

CHEMICAL COMMUNICATIONS

Discrete, soluble covalent organic boronate ester rectangles

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SUPPORTING INFORMATION

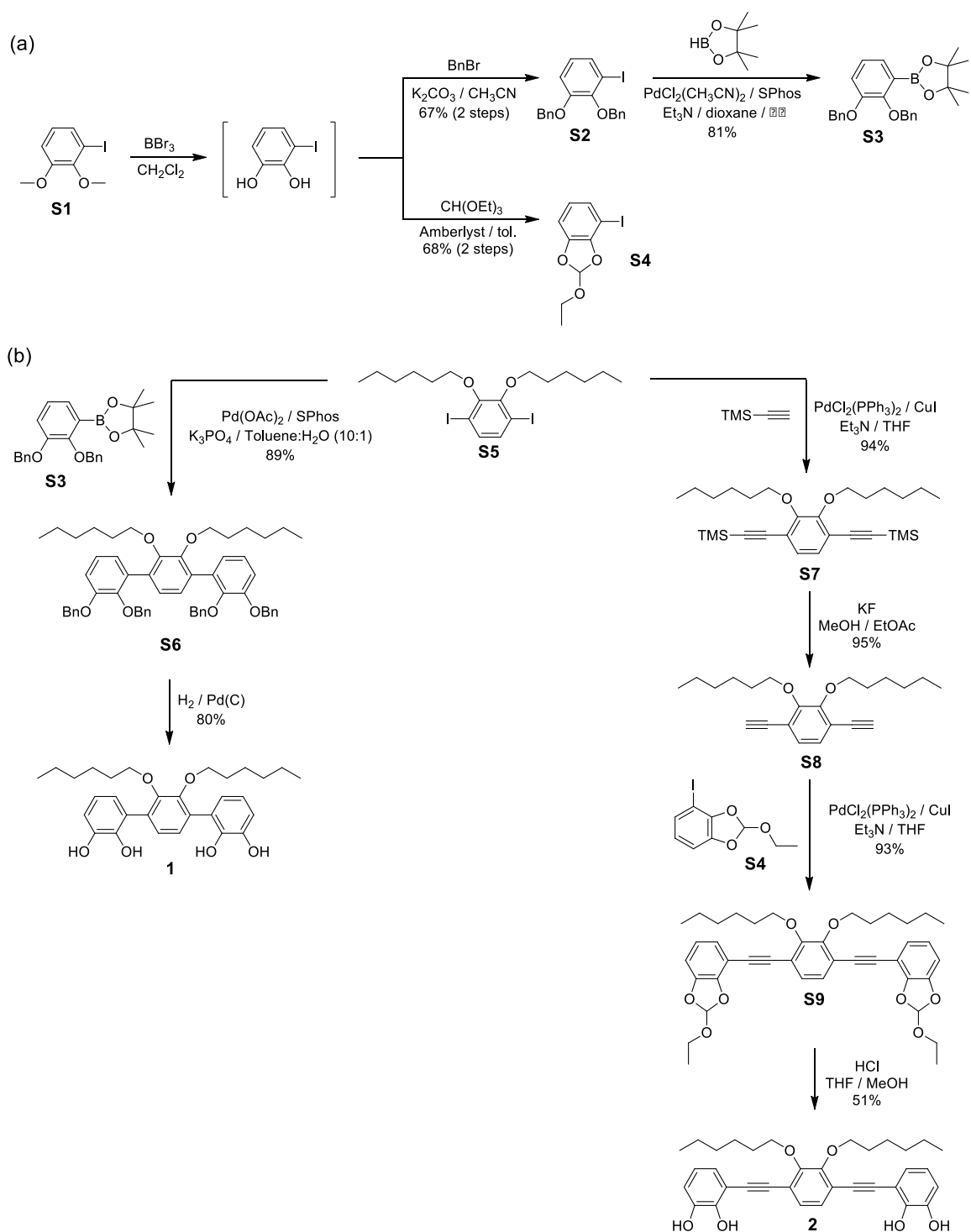
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I. General Synthetic Procedures

General Methods: Chemicals were purchased from Aldrich, Strem, Acros, TCI America, or Cambridge Isotope Labs and used as received. 1-Iodo-2,3-dimethoxybenzene **S1**,¹ and 2,3-bis(hexyloxy)-1,4-diiodobenzene **S5**² were prepared according to literature procedures. Solvents were dried using an Innovative Technologies SPS-400-5 solvent purification system. All reactions were carried out under an anhydrous N₂ atmosphere unless otherwise noted. Thin layer chromatography (TLC) was performed on alumina-backed sheets coated with silica gel 60 F254. Preparative TLC was performed on 20x20cm plates coated with a 1000 µm thick layer of 150 Å silica with F254 indicator. TLC plates were visualized using a UV/Vis lamp and/or by staining with iodine or *p*-anisaldehyde solution. Column chromatography was performed using glass columns over Dynamic Absorbents 60 Å, 32-63 µm silica gel. Melting points were determined on a Mettler Toledo Mel-Temp II melting point apparatus and are uncorrected. All ¹H and ¹³C NMR spectra were recorded with a Varian Mercury (300 MHz and 75 MHz, respectively) or Varian Unity Plus (400 MHz and 100 MHz, respectively) spectrometer using residual solvent as the internal standard. All chemical shifts are quoted using the δ scale and all coupling constants are expressed in Hertz (Hz). Infrared spectroscopic analysis was performed on a Perkin-Elmer Spectrum BX FT-IR system. UV/Vis spectroscopy was recorded on a Varian Cary 100 Bio UV-Visible spectrophotometer. Fluorescence data were gathered on a Jobin Yvon-SPEX FluoroMax-2. APCI and MALDI accurate mass spectrometric analysis of compounds **S2**, **S3**, **S4**, **S6**, **S7**, **S8**, **S9**, **1**, **2**, **3**, and **4** were performed at the UC Riverside Mass Spec Facility.

II. Synthesis of Compounds



S1: Prepared according to literature procedures.¹

S2: To a solution of **S1** (977 mg, 3.70 mmol) dissolved in dry dichloromethane (37 mL), boron tribromide (1.1 mL, 11.1 mmol) was added slowly under an inert atmosphere at 0 °C. The reaction mixture was allowed to return slowly to room temperature and stir for 3 hours, at which point the reaction was chilled to 0 °C and quenched with a minimum volume of water. The mixture was concentrated under reduced pressure, and the residue extracted with ethyl acetate (3x50 mL). The combined organic extracts were dried over MgSO₄ and concentrated in vacuo to yield solid 3-iodocatechol intermediate (870 mg). This solid was used directly in the following step without further purification. To a solution of 3-iodocatechol intermediate (870 mg, 3.69 mmol), potassium carbonate (2.04 g, 14.8 mmol), potassium iodide (123 mg, 0.738 mmol), in dry acetone (46 mL) was added benzyl bromide (1.1 mL, 9.22 mmol) under an inert atmosphere. The reaction solution was stirred under reflux for 12 hours. The solvent was evaporated under reduced pressure, water (50 mL) added, and the aqueous layer extracted with ethyl acetate (3x50 mL). The combined organic extracts were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The resulting residue was purified via column chromatography using a gradient starting with 9:1 hexanes:dichloromethane and increasing to 4:1 hexanes:dichloromethane, yielding white solid **S2** (1.01 g, 67%). Mp 62-64 °C; APCI-MS (m/z) [M+NH₄]⁺ calculated for C₂₀H₂₁NO₂I, 434.0612; found 434.0615 (ppm error = 0.8); ¹H NMR (CDCl₃, 300 MHz): δ 7.52-7.32 (m, 11H), 6.97 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.79 (t, *J* = 8.7 Hz, 1H), 5.12 (s, 2H), 5.04 (s, 2H); ¹³C NMR (CDCl₃, 75 MHz): 152.34, 148.56, 137.23, 136.75, 131.45, 129.01, 128.83, 128.53, 128.34, 128.32, 127.74, 126.24, 115.04, 93.49, 74.82, 71.37

S3: Modified from a literature procedure.² To a pressure flask charged with nitrogen was added **S2** (600 mg, 1.44 mmol), 2-dicyclohexylphosphino-2'-6'-dimethoxybiphenyl (Buchwald S-Phos ligand) (24 mg, 0.058 mmol), and bis(acetonitrile) palladium(II)chloride (3.7 mg, 0.014 mmol). The pressure flask was capped with a septum, evacuated and nitrogen filled three times before dry 1,4-dioxane (1 mL) and dry triethylamine (0.6 mL) were added. Pinacolborane (0.31 mL) was added quickly, and the flask immediately capped. The reaction was allowed to stir at 110 °C until the residue darkened and became thick (3 hours). The reaction mixture was filtered through Celite, eluting with ethyl acetate, and the filtrate concentrated under reduced pressure. The pure product was recrystallized from the reaction residue from dichloromethane/ethanol yielding colorless solid **S3** (546 mg, 81%). Mp = 83-84 °C; APCI-MS (m/z) [M+Na]⁺ calculated for C₂₆H₂₉BO₄Na, 439.2051; found 439.2054 (ppm error = 0.7); ¹H NMR (CDCl₃, 300 MHz): δ 7.47-7.28 (m, 11H), 7.04-6.96 (m, 2H), 5.05 (s, 2H), 4.98 (s, 2H),

1.26 (s, 12H); ^{13}C NMR (CDCl_3 , 75 MHz): 154.04, 152.14, 138.39, 137.49, 129.00, 128.70, 128.32, 128.06, 127.90, 127.73, 124.43, 118.52, 83.83, 76.06, 71.49

S4: To a solution of **S1** (1.0 g, 3.8 mmol) dissolved in dry dichloromethane (30 mL), was added boron tribromide (0.91 mL, 9.5 mmol) slowly under an inert atmosphere at 0 °C. The reaction mixture was allowed to return slowly to room temperature and stir for 3 hours, at which point the reaction was chilled to 0 °C and quenched with a minimum volume of water. The mixture was concentrated under reduced pressure, and the residue extracted with ethyl acetate (3x50 mL). The combined organic extracts were dried over MgSO_4 and concentrated in vacuo to yield solid 3-iodocatechol intermediate (0.9 g). This solid was taken up directly in dry toluene (38 mL). To this reaction solution was added ethyl orthoformate (1.9 mL, 11.4 mmol) and Amberlyst (19 mg, 5mg/mol intermediate), and the reaction mixture stirred at reflux for 12 hours. After cooling to room temperature, the reaction mixture was filtered through Celite (eluting with ethyl acetate). The filtrate was concentrated in vacuo onto silica, and the residue carried directly to column chromatography, eluting with 4:1 hexanes to dichloromethane to yield clear oil **S4** (744 mg, 68%). APCI-MS (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_9\text{H}_{10}\text{O}_3\text{I}$, 292.9669; found 292.968 (ppm error = 3.7); ^1H NMR (CDCl_3 , 300 MHz): δ 7.17 (dd, $J = 8.4, 1.2$ Hz, 1H), 6.91 (s, 1H), 6.82 (dd, $J = 7.5, 0.9$ Hz, 1H), 6.64 (t, $J = 7.8$ Hz, 1H), 3.74 (q, $J = 7.2$ Hz, 2H), 1.28 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz): 148.00, 145.25, 130.49, 123.58, 118.39, 108.37, 70.73, 59.88, 15.08

S5: Prepared according to literature procedures.²

S6: Modified from a literature procedure (4). To a mixture of **S5** (170 mg, 0.32 mmol), **S3** (400 mg, 0.96 mmol), and potassium carbonate (530 mg, 3.84 mmol) was added Buchwald SPhos palladacycle (24 mg, 0.038 mmol) under an inert atmosphere. Degassed solvents toluene (3.2 mL) and water (0.32 mL) were added and the solution stirred at 90°C for 48 hours. The reaction solution was allowed to cool; water (25 mL) was added, and extracted with ethyl acetate (3x25 mL). The combined organic extracts were dried over MgSO_4 and concentrated under reduced pressure. The crude material was purified through column chromatography using a gradient of 4:1 hexanes:dichloromethane moving to 2:1 hexanes:dichloromethane yielding 244 mg (0.29 mmol, 89%) colorless oil **S6**. APCI-MS (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{58}\text{H}_{63}\text{O}_6$, 855.4619; found 855.4615 (ppm error = -0.5); ^1H NMR (CDCl_3 , 300 MHz): δ 7.50-7.47 (m, 4H), 7.42-7.33 (m, 6H), 7.15-7.00 (m, 18H), 5.18 (s, 4H), 4.93 (s, 4H), 3.73 (t, $J = 6.5$ Hz, 4H), 1.39 (t, $J = 6.9$ Hz, 4H), 1.14-1.03 (m, 12H), 0.80 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (CDCl_3 , 75 MHz): 152.40, 150.81, 138.19, 137.48, 134.23, 133.33, 128.75, 128.34,

128.20, 128.10, 127.72, 127.64, 125.63, 124.21, 123.70, 113.96, 74.84, 73.55, 71.28, 31.82, 30.40, 25.75, 22.86, 14.31

S7: To a foil-wrapped 50mL Schlenk flask was added **S5** (300 mg, 0.566 mmol), trans-dichlorobis(triphenylphosphine)palladium (II) (79 mg, 0.113 mmol), and copper iodide (17 mg, 0.091 mmol) in that order. These solids were dissolved in a 1:1 solution of dry, degassed triethylamine (11 mL) and THF (11 mL), under nitrogen. To the reaction flask was added 0.32 mL (2.26 mmol) of tri-methyl-silylacetylene, and the solution was allowed to stir under nitrogen for 36 hours. The reaction mixture was concentrated under reduced pressure, and water (50 mL) was added. This aqueous layer was extracted with dichloromethane (3x50 mL), and the combined organic extracts washed with brine, dried over MgSO₄, and concentrated under reduced pressure to provide a black oil. The residue was purified by column chromatography with hexanes/dichloromethane (elutes 9:1) to afford 250 mg (0.531 mmol, 94%) of yellow oil **S7**. $R_f = 0.27$ (9:1 hexanes/CH₂Cl₂); APCI-MS (m/z) [M+Na]⁺ calculated for C₂₈H₄₆O₂NaSi₂, 493.2929; found 493.2936 (ppm error = 1.5); ¹H NMR (CDCl₃, 300 MHz): δ 7.06 (s, 2H), 4.07 (t, $J = 6.7$ Hz, 4H), 1.78-1.75 (m, 4H), 1.54-1.51 (m, 4H), 1.35-1.32 (m, 8H), 0.90 (t, $J = 7.0$ Hz, 6H); ¹³C NMR (CDCl₃, 75 MHz): 154.20, 128.13, 119.57, 100.97, 100.27, 74.37, 31.92, 30.51, 25.93, 22.79, 14.26, 0.13

S8: To a solution of **S7** (208 mg, 0.442 mmol) and potassium fluoride (154 mg, 2.65 mmol) in methanol (4.4 mL) was added ethyl acetate dropwise until the solution became homogenous. The reaction was stirred overnight at room temperature, then acidified with 1N HCl (12 mL). The methanol and ethyl acetate were evaporated in vacuo, and the aqueous mixture extracted with ethyl acetate (3x25 mL). The combined organic extracts were washed with brine, dried over MgSO₄, and concentrated under reduced pressure to yield orange oil **S8** (416 mg, 95%). APCI-MS (m/z) [M+H]⁺ calculated for C₂₂H₃₁O₂, 327.2319; found 327.2333 (ppm error = 4.4); ¹H NMR (CDCl₃, 300 MHz): δ 7.11 (s, 2H), 4.09 (t, $J = 6.6$ Hz, 4H), 3.31 (s, 2H), 1.78-1.75 (m, 4H), 1.54-1.51 (m, 4H), 1.35-1.32 (m, 8H), 0.90 (t, $J = 6.9$ Hz, 6H); ¹³C NMR (CDCl₃, 75 MHz): 154.52, 128.42, 119.00, 82.80, 79.75, 74.52, 31.87, 30.42, 25.89, 22.87, 14.29

S9: To a foil-wrapped 50mL Schlenk flask was added **S8** (150 mg, 0.459 mmol), **S4** (470 mg, 1.61 mmol), trans-dichlorobis(triphenylphosphine)palladium (II) (64 mg, 0.092 mmol), and copper iodide (14 mg, 0.073 mmol) in that order. These solids were dissolved in a 1:1 solution of dry, degassed triethylamine (9.2 mL) and THF (9.2 mL), under nitrogen, and the reaction allowed to stir for 48 hours. The reaction mixture was concentrated under reduced pressure, and water (25 mL) was added. The aqueous layer

was extracted with dichloromethane (3x25 mL), and the combined organic extracts washed with brine, dried over MgSO₄, and concentrated under reduced pressure onto silica. The residue was immediately subjected to column chromatography, eluting with 24:1 hexanes:ethyl acetate to yield bright yellow solid **S9** (280 mg, 93%). Mp = 89-90°C; LIFDI-MS (m/z) [M]⁺ calculated for C₄₀H₄₆O₈, 654.3187; found 654.3214 (ppm error = 4.1); ¹H NMR (CDCl₃, 75 MHz): δ 7.21 (s, 2H), 7.02-7.00 (m, 2H), 6.94 (s, 2H), 6.87-6.83 (m, 4H), 4.17 (t, *J* = 6.9 Hz, 4H), 3.76 (q, *J* = 6.9 Hz, 4H), 1.87-1.80 (m, 4H), 1.54-1.51 (m, 4H), 1.35-1.32 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (CDCl₃, 300 MHz): 153.94, 147.12, 146.24, 127.98, 125.05, 121.73, 119.51, 108.71, 104.99, 90.12, 88.88, 74.64, 59.51, 31.99, 30.57, 26.05, 22.88, 15.02, 14.29

1: To a Parr flask was added **S6** (240 mg, 0.28 mmol), tetrahydrofuran (5 mL), and 10% palladium on carbon (50 mg). The flask was placed on a Parr reactor and shaken for 4 hours under 45 psi hydrogen gas. The reaction residue was filtered through a pad of Celite, eluting with ethyl acetate, and the filtrate concentrated under reduced pressure. The reaction residue was subjected to column chromatography, eluting with dichloromethane to yield yellow oil **1** (111 mg, 80%). APCI-MS (m/z) [M+H]⁺ calculated for C₃₀H₃₉O₆, 495.2741; found 495.2732 (ppm error = -0.9); IR (powder, ATR) 3272.00, 2928.20, 1592.15, 1462.31, 1374.87, 1203.52, 1129.69, 1005.21, 770.03, 729.53 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.61 (s, 2H), 7.33 (s, 2H), 7.01-6.89 (m, 6H), 6.01 (s, 2H), 3.93 (t, *J* = 6.0 Hz, 4H), 1.66-1.58 (m, 4H), 1.34-1.15 (m, 12H), 0.87 (t, *J* = 6.0, 6H); ¹³C NMR (CDCl₃, 75 MHz): 148.30, 147.17, 140.57, 132.98, 128.48, 126.34, 122.40, 121.84, 114.75, 76.39, 31.60, 30.05, 25.62, 22.72, 14.12

2: To a solution of **S9** (130 mg, 0.199 mmol) in tetrahydrofuran (9.5 mL) was added concentrated HCl (0.5 mL) and allowed to stir overnight. Water (10 mL) was added, and the tetrahydrofuran evaporated under reduced pressure. The aqueous mixture was extracted with ethyl acetate (3x25 mL), and the combined organic extracts washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The resulting residue was subjected with column chromatography using a gradient starting with dichloromethane and increasing to 5% methanol in dichloromethane, yielding bright yellow solid **2** (55 mg, 51%). Mp = 89-90 °C; APCI-MS (m/z) [M+H]⁺ calculated for C₃₄H₃₉O₆, 543.2741; found 543.276 (ppm error = 3.5); IR (powder, ATR) 3310.81, 2926.60, 1617.17, 1581.61, 1465.64, 1438.01, 1374.96, 1332.25, 1226.08, 1065.31, 1008.93, 816.15, 776.00 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.22 (s, 2H), 6.92-6.88 (m, 4H), 6.76 (t, *J* = 9.0, 2H), 6.23 (s, 2H), 5.32 (s, 2H), 4.12 (t, *J* = 6.0 Hz, 4H), 1.80-1.69 (m, 4H), 1.42-1.33 (m, 4H), 1.27-1.16 (m, 8H), 0.79 (t, *J* = 9.0 Hz, 6H); ¹³C NMR; Solubility precluded collection of a ¹³C spectrum in CDCl₃; (CDCl₃:MeOD (10:1), 75

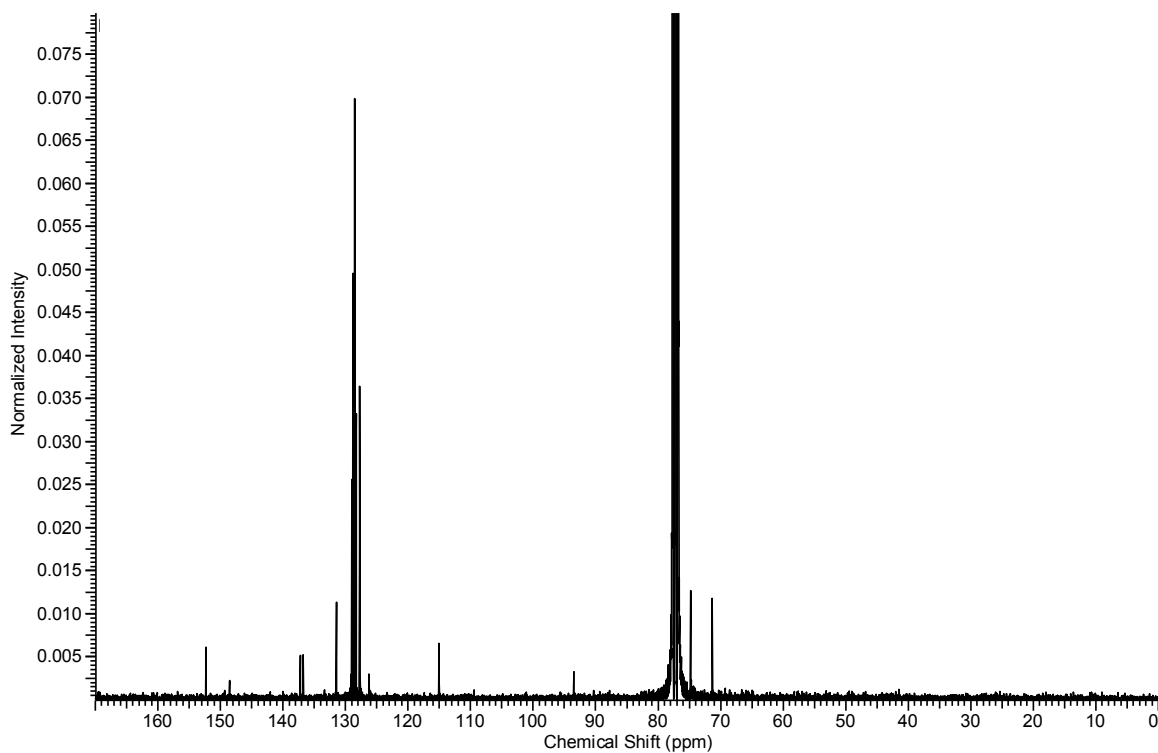
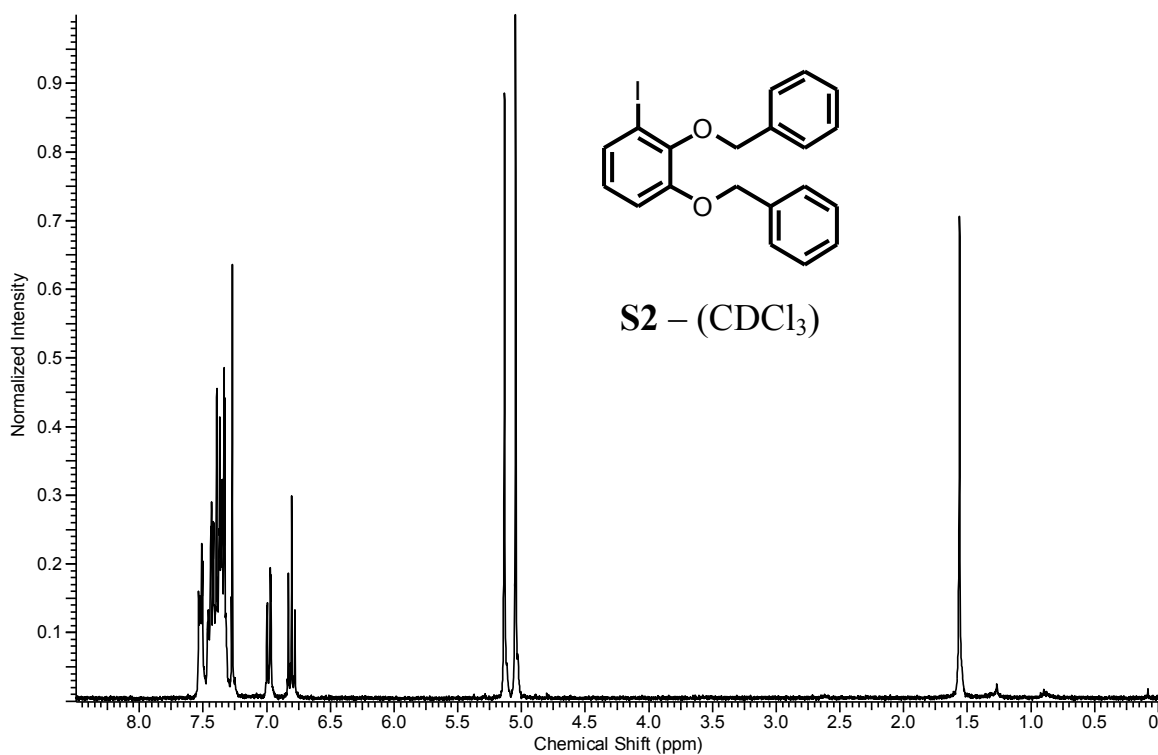
MHz): 152.88, 144.74, 127.98, 123.52, 120.36, 119.46, 116.36, 110.59, 90.83, 90.26, 74.94, 31.79, 30.30, 25.94, 22.72, 14.07

3: To a solution of **1** (40.9 mg, 0.083 mmol) and 1,4-benzenediboronic acid (13.7 mg, 0.083 mmol) in deuterated chloroform (8.3 mL) was added deuterated methanol (0.83 mL), and the solution allowed to stir at 50 °C for 3 hours. The reaction solution was allowed to cool slowly to room temperature and 4Å molecular sieves added. The solution was allowed to stir over sieves overnight, and the resulting cloudy solution decanted and concentrated under reduced pressure, yielding 47 mg (0.039 mmol, 94%) grey solid **3**. Mp = (>200°C); MALDI (m/z) [M+Na]⁺ calculated for C₇₂H₇₆B₄O₁₂Na, 1199.5601; found 1199.565 (ppm error = 4.1); IR (powder, ATR) 2927.80, 1521.06, 1364.98, 1325.50, 1246.59, 1198.83, 1145.13, 1083.55, 1018.85, 779.57, 738.10, 659.75 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 8.25 (s, 8H), 7.41-7.16 (m, 16H), 3.97 (t, J = 6.0 Hz, 8H), 1.53-1.44 (m, 8H), 1.35-1.27 (m, 8H), 1.17-1.04 (m, 16H), 0.76 (t, J = 6.0 Hz, 12H); low solubility precluded collection of a satisfactory ¹³C spectrum in pure CDCl₃, therefore the ¹³C spectrum was taken in (10:1) CDCl₃:MeOD (75 MHz): 150.32, 148.68, 146.66, 140.83, 132.89, 128.04, 126.39, 121.93, 114.80, 75.89, 31.57, 30.01, 25.55, 22.65, 14.09

4: To a solution of **2** (11.8 mg, 0.022 mmol) and 1,4-benzenediboronic acid (3.6 mg, 0.022 mmol) in deuterated chloroform (2.2 mL) was added deuterated methanol (0.22 mL), and the solution allowed to stir at 50 °C overnight. The reaction solution was allowed to cool slowly to room temperature and 4Å molecular sieves added. The solution was allowed to stir over sieves overnight, and the resulting solution decanted and concentrated under reduced pressure, yielding 14 mg (0.011 mmol, >99%) grey solid **4**. Mp = (>200°C); MALDI (m/z) [M]⁺ calculated for C₈₀H₇₆B₄O₁₂, 1272.5709; found 1272.5723 (ppm error = 1.1); IR (powder, ATR) 2926.32, 1627.59, 1521.72, 1437.45, 1368.13, 1333.21, 1249.99, 1141.49, 1019.44, 849.52, 732.30, 656.2 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 8.31 (s, 8H), 7.39-7.31 (m, 12H), 7.16 (t, J = 9.0 Hz, 4H), 4.33 (t, J = 6.0 Hz, 8H), 2.02-1.92 (m, 8H), 1.64-1.25 (m, 24H), 0.85 (t, J = 6.0 Hz, 12H); low solubility precluded collection of a satisfactory ¹³C spectrum in pure CDCl₃, therefore the ¹³C spectrum was taken in (10:1) CDCl₃:MeOD (75 MHz): 152.87, 144.74, 132.62, 127.98, 123.51, 120.51, 119.47, 116.35, 110.14, 90.82, 90.28, 74.95, 31.79, 30.30, 25.83, 22.72, 14.07

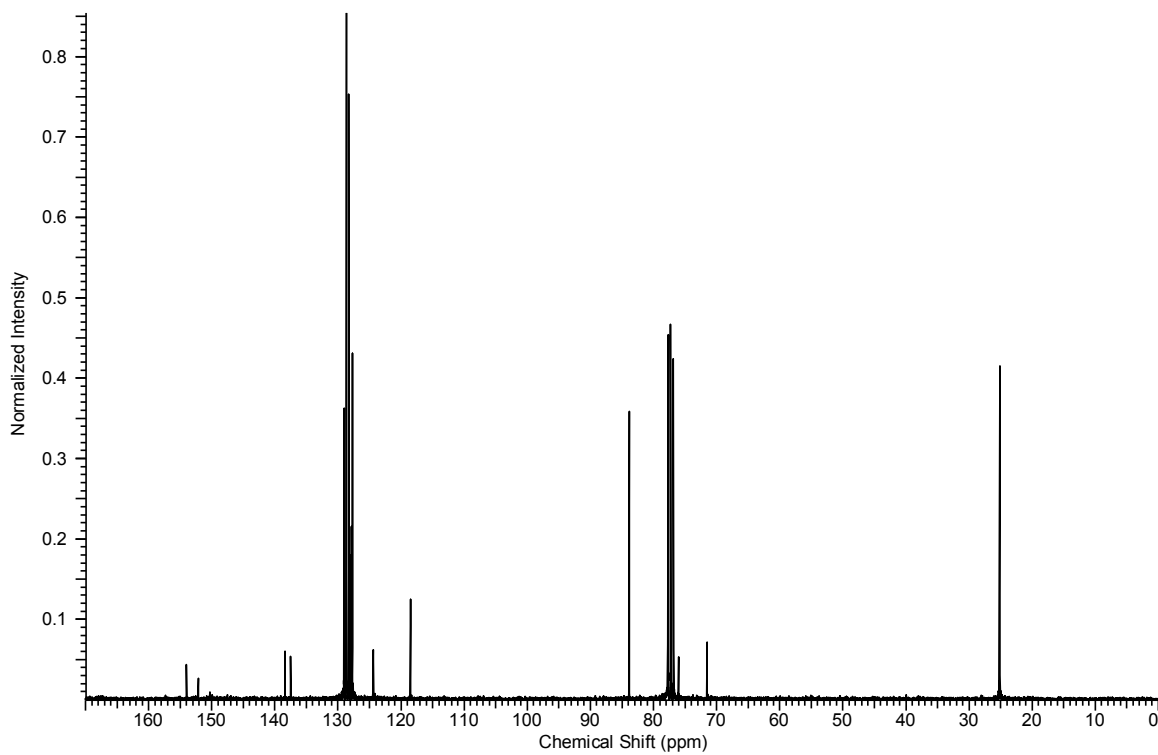
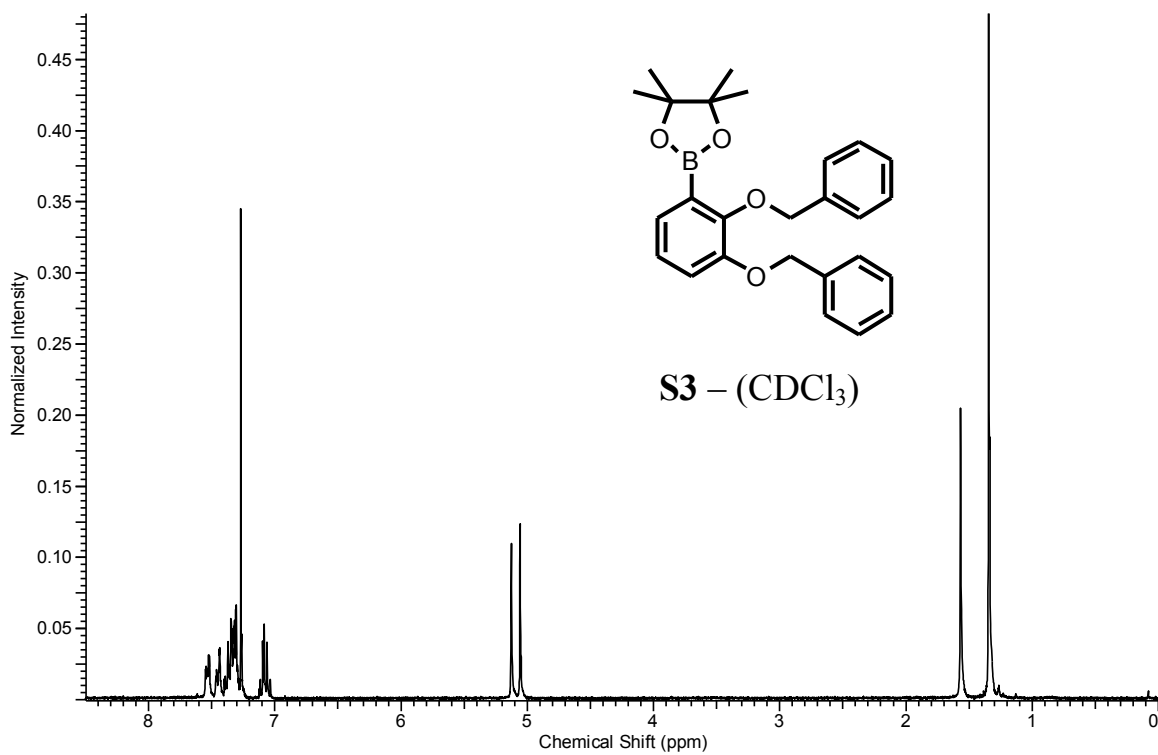
III. ^1H and ^{13}C NMR Spectra

S2



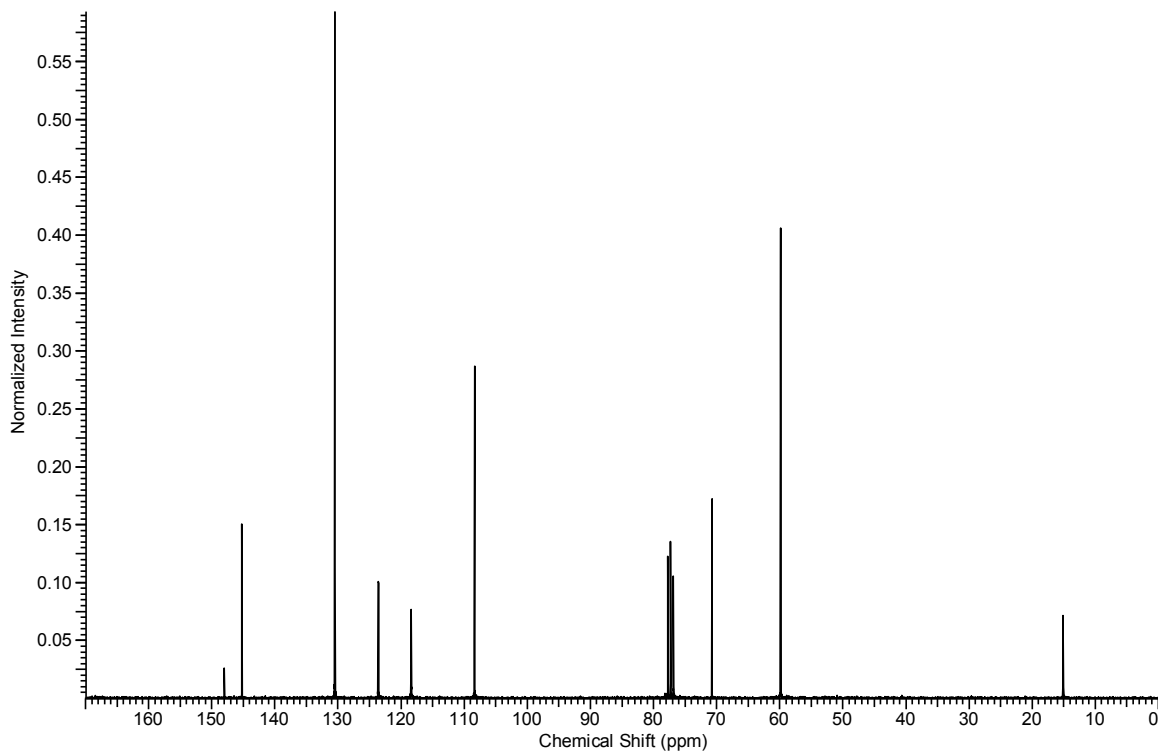
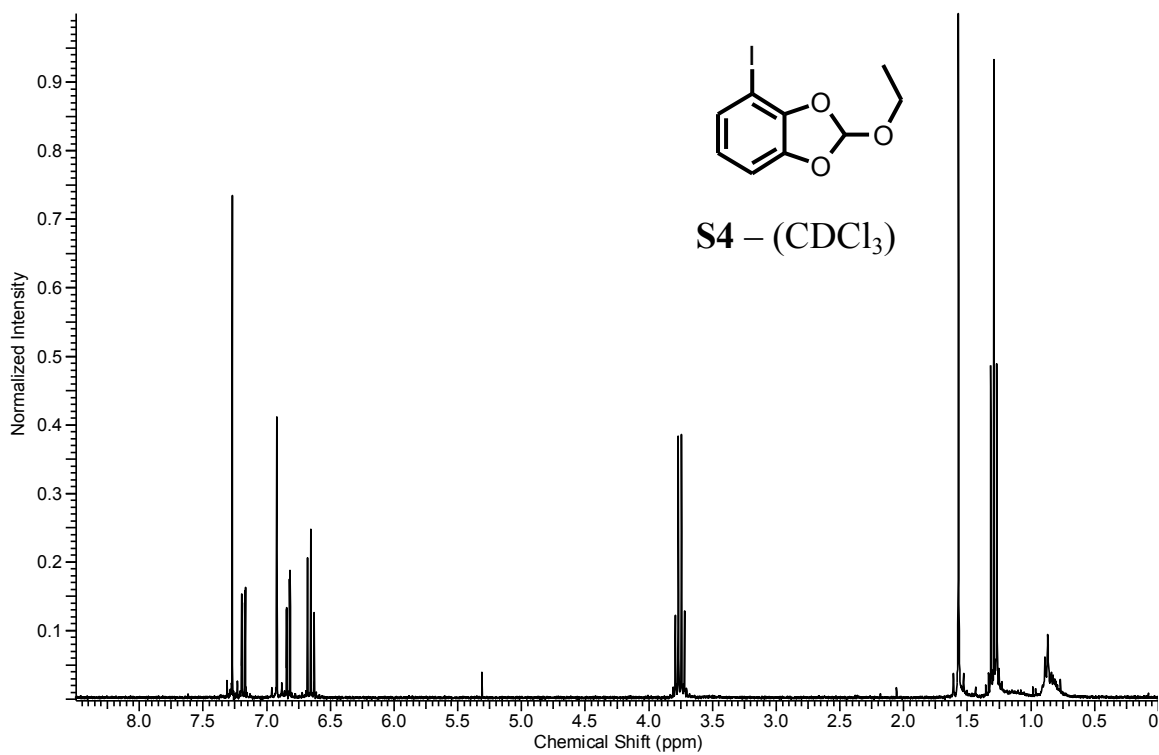
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S3



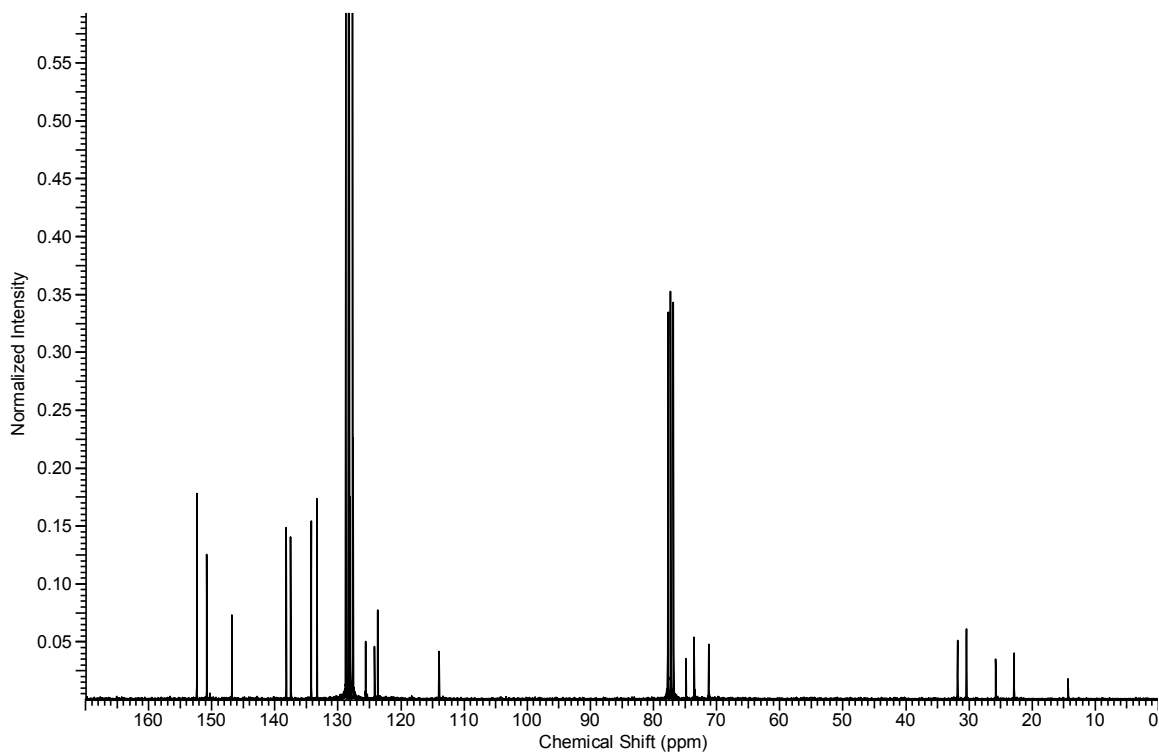
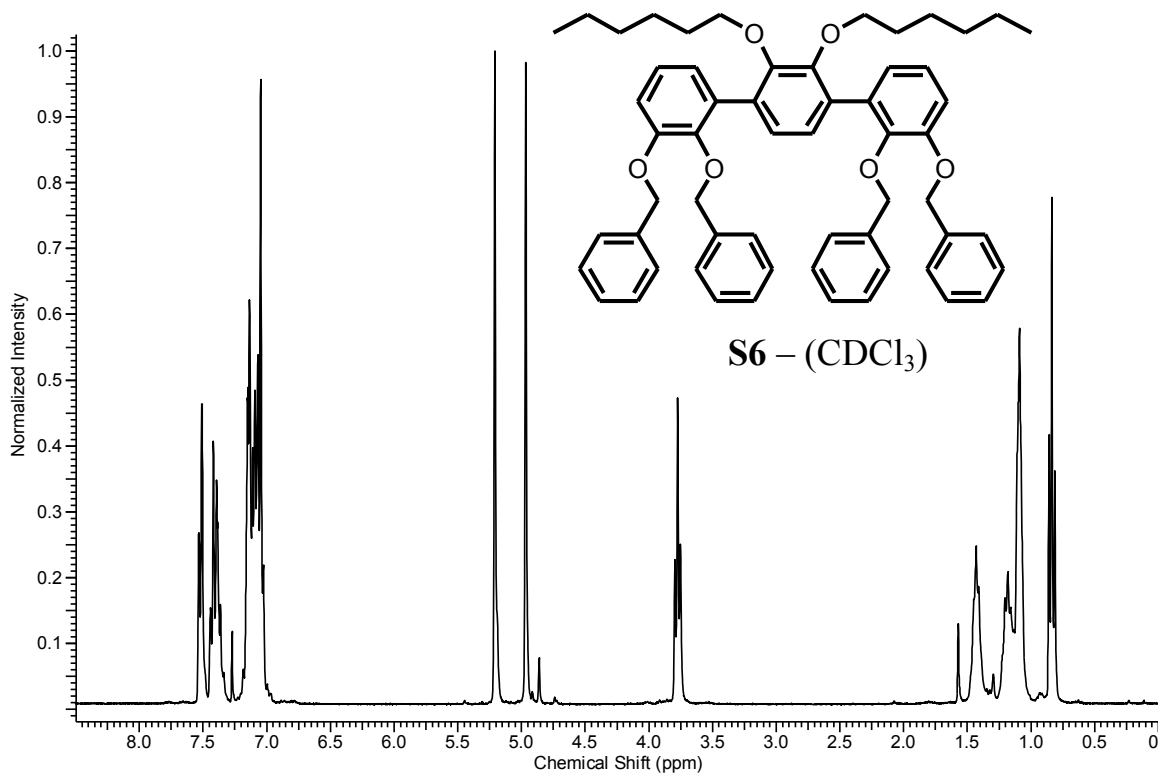
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S4



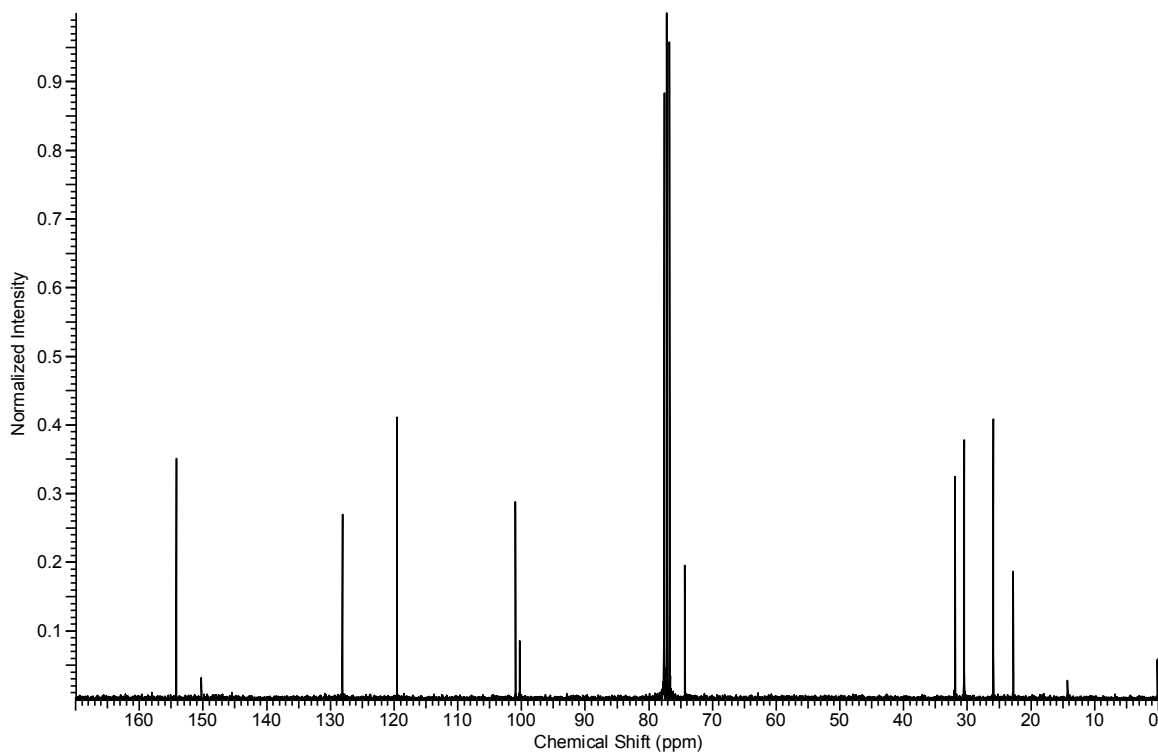
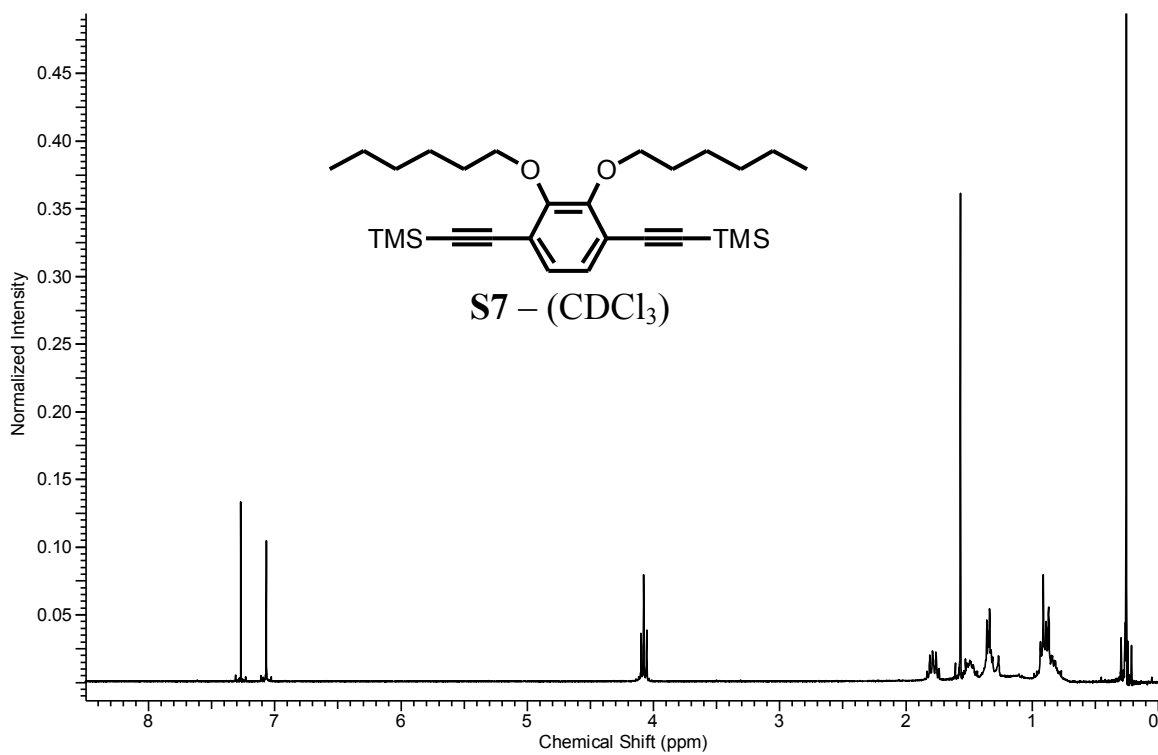
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S6



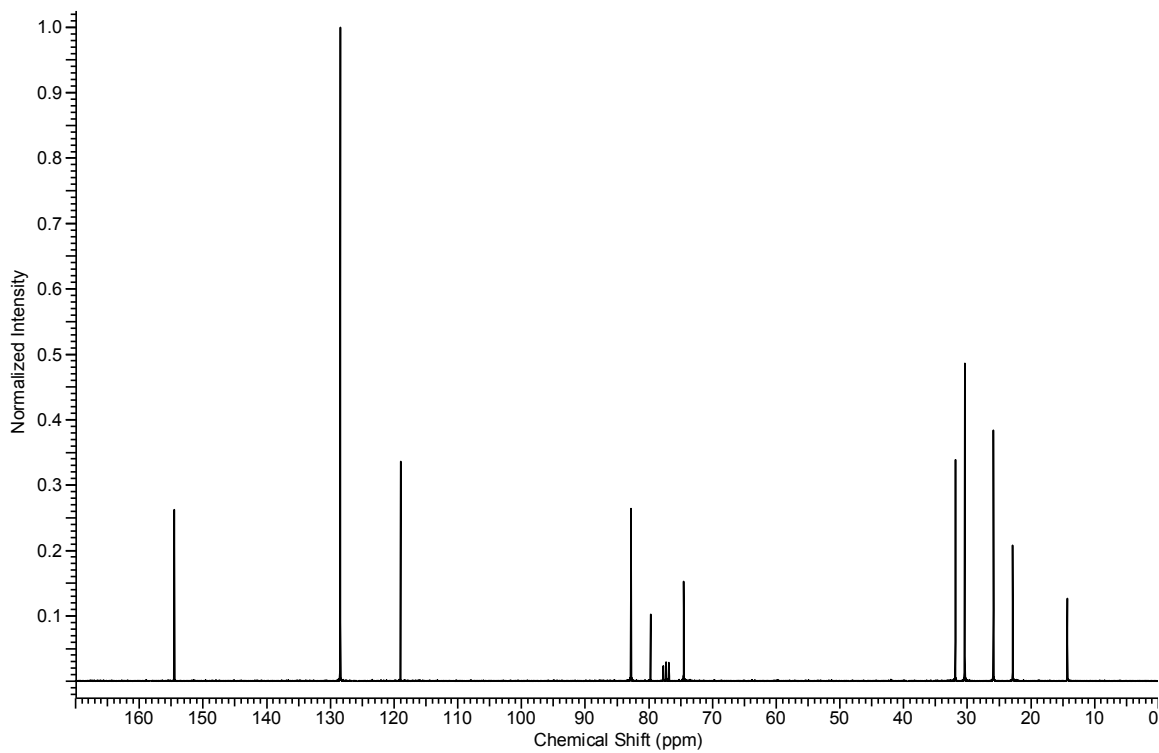
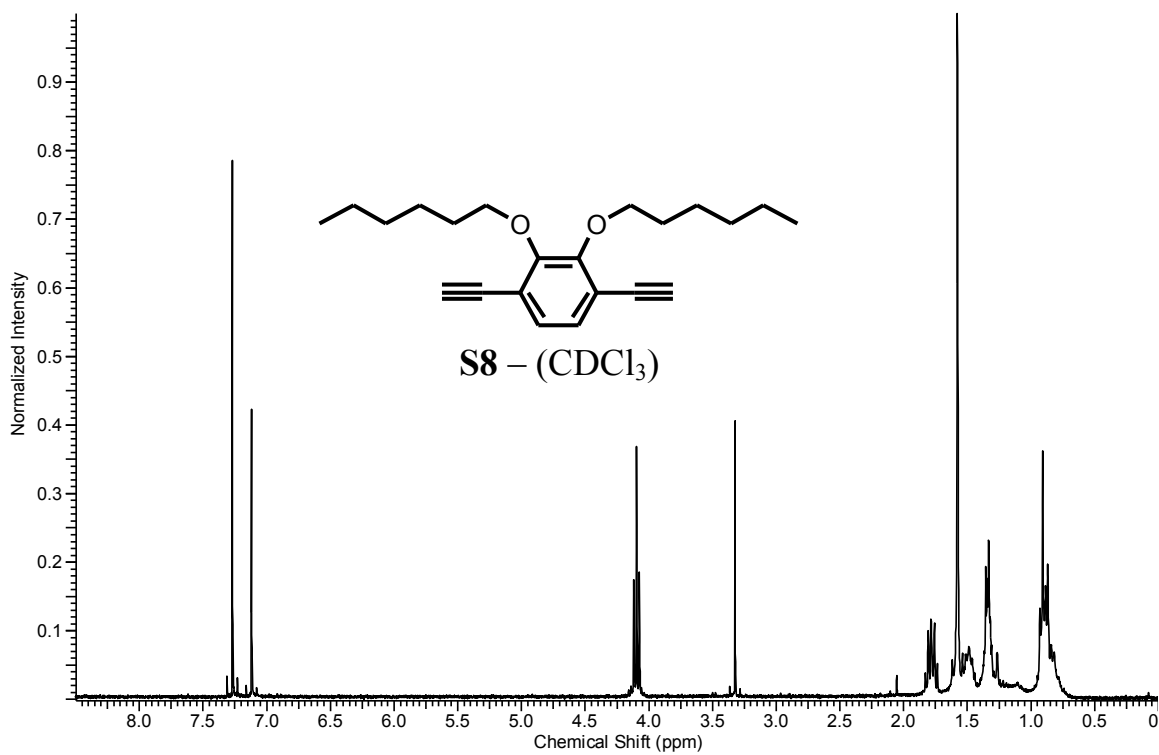
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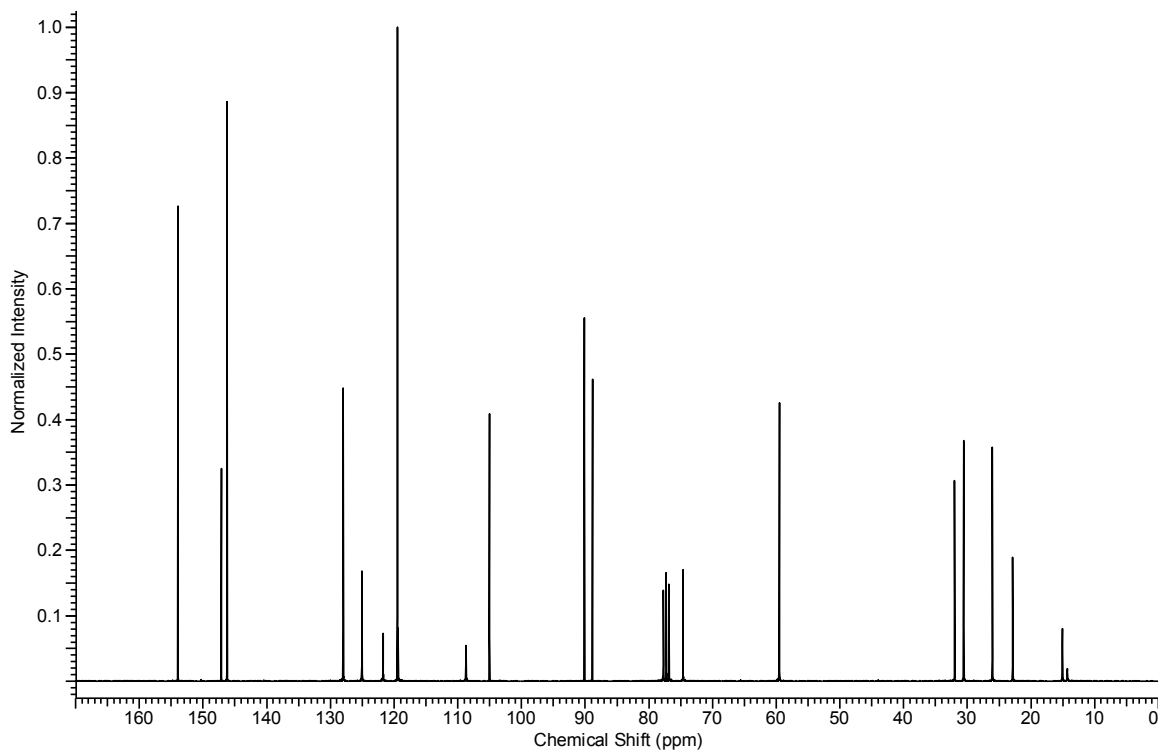
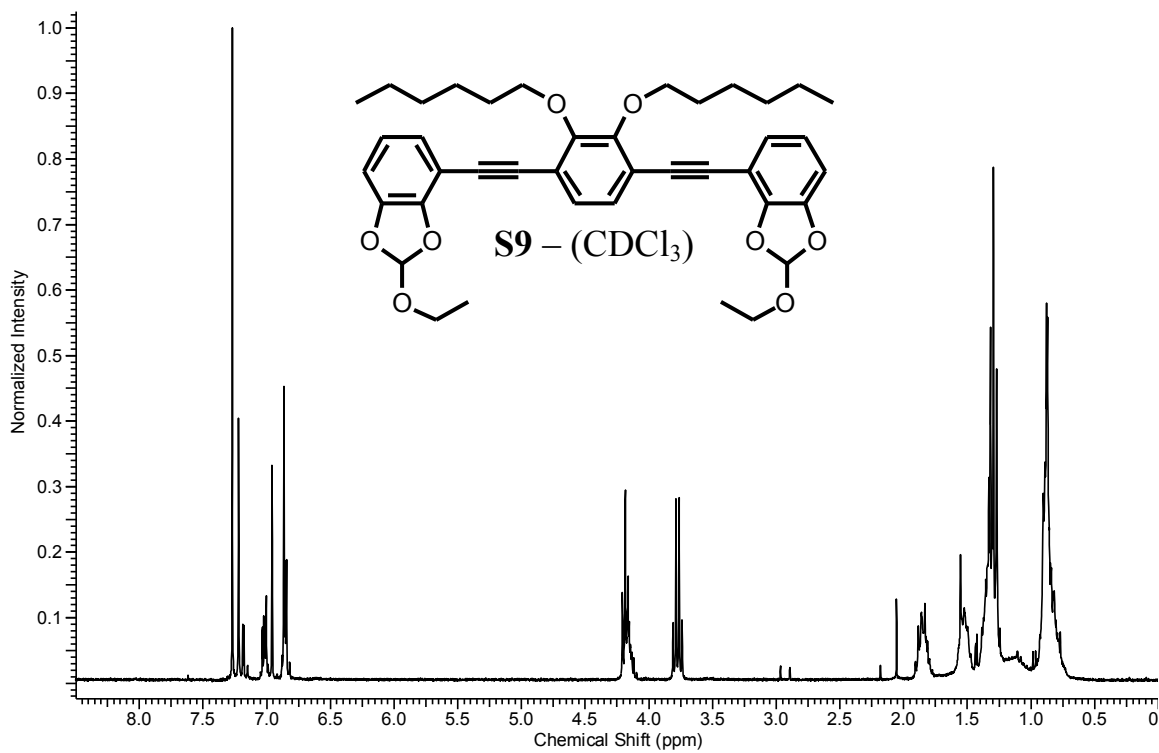
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S8



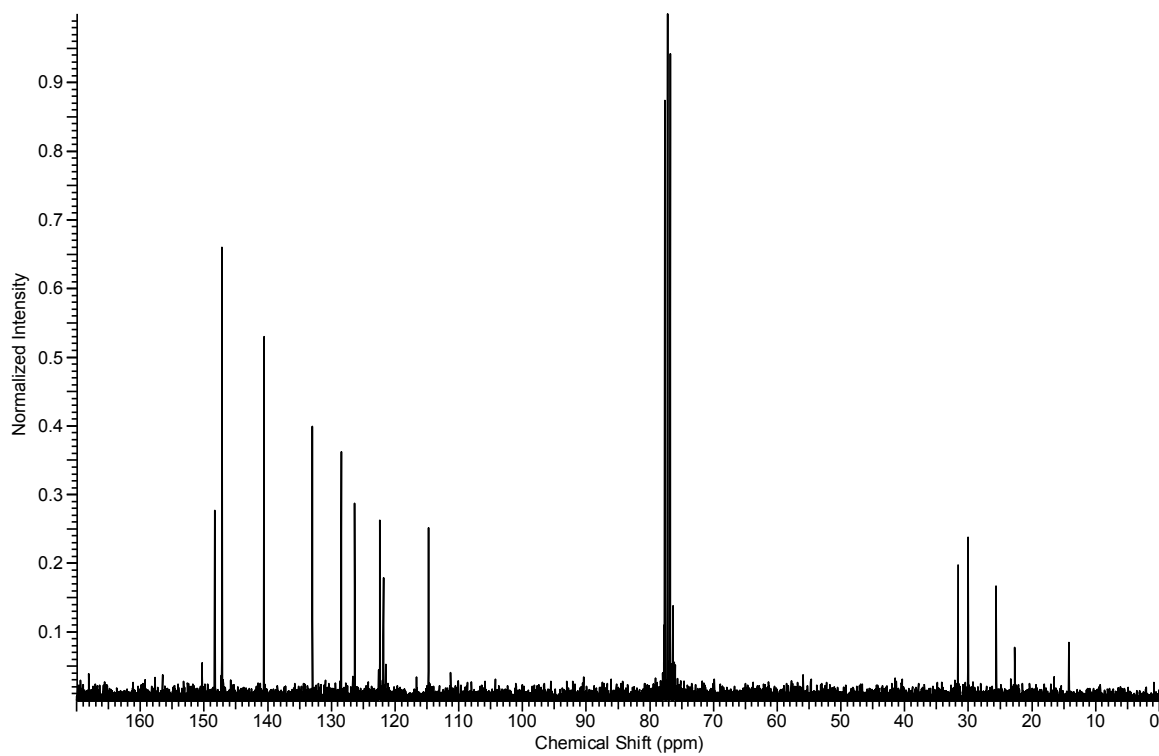
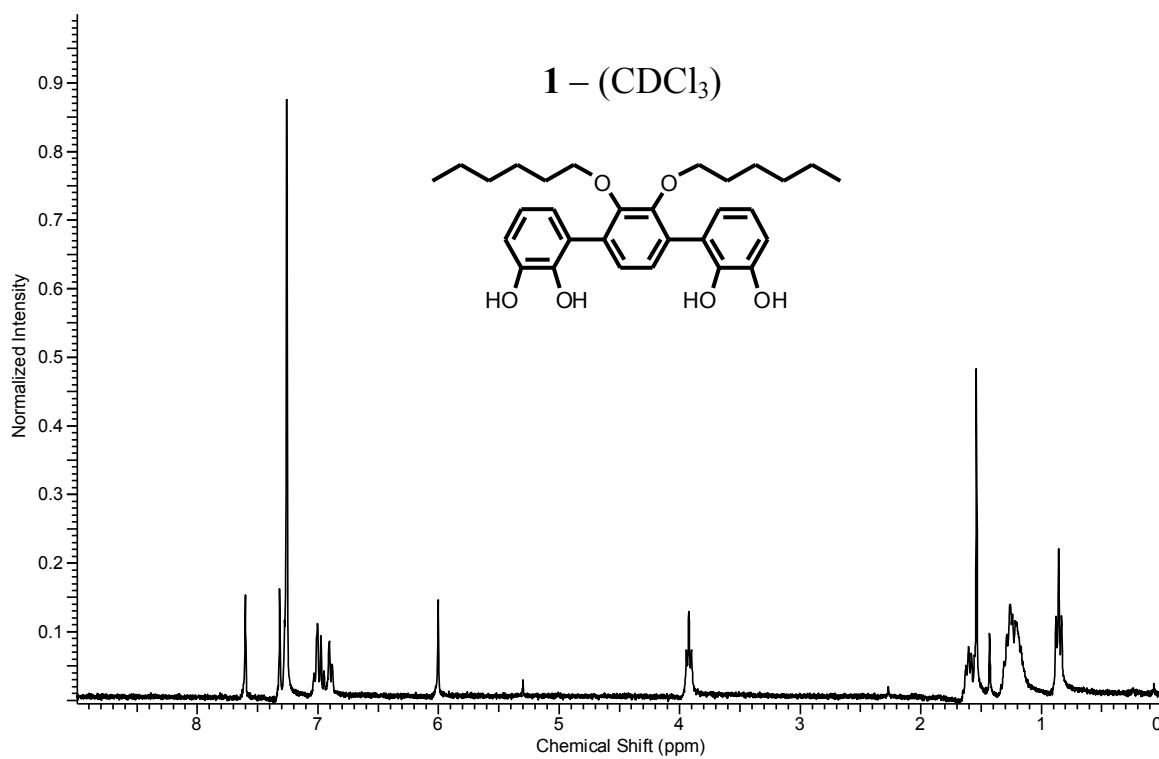
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S9

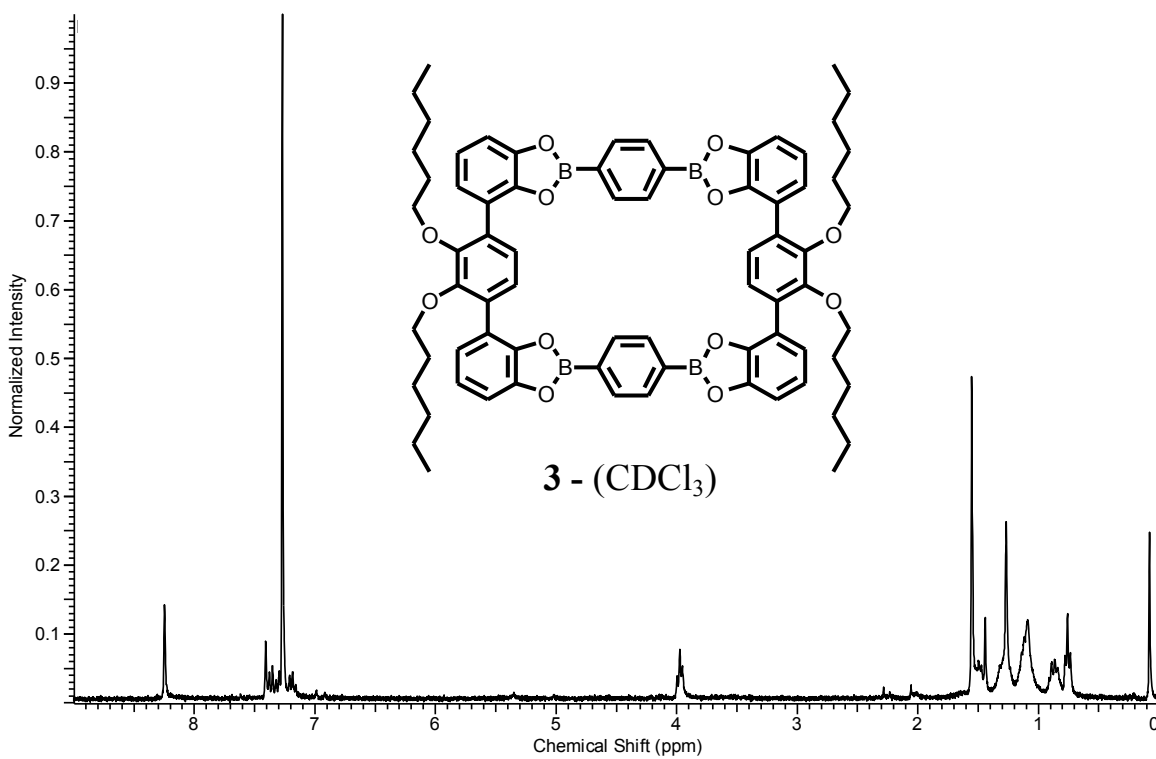


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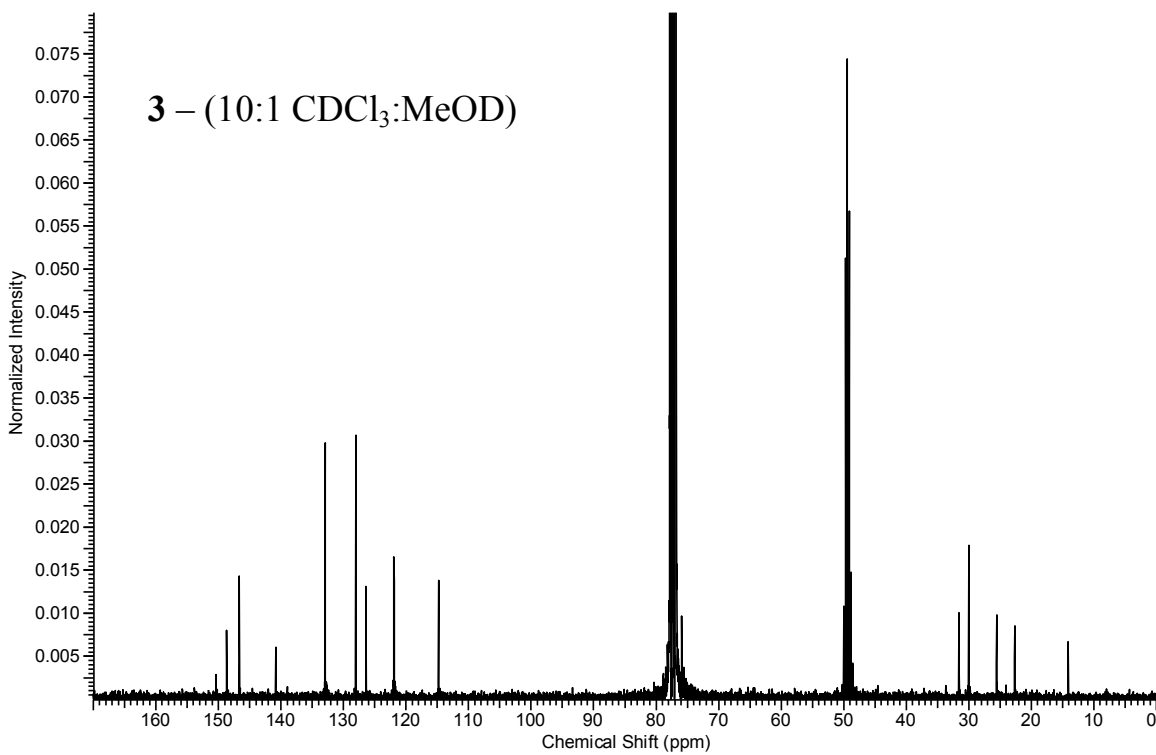
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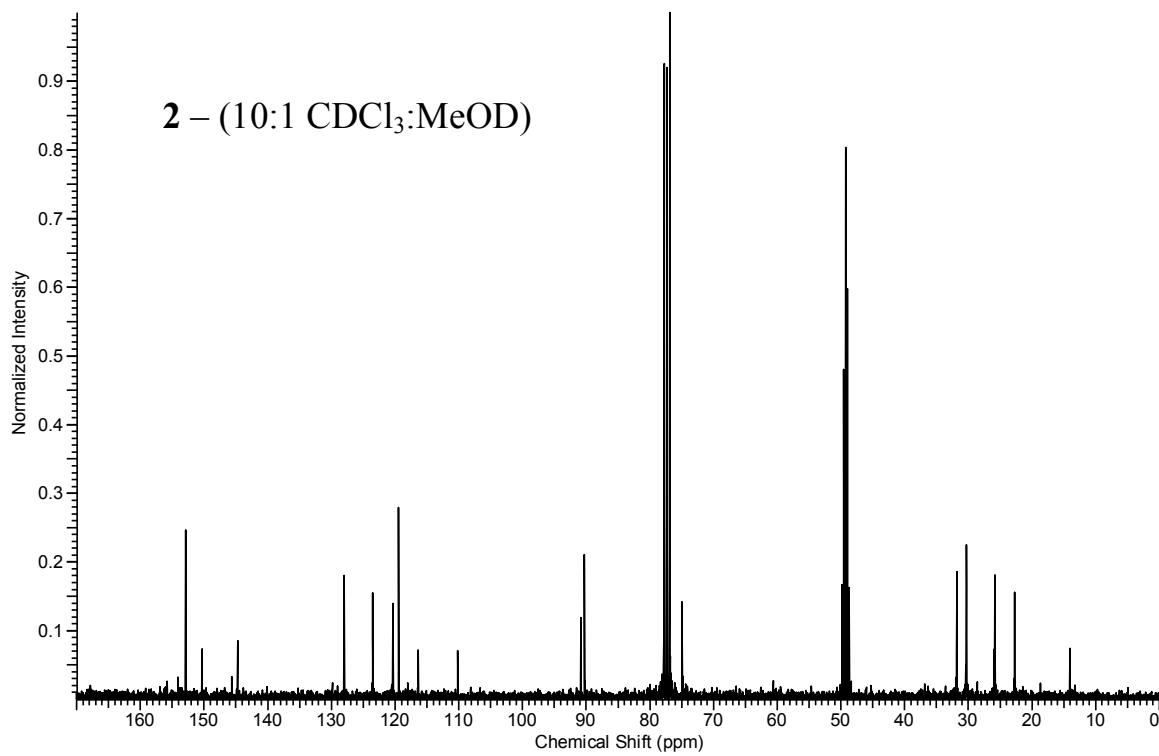
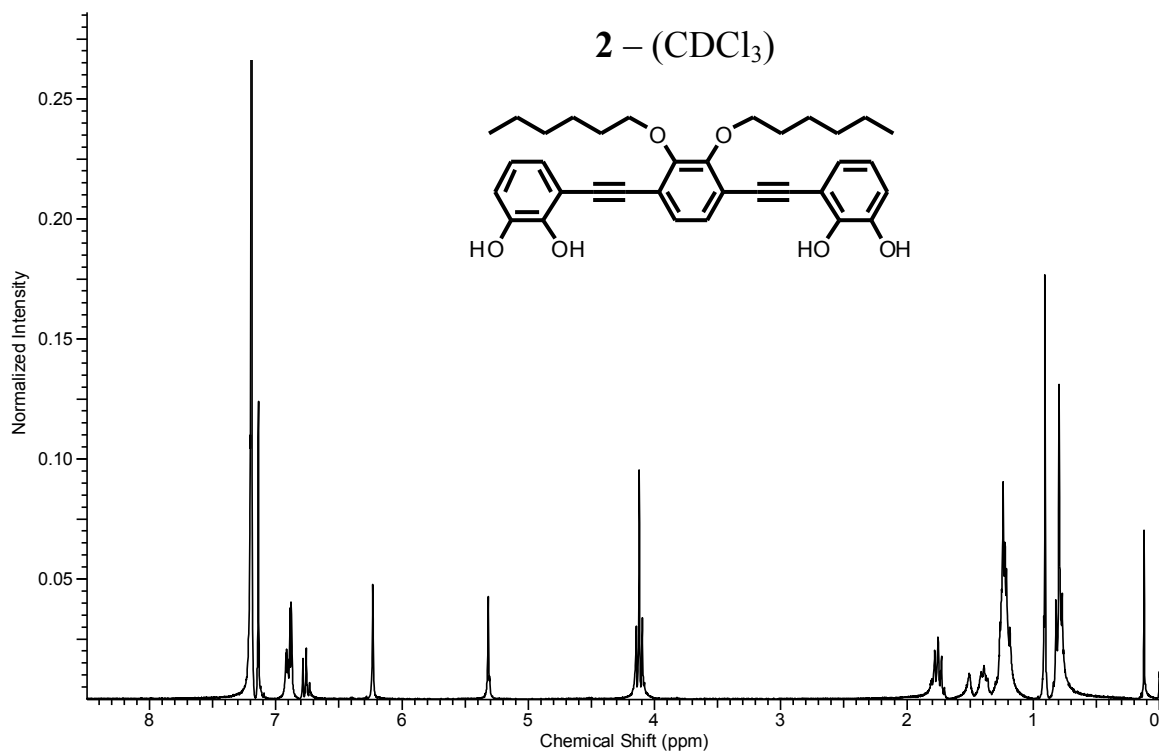
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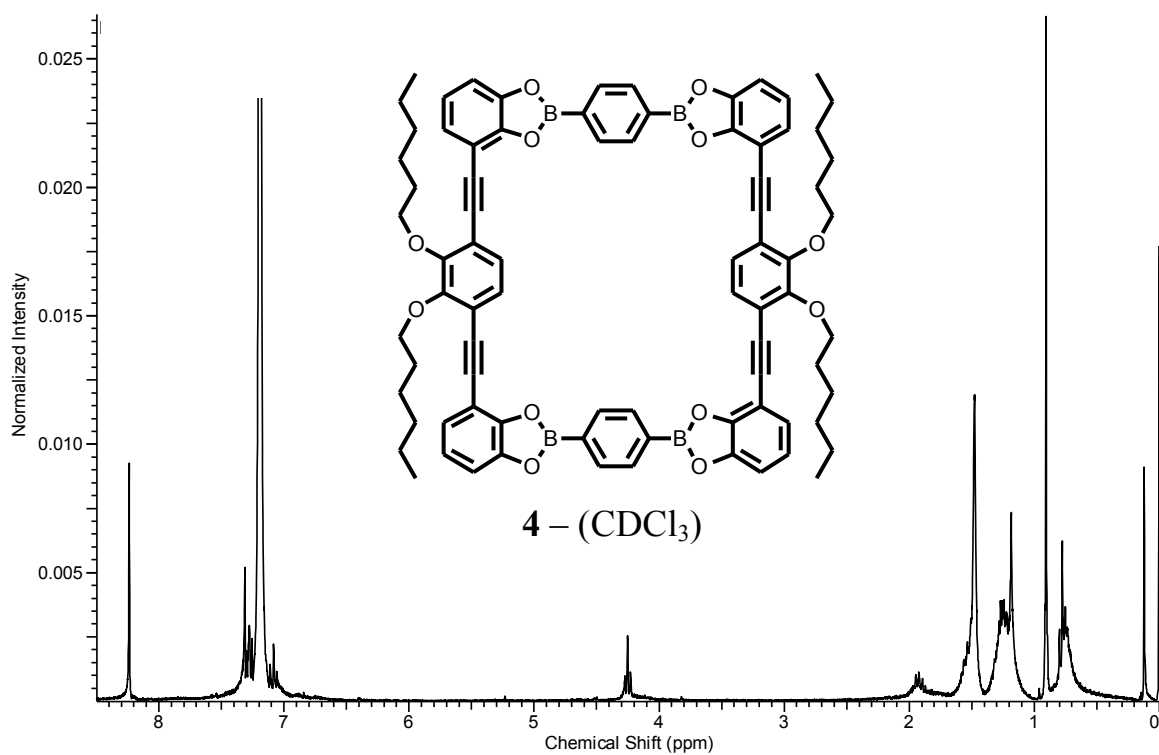
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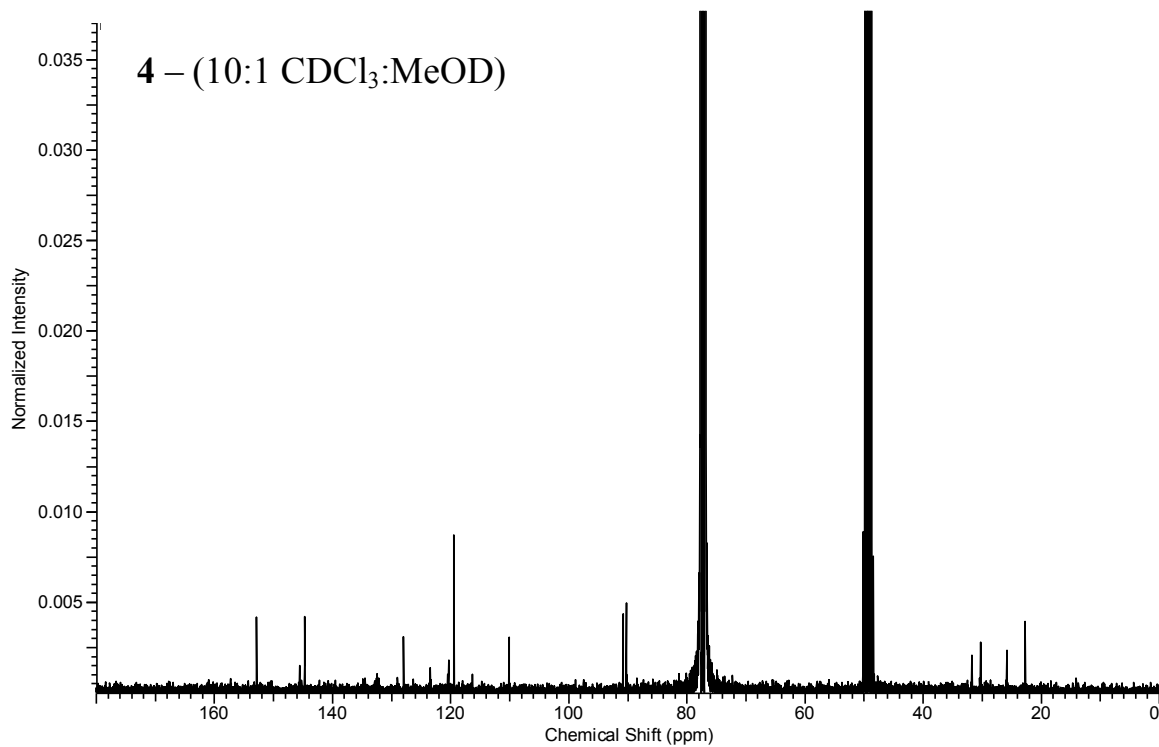
2



4



(Solubility precluded obtaining a satisfactory ¹³C spectrum of **5** in 100% CDCl₃)



Diagnostic ^1H NMR spectroscopic shifts supporting the dynamic assembly of boronate ester rectangle **4**:

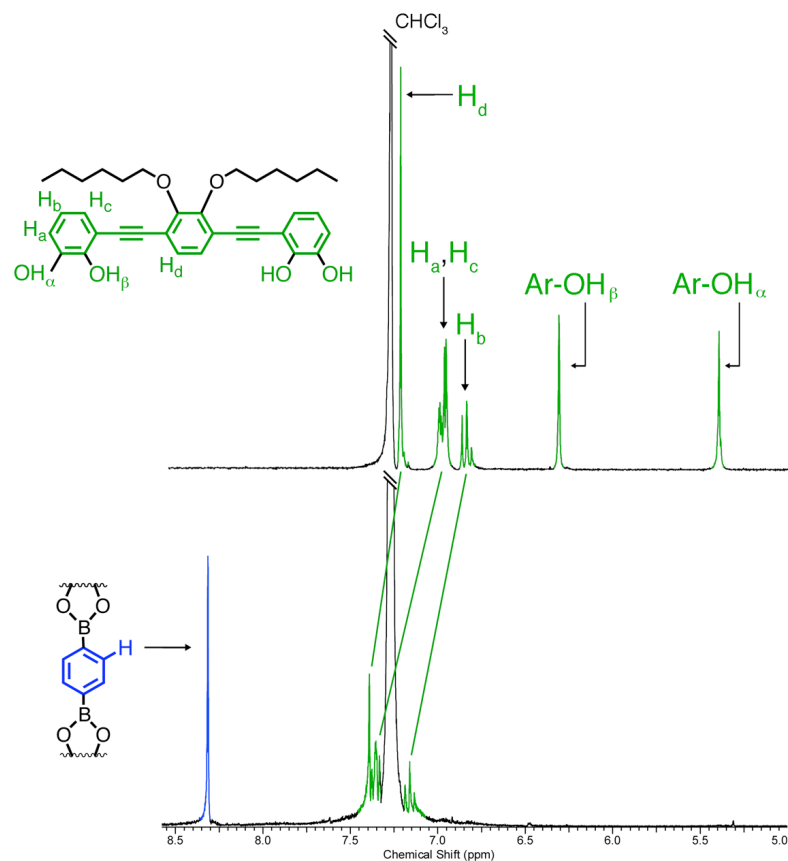


Figure S1. Partial ^1H NMR spectra (CDCl_3 , 298 K, 300 MHz) of bis catechol **2** (a) and boronate ester rectangle **4** (b) indicating shifts of proton signals H_a - H_d , the disappearance of Ar-OH_{α} and Ar-OH_{β} , and the appearance of a new singlet at 8.31 ppm corresponding to the central boronate aromatic proton. The analogous partial ^1H NMR spectra of bis catechol **1** and boronate ester rectangle **3** is displayed in Figure 2 of the main text.

IV. Infrared Spectra

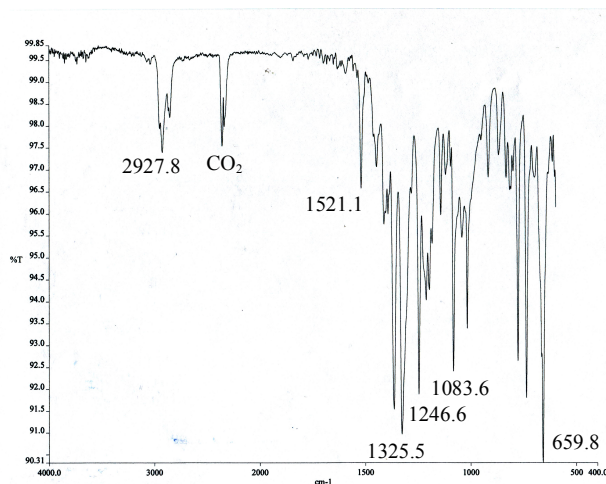
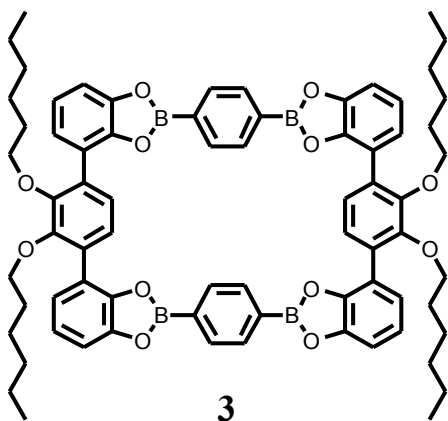
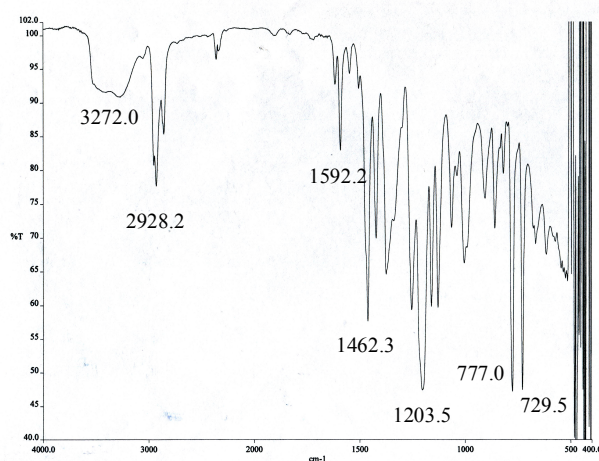
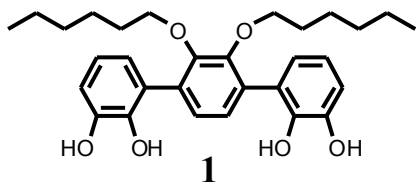
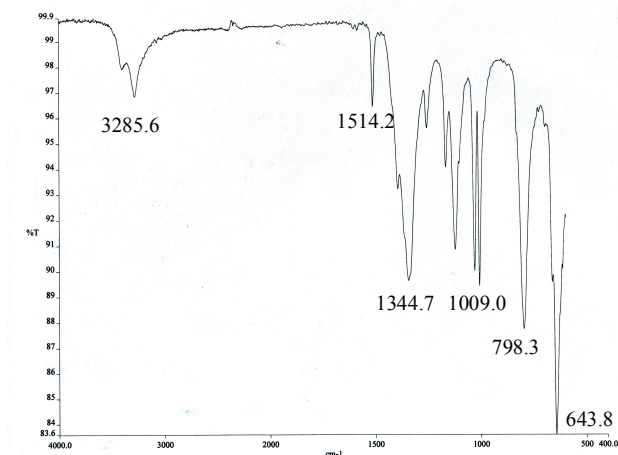
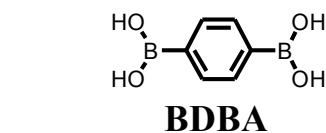


Figure S2. IR spectra of **BDBA** (top), linear bis-catechol **1** (middle), and boronate ester rectangle **3** (bottom). Labeled vibrational modes are in cm^{-1} .

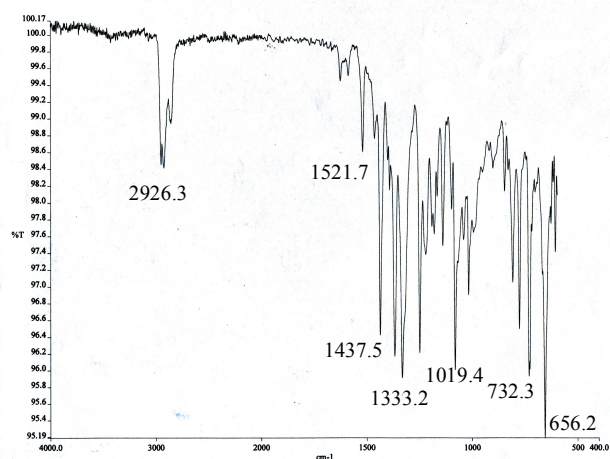
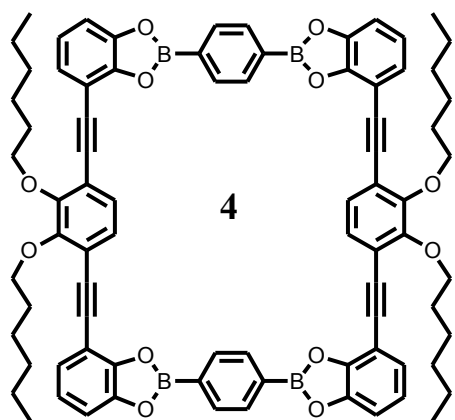
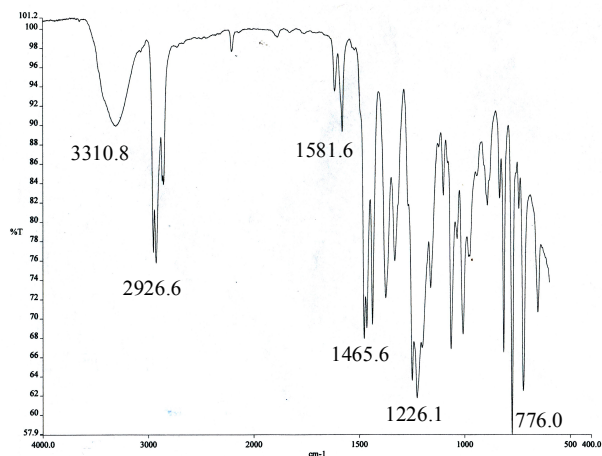
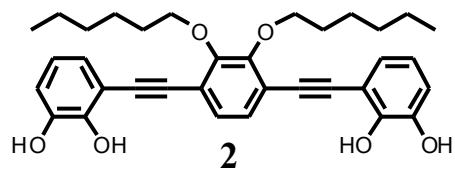
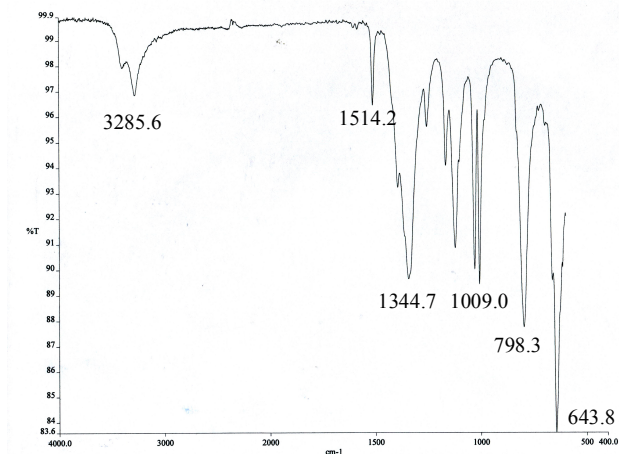
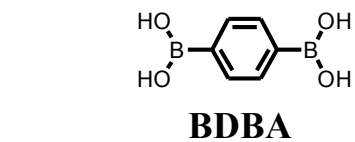
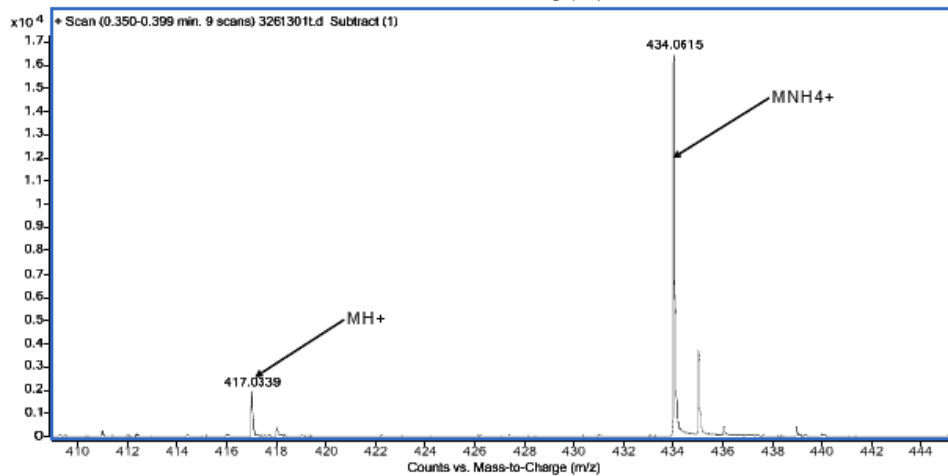
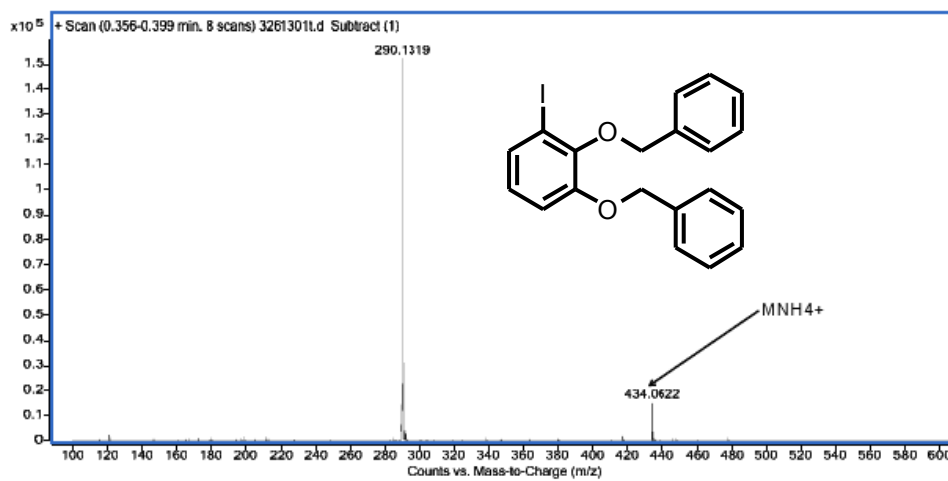


Figure S3. IR spectra of **BDBA** (top), linear bis-catechol **2** (middle), and boronate ester rectangle **4** (bottom). Labeled vibrational modes are in cm^{-1} .

V. Mass Spectrometric Data

S2

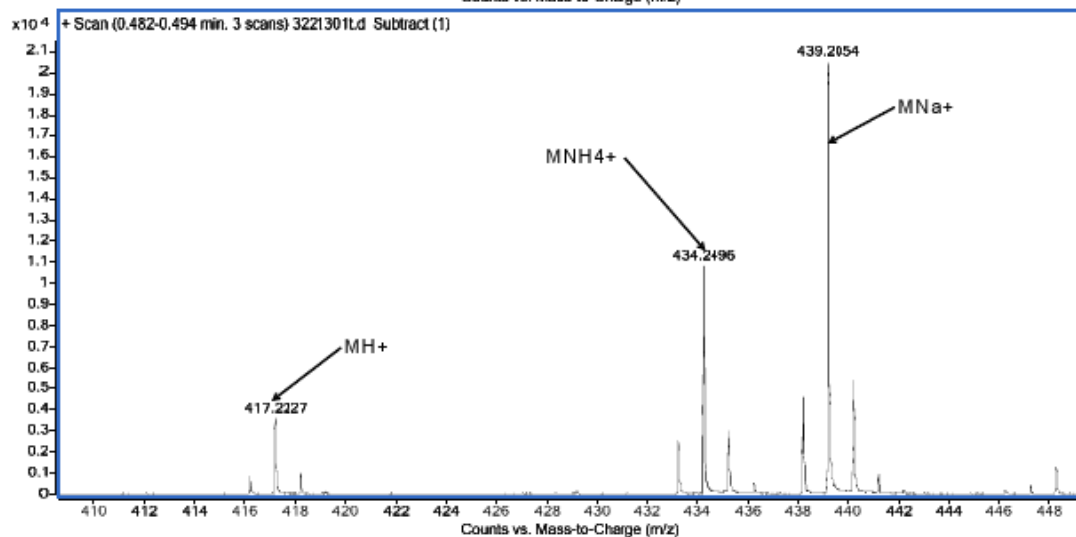
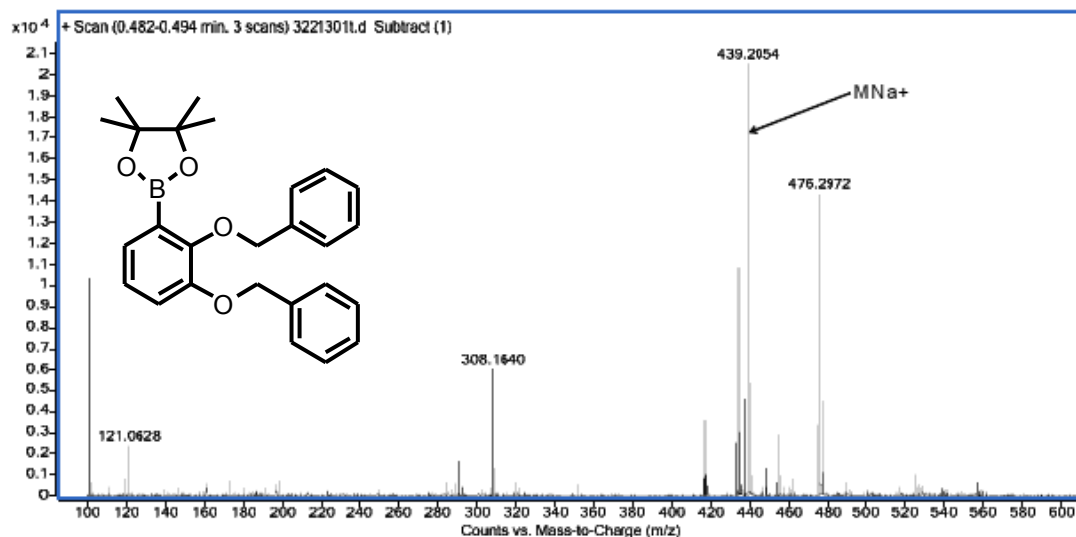


Measured Mass 434.0615

Element	Low Limit	High Limit
C	15	25
H	10	30
O	0	5
N	0	1
I	0	1

Formula	Calculated Mass	mDaError	ppmError	RDB
C20 H21 N O2 I	434.0612	0.3	0.8	10.5

S3.



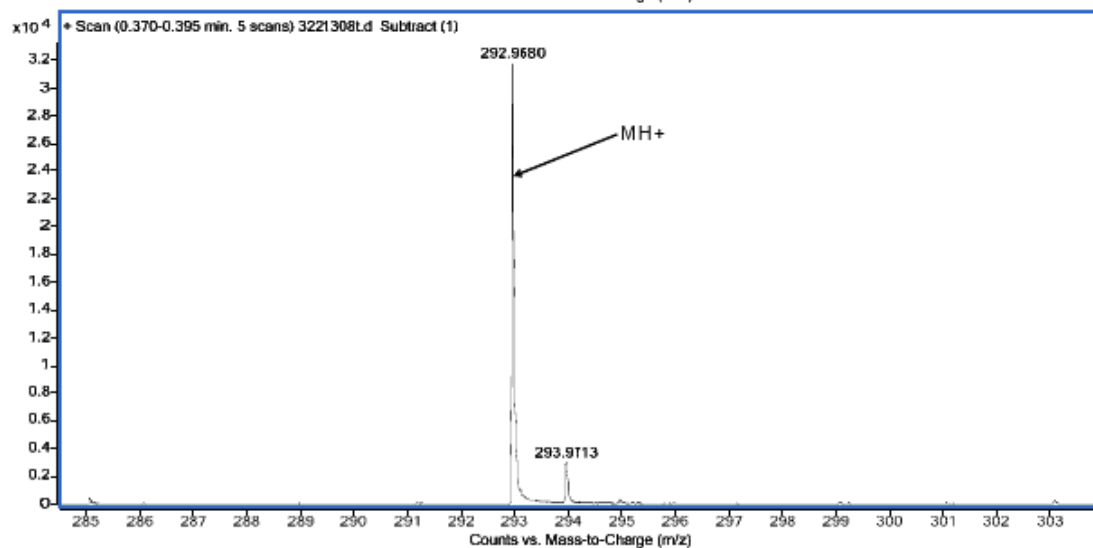
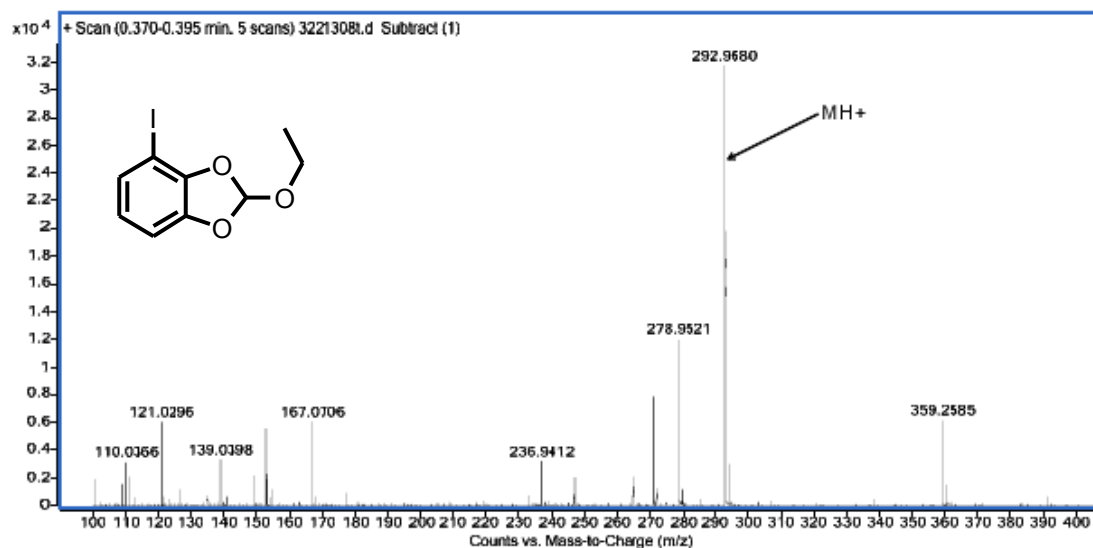
Measured Mass 439.2054

Element	Low Limit	High Limit
C	22	32
H	28	48
O	1	7
11B	0	1
Na	0	1

Formula	Calculated Mass	mDaError	ppmError	RDB
C ₂₆ H ₂₉ 11B O ₄ Na	439.2051	0.3	0.7	12.5
C ₂₈ H ₂₈ 11B O ₄	439.2075	-2.1	-4.8	15.5
C ₃₁ H ₂₈ O Na	439.2032	2.2	4.9	17.5

S24

S4.

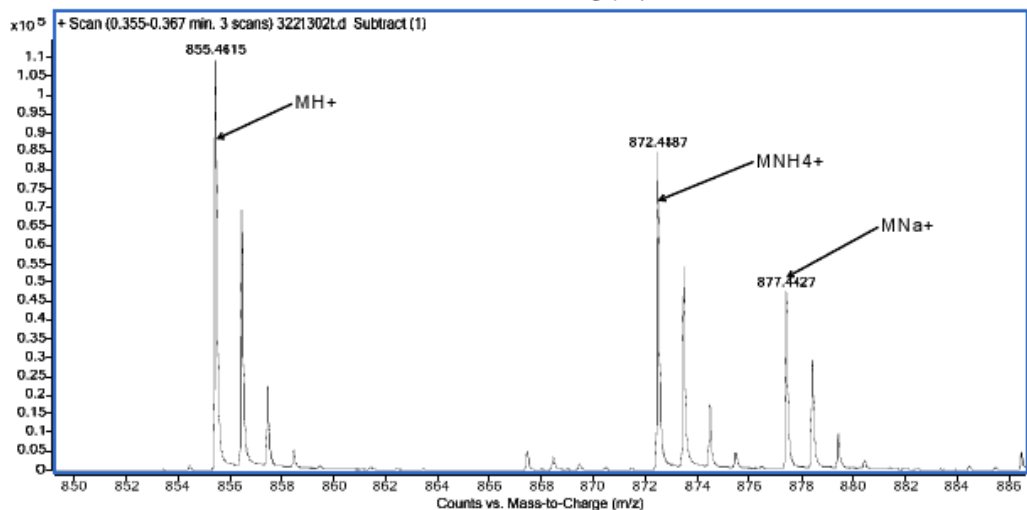
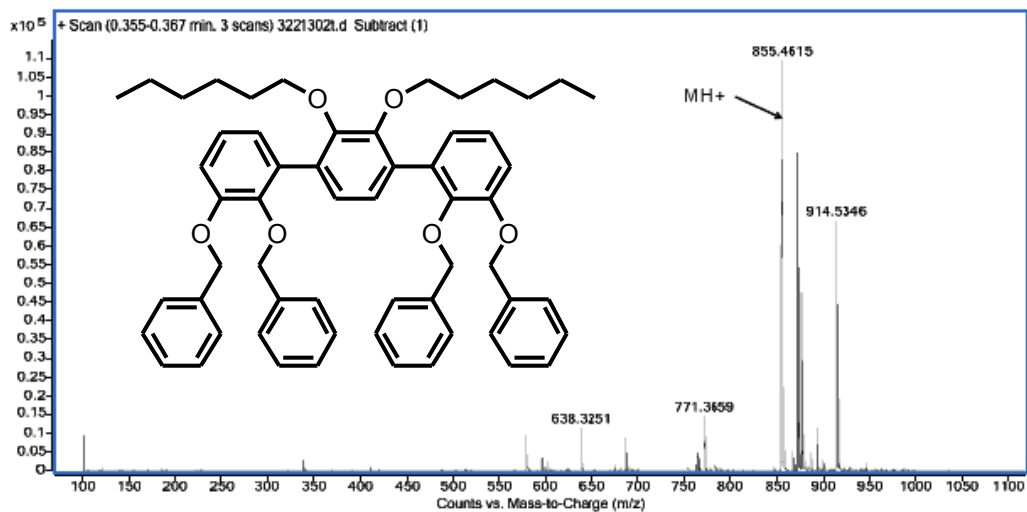


Measured Mass 292.968

<u>Element</u>	<u>Low Limit</u>	<u>High Limit</u>
C	4	14
H	0	20
O	0	5
I	0	1

<u>Formula</u>	<u>Calculated Mass</u>	<u>mDaError</u>	<u>ppmError</u>	<u>RDB</u>
C ₉ H ₁₀ O ₃ I	292.9669	1.1	3.7	4.5

S6.



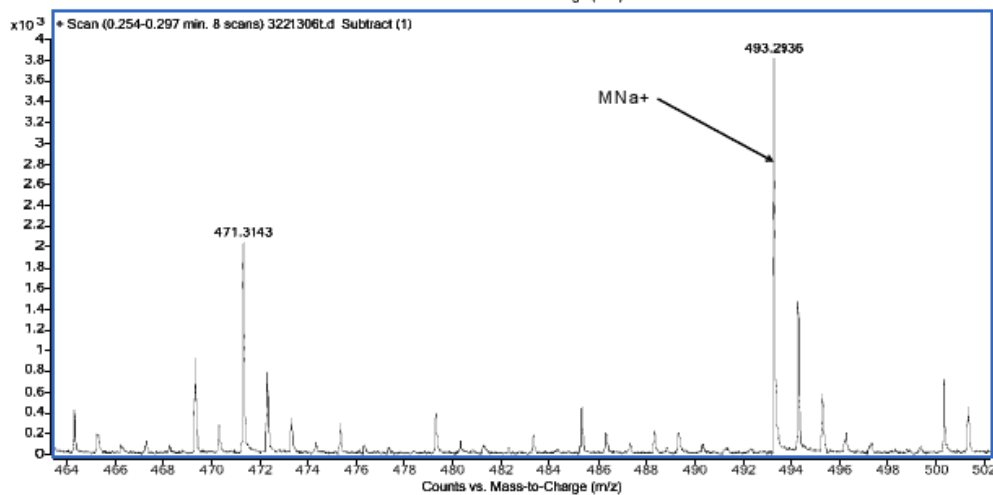
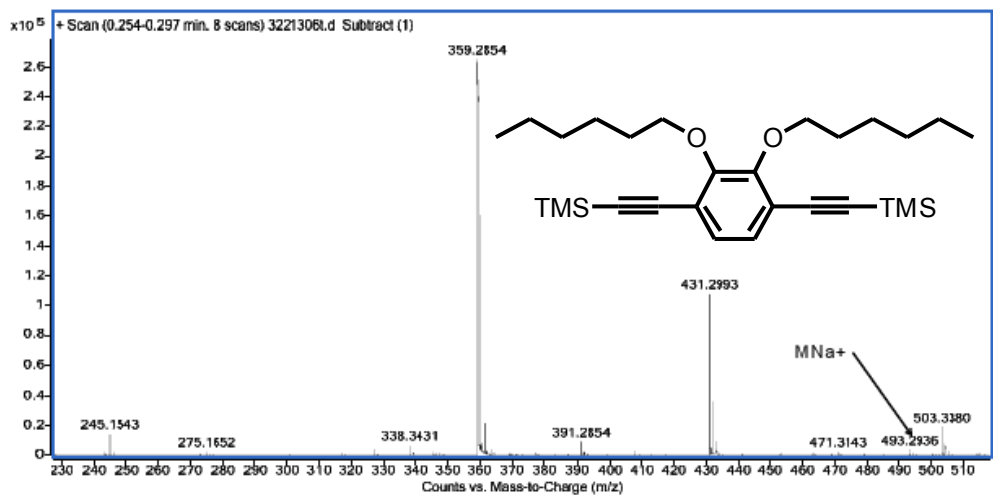
Measured Mass

855.4615

Element	Low Limit	High Limit
C	53	63
H	55	75
O	1	7

Formula	Calculated Mass	mDaError	ppmError	RDB
C ₅₈ H ₆₃ O ₆	855.4619	-0.4	-0.5	27.5

S7.

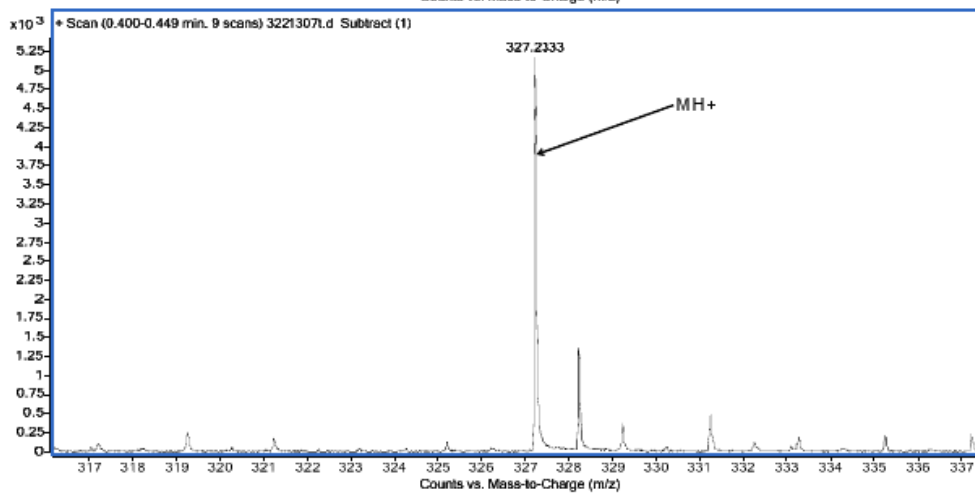
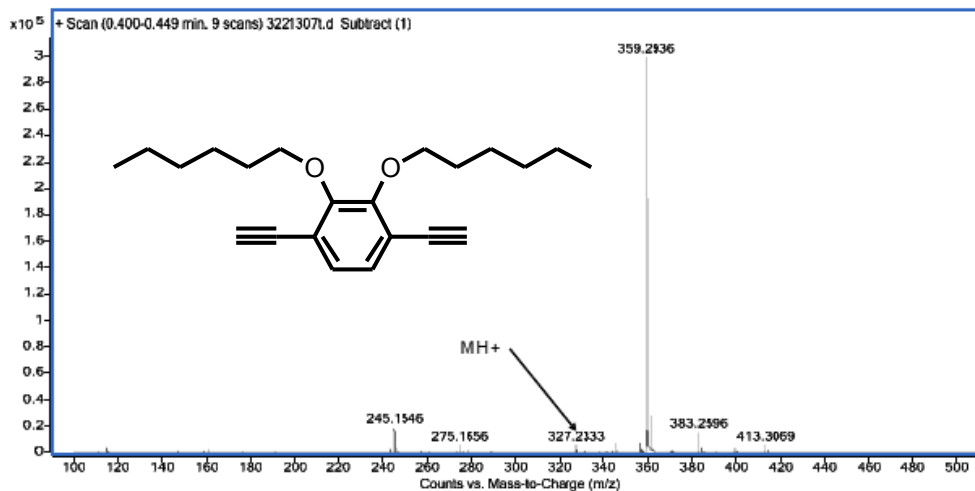


Measured Mass 493.2936

Element	Low Limit	High Limit
C	22	32
H	28	48
O	1	7
Si	0	2
Na	0	1

Formula	Calculated Mass	mDaError	ppmError	RDB
C28 H46 O2 Na Si2	493.2929	0.7	1.5	7.5
C29 H42 O5 Na	493.2924	1.2	2.3	8.5
C31 H41 O5	493.2949	-1.3	-2.5	11.5
C30 H45 O2 Si2	493.2953	-1.7	-3.4	10.5
C25 H46 O6 Na Si	493.2956	-2.0	-4.0	3.5

S8



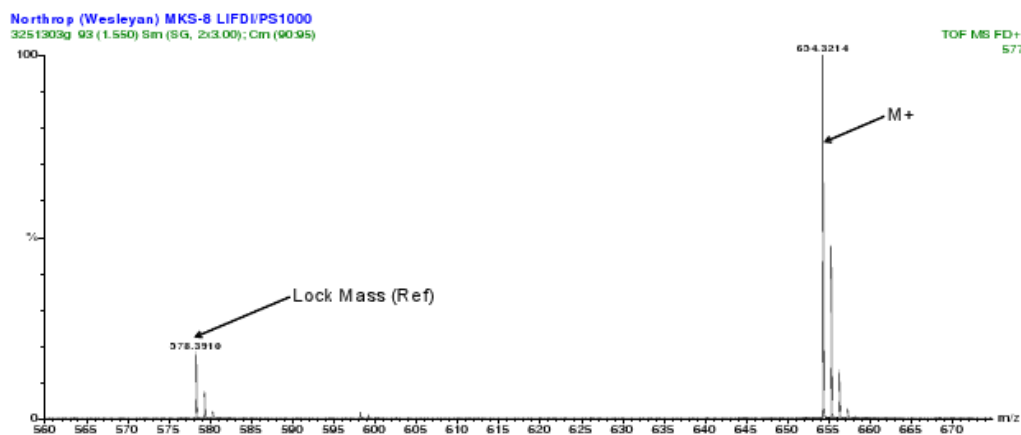
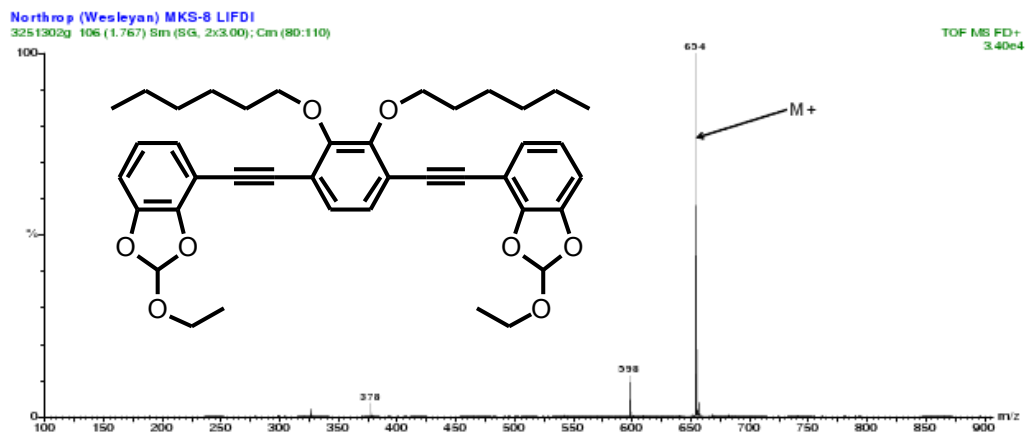
Measured Mass 327.2333

<u>Element</u>	<u>Low Limit</u>	<u>High Limit</u>
C	17	27
H	20	40
O	0	5

<u>Formula</u>	<u>Calculated Mass</u>	<u>mDaError</u>	<u>ppmError</u>	<u>RDB</u>
C ₂₂ H ₃₁ O ₂	327.2319	1.4	4.4	7.5

S28

S9.



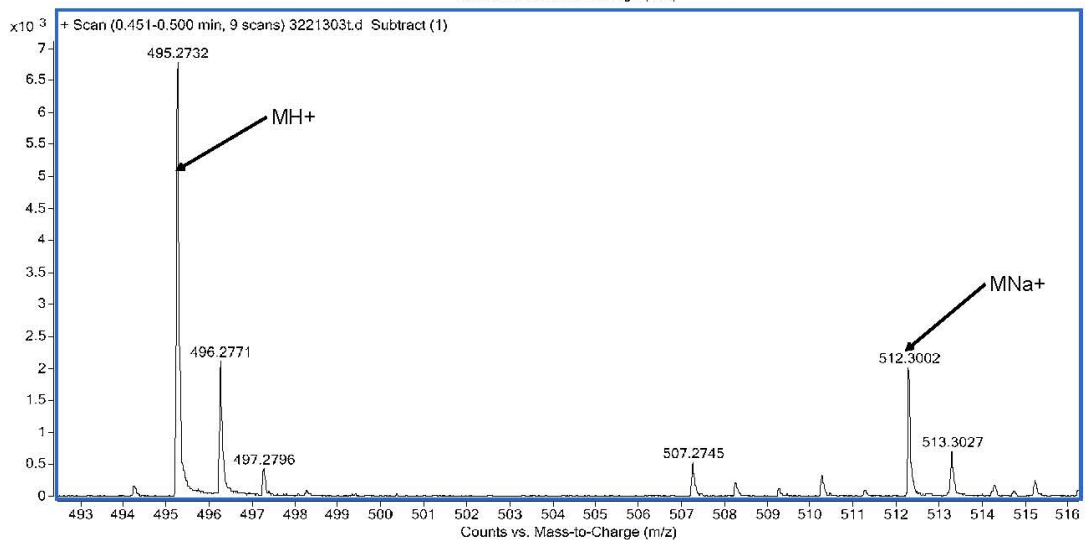
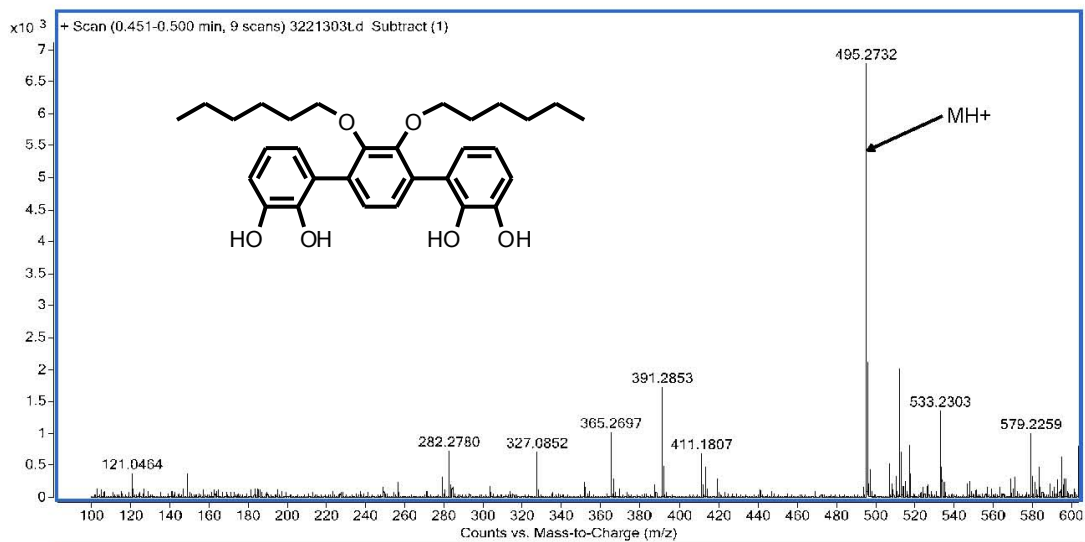
Measured Mass

654.3214

Element	Low Limit	High Limit
C	35	45
H	35	55
O	6	10

Formula	Calculated Mass	mDaError	ppmError	RDB
C40 H46 O8	654.3187	2.7	4.1	18

1.

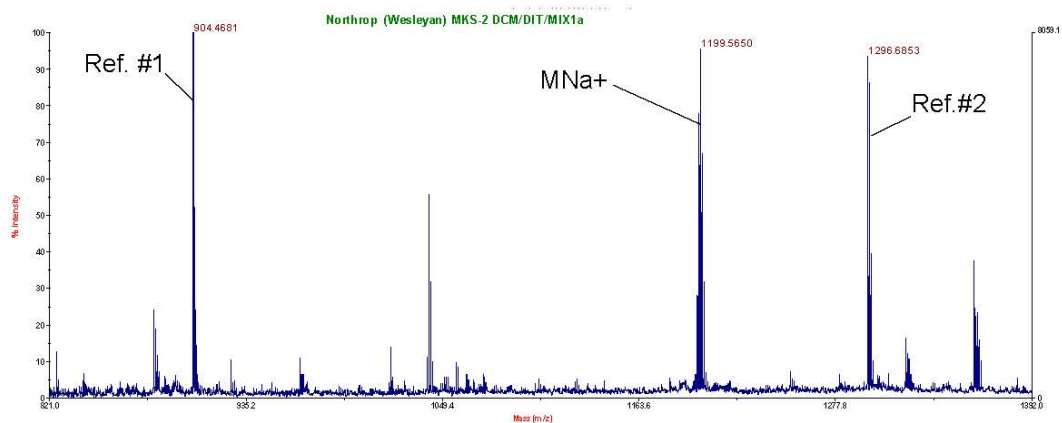
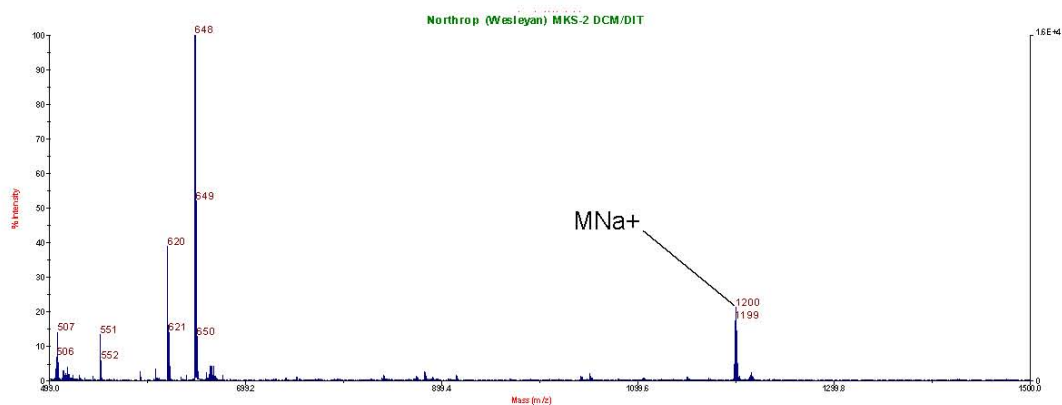


Measured Mass 495.2732

<u>Element</u>	<u>Low Limit</u>	<u>High Limit</u>
C	22	32
H	28	48
O	1	7

<u>Formula</u>	<u>Calculated Mass</u>	<u>mDaError</u>	<u>ppmError</u>	<u>RDB</u>
C30 H39 O6	495.2741	-0.9	-1.8	11.5

3.



Measured Mass

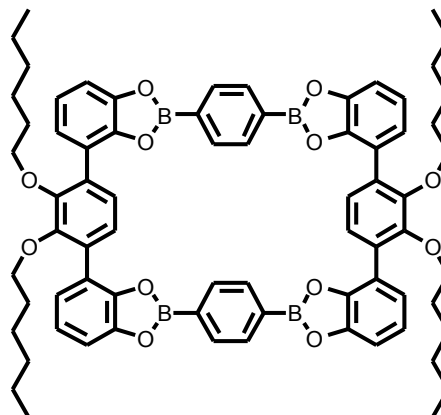
1199.565

Element

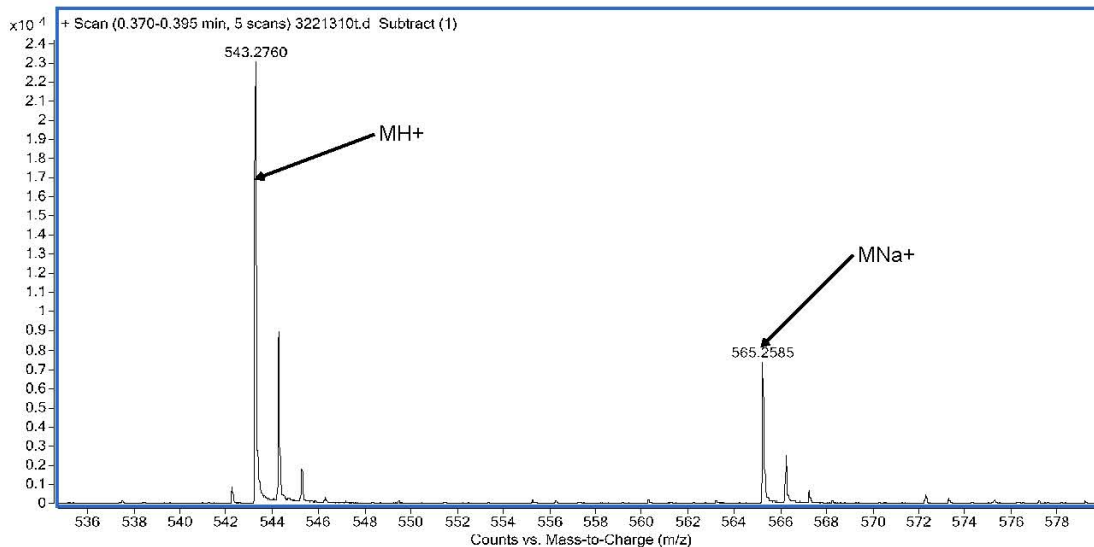
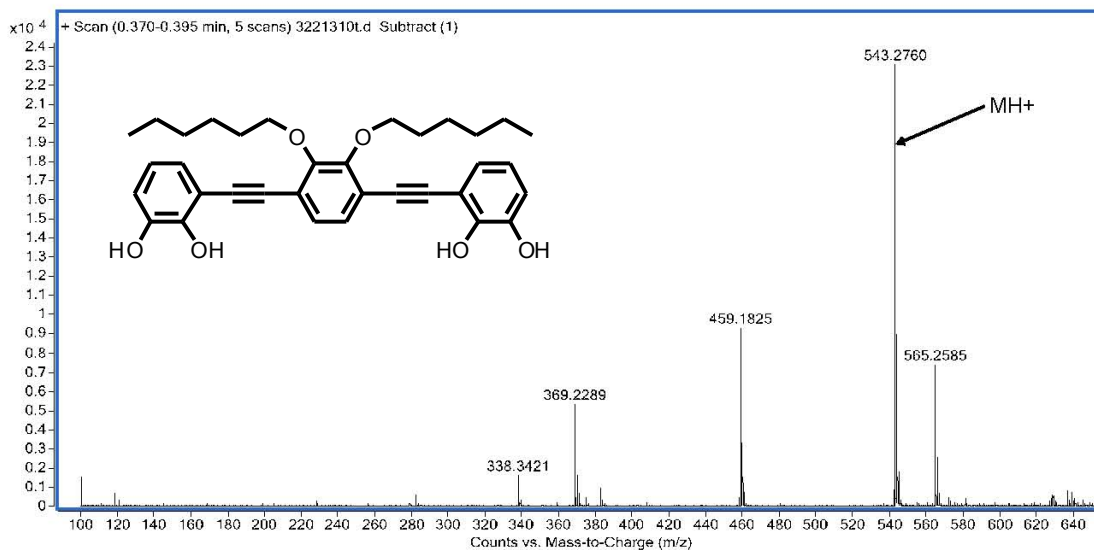
<u>Element</u>	<u>Low Limit</u>	<u>High Limit</u>
C	67	77
H	65	85
O	10	14
11B	3	5
Na	0	1

Formula

<u>Formula</u>	<u>Calculated Mass</u>	<u>mDaError</u>	<u>ppmError</u>	<u>RDB</u>
C70 H79 11B3 O14 Na	1199.5641	0.9	0.7	32.5
C72 H78 11B3 O14	1199.5665	-1.5	-1.3	35.5
C74 H75 11B4 O12	1199.5625	2.5	2.1	39.5
C72 H76 11B4 O12 Na	1199.5601	4.9	4.1	36.5



2.



Measured Mass

543.276

<u>Element</u>	<u>Low Limit</u>	<u>High Limit</u>
C	29	39
H	30	50
O	4	8

Formula
C34 H39 O6

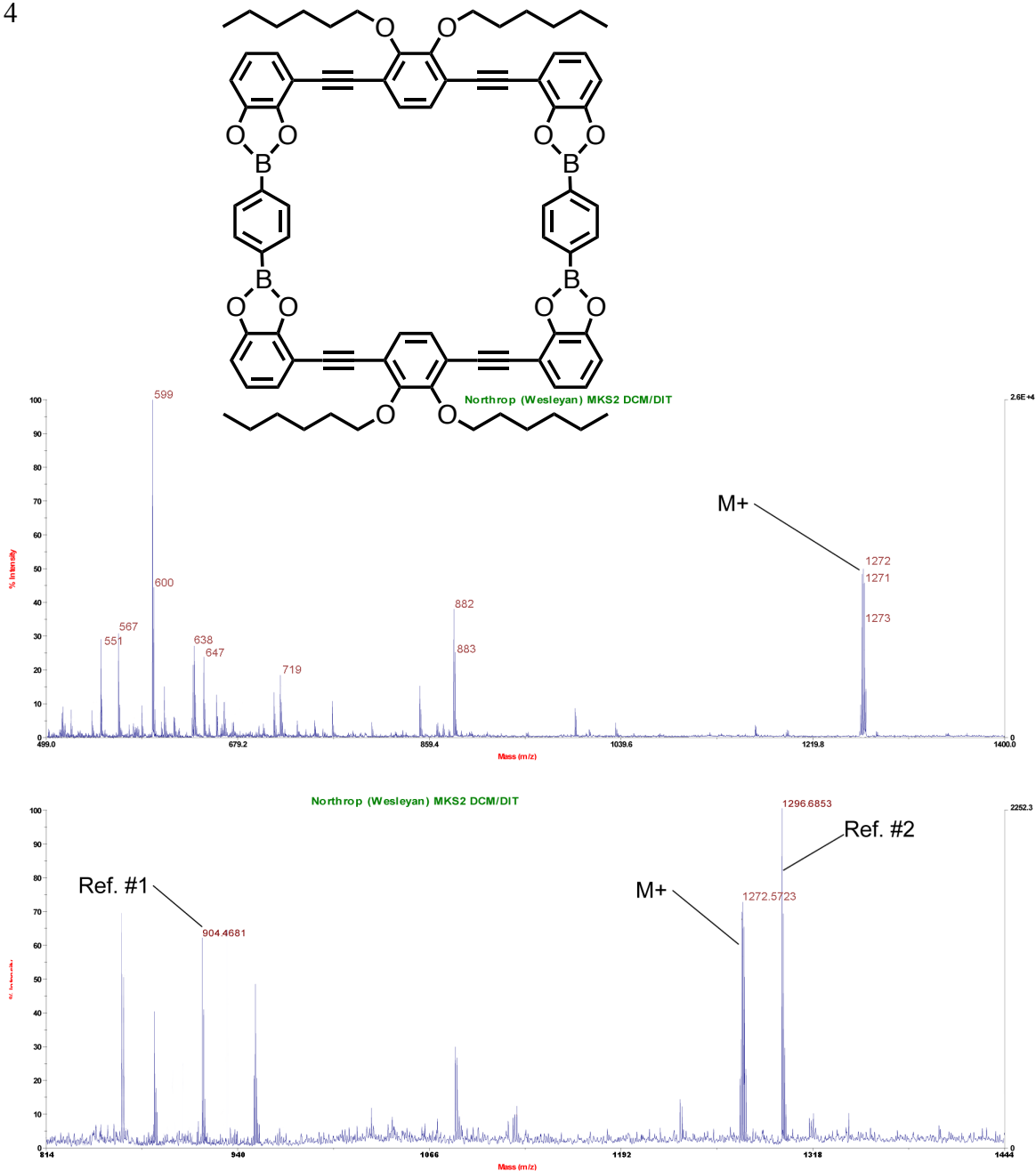
Calculated Mass
543.2741

mDaError
1.9

ppmError
3.5

RDB
15.5

4



Measured Mass

1272.5723

Element

Low Limit

High Limit

C

75

85

H

65

85

11B

3

5

O

10

14

Formula

Calculated Mass

mDaError

ppmError

RDB

C80 H76 11B4 O12

1272.5709

1.4

1.1

45

C79 H77 11B5 O12

1272.5880

-1.6

-1.3

44

C82 H79 11B3 O11

1272.5902

-1.8

-1.4

45

VI. UV/Vis & Fluorescence Spectroscopy

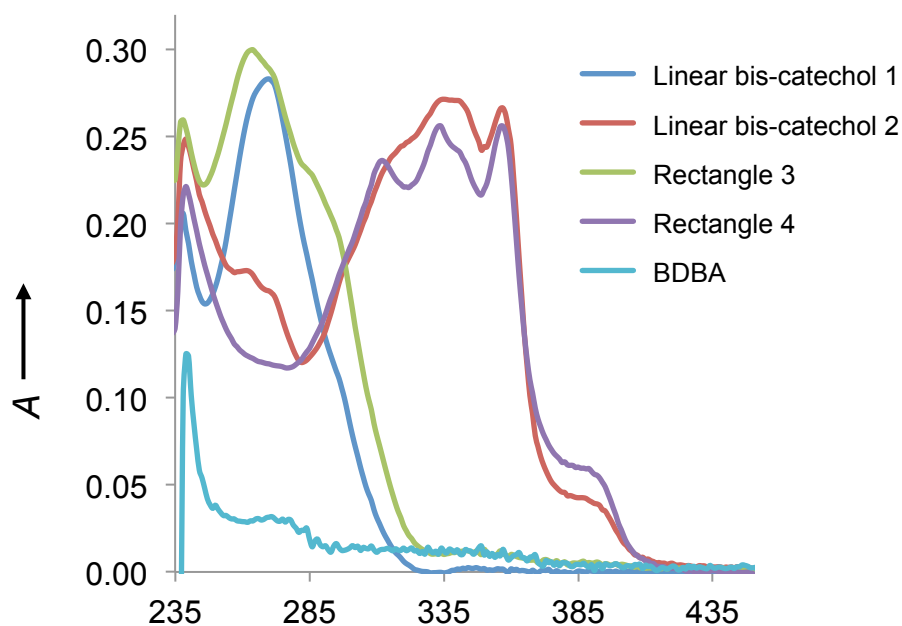


Figure S4. Overlaid UV/Vis spectra of bis-catechols **1** and **2**, boronate ester rectangles **3** and **4**, and **BDBA**. All spectra were collected in CHCl_3 (1.0×10^{-5} M) at 298 K.

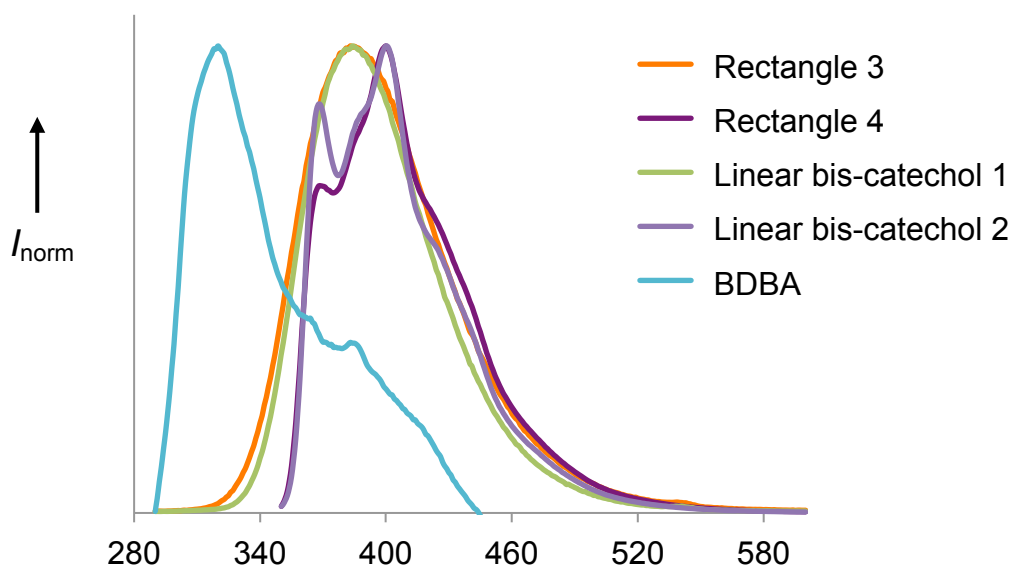


Figure S5. Overlaid normalized fluorescence spectra of bis-catechols **1** and **2**, boronate ester rectangles **3** and **4**, and **BDBA**. All spectra were collected in CHCl_3 (1.0×10^{-5} M) at 298 K. Compounds **1**, **3**, and **BDBA** were excited at $\lambda_{\text{ex}} = 270$ nm, compounds **2** and **4** were excited at $\lambda_{\text{ex}} = 320$ nm.

VII. Theoretical Modeling

The molecular structures of boronate ester rectangles **3** and **4**, with hexyloxy chains of replaced with methoxy groups, were constructed within the input mode of the program Maestro v9.9.109.⁵ Each rectangle was subjected to a 1000 step Monte Carlo Multiple Minimization (MCMM) conformational search using the OPLS force field⁶ in a solvent model for chloroform with a total number of 2000 iterations per minimization step in order to determine the lowest energy conformation of **3** and **4**.

The global energy minimum structures obtained for **3** and **4** were imported into the program Gaussian09.⁷ Optimizations of the ground state geometries were then carried out to full convergence at the B3LYP/6-31+g(d,p) level in a PCM solvent model for chloroform (Figure S6). Natural bond orbital (NBO)⁸ analysis was invoked using the pop=(full,nbo) keyword. HOMO-LUMO gaps were computed as the difference in energy between the highest energy occupied and lowest energy virtual orbitals obtained for each molecule from theoretical calculations. Molecular orbitals (see Figure 3 of the main text) were visualized using GaussView5.

Vibrational analyses were carried out at the B3LYP/6-31g(d) level and the resulting frequencies were used to aid in assigning relevant vibrational modes. Calculated frequencies were scaled by a factor of 0.960.⁹ Key boronate ester vibrational modes obtained from theoretical calculations, and their corresponding experimental modes, are given in Table S1 and Figure S7.

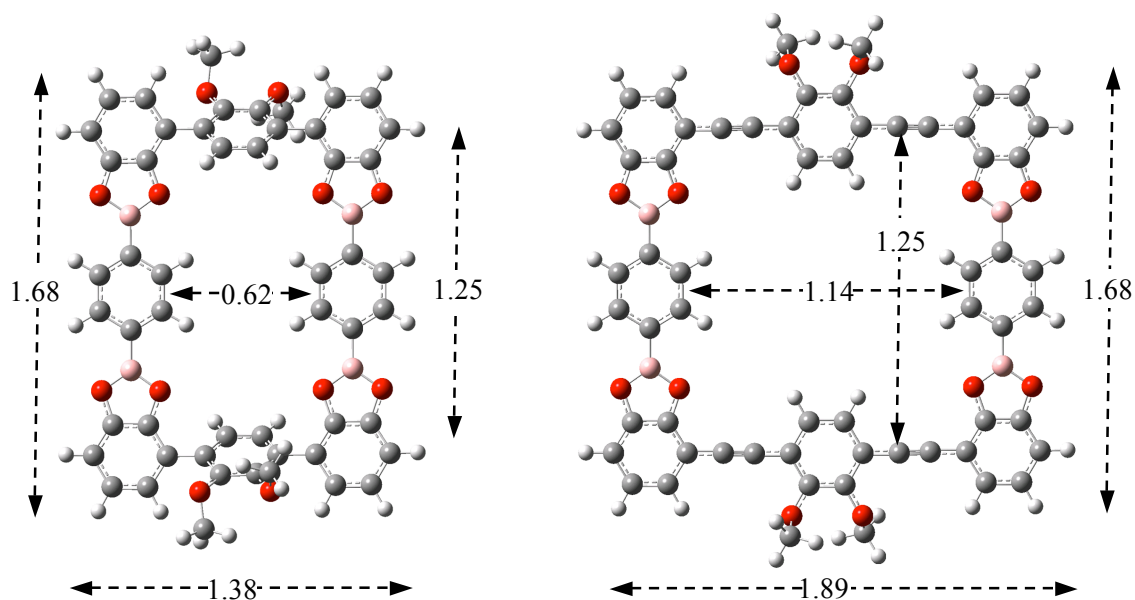


Figure S6. Exterior and interior dimensions of porous, shape persistent rectangles **3** and **4** as obtained from DFT calculations. All values are reported in nm.

Table S1. Comparison of computed and experimental B-O stretching frequencies and out of plane boronate ester vibrational frequencies that are characteristic of boronate esters. All values are reported in wavenumbers (cm^{-1}). Computed frequencies are scaled by 0.0960.

Assembly	B-O stretch (cm^{-1})		C-B-(O) ₂ out of plane bend (cm^{-1})	
	Experiment	Theory	Experiment	Theory
3	1325.50	1307.78	659.75	650.47
4	1333.21	1305.06	656.18	649.92

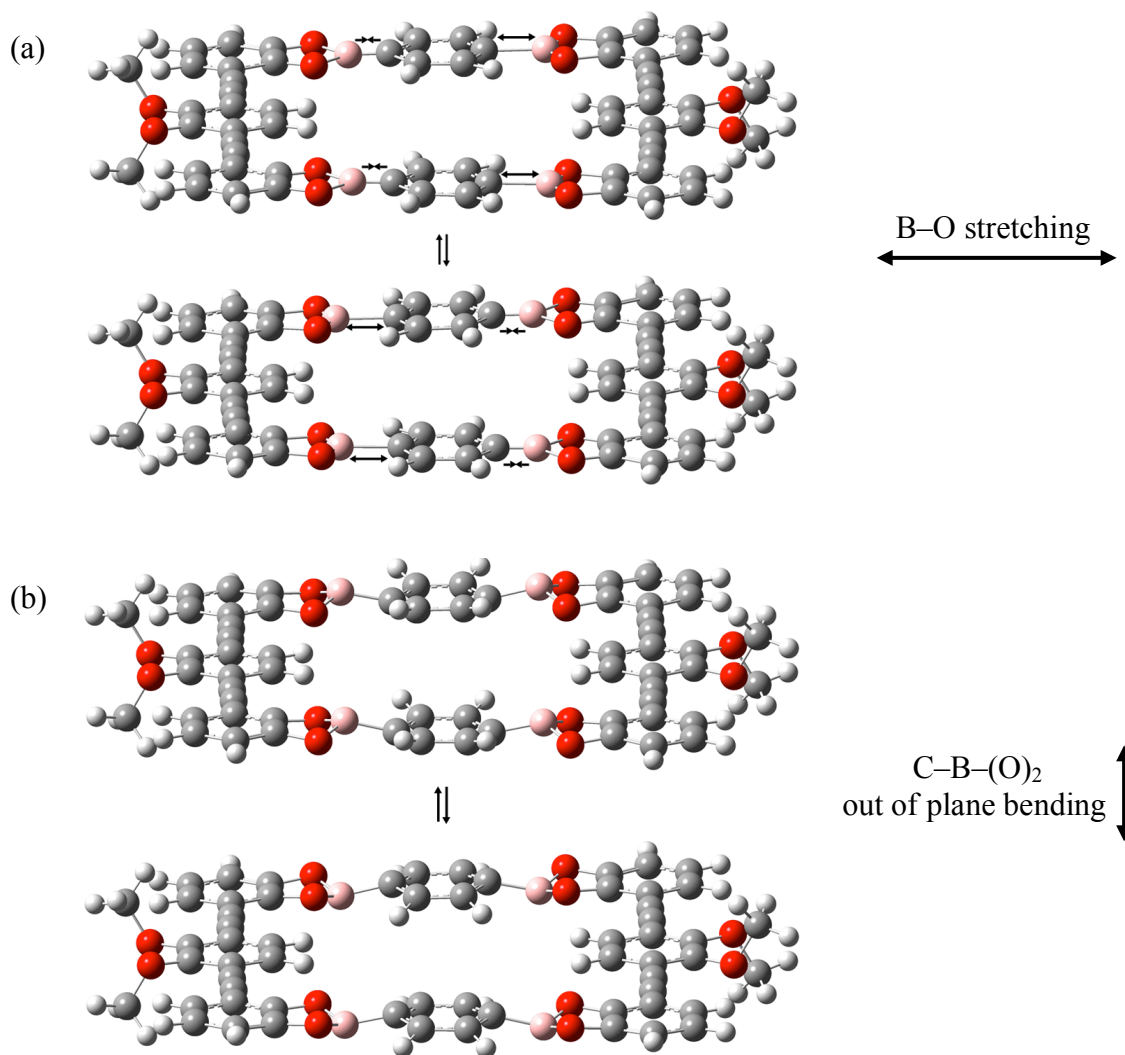


Figure S7. Snapshots at maximal and minimal displacements of (a) diagnostic B-O stretching and (b) boronate ester out of plane bending vibrational modes obtained from DFT calculations. Rectangle **4** is shown as a representative example; analogous modes were also found for rectangle **3**.

Stationary Point Summaries: Stationary points were optimized and energies calculated as described above. Geometries are given in Cartesian coordinates. Atoms are given by atomic number. Energies are given in Hartrees.

Rectangle 3:

6	5.399079	-0.664578	-1.354571	1	-4.744157	-1.173365	2.053941
6	6.248024	-1.427820	-0.535927	6	-6.211984	5.795685	0.375834
6	7.092847	-0.745493	0.362607	6	-7.411528	5.067317	0.431395
6	7.064761	0.662278	0.438566	6	-7.421874	3.669099	0.429020
6	6.237445	1.417521	-0.414190	6	-6.235771	2.903073	0.378922
6	5.401523	0.724559	-1.305569	6	-5.058610	3.649324	0.329485
1	4.744450	-1.173356	-2.054272	6	-5.050747	5.045772	0.323119
8	7.861577	-1.475174	1.238174	1	-6.192223	6.879822	0.372077
8	7.868384	1.297128	1.362631	1	-8.354758	5.602391	0.478505
1	4.753904	1.285551	-1.970653	1	-8.370347	3.146274	0.470574
6	6.155821	-5.797464	-0.826261	8	-3.754330	3.196448	0.250966
6	7.360975	-5.082471	-0.915029	8	-3.744245	5.489331	0.244782
6	7.395106	-3.688263	-0.813607	6	-6.155761	-5.797478	0.826155
6	6.231236	-2.911901	-0.622932	6	-5.014616	-5.037812	0.641519
6	5.047035	-3.644542	-0.549369	6	-5.046970	-3.644539	0.549344
6	5.014677	-5.037816	-0.641551	6	-6.231188	-2.911904	0.622842
1	6.116931	-6.878673	-0.898058	6	-7.395059	-3.688289	0.813433
1	8.289167	-5.623931	-1.068075	6	-7.360925	-5.082497	0.914848
1	8.348655	-3.180200	-0.898932	1	-6.116852	-6.878687	0.897948
8	3.757597	-3.181179	-0.359596	8	-3.708531	-5.468499	0.511710
8	3.708603	-5.468506	-0.511682	8	-3.757527	-3.181174	0.359628
6	6.212066	5.795664	-0.375768	1	-8.348620	-3.180245	0.898706
6	5.050822	5.045760	-0.323120	1	-8.289125	-5.623959	1.067833
6	5.058681	3.649309	-0.329560	6	-7.304967	1.376039	-2.684935
6	6.235837	2.903057	-0.378989	6	-9.289634	-1.314669	-1.151414
6	7.421949	3.669074	-0.429005	5	-2.946564	-4.314113	0.340441
6	7.411610	5.067288	-0.431323	6	1.411173	-4.303264	-0.160617
1	6.192322	6.879801	-0.371957	6	0.691922	-5.512392	-0.081024
8	3.744323	5.489318	-0.244787	6	-0.691852	-5.512389	0.081095
8	3.754395	3.196434	-0.251092	6	-1.411094	-4.303256	0.160704
1	8.370418	3.146236	-0.470542	6	-0.692736	-3.093922	0.076897
1	8.354842	5.602364	-0.478374	6	0.692824	-3.093926	-0.076786
6	9.289359	-1.314745	1.151992	5	2.946639	-4.314113	-0.340388
6	7.304271	1.376306	2.684955	1	1.223692	-6.457522	-0.144340
5	2.958791	4.339411	-0.197643	1	-1.223627	-6.457516	0.144399
6	-1.416591	4.335187	0.095703	1	-1.225305	-2.148826	0.134461
6	-0.695041	5.544531	0.047089	1	1.225399	-2.148833	-0.134332
6	0.695132	5.544527	-0.046967	1	9.638281	-1.528300	0.135010
6	1.416660	4.335180	-0.095811	1	9.592485	-0.305806	1.439324
6	0.695270	3.125717	-0.047230	1	9.711238	-2.046906	1.842176
6	-0.695224	3.125720	0.046885	1	7.111099	0.375697	3.085199
5	-2.958721	4.339429	0.197554	1	6.375486	1.957632	2.671503
1	-1.229457	6.489623	0.083188	1	8.045787	1.885803	3.302319
1	1.229566	6.489616	-0.082880	1	-7.112103	0.375342	-3.085109
1	1.229948	2.180765	-0.082668	1	-8.046600	1.885581	-3.302122
1	-1.229920	2.180772	0.082139	1	-6.376074	1.957205	-2.671879
6	-5.401322	0.724548	1.305339	1	-9.711718	-2.047040	-1.841251
6	-6.237380	1.417537	0.414102	1	-9.592860	-0.305816	-1.438961
6	-7.064849	0.662305	-0.438515	1	-9.638257	-1.527909	-0.134264
6	-7.092938	-0.745468	-0.362539				
6	-6.247983	-1.427827	0.535840				
6	-5.398890	-0.664586	1.354342				
1	-4.753584	1.285524	1.970319				
8	-7.868647	1.297146	-1.362416				
8	-7.861879	-1.475095	-1.237985				

B3LYP/6-31+g(d,p) HOMO: -0.23091

B3LYP/6-31+g(d,p) LUMO: -0.07313

B3LYP/6-31+g(d,p) enthalpy: -3005.8786695

B3LYP/6-31g(d) enthalpy: -3004.876006

B3LYP/6-31g(d) free energy: -3005.203159

Rectangle 4:

6	5.064041	-0.696709	-0.005715	6	-6.241160	5.482218	-0.009190
6	6.276740	-1.421469	-0.002213	6	-5.056539	6.225479	-0.007567
6	7.497369	-0.708031	0.007533	6	-5.052503	7.619437	-0.011415
6	7.498812	0.695026	-0.007215	1	-6.198881	9.451123	-0.019799
6	6.279651	1.410972	0.002190	1	-8.363650	8.178732	-0.023775
6	5.065465	0.688703	0.005373	1	-8.383981	5.715384	-0.018740
1	4.126401	-1.241640	-0.011489	8	-3.759635	5.766780	-0.002974
8	8.680885	-1.399767	-0.029327	8	-3.744340	8.061135	-0.009247
8	8.683733	1.384329	0.029973	6	-6.232947	-8.356725	0.016590
1	4.128944	1.235559	0.010891	6	-5.066538	-7.610986	0.011264
6	6.217662	-8.367127	-0.016744	6	-5.068243	-6.217024	0.007450
6	7.421259	-7.640745	-0.018752	6	-6.251617	-5.471781	0.009132
6	7.437520	-6.244793	-0.015219	6	-7.449252	-6.232351	0.015163
6	6.241160	-5.482218	-0.009211	6	-7.435327	-7.628329	0.018657
6	5.056539	-6.225479	-0.007584	1	-6.215980	-9.440751	0.019634
6	5.052503	-7.619437	-0.011432	8	-3.759114	-8.054869	0.009042
1	6.198881	-9.451123	-0.019820	8	-3.770577	-5.760492	0.002825
1	8.363650	-8.178731	-0.023801	1	-8.394825	-5.701359	0.018753
1	8.383981	-5.715383	-0.018767	1	-8.378618	-8.164737	0.023721
8	3.759635	-5.766780	-0.002986	6	-9.401082	1.453248	1.219327
8	3.744340	-8.061135	-0.009260	6	-9.404390	-1.436322	-1.218432
6	6.232947	8.356725	0.016572	5	-2.970164	-6.905384	0.004339
6	5.066538	7.610986	0.011247	6	1.412932	-6.903403	-0.002005
6	5.068243	6.217024	0.007433	6	0.689142	-8.112490	-0.001190
6	6.251617	5.471781	0.009112	6	-0.704006	-8.111325	0.000947
6	7.449252	6.232351	0.015140	6	-1.425775	-6.901030	0.001800
6	7.435327	7.628329	0.018635	6	-0.702207	-5.691891	0.000731
1	6.215980	9.440751	0.019617	6	0.691385	-5.693056	-0.000909
8	3.759114	8.054869	0.009029	5	2.957311	-6.910334	-0.004507
8	3.770577	5.760492	0.002811	1	1.223894	-9.058001	-0.002108
1	8.394825	5.701359	0.018728	1	-1.240339	-9.055940	0.001846
1	8.378618	8.164736	0.023698	1	-1.237055	-4.746437	0.001422
6	9.401083	-1.453248	1.219303	1	1.227814	-4.748498	-0.001570
6	9.404389	1.436321	-1.218456	1	9.652159	-0.446776	1.565826
5	2.970164	6.905384	0.004324	1	8.807753	-1.975984	1.977348
6	-1.412932	6.903403	-0.002001	1	10.313378	-2.015264	1.015481
6	-0.689142	8.112490	-0.001189	1	8.812339	1.960252	-1.976677
6	0.704006	8.111325	0.000943	1	9.653511	0.429334	-1.564891
6	1.425775	6.901030	0.001792	1	10.317771	1.996480	-1.014386
6	0.702207	5.691891	0.000725	1	-8.807751	1.975985	1.977371
6	-0.691385	5.693056	-0.000909	1	-10.313377	2.015264	1.015506
5	-2.957311	6.910334	-0.004497	1	-9.652157	0.446777	1.565851
1	-1.223894	9.058002	-0.002104	1	-10.317771	-1.996481	-1.014362
1	1.240339	9.055940	0.001840	1	-8.812340	-1.960254	-1.976652
1	1.237055	4.746437	0.001414	1	-9.653512	-0.429335	-1.564867
1	-1.227815	4.748498	-0.001568	6	-6.255318	-4.050789	0.005320
6	-5.064041	0.696709	-0.005695	6	-6.280786	-2.833095	0.002388
6	-6.276740	1.421469	-0.002191	6	-6.274953	2.843590	-0.002389
6	-7.497369	0.708031	0.007556	6	-6.247246	4.061236	-0.005346
6	-7.498812	-0.695026	-0.007215	6	6.255318	4.050789	0.005299
6	-6.279651	-1.410972	0.002212	6	6.280786	2.833094	0.002367
6	-5.065465	-0.688703	0.005392	6	6.274953	-2.843590	-0.002410
1	-4.126401	1.241640	-0.011471	6	6.247246	-4.061236	-0.005366
8	-8.680885	1.399767	-0.029303				
8	-8.683733	-1.384329	0.029997				
1	-4.128944	-1.235559	0.010909				
6	-6.217662	8.367127	-0.016724				
6	-7.421259	7.640745	-0.018728				
6	-7.437520	6.244793	-0.015195				

B3LYP/6-31+g(d,p) HOMO: -0.21627

B3LYP/6-31+g(d,p) LUMO: -0.08693

B3LYP/6-31+g(d,p) enthalpy: -3310.52855176

B3LYP/6-31g(d) enthalpy: -3309.459205

B3LYP/6-31g(d) free energy: -3309.631869

VIII. Supporting References

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