

SUPPORTING INFORMATION

One-flask Synthesis of Dibenzo-tetraaza[14]annulene Cyclic Congeners Bearing Buta-1,3-diyne Bridges.

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1. General information

Nuclear magnetic resonance experiments:

The NMR spectra were recorded using Mercury Varian (300 MHz) spectrometer at ambient temperature in DMSO-d₆ or CDCl₃ solvents. The chemical shifts are reported in parts per million (ppm) and the coupling constants J are given in hertz (Hz). Data are reported as follows: chemical shift, multiplicity (singlet, br.s –broad singlet, d – doublet, dd- doublet of doublets), coupling constant and integration. The residual signal of DMSO-d₆ solvent was used as an internal reference standard ($\delta_{\text{H}} = 2.500$ ppm and $\delta_{\text{C}} = 39.50$ ppm).

Mass spectrometry:

The mass spectrometry experiments were performed on a ESI-ITD mass spectrometer Esquire 3000 (Bruker-Daltonics, Bremen, Germany). The heated capillary temperature was set to 250°C. About 1 mg of sample was dissolved in 1 ml of CHCl₃ and the spray solution was prepared by adding 1 ml of CH₃OH (final ratio 1:1, v/v). After mixing, sample was injected by continuous infusion at a flow rate of 3 microliters/minute. Mass range applied was over the range from 300 to 1500 m/z. Scans were acquired for at least one minute. In case of heat sensitive samples temperature was set down to 150-160°C or to easily observed abnormalities in ion formation. About 1 mg of sample was dissolved in CHCl₃ and CH₃OH mixture (1:1 v/v).

Infrared spectroscopy (IR):

Fourier transform infrared (FT-IR) spectra were measured at room temperature in a transmission mode in the range of ν 4000-400 cm⁻¹ with a FTIR Bruker Equinox55 spectrometer. The KBr pellets were prepared by adding 0.8 mg of a sample powder to 200 mg of dry KBr. The powders were mixed homogeneously and compressed at a pressure of 10 kPa to form transparent pellets. Fourier transform infrared FT-IR ATR (Attenuated total reflection) spectra were recorded at room temperature with a FT-IR Thermo Fisher Nicolet IR200 spectrometer equipped with a diamond and operating in a single reflection mode.

UV-vis spectroscopy:

Electronic absorption spectra were obtained in chloroform or dichloromethane solutions using matched 1 cm quartz cuvettes and were recorded with a Hitachi U-3900H spectrophotometer.

Elemental analyses: Elemental analyses were conducted using an Euro-EA (EuroVector) and a VarioMicroCube microanalyzers. Samples were analyzed with standard parameters in a CHN mode.

Single crystal X-ray analysis:

Single crystal X-ray diffraction data were collected by the ω -scan technique using a KM4CCD κ -axis diffractometer with graphite-monochromated Cu-K α radiation ($\lambda = 1.54178$ Å) at room temperature. Data collection and data reduction were carried out with the Oxford Diffraction programs.¹ The crystal structure was solved by using direct methods with the SHELXS-2013 program.² Atomic scattering factors were taken from the International Tables for X-ray Crystallography. Positional parameters of non-H-atoms were refined by a full-matrix least-squares method with anisotropic thermal parameters by using the SHELXL-2016/6 program.³ Molecular graphics: Mercury,⁴ software used to geometry calculations: PLATON.⁵ Additional details of the data collection and refinement are listed in a Table S3 (*vide infra*).

¹ Oxford Diffraction (2006). CrysAlis CCD, CrysAlis RED. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

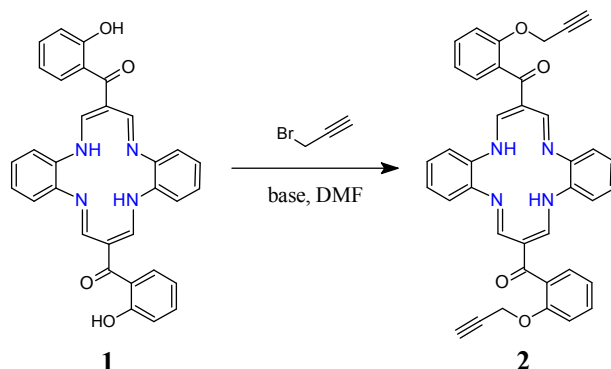
² G.M. Sheldrick, SHELXS-2013/1, Program for the Crystal Structure Solution. University Göttingen; Göttingen, Germany: 2013.

³ G.M. Sheldrick SHELXL, Program for the Refinement of Crystal Structures. University Göttingen; Göttingen, Germany: 2016.

⁴ C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood. J. Appl. Cryst. 41 (2008) 466.

2. Experimental procedures for the synthesis of starting macrocyclic precursors

2.1 Optimization of the reaction conditions for a synthesis of O,O'-bispropargylated ligand 2:

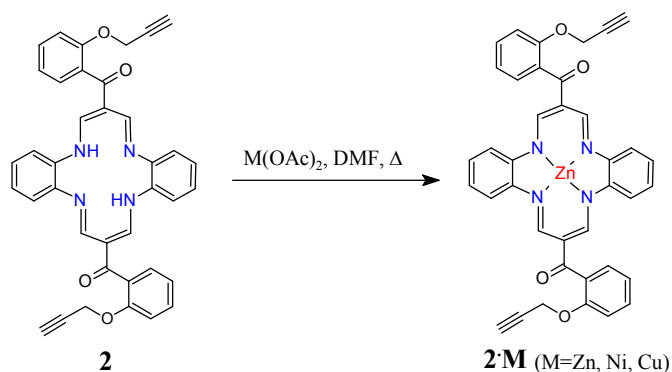


A single amount of macrocyclic ligand **1** (100 mg, 0.19 mmol), was added in to a suspension of anhydrous metal carbonate M_2CO_3 (0.57 mmol) in 5 ml of dry N,N-dimethylformamide. The resulting mixture was stirred at room temperature for 20 minutes. Then, propargyl bromide solution (0.068 ml, 0.64 mmol, 80% wt. % in toluene) was added to a clear red solution and the resulting mixture was stirred at room temperature for 24 h, or in the case of using sodium carbonate for 72 h. Orange precipitate was filtered off, washed with cold methanol and dried under a vacuum. The residue was recrystallized from dichloromethane to give orange needles.

Yields: 34.9% (Na_2CO_3), 54.2% (K_2CO_3), 64.7% (Cs_2CO_3), 0% NaOH, 0% KOH and 8.74% CsOH.

⁵ A.L. Spek, Acta Cryst. D65 (2009) 148.

2.2 Synthesis of O,O'-bispropargylated metal(II) complexes 2-M



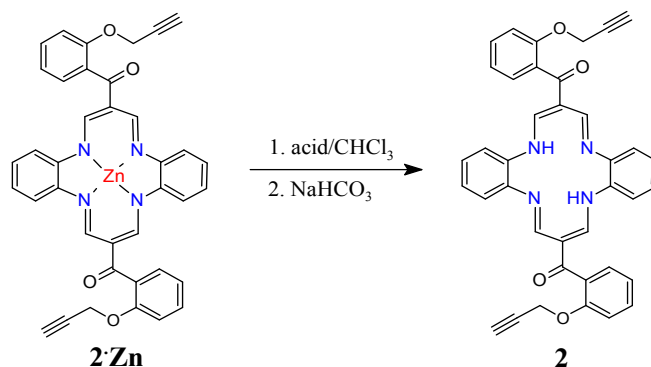
a) Nickel (II) complex **2·Ni**

A suspension of macrocyclic ligand **2** (100 mg, 0.164 mmol) in a solution of anhydrous copper(II) acetate (178 mg, 0.328 mmol) in 10 ml of dry N,N-dimethylformamide was heated at 90 °C for 6 hours. The reaction mixture was cooled down to room temperature and the resulting solid residue was removed by filtration, washed with methanol (2x20 ml) and dried under vacuum. Analytically pure product was obtained by recrystallization from a hot N,N-dimethylformamide. Brown powder was obtained in a 69% isolated yield (76 mg).

b) Copper (II) complex **2·Cu**

A suspension of macrocyclic ligand **2** (100 mg, 0.164 mmol) in a solution of nickel(II) acetate dihydrate (150 mg, 0.70 mmol) in 30 ml of dry N,N-dimethylformamide was heated at 70 °C until clear solution was obtained (ca. 5-6 h) and further heated at 70 °C for the next 2 h . The reaction mixture was cooled down to room temperature and the resulting solid residue was removed by filtration and dried under vacuum at 40° C. Orange needles was obtained in a 33% isolated yield (36 mg).

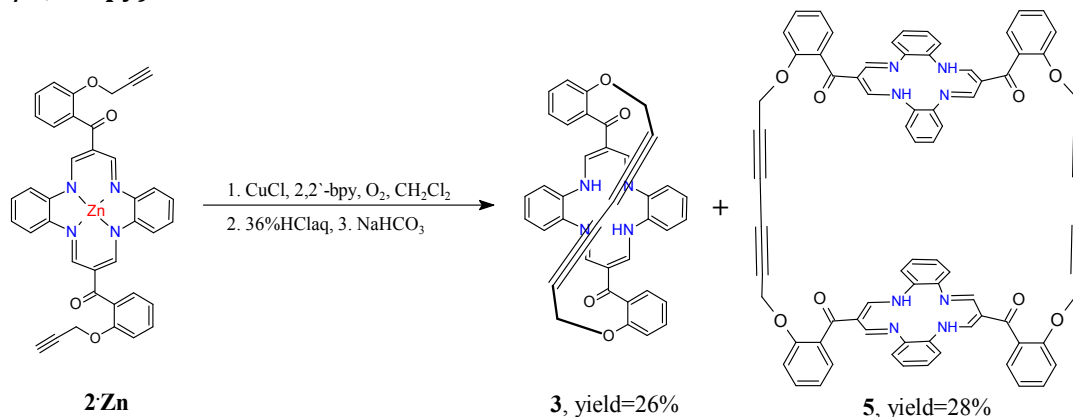
3. Stability studies of zinc(II) complex **2·Zn** under acidic conditions



To a solution of zinc complex **2·Zn** (10 mg, 0.015 mmol) in a 15 ml of CHCl_3 appropriate amount of acid was added in one portion (0.6 ml of CF_3COOH , 1 ml of glacial CH_3COOH and 1 ml of 36% HCl) and the mixture was stirred at room temperature for 1 hour. Next, the solution was washed twice with water (2 x 10ml) and neutralized with saturated NaHCO_3 solution. The organic phase was separated, dried over anhydrous MgSO_4 , filtered and evaporated to dryness. The ^1H NMR of crude reaction mixture sample evaporated to dryness and redissolved in CDCl_3 was recorded at this stage. The resulting mixture was also analyzed by TLC ($\text{CHCl}_3/\text{acetone}$, v:v. 6:1), $R_{f(2\cdot\text{Zn})}=0.2$, $R_{f(2)}=0.5$. Both the CF_3COOH and 36% HCl acids gave free base ligand **2** in a quantitative yields (>99%) as confirmed by both TLC and ^1H NMR analysis.

4. Experimental procedures for α,ω -diyne oxidative couplings:

4.1 General procedure for 2:Zn oxidative coupling under Glaser-Hay conditions (CuCl/2,2'-bpy)



Copper(I) chloride CuCl (189 mg, 1.91 mmol) and 2,2'-bipyridine (298 mg, 1.91 mmol) were added to a solution of zinc(II) complex **2** (200 mg, 0.299 mmol) in a 400 ml of freshly distilled dichloromethane. The reaction mixture was stirred at room temperature under a flux of dry air⁶ which slowly bubbled through the stirred solution until coupling was complete by TLC (ca. 15-20 h).⁷ The reaction was quenched by pouring the mixture into distilled water (100 ml). The organic phase was further washed with distilled water under vigorous stirring until the aqueous phase became colorless (ca. 4 x 200 ml). The reaction mixture was demetalated by treatment with concentrated 36% hydrochloric acid (30 ml) and stirred vigorously for 20 minutes. This clear yellow solution was washed twice with water (2 x 200 ml) and neutralized with saturated NaHCO₃ solution. The organic phase was separated, dried over anhydrous MgSO₄ and concentrated to ca. 50-60 ml under reduced pressure. The resulting solution was immediately adsorbed onto the top of the Al₂O₃ column and eluted first with CHCl₃:acetone v/v, 49:1 and then with CHCl₃:acetone v/v, 10:1. The first fraction was collected and evaporated to dryness under reduced pressure to give strapped ligand **3** as a dark red powder (46 mg, 0.076 mmol, isolated yield 26%). The second fraction containing cyclic dimer **5** was collected and concentrated under reduced pressure to a small volume (5 ml) and left at room temperature for 2 days. The orange precipitate was collected by filtration and dried in a vacuum to afford an analytically pure cyclic dimer **5** (51 mg, 0.042 mmol, isolated yield 28 %).

Monitoring of the reaction progress by FT-IR and ¹H NMR spectroscopy:

Small aliquots were routinely withdrawn during the reaction course at constant intervals, and after convenient reaction mixture workup FT-IR and ¹H NMR spectra were acquired. Infrared spectroscopy was used as an invaluable supportive tool for real-time analysis of alkyne coupling progression. The FT-IR spectra of the reference precursor **2** consist of the two characteristic absorption bands at ν 3221 and 2107 cm⁻¹ attributable to C $\equiv$ C and C-H stretches respectively, that gradually disappeared during coupling.

To follow the coupling progress, we focused on the diagnostic methylenoxy proton signals (4.6-4.8 ppm). The ¹H NMR spectrum of a reference ligand **2** displays a set of proton resonances at δ 2.36 and δ 4.74 ppm characteristic for AX₂ spin system of the propargylic moieties. As expected, the doublet resonance signal of **2** at δ 4.74 ppm gradually disappeared during coupling, and the

⁶ The air was dried over two interconnected drying tubes filled with anhydrous CaCl₂.

⁷ Actual volume of solvent was monitored and if necessary supplemented to a constant value of 400 ml.

final reaction mixture (Fig S1) showed two singlet resonance of 4.60 and 4.76 ppm assignable to the strapped ligand **3** and cyclic dimers **5**, respectively.

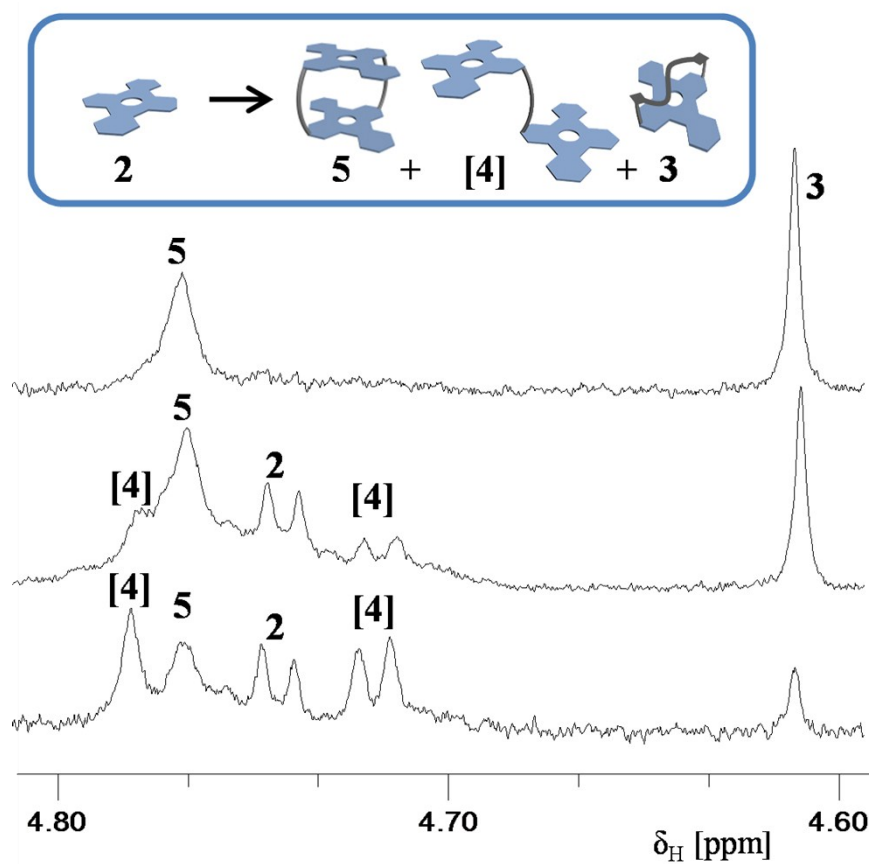
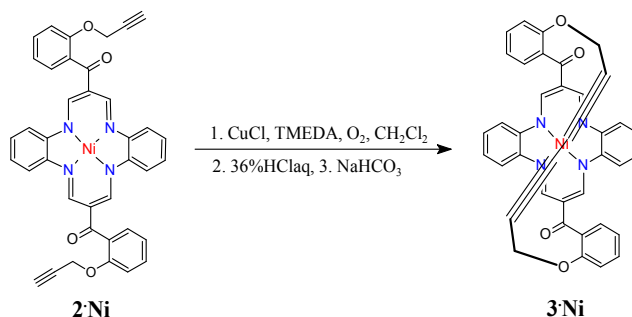


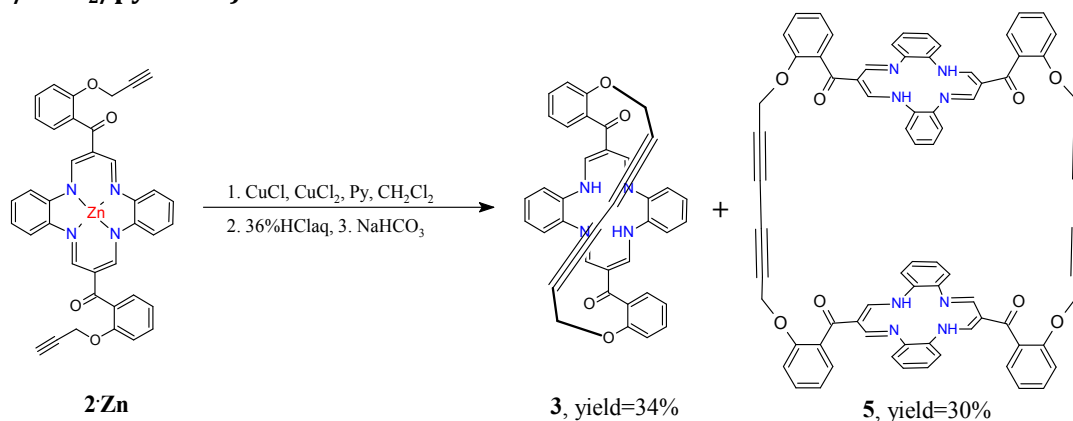
Figure S1. Diagnostic region of a ^1H NMR spectra (300MHz, CDCl_3) recorded for a series of crude acid-washed reaction mixture samples depicting the progress of **2:Zn** coupling ($\text{CuCl}\cdot 2,2'\text{-bpy}$, CH_2Cl_2 , dry air). The signals of methylenoxy ($-\text{OCH}_2\text{-C}\equiv\text{C}-$) moieties belonging to particular components are labelled in accordance with scheme 1.

4.2 General procedure for 2·Ni oxidative coupling under Glaser-Hay conditions (CuCl/TMEDA)



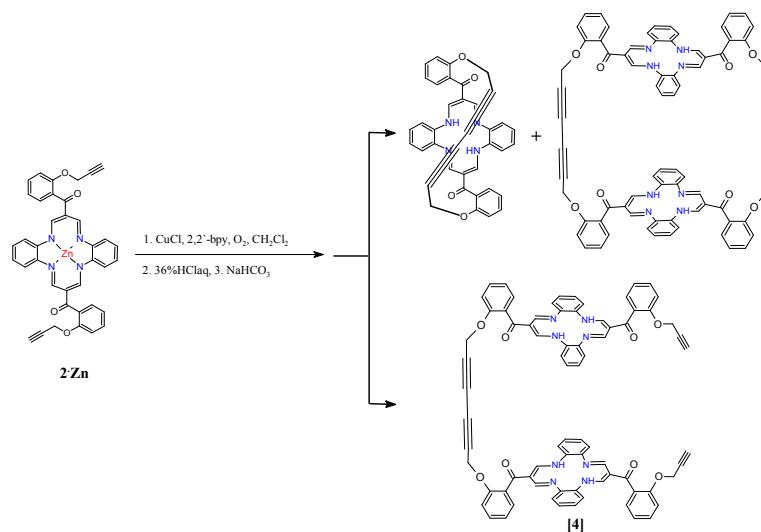
Copper(I) chloride CuCl (231 mg, 2.34 mmol) and N,N,N',N'-tetramethylethylenediamine TMEDA (0.35 ml, 2.34 mmol) were added to a solution of nickel(II) complex **2·Ni** (10 mg, 0.015 mmol) in a 100 ml of freshly distilled dichloromethane. The reaction mixture was stirred at room temperature under a flux of dry air which slowly bubbled through the stirred solution for 16 h. The reaction was quenched by pouring the mixture into distilled water (100 ml). The organic phase was additionally washed with distilled water and stirred vigorously until the aqueous phase became colorless (ca. 2 x 100 ml). The organic phase was separated, dried over anhydrous MgSO₄ and evaporated to dryness under reduced pressure. No signals attributable to the starting nickel(II) complex **2·Ni** can be found in both ¹H NMR and IR spectra.

4.3 General procedure for 2:Zn oxidative coupling under Glaser-Eglinton conditions (CuCl/CuCl₂/pyridine)



Copper(I) chloride CuCl (300 mg, 3.03 mmol) and copper(II) chloride CuCl₂·2H₂O (60 mg, 0.36 mmol) were added to a solution of zinc(II) complex **2·Zn** (200 mg, 0.299 mmol) in a 200 ml of dry pyridine. The flask was closed with a stopper and the reaction mixture was stirred at 273 K until the solution become dark-green (ca. 2 hours). The resulting mixture was left at 273 K for 7 days. The reaction mixture was quenched by pouring the mixture into 0.5 liter of ice water and extracted with dichloromethane (2 x 50 ml). The combined organic extracts were demetalated by treatment with concentrated 36% hydrochloric acid (50 ml) and stirred vigorously for 20 minutes. This clear yellow solution was washed twice with water (2 x 200ml) and neutralized with saturated NaHCO₃ solution. The organic phase was separated, dried over anhydrous MgSO₄ and concentrated to ca. 50 ml under reduced pressure. The resulting solution was immediately adsorbed onto the top of the Al₂O₃ column and eluted first with CHCl₃:acetone v/v, 49:1 and then with CHCl₃:acetone v/v, 10:1. The first fraction was collected and evaporated to dryness under reduced pressure to give strapped ligand **3** as a dark red powder (60 mg, 0.099 mmol, isolated yield 34%). The second fraction containing cyclic dimer **5** was collected and concentrated under reduced pressure to a volume of ca. 5 ml and left at room temperature for 24 hours. The orange precipitate was collected by filtration and dried in a vacuum to afford the analytically pure cyclic dimer **5** (55 mg, 0.045 mmol, isolated yield 30 %).

4.4 Isolation of a linear intermediate [4] from a mixture obtained under Glaser-Hay conditions (CuCl/2,2'-bpy)



Copper(I) chloride CuCl (189 mg, 1.91 mmol) and 2,2'-bipyridine (298 mg, 1.91 mmol) were added to a solution of zinc(II) complex **2·Zn** (200 mg, 0.299 mmol) in a 400 ml of freshly distilled dichloromethane. The reaction mixture was stirred at room temperature under a flux of dry air which slowly bubbled through the stirred solution until concentration of a linear intermediate reach maximum by TLC analysis. The reaction mixture was worked up as described previously in the general procedure described for the Glaser-Hay coupling. The unreacted starting ligand **2** and the strapped ligand **3** were first separated eluting with CHCl₃:acetone v/v, 49:1. Then second fraction of the linear intermediate **[4]** was then eluted with CHCl₃:acetone v/v, 20:1. Combined eluates were concentrated to ca. 10 ml and left at room temperature for 2 days. The resulting red solid was filtered off, dried in a vacuum and yielded an analytically pure linear dimer **[4]** as red crystals (72 mg, 0.060 mmol, isolated yield 40%).

5 Determination of kinetic effective molarity EM_k for 2·Zn oxidative couplings

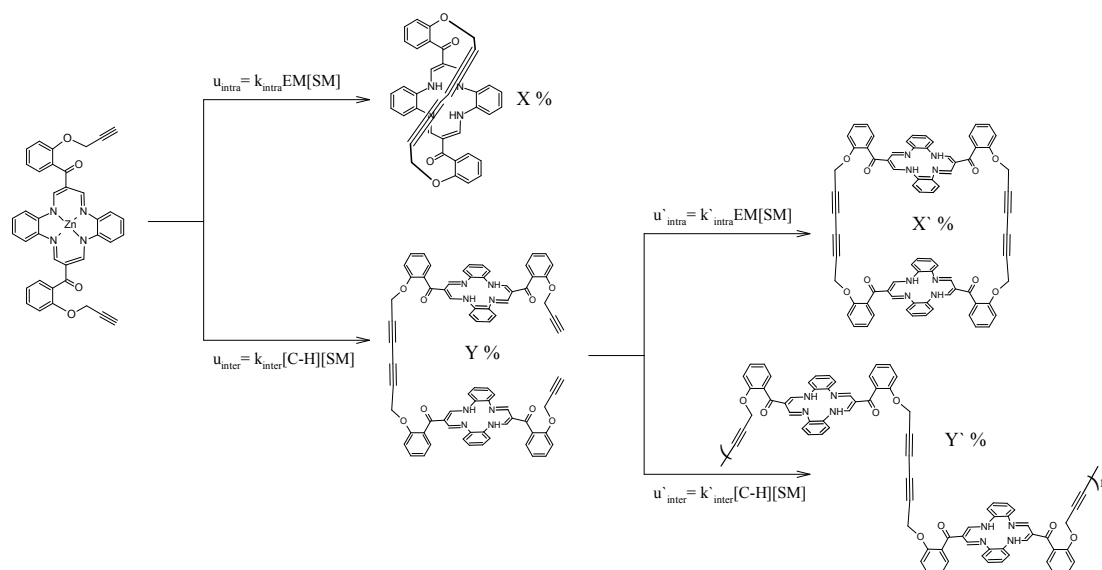


Table S1. Copper-catalyzed aerobic oxidations of bis-propargylated precursor **2·Zn**

Entry	Monomer 2·Zn [SM] ₀	Coupling conditions	Products distribution			$[EM]_{kin}$ [mM] ^b
			Strapped ligand (X) ^a	Open chain dimer (Y) ^b	X/Y	
1	1.50 mM	CuCl/TMEDA	44%	56%	0.786	1.18
2	1.50 mM	CuCl/CuCl ₂ /Py	34%	66%	0.515	0.77
3	10.00 mM	CuCl/CuCl ₂ /Py	5%	95%	0.0526	0.53
4	0.75 mM	CuCl/2,2'-bpy	26%	74%	0.351	0.26

^aIsolated yields, ^bEstimated yields according to a general mass balance formula: $Y\% = 100\% - X\%$

Kinetic effective molarity⁸ $[EM]_{kin}$ is defined as the critical concentration at which the rate of intramolecular coupling equals that of intermolecular coupling. $[EM]_{kin}$ provides a practical measure of the kinetic preference for cyclisation over oligomerization. Kinetic effective molarity can be calculated from the relative products distribution⁹:

$$\frac{X\%}{Y\%} = \frac{u_{intra}}{u_{inter}} = \frac{k_{intra}EM}{k_{inter}[SM]_0} = \frac{EM}{[SM]_0}$$

$$EM = (X/Y) \cdot [SM]_0$$

Where:

$[SM]_0$ – initial concentration of the starting precursor **2·Zn**

X % – isolated yield of intramolecular coupling product (strapped ligand **3**)

Y % – estimated content of all intermolecular coupling products (open-chain intermediate **4**, cyclic dimer **5** and higher oligomers)

⁸ (a) Mandolini, L. *Adv. Phys. Org. Chem.* **1986**, 22, 1. (b) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, 17, 183.

⁹ (a) Although ¹H NMR spectroscopy can be applied for effective molarity determination (see reference b), the accuracy of this method was largely influenced by overlapping oligomers signals and proved to be unreliable in the present system. Thus, all $[EM]_k$ values were estimated for isolated yields. (b) Mitchell, L.; Parkinson, J. A.; Percy, J. M.; Singh, K. J. *Org. Chem.* 2008, 73, 2389. (c) see also: Anderson, S.; Anderson, H. J.; Sanders, J. K. M. *J. Chem. Soc. Perkin Trans 1*, **1995**, 2255.

Thus aerobic oxidative coupling of 2-Zn precursor at initial concentration of 1.50 mmol/l performed in the presence of CuCl/TMEDA complex gave the kinetic effective molarity $[EM]_{kin}$:

$$\begin{aligned} X / Y &= v_{intra} / v_{inter} = k_{intra}EM / k_{inter}[SM]_0 = EM/[SM]_0 \\ [SM]_0 &= 1.5 \cdot 10^{-3} \text{ mol/l} = 1.50 \text{ mmol/l} \\ X/Y &= 44/56 = 0.786 \\ EM &= (X/Y) \cdot [SM]_0 = 0.78 \cdot 1.50 \text{ mmol/l} = 1.18 \text{ mmol/l} \end{aligned}$$

Similarly, aerobic oxidative coupling of Zn(II)-monomer precursor at initial concentration of 1.5 mmol/l performed in the presence of 2,2'-bpy-CuCl gave the kinetic effective molarity $[EM]_{kin}$:

$$\begin{aligned} X / Y &= v_{intra} / v_{inter} = k_{intra}EM / k_{inter}[SM]_0 = EM/[SM]_0 \\ [SM]_0 &= 1.5 \cdot 10^{-3} \text{ mol/l} = 1.50 \text{ mmol/l} \\ X/Y &= 26/74 = 0.351 \\ EM &= (X/Y) \cdot [SM]_0 = 0.35 \cdot 1.5 \text{ mmol/l} = 0.53 \text{ mmol/l} \end{aligned}$$

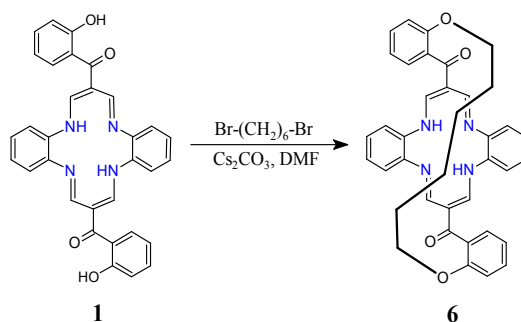
Table S2. Copper-catalyzed aerobic oxidations of open-chain intermediate complex **[4]Zn₂**

Entry	Open-chain dimer [4]Zn ₂ [SM] ₀ ^c	Coupling reagents	Products distribution			$[EM]_{kin}$ [mM] ^b
			Cyclic dimer (X') ^a	Higher oligomers (Y') ^b	X'/Y'	
1	(0.150 mmol-0.066 mmol) / 0.1 dm ³ = 0.84 mM	CuCl/TMEDA	16%	40%	0.400	0.33
2	(0.299 mmol-0.099 mmol) / 0.2 dm ³ = 1.00 mM	CuCl/CuCl ₂ /Py	30%	36%	0.833	0.83
3	(0.810 mmol-0.043 mmol) / 0.08 dm ³ = 0.77 mM	CuCl/CuCl ₂ /Py	17%	78%	0.218	0.17
4	(0.299 mmol-0.076 mmol) / 0.4 dm ³ = 0.56 mM	CuCl/2,2'-bpy	28%	46%	0.609	0.68

^aIsolated yields, ^bYields estimated according to a general mass balance formula: Y'%=100%-X%-X'%,

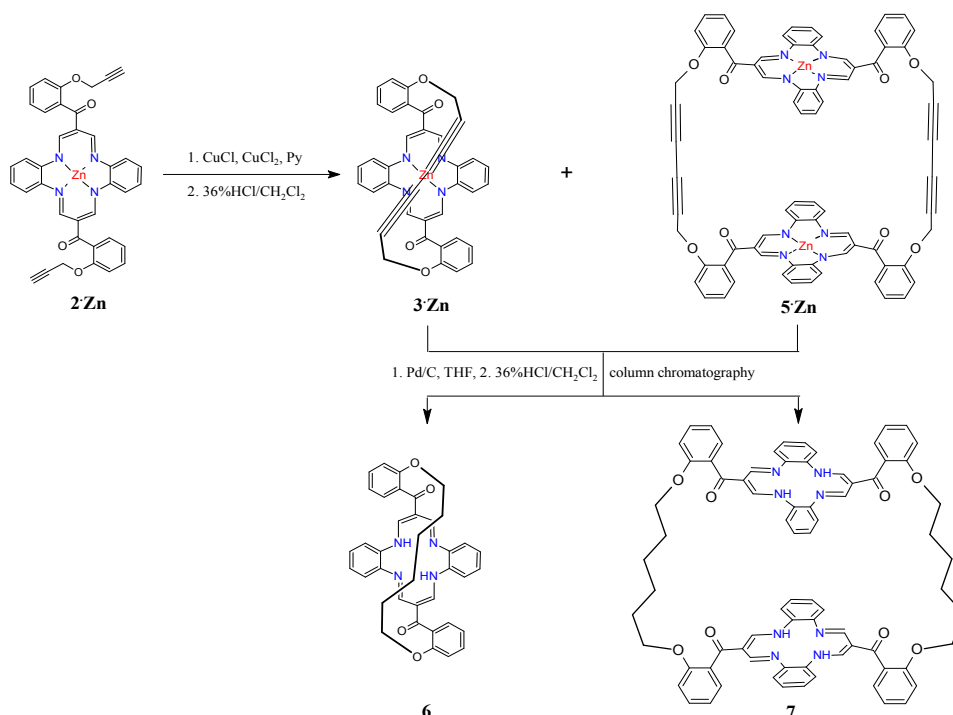
^cEstimated concentration according to a general formula: [(initial no. of moles of monomer - consumed no. of moles for strapped ligand 3 production)/fixed reaction volume].

6 General procedures for the synthesis of strapped ligand 6 via alkylation of 1



Starting ligand **1** (500 mg, 0.95 mmol) was added in a single amount to a suspension of anhydrous Cs_2CO_3 (800 mg, 2.44 mmol) in 60 ml of dry N,N-dimethylformamide. The resulting mixture was stirred at room temperature for 30 minutes. Then, 1,6-dibromohexane (0.22 ml, 1.42 mmol) was added in a single amount to a clear red solution and the resulting mixture was stirred at room temperature for 24 h. Orange precipitate was filtered off, washed with cold methanol and dried under vacuum. The residue was redissolved in dichloromethane (40 ml) and washed twice with distilled water (2x40 ml) to remove residual N,N-dimethylformamide. The organic phase was separated, dried over anhydrous MgSO_4 and concentrated to ca. 10 ml under reduced pressure. Concentrated solution was left at room temperature for 2 days. The resulting solid was filtered off, dried in a vacuum and yielded an analytically pure product (430mg, isolated yield 75%).

7 General procedures for a one-pot synthesis of strapped ligand 6 and cyclic dimer 7

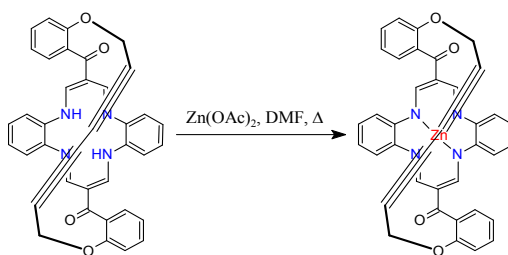


Copper(I) chloride CuCl (1.2 g, 12.12 mmol) and copper(II) chloride CuCl₂·2H₂O (240 mg, 1.44 mmol) were added to a solution of zinc(II) complex **2·Zn** (540 mg, 0.810 mmol) in a 80 ml of dry pyridine. The flask was closed with a stopper and the reaction mixture was stirred at 273 K until the solution become dark-green (ca. 2 hours). The resulting mixture was left at 273 K for 7 days. The reaction mixture was quenched by pouring the mixture into 0.5 liter of ice water and extracted with dichloromethane (2 x 50 ml). The combined organic extracts were dried over anhydrous MgSO₄, filtered and evaporated to dryness under reduced pressure. The crude mixture was redissolved in a hot THF (250 ml) and filtered on a fine frit to remove any insoluble residues.

Palladium on carbon (10wt%, 400 mg) was added in a one portion and the resulted suspension was stirred at room temperature under a flux of hydrogen for 5 h. The catalyst was filtered over a pad of Celite and the filtrate evaporated to dryness. The crude reaction mixture was dissolved in dichloromethane (50 ml), demetalated by treatment with concentrated 36% hydrochloric acid (25 ml) and stirred vigorously for 10 minutes. This clear yellow solution was washed twice with water (2 x 200ml) and neutralized with saturated NaHCO₃ solution. The organic phase was separated, dried over anhydrous MgSO₄ and concentrated to ca. 25 ml under reduced pressure. The resulting solution was adsorbed onto the top of the silica gel column and separated by the gradient elution chromatography (acetone:chloroform gradient v:v, 20:1→10:1).

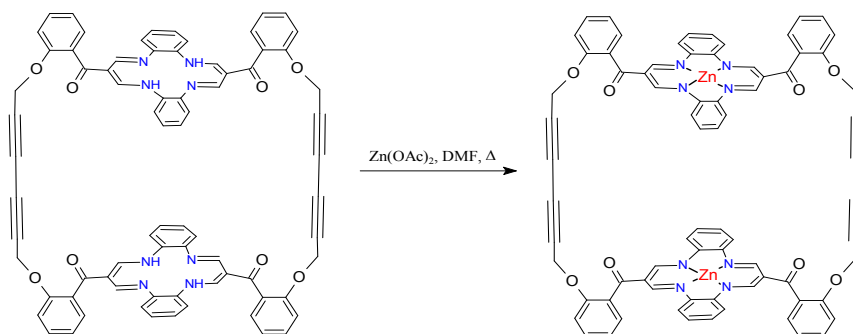
The first fraction was collected and evaporated to dryness under reduced pressure to give the strapped ligand **6** (26 mg, 0.043 mmol, isolated yield 5%). The second fraction was collected and evaporated to dryness under reduced pressure to give the cyclic dimer **7** (82 mg, 0.067 mmol, isolated yield 17%).

8 General procedure for the synthesis of strapped ligand zinc(II) complex 6·Zn



A single amount of strapped ligand **3** (100 mg, 0.083 mmol) was added to a solution of anhydrous zinc acetate (300.0 mg, 1.62 mmol) in 20 ml of dry N,N-dimethylformamide and was heated at 70 °C with stirring until the suspension disappeared and a clear deep-red solution was obtained (ca. 6-8h). The solution was cooled to room temperature, poured into dichloromethane (15 ml) and washed with cold distilled water (4x50 ml). The organic phase was separated and evaporated to dryness under reduced pressure. The resulting red solid was dried in a vacuum and yielded an analytically pure product (89 mg, isolated yield 80.5%).

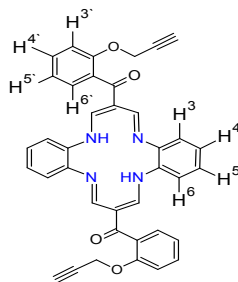
9 General procedure for the synthesis of cyclic dimer zinc(II) complex 5Zn_2



A single amount of cyclic dimer **5** (10 mg, 0.008 mmol) was added to a solution of anhydrous zinc acetate (10 mg, 0.06 mmol) in 20 ml of dry N,N-dimethylformamide and was heated at 90 °C with stirring until the suspension disappeared and a clear deep-red solution was obtained (ca. 8 h). The solution was cooled to room temperature and concentrated to ca. 5ml under reduced pressure. Distilled water was added in one portion (5 ml). The red precipitate was collected by filtration, washed with distilled water (2 x 10 ml) and dried under vacuum to afford the analytically pure product (9 mg, isolated yield 82%).

10 Characterization of the new compounds:

10.1 Characterization of O,O'-bispropargylated macrocyclic ligand 2



m.p.: 255 °C, orange needles.

UV-vis (CH₂Cl₂): λ 353 nm ($\epsilon = 8.5 \cdot 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 384 nm ($\epsilon = 3.6 \cdot 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$).

FTIR (ATR) ν (cm⁻¹): 3221 ($\equiv\text{C-H}$), 3112 ($=\text{C-H}$), 2921 (C-H), 2822 (C-H), 2107 ($\text{C}\equiv\text{C}$), 1642 (C=O), 1591 and 1561 (C=N and C=C macrocycle), 1450 and 1500 (C=C), 1254 (Ar-O-C), 1011 (Ar-O-C), 816, 744.

¹H NMR (300 MHz, CDCl₃, TMS) δ_{H} 2.36 (2 H, t, $J = 2.4$ Hz, $\text{C}\equiv\text{C-H}$), 4.74 (4 H, d, $J = 2.4$ Hz, OCH₂), 7.06-7.09 (2 H, m, H-5'), 7.11 (2 H, dd, $J = 0.9$ Hz, $J = 7.4$ Hz, H-3'), 7.15-7.22 (8 H, m, H-3,4,5,6), 7.4 (2 H, dd, $J = 1.6$ Hz, $J = 7.5$ Hz, H-6'), 7.47 (2 H, ddd, $J = 1.8$ Hz, $J = 7.4$ Hz, $J = 8.4$ Hz, H-4'), 8.59 (4 H, d, $J = 6.4$ Hz, N=C-H), 14.44 (2 H, t, $J = 6.5$ Hz, NH).

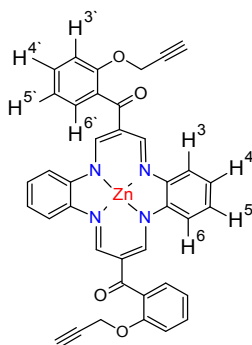
¹³C NMR (75 MHz, CDCl₃, TMS) δ_{C} 56.1 ($\text{C}\equiv\text{C-H}$); 75.9 ($\text{C}\equiv\text{C-H}$); 78.4 (OCH₂); 110.5; 113.1; 115.6; 122.0; 126.3; 129.4; 130.0; 130.9; 137.1; 153.0; 153.9; 192.5 (C=O).

¹H NMR (300 MHz, DMSO-d₆, TMS) δ_{H} 3.49 (2 H, t, $J = 2.3$ Hz, $\text{C}\equiv\text{C-H}$), 4.88 (4 H, d, $J = 2.3$ Hz, OCH₂), 7.12 (2 H, dt, $J = 0.8$ Hz, $J = 7.4$ Hz, H-3'), 7.16-7.36 (12 H, m, H-3,4,5,6,3',5',6'), 7.53 (2 H, ddd, $J = 1.8$ Hz, $J = 7.4$ Hz, $J = 8.4$ Hz, H-4'), 8.53 (4 H, d, $J = 6.4$ Hz, -N=C-H), 14.31 (2 H, t, $J = 6.4$ Hz, NH).

MS (ESI⁺): m/z (rel intensity) Mass calcd. for C₃₈H₂₉N₄O₄ [M+H]⁺ 605.2 (100%), found: 605.5 (100%) [M+H]⁺.

Elemental analysis: Anal. calcd. for. C₃₈H₂₈N₄O₄: C, 75.48; H, 4.67; N, 9.27; Found: C, 75.46; H, 4.65; N, 9.24.

10.2 Characterization of O,O'-bispropargylated macrocyclic complex 2·Zn



m.p.: > 260 °C, red needles.

UV-vis (CH₂Cl₃): λ 295 nm, 361 nm (ε = 6.3·10⁴ dm³·mol⁻¹·cm⁻¹), 400 nm (shoulder).

FTIR (ATR) ν (cm⁻¹): 3298 (≡C-H), 3057 (=C-H), 2113 (C≡C), 1619 (C=O), 1504 and 1480 (C=N and C=C macrocycle), 1601 and 1450 (C=C), 1392, 1345, 1310, 1285, 1264, 1210 (Ar-O-C), 1008 (Ar-O-C), 979, 915, 742 (C=C), 600.

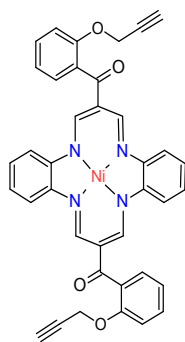
¹H NMR (300 MHz, DMSO-d₆, TMS) δ_H 3.46 (2 H, t, J = 2.3 Hz, C≡C-H), 4.83 (4 H, d, J = 2.3 Hz, OCH₂), 6.97-7.21 (14 H, br.m, H-3,4,5,6,3',5',6'), 7.47 (2 H, ddd, J = 1.8 Hz, J = 7.4, J = 8.4 Hz, H-4'), 8.53 (4 H, s, -N=C-H).

¹³C NMR (75 MHz, DMSO-d₆, TMS) δ_C 55.3; 78.3; 79.1; 109.6; 112.7; 114.7; 121.2; 125.8; 128.4; 130.0; 130.9; 140.3; 153.0; 154.7; 192.1.

MS (ESI⁺): m/z (rel intensity) Mass calcd. for C₃₈H₂₇N₄O₄Zn [M+H]⁺ 667.1 (100%), found: 667.7 (100%) [M+H]⁺.

Elemental analysis: Anal. calcd. for. C₃₈H₂₆N₄O₄Zn: C, 68.32; H, 3.92; N, 8.39; Found: C, 67.98; H, 3.80; N, 8.35.

10.3 Characterization of O,O'-bispropargylated macrocyclic complex 2·Ni



m.p.: 263-265 °C, orange needles.

UV-vis (CH₂Cl₂): λ 335 ($\epsilon = 3.9 \cdot 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 380 ($\epsilon = 2.5 \cdot 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 399 ($\epsilon = 3.5 \cdot 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 433 nm ($\epsilon = 8.7 \cdot 10^3 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$).

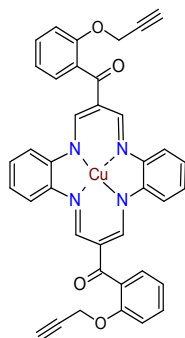
FTIR (KBr) ν (cm⁻¹): 3283 ($\equiv\text{C-H}$), 3069 ($=\text{C-H}$), 2921 (C-H), 2853 (C-H), 2111 (C $\equiv$ C), 1630 (C=O), 1569 and 1504 (C=N and C=C macrocycle), 1599 and 1450 (C=C, arom), 1420, 1345, 1315,, 1214 (Ar-O-C), 1022 (Ar-O-C), 934, 746 (C=C).

Complex 2·Ni is too insoluble to record ¹H and ¹³C NMR spectra.

MS (ESI⁺): m/z (rel intensity) Mass calcd. for C₃₈H₂₇N₄O₄Ni [M+H]⁺ 661.1 (100%), found: 661.5 (100%) [M+H]⁺.

Elemental analysis: Anal. calcd. for. C₃₈H₂₆N₄O₄Ni·0.5H₂O: C, 68.08; H, 4.06; N, 8.36; Found: C, 67.89; H, 3.93; N, 8.39.

10.4 Characterization of O,O`-bispropargylated macrocyclic complex 2·Cu



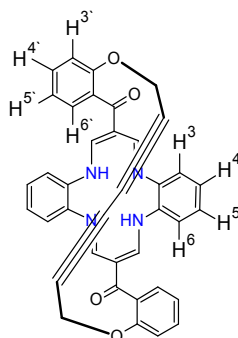
m.p.: > 260 °C, brown powder, insoluble in most organic solvents.

FTIR (KBr) ν (cm⁻¹): 3291 and 3228 ($\equiv$ C-H), 3072 (=C-H), 2925 (C-H), 2875 (C-H), 2111 (C $\equiv$ C), 1630 (C=O), 1566 and 1507 (C=N and C=C macrocycle), 1597 and 1451 (C=C, arom), 1412, 1338, 1217 (Ar-O-C), 1022 (Ar-O-C), 926, 750 (C=C).

Complex 2·Cu is both insoluble and paramagnetic, thus no NMR spectra could be obtained.

Elemental analysis: Anal. calcd. for. C₃₈H₂₆N₄O₄Cu: C, 68.51; H, 3.93; N, 8.41; Found: C, 68.32; H, 3.99; N, 8.39.

10.5 Characterization of strapped ligand 3



m.p.: > 260 °C, orange needles.

UV-vis (CHCl₃): λ 284, 364 nm.

FTIR (ATR) ν (cm⁻¹): 3063 and 3032 (=C-H), 2917 (C-H), 2858 (C-H), 1651 (C=O), 1598 and 1562 (C=N and C=C macrocycle), 1453 and 1499 (C=C), 1219 (Ar-O-C), 1005 (Ar-O-C), 748.

¹H NMR (300 MHz, CDCl₃, TMS) δ_{H} 4.60 (4 H, s, OCH₂), 6.84 (2 H, dd, J = 0.7 Hz, J = 8.3 Hz, H-3'), 7.09-7.22 (10 H, m, H-3,4,5,6,5'), 7.46 (2 H, ddd, J = 1.8 Hz, J = 7.5 Hz, J = 8.3 Hz, H-4'), 7.60 (2 H, dd, J = 1.7 Hz, J = 7.5 Hz, H-6'), 8.57 (4 H, d, J = 6.6 Hz, N=C-H), 14.54 (2 H, t, J = 6.6 Hz, NH).

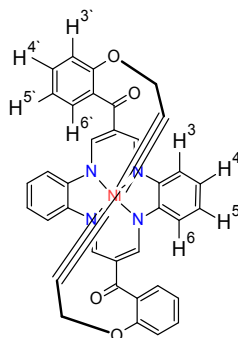
¹H NMR (300 MHz, DMSO-d₆, TMS) δ_{H} 4.86 (4 H, s, OCH₂), 7.09-7.22 and 7.47-7.56 (8 H, m, H-3,4,5,6,3',5'), 7.34-7.37 (4 H, m, H-4',6'), 8.53 (4 H, d, J = 6.5 Hz, N=C-H), 14.40 (2 H, t, J = 6.5 Hz, NH).

Strapped ligand 3 is too insoluble to record ¹³C NMR spectrum.

MS (ESI⁺): m/z (rel intensity) Mass calcd. for C₃₈H₂₇N₄O₄ [M+H]⁺ 603.2 (100%), found: 603.3 (100%) [M+H]⁺.

Elemental analysis: Anal. calcd. for. C₃₈H₂₆N₄O₄: C, 75.73; H, 4.35; N, 9.3; Found: C, 75.77; H, 4.30; N, 9.26.

10.6 Characterization of strapped ligand complex 3-Ni



m.p.: > 260 °C, red powder.

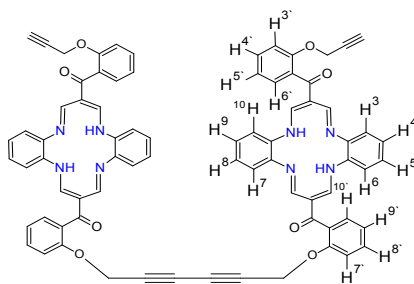
^1H NMR (300 MHz, DMSO- d_6 , TMS) δ_{H} 4.61 (4 H, s, OCH₂), 6.84 (2 H, d, J = 8.3 Hz, H-3'), 7.00 (4 H, m, H-3,6), 7.21 (2 H, dd, J = 6.3 Hz, J = 7.1 Hz, H-5'), 7.33 (4 H, m, H-4,5), 7.49 (2 H, ddd, J = 2.5 Hz, J = 7.2 Hz, J = 8.3 Hz, H-4'), 7.70 (2 H, dd, J = 2.1 Hz, J = 6.5 Hz, H-6'), 8.32 (4 H, s, N=C-H).

Strapped ligand complex 3-Ni is too insoluble to record a ^{13}C NMR spectrum.

MS (ESI+): m/z (rel intensity) Mass calcd. for C₃₈H₂₄N₄O₄NiNa [M+Na]⁺ 681.1 (100%), found: 681.4 (100%) [M+Na]⁺.

FTIR (HCB) ν (cm⁻¹): no peaks attributable to terminal C $\equiv$ C-H stretching can be observed.

10.7 Characterization of an open-chain intermediate [4]



m.p.: > 260 °C, red powder.

UV-vis (CH₂Cl₂): λ 353 and 384 nm.

FTIR (KBr) ν (cm⁻¹): 3456 (-NH), 3295 ($\equiv$ C-H), 3064 (=C-H), 2921 (C-H), 2853 (C-H), 1648 (C=O), 1599 and 1563 (C=N and C=C macrocycle), 1449 and 1499 (C=C), 1293, 1259, 1215 (Ar-O-C), 1143, 1001 (Ar-O-C), 911, 840 (N-H), 753.

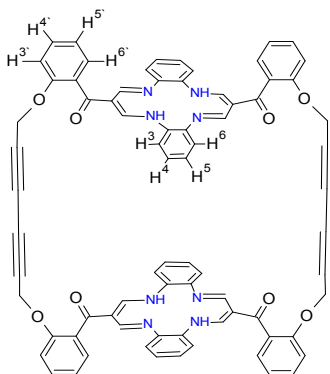
¹H NMR (300 MHz, CDCl₃, TMS) δ_{H} 2.36 (2 H, t, J = 2.4 Hz, C $\equiv$ C-H), 4.72 (4 H, d, J = 2.4 Hz, OCH₂), 4.78 (4 H, s, OCH₂), 7.02-7.17 (24 H, m, H-3,4,5,6,7,8,9,10,3',5',7',9'), 7.36-7.49 (8 H, m., H-4',6',8',10'), 8.54 (8 H, br.s, N=C-H), 14.36 (4 H, br.s, NH).

Compound [4] is too insoluble to record a ¹³C NMR spectrum.

MS (ESI⁺): m/z (rel intensity) Mass calcd. for C₇₆H₅₅N₈O₈ [M+H]⁺ 1207.4 (100%), found: 1207.4 (100%) [M+H]⁺.

Elemental analysis: Anal. calcd. for. C₇₆H₅₄N₈O₈·0.1CH₂Cl₂: C, 75.18; H, 4.49; N, 9.22; Found: C, 75.00; H, 4.29; N, 9.18.

10.8 Characterization of a cyclic dimer 5



m.p.: > 260 °C, orange powder.

UV-vis (CH₂Cl₂): λ 353 and 384 nm.

FTIR (KBr) ν (cm⁻¹): 3457 (-NH), 3066 (=C-H), 2859 (C-H), 1647 (C=O), 1599 and 1563 (C=N and C=C macrocycle), 1449 and 1499 (C=C), 1292, 1260, 1217 (Ar-O-C), 1143, 1000 (Ar-O-C), 911, 756 (C-H).

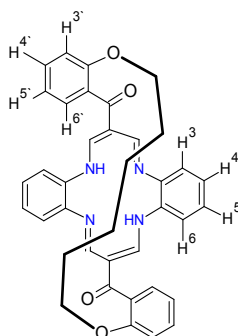
¹H NMR (300 MHz, CDCl₃, TMS) δ_H 4.76 (8 H, s, OCH₂), 7.00-7.17 (16 H, br.m., H-3,4,5,6), 7.07 (4 H, dd, J = 0.8 Hz, J = 8.4 Hz, H-3'), 7.14 (4 H, dt, J = 0.8 Hz, J = 7.4 Hz, H-5'), 7.40 (4 H, dd, J = 1.6 Hz, J = 7.4 Hz, H-6'), 7.46, (4 H, ddd, J = 1.8 Hz, J = 7.4, J = 8.4 Hz, H-4'), 8.53 (8 H, br.d, N=C-H), 14.37 (4 H, t, J = 6.5 Hz, NH). Pure cyclic dimer is poorly soluble in CDCl₃ therefore multiple scans are required to achieve satisfactory signal-to-noise ratio (S/N).

Cyclic dimer 5 is too insoluble to record a ¹³C NMR spectrum.

MS (ESI⁺): m/z (rel intensity) Mass calcd. for C₇₆H₅₃N₈O₈ [M+H]⁺ 1205.4 (100%), found: 1205.5 (100%) [M+H]⁺.

Elemental analysis: Anal. calcd. for. C₇₆H₅₂N₈O₈·0.5CH₂Cl₂: C, 73.64; H, 4.28; N, 8.98; Found: C, 73.56; H, 4.25; N, 8.99.

10.9 Characterization of strapped ligand 6



m.p.: > 260 °C, orange crystals

UV-vis (CHCl₃): λ 352 nm ($\epsilon = 2.57 \cdot 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 384 nm ($\epsilon = 1.26 \cdot 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$).

FTIR (KBr) ν (cm⁻¹): 3445 (-NH), 3061 (=C-H), 2921 and 2858 (C-H), 1652 (C=O), 1602 and 1562 (C=N and C=C macrocycle), 1486 and 1468 (C=C), 1450, 1424, 1296, 1245, 1216 (Ar-O-C), 1143, 1103, 910, 752 (C-H).

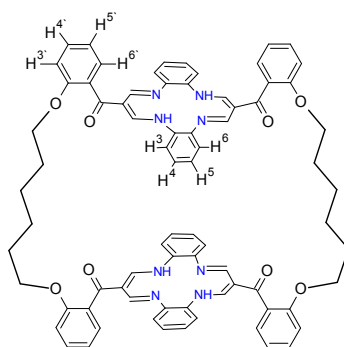
¹H NMR (300 MHz, CDCl₃, TMS) δ_{H} 1.28 (4 H, m, CH₂), 1.49 (4 H, m, CH₂), 3.82 (4 H, d, J = 5.6 Hz, OCH₂), 6.84 (2 H, dd, J = 0.6 Hz, J = 8.3 Hz, H-3'), 7.06-7.19 (10 H, m, H-3,4,5,6,5'), 7.43, (2 H, ddd, J = 1.8 Hz, J = 7.4 Hz, J = 8.3 Hz, H-4'), 7.57 (2 H, dd, J = 1.7 Hz, J = 7.5 Hz, H-6'), 8.49 (4 H, d, J = 6.5 Hz, N=C-H), 14.36 (2 H, t, J = 6.5 Hz, NH).

¹³C NMR (75 MHz, CDCl₃, TMS) δ_{C} 26.09; 26.15; 67.75 (OCH₂); 111.37; 111.73; 115.92; 121.06; 126.39; 129.04; 130.24; 131.93; 137.71; 153.28; 156.07; 193.03 (C=O).

MS (ESI⁺): m/z (rel intensity) Mass calcd. for C₃₈H₃₅N₄O₄ [M+H]⁺ 611.3 (100%), found: 611.5 (100%) [M+H]⁺.

Elemental analysis: Anal. calcd. for. C₃₈H₃₄N₄O₄: C, 74.73; H, 5.61; N, 9.17; Found: C, 74.87; H, 5.57; N, 9.17.

10.10 Characterization of cyclic dimer 7



m.p.: > 260 °C, orange powder

UV-vis (CHCl₃): λ 345 nm ($\epsilon = 5.45 \cdot 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 388 nm ($\epsilon = 2.28 \cdot 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$).

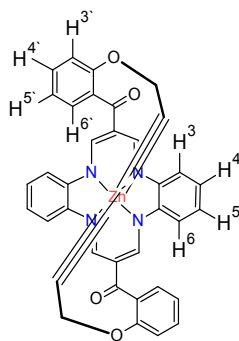
FTIR (ATR) ν (cm⁻¹): 3069 (=C-H), 2933 and 2858 (C-H), 1655 (C=O), 1564 (C=N and C=C macrocycle), 1484 (C=C), 1451, 1423, 1287, 1246 (Ar-O-C), 1141, 1103, 809, 813, 742 (C-H).

¹H NMR (300 MHz, CDCl₃, TMS) δ_{H} 1.03-1.44 (8 H, m, CH₂), 1.29-1.43 (8 H, m, CH₂), 3.63 (8 H, t, J = 6.2 Hz, OCH₂), 6.74 (4 H, d, J = 8.4 Hz, H-3'), 6.97-7.08 (20 H, m, H-3,4,5,6,5'), 7.30-7.36 (8 H, m, H-4',6'), 8.48 (8 H, J = 6.5 Hz, N=C-H), 14.32 (4 H, J = 6.8 Hz, NH).

MS (ESI⁺): m/z (rel intensity) Mass calcd. for C₇₆H₆₈N₈O₈Na [M+Na]⁺ 1243.5 (100%), found: 1243.6 (100%) [M+Na]⁺.

Elemental analysis: Anal. calcd. for. C₇₆H₆₈N₈O₈·0.25CHCl₃: C, 73.19; H, 5.50; N, 8.96; Found: C, 73.22; H, 5.81; N, 8.62.

10.11 Characterization of strapped ligand zinc(II) complex 3·Zn



m.p.: > 260 °C, red powder.

UV-vis (CH₂Cl₂): λ 362 nm.

FTIR (KBr) ν (cm⁻¹): 3031 (=C-H), 2926 (C-H), 2860 (C-H), 1650 (C=O), 1621, 1598 and 1576 (C=N and C=C macrocycle), 1550, 1522, 1482, 1452, 1394, 1330, 1310, 1013 (Ar-O-C), 757 (C-H).

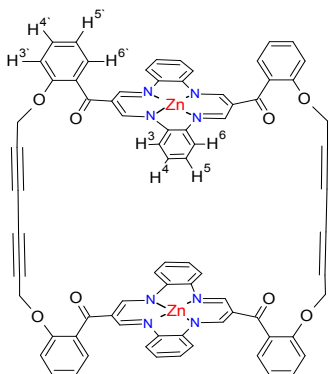
¹H NMR (300 MHz, DMSO-d₆, TMS) δ_{H} 4.79 (4 H, s, OCH₂), 7.05-7.20 (12 H, m., H-3,4,5,6,3',5'), 7.40 (2 H, dd, J = 1.6 Hz, J = 7.5 Hz, H-6'), 7.48 (2 H, ddd, J = 1.6, J = 7.6, J = 8.3 Hz, H-4'), 8.49 (4 H, s, N=C-H).

¹³C NMR (75 MHz, CDCl₃, TMS) δ_{C} 57.18; 69.22; 74.42; 109.89; 113.14; 114.66; 122.13; 125.69; 129.68; 130.68; 130.88; 140.96; 153.91; 155.44; 191.58;

MS (ESI⁺): m/z (rel intensity) Mass calcd. for C₃₈H₂₅N₄O₄Zn [M+H]⁺ 665.1 (100%), found: 665.5 (100%) [M+H]⁺.

Elemental analysis: Anal. calcd. for. C₃₈H₂₄N₄O₄Zn·0.5CH₂Cl₂: C, 65.27; H, 3.56; N, 7.91; Found: C, 65.44; H, 3.61; N, 7.87.

10.12 Characterization of cyclic dimer zinc(II) complex 5·Zn₂



m.p.: > 260 °C, red powder.

UV-vis (CH₂Cl₂): λ 362 nm.

FTIR (ATR) ν (cm⁻¹): 3058 (=C-H), 2924 (C-H), 2869 (C-H), 1621 (C=O), 1593 and 1571 (C=N and C=C macrocycle), 1543, 1517, 1482, 1447, 1393, 1336, 1310, 1268, 1207 (Ar-O-C), 1144, 1096, 1002 (Ar-O-C), 919, 749 (C-H).

¹H NMR (300 MHz, DMSO-d₆, TMS) δ_{H} 4.94 (8 H, s, OCH₂), 6.18-7.10 (20 H, br.m., H-3,4,5,6, 5'), 7.18 (4 H, d, J = 8.4 Hz, H-3'), 7.27 (4 H, dd, J = 1.6 Hz, J = 7.4 Hz, H-6'), 7.47, (4 H, ddd, J = 1.8 Hz, J = 7.5, J = 8.6 Hz, H-4'), 8.49 (8 H, br.s, N=C-H).

Cyclic dimer zinc(II) complex 5·Zn₂ is too insoluble to record a ¹³C NMR spectrum.

MS (ESI⁺): m/z (rel intensity) Mass calcd. for C₇₆H₄₉N₈O₈Zn₂ [M+H]⁺ 1329.2 (100%), found: 1329.1 (100%) [M+H]⁺.

Elemental analysis: Anal. calcd. for. C₇₆H₄₈N₈O₈Zn₂·0.5H₂O: C, 68.07; H, 3.68; N, 8.36; Found: C, 67.98; H, 3.79; N, 8.35.

11. Uv-vis spectroscopy

Uv-vis spectrum of the strapped zinc(II) complex **3·Zn** shows no red-shifting of the Soret band as compared to their **2·Zn** analog, that would be expected for ruffling macrocycle distortion.¹⁰ The hypsochromic shift have been observed in the tmtaa(Ni) complexes series, bearing bulky substituents at the diiminato chelate ring. This hypsochromic shift rises in part from distortions from planarity that reduce π -bond delocalization with increased degree of substitution.¹¹

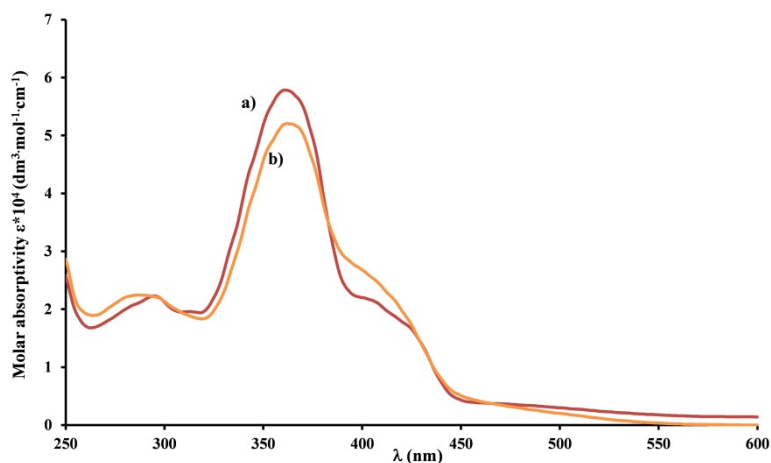


Figure S2. Uv-vis spectra comparison between a) **2·Zn** (25 μ M, red) and b) **3·Zn** (27 μ M, orange) complexes (CH_2Cl_2 , 298 K).

The general pattern of the electronic absorption Uv-vis spectra of both cofacial dimer **5** and its corresponding open-chain intermediate **[4]** resemble that of monomeric ligand **2**.

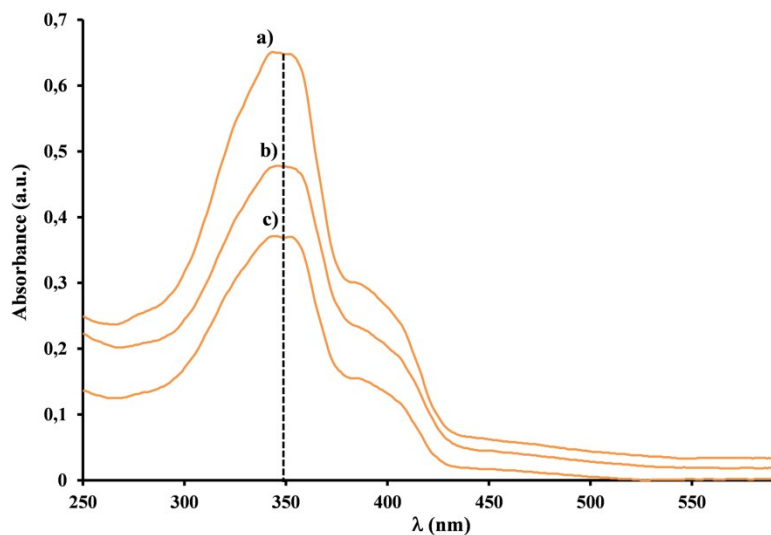


Figure S3. Comparison of the Uv-Vis spectra of: a) cyclic dimer **5** and b) its corresponding open-chain dimeric intermediate **[4]**, with c) monomeric ligand ($\sim 10^{-6}$ M, CH_2Cl_2 , 298 K).

¹⁰ Z. Zhou, Ch. Cao, Q. Liu, R. Jiang, *Org. Lett.*, 2010, **12**, 1780-1783; J. A. Shelnutt, X. Z. Song, J. G. Ma, S. L. Jia, W. Jentzen, C. J. Medforth, *J. Chem. Soc. Rev.*, 1998, **27**, 31-42.

¹¹ A. R. Cutler, C. S. Alleyne, D. Dolphin, *Inorg. Chem.*, 1985, **24**, 2276-2281.

12. Molecular models of cyclic dimers 5 and 7

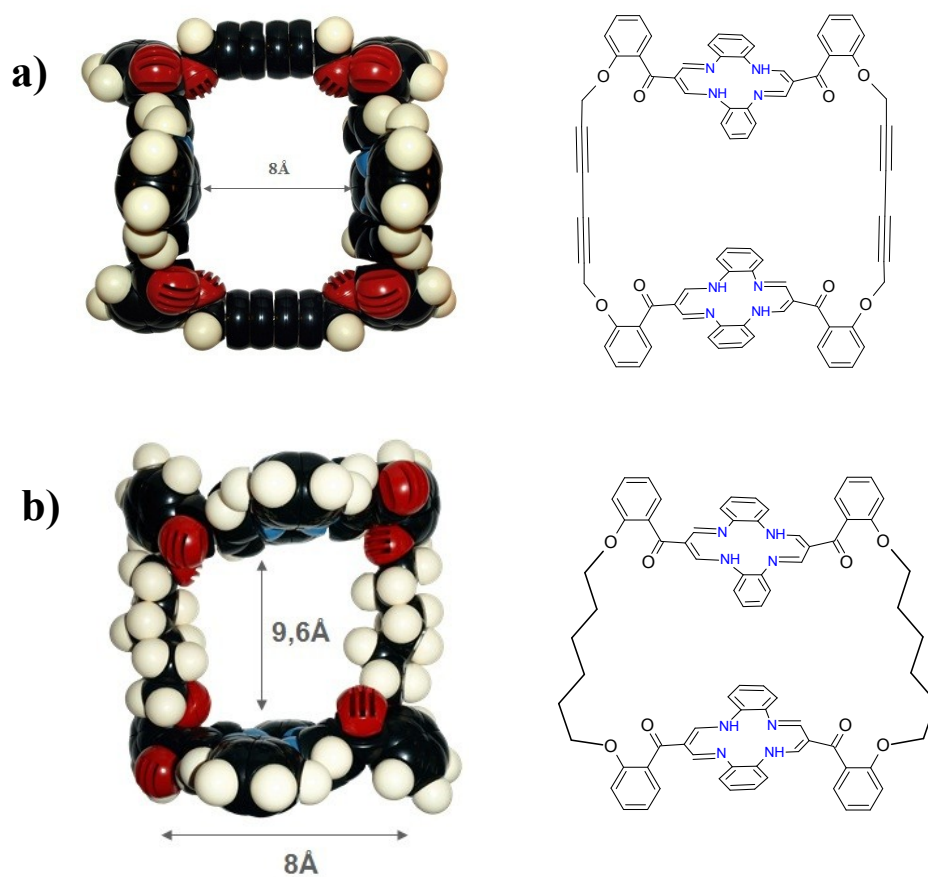


Figure S4. Corey-Pauling-Koltun (CPK) space filling models of cyclic dimers: a) **5** and b) **7** locked in extended conformations. Cross-cavity N...N distance estimation is indicated by the arrows.

13 X-ray structural analysis for zinc(II) complex **2·Zn**

The zinc(II) complex **2·Zn** ($\text{C}_{40}\text{H}_{32}\text{N}_4\text{O}_5\text{SZn}\cdot 3(\text{C}_2\text{H}_6\text{SO})$) crystallizes in the monoclinic *P*21 space group. The asymmetric part of unit cell contains one five-coordinated mononuclear **2·Zn** complex and three free lattice dimethyl sulfoxide molecules.

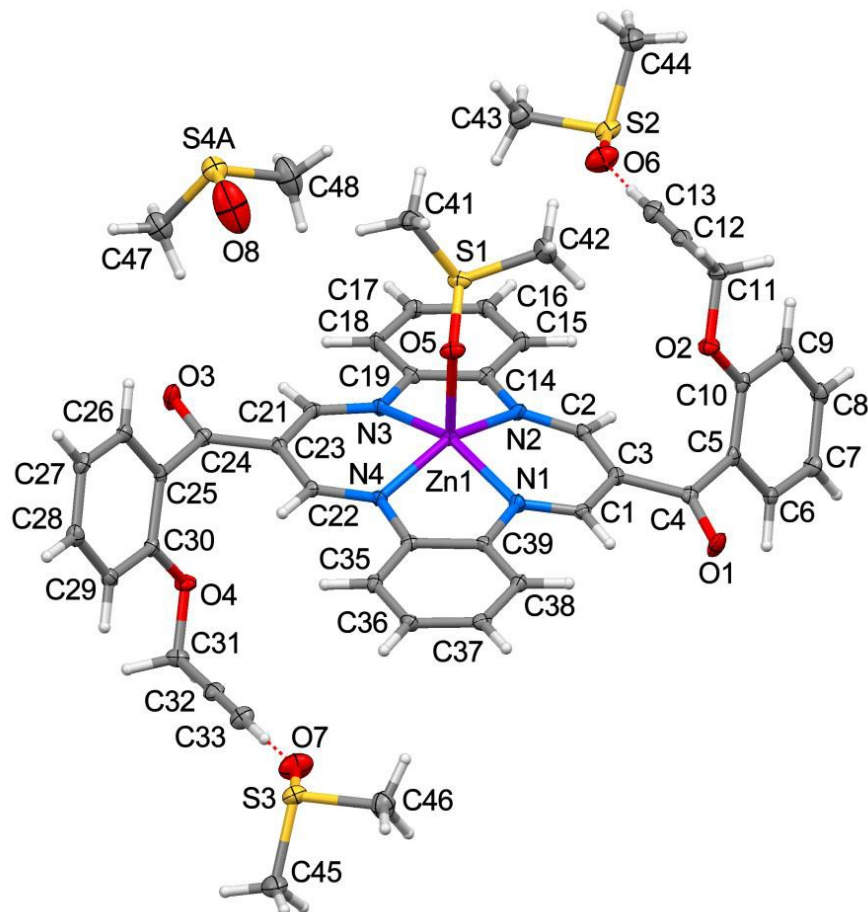


Figure S5. A view of the zinc(II) complex **2·Zn** with the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are drawn with an arbitrary radius. The intermolecular hydrogen bonds are shown as dashed lines.

The Zn–N bond lengths range from 2.019(3) to 2.034(3) Å, and Zn–O bond distance is 2.093(2) Å. Presence of the central zinc atom results in significant non-planarity of the 14-membered macrocyclic ring, which is up to 0.170(3) Å for the N2 atom.

Both dihedral angles between N₄ macrocycle mean plane and two substituted phenyl groups are 67.4(1)° within experimental error.

Propargyl groups are approximately oriented parallel to the N₄ macrocycle mean plane with the angles of 8.6(1)°. Both propargyl groups are involved in hydrogen bonds with uncoordinated dimethyl sulfoxide molecules with values of 3.089(4) Å and 164.6°, and 3.014(4) Å and 164.4°, for C13–H13...O6 and C33–H33...O7, respectively. A third uncoordinated dimethyl sulfoxide molecule exhibits a disorder of the sulfur atom over two positions in the ratio 0.820(4):0.180(4).

The crystal packing structure of the zinc(II) complex **2·Zn** is shown in Figure S6 below.

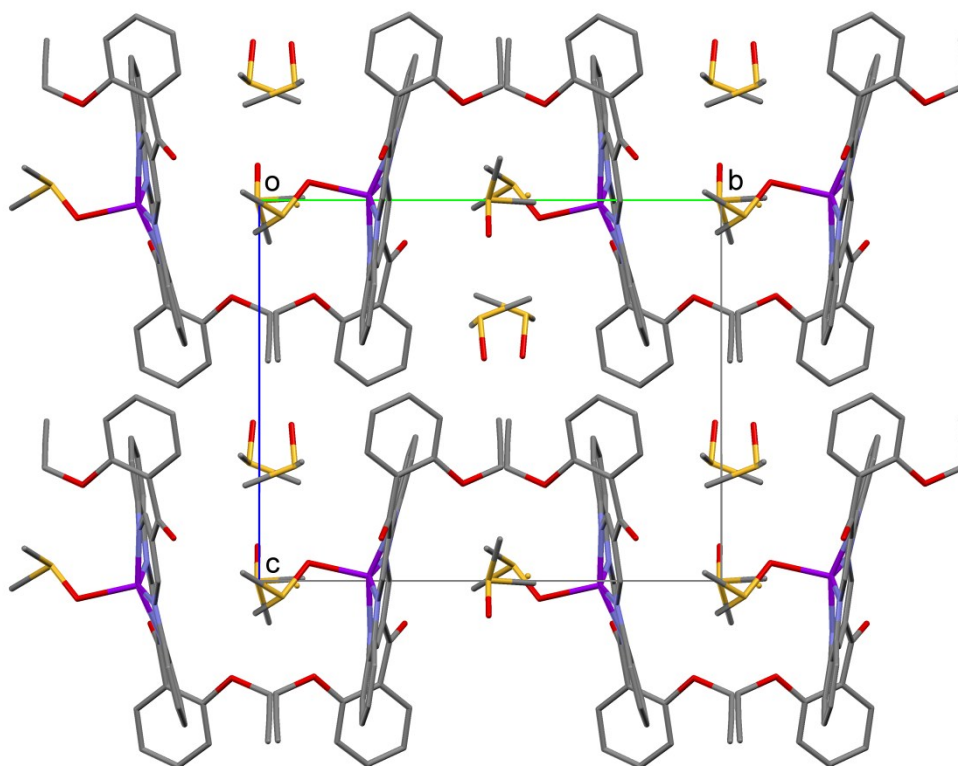


Figure S6. Molecular packing diagram of the zinc(II) complex **2·Zn** with DMSO solvent channels viewed down the a-axis.

Table S3. Crystal data and details of the structure determination for zinc(II) complex **2·Zn**

Chemical formula	C ₄₀ H ₃₂ N ₄ O ₅ SZn·3(C ₂ H ₆ OS)
Crystal system	monoclinic
Formula weight	980.57
Space group	<i>P2₁</i> (No. 4)
<i>a</i> (Å) <i>b</i> (Å) <i>c</i> (Å)	11.2639(12) 15.6341(17) 13.7495(15)
<i>V</i> (Å ³)	2272.3 (4)
<i>Z</i>	2
<i>D</i> _{calcd} (g cm ³)	1.433
<i>F</i> (000)	1024
<i>μ</i> (mm ⁻¹)	0.0782
Θ range (°)	1.6-25.0
Measured reflections	37301
Independent reflections	8020
Reflections with <i>I</i> > 2σ(<i>I</i>)	7875
<i>T</i> (K)	100
λ (Å)	0.71073 (Mo-K _α)
GooF on <i>F</i> ²	1.03
<i>R</i> , <i>wR</i> ²	0.0269, 0.0711
Δρ _{max} /Δρ _{min} (e Å ⁻³)	0.80/-0.36
β (°)	110.204(2)

14 X-ray structural analysis for strapped ligand 3

Strapped ligand **3** ($C_{38}H_{26}N_4O_4$) crystallizes in the space group *Pbcn* ($Z=8$) and contains one independent molecule in the asymmetric part of the unit cell (Figure S7).

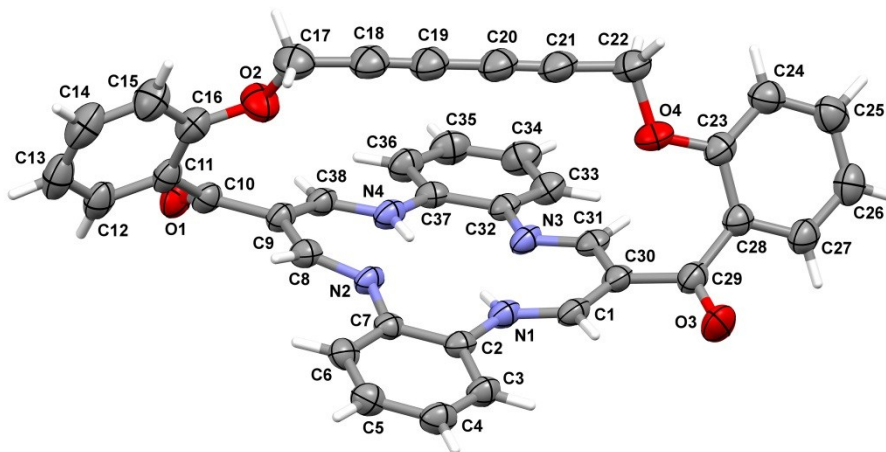


Figure S7. A view of the strapped ligand **3** with the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The 14-membered macrocyclic ring of **3** displays a slightly basket-like shaped deviation from coplanarity, described by dihedral angle between the two pentadiimine (N–C–C–C–N) planes of $19.76(4)^\circ$. A concave curvature of the DBTAA macrocyclic ring with the absence of the molecular symmetry results in the inherent chirality.¹² Due to a centrosymmetric space group the crystal in effect is a racemic mixture of the conformational enantiomers (Figure S8a).

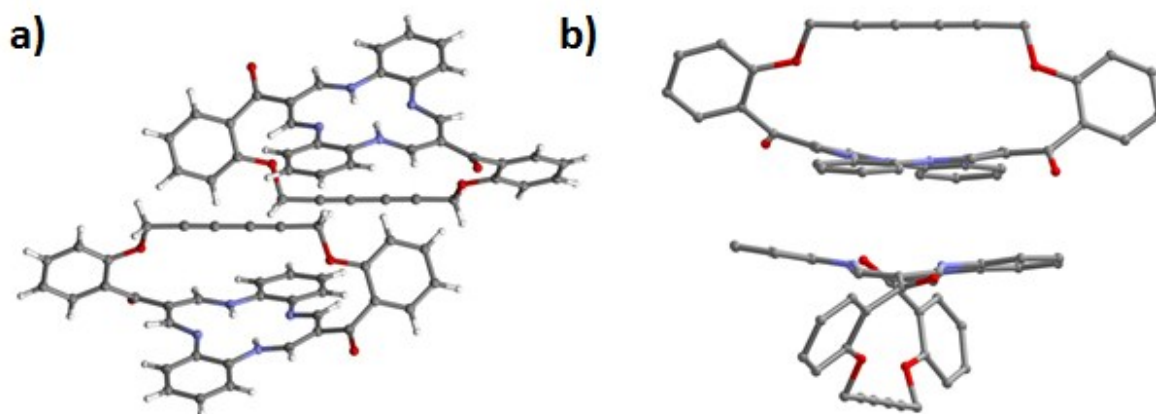


Figure S8. a) Two inherent enantiomers of strapped ligand **3** related in the crystal by an inversion centre, b) Self-recognition of two adjacent homochiral molecules of **3** via $\pi \cdots \pi$ -stacking. Hydrogen atoms have been omitted for clarity.

¹² Cort AD, Mandolini L, Pasquini C, Schiaffino L. *New J. Chem.* **2004**, 28, 1198–1199.

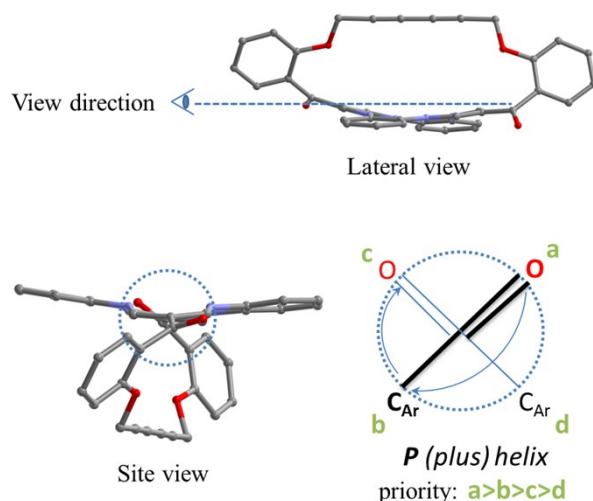


Figure S9. Assignment of strapped ligand **3** configuration: the priority letters a-d are arranged in the seniority order $a > b > c > d$.

The molecule has two substituted phenyl groups, which planes form with the N_4 macrocyclic ring different dihedral angles of 57.8 and 74.2°, despite that the 1,3-butadiyne bridge runs almost parallel to the N_4 macrocyclic ring mean plane with the closest distance of about 4 Å. Significant aromatic interactions occur on the opposite side of the chain between two adjacent macrocyclic rings at the distance of 3.3-3.4 Å (Figure S8b). The strapped ligand **3** has only hydrogen atom donors of carbon groups with a possibility to form intermolecular interactions with carbonyl oxygen atoms as well as intermolecular C–H $\cdots$ π contacts.¹³ Interactions with keto groups are distinctly different: C29–O3 has two weak C–H $\cdots$ O contacts of 2.89 and 2.91 Å, since C10–O1 shows three such contacts in the range of 2.65-2.72 Å. Even more clearly, the asymmetry of the molecule can be seen at interactions between 1,3-butadiyne bridges in adjacent molecules. The C22 methylene group form two significant interactions of C22–H22B $\cdots$ π_{ring} = 2.50 Å and C22–H22A $\cdots$ $\pi_{\text{C18-C19}}$ = 2.81 Å, since the corresponding C17 methylene group has acceptors at distances of 3.16 and 2.90 Å, respectively (Figure S10).

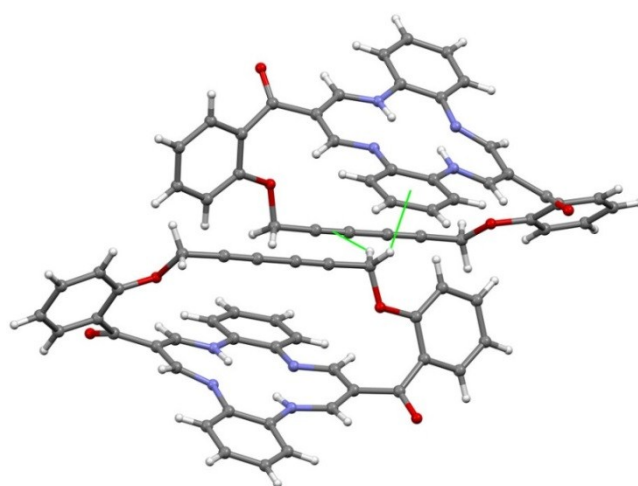


Figure S10. Intermolecular interaction C–H $\cdots$ π type between adjacent molecules of **3** marked as green lines.

¹³ Nishio, M.; Umezawa, Y.; Hirota, M.; Takeuchi, Y. *Tetrahedron* **1995**, 51, 8665.

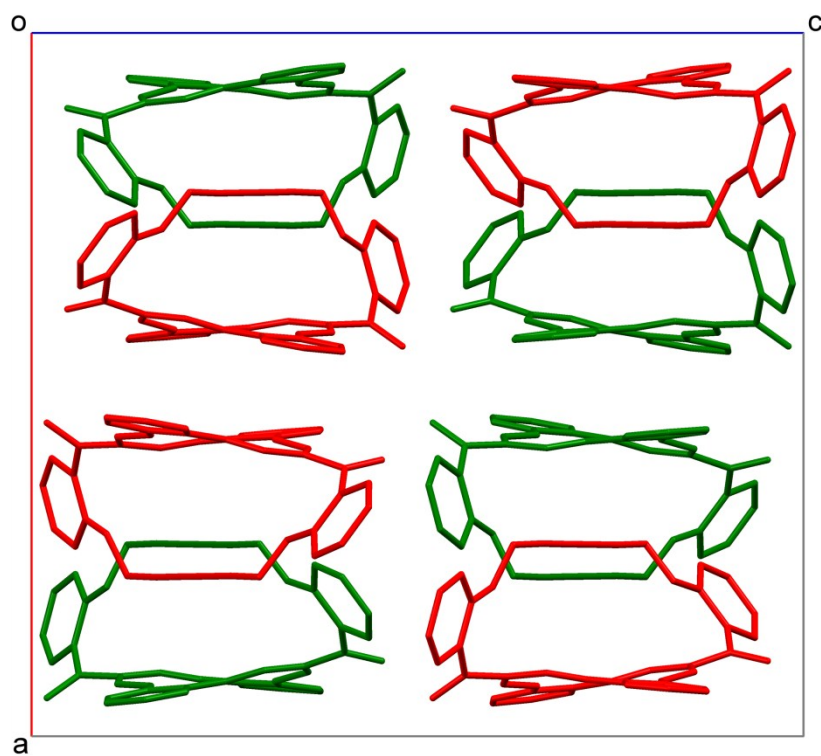
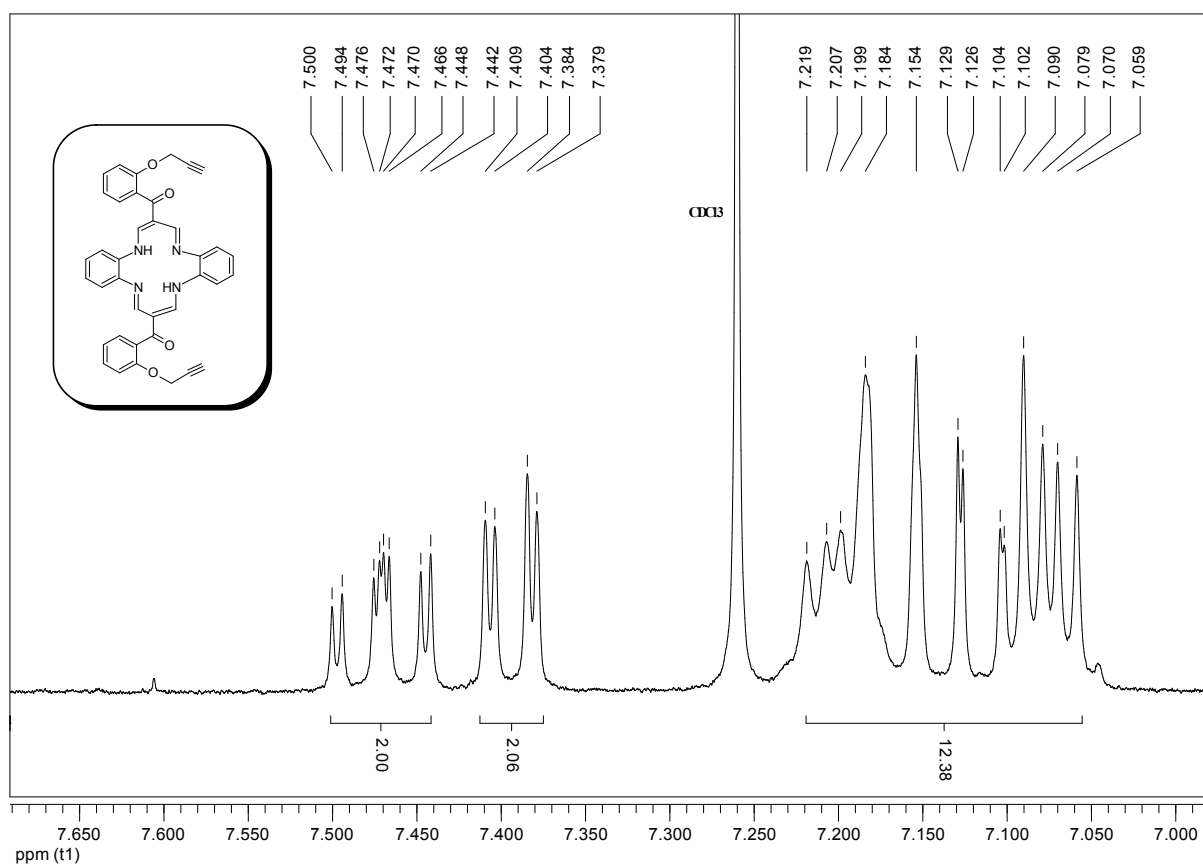
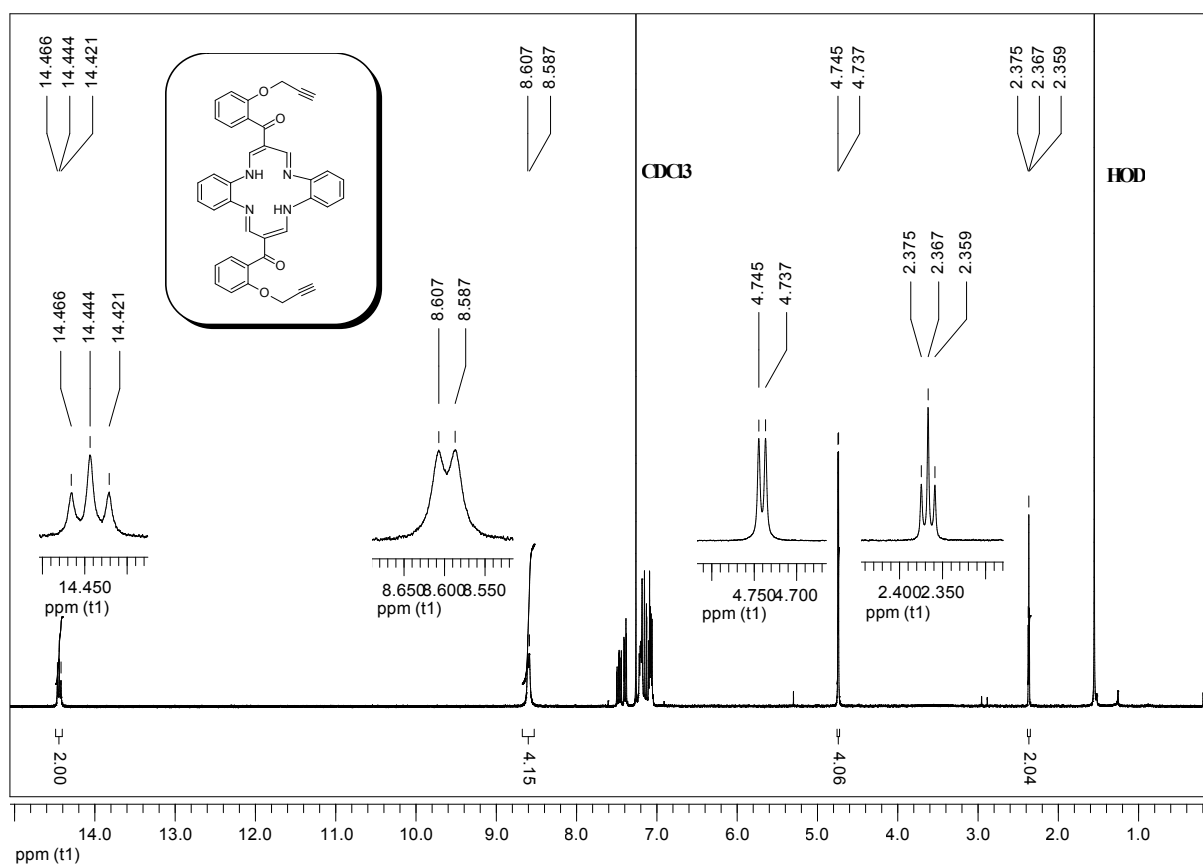


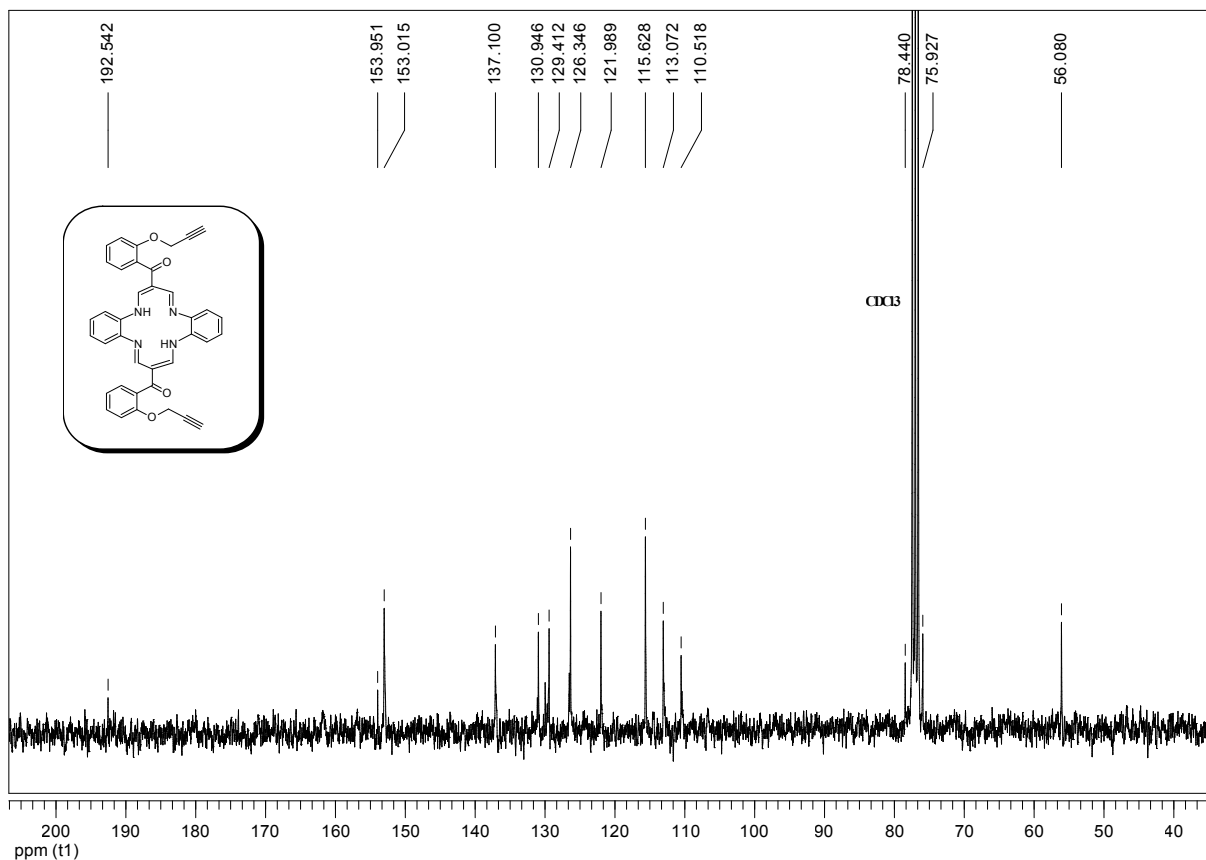
Figure S11. Molecular packing diagram of strapped ligand **3**, viewed down the *b*-axis, showing pairs of conformational enantiomers *M* (green) and *P* (red) and self-recognition of the two homochiral strapped ligands *via* a π - π stacking mechanism. Hydrogen atoms are omitted for clarity.

Table S4. Crystal data and details of the structure determination for strapped ligand **3**.

Chemical formula	C ₃₈ H ₂₆ N ₄ O ₄
Crystal system	orthorhombic
Formula weight	602.63
Space group	<i>Pbcn</i> (No. 60)
<i>a</i> (Å) <i>b</i> (Å) <i>c</i> (Å)	21.1618(16) 11.9414(11) 23.2097(17)
<i>V</i> (Å ³)	5865.1(8)
<i>Z</i>	8
<i>D</i> _{calcd} (g cm ³)	1.365
<i>F</i> (000)	2512
μ (mm ⁻¹)	0.090
Θ range (°)	1.8-25.0
Measured reflections	66233
Independent reflections	5176
Reflections with <i>I</i> >2 σ (<i>I</i>)	2230
<i>T</i> (K)	291
λ (Å)	0.71073 (Mo-K α)
GooF on <i>F</i> ²	0.95
<i>R</i> , <i>wR</i> ²	0.0404, 0.0619
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.18/-0.17

15 Copies of ^1H and ^{13}C NMR, FT-IR, ESI-MS and Uv-vis spectra



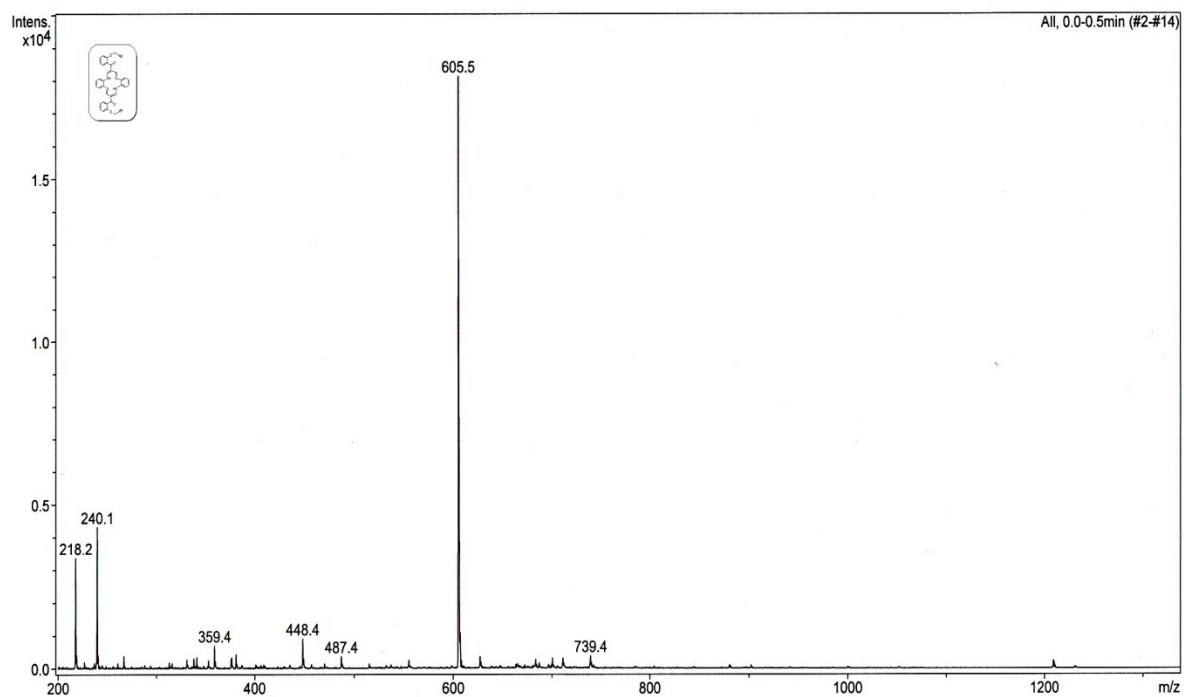


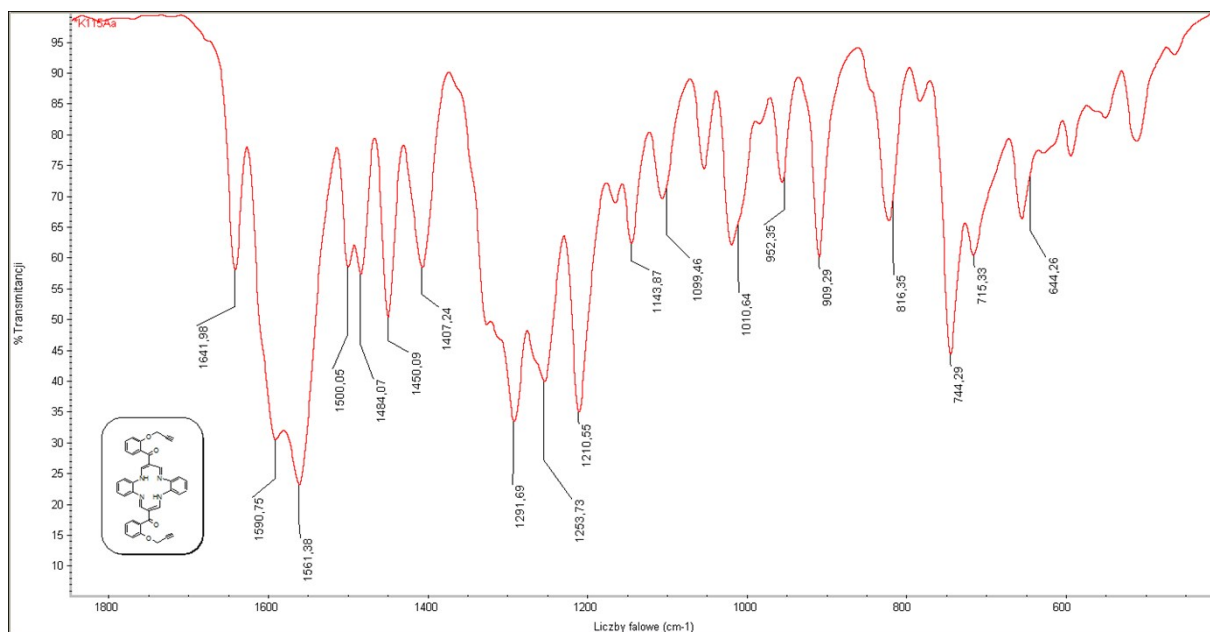
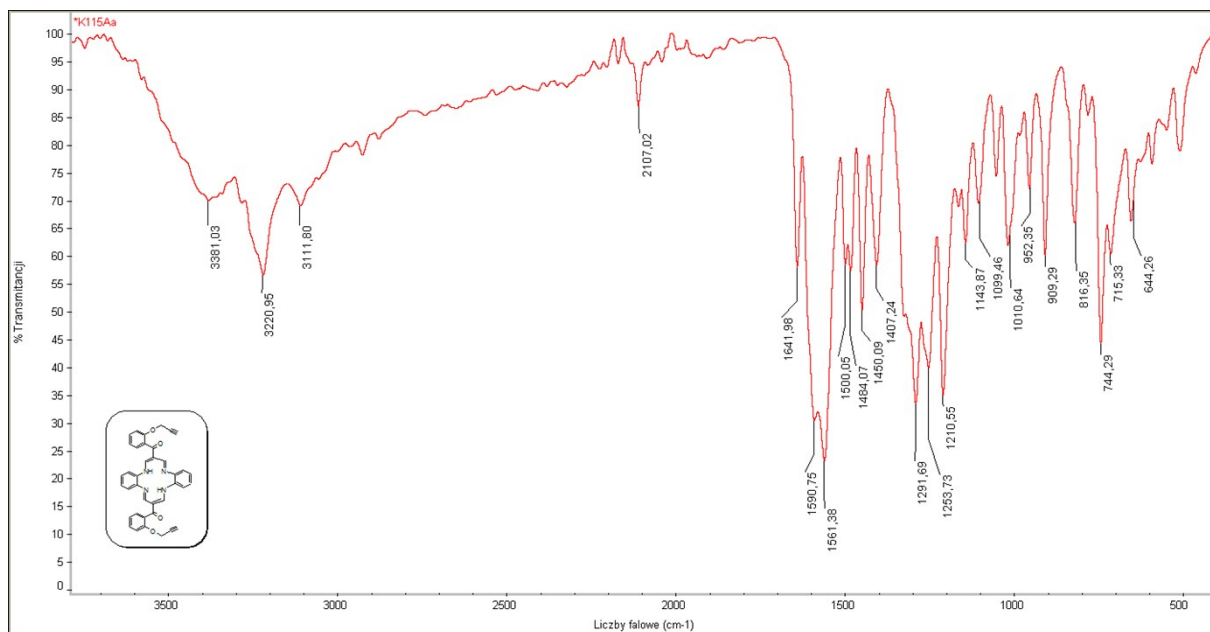
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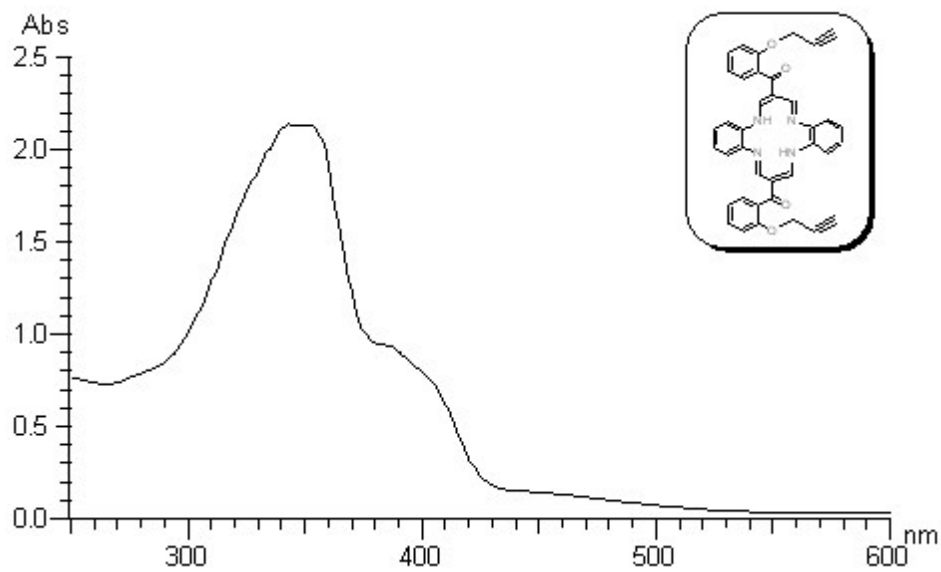
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ROESY spectroscopy

Diagnostic regions of the ROESY spectrum together with key connections, indicated in schematic representations by arrows, are shown in Fig. S13.

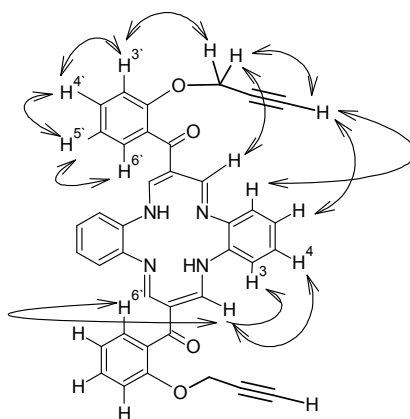


Figure S11. Schematic representation of the precursor ligand **2**, showing significant through-space connectivities assigned from the ROESY spectrum (see Figure S12).

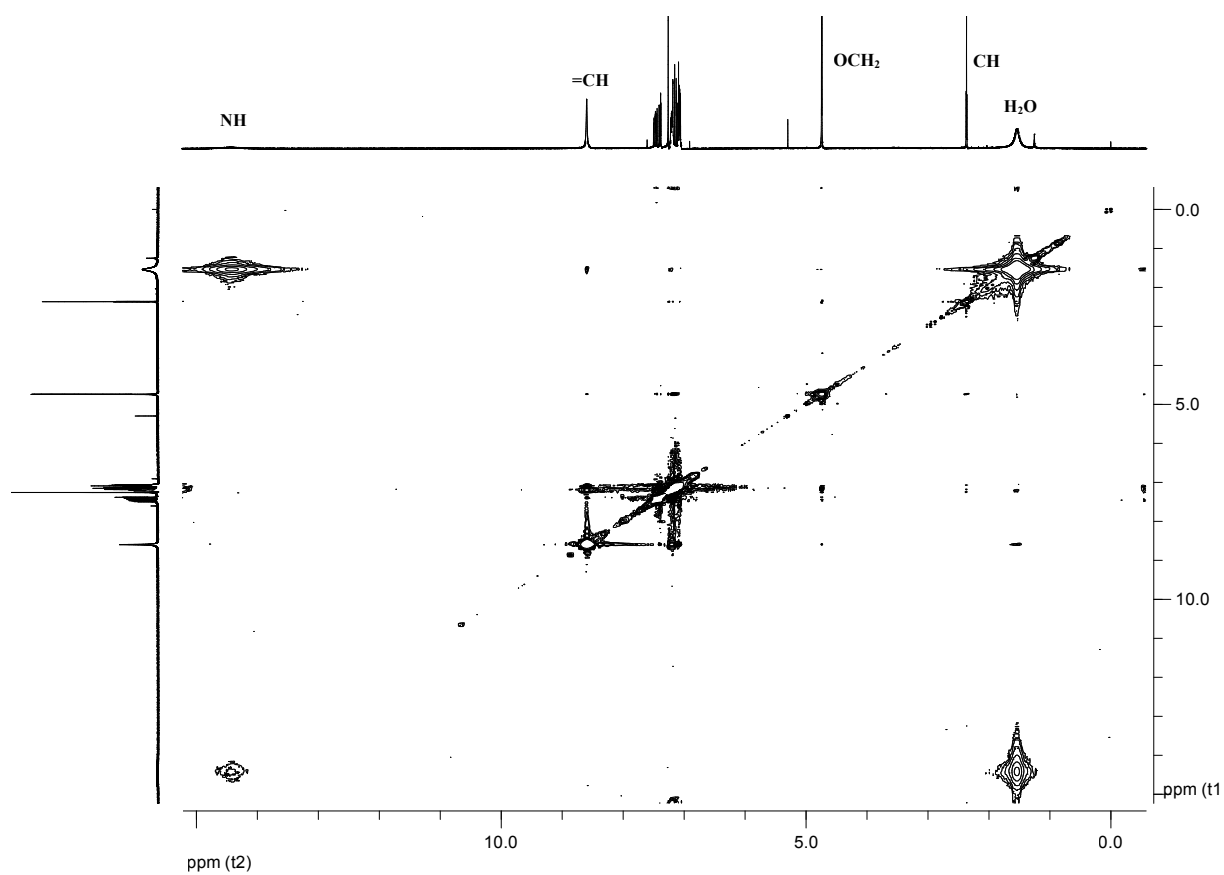
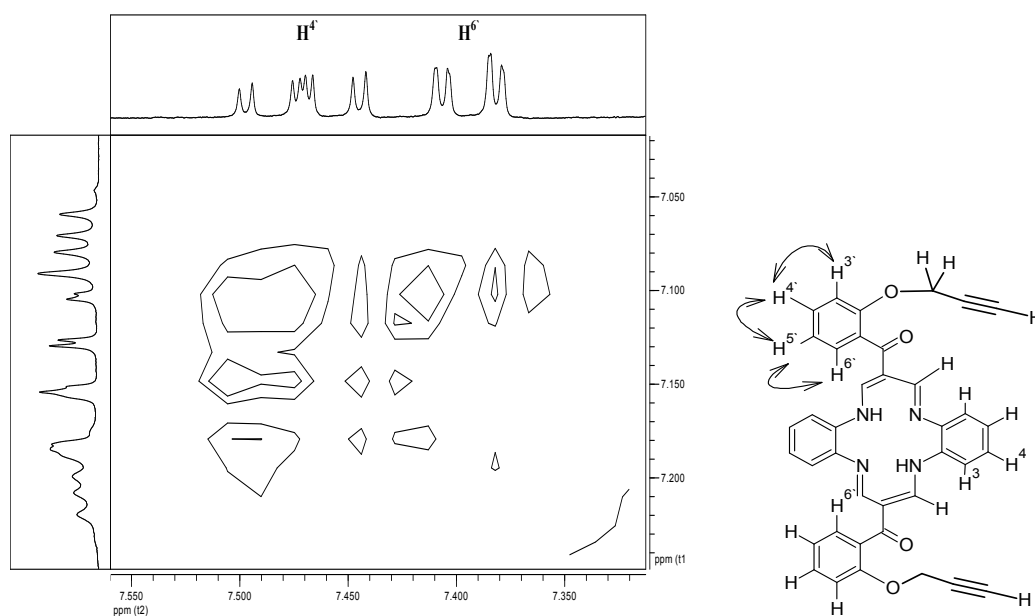
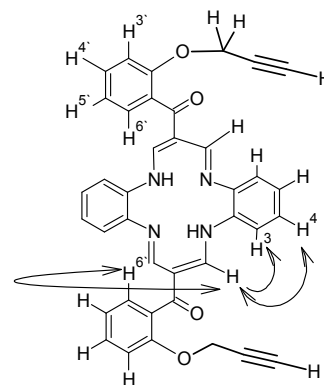
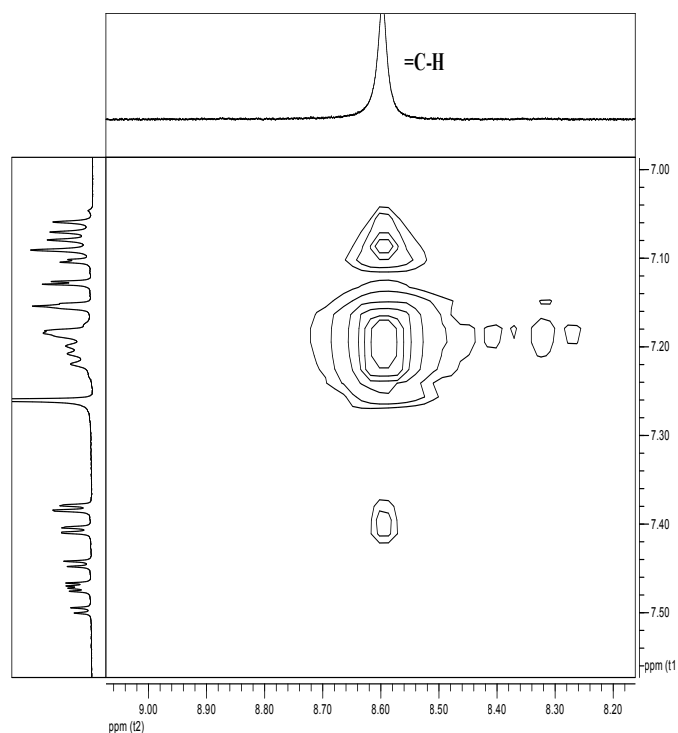


Figure S12. 2D-ROESY spectrum of the macrocyclic precursor **2** in CDCl_3 (0.003 mM) at 298 K.

a)



b)



c)

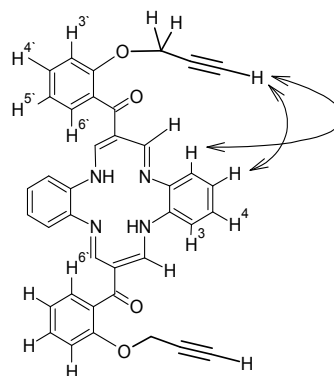
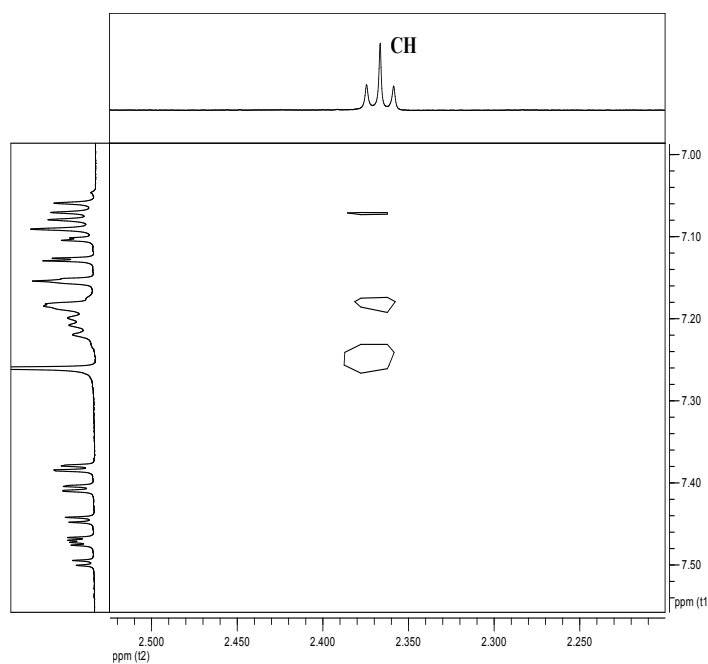
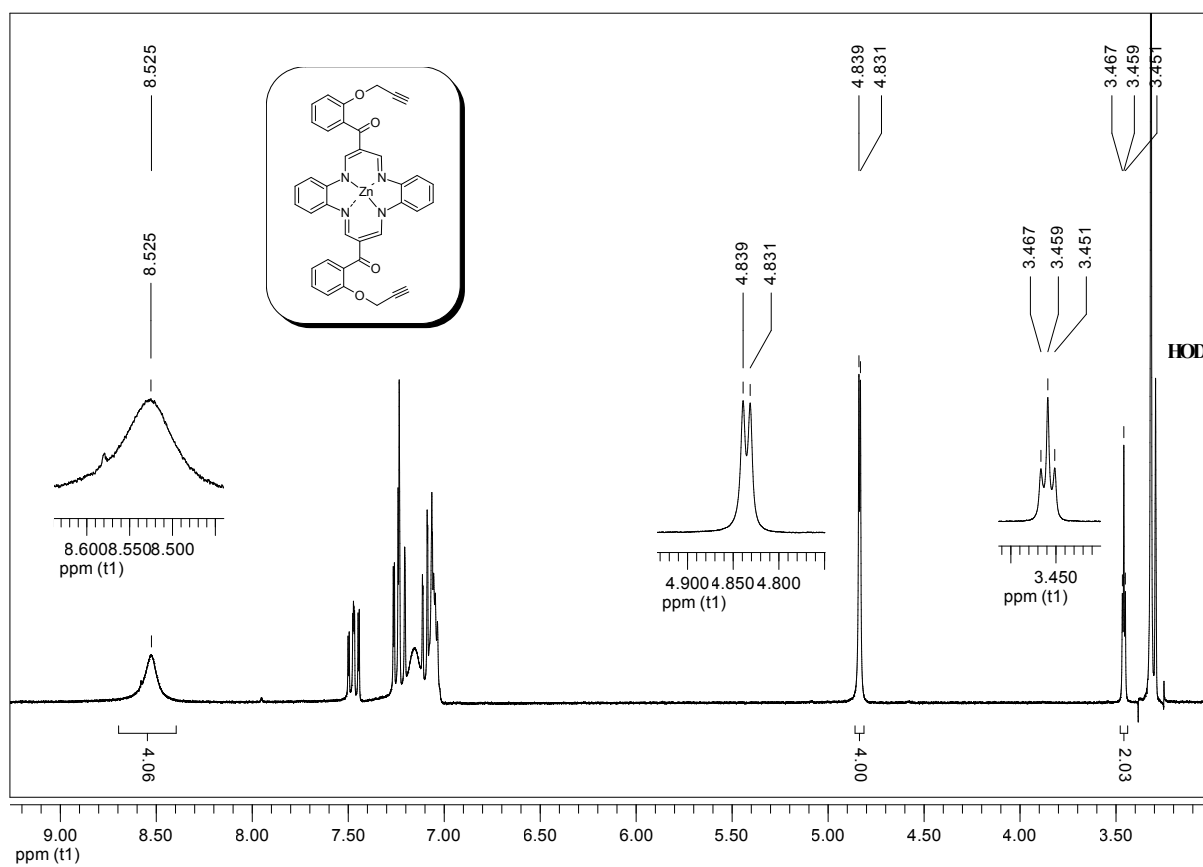
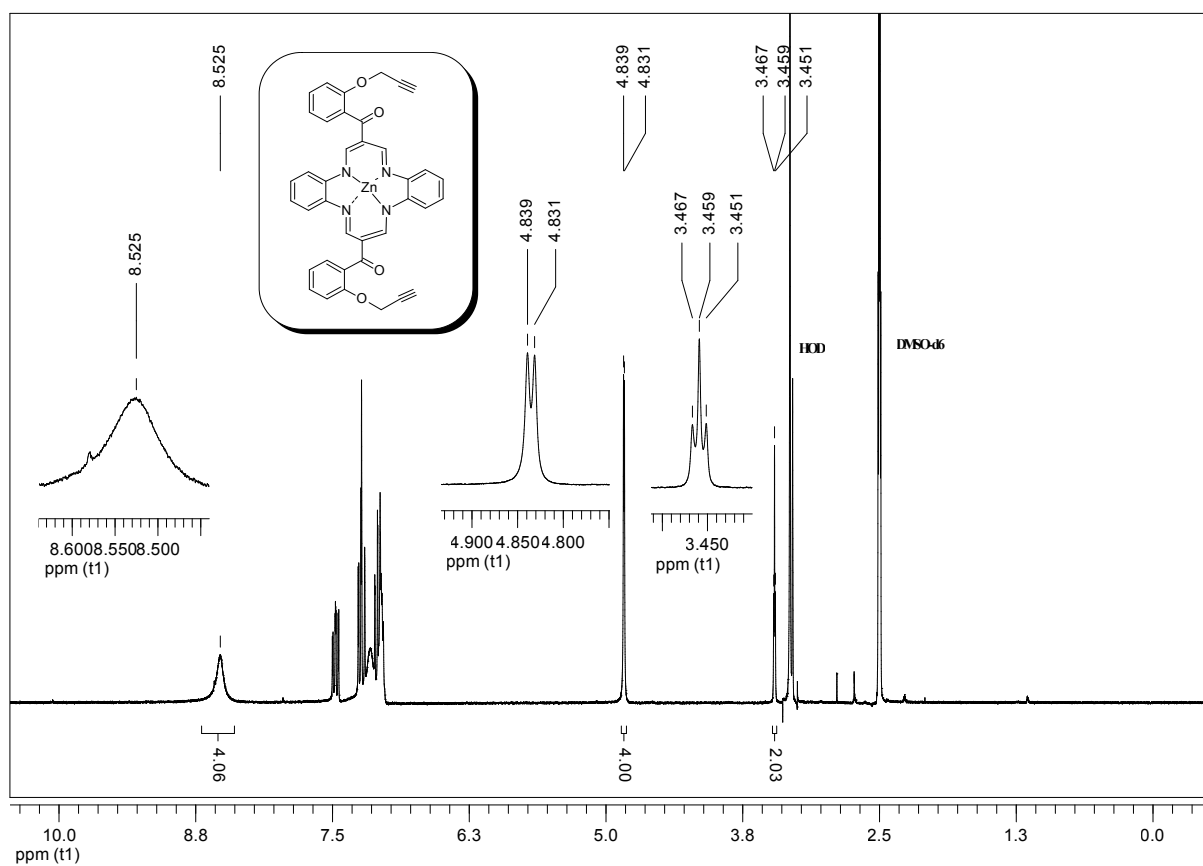
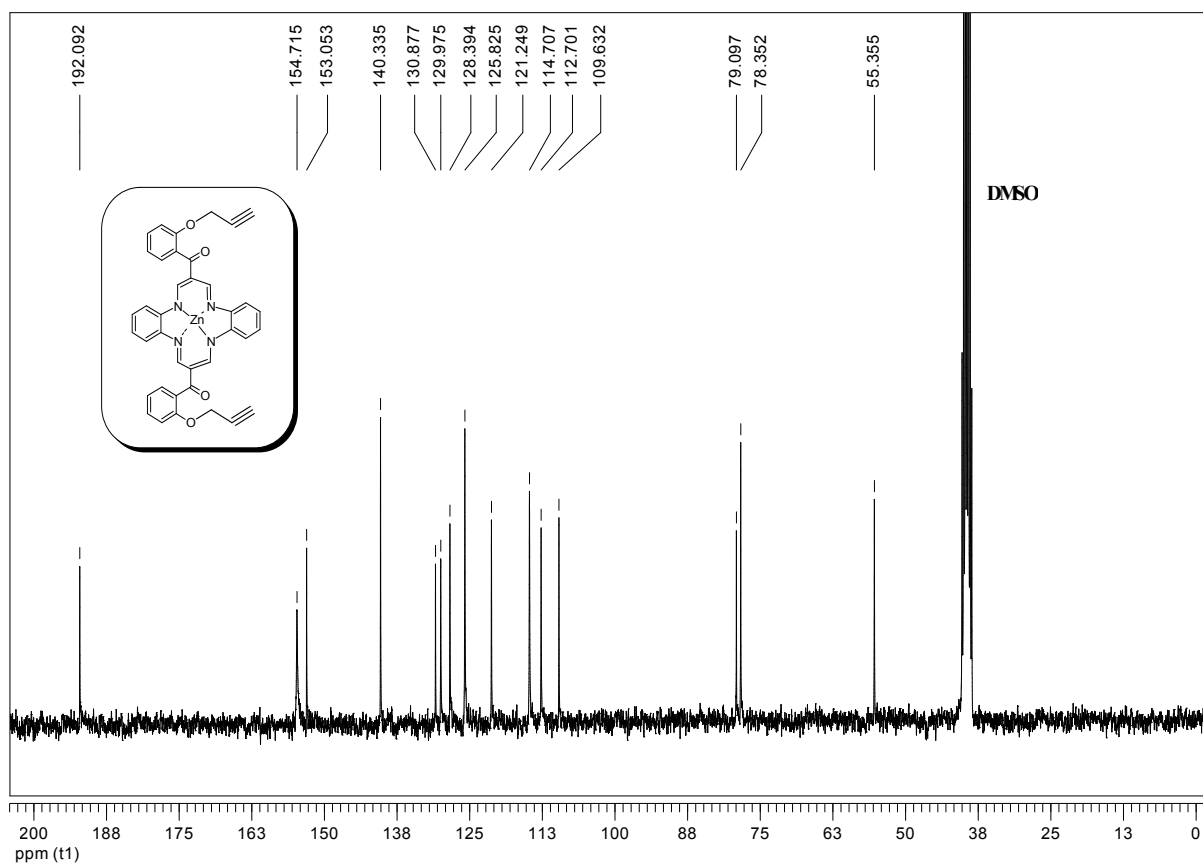
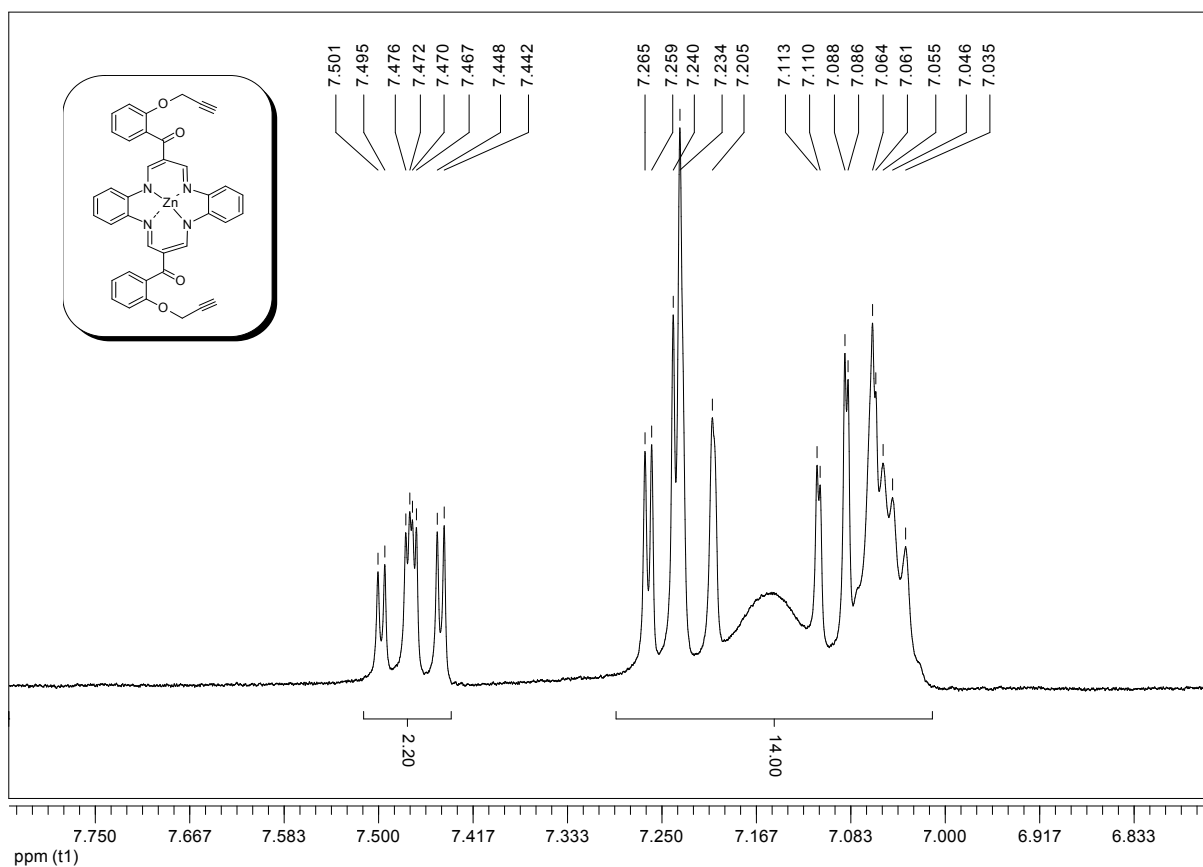


Figure S13. Partial contour plot of the two-dimensional ROESY spectrum of the macrocyclic precursor **2**, in CDCl_3 (0.003 mM) at 298 K, showing intramolecular cross-peaks observed between: a) aromatic protons $\text{H}^{3'}$ - $\text{H}^{6'}$ within benzoyl substituents, b) macrocyclic β -protons ($=\text{C}-\text{H}$) and aromatic protons, c) terminal acetylenic protons $\equiv\text{CH}$ and aromatic protons H^{3-4} .

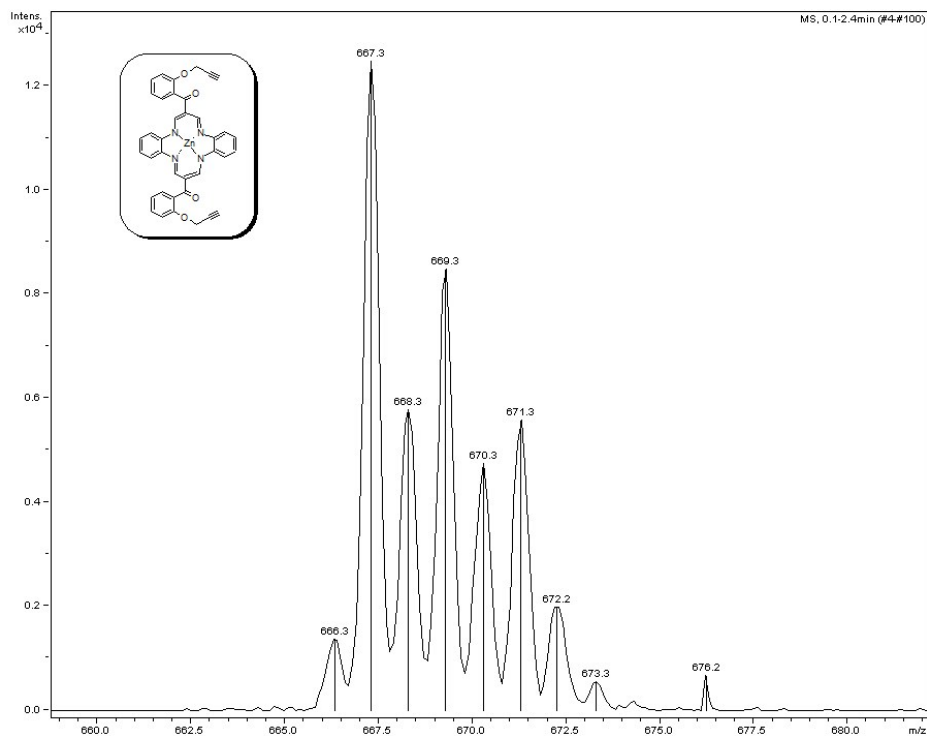
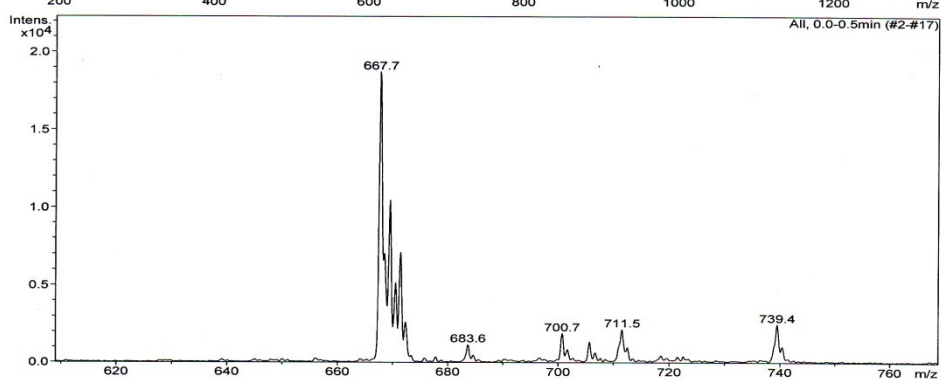
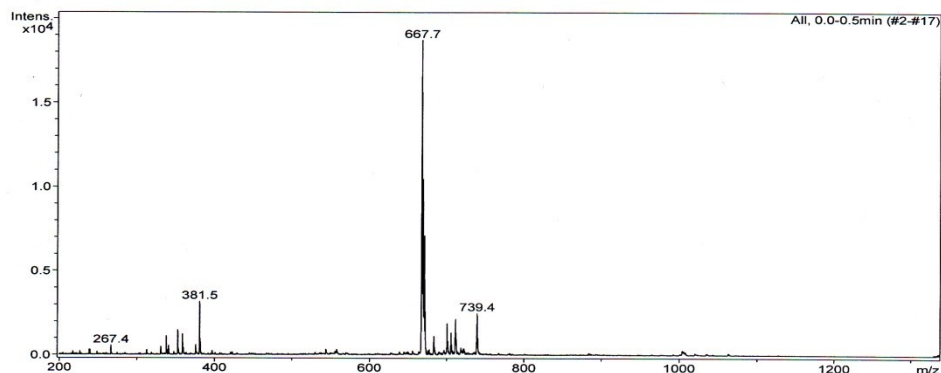


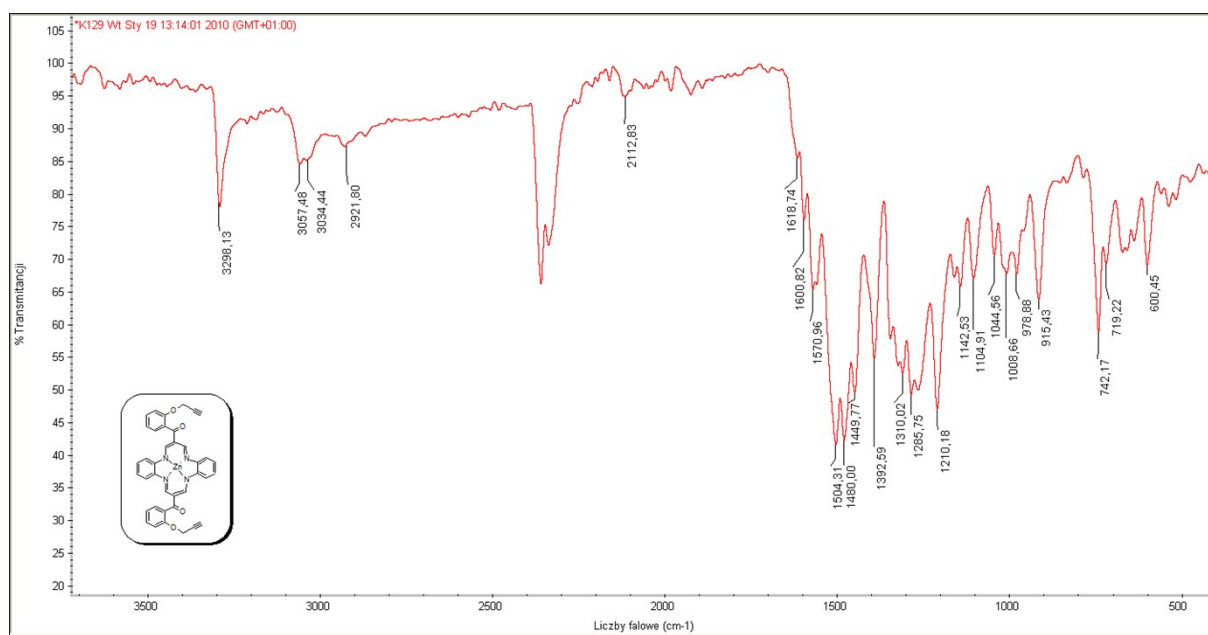
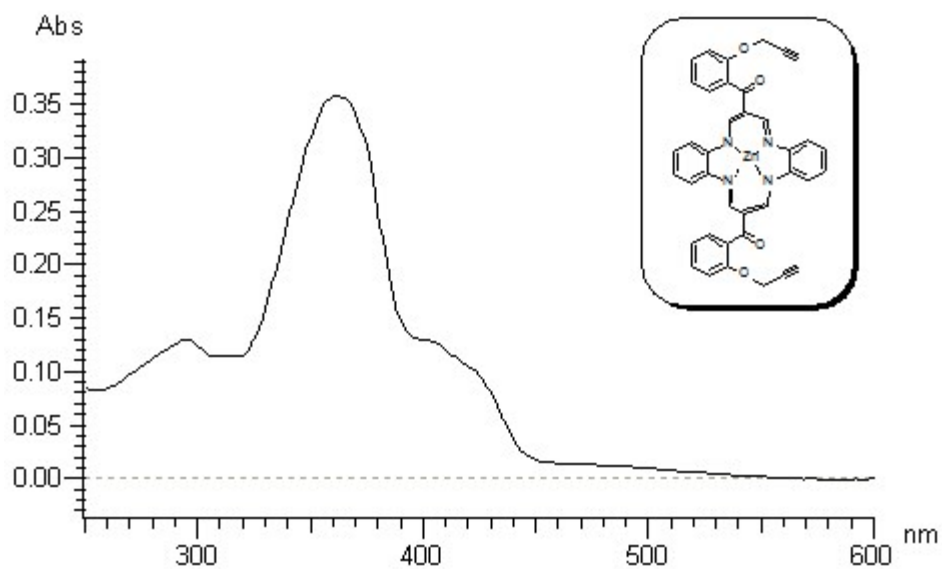


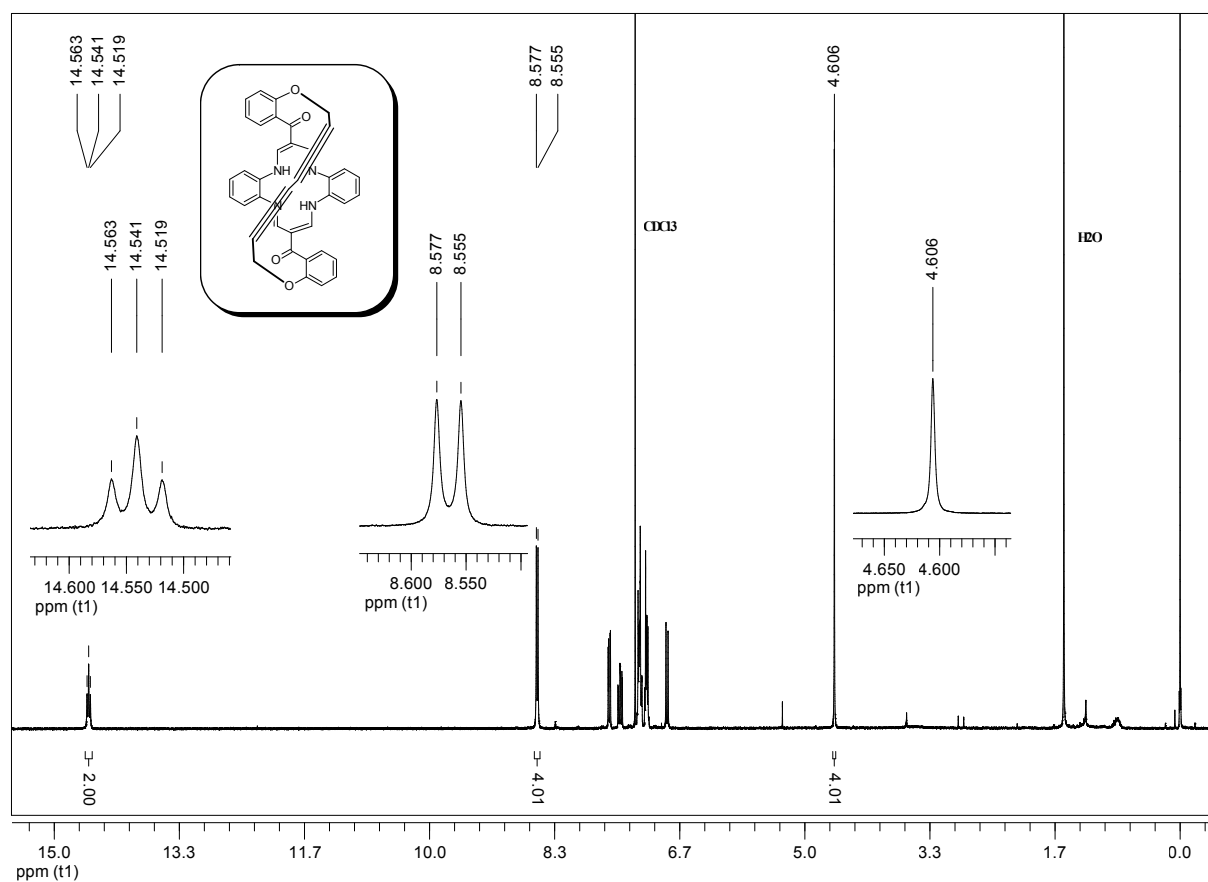
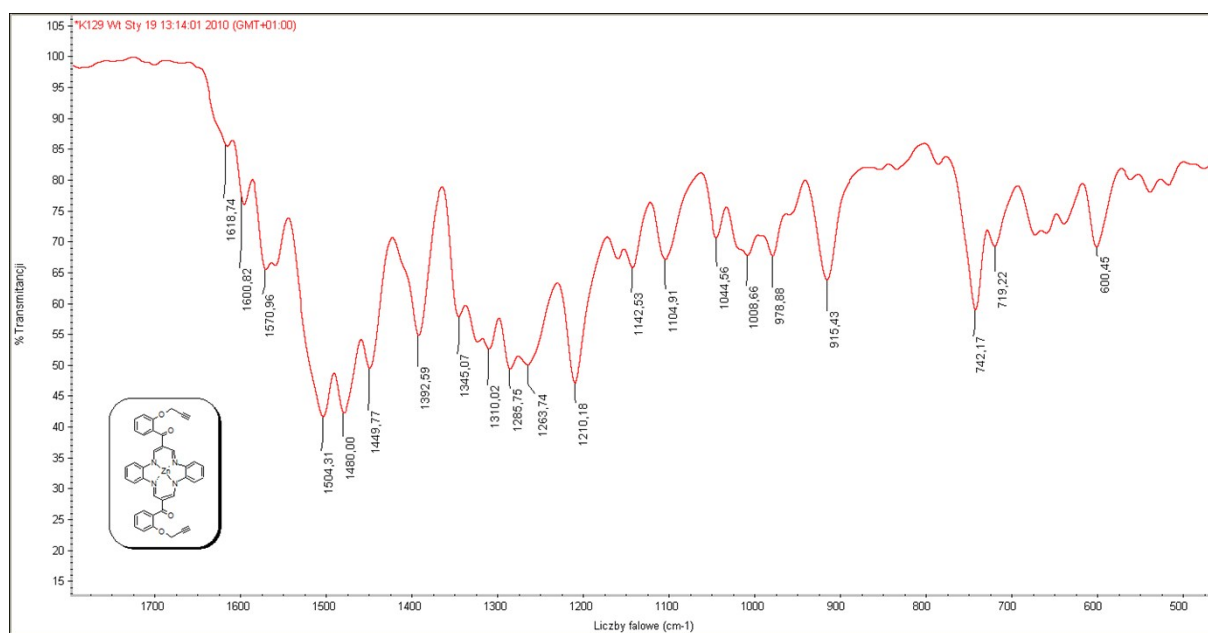
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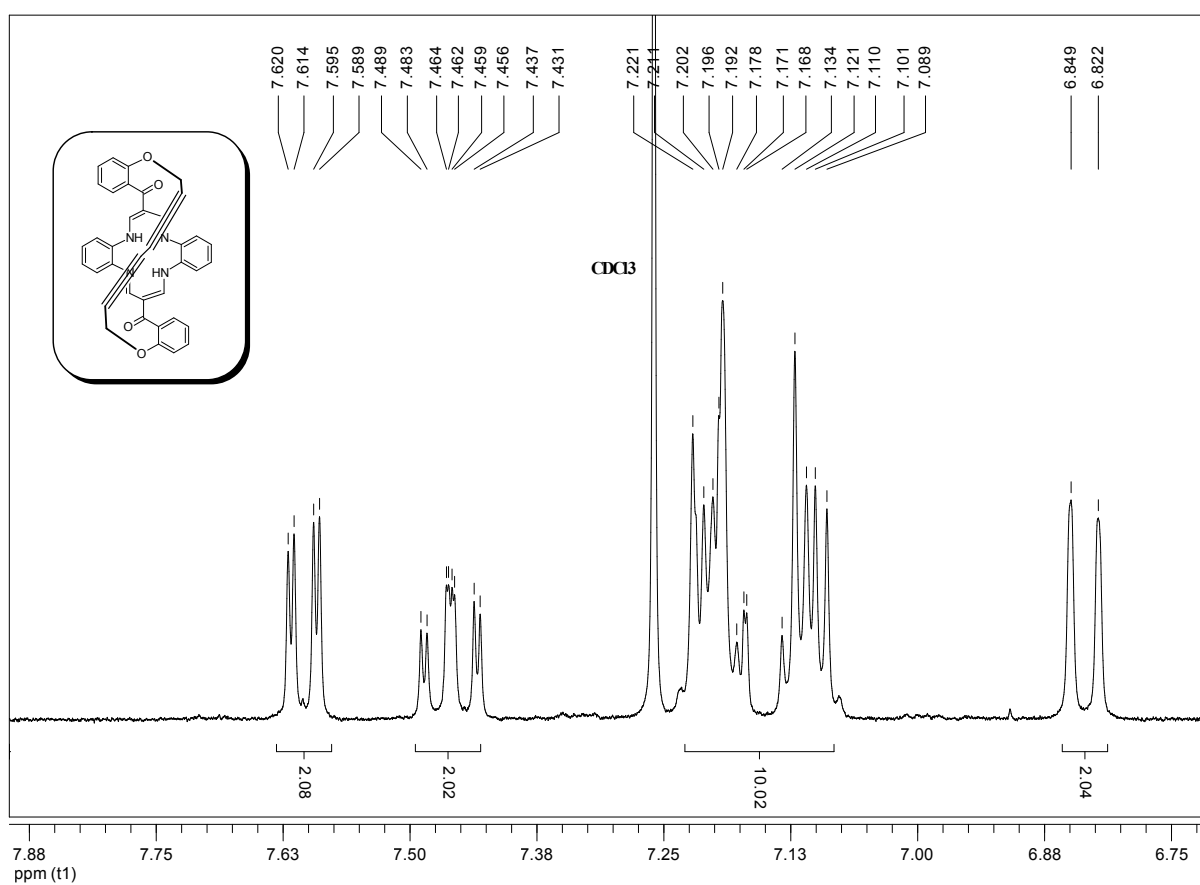
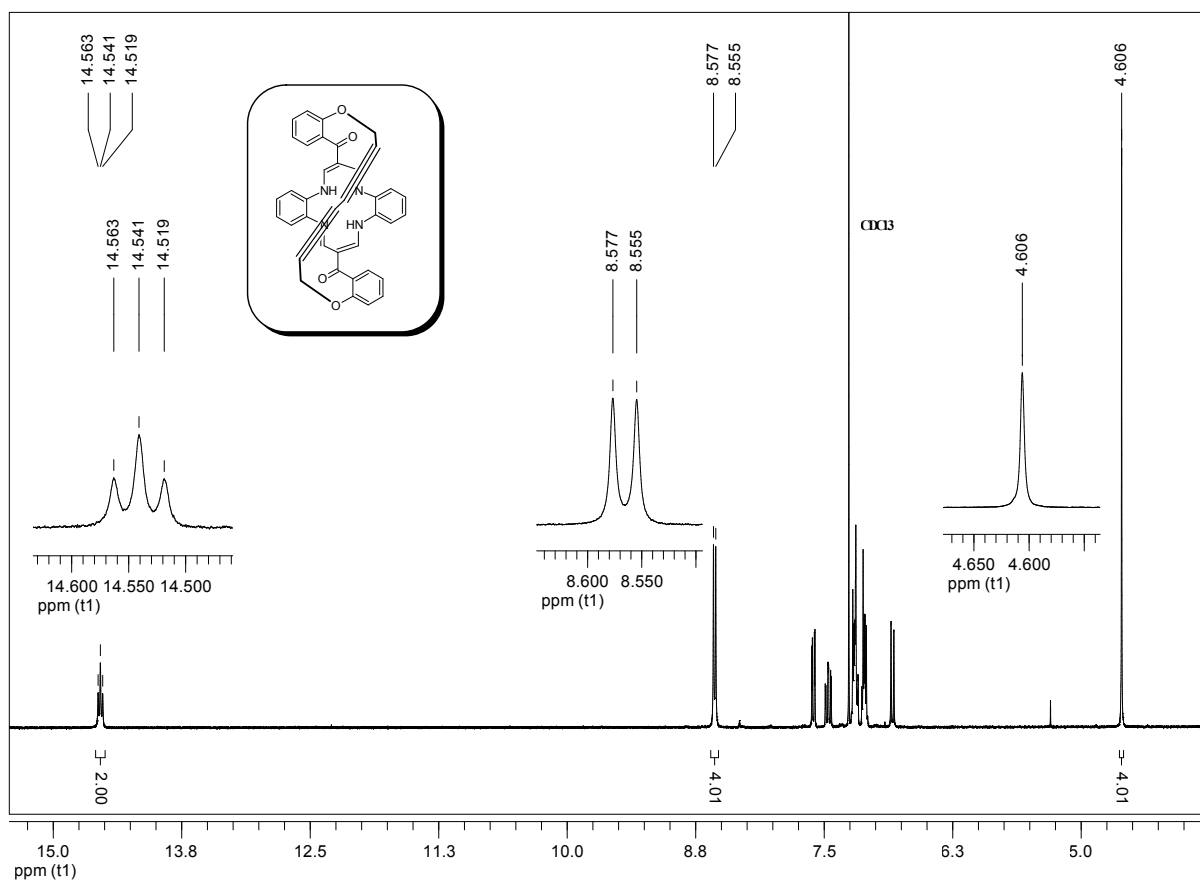
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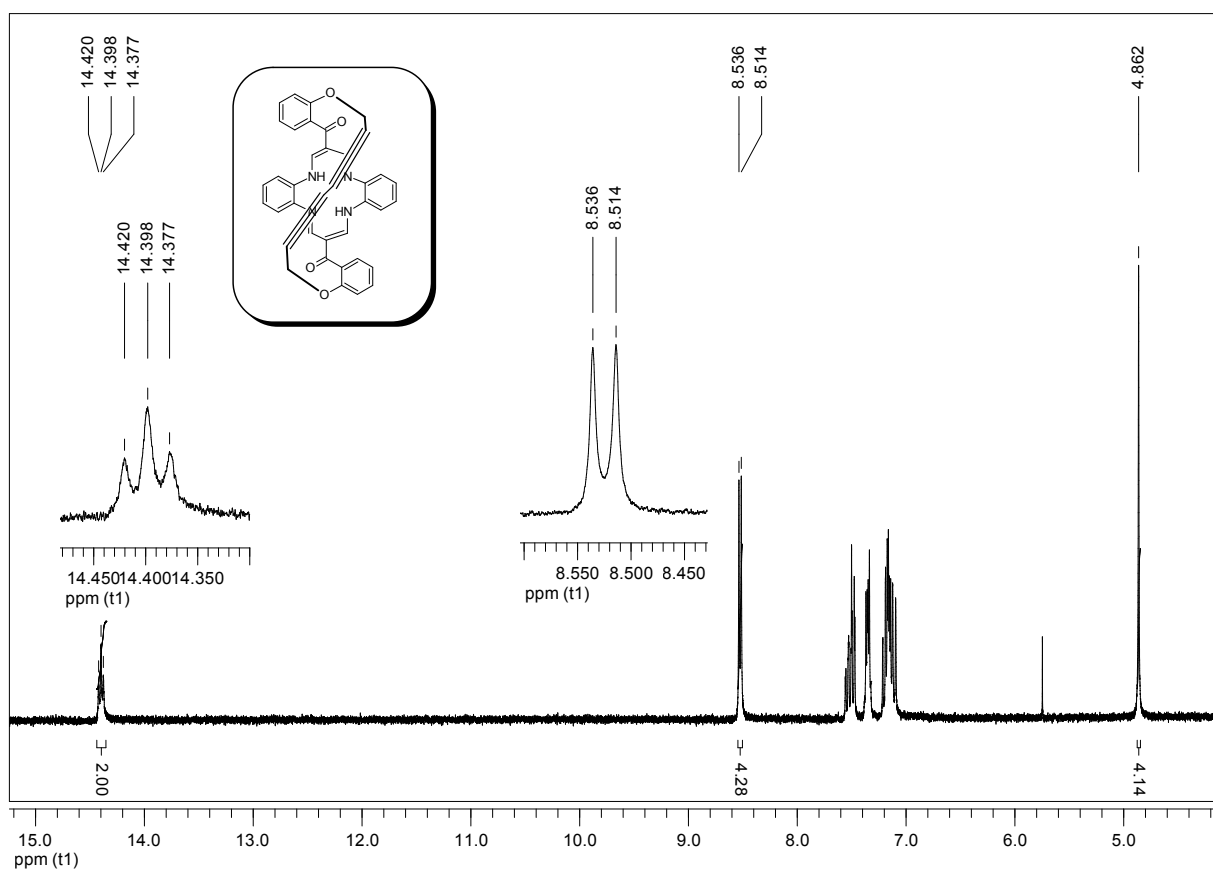
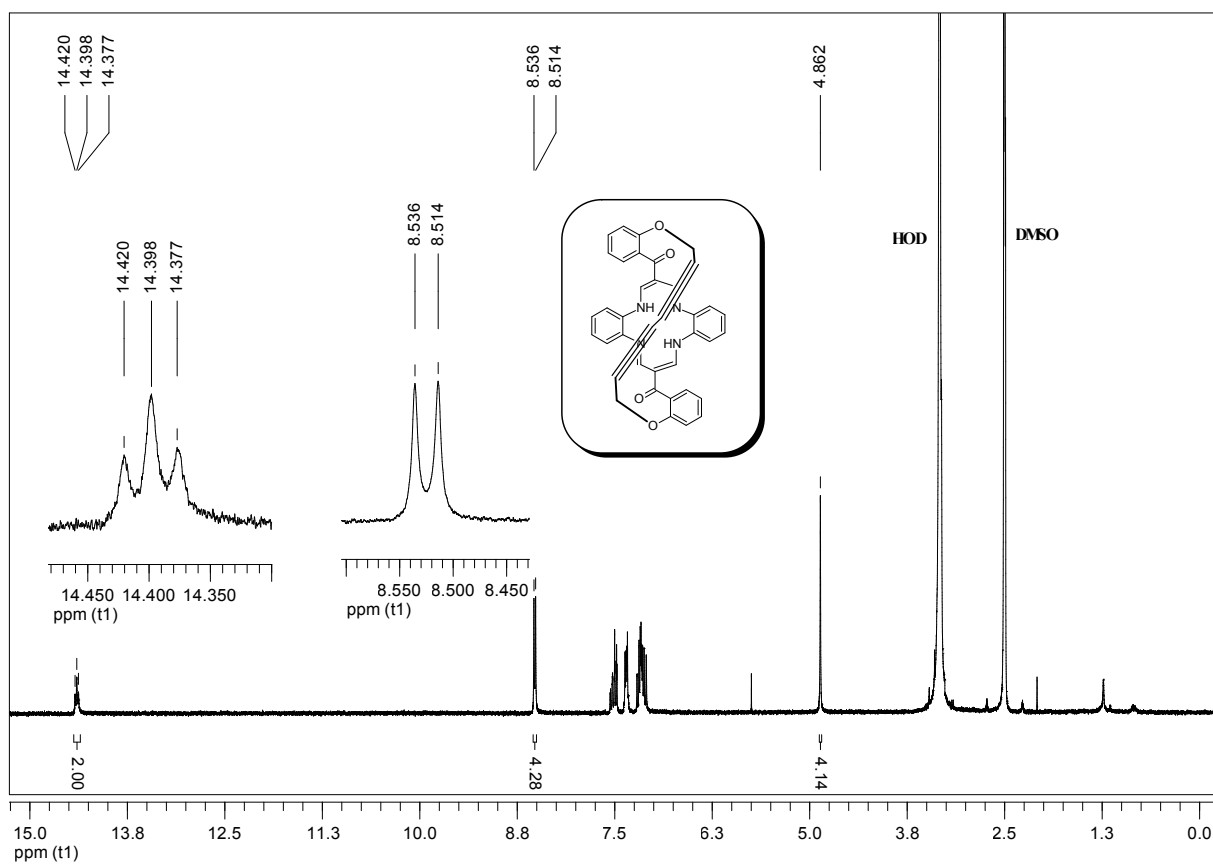
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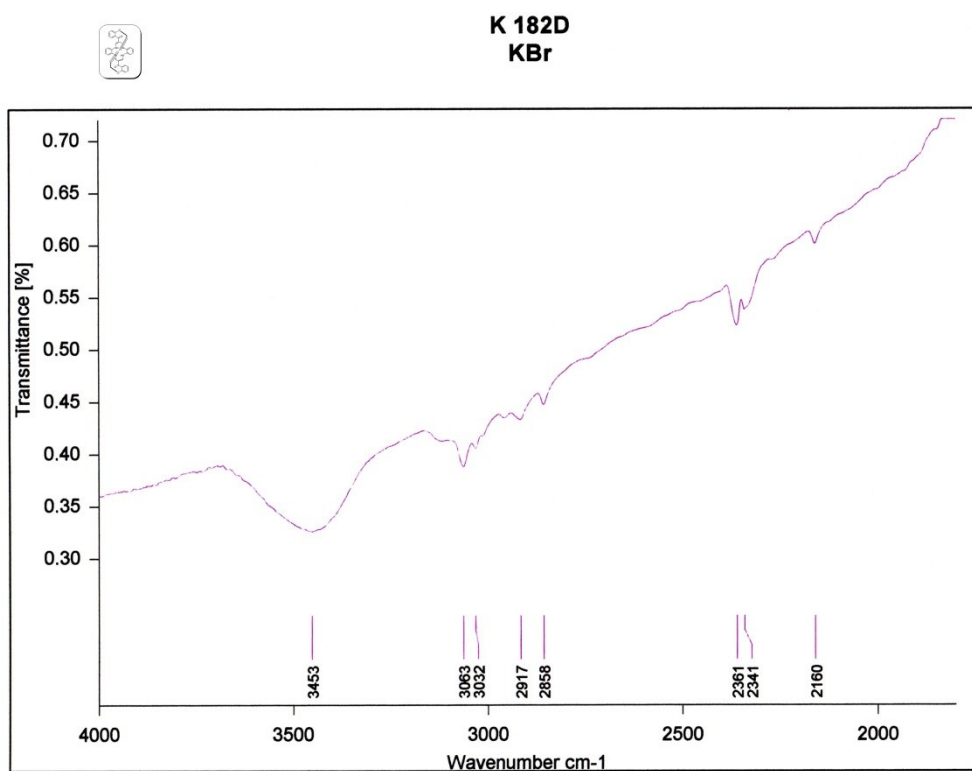
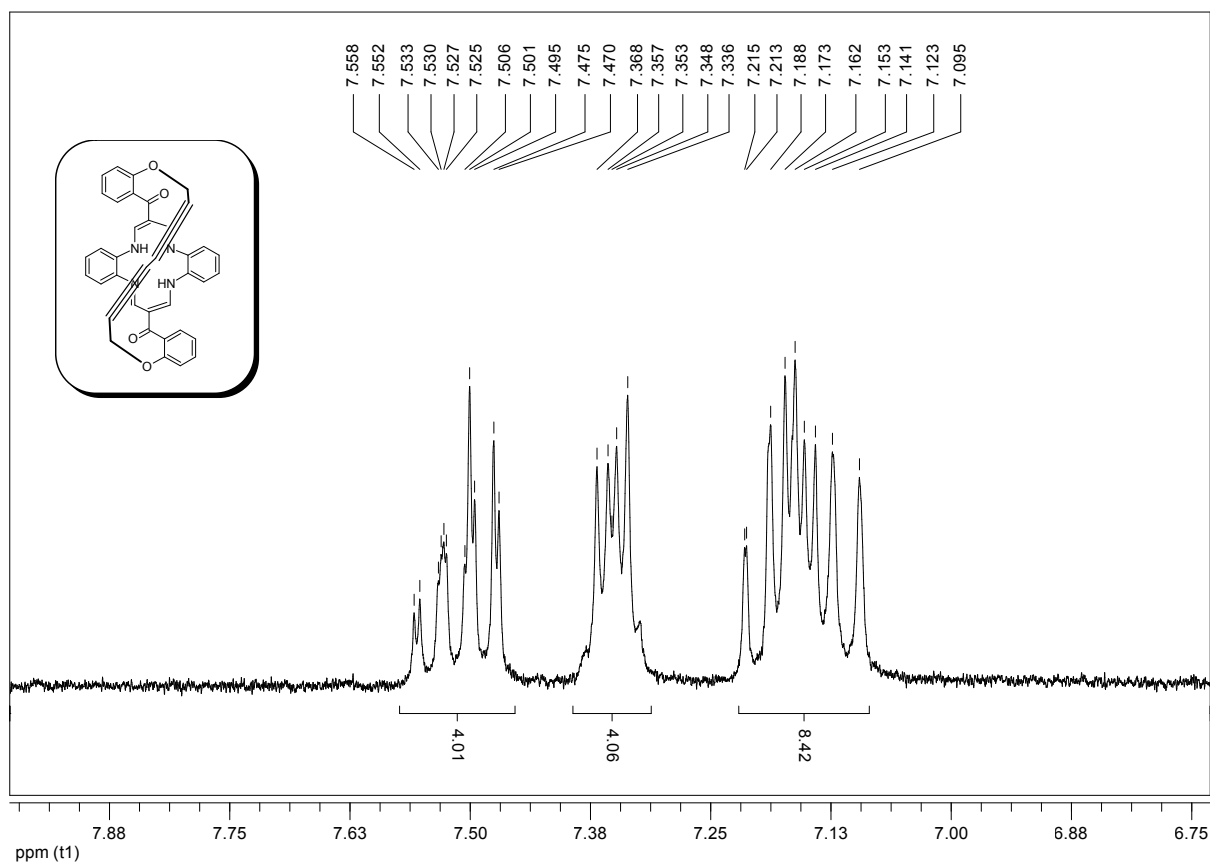






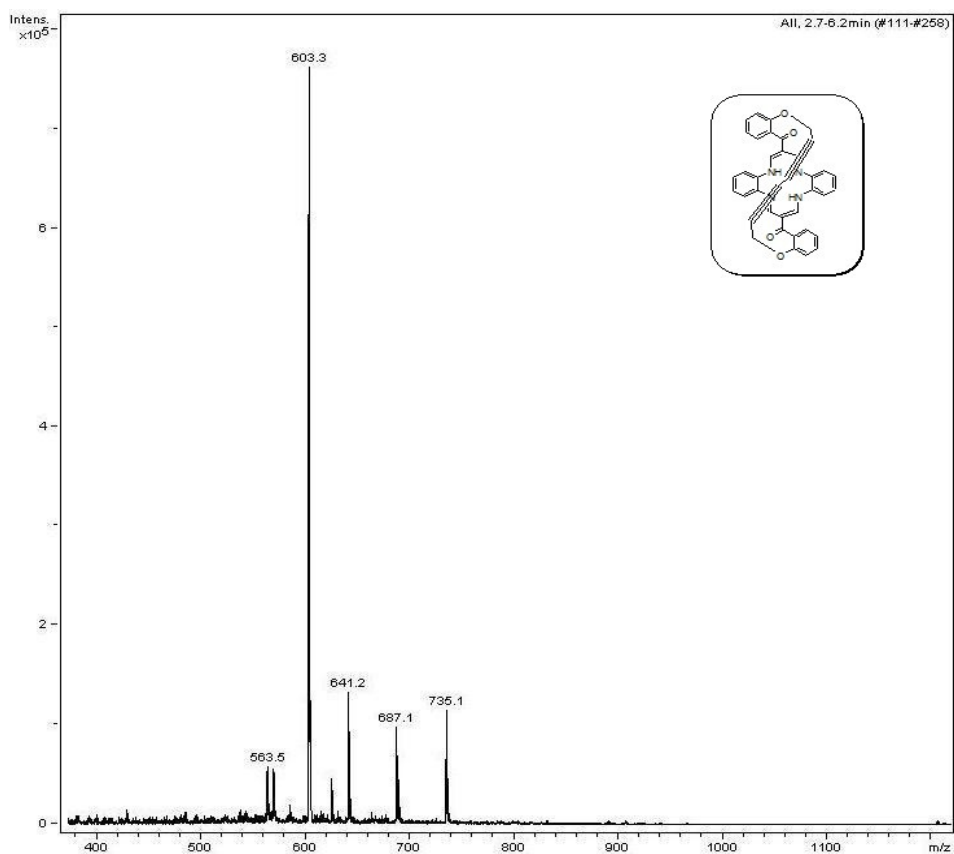
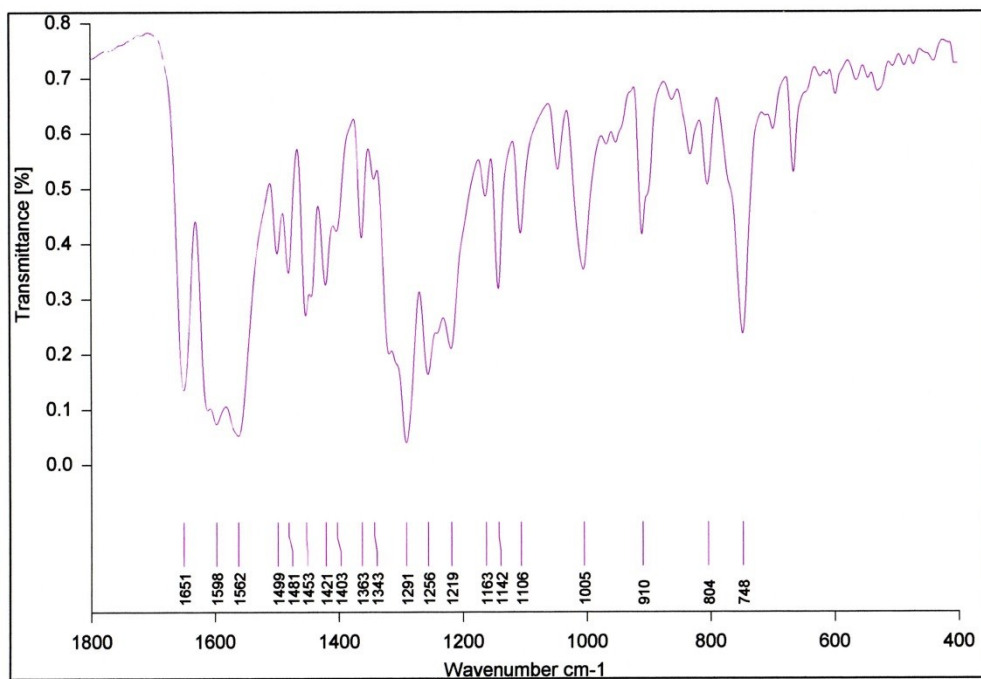


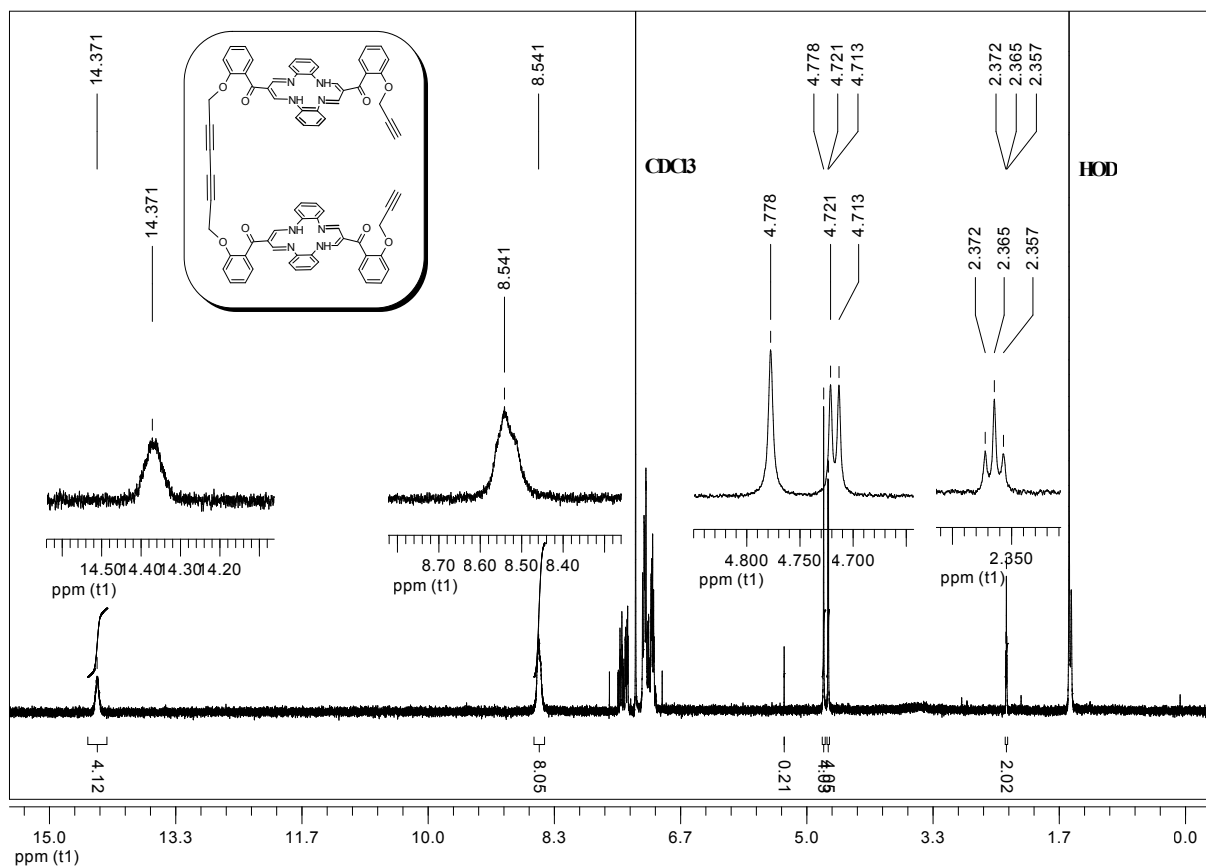
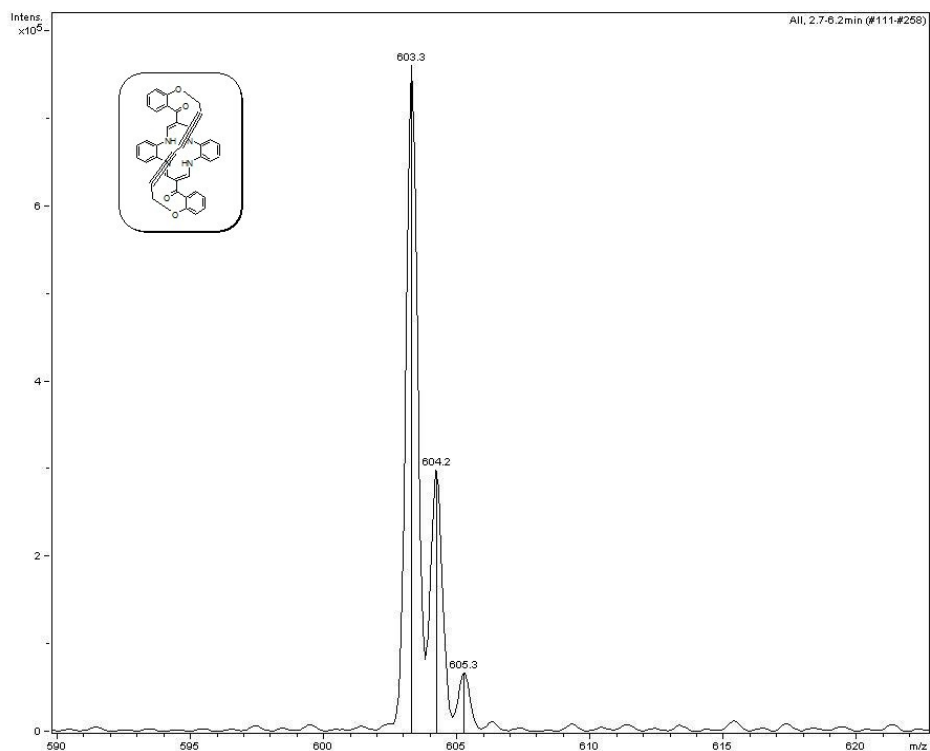






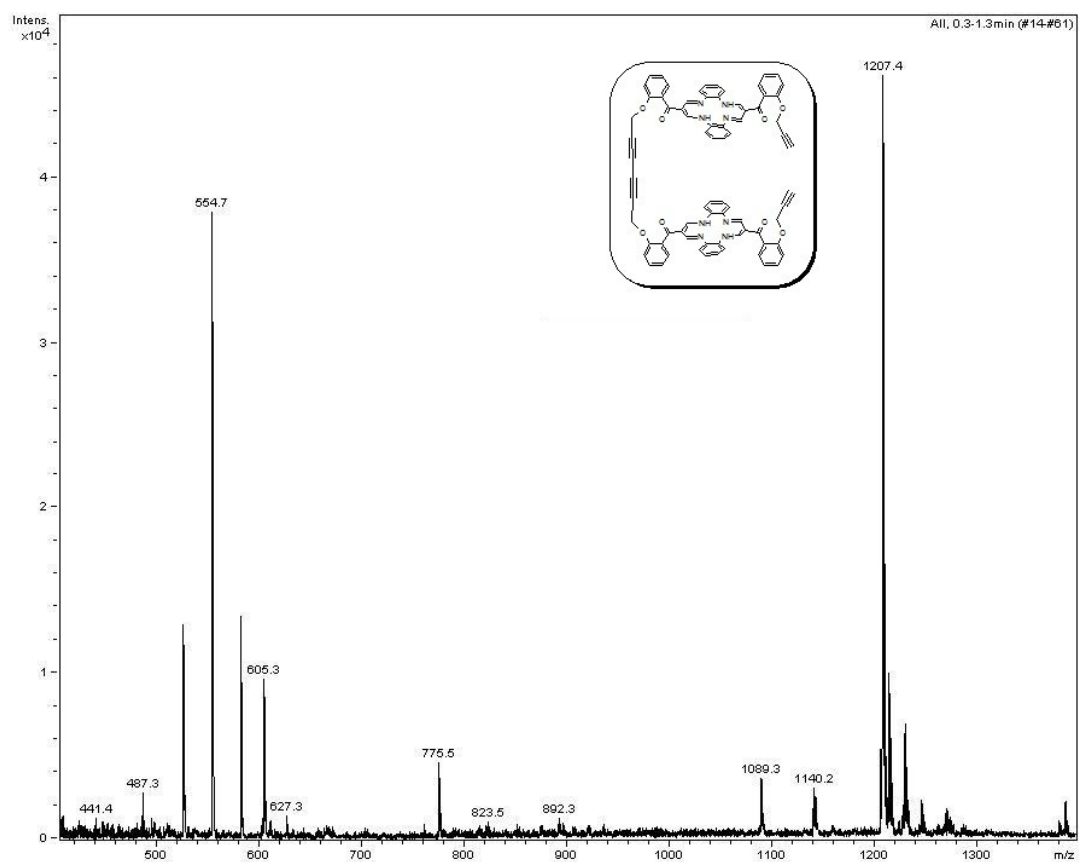
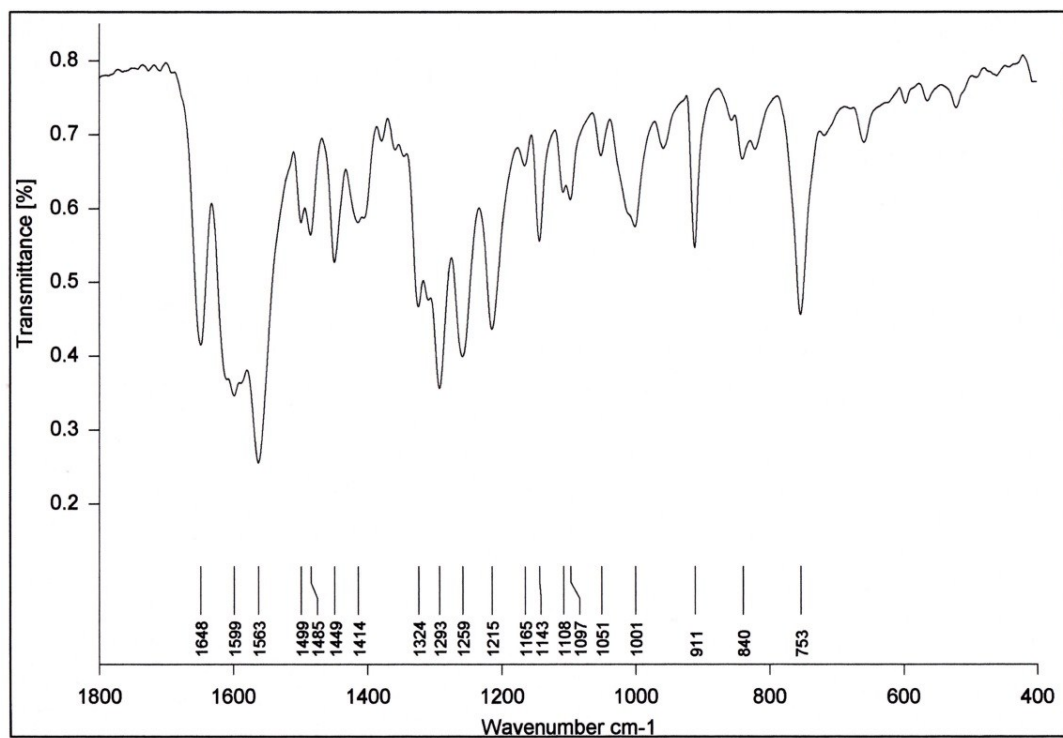
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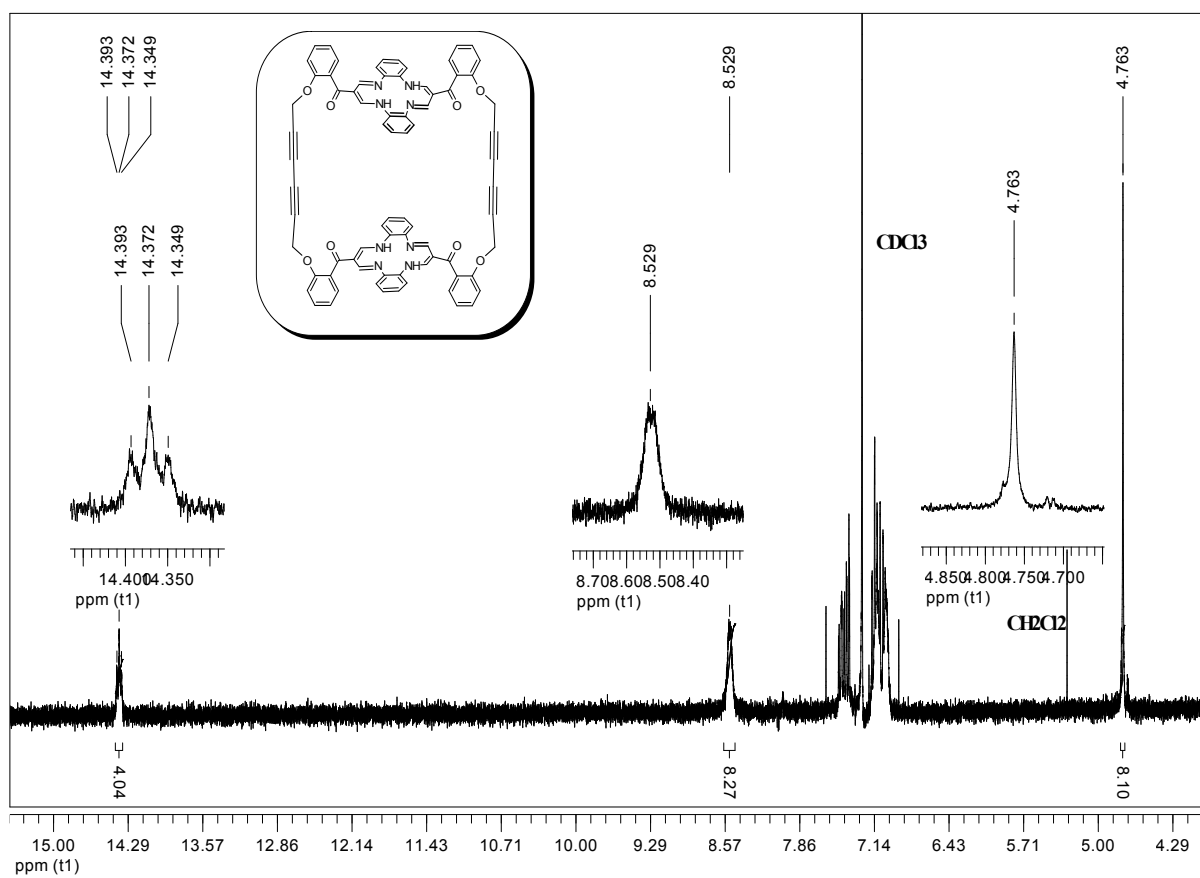
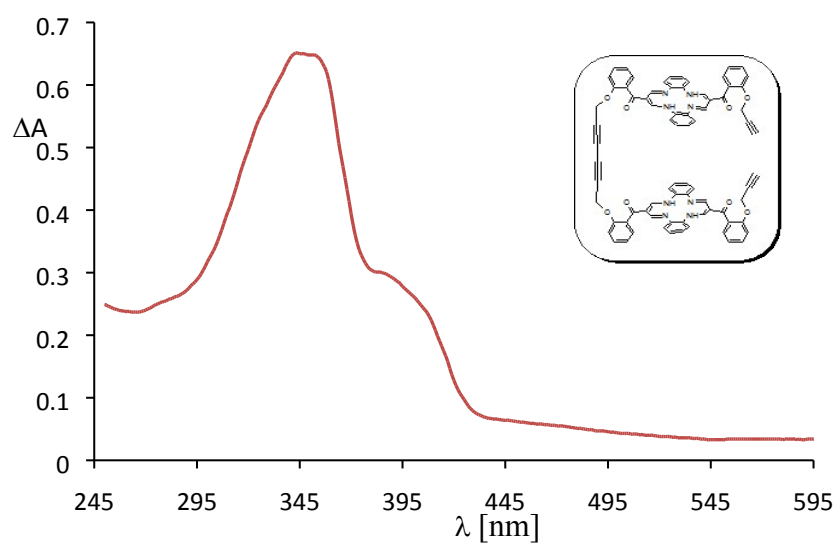


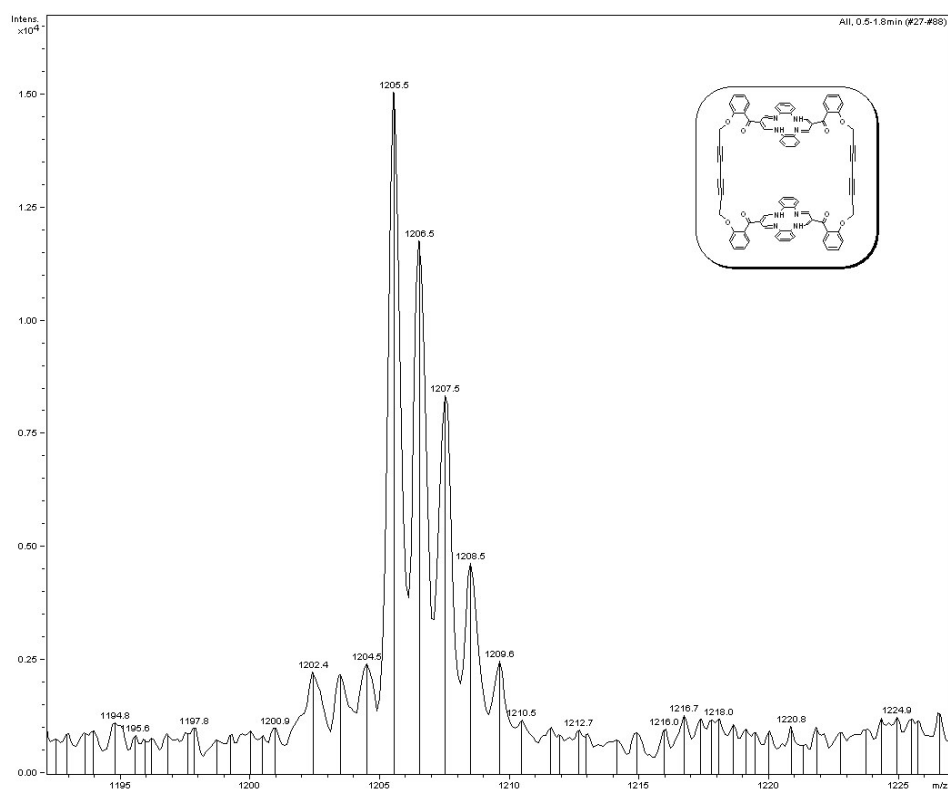
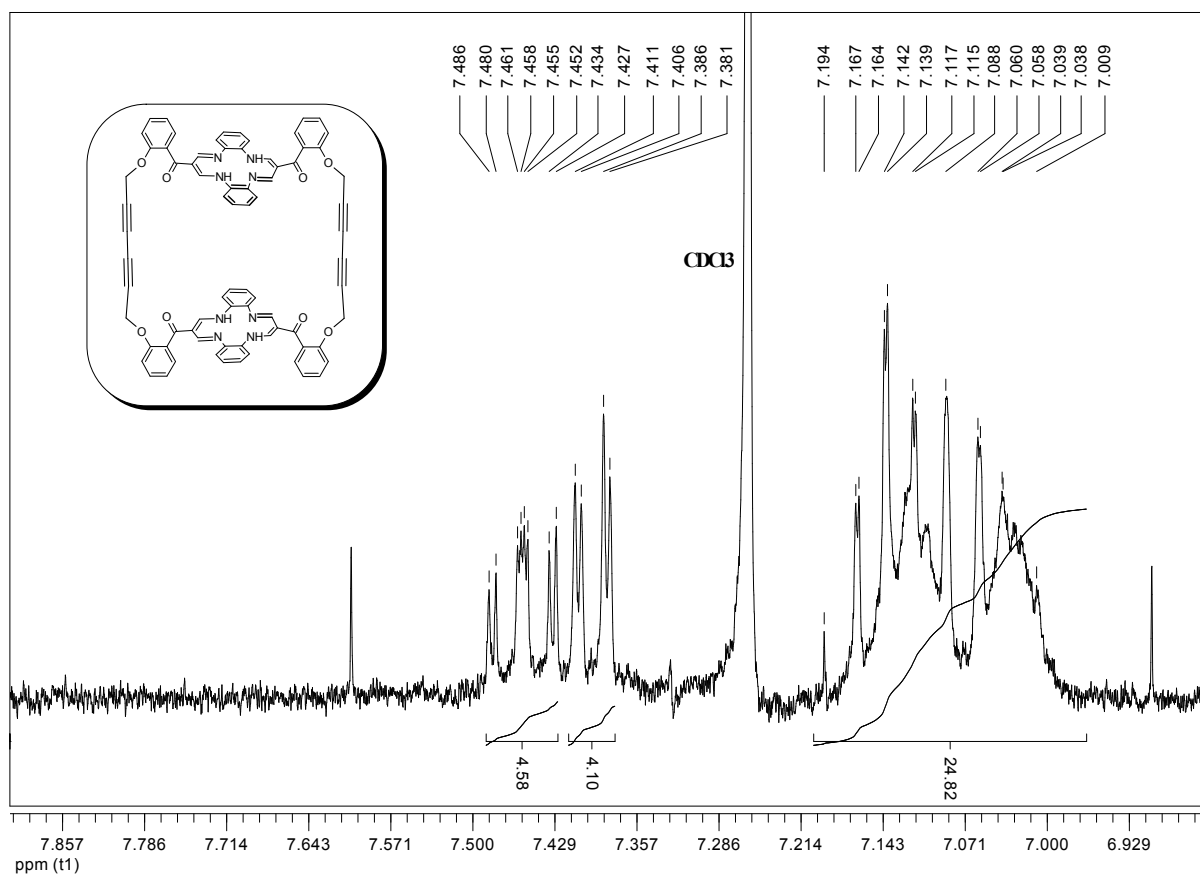


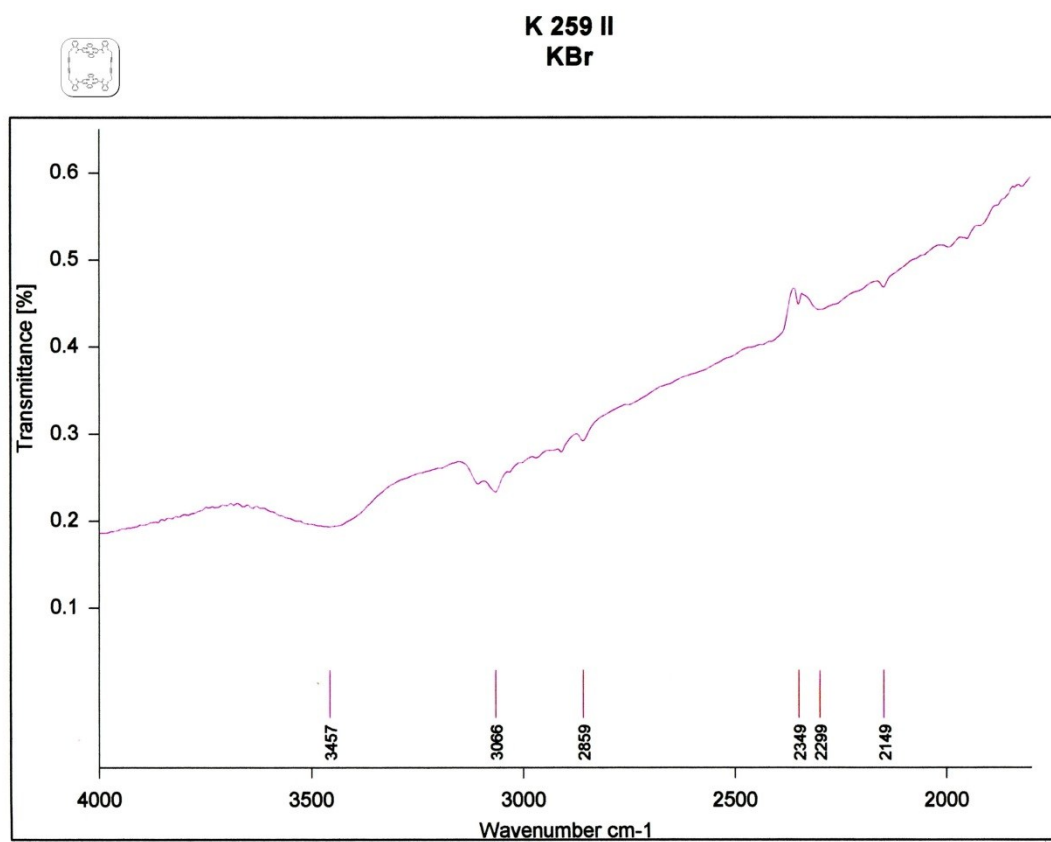
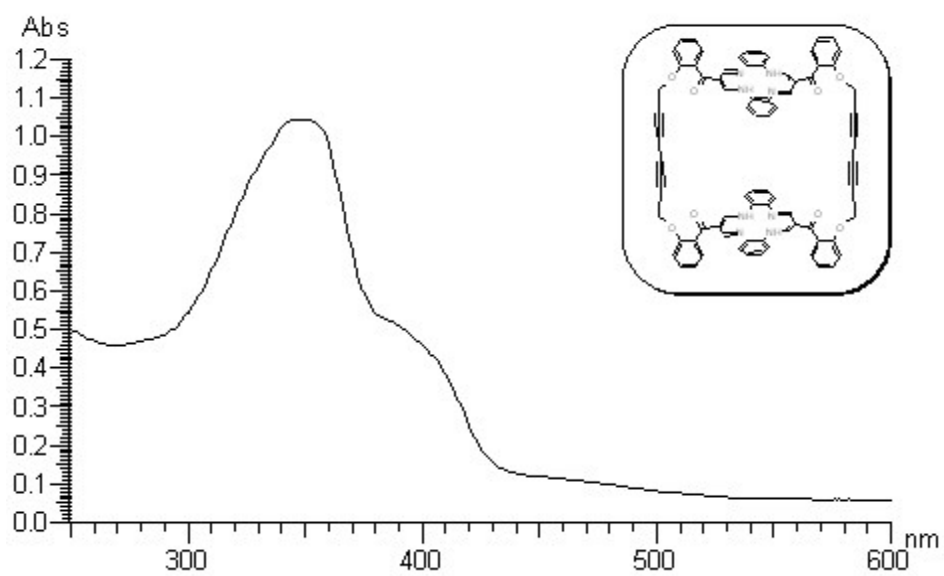


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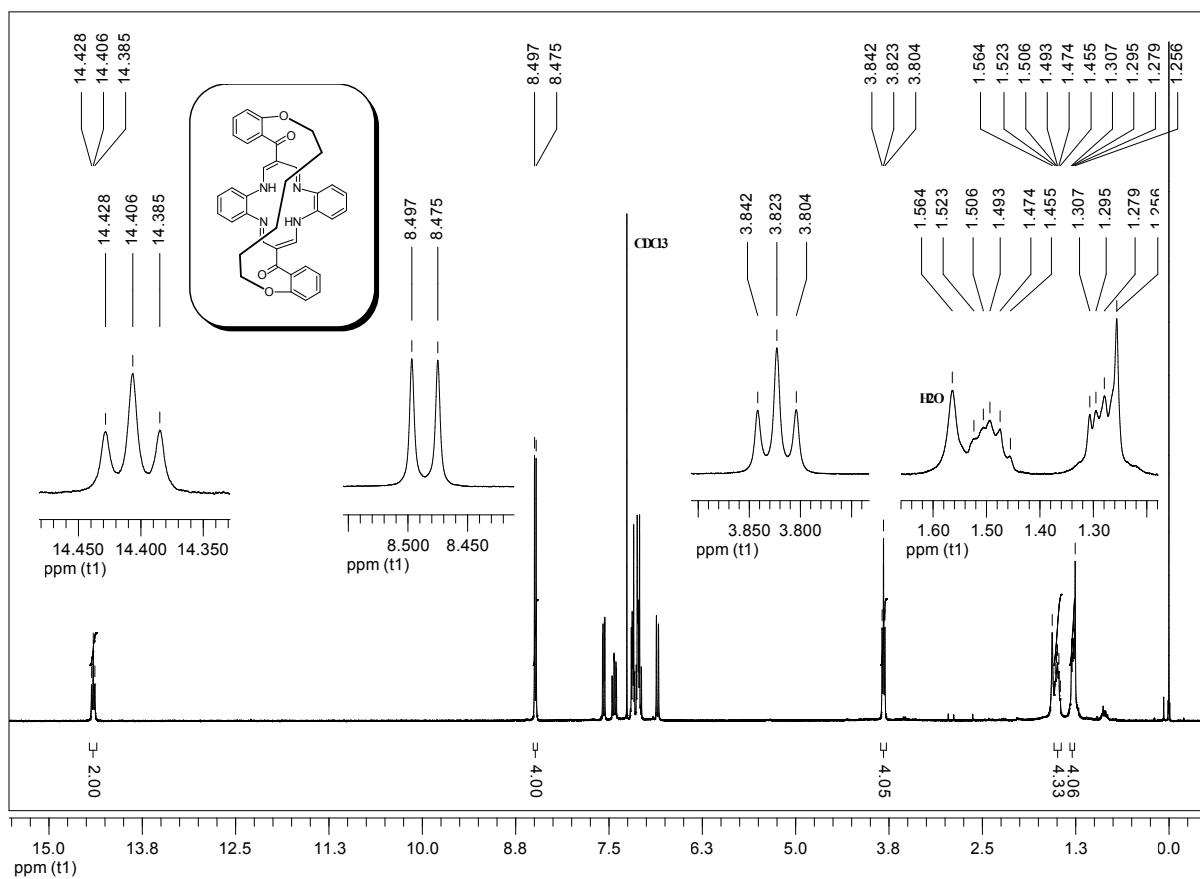
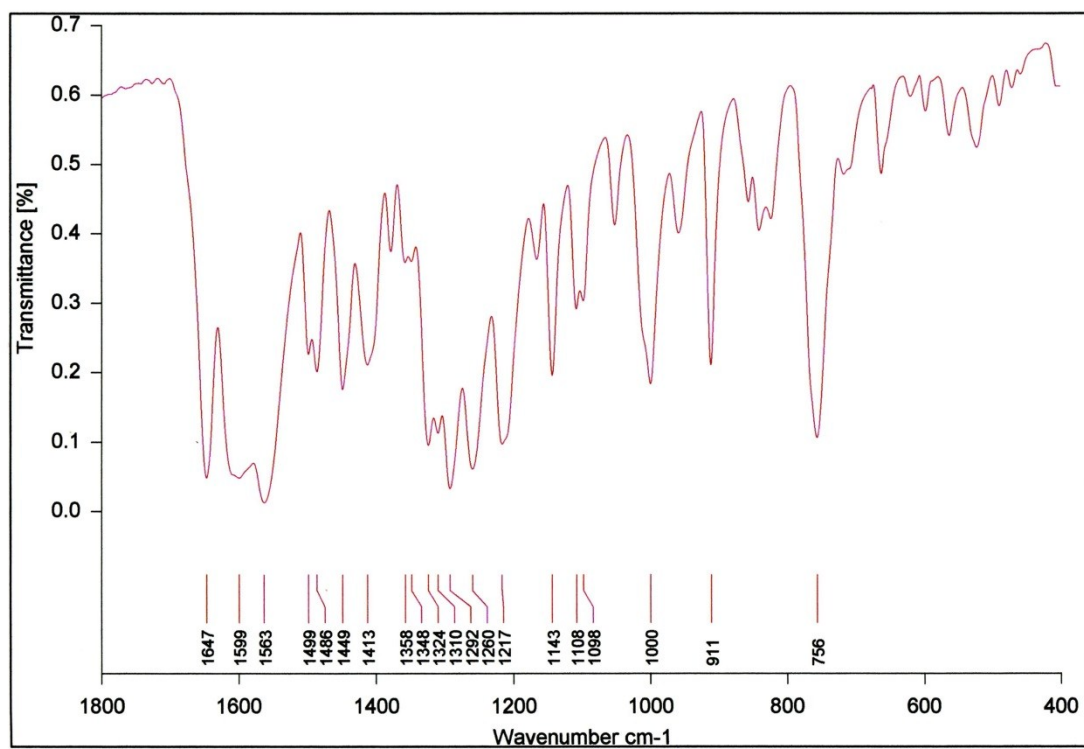


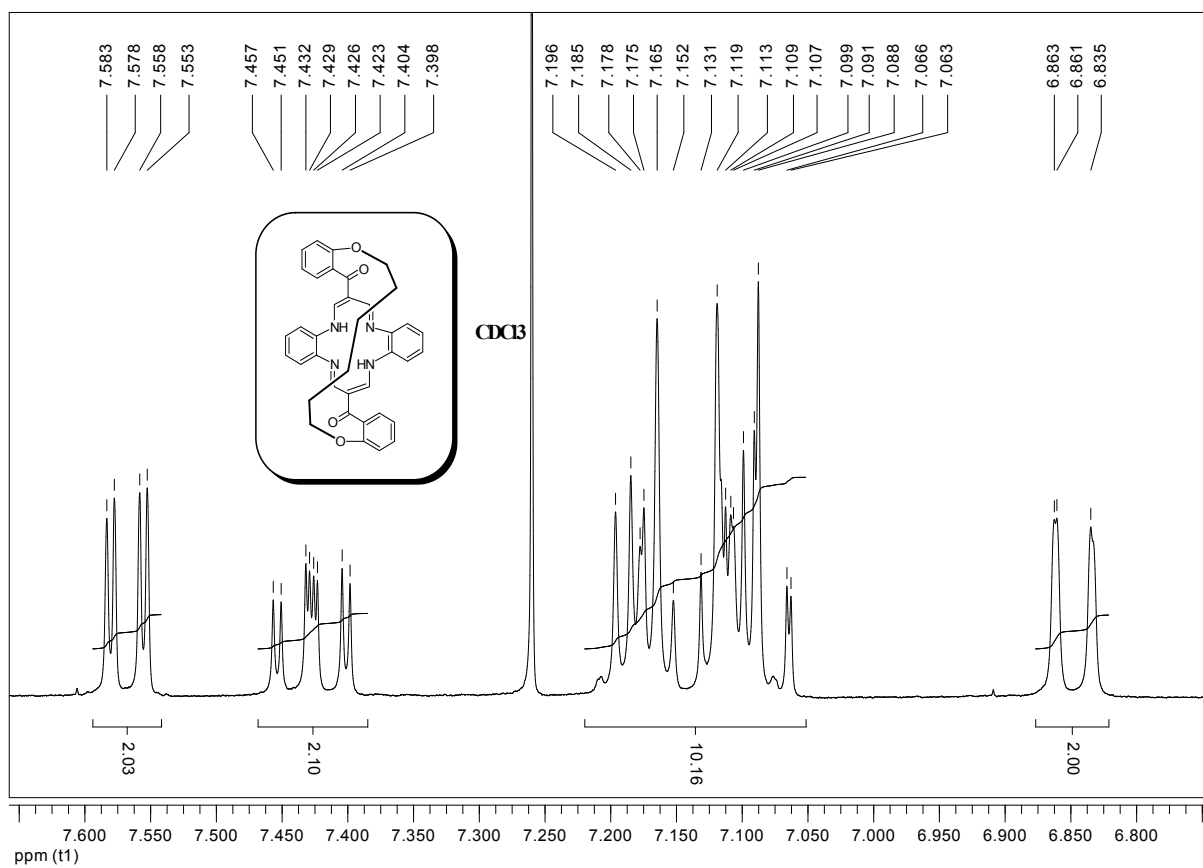
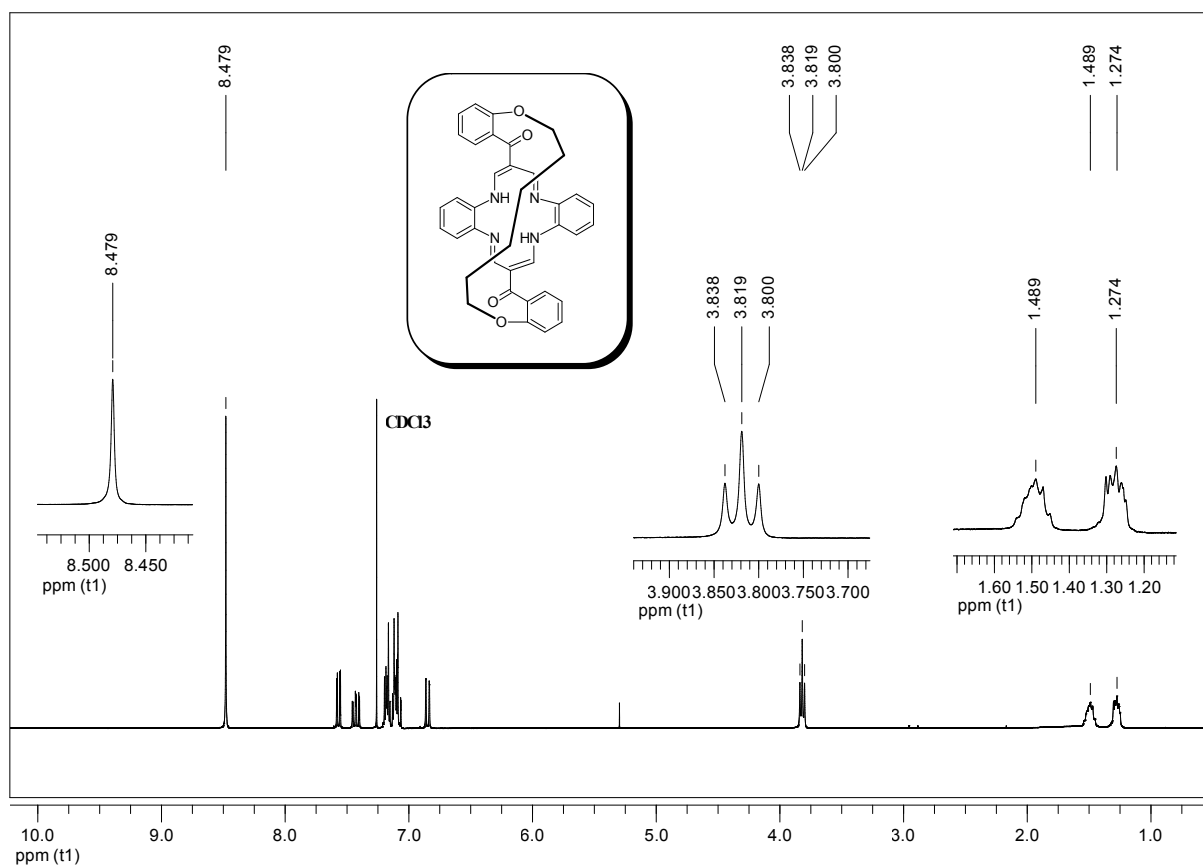


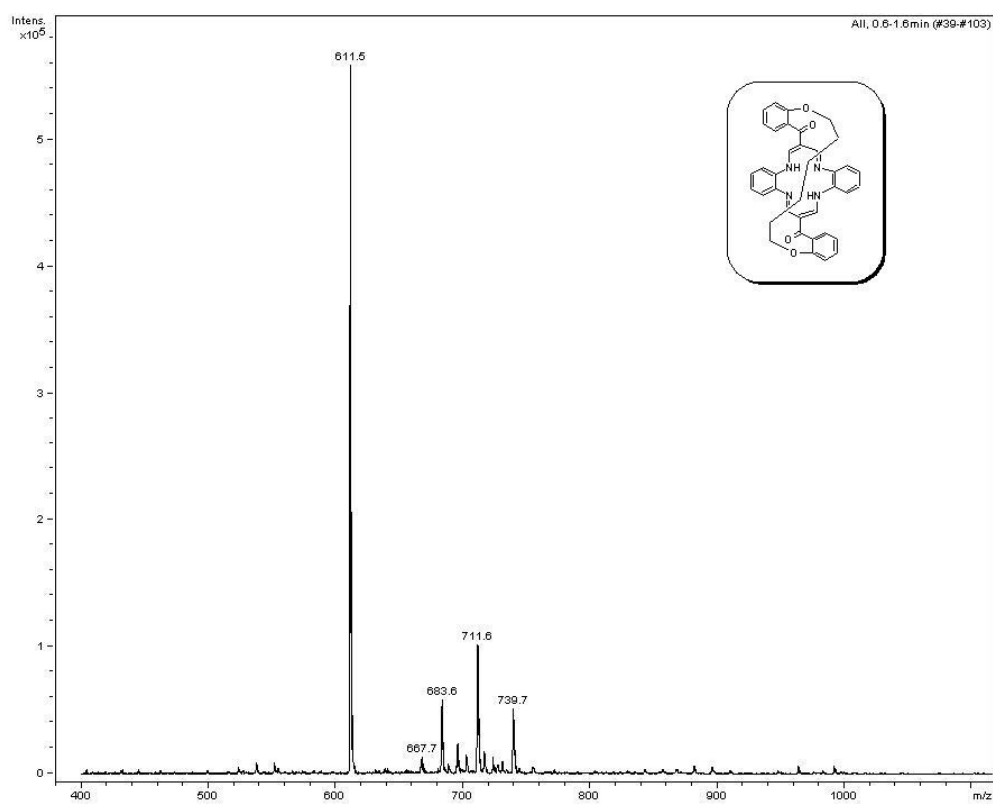
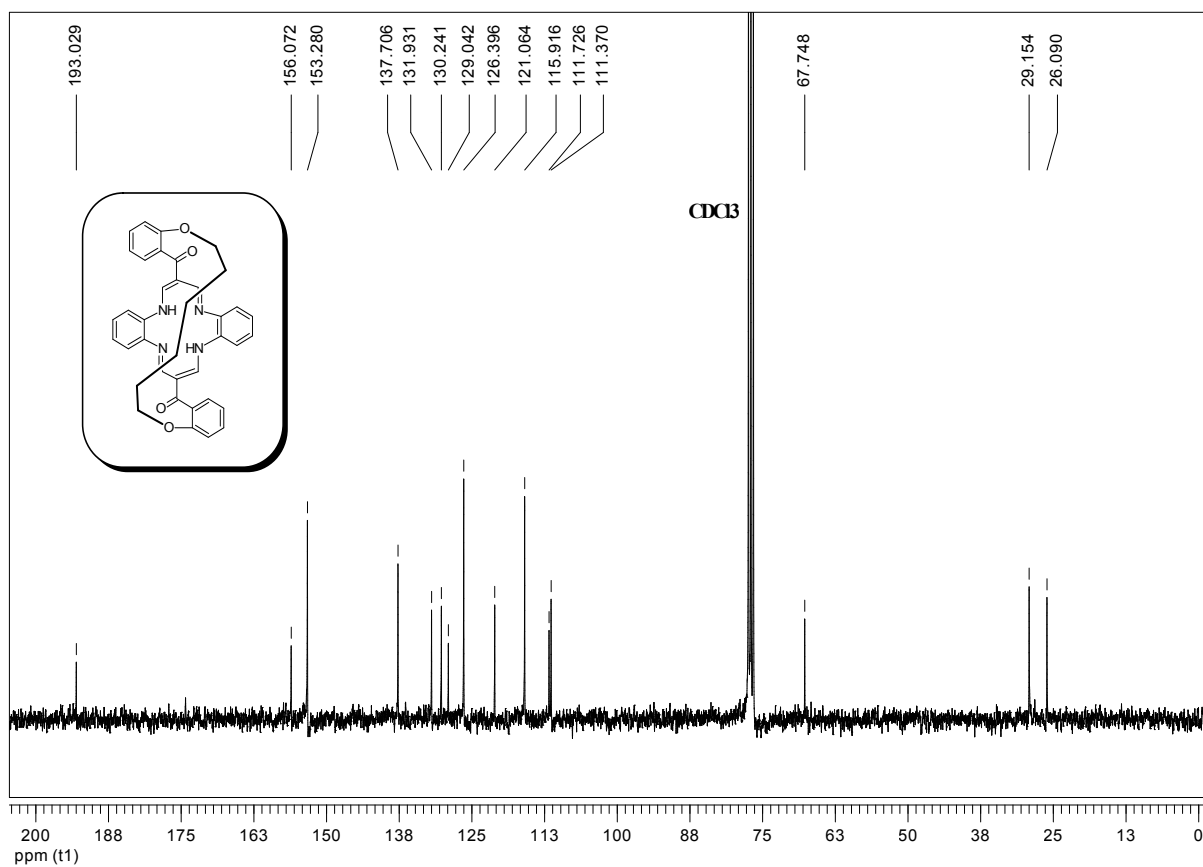


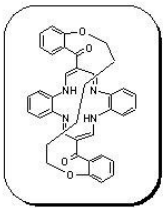


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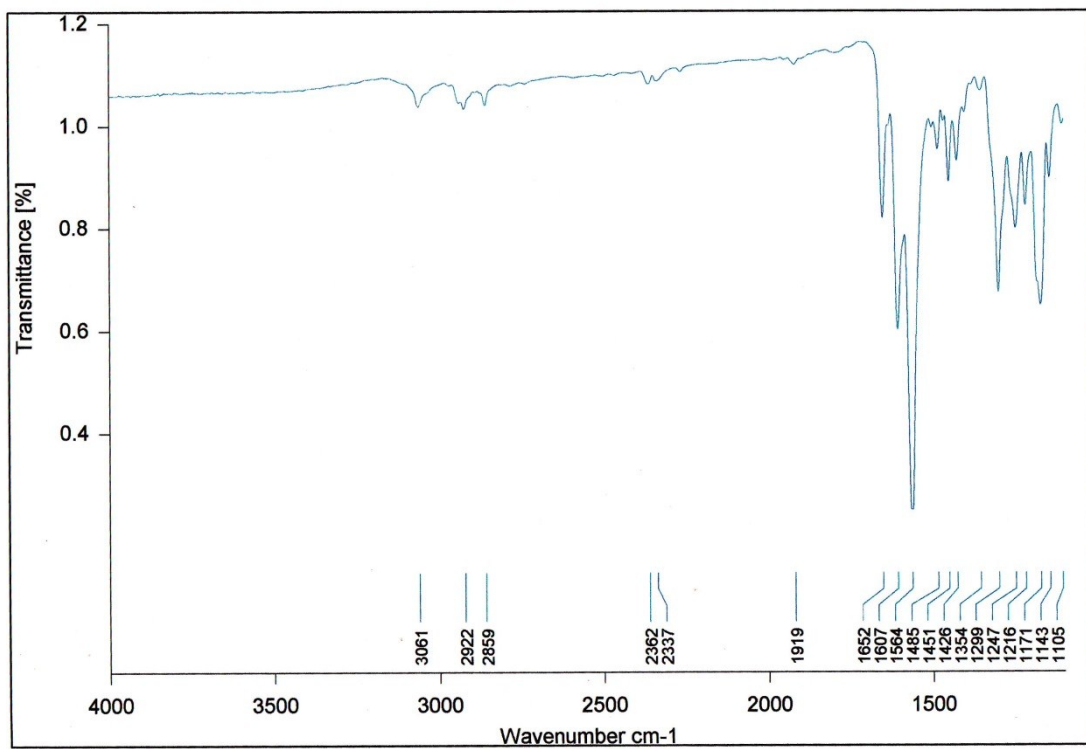






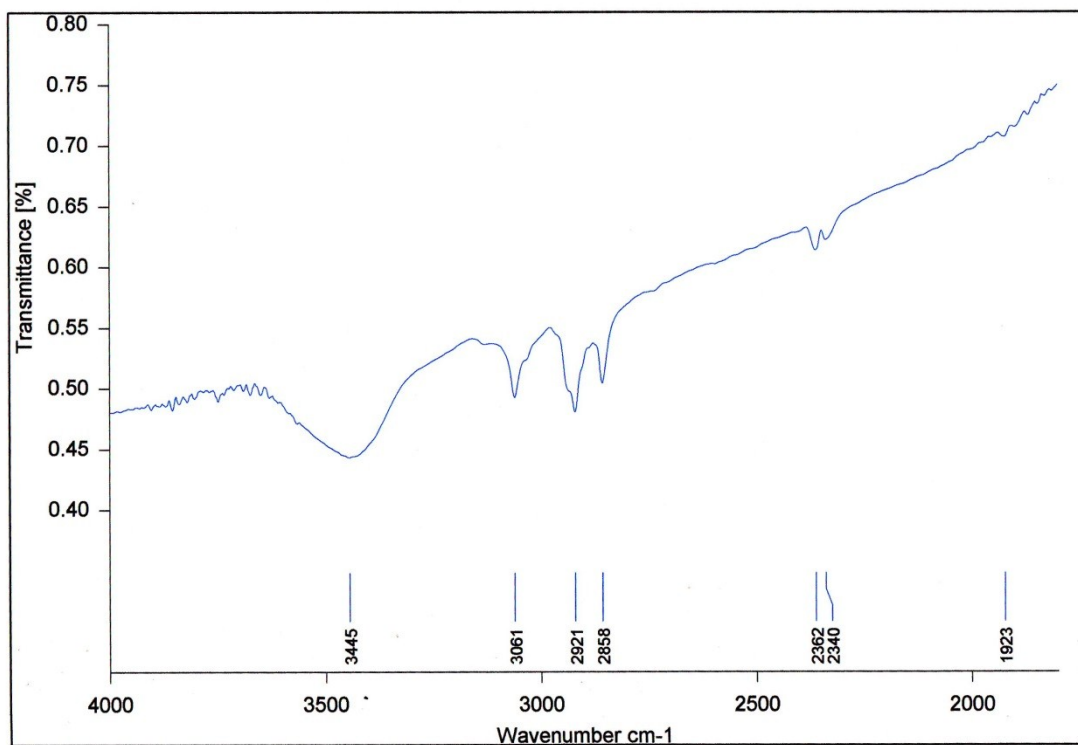


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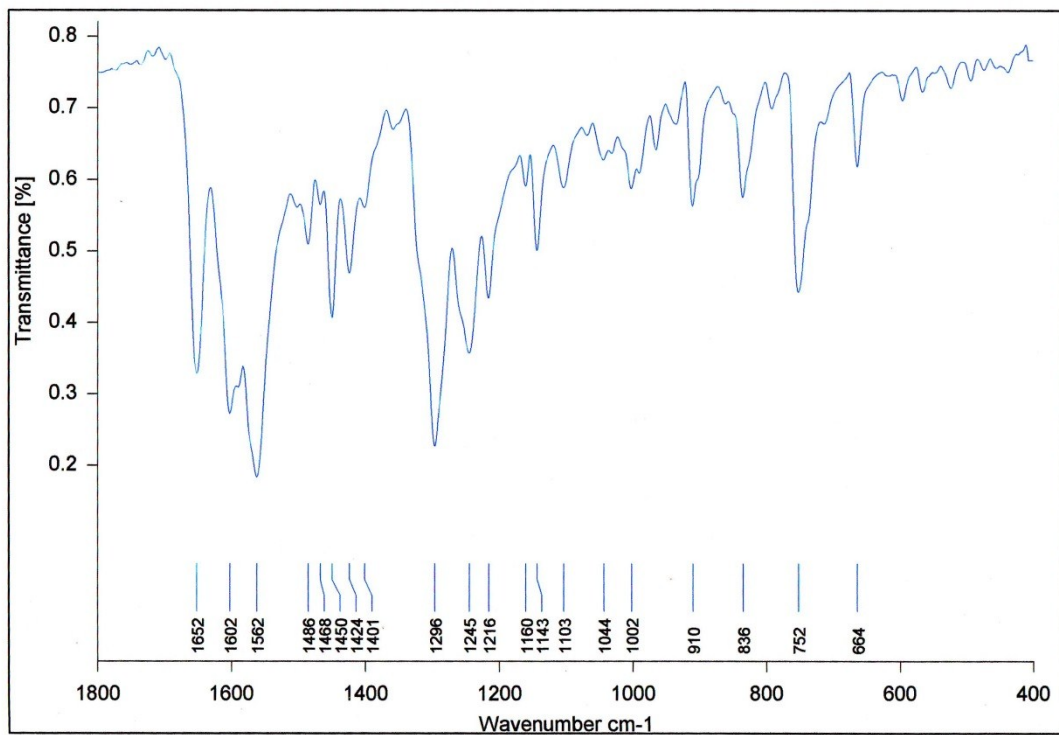


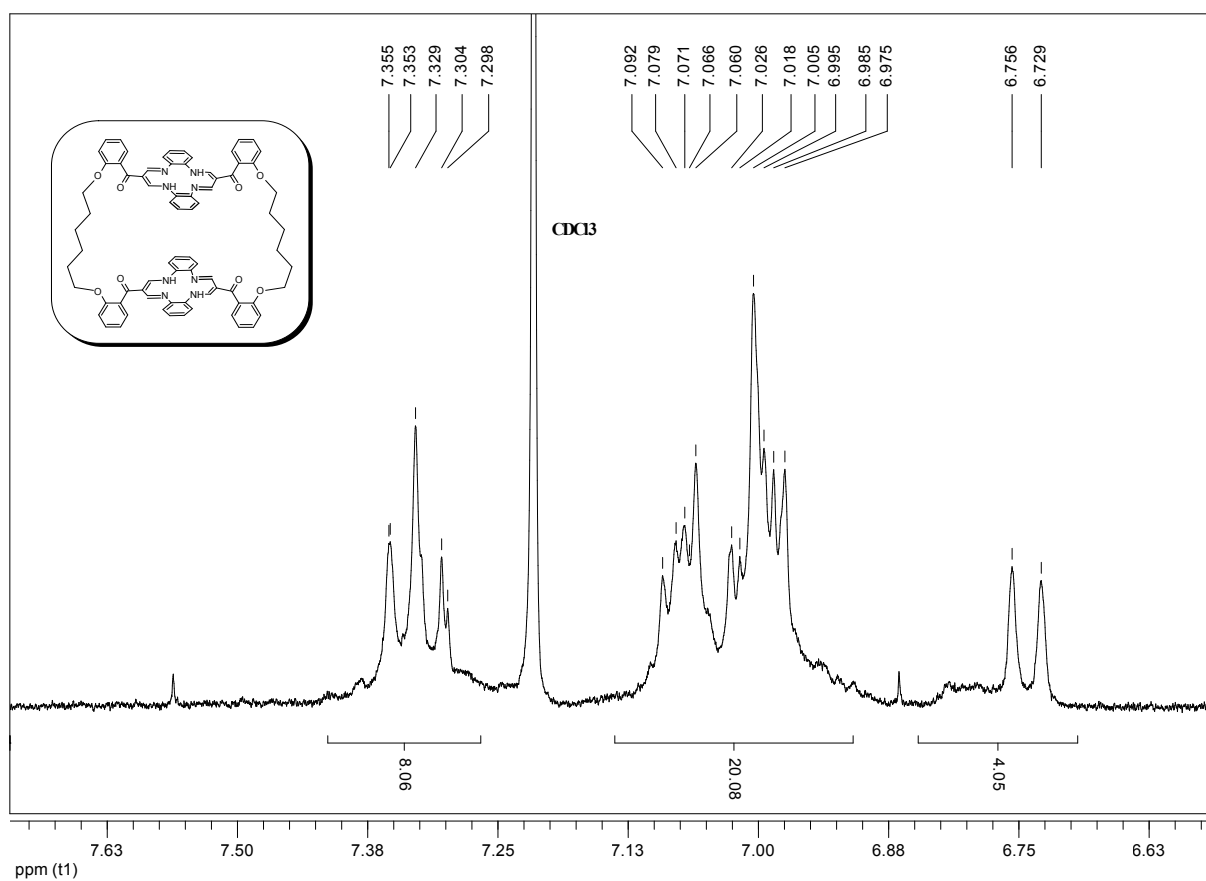
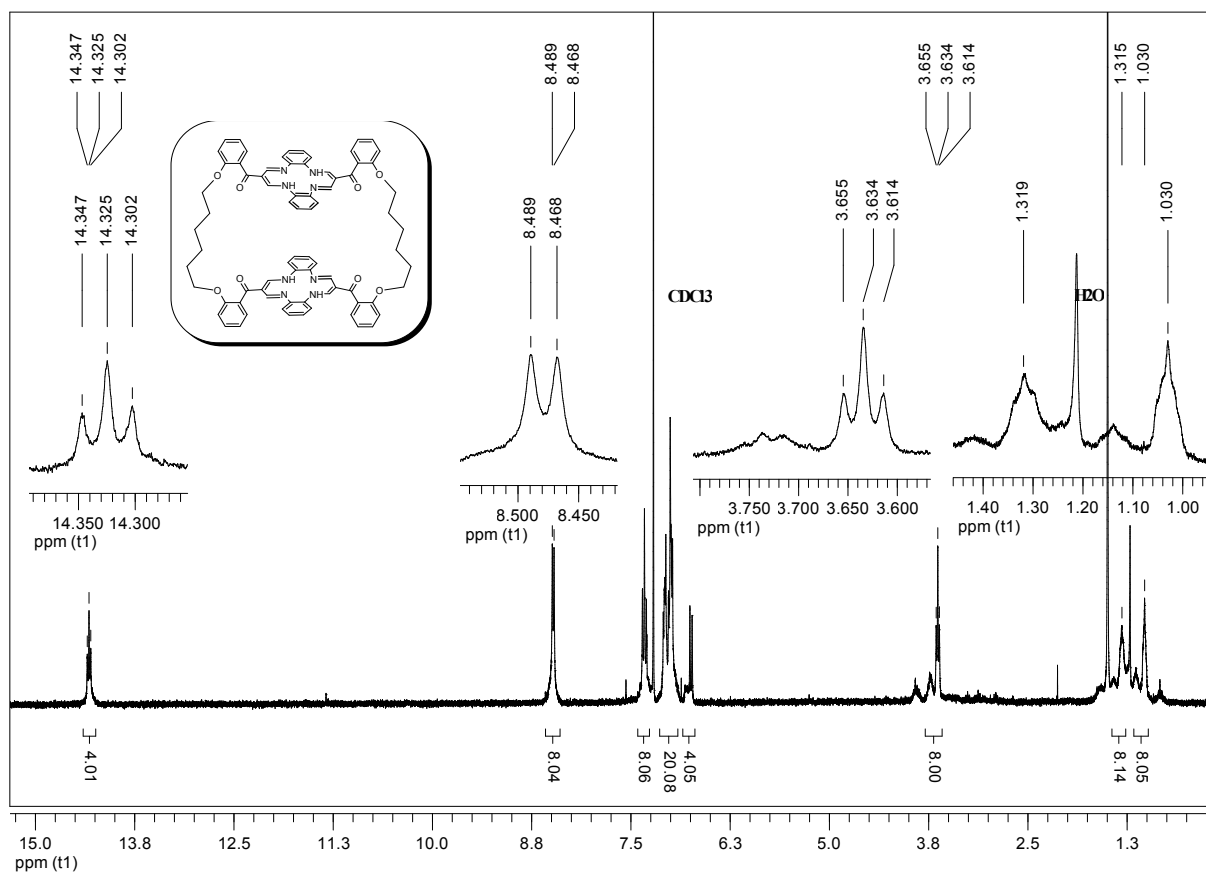


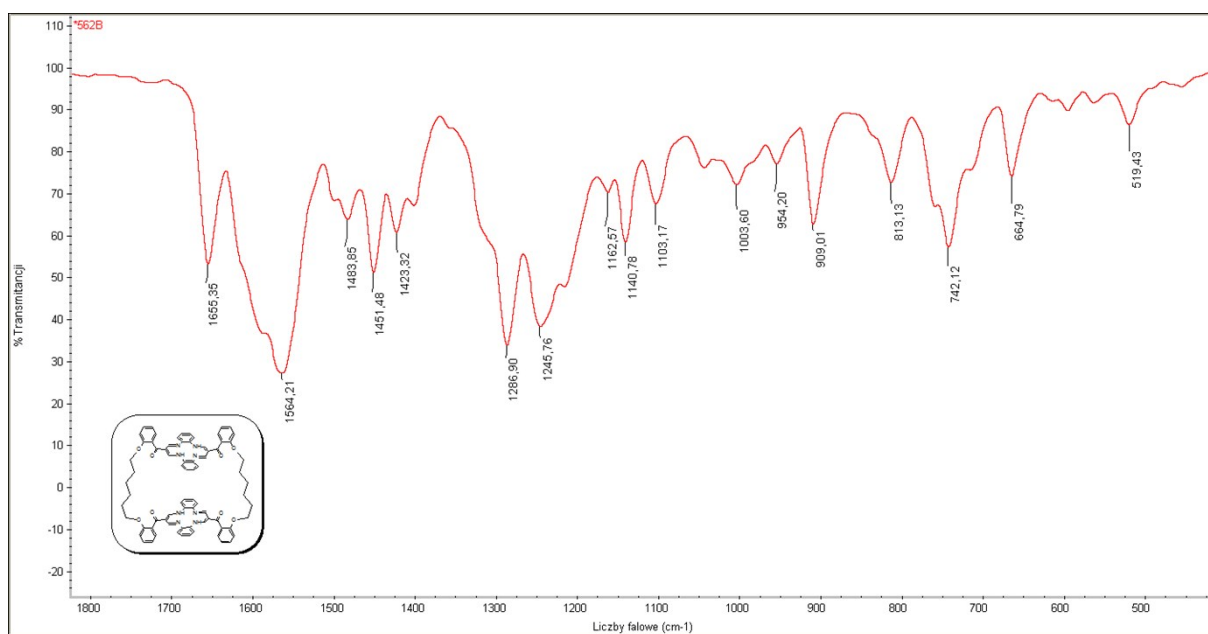
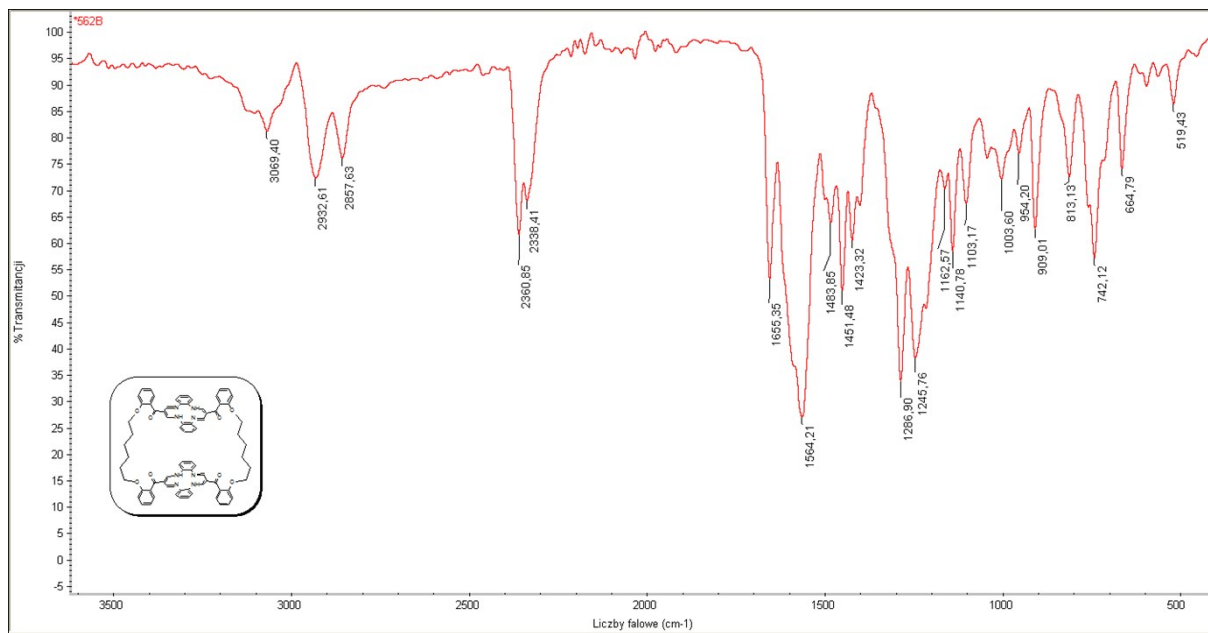
K 176
KBr



K 176
KBr

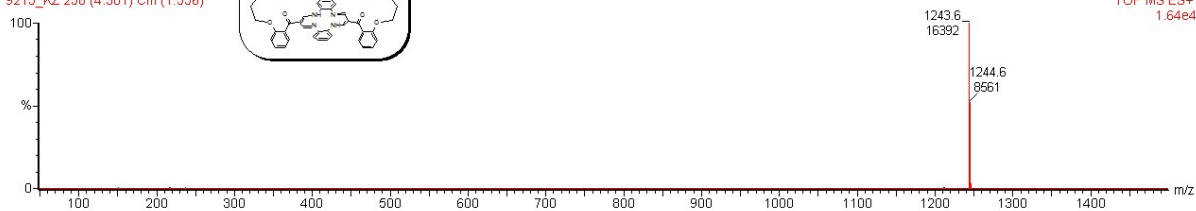
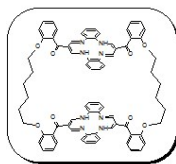






K562_B
LCT

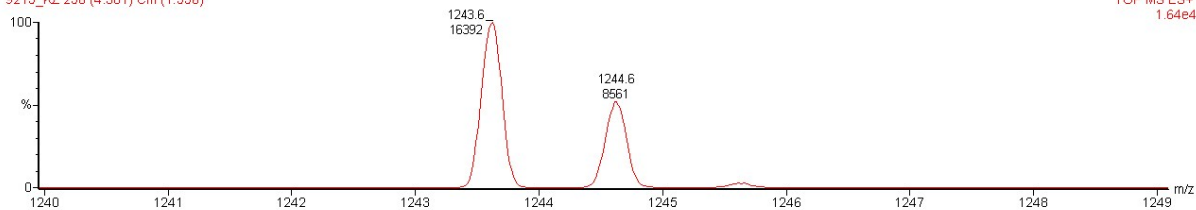
9215_KZ 258 (4.301) Cm (1.556)



13:48:29
07-Oct-2010
TOF MS ES+
1.64e4

K562_B
LCT

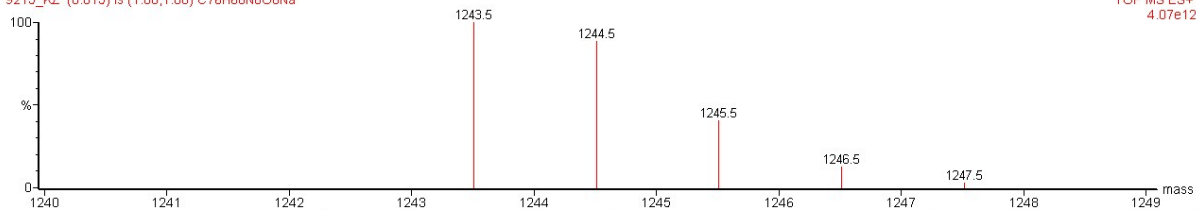
9215_KZ 258 (4.301) Cm (1.556)



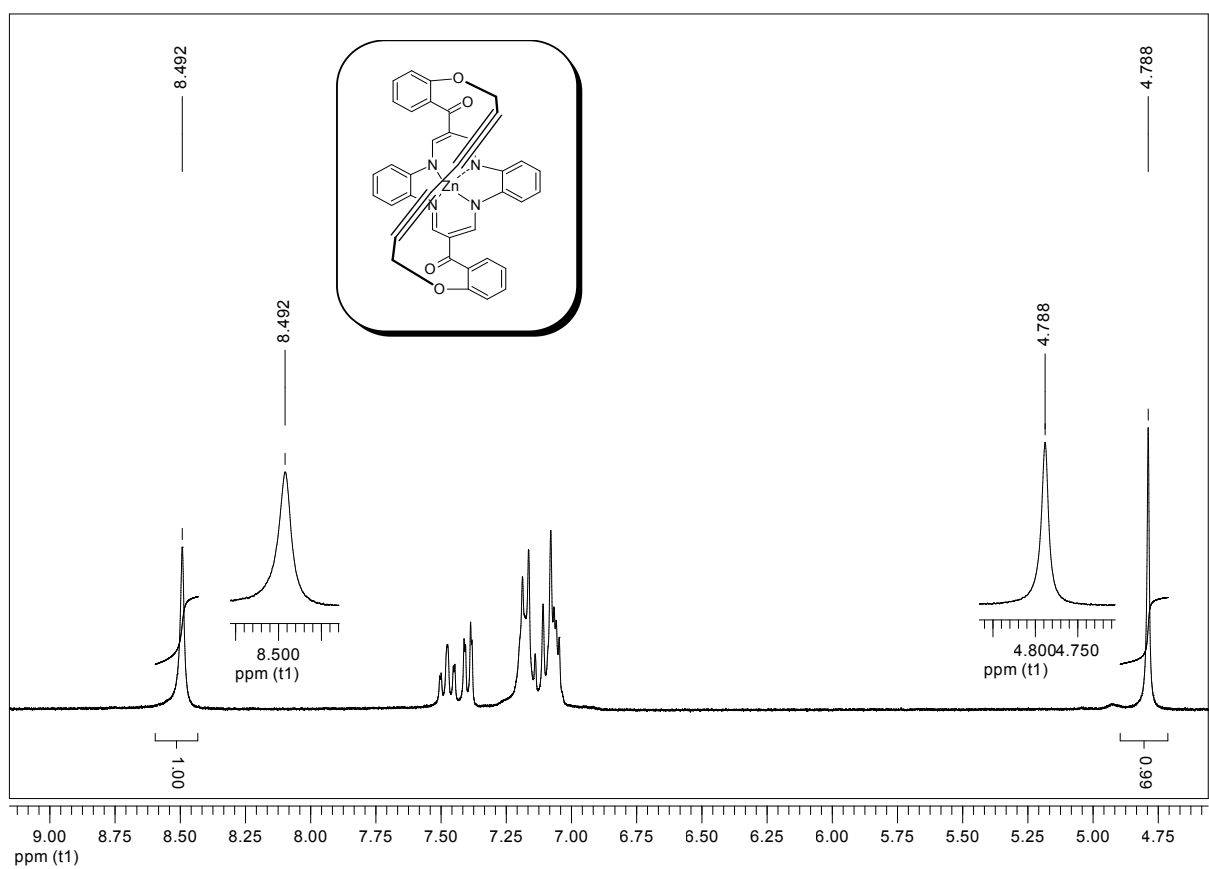
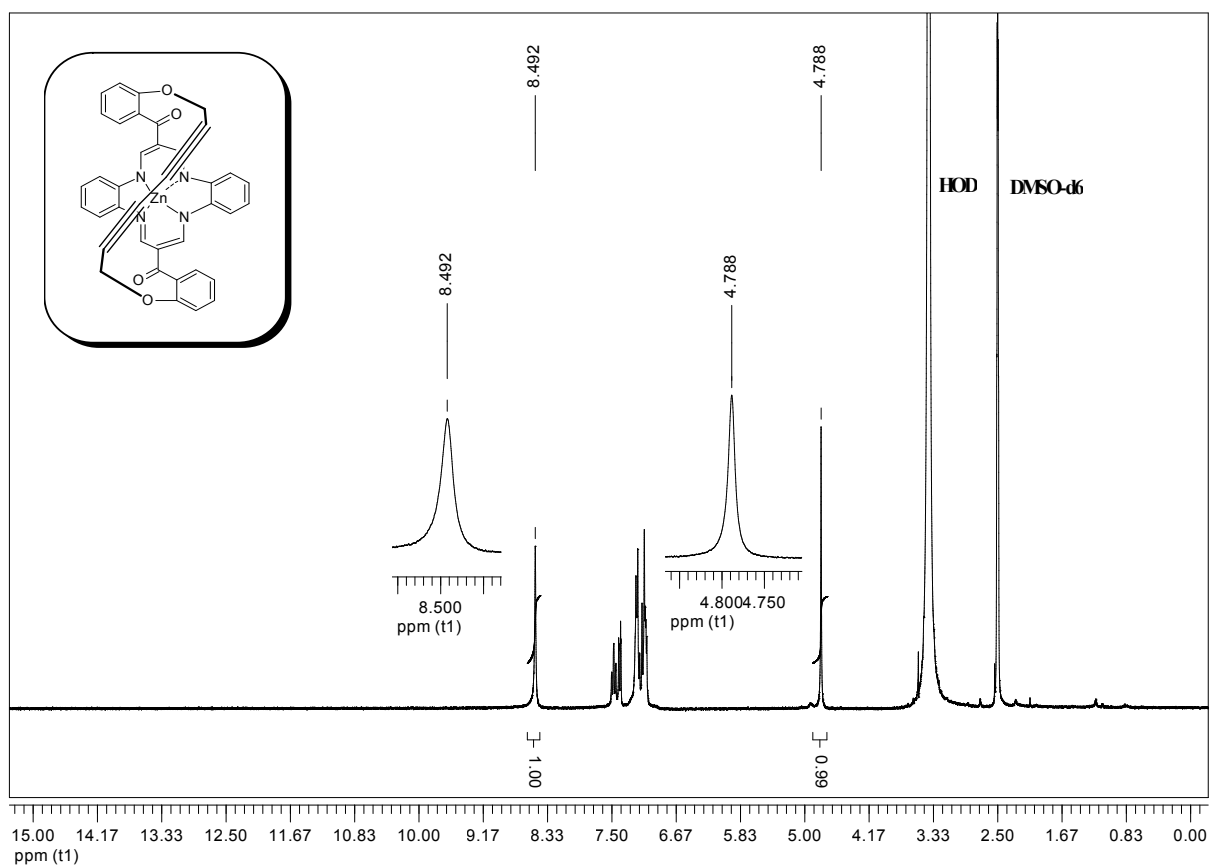
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07-Oct-2010
TOF MS ES+
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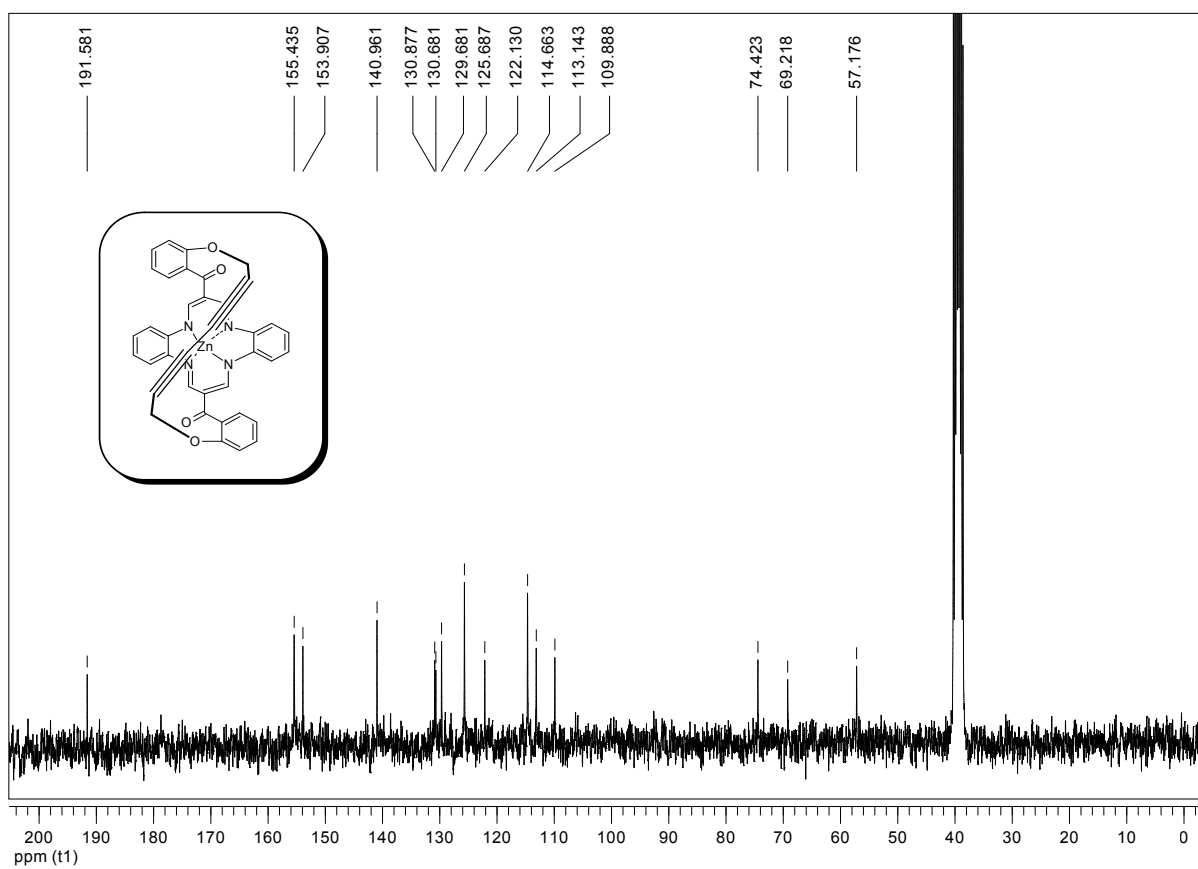
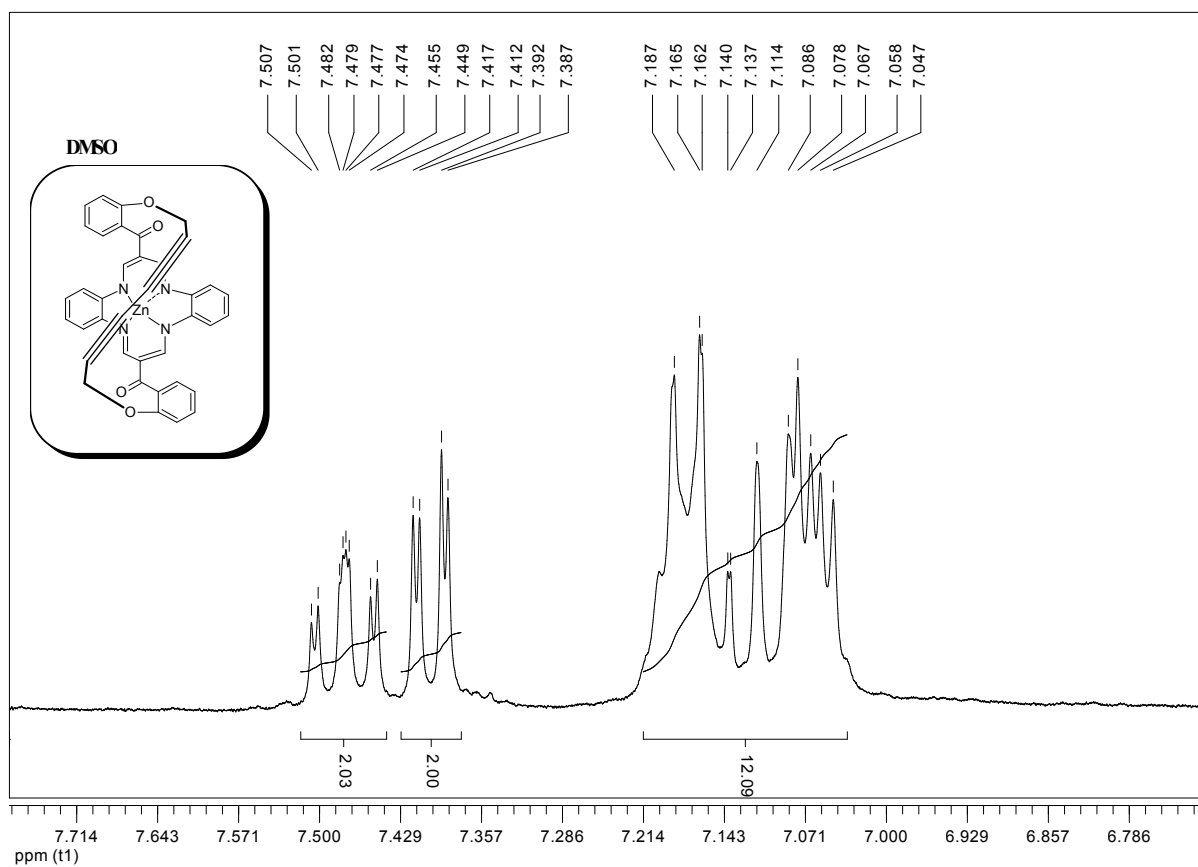
K562_B
LCT

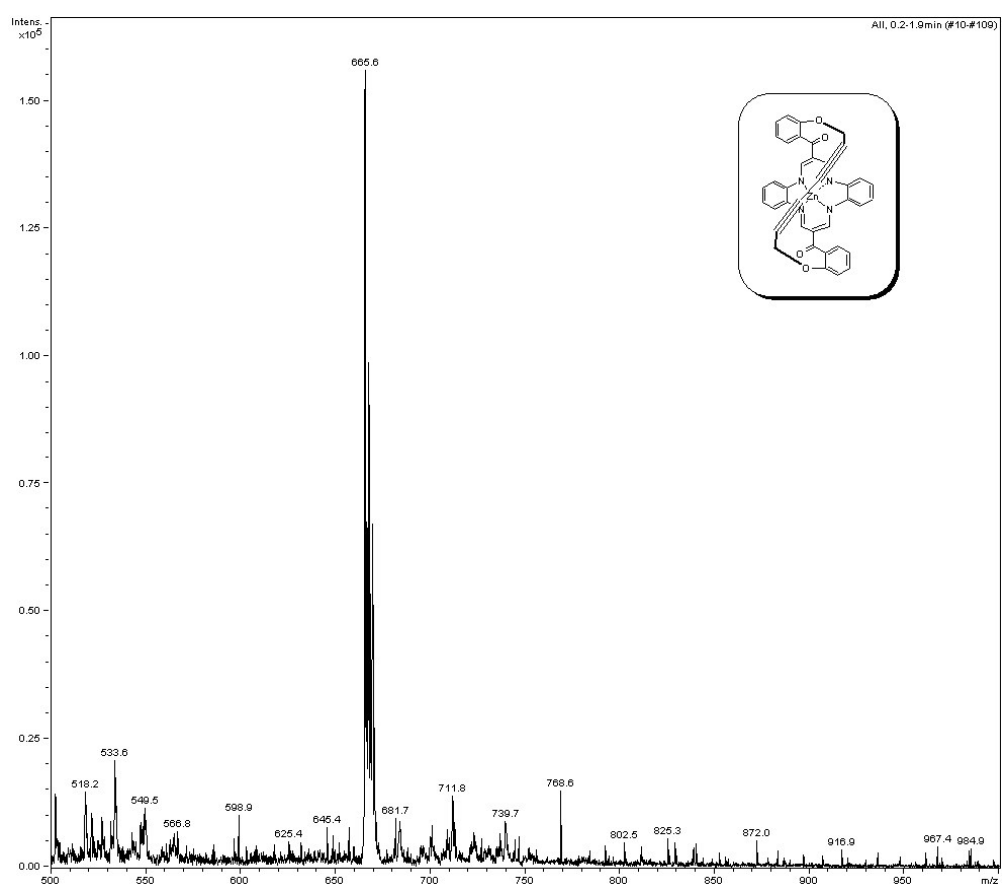
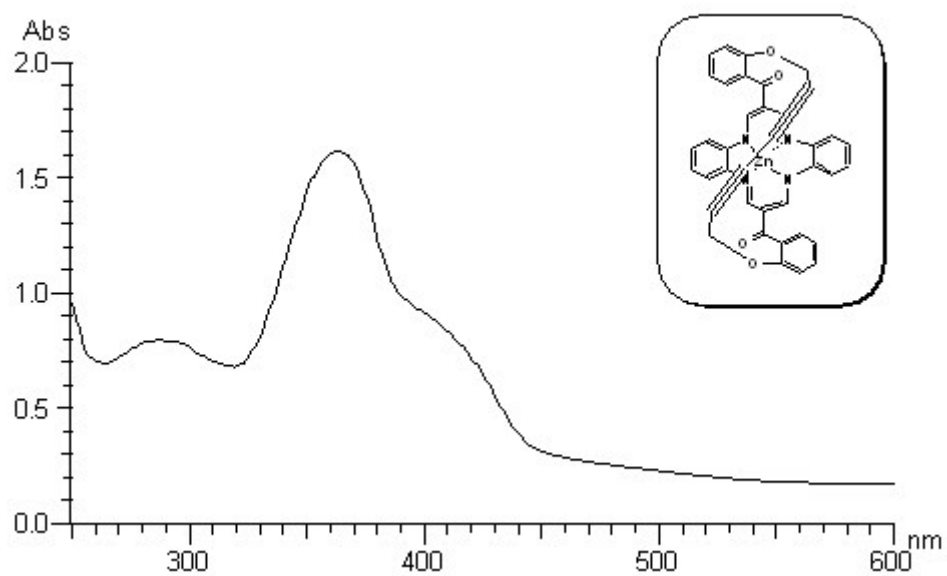
9215_KZ (0.015) Is (1.00,1.00) C76H68N8O8Na

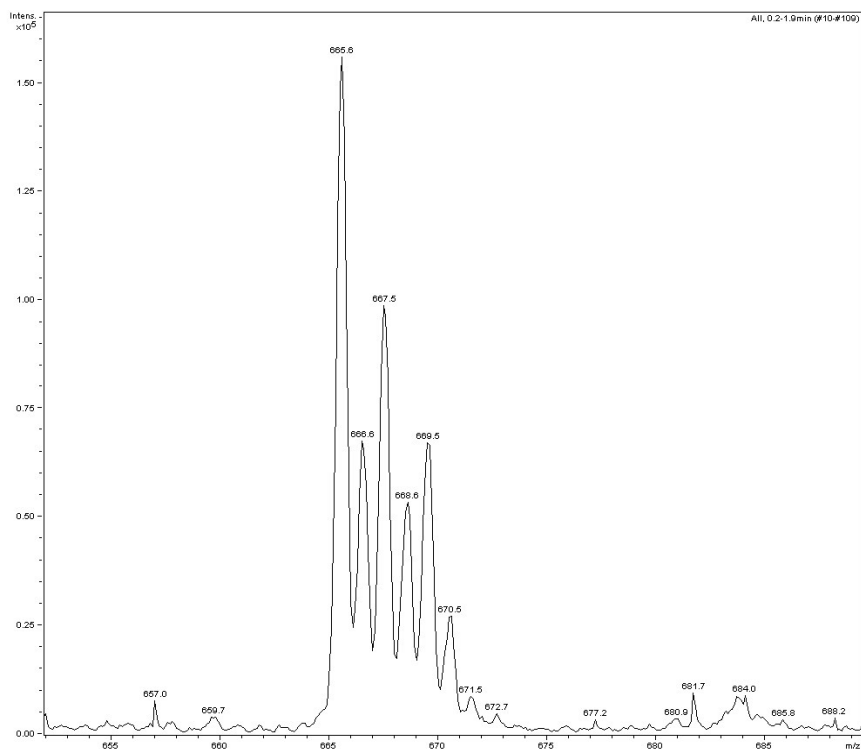


13:48:29
07-Oct-2010
TOF MS ES+
4.07e12

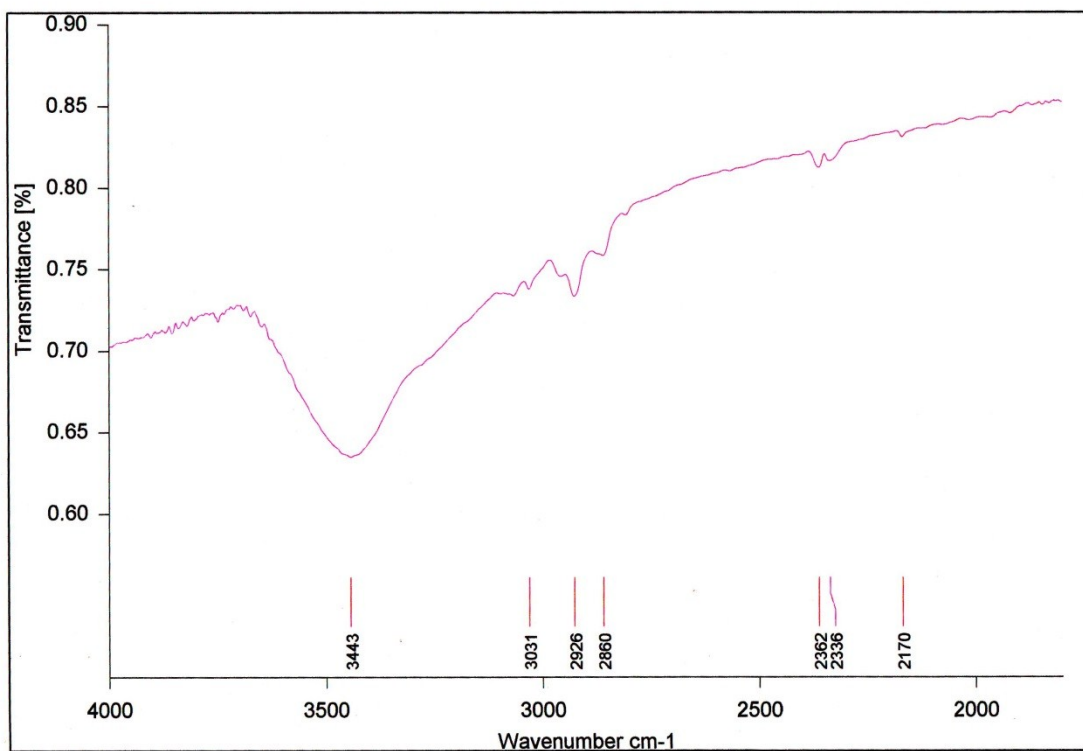








K 175
KBr





K 175
KBr

