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## **Section 1: General Methods**

Commercially available reagents were used as received. Dry solvents (THF, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and MeCN) for reactions were prepared using a MBraun MB-SPS-5 bench-top solvent purification system (SPS) under nitrogen (H<sub>2</sub>O content < 20 ppm). All other solvents were HPLC grade and were used without further purification. In the synthetic procedures, the solvents described as ‘dry solvent’ were purified using the SPS; if ‘dry’ is not stated, this means HPLC grade. Petroleum ether had a boiling point range of 40–60 °C. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA, 99%), diisopropylamine (99.5%), 3-chloroperbenzoic acid (*m*CPBA, ≤ 77%) and magnesium monoperoxyphthalate hexahydrate (MMPP, 80%) were purchased from Sigma-Aldrich and used as received. EDTA/NH<sub>3</sub> solution was prepared by saturating a 1:1 solution of water/aqueous 35% NH<sub>3</sub> solution with tetrasodium EDTA. Copper(I) chloride was prepared according to the published procedure<sup>[1]</sup> because CuCl prepared in this way has a finer particle size than commercial material, which is beneficial for Glaser coupling reactions.

Thin layer chromatography (TLC) was carried out on aluminum-backed silica gel plates with 0.2 mm thick silica gel 60 F254 (Merck) and visualized by UV irradiation at either 254 nm or 366 nm. Preparative flash column chromatography was carried out using flash silica gel 60 (230–400 mesh) obtained from Sigma-Aldrich, or on a Biotage Isolera One with a 200–400 nm UV detector.

Size exclusion chromatography (SEC) was carried out using Bio-Beads S-X1 or S-X3, 40–80 μm (Bio Rad). Analytical GPC was carried out on a VWR system equipped with a JAIGEL H-P pre-column, a JAIGEL-3H-A (8 × 500 mm) and a JAIGEL-4H-A (8 × 500 mm) column in series with THF + 1% pyridine as eluent with a flow rate of 1.0 mL/min. Semipreparative GPC was carried out on a Shimadzu recycling GPC system equipped with a LC-20 AD pump, SPD-20A UV detector and a JAIGEL H-P pre-column, a JAIGEL 3H (20 × 600 mm) and a JAIGEL 4H (20 × 600 mm) column in series with THF as the eluent at a flow rate of 3.5 mL/min.

<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on Bruker NEO 400, Bruker AVIII HD 500, Bruker AVIII HD 600 (Prodigy broadband cryoprobe), Avance NEO 600 (broadband helium cryoprobe), and AVIII 700 (<sup>1</sup>H/<sup>13</sup>C/<sup>15</sup>N TCI cryoprobe) spectrometers at 400 MHz, 500 MHz, 600 MHz, and 700 MHz (<sup>1</sup>H), 100 MHz, 126 MHz, 151 MHz, and 175 MHz (<sup>13</sup>C), and 162 MHz, 202 MHz, and 243 MHz (<sup>31</sup>P), respectively at 298 K. All chemical shifts are reported in ppm, coupling constants are reported in Hz and <sup>1</sup>H multiplicities are reported in accordance with the following: s = singlet; br s = broad singlet; d = doublet; t = triplet; q = quartet; and m = multiplet. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported relative to SiMe<sub>4</sub> (δ = 0). <sup>31</sup>P NMR spectra were externally referenced to an 85 % aqueous solution of H<sub>3</sub>PO<sub>4</sub> (δ<sub>P</sub> = 0.0 ppm) using the spectrometer reference values. <sup>1</sup>H NMR spectra were referenced to the residual solvent signal (CDCl<sub>3</sub>: 7.26 ppm, CD<sub>2</sub>Cl<sub>2</sub>: 5.32 ppm) and <sup>1</sup>H NMR assignments were made using the information provided by coupling constants and/or 2D NMR methods (COSY, NOESY, HSQC, HMBC). <sup>13</sup>C NMR spectra were referenced to the solvent signal (CD<sub>2</sub>Cl<sub>2</sub>: 53.84 ppm, CDCl<sub>3</sub>: 77.16 ppm). <sup>13</sup>C NMR spectra of cobalt carbonyl complex of alkynes often showed fewer than the expected number of peaks due to the broadness and low intensity (from the slow relaxation) of the carbons bound to cobalt and the overlap between the signals from the many carbon environments.

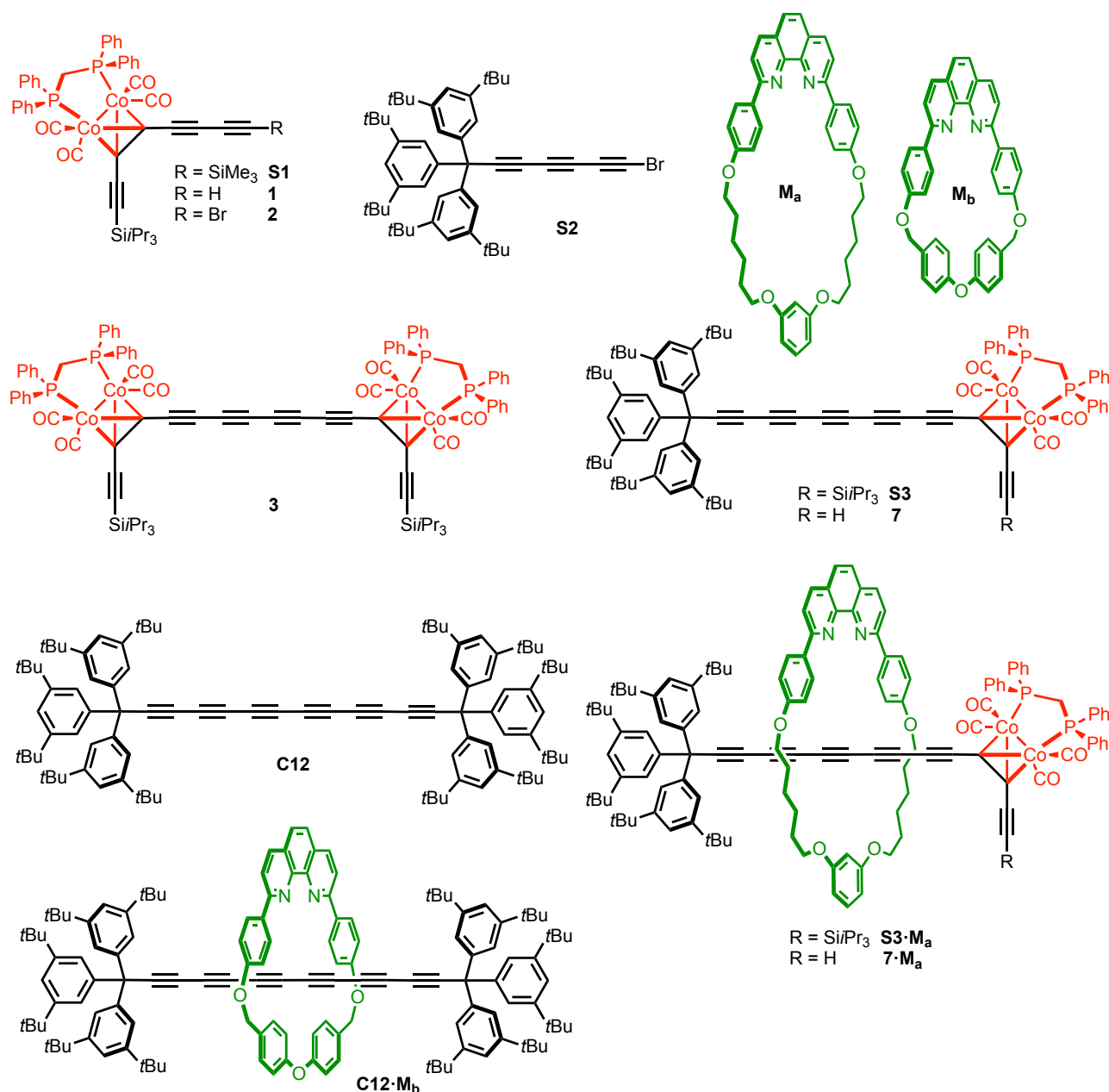
High-resolution mass spectrometry measurements were carried out by either: (i) electrospray ionization (ESI) mass spectrometry from 10 nM solutions of sample in 1:1 CH<sub>2</sub>Cl<sub>2</sub>:MeOH on a Thermo Scientific Q Exactive Hybrid Quadrupole-Orbitrap mass spectrometer using 90:10 MeOH:H<sub>2</sub>O (+0.1% formic acid) as the

mobile phase by the mass spectrometry service at the University of Oxford; or (ii) nanoelectrospray ionization (nESI) mass spectrometry from 10 nM solutions of sample in 4:4:1 CH<sub>2</sub>Cl<sub>2</sub>:MeOH:formic acid on a Waters Synapt G2-S spectrometer equipped with an Advion Biosciences Nanomate Triversa chip-based nanospray system in positive mode using MassLynx software (v4.1) by Mark F. Wyatt (Wyatt Analytical Ltd) and Paul J. Gates at the University of Bristol. The Nanomate was set to aspirate 5 μL of sample solution. MALDI-ToF spectra were measured on a Bruker MALDI Autoflex Speed mass spectrometer using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyldiene]malononitrile (DCTB) as the matrix.

UV-vis spectra were recorded in solution on a Perkin-Elmer Lambda 20 or Perkin-Elmer Lambda 25 spectrometer at 298 K, in fused silica cuvettes with a pathlength of 1 cm. Molar absorption coefficients ( $\epsilon$ , with units M<sup>-1</sup> cm<sup>-1</sup>) were determined from absorption spectra of solutions measured at appropriate concentrations to give an absorption in the range 0.5–1.5 with a path length of 1 cm.

Infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer with internal calibration range of 4000-600 cm<sup>-1</sup> and the sample being prepared as a thin film on a diamond ATR module.

Raman spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> solutions (typically 1 mM concentration) using a Bruker MultiRAM FT-Raman spectrometer. A continuous-wave Nd:YAG laser working at 1064 nm was employed for excitation. Raman scattering radiation was collected in a back-scattering configuration with a spectral resolution of 4 cm<sup>-1</sup>, and samples were held in a stationary fused silica NMR tube. Laser power was typically 50 mW and kept low to avoid sample degradation, spectra accumulation times were typically 64 accumulations.



**Figure 1.** Previously reported molecular structures (except for compound **2**) used in this work.

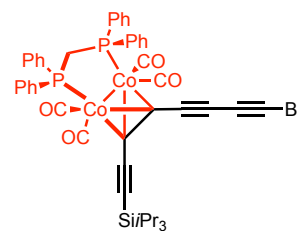
The supertrityl ( $\text{Tr}^*$ ) triyne bromide compound **S2**,<sup>[2]</sup> dicobalt masked tetrayne **S1** and **1**, phenanthroline macrocycles **M<sub>a</sub>**<sup>[3]</sup> and **M<sub>b</sub>**,<sup>[4]</sup> tetracobalt masked octayne **3**,<sup>[5]</sup> compounds **S3**, **S3·M<sub>a</sub>**, **7**, and **7·M<sub>a</sub>**,<sup>[6]</sup> and polyynes rotaxane **C12·M<sub>b</sub>**<sup>[7]</sup> and polyynes dumbbell **C12**<sup>[2]</sup> were synthesized as reported previously.

Unless otherwise noted in the individual procedures, complexes **M<sub>a</sub>·CuI**<sup>[6]</sup> and **M<sub>b</sub>·CuI**<sup>[8]</sup> were prepared as described in the literature. A typical procedure was described as follows: To a solution of macrocycle **M<sub>b</sub>** (400 mg, 0.716 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was added a solution of copper(I) iodide (136 mg, 0.716 mmol) in MeCN (20 mL), and the solution was stirred for 1 h at 20 °C. Solvent removal gave **M<sub>b</sub>·CuI** as a dark red solid. The complexes were used in the next reactions without further purification.

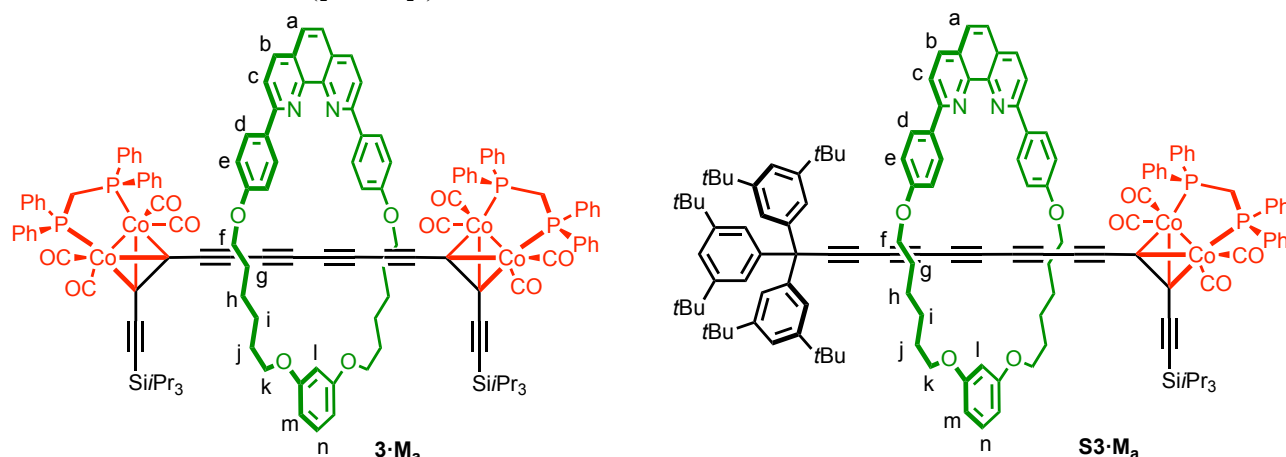
## Section 2: Synthetic Protocols

**CAUTION:** Some polyynes have been reported to be explosive. We have not experienced problems of this type, but all polyynes should be handled with care and not prepared on a large scale.

**Compound 2:** Potassium carbonate (0.18 g, 1.3 mmol) and 18-crown-6 (0.20 g, 0.77 mmol) were added to a solution of compound **S1** (0.24 g, 0.26 mmol) in THF (2 mL) and MeOH (2 mL), and the solution was stirred for 5 min at 20 °C. To the resulting solution was added a solution of CBr<sub>4</sub> (169 mg, 0.51 mmol) in THF (2 mL) and MeOH (2 mL). The mixture was stirred for 10 min at 20 °C and the reaction was monitored using TLC. Petroleum ether (10 mL) was added to the mixture and the solution passed through a short silica column (petroleum ether then petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> 9:1) to give compound **2** as a red solution. *As this compound decomposes rapidly upon drying, the yield of the reaction was determined by <sup>1</sup>H NMR spectroscopy: Compound **S1** (34 mg, 0.036 mmol) was treated with the procedure described above, and the yield of compound **2** (24.6 mg, 26.0 μmol, 72 % yield) was determined by NMR using an internal reference of ethyl acetate in CDCl<sub>3</sub>. The NMR solution was dried completely and resulted in a partially/completely decomposed solid (32 mg), assuming this mass was the intact compound **2**, the yield would be 94%. The difference between the two yields may be due to the decomposition when preparing the NMR sample as an insoluble solid was observed on the wall of the NMR tube.*



**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.42 (q, *J* = 6.2 Hz, 4H), 7.37 – 7.21 (m, 12H), 7.16 (d, *J* = 7.7 Hz, 4H), 3.51–3.32 (m, 2H, PCH<sub>2</sub>), 1.17–1.06 (m, 19H, *i*Pr<sub>3</sub>). **<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 203.4 (br, C=O), 201.5 (br, C=O), 136.6 (br), 134.0 (br), 132.4 (t, *J*<sub>C-P</sub> = 6.6 Hz), 131.5 (t, *J*<sub>C-P</sub> = 6.2 Hz), 130.1, 129.9, 128.6 (t, *J*<sub>C-P</sub> = 5.0 Hz), 128.4 (t, *J*<sub>C-P</sub> = 5.0 Hz), 108.7, 100.4, 81.0, 78.3, 67.9, 45.2 (C-Br), 35.9 (t, *J*<sub>C-P</sub> = 22.5 Hz, PCH<sub>2</sub>), 18.9 (SiCH(CH<sub>3</sub>)<sub>2</sub>), 11.6 (SiCH(CH<sub>3</sub>)<sub>2</sub>). **<sup>31</sup>P{<sup>1</sup>H} NMR** (243 MHz, CDCl<sub>3</sub>) δ<sub>P</sub> 38.66. **ESI HRMS *m/z***: calcd for C<sub>46</sub>H<sub>44</sub><sup>79</sup>BrCo<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Si ([M + H]<sup>+</sup>) 947.0326, found 947.0320.



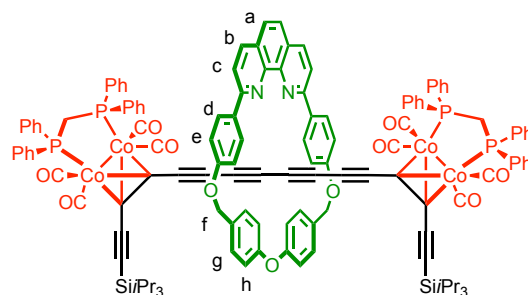
**Compound 3·Ma:** **Method 1.** Saito macrocycle **M<sub>a</sub>** (212 mg, 1.05 eq., 332 μmol) and copper(I) iodide (60.3 mg, 1.00 eq., 317 μmol) were combined and dissolved in a solution of dry MeCN (10.5 mL) and dry CH<sub>2</sub>Cl<sub>2</sub> (15.0 mL) and stirred for 1 h under argon at 20 °C. The solvent was removed under reduced pressure and the residual solid dissolved in dry THF (25 mL). Deprotected cobalt-masked tetrayne **1** (275 mg, 1.00 eq., 317 μmol), supertrityl triyne bromide **S2** (232 mg, 1.00 eq., 317 μmol) and potassium carbonate (219 mg, 5.00 eq., 1.58 mmol) were combined and evacuated of air and flushed with argon three times. The solids were cooled in liquid nitrogen, before adding the Cu-macrocycle complex **M<sub>a</sub>·CuI**, along with additional dry THF

(25 mL). The reaction mixture was thoroughly degassed (3 freeze-pump-thaw cycles) before warming to 60 °C and stirring under argon for 18 h. EDTA/NH<sub>3</sub> solution (40 mL) was added to the cooled reaction mixture and left to stir for 1 h. Et<sub>2</sub>O (50 mL) was added and the organic layer extracted. The aqueous layer was washed with Et<sub>2</sub>O (2 × 20 mL) and the combined organic extracts dried over Na<sub>2</sub>SO<sub>4</sub> before removing the solvent under reduced pressure. The crude product was subject to SiO<sub>2</sub> chromatography (petroleum ether/EtOAc, gradient elution from 0 to 33%), then size-exclusion chromatography (Bio-Rad S-X3, toluene) to yield Tr\* [2]rotaxane **S3**·**M<sub>a</sub>** (240 mg, 110 μmol, 35%)<sup>[6]</sup> and tetracobalt [2]rotaxane **3**·**M<sub>a</sub>** (101 mg, 42.5 μmol, 27%) as dark brown solids.

**Method 2.** To a solution of compound **S1** (50 mg, 0.053 mmol) in THF/MeOH (5 mL/5 mL) was added K<sub>2</sub>CO<sub>3</sub> (73.4 mg, 0.531 mmol) at 20 °C, and the solution was stirred for 10 min. This solution was passed through a silica plug (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether 1:1), which resulted in a solution of compound **1**. Without further purification, the resulting solution was concentrated to ca. 2 mL, and dry THF (ca. 10 mL) was added; then this resulting solution was again concentrated, and dry THF was added; repeating this three times gave a solution of compound **1** in THF (3 mL). Separately, compound **2** (0.064 mmol, assuming 100% yield) in dry THF (2 mL) was prepared from compound **S1** (50 mg, 0.053 mmol) as described above. Complex **M<sub>a</sub>**·CuI (48.5 mg, 0.059 mmol) and K<sub>2</sub>CO<sub>3</sub> (36.7 mg, 0.266 mmol) were added to a solution of compound **2** (0.064 mmol assuming 100% yield) and compound **1** (0.053 mmol, assuming 100% yield) in dry THF (5 mL), and the mixture was stirred at 60 °C for 20 h under an argon atmosphere. After cooling to room temperature, saturated aqueous EDTA/NH<sub>3</sub> solution (5 mL) was added and stirred for 1 h. CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and H<sub>2</sub>O (10 mL) were added, the layers were separated, and the aqueous phase was extracted with Et<sub>2</sub>O (2 × 20 mL). The organic phases were combined, washed with brine (20 mL), dried (MgSO<sub>4</sub>), and filtered. Solvent removal and purification by column chromatography (silica gel, petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 3:1, then petroleum ether/ethyl acetate, 4: 1) afforded compound **3**·**M<sub>a</sub>** (15 mg, 6.3 μmol, 13% based on compound **S1**) as a black solid.

<sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.52 (d, *J* = 8.5 Hz, 4H, H<sub>d</sub>), 8.20 (d, *J* = 8.4 Hz, 2H, H<sub>b</sub>), 8.05 (d, *J* = 8.4 Hz, 2H, H<sub>c</sub>), 7.69 (s, 2H, H<sub>a</sub>), 7.31 (s, 8H, Co Ar–H), 7.26 – 7.21 (m, 8H, Co Ar–H), 7.21 – 7.07 (m, 20H, Co Ar–H), 7.01 (t, *J* = 7.6 Hz, 8H, H<sub>e</sub> & Co Ar–H), 6.73 (t, *J* = 2.4 Hz, 1H, H<sub>i</sub>), 6.51 (dd, *J* = 8.1, 2.3 Hz, 2H, H<sub>m</sub>), 4.26 (t, *J* = 7.4 Hz, 4H, H<sub>f/k</sub>), 4.14 (t, *J* = 6.7 Hz, 4H, H<sub>k/f</sub>), 3.34 (s, 4H, P–CH<sub>2</sub>), 1.98 (p, *J* = 6.7 Hz, 4H, H<sub>g/j</sub>), 1.90 (p, *J* = 6.7 Hz, 4H, H<sub>j/g</sub>), 1.69 (d, *J* = 3.9 Hz, 8H, H<sub>h,i</sub>), 1.01 (s, 42H, Si–Pr). <sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 160.93 (O–C–C<sub>e</sub>), 160.77, 156.61 (N–C–C–N), 146.22 (C<sub>a</sub>–C–C<sub>b</sub>), 136.41 (C<sub>b</sub>), 133.56 (br, Ar–C), 132.20 (br, Ar–C), 131.82, 131.43 (br, Ar–C), 130.21, 129.83 (C<sub>n</sub>), 129.62 (C<sub>d</sub>), 129.20, 128.51 (t, *J*<sub>C–P</sub> = 4.8 Hz, Ar–C), 128.39 (t, *J*<sub>C–P</sub> = 4.8 Hz, Ar–C), 127.29, 125.36 (C<sub>a</sub>), 118.94 (C<sub>c</sub>), 115.08 (C<sub>e</sub>), 108.57 (C≡C), 108.13 (C<sub>m</sub>), 101.35 (C≡C), 99.44 (C<sub>i</sub>), 83.49 (C≡C), 82.08 (C≡C), 70.80 (C≡C), 68.35 (C<sub>f/k</sub>), 67.87 (C<sub>k/f</sub>), 67.30 (C≡C), 35.81 (P–CH<sub>2</sub>), 29.74 (C<sub>j/g</sub>), 29.39 (C<sub>g/j</sub>), 25.89 (C<sub>h/i</sub>), 25.84 (C<sub>i/h</sub>), 18.86 (CH(CH<sub>3</sub>)<sub>3</sub>), 11.56 (CH(CH<sub>3</sub>)<sub>3</sub>) (3 carbons not distinguished). **ESI HRMS** *m/z* = 1187.2710 [M+2H]<sup>2+</sup> (C<sub>134</sub>H<sub>130</sub>Co<sub>4</sub>N<sub>2</sub>O<sub>12</sub>P<sub>4</sub>Si<sub>2</sub><sup>2+</sup> requires 1187.2715).

**Compound 3·M<sub>b</sub>: Method 1.** To a solution of compound **S1** (270 mg, 0.287 mmol) in THF/MeOH (30 mL/10 mL) was added K<sub>2</sub>CO<sub>3</sub> (397 mg, 2.87 mmol) at 20 °C, and the solution



was stirred for 30 min. This solution was concentrated to ca. 5 mL and passed through a silica plug (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether 1:1), which resulted in a solution of compound **1**. Without further purification, the resulting solution was concentrated to ca. 5 mL, and dry THF (ca. 50 mL) was added; then this resulting solution was again concentrated, and dry THF was added; repeating this for three times gave a solution of compound **1** in THF (45 mL). Compound **S2** (180 mg, 0.246 mmol), complex **M<sub>b</sub>**·CuI (203 mg, 0.271 mmol), and K<sub>2</sub>CO<sub>3</sub> (170 mg, 1.23 mmol) were added into a Schlenk tube, and this mixture was vacuumed and refilled with a N<sub>2</sub> gas, repeating for three times. Compound **1** (0.287 mmol, assuming 100% yield) in the THF (45 mL) solution was transferred into the Schlenk tube, without further deoxygenation, this solution was stirred at a N<sub>2</sub> atmosphere at 65 °C for 18 h. After cooling to room temperature, saturated aqueous EDTA/NH<sub>3</sub> (10 mL) was added and stirred for 2 h. CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and H<sub>2</sub>O (20 mL) were added, the layers were separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 20 mL). The organic phases were combined, washed with brine (20 mL), dried (MgSO<sub>4</sub>), and filtered. Solvent was removed, and a short column chromatography (silica gel, petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> 1:1) was used to remove the less polar by-products, then the eluting solvent of ethyl acetate was used to give a mixture containing the desired products. Then a SEC (SX3, toluene) was used to remove the free macrocycle. Solvent removal and a final purification by column chromatography (silica gel, ethyl acetate/petroleum ether 1:5 to 1:1) afforded compound **3**·**M<sub>b</sub>** (55 mg, 24 μmol, 17% based on compound **S1**) and **S3**·**M<sub>b</sub>** (58 mg, 28 μmol, 11% based on compound **S2**) as black solids.

**Method 2.** To a solution of compound **S1** (200 mg, 0.213 mmol) in THF/MeOH (5 mL/2 mL) was added K<sub>2</sub>CO<sub>3</sub> (147 mg, 1.06 mmol), and the solution was stirred for 10 min at 20 °C. This solution was passed through a silica plug (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether 1:1), which resulted in a solution of compound **1**. Without further purification, the resulting solution was concentrated to ca. 5 mL, and dry THF (ca. 20 mL) was added; then this resulting solution was again concentrated, and dry THF was added; repeating this three times gave a solution of compound **1** in THF (20 mL). Separately, compound **2** (0.213 mmol, assuming 100% yield) in dry THF (20 mL) was prepared from compound **S1** (200 mg, 0.213 mmol) as described in the synthetic procedure. Complex **M<sub>b</sub>**·CuI (191 mg, 0.256 mmol) and K<sub>2</sub>CO<sub>3</sub> (147 mg, 1.06 mmol) were then added to the solution of compound **2** (0.213 mmol, assuming 100% yield) and compound **1** (0.213 mmol, assuming 100% yield) in dry THF (40 mL), and the mixture was stirred at 60 °C for 20 h under a N<sub>2</sub> atmosphere. After cooling to room temperature, saturated aqueous EDTA/NH<sub>3</sub> solution (20 mL) was added and stirred for 1 h. CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and H<sub>2</sub>O (20 mL) were added, the layers were separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 20 mL). The organic phases were combined, washed with brine (20 mL), dried (MgSO<sub>4</sub>), and filtered. Solvent removal and purification by column chromatography (silica gel, petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 3:1, then petroleum ether/ethyl acetate, 4: 1) afforded compound **3**·**M<sub>b</sub>** (73 mg, 32 μmol, 15% based on compound **S1**) as a black solid.

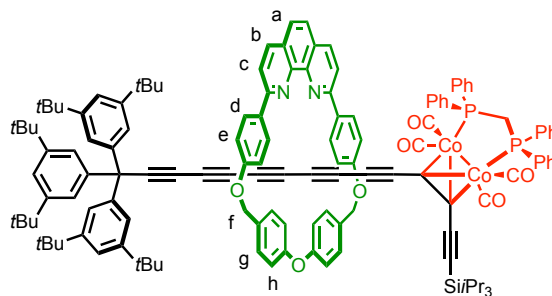
**IR** (ATR): 2943 (w, C–H), 2864 (w, C–H), 2150 (w, C≡C), 2104 (w, C≡C), 2036 (m, C=O), 2013 (s, C=O), 1988 (m, C=O) cm<sup>-1</sup>. **<sup>1</sup>H NMR** (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 8.21 (d, *J* = 8.3 Hz, 2H; H<sub>b</sub>), 8.08 (d, *J* = 8.7 Hz, 4H; H<sub>d</sub>), 7.92 (d, *J* = 8.3 Hz, 2H; H<sub>c</sub>), 7.73 (s, 2H; H<sub>a</sub>), 7.40–7.36 (m, 15H), 7.31–7.24 (m, 13H), 7.18–7.14 (m, 8H), 7.10–7.07 (m, 4H), 7.03–7.01 (m, 12H), 5.30 (s, 4H; H<sub>f</sub>), 3.43–3.33 (m, 4H; PCH<sub>2</sub>), 1.03–1.02 (m, 42H; *i*Pr<sub>3</sub>). **<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>C</sub> 204.2, 201.7, 160.0, 158.6, 158.1, 147.1, 137.2 (br), 136.3, 134.6, 134.2, 133.5 (br), 132.7 (t, *J*<sub>C-P</sub> = 6.1 Hz), 131.5 (t, *J*<sub>C-P</sub> = 6.1 Hz), 130.6, 130.1, 128.9 (t, *J*<sub>C-P</sub> = 4.9 Hz), 128.7 (t, *J*<sub>C-P</sub> = 4.9 Hz), 127.6, 127.5, 125.8, 122.8, 120.4, 116.8, 108.9, 101.3, 83.3, 82.5, 72.6, 71.0, 68.2, 67.9,

19.0, 11.9 (3 signals coincident or not observed).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{P}}$  38.2. **ESI HRMS  $m/z$ :** calcd for  $\text{C}_{130}\text{H}_{113}\text{Co}_4\text{N}_2\text{O}_{11}\text{P}_4\text{Si}_2$  ( $[\text{M} + \text{H}]^+$ ) 2293.4156, found 2293.4133.

**Compound  $\text{S3}\cdot\text{M}_b$ :** The titled compound  $\text{S3}\cdot\text{M}_b$  (58 mg, 28  $\mu\text{mol}$ , 11%) was obtained as a black solid as described in the above procedure using **Method 1**.

**IR (ATR):** 2960 (m, C–H), 2864 (w, C–H), 2034 (m, C=O), 2016 (s, C=O), 1991 (m, C=O)  $\text{cm}^{-1}$ .  **$^1\text{H}$  NMR** (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  8.22 (d,  $J = 8.3$  Hz, 2H;  $\text{H}_b$ ), 7.98 (d,  $J = 8.8$  Hz,

4H;  $\text{H}_d$ ), 7.90 (d,  $J = 8.3$  Hz, 2H;  $\text{H}_c$ ), 7.74 (s, 2H;  $\text{H}_a$ ), 7.40–7.37 (m, 4H;  $\text{PPh}_2\text{-H}$ ), 7.34–7.33 (m, 4H;  $\text{H}_g$ ), 7.30–7.26 (m, 13H;  $\text{H}_h$ , *para*-Tr\* and  $\text{PPh}_2\text{-H}$ ), 7.17–7.14 (m, 4H;  $\text{PPh}_2\text{-H}$ ), 7.10–7.07 (m, 2H;  $\text{PPh}_2\text{-H}$ ), 7.03–7.01 (m, 4H;  $\text{PPh}_2\text{-H}$ ), 6.96 (d,  $J = 8.8$  Hz, 4H;  $\text{H}_e$ ), 6.93 (d,  $J = 1.7$  Hz, 6H; *ortho*-Tr\*), 5.30, 5.27 (ABq,  $J = 15.0$  Hz, 4H;  $\text{H}_f$ ), 3.47–3.32 (m, 2H;  $\text{PCH}_2$ ), 1.18 (s, 54H; *t*Bu), 1.04–1.03 (m, 21H; *i*Pr<sub>3</sub>).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (151 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{C}}$  159.8, 158.5, 158.2, 150.7, 147.0, 144.0, 137.1 (br), 136.4, 134.5, 134.3, 133.3 (br), 132.7 (t,  $J_{\text{C-P}} = 6.1$  Hz), 131.5 (t,  $J_{\text{C-P}} = 6.1$  Hz), 130.6, 130.2, 130.1, 128.9 (t,  $J_{\text{C-P}} = 4.9$  Hz), 128.7 (t,  $J_{\text{C-P}} = 4.9$  Hz), 127.7, 127.6, 125.8, 124.0, 122.5, 120.9, 120.6, 116.6, 108.7, 101.6, 86.0, 82.0, 71.2, 70.7, 70.3, 68.2, 66.9, 65.2, 64.64, 64.55, 63.8, 57.8, 35.2, 31.5, 19.0, 11.9 (5 signals coincident or not observed).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{P}}$  38.3. **ESI HRMS  $m/z$ :** calcd for  $\text{C}_{133}\text{H}_{133}\text{Co}_2\text{N}_2\text{O}_7\text{P}_2\text{Si}$  ( $[\text{M} + \text{H}]^+$ ) 2078.8048, found 2078.8008.



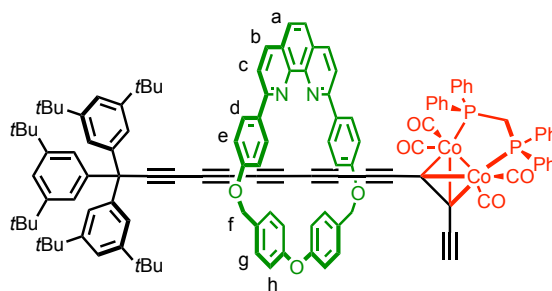
**Compound  $7\cdot\text{M}_b$ :** To compound  $\text{S3}\cdot\text{M}_b$  (45 mg, 0.022 mmol) in THF/ $\text{H}_2\text{O}$  (10/0.1 mL) was added TBAF (0.22 mL, 0.22 mmol, 1.0 M in THF). The solution was stirred at 20 °C, and the reaction was monitored by TLC analysis until deemed complete; ca. 1.5 h.  $\text{H}_2\text{O}$  (10 mL) and  $\text{CH}_2\text{Cl}_2$  (20 mL) were then added, the layers were separated, and the aqueous phase

was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10$  mL). The organic phases were combined, washed with brine (20 mL), dried ( $\text{MgSO}_4$ ), and filtered. Solvent removal and purification by column chromatography (silica gel, ethyl acetate/petroleum ether 1:2) afforded compound  $7\cdot\text{M}_b$  (31 mg, 16  $\mu\text{mol}$ , 75%) as a black solid.

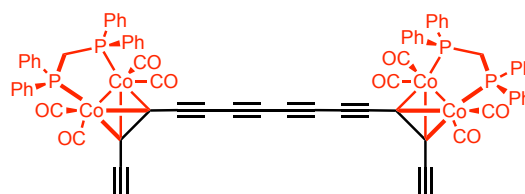
**$^1\text{H}$  NMR** (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  8.22 (d,  $J = 8.3$  Hz, 2H;  $\text{H}_b$ ), 7.99 (d,  $J = 8.8$  Hz, 4H;  $\text{H}_d$ ), 7.91 (d,  $J = 8.3$  Hz, 2H;  $\text{H}_c$ ), 7.74 (s, 2H;  $\text{H}_a$ ), 7.38–7.34 (m, 8H;  $\text{H}_g$  and  $\text{PPh}_2\text{-H}$ ), 7.31–7.26 (m, 13H;  $\text{H}_h$ , *para*-Tr\* and  $\text{PPh}_2\text{-H}$ ), 7.21–7.18 (m, 4H;  $\text{PPh}_2\text{-H}$ ), 7.10–7.07 (m, 6H;  $\text{PPh}_2\text{-H}$ ), 6.98 (d,  $J = 8.8$  Hz, 4H;  $\text{H}_e$ ), 6.95 (d,  $J = 1.8$  Hz, 6H; *ortho*-Tr\*), 5.31 (s, 4H;  $\text{H}_f$ ), 3.88 (t,  $J = 1.0$  Hz, 1H;  $\text{C}\equiv\text{CH}$ ), 3.51–3.28 (m, 2H;  $\text{PCH}_2$ ), 1.19 (s, 54H; *t*Bu).

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (100 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{C}}$  159.8, 158.5, 158.1, 150.7, 147.0, 144.0, 136.4, 134.5, 134.3, 132.4 (t,  $J_{\text{C-P}} = 6.1$  Hz), 131.7 (t,  $J_{\text{C-P}} = 6.1$  Hz), 130.6, 130.4, 130.1, 128.84 (t,  $J_{\text{C-P}} = 4.9$  Hz), 128.79 (t,  $J_{\text{C-P}} = 4.9$  Hz), 127.7, 127.6, 125.9, 123.9, 122.5, 120.9, 120.6, 116.6, 86.1, 86.0, 85.7, 82.2, 81.7, 71.1, 70.7, 70.3, 66.9, 65.1, 64.5, 63.9, 57.8, 35.2, 31.5 (8 signals coincident or not observed).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{P}}$  39.1.

**ESI HRMS  $m/z$ :** calcd for  $\text{C}_{124}\text{H}_{113}\text{Co}_2\text{N}_2\text{O}_7\text{P}_2$  ( $[\text{M} + \text{H}]^+$ ) 1922.6715, found 1922.6645.



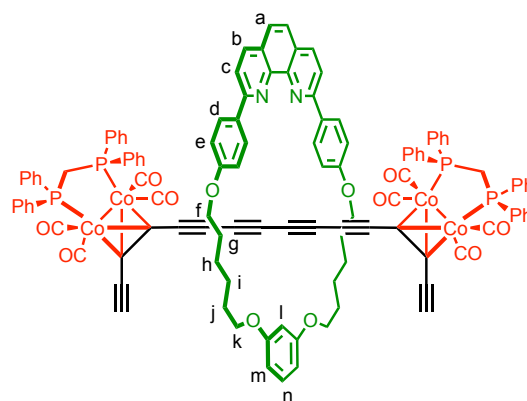
**Compound 4:** Tetracobalt tetrayne thread **3** (0.18 g, 1.0 eq., 0.10 mmol) was dissolved in dry THF (30 mL) containing water (0.30 mL). TBAF (1.0 M in THF, 1.0 mL, 10 eq., 1.0 mmol) was added dropwise and the mixture stirred at 20 °C for 30 min.



The reaction was quenched with addition of aqueous NH<sub>4</sub>Cl solution (20 mL), then Et<sub>2</sub>O (20 mL) was added, and the organic layer extracted. The aqueous layer was washed with Et<sub>2</sub>O (2 × 10 mL) and the combined extracts washed with brine (20 mL), then dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the crude material purified by silica chromatography (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, gradient elution from 0 to 100%) to yield deprotected tetracobalt tetrayne thread **4** (0.14 g, 0.98 mmol, 94%) as a red-brown solid.

<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 7.42 – 7.37 (m, 8H, Ar-H), 7.37 – 7.30 (m, 16H, Ar-H), 7.30 – 7.22 (m, 16H, Ar-H), 3.89 (t, *J* = 1.8 Hz, 2H, C≡CH), 3.47 (t, *J* = 10.5 Hz, 4H, P-CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>C</sub> 202.79 (C≡O), 135.68 (t, *J*<sub>C-P</sub> = 21.1 Hz, Ar-C), 134.50 (t, *J*<sub>C-P</sub> = 20.4 Hz, Ar-C), 132.29 (t, *J*<sub>C-P</sub> = 6.4 Hz, Ar-C), 131.95 (t, *J*<sub>C-P</sub> = 6.1 Hz, Ar-C), 130.66 (Ar-C), 130.49 (Ar-C), 128.88 (t, *J*<sub>C-P</sub> = 6.4 Hz, Ar-C), 85.81 (C≡CH), 85.69, 83.41, 82.28, 72.07 (Co-C), 70.66, 66.92, 65.24 (Co-C), 37.43 (t, *J*<sub>C-P</sub> = 21.3 Hz, P-CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>P</sub> 39.24. ESI HRMS *m/z* = 1420.9410 [M+H]<sup>+</sup> (C<sub>74</sub>H<sub>46</sub>Co<sub>4</sub>O<sub>8</sub>P<sub>4</sub><sup>+</sup> requires 1420.9398).

**Compound 4·M<sub>a</sub>:** Tetracobalt [2]rotaxane **3·M<sub>a</sub>** (35 mg, 1.0 eq., 15 μmol) was dissolved in THF (15 mL) containing water (0.15 mL). TBAF solution (1.0 M in THF, 0.15 mL, 10 eq., 0.15 mmol) was added dropwise and the mixture stirred at 20 °C for 30 min. The reaction was quenched with addition of aqueous NH<sub>4</sub>Cl solution (15 mL), then Et<sub>2</sub>O (10 mL) was added, and the organic layer extracted. The aqueous layer was washed with Et<sub>2</sub>O (2 × 5 mL) and the combined extracts washed with brine (10 mL), then dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the crude material purified by silica chromatography (petroleum ether/EtOAc, gradient elution from 0–40%) to yield deprotected tetracobalt [2]rotaxane **4·M<sub>a</sub>** (27 mg, 13 μmol, 88%) as a dark brown solid.



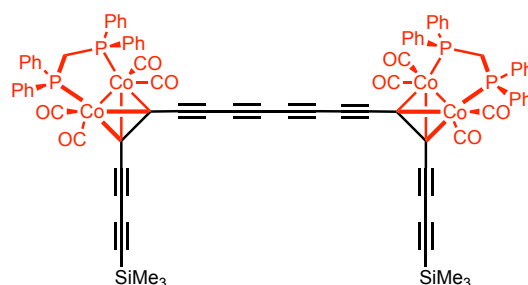
<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 8.52 (d, *J* = 8.9 Hz, 4H, H<sub>d</sub>), 8.26 (d, *J* = 8.4 Hz, 2H, H<sub>b</sub>), 8.10 (d, *J* = 8.5 Hz, 2H, H<sub>c</sub>), 7.74 (s, 2H, H<sub>a</sub>), 7.35 – 7.29 (m, 8H, Co Ar-H), 7.28 – 7.23 (m, 8H, H<sub>e</sub> & Co Ar-H), 7.23 – 7.18 (m, 16H, Co Ar-H), 7.17 – 7.13 (m, 4H, Co Ar-H), 7.11 – 7.05 (m, 9H, H<sub>n</sub> & Co Ar-H), 6.74 (t, *J* = 2.4 Hz, 1H, H<sub>i</sub>), 6.48 (dd, *J* = 8.2, 2.4 Hz, 2H, H<sub>m</sub>), 4.26 (t, *J* = 7.4 Hz, 4H, H<sub>l/k</sub>), 4.14 (t, *J* = 6.8 Hz, 4H, H<sub>k/f</sub>), 3.84 (s, 2H, C≡CH), 3.37 (dt, *J* = 22.4, 11.8 Hz, 4H, P-CH<sub>2</sub>), 1.98 (t, *J* = 7.2 Hz, 4H, H<sub>g/j</sub>), 1.91 (t, *J* = 6.8 Hz, 4H, H<sub>j/g</sub>), 1.74 – 1.66 (m, 8H, H<sub>h,i</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>C</sub> 161.18 (O-C-C<sub>e</sub>), 161.14, 156.40 (N-C-C-N), 146.51 (C<sub>a</sub>-C-C<sub>b</sub>), 136.82 (C<sub>b</sub>), 135.91 (t, *J*<sub>C-P</sub> = 25.5 Hz, Ar-C), 134.12 (t, *J*<sub>C-P</sub> = 20.3 Hz, Ar-C), 132.25 (t, *J*<sub>C-P</sub> = 6.5 Hz, Ar-C), 131.99, 131.79 (t, *J*<sub>C-P</sub> = 5.9 Hz, Ar-C), 130.63 (Ar-C), 130.32 (Ar-C), 129.82 (C<sub>n</sub>), 129.32 (C<sub>d</sub>), 128.77 (t, *J*<sub>C-P</sub> = 5.2 Hz, Ar-C), 127.75, 125.76 (C<sub>a</sub>), 119.17 (C<sub>c</sub>), 115.36 (C<sub>e</sub>), 108.13 (C<sub>m</sub>), 99.90 (C<sub>i</sub>), 86.28 (C≡CH), 85.61 (C≡C), 83.81 (C≡C), 82.21 (C≡C), 70.93 (C≡C), 68.68 (C<sub>k/f</sub>), 68.30 (C<sub>l/k</sub>), 67.38 (C≡C),

37.14 (t,  $J_{C-P} = 21.1$  Hz, P- $\underline{C}H_2$ ), 30.10 ( $C_{j/g}$ ), 29.67 ( $C_{g/i}$ ), 26.29 ( $C_{h/i}$ ), 26.19 ( $C_{i/h}$ ) (3 carbons not distinguished).  $^{31}P\{^1H\}$  NMR (202 MHz,  $CD_2Cl_2$ )  $\delta_P$  39.20. ESI HRMS  $m/z = 2061.2693$  [ $M+H$ ] $^+$  ( $C_{116}H_{89}Co_4N_2O_{12}P_4^+$  requires 2061.2688).

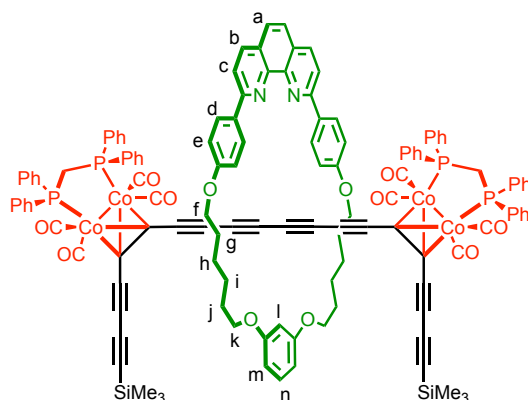
**Compound 5:** Deprotected tetracobalt thread **4** (240 mg, 1.0 eq., 0.17 mmol) was dissolved in dry  $CH_2Cl_2$  (250 mL). Trimethylsilyl acetylene (1.2 mL, 1.7 g, 50 eq., 8.5 mmol) and copper(I) chloride (0.75 g, 45 eq., 76 mmol) were added and  $O_2$  bubbled through the vigorously-stirred solution. TMEDA (1.0 mL, 40 eq., 6.8 mmol) was added to the reaction mixture.

Additional trimethylsilyl acetylene (1.2 mL, 50 eq., 8.5 mmol) was added over a period of 30 min via syringe pump. The reaction was monitored by TLC and, upon completion, was quenched by addition of water (100 mL). The organic layer was extracted and washed with water ( $2 \times 150$  mL), then brine (150 mL) before drying over  $Na_2SO_4$ . The solvent was removed under reduced pressure and the crude material initially purified by a  $SiO_2$  plug, flushing first with petroleum ether to remove the bis-TMS butadiyne, then 1:1 petroleum ether/ $CH_2Cl_2$ . The crude material was then subject to  $SiO_2$  chromatography (petroleum ether/EtOAc, gradient elution from 0 to 40%), to yield the TMS-protected extended thread **5** (0.18 g, 0.11 mmol, 66%) as a red solid.  $R_f$  (petroleum ether/EtOAc, 33%) = 0.60.

IR (ATR): 2958 (w, C-H), 2149 (m, C=C), 2037 (s, C=O), 2015 (s, C=O), 1992 (s, C=O)  $cm^{-1}$ .  $^1H$  NMR (600 MHz,  $CD_2Cl_2$ )  $\delta_H$  7.39 – 7.31 (m, 24H, Ar-H), 7.31 – 7.25 (m, 16H, Ar-H), 3.59 – 3.39 (m, 4H, P- $\underline{C}H_2$ ), 0.26 (s, 18H, SiMe<sub>3</sub>).  $^{13}C\{^1H\}$  NMR (151 MHz,  $CD_2Cl_2$ )  $\delta_C$  202.78 ( $\underline{C}\equiv O$ ), 202.12 ( $\underline{C}\equiv O$ ), 134.87 (q,  $J_{C-P} = 23.0$  Hz, Ar- $\underline{C}$ ), 132.13 (t,  $J_{C-P} = 6.2$  Hz, Ar- $\underline{C}$ ), 130.68 (d,  $J_{C-P} = 9.5$  Hz, Ar- $\underline{C}$ ), 129.01 (dt,  $J_{C-P} = 6.7, 3.2$  Hz, Ar- $\underline{C}$ ), 93.86, 89.85, 83.40, 83.09, 82.75, 80.30, 71.04, 69.84 (br, Co- $\underline{C}$ ), 67.07, 66.36 (br, Co- $\underline{C}$ ), 38.50 (t,  $J_{C-P} = 22.0$  Hz, P- $\underline{C}H_2$ ), -0.21 (SiMe<sub>3</sub>).  $^{31}P\{^1H\}$  NMR (243 MHz,  $CD_2Cl_2$ )  $\delta_P$  39.63. ESI HRMS  $m/z = 1615.0386$  [ $M+H$ ] $^+$  ( $C_{84}H_{63}Co_4O_8P_4Si_2^+$  requires 1615.0335).

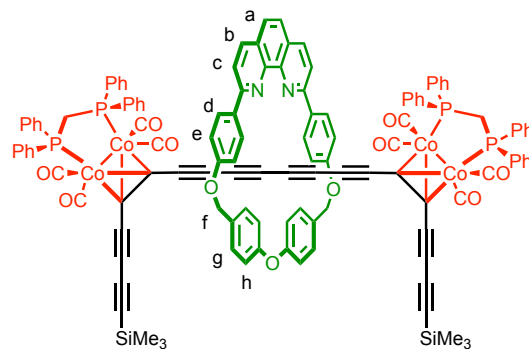


**Compound 5·M<sub>a</sub>:** Deprotected tetracobalt [2]rotaxane **4·M<sub>a</sub>** (30 mg, 1.0 eq., 15  $\mu$ mol) was dissolved in dry  $CH_2Cl_2$  (20 mL). TMS-acetylene (0.10 mL, 50 eq., 0.72 mmol) and copper(I) chloride (65 mg, 45 eq., 0.68 mmol) were added and the solution stirred vigorously in air for 2 min. TMEDA (68 mg, 87  $\mu$ L, 40 eq., 0.74 mmol) was added to the reaction mixture. The remaining TMS-acetylene (72 mg, 0.10 mL, 50 eq., 1.46 mmol) was added over a period of 30 min via syringe pump. Saturated aqueous EDTA/ $NH_3$  (5 mL) was added and stirred for 20 min. The organic layer was extracted and washed with water ( $2 \times 20$  mL), then brine (20 mL) before drying over  $Na_2SO_4$ . The solvent was removed under reduced pressure and the crude material purified by  $SiO_2$  chromatography (petroleum ether/EtOAc, gradient elution from 0 to 33%), to yield the extended tetracobalt [2]rotaxane **5·M<sub>a</sub>** (23 mg, 10  $\mu$ mol, 69%) as a red-brown solid.  $R_f$  (petroleum ether/EtOAc, 50%) = 0.68.



**IR** (ATR): 2981 (s, C–H), 2972 (s, C–H), 2889 (m, C–H), 2149 (m, C≡C), 2036 (s, C=O), 2017 (s, C=O), 1993 (s, C=O)  $\text{cm}^{-1}$ .  **$^1\text{H NMR}$**  (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  8.52 (d,  $J = 8.8$  Hz, 4H,  $\text{H}_{\text{d}}$ ), 8.25 (d,  $J = 8.5$  Hz, 2H,  $\text{H}_{\text{b}}$ ), 8.09 (d,  $J = 8.5$  Hz, 2H,  $\text{H}_{\text{c}}$ ), 7.73 (s, 2H,  $\text{H}_{\text{a}}$ ), 7.30 – 7.24 (m, 16H,  $\text{H}_{\text{e}}$  & Ar- $\underline{\text{H}}$ ), 7.24 – 7.18 (m, 16H, Ar- $\underline{\text{H}}$ ), 7.18 – 7.14 (m, 4H, Ar- $\underline{\text{H}}$ ), 7.13 – 7.08 (m, 9H,  $\text{H}_{\text{n}}$  & Ar- $\underline{\text{H}}$ ), 6.71 (t,  $J = 2.4$  Hz, 1H,  $\text{H}_{\text{i}}$ ), 6.49 (dd,  $J = 8.1$ , 2.3 Hz, 2H,  $\text{H}_{\text{m}}$ ), 4.28 (t,  $J = 7.3$  Hz, 4H,  $\text{H}_{\text{f/k}}$ ), 4.13 (t,  $J = 6.6$  Hz, 4H,  $\text{H}_{\text{k/f}}$ ), 3.38 (s, 4H, P- $\underline{\text{CH}_2}$ ), 2.01 (dd,  $J = 10.6$ , 3.8 Hz, 4H,  $\text{H}_{\text{g/j}}$ ), 1.93 (dd,  $J = 8.2$ , 4.7 Hz, 4H,  $\text{H}_{\text{j/g}}$ ), 1.73 (t,  $J = 3.5$  Hz, 8H,  $\text{H}_{\text{h,i}}$ ), 0.25 (s, 18H,  $\text{SiMe}_3$ ).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{C}}$  202.31 ( $\underline{\text{C}}=\text{O}$ , br), 161.24 (O- $\underline{\text{C}}-\text{C}_{\text{e}}$ ), 161.12, 156.36 (N- $\underline{\text{C}}-\underline{\text{C}}-\text{N}$ ), 146.50 ( $\text{C}_{\text{a}}-\underline{\text{C}}-\text{C}_{\text{b}}$ ), 136.80 ( $\text{C}_{\text{b}}$ ), 135.04 (t,  $J_{\text{C-P}} = 22.3$  Hz, Ar- $\underline{\text{C}}$ ), 134.41 (t,  $J_{\text{C-P}} = 21.4$  Hz, Ar- $\underline{\text{C}}$ ), 131.99 (t,  $J_{\text{C-P}} = 6.1$  Hz, Ar- $\underline{\text{C}}$ ), 130.68 (Ar- $\underline{\text{C}}$ ), 130.49 ( $\text{C}_{\text{n}}$ ), 129.85 (Ar- $\underline{\text{C}}$ ), 129.26 ( $\text{C}_{\text{d}}$ ), 128.89 (t,  $J_{\text{C-P}} = 5.0$  Hz, Ar- $\underline{\text{C}}$ ), 127.75, 125.76 ( $\text{C}_{\text{a}}$ ), 119.17 ( $\text{C}_{\text{c}}$ ), 115.39 ( $\text{C}_{\text{e}}$ ), 107.93 ( $\text{C}_{\text{m}}$ ), 100.16 ( $\text{C}_{\text{l}}$ ), 93.62, 89.95, 83.62, 83.10, 80.29, 71.29, 68.76 ( $\text{C}_{\text{k/f}}$ ), 68.26 ( $\text{C}_{\text{f/k}}$ ), 67.48, 60.63, 38.36 (t,  $J_{\text{C-P}} = 22.0$  Hz, P- $\underline{\text{CH}_2}$ ), 30.11 ( $\text{C}_{\text{j/g}}$ ), 29.70 ( $\text{C}_{\text{g/j}}$ ), 26.35 ( $\text{C}_{\text{h/i}}$ ), 26.29 ( $\text{C}_{\text{i/h}}$ ), 14.41, -0.20 ( $\text{SiMe}_3$ ) (2 carbons not distinguished).  **$^{31}\text{P}\{^1\text{H}\}$  NMR** (202 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{P}}$  39.61. **ESI HRMS**  $m/z = 2253.3412$  [ $\text{M}+\text{H}]^+$  ( $\text{C}_{126}\text{H}_{105}\text{Co}_4\text{N}_2\text{O}_{12}\text{P}_4\text{Si}_2^+$  requires 2253.3479).

**Compound 5·M<sub>b</sub>**: To compound 3·M<sub>b</sub> (100 mg, 0.0436 mmol) in THF/H<sub>2</sub>O (20/0.2 mL) was added TBAF (0.436 mL, 0.436 mmol, 1.0 M in THF). The solution was stirred at 20 °C, and the reaction was monitored by TLC analysis until deemed complete; ca. 2.5 h. H<sub>2</sub>O (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) were then added, the layers were separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The organic phases

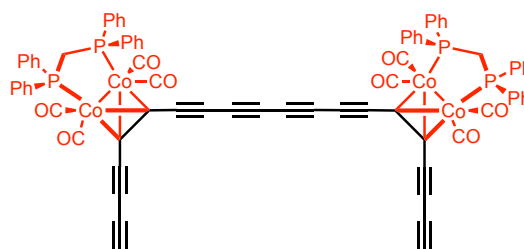


were combined, washed with brine (20 mL), dried ( $\text{MgSO}_4$ ), and filtered. Solvent removal and a silica column plug (ethyl acetate/petroleum ether 1:2) afforded deprotected intermediate 4·M<sub>b</sub> as a black solid, without further purification 4·M<sub>b</sub> was carried out through the next step. The Glaser-Hay catalyst was prepared by adding  $\text{CuCl}$  (170 mg, 1.74 mmol) to a solution of TMEDA (252 mg, 2.17 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL), and the solution was stirred for 5 min at 20 °C. To a solution of 4·M<sub>b</sub> (0.043 mmol, assuming 100% yield) and trimethylsilyl acetylene (426 mg, 4.34 mmol) in  $\text{CH}_2\text{Cl}_2$  (60 mL) was added the prepared Glaser-Hay catalyst, and the reaction mixture was stirred at 20 °C, during which a solution of trimethylsilyl acetylene (426 mg, 4.34 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was added to the above resulting solution at 20 °C over 3 h via a syringe pump. Saturated aqueous EDTA/ $\text{NH}_3$  (5 mL) was added and stirred for 30 min. H<sub>2</sub>O (20 mL) was added, the layers were separated, and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (2 × 20 mL). The organic phases were combined, washed with brine (20 mL), dried ( $\text{MgSO}_4$ ), and filtered. Solvent removal and purification by column chromatography (silica gel, ethyl acetate/petroleum ether 1:5 to 1:1) afforded compound 5·M<sub>b</sub> (53 mg, 24  $\mu\text{mol}$ , 56%) as a black solid.

**IR** (ATR): 2958 (w, C–H), 2153 (m, C≡C), 2036 (s, C=O), 2015 (s, C=O), 1991 (s, C=O)  $\text{cm}^{-1}$ .  **$^1\text{H NMR}$**  (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  8.22 (d,  $J = 8.4$  Hz, 2H;  $\text{H}_{\text{b}}$ ), 8.10 (d,  $J = 8.8$  Hz, 4H;  $\text{H}_{\text{d}}$ ), 7.93 (d,  $J = 8.4$  Hz, 2H;  $\text{H}_{\text{c}}$ ), 7.73 (s, 2H;  $\text{H}_{\text{a}}$ ), 7.40 (d,  $J = 8.7$  Hz, 4H;  $\text{H}_{\text{g}}$ ), 7.36 (d,  $J = 8.7$  Hz, 4H;  $\text{H}_{\text{h}}$ ), 7.32–7.28 (m, 13H), 7.25–7.19 (m, 17H), 7.11–7.10 (m, 10H), 7.05 (d,  $J = 8.8$  Hz, 4H;  $\text{H}_{\text{e}}$ ), 5.36 (s, 4H;  $\text{H}_{\text{f}}$ ), 3.44–3.35 (m, 4H; P- $\underline{\text{CH}_2}$ ), 0.26 (s, 18H;  $\text{SiCH}_3$ ).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{C}}$  160.0, 158.5, 158.0, 147.0, 136.3, 135.4, 135.2, 135.1, 134.6, 134.4, 134.2, 132.1 (t,  $J_{\text{C-P}} = 6.3$  Hz), 131.9 (t,  $J_{\text{C-P}} = 6.2$  Hz), 130.6, 130.4, 128.9–128.8 (m), 127.54, 127.48,

125.8, 122.7, 121.1, 120.4, 117.3, 116.8, 93.6, 90.0, 84.2, 82.9, 82.3, 80.5, 72.6, 71.0, 67.8, 38.8 (br), -0.2 (2 signals coincident or not observed).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{P}}$  39.3. **ESI HRMS  $m/z$** : calcd for  $\text{C}_{122}\text{H}_{89}\text{Co}_4\text{N}_2\text{O}_{11}\text{P}_4\text{Si}_2$  ( $[\text{M} + \text{H}]^+$ ) 2173.2278, found 2173.2286.

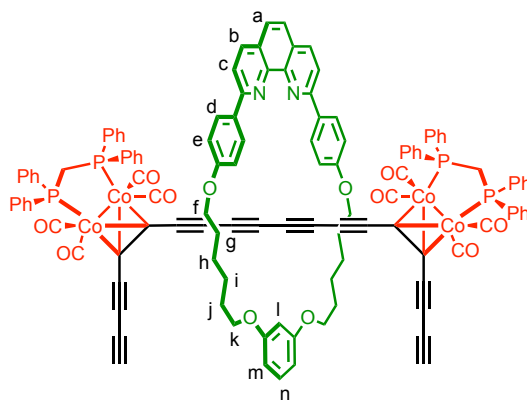
**Compound 6: Method 1.** Extended tetracobalt thread **5** (30 mg, 1.0 eq., 19  $\mu\text{mol}$ ) and  $\text{K}_2\text{CO}_3$  (39 mg, 15 eq., 0.28 mmol) were dissolved in a 1:1 solution of THF (5 mL) and MeOH (5 mL). Water (0.1 mL) was added and the solution stirred at 20 °C for 20 min before addition of water (15 mL) and  $\text{Et}_2\text{O}$  (15 mL). The organic layer was separated, washed with water (10 mL) then brine (10 mL). The organic extract was dried over  $\text{Na}_2\text{SO}_4$  and the solvent removed under reduced pressure to yield deprotected extended tetracobalt thread **6** (8.3 mg, 5.6  $\mu\text{mol}$ , 30%) as a red-brown solid.;  $R_{\text{f}}$  (petroleum ether/EtOAc, 33%) = 0.45.



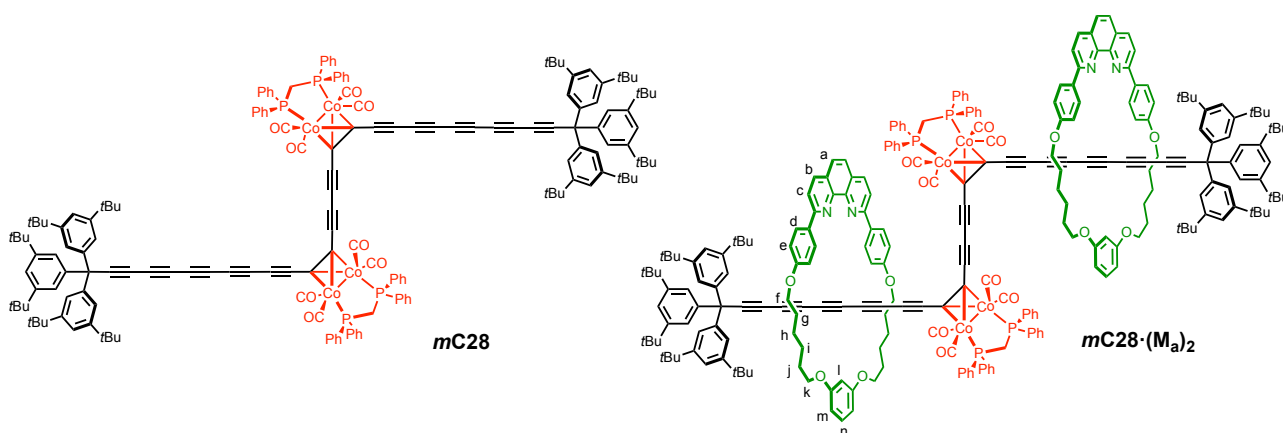
**Method 2.** Extended tetracobalt thread **5** (65 mg, 1.0 eq., 40  $\mu\text{mol}$ ) was dissolved in THF (25 mL) and water (0.25 mL, 1% v/v). TBAF solution (1.0 M in THF, 40  $\mu\text{L}$ , 1.0 eq., 40  $\mu\text{mol}$ ) solution was added and the mixture stirred at 20 °C for 5 min before addition of aqueous sat. aqueous  $\text{NH}_4\text{Cl}$  (25 mL).  $\text{Et}_2\text{O}$  (10 mL) was added and the organic layer extracted, washed with water (20 mL), then brine (20 mL). The combined organic extracts were dried over  $\text{Na}_2\text{SO}_4$  and the solvent reduced to minimal volume (~1–2 mL) under reduced pressure.  $\text{CHCl}_3$  (25 mL) was added, then the solvent reduced to minimal volume under reduced pressure (this process was repeated twice more). The solution of deprotected extended tetracobalt tetrayne thread **6** (55 mg, 38  $\mu\text{mol}$ , 94%) in  $\text{CHCl}_3$  was used directly in the next step. (*Note: This compound is unstable as a dry solid, but stable both in solution and on silica. This compound should be handled in solution. Method 2 allows a solution of thread 6 in  $\text{CHCl}_3$  to be obtained prior to the coupling step.*)

$^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  7.40 – 7.32 (m, 24H, Ar-H), 7.31 – 7.25 (m, 16H, Ar-H), 3.55 – 3.42 (m, 4H, P-CH<sub>2</sub>), 2.93 (s, 2H, C≡CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{C}}$  202.86 (C=O), 134.77 (br, Ar-C), 132.12 (t,  $J_{\text{C-P}}$  = 6.2 Hz, Ar-C), 130.71 (d,  $J_{\text{C-P}}$  = 7.7 Hz, Ar-C), 129.01 (q,  $J_{\text{C-P}}$  = 3.8 Hz, Ar-C), 83.32, 81.71, 78.88, 74.14 (C≡CH), 71.06, 70.09, 67.05, 38.55 (br, P-CH<sub>2</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{P}}$  39.68. **ESI HRMS  $m/z$**  = 1468.9429  $[\text{M} - \text{H}]^-$  ( $\text{C}_{78}\text{H}_{45}\text{Co}_4\text{O}_8\text{P}_4^-$  requires 1468.9425).

**Compound 6·M<sub>a</sub>:** Extended tetracobalt [2]rotaxane **5·M<sub>a</sub>** (22 mg, 1.0 eq., 9.8  $\mu\text{mol}$ ) and potassium carbonate (20 mg, 15 eq., 0.15 mmol) were dissolved in a 1:1 solution of THF (5 mL) and MeOH (5 mL). Water (0.05 mL) was added and the solution stirred at 20 °C for 20 min. The solvent was evaporated under reduced pressure and the crude material purified by  $\text{SiO}_2$  chromatography (petroleum ether/EtOAc, gradient elution from 0 to 50%) to yield deprotected extended tetracobalt [2]rotaxane **6·M<sub>a</sub>** (20 mg, 9.5  $\mu\text{mol}$ , 97%) as a red-brown solid.  $R_{\text{f}}$  (petroleum ether/EtOAc, 50%) = 0.49.

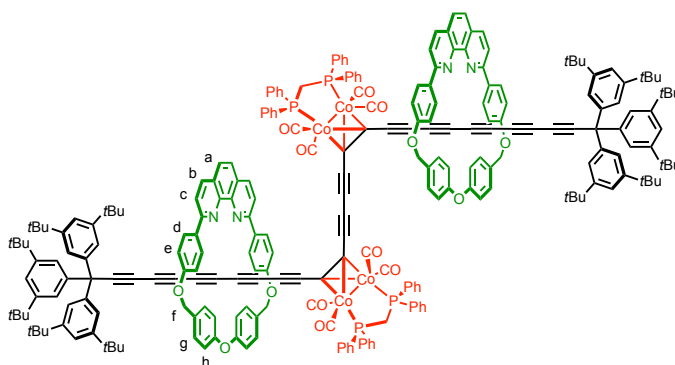


$^1\text{H NMR}$  (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  8.52 (d,  $J = 8.8$  Hz, 4H,  $\text{H}_d$ ), 8.25 (d,  $J = 8.4$  Hz, 2H,  $\text{H}_b$ ), 8.09 (d,  $J = 8.4$  Hz, 2H,  $\text{H}_c$ ), 7.73 (s, 2H,  $\text{H}_a$ ), 7.30 – 7.26 (m, 14H,  $\text{H}_e$  & Ar-H), 7.25 – 7.20 (m, 17H, Ar-H), 7.19 – 7.16 (m, 4H, Ar-H), 7.14 – 7.10 (m, 10H,  $\text{H}_n$  & Ar-H), 6.72 (t,  $J = 2.3$  Hz, 1H,  $\text{H}_l$ ), 6.49 (dd,  $J = 8.1, 2.3$  Hz, 2H,  $\text{H}_m$ ), 4.27 (t,  $J = 7.3$  Hz, 4H,  $\text{H}_{\text{f/k}}$ ), 4.13 (t,  $J = 6.7$  Hz, 4H,  $\text{H}_{\text{k/f}}$ ), 3.38 (s, 4H, P-CH<sub>2</sub>), 2.87 (s, 2H, C $\equiv$ CH), 2.00 (t,  $J = 9.1$  Hz, 4H,  $\text{H}_{\text{g/j}}$ ), 1.93 (t,  $J = 6.6$  Hz, 4H,  $\text{H}_{\text{j/g}}$ ), 1.73 (p,  $J = 3.5$  Hz, 8H,  $\text{H}_{\text{h,i}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{C}}$  202.55 (C $\equiv$ O, br), 161.24 (O-C-C<sub>e</sub>), 161.15, 156.39 (N-C-C-N), 146.53 (C<sub>a</sub>-C-C<sub>b</sub>), 136.81 (C<sub>b</sub>), 135.01 (t,  $J_{\text{C-P}} = 21.9$  Hz, Ar-C), 134.40 (t,  $J_{\text{C-P}} = 21.3$  Hz, Ar-C), 132.00 (t,  $J_{\text{C-P}} = 6.0$  Hz, Ar-C), 130.72 (Ar-C), 130.54 (C<sub>n</sub>), 129.86 (Ar-C), 129.28 (C<sub>d</sub>), 128.91 (td,  $J_{\text{C-P}} = 5.0, 2.3$  Hz, Ar-C), 127.77, 125.77 (C<sub>a</sub>), 119.18 (C<sub>c</sub>), 115.40 (C<sub>e</sub>), 107.97 (C<sub>m</sub>), 100.18 (C<sub>i</sub>), 83.59, 83.14, 82.02, 78.85, 74.03 (C $\equiv$ CH), 71.35, 70.12, 68.77 (C<sub>k/f</sub>), 68.29 (C<sub>f/k</sub>), 67.51, 38.43 (t,  $J_{\text{C-P}} = 21.8$  Hz, P-CH<sub>2</sub>), 30.11 (C<sub>j/g</sub>), 29.71 (C<sub>g/j</sub>), 26.36 (C<sub>h/i</sub>), 26.30 (C<sub>h/i</sub>) (Two C-Co resonances not observed due to extremely long relaxation times).  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{P}}$  39.63. ESI HRMS  $m/z = 2109.2695$  [ $\text{M} + \text{H}$ ]<sup>+</sup> (C<sub>120</sub>H<sub>89</sub>Co<sub>4</sub>N<sub>2</sub>O<sub>12</sub>P<sub>4</sub><sup>+</sup> requires 2109.2688).



Compounds **mC28** and **mC28·(M<sub>a</sub>)<sub>2</sub>** were synthesized as previously reported.<sup>[6]</sup>

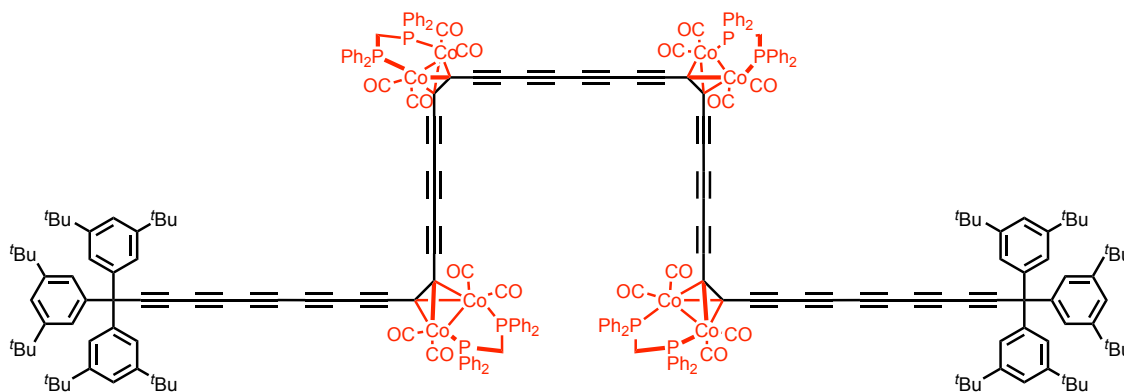
**Compound mC28·(M<sub>b</sub>)<sub>2</sub>**: To compound **7·M<sub>b</sub>** (50.0 mg, 0.026  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added a solution of  $\text{CuCl}$  (26 mg, 0.26 mmol) and TMEDA (39  $\mu\text{L}$ , 0.26 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL), and the solution was stirred at 20 °C for 40 min. Saturated aqueous EDTA/ $\text{NH}_3$  (5 mL) was added and stirred for 20 min.  $\text{H}_2\text{O}$  (20 mL) was then added, the layers were separated, and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10$  mL). The organic phases were combined, washed with brine (20 mL), dried ( $\text{MgSO}_4$ ), and filtered. Solvent removal and purification by column chromatography (silica gel, ethyl acetate/petroleum ether 1:5 to 1:1) afforded compound **mC28·(M<sub>b</sub>)<sub>2</sub>** (34 mg, 8.8  $\mu\text{mol}$ , 68%) as a black solid.



The organic phases were combined, washed with brine (20 mL), dried ( $\text{MgSO}_4$ ), and filtered. Solvent removal and purification by column chromatography (silica gel, ethyl acetate/petroleum ether 1:5 to 1:1) afforded compound **mC28·(M<sub>b</sub>)<sub>2</sub>** (34 mg, 8.8  $\mu\text{mol}$ , 68%) as a black solid.

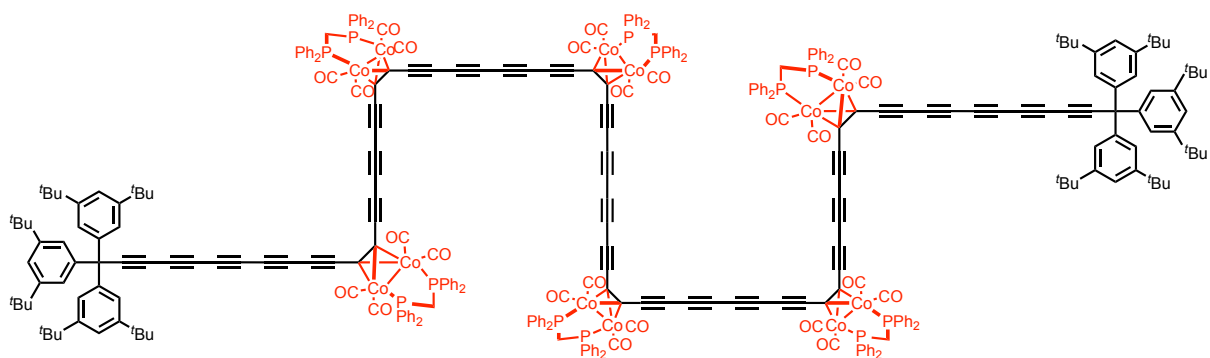
**IR** (ATR): 2962 (m, C-H), 2927 (m, C-H), 2871 (w, C-H), 2160 (w, C $\equiv$ C), 2033 (m, C=O), 2016 (s, C=O), 1991 (m, C=O)  $\text{cm}^{-1}$ . **UV-vis** ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ): 284 (193000), 318 (195000), 414 (104000), 582 (sh, 6510) nm.  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  8.15 (d,  $J = 8.3$  Hz, 4H;  $\text{H}_b$ ), 7.98 (d,  $J = 8.8$  Hz, 8H;  $\text{H}_d$ ), 7.85 (d,  $J = 8.3$  Hz, 4H;  $\text{H}_c$ ), 7.68 (s, 4H;  $\text{H}_a$ ), 7.31 (d,  $J = 8.6$  Hz, 8H;  $\text{H}_g$ ), 7.29 (t,  $J = 1.8$  Hz, 6H; *para*-Tr\*), 7.26 (d,  $J = 8.6$  Hz, 8H;  $\text{H}_h$ ), 7.25–7.21 (m, 18H; PPh<sub>2</sub>-H), 7.16–7.11 (m, 22H; PPh<sub>2</sub>-H), 6.97–6.94 (m, 20H;  $\text{H}_e$  and *ortho*-Tr\*),

5.26, 5.22 (ABq,  $J_{AB} = 15.6$  Hz, 8H; H<sub>i</sub>), 3.51–3.23 (m, 4H; PCH<sub>2</sub>), 1.18 (s, 54H; *t*Bu).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_{\text{C}}$  159.8, 158.5, 158.1, 150.7, 147.0, 144.0, 136.4, 135.3, 135.1, 134.9, 134.4, 134.3, 132.3 (t,  $J_{\text{C-P}} = 5.7$  Hz), 131.7 (t,  $J_{\text{C-P}} = 5.7$  Hz), 130.6, 130.5, 130.1, 129.00 (t,  $J_{\text{C-P}} = 4.9$  Hz), 128.85 (t,  $J_{\text{C-P}} = 4.9$  Hz), 127.6, 127.5, 125.8, 123.9, 122.5, 120.9, 120.6, 116.6, 88.2, 86.0, 85.9, 82.7, 82.0, 71.7, 70.6, 70.3, 67.2, 65.1, 64.6, 64.0, 60.6, 57.8, 35.2, 31.5 (2 signals coincident or not observed).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_{\text{P}}$  39.6. **ESI HRMS  $m/z$** : calcd for C<sub>248</sub>H<sub>223</sub>Co<sub>4</sub>N<sub>4</sub>O<sub>14</sub>P<sub>4</sub> ([M + H]<sup>+</sup>) 3842.3201, found 3842.3034. **GPC** (analytical, THF/pyridine 1% v/v) retention time: 36.18 min.



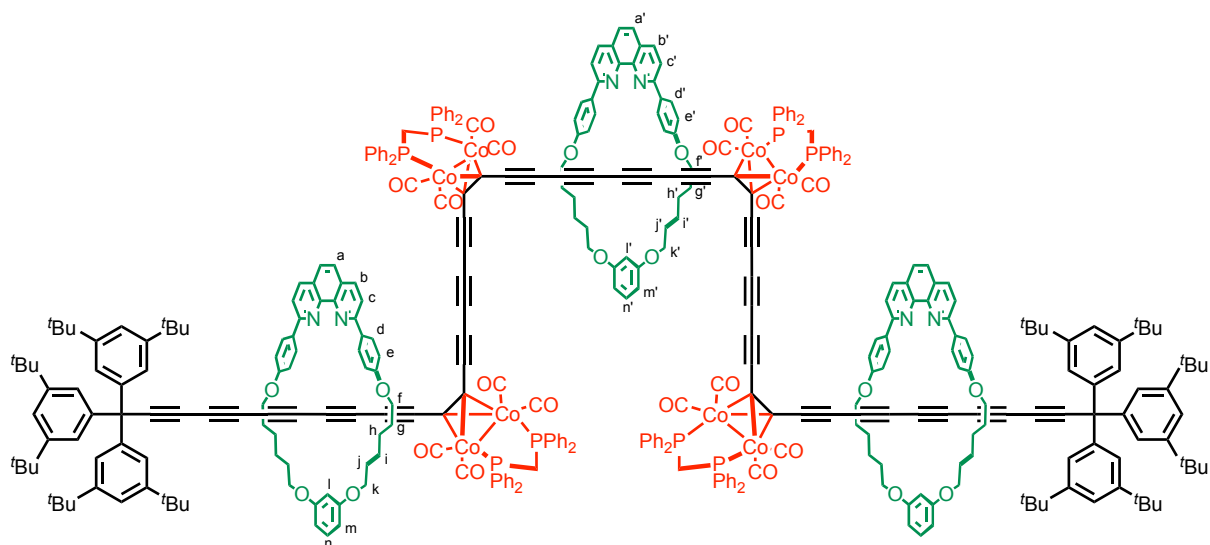
**Compound *m*C48**: Dry CHCl<sub>3</sub> (25 mL) and diisopropylamine (110 mg, 0.15 mL, 80 eq., 1.1 mmol) was added to bis(triphenylphosphine)palladium(II) dichloride (25 mg, 2.7 eq., 36  $\mu\text{mol}$ ), copper(I) iodide (34 mg, 13 eq., 0.18 mmol) and benzoquinone (44 mg, 30 eq., 0.41 mmol). The mixture was stirred in air before addition of a mixture of deprotected Tr\* cobalt thread **7** (56 mg, 3.0 eq., 41  $\mu\text{mol}$ ) and extended tetracobalt thread **6** (20 mg, 1.0 eq., 14  $\mu\text{mol}$ ) in dry CHCl<sub>3</sub> (5 mL). A drying tube was fitted and the reaction was stirred at 20 °C in air for 2 h. Water (30 mL) was added then the organic layer extracted and washed with water (30 mL) then brine (30 mL). The organic extract was dried over Na<sub>2</sub>SO<sub>4</sub>, then the solvent removed under reduced pressure. The crude material was purified by silica chromatography (petroleum ether/ CH<sub>2</sub>Cl<sub>2</sub>). The crude material was purified by recycling GPC (THF) to yield octacobalt ***m*C48** (29 mg, 6.9  $\mu\text{mol}$ , 51% with respect to compound **6**) and dodecacobalt ***m*C68** (7.0 mg, 1.2  $\mu\text{mol}$ , 18% with respect to compound **6**) as dark-brown solids.

**IR** (ATR): 2981 (s, C–H), 2971 (s, C–H), 2889 (m, C–H), 2152 (m, C=C), 2019 (s, C=O), 1996 (s, C=O) cm<sup>-1</sup>.  $^1\text{H}$  NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_{\text{H}}$  7.41 – 7.33 (m, 46H, Co Ar-H & Tr\* Ar-H), 7.33 – 7.28 (m, 30H, Co Ar-H), 7.28 – 7.24 (m, 10H, Co Ar-H), 6.97 (d,  $J = 1.8$  Hz, 12H, Tr\* Ar-H), 3.66 – 3.34 (m, 8H, P-CH<sub>2</sub>), 1.22 (s, 108H, *t*Bu).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_{\text{C}}$  202.34 (br, C=O), 150.80 (Tr\* Ar-C), 143.83 (Tr\* Ar-C), 135.13 – 134.22 (m, Co Ar-C), 132.29 – 131.91 (m, Co Ar-C), 130.94 – 130.65 (m, Co Ar-C), 129.14 – 128.90 (m, Co Ar-C), 123.99 (Tr\* Ar-C), 121.01 (Tr\* Ar-C), 87.03, 84.81, 84.73, 84.37, 84.30, 83.66, 83.36, 82.54, 82.17, 71.62, 71.42, 71.34, 70.16, 69.82, 67.29, 66.50, 64.54, 63.78, 63.69, 63.64, 57.84 (CAr<sub>3</sub>), 38.87 – 38.21 (m, P-CH<sub>2</sub>), 35.17 (C(CH<sub>3</sub>)<sub>3</sub>), 31.51 (C(CH<sub>3</sub>)<sub>3</sub>) (13 carbons not distinguished and  $^{31}\text{P}$ - $^{13}\text{C}$  couplings are not resolved due to overlapping signals).  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_{\text{P}}$  39.63.



**Compound *mC68*:** The titled compound *mC68* (7.0 mg, 1.2  $\mu\text{mol}$ , 18%) was obtained as a dark-brown solid as described in the above procedure.

**IR** (ATR): 2980 (m, C–H), 2970 (m, C–H), 2903 (w, C–H), 2149 (m, C $\equiv$ C), 2017 (s, C=O), 1995 (s, C=O)  $\text{cm}^{-1}$ .  **$^1\text{H}$  NMR** (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  7.40 – 7.33 (m, 69H, Co Ar–H & Tr\* Ar–H), 7.32 – 7.24 (m, 57H, Co Ar–H), 6.96 (d,  $J = 1.8$  Hz, 12H, Tr\* Ar–H), 3.62 – 3.35 (m, 12H, P–CH $_2$ ), 1.21 (s, 108H,  $^t\text{Bu}$ ).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (151 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{C}}$  201.12 (br, C $\equiv$ O), 150.80 (Tr\* Ar–C), 143.82 (Tr\* Ar–C), 135.13 – 134.22 (m, Co Ar–C), 132.35 – 131.86 (m, Co Ar–C), 130.97 – 130.62 (m, Co Ar–C), 129.25 – 128.78 (m, Co Ar–C), 123.99 (Tr\* Ar–C), 121.01 (Tr\* Ar–C), 87.02, 84.80, 84.74, 84.37, 84.30, 83.74, 83.63, 83.54, 83.45, 83.38, 83.35, 82.54, 71.61, 71.52, 71.48, 71.35, 70.16, 69.83, 67.35, 67.26, 67.18, 66.49, 64.53, 63.78, 63.68, 63.64, 57.84, 38.84 – 38.34 (m, P–CH $_2$ ), 35.17 (C(CH $_3$ ) $_3$ ), 31.51 (C(CH $_3$ ) $_3$ ) (24 carbons not distinguished and  $^{31}\text{P}$ – $^{13}\text{C}$  couplings are not resolved due to overlapping signals).  **$^{31}\text{P}\{^1\text{H}\}$  NMR** (243 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{P}}$  39.66.

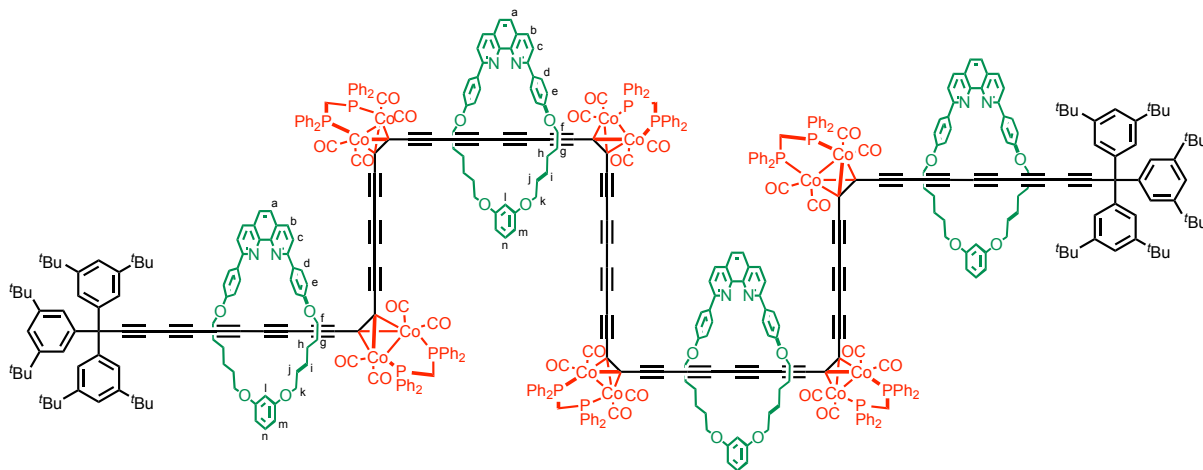


**Compound *mC48*·( $\text{M}_a$ ) $_3$ :** Dry  $\text{CHCl}_3$  (75 mL) and diisopropylamine (140 mg, 0.19 mL, 80 eq., 1.4 mmol) was added to bis(triphenylphosphine)palladium(II) dichloride (32 mg, 2.7 eq., 45  $\mu\text{mol}$ ), copper(I) iodide (43 mg, 13 eq., 0.22 mmol) and benzoquinone (55 mg, 30 eq., 0.51 mmol). The mixture was stirred in air before addition of a mixture of deprotected Tr\* [2]rotaxane  $7\cdot\text{M}_a$  (140 mg, 4.0 eq., 67  $\mu\text{mol}$ ) and deprotected extended tetracobalt [2]rotaxane  $6\cdot\text{M}_a$  (36 mg, 1.0 eq., 17  $\mu\text{mol}$ ) in dry  $\text{CHCl}_3$  (15 mL) over 1 hour via syringe pump. After complete addition, the reaction was stirred at 20  $^\circ\text{C}$  in air for a further 1 hour. EDTA/ $\text{NH}_3$  solution (75 mL) was then added, and the mixture stirred for 1 h. The organic layer was extracted, washed with water (50 mL) then brine (50 mL), before being dried over  $\text{Na}_2\text{SO}_4$  and the solvent removed under reduced pressure.

The crude material was purified by recycling GPC (THF) to yield octacobalt [4]rotaxane **mC48**·(**M<sub>a</sub>**)<sub>3</sub> (29.4 mg, 4.8 μmol, 28%), dodecacobalt [5]rotaxane **mC68**·(**M<sub>a</sub>**)<sub>4</sub> (11.1 mg, 1.34 μmol, 16%) and hexadecacobalt [6]rotaxane **mC88**·(**M<sub>a</sub>**)<sub>5</sub> (3.3 mg, 0.32 μmol, 6%) as dark-brown solids. (*Note: tetracobalt [3]rotaxane mC28·(**M<sub>a</sub>**)<sub>2</sub> is also formed, but not isolated.*)

**IR (ATR)** (only selected signals) 2961 (C–H), 2866 (C–H), 2149 (C≡C), 2019 (s, C=O), 1995 (s, C=O) cm<sup>-1</sup>.

**UV-vis** (CHCl<sub>3</sub>) λ<sub>max</sub> (ε) 589 (15200), 416 (153000), 319 (260000), 291 (292000) nm. **<sup>1</sup>H NMR** (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 8.49 (d, *J* = 8.3 Hz, 4H, H<sub>d'</sub>), 8.46 (d, *J* = 8.3 Hz, 8H, H<sub>d</sub>), 8.22 (d, *J* = 8.5 Hz, 4H, H<sub>b</sub>), 8.19 (d, *J* = 8.4 Hz, 2H, H<sub>b'</sub>), 8.09 – 7.99 (m, 6H, H<sub>c,c'</sub>), 7.71 (s, 4H, H<sub>a</sub>), 7.68 (s, 2H, H<sub>a'</sub>), 7.31 – 7.27 (m, 16H, Cr Ar-H), 7.26 – 7.17 (m, 65H, H<sub>c,e'</sub>, Co & Tr\* Ar-H), 7.15 – 7.10 (m, 17H, Co Ar-H), 7.09 – 7.05 (m, 3H, H<sub>n,n'</sub>), 6.91 (d, *J* = 1.8 Hz, 12H, Tr\* Ar-H), 6.73 (t, *J* = 2.4 Hz, 1H, H<sub>f</sub>), 6.64 (t, *J* = 2.4 Hz, 2H, H<sub>i</sub>), 6.48 (dd, *J* = 8.1, 2.2 Hz, 2H, H<sub>m'</sub>), 6.46 (dd, *J* = 8.1, 2.3 Hz, 4H, H<sub>m</sub>), 4.29 – 4.11 (m, 16H, H<sub>f,k</sub>), 4.07 (t, *J* = 6.6 Hz, 8H, H<sub>f,k'</sub>), 3.64 – 3.16 (m, 8H, P-CH<sub>2</sub>), 2.01 – 1.86 (m, 24H, H<sub>g,j</sub> & H<sub>g,j'</sub>), 1.75 – 1.70 (m, 8H, H<sub>f,i'</sub>), 1.66 (d, *J* = 5.5 Hz, 16H, H<sub>h,i</sub>), 1.14 (s, 108H, <sup>t</sup>Bu). **<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>C</sub> 201.65 (br, C≡O), 161.23, 161.16, 161.13, 161.07, 156.37, 150.70, 146.50, 143.81, 136.81, 134.97 (t, *J*<sub>C-P</sub> = 22.3 Hz), 134.61 – 134.02 (m), 132.25 – 131.67 (m), 130.75, 130.64, 130.60, 129.90, 129.09 – 128.84 (m), 127.76, 127.73, 125.77, 123.93, 120.94, 119.21, 115.41, 115.32, 107.98, 107.89, 100.33, 100.26, 86.88, 85.14, 84.72, 84.25, 83.89, 83.54, 82.84, 82.26, 77.96, 77.75, 77.54, 74.51, 74.25, 71.77, 71.68, 71.38, 70.45, 69.98, 68.77, 68.63, 68.31, 68.22, 67.78, 66.92, 64.82, 64.29, 64.08, 63.83, 57.84, 38.34 (br), 31.47, 30.15, 30.05, 29.74, 29.64, 26.40, 26.32, 26.28 (*4 carbonyl resonances not distinguished due to overlap and broadening; 12 Ar-C resonances not observed due to overlap*). **<sup>31</sup>P{<sup>1</sup>H} NMR** (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>P</sub> 39.54. **ESI HRMS** *m/z* = 3053.9266 [M+2H]<sup>2+</sup> (C<sub>376</sub>H<sub>342</sub>Co<sub>8</sub>N<sub>6</sub>O<sub>28</sub>P<sub>8</sub><sup>2+</sup> requires 3053.9034). **GPC** (analytical, THF/pyridine 1% v/v) retention time: 35.4 min.

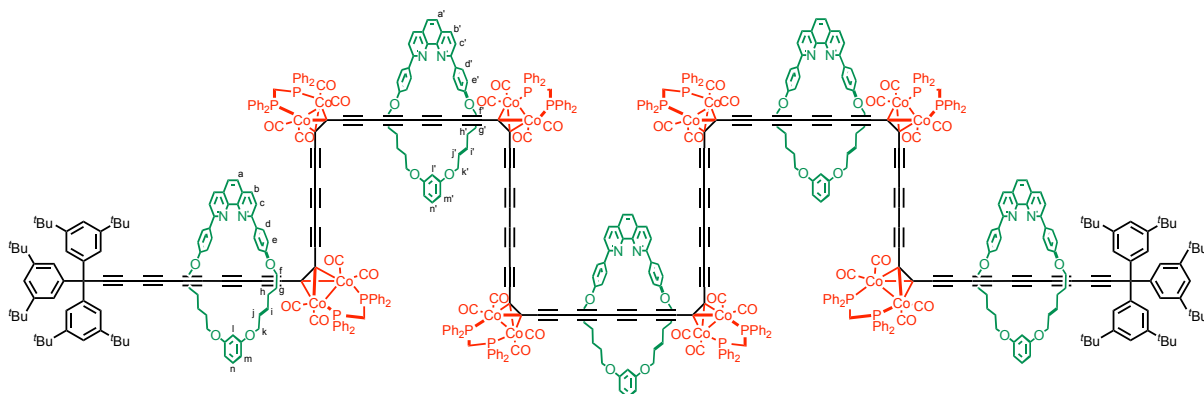


**Compound mC68**·(**M<sub>a</sub>**)<sub>4</sub>: The titled compound **mC68**·(**M<sub>a</sub>**)<sub>4</sub> (11.1 mg, 1.34 μmol, 16%) was obtained as a dark-brown solid as described in the above procedure.

**IR (ATR)** (only selected signals) 2951 (C–H), 2865 (C–H), 2148 (C≡C), 2019 (s, C=O), 1995 (s, C=O) cm<sup>-1</sup>.

**UV-vis** (CHCl<sub>3</sub>) λ<sub>max</sub> (ε) 592 (31500), 449 (286000), 422 (301000), 346 (417000), 322 (462000), 291 (520000) nm. **<sup>1</sup>H NMR** (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 8.50 (d, *J* = 8.8 Hz, 8H, H<sub>d</sub>), 8.45 (d, *J* = 8.9 Hz, 8H, H<sub>d</sub>), 8.21 (d, *J* = 8.4 Hz, 4H, H<sub>b</sub>), 8.18 (d, *J* = 8.4 Hz, 4H, H<sub>b</sub>), 8.04 (t, *J* = 8.0 Hz, 8H, H<sub>c</sub>), 7.70 (s, 4H, H<sub>a</sub>), 7.67 (s, 4H, H<sub>a</sub>), 7.31 – 7.16 (m, 118H, H<sub>c</sub>, Tr\* Ar-H & Co Ar-H), 7.16 – 7.05 (m, 28H, H<sub>n</sub> & Co Ar-H), 6.90 (d, *J* = 1.8 Hz, 12H, Tr\* Ar-H), 6.73 (t, *J* = 2.4 Hz, 2H, H<sub>i</sub>), 6.64 (t, *J* = 2.4 Hz, 2H, H<sub>i</sub>), 6.49 (dd, *J* = 8.1, 2.3 Hz, 4H, H<sub>m</sub>), 6.46 (dd, *J* = 8.1, 2.3 Hz, 4H, H<sub>m</sub>), 4.27 (t, *J* = 7.3 Hz, 8H, H<sub>f,k</sub>), 4.22 – 4.16 (m, 8H, H<sub>f,k</sub>), 4.13 (t, *J* = 6.6 Hz,

8H,  $H_{k(f)}$ , 4.06 (t,  $J = 6.6$  Hz, 8H,  $H_{k(f)}$ ), 3.58 – 3.26 (m, 12H, P-CH<sub>2</sub>), 2.03 – 1.84 (m, 32H,  $H_{g(j)}$ ), 1.78 – 1.61 (m, 32H,  $H_{h(i)}$ ), 1.13 (s, 108H, <sup>t</sup>Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_C$  161.22, 161.16, 161.13, 161.06, 156.36, 150.69, 146.50, 143.80, 136.81, 135.15 – 134.72 (m), 134.63 – 134.16 (m), 132.36 – 131.67 (m), 131.03 – 130.48 (m), 129.90, 129.29, 129.23, 129.14 – 128.77 (m), 127.75, 125.77, 123.92, 120.93, 119.21, 115.40, 115.31, 107.97, 107.88, 100.31, 100.26, 86.86, 85.12, 84.71, 84.61, 84.25, 83.98, 83.70, 83.47, 83.31, 77.96, 77.75, 77.54, 73.97, 71.99, 71.85, 71.69, 71.48, 71.37, 70.99, 70.42, 69.97, 68.76, 68.62, 68.31, 68.21, 67.85, 67.22, 67.15, 66.91, 64.81, 64.30, 64.07, 63.83, 57.83, 38.35, 37.25, 35.10, 31.46, 30.15, 30.05, 29.73, 29.64, 26.41, 26.35, 26.31, 26.27, 25.99 (9 Ar-C resonances not observed due to overlap; 6 Co-C resonances not observed due to their extremely long relaxation times and <sup>31</sup>P-<sup>13</sup>C couplings are not resolved due to overlapping signals). <sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_P$  39.60. ESI HRMS  $m/z = 2738.3530$  [M+3H]<sup>3+</sup> (C<sub>496</sub>H<sub>429</sub>Co<sub>12</sub>N<sub>8</sub>O<sub>40</sub>P<sub>12</sub><sup>3+</sup> requires 2738.3533). GPC (analytical, THF/pyridine 1% v/v) retention time: 34.6 min.

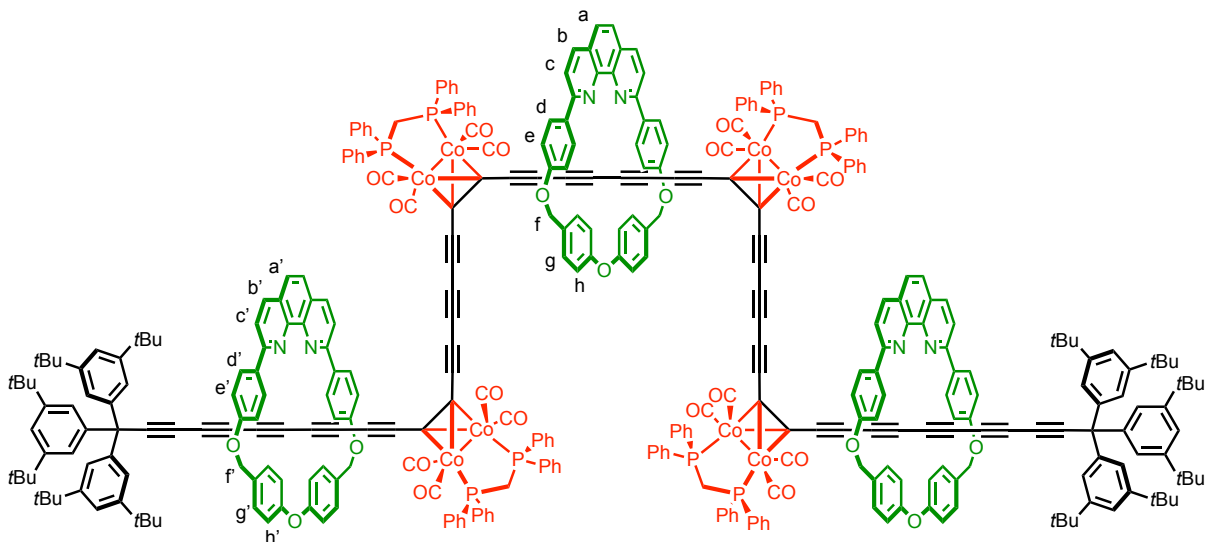


**Compound *mC88*·(*M<sub>a</sub>*)<sub>5</sub>:** The titled compound *mC88*·(*M<sub>a</sub>*)<sub>5</sub> (3.3 mg, 0.32  $\mu$ mol, 6%) was obtained as a dark-brown solid as described in the above procedure.

**IR (ATR)** (only selected signals) 2952 (C–H), 2866 (C–H), 2147 (C≡C), 2018 (s, C=O), 1995 (s, C=O) cm<sup>-1</sup>.

**UV-vis** (CHCl<sub>3</sub>)  $\lambda_{max}$  ( $\epsilon$ ) 592 (48200), 450 (454000), 424 (461000), 344 (620000), 323 (667000), 291 (741000) nm. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_H$  8.59 – 8.48 (m, 12H,  $H_d$ ), 8.45 (d,  $J = 8.6$  Hz, 8H,  $H_d$ ), 8.20 (dd,  $J = 18.8, 8.4$  Hz, 10H,  $H_{b,b'}$ ), 8.10 – 8.00 (m, 10H,  $H_{c,c'}$ ), 7.70 (d,  $J = 2.4$  Hz, 4H,  $H_a$ ), 7.66 (d,  $J = 3.3$  Hz, 6H,  $H_{a'}$ ), 7.31 – 7.16 (m, 153H,  $H_{c,e,e'}$ , Tr\* Ar-H & Co Ar-H), 7.10 (ddd,  $J = 31.4, 15.1, 7.8$  Hz, 38H,  $H_{n,n'}$  & Co Ar-H), 6.90 (d,  $J = 1.8$  Hz, 12H, Tr\* Ar-H), 6.77 – 6.71 (m, 3H,  $H_f$ ), 6.64 (t,  $J = 2.3$  Hz, 2H,  $H_i$ ), 6.49 (ddd,  $J = 8.3, 6.5, 2.3$  Hz, 6H,  $H_{m'}$ ), 6.46 (dd,  $J = 8.1, 2.3$  Hz, 4H,  $H_m$ ), 4.31 – 4.25 (m, 10H,  $H_{f,k(f),k'}$ ), 4.24 – 4.16 (m, 10H,  $H_{f,k(f),k'}$ ), 4.14 (td,  $J = 6.7, 3.7$  Hz, 10H,  $H_{k,f(k),f'}$ ), 4.06 (t,  $J = 6.6$  Hz, 10H,  $H_{k,f(k),f'}$ ), 3.69 – 3.16 (m, 16H, P-CH<sub>2</sub>), 2.03 – 1.85 (m, 40H,  $H_{g(j)}$  &  $H_{g(j)'}$ ), 1.77 – 1.63 (m, 40H,  $H_{h,i}$  &  $H_{h(i)'}$ ), 1.13 (s, 108H, <sup>t</sup>Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_C$  201.89 (br, C≡O), 161.21, 161.16, 161.12, 161.06, 156.34, 150.69, 146.50, 143.80, 136.80, 135.12 – 134.63 (m), 134.61 – 134.04 (m), 132.10 – 131.96 (m), 131.91, 131.86, 130.76, 130.74, 130.67, 130.61, 129.90, 129.28, 129.23, 129.02 – 128.92 (m), 127.75, 125.76, 123.92, 120.93, 119.20, 115.40, 115.31, 107.96, 107.88, 100.31, 100.26, 86.97, 86.86, 85.33, 85.13, 84.72, 84.24, 83.97, 83.77, 83.70, 83.51, 83.37, 82.84, 82.23, 77.96, 77.75, 77.53, 71.98, 71.88, 71.78, 71.69, 71.48, 71.38, 70.43, 69.97, 68.76, 68.61, 68.31, 68.20, 67.86, 67.82, 67.77, 67.71, 67.68, 67.53, 67.24, 66.91, 64.81, 64.29, 64.07, 63.83, 57.83, 38.95 – 38.13 (m), 35.10, 31.46, 30.15, 30.05, 29.74, 29.64, 26.41, 26.35, 26.31, 26.28 (carbonyl and 11 Ar-C resonances not distinguished due to overlap; 8 Co-C resonances not observed due to their extremely long

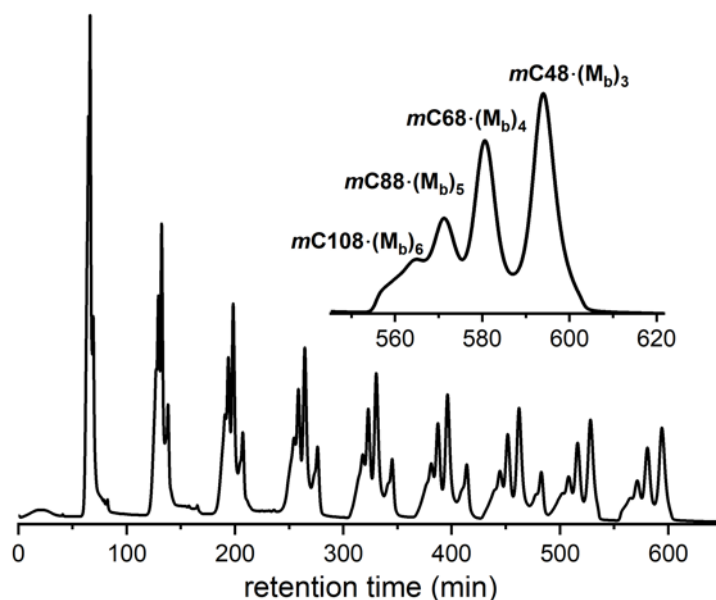
relaxation times;  $^{31}\text{P}$ - $^{13}\text{C}$  couplings are not resolved due to overlapping signals).  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{P}}$  39.63. **ESI HRMS**  $m/z = 2064.6663$  [ $\text{M}+5\text{H}$ ] $^{5+}$   $\text{C}_{616}\text{H}_{517}\text{Co}_{16}\text{N}_{10}\text{O}_{52}\text{P}_{16}$  $^{5+}$  requires 2064.6641). **GPC** (analytical, THF/pyridine 1% v/v) retention time: 34.0 min.



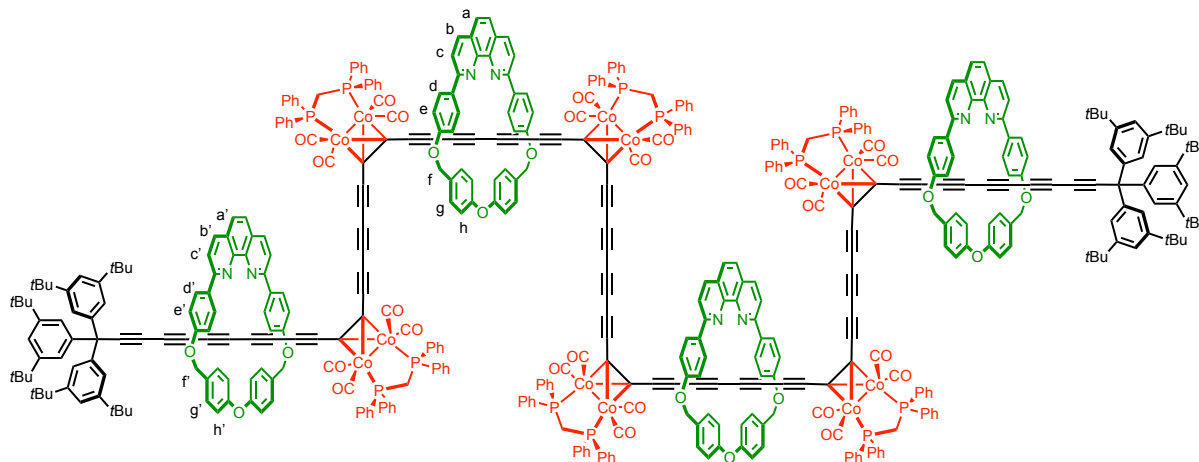
**Compound  $m\text{C48}\cdot(\text{M}_b)_3$ :** To compound  $5\cdot\text{M}_b$  (45 mg, 0.021 mmol) in THF/MeOH (10/10 mL) was added  $\text{K}_2\text{CO}_3$  (28.6 mg, 0.21 mmol), and the solution was stirred at rt for 1 h.  $\text{H}_2\text{O}$  (20 mL) and  $\text{CH}_2\text{Cl}_2$  (30 mL) were then added, the layers were separated, and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10$  mL). The organic phases were combined, washed with brine (20 mL), dried ( $\text{MgSO}_4$ ), and filtered. Solvent removal and purification by silica plug (ethyl acetate/petroleum ether 1:2) afforded a black solid  $6\cdot\text{M}_b$ , which was redissolved in  $\text{CHCl}_3$  (20 mL). To this resulting solution was added compound  $7\cdot\text{M}_b$  (60 mg, 0.031 mmol). Then, a solution of  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (44 mg, 0.062 mmol),  $\text{CuI}$  (59 mg, 0.31 mmol), benzoquinone (45 mg, 0.42 mmol), and diisopropylamine (0.24 mL, 1.7 mmol) in  $\text{CHCl}_3$  (10 mL) was added to the resulting solution, and this reaction mixture was stirred for 2 h at  $20^\circ\text{C}$ . Saturated aqueous EDTA/ $\text{NH}_3$  (25 mL) was added and stirred for 30 min.  $\text{H}_2\text{O}$  (20 mL) was added, the layers were separated, and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 20$  mL). The organic phases were combined, washed with brine (20 mL), dried ( $\text{MgSO}_4$ ), and filtered. Solvent removal and purification by recycling GPC (THF) afforded compound  $m\text{C48}\cdot(\text{M}_b)_3$  (19 mg,  $3.2\ \mu\text{mol}$ , 16%),  $m\text{C68}\cdot(\text{M}_b)_4$  (11 mg,  $1.4\ \mu\text{mol}$ , 14%),  $m\text{C88}\cdot(\text{M}_b)_5$  (5 mg,  $0.5\ \mu\text{mol}$ , 7%),  $m\text{C108}\cdot(\text{M}_b)_6$  (2.0 mg,  $0.17\ \mu\text{mol}$ , 3%), and  $m\text{C128}\cdot(\text{M}_b)_7$  (0.8 mg,  $0.06\ \mu\text{mol}$ , 1%) as black solids. (Note: tetracobalt [3]rotaxane  $m\text{C28}\cdot(\text{M}_b)_2$  is also formed, but not isolated.)

**IR** (ATR): 2963 (m, C-H), 2907 (w, C-H), 2868 (w, C-H), 2150 (w,  $\text{C}\equiv\text{C}$ ), 2036 (m,  $\text{C}=\text{O}$ ), 2018 (s,  $\text{C}=\text{O}$ ), 1994 (m,  $\text{C}=\text{O}$ )  $\text{cm}^{-1}$ . **UV-vis** ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ): 284 (304000), 318 (298000), 422 (183000), 582 (sh, 17900) nm.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  8.18 (d,  $J = 8.4$  Hz, 4H;  $\text{H}_b$ ), 8.17 (d,  $J = 8.4$  Hz, 2H;  $\text{H}_b$ ), 8.10 (d,  $J = 8.7$  Hz, 4H;  $\text{H}_d$ ), 7.98 (d,  $J = 8.8$  Hz, 8H;  $\text{H}_d$ ), 7.90 (d,  $J = 8.4$  Hz, 2H;  $\text{H}_c$ ), 7.88 (d,  $J = 8.4$  Hz, 4H;  $\text{H}_c$ ), 7.70 (s, 4H;  $\text{H}_a$ ), 7.67 (s, 2H;  $\text{H}_a$ ), 7.41 (s, 6H), 7.35–7.27 (m, 42H), 7.24–7.23 (m, 38H), 7.15–7.11 (m, 24H), 7.05 (d,  $J = 8.7$  Hz, 4H;  $\text{H}_e$ ), 6.97 (d,  $J = 8.8$  Hz, 8H;  $\text{H}_e$ ), 6.93 (d,  $J = 1.7$  Hz, 12H; *ortho*-Tr\*), 5.33 (s, 4H;  $\text{H}_f$ ), 5.30 (s, 8H;  $\text{H}_f$ ), 3.53–3.31 (m, 8H;  $\text{PCH}_2$ ), 1.17 (s, 108H; *t*Bu).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (151 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{C}}$  160.1, 159.8, 159.3, 158.6, 158.5, 158.1, 158.0, 150.73, 150.70, 147.01, 146.98, 144.0, 143.8 (br), 138.1 (br), 136.4, 135.1, 134.6, 134.5, 134.3, 132.2 (t,  $J_{\text{C-P}} = 6.3$  Hz), 132.1, 131.94 (t,  $J_{\text{C-P}} = 6.2$  Hz), 131.89, 131.85, 131.7, 130.64, 130.59, 130.2, 130.1, 129.01, 128.97, 128.9, 128.6, 128.5, 127.63, 127.55, 125.83, 125.78, 125.1,

123.9, 122.8, 122.5, 120.9, 120.6, 120.4, 116.9, 116.6, 116.2, 86.2, 84.8, 84.4, 83.4, 82.6, 81.7, 73.1, 71.9, 71.5, 71.0, 70.7, 70.3, 69.4, 68.2, 67.2, 65.1, 64.5, 64.1, 57.8, 35.1, 31.5 (12 signals coincident or not observed).  $^{31}\text{P}\{\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{P}}$  39.4. ESI HRMS  $m/z$ : calcd for  $\text{C}_{364}\text{H}_{295}\text{Co}_8\text{N}_6\text{O}_{25}\text{P}_8$  ( $[\text{M} + 3\text{H}]^{3+}$ ) 1957.4891, found 1957.5133. GPC (analytical, THF/pyridine 1% v/v) retention time: 35.15 min.



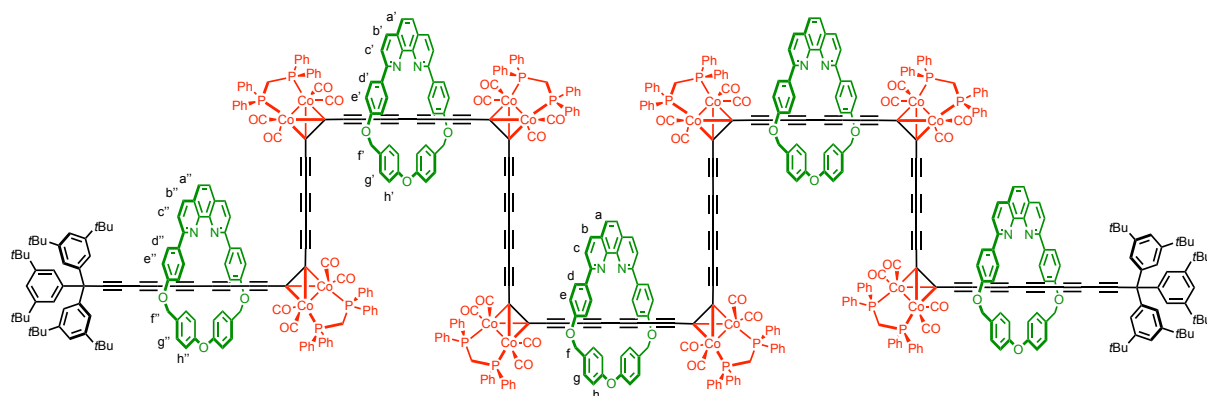
A typical recycling GPC trace of the crude reaction containing  $m\text{C}28\cdot(\text{M}_b)_2$ ,  $m\text{C}48\cdot(\text{M}_b)_3$ ,  $m\text{C}68\cdot(\text{M}_b)_4$ ,  $m\text{C}88\cdot(\text{M}_b)_5$ ,  $m\text{C}108\cdot(\text{M}_b)_6$ , and  $m\text{C}128\cdot(\text{M}_b)_7$  (eluting with THF at a flow rate of 3.5 mL/min,  $\lambda = 480$  nm).



**Compound  $m\text{C}68\cdot(\text{M}_b)_4$ :** The titled compound  $m\text{C}68\cdot(\text{M}_b)_4$  (11 mg, 1.4  $\mu\text{mol}$ , 14%) was obtained as a black solid as described in the above procedure.

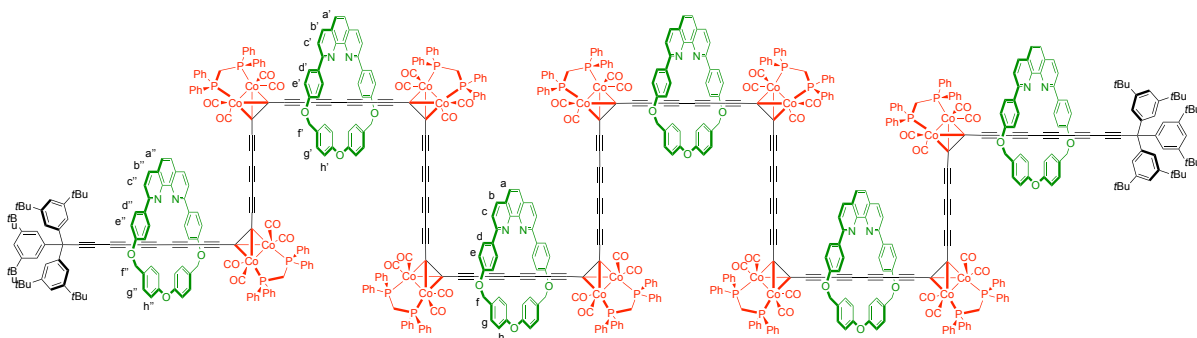
**IR** (ATR): 2962 (w, C–H), 2928 (w, C–H), 2869 (w, C–H), 2151 (w, C $\equiv$ C), 2036 (m, C=O), 2018 (s, C=O), 1994 (m, C=O)  $\text{cm}^{-1}$ . **UV-vis** ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ): 284 (386000), 318 (376000), 422 (260000), 582 (sh, 27500) nm.  **$^1\text{H}$  NMR** (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  8.18 (d,  $J = 8.3$  Hz, 4H;  $\text{H}_{\text{b}/\text{b}}$ ), 8.17 (d,  $J = 8.3$  Hz, 4H;  $\text{H}_{\text{b}'/\text{b}'}$ ), 8.10 (d,  $J = 8.8$  Hz, 8H;  $\text{H}_{\text{d}}$ ), 7.99 (d,  $J = 8.7$  Hz, 8H;  $\text{H}_{\text{d}'}$ ), 7.90 (d,  $J = 8.3$  Hz, 4H;  $\text{H}_{\text{c}/\text{c}'}$ ), 7.88 (d,  $J = 8.4$  Hz, 4H;  $\text{H}_{\text{c}'/\text{c}}$ ), 7.70 (s, 4H;  $\text{H}_{\text{a}'/\text{a}}$ ), 7.68 (s, 4H;  $\text{H}_{\text{a}/\text{a}'}$ ), 7.43–7.38 (m, 16H), 7.36–7.34 (m, 8H), 7.32–7.22 (m, 98H), 7.15–7.11 (m, 36H), 7.05 (d,  $J = 8.8$  Hz, 8H;  $\text{H}_{\text{e}}$ ), 6.97 (d,  $J = 8.7$  Hz, 8H;  $\text{H}_{\text{e}'}$ ), 6.94 (d,  $J = 1.8$  Hz, 12H; *ortho*-Tr\*), 5.35 (s, 8H;  $\text{H}_{\text{f}}$ ), 5.30 (s, 8H;  $\text{H}_{\text{f}'}$ ), 3.53–3.27 (m, 12H;  $\text{PCH}_2$ ), 1.18 (s, 108H; *t*Bu).  **$^{13}\text{C}\{\text{H}\}$  NMR** (151 MHz,

CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_c$  160.0, 159.8, 159.3, 158.6, 158.5, 158.1, 158.0, 150.7, 146.99, 146.96, 144.0, 136.4, 136.3, 135.2 (br), 135.0 (br), 134.9 (br), 134.6, 134.5, 134.44, 134.40, 134.29, 134.25, 132.20, 132.16, 132.11, 132.05, 132.01, 131.97, 131.93, 131.88, 131.8, 130.7, 130.64, 130.58, 130.2, 130.1, 129.01, 128.98, 128.95, 128.9, 127.6, 127.5, 125.82, 125.78, 123.9, 122.7, 122.5, 120.9, 120.6, 120.4, 116.8, 116.6, 86.1, 84.90, 84.87, 84.8, 84.6, 84.4, 83.7, 83.3, 82.7, 82.3, 81.7, 73.2, 73.0, 71.9, 71.5, 71.3, 71.2, 71.0, 70.7, 70.3, 68.2, 67.3, 67.1, 65.1, 64.5, 64.0, 57.8, 35.1, 31.5 (14 signals coincident or not observed and  $^{31}\text{P}$ - $^{13}\text{C}$  couplings are not resolved due to overlapping signals).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_p$  39.4. **ESI HRMS  $m/z$** : calcd for C<sub>480</sub>H<sub>366</sub>Co<sub>12</sub>N<sub>8</sub>O<sub>36</sub>P<sub>12</sub> ([M + 4H]<sup>4+</sup>) 1975.1510, found 1975.1534. **GPC** (analytical, THF/pyridine 1% v/v) retention time: 34.37 min.

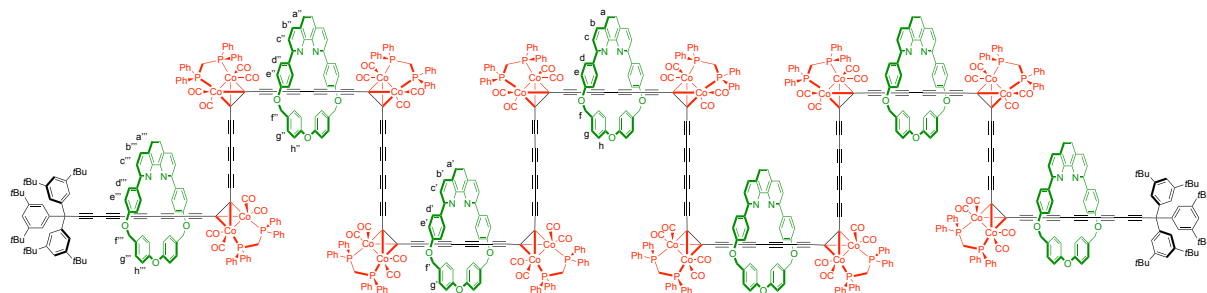


**Compound  $m\text{C88}\cdot(\text{M}_b)_5$** : The titled compound  $m\text{C88}\cdot(\text{M}_b)_5$  (5 mg, 0.5  $\mu\text{mol}$ , 7%) was obtained as a black solid as described in the above procedure.

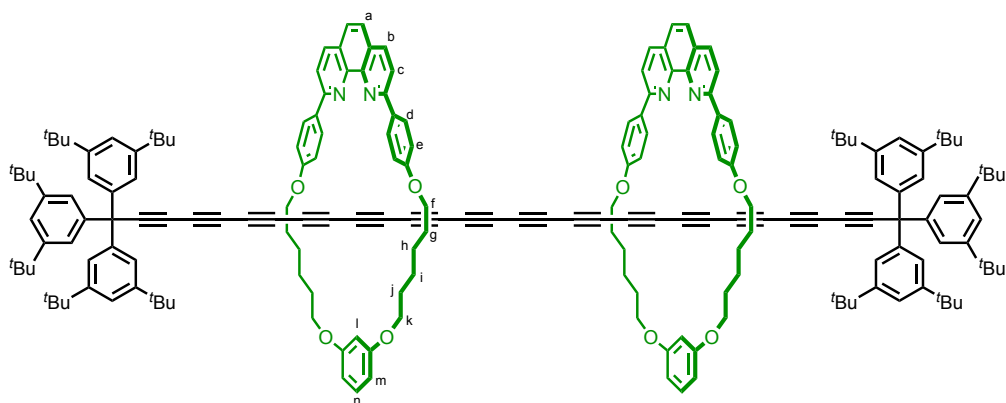
$^1\text{H}$  NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_H$  8.18 (d,  $J = 8.3$  Hz, 2H; H<sub>b</sub>), 8.18 (d,  $J = 8.3$  Hz, 4H; H<sub>b'/b''</sub>), 8.17 (d,  $J = 8.3$  Hz, 4H; H<sub>b''/b'</sub>), 8.09 (d,  $J = 8.7$  Hz, 8H; H<sub>d'</sub>), 8.08 (d,  $J = 8.8$  Hz, 4H; H<sub>d</sub>), 7.98 (d,  $J = 8.7$  Hz, 8H; H<sub>d''</sub>), 7.91 (d,  $J = 8.3$  Hz, 2H; H<sub>c</sub>), 7.90 (d,  $J = 8.3$  Hz, 4H; H<sub>c'/c''</sub>), 7.87 (d,  $J = 8.3$  Hz, 4H; H<sub>c''/c'</sub>), 7.693 (s, 4H; H<sub>a'/a''</sub>), 7.687 (s, 2H; H<sub>a</sub>), 7.68 (s, 4H; H<sub>a''/a'</sub>), 7.40–7.35 (m, 40H, H<sub>g'+g''+g'''+h'+h''</sub>), 7.32–7.22 (m, 134H), 7.14–7.11 (m, 48H), 7.05 (d,  $J = 8.8$  Hz, 12H; H<sub>e+e'</sub>), 6.97 (d,  $J = 8.7$  Hz, 8H; H<sub>e''</sub>), 6.93 (d,  $J = 1.8$  Hz, 12H; *ortho*-Tr\*), 5.35 (s, 4H; H<sub>f</sub>), 5.34 (s, 8H; H<sub>f'</sub>), 5.30 (s, 8H; H<sub>f''</sub>), 3.51–3.32 (m, 16H; PCH<sub>2</sub>), 1.17 (s, 108H; *t*Bu).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_c$  160.0, 159.8, 158.6, 158.53, 158.51, 158.1, 158.0, 150.7, 147.00, 146.96, 144.0, 136.4, 136.3, 134.9, 134.8, 134.7, 134.60, 134.57, 134.5, 134.29, 134.27, 134.25, 132.20, 132.16, 132.10, 132.05, 132.01, 131.97, 131.93, 131.88, 131.84, 131.80, 130.7, 130.2, 130.1, 129.01, 128.98, 128.95, 128.9, 127.6, 127.5, 125.82, 125.78, 123.9, 122.7, 122.6, 122.5, 120.9, 120.6, 120.4, 116.8, 116.6, 84.9, 84.6, 84.4, 83.7, 71.0, 70.7, 70.3, 68.2, 67.3, 57.8, 35.1, 31.5 (74 signals coincident or not observed and  $^{31}\text{P}$ - $^{13}\text{C}$  couplings are not resolved due to overlapping signals).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_p$  39.4. **ESI HRMS  $m/z$** : calcd for C<sub>596</sub>H<sub>437</sub>Co<sub>16</sub>N<sub>10</sub>O<sub>47</sub>P<sub>16</sub> ([M + 5H]<sup>5+</sup>) 1985.7480, found 1985.9485; calcd for C<sub>596</sub>H<sub>436</sub>Co<sub>16</sub>N<sub>10</sub>O<sub>47</sub>P<sub>16</sub> ([M + 4H]<sup>4+</sup>) 2481.9332, found 2481.8789; calcd for C<sub>596</sub>H<sub>435</sub>Co<sub>16</sub>N<sub>10</sub>O<sub>47</sub>P<sub>16</sub> ([M + 3H]<sup>3+</sup>) 3308.9085, found 3308.7858. **GPC** (analytical, THF/pyridine 1% v/v) retention time: 33.66 min.



**Compound  $mC108 \cdot (M_b)_6$ :** The titled compound  $mC108 \cdot (M_b)_6$  (2.0 mg, 0.17  $\mu\text{mol}$ , 3%) was obtained as a black solid as described in the above procedure.  $^1\text{H NMR}$  (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  8.18 (d,  $J = 8.4$  Hz, 4H;  $H_{b/b'}/b''$ ), 8.18 (d,  $J = 8.3$  Hz, 4H;  $H_{b/b'}/b''$ ), 8.17 (d,  $J = 8.2$  Hz, 4H;  $H_{b/b'}/b''$ ), 8.09 (d,  $J = 8.8$  Hz, 8H;  $H_{d/d'}$ ), 8.09 (d,  $J = 8.8$  Hz, 8H;  $H_{d/d'}$ ), 7.98 (d,  $J = 8.6$  Hz, 8H;  $H_{d'}$ ), 7.91 (d,  $J = 8.4$  Hz, 4H;  $H_{c/c'}/c''$ ), 7.90 (d,  $J = 8.3$  Hz, 4H;  $H_{c/c'}/c''$ ), 7.87 (d,  $J = 8.3$  Hz, 4H;  $H_{c/c'}/c''$ ), 7.69 (s, 4H;  $H_{a/a'}/a''$ ), 7.68 (s, 4H;  $H_{a/a'}/a''$ ), 7.67 (s, 4H;  $H_{a/a'}/a''$ ), 7.42–7.23 (m, 194H), 7.14–7.13 (m, 60H), 7.05–7.04 (m, 16H,  $H_{e+e'}$ ), 6.97 (d,  $J = 8.7$  Hz, 8H;  $H_{e''}$ ), 6.93 (d,  $J = 1.8$  Hz, 12H; *ortho*-Tr\*), 5.35 (s, 8H;  $H_f$ ), 5.34 (s, 8H;  $H_f$ ), 5.29 (s, 8H;  $H_f$ ), 3.51–3.33 (m, 20H;  $\text{PCH}_2$ ), 1.17 (s, 108H; *t*Bu).  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{P}}$  39.4. ESI HRMS  $m/z$ : calcd for  $\text{C}_{712}\text{H}_{508}\text{Co}_{20}\text{N}_{12}\text{O}_{58}\text{P}_{20}$  ( $[\text{M} + 6\text{H}]^{6+}$ ) 1992.9799, found 1992.9747; calcd for  $\text{C}_{712}\text{H}_{507}\text{Co}_{20}\text{N}_{12}\text{O}_{58}\text{P}_{20}$  ( $[\text{M} + 5\text{H}]^{5+}$ ) 2391.3744, found 2391.3302. GPC (analytical, THF/pyridine 1% v/v) retention time: 33.18 min.

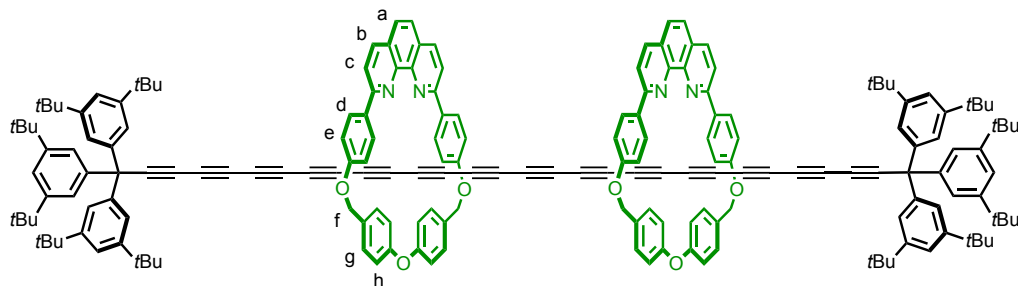


**Compound  $mC128 \cdot (M_b)_7$ :** The titled compound  $mC128 \cdot (M_b)_7$  (0.8 mg, 0.06  $\mu\text{mol}$ , 1%) was obtained as a black solid as described in the above procedure.  $^1\text{H NMR}$  (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{H}}$  8.18–8.16 (m, 14H;  $H_{b+b'+b''+b''}$ ), 8.10–8.08 (m, 20H;  $H_{d+d'+d''}$ ), 7.98 (d,  $J = 8.5$  Hz, 8H;  $H_{d''}$ ), 7.91–7.86 (m, 14H;  $H_{c+c'+c''+c''}$ ), 7.69–7.67 (m, 14H;  $H_{a+a'+a''+a''}$ ), 7.41–7.22 (m, 230H), 7.13 (m, 72H), 7.05–7.04 (m, 20H,  $H_{e+e'+e''}$ ), 6.96 (d,  $J = 8.6$  Hz, 8H;  $H_{e''}$ ), 6.93 (d,  $J = 1.8$  Hz, 12H; *ortho*-Tr\*), 3.49–3.34 (m, 24H;  $\text{PCH}_2$ ), 1.17 (s, 108H; *t*Bu) ( $\text{CH}_2$  from  $M_b$  overlapped with the solvent signal).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta_{\text{P}}$  39.4. ESI HRMS  $m/z$ : calcd for  $\text{C}_{828}\text{H}_{578}\text{Co}_{24}\text{N}_{14}\text{O}_{69}\text{P}_{24}$  ( $[\text{M} + 6\text{H}]^{6+}$ ) 2330.8347, found 2330.7774; calcd for  $\text{C}_{828}\text{H}_{577}\text{Co}_{24}\text{N}_{14}\text{O}_{69}\text{P}_{24}$  ( $[\text{M} + 5\text{H}]^{5+}$ ) 2796.8002, found 2796.6333. GPC (analytical, THF/pyridine 1% v/v) retention time: 32.88 min.



**Compound C28·(M<sub>a</sub>)<sub>2</sub>:** A solution of magnesium monoperoxyphthalate hexahydrate (93 mg, 80 wt%, 20 eq., 0.15 mmol) in MeOH (5.0 mL) was added dropwise using a syringe pump over a period of 2 h to a solution of cobalt-masked [3]rotaxane **mC28·(M<sub>a</sub>)<sub>2</sub>** (30 mg, 1.0 eq., 7.5 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The reaction was monitored using TLC and, upon reaching completion, was quenched using a sat aqueous NaHCO<sub>3</sub> solution (20 mL). The organic layer was washed with water and brine, then dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude mixture was purified by silica gel column chromatography (petroleum ether/EtOAc, gradient elution from 0 to 75%) to yield 14-yne [2]rotaxane **C28·(M<sub>a</sub>)<sub>2</sub>** (12 mg, 4.4 μmol, 59%) as a yellow solid.

**IR (ATR)** (only selected signals) 3006 (C–H), 2963 (C–H), 2200 (C≡C), 2130 (C≡C), 2013 (C≡C) cm<sup>-1</sup>. **UV-vis** (CHCl<sub>3</sub>) λ<sub>max</sub> (ε) 432 (346000), 401 (323000), 375 (205000), 355 (136000), 336 (99100), 289 (126000) nm. **<sup>1</sup>H NMR** (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 8.38 (d, *J* = 8.8 Hz, 8H, H<sub>d</sub>), 8.20 (d, *J* = 8.4 Hz, 4H, H<sub>b</sub>), 8.01 (d, *J* = 8.3 Hz, 4H, H<sub>c</sub>), 7.70 (s, 4H, H<sub>a</sub>), 7.33 (t, *J* = 1.8 Hz, 6H, Tr\* Ar-H), 7.09 (t, *J* = 8.8 Hz, 2H, H<sub>n</sub>), 7.04 (d, *J* = 8.8 Hz, 8H, H<sub>e</sub>), 6.94 (d, *J* = 1.8 Hz, 12H, Tr\* Ar-H), 6.45 – 6.41 (m, 4H, H<sub>l,m</sub>), 4.05 – 3.98 (m, 8H, H<sub>f</sub>), 3.93 – 3.86 (m, 8H, H<sub>k</sub>), 1.88 – 1.82 (m, 8H, H<sub>g</sub>), 1.80 – 1.73 (m, 8H, H<sub>j</sub>), 1.55 – 1.50 (m, 16H, H<sub>h,i</sub>), 1.22 (s, 108H, tBu). **<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>C</sub> 160.87, 160.81, 156.03 (C<sub>c</sub>-C<sub>g</sub>-N), 150.87, 146.41 (C<sub>a</sub>-C<sub>b</sub>), 143.47, 136.81 (C<sub>b</sub>), 132.16 (N-C<sub>c</sub>-C<sub>d</sub>), 130.02 (C<sub>k</sub>), 129.13 (C<sub>d</sub>), 127.78 (N-C<sub>e</sub>-C<sub>f</sub>-N), 125.82 (C<sub>a</sub>), 123.93, 121.13, 119.10 (C<sub>c</sub>), 115.05 (C<sub>e</sub>), 107.38 (C<sub>j</sub>), 100.81 (C<sub>i</sub>), 87.45, 69.17, 68.41 (C<sub>f,k</sub>), 68.08 (C<sub>k/f</sub>), 64.55, 64.27, 64.17, 64.06, 63.83, 63.60, 63.38, 63.17, 62.91, 62.74, 62.54, 62.25, 57.82 (CAr<sub>3</sub>), 35.15 (C(CH<sub>3</sub>)<sub>3</sub>), 31.46 (C(CH<sub>3</sub>)<sub>3</sub>), 29.95 (C<sub>j/g</sub>), 29.52 (C<sub>g/j</sub>), 26.34 (C<sub>h/i</sub>), 26.31 (C<sub>i/h</sub>). **ESI HRMS** *m/z* = 2772.6213 [M+H]<sup>+</sup> (C<sub>198</sub>H<sub>211</sub>N<sub>4</sub>O<sub>8</sub><sup>+</sup> requires 2772.6221). **Raman** (CH<sub>2</sub>Cl<sub>2</sub>, only most intense signal) 1940 (C≡C) cm<sup>-1</sup>.

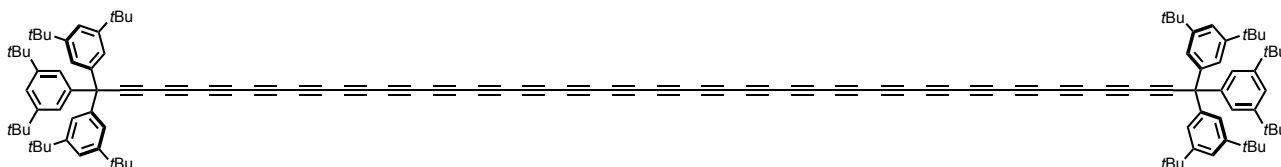


**Compound C28·(M<sub>b</sub>)<sub>2</sub>: Method 1.** To compound **mC28·(M<sub>b</sub>)<sub>2</sub>** (28 mg, 0.0073 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added *m*CPBA (18 mg, 77 wt%, 0.080 mmol), and the solution was stirred at 20 °C for 5 min. Saturated aqueous NaHCO<sub>3</sub> (5 mL) was added, and the solution was stirred for 5 min. H<sub>2</sub>O (20 mL) was added, the layers were separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The organic phases were combined, washed with brine (20 mL), dried (MgSO<sub>4</sub>), and filtered. Solvent removal and purification by

column chromatography (silica gel, ethyl acetate/petroleum ether 1:10 to 1:5) afforded compound **C28**·(**M<sub>b</sub>**)<sub>2</sub> (14 mg, 5.4 μmol, 74%) as a yellow-orange solid.

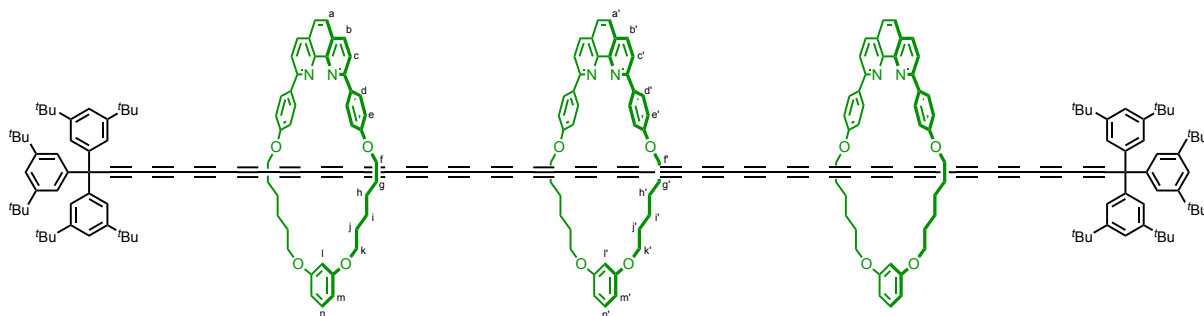
**Method 2.** To compound *m***C28**·(**M<sub>b</sub>**)<sub>2</sub> (15 mg, 0.0039 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6 mL) was added a solution of magnesium monoperoxyphthalate hexahydrate (97 mg, 80 wt%, 0.16 mmol) in MeOH (3 mL) via syringe pump over 1.5 h, while the solution was stirred at 20 °C. Saturated aqueous NaHCO<sub>3</sub> (2 mL) was added, and the solution was stirred for 5 min. H<sub>2</sub>O (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added, the layers were separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The organic phases were combined, washed with brine (20 mL), dried (MgSO<sub>4</sub>), and filtered. Solvent removal and purification by column chromatography (silica gel, ethyl acetate/petroleum ether 1:10 to 1:5) afforded compound **C28**·(**M<sub>b</sub>**)<sub>2</sub> (6.5 mg, 2.5 μmol, 64%) as a yellow-orange solid.

**IR** (ATR): 2963 (s, C–H), 2927 (m, C–H), 2867 (m, C–H), 2201 (w, C≡C), 2131 (w, C≡C), 2081 (w, C≡C), 2015 (w, C≡C), 1937 (w, C≡C) cm<sup>-1</sup>. **UV-vis** (CHCl<sub>3</sub>) λ<sub>max</sub> (ε): 275 (sh, 103000), 285 (118000), 297 (90400), 308 (78700), 320 (77100), 337 (83100), 354 (123000), 376 (224000), 401 (351000), 431 (386000) nm. **<sup>1</sup>H NMR** (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 8.18 (d, *J* = 8.3 Hz, 4H; H<sub>b</sub>), 7.84 (d, *J* = 8.3 Hz, 4H; H<sub>c</sub>), 7.78 (d, *J* = 8.7 Hz, 8H; H<sub>d</sub>), 7.71 (s, 4H; H<sub>a</sub>), 7.29 (t, *J* = 1.8 Hz, 6H; *para*-Tr\*), 7.03 (d, *J* = 8.4 Hz, 8H; H<sub>e</sub>), 6.91 (d, *J* = 1.8 Hz, 12H; *ortho*-Tr\*), 6.89 (d, *J* = 8.4 Hz, 8H; H<sub>h</sub>), 6.68 (d, *J* = 8.7 Hz, 8H; H<sub>c</sub>), 4.98, 4.89 (ABq, *J*<sub>AB</sub> = 15.0 Hz, 8H; H<sub>f</sub>), 1.18 (s, 108H; *t*Bu). **<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>C</sub> 159.6, 158.4, 157.8, 150.9 (Tr\*), 146.8, 143.5 (Tr\*), 136.6, 134.5, 134.1, 129.9, 127.8, 127.4, 126.0, 123.9 (Tr\*), 122.3, 121.1 (Tr\*), 120.6, 116.5, 87.1, 70.5, 69.3, 64.1, 63.93, 63.85, 63.80, 63.78, 63.7, 63.58, 63.4, 63.2, 62.9, 62.8, 62.6, 57.8, 35.2, 31.5. **ESI HRMS *m/z***: calcd for C<sub>190</sub>H<sub>179</sub>N<sub>4</sub>O<sub>6</sub> ([M + H]<sup>+</sup>) 2614.3885, found 2614.3861.



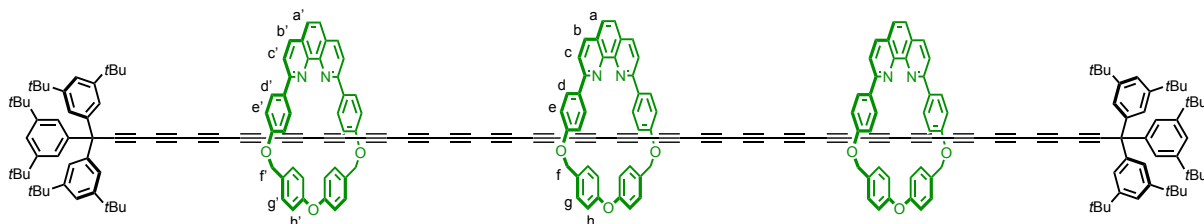
**Compound C48:** A solution of *m*CPBA (16 mg, 77 wt%, 24 eq., 70 μmol) in CD<sub>2</sub>Cl<sub>2</sub> (noted CH<sub>2</sub>Cl<sub>2</sub> also works, 1 mL) was added to a solution of octacobalt thread **13** (12 mg, 1.0 eq, 3.0 μmol) in CD<sub>2</sub>Cl<sub>2</sub> (noted CH<sub>2</sub>Cl<sub>2</sub> also works, 2 mL). Solvent removal and purification by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/pentane 1:4) afforded compound **C48** (2.9 mg, 1.7 μmol, 56%) as an orange-red solid.

**IR** (ATR) (only selected signals) 2962 (m, C–H), 2925 (m, C–H), 2854 (w, C–H), 2201 (vw, C≡C), 2096 (vw, C≡C), 2025 (vw, C≡C), 1942 (vw, C≡C), 1933 (vw, C≡C) cm<sup>-1</sup>. **UV-vis** (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>: 471, 438, 410, 387, 371, 356, 339, 326, 279 nm. **<sup>1</sup>H NMR** (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 7.27 (s, 6H, Tr\* Ar-H), 6.94 (s, 12H, Tr\* Ar-H), 1.18 (s, 108H, *t*Bu). **MALDI HRMS** (DCTB matrix) 1735.371 [M]<sup>-</sup> (C<sub>134</sub>H<sub>126</sub> requires 1734.986). **Raman** (CH<sub>2</sub>Cl<sub>2</sub>, only most intense signal) 1913 (C≡C) cm<sup>-1</sup>.



**Compound C48·(M<sub>a</sub>)<sub>3</sub>:** To a solution of cobalt-masked [4]rotaxane *m*C48·(M<sub>a</sub>)<sub>3</sub> (8.8 mg, 1.0 eq, 1.4 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL) was added dropwise a solution of magnesium monoperoxyphthalate hexahydrate (89 mg, 80 wt%, 100 eq., 144 μmol) in MeOH (4.0 mL) via syringe pump over a period of 2 h. The reaction was monitored using TLC and, once complete, was quenched using a sat. aqueous NaHCO<sub>3</sub> solution (~10 mL). The organic layer was washed with water and brine, then dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent removed under reduced pressure until a minimal amount (~0.5 mL) of solvent remained. The crude mixture was purified using silica gel column chromatography (petroleum ether/EtOAc, gradient elution from 0 to 75%) to yield 24-yne [4]rotaxane C48·(M<sub>a</sub>)<sub>3</sub> (1.0 mg, 0.27 μmol, 19%) as a red-orange solid after a quick removal of solvents. (*Note: the mass of the solid was determined as ca. 1.0 mg, 19% yield, but the solid has decomposed to some extent during drying.*)

**UV-vis** (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>: 478, 443, 415, 392, 372, 360, 344, 329, 289 nm. **<sup>1</sup>H NMR** (700 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 8.45 – 8.24 (br m, 12H, H<sub>d,d'</sub>), 8.20 – 8.10 (br m, 6H, H<sub>b,b'</sub>), 8.04 – 7.91 (br m, 6H, H<sub>c,c'</sub>), 7.69 – 7.60 (br m, 6H, H<sub>a,a'</sub>), 7.30 (t, *J* = 1.7 Hz, 6H, Tr\* Ar-H), 7.10 – 7.05 (m, 3H, H<sub>n,n'</sub>), 7.04 – 7.00 (m, 8H, H<sub>e</sub>), 6.96 – 6.93 (m, 4H, H<sub>e'</sub>), 6.91 (d, *J* = 1.8 Hz, 12H, Tr\* Ar-H), 6.43 – 6.39 (m, 6H, H<sub>n,n'</sub>), 6.36 (dd, *J* = 8.1, 2.4 Hz, 2H, H<sub>i</sub>), 6.33 (br s, 1H, H<sub>l</sub>), 4.03 – 3.99 (m, 8H, H<sub>f</sub>), 3.91 – 3.87 (m, 12H, H<sub>k,f</sub>), 3.79 (t, *J* = 6.4 Hz, 4H, H<sub>k'</sub>), 1.86 – 1.82 (m, 8H, H<sub>g</sub>), 1.78 – 1.74 (m, 12H, H<sub>j,g'</sub>), 1.69 – 1.67 (m, 4H, H<sub>j</sub>), 1.57 (br s, 16H, H<sub>h/h'/i/i'</sub>), 1.43 (br s, 8H, H<sub>h/h'/i/i'</sub>), 1.18 (s, 108H, tBu). **MALDI HRMS** (DCTB matrix) *m/z* = 1825.9779 [M+2H]<sup>2+</sup> (C<sub>260</sub>H<sub>254</sub>N<sub>6</sub>O<sub>12</sub><sup>2+</sup> requires 1825.9719). **Raman** (CH<sub>2</sub>Cl<sub>2</sub>, only most intense signal) 1910 (C≡C) cm<sup>-1</sup>.

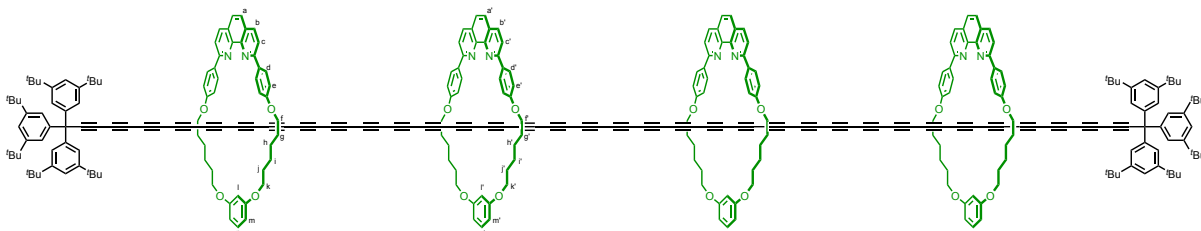


**Compound C48·(M<sub>b</sub>)<sub>3</sub>: Method 1.** To compound *m*C48·(M<sub>b</sub>)<sub>3</sub> (12 mg, 0.0020 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (12 mL) was added *m*CPBA (10 mg, 77 wt%, 0.045 mmol), and the solution was stirred at 20 °C for 10 min. Saturated aqueous NaHCO<sub>3</sub> (3 mL) was added, and the solution was stirred for 5 min. H<sub>2</sub>O (20 mL) was added, the layers were separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The organic phases were combined, washed with brine (20 mL), dried (MgSO<sub>4</sub>), and filtered. Solvent removal and purification by column chromatography (silica gel, ethyl acetate/petroleum ether 1:10 to 1:5) afforded compound C48·(M<sub>b</sub>)<sub>3</sub> (3.0 mg, 0.88 μmol, 43%) as an orange-red solid.

**Method 2.** To compound *m*C48·(M<sub>b</sub>)<sub>3</sub> (7.5 mg, 0.0013 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added a solution of magnesium monoperoxyphthalate hexahydrate (47 mg, 80wt%, 0.076 mmol) in MeOH (2 mL) via syringe pump over 1.5 h, while the solution was stirred at 20 °C. Saturated aqueous NaHCO<sub>3</sub> (2 mL) was added, and

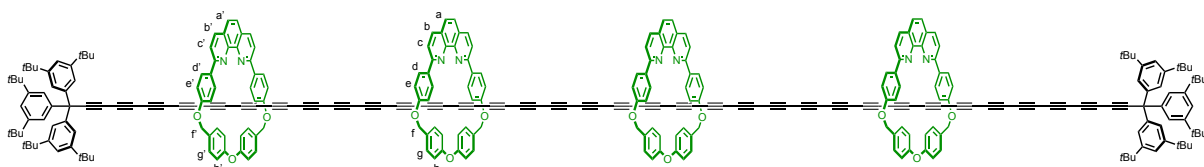
the solution was stirred for 5 min. H<sub>2</sub>O (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added, the layers were separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The organic phases were combined, washed with brine (20 mL), dried (MgSO<sub>4</sub>), and filtered. Solvent removal and purification by column chromatography (silica gel, ethyl acetate/petroleum ether 1:10 to 1:5) afforded compound **C48·(M<sub>b</sub>)<sub>3</sub>** (1.1 mg, 0.32 μmol, 25%) as an orange-red solid.

**IR** (ATR): 2958 (m, C–H), 2925 (m, C–H), 2854 (m, C–H), 2200 (w, C≡C), 2099 (w, C≡C), 2026 (w, C≡C), 1982 (w, C≡C), 1937 (w, C≡C), 1898 (w, C≡C), 800 (s) cm<sup>-1</sup>. **UV-vis** (CHCl<sub>3</sub>) λ<sub>max</sub> (ε): 283 (196000), 332 (188000), 344 (183000), 361 (170000), 394 (251000), 418 (438000), 447 (709000), 482 (706000) nm. **<sup>1</sup>H NMR** (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 8.23 (d, *J* = 8.3 Hz, 2H; H<sub>b</sub>), 8.15 (d, *J* = 8.3 Hz, 4H; H<sub>b'</sub>), 7.90 (d, *J* = 8.3 Hz, 2H; H<sub>c</sub>), 7.82 (d, *J* = 8.7 Hz, 4H; H<sub>d</sub>), 7.81 (d, *J* = 8.3 Hz, 4H; H<sub>c'</sub>), 7.79 (d, *J* = 8.7 Hz, 8H; H<sub>d'</sub>), 7.74 (s, 2H; H<sub>a</sub>), 7.67 (s, 4H; H<sub>a'</sub>), 7.30 (t, *J* = 1.8 Hz, 6H; *para*-Tr\*), 7.05 (d, *J* = 8.4 Hz, 8H; H<sub>g</sub>), 6.92 (d, *J* = 1.8 Hz, 12H; *ortho*-Tr\*), 6.87 (d, *J* = 8.4 Hz, 8H; H<sub>h</sub>), 6.82 (d, *J* = 8.3 Hz, 4H; H<sub>g</sub>), 6.67 (d, *J* = 8.7 Hz, 8H; H<sub>e</sub>), 6.54 (d, *J* = 8.3 Hz, 4H; H<sub>h</sub>), 6.53 (d, *J* = 8.7 Hz, 4H; H<sub>e</sub>), 4.93, 4.89 (ABq, *J*<sub>AB</sub> = 15.0 Hz, 8H; H<sub>f</sub>), 4.54 (s, 4H; H<sub>f</sub>), 1.19 (s, 108H; *t*Bu). **<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>C</sub> 159.8, 159.6, 158.4, 158.3, 157.7, 157.5, 150.9 (Tr\*), 146.9, 146.8, 143.5 (Tr\*), 136.8, 136.7, 134.64, 134.60, 134.1, 133.8, 129.8, 129.7, 127.9, 127.8, 127.4, 127.1, 126.1, 126.0, 124.0 (Tr\*), 122.5, 122.4, 121.1 (Tr\*), 120.6, 120.4, 116.7, 116.6, 87.4, 70.5, 69.2, 64.3, 64.03, 63.95, 63.89, 63.79, 63.75, 63.69, 63.60, 63.54, 63.46, 63.33, 63.14, 62.89, 62.83, 62.60, 62.40, 57.8, 35.2, 31.5 (6 sp<sup>1</sup>-carbon signals coincident or not observed). **MALDI HRMS (DCTB) *m/z***: calcd for C<sub>248</sub>H<sub>206</sub>N<sub>6</sub>O<sub>9</sub> ([M + 2H]<sup>2+</sup>) 1706.7952, found 1706.7972.



**Compound C68·(M<sub>a</sub>)<sub>4</sub>**: To a solution of cobalt-masked [5]rotaxane *m***C68·(M<sub>a</sub>)<sub>4</sub>** (4.0 mg, 1.0 eq, 0.49 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (6.0 mL) was added dropwise a solution of magnesium 2-carboperoxybenzoate hexahydrate (36 mg, 80 wt%, 120 eq., 58 μmol) in MeOH (5.0 mL) via syringe pump over a period of 2 h. The reaction was quenched using a sat. aqueous NaHCO<sub>3</sub> solution (~10 mL). The organic layer was washed with water and brine, then dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent removed under reduced pressure until a minimal amount (~0.5 mL) of solvent remained. The crude mixture was passed through a quick silica gel plug (EtOAc) to yield 34-yne [5]rotaxane **C68·(M<sub>a</sub>)<sub>4</sub>** as an orange-red solution. (*Note: The compound shows significant decomposition upon complete solvent removal.*)

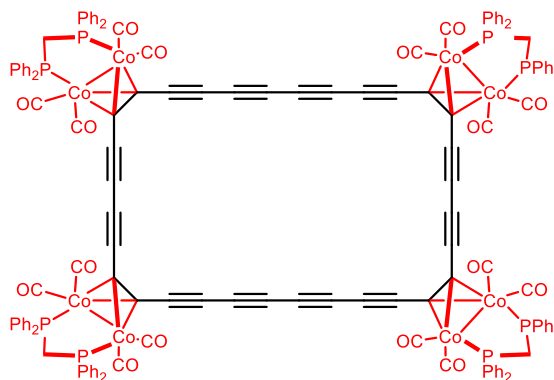
**UV-vis** (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>: 287, 329, 347, 369, 402, 425, 456, 492 nm. **MALDI HRMS (DCTB)** 4529.217 [M+H]<sup>+</sup> (C<sub>322</sub>H<sub>294</sub>N<sub>8</sub>O<sub>16</sub> requires 4529.251). **Raman** (CH<sub>2</sub>Cl<sub>2</sub>, only most intense signal) 1904 (C≡C) cm<sup>-1</sup>.



**Compound C68·(M<sub>b</sub>)<sub>4</sub>:** To compound *mcC68*·(M<sub>b</sub>)<sub>4</sub> (2.8 mg, 0.355 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL) was added a solution of magnesium monoperoxyphthalate (26.3 mg, 80% w/w, 42.5 μmol) in MeOH (1 mL) via syringe pump over 1.5 h, while the solution was stirred at 20 °C. Saturated aqueous NaHCO<sub>3</sub> (2 mL) was added, and the solution was stirred for 5 min. H<sub>2</sub>O (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added, the layers were separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The organic phases were combined, washed with brine (20 mL), dried (MgSO<sub>4</sub>), and filtered. Solvent removal, purification by a short column chromatography (silica gel, ethyl acetate/petroleum ether 1:5, then ethyl acetate/CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether 1:2:2) and washing with ethanol (3 × 5 mL) afforded compound **C68·(M<sub>b</sub>)<sub>4</sub>** (0.35 mg, 0.083 μmol, 23%) as an orange-red solid.

**UV-vis** (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>: 496, 460, 429, 403 (sh), 377 (sh), 352, 321, 282 nm. **<sup>1</sup>H NMR** (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 8.21 (d, *J* = 8.2 Hz, 4H; H<sub>b</sub>), 8.15 (d, *J* = 8.2 Hz, 4H; H<sub>b</sub><sup>′</sup>), 7.89 (d, *J* = 8.2 Hz, 4H; H<sub>c</sub>), 7.84 (d, *J* = 8.4 Hz, 8H; H<sub>d</sub>), 7.81 (d, *J* = 8.2 Hz, 4H; H<sub>c</sub><sup>′</sup>), 7.79 (d, *J* = 8.4 Hz, 8H; H<sub>d</sub><sup>′</sup>), 7.71 (s, 4H; H<sub>a</sub>), 7.67 (s, 4H; H<sub>a</sub><sup>′</sup>), 7.30 (t, *J* = 1.8 Hz, 6H; *para*-Tr\*), 7.06 (d, *J* = 8.2 Hz, 8H; H<sub>e</sub><sup>′</sup>), 6.92 (d, *J* = 1.8 Hz, 12H; *ortho*-Tr\*), 6.87 (d, *J* = 8.2 Hz, 8H; H<sub>b</sub><sup>′</sup>), 6.84 (d, *J* = 8.1 Hz, 8H; H<sub>g</sub>), 6.67 (d, *J* = 8.4 Hz, 8H; H<sub>e</sub><sup>′</sup>), 6.52 (d, *J* = 8.4 Hz, 4H; H<sub>c</sub>), 6.50 (d, *J* = 8.1 Hz, 4H; H<sub>h</sub>), 4.93, 4.90 (ABq, *J*<sub>AB</sub> = 14.8 Hz, 8H; H<sub>f</sub>), 4.51, 4.46 (ABq, *J*<sub>AB</sub> = 15.1 Hz, 8H; H<sub>f</sub>), 1.19 (s, 108H; *t*Bu). **ESI HRMS *m/z***: calcd for C<sub>306</sub>H<sub>234</sub>N<sub>8</sub>O<sub>12</sub> ([M + 4H]<sup>4+</sup>) 1053.7006, found 1053.7248; calcd for C<sub>306</sub>H<sub>233</sub>N<sub>8</sub>O<sub>12</sub> ([M + 3H]<sup>3+</sup>) 1404.5984, found 1404.5970. **MALDI HRMS (DCTB) *m/z***: calcd for C<sub>306</sub>H<sub>230</sub>N<sub>8</sub>O<sub>12</sub> ([M]<sup>+</sup>) 4210.7721, found 4210.904.

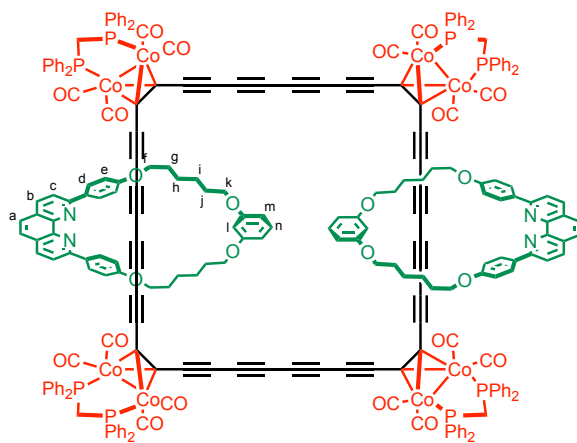
**mcC32:** Dry CHCl<sub>3</sub> (100 mL) and diisopropylamine (130 mg, 180 μL, 20 eq., 1.3 mmol) were added to deprotected tetracobalt tetrayne thread **3** (90 mg, 1.0 eq., 63 μmol), bis(triphenylphosphine)palladium(II) dichloride (30 mg, 0.67 eq., 42 μmol), copper(I) iodide (40 mg, 3.3 eq., 21 μmol) and benzoquinone (93 mg, 14 eq., 0.86 mmol). A drying tube was fitted, and reaction stirred at 20 °C in air for 24 h. The mixture was passed through a short silica plug (CHCl<sub>3</sub>) before removing the solvent under



reduced pressure. The crude material was purified by recycling GPC, then recrystallized from CHCl<sub>3</sub>/pentane to give the cyclic dimer **mcC32** (30 mg, 11 μmol, 35%) as a dark red crystalline solid.

**IR (ATR)** (only selected signals) 2923 (C–H), 2852 (C–H), 2148 (w, C≡C), 2035 (s, C=O), 2015 (s, C=O), 1990 (s, C=O) cm<sup>-1</sup>. **UV-vis** (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (*ε*) 557 (20900), 384 (180000), 326 (175000), 274 (181000) nm. **<sup>1</sup>H NMR** (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 7.59 – 7.36 (br m, 32H, Ar-H), 7.36 – 7.11 (br m, 48H, Ar-H), 3.72 – 3.25 (br m, 8H, P-CH<sub>2</sub>). **<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>C</sub> 202.67 (C≡O), 135.09 (br, Ar-C), 132.21, 130.63 (Ar-C), 128.97 (Ar-C), 88.34, 84.55 (br) 84.02, 82.62 (br), 70.58, 66.92, 38.52 (br, P-CH<sub>2</sub>) (2 carbons not distinguished and <sup>31</sup>P–<sup>13</sup>C couplings are not resolved due to overlapping signals). **<sup>31</sup>P{<sup>1</sup>H} NMR** (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>P</sub> 40.25. **GPC** (analytical, THF/pyridine 1% v/v) retention time = 43.02 min.

**[3]Catenane *mcC40*·(M<sub>a</sub>)<sub>2</sub>**: Dry CHCl<sub>3</sub> (40 mL) and diisopropylamine (29 mg, 40 μL, 40 eq., 0.28 mmol) was added to bis(triphenylphosphine)palladium(II) dichloride (6.6 mg, 1.3 eq., 9.5 μmol), copper(I) iodide (9.0 mg, 6.7 eq., 47 μmol) and benzoquinone (12 mg, 15 eq., 0.11 mmol). The mixture was stirred in air before addition of extended tetracobalt [2]rotaxane **6**·(M<sub>a</sub>)<sub>2</sub> (30 mg, 2.0 eq., 14 μmol) in dry CHCl<sub>3</sub> (10 mL) over 1 h via syringe pump. After complete addition, the reaction was stirred at 20 °C in air for a further 1 h. EDTA/NH<sub>3</sub> solution (25 mL) was then added and the mixture stirred for 1 h. The organic layer was extracted, washed with water (20 mL) The crude material was purified by recycling GPC (THF) to yield the octacobalt [3]catenane ***mcC40*·(M<sub>a</sub>)<sub>2</sub>** (6.0 mg, 1.4 μmol, 20% with respect to **6**·(M<sub>a</sub>)<sub>2</sub>) and hexadecacobalt [5]catenane ***mcC80*·(M<sub>a</sub>)<sub>4</sub>** (3.9 mg, 0.46 μmol, 13% with respect to **6**·(M<sub>a</sub>)<sub>2</sub>) as dark-brown solids.



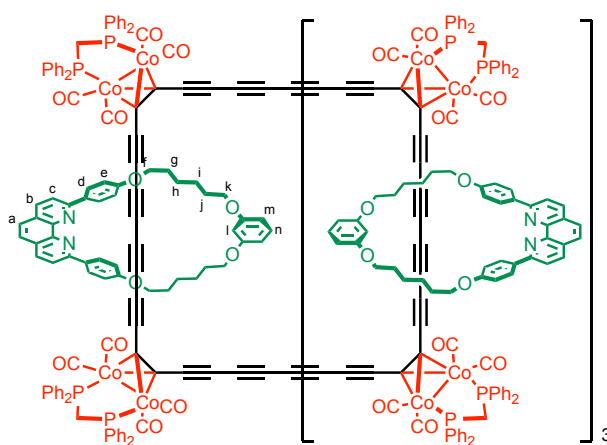
**IR (ATR)** (only selected signals) 2935 (C–H), 2145 (C≡C), 2019 (s, C=O), 1995 (s, C=O) cm<sup>-1</sup>. **UV-vis** (CHCl<sub>3</sub>) λ<sub>max</sub> (ε) 569 (24000), 406 (230000), 345 (246000), 327 (252000), 292 (291000) nm. **<sup>1</sup>H NMR** (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 8.54 (d, *J* = 8.3 Hz, 8H, H<sub>d</sub>), 8.23 (d, *J* = 8.4 Hz, 4H, H<sub>b</sub>), 8.08 (d, *J* = 8.6 Hz, 4H, H<sub>c</sub>), 7.72 (s, 4H, H<sub>a</sub>), 7.31 – 7.27 (m, 26H, H<sub>e</sub> & Ar-H), 7.27 – 7.20 (m, 38H, Ar-H), 7.20 – 7.16 (m, 8H, Ar-H), 7.16 – 7.07 (m, 18H, H<sub>n</sub> & Ar-H), 6.75 (s, 2H, H<sub>l</sub>), 6.52 (dd, *J* = 8.2, 2.3 Hz, 4H, H<sub>m</sub>), 4.26 (t, *J* = 7.3 Hz, 8H, H<sub>fk</sub>), 4.14 (d, *J* = 6.7 Hz, 8H, H<sub>k/f</sub>), 3.55 – 3.24 (m, 8H, P-CH<sub>2</sub>), 1.99 (t, *J* = 6.8 Hz, 8H, H<sub>g/j</sub>), 1.93 (t, *J* = 6.5 Hz, 8H, H<sub>j/g</sub>), 1.72 (br s, 16H, H<sub>n,i</sub>). **<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>C</sub> 202.14 (C=O, br), 161.28 (O-C-C<sub>e</sub>), 161.16, 156.31 (N-C-C-N), 146.51 (C<sub>a</sub>-C-C<sub>b</sub>), 136.82 (C<sub>b</sub>), 134.84 (t, *J*<sub>C-P</sub> = 21.7 Hz, Ar-C), 134.35 (t, *J*<sub>C-P</sub> = 21.5 Hz, Ar-C), 132.03 (d, *J*<sub>C-P</sub> = 6.5 Hz, Ar-C), 130.78 (Ar-C), 130.64 (C<sub>n</sub>), 129.96 (Ar-C), 129.28 (C<sub>d</sub>), 128.96 (t, *J*<sub>C-P</sub> = 4.9 Hz, Ar-C), 127.78, 125.81 (C<sub>a</sub>), 119.15 (C<sub>c</sub>), 115.44 (C<sub>e</sub>), 107.95 (C<sub>m</sub>), 100.33 (C<sub>i</sub>), 84.08, 83.71, 83.38, 83.21, 71.36, 71.11, 68.79 (C<sub>k/f</sub>), 68.30 (C<sub>fk</sub>), 67.60, 66.97, 38.98 (t, *J*<sub>C-P</sub> = 21.5 Hz, P-CH<sub>2</sub>), 30.11 (C<sub>j/g</sub>), 29.70 (C<sub>g/j</sub>), 26.38 (C<sub>h/i</sub>), 26.37 (C<sub>i/h</sub>). **<sup>31</sup>P{<sup>1</sup>H} NMR** (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>P</sub> 40.28. **ESI HRMS** *m/z* = 2107.2534 [M+2H]<sup>2+</sup> (C<sub>240</sub>H<sub>174</sub>Co<sub>8</sub>N<sub>4</sub>O<sub>24</sub>P<sub>8</sub><sup>2+</sup> requires 2107.2532). **GPC** (analytical, THF/pyridine 1% v/v) retention time: 36.8 min.

**[5]Catenane *mcC80*·(M<sub>a</sub>)<sub>4</sub>**: The titled compound ***mcC80*·(M<sub>a</sub>)<sub>4</sub>** (3.9 mg, 0.46 μmol, 13%) was obtained as a dark-brown solid as described in the above procedure.

**IR (ATR)** (only selected signals) 2961 (C–H), 2861 (C–H), 2146 (C≡C), 2018 (s, C=O), 1995 (s, C=O) cm<sup>-1</sup>.

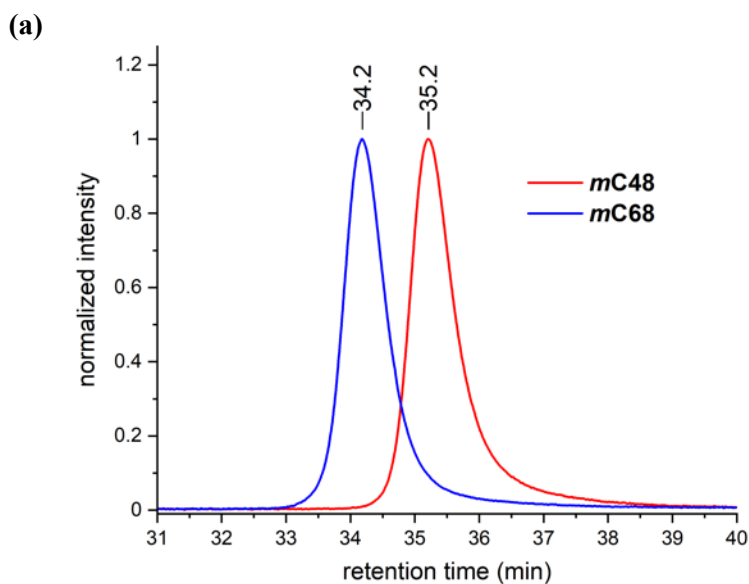
**UV-vis** (CHCl<sub>3</sub>) λ<sub>max</sub> (ε) 592 (35000), 444 (333000), 417 (353000), 346 (379000), 328 (392000), 291 (435000) nm. **<sup>1</sup>H NMR** (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ<sub>H</sub> 8.51 (d, *J* = 8.3 Hz, 16H, H<sub>d</sub>), 8.18 (d, *J* = 8.2 Hz, 8H, H<sub>b</sub>), 8.04

(d, *J* = 8.3 Hz, 8H, H<sub>c</sub>), 7.67 (s, 8H, H<sub>a</sub>), 7.31 – 7.17 (m, 140H, H<sub>e</sub> & Ar-H), 7.17 – 7.10 (m, 36H, Ar-H), 6.75

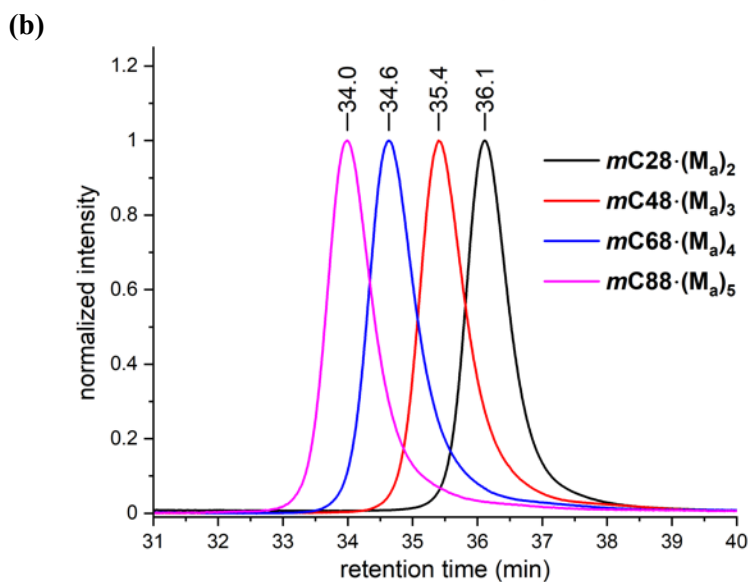


(s, 4H, H<sub>l</sub>), 6.51 (d,  $J = 8.1$  Hz, 8H, H<sub>m</sub>), 4.27 (t,  $J = 7.3$  Hz, 16H, H<sub>fk</sub>), 4.15 (t,  $J = 6.7$  Hz, 16H, H<sub>kf</sub>), 3.70 – 3.08 (m, 16H, P-CH<sub>2</sub>), 2.06 – 1.89 (m, 32H, H<sub>ig</sub>), 1.81 – 1.67 (m, 32H, H<sub>hi</sub>). **<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_c$  202.09 (C≡O, br), 161.26 (O-C-C<sub>e</sub>), 161.16, 156.31 (N-C-C-N), 146.50 (C<sub>a</sub>-C-C<sub>b</sub>), 136.81 (C<sub>b</sub>), 135.05 – 134.02 (m, Ar-C), 132.03 (d,  $J_{C-P} = 7.3$  Hz, Ar-C), 130.77 (Ar-C), 130.66 (C<sub>n</sub>), 129.93 (Ar-C), 129.29 (C<sub>d</sub>), 128.99 (t,  $J_{C-P} = 5.2$  Hz, Ar-C), 127.74, 125.79 (C<sub>a</sub>), 119.17 (C<sub>e</sub>), 115.41 (C<sub>e</sub>), 108.00 (C<sub>m</sub>), 100.23 (C<sub>l</sub>), 83.78 (br), 83.32, 77.55, 71.76, 71.45, 68.77 (C<sub>kf</sub>), 68.32 (C<sub>fk</sub>), 67.77, 67.19, 38.75 (br, P-CH<sub>2</sub>), 30.14 (C<sub>ig</sub>), 29.73 (C<sub>gj</sub>), 26.40 (C<sub>ih</sub>), 26.36 (C<sub>hi</sub>). **<sup>31</sup>P{<sup>1</sup>H} NMR** (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_p$  39.84. **ESI HRMS**  $m/z = 2107.2834$  [M+4H]<sup>4+</sup> (C<sub>480</sub>H<sub>348</sub>Co<sub>16</sub>N<sub>8</sub>O<sub>48</sub>P<sub>16</sub><sup>4+</sup> requires 2107.2532). **GPC** (analytical, THF/pyridine 1% v/v) retention time: 35.9 min.

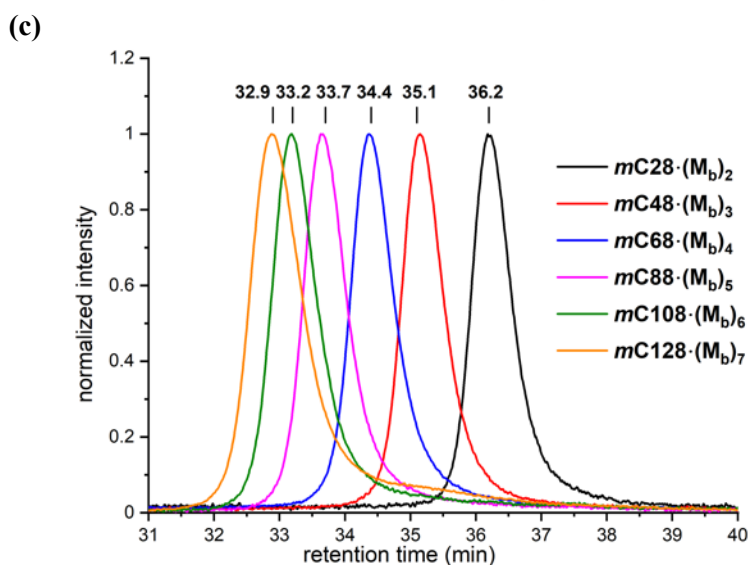
### Section 3: GPC Trace



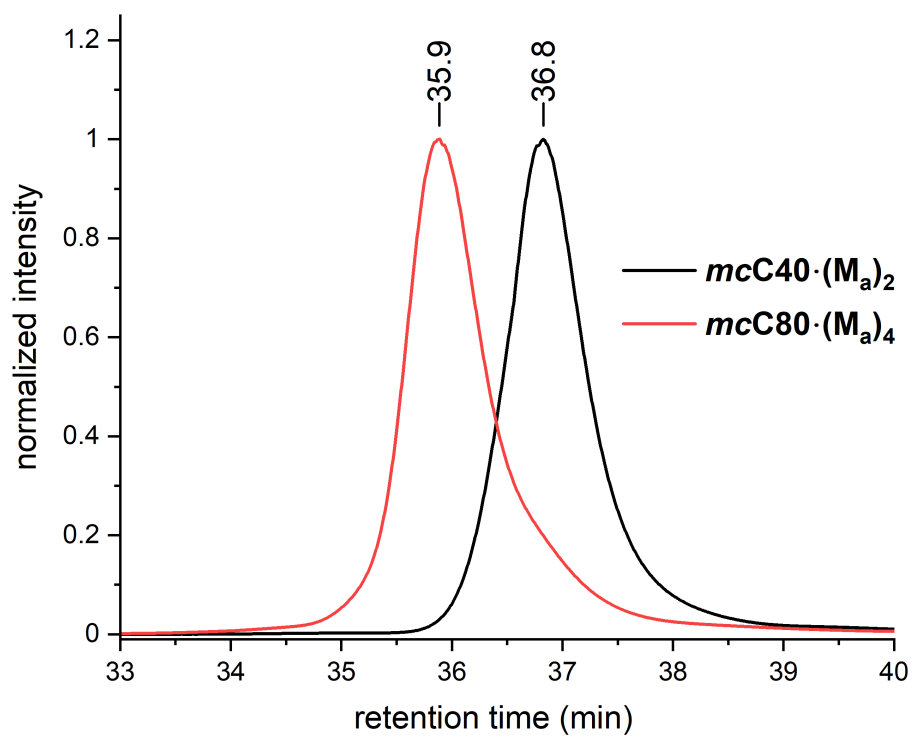
**Figure 2.** (a) Analytical GPC traces of masked thread compounds  $mC48$  and  $mC68$  (eluting with THF + 1% pyridine at a flow rate of 1.0 mL/min,  $\lambda = 525$  nm).



(b) Analytical GPC traces of masked polyrotaxanes  $mC28 \cdot (M_a)_2$ ,  $mC48 \cdot (M_a)_3$ ,  $mC68 \cdot (M_a)_4$ , and  $mC88 \cdot (M_a)_5$  (eluting with THF + 1% pyridine at a flow rate of 1.0 mL/min,  $\lambda = 525$  nm).



(c) Analytical GPC traces of masked polyrotaxanes  $mC28 \cdot (M_b)_2$ ,  $mC48 \cdot (M_b)_3$ ,  $mC68 \cdot (M_b)_4$ ,  $mC88 \cdot (M_b)_5$ ,  $mC108 \cdot (M_b)_6$ , and  $mC128 \cdot (M_b)_7$  (eluting with THF + 1% pyridine at a flow rate of 1.0 mL/min,  $\lambda = 480$  nm).

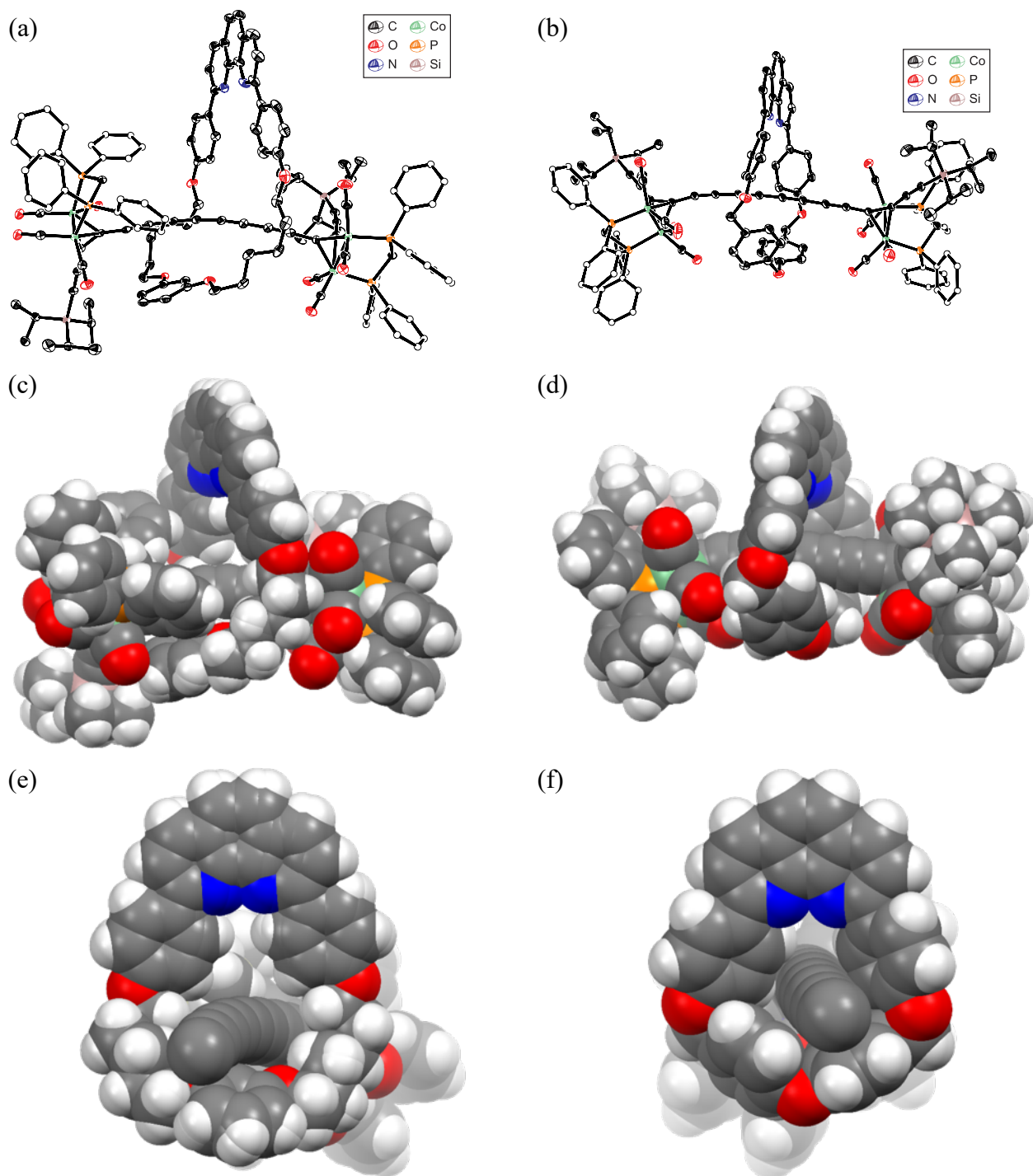


**Figure 3.** Analytical GPC traces of catenanes  $mcC40 \cdot (M_a)_2$  and  $mcC80 \cdot (M_a)_4$  (eluting with THF + 1% pyridine at a flow rate of 1.0 mL/min,  $\lambda = 525$  nm).

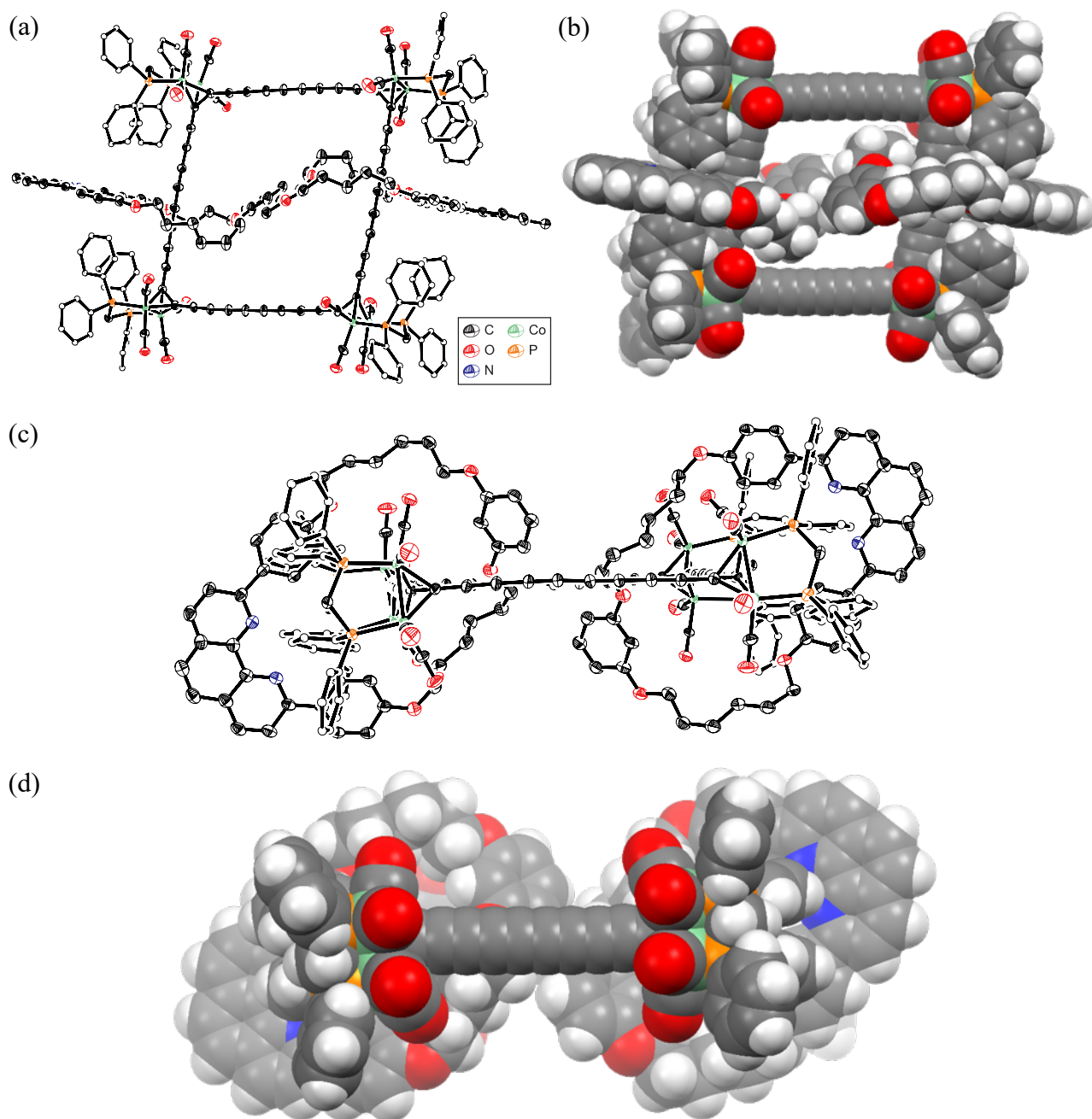
## Section 4: X-Ray Crystal Structures

Single crystal X-ray diffraction data for  $3 \cdot \mathbf{M}_a$  and  $3 \cdot \mathbf{M}_b$  were collected using beamline I19 at Diamond Light Source<sup>[9]</sup> and reduced using DIALS/XIA2.<sup>[10,11]</sup> Data for the [3]catenane  $mc\mathbf{C40} \cdot (\mathbf{M}_a)_2$  were collected using a (Rigaku) Oxford Diffraction Super-Nova A diffractometer and were reduced or CrysAlisPro. Structures were solved using SuperFlip<sup>[12]</sup> and refined using CRYSTALS<sup>[13,14]</sup> as detailed in the CIF.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2224109–2224111) and can be obtained via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)



**Figure 4.** X-ray crystallographic structure of tetracobalt [2]rotaxanes  $3 \cdot \mathbf{M}_a$  (left) and  $3 \cdot \mathbf{M}_b$  (right). For (a-b) ellipsoids are plotted at 30% probability, hydrogen atoms omitted and dppm phenyl rings plotted as spheres for clarity. Space-filling models (c-f) are presented to highlight difference in macrocyclic cavity size between  $\mathbf{M}_a$  and  $\mathbf{M}_b$ .



**Figure 5.** X-ray crystallographic structure of  $mcC40 \cdot (M_a)_2$ . For (a) and (c) ellipsoids are plotted at 30% probability, hydrogen atoms omitted and dppm phenyl rings plotted as spheres for clarity. Space-filling models are presented in (b) and (d).

## checkCIF/PLATON report, alerts and responses

### Tetracobalt [2]rotaxane 3·M<sub>a</sub> (CCDC 2224109)

The following ALERTS were generated.

#### **Alert level A**

PLAT027\_ALERT\_3\_A \_diffn\_reflns\_theta\_full value (too) Low ..... 21.30 Degree

**Author Response:** The sample was weakly diffracting and failed give diffraction beyond around 22 degrees. Further, as the sample suffered radiation damage, it was not possible to increase the acquisition time further to increase the diffraction limit. Despite the limited resolution, the final result gives useful information and the data quality does not affect the conclusions drawn.

---

#### **Alert level B**

PLAT029\_ALERT\_3\_B \_diffn\_measured\_fraction\_theta\_full value Low . 0.958 Why?

**Author Response:** Unfortunately, the sample suffered radiation damage so it was necessary to remove some of the data during processing leading to a reduced completeness. Despite the poor completeness, the final result gives useful information and the data quality does not affect the conclusions drawn.

PLAT911\_ALERT\_3\_B Missing FCF Refl Between Thmin & STh/L= 0.600 5800 Report

**Author Response:** Because the sample suffered radiation damage, it was necessary to remove some of the data during processing. These reflections were missing from all areas of the data and led to a reduced completeness. Despite this, the final result gives useful information and the data quality does not affect the conclusions drawn.

---

### Tetracobalt [2]rotaxane 3·M<sub>b</sub> (CCDC 2224110)

The following ALERTS were generated.

#### **Alert level B**

PLAT021\_ALERT\_4\_B Ratio Unique / Expected Reflections too High ... 1.555

**Author Response:** These materials suffer from radiation damage, so although the sample was weakly diffracting it was not possible to increase the exposure as it would damage the integrity of the crystal. Despite the limited resolution, the final result gives useful information and the data quality does not affect the conclusions drawn.

PLAT026\_ALERT\_3\_B Ratio Observed / Unique Reflections (too) Low .. 35% Check

**Author Response:** These materials suffer from radiation damage, so although the sample was weakly diffracting it was not possible to increase the exposure as it would damage the integrity of the crystal. Despite the limited resolution, the final result gives useful information and the data quality does not affect the conclusions drawn.

PLAT430\_ALERT\_2\_B Short Inter D...A Contact 027 ..027 . 2.79 Ang.

**Author Response:** Although these are close they are in an interdigitated arrangement suggesting this is a preferred configuration.

PLAT920\_ALERT\_1\_B Theta(Max) in CIF and FCF Differ by ..... 5.55 Degree

**Author Response:** Data beyond the diffraction limit were removed using the Wilson plot. Although these reflections are flagged correctly in the FCF file, they are still included in the file although not in the calculation for theta(max) in the CIF.

PLAT934\_ALERT\_3\_B Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers .. 9 Check

**Author Response:** The data were a little noisy, thought to be the result of a combination of radiation damage, solvent modelling and crystal quality. The worst of the outlying reflections were removed, though nine remained.

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[3]Catenane *mcC40*·(*M<sub>a</sub>*)<sub>2</sub> (CCDC 2224111)

The following ALERTS were generated.

**Alert level B**

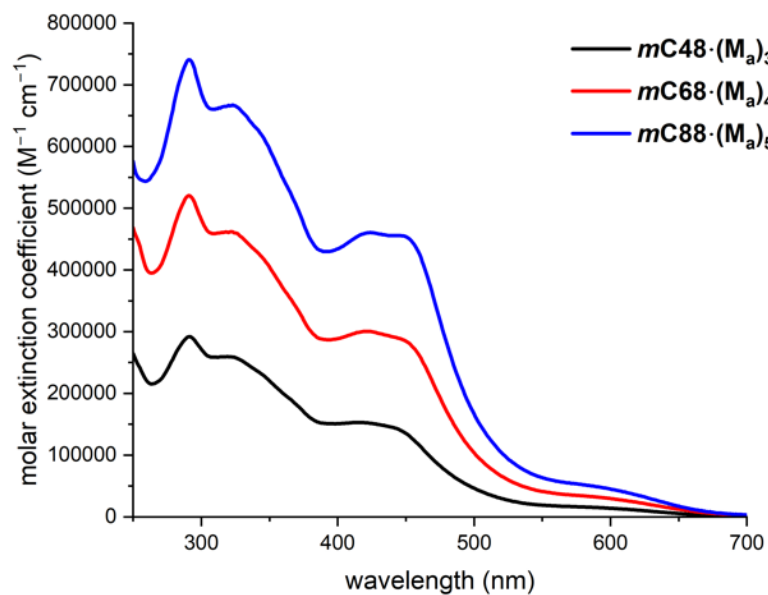
PLAT920\_ALERT\_1\_B Theta(Max) in CIF and FCF Differ by ..... 8.30 Degree

**Author Response:** Data beyond the diffraction limit were removed using the Wilson plot. Although these reflections are flagged correctly in the FCF file, they are still included in the file although not in the calculation for theta(max) in the CIF.

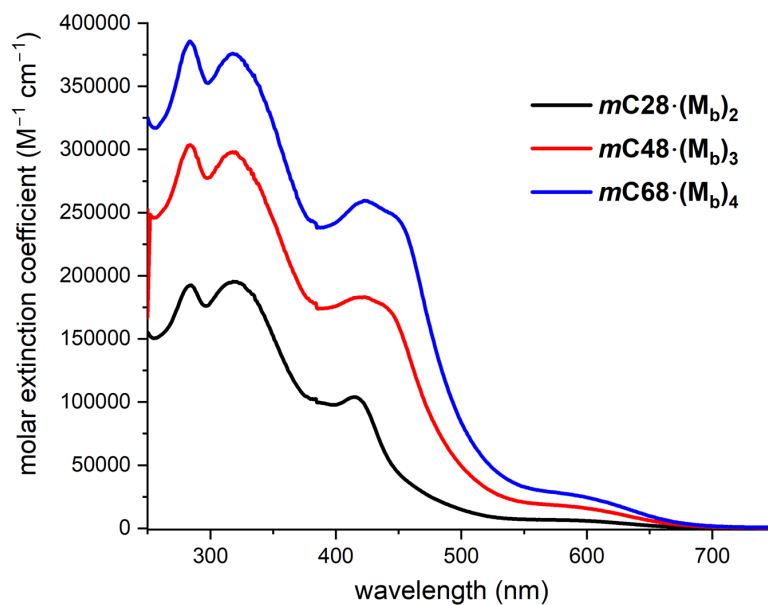
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## Section 5: UV-Visible Absorption Spectra

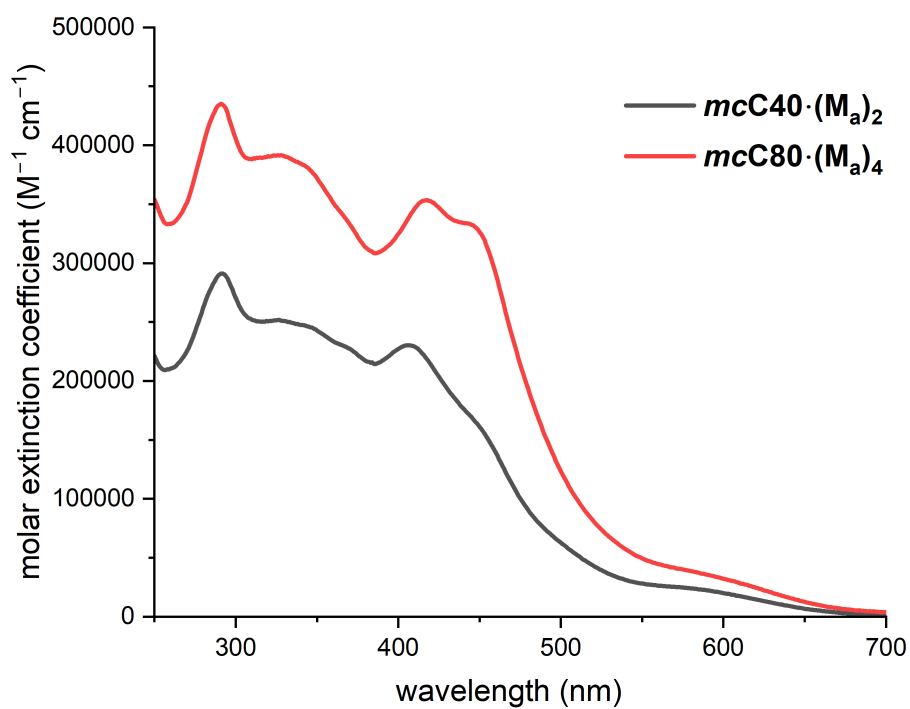
(a)



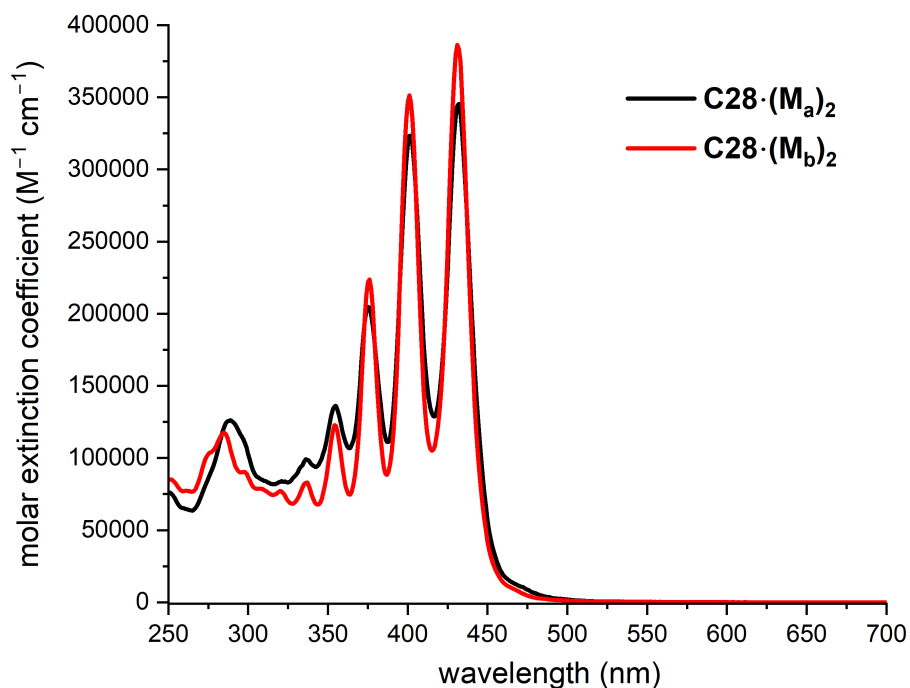
(b)



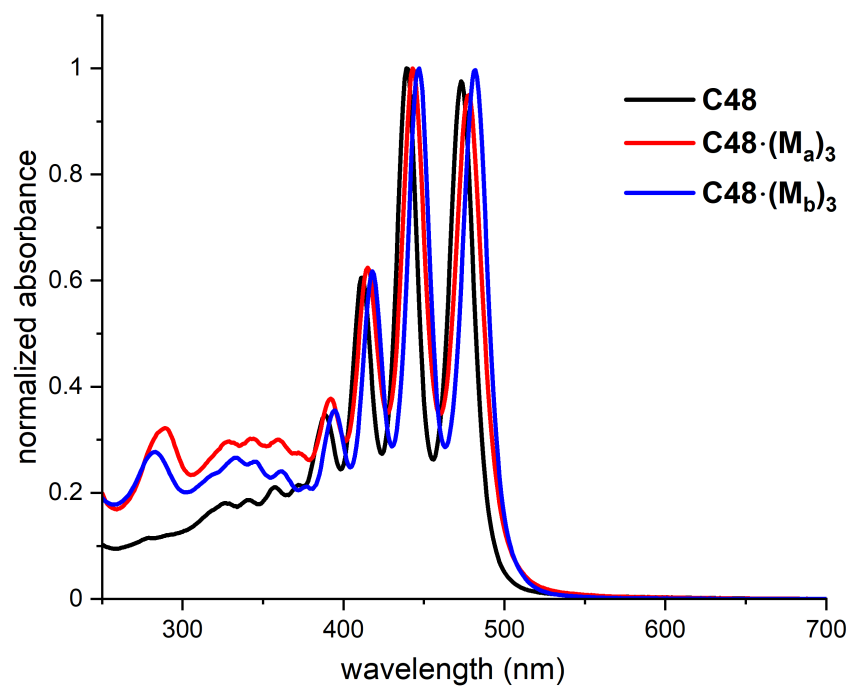
**Figure 6.** UV-vis spectra of masked polyrotaxanes (a)  $mC48 \cdot (M_a)_3$ ,  $mC68 \cdot (M_a)_4$ , and  $mC88 \cdot (M_a)_5$  and (b)  $mC28 \cdot (M_b)_2$ ,  $mC48 \cdot (M_b)_3$ , and  $mC68 \cdot (M_b)_4$  as measured in  $CHCl_3$  at room temperature.



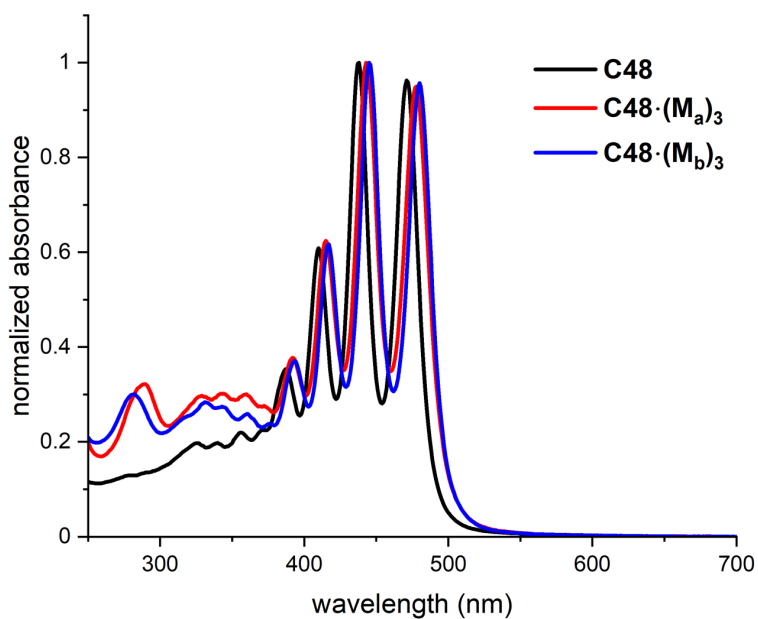
**Figure 7.** UV-vis spectra of masked catenanes  $mcC40 \cdot (M_a)_2$  and  $mcC80 \cdot (M_a)_4$  as measured in  $CHCl_3$  at room temperature.



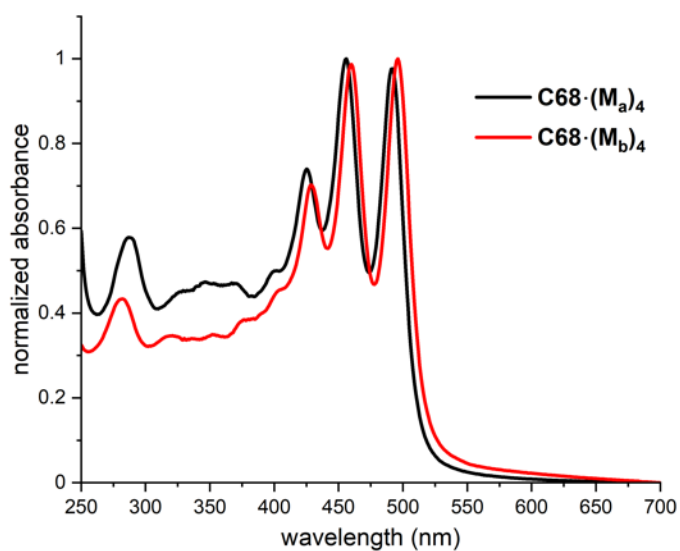
**Figure 8.** UV-vis spectra of polyyne [3]rotaxanes  $C28 \cdot (M_a)_2$  and  $C28 \cdot (M_b)_2$  as measured in  $CHCl_3$  at room temperature.



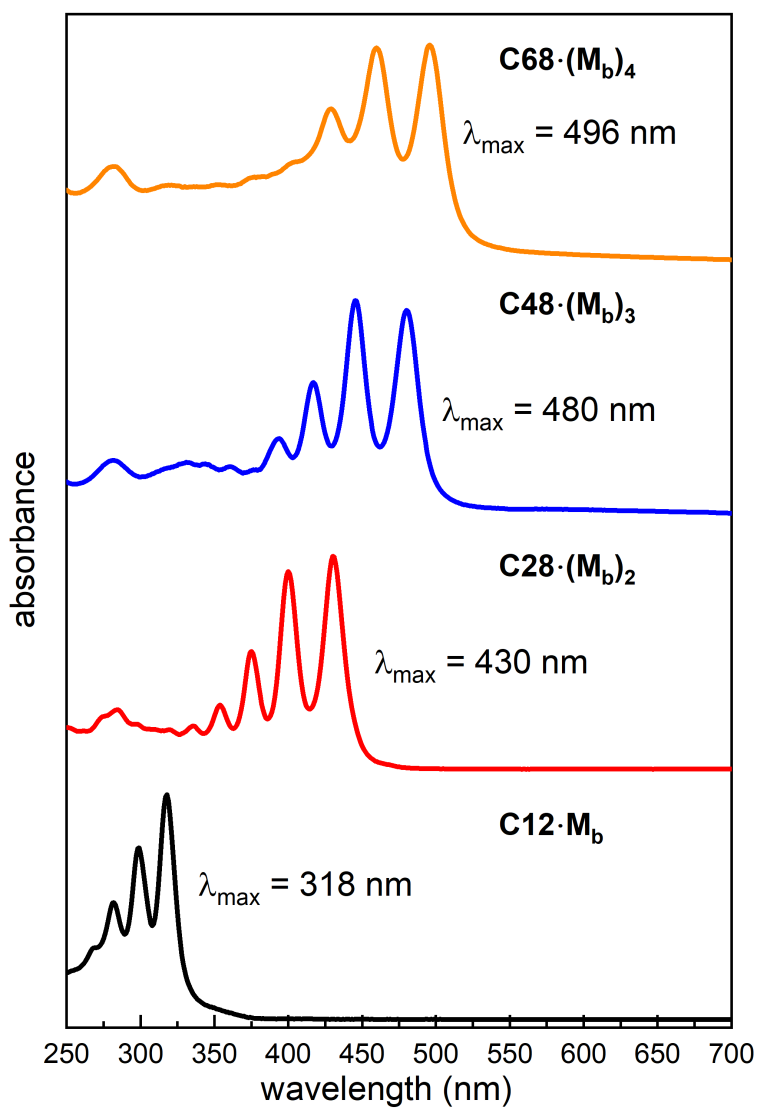
**Figure 9.** Normalized UV-vis spectra of polyynes **C48**, polyynes rotaxanes **C48·(M<sub>a</sub>)<sub>3</sub>** and **C48·(M<sub>b</sub>)<sub>3</sub>** as measured in CHCl<sub>3</sub> at room temperature.



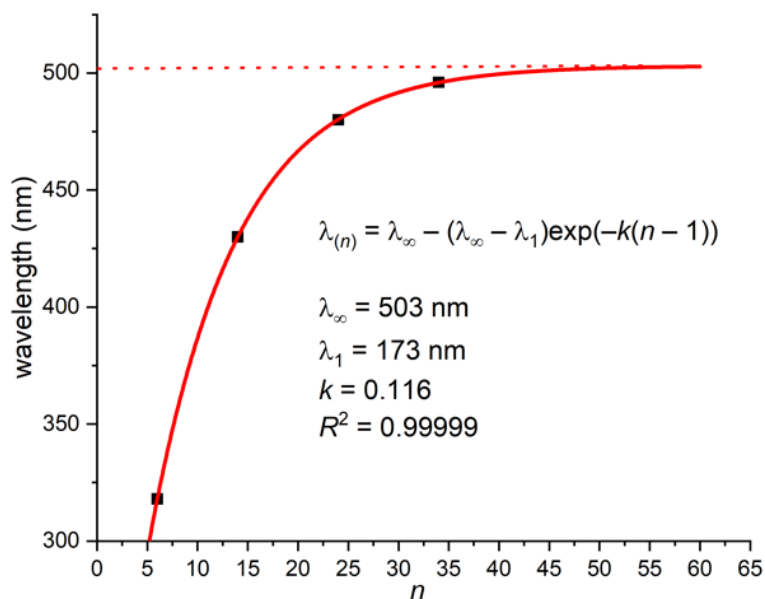
**Figure 10.** Normalized UV-vis spectra of polyynes **C48**, polyynes rotaxanes **C48·(M<sub>a</sub>)<sub>3</sub>** and **C48·(M<sub>b</sub>)<sub>3</sub>** as measured in CH<sub>2</sub>Cl<sub>2</sub> at room temperature.



**Figure 11.** Normalized UV-vis spectra of polyynes  $C68 \cdot (M_a)_4$  and  $C68 \cdot (M_b)_4$  as measured in  $CH_2Cl_2$  at room temperature.



**Figure 12.** UV-vis spectra of  $C12 \cdot M_b$ ,  $C28 \cdot (M_b)_2$ ,  $C48 \cdot (M_b)_3$ , and  $C68 \cdot (M_b)_4$  as measured in  $CH_2Cl_2$  at room temperature.



**Figure 13.** Convergence of  $\lambda_{\max}$  for the series of polyyne rotaxanes  $\text{C12}\cdot\text{M}_b$ ,  $\text{C28}\cdot(\text{M}_b)_2$ ,  $\text{C48}\cdot(\text{M}_b)_3$ , and  $\text{C68}\cdot(\text{M}_b)_4$  fitted to Meier equation  $\lambda(n) = \lambda_{\infty} - (\lambda_{\infty} - \lambda_1)e^{-k(n-1)}$ .

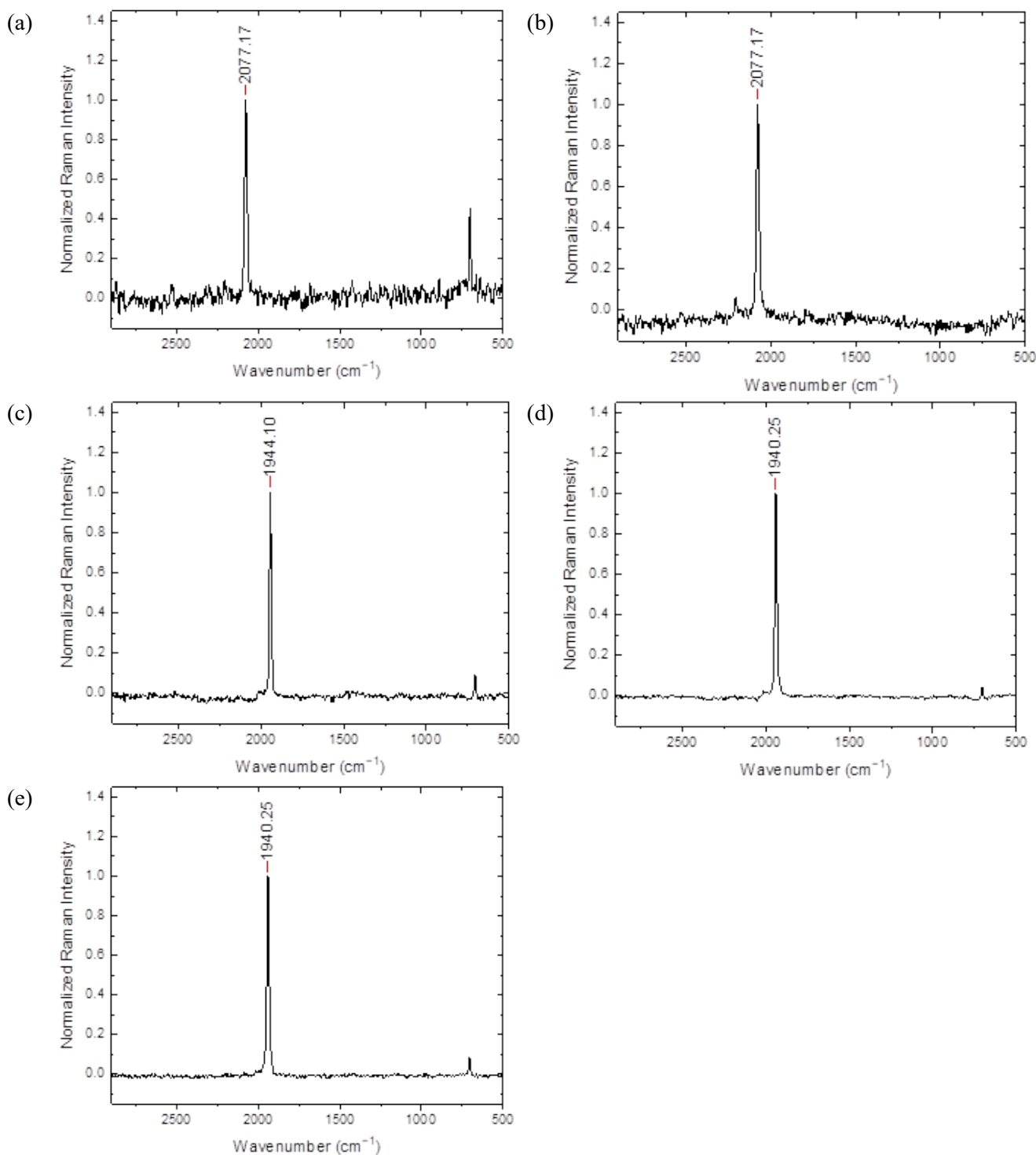
**Table 1.** Data analysis for **Figure 13** in the series of polyyne rotaxane with  $\text{M}_b$ .

$n$	$\lambda_{\max(\text{exp})}$	$\lambda_{\max(\text{cal})}$
6	318	318.0
14	430	429.9
24	480	480.2
34	496	495.9

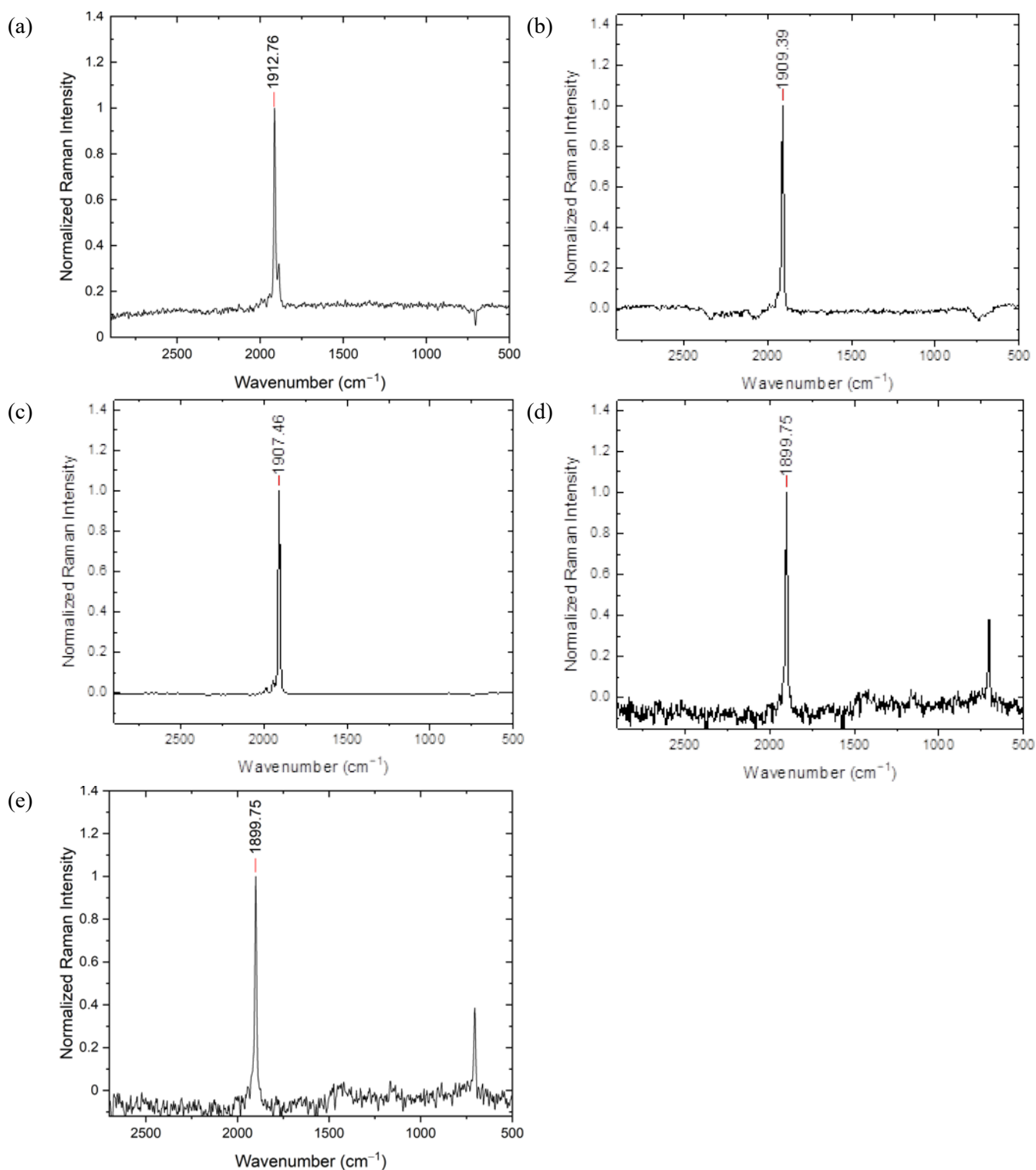
**Table 2.** Variables for equation  $\lambda(n) = \lambda_{\infty} - (\lambda_{\infty} - \lambda_1)e^{-k(n-1)}$  in **Figure 13** in the series of polyyne rotaxane incorporating  $\text{M}_b$ .

variable	value
$\lambda_{\infty}$	$503.1 \pm 0.3$
$\lambda_1$	$172.5 \pm 0.9$
$k$	$0.1160 \pm 0.0005$
$R^2$	0.99999

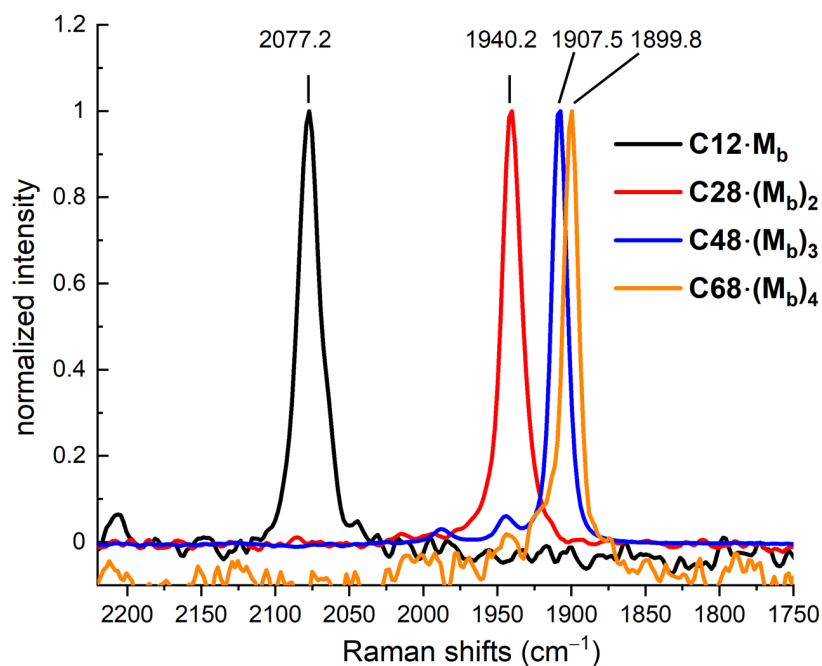
## Section 6: Raman Spectra



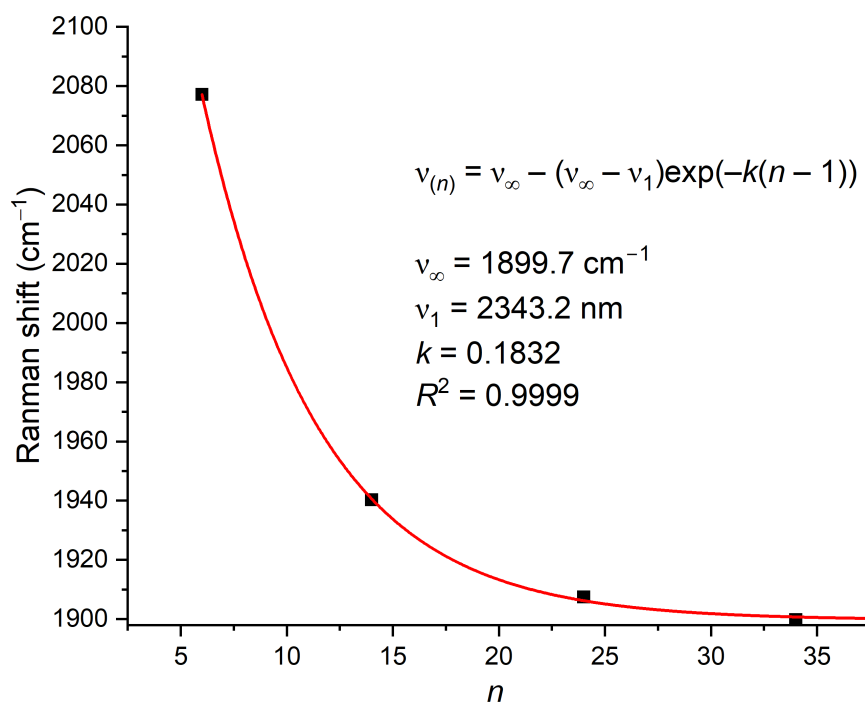
**Figure 14.** FT-Raman spectra of (a) polyyne dumbbell **C12**, laser power: 200 mW, 32 accumulations, (b) polyyne rotaxane **C12·M<sub>b</sub>**, laser power: 200 mW, 32 accumulations, (c) polyyne dumbbell **C28**, laser power: 200 mW, 64 accumulations, (d) polyyne rotaxane **C28·(M<sub>a</sub>)<sub>2</sub>**, laser power: 50 mW, 64 accumulations, and (e) polyyne rotaxane **C28·(M<sub>b</sub>)<sub>2</sub>**, laser power: 50 mW, 64 accumulations; all measured in CH<sub>2</sub>Cl<sub>2</sub> (ca. 1 mM) at room temperature; excitation: 1064 nm, spectral resolution: 4 cm<sup>-1</sup>. Prior to analysis and normalization, the Raman spectra were baseline-corrected by subtracting a third order polynomial curve, using Origin software. The peak at 704 cm<sup>-1</sup> can be assigned to the CH<sub>2</sub>Cl<sub>2</sub> solvent.



**Figure 15.** FT-Raman spectra of (a) **C48**, laser power: 100 mW, 32 accumulations; polyynes rotaxanes (b) **C48·(M<sub>a</sub>)<sub>3</sub>**, laser power: 100 mW, 32 accumulations, (c) **C48·(M<sub>b</sub>)<sub>3</sub>**, laser power: 50 mW, 64 accumulations, (d) **C68·(M<sub>a</sub>)<sub>4</sub>**, laser power: 50 mW, 64 accumulations and (e) **C68·(M<sub>b</sub>)<sub>4</sub>**, laser power: 100 mW, 128 accumulations; all measured in CH<sub>2</sub>Cl<sub>2</sub> (ca. 1 mM) at room temperature; excitation: 1064 nm, spectral resolution: 4 cm<sup>-1</sup>. Prior to analysis and normalization, the Raman spectra were baseline-corrected by subtracting a third order polynomial curve, using Origin software. The peak at 704 cm<sup>-1</sup> can be assigned to the CH<sub>2</sub>Cl<sub>2</sub> solvent.



**Figure 16.** Normalized FT-Raman spectra of  $C_{12}\cdot M_b$ ,  $C_{28}\cdot(M_b)_2$ ,  $C_{48}\cdot(M_b)_3$ , and  $C_{68}\cdot(M_b)_4$  as measured in  $CH_2Cl_2$  (ca. 1 mM) at room temperature; excitation: 1064 nm, spectral resolution:  $4\text{ cm}^{-1}$ .



**Figure 17.** Convergence of Raman shifts for the series of polyynes incorporating  $M_b$  by using the Meier equation  $v(n) = v_{\infty} - (v_{\infty} - v_1)e^{-k(n-1)}$ . The experimental Raman shift of compound  $C_{68}\cdot(M_b)_4$  happens to equal the predicted value of  $v_{\infty}$   $1900\text{ cm}^{-1}$  for infinite length, which illustrates the fact that the shift saturated at a length of ca. 68 sp-carbons.

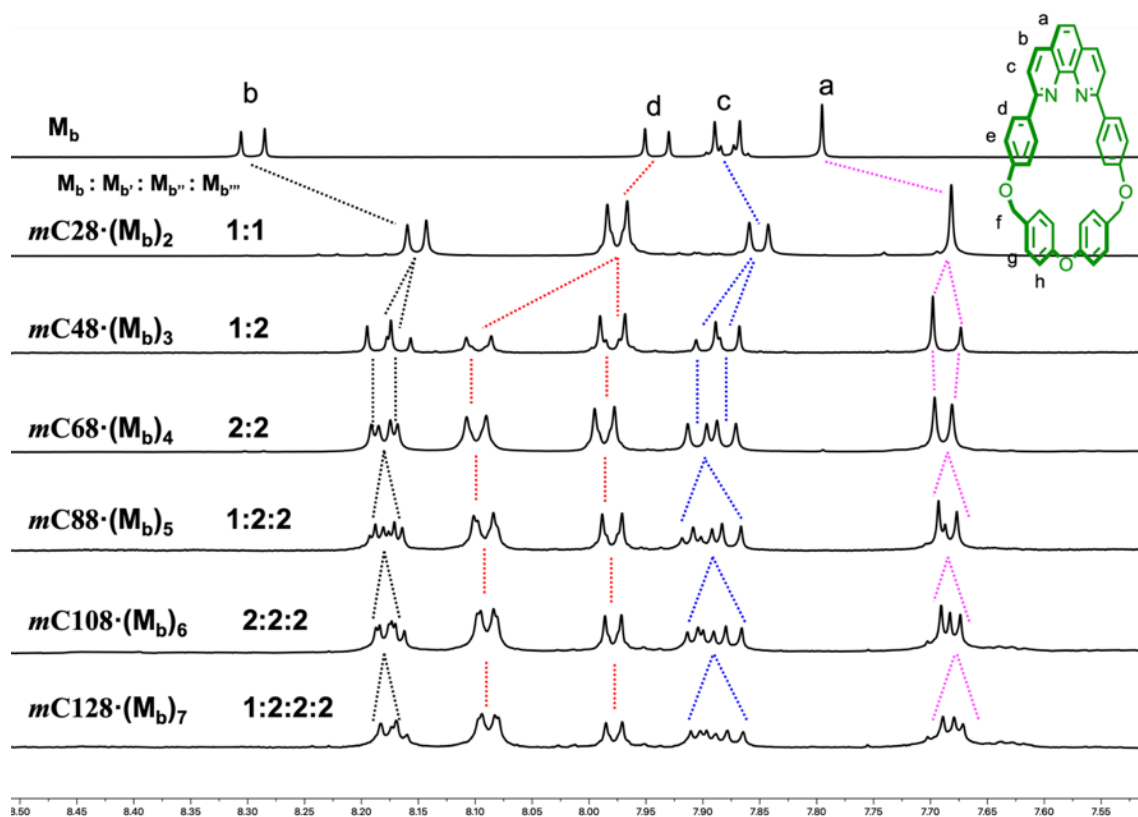
**Table 3.** Data analysis for **Figure 17** in the series of polyynes rotaxane incorporating **M<sub>b</sub>**.

<i>n</i>	<i>v</i> (exp)	<i>v</i> (cal)
6	2077.2	2077.2
14	1940.3	1940.7
24	1907.5	1906.2
34	1899.7	1900.7

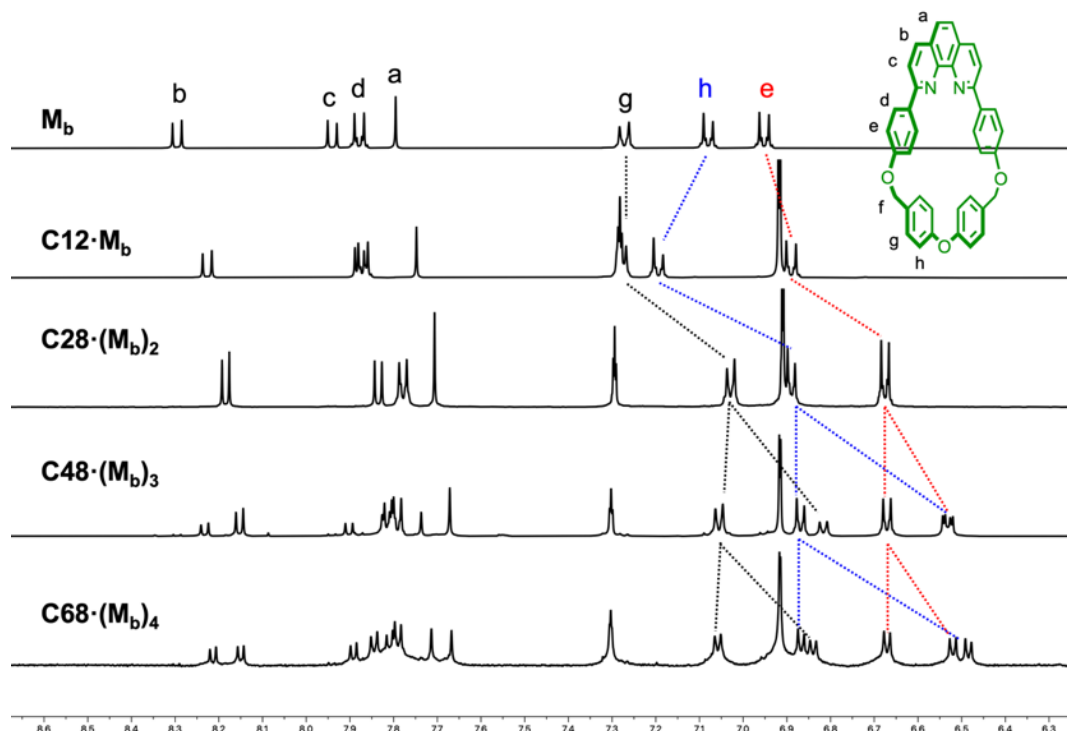
**Table 4.** Variables for equation  $v(n) = v_{\infty} - (v_{\infty} - v_1)e^{-k(n-1)}$  in **Figure 17** in the series of polyynes rotaxane incorporating **M<sub>b</sub>**.

<b>variable</b>	<b>value</b>
$v_{\infty}$	$1899.7 \pm 1.4$
$v_1$	$2343.2 \pm 14.8$
$k$	$0.1832 \pm 0.0067$
$R^2$	0.99987

## Section 7: Comparison of NMR Spectra



**Figure 18.** Comparison of partial  $^1\text{H}$  NMR spectra (8.5–7.5 ppm) of  $\text{M}_b$  (400 MHz) and masked poly[ $n$ ]rotaxanes ( $n = 3-8$ )  $m\text{C}28 \cdot (\text{M}_b)_2$  (500 MHz),  $m\text{C}48 \cdot (\text{M}_b)_3$  (400 MHz),  $m\text{C}68 \cdot (\text{M}_b)_4$  (500 MHz),  $m\text{C}88 \cdot (\text{M}_b)_5$  (500 MHz),  $m\text{C}108 \cdot (\text{M}_b)_6$  (600 MHz), and  $m\text{C}128 \cdot (\text{M}_b)_7$  (600 MHz) in  $\text{CD}_2\text{Cl}_2$ .

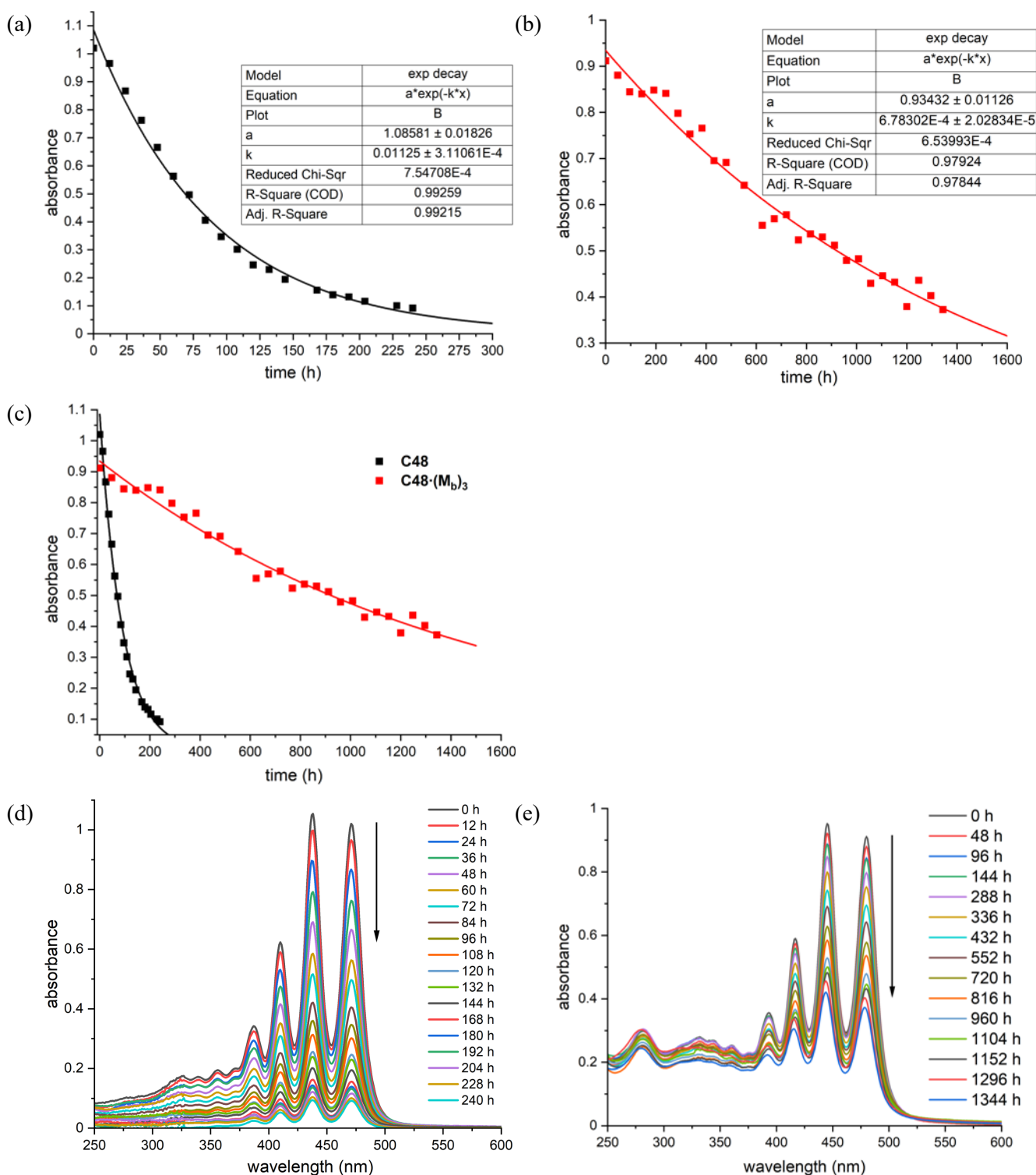


**Figure 19.** Comparison of partial  $^1\text{H}$  NMR spectra (8.6–6.3 ppm) of macrocycle  $\text{M}_b$  (400 MHz) and polyynes rotaxanes  $\text{C}12 \cdot \text{M}_b$  (400 MHz),  $\text{C}28 \cdot (\text{M}_b)_2$  (500 MHz),  $\text{C}48 \cdot (\text{M}_b)_3$  (500 MHz), and  $\text{C}68 \cdot (\text{M}_b)_4$  (600 MHz) in  $\text{CD}_2\text{Cl}_2$ .

## **Section 8: Solid-State Thermal Stability**

Stability tests were performed for solid-state samples of the polyynes dumbbell **C48** and polyynes rotaxanes **C48·(M<sub>b</sub>)<sub>3</sub>** at 30 °C. To perform this experiment, concentrated solutions of **C48** and **C48·(M<sub>b</sub>)<sub>3</sub>** in CH<sub>2</sub>Cl<sub>2</sub> were prepared, such that diluting 50 μL of the concentrated solution into 1.5 mL of CH<sub>2</sub>Cl<sub>2</sub> in a cuvette with a pathlength of 10 mm gave a UV-vis absorption spectrum with an optical density of ca. 1 at λ<sub>max</sub>. About 80 samples were prepared by transferring 50 μL of the concentrated solution into 80 vials. The solvent in each vial was evaporated and the residue was dried under high vacuum for ca. 10 min. These solid samples were then stored in an oven at 30 °C, wrapped with aluminum foil to shield from light. Three parallel measurements were recorded for each compound. **C48** and **C48·(M<sub>b</sub>)<sub>3</sub>** samples were dissolved in CH<sub>2</sub>Cl<sub>2</sub> and analyzed by UV-vis absorption spectroscopy at each 12 h interval and 48 h interval, respectively. Data points were averaged over three parallel measurements, because the solid films were formed unevenly on the wall of glass vials, resulting in some variation in the rate of decomposition.

The thermal decomposition was fitted to a first-order decay model,  $A(t) = a \cdot \exp(-kt)$ . For the polyynes dumbbell **C48**, the fit is excellent with  $R^2 = 0.99$ , giving the decaying rate of  $k = 0.01125 \text{ h}^{-1}$ ; half-life of  $t_{1/2} = 62 \text{ h}$  (**Figure 20a**). For the polyynes rotaxane **C48·(M<sub>b</sub>)<sub>3</sub>**, the fit is excellent with  $R^2 = 0.98$  giving  $k = 0.000678 \text{ h}^{-1}$ ; half lifetime of  $t_{1/2} = 1022 \text{ h}$  (**Figure 20b**). These results show that the polyynes rotaxane is 16.5 times more stable than the polyynes dumbbell. The plots in Figure 4 are the same as those in Figure 20a-c, except that in Figure 4 the absorbance is normalized, by dividing by  $a$ , to make it easier to compare the decay curves.



**Figure 20.** (a) Plot of UV-vis absorbance decay for solid-state polyne dumbbell **C48** monitored at  $\lambda_{\max} = 471$  nm over a period of 240 h at 30 °C, as measured in  $\text{CH}_2\text{Cl}_2$ . (b) Plot of UV-vis absorbance decay for solid-state polyne rotaxane **C48·(M<sub>b</sub>)<sub>3</sub>** monitored at  $\lambda_{\max} = 480$  nm over a period of 1344 h at 30 °C. An overlaid plot of absorbance of **C48** and **C48·(M<sub>b</sub>)<sub>3</sub>** from (a) and (b) is plotted in (c) to aid comparison. Selected UV-vis spectra during the decomposition process of (d) polyne dumbbell **C48** and (e) polyne rotaxane **C48·(M<sub>b</sub>)<sub>3</sub>**.

## Section 9: NMR Spectra

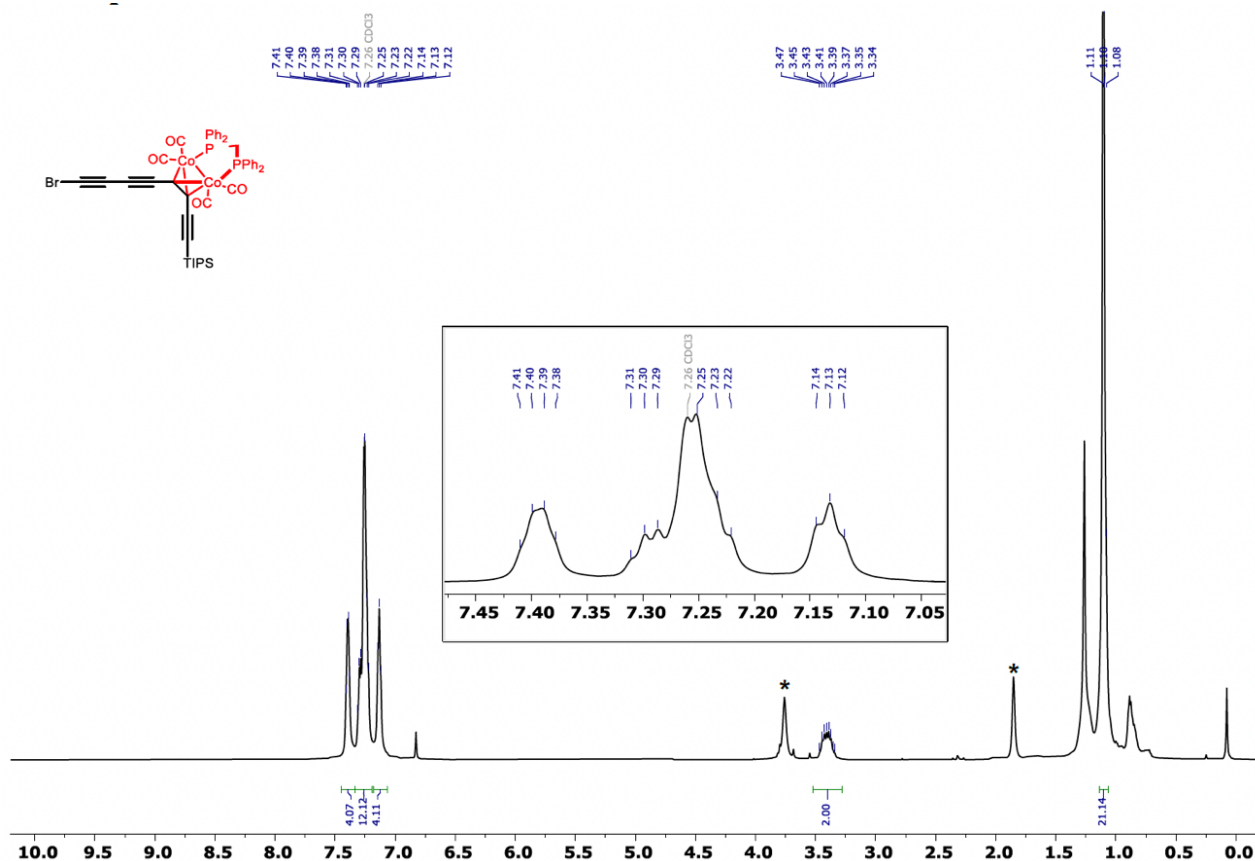


Figure 21.  $^1\text{H}$  NMR (600 MHz) spectrum of compound 2 in  $\text{CDCl}_3$  (\*indicates residual THF solvent).

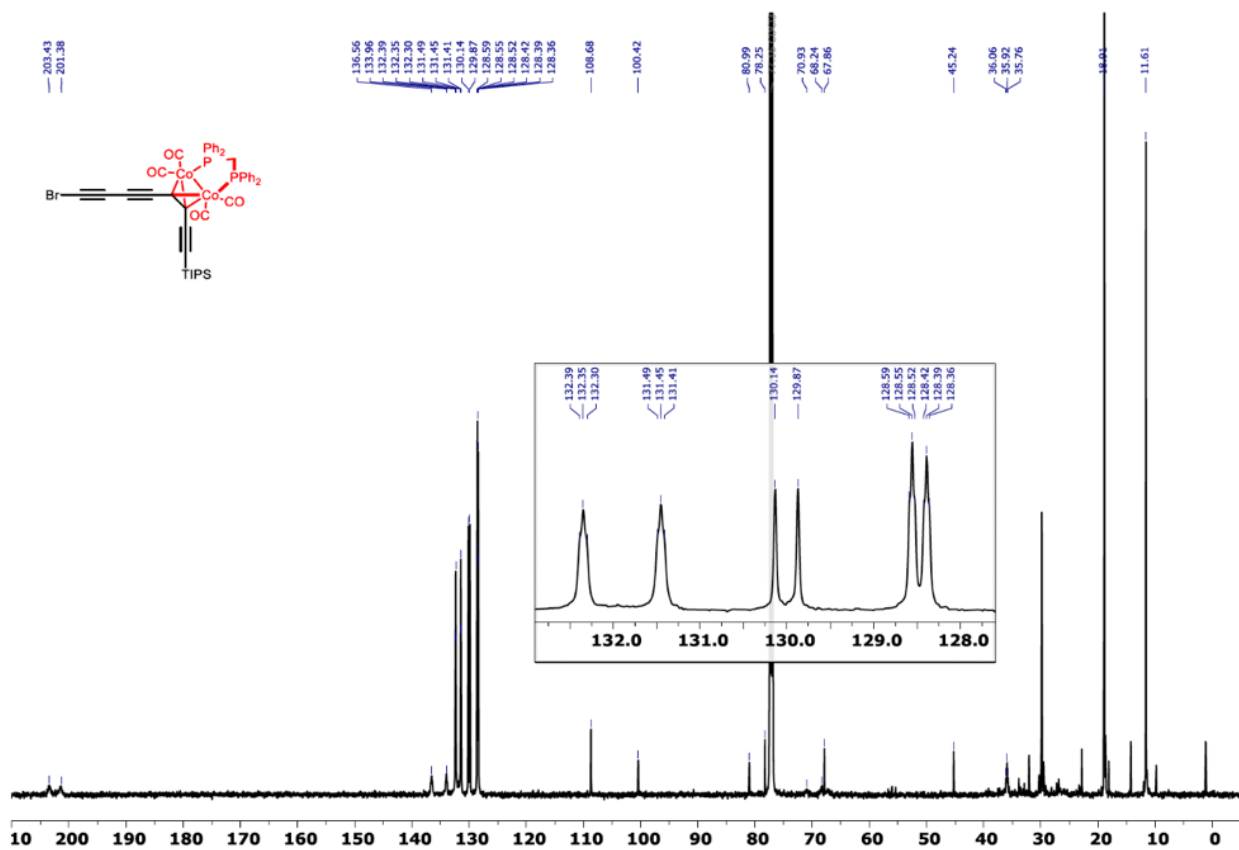


Figure 22.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound 2 in  $\text{CDCl}_3$ .

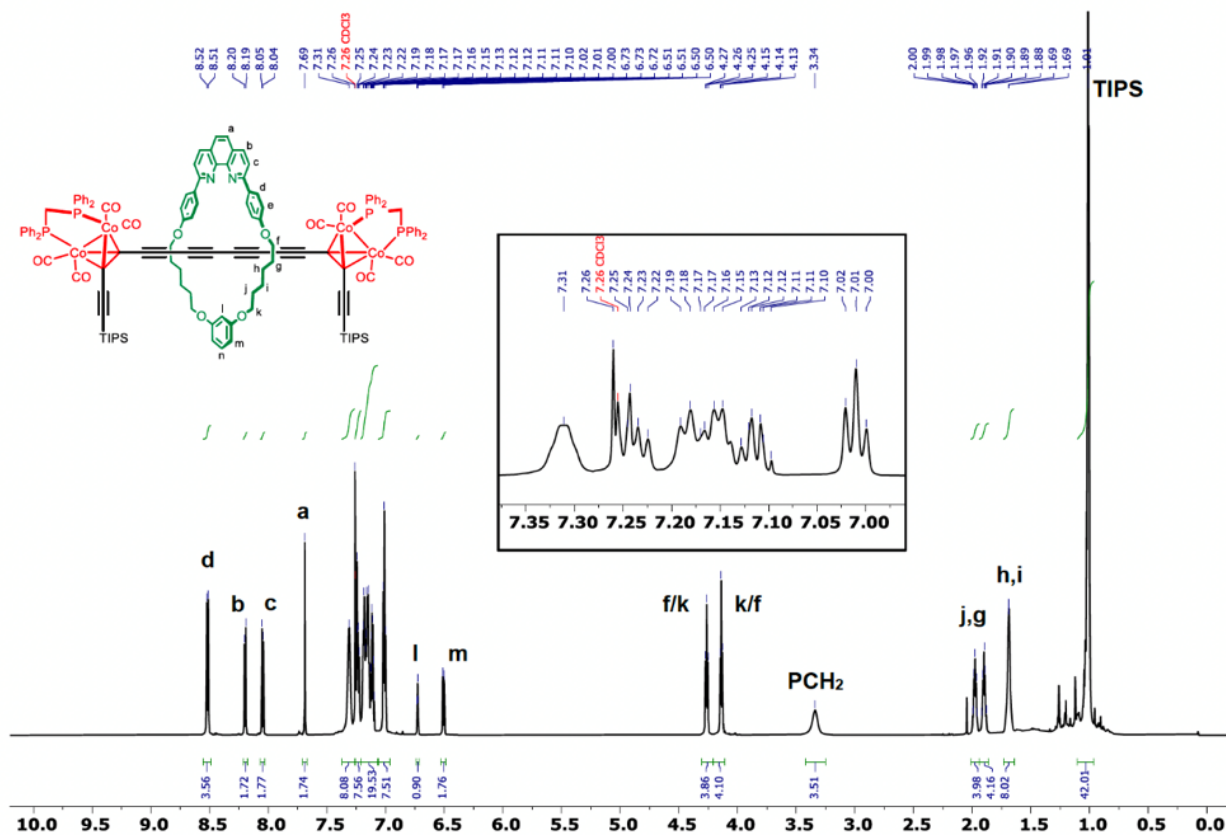


Figure 23.  $^1\text{H}$  NMR (600 MHz) spectrum of compound  $3 \cdot \text{M}_a$  in  $\text{CD}_2\text{Cl}_2$ .

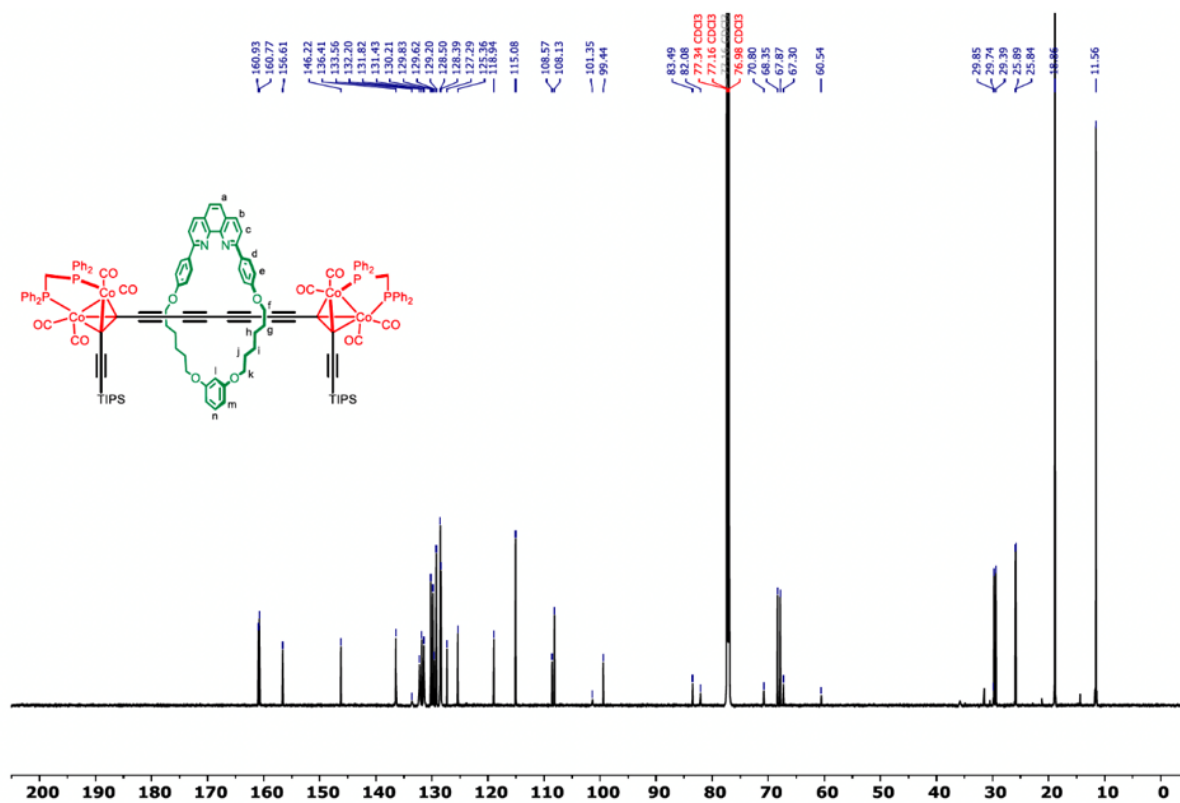


Figure 24.  $^{13}\text{C}\{^1\text{H}\}$  NMR (MHz) spectrum of compound  $3 \cdot \text{M}_a$  in  $\text{CD}_2\text{Cl}_2$ .

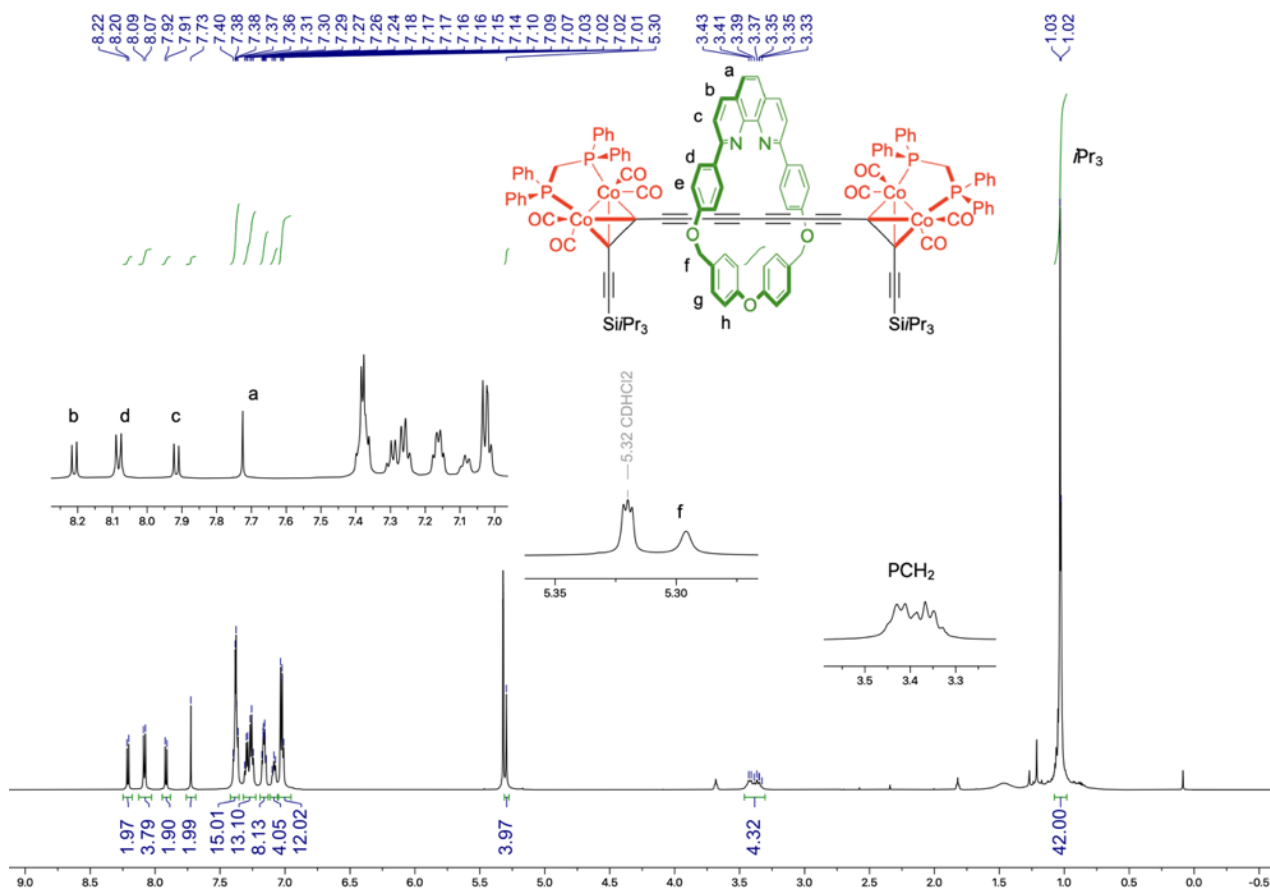


Figure 25.  $^1\text{H}$  NMR (600 MHz) spectrum of compound  $3 \cdot \text{M}_b$  in  $\text{CD}_2\text{Cl}_2$ .

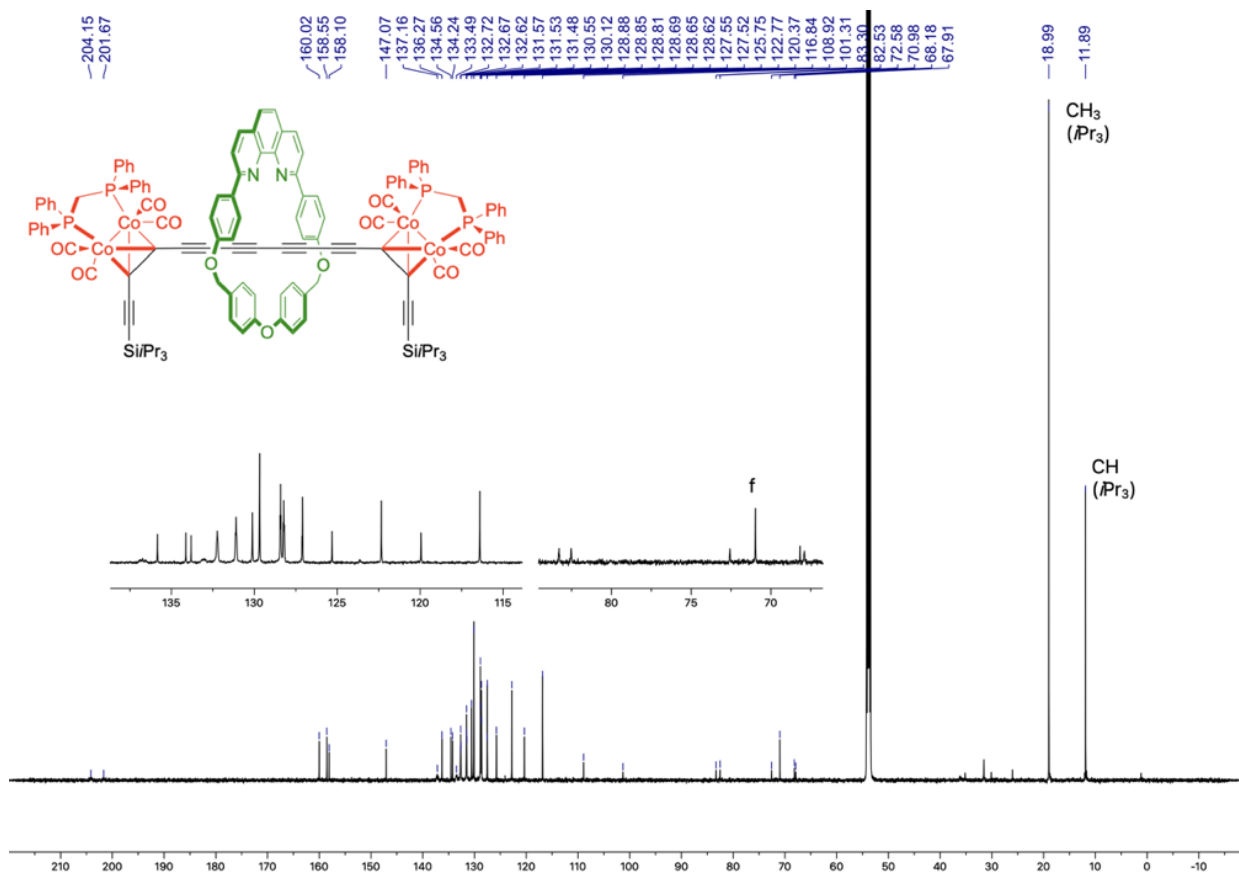


Figure 26.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound  $3 \cdot \text{M}_b$  in  $\text{CD}_2\text{Cl}_2$ .

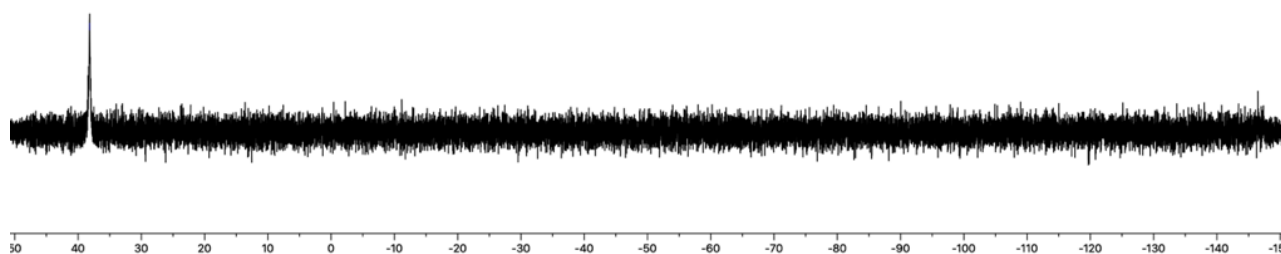


Figure 27.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz) spectrum of compound  $3 \cdot \text{M}_b$  in  $\text{CD}_2\text{Cl}_2$ .

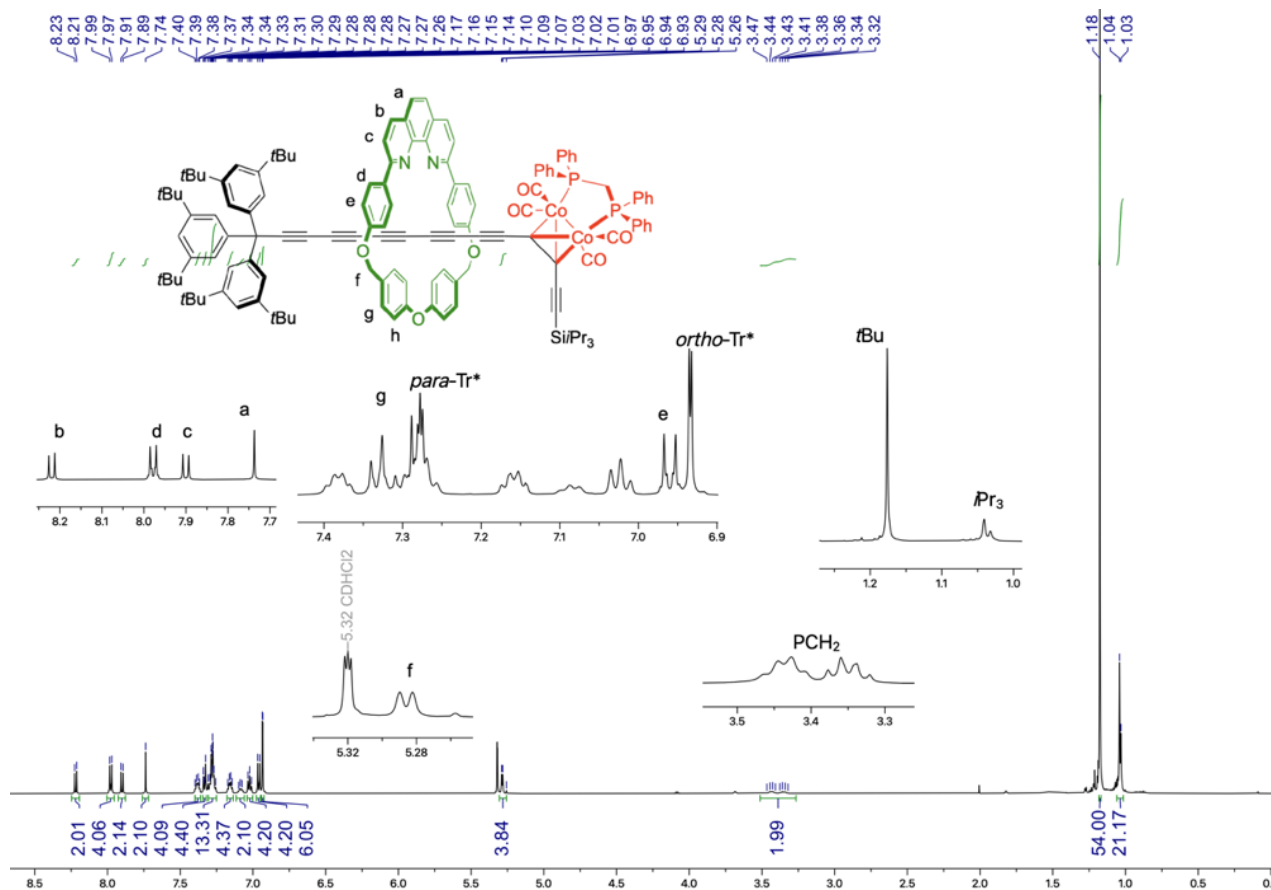
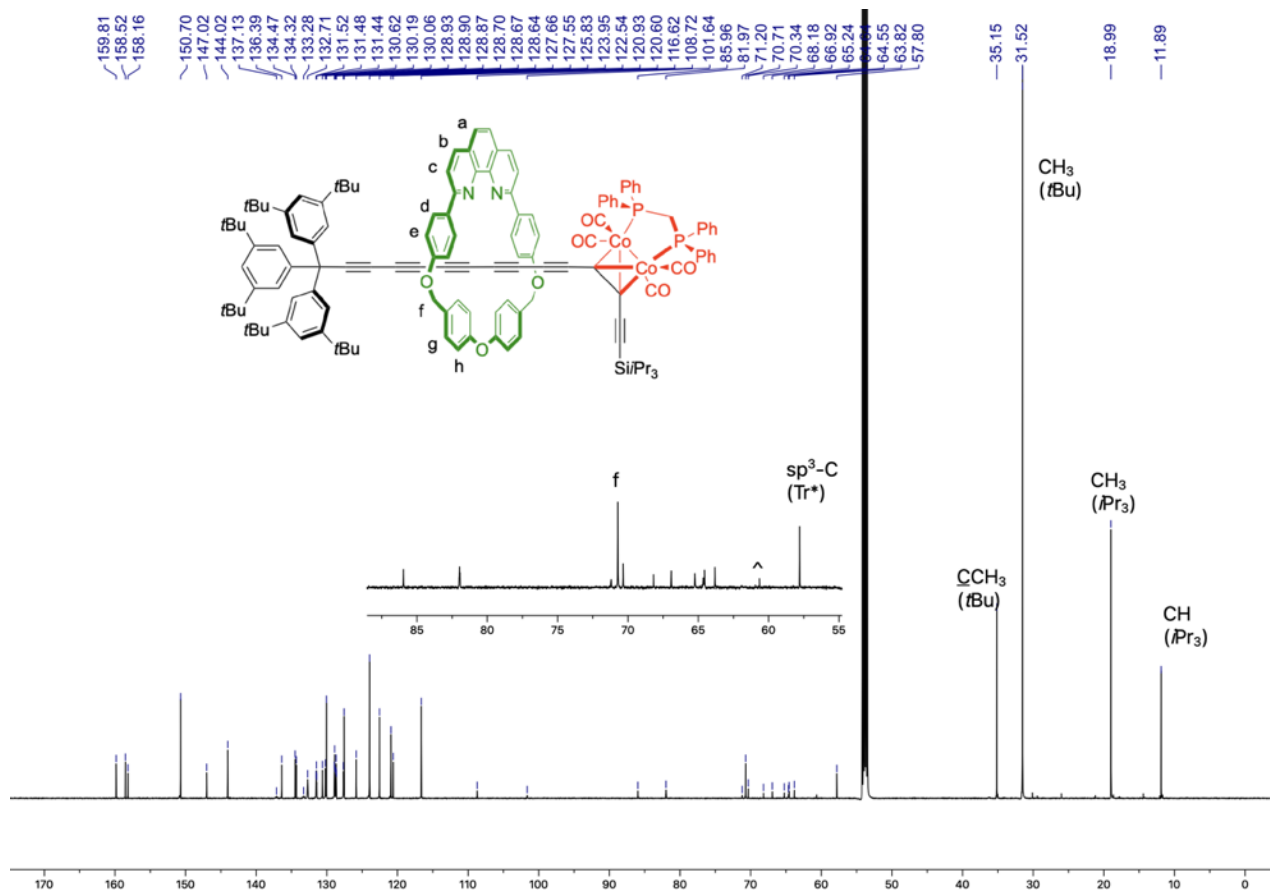
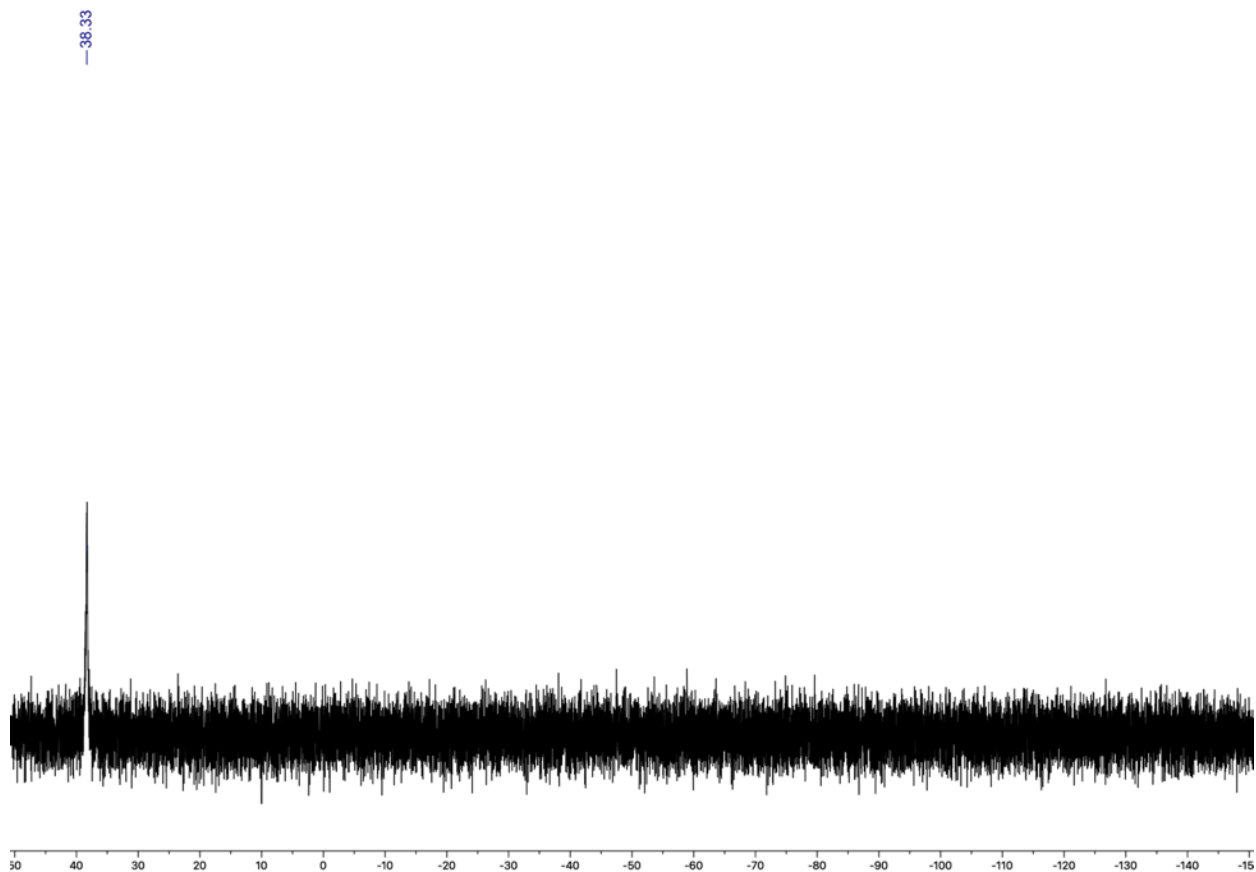


Figure 28.  $^1\text{H}$  NMR (600 MHz) spectrum of compound  $\text{S}3 \cdot \text{M}_b$  in  $\text{CD}_2\text{Cl}_2$ .



**Figure 29.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound  $\text{S3}\cdot\text{M}_b$  in  $\text{CD}_2\text{Cl}_2$  (^ indicates residual ethyl acetate).



**Figure 30.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz) spectrum of compound  $\text{S3}\cdot\text{M}_b$  in  $\text{CD}_2\text{Cl}_2$ .

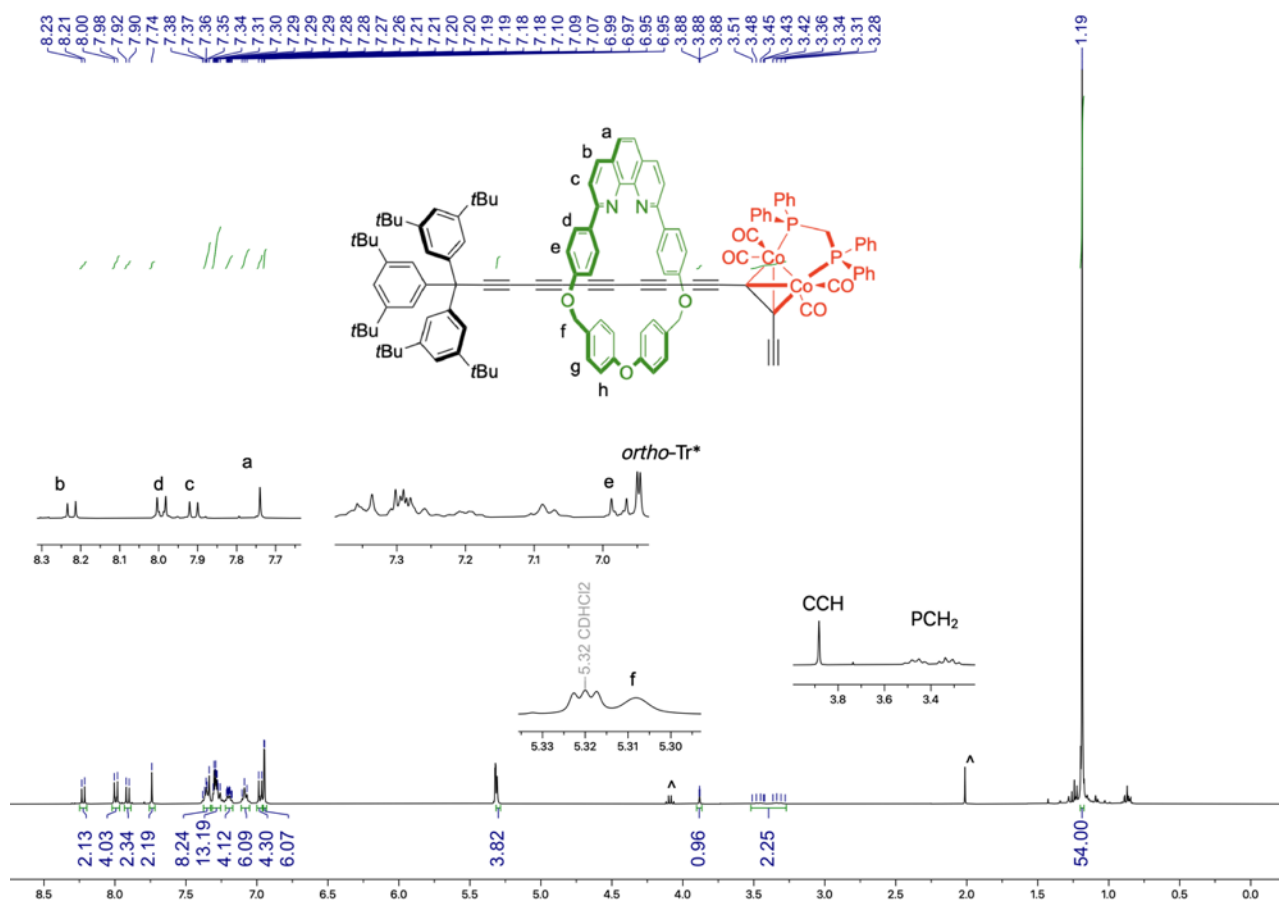


Figure 31.  $^1\text{H}$  NMR (400 MHz) spectrum of compound  $7 \cdot \text{M}_b$  in  $\text{CD}_2\text{Cl}_2$  (^ indicates residual ethyl acetate).

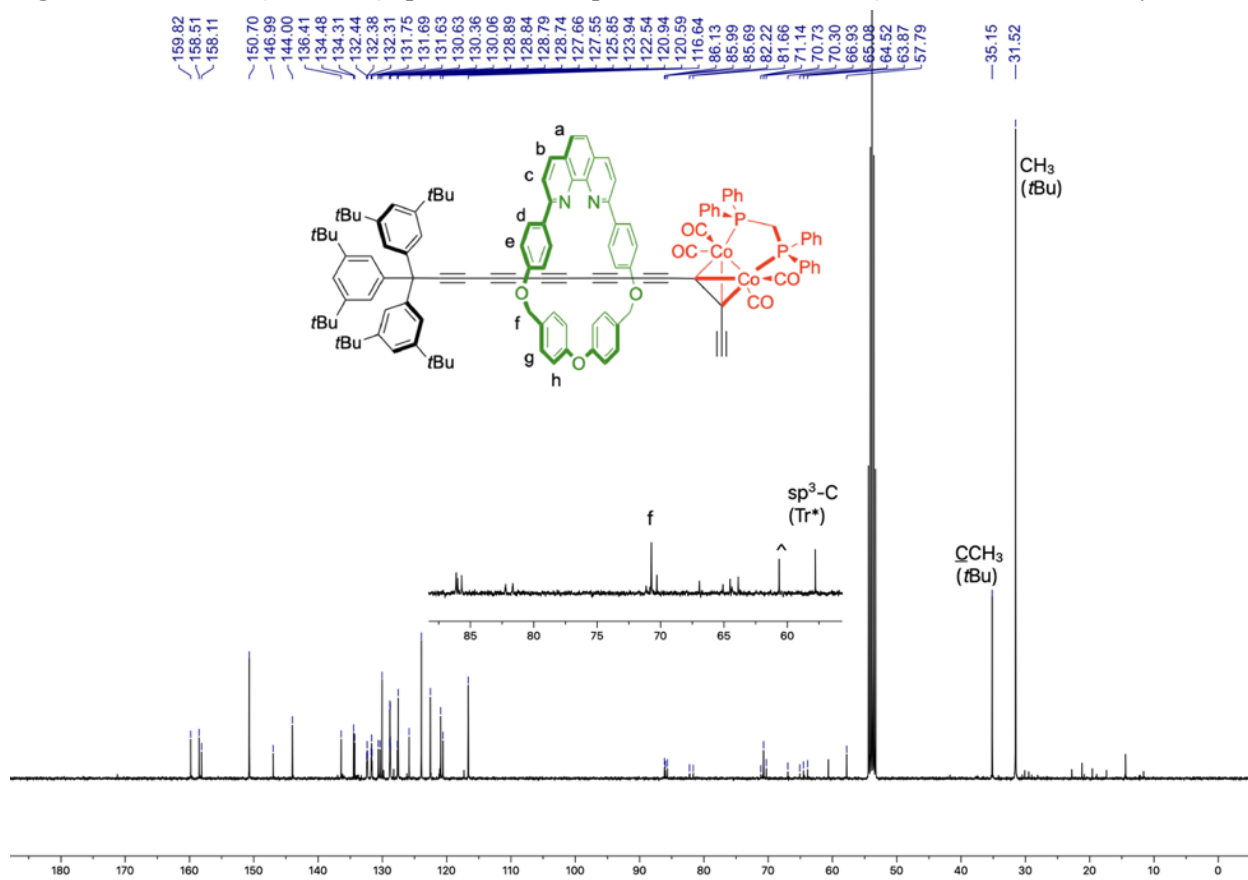


Figure 32.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz) spectrum of compound  $7 \cdot \text{M}_b$  in  $\text{CD}_2\text{Cl}_2$  (^ indicates residual ethyl acetate).



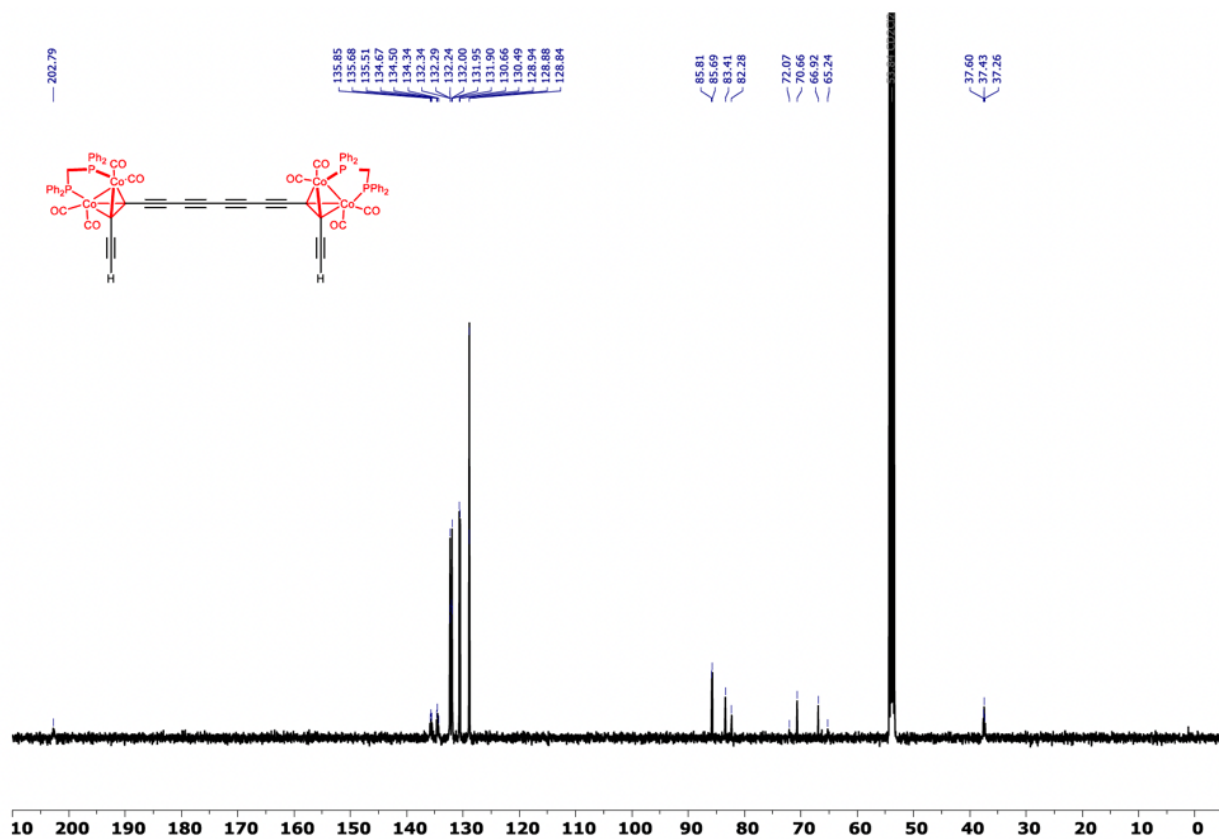


Figure 35.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz) spectrum of compound **4** in  $\text{CD}_2\text{Cl}_2$ .

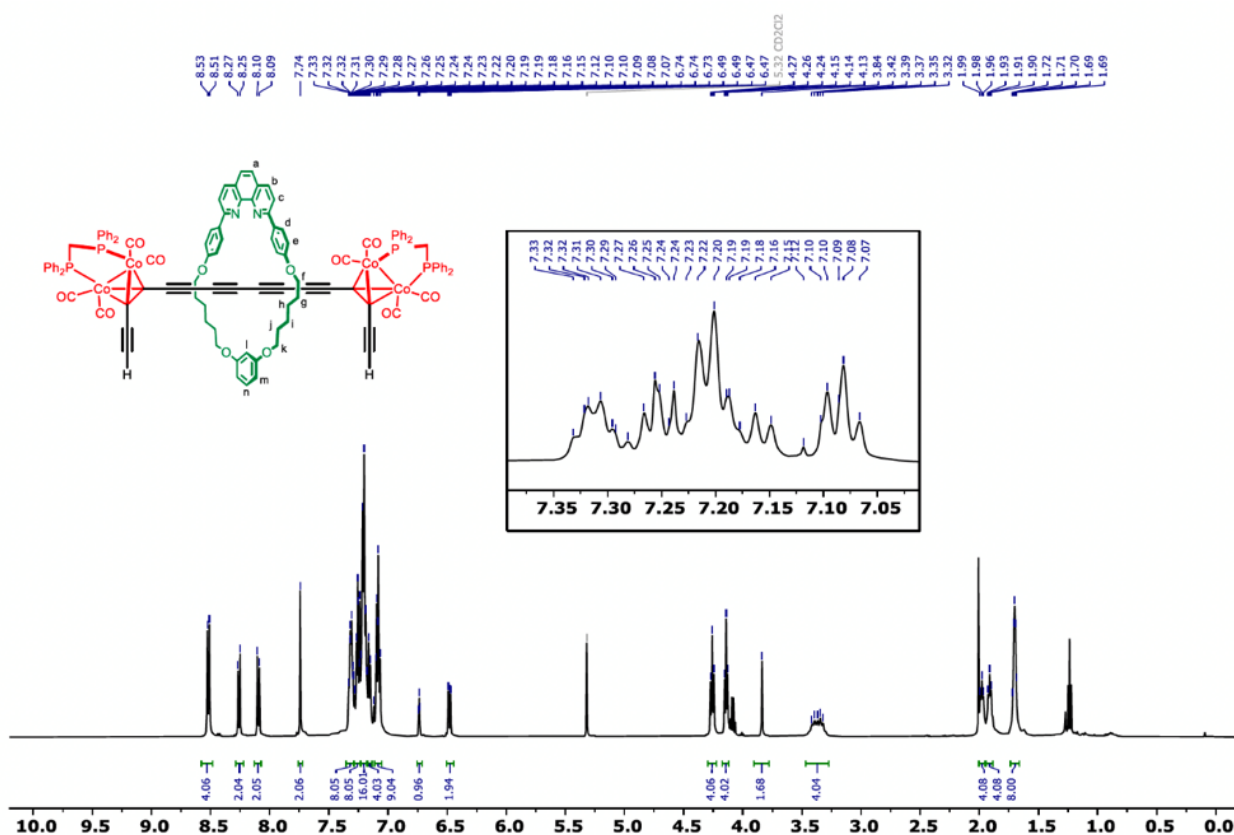


Figure 36.  $^1\text{H}$  NMR (500 MHz) spectrum of compound **4**· $\text{M}_a$  in  $\text{CD}_2\text{Cl}_2$ .

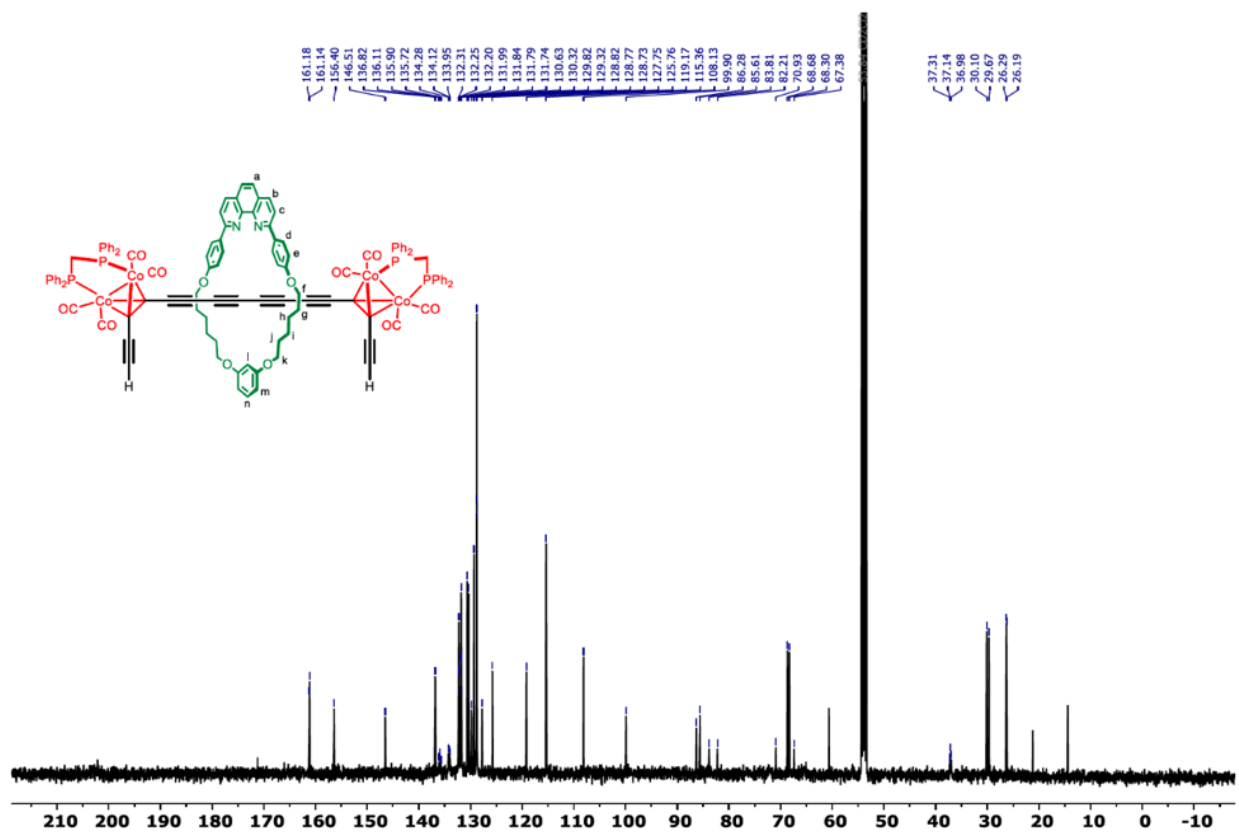


Figure 37.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz) spectrum of compound 4·Ma in  $\text{CD}_2\text{Cl}_2$ .

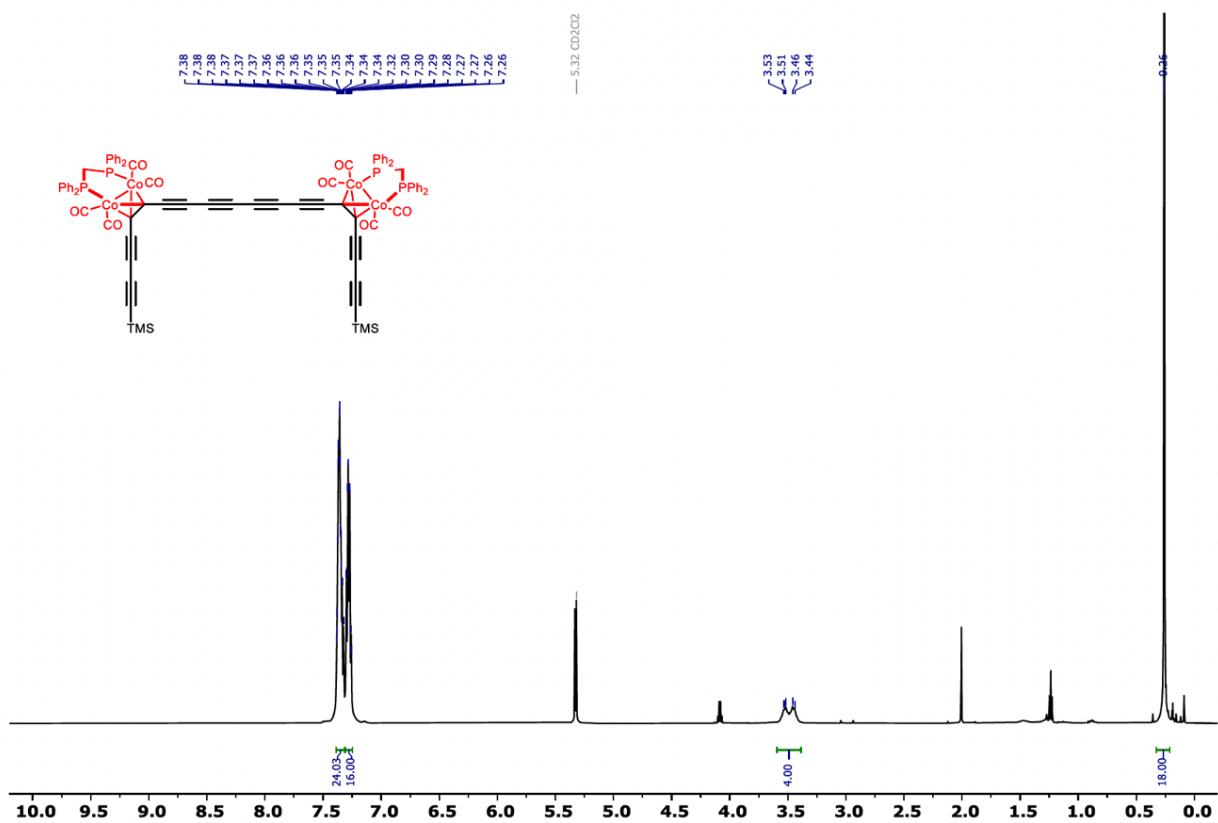


Figure 38.  $^1\text{H}$  NMR (600 MHz) spectrum of compound 5 in  $\text{CD}_2\text{Cl}_2$ .

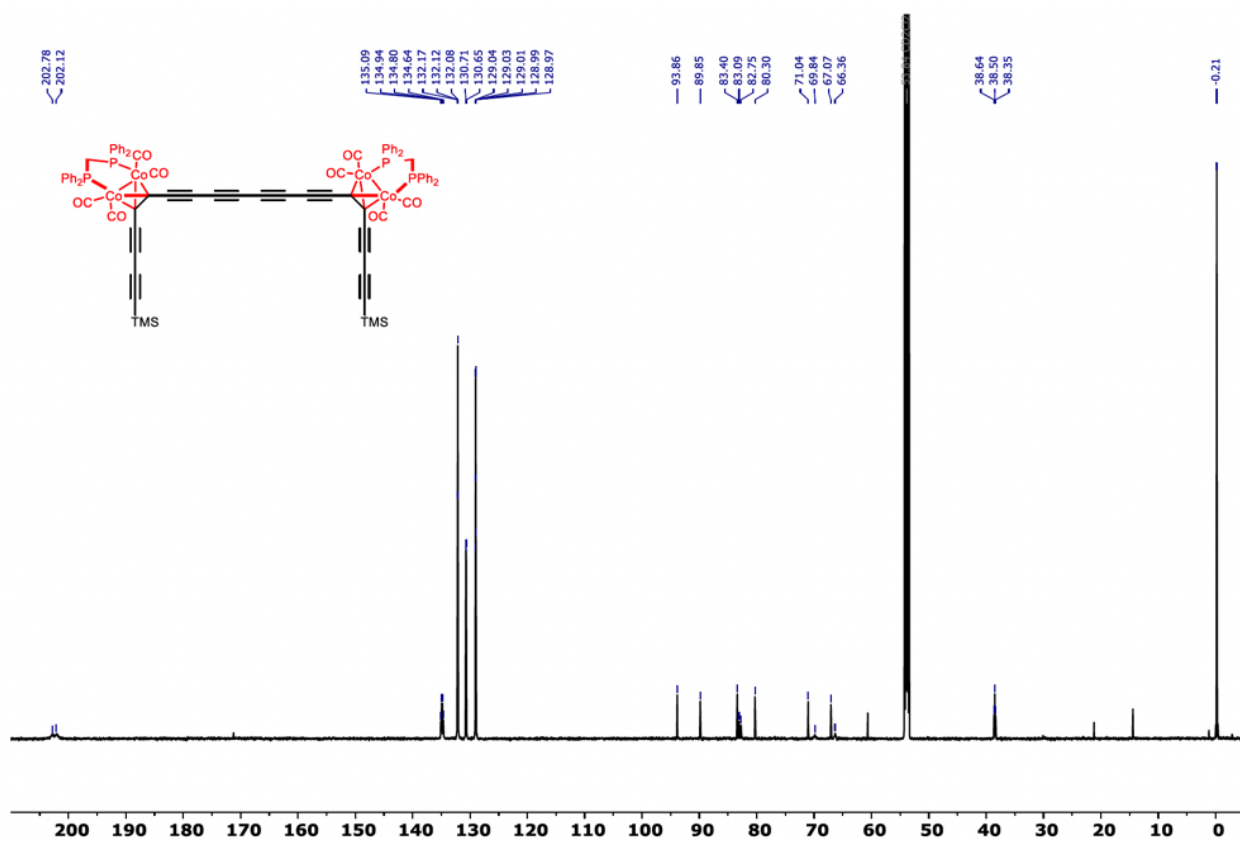


Figure 39.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound **5** in  $\text{CD}_2\text{Cl}_2$ .

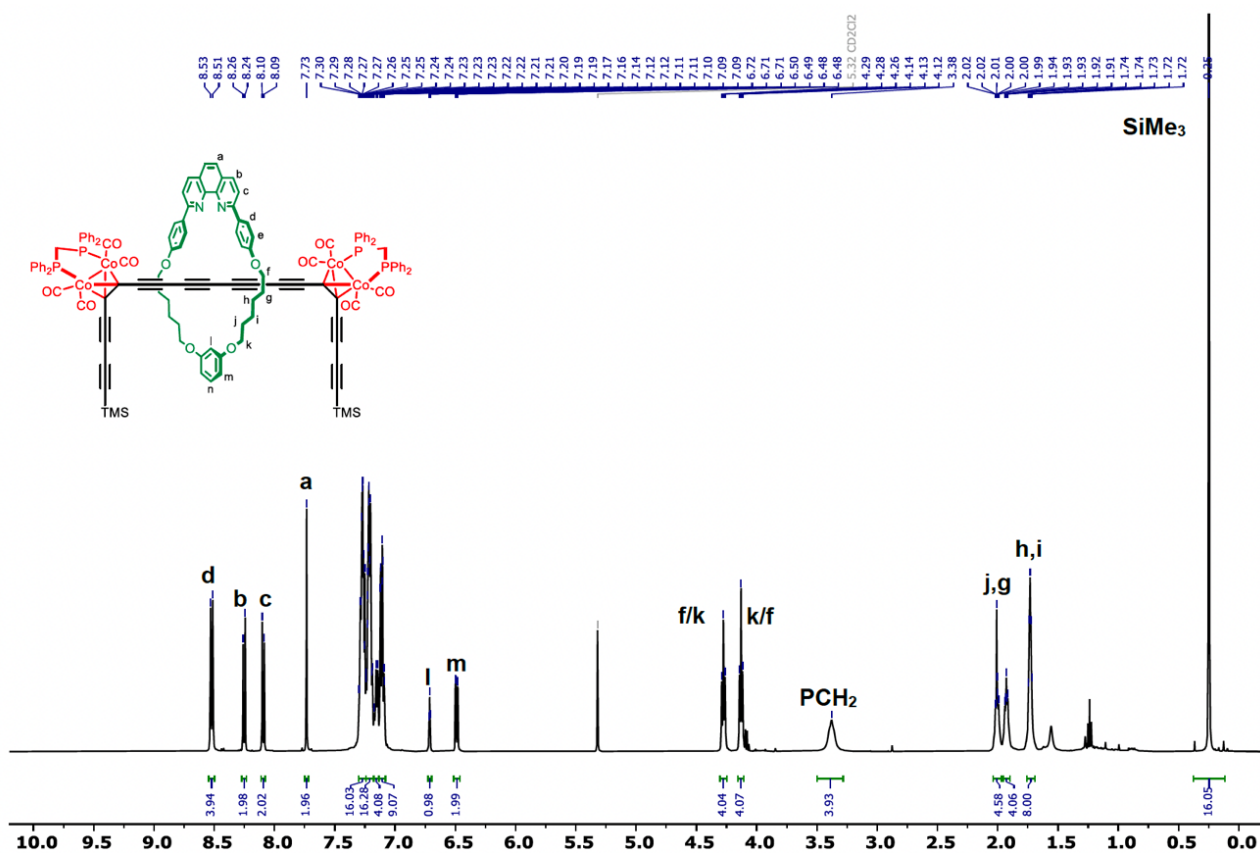


Figure 40.  $^1\text{H}$  NMR (500 MHz) spectrum of compound **5·M<sub>a</sub>** in  $\text{CD}_2\text{Cl}_2$ .

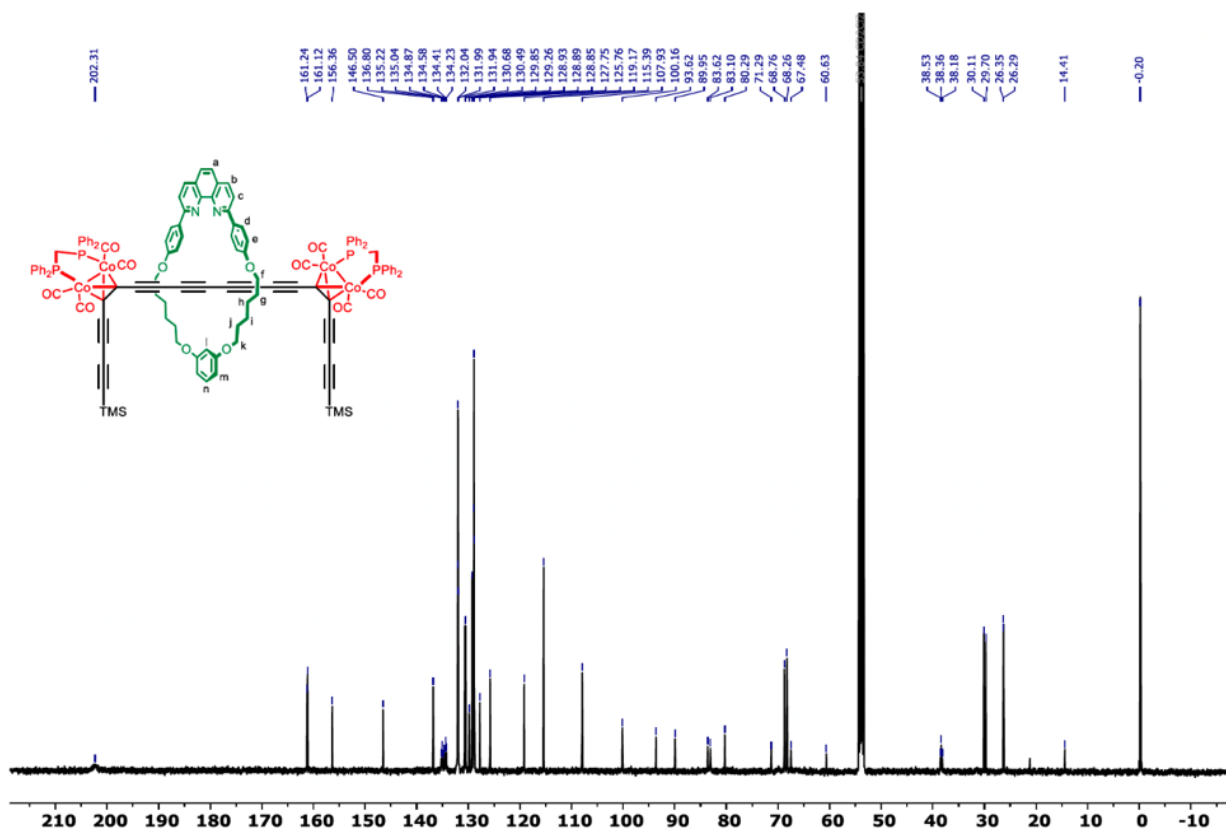


Figure 41.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz) spectrum of compound  $5 \cdot \text{M}_a$  in  $\text{CD}_2\text{Cl}_2$ .

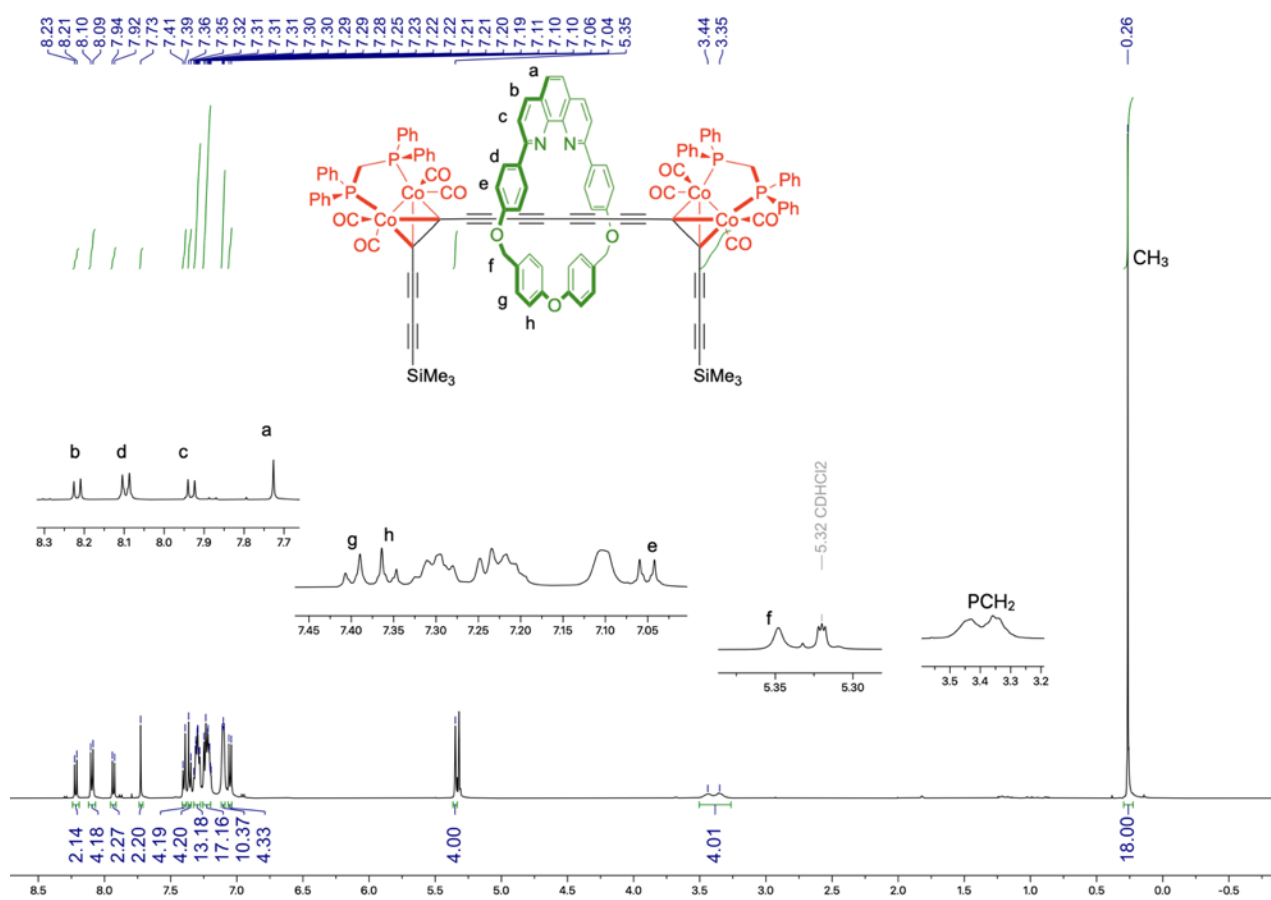


Figure 42.  $^1\text{H}$  NMR (500 MHz) spectrum of compound  $5 \cdot \text{M}_b$  in  $\text{CD}_2\text{Cl}_2$ .

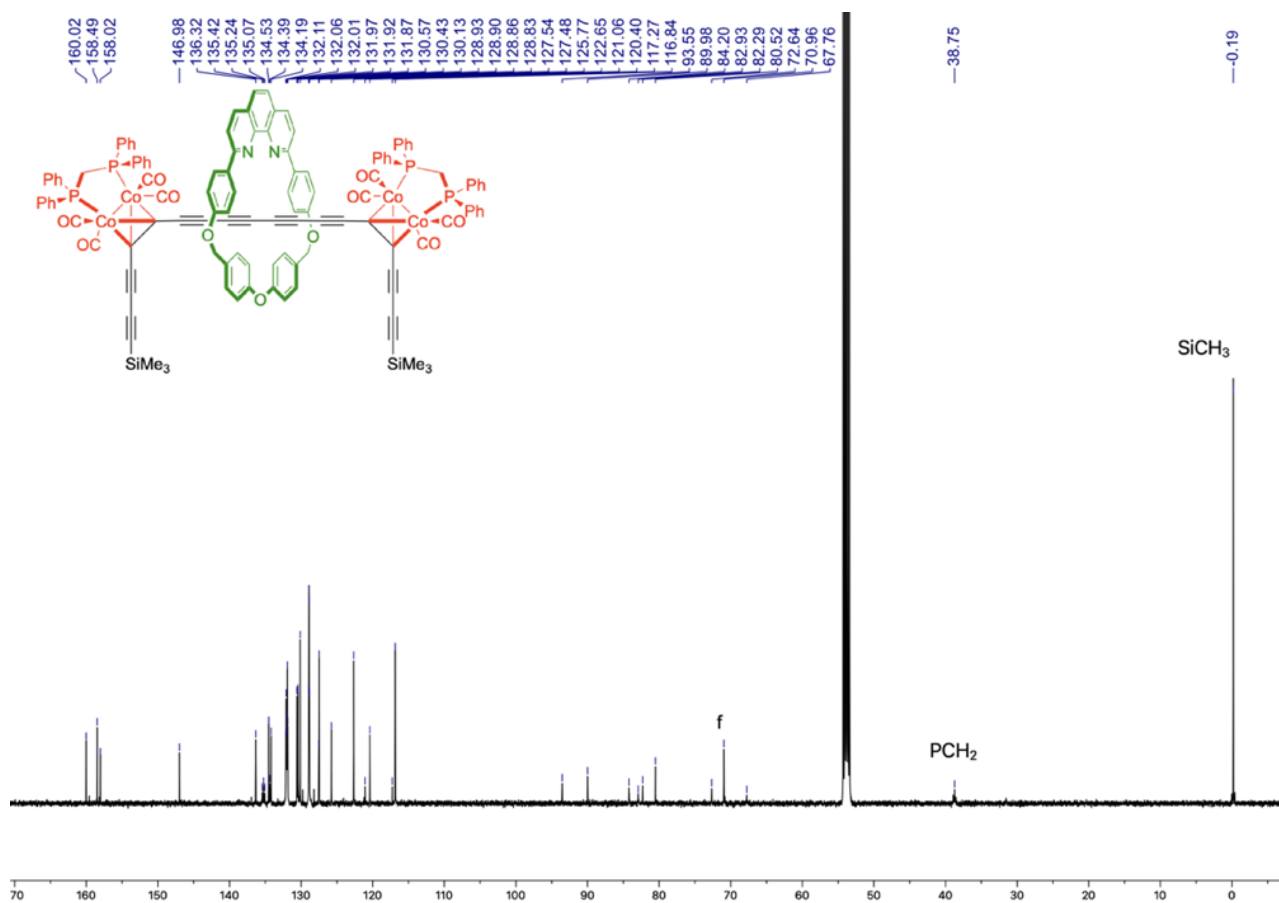


Figure 43.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz) spectrum of compound  $5 \cdot M_b$  in  $\text{CD}_2\text{Cl}_2$ .

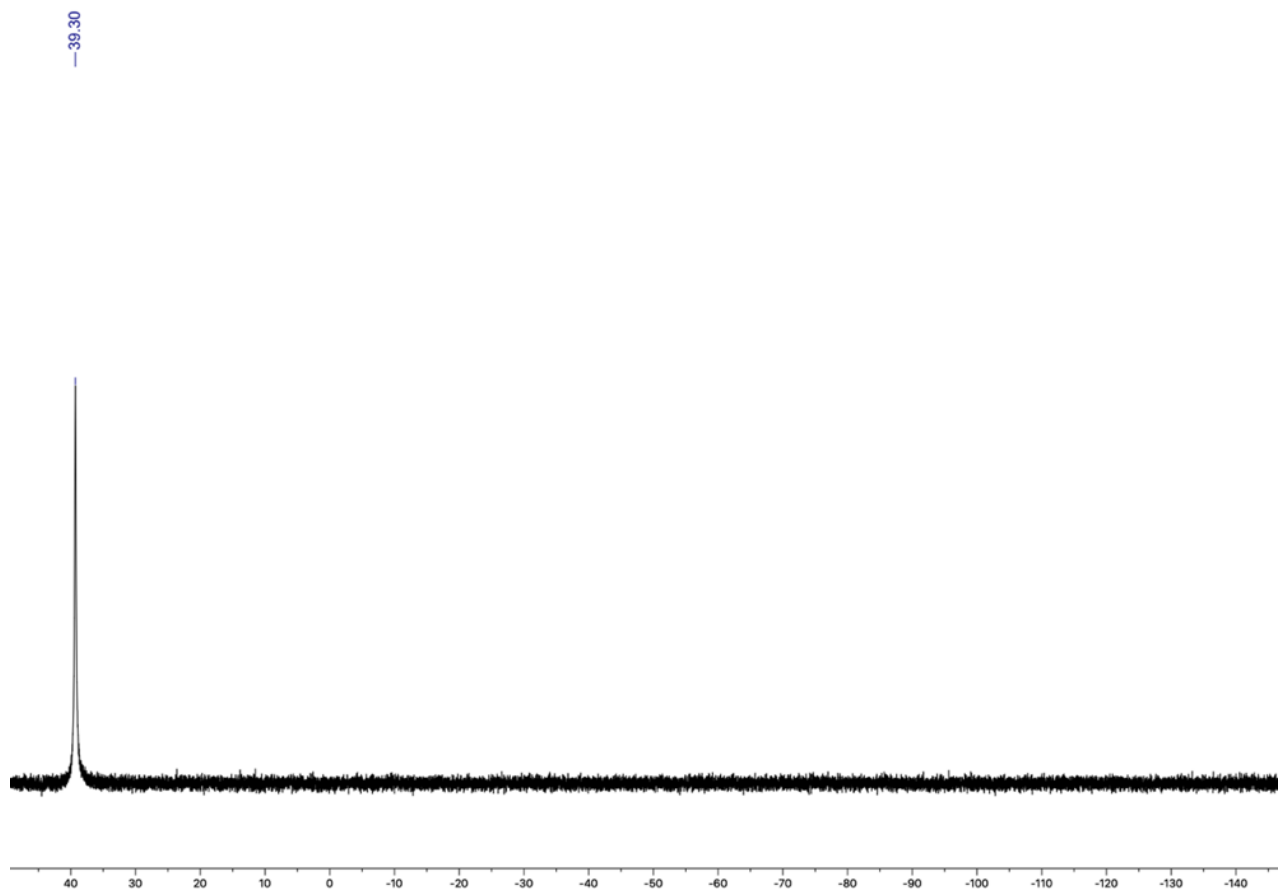
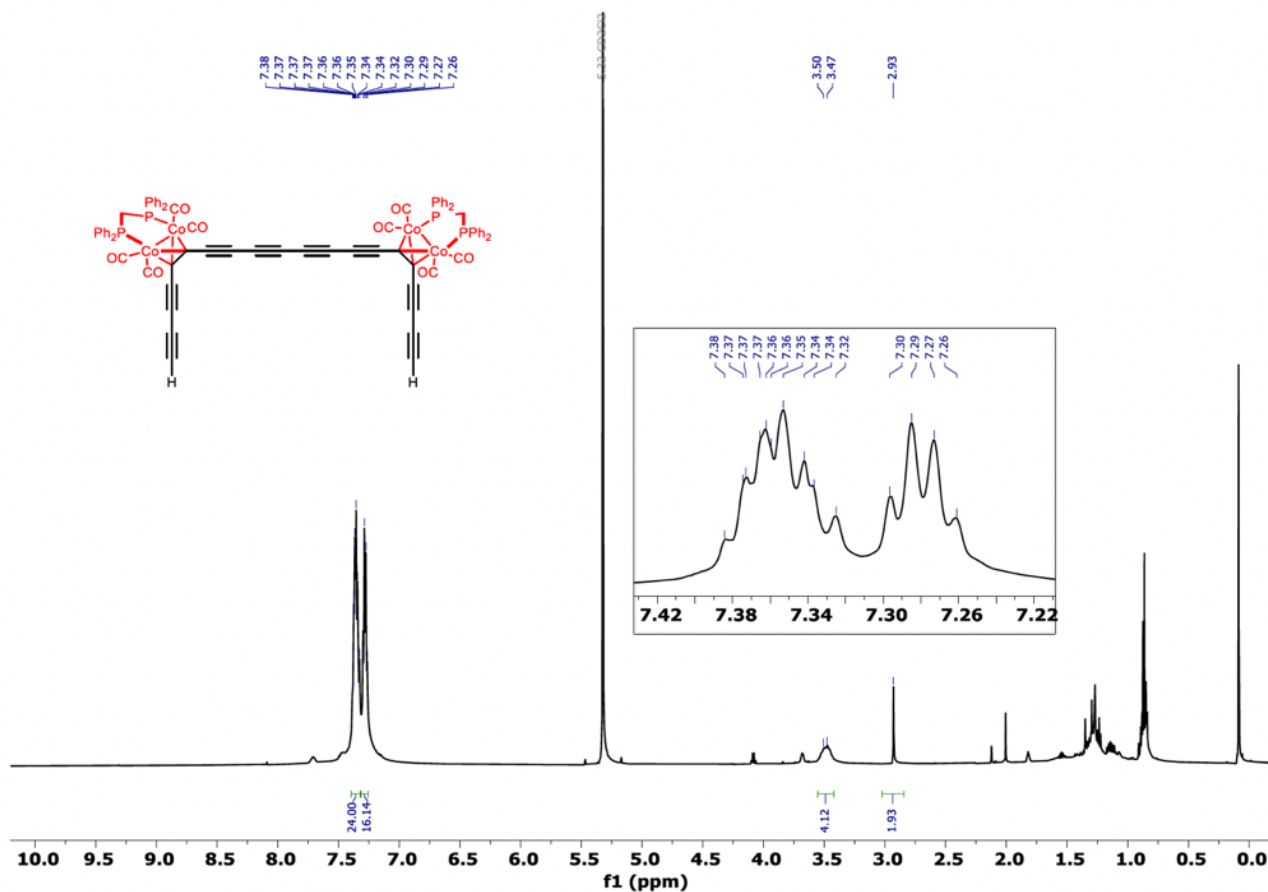
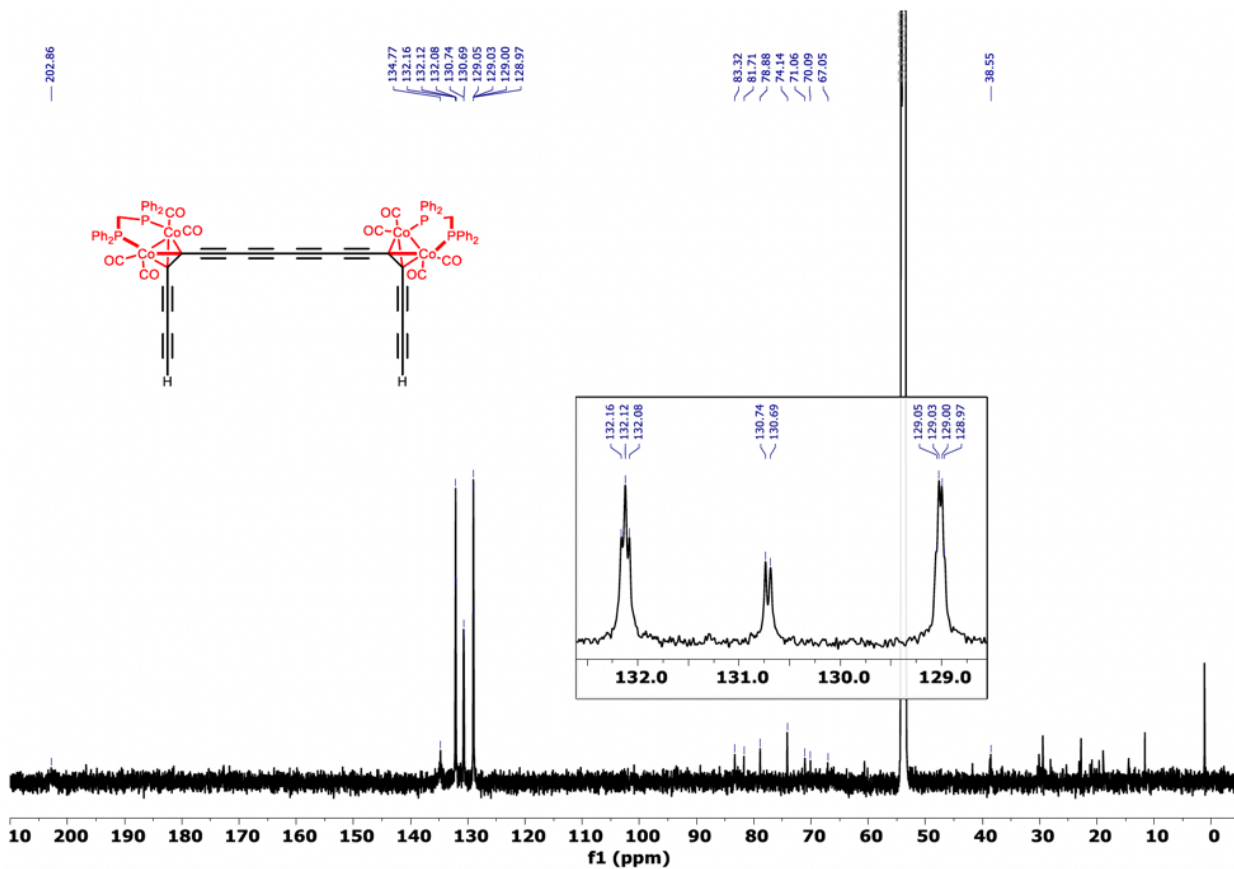


Figure 44.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz) spectrum of compound  $5 \cdot M_b$  in  $\text{CD}_2\text{Cl}_2$ .



**Figure 45.**  $^1\text{H}$  NMR (600 MHz) spectrum of compound 6 in  $\text{CD}_2\text{Cl}_2$ .



**Figure 46.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound 6 in  $\text{CD}_2\text{Cl}_2$ .

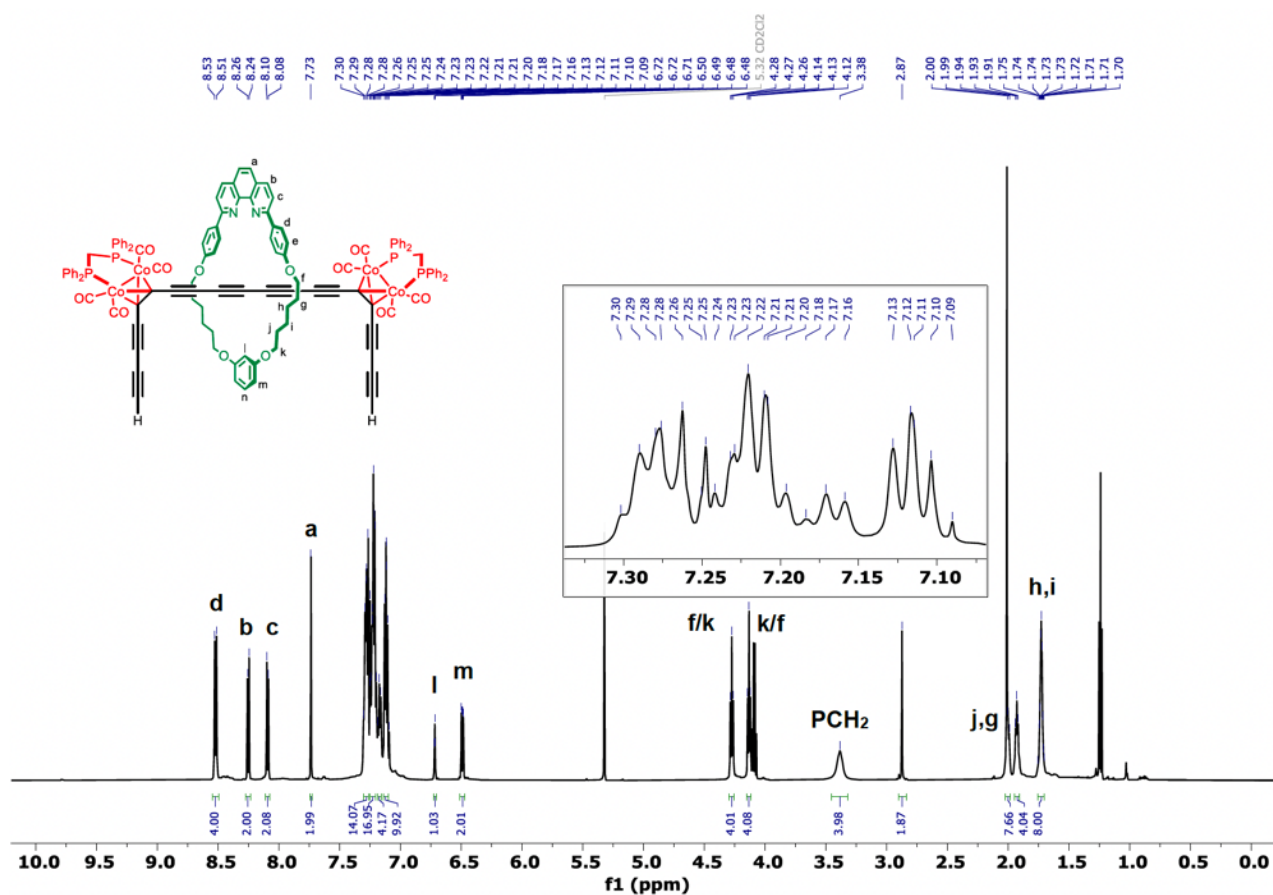


Figure 47.  $^1\text{H}$  NMR (500 MHz) spectrum of compound  $6 \cdot \text{M}_a$  in  $\text{CD}_2\text{Cl}_2$ .

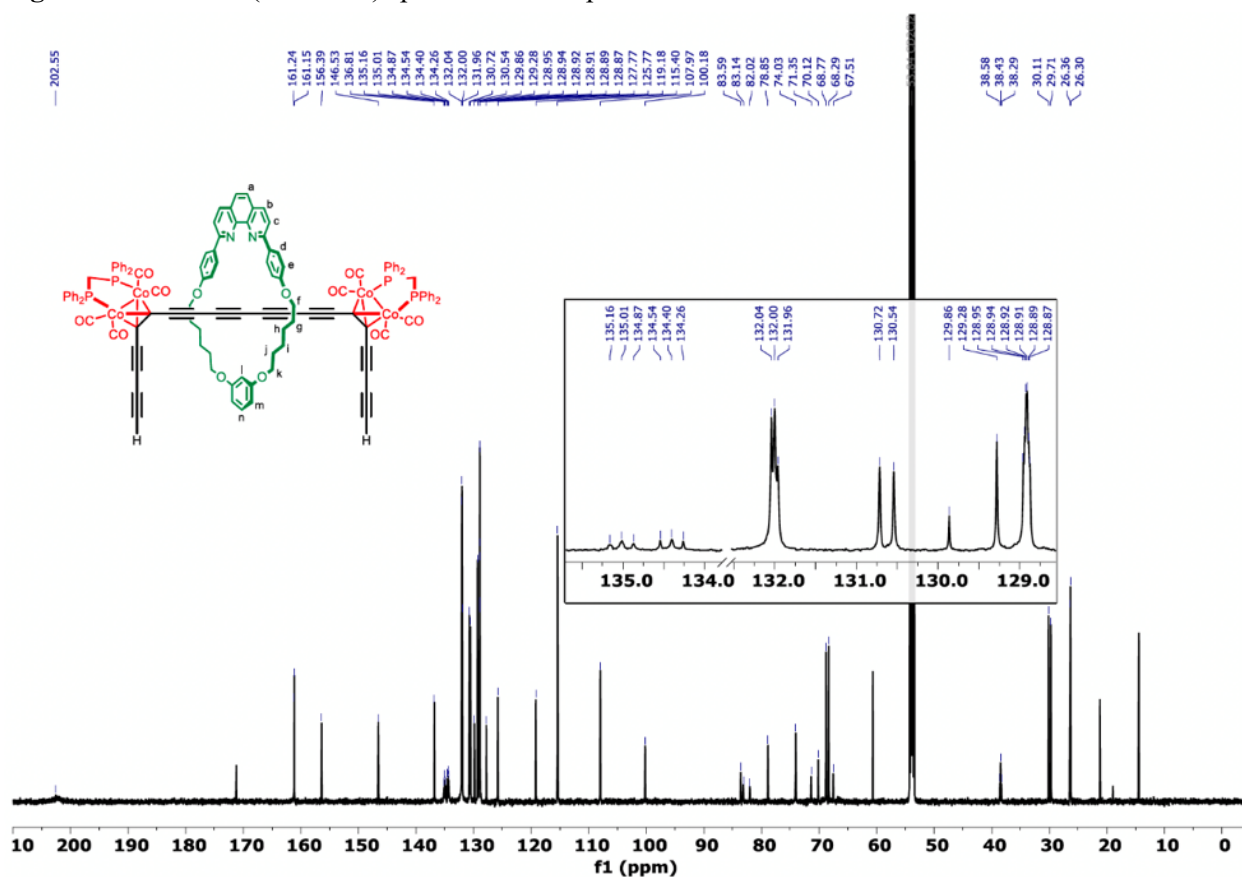


Figure 48.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz) spectrum of compound  $6 \cdot \text{M}_a$  in  $\text{CD}_2\text{Cl}_2$ .

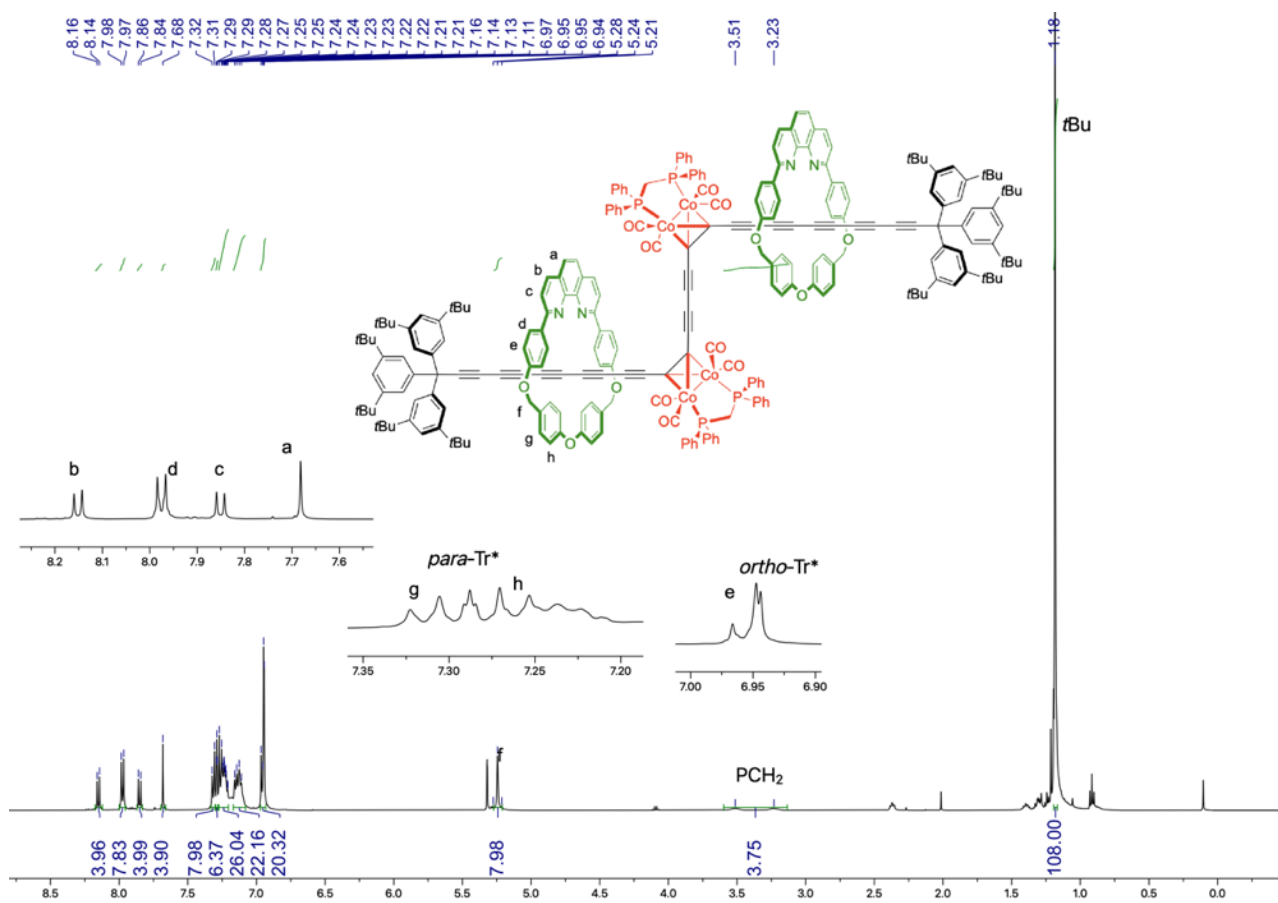


Figure 49.  $^1\text{H}$  NMR (500 MHz) spectrum of compound  $m\text{C}28 \cdot (\text{M}_b)_2$  in  $\text{CD}_2\text{Cl}_2$ .

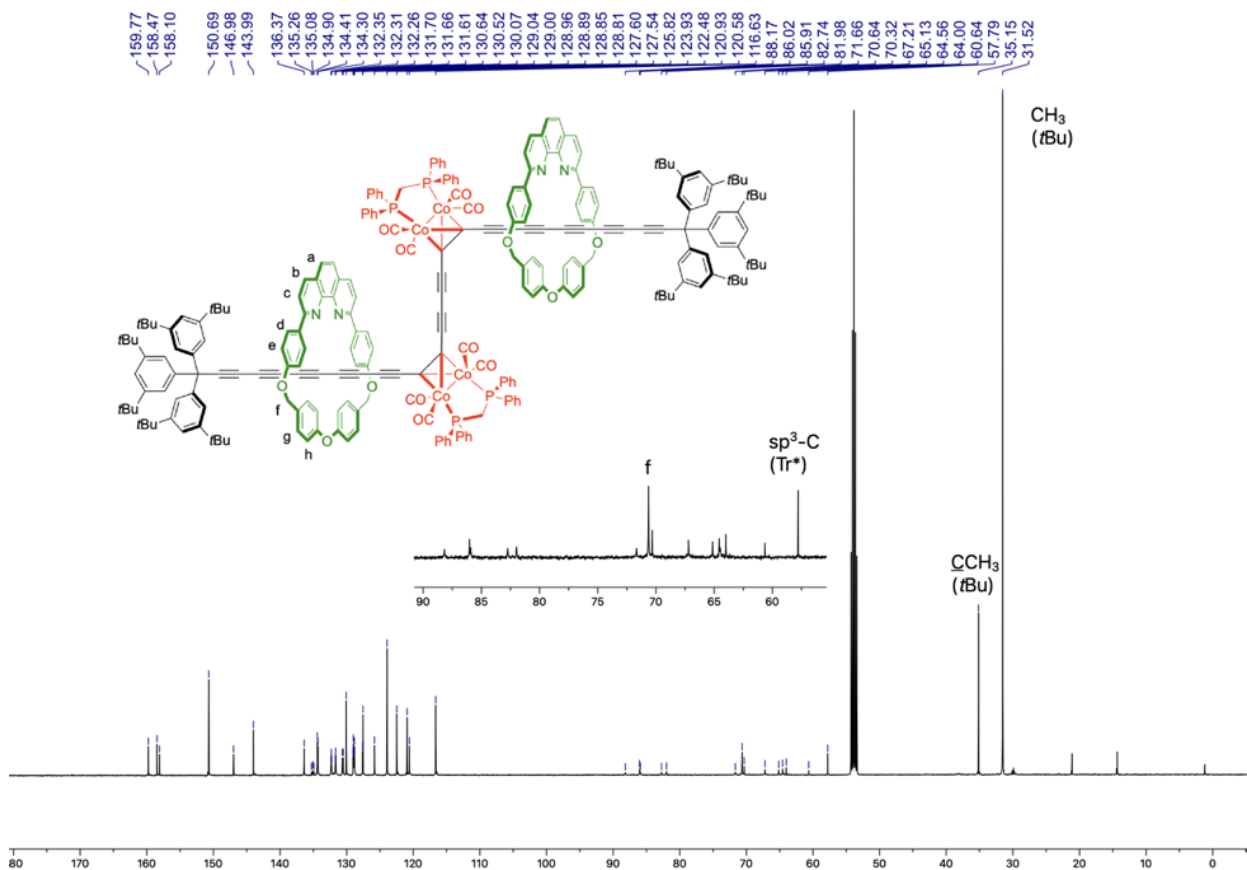


Figure 50.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz) spectrum of compound  $m\text{C}28 \cdot (\text{M}_b)_2$  in  $\text{CD}_2\text{Cl}_2$ .

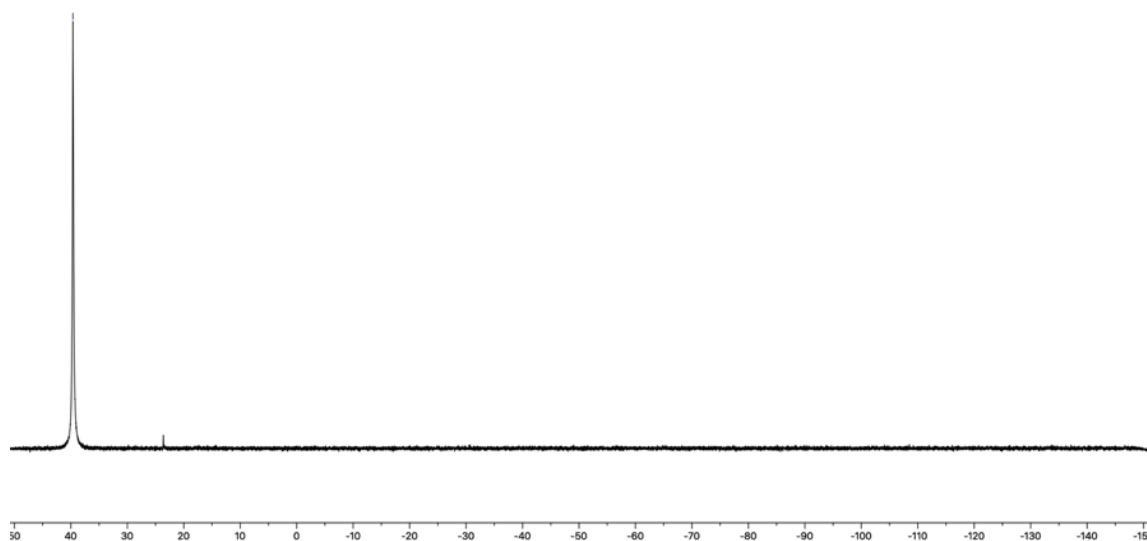


Figure 51.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz) spectrum of compound  $m\text{C}28 \cdot (\text{M}_b)_2$  in  $\text{CD}_2\text{Cl}_2$ .

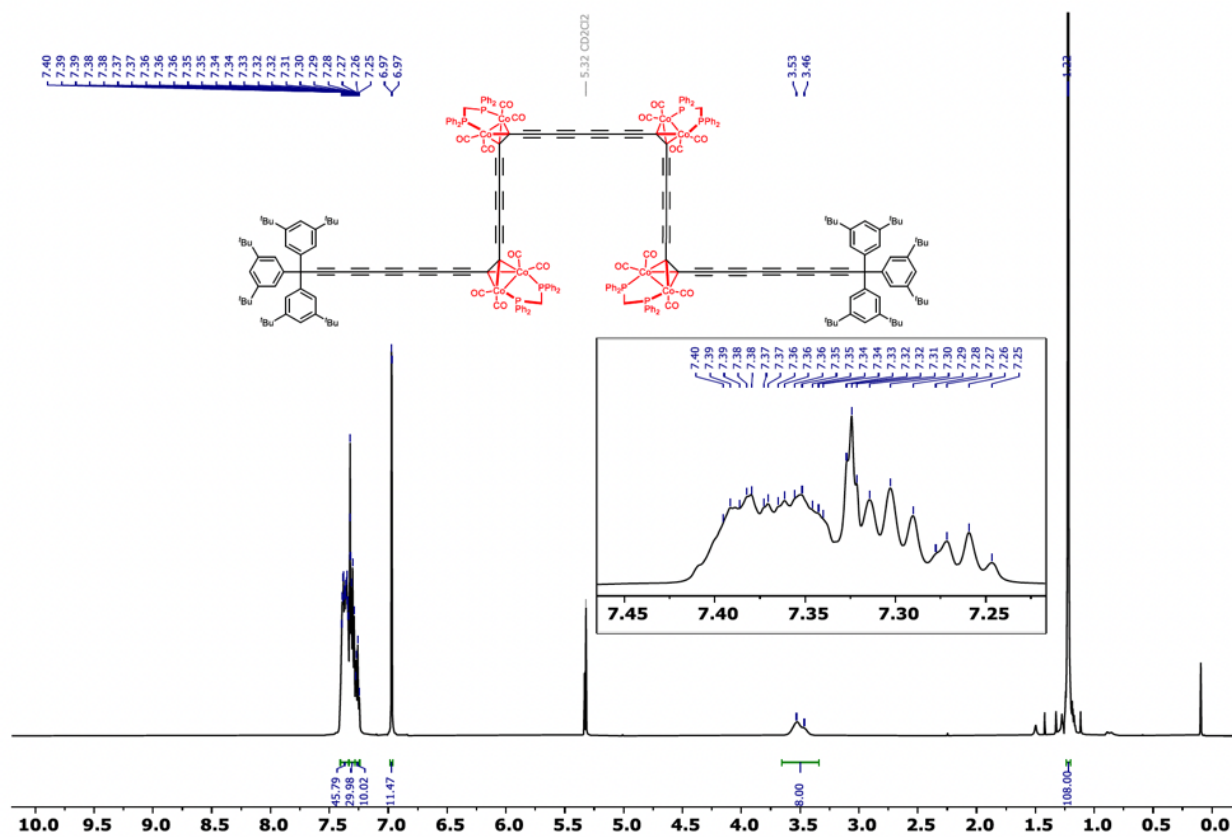


Figure 52.  $^1\text{H}$  NMR (600 MHz) spectrum of compound  $m\text{C}48$  in  $\text{CD}_2\text{Cl}_2$ .

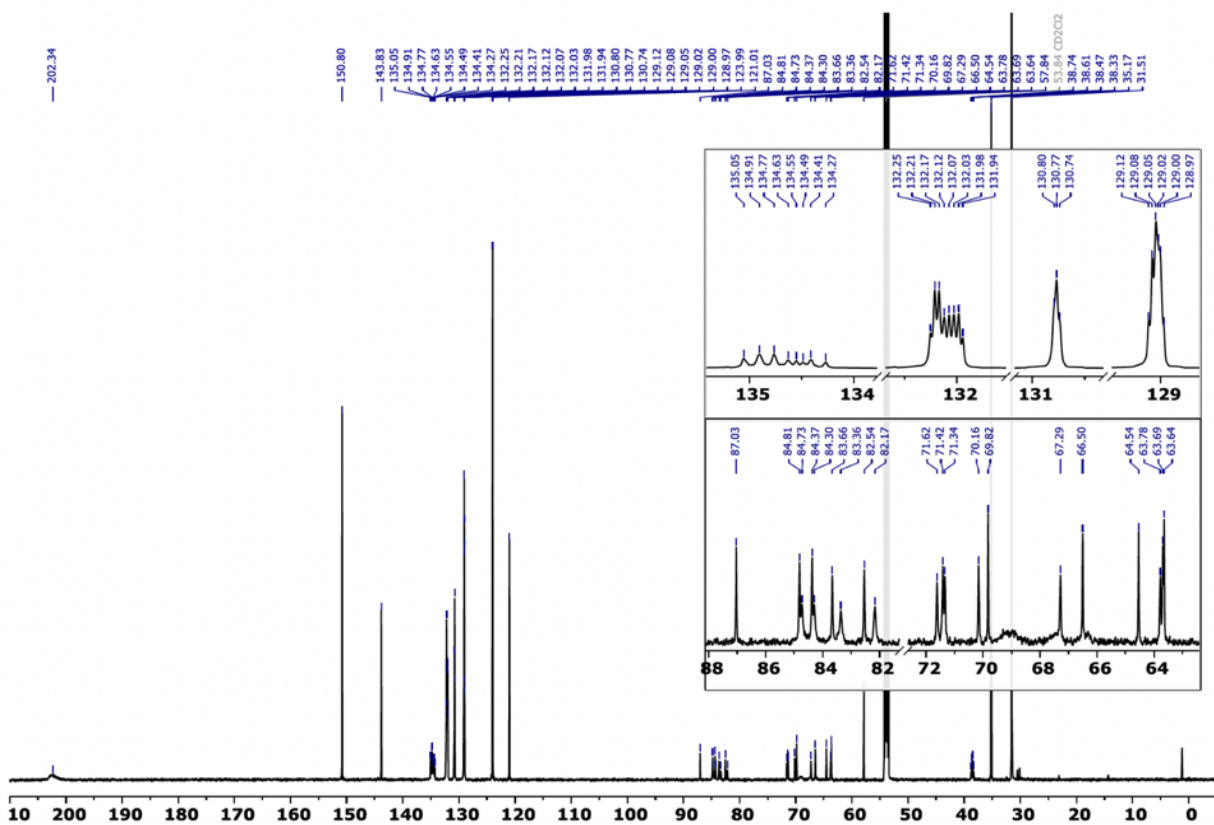


Figure 53. <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz) spectrum of compound *mC48* in CD<sub>2</sub>Cl<sub>2</sub>.

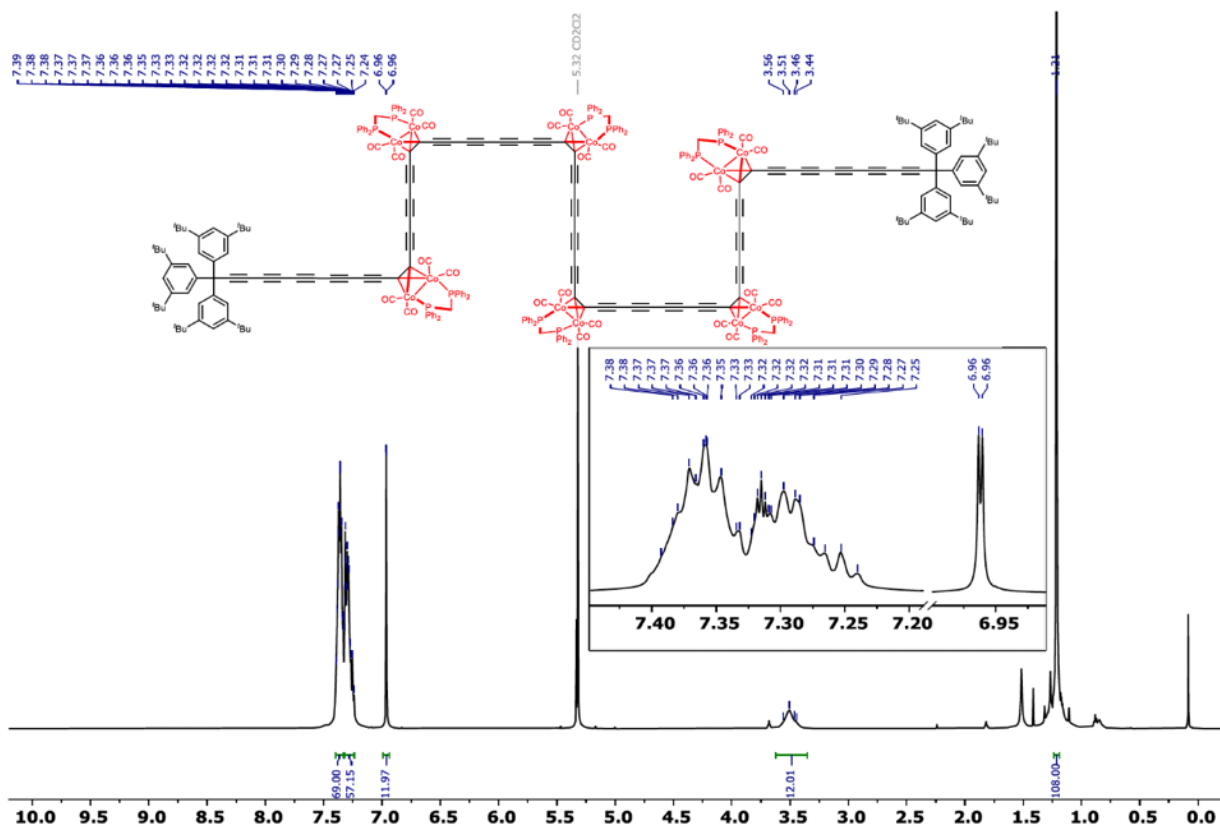


Figure 54. <sup>1</sup>H NMR (600 MHz) spectrum of compound *mC68* in CD<sub>2</sub>Cl<sub>2</sub>.



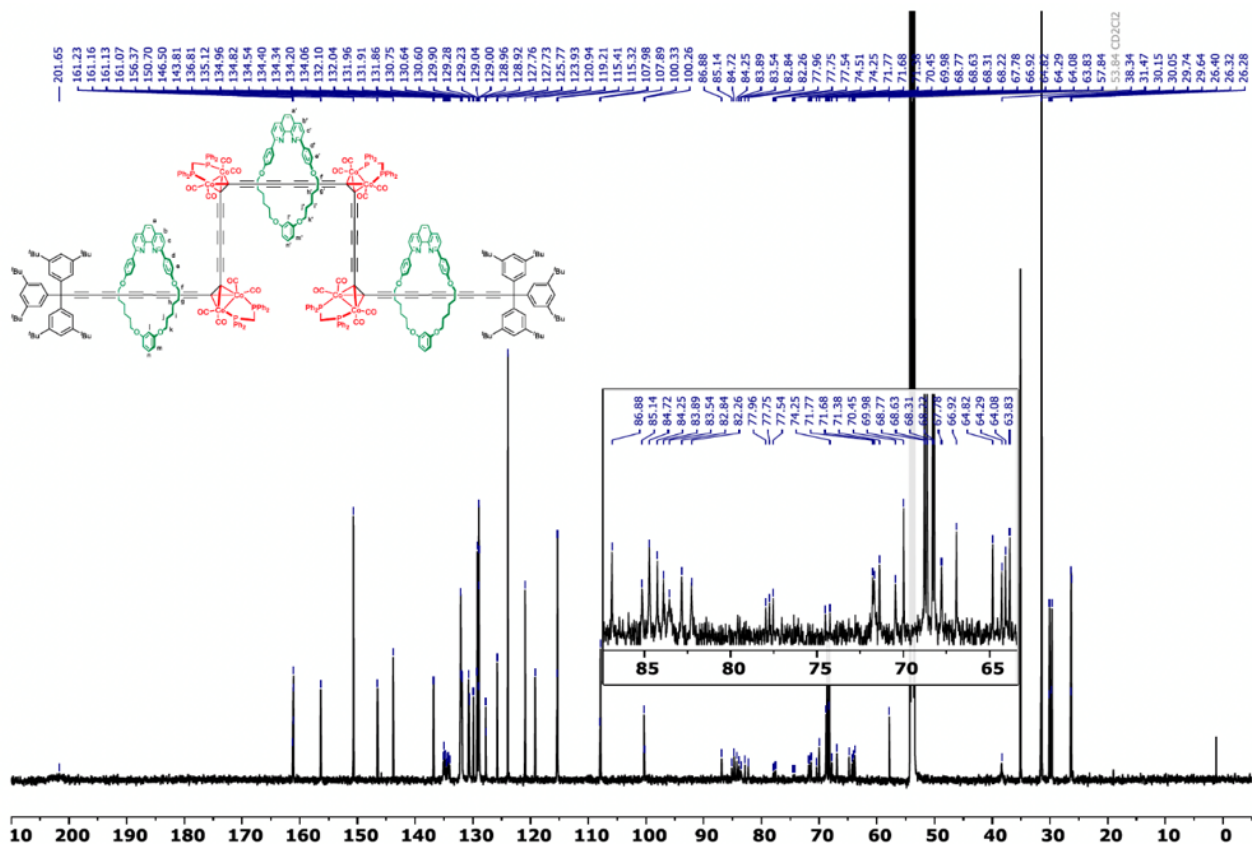


Figure 57.  $^{13}C\{^1H\}$  NMR (151 MHz) spectrum of compound  $mC48 \cdot (M_a)_3$  in  $CD_2Cl_2$ .

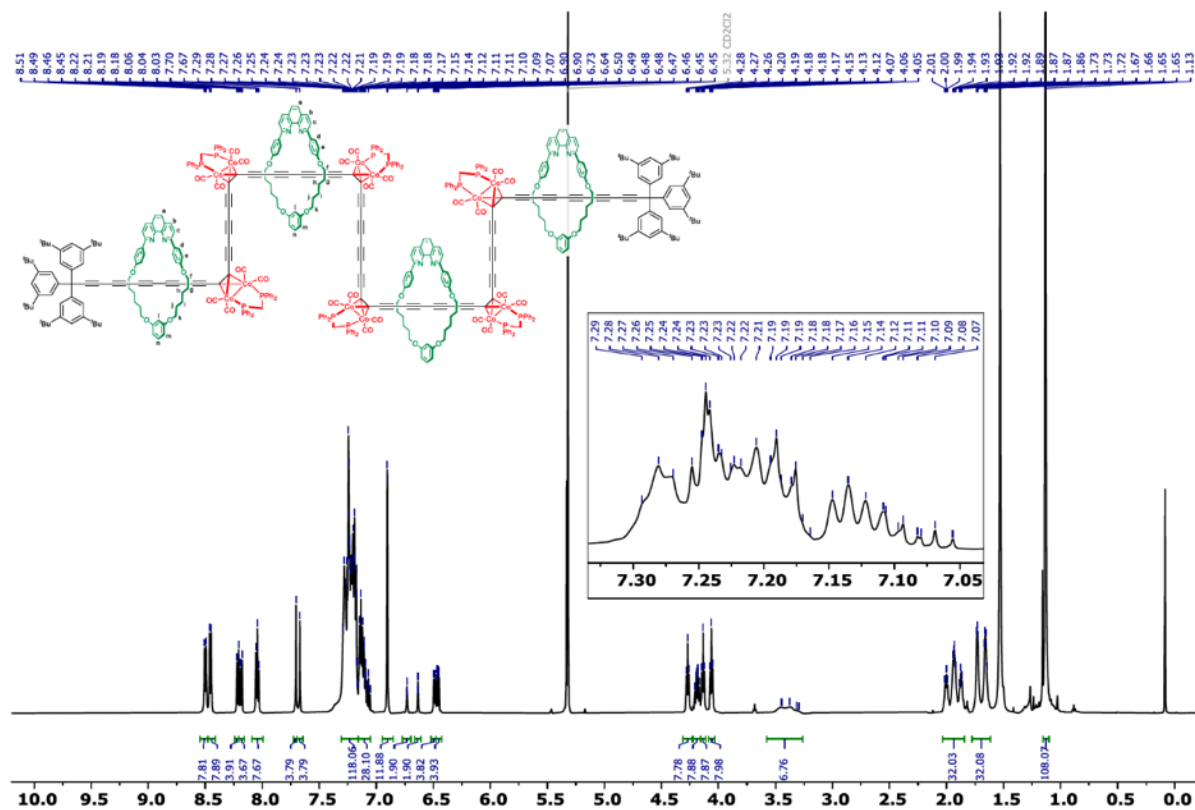


Figure 58.  $^1H$  NMR (600 MHz) spectrum of compound  $mC68 \cdot (M_a)_4$  in  $CD_2Cl_2$ .

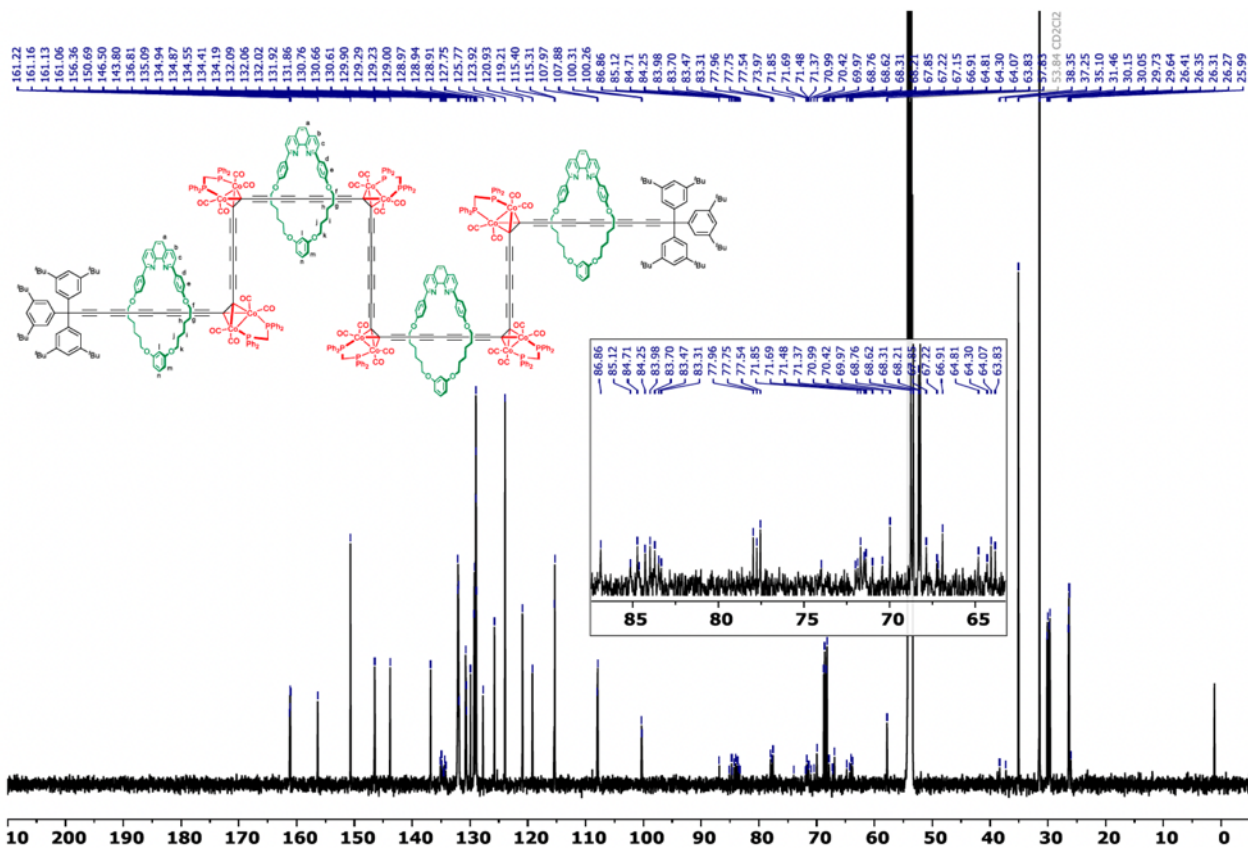


Figure 59.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound  $m\text{C68}\cdot(\text{M}_a)_4$  in  $\text{CD}_2\text{Cl}_2$ .

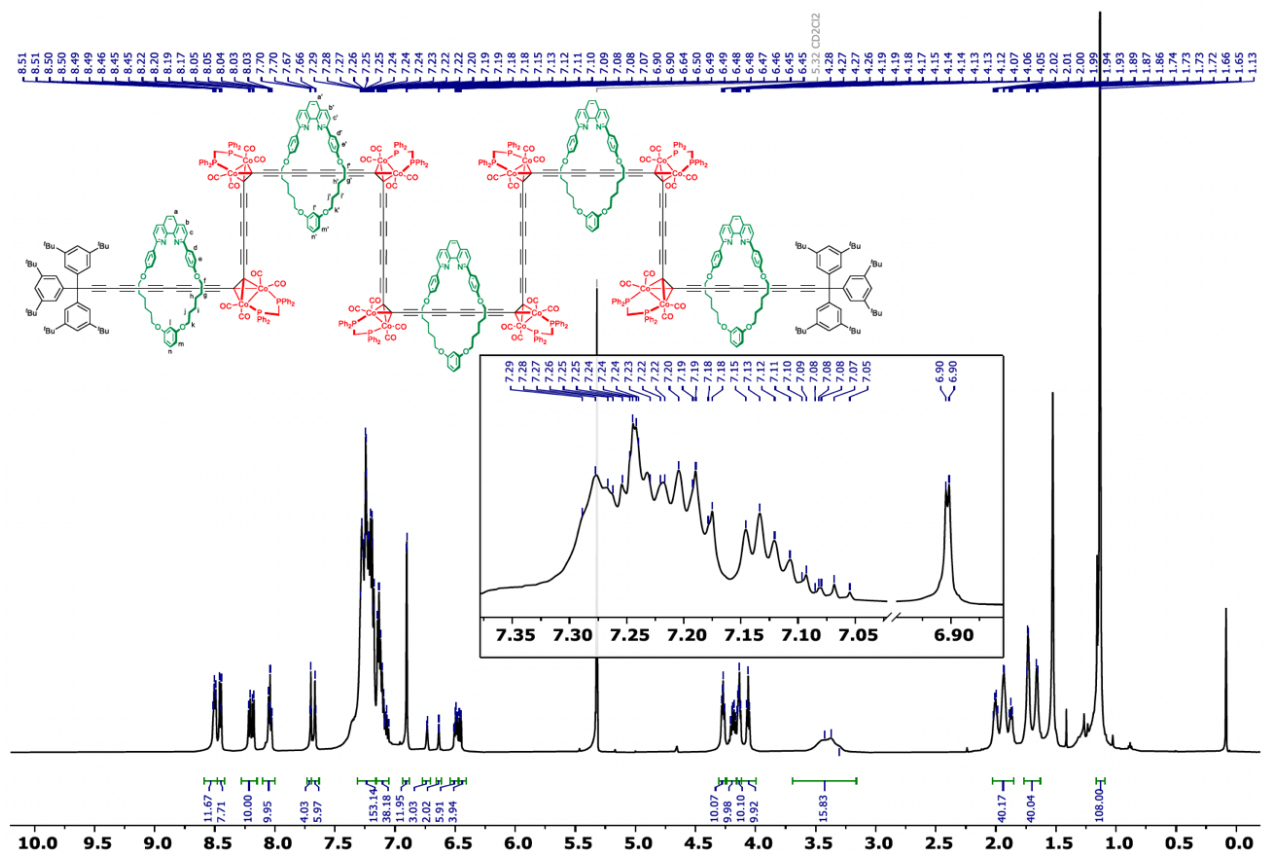


Figure 60.  $^1\text{H}$  NMR (600 MHz) spectrum of compound  $m\text{C88}\cdot(\text{M}_a)_5$  in  $\text{CD}_2\text{Cl}_2$ .

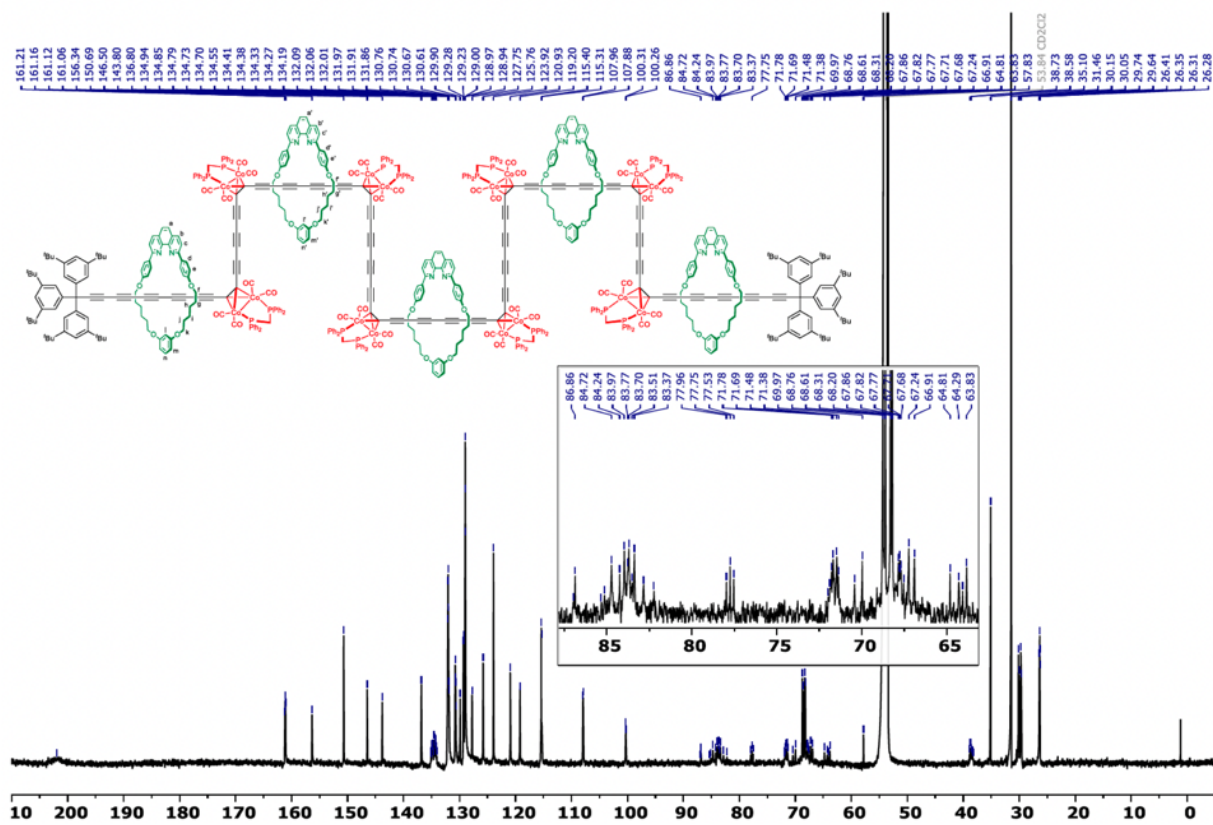


Figure 61.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound  $m\text{C88}\cdot(\text{M}_a)_5$  in  $\text{CD}_2\text{Cl}_2$ .

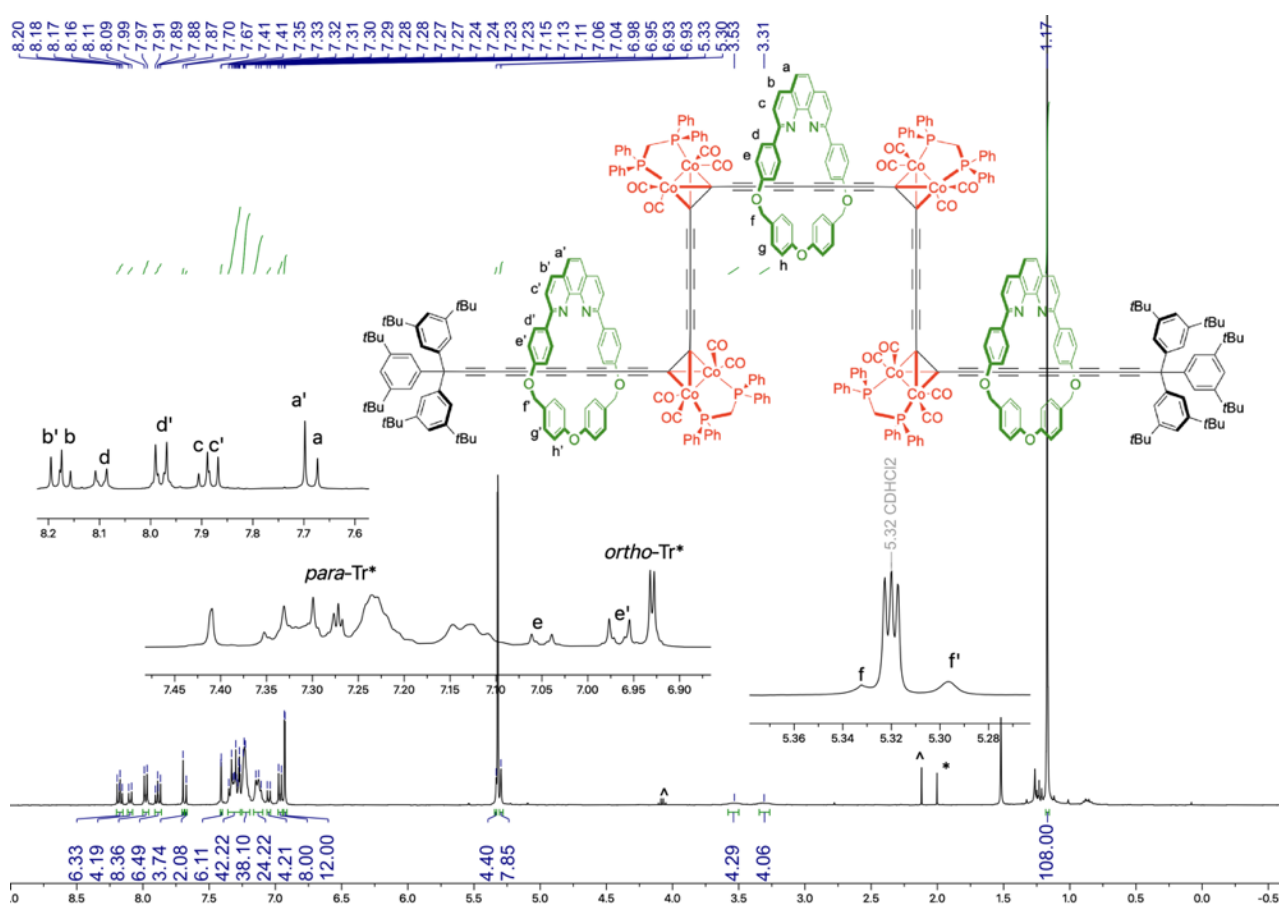
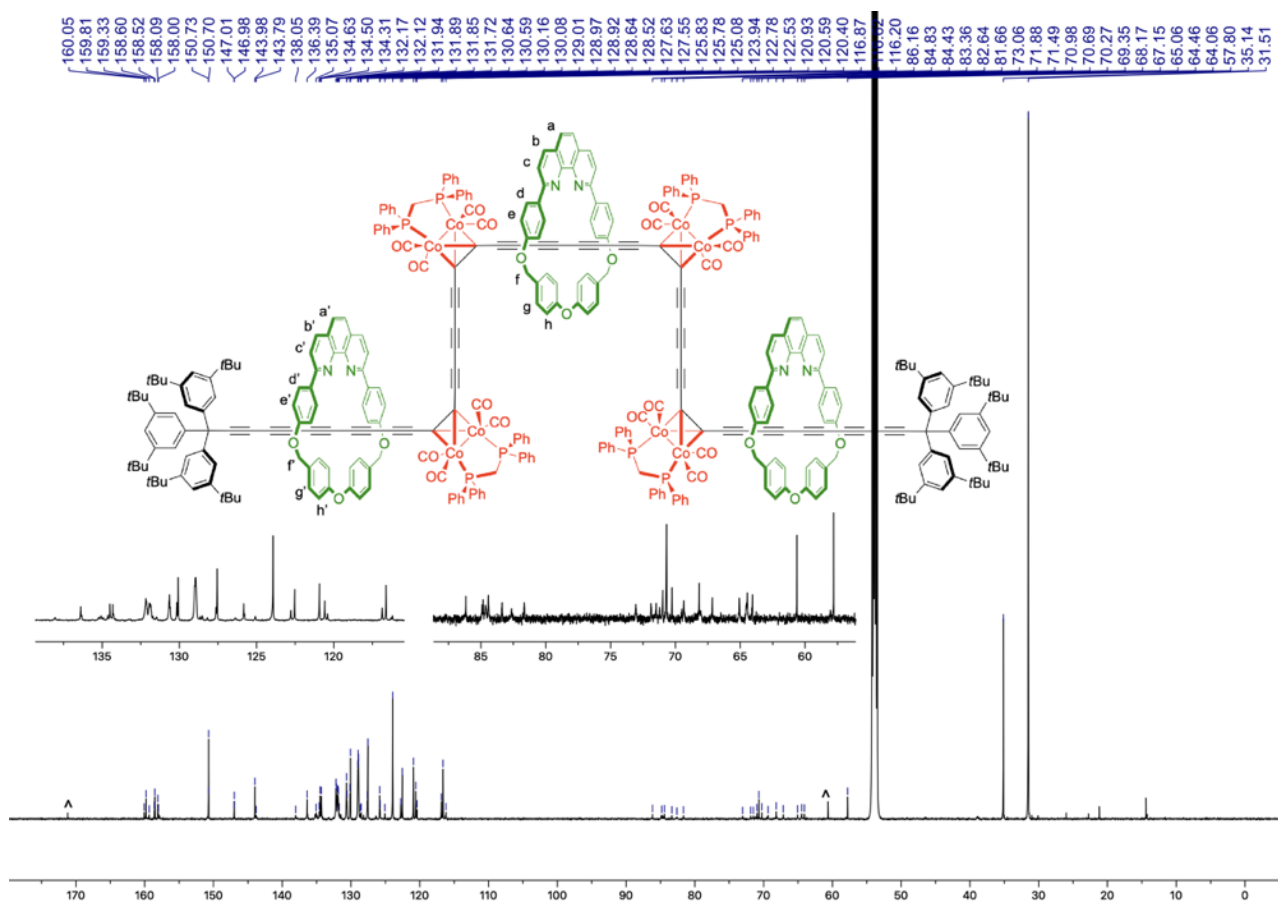
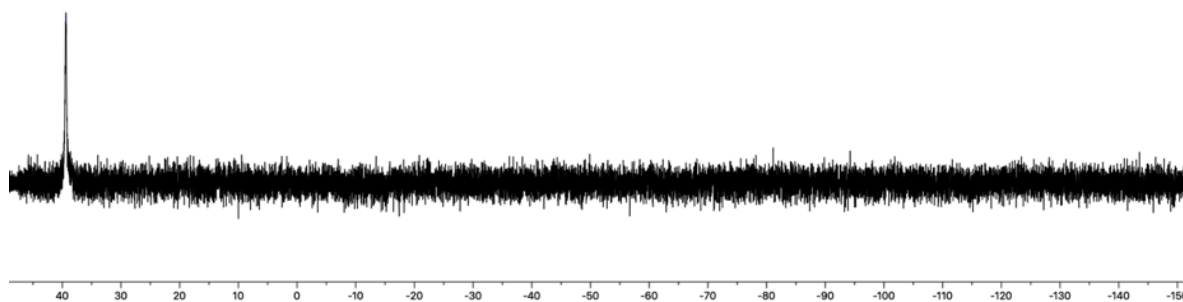


Figure 62.  $^1\text{H}$  NMR (400 MHz) spectrum of compound  $m\text{C48}\cdot(\text{M}_b)_3$  in  $\text{CD}_2\text{Cl}_2$  (^ and \* indicate ethyl acetate and acetone, respectively).

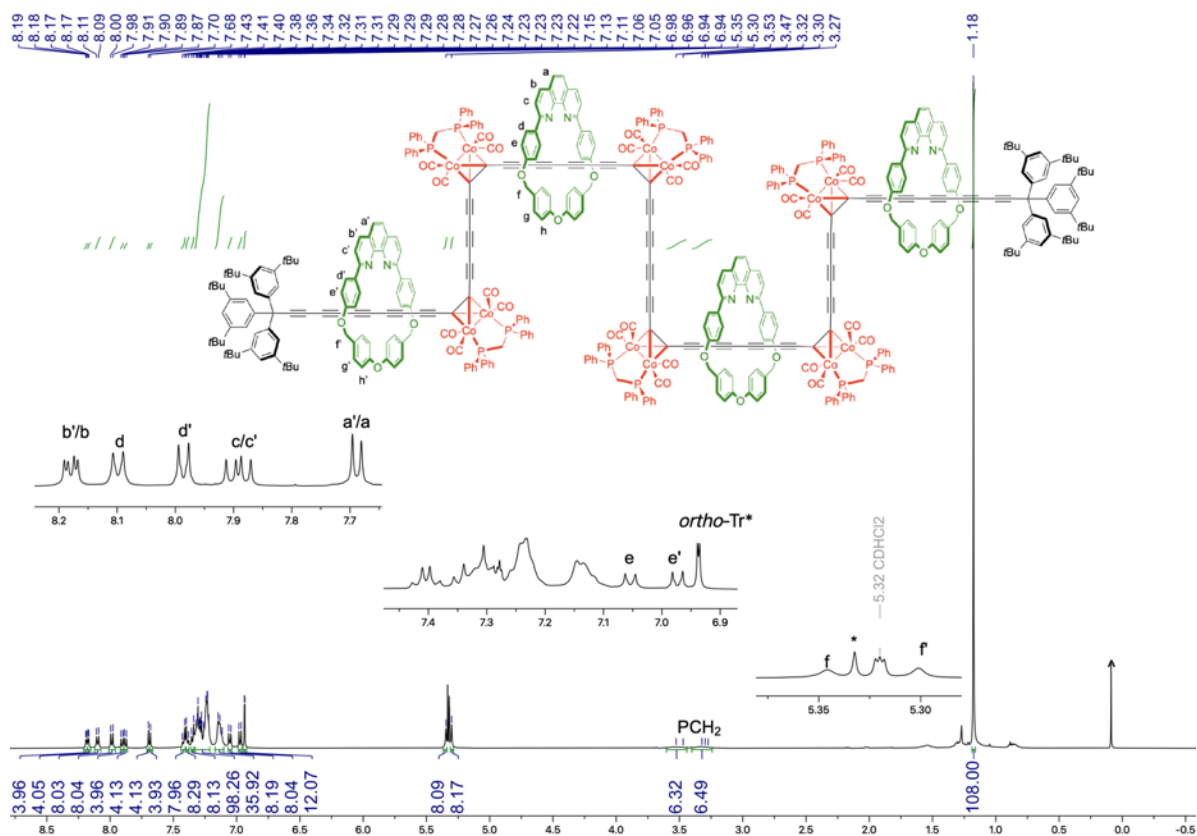


**Figure 63.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound  $m\text{C48}\cdot(\text{M}_b)_3$  in  $\text{CD}_2\text{Cl}_2$  (^ indicates ethyl acetate).

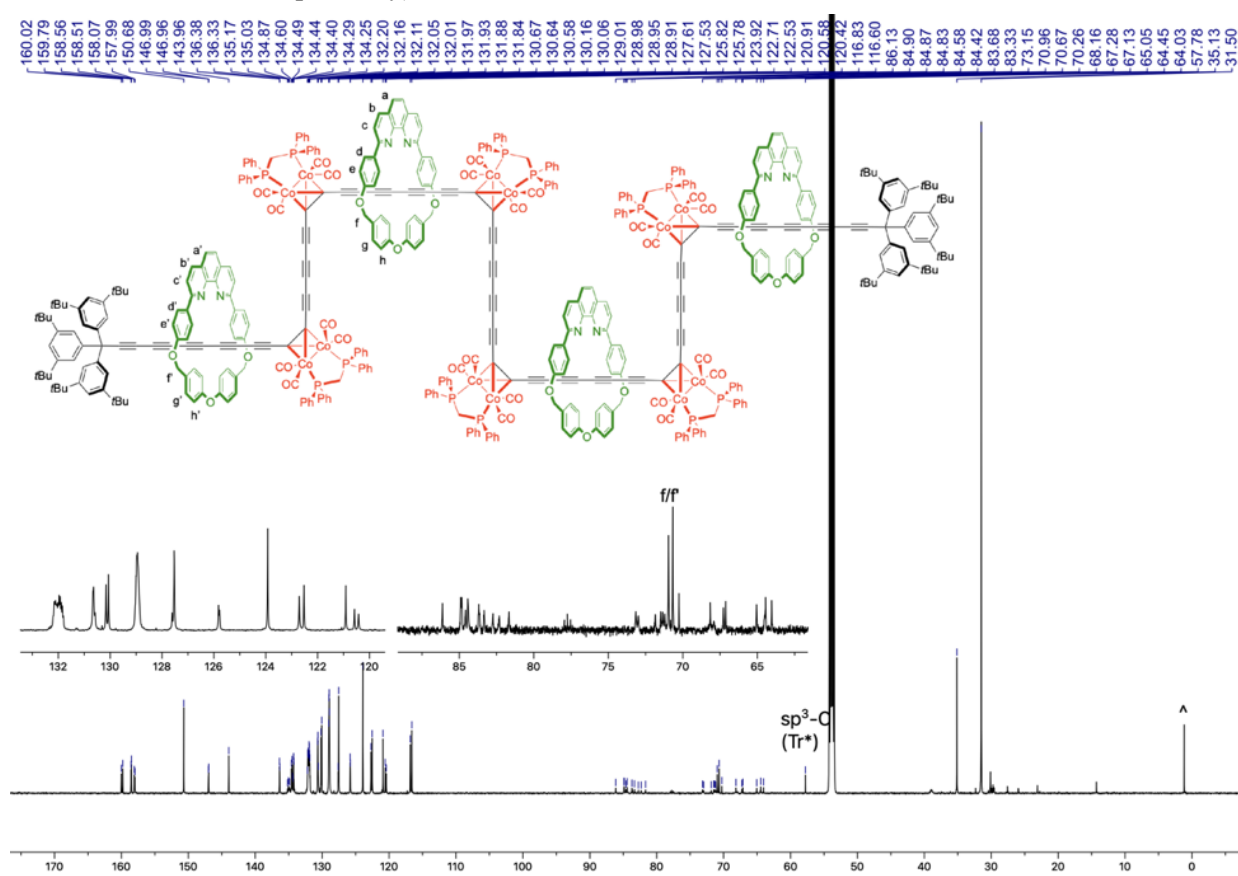
-39.40



**Figure 64.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz) spectrum of compound  $m\text{C48}\cdot(\text{M}_b)_3$  in  $\text{CD}_2\text{Cl}_2$ .



**Figure 65.**  $^1\text{H}$  NMR (500 MHz) spectrum of compound  $m\text{C68}\cdot(\text{M}_b)_4$  in  $\text{CD}_2\text{Cl}_2$  (^ and \* indicate silicon grease and residual  $\text{CH}_2\text{Cl}_2$ , respectively).



**Figure 66.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound  $m\text{C68}\cdot(\text{M}_b)_4$  in  $\text{CD}_2\text{Cl}_2$  (^ indicates silicon grease).

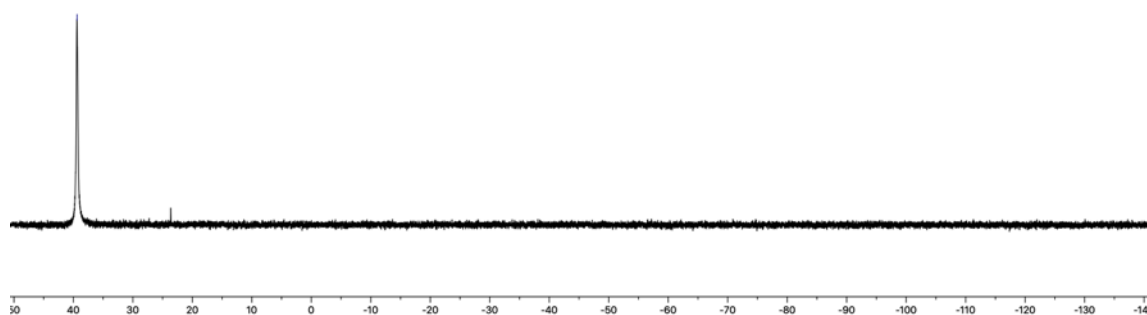


Figure 67.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz) spectrum of compound  $m\text{C68}\cdot(\text{M}_b)_4$  in  $\text{CD}_2\text{Cl}_2$ .

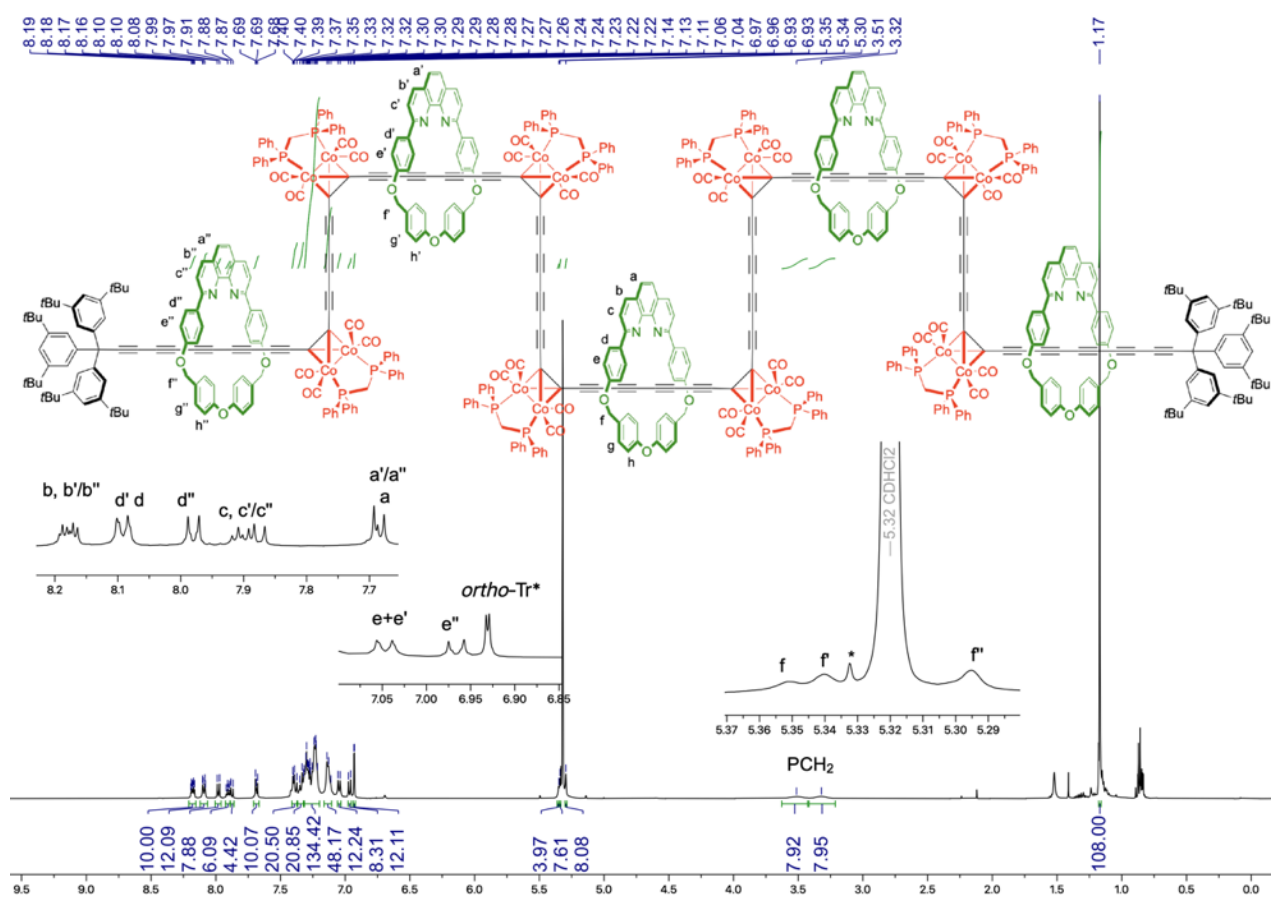


Figure 68.  $^1\text{H}$  NMR (500 MHz) spectrum of compound  $m\text{C88}\cdot(\text{M}_b)_5$  in  $\text{CD}_2\text{Cl}_2$  (\*indicates residual  $\text{CH}_2\text{Cl}_2$ ).

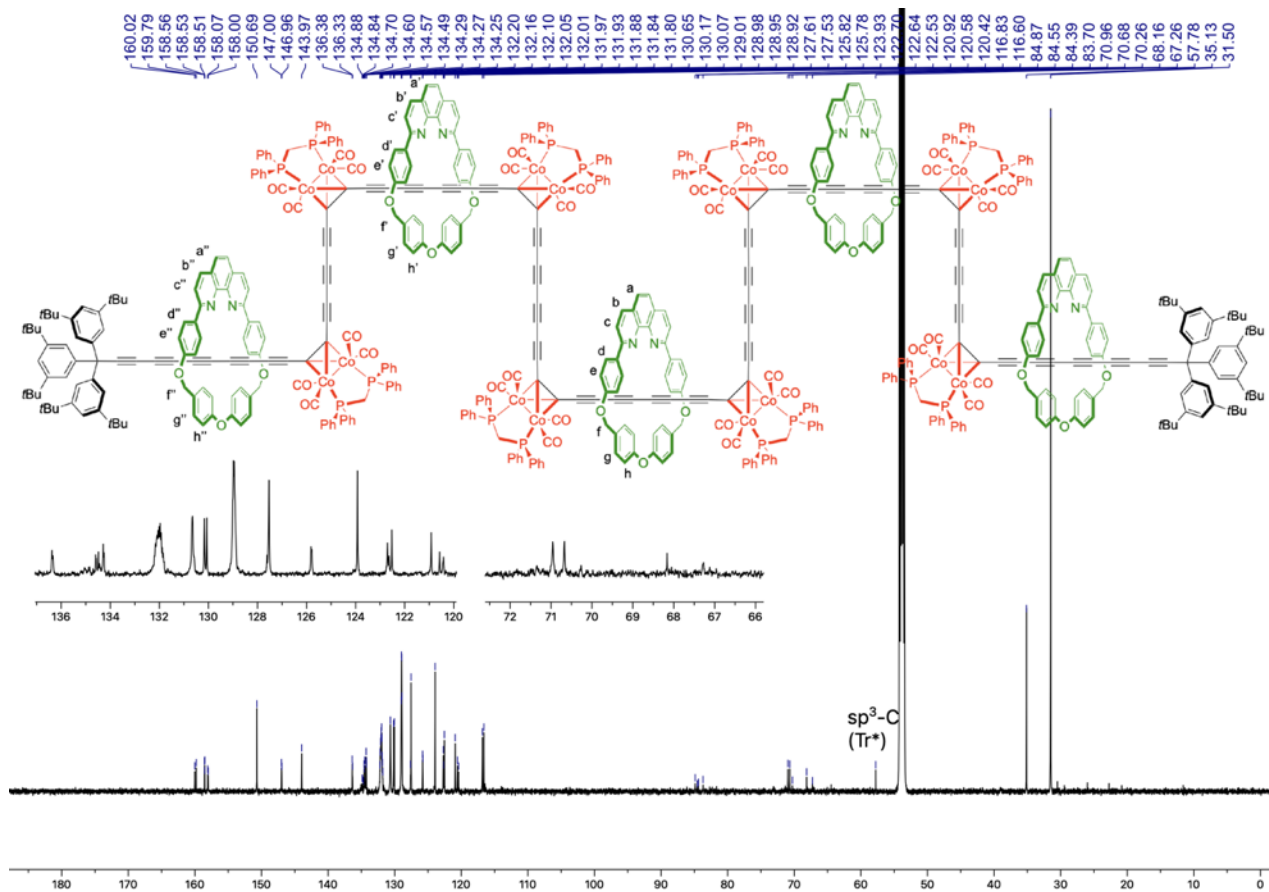


Figure 69.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound  $m\text{C88}\cdot(\text{M}_b)_5$  in  $\text{CD}_2\text{Cl}_2$ .

— 39.40

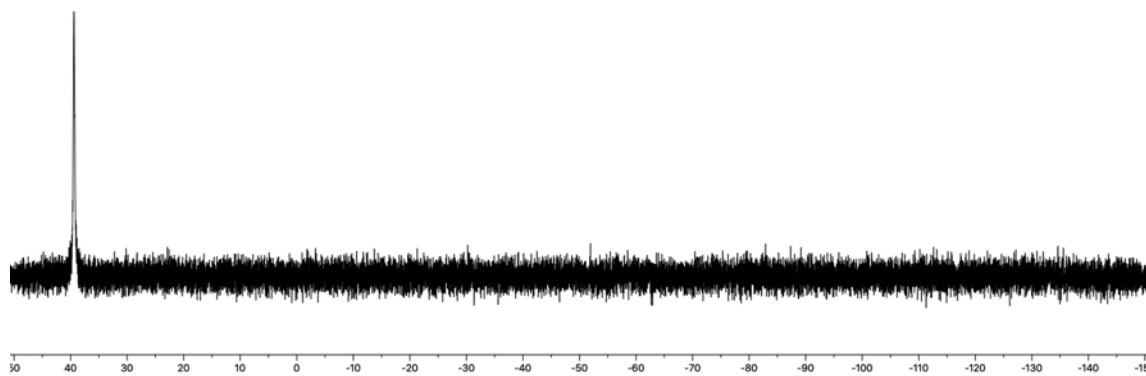
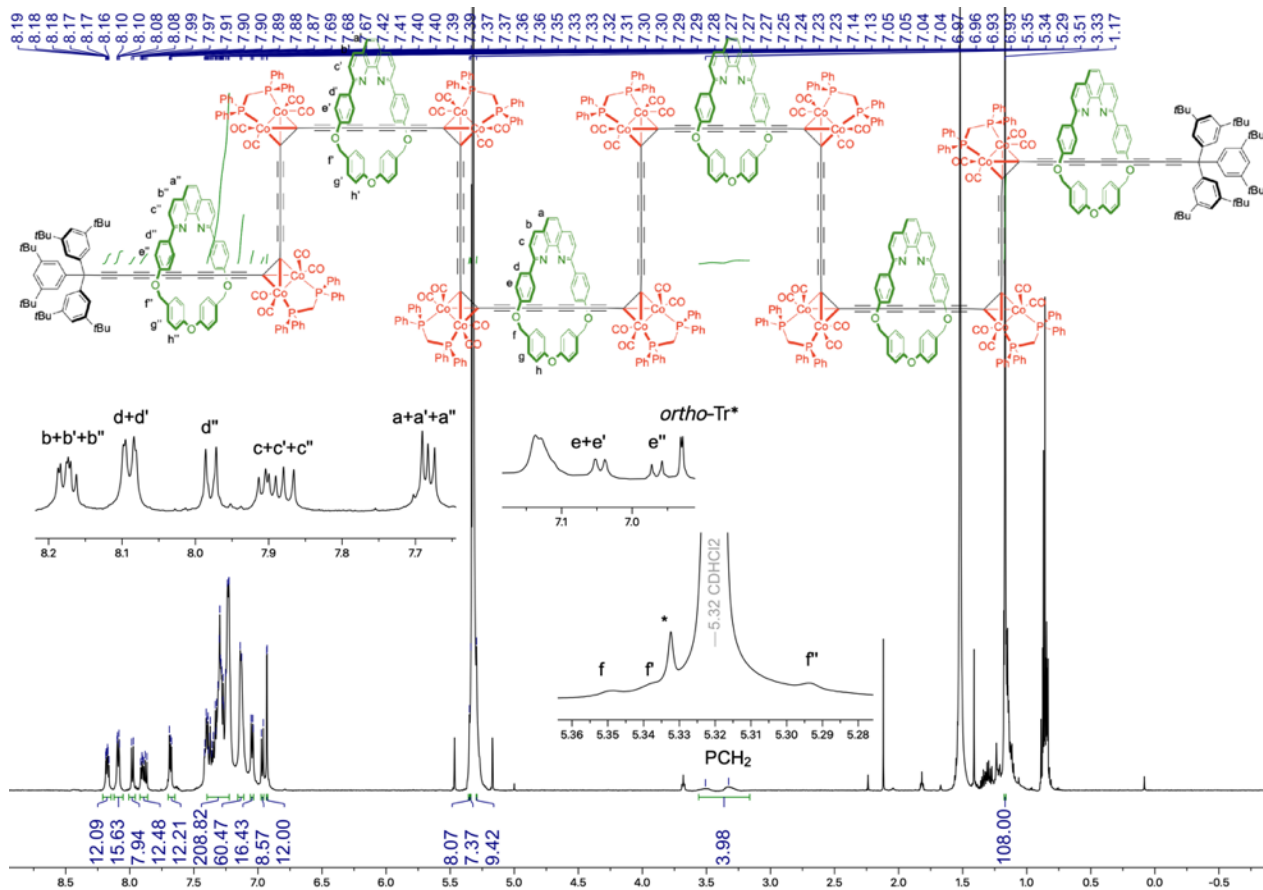
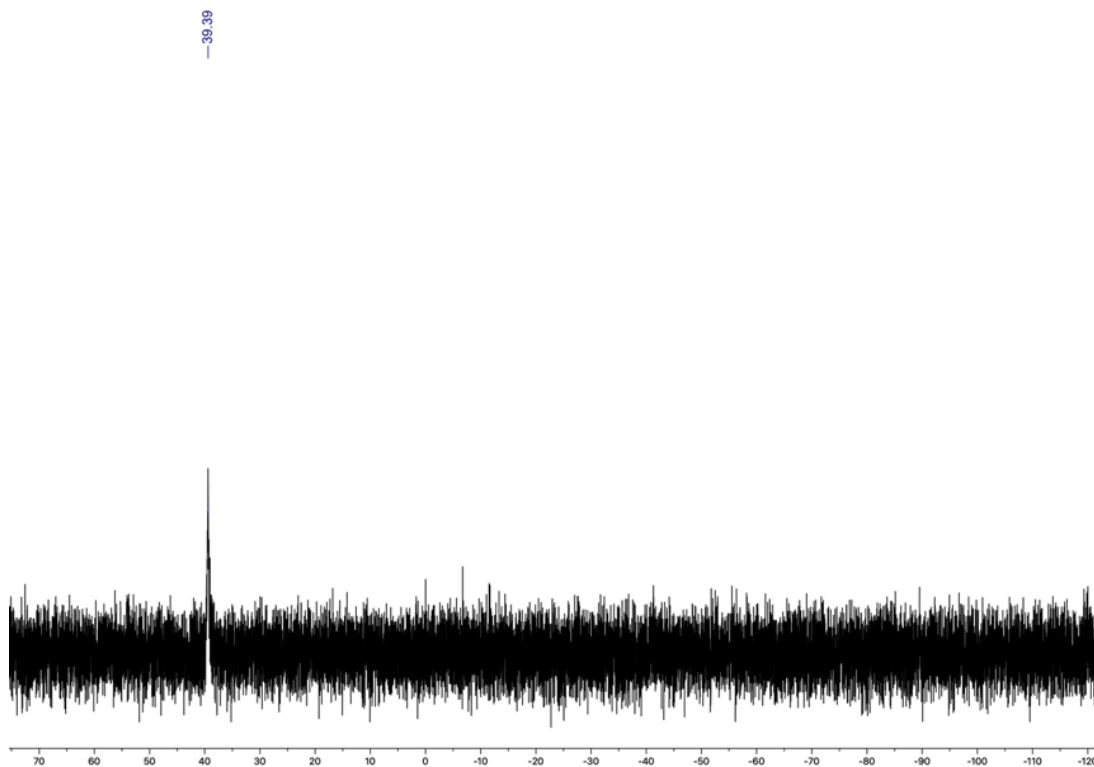


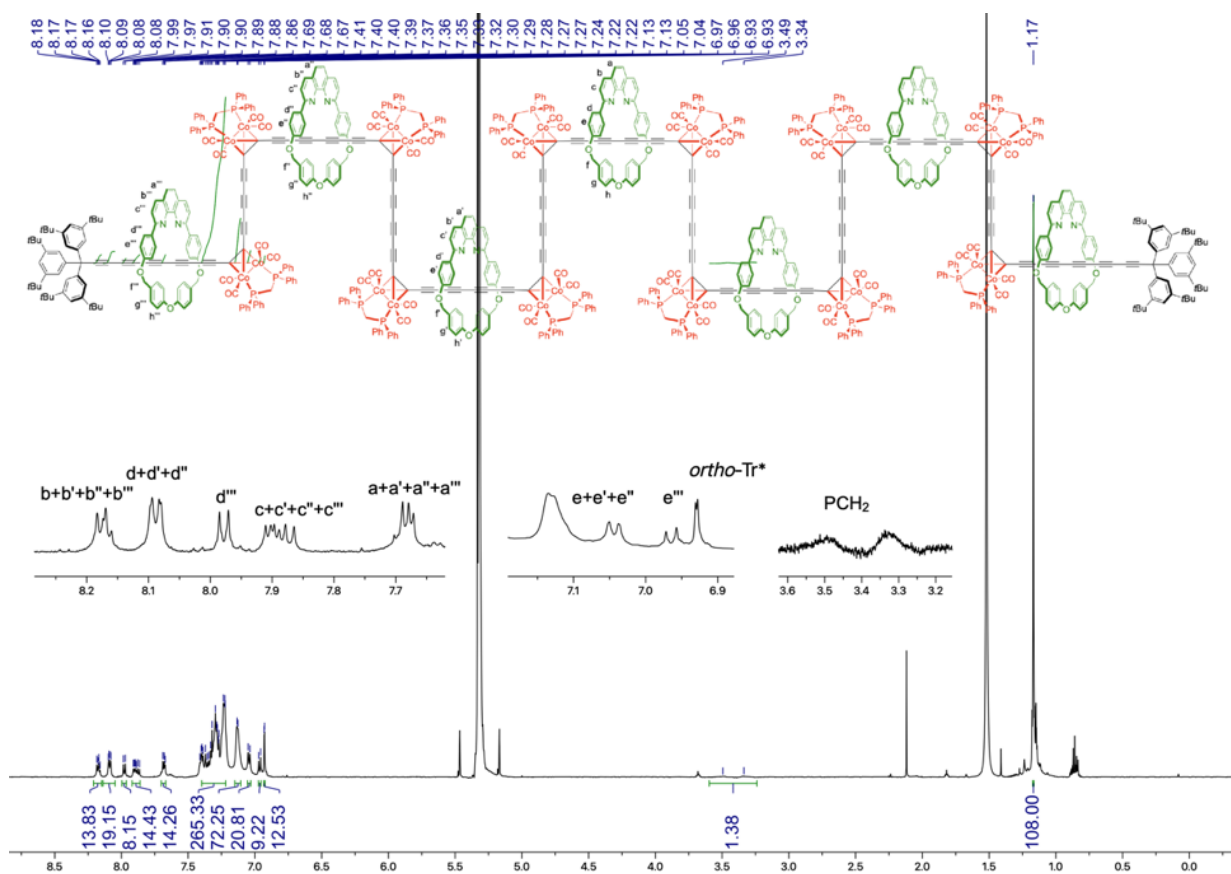
Figure 70.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz) spectrum of compound  $m\text{C88}\cdot(\text{M}_b)_5$  in  $\text{CD}_2\text{Cl}_2$ .



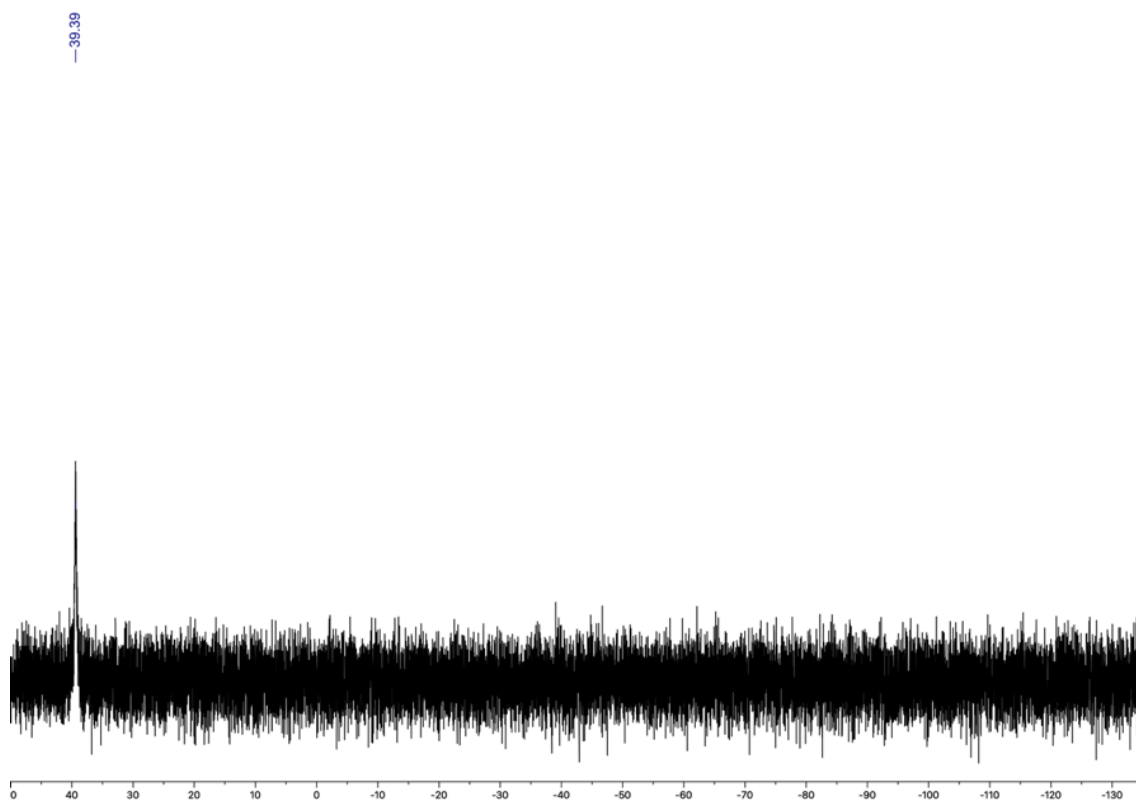
**Figure 71.**  $^1\text{H}$  NMR (600 MHz) spectrum of compound  $m\text{C108}\cdot(\text{M}_b)_6$  in  $\text{CD}_2\text{Cl}_2$  (\*indicates residual  $\text{CH}_2\text{Cl}_2$ ). The integration of  $\text{PCH}_2$  resonance was significantly less due to the long relaxing time required and phasing with less accuracy.



**Figure 72.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz) spectrum of compound  $m\text{C108}\cdot(\text{M}_b)_6$  in  $\text{CD}_2\text{Cl}_2$ .



**Figure 73.**  $^1\text{H}$  NMR (600 MHz) spectrum of compound  $m\text{C128}\cdot(\text{M}_b)_7$  in  $\text{CD}_2\text{Cl}_2$ . The methylene groups from the macrocycles were not resolved due to significant overlap with the residual  $\text{CH}_2\text{Cl}_2$ . The integration of  $\text{PCH}_2$  resonance was significantly less due to the long relaxing time required and phasing with less accuracy.



**Figure 74.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz) spectrum of compound  $m\text{C128}\cdot(\text{M}_b)_7$  in  $\text{CD}_2\text{Cl}_2$ .

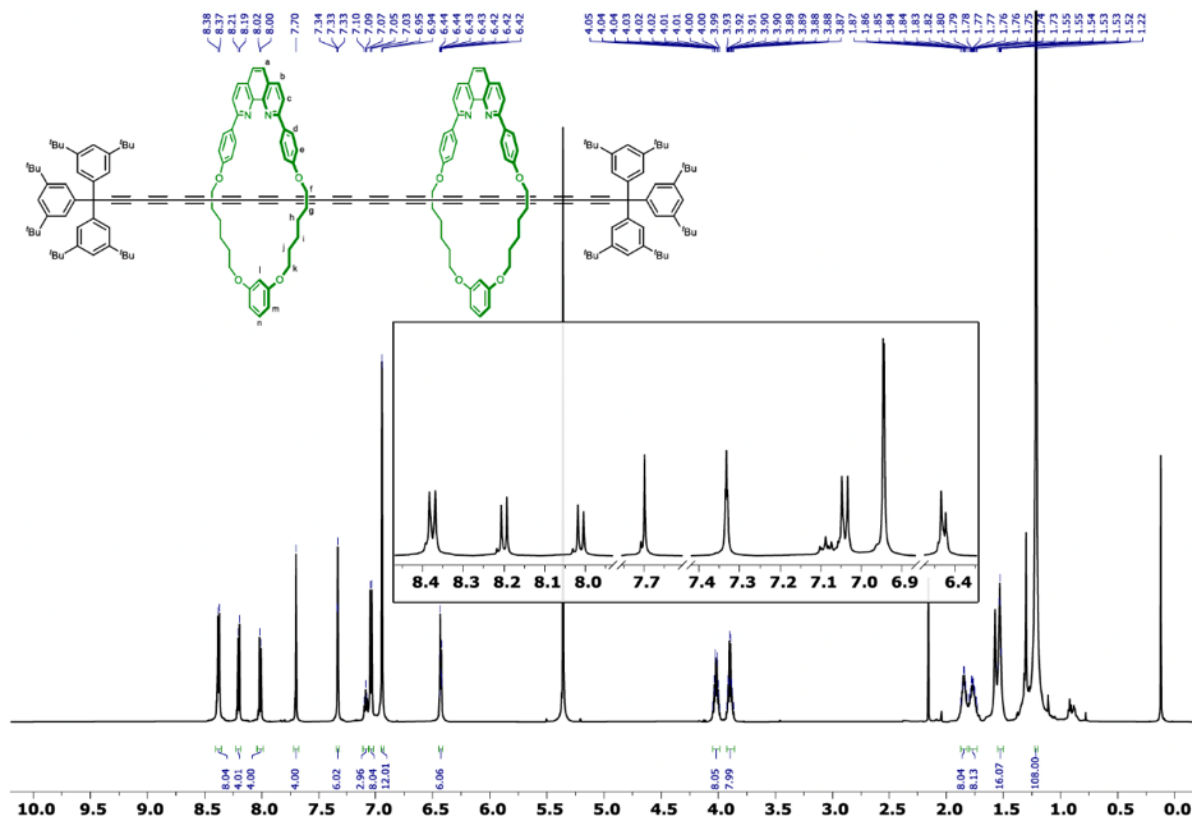


Figure 75.  $^1\text{H}$  NMR (600 MHz) spectrum of compound  $\text{C28}\cdot(\text{M}_a)_2$  in  $\text{CD}_2\text{Cl}_2$ .

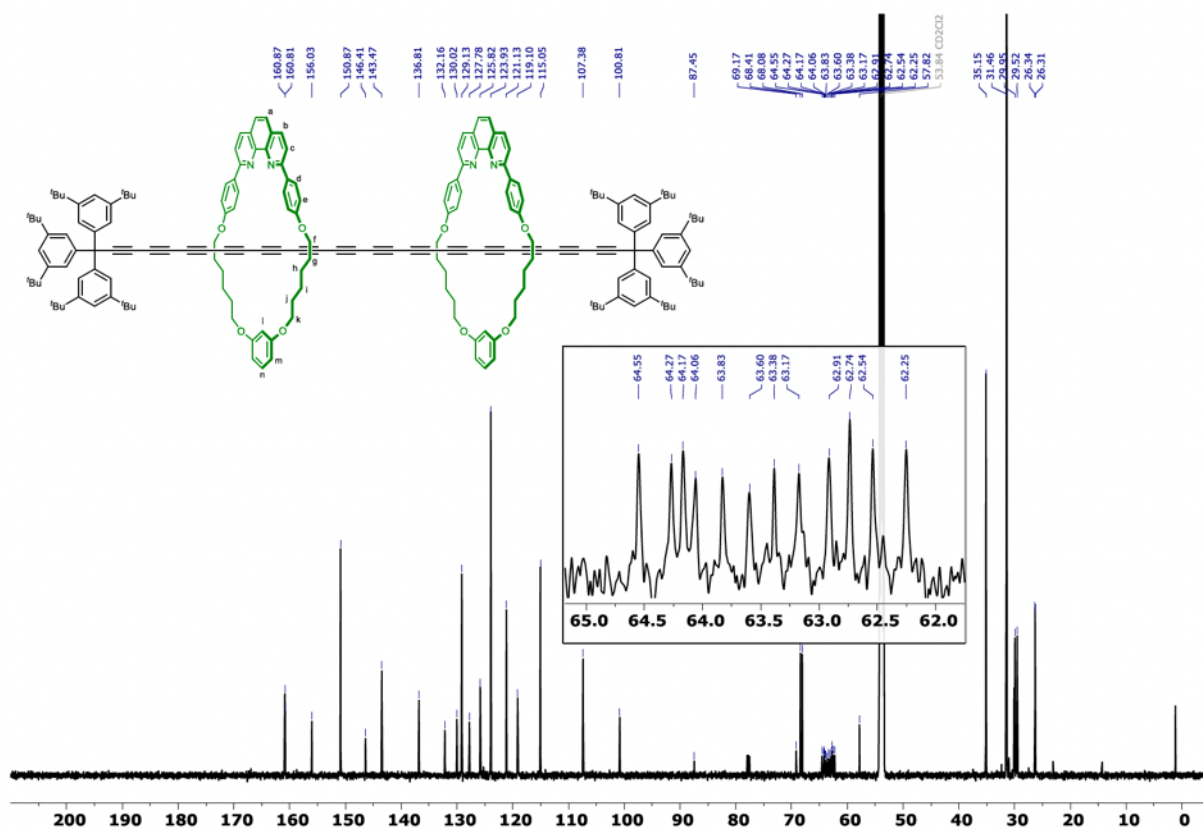


Figure 76.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound  $\text{C28}\cdot(\text{M}_a)_2$  in  $\text{CD}_2\text{Cl}_2$ .

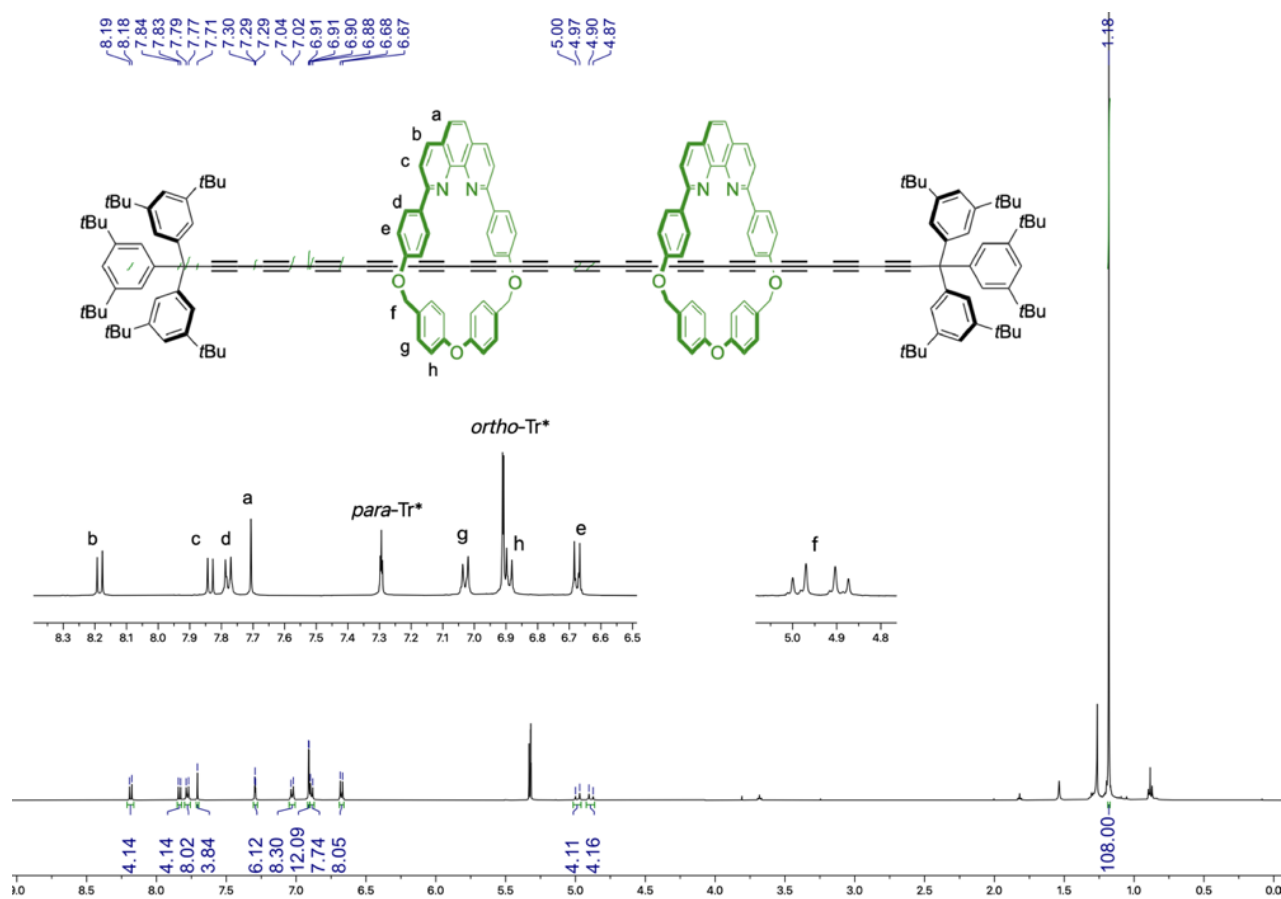


Figure 77.  $^1\text{H}$  NMR (500 MHz) spectrum of compound  $\text{C28}\cdot(\text{M}_b)_2$  in  $\text{CD}_2\text{Cl}_2$ .

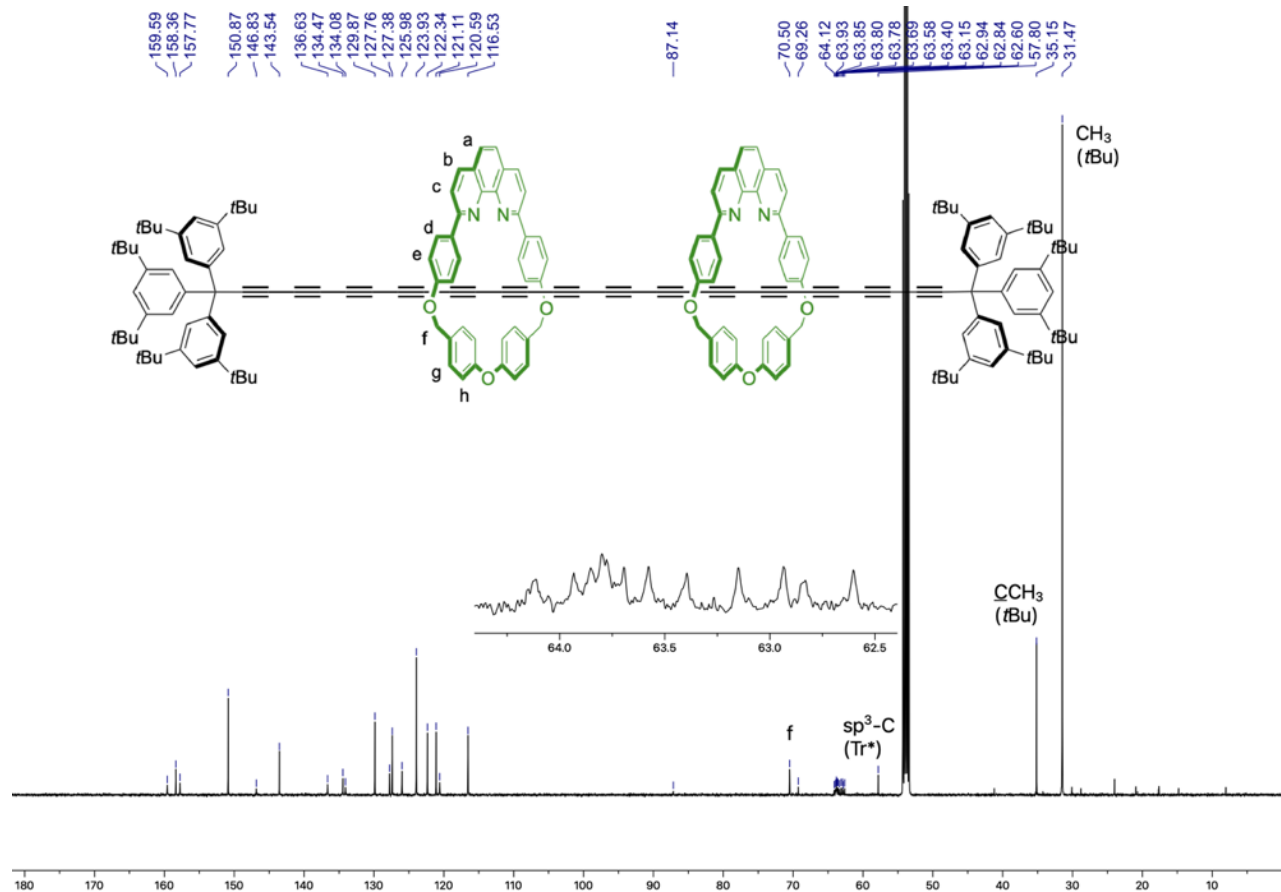
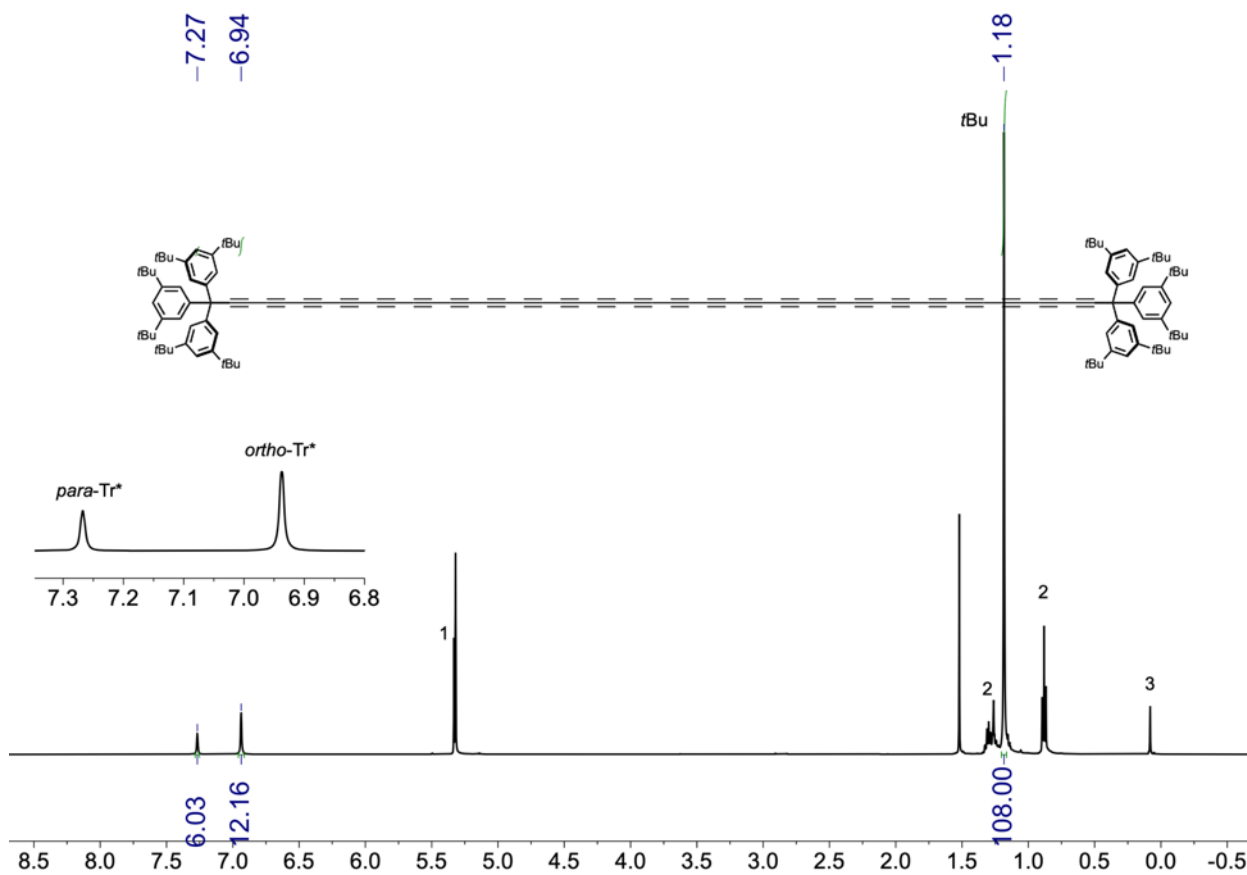
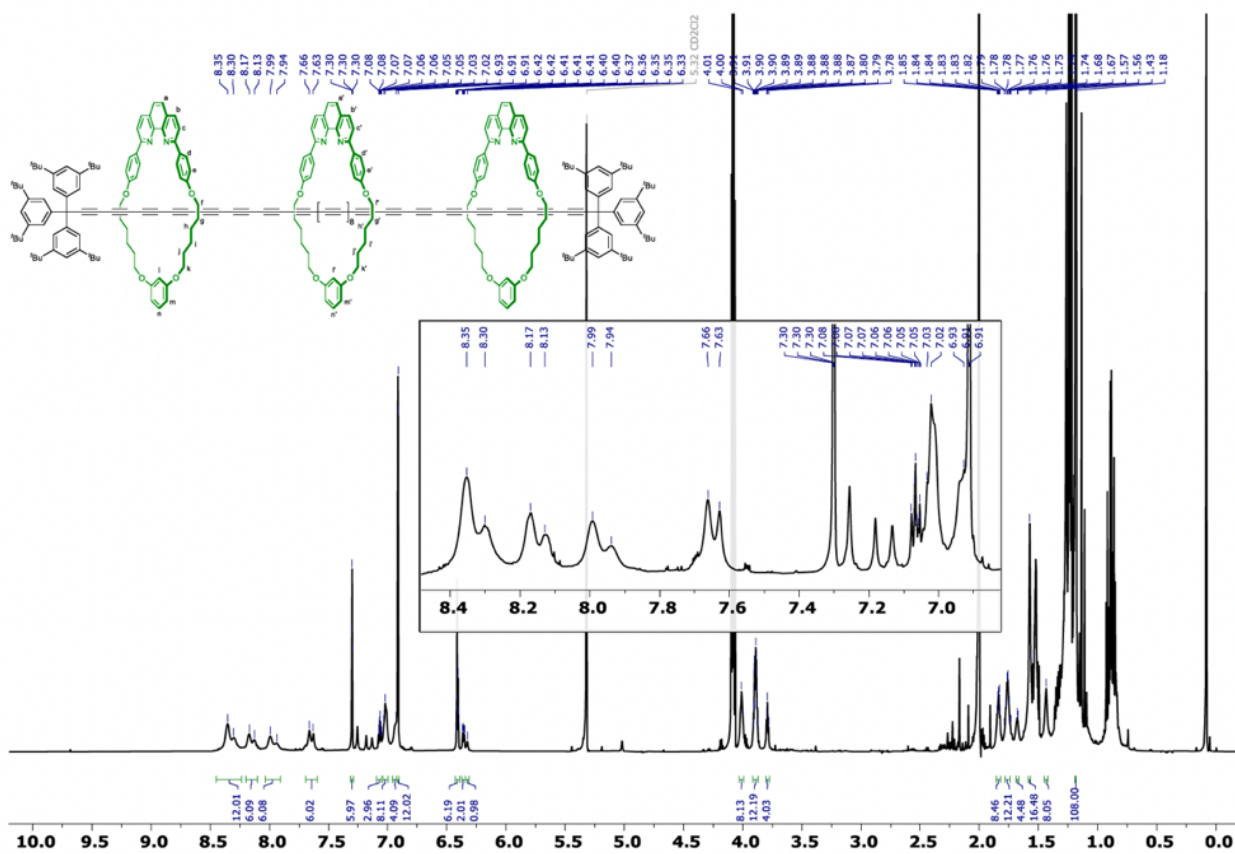


Figure 78.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz) spectrum of compound  $\text{C28}\cdot(\text{M}_b)_2$  in  $\text{CD}_2\text{Cl}_2$ .



**Figure 79.** <sup>1</sup>H NMR (500 MHz) spectrum of Tr\*[24] thread C48 in CD<sub>2</sub>Cl<sub>2</sub> (1, 2, and 3 indicate residual CH<sub>2</sub>Cl<sub>2</sub>, pentane, and silicon grease, respectively).



**Figure 80.** <sup>1</sup>H NMR (600 MHz) spectrum of compound C48·(M<sub>a</sub>)<sub>3</sub> in CD<sub>2</sub>Cl<sub>2</sub>.

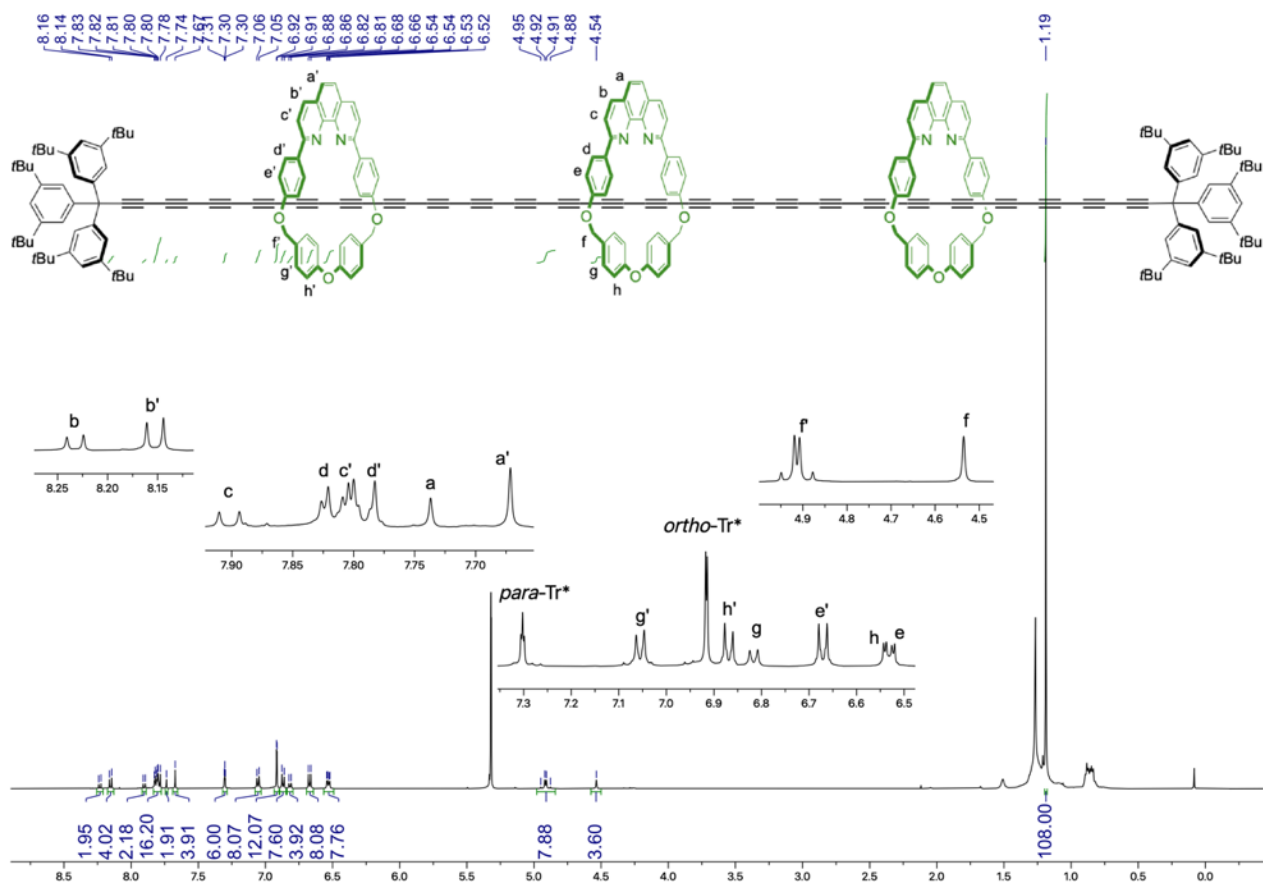


Figure 81. <sup>1</sup>H NMR (500 MHz) spectrum of compound C48·(M<sub>b</sub>)<sub>3</sub> in CD<sub>2</sub>Cl<sub>2</sub>.

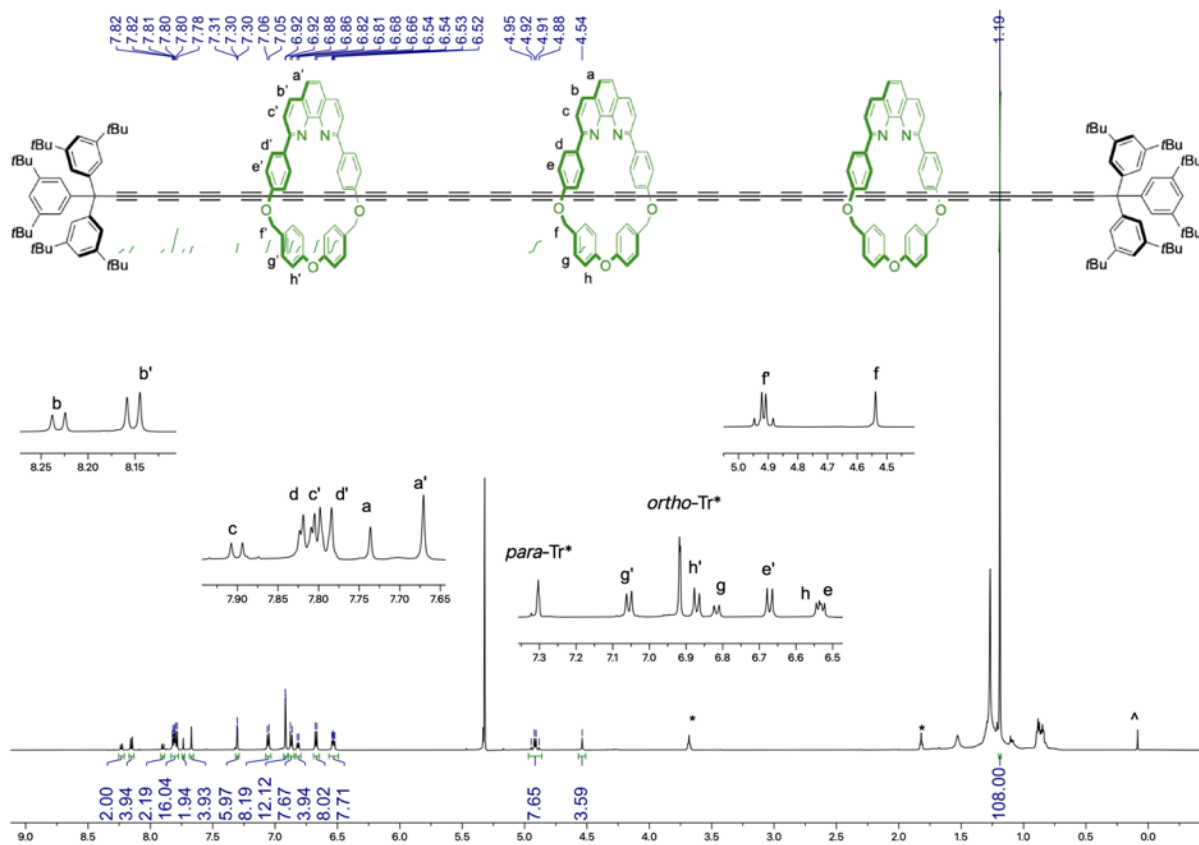
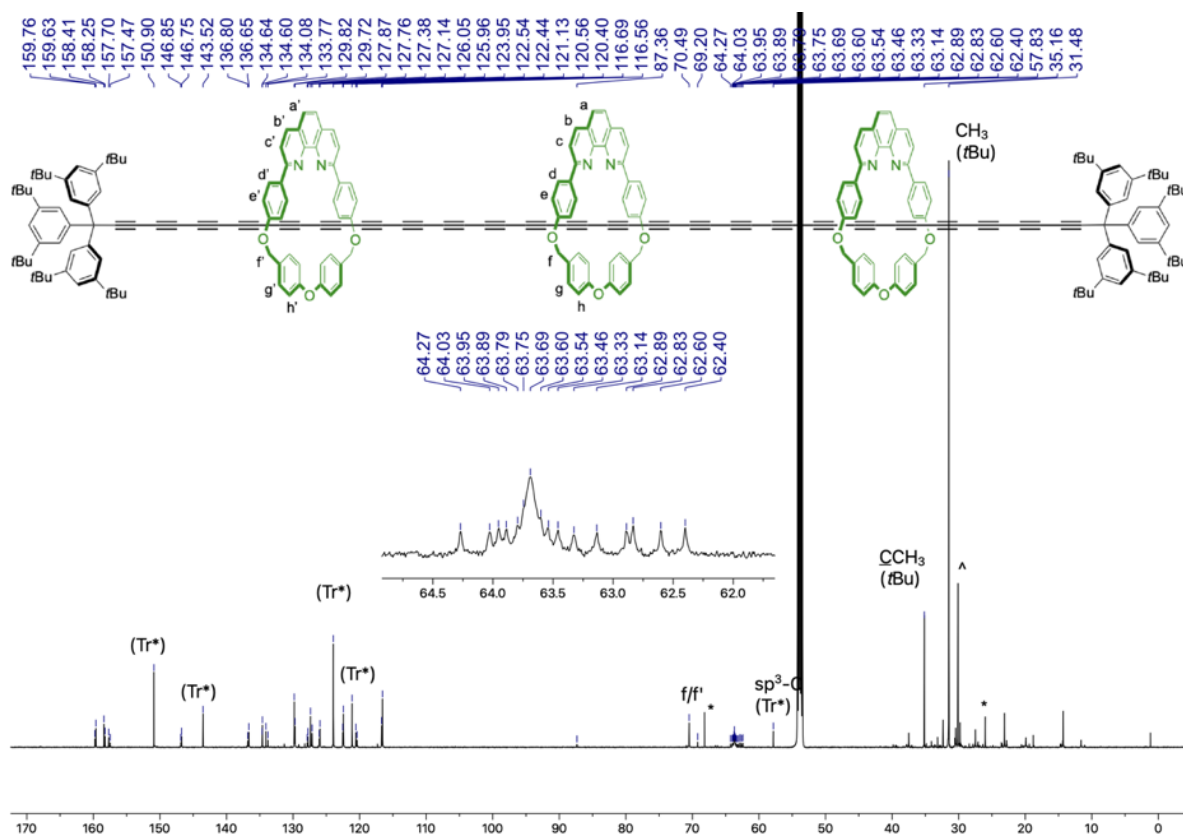
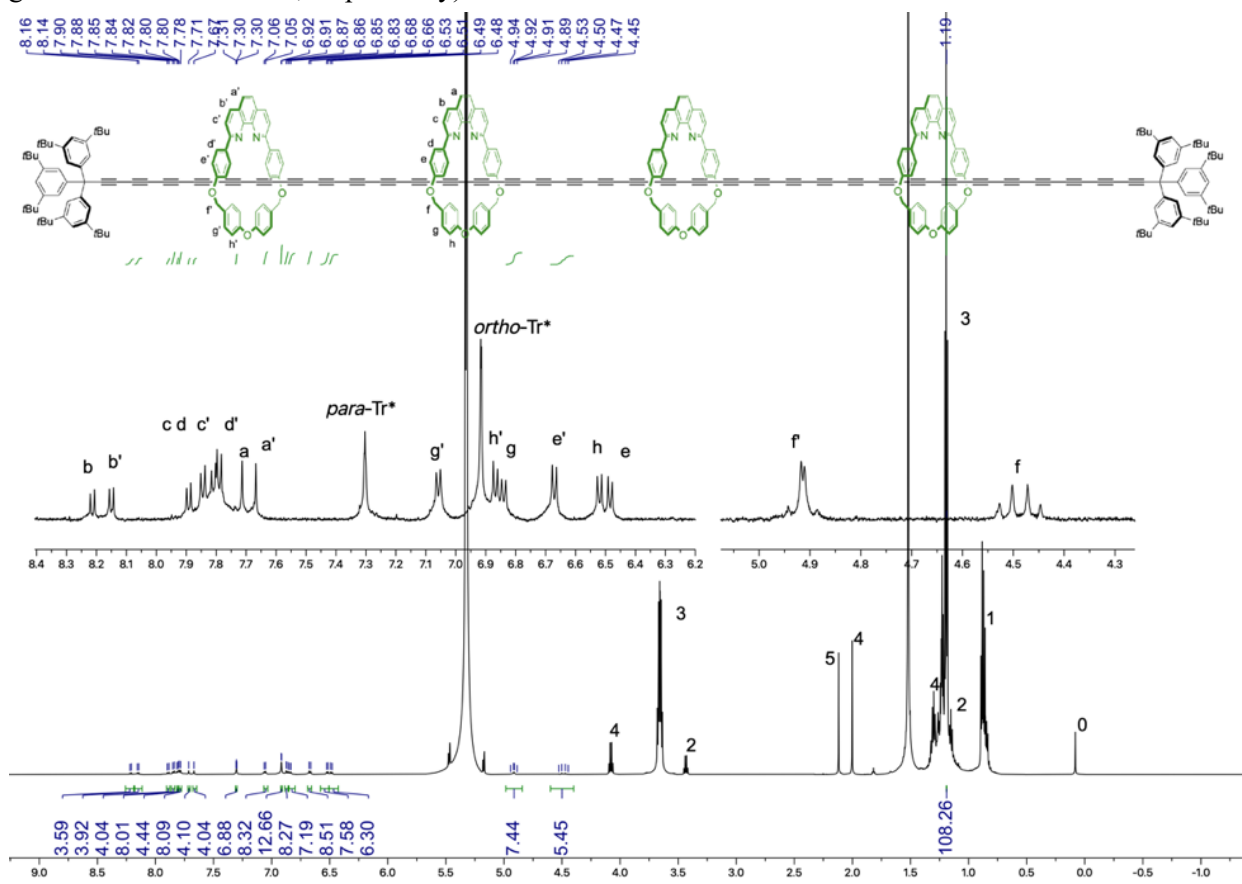


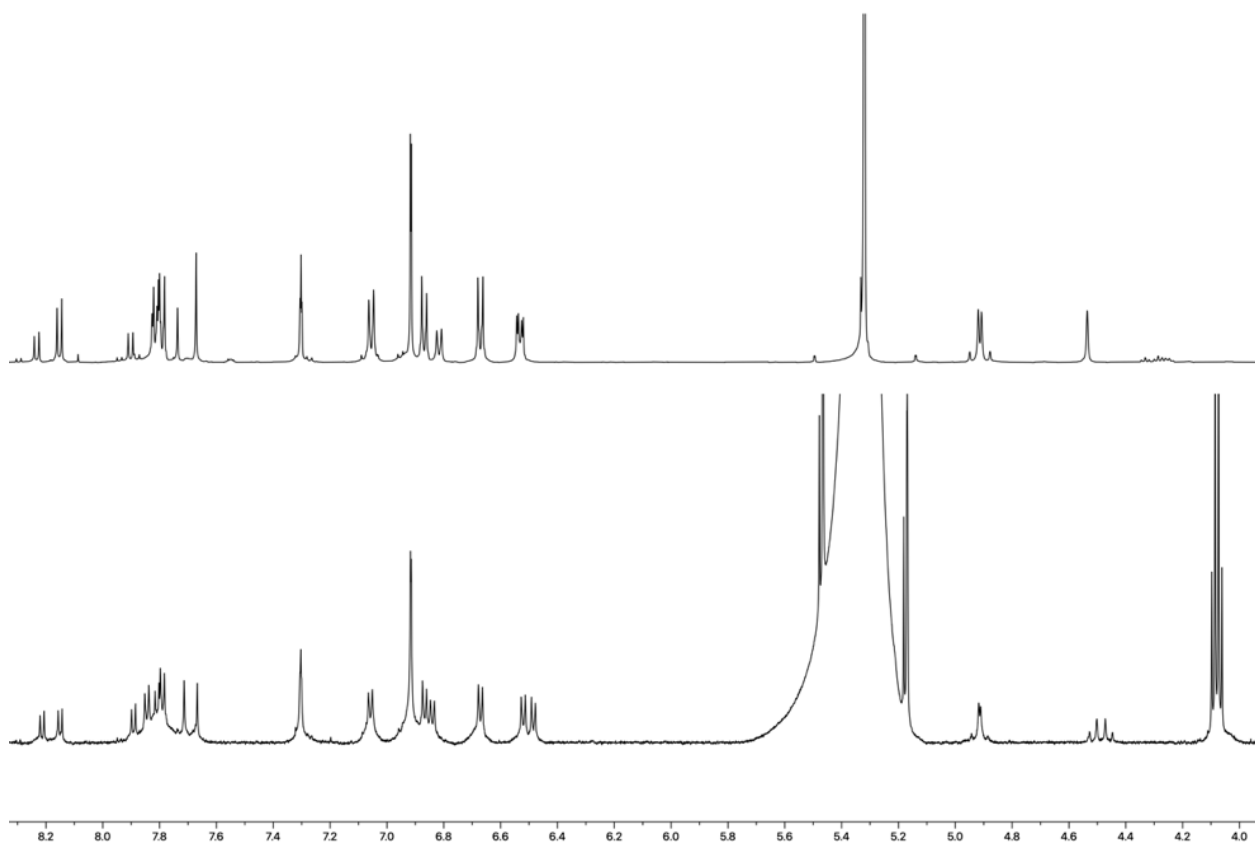
Figure 82. <sup>1</sup>H NMR (600 MHz) spectrum of compound C48·(M<sub>b</sub>)<sub>3</sub> in CD<sub>2</sub>Cl<sub>2</sub> (^ and \* indicate silicon grease and residual THF, respectively).



**Figure 83.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound **C48**·(**M<sub>b</sub>**)<sub>3</sub> in  $\text{CD}_2\text{Cl}_2$  (^and \*indicate silicon grease and residual THF, respectively).



**Figure 84.**  $^1\text{H}$  NMR (600 MHz) spectrum of compound **C68**·(**M<sub>b</sub>**)<sub>4</sub> in  $\text{CD}_2\text{Cl}_2$ . 0–5 denote the signals of silicon grease, petrol ether, diethyl ether, ethanol, ethyl acetate, and acetone, respectively.



**Figure 85.** Comparison of <sup>1</sup>H NMR (600 MHz) spectrum of compound C48·(Mb)<sub>3</sub> (top) and C68·(Mb)<sub>4</sub> (bottom) in CD<sub>2</sub>Cl<sub>2</sub>.

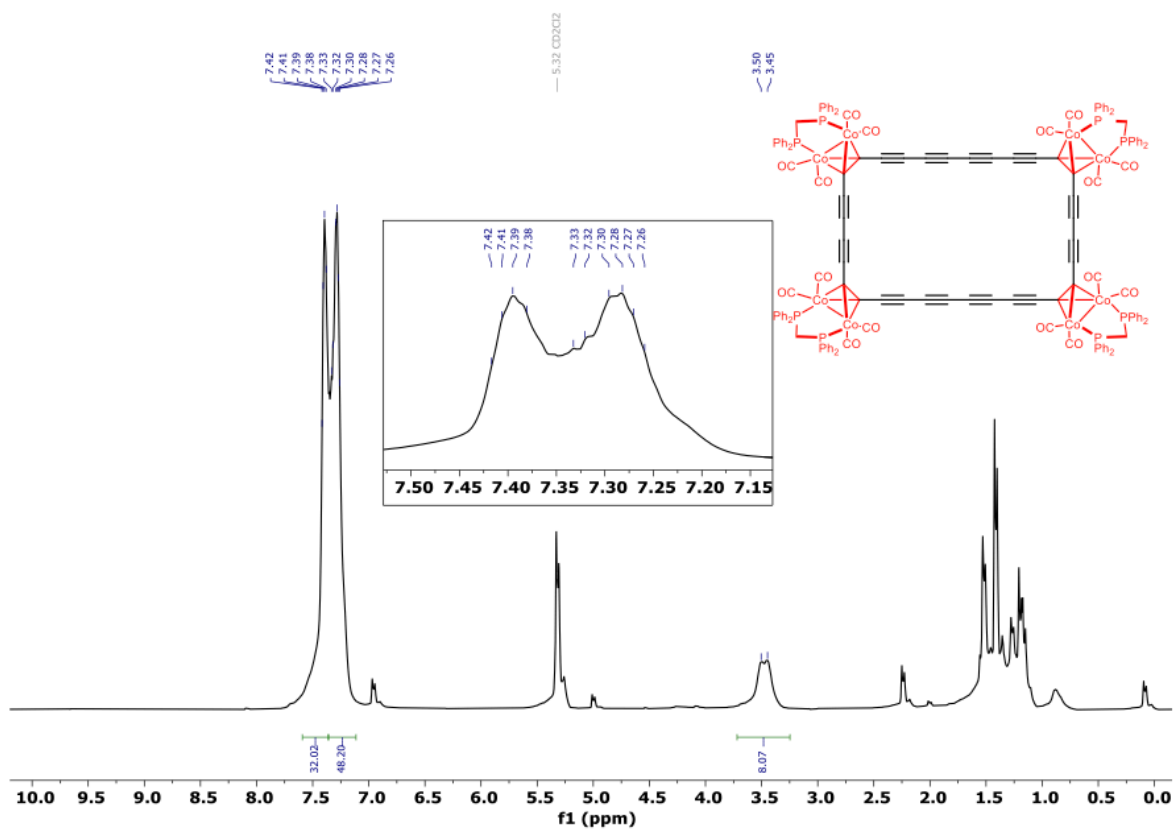


Figure 86.  $^1\text{H}$  NMR (600 MHz) spectrum of compound *mcC32* in  $\text{CD}_2\text{Cl}_2$ .

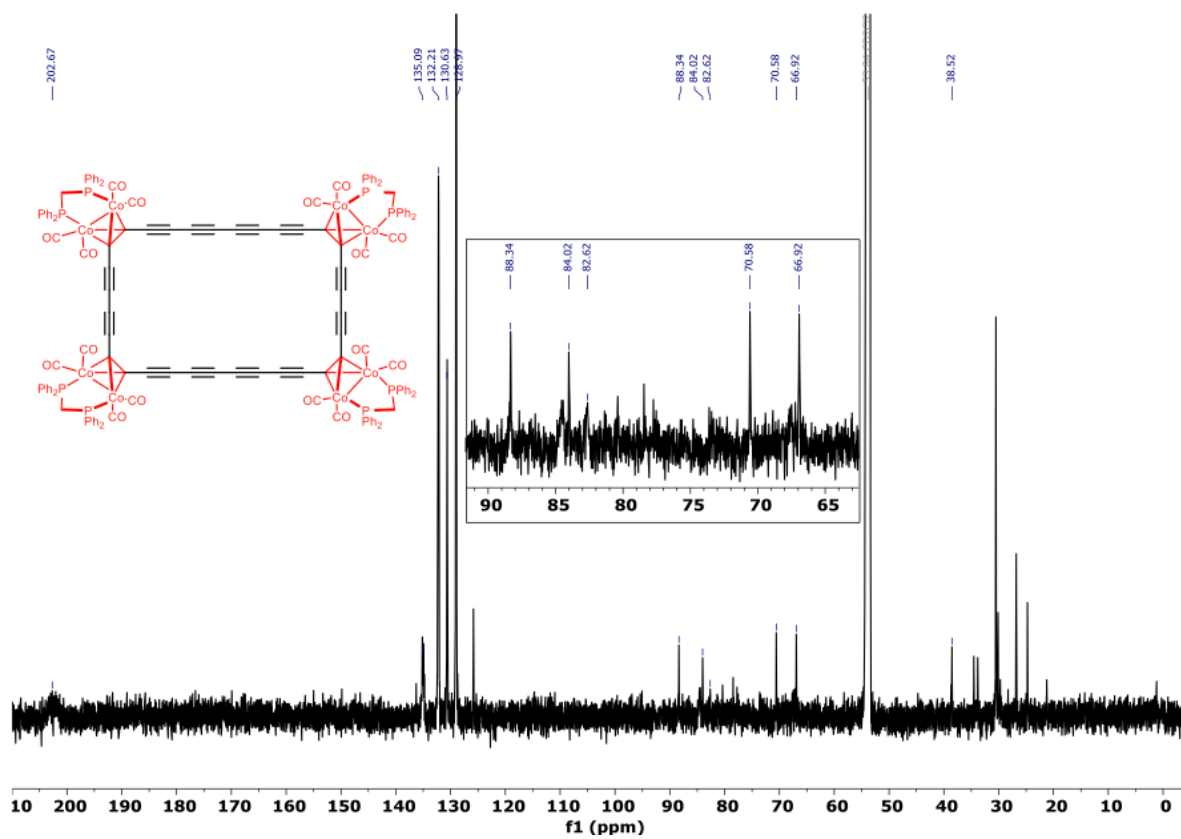


Figure 87.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound *mcC32* in  $\text{CD}_2\text{Cl}_2$ .

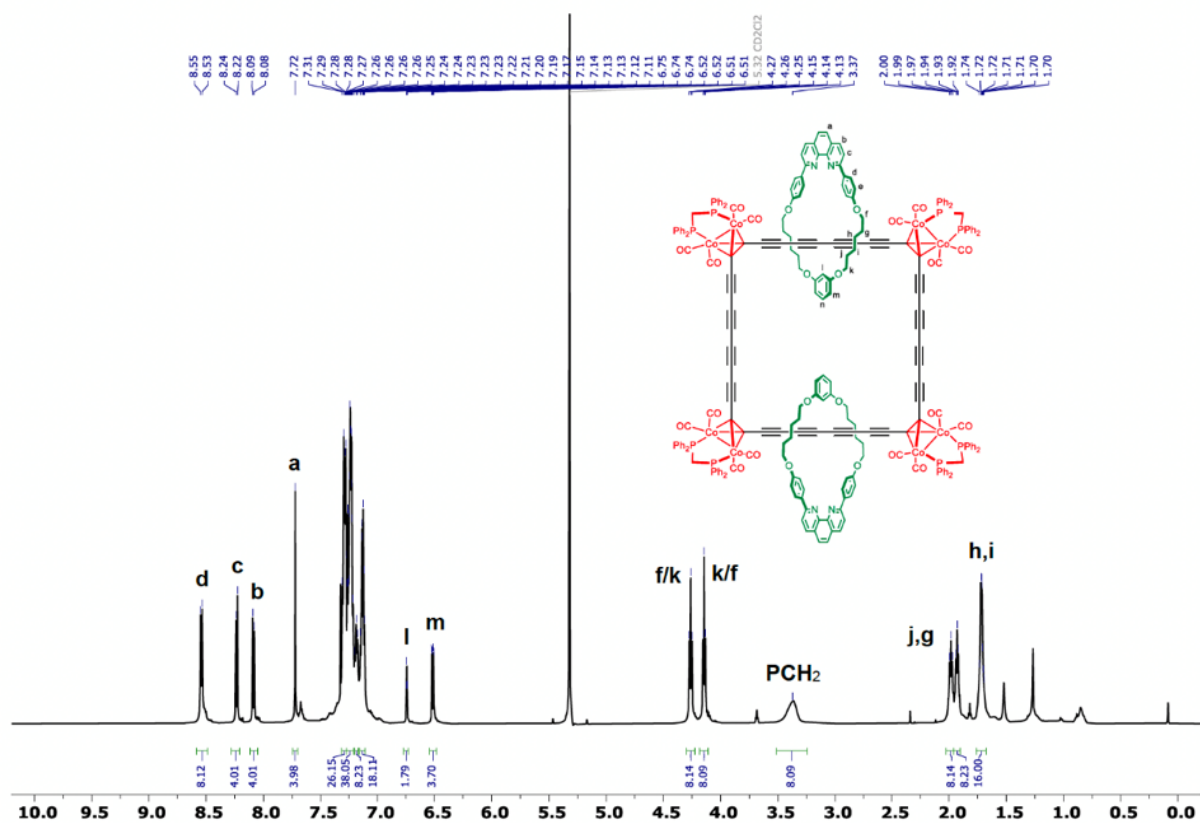


Figure 88.  $^1\text{H}$  NMR (600 MHz) spectrum of compound  $mcC40 \cdot (M_a)_2$  in  $\text{CD}_2\text{Cl}_2$ .

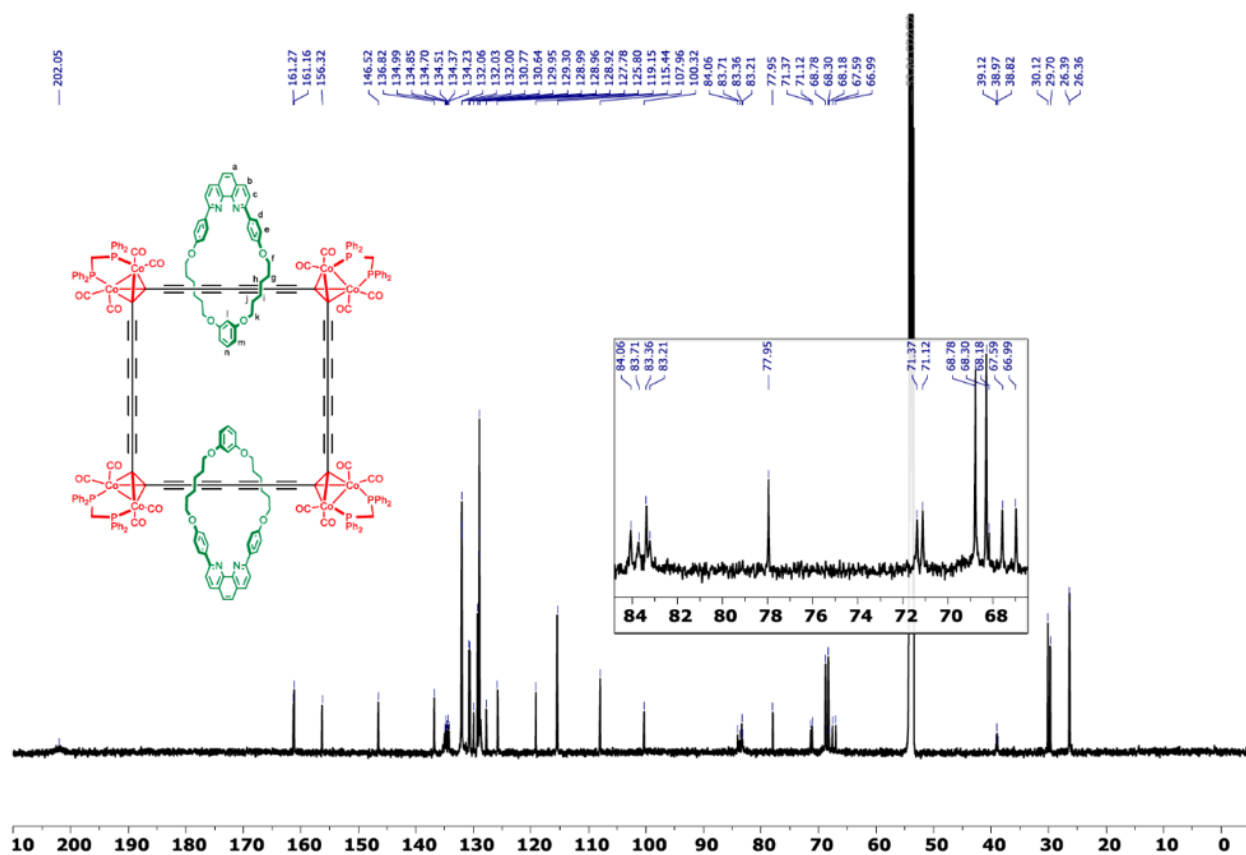
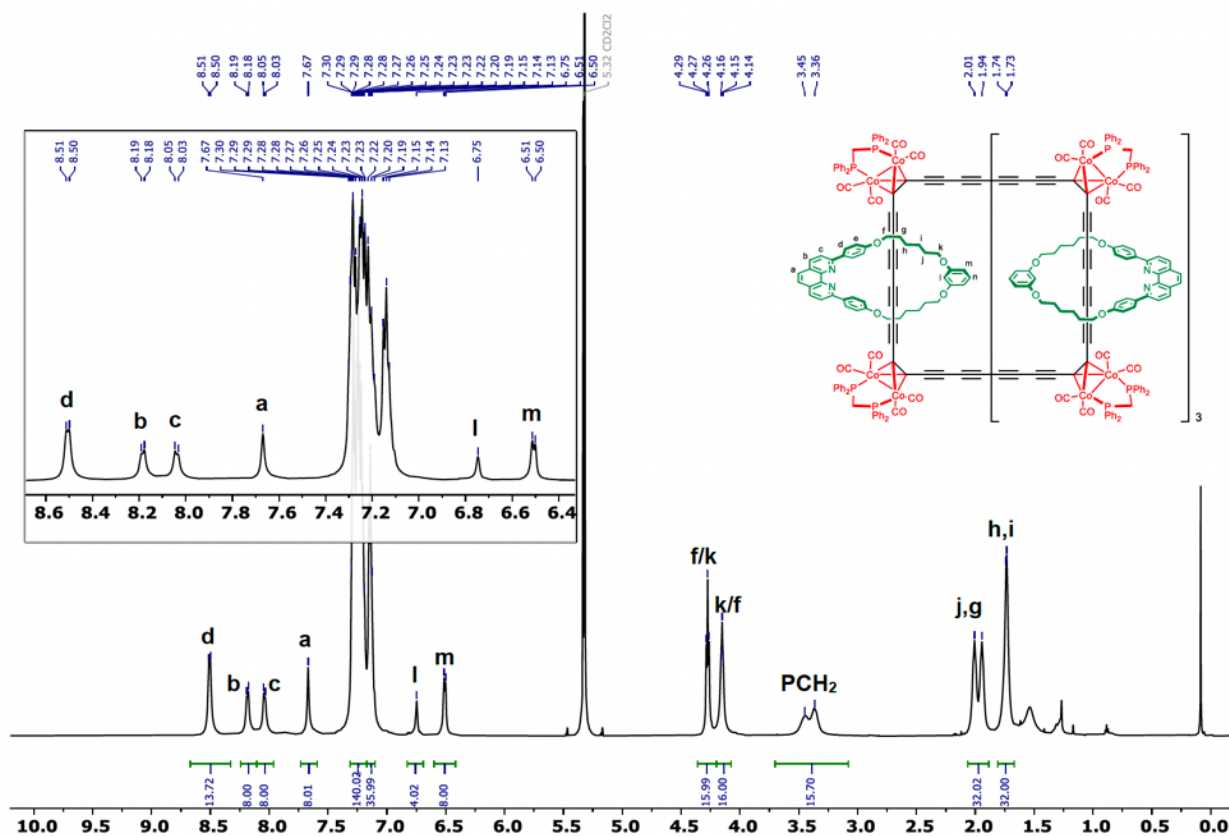
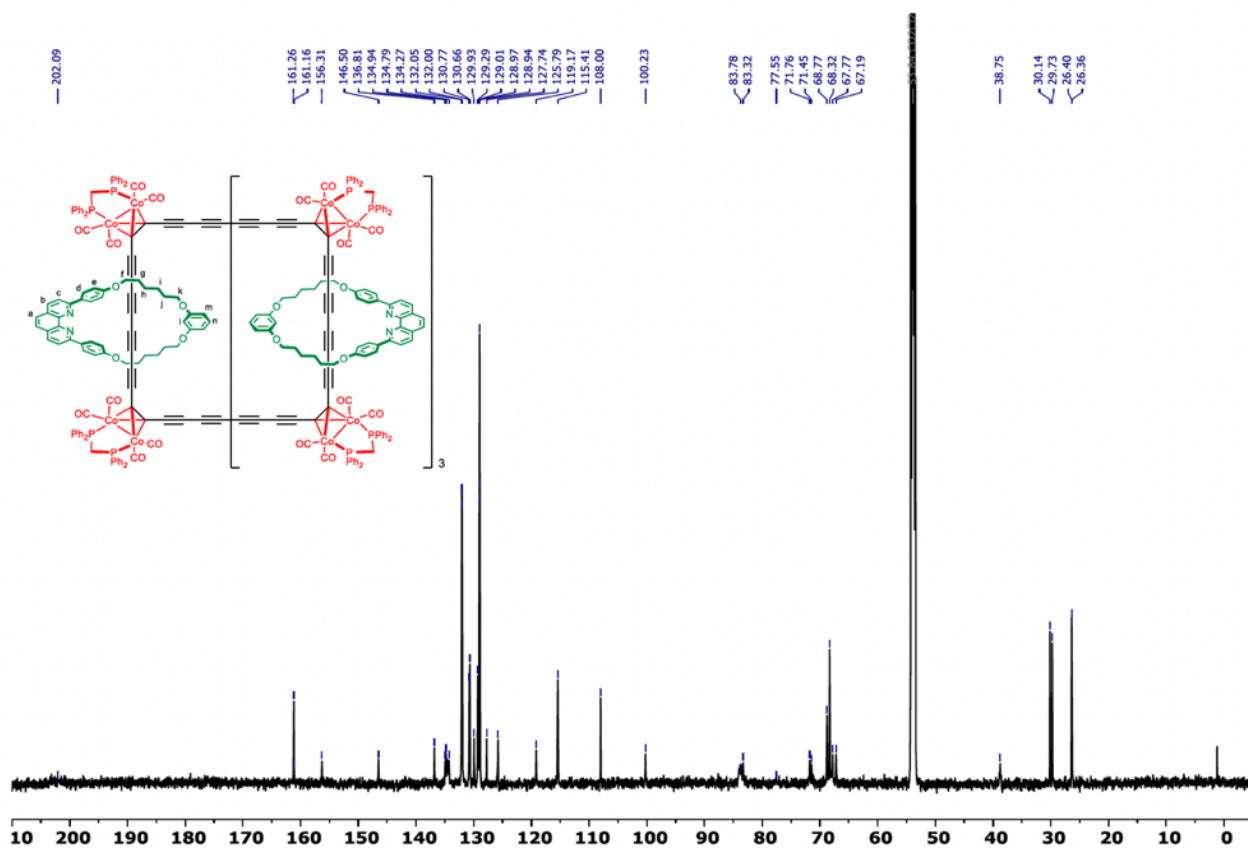


Figure 89.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound  $mcC40 \cdot (M_a)_2$  in  $\text{CD}_2\text{Cl}_2$ .



**Figure 90.**  $^1\text{H}$  NMR (600 MHz) spectrum of compound  $mcC80 \cdot (M_a)_4$  in  $\text{CD}_2\text{Cl}_2$ .



**Figure 91.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz) spectrum of compound  $mcC80 \cdot (M_a)_4$  in  $\text{CD}_2\text{Cl}_2$ .

## Section 10: Mass Spectra

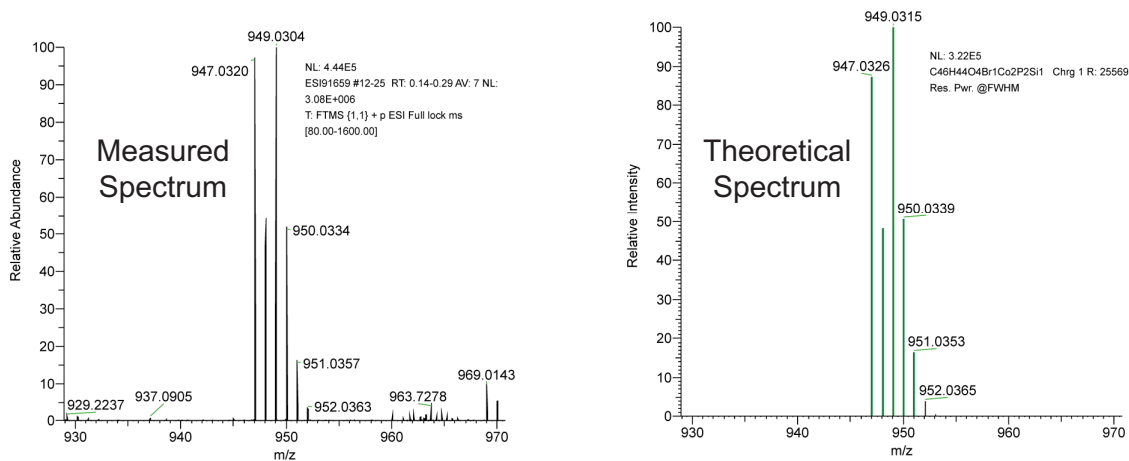


Figure 92. ESI high-resolution mass spectra of compound 2.

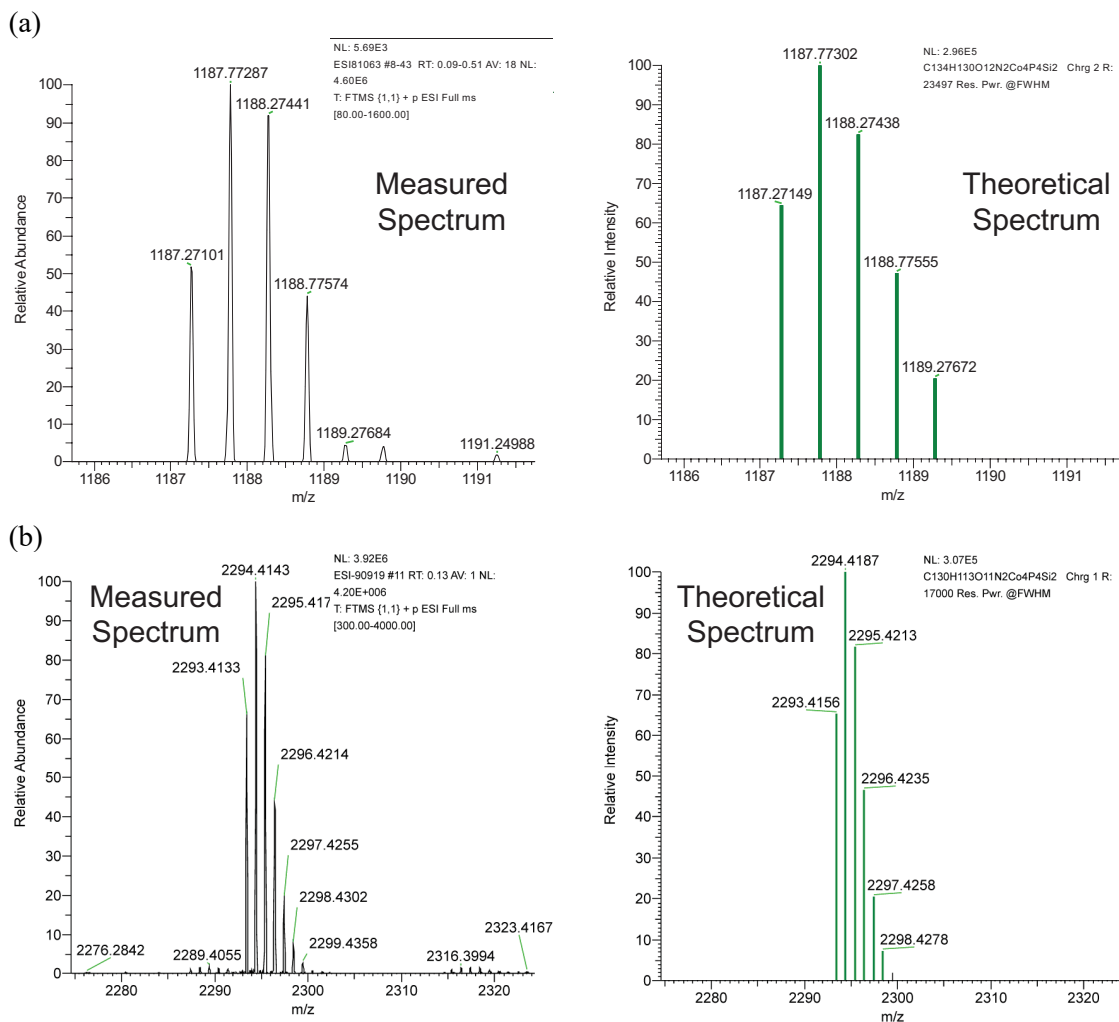


Figure 93. ESI high-resolution mass spectra of (a)  $3 \cdot M_a$  and (b)  $3 \cdot M_b$ .

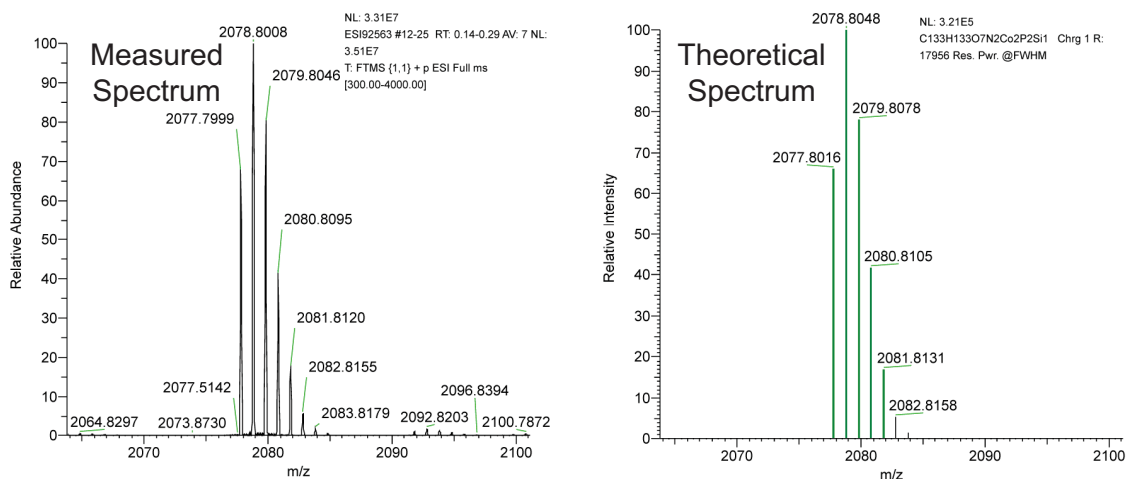


Figure 94. ESI high-resolution mass spectra of  $S3 \cdot M_b$ .

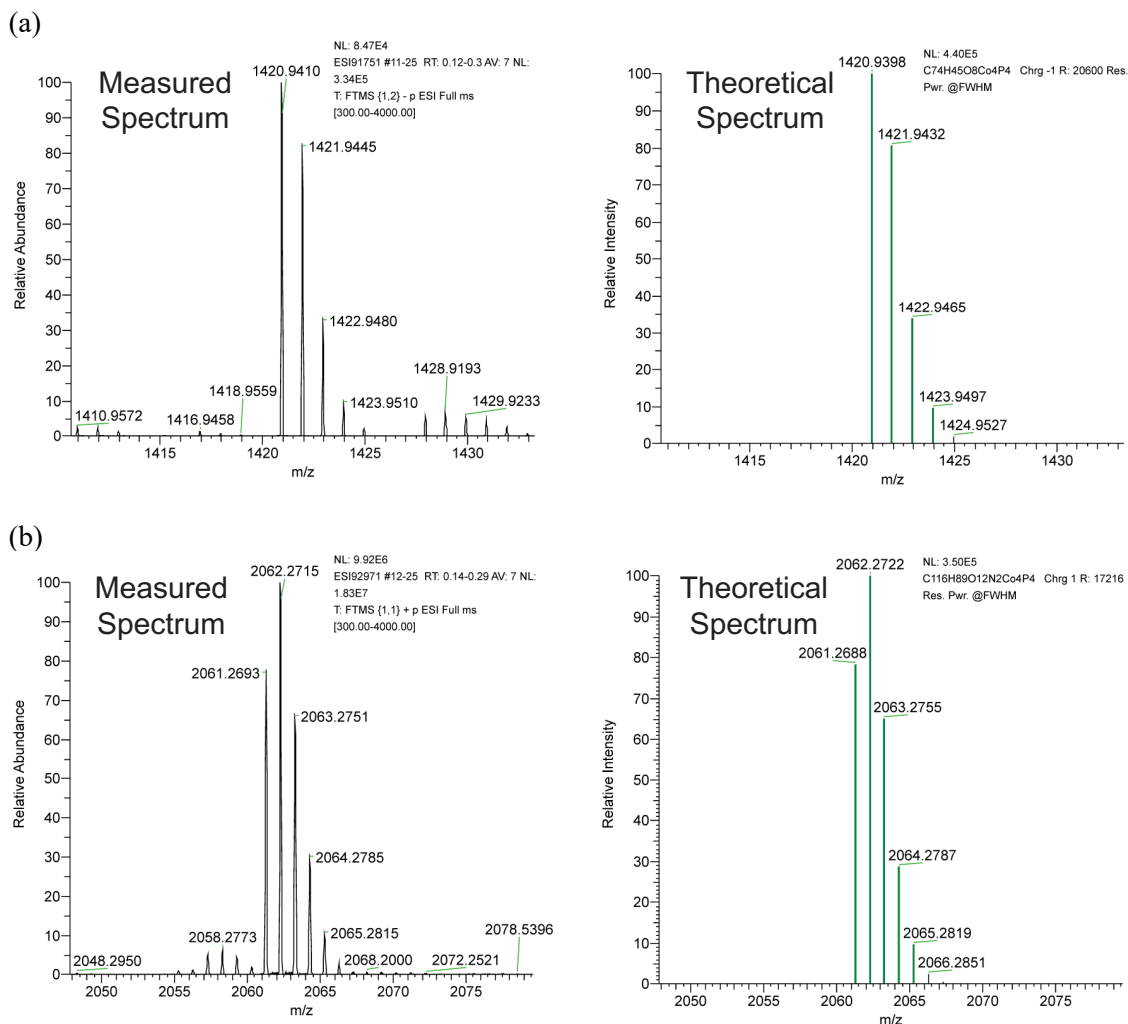
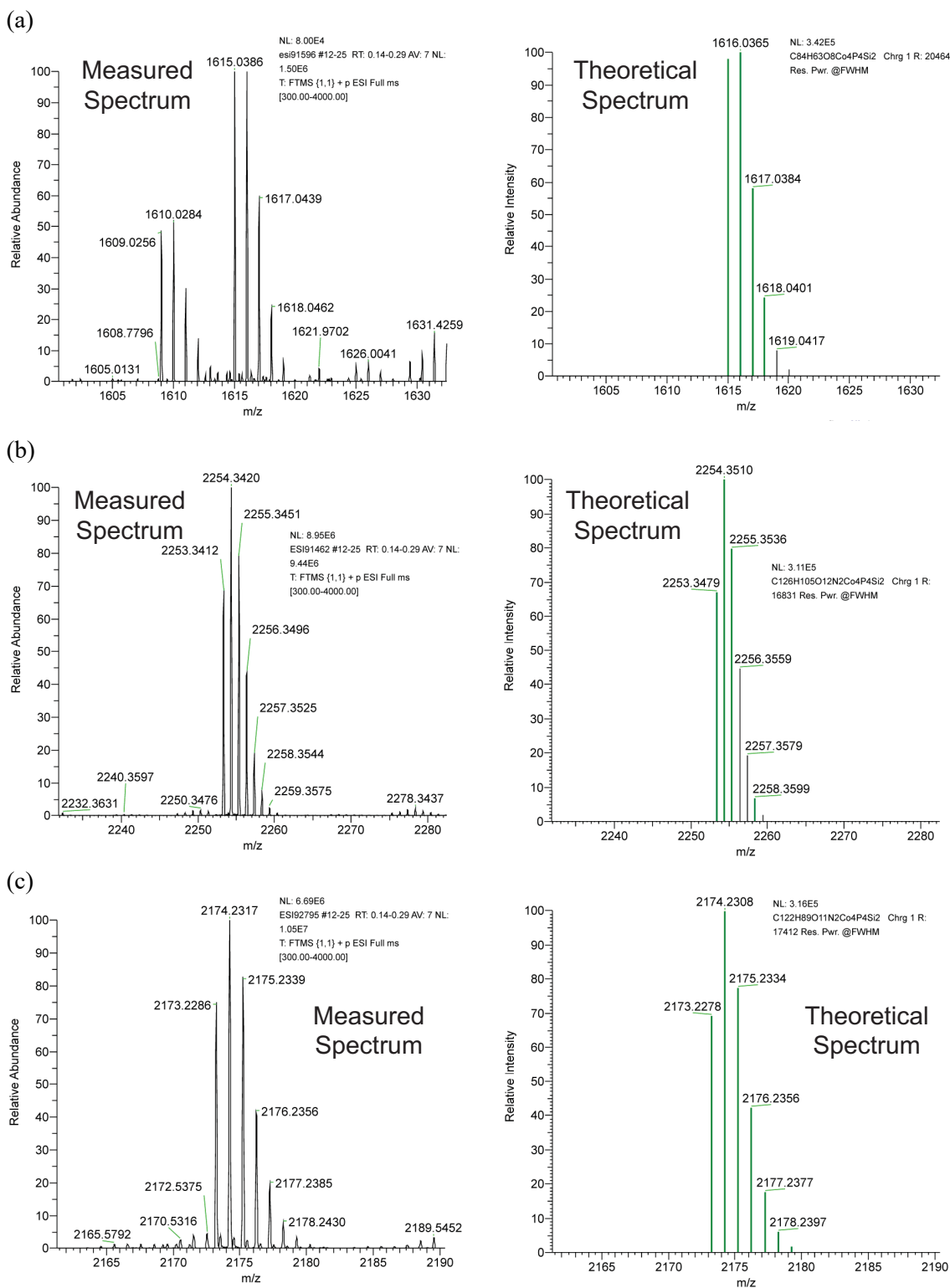
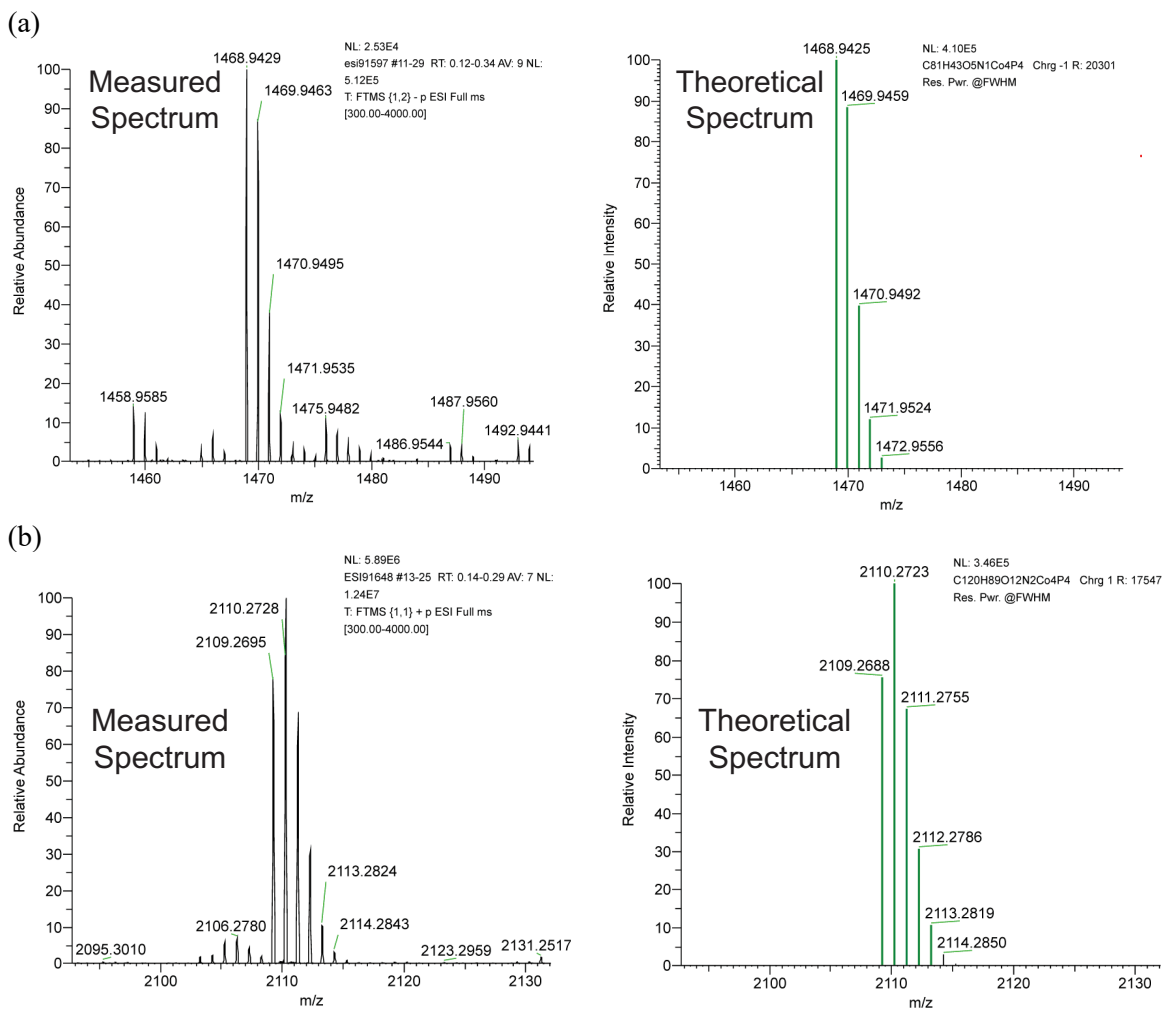


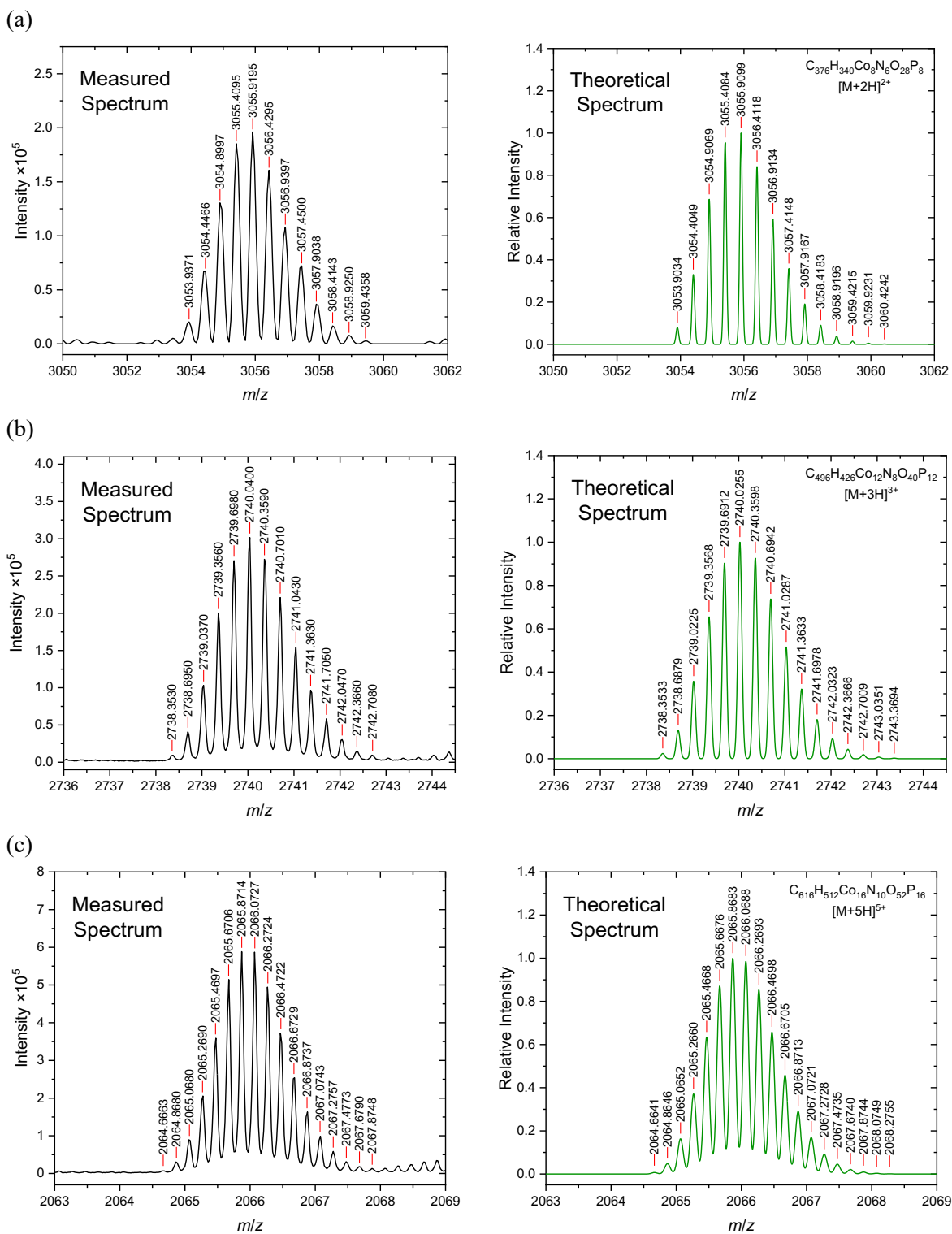
Figure 95. ESI high-resolution mass spectra of (a) compound 4 and (b)  $4 \cdot M_a$ .



**Figure 96.** ESI high-resolution mass spectra of (a) **5**, (b) **5·M<sub>a</sub>**, and (c) **5·M<sub>b</sub>**.



**Figure 97.** ESI high-resolution mass spectra of (a) **6** and (c) **6·M<sub>a</sub>**.



**Figure 98.** ESI high-resolution mass spectra of (a)  $mC48 \cdot (M_a)_3$ , (b)  $mC68 \cdot (M_a)_4$ , and (c)  $mC88 \cdot (M_a)_5$ .

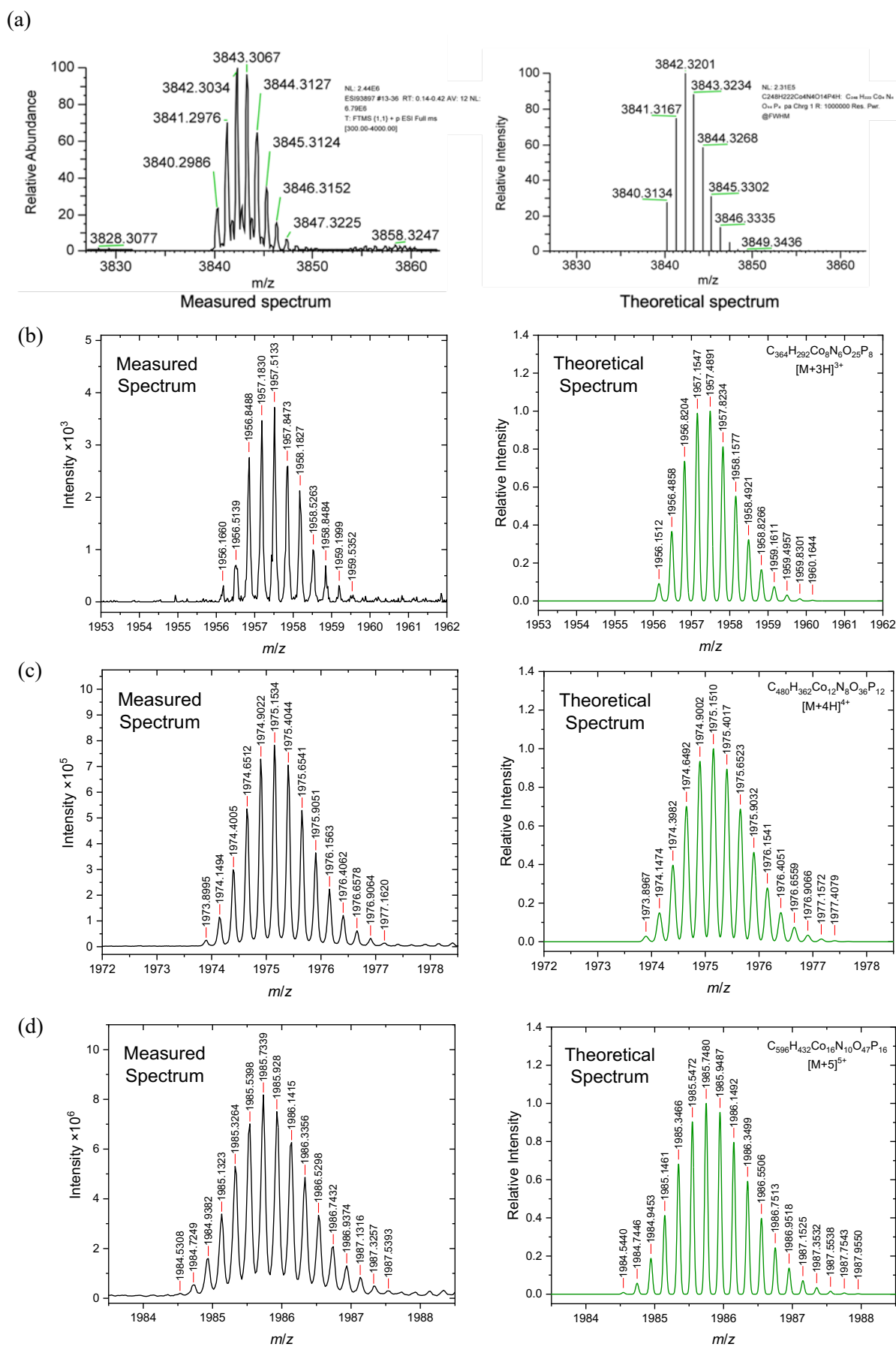
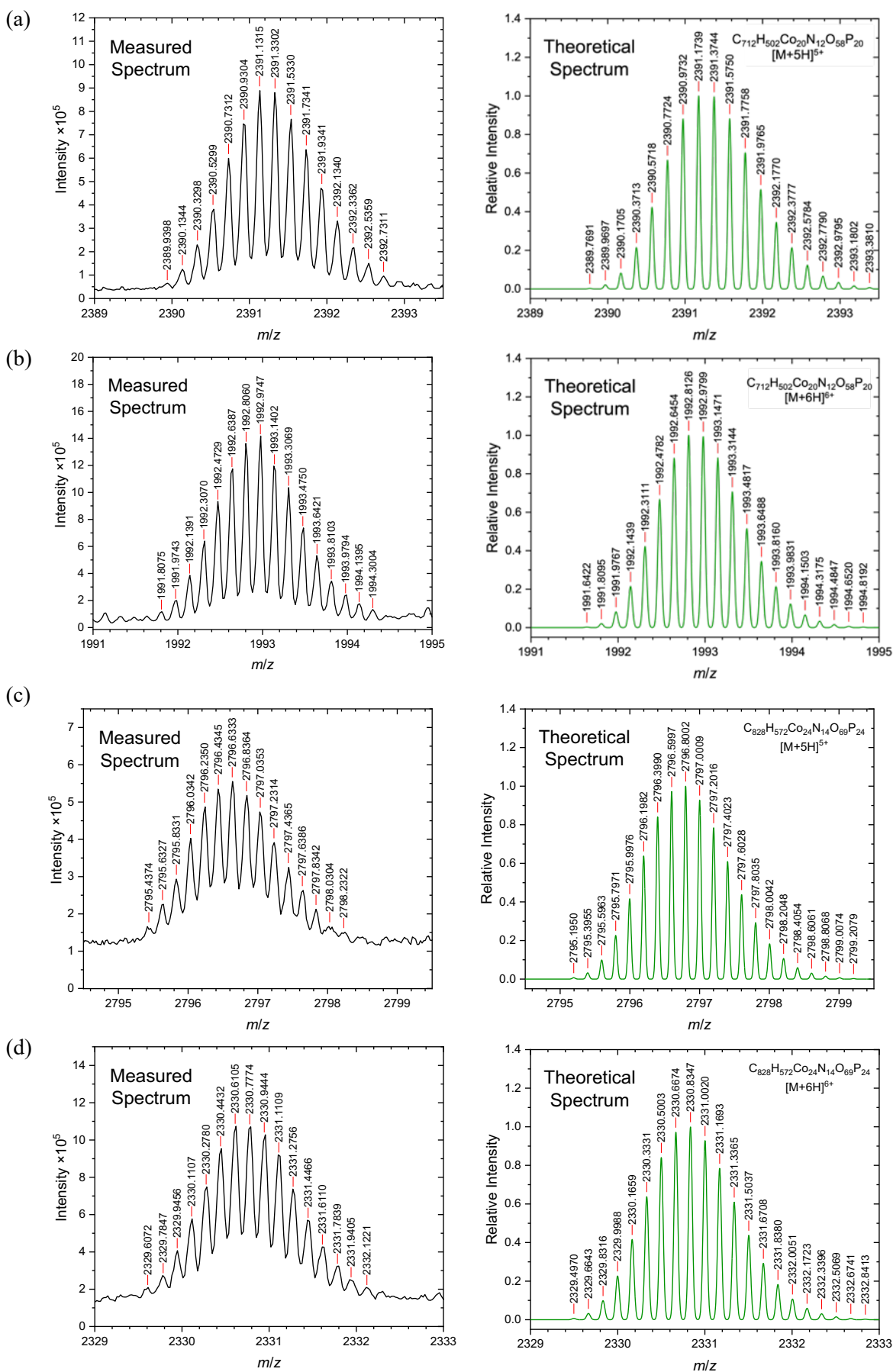
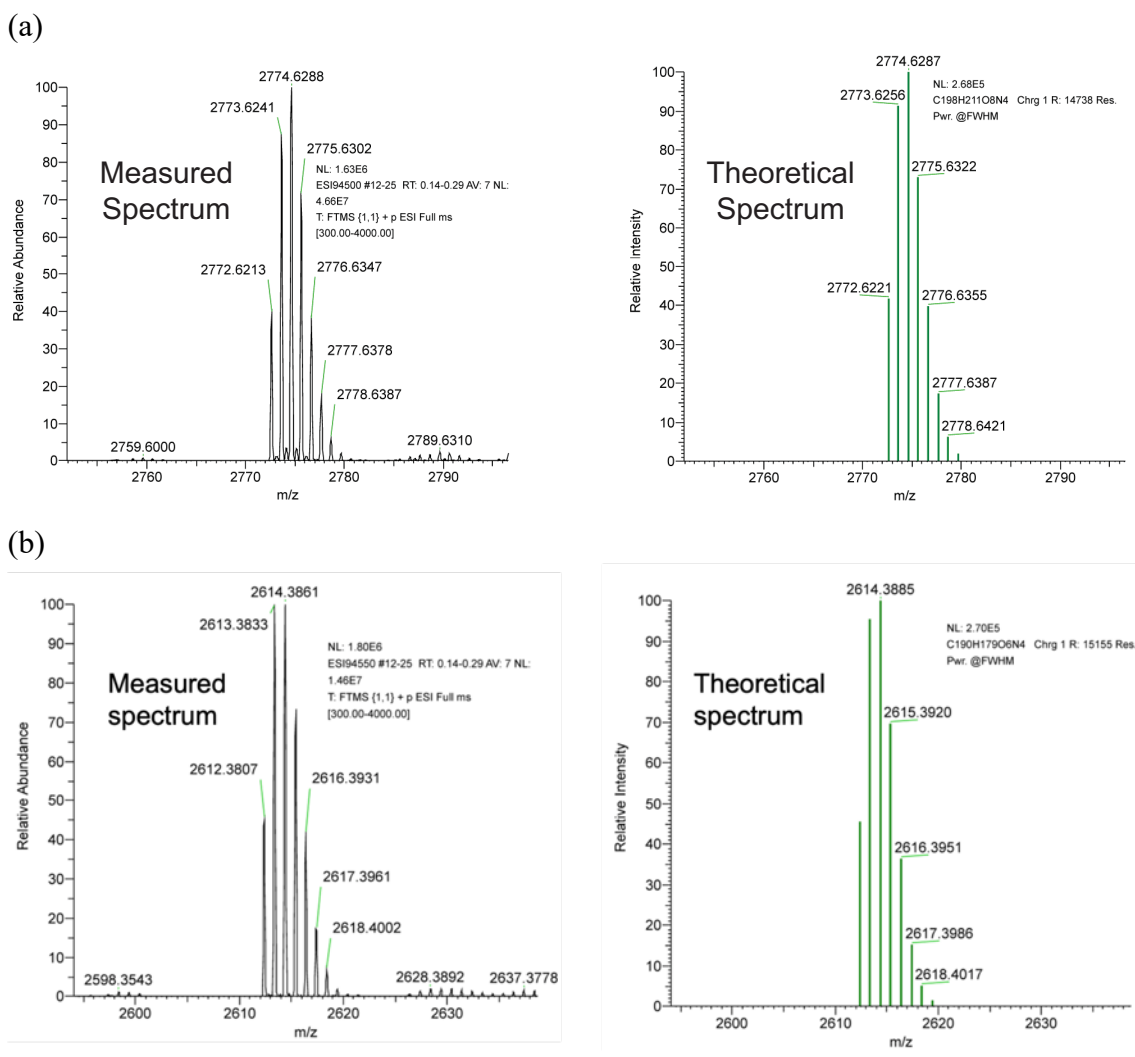


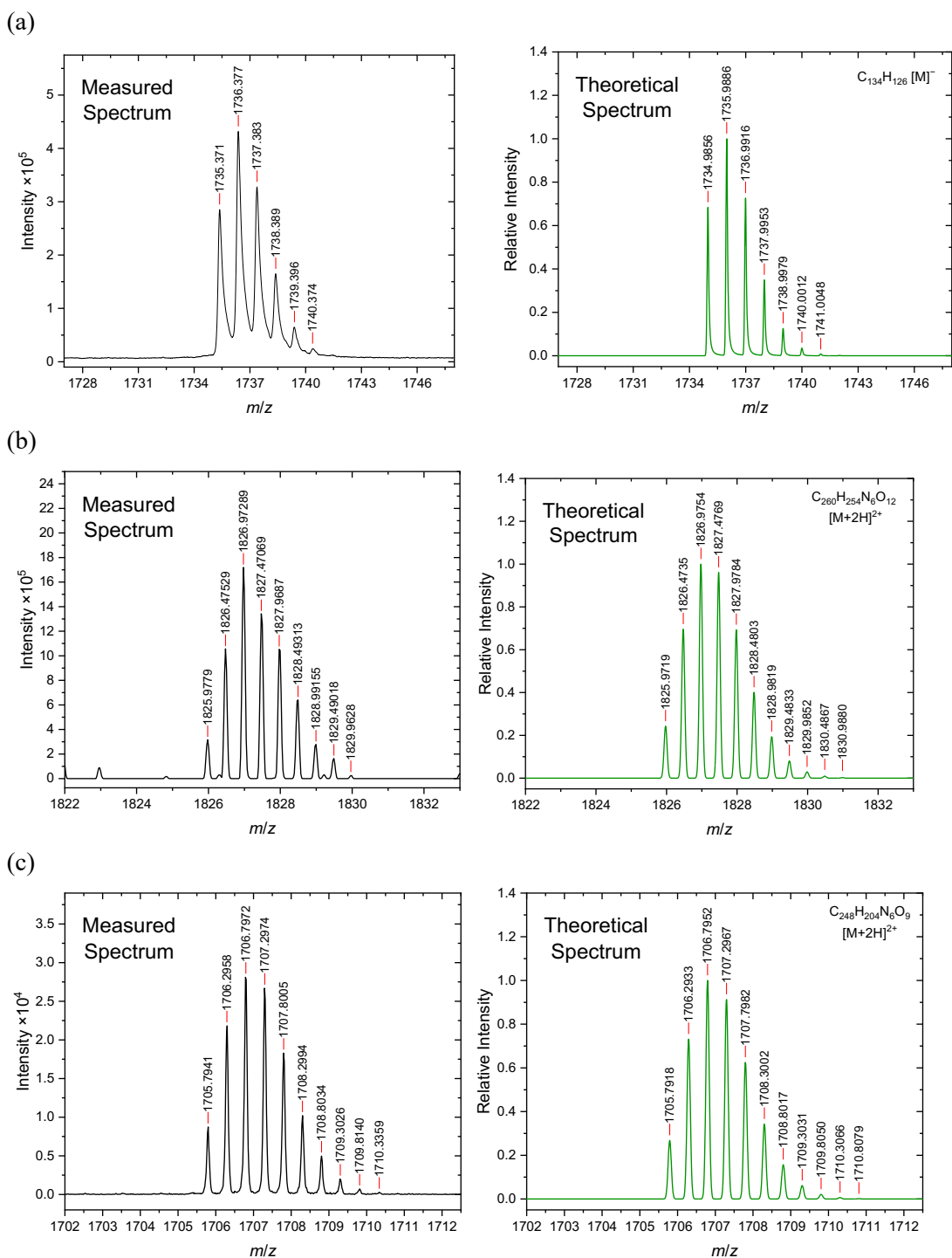
Figure 99. ESI high-resolution mass spectra of (a)  $mC28 \cdot (M_b)_2$ , (b)  $mC48 \cdot (M_b)_3$ , (c)  $mC68 \cdot (M_b)_4$ , and (d)  $mC88 \cdot (M_b)_5$ .



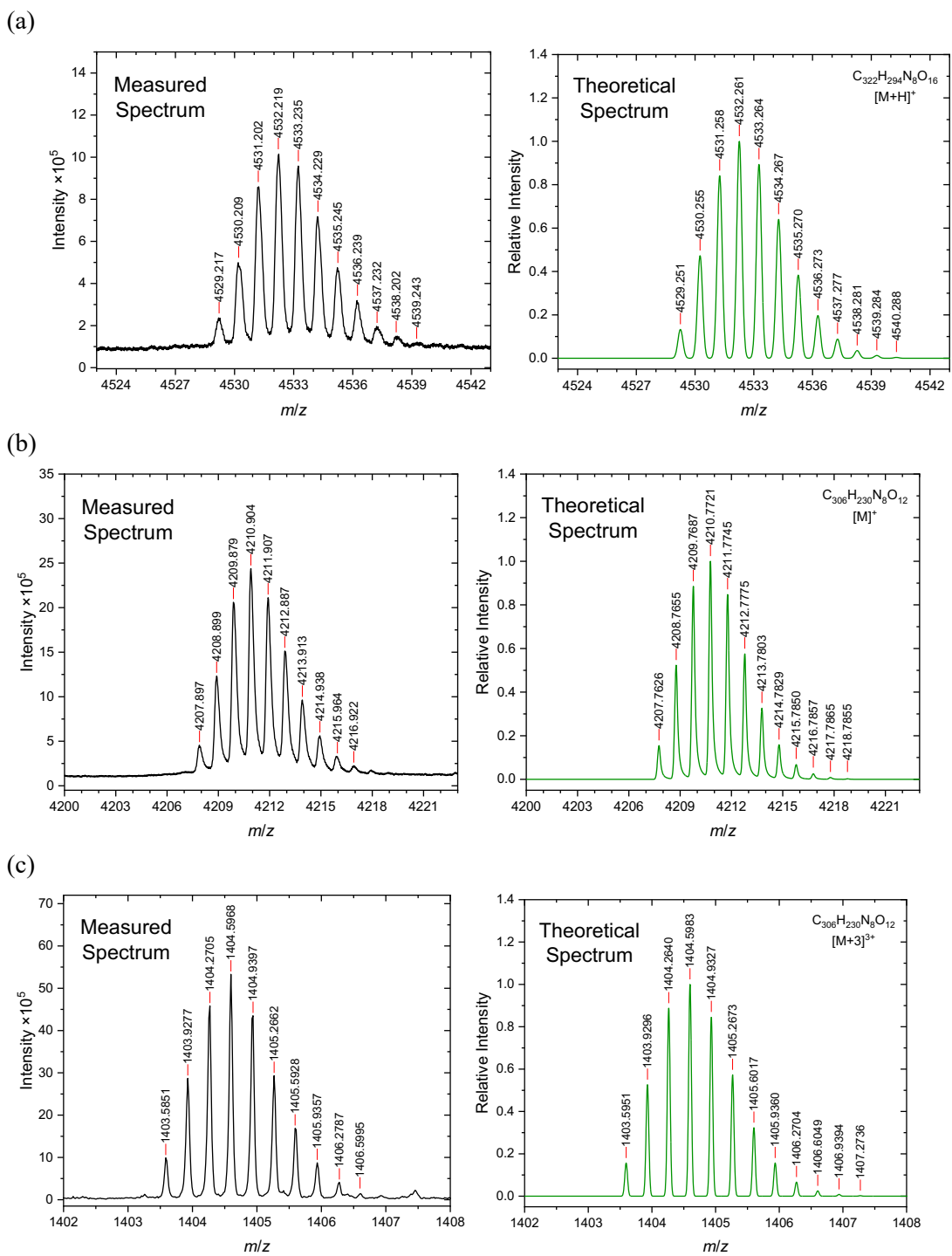
**Figure 100.** ESI high-resolution mass spectra of [7]rotaxane *mC108*·(**M<sub>b</sub>**)<sub>6</sub> in (a) 5<sup>+</sup> cation form and (b) 6<sup>+</sup> cation form and [8]rotaxane *mC128*·(**M<sub>b</sub>**)<sub>7</sub> in (c) 5<sup>+</sup> cation form and (d) 6<sup>+</sup> cation form.



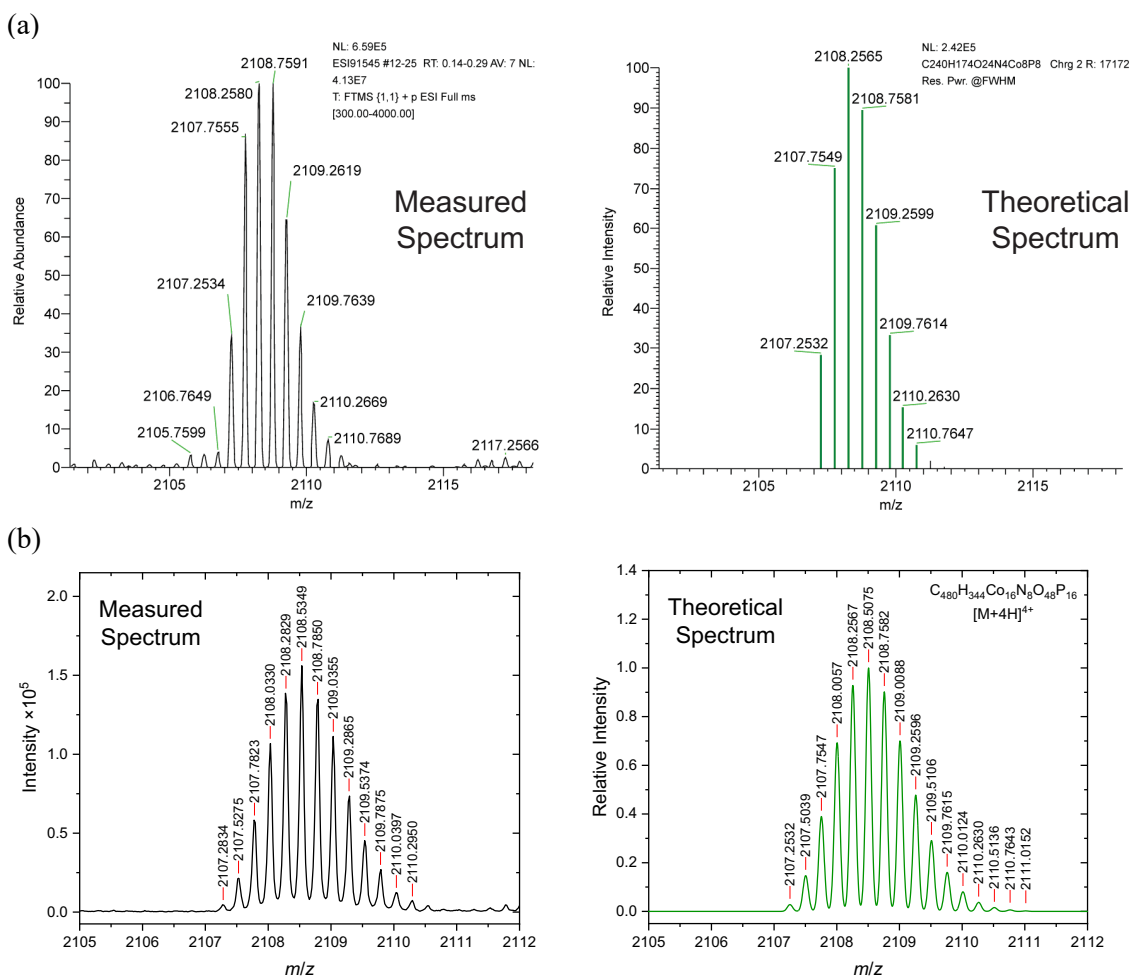
**Figure 101.** ESI high-resolution mass spectra of (a) C28·(M<sub>a</sub>)<sub>2</sub> and (b) C28·(M<sub>b</sub>)<sub>2</sub>.



**Figure 102.** MALDI-ToF mass spectrum high-resolution mass spectra of (a) polyynes dumbbell **C48**, (b) polyynes rotaxanes **C48·(M<sub>a</sub>)<sub>3</sub>**, and (c) **C48·(M<sub>b</sub>)<sub>3</sub>**.



**Figure 103.** MALDI-ToF mass spectrum high-resolution mass spectra of (a) polyynes  $C_{68} \cdot (M_a)_4$  and (b)  $C_{68} \cdot (M_b)_4$  as well as (c) ESI high-resolution mass spectra of  $C_{68} \cdot (M_b)_4$ .



**Figure 104.** ESI high-resolution mass spectra of (a) *mcC40·(M<sub>a</sub>)<sub>2</sub>* and (b) *mcC80·(M<sub>a</sub>)<sub>4</sub>*.

## Section 11: References

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