

Supplementary Information for:

Overcoming Strain-Induced Rearrangement Reactions: A Mild Dehydrative Aromatization Protocol for the Synthesis of Highly Distorted *para*-Phenylenes

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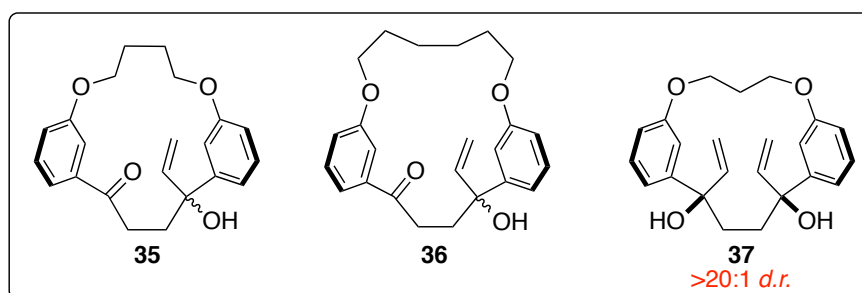
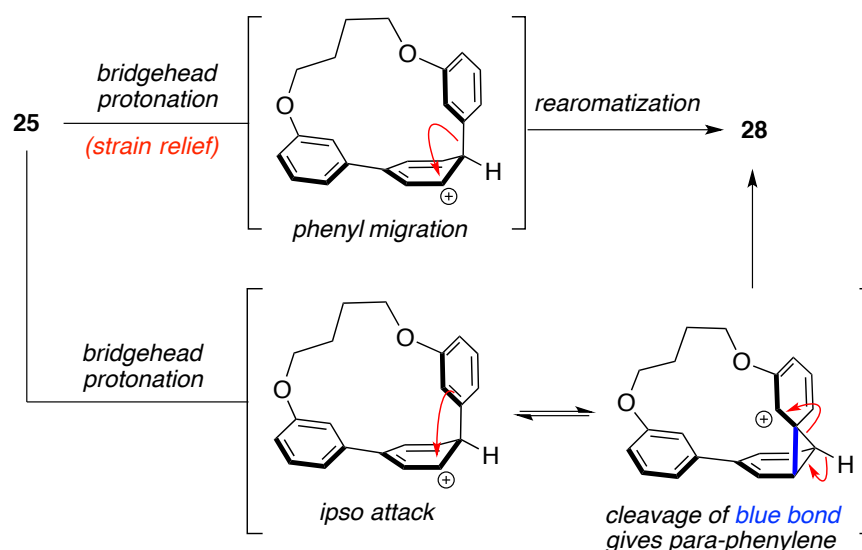


FIGURE SI-1: Structures/compounds not numbered in the manuscript that appear in the SI

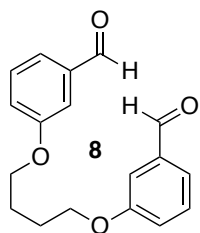


SCHEME SI-1: Proposed intermediate and possible mechanistic pathways for *p*-terphenyl to *m*-terphenyl rearrangement

General Experimental Conditions

All reactions were run in flame or oven-dried (120 °C) glassware and cooled under a positive pressure of ultra high pure nitrogen or argon gas. All chemicals were used as received from commercial sources, unless otherwise stated. Anhydrous reaction solvents were purified and dried by passing HPLC grade solvents through activated columns of alumina (Glass Contour SDS). All solvents used for chromatographic separations were HPLC grade (hexanes, ethyl acetate, dichloromethane, chloroform, methanol, and acetone). Chromatographic separations were performed using flash chromatography, as originally reported by Still and co-workers, on silica gel 60 (particle size 43-60 μm), and all chromatography conditions have been reported as height \times diameter in centimeters. Reaction progress was monitored by thin layer chromatography (TLC), on glass-backed silica gel plates (pH = 7.0). TLC plates were visualized using a handheld UV lamp (254 nm) and stained using an aqueous ceric ammonium molybdate (CAM) solution. Plates were dipped, wiped clean, and heated from the back of the plate. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at 400 or 600 MHz, calibrated using residual undeuterated solvent as an internal reference (CHCl_3 , δ 7.27 and 77.2 ppm), reported in parts per million relative to trimethylsilane (TMS, δ 0.00 ppm), and presented as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, t = triplet, m = multiplet, p = pentet), coupling constants (J , Hz). High-resolution mass spectrometric (HRMS) data were obtained using a quadrupole time-of-flight (Q-TOF) spectrometer and electrospray ionization (ESI).

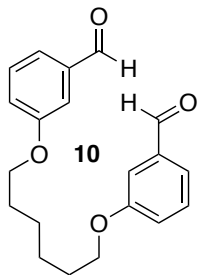
Experimental procedures and compound characterization data are presented in numerical order



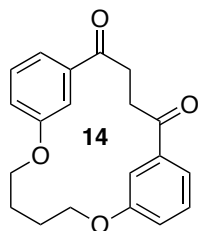
Dialdehyde 8: 1,4-Dibromobutane (**5**) (3.98 g, 18.4 mmol) was added to a stirred solution of 3-hydroxybenzaldehyde (5.01 g, 40.9 mmol), K_2CO_3 (5.66 g, 41.0 mmol) and TBAI (0.76 g, 2.1 mmol) in DMF (40 mL). The reaction was heated at 70 °C for 48 h, at which point water (100 mL) and 1 M HCl (50 mL) were added sequentially. The resulting mixture was extracted with ethyl acetate (3 \times 50 mL). The organic extracts

were combined and washed with saturated solution of NaHCO_3 (100 mL) and brine (100 mL), dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (18 \times 5.0 cm; chloroform, 2% to 5% acetone/chloroform) to afford **8** as white solid (4.75 g, 87%): R_f = 0.25 (chloroform); ^1H NMR (400 MHz, CDCl_3) δ 9.97 (s, 2H), 7.48-7.42 (m, 4H), 7.42-7.37 (m,

2H), 7.21-7.15 (m, 2H), 4.16-4.04 (m, 4H), 2.07-1.99 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.31, 159.67, 137.97, 130.24, 123.72, 122.09, 112.84, 67.87, 26.04; HRMS (ESI) calculated for $\text{C}_{18}\text{H}_{19}\text{O}_4$ ($[\text{M}+\text{H}]^+$) m/z = 299.1283, found 299.1290.

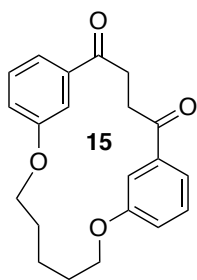


Dialdehyde 10: 1,6-Dibromohexane (**7**) (1.34 g, 5.49 mmol) was added to a stirred solution of 3-hydroxybenzaldehyde (2.03 g, 16.6 mmol) and K_2CO_3 (2.78 g, 20.1 mmol) in DMF (30 mL). The reaction was heated at 80 °C for 4 h, at which point water (75 mL) and 1 M HCl (30 mL) were added sequentially. The resulting mixture was extracted with ethyl acetate (3 \times 30 mL). The organic extracts were combined and washed with a saturated solution of NaHCO_3 (40 mL) and brine (40 mL), dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified via flash chromatography (18 cm \times 3.8 cm; 9:1 dichloromethane/hexanes, dichloromethane, and 1:9 acetone/dichloromethane) to afford **10** as white solid (1.47 g, 82%): R_f = 0.35 (dichloromethane); ^1H NMR (600 MHz, CDCl_3) δ 9.98 (s, 2H), 7.46-7.43 (m, 4H), 7.39 (s, 2H), 7.19-7.18 (m, 2H), 4.05 (t, J = 6.4 Hz, 4H), 1.88-1.82 (m, 4H), 1.60-1.55 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 192.2, 159.6, 137.8, 130.0, 123.5, 122.0, 112.7, 68.1, 29.1, 25.8; HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{23}\text{O}_4$ ($[\text{M}+\text{H}]^+$) m/z = 327.1596, found 327.1595.



Streamlined synthesis of macrocyclic diketone 14: Vinylmagnesium chloride (1.6 M in THF, 4.6 mL, 7.4 mmol) was added to a stirred solution of the dialdehyde **8** (1.02 g, 3.42 mmol) in THF (28 mL). After 10 min., the reaction was poured into water (50 mL) and further diluted with 1 M HCl (40 mL). The resulting mixture was extracted with dichloromethane (3 \times 20 mL). The combined organic extracts were washed with a saturated solution NaHCO_3 (30 mL) and water (30 mL), dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The pale yellow residue was dissolved in dichloromethane (224 mL), heated to 40 °C, followed by the addition of Hoveyda-Grubbs second-generation catalyst (0.052 g, 0.083 mmol). After 1 h, the reaction mixture was concentrated under reduced pressure. The dark brown residue was dissolved in 1:9 methanol/dichloromethane (34 mL), and sodium borohydride (0.380 g, 10.0 mmol) was added. After 3 h, the reaction was poured into water (50 mL) and further diluted with 1 M HCl (20 mL). The layers were separated and the aqueous phase was extracted with dichloromethane (2 \times 20 mL). The combined organic extracts were washed with water (20 mL), dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The dark brown residue was dissolved in dichloromethane (34

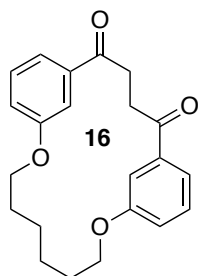
mL), followed by the sequential addition of NaHCO_3 (0.846 g, 10.1 mmol) and Dess-Martin periodinane (2.91 g, 6.86 mmol). After 30 min., the reaction was poured into water (50 mL). The layers were separated and the aqueous phase was extracted with dichloromethane (2×25 mL). The combined organic extracts were washed with water (30 mL), dried over Na_2SO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (15×2.5 cm, 3:7 EtOAc/hexanes) to afford 1,4-diketone **14** as a white solid (0.551 g, 51% from **8**): $R_f = 0.38$ (3:7 EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.51 (dd, $J = 7.8, 1.3$ Hz, 2H), 7.42-7.35 (m, 2H), 7.25-7.21 (m, 2H), 7.11 (ddd, $J = 8.2, 2.5, 1.0$ Hz, 2H), 4.22-4.17 (m, 4H), 3.09 (s, 4H), 2.00-1.93 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 199.77, 158.62, 137.57, 130.43, 120.89, 120.05, 115.89, 68.44, 36.22, 25.88; HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{21}\text{O}_4$ ($[\text{M}+\text{H}]^+$) $m/z = 325.1440$, found 325.1436.



Streamlined synthesis of 1,4-diketones 15: Vinylmagnesium chloride (1.6 M in THF, 5.5 mL, 8.8 mmol) was added to a stirred solution of **9** (1.24 g, 3.97 mmol) in THF (20 mL). After 10 min., the reaction was poured into water (100 mL) and further diluted with 1 M HCl (50 mL). The resulting mixture was extracted with dichloromethane (3×20 mL). The combined organic extracts were washed with a saturated solution

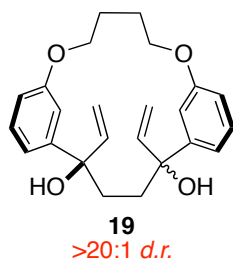
NaHCO_3 (30 mL) and water (30 mL), dried over MgSO_4 , filtered and concentrated under reduced pressure. The pale yellow residue was dissolved in dichloromethane (220 mL), heated to 40°C , followed by the addition of Hoveyda-Grubbs second-generation catalyst (0.062 g, 0.099 mmol). After 1 h, the reaction mixture was concentrated under reduced pressure. The dark brown residue was dissolved in 1:9 methanol/dichloromethane (30 mL) and sodium borohydride (0.619 g, 15.9 mmol) was added. After 3 h, the reaction was poured into water (50 mL) and further diluted with 1 M HCl (20 mL). The layers were separated and the aqueous phase was extracted with dichloromethane (2×20 mL). The combined organic extracts were washed with water (20 mL), dried over MgSO_4 , filtered and concentrated under reduced pressure. The dark brown residue was dissolved in dichloromethane (30 mL), followed by the sequential addition of NaHCO_3 (0.733 g, 8.73 mmol) and Dess-Martin periodinane (3.37 g, 7.89 mmol). After 30 min., the reaction was poured into water (50 mL). The layers were separated and the aqueous phase was extracted with dichloromethane (2×25 mL). The combined organic extracts were washed with water (30 mL), dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography ($12 \text{ cm} \times 2.5 \text{ cm}$; 3:7 EtOAc/hexanes) to afford 1,4-diketone **15** as a white solid (0.885 g, 66% from **9**): $R_f = 0.27$ (1:4

EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.49 (ddd, $J = 7.7, 1.7, 1.0$ Hz, 2H), 7.39-7.34 (m, 2H), 7.30 (dd, $J = 2.5, 1.6$ Hz, 2H), 7.07 (ddd, $J = 8.2, 2.5, 1.0$ Hz, 2H), 4.11 (t, $J = 6.2$ Hz, 4H), 3.21 (s, 4H), 1.84 (p, $J = 6.3$ Hz, 4H), 1.75-1.66 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 200.10, 159.05, 137.72, 130.32, 120.70, 119.58, 115.59, 68.01, 36.07, 27.93, 21.98; HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{23}\text{O}_4$ ($[\text{M}+\text{H}]^+$) $m/z = 339.1596$, found 339.1598.



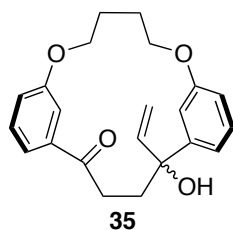
Streamlined synthesis of 1,4-diketones 16: Vinylmagnesium chloride (1.6 M in THF, 4.8 mL, 7.7 mmol) was added to a stirred solution of **10** (1.19 g, 3.65 mmol) in THF (20 mL). After 10 min., the reaction was poured into water (100 mL) and further diluted with 1 M HCl (50 mL). The resulting mixture was extracted with dichloromethane (3 \times 20 mL). The combined organic extracts were washed with a saturated solution of

NaHCO_3 (40 mL) and water (40 mL), dried over MgSO_4 , filtered and concentrated under reduced pressure. The pale yellow residue was dissolved in dichloromethane (240 mL), heated to 40 $^\circ\text{C}$, followed by the addition of Hoveyda-Grubbs second-generation catalyst (0.067 g, 0.107 mmol). After 1 h, the reaction mixture was concentrated under reduced pressure. The dark brown residue was dissolved in 1:9 methanol/dichloromethane (36 mL), and sodium borohydride (0.652 g, 17.2 mmol) was added. After 3 h, the reaction was poured into water (50 mL) and further diluted with 1 M HCl (30 mL). The layers were separated and the aqueous phase was extracted with dichloromethane (2 \times 20 mL). The combined organic extracts were washed with water (20 mL), dried over MgSO_4 , filtered and concentrated under reduced pressure. The dark brown residue was dissolved in dichloromethane (30 mL), followed by the sequential addition of NaHCO_3 (0.613 g, 7.30 mmol) and Dess-Martin periodinane (3.09 g, 7.30 mmol). After 30 min., the reaction was poured into water (50 mL). The layers were separated and the aqueous phase was extracted with dichloromethane (2 \times 25 mL). The combined organic extracts were washed with water (30 mL), dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (12 cm \times 2.5 cm; 3:7 EtOAc/hexanes) to afford 1,4-diketone **16** as a white solid (0.681 g, 53% from **10**): $R_f = 0.42$ (2:3 EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.55 (ddd, $J = 7.7, 1.7, 1.0$ Hz, 2H), 7.43-7.35 (m, 4H), 7.09 (ddd, $J = 8.2, 2.5, 1.0$ Hz, 2H), 4.08 (t, $J = 5.8$ Hz, 4H), 3.20 (s, 4H), 1.87-1.77 (m, 4H), 1.67-1.59 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 199.67, 159.33, 137.50, 130.36, 120.52, 118.54, 116.23, 67.91, 35.80, 28.24, 25.29; HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{25}\text{O}_4$ ($[\text{M}+\text{H}]^+$) $m/z = 353.1753$, found 353.1753.



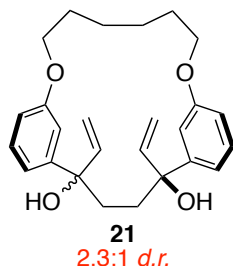
Allylic alcohol 19: 1,4-diketone **12** (0.298 g, 0.925 mmol), as a solution in THF (7.5 mL) was added to a stirred 65 °C solution of vinylmagnesium chloride (1.6 M in THF, 1.8 mL, 2.8 mmol). After 1 min., the reaction mixture was poured into water (20 mL) and further diluted with 1 M HCl (20 mL). The resulting mixture was extracted with dichloromethane (3 × 10 mL). The organic extracts were combined

and washed with a saturated solution of NaHCO₃ (20 mL) and brine (20 mL), then dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The solid residue was purified by flash chromatography (15 × 2.5 cm, 1:4 EtOAc/hexanes) to give hydroxyketone **35** (0.048 g, 15%) and allylic alcohol **19** (0.220 g, 63%; 77% based on recovered **35**) predominately as the *syn*-diastereomer (> 20:1 d.r.).



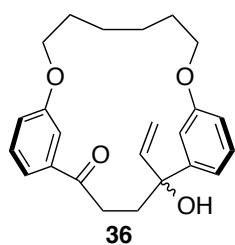
Hydroxy ketone 35: *R*_f = 0.35 (1:4 EtOAc/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.53 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.38-7.30 (m, 2H), 7.12 (ddd, *J* = 7.7, 1.7, 0.9 Hz, 1H), 7.04 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 1H), 6.96-6.93 (m, 1H), 6.92-6.90 (m, 1H), 6.88 (dd, *J* = 2.5, 1.0 Hz, 1H), 6.86 (dd, *J* = 2.5, 1.0 Hz, 1H), 5.31 (dd, *J* = 17.3, 0.9 Hz, 1H), 5.15 (dd, *J* = 10.7, 0.8 Hz, 1H), 4.27-4.17 (m, 2H), 4.18-4.10 (m, 1H), 4.03-3.93 (m, 1H), 2.79-2.56 (m, 2H), 2.44-2.24 (m, 2H), 2.13-1.88 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 201.84, 158.68, 158.59, 145.39, 144.29, 137.62, 129.98, 129.74, 120.38, 119.80, 118.30, 115.98, 113.38, 113.34, 113.05, 77.07, 69.16, 67.06, 39.19, 33.75, 26.45, 25.80; HRMS (ESI) calculated for C₂₂H₂₃O₃ ([M-(H₂O)+H]⁺) *m/z* = 335.1647, found 335.1647.

Allylic alcohol 19: *R*_f = 0.22 (1:4 EtOAc/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.17 (m, 2H), 6.98-6.90 (m, 2H), 6.80 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 2H), 6.72-6.64 (m, 2H), 6.19 (dd, *J* = 17.2, 10.7 Hz, 2H), 5.32 (dd, *J* = 17.3, 1.3 Hz, 2H), 5.16 (dd, *J* = 10.7, 1.3 Hz, 2H), 4.15-4.00 (m, 4H), 3.08 (s, 2H), 2.04-1.90 (m, 4H), 1.84-1.65 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 158.71, 146.45, 143.18, 143.16, 129.16, 129.14, 118.47, 113.54, 113.31, 113.29, 112.81, 76.86, 67.50, 36.77, 26.03; HRMS (ESI) calculated for C₂₄H₂₅O₂ ([M-(2H₂O)+H]⁺) *m/z* = 345.1855, found 345.1868.



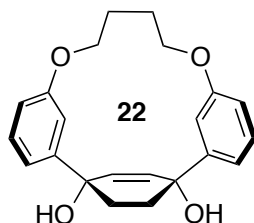
Allylic alcohol 21: 1,4-diketone **12** (0.560 g, 1.59 mmol), as a solution in THF (10 mL), was added to a stirred 65 °C solution vinylmagnesium chloride (1.6 M in

THF, 5.2 mL, 8.3 mmol). After 1 h, the reaction mixture was poured into water (100 mL) and further diluted with 1 M HCl (30 mL). The resulting mixture was extracted with dichloromethane (3 × 30 mL). The organic extracts were combined and washed with a saturated solution of NaHCO₃ (30 mL) and brine (30 mL), dried over anhydrous MgSO₄ and concentrated under reduced pressure. The solid residue was purified by flash chromatography (15 × 2.5 cm, 1:4 EtOAc/hexanes) to give hydroxyketone **36** (0.250 g, 41%) and allylic alcohol **21** (0.310 g, 47%; 86% based on recovery of **36**) as an inseparable mixture of diastereomers (2.3:1 *d.r.*):



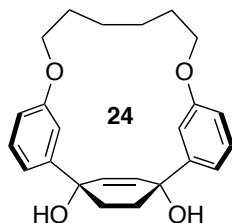
Hydroxy ketone 36: R_f = 0.33 (1:4 EtOAc/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 7.58-7.52 (m, 1H), 7.37-7.32 (m, 1H), 7.29-7.24 (m, 1H), 7.21 (s, 1H), 7.12 (s, 1H), 7.06 (dd, J = 8.1, 2.4 Hz, 1H), 6.93 (dd, J = 7.7, 1.6 Hz, 1H), 6.79 (dd, J = 8.1, 2.6 Hz, 1H), 6.26 (dd, J = 17.3, 10.7 Hz, 1H), 5.36 (d, J = 17.4 Hz, 1H), 5.17 (d, J = 10.6 Hz, 1H), 4.12-3.96 (m, 4H), 2.95 (dt, J = 15.5, 7.6 Hz, 1H), 2.57 (dt, J = 15.1, 6.6 Hz, 1H), 2.45 (dt, J = 14.8, 7.6 Hz, 1H), 2.33-2.19 (m, 1H), 2.09 (s, 1H), 1.97-1.74 (m, 4H), 1.69-1.56 (m, 4H); ¹³C NMR (151 MHz, CDCl₃) δ 201.35, 159.19, 158.89, 145.49, 144.45, 138.18, 129.74, 129.45, 120.02, 118.67, 118.00, 116.16, 112.99, 112.76, 111.58, 76.61, 67.99, 66.45, 37.18, 33.02, 28.09, 27.90, 24.66, 24.33; HRMS (ESI) calculated for C₂₄H₂₉O₄ ([M+H]⁺) m/z = 381.2066, found 381.2075.

Allylic alcohol 21 (major isomer): R_f = 0.14 (1:4 EtOAc/hexanes), 0.59 (1:1 EtOAc/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 7.31 (d, J = 8.0 Hz, 2H), 7.19 (dd, J = 7.7, 1.7 Hz, 2H), 6.80 (dd, J = 8.2, 2.4 Hz, 2H), 6.59-6.54 (m, 2H), 6.08 (dd, J = 17.3, 10.6 Hz, 2H), 5.18 (d, J = 17.3 Hz, 2H), 5.01 (d, J = 10.6 Hz, 2H), 4.11-4.03 (m, 2H), 3.98-3.94 (m, 2H), 2.51 (s, 2H), 2.02-1.94 (m, 2H), 1.93-1.86 (m, 2H), 1.83-1.76 (m, 4H), 1.73-1.56 (m, 4H); ¹³C NMR (151 MHz, CDCl₃) δ 159.2, 146.2, 145.7, 129.4, 117.4, 113.2, 112.3, 111.3, 76.8, 66.8, 35.6, 28.4, 24.7; HRMS (ESI) calculated for C₂₆H₃₃O₄ ([M+H]⁺) m/z = 409.2379, found 409.2380.



Cyclohex-2-ene-1,4-diol 22: Grubbs' second-generation catalyst (0.023 g, 0.026 mmol) was added to a stirred solution of **19** (>20:1 *d.r.*; 0.201 g, 0.526 mmol) in dichloromethane (35 mL) and the reaction was heated to 40 °C. After 2 h, the solvent was removed under reduced pressure and residue was purified by flash chromatography (15 × 2.5 cm, 1:1 EtOAc/hexanes) to give compound **22** as an off-white solid (0.159 g,

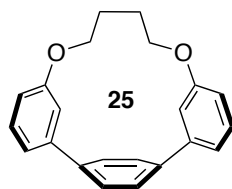
86%); R_f = 0.27 (1:1 EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.27 (m, 4H), 7.05-6.99 (m, 2H), 6.80 (ddd, J = 7.7, 2.5, 1.4 Hz, 2H), 6.08 (s, 2H), 4.26-4.11 (m, 2H), 4.06-3.93 (m, 2H), 2.17 (s, 2H), 2.14-1.98 (m, 4H), 1.97-1.78 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.64, 147.77, 134.96, 130.23, 117.59, 114.70, 113.81, 73.25, 69.81, 37.00, 26.98. HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{23}\text{O}_3$ ($[\text{M}-(\text{H}_2\text{O})+\text{H}]^+$) m/z = 335.1647, found 335.1641.



Cyclohex-2-ene-1,4-diol 22: Grubbs' second-generation catalyst (0.020 g, 0.023 mmol) was added to a stirred solution of **21** (2.3:1 *d.r.*; 0.380 g, 0.930 mmol) in dichloromethane (23 mL) and the reaction was heated to 40 °C. After 2 h, the solvent was removed under reduced pressure and residue was purified by flash chromatography (15 x 2.5 cm, 3:7 EtOAc/hexanes) to give compound **24** as an off-white solid (0.225 g, 59%, 85% based on recovered *anti*-**21**) and (uncyclized) *anti*-**21** (0.106 g, 92% recovery).

anti-**21**: R_f = 0.33 (1:4 EtOAc/hexanes); ^1H NMR (600 MHz, CDCl_3) δ 7.30-7.23 (m, 2H), 7.15-7.10 (m, 2H), 6.79-6.73 (m, 2H), 6.58-6.52 (m, 2H), 6.06 (dd, J = 17.2, 10.6 Hz, 2H), 5.15 (dd, J = 17.2, 1.0 Hz, 2H), 5.00 (dd, J = 10.6, 1.0 Hz, 2H), 4.03 (dt, J = 9.3, 4.8 Hz, 2H), 3.94 (td, J = 9.2, 3.9 Hz, 2H), 2.00 (s, 2H), 1.95-1.88 (m, 2H), 1.88-1.80 (m, 2H), 1.79-1.72 (m, 1H), 1.69-1.50 (m, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 159.15, 146.18, 145.66, 129.43, 117.42, 113.21, 112.31, 111.30, 76.80, 66.75, 35.64, 28.38, 24.71; HRMS (ESI) calculated for $\text{C}_{26}\text{H}_{33}\text{O}_4$ ($[\text{M}+\text{H}]^+$) m/z = 409.2379, found 409.2372.

Cyclohex-2-ene-1,4-diol 22: R_f = 0.29 (1:1 EtOAc/hexanes); ^1H NMR (600 MHz, CDCl_3) δ 7.32-7.26 (m, 4H), 6.93-6.88 (m, 2H), 6.80-6.74 (m, 2H), 5.96 (s, 2H), 4.02-3.94 (m, 4H), 2.54 (s, 2H), 2.08-2.03 (m, 2H), 1.86-1.74 (m, 6H), 1.63-1.55 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.83, 147.84, 134.66, 130.13, 117.49, 113.76, 112.62, 72.98, 67.62, 36.33, 27.78, 24.63; HRMS (ESI) calculated for $\text{C}_{24}\text{H}_{27}\text{O}_3$ ($[(\text{M}-\text{H}_2\text{O})+\text{H}]^+$) m/z = 363.1960, found 363.1968.



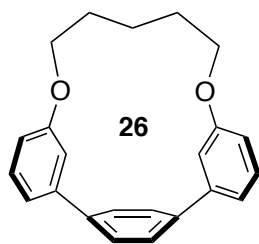
1,6-dioxo[6](3,3')-p-Terphenylenophane (25): *p*-Toluene sulfonic acid monohydrate (0.130 g, 0.684 mmol) was added to a stirred solution of **22** (0.040 g, 0.11 mmol) in toluene (6 mL). The reaction was heated at 50 °C for 10 h and then to 60 °C for 5 h.

After 15 h, a saturated solution of NaHCO_3 (20 mL) was added. The layers were separated and the aqueous phase was extracted with dichloromethane (2 x 10 mL). The organic extracts

were combined and washed with brine (20 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 1.3 cm, 5% EtOAc/hexanes) to afford **25** as a white solid (0.015 g, 42%); *R*_f = 0.43 (5% EtOAc/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 7.37 (s, 4H), 7.36-7.32 (m, 2H), 7.26-7.24 (m, 2H), 6.78 (dd, *J* = 8.4, 2.7 Hz, 2H), 5.31 (d, *J* = 2.9 Hz, 2H), 3.95-3.89 (s, 4H), 1.46-1.40 (m, 4H); ¹³C NMR (151 MHz, CDCl₃) δ 156.29, 144.82, 144.55, 130.30, 117.70, 115.81, 115.69, 67.29, 22.77; HRMS (EI) calculated for C₂₂H₂₁O₂ (M⁺) *m/z* = 316.1463, found 316.1437.

Alternate procedure for 25 (Table 1, entry 4): Sodium hydrogen sulfate monohydrate (0.008 g, 0.06 mmol) was added to a stirred 130 °C solution of **22** (0.010 g, 0.028 mmol) and *o*-chloranil (0.035 g, 0.14 mmol) in DMSO (0.75 mL) and xylenes (2 mL). After 24 h, the reaction mixture was cooled to room temperature and a saturated solution of NaHCO₃ (10 mL) and dichloromethane (10 mL) were added. The layers were separated and the aqueous phase was extracted with dichloromethane (2 × 10 mL). The organic extracts were combined, filtered through a pad of Celite (2 cm), and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (7.5 × 0.6 cm; 5% EtOAc/hexanes) to afford the **25** as a white solid (0.0032 g, 36%). A trace amount of the [6]MTPP isomer was observed in the ¹H NMR spectrum of **25**.

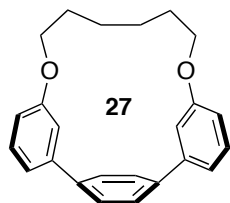
Alternate procedure for 25 (Table 1, entry 10): Burgess reagent (0.021 g, 0.088 mmol) was added to a stirred solution of **22** (0.010 g, 0.028 mmol) in toluene (2 mL) at 80 °C. After 15 min., the reaction was cooled to room temperature, water (10 mL) was added, and the resulting mixture was stirred for 5 min. The layers were separated and the mixture was extracted with dichloromethane (3 × 5 mL). The organic extracts were combined and washed with brine (10 mL), dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography (12 × 1.3 cm, 1:1 dichloromethane/hexanes) to afford **25** as a white solid (0.005 g, 56%).



1,7-dioxa[7](3,3')-p-Terphenylenophane (26) (Table 1, entry 11): Burgess reagent (0.050 g, 0.21 mmol) was added to a stirred solution of **23** (0.026 g, 0.071 mmol) in toluene (3 mL) at 80 °C. After 15 min., the reaction was cooled to room temperature, water (10 mL) was added, and the resulting mixture was stirred for 5 min. The layers were separated and the mixture was extracted with

dichloromethane (3 × 10 mL). The organic extracts were combined and washed with brine (10 mL),

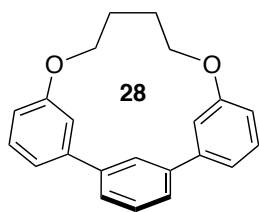
dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (12 \times 1.3 cm, 1:1 dichloromethane/hexanes) to afford **26** as a white solid (0.016 g, 68%): R_f = 0.32 (1:19 EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.44 (s, 4H), 7.35 (dd, J = 8.2, 7.4 Hz, 2H), 7.30-7.24 (m, 2H), 6.78 (ddd, J = 8.3, 2.8, 1.0 Hz, 2H), 5.81 (dd, J = 2.8, 1.5 Hz, 2H), 4.10-4.05 (m, 4H), 1.51-1.42 (m, 4H), 1.21-1.12 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 157.2, 144.7, 144.1, 130.6, 129.5, 118.7, 115.9, 115.4, 68.5, 26.8, 23.3; HRMS (EI) calculated for $\text{C}_{23}\text{H}_{22}\text{O}_2$ ($[\text{M}]^+$) m/z = 330.1618, found, 330.1620.



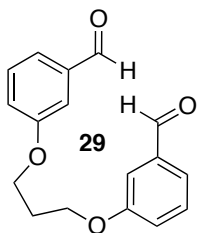
1,8-dioxa[8](3,3'')-p-Terphenylenophane (27): *p*-Toluene sulfonic acid monohydrate (0.502 g, 2.92 mmol) was added to a stirred solution of **24** (0.184 g, 0.484 mmol) in toluene (20 mL) and the reaction was heated to 60 $^\circ\text{C}$. After 2 h, a saturated solution of NaHCO_3 (20 mL) was added to the reaction. The layers were separated

and the aqueous phase was extracted with dichloromethane (3 \times 15 mL). The organic extracts were combined and washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (15 \times 1.3 cm, 1:1 dichloromethane/hexanes) to afford **27** as a white solid (0.120 g, 74%): R_f = 0.41 (1:1 dichloromethane/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.39 (s, 4H), 7.36 (dd, J = 8.3, 7.4 Hz, 2H), 7.26-7.20 (m, 2H), 6.84 (ddd, J = 8.3, 2.7, 0.9 Hz, 2H), 5.92 (dd, J = 2.8, 1.4 Hz, 2H), 4.08-3.99 (m, 4H), 1.62-1.50 (m, 4H), 1.12-1.04 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 156.86, 144.54, 143.59, 130.21, 128.76, 117.46, 116.63, 115.88, 68.42, 27.81, 27.63; HRMS (EI) calculated for $\text{C}_{24}\text{H}_{24}\text{O}_2$ ($[\text{M}]^+$) m/z = 344.1931 found 344.1896.

Alternate procedure for 28 (Table 1, entry 13): Burgess reagent (0.058 g, 0.24 mmol) was added to a stirred solution of **24** (0.021 g, 0.082 mmol) in toluene (3 mL) at 80 $^\circ\text{C}$. After 15 min., the reaction was cooled to room temperature, water (10 mL) was added, and the resulting mixture was stirred for 5 min. The layers were separated and the mixture was extracted with dichloromethane (3 \times 10 mL). The organic extracts were combined and washed with brine (10 mL), dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (12 \times 1.3 cm, 1:1 dichloromethane/hexanes) to afford **25** as a white solid (0.017 g, 60%).

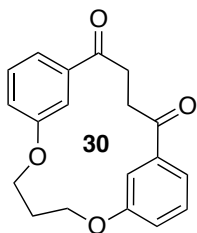


1,6-dioxo[6](3,3'')m-Terphenylophane (28): *para*-Toluenesulfonic acid monohydrate (0.033 g, 0.17 mmol) was added to a stirred 70 °C of **25** (0.011 g, 0.035 mmol) in toluene (2 mL). After 12 h, a saturated solution of NaHCO₃ (10 mL) was added to the reaction. The layers were separated and the aqueous phase was extracted with dichloromethane (3 × 5 mL). The organic extracts were combined and washed with brine (10 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography (7 × 0.5 cm, 1:1 dichloromethane/hexanes) to afford **28** as a white solid (0.060 g, 55%): *R_f* = 0.31 (5% EtOAc/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 8.33-8.27 (m, 1H), 7.66 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.52-7.45 (m, 1H), 7.40-7.34 (m, 4H), 7.34-7.30 (m, 2H), 6.95-6.89 (m, 2H), 4.36-4.22 (m, 4H), 2.08 (t, *J* = 4.2 Hz, 4H); ¹³C NMR (151 MHz, CDCl₃) δ 158.73, 141.71, 140.49, 131.38, 130.47, 129.34, 124.04, 117.44, 116.85, 114.30, 69.01, 24.25; HRMS (EI) calculated for C₂₂H₂₁O₂ (M⁺) *m/z* = 316.1463, found 316.1442.



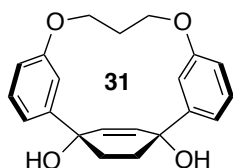
Dialdehyde 29: 1,3-Dibromopropane (2.76 g, 13.6 mmol) was added to a stirred solution of 3-hydroxybenzaldehyde (5.00 g, 40.9 mmol), K₂CO₃ (6.50 g, 47.1 mmol) and TBAI (0.375 g, 1.01 mmol) in DMF (75 mL). The reaction was heated at 70 °C for 15 h, at which point water (100 mL) and 1 M HCl (50 mL) were added sequentially. The resulting mixture was extracted with ethyl acetate (3 × 50 mL). The organic extracts

were combined and washed with saturated solution of NaHCO₃ (100 mL) and brine (100 mL), dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified via flash chromatography (16 cm × 5.0 cm; dichloromethane, and 2% acetone/dichloromethane) to afford **2** as colorless oil. (2.80 g, 72%): *R_f* = 0.27 (dichloromethane); ¹H NMR (400 MHz, CDCl₃) δ 9.80 (s, 2H), 7.30-7.28 (m, 4H), 7.25-7.23 (m, 2H), 7.06-6.98 (m, 2H), 4.07 (t, *J* = 6.1 Hz, 4H), 2.15 (p, *J* = 6.1 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 192.17, 159.44, 137.88, 130.19, 123.70, 121.97, 112.82, 64.60, 29.14; HRMS (ESI) calculated for C₁₇H₁₇O₄ ([M+H]⁺) *m/z* = 285.1127, found 285.1124.



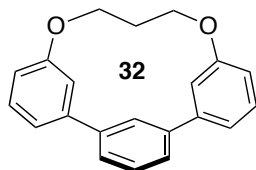
Streamlined synthesis of macrocyclic diketone 30: Vinylmagnesium chloride (1.6 M in THF, 2.5 mL, 4.0 mmol) was added to a stirred 0 °C solution of dialdehyde **2** (0.500 g, 1.76 mmol) in THF (10 mL). After 30 min, the reaction mixture was poured into water (50 mL) and further diluted with 1 M HCl (30 mL). The resulting mixture was

extracted with dichloromethane (3 × 15 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (30 mL) and brine (30 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The pale yellow residue was dissolved in dichloromethane (150 mL), stirred and heated to 40 °C, followed by the addition of Hoveyda-Grubbs second-generation catalyst (0.040 g, 0.060 mmol). After 2 h, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was dissolved in 1:9 methanol/dichloromethane (15 mL) and sodium borohydride (0.230 g, 5.88 mmol) was added. After 1 h, the reaction mixture was poured into water (100 mL) and the layers were separated. The aqueous phase was extracted with dichloromethane (2 × 20 mL) and the combined organic extracts were washed with water (20 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was dissolved in dichloromethane (20 mL), followed by the sequential addition of NaHCO₃ (0.270 g, 3.21 mmol) and Dess-Martin periodinane (1.45 g, 3.20 mmol). After 2 h, a 10% aqueous solution of Na₂S₂O₃ (50 mL) was added and stirring was continued for 10 min. The resulting mixture was extracted with dichloromethane (3 × 20 mL). The organic extracts were combined and washed with water (50 mL) and brine (50 mL), dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified via flash chromatography (15 cm × 2.5 cm; 3:7 ethyl acetate/hexane) to give 1,4-diketone **30** as a beige solid (0.120 g, 22%, over 4 steps): *R*_f = 0.38 (2:3 ethyl acetate/hexane); ¹H NMR (600 MHz, CDCl₃) δ 7.42 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.36-7.29 (m, 2H), 7.24-7.20 (m, 2H), 7.10 (ddd, *J* = 8.1, 2.6, 1.0 Hz, 2H), 4.34 (t, *J* = 6.1 Hz, 4H), 3.11 (s, 4H), 2.19 (p, *J* = 6.1 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 200.85, 159.14, 138.03, 130.43, 121.57, 121.39, 117.10, 66.38, 36.42, 29.09.



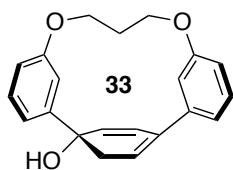
Cyclohex-2-ene-1,4-diol 31: Vinylmagnesium chloride (1.6 M in THF, 0.45 mL, 0.70 mmol) was added to a stirred solution of 1,4-diketone **30** (0.100 g, 0.322 mmol), in THF (4 mL) at 65 °C. After 30 min., the reaction mixture was cooled to room temperature, poured into water (20 mL), and further diluted with 1 M HCl (10 mL). The resulting mixture was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (30 mL) and brine (30 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The pale yellow residue was dissolved in dichloromethane (10 mL), the Grubbs second-generation catalyst (0.007g, 0.008 mmol) was added, and the reaction was heated to 40 °C. After 2 h, the reaction was cooled to room temperature and the solvent was removed

under reduced pressure. The brown residue was purified by flash chromatography (15 × 1.3 cm, 3:2 EtOAc/hexane) to give compound **37** as an off-white solid (0.065 g, 60%); R_f = 0.41 (7:3 EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.30 (m, 4H), 7.03-6.99 (m, 2H), 6.92-6.84 (m, 2H), 6.14 (s, 2H), 4.46-4.30 (m, 2H), 4.29-4.23 (m, 2H), 2.29-2.08 (m, 6H), 1.84-1.71 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.88, 146.95, 142.95, 129.36, 119.04, 115.62, 114.07, 113.62, 76.93, 65.44, 37.24, 27.78; HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{21}\text{O}_3([\text{M}-(\text{H}_2\text{O})+\text{H}]^+)$ m/z = 321.1491, found 321.1493.



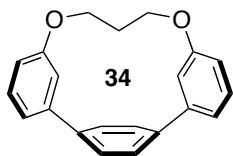
1,5-dioxolane[5](3,3'')m-Terphenylphane (32): *para*-Toluenesulfonic acid monohydrate (0.060 g, 0.31 mmol) was added to a stirred 60 °C of **31** (0.012 g, 0.038 mmol) in toluene (2.5 mL). After 3 h, the reaction was heated to 70 °C for an

additional 1 h, followed by the addition of a saturated solution of NaHCO_3 (10 mL). The layers were separated and the aqueous phase was extracted with dichloromethane (3 × 5 mL). The organic extracts were combined and washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (7 × 0.5 cm, 1:1 dichloromethane/hexanes) to afford **32** as a white solid (0.004 g, 40%); R_f = 0.41 (2:3 dichloromethane/hexanes); ^1H NMR (600 MHz, CDCl_3) δ 7.62 (dd, J = 7.5, 2.0 Hz, 2H), 7.50 (d, J = 2.1 Hz, 1H), 7.46-7.40 (m, 1H), 7.35-7.29 (m, 2H), 7.28 (s, 1H), 7.07-7.02 (m, 2H), 6.92 (dd, J = 8.2, 2.8 Hz, 2H), 4.36-4.19 (m, 4H), 2.65 (s, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 157.24, 144.91, 142.84, 142.64, 129.70, 127.63, 123.74, 118.28, 117.98, 116.15, 64.23, 24.77; HRMS (EI) calculated for $\text{C}_{21}\text{H}_{18}\text{O}_2 (\text{M}^+)$ m/z = 302.1307, found 302.1336.



Tin(II) chloride dihydrate (0.053 g, 0.230 mmol) was added to a stirred solution of **31** (0.008 g, 0.023 mmol) in 1:1 THF/PhMe (4 mL) at 80 °C. After 12 h, the reaction was cooled to room temperature and 3 M NaOH (5 mL) was added, followed by dichloromethane (10 mL). The layers were separated and the aqueous phase was extracted with dichloromethane (3 × 5 mL). The combined organic extracts was washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The off-white residue was purified by flash chromatography (4.0 × 0.7 cm, dichloromethane to 2% acetone/dichloromethane) to give compound **33** as colorless solid (0.006 g, 78%); R_f = 0.41 (1% acetone/dichloromethane); ^1H NMR (600 MHz, CDCl_3) δ 7.41 (dd, J = 2.5, 1.7 Hz, 1H), 7.34-7.24 (m, 2H), 7.22-7.15 (m, 1H), 6.91 (ddd, J = 7.8, 2.6, 1.2 Hz, 1H), 6.84 – 6.80 (m, 1H), 6.79-6.72 (m, 2H), 6.36 (dd, J = 9.6, 0.9 Hz, 1H), 6.12 (dt, J = 9.6, 1.3 Hz, 1H), 5.66 (ddd, J = 7.0, 2.8, 1.4 Hz, 1H), 4.52-4.40 (m, 1H), 4.41-4.15 (m, 3H), 2.97-2.84 (m, 1H), 2.71 (ddd,

$J = 16.0, 7.0, 1.9$ Hz, 1H), 2.16 (s, 1H), 2.06-1.91 (m, 1H), 1.88-1.76 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 156.98, 156.95, 145.10, 142.78, 139.09, 135.73, 130.31, 130.20, 129.11, 124.46, 120.22, 117.53, 116.56, 116.36, 116.05, 111.99, 75.50, 65.96, 64.25, 39.18, 26.69; HRMS (EI) calculated for $\text{C}_{21}\text{H}_{20}\text{O}_3$ (M^+) $m/z = 320.1412$, found 320.1410

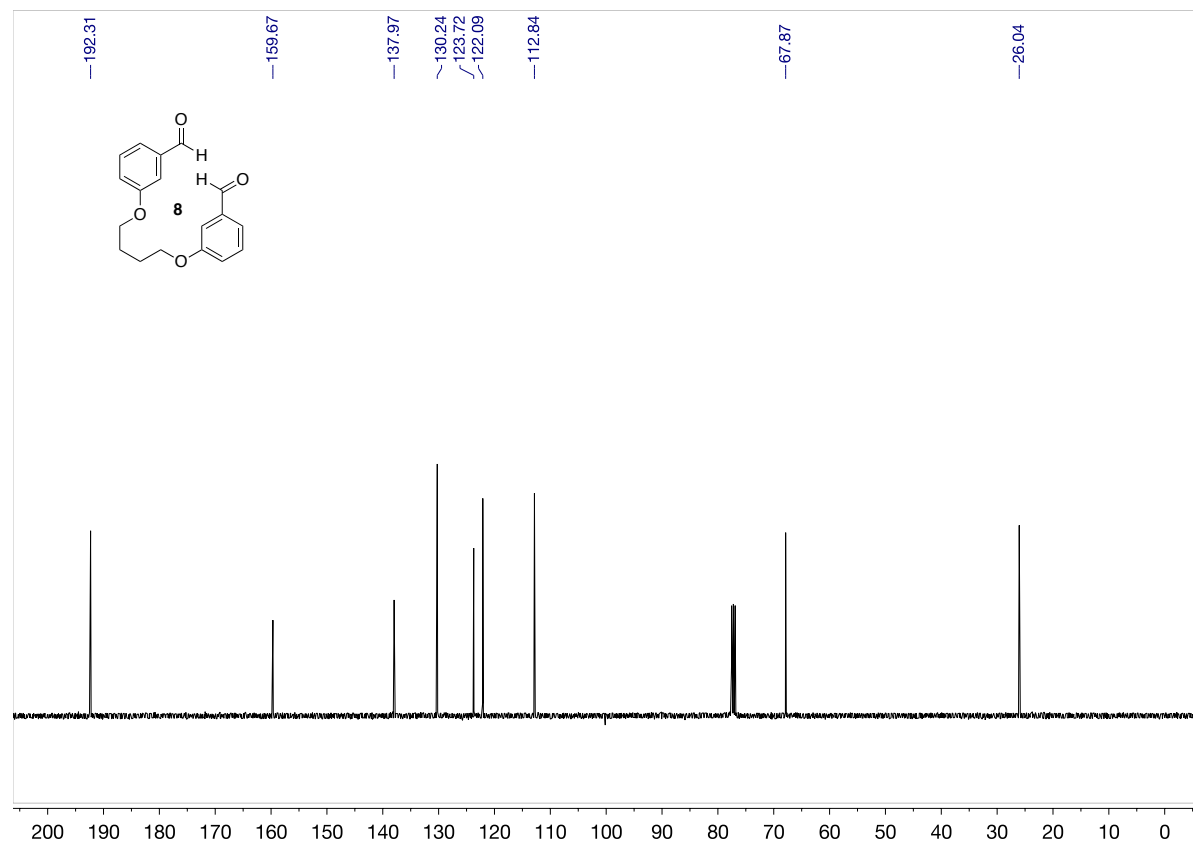
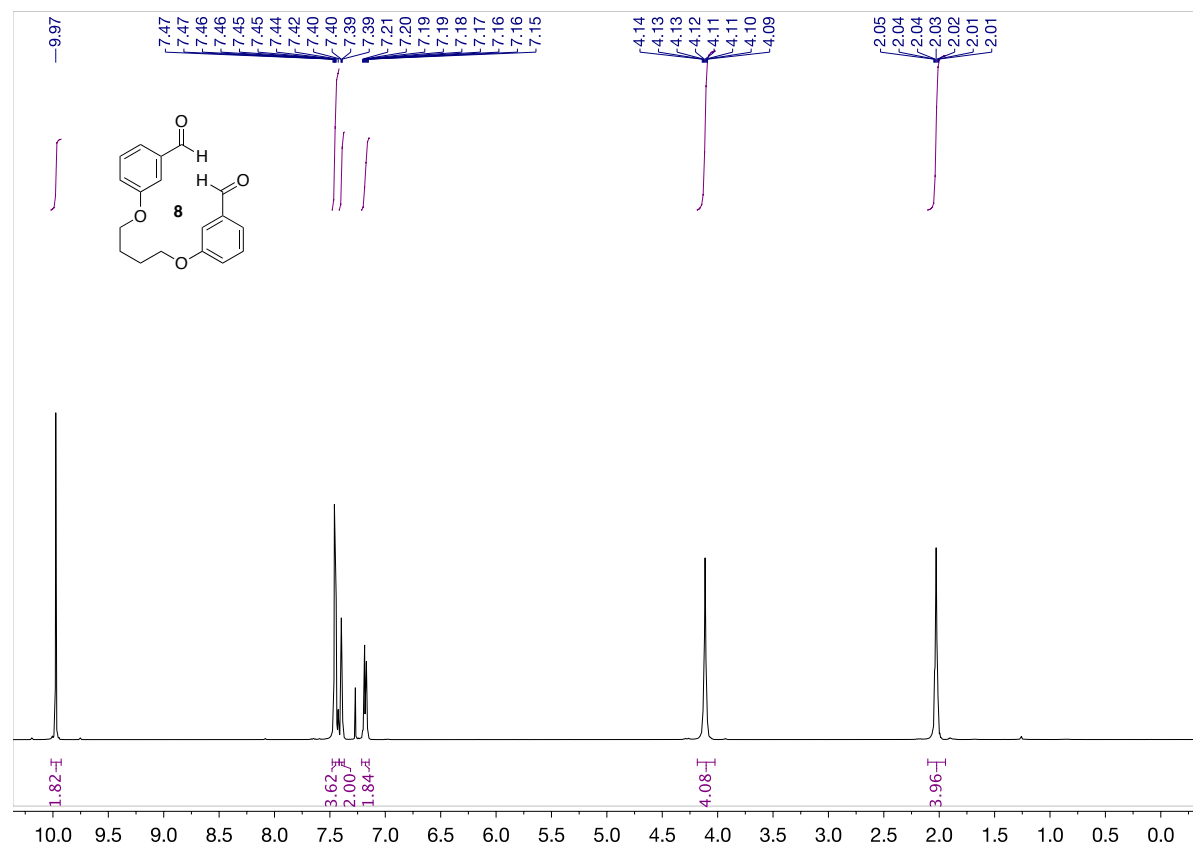


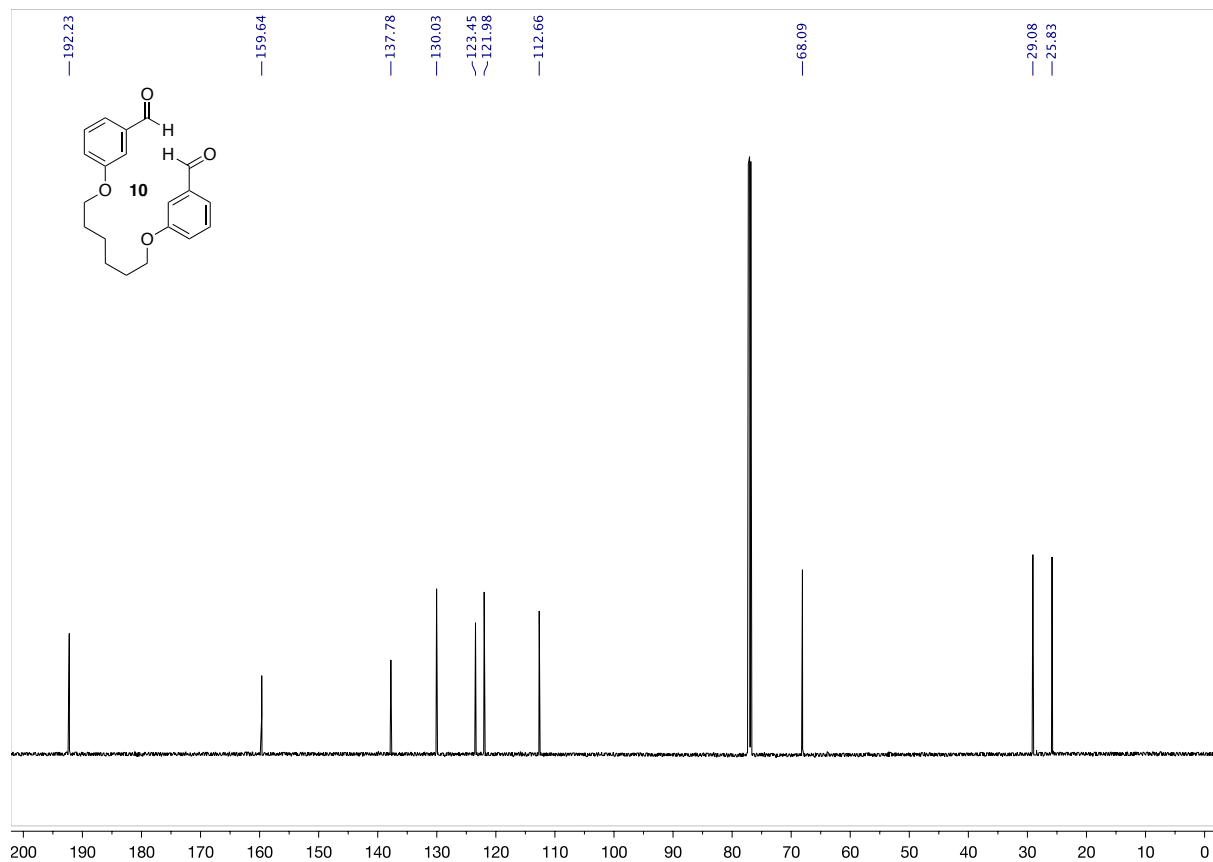
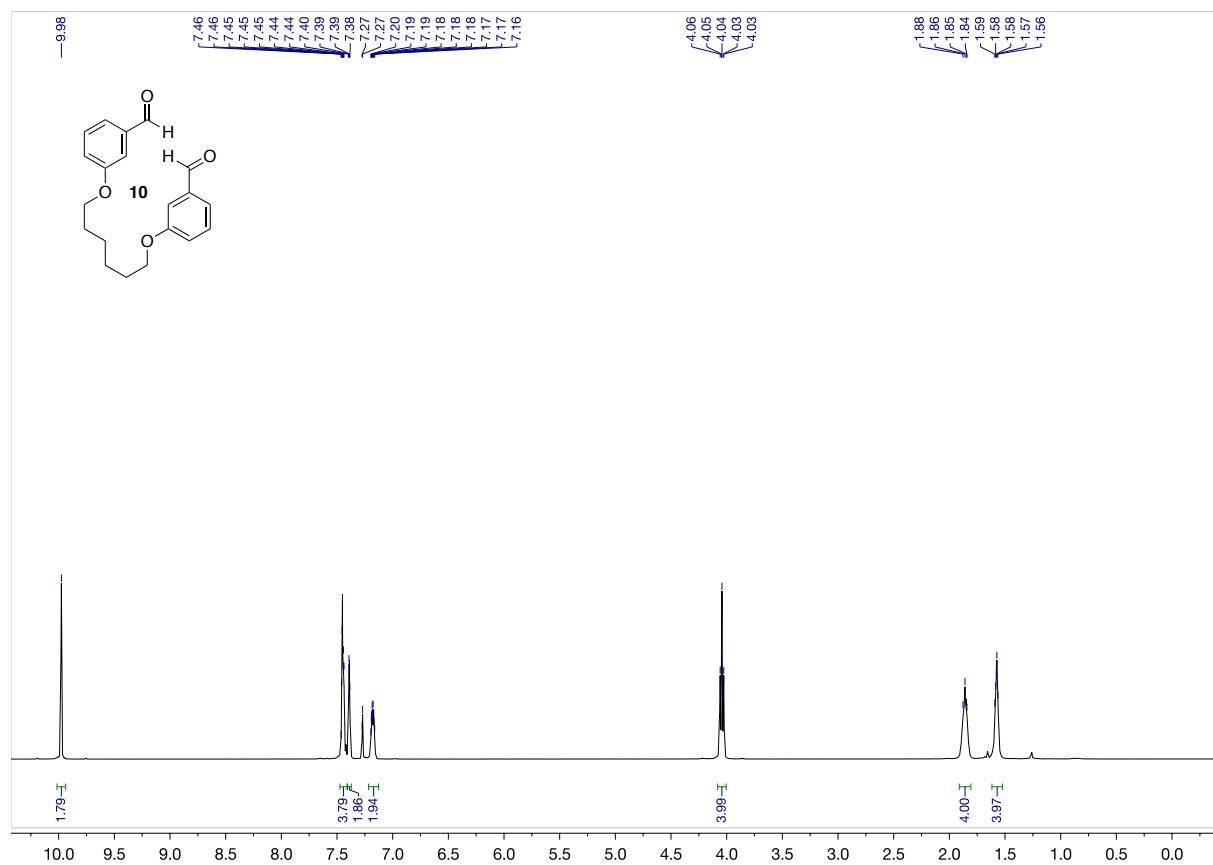
1,5-dioxo[5](3,3'')p-terphenylenophane (34) (Table 1, entry 9): Burgess reagent (0.126 g, 0.530 mmol) was added to a stirred solution of **31** (0.044 g, 0.130 mmol) in toluene (2.5 mL) at 80 °C. After 15 min., the reaction was cooled to room

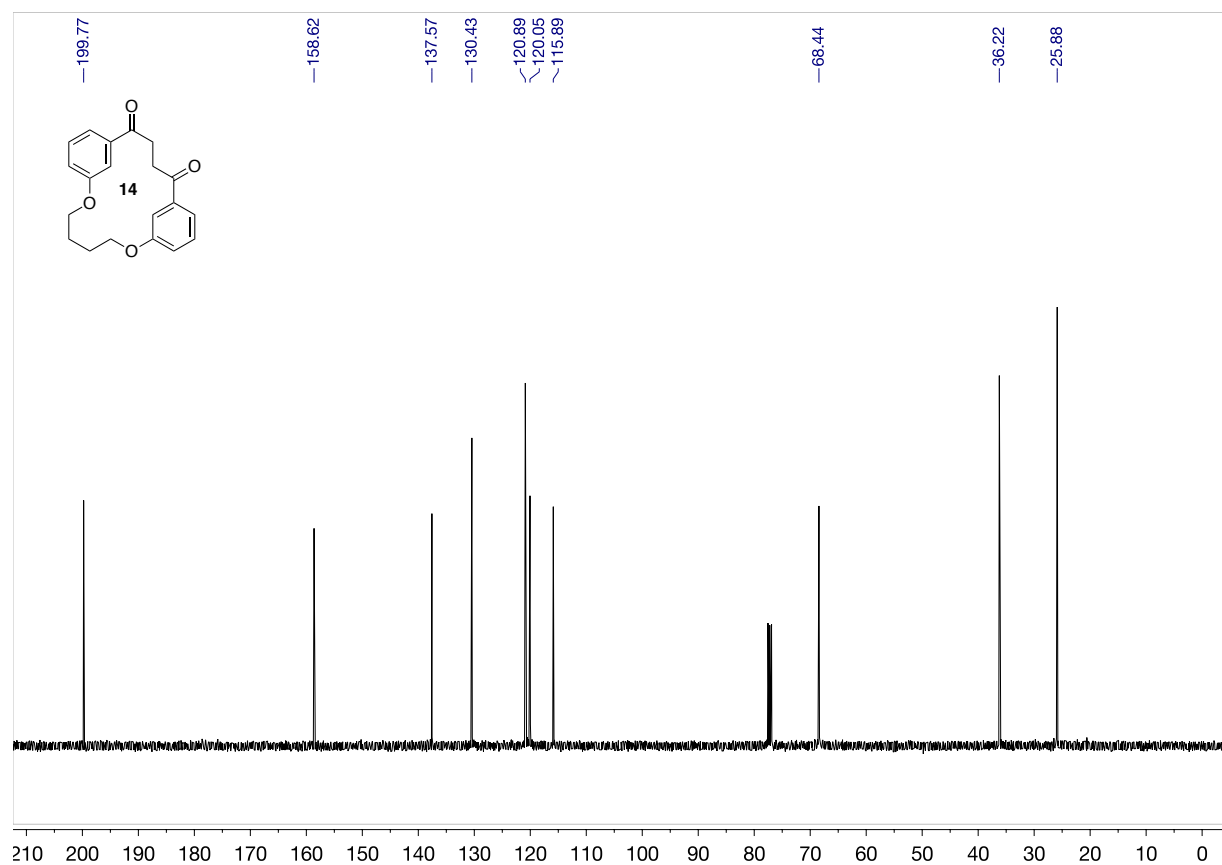
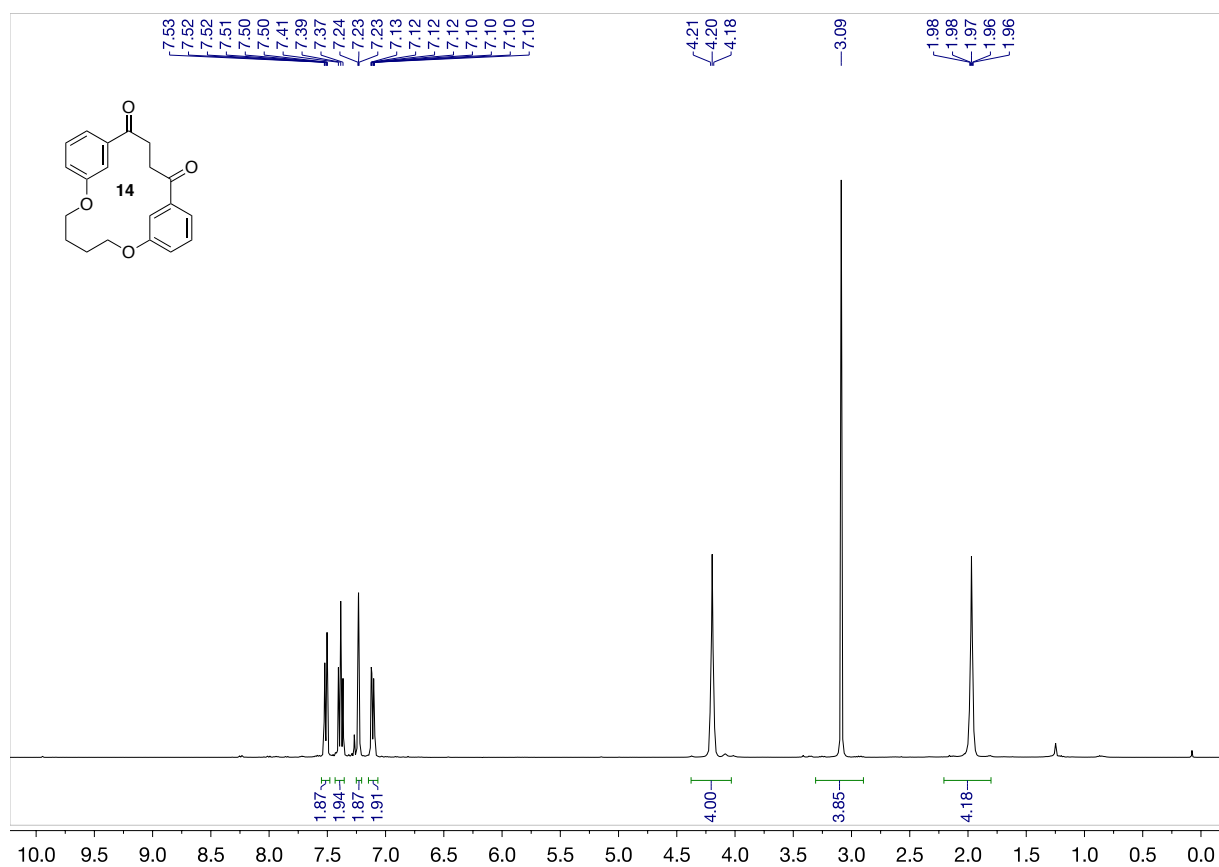
temperature, water (20 mL) was added, and the resulting mixture was stirred for 5 min. The layers were separated and the mixture was extracted with dichloromethane (3×10 mL). The organic extracts were combined and washed with brine (10 mL), dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (12 \times 1.3 cm, 1:1 dichloromethane/hexanes) to afford **34** as a white solid (0.023 g, 58%): $R_f = 0.43$ (2:3 dichloromethane/hexane); ^1H NMR (600 MHz, CDCl_3) δ 7.42 (s, 4H), 7.33-7.26 (m, 2H), 7.25-7.21 (m, 2H), 6.72 (dd, $J = 8.3, 2.8$ Hz, 2H), 5.35 (s, 2H), 4.12-3.81 (m, 4H), 1.96-1.86 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 157.25, 145.19, 145.13, 131.75, 130.53, 118.50, 115.48, 115.42, 64.67, 25.16; HRMS (EI) calculated for $\text{C}_{21}\text{H}_{18}\text{O}_2$ (M^+) $m/z = 302.1307$, found 302.1336.

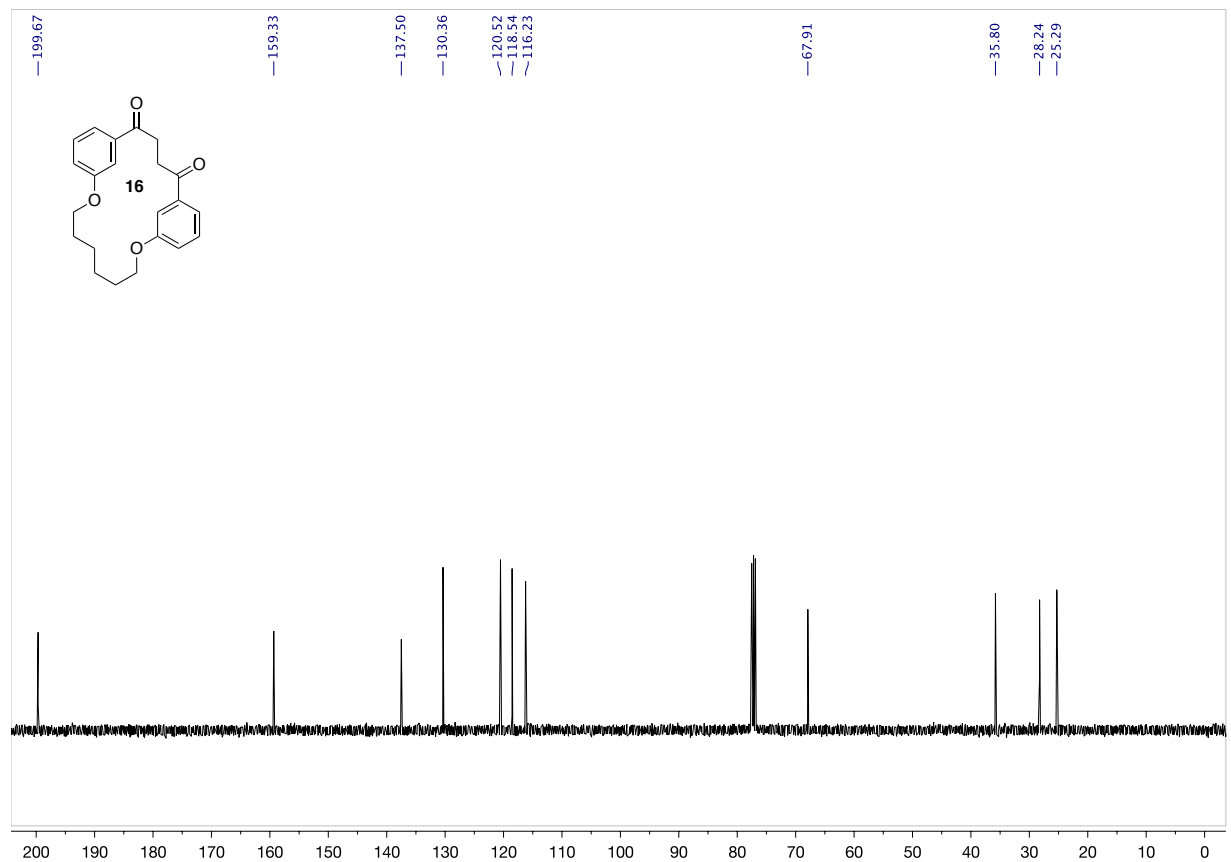
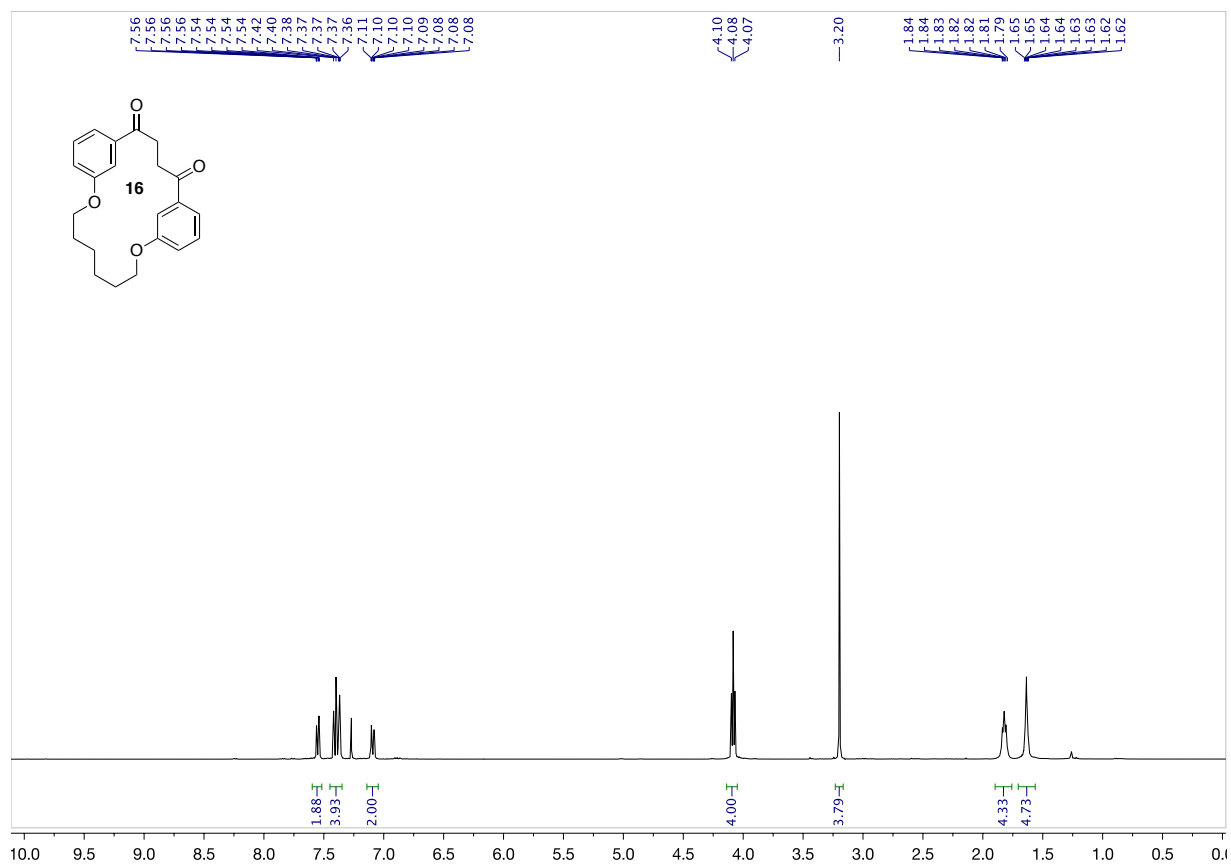
Alternate procedure for 34 (Table 1 entry 8): Trifluoromethanesulfonic anhydride 0.088 g, 0.31 mmol) and pyridine (0.5 mL) were added to a stirred solution of **33** (0.020 g, 0.062 mmol) in dichloromethane (2 mL) at 0 °C. After 30 min., the cooling bath was removed and the reaction was warmed to room temperature, poured into water (10 mL), and further diluted by 1 M HCl (5 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (2×10 mL). The combined organic extracts were washed with saturated solution of NaHCO_3 (10 mL), brine (10 mL), dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was purified by flash chromatograph (12 \times 0.5 cm, 2:3 dichloromethane/hexanes) to afford **34** as a white solid (0.003 g, 16%).

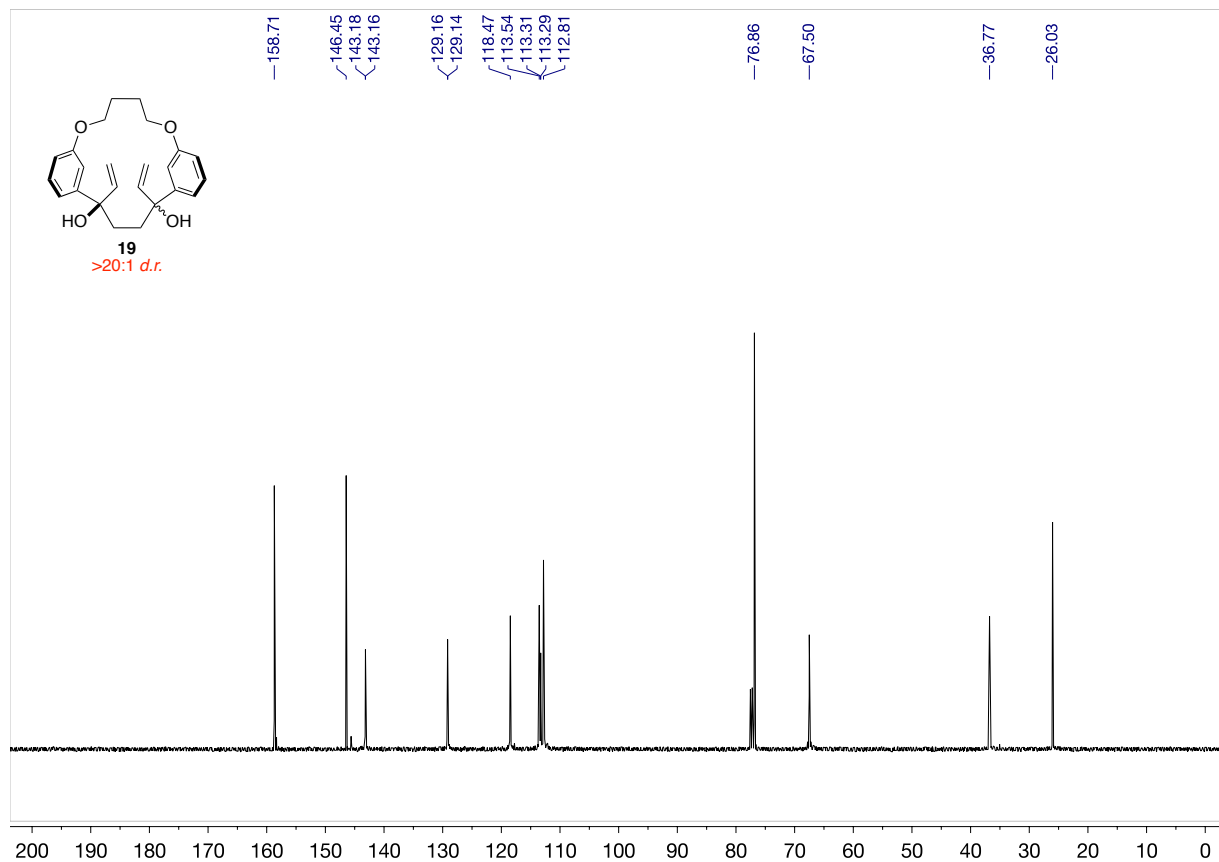
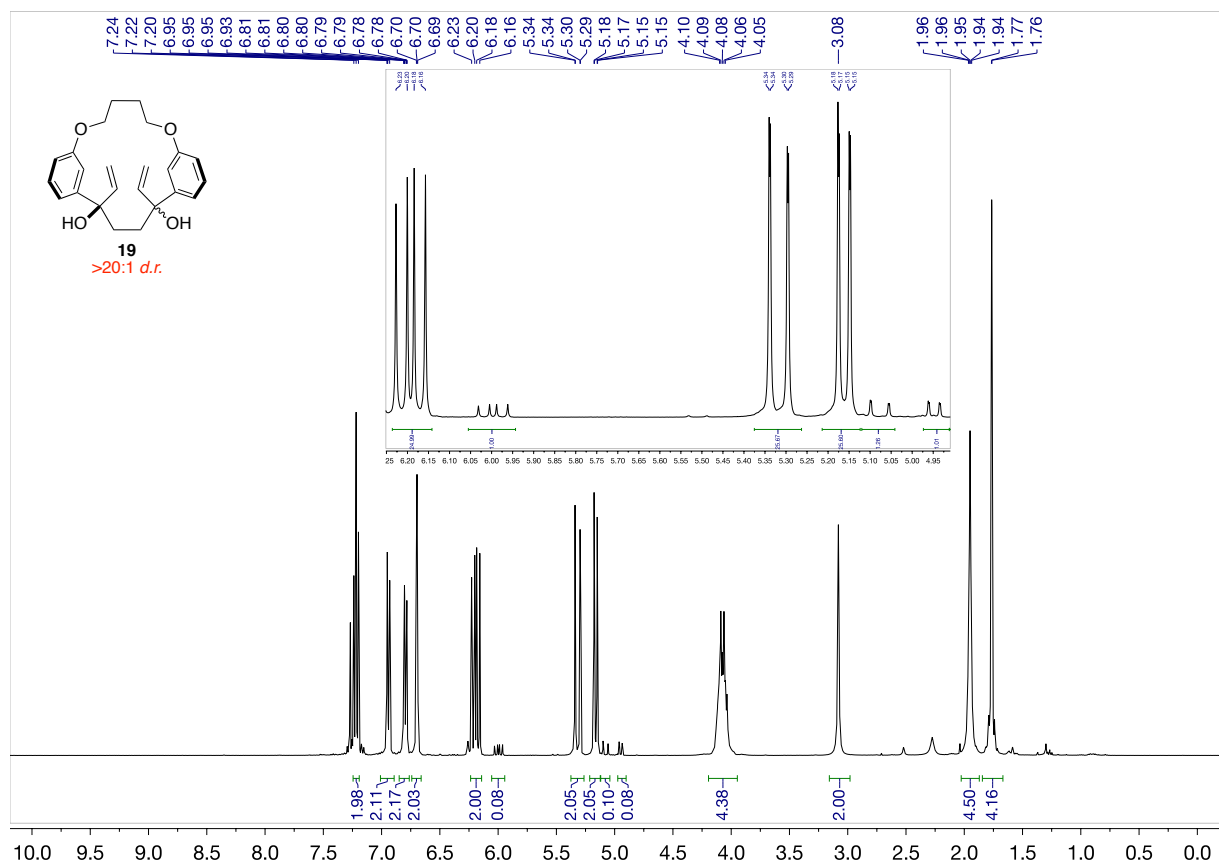
^1H and ^{13}C NMR Spectra (listed in numerical order)

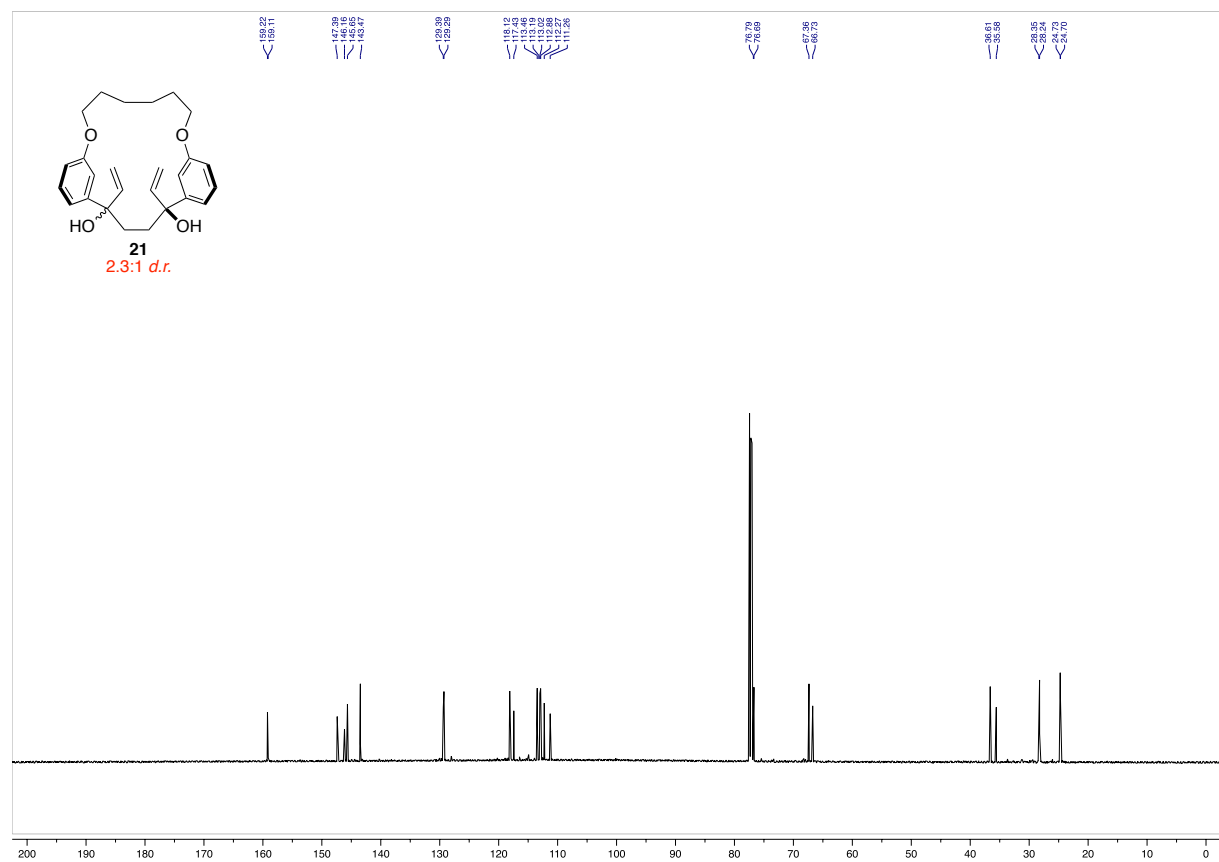
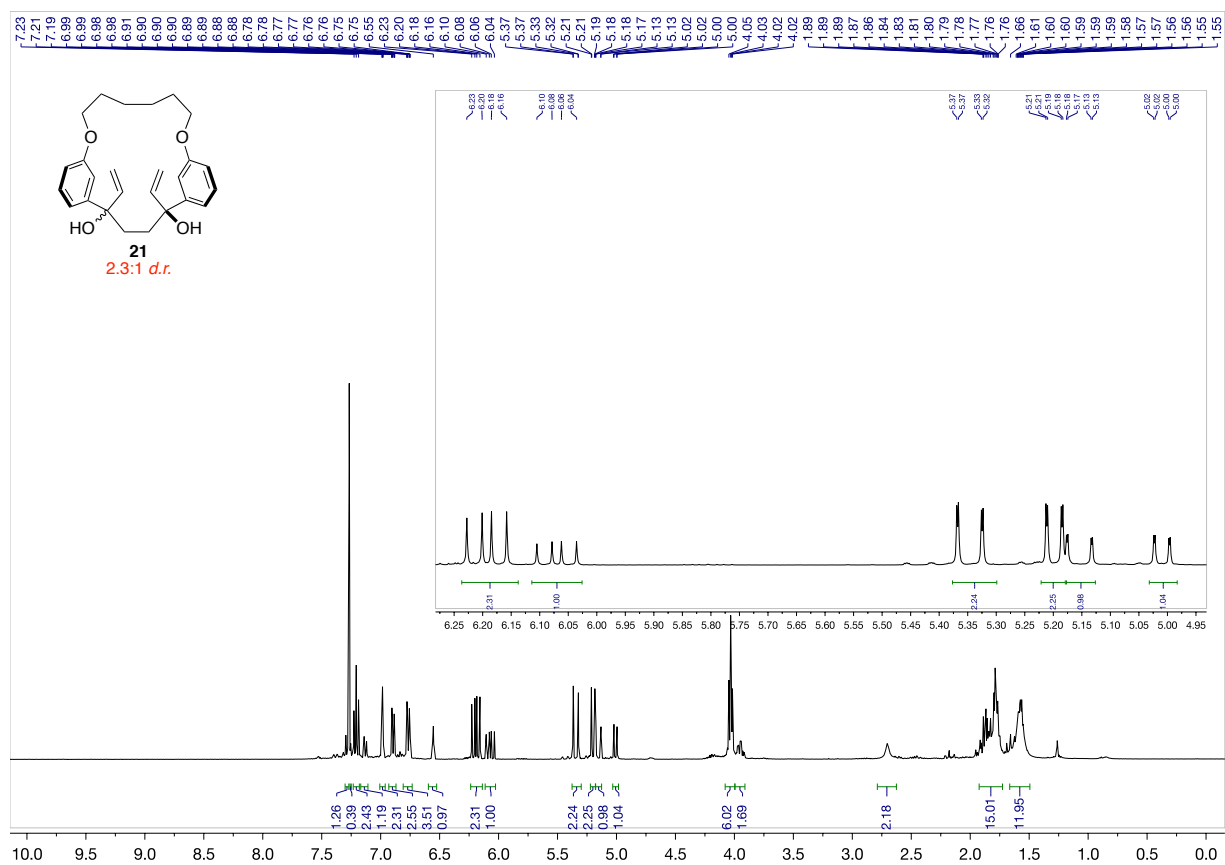


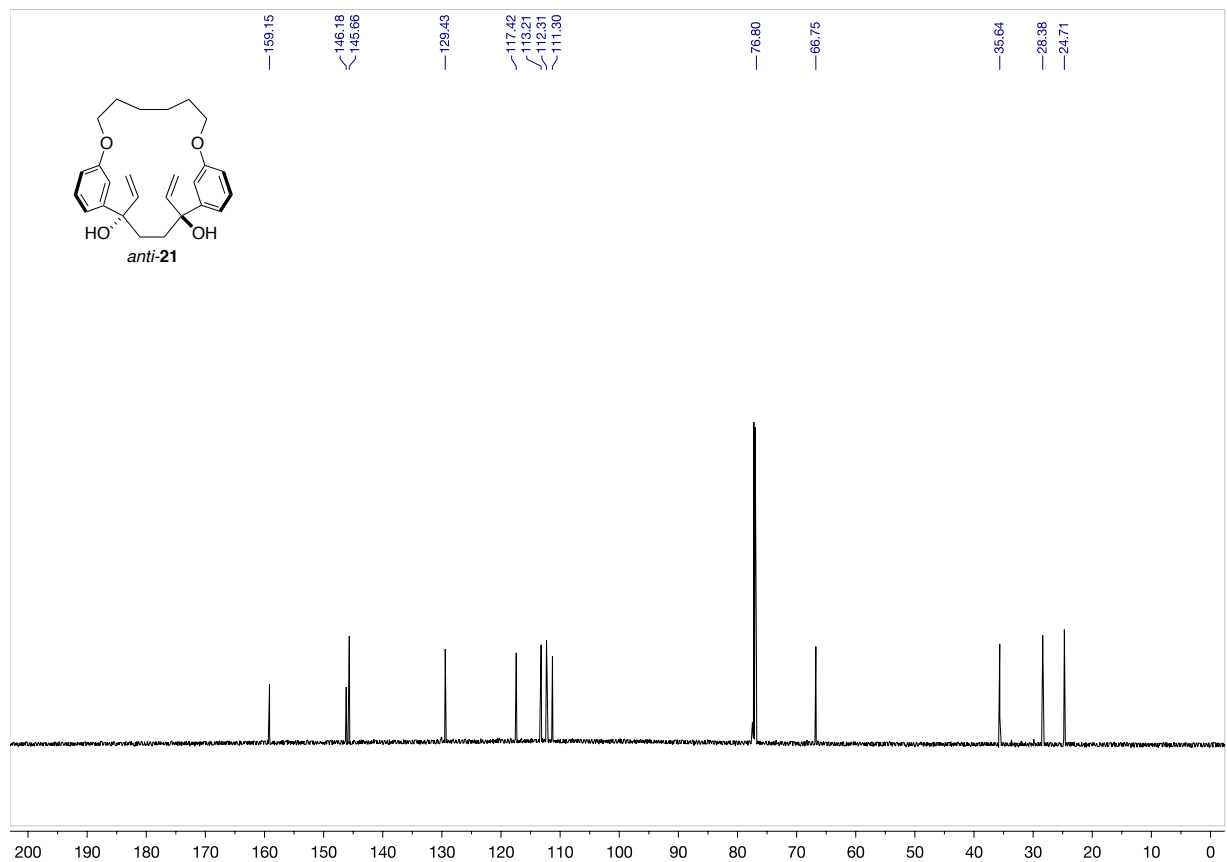
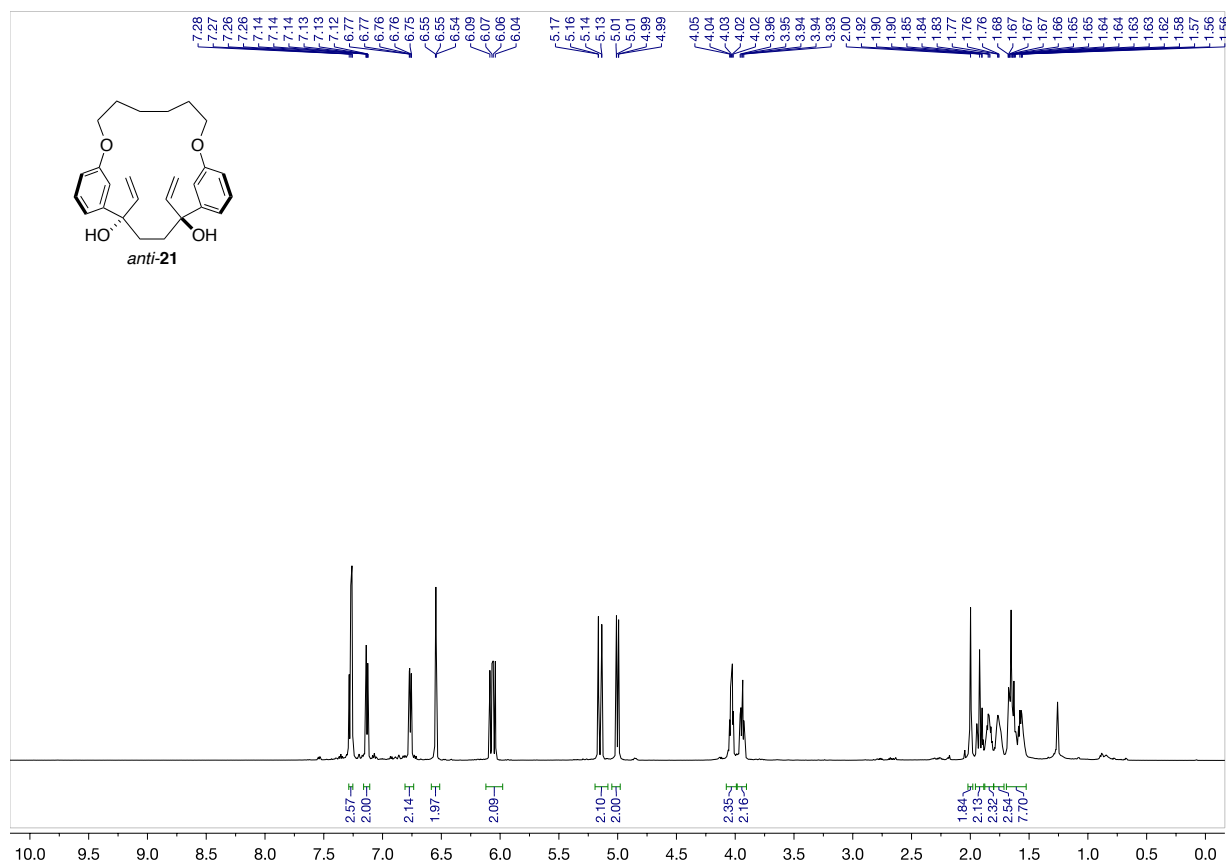


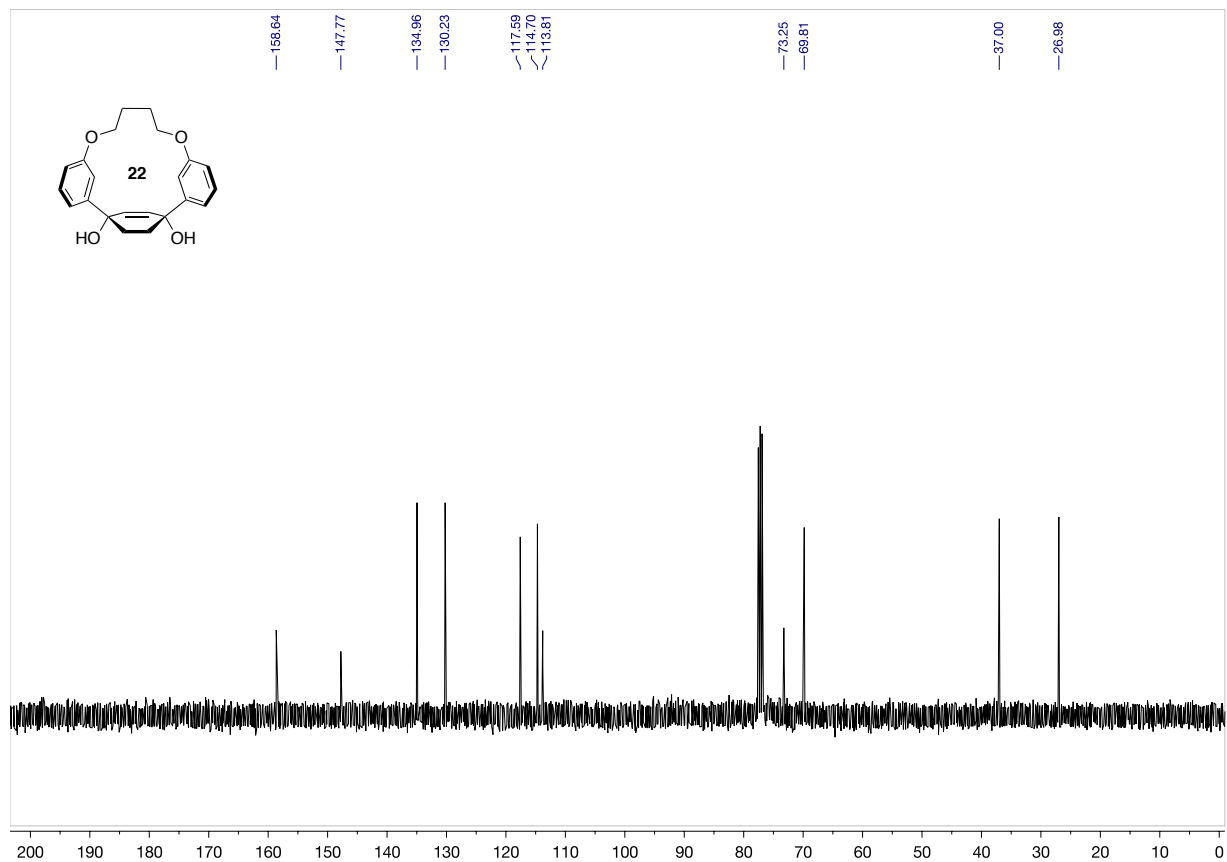
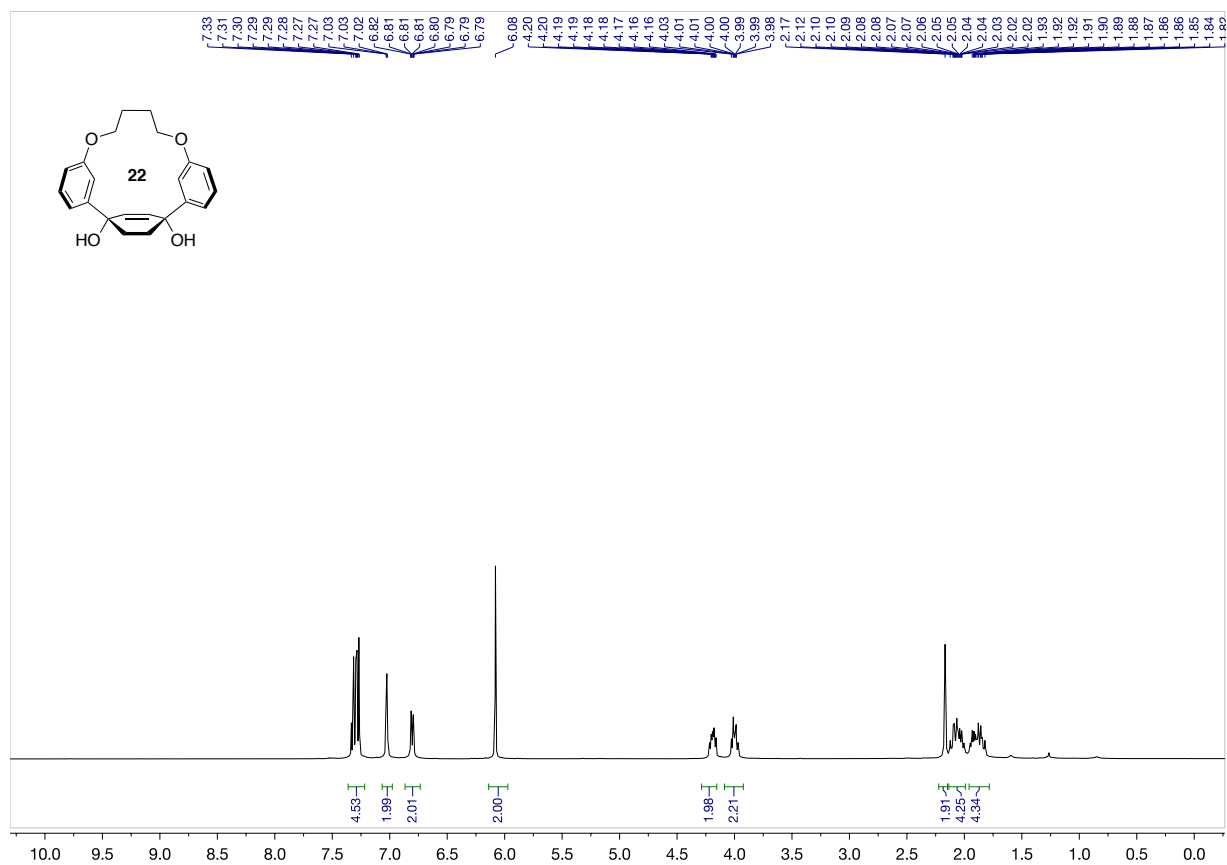


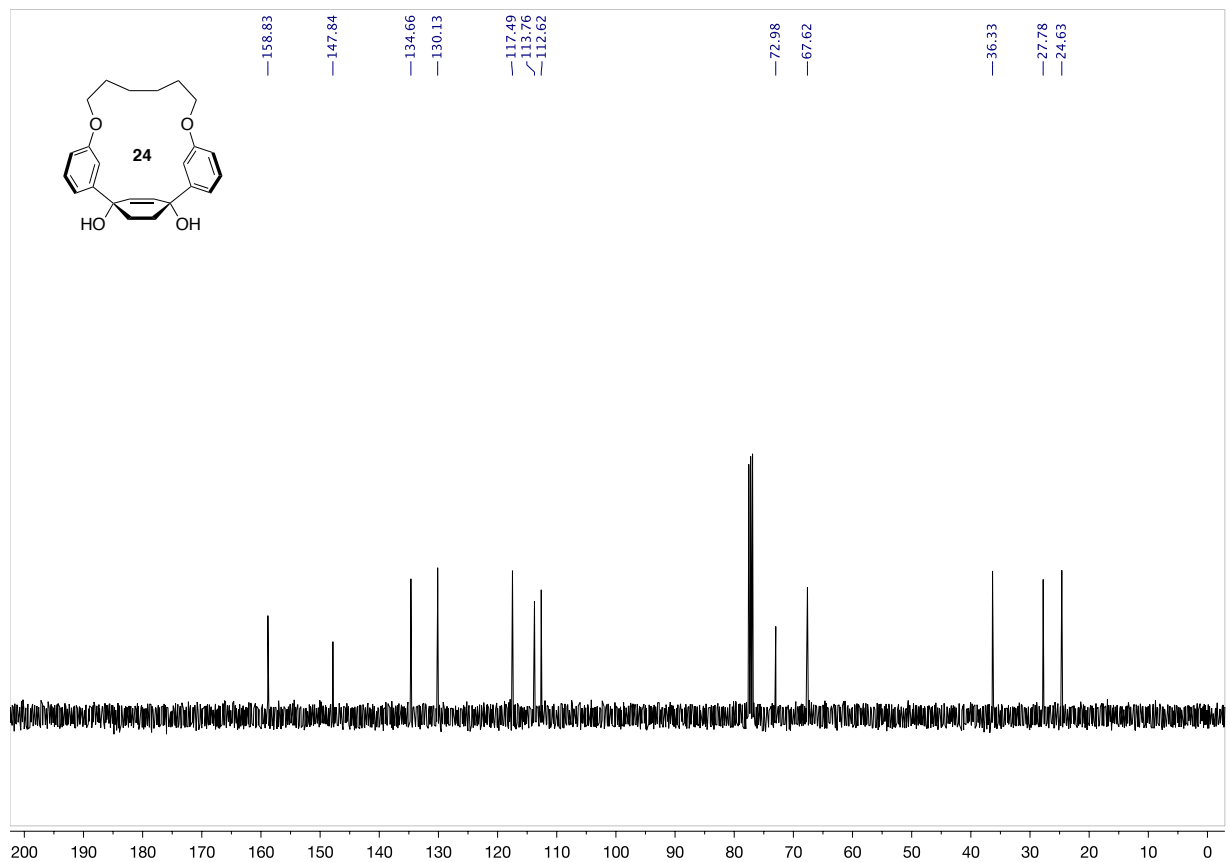
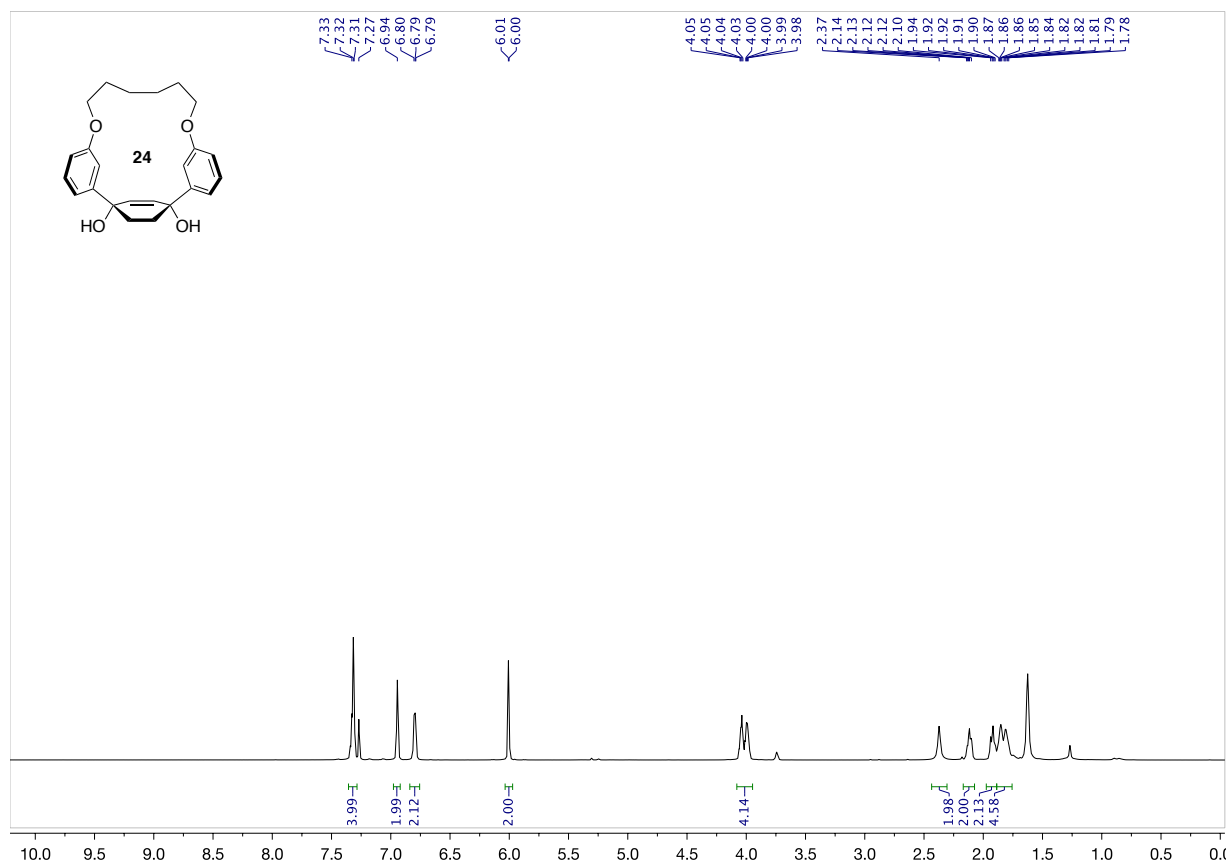


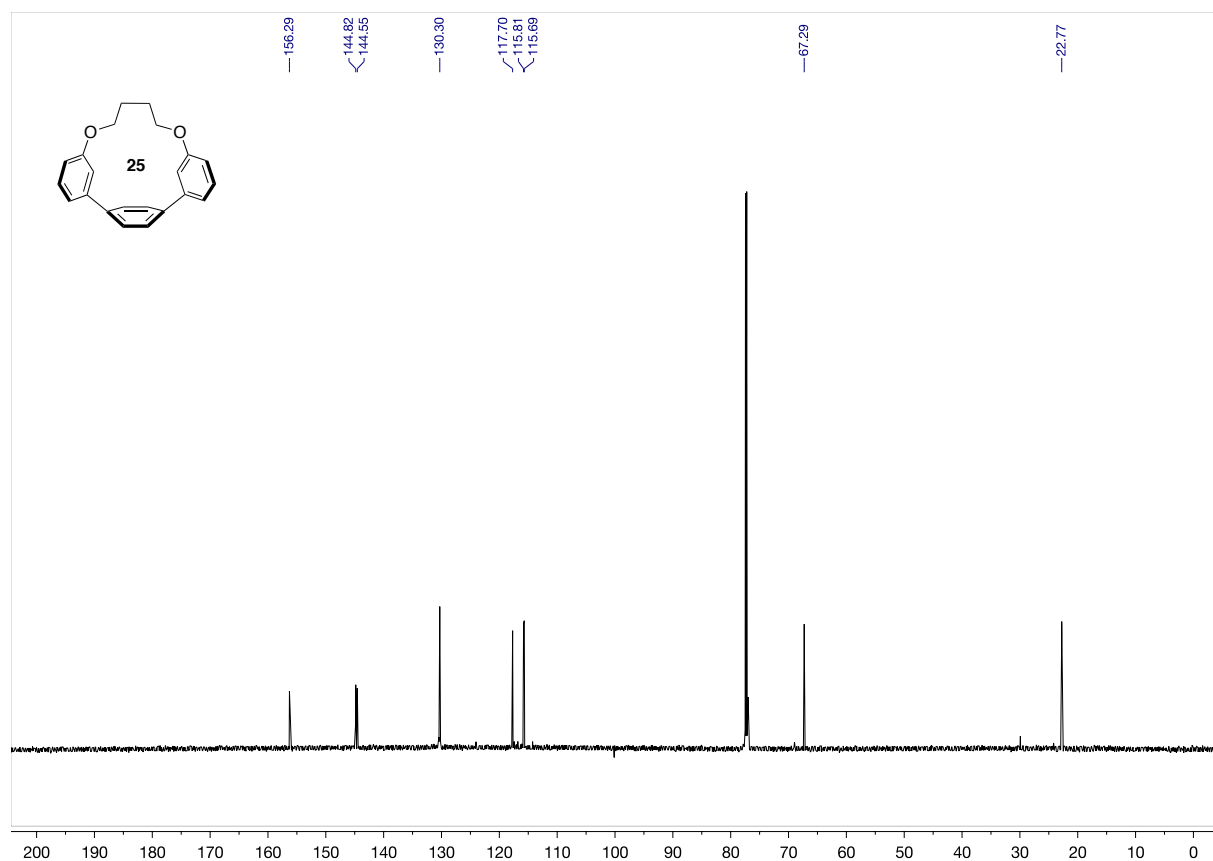
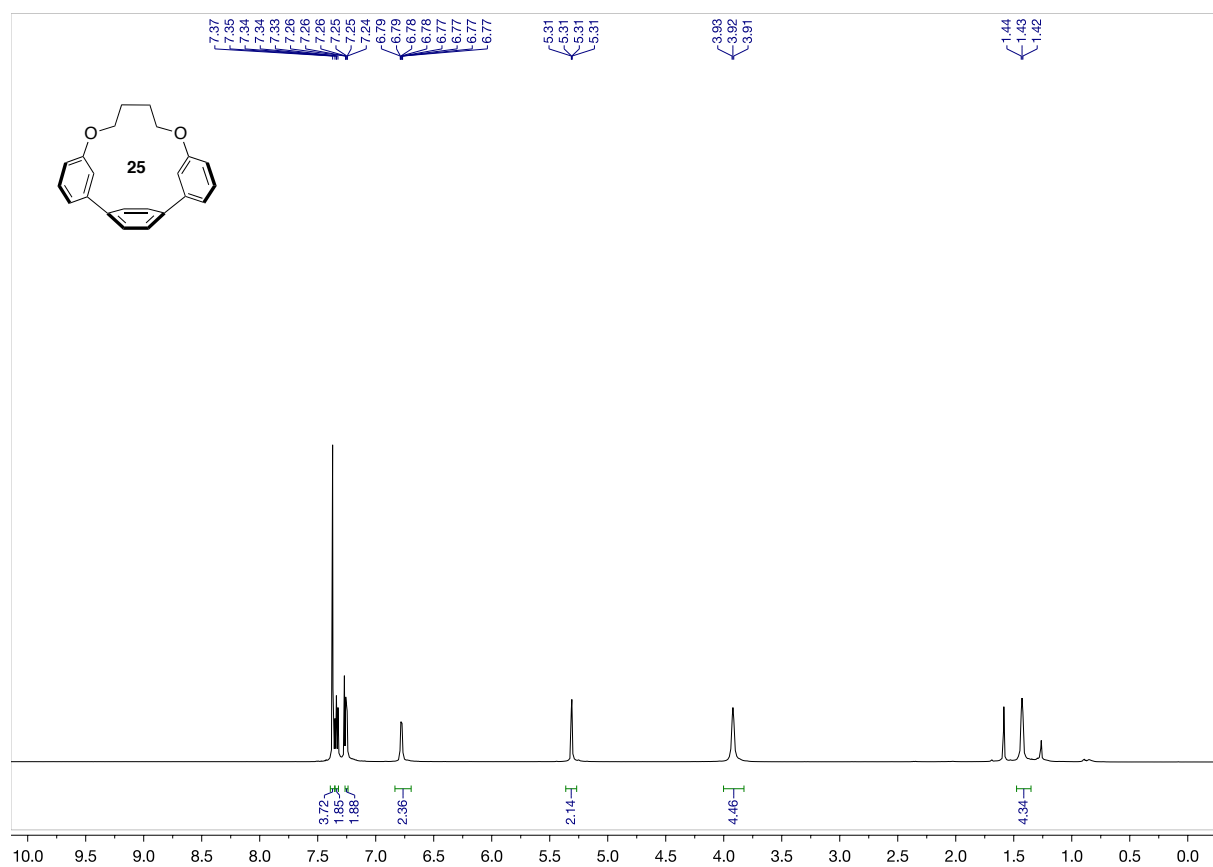


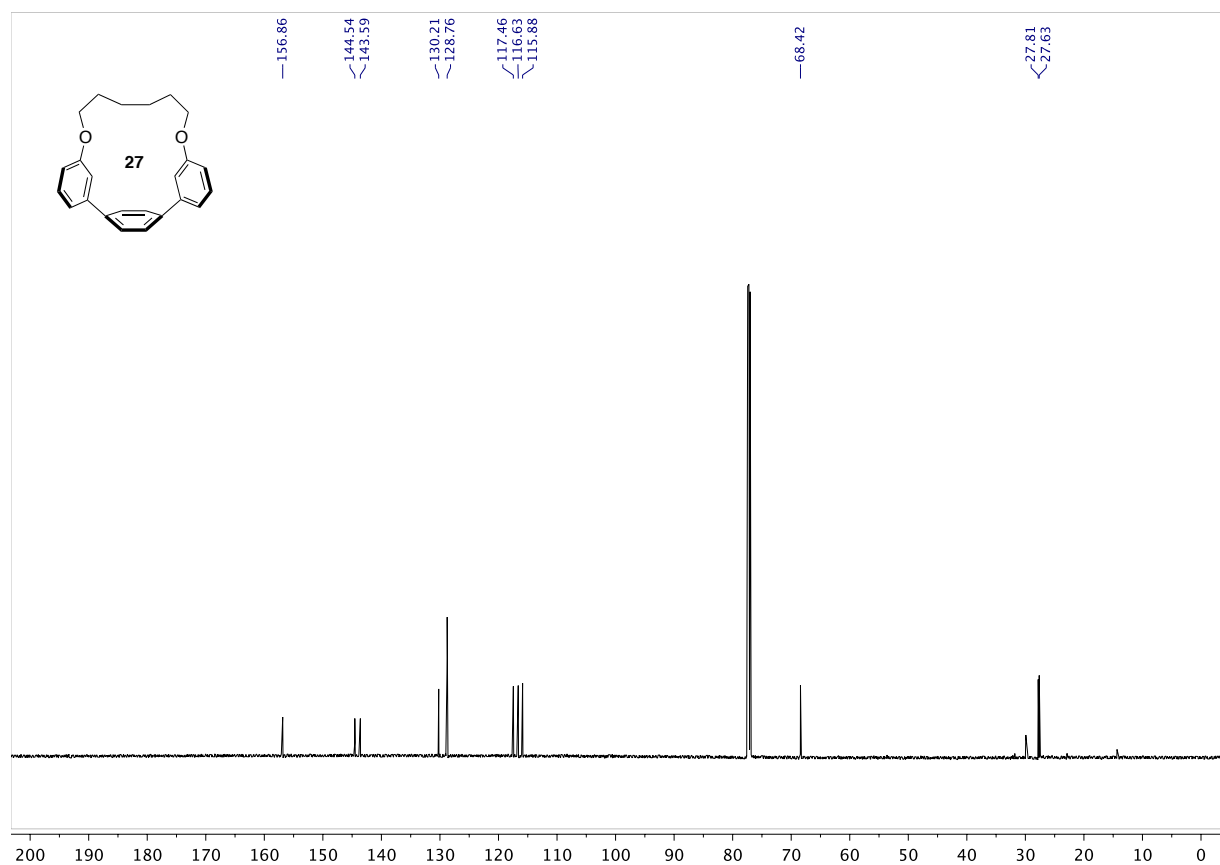
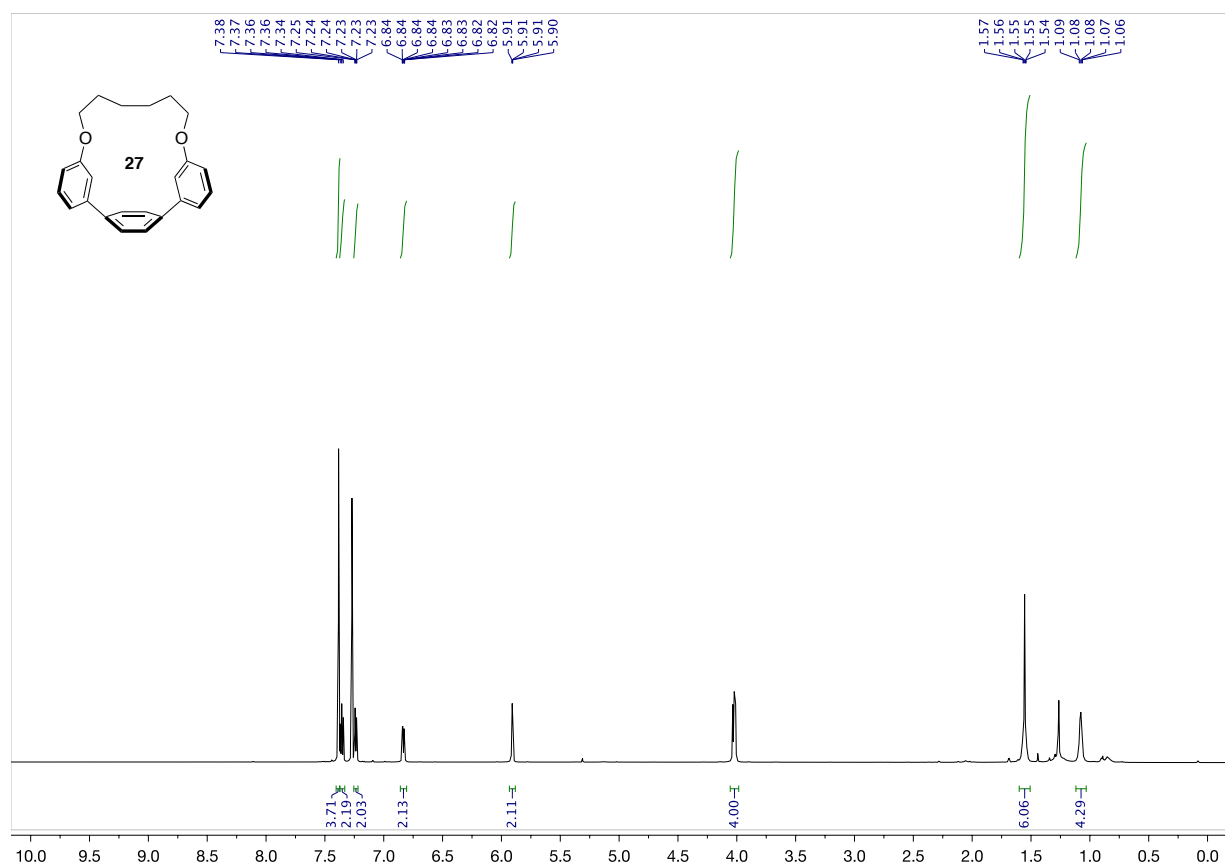


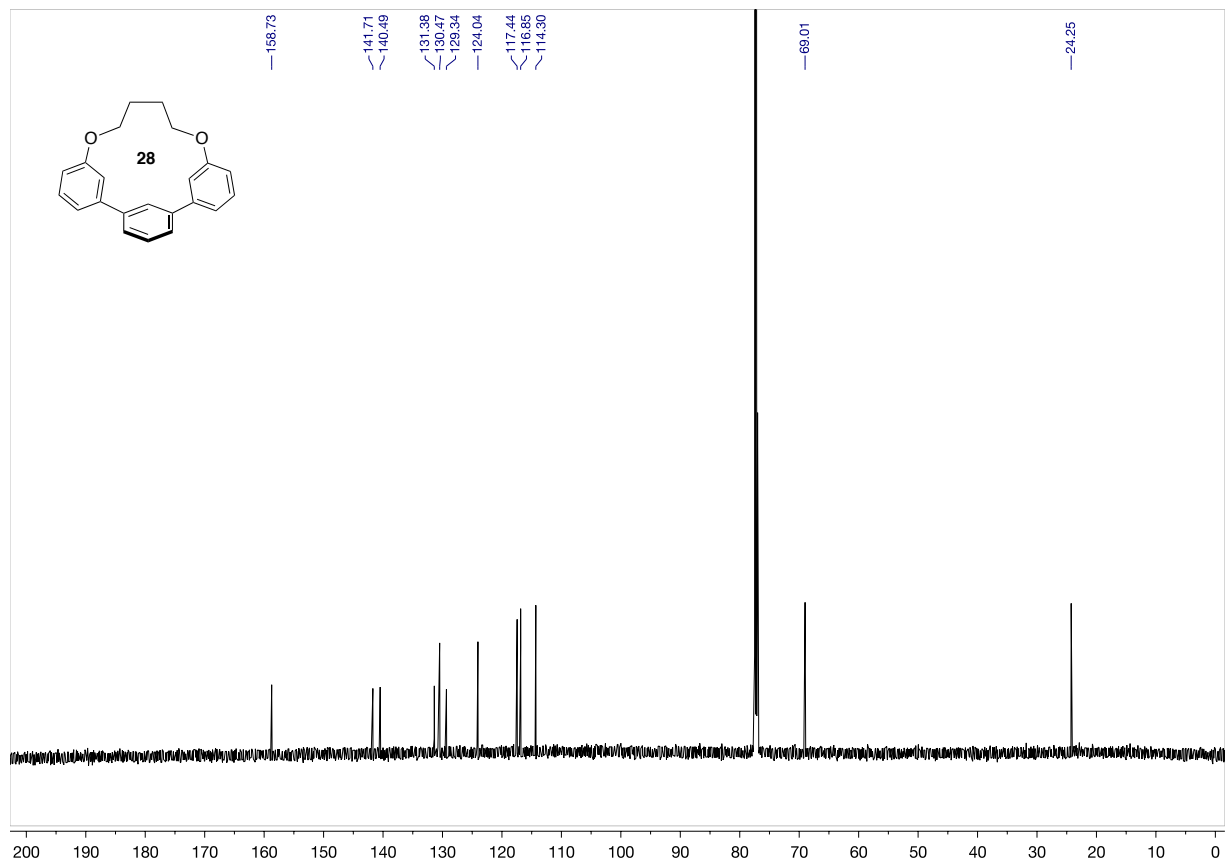
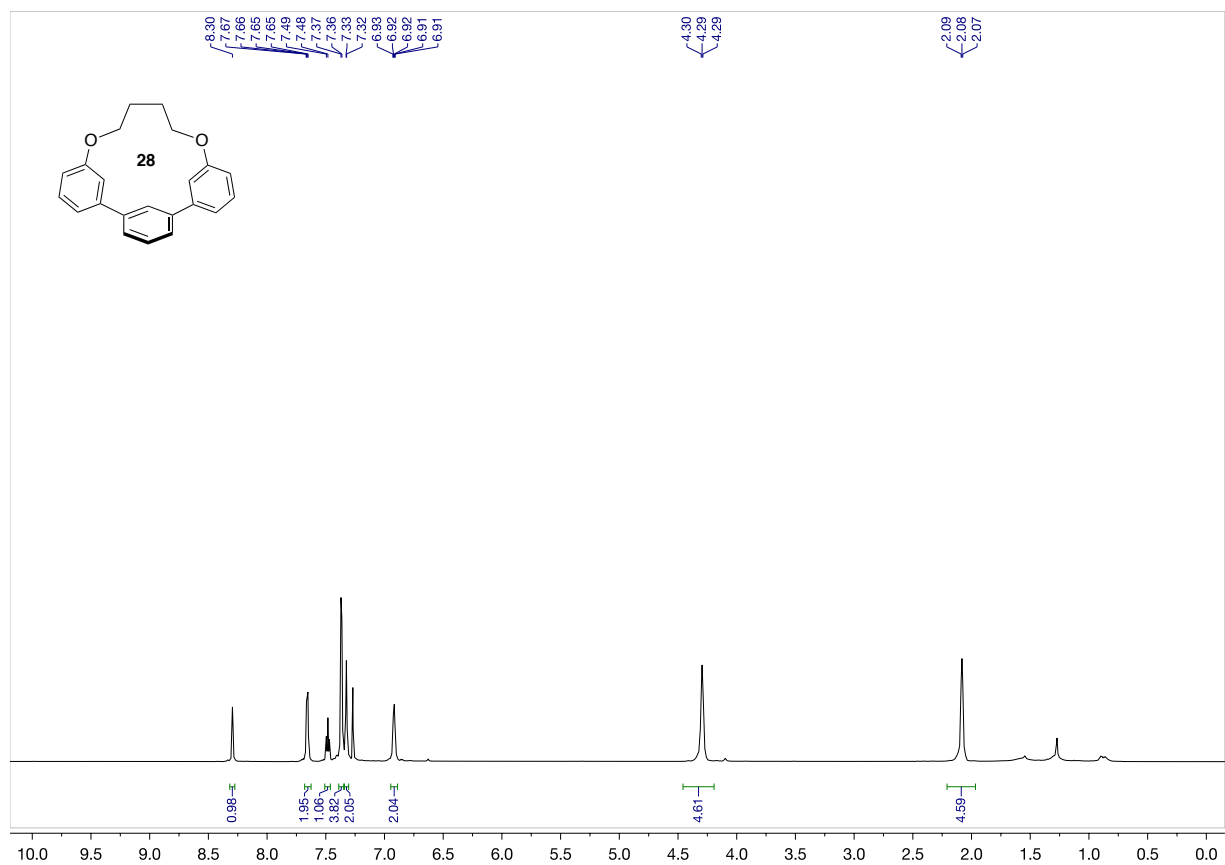


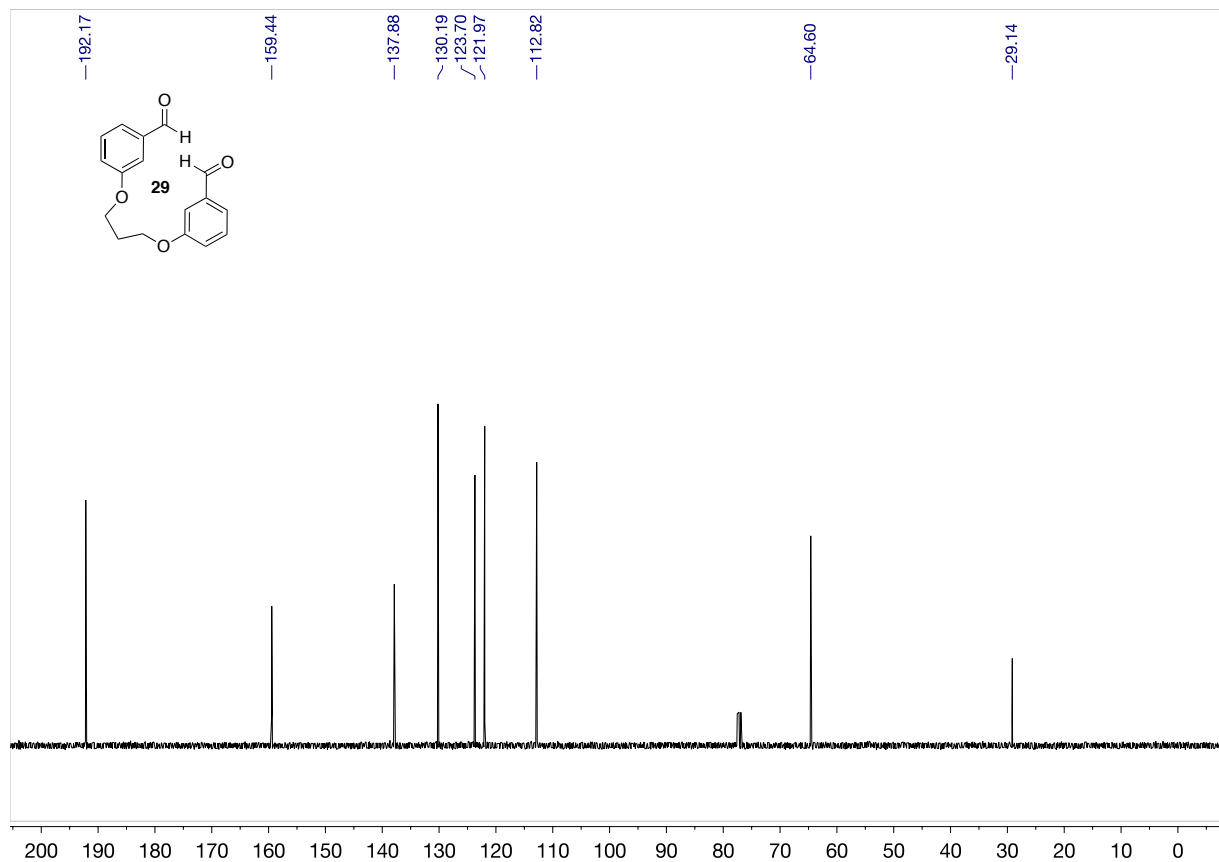
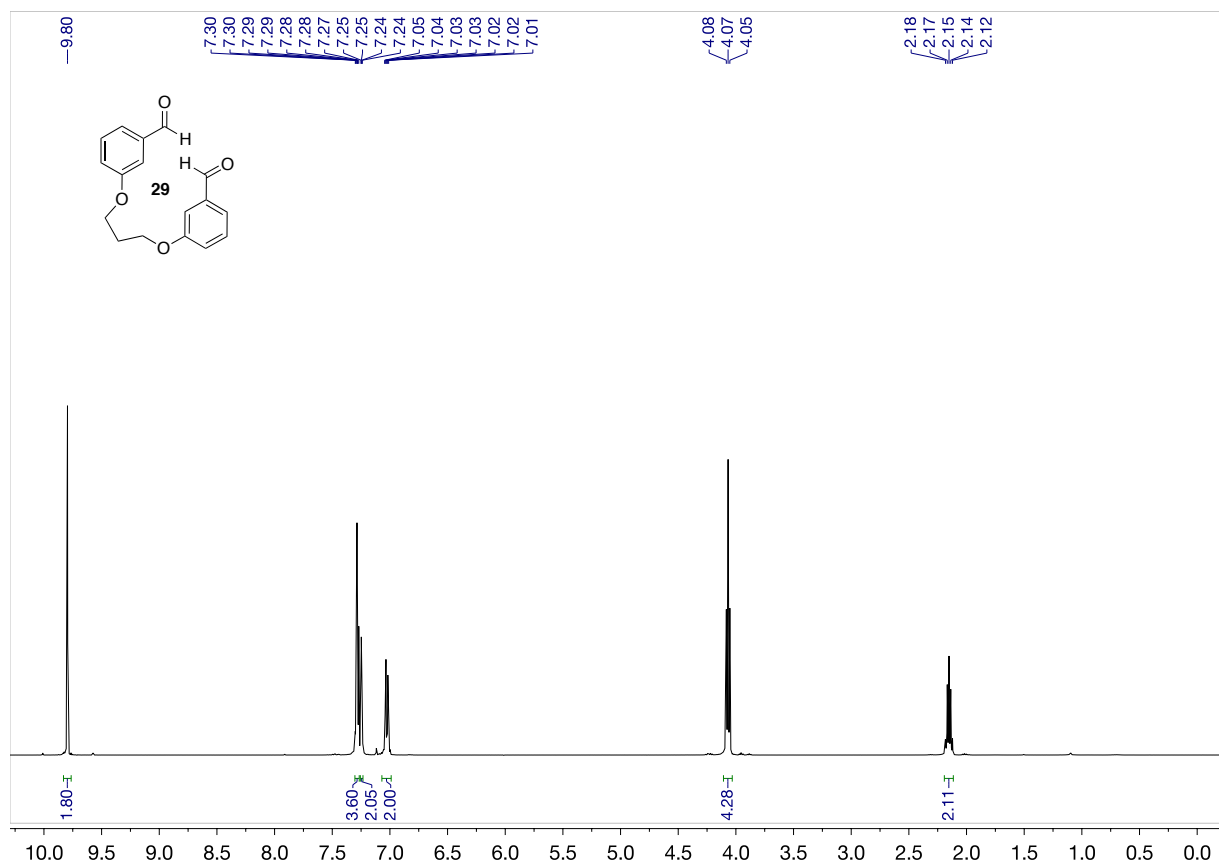


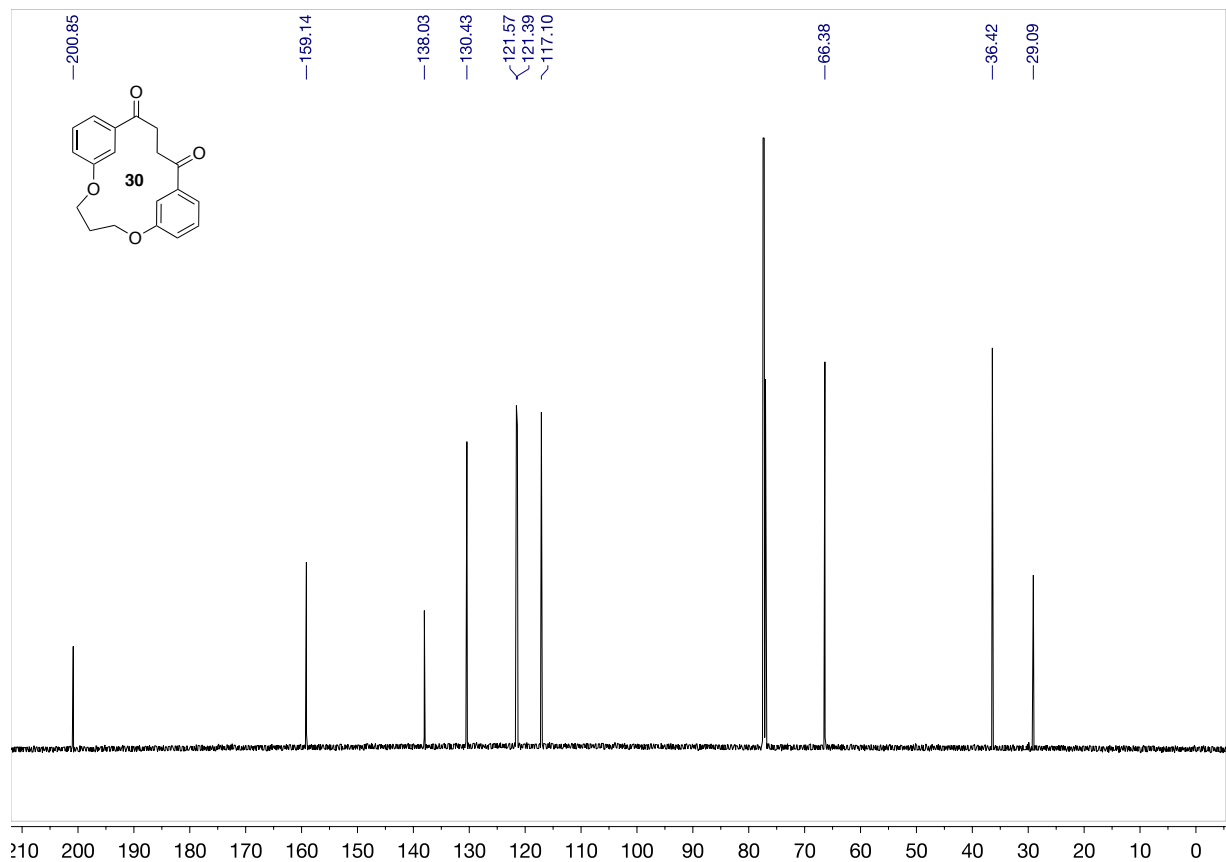
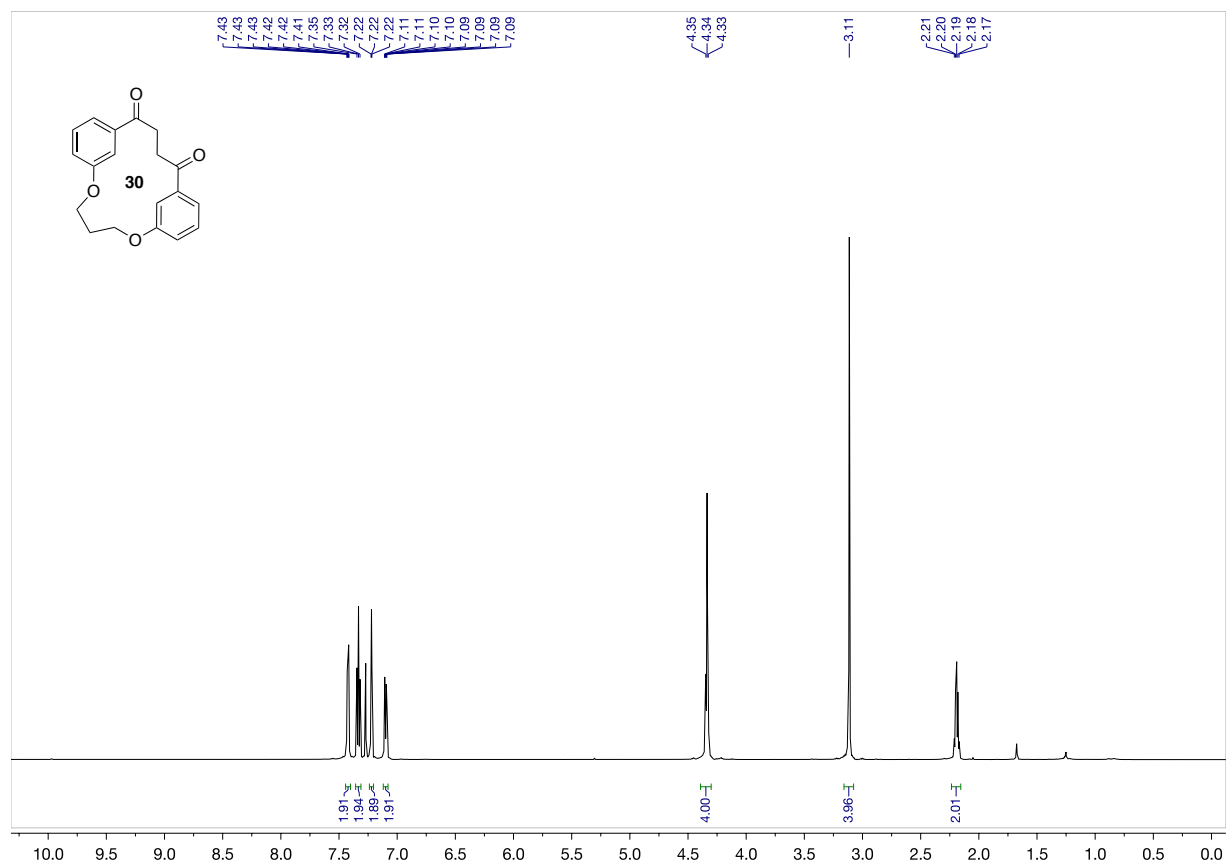


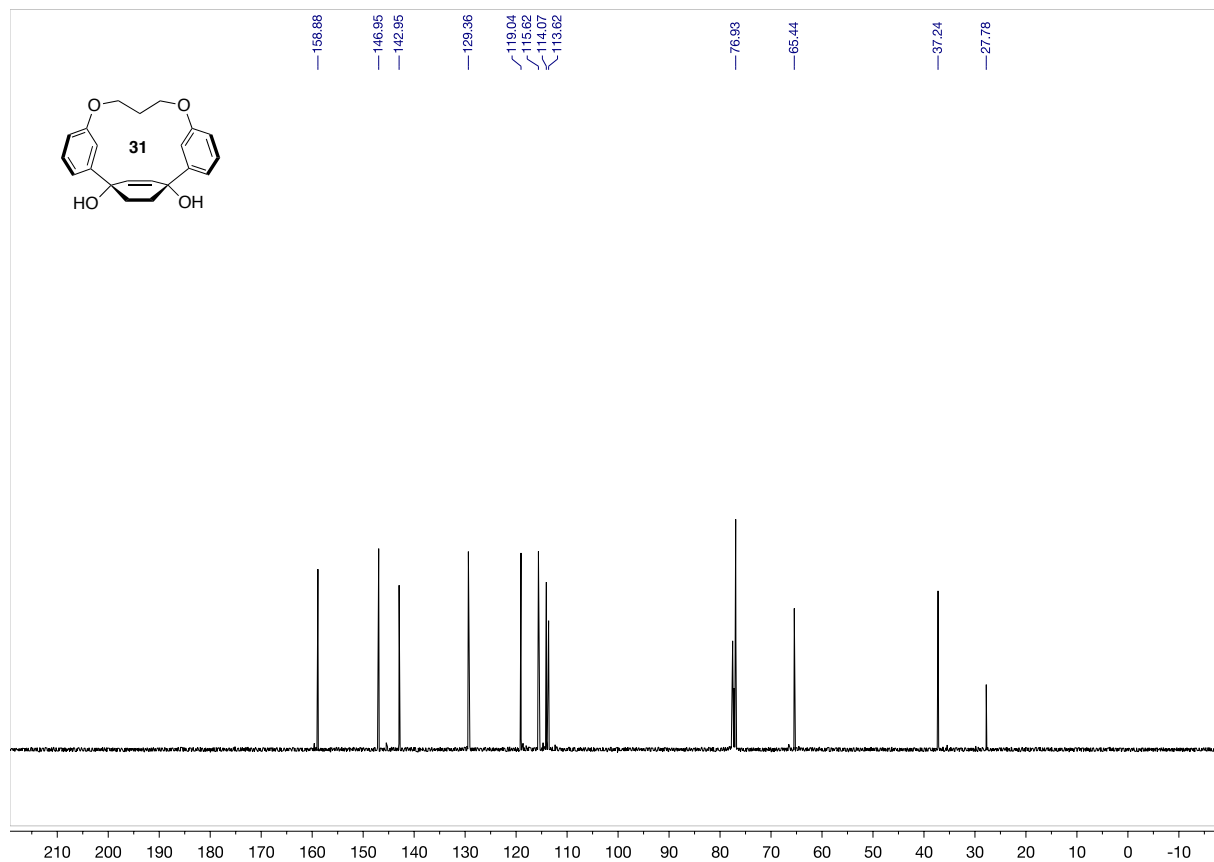
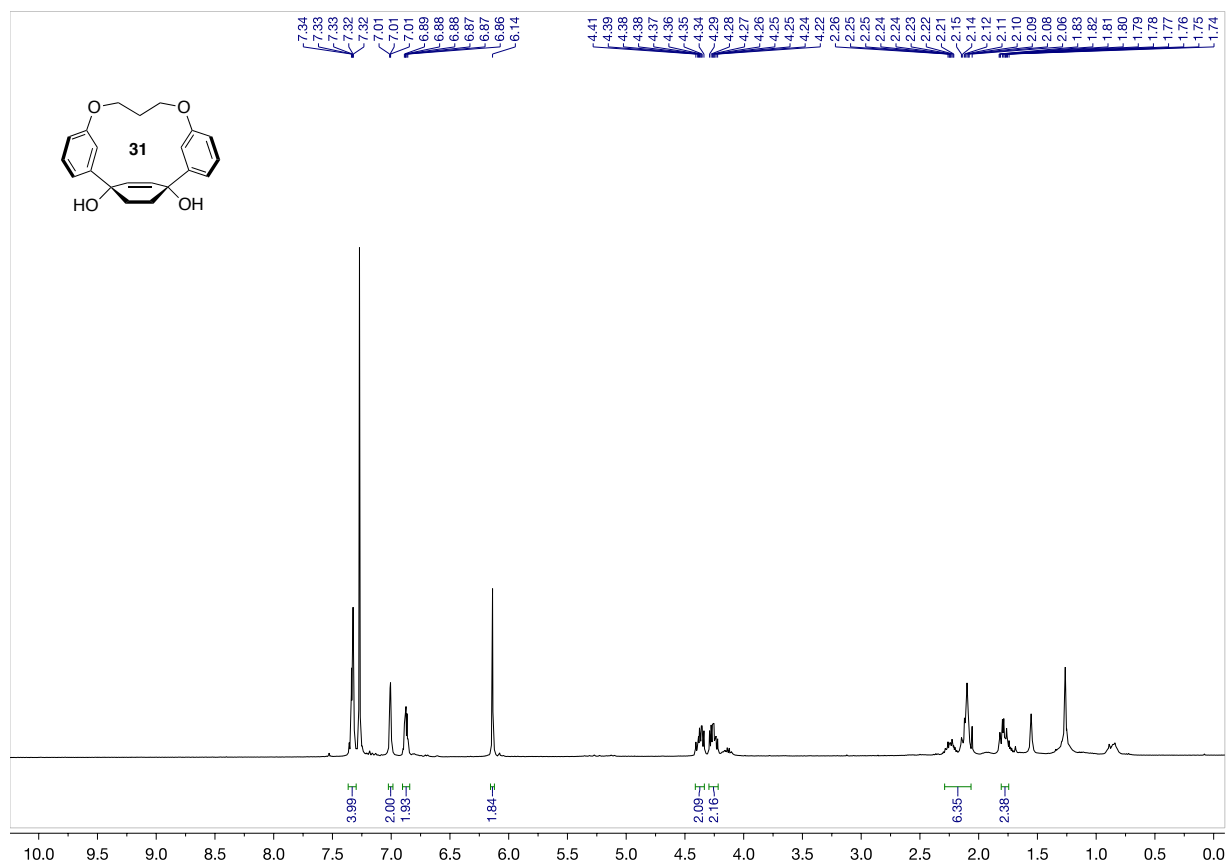


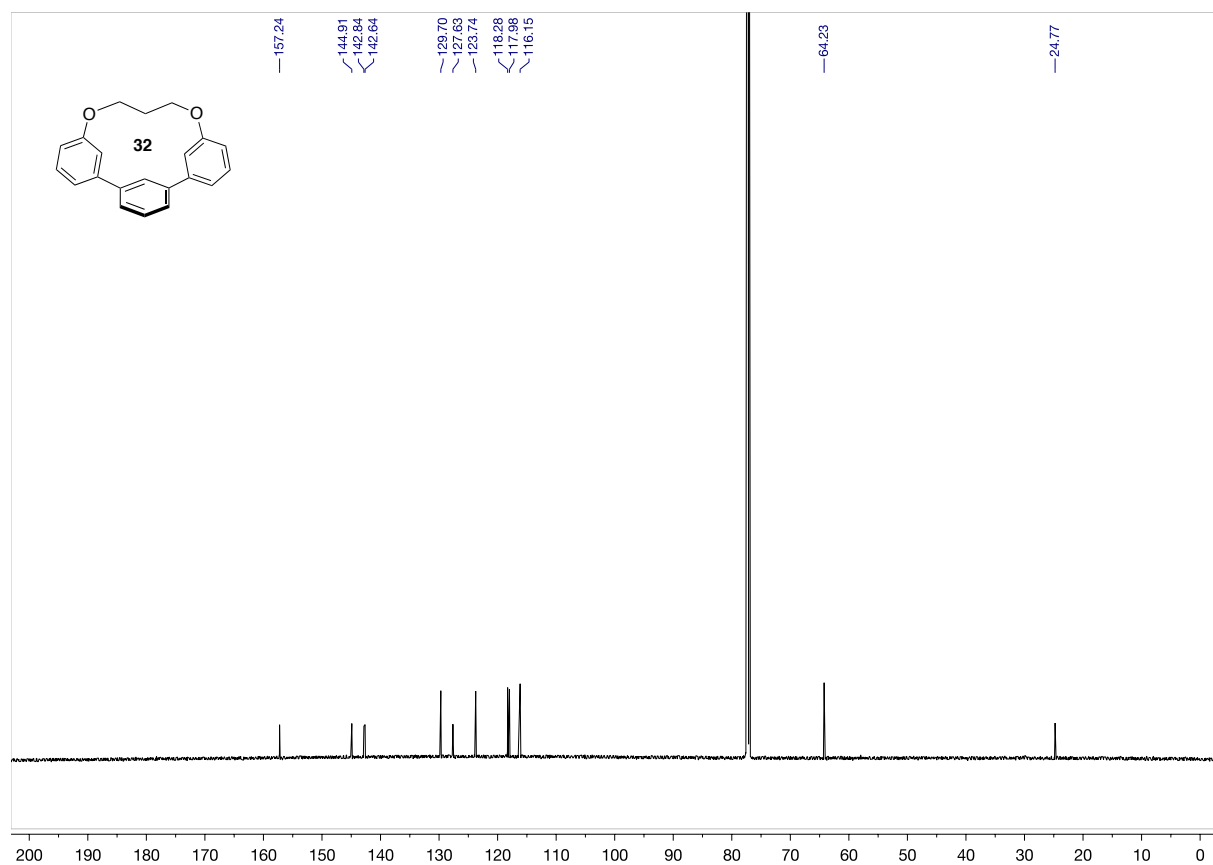
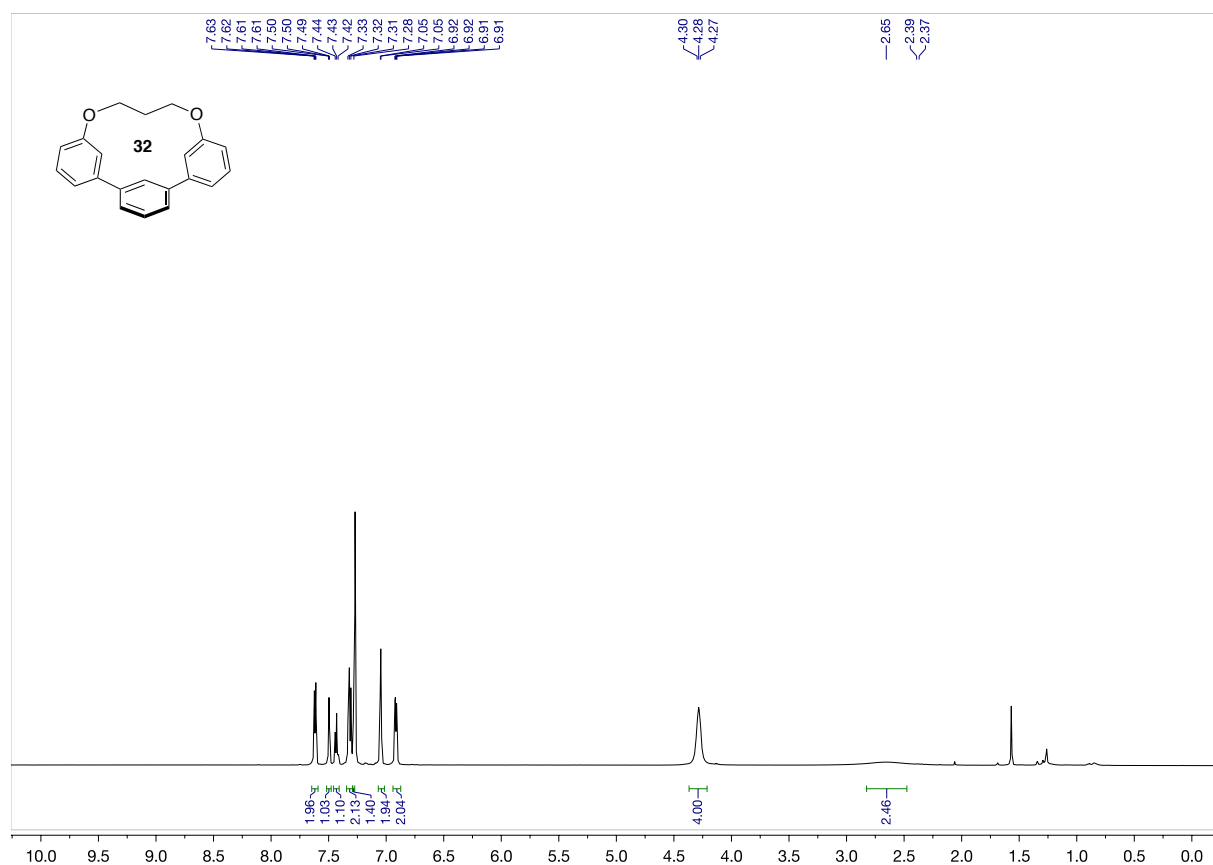


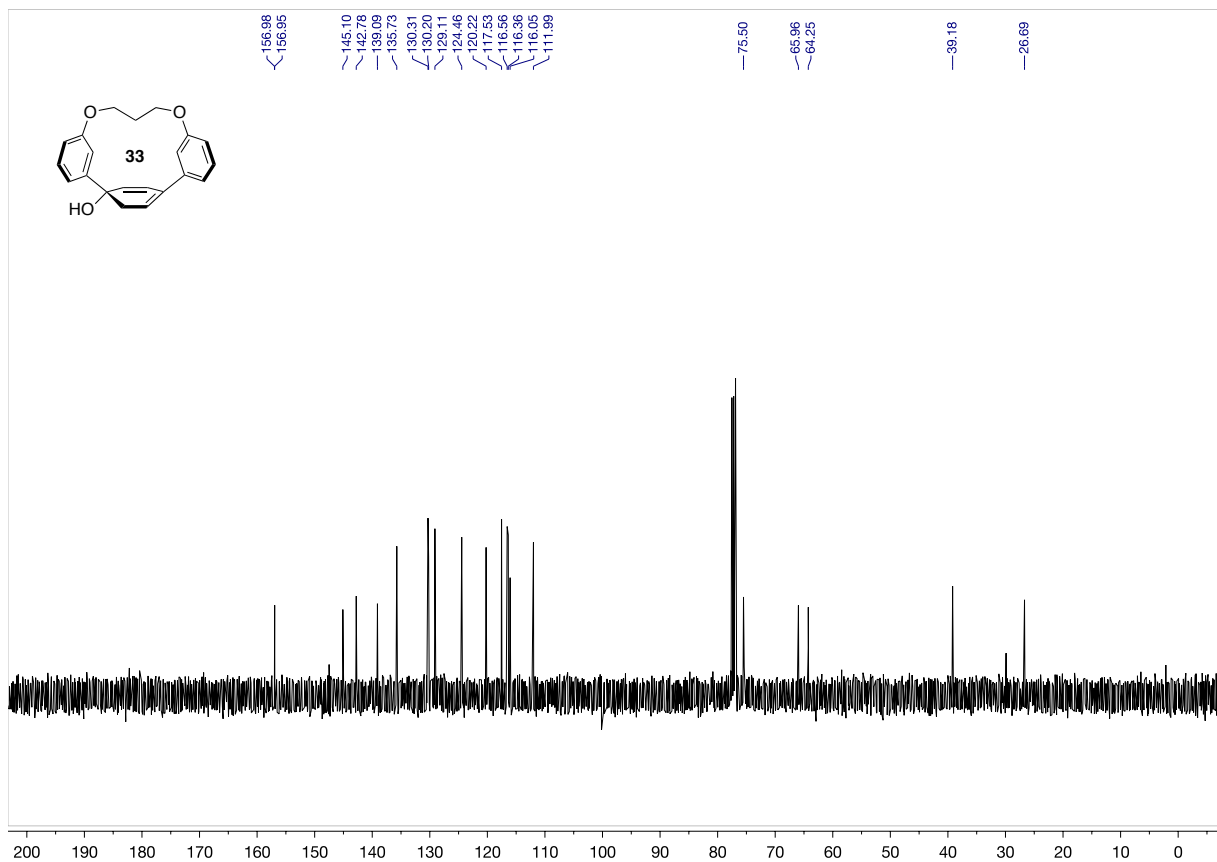
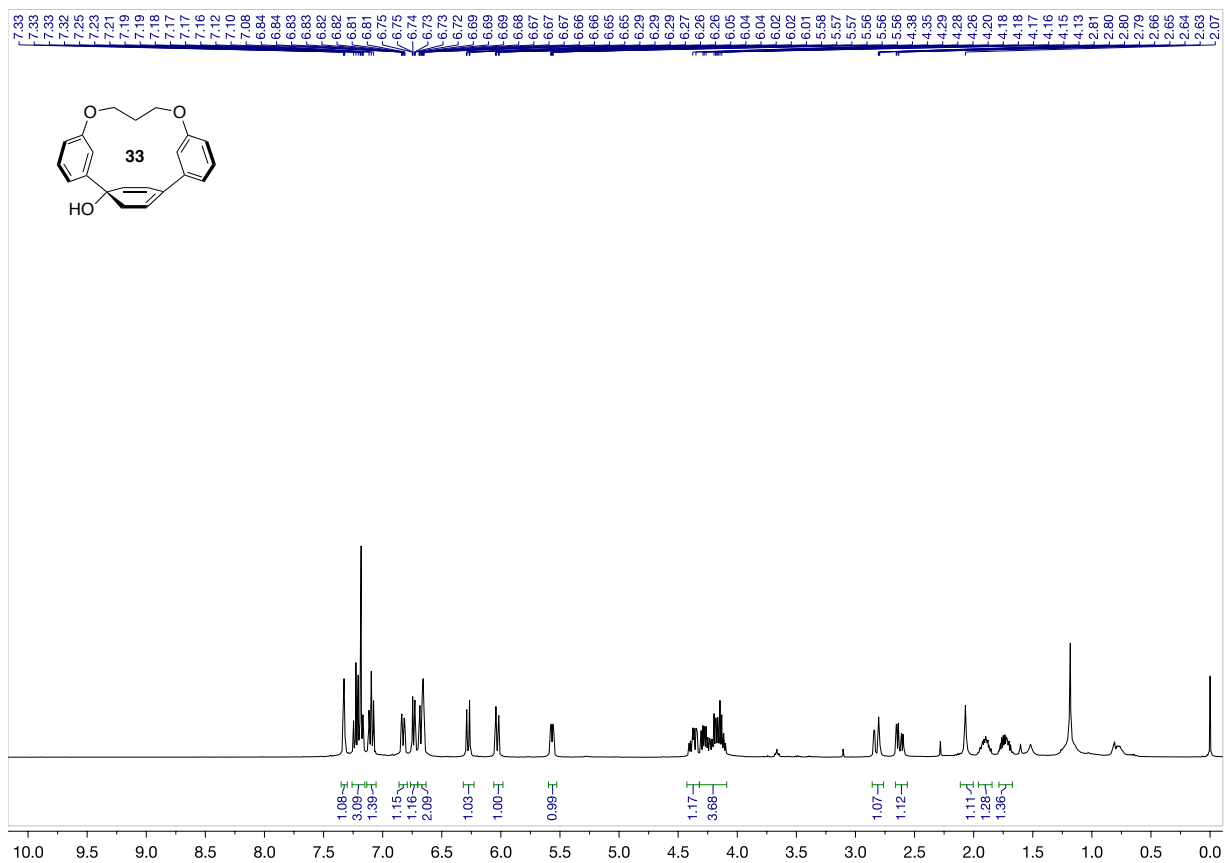


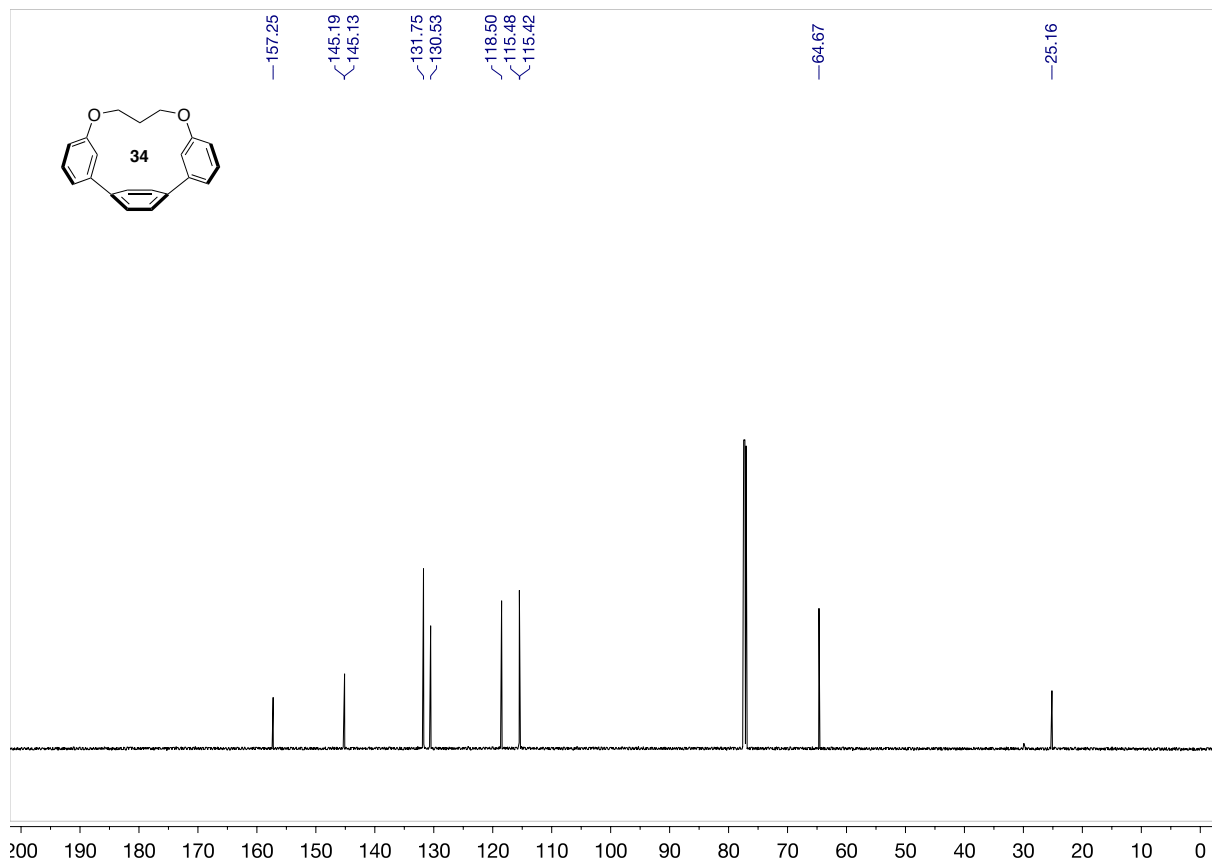
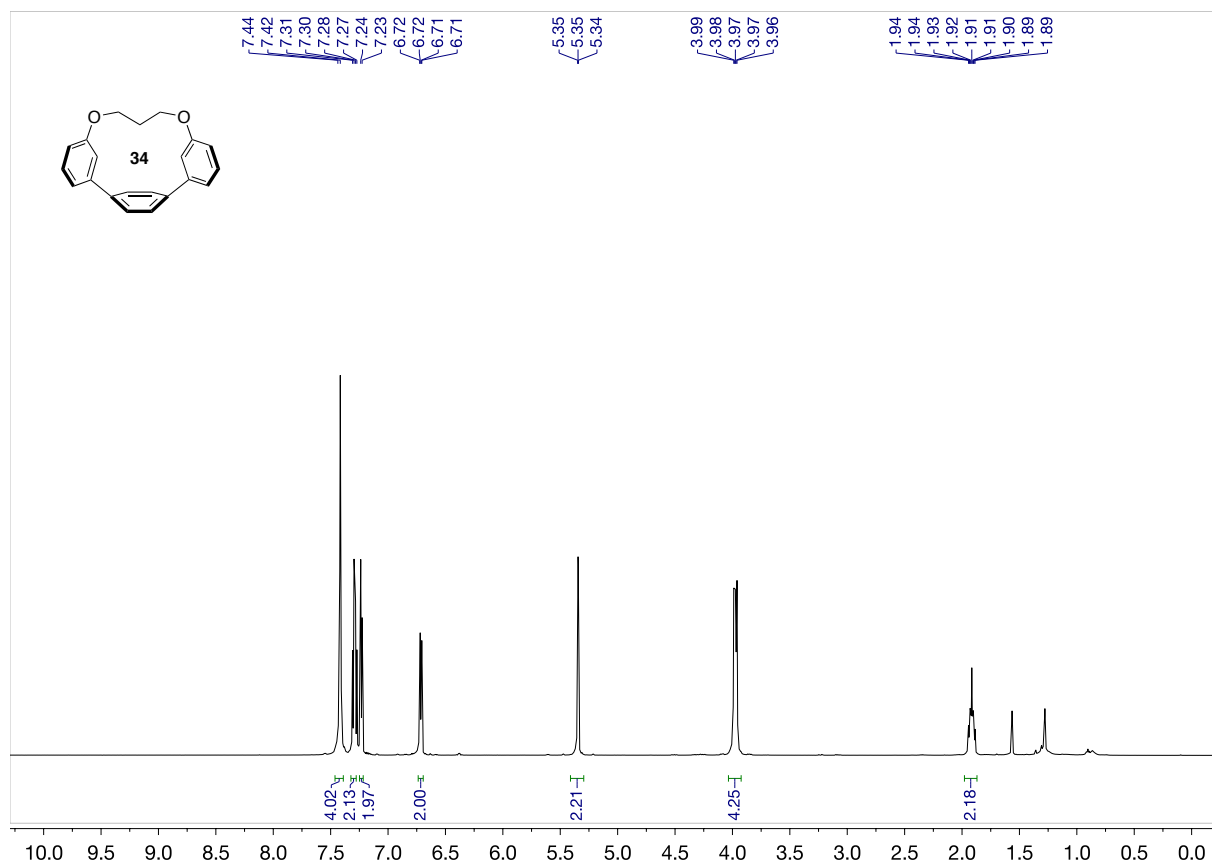


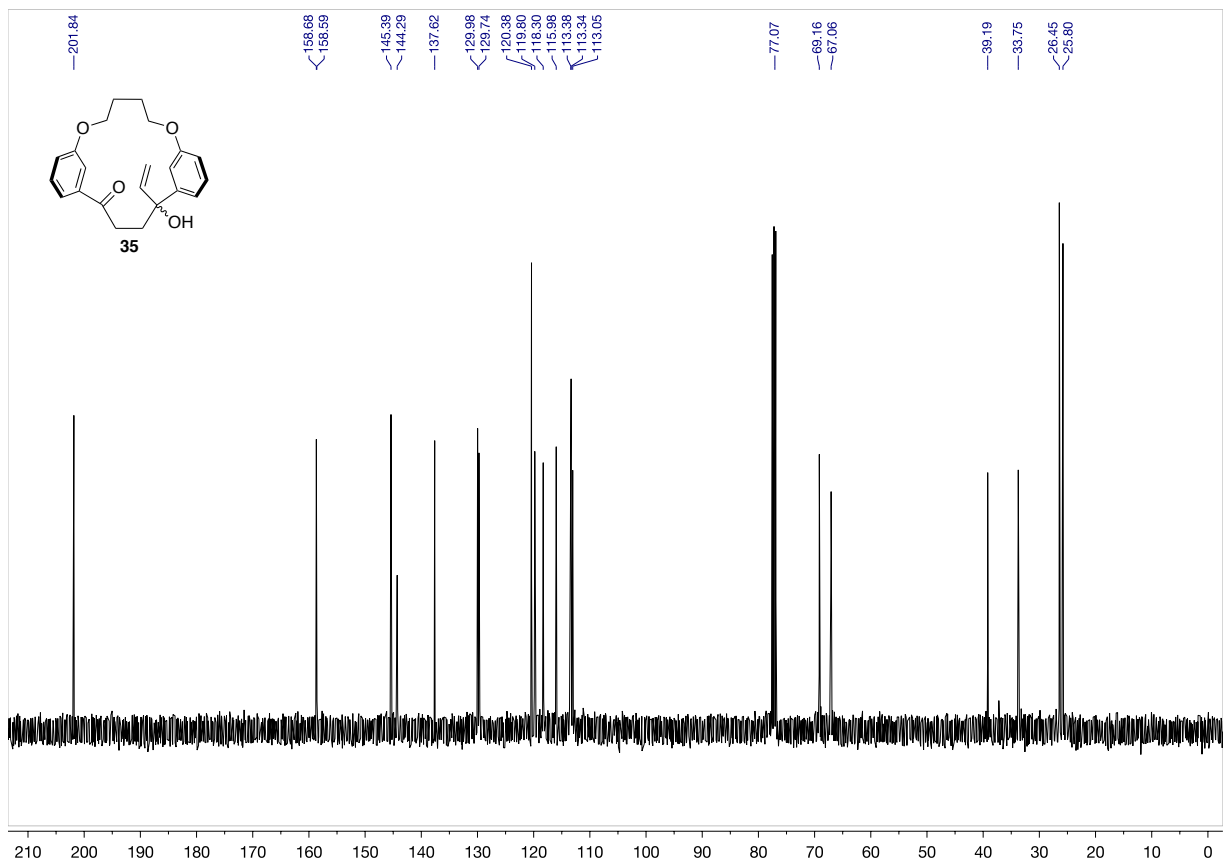
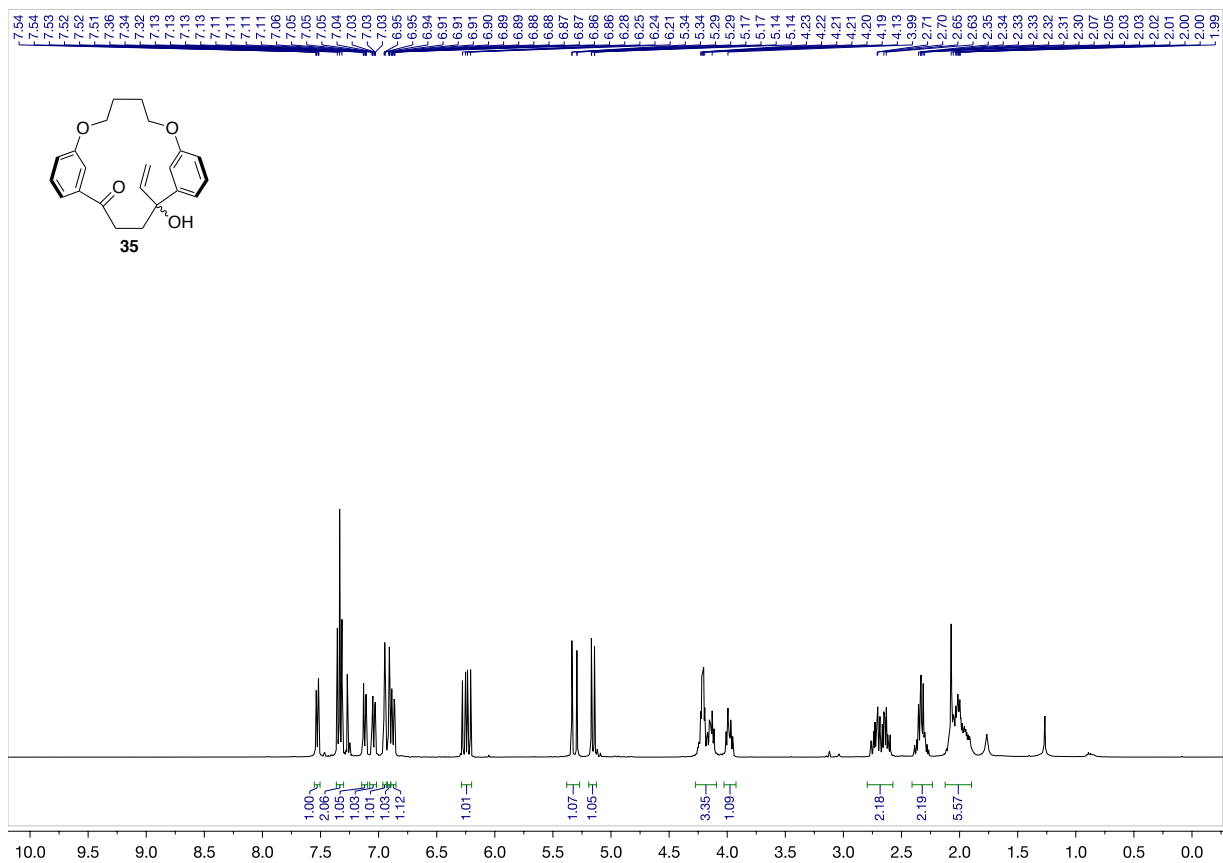


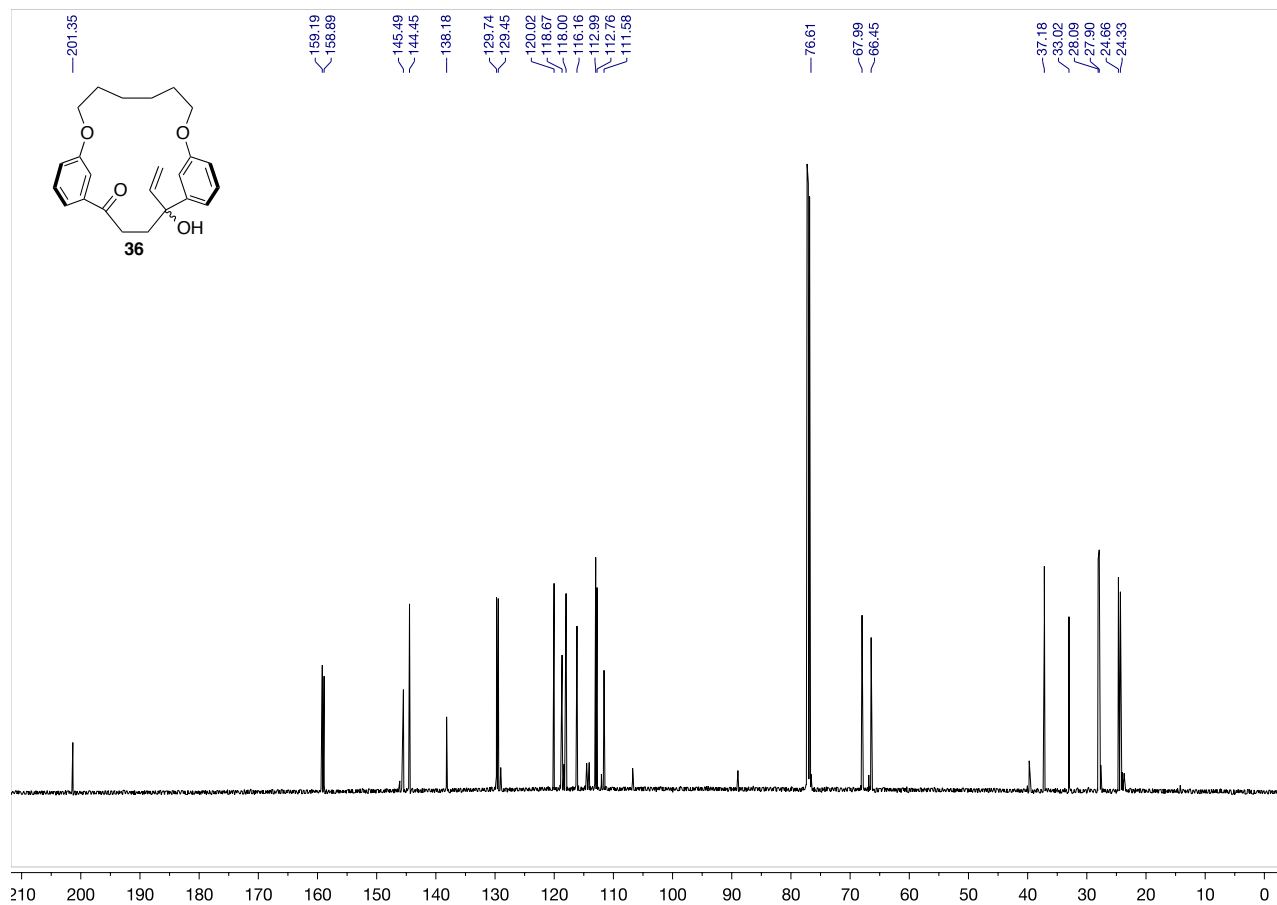
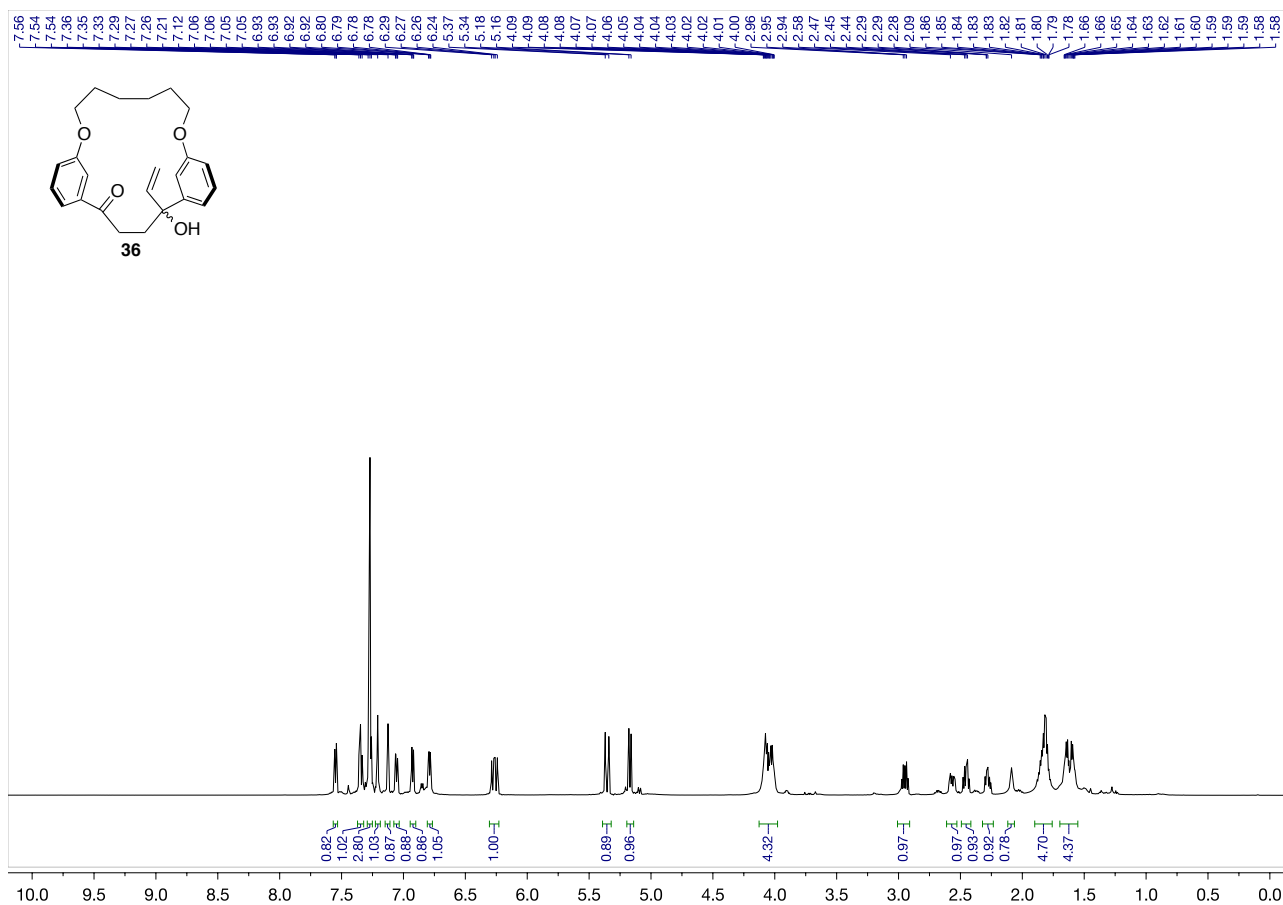


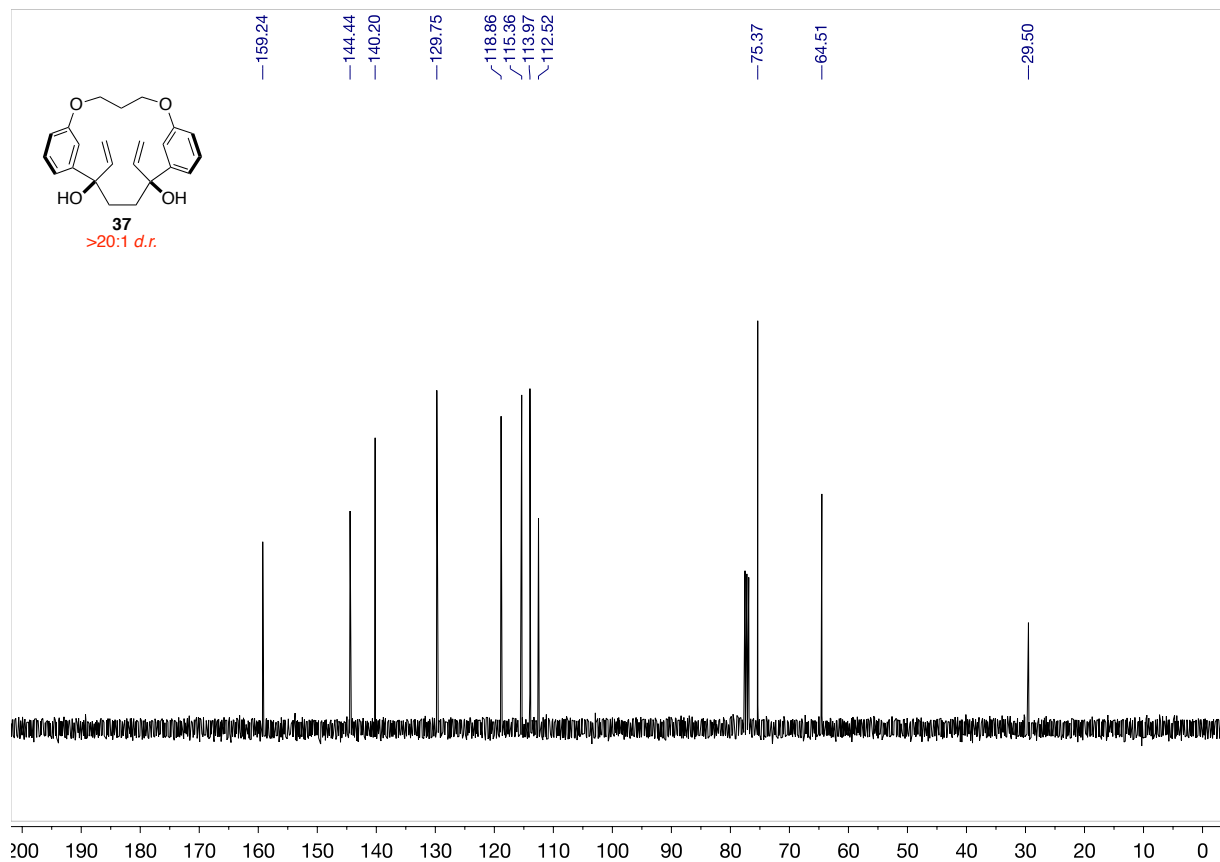
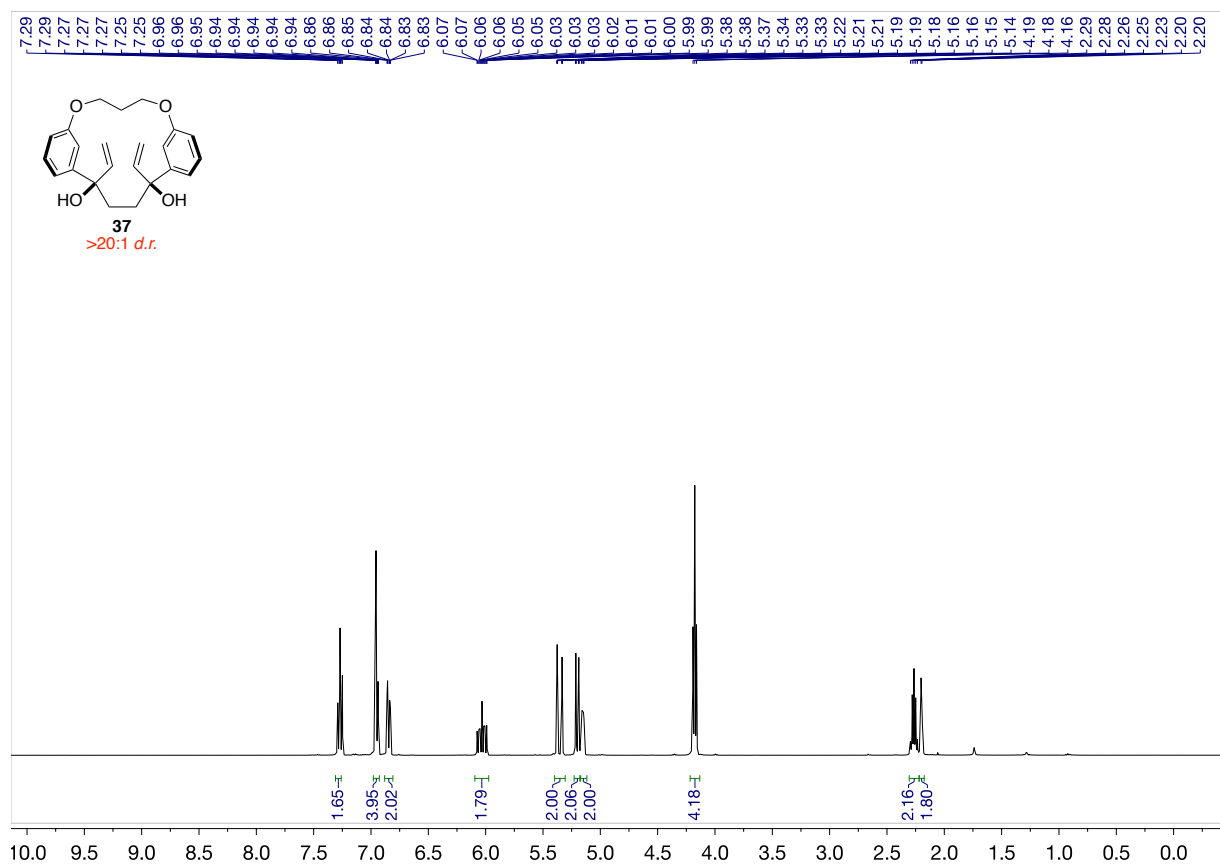












X-ray Crystal Structure and Relevant Data for Compound 34

Table SI-1: Crystal Data and Structure Refinement for (Merner060815) Compound 34

| | | |
|-----------------------------------|--|---------------------|
| Identification code | Merner060815 | |
| Empirical formula | C ₂₁ H ₁₈ O ₂ | |
| Formula weight | 304.37 | |
| Temperature | 180(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P b c a | |
| Unit cell dimensions | a = 19.549(2) Å | $\alpha = 90^\circ$ |
| | b = 8.1172(8) Å | $\beta = 90^\circ$ |
| | c = 19.927(2) Å | $\gamma = 90^\circ$ |
| Volume | 3162.1(6) Å ³ | |
| Z | 8 | |
| Density (calculated) | 1.279 g/cm ³ | |
| Absorption coefficient | 0.081 mm ⁻¹ | |
| F(000) | 1296 | |
| Crystal size | 0.17 x 0.22 x 0.25 mm ³ | |
| Theta range for data collection | 2.04 to 28.35° | |
| Index ranges | -25 ≤ h ≤ 26, -10 ≤ k ≤ 9, -26 ≤ l ≤ 25 | |
| Reflections collected | 31449 | |
| Independent reflections | 3941 [R(int) = 0.0561] | |
| Completeness to theta = 28.35° | 99.7% | |
| Absorption correction | Multiscan | |
| Max. and min. transmission | 0.9860 and 0.9800 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 3941 / 0 / 220 | |
| Goodness-of-fit on F ² | 1.212 | |
| Final R indices [I > 2σ(I)] | R1 = 0.0602, wR2 = 0.1070 | |
| R indices (all data) | R1 = 0.0725, wR2 = 0.1120 | |
| Largest diff. peak and hole | 0.245 and -0.196 | |

Table SI-2: Bond Lengths and Angles for (Merner060815) Compound 34

| | |
|---------|----------|
| O1-C26 | 1.378(2) |
| O1-C2 | 1.442(2) |
| O8-C21 | 1.380(2) |
| O8-C4 | 1.446(2) |
| C9-C10 | 1.385(3) |
| C9-C21 | 1.393(2) |
| C21-C20 | 1.381(2) |
| C20-C22 | 1.404(2) |
| C22-C11 | 1.381(2) |

| | |
|---------|----------|
| C22-C23 | 1.502(2) |
| C23-C12 | 1.399(2) |
| C23-C19 | 1.401(2) |
| C19-C18 | 1.385(2) |
| C18-C24 | 1.402(2) |
| C24-C13 | 1.397(2) |
| C24-C25 | 1.493(2) |
| C25-C14 | 1.388(2) |
| C25-C17 | 1.408(2) |
| C14-C15 | 1.389(3) |
| C15-C16 | 1.382(3) |
| C16-C26 | 1.396(2) |
| C26-C17 | 1.381(2) |
| C2-C3 | 1.532(2) |
| C3-C4 | 1.528(2) |
| C13-C12 | 1.393(2) |
| C11-C10 | 1.397(3) |

| | |
|-------------|------------|
| C26-O1-C2 | 118.22(13) |
| C21-O8-C4 | 117.43(13) |
| C10-C9-C21 | 119.00(16) |
| O8-C21-C20 | 122.78(15) |
| O8-C21-C9 | 118.17(15) |
| C20-C21-C9 | 119.04(16) |
| C21-C20-C22 | 122.07(16) |
| C11-C22-C20 | 118.72(16) |
| C11-C22-C23 | 131.59(16) |
| C20-C22-C23 | 109.46(14) |
| C12-C23-C19 | 117.73(16) |
| C12-C23-C22 | 117.76(15) |
| C19-C23-C22 | 117.27(15) |
| C18-C19-C23 | 120.23(16) |
| C19-C18-C24 | 119.54(16) |
| C13-C24-C18 | 117.81(17) |
| C13-C24-C25 | 118.04(15) |
| C18-C24-C25 | 118.95(16) |
| C14-C25-C17 | 118.71(17) |
| C14-C25-C24 | 128.43(17) |
| C17-C25-C24 | 111.69(15) |
| C25-C14-C15 | 119.29(18) |
| C16-C15-C14 | 121.99(17) |
| C15-C16-C26 | 119.10(17) |
| O1-C26-C17 | 123.68(16) |
| O1-C26-C16 | 117.00(16) |
| C17-C26-C16 | 119.28(17) |
| O1-C2-C3 | 114.53(15) |

| | |
|-------------|------------|
| C4-C3-C2 | 108.95(14) |
| O8-C4-C3 | 115.00(14) |
| C26-C17-C25 | 121.48(16) |
| C12-C13-C24 | 120.11(16) |
| C13-C12-C23 | 119.46(16) |
| C22-C11-C10 | 119.08(17) |
| C9-C10-C11 | 122.05(17) |

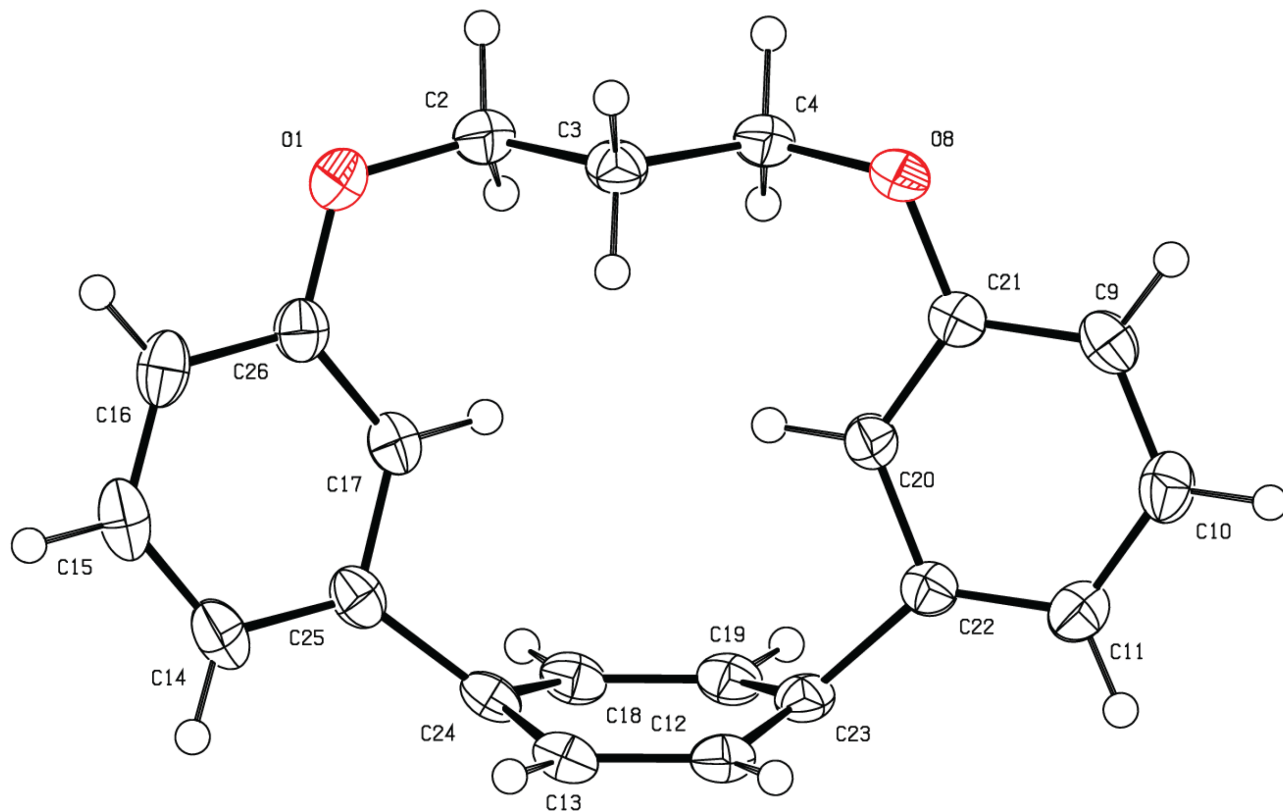


FIGURE SI-2: X-ray crystal structure of compound **34**

Table SI-1: Crystal Data and Structure Refinement for (**Merner121114**) Compound **28**

| | | |
|----------------------|--|---------------------|
| Identification code | Merner121114 | |
| Empirical formula | C ₂₂ H ₂₀ O ₂ | |
| Formula weight | 316.40 | |
| Temperature | 180.45 K | |
| Crystal system | Monoclinic | |
| Space group | P2 ₁ /n | |
| Unit cell dimensions | a = 12.5333(3) Å | $\alpha = 90^\circ$ |

| | | |
|-----------------------------------|--|---------------------|
| | $b = 7.8729(2) \text{ \AA}$ | $\beta = 91^\circ$ |
| | $c = 16.2274(4) \text{ \AA}$ | $\gamma = 90^\circ$ |
| Volume | $1600.48(7) \text{ \AA}^3$ | |
| Z | 4 | |
| Density (calculated) | 1.3130 g/cm^3 | |
| Absorption coefficient | 0.083 mm^{-1} | |
| F(000) | 672.3 | |
| Crystal size | $0.5 \times 0.4 \times 0.2 \text{ mm}^3$ | |
| Theta range for data collection | $4.04 \text{ to } 74.34^\circ$ | |
| Index ranges | $-21 \leq h \leq 20, -13 \leq k \leq 13, -27 \leq l \leq 27$ | |
| Reflections collected | 47977 | |
| Independent reflections | 8058 [R(int) = 0.0586, R(sigma) = 0.0452] | |
| Data / restraints / parameters | 8058 / 0 / 217 | |
| Goodness-of-fit on F ² | 1.099 | |
| Final R indices [I > 2sigma(I)] | R1 = 0.0682, wR2 = 0.1560 | |
| R indices (all data) | R1 = 0.0984, wR2 = 0.1826 | |
| Largest diff. peak and hole | 0.70 and -0.47 | |

Table SI-3: Bond Lengths and Angles for (Merner121114) Compound 28

| | |
|-----------|----------|
| O1-C0aa | 1.371(2) |
| O1-C2 | 1.449(2) |
| O8-C5 | 1.446(2) |
| O8-C7 | 1.374(2) |
| C15-C0aa | 1.402(2) |
| C15-C14 | 1.389(2) |
| C16-C0aa | 1.389(2) |
| C2-C3 | 1.536(2) |
| C3-C4 | 1.536(2) |
| C4-C5 | 1.532(2) |
| C7-C9 | 1.400(2) |
| C7-C20 | 1.391(2) |
| C9-C10 | 1.388(2) |
| C14-C13 | 1.397(2) |
| C13-C3aa | 1.400(2) |
| C16-C3aa | 1.406(2) |
| C3aa-C4aa | 1.488(2) |
| C20-C1aa | 1.405(2) |
| C1aa-C5aa | 1.490(2) |
| C1aa-C11 | 1.395(2) |
| C5aa-C19 | 1.401(2) |
| C12-C4aa | 1.399(2) |
| C4aa-C17 | 1.402(2) |
| C17-C18 | 1.398(2) |

| | |
|---------------|------------|
| C18-C19 | 1.394(2) |
| C11-C10 | 1.399(2) |
| C2-O1-C0aa | 116.75(9) |
| C7-O8-C5 | 117.99(9) |
| C14-C15-C0aa | 118.66(11) |
| C15-C0aa-O1 | 117.83(10) |
| C16-C0aa-O1 | 122.70(11) |
| C16-C0aa-C15 | 119.45(12) |
| C2-C3-O1 | 114.34(10) |
| C4-C3-C2 | 111.52(10) |
| C5-C4-C3 | 112.70(11) |
| C4-C5-O8 | 112.90(11) |
| C9-C7-O8 | 117.14(11) |
| C20-C7-O8 | 123.94(11) |
| C20-C7-C9 | 118.91(12) |
| C10-C9-C7 | 119.77(11) |
| C13-C14-C15 | 121.99(11) |
| C13-C24-C18 | 119.73(10) |
| C3aa-C13-C14 | 117.93(10) |
| C4aa-C3aa-C13 | 124.74(11) |
| C4aa-C3aa-C16 | 117.09(9) |
| C3aa-C16-C0aa | 122.18(11) |
| C1aa-C20-C7 | 121.30(11) |
| C5aa-C1aa-C20 | 115.27(18) |
| C11-C1aa-C20 | 119.47(11) |
| C11-C1aa-C5aa | 125.09(11) |
| C12-C5aa-C1aa | 115.29(10) |
| C19-C5aa-C12 | 118.34(10) |
| C4aa-C12-C5aa | 123.12(10) |
| C12-C4aa-C3aa | 118.00(10) |
| C17-C4aa-C3aa | 124.22(10) |
| C17-C4aa-C12 | 117.21(10) |
| C18-C17-C4aa | 120.09(10) |
| C19-C18-C17 | 121.52(11) |
| C18-C19-C5aa | 119.18(12) |
| C10-C11-C1aa | 118.89(12) |
| C11-C10-C9 | 121.55(12) |

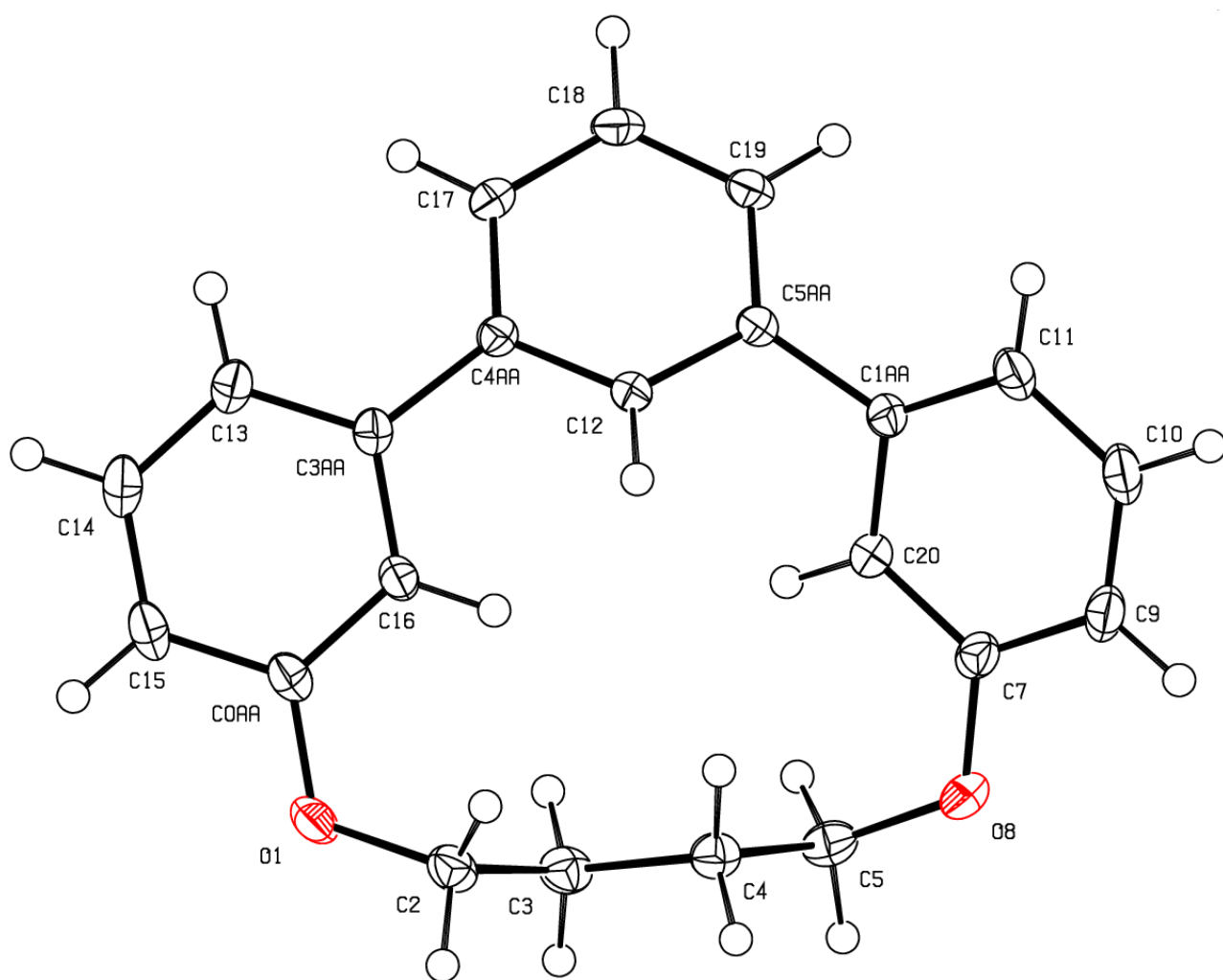


FIGURE SI-3: X-ray crystal structure of compound 28

DFT Computed Strain Energies of 31 and 34

Full geometry optimization using the geometry from the CIF of **34** as a starting guess was performed using the B3LYP functional in conjunction with a 6-31G(d) basis set. The harmonic vibrational analysis was done at the same level to verify the nature of the stationary point. All of the electronic calculations were performed with Gaussian 09¹ package of programs.

Cartesian Coordinates for **31** (in Å):

| | | | |
|---|------------|------------|------------|
| C | 0.3212660 | 2.7493050 | -0.0453390 |
| H | 0.5628480 | 2.2260540 | -0.9830630 |
| H | 0.3868140 | 2.0230740 | 0.7656570 |
| C | 1.3645940 | 3.8134910 | 0.2380560 |
| H | 1.1964530 | 4.2491770 | 1.2294520 |
| H | 1.3286080 | 4.6288670 | -0.4951910 |
| C | 2.7511280 | 3.1445680 | 0.1691690 |
| H | 3.0038250 | 2.9129420 | -0.8720530 |
| H | 3.5222540 | 3.8097520 | 0.5701870 |
| C | 3.7852380 | 0.4135700 | -0.6593360 |
| H | 4.5455890 | 1.1438780 | -0.9195320 |
| C | 3.7792020 | -0.8501160 | -1.2566500 |
| H | 4.5414470 | -1.0945860 | -1.9918820 |
| C | 2.8174130 | -1.7988090 | -0.9178490 |
| H | 2.8345970 | -2.7801400 | -1.3814740 |
| C | -0.1690700 | -2.1574780 | 1.4915120 |
| H | 0.2253650 | -2.2545950 | 2.5032360 |
| C | -1.4251280 | -1.7360260 | 1.3102530 |
| H | -2.0536680 | -1.5014170 | 2.1674850 |
| C | -3.9485900 | 0.2517810 | -0.1915970 |
| H | -4.7181960 | -0.5108470 | -0.1931570 |
| C | -4.2848820 | 1.6134600 | -0.2351330 |
| H | -5.3325700 | 1.9006140 | -0.2777970 |
| C | -3.3129450 | 2.6108900 | -0.2156330 |
| H | -3.5787150 | 3.6632990 | -0.2369020 |
| C | -1.6270970 | 0.8893910 | -0.1399920 |
| H | -0.5952630 | 0.5799690 | -0.1027110 |
| C | -1.1311970 | -1.8995930 | -1.2039300 |
| H | -1.7444830 | -2.2248080 | -2.0509350 |
| H | -0.6049580 | -0.9975070 | -1.5289930 |
| C | -0.0924760 | -2.9678500 | -0.8463340 |
| H | 0.5507580 | -3.1710620 | -1.7085080 |
| H | -0.5764160 | -3.9168520 | -0.5826090 |
| C | 1.8593210 | -0.2450900 | 0.6552210 |
| H | 1.1293830 | 0.0083000 | 1.4160000 |

| | | | |
|---|------------|------------|------------|
| C | 2.8157150 | 0.7193440 | 0.2987620 |
| C | 1.8291710 | -1.4997650 | 0.0352870 |
| C | 0.7682730 | -2.5695350 | 0.3712640 |
| C | -2.1041710 | -1.5566990 | -0.0393240 |
| C | -2.6038140 | -0.1112260 | -0.1455760 |
| C | -1.9610920 | 2.2440040 | -0.1595640 |
| H | 2.1206790 | -3.5544940 | 1.4020730 |
| H | -2.9602900 | -3.3030080 | 0.1494380 |
| O | -1.0143240 | 3.2407660 | -0.1153490 |
| O | 2.7833510 | 1.9332760 | 0.9542970 |
| O | 1.4453800 | -3.7878210 | 0.7441140 |
| O | -3.2605580 | -2.4090100 | -0.0778510 |

Cartesian Coordinates for *p*-terphenyl precursor of **31** (in Å):

| | | | |
|---|------------|------------|------------|
| C | 4.0938360 | 2.3203580 | -0.2895740 |
| H | 4.7114240 | 3.2018340 | -0.4396960 |
| C | 4.5106410 | 1.0780030 | -0.7740900 |
| H | 5.4558050 | 0.9888220 | -1.3035800 |
| C | 3.7188600 | -0.0524580 | -0.5795430 |
| H | 4.0467160 | -1.0191730 | -0.9499840 |
| C | 0.6683050 | -1.1281390 | 1.4258760 |
| H | 1.1189150 | -1.1549740 | 2.4186910 |
| C | -0.6604510 | -1.0390050 | 1.3071900 |
| H | -1.2902580 | -1.0232530 | 2.1946540 |
| C | -3.8375350 | -0.3927280 | -0.3698930 |
| H | -4.0494110 | -1.4293470 | -0.6026870 |
| C | -4.8585410 | 0.5601300 | -0.3966920 |
| H | -5.8686490 | 0.2547650 | -0.6580880 |
| C | -4.5901970 | 1.8936820 | -0.0886440 |
| H | -5.3868130 | 2.6327770 | -0.1082950 |
| C | -2.2693220 | 1.3203550 | 0.2726540 |
| H | -1.2600750 | 1.6259920 | 0.5374600 |
| C | -0.4042270 | -0.7750700 | -1.1812630 |
| H | -0.9096890 | -1.0207090 | -2.1210590 |
| H | -0.1622310 | 0.2935320 | -1.2142040 |
| C | 0.8848070 | -1.5867140 | -1.0292740 |
| H | 1.5430460 | -1.4391260 | -1.8913950 |
| H | 0.6590090 | -2.6600150 | -0.9868440 |
| C | 2.0886720 | 1.2851140 | 0.5864590 |
| H | 1.1535990 | 1.3710860 | 1.1316950 |
| C | 2.8811930 | 2.4192950 | 0.3914310 |
| C | 2.4937190 | 0.0361220 | 0.1005730 |
| C | 1.6435830 | -1.2336100 | 0.2670970 |
| C | -1.3942800 | -1.0447570 | -0.0228810 |

| | | | |
|---|------------|------------|------------|
| C | -2.5301470 | -0.0221220 | -0.0364780 |
| C | -3.2885870 | 2.2712480 | 0.2476700 |
| H | 3.1189280 | -2.1203240 | 1.2147190 |
| H | -1.3170260 | -2.9992820 | 0.0087150 |
| O | 2.5089670 | -2.3643380 | 0.4987390 |
| O | -2.0025680 | -2.3414970 | -0.1843790 |
| H | -3.0657640 | 3.3065400 | 0.4930230 |
| H | 2.5493010 | 3.3793090 | 0.7782900 |

Cartesian Coordinates for alkoxy bridging group of **31** (in Å):

| | | | |
|---|------------|------------|------------|
| C | 1.0016090 | -0.3573120 | 0.2886430 |
| H | 0.9827770 | -0.3976060 | 1.3921430 |
| H | 0.6823180 | -1.3458830 | -0.0834540 |
| C | 0.0375080 | 0.7147830 | -0.2039330 |
| H | 0.0637950 | 0.7379960 | -1.2995760 |
| H | 0.3934530 | 1.6905240 | 0.1524140 |
| C | -1.4046250 | 0.5057520 | 0.2635150 |
| H | -1.4508640 | 0.4962440 | 1.3656130 |
| H | -2.0223160 | 1.3428360 | -0.0760810 |
| O | 2.3002940 | -0.0319070 | -0.1910680 |
| O | -2.0185440 | -0.6605370 | -0.2811930 |
| H | 2.9093110 | -0.7292060 | 0.0952710 |
| H | -1.6194180 | -1.4346830 | 0.1424080 |

Cartesian Coordinates for **34** (in Å):

| | | | |
|---|------------|------------|------------|
| O | 2.5008600 | 2.4769540 | -0.0663690 |
| O | -2.5014700 | 2.4767900 | -0.0661030 |
| C | -4.1810510 | 0.9095340 | -0.6688080 |
| H | -4.7964100 | 1.7394290 | -1.0019400 |
| C | -2.9197620 | 1.1707590 | -0.1102330 |
| C | -2.1481990 | 0.1000130 | 0.3274770 |
| H | -1.1628060 | 0.2712500 | 0.7349810 |
| C | -2.5507840 | -1.2384260 | 0.1382700 |
| C | -1.4005580 | -2.1747890 | 0.3530230 |
| C | -0.6964980 | -2.1262590 | 1.5686650 |
| C | 0.6970860 | -2.1262570 | 1.5685580 |
| C | 1.4009580 | -2.1748010 | 0.3528020 |
| C | 2.5510250 | -1.2382610 | 0.1379540 |
| C | 3.8009490 | -1.4923690 | -0.4263360 |
| H | 4.1368800 | -2.5121720 | -0.5901390 |
| C | 4.6098300 | -0.4092790 | -0.8028310 |
| H | 5.5890240 | -0.6012880 | -1.2340140 |

| | | | |
|---|------------|------------|------------|
| C | 4.1810410 | 0.9101030 | -0.6686090 |
| H | 4.7963420 | 1.7401210 | -1.0015280 |
| C | 2.9194940 | 1.1710300 | -0.1104680 |
| C | 1.2702900 | 2.8011090 | 0.5947750 |
| H | 1.3708210 | 3.8625900 | 0.8413240 |
| H | 1.2084350 | 2.2507010 | 1.5436210 |
| C | -0.0003560 | 2.5756450 | -0.2525400 |
| H | -0.0003810 | 3.2626500 | -1.1058070 |
| H | -0.0004650 | 1.5632290 | -0.6645240 |
| C | -1.2709150 | 2.8012130 | 0.5949060 |
| H | -1.2089050 | 2.2510100 | 1.5438660 |
| H | -1.3715240 | 3.8627310 | 0.8412410 |
| C | 2.1480260 | 0.1000840 | 0.3268960 |
| H | 1.1624350 | 0.2710810 | 0.7340060 |
| C | 0.6983360 | -2.6030540 | -0.7856340 |
| C | -0.6981190 | -2.6030650 | -0.7855200 |
| C | -3.8004470 | -1.4928280 | -0.4265040 |
| H | -4.1360110 | -2.5127210 | -0.5904740 |
| C | -4.6094880 | -0.4099420 | -0.8032070 |
| H | -5.5884960 | -0.6021560 | -1.2347140 |
| H | -1.2284750 | -1.8857580 | 2.4860930 |
| H | -1.2239940 | -2.7029460 | -1.7318650 |
| H | 1.2240680 | -2.7029390 | -1.7320590 |
| H | 1.2292030 | -1.8857230 | 2.48588 |

Cartesian Coordinates for alkoxy bridging group of **34** (in Å):

| | | | |
|---|------------|------------|------------|
| O | 2.4612860 | -0.2841330 | -0.1052280 |
| O | -2.4612860 | -0.2841330 | -0.1052270 |
| C | 1.2781130 | 0.4911610 | 0.0459260 |
| H | 1.3095390 | 1.2271150 | -0.7649240 |
| H | 1.2914070 | 1.0549930 | 0.9941160 |
| C | 0.0000000 | -0.3454170 | -0.0538550 |
| H | 0.0000000 | -0.8947320 | -1.0022630 |
| H | 0.0000000 | -1.0978860 | 0.7523190 |
| C | -1.2781130 | 0.4911610 | 0.0459260 |
| H | -1.2914070 | 1.0549940 | 0.9941150 |
| H | -1.3095390 | 1.2271150 | -0.7649250 |
| H | -2.4862720 | -0.9234540 | 0.6236060 |
| H | 2.4862760 | -0.9234500 | 0.6236090 |

Cartesian Coordinates for *p*-terphenyl system of **34** (in Å):

| | | | |
|---|------------|-----------|------------|
| C | -5.7300110 | 0.0001460 | -0.0001880 |
| H | -6.8166550 | 0.0001850 | -0.0001910 |

| | | | |
|---|------------|------------|------------|
| C | -5.0259130 | 1.1822850 | -0.2365940 |
| C | -3.6319500 | 1.1815670 | -0.2373110 |
| H | -3.0949770 | 2.1018100 | -0.4500820 |
| C | -2.9087790 | -0.0000600 | 0.0000040 |
| C | -1.4246130 | -0.0001210 | 0.0001530 |
| C | -0.6956500 | 1.0835930 | 0.5181180 |
| C | 0.6956500 | 1.0835920 | 0.5181180 |
| C | 1.4246130 | -0.0001210 | 0.0001530 |
| C | 2.9087790 | -0.0000600 | 0.0000040 |
| C | 3.6321460 | -1.1815610 | 0.2373210 |
| H | 3.0953000 | -2.1018500 | 0.4502030 |
| C | 5.0260970 | -1.1820670 | 0.2363700 |
| H | 5.5633960 | -2.1068890 | 0.4299920 |
| C | 5.7300110 | 0.0001460 | -0.0001880 |
| H | 6.8166540 | 0.0001850 | -0.0001900 |
| C | 5.0259120 | 1.1822860 | -0.2365910 |
| C | 3.6319490 | 1.1815670 | -0.2373080 |
| H | 3.0949760 | 2.1018110 | -0.4500760 |
| C | 0.6956480 | -1.0838220 | -0.5178670 |
| C | -0.6956470 | -1.0838220 | -0.5178660 |
| C | -3.6321460 | -1.1815600 | 0.2373240 |
| H | -3.0953000 | -2.1018490 | 0.4502080 |
| C | -5.0260970 | -1.1820670 | 0.2363730 |
| H | -5.5633950 | -2.1068890 | 0.4299970 |
| H | -1.2267650 | 1.9225390 | 0.9592850 |
| H | -1.2267790 | -1.9227620 | -0.9590250 |
| H | 1.2267790 | -1.9227620 | -0.9590250 |
| H | 1.2267660 | 1.9225380 | 0.9592850 |
| H | -5.5630360 | 2.1071990 | -0.4302730 |
| H | 5.5630350 | 2.1072000 | -0.4302670 |

[1.] Gaussian 09, *Revision D.01*: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.