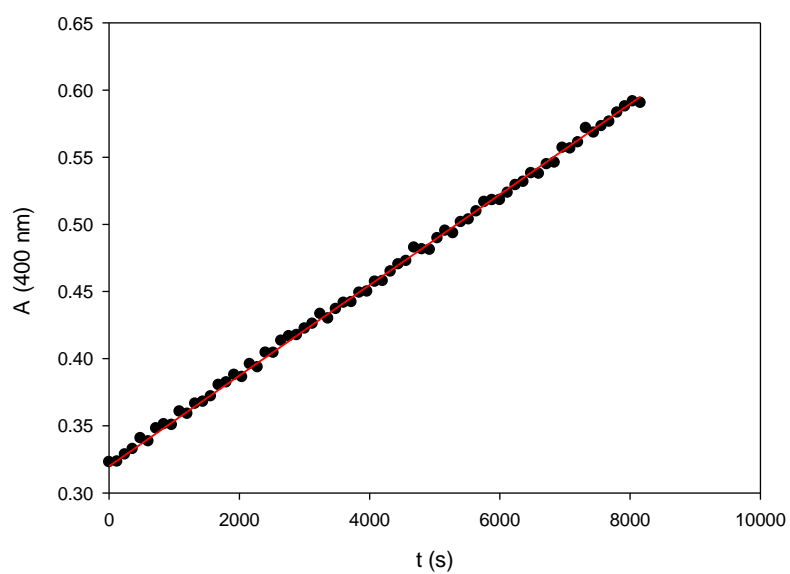
cat 3 3e-5 M



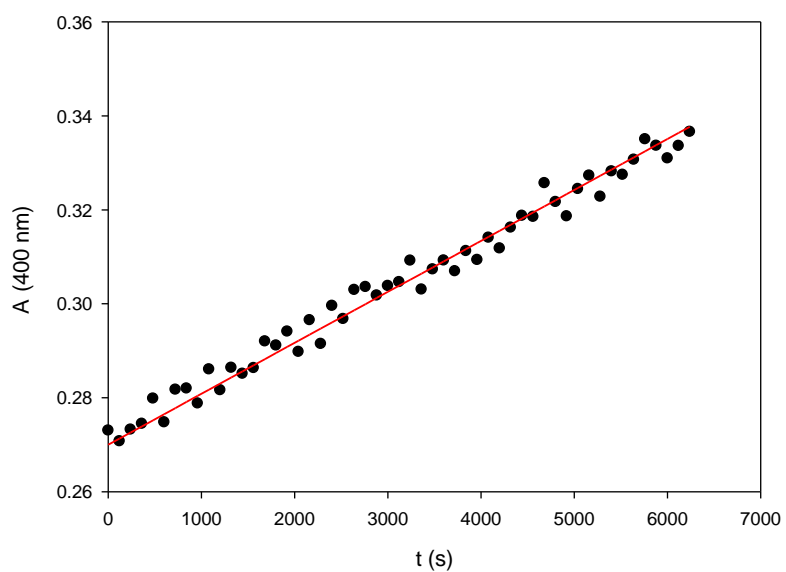
cat 3 6e-5 M



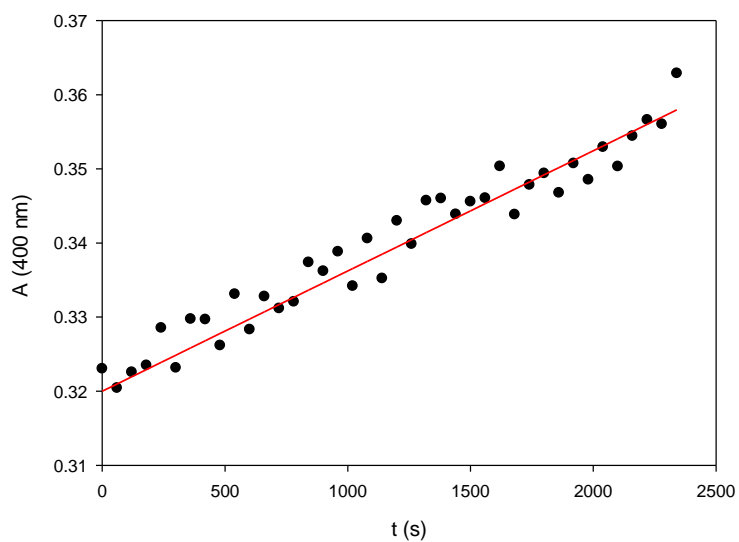
cat 3 1.1e-4 M



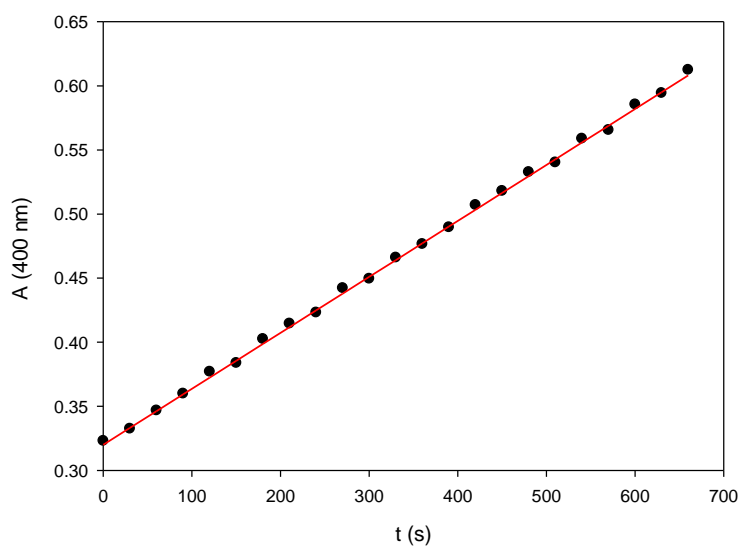
cat 4 1.5e-5 M



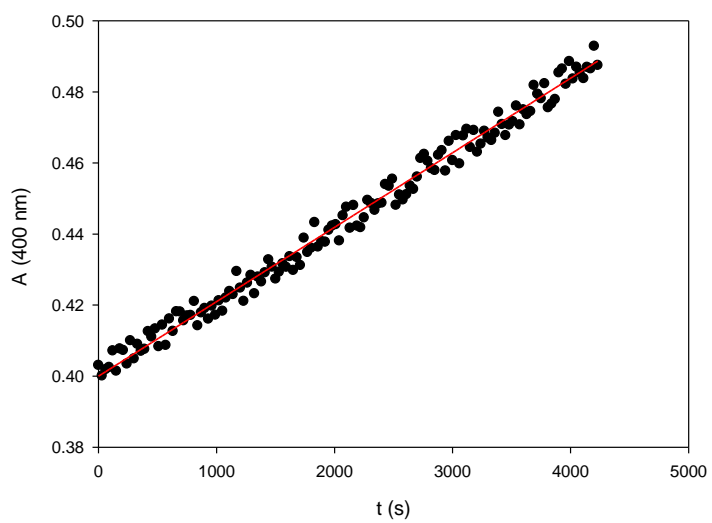
cat 4 4.5e-5 M



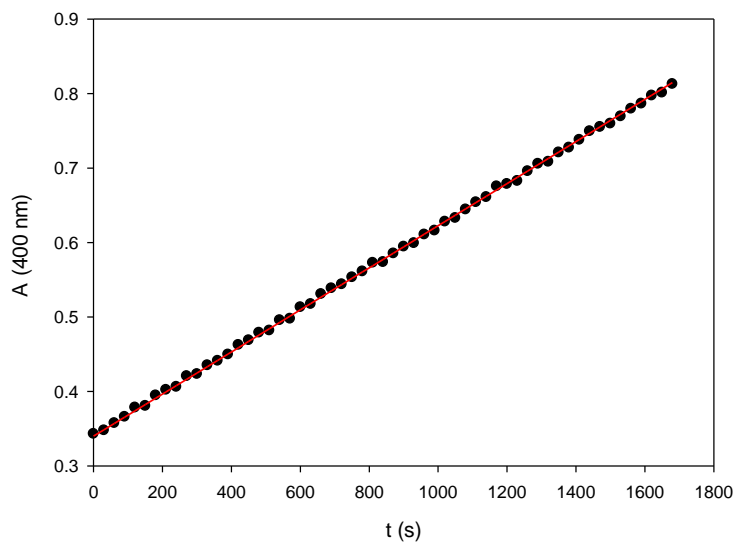
cat 4 5e-4 M



cat 1 2e-4 M



cat 1 1.8e-3 M

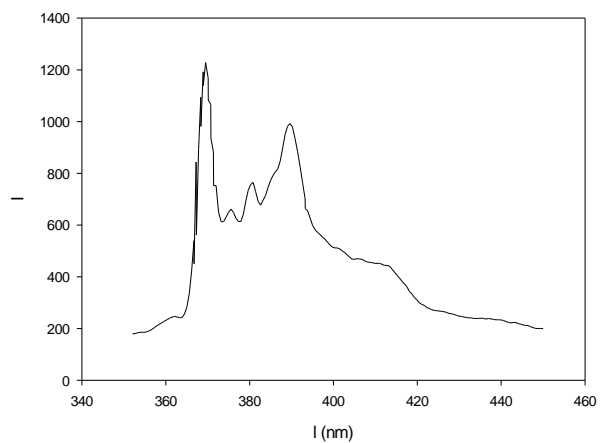


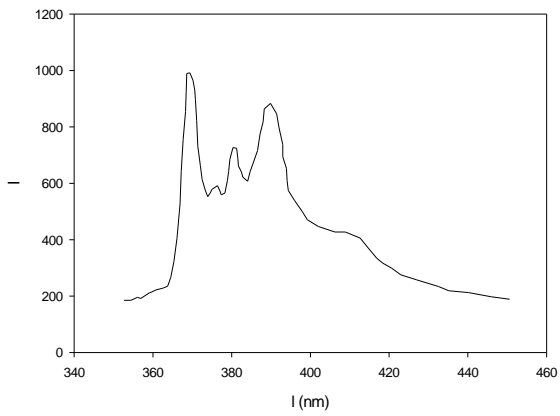
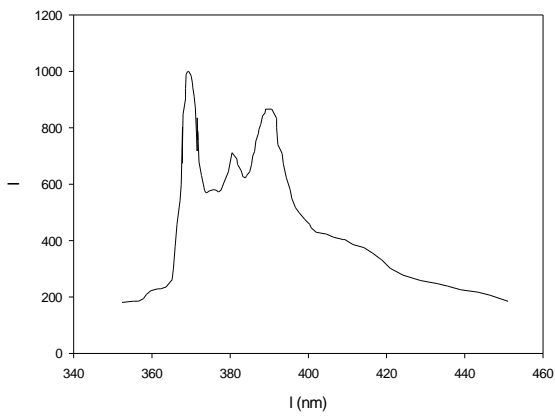
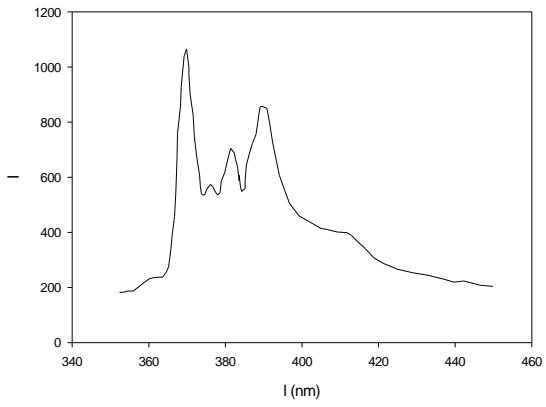
S.4 Fluorescence Titration

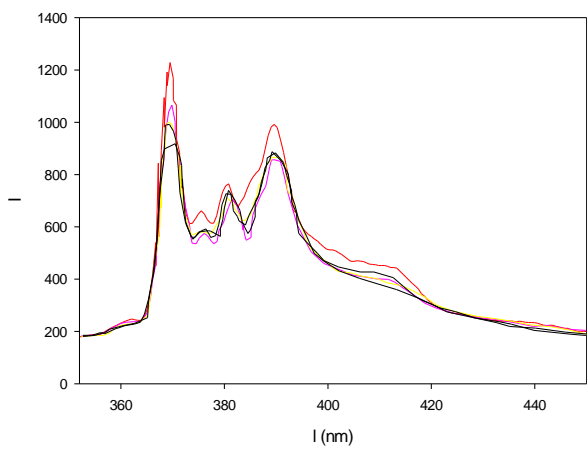
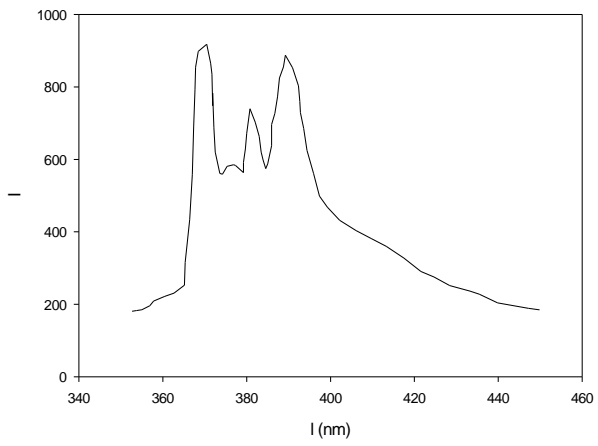
Points of titrations in Figure 2

LogC	C	I ₁ /I ₃
6.3010	5.0000e-7	1.8000
5.8239	1.5000e-6	1.8500
5.3979	4.0000e-6	1.7500
5.0706	8.5000e-6	1.7200
4.6021	2.5000e-5	1.8300
4.1549	7.0000e-5	1.6500
4.0000	1.0000e-4	1.6000
3.5229	3.0000e-4	1.3500
3.3979	4.0000e-4	1.2000

Emission spectra of pyrene in the titration experiment (see above).

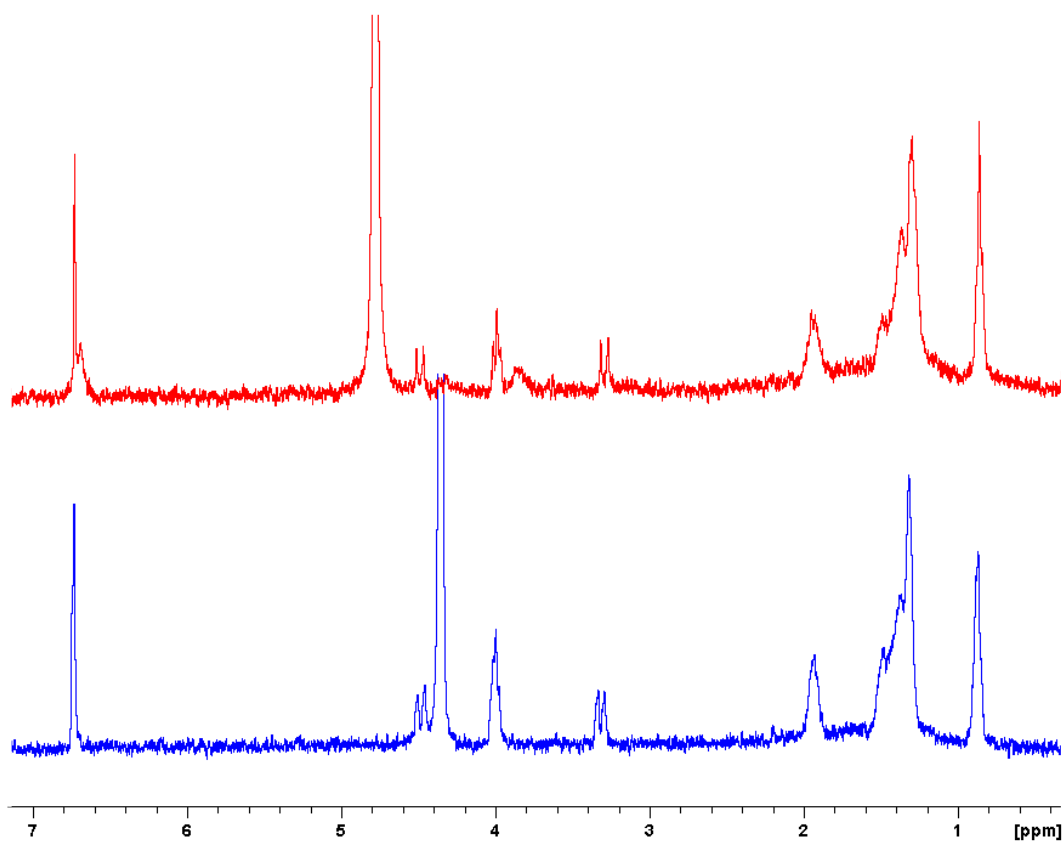




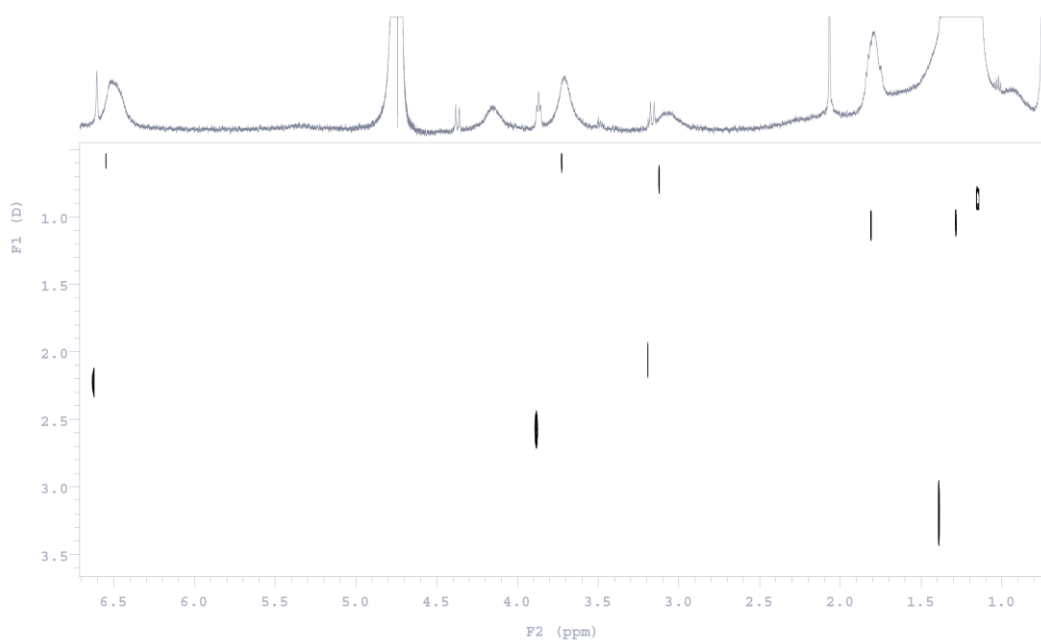


Overlapped spectra

S.5 ^1H NMR spectra of the aggregate and DOSY experiment



^1H NMR (300 MHz, D_2O) spectra of **3** (0.2 mM) recorded at 298 K (red) and 333 K (blue). The spectra clearly show a slow equilibrium between the compound in the solution and in the aggregate.



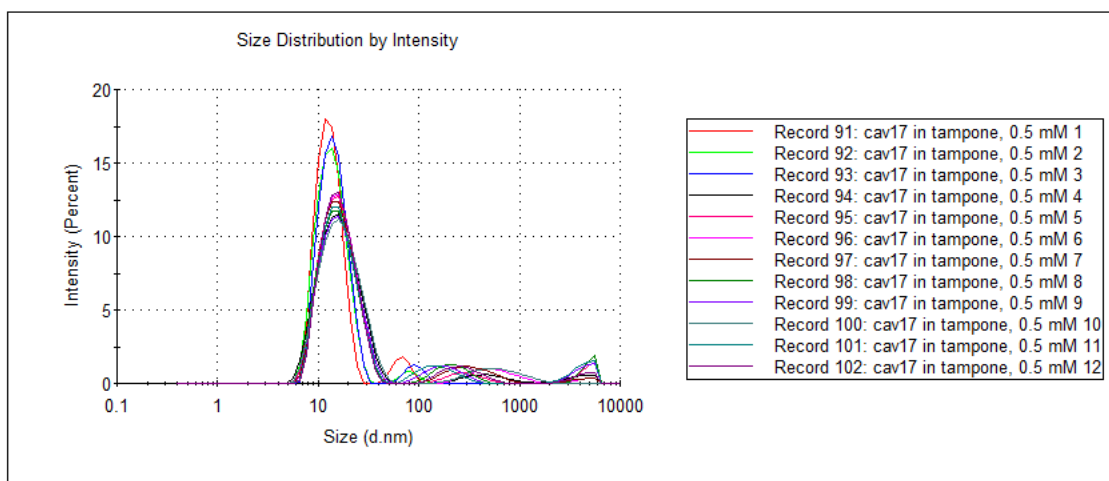
DOSY spectrum (600 MHz, 298 K) in D_2O of **3**. The spectrum shows a significant difference in dimensions for the aggregate and for the monomer.

S.6 Dynamic Light Scattering Measurements

Sample Name: cav17 in tampone, 0.5 mM 12
SOP Name: mansettings.nano
File Name: CAV17 29-04-2022.dts
Record Number: 102
Material RI: 1.45
Material Absorbtion: 0.001
Dispersant Name: Water
Dispersant RI: 1.330
Viscosity (cP): 0.8872
Measurement Date and Time: lunedì 2 maggio 2022 10:11:45

Temperature (°C): 25.1
Count Rate (kcps): 198.7
Cell Description: Disposable micro cuvette (40µl)
Duration Used (s): 80
Measurement Position (mm): 3.00
Attenuator: 8

	Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 16.72	Peak 1: 16.65	88.2	6.262
Pdl: 0.286	Peak 2: 276.8	8.6	115.5
Intercept: 0.927	Peak 3: 4324	3.1	964.2
Result quality : Good			



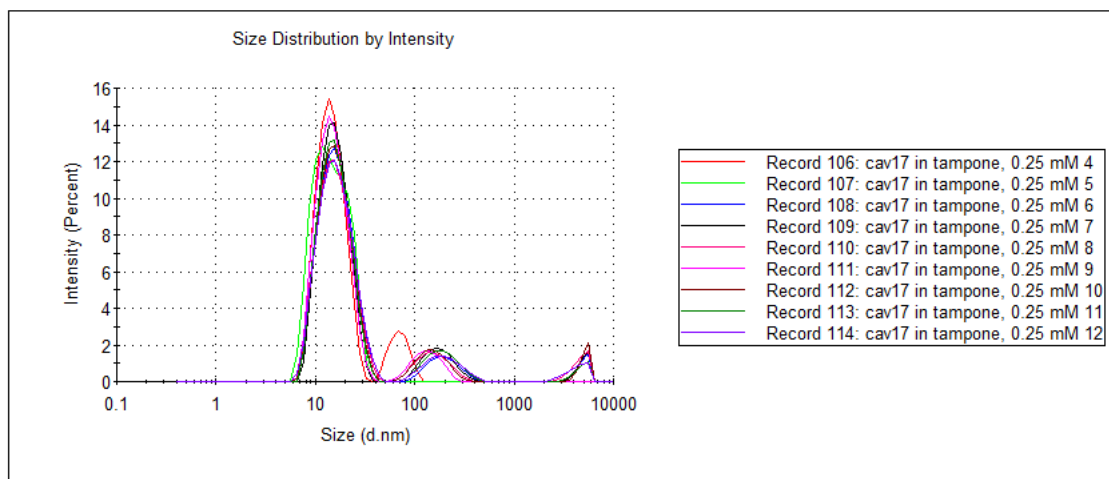
DLS measurement of a buffered solution of **3** (0.5 mM)

Sample Name: cav17 in tampone, 0.25 mM 12
SOP Name: mansettings.nano
File Name: CAV17 29-04-2022.dts
Record Number: 114
Material RI: 1.45
Material Absorbtion: 0.001
Dispersant Name: Water
Dispersant RI: 1.330
Viscosity (cP): 0.8872
Measurement Date and Time: lunedì 2 maggio 2022 10:58:13

Temperature (°C): 25.0
Count Rate (kcps): 306.1
Cell Description: Disposable micro cuvette (40µl)
Duration Used (s): 60
Measurement Position (mm): 3.00
Attenuator: 9

	Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 17.43	Peak 1: 16.97	85.6	6.727
Pdl: 0.320	Peak 2: 202.9	10.4	83.61
Intercept: 0.907	Peak 3: 4384	4.0	935.9

Result quality : Good



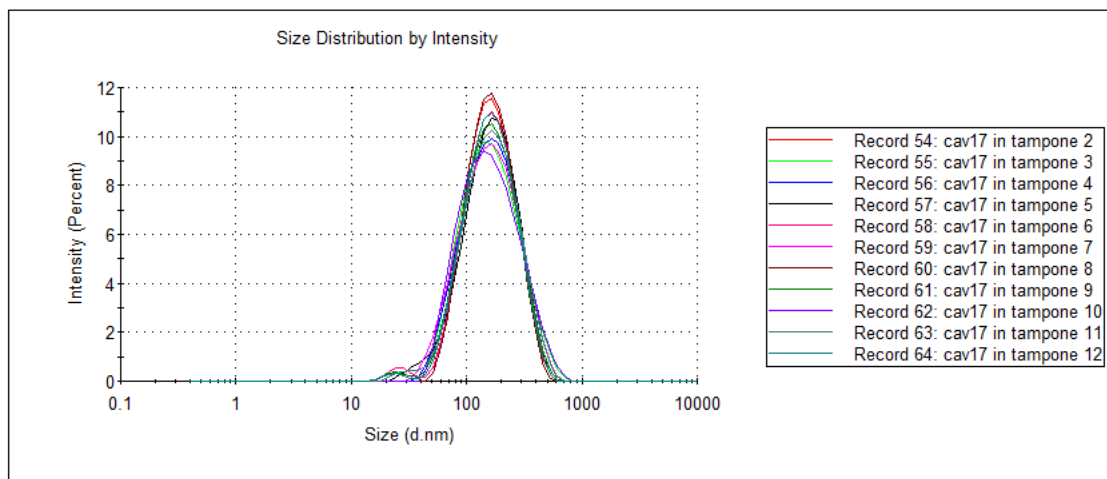
DLS measurement of a buffered solution of **3** (0.25 mM)

Sample Name: cav17 in tampone 2
SOP Name: mansettings.nano
File Name: CAV17 29-04-2022.dts
Record Number: 54
Material RI: 1.45
Material Absorbtion: 0.001
Dispersant Name: Water
Dispersant RI: 1.330
Viscosity (cP): 0.8872
Measurement Date and Time: lunedì 2 maggio 2022 08:37:39

Temperature (°C): 25.0
Count Rate (kcps): 380.7
Cell Description: Disposable micro cuvette (40µl)
Duration Used (s): 60
Measurement Position (mm): 3.00
Attenuator: 7

	Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 138.9	Peak 1: 178.4	100.0	84.96
Pdl: 0.208	Peak 2: 0.000	0.0	0.000
Intercept: 0.941	Peak 3: 0.000	0.0	0.000

Result quality : Good



DLS measurement of the same sample of **3** after 60 h.