Electronic Supplementary Information

A Planarized 9-Phenylanthracenes: A Simple Electron-Donating Building Block for Fluorescence Materials

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1. Experimental Details

General. Melting points (mp) were determined with a Yanaco MP-S3 instrument. Thermogravimetric analysis (TGA) was performed on a SII Exstar 6000 TG/DTA 6200 (Seiko) apparatus at a heating rate of 5 °C/min under a nitrogen atmosphere. ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were measured with a JEOL AL-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 128 MHz for ^{11}B, and 376 MHz for ^{19}F) in $CDCl_3$, CD_2Cl_2, 1,1,2,2-tetrachloroethane-d_2 or acetone-d_6. ^{13}C NMR spectra (150 MHz) of the compounds **10** and **12** were measured with a JEOL ECA 600 II spectrometer equipped with an UltraCOOL probe in $CDCl_3$. Chemical shifts are reported in δ ppm using $CHCl_3$ (7.26 ppm), CH_2Cl_2 (5.32 ppm), 1,1,2,2-tetrachloroethane (5.98 ppm), acetone (2.05 ppm) for ^{1}H NMR spectra and $CDCl_3$ (77.16 ppm), CD_2Cl_2 (53.84 ppm), 1,1,2,2-tetrachloroethane-d_2 (73.78 ppm), or acetone-d_6 (29.84 and 206.26 ppm) for ^{13}C NMR spectra as an internal standard. ^{11}B NMR and ^{19}F NMR spectra are reported using $BF_3{\cdot}OEt_2$ and CF_3CO_2H as an external standard. Mass spectrometry was performed with a Bruker Daltonics micrOTOF Focus with the APCI ionization method. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thickness of silica gel 60F_{254} (Merck). Column chromatography was performed using silica gel PSQ 100B (Fuji Silysia Chemical). Recycling preparative gel permeation chromatography (GPC) was performed with a LC-918 equipped with polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) using chloroform as an eluent. Dry THF, diethyl ether and DMF were purchased from Kanto Chemical. Dry 1,2-dichloroethane was purchased from Aldrich. Dry toluene was purchased from Kanto Chemical. Commercially available solvents and reagents were used as received. 2-Bromo-1,3-di(2-propenyl)benzene[1] and 1,4-diethynyltetrafluorobenzene[2] were prepared as described in the literature. All reactions were carried out under a nitrogen atmosphere.

9-[2,6-Di(2-propenyl)phenyl]anthracene (5). To a solution of 2-bromo-1,3-di(2-propenyl)benzene (3.55 g, 15.0 mmol) in diethyl ether (30 mL) was added a pentane solution of *t*-BuLi (1.77 M, 17.0 mL, 30.1 mmol) dropwise at –78 °C. After stirring for 1 h, the reaction mixture was warmed to room temperature and added dropwise to a suspension of anthrone (2.93 g, 15.1 mmol) in toluene (60 mL). The mixture was refluxed with stirring for 21 h. After cooling to room temperature, a saturated aqueous solution of NH_4Cl (40 mL) was added. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The organic extracts were dried over $MgSO_4$. After filtration, volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel using 4/1 hexane/toluene as an eluent (R_f = 0.48) to give 2.21 g (6.61

mmol) of **5** in 44% yield as white solids: mp. 182–183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 6H), 4.47–4.48 (m, 2H), 4.49–4.50 (m, 2H), 7.28–7.42 (m, 6H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 8.42 (s, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 24.4, 115.5, 126.1, 126.12, 127.6, 128.4, 128.5, 129.1, 129.41, 129.43, 131.9, 132.4, 134.3 146.3, 146.5; HRMS (APCI, positive) *m/z* calcd for $C_{26}H_{22}$ 334.1716, found: 334.1724.

Planarized 9-phenylanthracene 2. A mixture of **5** (1.34 g, 4.01 mmol) and $Sc(OTf)_3$ (966 mg, 1.96 mmol) in 1,2-dichloroethane (1 L) was refluxed with stirring for 4 h. After cooling to room temperature, water (300 mL) was added to the mixture. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with brine and dried over $MgSO_4$. After filtration, the mixture was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using 4/1 hexane/chloroform as an eluent (R_f = 0.50), followed by GPC to give 827 mg (2.47 mmol) of **2** in 62% yield as yellow solids: mp. 260 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79 (s, 12H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.51–7.60 (m, 6H), 7.84 (d, *J* = 8.0 Hz, 2H), 8.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.4, 39.1, 122.4, 122.6, 123.6, 125.0, 125.9, 126.0, 126.1, 126.4, 128.1, 131.7, 143.8, 144.1; HRMS (APCI, positive) *m/z* calcd for $C_{26}H_{22}$ 334.1716, found: 334.1707.

10-Bromo-substituted planarized 9-phenylanthracene 6. A mixture of **2** (337 mg, 1.01 mmol) and *N*-bromosuccinimide (215 mg, 1.21 mmol) in dichloromethane (20 mL) was stirred for 2 h at room temperature. After addition of water (10 mL), the organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over $MgSO_4$. After filtration, the mixture was concentrated under reduced pressure and purified by column chromatography on silica gel using 4/1 hexane/toluene as an eluent (R_f = 0.55) to give 355 mg (0.861 mmol) of **6** in 85% yield as yellow solids: mp. 280 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79 (s, 12H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.63–7.67 (m, 4H), 8.47 (dd, *J* = 7.6 Hz and *J* = 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ36.3, 39.4, 122.6, 123.0, 123.2, 124.5, 124.9, 125.6, 126.0, 127.5, 128.5, 130.5, 144.10, 144.15; HRMS (APCI, positive) *m/z* calcd for $C_{26}H_{21}{}^{79}Br$ 412.0827, found: 412.0821.

10-Dimesitylboryl-substituted planarized 9-phenylanthracene 7. To a solution of **6** (103 mg, 0.250 mmol) in THF (5 mL) was added a pentane solution of *t*-BuLi (1.77 M, 0.28 mL, 0.50 mmol) at –78 °C.

After stirring for 15 min, a solution of dimesitylfluoroborane (67.2 mg, 0.251 mmol) in THF (2 mL) was added. The mixture was allowed to warm to room temperature and futher heated under refluxing conditions for 20 h. After cooling to room temperature, water (10 mL) was added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using 4/1 hexane/chloroform as an eluent ($R_f = 0.35$) to give 73.8 mg (0.127 mmol) of **7** in 51% yield as yellow solids: mp. 250 °C (decomp.); ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2, 80 °C) δ 1.80 (s, 12H), 1.97 (s, 12H), 2.32 (s, 6H), 6.79 (s, 4H), 7.29 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H), 7.54–7.61 (m, 4H), 7.98 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ21.4, 23.6, 36,1, 39.3, 122.1, 123.2, 124.7, 125.2, 126.6, 128.3, 129.1, 134.0, 139.6, 140.97, 140.99, 141.2, 143.8, 144.4, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 75.6; HRMS (APCI, positive) m/z calcd for $C_{44}H_{43}B$: 582.3452, found: 582.3475.

10-Formyl-substituted planarized 9-phenylanthracene 8. To a solution of **6** (203 mg, 0.492 mmol) in THF (10 mL) was added a pentane solution of t-BuLi (1.61 M, 0.62 mL, 1.0 mmol) dropwise at –78 °C. After stirring for 30 min, DMF (0.12 mL, 1.5 mmol) was added. The mixture was stirred for 1 h at the same temperature. After addition of water (10 mL), the organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The mixture was purified by column chromatography on silica gel using 1/1 hexane/chloroform as an eluent ($R_f = 0.39$) to give 82.3 mg (0.227 mmol) of **8** in 46% yield as orange solids: mp. 260 °C (decomp.); ^{1}H NMR (400 MHz, acetone-d_6) δ 1.82 (s, 12H), 7.56 (t, J = 8.0 Hz, 1H), 7.77–7.81 (m, 4H), 7.89 (t, J = 7.2 Hz, 2H), 8.91 (d, J = 8.8 Hz, 2H), 11.45 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.1, 39.4, 121.3, 122.8, 123.2, 124.8, 125.0, 125.1, 128.9, 129.8, 130.3, 132.4, 144.6, 145.6, 193.3; HRMS (APCI) m/z calcd for $C_{27}H_{22}O$ 362.1665, found: 362.1655.

10-Cyano-substituted planarized 9-phenylanthracene 9. To a stirring solution of **8** (100 mg, 0.276 mmol) in 28% aqueous ammonia (5 mL) and THF (10 mL) was added iodine (227 mg, 0.894 mmol) one portion. The mixture was stirred at 60 °C for 22 h. After cooling to room temperature, a saturated aqueous solution of sodium thiosulfate (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was purified by column chromatography on silica gel using 1/1 hexane/chloroform as an eluent (R_f = 0.33) to give 60.7 mg (0.169 mmol) of **9** in 61% yield as orange solids: mp. 275–276 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 12H), 7.50 (t, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.71–7.78 (m, 4H), 8.32 (dd, J = 8.4 Hz and J = 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.4, 39.4, 104.5, 118.5, 122.7, 123.40, 123.44, 124.6, 125.34, 125.35, 129.0, 130.0, 133.6, 144.9, 145.5; HRMS (APCI) *m*/*z* calcd for $C_{27}H_{22}N$ 359.1674, found: 359.1685.

Bis(planarized 9-phenylanthryl)-capped 1,4-diethynyl-2,3,4,5-tetrafluorophenylene 10. A mixture of **6** (106 mg, 0.256 mmol), 1,4-diethynyltetrafluorobenzene (25.6 mg, 0.129 mmol), $Pd(PhCN)_2Cl_2$ (7.2 mg, 0.010 mmol), P(*t*-Bu)$_3$ (5.4 mg, 0.027 mmol), CuI (4.0 mg, 0.021 mmol), and HN(*i*-Pr)$_2$ (0.5 mL, 3.57 mmol) in toluene (10 mL) was refluxed with stirring for 44 h. After cooling to room temperature, water (5 mL) was added. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was washed with $CHCl_3$ and dried *in vacuo* to give 10.2 mg (0.012 mmol) of **10** as a pure form in 9% yield as dark red solids: mp. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 (s, 24H), 7.46 (t, ^3J = 8.0 Hz 2H), 7.63 (d, J = 8.0 Hz, 4H), 7.71–7.78 (m, 8H), 8.62 (d, J = 8.0 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 36.4, 39.3, 87.0, 102.3, 114.8, 122.2, 123.1, 123.2, 124.5, 125.1, 125.4, 125.9, 127.9, 120.1, 133.1, 144.5, 145.0, 145.7, 147.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –54.1 (s); HRMS (APCI) *m*/*z* calcd for $C_{62}H_{42}F_4$ 862.3217 found: 863.3200.

Tris(planarized 9-phenylanthryl)borane 11. To a solution of **6** (124 mg, 0.301 mmol) in THF (6 mL) was added a pentane solution of *t*-BuLi (1.77 M, 0.34 mL, 0.60 mmol) dropwise at –78 °C. After stirring for 2 h, a solution of $BF_3{\cdot}OEt_2$ (0.013 mL, 0.10 mmol) in THF (2 mL) was added. The mixture was stirred for 19 h at room temperature. After addition of water (10 mL), the precipitates was collected by filtration and washed successively with water and diethyl ether, and dried *in vacuo* to give 43.1 mg (0.0426 mmol) of **11** in 43% yield as red solids: mp. >300 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.74 (s, 36H), 7.01 (t, J = 8.0 Hz, 6H), 7.43 (t, J = 7.6 Hz, 3H), 7.48 (d, J = 7.6 Hz, 6H), 7.60 (d, J = 8.0 Hz, 6H), 8.20 (d, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.2, 39.5, 122.6, 123.6, 125.1, 126.16, 126.20, 126.3, 126.9, 128.9, 134.8, 144.5, 144.9, one signal for the carbon atom bound to the boron atom were not observed due to the quadrupolar relaxation; HRMS (APCI) *m*/*z* calcd for $C_{78}H_{63}{}^{11}B$ 1010.5017, found: 1010.5067.

1,2,4,5-Tetrafluoro-3,6-bis[(9-phenylanthryl)ethynyl]benzene 12. A mixture of 9-bromo-10-phenylanthracene (0.255 mmol, 85.0 mg), 1,4-diethynyltetrafluorobenzene (0.126 mmol, 25.0 mg), $Pd(PPh_3)_2Cl_2$ (0.0256 mmol, 18.0 mg), CuI (0.121 mmol, 24.0 mg), and $HN(i\text{-}Pr)_2$ (0.5 mL, 3.57 mmol) in THF (10 mL) was refluxed with stirring for 90 h. After cooling to room temperature, the solution was filtered to remove precipitates of diisopropylammonium bromide and the mixture solution was washed with water. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over Na_2SO_4. After filtration, the mixture was concentrated under reduced pressure and purified by column chromatography on silica gel using 10/1 hexane/chloroform as an eluent (R_f = 0.25) to give 8.1 mg (0.0115 mmol) of **12** in 9% yield as orange solids: mp. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.47 (m, 8H), 7.58–7.62 (m, 6H), 7.67–7.73 (m, 8H), 8.77 (d, ^3J = 8.8 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 86.6, 101.3, 115.6, 126.0, 126.6, 127.3, 127.4, 127.5, 127.8, 128.0, 128.6, 130.1, 131.2, 131.6, 132.8, 138.4, 140.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –53.7 (s); HRMS (APCI) *m/z* calcd for $C_{50}H_{26}F_4$ 702.1965 found: 702.1961.

2. Photophysical Properties

UV-vis absorption spectra and fluorescence spectra were measured with a Shimadzu UV-3150 spectrometer and a Hitachi F-4500 spectrometer, respectively, in spectral grade solvents. Fluorescence quantum yields were determined with a Hamamatsu Absolute PL Quantum Yield spectrometer C11347 and C9920-02 calibrated integrating sphere system. Fluorescence lifetime was measured with a Hamamatsu Picosecond fluorescence measurement system C4780.

Table S1 Photophysical Data for **2** and **3** in Cyclohexane

compd	λ_{abs} / nm	ε / M^{-1}cm^{-1}	λ_{em} / nm	Stokes shift / cm^{-1}	Φ_F[a]	τ / ns	k_r / 10^7 s^{-1}	k_{nr} / 10^7 s^{-1}
2	443	21900	446	152	0.92	9.7	9.48	0.825
3	384	9400	394	661	0.51	6.6	7.73	7.42

[a] Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within ±3% error.

Table S2 Photophysical Data for **7–12** in Various Solvents

compd	solvent	λ_{abs} / nm	ε / M^{-1}cm^{-1}	λ_{em} / nm	Stokes shift / cm^{-1}	Φ_F[a]
7	cyclohexane	486	18900	527	1600	0.88
	THF	485	21800	540	2100	0.80
	DMF	486	16100	549	2360	0.69
	acetone	483	16700	545	2360	0.63
8	cyclohexane	469	13800	573	3850	0.45
	THF	474	13600	596	4340	0.34
	DMF	476	13300	617	4830	0.25
	acetone	471	13400	607	4750	0.25
9	cyclohexane	477	13000	489	514	0.94
	THF	484	12700	506	1020	0.88
	DMF	488	11200	519	1220	0.84
	acetone	483	11100	512	1170	0.87
10	toluene	554	77300	571	538	0.72
	THF	553	67700	583	930	0.67
11	cyclohexane	547	23400	632	2460	0.21
	THF	552	29300	646	2640	0.03

12	toluene	479	35700	495	675	0.89

[a] Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within ±3% error.

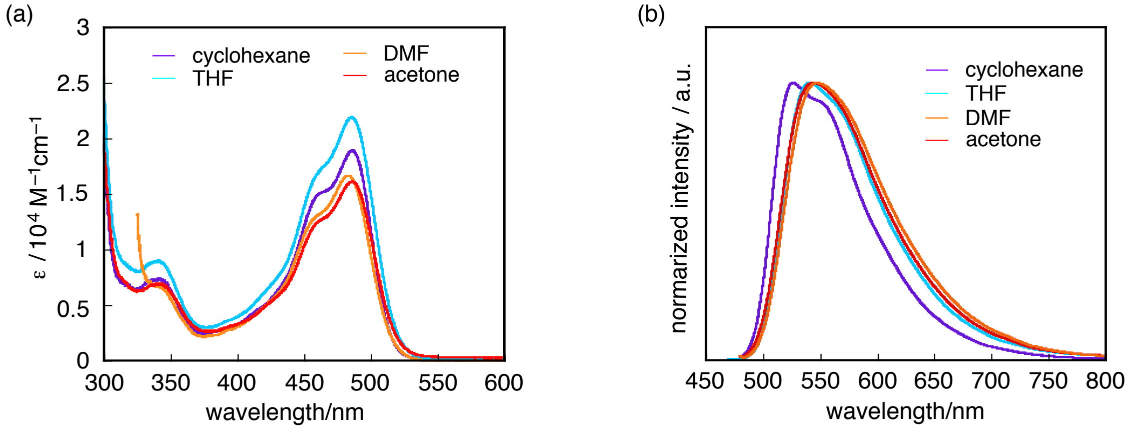

Fig. S1 (a) UV-vis absorption and (b) fluorescence spectra of **7** in various solvents.

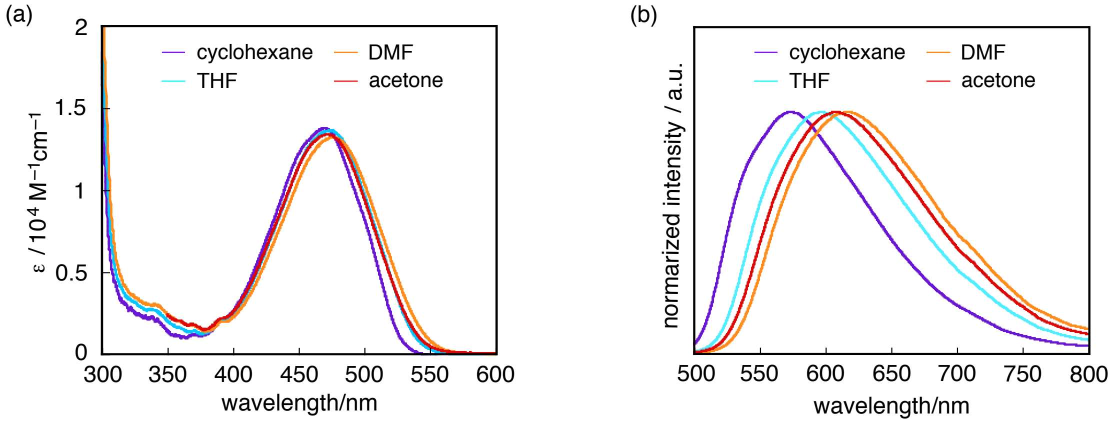

Fig. S2 (a) UV-vis absorption and (b) fluorescence spectra of **8** in various solvents.

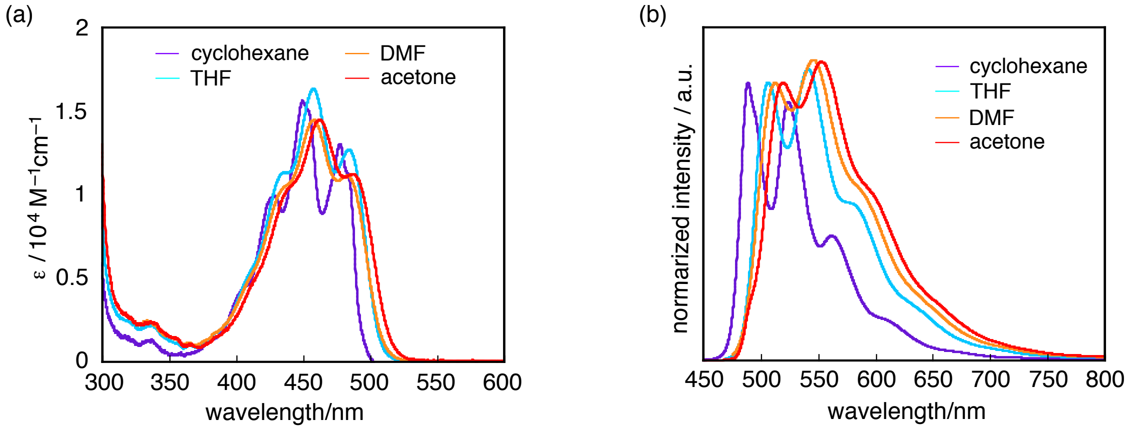

Fig. S3 (a) UV-vis absorption and (b) fluorescence spectra of **9** in various solvents.

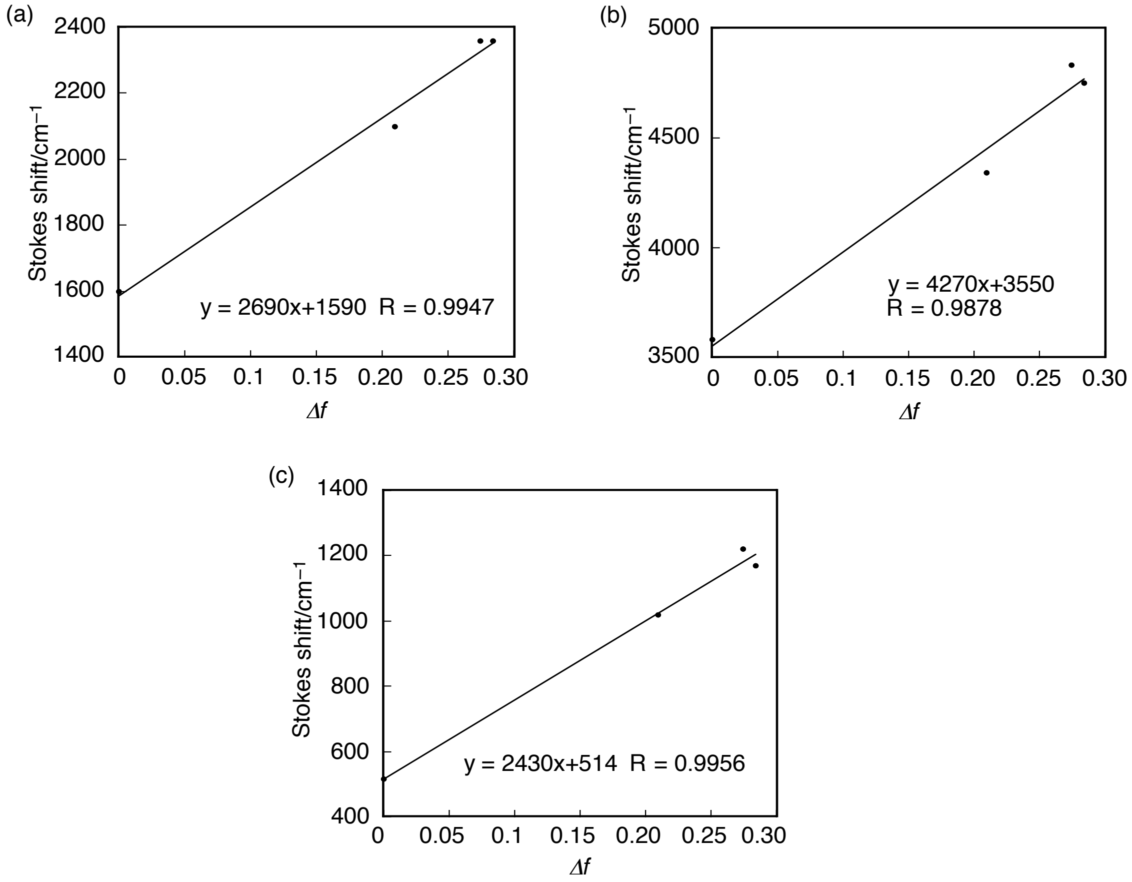

Fig. S4 Lippert-Mataga plots of (a) **7**, (b) **8**, and (c) **9**.

Table S3 Dipole Moments (μ_e) of **7**–**9** in the Excited State Obtained Based on the Lippert-Mataga Plots

compd	radius[a] / Å	gradient / cm^{-1}	$\Delta\mu_{e-g}$ / D	μ_g[b] / D	μ_e / D
7	6.67	2690	8.89	0.32	9.21
8	5.63	4270	8.69	4.92	13.7
9	5.78	2430	6.82	6.04	12.9

[a]Calculated at the MP2/6-31G(d) level. [b]Calculated at the B3LYP/6-31G(d) level.

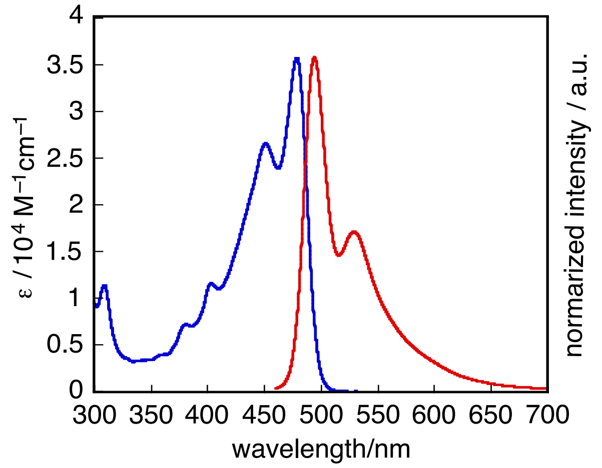

Fig. S5 UV-vis absorption (blue) and fluorescence spectra (red) of **12** in toluene.

3. Cyclic Voltammetry

Cyclic voltammetry (CV) was performed on an ALS/chi-617A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a Ag/AgNO$_3$ reference electrode. The measurements were carried out under an argon atmosphere using a THF solution of sample with a concentration of 0.1 mM, and 0.1 M tetrabutylammonium hexafluorophosphate (Bu$_4$N$^+$PF$_6^-$) as a supporting electrolyte with a scan rate of 0.1 V/s. The redox potentials were calibrated with ferrocene as an internal standard.

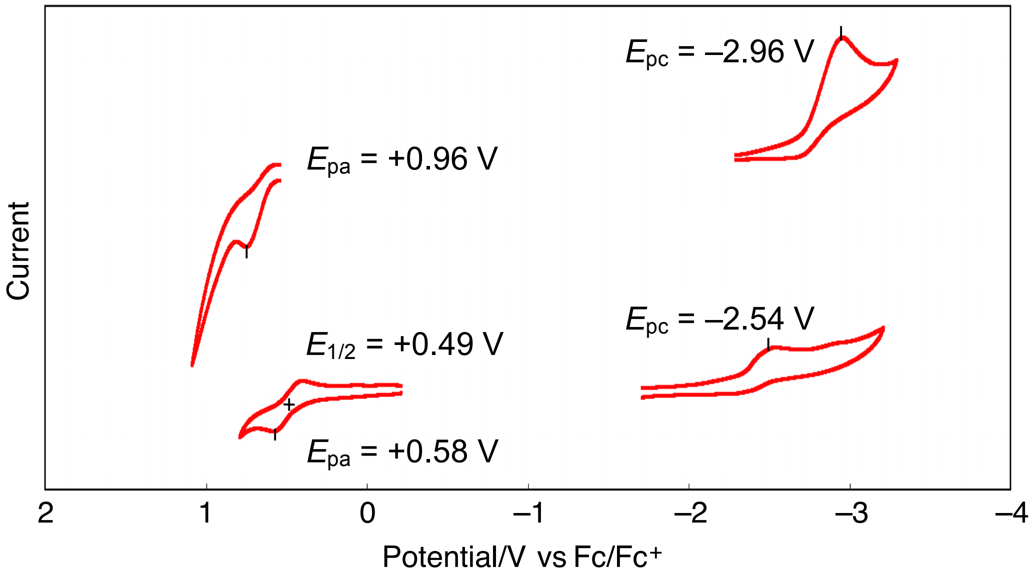

Fig. S6 Cyclic voltammograms of **3** (top) and **2** (bottom) in THF with Bu$_4$N$^+$PF$_6^-$ (0.1 M) as a supporting electrolyte at a scan rate of 0.1 V/s.

4. Thermogravimetric Analysis

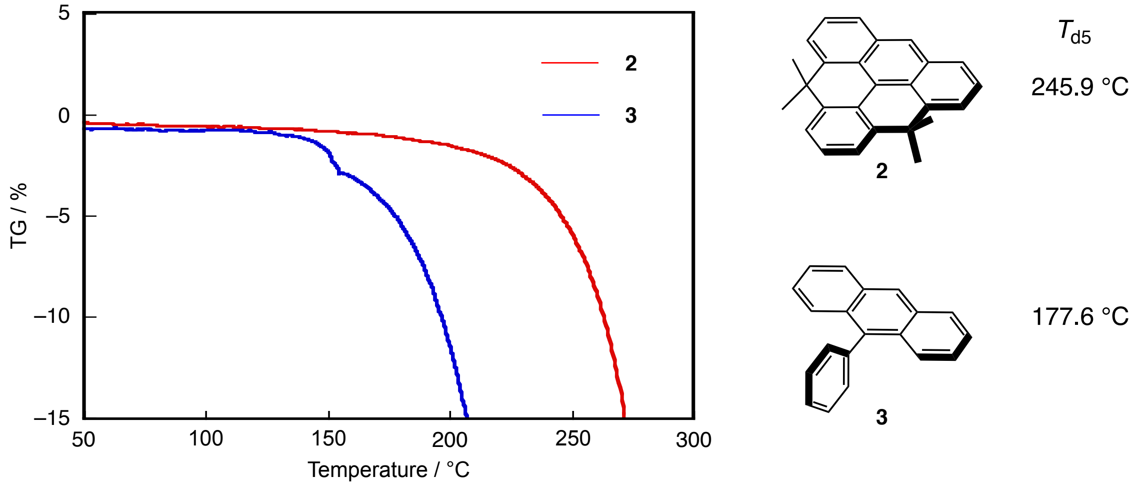

Fig. S7 Thermogravimetric analysis of **2** (red line) and **3** (blue line) with their 5% weight loss temperatures.

5. X-Ray Crystallographic Analysis

Structural analysis of 2. Single crystals of **2** were grown by slow evaporation from diethyl ether. The intensity data were collected on a Rigaku Saturn CCD diffractometer with VariMax monochromator MoKα radiation (λ = 0.71070 Å) at 123 K. A total of 5694 reflections were measured at the maximum 2θ angle of 50°, of which 1543 were independent reflections (R_{int} = 0.0239). The structure was solved by direct methods (SHELXS-97)[3] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[3] While all hydrogen atoms were placed using AFIX instructions, all the other atoms were refined anisotropically. The crystal data are as follows: $C_{26}H_{22}$; FW = 334.44, Orthorhombic, $C222_1$, a = 9.937(4) Å, b = 17.673(7) Å, c = 10.223(4) Å, V = 1795.3(12) Å^3, Z = 4, D_{calcd} = 1.237 g cm^{-3}. The refinement converged to R_1 [I>2σ(I)] = 0.0392, wR_2 (all data) = 0.1054, GOF = 1.107.

Structural analysis of 3. Single crystals of **3** were grown by slow evaporation from dichloromethane. The intensity data were collected on a Rigaku Saturn CCD diffractometer with VariMax monochromator MoKα radiation (λ = 0.71070 Å) at 123 K. A total of 4223 reflections were measured at the maximum 2θ angle of 50°, of which 2241 were independent reflections (R_{int} = 0.0614). The structure was solved by direct methods (SHELXS-97)[3] and refined by full-matrix least-squares procedures on F^2 for all reflections (SIR2002/SIR2004).[3] While all hydrogen atoms were placed using AFIX instructions, all other atoms were refined anisotropically. The crystal data are as follows: $C_{20}H_{14}$; FW = 254.31, Triclinic, P-1, a = 6.247(6) Å, b = 10.259(11) Å, c = 10.779(11) Å, V = 654.7(12) Å^3, Z = 2, D_{calcd} = 1.290 g cm^{-3}. The refinement converged to R_1 [I>2σ(I)] = 0.1195, wR_2 (all data) = 0.2975, GOF = 0.962.

Crystallographic data of **2** and **3** have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1427121 and 1427122. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

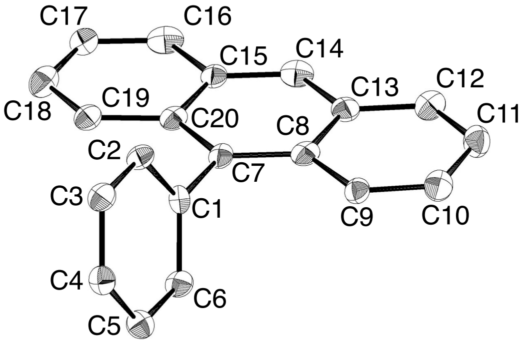

Fig. S8 *ORTEP* drawing of **3** (50% probability for thermal ellipsoids). Selected bond length (Å) and angle (deg): C1–C7, 1.501(5); C8–C7–C1–C6, –73.2(5).

6. Theoretical Calculations

Theoretical calculations of **2**, **3, 7, 8, 9, 10,** and **11** in the ground state were conducted using the Gaussian 09 program.[4] The geometries optimized at the B3LYP/6-31G(d) level of theory were used for the TD-DFT calculations at the B3LYP/6-31G(d) level of theory.

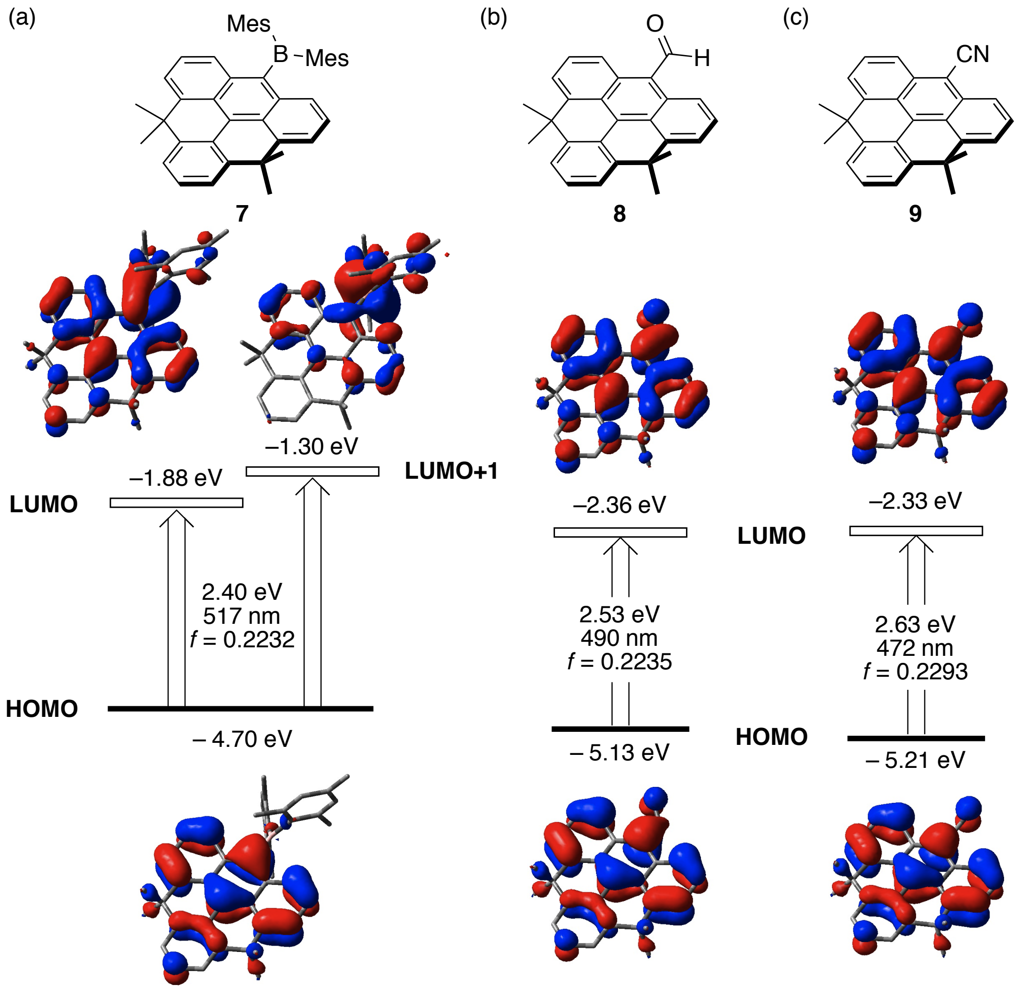

Fig. S9 Kohn-Sham plots and energy levels of frontier molecular orbitals of (a) **7**, (b) **8**, and (c) **9**, together with the transition energies obtained by the TD DFT calculations at the B3LYP/6-31G(d) level of theory.

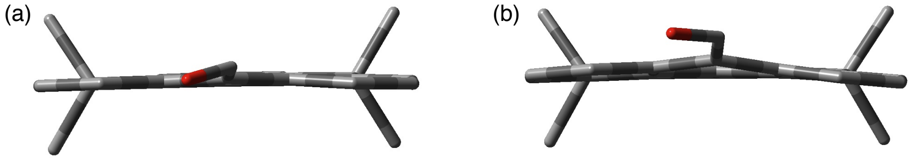

Fig. S10 Optimized structures of **8** calculated at the CAM-B3LYP/6-31G(d) level of theory (a) in the ground state (S_0) and (b) in the lowest excited singlet state (S_1).

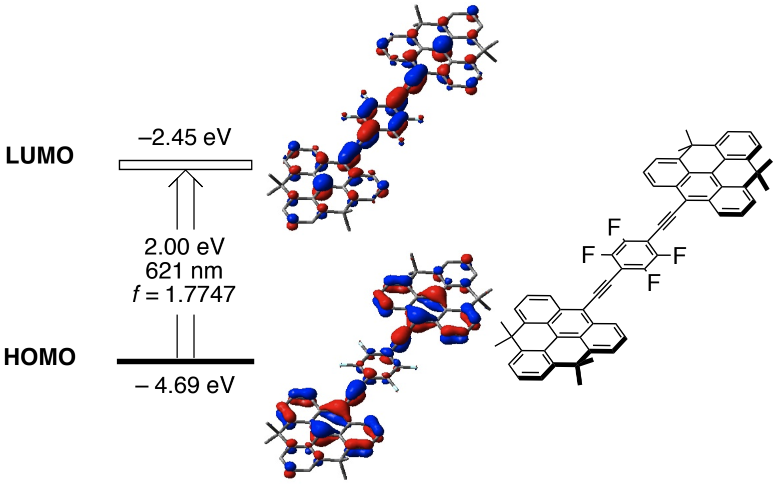

Fig. S11 Kohn-Sham plots and energy levels of HOMO and LUMO of **10**, together with the transition energy obtained by the TD DFT calculation at the B3LYP/6-31G(d) level of theory.

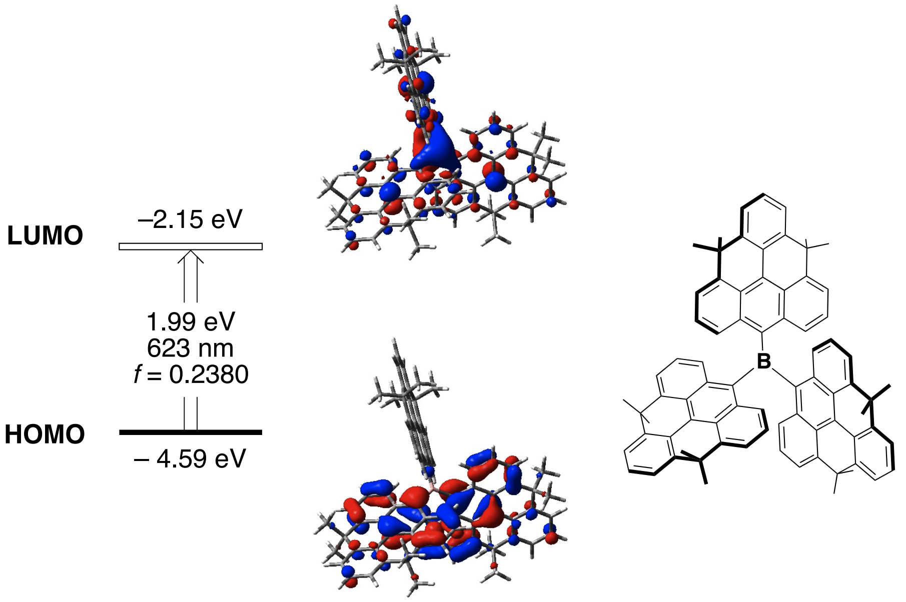

Fig. S12 Kohn-Sham plots and energy levels of HOMO and LUMO of **11** together with the transition energy obtained by the TD DFT calculation at the B3LYP/6-31G(d) level of theory.

7. References

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8. NMR Spectra

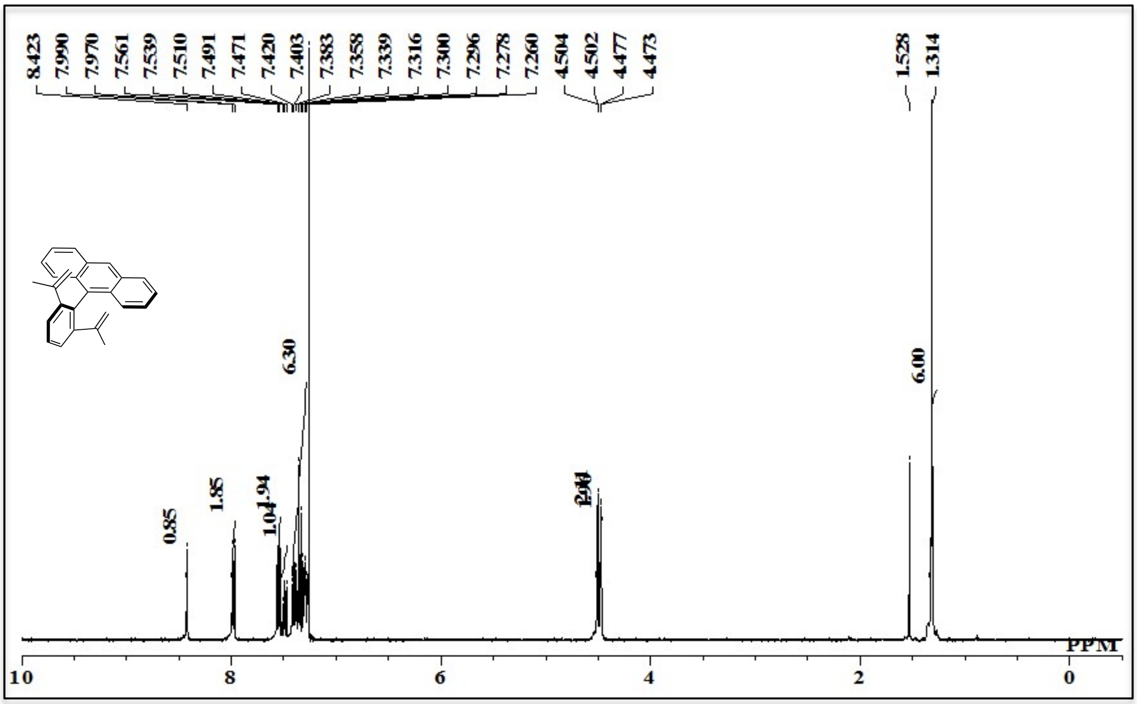

Fig. S13 ^{1}H NMR spectrum (400 MHz) of **5** in $CDCl_3$.

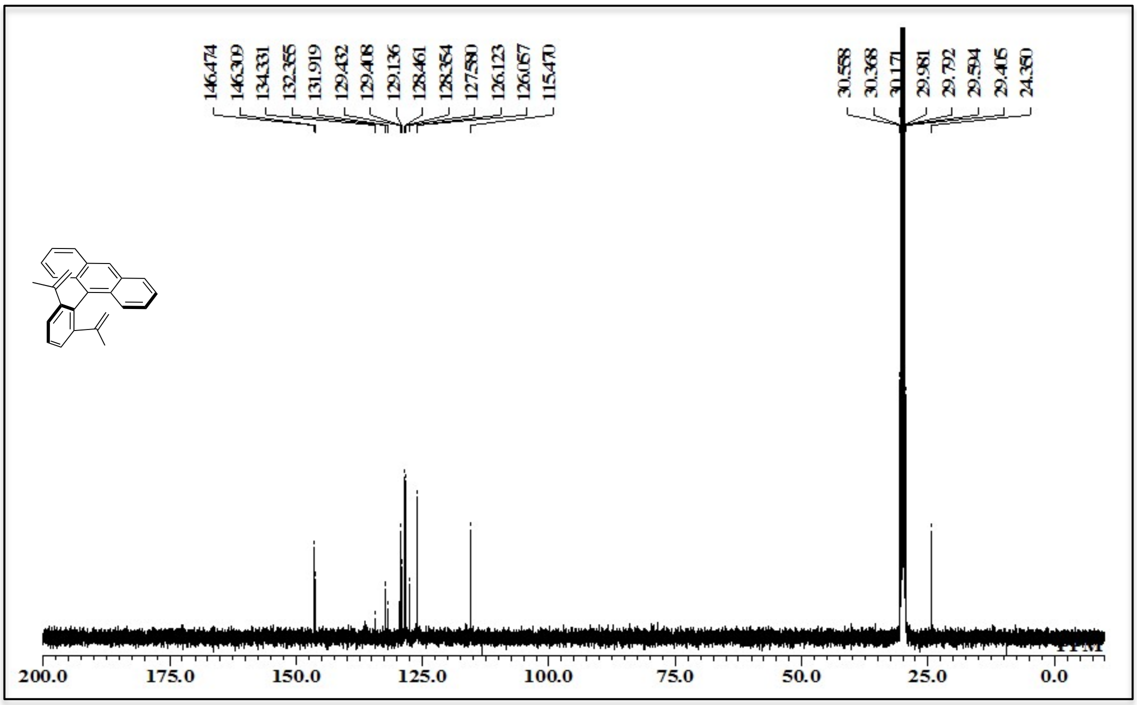

Fig. S14 ^{13}C NMR spectrum (100 MHz) of **5** in acetone-d_6.

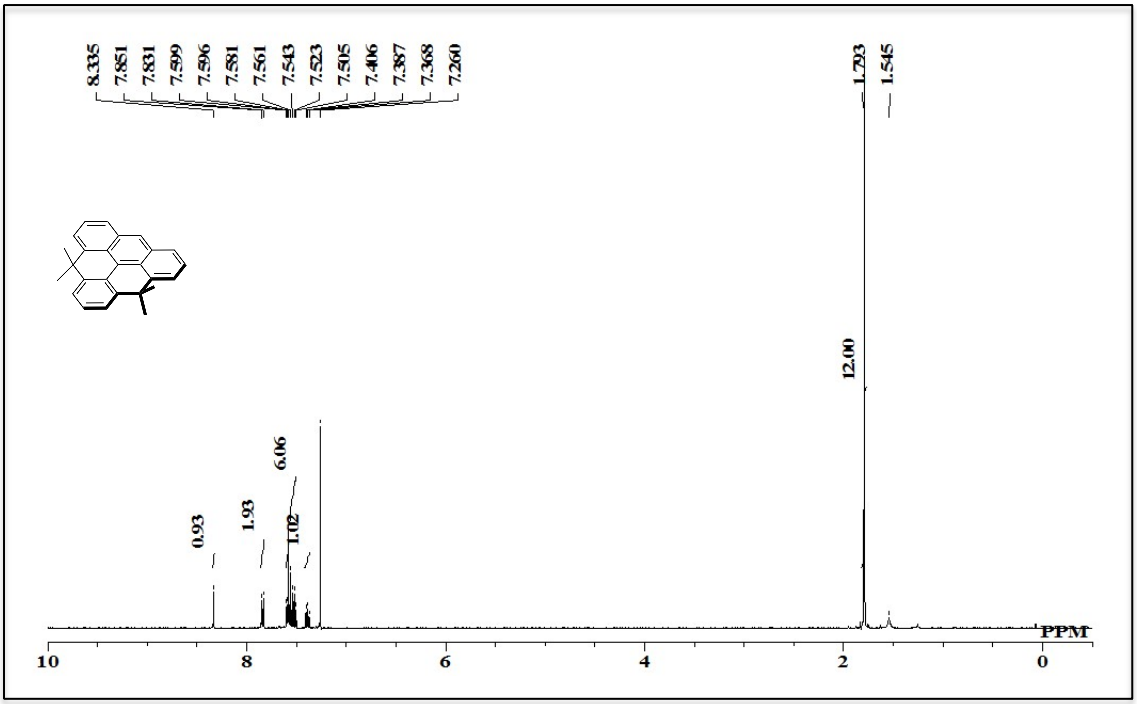

Fig. S15 ^{1}H NMR spectrum (400 MHz) of **2** in CDCl$_3$.

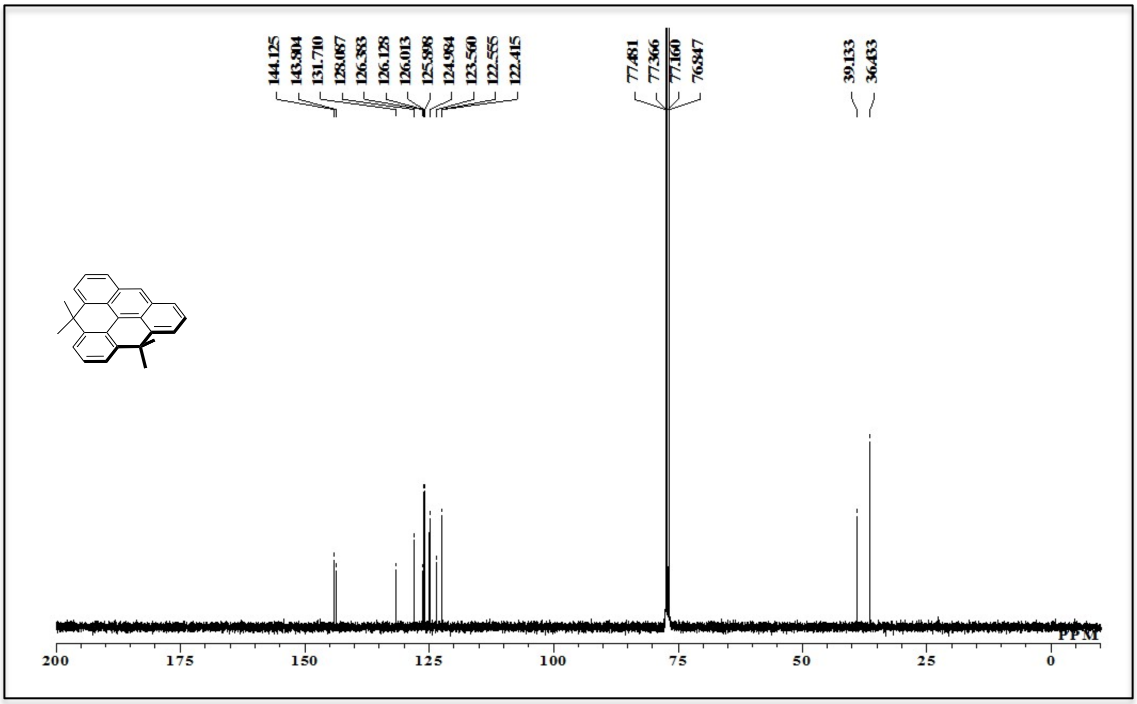

Fig. S16 ^{13}C NMR spectrum (100 MHz) of **2** in CDCl$_3$.

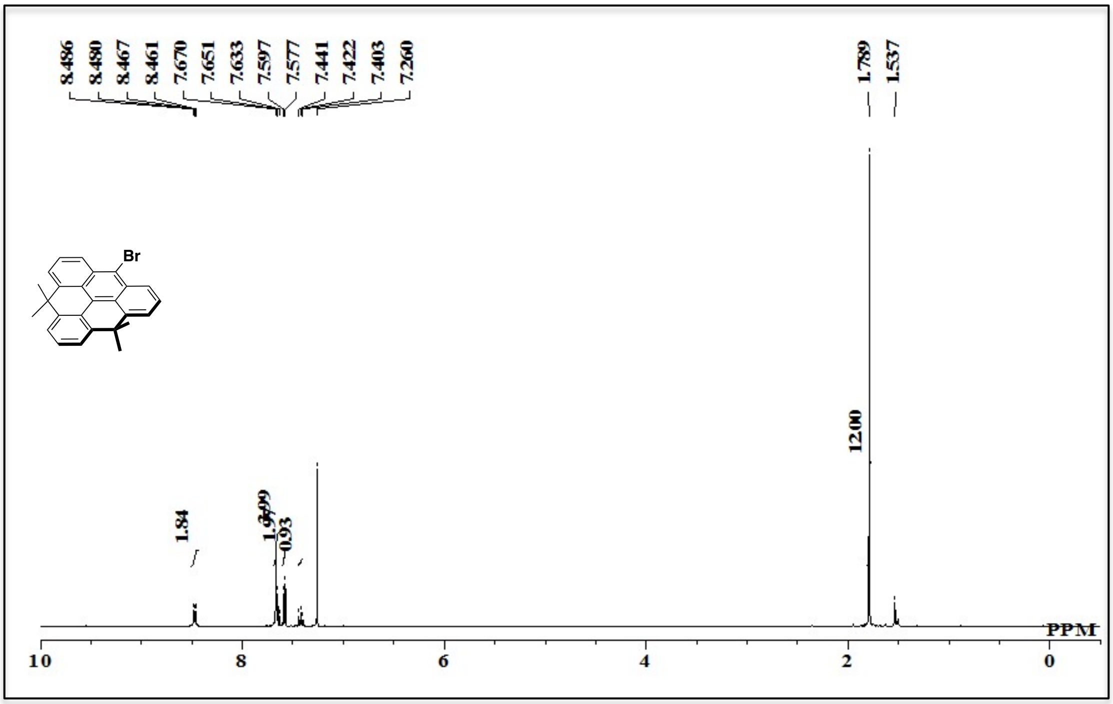

Fig. S17 ^{1}H NMR spectrum (400 MHz) of **6** in $CDCl_3$.

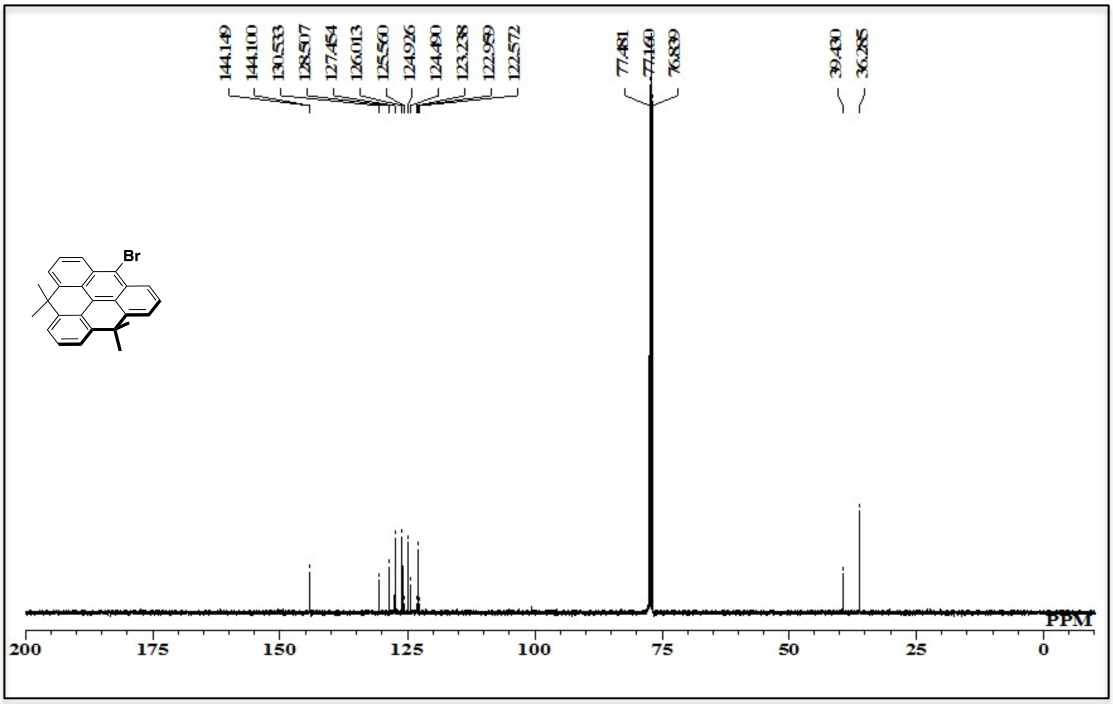

Fig. S18 ^{13}C NMR spectrum (100 MHz) of **6** in $CDCl_3$.

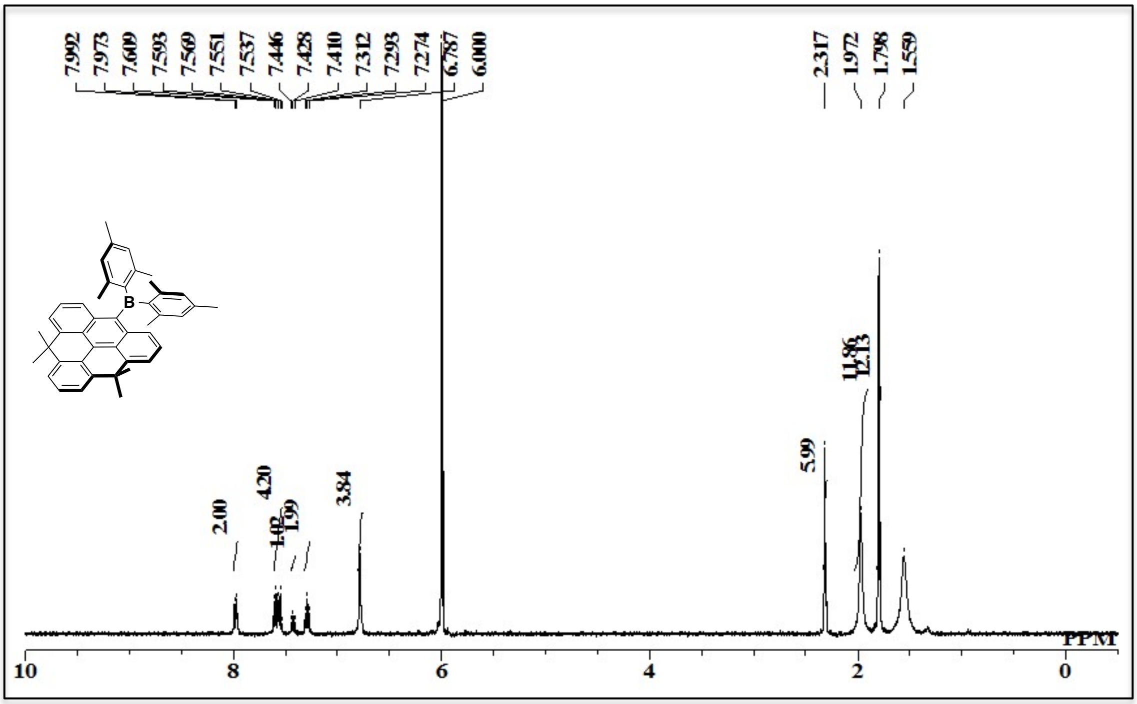

Fig. S19 ^{1}H NMR spectrum (400 MHz) of **7** in 1,1,2,2-tetrachloroethane-d_2.

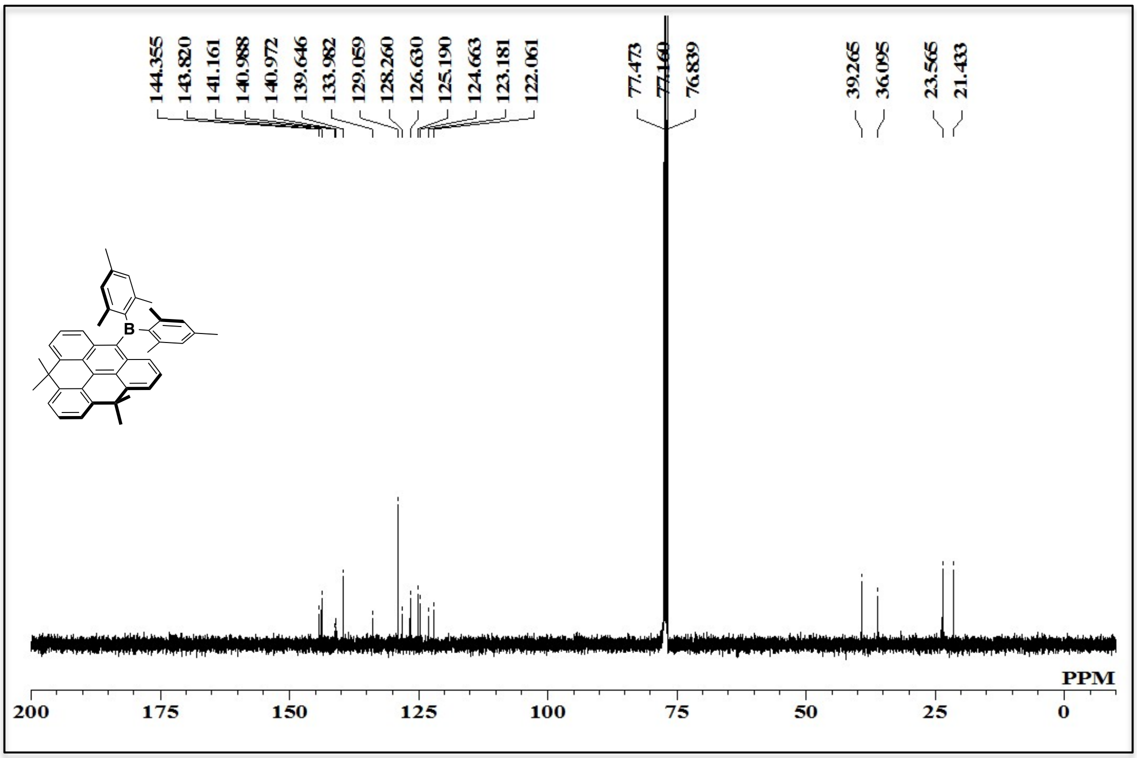

Fig. S20 ^{13}C NMR spectrum (100 MHz) of **7** in $CDCl_3$.

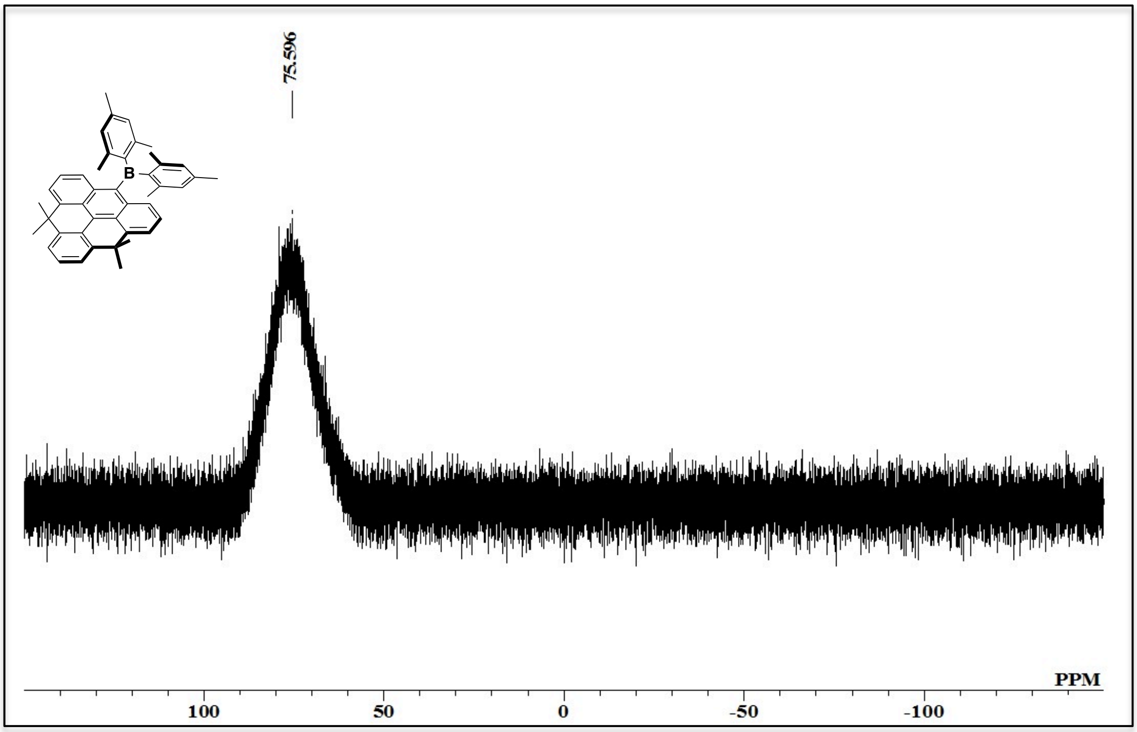

Fig. S21 ^{11}B NMR spectrum (128 MHz) of **7** in CDCl$_3$.

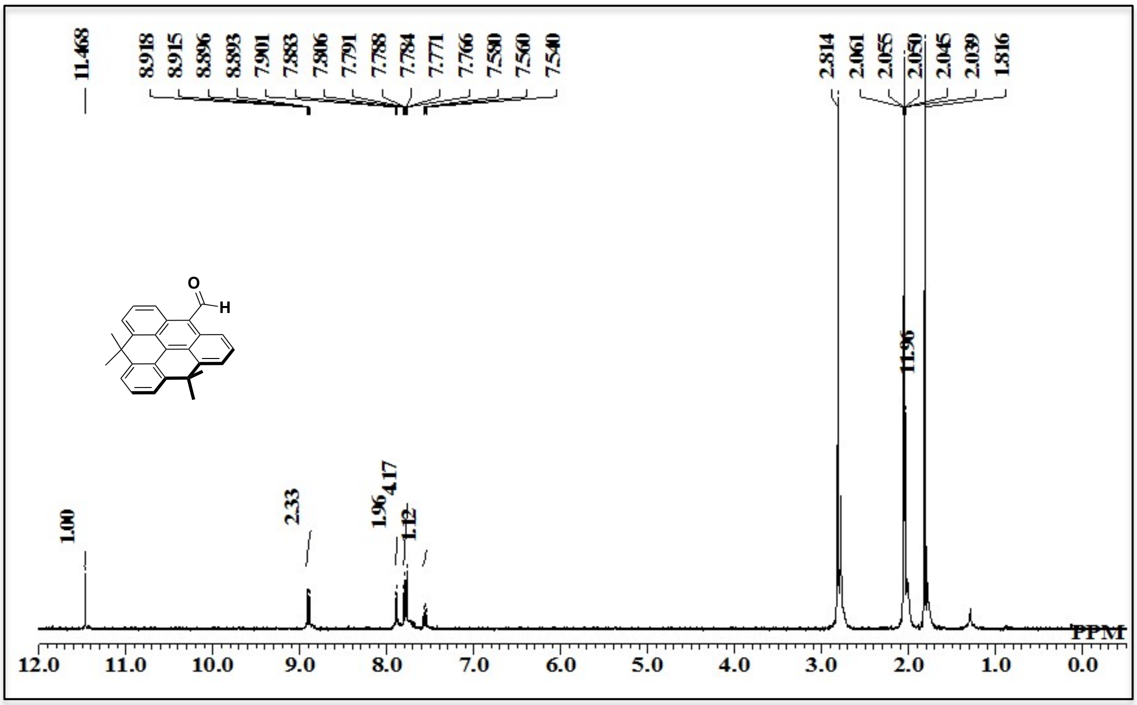

Fig. S22 ^{1}H NMR spectrum (400 MHz) of **8** in acetone-d_6.

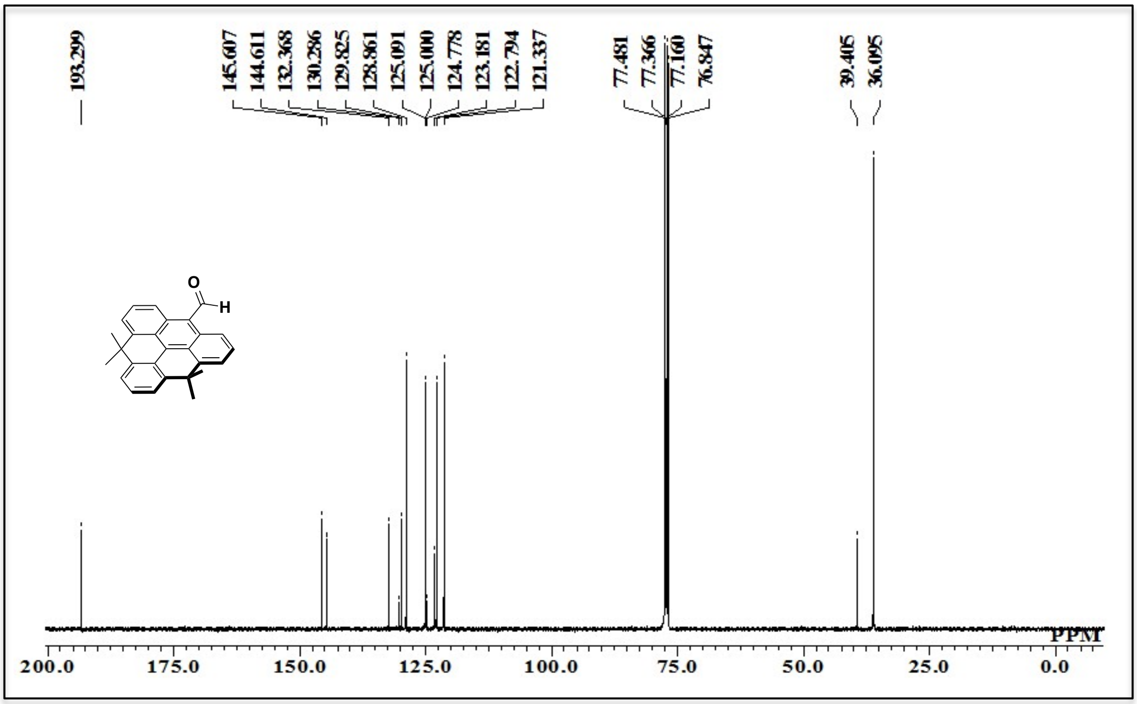

Fig. S23 ^{13}C NMR spectrum (100 MHz) of **8** in $CDCl_3$.

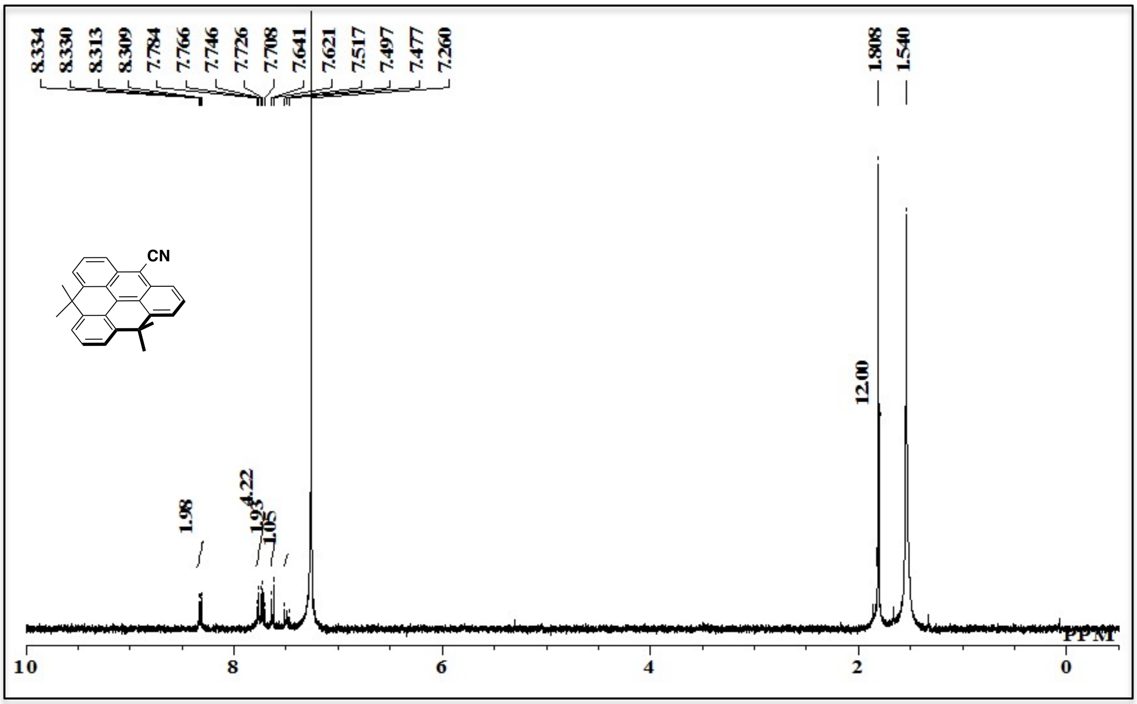

Fig. S24 ^{1}H NMR spectrum (400 MHz) of **9** in $CDCl_3$.

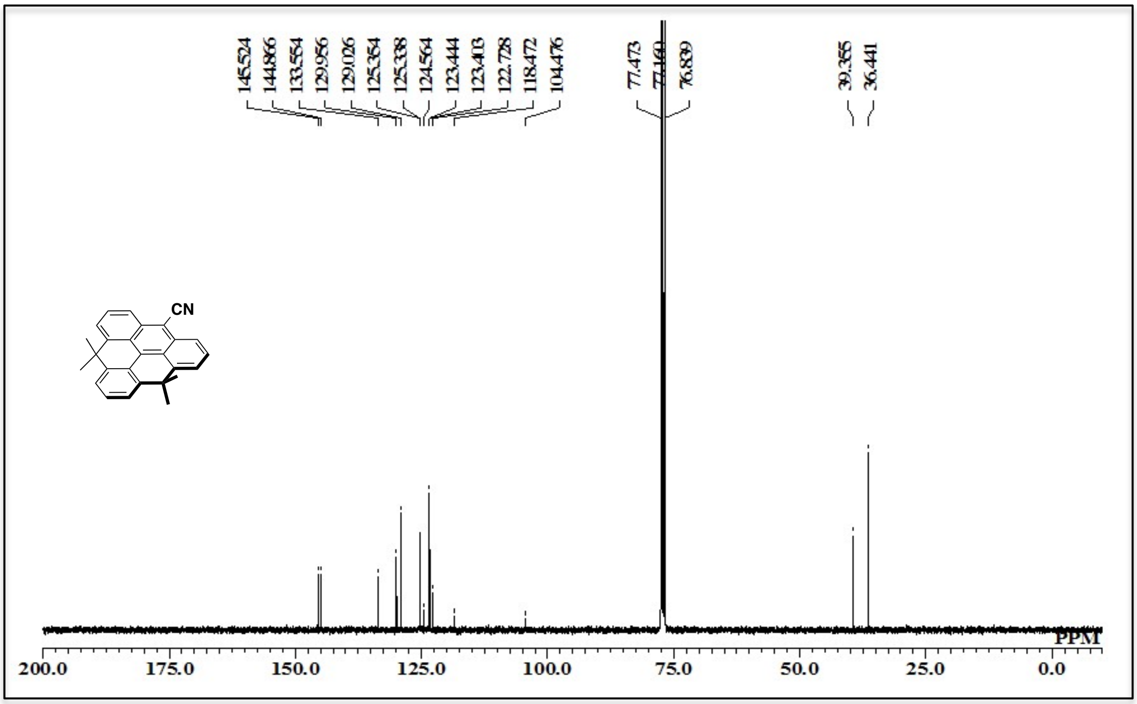

Fig. S25 ^{13}C NMR spectrum (100 MHz) of **9** in $CDCl_3$.

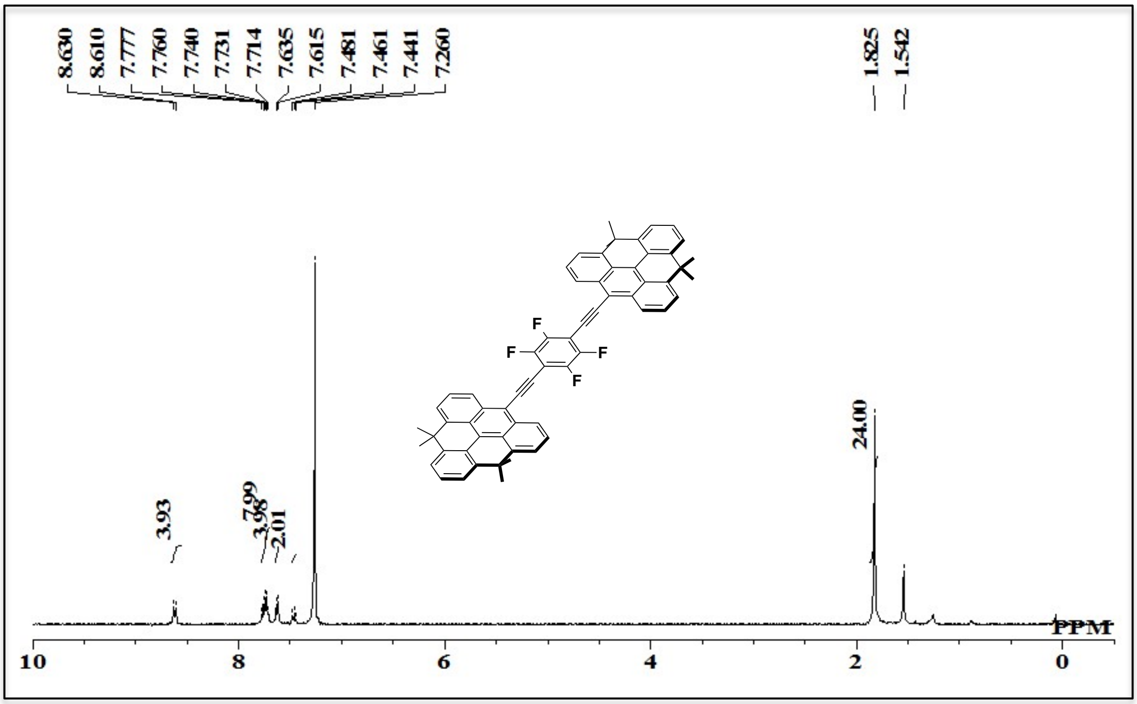

Fig. S26 ^{1}H NMR spectrum (400 MHz) of **10** in $CDCl_3$.

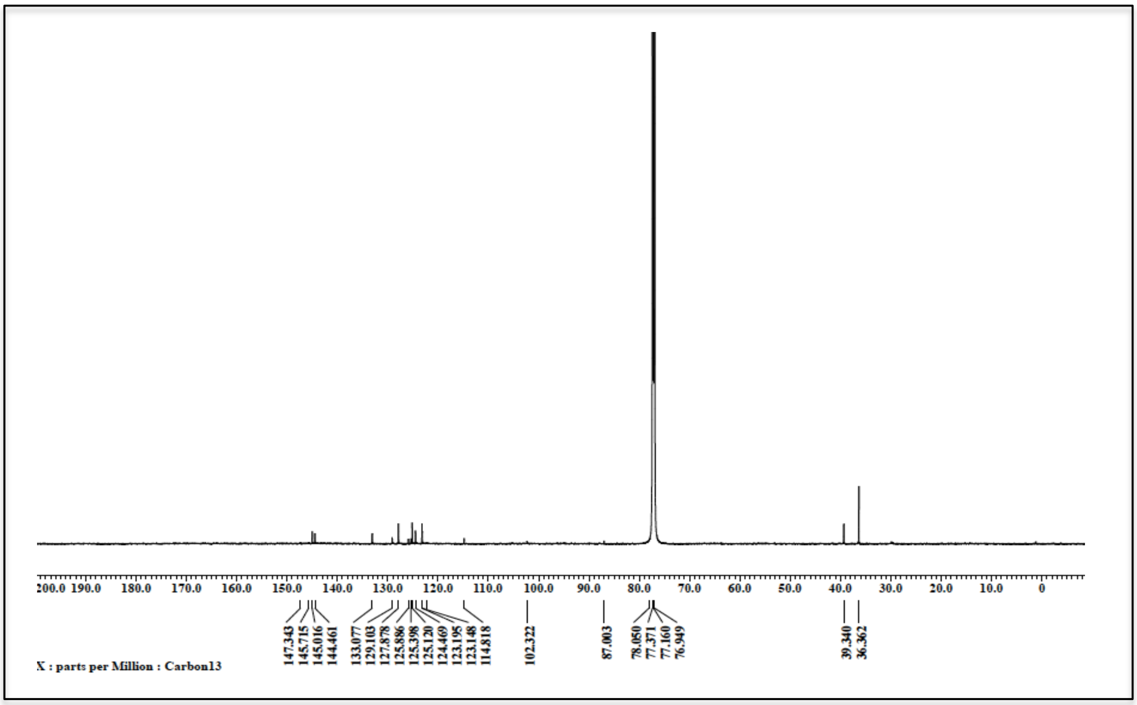

Fig. S27 ^{13}C NMR spectrum (150 MHz) of **10** in $CDCl_3$.

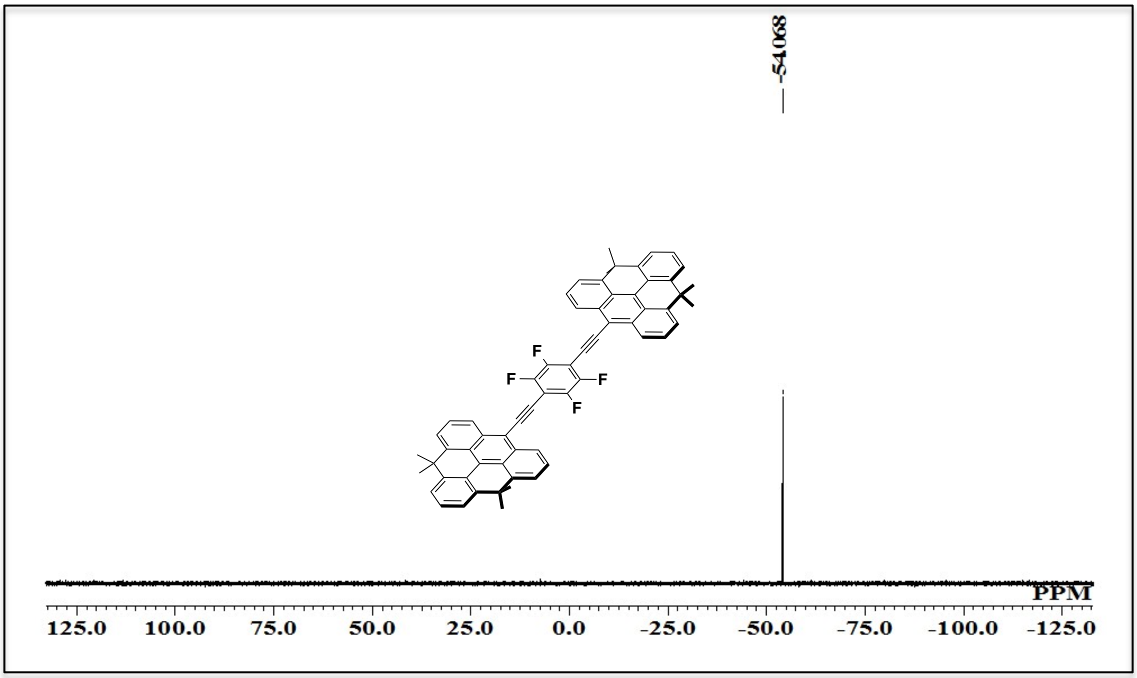

Fig. S28 ^{19}F NMR spectrum (376 MHz) of **10** in $CDCl_3$.

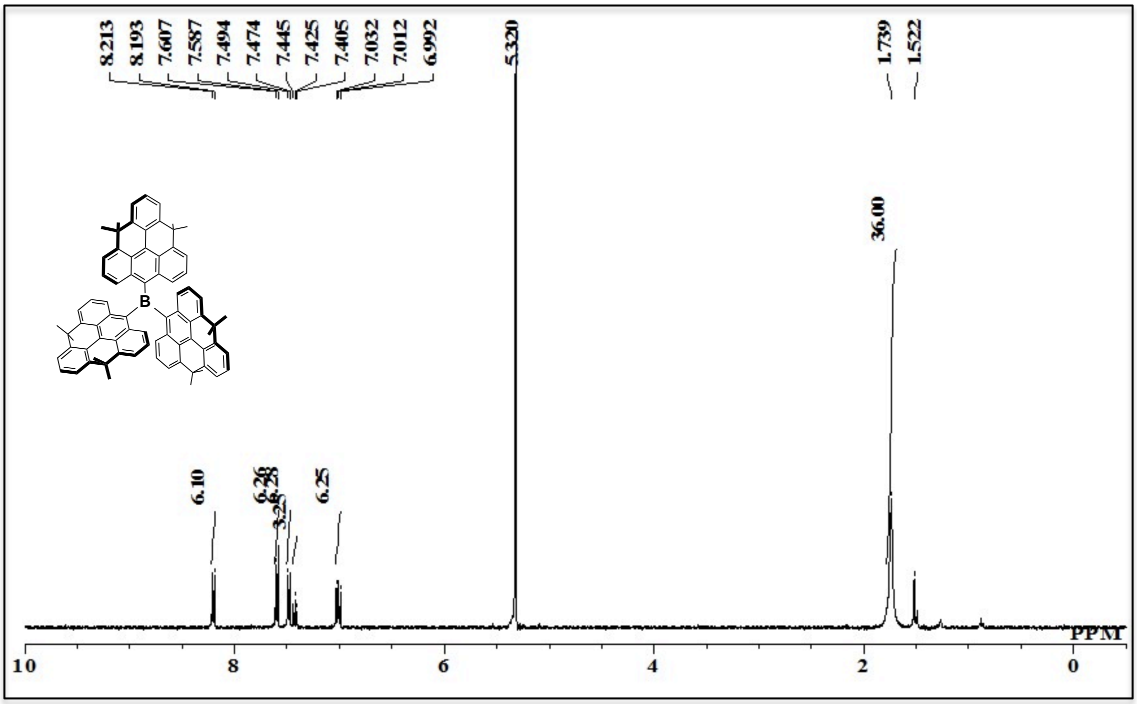

Fig. S29 ^{1}H NMR spectrum (400 MHz) of **11** in CD_2Cl_2.

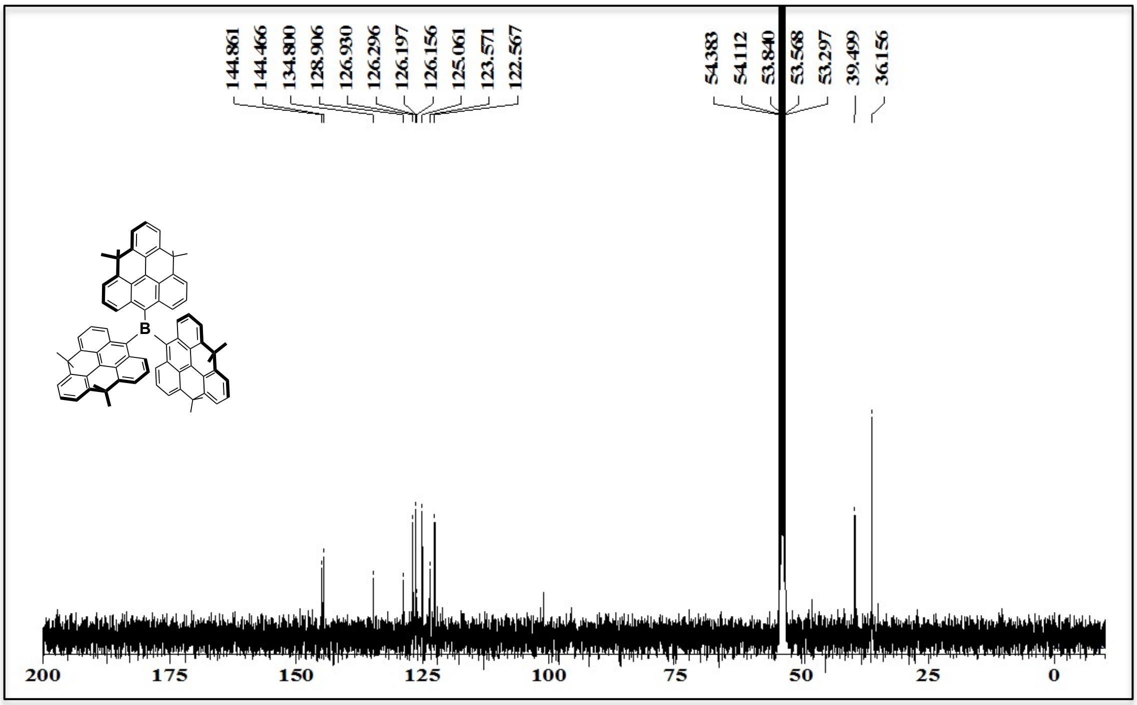

Fig. S30 ^{13}C NMR spectrum (100 MHz) of **11** in CD_2Cl_2.

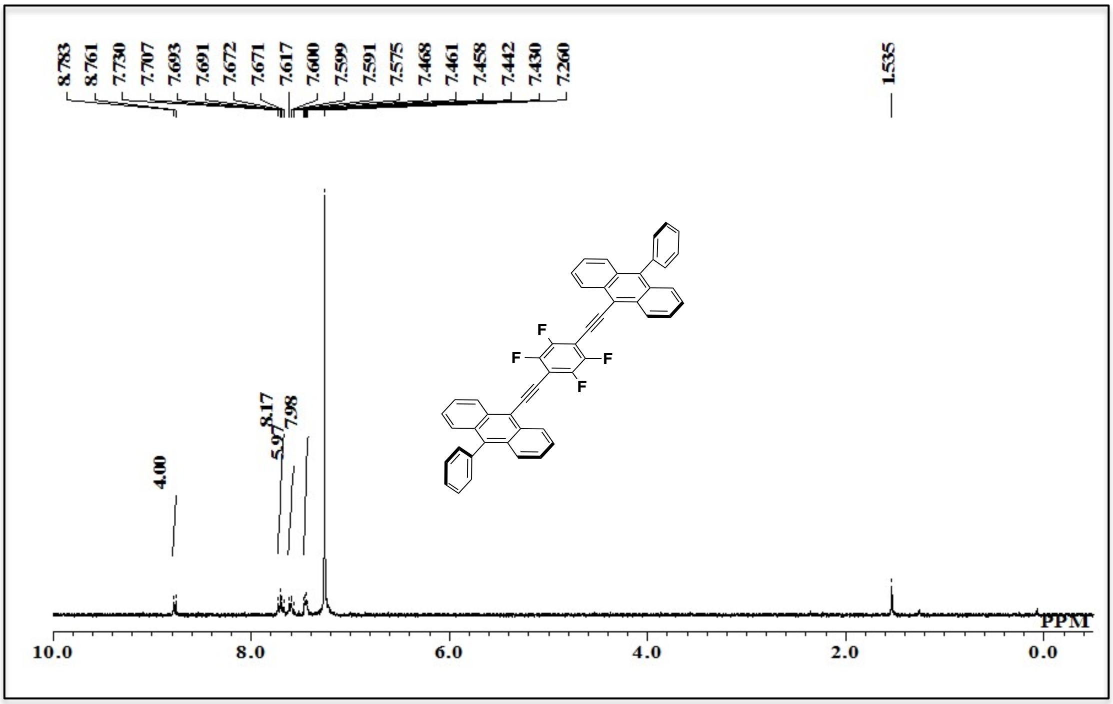

Fig. S31 ^{1}H NMR spectrum (400 MHz) of **12** in $CDCl_3$.

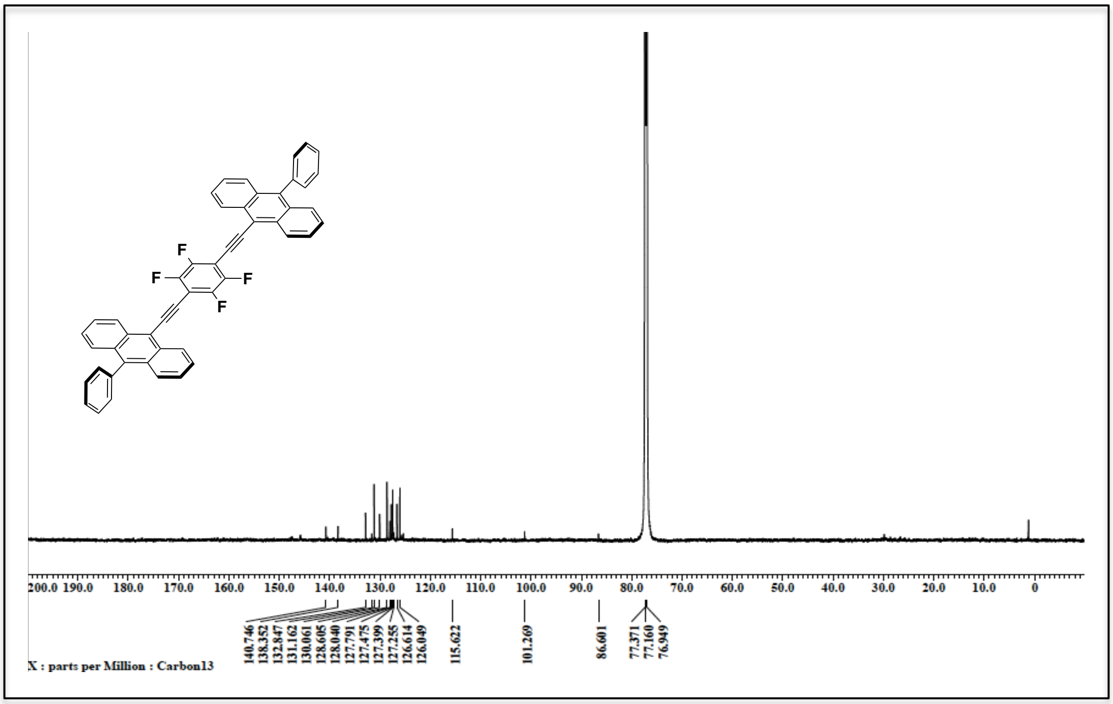

Fig. S32 ^{13}C NMR spectrum (150 MHz) of **12** in $CDCl_3$.

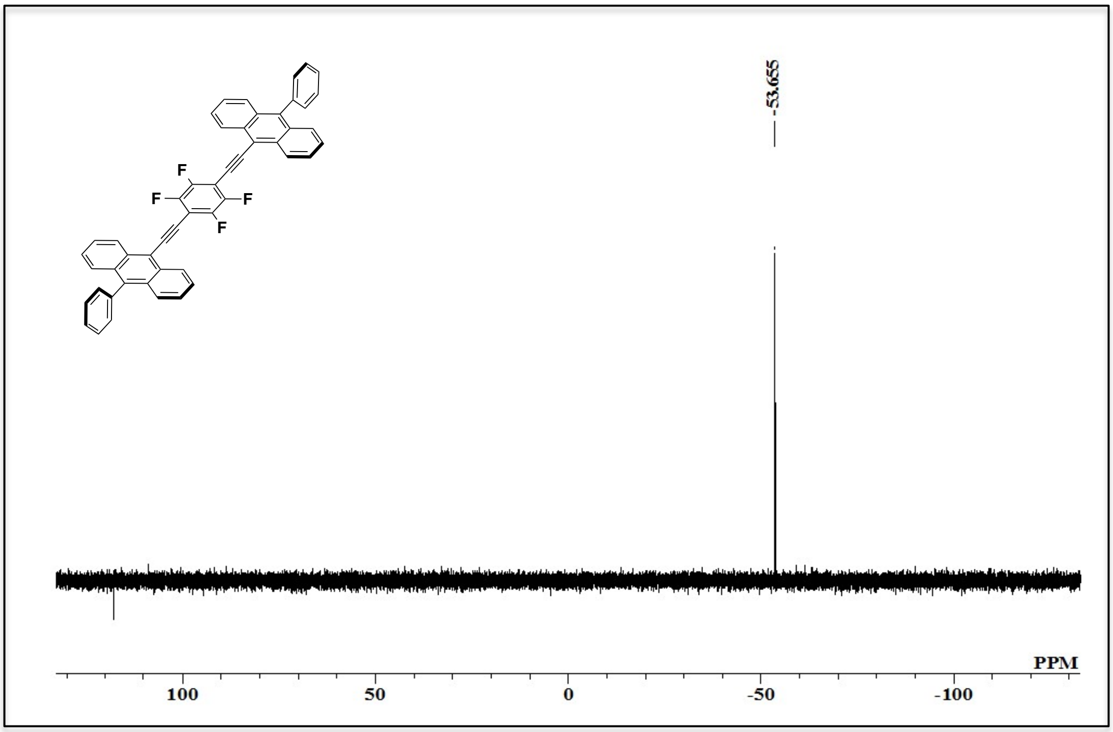

Fig. S33 ^{19}F NMR spectrum (376 MHz) of **12** in $CDCl_3$.