Supporting information

Expanding the Scope of Peropyrenes and Teropyrenes Through a Facile $InCl_3$-catalyzed Multifold Alkyne Benzannulation

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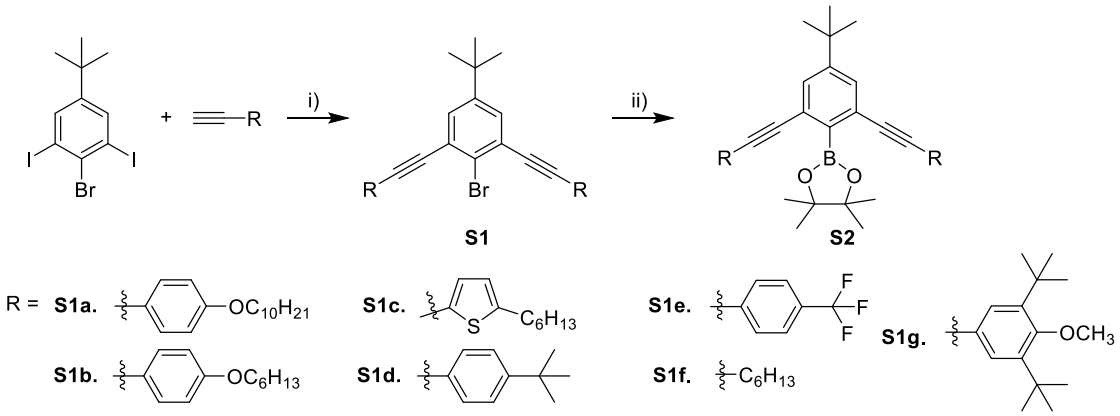
1. General experimental section

All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under nitrogen. Anhydrous tetrahydrofuran (THF) and dichloromethane (DCM) were obtained by passing the solvent (HPLC grade) through an activated alumina column on a PureSolv MD 5 solvent drying system. ^{1}H and ^{13}C NMR spectra were recorded on Varian 400 MHz or Varian 500 MHz NMR Systems Spectrometers. Spectra were recorded in deuterated chloroform ($CDCl_3$) and toluene (d_8-toluene). Tetramethylsilane (TMS, set to 0 ppm) was used as an internal standard for chemical shifts or referenced to the residual protio-solvent $CDCl_3$ peaks (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C, respectively) and d_8-toluene peaks (2.08 ppm for ^{1}H and 20.43 ppm for ^{13}C <CD_2H>, respectively). Chemical shifts are reported in part per million (ppm) from low to high frequency and referenced to the residual solvent resonance. The ^{13}C NMR signals of carbon atoms linked directly to boron were not detected due to the quadrupolar relaxation rate of boron. Coupling constants (J) are reported in Hz. The multiplicity of ^{1}H signals are indicated as: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, br-s = broad singlet. High resolution ESI or APPI mass spectra were recorded using an Agilent 6230 TOF MS. TLC was carried out on silica gel 60 F254 glass plates; visualization by UV or visible light. Purification of reaction products was carried out by flash chromatography using silica gel 60 (230-400 mesh).

2. Synthesis and characterization

Note: For compounds **S1a-c**, **S2a-c**, **1a-c**, **2a-c**, **3a-b**, **4a-b**, **5a**, and **6a**, all the data matched with those were reported before.[1]

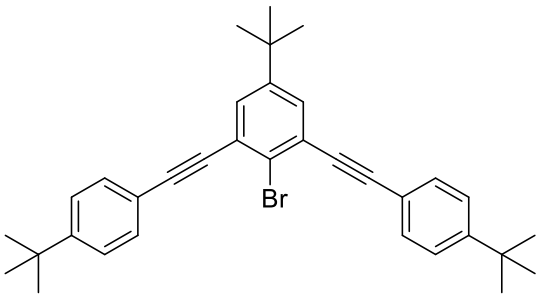
2.1 Synthesis of compound S2



Scheme S1: Conditions: i) $Pd(PPh_3)_2Cl_2$, CuI, THF/Et_3N, r.t., 14 h; ii) (a) *n*-butyl lithium (*n*-BuLi), THF, –78 °C, 30 min; (b) isopropoxyboronic acid pinacol ester, –78 °C to r.t.

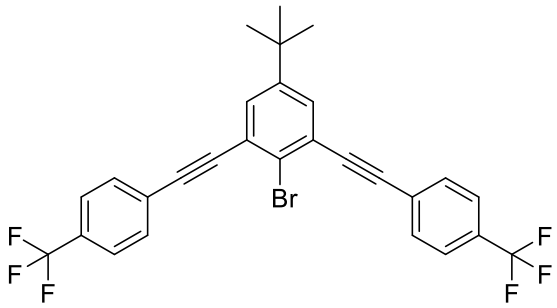
General procedure A for the synthesis of compounds **S1**:

To the solution of 2-bromo-5-(*tert*-butyl)-1,3-diiodobenzene (4.65 g, 10.0 mmol, 1.00 equiv) and terminal alkyne (25 mmol, 2.5 equiv) in Et_3N (40 mL) and THF (80 mL), were added $Pd(PPh_3)_2Cl_2$ (70.0 mg, 0.100 mmol) and CuI (38.0 mg, 0.200 mmol). The resulting mixture was stirred under a N_2 atmosphere at room temperature for 14 h. The ammonium salt was then removed by filtration. The solvent was removed under reduced pressure and the residue was purified by column chromatography.

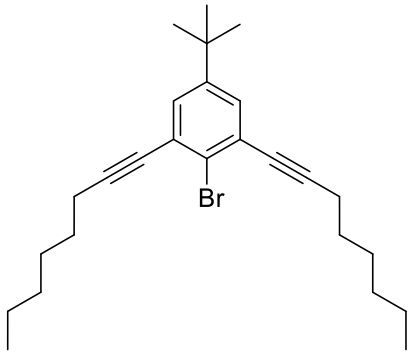


Purification by column chromatography (silica gel, hexane) to give pure **S1d** as light yellow oil (4.15 g, yield 79 %). R_f = 0.1 (hexane); FTIR (neat) 2961, 2209, 1565, 1504 cm^{-1}; ^1H NMR (400 MHz,

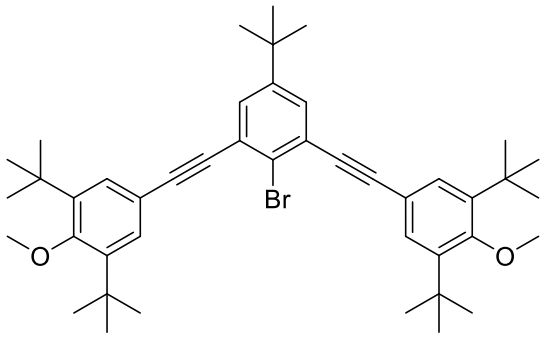
$CDCl_3$) δ 7.58 – 7.54 (m, 4H), 7.53 (s, 2H), 7.43 – 7.38 (m, 4H), 1.39 – 1.33 ppm (m, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 150.2, 131.6, 130.1, 126.1, 125.53, 125.49, 120.0, 93.7, 88.2, 35.0, 34.7, 31.3, 31.2 ppm; HRMS (ESI, positive) *m/z* calcd for $C_{34}H_{38}Br$ $[M+H]^+$ 525.2151, found 525.2176.



Purification by column chromatography (silica gel, hexane) to give pure **S1e** as white solid (4.71 g, yield 86%). R_f = 0.2 (hexane); FTIR (neat) 2969, 2213, 1930, 1687, 1613 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.68 (m, 4H), 7.67 – 7.61 (m, 4H), 7.59 (s, 2H), 1.36 ppm (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 132.1, 131.0, 130.5 (q, ^2J(C,F) = 32.5 Hz), 126.8, 126.7, 125.5, 125.49 (q, ^1J(C,F) = 3.8 Hz), 124.0 (q, ^3J(C,F) = 271.3 Hz), 92.2, 90.7, 34.8, 31.1 ppm; HRMS (ESI, positive) *m/z* calcd for $C_{28}H_{19}BrF_6Na$ $[M+Na]^+$ 571.0467, found 571.0474.



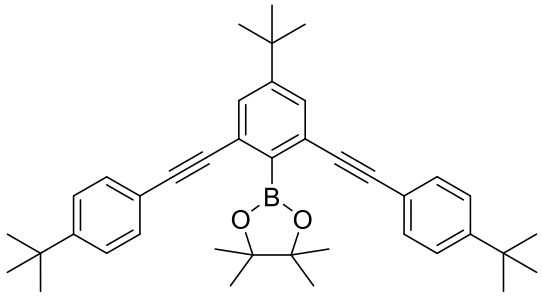
Purification by column chromatography (silica gel, hexane) to give pure **S1f** as light yellow oil (3.00 g, yield 70 %). R_f = 0.2 (hexane); FTIR (neat) 2955, 2928, 2857, 2232, 1565 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 2H), 2.46 (t, *J* = 7.0 Hz, 4H), 1.68 – 1.59 (m, 4H), 1.55 – 1.46 (m, 4H), 1.40 – 1.30 (m, 8H), 1.27 (s, 9H), 0.91 ppm (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 129.7, 126.3, 125.2, 95.0, 80.2, 34.5, 31.5, 31.1, 28.73, 28.70, 22.7, 19.8, 14.2 ppm; HRMS (ESI, positive) *m/z* calcd for $C_{26}H_{38}Br$ $[M+H]^+$ 429.2151, found 429.2159.



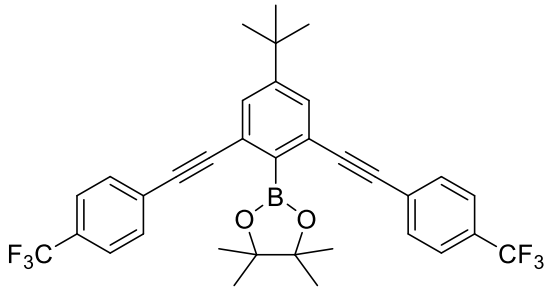
Purification by column chromatography (silica gel, hexane) to give pure **S1g** as light yellow oil (5.03 g, yield 72 %). R_f = 0.2 (hexane); FTIR (neat) 2962, 2871, 2212, 1735, 1562 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 2H), 7.51 (s, 4H), 3.71 (s, 6H), 1.46 (s, 36H), 1.35 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 150.1, 144.3, 130.4, 130.0, 126.1, 125.3, 117.3, 94.4, 87.4, 64.6, 35.9, 34.7, 32.1, 31.2 ppm; HRMS (ESI, positive) *m/z* calcd for $C_{44}H_{58}BrO_2$ $[M+H]^+$ 697.3615, found 697.3608.

General procedure B for synthesis of compounds **S2**:

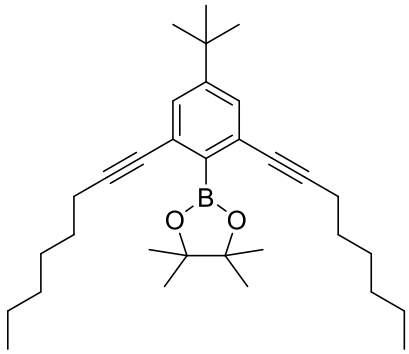
To a solution of **S1** (5 mmol) in THF (50 mL) at −78 °C was added a solution of n-butyllithium in hexanes (2 mL, 2.5 M, 5.00 mmol). After stirring for 30 min at −78 °C, isopropoxyboronic acid pinacol ester (930 mg, 5.00 mmol) was added, the reaction removed from the cooling bath and warmed to room temperature. Upon reaching room temperature the reaction was quenched by the addition of H_2O, and then extracted with DCM. The extract was washed with water, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography.



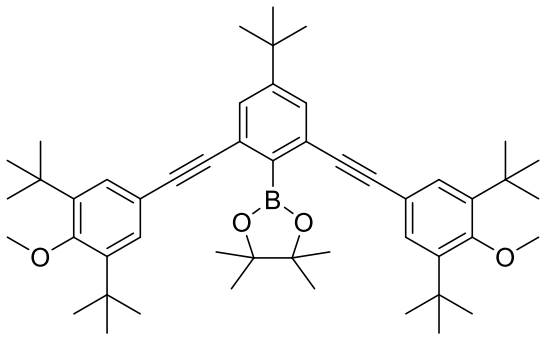
Purification by column chromatography (silica gel, hexane:DCM = 2:1, v/v) to give **S2d** as light yellow foam solid (2.20 g, yield 77 %). R_f = 0.2 (hexane/DCM 2:1); FTIR (neat) 2962, 2208, 1909, 1776, 1586, 1537, 1462, 1363, 1318, 1266, 1133, 1108, 1054, 963, 855, 833 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 2H), 7.50 – 7.46 (m, 4H), 7.39 – 7.35 (m, 4H), 1.40 (s, 12H), 1.34 (s, 18H), 1.33 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 151.5, 131.4, 129.1, 126.8, 125.4, 120.6, 90.1, 89.6, 84.3, 34.9, 34.8, 31.3, 31.1, 25.2 ppm; HRMS (ESI, positive) *m/z* calcd for $C_{40}H_{50}BO_2$ $[M+H]^+$ 573.3898, found 573.3925.



Purification by column chromatography (silica gel, hexane:DCM = 3:1, v/v) to give **S2e** as light yellow solid (1.16 g, yield 39 %). R_f = 0.4 (hexane/DCM 2:1); FTIR (neat) 2279, 2205, 1929, 1615 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 8H), 7.57 (s, 2H), 1.37 (s, 12H), 1.34 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 131.9, 130.1 (q, *J*(C,F) = 32.0 Hz), 129.8, 127.4, 126.3, 125.4 (q, *J*(C,F) = 3.8 Hz), 124.1 (q, *J*(C,F) = 264.5 Hz), 92.5, 88.7, 84.5, 34.9, 31.1, 25.1 ppm; HRMS (ESI, positive) *m/z* calcd for $C_{34}H_{31}BF_6O_2Na$ $[M+Na]^+$ 619.2214, found 619.2251.



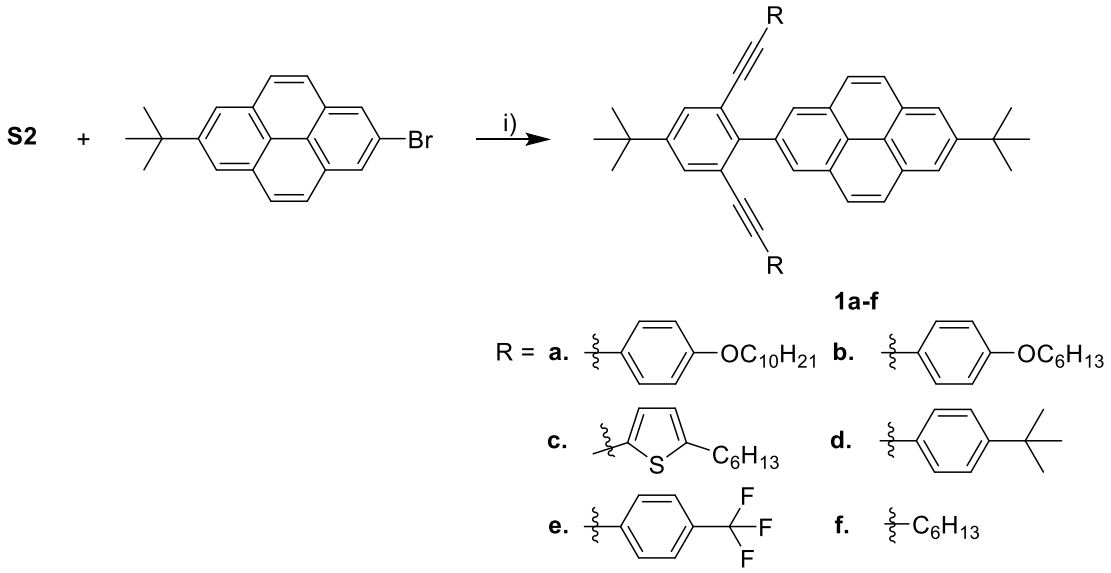
Purification by column chromatography (silica gel, hexane:DCM = 4:1, v/v) to give **S2f** as light yellow oil (1.86 g, yield 78 %). R_f = 0.25 (hexane/DCM 4:1); FTIR (neat) 2955, 2929, 2858, 2228, 1558, 1460, 1333, 1312, 1149, 1132, 1057, 879 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 2H), 2.37 (t, *J* = 7.2 Hz, 4H), 1.64 – 1.54 (m, 4H), 1.50 – 1.41 (m, 4H), 1.39 (s, 12H), 1.34 – 1.27 (m, 8H), 1.25 (s, 9H), 0.89 ppm (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 128.1, 126.9, 90.7, 84.0, 81.3, 34.6, 31.5, 31.1, 28.90, 28.86, 25.0, 22.7, 19.8, 14.2 ppm; HRMS (ESI, positive) *m/z* calcd for $C_{32}H_{49}BO_2Na$ $[M+Na]^+$ 499.3718, found 499.3749.



Purification by column chromatography (silica gel, hexane:DCM = 3:1, v/v) to give **S2g** as light yellow oil (2.03 g, yield 54 %). R_f = 0.25 (hexane/DCM 3:1); FTIR (neat) 2963, 2869, 2206, 1587 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 2H), 7.43 (s, 4H), 3.69 (s, 6H), 1.43 (s, 36H), 1.42 (s, 12H), 1.33 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 152.2, 144.0, 130.3, 128.9, 126.8, 117.9, 90.7, 88.7, 84.3, 64.5, 35.9,

34.8, 32.1, 31.2, 25.2 ; HRMS (ESI, positive): *m/z* calcd for $C_{50}H_{69}BO_4Na$ $[M+Na]^+$ 767.5181, found 766.5203.

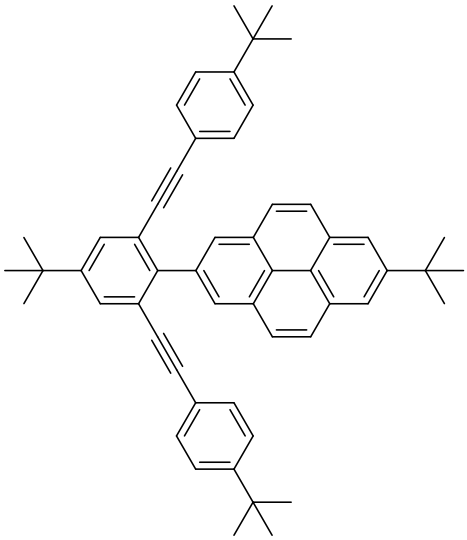
2.2 Synthesis of compound 1



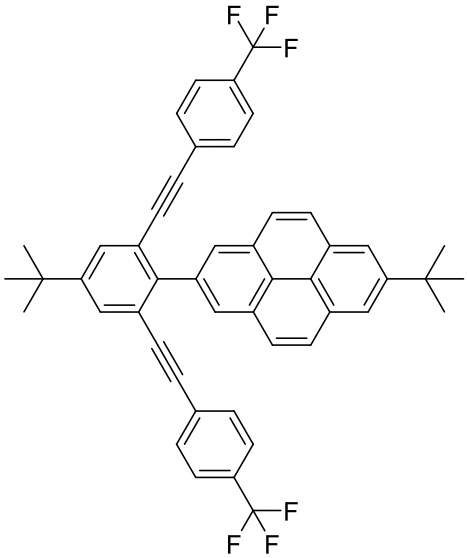
Scheme S2: Conditions: i) $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, 80 °C, 24 h

General procedure C for synthesis of compounds **1**:

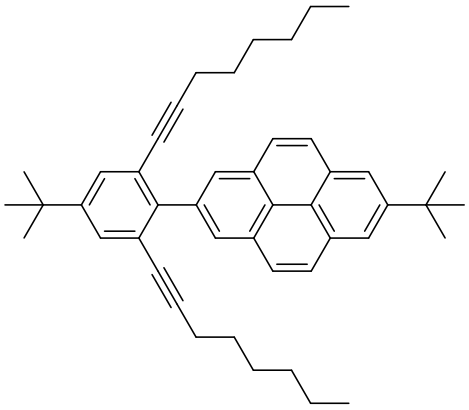
2-Bromo-7-(*tert*-butyl)pyrene (168 mg, 0.500 mmol), 2,6-diynylphenyl borate **S2** (0.600 mmol) and K_2CO_3 (138 mg, 1.00 mmol) were dissolved in THF (20 mL) and water (4 mL) solution. $Pd(PPh_3)_4$ (29.0 mg, 0.0250 mmol) was added to the solution before degassing the mixture via bubbling nitrogen for 30 min. The resulting mixture was stirred under a N_2 atmosphere at 80 °C for 24 h. After the reaction was complete, the mixture was diluted with DCM, washed with H_2O and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography.



Purification by flash column chromatography (silica gel, hexane:DCM = 10:1, v/v) yielded pure **1d** as a light yellow solid (165 mg, yield 47%). R_f = 0.4 (hexane/DCM 7:1); FTIR (neat) 2960, 2902, 2245, 1905, 1606, 1555, 1512 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 2H), 8.29 (s, 2H), 8.16 (d, *J* = 9.0 Hz, 2H), 8.12 (d, *J* = 9.0 Hz, 4H), 7.76 (s, 2H), 7.17 – 7.08 (m, 4H), 7.06 – 6.98 (m, 4H), 1.65 (s, 9H), 1.48 (s, 9H), 1.21 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 150.3, 149.1, 143.2, 136.3, 131.4, 131.2, 130.3, 129.8, 127.8, 127.6, 127.5, 125.3, 124.1, 123.5, 123.2, 122.1, 120.2, 92.5, 89.2, 35.4, 34.80, 34.79, 32.2, 31.4, 31.2 ppm; HRMS (APPI, positive): calcd for $C_{54}H_{54}$ $[M]^+$ 702.4220, found 702.4236.

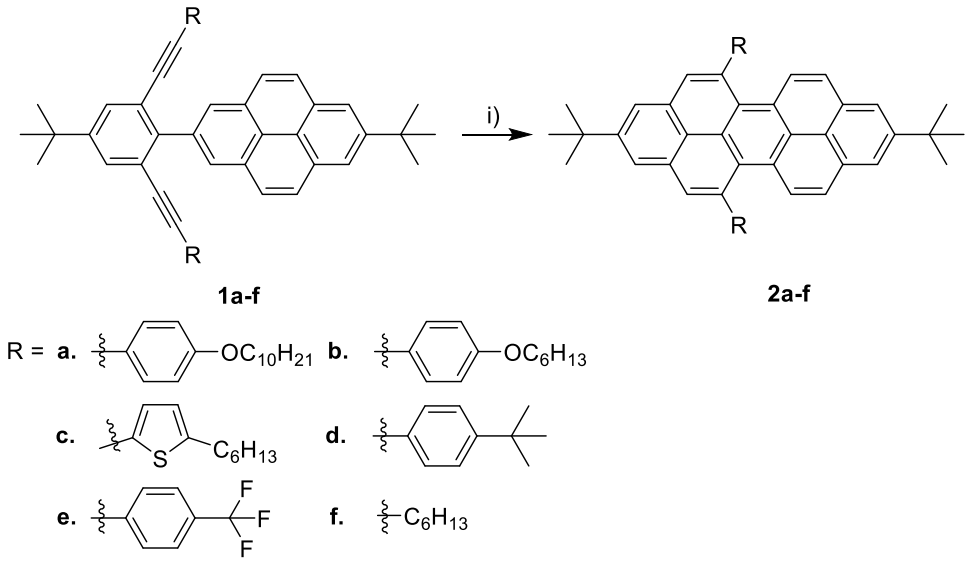


Purification by column chromatography (silica gel, hexane:DCM = 20:1, v/v) to give **1e** as light yellow solid (167 mg, yield 46 %). R_f = 0.5 (hexane/DCM 10:1); FTIR (neat) 2964, 2210, 1614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 2H), 8.29 (s, 2H), 8.11 (br-s, 4H), 7.79 (s, 2H), 7.39 – 7.30 (m, 4H), 7.16 – 7.04 (m, 4H), 1.63 (s, 9H), 1.48 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 149.5, 144.2, 135.8, 131.6, 131.4, 130.6, 130.4, 129.8 (q, ^2J(C,F) = 32.4 Hz), 128.0, 127.4, 127.1, 126.9, 125.2 (q, ^1J(C,F) = 3.8 Hz), 124.2, 123.9 (q, ^3J(C,F) = 270.6 Hz), 123.1, 122.9, 122.5, 92.0, 91.1, 35.5, 34.9, 32.1, 31.3 ppm; HRMS (ESI, positive) *m/z* calcd for $C_{48}H_{37}F_6$ $[M+H]^+$ 727.2794, found 727.2821.



Purification by flash column chromatography (silica gel, hexane:DCM = 15:1, v/v) yielded pure **1f** as a light yellow solid (103 mg, yield 34%). R_f = 0.4 (hexane/DCM 12:1); FTIR (neat) 2951, 2931, 2866, 2231, 1756, 1605, 1555 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 2H), 8.24 (s, 2H), 8.08 (br-s, 4H), 7.58 (s, 2H), 2.08 (t, *J* = 6.9 Hz, 4H), 1.62 (s, 9H), 1.42 (s, 9H), 1.14 – 1.04 (m, 4H), 0.87 – 0.60 (m, 12H), 0.49 ppm (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 148.9, 143.7, 137.0, 131.3, 130.3, 129.0, 127.7, 127.3, 127.1, 124.0, 123.9, 123.2, 122.1, 93.5, 80.7, 35.4, 34.6, 32.1, 31.3, 28.42, 28.38, 22.3, 19.5, 13.9 (one alkyl peak missing due to coincidental overlap) ppm; HRMS (ESI, positive) *m/z* calcd for $C_{46}H_{55}$ $[M+H]^+$ 607.4298, found 607.4313.

2.3 Synthesis of peropyrenes 2

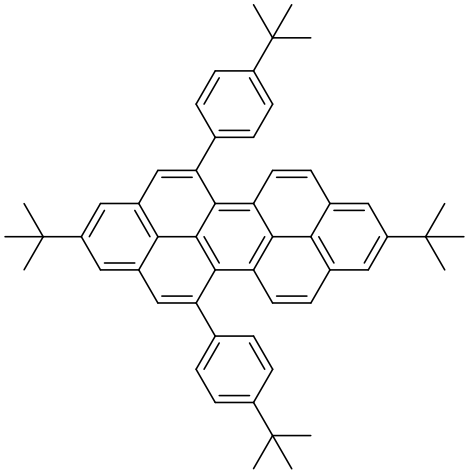


Scheme S3: Conditions: i) $InCl_3$, toluene, 100 °C.

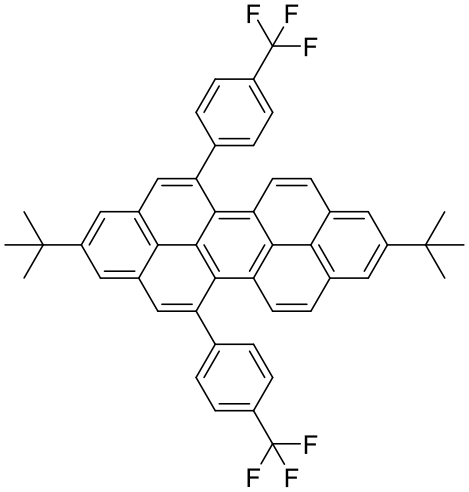
General procedure E for synthesis of compounds **2**:

A flame-dried round-bottom flask was charged with a magnetic stirring bar, the

corresponding precursors **4** (0.0300 mmol) and anhydrous toluene (3 mL). $InCl_3$ (2.00 mg, 0.3 equiv., 0.00900 mmol) was added to the solution before degassing the mixture via bubbling nitrogen for 30 min, then the resulting mixture was heated at 100°C under a N_2 atmosphere. After reaction completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography.

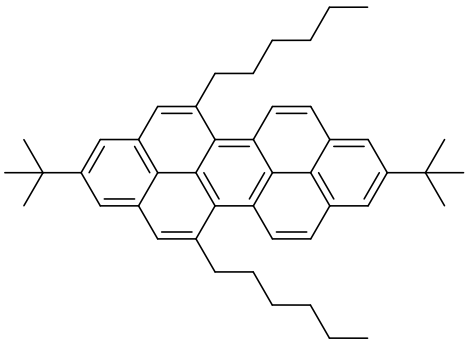


Purification by flash column chromatography (silica gel, hexane:DCM = 10:1, v/v) yielded pure **2d** as an orange solid (19.0 mg, yield 91%). R_f = 0.4 (hexane/DCM 8:1); FTIR (neat) 2953, 2901, 2864, 1628, 1578, 1509 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 2H), 8.25 (s, 2H), 8.22 (s, 2H), 8.22 (d, *J* = 9.5 Hz, 2H), 7.72 (d, *J* = 9.5 Hz, 2H), 7.58 – 7.45 (m, 8H), 1.63 (s, 9H), 1.60 (s, 9H), 1.49 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 149.7, 149.2, 143.2, 139.6, 131.3, 131.0, 130.9, 128.8, 128.4, 126.0, 125.9, 125.5, 124.8, 124.6, 124.4, 122.72, 122.68, 122.4, 121.8, 35.3, 35.3, 34.8, 32.1, 32.0, 31.7 ppm; HRMS (APPI, positive): *m/z* calcd for $C_{54}H_{54}$ $[M]^+$ 702.4220, found 702.4226.



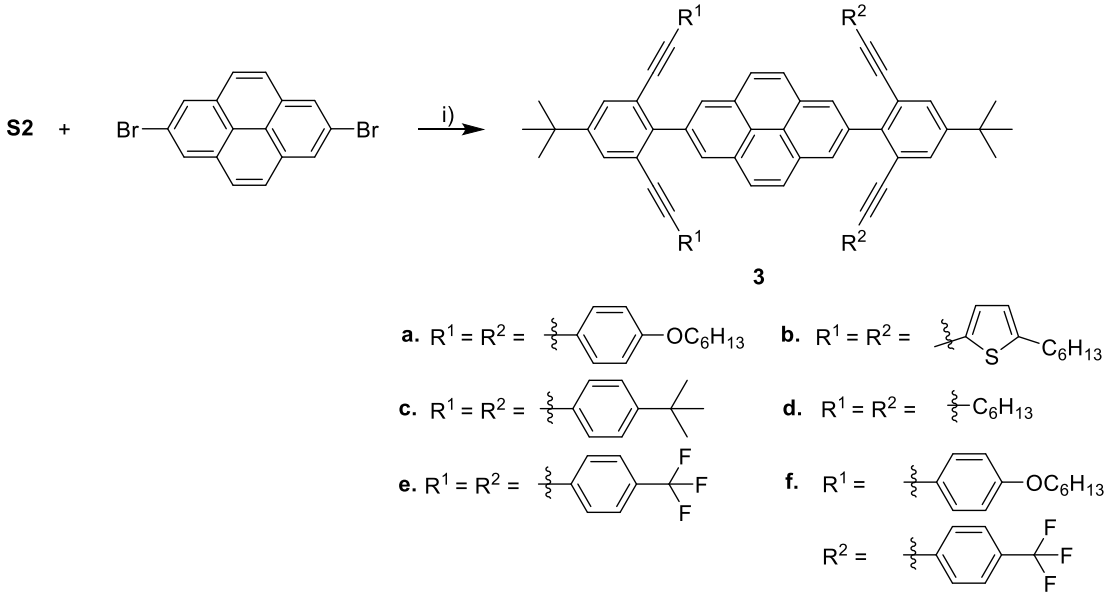
Reaction was performed with 50 mol % $InCl_3$ in xylene at 150 °C for 24 hours. Purification by flash column chromatography (silica gel, hexane:DCM = 20:1, v/v) yielded pure **2e** as an orange solid (15.7 mg, yield 72%). R_f = 0.5 (hexane/DCM 10:1); FTIR (neat) 2963, 1614, 1580 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 2H), 8.26 (s, 2H), 8.23 (s, 2H), 8.05 (d, *J* = 9.3 Hz, 2H), 7.80 (d, *J* = 9.4 Hz, 2H), 7.78 – 7.41 (m, 4H), 7.69 – 7.65 (m, 4H), 1.63 (s, 9H), 1.59 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 149.8, 149.58, 149.57, 138.2, 131.9, 130.71, 130.67, 129.5, 129.3 (q, ^2J(C,F) = 32.3 Hz), 128.1, 126.1 (q,

^1J(C,F) = 3.7 Hz), 125.7, 125.4, 124.6 (q, ^3J(C,F) = 279.8 Hz), 124.5, 123.8, 123.7, 123.1, 122.5, 122.2, 35.43, 35.38, 32.02, 32.01 ppm; HRMS (ESI, positive) *m/z* calcd for $C_{48}H_{36}F_6$ $[M]^+$ 726.2716, found 726.2728.



Purification by flash column chromatography (silica gel, hexane:DCM = 15:1, v/v) yielded pure **2f** as an orange solid (15.6 mg, yield 87%). R_f = 0.6 (hexane/DCM 10:1); FTIR (neat) 2954, 2926, 2857, 1629, 1577 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 9.3 Hz, 2H), 8.37 (s, 2H), 8.27 (s, 2H), 8.23 – 8.16 (m, 4H), 3.76 – 3.68 (m, 4H), 1.98 (m, 4H), 1.66 (s, 9H), 1.65 (s, 9H), 1.52 – 1.48 (m, 4H), 1.39 – 1.32 (m, 8H), 0.89 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.22, 149.16, 138.7, 131.04, 130.95, 129.2, 127.1, 126.6, 125.2, 125.1, 124.8, 123.9, 123.0, 122.4, 121.5, 120.5, 38.5, 35.4, 35.3, 32.13, 32.11, 31.9, 31.8, 29.8, 22.8, 14.2 ppm; HRMS (ESI, positive) *m/z* calcd for $C_{46}H_{55}$ $[M+H]^+$ 607.4298, found 607.4311.

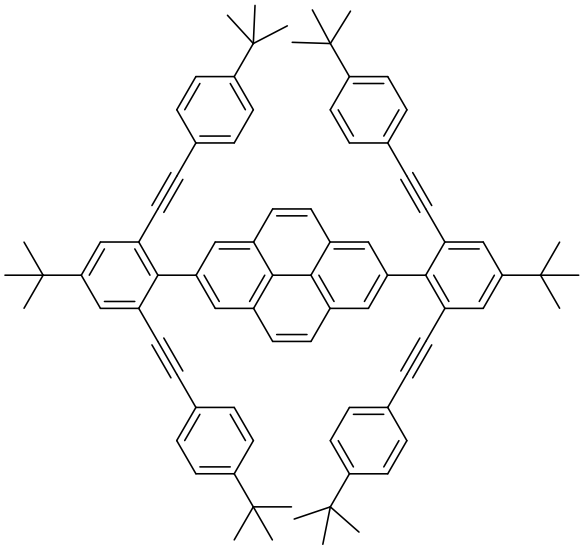
2.4 Synthesis of compound 3



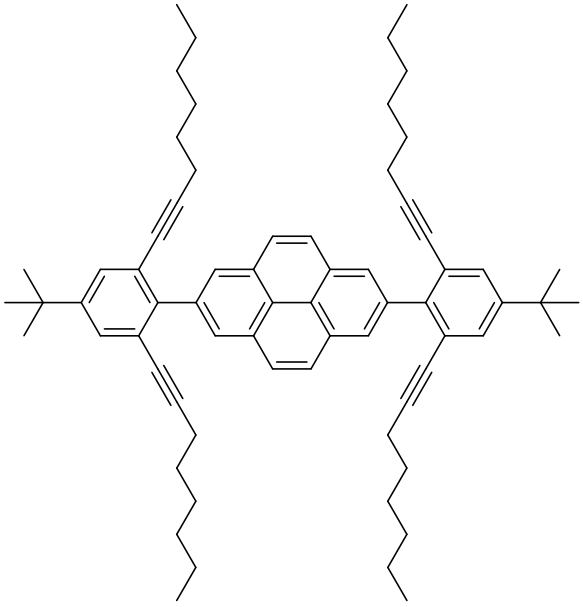
Scheme S4: Conditions: i) $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, 80 °C, 48 h.

General procedure D for synthesis of compounds **3**:

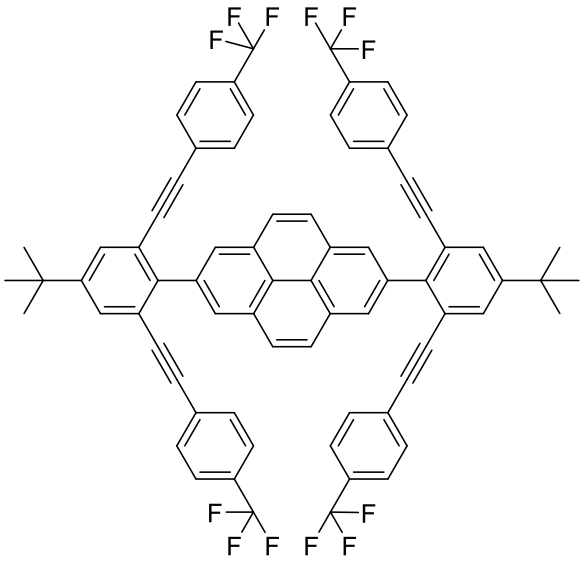
2,7-Dibromopyrene (144 mg, 0.400 mmol), 2,6-diynylphenyl borate **S2** (1.00 mmol) and K_2CO_3 (221 mg, 1.60 mmol) were dissolved in THF (20 mL) and water (4 mL) solution. $Pd(PPh_3)_4$ (46.0 mg, 0.0400 mmol) was added to the solution before degassing the mixture via bubbling nitrogen for 30 min. The resulting mixture was stirred under a N_2 atmosphere at 80 °C for 48 h. After the reaction was complete, the mixture was diluted with DCM, washed with H_2O and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography.



Purification by flash column chromatography (silica gel, hexane:DCM = 8:1, v/v) yielded pure **3c** as a yellow solid (249 mg, yield 57%). R_f = 0.3 (hexane/DCM 6:1); FTIR (neat) 2959, 2902, 2206, 1779, 1502 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 4H), 8.24 (s, 4H), 7.81 (s, 4H), 7.20 – 6.98 (m, 16H), 1.51 (s, 18H), 1.20 ppm (s, 36H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 150.4, 142.9, 136.4, 131.2, 130.8, 130.0, 127.8, 127.6, 125.4, 124.4, 123.5, 120.1, 92.6, 89.3, 34.803, 34.797, 31.4, 31.2 ppm; HRMS (APPI, positive): calcd for $C_{84}H_{82}$ $[M]^+$ 1090.6411, found 1090.6416.

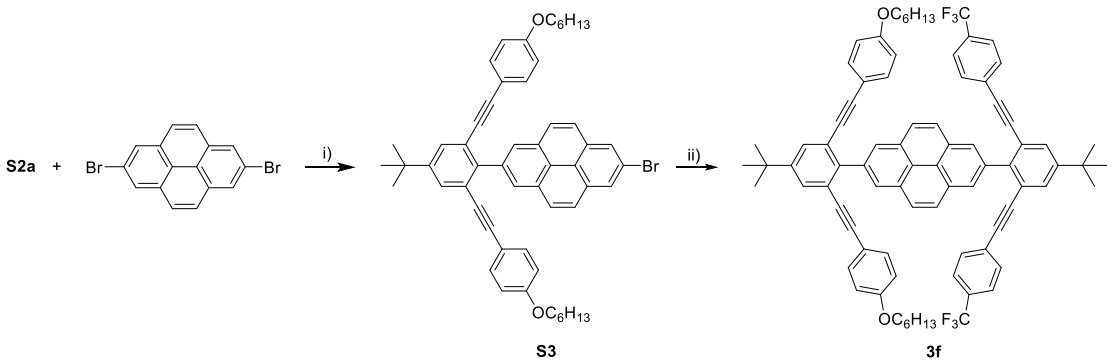


Purification by flash column chromatography (silica gel, hexane:DCM = 15:1, v/v) yielded pure **3d** as a yellow solid (144 mg, yield 40%). R_f = 0.3 (hexane/DCM 12:1); FTIR (neat) 2953, 2927, 2854, 2229, 1587, 1542 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 4H), 8.08 (s, 4H), 7.58 (s, 4H), 2.09 (t, *J* = 7.0 Hz, 8H), 1.41 (s, 18H), 1.26 – 1.15 (m, 8H), 0.98 – 0.83 (m, 24H), 0.60 ppm (t, *J* = 6.7 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 143.2, 136.9, 130.6, 129.4, 127.4, 127.3, 124.2, 123.9, 93.3, 80.8, 34.6, 31.33, 31.32, 28.5, 28.4, 22.4, 19.5, 14.0 ppm; HRMS (APPI, positive): calcd for $C_{68}H_{82}$ $[M]^+$ 899.6411, found 899.6420.



Purification by flash column chromatography (silica gel, hexane:DCM = 20:1, v/v) yielded pure **3e** as a light yellow solid (46.0 mg, yield 10%). R_f = 0.3 (hexane/DCM 15:1); FTIR (neat) 2957, 2927, 2210, 1613, 1508 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 4H), 8.19 (s, 4H), 7.82 (s, 4H), 7.31 – 7.35 (m, 8H), 7.21 – 7.16 (m, 8H), 1.49 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 143.6, 136.3, 131.6, 130.9, 130.8, 130.0 (q, ^2J(C,F) = 32.6 Hz), 127.8, 127.5, 126.8, 125.2 (q, ^1J(C,F) = 4.0 Hz), 124.4, 122.9, 91.9, 91.1, 34.9, 31.3 ppm {CF_3 peak was hard to detect due to low solubility}; HRMS (APPI, positive): calcd for $C_{72}H_{46}F_{12}$ $[M]^+$ 1138.3402, found 1138.3431.

2.5 Synthesis of compound 3f



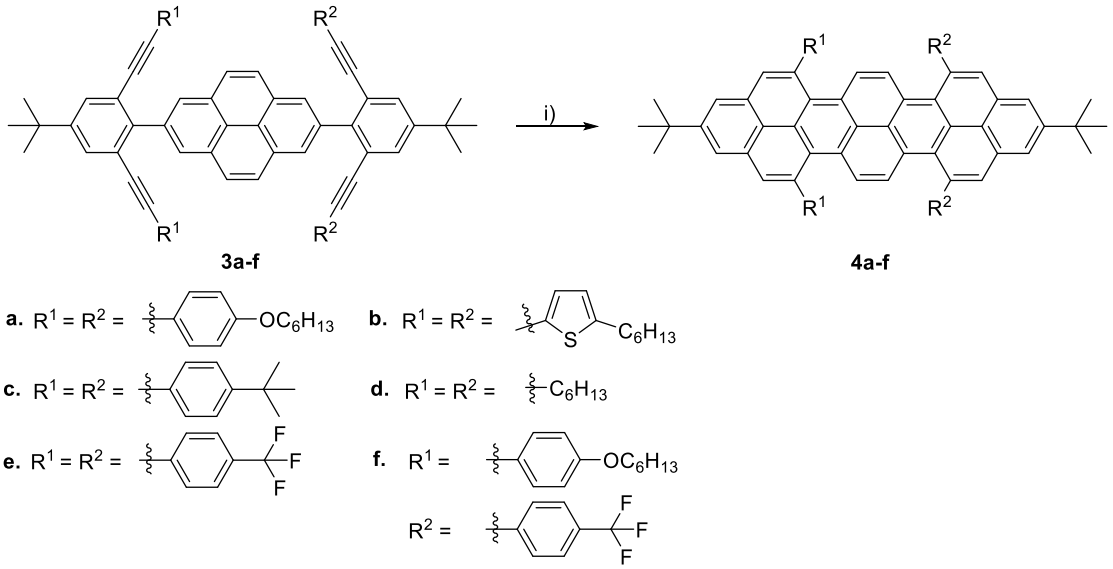
Scheme S5: Conditions: i) $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, 80 °C, 12 h. ii) **S2e**, $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, 80 °C, 12 h.

Compound **S3**:

2,7-dibromopyrene (360 mg, 1.00 mmol), 2,6-diynylphenyl borate **S2a** (661 mg, 1.00 mmol) and K_2CO_3 (276 mg, 2.00 mmol) were dissolved in THF (20 mL) and water (4 mL) solution. $Pd(PPh_3)_4$ (116 mg, 0.100 mmol) was added to the solution before degassing the mixture via bubbling nitrogen for 30 min. The resulting mixture was stirred under a N_2 atmosphere at 80 °C for 12 h. After the reaction was complete, the mixture was diluted with DCM, washed with H_2O and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexane:DCM = 5:1, v/v) yielded pure **S3** as a yellow solid (211 mg, yield 26%). R_f = 0.2 (hexane/DCM 5:1); FTIR (neat) 2951, 2927, 2857, 2204, 1603, 1506, 1466, 1243, 1169, 1022, 880, 828 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 2H), 8.30 (s, 2H), 8.18 (d, *J* = 9.0 Hz, 2H), 7.99 (d, *J* = 9.0 Hz, 2H), 7.79 (s, 2H), 7.06 – 6.95 (m, 4H), 6.69 – 6.57 (m, 4H), 3.82 (t, *J* = 6.6 Hz, 4H), 1.74 – 1.65 (m, 4H), 1.50 (s, 9H), 1.38 – 1.24 (m, 12H), 0.91 ppm (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 150.6, 142.3, 137.2, 133.0, 132.8, 130.1, 129.4, 129.0, 128.5, 127.0, 126.2, 123.7, 123.6, 123.4, 120.0, 114.9, 114.4, 92.7, 88.4, 68.0, 34.8, 31.6, 31.3, 29.2, 25.7, 22.7, 14.1 ppm; HRMS (APPI, positive): calcd for $C_{54}H_{53}BrO_2$ $[M]^+$ 812.3223, found 812.3243.

Compound **3f** was prepared following general procedure D, using compound **S3** and **S2e** as starting material. R_f = 0.2 (hexane/DCM 6:1); FTIR (neat) 2956, 2210, 1606, 1508 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 2H), 8.58 (s, 2H), 8.24 (d, *J* = 8.9 Hz, 2H), 8.19 (d, *J* = 8.9 Hz, 2H), 7.85 (s, 2H), 7.76 (s, 2H), 7.40 – 7.33 (m, 4H), 7.24 – 7.18 (m, 4H), 7.10 – 7.02 (m, 4H), 6.65 – 6.58 (m, 4H), 3.78 (t, *J* = 6.6 Hz, 4H), 1.71 – 1.61 (m, 4H), 1.51 (s, 9H), 1.49 (s, 9H), 1.37 – 1.26 (m, 12H), 0.87 ppm (t, *J* = 6.9 Hz, 6H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 150.8, 150.5, 143.8, 142.3, 137.1, 136.0, 132.9, 131.6, 130.9, 130.7, 129.9 (q, ^2J(C,F) = 32.5 Hz), 129.6, 128.2, 128.0, 127.4, 127.2, 126.90, 125.89, 125.3 (q, ^1J(C,F) = 3.8 Hz), 124.5, 124.3, 123.9 (q, ^3J(C,F) = 270.9 Hz), 123.7, 122.9, 115.0, 92.6, 92.0, 91.2, 88.6, 68.0, 34.9, 34.8, 31.6, 31.4, 31.3, 29.2, 25.7, 22.7, 14.1 ppm; HRMS (APPI, positive): calcd for $C_{82}H_{72}F_6O_2$ $[M]^+$ 1202.5431, found 1202.5435.

2.6 Synthesis of teropyrenes 4

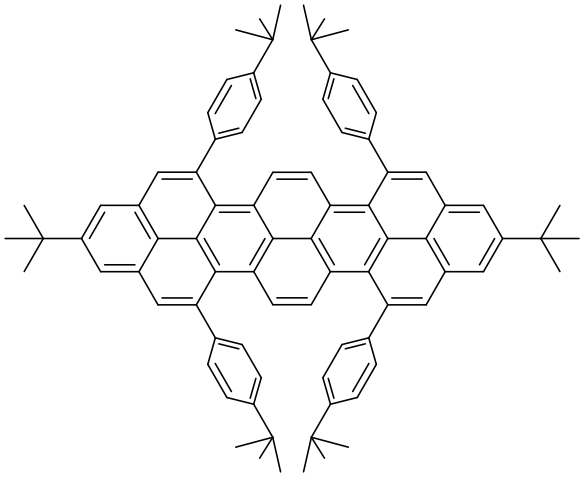


Scheme S6: Conditions: i) $InCl_3$, toluene, 80 °C or 100°C.

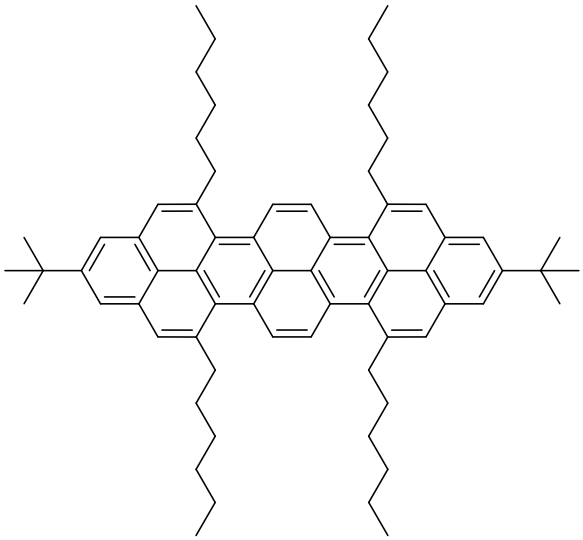
General procedure F for synthesis of compounds **4:**

A flame-dried round-bottom flask was charged with a magnetic stirring bar, the corresponding precursors **3** (0.0300 mmol) and anhydrous toluene (6 mL). $InCl_3$ (3.3 mg, 0.5 equiv., 0.0150 mmol) was added to the solution before degassing the mixture

via bubbling nitrogen for 30 min, then the resulting mixture was heated at 100°C under a N_2 atmosphere. After reaction completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography.

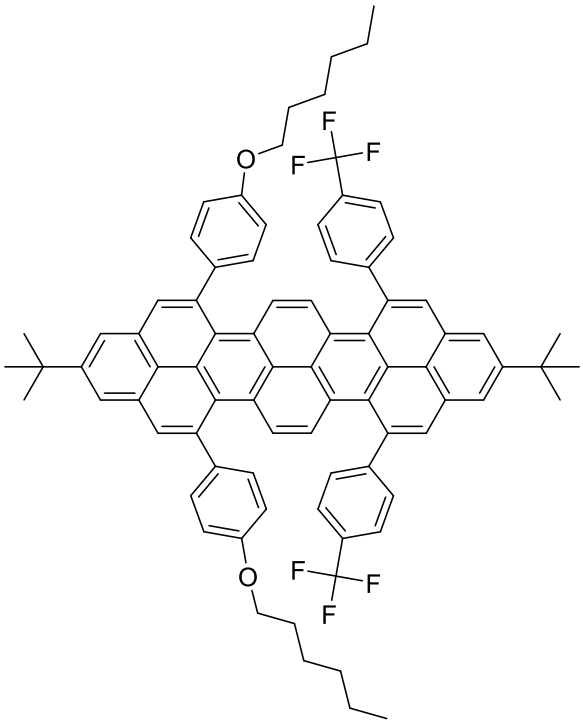


Purification by flash column chromatography (silica gel, hexane:DCM = 10:1, v/v) yielded pure **4c** as a purple solid (29.8 mg, yield 90%). R_f = 0.5 (hexane/DCM 6:1); FTIR (neat) 2952, 2901, 2865, 1616, 1575, 1506 cm^{-1}; ^1H NMR (400 MHz, toluene-d_8) δ 8.33 (s, 4H), 8.22 (s, 4H), 8.06 (s, 4H), 7.37 – 7.29 (m, 8H), 7.28 – 7.21 (m, 8H), 1.58 (s, 18H), 1.26 ppm (s, 36H); ^{13}C NMR (100 MHz, toluene-d_8) δ 149.8, 149.5, 143.5, 140.0, 131.8, 131.6, 129.1, 126.7, 126.20, 126.19, 126.0, 125.8, 125.0, 122.9, 122.4, 35.3, 34.6, 32.0, 31.5 ppm; HRMS (APPI, positive): calcd for $C_{84}H_{82}$ $[M]^+$ 1090.6411, found 1090.6415.



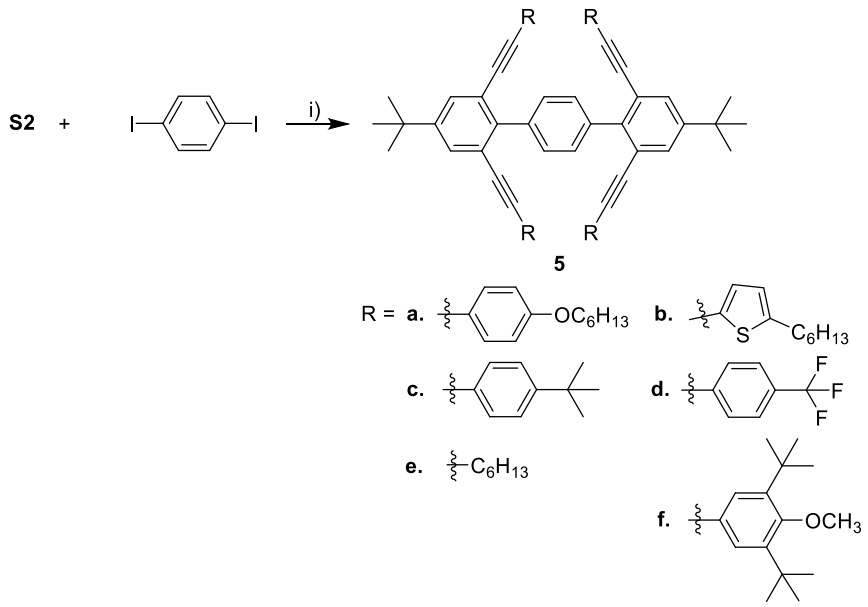
Purification by flash column chromatography (silica gel, hexane:DCM = 10:1, v/v) yielded pure **4d** as a purple solid (20.3 mg, yield 75%). R_f = 0.5 (hexane/DCM 6:1); FTIR (neat) 2951, 2921, 2853, 1694, 1577 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 4H), 8.32 (s, 4H), 8.28 (s, 4H), 3.97 – 3.79 (m, 8H), 2.11 (m, 8H), 1.68 (s, 18H), 1.65 – 1.59 (m, 8H), 1.49 – 1.35 (m, 16H), 0.93 ppm (t, J = 7.2 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 139.2, 131.1, 129.3, 126.9, 125.4, 124.6, 124.0, 123.7, 121.6, 120.4, 38.5, 35.4, 32.1,

32.0, 30.0, 22.9, 14.3 (one alkyl peak missing due to coincidental overlap) ppm; HRMS (APPI, positive): calcd for $C_{68}H_{83}$ $[M]^+$ 898.6411, found 898.6423.



Purification by flash column chromatography (silica gel, hexane:DCM = 5:1, v/v) yielded pure **4f** as a purple solid (31.8 mg, yield 88%). R_f = 0.2 (hexane/DCM 5:1); FTIR (neat) 2955, 2861, 1792, 1704, 1606, 1505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 2H), 8.33 (s, 2H), 8.24 – 8.11 (m, 6H), 7.89 (d, *J* = 9.8 Hz, 2H), 7.78 – 7.59 (m, 8H), 7.45 – 7.35 (m, 4H), 7.02 – 6.91 (m, 4H), 4.06 (t, *J* = 6.7 Hz, 4H), 1.94 – 1.83 (m, 4H), 1.63 (s, 9H), 1.62 (s, 9H), 1.45 – 1.35 (m, 8H), 0.95 ppm (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 150.3, 150.0, 149.51, 149.49, 139.3, 138.4, 138.1, 132.3, 131.9, 131.1, 130.8, 130.0, 129.4, 129.1 (q, ^2J(C,F) = 32.2 Hz), 126.1, 126.0 (q, ^1J(C,F) = 3.6 Hz), 125.85, 125.81, 125.78, 125.7, 125.1, 124.7, 124.6 (q, ^3J(C,F) = 270.4 Hz), 124.4, 123.6, 123.5, 122.9, 122.1, 121.3, 115.0, 68.3, 35.42, 35.39, 32.03, 32.00, 31.9, 29.5, 25.9, 22.8, 14.2 ppm; HRMS (APPI, positive): calcd for $C_{82}H_{72}F_6O_2$ $[M]^+$ 1202.5431, found 1202.5427.

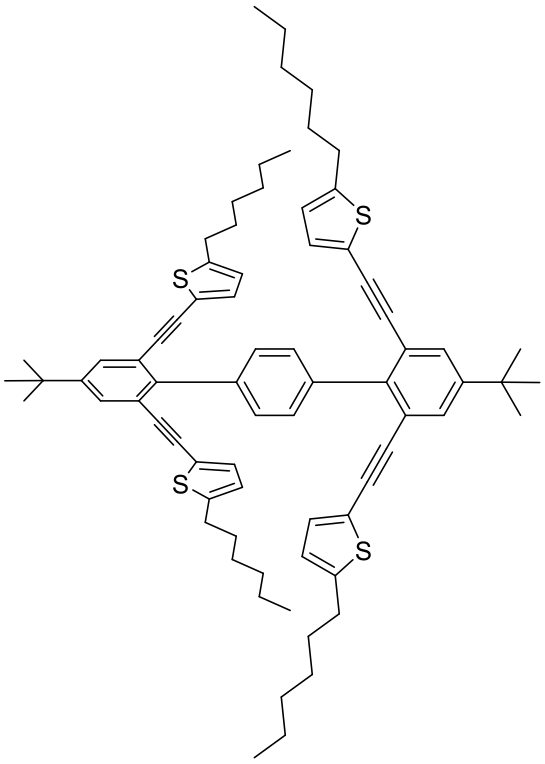
2.7 Synthesis of compounds 5



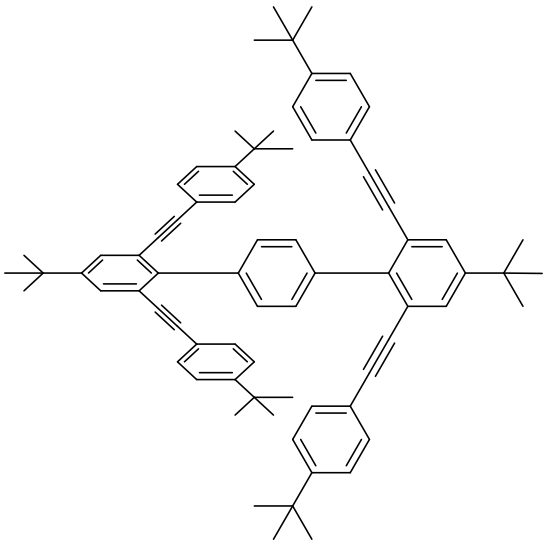
Scheme S7: Conditions: i) $Pd(PPh_3)_4$, $AgCO_3$, THF, 80 °C, 48 h.

General procedure E for synthesis of compounds **5**:

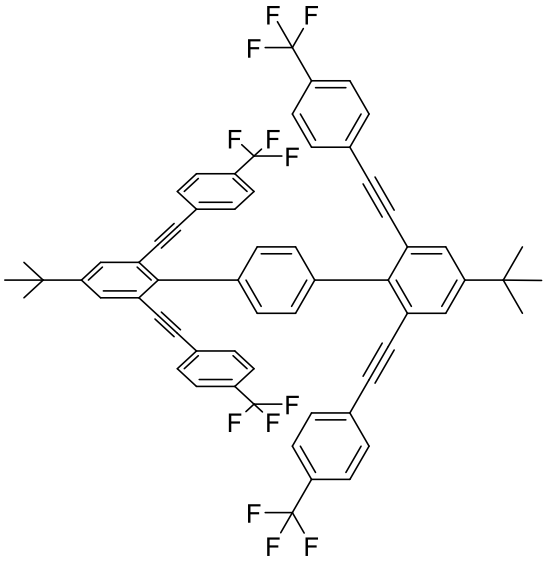
1,4-diiodobenzene (132 mg, 0.40 mmol, 1.0 equiv.), 2,6-diynylphenyl borate **S2** (1.00 mmol, 2.5 equiv.) and Ag_2CO_3 (442 mg, 1.6 mmol, 4 equiv.) were dissolved in anhydrous THF (60 mL). $Pd(PPh_3)_4$ (46 mg, 0.04 mmol, 0.1 equiv.) was added to the solution before degassing the mixture via bubbling nitrogen for 30 min. The resulting mixture was stirred under a N_2 atmosphere at 80 °C for 48 h. After the reaction was complete, the mixture was diluted with DCM, washed with H_2O and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography to give compound **5**.



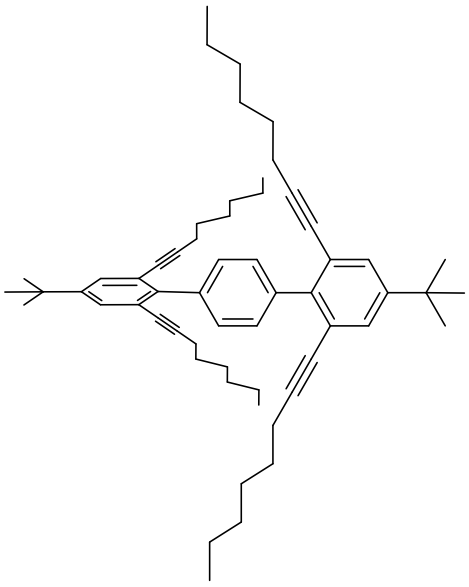
Purification by flash column chromatography (silica gel, hexane:DCM = 20:1, v/v) yielded pure **5b** as a yellow solid (137 mg, yield 31%). R_f = 0.3 (hexane/DCM 20:1); FTIR (neat) 2965, 2899, 2211, 1789 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 4H), 7.62 (s, 4H), 6.69 (d, *J* = 3.6 Hz, 4H), 6.42 (d, *J* = 3.6 Hz, 4H), 2.64 (t, *J* = 7.7 Hz, 8H), 1.61 – 1.50 (m, 8H), 1.44 (s, 18H), 1.40 – 1.10 (m, 24H), 0.90 ppm (t, *J* = 6.6 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 148.2, 143.3, 138.3, 132.1, 129.5, 128.4, 124.1, 123.2, 120.4, 92.5, 86.9, 34.7, 31.7, 31.5, 31.3, 30.3, 28.8, 22.7, 14.2 ppm; HRMS (APPI, positive): calcd for $C_{74}H_{86}S_4$ $[M]^+$ 1102.5607, found 1102.5625.



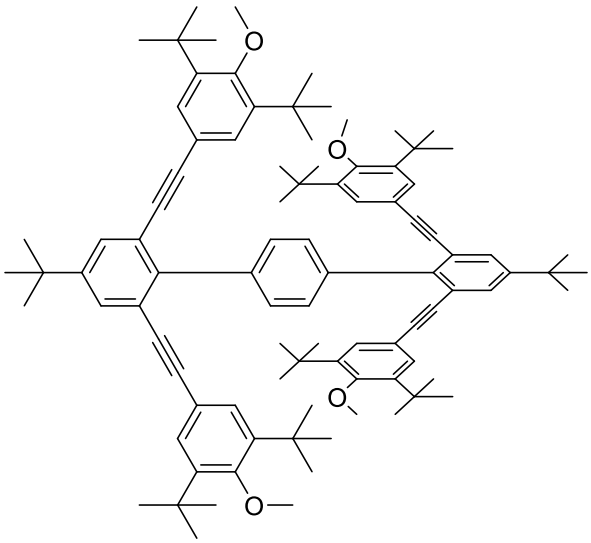
Purification by flash column chromatography (silica gel, hexane:DCM = 20:1, v/v) yielded pure **5c** as a yellow solid (155 mg, yield 40%). R_f = 0.3 (hexane/DCM 15:1); FTIR (neat) 2961, 2903, 2867, 2208, 1905, 1787, 1659, 1586, 1539, 1503 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 4H), 7.73 (s, 4H), 7.08 – 7.04 (m, 8H), 7.04 – 6.98 (m, 8H), 1.50 (s, 18H), 1.15 ppm (s, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 150.1, 144.2, 138.9, 131.3, 129.6, 129.0, 125.0, 123.5, 120.1, 93.1, 88.8, 34.8, 34.6, 31.4, 31.2 ppm; HRMS (APPI, positive): calcd for $C_{74}H_{78}$ $[M]^+$ 966.6098, found 966.6127.



Purification by flash column chromatography (silica gel, hexane:DCM = 20:1, v/v) yielded pure **5d** as a yellow solid (224 mg, yield 55%). R_f = 0.25 (hexane/DCM 20:1); FTIR (neat) 2967, 2904, 2870, 2207, 1615 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 4H), 7.76 (s, 4H), 7.22 – 7.15 (m, 8H), 7.14 – 7.06 (m, 8H), 1.50 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 144.9, 139.2, 131.7, 131.5, 129.9, 129.6, 129.5 (q, ^2J(C,F) = 32.4 Hz), 125.0 (q, ^1J(C,F) = 3.8 Hz), 123.8 (q, ^3J(C,F) = 270.6 Hz), 122.7, 91.6, 91.5, 34.9, 31.3 ppm; HRMS (APPI, positive): calcd for $C_{62}H_{42}F_{12}$ $[M]^+$ 1014.3089, found 1014.3097.

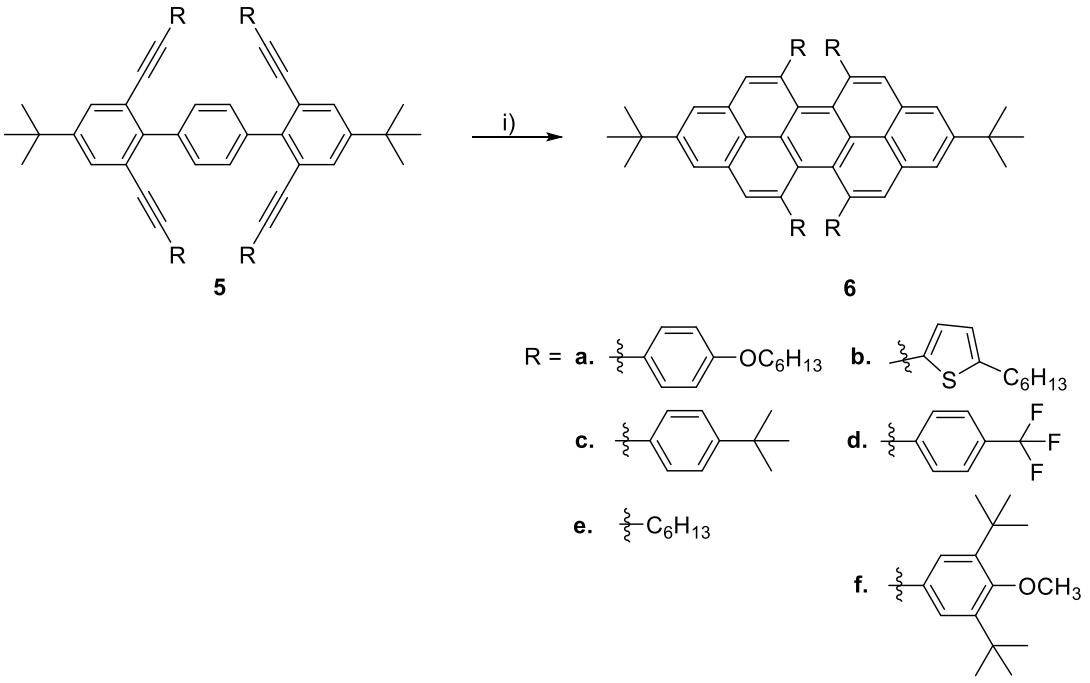


Purification by flash column chromatography (silica gel, hexane:DCM = 20:1, v/v) yielded pure **5e** as a yellow solid (68 mg, yield 22%). R_f = 0.3 (hexane/DCM 20:1); FTIR (neat) 2955, 2930, 2857, 2230, 1589 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 4H), 7.45 (s, 4H), 2.19 (t, J = 7.0 Hz, 8H), 1.42 – 1.36 (m, 8H), 1.34 (s, 18H), 1.29 – 1.16 (m, 24H), 0.80 ppm (t, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 143.5, 138.0, 129.2, 129.1, 123.4, 93.1, 80.6, 34.5, 31.5, 31.3, 28.8, 28.7, 22.7, 19.6, 14.2 ppm; HRMS (APPI, positive): calcd for $C_{58}H_{78}$ $[M]^+$ 774.6098, found 774.6127.



Purification by flash column chromatography (silica gel, hexane:DCM = 10:1, v/v) yielded pure **5f** as a yellow solid (225 mg, yield 43%). R_f = 0.4 (hexane/DCM 10:1); FTIR (neat) 2961, 2870, 2211, 1591, 1536 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 4H), 7.64 (s, 4H), 7.10 (s, 8H), 3.54 (s, 12H), 1.45 (s, 18H), 1.22 ppm (s, 72H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 149.8, 143.8, 143.6, 143.3, 138.1, 130.0, 129.0, 123.2, 117.9, 93.3, 88.6, 64.3, 35.7, 34.8, 31.9, 31.4 ppm; HRMS (APPI, positive): calcd for $C_{94}H_{118}O_4$ $[M]^+$ 1310.9025, found 1310.9028.

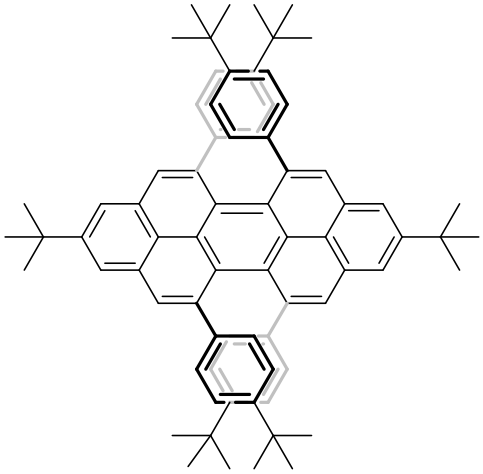
2.8 Synthesis of chiral peropyrenes 6



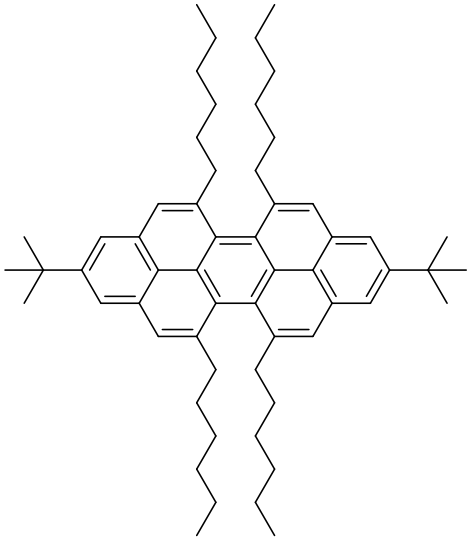
Scheme S8: Conditions: i) $InCl_3$, toluene, 120 °C.

General procedure G for synthesis of compounds **6**:

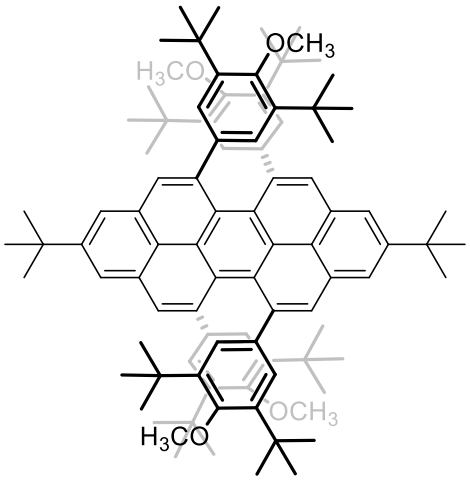
A flame-dried round-bottom flask was charged with a magnetic stirring bar, the corresponding precursors **3** (0.0200 mmol) and anhydrous toluene (4 mL). $InCl_3$ (4.42 mg, 1.0 equiv., 0.0200 mmol) was added to the solution before degassing the mixture via bubbling nitrogen for 30 min, then the resulting mixture was heated at 120 °C under a N_2 atmosphere. After reaction completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography.



Purification by flash column chromatography (silica gel, hexane:DCM = 70:1, v/v) yielded pure **6c** as an orange solid (7.00 mg, yield 52%). R_f = 0.3 (hexane/DCM 20:1); FTIR (neat) 3029, 2960, 2867, 1724, 1619, 1575, 1510, 1475, 1462, 1362, 1268, 1228, 1110, 1019, 897, 831, 732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 4H), 7.85 (s, 4H), 6.95 –7.19 (br, 8H), 6.50 – 6.90 (br, 8H), 1.64 (s, 18H), 1.42 ppm (m, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 148.6, 140.8, 140.2, 131.5, 128.7, 127.4 (br), 126.7 (br), 126.2, 123.9, 123.0, 120.7, 35.4, 34.6, 32.1, 31.7 ppm; HRMS (APPI, positive): calcd for $C_{74}H_{78}$ $[M]^+$ 966.6098, found 966.6126.



Purification by flash column chromatography (silica gel, hexane) yielded pure **6e** as an orange solid (1.20 mg, yield 8 %). R_f = 0.6 (hexane); FTIR (neat) 2954, 2923, 2852, 1732, 1462, 1377, 1361, 1074 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 4H), 7.97 (s, 4H), 3.48 – 3.60 (m, 4H), 3.28 – 3.41 (m, 4H), 1.63 (s, 18H), 1.19 – 0.58 (m, 36H), 0.47 ppm (t, J = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 139.5, 131.7, 125.5, 124.11, 124.06, 121.5, 119.9, 36.4, 35.4, 33.3, 32.2, 31.4, 28.8, 22.5, 13.9 ppm; HRMS (APPI, positive): calcd for $C_{58}H_{78}$ $[M+H]^+$ 774.6098, found 774.6128.



Purification by flash column chromatography (silica gel, hexane) yielded pure **6f** as an orange solid (15.5 mg, yield 59 %). R_f = 0.6 (hexane/DCM 7:1); FTIR (neat) 2958, 2926, 2868, 1463, 1416, 1394, 1362, 1261, 1225, 1115, 1013, 882 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 4H), 7.83 (s, 4H), 7.40 – 6.70 (br, 8H), 3.65 (s, 12H), 1.64 (s, 18H), 1.44 – 0.85 ppm (br, 72H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 149.4, 142.6 (br), 139.6, 137.2, 131.4, 128.7, 125.7, 125.5 (br), 123.5, 122.8, 120.2, 63.6, 35.4, 35.1, 32.1, 31.8 ppm; HRMS (APPI, positive): calcd for $C_{94}H_{118}O_4$ $[M]^+$ 1310.9025, found 1310.9036.

3. Absorption and fluorescence Spectra of 2, 4, and 6

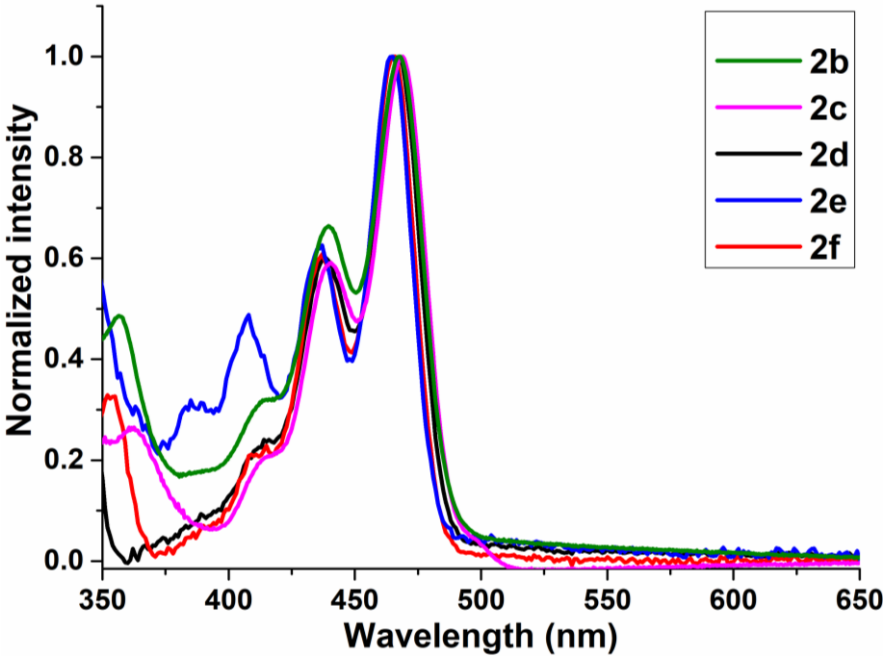


Figure S1. Normalized UV-vis absorption spectra of peropyrenes **2**.

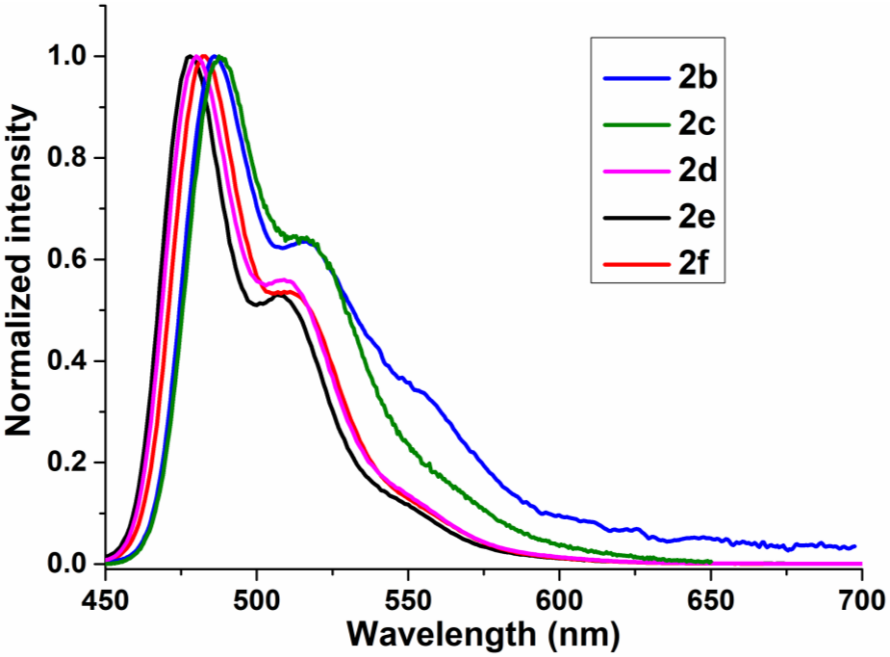


Figure S2. Normalized fluorescence spectra of peropyrenes **2**.

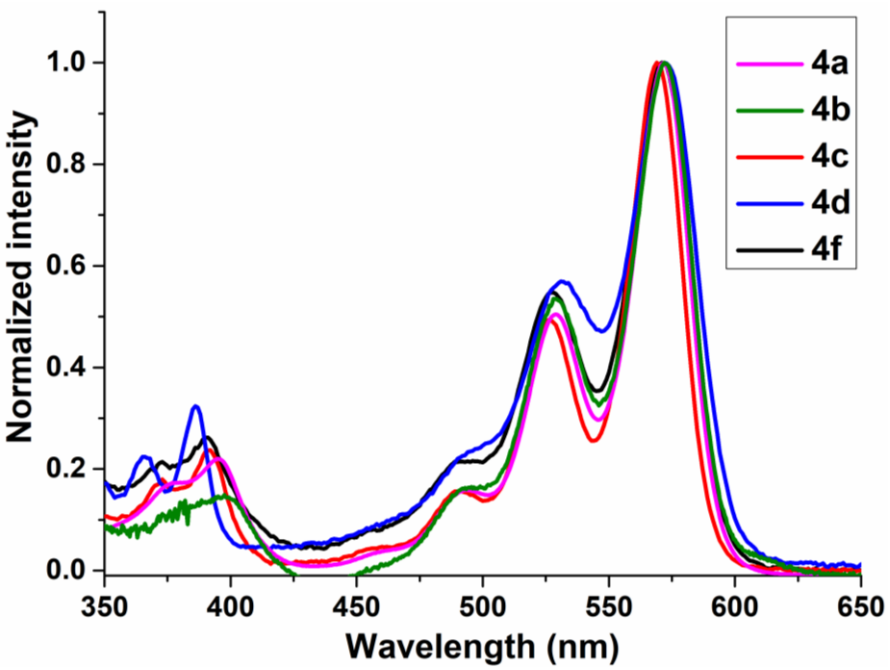


Figure S3. Normalized UV-vis absorption spectra of teropyrenes **4**.

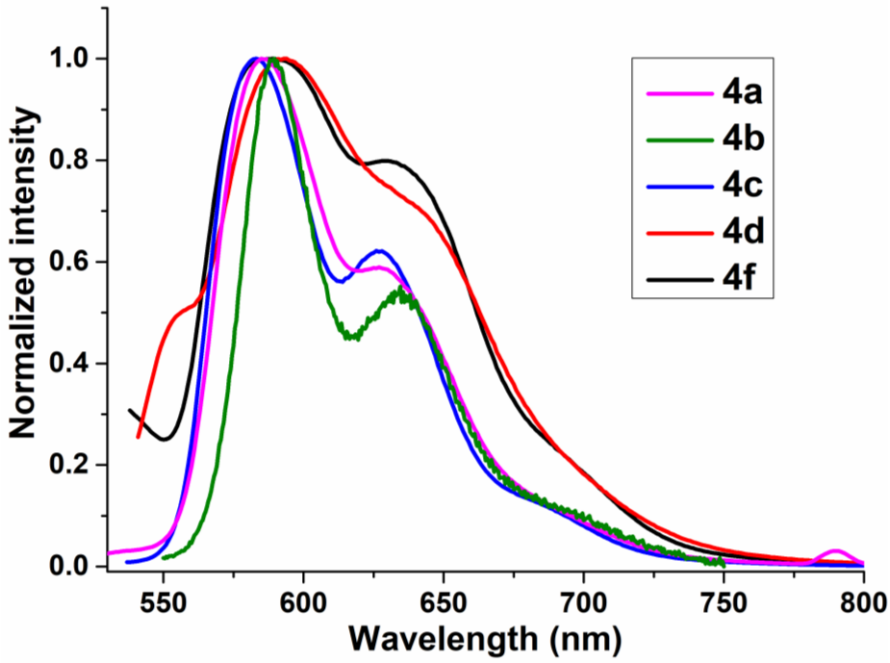


Figure S4. Normalized fluorescence spectra of teropyrenes **4**.

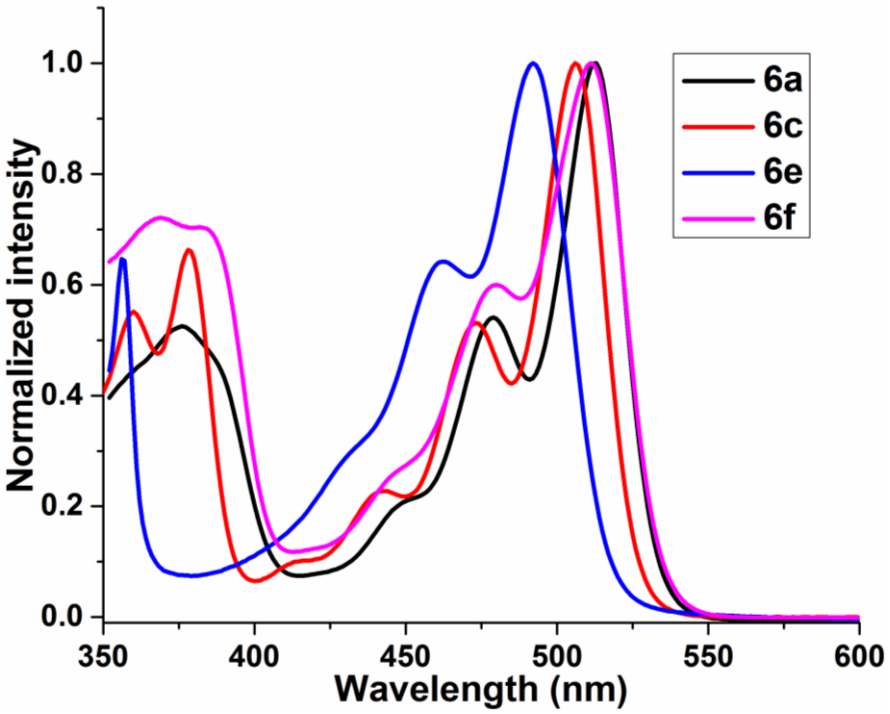


Figure S5. Normalized UV-vis absorption spectra of chiral peropyrenes **6**.

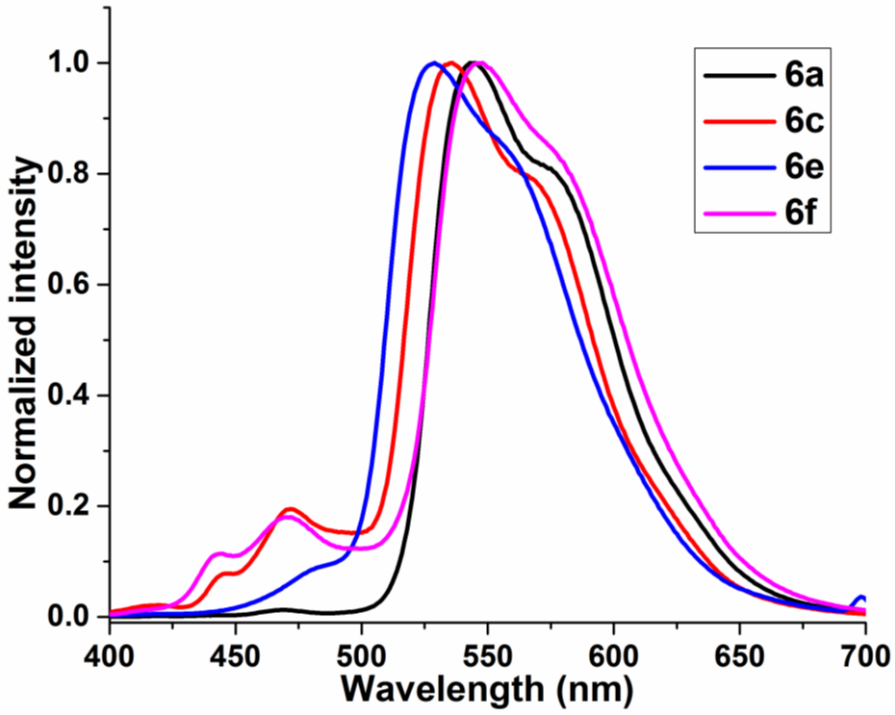


Figure S6. Normalized fluorescence spectra of chiral peropyrenes **6**.

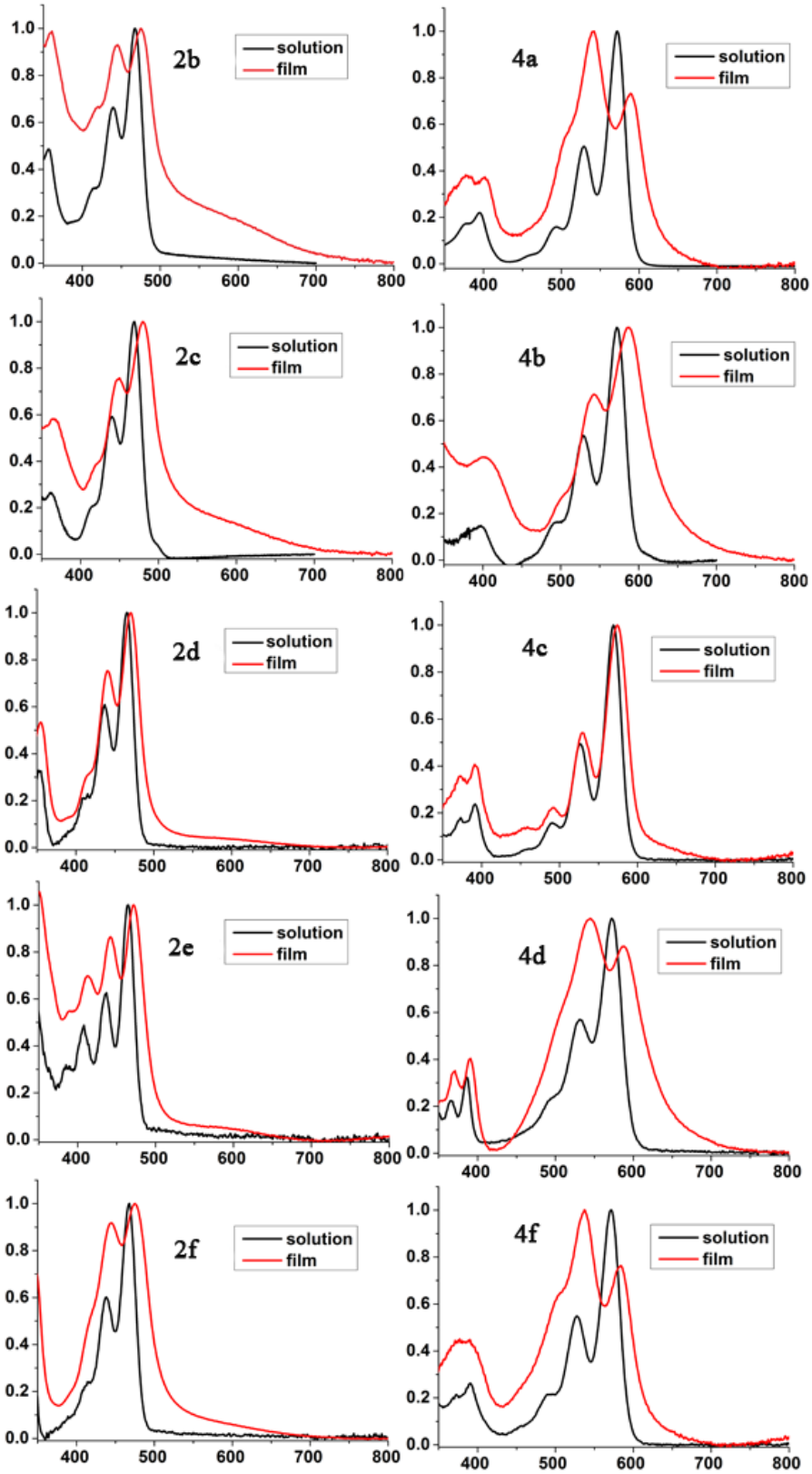


Figure S7. Normalized UV-vis absorption spectra of peropyrenes **2** and peropyrenes **4** in solution and solid state.

4. Electrochemistry

Chemicals. Anhydrous benzene (Bz, 99.8%, Sigma-Aldrich), acetonitrile (MeCN, HPLC grade, Pharmco-Aaper) and prepurified tetrahydrofuran (THF) were purified following the procedures described below. Tetra-*n*-butylammonium perchlorate (TBAP, Alfa Aesar) was recrystallized from EtOH (95%), dried at 90 °C in a vacuum oven for 12 hours and kept an Ar glovebox before use. All solutions used for electrochemistry measurements were prepared in the glovebox under an argon atmosphere with O_2 and H_2O content< 0.1 ppm.

Apparatus and Instrumentation. Cyclic voltammetry (CV) experiments were carried out in the glovebox using a conventional three-electrode cell connected to a CH Instruments Electrochemical Workstation 760 (Austin, TX). A Pt disk (0.134 cm in diameter) was used as working electrode. Before each measurement, the working electrode was polished on a felt pad with 0.05 μm alumina (Buehler), sonicated in water and methanol for 10 min in each solvent, and dried in an oven at 90 °C. A Pt coil and a Ag wire served as a counter electrode and a quasi-reference electrode (QRE), respectively. The CVs were run with the QRE and the potentials were calibrated against SCE by adding ferrocene (Fc) as an internal standard, taking $E°_{Fc/Fc+}$ = 0.424 V vs SCE.[2] The voltammetric measurements were performed in either Bz/MeCN mixture of 5:1 (v/v) or THF to provide a solvent with an adequate potential window with THF being used for oxidations less positive than 1 V vs SCE. Table S1 lists the solvents used for the compounds studied in this work. In all cases the supporting electrolyte was 0.1 M TBAP.

Electrochemical Simulation. Digital simulations of CVs were performed with DigiElch Software package 7.F (ElchSoft, Germany) to fit the experimental results. The fitting provided the best measure of the E^0 for the reductions and oxidations and the value from the fitting was used as an estimate of the HOMO and LUMO energy levels of compounds.

THF purification process. 60 ml of THF pretreated with a commercial solvent purification system, were transferred with a cleaned, dried syringe to a round-bottom flask of the distillation apparatus. Next, 1.0 M lithium aluminum hydride (LAH, Sigma-Aldrich) in THF (6 ml) was added to the round-bottom flask. The LAH solution is flammable, corrosive and toxic and should be handled with care. This solution was distilled under an Ar atmosphere to collect the 10-80% fraction. The distillate was transferred immediately to the Ar glovebox and stored on activated alumina powder (MP biomedicals, Inc).

Benzene purification process. First, 50 ml of concentrated H_2SO_4 was added to 200 ml of anhydrous benzene (99.8%) and vigorously shaken for 20 min to remove any possible thiophene. The separated benzene phase was washed with 50 mL of de-ionized water (18 MΩ cm, Barnstead Nanopure) twice. The benzene was washed with 50 ml of 0.1 M NaOH solution three times (to neutralize possible H_2SO_4 residue and washed with 50 ml of milli-Q water three times. The benzene was pre-dried by passing over activated Na_2SO_4 (baked at 200 °C, 1h) and refluxed for 6 hours over metallic Na under a nitrogen line. The 10-80% fraction of distillate was collected into a flask containing activated alumina (baked at 400 °C, 4h) and stored in the Ar glovebox.

Acetonitrile purification process. The details of the purification will be given elsewhere.[2] Briefly, to remove metal ions, MeCN (HPLC grade) was mixed with EDTA in a round-bottom flask and stirred for 18 hours. After sedimentation, the top solution were distilled to collect 5-95% fraction. The distillate was passed through two consecutive columns of activated molecular sieves and activated chromatographic alumina to remove possible organic impurities and to pre-dry the solvent. The MeCN was refluxed for 2 hours over CaH_2 under argon atmosphere. The 10-80% fraction of distillate was collected into a flask containing activated alumina and stored in the glovebox.

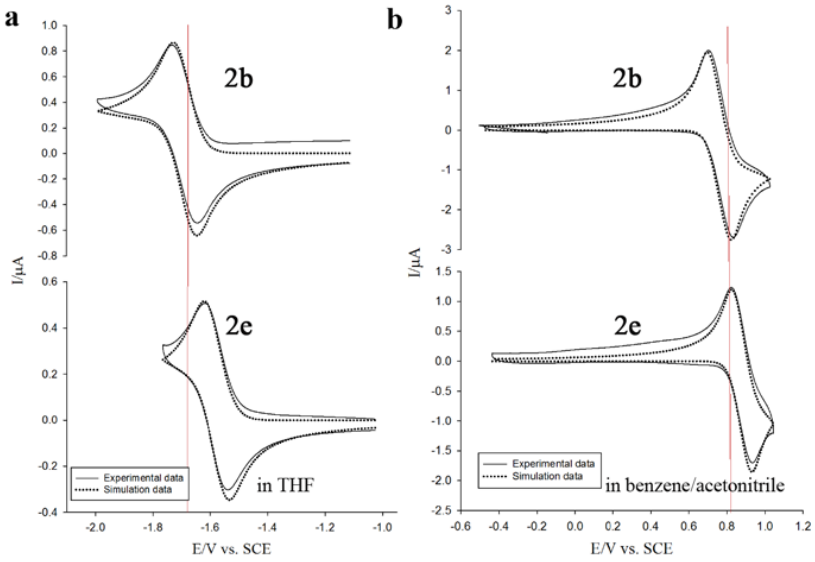


Figure S8. Cyclic voltammograms of **2b** and **2e**. (····) Shows the simulation results for a one-electron reduction and oxidation, respectively with the E^0_{ox} values given in table 5 in manuscript. Note that the potentials lines mark the E^0 of **2b** for the oxidation (A) and reduction (B) cases.

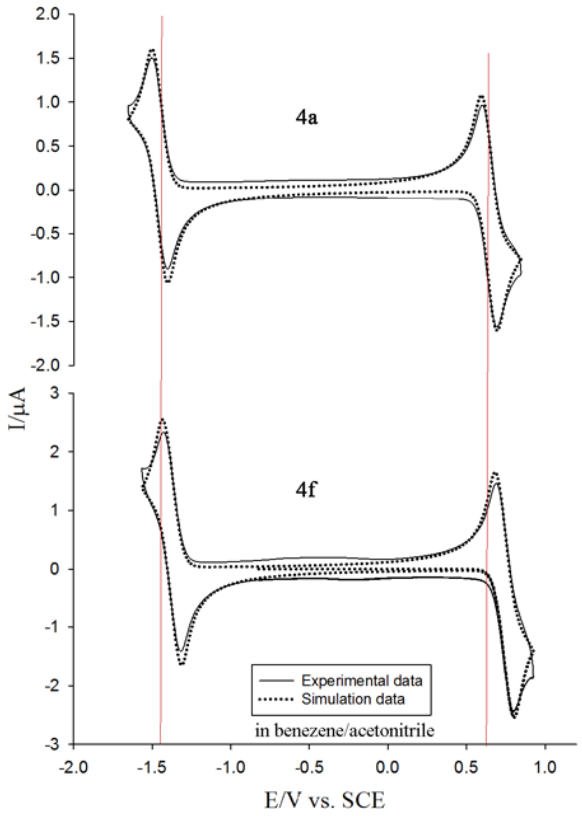


Figure S9. Cyclic voltammograms of 0.8 mM **4a** and **4f** in benzene/acetonitrile (5:1) mixture with 0.1 M TBAP as the supporting electrolyte. All other conditions as in Figure S8.

Table S1. Solvents used for electrochemical measurements.

Compounds	Oxidation	Reduction
2	Benzene + MeCN	THF
4	Benzene + MeCN	Benzene + MeCN
6	Benzene + MeCN	THF

5. X-ray crystallographic data

Single crystals of peropyrene **2a**, teropyrene **4c**, and chiral peropyrene **6f** were obtained by slow diffusion of methanol into their d-chloroform solution; Single crystals of teropyrene **4d** obtained by slow diffusion of methanol into its $C_2H_4Cl_2$ solution.

Table S2. Crystal data for peropyrene **2a** (CCDC number: 1826979).

Empirical formula	$C_{66}H_{78}O_2$	
Formula weight	903.28	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.134(3) Å	α= 70.214(5)°.
	b = 13.857(4) Å	β= 75.507(5)°.
	c = 17.116(4) Å	γ = 73.496(5)°.
Volume	2558.1(11) $Å^3$	
Z	2	
Density (calculated)	1.173 Mg/m^3	
Absorption coefficient	0.068 mm^{-1}	
F(000)	980	
Crystal size	0.086 x 0.072 x 0.063 mm^3	
Theta range for data collection	1.283 to 25.403°.	
Index ranges	-14<=h<=14, -16<=k<=16, -20<=l<=20	
Reflections collected	44928	
Independent reflections	9269 [R(int) = 0.1182]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9269 / 48 / 641	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0604, wR2 = 0.1323	
R indices (all data)	R1 = 0.1305, wR2 = 0.1658	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.397 and -0.328 e.$Å^{-3}$	

Table S3. Crystal data for peropyrene **4c** (CCDC number: 1826980).

Empirical formula	$C_{128}H_{123}O_2$	
Formula weight	1686.25	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 32.0480(19) Å	α= 90°.
	b = 25.4121(15) Å	β= 102.8650(11)°.
	c = 26.3829(15) Å	γ = 90°.
Volume	20947(2) $Å^3$	
Z	8	
Density (calculated)	1.069 Mg/m^3	
Absorption coefficient	0.061 mm^{-1}	
F(000)	7228	
Crystal size	0.079 x 0.065 x 0.046 mm^3	
Theta range for data collection	1.387 to 24.999°.	
Index ranges	-38<=h<=38, -30<=k<=30, -31<=l<=28	
Reflections collected	150691	
Independent reflections	18441 [R(int) = 0.1760]	
Completeness to theta = 24.999°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18441 / 142 / 1262	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0833, wR2 = 0.2135	
R indices (all data)	R1 = 0.1598, wR2 = 0.2440	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.108 and -0.458 e.$Å^{-3}$	

Table S4. Crystal data for peropyrene **4d** (CCDC number: 1826981).

Empirical formula	$C_{68}H_{74}$
Formula weight	891.27
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1

Unit cell dimensions	a = 9.3311(6) Å	α= 103.7940(10)°.
	b = 9.8219(6) Å	β= 94.9920(10)°.
	c = 16.1042(10) Å	γ = 112.5660(10)°.
Volume	1297.14(14) $Å^3$	
Z	1	
Density (calculated)	1.141 Mg/m^3	
Absorption coefficient	0.064 mm^{-1}	
F(000)	482	
Crystal size	0.244 x 0.158 x 0.024 mm^3	
Theta range for data collection	2.333 to 27.103°.	
Index ranges	-11<=h<=11, -12<=k<=12, -20<=l<=20	
Reflections collected	26460	
Independent reflections	5718 [R(int) = 0.0487]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6312	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5718 / 56 / 351	
Goodness-of-fit on F^2	1.100	
Final R indices [I>2sigma(I)]	R1 = 0.0640, wR2 = 0.1856	
R indices (all data)	R1 = 0.0998, wR2 = 0.2030	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.607 and -0.334 $e.Å^{-3}$	

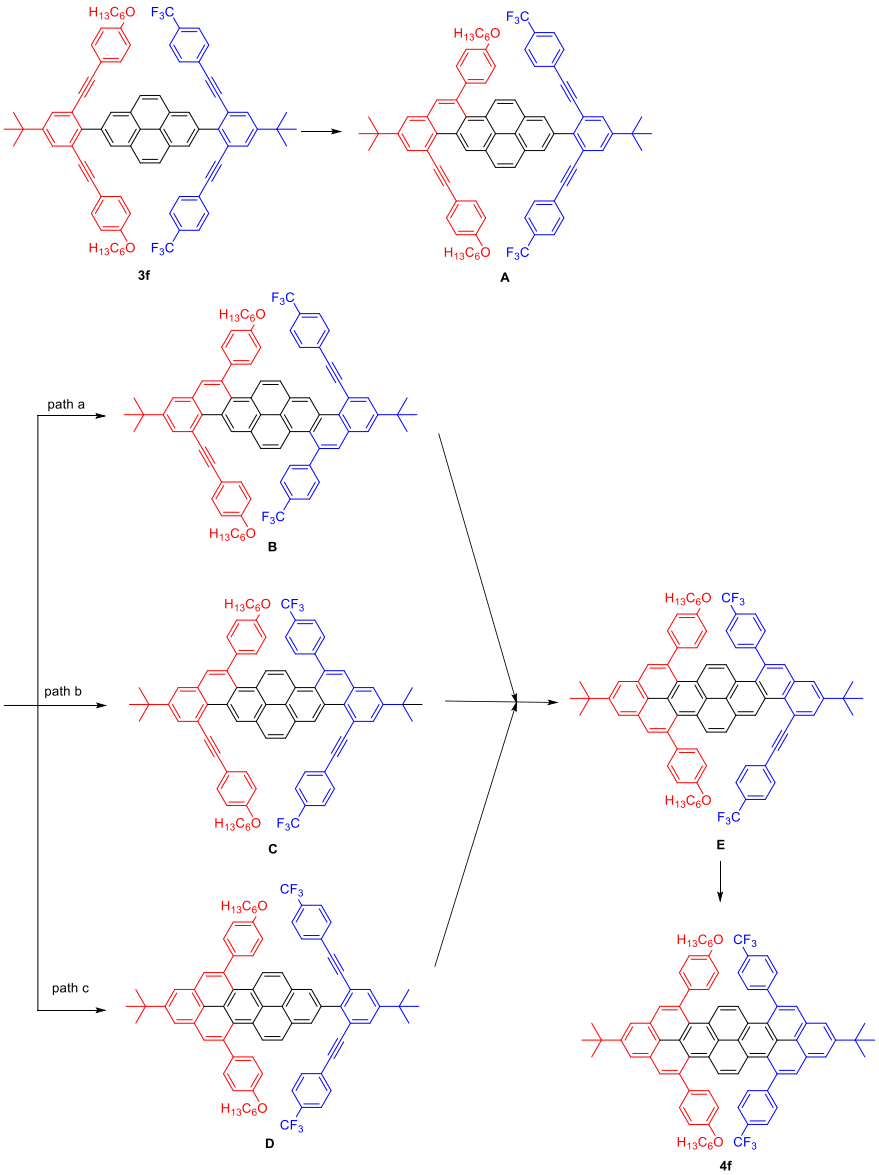
Table S5. Crystal data for peropyrene **6f** (CCDC number: 1826982).

Empirical formula	C95.50 H118 Cl4.50 O4.93	
Formula weight	1504.30	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 15.3329(8) Å	α= 90°.
	b = 18.3488(10) Å	β= 99.6319(10)°.
	c = 15.6332(8) Å	γ = 90°.
Volume	4336.2(4) $Å^3$	
Z	2	
Density (calculated)	1.152 Mg/m^3	
Absorption coefficient	0.202 mm^{-1}	

F(000)	1614
Crystal size	0.085 x 0.043 x 0.013 mm^3
Theta range for data collection	1.321 to 25.000°.
Index ranges	-18<=h<=18, -21<=k<=21, -18<=l<=18
Reflections collected	63552
Independent reflections	15279 [R(int) = 0.0592]
Completeness to theta = 25.000°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6807
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15279 / 209 / 1113
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0787, wR2 = 0.2132
R indices (all data)	R1 = 0.1041, wR2 = 0.2326
Absolute structure parameter	0.54(14)
Extinction coefficient	n/a
Largest diff. peak and hole	1.751 and -0.408 e.$Å^{-3}$

6. Possible cyclization progression in compound 3f

Since electron-rich alkynes cyclize faster, it is most likely that one of these electron-rich alkyne groups cyclize first to produce a mono-cyclized intermediate **A**. The electron-rich aryl groups in (shown in red) are conjugated with the benzopycene backbone of **A** making the second cyclization easier, which would lead to three possible intermediates **B**, **C**, or **D**. All of these intermediates would undergo a third alkyne cyclization to arrive at intermediate **E** that has two electron-rich aryl groups partially conjugated with the backbone, making the cyclization of the remaining electron-poor alkyne more facile.



Scheme S9. Synthesis of teropyrene 4f with possible intermediates

7. ^{1}H and ^{13}C NMR spectra for new compounds

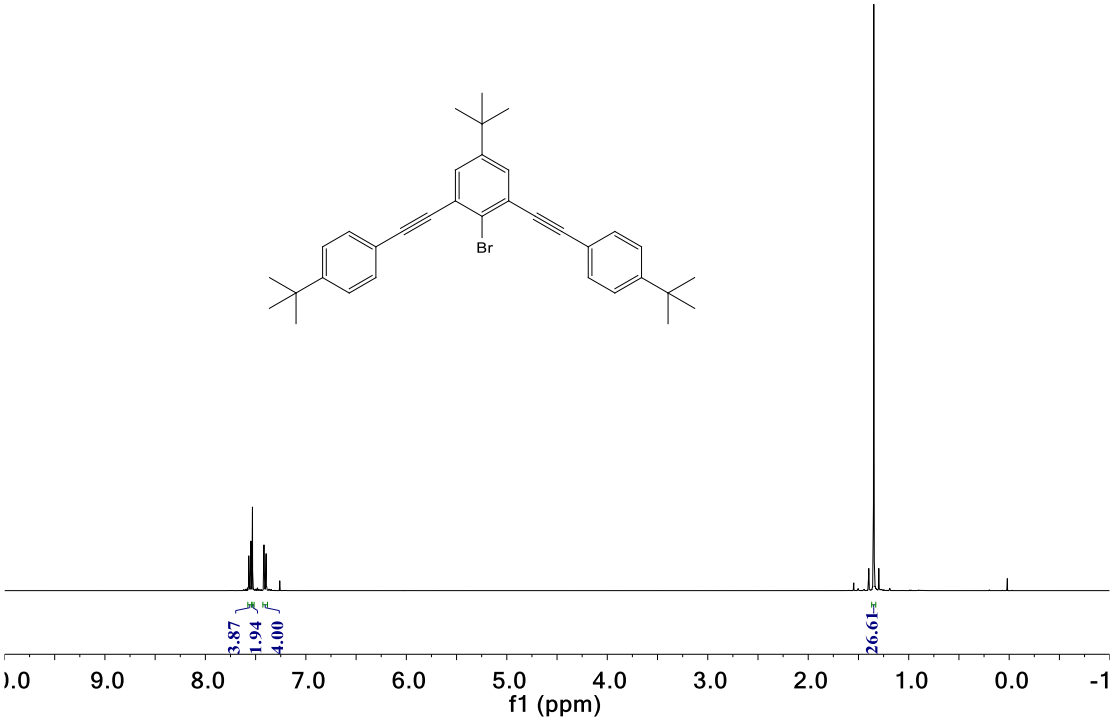


Figure S10. ^{1}H NMR spectrum for compound **S1d** in $CDCl_3$ at 298 K.

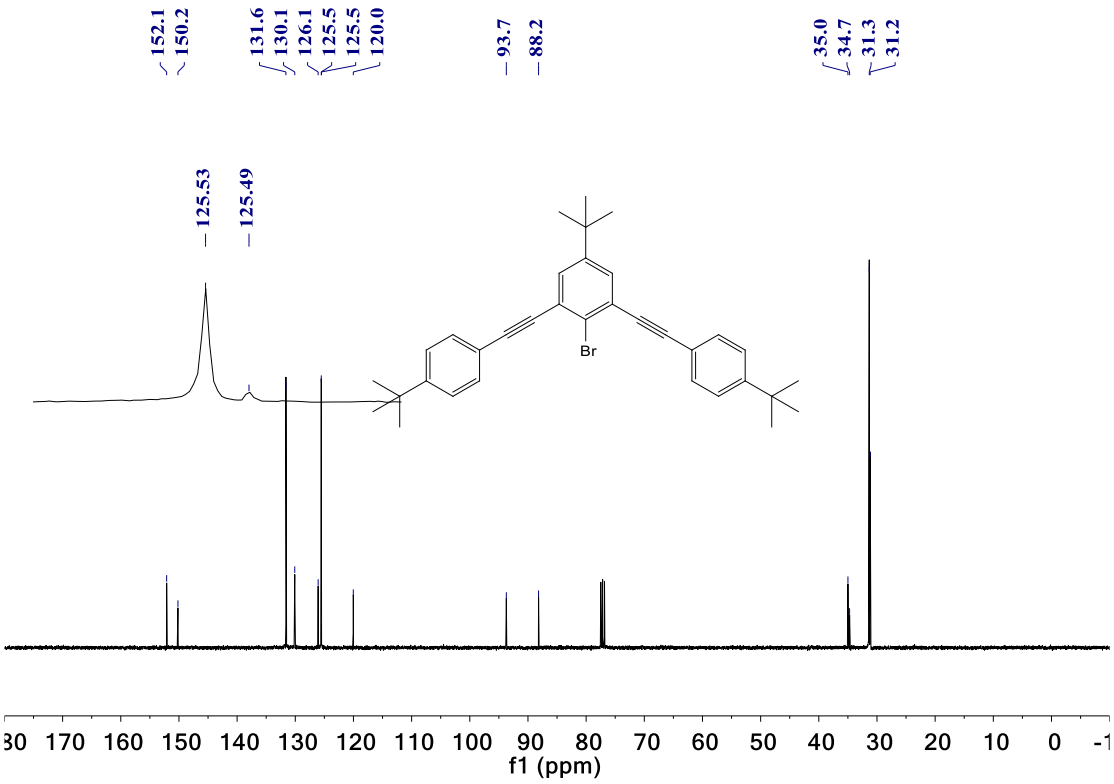


Figure S11. ^{1}H NMR spectrum for compound **S1d** in $CDCl_3$ at 298 K.

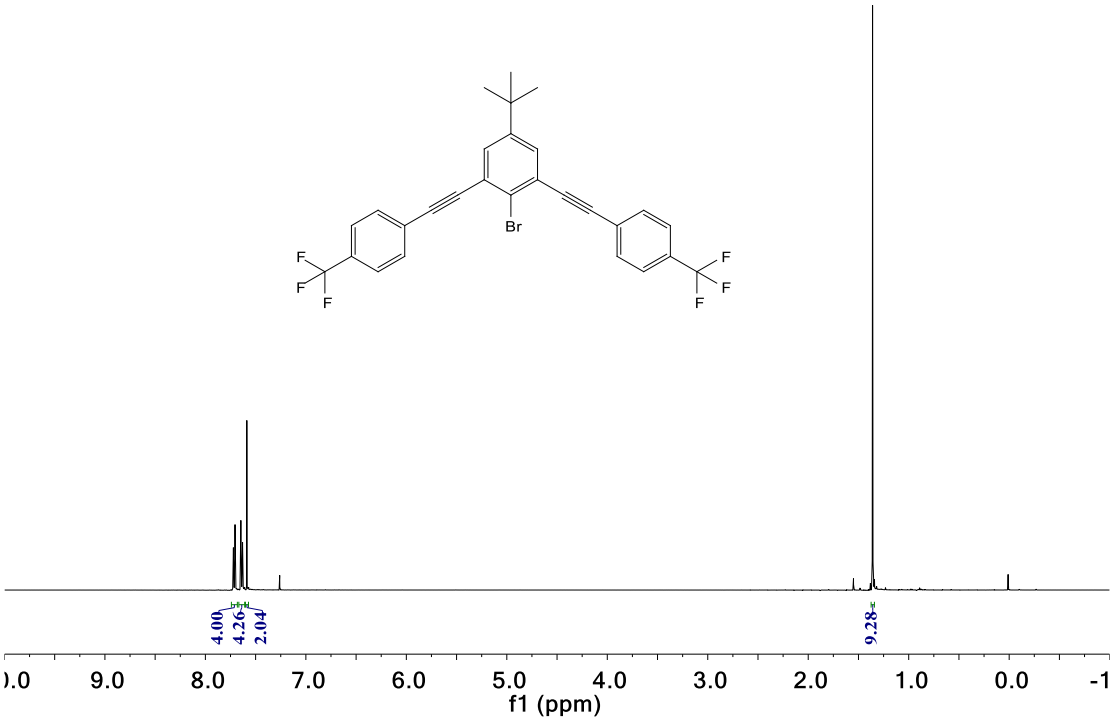


Figure S12. ^{1}H NMR spectrum for compound **S1e** in $CDCl_3$ at 298 K.

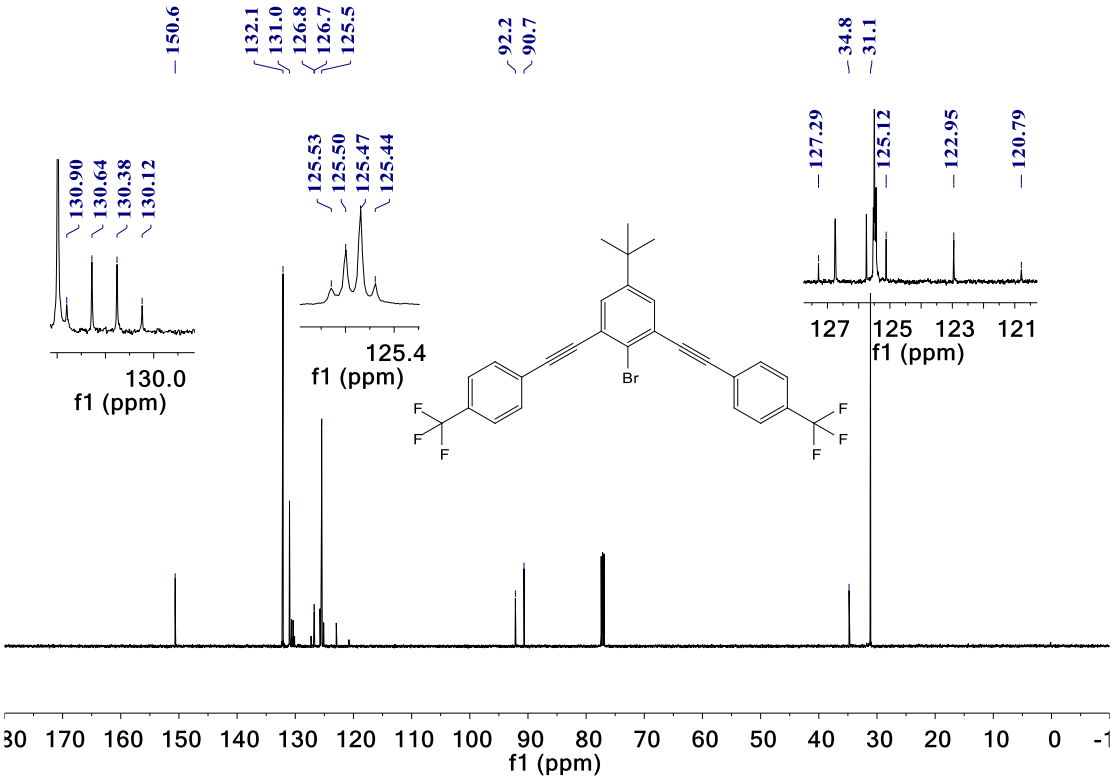


Figure S13. ^{13}C NMR spectrum for compound **S1e** in $CDCl_3$ at 298 K.

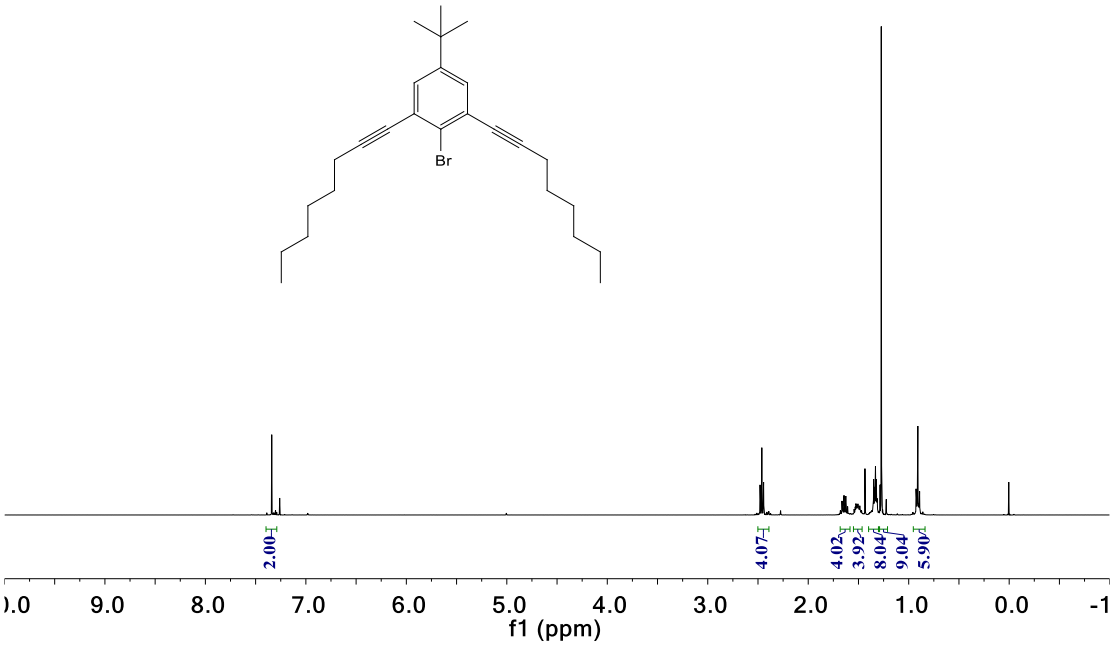


Figure S14. ^{1}H NMR spectrum for compound **S1f** in $CDCl_3$ at 298 K.

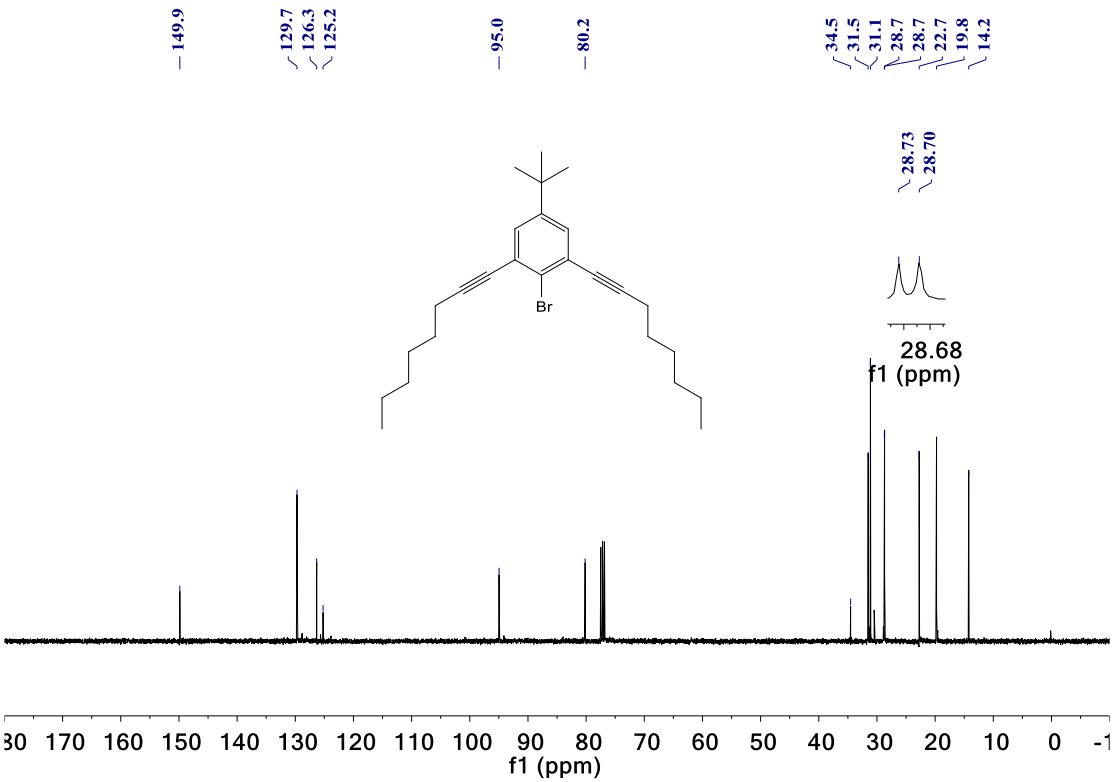


Figure S15. ^{13}C NMR spectrum for compound **S1f** in $CDCl_3$ at 298 K.

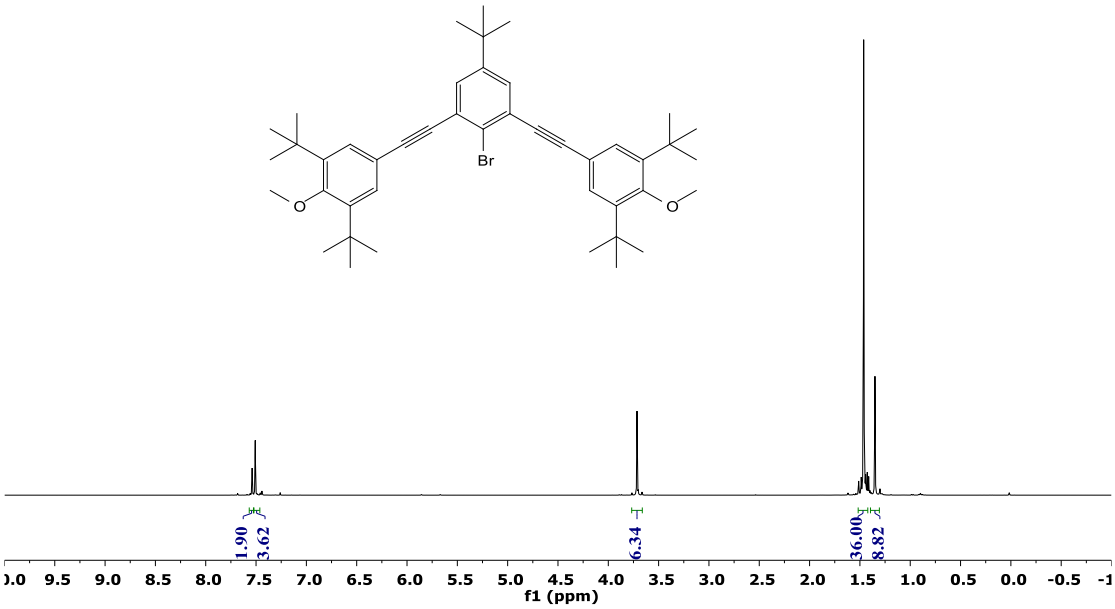


Figure S16. ^{1}H NMR spectrum for compound **S1g** in $CDCl_3$ at 298 K.

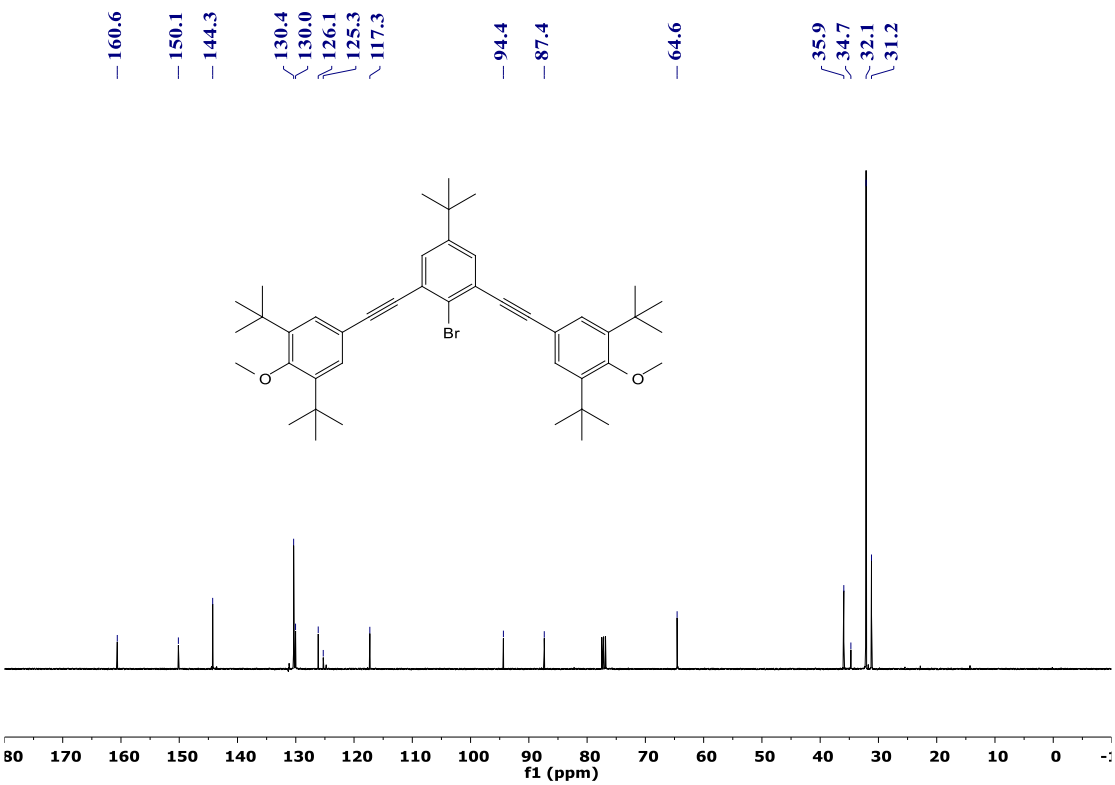


Figure S17. ^{13}C NMR spectrum for compound **S1g** in $CDCl_3$ at 298 K.

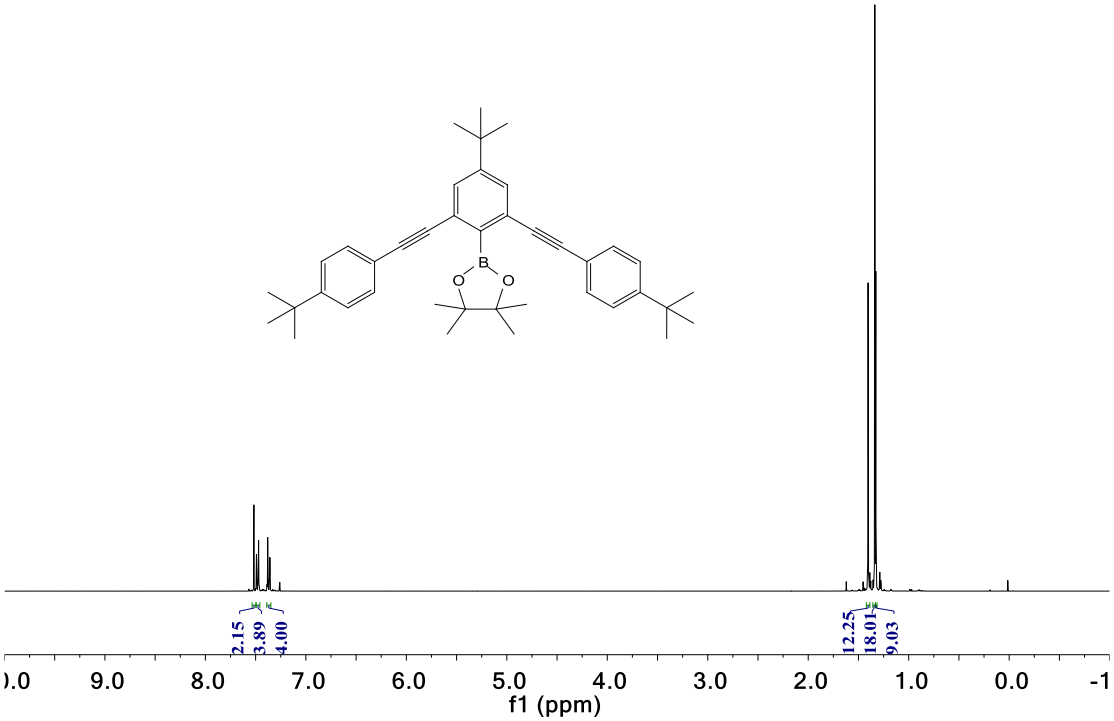


Figure S18. ^{1}H NMR spectrum for compound **S2d** in $CDCl_3$ at 298 K.

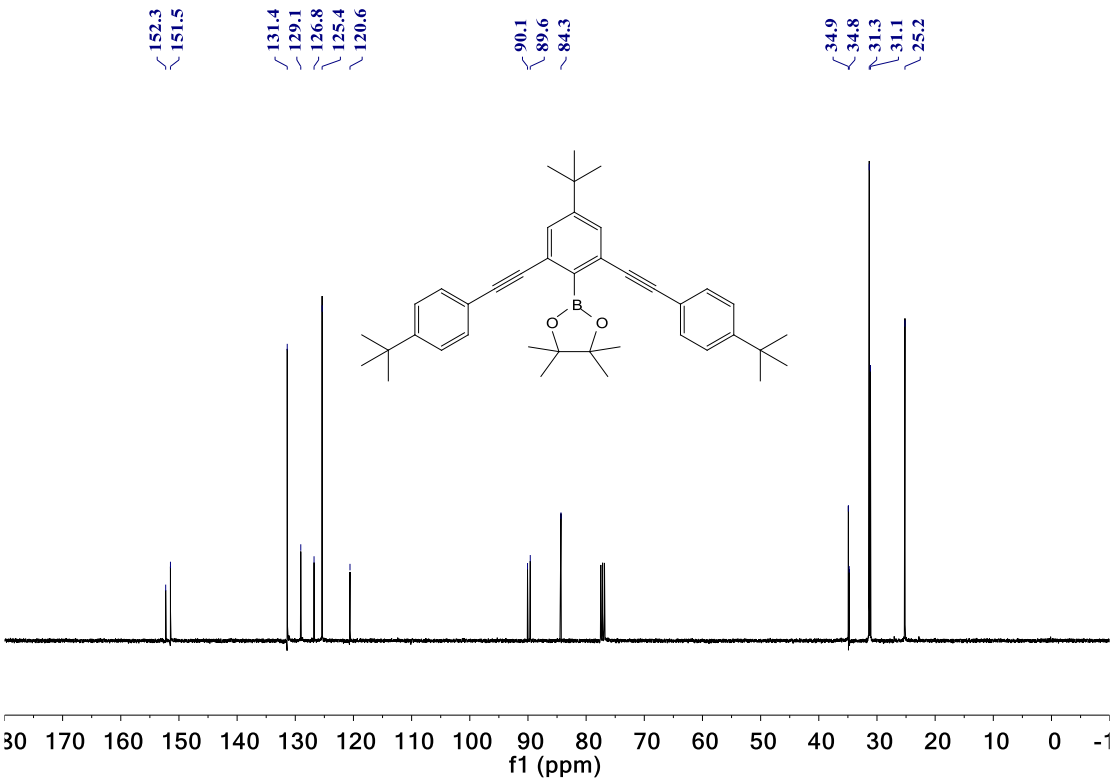


Figure S19. ^{13}C NMR spectrum for compound **S2d** in $CDCl_3$ at 298 K.

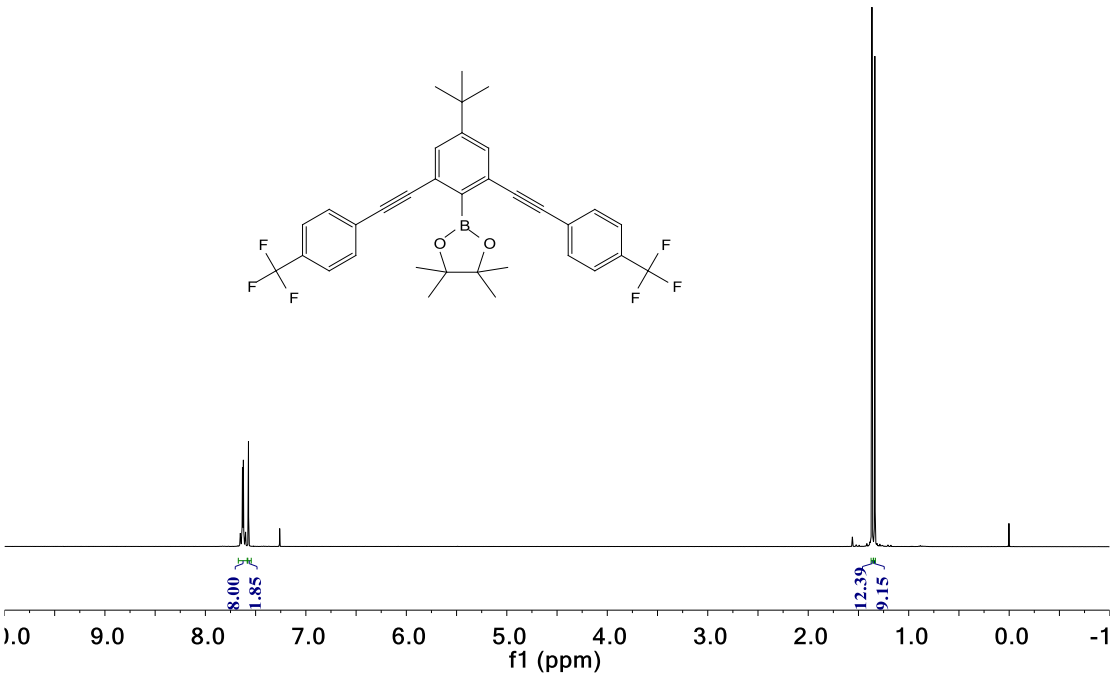


Figure S20. ^{1}H NMR spectrum for compound **S2e** in $CDCl_3$ at 298 K.

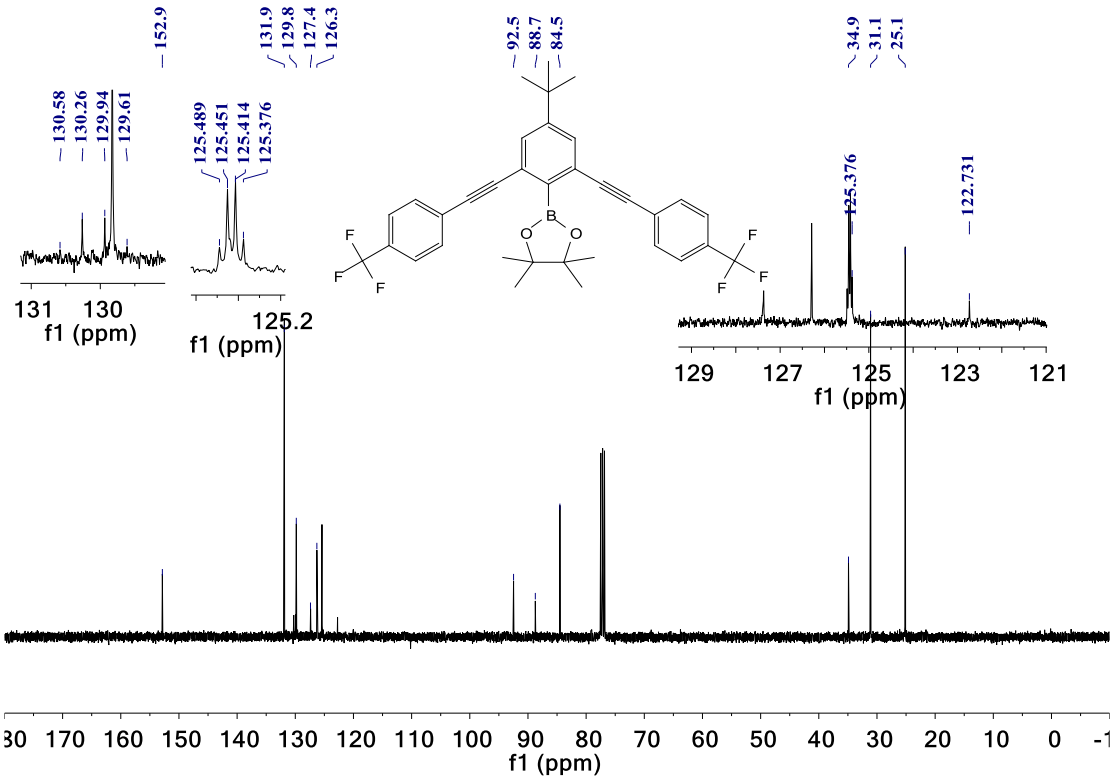


Figure S21. ^{13}C NMR spectrum for compound **S2e** in $CDCl_3$ at 298 K.

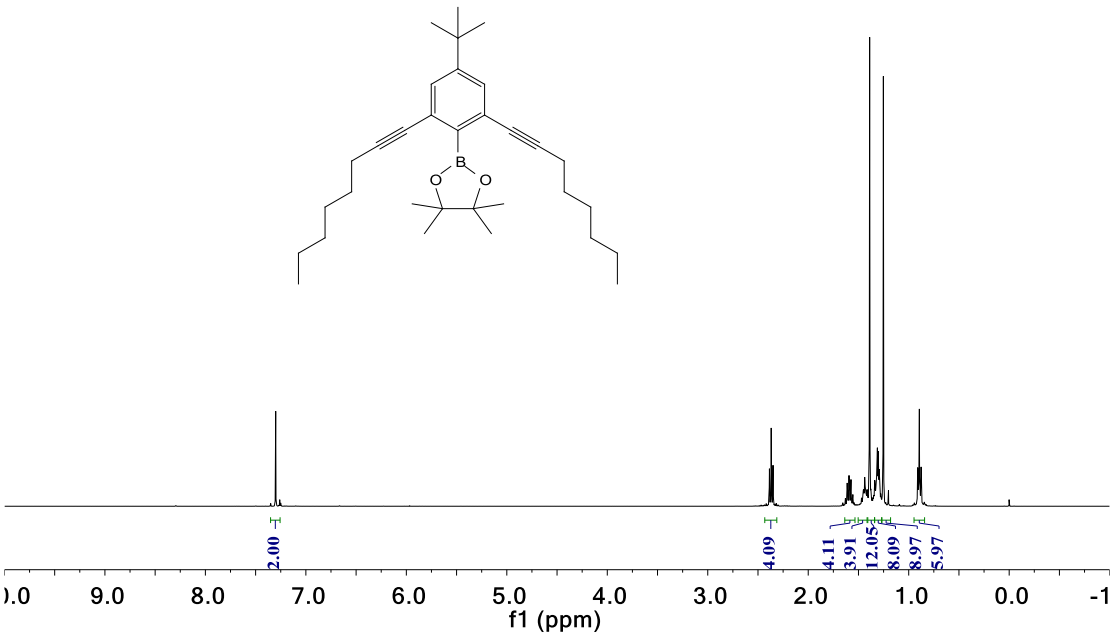


Figure S22. ^{1}H NMR spectrum for compound **S2f** in $CDCl_3$ at 298 K.

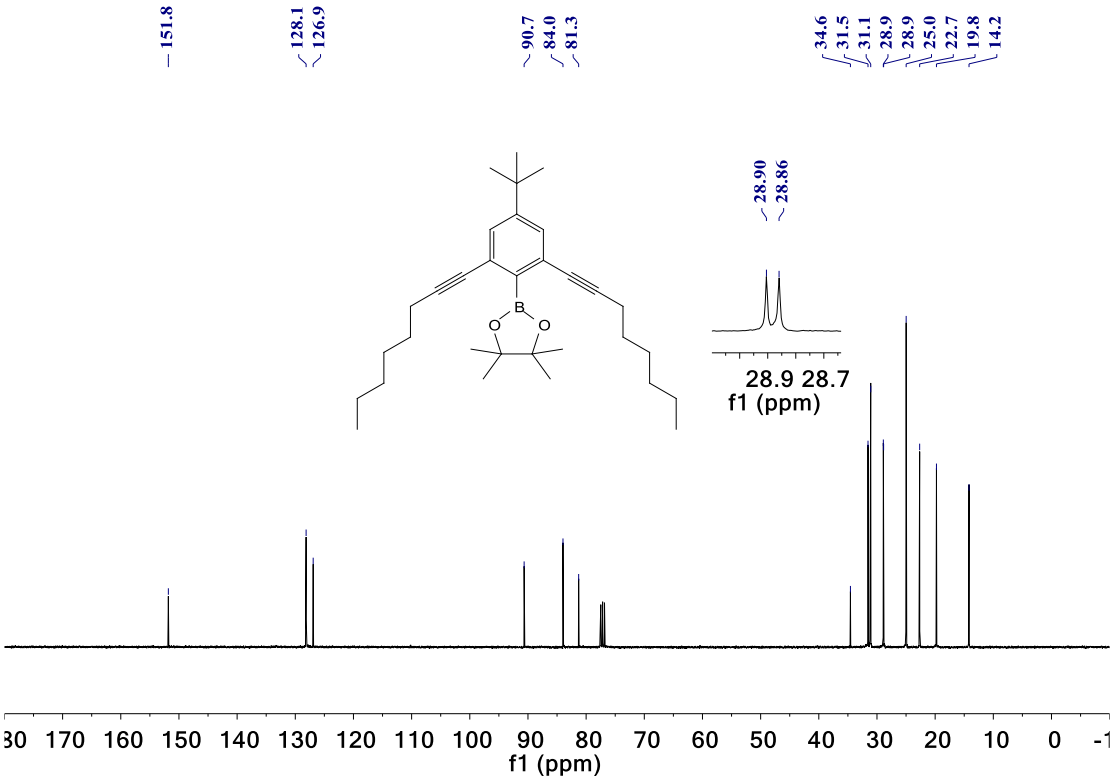


Figure S23. ^{13}C NMR spectrum for compound **S2f** in $CDCl_3$ at 298 K.

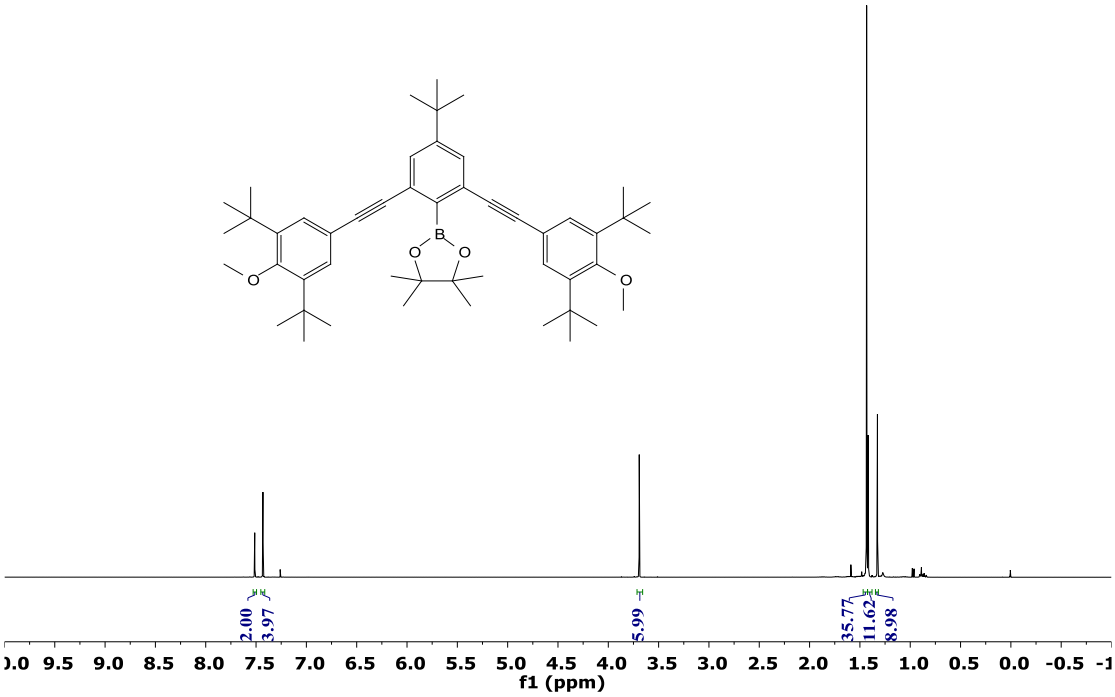


Figure S24. ^{1}H NMR spectrum for compound **S2g** in $CDCl_3$ at 298 K.

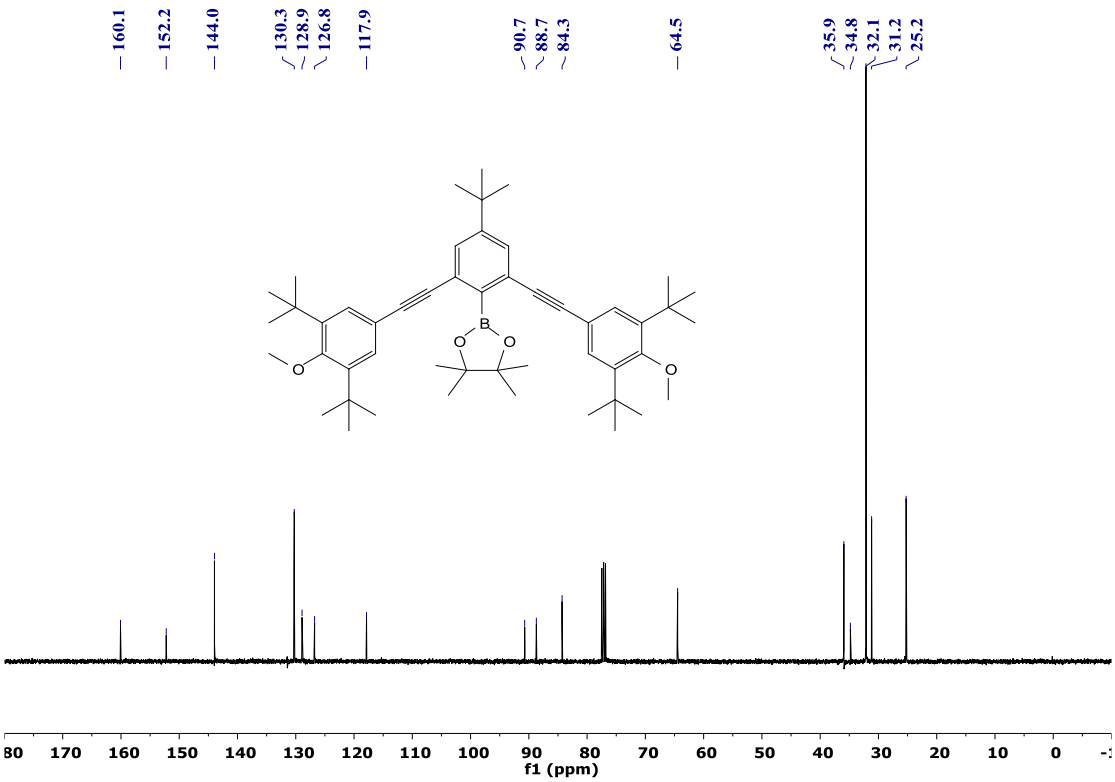


Figure S25. ^{13}C NMR spectrum for compound **S2g** in $CDCl_3$ at 298 K.

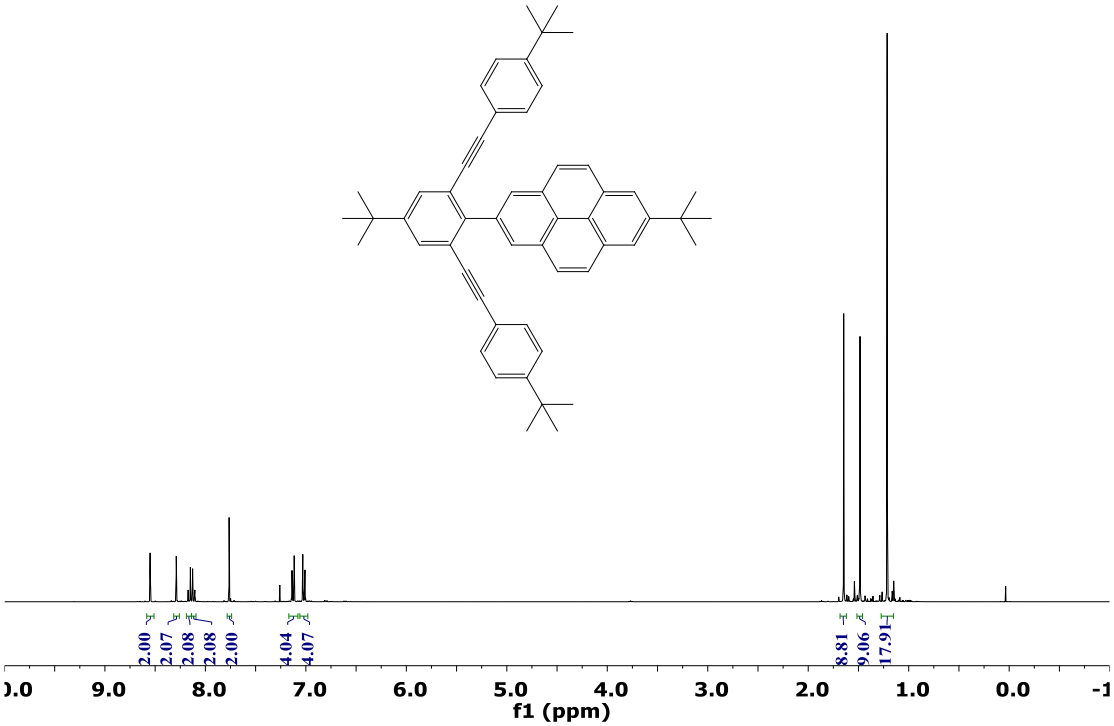


Figure S26. ^{1}H NMR spectrum for compound **1d** in $CDCl_3$ at 298 K.

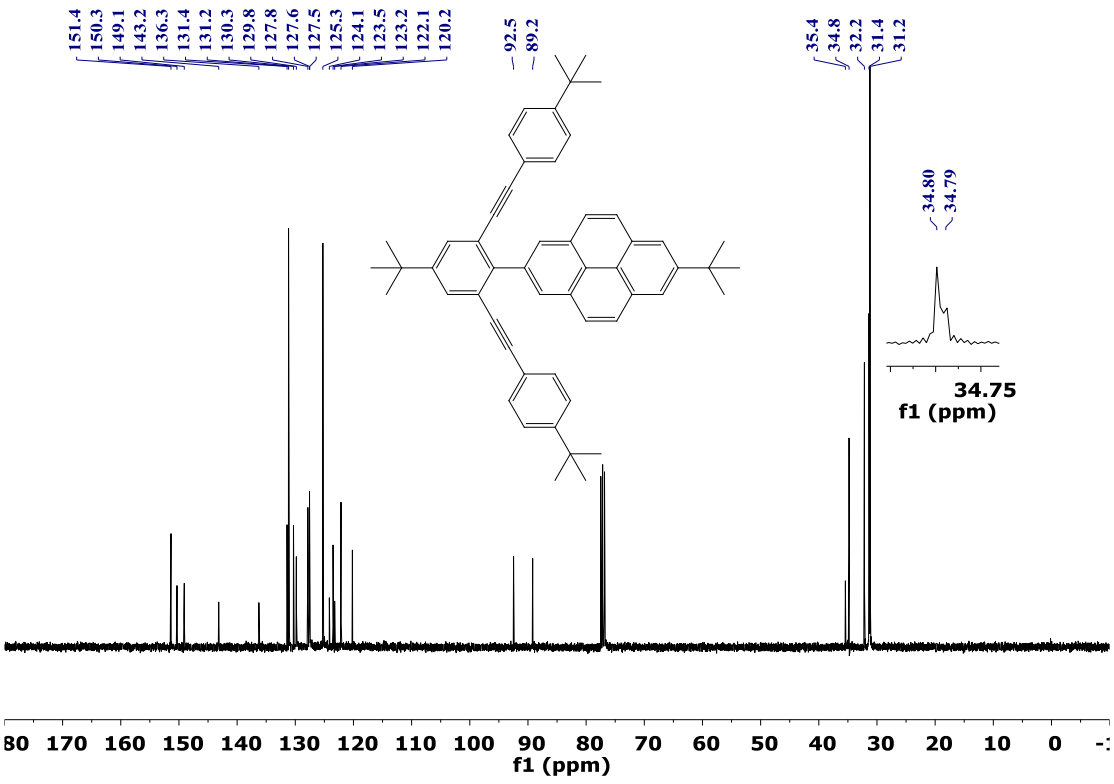


Figure S27. ^{13}C NMR spectrum for compound **1d** in $CDCl_3$ at 298 K.

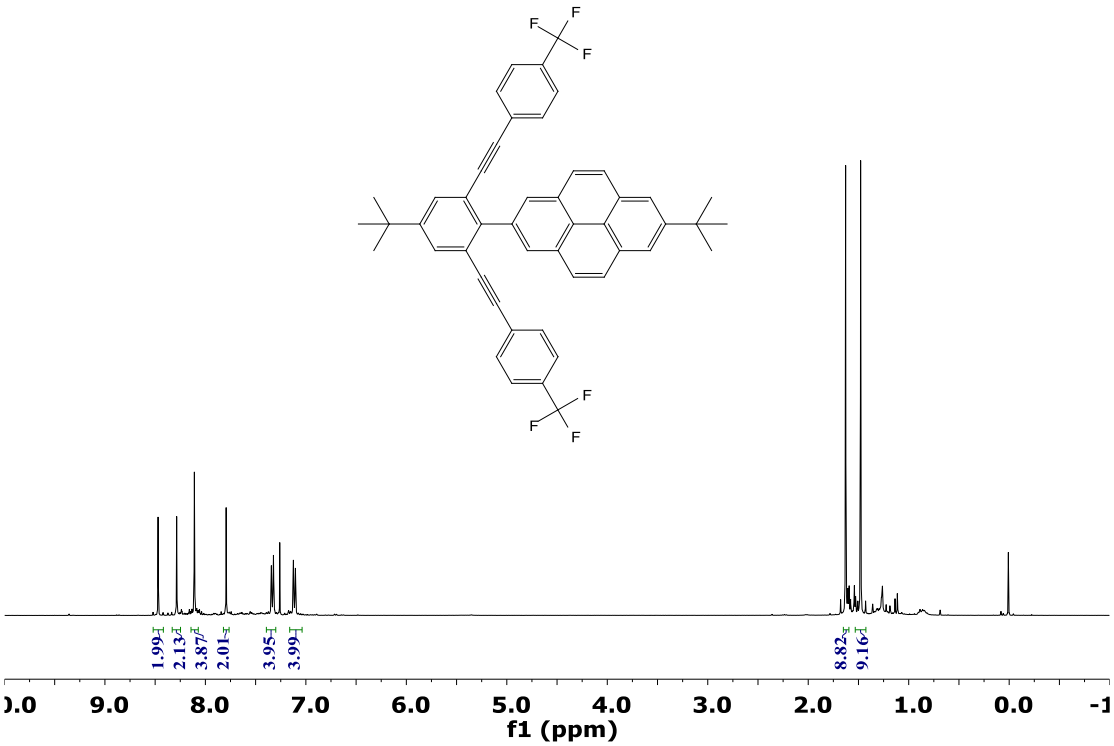


Figure S28. ^{1}H NMR spectrum for compound **1e** in $CDCl_3$ at 298 K.

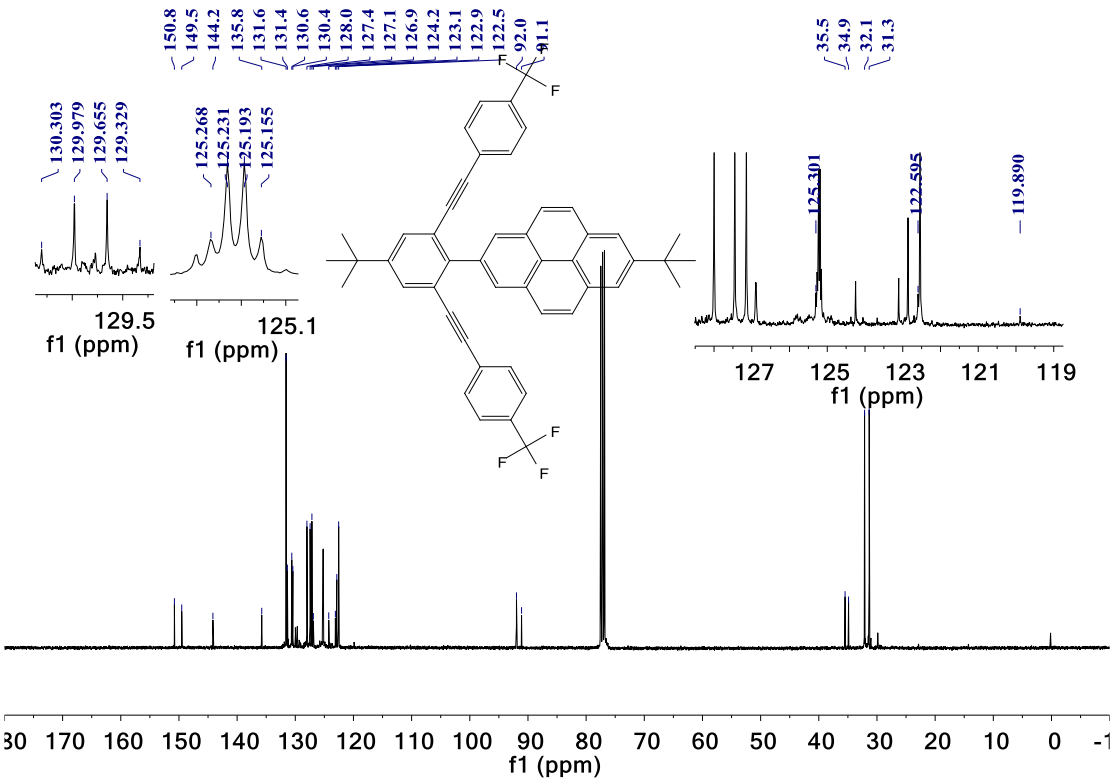


Figure S29. ^{13}C NMR spectrum for compound **1e** in $CDCl_3$ at 298 K.

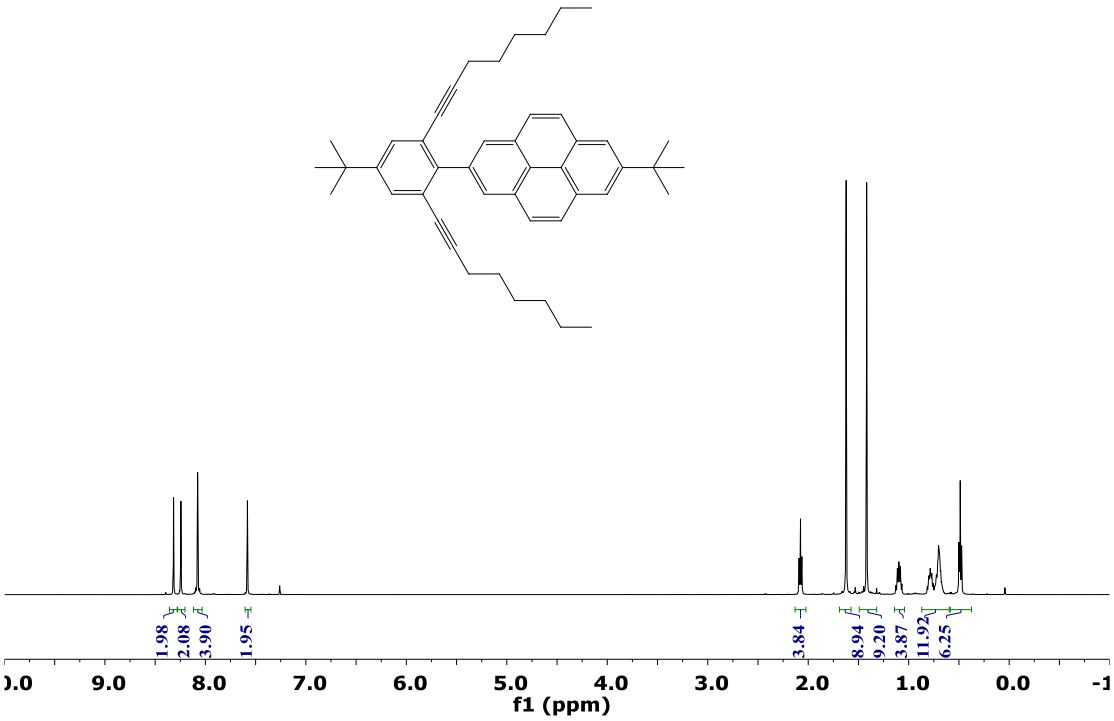


Figure S30. ^{1}H NMR spectrum for compound **1f** in $CDCl_3$ at 298 K.

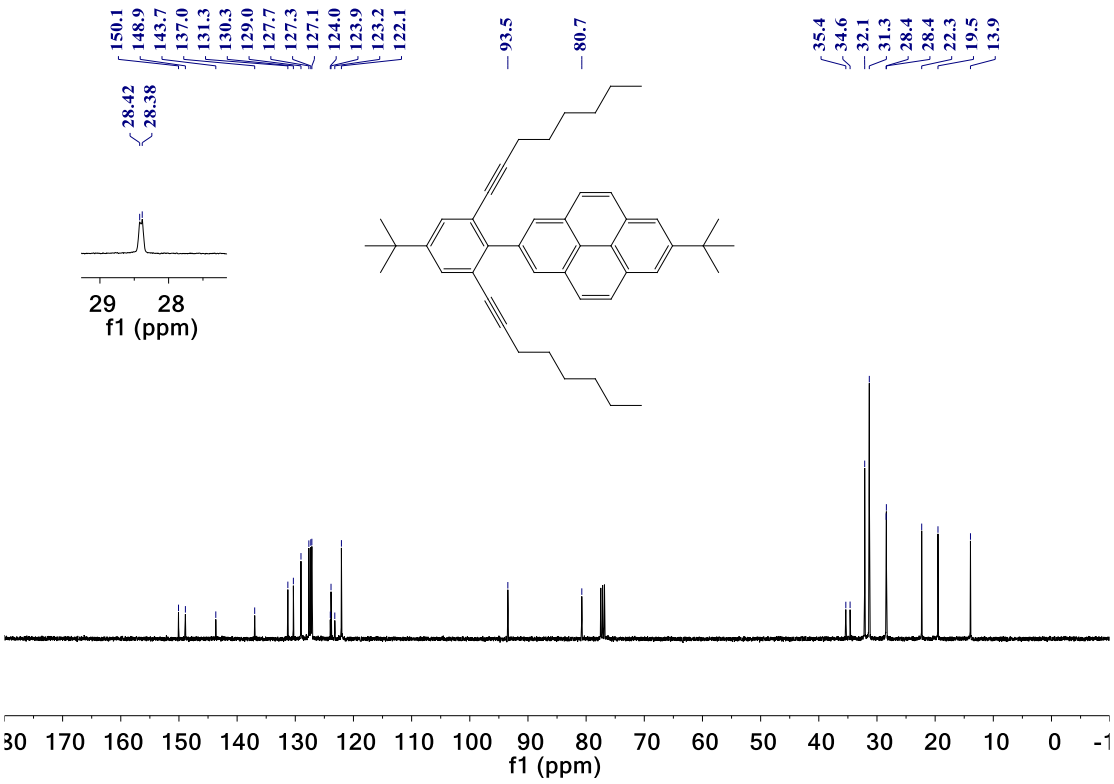


Figure S31. ^{13}C NMR spectrum for compound **1f** in $CDCl_3$ at 298 K.

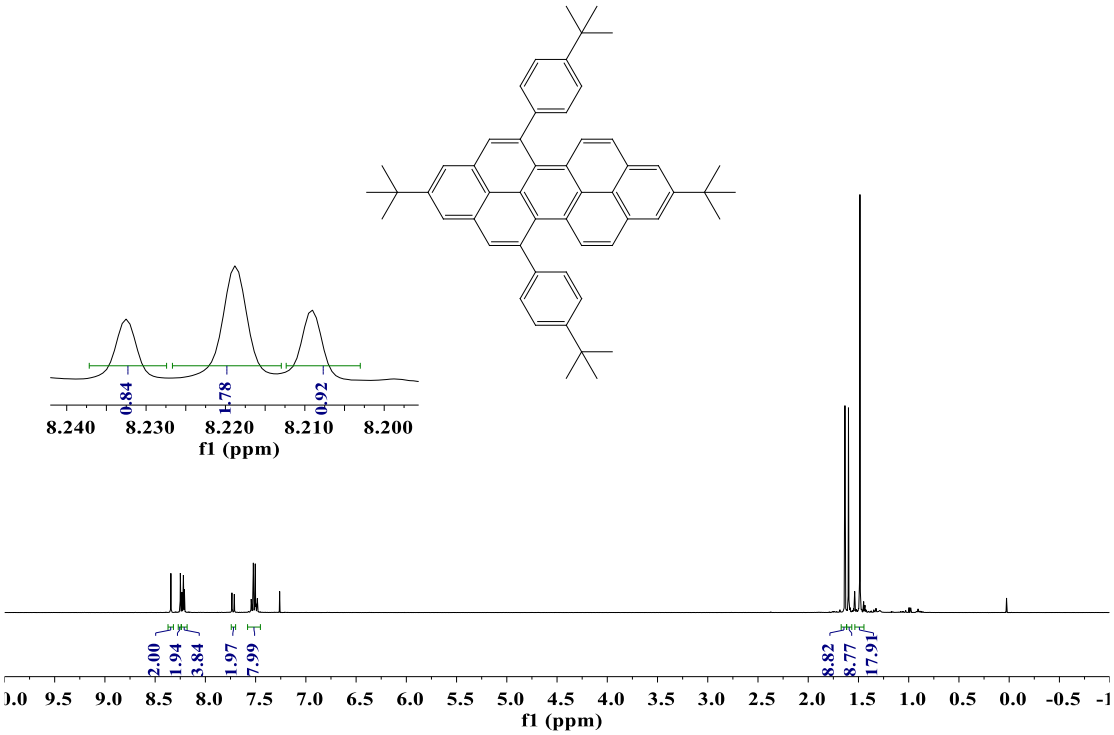


Figure S32. ^{1}H NMR spectrum for compound **2d** in $CDCl_3$ at 298 K.

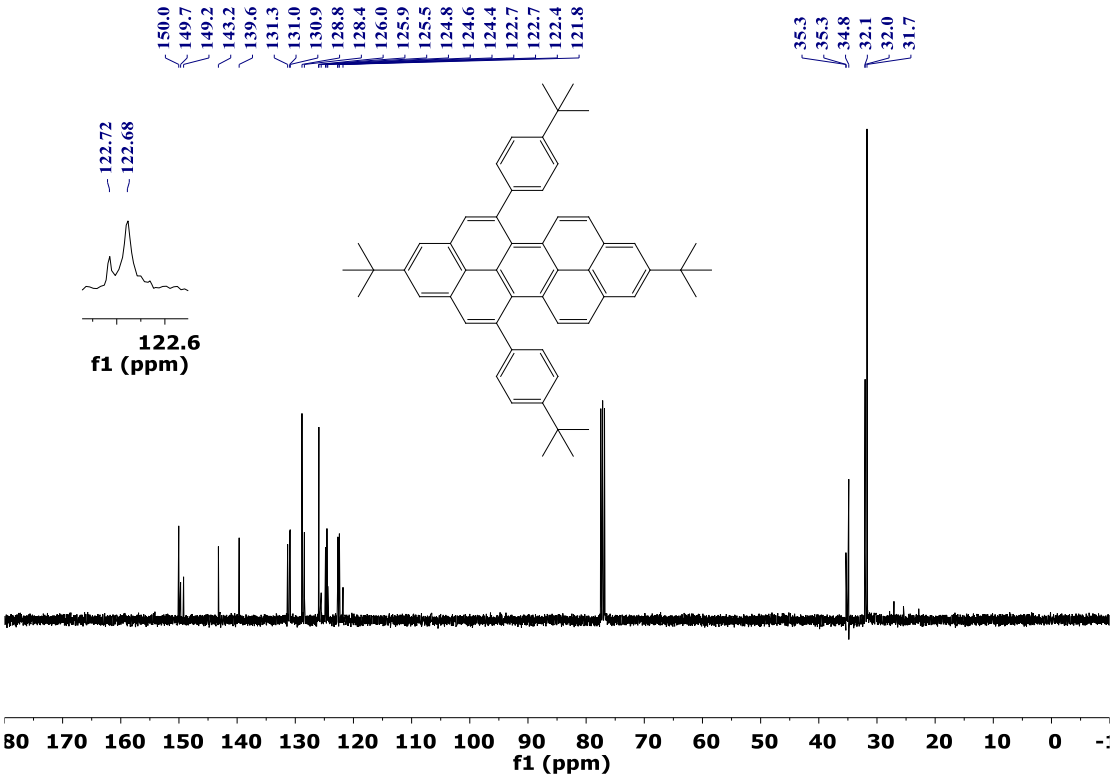


Figure S33. ^{13}C NMR spectrum for compound **2d** in $CDCl_3$ at 298 K.

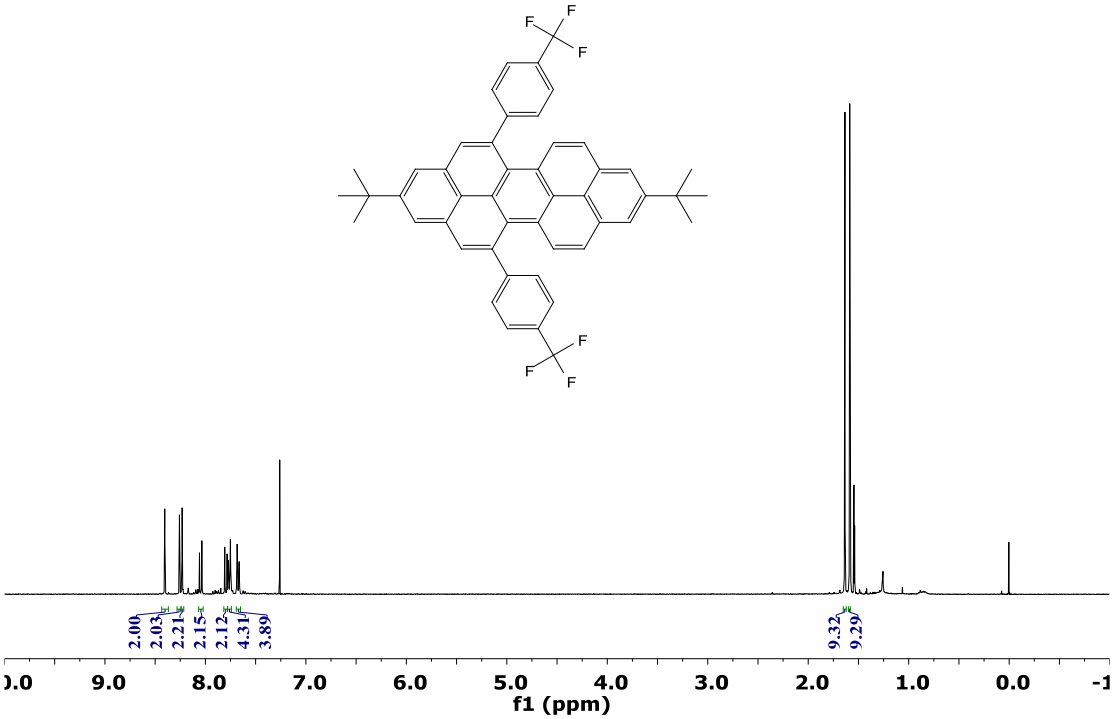


Figure S34. ^{1}H NMR spectrum for compound **2e** in $CDCl_3$ at 298 K.

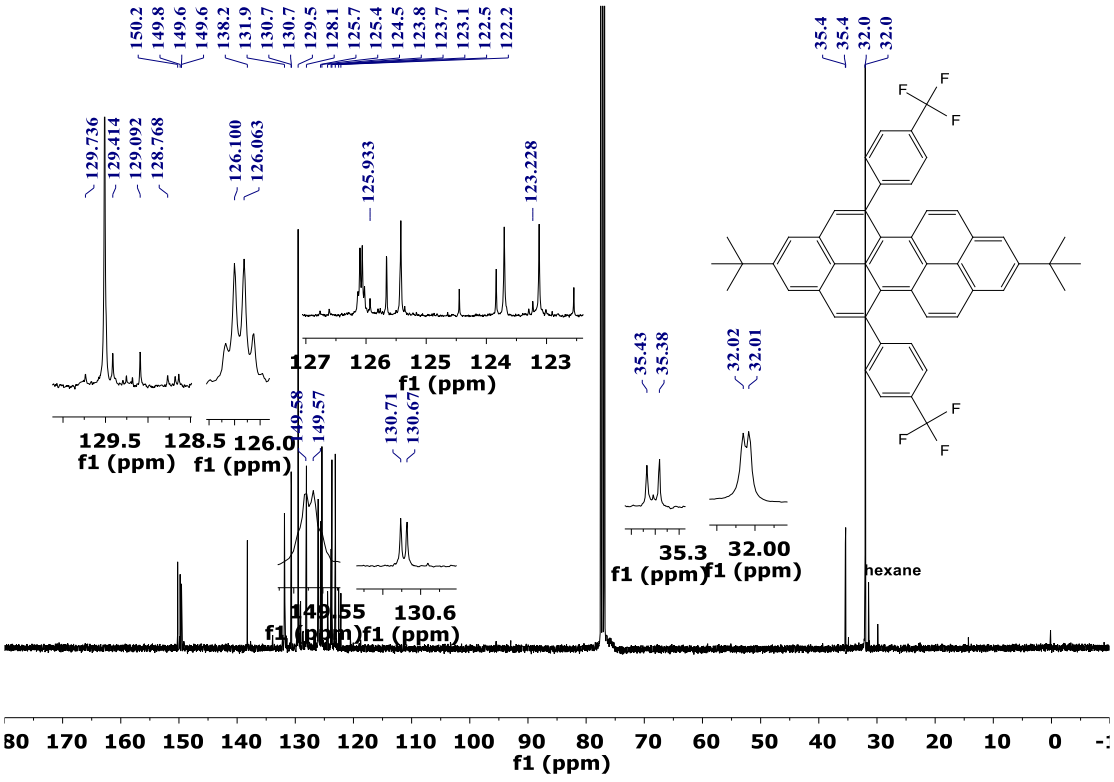


Figure S35. ^{13}C NMR spectrum for compound **2e** in $CDCl_3$ at 298 K.

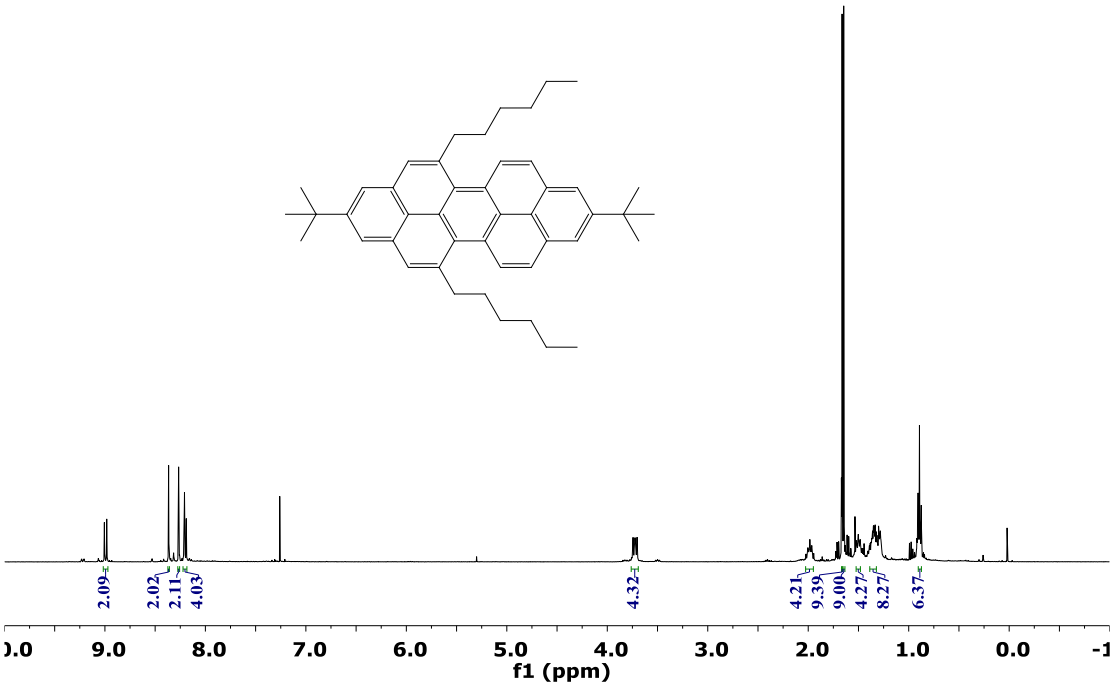


Figure S36. ^{1}H NMR spectrum for compound **2f** in $CDCl_3$ at 298 K.

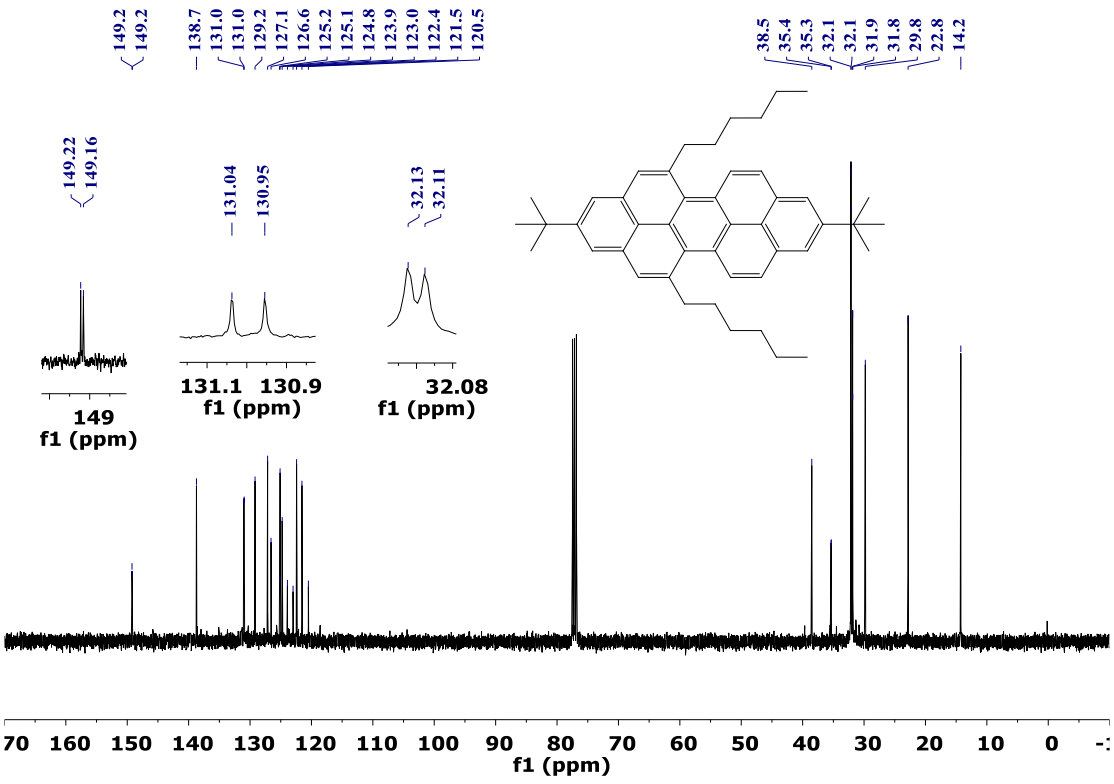


Figure S37. ^{13}C NMR spectrum for compound **2f** in $CDCl_3$ at 298 K.

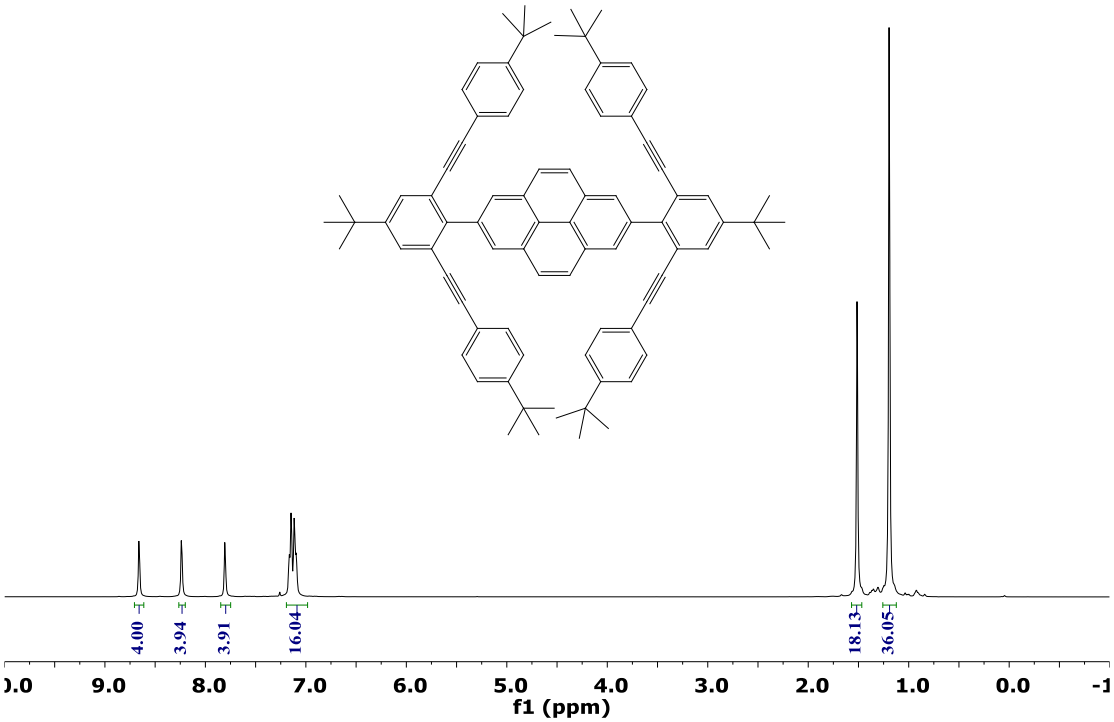


Figure S38. ^{1}H NMR spectrum for compound **3c** in $CDCl_3$ at 298 K.

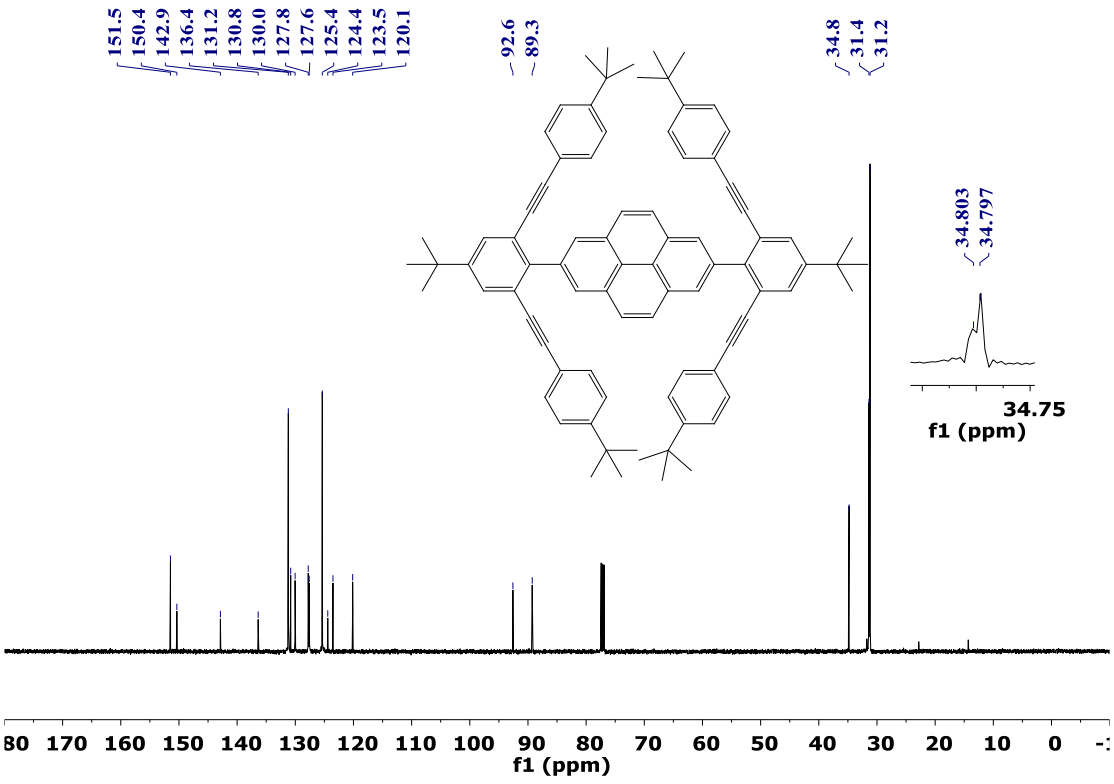


Figure S39. ^{13}C NMR spectrum for compound **3c** in $CDCl_3$ at 298 K.

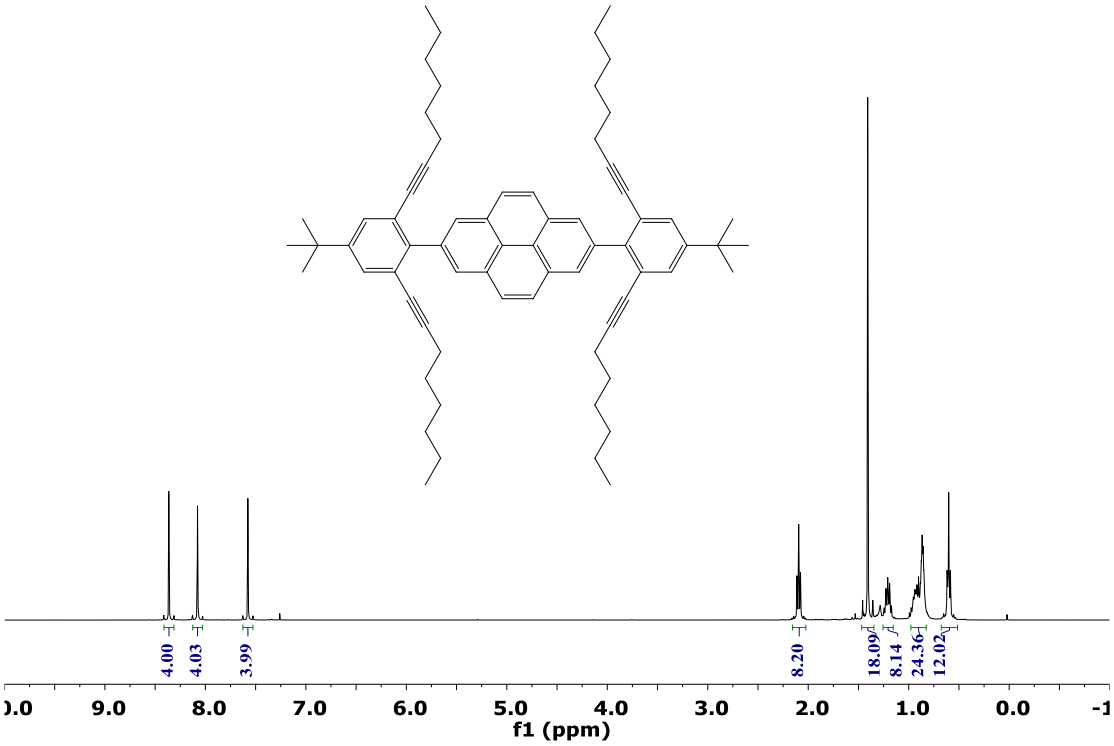


Figure S40. ^{1}H NMR spectrum for compound **3d** in $CDCl_3$ at 298 K.

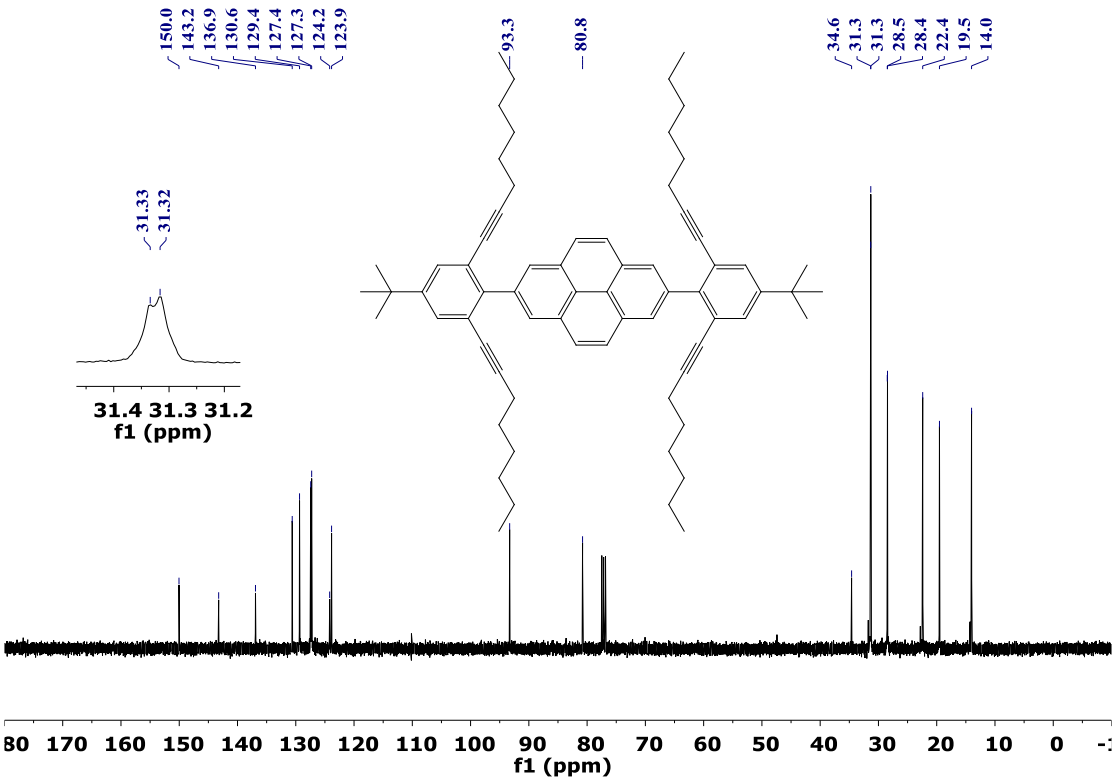


Figure S41. ^{13}C NMR spectrum for compound **3d** in $CDCl_3$ at 298 K.

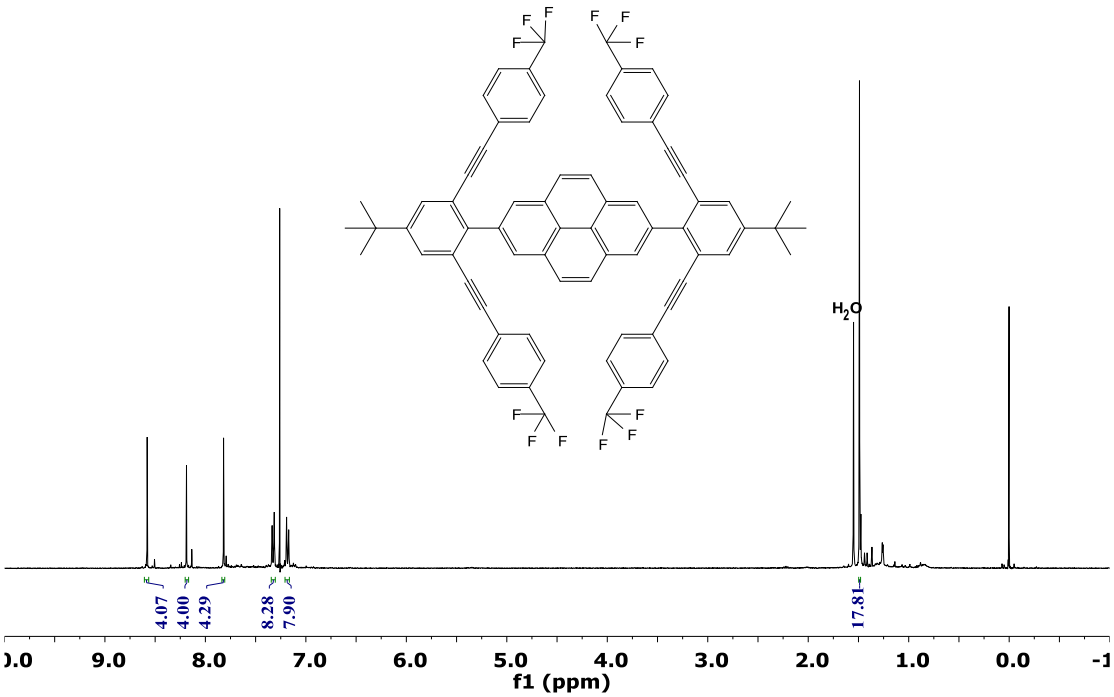


Figure S42. ^{1}H NMR spectrum for compound **3e** in $CDCl_3$ at 298 K.

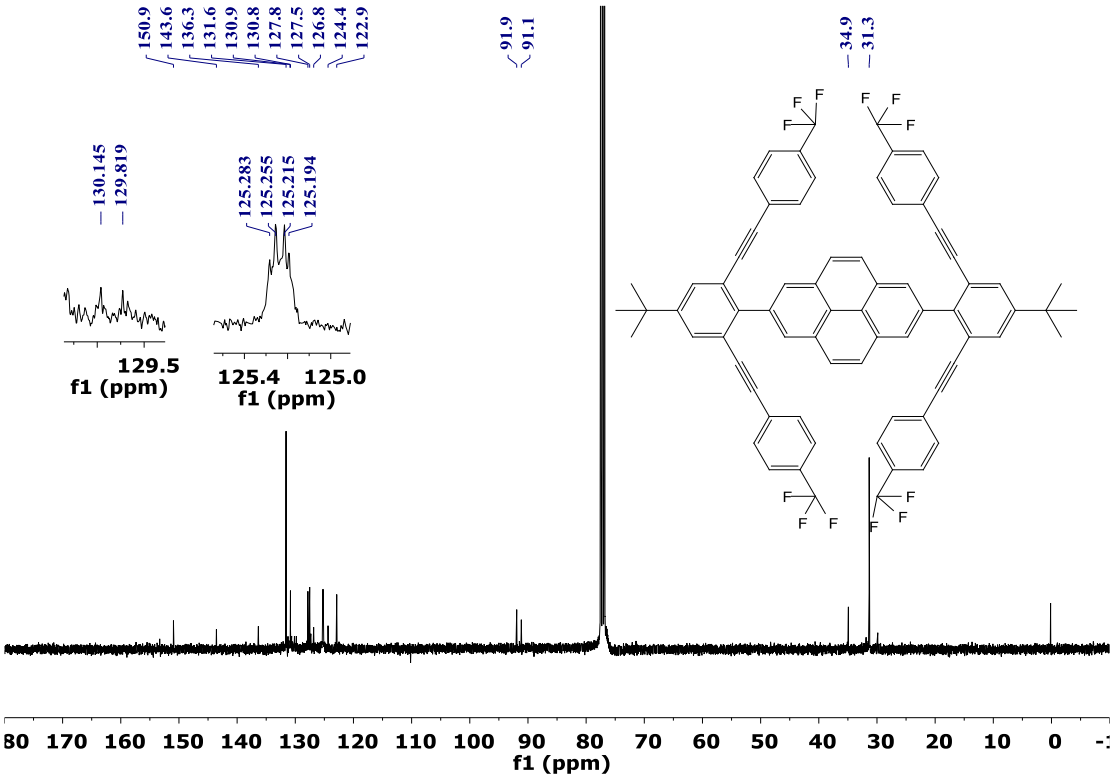


Figure S43. ^{13}C NMR spectrum for compound **3e** in $CDCl_3$ at 298 K.

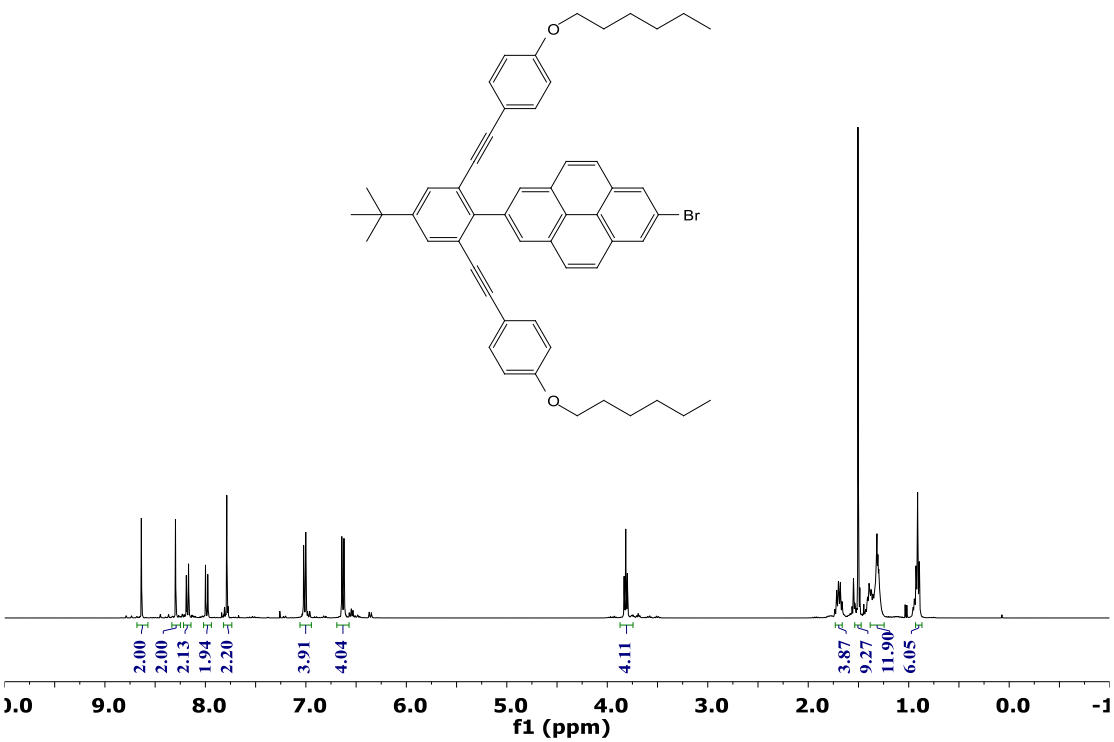


Figure S44. ^{1}H NMR spectrum for compound **S3** in $CDCl_3$ at 298 K.

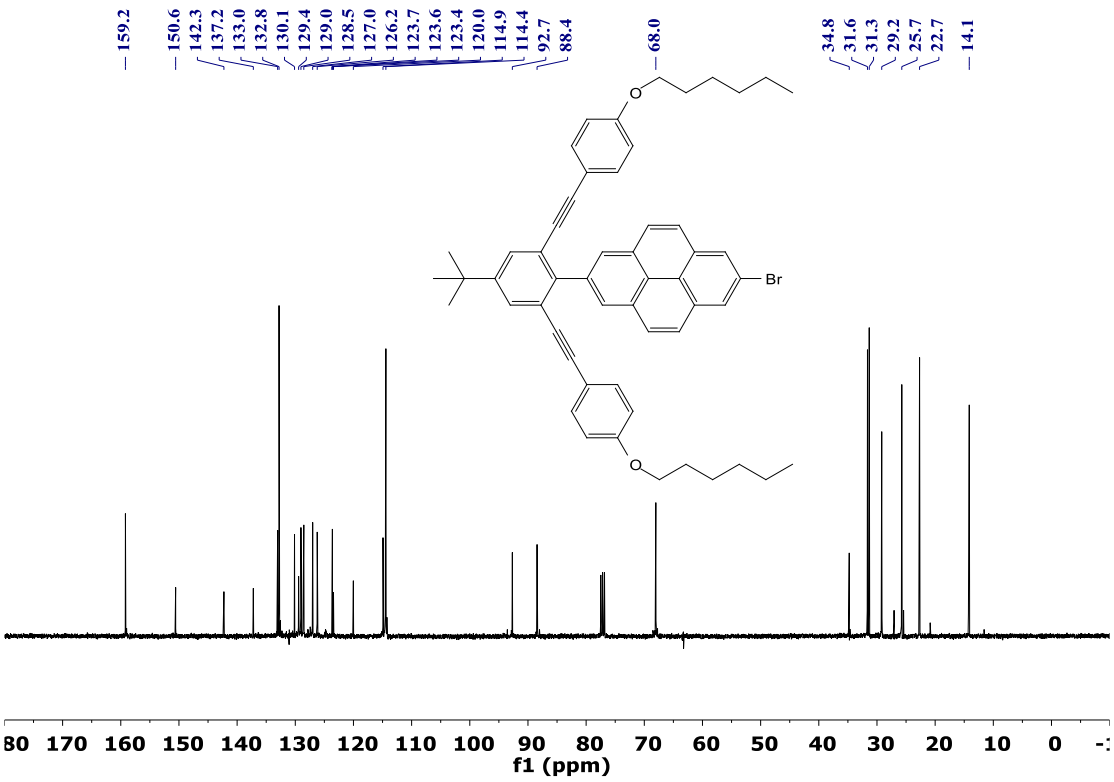


Figure S45. ^{13}C NMR spectrum for compound **S3** in $CDCl_3$ at 298 K.

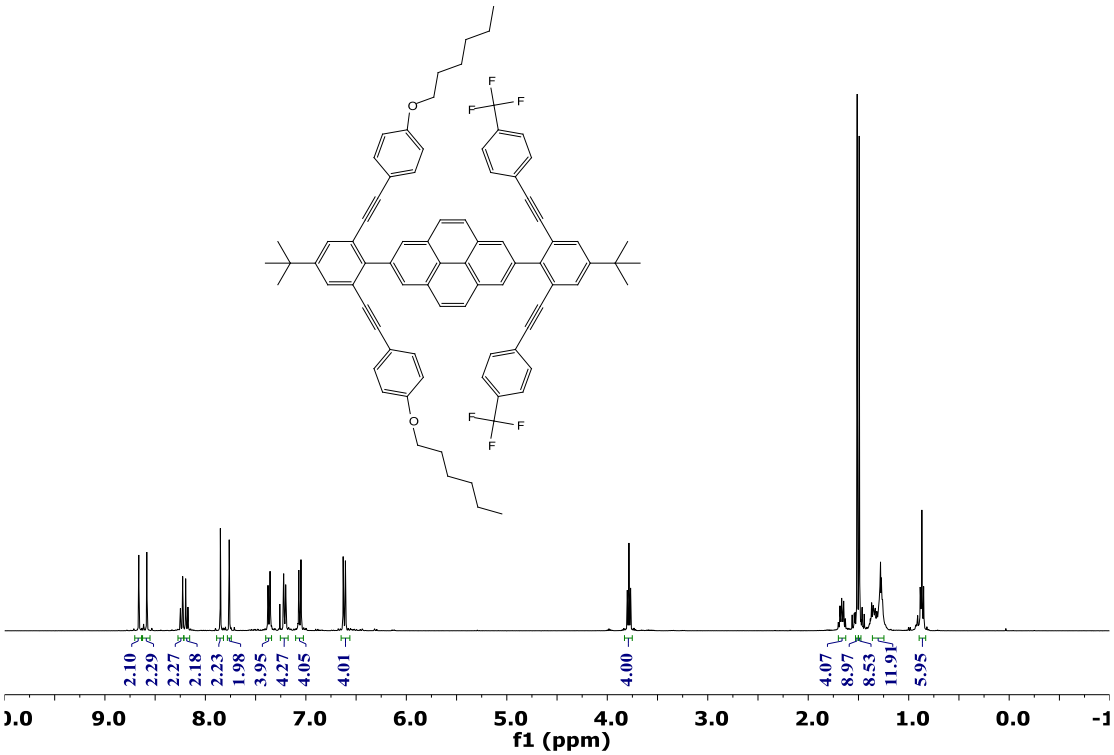


Figure S46. ^{1}H NMR spectrum for compound **3f** in $CDCl_3$ at 298 K.

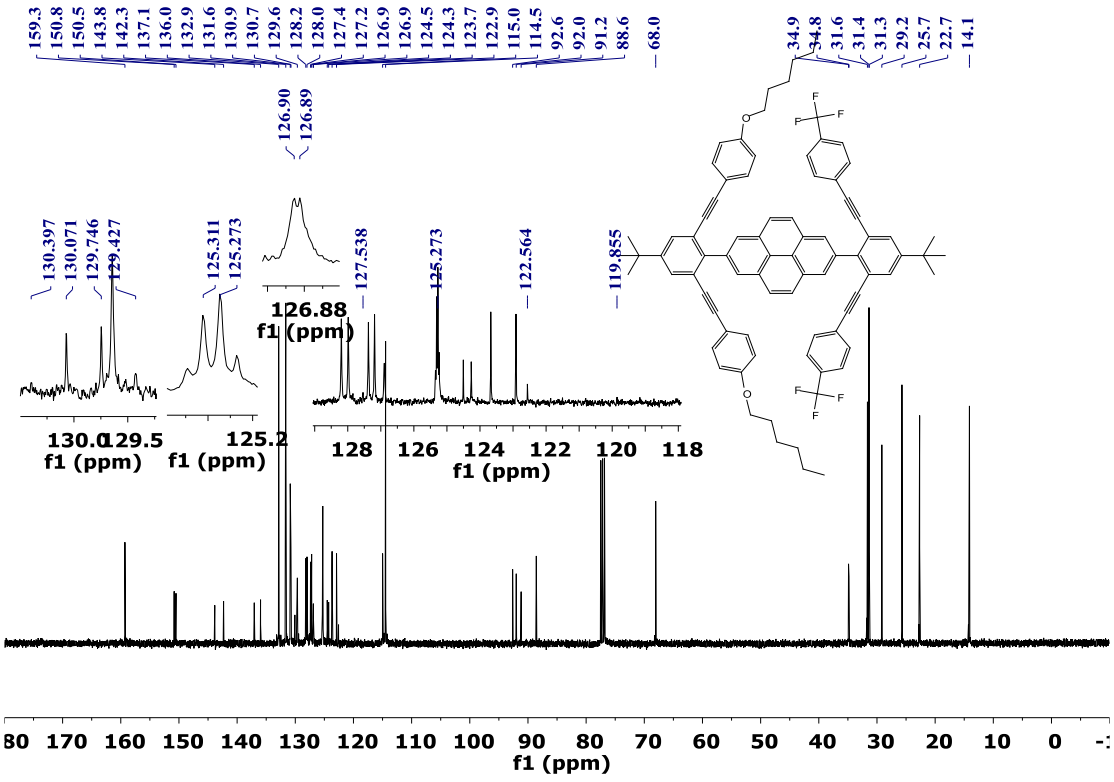


Figure S47. ^{13}C NMR spectrum for compound **3f** in $CDCl_3$ at 298 K.

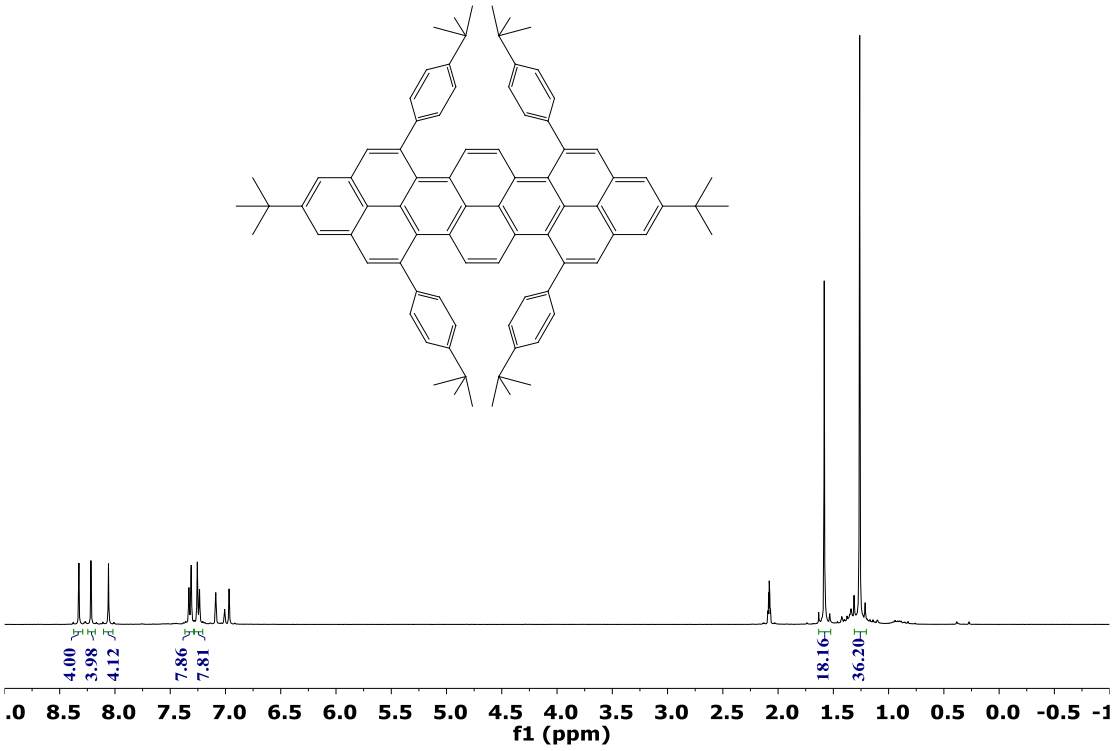


Figure S48. ^{1}H NMR spectrum for compound **4c** in toluene-d_8 at 298 K.

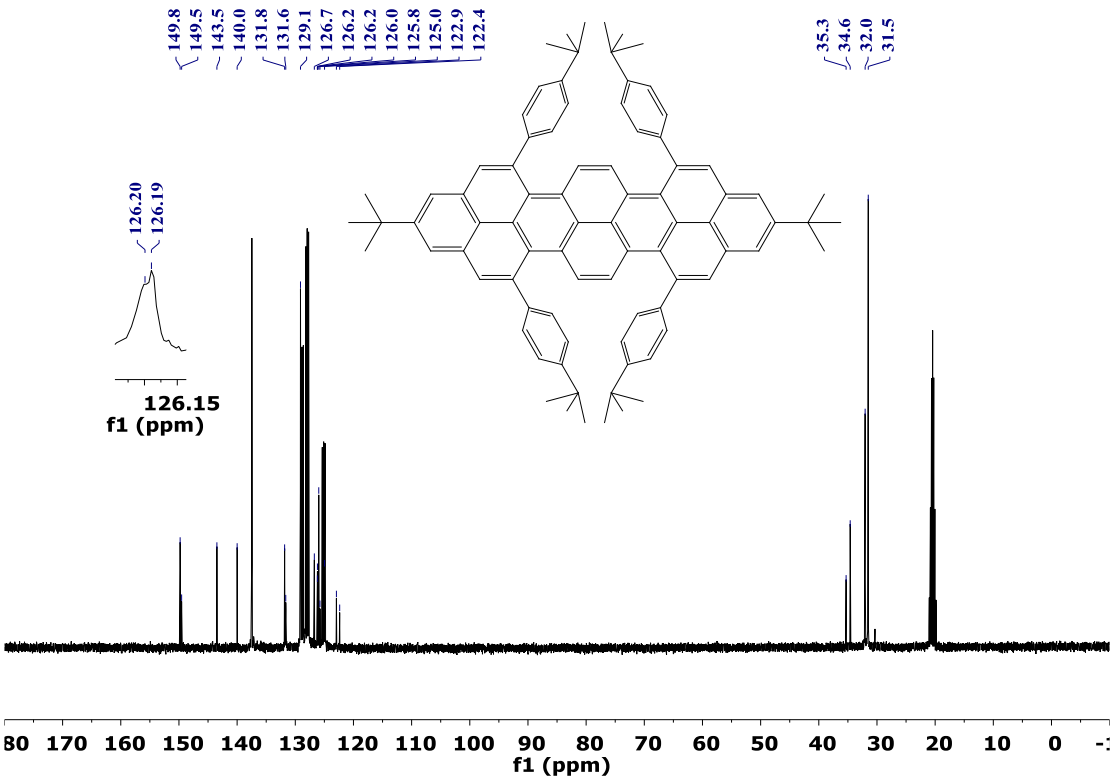


Figure S49. ^{13}C NMR spectrum for compound **4c** in toluene-d_8 at 298 K.

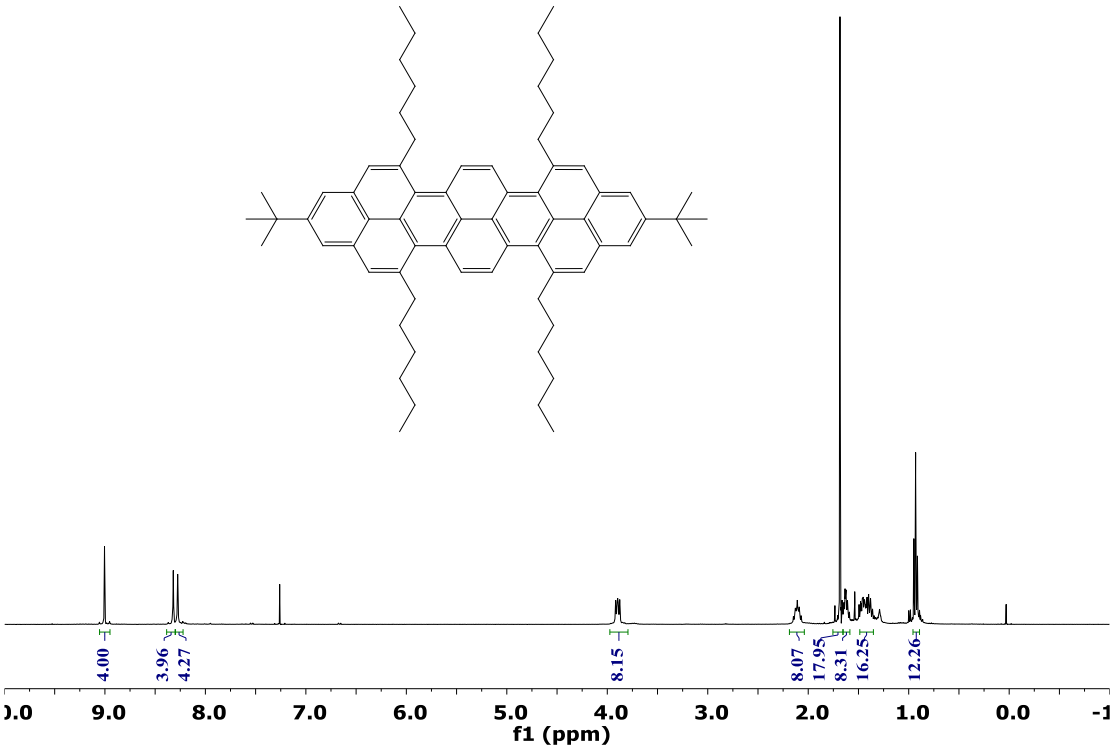


Figure S50. ^{1}H NMR spectrum for compound **4d** in $CDCl_3$ at 298 K.

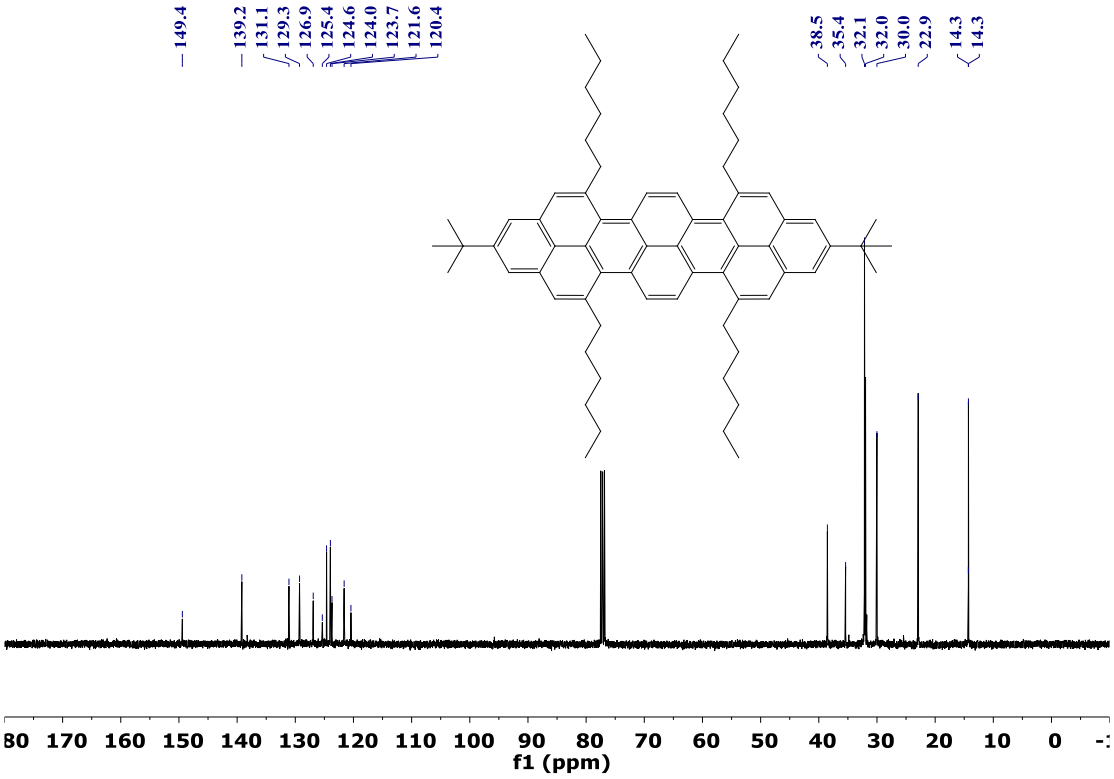


Figure S51. ^{13}C NMR spectrum for compound **4d** in $CDCl_3$ at 298 K.

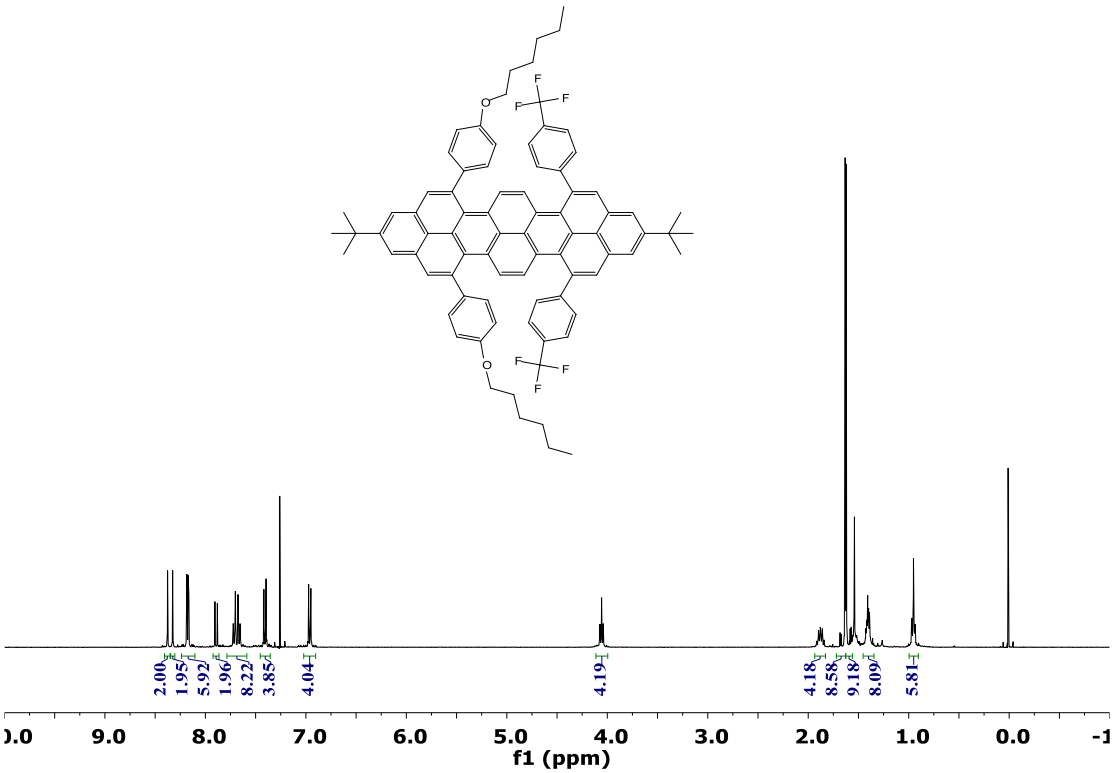


Figure S52. ^{1}H NMR spectrum for compound **4f** in $CDCl_3$ at 298 K.

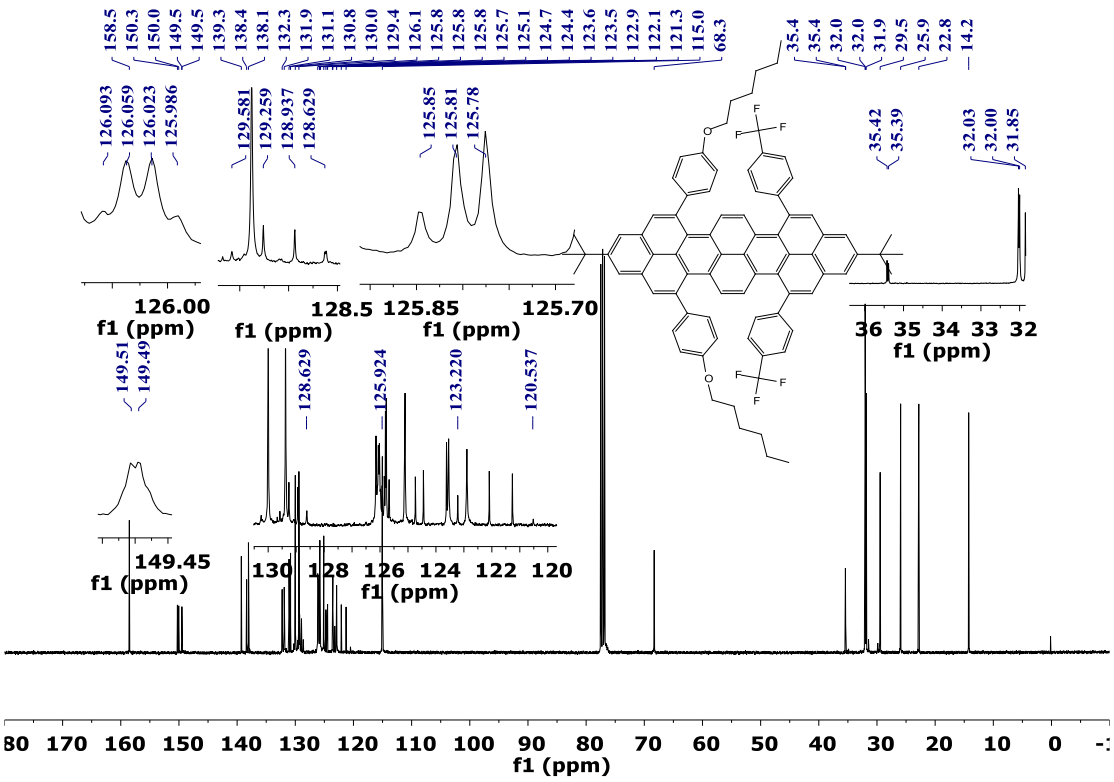


Figure S53. ^{13}C NMR spectrum for compound **4f** in $CDCl_3$ at 298 K.

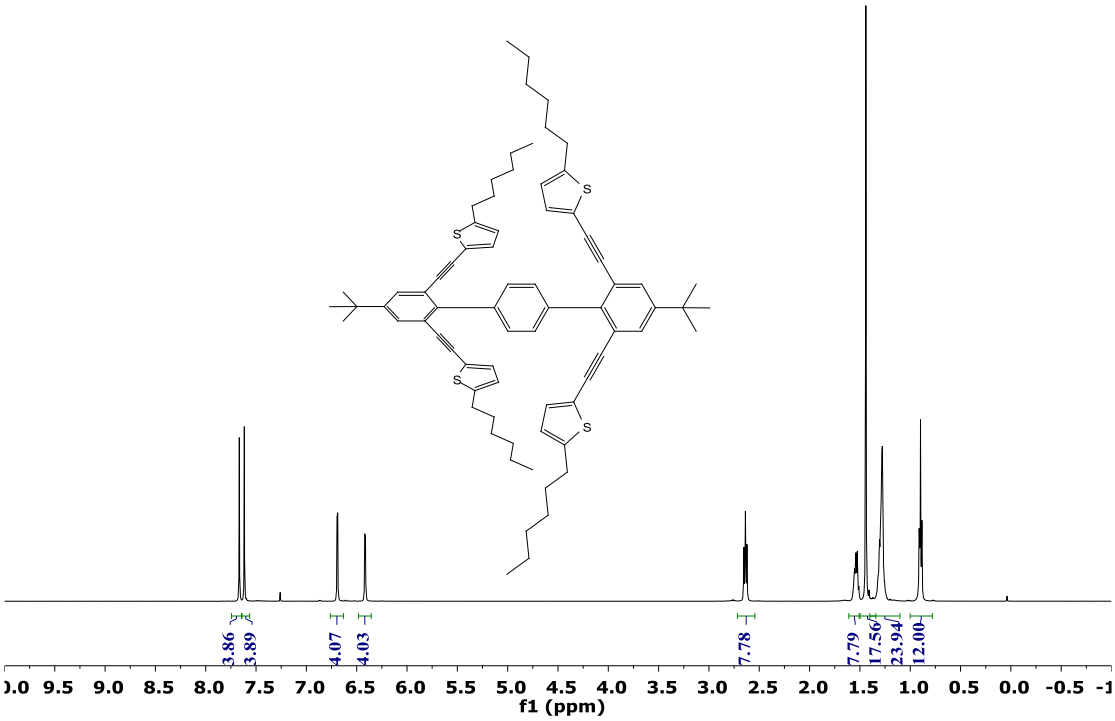


Figure S54. ^{1}H NMR spectrum for compound **5b** in $CDCl_3$ at 298 K.

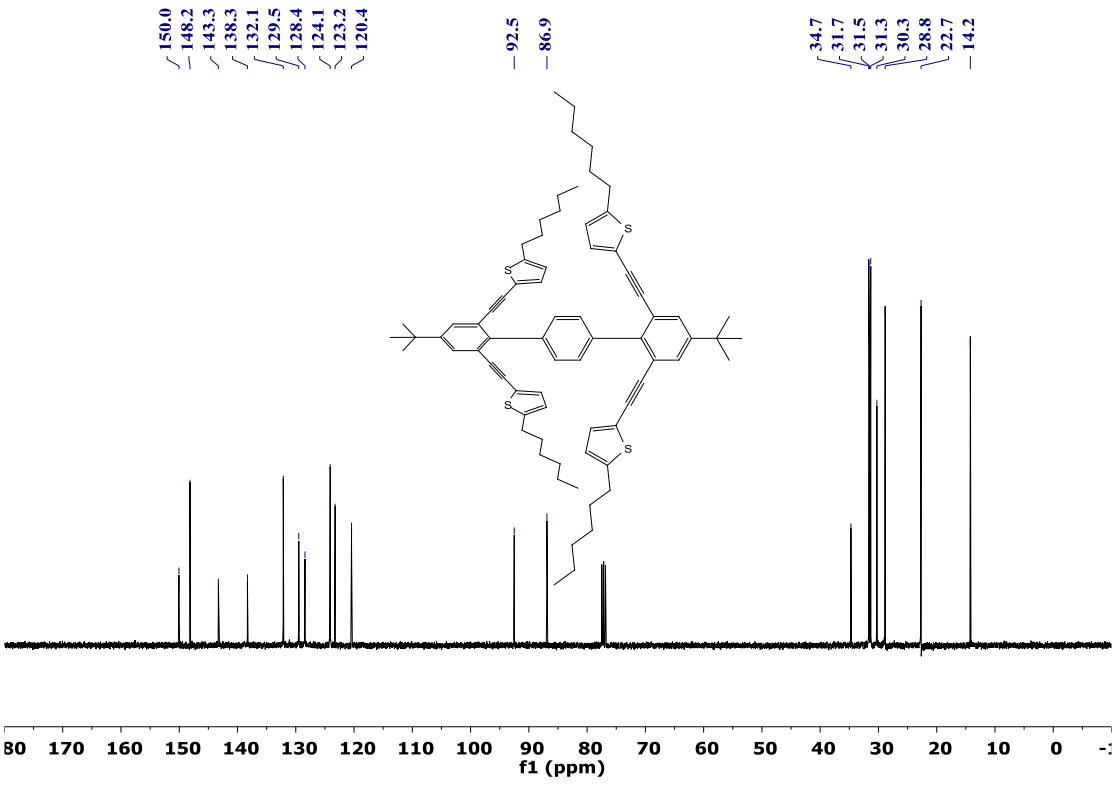


Figure S55. ^{13}C NMR spectrum for compound **5b** in $CDCl_3$ at 298 K.

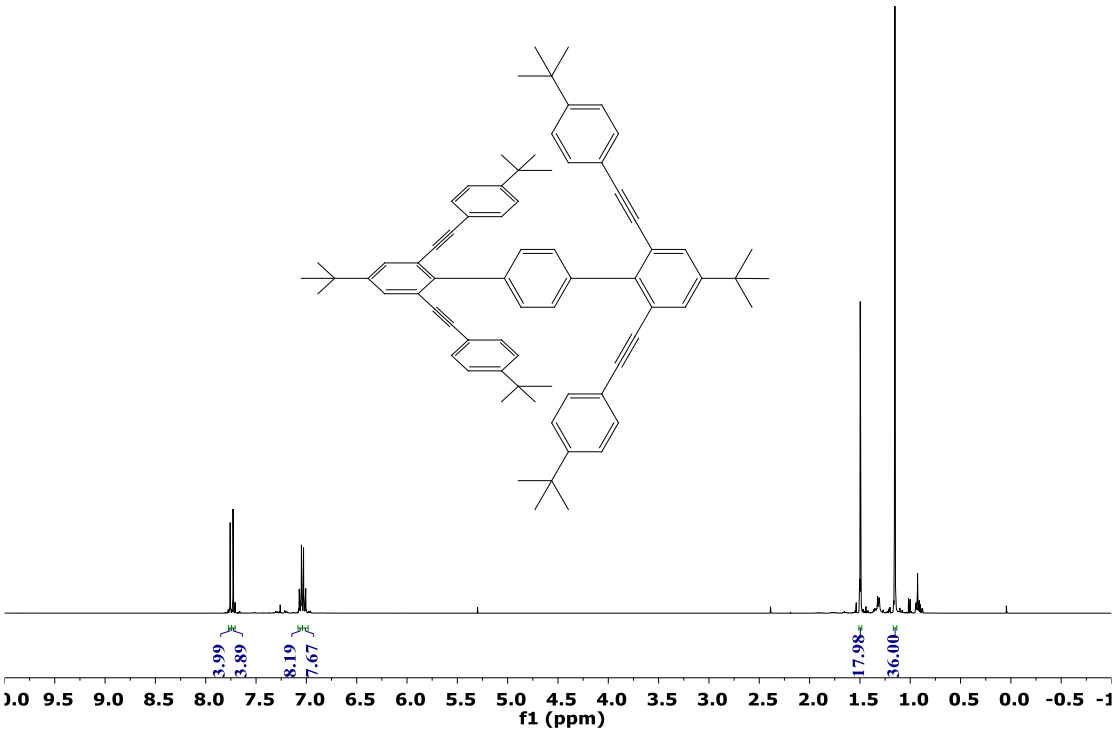


Figure S56. ^{1}H NMR spectrum for compound **5c** in $CDCl_3$ at 298 K.

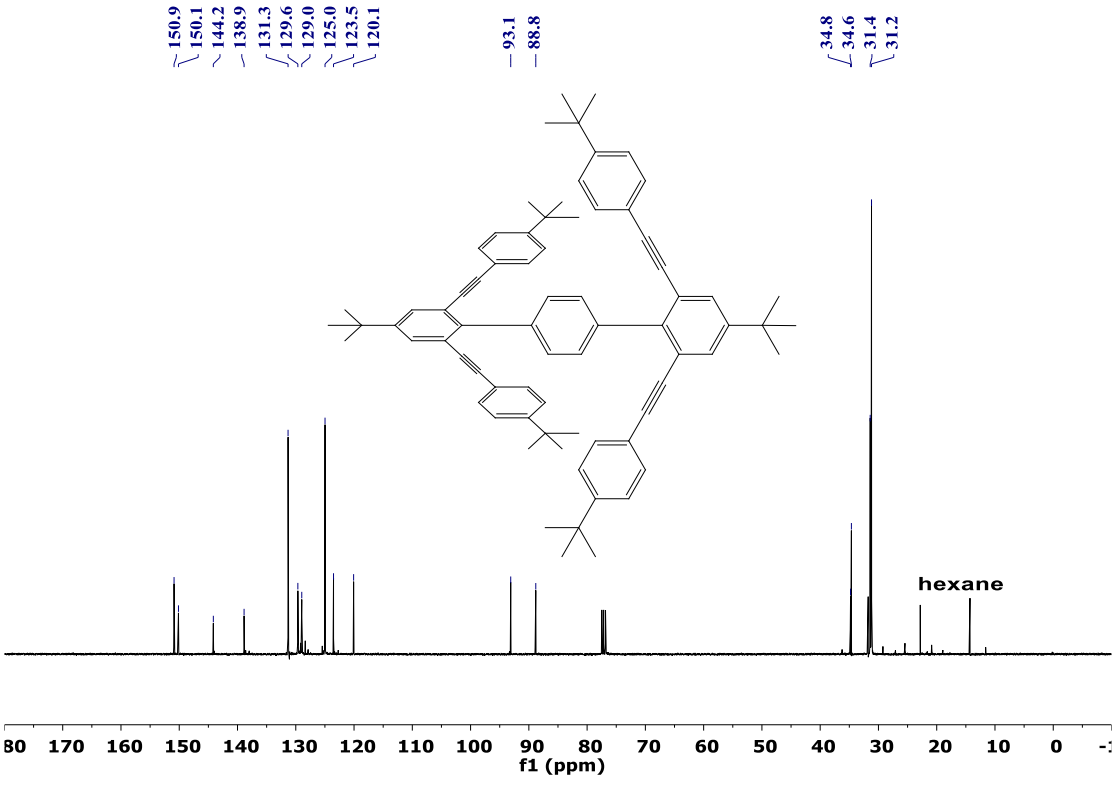


Figure S57. ^{13}C NMR spectrum for compound **5c** in $CDCl_3$ at 298 K.

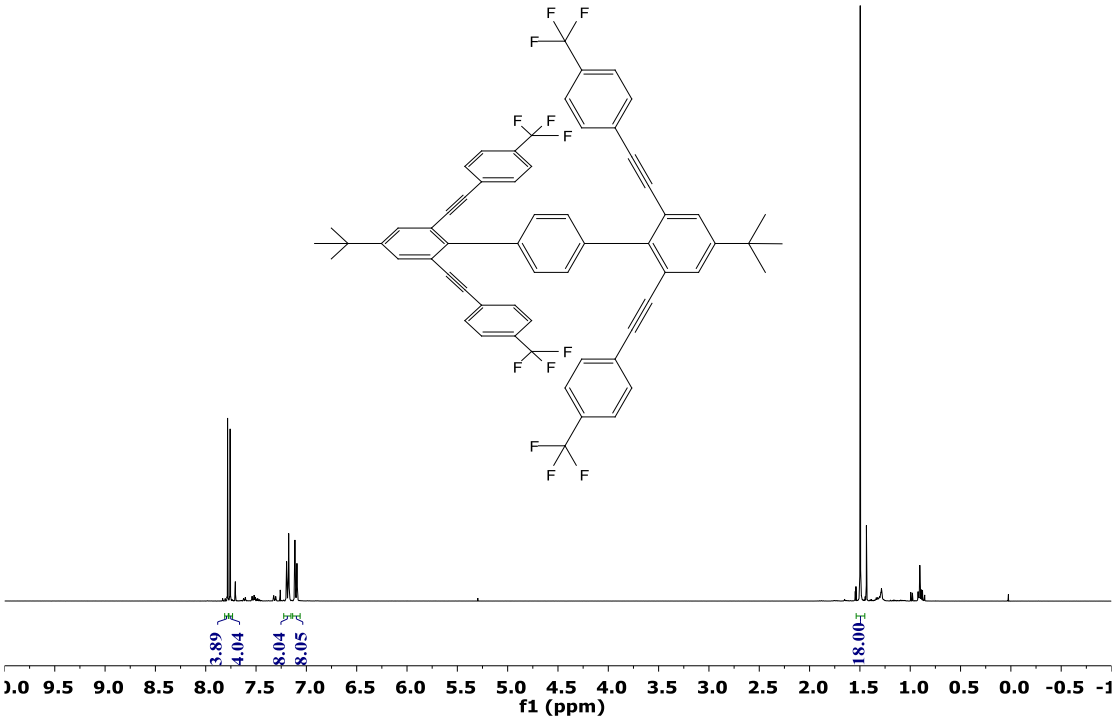


Figure S58. ^{1}H NMR spectrum for compound **5d** in $CDCl_3$ at 298 K.

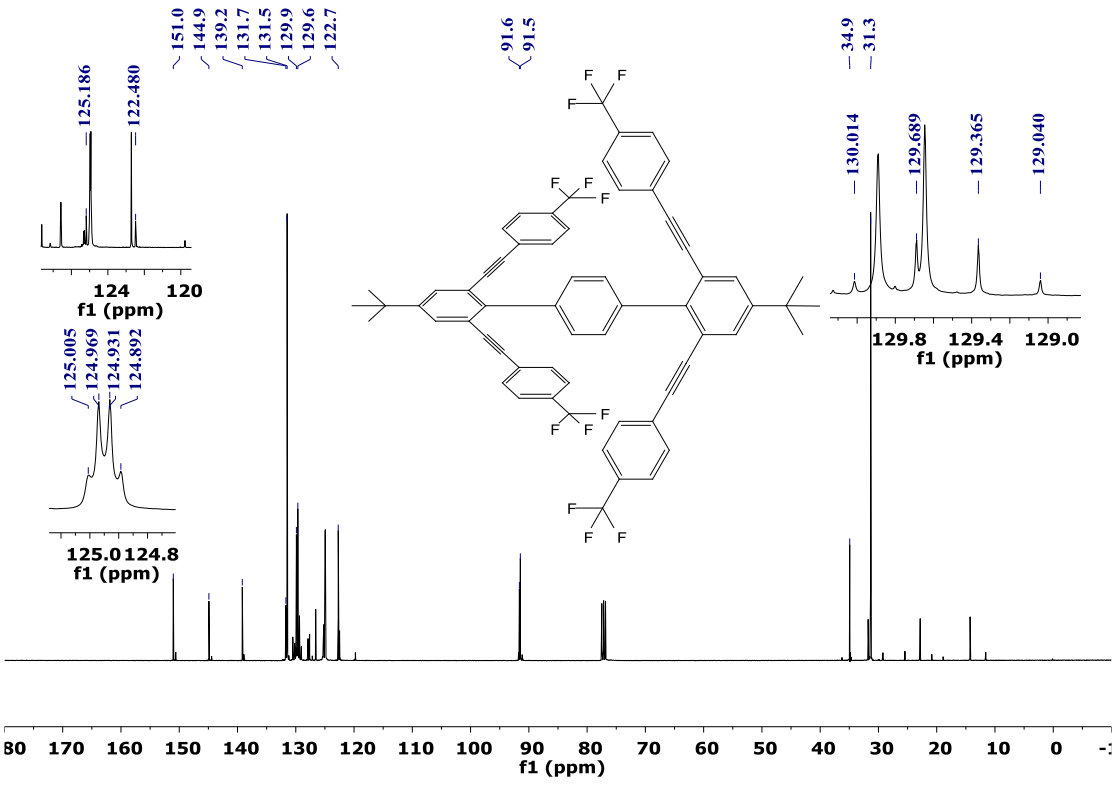


Figure S59. ^{13}C NMR spectrum for compound **5d** in $CDCl_3$ at 298 K.

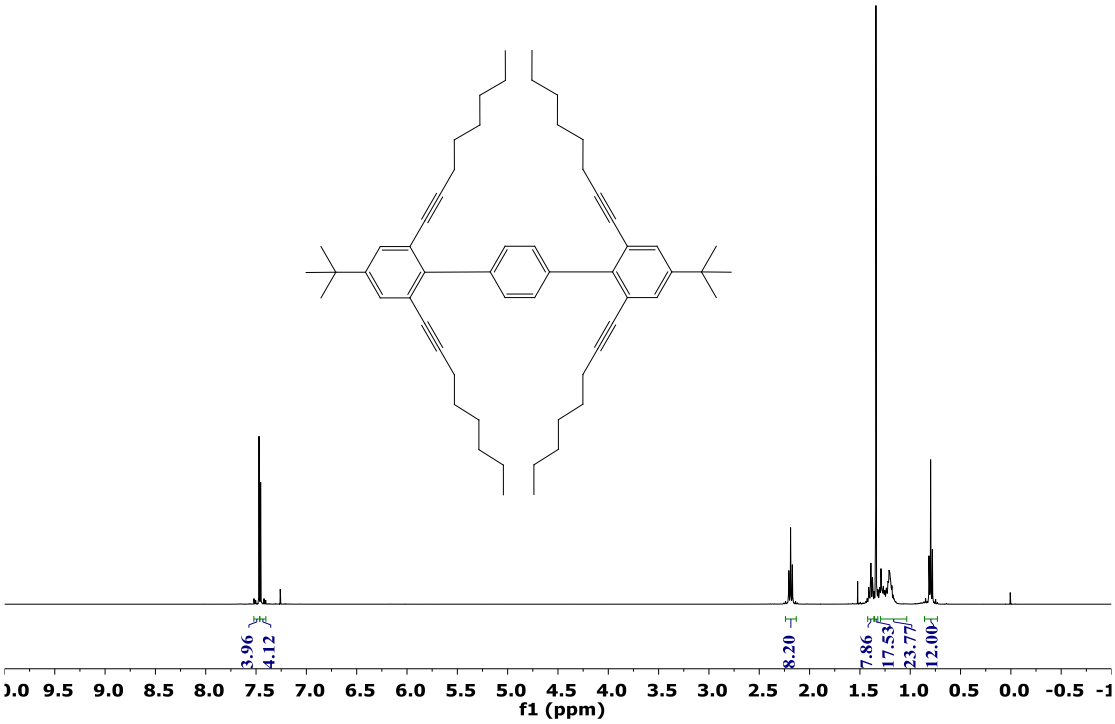


Figure S60. ^{1}H NMR spectrum for compound **5e** in $CDCl_3$ at 298 K.

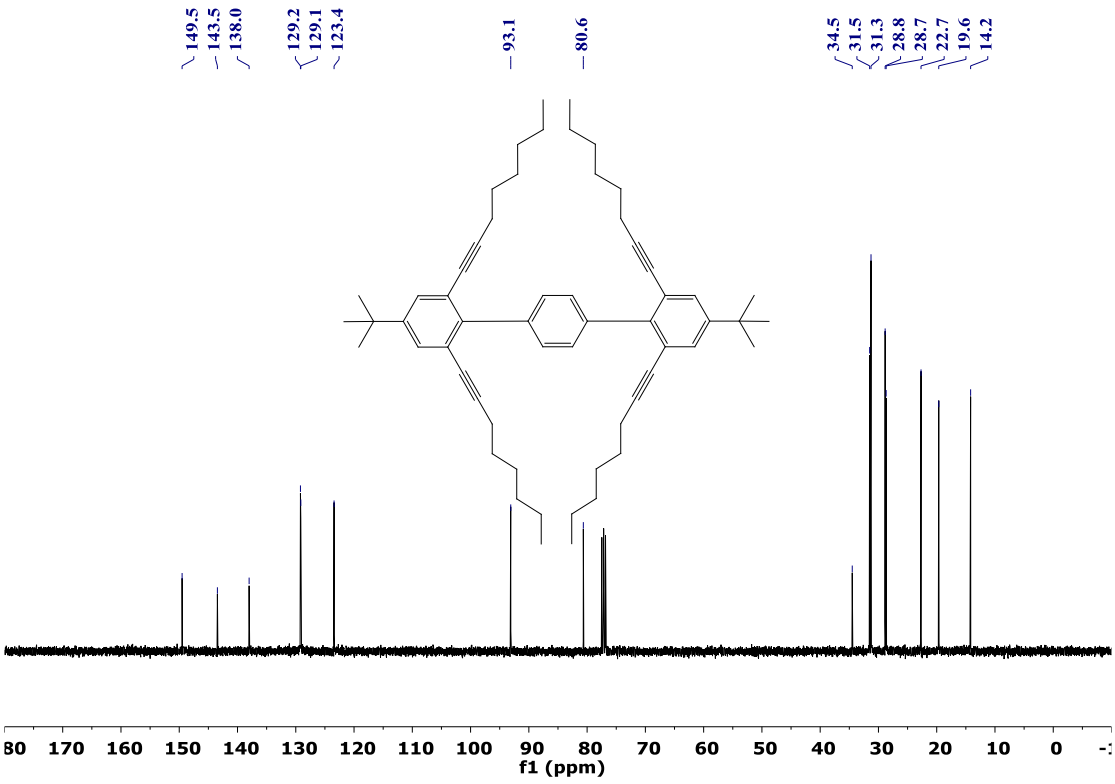


Figure S61. ^{13}C NMR spectrum for compound **5e** in $CDCl_3$ at 298 K.

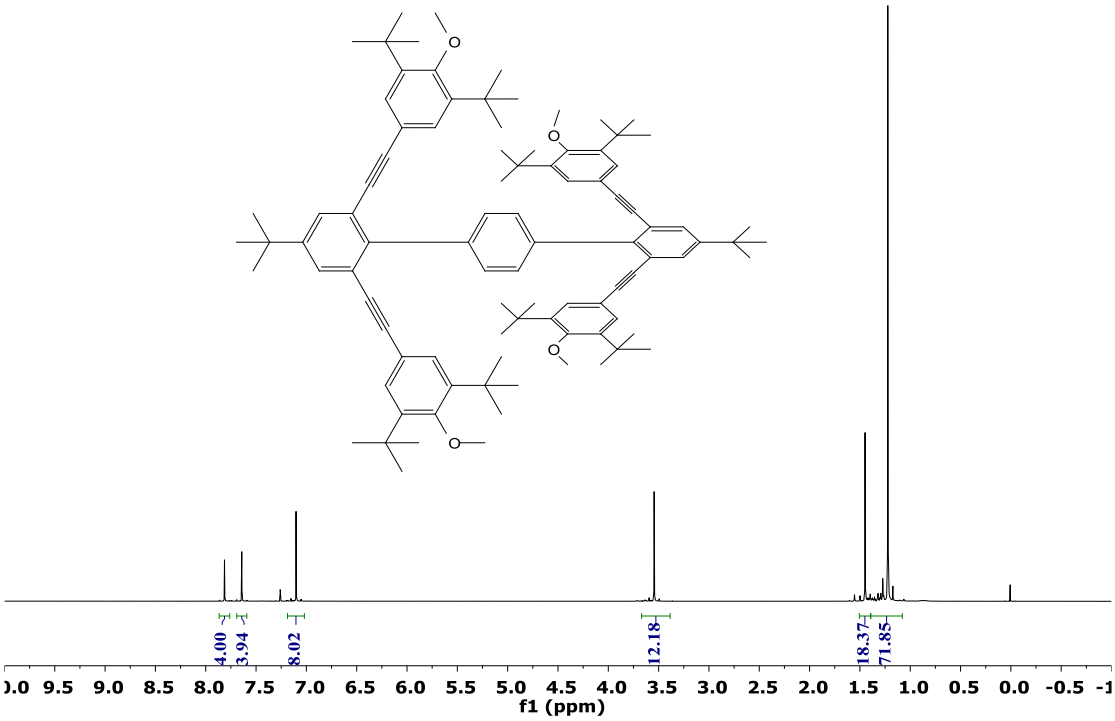


Figure S62. ^{1}H NMR spectrum for compound **5f** in $CDCl_3$ at 298 K.

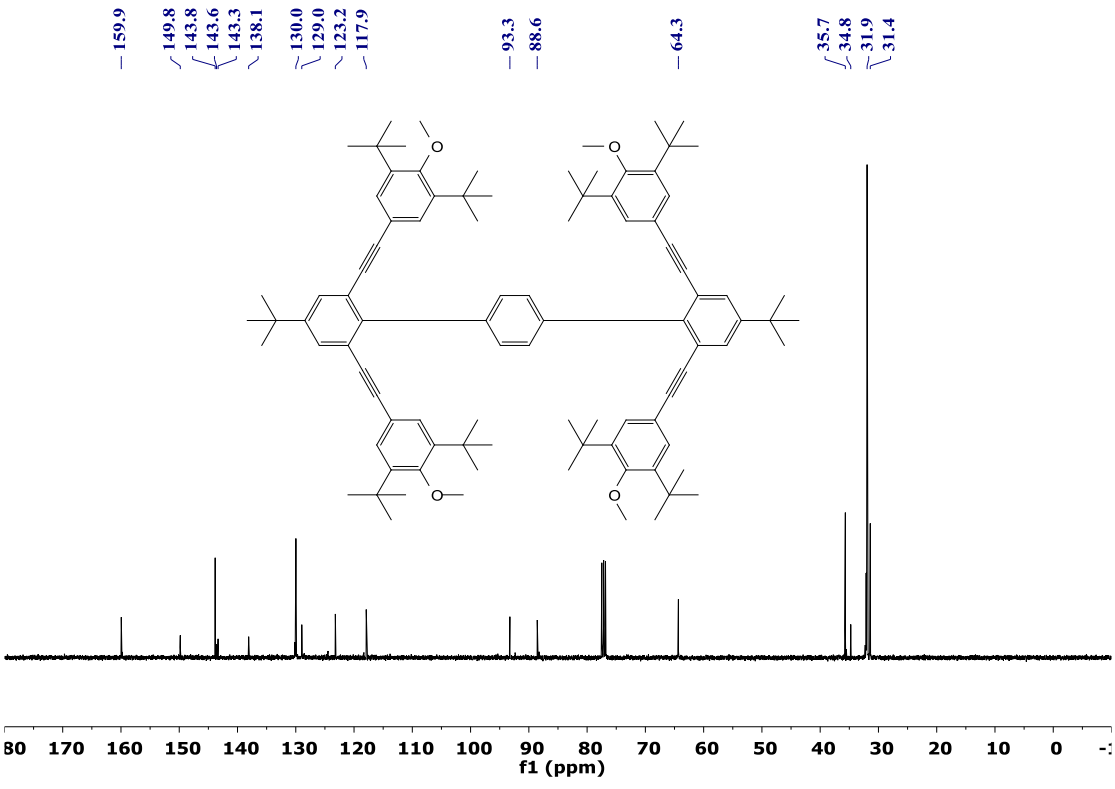


Figure S63. ^{13}C NMR spectrum for compound **5f** in $CDCl_3$ at 298 K.

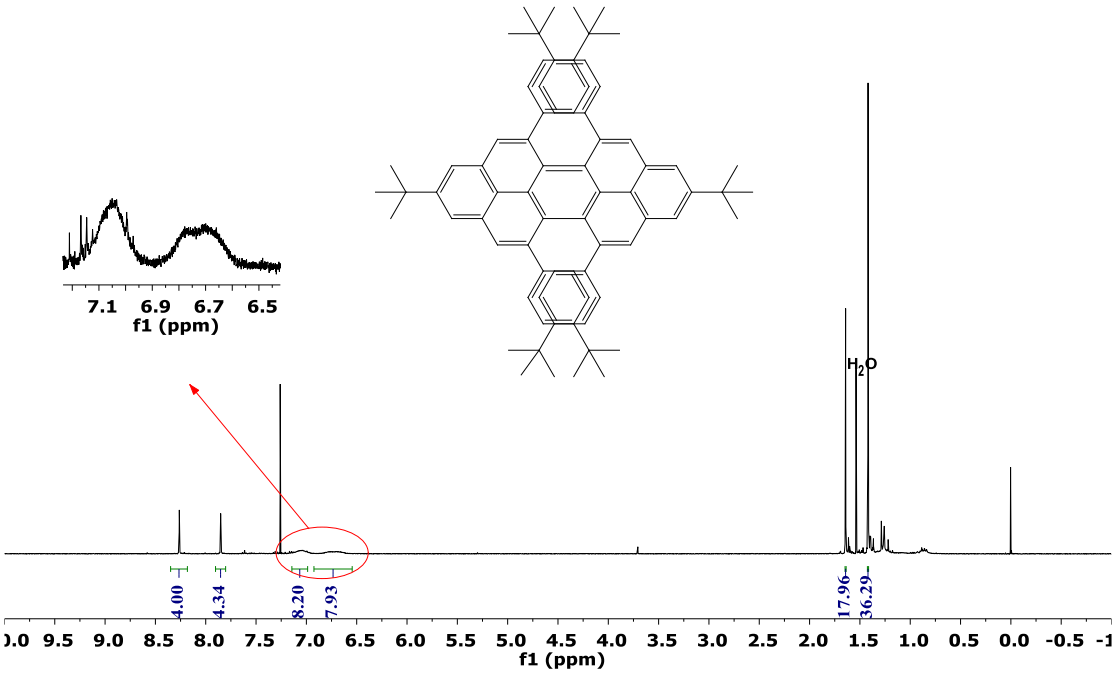


Figure S64. ^{1}H NMR spectrum for compound **6c** in $CDCl_3$ at 298 K.

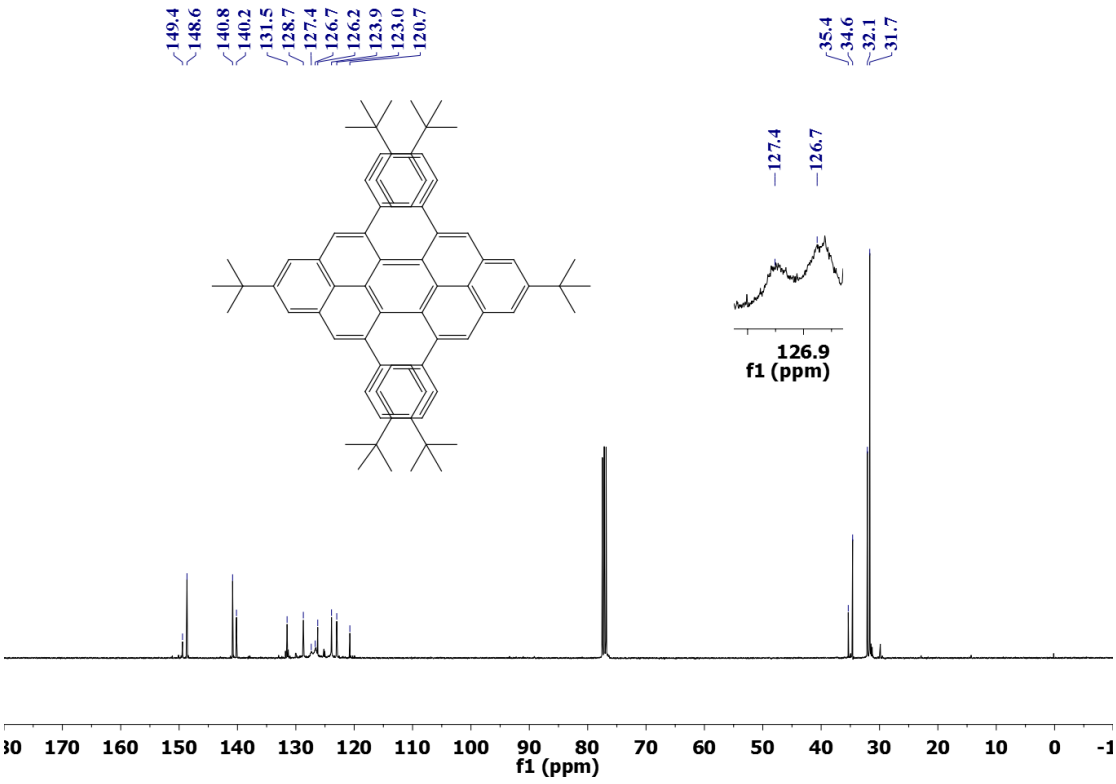


Figure S65. ^{13}C NMR spectrum for compound **6c** in $CDCl_3$ at 298 K.

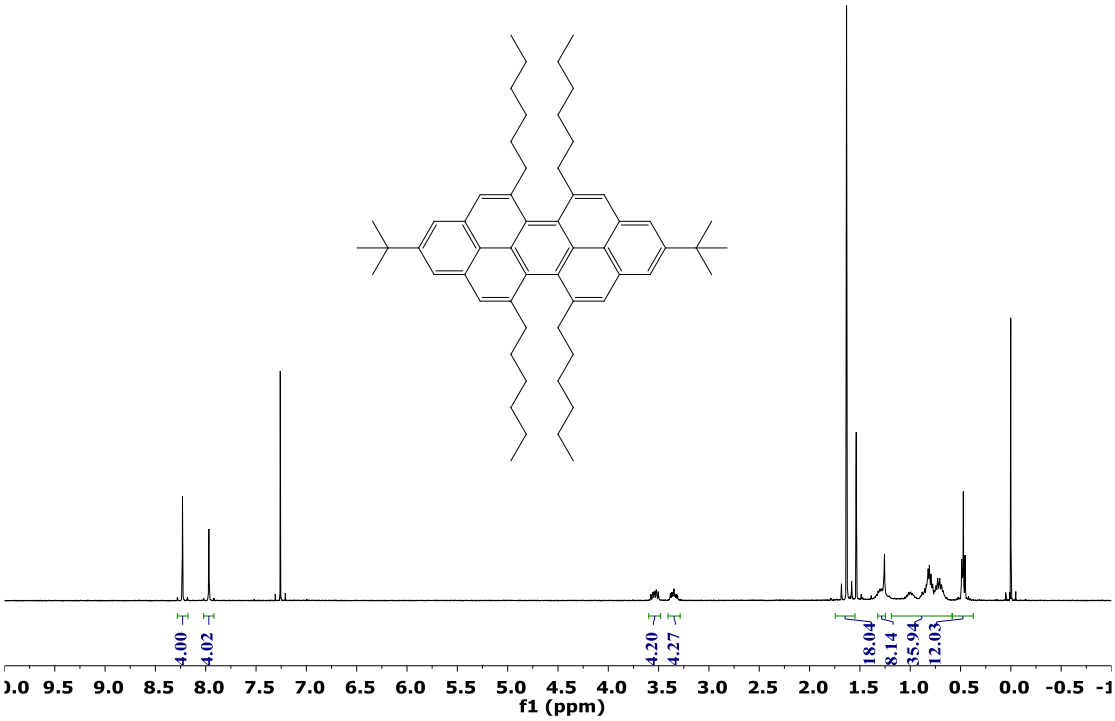


Figure S66. ^{1}H NMR spectrum for compound **6e** in $CDCl_3$ at 298 K.

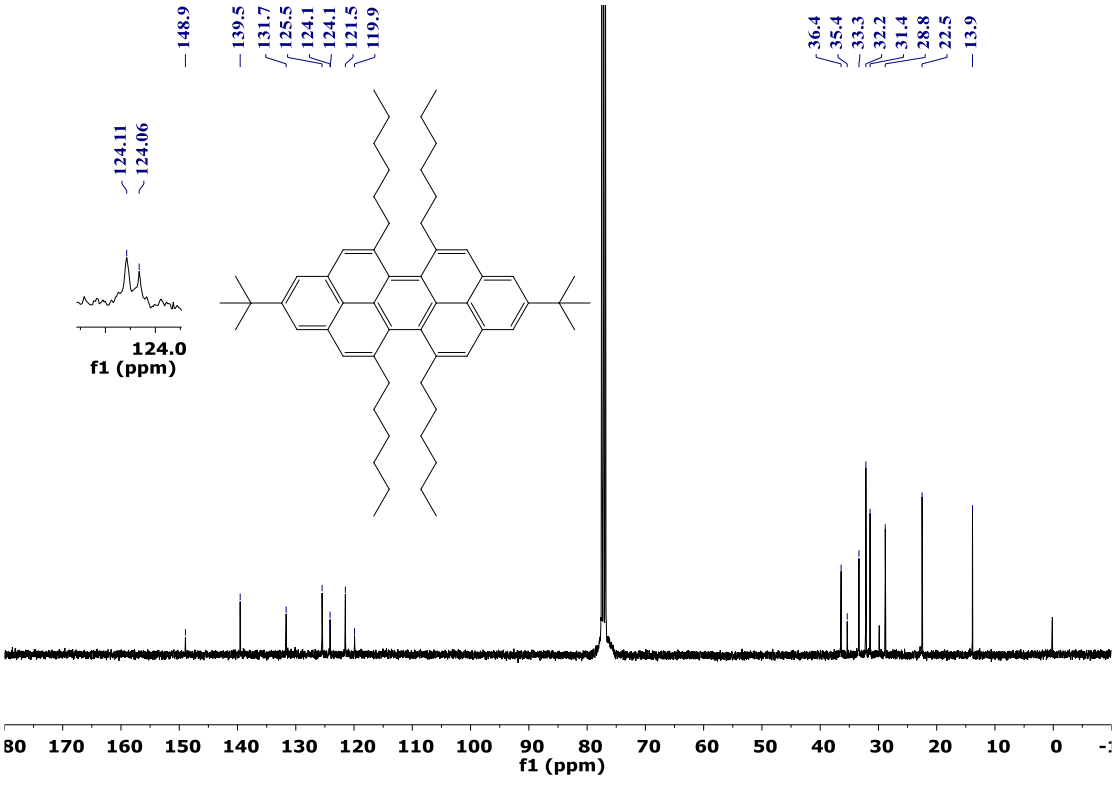


Figure S67. ^{13}C NMR spectrum for compound **6e** in $CDCl_3$ at 298 K.

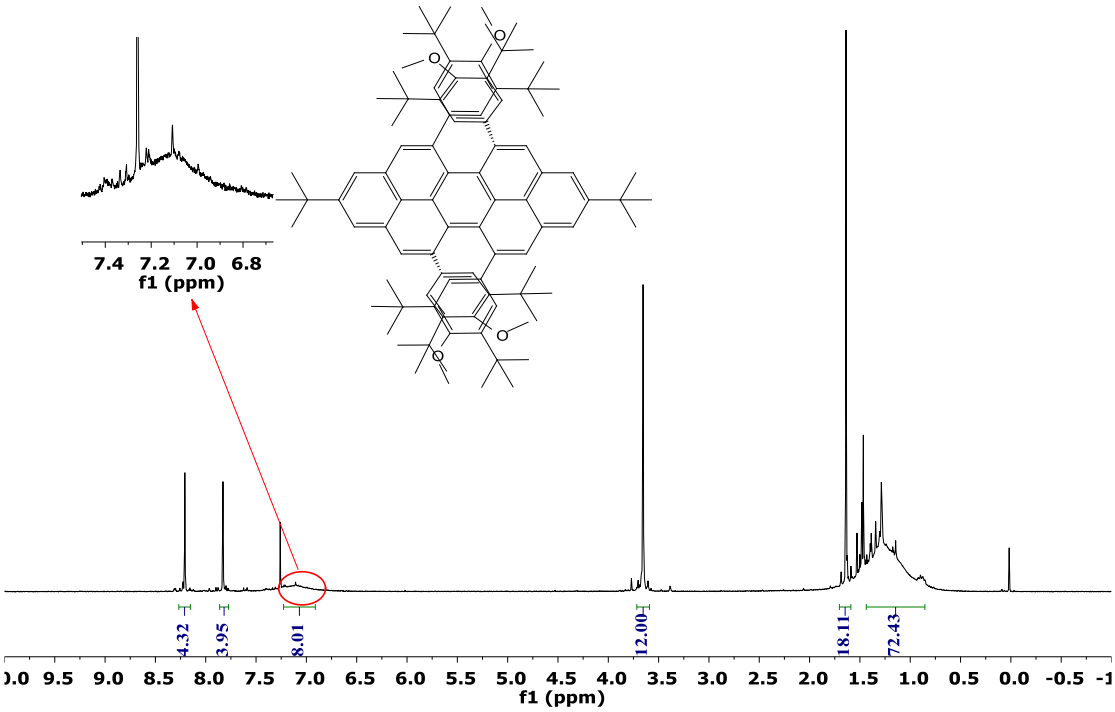


Figure S68. ^{1}H NMR spectrum for compound **6f** in $CDCl_3$ at 323 K.

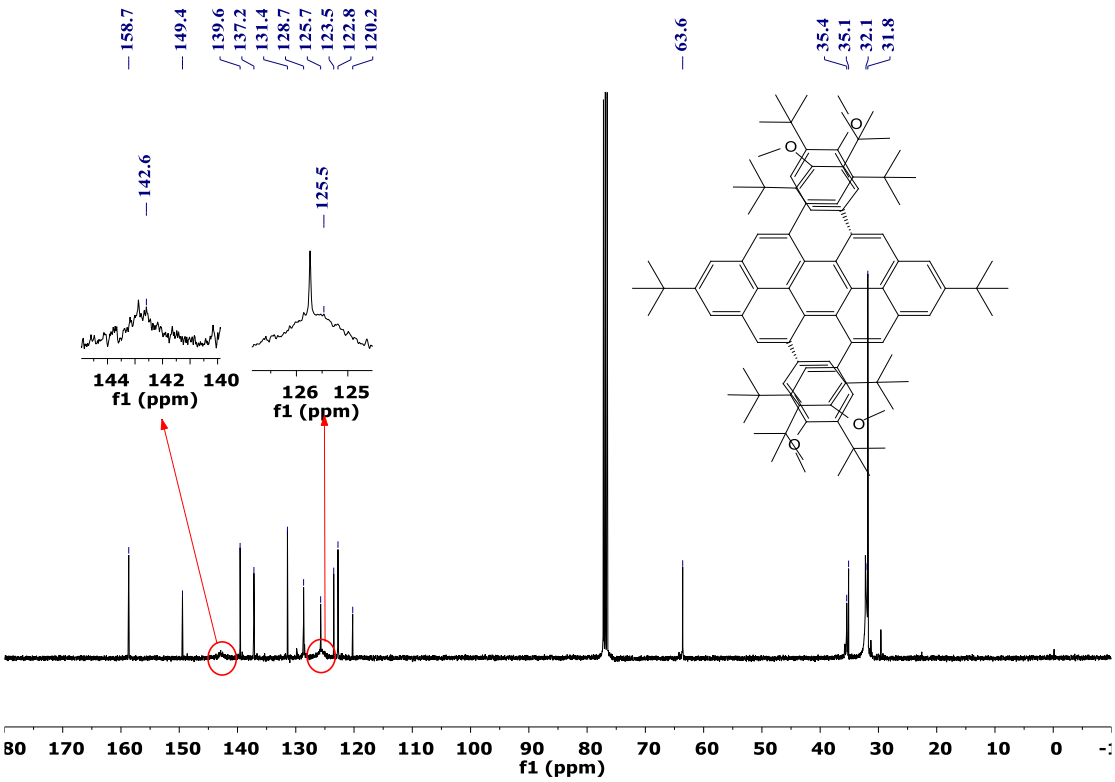


Figure S69. ^{13}C NMR spectrum for compound **6f** in $CDCl_3$ at 323 K.

8. References

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