Templated synthesis of a large and flexible covalent porphyrinic cage bearing orthogonal recognition sites

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Supporting Information

Contents

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1 General Procedures

Dry solvents were distilled from suitable drying agents (tetrahydrofurane from sodium/benzophenone, dichloromethane and chloroform from calcium hydride). Thin layer chromatography was carried out using pre-coated polymeric sheets of silica gel (Macheray-Nagel, POLYGRAM, SIL G/UV254). Preparative column chromatography was carried out using silica gel (Merck Kieselgel, silica gel 60, 0.063– 0.200 mm). The size exclusion column chromatography was carried out using Bio-Beads® S-X1 beads were swollen in toluene during one night before use. All chemicals were of best commercially available grade and used without further purification.

Mass spectra were obtained by using a Bruker MicroTOF spectrometer (ES-MS).

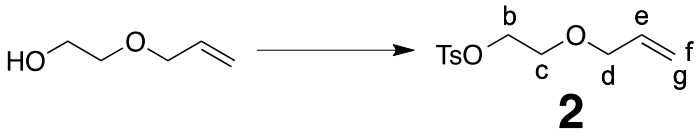
UV-visible spectra were recorded with a Kontron Instruments UVIKON 860 spectrometer at 21°C with a 1 cm path cell.

Nuclear Magnetic Resonance (NMR) spectra for ^{1}H and ^{13}C were acquired on Bruker AVANCE 300, 400, 500 or 600 spectrometers. The spectra were referenced to residual proton–solvent references (^{1}H: CD_2Cl_2 at 5.32 ppm, $CDCl_3$ at 7.26 ppm; ^{13}C: $CDCl_3$ at 77.16 ppm). In the assignments, the chemical shift (in ppm) is given first, followed, in brackets, by the assignment, the multiplicity of the signal (s: singlet, d: doublet, q: quadruplet, m: multiplet, bs: broad singlet), the value of the coupling constants in Hertz if applicable, and finally the number of protons implied. NMR experiments.

Measures of self-diffusion coefficients were performed on a BRUKER 600 MHz spectrometer - Avance III, equipped with a high strength z gradient probe DOTY Scientific, developing a pulse field gradient of 50 G/cm/A. The gradient coil is cooled by air flow and the sample was thermostated at 298 or 300 K. Diffusion NMR data were acquired using a Stimulated Echo pulse sequence with bipolar z gradients. Limited Eddy current Delay was fixed to 5 ms. The gradient strength varied linearly between 6 and 305 G / cm in 30 experiments. The diffusion time and the duration of the sinusoidal gradients were optimized for each sample. Typically the diffusion time was set between 8 and 10 ms, and the half-gradient delay between 600 and 900 ºs. The gradient recovery delay was set to 100 ºs. A recycling delay of 3 s was respected between scans. DOSY NMR Processing. DOSY spectra are generated by the DOSY module of the software NMRNotebook, using Inverse Laplace Transform (ILT) driven by maximum entropy, to build the diffusion dimension. An exponential line broadening apodization of 1 Hz was applied to the spectral axis and baseline offset was corrected before DOSY calculation. Intensities of selected NMR peaks were processed by ILT. The final DOSY spectra were obtained with 128 points in the diffusion dimension and 1000 MaxEnt iterations. Dynamic viscometry. Solvent viscosities at different temperatures were measured using a falling ball micro-viscometer Anton Paar, at 298 and 300 K (thermostat Peltier effect).

2 Experimental Procedures

2.1 Synthesis of the allyloxyethyl tosylate (2)

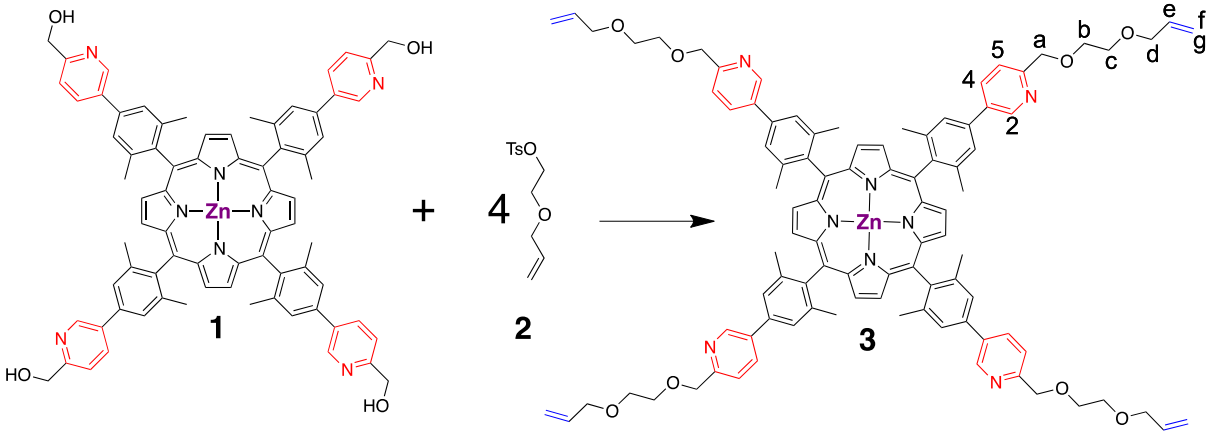


2

In a dry round bottom flask, allyloxyethanol (506 mg, 4.96 mmol, 1 eq), DMAP (18.2 mg, 0.147 mmol, 3 mol%) and triethylamine (3.45 mL, 24.8 mmol, 5 eq) were added in 10 mL of freshly distilled dichloromethane. This solution was cooled at 0°C and was degassed (3 cycles). Then tosyl chloride (2.36 g, 12.4 mmol, 2.5 eq) was added portion wise, 0,5 hour later the ice bath was removed and the reaction was let over argon at room temperature overnight. The reaction was then poured in a mixture of HCl (10%) and ice. The resulting solution was extracted with dichloromethane. The organic layer was then washed with water and brine. The organic layer was dried and evaporated. The residual oil was purified by chromatography on silica gel using dichloromethane/methanol (100/0.5 to 95/5) as the mobile phase. Removal of the solvent furnished 1.17 g (92% yield) of **2** as a pale yellow oil.

NMR ^{1}H (300 MHz) ($CDCl_3$) : δ = 7.79 (H ortho, d, J = 7.9 Hz, 2H), 7.32 (H meta, d, J = 7.9 Hz, 2H), 5.80 (He, ddt, J = 17.2 Hz, 10.4 Hz, 5.7 Hz, 1H), 5.20 (Hg, dq, J = 17.2 Hz, 1.6 Hz, 1H), 5.14 (Hf, dq, J = 10.4 Hz, 1.5 Hz, 1H), 4.15 (Hb, t, J = 4.8 Hz, 2H), 3.93 (Hd, dt, J = 5.7 Hz, 1.5 Hz, 2H), 3.61 (Hc, t, J = 4.8 Hz, 2H), 2.43 (H_3C-Ar, s, 3H).

2.2 Synthesis of the zinc(II) *meso*-tetrakis[2,6-dimethyl-4-(6-((2-allyloxy)ethoxy)methylpyrid-3-yl)phenyl]porphyrin (3)



In a dry round bottom flask containing anhydrous DMF (1.1 mL) **1**[1] (26 mg, 21.3 µmol, 1 eq) was added. After complete dissolution sodium hydride (8.5 mg, 213 µmol, 10 eq) was added portion wise. Reaction's color changed from dark violet to a dark greenish violet. Then **2** (55 mg, 213 µmol, 10 eq) was injected in the reaction and the mixture was allowed to heat at 70°C overnight under argon. The DMF was evaporated and the residue was dissolved in dichloromethane. This solution was then washed with water and brine. The organic layers were combined and volatiles were evaporated. The crude solid was purified by chromatography on silica gel using dichloromethane/methanol (100/0.5 to 95/5) as the mobile phase. Removal of the solvent furnished 28 mg (84% yield) of **3** as a dark purple solid.

NMR ^{1}H (300 MHz) (CD_2Cl_2) : δ = 8.79 (H pyr, s, 8H), 7.95 (H_4, d, *J* = 7.9 Hz, 4H), 7.80 (H_2, bs, 4H), 7.50 (H_{Ar}, s, 8H), 7.33 (H_5, d, *J* = 8.0 Hz, 4H), 5.89 (He, ddt, J = 17.3 Hz, 10.4

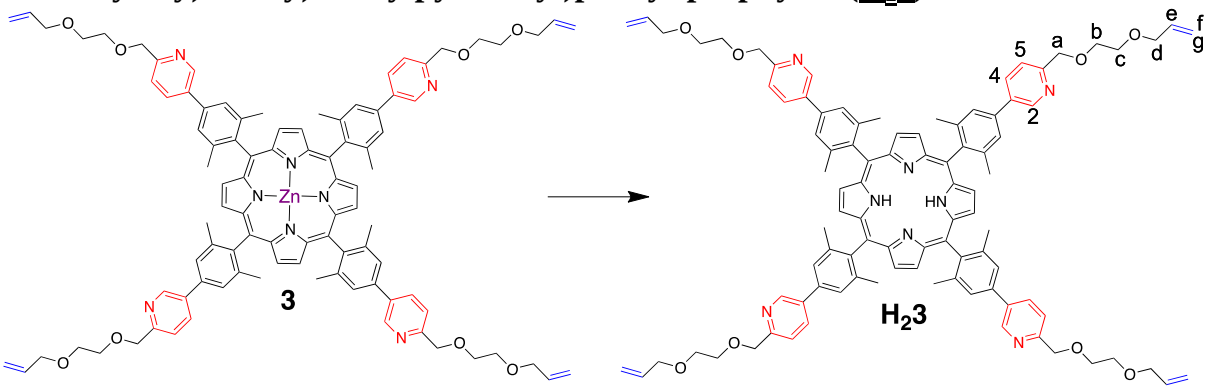
Hz, 5.5 Hz, 4H), 5.25 (Hg, dq, J = 17.3 Hz, 1.7 Hz, 4H), 5.14 (Hf, dq, J = 10.4 Hz, 1.5 Hz, 4H), 3.97 (Hd, dt, J = 5.5 Hz, 1.6 Hz, 8H), 3.77 (Ha, bs, 8H), 3.53 (Hb, Hc, m, 16H), 1.96 (H_3C-Ar, s, 24H).

NMR ^{13}C (75 MHz) ($CDCl_3$) : δ = 157.0, 149.7, 147.1, 142.2, 140.5, 137.0, 135.6, 135.5, 134.8, 131.3, 125.7, 121.5, 118.0, 117.3, 73.33, 72.42, 70.41, 69.47, 22.19.

HR ES-MS: [M^+] m/z (%) = 1554.675 (100) (exp), (calcd. for $C_{96}H_{96}N_8O_8Zn_2$ 1554.665).

UV-vis (toluene): λ(nm) (log(ε)) 423 (5.57), 550 (4.26), 586 (3.39)

2.3 Synthesis of the *meso*-tetrakis[2,6-dimethyl-4-(6-((2-allyloxy)ethoxy)methylpyrid-3-yl)phenyl]porphyrin ($\underline{H_2}$**3**)

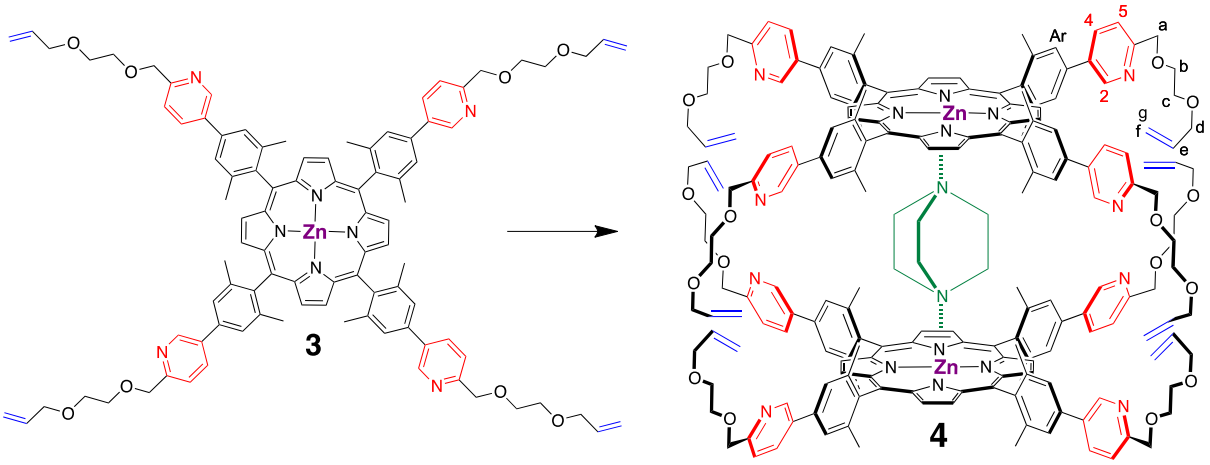


To a stirred solution of **3** (10 mg, 6.43 µmol) in dichloromethane (15mL), was added dropwise a 50% (v/v) solution of trifluoroacetic acid in dichloromethane until the solution's color changed from deep purple to green. The green solution was then poured into a separatory funnel containing a saturated solution of sodium carbonate (15 mL), after mixing the organic layer's color changed from green to purple. The aqueous layer was removed, and the organic phase was washed three times with distilled water, the pH of the last aqueous layer was measured (pH=7) and the organic phase was dried over $MgSO_4$. The mixture was filtered and then evaporated affording compound $\underline{\mathbf{H_2}}\mathbf{3}$ as a purple solid (9.6 mg, 100 % yield).

NMR ^1H (300 MHz) ($CDCl_3$) : δ = 9.08 (H_2, d, *J* = 2.1 Hz, 4H), 8.70 (H pyr, s, 8H), 8.20 (H_4, dd, *J* = 8.1 Hz, 2.2 Hz, 4H), 7.68 (H_{Ar}, s, 8H), 7.68 (H_5, d, *J* = 8.0 Hz, 4H), 5.97 (He, ddt, J = 17.3 Hz, 10.5 Hz, 5.7 Hz, 4H), 5.33 (Hg, dq, J = 17.2 Hz, 1.6 Hz, 4H), 5.22 (Hf, dq, J = 10.4 Hz, 1.4 Hz, 4H), 4.83 (Ha, s, 8H), 4.10 (Hd, dt, J = 5.6 Hz, 1.4 Hz, 8H), 3.79 (Hb, Hc, m, 16H), 1.96 (H_3C-Ar, s, 24H), -2,43 (NH, s, 2H).

UV-vis (dichloromethane/acetonitrile): λ(nm) 418, 514, 546, 590, 646

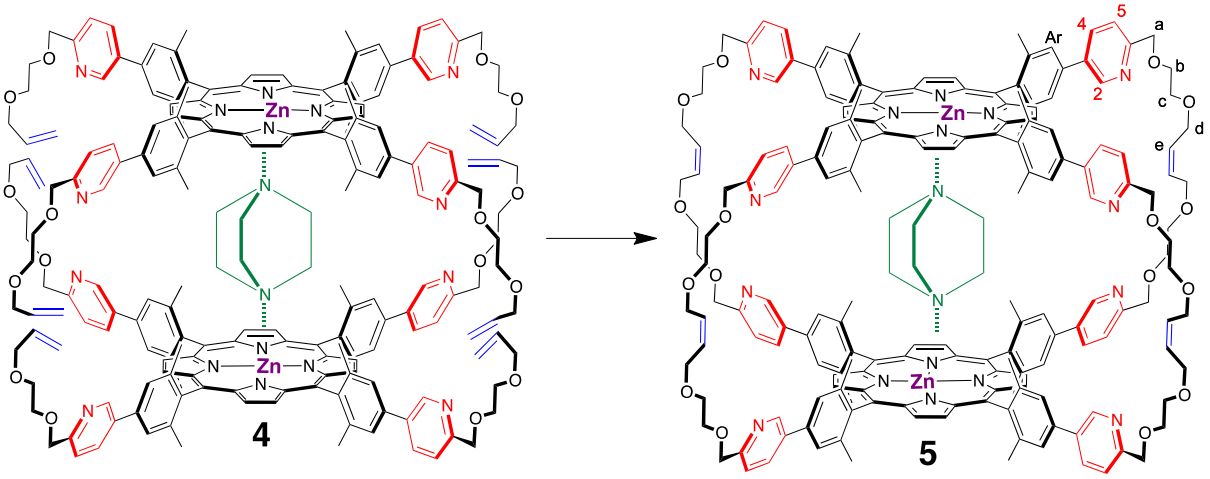
2.4 Synthesis of the DABCO-templated dimer (4)



In a dry round bottom flask under argon, **3** (3.7 mg, 2.38 µmol, 1 eq) was dissolved in 500 µL of deuterated dichloromethane. A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO) in DCM-d2 (1.05 mM, 113 µL, 0.5 eq) was then injected. The resulting mixture was poured into a NMR-tube and then a spectrum was recorded.

NMR ^{1}H (500 MHz) (CD_2Cl_2, 193K) : δ = 9.04 (H_2, s, 8H), 8.37 (H pyr, s, 16H), 8.22 (H_4, d, *J* = 7.09 Hz, 8H), 7.79 (H_{Arout}, s, 8H), 7.65 (H_5, d, *J* = 7.34 Hz, 8H), 7.50 (H_{Arin}, s, 8H), 5.95 (He, m, 8H), 5.32 (Hg, m, 8H), 5.20 (Hf, bd, J = 10.7 Hz, 8H),4.74 (Ha, s, 16H), 4.03 (Hd, m, 16H), 3.78 (Hb, m, 16H), 3.68 (Hc, m, 16H), 1.89 (H_3C-Ar out, bs, 24H), 1.18 (H_3C-Ar in, bs, 24H), -4.06 (H_{DABCO}, s, 12H).

2.5 Synthesis of the DABCO-included cage (5)



In a dry round bottom flask under argon, **3** (37 mg, 23.8 µmol, 1 eq) was dissolved in freshly distilled DCM. A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO) (1.05 mM, 1.13 mL, 0.5 eq) was injected into the porphyrin solution. The mixture was then degassed (three vacuum/argon cycles), and second generation Grubbs' catalyst was quickly added (10.1 mg, 11.9 µmol, 0.5 eq). The reaction was allowed to react at room temperature, after 4 hours of reaction a second part of catalyst was added (10.1 mg, 11.9 µmol, 0.5 eq), then reaction was stirred for 14 hours. Then the reaction mixture was then poured into a separatory funnel containing distillated water (50 mL), and the organic layer was extracted and then washed with brine. The solvent was evaporated under vacuum and toluene (5 mL) was added. The

resulting solution was then deposed on a Bio-Beads® column eluted with toluene, and the purple band was collected and evaporated affording compound **5** (20.8 mg, 56 % yield).

NMR ^{1}H (300 MHz) (CD_2Cl_2) : δ = 9.05 (H_2, d, *J* = 1,54 Hz, 8H), 8.41 (H pyr, s, 16H), 8.26 (H_4, dd, *J* = 8.13 Hz, 2,34 Hz, 8H), 7.75 (H_{Arout}, s, 8H), 7.69 (H_5, d, *J* = 8.11 Hz, 8H), 7.61 (H_{Arin}, s, 8H), 5.95 (He, m, 8H), 4.78 (Ha, s, 16H), 4.16 (Hd, m, 16H), 3.83 (Hb, m, 16H), 3.77 (Hc, m, 16H), 1.76 (H_3C-Ar out, bs, 24H), 1.46 (H_3C-Ar in, bs, 24H), -4.07 (H_{DABCO}, s, 8H), -4.13 (H_{DABCO}, s, 4H).

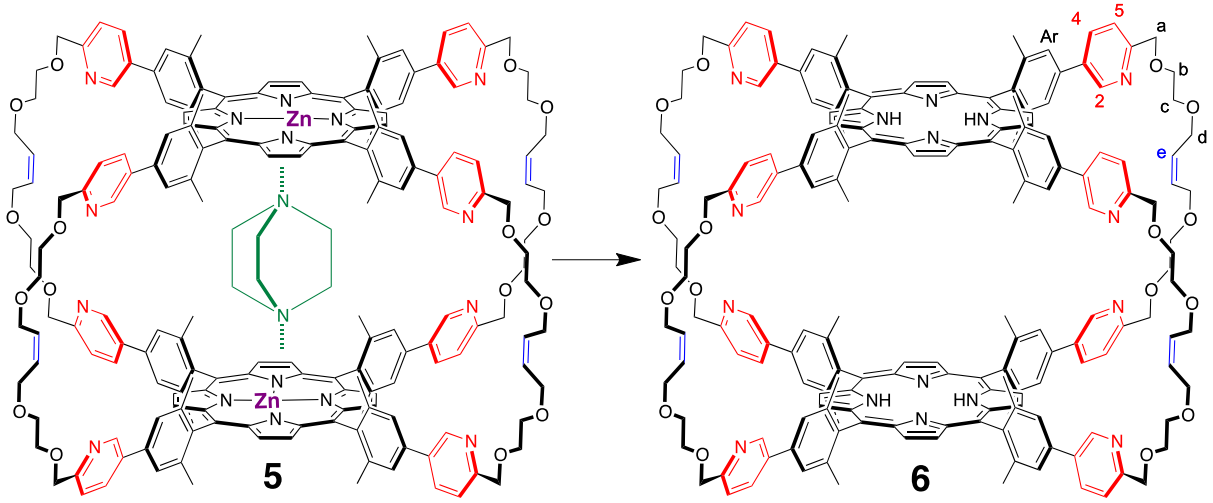
NMR ^{13}C (150 MHz) ($CDCl_3$) : δ = 157.5, 149.2, 147.7, 141.9, 140.8, 139.0, 137.4, 135.5, 130.7, 129.8, 125.7, 121.8, 117.2, 74.25, 71.71, 70.66, 70.63, 21.77

ES-MS: [M(without DABCO)+2Na^+] m/z (%) = 1522.600 (100) (exp), (calcd. for $C_{184}H_{176}N_{16}O_{16}Zn_2Na_2$ 1522.600).

HR ES-MS: [M(without DABCO)+Na^++H^+] m/z (%) = 1511.094 (100) (exp), (calcd. for $C_{184}H_{176}N_{16}O_{16}Zn_2HNa$ 1511.101).

UV-vis (toluene): λ(nm) (log(ε)) 426 (6.11), 562 (4.66), 601 (4.33)

2.6 Synthesis of the cage (6)



To a stirred solution of **5** (15 mg, 4.82 µmol) in dichloromethane (15mL), was added dropwise a 50% (v/v) solution of trifluoroacetic acid in dichloromethane until the solution's color changed from deep purple to green. The green solution was then poured into a separatory funnel containing a saturated solution of sodium carbonate (15 mL), after mixing the organic layer's color changed from green to purple. The aqueous layer was removed, and the organic phase was washed three times with distilled water, the pH of the last aqueous layer was measured (pH=7) and the organic phase was dried over $MgSO_4$. The mixture was filtered and then evaporated. The residue was then deposed on a Bio-Beads® column eluted with toluene, and the purple band was collected and evaporated affording compound **6** as a purple solid (13.8 mg, 100 % yield).

NMR ^{1}H (300 MHz) ($CDCl_3$) : δ = 8.98 (H_2, d, *J* = 1.66 Hz, 8H), 8.37 (H pyr, s, 16H), 8.13 (H_4, dd, *J* = 8.24 Hz, 2.12 Hz, 8H), 7.70 (H_5, d, *J* = 7.88 Hz, 8H), 7.58 (H_{Arout}, s, 8H), 7.23 (H_{Arin}, s, 8H), 5.95 (He, m, 8H), 4.86 (Ha, s, 16H), 4.16 (Hd, m, 16H), 3.85 (Hb, m, 16H), 3.78 (Hc, m, 16H), 1.85 (H_3C-Ar_{out}, bs, 24H), 0.96 (H_3C-Ar_{in}, bs, 24H), -2.92 (N-H, s, 4H)

ES-MS: : $[M+2H^+]$ m/z (%) = 1436.691 (100) (exp), (calcd. for $C_{184}H_{180}N_{16}O_{16}Zn_2H_2$ 1436.699), $[M+H^+]$ 2872.375(exp), (calcd. for $C_{184}H_{180}N_{16}O_{16}Zn_2H$ 2872.391).

HR ES-MS: $[M+2H^+]$ m/z (%) = 1436.691 (100) (exp), (calcd. for $C_{184}H_{180}N_{16}O_{16}Zn_2H_2$ 1436.699).

UV-vis (dichloromethane/acetonitrile): λ(nm) (log(ε)) 415 (5.88), 514, 546, 590, 646

3 Compounds characterizations

3.1 allyloxyethyl tosylate (2)

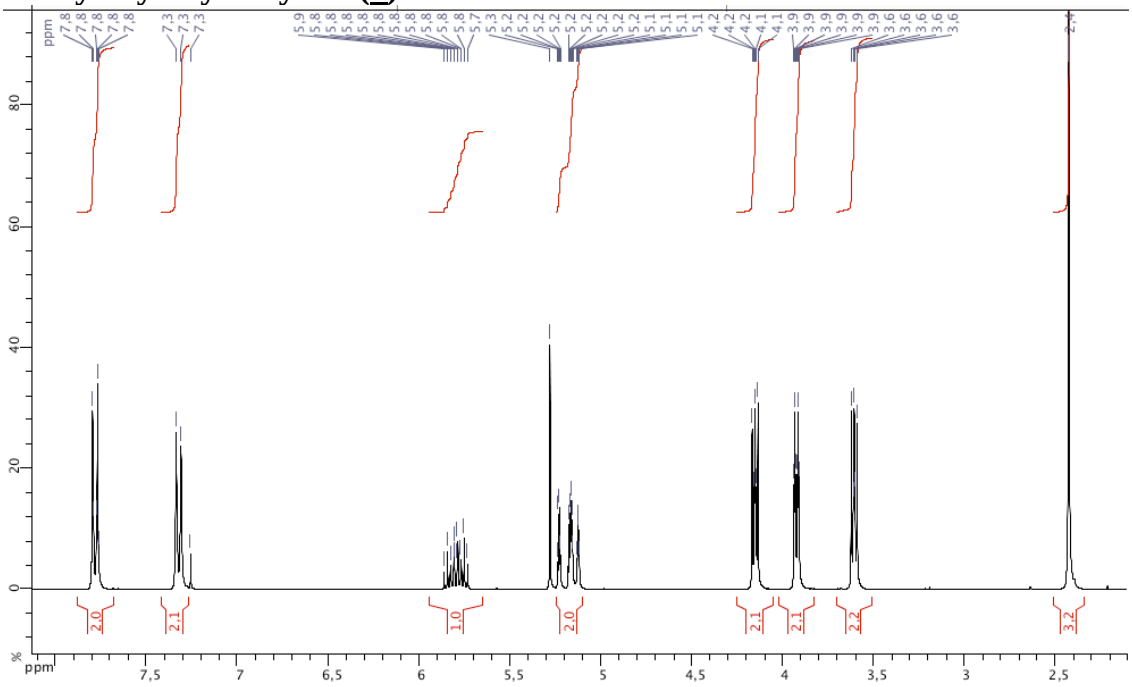


Figure 1. ^{1}H-NMR spectrum of 2 in $CDCl_3$ at 298K (300 MHz).

3.2 *meso*-tetrakis[2,6-dimethyl-4-(6-((2-allyloxy)ethoxy)methylpyrid-3-yl)phenyl]porphyrin (3)

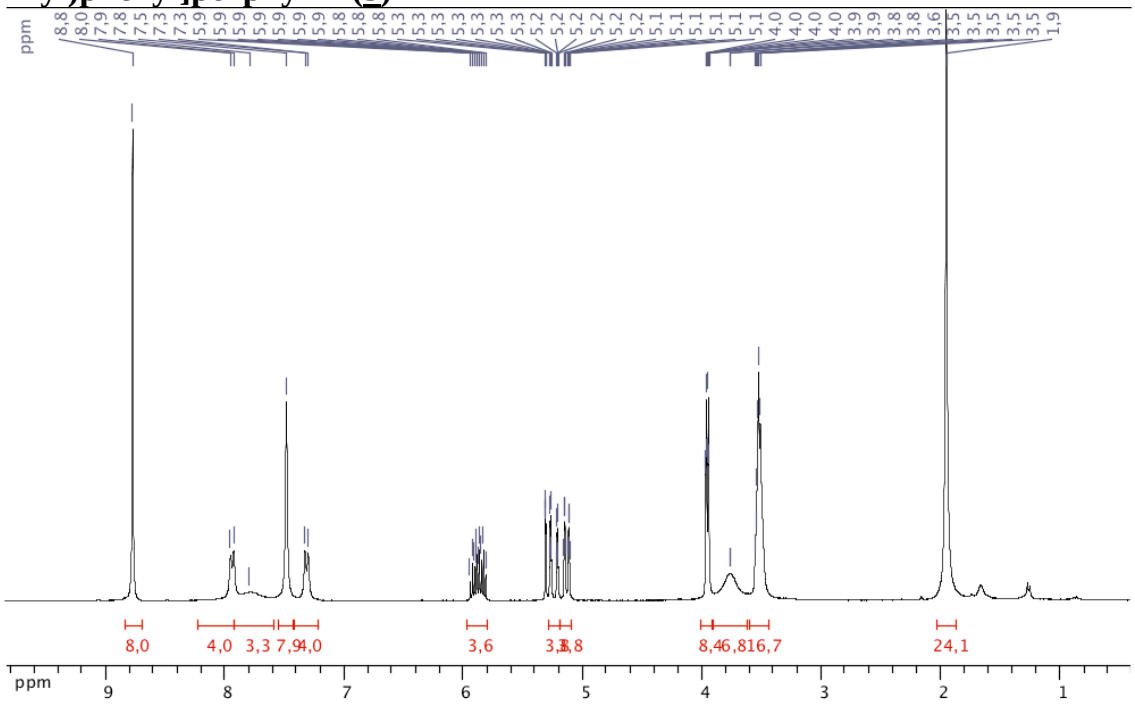


Figure 2. ^{1}H-NMR spectrum of 3 in CD_2Cl_2 at 298K (300 MHz).

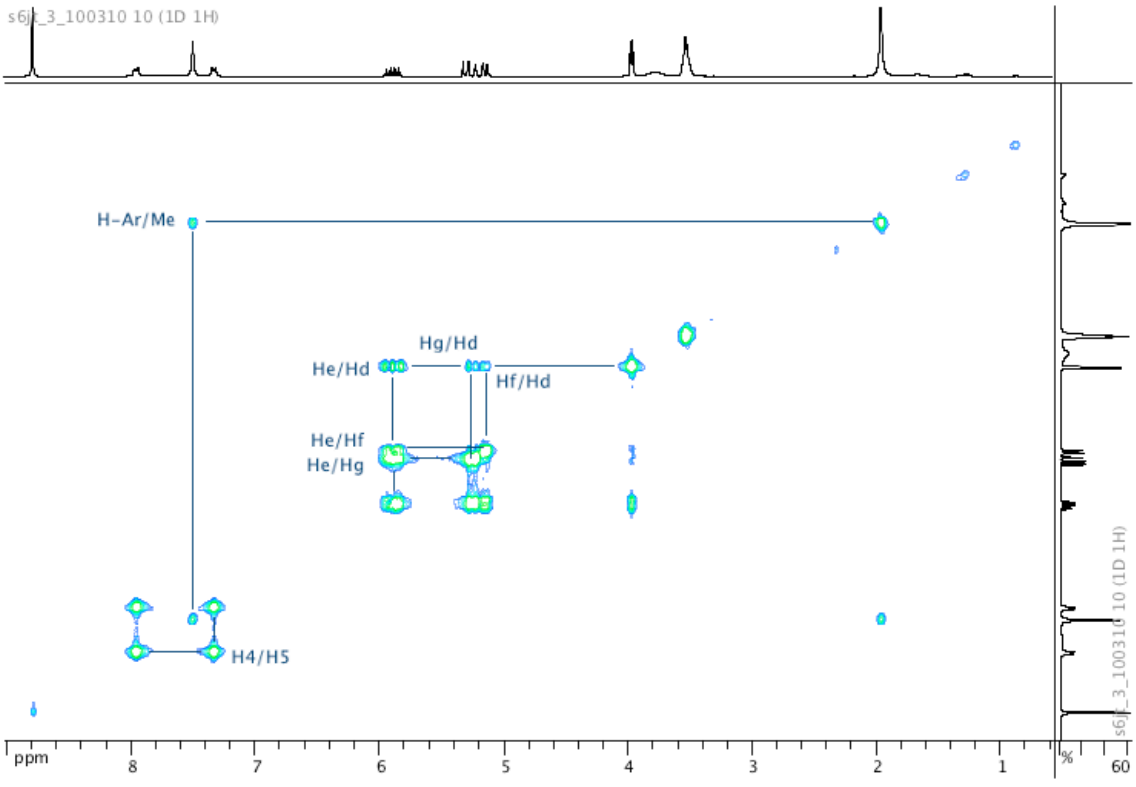


Figure 3. COSY ^{1}H/^{1}H-NMR spectrum of 3 in CD_2Cl_2 at 298K (300 MHz).

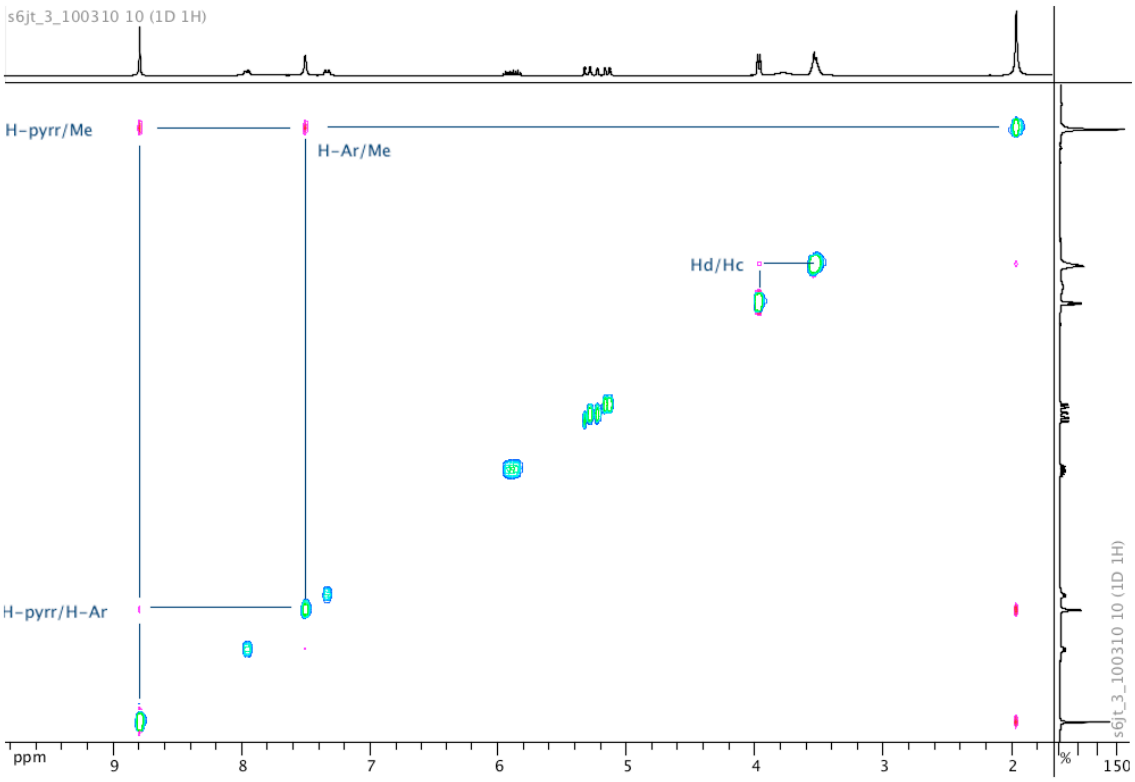


Figure 4. ROESY $^{1}H/^{1}H$-NMR spectrum of 3 in CD_2Cl_2 at 298K (300 MHz).

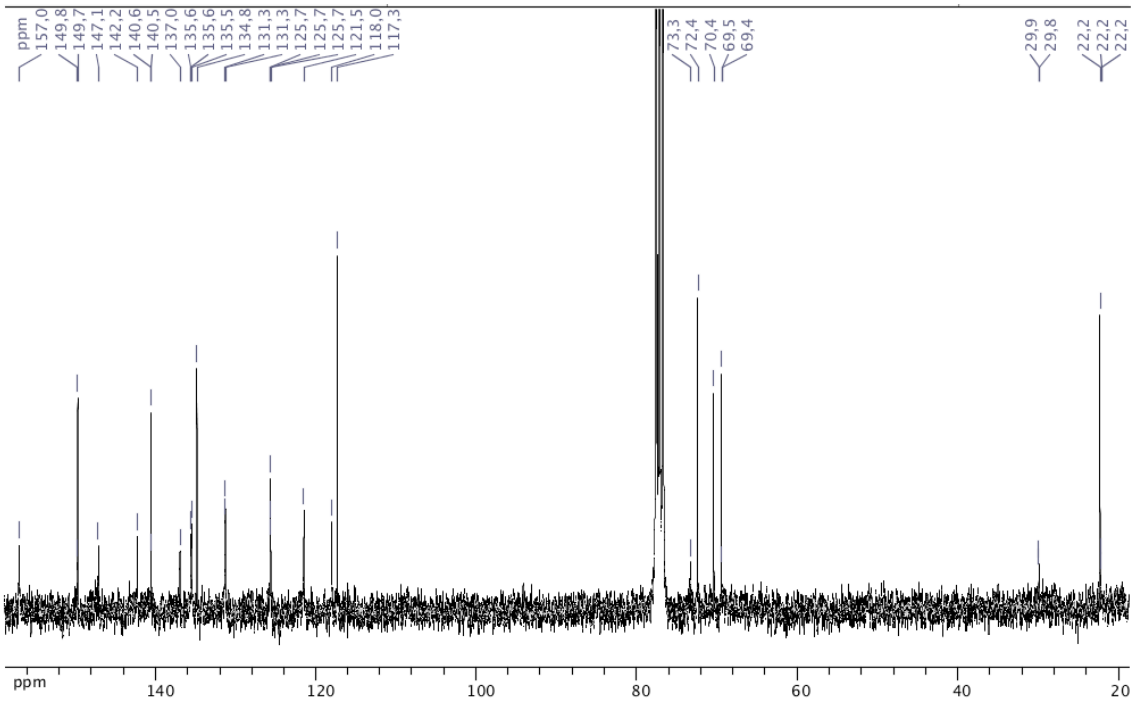


Figure 5. ^{13}C-NMR spectrum of 3 in $CDCl_3$ at 298K (75 MHz).

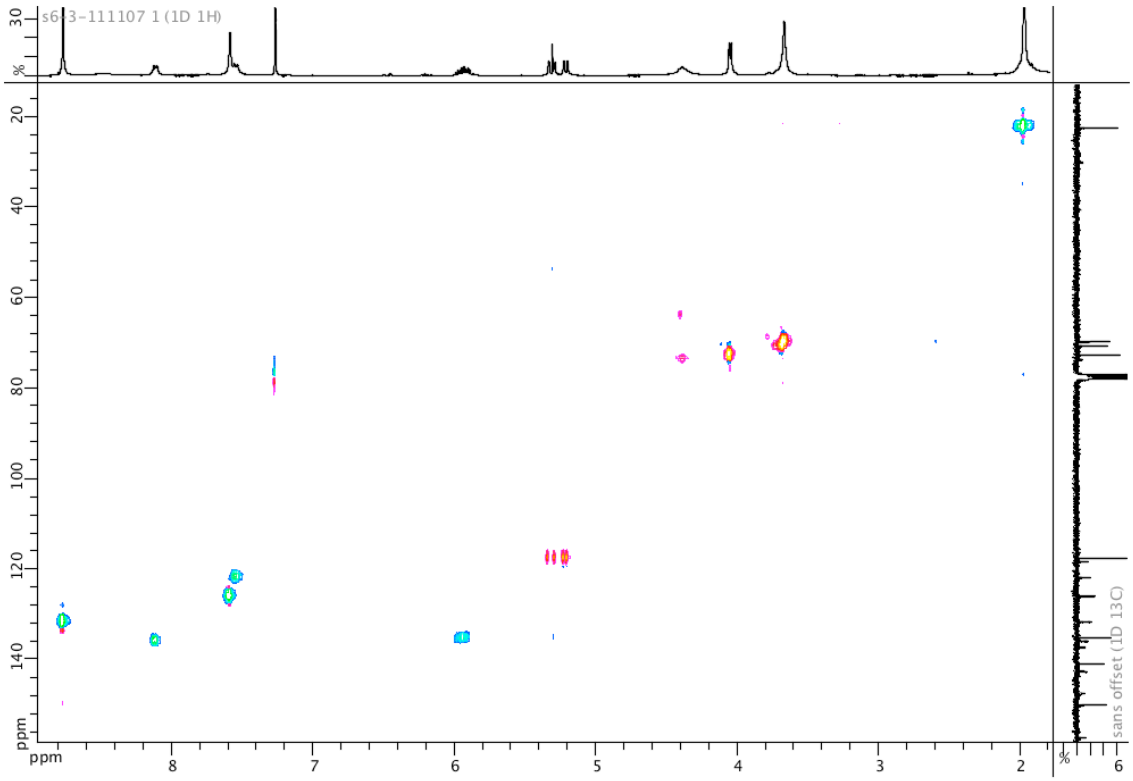


Figure 6. HSQC $^{1}H/^{13}C$-NMR spectrum of 3 in $CDCl_3$ at 298K (300 MHz).

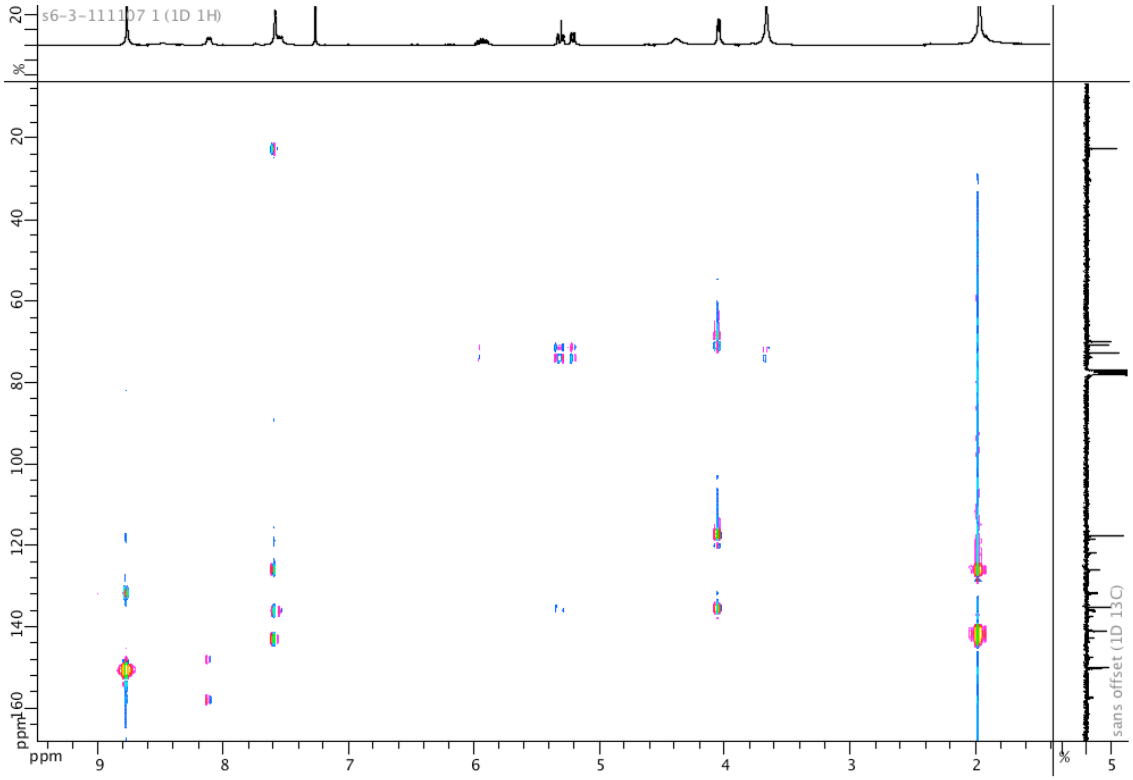


Figure 7. HMBC 1H/13C-NMR spectrum of 3 in CDCl3 at 298K (300 MHz).

Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name	O15447ML.d	Acquisition Date	9/28/2011 9:55:26 AM
Method	esi wide pos.m	Operator	Administrator
Sample Name	TalkP	Instrument	micrOTOF
Comment			

Acquisition Parameter

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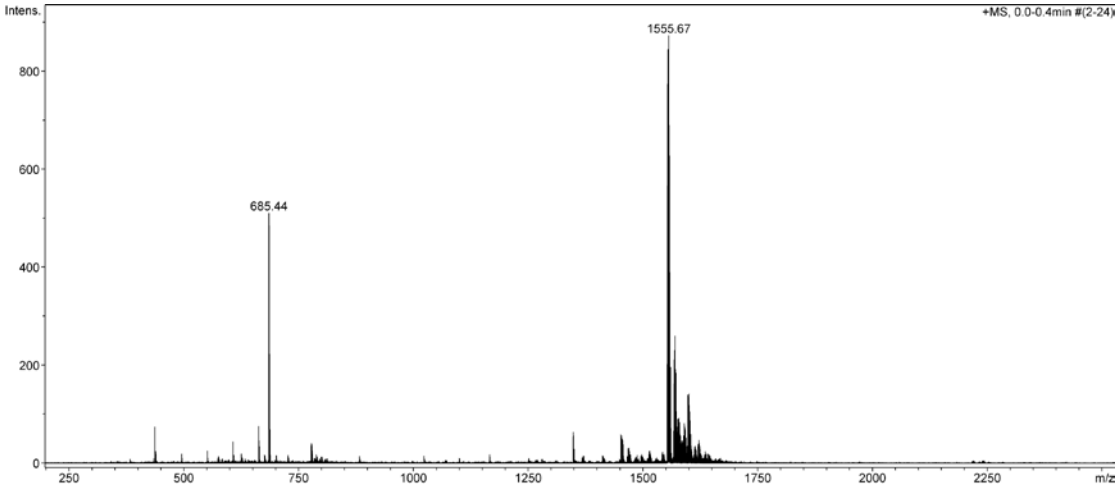

Bruker Daltonics DataAnalysis 3.1 printed: 9/28/2011 10:01:34 AM Page 1 of 1

Figure 8. ES-MS spectrum of 3.

Mass Spectrum Molecular Formula Report

Analysis Info

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Method	esi wide pos.m	Operator	Administrator
Sample Name	TalkP	Instrument	micrOTOF 66
Comment			

Acquisition Parameter

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Scan Begin	50 m/z	Hexapole RF	300.0 V	Set Pulsar Push	799 V
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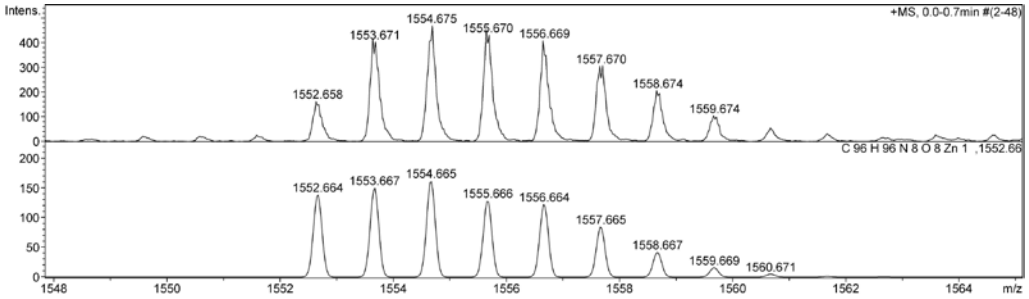
		Hexapole 1	24.3 V	Set Flight Tube	8600 V
				Set Detector TOF	2050 V



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C 96 H 95 N 8 O 8 Zn 1	0.42	1551.656	0.97	-7.76	53.50	ok	even
C 96 H 94 N 8 O 8 Zn 1	0.59	1550.648	-5.03	-12.00	54.00	-	odd
C 96 H 93 N 8 O 8 Zn 1	0.70	1549.640	-9.79	-16.79	54.50	ok	even

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Figure 9. HRMS spectrum of compound 3.

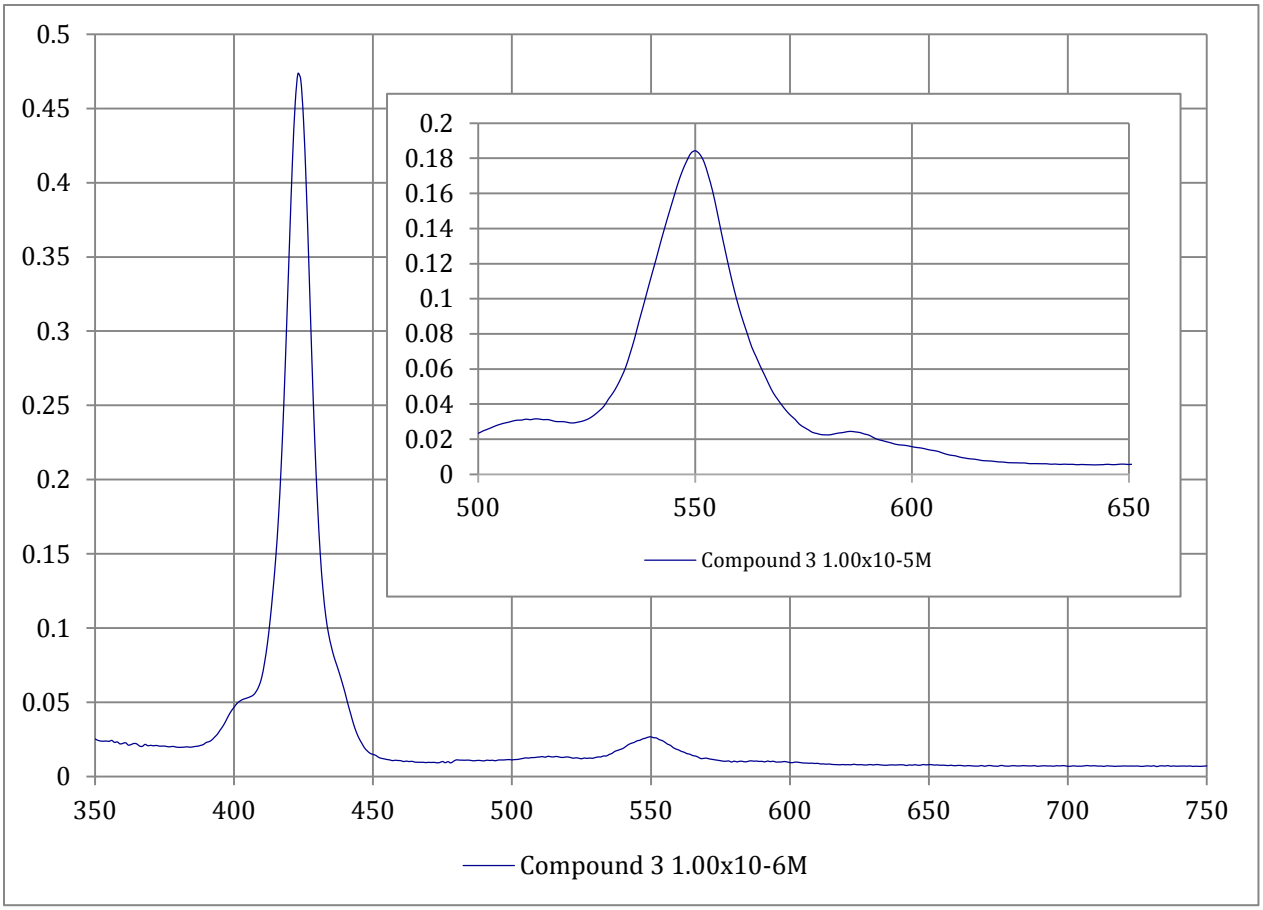

Figure 10. UV-vis. absorption spectra of 3 in toluene.

3.3 *meso*-tetrakis[2,6-dimethyl-4-(6-((2-allyloxy)ethoxy)methylpyrid-3-yl)phenyl]porphyrin ($H_2$3)

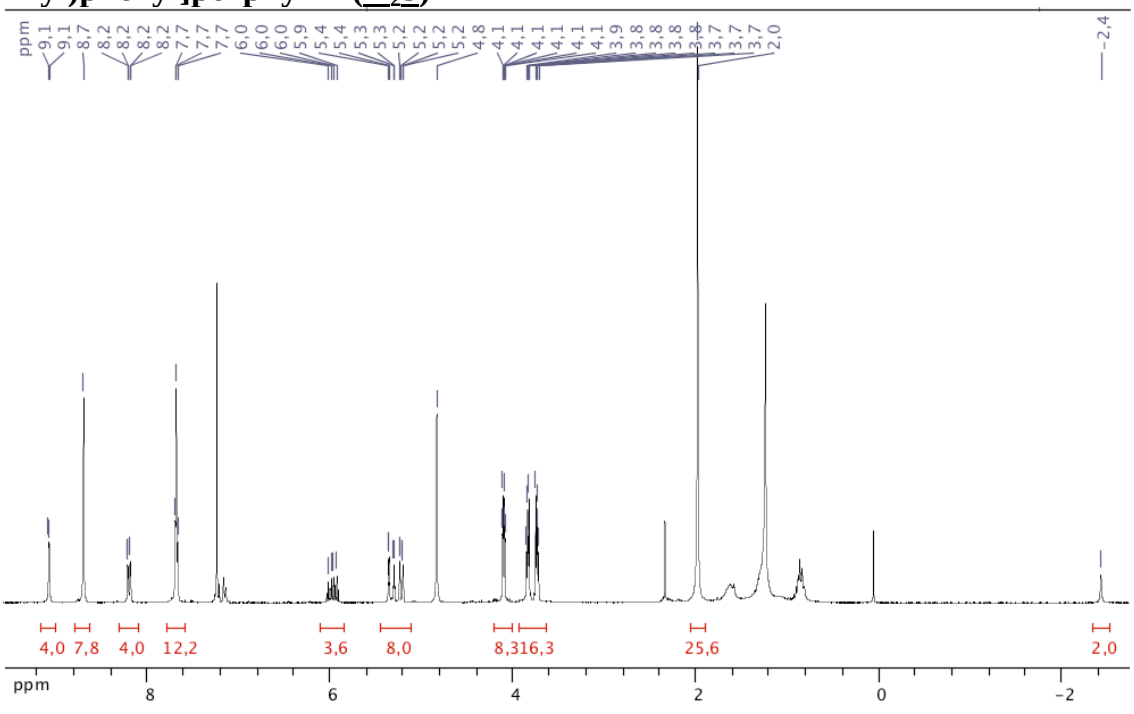

Figure 11. ^{1}H-NMR spectrum of $H_2$3 in $CDCl_3$ at 298K (300 MHz).

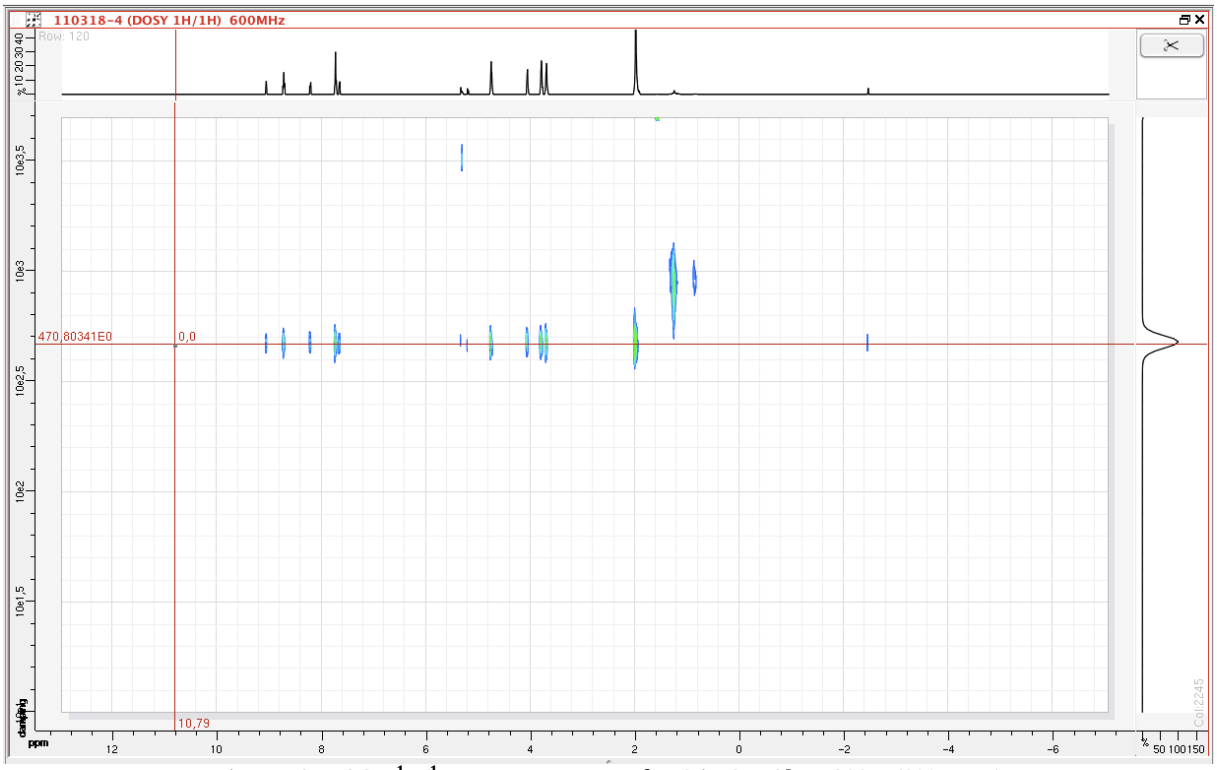

Figure 12. DOSY $^{1}H/^{1}H$-NMR spectrum of H23 in CD_2Cl_2 at 298K (600 MHz) D = 470 µm^2.s^{-1}.

3.4 DABCO-templated dimer (4)

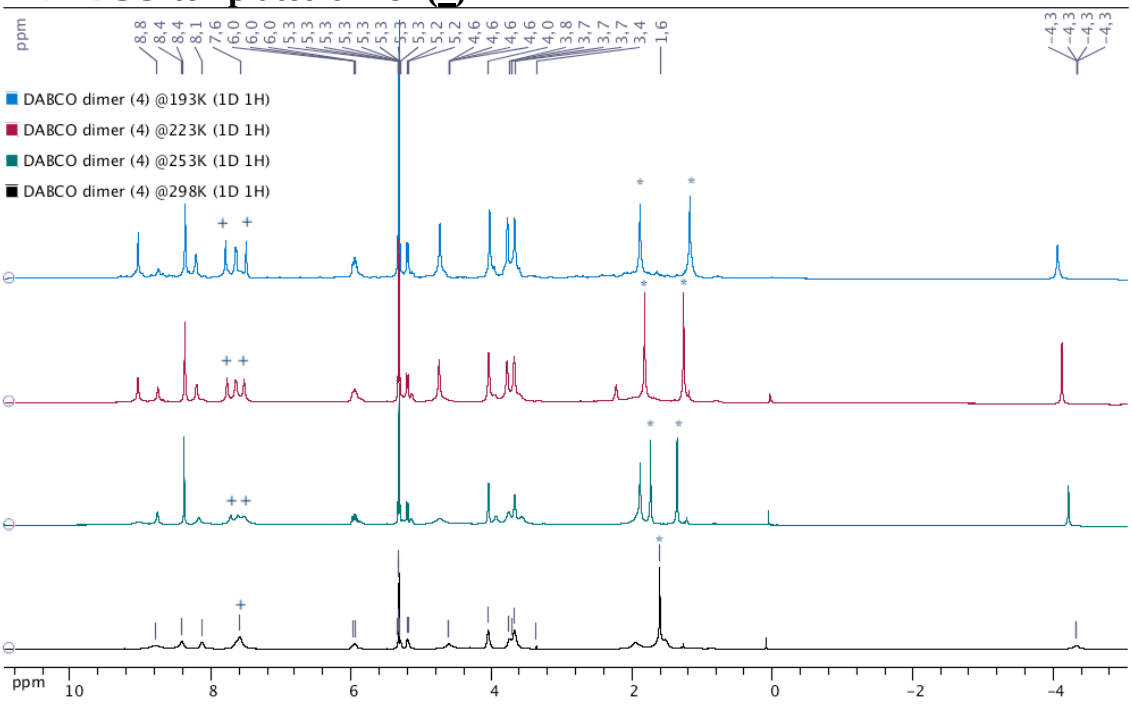

Figure 13. Variable temperature ^{1}H-NMR spectra of 4 in CD_2Cl_2 (500MHz) signal splitting +: HAr protons *: HMe protons.

3.5 DABCO-included cage (5)

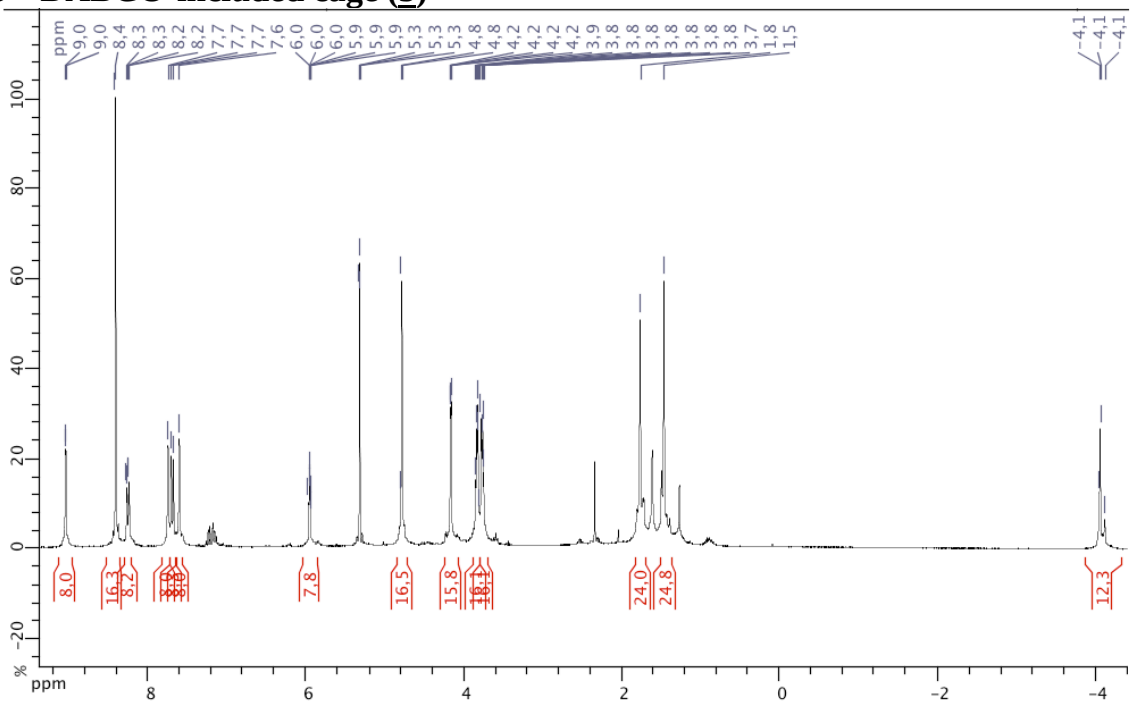

Figure 14. ^{1}H-NMR spectrum of 5 in CD_2Cl_2 at 298K (300 MHz).

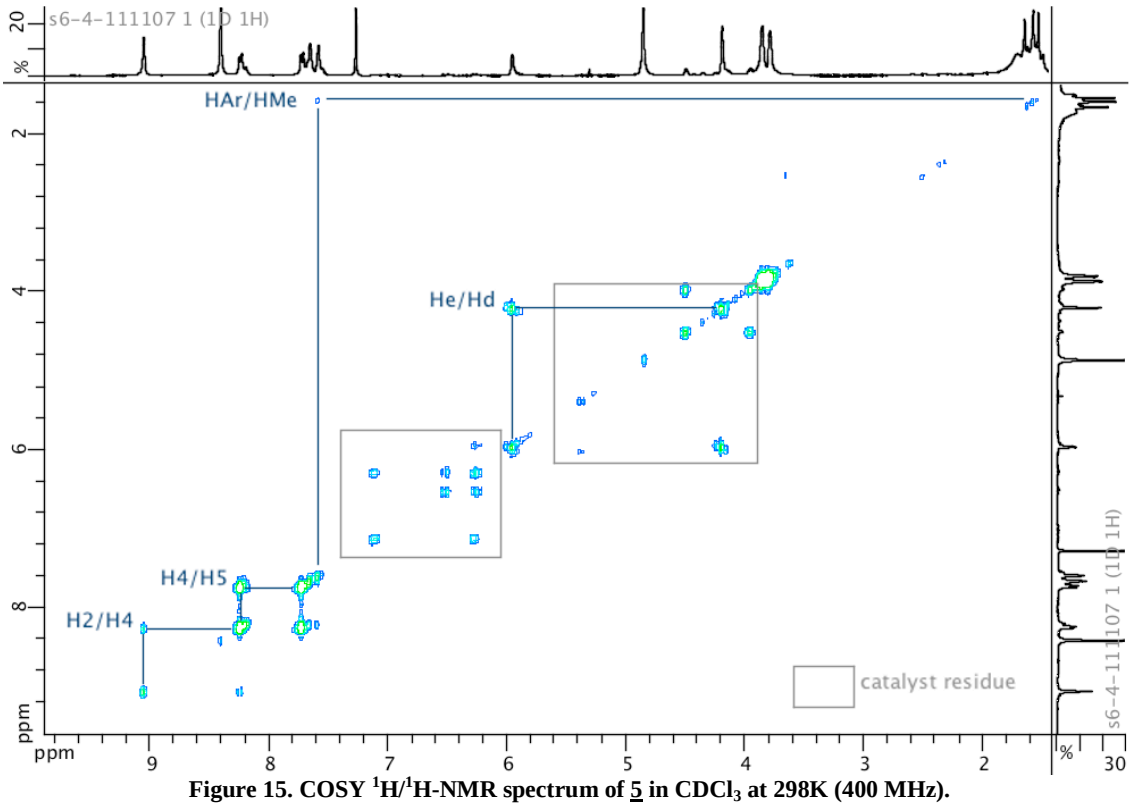

Figure 15. COSY ^{1}H/^{1}H-NMR spectrum of 5 in $CDCl_3$ at 298K (400 MHz).

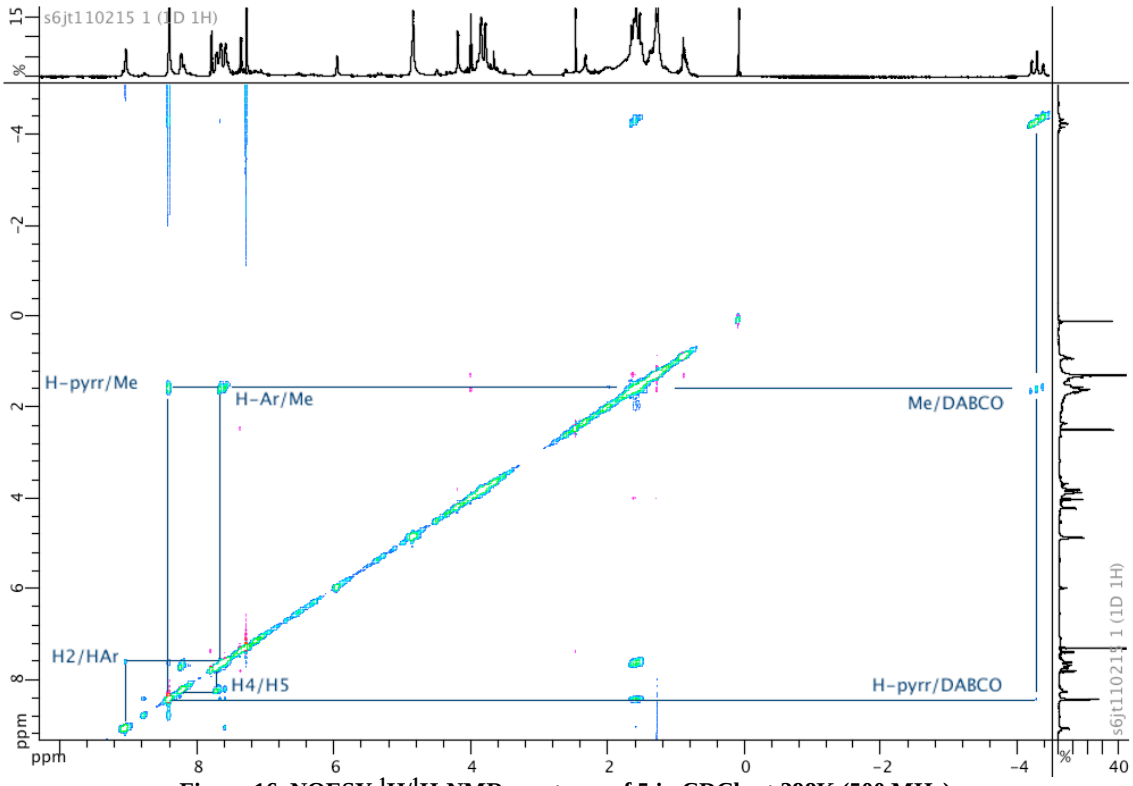

Figure 16. NOESY $^{1}H/^{1}H$-NMR spectrum of 5 in $CDCl_3$ at 298K (500 MHz).

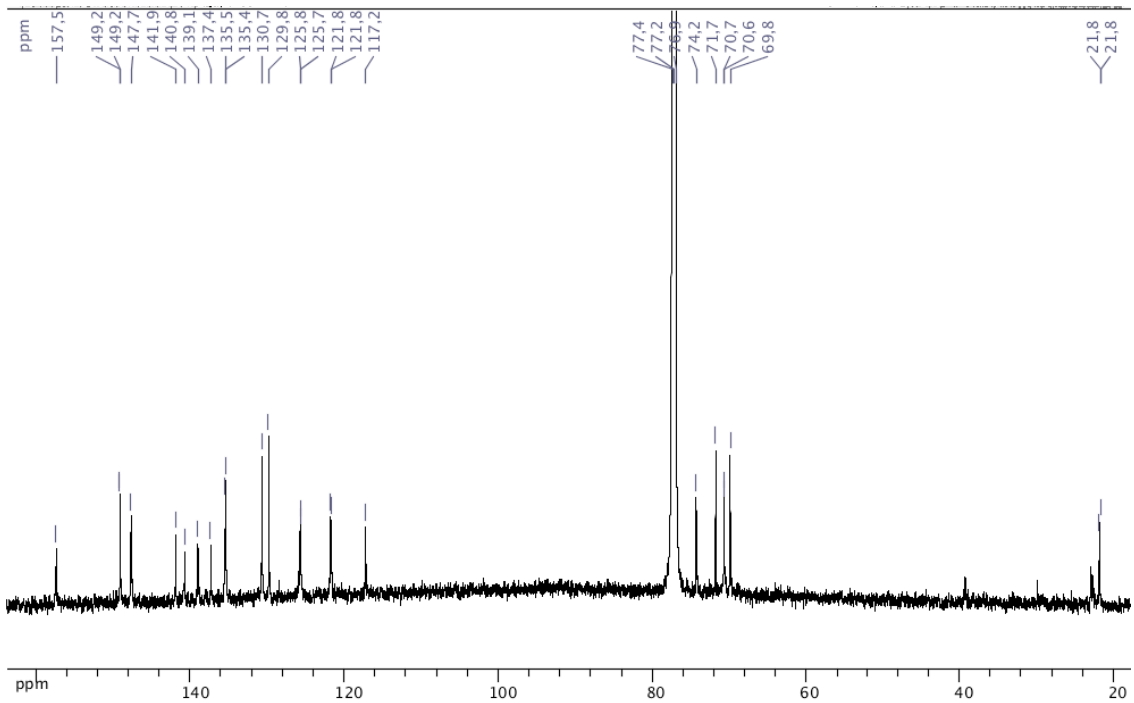

Figure 17. ^{13}C-NMR spectrum of 5 in $CDCl_3$ at 298K (150 MHz).

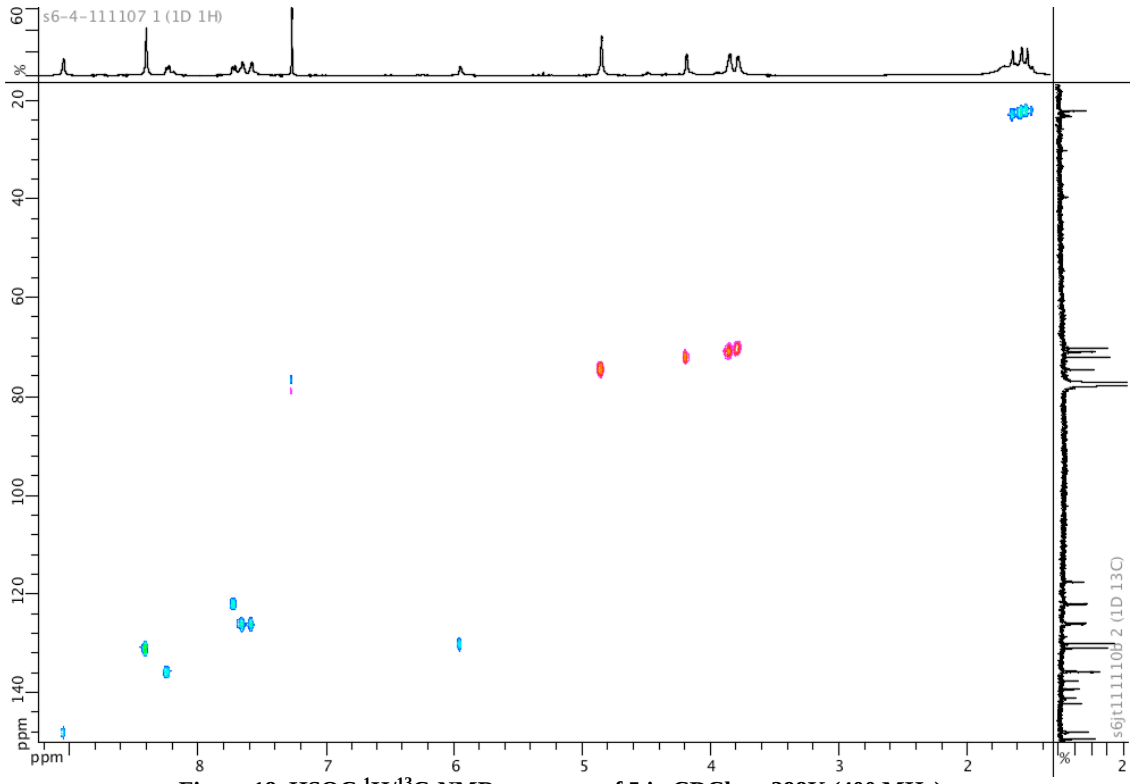

Figure 18. HSQC $^{1}H/^{13}C$-NMR spectrum of 5 in $CDCl_3$ at 298K (400 MHz).

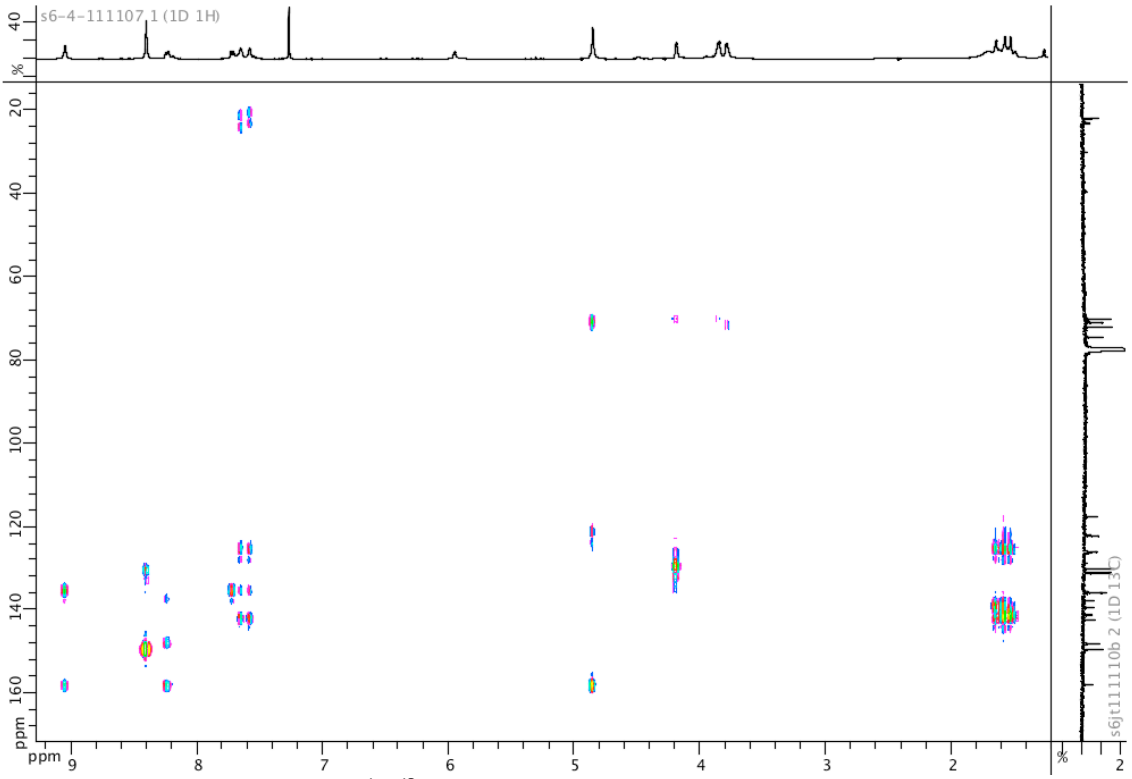

Figure 19. HMBC $^{1}H/^{13}C$-NMR spectrum of 5 in $CDCl_3$ at 298K (400 MHz).

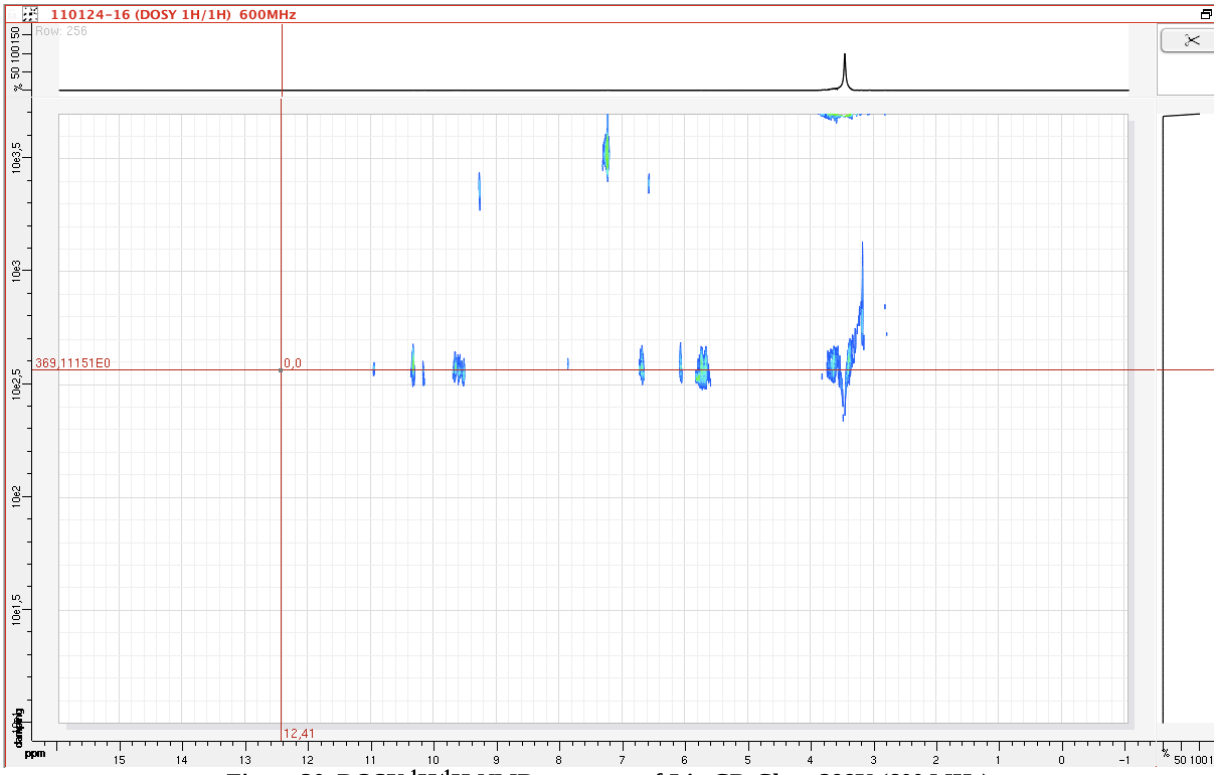

Figure 20. DOSY $^{1}H/^{1}H$-NMR spectrum of 5 in CD_2Cl_2 at 298K (600 MHz) D = 369 µm^2.s^{-1}.

Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name	O15769ML.d	Acquisition Date	11/7/2011 11:59:05 AM
Method	esi wide pos.m	Operator	Administrator
Sample Name	Zn2 cage lourd	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	350.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	350.0 V
Scan Range	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	517 °C

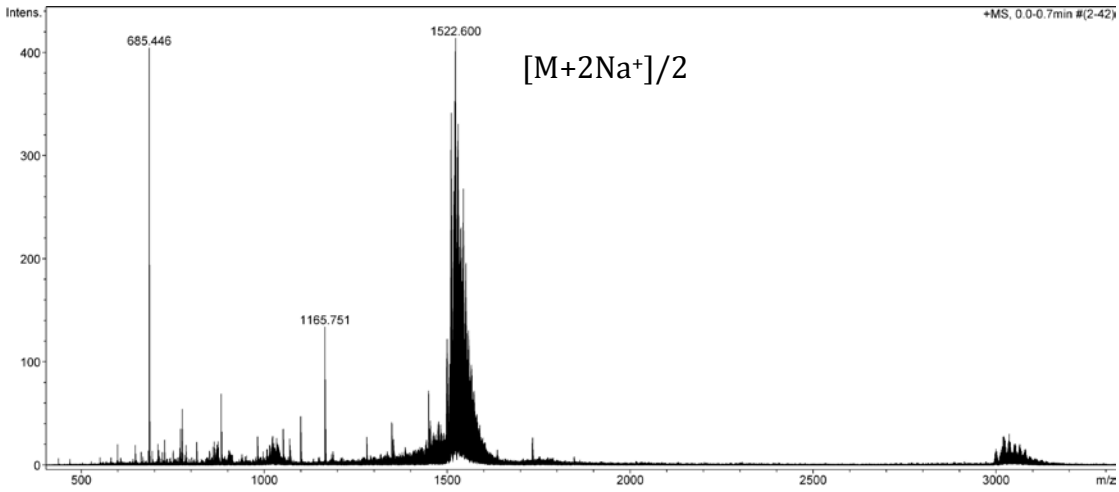

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Figure 21. ES-MS spectrum of 5.

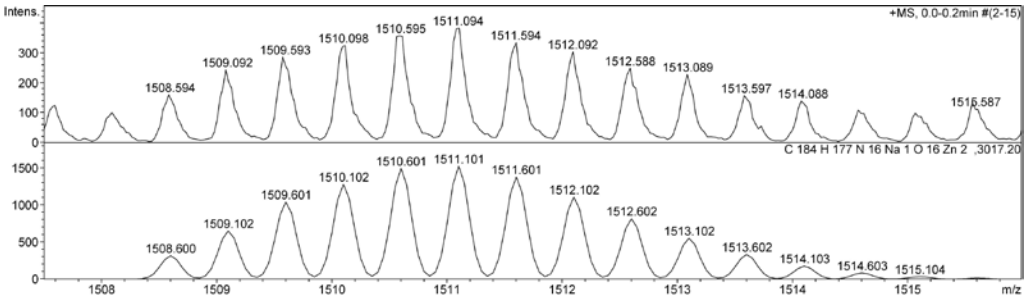
Mass Spectrum Molecular Formula Report

Analysis Info

Analysis Name	D:\Data\Service masse\O15768ML.d	Acquisition Date	11/7/2011 11:53:51 AM
Method	esi wide pos.m	Operator	Administrator
Sample Name	Zn2 cage	Instrument	micrOTOF 66
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	79 V
Scan Range	n/a	Capillary Exit	250.0 V	Set Pulsar Pull	799 V
Scan Begin	50 m/z	Hexapole RF	300.0 V	Set Pulsar Push	799 V
Scan End	3000 m/z	Skimmer 1	50.0 V	Set Reflector	1700 V
		Hexapole 1	24.3 V	Set Flight Tube	8600 V
				Set Detector TOF	2050 V



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 184 H 177 N 16 Na 1 O 16 Zn 2	0.15	1508.600	5.09	6.29	104.00	ok	even
C 184 H 176 N 16 Na 1 O 16 Zn 2	0.20	1508.096	2.52	3.47	104.50	-	odd
C 184 H 178 N 16 Na 1 O 16 Zn 2	0.21	1509.104	7.66	9.01	103.50	-	odd
C 184 H 179 N 16 Na 1 O 16 Zn 2	0.30	1509.608	10.48	12.11	103.00	ok	even
C 184 H 180 N 16 Na 1 O 16 Zn 2	0.39	1510.112	12.92	15.12	102.50	-	odd
C 184 H 181 N 16 Na 1 O 16 Zn 2	0.48	1510.616	15.54	18.46	102.00	ok	even

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Figure 22. HRMS spectrum of compound 5.

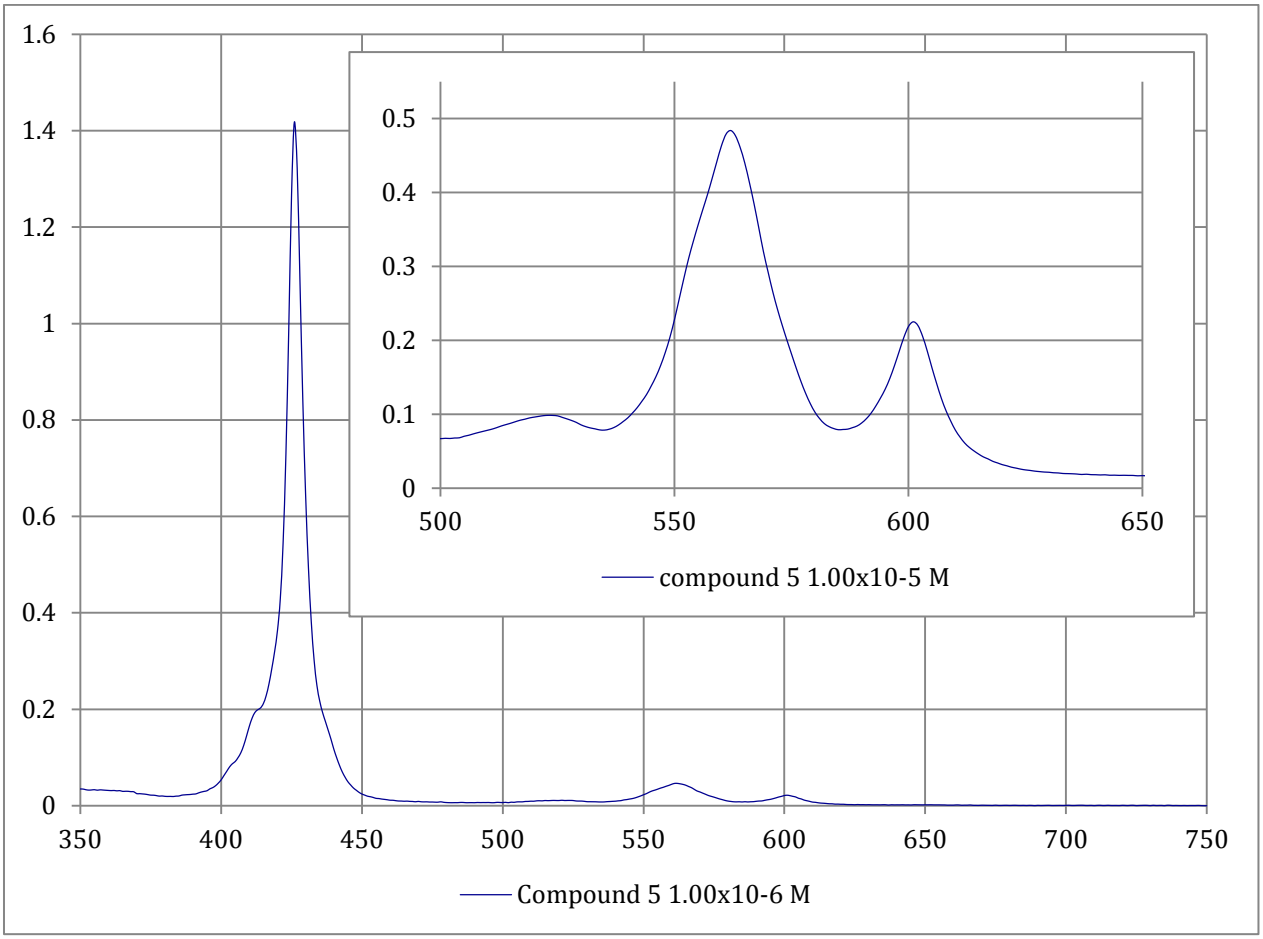

Figure 23. UV-vis. absorption spectra of 5 in toluene.

3.6 cage (6)

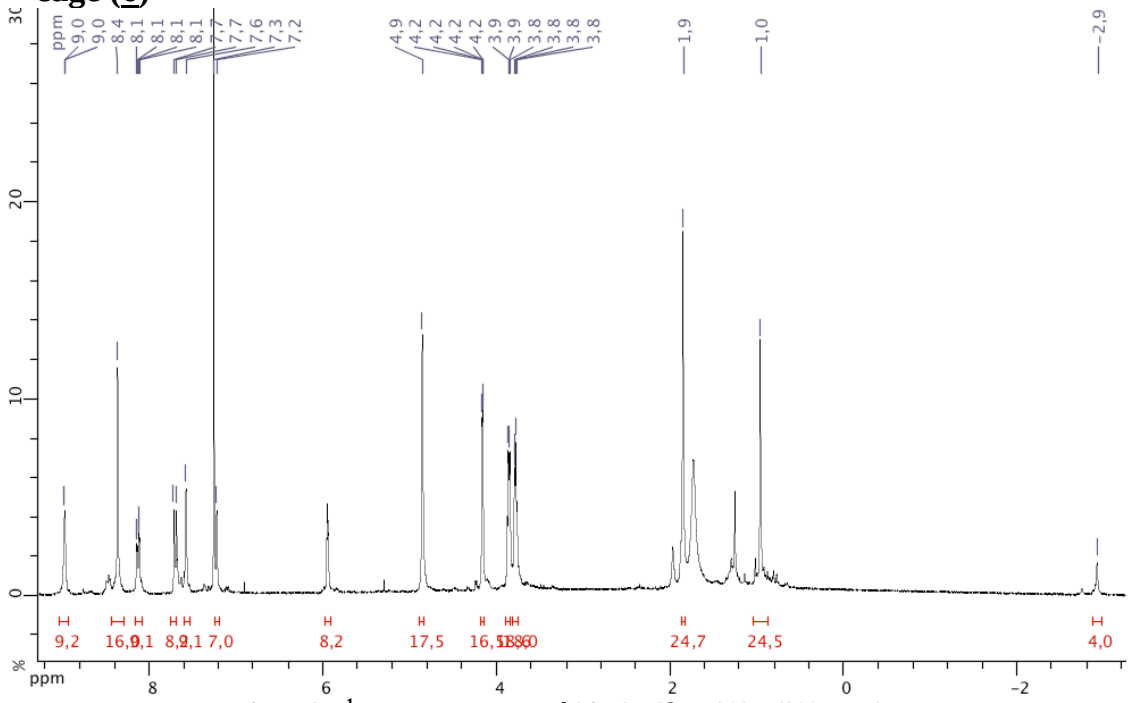

Figure 24. ^{1}H-NMR spectrum of 6 in $CDCl_3$ at 298K (300 MHz).

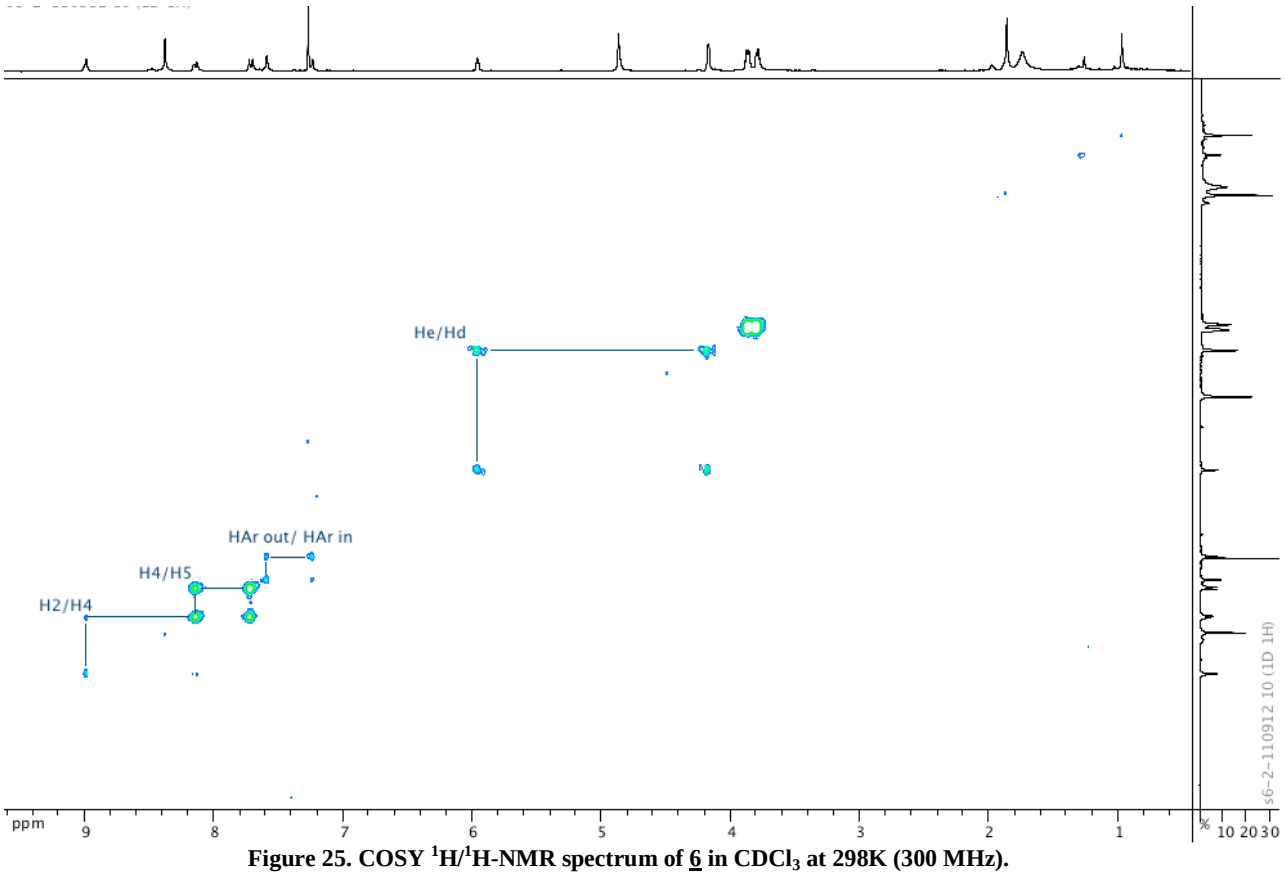

Figure 25. COSY ^{1}H/^{1}H-NMR spectrum of 6 in $CDCl_3$ at 298K (300 MHz).

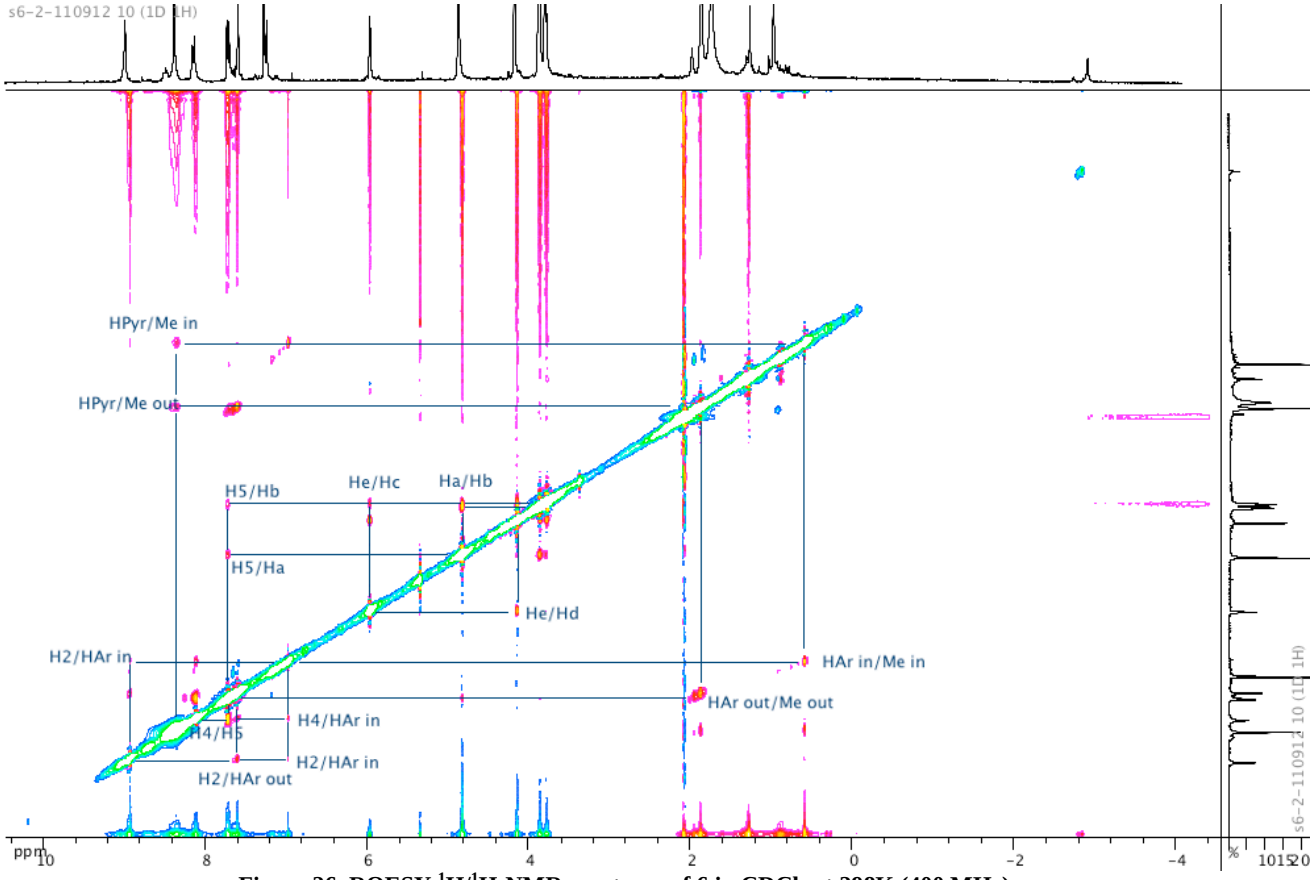

Figure 26. ROESY $^{1}H/^{1}H$-NMR spectrum of 6 in $CDCl_3$ at 298K (400 MHz).

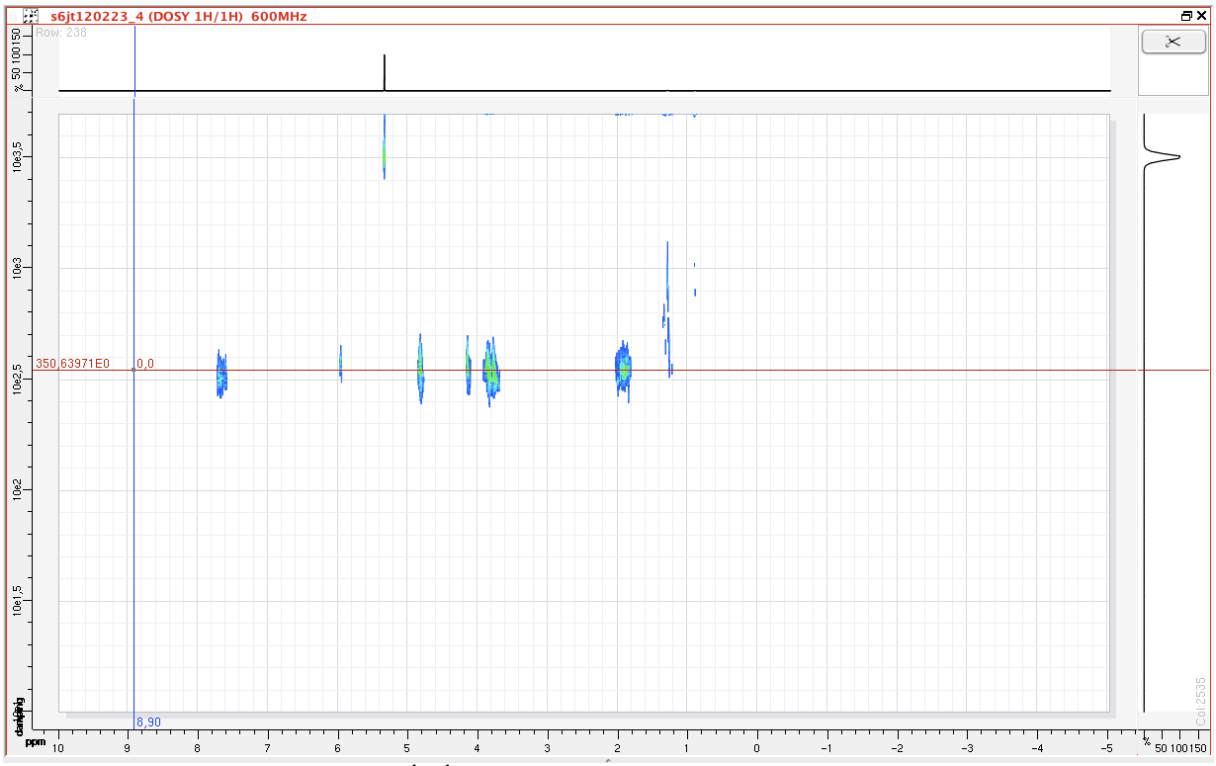

Figure 27. DOSY $^{1}H/^{1}H$-NMR spectrum of 6 in CD_2Cl_2 at 298K (600 MHz)
D = 350 µm^2.s^{-1}.

Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name	O15450ML.d	Acquisition Date	9/28/2011 10:45:15 AM
Method	esi wide pos.m	Operator	Administrator
Sample Name	H4 cage	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	146 nA
Ion Polarity	Positive	Set Capillary Exit	350.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	300.0 V
Scan Range	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	518 °C

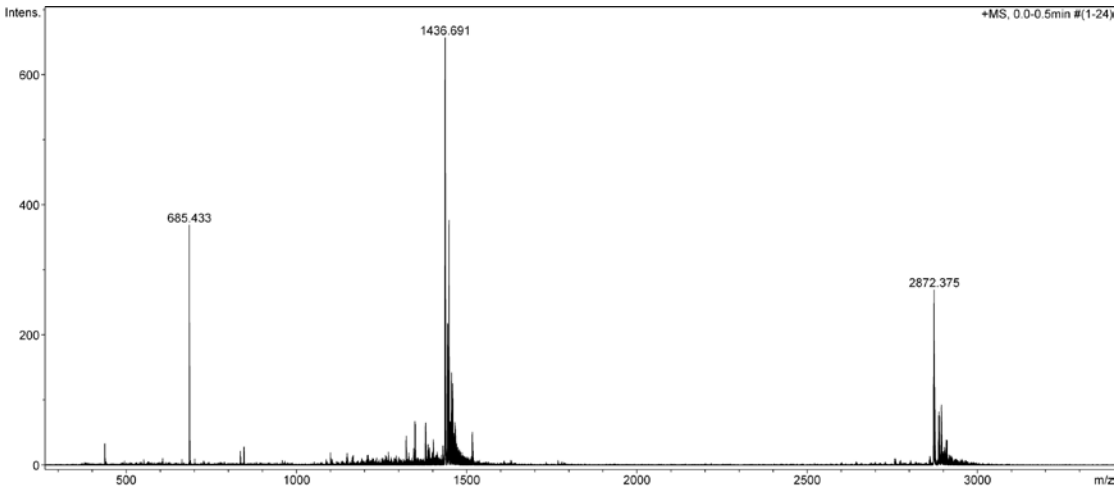

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Figure 28. ES-MS spectrum of 6.

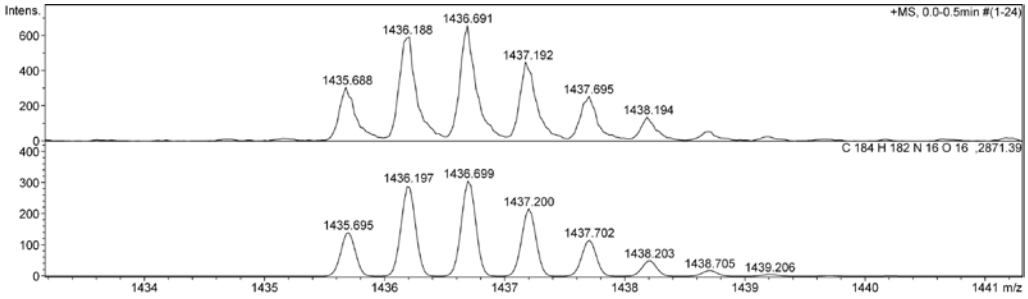
Mass Spectrum Molecular Formula Report

Analysis Info

Analysis Name	D:\Data\Service masse\O15450ML.d	Acquisition Date	9/28/2011 10:45:15 AM
Method	esi wide pos.m	Operator	Administrator
Sample Name	H4 cage	Instrument	micrOTOF 66
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	79 V
Scan Range	n/a	Capillary Exit	350.0 V	Set Pulsar Pull	799 V
Scan Begin	50 m/z	Hexapole RF	300.0 V	Set Pulsar Push	799 V
Scan End	5000 m/z	Skimmer 1	50.0 V	Set Reflector	1700 V
		Hexapole 1	24.3 V	Set Flight Tube	8600 V
				Set Detector TOF	2050 V



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 184 H 182 N 16 O 16	0.03	1435.695	5.48	5.72	102.00	ok	even
C 184 H 181 N 16 O 16	0.30	1435.192	3.87	4.00	102.50	-	odd
C 184 H 180 N 16 O 16	0.53	1434.688	2.25	2.28	103.00	ok	even
C 184 H 179 N 16 O 16	0.68	1434.184	0.62	0.68	103.50	-	odd
C 184 H 176 N 16 O 16	0.70	1432.672	-4.33	-4.13	105.00	ok	even
C 183 H 188 N 16 O 16	0.70	1432.719	28.37	28.46	98.00	ok	even
C 184 H 178 N 16 O 16	0.75	1433.680	-1.02	-0.91	104.00	ok	even
C 184 H 177 N 16 O 16	0.75	1433.176	-2.67	-2.60	104.50	-	odd

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Figure 29. HRMS spectrum of compound 6.

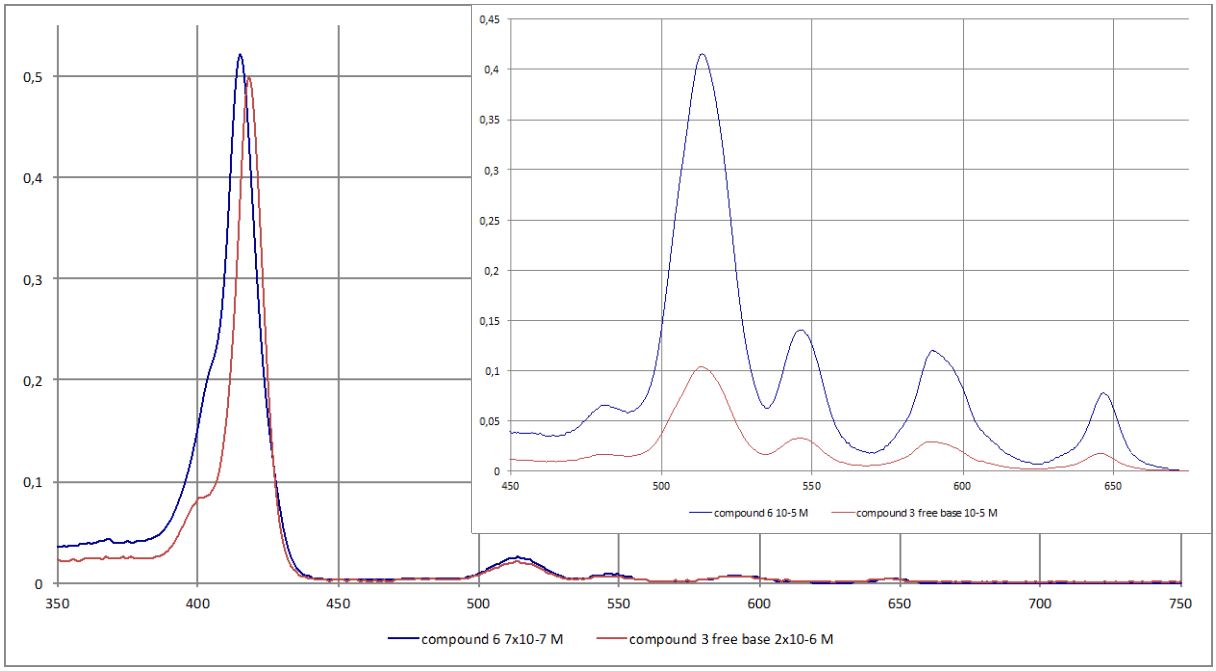

Figure 30. UV-vis. absorption spectra of 6 (in blue) and $H_2$3 (in red) both in DCM/MeCN (2/1).

4 Crystallographic data of 5

4.1 Experimental data:

XRD data were collected on a Bruker-Nonius KappaCCD diffractometer with Apex-II detector at T = 123.0(1) K with graphite monochromatized Mo-$K\alpha$ radiation (λ = 0.71073 Å). Collect software[2] was used for data measurement, and DENZO-SMN[3] was used for processing. The structures were solved by direct methods with SIR-97[4] and refined by full-matrix least-squares methods using WinGX software[5], which utilizes the SHELXL-97 module.[6] Multi-scan absorption correction (SADABS[7]) was applied on all data. The positions of carbon-bound hydrogen atoms were calculated and refined as riding on the parent carbon atoms with $U_H = 1.2\ U_C$ (or $U_H = 1.5\ U_C$ in the case of methyl groups).

The crystal structure of **5** was found to contain two symmetrically independent molecules of **5**, of which 1/4 of each is a part of the asymmetric unit. These differ by their position relatively to the symmetry elements, namely, the zinc atoms lie on a twofold axis in one and on a mirror plane in the other one. For both of these the DABCO molecules were found to be disordered around respective symmetry elements and were modelled in two positions with 50% occupancies. Restraints were used both for the geometry (DFIX and DANG were used to tie equivalent interatomic distances to free variables) and the anisotropic displacement parameters (DELU, SIMU). Also, geometries of porphyrin cores and 2,6-dimethylphenyl rings were restrained (SADI) and then refined anisotropically. Pyridine rings were refined as rigid bodies (AFIX 66) with common isotropic atomic displacement parameters for all the atoms in each ring (EADP). The flexible polyether chains were found to be badly disordered and thus the geometry had to be heavily restrained (DFIX, DANG) using values obtained from CSD.[8] One of the chains was modelled in two conformations, each with 50% occupancy. All the atoms in all the chains were refined with equal (EADP) isotropic atomic displacement parameters. The structure was found to possess large voids containing disordered solvent which could not be modelled explicitly. The associated electron density was thus removed using SQUEEZE procedure in PLATON.[9]

4.2 CheckCIF report

A-level alerts:
RFACR01_ALERT_3_A The value of the weighted R factor is > 0.45
Weighted R factor given 0.458
PLAT084_ALERT_2_A High wR2 Value 0.46
PLAT602_ALERT_2_A VERY LARGE Solvent Accessible VOID(S) in Structure !

Response:
The structure contains severely disordered parts (pyridine rings, polyether chains) and large voids filled with disordered solvent.

A-level alert:
PLAT026_ALERT_3_A Ratio Observed / Unique Reflections too Low .... 24 Perc.

Response:
The crystal was weakly diffracting.

A-level alert:

PLAT201_ALERT_2_A Isotropic non-H Atoms in Main Residue(s) 39

Response:
Due to severe disorder, pyridine rings and polyether chains were refined isotropically

A-level alert:
PLAT241_ALERT_2_A Check High Ueq as Compared to Neighbors for C1J

Response:
C1J is the first atom in the polyether chain and is bound to the pyridine ring. Since the polyether chains were modelled so that all the atoms in all the chains have identical isotropic ADP, the difference in ADP between C1J and the atom in the pyridine ring to which it is bound (C12H) is rather significant.

B-level alert:
RFACG01_ALERT_3_B The value of the R factor is > 0.15
R factor given 0.169
PLAT049_ALERT_1_B Calculated Density less than 1.0 gcm-3 ..... 0.9448
PLAT082_ALERT_2_B High R1 Value 0.17

Response:
The structure contains severely disordered parts (pyridine rings, polyether chains) and large voids filled with disordered solvent.

B-level alerts:
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.9 Ratio
PLAT220_ALERT_2_B Large Non-Solvent N Ueq(max)/Ueq(min) ... 4.4 Ratio
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 5.0 Ratio

Response:
The atoms in the disordered regions of the model have high ADPs compared to the ones in the ordered regions of the model.

B-level alerts:
PLAT241_ALERT_2_B Check High Ueq as Compared to Neighbors for C1I
PLAT242_ALERT_2_B Check Low Ueq as Compared to Neighbors for C12H
PLAT242_ALERT_2_B Check Low Ueq as Compared to Neighbors for C12B
PLAT242_ALERT_2_B Check Low Ueq as Compared to Neighbors for C12C

Response:
C1I is the first atom in the polyether chain and is bound to the pyridine ring. Atoms C12B, C12C, C12H belong to the pyridine rings and are the atoms to which polyether chains are bound. Since the polyether chains were modelled so that all the atoms in all the chains have identical isotropic ADP and the pyridine rings were modelled so that all the atoms in each ring have the same isotropic ADP, significant differences in ADP arose between such pairs of atoms. Thus, this situation reflects the way the structure was modelled.

B-level alert:
PLAT241_ALERT_2_B Check High Ueq as Compared to Neighbors for C3G

Response:
C3G is a member of the 2,6-dimethylphenyl ring which has some rotational freedom.

B-level alert:
PLAT241_ALERT_2_B Check High Ueq as Compared to Neighbors for C9G

Response:
C9G is a member of the pyridine ring which is badly disordered and whose atoms have been modelled with common isotropic ADP. Since this atom is bound to a better-ordered 2,6-dimethylphenyl ring, there is a significant difference between the ADPs of C9G and it's neighbour in the 2,6-dimethylphenyl ring (C4G).

B-level alerts:
PLAT420_ALERT_2_B D-H Without Acceptor *O5K - *H6D2 ... ?
PLAT420_ALERT_2_B D-H Without Acceptor *O5D - *H4K1 ... ?
PLAT420_ALERT_2_B D-H Without Acceptor *O2L - *H1E1 ... ?
PLAT420_ALERT_2_B D-H Without Acceptor *O5L - *H4E1 ... ?
PLAT420_ALERT_2_B D-H Without Acceptor *O2E - *H1L2 ... ?

Response:
These atom pairs do not correspond to hydroxyl groups but are pairs of oxygen atoms from one disorder component and the hydrogen atoms from another disorder component, wrongly assumed to be bonded by CheckCIF.

B-level alert:
PLAT430_ALERT_2_B Short Inter D...A Contact N4A .. N4A .. 2.66 Ang.

Response:
This is the standard N···N distance in DABCO.

B-level alert:
PLAT910_ALERT_3_B Missing # of FCF Reflections Below Th(Min) 15

Response:
Some reflections had to be omitted in the refinement for technical reasons.

B-level alert:
PLAT934_ALERT_3_B Number of (Iobs-Icalc)/SigmaW .gt. 10 Outliers . 1

Response:
A consequence of the bad crystal quality.

B-level alert:
PLAT973_ALERT_2_B Large Calcd. Positive Residual Density on Zn2 1.82 eA-3
PLAT973_ALERT_2_B Large Calcd. Positive Residual Density on Zn1 1.78 eA-3

Response:
A consequence of the bad crystal quality.

5 References

1. J. Taesch, T. T. Dang and V. Heitz, *Tetrahedron Lett.*, 2012, **53**, 333.
2. R.W. Hooft, *COLLECT*, Nonius BV, Delft,The Netherlands **1998**.
3. Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, Macromolecular Crystallography, Part A, 307.
4. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115.
5. L. J. Farrugia, *J. Appl. Crystallogr.*, **1999**, *32*, 837.
6. G. M. Sheldrick, *SHELXL-97 – A program for the Refinement of Crystal Structures*, University of Göttingen, Germany **1997,** release 97-2.
7. G.M. Sheldrick, *SADABS*, Version 2008/2, Universität Göttingen: Göttingen, Germany ***2008***.
8. Cambridge Structural Database (version 1.14, 2012), The Cambridge Crystallographic Data Centre, Cambridge, UK.
9. A.L. Spek, PLATON, *Acta Cryst.*, **2009**, *D65*, 148-155.