Supporting Information

A High Yielding and Divergent Paradigm for the Synthesis of D_{2h}-Symmetric Octakis-Substituted Pentiptycenequinones

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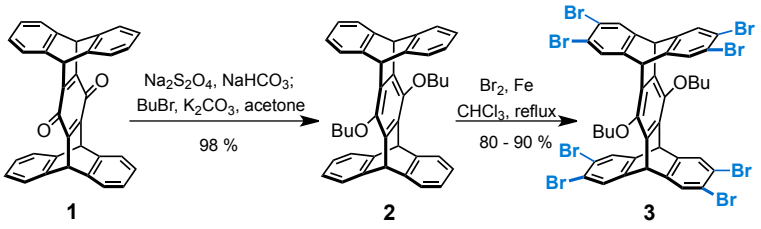
General Information.

All reactions were performed under an inert atmosphere of argon unless otherwise stated. Chemicals were purchased from commercially available sources and used without further purification unless otherwise noted. Nuclear magnetic resonance (NMR) spectra for ^{1} H were obtained at 300, 400 or 500 MHz as noted using Bruker NMR spectrometers. All ^{13}C NMR measurements were carried out at 125 MHz. Chemical shifts are reported in ppm on the δ-scale using the residual natural abundance isotopes of the solvents as references. $CDCl_3$ was calibrated at δ7.26 and δ77.16 for ^{1}H and ^{13}C, respectively. IR spectral data was recorded in cm^{-1} using an Attenuated Total Reflectance (ATR)-IR Spectrometer. High resolution mass spectrometry was performed using electrospray ionization with a time of flight (ESI-TOF), DART or MALDI mass spectrometer, as noted. 2,4,6-trivinylcyclotriboroxane-pyridine complex **6** and 4-tetraphenyliodide **7** were prepared according to previously reported literature procedure.[1,2]

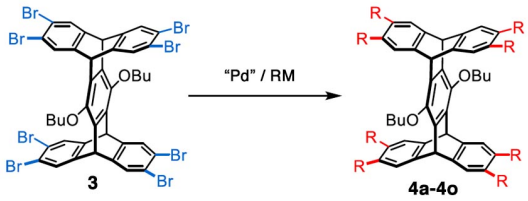
Synthetic Procedures.

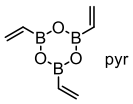


Synthesis of 2. Pentiptycene quinone **1** (800 mg, 1.74 mmol) was suspended in THF (8 mL). Sodium dithionite (2.6 g, 14.77 mmol) was dissolved in H_2O (12 mL). Aqueous solution was added to suspended starting material and the biphasic mixture was heated to 40°C while stirring vigorously for 1.5 hours—or until suspended solid in organic layer had completely dissolved and yellow color had paled. Reaction was cooled to room temperature and transferred to separatory funnel. Aqueous layer was removed and organic layer was washed with brine (3x25 mL) and dried with Na_2SO_4. Solvent was removed under reduced pressure to yield off-white solid. This solid, along with freshly dehydrated K_2CO_3 (1.2 g, 8.686 mmol) and a catalytic amount of 18-crown-6 (5 mg) was suspended in anhydrous acetone (75 mL) in a dry roundbottom. Bromobutane (940 µL, 8.68 mmol) was added and reaction was heated to reflux for 14 hours. Reaction was cooled to roomed temperature and solvent was removed under reduced pressure. CH_2Cl_2 (50 mL) was added and mixture was filtered. Solid was washed thoroughly with CH_2Cl_2 until filtrate no longer contained product by TLC analysis. Combined washes were washed with H_2O (3x50mL), dried with $MgSO_4$, and evaporated under reduced pressure to yield crude product. Crude product was purified by flash column chromatography (25% DCM in hexane gradient to 50% DCM in hexane) to yield pure product as white powder (979 mg, 98%). m.p. 284.1-286.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (dd, *J*= 5.3, 3.2 Hz, 8H), 6.93 (dd, *J*= 5.4, 3.2 Hz, 8H), 5.64 (s, 4H), 3.91 (t, *J*= 6.7 Hz, 4H), 1.99 (m, 4H), 1.72 (m, 4H), 1.14 (t, *J*= 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.2, 145.5, 136.4, 125.2, 123.7, 76.1, 48.5, 32.8, 19.9, 14.3; IR (cm^{-1}): 3067, 3018, 2955, 1480, 1459, 1376, 1301, 1257, 1067, 1024, 751, 554; HRMS (ESI) calcd for $C_{42}H_{39}O_2$ $[M+H]^+$ 575.2950, found 575.2946.

Synthesis of 3. A flame dried 10 mL schlenck flask was charged with compound **2** (70 mg, 0.122 mmol) and a catalytic amount of iron filings (9 mg). The reaction flask was evacuated and backfilled with argon three times. Anhydrous dichloromethane (8 mL) was added and reaction was stirred for five minutes until starting material was fully dissolved. Freshly distilled Br_2 (55 µL, 1.06 mmol) was added, and reaction was heated to reflux under an argon atmosphere for 90 minutes. Reaction was cooled first to room temperature and then to 0°C. K_2CO_3 (~50 mg) was added and reaction was allowed to warm to room temperature and continue stirring for 10 hours. Solvent was removed under reduce pressure. Solid was taken up in hot chloroform (~75 mL) in order to dissolve the maximum amount of solid. Suspension was filtered through a sort silica pad. Solvent was removed under reduced pressure to yield crude product as pale yellow solid. Solid was then washed with acetone and a minimal amount of cold dichloromethane followed by collection by centrifugation to yield product as white powder (116 mg, 79. A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (s, 8H), 5.50 (s, 4H), 3.87 (t, *J*= 8.9 Hz, 4H), 1.94 (m, 4H), 1.70 (m, 4H), 1.15 (t, *J*= 9.7 Hz, 6H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4, 145.0. 135.5, 128.9, 121.5, 76.6, 46.7, 32.8, 19.9, 14.3; IR (cm^{-1}): 2951, 2866, 1465, 1436,1359, 1266, 1065, 1028, 917, 858, 786, 532; HRMS (MALDI-TOF) calcd for $C_{42}H_{30}Br_8O_2$ $[M]^+$ 1205.5631, found 1205.5664.

Synthesis of compounds 4a – 4o



product	—R	coupling partner	yield (%)
4a	—Me	$AlMe_3$	94
4b	—≡—Ph	≡—Ph	77
4c	—≡—C$_6$H$_4$—^{t}Bu	≡—C$_6$H$_4$—^{t}Bu	65
4d	—2-thienyl	Bu_3Sn—2-thienyl	76
4e	—C$_6$H$_5$	Bu_3Sn—C$_6$H$_5$	83
4f	—CH=CH$_2$	Bu_3Sn—CH=CH$_2$	70
4g	—2-furyl	Bu_3Sn—2-furyl	65
4h	—Ph	$PhB(OH)_2$	93
4i	—C$_6$H$_4$—OMe	$(HO)_2B$—C$_6$H$_4$—OMe	69
4j	—C$_6$H$_4$—CHO	$(HO)_2B$—C$_6$H$_4$—CHO	74
4k	—3-pyridyl	$(HO)_2B$—3-pyridyl	91
4l	—C$_6$H$_4$—CPh$_3$	Bpin—C$_6$H$_4$—CPh$_3$	85
4m	—C$_6$H$_4$—F	Bpin—C$_6$H$_4$—F	82
4n	—CH=CH$_2$		91
4o	—C$_6$H$_4$—CO$_2$Et	$(HO)_2B$—C$_6$H$_4$—CO$_2$Et	76

Synthesis of 4a. A flame dried 50 mL schlenck flask and condenser system was charged with **3** (150 mg, 0.124 mmol). The flask was evacuated and backfilled with argon three times. Anhydrous THF (24 mL) was added and suspension was thoroughly degassed. $PdCl_2(PPh_3)_2$ (35 mg, 0.0498 mmol) was added and mixture was further degassed. Reaction was heated to 60°C and allowe to stir for 30mins. 2 M $AlMe_3$ in hexanes (1 mL, 1.99 mmol) was added and reaction was heated to reflux for 12 hours. Reaction was

cooled down to 0^0C and 2 M HCl was added dropwise until bubbling ceased. Organics were washed with Brine 3x, dried over $MgSO_4$ and evaporated under reduced pressure. Product was purified by flash column chromatography (15% DCM in Hexane) to yield product as white solid (80 mg, 94%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (s, 8H), 5.47 (s, 4H), 3.88 (t, *J*= 6.7 Hz, 4H), 2.07 (s, 24H), 1.98 (m, 4H), 1.71 (m, 4H), 1.14 (t, *J*= 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.8, 143.4, 136.8, 132.7, 125.0, 75.9, 47.6, 32.9, 19.9, 19.5, 14.4; IR (cm^{-1}): 2959, 2918, 2852, 1463, 1261, 1068, 1026, 860, 799, 556; HRMS (ESI) calcd for $C_{50}H_{55}O_2$ $[M+H]^+$ 687.4202, found 687.4228.

Synthesis of 4b. To a 100 mL round bottom flask were added anhydrous DMF (5 mL), NEt_3 (1 mL), **3** (120.6 mg, 0.100 mmol), and PPh_3 (15.7 mg, 0.060 mmol). The resulting mixture was cooled down to -78 °C before it was connected to vacuum for 30 min. It was then allowed to warm up to room temperature under Argon atmosphere. Phenylacetylene (490 mg, 4.80 mmol), $Pd(PPh_3)_4$ (34.7 mg, 0.030 mmol), and CuI (5.7 mg, 0.030 mmol) were added into the reaction flask, and the reaction mixture was cooled down in a dry ice-acetone bath before it was connected to vacuum again for 5 min. The flask was then gradually heated up and the reaction was stirred at 65 °C under argon for 48 hours. A 1:1 water-acetone mixture (20 mL) was added in to quench the reaction and the crude product was collected by filtration. The obtained solids were further washed with excess of water and acetone, and they were proved to be pure by ^{1}H NMR (106 mg, 77 %) after solvent removal. A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (s, 8H), 7.50 (m, 16H), 7.30 (m, 24H), 5.67 (s, 4H), 3.99 (t, *J*= 6.4 Hz, 4H), 2.06-2.00 (m, 4H), 1.87-1.79 (m, 4H), 1.23 (t, *J*= 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4, 144.3, 135.6, 131.8, 128.45, 128.43, 127.0, 123.5, 123.4, 93.2, 88.6, 76.5, 47.8, 33.0, 20.1, 14.4; IR (cm^{-1}): 2936, 2860, 1596, 1493, 1460, 1255, 1060, 1027, 912, 752, 688, 564, 529, 456; HRMS (ESI) calcd for $C_{106}H_{70}O_2Na$ $[M+Na]^+$ 1397.5268, found 1397.5284.

Synthesis of 4c. To a 15 mL round bottom flask was added **3** (30.0 mg, 0.0249 mmol), dry DMF (5 mL) and Et_3N (1 mL). The mixture was freeze pump thawed (1x). $Pd(PPh_3)_4$ (28.8 mg, 24.9 µmol), CuI (8.5 mg, 44.6 µmol) PPh_3 (25.5 mg, 97.2 µmol) and 4- *tert*butylphenyl acetylene (0.82 mL, 3.98 mmol) were added to the suspension. The reaction was freeze pump thawed again (1x) and then heated to 65 °C for 48 hours and then cooled to room temperature. The solvent was then removed under reduced pressure leaving a crude brown solid. The crude product was purified via flash column chromatography (1% DCM in Hexanes) to yield **4c** as light brown solid (29.6 mg, 65%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (s, 8H), 7.44 (d, *J* = 8.4 Hz, 16H), 7.33 (d, *J* = 8.6 Hz, 16H), 5.65 (s, 4H), 3.97 (t, *J* = 6.5 Hz, 4H), 2.06 – 1.99 (m, 4H), 1.88 – 1.77 (m, 4H), 1.31 (s, 72H), 1.23 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.6, 146.3, 144.2, 135.6, 131.5, 127.0, 125.4, 123.5, 120.6, 93.2, 88.1, 76.5, 47.7, 34.9, 33.0, 31.3, 20.1, 14.4; IR (cm^{-1}): 3036, 2959, 1504; HRMS (MALDI-TOF) calcd for $C_{138}H_{134}O_2$ $[M+Na]^+$ 1846.028, found 1846.033.

Synthesis of 4d. To a 15 mL roundbottom flask was added DMF (3 mL), **3** (30.0 mg, 0.0248 mmol) and 2-tributylstannyl thiophene (79µL, 0.249 mmol). Suspension was thoroughly degassed by freeze pump thaw method (2x). $PdCl_2(PPh_3)_2$ (7 mg, 0.010 mmol) was added and reaction was further degassed via one more round of freeze pump thaw and backfilled with argon. Reaction was heated to 130°C for 16 hours. Reaction was cooled to room temperature. Solvent was evaporated under reduced pressure to yield brown solid/film. Solid was taken up in DCM (20 mL). Solution was washed with H_2O, dried over $MgSO_4$ and

evaporated under reduced pressure. Solid was purified via flash column chromatography (25% DCM in hexane) to yield product as off-white solid (23.4 mg, 76%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (s, 8H), 7.20 (dd, *J*= 5.1, 1.2 Hz, 8H), 6.89 (dd, *J*= 5.1, 3.5 Hz, 8H), 6.76 (dd, *J*= 3.6, 1.2 Hz, 8H), 5.78 (s, 4H), 4.01 (t, *J*= 6.7 Hz, 4H), 1.98-2.05 (m, 4H), 1.69-1.78 (m, 4H), 1.11 (t, *J*= 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4, 144.6, 142.7, 136.1, 131.2, 127.2, 126.9, 126.5, 126.0, 76.5, 47.7, 32.8, 20.0, 14.3; IR (cm^{-1}): 3105, 2959, 2928, 2889, 1489, 1273, 1249, 1035, 907, 849, 830, 694; HRMS (MALDI-TOF) calcd for $C_{74}H_{54}O_2S_8$ $[M]^+$: 1230.1890, found 1230.1852.

Synthesis of 4e. To a 10 mL Schlenk flask was added **3** (30.0 mg, 0.0249 mmol) and DMF (3.5 mL). The mixture was freeze pump thawed (2x). $PdCl_2(PPh_3)_2$ (7.1 mg, 10.1 µmol) was added to the mixture and the reaction was freeze pump thawed again (1x). Finally, 4-(tributylstannyl)toluene (103 mg, 270 µmol) was added to and the reaction was freeze pump thawed (1x). The reaction was heated for 16 hours at 95 °C under argon, then cooled to room temperature and concentrated under reduced pressure, leaving the crude mixture as a brown solid. The crude product was purified via flash column chromatography (10% DCM in Hexanes) to yield a glassy white solid. Solid rinsed with cold hexanes to yield product **x** as a white solid (26.8 mg, 83%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (s, 8H), 6.95 (d, *J* = 8.2 Hz, 16H), 6.92 (d, *J* = 8.2 Hz, 16H), 5.77 (s, 4H), 3.98 (t, *J* = 6.4 Hz, 4H), 2.27 (s, 24H), 2.01-1.95 (m, 4H), 1.79- 1.72 (m, 4H), 1.09 (t, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4, 144.4, 138.8, 137.5, 136.5, 135.9, 129.9, 128.6, 126.1, 76.2, 48.0, 32.9, 21.3, 20.1, 14.3; IR (cm^{-1}): 3036, 2959, 1504; HRMS (MALDI-TOF) calcd for $C_{98}H_{86}O_2$ $[M+H]^+$ 1295.671, found 1295.673.

Synthesis of 4f. To a 5 mL roundbottom flask was added **3** (34.5 mg, 0.0286 mmol) suspended in DMF (3.5 mL). Suspension was degassed via freeze-pump-thaw method (2x). Allyltributylstannane (89µL, 0.286 mmol) was added and suspension was cooled to -78°C and stirred under vacuum for 5 minutes, followed by being backfilled with argon. $PdCl_2(PPh_3)_2$ (8.0 mg, 0.011 mmol) was added and suspension was stirred under vacuum at -78°C for 5 more minutes, and backfilled with argon. Reaction was heated to 95°C for 14 hours. Reaction was allowed to cool to room temperature. Solvent was removed under reduced pressure. Reaction mixture was filtered through short silica pad followed by purification by flash column chromatography (25% DCM in Hexanes) to yield white solid product with tin impurities. Solid was washed with hexane and collected by centrifugation to yield pure white solid product. Remainder of product was crystallized from hexane wash by slow evaporation to a minimal amount of solvent and cooling in refrigerator for 12 hours to complete the crystallization. Crystals were added to original solid to yield pure product as white solid (17.9 mg, 70%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (s, 8H), 5.81(ddt, *J*= 16.7 Hz, 10.4 Hz, 6.5 Hz, 8H), 5.52 (s, 4H), 4.94-4.99 (m, 16H), 3.87 (t, *J*= 7.0 Hz, 4H), 3.24 (d, *J*=6.5 Hz, 16 H), 1.92-1.99 (m, 4H), 1.58-1.67 (m, 4H), 1.10 (t, *J*= 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.0, 143.9, 137.2, 136.6, 134.4, 124.7, 115.9, 76.0, 47.7, 37.1, 32.7, 19.7, 14.3; IR (cm^{-1}): 3078, 3005, 2960, 2932, 1638, 1467, 1265, 1071, 1028, 995, 906, 734, 558; HRMS (ESI) calcd for $C_{66}H_{71}O_2$ $[M+H]^+$ 895.5454, found 895.5490.

Synthesis of 4g. To a 10 mL roundbottom flask was added DMF (3 mL) and **3** (30.6 mg, 0.0254 mmol). Suspension was deoxygenate via free ze pump thaw method (2x). 2-tributylstannyl furan (80µL, 0.254 mmol) was added and suspension was further deoxygenated with one more cycle. $PdCl_2(PPh_3)_2$ (7.1 mg, 0.010 mmol) was added and reaction was further degassed via one final round of freeze pump thaw and backfilled with argon. Reaction was heated to 130°C for 16 hours. Reaction was evaporated under reduced pressure to yield crude product brown solid/film. Solid was purified by flash column

chromatography (35% DCM in hexane gradient to 40% DCM in hexane) to yield product as white solid still containing aliphatic impurities by NMR. Product was further purified by trituration with hexanes and finally collected by centrifugation to yield product as white solid (18.1 mg, 65%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (s, 8H), 7.37 (dd, *J*= 1.8, 0.8 Hz, 8H), 6.34 (dd, *J*= 3.4, 1.8 Hz, 8H), 5.89 (dd, *J*= 3.3, 0.8 Hz, 8H), 5.77 (s, 4H), 4.00 (t, *J*= 6.7 Hz, 4H), 1.98-2.06 (m, 4H), 1.70-1.80 (m, 4H), 1.14 (t, *J*= 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.0, 146.3, 144.7, 141.7, 136.0, 126.5, 124.3, 111.4, 108.2, 76.4, 47.9, 32.9, 20.0, 14.3; IR (cm^{-1}): 3118, 2958, 2931, 1499, 1457, 1274, 1155,1008, 905, 809, 731, 594; HRMS (ESI) calcd for $C_{74}H_{55}O_{10}$ $[M+H]^+$ 1103.3795, found 1103.3790.

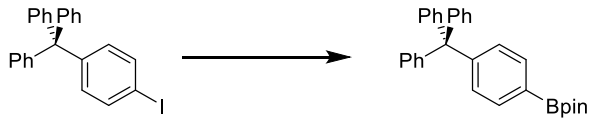
Synthesis of 4h. A flame dried 50 mL schlenk flask was charged with phenylboronic acid (162 mg, 1.33 mmol) and K_3PO_4 (563 mg, 2.65 mmol). The flask was evacuated and backfilled with argon three times. Anhydrous THF (12 mL) was added and reaction was degassed with argon. $Pd(P\mathit{t}Bu_3)_2$ (17 mg, 0.033 mmol) was added and reaction was further degassed. **3** (100 mg, 0.083 mmol) was added and reaction was further degassed. Reaction mixture was heated to 40°C and stirred for 14 hours. Reaction was cooled to room temperature. Reaction mixture was washed with saturated NH_4Cl solution (3x20 mL), dried with $MgSO_4$ and concentrated under reduced pressure to yield crude product. Crude product was purified by flash column chromatography (30% DCM in Hexane gradient to 40% DCM in Hexane) to yield product as white solid (91 mg, 93%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (s, 8H), 7.15-7.14 (m, 24H), 7.05-7.02 (m, 16H), 5.84, (s, 4H), 4.02 (t, *J*= 6.4 Hz, 4H), 2.05-1.97 (m, 4H), 1.81-1.72 (m, 4H), 1.09 (t, *J*= 7.3 Hz, 6H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.5, 144.6, 141.6, 137.8, 136.5, 130.1, 127.9, 126.4, 126.1, 76.3, 48.0, 32.9, 20.1, 14.3; IR (cm^{-1}): 3021, 2923, 2855, 1600, 1464, 1276, 1248, 1072, 763, 700, 574; HRMS (ESI) calcd for $C_{90}H_{74}NO_2$ $[M+NH_4]^+$ 1200.5714, found 1200.5734.

Synthesis of 4i. To a 15 mL sealed tube was added THF (5mL), H_2O (2mL), **3** (29.3 mg, 0.0243 mmol), 4-methoxyphenylboronic acid (118 mg, 0.777 mmol) and K_2CO_3 (137 mg, 0.992 mmol). Suspension was thoroughly degassed with Argon. $Pd(PPh_3)_4$ (11.5 mg, 9.9μmol) was added and reaction was further degassed, before being sealed under argon. Reaction was heated to 95°C for 14 hours. Reaction was cooled to room temperature. Aqueous layer was removed. Organics were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. Crude product was purified by flash column chromatography (70% DCM in hexane slow gradient to DCM) to yield pale yellow solid. Solid was suspended in acetone/MeOH mixture and collected via centrifugation (2x) to yield pure product as white powder (23.7 mg, 69%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (s, 8H), 6.95 (d, *J* = 8.8 Hz, 16H), 6.70 (d, *J*= 8.8 Hz, 16 H), 5.78 (s, 4H), 4.00 (t, *J*= 6.5 Hz, 4H), 3.75 (s, 24H), 1.97-2.04 (m, 4H), 1.71-1.81 (m, 4H), 1.10 (t, *J*=7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.2, 146.4, 144.3, 137.1, 136.5, 134.2, 131.1, 126.0, 113.4, 76.2, 55.3, 48.0, 32.9, 20.1, 14.3; IR (cm^{-1}): 2958, 2932, 2834, 1608, 1513, 1464, 1291, 1244, 1177, 1034, 908, 831, 732, 558; HRMS (MALDI-TOF) calcd for $C_{98}H_{86}O_{10}$ $[M]^+$ 1422.6221, found 1422.6220.

Synthesis of 4j. To a 10 mL sealed tube was added THF (6mL), H_2O (2mL), **3** (30.0 mg, 0.0249 mmol), freshly recrystallized 4-formylphenylboronic acid (45 mg, 0.299 mmol) and K_2CO_3 (138 mg, 1.00 mmol). Suspension was thoroughly degassed with Argon. $Pd(PPh_3)_4$ (11.5 mg, 0.010) was added and reaction was further degassed, before being sealed under argon. Reaction was stirred in sealed tube at 95°C for 15 hours. Reaction became a solution that stayed in solution upon cooling to room temperature. Aqueous layer was removed. Organics were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. Crude product was purified by flash column chromatography (DCM slow gradient to 5% diethyl ether in DCM) to yield product as white solid (26.1 mg, 74%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.95 (s, 8H), 7.70 (d, *J* = 8.4 Hz, 16H), 7.52 (s, 8H), 7.18 (d, *J*= 8.2 Hz, 16 H), 5.93 (s, 4H), 4.06 (t, *J*= 6.6 Hz,

4H), 2.01-2.08 (m, 4H), 1.70-1.79 (m, 4H), 1.08 (t, *J*=7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.8, 147.0, 146.7, 145.3, 137.0, 136.2, 134.9, 130.6, 129.7, 126.1, 76.0, 48.0, 32.8, 20.0, 14.3; IR (cm^{-1}): 2959. 2828, 1699, 1602, 1465, 1209, 1168, 830; HRMS (MALDI-TOF) calcd for $C_{98}H_{70}O_{10}$ $[M]^+$ 1406.4969, found 1406.4902.

Synthesis of 4k. To a 15 mL sealed tube was added THF (6mL), H_2O (2mL), **3** (29.9 mg, 0.0248 mmol), 4-pyridinylboronic acid (111.8 mg, 0.793 mmol) and K_2CO_3 (137 mg, 0.992 mmol). Suspension was thoroughly degassed with Argon. $Pd(PPh_3)_4$ (11.5 mg, 9.9μmol) was added and reaction was further degassed, before being sealed under argon. Reaction was heated to 90°C for 12 hours. Reaction was allowed to cool to room temperature. Aqueous layer was removed, and organics were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Crude material was purified by flash column chromatography (1% Et_3N in DCM gradient to 1% Et_3N and 8% MeOH in DCM) to yield white solid containing 1:1 ratio of desired product to triethyl ammonium. Solid was freebased by dissolving in DCM and washing with $NaHCO_3$ and drying over $MgSO_4$. Solvent was removed under reduced pressure to yield product as white solid (26.9 mg, 91%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 5.8 Hz, 16H), 7.48 (s, 8H), 6.94 (d, *J*= 6.1 Hz, 16 H), 5.92 (s, 4H), 4.04 (t, *J*= 6.6 Hz, 4H), 2.00-2.08 (m, 4H), 1.70-1.79 (m, 4H), 1.09 (t, *J*=7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.9, 148.2, 146.8, 145.7, 136.0, 135.6, 126.0, 124.6, 76.7, 47.9, 32.8, 20.0, 14.3; IR (cm^{-1}): 3025, 2958, 2872, 1598, 1465, 826, 730, 578; HRMS (MALDI-TOF) calcd for $C_{82}H_{63}N_8O_2$ $[M+H]^+$ 1191.5074, found 1191.5106.



7 **8**

Synthesis of TetraphenylBpin 8.[3] To a 25 mL round bottom flask was added tetraphenylmethyl iodide **7** (300mg, 0.672mmol), B_2Pin_2 (295mg, 1.16 mmol) and KOAc (198 mg, 2.016 mmol) were taken up in DMF (16mL). Suspension was deoxygenated by freeze-pump-thaw method. $Pd(OAc)_2$ (7.5 mg, 0.0336 mmol) was added, and solution was further deoxygenated. Reaction was heated to 100°C for 12 hours. Reaction mixture was filtered through celite pad. Solvent was removed under reduce pressure. Solid was taken up in ether/water mixture. Aqueous layer was removed and organics were washed with aqueous NH_4Cl (3x). Organics were dried over $MgSO_4$ and concentrated under reduced pressure to yield pale brown solid as crude product. Crude product was purified by flash column chromatography (20% DCM in hexane) to yield white solid. Solid was triturated with MeOH to remove remaining B_2Pin_2 reagent to yield pure product as white solid (202mg, 67%). m.p. 241-243°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J*= 8.4 Hz, 2H), 7.24-7.15 (m, 17H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.1, 146.8, 134.1, 131.3, 130.7, 127.6, 126.0, 83.9, 65.3, 25.0; IR (cm^{-1}): 3083, 2976, 1609, 1492, 1397, 1381, 1144, 750, 701; HRMS (DART) calcd for $C_{31}H_{32}BO_2$ $[M+H]^+$ 447.2495, found 447.24787.

Synthesis of 4l. To a 20 mL sealed tube was added THF (9mL), H_2O (3mL), **3** (65 mg, 0.054 mmol), **8** (289 mg, 0.647 mmol) and K_2CO_3 (298 mg, 2.156 mmol). Suspension was thoroughly degassed with Argon. $Pd(PPh_3)_4$ (25 mg, 0.0216) was added and reaction was further degassed, before being sealed under argon. Reaction was stirred in sealed tube at 95°C for 13 hours. Reaction became a solution that stayed in solution upon cooling to room temperature. Aqueous layer was removed, and organics were dried over $MgSO_4$ and evaporated under reduced pressure. Solid was then taken up in biphasic DCM/ H_2O mixture. Organic layer was washed with H_2O (3x), dried—once again—over $MgSO_4$, and concentrated under reduced pressure. Crude brown solid was purified by flash column chromatography

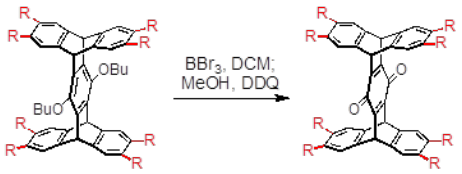
(20% DCM in Hexanes) to yield white solid, which contained a mixture of desired product **4l** and **8**. Bpin **8** could then be removed by triturating solid with hexanes and filtered until filtrate, was clean by TLC to yield pure **4l** as white solid. (143 mg, 85%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (s, 8H), 7.09-7.16 (m, 120H), 6.94 (d, *J*= 8.6 Hz, 16H), 6.84 (d, *J*= 8.5 Hz, 16H), 5.77 (s, 4H), 3.99 (t, *J*= 6.3 Hz, 4H), 2.01-1.95 (m, 4H), 1.78-1.69 (m, 4H), 1.06 (t, *J*= 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.8, 146.4, 144.9, 144.5, 139.1, 137.5, 136.4, 131.3, 130.6, 129.2, 127.5, 126.0, 125.7, 76.2, 64.8, 48.0, 32.9, 20.1, 14.3; IR (cm^{-1}): 3056, 3028, 2927, 1597, 1491, 1446, 1034, 830, 748, 699; HRMS (MALDI-TOF) calcd for $C_{242}H_{182}O_2$ $[M]^+$ 3119.4140 , found 3119.464.

Synthesis of 4m. To a 10 mL sealed tube was added THF (5mL), H_2O (2mL), **3** (28.7 mg, 0.0238 mmol), 4-fluorophenylboronic acid, pinacol ester (60.5 µL, 0.286 mmol) and K_2CO_3 (132 mg, 0.952 mmol). Suspension was thoroughly degassed with Argon. $Pd(PPh_3)_4$ (11.0 mg, 9.5µmol) was added and reaction was further degassed, before being sealed under argon. Reaction was stirred in sealed tube at 95°C for 15 hours. Aqueous layer was removed. Organic layer was washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure to yield crude product. Solid was purified by flash column chromatography (30% DCM in hexane) to yield white solid mixture of product and unreacted Bpin starting material. Solid was washed with hexane and collected by centrifugation to yield pure product as white solid (25.8 mg, 82%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 8H), 6.84-6.88 (m, 16H), 6.94-6.98 (m, 16H), 5.82 (s, 4H), 4.02 (t, *J*= 6.7 Hz, 4H), 1.98-2.05 (m, 4H), 1.69-1.78 (m, 4H), 1.08 (t, *J*= 7.3 Hz, 6H); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -116.4 (tt, *J*= 8.6 Hz, 5.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161. 8 (d, *J*= 246.3 Hz), 146.5, 144.7, 137.2 (d, *J*= 3.3 Hz), 136.8, 136.4, 131.5 (d, *J*= 7.9 Hz), 126.0, 115.1 (d, *J*= 21.3 Hz), 76.4, 47.9, 32.9, 20.0, 14.3; IR (cm^{-1}): 2959, 2832, 1605, 1511, 1466, 1226, 1158, 835, 542; HRMS (MALDI-TOF) calcd for $C_{90}H_{62}F_8O_2$ $[M]^+$ 1326.4622, found 1326.4596.

Synthesis of 4n. **3** (70 mg, 0.058 mmol), 2,4,6-trivinylcyclotriboroxane-pyridine (84 mg, 0.348 mmolo) and K_2CO_3 (64 mg, 0.464 mmol) were suspended in a biphasic mixture of THF (3 mL), dimethoxyethane (1.5 mL) and H_2O (0.75 mL) in a 10 mL sealed tube. Mixture was thoroughly degassed with argon. PPh_3 (15 mg, 0.058 mmol) and $Pd(OAc)_2$ (5.2 mg, 0.023 mmol) was added and reaction was further degassed. Sealed tube was closed and stirred in sand bath at 70°C for 4 hours. Reaction could be visually monitored as was completed once all solids had gone into solution and reaction resembled a biphasic solvent system. At this point, reaction was cooled to room temperature. Aqueous layer was removed and organics were evaporated under reduced pressure. Residue was dissolved in biphasic mixture of ethyl acetate (40 mL) and brine (30 mL). Aqueous layer was removed and organics were washed with brine two more times before being dried with Na_2SO_4 and concentrated under reduced pressure. Residue was taken up in a 1:1 mixture of DCM and hexanes and ***quickly*** flushed through a silica plug.[4] Solvent was then concentrated under reduced pressure to yield pale yellow solid as crude product. Crude material could then be recrystallized from hexanes to yield pure product as white solid (41.2 mg, 91%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 8H), 6.87 (dd, *J*= 17.4, 11.0 Hz, 8H), 5.64 (s, 4H), 5.50 (dd, *J*= 17.4, 1.2 Hz, 8H), 5.21 (dd, *J*= 11.0, 1.2 Hz, 8H), 3.96 (t, *J*= 6.8 Hz, 4H), 2.06-1.98 (m, 4H), 1.78-1.65 (m, 4H), 1.14 (t, *J*= 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.0, 144.5, 136.1, 134.8, 133.4, 121.5, 115.9, 76.3, 48.0, 32.8, 19.8, 14.3; IR (cm^{-1}): 2954, 2927, 2867, 1624, 1463, 1425, 1271, 1247, 1067, 1029, 986, 903, 750, 555; HRMS (ESI) calcd for $C_{58}H_{55}O_2$ $[M+H]^+$ 783.4202, found 783.4224.

Synthesis of 4o. To a 10 mL pressure tube was added **3** (30.4 mg, 25.2 µmol), 4-ethoxycarbonylphenyl-boronic acid (90.1 mg, 464 µmol), K_2CO_3 (156 mg, 1.13 mmol) and $Pd(PPh_3)_4$ (13.0 mg, 11.3 µmol) followed by THF (6 mL) and water (2 mL). The suspension was degassed by the freeze pump thaw method (1x). The reaction vessel was sealed and heated at 90 °C for 16 hours and then cooled to room

temperature. THF (20 mL) was added and the organic layer was washed with brine, dried over magnesium sulfate and concentrated en vacuo to yield a brown solid. The crude mixture was purified via flash column chromatography (10% EtOAc in Hexane) to yield **4o** as a white solid (33.9 mg, 76%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.5 Hz, 16H), 7.48 (s, 8H), 7.08 (d, *J* = 8.5 Hz, 16H), 5.89 (s, 4H), 4.34 (q, *J* = 7.1 Hz, 16H) 4.04 (t, *J* = 6.6 Hz, 4H) 2.07–1.98 (m, 4H), 1.79–1.66 (m, 4H), 1.37 (t, *J* = 7.1 Hz, 24H), 1.08 (t, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.6, 146.6, 145.6, 145.1, 137.1, 136.3, 130.0, 129.5, 128.9, 126.1, 76.6, 61.1, 48.0, 32.8, 20.0, 14.5, 14.3; IR (cm^{-1}): 3044, 2958, 1713, 1608; HRMS (MALDI-TOF) cacld for $C_{114}H_{102}O_{18}$ $[M+Na]^+$ 1781.6965, found 1781.6905.



Synthesis of 5a. A flame dried 25mL round bottom was charged with pentiptycene **4a** (50mg, 0.073), dissolved in anhydrous DCM (19mL). Solution was cooled to -78°C. BBr_3 (510 µL, 0.51 mmol, 1M in DCM) was added dropwise. Upon completion of addition dry ice bath was removed and reaction was allowed to gradually warm to room temperature and stir until TLC showed complete dealkylation (45 minutes). Reaction was then cooled to 0°C. MeOH (100 µL) was added dropwise. DDQ (41 mg, 0.18 mmol). Reaction was allowed towarm to room temperature, and stir for a further 20 minutes. Aqueous sodium bicarbonate was added and stirred. Sufficient DCM was added to fully dissolve all solids. Biphasic mixture was extracted with DCM. Organics were dried over $MgSO_4$. Crude product was purified by flash column chromatograph (35% DCM in Hexane) to yield product as orange solid (35 mg, 85%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (s, 8H), 5.57 (s, 4H), 2.09 (s, 24H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.4, 151.6, 141.7, 133.3, 125.6, 46.6, 19.5; IR (cm^{-1}): 2965, 1644, 1594, 1471, 1457, 1301, 1199, 902, 750, 728, 570; HRMS (ESI) calcd for $C_{42}H_{37}O_2$ $[M+H]^+$ 573.2794, found 573.2786.

Synthesis of 5h. A flame dried 15mL round bottom was charged with pentiptycene **4h** (32mg, 0.027 mmol), dissolved in anhydrous DCM (7mL). Solution was cooled to -78°C. BBr_3 (190 µL, 0.190 mmol, 1M in DCM) was added dropwise. Upon completion of addition dry ice bath was removed and reaction was allowed to gradually warm to room temperature and stir until TLC showed complete dealkylation (65 minutes). Reaction was then cooled to 0°C. MeOH (100 µL) was added dropwise. DDQ (12.3 mg, 0.054 mmol) was added and reaction was allowed towarm to room temperature, and stir for a further 20 minutes. Aqueous sodium bicarbonate was added and stirred. Sufficient DCM was added to fully dissolve all solids. Biphasic mixture was extracted with DCM. Organics were dried over $MgSO_4$. Crude product was purified by flash column chromatograph (40% DCM in Hexane) to yield product as orange solid (24 mg, 83%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (s, 8H), 7.15 (m, 24H), 7.03 (m, 16H), 5.94 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.0, 151.2, 142.8, 141.1, 138.2, 130.0, 128.0, 126.8, 126.7, 47.0; IR (cm^{-1}): 2920, 2851, 1641, 1592, 1463, 1129, 910, 758, 698, 584, 565, 525; HRMS (ESI) calcd for $C_{82}H_{53}O_2$ $[M+H]^+$ 1069.4045, found 1069.4027.

Synthesis of 5l. A flame dried 10mL schlenk flask was charged with pentiptycene **4l** (45mg, 0.0144 mmol) dissolved in anhydrous DCM (3mL). Solution was cooled to -78°C. BBr_3 (101 µL, 0.101 mmol, 1M in DCM) was added dropwise. Upon completion of addition, reaction was allowed to gradually warm to room temperature and stir until TLC showed complete dealkylation (2 hours and 35 minutes). Reaction

mixture was then cooled to 0^0C and MeOH (~50 μL) was added slowly. DDQ (6.5 mg, 0.029 mmol) was added and ice bath was removed in order to allow reaction to warm to room temperature, and stir for a further 20 minutes. Aqueous sodium bicarbonate was added and stirred. Sufficient DCM was added to fully dissolve all solids. Biphasic mixture was extracted with DCM (2x). Organics were dried over $MgSO_4$. Crude product was purified by flash column chromatography (30% DCM in Hexane) to yield product as orange solid (37 mg, 84%). A melting point determination was not possible because the solid decomposed when heated to 350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (s, 8H), 7.16-7.08 (m, 120H), 6.94 (d, *J*= 8.6 Hz, 16H), 6.83 (d, *J*= 8.6 Hz, 16H), 5.87 (s, 4H) ^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.0, 151.1, 146.8, 145.2, 142.7, 138.7, 137.9, 131.3, 130.7, 129.1, 127.5, 126.4, 126.0, 64.8, 47.0; IR (cm^{-1}): 2921, 2851, 1648, 1594, 1491, 1403, 1371, 1181, 1083, 831, 735, 700; HRMS (MALDI-TOF) calcd for $C_{2342}H_{164}O_2$ $[M]^+$ 3005. 2731, found 3005.277.

Figure S1. ^{1}H NMR of compound 2 in $CDCl_3$ at 400 MHz

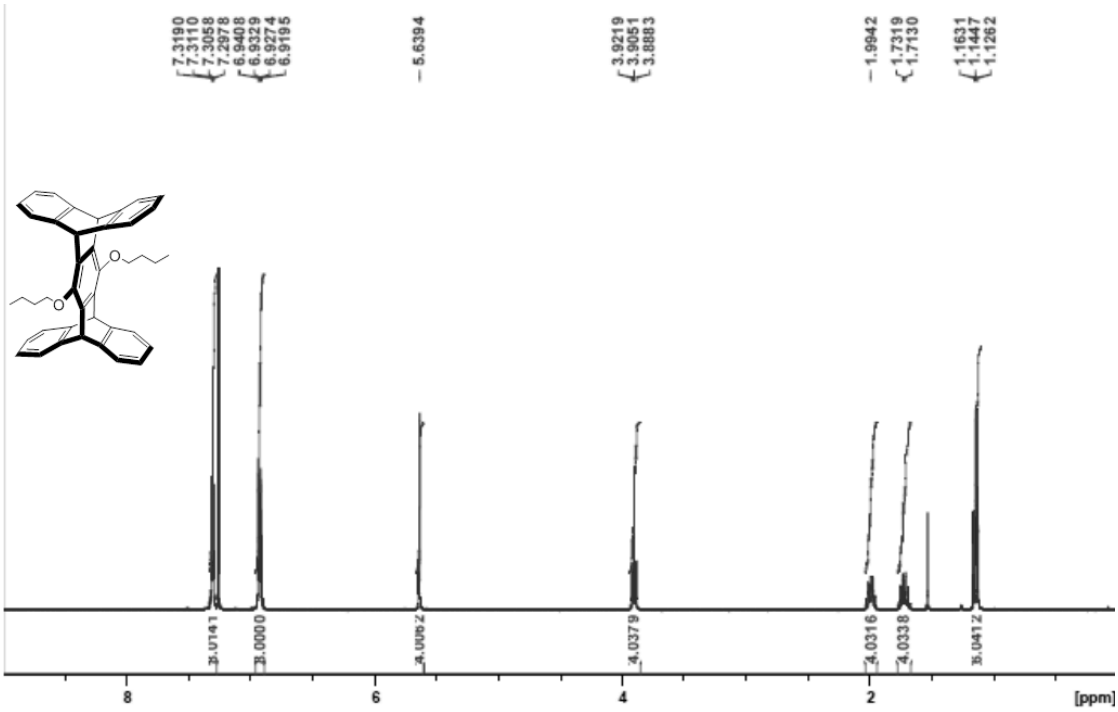


Figure S2. ^{13}C NMR of compound 2 in $CDCl_3$ at 125 MHz

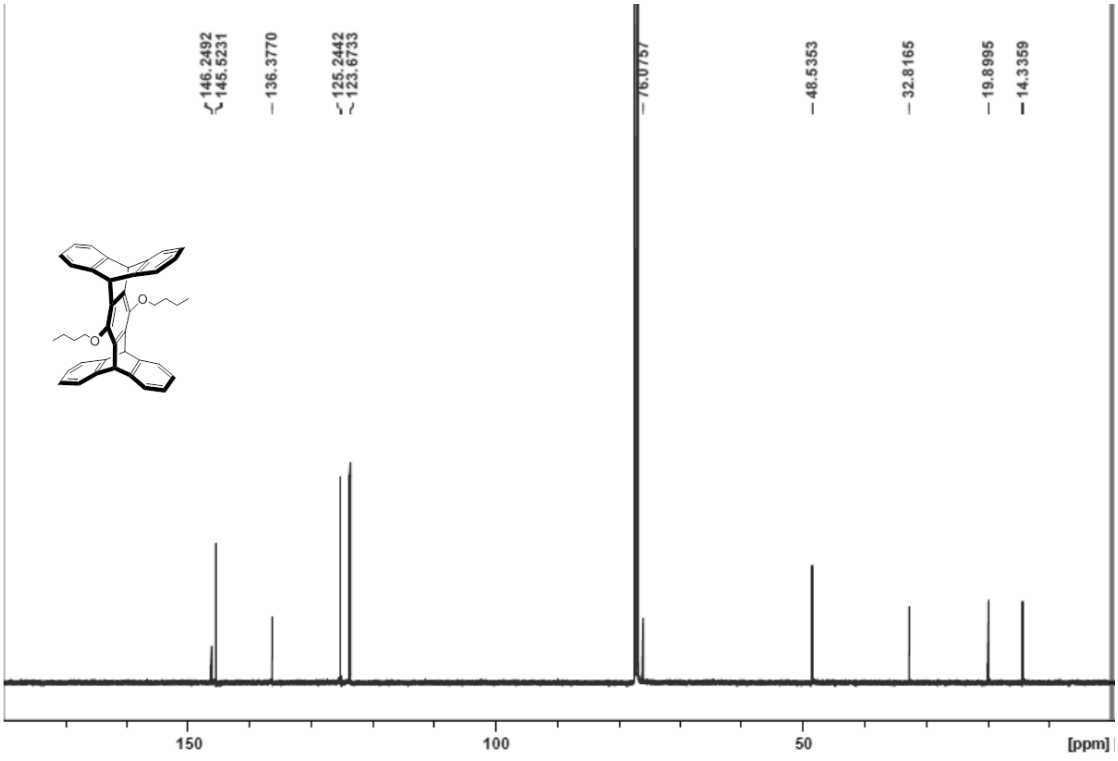


Figure S3. ^{1}H NMR of compound 3 in $CDCl_3$ at 400 MHz

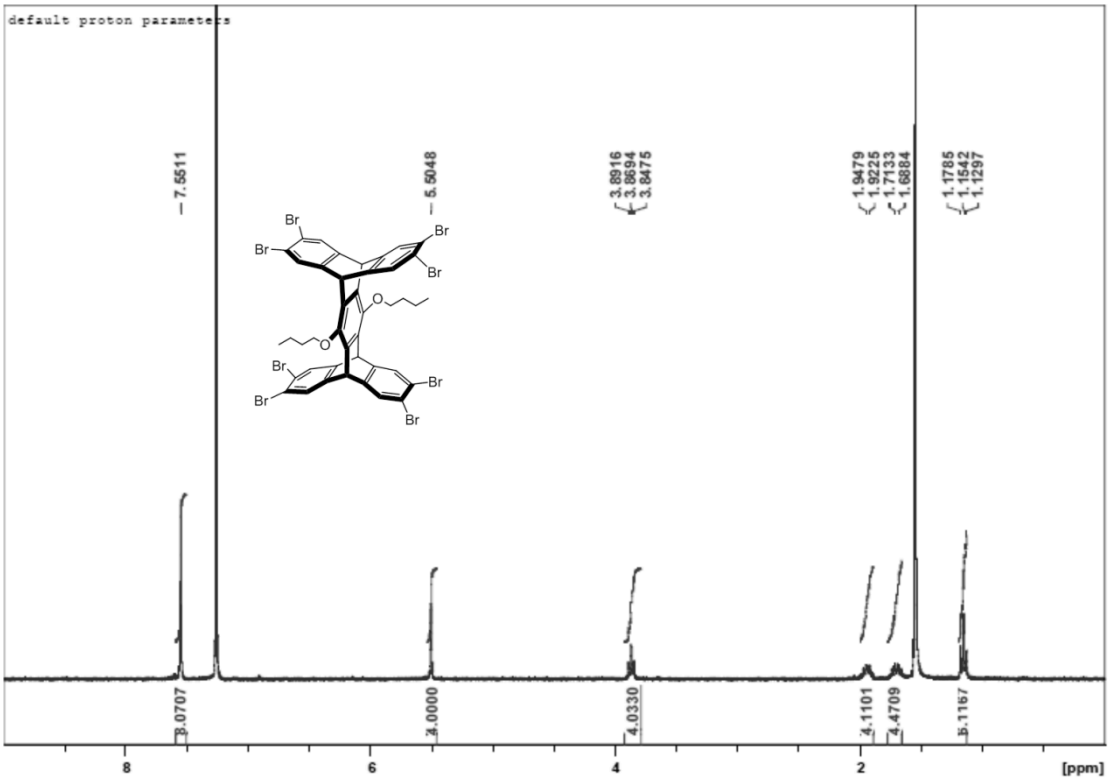


Figure S4. ^{13}C NMR of compound 3 in $CDCl_3$ at 125 MHz

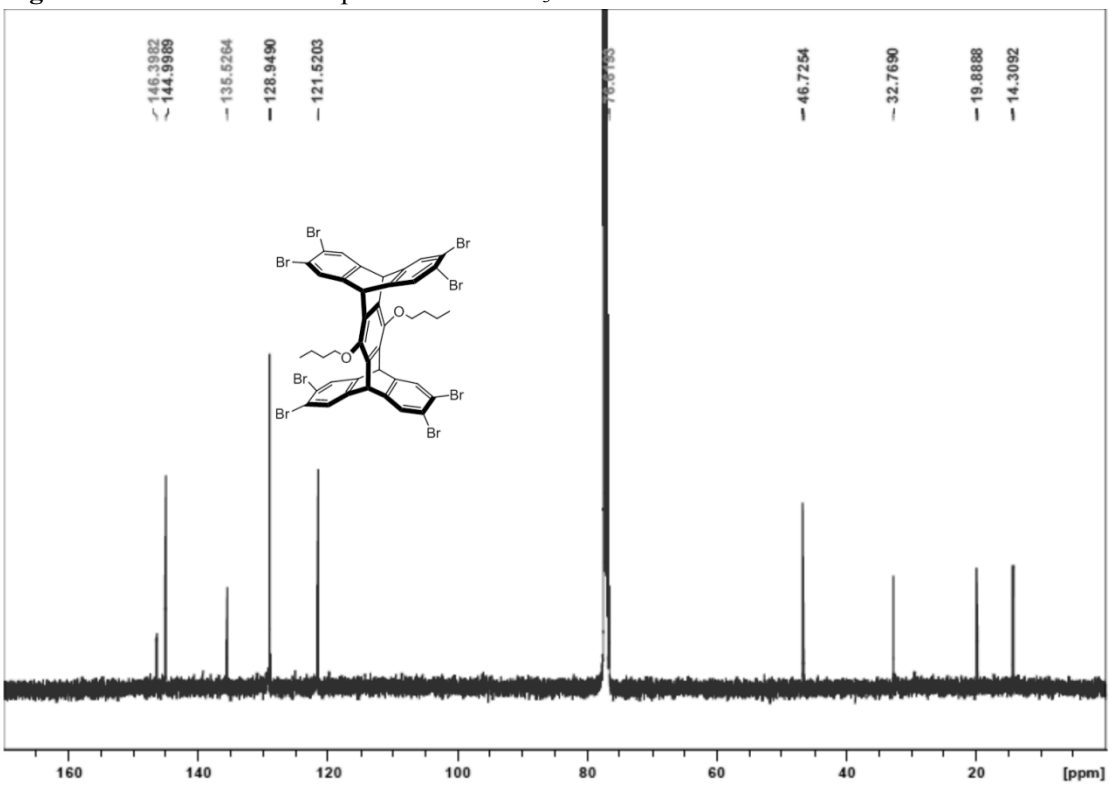


Figure S5. ^{1}H NMR of compound 4a in $CDCl_3$ at 400 MHz

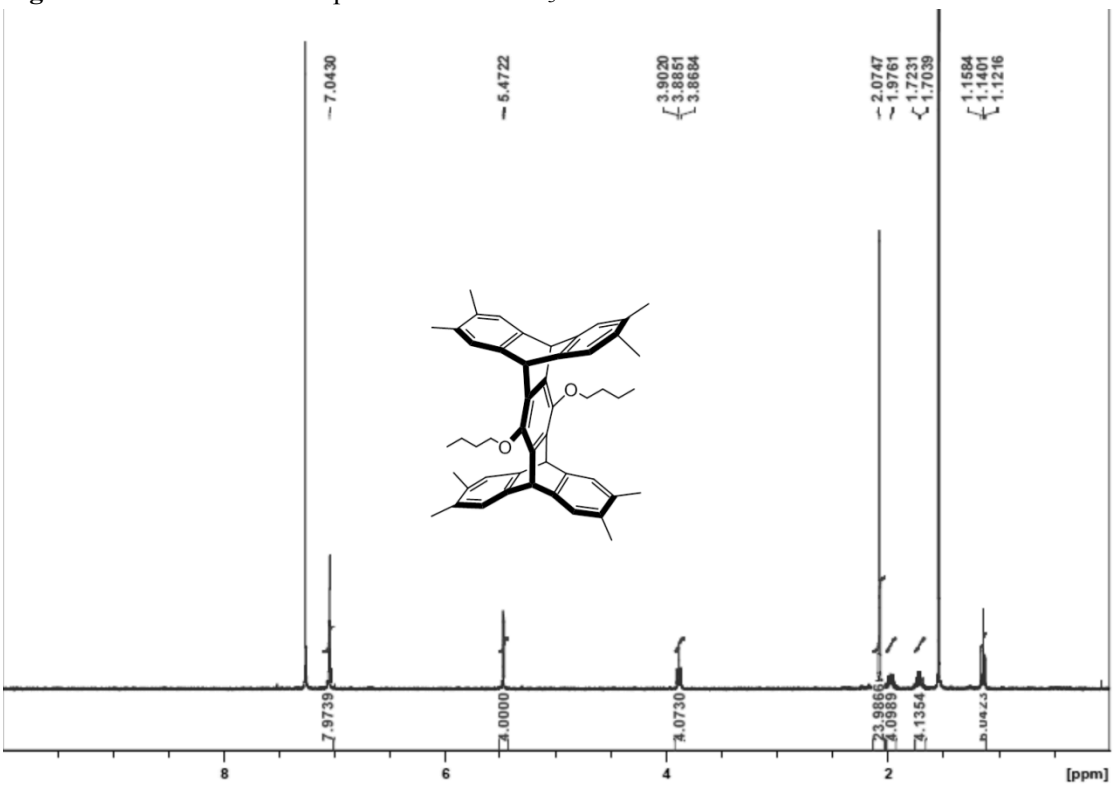


Figure S6. ^{13}C NMR of compound 4a in $CDCl_3$ at 125 MHz

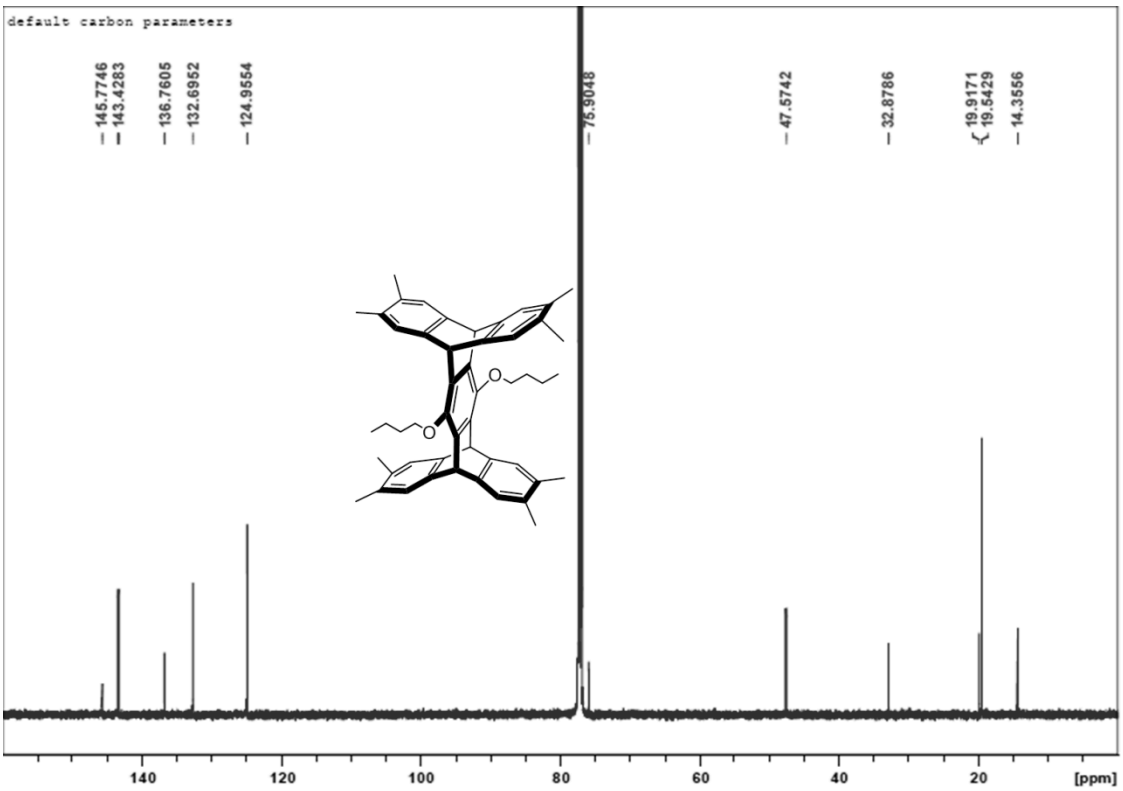


Figure S7. ^{1}H NMR of compound 4b in $CDCl_3$ at 400 MHz

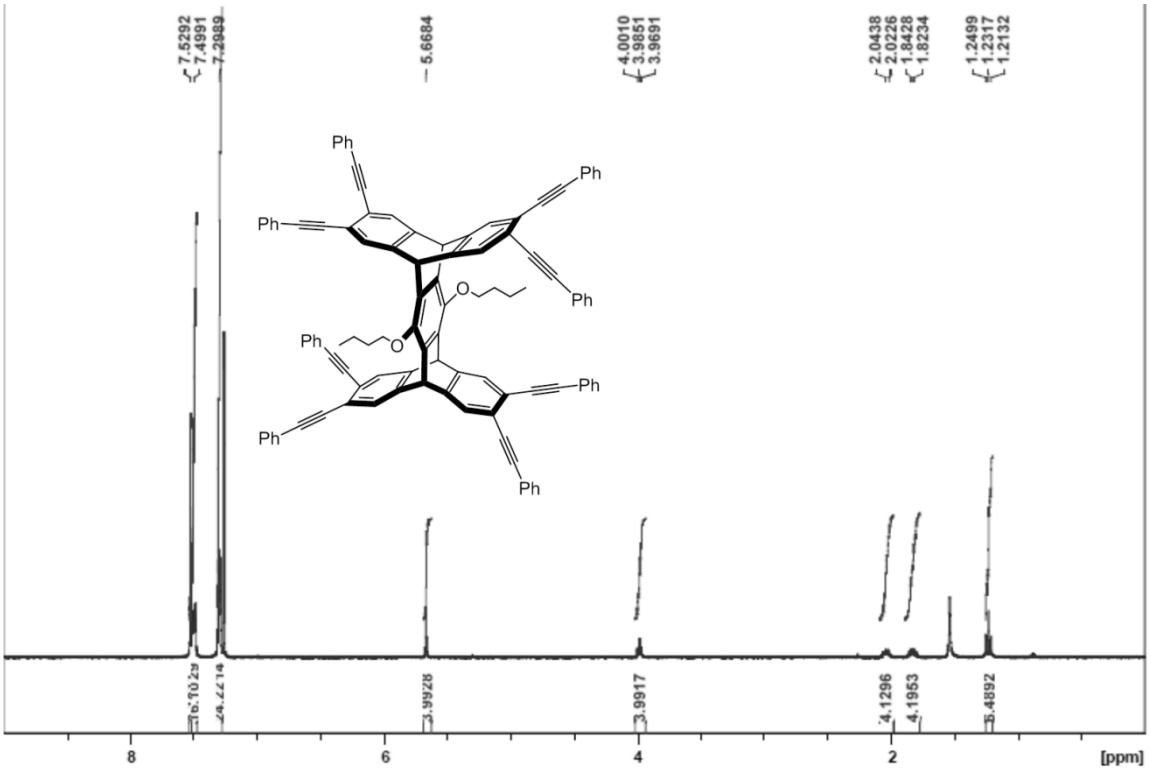


Figure S8. ^{13}C NMR of compound 4b in $CDCl_3$ at 125 MHz

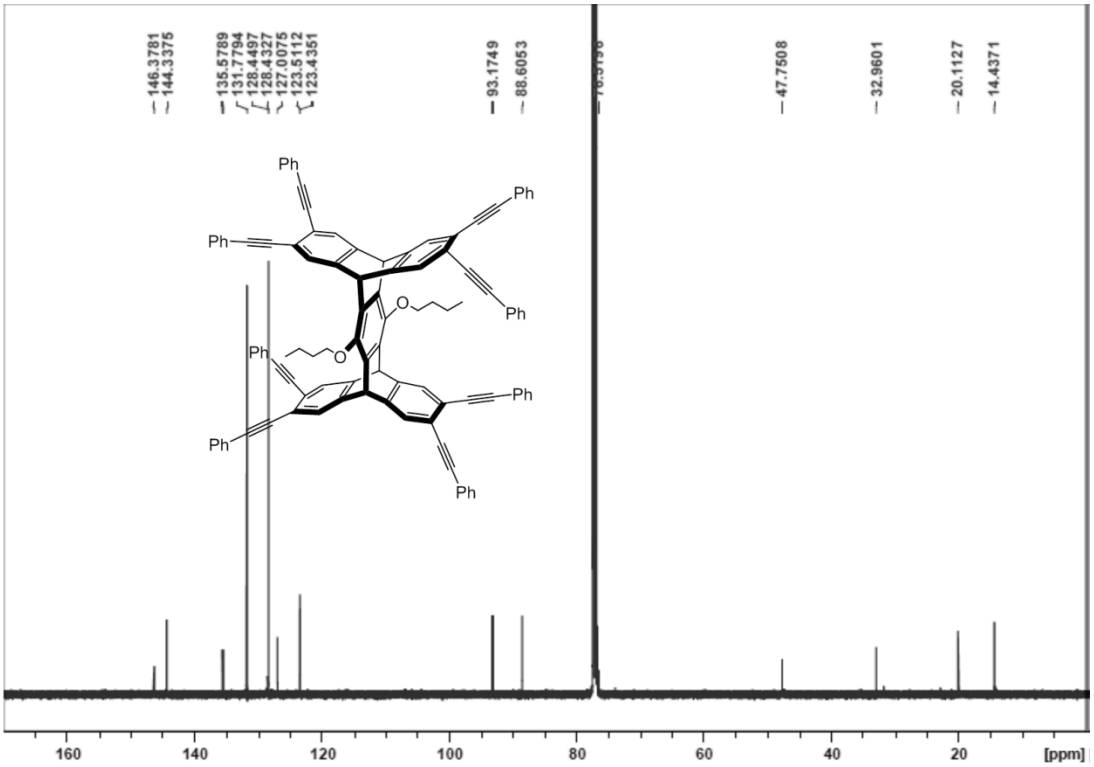


Figure S9. ^{1}H NMR of compound 4c in $CDCl_3$ at 500 MHz

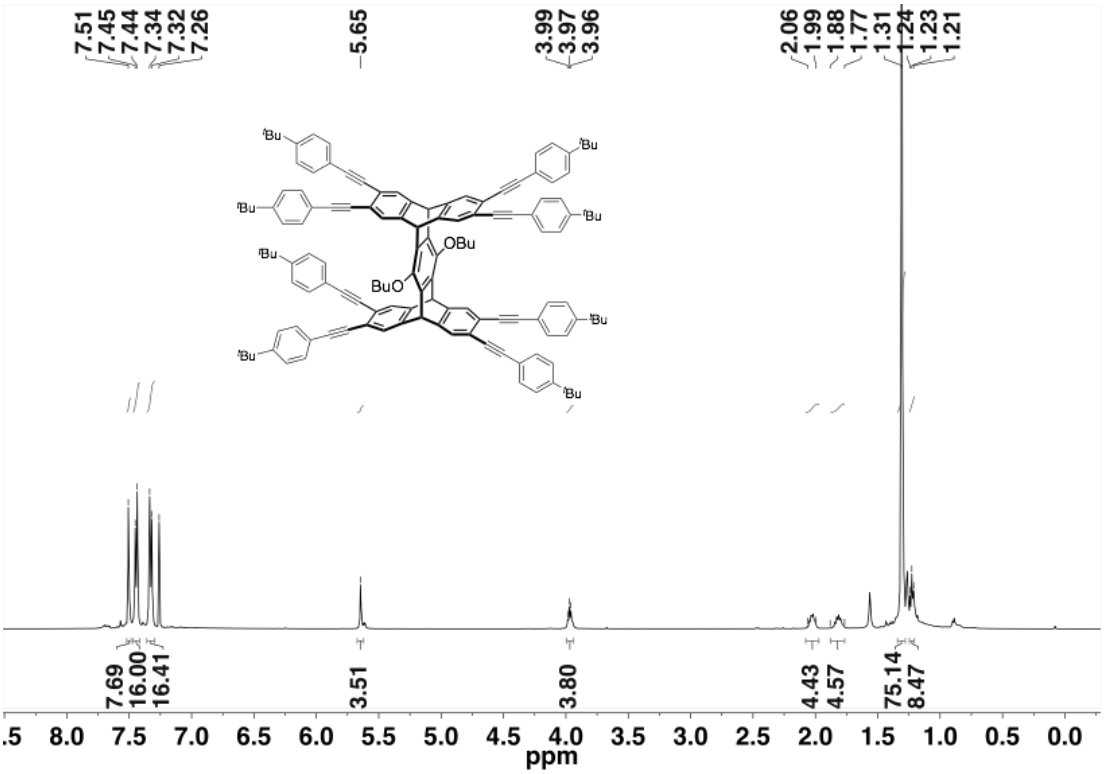


Figure S10. ^{13}C NMR of compound 4c in $CDCl_3$ at 125 MHz

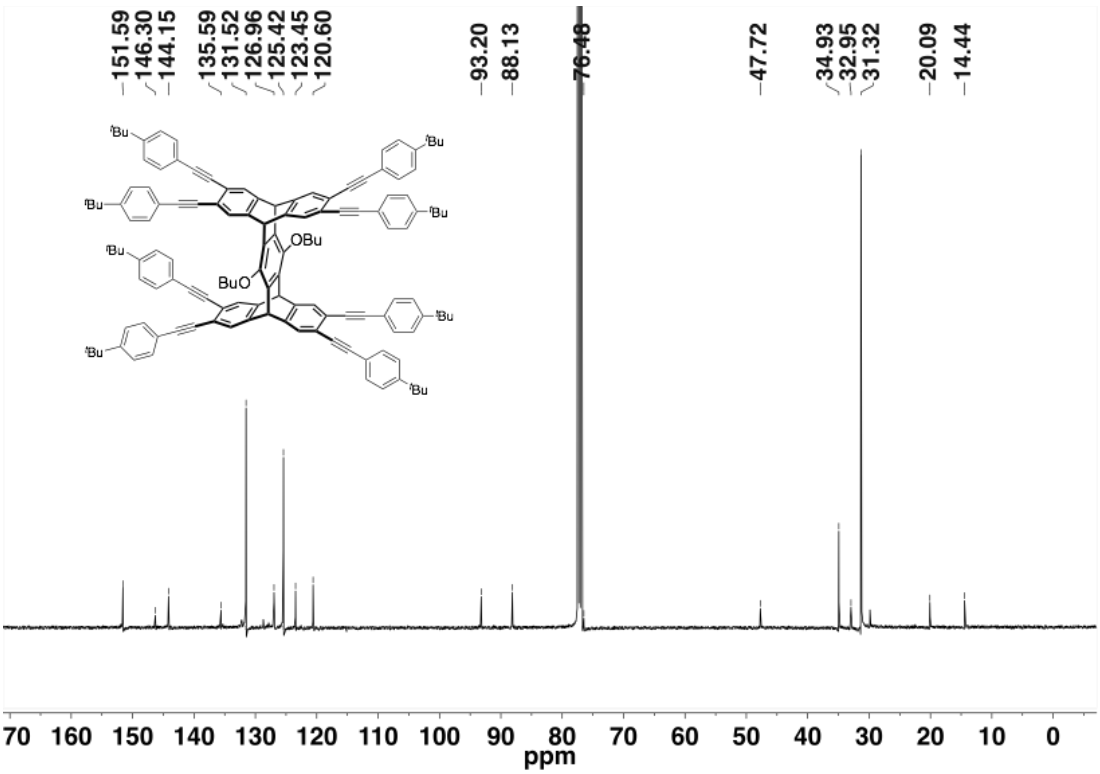


Figure S11. ^{1}H NMR of compound 4d in $CDCl_3$ at 400 MHz

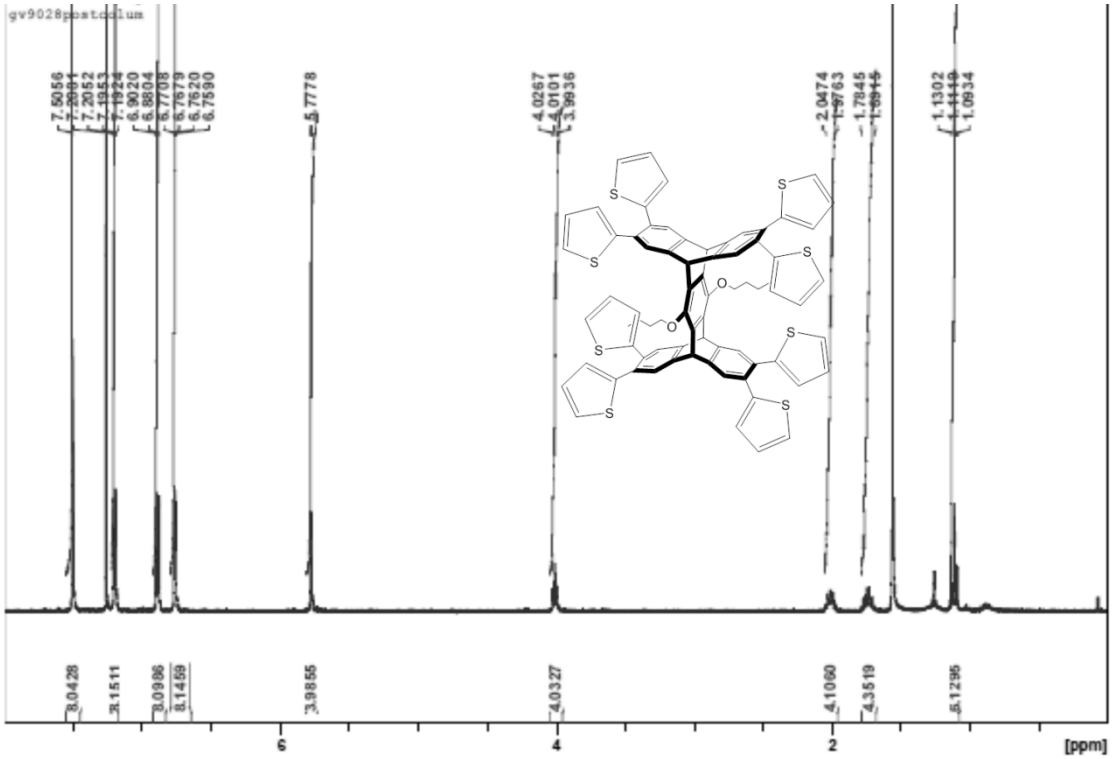


Figure S12. ^{13}C NMR of compound 4d in $CDCl_3$ at 125 MHz

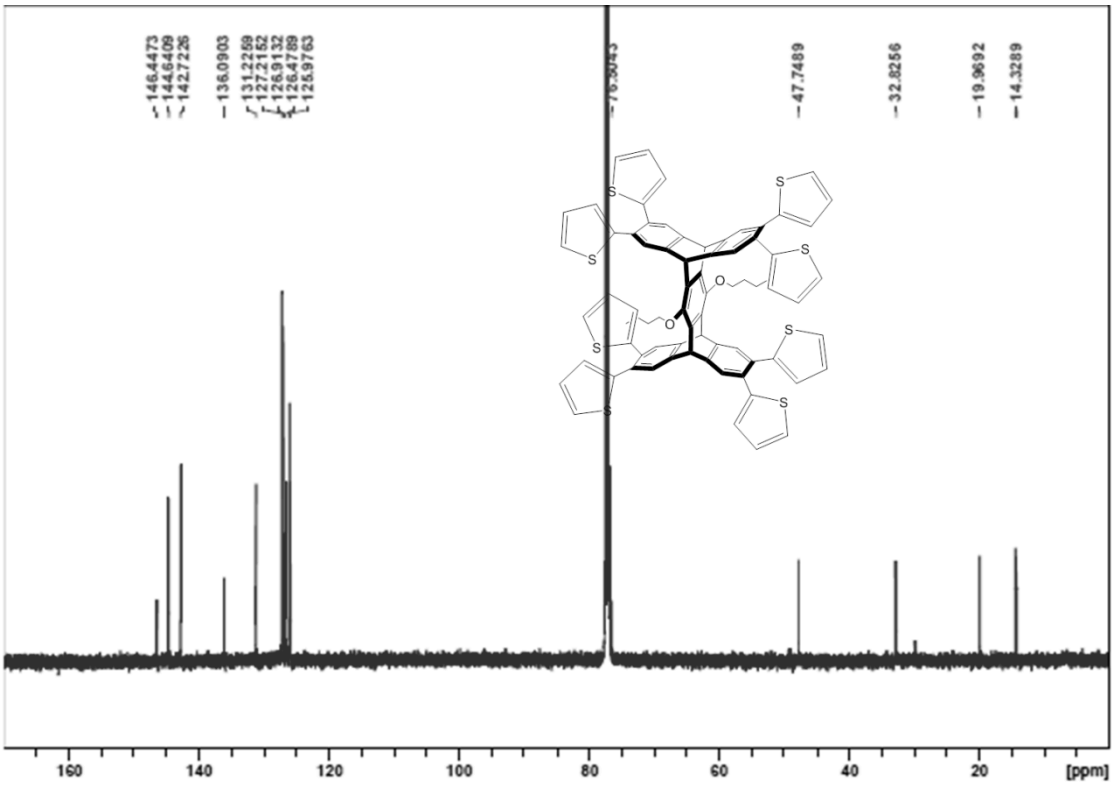


Figure S13. ^{1}H NMR of compound 4e in $CDCl_3$ at 500 MHz

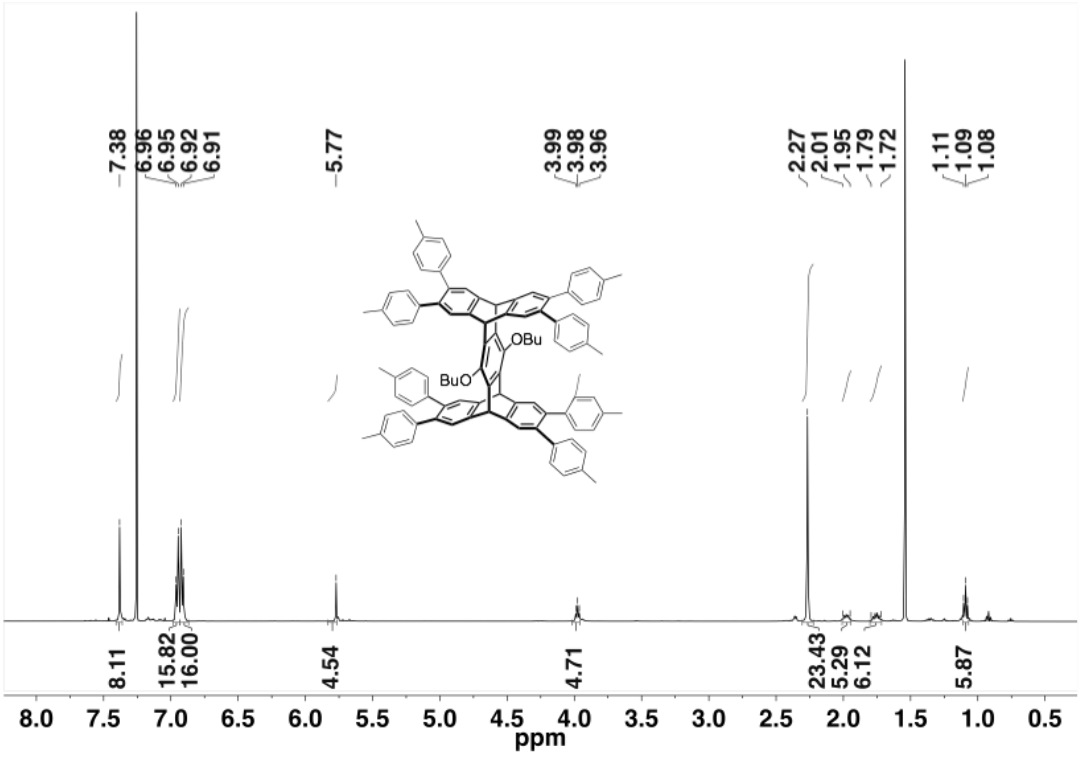


Figure S14. ^{13}C NMR of compound 4e in $CDCl_3$ at 125 MHz

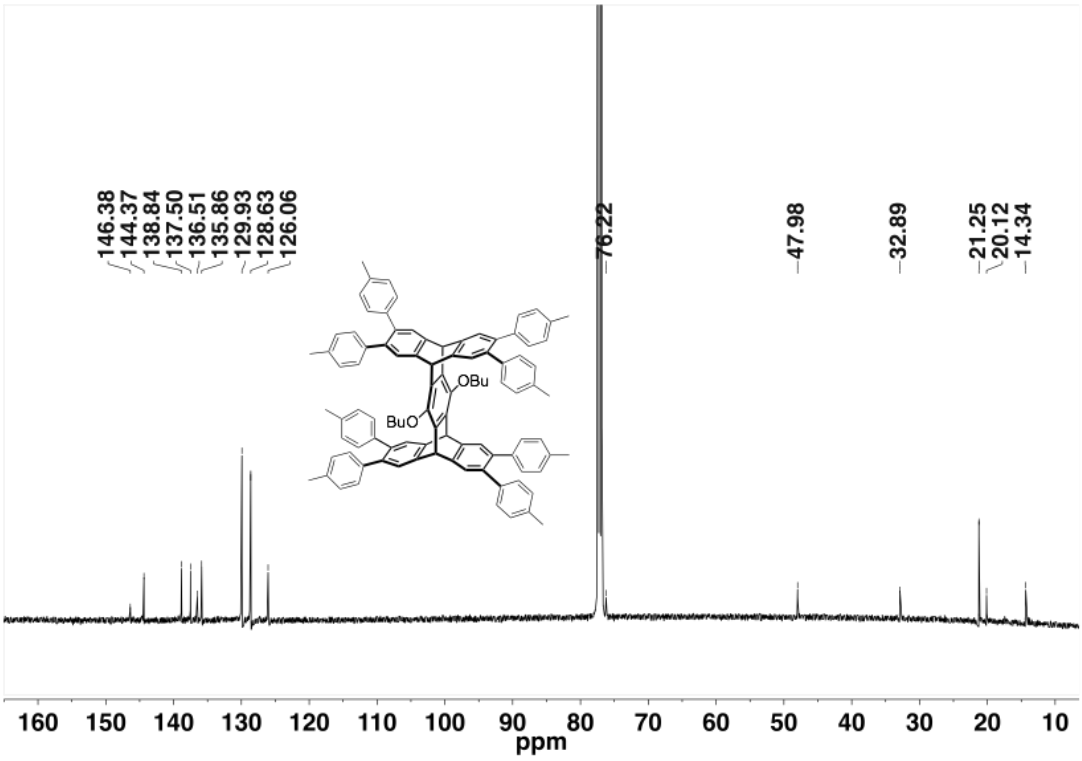


Figure S15. ^{1}H NMR of compound 4f in $CDCl_3$ at 400 MHz

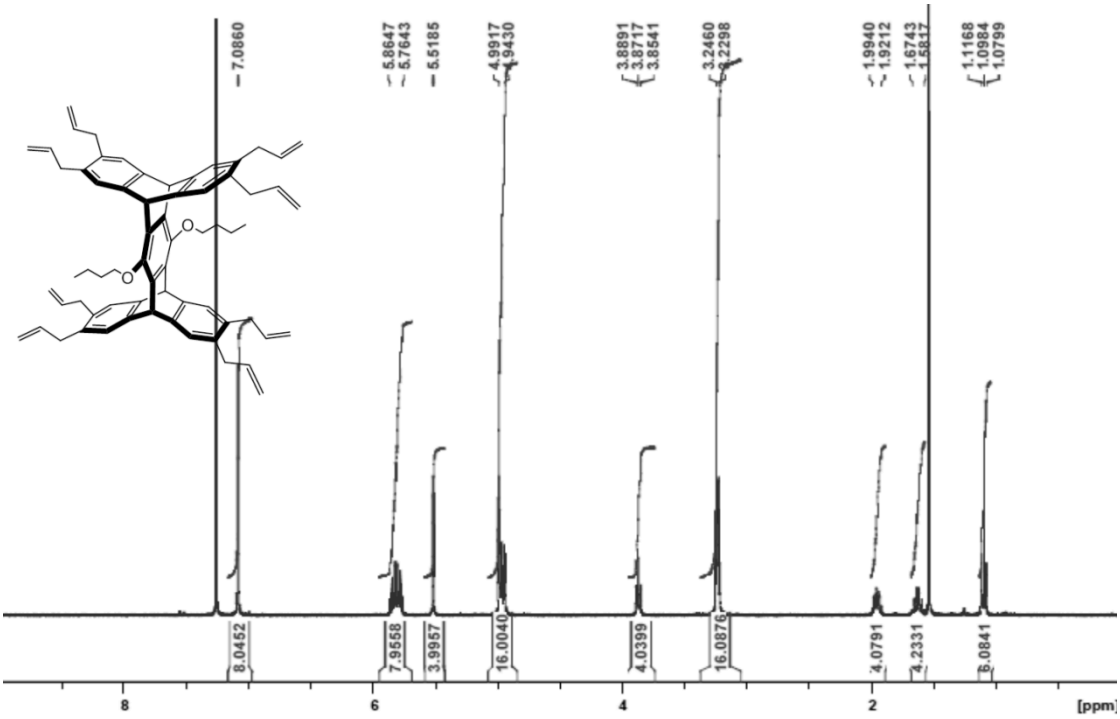


Figure S16. ^{13}C NMR of compound 4f in $CDCl_3$ at 125 MHz

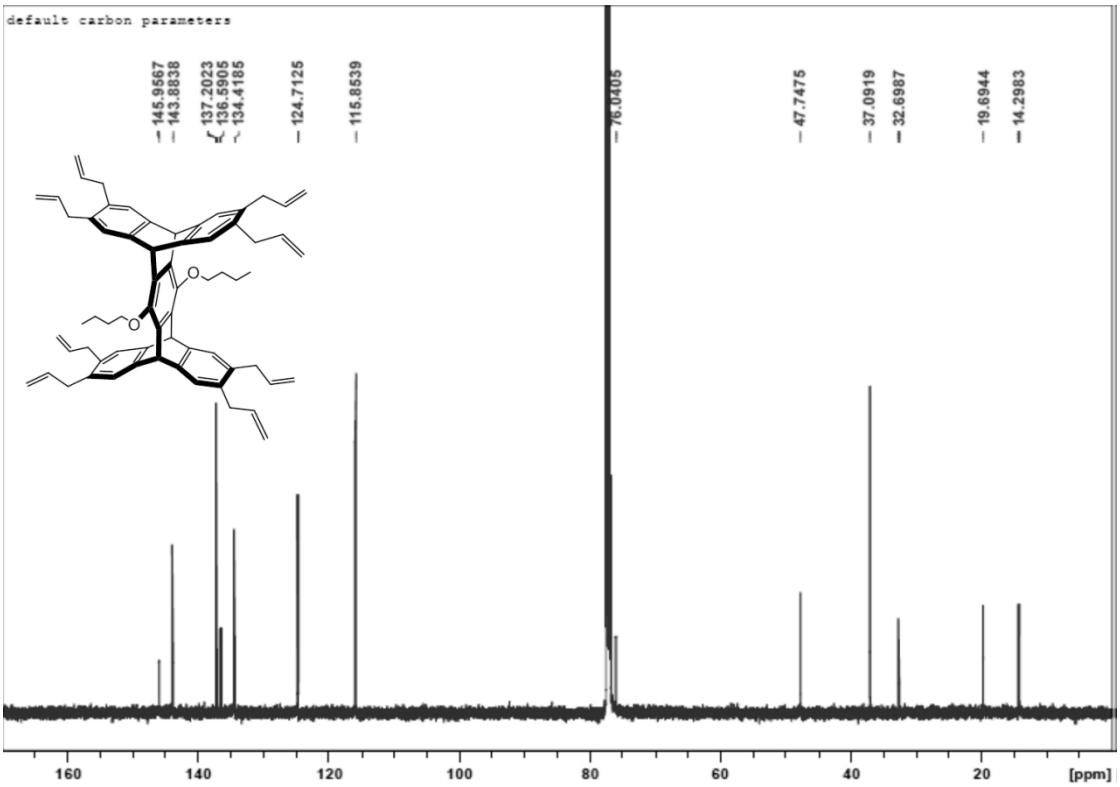


Figure S17. ^{1}H NMR of compound 4g in $CDCl_3$ at 400 MHz

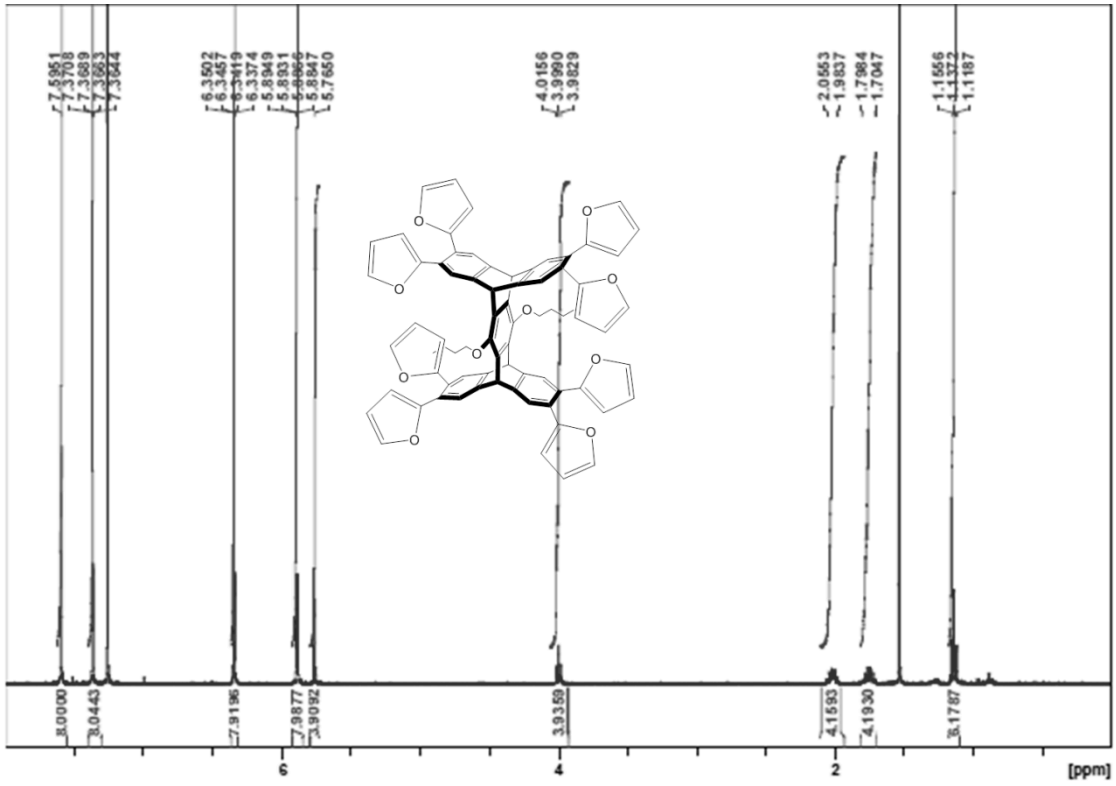


Figure S18. ^{13}C NMR of compound 4g in $CDCl_3$ at 125 MHz

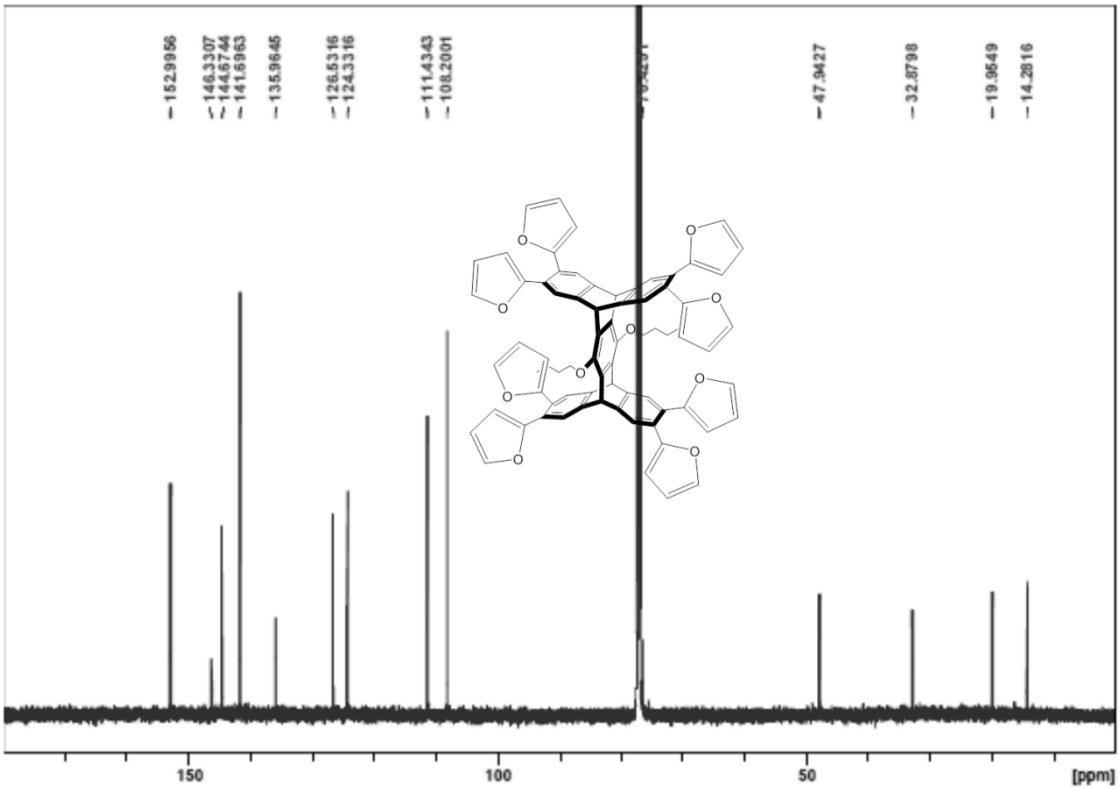


Figure S19. ^{1}H NMR of compound 4h in $CDCl_3$ at 400 MHz

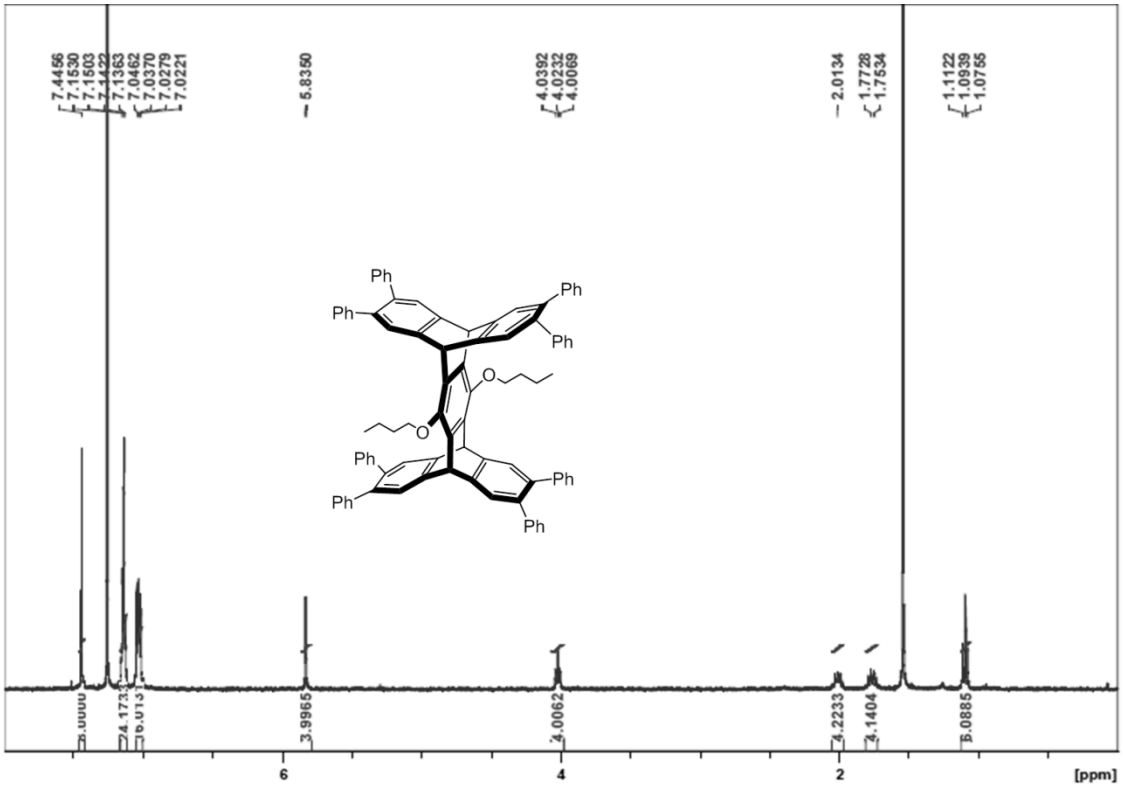


Figure S20. ^{13}C NMR of compound 4h in $CDCl_3$ at 125 MHz

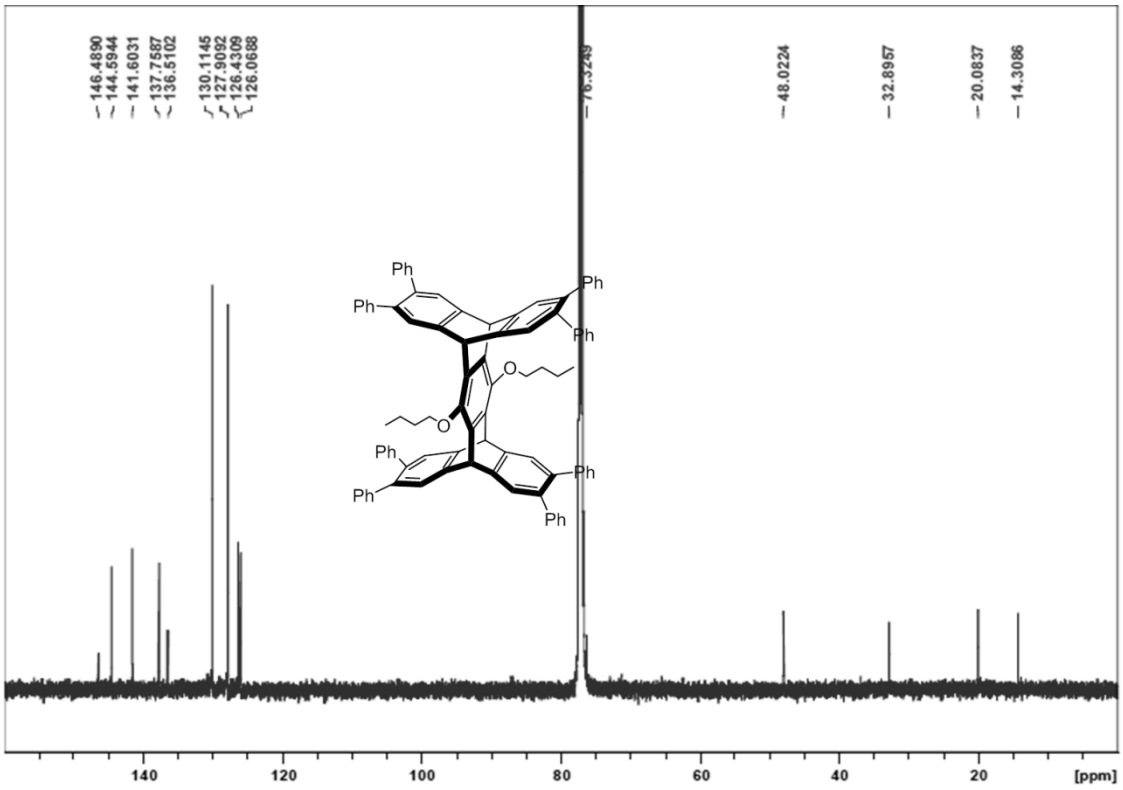


Figure S21. ^{1}H NMR of 4i in $CDCl_3$ at 400 MHz

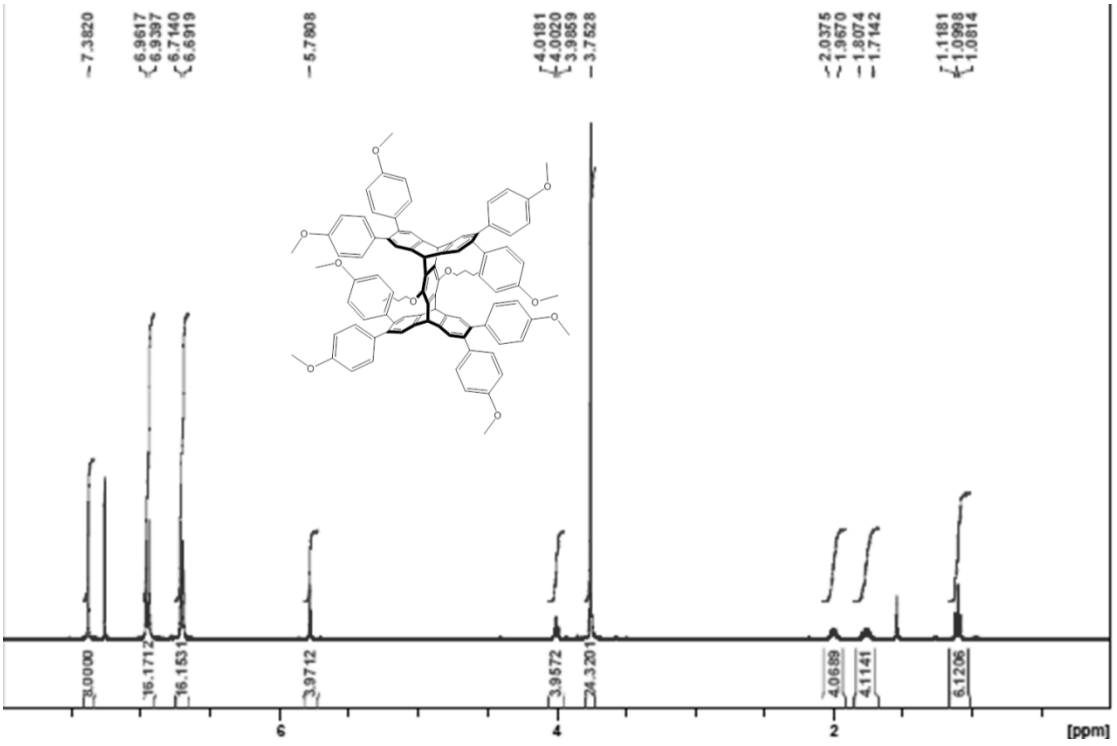


Figure S22. ^{13}C NMR of 4i in $CDCl_3$ at 125 MHz

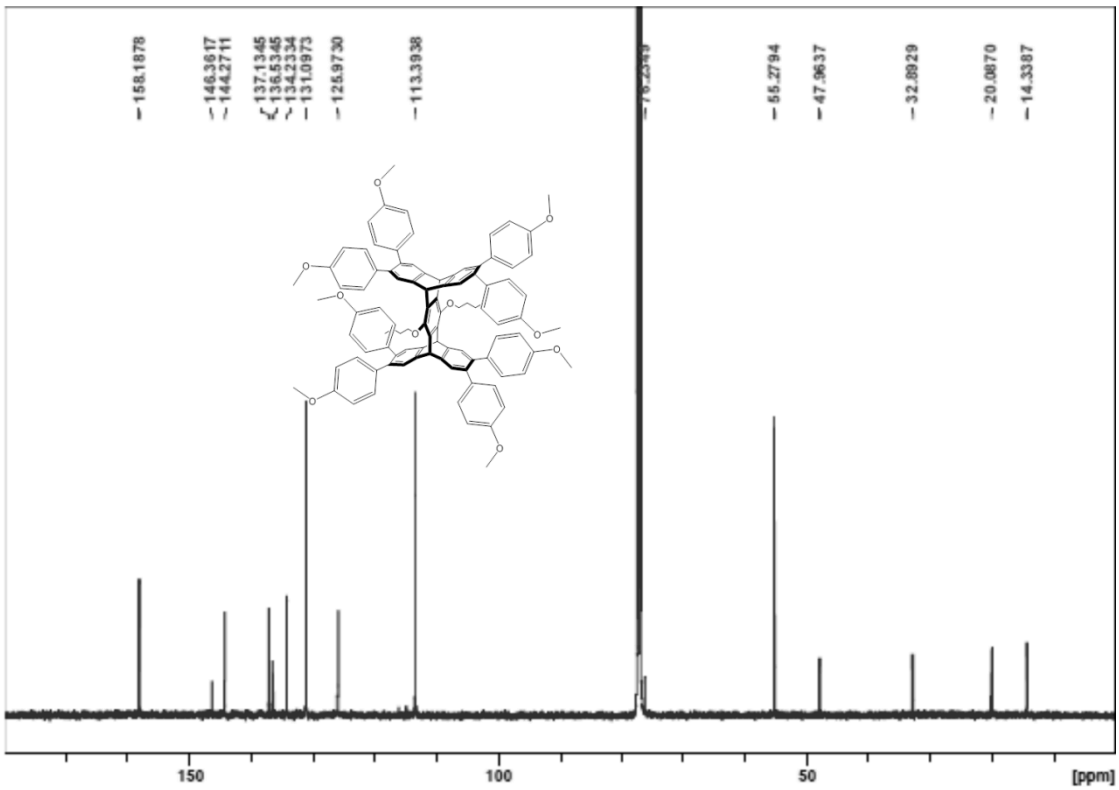


Figure S23. ^{1}H NMR of 4j in $CDCl_3$ at 400 MHz

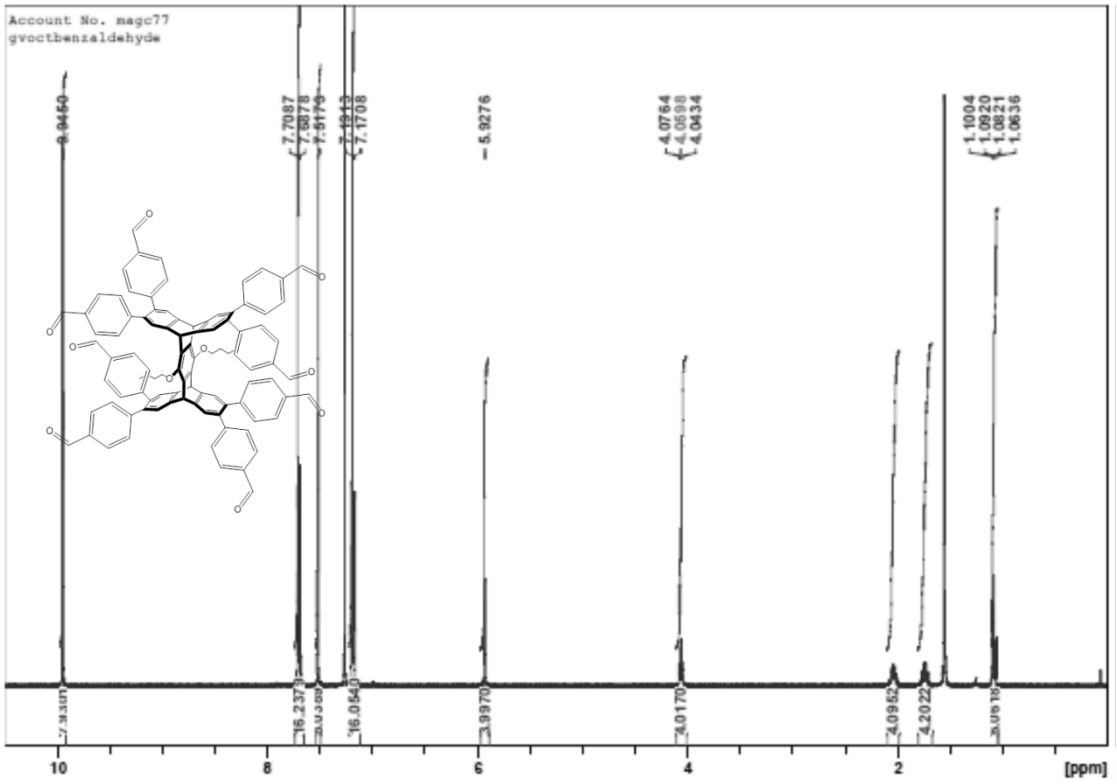


Figure S24. ^{13}C NMR of 4j in $CDCl_3$ at 125 MHz

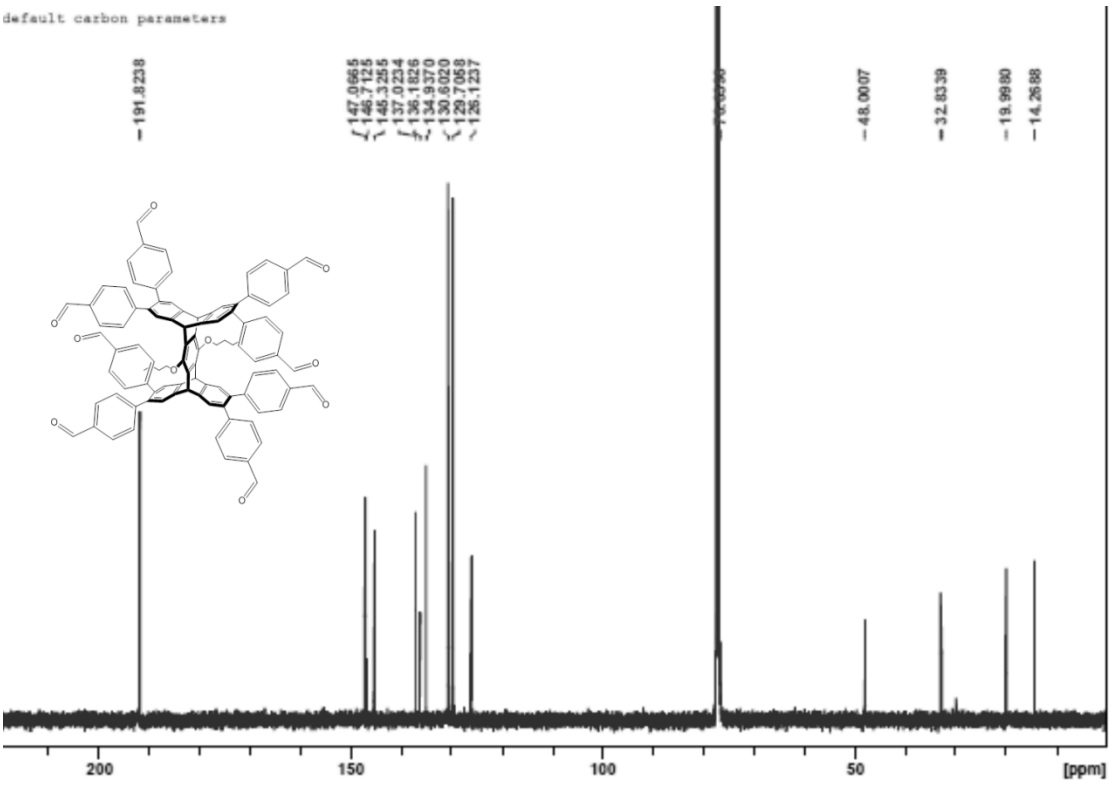


Figure S25. ^{1}H NMR of 4k in $CDCl_3$ at 400 MHz

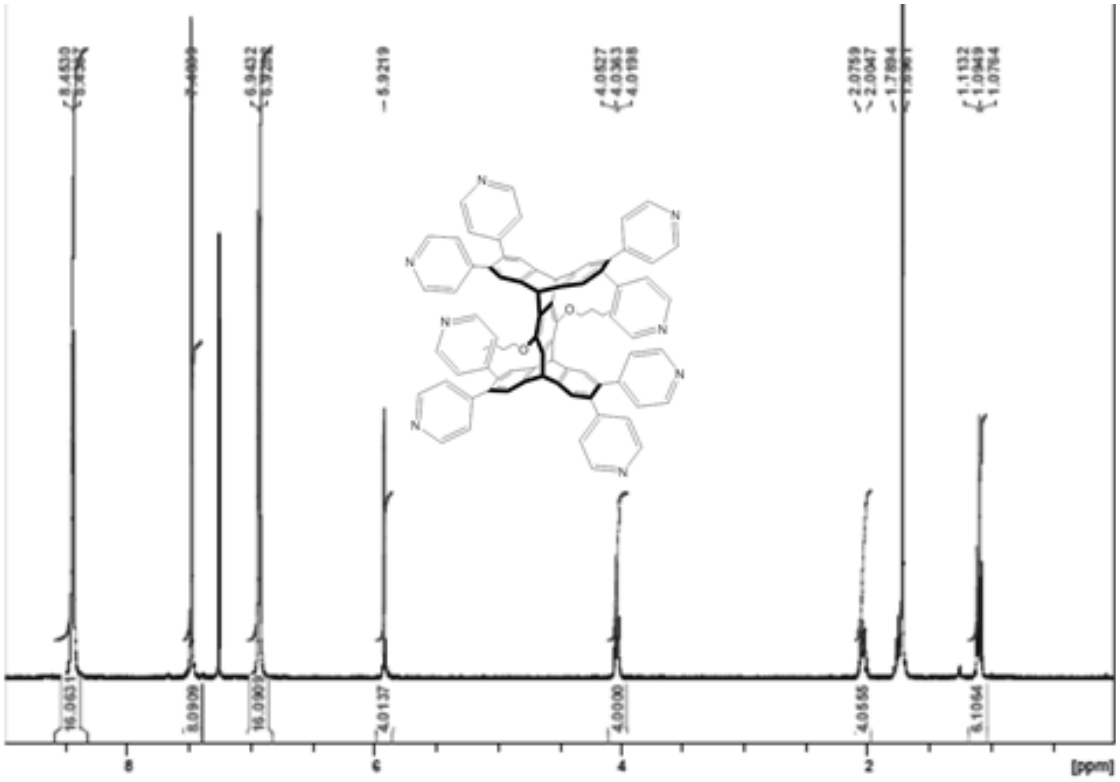


Figure S26. ^{13}C NMR of 4k in $CDCl_3$ at 125 MHz

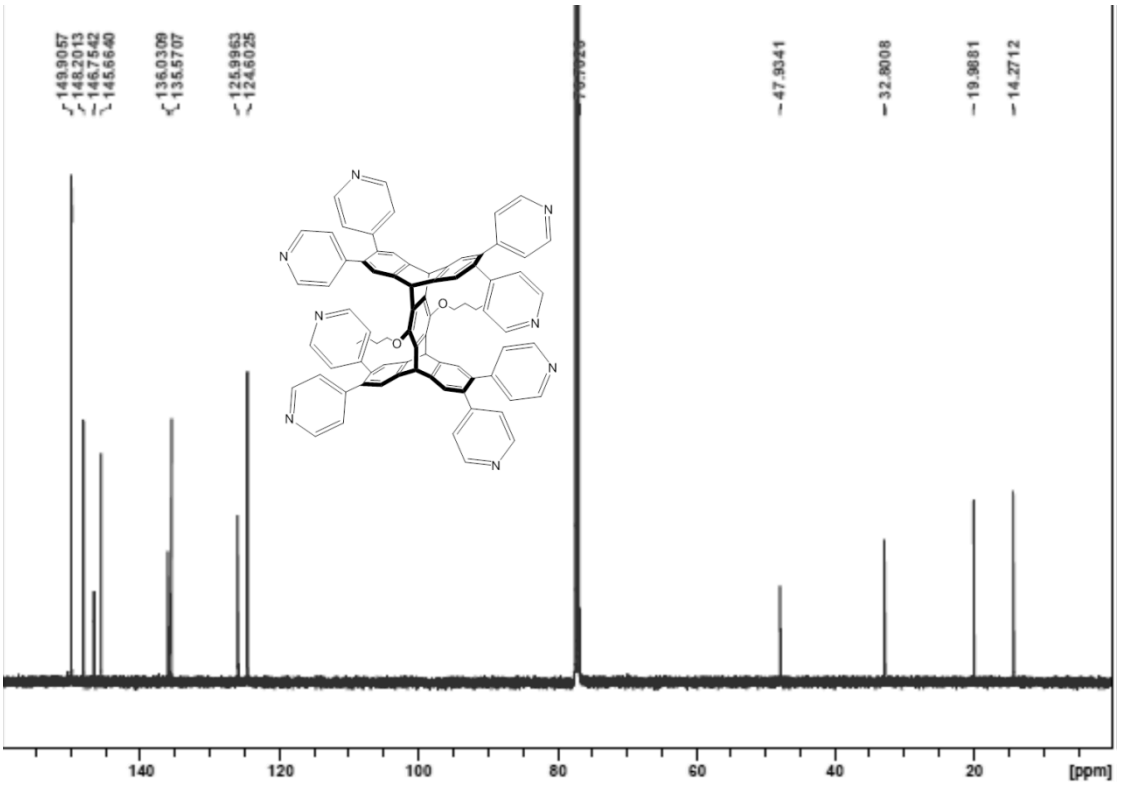


Figure S27. ^{1}H NMR of compound **8** in $CDCl_3$ at 400 MHz

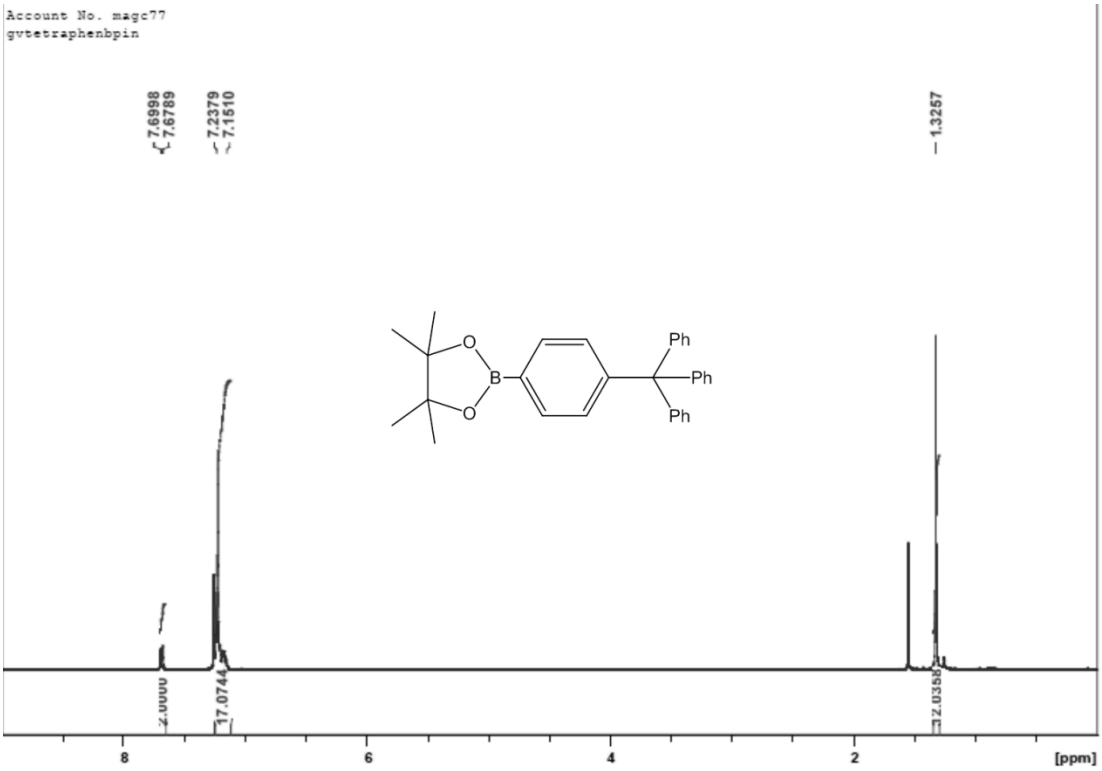


Figure S28. ^{13}C NMR of compound **8** in $CDCl_3$ at 125 MHz

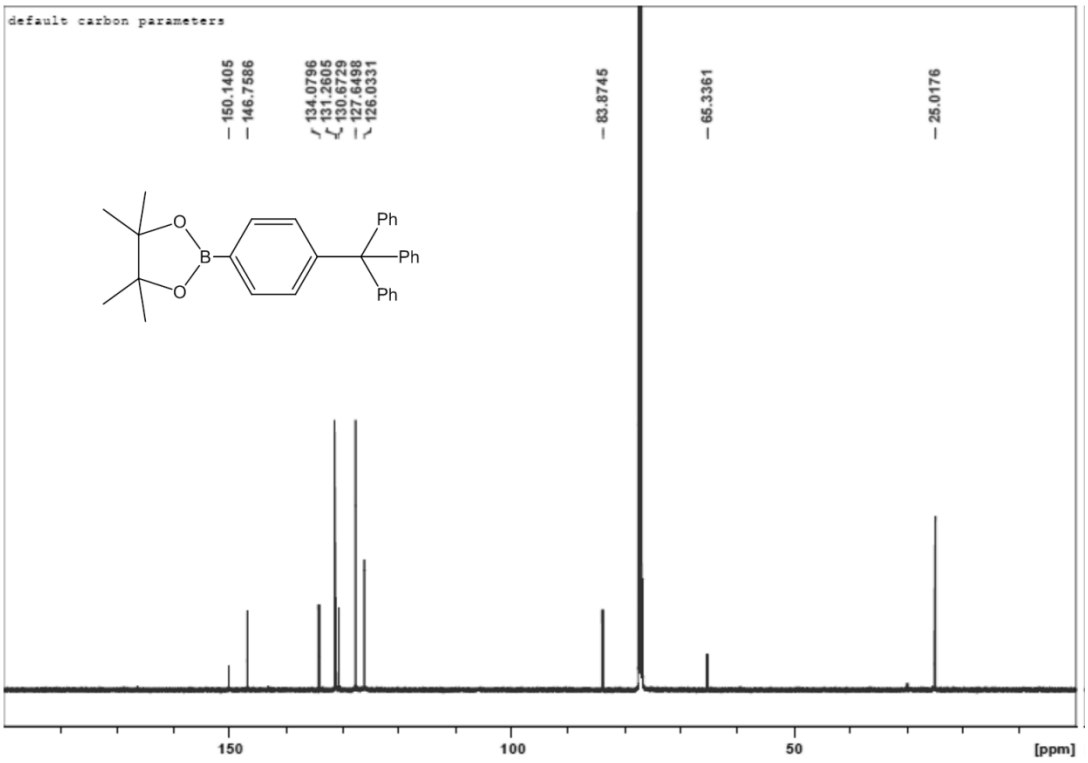


Figure S29. ^{1}H NMR of compound 4l in $CDCl_3$ at 400 MHz

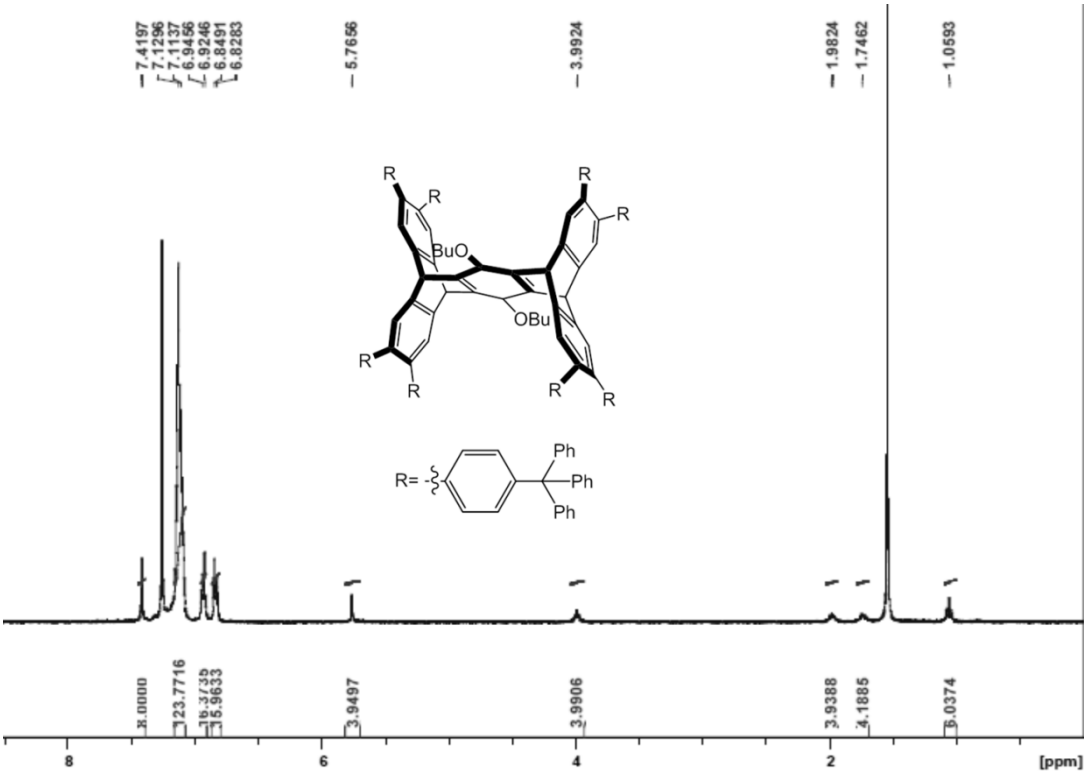


Figure S30. ^{13}C NMR of compound 4l in $CDCl_3$ at 125 MHz

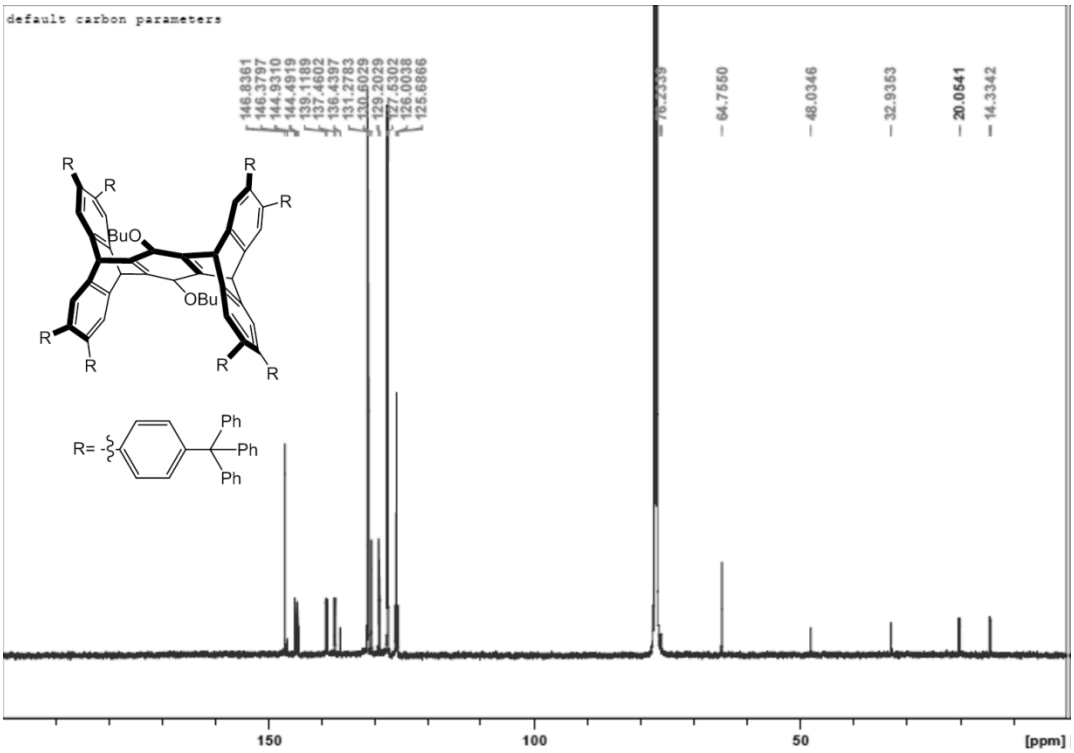


Figure S31. ^{1}H NMR of **4m** in $CDCl_3$ at 400 MHz

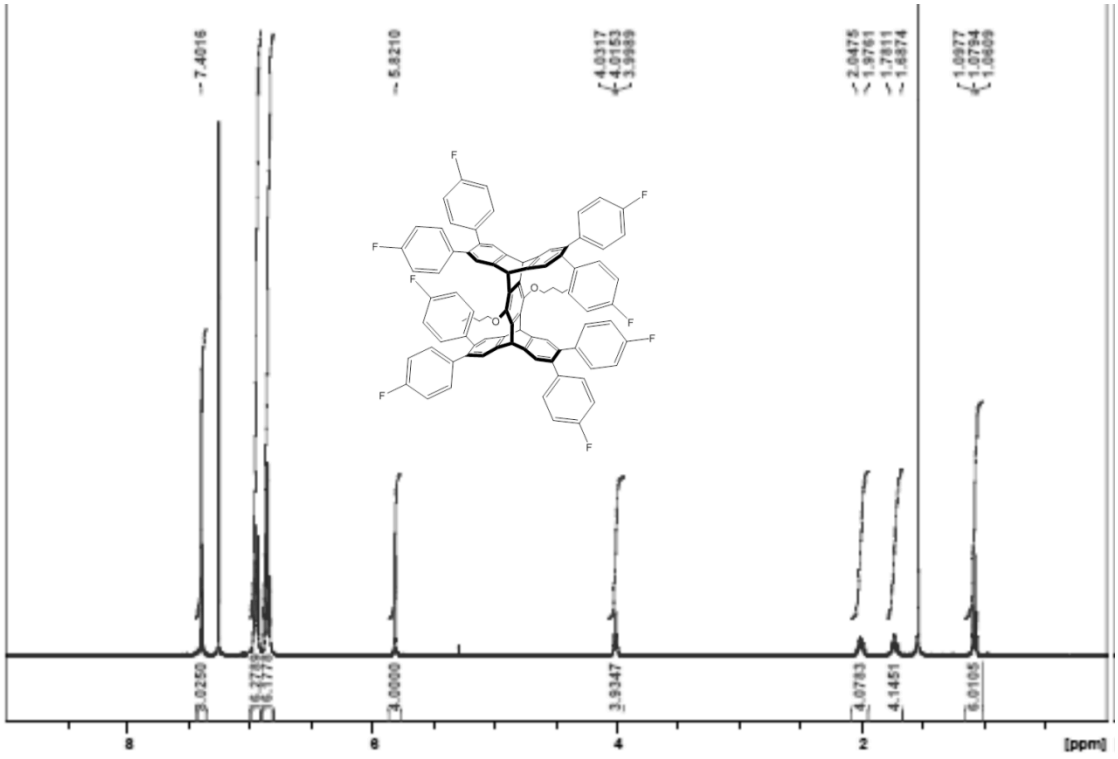


Figure S32. ^{13}C NMR of **4m** in $CDCl_3$ at 125 MHz

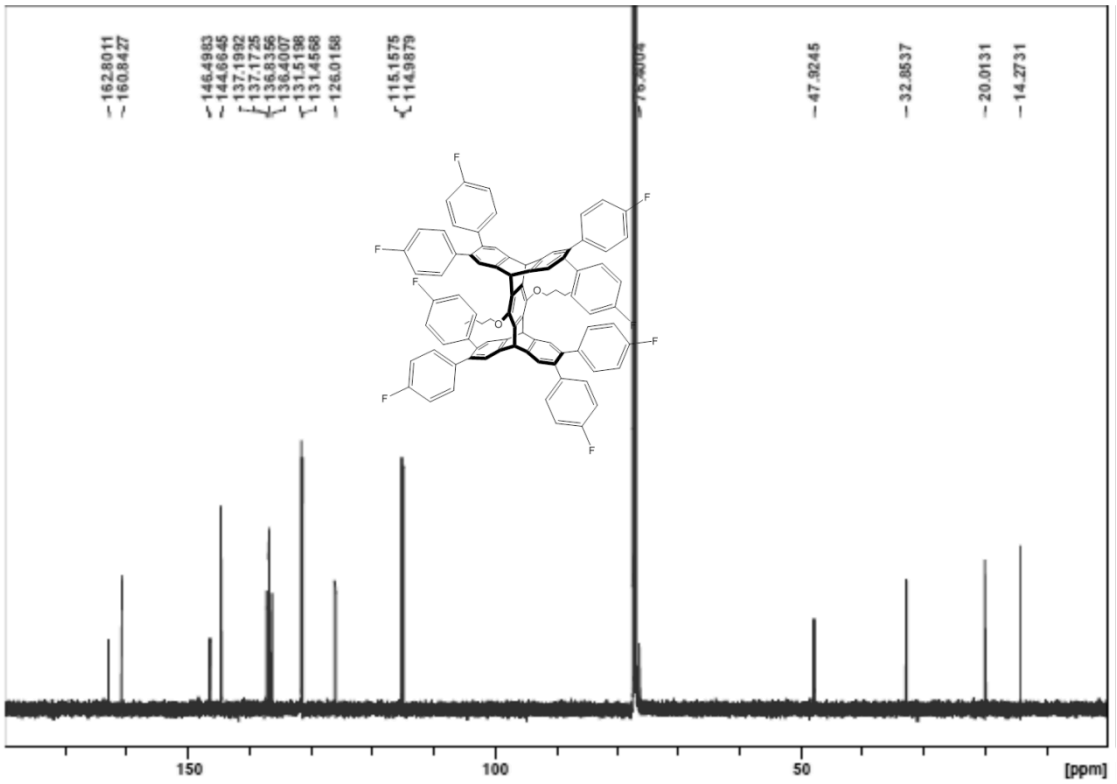


Figure S33. ^{19}F NMR of **4m** in $CDCl_3$ at 376 MHz (proton decoupled)

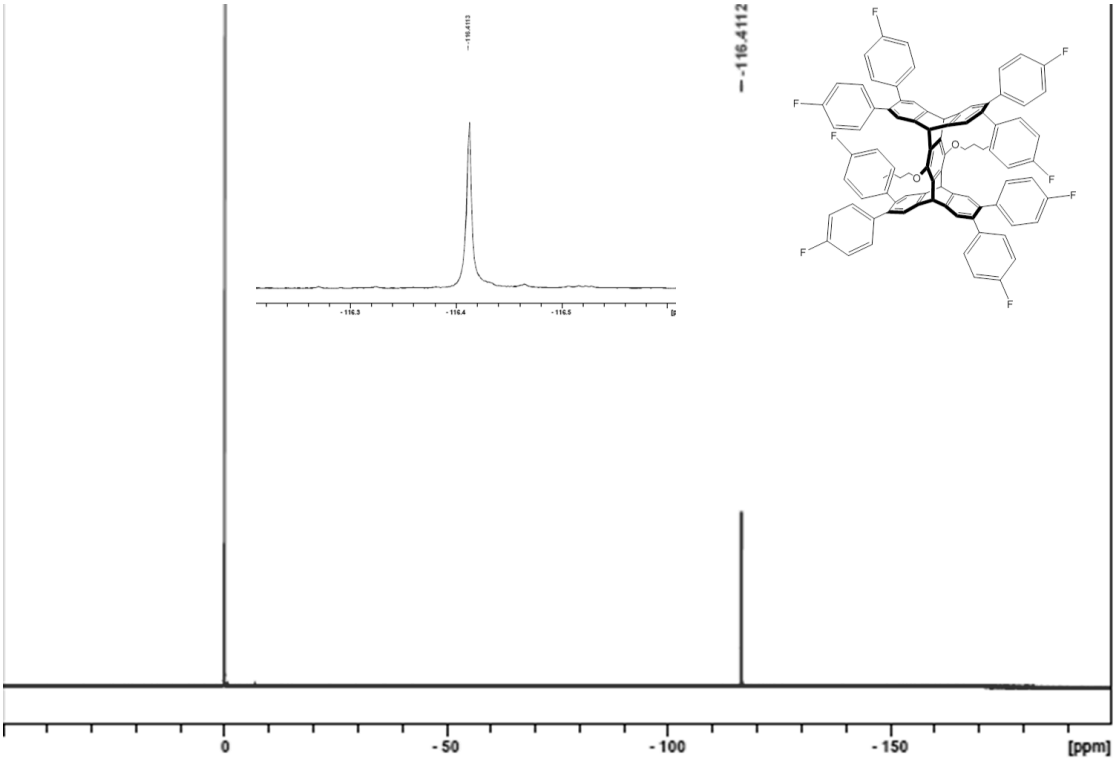


Figure S34. ^{19}F NMR of **4m** in $CDCl_3$ at 376 MHz

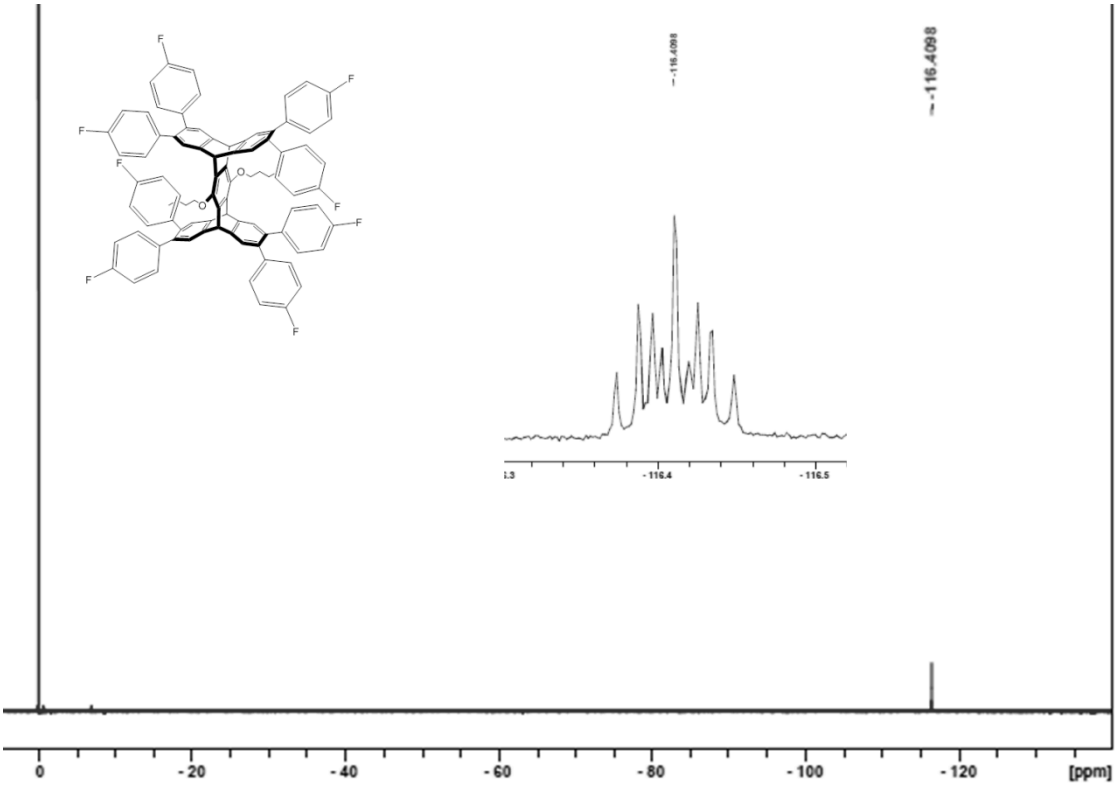


Figure S35. ^{1}H NMR of compound 4n in $CDCl_3$ at 400 MHz

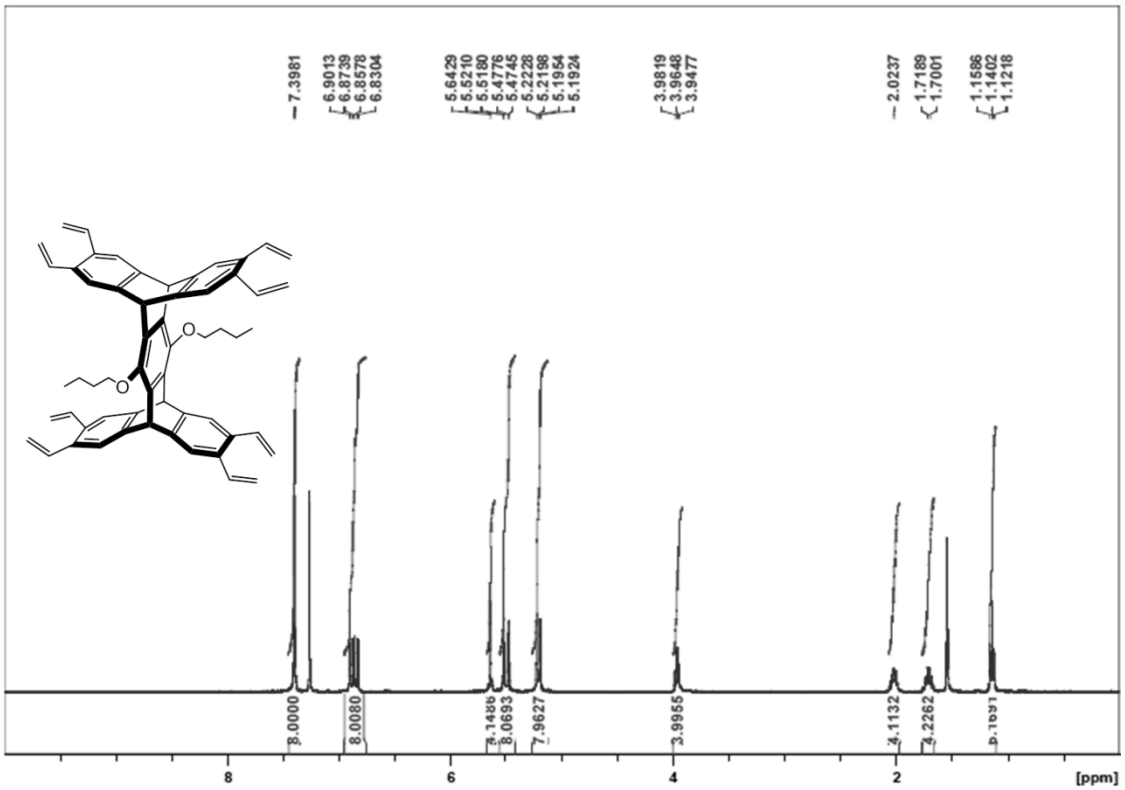


Figure S36. ^{13}C NMR of compound 4n in $CDCl_3$ at 125 MHz

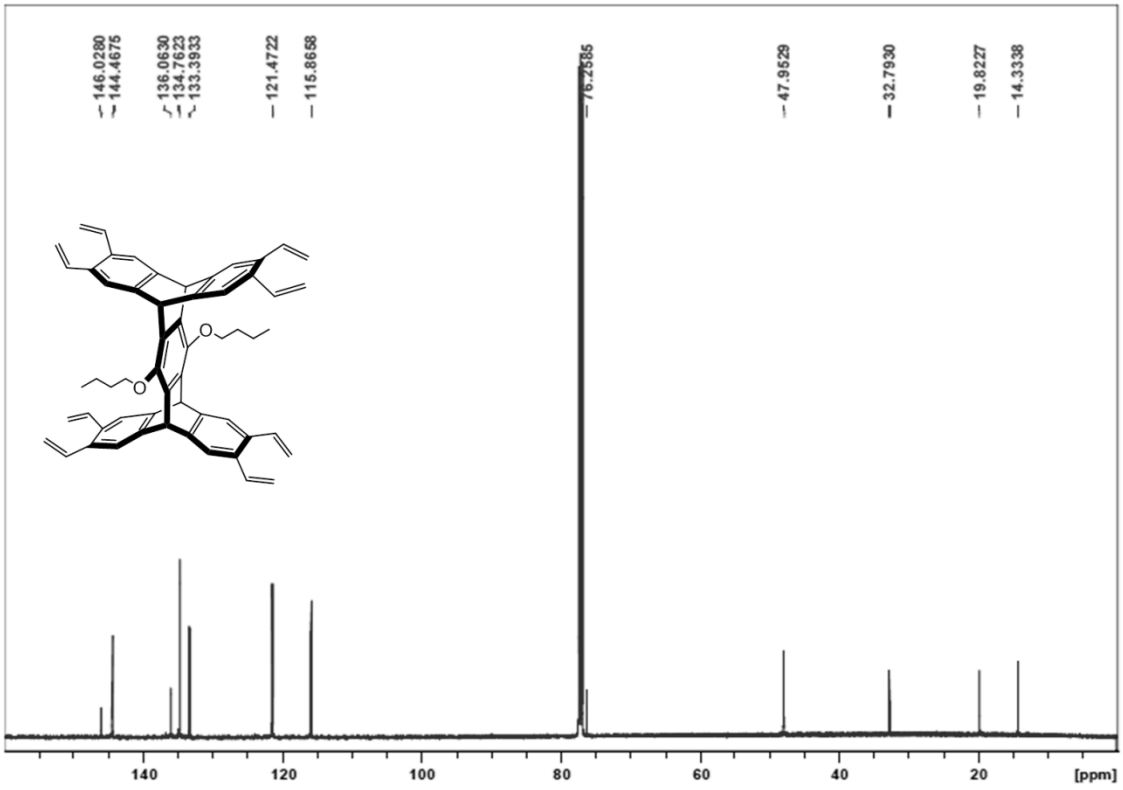


Figure S37. ^{1}H NMR of compound 4o in $CDCl_3$ at 300 MHz

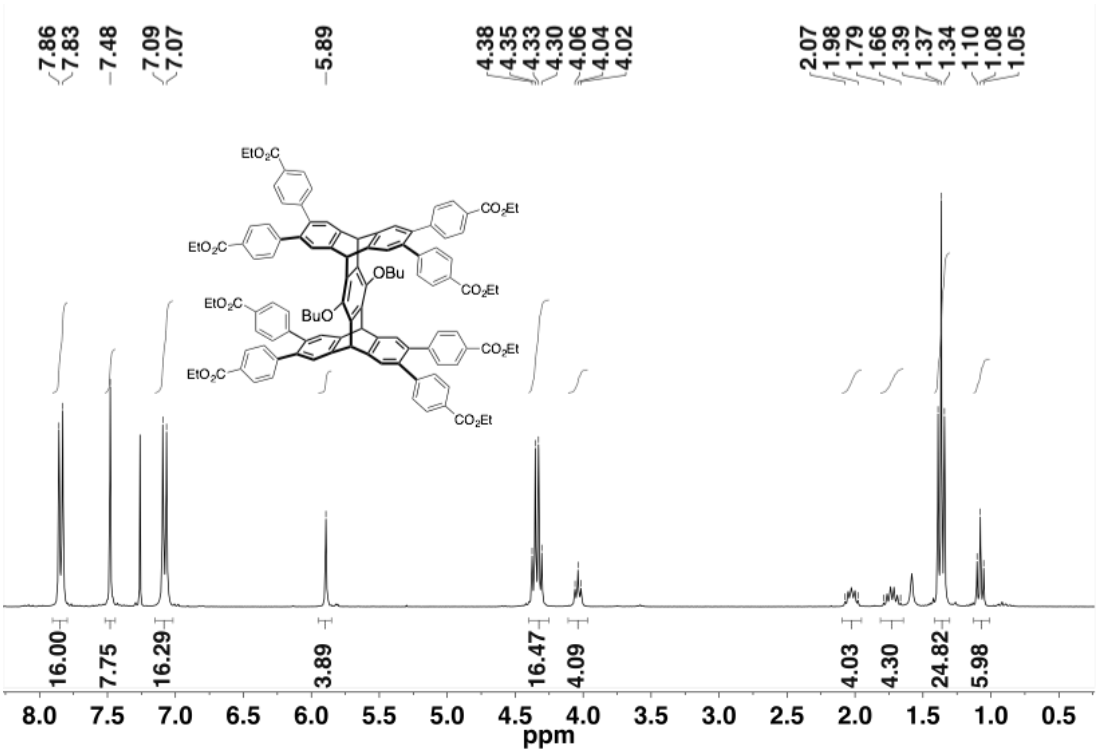


Figure S38. ^{13}C NMR of compound 4o in $CDCl_3$ at 125 MHz

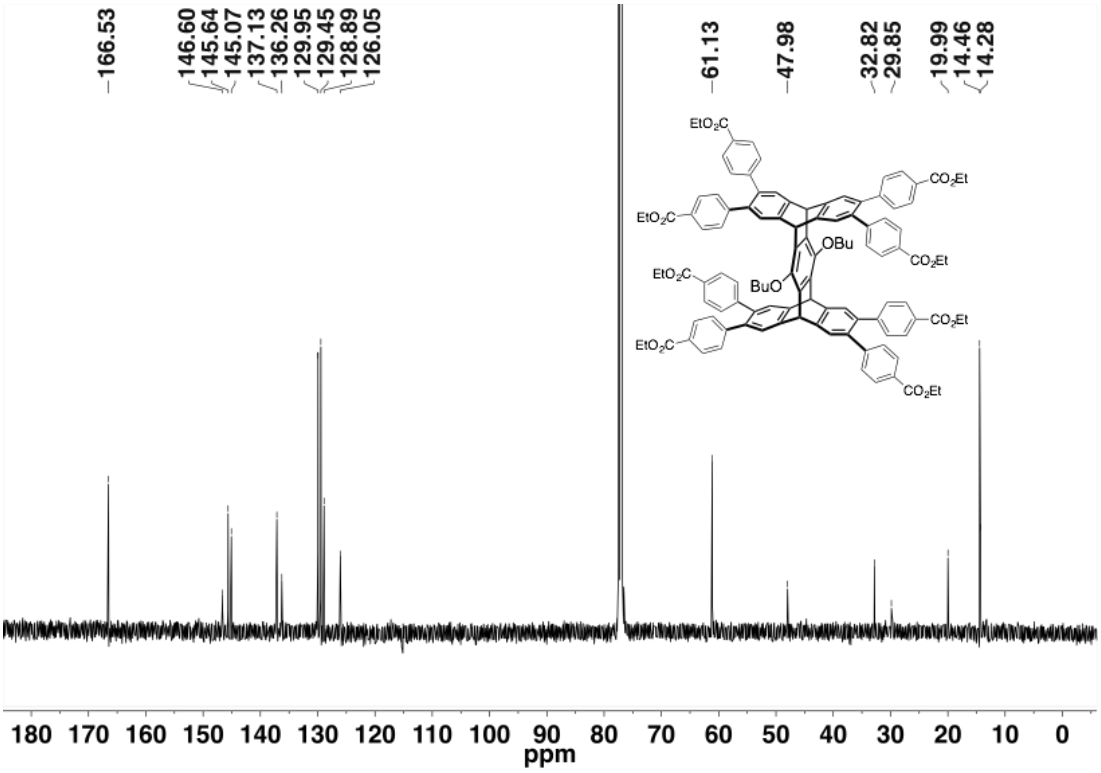


Figure S39. ^{1}H NMR of compound 5a in $CDCl_3$ at 400 MHz

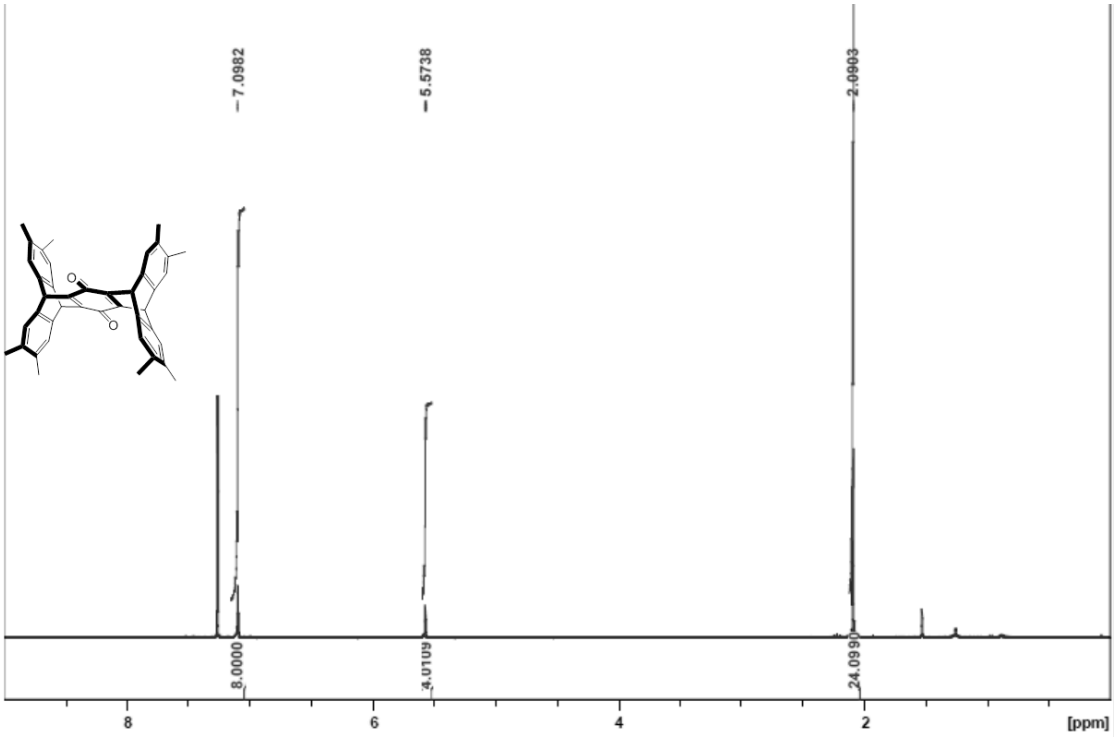


Figure S40. ^{13}C NMR of compound 5a in $CDCl_3$ at 125 MHz

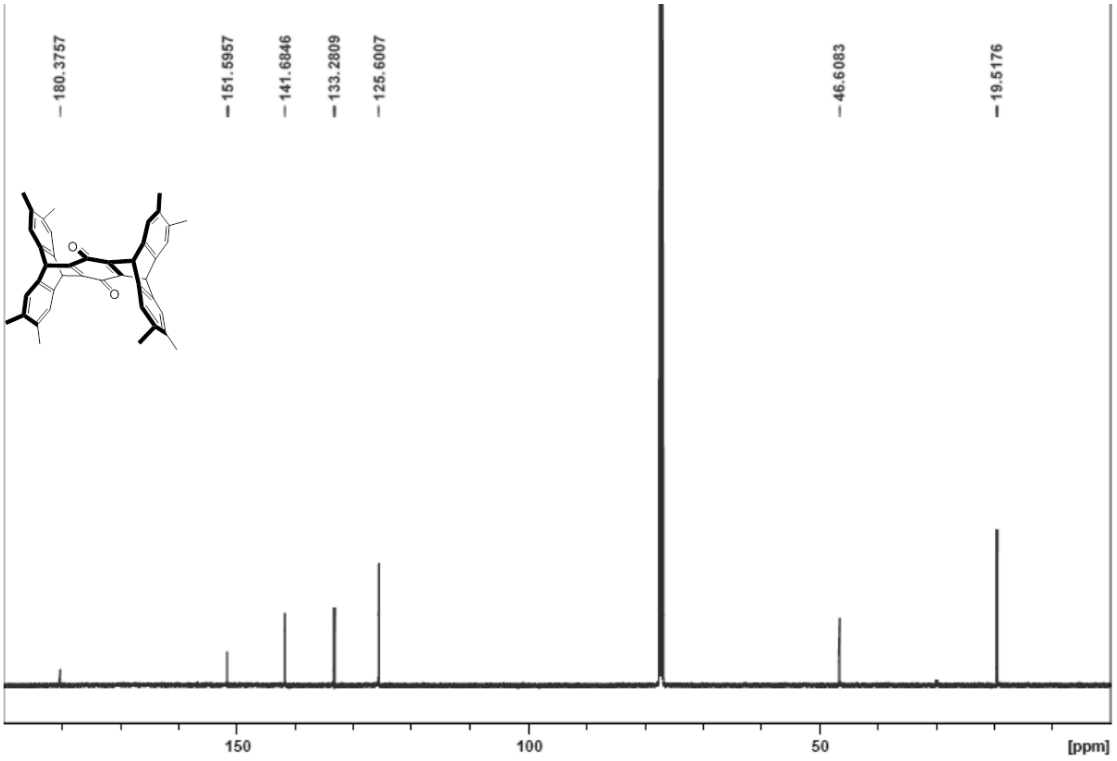


Figure S41. ^{1}H NMR of compound 5h in $CDCl_3$ at 400 MHz

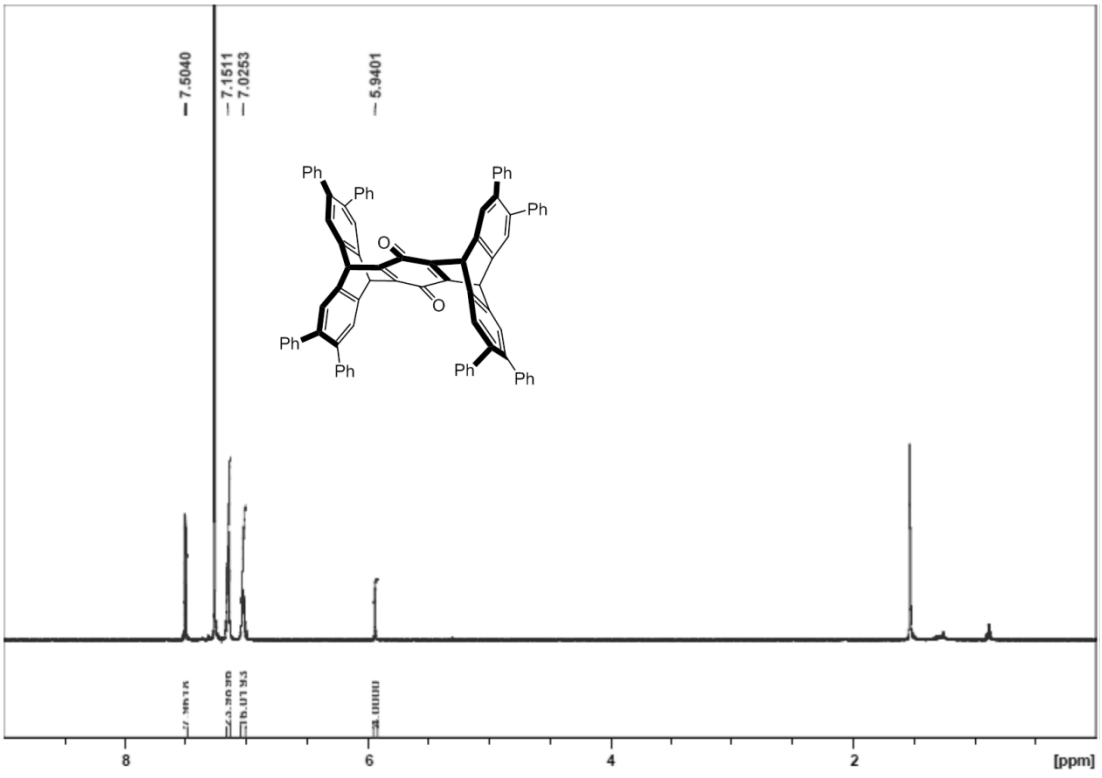


Figure S42. ^{13}C NMR of compound 5h in $CDCl_3$ at 125 MHz

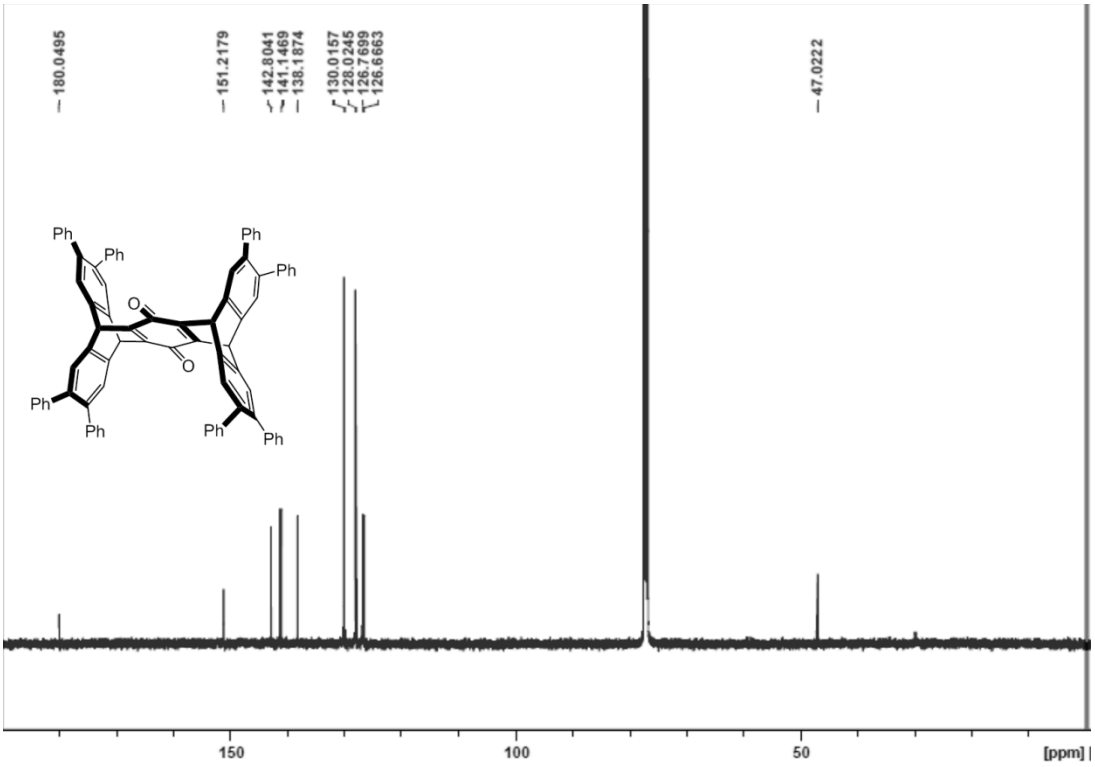


Figure S43. ^{1}H NMR of compound 5l in $CDCl_3$ at 500 MHz

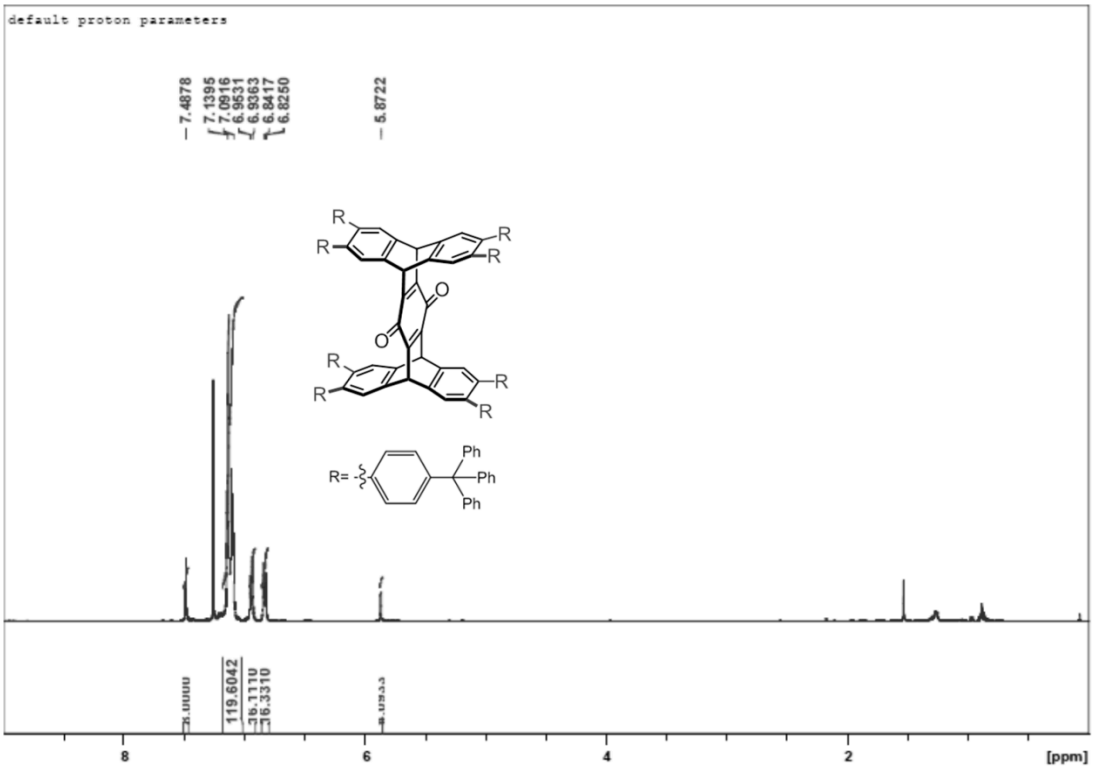
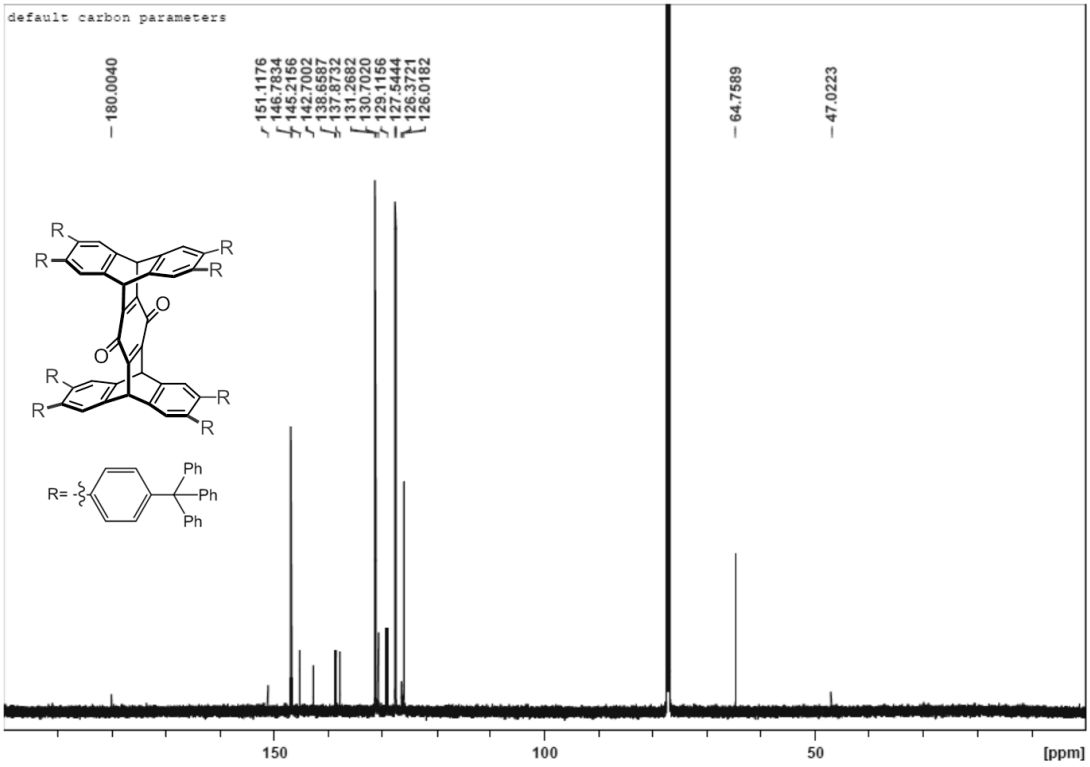


Figure S44. ^{13}C NMR of compound 5l in $CDCl_3$ at 125 MHz



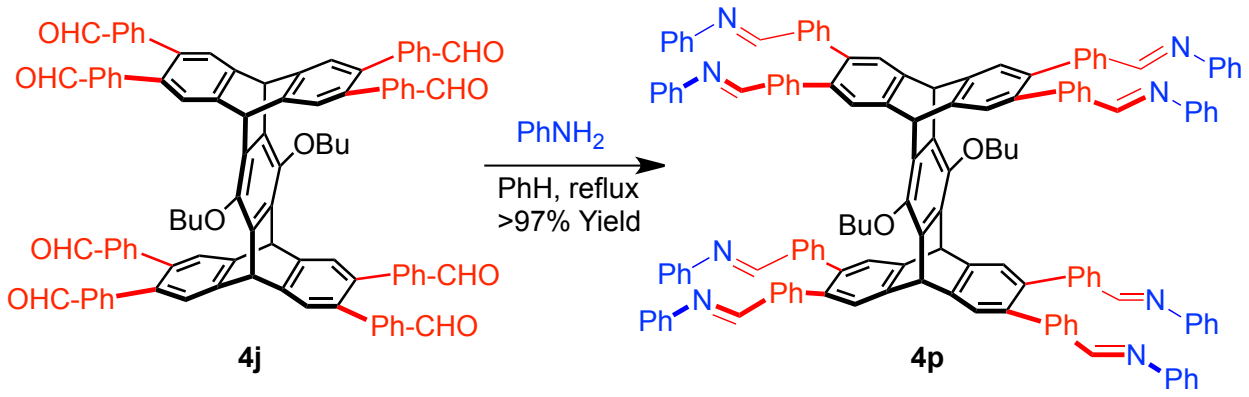
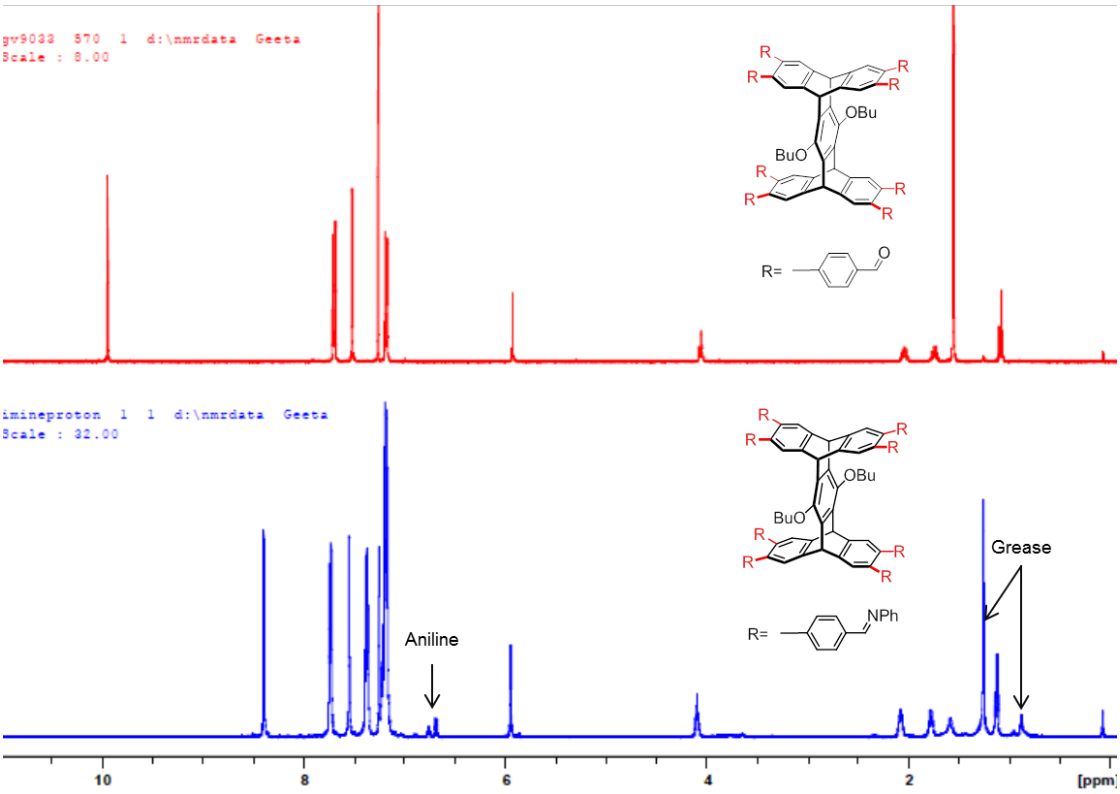


Figure S45. ^{1}H NMR of imine formation in $CDCl_3$ at 400 MHz



4j (11.4 mg, 0.0081 mmol) was suspended in PhH (7 mL). Aniline (47.2µL, 0.518 mmol) was added and reaction was heated to reflux through a soxhelet extractor with a layer of $MgSO_4$ for 12 hours. The reaction mixture was concentrated under reduced pressure to show clean conversion by NMR with an estimate yield ≥97%.

Figure S46. ATR IR of Compound 2

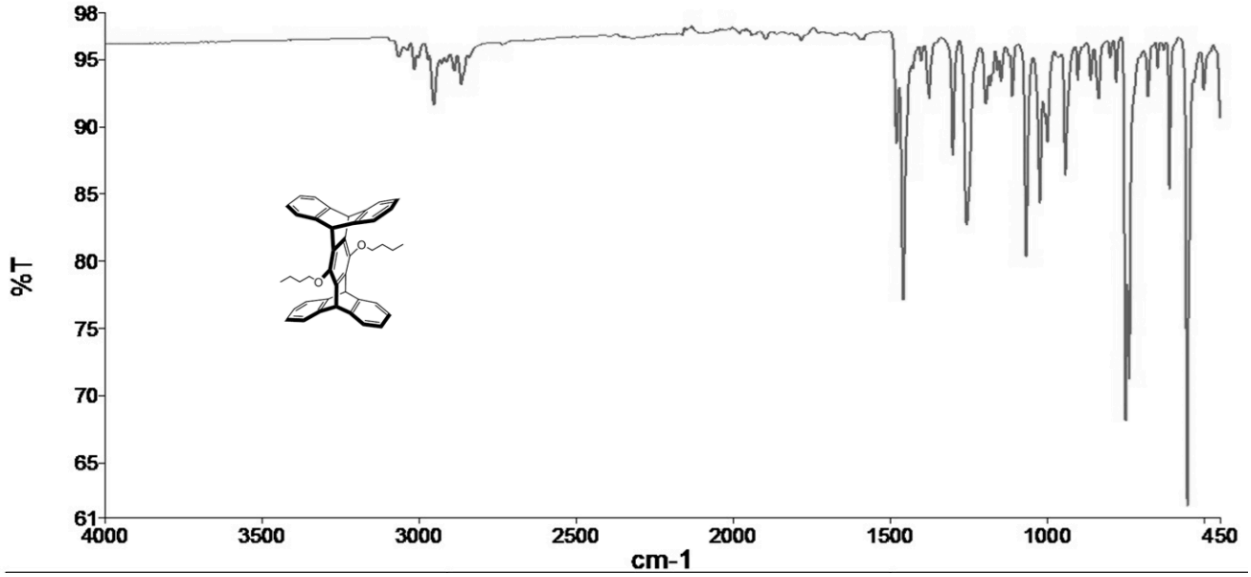


Figure S47. ATR IR of Compound 3

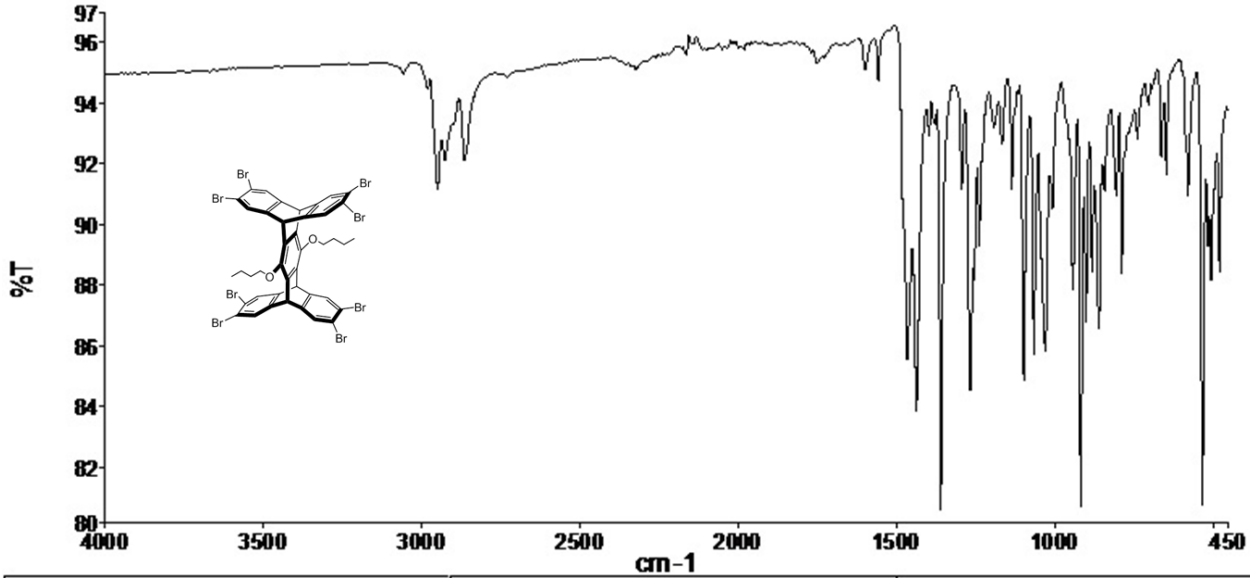


Figure S48. ATR IR of Compound 4a

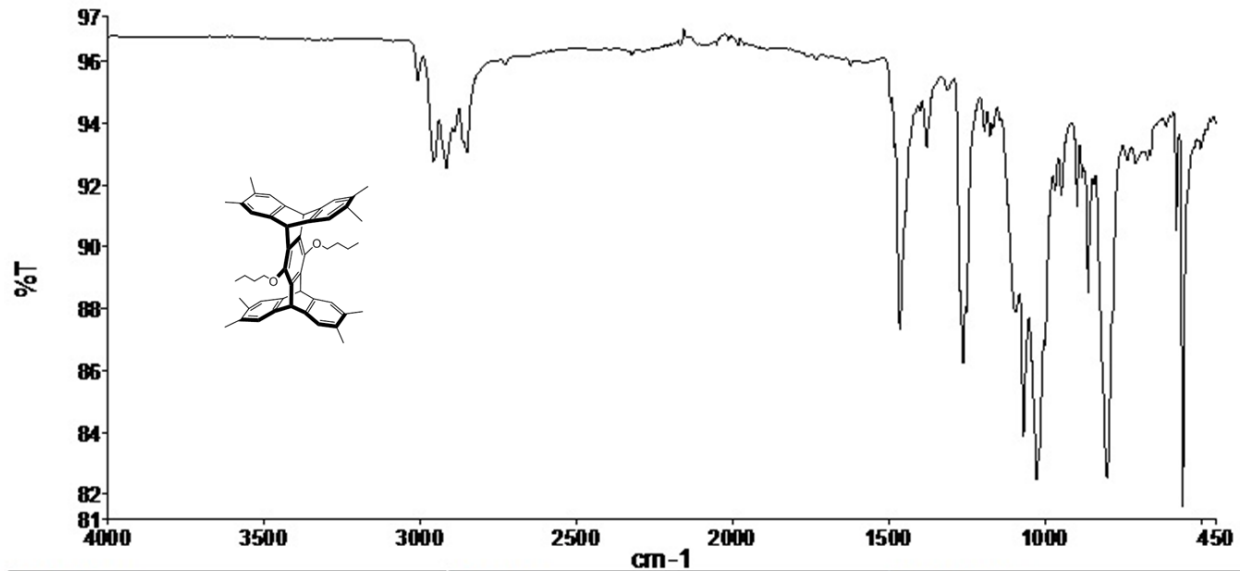


Figure S49. ATR IR of Compound 4b

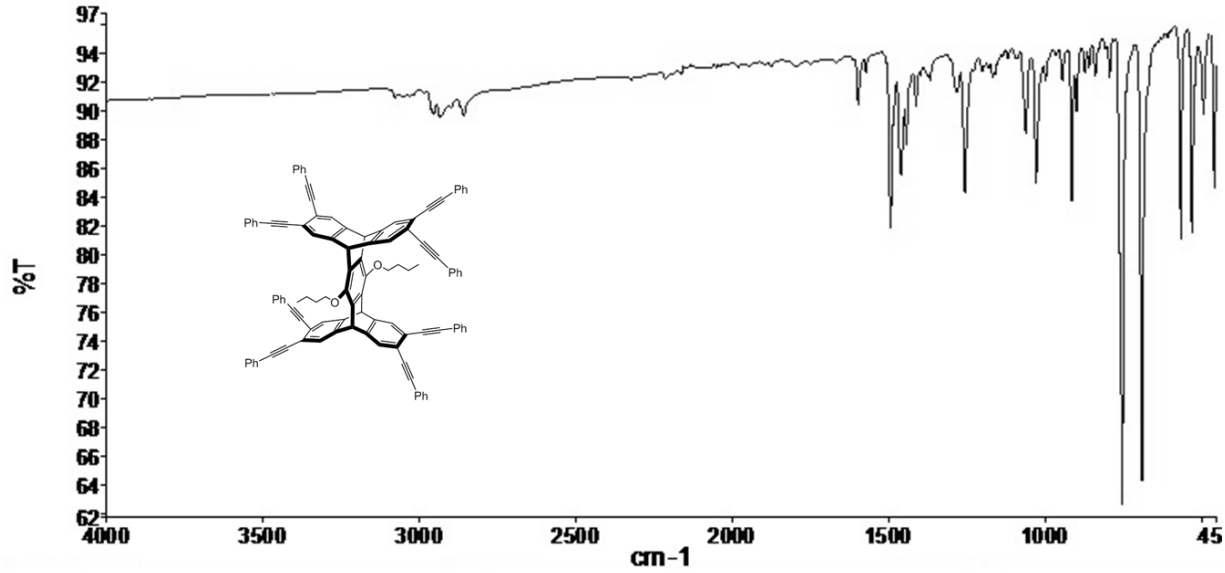


Figure S50. ATR IR of Compound 4c

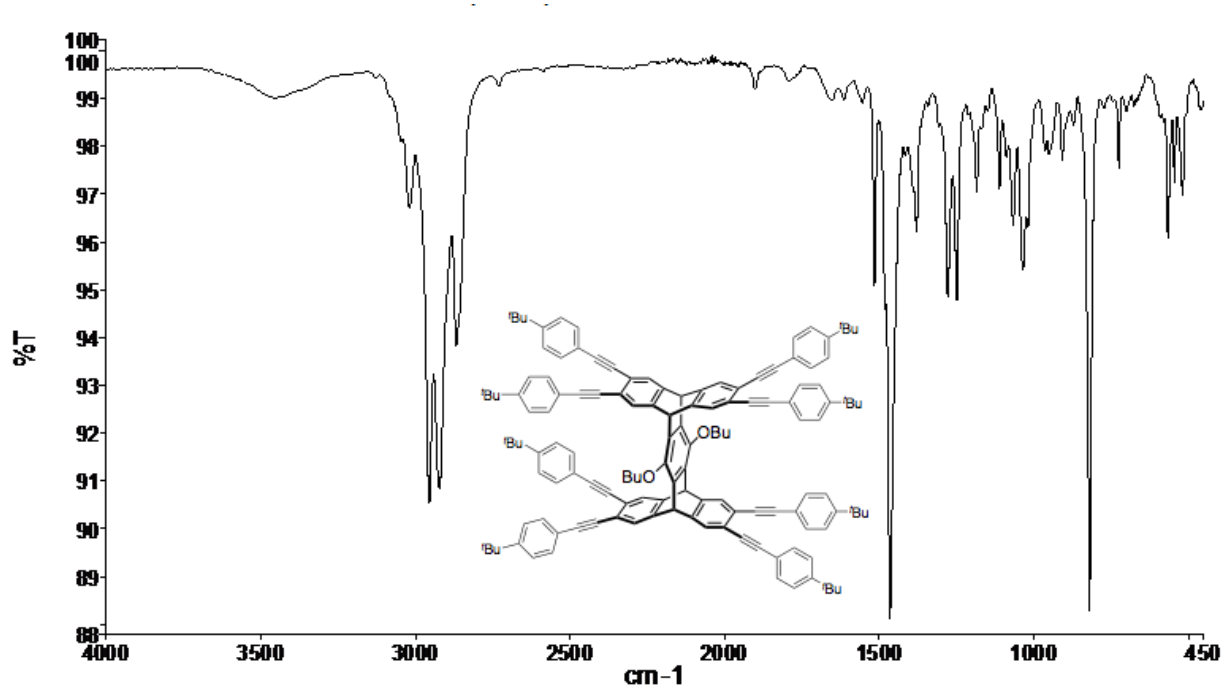


Figure S51. ATR IR of Compound 4d

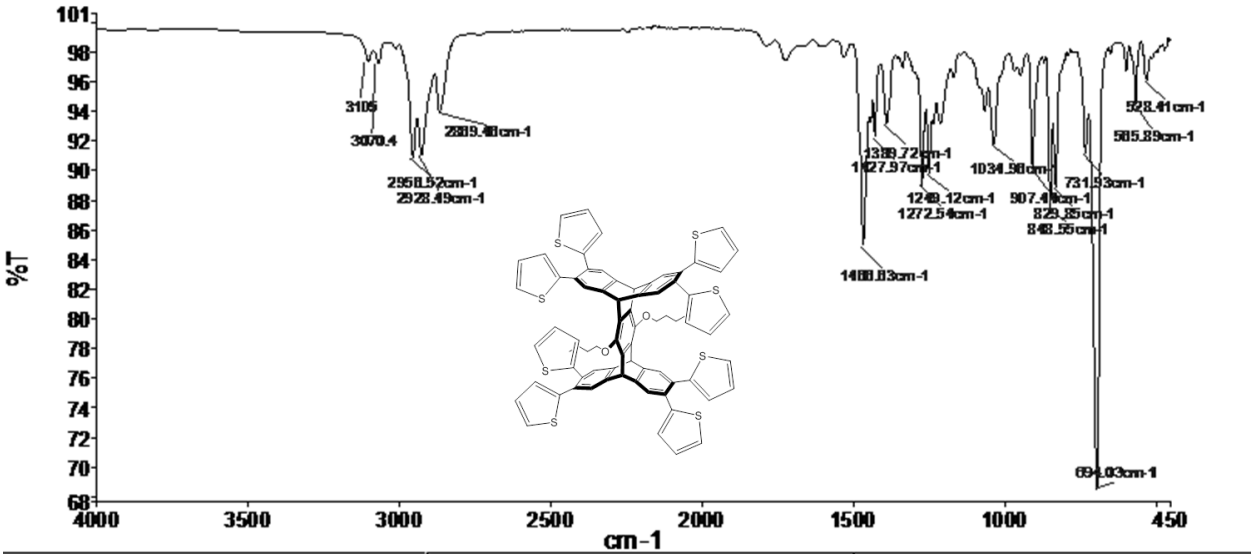


Figure S52. ATR IR of Compound 4e

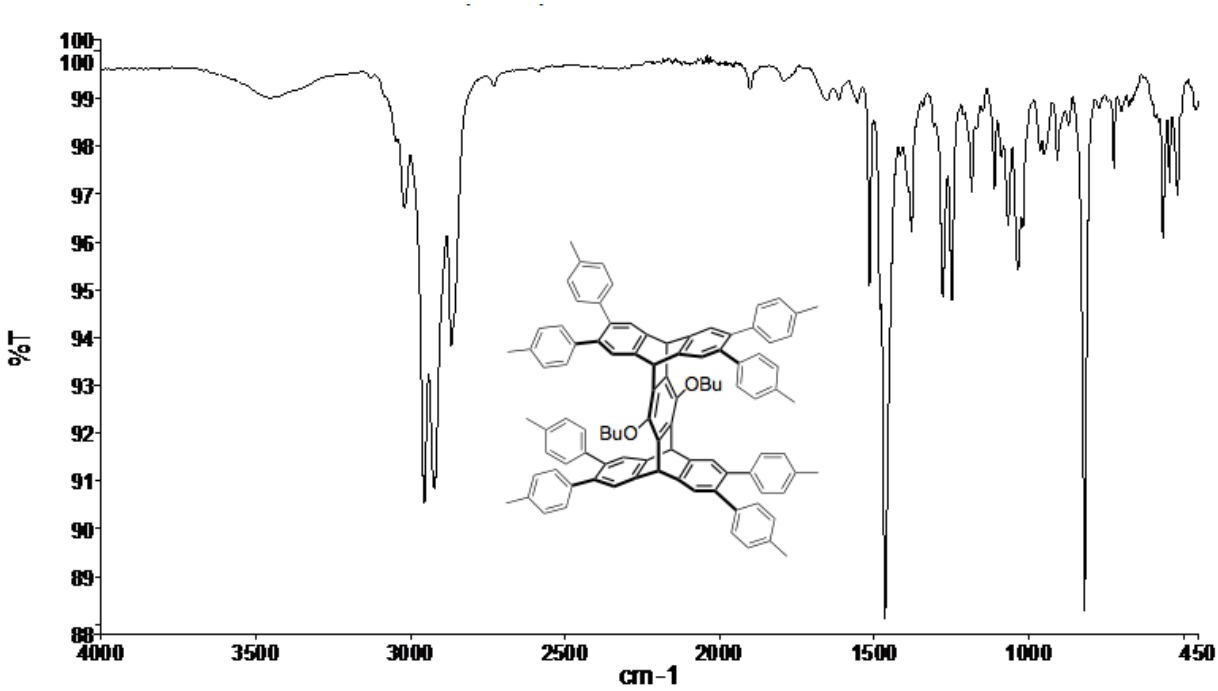


Figure S53. ATR IR of Compound 4f

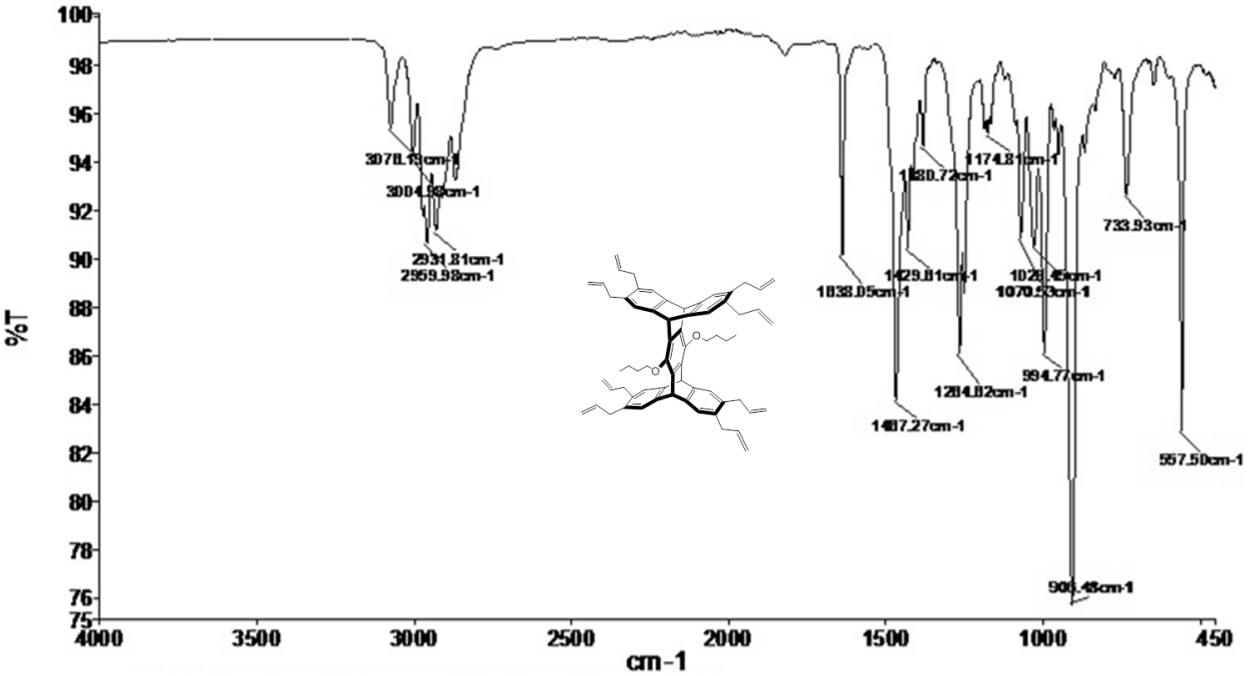


Figure S54. ATR IR of Compound 4g

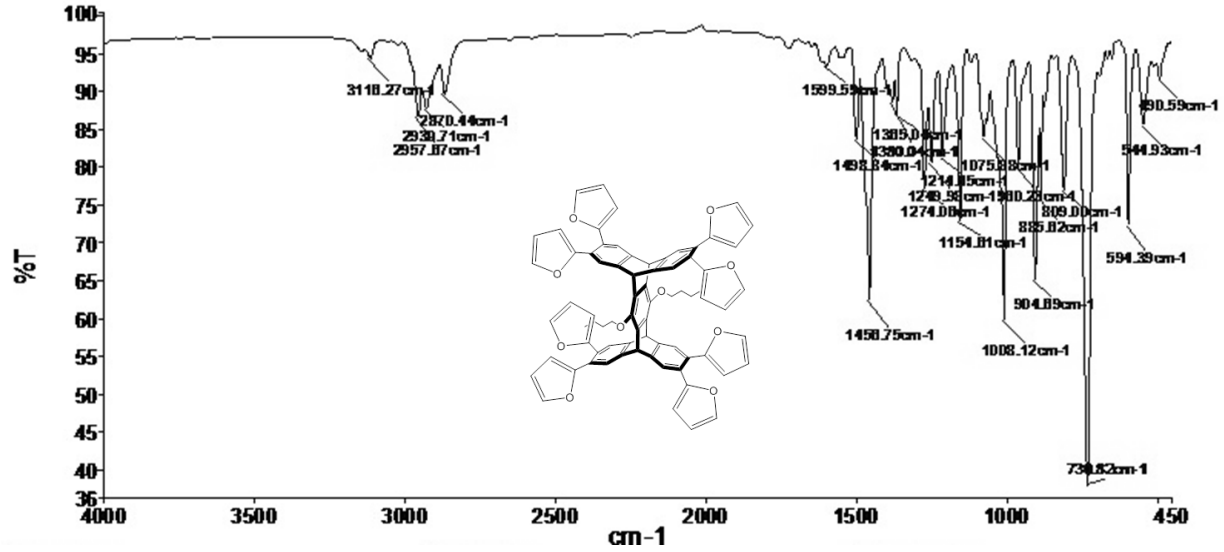


Figure S55. ATR IR of Compound 4h

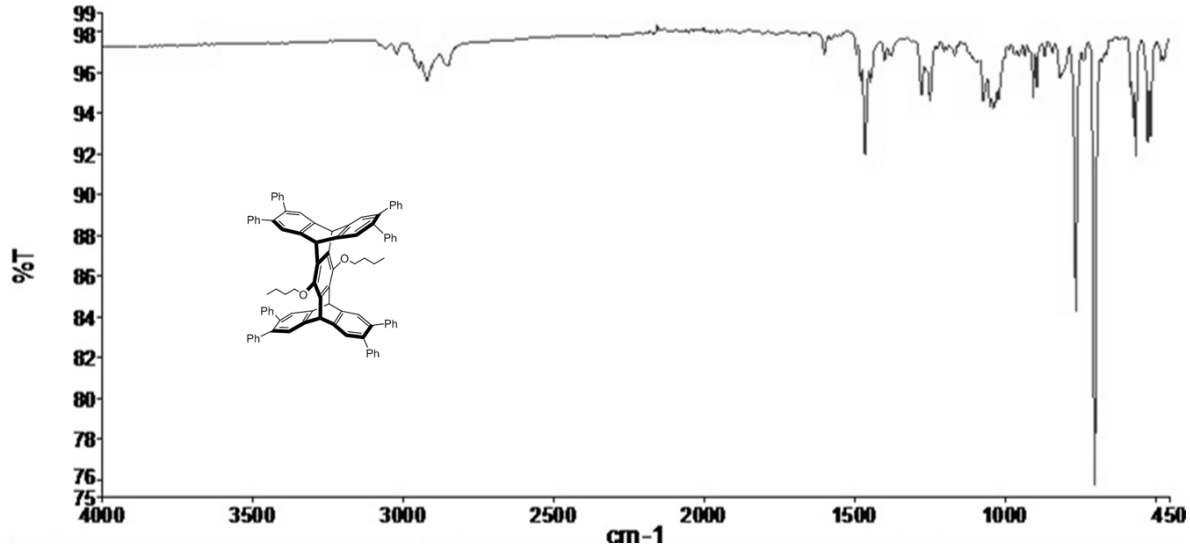


Figure S56. ATR IR of Compound 4i

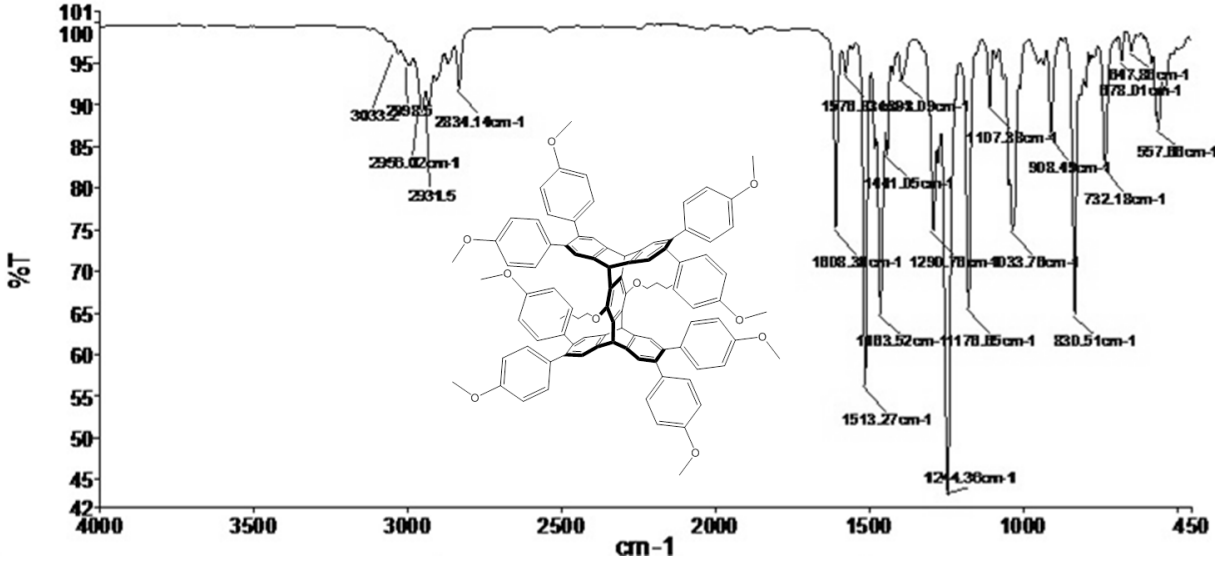


Figure S57. ATR IR of Compound 4j

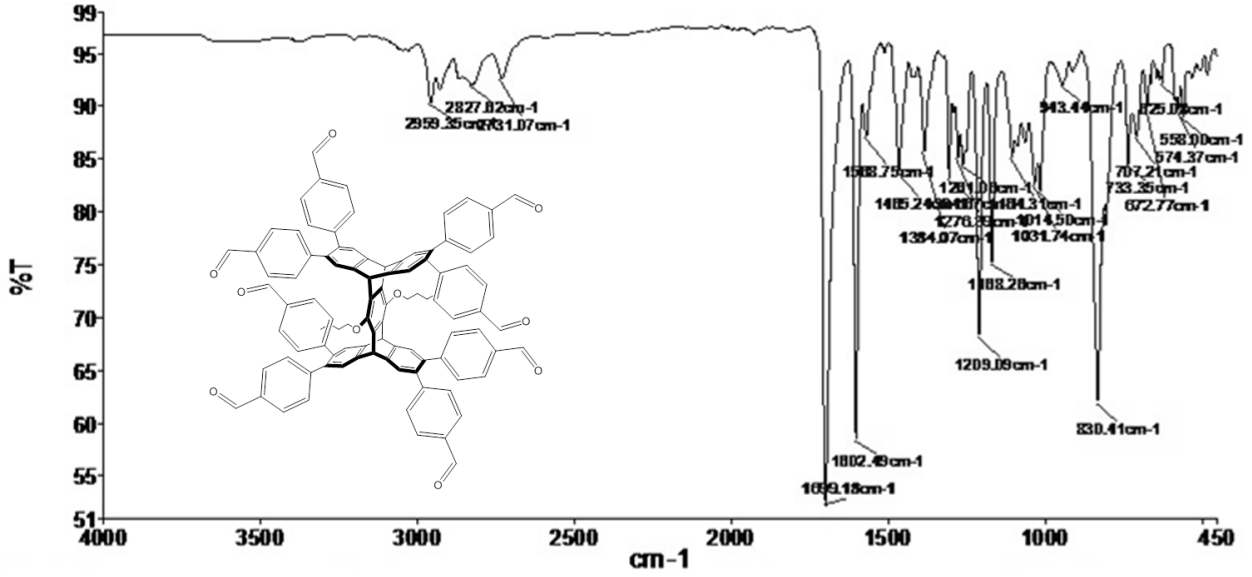


Figure S58. ATR IR of Compound 4k

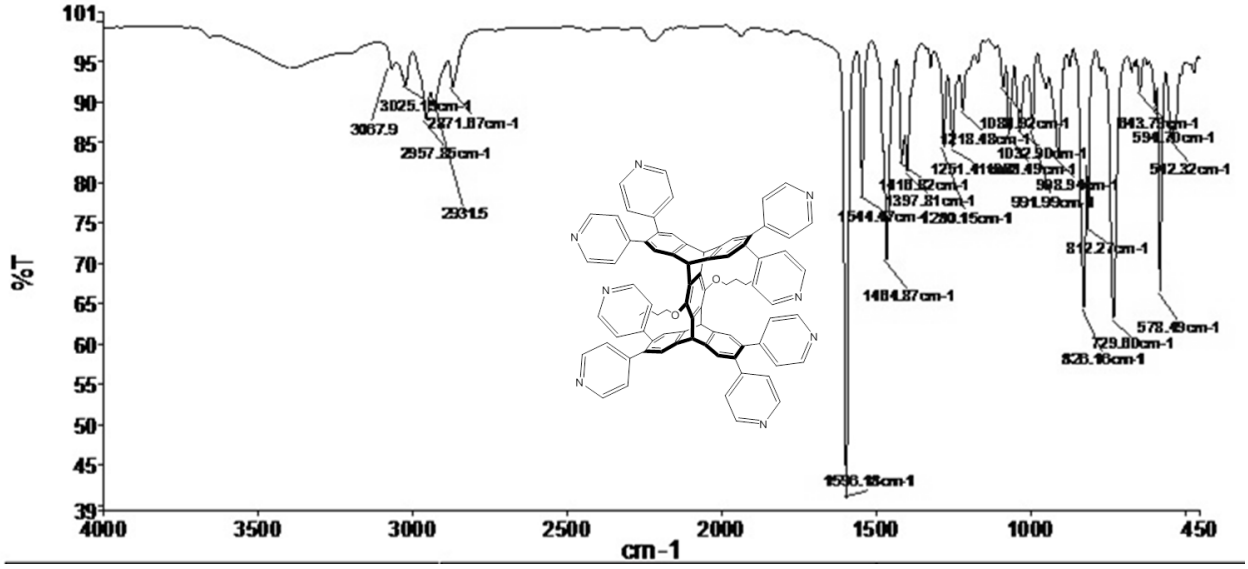


Figure S59. ATR IR of Compound 8

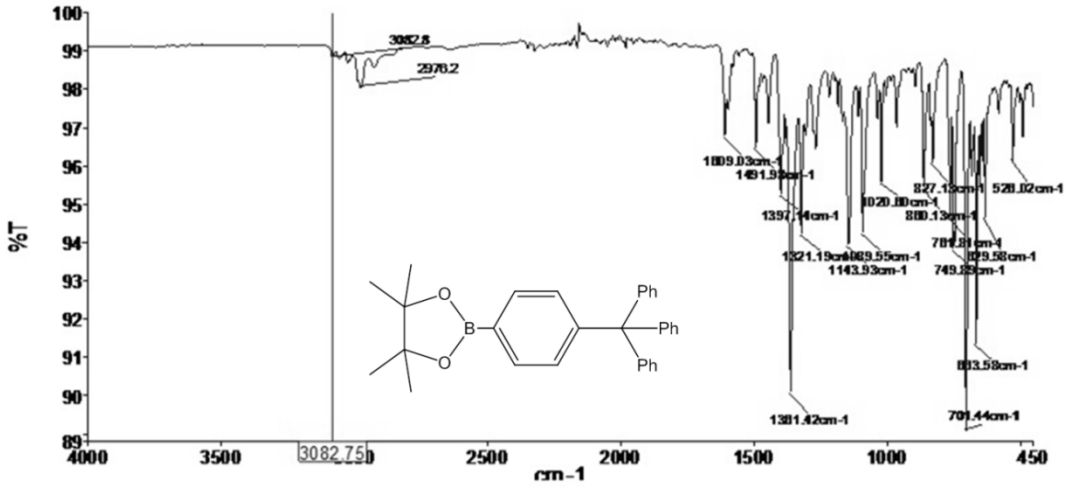


Figure S60. ATR IR of Compound 4l

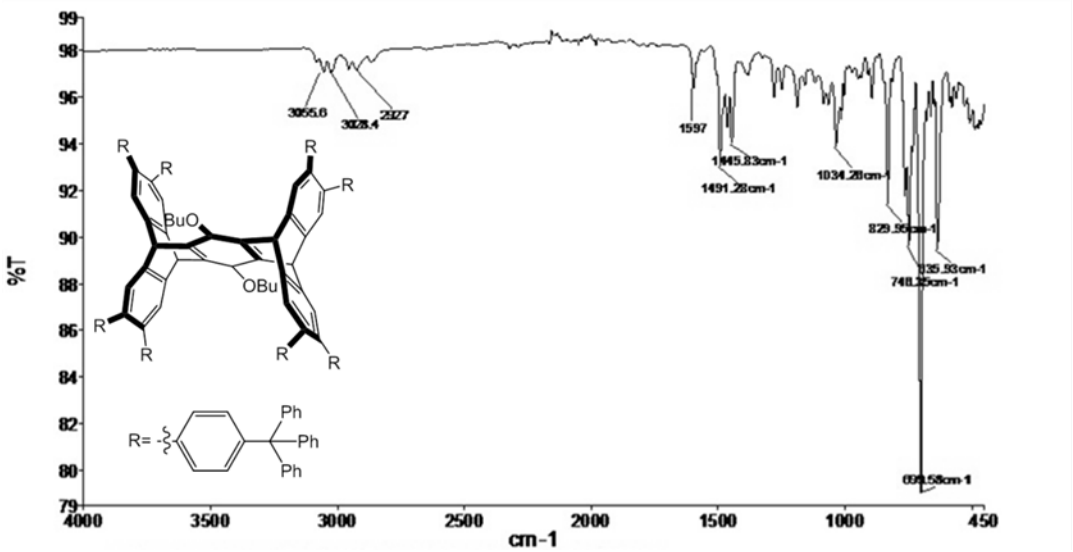


Figure S61. ATR IR of Compound 4m

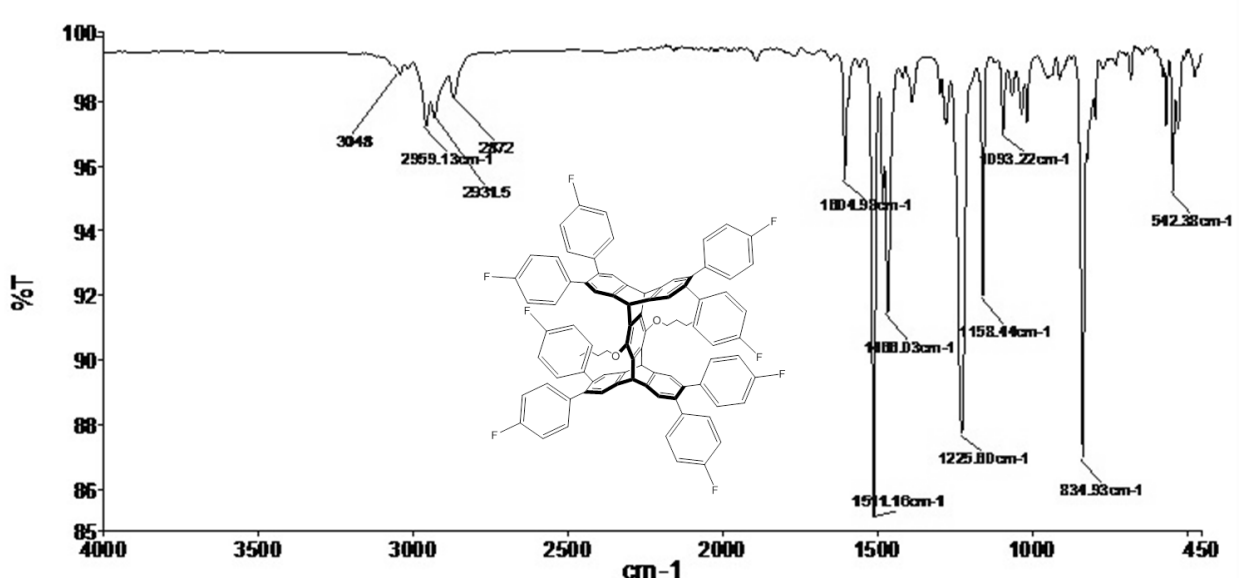


Figure S62. ATR IR of Compound 4n

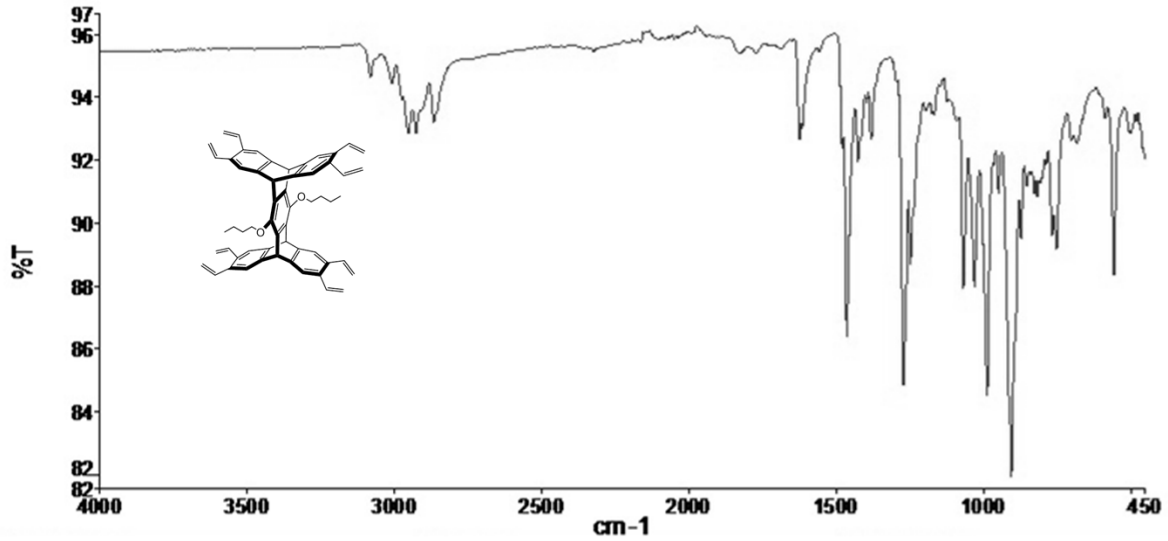


Figure S63. ATR IR of Compound 4o

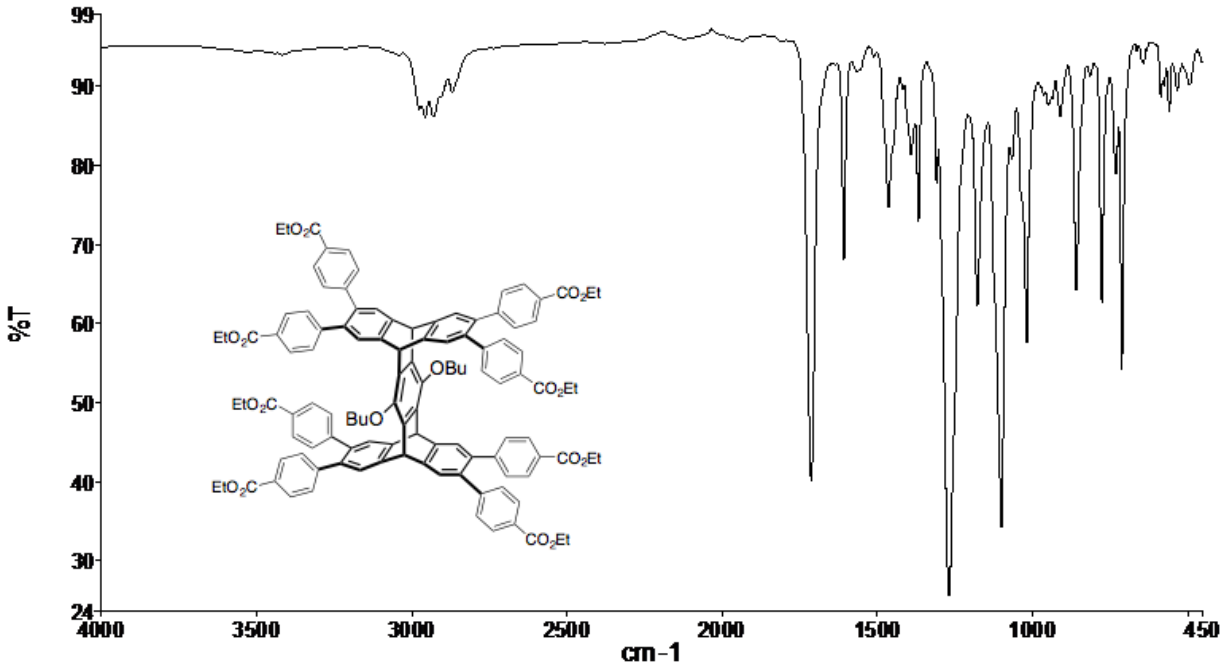


Figure S64. ATR IR of Compound 5a

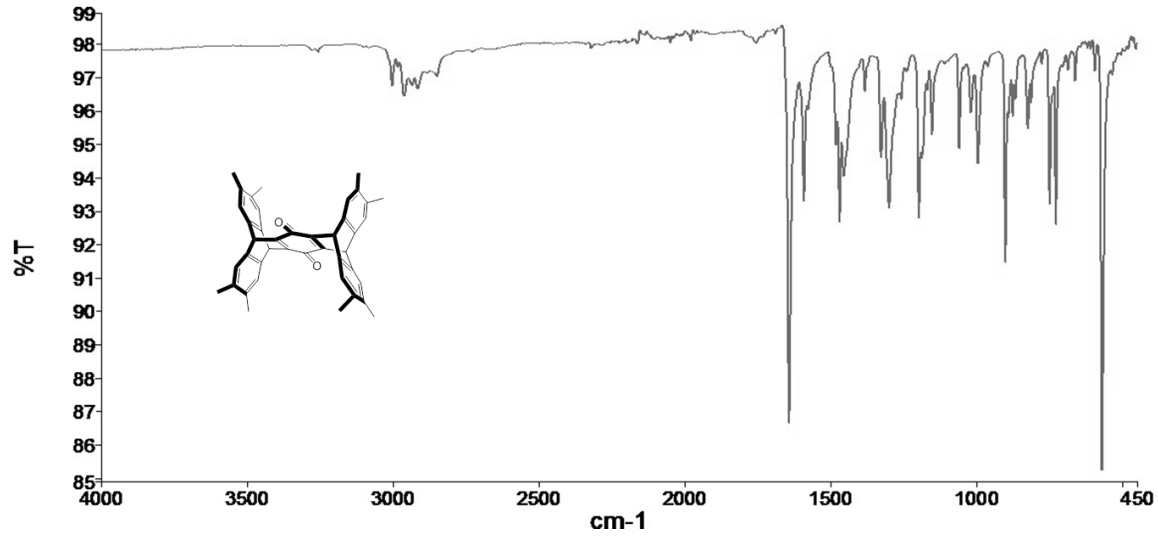


Figure S65. ATR IR of Compound 5h

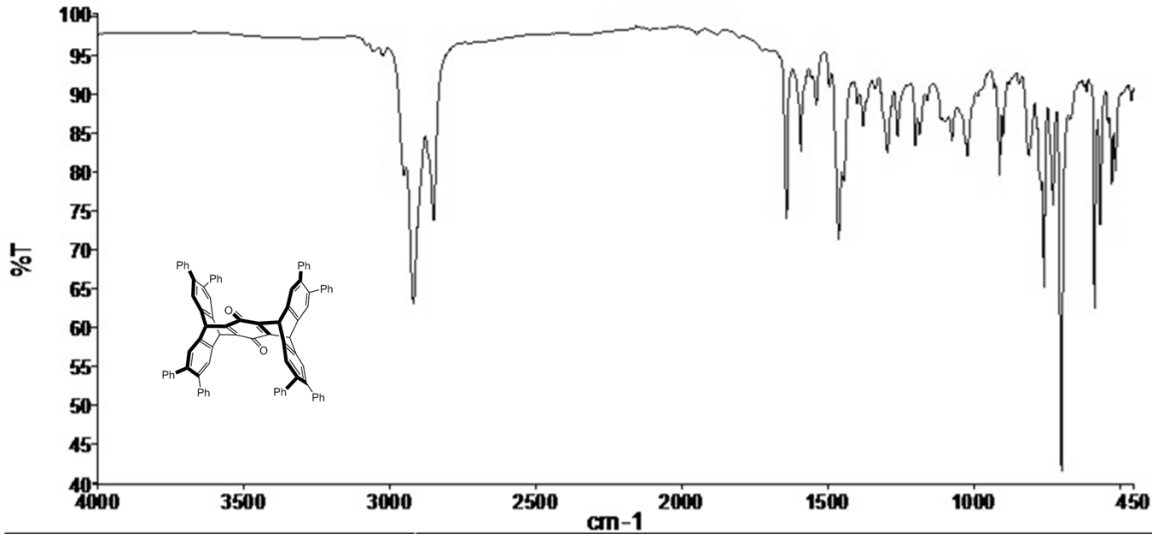
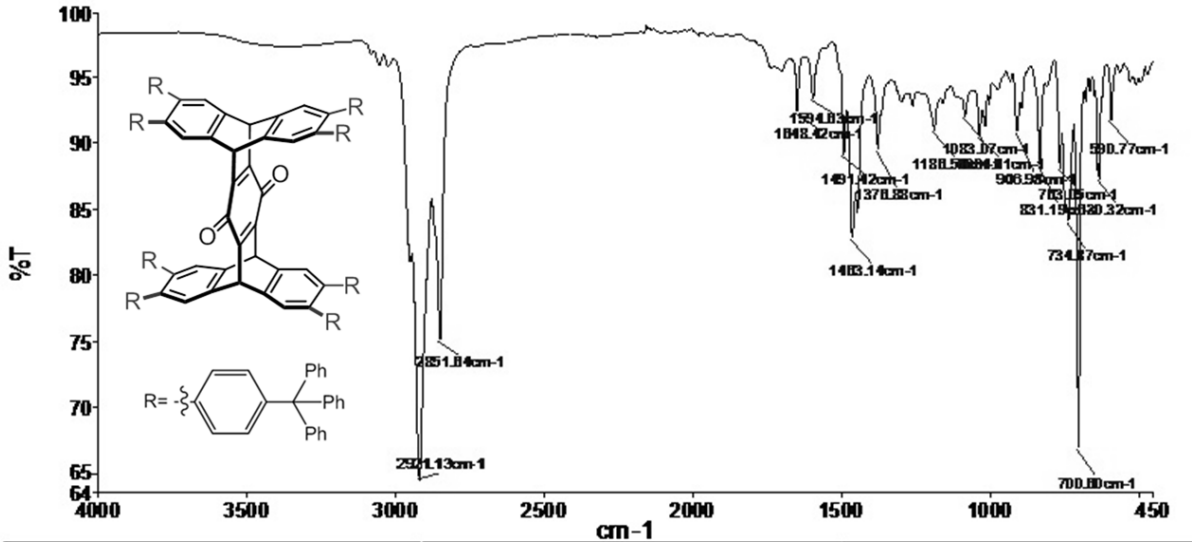


Figure S66. ATR IR of Compound 5l



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[4] It should be noted that the octavinyl derivative proved to be sensitive to a variety of conditions including high heat, light and and SiO_2. As a result, attempts to completely purify the product by traditional column chromatography resulted in drastically depressed yields due to decomposition of the material from prolonged exposure to SiO_2.