Supporting Information for:

Efficient Stannole Cycloaddition-Aromatization Cascades with Arynes for the Synthesis of Polycyclic Aromatic Hydrocarbons

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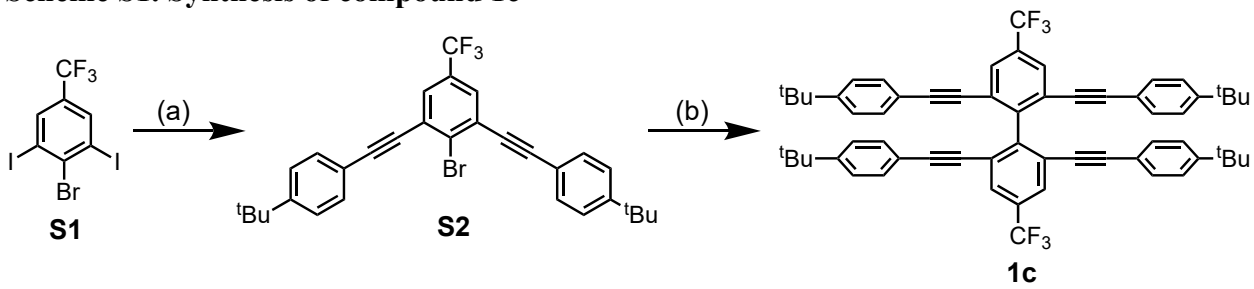
General Details

Unless otherwise stated, all manipulations were conducted in dry solvents under an inert atmosphere of nitrogen, using either standard Schlenk techniques or a glovebox. Pentane, toluene, tetrahydrofuran (THF), diethyl ether, acetonitrile (MeCN), and dichloromethane (CH_2Cl_2) were dried using a JC Meyers Phoenix SDS solvent purification system. Benzene-d_6, $CDCl_3$, and were freed from oxygen with vigorous nitrogen bubbling for 30 minutes, and then dried for at least 48 h over 3 Å molecular sieves (5% by mass). CD_2Cl_2 was freed from oxygen via freeze-pump-thaw three times, and then dried for at least 48 h over 3 Å molecular sieves (5% by mass). All reaction solvents were stored over 3 Å molecular sieves. All substrates, internal standards, or catalysts were used as received (or synthesized) unless otherwise noted. CuCl was purified by reported methods,[1] dried under vacuum at 200 °C overnight in the absence of light, then ground in a mortar and pestle in a glovebox for all reactions in this manuscript. Compounds **S1**,[2] **S3**,[3] **S4**,[4] **S5**,[5] **S6**,[6] **1a**,[7] **1b**,[8] and $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$[9] were synthesized by literature procedures. Celite® was dried in an oven at 150 °C for at least 24 hours, then brought into a glove-box. NMR spectra were recorded on 300, 400, 500, or 600 MHz spectrometers. Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks for ^{1}H-NMR spectra (δ = 7.26 ppm for $CDCl_3$, = 5.32 ppm for CD_2Cl_2 and δ = 7.16 for C_6D_6) and ^{13}C-NMR spectra (δ = 77.16 ppm for $CDCl_3$, δ = 128.06 for C_6D_6). NMR spectra are shown using MestReNova NMR processing software. Column chromatography was carried out using Fisher Chemical 40–63μm, 230–400 mesh silica gel.

Synthetic procedures and basic characterization data

Synthesis of oligoynes

Scheme S1. Synthesis of compound 1c



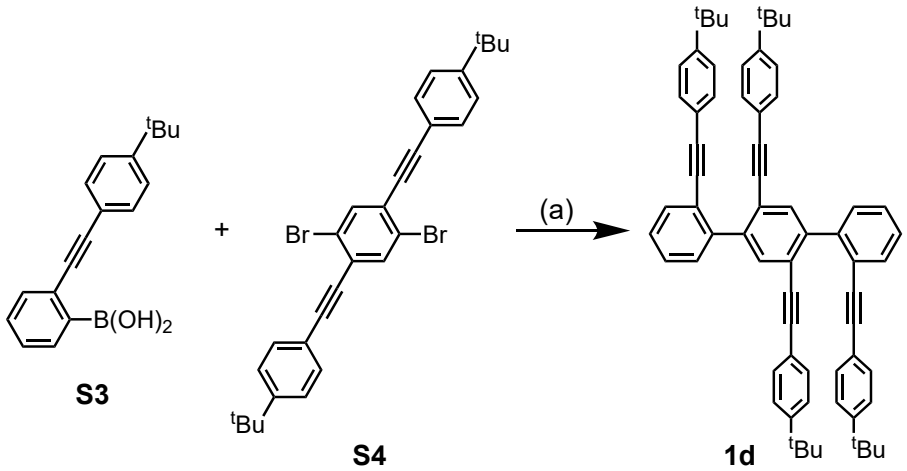
Reagents and conditions: (a) 4-(tertbutyl)phenylacetylene (2.1 equivs), CuI (0.05 equivs), $Pd(PPh_3)_4$ (0.02 equivs), triethylamine, THF, 23 ˚C, 92%; (b) i) ^{t}BuLi (2.0 equivs), CuCN (0.5 equivs), Et_2O, -78 ˚C, ii) 1,4-benzoquinone (1.6 equivs), 23 ˚C, 62%.

1-bromo-4-trifluoromethyl-2,6-(1-ethynyl-4-tertbutylphenyl)benzene (S2). A 150 mL schlenk flask was charged with **S1** (6.48 g, 13.6 mmol, 1 equiv), $Pd(PPh_3)_4$ (0.31 g, 0.27 mmol, 0.02 equivs), copper iodide (0.14 g, 0.70 mmol, 0.05 equivs), triethylamine (30 mL), and tetrahydrofuran (50 mL). 4-(tertbutyl)phenylacetylene (4.51 g, 28.5 mmol, 2.1 equivs) was then added, the flask was sealed, and the solution was stirred at RT for 18 h. The reaction mixture was then diluted with 200 mL dichloromethane and washed with 2 M aqueous HCl 3x100 mL, dried over $MgSO_4$, and concentrated via rotary evaporation. The crude solid was dissolved in 120 mL hexanes, filtered through a short plug of silica, and concentrated to dryness via rotary evaporation to afford **S2** (6.70 g, 92%) as a pale yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (s, 2H), 7.53-7.56 (m, 4 H), 7.40-7.43 (m, 4 H), 1.34 (s, 18 H) **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.8, 132.2, 131.8, 129.8 (q, J = 33 Hz), 128.5 (q, J = 4 Hz), 127.7, 125.6, 123.4 (q, J = 273 Hz), 119.3, 96.2, 86.7, 35.0, 31.3 **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{31}H_{28}F_3Br$, 536.1326; found, 536.1323.

Tetrayne 1c. A 500 mL Schlenk flask was charged with **S2** (5.00 g, 9.80 mmol, 1.00 equiv) and diethyl ether (135 mL), and the stirred solution was cooled to -78 ˚C with a CO_2(s)/acetone bath. To this solution was added *tert*-butyllithium* (1.7 M in hexanes, 11.0 mL, 9.80 mmol, 2.00 equivs) by addition funnel over 15 min and the resulting mixture was stirred for a further 1 h at –78 °C. Copper(I) cyanide (0.42 g, 4.65 mmol, 0.50 equivs) was added, the reaction mixture was stirred at -78 ˚C for an additional 1 h, and the flask was removed from the CO_2(s)/acetone bath and allowed to warm to RT. 1,4-benzoquinone (1.61 g, 14.9 mmol, 1.60 equivs) was added, and the reaction mixture was stirred for 2 h. The solution was then poured into 500 mL of 1 M aqueous HCl, the organic layer was separated, and the aqueous layer was washed with 2x100 mL ethyl acetate. The organic layers were combined, dried over $MgSO_4$, and concentrated to dryness via rotary evaporator. The crude product was purified by column chromatography (100% hexanes) and subsequently recrystallized from toluene at -78 ˚C to afford **1c** (2.65 g, 62%) as pale yellow crystals. **^{1}H NMR (400 MHz, C_6D_6)** δ 7.96 (s, 4 H), 7.24 (m, 8 H), 7.02 (m, 8 H), 1.04 (s, 36 H) **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.3, 147.4, 131.5, 130.8 (q, J = 33 Hz), 127.3 (q, J = 4 Hz), 125.6, 125.4, 123.8 (q, J = 273 Hz), 119.6, 95.2, 86.0, 34.9, 31.2 **HRMS–ESI (m/z):** $[M+H]^+$ calcd for $C_{62}H_{57}F_6$, 915.4359; found, 915.4374.

*NOTE: *tert*-butyllithium is highly pyrophoric and should be handled with care.

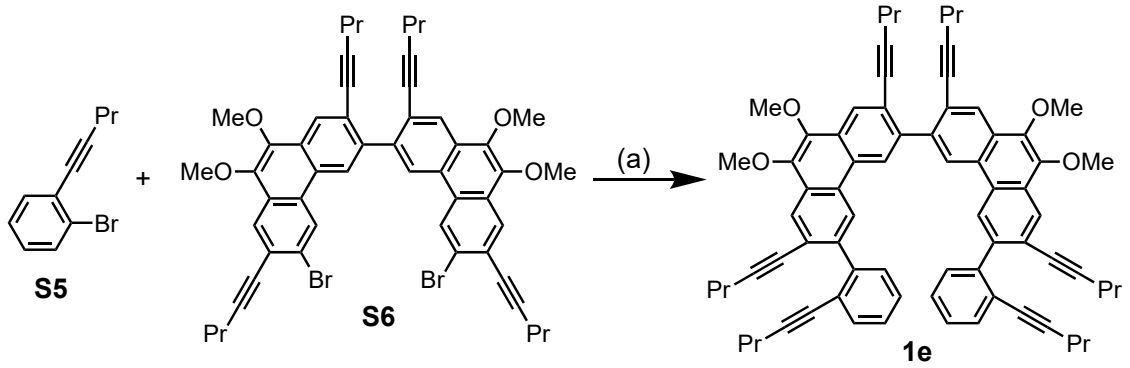
Scheme S2. Synthesis of compound 1d



Reagents and conditions: $PdCl_2(PPh_3)_2$ (0.06 equivs), K_2CO_3 (2.5 equivs), toluene, EtOH, H_2O, 90 ˚C, 33%.

Tetrayne 1d. A 150 mL Teflon stoppered flask was charged with **S3** (675 mg, 2.43 mmol, 2.50 equivs), **S4** (533 mg, 0.97 mmol, 1.00 equiv), $PdCl_2(PPh_3)_2$ (41 mg, 0.058 mmol, 0.06 equivs), K_2CO_3 (336 mg, 2.43 mmol, 2.5 equivs), toluene (23 mL), ethanol (23 mL), and water (6 mL). The flask was sealed with a Teflon stopper, and the stirred solution was heated to 90 ˚C for 3 h. The mixture was allowed to cool to RT and was diluted with 100 mL dichloromethane and 100 mL water. The organic layer was separated, and the aqueous layer was extracted with 100 mL of dichloromethane. The combined organic phases were washed with 100 mL 1.5 M HCl and 100 mL brine, dried over $MgSO_4$, and concentrated by rotary evaporator. The crude product was purified by column chromatography (0-25% toluene in hexanes) and concentrated by rotary evaporator. The resulting beige solid was triturated with hexanes (3x10 mL) to afford **1d** (305 mg, 33%) as a white powder. **^{1}H NMR (400 MHz, CD_2Cl_2)** δ 7.96 (s, 2 H), 7.69-7.74 (m, 4 H), 7.43-7.51 (m, 4 H), 7.25-7.30 (m, 8 H), 7.14-7.19 (m, 8 H), 1.28 (s, 18 H), 1.18 (s, 18 H) **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.5, 151.1, 142.0, 141.8, 134.1, 132.2, 131.4, 131.3, 130.6, 127.7, 127.5, 125.3, 125.2, 123.3, 122.3, 120.6, 120.4, 94.3, 93.6, 88.8, 88.5, 34.9, 34.7, 31.3, 31.2 **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{66}H_{62}$, 854.4852; found, 854.4836.

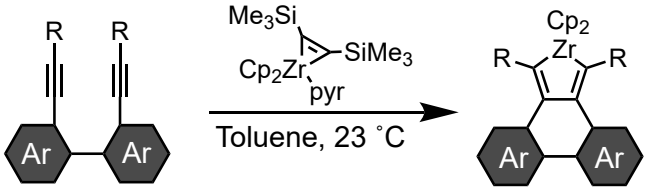
Scheme S3. Synthesis of compound 1e



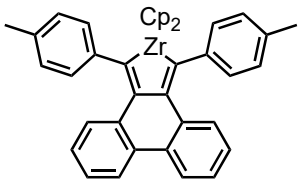
Reagents and conditions: nBuLi (2.50 equivs), $ZnCl_2$ (2.60 equivs), $Pd(PPh_3)_4$ (0.05 equivs), THF, 65 ˚C, 50%.

Hexayne 1e. A 125 mL Schlenk flask was charged with **S5** (1.43 g, 6.38 mmol, 2.60 equiv) and tetrahydrofuran (20 mL) and the solution was cooled to –78 °C with a CO_2(s)/acetone bath. To this solution was added *n*-butyllithium (1.60 M in hexanes, 3.83 mL, 6.13 mmol, 2.50 equiv) by syringe over 20 min and the resulting mixture was stirred for a further 10 min at –78 °C. To this mixture was added $ZnCl_2$ (1.05 M in THF, 6.13 mL, 6.38 mmol, 2.60 equiv) by syringe over 5 min, and subsequently the flask was removed from the cold bath and warmed to RT over 1 h. At this time **S6** (2.20 g, 2.45 mmol, 1.00 equiv) and $Pd(PPh_3)_4$ (142 mg, 0.123 mmol, 0.050 equiv), were added against a flow of N_2, the Schlenk flask was sealed, and the mixture was stirred at 65 ˚C for 18 h. The solution was then exposed to air and diluted with aqueous ammonium chloride (40 mL). The crude product was extracted with CH_2Cl_2 (3x20 mL), dried over $MgSO_4$, and solvents were removed by rotary evaporation. The crude product was purified by column chromatography (33-50% CH_2Cl_2 in hexanes) and subsequently crystallized from hexanes at -30 ˚C to afford **1e** (1.25 g, 50%) as off-white crystals. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.64 (s, 2H), 8.56 (s, 2H), 8.34 (s, 2H), 8.33 (s, 2H), 7.73-7.68 (m, 2H), 7.46-7.38 (*overlapped* m, 6H), 7.29-7.22 (m, 2H), 4.13 (s, 6H), 4.12 (s, 6H), 2.27-2.24 (t, J = 6.9 Hz, 4H), 2.15-2.11 (t, J = 6.9 Hz, 4H), 2.02-1.99 (t, J = 6.8 Hz, 4H), 1.46-1.39 (m, 4H), 1.32-1.23 (m, 4H), 1.19-1.10 (m, 4H), 0.88-0.82 (t, J = 7.6 Hz, 6H), 0.66-0.62 (t, J = 7.5 Hz, 6H), 0.52-0.48 (t, J = 7.4 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.88, 143.78, 143.25, 140.66, 140.61, 132.20, 130.32, 128.48, 128.40, 127.31, 127.28, 127.22, 126.88, 126.00, 125.96, 124.70, 123.92, 123.16, 122.81, 94.31, 94.11, 93.60, 80.72, 80.65, 80.31, 61.23, 61.22, 22.09, 22.05, 21.95, 21.73, 21.65, 21.44, 13.50, 13.32, 13.15. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{74}H_{70}O_4$, 1022.5274; found, 1022.5278.

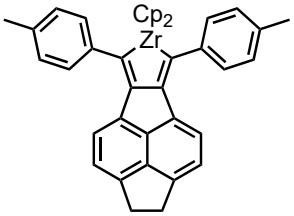
Synthesis of zirconacyclopentadienes



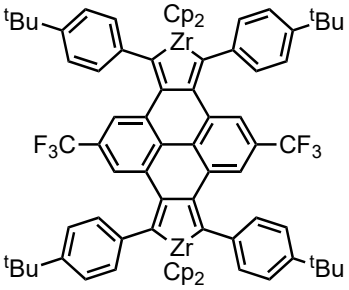
Procedure: In a glovebox, $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ (1.1 equivs per diyne) and the appropriate oligoyne (1.0 equiv) were weighed into separate flasks. To each flask was then added equal volumes of benzene, and a stir bar was added to the solution containing zirconium. To the stirring solution of $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ was added the benzene solution of the diyne. The reaction mixture was stirred for 10 minutes, concentrated to 25% of the original volume, and diluted with pentane back to the original volume of the solution. The precipitate was collected on a fritted funnel, washed with pentane (2 x 5 mL), and dried under vacuum to afford pure zirconacyclopentadiene.



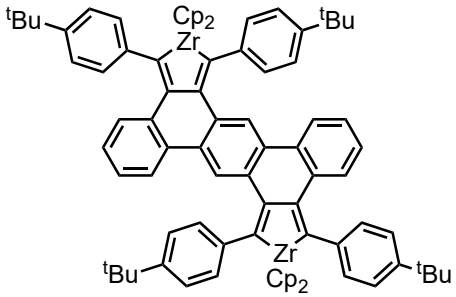
S7. This compound was synthesized according to the procedure outlined above using the following amounts: **1a** (1.20 g, 3.14 mmol), $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ (1.63 g, 3.45 mmol), benzene (15 mL). **S7** (1.60 g, 85%) was isolated as a dark brown/red powder. **^{1}H NMR (600 MHz, C_6D_6):** δ 7.80 (dd, *J* = 7.90, 0.9 Hz, 2H), 7.71 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.01-6.95 (*overlapped* m, 2H), 6.99 (d, *J* = 8.0 Hz, 4H), 6.83 (dt, *J* = 7.9, 0.9 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 4H), 2.19 (s, 6H). **^{13}C NMR (151 MHz, C_6D_6):** δ 197.2, 146.1, 139.3, 133.8, 132.9, 132.2, 130.1, 128.4, 127.0, 126.7, 126.6, 124.3, 112.1, 21.2. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{40}H_{32}Zr$, 602.1551; found, 602.1550.



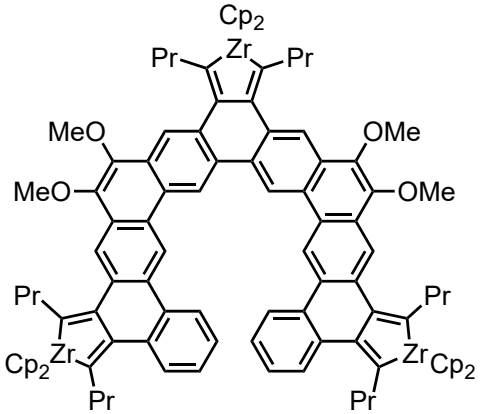
S8. This compound was synthesized according to the procedure outlined above using the following amounts: **1b** (300 mg, 0.78 mmol), $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ (395 mg, 1.56 mmol), benzene (3 mL). **S8** (440 mg, 94%) was isolated as a bright orange powder. **^{1}H NMR (400 MHz, C_6D_6)** δ 7.34 – 7.31 (d, *J* = 8.2 Hz, 4H), 7.29-27 (d, *J* = 8.2 Hz, 4H), 7.09-7.07 (d, *J* = 7.1 Hz, 2H), 6.98-6.96 (d, *J* = 7.1 Hz, 2H), 5.90 (s, 10H), 2.92 (s, 4H), 2.34 (s, 6H). **^{13}C NMR (101 MHz, C_6D_6)** δ 193.32, 148.25, 142.05, 138.74, 136.95, 134.69, 133.57, 130.12, 128.35, 128.22, 128.06, 127.90, 125.03, 121.07, 120.70, 111.66, 31.94, 21.30. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{40}H_{32}Zr$, 602.1551; found, 602.1549.



S9. This compound was synthesized according to the procedure outlined above using the following amounts: **1c** (3.14 g, 3.43 mmol), $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ (3.39 g, 7.20 mmol), benzene (70 mL). **S7** (3.80 g, 82%) was isolated as a maroon powder. **^{1}H NMR (600 MHz, C_6D_6)** δ 7.44 (s, 4 H), 7.24-7.28 (m, 8 H), 6.73-6.77 (m, 8 H), 5.95 (s, 20 H), 1.34 (s, 36 H)**. ^{13}C NMR (151 MHz, THF-*d8*)** δ 201.5, 147.4, 146.4, 139.2, 133.7, 131.4, 127.5 (q, *J* = 31 Hz), 126.79, 126.3, 126.0 (q, *J* = 4 Hz), 125.1 (q, *J* = 272 Hz), 113.4, 35.0, 31.9. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{82}H_{76}F_6Zr_2$, 1354.3945; found, 1354.3942.

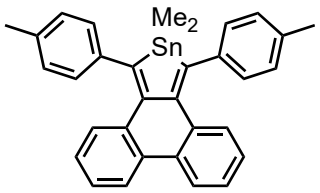


S10. This compound was synthesized according to the procedure outlined above using the following amounts: **1d** (1.50 g, 1.75 mmol), $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ (1.73 g, 3.68 mmol), benzene (18 mL). **S10** (1.90 g, 83%) was isolated as a dark purple powder**. ^{1}H NMR (600 MHz, C_6D_6)** δ 8.20 (s, 2 H), 7.65 (d, J = 8.1, 2 H), 7.25 (m, 8 H), 7.10 (t, J = 7.5, 2 H), 6.99 (d, J = 8.1, 2 H), 6.79 (m, 10 H), 6.00 (s, 20 H), 1.34 (s, 18 H), 1.28 (s, 18 H). **^{13}C NMR (151 MHz, C_6D_6)** δ 198.10, 196.53, 147.03, 146.21, 146.12, 145.95, 139.59, 139.42, 134.59, 133.74, 132.21, 131.97, 131.44, 129.33, 128.88, 126.87, 126.37, 126.35, 126.28, 126.10, 124.96, 112.12, 34.45, 34.38, 31.83, 31.68. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{86}H_{82}Zr_2$, 1294.4511; found, 1294.4518.



S11. This compound was synthesized according to the procedure outlined above using the following amounts: **1e** (1.02 g, 1.00 mmol), $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ (1.60 g, 3.30 mmol), benzene (10 mL). **S11** (1.43 g, 85%) was isolated as an orange powder. **^{1}H NMR (400 MHz, C_6D_6)** δ 9.52 (s, 2H), 9.31 (s, 2H), 8.72 (s, 2H), 8.64 (s, 2H), 8.11-8.09 (d, *J* = 7.8 Hz, 2H), 7.60-7.58 (d, *J* = 7.6 Hz, 2H), 7.50-7.47 (t, *J* = 7.6 Hz, 2H), 7.39-7.35 (t, *J* = 7.8 Hz, 2H), 6.07 (s, 10H), 5.99 (s, 20H), 4.09 (s, 6H), 4.09 (s, 6H), 3.44-3.37 (m, 8H), 3.03-3.01 (m, 4H), 1.36-1.32 (m, 12H), 0.98-0.91 (m, 18H). **^{13}C NMR (151 MHz, C_6D_6)** δ 200.04, 199.11, 150.34, 145.18, 145.08, 135.67, 135.32, 134.08, 133.78, 133.66, 129.57, 128.89, 128.74, 128.60, 127.05, 124.91, 123.54, 123.35, 123.24, 119.40, 118.93, 118.85, 118.45, 118.33, 114.21, 109.18, 109.07, 61.23, 61.21, 44.55, 44.40, 44.17, 27.31, 27.25, 27.18, 15.17, 15.15, 15.14. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{104}H_{100}O_4Zr_3$, 1682.4763; found, 1682.4758.

Synthesis of stannoles:



Stannole 2a.

*From isolated zirconacyclopentadiene **S7**:*

A 125 mL round bottom flask flask was charged with zirconacycle **S7** (0.400 g, 0.662 mmol, 1.00 equiv), Me_2SnCl_2 (0.160 g, 0.7285 mmol, 1.1 equivs), CuCl (0.066 g, 0.662 mmol, 1.00 equiv), and LiCl (0.059 g, 1.39 mmol, 2.10 equiv). To the flask was then added toluene (10 mL) and the reaction mixture was stirred ***vigorously*** for ~ 1 h. The solution was filtered through celite, concentrated to dryness in vacuo, and the crude solid was suspended in acetonitrile (5 mL). The precipitate was collected on a fritted funnel, washed with acetonitrile (2x3 mL), and dried under vacuum to yield **2a** (0.285 g, 81%) as a bright orange crystalline solid.

*From diyne **1a** with $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$:*

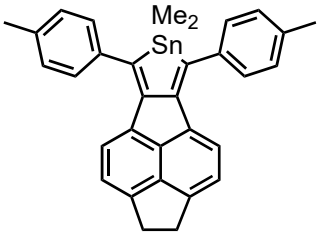
A 125 mL round bottom flask was charged with **1a** (0.253 g, 0.662 mmol, 1.00 equiv), $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ (0.342 g, 0.728 mmol, 1.10 equivs), and toluene (10 mL). The reaction mixture was stirred for 10 minutes. Me_2SnCl_2 (0.160 g, 0.7285 mmol, 1.1 equivs), CuCl (0.066 g, 0.662 mmol, 1.00 equiv), and LiCl (0.059 g, 1.39 mmol, 2.10 equiv) were then added to the stirred reaction mixture in one portion and the mixture was stirred vigorously for 1 h. The solution was filtered through celite, concentrated to dryness in vacuo, and the crude solid was suspended in acetonitrile (5 mL). The precipitate was collected on a fritted funnel, washed with acetonitrile (2x3 mL), and dried under vacuum to yield **2a** (0.246 g, 70%) as an orange solid.

*From diyne **1a** via the Negishi protocol:*

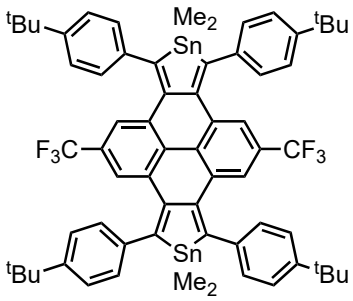
A 125 mL schlenk flask was charged with **1a** (0.253 g, 0.662 mmol, 1.00 equiv), Cp_2ZrCl_2 (0.212 g, 0.728 mmol, 1.10 equivs) and THF (10 mL), and the solution was cooled to -78 ˚C with a CO_2(s)/acetone bath. To this solution was added *n*-butyllithium (1.60 M in hexanes, 0.894 mL,

1.43 mmol, 2.20 equiv) by syringe over 20 min, the resulting mixture was stirred for a further 10 min at –78 °C, and then warmed to RT over 1 h. Me_2SnCl_2 (0.160 g, 0.7285 mmol, 1.1 equivs), CuCl (0.066 g, 0.662 mmol, 1.00 equiv), and LiCl (0.059 g, 1.39 mmol, 2.10 equiv) were then added to the stirred reaction mixture in one portion and the mixture was stirred vigorously for 1 h. The solution was filtered through celite, concentrated to dryness in vacuo, and the crude solid was suspended in acetonitrile (5 mL). The precipitate was collected on a fritted funnel, washed with acetonitrile (2x3 mL), and dried under vacuum to yield **2a** (0.232 g, 68%) as an orange solid.

^{1}H NMR (600 MHz, C_6D_6): δ 7.83 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 4H), 6.98 (dt, *J* = 8.1, 1.1 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 4H), 6.75 (dt, *J* = 8.1, 1.2 Hz, 2H), 2.10 (s, 6H), 0.38 (s, $J_{Sn,H}$ = 27.8 Hz, 6H). **^{13}C NMR (151 MHz, C_6D_6):** δ 146.5, 146.4, 143.0, 135.3, 135.2, 133.8, 131.4, 130.4, 128.6, 128.4, 127.7, 127.0, 124.5, 21.2, -7.6. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{32}H_{28}Sn$, 532.1213; found, 532.1212.



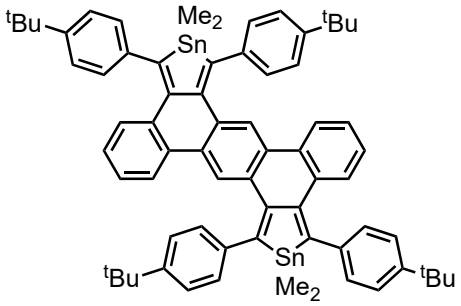
Stannole 2b. A teflon stoppered flask was charged with **S8** (0.160 g, 0.265 mmol, 1.00 equiv), Me_2SnCl_2 (0.070 g, 0.318 mmol, 1.10 equivs), CuCl (0.157 g, 1.58 mmol, 6.00 equivs), and toluene (6 mL), and sealed with a teflon stopper. The vigorously stirred reaction heated at 80 ˚C for 24 h. The reaction mixture was then filtered through celite, concentrated to 1 mL, and diluted with acetonitrile (5 mL). The precipitate was collected on a fritted funnel and washed with acetonitrile (2x3 mL) to afford **2b** (0.132 g, 73%) as a bright yellow powder. **^{1}H NMR (600 MHz, Benzene-d_6)** δ 7.83-7.82 (d, *J* = 7.3 Hz, 2H), 7.58-7.57 (d, *J* = 8.0 Hz, 4H), 7.13-7.12 (d, *J* = 8.0 Hz, 2H), 7.03-7.01 (d, *J* = 7.3 Hz, 2H), 2.95 (s, 4H), 2.22 (s, 6H), 0.38 (s, 6H). **^{13}C NMR (151 MHz, C_6D_6)** δ 152.16, 143.85, 142.28, 141.95, 141.24, 139.12, 135.79, 132.12, 129.86, 127.65, 121.24, 120.78, 32.04, 21.32, -7.46. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{32}H_{28}Sn$, 532.1213; found, 532.1211.



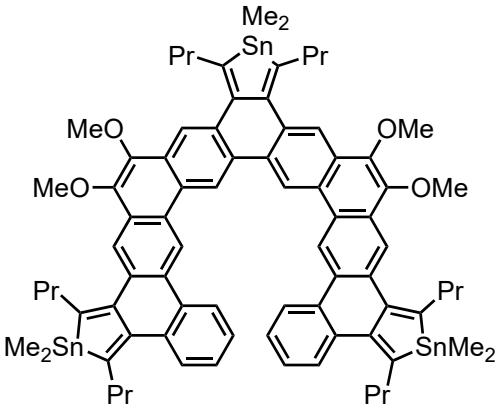
Stannole 2c. A 125 mL round bottom flask was charged with **S9** (1.10 g, 0.900 mmol, 1.00 equiv), Me_2SnCl_2 (0.435 g, 1.98 mmol, 2.2 equivs), CuCl (0.534 g, 5.40 mmol, 6.00 equivs), $ZnCl_2$ (0.245 g, 1.80 mmol, 2.00 equivs),* and toluene (20 mL) and stirred vigorously at RT for 2 h. The reaction

mixture was then filtered through celite, concentrated to 2 mL, and diluted with acetonitrile (10 mL). The precipitate was collected on a fritted funnel and washed with acetonitrile (2x5 mL) to afford **2c** (0.687 g, 70%) as a bright orange/red crystalline solid. ^{1}H NMR (600 MHz, Benzene-d_6) δ 7.67 (s, 4H), 7.30 – 7.25 (m, 8H), 7.21 – 7.17 (m, 8H), 1.26 (s, 36H), 0.35 (s, 12H). ^{13}C NMR (151 MHz, C_6D_6) δ 150.68, 149.48, 143.94, 142.61, 133.61, 133.24, 126.98, 126.11, 124.85, 123.48, 115.88, 34.58, 31.36, 0.08, -8.17. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{66}H_{68}F_6Sn_2$, 1214.3269; found, 1214.3273.

*NOTE: it was determined that formation of stannole **2c** required the presence of a Lewis acid to proceed, unlike for other stannoles. BPh_3 (50% yield), $AlEt_3$ (75% yield), and $ZnCl_2$ (82% yield) were all found to successfully generate the product.



Stannole 2d. In a glovebox, a round bottom flask was charged with zirconacycle **S10** (0.570 g, 0.439 mmol, 1.00 equiv), Me_2SnCl_2 (0.212 g, 0.966 mmol, 2.20 equivs), CuCl (0.086 g, 0.878 mmol, 2.00 equivs), LiCl (0.074 g,1.76 mmol, 4.00 equivs) and toluene (12 mL) and stirred vigorously at RT for 1 h. The reaction mixture was then filtered through celite, concentrated to 1 mL, and diluted with acetonitrile (7 mL). The precipitate was collected on a fritted funnel and washed with acetonitrile (2x3 mL) to afford **2c** (0.349 g, 69%) as a dark red-brown powder. **^{1}H NMR (600 MHz, C_6D_6)** δ 8.28 (s, 2H), 7.85-7.83 (m, 2H), 7.43-7.37 (m, 4H), 7.37-7.32 (m, 4H), 7.27-7.21 (m, 8H), 7.07-7.04 (m, 2H), 6.90-6.89 (m, 2H), 6.73-6.70 (m, 2H), 1.27 (s, 18H), 1.22 (s, 18H), 0.40 (s, 12H).**^{13}C NMR (151 MHz, C_6D_6)** δ 148.57, 148.51, 147.09, 146.97, 146.78, 146.14, 143.72, 143.18, 135.39, 133.76, 133.68, 133.07, 131.25, 127.18, 126.89, 126.84, 126.64, 124.83, 115.73, 34.58, 34.55, 31.61, 31.46, -7.47. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{70}H_{74}Sn_2$, 1154.3834; found, 1154.3834.



Stannole 2e. In a glovebox, a round bottom flask was charged with zirconacycle **S11** (0.240 g, 0.1422 mmol, 1.00 equiv), Me_2SnCl_2 (0.103 g, 0.469 mmol, 3.30 equivs), CuCl (0.042 g, 0.427 mmol, 3.00 equivs), and toluene (15 mL) and stirred vigorously at RT for 15 min.* The reaction mixture was then filtered through celite, concentrated to dryness in vacuo, and suspended in acetonitrile (3 mL). The precipitate was collected on a fritted funnel and washed with acetonitrile (2x1 mL) to afford **2e** (0.126 g, 60%) as a bright green-yellow powder. **^{1}H NMR (400 MHz, C_6D_6)** δ 9.59 (s, 2H), 9.44 (s, 2H), 9.01 (s, 2H), 8.92 (s, 2H), 8.25-8.22 (m, 2H), 7.94-7.92 (m, 2H), 7.38-7.34 (m, 2H), 7.32-7.28 (m, 2H), 3.96 (s, 6H), 3.93 (s, 6H), 3.43-3.39 (m, 4H), 3.37-3.33 (m, 4H), 3.03-2.99 (m, 4H), 1.73-1.66 (m, 8H), 1.58-1.53 (m, 2H), 1.04-0.99 (m, 12H), 0.91-0.87 (m, 6H), 0.51 (s, 6H), 0.48 (s, 12H). **^{13}C NMR (151 MHz, C_6D_6)** δ 150.51, 150.07, 147.27, 147.06, 146.84, 145.01, 144.94, 135.12, 134.92, 133.76, 133.54, 133.23, 133.14, 130.53, 129.55, 129.42, 129.32, 128.86, 128.77, 128.47, 127.24, 124.65, 124.45, 119.50, 118.83, 60.92, 60.90, 39.19, 38.97, 38.64, 29.31, 29.02, 14.33, 14.32, 14.21, -7.16, -7.27. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{80}H_{88}O_4Sn_2$, 1472.3749; found, 1472.3750.

*NOTE: The reaction length is very important for achieving full conversion and reproducibly high yields. If the reaction is allowed to stir too long (>20 min) the product begins to decompose, complicating work up and isolation significantly; however, appreciably shorter reaction times (<10 min) do not facilitate complete consumption of the starting zirconacycle.

Diels-Alder with Benzyne Precursors:

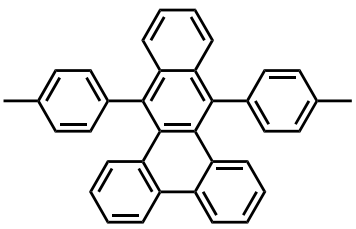
Procedure A (using 1-SiMe$_3$-2-OTf arenes):

A flask was charged with the desired stannole (1.0 equiv), benzyne precursor (1.1 equiv per stannole), tetrabutylammonium difluorotriphenylsilicate (TBAT) (3.3 equiv per stannole), dimethylacetylenedicarboxylate (DMAD) (3 equiv per stannole), and benzene. The stirred reaction mixture was heated to 60 ˚C for 12 h and then cooled to RT. The solution was then concentrated to dryness via rotary evaporator and purified by column chromatography.

Procedure B (using 1,2-dihaloarenes):

A flask was charged with the desired stannole (1.0 equiv), benzyne precursor (1.2 equivs per stannole), and toluene and stirred vigorously*. To this solution was added *n*-butyllithium (1.3 equivs per stannole) dropwise over 15 min. The reaction mixture was quenched with aqueous ammonium chloride, extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated to dryness via rotary evaporation. The crude solid was purified by column chromatography.

*NOTE: complete dissolution of both starting materials prior to the addition of nBuLi is necessary for achieving full conversion.



PAH 3a.

From procedure A:

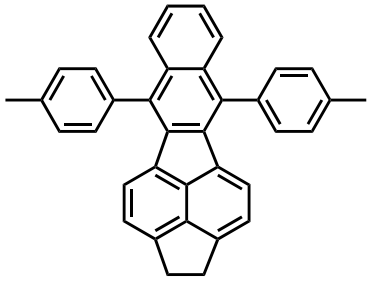
This compound was synthesized according to procedure A outlined above using the following amounts: **2a** (0.200 g, 0.376 mmol), 2-($SiMe_3$)C_6H_4(OTf) (0.120 g, 0.414 mmol), TBAT (0.670 g, 1.24 mmol), DMAD (0.160 g, 1.13 mmol), benzene (2 mL). Eluent: 15% CH_2Cl_2 in hexanes. **3a** (0.110 g, 68%, ≥98% purity) was isolated as a white powder.

From procedure B:

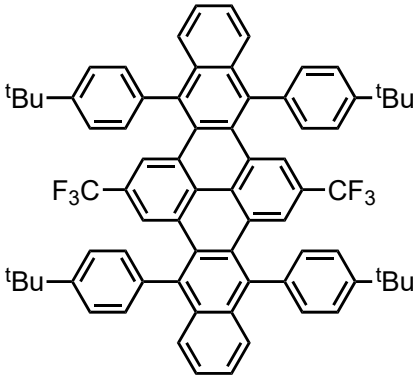
This compound was synthesized according to procedure B outlined above using the following amounts: **2a** (0.200 g, 0.376 mmol), 1,2-dibromobenzene (0.106 g, 0.451 mmol), nBuLi (1.00 M in hexanes, 0.489 mL, 0.489 mmol), benzene (2 mL). Eluent: 15% CH_2Cl_2 in hexanes. **3a** (0.124 g, 72%, ≥98% purity) was isolated as a white powder.

3a was also synthesized via procedure B on 0.038 mmol scale from 2-chloro-bromobenzene (0.009 g, 0.045 mmol, 83%) and 2-fluoro-bromobenzene (0.008 g, 0.045 mmol, 81%) using identical conditions to those described for 1,2-dibromobenzene.

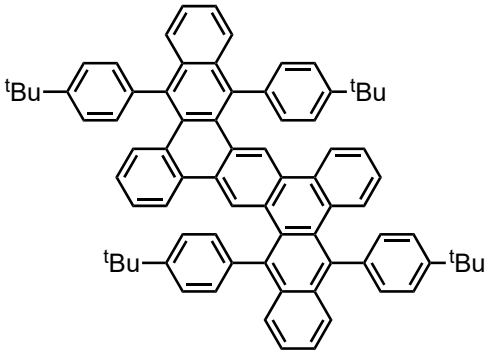
In all cases, ^{1}H NMR spectroscopy of **2a** matched reported chemical shifts from the literature.[9]



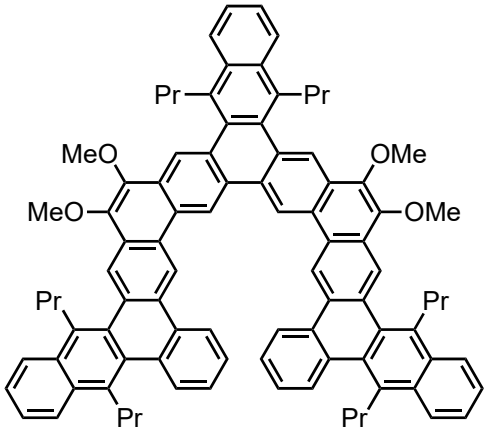
3b. This compound was synthesized according to procedure B outlined above using the following amounts: **2b** (0.200 g, 0.376 mmol), 1,2-dibromobenzene (0.106 g, 0.451 mmol), nBuLi (1.00 M in hexanes, 0.489 mL, 0.489 mmol), benzene (2 mL). Eluent: 15% CH_2Cl_2 in hexanes. **3b** (0.133 g, 75%, ≥98% purity) was isolated as a pale yellow powder**. ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72-7.70 (m, 2H), 7.47 (*apparent* s, 8H), 7.39-7.37 (m, 2H), 7.17-7.16 (d, J = 7.1 Hz, 2H), 6.73-6.71 (d, J = 7.1 Hz, 2H), 3.44 (s, 4H), 2.59 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 145.11, 137.49, 136.83, 136.33, 134.89, 134.37, 132.76, 132.63, 130.16, 129.90, 126.89, 125.48, 123.96, 120.94, 32.25, 21.69. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{36}H_{26}$, 458.2035; found, 458.2035.



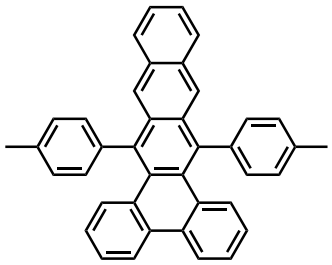
3c. This compound was synthesized according to procedure A outlined above using the following amounts: **2c** (0.250 g, 0.206 mmol), 2-($SiMe_3$)C_6H_4(OTf) (0.147 g, 0.495 mmol), TBAT (0.534 g, 0.990 mmol), DMAD (0.087 g, 0.617 mmol), benzene (5 mL). Eluent: 33% CH_2Cl_2 in hexanes. **3c** (0.088 g, 40%, 94% purity) was isolated as a pale-yellow powder. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.00-7.97 (m, 4H), 7.58 (s, 4H), 7.57-7.55 (d, *J* = 8.3 Hz, 8H), 7.50-7.47 (m, 4H), 7.37-7.35 (d, *J* = 8.3 Hz, 8H), 1.43 (s, 36H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 151.26, 137.86, 137.22, 132.59, 131.19, 130.08, 129.68, 128.01, 127.27, 126.60, 126.43, 126.38, 125.70, 125.49, 125.05, 125.02, 124.79, 122.98, 34.87, 31.52. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{74}H_{64}F_6$, 1066.4912; found, 1066.4914.



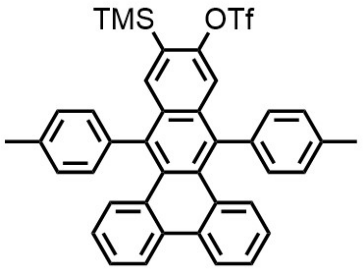
3d. This compound was synthesized according to procedure A outlined above using the following amounts: **2d** (0.150 g, 0.130 mmol), 2-($SiMe_3$)C_6H_4(OTf) (0.093 g, 0.312 mmol), TBAT (0.337 g, 0.625 mmol), DMAD (0.055 g, 0.390 mmol), benzene (5 mL). Eluent: 33% CH_2Cl_2 in hexanes. **3d** (0.121 g, 70%, 95% purity) was isolated as a pale-yellow powder. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.64 (s, 2H), 7.99-7.98 (m, 2H), 7.93-7.92 (m, 2H), 7.73-7.70 (d, *J* = 8.3 Hz, 4H), 7.67-7.65 (d, *J* = 8.3 Hz, 4H), 7.48-7.43 (*overlapped* m, 8H), 7.40-7.38 (d, J = 8.27 Hz, 4H), 7.34-7.32 (m, 2H) 7.14-7.10 (m, 2H), 7.02-7.00 (m, 2H), 6.86-6.82 (m, 2H), 1.50 (s, 18H), 1.40 (s, 18H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 150.73, 139.38, 138.56, 135.60, 135.19, 135.17, 135.15, 132.84, 132.49, 132.37, 132.07, 131.72, 130.98, 130.74, 130.55, 130.17, 129.53, 129.03, 128.23, 127.06, 126.97, 126.55, 126.53, 126.48, 125.89, 125.65, 125.61, 125.52, 124.44, 31.83, 31.62. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{78}H_{70}$, 1006.5478; found, 1006.5480.



3e. This compound was synthesized according to procedure B outlined above using the following amounts: **2e** (0.200 g, 0.136 mmol), 1,2-dibromobenzene (0.114 g, 0.489 mmol), nBuLi (1.00 M in hexanes, 0.476 mL, 0.476 mmol), benzene (2 mL). Eluent: 35% CH_2Cl_2 in hexanes. **3e** (0.094 g, 55%, 92% purity) was isolated as a yellow powder. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.08 (s, 2H), 10.00 (s, 2H), 9.02 (s, 2H), 8.97 (s, 2H), 8.93-8.91 (m, 2H), 8.35-8.32 (m, 4H), 8.31-8.28 (m, 2H), 8.11-8.09 (m, 2H), 7.66-7.60 (*overlapped* m, 8H), 7.57-7.55 (m, 2H), 4.21 (s, 6H), 4.19 (s, 6H), 3.90-3.80 (*overlapped* m, 12H), 2.30-2.23 (*overlapped* m, 8H), 1.96 (b, 4H), 1.29-1.26 (m, 6H), 1.24-1.22 (m, 6H), 1.08-1.05 (m, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 144.37, 144.30, 132.81, 132.69, 132.54, 132.43, 132.42, 132.31, 132.23, 131.98, 131.56, 130.91, 130.87, 130.57, 130.42, 130.35, 130.10, 128.66, 128.38, 128.28, 127.86, 127.64, 126.78, 125.99, 125.94, 125.89, 125.58, 125.50, 125.47, 124.06, 123.82, 123.63, 118.17, 117.72, 61.13, 61.13, 34.38, 34.34, 34.26, 25.49, 25.21, 25.16, 14.82, 14.77, 14.70. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{92}H_{82}O_4$, 1250.6213; found, 1250.6212.

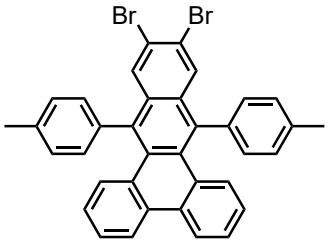


PAH 4. This compound was synthesized according to procedure A outlined above using the following amounts: **2a** (0.100 g, 0.188 mmol), 2-($SiMe_3$)-3-(OTf)naphthalene (0.079 g, 0.226 mmol), TBAT (0.335 g, 0.621 mmol), DMAD (0.080 g, 0.564 mmol), benzene (6 mL). Eluent: 10% CH_2Cl_2 in hexanes. **4** (0.073 g, 76%, ≥98% purity) was isolated as a bright yellow powder**.** **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.53 (s, 2H), 8.21-8.19 (m, 2H), 7.93-7.91 (m, 2H), 7.56-7.52 (m, 4H), 7.50-7.48 (*overlapped* m, 4H), 7.44-7.42 (m, 2H), 7.41-7.39 (m, 4H), 7.35-7.32 (m, 2H), 7.00-6.97 (m, *2H*), 2.56 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.80, 137.62, 135.34, 135.06, 132.86, 132.43, 132.04, 131.54, 130.86, 130.02, 128.54, 127.84, 127.05, 126.08, 125.79, 125.51, 123.53, 21.63. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{40}H_{28}$, 508.2191; found, 508.2190.

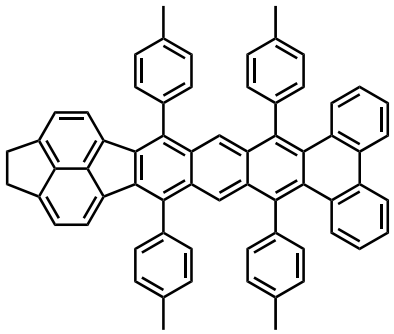


PAH 8. This compound was synthesized according to procedure A outlined above using the following amounts: **2a** (0.150 g, 0.130 mmol), 2,5-($SiMe_3$)-1,4-(OTf)C_6H_4 (0.093 g, 0.312 mmol)*, TBAT (0.337 g, 0.625 mmol), DMAD (0.055 g, 0.390 mmol), benzene (5 mL). Eluent: 33% CH_2Cl_2 in hexanes. **8** (0.132 g, 76%)* was isolated as a pale-yellow powder. **^{1}H NMR (600 MHz, C_6D_6):** δ 8.28 (dd, *J* = 8.0 Hz, 2H), 8.17 (s, 1H), 7.88 (s, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 7.1 Hz, 2H), 7.43-7.31 (m, 11H), 7.28-7.24 (m, 4H), 7.02 (t, *J* = 7.7 Hz, 2H), 2.51 (s, 3H), 2.50 (s, 3H), 0.34 (s, 9H). **^{13}C NMR (151 MHz, C_6D_6):** δ 152.8, 138.0, 137.9, 137.8, 137.7, 137.2, 135.6, 135.5, 135.4, 135.3, 133.0, 132.4, 132.3, 132.1, 131.3, 131.1, 130.9, 130.7, 130.6, 130.5, 130.2, 130.04, 130.02, 129.93, 129.88, 127.8, 127.4, 127.2, 126.09, 126.06, 123.49, 123.46, 118.6 (q, $J_{C,F}$ = 320.5 Hz, CF3), 116.0, 21.6, 21.6, -0.6. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{40}H_{33}F_3O_3SSi$, 678.1872; found, 678.1875.

*NOTE: use of a larger excess of 2,5-($SiMe_3$)-1,4-(OTf)C_6H_4 (0.169 g, 0.567 mmol) while keeping all other parameters constant moderately improved the yield of **8** (0.147 g, 85%).



PAH 9. A flask was charged with **2a** (0.250 g, 0.470 mmol, 1.00 equiv), 1,2,4,5-tetrabromobenzene (0.370 g, 0.940 mmol, 2.00 equivs), and benzene (5 mL) and stirred vigorously until all components were fully dissolved. To this solution was added *n*-butyllithium (1.00 M in hexanes, 0.517 mL, 0.517 mmol, 1.1 equivs) dropwise over 15 min. The reaction mixture was quenched with aqueous ammonium chloride, extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated to dryness via rotary evaporation. The excess 1,2,4,5-tetrabromobenzene was removed from the crude product by sublimation *in vacuo*. The remaining crude product was dissolved in CH_2Cl_2 (5 mL) and precipitated from solution by the addition of MeOH (15 mL). The precipitate was collected on a fritted funnel to afford **3a** (0.191 g, 66%) as a light peach-colored powder. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26-8.24 (d, *J* = 8.5 Hz, 2H), 8.20 (s, 2H), 7.51-7.49 (d, *J* = 8.5 Hz, 2H), 7.37-7.35 (*overlapped* m, 10H), 7.01-7.00 (m, 2H), 2.50 (s, 6H). **^{13}C NMR (151 MHz, C_6D_6)** δ 138.03, 137.96, 134.82, 132.72, 132.69, 132.43, 131.82, 131.64, 131.03, 130.97, 130.36, 128.22, 128.06, 127.90, 127.66, 126.37, 123.92, 122.75, 21.28. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{36}H_{24}Br_2$, 678.1872; found, 678.1875.

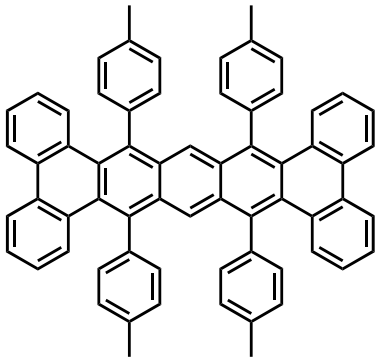


PAH 10.

*From **8**:* A teflon stoppered flask was charged with **2b** (0.053 g, 0.100 mmol, 1.00 equiv), **8** (0.075 g, 0.110 mmol, 1.1 equivs), TBAT (0.178 g, 0.330 mmol, 3.30 equivs), DMAD (0.021 g, 0.150 mmol, 1.50 equivs), benzene (2 mL). The flask was sealed and heated to 60 ˚C for 24 h. The reaction mixture was cooled to RT and concentrated via rotary evaporation. The crude solid was purified by preparatory thin layer chromatography (25% CH_2Cl_2 in hexanes) to afford **10** (0.060 g, 72%, 90% purity) was isolated as an orange powder.

*From **9**:* A flask was charged with **2b** (0.053 g, 0.100 mmol, 1.00 equiv), **9** (0.074 g, 0.120 mmol, 1.20 equivs), and benzene (1 mL) and stirred vigorously until all components were fully dissolved. To this solution was added *n*-butyllithium (1.00 M in hexanes, 0.120 mL, 0.120 mmol, 1.20 equivs) dropwise over 15 min. The reaction mixture was quenched with aqueous ammonium chloride, extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated to dryness via rotary evaporation. The crude product was purified by preparatory thin layer chromatography (25% CH_2Cl_2 in hexanes) to afford **3a** (0.050 g, 60%) as an orange powder.

^{1}H NMR (400 MHz, C_6D_6) δ 9.59 (s, 2H), 9.44 (s, 2H), 9.01 (s, 2H), 8.92 (s, 2H), 8.25-8.22 (m, 2H), 7.94-7.92 (m, 2H), 7.38-7.34 (m, 2H), 7.32-7.28 (m, 2H), 3.96 (s, 6H), 3.93 (s, 6H), 3.43-3.39 (m, 4H), 3.37-3.33 (m, 4H), 3.03-2.99 (m, 4H), 1.73-1.66 (m, 8H), 1.58-1.53 (m, 2H), 1.04-0.99 (m, 12H), 0.91-0.87 (m, 6H), 0.51 (s, 6H), 0.48 (s, 12H). **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{66}H_{46}$, 838.3600; found, 838.3603.

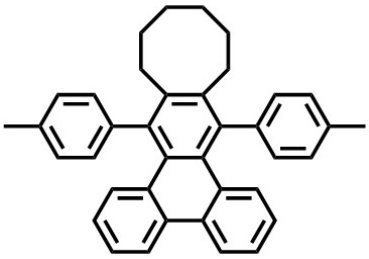


PAH 11. A flask was charged with **2a** (0.250 g, 0.470 mmol, 1.00 equiv), 1,2,4,5-tetrabromobenzene (0.093 g, 0.235 mmol, 0.50 equivs), and benzene (5 mL) and stirred vigorously until all components were fully dissolved. To this solution was added *n*-butyllithium (1.00 M in

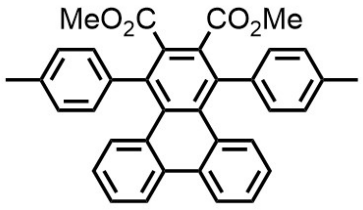
hexanes, 0.517 mL, 0.517 mmol, 1.1 equivs) dropwise over 15 min. Over the course of the reaction a bright orange crystalline solid precipitated from the reaction mixture. Upon completion, the precipitate was collected on a fritted funnel and washed with THF (5x5 mL) to afford **11** (0.078 g, 40%) as a bright orange crystalline solid. **Anal. Calcd for $C_{66}H_{46}$:** C, 94.5; H, 5.5. Found: C, 94.6; H, 5.4. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{66}H_{46}$, 838.3600; found, 838.3606.

Diels Alder cycloaddition with alkynes:

Procedure: A flask was charged with stannole **2a** (1.0 equiv), the desired alkyne (1.1 equivs), and toluene. The flask was sealed, and the stirred reaction mixture was heated to 100 ˚C for 24 h. The solution was cooled to RT and concentrated to dryness via rotary evaporation. The crude product was purified by column chromatography.

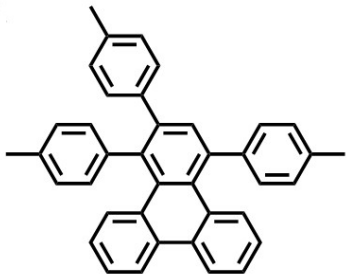


PAH 5. This compound was synthesized according to the procedure outlined above using the following amounts: **2a** (0.100 g, 0.188 mmol), cyclooctyne (0.022 g, 0.206 mmol), toluene (2 mL). Eluent: 5% CH_2Cl_2 in hexanes. **5** (0.085 g, 97%, ≥98% purity) was isolated as an off-white powder. **^{1}H NMR (600 MHz, C_6D_6):** δ 8.36 (dd, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 4H), 7.21 (d, *J* = 7.8 Hz, 4H), 7.02 (t, *J* = 7.8 Hz, 2H), 2.97-2.89 (m, 4H), 2.44 (s, 6H), 1.56 (br m, 4H), 1.48 (br m, 4H). **^{13}C NMR (151 MHz, C_6D_6):** δ 140.9, 139.8, 137.5, 136.4, 131.6, 131.30, 131.27, 130.4, 129.8, 129.3, 125.8, 125.3, 123.0, 31.8, 28.9, 26.0, 21.4. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{38}H_{34}$, 490.2661; found, 490.2662.

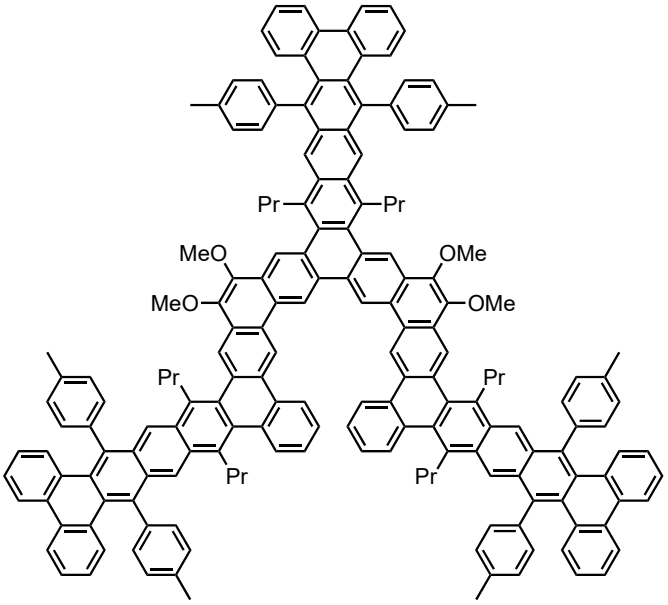


PAH 6. This compound was synthesized according to the procedure outlined above using the following amounts: **2a** (0.100 g, 0.188 mmol), dimethylacetylenedicarboxylate (0.029 g, 0.206 mmol), toluene (2 mL). Eluent: 30% CH_2Cl_2 in hexanes. **6** (0.088 g, 89%, 97% purity) was isolated as an off-white powder. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.40 (dd, *J* = 8.3, 0.7 Hz, 2H), 7.58 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.44 (dt, *J* = 7.5, 1.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 4H), 7.20 (d, *J* = 8.0 Hz, 4H), 7.06 (dt, *J* = 7.7, 1.2 Hz, 2H), 3.57 (s, 6H), 2.41 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ

169.6, 138.5, 137.8, 136.2, 132.9, 132.0, 131.4, 130.00, 129.97, 129.95, 127.5, 125.9, 123.3, 52.5, 21.5. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{36}H_{28}O_4$, 524.1988; found, 524.1985.



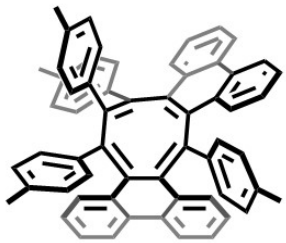
PAH 7. This compound was synthesized according to the procedure outlined above using the following amounts: **2a** (0.100 g, 0.188 mmol), 4-ethynyltoluene (0.024 g, 0.206 mmol), toluene (2 mL). Eluent: 10% CH_2Cl_2 in hexanes. **7** (0.039 g, 42%, 96% purity) was isolated as an off-white powder. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 8.41 (dd, *J* = 7.6, 3.7 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.61 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.43 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.40-7.36 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.10 (td, *J* = 7.6, 1.1 Hz, 1H), 7.03-6.94 (m, 9H), 2.42 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H). **^{13}C NMR (151 MHz, C_6D_6):** δ 141.7, 140.2, 139.2, 139.0, 138.0, 137.0, 136.5, 136.2, 135.8, 132.7, 132.1, 132.1, 131.7, 131.5, 131.2, 130.5, 130.2, 130.0, 129.92, 129.87, 129.8, 129.7, 129.3, 128.6, 126.6, 126.4, 125.6, 125.3, 123.3, 21.43, 21.39, 21.3. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{39}H_{30}$, 498.2348; found, 498.2346.



PAH 12. A flask was charged with stannole **2e** (0.060 g, 0.040 mmol, 1.00 equiv), **9** (0.083 g, 0.135 mmol, 3.30 equivs), and 1-chloronaphthalene (1 mL) and stirred vigorously until all components were dissolved. To this solution was added *n*-butyllithium (1.00 M in hexanes, 0.128 mL, 0.128 mmol, 3.20 equivs) dropwise over 15 min. To the reaction mixture was added 10 mL pentane, and the precipitate was collected on a fritted funnel and washed with pentane (3x3 mL).

The crude solid was purified by preparatory thin layer chromatography (35% DCM in Hexanes) to afford **12** (0.025 g, 27%) as a bright orange powder. **^{1}H NMR (600 MHz, C_6D_6)** δ 10.13 (s, 1H), 10.02 (s, 1H), 9.28 (d, *J* = 6.9 Hz, 2H), 9.20 (d, *J* = 3.3 Hz, 3H), 9.11 (s, 1H), 8.30 (d, *J* = 8.6 Hz, 1H), 8.20 – 8.01 (m, 18H), 7.56 (d, *J* = 8.1 Hz, 10H), 7.48 (d, *J* = 8.1 Hz, 3H), 7.36 (d, *J* = 8.3 Hz, 4H), 7.32 (d, *J* = 7.4 Hz, 4H), 7.29 (s, 11H), 7.27 – 7.23 (m, 6H), 6.93 – 6.88 (m, 3H), 3.85 (d, *J* = 3.4 Hz, 6H), 2.30 – 2.24 (m, 16H), 2.11 (s, 7H), 1.17 – 1.01 (m, 22H). **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{182}H_{142}O_4$, 2392.0942; found, 2392.0942*.

*NOTE: There is an additional small peak in the MALDI spectrum at 2426.1199 (Figure S54). This corresponds to **12** + 34 amu, which we tentatively attribute to the addition of oxygen across one tetrabenzopentacene unit and subsequent protonation under MALDI conditions. Due to the high light and oxygen sensitivity of the compound, we believe this occurs during spotting the sample and/or loading of the plate rather than as a function of an impurity present in the bulk material.



COT 13. A flask was charged with stannole **2b** (0.150 g, 0.282 mmol) and mesitylene (4 mL). The flask was sealed, and the stirred reaction mixture was heated to 160 ˚C for 72 h. The solution was cooled to RT and concentrated to dryness via rotary evaporator to afford **13** (0.105 g, 98%, ≥98% purity) as a pale-yellow solid. Single crystals suitable for x-ray diffraction were grown by slow evaporation of a saturated CH_2Cl_2/hexanes solution. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.80-8.77 (m, 2H), 8.64 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.86-7.83 (*overlapped* m, 2H), 7.80-7.78 (m, 1H), 7.56-7.55 (d, *J* = 8.3 Hz, 1H), 7.40-7.35 (*overlapped* m, 2H), 7.14-7.13 (*overlapped* m, 3H), 7.09-7.06 (*overlapped* m, 3H), 6.89-6.88 (d, *J* = 7.9 Hz, 2H), 6.84-6.82 (d, *J* = 8.2 Hz, 2H), 6.75-6.74 (d, *J* = 7.9 Hz, 2H), 6.67-6.65 (d, *J* = 8.1 Hz, 2H), 6.60-6.55 (m, 5H), 6.51 (m, 2H), 6.10-6.09 (d, *J* = 7.5 Hz, 1H), 2.22 (s, 3H), 2.14 (s, 6H), 2.13 (s, 6H), 2.04 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 143.35, 141.44, 140.33, 139.04, 138.08, 137.98, 137.33, 137.24, 136.85, 136.26, 136.23, 136.20, 136.12, 136.02, 135.78, 135.45, 135.36, 134.86, 134.31, 131.76, 131.72, 131.07, 130.78, 130.73, 130.68, 130.43, 130.35, 130.12, 128.80, 128.56, 128.52, 128.49, 128.45, 128.12, 128.07, 127.96, 127.51, 127.47, 126.96, 126.86, 126.73, 126.64, 126.45, 126.42, 126.38, 125.73, 124.14, 123.36, 122.90, 122.33, 21.32, 21.25, 21.23, 21.18. **HRMS–EI (m/z):** $[M]^+$ calcd for $C_{60}H_{44}$, 764.3443; found, 764.3444.

General Considerations for Reproducible Stannole Synthesis

We have found that several reaction parameters are particularly important to ensure reproducible results for the generation of stannoles and their subsequent cycloadditions which are highlighted here.

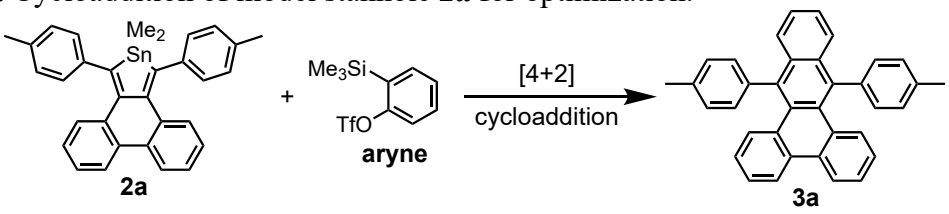
Due to the heterogeneous nature of the reaction, vigorous, efficient stirring is absolutely necessary to ensure reliable results from stannole generation. The reaction vessel used to run these reactions should be ~5x the volume of solvent and the stir bar should be an appropriate size for the reaction vessel, resulting in a powerful vortex that evenly disperses the insoluble components. It is important that stirring remain strong for the duration of the reaction.

Commercial CuCl can contain a wide range of impurities that may adversely impact the reaction. While some batches appeared to work appropriately as-received, others gave significantly decreased yields, and in some cases no product formation at all. Notably, during the synthesis of stannole **2a**, impure CuCl appears to mediate the formation of COT **13** as a major side product. To avoid this issue, commercial CuCl was recrystallized by dissolution in concentrated HCl and precipitation by addition of deionized H_2O. It was subsequently filtered, washed with ethanol followed by diethyl ether, dried under vacuum at 200 ˚C overnight, and stored in a glovebox.

Optimization of [4+2] Cycloaddition with *o*-$SiMe_3$-OTf arenes

Optimization of cycloaddition conditions was carried out using model system **2a** and 2-$(SiMe_3)C_6H_4(OTf)$. Stannole **2a** was held at a constant concentration of 18.8 mM and equivalents of other reagents are stated in reference to this. All reactions were run for 24 h. All yields were determined *in-situ* via ^{1}H NMR spectroscopy using dimethyl sulfone as an internal standard.

Scheme S1. Cycloaddition of model stannole **2a** for optimization.



Aryne equivs	F⁻ Source	F⁻ equivs	Stannylene Trap	Trap equivs	Solvent	Temperature (˚C)	Yield (%)
1	TBAT	1.1	none	-	THF	23	71
1	TBAT	3	none	-	THF	23	73
1.1	TBAT	3.3	none	-	THF	23	76
1.1	TBAT	3.3	none	-	DCM	23	15
1.1	TBAT	3.3	none	-	Toluene	60	78
1.1	CsF	3.3	none	-	THF	50	37
1.1	TMAF	3.3	none	-	THF	23	52
1.1	KF/NBu_4Cl	3.3	none	-	THF	23	4

1.1	**TBAT**	**3.3**	**DMAD**	**1.5**	**Toluene**	**60**	**88**
1.1	TBAT	3.3	DMAD	3	Toluene	60	87
1.1	TBAT	3.3	DMAD	5	Toluene	60	84
1.1	TBAT	3.3	diphenyldisulfide	3	Toluene	60	78
1.1	TBAT	3.3	butylbromide	10	Toluene	60	76
1.1	TBAT	3.3	diacetyl	3	Toluene	60	76

Table S1. Optimization of [4+2] cycloaddition of **2a** with *o*-$SiMe_3$-OTf arenes.

^{1}H and $^{13}C\{^{1}H\}$NMR spectra

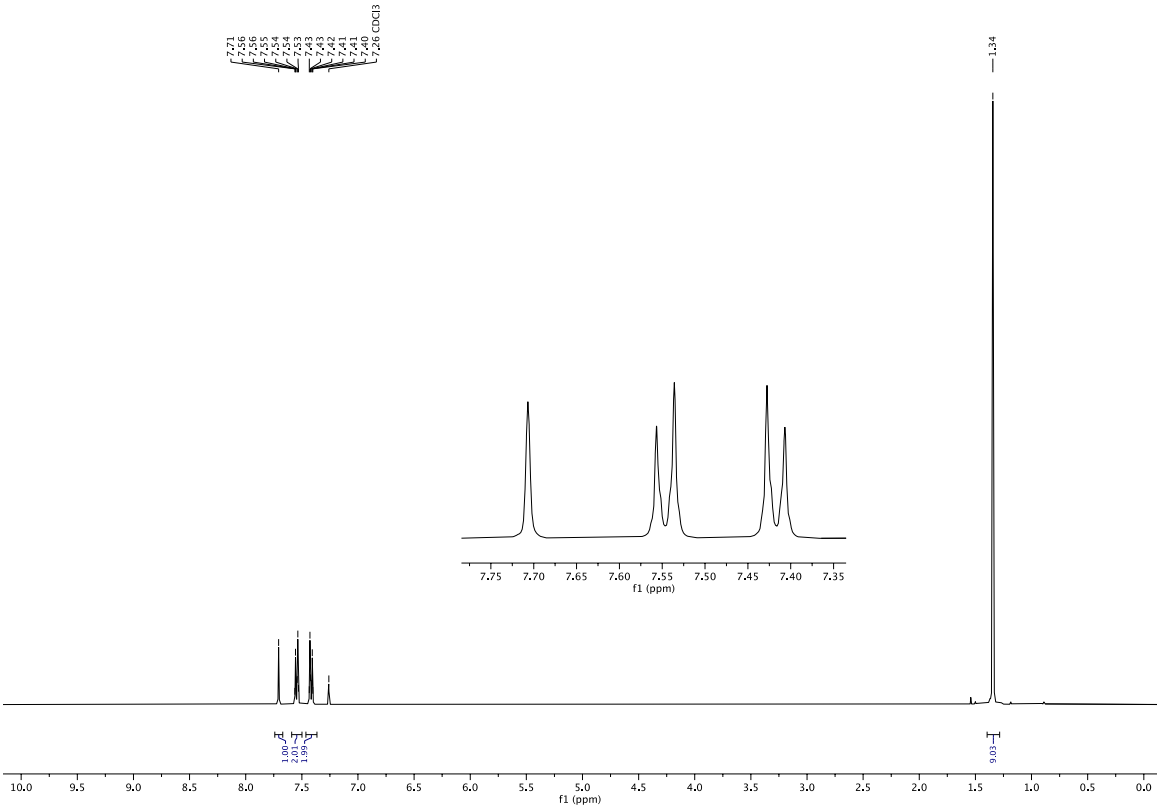


Figure S1. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **S2**.

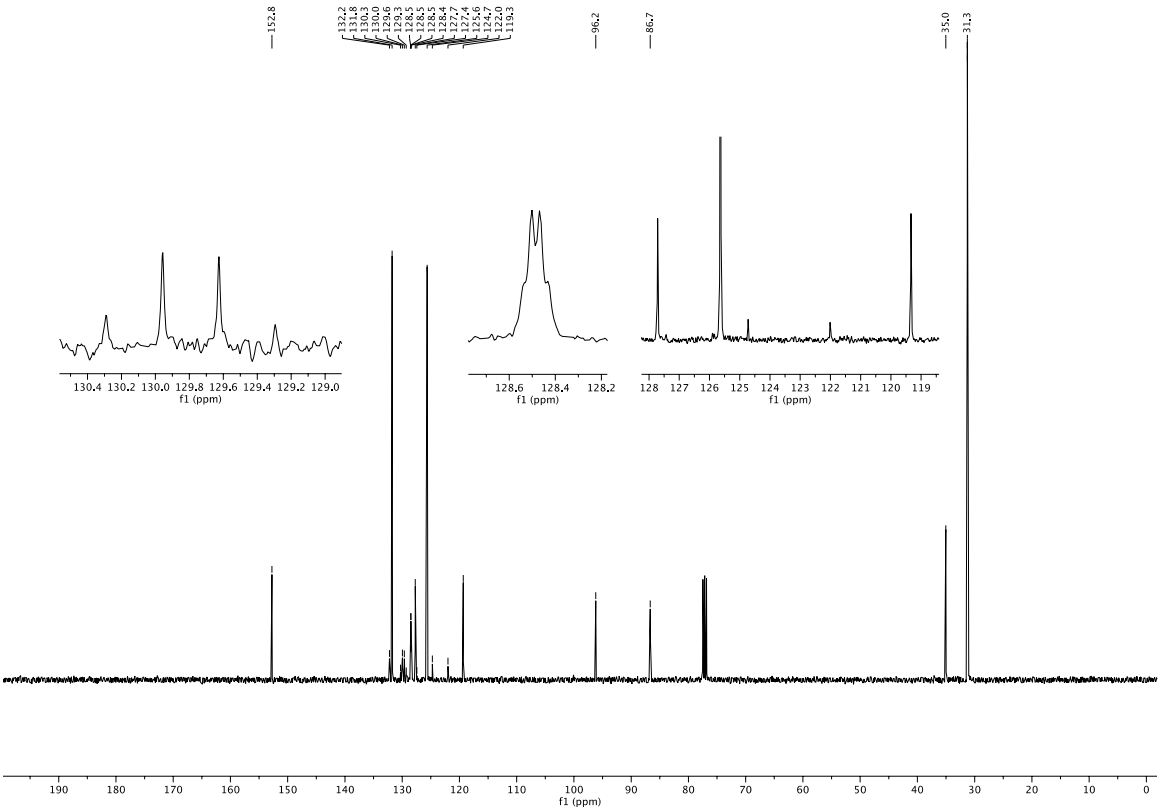


Figure S2. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, $CDCl_3$) of **S2**.

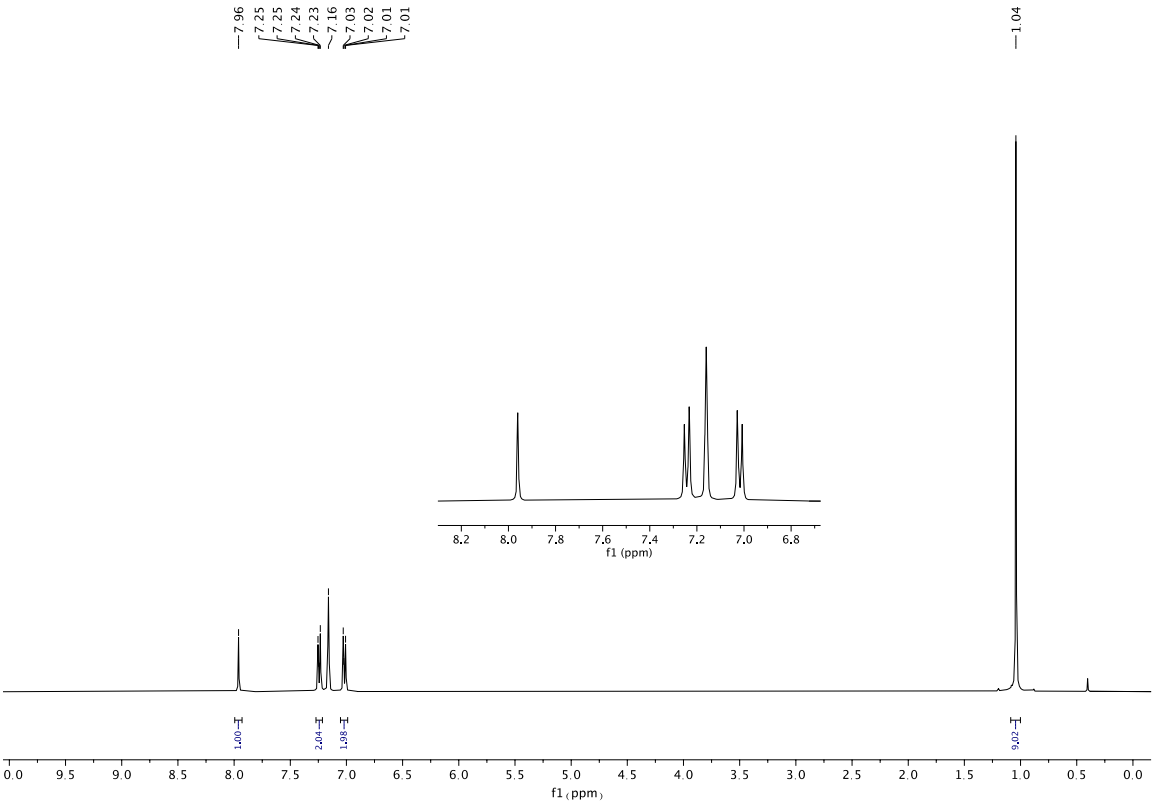


Figure S3. ^{1}H NMR Spectrum (400 MHz, C_6D_6) of **1c**.

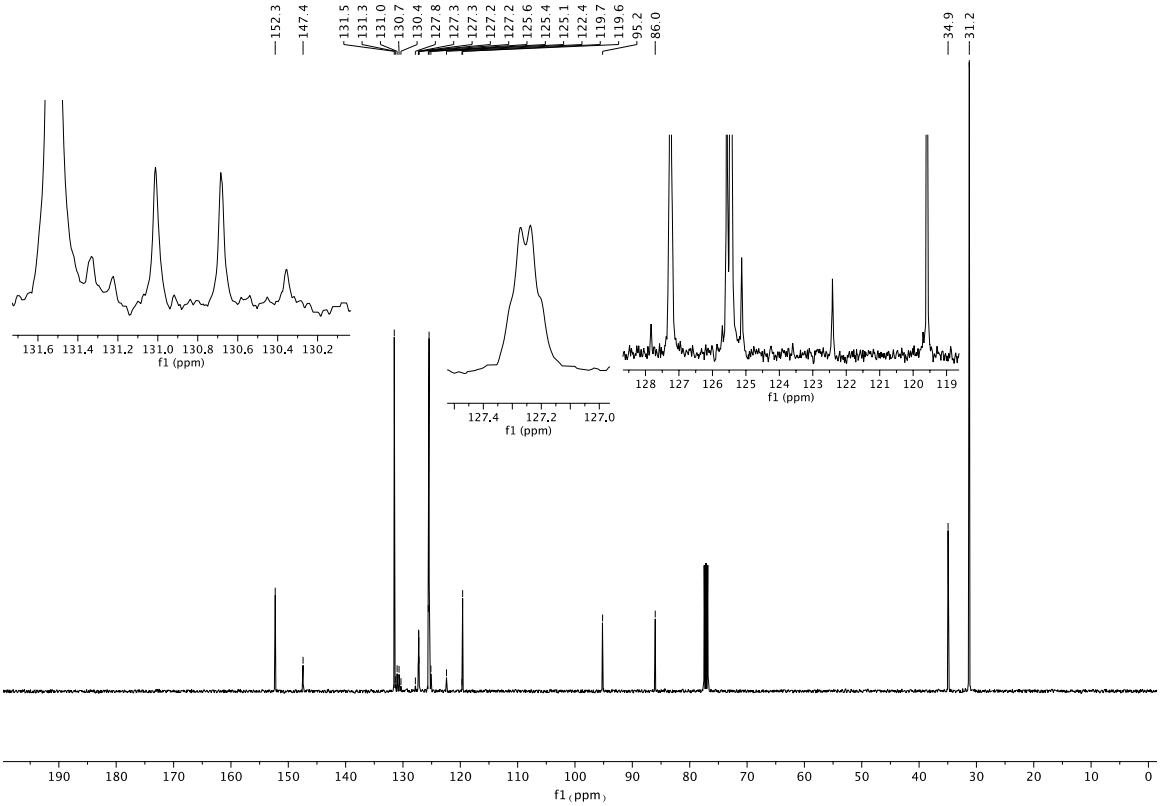


Figure S4. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-d) of **1c**.

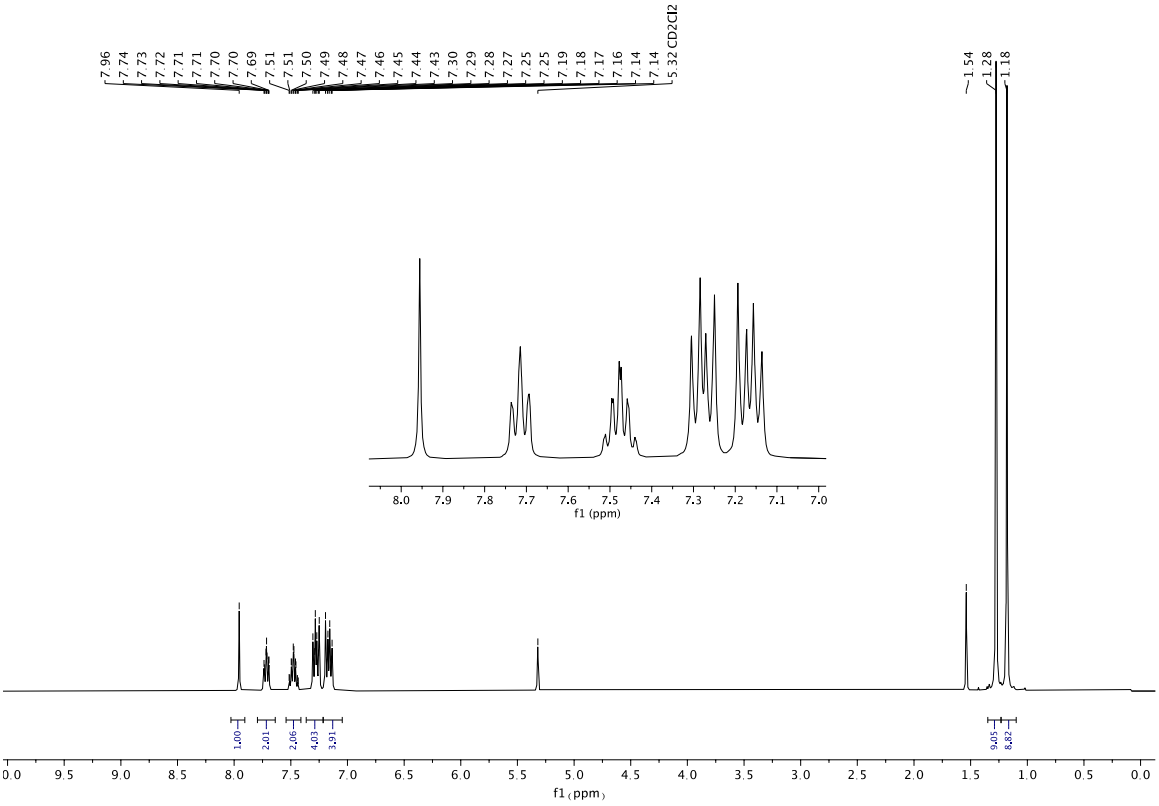


Figure S5. ^{1}H NMR Spectrum (400 MHz, CH_2Cl_2) of **1d**.

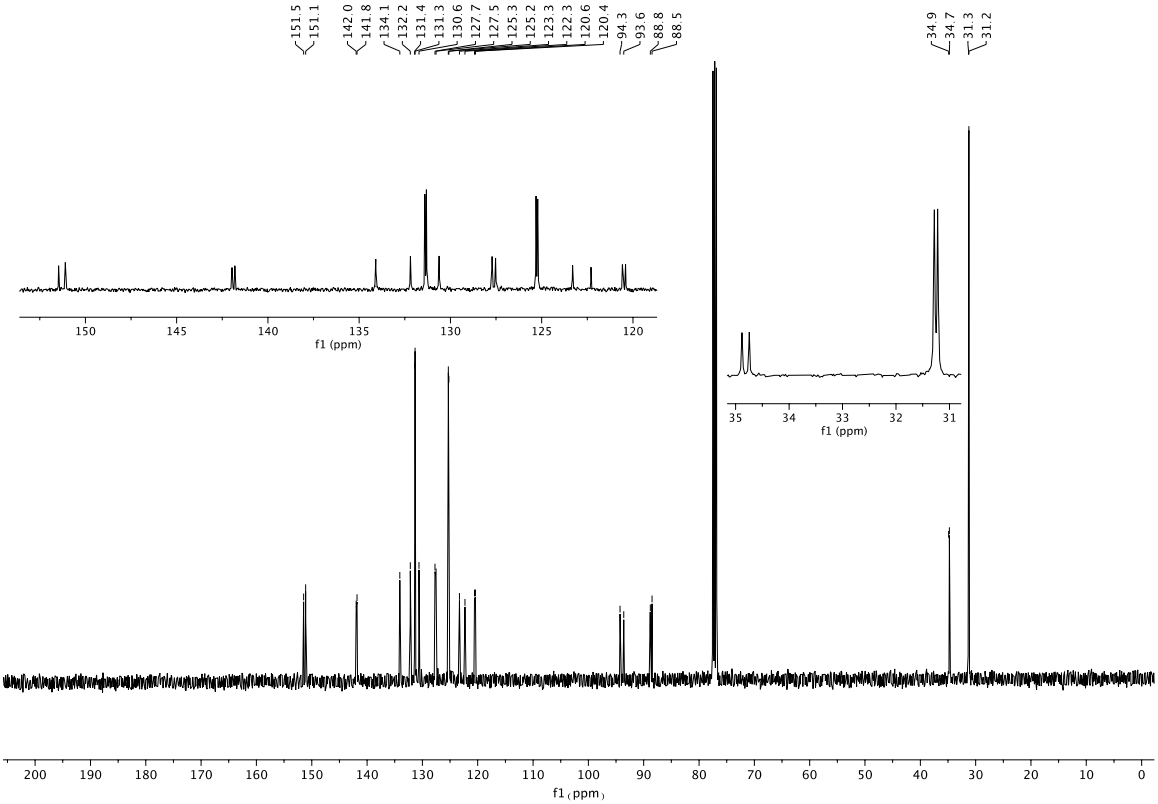


Figure S6. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, $CDCl_3$) of **1d**.

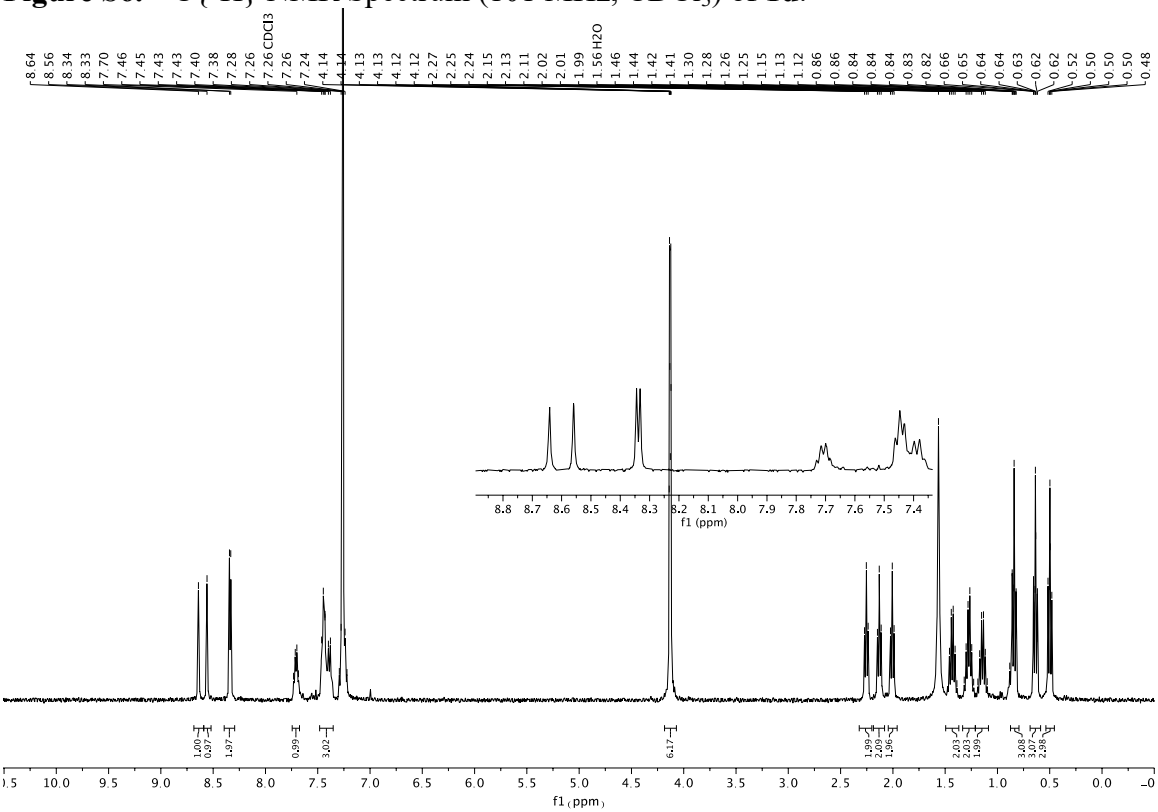


Figure S7. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **1e**.

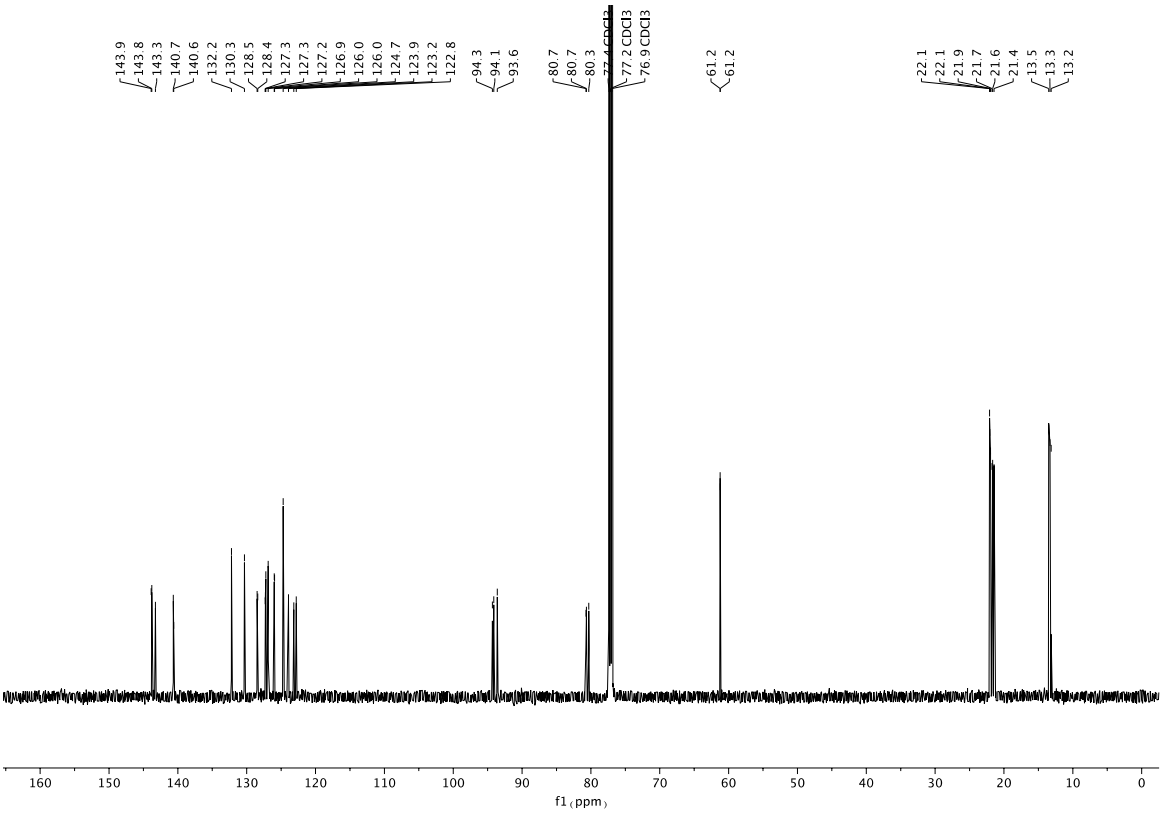


Figure S8. ^{13}C NMR Spectrum (500 MHz, $CDCl_3$) of **1e**.

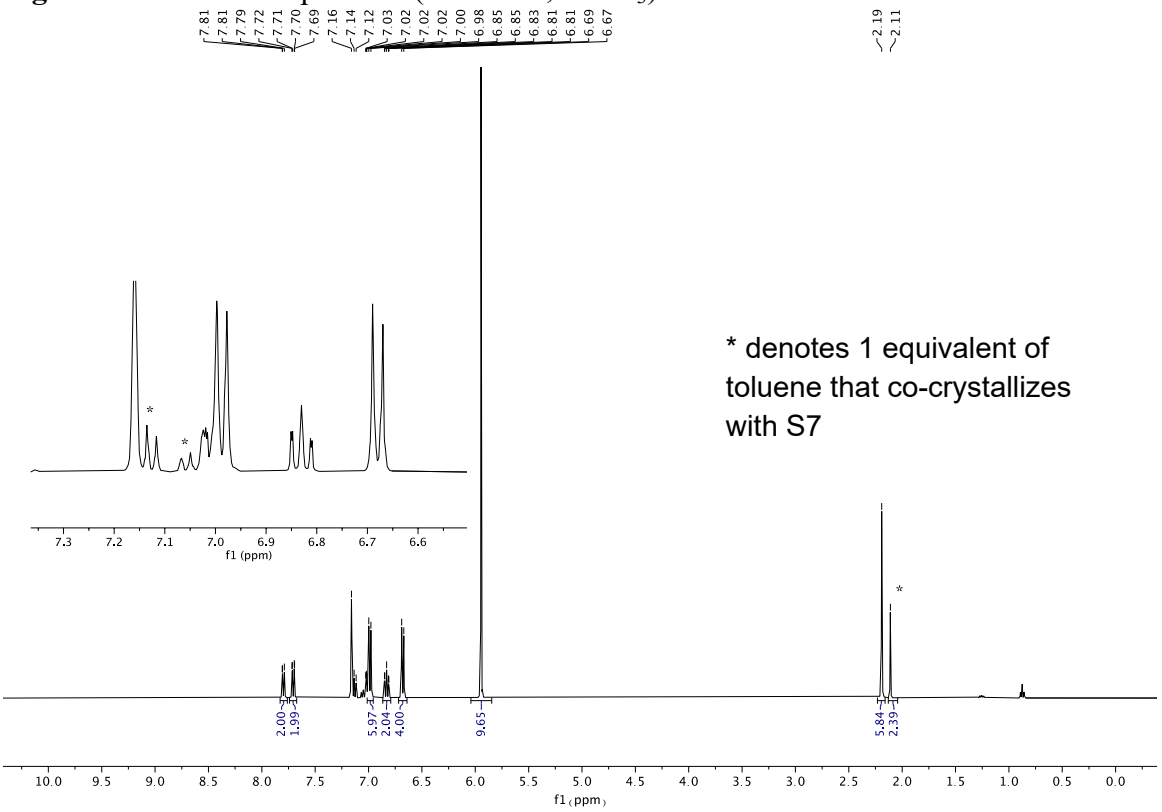


Figure S9. ^{1}H NMR Spectrum (600 MHz, C_6D_6) of **S7**.

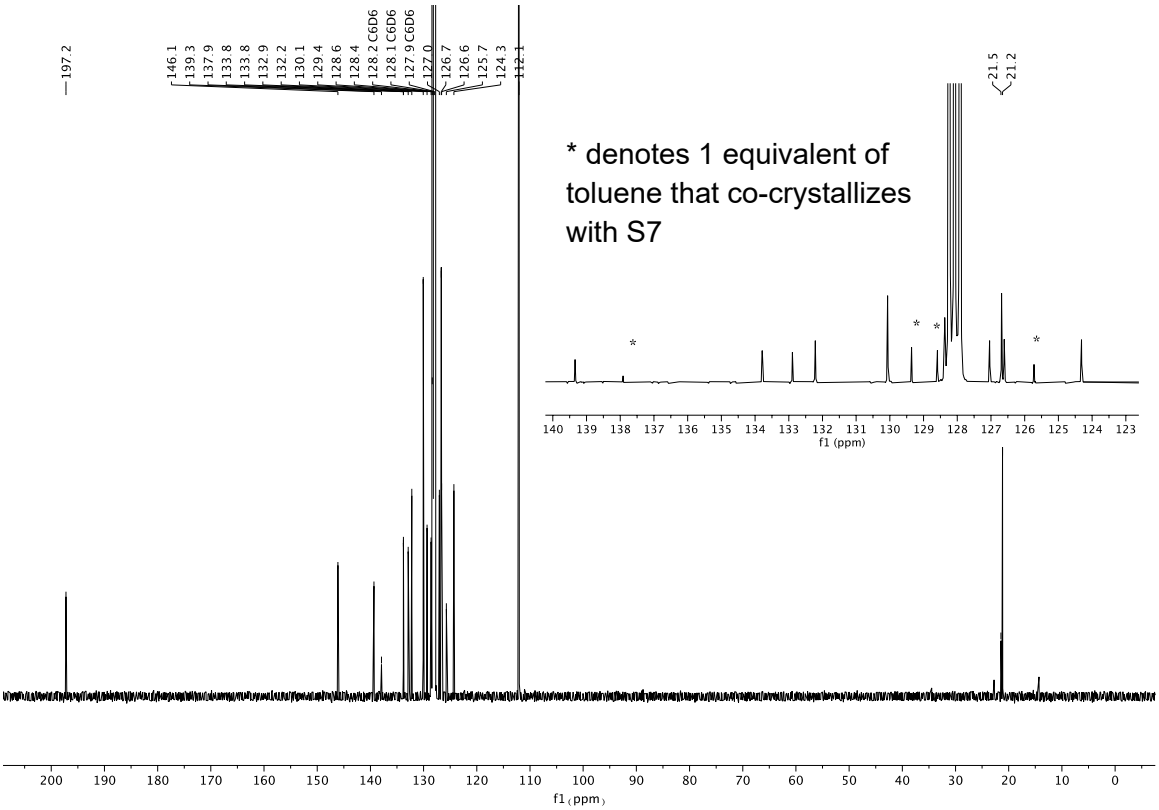


Figure S10. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, C_6D_6) of **S7**.

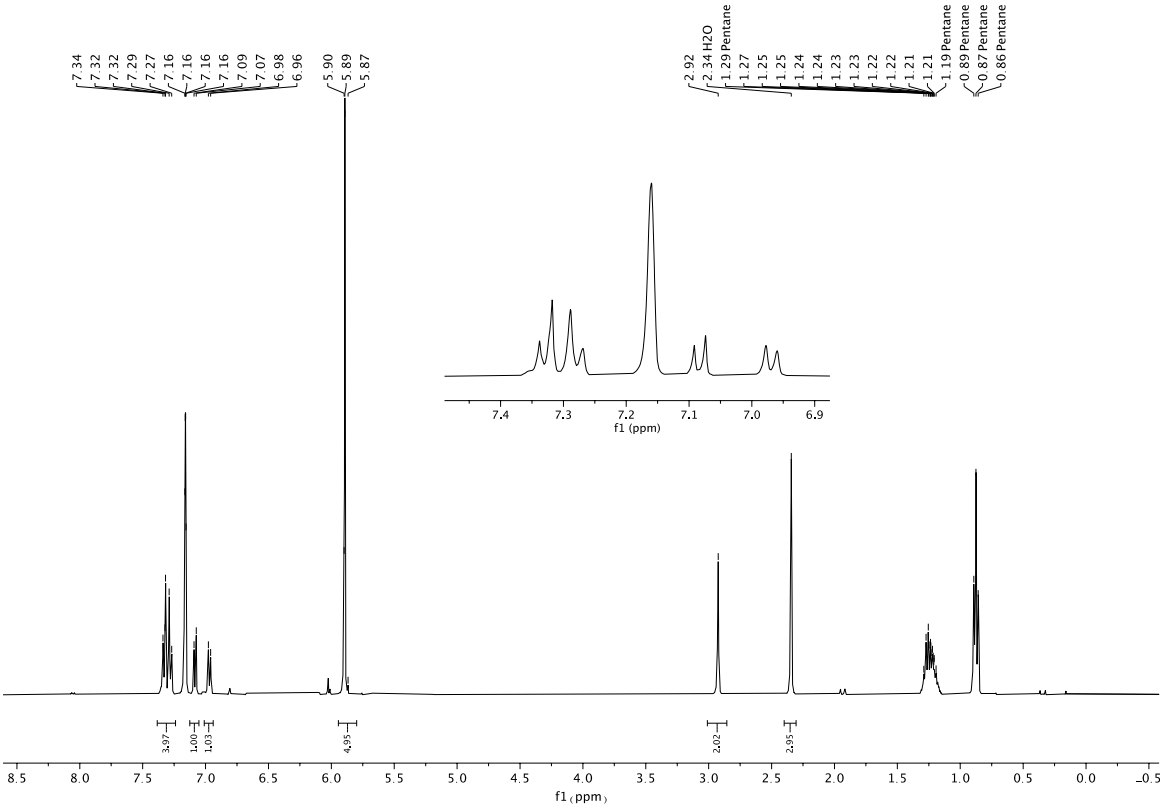


Figure S11. ^{1}H NMR Spectrum (400 MHz, C_6D_6) of **S8**.

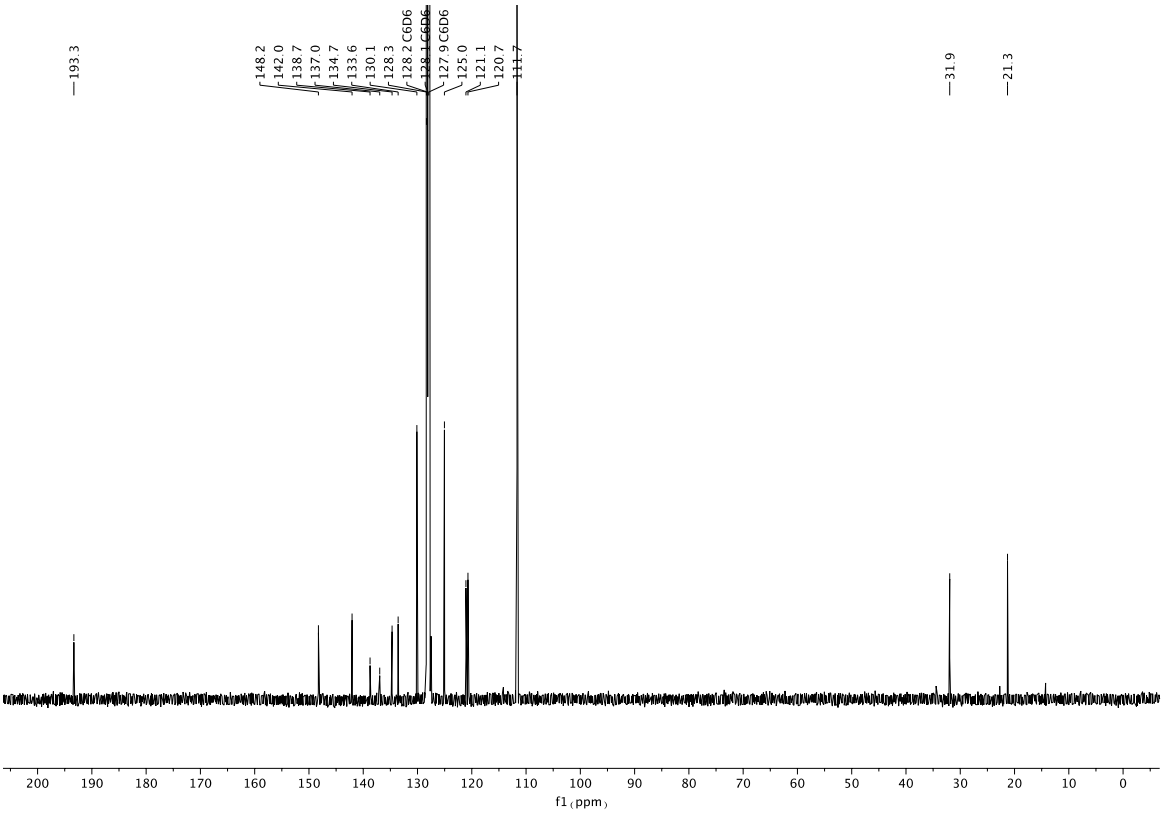


Figure S12. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, C_6D_6) of **S8**.

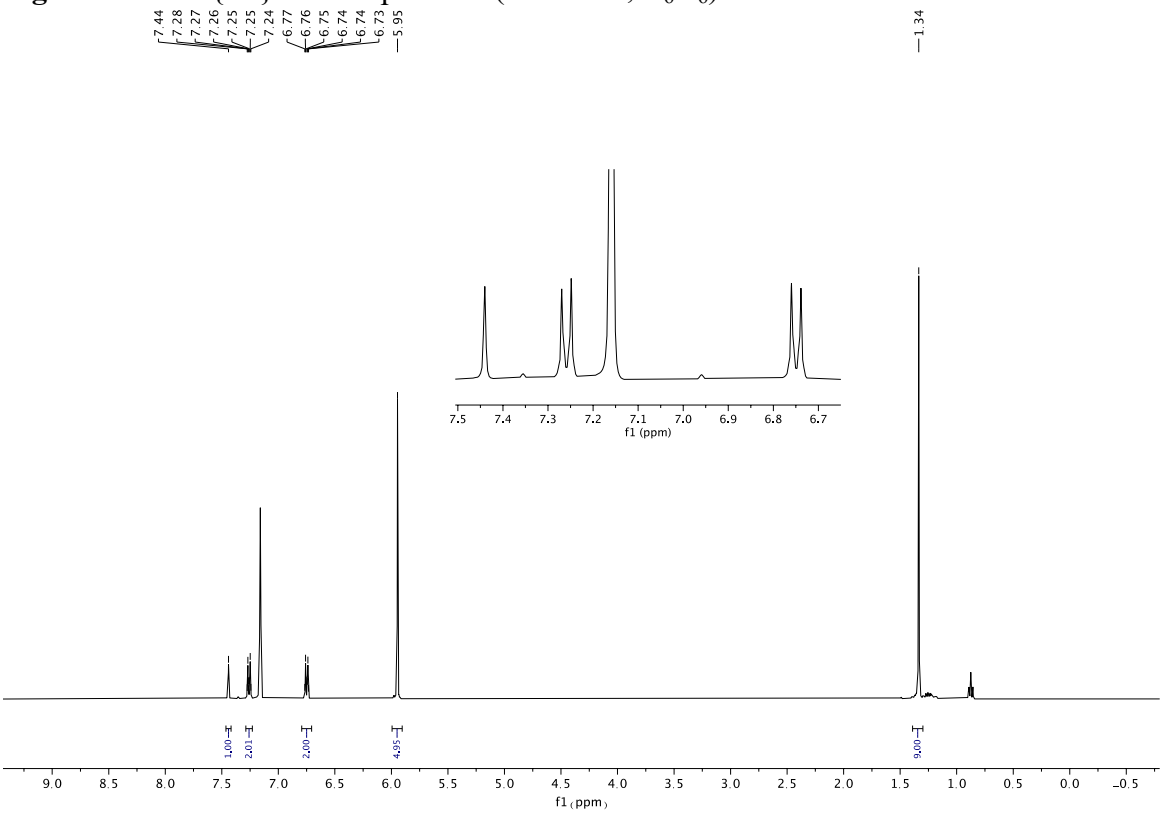


Figure S13. ^{1}H NMR Spectrum (600 MHz, C_6D_6) of **S9**.

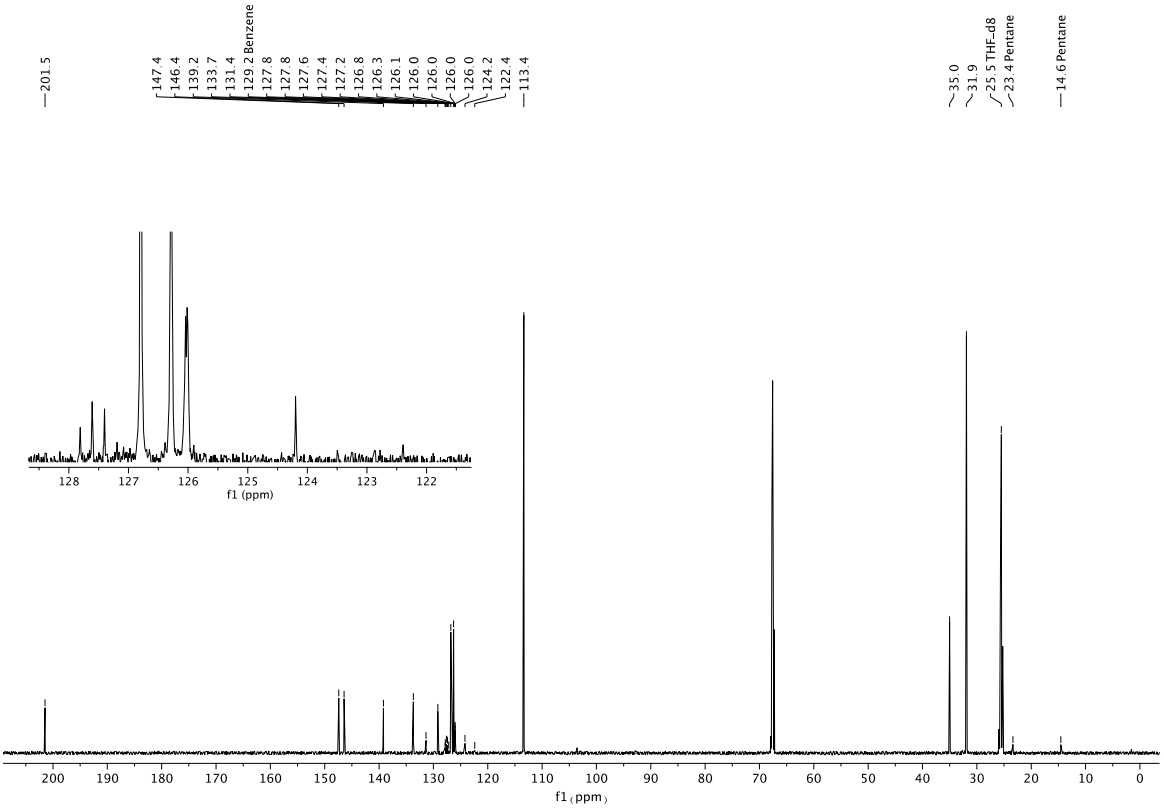


Figure S14. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, THF-*d8*) of **S9**.

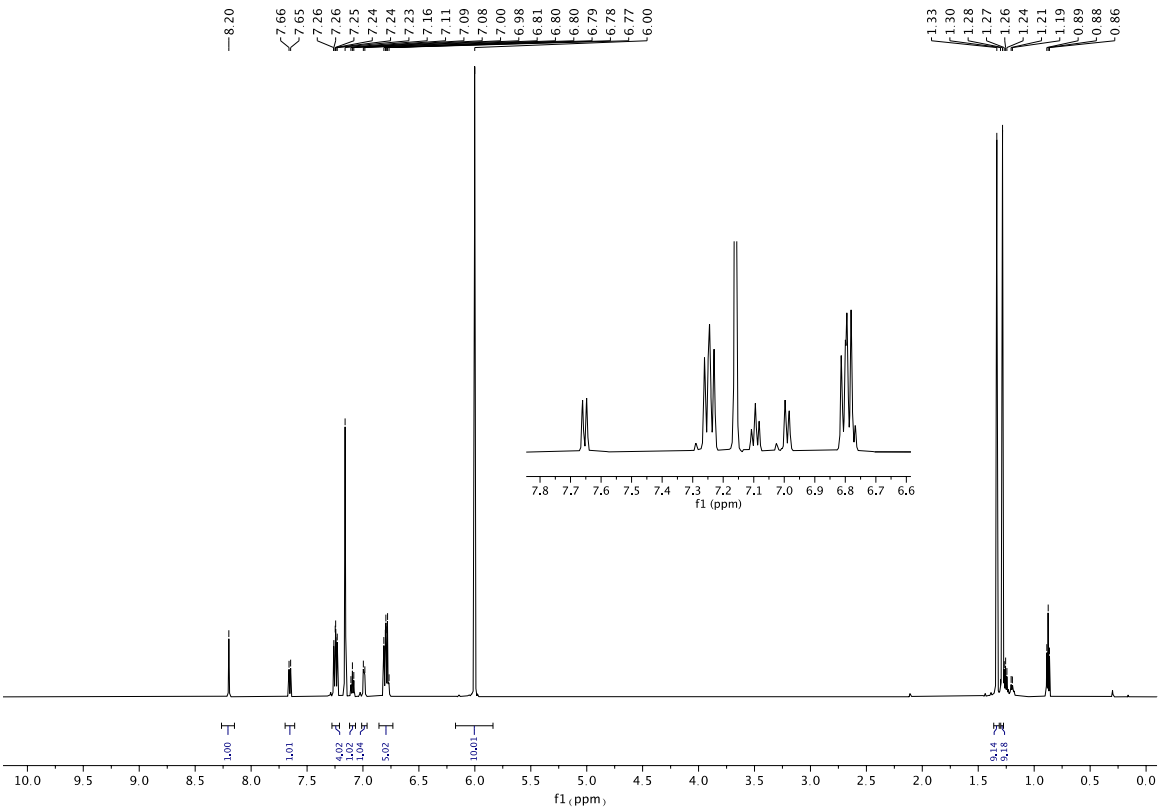


Figure S15. ^{1}H NMR Spectrum (600 MHz, C_6D_6) of **S10**.

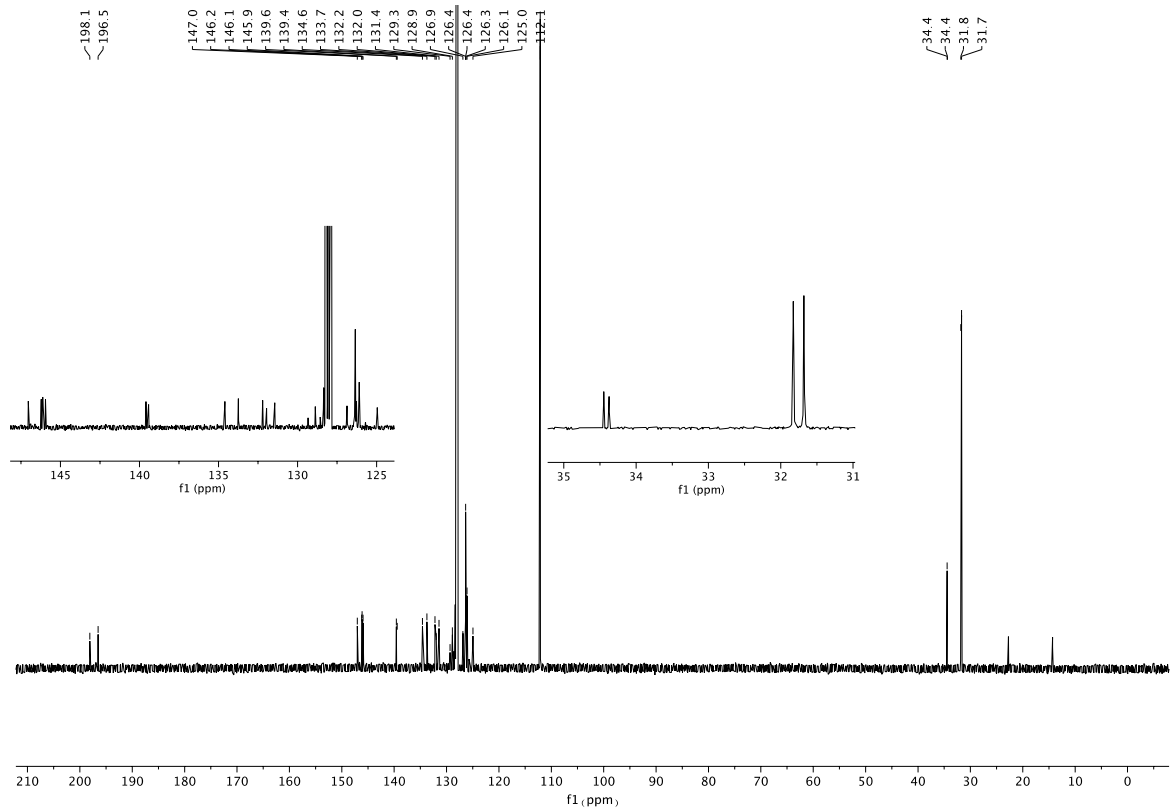


Figure S16. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, C_6D_6) of **S10**.

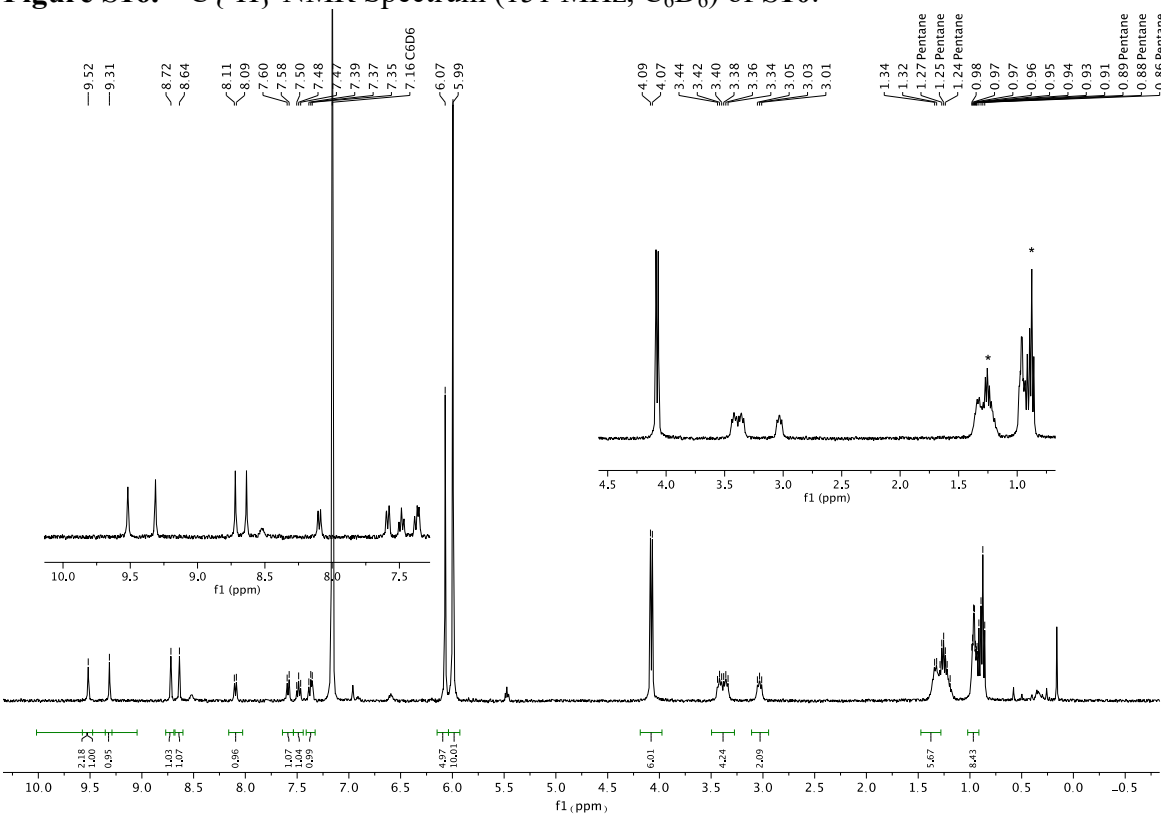


Figure S17. ^{1}H NMR Spectrum (400 MHz, C_6D_6) of **S11**.

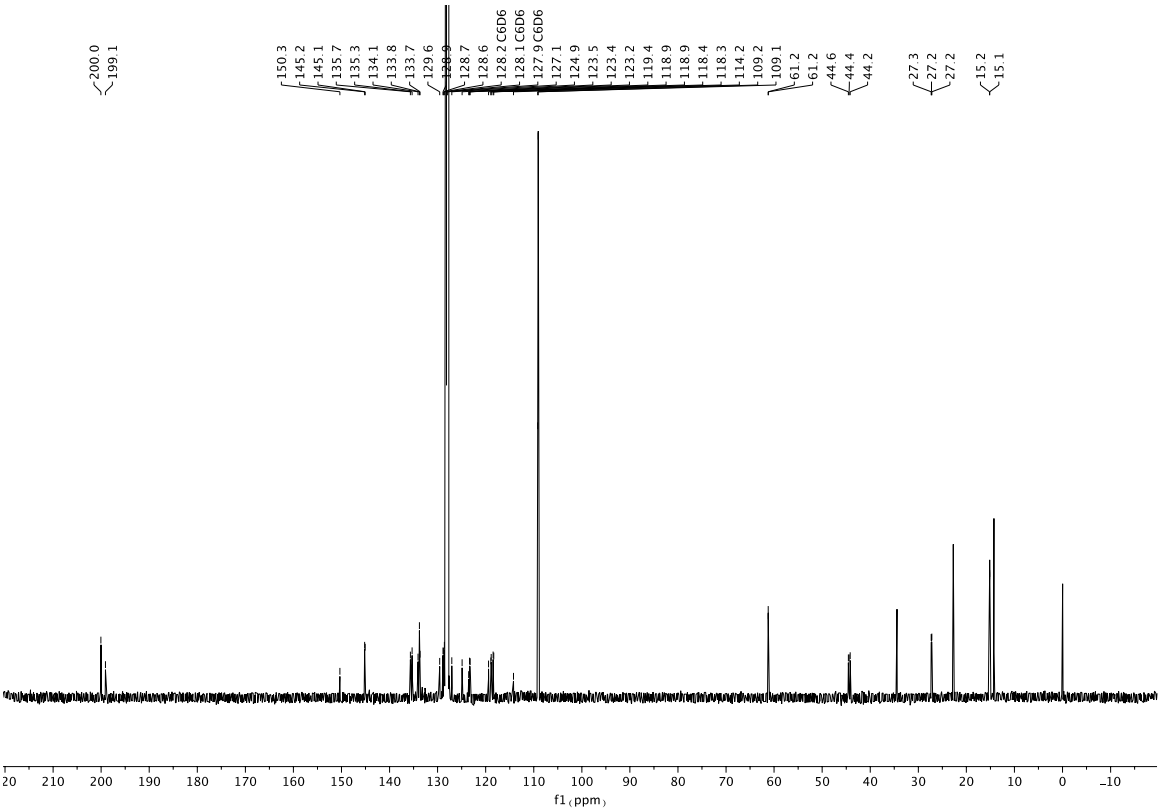


Figure S18. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, C_6D_6) of **S11**.

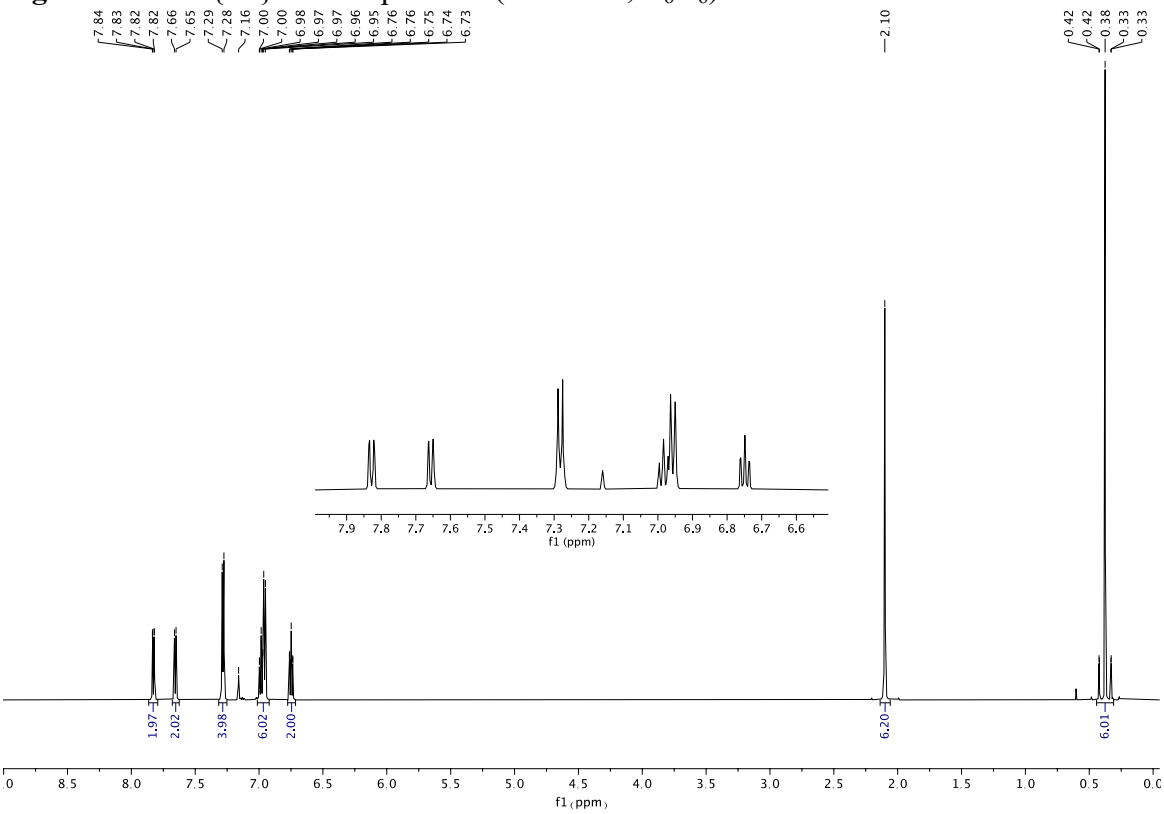


Figure S19. ^{1}H NMR Spectrum (600 MHz, C_6D_6) of **2a**.

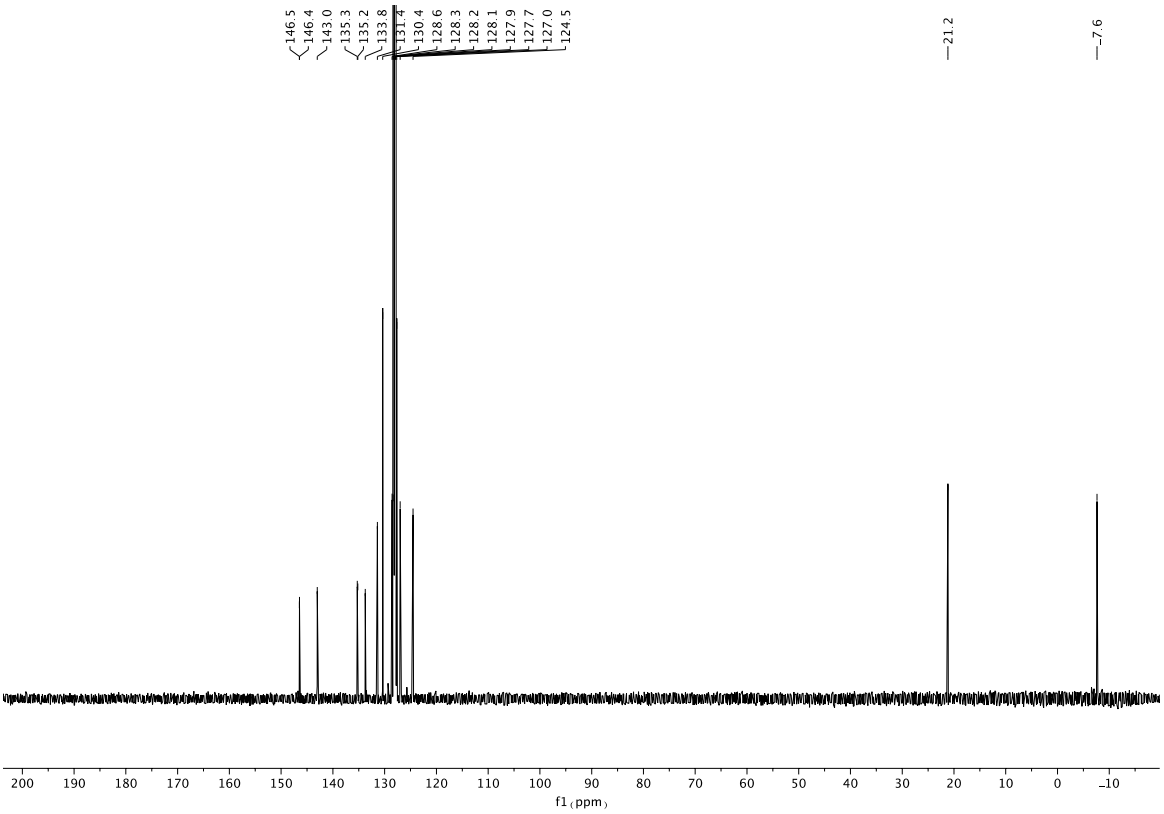


Figure S20. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, C_6D_6) of **2a**.

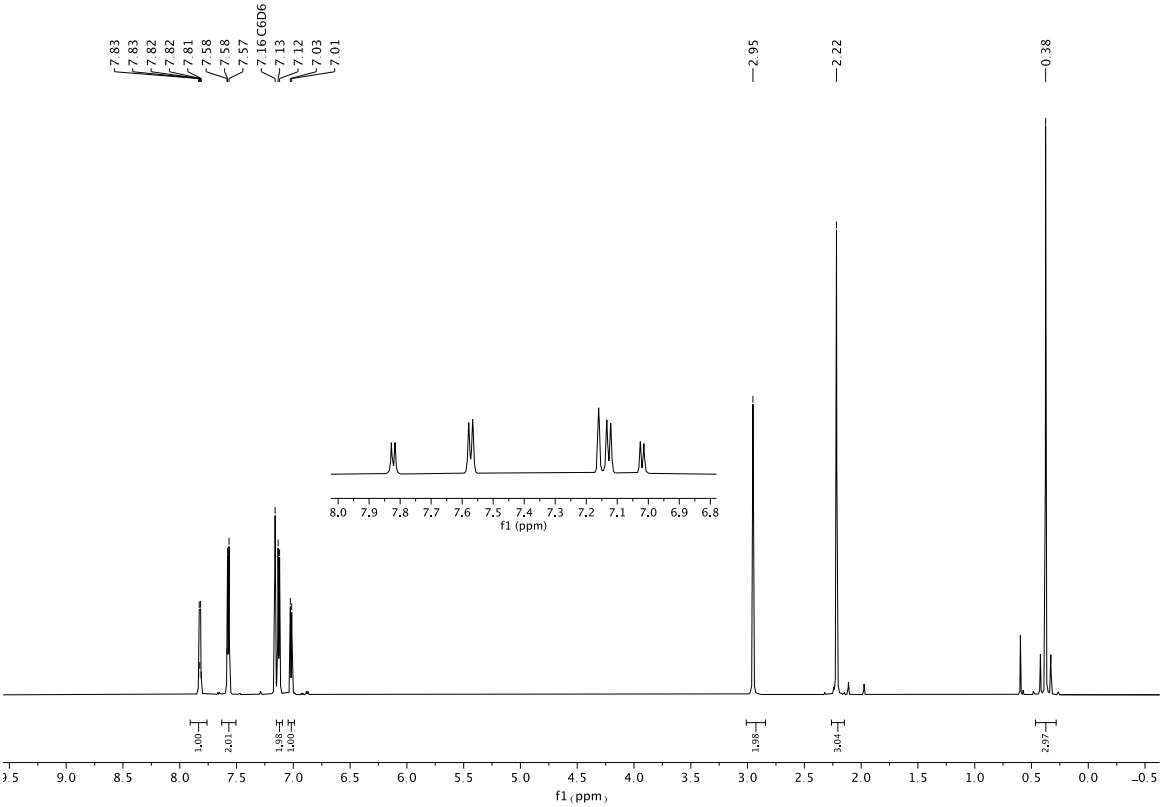


Figure S21. ^{1}H NMR Spectrum (600 MHz, C_6D_6) of **2b**.

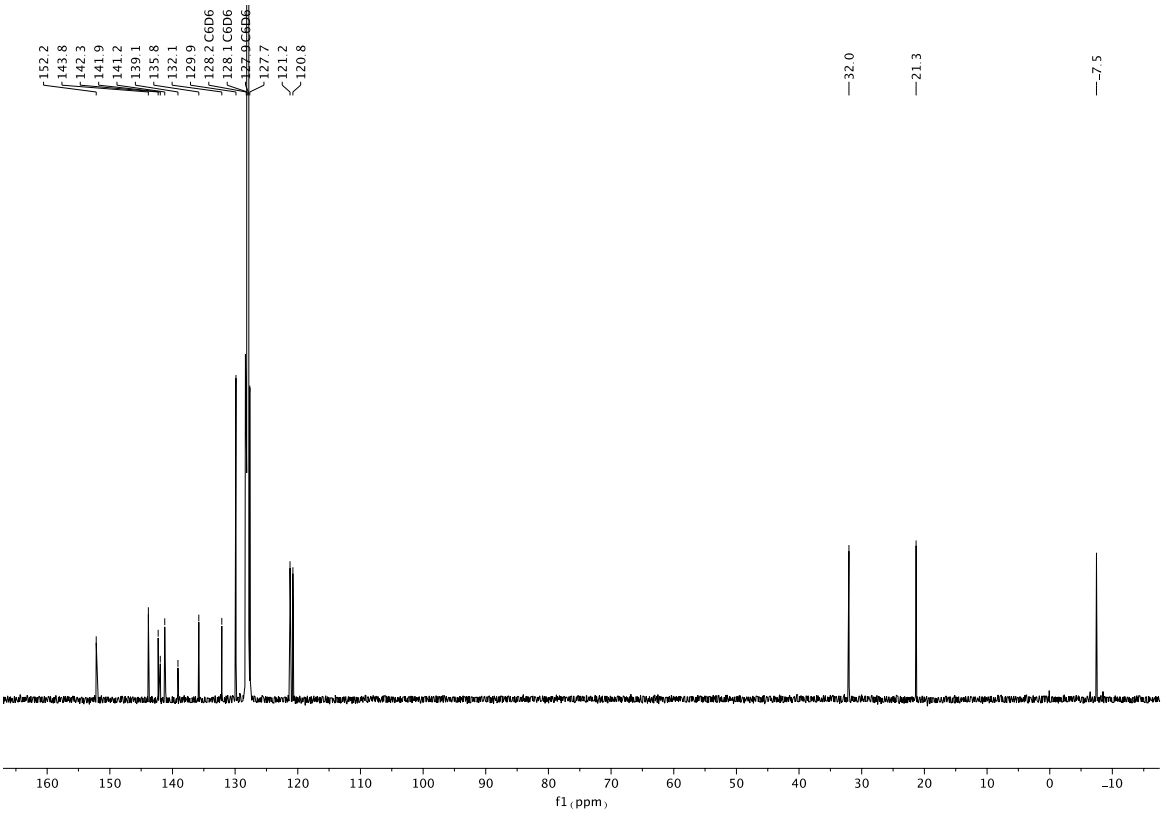


Figure S22. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, C_6D_6) of **2b**.

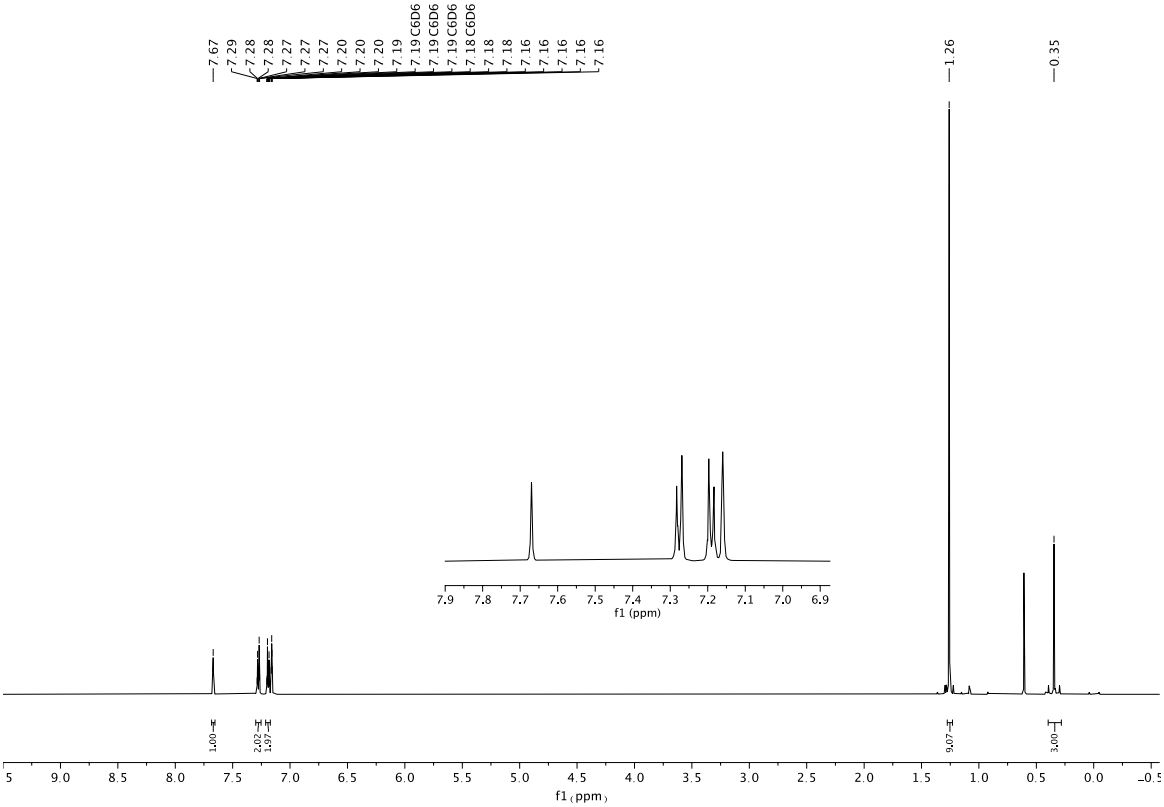


Figure S23. ^{1}H NMR Spectrum (600 MHz, C_6D_6) of **2c**.

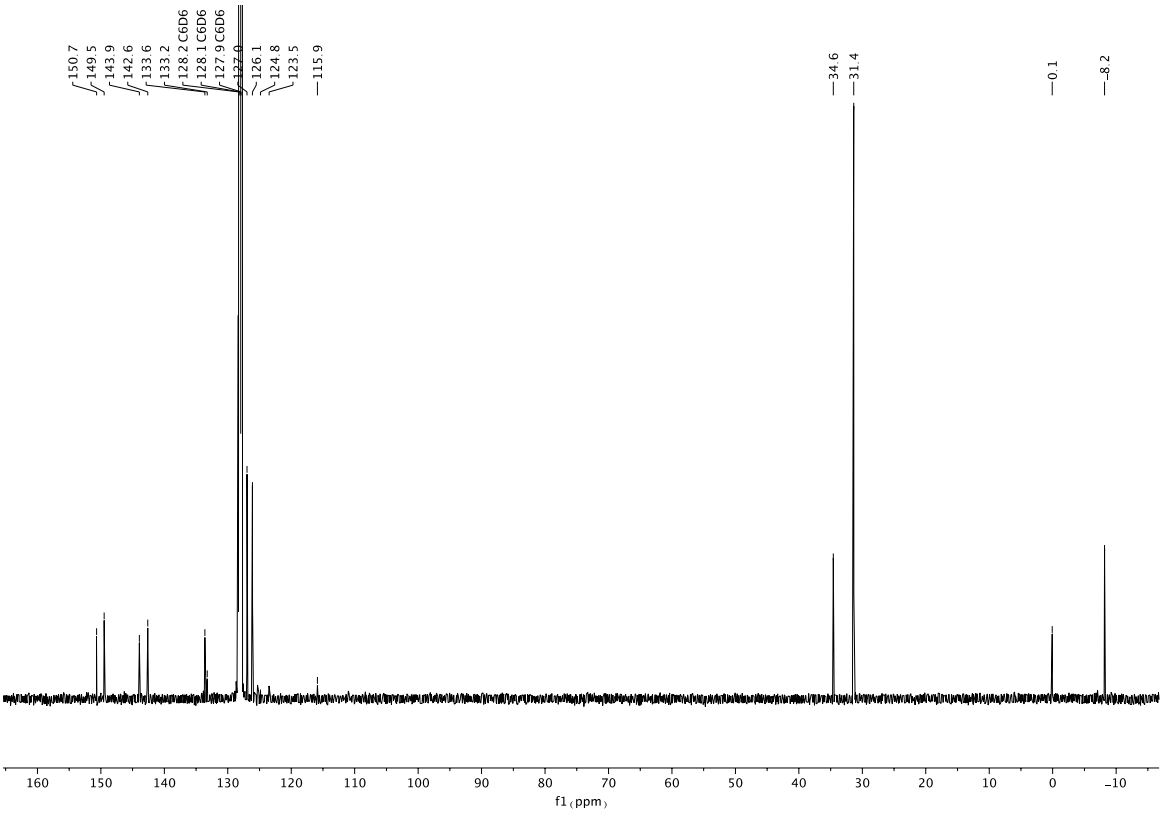


Figure S24. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, C_6D_6) of **2c**.

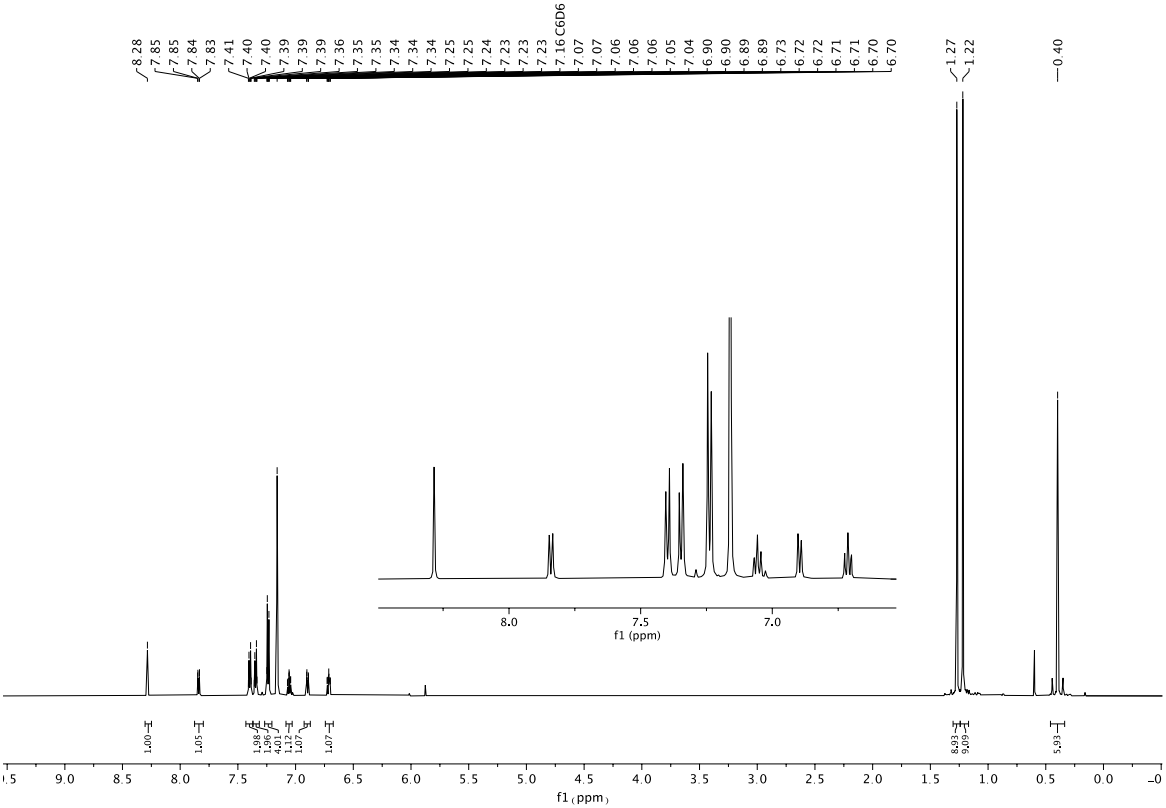


Figure S25. ^{1}H NMR Spectrum (600 MHz, C_6D_6) of **2d**.

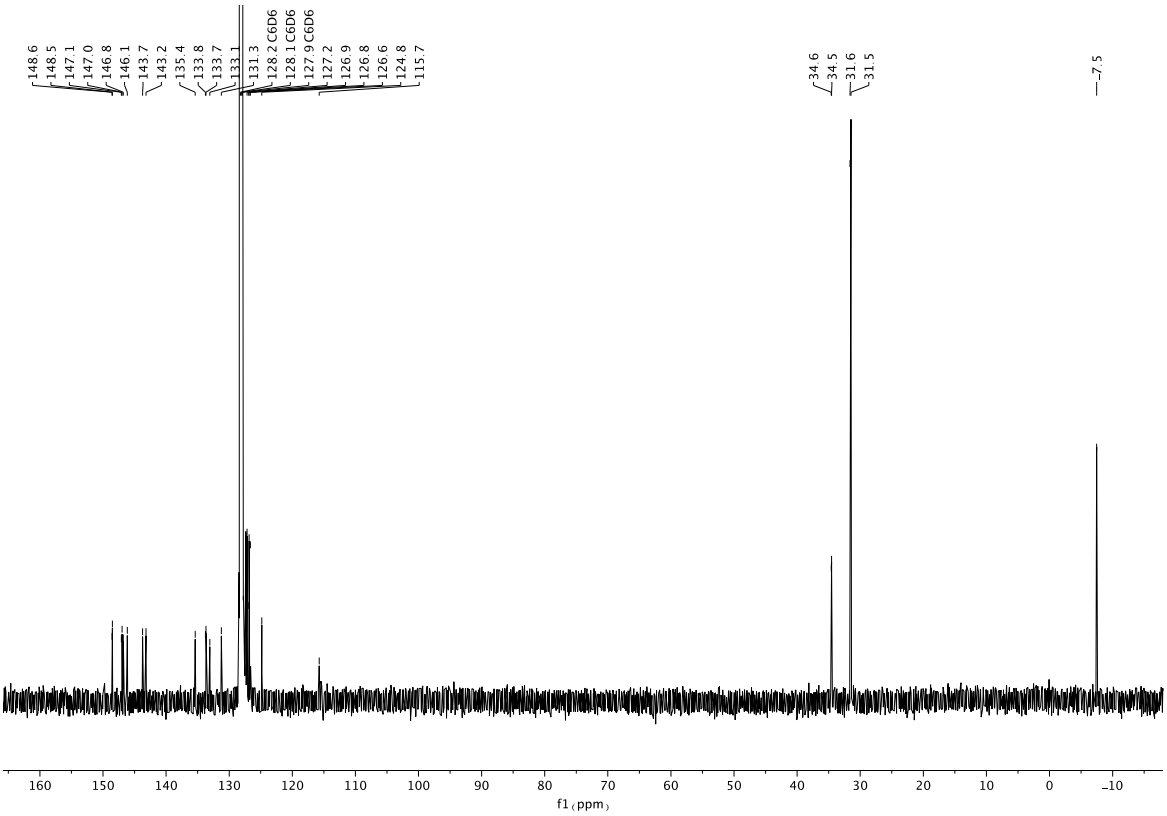


Figure S26. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, C_6D_6) of **2d**.

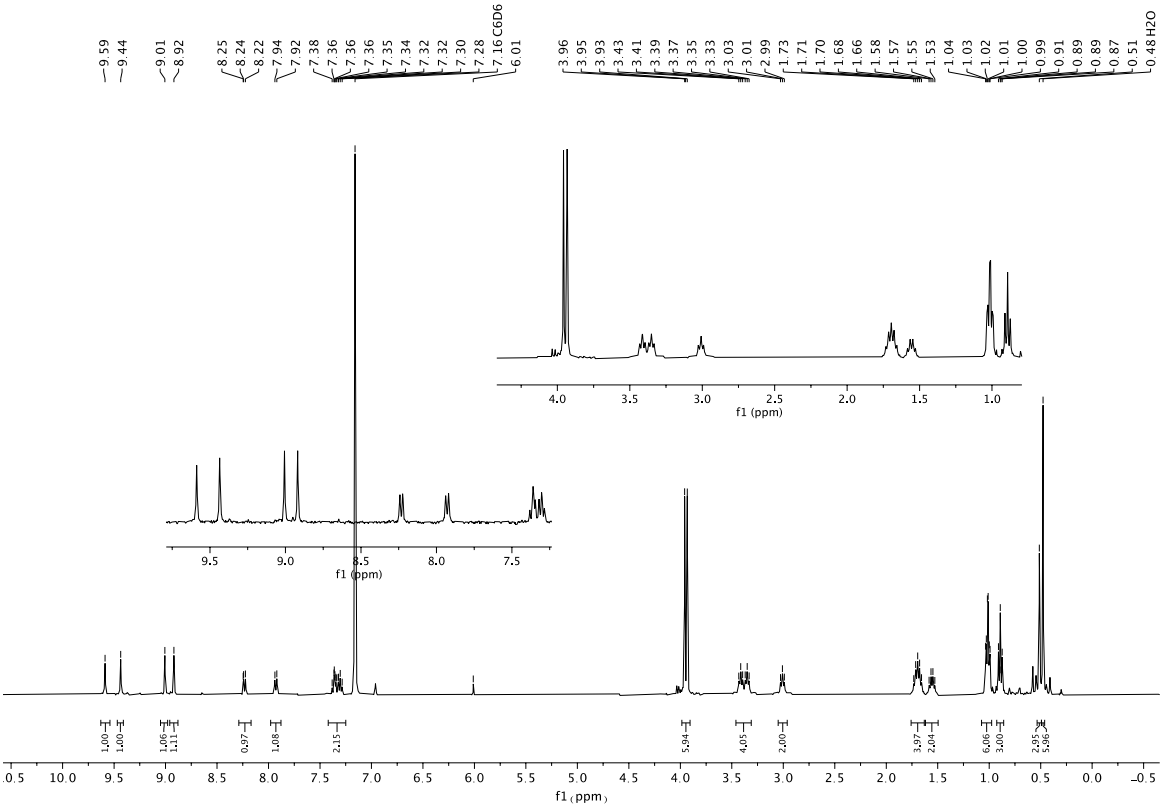


Figure S27. ^{1}H NMR Spectrum (400 MHz, C_6D_6) of **2e**.

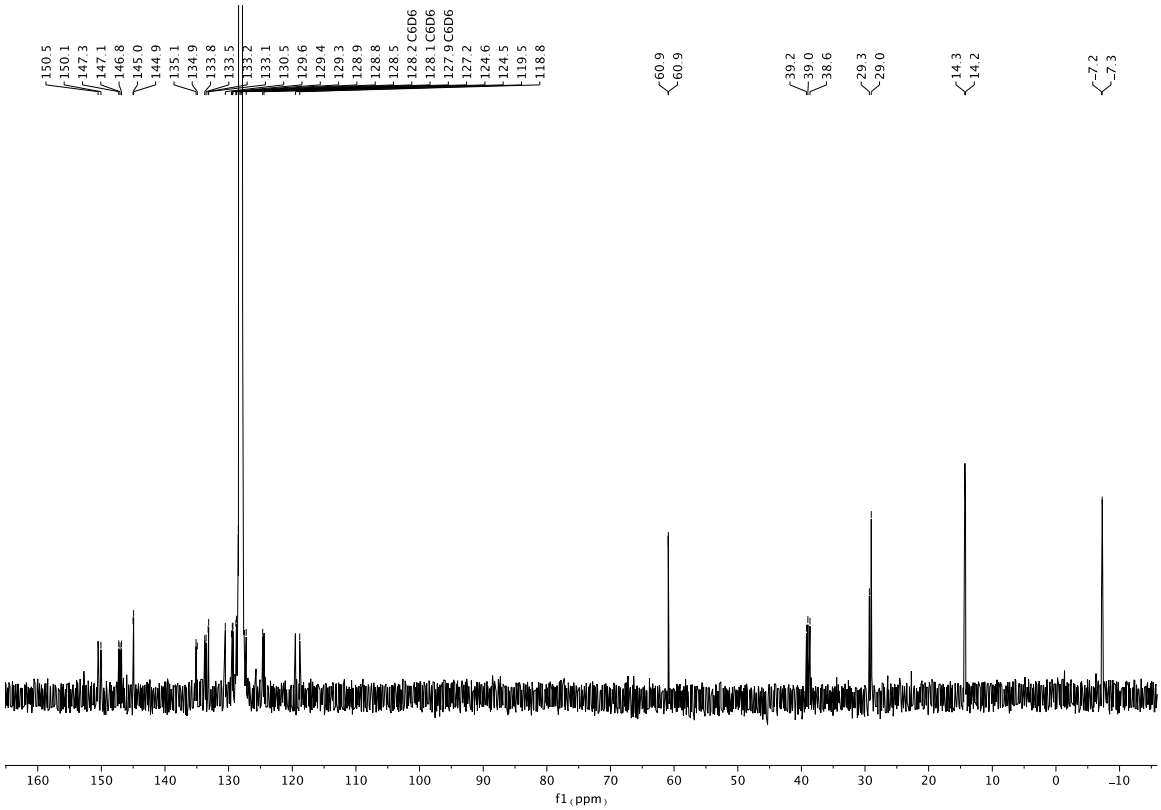


Figure S28. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, C_6D_6) of **2e**.

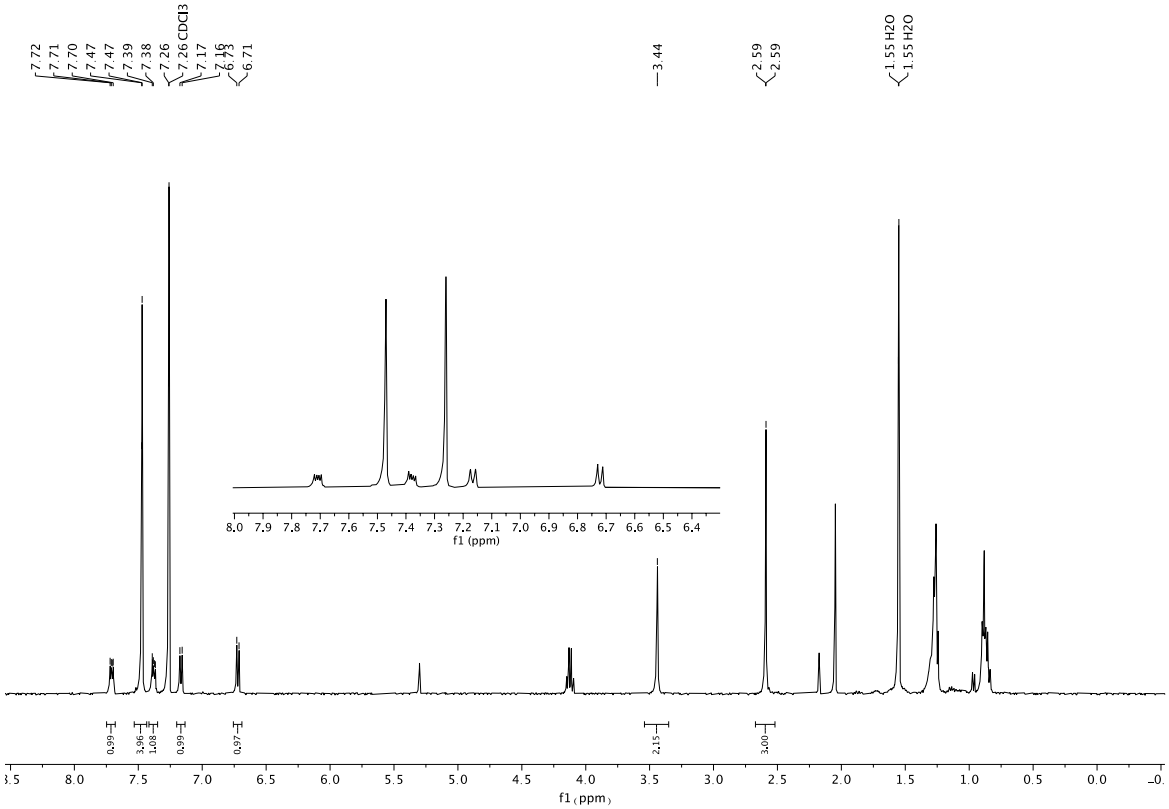


Figure S29. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **3b**.

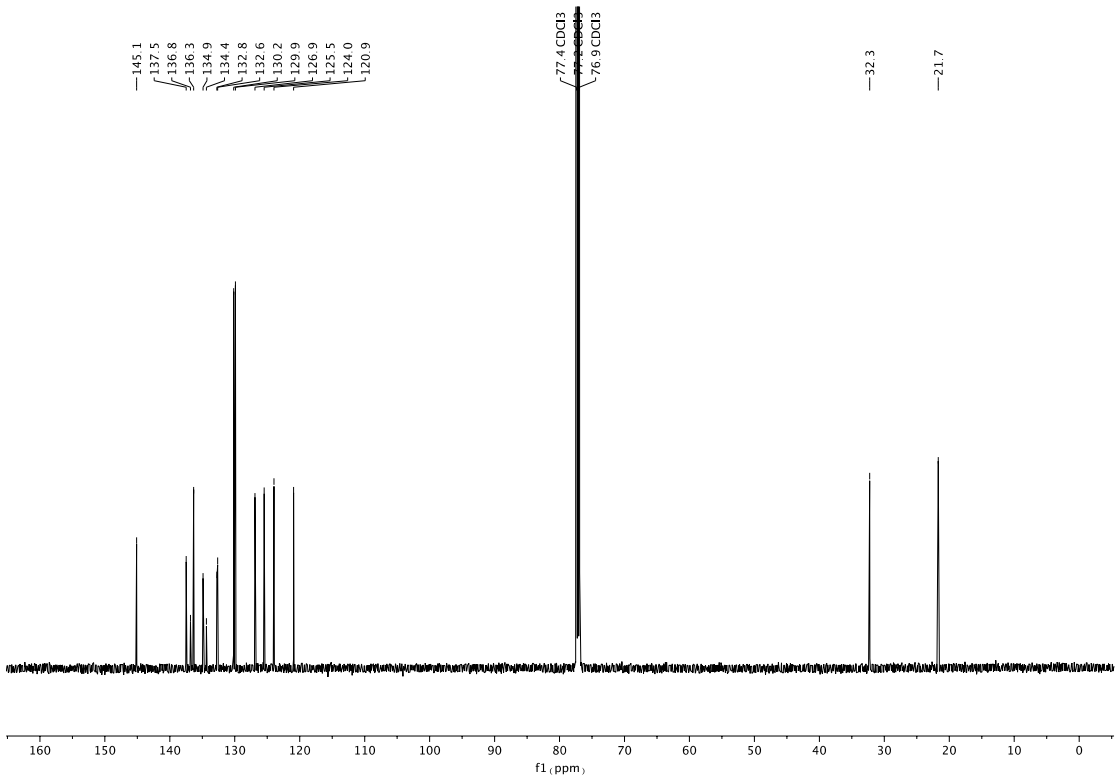


Figure S30. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, $CDCl_3$) of **3b**.

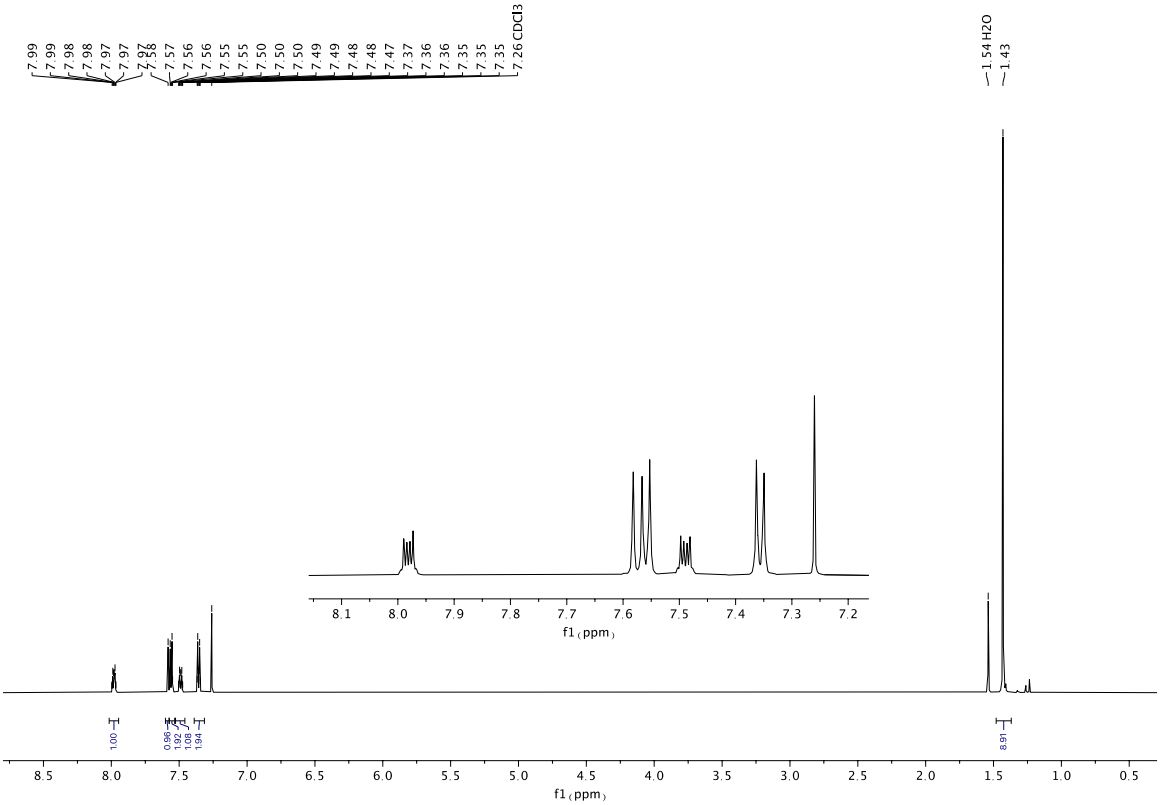


Figure S31. ^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **3c**.

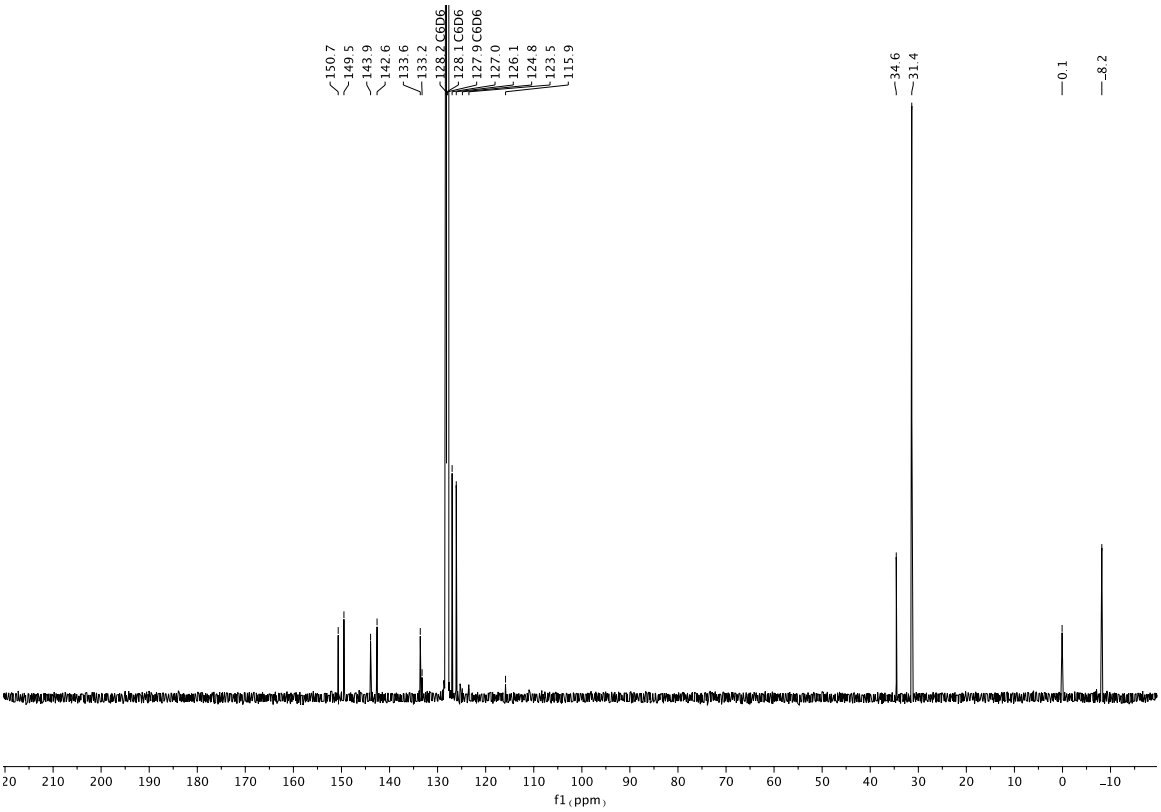


Figure S32. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, $CDCl_3$) of **3c**.

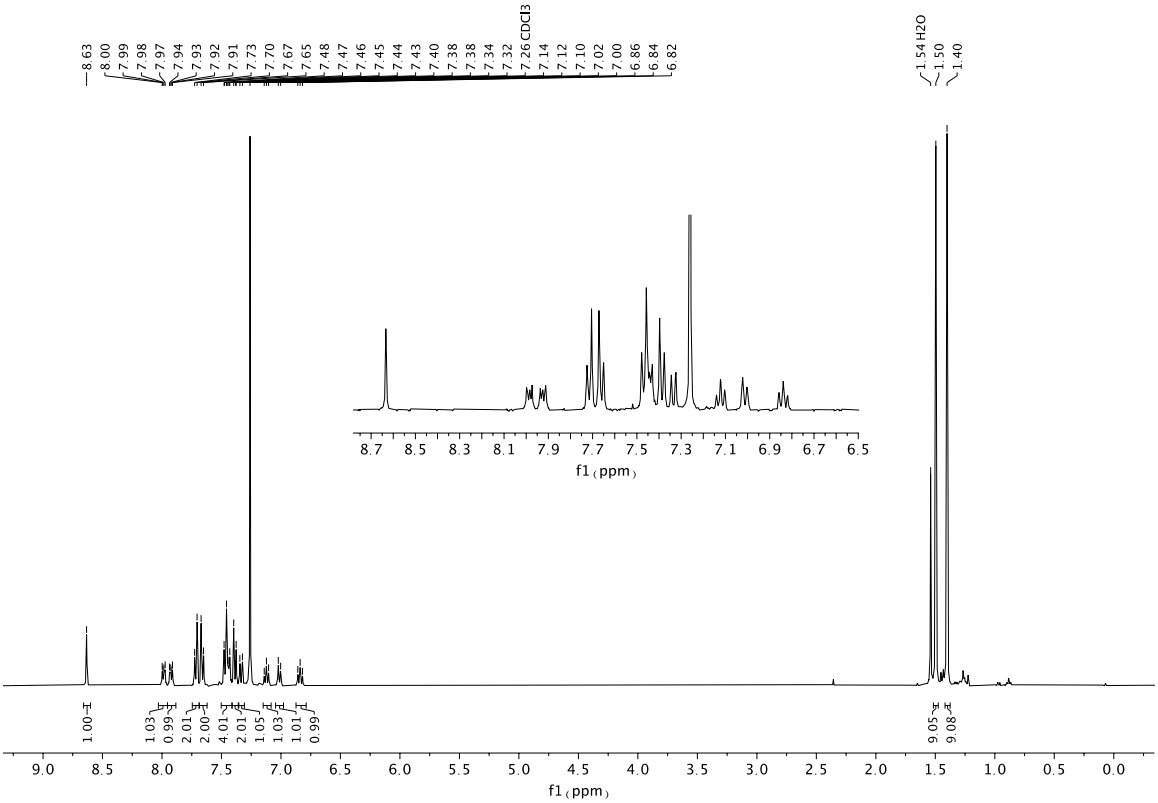


Figure S33. ^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **3d**.

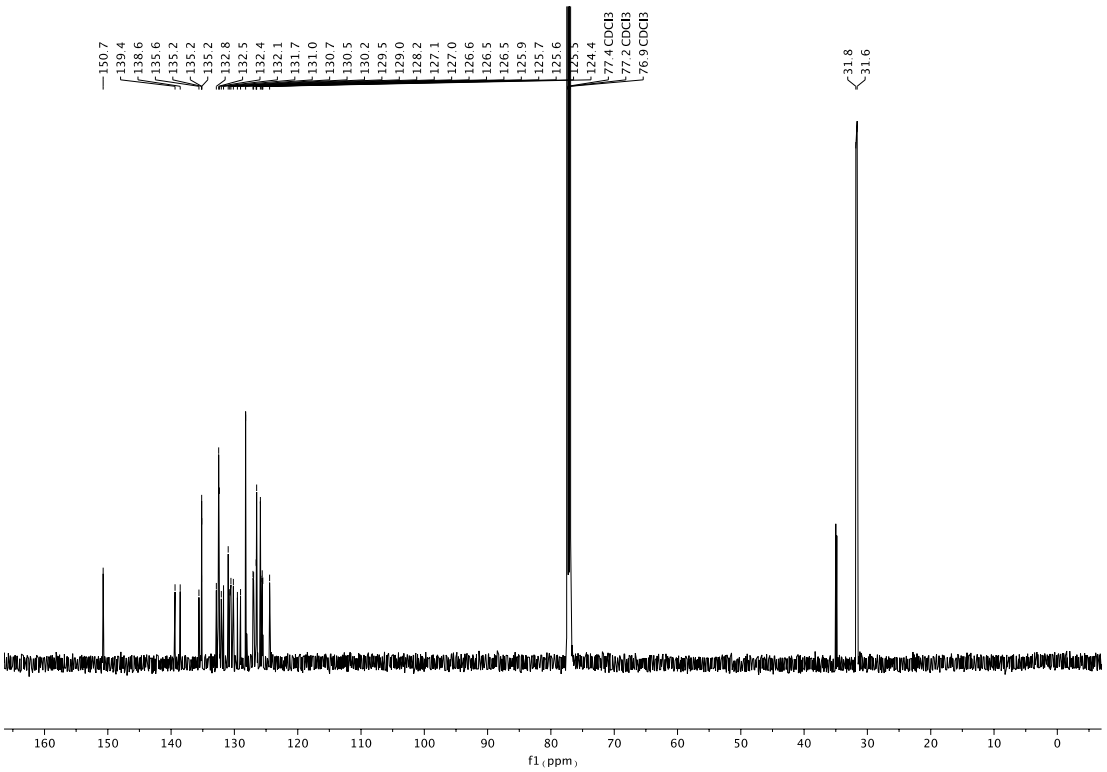


Figure S34. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, $CDCl_3$) of **3d**.

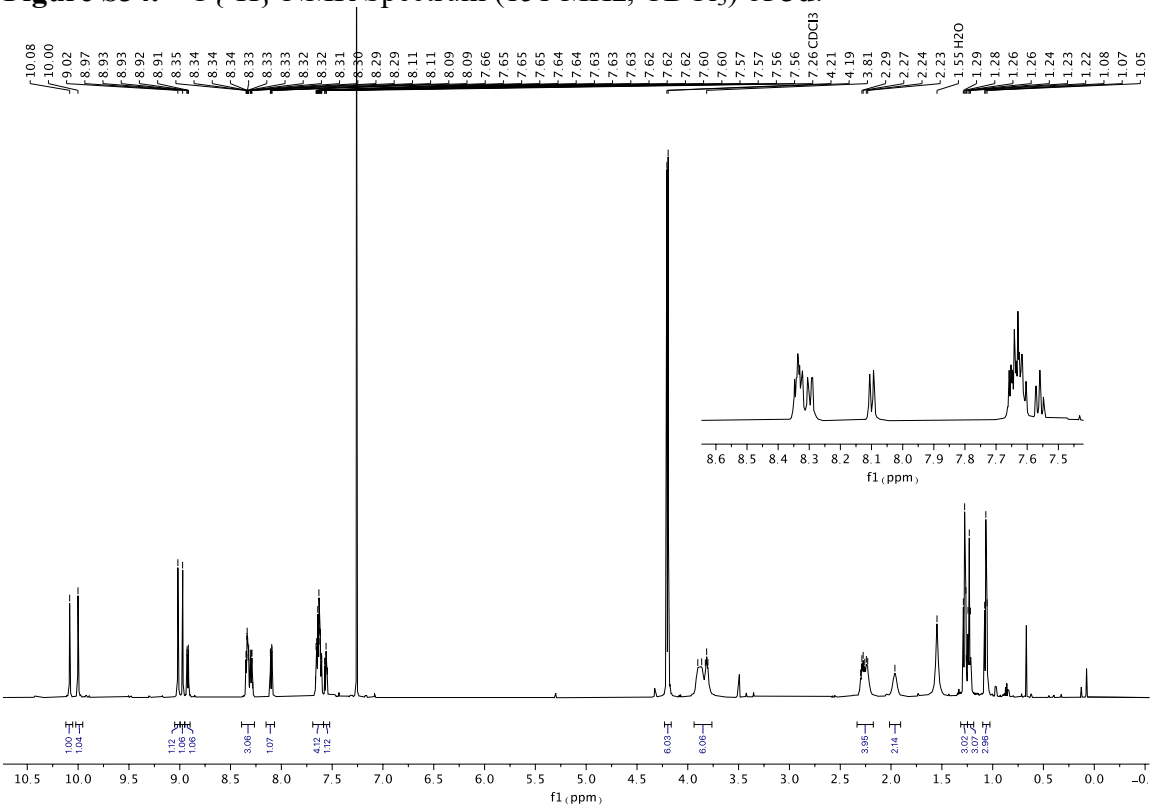


Figure S35. ^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **3e**.

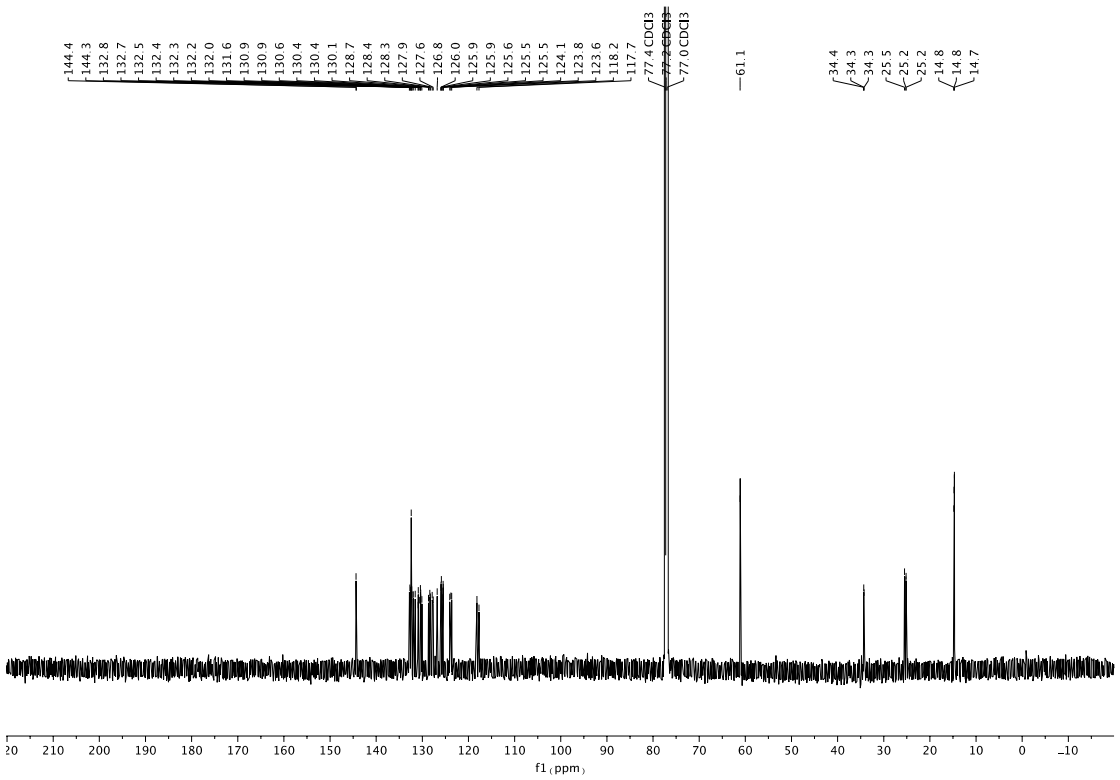


Figure S36. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, $CDCl_3$) of **3e**.

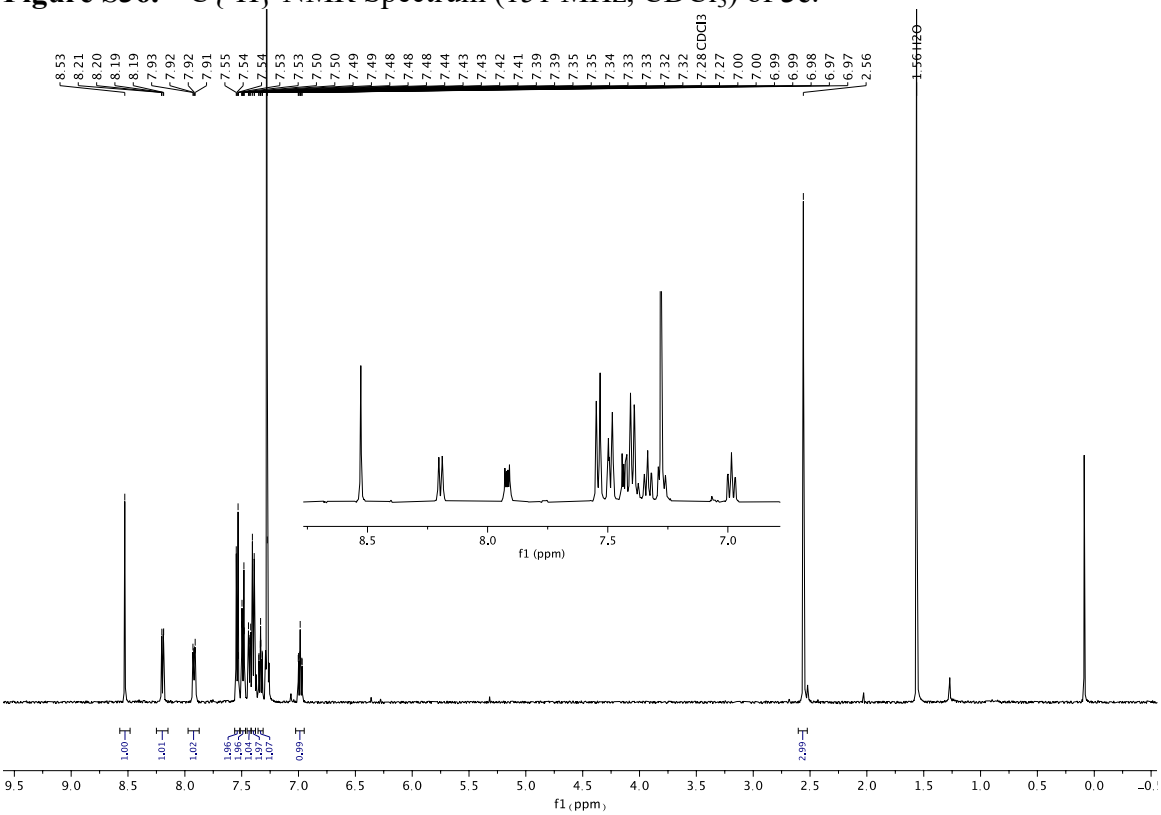


Figure S37. ^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **4**.

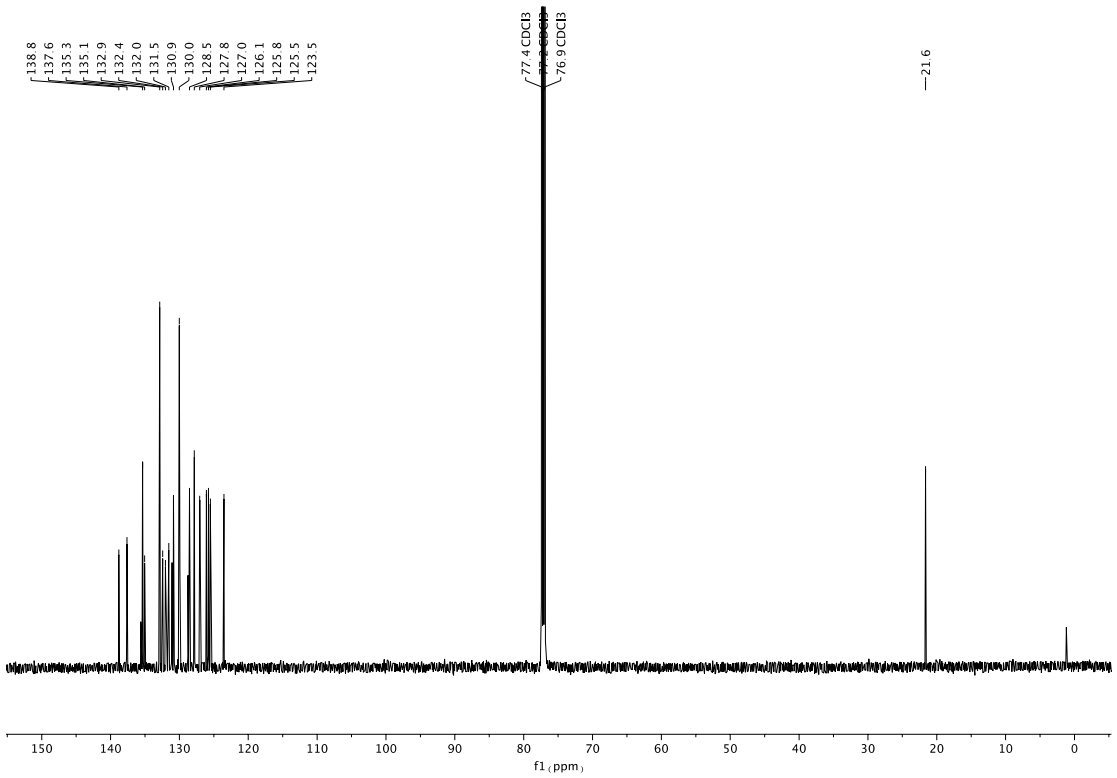


Figure S38. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, $CDCl_3$) of **4**.

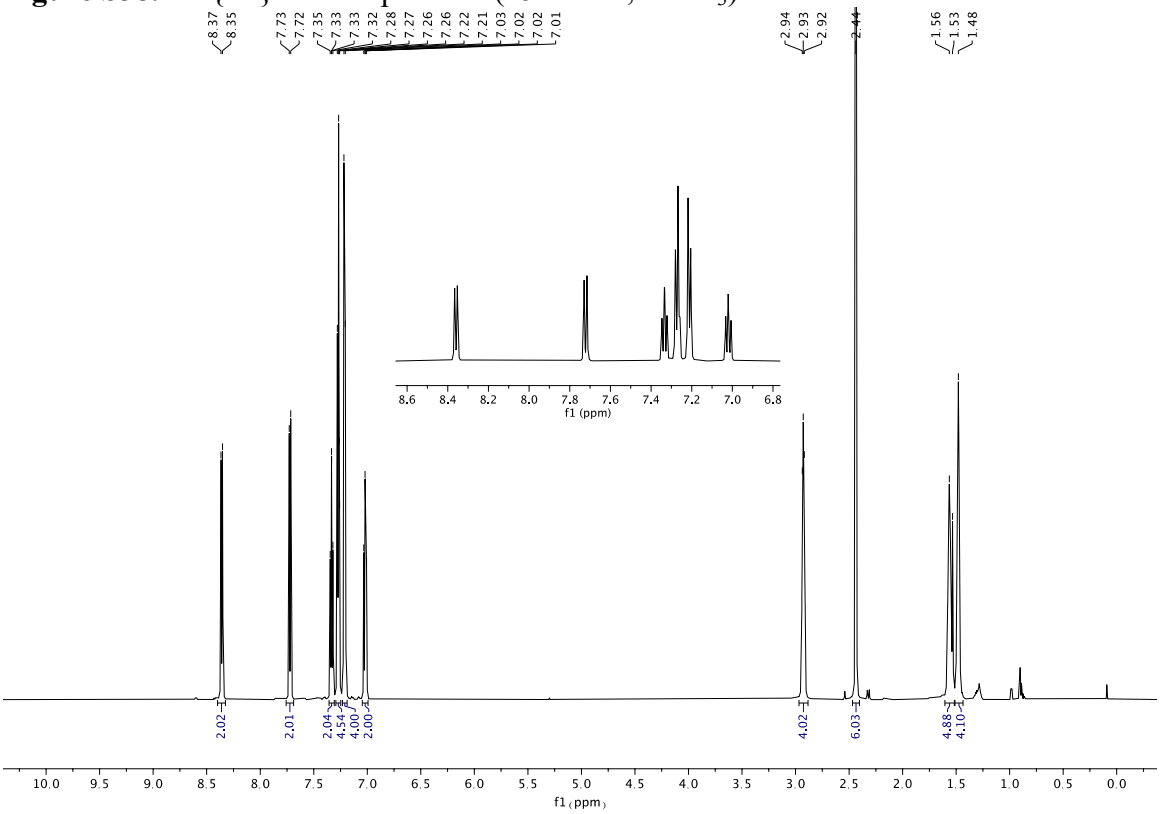


Figure S39. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of **5**.

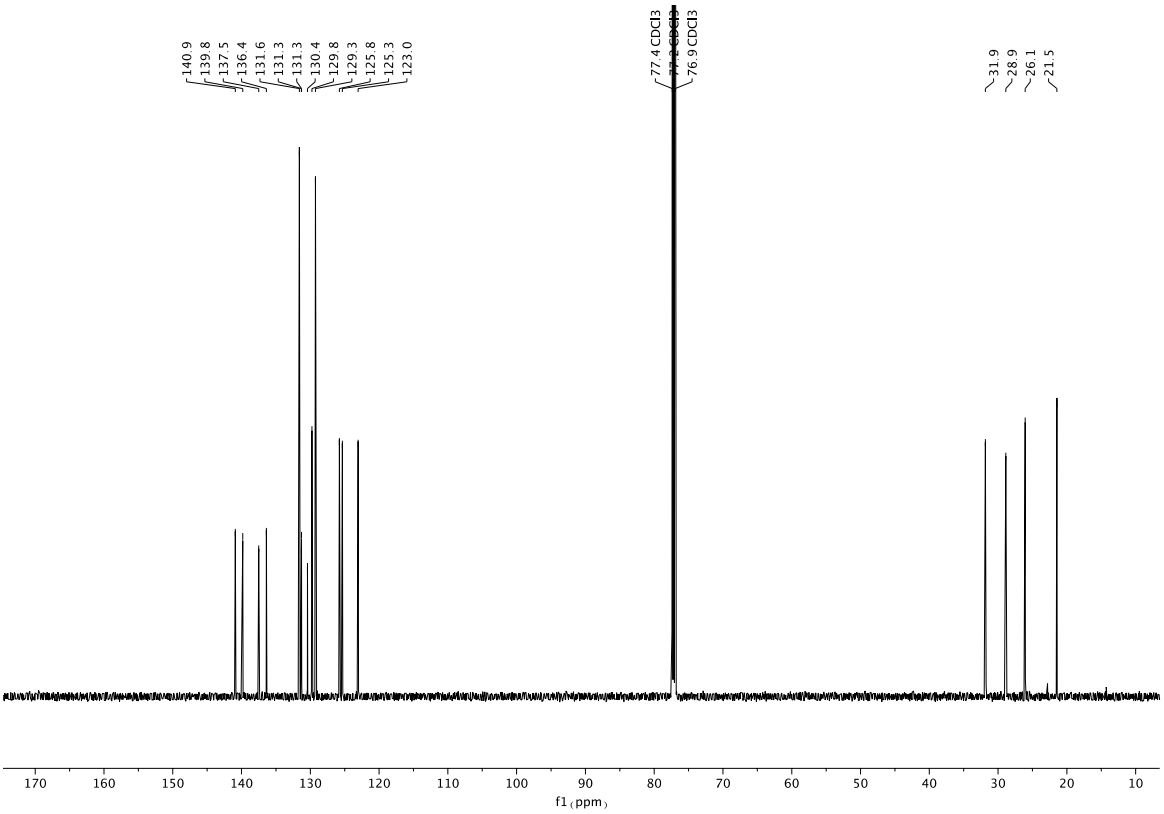


Figure S40. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, $CDCl_3$) of **5**.

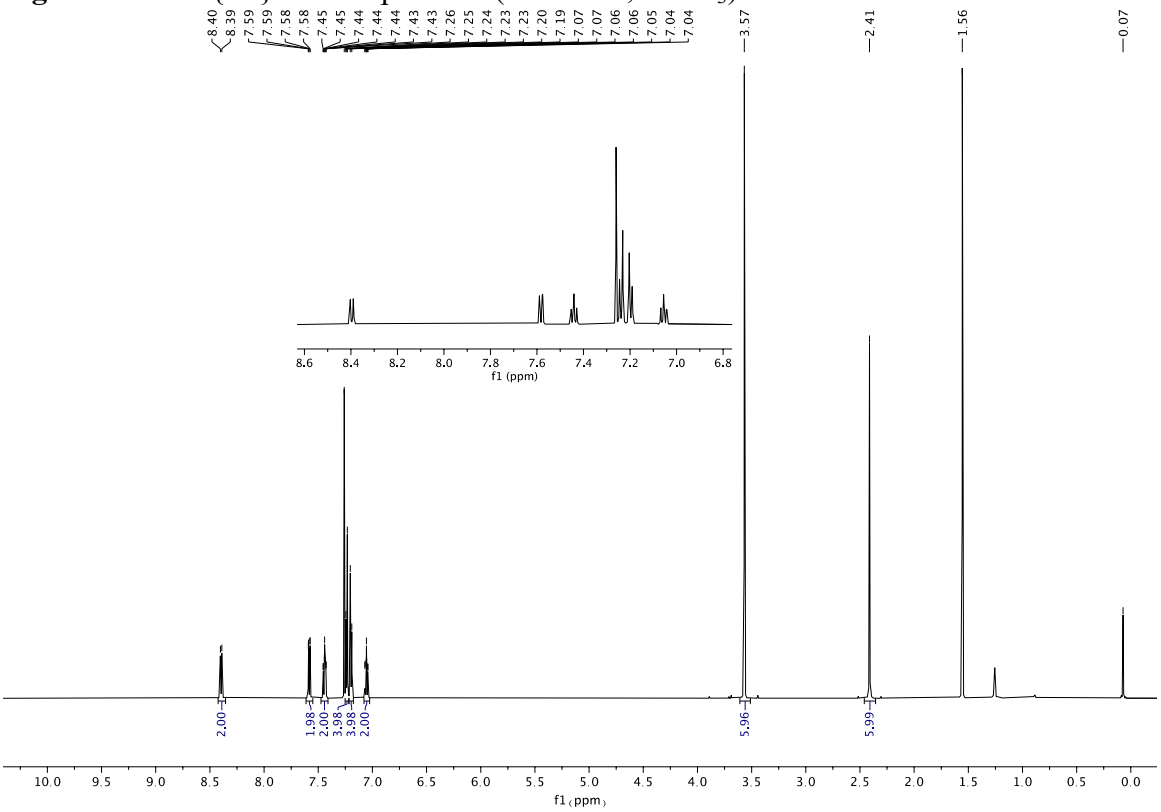


Figure S41. ^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **6**.

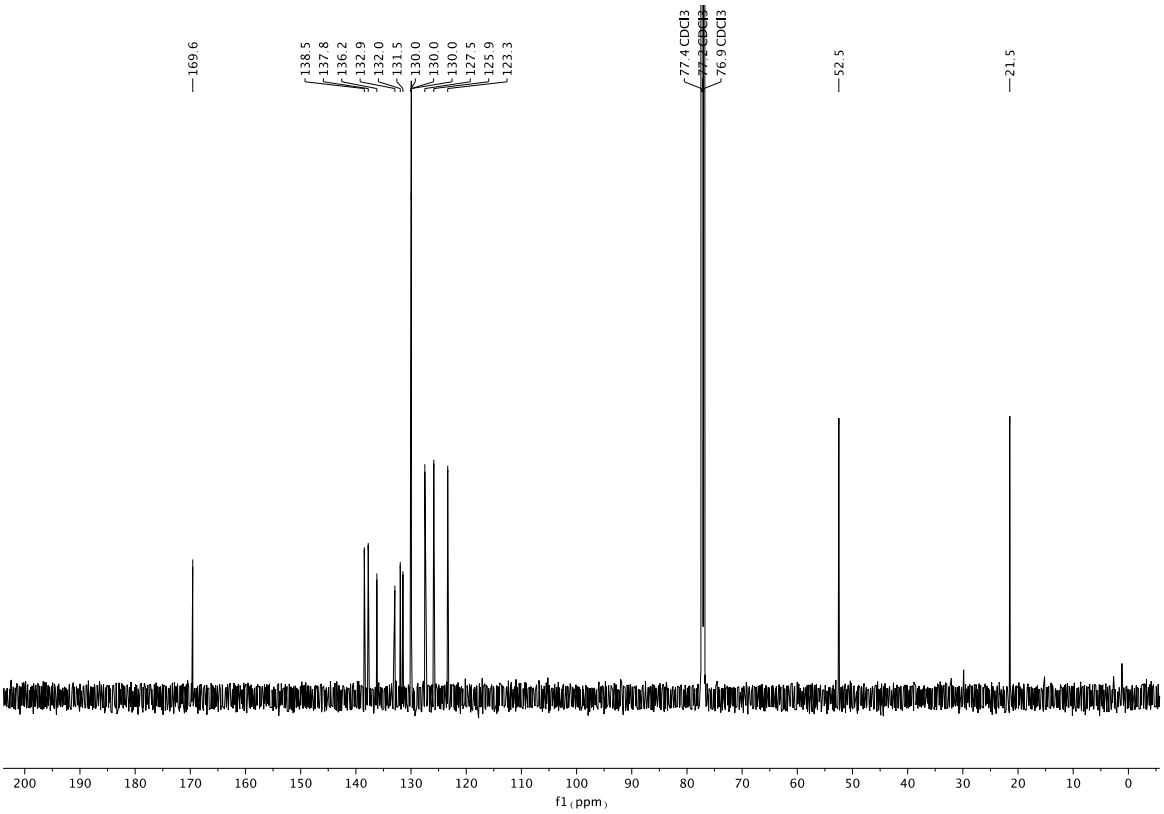


Figure S42. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, $CDCl_3$) of **6**.

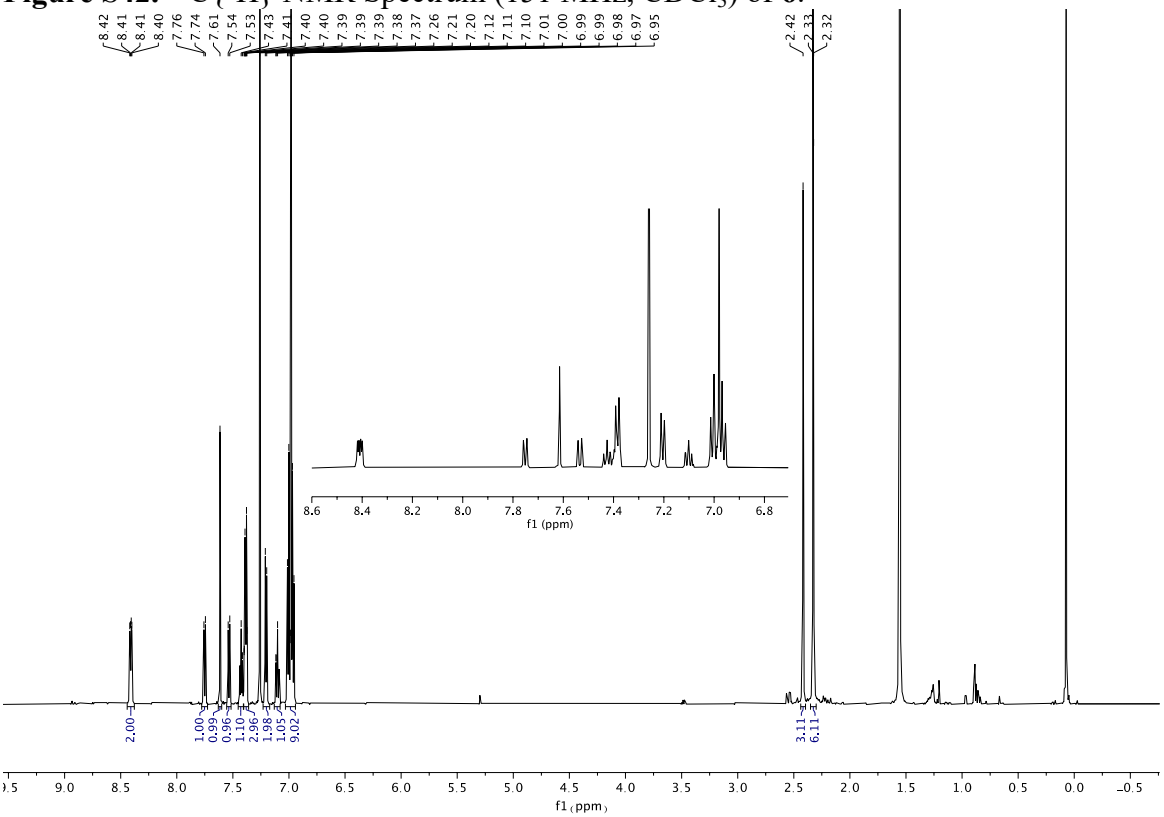


Figure S43. ^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **7**.

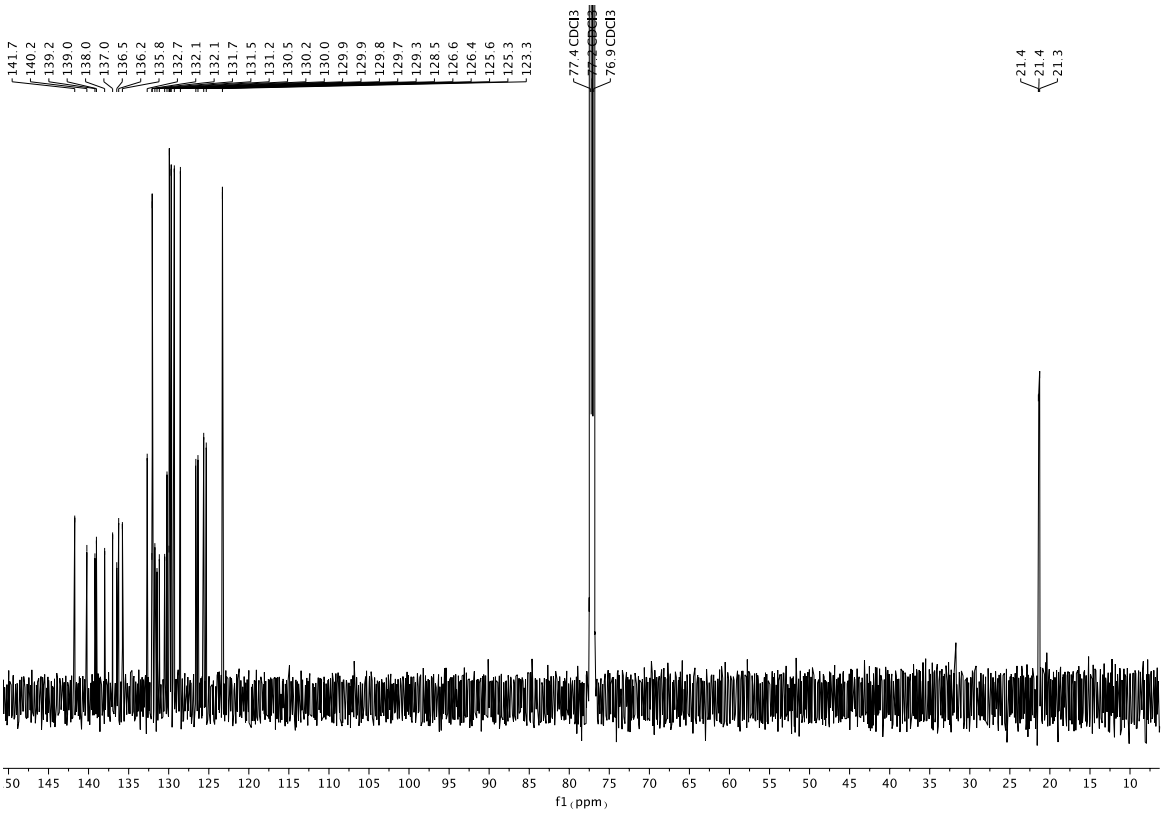


Figure S44. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, $CDCl_3$) of **7**.

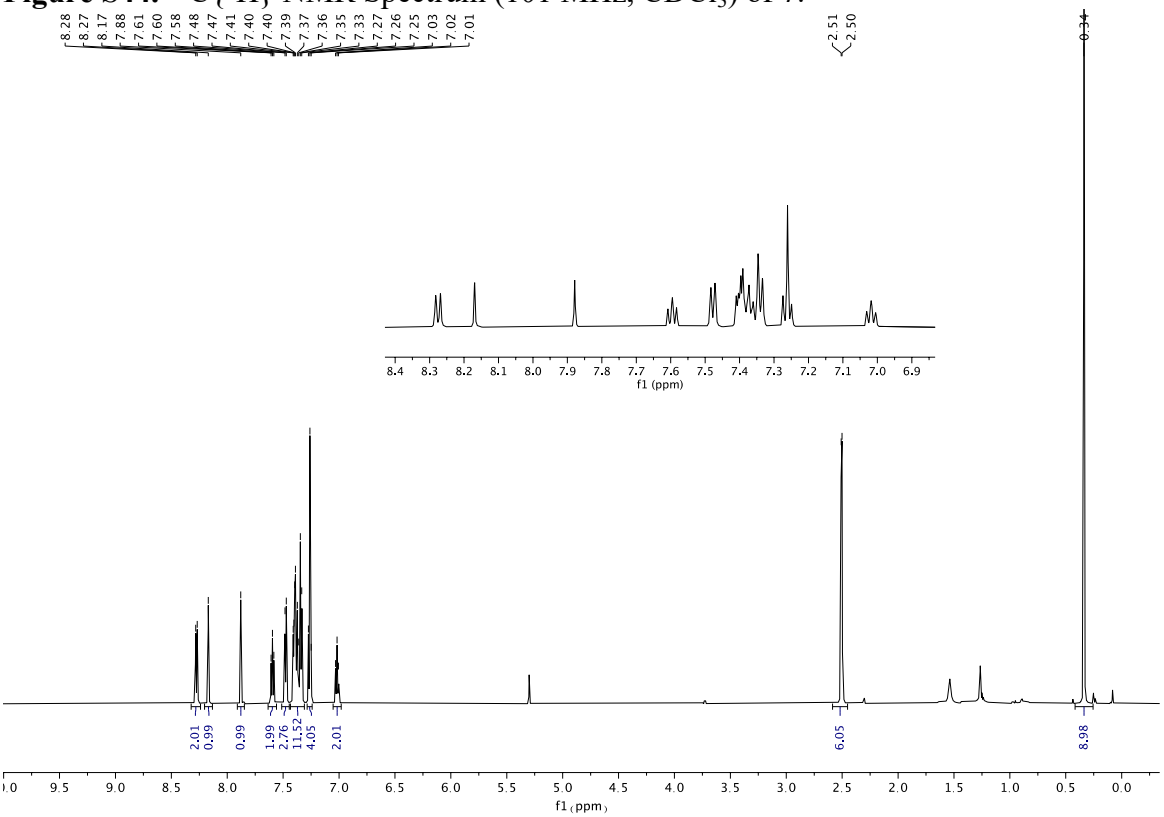


Figure S45. ^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **8**.

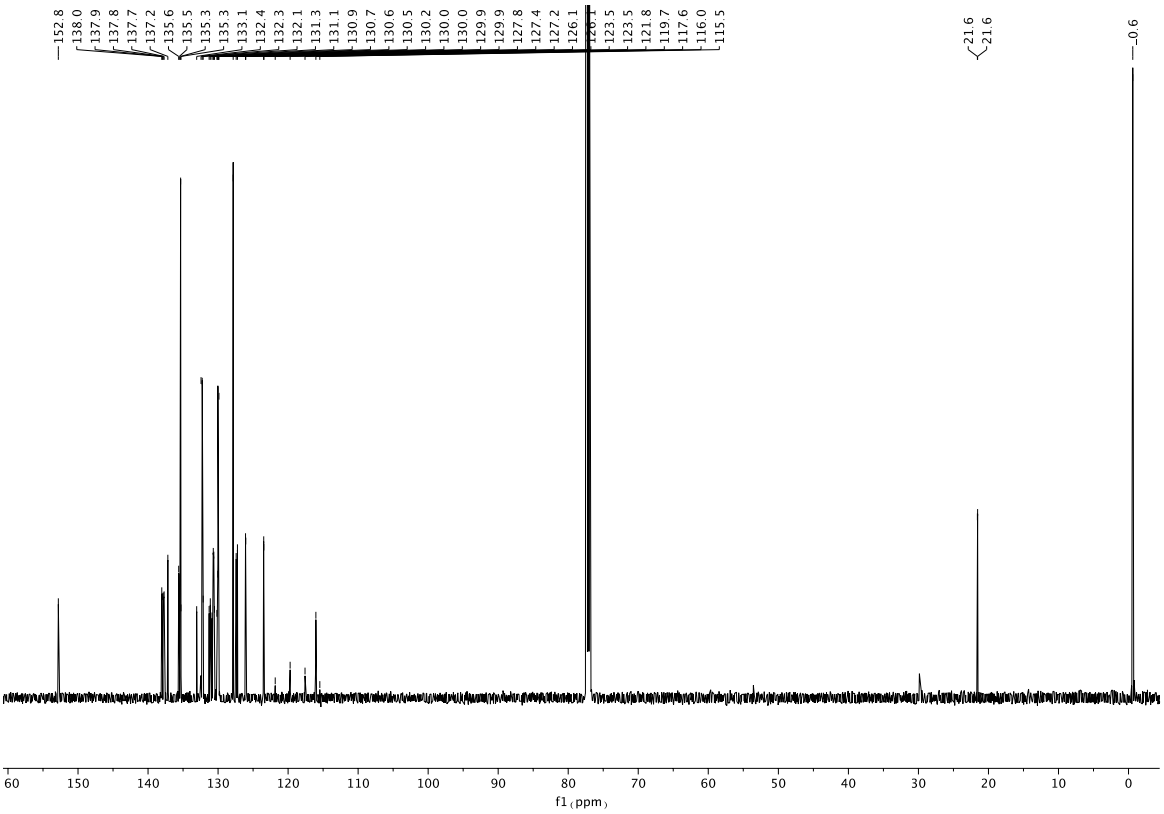


Figure S46. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, $CDCl_3$) of **8**.

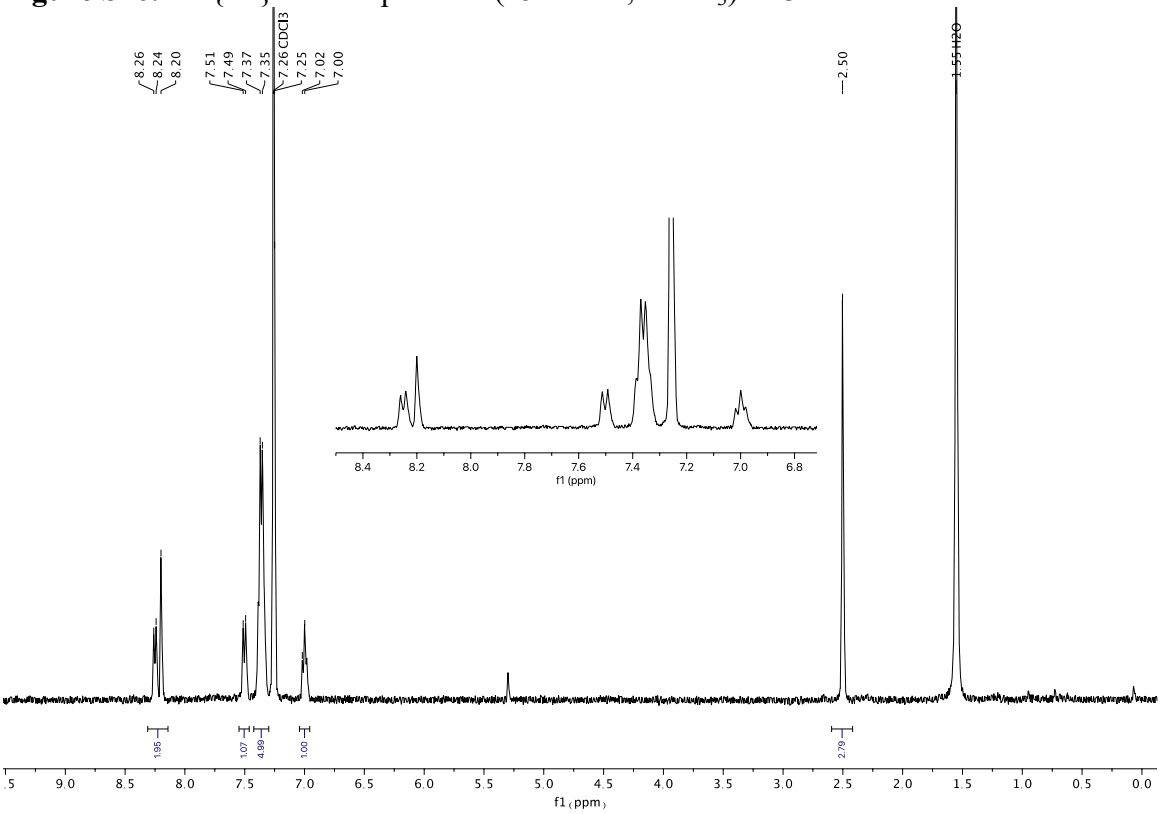


Figure S47. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **9**.

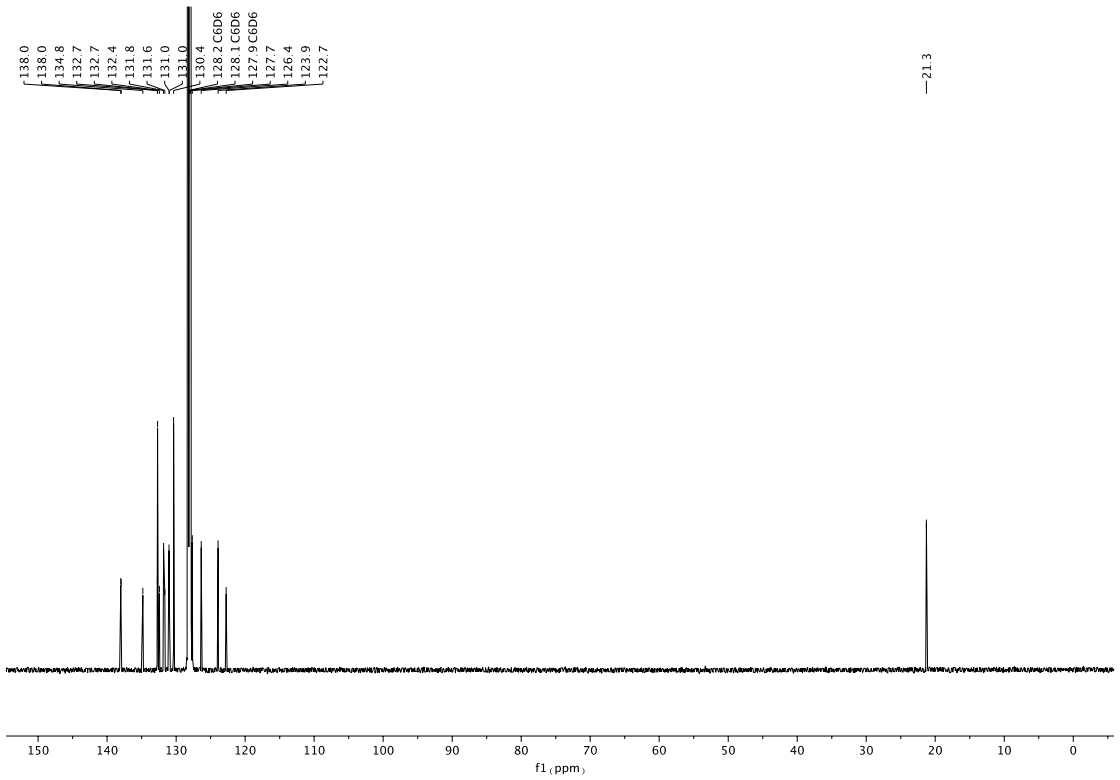


Figure S48. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, C_6D_6) of **9**.

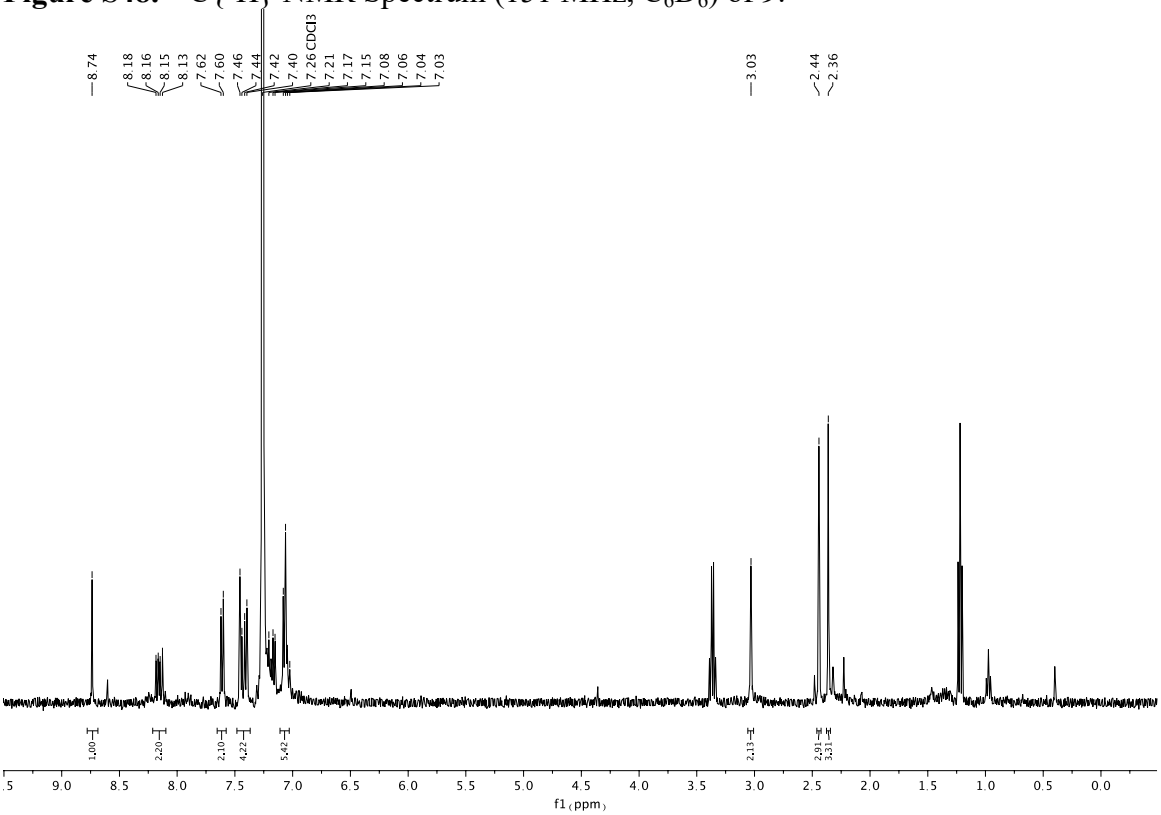


Figure S49. ^{1}H NMR Spectrum (400 MHz, C_6D_6) of **10**.

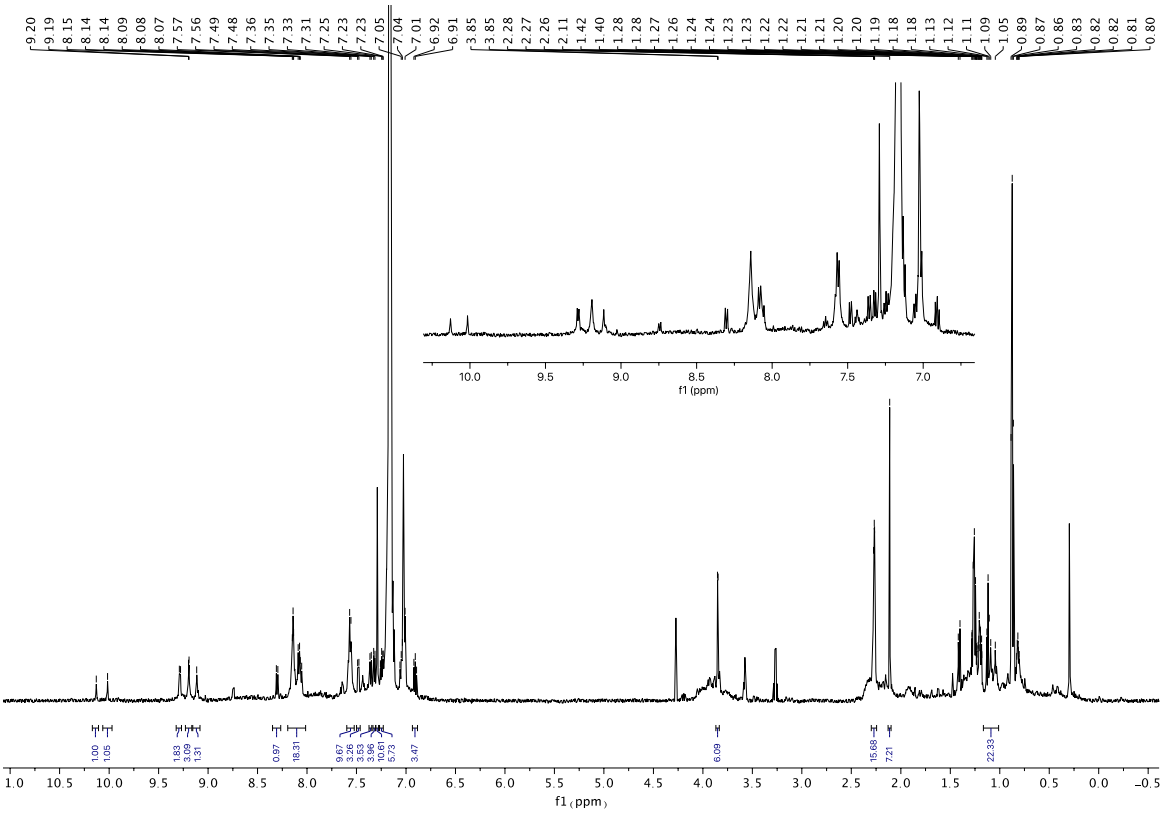


Figure S50. ^{1}H NMR Spectrum (600 MHz, C_6D_6) of **12**.

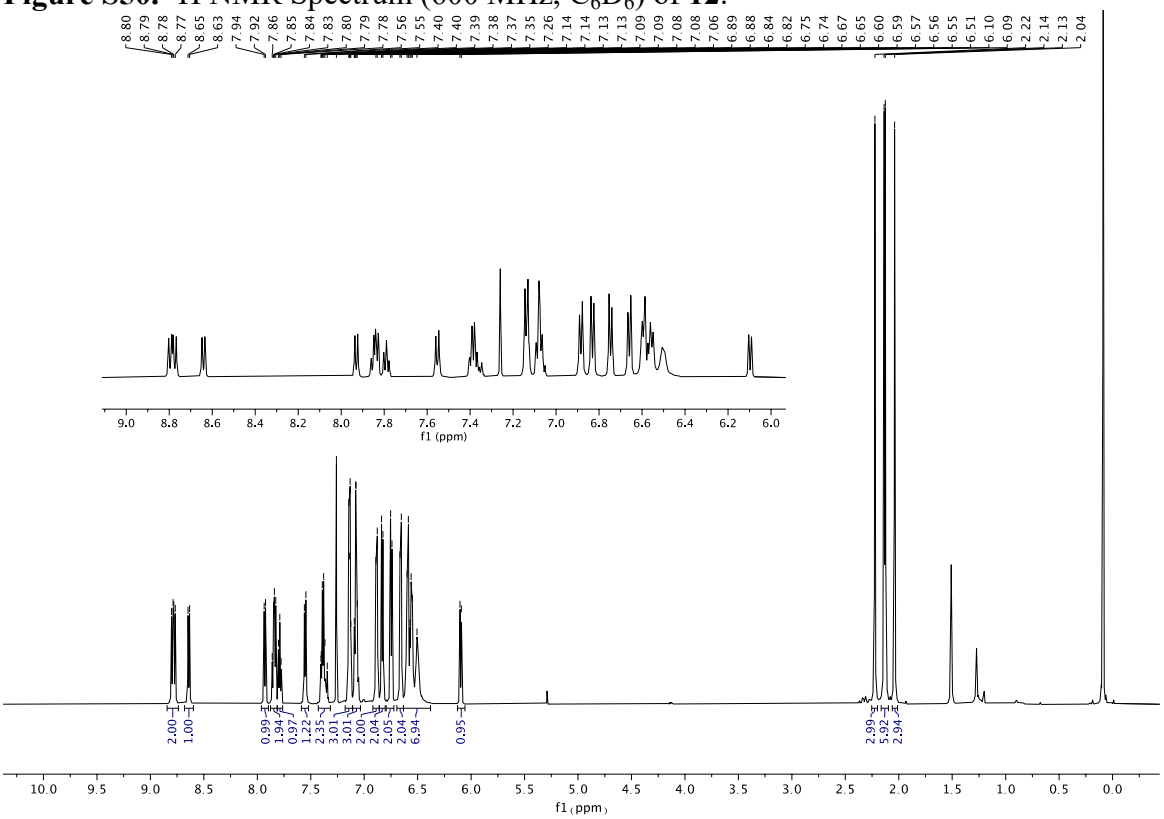


Figure S51. ^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of **13**.

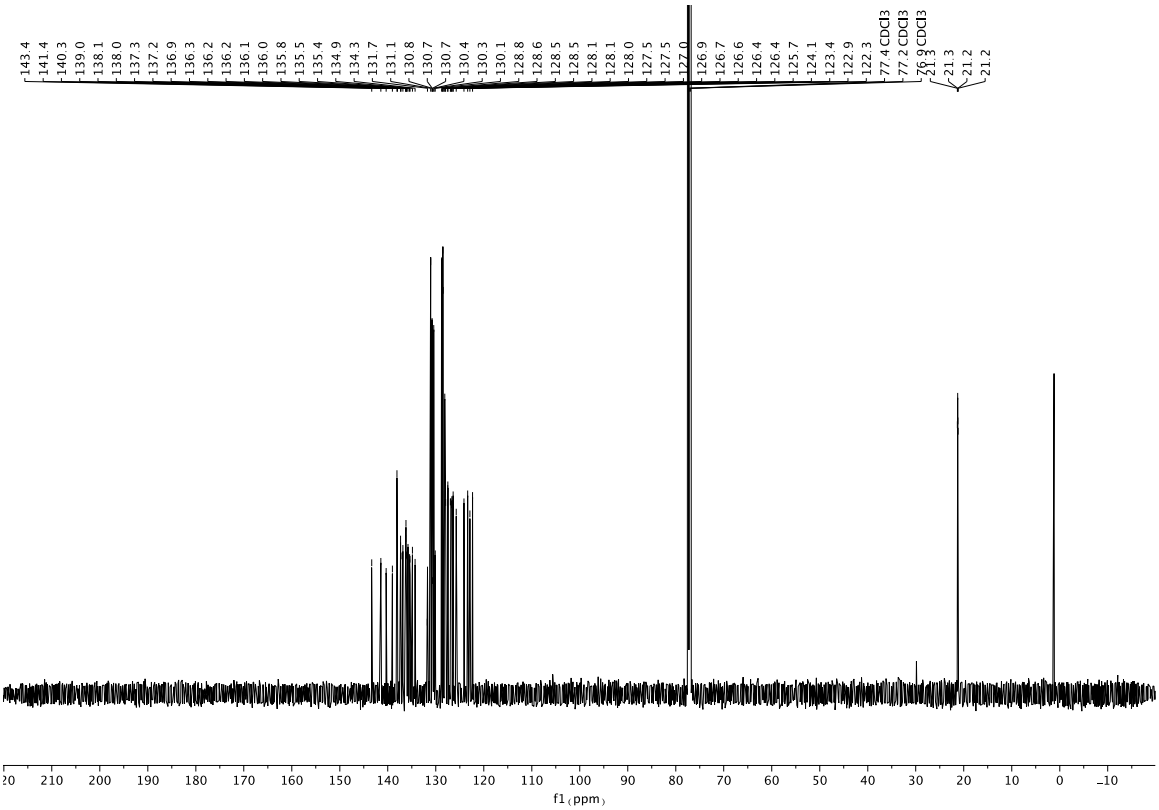


Figure S52. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, $CDCl_3$) of **13**.

MALDI-TOF Spectrometry

Mass spectrometry of all compounds was performed *via* matrix-assisted laser desorption ionization – time of flight (MALDI-TOF) at the LBNL Catalysis Lab at UC Berkeley, using TCNQ as the matrix. Isotope patterns were calculated with Adaptas Solutions' Isotope Distribution Calculator (https://www.sisweb.com/mstools/isotope.htm).

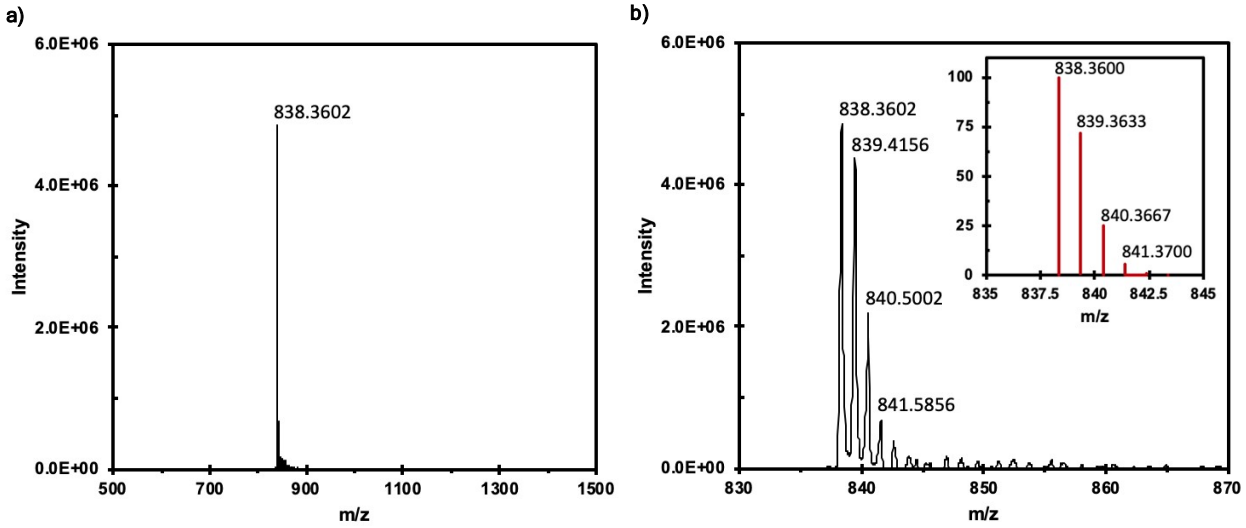


Figure S53. MALDI-TOF spectra of **11** from a) 500-1500 amu, and b) 830-870 amu. Inset depicts the calculated masses and isotope pattern of **11**.

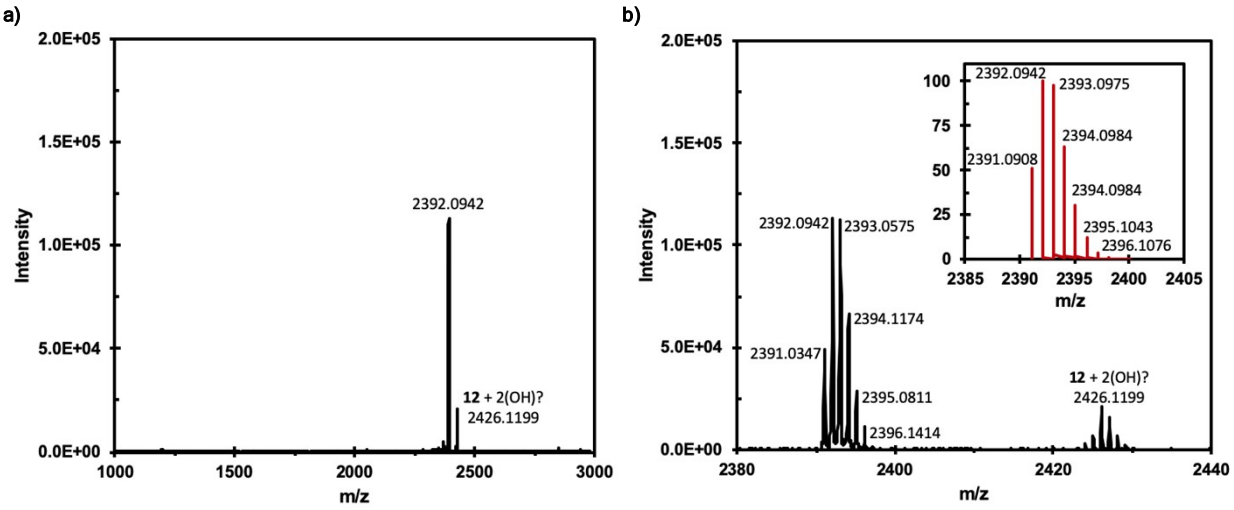


Figure S54. MALDI-TOF spectra of **12** from a) 500-3000 amu, and b) 2380-2440 amu. Inset depicts the calculated masses and isotope pattern of **12**.

Steady-State Spectroscopy

UV-Vis and fluorescence spectroscopies were performed on a Varian 5000 UV-Vis-NIR spectrometer and Nanolog Spectrofluorimeter respectively using quartz cuvettes with a path length of 1 cm. Dry, degassed THF was used as the solvent for **3b**, **3c**, **3d**, **3e**, **4**, and **12**, and 1-chloronaphthalene was used as the solvent for **11**. UV-vis and fluorescence spectra for all compounds were acquired at $5x10^{-6}$ M and acquired in duplicate. Molar absorptivity (ε) was calculated using the Beer-Lambert Law.

X-ray Crystallography

X-ray diffraction data for **13** was collected at the UC Berkeley CheXRay crystallographic facility on a Rigaku Pilatus 200K diffractometer using Cu Kα radiation with a wavelength of 1.5418 Å. Crystals of **13** were kept at 100 K throughout collection. Data collection, integration, scaling, and space group determination for **13** was performed with Rigaku CrysAlis Pro (v. 40_64.84a) software. Structures were solved by SHELXT-2014[10] and refined with SHELXL-2014,[11] with refinement of F^2 on all data by full-matrix least squares, using the OLEX2 interface.[12] The 3D molecular structure figures were visualized with Mercury 3.7.

Details of structure solution and refinement for 13:

All non-hydrogen atoms in the solid-state molecular structure of **13** were refined anisotropically. Hydrogen atoms were placed in calculated positions using a riding model and refined isotropically. The asymmetric unit contains one molecule of chloroform which was disordered across two positions. The relative occupancies of these components were modeled using free variables. The anisotropic displacement parameters of atoms Cl3 and Cl3A were fixed to be equal using the EADP constraint. A disordered, partially occupied (occu = 0.66) molecule of chloroform occupying a special position was accounted for with SQUEEZE.

Empirical formula	$C_{61}H_{45}Cl_3$+0.66[$CHCl_3$]
Formula weight	884.32
Temperature/K	100
Crystal system	Triclinic
Space group	*P*–1
a/Å	13.13230(10)
b/Å	14.2033(2)
c/Å	14.70790(10)
α/°	94.6060(10)
β/°	111.0410(10)
γ/°	97.9730(10)
Volume/Å^3	2510.43(5)
Z	2
ρ_{calc}g/cm^3	1.170
μ/mm^{-1}	1.931
F(000)	924.0
Crystal size/mm^3	0.11 × 0.08 × 0.065
Radiation	CuKα (λ = 1.54184 Å)
2θ range for data collection/°	6.346 to 149.004
Index ranges	$-16 \le h \le 16$, $-17 \le k \le 17$, $-18 \le l \le 18$
Reflections collected	100149

Table S2. Crystal data and structure refinement for **13**.

References

(1) Österlöf, J. Acta. Chem. Scand. **1950**, *4*, 374-385.

(2) Levi, Z.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 2796–2797.

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