Expanded Cyclotetrabenzoins

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Supporting Information

General Methods and Materials

All reactions were performed under inert atmosphere in oven-dried glassware. Reagents were purchased from commercial suppliers: 3-ethyl-5-(2-hydroxylethyl)-4-methylthiazolium bromide (Thermo-Fischer Scientific), 2,6-naphthalenedicarboxylic Acid (TCI), triethylamine (Thermo-Fischer Scientific), Ac_2O (Sigma-Aldrich), $LiAlH_4$ and H_2SO_4 (Macron Fine Chemicals) and used without further purification, except for 4,4'-biphenyldicarbaldehyde, which was purified by recrystallization from EtOH. Solvents were used as received, except PhMe, which was dried over activated alumina in an mBraun solvent purification system. Compound 2,7-naphthalenedialdehyde was prepared according to the literature procedure.[1]

Column chromatography was carried out on silica gel 60, 32–63 mesh. Analytical TLC was performed on J. T. Baker or Merck plastic-backed silica gel IB-F plates. NMR spectra were obtained on Bruker Avance 300, Bruker Avance 400, Bruker Avance DRX 500, JEOL ECA-500, and ECA-600 spectrometers, with working frequencies (for ^{1}H NMR nuclei) of 300, 400, 500, 500, and 600 MHz, respectively. All ^{13}C NMR spectra were recorded with simultaneous decoupling of ^{1}H nuclei. ^{1}H NMR chemical shifts are reported in ppm units relative to the residual signal of the solvent ($CDCl_3$: 7.26 ppm, DMSO-d_6: 2.50 ppm). All NMR spectra were recorded at 25 °C.

Mass spectrometric measurements were performed by the Mass Spectrometry Facility of the Department of Chemistry and Biochemistry at the University of Texas at Austin. Mass spectra of aldehydes **1c**, **5a**–**5c,** and **6** and corresponding intermediate compounds were recorded on a Finnigan MAT 95 (70 eV) using EIMS (electron ionization mass spectrometry) or FAB-MS (fast atom bombardment mass spectrometry) with 3-nitrobenzyl alcohol as a matrix. Mass spectra of **3c** was recorded on ThermoFisher QExactive Plus using ESI MS (electrospray ionization mass spectrometry). The molecule ion peak $[M]^+$ or peak of the pseudo molecule $[M + H]^+$ are indicated as mass per charge ratio (m/z) and their intensity is given in percent, relative to the main peak (100 %) for EIMS. Structure of **7** was solved as iodide adduct $[M+I]^-$ by HR-ESI MS (high resolution electrospray ionization mass spectrometry) using a Thermo Scientific LTQ Orbitrap XL at KIT. The measurements were performed in negative mode with a CH_2Cl_2:MeOH (1:1) solution of **7** with 1%1 mM solution of CsI in MeOH added. Collision induced dissociation (CID) of $[M+I]^-$ indicates sequential loss of up to 24 CO

molecules. Infrared spectra were recorded on either Nicolet iS10 FT-IR or Bruker IFS 88 spectrometer; both were equipped with an ATR probe. The UV-vis absorption spectra were measured using a Cary 5000 UV-Vis-NIR spectrophotometer from Agilent Technology. The measurement was performed for the 8.9 μM solutions in CH_2Cl_2 as a solvent in the range from 700 nm to 220 nm and using the cuvettes with a thickness of 1 cm. Melting points were measured in open capillary tubes using either a Barnstead International Mel-TEMP apparatus or Stanford Research Systems Optimelt and are uncorrected.

All single X-ray diffusion measurements were performed by Dr. Xiqu Wang (UH) by using a Bruker DUO platform diffractometer equipped with a 4K CCD APEX II detector and an Incoatec 30 Watt Cu microsource with compact multilayer optics. Data were collected using a narrow-frame algorithm with scan widths of 0.50% in omega and an exposure time of 20 s per frame at 4 cm detector distance. The data were integrated using the Bruker SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to the variation in the path length through the detector faceplate. The data were scaled, and an absorption correction was applied using SADABS. The structure was solved with SHELXT 2014, and refined with SHELXL 2014 using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters, and all the H atoms were calculated in idealized positions and refined riding on their parent atoms. The highly disordered solvent molecules could not be determined reliably and their contributions to the electron density were treated using the PLATON/SQUEEZE program. The chemical formulas and calculated density correspond to the ordered molecules only.

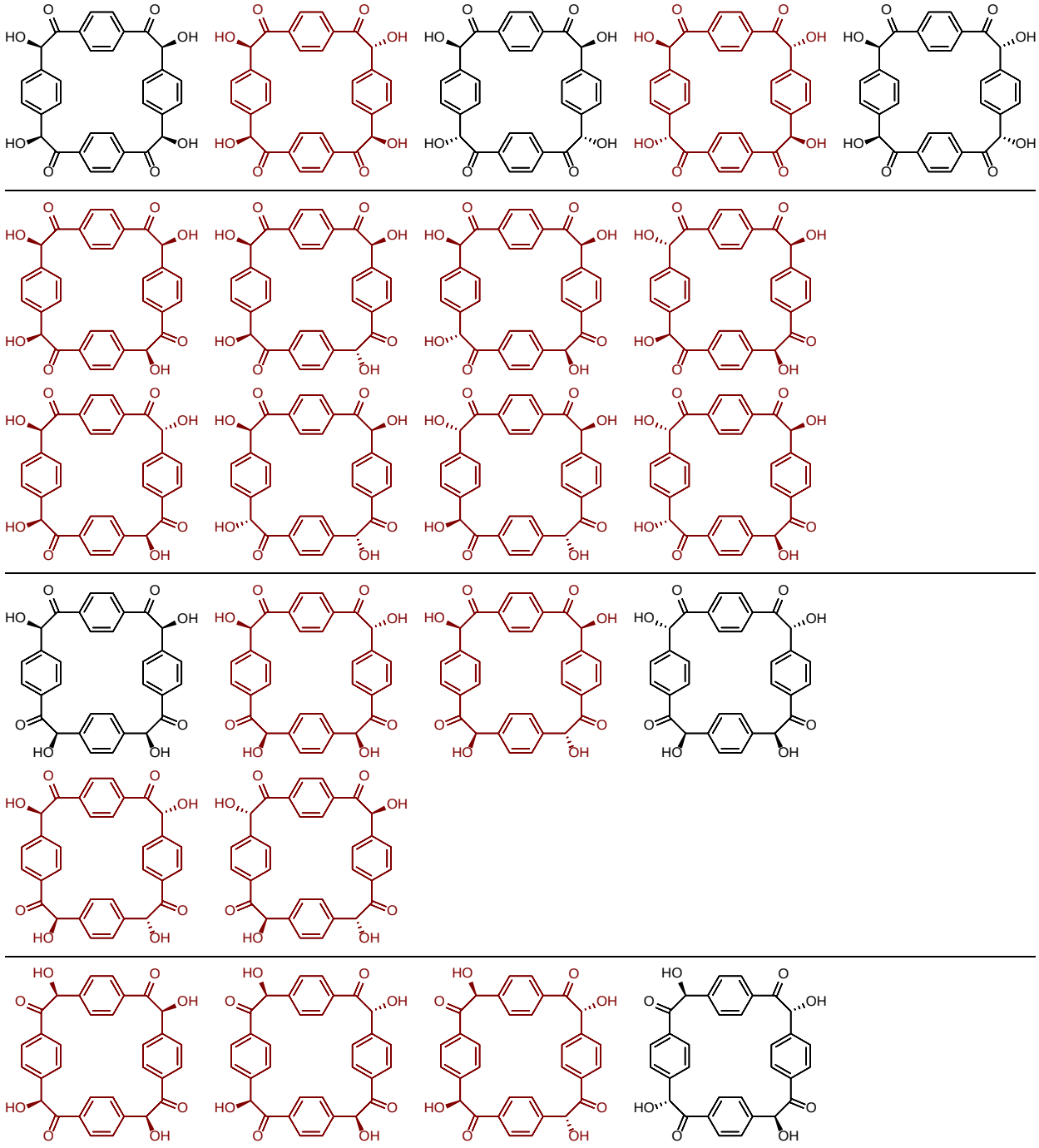
Gas adsorption isotherms were measured volumetrically using a surface analyser ThermoScientific Surfer Gas adsorption Porosimeter. A liquid nitrogen bath (77K) was used and the N_2 gas used was UHP grade. For measurement of the specific surface areas (S_{BET}, m^2/g) the BET method was applied. None of the examined samples showed any porosity.

Experiments are presented in the order that follows the discussion of the manuscript.

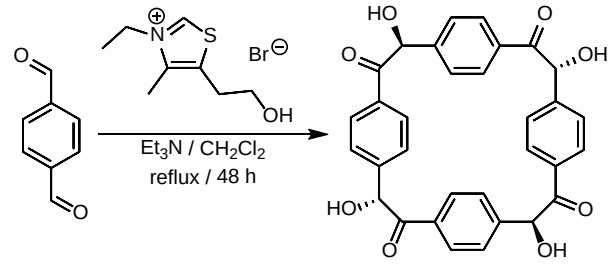
Compound numbers are identical to those in the main text of the manuscript.

Possible Regio- and Stereoisomers of 2a

Figure S1. Possible regio- and stereosiomers of cyclotetrabenzoin **2a**. Isomers highlighted in red are chiral and therefore exist as two enantiomers.



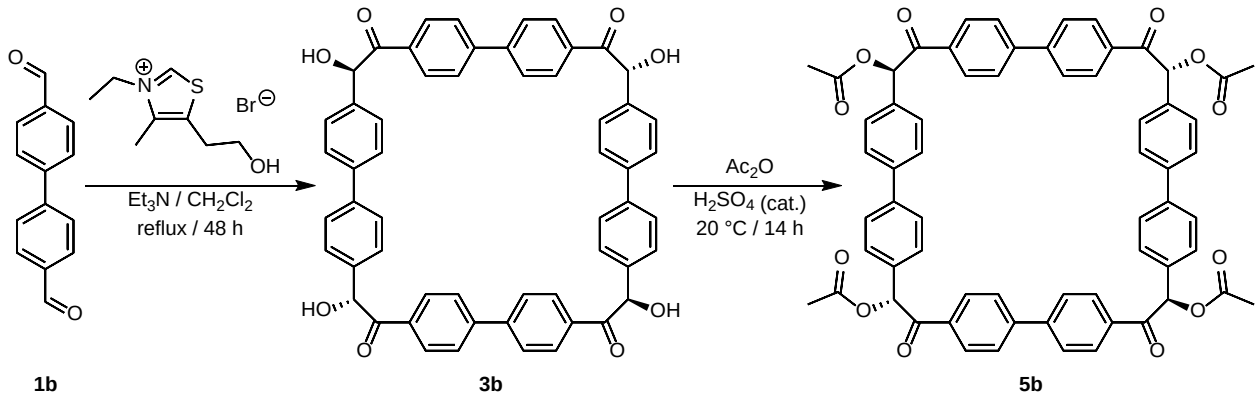
Synthesis of Cyclotetrabenzoin 2a Using an NHC Catalyst



1a **2a**

Terephthalaldehyde (**1a**, 134 mg, 1.00 mmol) and 3-ethyl-5-(2-hydroxyethyl)-4-methyl thiazolium bromide (50 mg, 0.199 mmol) were dissolved in CH_2Cl_2 (40 mL), and the solution was then heated to boiling in an oil bath. Then, Et_3N (0.1 mL) was added and the solution was heated at reflux for 72 h. The resulting precipitate was filtered, washed three times with CH_2Cl_2 (25 mL) and dried. Cyclotetrabenzoin **2a** was isolated from the resulting solid by recrystallization from DMSO and MeOH (25 mg, 19% yield), following the procedure previously developed to purify **2a** obtained in the cyanide-catalyzed reaction.[2] The recrystallized material was proven to be identical (by ^{1}H NMR spectroscopy) to the one prepared in the cyanide-catalyzed reaction.

Synthesis of Cyclotetrabenzoin 5b

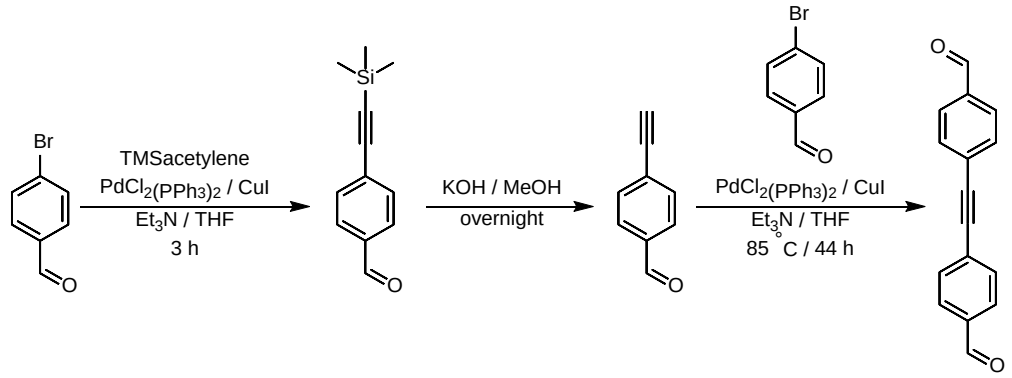


1b **3b** **5b**

A solution of 4,4'-biphenyldicarbaldehyde (**1b**, 2.11 g, 10.0 mmol) and 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide (500 mg, 1.98 mmol) in CH_2Cl_2 (40 mL) was heated to reflux (oil bath) under a nitrogen atmosphere. Then, Et_3N (2.00 mL, 1.45 g, 14.3 mmol) was injected and the reaction mixture was kept at reflux for 48 h. While still hot, the solution was filtered, and the residue was washed with CH_2Cl_2, EtOH, and Et_2O. After drying, ~1.19 g of crude product **3b** was obtained as a white to beige powder (mp >300 °C, decomp.). IR: $\tilde{\nu}$ = 3400, 1680 cm^{-1}.

Crude biphenyl cyclotetrabenzoin (**3b**, 1.19 g, 1.42 mmol) was stirred in Ac_2O (8.0 mL, 8.64 g, 84.5 mmol) until the mixture turned homogeneous. A catalytic amount of H_2SO_4 (4 drops) was added and the mixture was stirred for 18 h at room temperature. Then, the mixture was neutralized with 1M solution of NaOH (3 mL). The mixture was poured into CH_2Cl_2 (100 mL), transferred to a separatory funnel, and washed with deionized H_2O (100 mL). The organic layer was removed via rotary evaporator to provide a yellow, glassy solid. The crude product was purified by column chromatography on silica gel, eluting with an 8:2 EtOAc/hexanes mixture. After evaporation, compound **5b** (622 mg, 0.62 mmol, 24% overall yield) was collected as a white solid (mp >300 °C, decomp.). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06–7.85 (m, 8H), 7.63–7.42 (m, 24H), 6.95–6.80 (m, 4H), 2.23 (s, 12H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 192.9–192.4 (m), 170.6, 170.4, 168.9, 144.9–144.7 (m), 144.2–144.0 (m) 141.1–141.0 (m), 140.9–140.8 (m), 140.7, 140.6, 140.5, 140.4, 140.3–140.2 (m), 133.9–133.7 (m), 133.4–133.3 (m), 133.1–133.0 (m), 129.6–129.4 (m), 128.1–127.6 (m), 127.4–127.1 (m), 77.7, 20.9 ppm. IR: $\tilde{\nu}$ 3000–2800, 1739, 1692 cm^{-1}. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{64}H_{48}O_{12}K$ 1047.2783; Found 1047.2777. Single crystals of **5b** suitable for X-ray diffraction analysis were grown by diffusion of MeOH into its THF solution.

Synthesis of 4,4'-(ethyne-1,2-diyl)dibenzaldehyde 1c



1c

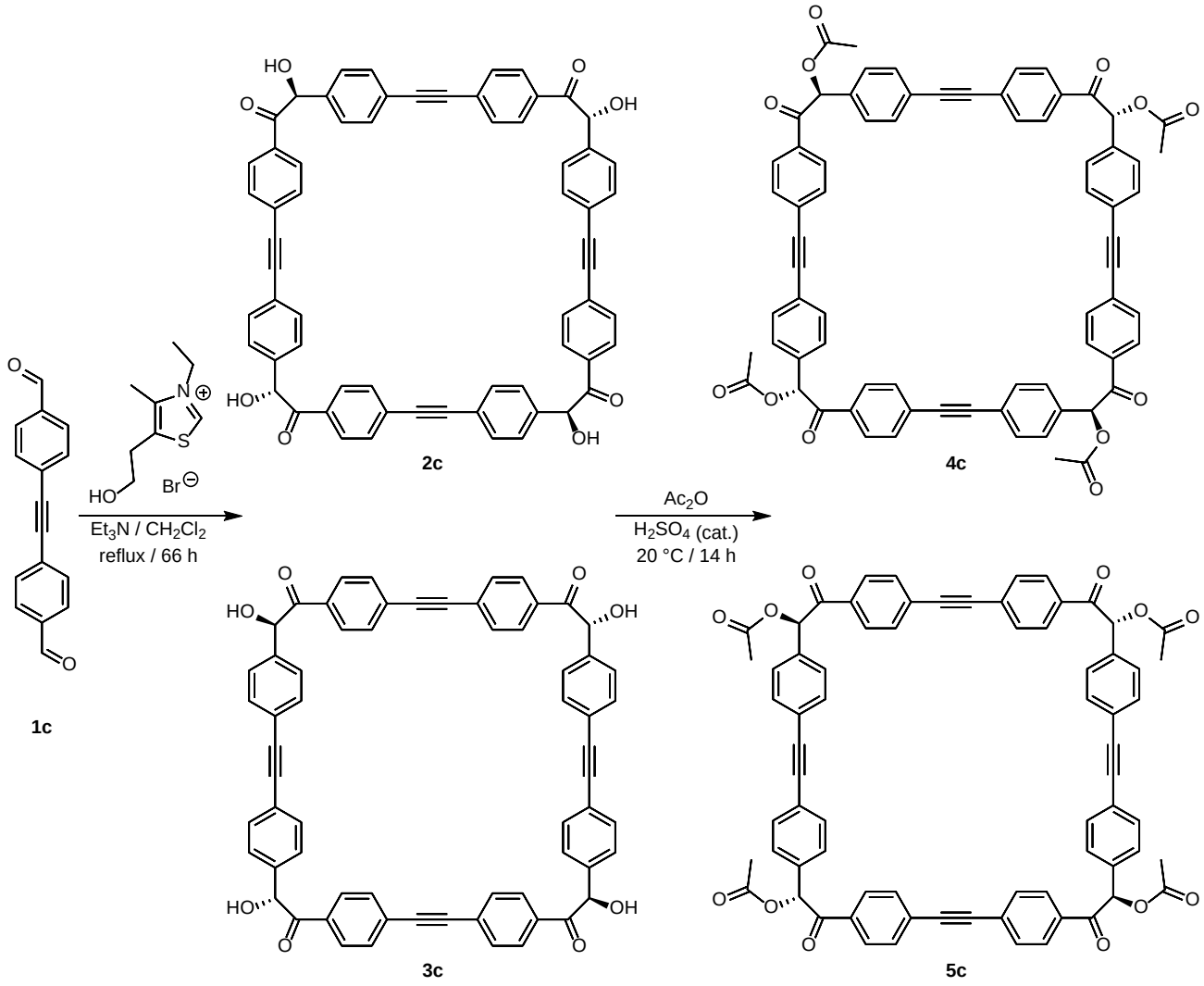
Synthesis was performed according to a literature procedure,[3] with some modifications. In a round bottom flask, 4-bromobenzaldehyde (5.00 g, 27.0 mmol), $PdCl_2(PPh_3)_2$ (379 mg, 540 µmol), and CuI (206 mg, 1.08 mmol) were dissolved in dry THF (30 mL). Et_3N (4.10 g, 5.62 mL, 40.5 mmol) and trimethylsilylacetylene (2.79 g, 4.04 mL, 28.4 mmol) were added, and the reaction mixture was stirred for 3 h at room temperature. The reaction progress was monitored via TLC. After full conversion was achieved, the volatiles were removed under reduced pressure. The obtained crude product was purified by column chromatography on silica gel, eluting with cyclohexane/EtOAc mixture. After evaporation, 4-((trimethylsilyl)ethynyl)benzaldehyde (5.42 g, 26.8 mmol, 99 %) was collected as a dark yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.82 (d, J=8.4 Hz, 2H), 7.61 (d, J=8.1 Hz, 2H), 0.29–0.27 (m, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 135.6, 132.5, 129.4, 129.3, 103.8, 99.0, 0.00 ppm. IR: $\tilde{\nu}$ 2956–2737, 2156, 1698 cm^{-1}. EIMS (70 eV), m/z (%): 202 (24) $[M+H]^+$.

4-((Trimethylsilyl)ethynyl)benzaldehyde (3.00 g, 14.8 mmol) was dissolved in MeOH (100 mL), followed by the addition of KOH (1.04 g, 18.5 mmol). The reaction mixture was stirred overnight at room temperature. The reaction progress was monitored via TLC. After full conversion was achieved, brine was added and the product was extracted with EtOAc (3×100 mL). The combined organic phases were dried over Na_2SO_4. All volatiles were removed and the crude product was purified by column chromatography on silica gel, eluting with a cyclohexane/EtOAc mixture. After evaporation, 4-ethynylbenzaldehyde (1.92 g, 14.8 mmol, 89%) was collected as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 7.85 (d, J=8.4 Hz, 2H), 7.65 (d, J=8.3 Hz, 2H), 3.30 (s, 1H) ppm. ^{13}C NMR

(75 MHz, $CDCl_3$): δ 191.3, 135.9, 132.7 (2C), 129.5 (2C), 128.3, 82.6, 81.0 ppm. IR: $\tilde{\nu}$ 3215, 2838–2739, 2099, 1682 cm^{-1}. EIMS (70 eV), *m/z* (%): 130 (100) $[M+H]^+$.

In a round bottom flask, 4-ethynylbenzaldehyde (2.14 g, 16.4 mmol), 4-bromobenzaldehyde (3.04 g, 16.4 mmol), $PdCl_2(PPh_3)_2$ (346 mg, 493 μmol), and CuI (125 mg, 657 μmol) were dissolved in dry THF (119 mL). Et_3N (29.0 g, 39.7 mL, 287 mmol) was added, and the reaction mixture was heated in an 85 °C oil bath for 44 h. The reaction progress was monitored via TLC. After full conversion was achieved, the reaction mixture was cooled down and the volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with CH_2Cl_2. After evaporation, 4,4'-(ethyne-1,2-diyl)dibenzaldehyde **1c** (3.06 g, 13.1 mmol, 79%) was collected as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 10.05 (s, 2H), 7.91 (d, *J*=8.1 Hz, 4H), 7.72 (d, *J*=8.1 Hz, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.3, 135.9, 132.3, 129.6, 128.7, 92.1 ppm. IR: $\tilde{\nu}$ 2948–2844, 1696 cm^{-1}. EIMS (70 eV), *m/z* (%): 234 (100) $[M+H]^+$. HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{16}H_{10}O_2$ 234.0675; Found 234.0677. Spectral dara are identical to a previous literature report.[3]

Synthesis of Cyclotetrabenzoins 4c and 5c



A solution of 4,4'-(ethyne-1,2-diyl)dibenzaldehyde (**1c**, 2.00 g, 8.54 mmol) and 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide (1.22 g, 4.84 mmol) in CH_2Cl_2 (167 mL) was heated to reflux in an oil bath. Then, Et_3N (1.7 mL) was injected and the reaction mixture was heated at reflux for 66 h. While still hot, the solution was filtered, and the residue was washed with CH_2Cl_2, EtOH, and Et_2O. After drying, 1.39 g of crude products **2c**/**3c** was obtained as a yellow powder (mp: >300 °C, decomp.). IR: $\tilde{\nu}$ 3452, 3424, 2215, 1677 cm^{-1}.

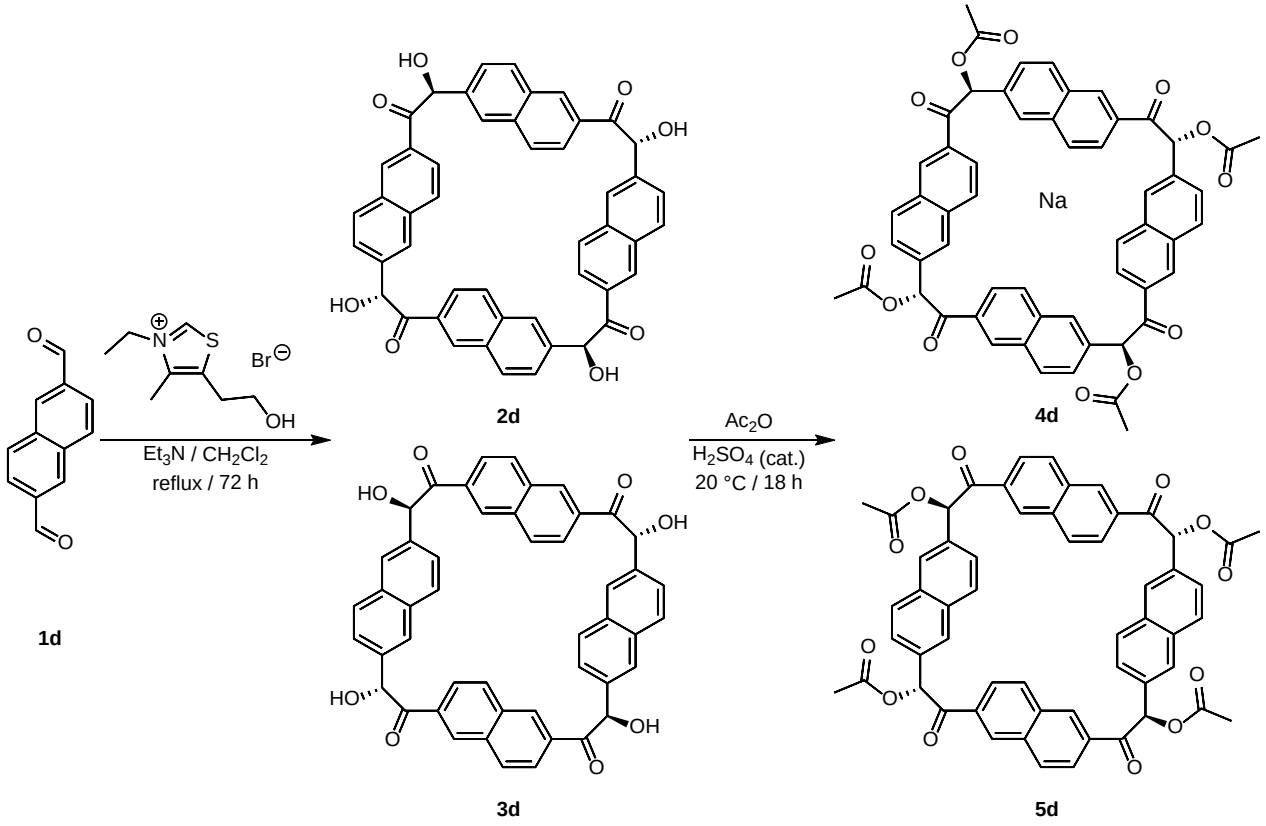
Crude tolane cyclotetrabenzoins **2c** and **3c** (1.20 g, 1.28 mmol) were stirred in Ac_2O (75 mL, 81.0 g, 793 mmol) until the mixture turned homogeneous. Catalytic amount of H_2SO_4 (6 drops) was added and the mixture was stirred for 18 h at room temperature. The mixture was poured into CH_2Cl_2 (200 mL),

transferred to a separatory funnel, washed three times with deionized H_2O (150 mL), and twice with brine (100 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent removed via rotary evaporator to provide a yellow, glassy solid. This solid was purified by column chromatography on silica gel, eluting with a CH_2Cl_2/EtOAc mixture. After evaporation, a mixture of compounds **4c** and **5c** (467 mg, 0.422 mmol, 23% overall yield) was collected as a pale yellow solid (mp >300 °C, decomp.). This mixture could be separated by HPLC (column: reverse phase VDSpher C18 M-SE 5μm; 250×4.0 mm; flow rate: 1 mL/min; injection volume: 5 μL; detector: 280 nm; solvent gradient: 0–10 min, MeCN 80 to 100%; 10–21 min, MeCN 100%; 21–25 min, MeCN 100 to 5%) on an analytical scale, but not preparative. In the absence of X-ray crystal structures, our assignments of structures of **4c** and **5c** are tentative: we cannot tell which compound is which.

Compound **4c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (m, 8H), 7.47 (m, 16H), 7.40 (m, 8H), 6.82 (m, 4H), 2.23 (t, J=2.7 Hz, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4 (m), 170.5 (m), 133.6 (m), 132.7, 132.6, 132.0, 129.0, 128.9, 128.4, 128.0, 124.3, 124.0, 92.1 (m), 89.8 (m), 21.0 (m) ppm. IR: $\tilde{\nu}$ 2927–2853, 1742, 1694 cm^{-1}. ESI-MS (m/z): 1127 (100) $[M+Na]^+$. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{72}H_{48}O_{12}Na$ 1127.3043; Found 1127.3092.

Compound **5c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (m, 8H), 7.48 (m, 16H), 7.40 (m, 8H), 6.82 (m, 4H), 2.23 (t, J=2.7 Hz, 12H) ppm. IR: $\tilde{\nu}$ 2927–2853, 1742, 1694 cm^{-1}. ESI-MS (m/z): 1127 (100) $[M+Na]^+$. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{72}H_{48}O_{12}Na$ 1127.3043; Found 1127.3092. Because of the miniscule amount of pure **5c** that was obtained, a satisfactory ^{13}C NMR spectrum could not be obtained.

Synthesis of Cyclotetrabenzoins 4d and 5d



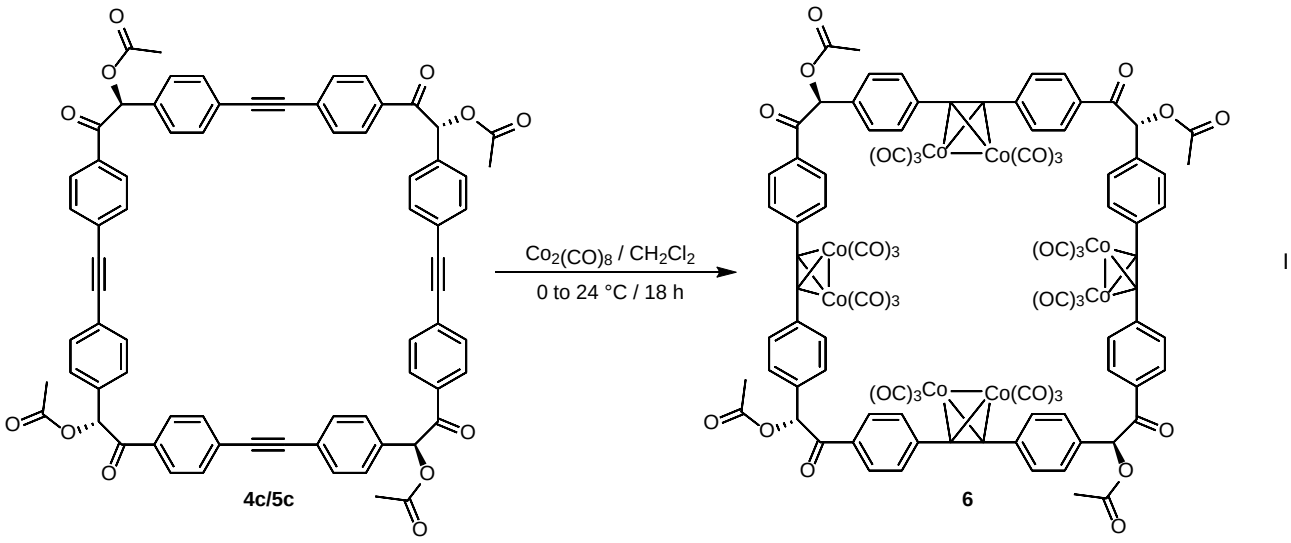
A solution of 2,7-naphthalene dialdehyde (**1d**, 1.33 g, 7.24 mmol) and 3-ethyl-5-(2-hydroxyethyl)-4-methyl thiazolium bromide (380 mg, 1.51 mmol) in CH_2Cl_2 (40 mL) was boiled (oil bath) with stirring until all solids dissolved. Then, Et_3N (1.50 mL, 1.10 g, 10.8 mmol) was injected and the solution was kept at reflux for 72 h. While hot, the solution was filtered and washed with CH_2Cl_2, EtOH, and Et_2O. After drying, the collected solids were stirred in a round-bottom flask with Ac_2O (3.70 mL, 4.00 g, 39.2 mmol) and a catalytic amount of H_2SO_4 (6 drops) at room temperature overnight. The mixture was then neutralized with 1M solution of NaOH (1.50m mL). The resulting solution was then poured into CH_2Cl_2 (100 mL) and washed three times with H_2O (25 mL each) and once with brine (25 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated with a rotary evaporator. The crude product was purified by column chromatography on silica gel, eluting with 1:1 hexanes/EtOAc mixture. After evaporation, compounds **4d** (R_f=0.27, 111 mg, 122 mmol, 9% overall yield) and **5d** (R_f=0.35, 61 mg, 67.2 mmol, 5% overall yield) were collected as white solids (mp >300 °C, decomp.).

Single crystals of **4d** suitable for X-ray diffraction grew from one of the column fractions, eluted with EtOAc/CH_2Cl_2, after overnight evaporation.

Compound **4d:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.36–8.22 (m, 4H), 7.99–7.60 (m, 16H), 7.53–7.41 (m, 4H), 7.14–7.06 (m, 4H), 2.25–2.21 (m, 12H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.5, 192.3, 192.0, 191.8, 170.7, 170.5, 135.5, 135.4, 135.3, 134.5, 134.3, 133.9, 133.8, 133.5, 133.3, 133.0, 132.7, 132.6, 132.4, 132.2, 132.0, 131.9, 131.7, 131.2, 131.0, 130.7, 130.6, 130.3, 130.0, 129.0, 129.5, 129.2, 129.0, 128.9, 128.7, 127.9, 127.0, 126.9, 126.8, 126.5, 126.2, 125.1, 125.0, 124.8, 124.7, 78.0, 77.8, 77.6, 20.9 ppm. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{56}H_{40}O_{12}Na$ 927.2417; Found 927.2423.

Compound **5d**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (d, J = 9.7 Hz, 1H), 8.23 (t, J = 8.6 Hz, 2H), 8.16 (d, J = 9.7 Hz, 1H), 7.95–7.86 (m, 4H), 7.82–7.65 (m, 4H), 7.51–7.42 (m, 12H), 7.51–7.42 (m, 4H), 7.13–7.07 (m, 4H), 2.23 (t, J = 9.2 Hz, 12H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.3, 192.3, 192.0, 170.6, 170.5, 135.5, 134.2, 134.1, 134.0, 133.5, 133.4, 133.3, 132.3, 132.0, 131.9, 131.0, 130.4, 130.3, 130.2, 129.9, 129.7, 129.6, 129.0, 128.9, 128.9, 128.8, 126.6, 126.5, 126.4, 125.2, 125.0, 124.9, 124.8, 77.8, 77.7, 77.6, 20.9 ppm. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{56}H_{40}O_{12}Na$ 927.2417; Found 927.2428.

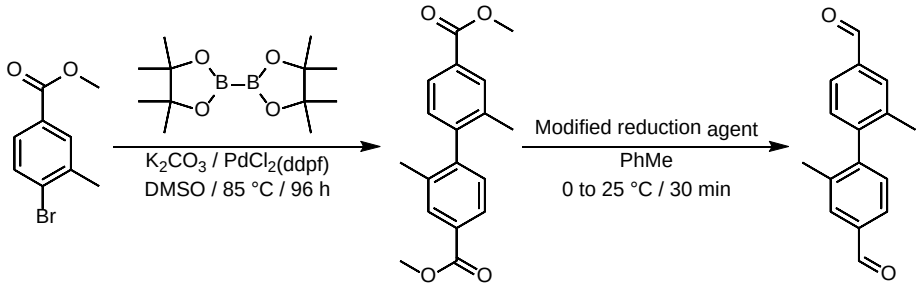
Synthesis of Complex 6



A mixture of acetylated cyclotetrabenzoins **4c** and **5c** (50.0 mg, 45.2 μmol) and $Co_2(CO)_8$ (62.2 mg, 181 μmol) was dissolved in CH_2Cl_2 (5 mL) at 0 °C. The reaction mixture was stirred at 0 °C and the reaction progress was monitored via thin-layer chromatography. After 2 h, the reaction mixture was left to warm up to 24 °C and the stirring was continued overnight. The volatiles were removed via rotary evaporator and the crude product was purified by column chromatography on silica gel, eluting with CH_2Cl_2/EtOAc mixture. After evaporation, compound **6** (55.4 mg, 24.6 μmol, 54 %) was collected as a red solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05–7.89 (m, 8H), 7.65–7.41 (m, 24H), 6.86–6.78 (m, 4H), 2.22 (m, 12H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.6 (m), 192.7, 170.6, 144.9 (m), 139.7 (m), 138.2, 137.5, 133.8, 133.2, 129.9, 129.7, 129.4, 20.9 ppm. Due to the low noise-to-signal ratio, one ^{13}C NMR signal could not be identified despite more than 8,000 collected scans. IR: $\tilde{\nu}$ 2933, 2092, 2053, 2003, 1742, 1691 cm^{-1}. HRMS (ESI) m/z: $[M+I]^-$ Calcd for $C_{96}H_{48}Co_8O_{36}I$ 2375.5660; Found 2375.5651.

Synthesis of Compounds 1f and 1h

General procedure for the preparation of the modified reduction agent.[4] An argon-flushed vial was charged with *cis*-2,6-dimethylmorpholine (9.70 mL, 78.7 mmol) and PhMe (84.0 mL). The mixture was stirred and cooled down to 0 °C. The SMEAH solution (15.0 mL, 3.4 N in PhMe, 52.5 mmol, 1.00) was added dropwise and stirred at 0 °C for 1 h to give a colorless homogenous solution.

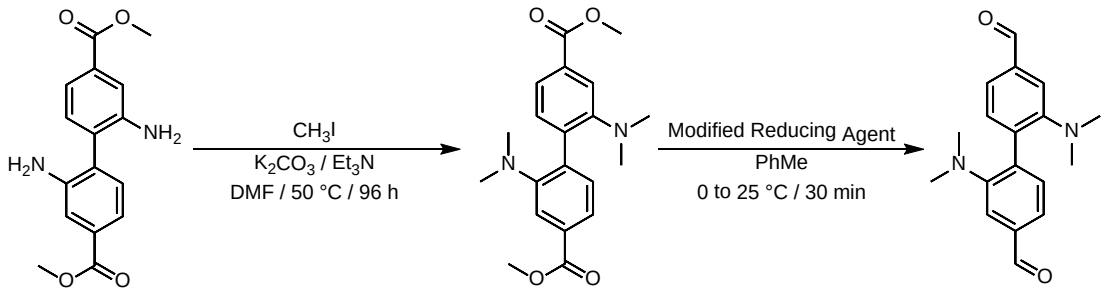


1f

Synthesis of compound **1f** was performed according to a literature procedure.[5] Bis(pinacolato)diboron (1.09 g, 4.31 mmol), 4-bromo-3-methylbenzoic acid methyl ester (2.10 g, 9.81 mmol), K_2CO_3 (3.78 g, 27.4 mmol), and [$PdCl_2$(dppf)] (0.126 g, 0.172 mmol, 4 mol%) were placed into a round bottom flask. Degassed DMSO (15.4 mL) was added by syringe. The mixture was stirred and heated in an 85 °C oil bath for 4 d. After cooling, the mixture was poured into H_2O (240 mL) and extracted with CH_2Cl_2 (3×67 mL) and EtOAc (3×100 mL). The combined extracts were washed with H_2O (3×80 mL) and brine (3×80 mL) and dried over anhydrous Na_2SO_4. The solution was filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel eluting with a cyclohexane/EtOAc mixture. After evaporation, 2,2'-dimethyl-1,1'-biphenyl-4,4'-dicarboxylic acid dimethyl ester (1.12 g, 3.76 mmol, 87 %) was collected as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, J=1.7 Hz, 2H), 7.90 (dd, J=7.9, 1.7 Hz, 2H) 7.16 (d, J=7.9 Hz, 2H), 3.94 (s, 6H), 2.08 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.1, 145.4, 135.9, 131.2, 129.5, 129.0, 127.0, 52.1, 19.7 ppm. IR: $\tilde{\nu}$ 2952, 1710 cm^{-1}. EIMS (70 eV), m/z (%): 299 (19) [M+H]$^+$, 298 (100) [M]$^+$.

2,2'-Dimethyl-1,1'-biphenyl-4,4'-dicarboxylic acid dimethyl ester (500 mg, 1.68 mmol) was dissolved in PhMe (17.1 mL) and the solution was cooled to 0 °C. The modified reduction agent (25.1 mL, 12.0

mmol) was added dropwise to prevent a rise in temperature. After addition, the mixture was stirred for 30 min at room temperature. The reaction was stopped with aqueous 1N HCl (4.00 mL). The mixture was poured into H_2O (50.0 mL) and extracted with EtOAc (3×30 mL). The combined organic layers were washed with H_2O (3×75 mL) and brine (3×75 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel, eluting with a cyclohexane/EtOAc mixture. After evaporation, compound **1f** (348 mg, 1.46 mmol, 87 %) was collected as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.04 (s, 2H), 7.83 (d, *J*=1.7 Hz, 2H), 7.77 (dd, *J*=7.7, 1.7 Hz, 2H,), 7.26 (d, *J*=7.7 Hz, 2H), 2.12 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.1, 146.8, 136.6, 135.9, 131.3, 129.5, 127.4, 19.7 ppm. IR: $\tilde{\nu}$ 2815, 2725, 1688 cm^{-1}. EIMS (70 eV), *m/z* (%): 239 (19) $[M+H]^+$, 238 (100) $[M]^+$. Spectral data matched a previous literature report.[5]



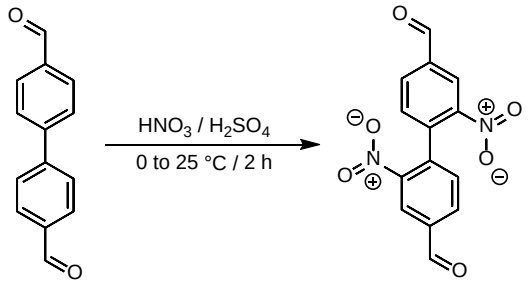
1h

Iodomethane (0.733 mL, 1.67 g, 11.8 mmol) was added dropwise to a stirred suspension of 2,2'-diaminobiphenyl-4,4'-dicarboxylic acid dimethyl ester (0.807 g, 2.69 mmol) and K_2CO_3 (2.21 g, 16.0 mmol) in DMF (10 mL). The mixture was stirred at room temperature and the reaction progress was monitored through thin-layer chromatography. After 18 h, 0.5 mL of Et_3N were added, and the mixture was stirred at 50 °C, with an oil bath as a heat source. After 24 h, MeI (0.733 mL, 1.67 g, 11.8 mmol) was added and the mixture was stirred at 50 °C (oil bath) for 96 h. It was then cooled down and diluted with H_2O (10.0 mL) and NH_4Cl (10.0 mL). The solution was extracted with EtOAc (3×20 mL) and the combined organic extracts were washed with H_2O (3×10 mL) and brine (3×10 mL). The organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel eluting with a cyclohexane/EtOAc mixture (+0.1% Et_3N). After evaporation, 2,2'-dimethyldiamino-1,1'-biphenyl-4,4'-dicarboxylic acid

dimethyl ester (670 mg, 1.88 mmol, 79 %) was collected as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (d, J=1.7 Hz, 2H), 7.59 (dd, J=8.1, 1.5 Hz, 2H), 7.44 (d, J=8.0 Hz, 2H), 3.91 (s, 6H), 2.59 (s, 12H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 150.2, 136.6, 131.1, 129.7, 121.8, 119.2, 52.1, 42.7 ppm. IR: $\tilde{\nu}$ 2942, 2833, 2783, 1715 cm^{-1}. EIMS (70 eV), m/z (%): 356 (0.28) $[M]^+$.

2,2'-Dimethyldiaminobiphenyl-4,4'-dicarboxylic acid dimethyl ester (540 mg, 1.52 mmol) was dissolved in PhMe (15.0 mL) and cooled to 0 °C. The modified reduction agent (22.8 mL, 10.9 mmol) was added dropwise to prevent a rise in temperature. After addition, the mixture was stirred for 30 min at room temperature. The reaction was stopped with aqueous 1N HCl (3.70 mL). The mixture was poured into H_2O (50 mL) and extracted with EtOAc (3×30 mL). The combined organic layers were washed with H_2O (3×75 mL) and brine (3×75 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel eluting with cyclohexane/EtOAc mixture. After evaporation, compound **1h** (370 mg, 1.23 mmol, 86 %) was collected as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.99 (s, 2H), 7.57 (d, J=7.8 Hz, 2H), 7.53 (d, J=1.6 Hz, 2H), 7.44 (dd, J=7.8, 1.6 Hz, 2H), 2.64 (s, 12H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.3, 150.7, 137.8, 136.4, 131.6, 122.9, 117.9, 42.7 ppm. IR: $\tilde{\nu}$ 2841, 2784, 1691 cm^{-1}. EIMS (70 eV), m/z (%): 296 (27) $[M]^+$. Spectral data matches a previous literature report.[6]

Synthesis of Compound 1g

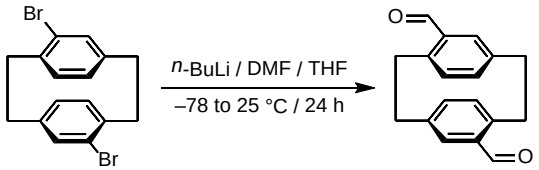


1g

The synthesis was performed according to a literature procedure.[6] Nitric (1.29 mL, 1.80 g, 28.6 mmol) and sulfuric (1.67 mL, 3.02 g, 30.8 mmol) acids were mixed, cooled to −5 °C, and stirred vigorously. 1,1'-Biphenyl-4,4'-dialdehyde (363 mg, 1.73 mmol) was slowly added to prevent the temperature from exceeding 0 °C. After addition, the mixture was stirred for 1 h at 0 °C and 1 h at room

temperature. The mixture was then poured into iced H_2O (46 mL), and the precipitated solid was obtained through filtration and dissolved in $CHCl_3$ (50 mL). This solution was dried over anhydrous Na_2SO_4. The solution was heated at reflux with silica gel (300 mg) and filtered hot twice. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel, eluting with a cyclohexane/EtOAc mixture. After evaporation, compound **1g** (357 mg, 1.19 mmol, 69 %) was collected as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.16 (s, 2H), 8.75 (d, J=1.6 Hz, 2H), 8.25 (dd, J=7.8, 1.6 Hz, 2H), 7.51 (d, J=7.8 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.1, 147.3, 138.6, 137.2, 133.5, 131.5, 126.0 ppm. IR: $\tilde{\nu}$ 3079, 2949, 1699 cm^{-1}. EIMS (70 eV), *m/z* (%): 300 (6) $[M]^+$, 254 (100) $[C_{14}H_8NO_4]^+$. Spectral data matches a previous literature report.[6]

Synthesis of Compound 1i



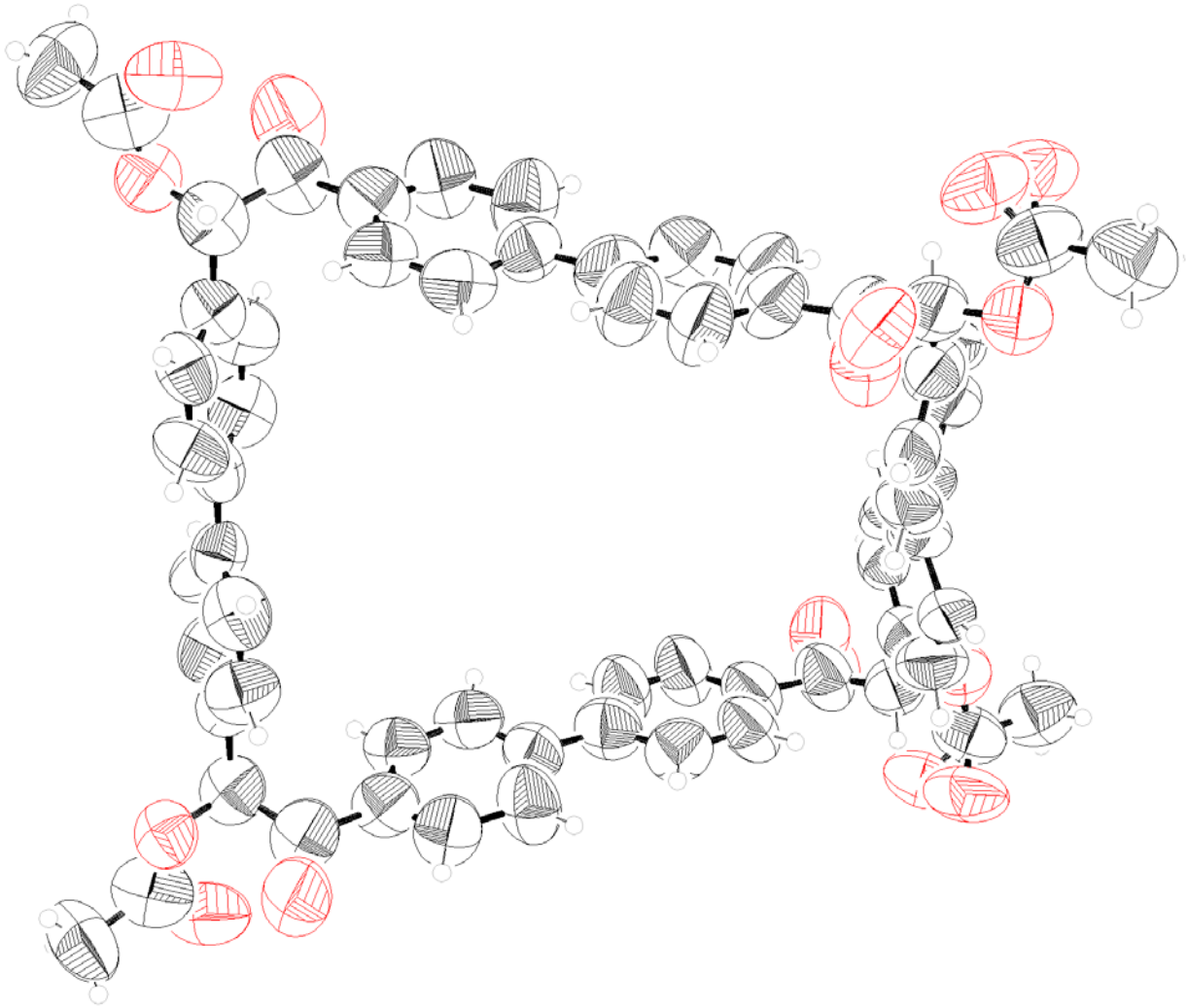
1i

Synthesis followed a published literature procedure.[7] 4,16-Dibromo[2.2]paracyclophane (0.864 g, 2.36 mmol) was dissolved in degassed THF (22.5 mL). The solution was stirred and cooled to −78 °C and then *n*-BuLi solution (3.14 mL, 2.5 M, 0.503 g, 7.86 mmol) was added dropwise. The mixture was stirred at −78 °C for 2 h, then DMF (2.72 mL, 2.59 g, 35.4 mmol) was added dropwise and the mixture was left to warm up room temperature overnight. The solution was washed with brine (3×7.5 mL) and $NaHCO_3$ (3×7.5 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with an *n*-hexane/CH_2Cl_2 mixture. After evaporation, compound **1i** (195 mg, 0.737 mmol, 31 %) was collected as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.93 (s, 2H), 7.05 (d, J=2.0 Hz, 2H), 6.63 (dd, J=7.8, 2.0 Hz, 2H), 6.52 (d, J=7.8 Hz, 2H), 4.13 (ddd, J=12.9, 10.2, 2.4 Hz, 2H), 3.29 (ddd, J=13.1, 10.6, 2.4 Hz, 2H), 3.15 (ddd, J=13.1, 10.1, 5.8 Hz, 2H), 3.01 (ddd, J=13.1, 10.6, 5.8 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.9, 142.9, 140.5, 137.0, 136.8, 136.6, 135.2, 34.4, 32.8 ppm. IR: $\tilde{\nu}$ 2930–2747, 1668 cm^{-1}. EIMS (70 eV), *m/z* (%): 264 (17) $[M]^+$. Spectral data match a previous literature report.[8]

Crystal Data and Structure Refinement Parameters for Compound 5b

Empirical formula	$C_{64}H_{48}O_{12}$	
Formula weight	1009.02 g mol^{-1}	
Temperature	123(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	*F*dd2	
Unit cell dimensions	a = 13.3250(4) Å	α = 90°
	b = 25.7868(7) Å	β = 90°
	c = 51.1388(15) Å	γ = 90°
Volume	17571.8(9) $Å^3$	
Z	8	
Density (calculated)	0.763 Mg m^{-3}	
Absorption coefficient	0.429 mm^{-1}	
$F(000)$	4224	
Crystal size	0.16×0.14×0.01 mm^3	
Theta range for data collection	3.833 to 66.694°	
Index ranges	$-11 \le h \le 15$, $-30 \le k \le 20$, $-52 \le l \le 58$	
Reflections collected	16314	
Independent reflections	6701 [R(int) = 0.0288]	
Completeness to theta = 66.694°	98.3 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7528 and 0.5708	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6701 / 310 / 364	
Goodness-of-fit on F^2	1.224	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0640, wR_2 = 0.1670	
R indices (all data)	R_1 = 0.1215, wR_2 = 0.1934	
Absolute structure parameter	0.7(5)	
Largest diff. peak and hole	0.133 and −0.128 e^- $Å^{-3}$	

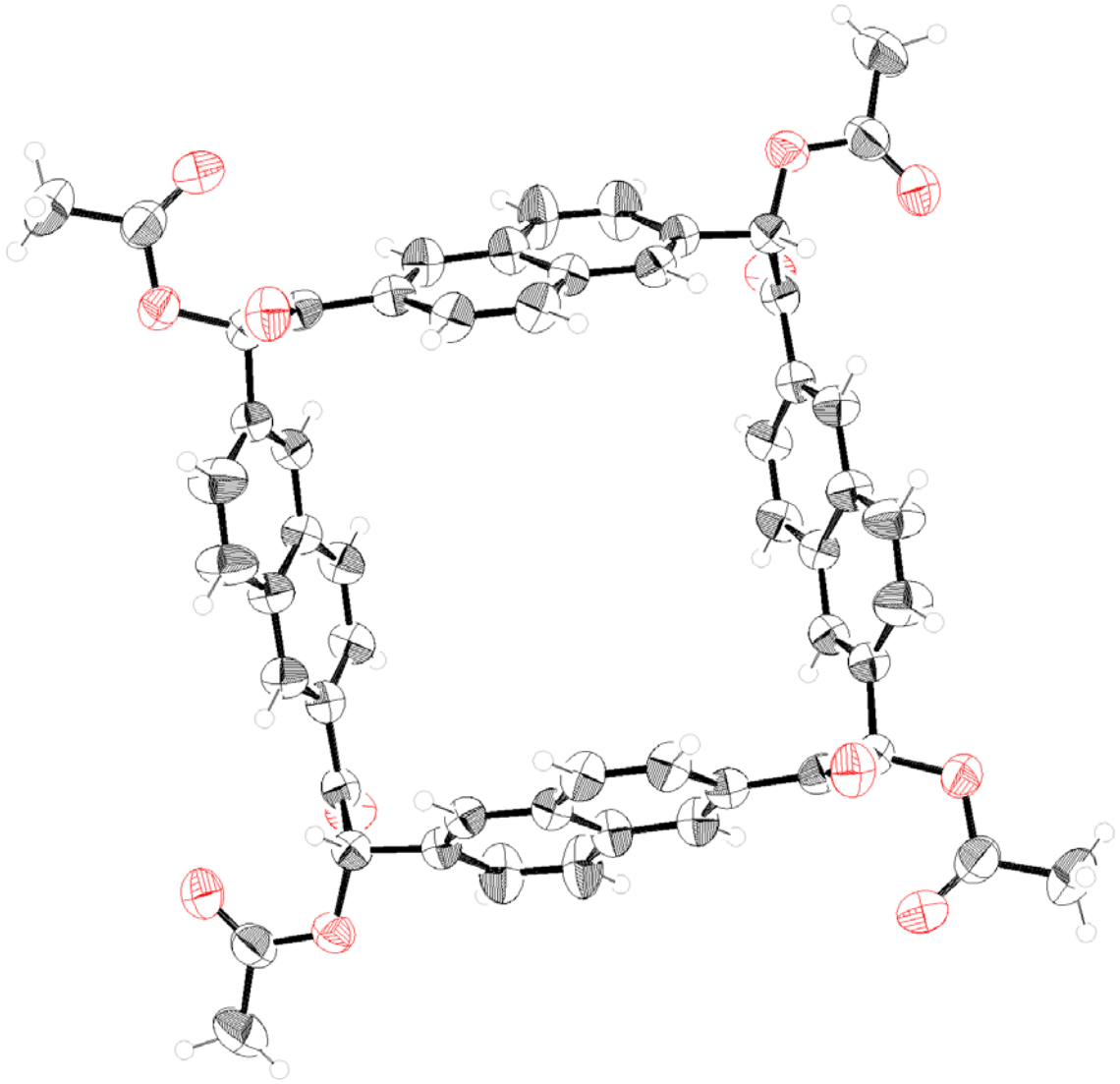
Figure S2. Thermal ellipsoid plot of the X-ray crystal structure of compound **5b**. Ellipsoids shown at 50% probability.



Crystal Data and Structure Refinement Parameters for Compound 4d

Empirical formula	$C_{56}H_{40}O_{12}$	
Formula weight	904.88 g mol^{-1}	
Temperature	123(2) K	
Wavelength	1.54178 Å	
Crystal system	Tetragonal	
Space group	$I\bar{4}$	
Unit cell dimensions	a = 16.0194(7) Å	α = 90°
	b = 16.0194(7) Å	β = 90°
	c = 10.8949(5) Å	γ = 90°
Volume	2795.9(3) Å^3	
Z	2	
Density (calculated)	1.075 Mg m^{-3}	
Absorption coefficient	0.623 mm^{-1}	
F(000)	944	
Crystal size	0.09×0.07×0.06 mm^3	
Theta range for data collection	3.902 to 68.262°	
Index ranges	$-19 \le h \le 18$, $-19 \le k \le 19$, $-13 \le l \le 12$	
Reflections collected	9810	
Independent reflections	2555 [R(int) = 0.0273]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7531 and 0.6447	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2555 / 0 / 156	
Goodness-of-fit on F^2	1.068	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0405, wR_2 = 0.1115	
R indices (all data)	R_1 = 0.0432, wR_2 = 0.1138	
Absolute structure parameter	0.2(3)	
Largest diff. peak and hole	0.149 and −0.162 e$^-$ Å^{-3}	

Figure S3. Thermal ellipsoid plot of the X-ray crystal structure of compound **4d**. Ellipsoids shown at 50% probability.



^{1}H and ^{13}C NMR Spectra of Cyclotetrabenzoin 5b

Figure S4. ^{1}H NMR Spectrum of compound **5b** (600 MHz, $CDCl_3$, 25 °C).

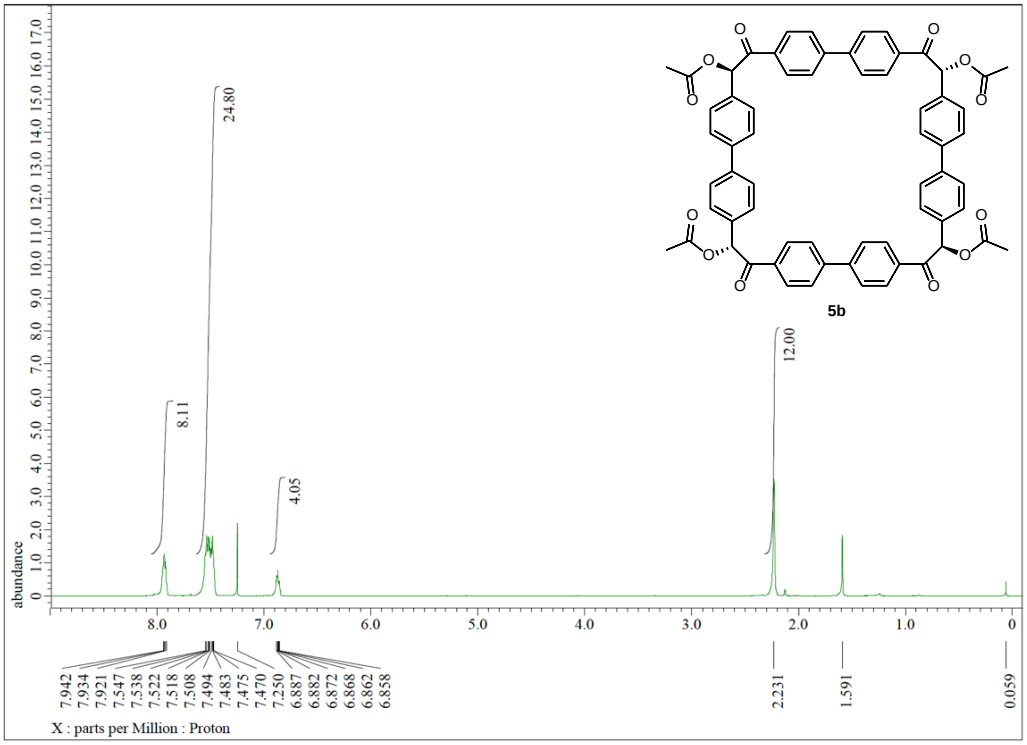
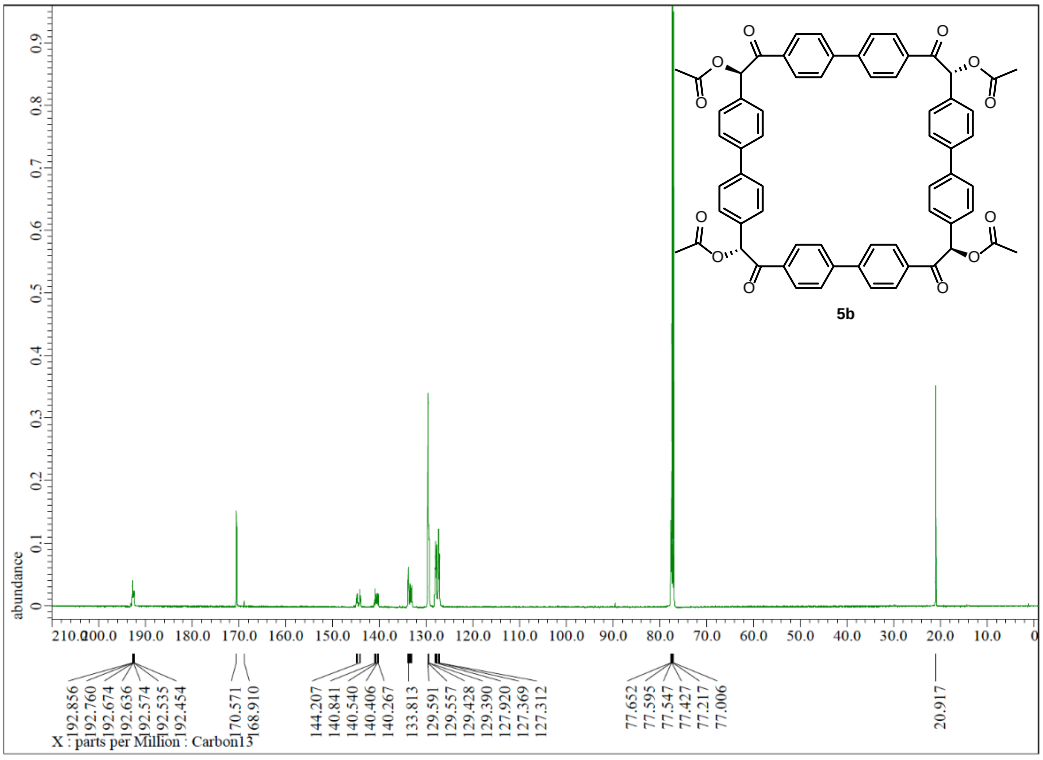


Figure S5. ^{13}C NMR Spectrum of compound **5b** (150 MHz, $CDCl_3$, 25 °C).



^{1}H and ^{13}C NMR Spectra of Cyclotetrabenzoins 4c and 5c

Figure S6. ^{1}H NMR Spectrum of compound **4c** (400 MHz, $CDCl_3$, 25 °C).

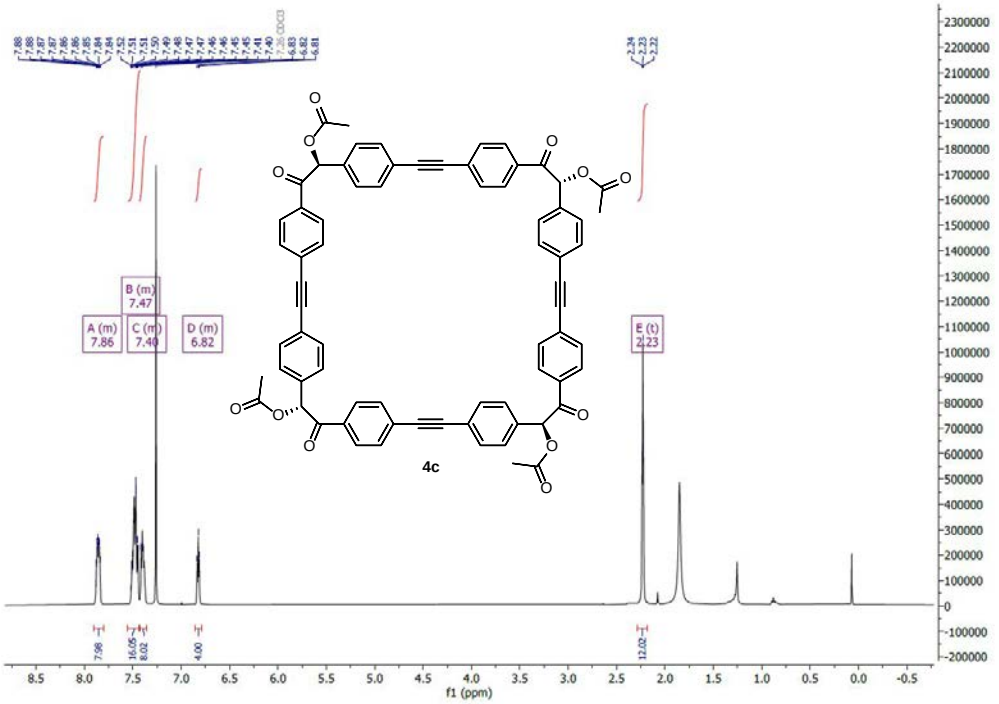


Figure S7. ^{13}C NMR Spectrum of compound **4c** (100 MHz, $CDCl_3$, 25 °C).

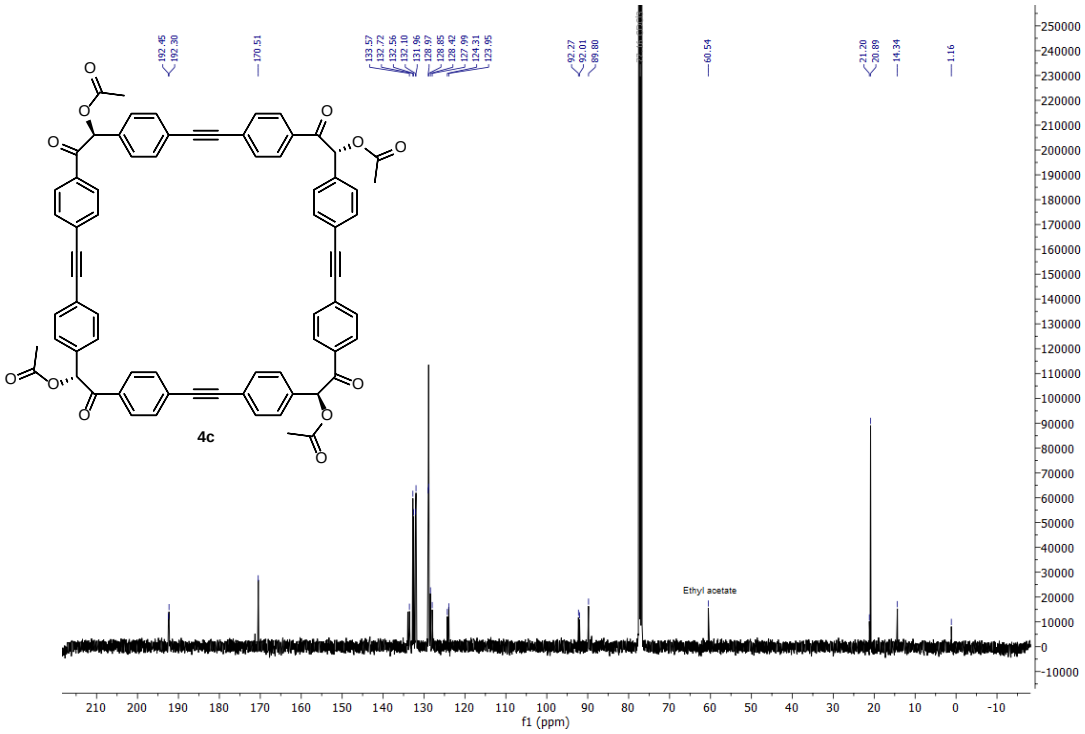
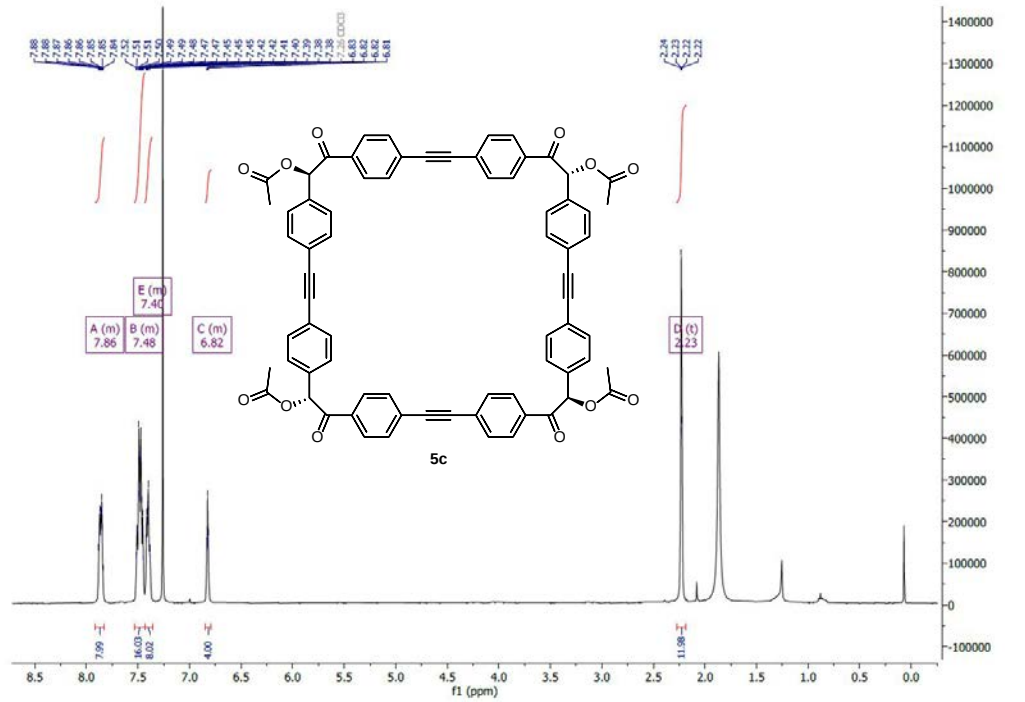


Figure S8. ^{1}H NMR Spectrum of compound **5c** (400 MHz, $CDCl_3$, 25 °C).



^{1}H and ^{13}C NMR Spectra of Cyclotetrabenzoin 4d and 5d

Figure S10. ^{1}H Spectrum of compound **4d** (500 MHz, $CDCl_3$, 25 °C).

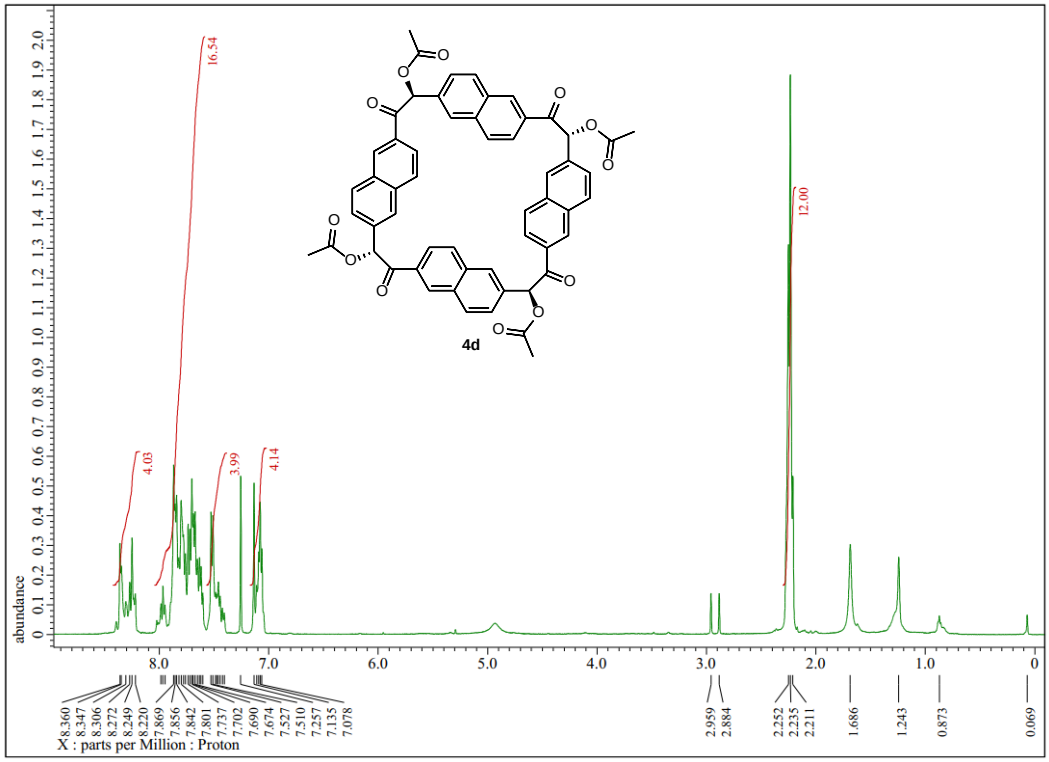


Figure S11. ^{13}C Spectrum of compound **4d** (125 MHz, $CDCl_3$, 25 °C).

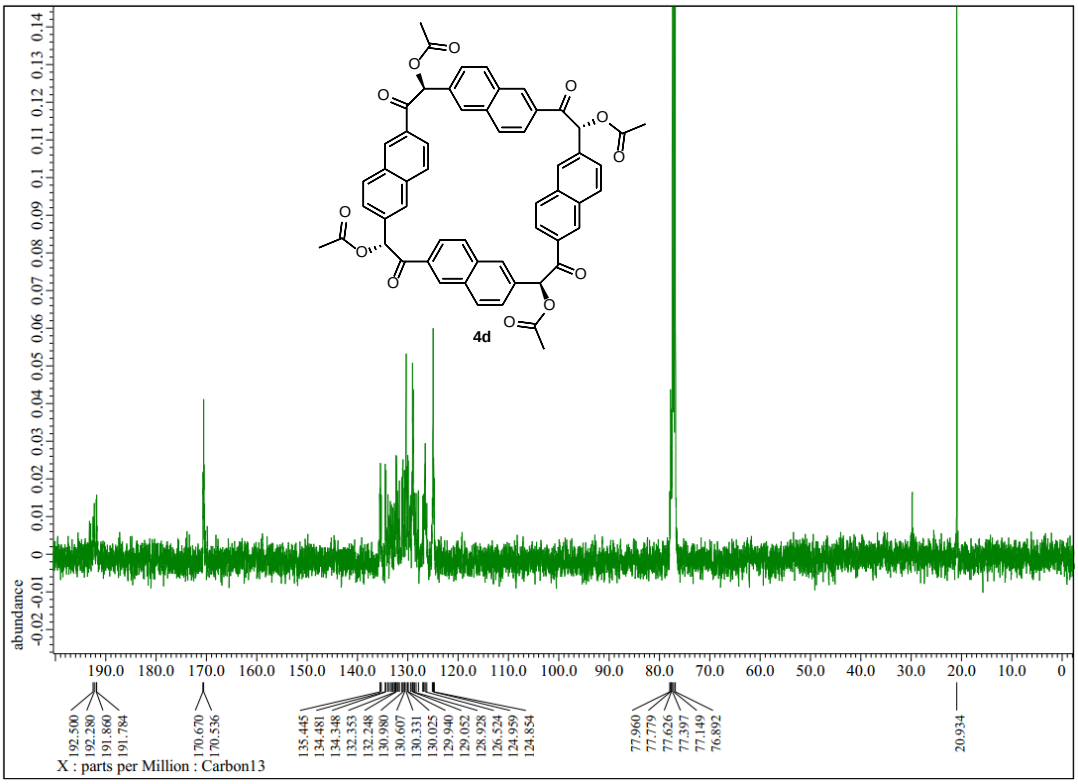


Figure S12. ^{1}H Spectrum of compound **5d** (500 MHz, $CDCl_3$, 25 °C).

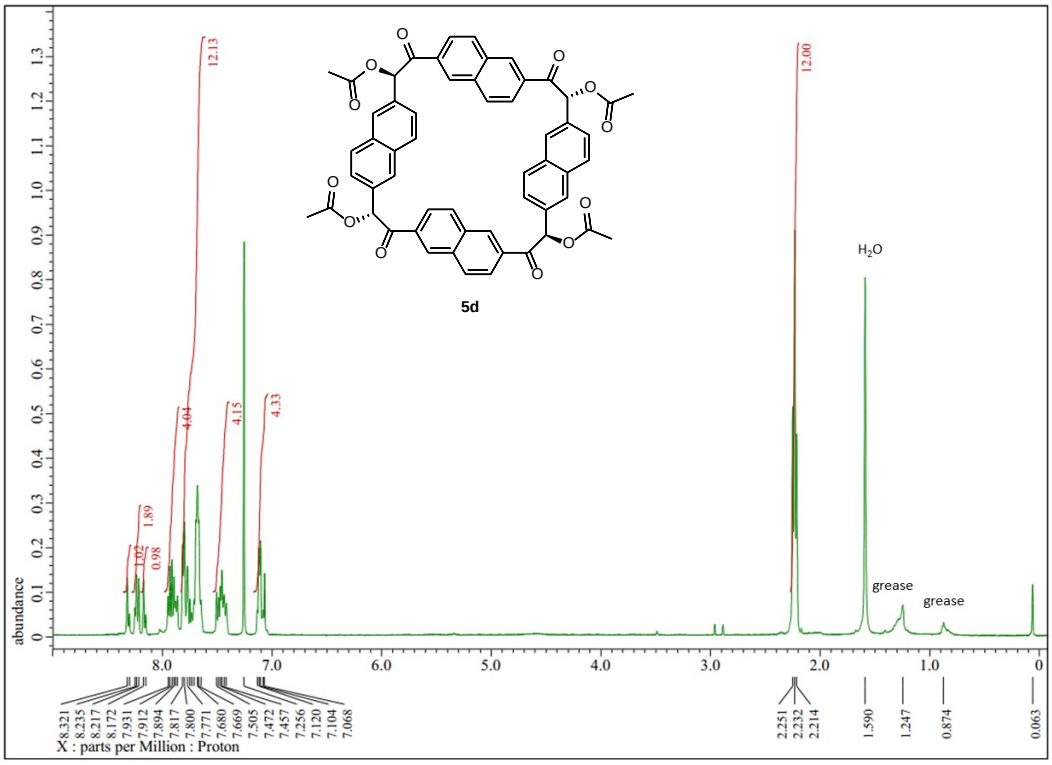
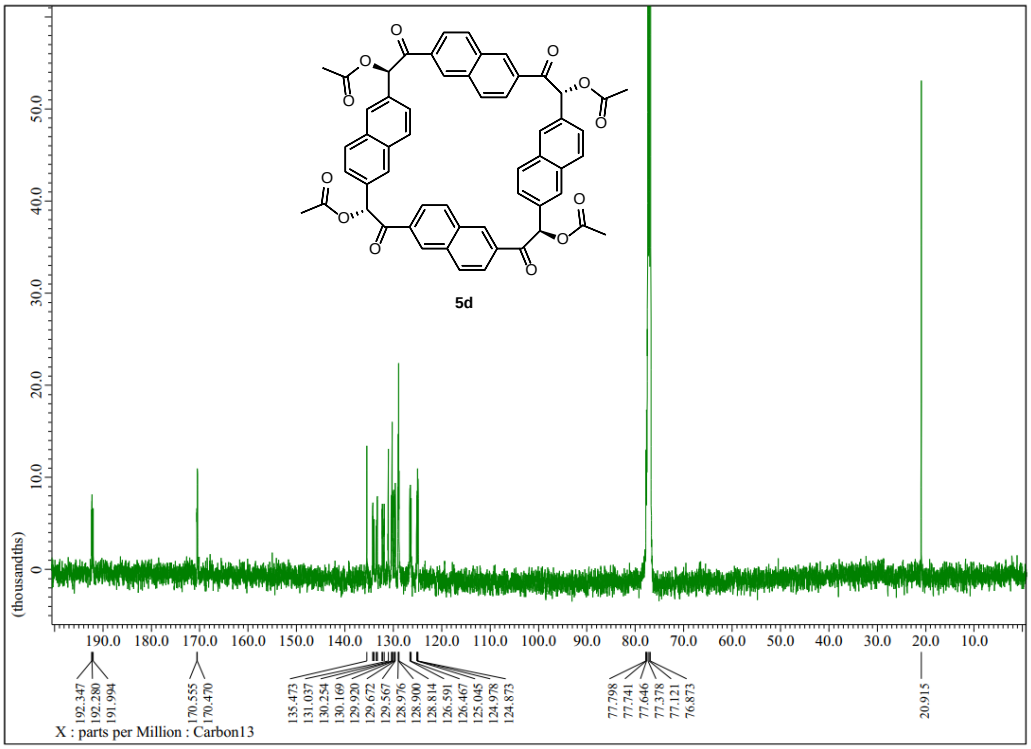


Figure S13. ^{13}C Spectrum of compound **5d** (125 MHz, $CDCl_3$, 25 °C).



^{1}H, ^{13}C NMR, IR, and HR-ESI Mass Spectra of Complex 6

Figure S14. ^{1}H NMR Spectrum of compound **6** (500 MHz, $CDCl_3$, 25 °C).

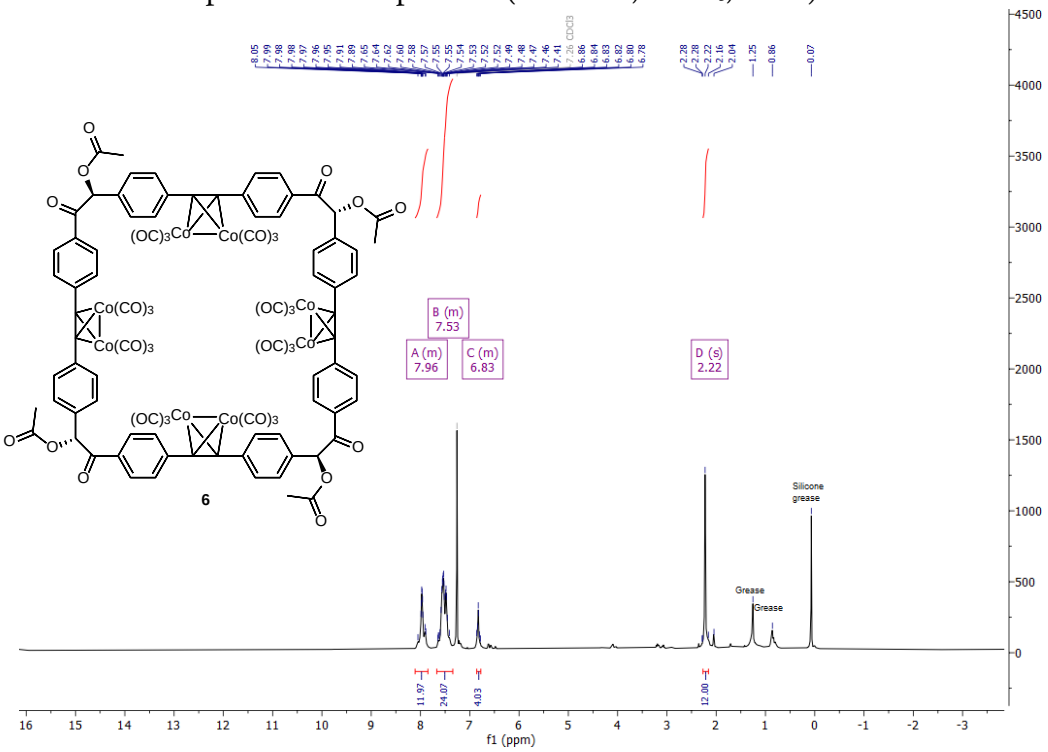


Figure S15. ^{13}C NMR Spectrum of compound **6** (125 MHz, $CDCl_3$, 25 °C).

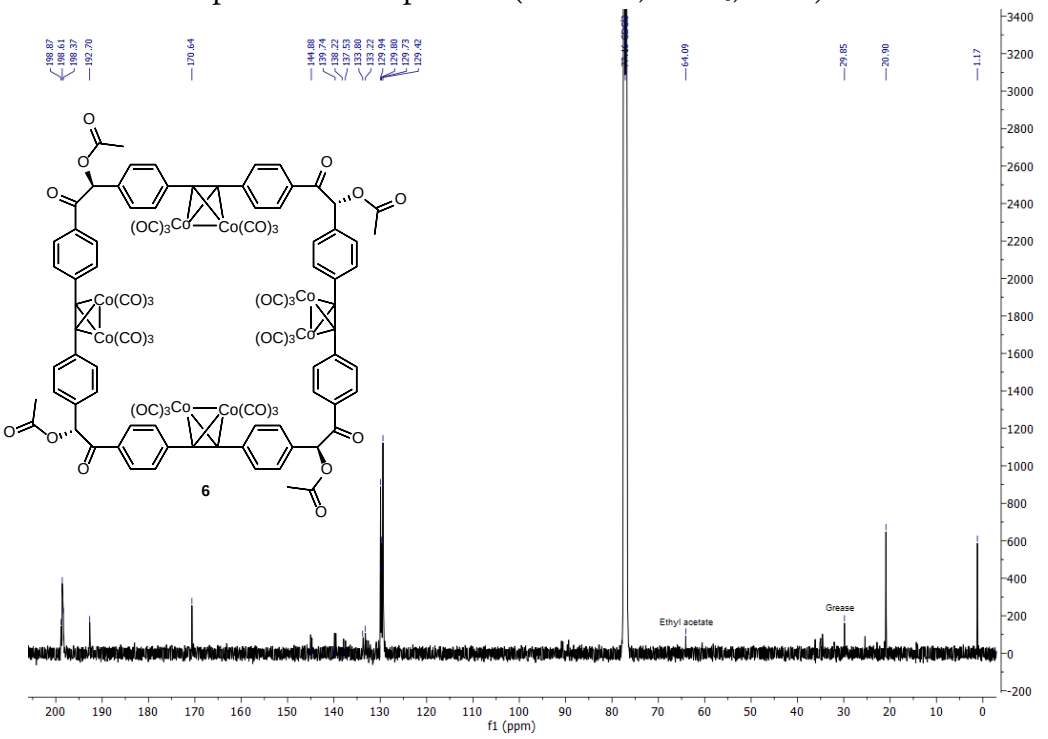


Figure S16. Comparison of the IR spectra of compounds **4c**/**5c** and **6**.

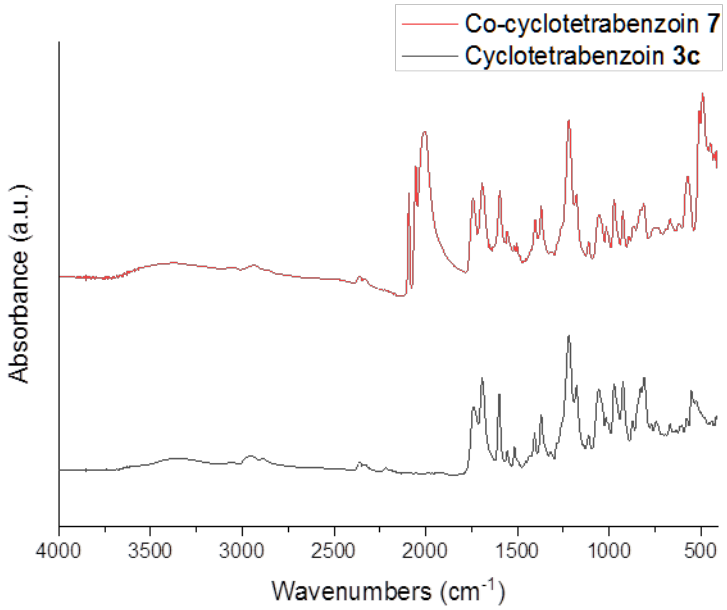


Figure S17. Comparison of the UV-vis spectra of compounds **4c**/**5c** and **6** (8.9 μM solutions in CH_2Cl_2).

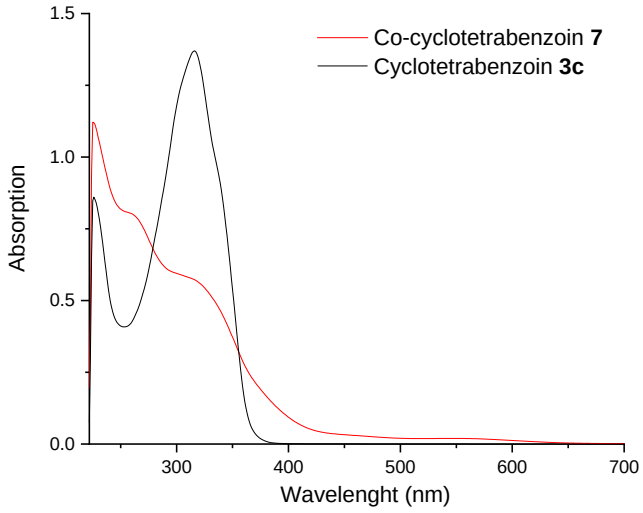


Figure S18. Comparison of ^{1}H NMR spectra of compounds **4c**/**5c** and **6**

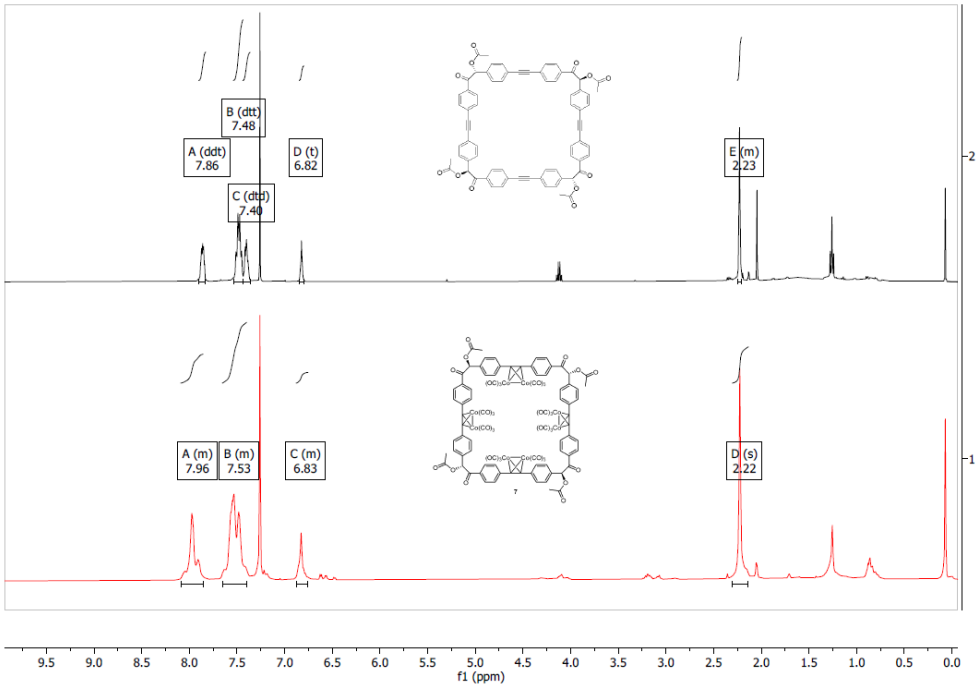


Figure S19. Comparison of ^{13}C NMR spectra of compounds **4c**/**5c** and **6**

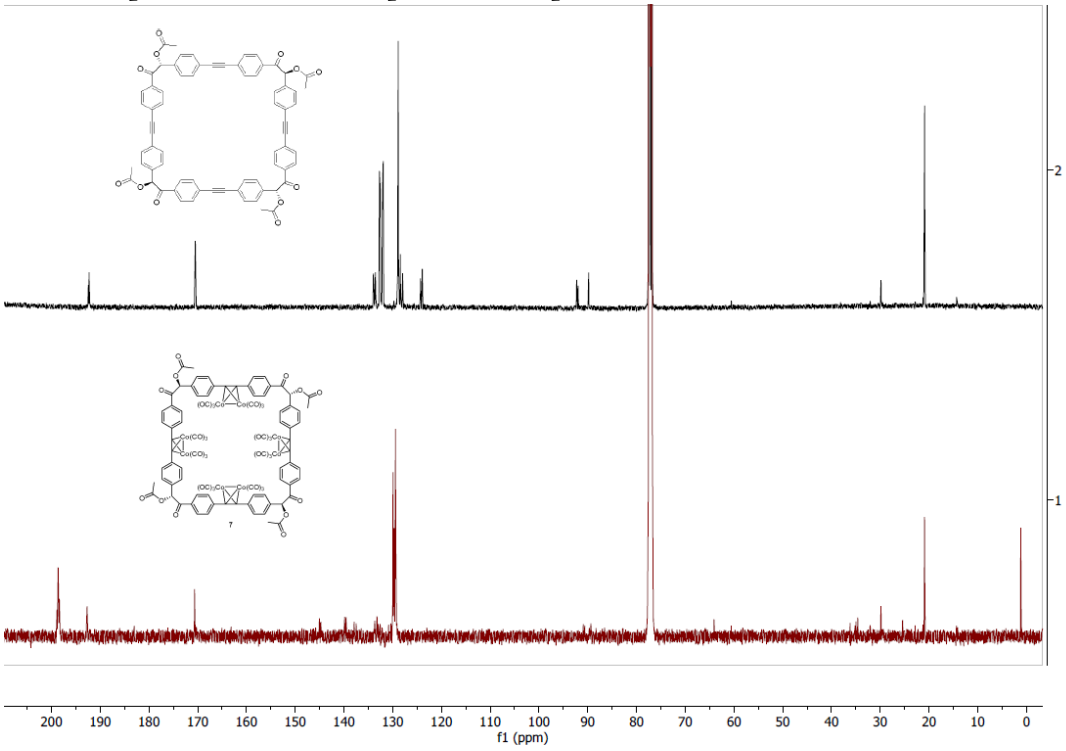
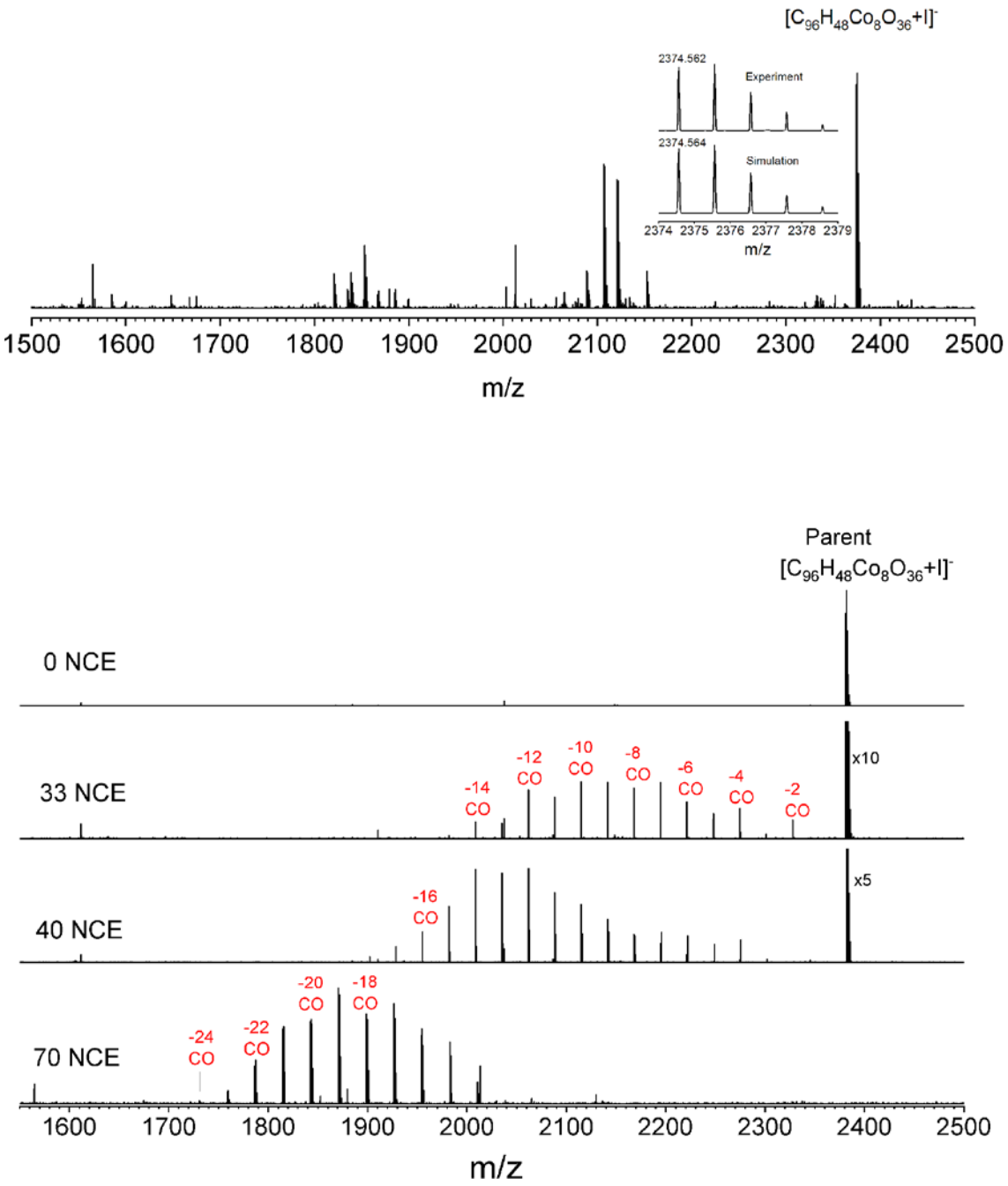


Figure S20. HR-ESI MS spectra of compound **6.**



Top trace: ESI-MS of **6** as iodide adduct, negative mode.

Bottom traces: Collision-induced dissociation of [**6**+I]$^-$ at four different activation energies (in machine units of "normalized collision energy", NCE) indicating loss of up to 24 CO molecules.

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