## Supporting Information for

# 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 $\left(120^{\circ} \mathrm{C}\right)$ 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 $\mu \mathrm{m}$ ), 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 ( $\mathrm{pH}=7.0$ ). 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. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ nuclear magnetic resonance (NMR) spectra were recorded at 400 or 600 MHz , calibrated using residual undeuterated solvent as an internal reference $\left(\mathrm{CHCl}_{3}, \delta 7.27\right.$ and 77.2 ppm ), reported in parts per million relative to trimethylsilane (TMS, $\delta 0.00 \mathrm{ppm}$ ), and presented as follows: chemical shift ( $\delta, \mathrm{ppm}$ ), multiplicity ( $\mathrm{s}=$ singlet, br $\mathrm{s}=$ broad singlet, $\mathrm{d}=$ doublet, dd = doublet of doublets, $t=$ triplet, $m=$ multiplet), coupling constants $(J, H z)$. 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 ( $0.731 \mathrm{~g}, 6.89 \mathrm{mmol}$, as an aqueous solution, $3 \mathrm{~mL} \mathrm{H} \mathrm{H}_{2} \mathrm{O}$ ) and 4-tertbutylphenylboronic acid ( $0.332 \mathrm{~g}, 1.85 \mathrm{mmol}$ ) were added sequentially to a stirred solution of $56(0.140 \mathrm{~g}, 0.231 \mathrm{mmol})$ in toluene $(9 \mathrm{~mL})$, 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) ( $0.027 \mathrm{~g}, 0.023 \mathrm{mmol}$ ) was added, and nitrogen gas was once again passed over the reaction mixture for 2 min . The reaction was heated to $90{ }^{\circ} \mathrm{C}$ for 16 h and then cooled to room temperature. Once cooled, water $(40 \mathrm{~mL})$ and $1 \mathrm{M} \mathrm{HCl}(10 \mathrm{~mL})$ were added to the reaction mixture and the layers were separated. The aqueous phase was extracted with dichloromethane ( $3 \times 10 \mathrm{~mL}$ ), and the combined organic extracts were washed with brine ( 30 mL ), dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $15 \times 2.5 \mathrm{~cm}, 3-8 \%$ ethyl acetate/hexanes) to yield 7 as a white solid $(0.160 \mathrm{~g}, 85 \%)$ : $R_{f}=0.42$ (1:19 ethyl acetate/hexanes); ${ }^{1} \mathrm{H} \mathrm{NMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.60-7.58(\mathrm{~m}$, $4 \mathrm{H}), 7.49-7.47(\mathrm{~m}, 6 \mathrm{H}), 7.28-7.27(\mathrm{~m}, 4 \mathrm{H}), 7.13(\mathrm{~s}, 4 \mathrm{H}), 7.11-7.10(\mathrm{~m}, 4 \mathrm{H}), 7.07(\mathrm{~s}, 2 \mathrm{H}), 3.92(\mathrm{~s}, 6 \mathrm{H}), 1.40(\mathrm{~s}$, $18 \mathrm{H}), 1.33(\mathrm{~s}, 18 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(151 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 155.74,150.05,149.25,140.32,140.02,138.13,135.15$, $133.42,133.24,129.79,129.73,129.64,129.33,125.26,124.81,113.31,55.98,34.77,34.59,31.60,31.58$; HRMS (EI) calc'd for $\mathrm{C}_{60} \mathrm{H}_{66} \mathrm{O}_{2}\left([\mathrm{M}]^{+}\right) \mathrm{m} / \mathrm{z}=818.5063$, found 818.5024 .

[5]helicene (8): A solution of iron(III) chloride ( $0.16 \mathrm{~g}, 0.96 \mathrm{mmol}$ ) in dichloromethane/nitromethane (9:1) was added dropwise to a stirred $0{ }^{\circ} \mathrm{C}$ solution of 7 $(0.040 \mathrm{~g}, 0.048 \mathrm{mmol})$ in dichloromethane $(8 \mathrm{~mL})$. 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 $(10 \mathrm{~mL})$ were added to the reaction. The layers were separated and the aqueous phase extracted with dichloromethane $(2 \times 10 \mathrm{~mL})$. The combined organic extracts were washed with brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography $(15 \times 1.3 \mathrm{~cm}, 5 \%$ to $8 \%$ ethyl acetate/hexanes) to yield tetrabenz(a,c,h,j)anthracene 9 as a white solid ( $0.003 \mathrm{~g}, 7 \%$ ) and 8 as a yellow solid ( $0.026 \mathrm{~g}, 65 \%$ ).
tetrabenz(a,c,h,j)anthracene 9: $\mathrm{R}_{f}=0.30$ (1:19 ethyl acetate/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 9.89(\mathrm{~s}, 2 \mathrm{H})$, $8.93(\mathrm{~d}, \mathrm{~J}=2.0 \mathrm{~Hz}, 2 \mathrm{H}), 8.60(\mathrm{~s}, 2 \mathrm{H}), 8.56(\mathrm{~d}, \mathrm{~J}=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 8.39(\mathrm{~s}, 2 \mathrm{H}), 7.76(\mathrm{dd}, J=8.5,1.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.74-$ $7.72(\mathrm{~m}, 4 \mathrm{H}), 7.59-7.57(\mathrm{~m}, 4 \mathrm{H}), 4.20(\mathrm{~s}, 6 \mathrm{H}), 1.59(\mathrm{~s}, 18 \mathrm{H}), 1.44(\mathrm{~s}, 18 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (151 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta$ $156.26,150.40,149.28,135.58,131.50,130.20,129.57,129.24,128.68,128.63,128.06,126.30,125.81,125.38$, 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 $\mathrm{C}_{60} \mathrm{H}_{62} \mathrm{O}_{2}$ ([M] ${ }^{+}$) $m / z=814.4750$, found 814.4788 .
[5]helicene 9: $\mathrm{R}_{f}=0.17$ (1:19 ethyl acetate/hexanes); ${ }^{1} \mathrm{H} \mathrm{NMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.64(\mathrm{~d}, \mathrm{~J}=2.1 \mathrm{~Hz}, 4 \mathrm{H}), 8.46$ (d, $J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 8.26(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 2 \mathrm{H}), 8.12(\mathrm{~s}, 2 \mathrm{H}), 7.75(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 4 \mathrm{H}), 7.59-7.54(\mathrm{~m}, 6 \mathrm{H}), 4.13(\mathrm{~s}$, $6 \mathrm{H}), 1.45(\mathrm{~s}, 18 \mathrm{H}), 1.11(\mathrm{~s}, 18 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (151 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 156.36,150.36,146.88,135.72,131.41,130.20$,
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 $\mathrm{C}_{60} \mathrm{H}_{62} \mathrm{O}_{2}\left([\mathrm{M}]^{+}\right) \mathrm{m} / \mathrm{z}=814.4750$, found 814.4772 .


Tetrabenzanthracene 10: A solution of boron tribromide ( $0.014 \mathrm{~g}, 0.056 \mathrm{mmol}, 0.28$ $\mathrm{M})$ in dichloromethane was added dropwise to a stirred $0^{\circ} \mathrm{C}$ solution of $29 \mathrm{~B}(0.006 \mathrm{~g}$, 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 ( $3 \times 5 \mathrm{~mL}$ ). The combined organic extracts were washed with brine ( 10 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The white solid residue was dissolved in acetone ( 4 mL ) and methyl iodide ( $0.004 \mathrm{~g}, 0.028 \mathrm{mmol}$ ) was added at room temperature. The reaction was heated to $56{ }^{\circ} \mathrm{C}$ 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 ( $3 \times 5 \mathrm{~mL}$ ), and the combined organic extracts were washed with brine ( 10 mL ), dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $5 \times 0.7 \mathrm{~cm}, 3: 7$ dichloromethane/hexanes) to yield 10 as a white solid $(0.002 \mathrm{~g}, 35 \%), R_{f}=0.56\left(2: 3\right.$ dichloromethane/hexanes); ${ }^{1} \mathrm{H} \mathrm{NMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 10.00(\mathrm{~s}$, $1 \mathrm{H}), 9.73(\mathrm{~s}, 1 \mathrm{H}), 8.95(\mathrm{~d}, \mathrm{~J}=2.0 \mathrm{~Hz}, 2 \mathrm{H}), 8.58(\mathrm{~s}, 2 \mathrm{H}), 8.54(\mathrm{~d}, \mathrm{~J}=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 8.32(\mathrm{~s}, 2 \mathrm{H}), 7.78-7.70(\mathrm{~m}, 6 \mathrm{H})$, $7.61-7.54(\mathrm{~m}, 4 \mathrm{H}), 4.12(\mathrm{~s}, 6 \mathrm{H}), 1.60(\mathrm{~s}, 19 \mathrm{H}), 1.44(\mathrm{~s}, 19 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (151 MHz, CDCl ${ }_{3}$ ) $\delta 156.24,150.43$, $149.39,135.61,131.52,130.16,129.61,129.43,128.75,128.47,128.02,126.34,125.89,125.43,124.35,123.14$, 119.34, 117.83, 117.53, 104.18, 55.76, 35.28, 34.87, 31.66, 31.57, 29.92. HRMS (El) calc'd for $\mathrm{C}_{60} \mathrm{H}_{62} \mathrm{O}_{2}$ ([M] ${ }^{+}$) $m / z=814.4750$, found 814.4788.


1,9-dioxa[9](3,3%22)p-Terphenylenophane (13): p-Toluene sulfonic acid monohydrate $(0.174 \mathrm{~g}, 0.913 \mathrm{mmol})$ was added to a stirred solution of $47(0.060 \mathrm{~g}, 0.15 \mathrm{mmol})$ in toluene ( 6 mL ), and the reaction was heated at $65^{\circ} \mathrm{C}$. After 1 h , the reaction was poured into water ( 50 mL ) and further diluted with a saturated solution of $\mathrm{NaHCO}_{3}(15 \mathrm{~mL})$. The layers were separated and the aqueous phase extracted with dichloromethane ( $3 \times 10 \mathrm{~mL}$ ). The combined organic extracts were washed with brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $15 \times 1.3$ $\mathrm{cm}, 50 \%$ dichloromethane/hexanes) to afford 13 as a white solid ( $0.038 \mathrm{~g}, 70 \%$ ): $R_{f}=0.50$ (1:1 dichloromethane/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.52(\mathrm{~s}, 4 \mathrm{H}), 7.38-7.34(\mathrm{~m}, 2 \mathrm{H}), 7.28(\mathrm{~d}, \mathrm{~J}=5.9 \mathrm{~Hz}, 2 \mathrm{H}), 6.85$ (dd, $J=8.3,2.7 \mathrm{~Hz}, 2 \mathrm{H}), 6.37-6.36(\mathrm{~m}, 2 \mathrm{H}), 4.13-4.11(\mathrm{~m}, 4 \mathrm{H}), 1.67-1.61(\mathrm{~m}, 4 \mathrm{H}), 1.36-1.31(\mathrm{~m}, 4 \mathrm{H}), 1.09$ $-1.04(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(151 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ ס 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 $\mathrm{C}_{25} \mathrm{H}_{26} \mathrm{O}_{2}\left([\mathrm{M}]^{+}\right) \mathrm{m} / \mathrm{z}=358.1933$, found 358.1925.


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1,10-dioxa[10](3,3%22)p-Terphenylenophane (14): $p$-Toluene sulfonic acid monohydrate $(0.180 \mathrm{~g}, 0.944 \mathrm{mmol})$ was added to a stirred solution of $48(0.077 \mathrm{~g}, 0.19 \mathrm{mmol})$ in toluene ( 5.0 mL ), and the reaction was heated at $60^{\circ} \mathrm{C}$. After 30 min , the reaction was cooled and poured into water ( 50 mL ) and then further diluted with a saturated solution of $\mathrm{NaHCO}_{3}(15 \mathrm{~mL})$. The layers were separated and the aqueous phase extracted with dichloromethane $(3 \times 10 \mathrm{~mL})$. The combined organic extracts were washed with brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatograph ( $15 \times 1.3 \mathrm{~cm}, 50 \%$ dichloromethane/hexanes) to afford 14 as a white solid ( 0.031 g , $44 \%$ ); $R_{f}=0.48$ ( $1: 1$ dichloromethane/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.56(\mathrm{~s}, 4 \mathrm{H}), 7.36$ (dd, $J=8.2,7.4$ $\mathrm{Hz}, 2 \mathrm{H}$ ), $7.29-7.25(\mathrm{~m}, 2 \mathrm{H}), 6.86$ (ddd, $J=8.2,2.7,1.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.63(\mathrm{dd}, J=2.7,1.5 \mathrm{~Hz}, 2 \mathrm{H}), 4.20-4.16(\mathrm{~m}$, $4 \mathrm{H}), 1.72-1.65(\mathrm{~m}, 4 \mathrm{H}), 1.35-1.30(\mathrm{~m}, 4 \mathrm{H}), 1.27-1.20(\mathrm{~m}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 MHz, CDCl $\left.)^{2}\right)$ б $158.32,143.42$, 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 $\mathrm{C}_{26} \mathrm{H}_{28} \mathrm{O}_{2}$ ([M] ${ }^{+}$) $m / z=372.2089$, found 372.2099.


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1,11-dioxa [11] (3,3")p-Terphenylenophane (15): p-Toluene sulfonic acid monohydrate $(0.126 \mathrm{~g}, 0.660 \mathrm{mmol})$ was added to a stirred solution of compound 49 (mixture of diastereomers) $(0.069 \mathrm{~g}, 0.17 \mathrm{mmol})$ in toluene $(15 \mathrm{~mL})$, and the reaction was heated at
$80^{\circ} \mathrm{C}$. 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 $\mathrm{NaHCO}_{3}(10 \mathrm{~mL})$. The layers were separated and the aqueous phase extracted with ethyl acetate $(3 \times 10 \mathrm{~mL})$. The combined organic extracts were washed with brine ( 15 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $15 \times 1.3 \mathrm{~cm}, 5 \%$ ethyl acetate/hexanes) to afford 15 as a white solid ( $0.047 \mathrm{~g}, 72 \%$ ); $R_{f}=0.39$ (1:19 ethyl acetate/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.60(\mathrm{~s}, 4 \mathrm{H}), 7.41-7.33(\mathrm{~m}, 2 \mathrm{H}), 7.24(\mathrm{~d}, \mathrm{~J}=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.97$ (s, 2H), 6.89 (dd, $J=8.2,2.5 \mathrm{~Hz}, 2 \mathrm{H}), 4.19(\mathrm{t}, J=8.3 \mathrm{~Hz}, 4 \mathrm{H}), 1.98-1.83(\mathrm{~m}, 4 \mathrm{H}), 1.60-1.52(\mathrm{~m}, 4 \mathrm{H}), 1.42-$ $1.28(\mathrm{~m}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 158.69,143.08,141.65,130.30,128.21,117.63,116.32,113.54$, $67.16,32.25,31.91,27.77,25.41$; HRMS (EI) calc'd for $\mathrm{C}_{27} \mathrm{H}_{30} \mathrm{O}_{2}\left([\mathrm{M}]^{+}\right) \mathrm{m} / \mathrm{z}=386.2246$, found 386.2057.


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1,12-dioxa[12](3,3')p-Terphenylenophane (16): p-Toluene sulfonic acid monohydrate ( $0.164 \mathrm{~g}, 0.595 \mathrm{mmol}$ ) was added to a stirred solution of compound 50 (mixture of diastereomers) ( $0.052 \mathrm{~g}, 0.12 \mathrm{mmol}$ ) in toluene $(4.0 \mathrm{~mL})$, and the reaction was heated at 65 ${ }^{\circ} \mathrm{C}$. 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 $\mathrm{NaHCO}_{3}(10 \mathrm{~mL})$. The layers were separated and the aqueous phase extracted with dichloromethane ( $3 \times 10 \mathrm{~mL}$ ). The combined organic extracts were washed with brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $15 \times 1.3 \mathrm{~cm}, 50 \%$ dichloromethane/hexanes) to afford 16 as a white solid ( $0.031 \mathrm{~g}, 65 \%$ ): $R_{f}=0.55$ ( $1: 1$ dichloromethane/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.66(\mathrm{~s}, 4 \mathrm{H}), 7.41-7.32(\mathrm{~m}, 2 \mathrm{H}), 7.26(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.07-7.01(\mathrm{~m}, 2 \mathrm{H}), 6.90$ (dd, $J=8.1,2.5 \mathrm{~Hz}, 2 \mathrm{H}), 4.25-4.16(\mathrm{~m}, 4 \mathrm{H}), 1.97-1.85(\mathrm{~m}, 4 \mathrm{H}), 1.51-1.44(\mathrm{~m}, 8 \mathrm{H}), 1.42-1.35(\mathrm{~m}, 4 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 158.87,142.38,141.02,130.29,127.86,118.04,116.77,112.99,68.28,31.05,29.75$, 26.96, 25.78; HRMS (ESI) calculated for $\mathrm{C}_{28} \mathrm{H}_{33} \mathrm{O}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=401.2475$, found 401.2481 .


4,4",6,6"-tetrabromo-1,8-dioxa[8](3,3%22)p-terphenylophane (18): Bromine (0.368 $\mathrm{g}, 2.32 \mathrm{mmol})$ was added to a stirred solution of $12^{1}(0.100 \mathrm{~g}, 0.291 \mathrm{mmol})$ in 1,2dichlorobenzene $(5.0 \mathrm{~mL})$ at room temperature. The resulting mixture was heated to $80^{\circ} \mathrm{C}$ 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 $5 \% \mathrm{NaHSO}_{3}(10 \mathrm{~mL})$ was added, and the resulting mixture was stirred for 5 min . The layers were separated and the aqueous phase extracted with dichloromethane $(3 \times 10 \mathrm{~mL})$. The combined organic extracts were washed with a saturated solution of Na $\mathrm{HCO}_{3}(15 \mathrm{~mL})$ and brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure to afford 18 as a white solid ( $0.180 \mathrm{~g}, 95 \%$ ): $R_{f}=0.31$ ( $3: 7$ dichloromethane/hexanes). ${ }^{1} \mathrm{H} \mathrm{NMR}(600 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 7.81(\mathrm{~s}, 2 \mathrm{H}), 7.42(\mathrm{~s}, 4 \mathrm{H}), 5.87(\mathrm{~s}, 2 \mathrm{H}), 4.09(\mathrm{t}, \mathrm{J}=7.4 \mathrm{~Hz}, 4 \mathrm{H}), 1.58-1.56(\mathrm{~m}, 4 \mathrm{H}), 1.08-1.05(\mathrm{~m}, 4 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR (151 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 153.02,143.01,142.19,136.41,129.07,119.30,110.93,110.18,69.74,27.55$, 27.44; HRMS (EI) calc'd for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{O}_{2} \mathrm{Br}_{4}\left([\mathrm{M}]^{+}\right) \mathrm{m} / \mathrm{z}=655.8197$, found 655.8224.


4,4", 6,6"- tetrabromo-1,9-dioxa[9](3,3%22)p-terphenylophane (19): Bromine (0.71 $\mathrm{g}, 4.4 \mathrm{mmol})$ was added to a stirred solution of $13(0.020 \mathrm{~g}, 0.056 \mathrm{mmol})$ in $1,2-$ dichlorobenzene ( 2.0 mL ). The resulting mixture was heated to $70{ }^{\circ} \mathrm{C}$ 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 $5 \% \mathrm{NaHSO}_{3}(10 \mathrm{~mL})$ was added, and the resulting mixture was stirred for 10 min . The layers were separated and the aqueous phase extracted with dichloromethane ( $2 \times$ 15 mL ). The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}(20 \mathrm{~mL})$ and brine (20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure to yield 19 as a white solid ( $0.038 \mathrm{~g}, 95 \%$ ): $R_{f}=0.34$ (3:7 dichloromethane/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.80(\mathrm{~s}, 2 \mathrm{H}), 7.45(\mathrm{~s}, 4 \mathrm{H})$, $6.23(\mathrm{~s}, 2 \mathrm{H}), 4.13-4.10(\mathrm{~m}, 3 \mathrm{H}), 1.72-1.67(\mathrm{~m}, 4 \mathrm{H}), 1.29-1.24(\mathrm{~m}, 4 \mathrm{H}), 1.16-1.09(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (151 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 153.50,142.55,141.59,136.20,128.86,118.34,110.79,110.27,69.03,29.71,26.45,25.74$; $\operatorname{HRMS}(\mathrm{APCl})$ calc'd for $\mathrm{C}_{25} \mathrm{H}_{22} \mathrm{O}_{2} \mathrm{Br}_{5}\left([\mathrm{M}+\mathrm{Br}]^{-}\right) \mathrm{m} / \mathrm{z}=748.7537$, found 748.7537.


4,4",6,6"-tetrabromo-1,10-dioxa[10](3,3%22)p-terphenylophane (20): Bromine $(0.178 \mathrm{~g}, 1.12 \mathrm{mmol})$ was added to a stirred solution of $14(0.052 \mathrm{~g}, 0.14 \mathrm{mmol})$ in 1,2 -dichlorobenzene ( 6 mL ). The resulting mixture was heated to $80^{\circ} \mathrm{C}$ 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 $5 \% \mathrm{NaHSO}_{3}(20 \mathrm{~mL})$ was added, and the resulting mixture was stirred for 10 min . The layers were separated and the aqueous phase was extracted with dichloromethane $(3 \times 15 \mathrm{~mL})$. The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}(20 \mathrm{~mL})$ and brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure to yield 20 as a white solid ( $0.090 \mathrm{~g}, 93 \%$ ): $R_{f}=0.37$ (3:7 dichloromethane/hexanes); ${ }^{1} \mathrm{H}$ NMR $\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.82(\mathrm{~s}, 2 \mathrm{H}), 7.51(\mathrm{~s}, 4 \mathrm{H}), 6.48(\mathrm{~s}, 2 \mathrm{H}), 4.18(\mathrm{t}, \mathrm{J}=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 1.74-1.69(\mathrm{~m}, 4 \mathrm{H}), 1.31-$ $1.29(\mathrm{~m}, 4 \mathrm{H}), 1.23-1.20(\mathrm{~m}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(151 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 154.22,142.26,141.19,136.63,128.99,118.33$, 111.12, 110.87, 69.93, 29.42, 27.29, 25.92; HRMS (APCI) calc'd for $\mathrm{C}_{26} \mathrm{H}_{24} \mathrm{O}_{2} \mathrm{Br}_{5}\left([\mathrm{M}+\mathrm{Br}]^{-}\right) \mathrm{m} / \mathrm{z}=762.7693$, found 762.7702 .


4,4", 6,6"-tetrabromo-1,11-dioxa [11] (3,3")p-terphenylophane (21): Bromine $(0.150 \mathrm{~g}, 0.939 \mathrm{mmol})$ 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 $80{ }^{\circ} \mathrm{C}$ 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 $5 \% \mathrm{NaHSO}_{3}(10 \mathrm{~mL})$ was added, and the resulting mixture was stirred for 10 min . The layers were separated and the aqueous phase was extracted with dichloromethane $(3 \times 10 \mathrm{~mL})$. The combined organic extracts were washed with a saturated solution of Na $\mathrm{HCO}_{3}(20 \mathrm{~mL})$ and brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure to yield 21 as a white solid ( $0.042 \mathrm{~g}, 92 \%$ ): $R_{f}=0.37$ (3:7 dichloromethane/hexanes); ${ }^{1} \mathrm{H} \mathrm{NMR}(600 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 7.84(\mathrm{~s}, 2 \mathrm{H}), 7.53(\mathrm{~s}, 4 \mathrm{H}), 6.76(\mathrm{~s}, 2 \mathrm{H}), 4.23-4.20(\mathrm{~m}, 4 \mathrm{H}), 1.87-1.82(\mathrm{~m}, 4 \mathrm{H}), 1.41-1.26(\mathrm{~m}, 10 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR (151 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 154.09,141.94,140.58,136.99,129.19,116.37,111.49,111.38,68.05,31.73$, 31.28, 27.41, 25.00; HRMS (EI) calc'd for $\mathrm{C}_{27} \mathrm{H}_{26} \mathrm{Br}_{4} \mathrm{O}_{2}\left([\mathrm{M}]^{+}\right) \mathrm{m} / \mathrm{z}=697.8666$, found 697.8684 .


4,4", 6,6"-tetrabromo-1,12-dioxa [12] (3,3")p-terphenylophane (22): Bromine ( $0.052 \mathrm{~g}, 0.32 \mathrm{mmol}$ ) 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 $80{ }^{\circ} \mathrm{C}$ 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 $5 \% \mathrm{NaHSO}_{3}(10 \mathrm{~mL})$ was added, and the resulting mixture was stirred for 10 min . The layers were separated and the aqueous phase was extracted with dichloromethane $(3 \times 10 \mathrm{~mL})$. The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}(15 \mathrm{~mL})$ and brine $(20 \mathrm{~mL})$, dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure to yield 22 as a white solid ( $0.029 \mathrm{~g},>95 \%$ ): $R_{f}=0.40$ (3:7 dichloromethane/hexanes); ${ }^{1} \mathrm{H}$ NMR ( 600 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.84(\mathrm{~s}, 2 \mathrm{H}), 7.53(\mathrm{~s}, 4 \mathrm{H}), 6.78(\mathrm{~s}, 2 \mathrm{H}), 4.22-4.19(\mathrm{~m}, 4 \mathrm{H}), 1.88-1.83(\mathrm{~m}, 4 \mathrm{H}), 1.42-1.39(\mathrm{~m}$, $4 \mathrm{H}), 1.37-1.33(\mathrm{~m}, 4 \mathrm{H}), 1.30-1.26(\mathrm{~m}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 154.28,141.81,140.43,137.04$, 129.17, 117.02, 112.09, 111.95, 69.27, 30.35, 29.19, 26.75, 25.38; HRMS (APCI) calc'd for $\mathrm{C}_{28} \mathrm{H}_{28} \mathrm{O}_{2} \mathrm{Br}_{5}$ ( $[\mathrm{M}+\mathrm{Br}]^{-}$) $m / z=794.7965$, found 794.7942.


4,4",6,6"-tetrakis(4-t-butylphenyl)-1,7-dioxa[7](3,3%22)p-terphenylenophane (23): Sodium carbonate ( $0.590 \mathrm{~g}, 5.55 \mathrm{mmol}$ ) and 4-tert-butlyphenylboronic acid ( 0.272 g , $1.51 \mathrm{mmol})$ were added sequentially to a stirred solution of $17^{2}(0.121 \mathrm{~g}, 0.185 \mathrm{mmol})$ in toluene $(9 \mathrm{~mL})$, 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) ( $0.032 \mathrm{~g}, 0.028 \mathrm{mmol}$ ) was added, and nitrogen gas was once again passed over the reaction mixture for 3 min . The reaction was heated to $90{ }^{\circ} \mathrm{C}$ for 14 h and then cooled to room temperature. Once cooled, water ( 20 mL ) and $1 \mathrm{M} \mathrm{HCl}(10 \mathrm{~mL})$ were added and the layers separated. The aqueous phase was extracted with dichloromethane ( $3 \times 15 \mathrm{~mL}$ ), and the combined organic extracts were washed with brine ( 20 mL ), dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, 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 ( $0.132 \mathrm{~g}, 83 \%$ ): $R_{f}=0.27$ (1:19 ethyl acetate/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.58-7.53(\mathrm{~m}, 8 \mathrm{H}), 7.51$ (s, $2 \mathrm{H}), 7.45-7.43(\mathrm{~m}, 4 \mathrm{H}), 7.38-7.36(\mathrm{~m}, 4 \mathrm{H}), 7.27(\mathrm{~d}, J=4.5 \mathrm{~Hz}, 4 \mathrm{H}), 6.02(\mathrm{~s}, 2 \mathrm{H}), 4.13(\mathrm{t}, J=7.4 \mathrm{~Hz}, 4 \mathrm{H}), 1.59$ $-1.53(\mathrm{~m}, 4 \mathrm{H}), 1.37(\mathrm{~s}, 18 \mathrm{H}), 1.32(\mathrm{~s}, 18 \mathrm{H}), 1.27-1.21(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (151 MHz, CDCl $\left.{ }_{3}\right) \delta 153.36,150.02$,
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 (El) calc'd for $\mathrm{C}_{63} \mathrm{H}_{70} \mathrm{O}_{2}\left(\mathrm{M}^{+}\right) \mathrm{m} / \mathrm{z}=858.5376$, found 858.5389.
 $\mathrm{mL})$ layers separated. The aqueous phase was extracted with dichloromethane ( $3 \times 15$ mL ), and the combined organic extracts were washed with brine ( 20 mL ), dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, 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 ( $0.120 \mathrm{~g}, 92 \%$ ): $R_{f}=0.39$ (1:19 ethyl acetate/hexanes); ${ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.59-7.52(\mathrm{~m}, 10 \mathrm{H}), 7.46(\mathrm{~d}, \mathrm{~J}=7.3 \mathrm{~Hz}, 4 \mathrm{H}), 7.39-7.37(\mathrm{~m}, 4 \mathrm{H}), 7.28(\mathrm{~d}, \mathrm{~J}=4.6 \mathrm{~Hz}, 4 \mathrm{H}), 6.15$ $(\mathrm{s}, 2 \mathrm{H}), 4.10(\mathrm{t}, \mathrm{J}=7.3 \mathrm{~Hz}, 4 \mathrm{H}), 1.71-1.67(\mathrm{~m}, 4 \mathrm{H}), 1.39-1.36(\mathrm{~m}, 36 \mathrm{H}), 1.19-1.16(\mathrm{~m}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 153.07,149.97,149.43,143.08,140.86,137.42,135.16,132.78,130.78,129.55,129.47,129.27$, 125.34, 125.25, 119.27, 68.68, 34.76, 34.69, 31.61, 28.20, 27.43; HRMS (ESI) calc'd for $\mathrm{C}_{64} \mathrm{H}_{73} \mathrm{O}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=$ 873.5611, found 873.5646.


4,4",6,6"-tetrakis(4-t-butylphenyl)-1,9-dioxa[9](3,3%22)p-terphenylenophane (25): Sodium carbonate ( $0.283 \mathrm{~g}, 2.67 \mathrm{mmol}$ as an aqueous solution, 2 mL of $\mathrm{H}_{2} \mathrm{O}$ ) and 4-tert-butylphenylboronic acid ( $0.125 \mathrm{~g}, 0.712 \mathrm{mmol}$ ) were added sequentially to a stirred solution of $19(0.061 \mathrm{~g}, 0.089 \mathrm{mmol})$ in toluene $(6 \mathrm{~mL})$ and ethanol $(1.5 \mathrm{~mL})$ 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 $90^{\circ} \mathrm{C}$ for 6 h and then cooled to room temperature. Once cooled, water $(10 \mathrm{~mL})$ and $1 \mathrm{M} \mathrm{HCl}(10 \mathrm{~mL})$ were added and the layers separated. The aqueous phase was extracted with dichloromethane $(3 \times 10 \mathrm{~mL})$, and the combined organic extracts were washed with brine ( 20 mL ), dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $15 \times 1.3 \mathrm{~cm}, 1: 19$ ethyl acetate/hexanes) to yield 25 as a white solid ( $0.061 \mathrm{~g}, 77 \%$ ): $R_{f}=0.38$ ( $1: 19$ ethyl acetate/hexanes); ${ }^{1} \mathrm{H} \mathrm{NMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.58(\mathrm{~d}, \mathrm{~J}=8.2$ $\mathrm{Hz}, 4 \mathrm{H}), 7.50(\mathrm{~s}, 2 \mathrm{H}), 7.47-7.43(\mathrm{~m}, 8 \mathrm{H}), 7.32(\mathrm{~d}, \mathrm{~J}=8.3 \mathrm{~Hz}, 4 \mathrm{H}), 7.27(\mathrm{~s}, 2 \mathrm{H}), 6.53(\mathrm{~s}, 2 \mathrm{H}), 4.17-4.14(\mathrm{~m}, 4 \mathrm{H})$, $1.79(\mathrm{t}, \mathrm{J}=7.9 \mathrm{~Hz}, 4 \mathrm{H}), 1.38(\mathrm{~s}, 18 \mathrm{H}), 1.36-1.32(\mathrm{~m}, 4 \mathrm{H}), 1.31(\mathrm{~s}, 18 \mathrm{H}), 1.29-1.28(\mathrm{~m}, 2 \mathrm{H}), 1.22-1.16(\mathrm{~m}$, $2 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR (151 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 153.96,149.94,149.42,142.15,140.54,137.34,135.13,132.82,131.15$, $129.63,129.39,129.30,129.26,125.24,125.09,118.67,68.92,34.74,34.60,31.59,31.53,30.44,27.53,27.16 ;$ HRMS (APCI) calc'd for $\mathrm{C}_{65} \mathrm{H}_{75} \mathrm{O}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=887.5767$, found 887.5747.


4,4",6,6"-tetrakis(4-t-butylphenyl)-1,10-dioxa[10](3,3%22)p-terphenylenophane (26): Sodium carbonate ( $0.390 \mathrm{~g}, 3.69 \mathrm{mmol}$, as an aqueous solution, 2 mL of $\mathrm{H}_{2} \mathrm{O}$ ) and 4-tert-butylphenylboronic acid ( $0.165 \mathrm{~g}, 0.917 \mathrm{mmol}$ ) were added sequentially to a stirred solution of $20(0.084 \mathrm{~g}, 0.12 \mathrm{mmol})$ 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) ( $0.020 \mathrm{~g}, 0.017 \mathrm{mmol}$ ) was added, and nitrogen gas was once again passed over the reaction mixture for 2 min . The reaction was heated to $90^{\circ} \mathrm{C}$ for 3 h and then cooled to room temperature. Once cooled, water ( 20 mL ) and $1 \mathrm{M} \mathrm{HCl}(10 \mathrm{~mL})$ were added to the reaction mixture, and the layers were separated. The aqueous phase was extracted with dichloromethane ( $3 \times 15 \mathrm{~mL}$ ), and the combined organic extracts were washed with brine ( 30 mL ), dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $15 \times 1.3 \mathrm{~cm}, 25 \%$ to $40 \%$ dichloromethane/hexanes) to yield 26 as a white solid ( $0.085 \mathrm{~g}, 78 \%$ ): $R_{f}=0.39$ ( $3: 7$ dichloromethane/hexanes); ${ }^{1} \mathrm{H}$

NMR (600 MHz, CDCl ${ }_{3}$ ) $\delta 7.58(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 4 \mathrm{H}), 7.49(\mathrm{~s}, 2 \mathrm{H}), 7.46(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 4 \mathrm{H}), 7.38(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 4 \mathrm{H})$, $7.29(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 4 \mathrm{H}), 7.23(\mathrm{~s}, 4 \mathrm{H}), 6.73(\mathrm{~s}, 2 \mathrm{H}), 4.22(\mathrm{t}, J=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 1.82-1.77(\mathrm{~m}, 4 \mathrm{H}), 1.39-1.34(\mathrm{~m}$, $22 \mathrm{H}), 1.31-1.29(\mathrm{~m}, 22 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (151 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 154.32,149.90,149.36,141.59,140.19,137.42$, $135.20,133.16,131.29,129.63,129.36,129.29,125.21,124.98,117.84,68.70,34.74,34.57,31.58,29.48$, 27.73, 25.86; HRMS (APCI) calc'd for $\mathrm{C}_{66} \mathrm{H}_{77} \mathrm{O}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=901.5924$, found 901.5881.
 rated. The aqueous phase was extracted with dichloromethane ( $3 \times 10 \mathrm{~mL}$ ), and the combined organic extracts were washed with brine ( 10 mL ), dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $14 \times 1.0 \mathrm{~cm}, 10 \%$ to $30 \%$ dichloromethane/hexanes) to yield 27 as a white solid ( $0.022 \mathrm{~g}, 70 \%$ ): $R_{f}=0.40$ ( $3: 7$ dichloromethane/hexanes); ${ }^{1} \mathrm{H} \mathrm{NMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $7.59(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 7.47-7.45(\mathrm{~m}, 6 \mathrm{H}), 7.31-7.27(\mathrm{~m}, 12 \mathrm{H}), 6.92(\mathrm{~s}, 2 \mathrm{H}), 4.24(\mathrm{t}, \mathrm{J}=8.3 \mathrm{~Hz}, 4 \mathrm{H}), 1.97-$ $1.92(\mathrm{~m}, 4 \mathrm{H}), 1.55-1.51(\mathrm{~m}, 4 \mathrm{H}), 1.44-1.41(\mathrm{~m}, 2 \mathrm{H}), 1.39(\mathrm{~s}, 18 \mathrm{H}), 1.38-1.36(\mathrm{~m}, 2 \mathrm{H}), 1.34(\mathrm{~s}, 18 \mathrm{H}), 1.31-$ $1.29(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(151 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 154.17,149.87,149.20,140.96,139.81,137.75,135.30,134.03$, $131.63,129.58,129.56,129.53,129.31,125.19,124.85,115.93,67.22,34.74,34.58,31.70,31.60,31.36,31.18$, 27.90, 25.32; HRMS (APCI) calc'd for $\mathrm{C}_{67} \mathrm{H}_{79} \mathrm{O}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=915.6080$, found 915.6055.


4,4",6,6"-tetrakis(4-t-butylphenyl) 1,12-dioxa[12](3,3%22)p-terphenylenophane (28): Sodium carbonate ( $0.110 \mathrm{~g}, 1.05 \mathrm{mmol}$, as an aqueous solution, 1 mL of $\mathrm{H}_{2} \mathrm{O}$ ) and 4-tert-butylpheny boronic acid ( $0.061 \mathrm{~g}, 0.34 \mathrm{mmol}$ ) were added sequentially to a stirred solution of $22(0.030 \mathrm{~g}, 0.042 \mathrm{mmol})$ 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) ( $0.005 \mathrm{~g}, 0.004 \mathrm{mmol}$ ) was added, and nitrogen gas was once again passed over the reaction mixture for 2 min . The reaction was heated to $90^{\circ} \mathrm{C}$ 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 $(3 \times 10 \mathrm{~mL})$, and the combined organic extracts were washed with brine ( 20 mL ), dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (14 $\times 1.0 \mathrm{~cm}, 100 \%$ hexanes to $40 \%$ dichloromethane/hexanes) to yield 27 as a white solid ( $0.028 \mathrm{~g}, 74 \%$ ): $R_{f}=0.41$ (3:7 dichloromethane/hexanes); ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.60-7.57(\mathrm{~m}, 4 \mathrm{H}), 7.47-7.46(\mathrm{~m}, 2 \mathrm{H}), 7.46-7.45(\mathrm{~m}, 2 \mathrm{H}), 7.43(\mathrm{~s}, 2 \mathrm{H}), 7.27-7.26(\mathrm{~m}$, $12 \mathrm{H}), 6.93(\mathrm{~s}, 2 \mathrm{H}), 4.22-4.18(\mathrm{~m}, 4 \mathrm{H}), 1.95-1.91(\mathrm{~m}, 4 \mathrm{H}), 1.46-1.40(\mathrm{~m}, 7 \mathrm{H}), 1.39-1.37(\mathrm{~m}, 21 \mathrm{H}), 1.36-$ 1.32 (m, 20H); ${ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 154.39,149.87,149.20,140.82,139.76,137.89,135.34,134.07$, $132.07,129.95,129.58,129.49,129.29,125.17,124.83,116.70,68.42,34.74,34.59,31.71,31.60,30.06,29.03$, 27.57, 25.54; HRMS (ESI) calc'd for $\mathrm{C}_{68} \mathrm{H}_{81} \mathrm{O}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=929.6237$, found 929.6283.


Macrocycle 29B: A solution of Iron (III) chloride ( $0.088 \mathrm{~g}, 0.054 \mathrm{mmol}$ ) in dichloromethane/nitromethane (9:1) was added dropwise to a stirred $0{ }^{\circ} \mathrm{C}$ solution of 23 $(0.024 \mathrm{~g}, 0.028 \mathrm{mmol})$ in dichloromethane $(5 \mathrm{~mL})$. 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 $(5 \mathrm{~mL})$ were added. The layers were separated and the aqueous phase extracted with dichloromethane $(2 \times 10 \mathrm{~mL})$. The combined organic extracts were washed with brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography ( $6 \times 1.0$ $\mathrm{cm}, 30 \%$ dichloromethane/hexanes) to yield 29 B as a white solid ( $0.021 \mathrm{~g}, 90 \%$ ): $R_{f}=0.37$ (3:7 dichloro-
methane/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 9.52(\mathrm{~s}, 1 \mathrm{H}), 9.19(\mathrm{~s}, 1 \mathrm{H}), 8.68(\mathrm{~d}, \mathrm{~J}=2.0 \mathrm{~Hz}, 2 \mathrm{H}), 8.26-8.24$ $(\mathrm{m}, 4 \mathrm{H}), 7.70-7.68(\mathrm{~m}, 4 \mathrm{H}), 7.66-7.63(\mathrm{~m}, 4 \mathrm{H}), 7.57-7.55(\mathrm{~m}, 4 \mathrm{H}), 3.78(\mathrm{t}, \mathrm{J}=7.2 \mathrm{~Hz}, 4 \mathrm{H}), 1.84-1.76(\mathrm{~m}$, 4 H ), $1.53(\mathrm{~s}, 18 \mathrm{H}), 1.46(\mathrm{~s}, 18 \mathrm{H}), 1.29-1.26(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 155.25,150.16,148.96$, $135.74,130.94,129.88,129.52,129.17,128.83,127.87,127.86,125.79,125.50,125.34,123.55,122.96,119.10$, 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 $\mathrm{C}_{63} \mathrm{H}_{66} \mathrm{O}_{2}$ $\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=855.5141$, found 855.5167 .


Macrocycle 30B: A solution of Iron (III) chloride ( $0.092 \mathrm{~g}, 0.056 \mathrm{mmol}$ ) in dichloromethane/nitromethane ( $9: 1$ ) was added dropwise to a stirred $0{ }^{\circ} \mathrm{C}$ solution of 24 $(0.025 \mathrm{~g}, 0.027 \mathrm{mmol})$ in dichloromethane $(5 \mathrm{~mL})$. 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 $(5 \mathrm{~mL})$ were added. The layers were separated and the aqueous phase was extracted with dichloromethane ( $2 \times 10 \mathrm{~mL}$ ). The combined organic extracts were washed with brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $14 \times 1.0 \mathrm{~cm}$, $20 \%-35 \%$ dichloromethane/hexanes) to yield 30B as a white solid ( $0.020 \mathrm{~g}, 80 \%$ ): $R_{f}=0.49$ ( $2: 3$ dichloromethane/hexanes); ${ }^{1} \mathrm{H}$ NMR $\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 9.68(\mathrm{~s}, 1 \mathrm{H}), 9.22(\mathrm{~s}, 1 \mathrm{H}), 8.74(\mathrm{~s}, 2 \mathrm{H}), 8.25(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 2 \mathrm{H})$, $8.20(\mathrm{~s}, 2 \mathrm{H}), 7.78(\mathrm{~s}, 2 \mathrm{H}), 7.70-7.67(\mathrm{~m}, 6 \mathrm{H}), 7.57(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 3.76-3.73(\mathrm{~m}, 4 \mathrm{H}), 1.68-1.65(\mathrm{~m}, 4 \mathrm{H})$, $1.54(\mathrm{~s}, 18 \mathrm{H}), 1.49(\mathrm{~s}, 18 \mathrm{H}), 1.18-1.16(\mathrm{~m}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $151 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 155.60,150.05,148.87,135.89$, 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 $\mathrm{C}_{64} \mathrm{H}_{68} \mathrm{O}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=$ 869.5298, found 869.5266.


Macrocycle 31B: A solution of Iron (III) chloride ( $0.030 \mathrm{~g}, 0.18 \mathrm{mmol}$ ) in dichloromethane/nitromethane ( $9: 1$ ) was added dropwise to a stirred $0{ }^{\circ} \mathrm{C}$ solution of 25 $(0.015 \mathrm{~g}, 0.017 \mathrm{mmol})$ in dichloromethane $(3 \mathrm{~mL})$. 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 ( $0.030 \mathrm{~g}, 0.18 \mathrm{mmol}$ ) 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 $(2 \times 10 \mathrm{~mL})$. The combined organic extracts were washed with brine ( 10 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $15 \times 1.0 \mathrm{~cm}$, $30 \%$ dichloromethane/hexanes) to yield 31B as a white solid ( $0.012 \mathrm{~g}, 80 \%$ ): $R_{f}=0.42$ (2:3 dichloromethane/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 9.98(\mathrm{~s}, 1 \mathrm{H}), 9.61(\mathrm{~s}, 1 \mathrm{H}), 8.93(\mathrm{~d}, \mathrm{~J}=2.1 \mathrm{~Hz}, 2 \mathrm{H}), 8.54-8.49$ $(\mathrm{m}, 4 \mathrm{H}), 8.30(\mathrm{~s}, 2 \mathrm{H}), 7.75-7.71(\mathrm{~m}, 6 \mathrm{H}), 7.57-7.55(\mathrm{~m}, 4 \mathrm{H}), 4.38-4.33(\mathrm{~m}, 4 \mathrm{H}), 2.08-2.00(\mathrm{~m}, 4 \mathrm{H}), 1.59(\mathrm{~s}$, $18 \mathrm{H}), 1.45(\mathrm{~s}, 18 \mathrm{H}), 1.31-1.26(\mathrm{~m}, 6 \mathrm{H})$ ) ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 155.41,150.17,149.16,135.90,131.87$, 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 $\mathrm{C}_{65} \mathrm{H}_{71} \mathrm{O}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=$ 883.5454 , found 883.5446 .


Macrocycles 32A and 32B: A solution of Iron (III) chloride ( $0.329 \mathrm{~g}, 2.03 \mathrm{mmol}$ ) in dichloromethane/nitromethane (9:1) was added dropwise to a stirred solution of $26(180 \mathrm{mg}, 0.20 \mathrm{mmol})$ in dichloromethane ( 50 mL ) under argon. After 15 min , methanol $(10 \mathrm{~mL})$ and water $(20 \mathrm{~mL})$ were added.. The organic layers were separated, and the aqueous phase was extracted with dichloromethane $(3 \times 15) \mathrm{mL}$. The combined organic extracts were washed with brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography ( $20 \times 2.5 \mathrm{~cm}, 1: 19 \mathrm{EtOAC} / \mathrm{Hexanes}$ ) to yield 32B $(0.078 \mathrm{~g}, 43 \%)$ as a white solid and $32 \mathrm{~A}(0.016 \mathrm{~g}, 9 \%)$ as a yellow solid.

Macrocycle 32B: $R_{f}=0.44$ (1:19 EtOAC/Hexanes); ${ }^{1} \mathrm{H}$ NMR; ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 9.91(\mathrm{~s}, 1 \mathrm{H}), 9.56(\mathrm{~s}, 1 \mathrm{H}), 8.8$ (s, 2H), $8.44-8.42(\mathrm{~m}, 4 \mathrm{H}), 8.07(\mathrm{~s}, 2 \mathrm{H}), 7.78(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 4 \mathrm{H}), 7.73(\mathrm{dd}, J=8.5,1.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.56(\mathrm{~d}, \mathrm{~J}=7.9$ $\mathrm{Hz}, 4 \mathrm{H}), 4.00-3.99(\mathrm{~m}, 4 \mathrm{H}), 1.85-1.83(\mathrm{~m}, 4 \mathrm{H}), 1.57(\mathrm{~s}, 18 \mathrm{H}), 1.46(\mathrm{~s}, 18 \mathrm{H}), 1.37-1.33(\mathrm{~m}, 4 \mathrm{H}), 1.28-1.25$
(m, 4H); ${ }^{13} \mathrm{C}$ NMR (151 MHz, $\left.\mathrm{CDCl}_{3}\right) ~ \delta 155.64,150.16,149.09,135.70,131.06,129.86,129.62,129.18,128.66$, $128.25,127.94,125.98,125.71,125.29,123.99,123.14,119.14,117.59,117.15,104.91,69.24,35.19,34.83$, 31.67, 31.50, 30.10, 29.51, 25.55; HRMS (APCI) calc'd for $\mathrm{C}_{66} \mathrm{H}_{73} \mathrm{O}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=897.5611$, found 897.5622.

Macrocycle 32A: $R_{f}=0.23$ (1:19 EtOAC/Hexanes; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $8.62(\mathrm{~s}, 2 \mathrm{H}), 8.49(\mathrm{~d}, \mathrm{~J}=2.0 \mathrm{~Hz}$, $2 \mathrm{H}), 8.45(\mathrm{~d}, \mathrm{~J}=8.9 \mathrm{~Hz}, 4 \mathrm{H}), 7.91(\mathrm{~s}, 2 \mathrm{H}), 7.71-7.69(\mathrm{~m}, 4 \mathrm{H}), 7.62-7.60(\mathrm{~m}, 2 \mathrm{H}), 7.54-7.52(\mathrm{~m}, 4 \mathrm{H}), 4.55-4.40(\mathrm{~m}$, $4 \mathrm{H}), 1.64(\mathrm{q}, \mathrm{J}=7.0,5.7 \mathrm{~Hz}, 4 \mathrm{H}), 1.51-1.43(\mathrm{~m}, 4 \mathrm{H}), 1.42(\mathrm{~s}, 18 \mathrm{H}), 1.37-1.35(\mathrm{~m}, 2 \mathrm{H}), 1.27-1.22(\mathrm{~m}, 2 \mathrm{H}), 1.20(\mathrm{~s}$, $18 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 153.11,150.05,146.45,135.41,131.63,131.21,130.53,129.44,129.27$, $128.73,128.26,125.96,125.52,125.41,125.16,123.89,123.04,121.83,110.20,67.92,34.66,34.63,31.44$, 31.06, 31.01, 27.86, 27.76; HRMS (EI) calc'd for $\mathrm{C}_{66} \mathrm{H}_{72} \mathrm{O}_{2}\left([\mathrm{M}]^{+}\right) \mathrm{m} / \mathrm{z}=896.5532$, found 896.5496 .


Macrocycle 33A: A solution of Iron (III) chloride ( $0.012 \mathrm{~g}, 0.070 \mathrm{mmol}$ ) in dichloromethane/nitromethane (9:1) was added dropwise to a stirred $0{ }^{\circ} \mathrm{C}$ solution of $27(0.006 \mathrm{~g}, 0.007 \mathrm{mmol})$ 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 ( $3 \times 5 \mathrm{~mL}$ ). The combined organic extracts were washed with brine ( 10 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $5 \times 1.0 \mathrm{~cm}, 30 \%$ dichloromethane/hexanes) to yield 33 A as a white solid ( $0.005 \mathrm{~g}, 80 \%$ ): $R_{f}=0.32$ ( $3: 7$ dichloromethane/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $8.64(\mathrm{~s}, 2 \mathrm{H}), 8.55(\mathrm{~s}, 2 \mathrm{H}), 8.47(\mathrm{~d}, \mathrm{~J}=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 8.39(\mathrm{~d}, \mathrm{~J}=2.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.97(\mathrm{~s}, 2 \mathrm{H}), 7.73(\mathrm{~d}, \mathrm{~J}=7.9 \mathrm{~Hz}, 4 \mathrm{H})$, $7.59-7.54(\mathrm{~m}, 6 \mathrm{H}), 4.50-4.39(\mathrm{~m}, 4 \mathrm{H}), 1.89-1.78(\mathrm{~m}, 4 \mathrm{H}), 1.67-1.62(\mathrm{~m}, 4 \mathrm{H}), 1.57-1.53(\mathrm{~m}, 4 \mathrm{H}), 1.43(\mathrm{~s}$, $18 \mathrm{H}), 1.32-1.29(\mathrm{~m}, 2 \mathrm{H}), 1.14(\mathrm{~s}, 18 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (151 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 153.76,150.26,146.52,135.68,131.62$, $130.70,129.99,129.82,129.51,128.65,128.42,126.69,125.99,125.43,125.39,124.13,123.17,121.80,108.11$, 69.52, 34.83, 34.70, 33.33, 32.19, 31.63, 31.15, 28.65, 27.45; HRMS (APCI) calc'd for $\mathrm{C}_{67} \mathrm{H}_{75} \mathrm{O}_{2}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=$ 911.5767, found 911.5812.


Macrocycle 34A : A solution of Iron (III) chloride ( $0.035 \mathrm{~g}, 0.21 \mathrm{mmol}$ ) in dichloromethane/nitromethane (9:1,) was added dropwise to a stirred $0^{\circ} \mathrm{C}$ solution of $28(0.010 \mathrm{~g}, 0.011 \mathrm{mmol})$ 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 $(3 \times 5 \mathrm{~mL})$. The combined organic extracts were washed with brine ( 10 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $5 \times 1.0 \mathrm{~cm}, 5 \%$ ethyl acetate/hexanes) to yield 34A as a white solid ( $0.008 \mathrm{~g}, 80 \%$ ): $R_{f}=0.35$ ( $1: 19$ ethyl acetate/hexanes) ${ }^{1} \mathrm{H} \mathrm{NMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.66(\mathrm{~s}$, $2 \mathrm{H}), 8.58(\mathrm{~s}, 2 \mathrm{H}), 8.47(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 8.38(\mathrm{~d}, J=1.9 \mathrm{~Hz}, 2 \mathrm{H}), 8.11(\mathrm{~s}, 2 \mathrm{H}), 7.74(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 4 \mathrm{H}), 7.57-$ $7.55(\mathrm{~m}, 6 \mathrm{H}), 4.50-4.42(\mathrm{~m}, 4 \mathrm{H}), 2.10-2.07(\mathrm{~m}, 4 \mathrm{H}), 1.89-1.86(\mathrm{~m}, 4 \mathrm{H}), 1.71-1.69(\mathrm{~m}, 4 \mathrm{H}), 1.65-1.63(\mathrm{~m}$, $4 \mathrm{H}), 1.44(\mathrm{~s}, 18 \mathrm{H}), 1.35-1.30(\mathrm{~m}, 4 \mathrm{H}), 1.13(\mathrm{~s}, 18 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (151 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 154.20,150.23,146.57$, $135.74,131.44,130.20,1$ 刀о $95,129.69,129.55,128.75,128.12,126.94,126.00,125.35,124.05,123.07,121.80$, 106.59, 68.40, 34.82, $34 \quad 31.87,31.63,31.13,30.84,29.89,26.57,26.40$; HRMS (APCI) calc'd for $\mathrm{C}_{65} \mathrm{H}_{75} \mathrm{O}_{2}$ $\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=925.5924$, round 925.59.


35

Dialdehyde 35: 1,7-Dibromoheptane ( $6.12 \mathrm{~g}, 23.7 \mathrm{mmol}$ ) was added to a stirred solution of 3hydroxybenzaldehyde ( $5.20 \mathrm{~g}, 42.6 \mathrm{mmol}$ ), $\mathrm{K}_{2} \mathrm{CO}_{3}(11.4 \mathrm{~g}, 82.8 \mathrm{mmol})$ and tetrabutylammonium iodide ( $0.875 \mathrm{~g}, 2.37 \mathrm{mmol}$ ) in DMF ( 50 mL ) at room temperature. The reaction was heated at $80^{\circ} \mathrm{C}$ for 24 h , at which point water $(50 \mathrm{~mL})$ and $1 \mathrm{M} \mathrm{HCl}(50 \mathrm{~mL})$ were added sequentially . The resulting solution was extracted with ethyl acetate $(3 \times 50 \mathrm{~mL})$. The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}(50 \mathrm{~mL})$ and brine ( 50 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $16 \times 3.8 \mathrm{~cm}$; $60 \%$ dichloromethane/hexanes to dichloromethane) to afford 35 as a white solid ( $5.19 \mathrm{~g}, 72 \%$ ): $R_{f}=0.30$ ( $7: 3$ dichloromethane/hexanes);
${ }^{1} \mathrm{H}$ NMR (400 MHz, CDCl $\mathrm{Cl}_{3}$ ) $9.98(\mathrm{~s}, 2 \mathrm{H}), 7.46-7.41(\mathrm{~m}, 4 \mathrm{H}), 7.40-7.38(\mathrm{~m}, 2 \mathrm{H}), 7.21-7.15(\mathrm{~m}, 2 \mathrm{H}), 4.03(\mathrm{t}, \mathrm{J}$ $=6.5 \mathrm{~Hz}, 4 \mathrm{H}), 1.83(\mathrm{dt}, J=8.3,6.3 \mathrm{~Hz}, 4 \mathrm{H}), 1.57-1.44(\mathrm{~m}, 6 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 192.45,159.88$, 137.98, 130.23, 123.63, 122.20, 112.87, 68.40, 29.29, 29.28, 26.18; HRMS (ESI) calc'd for $\mathrm{C}_{21} \mathrm{H}_{25} \mathrm{O}_{4}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}$ $=341.1747$, found 341.1747.


36

Dialdehyde 36: 1,8-Dibromooctane ( $5.98 \mathrm{~g}, 22.0 \mathrm{mmol}$ ) was added to a stirred solution of 3hydroxy benzaldehyde ( $5.10 \mathrm{~g}, 41.8 \mathrm{mmol}$ ), $\mathrm{K}_{2} \mathrm{CO}_{3}(7.58 \mathrm{~g}, 54.9 \mathrm{mmol})$ and tetrabutylammonium iodide ( $0.811 \mathrm{~g}, 2.20 \mathrm{mmol}$ ) in DMF ( 70 mL ). The reaction was heated at $80^{\circ} \mathrm{C}$ for 26 h , at which point the reaction was cooled to room temperature and water ( 50 mL ) and 1 M HCl $(50 \mathrm{~mL})$ were added sequentially. The aqueous phase was extracted with dichloromethane (3 $\times 20 \mathrm{~mL}$ ). The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}$ $(25 \mathrm{~mL})$ and brine ( 25 mL ), dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (15 $\times 5 \mathrm{~cm}$; 70\% dichloromethane/hexanes to dichloromethane) to afford 36 as white solid ( $5.20 \mathrm{~g}, 70 \%$ ); $R_{f}=0.21$ (7:3 dichloromethane/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 9.97(\mathrm{~s}, 2 \mathrm{H}), 7.45-7.41(\mathrm{~m}, 4 \mathrm{H})$, $7.39(\mathrm{~d}, \mathrm{~J}=2.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.19-7.16(\mathrm{~m}, 2 \mathrm{H}), 4.04-4.00(\mathrm{~m}, 4 \mathrm{H}), 1.85-1.78(\mathrm{~m}, 4 \mathrm{H}), 1.51-1.39(\mathrm{~m}, 8 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 192.42,159.87,137.95,130.20,123.56,122.17,112.87,68.42,29.46,29.30,26.14 ;$ HRMS (APCI) calc'd for $\mathrm{C}_{22} \mathrm{H}_{26} \mathrm{O}_{4} \mathrm{Na}\left([\mathrm{M}+\mathrm{Na}]^{+}\right) \mathrm{m} / \mathrm{z}=377.1723$, found 377.1725.


37

Dialdehyde 37: 1,9-Dibromononane ( $2.28 \mathrm{~g}, 7.96 \mathrm{mmol}$ ) was added to a stirred solution of 3hydroxy benzaldehyde ( $1.90 \mathrm{~g}, 15.6 \mathrm{mmol}$ ), $\mathrm{K}_{2} \mathrm{CO}_{3}(2.82 \mathrm{~g}, 20.4 \mathrm{mmol})$ and tetrabutylammonium iodide ( $0.303 \mathrm{~g}, 0.821 \mathrm{mmol}$ ) in DMF ( 37 mL ). The reaction was heated at $80^{\circ} \mathrm{C}$ for 24 h , at which point water ( 20 mL ) and $1 \mathrm{M} \mathrm{HCl}(10 \mathrm{~mL})$ were added sequentially. The aqueous phase was extracted with dichloromethane ( $3 \times 25 \mathrm{~mL}$ ). The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}(30 \mathrm{~mL})$ and brine ( 30 mL ), dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $15 \times 5 \mathrm{~cm} ; 60 \%$ dichloromethane/hexanes to dichloromethane) to afford 37 as a white solid ( $2.71 \mathrm{~g}, 90 \%$ ); $R_{f}=0.39$ ( $3: 2$ dichloromethane/hexanes); ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDCl}_{3}\right)$ ס $9.97(\mathrm{~s}, 2 \mathrm{H}), 7.46-7.41(\mathrm{~m}, 4 \mathrm{H}), 7.39-7.38(\mathrm{~m}, 2 \mathrm{H}), 7.20-7.15(\mathrm{~m}, 2 \mathrm{H}), 4.02(\mathrm{t}, \mathrm{J}$ $=6.5 \mathrm{~Hz}, 4 \mathrm{H}), 1.85-1.78(\mathrm{~m}, 4 \mathrm{H}), 1.50-1.46(\mathrm{~m}, 4 \mathrm{H}), 1.41-1.36(\mathrm{~m}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 192.47,159.93,137.99,130.23,123.60,122.22,112.91,68.49,29.69,29.50,29.35,26.22$; HRMS (APCI) calc'd for $\mathrm{C}_{23} \mathrm{H}_{29} \mathrm{O}_{4}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=369.2060$, found 369.2063.


38

Dialdehyde 38: 1,10-Dibromodecane ( $1.15 \mathrm{~g}, 3.84 \mathrm{mmol}$ ) was added to a stirred solution of 3-hydroxy benzaldehyde ( $0.890 \mathrm{~g}, 7.29 \mathrm{mmol}$ ), $\mathrm{K}_{2} \mathrm{CO}_{3}(1.32 \mathrm{~g}, 9.59 \mathrm{mmol})$ and tetrabutylammonium iodide ( $0.141 \mathrm{~g}, 0.383 \mathrm{mmol}$ ) in DMF ( 15 mL ). The reaction was heated at 80 ${ }^{\circ} \mathrm{C}$ for 24 h , at which point water $(20 \mathrm{~mL})$ and $1 \mathrm{M} \mathrm{HCl}(10 \mathrm{~mL})$ were added sequentially. The aqueous phase was extracted with dichloromethane $(3 \times 15 \mathrm{~mL})$. The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}(20 \mathrm{~mL})$ and brine ( 15 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $15 \times 2.5 \mathrm{~cm} ; 60 \%$ to $90 \%$ dichloromethane/hexanes) to afford 38 as a white solid ( $0.857 \mathrm{~g}, 62 \%$ ): $R_{f}=0.26$ (3:2 dichloromethane/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 9.97(\mathrm{~s}, 2 \mathrm{H}), 7.47-7.41(\mathrm{~m}, 4 \mathrm{H}), 7.40-7.37(\mathrm{~m}, 2 \mathrm{H}), 7.21-7.14(\mathrm{~m}$, $2 \mathrm{H}), 4.02(\mathrm{t}, \mathrm{J}=6.6 \mathrm{~Hz}, 4 \mathrm{H}), 1.87-1.76(\mathrm{~m}, 4 \mathrm{H}), 1.53-1.42(\mathrm{~m}, 4 \mathrm{H}), 1.40-1.34(\mathrm{~m}, 8 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 192.46,159.91,137.97,130.21,123.57,122.20,112.90,68.49,29.69$, 29.55, 29.33, 26.21; HRMS (ESI) calc'd for $\mathrm{C}_{24} \mathrm{H}_{31} \mathrm{O}_{4}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=383.2217$, found 383.2218 .


39

1,4-Diketone 39: Vinylmagnesium chloride (1.6 M in THF, $6.2 \mathrm{~mL}, 7.5 \mathrm{mmol}$ ) was added to a stirred $0{ }^{\circ} \mathrm{C}$ solution of dialdehyde $35(1.52 \mathrm{~g}, 4.48 \mathrm{mmol})$ in dichloromethane ( 50 mL ). After 1 h , the reaction mixture was poured into water $(100 \mathrm{~mL})$ and further diluted with $1 \mathrm{M} \mathrm{HCl}(50$ $\mathrm{mL})$. The aqueous phase was extracted with dichloromethane $(3 \times 25 \mathrm{~mL})$. The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}(30 \mathrm{~mL})$ and brine $(30 \mathrm{~mL})$, dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was dissolved in dichloromethane ( 300 mL ) and Hoveyda-Grubbs second-generation catalyst ( $0.085 \mathrm{~g}, 0.13 \mathrm{mmol}$ ) was added. The reaction was heated at $40{ }^{\circ} \mathrm{C}$ 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 ( $0.851 \mathrm{~g}, 22.4 \mathrm{mmol}$ ) was added. After 11 h , the reaction mixture was poured into water ( 200 mL ) and further diluted with $1 \mathrm{M} \mathrm{HCl}(20$ mL ). The layers were separated and the aqueous phase was extracted with dichloromethane ( $3 \times 20 \mathrm{~mL}$ ). The combined organic extracts were washed with water ( 30 mL ) and brine ( 30 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The dark brown residue was dissolved in dichloromethane (45 mL ) followed by the addition of pyridinium chlorochromate ( $2.90 \mathrm{~g}, 13.4 \mathrm{mmol}$ ). 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 $(3 \times 20 \mathrm{~mL})$. The fitrate was concentrated under reduced pressure to give a brown residue, which was purified by flash chromatography ( $20 \times 2.5 \mathrm{~cm}$, dichloromethane) to afford 1,4-diketone 39 as a white solid ( $0.61 \mathrm{~g}, 37 \%$ from 35 ): $R_{f}=0.37$ (dichloromethane); ${ }^{1} \mathrm{H} \mathrm{NMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.48(\mathrm{~d}, \mathrm{~J}=7.6 \mathrm{~Hz}$, $2 \mathrm{H}), 7.41-7.37(\mathrm{~m}, 2 \mathrm{H}), 7.37-7.31(\mathrm{~m}, 2 \mathrm{H}), 7.07(\mathrm{dd}, J=8.2,2.6 \mathrm{~Hz}, 2 \mathrm{H}), 4.09(\mathrm{t}, \mathrm{J}=6.6 \mathrm{~Hz}, 4 \mathrm{H}), 3.31(\mathrm{~s}, 4 \mathrm{H})$, $1.80-1.76(\mathrm{~m}, 4 \mathrm{H}), 1.49-1.43(\mathrm{~m}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (151 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 200.30,159.13,138.16,130.11,120.99$, $120.59,114.07,68.07,35.25,28.08,27.92,25.43$; HRMS (ESI) calc'd for $\mathrm{C}_{23} \mathrm{H}_{27} \mathrm{O}_{4}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=367.1904$, found 367.1892 .


40

1,4-Diketone 40: Vinylmagnesium chloride ( 1.6 M in THF, $16 \mathrm{~mL}, 26 \mathrm{mmol}$ ) was added to a stirred $0{ }^{\circ} \mathrm{C}$ solution of dialdehyde $36(4.15 \mathrm{~g}, 11.6 \mathrm{mmol})$ in dichloromethane ( 80 mL ). After 30 min , the reaction mixture was poured into water ( 30 mL ) and further diluted with 1 M HCl $(20 \mathrm{~mL})$. The aqueous phase was extracted with dichloromethane ( $3 \times 20 \mathrm{~mL}$ ). The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}(20 \mathrm{~mL})$ and brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The white residue was dissolved in dichloromethane ( 800 mL ), and Hoveyda-Grubbs secondgeneration catalyst ( $0.217 \mathrm{~g}, 0.347 \mathrm{mmol}$ ) was added. The reaction was heated at $40^{\circ} \mathrm{C}$ 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 $(120 \mathrm{~mL})$, and sodium borohydride $(2.20 \mathrm{~g}, 58.0 \mathrm{mmol})$ was added. After 14 h , the reaction mixture was poured into water $(50 \mathrm{~mL})$ and further diluted with $1 \mathrm{M} \mathrm{HCl}(20 \mathrm{~mL})$. The layers were separated and the aqueous phase extracted with dichloromethane $(3 \times 20 \mathrm{~mL})$. The combined organic extracts were washed with a saturated Na $\mathrm{HCO}_{3}$ solution ( 30 mL ) and brine ( 30 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The dark brown residue was dissolved in dichloromethane ( 120 mL ), followed by addition of pyridinium chlorochromate $(7.50 \mathrm{~g}, 34.8 \mathrm{mmol})$. 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 $(2.5 \mathrm{~cm})$ and washed with diethyl ether ( $3 \times 10 \mathrm{~mL}$ ). The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography ( $17 \times$ $3.8 \mathrm{~cm}, 20 \%$ ethyl acetate/hexanes) to afford 1,4-diketone 40 as a white solid ( $1.80 \mathrm{~g}, 41 \%$ from 36 ); $R_{f}=0.38$ (1:4 ethyl acetate/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.53-7.49(\mathrm{~m}, 4 \mathrm{H}), 7.38-7.34(\mathrm{~m}, 2 \mathrm{H}), 7.09$ (ddd, $\mathrm{J}=$ $8.2,2.4,1.1 \mathrm{~Hz}, 2 \mathrm{H}), 4.11(\mathrm{t}, \mathrm{J}=6.8 \mathrm{~Hz}, 4 \mathrm{H}), 3.34(\mathrm{~s}, 4 \mathrm{H}), 1.82-1.75(\mathrm{~m}, 4 \mathrm{H}), 1.51-1.39(\mathrm{~m}, 8 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 200.12,159.11,138.19,130.08,120.81,120.49,114.15,68.24,34.99,28.46,28.06,25.28$; HRMS (ESI) calc'd for $\mathrm{C}_{24} \mathrm{H}_{29} \mathrm{O}_{4}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=381.2060$, found 381.2066.


41

1,4-Diketone 41: Vinylmagnesium chloride ( 1.6 M in THF, $10 \mathrm{~mL}, 17 \mathrm{mmol}$ ) was added to a stirred $0{ }^{\circ} \mathrm{C}$ solution of dialdehyde $37(2.56 \mathrm{~g}, 6.96 \mathrm{mmol})$ in dichloromethane ( 50 mL ). After 30 min , the reaction mixture was poured into water $(130 \mathrm{~mL})$ and further diluted with 1 M HCl $(30 \mathrm{~mL})$. The aqueous phase was extracted with dichloromethane ( $3 \times 30 \mathrm{~mL}$ ). The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}(30 \mathrm{~mL})$ and brine ( 30 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The white residue was dissolved in dichloromethane ( 470 mL ), and Hoveyda-Grubbs secondgeneration catalyst ( $0.131 \mathrm{~g}, 0.209 \mathrm{mmol}$ ) was added. The reaction was heated at $40{ }^{\circ} \mathrm{C}$ 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 $(70 \mathrm{~mL})$ and sodium borohydride ( $1.59 \mathrm{~g}, 41.8 \mathrm{mmol}$ ) was added. After 5 h , the reaction mixture was poured into water ( 100 mL ) and further diluted with $1 \mathrm{M} \mathrm{HCl}(25 \mathrm{~mL})$. The layers were separated and the aqueous phase extracted with dichloromethane $(3 \times 30 \mathrm{~mL})$. The combined organic extracts were washed with a saturated $\mathrm{NaHCO}_{3}$ solution ( 30 mL ) and brine ( 30 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The dark brown residue was dissolved in dichloromethane ( 70 mL ), followed by addition of pyridinium chlorochromate ( $4.50 \mathrm{~g}, 20.8 \mathrm{mmol}$ ). 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 $(2.5 \mathrm{~cm})$ and washed with diethyl ether
$(3 \times 20 \mathrm{~mL})$. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography ( $15 \times 3.8 \mathrm{~cm}, 20 \%$ ethyl acetate/hexanes) to afford 1,4 -diketone 41 as a white solid ( $0.83 \mathrm{~g}, 30 \%$ from 37): $R_{f}=0.45$ (1:4 ethyl acetate/hexanes); ${ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.51-7.49(\mathrm{~m}, 4 \mathrm{H}), 7.38-7.34(\mathrm{~m}, 2 \mathrm{H})$, $7.10-7.07(\mathrm{~m}, 2 \mathrm{H}), 4.10(\mathrm{t}, \mathrm{J}=6.8 \mathrm{~Hz}, 4 \mathrm{H}), 3.37(\mathrm{~s}, 4 \mathrm{H}), 1.81-1.74(\mathrm{~m}, 4 \mathrm{H}), 1.45-1.35(\mathrm{~m}, 10 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 200.19,159.12,138.48,129.95,121.29,120.53,113.37,68.27,34.58,28.80,28.58,28.22$, 25.43; HRMS (ESI) calc'd for $\mathrm{C}_{25} \mathrm{H}_{31} \mathrm{O}_{4}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=395.2217$, found 395.2229.


42

1-4,Diketone 42: Vinylmagnesium chloride ( 1.6 M in THF, $3.1 \mathrm{~mL}, 4.8 \mathrm{mmol}$ ) was added to a stirred $0^{\circ} \mathrm{C}$ solution of dialdehyde $38(0.740 \mathrm{~g}, 1.94 \mathrm{mmol})$ in dichloromethane ( 20 mL ). After 30 min , the reaction mixture was poured into water $(20 \mathrm{~mL})$ and further diluted with 1 M HCl $(10 \mathrm{~mL})$. The aqueous phase was extracted with dichloromethane $(3 \times 20 \mathrm{~mL})$. The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}(20 \mathrm{~mL})$ and brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The white residue was dissolved in dichloromethane ( 130 mL ), and Hoveyda-Grubbs secondgeneration catalyst ( $0.062 \mathrm{~g}, 0.099 \mathrm{mmol}$ ) was added. The reaction was heated at $40^{\circ} \mathrm{C}$ 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 $(20 \mathrm{~mL})$ and sodium borohydride ( $0.442 \mathrm{~g}, 11.6 \mathrm{mmol}$ ) was added. After 9 h , the reaction mixture was poured into water ( 50 mL ) and further diluted with $1 \mathrm{M} \mathrm{HCl}(15 \mathrm{~mL})$. The layers were separated and the aqueous phase extracted with dichloromethane $(3 \times 15 \mathrm{~mL})$. The combined organic extracts were washed with a saturated $\mathrm{NaHCO}_{3}$ solution ( 20 mL ) and brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The dark brown residue was dissolved in dichloromethane ( 20 mL ), followed by addition of pyridinium chlorochromate ( $1.25 \mathrm{~g}, 5.81 \mathrm{mmol}$ ). The reaction was stirred for 30 h , at which point silica gel was added, and the slurry was passed through a pad of Celite $(2.5 \mathrm{~cm})$ and washed with diethyl ether ( $3 \times 15 \mathrm{~mL}$ ). The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography ( $15 \times$ $3.8 \mathrm{~cm}, 20 \%$ ethyl acetate/hexanes) to afford 1,4-diketone 42 as a white solid ( $0.20 \mathrm{~g}, 26 \%$ from 38 ), $R_{f}=0.45$ (1:4 ethyl acetate/hexanes); ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.53-7.48(\mathrm{~m}, 4 \mathrm{H}), 7.39-7.32(\mathrm{~m}, 2 \mathrm{H}), 7.10$ (ddd, $\mathrm{J}=$ $8.2,2.4,1.3 \mathrm{~Hz}, 2 \mathrm{H}), 4.10(\mathrm{t}, \mathrm{J}=7.0 \mathrm{~Hz}, 4 \mathrm{H}), 3.37(\mathrm{~s}, 4 \mathrm{H}), 1.83-1.74(\mathrm{~m}, 4 \mathrm{H}), 1.48-1.41(\mathrm{~m}, 4 \mathrm{H}), 1.35-1.29$ $(\mathrm{m}, 8 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 200.23,159.25,138.62,129.89,121.40,120.53,113.15,68.22,34.56$, 29.28, 28.63, 28.41, 25.70; HRMS (ESI) calc'd for $\mathrm{C}_{26} \mathrm{H}_{33} \mathrm{O}_{4}\left([\mathrm{M}+\mathrm{H}]^{+}\right) \mathrm{m} / \mathrm{z}=409.2373$, found 409.2375.


Cyclohex-2-ene-1,4-diol 47: Vinylmagnesium chloride ( 1.6 M in THF, $1.2 \mathrm{~mL}, 1.9 \mathrm{mmol}$ ) was added to a stirred solution of 1,4-diketone 39 ( $0.270 \mathrm{~g}, 0.738 \mathrm{mmol}$ ) in dichloromethane (8 mL ) at $40^{\circ} \mathrm{C}$. After 30 min , the reaction mixture was poured into water ( 50 mL ) and further diluted with $1 \mathrm{M} \mathrm{HCl}(30 \mathrm{~mL})$. The aqueous phase was extracted with dichloromethane $(3 \times$ 15 mL ). The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}$ $(20 \mathrm{~mL})$ and brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $20 \times 2.5 \mathrm{~cm}, 20 \%$ ethyl acetate/hexanes) to afford allylic alcohol 43 ( $0.145 \mathrm{~g}, 47 \%$ ) as an inseparable mixture of diastereomers (73:27 d.r.); $\quad R_{f}=0.23$ (1:4 ethyl acetate/hexane). The mixture of diastereomers was carried forward without purification. Grubbs second-generation catalyst ( $0.011 \mathrm{~g}, 0.013 \mathrm{mmol}$ ) was added to a stirred solution of $43(0.110 \mathrm{~g}, 0.260 \mathrm{mmol})$ in dichloromethane $(7 \mathrm{~mL})$, and the reaction was heated to $40^{\circ} \mathrm{C}$. After 2 h , the reaction was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography ( $18 \times 1.3 \mathrm{~cm}, 30 \%$ to $40 \%$ ethyl acetate/hexanes) to afford compound anti-43 as a colorless oil ( $0.027 \mathrm{~g}, 26 \%$ ) and 47 as an off-white solid ( $0.066 \mathrm{~g}, 64 \%$ ).

Anti-allylic-1,4-diol 43 (anti-43): $R_{f}=0.23$ (1:4 ethyl acetate/hexane); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) 7.27-7.22 (m, $2 \mathrm{H}), 7.08(\mathrm{ddd}, \mathrm{J}=7.7,1.8,1.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.78(\mathrm{ddd}, J=8.2,2.5,1.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.72(\mathrm{t}, \mathrm{J}=2.1 \mathrm{~Hz}, 2 \mathrm{H}), 6.11(\mathrm{dd}, \mathrm{J}=$ $17.2,10.6 \mathrm{~Hz}, 2 \mathrm{H}), 5.22(\mathrm{dd}, J=17.2,1.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.08(\mathrm{dd}, J=10.6,1.0 \mathrm{~Hz}, 2 \mathrm{H}), 4.01-3.91(\mathrm{~m}, 4 \mathrm{H}), 1.98(\mathrm{br} \mathrm{s}$, 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); ${ }^{13} \mathrm{C}$ NMR ( $151 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) 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 $\mathrm{C}_{27} \mathrm{H}_{34} \mathrm{O}_{4} \mathrm{Na}\left(\left[\mathrm{M}+\mathrm{Na}^{+}\right) \mathrm{m} / \mathrm{z}=445.2349\right.$, found 445.2366.

Cyclohex-2-ene-1,4-diol 47: $R_{f}=0.13$ (3:7 ethyl acetate/hexanes); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.35-7.31$ ( m , $4 \mathrm{H}), 6.90-6.88(\mathrm{~m}, 2 \mathrm{H}), 6.84-6.79(\mathrm{~m}, 2 \mathrm{H}), 6.08(\mathrm{~s}, 2 \mathrm{H}), 4.07-3.93(\mathrm{~m}, 4 \mathrm{H}), 2.22-2.13(\mathrm{~m}, 2 \mathrm{H}), 1.95-1.86$ $(\mathrm{m}, 7 \mathrm{H}), 1.64-1.55(\mathrm{~m}, 7 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(151 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 158.60,147.80,134.57,129.90,117.24,112.90$,
112.38, 72.62, 68.04, 36.35, 27.76, 27.39, 26.14; HRMS (ESI) calc'd for $\left.\mathrm{C}_{25} \mathrm{H}_{29} \mathrm{O}_{3}\left(\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}\right)+\mathrm{H}\right]^{+}\right) \mathrm{m} / \mathrm{z}=377.2111$, found 377.2102 .


Cyclohex-2-ene-1,4-diol 48: Vinylmagnesium chloride ( 1.6 M in THF, $0.50 \mathrm{~mL}, 0.81 \mathrm{mmol}$ ) was added to a stirred solution of 1,4-diketone $40(0.122 \mathrm{~g}, 0.322 \mathrm{mmol})$ in dichloromethane $(3.0 \mathrm{~mL})$ at $40^{\circ} \mathrm{C}$. After 30 min , the reaction mixture was poured into water ( 10 mL ) and further diluted with $1 \mathrm{M} \mathrm{HCl}(10 \mathrm{~mL})$. The aqueous phase was extracted with dichloromethane $(3 \times 10 \mathrm{~mL})$. The combined organic extracts were washed with a saturated solution of Na $\mathrm{HCO}_{3}(10 \mathrm{~mL})$ and brine ( 10 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, 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 ( $0.008 \mathrm{~g}, 0.01 \mathrm{mmol}$ ) was added. The reaction was heated at $40^{\circ} \mathrm{C}$. After 2.5 h , the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography ( $15 \times 1.3 \mathrm{~cm}, 5 \%$ to $10 \%$ acetone/dichloromethane) to afford anti-44 as colorless oil ( $0.019 \mathrm{~g}, 13 \%$ ) and compound 48 as an offwhite solid ( $0.076 \mathrm{~g}, 58 \%$ ).

Anti-allylic-1,4-diol 44 (anti-44): $R_{f}=0.41$ (1:19 acetone/dichloromethane); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.28-$ 7.24 (m, 2H), 7.04 (ddd, $J=7.8,1.8,0.9 \mathrm{~Hz}, 2 \mathrm{H}$ ), $6.83-6.82(\mathrm{~m}, 2 \mathrm{H}), 6.75$ (ddd, $J=8.2,2.5,0.9 \mathrm{~Hz}, 2 \mathrm{H}$ ), 6.12 (dd, $J=17.3,10.7 \mathrm{~Hz}, 2 \mathrm{H}), 5.24(\mathrm{dd}, J=17.2,1.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.09(\mathrm{dd}, J=10.6,1.0 \mathrm{~Hz}, 2 \mathrm{H}), 3.98(\mathrm{t}, J=5.7 \mathrm{~Hz}, 4 \mathrm{H})$, 1.96-1.90 (m, 3H), 1.85-1.74 (m, 6H) 1.60-1.38 (m, 9H); ${ }^{13} \mathrm{C}$ NMR (101 MHz, CDCl ${ }_{3}$ ) 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 $\left.\mathrm{C}_{28} \mathrm{H}_{33} \mathrm{O}_{2}\left(\left[\mathrm{M}-2 \mathrm{H}_{2} \mathrm{O}\right)+\mathrm{H}\right]^{+}\right) \mathrm{m} / \mathrm{z}=401.2474$, found 401.2484.

Cyclohex-2-ene-1,4-diol 48: $R_{f}=0.12$ (1:19 acetone/dichloromethane); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.39$ - 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$1.93(\mathrm{~m}, 2 \mathrm{H}), 1.85-1.67(\mathrm{~m}, 6 \mathrm{H}), 1.54-1.48(\mathrm{~m}, 6 \mathrm{H}){ }^{\text { }}{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 158.77,147.85,134.49$, 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 $\mathrm{C}_{26} \mathrm{H}_{28} \mathrm{O}_{2}$ ([M$\left.2 \mathrm{H}_{2} \mathrm{O}^{+}\right) \mathrm{m} / \mathrm{z}=372.2089$, found 372.2121 .

Cyclohex-2-ene-1,4-diols 49: Vinylmagnesium chloride ( 1.6 M in THF, $0.44 \mathrm{~mL}, 0.71 \mathrm{mmol}$ ) was added to a stirred solution of 1,4 -diketone $37(0.127 \mathrm{~g}, 0.322 \mathrm{mmol})$ in dichloromethane $(3.0 \mathrm{~mL})$ at $40^{\circ} \mathrm{C}$. After 30 min , the reaction mixture was poured into water ( 10 mL ) and further diluted with $1 \mathrm{M} \mathrm{HCl}(10 \mathrm{~mL})$. The aqueous phase was extracted with dichloromethane ( $3 \times 10 \mathrm{~mL}$ ). The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}(10 \mathrm{~mL})$ and brine ( 10 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The white residue was dissolved in dichloromethane ( 7.0 mL ), and Grubbs' second-generation catalyst ( $0.014 \mathrm{~g}, 0.016 \mathrm{mmol}$ ) was added. The reaction was heated at $40^{\circ} \mathrm{C}$. 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 ( $15 \times 1.3 \mathrm{~cm}, 10 \%$ to $25 \%$ acetone/chloroform) to afford anti 49 ( $0.026 \mathrm{~g}, 19 \%$ ) and syn $49(0.050 \mathrm{~g}, 38 \%)$ as offwhite solids (d.r. syn/anti $=71: 29$ ).

anti-49: $R_{f}=0.47$ (1:9 acetone/chloroform); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) 7.31-7.27 (m, $2 \mathrm{H}), 7.23(\mathrm{t}, \mathrm{J}=2.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.12(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.85(\mathrm{dd}, \mathrm{J}=8.2,2.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.00$ (s, 2H), $4.21-4.14(\mathrm{~m}, 4 \mathrm{H}), 2.44(\mathrm{~d}, J=10.0 \mathrm{~Hz}, 2 \mathrm{H}), 2.07(\mathrm{~d}, J=10.0 \mathrm{~Hz}, 2 \mathrm{H}), 1.90-$ $1.77(\mathrm{~m}, 6 \mathrm{H}), 1.53-1.39(\mathrm{~m}, 10 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $151 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 158.60$, 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 $\mathrm{C}_{27} \mathrm{H}_{30} \mathrm{O}_{2}\left(\left[\mathrm{M}-2 \mathrm{H}_{2} \mathrm{O}\right]^{+}\right) \mathrm{m} / \mathrm{z}=386.2245$, found 386.2254.

syn-49: $R_{f}=0.18\left(1: 9\right.$ acetone/chloroform); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $7.34-7.27(\mathrm{~m}, 4 \mathrm{H})$, $6.87(\mathrm{t}, \mathrm{J}=2.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.79(\mathrm{dt}, J=7.7,1.9 \mathrm{~Hz}, 2 \mathrm{H}), 6.11(\mathrm{~s}, 2 \mathrm{H}), 4.02-3.92(\mathrm{~m}, 4 \mathrm{H}), 2.25$ $(\mathrm{d}, J=3.2 \mathrm{~Hz}, 2 \mathrm{H}), 2.21-2.14(\mathrm{~m}, 2 \mathrm{H}), 1.95-1.91(\mathrm{~m}, 2 \mathrm{H}), 1.79(\mathrm{qt}, J=10.9,5.3 \mathrm{~Hz}, 4 \mathrm{H})$, $1.60(\mathrm{dt}, \mathrm{J}=13.5,6.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.55-1.37(\mathrm{~m}, 8 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $151 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) ठ 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 $\mathrm{C}_{27} \mathrm{H}_{30} \mathrm{O}_{2}\left(\left[\mathrm{M}-2 \mathrm{H}_{2} \mathrm{O}\right]^{+}\right) \mathrm{m} / \mathrm{z}=386.2245$, found 386.2245.

Cyclohex-2-ene-1,4-diols 50: Vinylmagnesium chloride ( 1.6 M in THF, $0.75 \mathrm{~mL}, 1.2 \mathrm{mmol}$ ) was added to a stirred solution of 1,4 -diketone $42(0.165 \mathrm{~g}, 0.415 \mathrm{mmol})$ in dichloromethane ( 5.0 mL ) at $40{ }^{\circ} \mathrm{C}$. After 30 min , the reaction mixture was poured into water $(10 \mathrm{~mL})$ and further diluted with $1 \mathrm{M} \mathrm{HCl}(10 \mathrm{~mL})$. The aqueous phase was extracted with dichloromethane $(3 \times 10 \mathrm{~mL})$. The combined organic extracts were washed with a saturated solution of $\mathrm{NaHCO}_{3}(10 \mathrm{~mL})$ and brine ( 10 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The white residue was dissolved in dichloromethane ( 5.0 mL ), and Grubbs' second-generation catalyst ( $0.009 \mathrm{~g}, 0.01 \mathrm{mmol}$ ) was added. The reaction was heated at $40^{\circ} \mathrm{C}$. 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 purified by flash chromatography ( $16 \times 1.3 \mathrm{~cm}, 10 \%$ to $25 \%$ acetone/dichloromethane) to give anti 50 ( $0.016 \mathrm{~g}, 18 \%$ ) 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); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.30-$ $7.24(\mathrm{~m}, 2 \mathrm{H}), 7.23-7.20(\mathrm{~m}, 2 \mathrm{H}), 7.14-7.09(\mathrm{~m}, 2 \mathrm{H}), 6.84$ (ddd, $J=8.2,2.6,1.0 \mathrm{~Hz}$, $2 \mathrm{H}), 5.93(\mathrm{~s}, 2 \mathrm{H}), 4.123-4.09(\mathrm{~m}, 4 \mathrm{H}), 2.38-2.29(\mathrm{~m}, 2 \mathrm{H}), 2.07-2.00(\mathrm{~m}, 2 \mathrm{H}), 1.91(\mathrm{~s}$, 2H), $1.89-1.73(\mathrm{~m}, 4 \mathrm{H}), 1.49-1.37(\mathrm{~m}, 12 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 158.70$, $148.63,134.43,129.75,117.17,116.89,110.42,72.31,68.28,35.80,30.25,29.41$, 27.57, 25.57; HRMS (ESI) calc'd for anti $\left.50 \mathrm{C}_{28} \mathrm{H}_{35} \mathrm{O}_{3}\left(\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}\right)+\mathrm{H}\right]^{+}\right) \mathrm{m} / \mathrm{z}=419.2580$, found 419.2586.

syn-50: $R_{f}=0.11$ (1:19 acetone/dichloromethane); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.38$ $7.29(\mathrm{~m}, 4 \mathrm{H}), 6.91-6.85(\mathrm{~m}, 2 \mathrm{H}), 6.83-6.76(\mathrm{~m}, 2 \mathrm{H}), 6.08(\mathrm{~s}, 2 \mathrm{H}), 4.01-3.90(\mathrm{~m}, 4 \mathrm{H})$, $2.27-2.13(\mathrm{~m}, 4 \mathrm{H}), 2.05-1.93(\mathrm{~m}, 2 \mathrm{H}), 1.76(\mathrm{tt}, \mathrm{J}=6.8,3.7 \mathrm{~Hz}, 4 \mathrm{H}), 1.56-1.47(\mathrm{~m}$, 2 H ), $1.43-1.34(\mathrm{~m}, 10 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 158.98,148.09,134.74,130.06$, 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 $\left.50 \mathrm{C}_{28} \mathrm{H}_{35} \mathrm{O}_{3}\left(\left[\mathrm{M}-\mathrm{H}_{2} \mathrm{O}\right)+\mathrm{H}\right]^{+}\right) \mathrm{m} / \mathrm{z}=419.2580$, found 419.2583 .


4,4",6,6"-tetrabromo-3,3"-dimethoxy-p-terphenyl (56): Bromine ( $0.480 \mathrm{~g}, 3.00$ mmol ) was added to a stirred solution of 3,3 "-dimethoxy- $p$-terphenyl ( $0.080 \mathrm{~g}, 0.28$ $\mathrm{mmol})$ in 1,2-dichlorobenzene $(5 \mathrm{~mL})$. The resulting mixture was heated to $70^{\circ} \mathrm{C}$ 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 dichloromethane ( 15 mL ), a solution of $5 \% \mathrm{NaHSO}_{3}(15 \mathrm{~mL})$ was added, and the resulting mixture was stirred for 10 min . The layers were separated and the aqueous phase extracted with dichloromethane ( $3 \times 10 \mathrm{~mL}$ ). The combined organic extracts were washed with brine ( 20 mL ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography ( $15 \times 2.5 \mathrm{~cm}, 10 \%$ to $40 \%$ dichloromethane/hexanes) to yield 56 as a pale yellow solid ( $0.096 \mathrm{~g}, 57 \%$ ): $R_{f}=0.51$ ( $2: 3$ dichloromethane/hexane); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.86(\mathrm{~s}, 2 \mathrm{H}), 7.49(\mathrm{~s}, 4 \mathrm{H}), 6.92(\mathrm{~s}, 2 \mathrm{H}), 3.92(\mathrm{~s}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $151 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 155.43, 142.20, 140.19, 136.83, 129.16, 114.49, 113.19, 111.62, 56.73; HRMS (EI) calc'd for $\mathrm{C}_{20} \mathrm{H}_{14} \mathrm{O}_{2} \mathrm{Br}_{4}$ ([M] ${ }^{+}$) $m / z=605.7686$, found 605.7662.

## 4. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra













SI-19







| $\begin{aligned} & \stackrel{8}{\circ} \\ & \stackrel{\omega}{n} \\ & \stackrel{1}{1} \end{aligned}$ |  |  |  | $\begin{aligned} & 0 \\ & \stackrel{0}{i} \\ & i \end{aligned}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |



| 210 | 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |











-154.28
-141.81
$乙_{140.43}$
-137.04
-129.17

-117.02
$\mathcal{L}_{111.95}^{112.09}$
N

wivmump

| T | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |  | 1 | 1 | 1 |  | 1 | 1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 210 | 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |





SI-30



SI-32



SI-34


SI-35



SI-37








| \% | 命 | $\stackrel{y}{4}$ | $\begin{aligned} & \text { İ } \\ & \text { /ి } \end{aligned}$ | $\begin{aligned} & \mathbb{8 N} \\ & \mathbb{N} \underset{\sim}{\top} \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: |




| - | 1 | 1 | T | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | , | 1 | 1 | 1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 210 | 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |





| T | 1 | T | T | 1 | , | T | , | T | 1 | T | 1 | 1 | 1 | 1 | T | T | T | 1 | 1 | , | 1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 210 | 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |




| $\begin{aligned} & \stackrel{g}{+} \\ & \stackrel{8}{\circ} \end{aligned}$ |  |  |  |
| :---: | :---: | :---: | :---: |



| , | , | T | T | 1 | 1 | T | $\uparrow$ | , | T | 1 | 1 | 1 | 1 | , | T | T | T | 1 | 1 | $\uparrow$ | 1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 210 | 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |






| , | , | T | T | 1 | 1 | T | $\uparrow$ | , | T | 1 | 1 | 1 | 1 | , | T | T | T | 1 | 1 | $\uparrow$ | 1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 210 | 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |



| 1 | 1 | 1 | T | 1 | 1 | 1 | 1 | 1 | T | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 210 | 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |



















| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 210 | 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |





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

Full geometry optimization was performed using the B3LYP functional in conjunction with a $6-31 \mathrm{G}(\mathrm{d})$ 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

|  |  |  |  |
| :--- | ---: | ---: | ---: |
| C | -4.40738900 | -2.11846100 | -0.90084700 |
| C | -3.20672200 | -1.75653600 | -1.49289200 |
| C | -2.78145600 | -0.41804000 | -1.54507200 |
| C | -3.63321900 | 0.59878500 | -1.07001500 |
| C | -4.89076300 | 0.22143300 | -0.56272500 |
| H | -5.30233500 | -1.10819700 | -0.44407200 |
| C | -2.51514500 | -2.52436000 | -1.80345200 |
| C | 1.39958300 | 0.04152500 | -1.65694700 |
| C | 2.80729400 | -0.11047100 | -1.31306500 |
| C | 3.52383800 | -1.26681300 | -1.68391600 |
| C | 3.45128500 | 0.83633600 | -0.43305300 |
| H | 4.80011300 | -1.52659100 | -1.22813000 |
| C | 3.06348400 | -2.04126200 | -2.28113600 |
| C | 4.79567600 | 0.60061700 | -0.12078500 |
| H | 5.49250300 | -0.56152200 | -0.45120000 |
| C | 5.31985800 | 1.33172700 | 0.48300000 |
| C | -1.38856400 | -0.12576500 | -1.85473500 |
| C | -0.81347600 | 1.06746200 | -1.36312600 |
| C | 0.60390600 | 1.06147800 | -1.06894600 |
| H | -0.56953000 | -1.05753400 | -2.52733600 |
| C | -1.02321000 | -1.86743700 | -3.08958400 |
| H | 0.7907400 | -0.91772300 | -2.50536600 |
| H | 1.39821100 | -1.59912000 | -3.08711700 |
| O | -5.57075900 | 0.98963600 | -0.20804800 |
| C | -4.74702400 | -3.42254900 | -0.66192000 |
| H | 0.03091900 | -4.49775500 | 0.04789300 |
| H | 0.04654700 | -4.89596400 | 1.07245900 |
| C | 0.01477200 | -3.40287500 | 0.14444400 |
| H | -1.25843000 | -4.93618900 | -0.67012000 |
| H | -1.21644100 | -4.55132000 | -1.70049900 |
| C | -1.28626300 | -6.03118500 | -0.76317900 |
| H | -2.55021800 | -4.42368100 | 0.00071100 |
| H | -2.76968000 | -5.00317800 | 0.90537400 |
| C | -2.38778900 | -3.93338200 | 0.3335600 |
| H | -3.77767000 | -4.44705200 | -0.93914800 |
| H | -4.34298700 | -5.37595900 | -0.83059600 |
| O | -3.46724600 | -4.37635300 | -1.99079600 |
| C | 5.37835300 | -2.73878600 | -1.54634500 |
| H | 1.31596900 | -4.90958300 | -0.69277100 |
| H | 1.20792000 | -4.65018100 | -1.75693200 |
| C | 1.43053900 | -6.00322400 | -0.66013400 |
| H | 2.59061200 | -4.23308200 | -0.15778300 |
| H | 2.45661800 | -3.14645000 | -0.20235800 |
| C | 2.72395300 | -4.47883300 | 0.90590300 |
| H | 3.85953400 | -4.64292200 | -0.93171700 |
| H | 3.68215200 | -4.58956800 | -2.01432200 |
| C | 4.07021900 | -5.70026100 | -0.71625800 |
| H | 5.14297200 | -3.83815000 | -0.63781400 |
| H | 6.01753900 | -4.48036900 | -0.77588800 |
|  | 5.15801600 | -3.46982300 | 0.39627000 |
|  |  |  |  |


| C | -3.14278500 | 1.97238800 | -1.14926500 |
| :---: | :---: | :---: | :---: |
| C | -1.74571000 | 2.20695300 | -1.27685400 |
| C | -4.00914500 | 3.08257200 | -1.17031800 |
| C | -1.29911300 | 3.52756200 | -1.51322100 |
| C | -3.53616700 | 4.36608600 | -1.37402800 |
| H | -5.07956200 | 2.92320100 | -1.07922400 |
| C | -2.16142700 | 4.61752600 | -1.57932400 |
| H | -0.23908800 | 3.67298900 | -1.67521500 |
| H | -4.24999100 | 5.18386200 | -1.41481500 |
| C | 2.65739000 | 1.91425000 | 0.10251100 |
| C | 1.24497300 | 1.94680600 | -0.07808600 |
| C | 3.23428400 | 2.84922600 | 0.99122600 |
| C | 0.48910800 | 2.75197100 | 0.81249400 |
| C | 2.46666200 | 3.68601300 | 1.77290600 |
| H | 4.31289800 | 2.89972100 | 1.08994400 |
| C | 1.05723400 | 3.60780900 | 1.74679600 |
| H | 2.96536500 | 4.37499400 | 2.44869200 |
| C | -1.68532500 | 6.04179700 | -1.91912400 |
| C | -2.30094900 | 6.46723700 | -3.27444000 |
| H | -3.39579300 | 6.45967600 | -3.24295400 |
| H | -1.98007800 | 7.48259800 | -3.53851400 |
| H | -1.98511500 | 5.79089500 | -4.07676700 |
| C | -0.15221500 | 6.13659800 | -2.03535800 |
| H | 0.34751100 | 5.83401500 | -1.10825100 |
| H | 0.23490700 | 5.51286500 | -2.84880000 |
| H | 0.13809500 | 7.17152800 | -2.24911100 |
| C | -2.14803200 | 7.02992500 | -0.82260900 |
| H | -3.23777900 | 7.04752800 | -0.71705000 |
| H | -1.72275800 | 6.76624400 | 0.15221400 |
| H | -1.82377300 | 8.04829200 | -1.06914300 |
| H | -0.58532300 | 2.67281200 | 0.77221400 |
| C | 0.22792200 | 4.42906700 | 2.74964400 |
| C | 0.61575700 | 4.01057300 | 4.18892300 |
| H | 1.67861800 | 4.18026800 | 4.39143700 |
| H | 0.03959000 | 4.58836900 | 4.92217300 |
| H | 0.40917700 | 2.94731800 | 4.35580100 |
| C | -1.28737700 | 4.21171600 | 2.58089400 |
| H | -1.63610500 | 4.49855200 | 1.58316100 |
| H | -1.56877800 | 3.16631200 | 2.75090000 |
| H | -1.83012100 | 4.82155800 | 3.31228000 |
| C | 0.52864900 | 5.93516400 | 2.56361900 |
| H | 1.58871400 | 6.16405800 | 2.71674000 |
| H | 0.25806800 | 6.26924900 | 1.55561600 |
| H | -0.04612400 | 6.52995700 | 3.28408700 |
| C | -6.60985900 | -1.42792100 | 0.18471400 |
| C | -7.47588600 | -2.40058900 | -0.34425400 |
| C | -7.04601700 | -0.73002700 | 1.31947900 |
| C | -8.71650200 | -2.64534300 | 0.23347500 |
| H | -7.17425400 | -2.96474000 | -1.21995500 |
| C | -8.29165600 | -0.98240800 | 1.89625200 |
| H | -6.39257300 | 0.00934900 | 1.77500400 |
| C | -9.16149000 | -1.94491300 | 1.36860500 |
| H | -9.35373900 | -3.40141100 | -0.21773000 |
| H | -8.57189900 | -0.41603200 | 2.77775000 |
| C | 6.88000200 | -0.77059100 | 0.03659900 |
| C | 7.88011400 | -1.32394000 | -0.78275400 |
| C | 7.24966400 | -0.38972800 | 1.33424600 |
| C | 9.18313900 | -1.47005500 | -0.31968000 |
| H | 7.6 | -1.63576700 | 0 |


| C | 8.55913800 | -0.54187300 | 1.79267500 |
| :--- | ---: | ---: | ---: |
| H | 6.49788700 | 0.01397600 | 2.00742100 |
| C | 9.56172000 | -1.08347700 | 0.97824900 |
| H | 9.92337200 | -1.89366700 | -0.99332300 |
| H | 8.78528600 | -0.23505900 | 2.80806900 |
| C | 11.01654300 | -1.26641000 | 1.44516300 |
| C | 11.95866900 | -0.45884000 | 0.52323000 |
| H | 13.00198200 | -0.58133800 | 0.83823100 |
| H | 11.88466400 | -0.77856700 | -0.52047000 |
| H | 11.71842100 | 0.61284300 | 0.55996100 |
| C | 11.39688600 | -2.76461100 | 1.37409500 |
| H | 12.43526500 | -2.91073900 | 1.6964900 |
| H | 10.75102200 | -3.36398100 | 2.02596500 |
| H | 11.30477900 | -3.16077300 | 0.35743600 |
| C | 11.23242000 | -0.78541300 | 2.89256600 |
| H | 11.00690300 | 0.28110100 | 3.00594200 |
| H | 10.61403900 | -1.34359900 | 3.60478000 |
| H | 12.27994600 | -0.93333300 | 3.17851800 |
| C | -10.54203800 | -2.25333800 | 1.97434400 |
| C | -11.63973600 | -1.98594300 | 0.91696400 |
| H | -11.50457100 | -2.60487100 | 0.02383100 |
| H | -12.63117900 | -2.20865900 | 1.33052900 |
| H | -11.63113000 | -0.93672500 | 0.60027100 |
| C | -10.59712400 | -3.73899900 | 2.40337600 |
| H | -11.57904300 | -3.97726600 | 2.83080600 |
| H | -10.42919000 | -4.41378300 | 1.55750600 |
| H | -9.83469500 | -3.95639900 | 3.16009600 |
| C | -10.84657200 | -1.38614900 | 3.21055100 |
| H | -10.11166200 | -1.5514500 | 4.01392800 |
| H | -10.85115200 | -0.31736600 | 2.9679100 |
| H | -11.83737700 | -1.63947700 | 3.60453200 |

## Compound 26

|  |  |  |  |
| :--- | ---: | ---: | ---: |
| C | 0.05655500 | -4.93894500 | 1.87460400 |
| C | -0.13737000 | -3.60184700 | 1.52358700 |
| C | 0.86769000 | -2.84610400 | 0.89538700 |
| C | 2.13239800 | -3.42409900 | 0.65917300 |
| C | 2.31945900 | -4.76275100 | 1.05959900 |
| H | 1.31133600 | -5.51876600 | 1.64297000 |
| H | -1.10227200 | -3.13147800 | 1.65764900 |
| C | 1.47550500 | -6.55364900 | 1.92672600 |
| C | -1.09938000 | 0.65620100 | -0.63034500 |
| C | -2.17106900 | 1.55382800 | -1.15596300 |
| C | -3.18138000 | 0.90860700 | -1.88365600 |
| C | -2.31931400 | 2.92581500 | -0.84215900 |
| H | -4.35138700 | 1.56151300 | -2.26457000 |
| C | -3.08852200 | -0.14926000 | -2.10426400 |
| C | -3.49337600 | 3.57528000 | -1.26598500 |
| H | -4.50789000 | 2.91598500 | -1.95715500 |
| H | -3.60043200 | 4.63712900 | -1.06193100 |
| C | -5.40024700 | 3.45077600 | -2.26899200 |
| C | 0.40792700 | -1.51802900 | 0.38713100 |
| H | -0.20632400 | -0.59629800 | 1.24989800 |
| C | -0.15579100 | -0.75877500 | 2.32369700 |
| H | -0.93754100 | 0.47962700 | 0.75213700 |
| C | -1.44820900 | 1.14759700 | 1.43968600 |
| H | 0.35349900 | -1.26522300 | -0.99173200 |
| C | 0.84149700 | -1.94963700 | -1.67951700 |
| H | -0.39815300 | -0.20360200 | -1.49051000 |
| H | -0.49008600 | -0.07095500 | -2.56558700 |
| O | 3.29636800 | -5.21581100 | 0.91464600 |
| C | -0.90682800 | -5.74509500 | 2.41346800 |
| H | -4.68738400 | -3.43775800 | 0.12833500 |
| H | -5.31755900 | -4.24297100 | -0.27524000 |
| C | -3.87580900 | -3.29111400 | -0.5995500 |
| H | -4.06748200 | -3.86729800 | 1.46858500 |
| H | -3.57650200 | -2.98773300 | 1.91190700 |
| C | -4.85878100 | -4.15631500 | 2.17523600 |
| H | -3.02515300 | -4.99167300 | 1.34293600 |
| H | -3.50231900 | -5.93679000 | 1.05574500 |
| C | -2.33341400 | -4.3959900 | 0.53154000 |
| H | -2.21094800 | -5.19233500 | 2.63603700 |
| H | -2.69775900 | -5.90938000 | 3.30254000 |
| O | -2.11469100 | -4.24665700 | 3.18692700 |
| C | -5.29855400 | 0.83343500 | -2.95216400 |
| H | -5.49048200 | -2.13121200 | 0.23259300 |
| H | -4.87029600 | -1.38889900 | 0.75627400 |
| C | -6.37787300 | -2.28431400 | 0.86426300 |
| C | -5.90443000 | -1.53594100 | -1.12263900 |
| H | -5.02401400 | -1.49377700 | -1.77498500 |
| H | -6.62512300 | -2.19610100 | -1.62625200 |
| C | -6.49181200 | -0.12072000 | -0.99466000 |
| H | -5.88496500 | 0.46042900 | -0.28763300 |
| H | -7.50288300 | -0.16256000 | -0.56529500 |
| H | -6.57421200 | 0.66104000 | -2.30892000 |
| -7.04259300 | 1.63982200 | -2.13360900 |  |
| -7.17754800 | 0.12826500 | -3.05073100 |  |
|  | 3.606607800 | -2.69049600 | 0.02561100 |


|  |  |  |  |
| :--- | ---: | ---: | ---: |
| C | 4.69050500 | -0.72612900 | -0.17479200 |
| H | 3.02911400 | -0.88164800 | 1.17327500 |
| C | 5.13202600 | -2.64065200 | -1.53521200 |
| H | 3.80453100 | -4.30830000 | -1.29414900 |
| C | 5.48256000 | -1.33300700 | -1.15906000 |
| H | 4.91533800 | 0.27975200 | 0.16279600 |
| H | 5.70792700 | -3.15653500 | -2.29908700 |
| C | -1.28852800 | 3.70724900 | -0.10689400 |
| C | 0.07264100 | 3.63070600 | -0.43188300 |
| C | -1.65547700 | 4.59097200 | 0.92214500 |
| C | 1.02208400 | 4.40083000 | 0.24017600 |
| H | 0.39587000 | 2.96889400 | -1.22949300 |
| C | -0.70386100 | 5.3569000 | 1.59011600 |
| H | -2.70002300 | 4.66529800 | 1.21406700 |
| C | 0.66187600 | 5.28302000 | 1.26815600 |
| H | -1.03799000 | 6.01845100 | 2.38402800 |
| C | 6.68437300 | -0.63502600 | -1.82037400 |
| C | 7.96733600 | -1.46017700 | -1.56086000 |
| H | 7.88798900 | -2.47477800 | -1.96507600 |
| H | 8.83313800 | -0.97969100 | -2.03320900 |
| H | 8.16855800 | -1.54366600 | -0.48672800 |
| C | 6.91053200 | 0.78676900 | -1.27236100 |
| H | 6.04547900 | 1.43532700 | -1.45170300 |
| H | 7.1649700 | 0.78096500 | -0.19593700 |
| H | 7.77364800 | 1.24194300 | -1.77131800 |
| C | 6.44429200 | -0.53010500 | -3.34541900 |
| H | 6.31699700 | -1.51516400 | -3.80650600 |
| H | 5.54478800 | 0.05793500 | -3.56057900 |
| H | 7.29603800 | -0.04064900 | -3.83385100 |
| H | 2.06031800 | 4.30578000 | -0.05842000 |
| C | 1.68219700 | 6.14571500 | 2.03204000 |
| C | 1.32989500 | 7.64168600 | 1.85265700 |
| H | 0.32799400 | 7.87261600 | 2.22950600 |
| H | 2.04445400 | 8.27052900 | 2.39803500 |
| H | 1.36301800 | 7.92783300 | 0.79520300 |
| C | 3.12307800 | 5.92957100 | 1.53199200 |
| H | 3.44753200 | 4.89055300 | 1.65937400 |
| H | 3.23185300 | 6.19492100 | 0.47423700 |
| H | 3.81109100 | 6.56271600 | 2.10363500 |
| C | 1.63614900 | 5.78668500 | 3.53652700 |
| H | 0.64384200 | 5.95883100 | 3.9663700 |
| H | 1.89072900 | 4.33259300 | 3.69544400 |
| H | 2.35345400 | 6.39847700 | 4.09748200 |
|  |  |  |  |

## Compound 7:

|  |  |  |  |
| :--- | ---: | ---: | ---: |
| C | -5.28389700 | -2.96408500 | 0.86272800 |
| C | -3.89177900 | -2.92667900 | 0.73307500 |
| C | -3.20735400 | -1.77021200 | 0.34015400 |
| C | -3.95903900 | -0.59552700 | 0.05821300 |
| C | -5.35299300 | -0.66102000 | 0.18846100 |
| H | -6.02770900 | -1.81553800 | 0.58432000 |
| H | -3.34605700 | -3.84692600 | 0.91257400 |
| C | -7.10785100 | -1.80128600 | 0.67419700 |
| C | 1.08054200 | -2.25646400 | -0.0 .0692300 |
| C | 2.53015700 | -2.55454500 | -0.29175000 |
| C | 3.86482700 | -3.87334600 | -0.60802200 |
| C | 3.54810600 | -1.56756000 | -0.24962400 |
| H | 4.17979400 | -4.24803000 | -0.90947700 |
| C | 2.09120000 | -4.63332500 | -0.6567600 |
| C | 4.85484700 | -1.96477000 | -0.56701300 |
| H | 5.18550000 | -3.27820600 | -0.90064800 |
| C | 6.21539100 | -3.52844100 | -1.12842500 |
| C | -1.72362400 | -1.87326400 | 0.20792700 |
| H | -1.02338200 | -1.33700200 | -0.88630700 |
| C | -1.56255100 | -0.79180300 | -1.65332100 |
| H | 0.35150500 | -1.51408900 | -1.01777900 |
| C | 0.86488500 | -1.09803700 | -1.88014000 |
| H | -0.98400700 | -2.59209500 | 1.16231700 |
| C | -1.49060000 | -2.99869500 | 2.03314100 |
| H | 0.38691800 | -2.79403300 | 1.01544300 |
| H | 0.92913400 | -3.37054300 | 1.76077800 |
| H | 5.64872100 | -1.22463800 | -0.51793800 |
| C | -5.93085100 | 0.23886900 | -0.00298900 |
| C | 3.32911300 | -0.15898600 | 0.18370400 |
| C | 2.66794400 | 0.15006500 | 1.38431100 |
| C | 3.88066100 | 0.90952100 | -0.53606700 |
| H | 2.59910100 | 1.45877000 | 1.85083400 |
| C | 2.22972100 | -0.64833600 | 1.97480200 |
| H | 3.80432800 | 2.22225100 | -0.06603100 |
| C | 4.38077100 | 0.71237300 | -1.48111300 |
| H | 3.17741600 | 2.53057800 | 1.14842200 |
| H | 2.10173900 | 1.64045900 | 2.79997100 |
| C | 4.25477100 | 3.00737400 | -0.66374600 |
| C | -3.36888200 | 0.70878700 | -0.35702100 |
| C | -2.33795500 | 1.33812500 | 0.35973800 |
| C | -3.87553700 | 1.38175200 | -1.47710800 |
| H | -1.83831900 | 2.57342300 | -0.03929300 |
| C | -1.92387400 | 0.85362300 | 1.23887700 |
| H | -3.37342700 | 2.62350700 | -1.87105700 |
| C | -4.66541000 | 0.91804300 | -2.06269700 |
| H | -2.33968800 | 3.25087900 | -1.16557400 |
| H | -1.03619700 | 3.01541800 | 0.54511900 |
| H | -3.80041600 | 3.09366200 | -2.75027900 |
| C | -1.74366400 | 4.60675000 | -1.58373200 |
| C | -2.47276400 | 5.21962200 | -2.79476100 |
| H | -3.53463500 | 5.39332300 | -2.58577800 |
| H | -2.02205400 | 6.18645600 | -3.04627900 |
| H | -2.39854500 | 4.58172800 | -3.68273100 |
| -0.25682000 | 4.41186200 | -1.96625400 |  |
| 0.19726200 | 5.37187300 | -2.24252500 |  |
| 0.32473200 | 3.98820800 | -1.14089000 |  |


|  |  |  |  |
| :--- | ---: | ---: | ---: |
| C | -1.84727100 | 5.60780900 | -0.40880100 |
| H | -1.41938000 | 6.57664300 | -0.69465000 |
| H | -2.89321400 | 5.76918600 | -0.12355400 |
| H | -1.31053900 | 5.25696900 | 0.47842400 |
| C | 3.14941900 | 3.95054000 | 1.74296800 |
| C | 1.69581100 | 4.37145100 | 2.05963400 |
| H | 1.21265300 | 3.68595300 | 2.76337400 |
| H | 1.67797200 | 5.37266000 | 2.50742800 |
| H | 1.08982100 | 4.39987600 | 1.14703200 |
| C | 3.97459100 | 3.9603200 | 3.05295100 |
| H | 5.01534600 | 3.67501000 | 2.86147200 |
| H | 3.97204900 | 4.96156500 | 3.50109100 |
| H | 3.56794000 | 3.26076800 | 3.79128300 |
| C | 3.75104200 | 4.99815300 | 0.78695900 |
| H | 4.80614600 | 4.79620200 | 0.57091800 |
| H | 3.20875500 | 5.03920100 | -0.16471800 |
| H | 3.69418500 | 5.99233200 | 1.24468800 |
| O | 4.36787900 | -5.56818600 | -1.20430300 |
| O | -5.81011200 | -4.16302400 | 1.25238000 |
| C | 5.67792500 | -5.99817800 | -1.53575600 |
| H | 5.60013800 | -7.06810700 | -1.73783800 |
| H | 6.05705800 | -5.48710000 | -2.4308900 |
| H | 6.37910700 | -5.83662500 | -0.70602600 |
| C | -7.21908100 | -4.26396900 | 1.37655000 |
| H | -7.42011300 | -5.29177000 | 1.68460000 |
| H | -7.60893700 | -3.57533100 | 2.13814600 |
| H | -7.72452800 | -4.06653900 | 0.42169400 |

## Compound 8:

| C | -4.98584500 | -3.11191600 | -0.58925100 |
| :---: | :---: | :---: | :---: |
| C | -3.60435000 | -3.14116500 | -0.42828300 |
| C | -2.88249400 | -1.99825500 | -0.04473100 |
| C | -3.58831300 | -0.78813700 | 0.19808800 |
| C | -4.98195800 | -0.78008700 | 0.00738400 |
| C | -5.68464600 | -1.91161400 | -0.37876600 |
| H | -3.10608800 | -4.07730900 | -0.64891000 |
| H | -6.75762000 | -1.85239800 | -0.52002200 |
| C | 1.41862200 | -2.01022100 | -0.03121200 |
| C | 2.88248900 | -1.99826600 | 0.04471100 |
| C | 3.60434100 | -3.14118000 | 0.42826200 |
| C | 3.58831300 | -0.78815000 | -0.19810900 |
| C | 4.98583500 | -3.11193600 | 0.58922900 |
| H | 3.10607500 | -4.07732100 | 0.64889200 |
| C | 4.98195900 | -0.78010600 | -0.00740800 |
| C | 5.68464200 | -1.91163700 | 0.37874000 |
| H | 6.75761700 | -1.85242700 | 0.51999000 |
| C | -1.41862700 | -2.01021600 | 0.03119400 |
| C | -0.70773600 | -0.79119500 | 0.14127600 |
| C | 0.70773500 | -0.79119700 | -0.14128500 |
| C | -0.68572000 | -3.21873700 | -0.03228400 |
| H | -1.20753500 | -4.16811200 | -0.06332400 |
| C | 0.68571000 | -3.21874000 | 0.03225900 |
| H | 1.20752200 | -4.16811800 | 0.06329000 |
| H | 5.53810800 | 0.14047700 | -0.14862500 |
| H | -5.53810300 | 0.14050000 | 0.14860000 |
| C | 2.85291100 | 0.37119400 | -0.69335100 |
| C | 3.50918300 | 1.47622100 | -1.27757200 |
| C | 1.43497500 | 0.37312600 | -0.67120900 |
| C | 2.80987500 | 2.51622300 | -1.85675700 |
| H | 4.59308700 | 1.49624800 | -1.31886500 |
| C | 0.75050800 | 1.42929900 | -1.32136100 |
| C | 1.39874900 | 2.50403700 | -1.91580100 |
| H | 3.36745500 | 3.33205400 | -2.30819000 |
| H | -0.32702300 | 1.37170300 | -1.37126300 |
| C | -2.85290900 | 0.37120300 | 0.69333800 |
| C | -3.50917800 | 1.47623000 | 1.27756100 |
| C | -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 |
| C | -1.39874100 | 2.50403800 | 1.91579800 |
| H | -3.36744700 | 3.33205500 | 2.30819200 |
| H | 0.32702600 | 1.37169300 | 1.37127200 |
| C | 0.65237700 | 3.62799300 | -2.65606600 |
| C | 1.03092200 | 4.99618300 | -2.04106400 |
| H | 0.51277600 | 5.80656400 | -2.56828000 |
| H | 0.74687900 | 5.04375200 | -0.98353200 |
| H | 2.10613000 | 5.19350500 | -2.10645000 |
| C | -0.87779400 | 3.47197000 | -2.57339700 |
| H | -1.36169300 | 4.30658300 | -3.09359000 |
| H | -1.21973800 | 2.54606600 | -3.04925400 |
| H | -1.23310500 | 3.47303000 | -1.53695700 |
| C | 1.06150000 | 3.61288700 | -4.14882200 |
| H | 2.13912700 | 3.76139700 | -4.27698200 |
| H | 0.79806900 | 2.65744700 | -4.61648100 |
| H | 0.54627500 | 4.41298600 | -4.69477800 |


|  |  |  |  |
| :--- | ---: | ---: | ---: |
| C | -0.65236600 | 3.62797400 | 2.65609100 |
| C | 0.87780000 | 3.47175100 | 2.57371400 |
| H | 1.36171100 | 4.30642200 | 3.09380400 |
| H | 1.21955700 | 2.54591400 | 3.04983600 |
| H | 1.23328400 | 3.47253600 | 1.53733300 |
| C | -1.06176400 | 3.61305200 | 4.14877300 |
| H | -0.54656200 | 4.41315300 | 4.69474800 |
| H | -2.13940100 | 3.76167800 | 4.27671700 |
| H | -0.79851300 | 2.65763100 | 4.61657300 |
| C | -1.03062300 | 4.99615800 | 2.04089800 |
| H | -2.10580900 | 5.19365100 | 2.10611400 |
| H | -0.51242800 | 5.80651300 | 2.56810500 |
| H | -0.74642400 | 5.04357800 | 0.98340100 |
| O | -5.56587000 | -4.28851000 | -0.9723500 |
| O | 5.56585600 | -4.28853300 | 0.97232700 |
| C | 6.96971500 | -4.31295200 | 1.17129400 |
| H | 7.27835700 | -3.62537900 | 1.97012400 |
| H | 7.21210100 | -5.33602000 | 1.46498300 |
| H | 7.51435000 | -4.06290300 | 0.25102400 |
| C | -6.96974100 | -4.31294600 | -1.17123500 |
| H | -7.27844100 | -3.62539200 | -1.97006000 |
| H | -7.21213500 | -5.33602100 | -1.46488700 |
| H | -7.51431800 | -4.06288200 | -0.25093700 |

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

## Compound 8:

Excited State
$216->223$
$217->221$
$217->222$
$218->221$
$219->220$

Excited State
215 -> 224
217 -> 221
218 -> 221 219 -> 220

Excited State
214 -> 221
216 -> 221
216 -> 222
217 -> 220
217 -> 223
218 -> 220
218 -> 223
219 -> 221
219 -> 222 219 -> 224

Excited State
215 -> 220
216 -> 221
216 -> 222
217 -> 220
217 -> 223
218 -> 220
218 -> 223
219 -> 221
219 -> 222
219 -> 224
Excited State 218 -> 220 219 -> 221

Excited State 218 -> 220 219 -> 221

Excited State
210 -> 221
212 -> 226
213 -> 227
214 -> 224
215 -> 220
216 -> 221
216 -> 222
217 -> 220
217 -> 223

1: Triplet-A 0.13361
0.11768
0.12945
0.47322
$-0.41362$
2: Triplet-A -0.10444 0.10240 0.42875 0.48609

3: Triplet-A 0.11919
0.15547
$-0.14695$
-0.20069
-0.10134
-0.32601
0.13540
0.41641
0.12227
0.10658

4: Triplet-A
-0.16655
0.11499
-0.20207
-0.21773
-0.14770
0.31822
0.19059
-0.26992
0.13903
0.23299

5: Triplet-A
0.50513
0.45429

6: Singlet-A
0.49439
0.49070

7: Triplet-A 0.11113
$-0.11432$
0.11019
$-0.13383$
-0.26407
-0.22466
0.16223
$-0.17035$
0.15226
$2.3658 \mathrm{eV} 524.06 \mathrm{~nm} \mathrm{f}=0.0000<\mathrm{S}^{* *} 2>=2.000$
$2.8795 \mathrm{eV} 430.57 \mathrm{~nm} \mathrm{f}=0.0000<S^{* *} 2>=2.000$
2.8827 eV $430.09 \mathrm{~nm} \mathrm{f}=0.0000<\mathrm{S}^{* *} 2>=2.000$
$3.0707 \mathrm{eV} 403.77 \mathrm{~nm} \mathrm{f}=0.0000<\mathrm{S}^{* *} 2>=2.000$
$3.1521 \mathrm{eV} 393.34 \mathrm{~nm} \mathrm{f}=0.0000<S^{* *} 2>=2.000$
$3.2654 \mathrm{eV} 379.69 \mathrm{~nm} \mathrm{f}=0.0000<\mathrm{S}^{* *} 2>=0.000$
$3.3401 \mathrm{eV} 371.20 \mathrm{~nm} \mathrm{f}=0.0000<S^{* *} 2>=2.000$

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

## Compound 32A:

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


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

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[^0]:    ${ }^{1}$ 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.

