Supplementary Information

Synthesis of electron-poor hexa-*peri*-hexabenzocoronene

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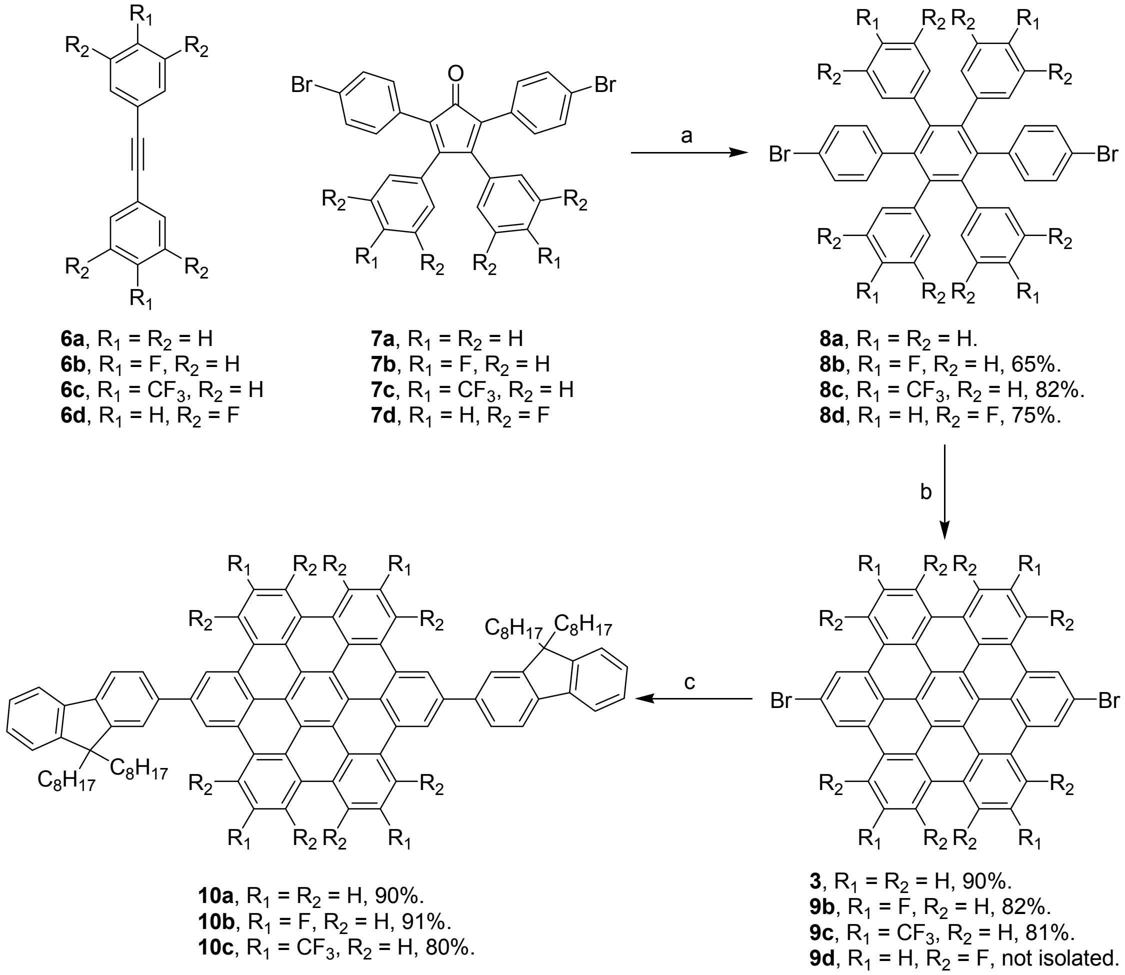
Contents

Experimental Procedures

All reactions were performed using anhydrous solvent under an inert atmosphere unless stated otherwise. Silica gel (Merck 9385 Kieselgel 60) was used for flash chromatography. Thin layer chromatography was performed on Merck Kieselgel 60 silica gel on glass (0.25 mm thick). ^{1}H and ^{13}C NMR spectroscopy were carried out using either the Varian Inova-400 (400 MHz) or the Varian Inova-500 (500 MHz). Electrospray (ESI) high resolution mass spectra (HRMS) were recorded with a Thermo-Finnigan 7T LTQ-FTMS spectrometer and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Reflex 2 (DCTB as matrix). IR spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer while UV-vis spectra were recorded using a Cary 50 UV-vis spectrometer. Photoluminescence was measured with a Varian Cary Eclipse fluorimeter. Melting points were determined on a Büchi 510 melting point apparatus. Elemental analyses were obtained commercially through Chemical & Analytical Services Pty. Ltd. (Australia) an Exeter Analytical CE–440 elemental analyzer. Thermal gravimetric analysis (TGA) experiments were carried out with a Mettler Toledo TGA/SDTA851e and differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Sapphire DSC. Electrochemical measurements were recorded on a Solartron 1287A Potentiostat/Galvanostat. Diphenylacetylene **6a** and benzil **11a** are commercially available and compounds **6b**,[1] **6c**,[1] **7a**,[2] **8a**,[2] and **12**[3] have been reported in the literature. Compound **10a** has also been reported previously by our group obtained via a different synthetic route.[4]



6a, $R_1 = R_2 = H$
6b, $R_1 = F, R_2 = H$
6c, $R_1 = CF_3, R_2 = H$
6d, $R_1 = H, R_2 = F$

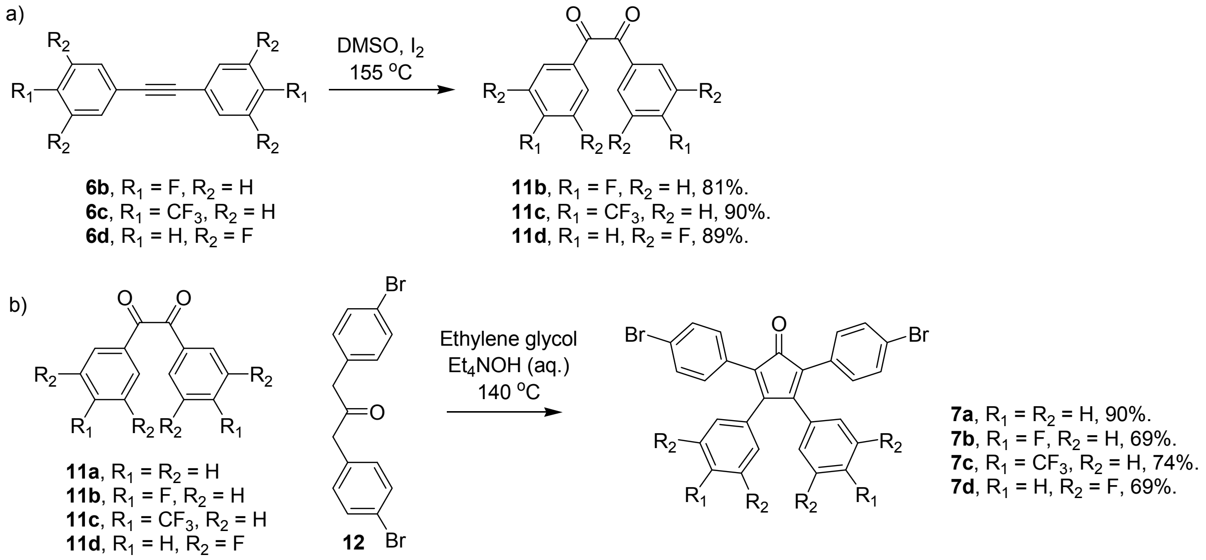
7a, $R_1 = R_2 = H$
7b, $R_1 = F, R_2 = H$
7c, $R_1 = CF_3, R_2 = H$
7d, $R_1 = H, R_2 = F$

8a, $R_1 = R_2 = H$.
8b, $R_1 = F, R_2 = H$, 65%.
8c, $R_1 = CF_3, R_2 = H$, 82%.
8d, $R_1 = H, R_2 = F$, 75%.

10a, $R_1 = R_2 = H$, 90%.
10b, $R_1 = F, R_2 = H$, 91%.
10c, $R_1 = CF_3, R_2 = H$, 80%.

3, $R_1 = R_2 = H$, 90%.
9b, $R_1 = F, R_2 = H$, 82%.
9c, $R_1 = CF_3, R_2 = H$, 81%.
9d, $R_1 = H, R_2 = F$, not isolated.

Scheme S1. Synthesis of electron-poor hexa-*peri*-hexabenzocoronenes.



6b, $R_1 = F, R_2 = H$
6c, $R_1 = CF_3, R_2 = H$
6d, $R_1 = H, R_2 = F$

11b, $R_1 = F, R_2 = H$, 81%.
11c, $R_1 = CF_3, R_2 = H$, 90%.
11d, $R_1 = H, R_2 = F$, 89%.

11a, $R_1 = R_2 = H$
11b, $R_1 = F, R_2 = H$
11c, $R_1 = CF_3, R_2 = H$
11d, $R_1 = H, R_2 = F$

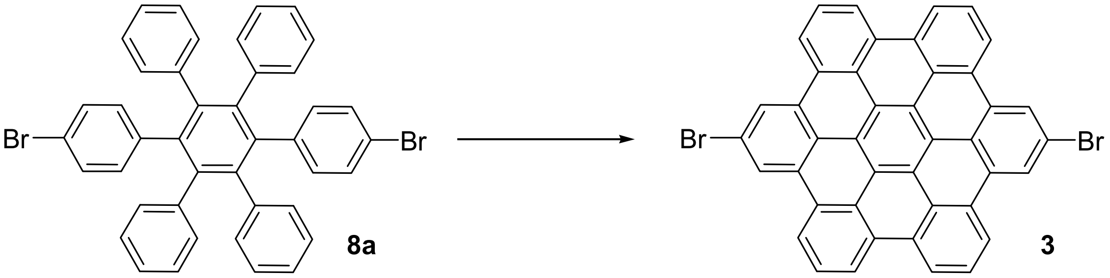
12

7a, $R_1 = R_2 = H$, 90%.
7b, $R_1 = F, R_2 = H$, 69%.
7c, $R_1 = CF_3, R_2 = H$, 74%.
7d, $R_1 = H, R_2 = F$, 69%.

Scheme S2. a) Synthesis of dione **11b-d** and b) synthesis of cyclopentadienone **7a-d**.

2,11-Dibromohexabenzo[bc,ef,hi,kl,no,qr]coronene 3

Intramolecular oxidative cyclodehydrogenation of 4-bromo-4'-(4-bromophenyl)-3',5',6'-triphenyl-1,1':2',1''-terphenyl ***8a*** *under various conditions*



Method	Oxidant (6 eq.)	Acid (6 eq.)	Solvent (30 mL)	Yield %
A	$FeCl_3$	-	CH_2Cl_2(25 mL)/$MeNO_2$(5 mL)	3
B	$FeCl_3$	CF_3SO_3H	CH_2Cl_2 (25 mL)/$MeNO_2$(5 mL)	49
C	DDQ	CF_3COOH	CH_2Cl_2 (30 mL)	0
D	DDQ	CH_3SO_3H	CH_2Cl_2 (30 mL)	0
E	DDQ	CF_3SO_3H	CH_2Cl_2 (30 mL)	94

General procedure for Method A and B

To oven dried 100 mL round bottom flask cooled under nitrogen was added 4-bromo-4'-(4-bromophenyl)-3',5',6'-triphenyl-1,1':2',1''-terphenyl **8a** (250 mg, 0.36 mmol) and dry CH_2Cl_2 (25 mL). $FeCl_3$ (352 mg, 2.16 mmol) dissolved in dry nitromethane (5 mL) was added drop-wise to the stirring mixture under nitrogen flow and allowed to stir for 2 hr. For method B, CF_3SO_3H (0.2 mL, 2.16 mmol) was added after the addition of $FeCl_3$. For method A the reaction mixture was poured into methanol and the precipitate were filtered and washed with methanol. For method B the reaction was quenched with saturated potassium carbonate solution and the solvent was removed under reduced pressure. The solids were filtered and washed with HCl (10% aq.) followed by methanol to give the crude solid. Soluble starting material and by-products were removed by washing with chloroform.

General procedure for Method C, D & E

To oven dried 100 ml round bottom flask cooled under nitrogen was added 4-bromo-4'-(4-bromophenyl)-3',5',6'-triphenyl-1,1':2',1''-terphenyl **8a** (250 mg, 0.36 mmol), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 492 mg, 2.16 mmol) and dry CH_2Cl_2 (30 mL). Acid (2.16 mmol) was added to the reaction mixture and allowed to stir for 2 hr under nitrogen atmosphere. The reaction mixture was quenched with saturated potassium carbonate solution and CH_2Cl_2 was removed under reduced pressure. The solids were filtered and washed with water followed by methanol to give the crude solid. Soluble starting material and byproducts were removed by washing with chloroform.

*Procedure for HBC **3** in multi-gram scale*

To a slurry of 4-bromo-4'-(4-bromophenyl)-3',5',6'-triphenyl-1,1':2',1''-terphenyl **8a** (15.0 g, 21.66 mmol) and DDQ (28.6 g, 130 mmol) in CH_2Cl_2 (750 mL) under nitrogen at 0 °C was added CF_3SO_3H (11.4 mL, 19.5 g, 130 mmol). The dark slurry was stirred for 3 hours then the reaction mixture poured into saturated K_2CO_3 solution. The CH_2Cl_2 was removed under vacuum. The yellow insoluble product was collected by gravity filtration. The product was washed with H_2O, MeOH until the wash was colourless then CH_2Cl_2 and dried under air, then vacuum to give a crude product. Yield 13.14 g (91.3%). The solubility of the product was too low for NMR spectroscopy.

DSC: T_m = 393 °C. FT-IR (neat, cm^{-1}): 1575, 1354, 1022, 844, 813. MALDI-MS (*m/z*): M^+ 680.0. Elemental analysis: calcd. for $C_{42}H_{16}Br_2$, C 74.14, H 2.37, Br 23.49; found, C 63.79, H 2.09. There is a large discrepency between the calculated and measured elemental composition which may be a result of incomplete material combustion in the experiment.

2,5-Bis(9,9-dioctyl-9H-fluoren-2-yl)hexabenzo[bc,ef,hi,kl,no,qr]coronene 10a

Dibromo-HBC **3** (4.59 g, 7.29 mmol) and 9,9-dioctylfluorene-2-boronic acid pinacol ester (7.53 g, 14.57 mmol) was dispersed in toluene (100 mL) and thoroughly degassed by bubbling with nitrogen gas. Degassed solution of Et_4NOH (20 mL, 1 M) and tetrakis(triphenylphosphine)palladium(0) (840 mg, 0.729 mmol) was added and the reaction was heated at 90 °C for 14 h under N_2. The reaction was cooled, filtered through celite and the product extracted with toluene (100 mL). The toluene solution was dried with $MgSO_4$ and filtered through a plug of silica. The volume of the resulting yellow solution was reduced under vacuum and the product was precipitated with MeOH. A yellow solid (8.47 g, 89% yield) was obtained after filtration and drying under vacuum.

TGA, T_{decomp} (5% mass loss) = 409 °C. DSC, T_g = 125 °C. UV-vis: λ_{max} chloroform solution (ε, $M^{-1}cm^{-1}$) = 365 nm (1.8×10^5). ^{1}H NMR (500 MHz, 6.25 mM, $CDCl_3$, 20 °C, δ): 0.82 (t, *J* = 7 Hz, 12H, $-CH_3$), 1.01 (br, 4H, $-CH_2-$), 1.15 (br, 4H, $-CH_2-$), 1.24 (br, 40H, $-CH_2-$), 2.40 (m, 8H, $-CH_2-$), 7.31 (t, *J* = 7 Hz, 2H, HBC-H), 7.42 (t, *J* = 7 Hz, 2H, HBC-H), 7.55 (m, 6H, fluorene-H), 7.76 (d, *J* = 7 Hz, 2H, fluorene-H), 7.94 (m, 8H, fluorene-H and HBC-H), 8.06 (d, *J* = 8 Hz, 4H, HBC-H), 8.12 (d, *J* = 8 Hz, 2H, HBC-H), 8.15 (s, 2H, HBC-H), 8.31 (s, 2H, HBC-H). ^{13}C NMR (125 MHz, 75 mM, $CDCl_3$, 20 °C, δ): 151.4, 151.1, 141.2, 140.6, 140.3, 136.3, 128.3 (2), 128.2, 128.1, 126.5, 124.4, 123.1, 122.8, 122.0, 121.4, 120.2, 120.0 (3), 119.8 (2), 118.4, 118.1, 118.0, 117.6, 55.4, 40.9, 31.9, 30.4, 29.6, 29.5, 24.4, 22.7, 14.2. FT-IR (neat, cm^{-1}): 3059, 2953, 2924, 2851, 1610, 1584, 1455, 1373, 1366, 1083, 1022, 866, 826, 781, 740, 684. MS-MALDI (*m/z*): M$^+$ 1298.68. Elemental analysis: calcd. for $C_{100}H_{98}$, C 92.4, H 7.6; found C 92.4, H 7.6. The characterization data is identical to a previous report for compound **10a** obtained via a different synthetic route.[4]

1,2-Bis(4-fluorophenyl)ethane-1,2-dione 11b

1,2-Bis(4-fluorophenyl)acetylene **6b** (2.14 g, 10 mmol) and iodine (1.3 g, 5 mmol) were dissolved in DMSO (10 mL). The reaction was heated to 155 °C for 14 h under N_2 and cooled to room temperature. The reaction was poured into an aqueous solution of sodium thiosulfate (50 mL, 1 M) and the resulting precipitated was collected and washed with water (100 mL). The solid was dissolved in dichloromethane (50 mL) and washed with water (50 mL). The crude product was purified by column chromatography (SiO_2, dichloromethane/petroleum spirits 40-60 °C 1:1, $R_f = 0.3$) and a yellow crystalline solid (2 g, 81% yield) was obtained.

m.p. 122 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 7.18-7.21 (td, 4H, Ar), 8.01-8.04 (td, 4H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 116.3, 116.6, 129.4, 132.8, 132.9, 165.0, 168.8, 192.2. FT-IR (neat, cm^{-1}): 1665 (C=O), 1598, 1506, 1228, 1156, 886, 843. HRMS-ESI (*m/z*), calcd. for $C_{14}H_8F_2O_2$: M+Ag$^+$ 352.95378, found 352.95380. The characterization data is identical to a previous report for compound **11b** obtained via a different synthetic route.[5]

Cyclopentadienone 7b

1,2-Bis(4-fluorophenyl)ethane-1,2-dione **11b** (0.5 g, 2 mmol), diphenylacetone **12** (0.75 g, 2 mmol) and ethylene glycol (2 mL) were placed in a Schlenk tube (25 mL). The mixture was heated to 140 °C and Et_4NOH (0.1 mL, 1 M aq.) was added. The reaction was stirred at 140 °C for 1 h and allowed to cool to room temperature. Methanol (10 mL) was added and the resulting precipitate was collected and washed with methanol (50 mL). A purple solid (0.8 g, 69% yield) was obtained after drying under vacuum.

DSC: T_m = 286 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 6.89 (td, 4H, Ar), 6.94 (td, 4H, Ar), 7.07 (d, *J* 7 Hz, 4H, Ar), 7.39 (d, *J* 7 Hz, 4H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ):

115.59, 115.76, 122.24, 124.61, 128.30, 128.32, 129.13, 131.17, 131.48, 131.55, 131.61, 153.47, 161.87, 163.86, 199.01. FT-IR (neat, cm^{-1}): 1712 (C=O), 1601, 1505, 1487, 1235, 1159, 1072, 1010, 850, 761. HRMS-ESI (*m/z*), calcd. for $C_{29}H_{16}Br_2F_2O$: M+Ag$^+$ 684.85609, found 684.85657.

Hexaphenylbenzene 8b

Cyclopentadienone **7b** (0.578 g, 1 mmol) and 1,2-bis(4-fluorophenyl)acetylene **6b** (0.214 g, 1 mmol) and diphenyl ether (0.5 mL) were placed in a Schlenk tube (10 mL). The reaction was heated to 250 °C for 2 h or until the purple colour of the cyclopentadienone disappeared. The reaction was cooled to room temperature and the solid was dispersed in methanol (10 mL). A colourless crystalline solid (0.5 g, 65% yield) was obtained after filtration and drying under vacuum.

DSC: T_m = 282 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 6.61 (d, *J* 8.5 Hz, 4H, Ar), 6.65 (td, 8H, Ar), 6.72 (td, 8H, Ar), 7.04 (d, *J* 8.5 Hz, 4H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 110.00, 114.11, 114.27, 119.96, 130.24, 132.46, 132.53, 132.63, 135.67, 138.92, 139.79, 159.84, 161.80. FT-IR (neat, cm^{-1}): 1510, 1222, 1161, 1013, 815, 758. HRMS-ESI (*m/z*), calcd. for $C_{42}H_{24}Br_2F_4$: M+Ag$^+$ 870.92059, found 870.92133.

HBC 9b

Hexaphenylbenzene **8b** (1 g, 1.3 mmol) was dissolved in dichloromethane (100 mL) and cooled to 0 °C. DDQ (2 g, 8.8 mmol) was added followed by trifluoromethanesulfonic acid (2.7 g, 18 mmol). The reaction was stirred at 25 °C for 14 h under N_2 and was then quenched by the addition of methanol (200 mL). The resulting precipitate was collected by filtration and washed with methanol (100 mL). A yellow solid (0.8 g, 82% yield) was obtained after drying under vacuum. The solubility of the product was too low in common organic solvents. As a result, NMR spectrum was not recorded.

DSC: no thermal transitions detected up to 500 °C. FT-IR (neat, cm^{-1}): 1608, 1583, 1416, 1369, 1158, 1009, 920, 852. MALDI-TOF MS (*m/z*): M$^+$ 752.0. Elemental analysis: calcd. for $C_{42}H_{12}Br_2F_4$, C 67.05, H 1.61; found C 67.09, H 1.76.

Fluorenyl HBC 10b

HBC **9b** (150 mg, 0.2 mmol) and 9,9-dioctylfluorene-2-boronic acid pinacol ester (250 mg, 0.5 mmol) was dissolved in toluene (20 mL) and thoroughly degassed by bubbling with nitrogen gas. Degassed solution of Et_4NOH (5 mL, 1 M aq.) and tetrakis-(triphenylphosphine)palladium(0) (12 mg, 5 mol%) was added and the reaction was heated at 90 °C for 14 h under N_2. The reaction was cooled and the product extracted with toluene (20 mL). The toluene solution was dried with $MgSO_4$ and filtered through a plug of silica. The volume of the resulting yellow solution was reduced under vacuum and the product was precipitated with MeOH. A yellow solid (250 mg, 91% yield) was obtained after filtration and drying under vacuum.

TGA, T_{decomp} (5% mass loss) = 404 °C. DSC, No thermal transitions in the measured temperature range (25 °C – 350 °C). UV-vis: λ_{max} chloroform solution (ε, $M^{-1}cm^{-1}$) = 364 nm (9.4×10^4). ^1H NMR (500 MHz, $CDCl_3$, 60 mM, 20 °C, δ): 0.71 (br, 20H, $-CH_2-$ and CH_3), 0.9-1.2 (br m, 40H, $-CH_2-$), 1.95 (m, 8H, $-CH_2-$), 5.83-7.08 (br, ArH), 7.33 (br, ArH), 7.55 (br, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, 60 mM, 20 °C, δ): 14.03, 22.52, 23.87, 23.90, 23.92, 29.01, 29.09, 29.70, 29.71, 29.79, 31.64, 39.92, 55.16, 105.92 (br), 114.25 (br), 118.23 (br), 119.80 (br), 120.68 (br), 122.96 (br), 126.07 (br), 128.93 (br), 138.60 (br), 140.53 (br), 151.08 (br), 151.65 (br), 158.05 (br), 160.24 (br). Both ^1H and ^{13}C NMR showed broadened resonances in chloroform solution independent of concentration. This is indicative of strong aggregation behavior in solution. FT-IR (neat, cm^{-1}): 2928, 2854, 1610, 1370, 1159, 1009, 849. MALDI-TOF MS (*m/z*): M^+ 1371.7. Elemental analysis: calcd. for $C_{100}H_{94}F_4$, C 87.55, H 6.91; found C 87.69, H 6.94.

1,2-Bis(4-(trifluoromethyl)phenyl)ethane-1,2-dione 11c

1,2-Bis(4-(trifluoromethyl)phenyl)acetylene **6c** (0.5 g, 1.6 mmol) and iodine (250 mg, 1 mmol) were dissolved in DMSO (5 mL). The reaction was heated to 155 °C for 14 h under N_2 and cooled to room temperature. The reaction was poured into an aqueous solution of sodium thiosulfate (50 mL, 1 M) and the resulting precipitated was collected and washed with water (100 mL). The solid was dissolved in dichloromethane (50 mL) and washed with water (50 mL). The crude product was purified by column chromatography (SiO_2, dichloromethane/petroleum spirits 40-60 °C 1:1, $R_f = 0.3$) and a yellow crystalline solid (0.5 g, 90% yield) was obtained.

m.p. 143 °C. ^1H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 7.81 (d, *J* 8 Hz, 4H, Ar), 8.12 (d, *J* 8 Hz, 4H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 119.99, 122.16, 124.33, 126.11, 126.14, 126.17, 126.20, 126.27, 126.51, 130.07, 130.24, 130.33, 135.21, 135.22, 135.79, 136.05, 136.32, 136.58, 191.87. FT-IR (neat, cm^{-1}): 1673 (C=O), 1329, 1176, 1126, 1067. The characterization data is identical to a previous report for compound **11c** obtained via a different synthetic route.[6]

Cyclopentadienone 7c

1,2-Bis(4-(trifluoromethyl)phenyl)ethane-1,2-dione **11c** (0.5 g, 1.44 mmol), diphenylacetone **12** (0.53 g, 1.44 mmol) and ethylene glycol (1 mL) were placed in a Schlenk tube (25 mL). The mixture was heated to 140 °C and Et_4NOH (0.1 mL, 1 M aq.) was added. The reaction was stirred at 140 °C for 1 h and allowed to cool to room temperature. Methanol (10 mL) was added and the resulting precipitate was collected and washed with methanol (50 mL). A purple solid (0.7 g, 74% yield) was obtained after drying under vacuum.

DSC: T_m = 242 °C, T_c = 189 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 7.03 (d, *J* 8.5 Hz, 4H, Ar), 7.05 (d, *J* 8.5 Hz, 4H, Ar), 7.41 (d, *J* 8.5 Hz, 4H, Ar), 7.50 (d, *J* 8.5 Hz, 4H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 122.80, 125.45, 125.48, 125.51, 125.54, 125.74, 128.50, 129.42, 130.92, 131.54, 131.66, 135.95, 152.58, 198.48. FT-IR (neat, cm^{-1}): 1716 (C=O), 1488, 1320, 1166, 1125, 1067, 856, 758. HRMS-ESI (*m/z*), calcd. for $C_{31}H_{16}Br_2F_6O$: M+Ag$^+$ 784.84971, found 784.85051.

Hexaphenylbenzene 8c

Cyclopentadienone **7c** (0.3 g, 0.44 mmol) and 1,2-bis(4-(trifluoromethyl)phenyl)acetylene **6c** (0.139 g, 0.44 mmol) and diphenyl ether (0.5 mL) were placed in a Schlenk tube (10 mL). The reaction was heated to 250 °C for 2 h or until the purple colour of the cyclopentadienone disappeared. The reaction was cooled to room temperature and the solid was dispersed in methanol (10 mL). A colourless crystalline solid (0.35 g, 82% yield) was obtained after filtration and drying under vacuum.

DSC: T_m = 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 6.64 (d, *J* 8.5 Hz, 4H, Ar), 6.90 (d, *J* 8 Hz, 8H, Ar), 7.05 (d, *J* 8.5 Hz, 8H, Ar), 7.20 (d, *J* 8.5 Hz, 4H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 120.75, 122.70, 124.19, 124.22, 124.25, 124.27, 124.86, 128.36, 128.62, 130.56, 131.18, 132.37, 139.53, 139.75, 142.90. FT-IR (neat, cm^{-1}): 1322, 1119, 1066. HRMS-ESI (*m/z*), calcd. for $C_{46}H_{24}Br_2F_{12}$: M+Ag$^+$ 1070.90781, found 1070.90892.

HBC 9c

Hexaphenylbenzene **8c** (0.5 g, 0.52 mmol) was dissolved in dichloromethane (100 mL) and cooled to 0 °C. DDQ (0.82 g, 3.6 mmol) was added followed by trifluoromethanesulfonic acid (1.08 g, 7.2 mmol). The reaction was stirred at 25 °C for 14 h under N_2 and was then quenched by the addition of methanol (200 mL). The resulting precipitate was collected by filtration and washed with methanol (100 mL). A yellow solid (0.4 g, 81% yield) was obtained after drying under vacuum. The solubility of the product was too low in common organic solvents. As a result, NMR spectrum was not recorded.

DSC: no thermal transitions detected up to 500 °C. FT-IR (neat, cm^{-1}): 1323, 1279, 1127, 880. MALDI-TOF MS (*m/z*): M^+ 952.2. Elemental analysis: calcd. for $C_{46}H_{12}Br_2F_{12}$, C 58.01, H 1.27; found C 57.98, H 1.40.

Fluorenyl HBC 10c

HBC **9c** (150 mg, 0.16 mmol) and 9,9-dioctylfluorene-2-boronic acid pinacol ester (200 mg, 0.4 mmol) was dissolved in toluene (20 mL) and thoroughly degassed by bubbling with nitrogen gas. Degassed solution of Et_4NOH (5 mL, 1 M aq.) and tetrakis-(triphenylphosphine)palladium(0) (10 mg, 5 mol%) was added and the reaction was heated at 90 °C for 14 h under N_2. The reaction was cooled and the product extracted with toluene (20 mL). The toluene solution was dried with $MgSO_4$ and filtered through a plug of silica. The volume of the resulting yellow solution was reduced under vacuum and the product was precipitated with MeOH. An orange solid (200 mg, 80% yield) was obtained after filtration and drying under vacuum.

TGA, T_{decomp} (5% mass loss) = 286 °C. DSC, No thermal transitions in the measured temperature range (25 °C – 250 °C). UV-vis: λ_{max} chloroform solution (ε, $M^{-1}cm^{-1}$) = 371 nm (3.9×10^4). ^1H NMR (500 MHz, $CDCl_3$, 50 mM, 20 °C, δ): 0.6-1.2 (br, 60H, $-CH_2-$ and CH_3), 2.03 (br, 8H, $-CH_2-$), 6.0-6.7 (br, ArH), 6.9-7.5 (br, ArH). ^{13}C NMR (125 MHz, $CDCl_3$, 50 mM, 20 °C, δ): 13.90, 22.44, 23.80, 28.87, 28.88, 28.90, 29.19, 31.54, 31.55, 40.34, 55.14, 109.99, 110.10 (br), 119.66, 119.81, 122.90 (br), 125.99 (br), 126.74 (br), 140.25, 140.47, 150.97, 151.42, 168.93. Both ^1H and ^{13}C NMR showed broadened resonances in chloroform solution independent of concentration. This is indicative of strong aggregation behavior in solution. FT-IR (neat, cm^{-1}): 2926, 2854, 1610, 1353, 1280, 1120, 875, 741. MALDI-TOF MS (*m/z*): M^+ 1571.6. Elemental analysis: calcd. for $C_{104}H_{94}F_{12}$, C 79.47, H 6.03; found C 79.49, H 6.23.

1,2-Bis(3,5-difluorophenyl)acetylene 6d

3,5-Difluoroiodobenzene (2.4 g, 10 mmol), copper iodide (100 mg), $Pd(PPh_3)_2Cl_2$ (200 mg) and 1,8-diazabicycloundec-7-ene (10 g, 66 mmol) were added to toluene (50 mL). The mixture was degassed by bubbling nitrogen gas and trimethylsilylacetylene (0.5 g, 5.1 mmol) was added. This was followed by the addition of water (0.1 mL). The reaction mixture was stirred at 60 °C for 14 h and the crude product was extract with toluene. A colourless crytalline solid (1.1 g, 80% yield) was obtained after purification by column chromatography (SiO_2, dichloromethane/petroleum spirits 40-60 °C 1:3, $R_f = 0.7$).

m.p. 71 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 6.85 (tt, 2H, Ar), 7.05 (dt, 4H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 88.69, 88.73, 88.77, 104.84, 105.09, 105.34, 114.56, 114.64, 114.75, 114.83, 124.95, 161.42, 161.55, 163.90, 164.03. FT-IR (neat, cm^{-1}): 1615, 1585, 1428, 1368, 1180, 1122, 990, 856.

1,2-Bis(3,5-difluorophenyl)ethane-1,2-dione 11d

1,2-Bis(3,5-difluorophenyl)acetylene **6d** (0.5 g, 2 mmol) and iodine (250 mg, 1 mmol) were dissolved in DMSO (5 mL). The reaction was heated to 155 °C for 14 h under N_2 and cooled to room temperature. The reaction was poured into an aqueous solution of sodium thiosulfate (50 mL, 1 M) and the resulting precipitated was collected and washed with water (100 mL). The solid was dissolved in dichloromethane (50 mL) and washed with water (50 mL). The crude product was purified by column chromatography (SiO_2, dichloromethane/petroleum spirits 40-60 °C 1:1, $R_f = 0.3$) and a yellow crystalline solid (0.5 g, 89% yield) was obtained.

m.p. 137 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 7.12 (tt, 2H, Ar), 7.49 (dt, 4H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 110.44, 110.64, 110.84, 112.79, 112.85, 112.95, 113.01, 134.95, 135.01, 135.08, 162.10, 162.19, 164.12, 164.21, 189.64. FT-IR (neat, cm^{-1}): 1678 (C=O), 1591, 1437, 1327, 1135, 979, 869.

Cyclopentadienone 7d

1,2-Bis(3,5-difluorophenyl)ethane-1,2-dione **11d** (0.2 g, 0.71 mmol), diphenylacetone **12** (0.26 g, 0.71 mmol) and ethylene glycol (1 mL) were placed in a Schlenk tube (25 mL). The mixture was heated to 140 °C and Et_4NOH (0.1 mL, 1 M aq.) was added. The reaction was stirred at 140 °C for 1 h and allowed to cool to room temperature. Methanol (10 mL) was added and the resulting precipitate was collected and washed with methanol (50 mL). A purple solid (0.3 g, 69% yield) was obtained after drying under vacuum.

DSC: T_m = 240 °C, T_c = 180 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 6.48 (dt, 4H, Ar), 6.79 (tt, 2H, Ar), 7.07 (d, *J* 8.5 Hz, 4H, Ar), 7.43 (d, *J* 8.5 Hz, 4H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 104.64, 104.84, 105.04, 111.78, 111.83, 111.93, 111.99, 123.06, 125.60, 128.12, 131.42, 131.51, 131.72, 135.39, 151.50, 161.88, 161.98, 163.87, 163.98, 198.18. FT-IR (neat, cm^{-1}): 1715 (C=O), 1619, 1586, 1489, 1431, 1346, 1122, 990, 751. HRMS-ESI (*m/z*), calcd. for $C_{29}H_{14}Br_2F_4O$: M+Ag$^+$ 720.83725, found 720.83801.

Hexaphenylbenzene 8d

Cyclopentadienone **7d** (0.1 g, 0.16 mmol) and 1,2-bis(3,5-difluorophenyl)acetylene **6d** (41 mg, 0.16 mmol) and diphenyl ether (0.5 mL) were placed in a Schlenk tube (10 mL). The reaction was heated to 250 °C for 2 h or until the purple colour of the cyclopentadienone disappeared. The reaction was cooled to room temperature and the solid was dispersed in methanol (10 mL). A colourless crystalline solid (0.1 g, 75% yield) was obtained after filtration and drying under vacuum.

DSC: T_m = 268 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 6.37 (dt, 8H, Ar), 6.46 (tt, 4H, Ar), 6.71 (d, *J* 7 Hz, 4H, Ar), 7.15 (d, *J* 7 Hz, 4H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C, δ): 102.18, 102.43, 102.68, 113.59, 113.66, 113.78, 113.85, 121.12, 130.78, 131.85, 137.06, 138.87, 138.88, 139.44, 141.90, 160.70, 160.83, 163.19, 163.32. FT-IR (neat, cm^{-1}): 1619, 1595, 1414, 1288, 1124, 1013, 992, 847. HRMS-ESI (*m/z*), calcd. for $C_{42}H_{20}Br_2F_8$: M+Ag$^+$ 942.88290, found 942.88364.

NMR Data – Compound **7b**

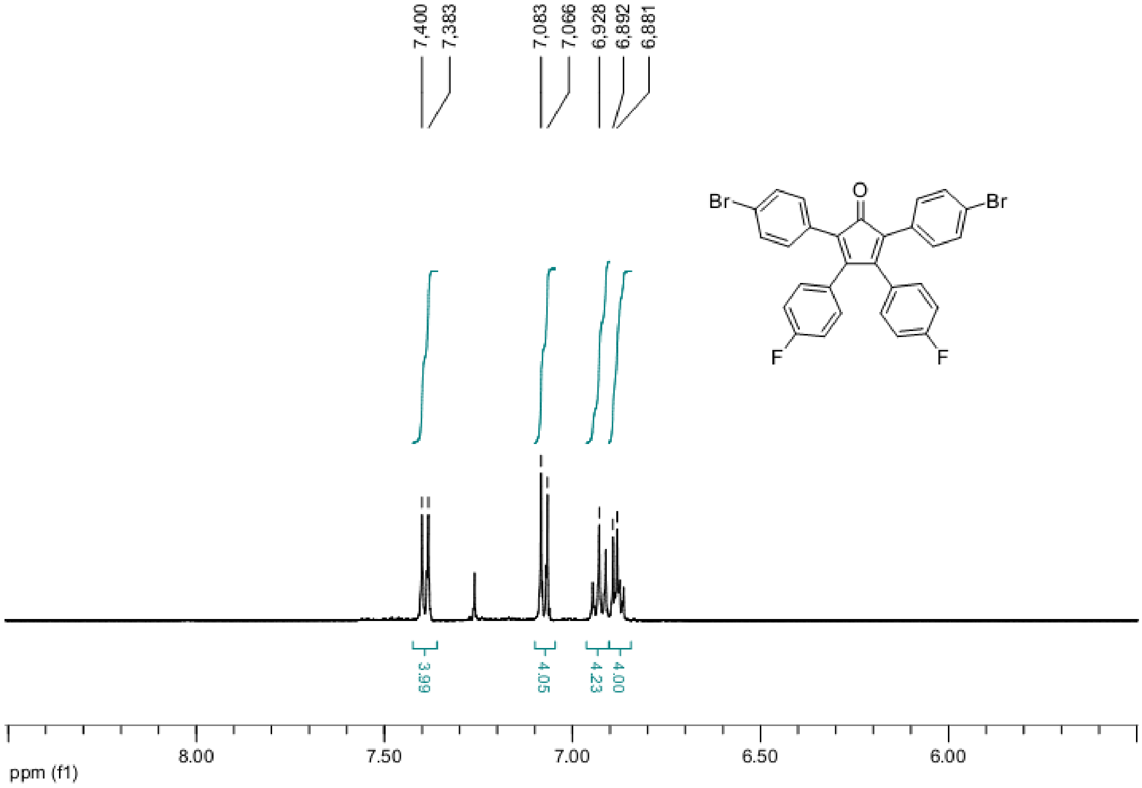


Figure S1. ^{1}H NMR (500 MHz) spectrum of compound **7b** in $CDCl_3$.

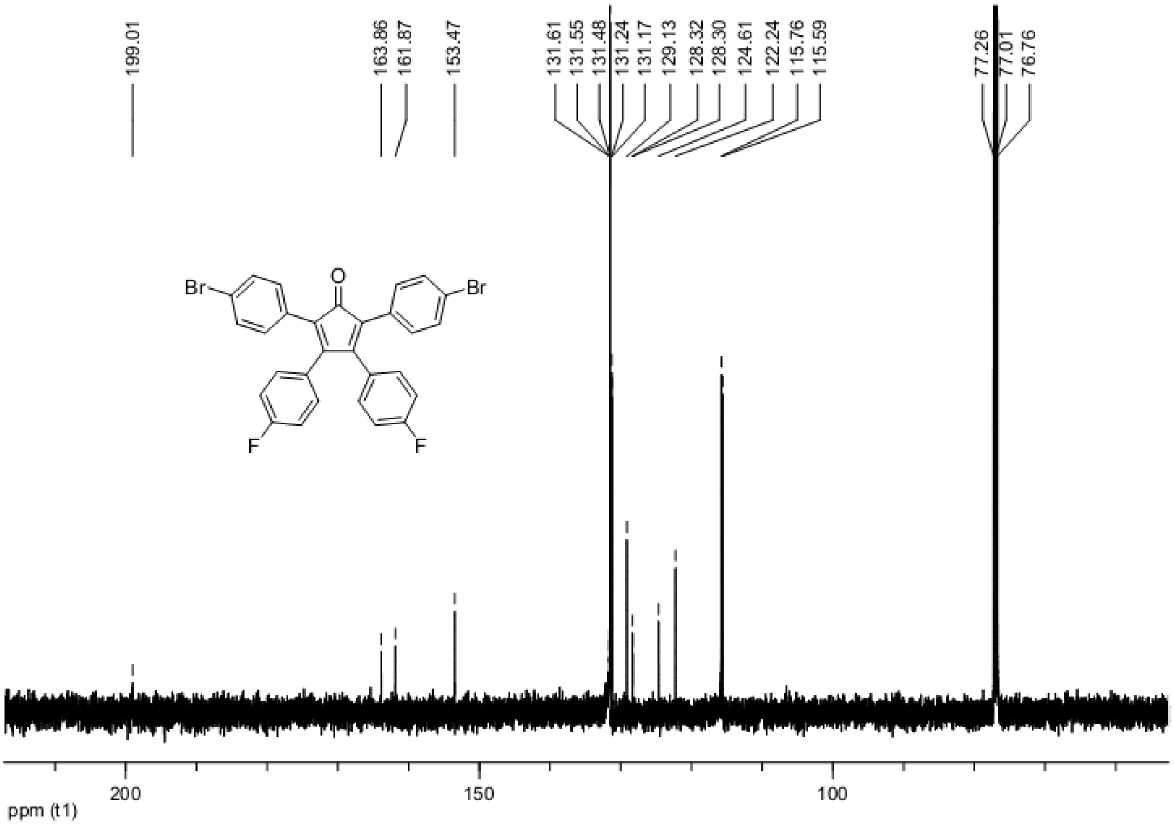


Figure S2. ^{13}C NMR (125 MHz) spectrum of compound **7b** in $CDCl_3$.

NMR Data – Compound **8b**

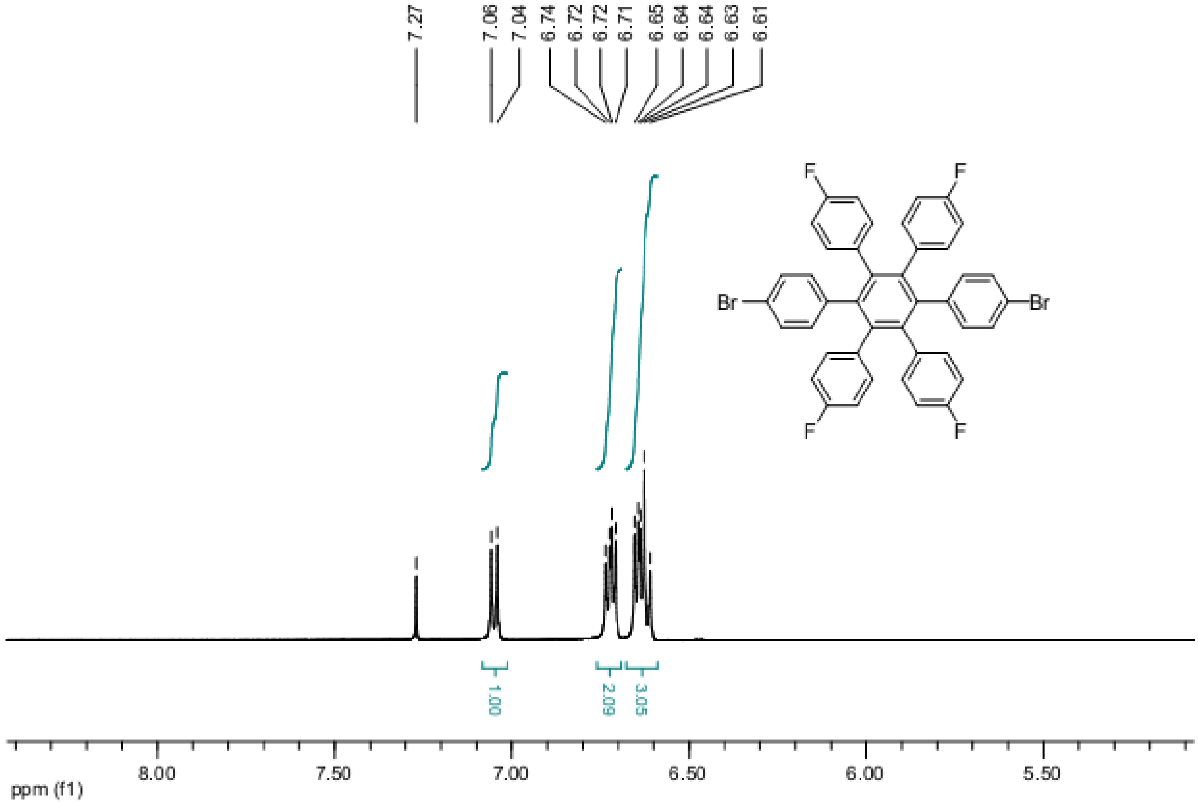


Figure S3. ^{1}H NMR (500 MHz) spectrum of compound **8b** in $CDCl_3$.

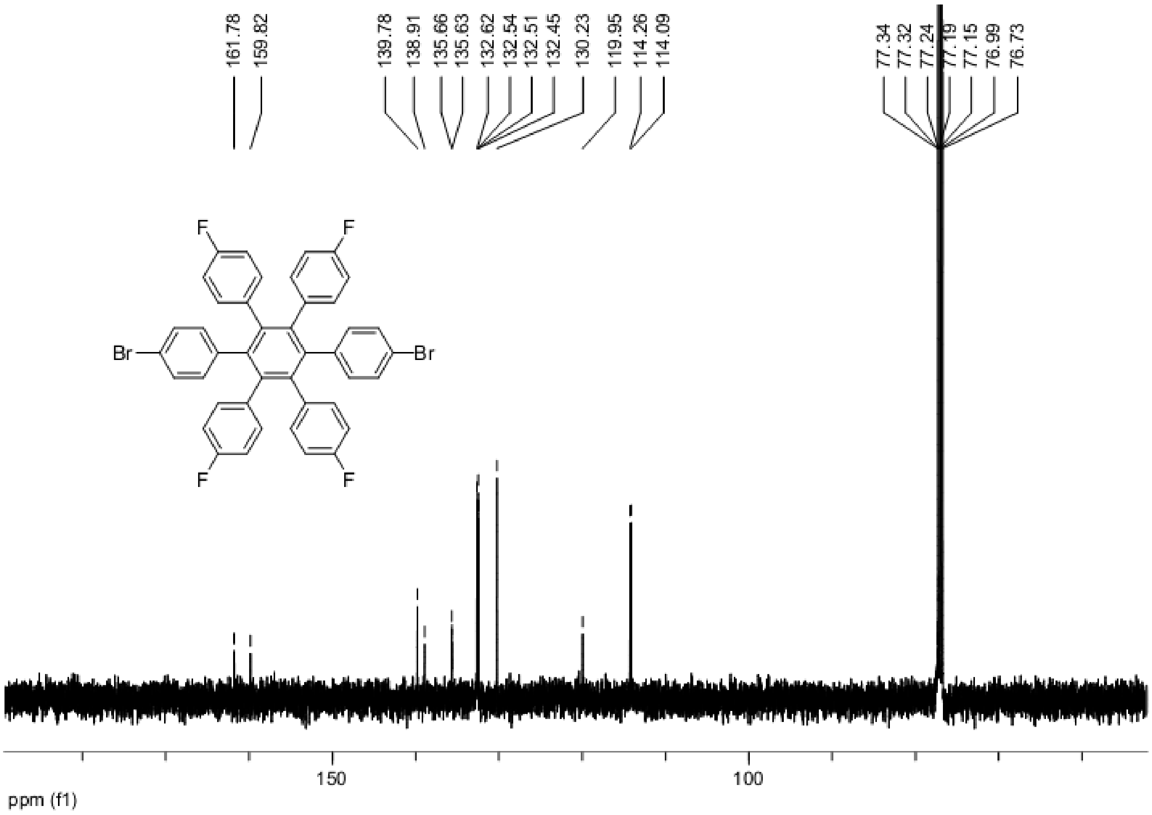


Figure S4. ^{13}C NMR (125 MHz) spectrum of compound **8b** in $CDCl_3$.

NMR Data – Compound **11c**

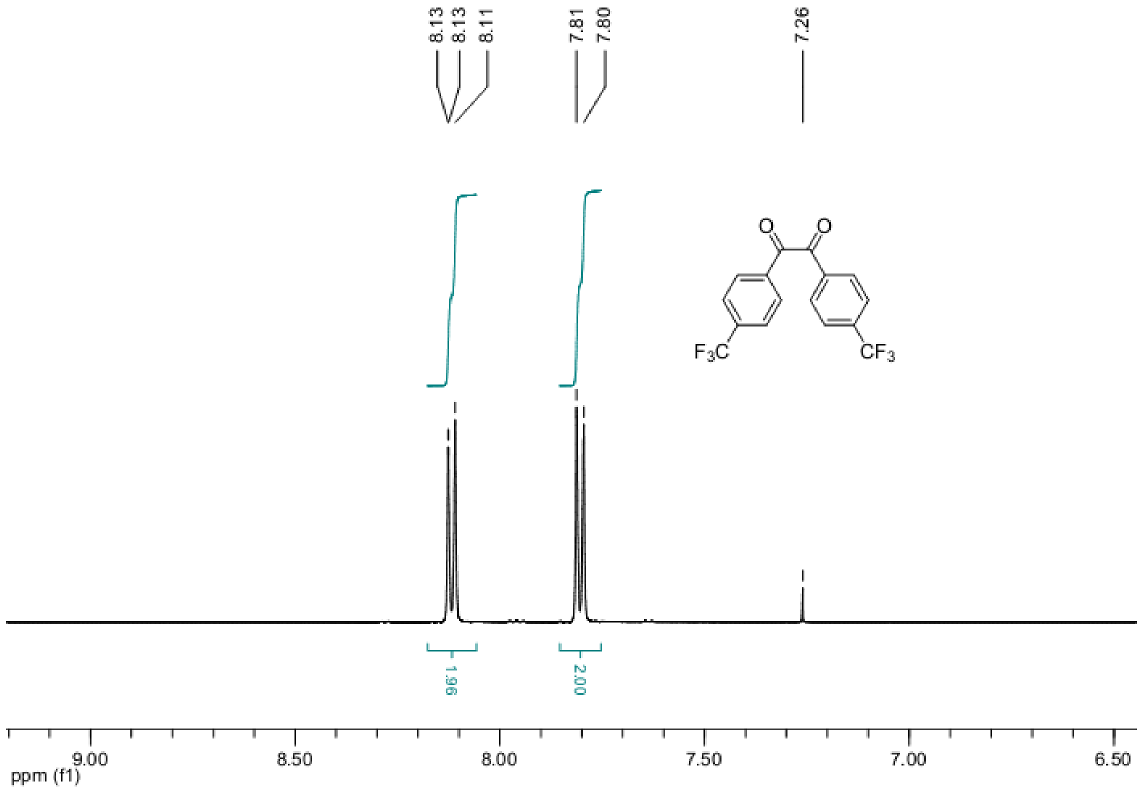


Figure S5. ^{1}H NMR (500 MHz) spectrum of compound **11c** in $CDCl_3$.

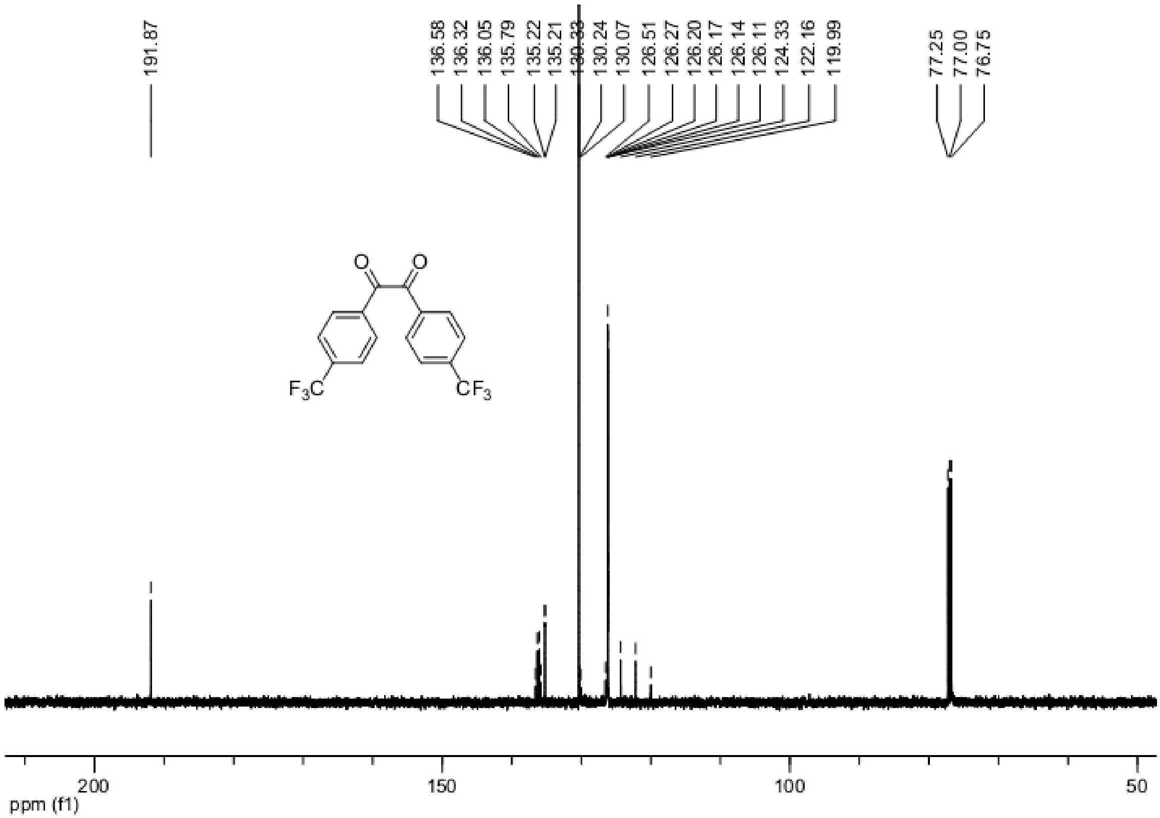


Figure S6. ^{13}C NMR (125 MHz) spectrum of compound **11c** in $CDCl_3$.

NMR Data – Compound **7c**

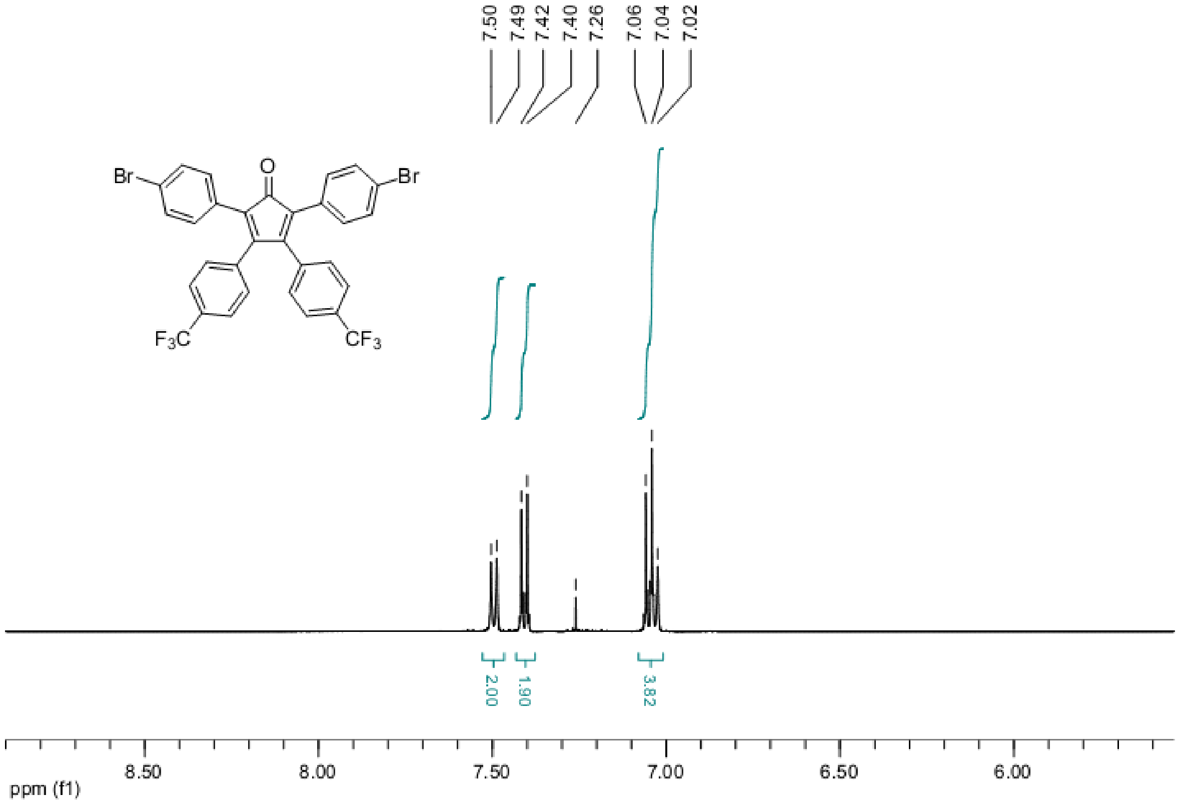


Figure S7. ^{1}H NMR (500 MHz) spectrum of compound **7c** in $CDCl_3$.

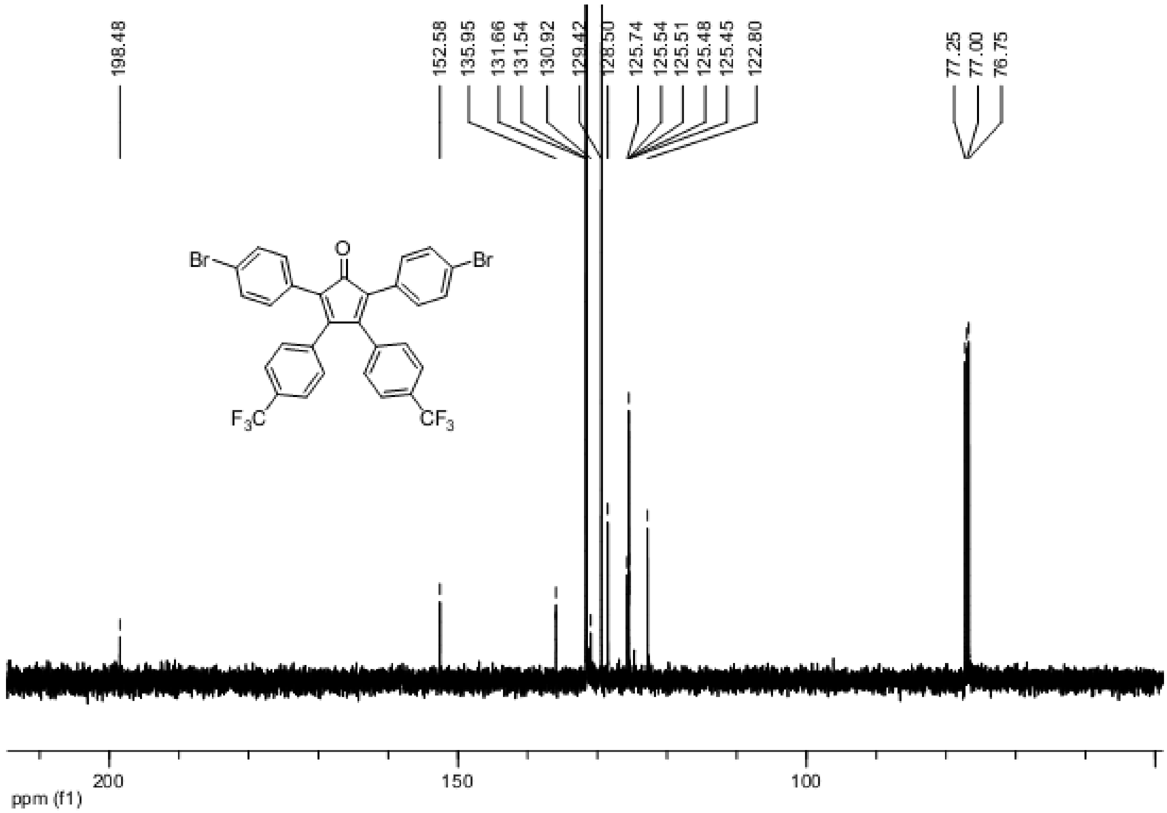


Figure S8. ^{13}C NMR (125 MHz) spectrum of compound **7c** in $CDCl_3$.

NMR Data – Compound **8c**

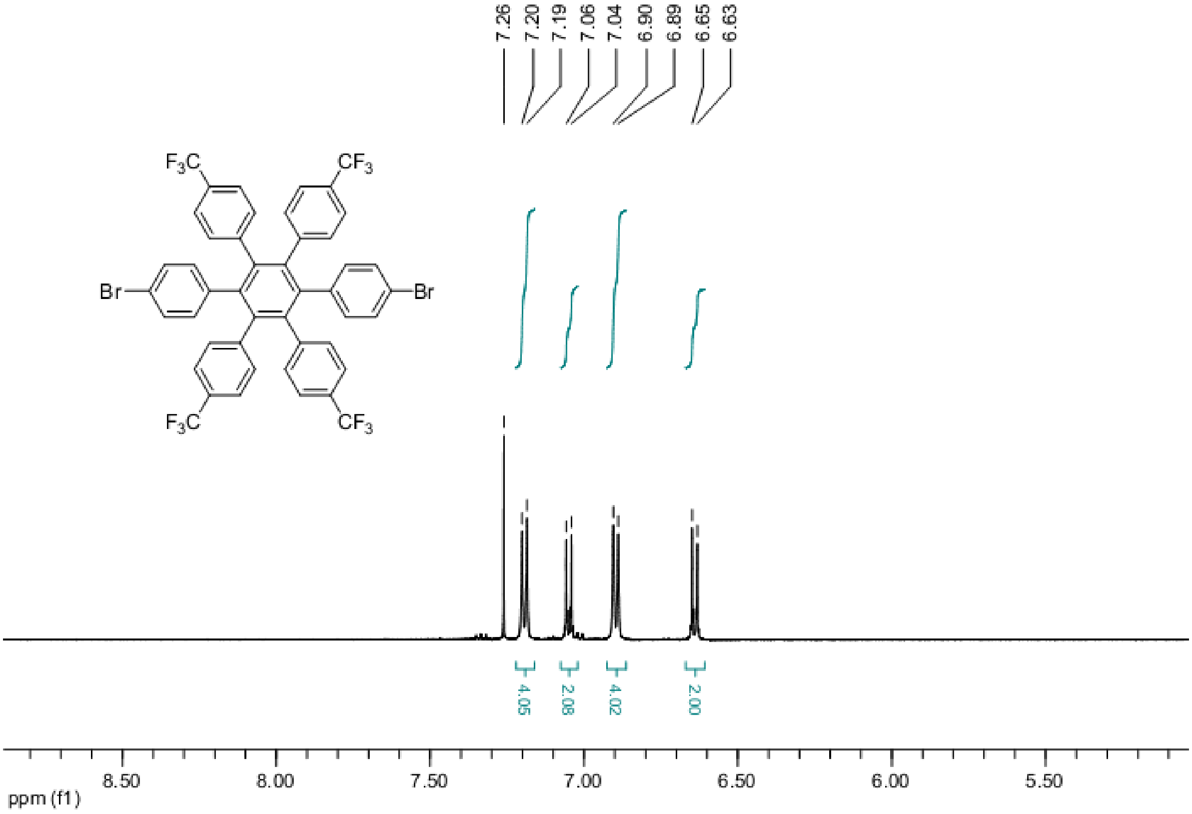


Figure S9. ^{1}H NMR (500 MHz) spectrum of **8c** in $CDCl_3$.

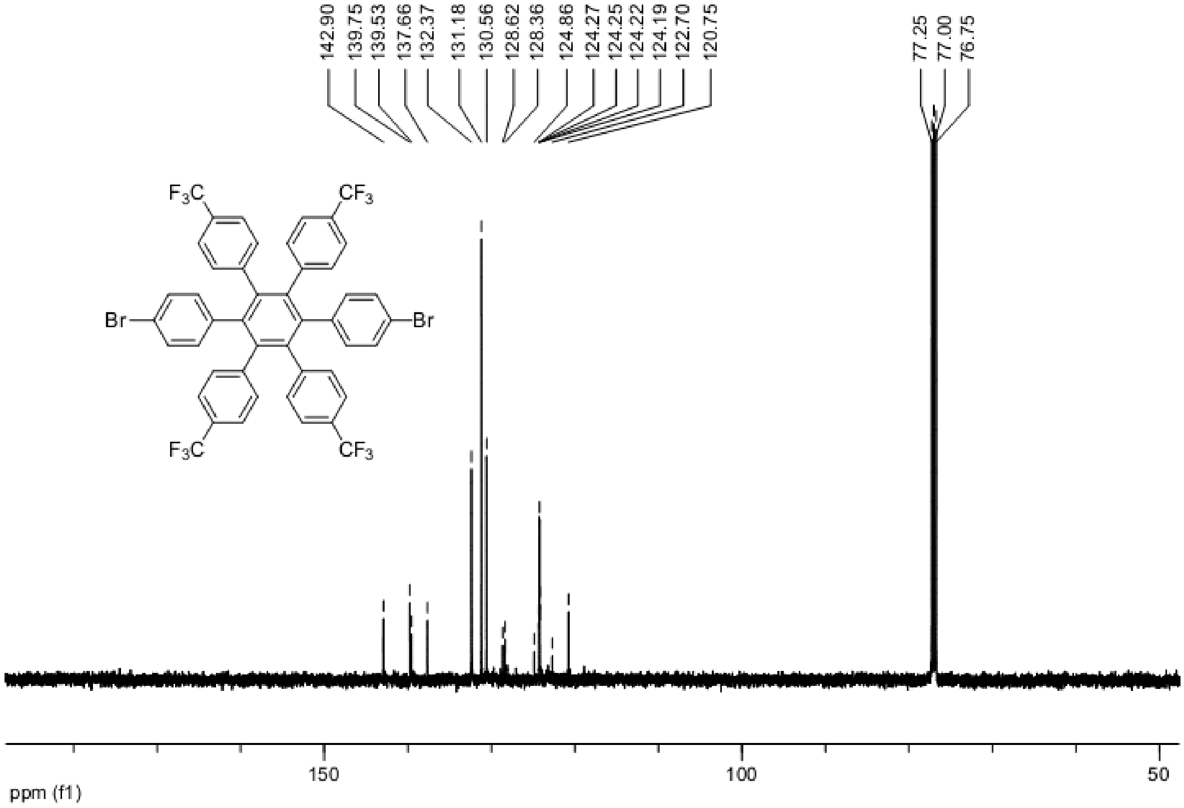


Figure S10. ^{13}C NMR (125 MHz) spectrum of **8c** in $CDCl_3$.

NMR Data – Compound **6d**

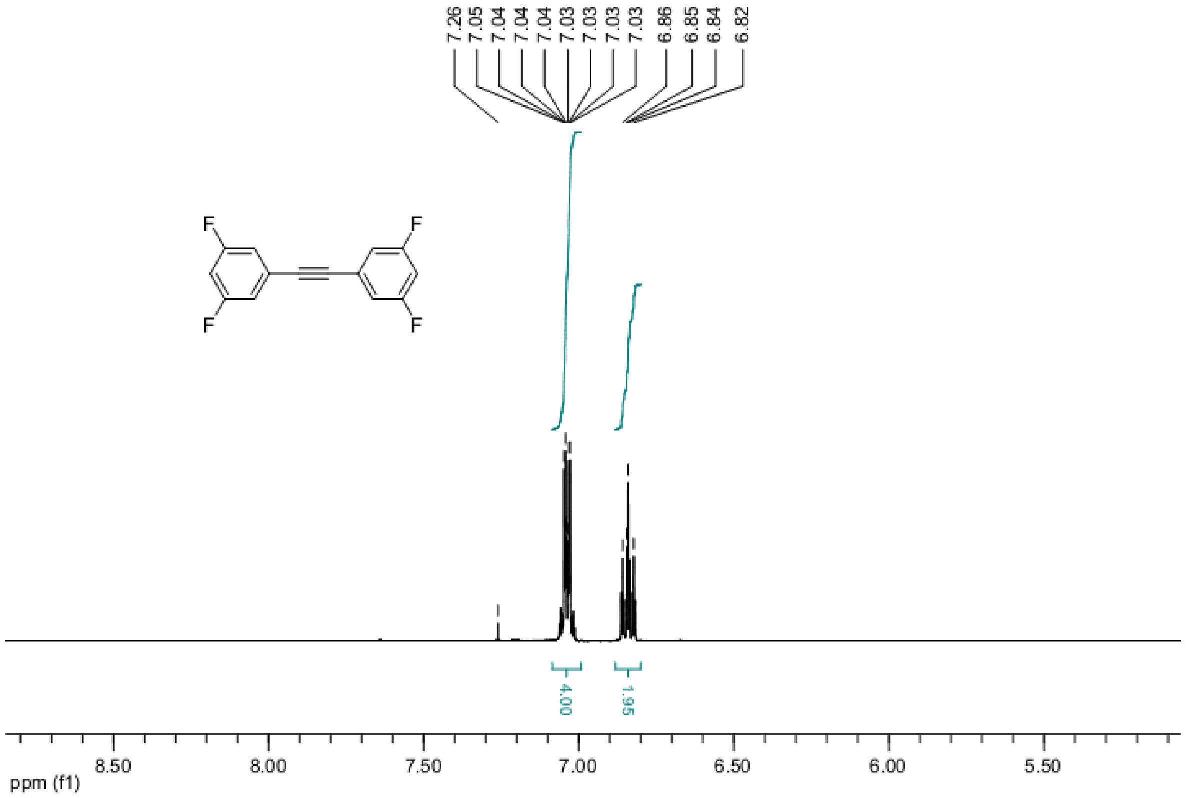


Figure S11. ^{1}H NMR (500 MHz) spectrum of compound **6d** in $CDCl_3$.

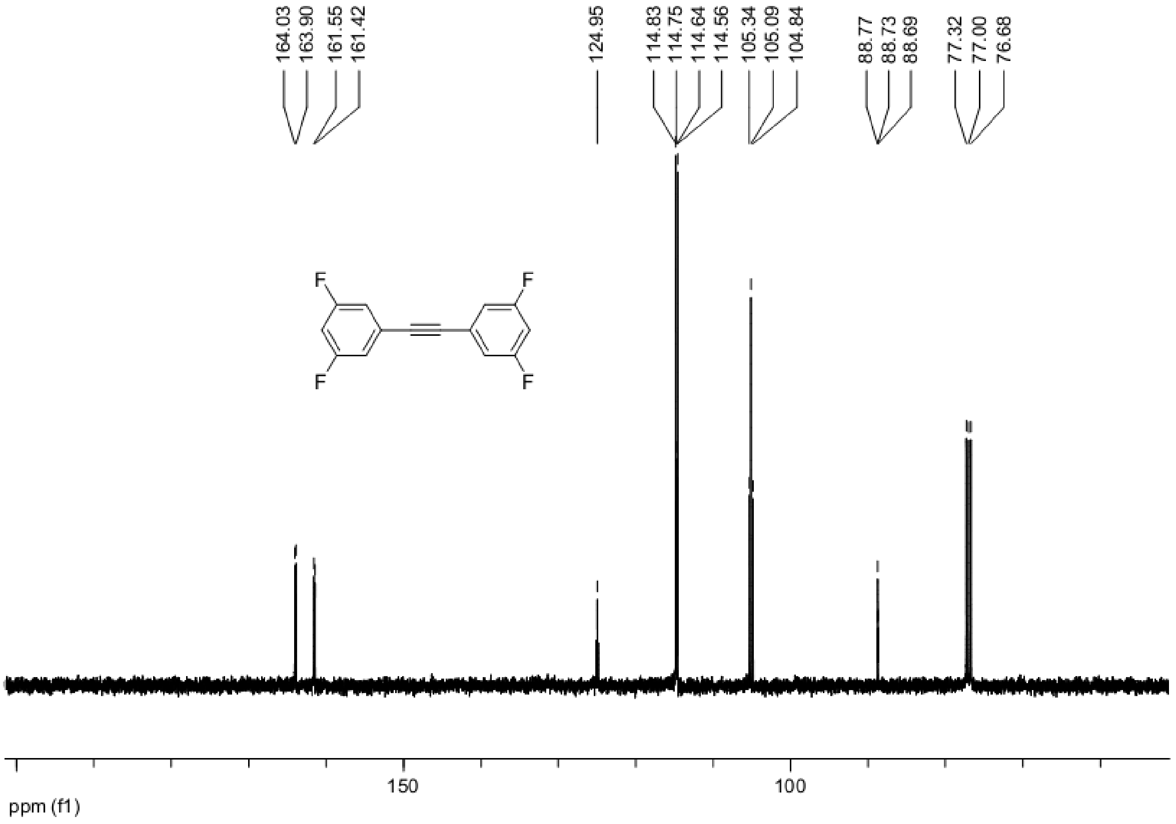


Figure S12. ^{13}C NMR (125 MHz) spectrum of compound **6d** in $CDCl_3$.

NMR Data – Compound **11d**

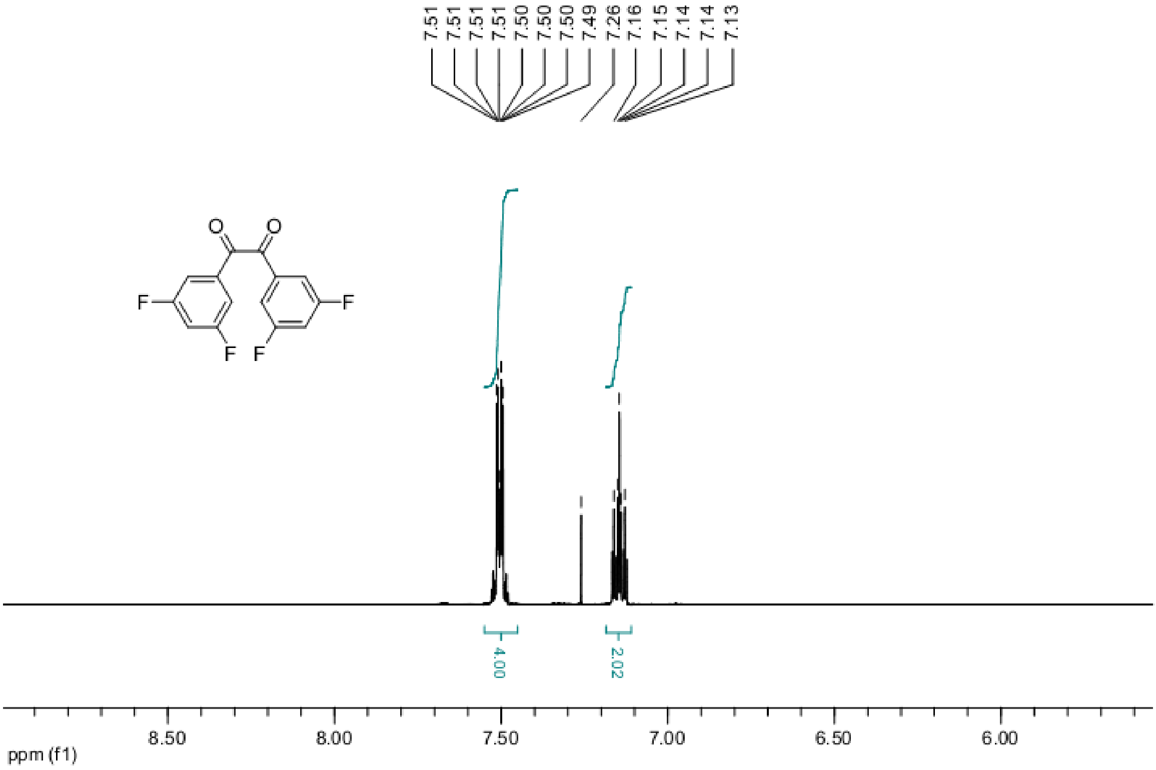


Figure S13. ^{1}H NMR (500 MHz) spectrum of compound **11d** in $CDCl_3$.

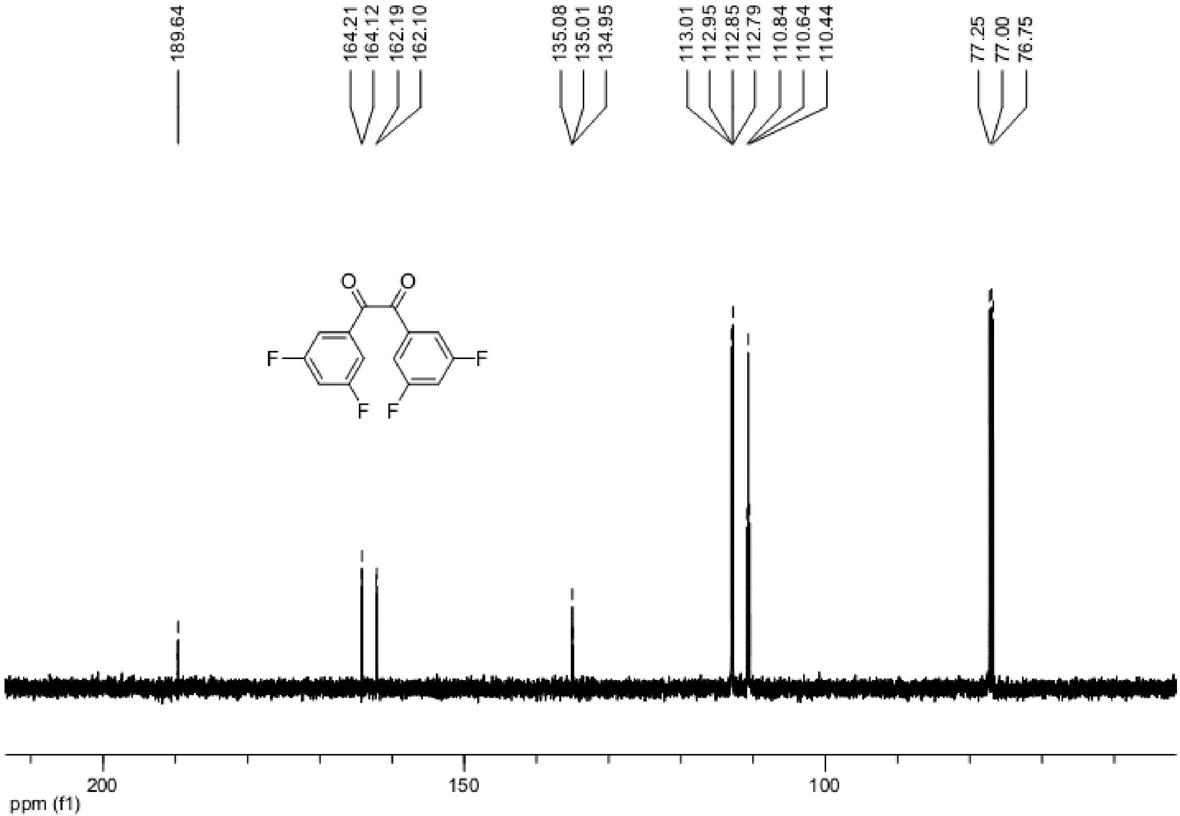


Figure S14. ^{13}C NMR (125 MHz) spectrum of compound **11d** in $CDCl_3$.

NMR Data – Compound **7d**

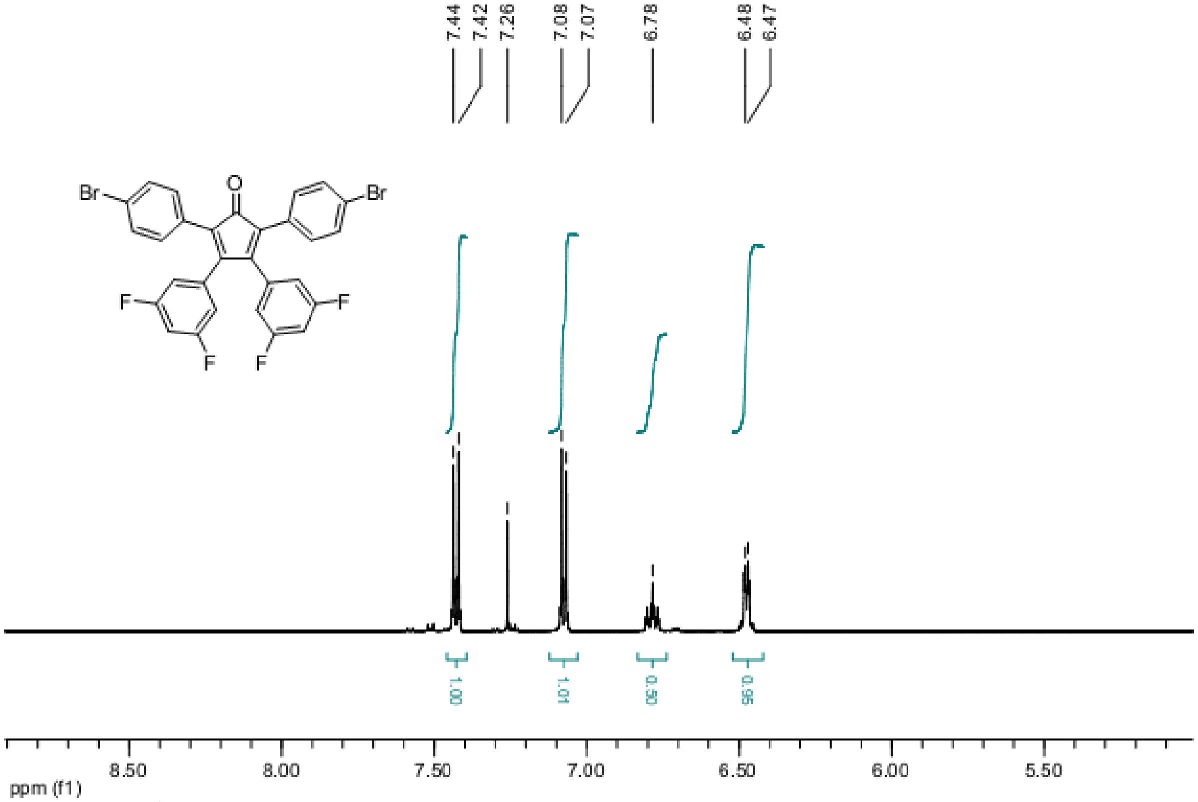


Figure S15. ^{1}H NMR (500 MHz) spectrum of compound **7d** in $CDCl_3$.

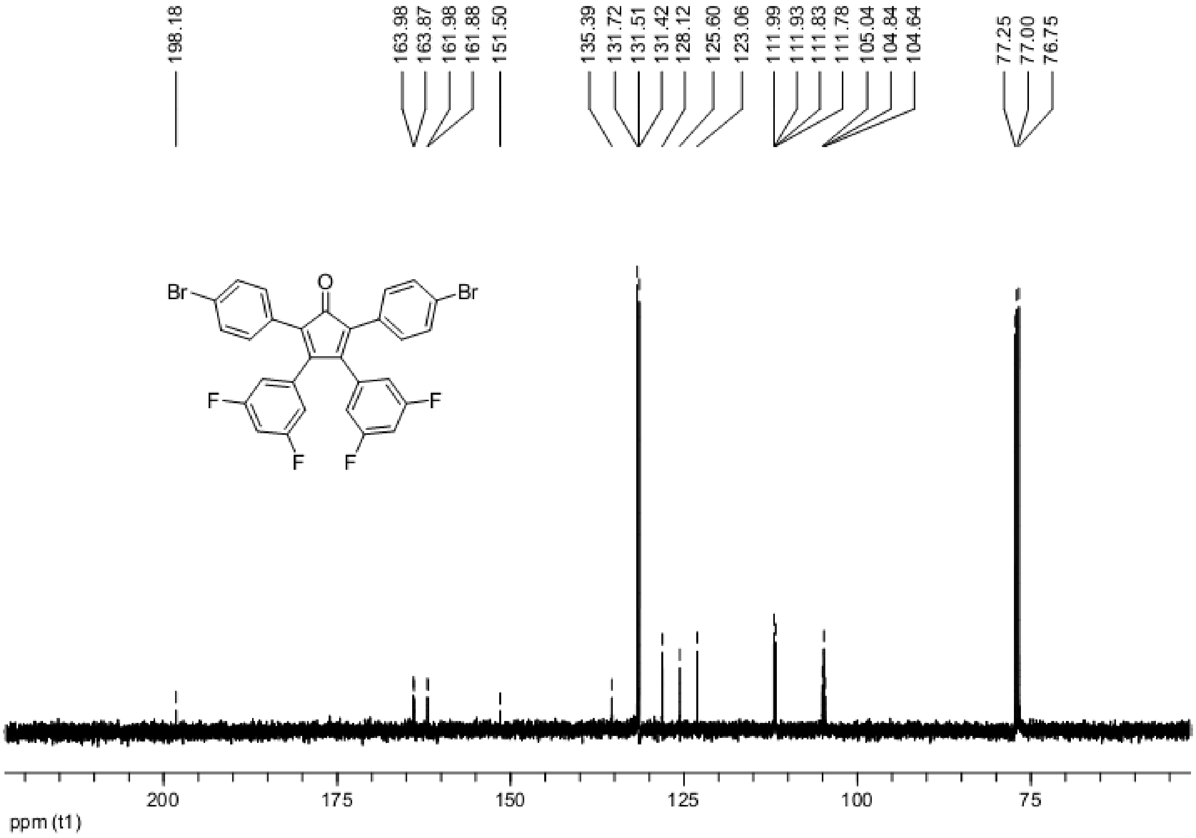


Figure S16. ^{13}C NMR (125 MHz) spectrum of compound **7d** in $CDCl_3$.

NMR Data – Compound **8d**

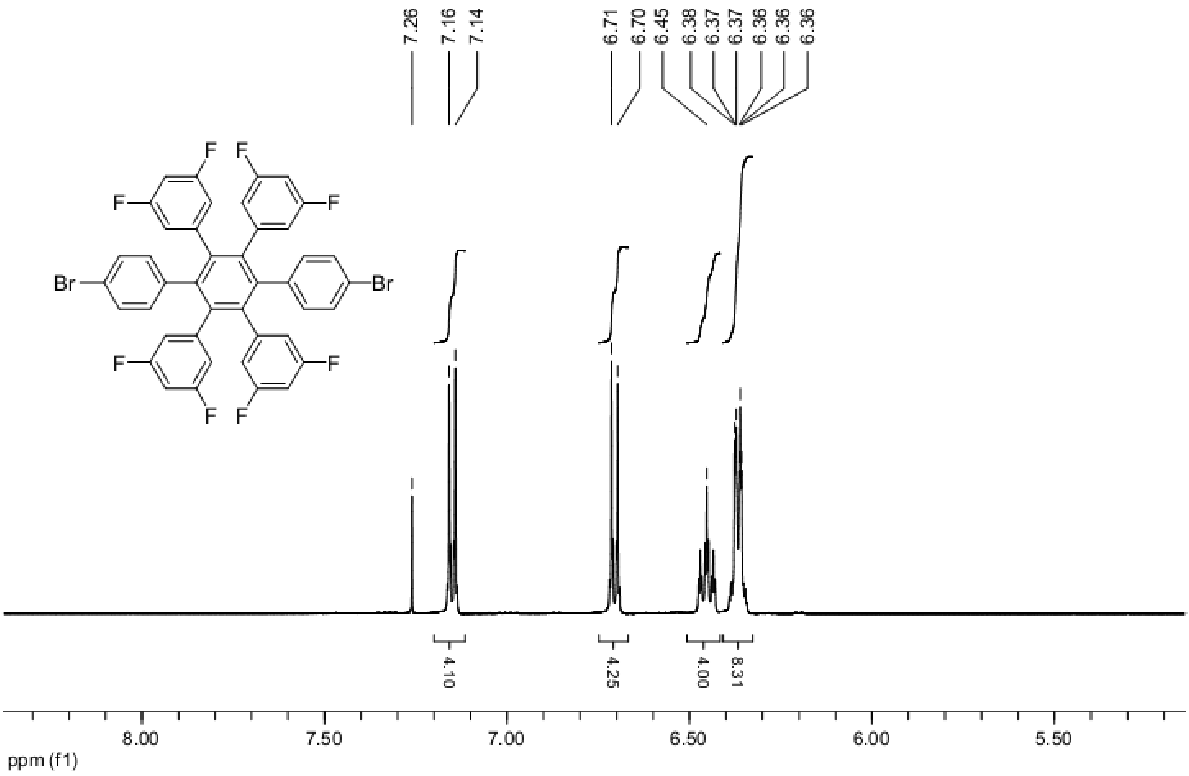


Figure S17. ^{1}H NMR (500 MHz) spectrum of compound **8d** in $CDCl_3$.

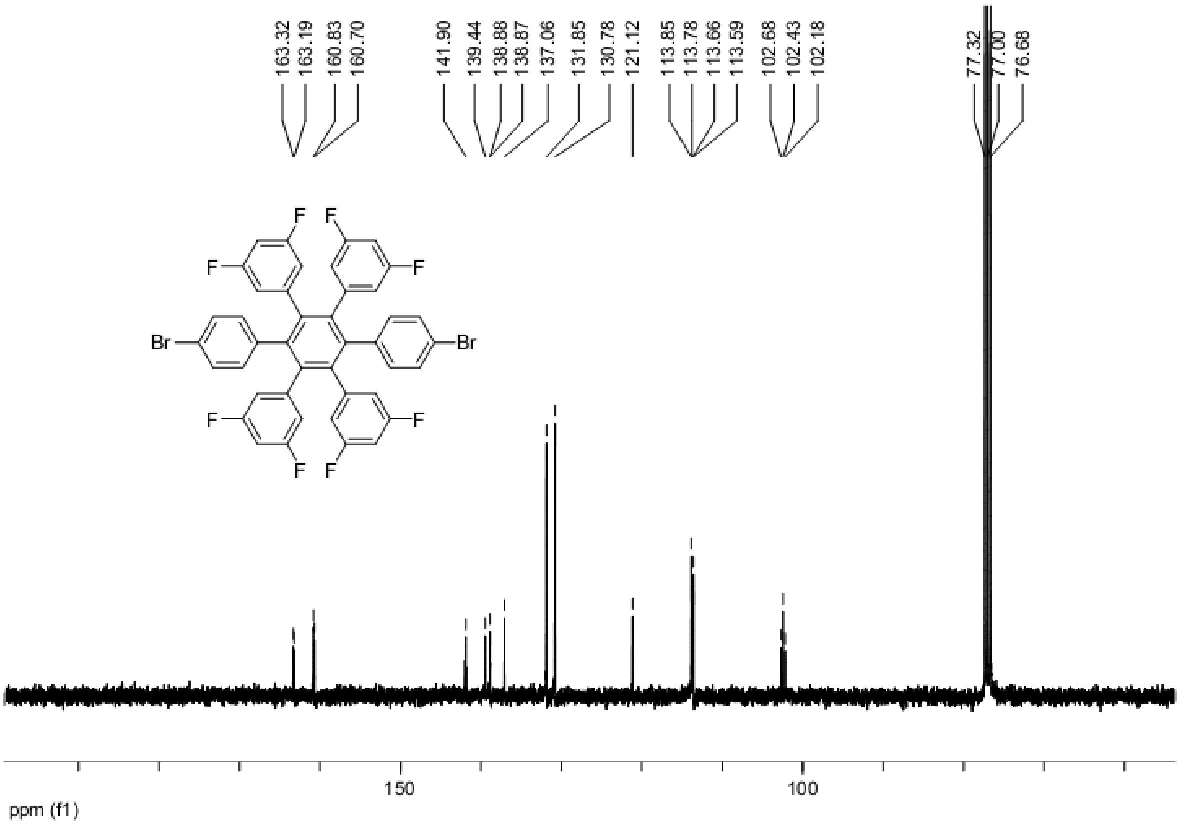


Figure S18. ^{13}C NMR (125 MHz) spectrum of compound **8d** in $CDCl_3$.

NMR Data – Compound **10b**

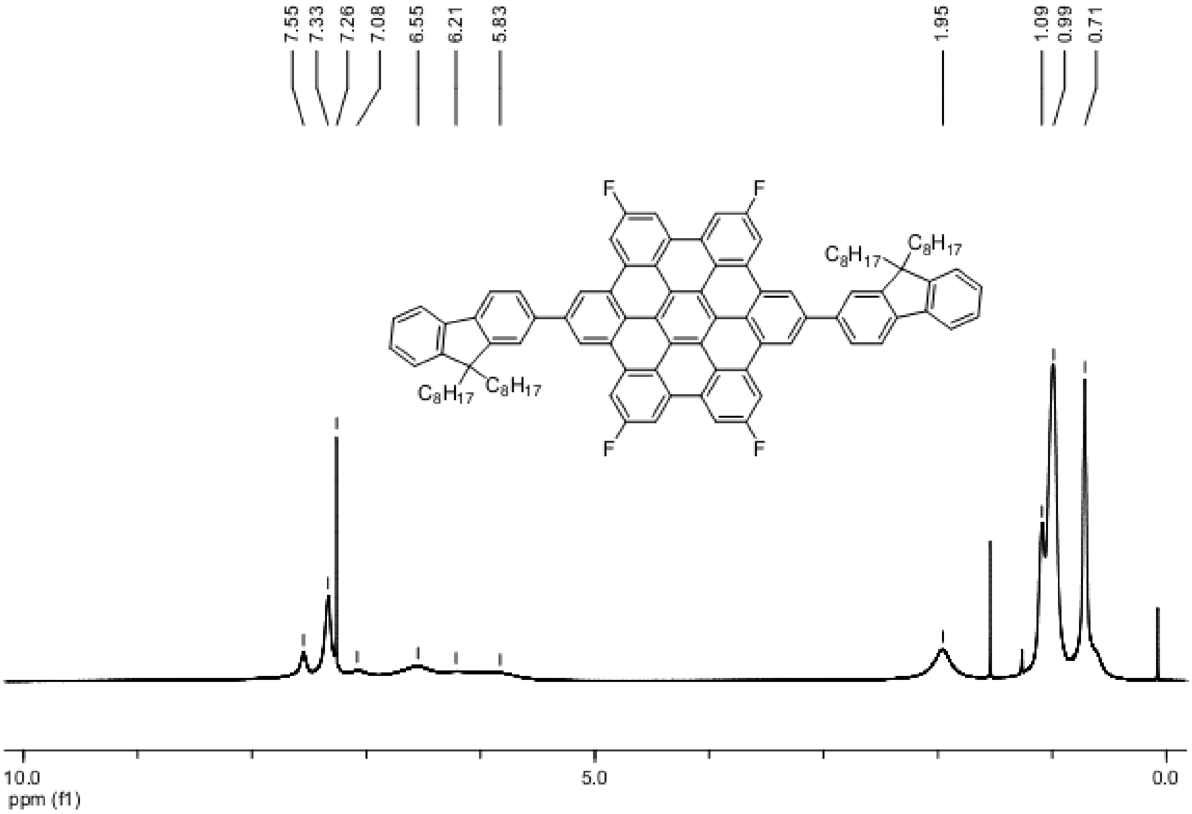


Figure S19. ^{1}H NMR (500 MHz) spectrum of compound **10b** in CDCl$_3$ (60 mM).

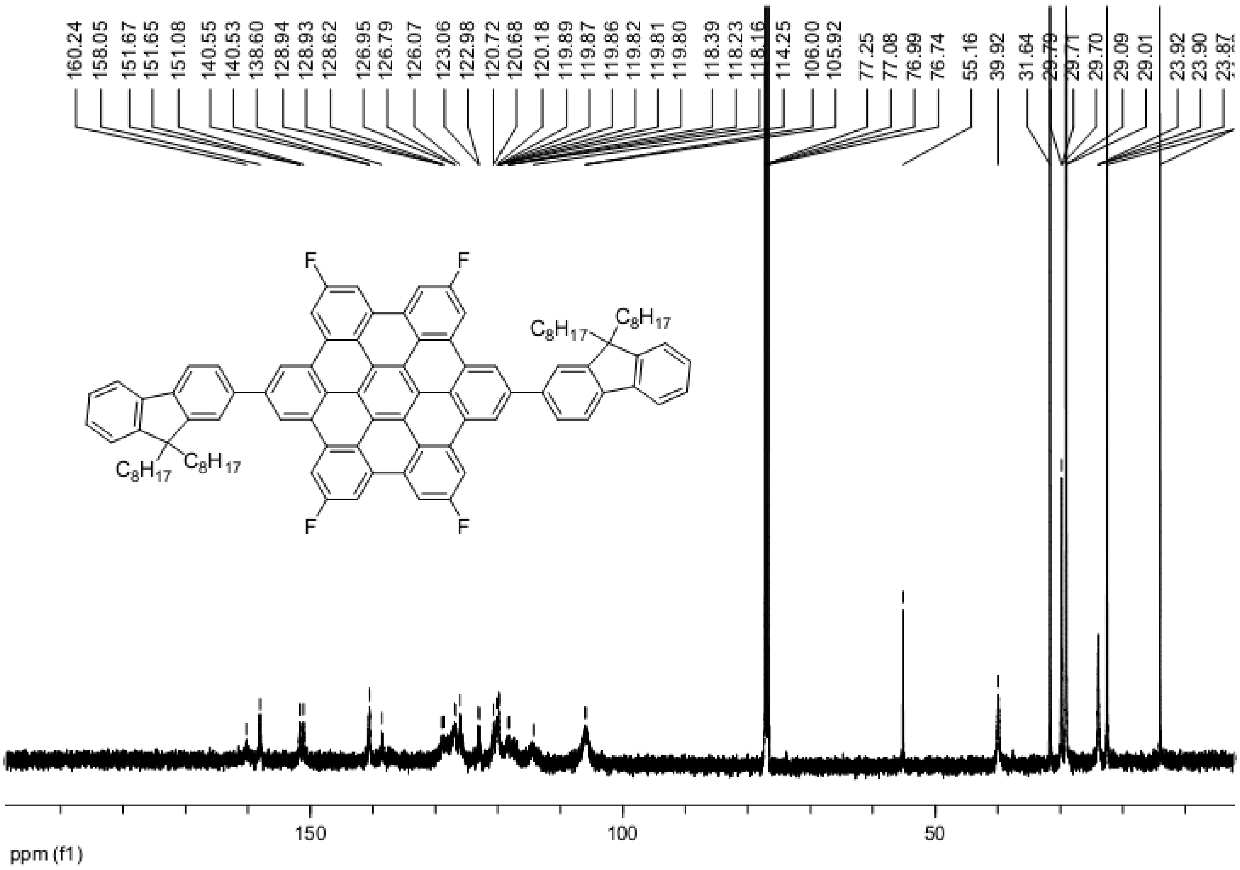


Figure S20. ^{13}C NMR (125 MHz) spectrum of compound **10b** in CDCl$_3$ (60 mM).

NMR Data – Compound **10c**

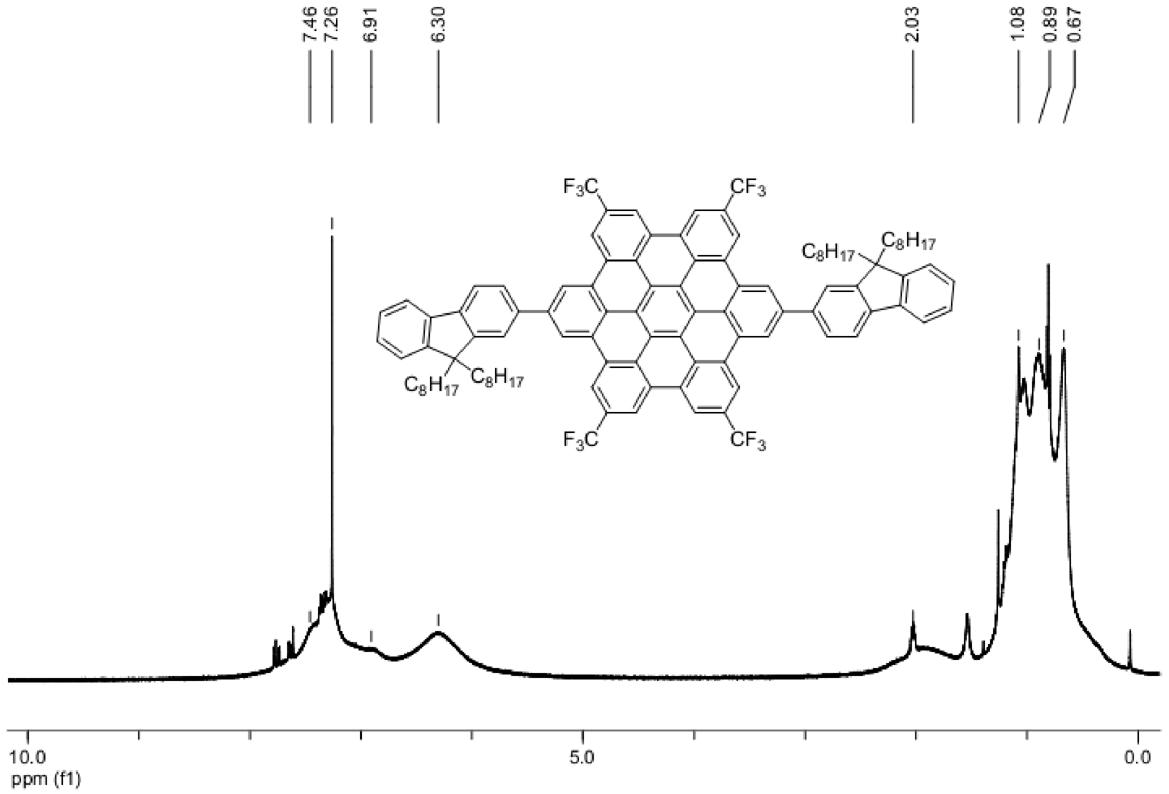


Figure S21. ^{1}H NMR (500 MHz) spectrum of compound **10c** in $CDCl_3$.

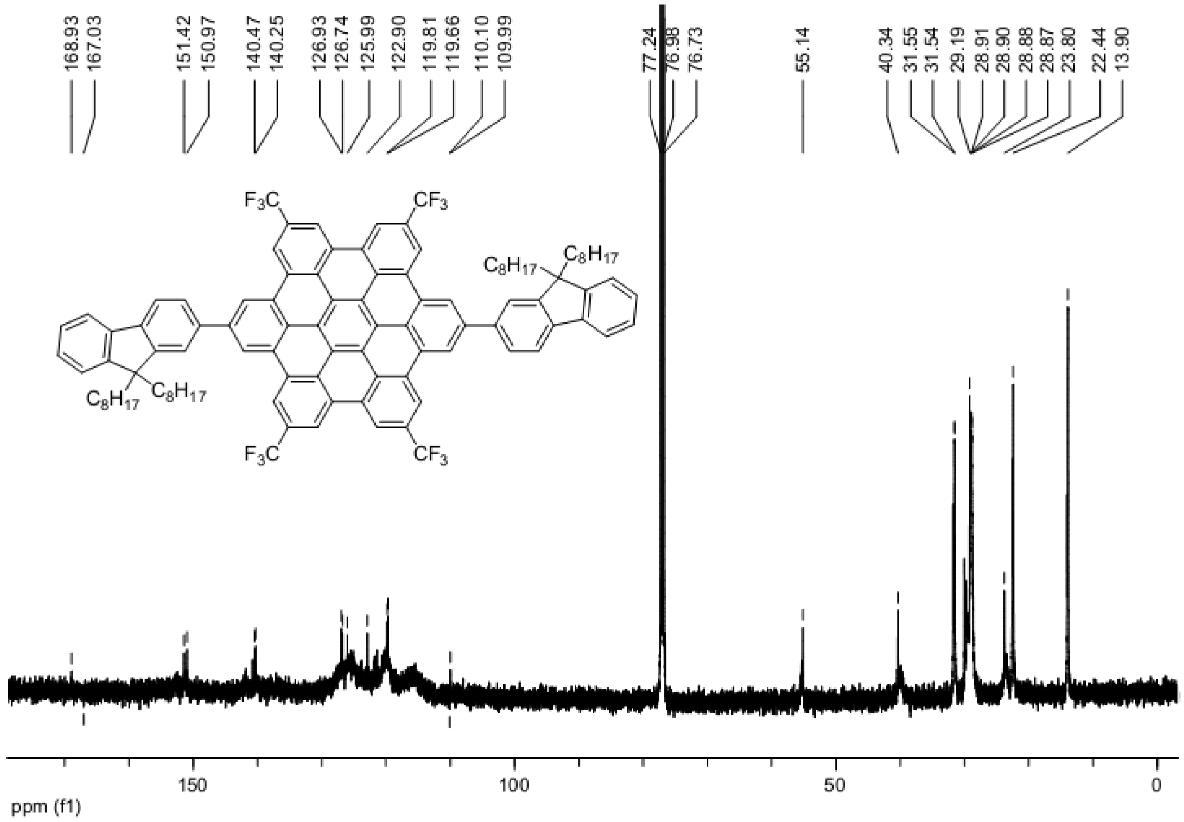


Figure S22. ^{13}C NMR (125 MHz) spectrum of compound **10c** in $CDCl_3$.

Matrix-assisted laser desorption ionization mass spectrum (MALDI-MS) of HBC derivatives

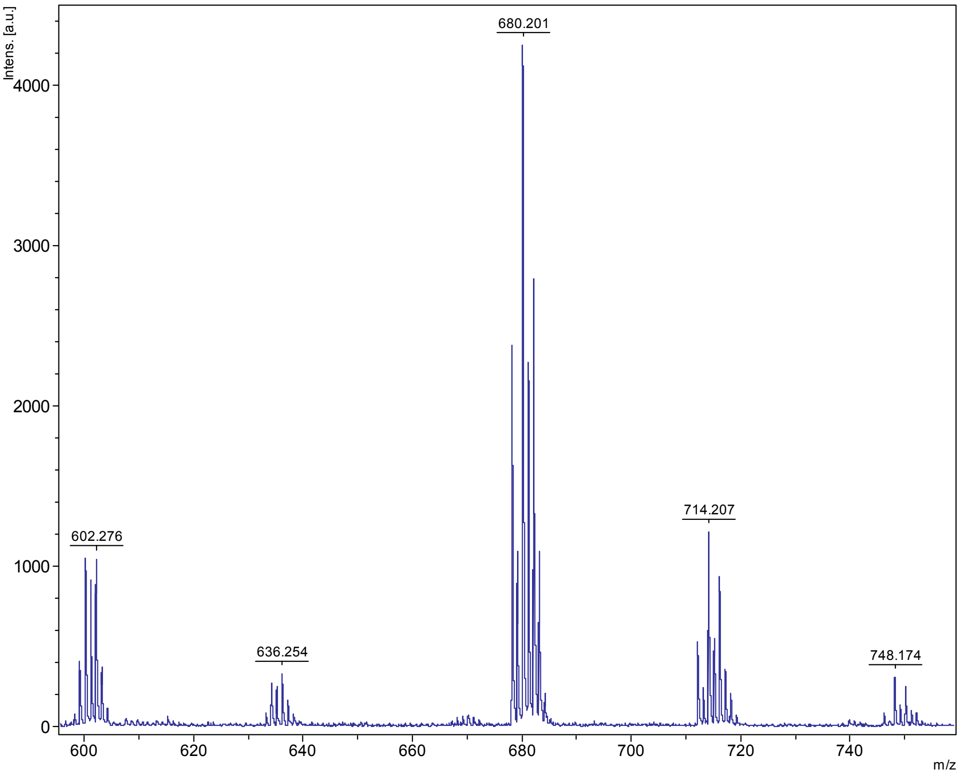


Figure S23. MALDI-MS of HBC derivative **3** (680 m/z) synthesised using $FeCl_3/CF_3SO_3H$. Chlorinated products were observed (714 and 748 m/z).

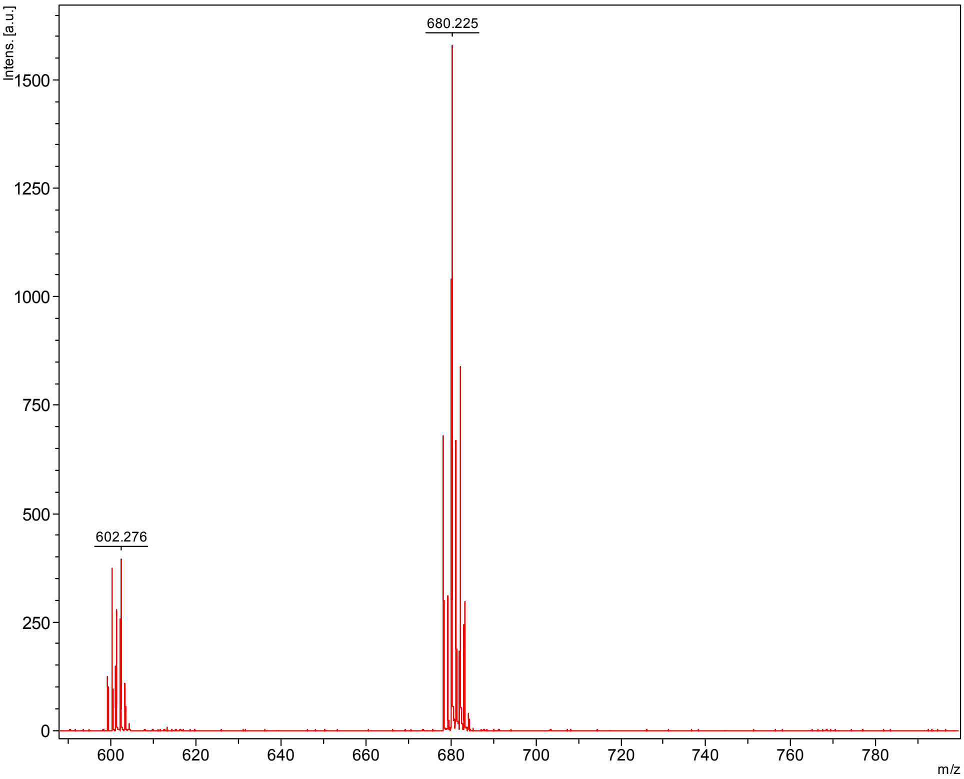


Figure S24. MALDI-MS of HBC derivative **3** (680 m/z) synthesised using DDQ/CF_3SO_3H. No chlorinated products were detected.

Thermal properties – TGA and DSC

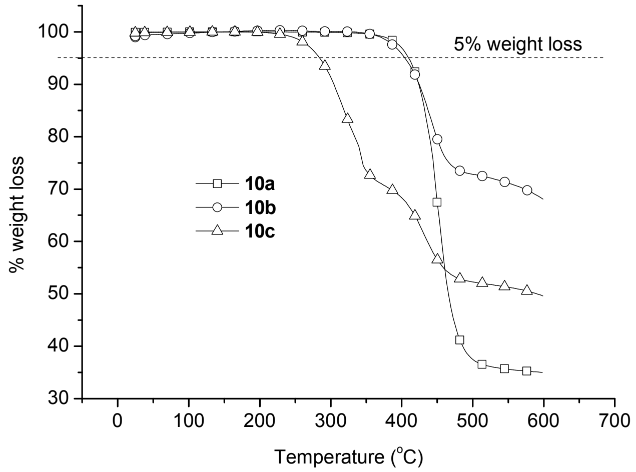


Figure S25. Thermal gravimetric analysis plots of fluorenyl HBC compounds **10a-c** showing percentage weight loss.

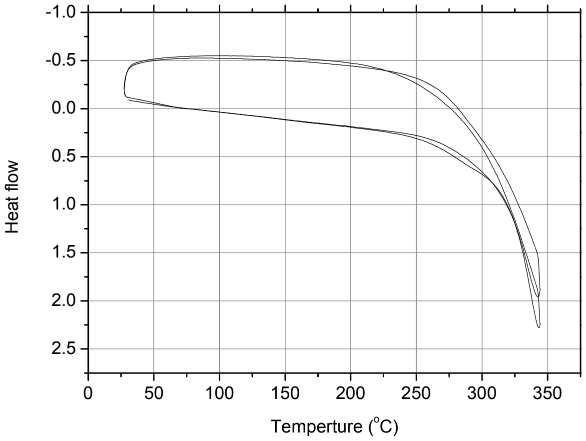


Figure S26. Differential scanning calorimetry data for HBC **10b** showing the second and third heat-cool cycles (10 °C/min).

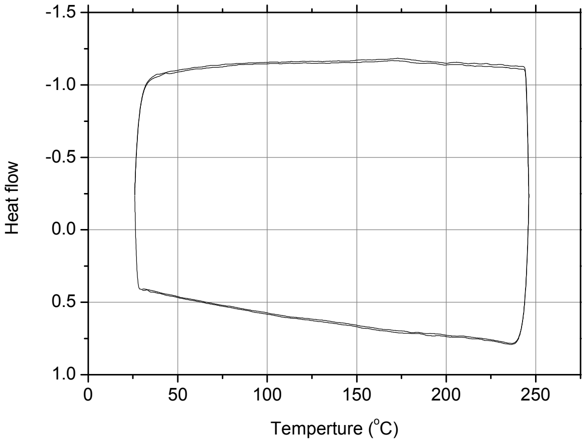


Figure S27. Differential scanning calorimetry data for HBC **10c** showing the second and third heat-cool cycles (10 °C/min).

UV-vis and fluorescence spectral data

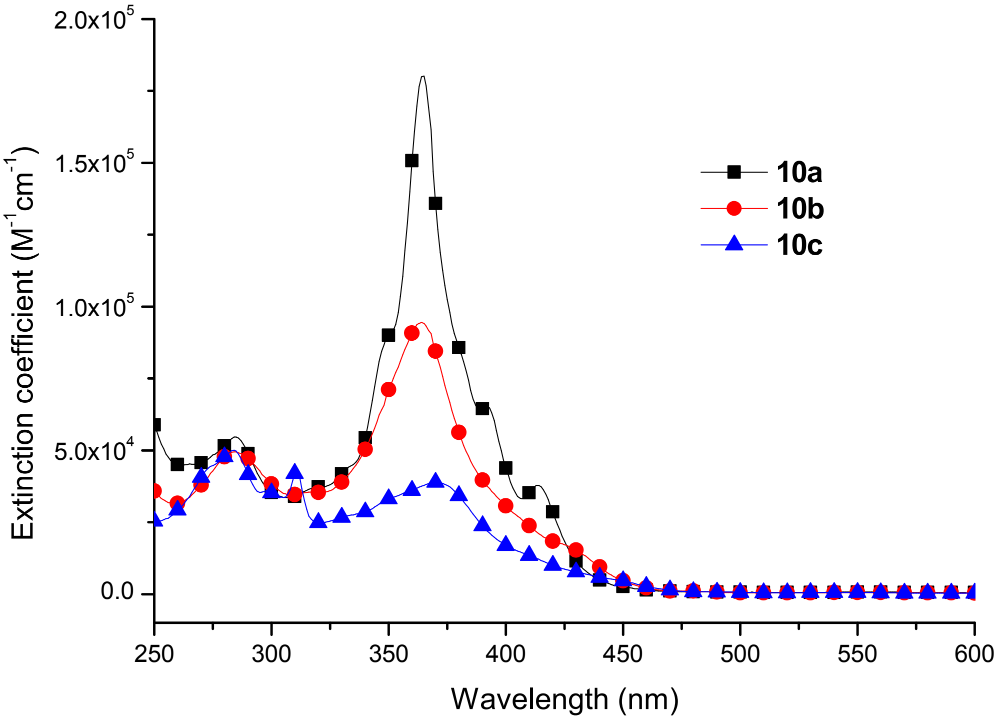


Figure S28. UV-vis spectrum of HBC compounds **10a-c** in chloroform solution.

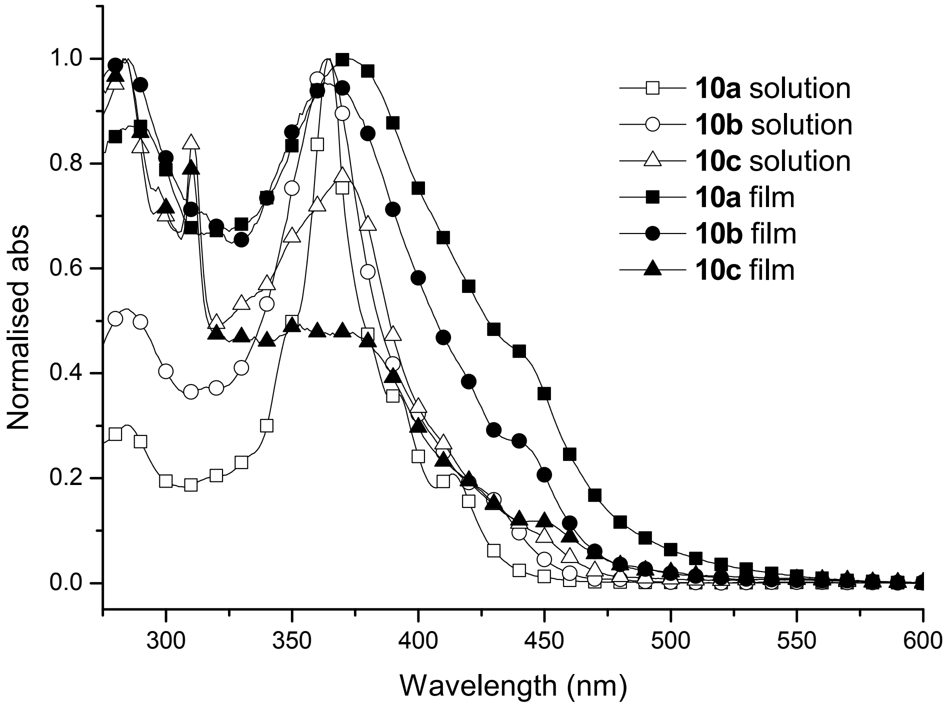


Figure S29. Normalized UV-vis spectrum of HBC compounds **10a-c** in solution and in solid state.

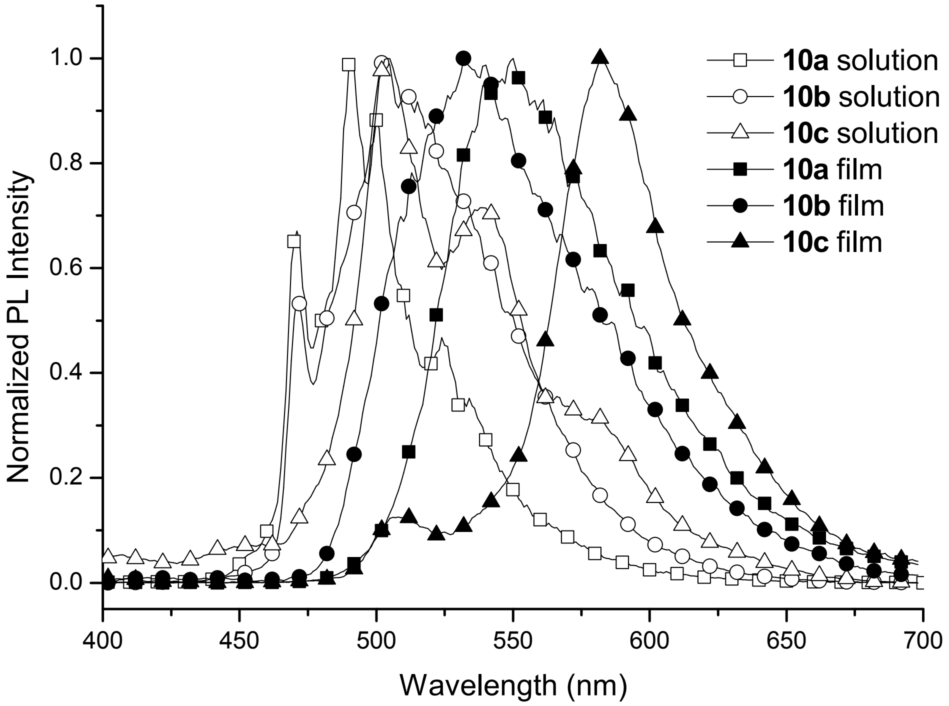


Figure S30. Normalized photoluminescence spectrum of HBC compounds **10a-c** in solution and in solid state.

Electrochemistry of fluorenyl HBC compounds 10a-c

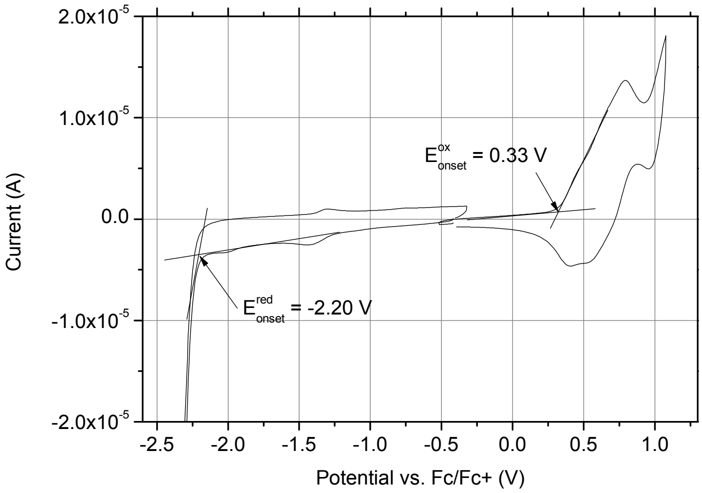


Figure S31. CV curve of **10a** in chlorobenzene/MeCN 10:1, 1 × 10^{-3} M, Bu_4NPF_6 (0.1 M), 295 K, scan rate = 50 mV·s^{-1}, versus Fc/Fc^+;

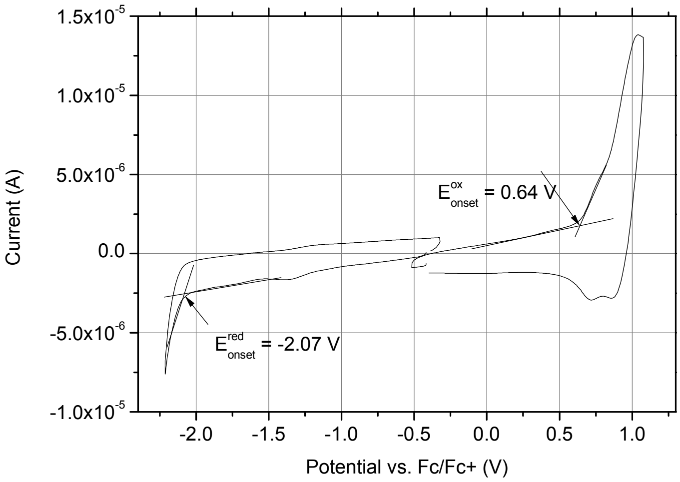


Figure S32. CV curve of **10b** in chlorobenzene/MeCN 10:1, 1 × 10^{-3} M, Bu_4NPF_6 (0.1 M), 295 K, scan rate = 50 mV·s^{-1}, versus Fc/Fc^+.

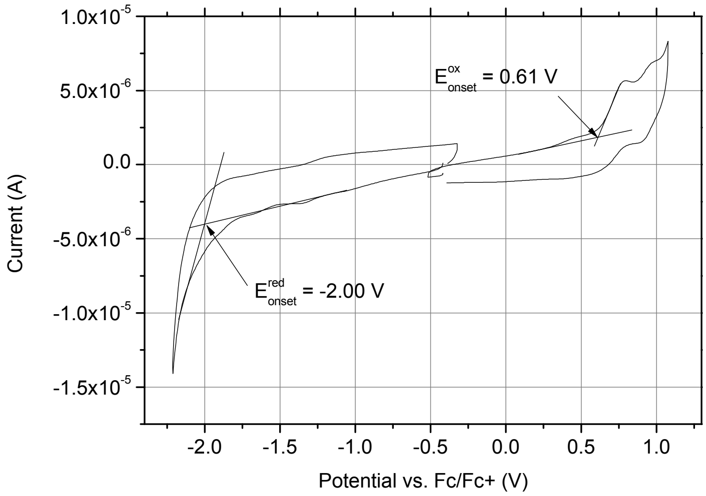


Figure S33. CV curve of **10c** in chlorobenzene/MeCN 10:1, 1 × 10^{-3} M, Bu_4NPF_6 (0.1 M), 295 K, scan rate = 50 mV·s^{-1}, versus Fc/Fc^+.

DFT calculations and energy level diagram

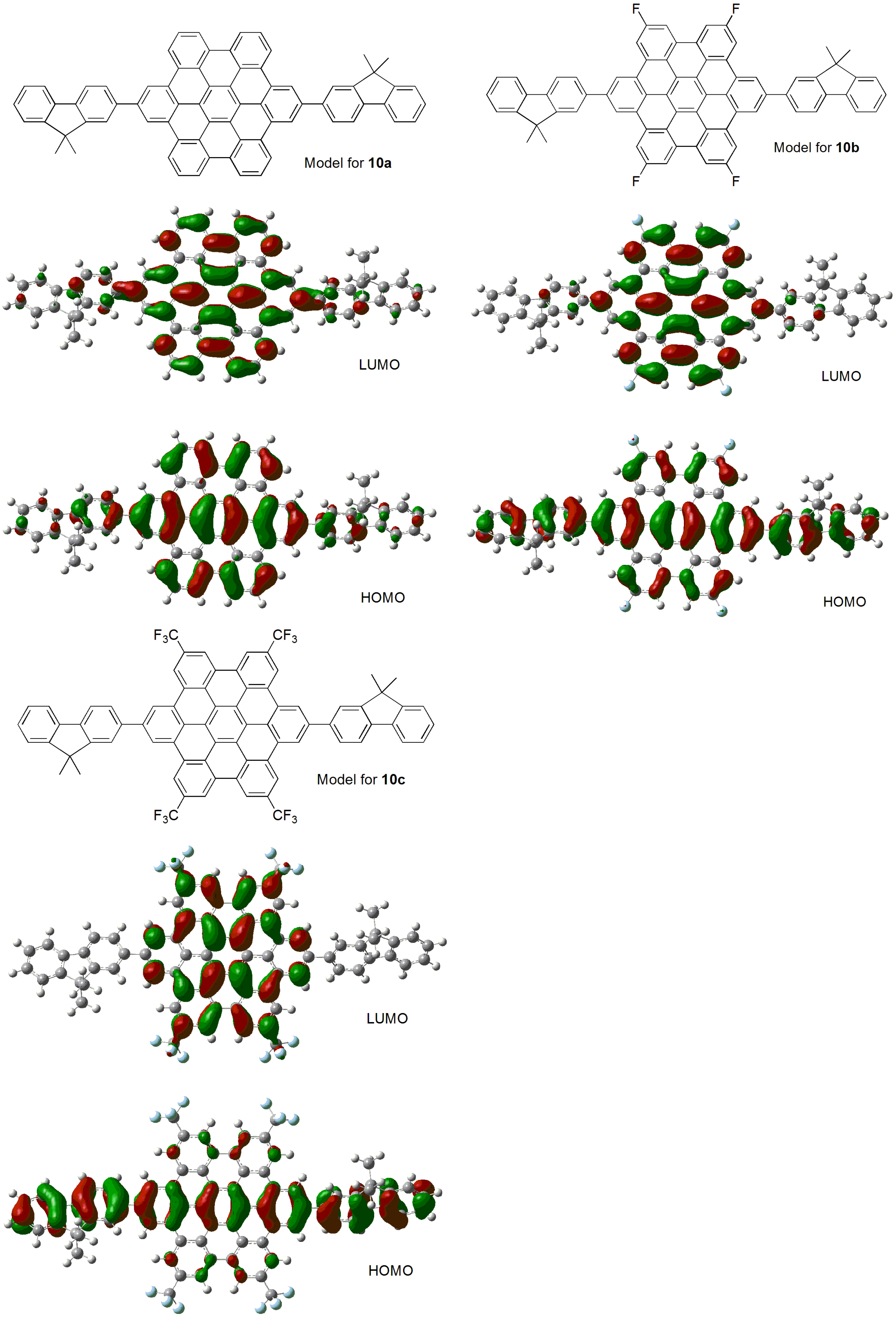


Figure S34. Models for HBC compounds **10a-c** and frontier orbital distribution calculated with DFT at the B3LYP/6-31G level using Gaussian 09W.[7]

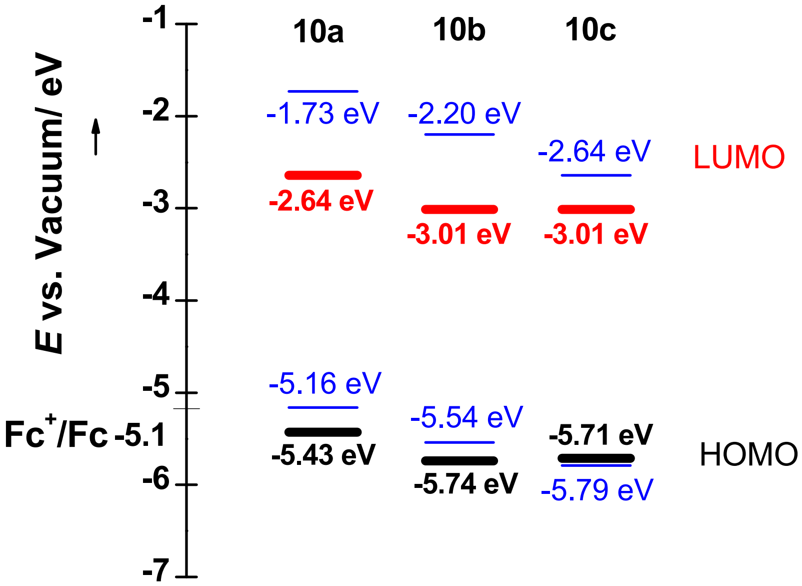


Figure S35. Energy level diagram of HBC compounds **10a-c** derived from electrochemical and UV-vis absorption data. Calculated energies are in blue.

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