Pi-Extension of Strained Benzenoid Macrocycles Using the Scholl Reaction

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SCHEME SI-1: Synthesis of *p*-terphenyl-containing macrocycles presented in Scheme 3

2.



SCHEME SI-2: Synthesis of (non-macrocyclic) p-terphenyl model compound 7

3. General experimental conditions, procedures and characterization data

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, dichloromethane, nitromethane, toluene, ethanol, and water, that were used in Scholl or Suzuki reactions were purged with nitrogen or argon gas for 30 min prior to use.* 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 × 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 ¹³C nuclear magnetic resonance (NMR) spectra were recorded at 400 or 600 MHz, calibrated using residual undeuterated solvent as an internal reference (CHCl₃, 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, br s = broad singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet), 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).

New compounds: procedures and characterization data (listed in chronological order)



4,4",6,6"-tetrakis(4-t-butylphenyl)-3,3"-dimethoxy-p-terphenyl (7): Sodium carbonate (0.731 g, 6.89 mmol, as an aqueous solution, 3 mL H₂O) and 4-tertbutylphenylboronic acid (0.332 g, 1.85 mmol) were added sequentially to a stirred solution of 56 (0.140 g, 0.231 mmol) in toluene (9 mL), and ethanol (1.5 mL) at room temperature. After the addition was complete, a stream of nitrogen gas was passed over the reaction mixture for 3 min. Tetrakis(triphenylphosphine)palladium(0) (0.027 g, 0.023 mmol) was added, and nitrogen gas was once again passed over the reaction mixture for 2 min. The reaction was heated to 90 °C for 16 h and then cooled to room temperature.

Once cooled, water (40 mL) and 1 M HCl (10 mL) were added to the reaction mixture and the layers were separated. The aqueous phase was extracted with dichloromethane (3 × 10 mL), and the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 2.5 cm, 3-8% ethyl acetate/hexanes) to yield **7** as a white solid (0.160 g, 85%): R_f = 0.42 (1:19 ethyl acetate/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 7.60 – 7.58 (m, 4H), 7.49 – 7.47 (m, 6H), 7.28 – 7.27 (m, 4H), 7.13 (s, 4H), 7.11 – 7.10 (m, 4H), 7.07 (s, 2H), 3.92 (s, 6H), 1.40 (s, 18H), 1.33 (s, 18H); ¹³C NMR (151 MHz, CDCl₃) δ 155.74, 150.05, 149.25, 140.32, 140.02, 138.13, 135.15, 133.42, 133.24, 129.79, 129.73, 129.64, 129.33, 125.26, 124.81, 113.31, 55.98, 34.77, 34.59, 31.60, 31.58; HRMS (EI) calc'd for C₆₀H₆₆O₂ ([M]⁺) *m/z* = 818.5063, found 818.5024.



[5]helicene (8): A solution of iron(III) chloride (0.16 g, 0.96 mmol) in dichloromethane/nitromethane (9:1) was added dropwise to a stirred 0 °C solution of 7 (0.040 g, 0.048 mmol) in dichloromethane (8 mL). During the addition, a gentle stream of argon gas was passed through the reaction vessel, after which an argonfilled balloon was placed over the reaction. After 1 h, methanol (10 mL) and water (10 mL) were added to the reaction. The layers were separated and the aqueous phase extracted with dichloromethane (2 × 10 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 1.3 cm, 5% to 8% ethyl acetate/hexanes) to yield tetrabenz(*a*,*c*,*h*,*j*)anthracene

9 as a white solid (0.003 g, 7%) and **8** as a yellow solid (0.026 g, 65%).

tetrabenz(a,c,h,j)anthracene **9**: $R_f = 0.30$ (1:19 ethyl acetate/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 9.89 (s, 2H), 8.93 (d, J = 2.0 Hz, 2H), 8.60 (s, 2H), 8.56 (d, J = 8.6 Hz, 2H), 8.39 (s, 2H), 7.76 (dd, J = 8.5, 1.9 Hz, 2H), 7.74 – 7.72 (m, 4H), 7.59 – 7.57 (m, 4H), 4.20 (s, 6H), 1.59 (s, 18H), 1.44 (s, 18H); ¹³C NMR (151 MHz, CDCl₃) δ 156.26, 150.40, 149.28, 135.58, 131.50, 130.20, 129.57, 129.24, 128.68, 128.63, 128.06, 126.30, 125.81, 125.38, 124.26, 123.16, 119.18, 117.66, 104.15, 55.63, 35.24, 34.83, 31.74, 31.61; HRMS (EI) calc'd for $C_{60}H_{62}O_2$ ([M]⁺) m/z = 814.4750, found 814.4788.

[5]helicene **9**: $R_f = 0.17$ (1:19 ethyl acetate/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 8.64 (d, J = 2.1 Hz, 4H), 8.46 (d, J = 8.7 Hz, 2H), 8.26 (d, J = 2.0 Hz, 2H), 8.12 (s, 2H), 7.75 (d, J = 8.1 Hz, 4H), 7.59 – 7.54 (m, 6H), 4.13 (s, 6H), 1.45 (s, 18H), 1.11 (s, 18H); ¹³C NMR (151 MHz, CDCl₃) δ 156.36, 150.36, 146.88, 135.72, 131.41, 130.20,

130.03, 129.97, 129.65, 129.00, 127.77, 127.51, 126.00, 125.39, 125.20, 124.66, 123.06, 121.50, 104.41, 56.05, 34.86, 34.65, 31.66, 31.16; HRMS (EI⁺) calc'd for $C_{60}H_{62}O_2$ ([M]⁺) m/z = 814.4750, found 814.4772.



Tetrabenzanthracene 10: A solution of boron tribromide (0.014 g, 0.056 mmol, 0.28 M) in dichloromethane was added dropwise to a stirred 0 °C solution of **29B** (0.006 g, 0.007 mmol) in dichloromethane (2 mL). After the addition, the reaction was warmed to room temperature. After 1 h the reaction was poured into ice water (10 mL) and stirred for 5 min. The layers were separated and the aqueous phase extracted with dichloromethane (3 × 5 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The white solid residue was dissolved in acetone (4 mL) and methyl iodide (0.004 g, 0.028 mmol) was added at room temperature. The reaction was heated to

56 °C for 14 h and then cooled to room temperature. Once cooled, water (10 mL) was added and the layers separated. The aqueous phase was extracted with dichloromethane (3 × 5 mL), and the combined organic extracts were washed with brine (10 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (5 × 0.7 cm, 3:7 dichloromethane/hexanes) to yield **10** as a white solid (0.002 g, 35%), R_f = 0.56 (2:3 dichloromethane/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 10.00 (s, 1H), 9.73 (s, 1H), 8.95 (d, *J* = 2.0 Hz, 2H), 8.58 (s, 2H), 8.54 (d, *J* = 8.6 Hz, 2H), 8.32 (s, 2H), 7.78 – 7.70 (m, 6H), 7.61 – 7.54 (m, 4H), 4.12 (s, 6H), 1.60 (s, 19H), 1.44 (s, 19H); ¹³C NMR (151 MHz, CDCl₃) δ 156.24, 150.43, 149.39, 135.61, 131.52, 130.16, 129.61, 129.43, 128.75, 128.47, 128.02, 126.34, 125.89, 125.43, 124.35, 123.14, 119.34, 117.83, 117.53, 104.18, 55.76, 35.28, 34.87, 31.66, 31.57, 29.92. HRMS (EI) calc'd for C₆₀H₆₂O₂ ([M]⁺) *m/z* = 814.4750, found 814.4788.



1,9-dioxa[9](3,3")p-Terphenylenophane (13): *p*-Toluene sulfonic acid monohydrate (0.174 g, 0.913 mmol) was added to a stirred solution of **47** (0.060 g, 0.15 mmol) in toluene (6 mL), and the reaction was heated at 65 °C. After 1 h, the reaction was poured into water (50 mL) and further diluted with a saturated solution of NaHCO₃ (15 mL). The layers were separated and the aqueous phase extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous MgSO₄,

filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (15×1.3 cm, 50% dichloromethane/hexanes) to afford **13** as a white solid (0.038 g, 70%): $R_f = 0.50$ (1:1 dichloromethane/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 7.52 (s, 4H), 7.38 – 7.34 (m, 2H), 7.28 (d, J = 5.9 Hz, 2H), 6.85 (dd, J = 8.3, 2.7 Hz, 2H), 6.37 – 6.36 (m, 2H), 4.13 – 4.11 (m, 4H), 1.67 – 1.61 (m, 4H), 1.36 – 1.31 (m, 4H), 1.09 – 1.04 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 157.78, 143.82, 142.70, 130.47, 128.50, 116.82, 116.75, 115.91, 68.87, 30.84, 28.08, 27.27; HRMS (EI) calc'd for C₂₅H₂₆O₂ ([M]⁺) m/z = 358.1933, found 358.1925.



1,10-dioxa[10](3,3")*p*-Terphenylenophane (14): *p*-Toluene sulfonic acid monohydrate (0.180 g, 0.944 mmol) was added to a stirred solution of **48** (0.077 g, 0.19 mmol) in toluene (5.0 mL), and the reaction was heated at 60 °C. After 30 min, the reaction was cooled and poured into water (50 mL) and then further diluted with a saturated solution of NaHCO₃ (15 mL). The layers were separated and the aqueous phase extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with brine

(20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatograph (15 × 1.3 cm, 50% dichloromethane/hexanes) to afford **14** as a white solid (0.031 g, 44%); $R_f = 0.48$ (1:1 dichloromethane/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.56 (s, 4H), 7.36 (dd, J = 8.2, 7.4 Hz, 2H), 7.29 – 7.25 (m, 2H), 6.86 (ddd, J = 8.2, 2.7, 1.0 Hz, 2H), 6.63 (dd, J = 2.7, 1.5 Hz, 2H), 4.20 – 4.16 (m, 4H), 1.72 – 1.65 (m, 4H), 1.35 – 1.30 (m, 4H), 1.27 – 1.20 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 158.32, 143.42, 142.21, 130.38, 128.26, 116.94, 115.99, 115.70, 68.26, 30.05, 27.67, 26.47. HRMS (EI) calc'd for C₂₆H₂₈O₂ ([M]⁺) m/z = 372.2089, found 372.2099.



1,11-dioxa [11] (3,3')*p*-Terphenylenophane (15): *p*-Toluene sulfonic acid monohydrate (0.126 g, 0.660 mmol) was added to a stirred solution of compound **49** (mixture of diastereomers) (0.069 g, 0.17 mmol) in toluene (15 mL), and the reaction was heated at

80 °C. After 2 h, the reaction was cooled to room temperature and poured into water (10 mL) and then further diluted with a saturated solution of NaHCO₃ (10 mL). The layers were separated and the aqueous phase extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with brine (15 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 1.3 cm, 5% ethyl acetate/hexanes) to afford **15** as a white solid (0.047 g, 72%); R_f = 0.39 (1:19 ethyl acetate/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.60 (s, 4H), 7.41 – 7.33 (m, 2H), 7.24 (d, *J* = 7.5 Hz, 2H), 6.97 (s, 2H), 6.89 (dd, *J* = 8.2, 2.5 Hz, 2H), 4.19 (t, *J* = 8.3 Hz, 4H), 1.98 – 1.83 (m, 4H), 1.60 – 1.52 (m, 4H), 1.42 – 1.28 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 158.69, 143.08, 141.65, 130.30, 128.21, 117.63, 116.32, 113.54, 67.16, 32.25, 31.91, 27.77, 25.41; HRMS (EI) calc'd for C₂₇H₃₀O₂ ([M]⁺) *m/z* = 386.2246, found 386.2057.



1,12-dioxa[12](3,3")*p***-Terphenylenophane (16):** *p***-**Toluene sulfonic acid monohydrate (0.164 g, 0.595 mmol) was added to a stirred solution of compound **50** (mixture of diastereomers) (0.052 g, 0.12 mmol) in toluene (4.0 mL), and the reaction was heated at 65 °C. After 2.5 h, the reaction was cooled to room temperature and poured into water (40 mL) and then further diluted with a saturated solution of NaHCO₃ (10 mL). The layers were separated and the aqueous phase extracted with dichloromethane (3 × 10 mL).

The combined organic extracts were washed with brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 1.3 cm, 50% dichloromethane/hexanes) to afford **16** as a white solid (0.031 g, 65%): R_f = 0.55 (1:1 dichloromethane/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 4H), 7.41 – 7.32 (m, 2H), 7.26 (d, *J* = 7.5 Hz, 2H), 7.07 – 7.01 (m, 2H), 6.90 (dd, *J* = 8.1, 2.5 Hz, 2H), 4.25 – 4.16 (m, 4H), 1.97 – 1.85 (m, 4H), 1.51 – 1.44 (m, 8H), 1.42 – 1.35 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 158.87, 142.38, 141.02, 130.29, 127.86, 118.04, 116.77, 112.99, 68.28, 31.05, 29.75, 26.96, 25.78; HRMS (ESI) calculated for C₂₈H₃₃O₂ ([M+H]⁺) *m/z* = 401.2475, found 401.2481.



4,4",6,6"-tetrabromo-1,8-dioxa[8](3,3")p-terphenylophane (**18**): Bromine (0.368 g, 2.32 mmol) was added to a stirred solution of **12**¹ (0.100 g, 0.291 mmol) in 1,2-dichlorobenzene (5.0 mL) at room temperature. The resulting mixture was heated to 80 °C for 2 hours and then cooled to room temperature under a stream of nitrogen gas. After complete evaporation of the solvent, the residue was dissolved in dichloromethane (20 mL), an aqueous solution of 5% NaHSO₃ (10 mL) was added,

and the resulting mixture was stirred for 5 min. The layers were separated and the aqueous phase extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with a saturated solution of Na-HCO₃ (15 mL) and brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure to afford **18** as a white solid (0.180 g, 95%): R_f = 0.31 (3:7 dichloromethane/hexanes). ¹H NMR (600 MHz, CDCl₃) δ 7.81 (s, 2H), 7.42 (s, 4H), 5.87 (s, 2H), 4.09 (t, *J* = 7.4 Hz, 4H), 1.58 – 1.56 (m, 4H), 1.08 – 1.05 (m, 4H); ¹³C NMR (151 MHz, CDCl₃) δ 153.02, 143.01, 142.19, 136.41, 129.07, 119.30, 110.93, 110.18, 69.74, 27.55, 27.44; HRMS (EI) calc'd for C₂₄H₂₀O₂Br₄ ([M]⁺) *m/z* = 655.8197, found 655.8224.



4,4", 6,6"- *tetrabromo-1,9-dioxa[9](3,3")p-terphenylophane* (**19**): Bromine (0.71 g, 4.4 mmol) was added to a stirred solution of **13** (0.020 g, 0.056 mmol) in 1,2-dichlorobenzene (2.0 mL). The resulting mixture was heated to 70 °C for 6 h and then cooled to room temperature under a stream of nitrogen gas. After complete evaporation of the solvent, the residue was dissolved in dichloromethane (10 mL), an aqueous solution of 5% NaHSO₃ (10 mL) was added, and the resulting mixture

was stirred for 10 min. The layers were separated and the aqueous phase extracted with dichloromethane (2 × 15 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (20 mL) and brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure to yield **19** as a white solid (0.038 g, 95%): R_f = 0.34 (3:7 dichloromethane/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 7.80 (s, 2H), 7.45 (s, 4H), 6.23 (s, 2H), 4.13 – 4.10 (m, 3H), 1.72 – 1.67 (m, 4H), 1.29 – 1.24 (m, 4H), 1.16 – 1.09 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 153.50, 142.55, 141.59, 136.20, 128.86, 118.34, 110.79, 110.27, 69.03, 29.71, 26.45, 25.74; HRMS (APCI) calc'd for C₂₅H₂₂O₂Br₅ ([M+Br]⁻) m/z = 748.7537, found 748.7537.



4,4",6,6"-tetrabromo-1,10-dioxa[10](3,3")p-terphenylophane (**20**): Bromine (0.178 g, 1.12 mmol) was added to a stirred solution of **14** (0.052 g, 0.14 mmol) in 1,2-dichlorobenzene (6 mL). The resulting mixture was heated to 80 °C for 12

h and then cooled to room temperature under a stream of nitrogen gas. After complete evaporation of the solvent, the residue was dissolved in dichloromethane (15 mL), an aqueous solution of 5% NaHSO₃ (20 mL) was added, and the resulting mixture was stirred for 10 min. The layers were separated and the aqueous phase was extracted with dichloromethane (3 × 15 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (20 mL) and brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure to yield **20** as a white solid (0.090 g, 93%): $R_f = 0.37$ (3:7 dichloromethane/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 7.82 (s, 2H), 7.51 (s, 4H), 6.48 (s, 2H), 4.18 (t, J = 8.0 Hz, 4H), 1.74 – 1.69 (m, 4H), 1.31 – 1.29 (m, 4H), 1.23 – 1.20 (m, 4H); ¹³C NMR (151 MHz, CDCl₃) δ 154.22, 142.26, 141.19, 136.63, 128.99, 118.33, 111.12, 110.87, 69.93, 29.42, 27.29, 25.92; HRMS (APCI) calc'd for C₂₆H₂₄O₂Br₅ ([M+Br]⁻) m/z = 762.7693, found 762.7702.



4,4", **6,6"**-tetrabromo-1,11-dioxa [11] (3,3")p-terphenylophane (21): Bromine (0.150 g, 0.939 mmol) was added to a stirred solution of [11]PTPP (15) (0.025 g, 0.065 mmol) in 1,2-dichlorobenzene (5 mL). The resulting mixture was heated to 80 °C for 2.5 h and then cooled to room temperature under a stream of nitrogen gas. After evaporation of the solvent, the residue was dissolved in dichloromethane (10 mL), an aqueous solution of 5% NaHSO₃ (10 mL) was added, and

the resulting mixture was stirred for 10 min. The layers were separated and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with a saturated solution of Na-HCO₃ (20 mL) and brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure to yield **21** as a white solid (0.042 g, 92%): $R_f = 0.37$ (3:7 dichloromethane/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 7.84 (s, 2H), 7.53 (s, 4H), 6.76 (s, 2H), 4.23 – 4.20 (m, 4H), 1.87 – 1.82 (m, 4H), 1.41 – 1.26 (m, 10H); ¹³C NMR (151 MHz, CDCl₃) δ 154.09, 141.94, 140.58, 136.99, 129.19, 116.37, 111.49, 111.38, 68.05, 31.73, 31.28, 27.41, 25.00; HRMS (EI) calc'd for C₂₇H₂₆Br₄O₂ ([M]⁺) *m/z* = 697.8666, found 697.8684.



4,4", **6,6"-tetrabromo-1,12-dioxa [12]** (**3,3"**)*p*-terphenylophane (**22**): Bromine (0.052 g, 0.32 mmol) was added to a stirred solution of [12]PTPP (**16**) (0.016 g, 0.040 mmol) in 1,2-dichlorobenzene (2 mL). The resulting mixture was heated to 80 °C for 3 h and then cooled to room temperature under a stream of nitrogen gas. After complete evaporation of the solvent, the residue was dissolved in dichloromethane (10 mL), an aqueous solution of 5% NaHSO₃ (10 mL) was added,

and the resulting mixture was stirred for 10 min. The layers were separated and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (15 mL) and brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure to yield **22** as a white solid (0.029 g, >95%): $R_f = 0.40$ (3:7 dichloromethane/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 7.84 (s, 2H), 7.53 (s, 4H), 6.78 (s, 2H), 4.22 – 4.19 (m, 4H), 1.88 – 1.83 (m, 4H), 1.42 – 1.39 (m, 4H), 1.37 – 1.33 (m, 4H), 1.30 –1.26 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 154.28, 141.81, 140.43, 137.04, 129.17, 117.02, 112.09, 111.95, 69.27, 30.35, 29.19, 26.75, 25.38; HRMS (APCI) calc'd for C₂₈H₂₈O₂Br₅ ([M+Br]⁻) m/z = 794.7965, found 794.7942.



4,4",6,6"-tetrakis(4-t-butylphenyl)-1,7-dioxa[7](3,3")p-terphenylenophane (23): Sodium carbonate (0.590 g, 5.55 mmol) and 4-*tert*-butyphenylboronic acid (0.272 g, 1.51 mmol) were added sequentially to a stirred solution of **17**² (0.121 g, 0.185 mmol) in toluene (9 mL), water (3 mL), and ethanol (1.5 mL) at room temperature. After the addition was complete, a stream of nitrogen gas was passed over the reaction mixture for 3 min. Tetrakis(triphenylphosphine)palladium(0) (0.032 g, 0.028 mmol) was added, and nitrogen gas was once again passed over the reaction mixture for 3 min. The reaction was heated to 90 °C for 14 h and then cooled to room temperature. Once cooled, water (20 mL) and 1 M HCl (10 mL) were added and the layers separated.

The aqueous phase was extracted with dichloromethane (3 × 15 mL), and the combined organic extracts were washed with brine (20 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (5-20% ethyl acetate/hexanes) to yield **23** as a white solid (0.132 g, 83%): $R_f = 0.27$ (1:19 ethyl acetate/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.53 (m, 8H), 7.51 (s, 2H), 7.45 – 7.43 (m, 4H), 7.38 – 7.36 (m, 4H), 7.27 (d, J = 4.5 Hz, 4H), 6.02 (s, 2H), 4.13 (t, J = 7.4 Hz, 4H), 1.59 – 1.53 (m, 4H), 1.37 (s, 18H), 1.32 (s, 18H), 1.27 – 1.21 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 153.36, 150.02,

149.57, 143.98, 140.97, 137.12, 134.98, 132.65, 130.27, 129.97, 129.47, 129.24, 129.03, 125.44, 125.27, 120.40, 68.84, 34.77, 34.69, 31.59, 27.15, 23.37; HRMS (EI) calc'd for $C_{63}H_{70}O_2$ (M⁺) m/z = 858.5376, found 858.5389.



4,4",6,6"-tetrakis(4-t-butylphenyl)-1,8-dioxa[8](3,3")p-terphenylenophane (24): Sodium carbonate (0.480 g, 4.50 mmol) and 4-*tert*-butylphenylboronic acid (0.215 g, 1.20 mmol) were added sequentially to a stirred solution of **18** (0.101 g, 0.150 mmol) in toluene (6 mL), water (2 mL), and ethanol (1 mL) at room temperature. After the addition was complete, a stream of nitrogen gas was passed over the reaction mixture for 3 min. Tetrakis(triphenylphosphine)palladium(0) (0.021 g, 0.015 mmol) was added, and nitrogen gas was once again passed over the reaction mixture for 3 min. The reaction was heated to 90 °C for 7 h and then cooled to room temperature. Once cooled, water (20 mL) and 1 M HCI (10 mL) were added and the layers separated. The aqueous phase was extracted with dichloromethane (3 × 15

mL), and the combined organic extracts were washed with brine (20 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (5-20% ethyl acetate/hexanes) to yield **24** as a white solid (0.120 g, 92%): $R_f = 0.39$ (1:19 ethyl acetate/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.52 (m, 10H), 7.46 (d, J = 7.3 Hz, 4H), 7.39 – 7.37 (m, 4H), 7.28 (d, J = 4.6 Hz, 4H), 6.15 (s, 2H), 4.10 (t, J = 7.3 Hz, 4H), 1.71 – 1.67 (m, 4H), 1.39 – 1.36 (m, 36H), 1.19 – 1.16 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 153.07, 149.97, 149.43, 143.08, 140.86, 137.42, 135.16, 132.78, 130.78, 129.55, 129.47, 129.27, 125.34, 125.25, 119.27, 68.68, 34.76, 34.69, 31.61, 28.20, 27.43; HRMS (ESI) calc'd for C₆₄H₇₃O₂ ([M+H]⁺) *m/z* = 873.5611, found 873.5646.



4,4",6,6"-tetrakis(4-t-butylphenyl)-1,9-dioxa[9](3,3")p-terphenylenophane (25): Sodium carbonate (0.283 g, 2.67 mmol as an aqueous solution, 2 mL of H₂O) and 4-tert-butylphenylboronic acid (0.125 g, 0.712 mmol) were added sequentially to a stirred solution of 19 (0.061 g, 0.089 mmol) in toluene (6 mL) and ethanol (1.5 mL) at room temperature. After the addition was complete, a stream of nitrogen gas was passed over the reaction mixture for 3 min. Tetrakis(triphenylphosphine)palladium(0) (0.016 g, 0.014 mmol) was added, and nitrogen gas was once again passed over the reaction mixture for 3 min. The reaction was heated to 90 °C for 6 h and then cooled to room temperature. Once cooled, water (10 mL) and 1 M HCl (10 mL) were added and the layers separated.

The aqueous phase was extracted with dichloromethane (3 × 10 mL), and the combined organic extracts were washed with brine (20 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 1.3 cm, 1:19 ethyl acetate/hexanes) to yield **25** as a white solid (0.061 g, 77%): R_f = 0.38 (1:19 ethyl acetate/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 7.58 (d, *J* = 8.2 Hz, 4H), 7.50 (s, 2H), 7.47 – 7.43 (m, 8H), 7.32 (d, *J* = 8.3 Hz, 4H), 7.27 (s, 2H), 6.53 (s, 2H), 4.17 – 4.14 (m, 4H), 1.79 (t, *J* = 7.9 Hz, 4H), 1.38 (s, 18H), 1.36 – 1.32 (m, 4H), 1.31 (s, 18H), 1.29 – 1.28 (m, 2H), 1.22 – 1.16 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 153.96, 149.94, 149.42, 142.15, 140.54, 137.34, 135.13, 132.82, 131.15, 129.63, 129.39, 129.30, 129.26, 125.24, 125.09, 118.67, 68.92, 34.74, 34.60, 31.59, 31.53, 30.44, 27.53, 27.16; HRMS (APCI) calc'd for C₆₅H₇₅O₂ ([M+H]⁺) *m/z* = 887.5767, found 887.5747.



4,4",6,6"-tetrakis(4-t-butylphenyl)-1,10-dioxa[10](3,3")p-terphenylenophane

(26): Sodium carbonate (0.390 g, 3.69 mmol, as an aqueous solution, 2 mL of H_2O) and 4-*tert*-butylphenylboronic acid (0.165 g, 0.917 mmol) were added sequentially to a stirred solution of **20** (0.084 g, 0.12 mmol) in toluene (6 mL) and ethanol (1.5 mL) at room temperature. After the addition was complete, a stream of nitrogen gas was passed over the reaction mixture for 2 min. Tetrakis(triphenylphosphine)palladium(0) (0.020 g, 0.017 mmol) was added, and nitrogen gas was once again passed over the reaction mixture for 2 min. The reaction was heated to 90 °C for 3 h and then cooled to room temperature. Once cooled, water (20 mL) and 1 M HCI (10 mL) were added to the reaction mixture,

and the layers were separated. The aqueous phase was extracted with dichloromethane (3 × 15 mL), and the combined organic extracts were washed with brine (30 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 1.3 cm, 25% to 40% dichloromethane/hexanes) to yield **26** as a white solid (0.085 g, 78%): $R_f = 0.39$ (3:7 dichloromethane/hexanes); ¹H

NMR (600 MHz, CDCl₃) δ 7.58 (d, *J* = 8.1 Hz, 4H), 7.49 (s, 2H), 7.46 (d, *J* = 7.9 Hz, 4H), 7.38 (d, *J* = 8.0 Hz, 4H), 7.29 (d, *J* = 7.9 Hz, 4H), 7.23 (s, 4H), 6.73 (s, 2H), 4.22 (t, *J* = 8.0 Hz, 4H), 1.82 – 1.77 (m, 4H), 1.39 – 1.34 (m, 22H), 1.31 – 1.29 (m, 22H); ¹³C NMR (151 MHz, CDCl₃) δ 154.32, 149.90, 149.36, 141.59, 140.19, 137.42, 135.20, 133.16, 131.29, 129.63, 129.36, 129.29, 125.21, 124.98, 117.84, 68.70, 34.74, 34.57, 31.58, 29.48, 27.73, 25.86; HRMS (APCI) calc'd for C₆₆H₇₇O₂ ([M+H]⁺) *m/z* = 901.5924, found 901.5881.



4,4",6,6"-tetrakis(4-t-butylphenyl)-1,11-dioxa[11](3,3")p-terphenylenophane (**27**): Sodium carbonate (0.111 g, 1.05 mmol, as an aqueous solution, 1 mL of H_2O) and 4-*tert*-butylphenylboronic acid (0.052 g, 0.29 mmol) were added sequentially to a stirred solution of **21** (0.025 g, 0.036 mmol) in toluene (3 mL) and ethanol (1 mL) at room temperature. After the addition was complete, a stream of nitrogen gas was passed over the reaction mixture for 2 min. Tetrakis(triphenylphosphine)palladium(0) (0.007 g, 0.005 mmol) was added, and nitrogen gas was once again passed over the reaction mixture for 2 min. The reaction was heated to 80 °C for 14 h and then cooled to room temperature.

Once cooled, water (10 mL) and 1 M HCl (5 mL) were added to the reaction mixture, and the layers were separated. The aqueous phase was extracted with dichloromethane (3 × 10 mL), and the combined organic extracts were washed with brine (10 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (14 × 1.0 cm, 10% to 30% dichloromethane/hexanes) to yield **27** as a white solid (0.022 g, 70%): $R_f = 0.40$ (3:7 dichloromethane/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 7.59 (d, J = 8.0 Hz, 4H), 7.47 – 7.45 (m, 6H), 7.31 – 7.27 (m, 12H), 6.92 (s, 2H), 4.24 (t, J = 8.3 Hz, 4H), 1.97 – 1.92 (m, 4H), 1.55 – 1.51 (m, 4H), 1.44 – 1.41 (m, 2H), 1.39 (s, 18H), 1.38 – 1.36 (m, 2H), 1.34 (s, 18H), 1.31 – 1.29 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 154.17, 149.87, 149.20, 140.96, 139.81, 137.75, 135.30, 134.03, 131.63, 129.58, 129.56, 129.53, 129.31, 125.19, 124.85, 115.93, 67.22, 34.74, 34.58, 31.70, 31.60, 31.36, 31.18, 27.90, 25.32; HRMS (APCI) calc'd for C₆₇H₇₉O₂ ([M+H]⁺) *m/z* = 915.6080, found 915.6055.



4,4",6,6"-tetrakis(4-t-butylphenyl) 1,12-dioxa[12](3,3")p-terphenylenophane (28): Sodium carbonate (0.110 g, 1.05 mmol, as an aqueous solution, 1 mL of H_2O) and 4-*tert*-butylpheny boronic acid (0.061 g, 0.34 mmol) were added sequentially to a stirred solution of **22** (0.030 g, 0.042 mmol) in toluene (3 mL and ethanol (1 mL) at room temperature. After the addition was complete, a stream of nitrogen gas was passed over the reaction mixture for 3 min. Tetrakis(triphenylphosphine)palladium(0) (0.005 g, 0.004 mmol) was added, and nitrogen gas was once again passed over the reaction mixture for 2 min. The reaction was heated to 90 °C for 7 h and then cooled to room temperature. Once cooled, water (20 mL) was added to the reaction, and the layers were separated.

The aqueous phase was extracted with dichloromethane (3 × 10 mL), and the combined organic extracts were washed with brine (20 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (14 × 1.0 cm, 100% hexanes to 40% dichloromethane/hexanes) to yield **27** as a white solid (0.028 g, 74%): $R_f = 0.41$ (3:7 dichloromethane/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.57 (m, 4H), 7.47 – 7.46 (m, 2H), 7.46 – 7.45 (m, 2H), 7.43 (s, 2H), 7.27 – 7.26 (m, 12H), 6.93 (s, 2H), 4.22 – 4.18 (m, 4H), 1.95 – 1.91 (m, 4H), 1.46 – 1.40 (m, 7H), 1.39 – 1.37 (m, 21H), 1.36 – 1.32 (m, 20H); ¹³C NMR (101 MHz, CDCl₃) δ 154.39, 149.87, 149.20, 140.82, 139.76, 137.89, 135.34, 134.07, 132.07, 129.95, 129.58, 129.49, 129.29, 125.17, 124.83, 116.70, 68.42, 34.74, 34.59, 31.71, 31.60, 30.06, 29.03, 27.57, 25.54; HRMS (ESI) calc'd for C₆₈H₈₁O₂ ([M+H]⁺) *m/z* = 929.6237, found 929.6283.



Macrocycle 29B: A solution of Iron (III) chloride (0.088g, 0.054 mmol) in dichloromethane/nitromethane (9:1) was added dropwise to a stirred 0 °C solution of **23** (0.024 g, 0.028 mmol) in dichloromethane (5 mL). During the addition, a gentle stream of argon gas was passed through the reaction vessel, after which an argonfilled balloon was placed over the reaction. After 20 min, methanol (5 mL) and water (5 mL) were added. The layers were separated and the aqueous phase extracted with dichloromethane (2 × 10 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography (6 × 1.0

cm, 30% dichloromethane/hexanes) to yield **29B** as a white solid (0.021 g, 90%): $R_f = 0.37$ (3:7 dichloro-

methane/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 9.52 (s, 1H), 9.19 (s, 1H), 8.68 (d, *J* = 2.0 Hz, 2H), 8.26 – 8.24 (m, 4H), 7.70 – 7.68 (m, 4H), 7.66 – 7.63 (m, 4H), 7.57 – 7.55 (m, 4H), 3.78 (t, *J* = 7.2 Hz, 4H), 1.84 – 1.76 (m, 4H), 1.53 (s, 18H), 1.46 (s, 18H), 1.29 – 1.26 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 155.25, 150.16, 148.96, 135.74, 130.94, 129.88, 129.52, 129.17, 128.83, 127.87, 127.86, 125.79, 125.50, 125.34, 123.55, 122.96, 119.10, 118.42, 117.18, 105.75, 70.47, 35.09, 34.82, 31.66, 31.51, 29.89, 27.25, 24.32; HRMS (ESI) calc'd for C₆₃H₆₆O₂ ([M+H]⁺) *m/z* = 855.5141, found 855.5167.



Macrocycle 30B: A solution of Iron (III) chloride (0.092 g, 0.056 mmol) in dichloromethane/nitromethane (9:1) was added dropwise to a stirred 0 °C solution of **24** (0.025 g, 0.027 mmol) in dichloromethane (5 mL). During the addition, a gentle stream of argon gas was passed through the reaction vessel, after which an argonfilled balloon was placed over the reaction. After 20 min, methanol (5 mL) and water (5 mL) were added. The layers were separated and the aqueous phase was extracted with dichloromethane (2 × 10 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (14 × 1.0 cm,

20%-35% dichloromethane/hexanes) to yield **30B** as a white solid (0.020 g, 80%): $R_f = 0.49$ (2:3 dichloromethane/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 9.68 (s, 1H), 9.22 (s, 1H), 8.74 (s, 2H), 8.25 (d, J = 8.4 Hz, 2H), 8.20 (s, 2H), 7.78 (s, 2H), 7.70 – 7.67 (m, 6H), 7.57 (d, J = 8.0 Hz, 4H), 3.76 – 3.73 (m, 4H), 1.68 – 1.65 (m, 4H), 1.54 (s, 18H), 1.49 (s, 18H), 1.18 – 1.16 (m, 4H); ¹³C NMR (151 MHz, CDCl₃) δ 155.60, 150.05, 148.87, 135.89, 131.14, 129.72, 129.54, 129.01, 128.62, 127.85, 127.81, 125.77, 125.54, 125.33, 123.60, 123.05, 118.93, 117.11, 105.37, 69.90, 35.10, 34.83, 31.69, 31.57, 31.47, 27.49, 24.98; HRMS (ESI) calc'd for C₆₄H₆₈O₂ ([M+H]⁺) *m/z* = 869.5298, found 869.5266.



Macrocycle 31B: A solution of Iron (III) chloride (0.030 g, 0.18 mmol) in dichloromethane/nitromethane (9:1) was added dropwise to a stirred 0 °C solution of **25** (0.015 g, 0.017 mmol) in dichloromethane (3 mL). During the addition, a gentle stream of argon gas was passed through the reaction vessel, after which an argonfilled balloon was placed over the reaction. After 30 min, additional Iron (III) chloride solution (0.030 g, 0.18 mmol) was added. After 1 h, methanol (5 mL) and water (5 mL) were added. The layers were separated and the aqueous phase extracted with dichloromethane (2 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 1.0 cm,

30% dichloromethane/hexanes) to yield **31B** as a white solid (0.012 g, 80%): $R_f = 0.42$ (2:3 dichloromethane/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 9.98 (s, 1H), 9.61 (s, 1H), 8.93 (d, J = 2.1 Hz, 2H), 8.54 – 8.49 (m, 4H), 8.30 (s, 2H), 7.75 – 7.71 (m, 6H), 7.57 – 7.55 (m, 4H), 4.38 – 4.33 (m, 4H), 2.08 – 2.00 (m, 4H), 1.59 (s, 18H), 1.45 (s, 18H), 1.31 – 1.26 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 155.41, 150.17, 149.16, 135.90, 131.87, 130.03, 129.63, 129.31, 128.73, 128.41, 127.97, 126.22, 125.72, 125.33, 124.14, 123.11, 119.21, 117.18, 105.74, 100.18, 68.71, 35.21, 34.85, 31.69, 31.53, 28.14, 27.85, 25.54; HRMS (APCI) calc'd for C₆₅H₇₁O₂ ([M+H]⁺) *m/z* = 883.5454, found 883.5446.



Macrocycles 32A and 32B: A solution of Iron (III) chloride (0.329 g, 2.03 mmol) in dichloromethane/nitromethane (9:1) was added dropwise to a stirred solution of **26** (180 mg, 0.20 mmol) in dichloromethane (50 mL) under argon. After 15 min, methanol (10 mL) and water (20 mL) were added.. The organic layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 15) mL. The combined organic extracts were washed with brine (20 mL), dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (20 x 2.5 cm, 1:19 EtOAC/Hexanes) to yield **32B** (0.078 g, 43%) as a white solid and 32A (0.016 g, 9%) as a yellow solid.

Macrocycle **32B**: $R_f = 0.44$ (1:19 EtOAC/Hexanes); ¹H NMR; (600 MHz, CDCl₃) δ 9.91 (s, 1H), 9.56 (s, 1H), 8.8 (s, 2H), 8.44 – 8.42 (m, 4H), 8.07 (s, 2H), 7.78 (d, J = 7.9 Hz, 4H), 7.73 (dd, J = 8.5, 1.8 Hz, 2H), 7.56 (d, J = 7.9 Hz, 4H), 4.00 – 3.99 (m, 4H), 1.85 – 1.83 (m, 4H), 1.57 (s, 18H), 1.46 (s, 18H), 1.37 – 1.33 (m, 4H), 1.28 – 1.25

(m, 4H); ¹³C NMR (151 MHz, CDCl₃) δ 155.64, 150.16, 149.09, 135.70, 131.06, 129.86, 129.62, 129.18, 128.66, 128.25, 127.94, 125.98, 125.71, 125.29, 123.99, 123.14, 119.14, 117.59, 117.15, 104.91, 69.24, 35.19, 34.83, 31.67, 31.50, 30.10, 29.51, 25.55; HRMS (APCI) calc'd for $C_{66}H_{73}O_2$ ([M+H]⁺) *m/z* = 897.5611, found 897.5622.

Macrocycle **32A**: $R_f = 0.23$ (1:19 EtOAC/Hexanes; ¹H NMR (400 MHz, CDCl₃) 8.62 (s, 2H), 8.49 (d, J = 2.0 Hz, 2H), 8.45 (d, J = 8.9 Hz, 4H), 7.91 (s, 2H), 7.71-7.69 (m, 4H), 7.62 -7.60 (m, 2H), 7.54-7.52 (m, 4H), 4.55-4.40 (m, 4H), 1.64 (q, J = 7.0, 5.7 Hz, 4H), 1.51-1.43 (m, 4H), 1.42 (s, 18H), 1.37-1.35 (m, 2H), 1.27-1.22 (m, 2H), 1.20 (s, 18H); ¹³C NMR (101 MHz, CDCl₃) δ 153.11, 150.05, 146.45, 135.41, 131.63, 131.21, 130.53, 129.44, 129.27, 128.73, 128.26, 125.96, 125.52, 125.41, 125.16, 123.89, 123.04, 121.83, 110.20, 67.92, 34.66, 34.63, 31.44, 31.06, 31.01, 27.86, 27.76; HRMS (EI) calc'd for C₆₆H₇₂O₂ ([M]⁺) m/z = 896.5532, found 896.5496.



Macrocycle 33A: A solution of Iron (III) chloride (0.012 g, 0.070 mmol) in dichloromethane/nitromethane (9:1) was added dropwise to a stirred 0 °C solution of **27** (0.006 g, 0.007 mmol) in dichloromethane (3 mL). During the addition, a gentle stream of argon gas was passed through the reaction vessel, after which an argon-filled balloon was placed over the reaction. After 30 min, methanol (5 mL) and water (5 mL) were added to the reaction. The layers were separated and the aqueous phase extracted with dichloromethane (3 × 5 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (5 × 1.0 cm, 30% dichloromethane/hexanes) to

yield **33A** as a white solid (0.005 g, 80%): $R_f = 0.32$ (3:7 dichloromethane/hexanes); ¹H NMR (600 MHz, CDCl₃) δ 8.64 (s, 2H), 8.55 (s, 2H), 8.47 (d, J = 8.6 Hz, 2H), 8.39 (d, J = 2.0 Hz, 2H), 7.97 (s, 2H), 7.73 (d, J = 7.9 Hz, 4H), 7.59 – 7.54 (m, 6H), 4.50 – 4.39 (m, 4H), 1.89 – 1.78 (m, 4H), 1.67 – 1.62 (m, 4H), 1.57 – 1.53 (m, 4H), 1.43 (s, 18H), 1.32 – 1.29 (m, 2H), 1.14 (s, 18H); ¹³C NMR (151 MHz, CDCl₃) δ 153.76, 150.26, 146.52, 135.68, 131.62, 130.70, 129.99, 129.82, 129.51, 128.65, 128.42, 126.69, 125.99, 125.43, 125.39, 124.13, 123.17, 121.80, 108.11, 69.52, 34.83, 34.70, 33.33, 32.19, 31.63, 31.15, 28.65, 27.45; HRMS (APCI) calc'd for C₆₇H₇₅O₂ ([M+H]⁺) m/z = 911.5767, found 911.5812.



Macrocycle 34A : A solution of Iron (III) chloride (0.035 g, 0.21 mmol) in dichloromethane/nitromethane (9:1,) was added dropwise to a stirred 0 °C solution of **28** (0.010 g, 0.011 mmol) in dichloromethane (4 mL). During the addition, a gentle stream of argon gas was passed through the reaction vessel, after which an argon-filled balloon was placed over the reaction. After 30 min, methanol (5 mL) and water (5 mL) were added to the reaction. The layers were separated and the aqueous phase extracted with dichloromethane (3 × 5 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (5 × 1.0 cm, 5% ethyl acetate/hexanes) to yield

34A as a white solid (0.008 g, 80%): $R_f = 0.35$ (1:19 ethyl acetate/hexanes) ¹H NMR (600 MHz, CDCl₃) δ 8.66 (s, 2H), 8.58 (s, 2H), 8.47 (d, J = 8.6 Hz, 2H), 8.38 (d, J = 1.9 Hz, 2H), 8.11 (s, 2H), 7.74 (d, J = 7.9 Hz, 4H), 7.57 – 7.55 (m, 6H), 4.50 – 4.42 (m, 4H), 2.10 – 2.07 (m, 4H), 1.89 – 1.86 (m, 4H), 1.71 – 1.69 (m, 4H), 1.65 – 1.63 (m, 4H), 1.44 (s, 18H), 1.35 – 1.30 (m, 4H), 1.13 (s, 18H); ¹³C NMR (151 MHz, CDCl₃) δ 154.20, 150.23, 146.57, 135.74, 131.44, 130.20, ¹²⁰ $^{\circ}$ 5, 129.69, 129.55, 128.75, 128.12, 126.94, 126.00, 125.35, 124.05, 123.07, 121.80, 106.59, 68.40, 34.82, 34 31.87, 31.63, 31.13, 30.84, 29.89, 26.57, 26.40; HRMS (APCI) calc'd for C₆₅H₇₅O₂ ([M+H]⁺) m/z = 925.5924, round 925.59.



Dialdehyde 35: 1,7-Dibromoheptane (6.12 g, 23.7 mmol) was added to a stirred solution of 3hydroxybenzaldehyde (5.20 g, 42.6 mmol), K_2CO_3 (11.4 g, 82.8 mmol) and tetrabutylammonium iodide (0.875 g, 2.37 mmol) in DMF (50 mL) at room temperature. The reaction was heated at 80 °C for 24 h, at which point water (50 mL) and 1 M HCl (50 mL) were added sequentially. The resulting solution was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (50 mL) and brine (50 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (16 × 3.8 cm; 60% dichloromethane/hexanes to dichloromethane) to afford **35** as a white solid (5.19 g, 72%): $R_f = 0.30$ (7:3 dichloromethane/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 9.98 (s, 2H), 7.46 – 7.41 (m, 4H), 7.40 – 7.38 (m, 2H), 7.21 – 7.15 (m, 2H), 4.03 (t, J = 6.5 Hz, 4H), 1.83 (dt, J = 8.3, 6.3 Hz, 4H), 1.57 – 1.44 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 192.45, 159.88, 137.98, 130.23, 123.63, 122.20, 112.87, 68.40, 29.29, 29.28, 26.18; HRMS (ESI) calc'd for C₂₁H₂₅O₄ ([M+H]⁺) *m/z* = 341.1747, found 341.1747.



Dialdehyde 36: 1,8-Dibromooctane (5.98 g, 22.0 mmol) was added to a stirred solution of 3hydroxy benzaldehyde (5.10 g, 41.8 mmol), K₂CO₃ (7.58 g, 54.9 mmol) and tetrabutylammonium iodide (0.811 g, 2.20 mmol) in DMF (70 mL). The reaction was heated at 80 °C for 26 h, at which point the reaction was cooled to room temperature and water (50 mL) and 1 M HCI (50 mL) were added sequentially. The aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (25 mL) and brine (25 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 5 cm; 70% dichloromethane/hexanes to dichloromethane) to afford **36** as white solid (5.20 g, 70%); R_f = 0.21 (7:3 dichloromethane/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 9.97 (s, 2H), 7.45 – 7.41 (m, 4H),

7.39 (d, J = 2.5 Hz, 2H), 7.19 – 7.16 (m, 2H), 4.04 – 4.00 (m, 4H), 1.85 – 1.78 (m, 4H), 1.51 – 1.39 (m, 8H); ¹³C NMR (101 MHz, CDCl₃) δ 192.42, 159.87, 137.95, 130.20, 123.56, 122.17, 112.87, 68.42, 29.46, 29.30, 26.14; HRMS (APCI) calc'd for C₂₂H₂₆O₄Na ([M+Na]⁺) m/z = 377.1723, found 377.1725.



Dialdehyde 37: 1,9-Dibromononane (2.28 g, 7.96 mmol) was added to a stirred solution of 3-hydroxy benzaldehyde (1.90 g, 15.6 mmol), K₂CO₃ (2.82 g, 20.4 mmol) and tetrabutylammonium iodide (0.303 g, 0.821 mmol) in DMF (37 mL). The reaction was heated at 80 °C for 24 h, at which point water (20 mL) and 1 M HCl (10 mL) were added sequentially. The aqueous phase was extracted with dichloromethane (3 × 25 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (30 mL) and brine (30 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 5 cm; 60% dichloromethane/hexanes to dichloromethane) to afford **37** as a white solid (2.71 g, 90%); $R_f = 0.39$ (3:2 dichloromethane/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 9.97 (s, 2H), 7.46 – 7.41 (m, 4H), 7.39 – 7.38 (m, 2H), 7.20 – 7.15 (m, 2H), 4.02 (t, J = 6.5 Hz, 4H), 1.85 – 1.78 (m, 4H), 1.50 – 1.46 (m, 4H), 1.41 – 1.36 (m, 6H); ¹³C NMR (101

MHz, CDCl₃) δ 192.47, 159.93, 137.99, 130.23, 123.60, 122.22, 112.91, 68.49, 29.69, 29.50, 29.35, 26.22; HRMS (APCI) calc'd for C₂₃H₂₉O₄ ([M+H]⁺) *m/z* = 369.2060, found 369.2063.



Dialdehyde 38: 1,10-Dibromodecane (1.15 g, 3.84 mmol) was added to a stirred solution of 3-hydroxy benzaldehyde (0.890 g, 7.29 mmol), K_2CO_3 (1.32 g, 9.59 mmol) and tetrabutylammonium iodide (0.141 g, 0.383 mmol) in DMF (15 mL). The reaction was heated at 80 °C for 24 h, at which point water (20 mL) and 1 M HCl (10 mL) were added sequentially. The aqueous phase was extracted with dichloromethane (3 × 15 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (20 mL) and brine (15 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 2.5 cm; 60% to 90% dichloromethane/hexanes) to afford **38** as a white solid (0.857 g, 62 %): $R_f = 0.26$ (3:2 dichloromethane/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 9.97 (s, 2H), 7.47 – 7.41 (m, 4H), 7.40 – 7.37 (m, 2H), 7.21 – 7.14 (m, 2H), 4.02 (t, J = 6.6 Hz, 4H), 1.87 – 1.76 (m, 4H), 1.53 – 1.42 (m, 4H), 1.40 – 1.34 (m, 8H);

¹³C NMR (101 MHz, CDCl₃) δ 192.46, 159.91, 137.97, 130.21, 123.57, 122.20, 112.90, 68.49, 29.69, 29.55, 29.33, 26.21; HRMS (ESI) calc'd for C₂₄H₃₁O₄ ([M+H]⁺) m/z = 383.2217, found 383.2218.



1,4-Diketone 39: VinyImagnesium chloride (1.6 M in THF, 6.2 mL, 7.5 mmol) was added to a stirred 0 °C solution of dialdehyde **35** (1.52 g, 4.48 mmol) in dichloromethane (50 mL). After 1 h, the reaction mixture was poured into water (100 mL) and further diluted with 1 M HCl (50 mL). The aqueous phase was extracted with dichloromethane (3×25 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (30 mL) and brine (30 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was dissolved in dichloromethane (300 mL) and Hoveyda-Grubbs second-generation catalyst (0.085 g, 0.13 mmol) was added. The reaction was heated at 40 °C for 3 h, after which the

reaction mixture was cooled to room temperature and concentrated under reduced pressure. The dark brown residue was dissolved in 1:9 methanol/dichloromethane (50 mL), and sodium borohydride (0.851 g, 22.4 mmol) was added. After 11 h, the reaction mixture was poured into water (200 mL) and further diluted with 1 M HCl (20 mL). The layers were separated and the aqueous phase was extracted with dichloromethane ($3 \times 20 \text{ mL}$). The combined organic extracts were washed with water (30 mL) and brine (30 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The dark brown residue was dissolved in dichloromethane (45 mL) followed by the addition of pyridinium chlorochromate (2.90 g, 13.4 mmol). The reaction was stirred for 4 h, at which point silica gel was added to the reaction, and the slurry was passed through a pad of Celite (2.5 cm) and washed with diethyl ether ($3 \times 20 \text{ mL}$). The fitrate was concentrated under reduced pressure to give a brown residue, which was purified by flash chromatography ($20 \times 2.5 \text{ cm}$, dichloromethane) to afford 1,4-diketone **39** as a white solid (0.61 g, 37% from **35**): $R_f = 0.37$ (dichloromethane); ¹H NMR (600 MHz, CDCl_3) δ 7.48 (d, J = 7.6 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.37 – 7.31 (m, 2H), 7.07 (dd, J = 8.2, 2.6 Hz, 2H), 4.09 (t, J = 6.6 Hz, 4H), 3.31 (s, 4H), 1.80 – 1.76 (m, 4H), 1.49 – 1.43 (m, 6H); ¹³C NMR (151 MHz, CDCl_3) δ 200.30, 159.13, 138.16, 130.11, 120.99, 120.59, 114.07, 68.07, 35.25, 28.08, 27.92, 25.43; HRMS (ESI) calc'd for C₂₃H₂₇O₄ ([M+H]⁺) *m/z* = 367.1904, found 367.1892.



1,4-Diketone 40: Vinylmagnesium chloride (1.6 M in THF, 16 mL, 26 mmol) was added to a stirred 0 °C solution of dialdehyde **36** (4.15 g, 11.6 mmol) in dichloromethane (80 mL). After 30 min, the reaction mixture was poured into water (30 mL) and further diluted with 1 M HCl (20 mL). The aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (20 mL) and brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The white residue was dissolved in dichloromethane (800 mL), and Hoveyda-Grubbs second-generation catalyst (0.217 g, 0.347 mmol) was added. The reaction was heated at 40 °C for 5 h, after which the reaction mixture was cooled to room temperature and concentrated under reduced pressure.

(120 mL), and sodium borohydride (2.20 g, 58.0 mmol) was added. After 14 h, the reaction mixture was poured into water (50 mL) and further diluted with 1 M HCl (20 mL). The layers were separated and the aqueous phase extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with a saturated Na-HCO₃ solution (30 mL) and brine (30 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The dark brown residue was dissolved in dichloromethane (120 mL), followed by addition of pyridinium chlorochromate (7.50 g, 34.8 mmol). The reaction was stirred for 6 h, at which point silica gel was added to the reaction, and the slurry was passed through a pad of Celite (2.5 cm) and washed with diethyl ether (3 × 10 mL). The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (17 × 3.8 cm, 20% ethyl acetate/hexanes) to afford 1,4-diketone **40** as a white solid (1.80 g, 41% from **36**); R_f = 0.38 (1:4 ethyl acetate/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.49 (m, 4H), 7.38 – 7.34 (m, 2H), 7.09 (ddd, J = 8.2, 2.4, 1.1 Hz, 2H), 4.11 (t, J = 6.8 Hz, 4H), 3.34 (s, 4H), 1.82 - 1.75 (m, 4H), 1.51 – 1.39 (m, 8H); ¹³C NMR (101 MHz, CDCl₃) δ 200.12, 159.11, 138.19, 130.08, 120.81, 120.49, 114.15, 68.24, 34.99, 28.46, 28.06, 25.28; HRMS (ESI) calc'd for C₂₄H₂₉O₄ ([M+H]⁺) m/z = 381.2060, found 381.2066.



1,4-Diketone 41: Vinylmagnesium chloride (1.6 M in THF, 10 mL, 17 mmol) was added to a stirred 0 °C solution of dialdehyde **37** (2.56 g, 6.96 mmol) in dichloromethane (50 mL). After 30 min, the reaction mixture was poured into water (130 mL) and further diluted with 1 M HCl (30 mL). The aqueous phase was extracted with dichloromethane (3 × 30 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (30 mL) and brine (30 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The white residue was dissolved in dichloromethane (470 mL), and Hoveyda-Grubbs second-generation catalyst (0.131 g, 0.209 mmol) was added. The reaction was heated at 40 °C for 3 h, after which the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The dark brown residue was dissolved in 1:9 methanol/dichloromethane (70 mL) and sodium borohydride (1.59 g, 41.8 mmol) was added. After 5 h, the reaction mix-

ture was poured into water (100 mL) and further diluted with 1 M HCl (25 mL). The layers were separated and the aqueous phase extracted with dichloromethane (3×30 mL). The combined organic extracts were washed with a saturated NaHCO₃ solution (30 mL) and brine (30 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The dark brown residue was dissolved in dichloromethane (70 mL), followed by addition of pyridinium chlorochromate (4.50 g, 20.8 mmol). The reaction was stirred for 4 h, at which point silica gel was added to the reaction, and the slurry was passed through a pad of Celite (2.5 cm) and washed with diethyl ether

(3 × 20 mL). The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 3.8 cm, 20% ethyl acetate/hexanes) to afford 1,4-diketone **41** as a white solid (0.83 g, 30% from **37**): $R_f = 0.45$ (1:4 ethyl acetate/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.49 (m, 4H), 7.38 – 7.34 (m, 2H), 7.10 – 7.07 (m, 2H), 4.10 (t, J = 6.8 Hz, 4H), 3.37 (s, 4H), 1.81 – 1.74 (m, 4H), 1.45 – 1.35 (m, 10H); ¹³C NMR (101 MHz, CDCl₃) δ 200.19, 159.12, 138.48, 129.95, 121.29, 120.53, 113.37, 68.27, 34.58, 28.80, 28.58, 28.22, 25.43; HRMS (ESI) calc'd for C₂₅H₃₁O₄ ([M+H]⁺) m/z = 395.2217, found 395.2229.



1-4,Diketone 42: Vinylmagnesium chloride (1.6 M in THF, 3.1 mL, 4.8 mmol) was added to a stirred 0 °C solution of dialdehyde **38** (0.740 g, 1.94 mmol) in dichloromethane (20 mL). After 30 min, the reaction mixture was poured into water (20 mL) and further diluted with 1 M HCl (10 mL). The aqueous phase was extracted with dichloromethane (3×20 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (20 mL) and brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The white residue was dissolved in dichloromethane (130 mL), and Hoveyda-Grubbs second-generation catalyst (0.062 g, 0.099 mmol) was added. The reaction was heated at 40 °C for 5 h, after which the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The dark brown residue was dissolved in 1:9 methanol/dichloromethane (20 mL) and sodium borohydride (0.442 g, 11.6 mmol) was added. After 9 h, the reaction mix-

ture was poured into water (50 mL) and further diluted with 1 M HCl (15 mL). The layers were separated and the aqueous phase extracted with dichloromethane (3 × 15 mL). The combined organic extracts were washed with a saturated NaHCO₃ solution (20 mL) and brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The dark brown residue was dissolved in dichloromethane (20 mL), followed by addition of pyridinium chlorochromate (1.25 g, 5.81 mmol). The reaction was stirred for 30 h, at which point silica gel was added, and the slurry was passed through a pad of Celite (2.5 cm) and washed with diethyl ether (3 × 15 mL). The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 3.8 cm, 20% ethyl acetate/hexanes) to afford 1,4-diketone **42** as a white solid (0.20 g, 26% from **38**), R_f = 0.45 (1:4 ethyl acetate/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.48 (m, 4H), 7.39 – 7.32 (m, 2H), 7.10 (ddd, *J* = 8.2, 2.4, 1.3 Hz, 2H), 4.10 (t, *J* = 7.0 Hz, 4H), 3.37 (s, 4H), 1.83 – 1.74 (m, 4H), 1.48 – 1.41 (m, 4H), 1.35 – 1.29 (m, 8H); ¹³C NMR (101 MHz, CDCl₃) δ 200.23, 159.25, 138.62, 129.89, 121.40, 120.53, 113.15, 68.22, 34.56, 29.28, 28.63, 28.41, 25.70; HRMS (ESI) calc'd for C₂₆H₃₃O₄ ([M+H]⁺) *m/z* = 409.2373, found 409.2375.



Cyclohex-2-ene-1,4-diol 47: VinyImagnesium chloride (1.6 M in THF, 1.2 mL, 1.9 mmol) was added to a stirred solution of 1,4-diketone **39** (0.270 g, 0.738 mmol) in dichloromethane (8 mL) at 40 °C. After 30 min, the reaction mixture was poured into water (50 mL) and further diluted with 1 M HCI (30 mL). The aqueous phase was extracted with dichloromethane (3 × 15 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (20 mL) and brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (20 × 2.5 cm, 20% ethyl acetate/hexanes) to afford allylic alcohol **43** (0.145 g, 47%) as an inseparable mixture of

diastereomers (73:27 *d.r.*); $R_f = 0.23$ (1:4 ethyl acetate/hexane). The mixture of diastereomers was carried forward without purification. Grubbs second-generation catalyst (0.011 g, 0.013 mmol) was added to a stirred solution of **43** (0.110 g, 0.260 mmol) in dichloromethane (7 mL), and the reaction was heated to 40 °C. After 2 h, the reaction was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography (18 × 1.3 cm, 30% to 40% ethyl acetate/hexanes) to afford compound *anti*-**43** as a colorless oil (0.027 g, 26%) and **47** as an off-white solid (0.066 g, 64%).

Anti-allylic-1,4-diol 43 (*anti-***43**): R_f =0.23 (1:4 ethyl acetate/hexane); ¹H NMR (400 MHz, CDCl₃) 7.27-7.22 (m, 2H), 7.08 (ddd, *J* = 7.7, 1.8, 1.0 Hz, 2H), 6.78 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 2H), 6.72 (t, *J* = 2.1 Hz, 2H), 6.11 (dd, *J* = 17.2, 10.6 Hz, 2H), 5.22 (dd, *J* = 17.2, 1.0 Hz, 2H), 5.08 (dd, *J* = 10.6, 1.0 Hz, 2H), 4.01-3.91 (m, 4H), 1.98 (br s, 2H) 1.95-1.80 (m, 6H), 1.78-1.68 (m, 2H), 1.60-1.51 (m, 4H), 1.50-1.43 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) 159.21, 146.51, 145.09, 129.54, 117.67, 113.36, 112.70, 111.33, 76.72, 67.27, 35.70, 28.04, 26.95, 25.66; HRMS (ESI) calc'd for C₂₇H₃₄O₄Na ([M+Na⁺) *m/z* = 445.2349, found 445.2366.

Cyclohex-2-ene-1,4-diol 47: $R_f = 0.13$ (3:7 ethyl acetate/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.31 (m, 4H), 6.90 – 6.88 (m, 2H), 6.84 – 6.79 (m, 2H), 6.08 (s, 2H), 4.07 – 3.93 (m, 4H), 2.22 – 2.13 (m, 2H), 1.95 – 1.86 (m, 7H), 1.64 – 1.55 (m, 7H); ¹³C NMR (151 MHz, CDCl₃) δ 158.60, 147.80, 134.57, 129.90, 117.24, 112.90,

112.38, 72.62, 68.04, 36.35, 27.76, 27.39, 26.14; HRMS (ESI) calc'd for $C_{25}H_{29}O_3$ ([M- H_2O)+H]⁺) m/z = 377.2111, found 377.2102.



Cyclohex-2-ene-1,4-diol 48: Vinylmagnesium chloride (1.6 M in THF, 0.50 mL, 0.81 mmol) was added to a stirred solution of 1,4-diketone **40** (0.122 g, 0.322 mmol) in dichloromethane (3.0 mL) at 40 °C. After 30 min, the reaction mixture was poured into water (10 mL) and further diluted with 1 M HCl (10 mL). The aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with a saturated solution of Na-HCO₃ (10 mL) and brine (10 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure to afford allylic alcohol **44** as an inseparable mixture of diastereomers (*68:32 d.r.*); *R*_f = 0.41 (1:19 acetone/dichloromethane). The mixture of diastereomers with hydroxy ketone was carried forward and separated after the next synthetic step. The

residue was dissolved in dichloromethane (8.0 mL), and Grubbs' second-generation catalyst (0.008 g, 0.01 mmol) was added. The reaction was heated at 40 °C. After 2.5 h, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 1.3 cm, 5% to 10% acetone/dichloromethane) to afford *anti*-44 as colorless oil (0.019 g, 13%) and compound **48** as an off-white solid (0.076 g, 58%).

Anti-allylic-1,4-diol 44 (anti-44): $R_f = 0.41$ (1:19 acetone/dichloromethane); ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.24 (m, 2H), 7.04 (ddd, J = 7.8, 1.8, 0.9 Hz, 2H), 6.83-6.82 (m, 2H), 6.75 (ddd, J = 8.2, 2.5, 0.9 Hz, 2H), 6.12 (dd, J = 17.3, 10.7 Hz, 2H), 5.24 (dd, J = 17.2, 1.0 Hz, 2H), 5.09 (dd, J = 10.6, 1.0 Hz, 2H), 3.98 (t, J = 5.7 Hz, 4H), 1.96-1.90 (m, 3H), 1.85-1.74 (m, 6H) 1.60-1.38 (m, 9H); ¹³C NMR (101 MHz, CDCl₃) 159.25, 146.89, 144.89, 129.53, 117.73, 113.05, 112.70, 111.79, 76.75, 67.61, 35.68, 28.65, 27.98, 25.11; HRMS (ESI) calc'd for $C_{28}H_{33}O_2$ ([M-2H₂O)+H]⁺) *m/z* = 401.2474, found 401.2484.

Cyclohex-2-ene-1,4-diol 48: $R_f = 0.12$ (1:19 acetone/dichloromethane); ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.31 (m, 4H), 6.95 – 6.93 (m, 2H), 6.82 – 6.75 (m, 2H), 6.01 (s, 2H), 4.03 – 3.91 (m, 4H), 2.20 – 2.12 (m, 4H), 2.00 – 1.93 (m, 2H), 1.85 – 1.67 (m, 6H), 1.54 – 1.48 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 158.77, 147.85, 134.49, 129.87, 116.97, 114.53, 110.45, 72.60, 67.55, 36.15, 28.57, 26.96, 24.28; HRMS (EI) calc'd for C₂₆H₂₈O₂ ([M-2H₂O]⁺) *m/z* = 372.2089, found 372.2121.

Cyclohex-2-ene-1,4-diols 49: VinyImagnesium chloride (1.6 M in THF, 0.44 mL, 0.71 mmol) was added to a stirred solution of 1,4-diketone **37** (0.127 g, 0.322 mmol) in dichloromethane (3.0 mL) at 40 °C. After 30 min, the reaction mixture was poured into water (10 mL) and further diluted with 1 M HCl (10 mL). The aqueous phase was extracted with dichloromethane (3×10 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (10 mL) and brine (10 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The white residue was dissolved in dichloromethane (7.0 mL), and Grubbs' second-generation catalyst (0.014 g, 0.016 mmol) was added. The reaction was heated at 40 °C. The reaction was monitored by TLC, and it was observed that both syn and anti-isomers cyclized. After 19 h, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 1.3 cm, 10% to 25% acetone/chloroform) to afford *anti* **49** (0.026 g, 19%) and *syn* **49** (0.050 g, 38%) as off-white solids (*d.r. syn/anti* = 71:29).



anti-49: $R_f = 0.47$ (1:9 acetone/chloroform); ¹H NMR (600 MHz, CDCl₃) 7.31 - 7.27 (m, 2H), 7.23 (t, J = 2.0 Hz, 2H), 7.12 (d, J = 7.6 Hz, 2H), 6.85 (dd, J = 8.2, 2.5 Hz, 2H), 6.00 (s, 2H), 4.21 - 4.14 (m, 4H), 2.44 (d, J = 10.0 Hz, 2H), 2.07 (d, J = 10.0 Hz, 2H), 1.90 - 1.77 (m, 6H), 1.53 - 1.39 (m, 10H). ¹³C NMR (151 MHz, CDCl₃) δ 158.60, 149.11, 134.59, 129.68, 116.96, 116.24, 109.85, 71.85, 67.85, 35.51, 29.86, 29.84, 27.58, 25.37; HRMS (EI) calc'd for $C_{27}H_{30}O_2$ ([M-2H₂O]⁺) m/z = 386.2245, found 386.2254.



syn-**49**: $R_f = 0.18$ (1:9 acetone/chloroform); ¹H NMR (600 MHz, CDCl₃) 7.34 - 7.27 (m, 4H), 6.87 (t, J = 2.0 Hz, 2H), 6.79 (dt, J = 7.7, 1.9 Hz, 2H), 6.11 (s, 2H), 4.02 - 3.92 (m, 4H), 2.25 (d, J = 3.2 Hz, 2H), 2.21 - 2.14 (m, 2H), 1.95 -1.91 (m, 2H), 1.79 (qt, J = 10.9, 5.3 Hz, 4H), 1.60 (dt, J = 13.5, 6.8 Hz, 2H), 1.55 - 1.37 (m, 8H). ¹³C NMR (151 MHz, CDCl₃) δ 158.93, 148.09, 134.78, 130.07, 117.51, 113.56, 111.63, 72.64, 67.71, 36.47, 29.28, 27.95, 27.75, 25.67; HRMS (EI) calc'd for $C_{27}H_{30}O_2$ ([M-2H₂O]⁺) m/z = 386.2245, found 386.2245.

Cyclohex-2-ene-1,4-diols **50**: VinyImagnesium chloride (1.6 M in THF, 0.75 mL, 1.2 mmol) was added to a stirred solution of 1,4-diketone **42** (0.165 g, 0.415 mmol) in dichloromethane (5.0 mL) at 40 °C. After 30 min, the reaction mixture was poured into water (10 mL) and further diluted with 1 M HCl (10 mL). The aqueous phase was extracted with dichloromethane (3×10 mL). The combined organic extracts were washed with a saturated solution of NaHCO₃ (10 mL) and brine (10 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The white residue was dissolved in dichloromethane (5.0 mL), and Grubbs' second-generation catalyst (0.009 g, 0.01 mmol) was added. The reaction was heated at 40 °C. The reaction was monitored by TLC and it was observed that both syn and anti-diastereomers cyclized. After 2.5 h, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was cooled to room temperature and concentrated under reduced pressure. The residue was for 25% acetone/dichloromethane) to give **anti 50** (0.016 g, 18%) and *syn* **50** (0.037 g, 41%) as off-white solids (*d.r. syn/anti* = 70:30)



anti-**50**: $R_f = 0.55$ (1:19 acetone/dichloromethane); ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.24 (m, 2H), 7.23 – 7.20 (m, 2H), 7.14 – 7.09 (m, 2H), 6.84 (ddd, J = 8.2, 2.6, 1.0 Hz, 2H), 5.93 (s, 2H), 4.123 – 4.09 (m, 4H), 2.38 – 2.29 (m, 2H), 2.07 – 2.00 (m, 2H), 1.91 (s, 2H), 1.89 – 1.73 (m, 4H), 1.49 – 1.37 (m, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 158.70, 148.63, 134.43, 129.75, 117.17, 116.89, 110.42, 72.31, 68.28, 35.80, 30.25, 29.41, 27.57, 25.57; HRMS (ESI) calc'd for *anti* **50** C₂₈H₃₅O₃ ([M-H₂O)+H]⁺) *m/z* = 419.2580, found 419.2586.



syn-**50**: $R_f = 0.11$ (1:19 acetone/dichloromethane); ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.29 (m, 4H), 6.91 – 6.85 (m, 2H), 6.83 – 6.76 (m, 2H), 6.08 (s, 2H), 4.01 – 3.90 (m, 4H), 2.27 – 2.13 (m, 4H), 2.05 – 1.93 (m, 2H), 1.76 (tt, J = 6.8, 3.7 Hz, 4H), 1.56 – 1.47 (m, 2H), 1.43 – 1.34 (m, 10H); ¹³C NMR (101 MHz, CDCl₃) δ 158.98, 148.09, 134.74, 130.06, 117.50, 113.95, 111.58, 72.52, 67.82, 36.23, 29.03, 27.51, 27.23, 25.41; HRMS (ESI) calc'd for *syn* **50** C₂₈H₃₅O₃ ([M-H₂O)+H]⁺) m/z = 419.2580, found 419.2583.



4,4",6,6"-tetrabromo-3,3"-dimethoxy-p-terphenyl (**56**): Bromine (0.480 g, 3.00 mmol) was added to a stirred solution of 3,3"-dimethoxy-*p*-terphenyl (0.080 g, 0.28 mmol) in 1,2-dichlorobenzene (5 mL). The resulting mixture was heated to 70 °C for 2 h and then cooled to room temperature under a stream of nitrogen gas. After complete evaporation of the solvent, the residue was dissolved in dichloro-

methane (15 mL), a solution of 5% NaHSO₃ (15 mL) was added, and the resulting mixture was stirred for 10 min. The layers were separated and the aqueous phase extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with brine (20 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (15 × 2.5 cm, 10% to 40% dichloromethane/hexanes) to yield **56** as a pale yellow solid (0.096 g, 57%): R_f = 0.51 (2:3 dichloromethane/hexane); ¹H NMR (600 MHz, CDCl₃) δ 7.86 (s, 2H), 7.49 (s, 4H), 6.92 (s, 2H), 3.92 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 155.43, 142.20, 140.19, 136.83, 129.16, 114.49, 113.19, 111.62, 56.73; HRMS (EI) calc'd for C₂₀H₁₄O₂Br₄ ([M]⁺) m/z = 605.7686, found 605.7662.

4. ¹H and ¹³C NMR spectra













160 150 140 130 120 110 100

210 200 190 180 170

















































































5. Cartesian Coordinates for 7, 8, 26, and 32A in Å

Full geometry optimization 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 16 package of programs.

Compound 32A

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Compound 26

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н	1.89072900	4.73259300	3.69544400
Н	2.35345400	6.39847700	4.09748200

Compound 7:

С	-5.28389700	-2.96408500	0.86272800
С	-3.89177900	-2.92667900	0.73307500
С	-3.20735400	-1.77021200	0.34015400
С	-3.95903900	-0.59552700	0.05821300
С	-5.35299300	-0.66102000	0.18846100
Ċ	-6.02770900	-1.81553800	0.58432000
Ĥ	-3 34605700	-3 84692600	0 91257400
Н	-7 10785100	-1 80128600	0 67419700
C C	1 08054200	-2 25646400	-0.07602300
C C	2 52015700	2 55454500	0.20175000
C	2.55015700	2 97224600	-0.29175000
	2.00402700	-3.87334000	-0.00802200
	3.54610600	-1.50750000	-0.24962400
	4.17979400	-4.24803000	-0.90947700
H	2.09120000	-4.63332500	-0.65567600
C	4.85484700	-1.96477000	-0.56701300
С	5.18550000	-3.27820600	-0.90064800
Н	6.21539100	-3.52844100	-1.12842500
С	-1.72362400	-1.87326400	0.20792700
С	-1.02338200	-1.33700200	-0.88630700
Н	-1.56255100	-0.79180300	-1.65332100
С	0.35150500	-1.51408900	-1.01777900
Н	0.86488500	-1.09803700	-1.88014000
С	-0.98400700	-2.59209500	1.16231700
н	-1.49060000	-2.99869500	2.03314100
C	0 38691800	-2 79403300	1 01544300
Ĥ	0.92913400	-3 37054300	1 76077800
н	5 64872100	-1 22463800	-0 51793800
н	-5 03085100	0 23886000	
C C	3 32011300	0.25000500	0.18370400
	2,66704400	-0.15696600	0.10370400
	2.00794400	0.15000500	1.30431100
	3.00000100	0.90952100	-0.55000700
	2.59910100	1.45877000	1.85083400
Н	2.22972100	-0.64833600	1.97480200
С	3.80432800	2.22225100	-0.06603100
Н	4.38077100	0.71237300	-1.48111300
С	3.17741600	2.53057800	1.14842200
Н	2.10173900	1.64045900	2.79997100
Н	4.25477100	3.00737400	-0.66374600
С	-3.36888200	0.70878700	-0.35702100
С	-2.33795500	1.33812500	0.35973800
С	-3.87553700	1.38175200	-1.47710800
С	-1.83831900	2.57342300	-0.03929300
Н	-1.92387400	0.85362300	1.23887700
С	-3.37342700	2.62350700	-1.87105700
H	-4 66541000	0.91804300	-2 06269700
C	-2 33968800	3 25087900	-1 16557400
Ч	-2.00000000	3 015/1800	0 5/511000
	3 800/1600	3.00366200	2 75027000
11 C	1 74266400	3.09300200	1 5027200
	-1.74300400	4.00070000	-1.30373200
	-2.4/2/6400	5.21962200	-2.79476100
Н	-3.53463500	5.39332300	-2.58577800
н	-2.02205400	6.18645600	-3.0462/900
Н	-2.39854500	4.58172800	-3.68273100
С	-0.25682000	4.41186200	-1.96625400
Н	0.19726200	5.37187300	-2.24252500
Н	0.32473200	3.98820800	-1.14089000
Н	-0.16001600	3.73173400	-2.82029300

С	-1.84727100	5.60780900	-0.40880100
Н	-1.41938000	6.57664300	-0.69465000
Н	-2.89321400	5.76918600	-0.12355400
Н	-1.31053900	5.25696900	0.47842400
С	3.14941900	3.95054000	1.74296800
С	1.69581100	4.37145100	2.05963400
Н	1.21265300	3.68595300	2.76337400
Н	1.67797200	5.37266000	2.50742800
Н	1.08982100	4.39987600	1.14703200
С	3.97459100	3.96003200	3.05295100
Н	5.01534600	3.67501000	2.86147200
Н	3.97204900	4.96156500	3.50109100
Н	3.56794000	3.26076800	3.79128300
С	3.75104200	4.99815300	0.78695900
Н	4.80614600	4.79620200	0.57091800
Н	3.20875500	5.03920100	-0.16471800
Н	3.69418500	5.99233200	1.24468800
0	4.36787900	-5.56818600	-1.20430300
0	-5.81011200	-4.16302400	1.25238000
С	5.67792500	-5.99817800	-1.53575600
Н	5.60013800	-7.06810700	-1.73783800
Н	6.05705800	-5.48710000	-2.43087900
Н	6.37910700	-5.83662500	-0.70602600
С	-7.21908100	-4.26396900	1.37655000
Н	-7.42011300	-5.29177000	1.68460000
Н	-7.60893700	-3.57533100	2.13814600
Н	-7.72452800	-4.06653900	0.42169400

Compound 8:

С	-4.98584500	-3.11191600	-0.58925100
С	-3.60435000	-3.14116500	-0.42828300
С	-2.88249400	-1.99825500	-0.04473100
С	-3.58831300	-0.78813700	0.19808800
Ċ	-4.98195800	-0.78008700	0.00738400
C C	-5 68464600	-1 91161400	-0.37876600
н	-3 10608800	-4 07730900	-0.64891000
н	-6 75762000	-1 85230800	-0 52002200
C C	1 / 19622000	2 01022100	0.02121200
	2 99249000	-2.01022100	-0.03121200
	2.00240900	-1.99626600	0.04471100
	3.60434100	-3.14118000	0.42826200
	3.58831300	-0.78815000	-0.19810900
C	4.98583500	-3.11193600	0.58922900
H	3.10607500	-4.07732100	0.64889200
С	4.98195900	-0.78010600	-0.00740800
С	5.68464200	-1.91163700	0.37874000
Н	6.75761700	-1.85242700	0.51999000
С	-1.41862700	-2.01021600	0.03119400
С	-0.70773600	-0.79119500	0.14127600
С	0.70773500	-0.79119700	-0.14128500
С	-0.68572000	-3.21873700	-0.03228400
Н	-1.20753500	-4.16811200	-0.06332400
С	0.68571000	-3.21874000	0.03225900
Н	1.20752200	-4.16811800	0.06329000
н	5.53810800	0.14047700	-0.14862500
Н	-5.53810300	0.14050000	0.14860000
C	2.85291100	0.37119400	-0.69335100
C C	3 50918300	1 47622100	-1 27757200
C C	1 43497500	0.37312600	-0.67120900
C	2 80987500	2 51622300	-1 85675700
н	4 59308700	1 49624800	-1 31886500
C C	0 75050800	1 /2020000	-1 32136100
C	1 3087/000	2 50403700	1 01580100
	2 26745500	2.30403700	2 20810000
	0.22702200	3.33203400	-2.30019000
	-0.32702300	1.37170300	-1.37120300
	-2.65290900	0.37120300	0.09333600
	-3.50917800	1.47623000	1.27750100
	-1.43497300	0.37312800	0.67120300
C	-2.80986800	2.51622900	1.85674900
H	-4.59308200	1.49626000	1.31885200
C	-0.75050400	1.42929400	1.32136500
С	-1.39874100	2.50403800	1.91579800
Н	-3.36744700	3.33205500	2.30819200
Н	0.32702600	1.37169300	1.37127200
С	0.65237700	3.62799300	-2.65606600
С	1.03092200	4.99618300	-2.04106400
Н	0.51277600	5.80656400	-2.56828000
Н	0.74687900	5.04375200	-0.98353200
Н	2.10613000	5.19350500	-2.10645000
С	-0.87779400	3.47197000	-2.57339700
Н	-1.36169300	4.30658300	-3.09359000
Н	-1.21973800	2.54606600	-3.04925400
Н	-1.23310500	3.47303000	-1.53695700
С	1.06150000	3.61288700	-4.14882200
Ĥ	2.13912700	3,76139700	-4.27698200
H	0.79806900	2,65744700	-4.61648100
Н	0.54627500	4.41298600	-4.69477800
	J.J.J.J., 0000		

С	-0.65236600	3.62797400	2.65609100
С	0.87780000	3.47175100	2.57371400
Н	1.36171100	4.30642200	3.09380400
Н	1.21955700	2.54591400	3.04983600
Н	1.23328400	3.47253600	1.53733300
С	-1.06176400	3.61305200	4.14877300
Н	-0.54656200	4.41315300	4.69474800
Н	-2.13940100	3.76167800	4.27671700
Н	-0.79851300	2.65763100	4.61657300
С	-1.03062300	4.99615800	2.04089800
Н	-2.10580900	5.19365100	2.10611400
Н	-0.51242800	5.80651300	2.56810500
Н	-0.74642400	5.04357800	0.98340100
0	-5.56587000	-4.28851000	-0.97235600
0	5.56585600	-4.28853300	0.97232700
С	6.96971500	-4.31295200	1.17129400
Н	7.27835700	-3.62537900	1.97012400
Н	7.21210100	-5.33602000	1.46498300
Н	7.51435000	-4.06290300	0.25102400
С	-6.96974100	-4.31294600	-1.17123500
Н	-7.27844100	-3.62539200	-1.97006000
Н	-7.21213500	-5.33602100	-1.46488700
Н	-7.51431800	-4.06288200	-0.25093700

6. Excitation energies and oscillator strengths for Compounds 8 and 32A:

Compound 8:

Excited State 216 -> 223 217 -> 221 217 -> 222 218 -> 221 219 -> 220	1: Triplet-A 0.13361 0.11768 0.12945 0.47322 -0.41362	2.3658 eV	524.06 nm	f=0.0000	<\$**2>=2.000
Excited State 215 -> 224 217 -> 221 218 -> 221 219 -> 220	2: Triplet-A -0.10444 0.10240 0.42875 0.48609	2.8795 eV	430.57 nm	f=0.0000	<s**2>=2.000</s**2>
Excited State 214 -> 221 216 -> 221 216 -> 222 217 -> 220 217 -> 223 218 -> 220 218 -> 223 219 -> 221 219 -> 222 219 -> 224	3: Triplet-A 0.11919 0.15547 -0.14695 -0.20069 -0.10134 -0.32601 0.13540 0.41641 0.12227 0.10658	2.8827 eV	430.09 nm	f=0.0000	<s**2>=2.000</s**2>
Excited State 215 -> 220 216 -> 221 216 -> 222 217 -> 220 217 -> 223 218 -> 220 218 -> 223 219 -> 221 219 -> 222 219 -> 224	4: Triplet-A -0.16655 0.11499 -0.20207 -0.21773 -0.14770 0.31822 0.19059 -0.26992 0.13903 0.23299	3.0707 eV	403.77 nm	f=0.0000	<s**2>=2.000</s**2>
Excited State 218 -> 220 219 -> 221	5: Triplet-A 0.50513 0.45429	3.1521 eV	393.34 nm	f=0.0000	<s**2>=2.000</s**2>
Excited State 218 -> 220 219 -> 221	6: Singlet-A 0.49439 0.49070	3.2654 eV	379.69 nm	f=0.0000	<s**2>=0.000</s**2>
Excited State 210 -> 221 212 -> 226 213 -> 227 214 -> 224 215 -> 220 216 -> 221 216 -> 222 217 -> 220 217 -> 223	7: Triplet-A 0.11113 -0.11432 0.11019 -0.13383 -0.26407 -0.22466 0.16223 -0.16223 -0.17035 0.15226	3.3401 eV	371.20 nm	f=0.0000	<s**2>=2.000</s**2>

217 -> 225 218 -> 223 219 -> 222 219 -> 224	-0.11137 -0.18216 -0.14013 0.29005				
Excited State 218 -> 221 219 -> 220	8: Singlet-A -0.40627 0.56821	3.4188 eV	362.65 nm	f=0.3159	<s**2>=0.000</s**2>
Excited State 218 -> 221 218 -> 222 219 -> 220	9: Singlet-A 0.55489 0.11947 0.38782	3.5977 eV	344.62 nm	f=1.2793	<s**2>=0.000</s**2>
Excited State 218 -> 220 219 -> 221 219 -> 222	10: Singlet-A -0.46826 0.47458 0.14909	3.7233 eV	333.00 nm	f=0.1352	<s**2>=0.000</s**2>
Excited State 216 -> 220 217 -> 221 218 -> 221 218 -> 222 219 -> 223	11: Singlet-A 0.34909 0.50526 0.10083 -0.20405 0.20519	3.7754 eV	328.40 nm	f=0.1141	<s**2>=0.000</s**2>
Excited State 215 -> 220 217 -> 220 218 -> 223 219 -> 222	12: Singlet-A -0.13052 0.62653 -0.11825 0.22731	3.8403 eV	322.85 nm	f=0.0029	<s**2>=0.000</s**2>

Compound 32A:

Excited State 239 -> 245 240 -> 244 241 -> 243 241 -> 244 242 -> 243	1:	Triplet-A -0.12175 0.18535 -0.17170 0.35141 0.45572	2.3458 e	V 528.53 ni	m f=0.000)0 <s**2>=2.00</s**2>	0
Excited State 239 -> 244 240 -> 243 241 -> 243 241 -> 244 242 -> 243 242 -> 244	2:	Triplet-A 0.11965 0.13847 0.21664 -0.37895 0.38521 0.22649	2.8493 e\	√ 435.15 nn	n f=0.000	0 <s**2>=2.000</s**2>)
Excited State 239 -> 243 239 -> 245 240 -> 243 240 -> 244 241 -> 243 241 -> 243 241 -> 244 241 -> 245 242 -> 244 242 -> 246	3:	Triplet-A -0.11834 -0.21179 0.20595 0.25088 0.12365 0.17474 -0.10998 -0.23419 0.30503 0.14166	2.8707 eV	431.89 nm	f=0.0000	<s**2>=2.000</s**2>	
Excited State 238 -> 243 239 -> 245 240 -> 243 241 -> 243 241 -> 244 241 -> 247 242 -> 244 242 -> 246 242 -> 247	4:	Triplet-A 0.11840 0.10848 -0.17723 0.44048 0.18845 -0.13731 0.22749 -0.18471 -0.16059	3.0028 eV	412.90 nm	f=0.0000	<s**2>=2.000</s**2>	
Excited State 239 -> 245 241 -> 243 242 -> 244	5:	Triplet-A 0.11265 -0.39799 0.49115	3.0838 eV	402.05 nm	f=0.0000	<s**2>=2.000</s**2>	
Excited State 241 -> 243 242 -> 243 242 -> 244	6:	Singlet-A -0.45118 -0.20054 0.47698	3.2220 eV	384.80 nm	f=0.0157	<s**2>=0.000</s**2>	
Excited State 238 -> 243 239 -> 243 239 -> 245 240 -> 243 240 -> 244 241 -> 243 241 -> 244 241 -> 245	7:	Triplet-A -0.16587 0.11327 0.15704 0.35482 -0.16824 0.13679 0.10438 0.12034	3.2693 eV	379.23 nm	f=0.0000	<s**2>=2.000</s**2>	

241 -> 247 242 -> 245 242 -> 246	-0.14729 -0.17154 0.22899				
Excited State 241 -> 243 241 -> 244 242 -> 243 242 -> 244	8: Singlet-A -0.13103 0.24463 0.61879 0.16693	3.3326 eV	372.03 nm	f=0.4949	<s**2>=0.000</s**2>
Excited State 240 -> 243 241 -> 244 242 -> 243	9: Singlet-A 0.17025 0.60323 -0.22233	3.5282 eV	351.40 nm	f=0.5427	<s**2>=0.000</s**2>
Excited State 240 -> 243 240 -> 244 241 -> 243 242 -> 244 242 -> 247	10: Singlet-A -0.18909 -0.12864 0.47139 0.42002 0.12135	3.6133 eV	343.13 nm	f=0.0987	<s**2>=0.000</s**2>
Excited State 239 -> 243 239 -> 244 240 -> 243 240 -> 244 241 -> 244 242 -> 243 242 -> 244 242 -> 244 242 -> 245 242 -> 247	11: Singlet-A 0.27672 0.13878 0.44192 -0.27851 -0.23185 0.11648 0.10279 0.13286 -0.10004	3.7364 eV	331.83 nm	f=0.4949	<s**2>=0.000</s**2>
Excited State 238 -> 243 239 -> 243 240 -> 243 240 -> 245 242 -> 244 242 -> 245	12: Singlet-A -0.11345 0.49777 -0.34839 0.12988 -0.12589 0.22468	3.7829 eV	327.75 nm	f=0.0364	<s**2>=0.000</s**2>

¹ Mitra, N. K.; Meudom, R.; Corzo, H. H.; Gorden, J. D.; Merner, B. L. *J. Am. Chem. Soc.* **2016**, *138*, 3235-3240. ² Mitra, N. K.; Meudom, R.; Gorden, J. D.; Merner, B. L. *Org. Lett.* **2015**, *17*, 2700-2703.