Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

Fully Fused Boron-Doped Polycyclic Aromatic Hydrocarbons: Their Synthesis, Structure–Property Relationships, and Self-Assembly Behavior in Aqueous Media

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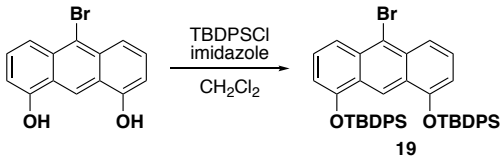
1. Experimental Details

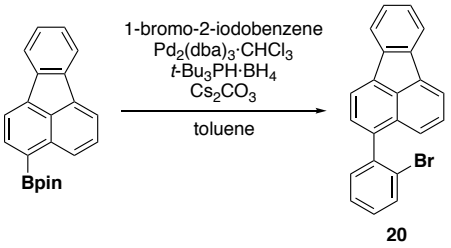
General procedures. Melting points (Mp.) or decomposition temperatures were determined with a Yanaco MP-S3 instrument (MP-S3). ^{1}H, ^{13}C{^{1}H}, and ^{11}B{^{1}H} NMR spectra were recorded with a JEOL JNM-ECA 500 II spectrometer in $CDCl_3$, CD_2Cl_2, or acetone-d_6 (500 MHz for ^{1}H, 126 MHz for ^{13}C, and 160 MHz for ^{11}B). ^{13}C{^{1}H} NMR spectra of some compounds were also recorded with a JEOL ECA 600II spectrometer equipped with an UltraCOOL probe (151 MHz). The chemical shifts in ^{1}H NMR spectra are reported in δ ppm using the residual protons of the solvents, $CHCl_3$ (δ 7.26) in $CDCl_3$, CH_2Cl_2 (δ 5.32) in CD_2Cl_2, or $(CH_3)_2CO$ (δ 2.05) in acetone-d_6, as an internal standard. The chemical shifts in ^{13}C NMR spectra are reported using the solvent signals of $CDCl_3$ (δ 77.16) or acetone-d_6 (δ 29.84) as an internal standard. The chemical shifts in ^{11}B NMR spectra are reported using BF_3·OEt (δ 0.00) as an external standard. Mass spectra were measured with a Bruker micrOTOF Focus spectrometry system with the ionization method of APCl or a ThermoFisher Scientific Exactive with the ionization method of ESI. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm thickness of silica gel 60F_{254} (Merck). Column chromatography was performed using neutral silica gel PSQ60B (Fuji Silysia Chemicals). Recycling preparative gel permeation chromatography (GPC) was performed with a LaboACE LC-5060 equipped with polystyrene gel columns (JAIGEL-2HR, Japan Analytical Industry) using chloroform as an eluent. Anhydrous CH_2Cl_2, 1,2-dichloroethane, toluene, and DMF were purchased from Kanto Chemicals and further purified by Glass Contour Solvent Systems. Nitromethane was distilled from CaH_2 prior to use. 1-(2-Bromophenyl)naphthalene,[1] 9-(2-bromophenyl)phenanthrene,[2] 2-(fluoranthen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane,[3] 1-(2,6-dibromophenyl)naphthalene,[4] 10-bromo-1,8-bis(2,4,6-trimethylphenoxy)anthracene,[5] 10-bromo-1,8-anthracenediol,[6] and 2,5,8,11,14,17-hexaoxanonadecan-19-yl 4-methylbenzenesulfonate[7] were prepared according to the literature methods. All reactions were performed with dry glassware and under a nitrogen atmosphere.



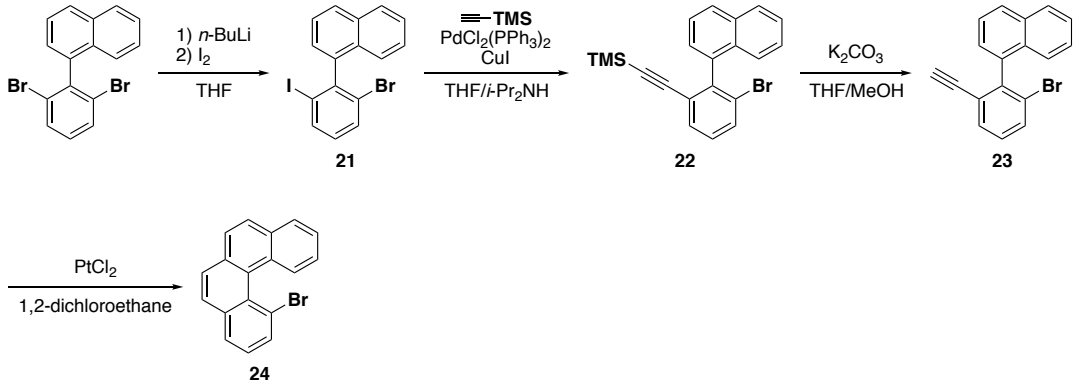
19

10-Bromo-1,8-bis(*t*-butyldiphenylsiloxy)anthracene (19). To a solution of 9-bromo-4,5-anthracenediol (1.33 g, 4.60 mmol) and imidazole (1.25 g, 18.4 mmol) in CH_2Cl_2 (40 mL) was added *t*-butyldiphenylsilyl chloride (3.60 mL, 13.8 mmol) at room temperature. After stirring at the same temperature for 3 h, the resulting mixture was filtered through a pad of Celite® and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (9/1 hexane/CH_2Cl_2, R_f = 0.30) to give 2.68 g (3.49 mmol, 76%) of **19** as a yellow solid: Mp. 239.8–240.5 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 9.88 (s, 1H), 8.05 (d, J = 9.2 Hz, 2H), 7.89 (dd, J = 7.7, 1.5 Hz, 8H), 7.53–

7.44 (m, 12H), 7.21 (dd, J = 9.2, 7.7 Hz, 2H), 6.53 (d, J = 7.7 Hz, 2H), 1.25 (s, 18H); $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) δ 152.0, 135.6, 132.2, 130.2, 128.1, 127.2, 126.8, 122.8, 120.5, 116.7, 112.3, 26.9, 19.7, one signal was not observed due to the overlap with other signals; HRMS (APCI) *m/z* calcd for $C_{46}H_{45}BrO_2Si_2$ $[M]^+$ 764.2136, found: 764.2114.



3-(2-Bromophenyl)fluoranthene (20). A mixture of 2-(fluoranthen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.12 mg, 3.41 mmol), 1-bromo-2-iodobenzene (1.59 g, 5.61 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (177 mg, 0.171 mmol), t-$Bu_3PH{\cdot}BF_4$ (49.4 mg, 0.170 mmol) and Cs_2CO_3 (1.81 g, 5.12 mmol) in toluene was stirred at 115 °C for 24 h. After cooling the reaction mixture to room temperature, water was added. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (9/1 hexane/CH_2Cl_2, R_f = 0.32) to give 500 mg (1.40 mmol, 41%) of **20** as a pale yellow solid. The spectral data of the product were consistent with those reported in the literature.[8]



1-(2-Bromo-6-iodophenyl)naphthalene (21). To a solution of 1-(2,6-dibromophenyl)naphthalene (1.57 g, 4.34 mmol) in THF (20 mL) was added a hexane solution of n-BuLi (1.56 M in hexane, 2.92 mL, 4.56 mmol) dropwise at –78 °C. After stirring at the same temperature for 2 h, a solution of I_2 (2.20 g, 8.68 mmol) in THF (10 mL) was added dropwise at –78 °C. The mixture was allowed to warm to room temperature followed by stirring for 2 h. After a saturated NaS_2O_3 aqueous solution was added, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined

organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (hexane, R_f = 0.48) to give 1.66 g (4.06 mmol, 94%) of **21** as a colorless solid: Mp. 119.4–120.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99–7.93 (m, 3H), 7.75–7.73 (m, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.53–7.50 (m, 1H), 7.45–7.42 (m, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.30–7.28 (m, 1H), 6.99 (t, J = 8.0 Hz, 1H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 145.1, 142.6, 138.4, 133.7, 132.8, 130.8, 130.7, 128.8, 128.6, 127.0, 126.6, 126.2, 125.5, 125.0, 124.0, 101.4; HRMS (APCI) *m/z* calcd for $C_{16}H_{10}BrI$ $[M]^+$ 407.9005, found: 407.9018.

1-Bromo-2-naphtyl-3-(trimethylsilylethynyl)benzene (22). To a solution of **21** (818 mg, 2.00 mmol), $PdCl_2(PPh_3)_2$ (21.1 mg, 30.1 μmol), and CuI (5.7 mg, 29.9 μmol) in THF (5 mL) and *i*-Pr_2NH (5 mL) was added trimethylsilylacetylene (235 mg, 2.40 mmol) dropwise at room temperature. After stirring at the same temperature for 24 h, the resulting mixture was filtered through a pad of Celite® and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (hexane, R_f = 0.40) to give 658 mg (1.73 mmol, 86%) of **22** as a colorless oil: ^{1}H NMR (500 MHz, acetone-d_6) δ 8.00–7.98 (m, 2H), 7.84–7.82 (m, 1H), 7.62–7.59 (m, 2H), 7.53–7.50 (m, 2H), 7.45–7.40 (m, 2H), 7.36–7.32 (m, 2H), –0.32 (s, 9H); ^{13}C{H} NMR (126 MHz, acetone-d_6) δ 144.9, 138.8, 134.6, 133.9, 132.3, 131.7, 130.2, 129.1, 128.0, 126.9, 126.6, 126.1, 125.1, 104.1, 99.8, –0.6, two signals were not observed due to the overlap with other signals; HRMS (APCI) *m/z* calcd for $C_{21}H_{19}BrSi$ $[M]^+$ 378.0434, found: 378.0420.

1-Bromo-2-naphtyl-3-ethynylbenzene (23). A mixture of **22** (574 mg, 1.51 mmol) and K_2CO_3 (835 mg, 6.04 mmol) in THF (5 mL) and MeOH (5 mL) was stirred at room temperature for 4 h. The reaction mixture was filtered through a pad of Celite® and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (hexane, R_f = 0.35) to give 445 mg (1.45 mmol, 96%) of **23** as a colorless solid: Mp. 97.0–97.5 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 7.99 (dd, J = 8.4, 2.3 Hz, 2H), 7.86–7.84 (m, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.54–7.51 (m, 1H), 7.44 (td, J = 7.9, 2.0 Hz, 2H), 7.37 (d, J = 6.1 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 3.30 (s, 1H); ^{13}C{H} NMR (126 MHz, acetone-d_6) δ 144.5, 138.6, 134.6, 134.1, 133.0, 132.3, 130.3, 129.3, 129.2, 128.0, 127.1, 126.8, 126.2, 126.0, 125.9, 125.5, 83.3, 82.3; HRMS (APCI) *m/z* calcd for $C_{18}H_{11}Br$ $[M]^+$ 306.0039, found: 306.0034.

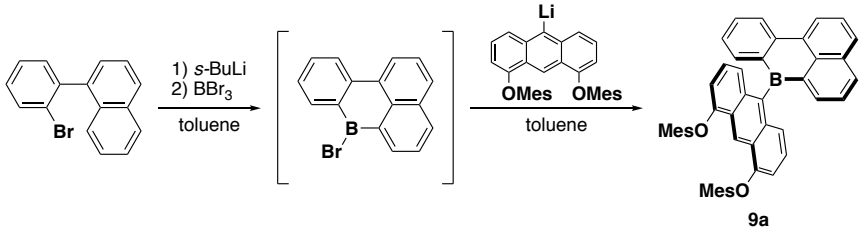
1-Bromobenzo[*c*]phenanthrene (24). A mixture of **23** (614 mg, 2.00 mmol) and $PtCl_2$ (42.5 mg, 0.160 mmol) in 1,2-dichloroethane was stirred at 100 °C for 72 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite® and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (hexane, R_f = 0.50) to give 242 mg (0.786 mmol, 39%) of **24** as a colorless solid: Mp. 147.4–148.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ

8.29 (d, J = 6.9 Hz, 1H), 8.01–7.97 (m, 3H), 7.94 (d, J = 7.7 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.63–7.58 (m, 2H), 7.51 (t, J = 7.7 Hz, 1H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 135.7, 133.1, 132.34, 132.31, 131.9, 129.0, 128.7, 127.5, 127.4, 127.3, 127.0, 126.72, 126.68, 126.1, 125.6, 124.7, 121.8, one signal was not observed due to the overlap with other signals; HRMS (APCI) *m/z* calcd for $C_{18}H_{11}Br$ $[M]^+$ 306.0039, found: 306.0040.

A general procedure for preparation of cyclization precursors.

Preparation of lithiated anthracene derivatives: To a solution of 1,8-di(mesityloxy)- or 1,8-bis(*t*-butyldiphenylsiloxy)-10-bromoanthracene in toluene (0.10 M) was added a cyclohexane solution of *s*-BuLi (1.23 M in cyclohexane, 1.0 equiv) dropwise at 0 °C. After stirring at the same temperature for 0.5 h, the mixture was directly used for the reaction with bromoboranes prepared as follows.

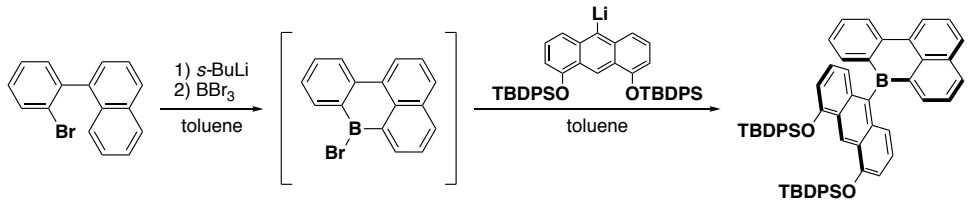
To a solution of bromobiaryl in toluene (0.20 M) was added a cyclohexane solution of *s*-BuLi (1.23 M, 1.05 equiv) dropwise at 0 °C. After stirring at the same temperature for 2 h, BBr_3 (1.1 equiv) was added to the mixture at –78 °C. The resulting mixture was stirred at –78 °C for 0.5 h, at 0 °C for 0.5 h, and then at 60 °C for 24 h. After cooling to room temperature, all volatiles were removed in *vacuo*. The resulting mixture was dissolved in toluene (0.10 M), and this mixture was added to a toluene solution of the lithiated anthracenes at 0 °C. After stirring at room temperature for 0.5 h, water was added to the mixture. The organic layer was separated and the aqueous layer was extracted with toluene. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting mixture was successively washed with hexane and MeOH to afford the cyclization precursors.



9a

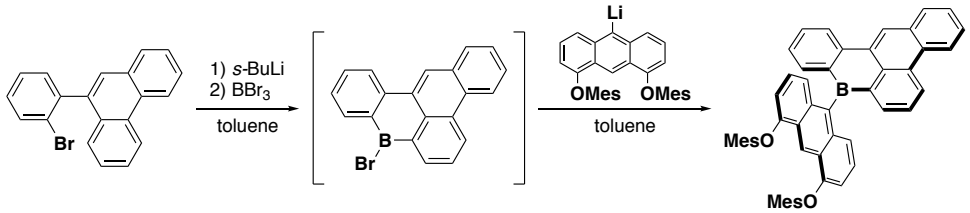
7-[4,5-Di(mesityloxy)anthracen-9-yl]-7*H*-benzo[*e*]naphtho[1,8-*bc*]borinine (9a). The titled compound was prepared according to the general procedure using 1-(2-bromophenyl)naphthalene (283 mg, 1.00 mmol) and 10-bromo-1,8-di(mesityloxy)anthracene (525 mg, 1.00 mmol) in 47% yield (306 mg, 0.465 mmol) as a yellow solid: Mp. >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.88 (d, J = 6.9 Hz, 1H), 8.67 (d, J = 8.4 Hz, 1H), 8.28–8.27 (m, 1H), 8.12 (d, J = 7.7 Hz, 1H), 8.03 (dd, J = 6.9, 1.5 Hz, 1H), 7.84 (t, J = 8.0 Hz, 1H), 7.78–7.75 (m, 1H), 7.71 (dd, J = 7.7, 1.5 Hz, 1H), 7.56 (t, J = 7.3 Hz, 1H), 7.29 (t, J = 7.3 Hz, 1H), 7.07 (d, J = 8.4 Hz, 2H), 6.98 (s, 4H), 6.90 (t, J = 8.0 Hz, 2H), 6.26 (d, J = 7.7 Hz, 2H), 2.35 (s, 6H), 2.24 (s, 12H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 154.2, 149.4, 143.6, 141.9, 140.9, 139.9, 137.8, 136.7, 136.0, 135.6, 134.5, 133.8, 133.0, 132.4, 131.6,

131.3, 130.8, 129.7, 127.3, 126.5, 126.2, 126.0, 124.5, 123.7, 123.6, 115.5, 103.9, 21.0, 16.4, one signal was not observed due to the overlap with other signals; $^{11}B\{H\}$ NMR (160 MHz, $CDCl_3$) δ 65.8; HRMS (APCI) *m/z* calcd for $C_{48}H_{39}BO_2$ $[M]^+$ 658.3038, found: 658.3007.



9b

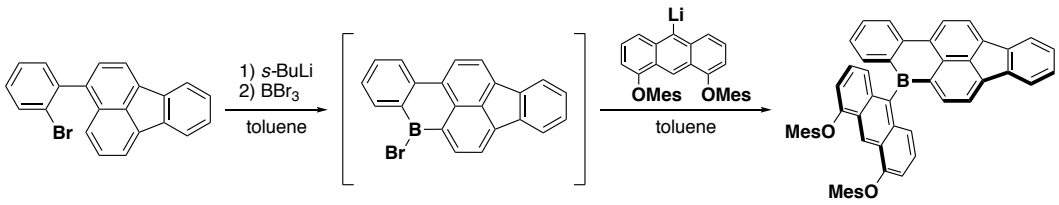
7-[4,5-Bis(*t*-butyldiphenylsiloxy)anthracen-9-yl]-7*H*-benzo[*e*]naphtho[1,8-*bc*]borinine (9b). The titled compound was prepared according to the general procedure using 1-(2-bromophenyl)naphthalene (566 mg, 2.00 mmol) and 10-bromo-1,8-bis(*t*-butyldiphenylsiloxy)anthracene (1.53 g, 2.00 mmol) in 32% yield (581 mg, 0.646 mmol) as a yellow solid: Mp. 226.0–226.8 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.83 (d, J = 7.7 Hz, 1H), 8.63 (d, J = 7.7 Hz, 1H), 8.25–8.23 (m, 1H), 8.09 (d, J = 7.7 Hz, 1H), 7.98–7.96 (m, 1H), 7.91 (m, 8H), 7.81 (t, J = 7.7 Hz, 1H), 7.75–7.72 (m, 1H), 7.65 (dd, J = 7.7, 1.5 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.45–7.37 (m, 12H), 7.28 (d, J = 7.7 Hz, 1H), 6.96 (d, J = 8.4 Hz, 2H), 6.64 (t, J = 8.0 Hz, 2H), 6.36 (d, J = 6.9 Hz, 2H), 1.29 (s, 18H); $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) δ 151.9, 143.4, 141.8, 141.4, 139.8, 137.7, 136.6, 136.0, 135.8, 135.6, 133.7, 133.0, 132.61, 132.56, 132.4, 131.6, 130.8, 130.0, 128.0, 127.2, 126.4, 126.2, 125.92, 125.89, 124.2, 123.6, 115.7, 111.5, 27.0, 19.8; $^{11}B\{H\}$ NMR (160 MHz, $CDCl_3$) δ 65.6; HRMS (APCI) *m/z* calcd for $C_{62}H_{55}BO_2Si_2$ $[M]^+$ 898.3828, found: 898.3835.



16

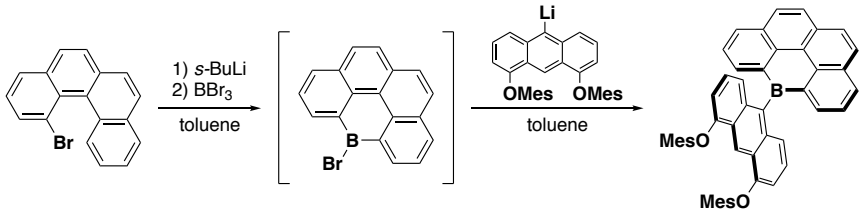
8-[4,5-Di(mesityloxy)anthracen-9-yl]-8*H*-benzo[*e*]phenanthro[1,10-*bc*]borinine (16). The titled compound was prepared according to the general procedure using 9-(2-bromophenyl)phenanthrene (333 mg, 1.00 mmol) and 10-bromo-1,8-di(mesityloxy)anthracene (525 mg, 1.00 mmol) in 32% yield (229 mg, 0.323 mmol) as a yellow solid: Mp. >300 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 9.93 (s, 1H), 9.18 (s, 1H), 9.15–9.14 (m, 1H), 8.81 (t, J = 8.8 Hz, 2H), 8.19 (d, J = 6.9 Hz, 1H), 8.06–8.05 (m, 1H), 7.82–7.69 (m, 5H), 7.33 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 9.2 Hz, 2H), 6.98 (s, 4H), 6.92 (t, J = 8.0 Hz, 2H), 6.27 (d, J = 6.9 Hz, 2H), 2.35 (s, 6H), 2.26 (s, 12H); $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) δ 154.3,

149.4, 142.0, 141.8, 141.0, 139.7, 137.7, 135.9, 135.8, 134.5, 133.8, 132.1, 131.9, 131.5, 131.3, 130.8, 130.1, 130.0, 129.9, 129.7, 128.2, 128.1, 127.5, 127.2, 126.7, 124.6, 123.8, 123.5, 122.8, 115.6, 103.9, 21.0, 16.5; ^{11}B{H} NMR (160 MHz, $CDCl_3$) δ 65.9; HRMS (APCI) *m/z* calcd for $C_{52}H_{41}BO_2$ $[M]^+$ 708.3194, found: 708.3189.



20 **17**

5-[4,5-Di(mesityloxy)anthracen-9-yl]-5*H*-benzo[*e*]fluorantheno[3,4-*bc*]borinine (17). The titled compound was prepared according to the general procedure using compound **20** (357 mg, 1.00 mmol) and 10-bromo-1,8-di(mesityloxy)anthracene (525 mg, 1.00 mmol) in 26% yield (191 mg, 0.261 mmol) as an orange solid: Mp. >300 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.88 (s, 1H), 8.54 (d, J = 7.7 Hz, 1H), 8.42 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 7.7 Hz, 1H), 7.80–7.67 (m, 2H), 7.72–7.70 (m, 2H), 7.68–7.64 (m, 1H), 7.50 (dd, J = 7.7, 1.5 Hz, 1H), 7.34–7.31 (m, 1H), 7.27–7.24 (m, 1H), 7.19–7.14 (m, 3H), 7.00 (s, 4H), 6.98 (dd, J = 8.8, 7.3 Hz, 2H), 6.27 (d, J = 6.9 Hz, 2H), 2.34 (s, 6H), 2.23 (s, 12H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 154.3, 149.4, 145.0, 144.2, 141.4, 141.2, 141.0, 140.5, 140.3, 139.1, 138.7, 136.3, 135.7, 134.5, 134.1, 134.0, 133.3, 131.3, 130.4, 129.7, 129.4, 128.3, 127.8, 126.5, 124.7, 123.7, 123.3, 122.9, 122.3, 120.9, 120.4, 115.6, 104.0, 21.0, 16.4, one signal was not observed due to the overlap with the other signals; ^{11}B{H} NMR (160 MHz, $CDCl_3$) δ 65.7; HRMS (APCI) *m/z* calcd for $C_{54}H_{41}BO_2$ $[M]^+$ 733.3272, found: 733.3245.



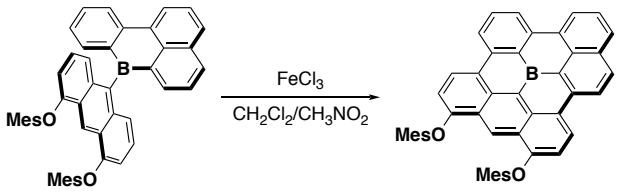
24 **18**

6-[4,5-Di(mesityloxy)anthracene-9-yl]-6*H*-6-borabenzo[*cd*]pyrene (18). The titled compound was prepared according to the general procedure using compound **24** (307 mg, 1.00 mmol) and 10-bromo-1,8-di(mesityloxy)anthracene (526 mg, 1.00 mmol) in 22% yield (150 mg, 22.0 μmol) as a yellow solid: Mp. >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.43 (d, J = 7.7 Hz, 2H), 8.28–8.20 (m, 6H), 7.71 (t, J = 7.3 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.98 (s, 4H), 6.87 (t, J = 8.0 Hz, 2H), 6.26 (d, J = 6.9 Hz, 2H), 2.35 (s, 6H), 2.26 (s, 12H); ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 154.2, 149.5, 142.6, 141.1, 136.5, 136.0, 134.5, 134.1, 132.2, 131.3, 131.2, 129.7, 129.3, 127.4, 126.4, 124.4, 124.2,

123.8, 115.6, 103.8, 21.0, 16.5, two signals were not observed due to the overlap with other signals; $^{11}B\{H\}$ NMR (160 MHz, $CDCl_3$) δ 65.0; HRMS (APCI) *m/z* calcd for $C_{50}H_{39}BO_2$ $[M]^+$ 682.3038, found: 682.3023.

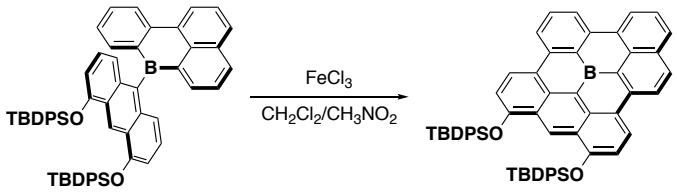
A general procedure for preparation of fully fused boron-doped PAHs.

To a solution of the cyclization precursor in CH_2Cl_2 (0.50 mM) was added a CH_3NO_2 solution of $FeCl_3$ (8.0 equiv) dropwise at 0 °C. After stirring at room temperature for 0.5 h, MeOH was added to the reaction mixture. After removal of solvents, the mixture was subjected to silica gel column chromatography (hexane/toluene) to afford fully fused boron-doped PAHs.



9a **10a**

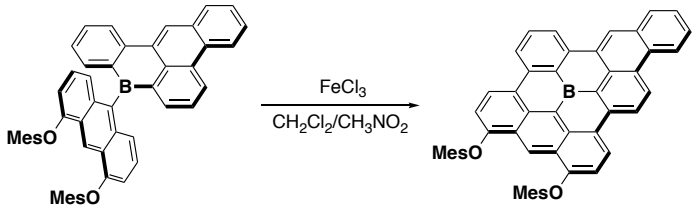
Compound 10a. This compound was prepared according to the general procedure using compound **9a** (132 mg, 0.200 mmol) in 48% yield (63.3 mg, 96.7 μmol) as a purple solid: mp. >300 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 10.61 (s, 1H), 9.05 (d, J = 8.4 Hz, 1H), 8.94 (d, J = 7.7 Hz, 1H), 8.86 (d, J = 8.4 Hz, 1H), 8.81 (d, J = 8.4 Hz, 1H), 8.72 (d, J = 8.4 Hz, 1H), 8.62 (d, J = 7.7 Hz, 1H), 8.39 (d, J = 9.2 Hz, 1H), 8.14 (d, J = 7.7 Hz, 1H), 8.02 (t, J = 8.0 Hz, 1H), 7.85 (t, J = 7.7 Hz, 1H), 7.06 (s, 2H), 7.05 (s, 2H), 6.84 (d, J = 7.7 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.28 (s, 6H), 2.27 (s, 6H); $^{13}C\{H\}$ NMR (151 MHz, $CDCl_3$) δ 158.5, 157.0, 149.0, 148.9, 140.5, 140.4, 140.1, 135.3, 135.2, 134.0, 133.9, 133.3, 132.2, 131.8, 131.5, 131.2, 131.1, 131.0, 130.6, 130.04, 129.99, 129.7, 128.8, 128.5, 127.3, 126.5, 126.2, 125.6, 125.0, 123.2, 122.6, 121.9, 121.8, 121.6, 106.2, 21.1, 16.49, 16.47, one signal for the carbon atom bound to the boron atom was not observed due to the quadrupolar relaxation and another three signals were not observed due to the overlap with other signals; $^{11}B\{H\}$ NMR (160 MHz, $CDCl_3$) δ 43.1; HRMS (APCI) *m/z* calcd for $C_{48}H_{35}BO_2$ $[M]^+$ 654.2725, found: 654.2706.



9b **10b**

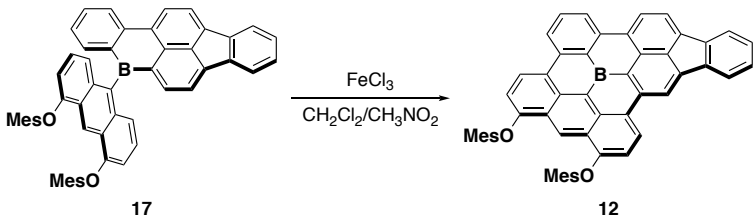
Compound 10b. This compound was prepared according to the general procedure using compound **9b** (90.0 mg, 0.100 mmol) in 64% yield (57.3 mg, 64.0 μmol) as a purple solid: Mp. 291.0–291.5 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.86 (d, J = 7.7 Hz, 1H), 8.75 (d, J = 8.4 Hz, 1H), 8.63 (m, 2H), 8.56 (d, J = 8.4 Hz, 1H), 8.45 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 9.2 Hz, 1H), 8.07 (d, J = 7.7 Hz, 1H), 7.97–7.90 (m, 10H), 7.79 (t, J = 7.7 Hz, 1H), 7.50–7.41 (m, 12H), 6.90 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 7.7 Hz, 1H), 1.34 (s, 9H), 1.33 (s, 9H); ^{13}C{H} NMR (151 MHz, $CDCl_3$) δ 156.8, 155.2, 140.32, 140.27, 140.0, 135.7, 133.9, 133.2, 133.0, 132.1, 131.94, 131.87, 131.78, 131.69, 131.25, 131.21, 130.42, 130.36, 129.4, 129.0, 128.34, 128.29, 128.25, 127.0, 126.8, 125.7, 125.5, 125.3, 124.8, 121.9, 121.6, 121.5, 113.6, 26.90, 26.88, 19.9, one signal for the carbon atom bound to the boron atom was not observed due to the quadrupolar relaxation and another six signals were not observed due to the overlap with other signals; ^{11}B{H} NMR (160 MHz, $CDCl_3$) δ 40.8; HRMS (APCI) *m/z* calcd for $C_{62}H_{51}BO_2Si_2$ $[M]^+$ 894.3515, found: 894.3493.



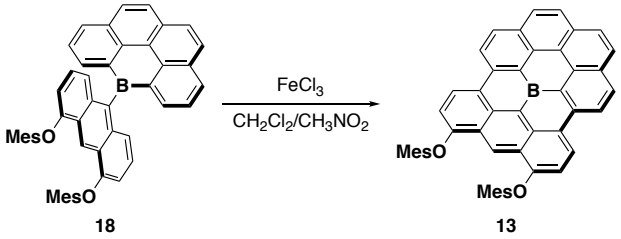
16 11

Compound 11. This compound was prepared according to the general procedure using compound **16** (70.9 mg, 0.100 mmol) in 34% yield (24.0 mg, 34.1 μmol) as a purple solid: Mp. >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.58 (s, 1H), 9.23–9.20 (m, 2H), 9.02 (d, J = 7.7 Hz, 1H), 8.94–8.89 (m, 2H), 8.82 (d, J = 8.4 Hz, 1H), 8.78 (d, J = 8.4 Hz, 1H), 8.59 (d, J = 7.7 Hz, 1H), 8.21 (d, J = 7.7 Hz, 1H), 8.01 (t, J = 8.0 Hz, 1H), 7.79 (t, J = 7.7 Hz, 1H), 7.72 (t, J = 6.9 Hz, 1H), 7.06 (s, 2H), 7.05 (s, 2H), 6.83 (d, J = 7.7 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 2.413 (s, 3H), 2.405 (s, 3H), 2.284 (s, 6H), 2.276 (s, 6H); ^{13}C{H} NMR (151 MHz, $CDCl_3$) δ 158.0, 157.0, 149.1, 149.0, 140.8, 140.2, 139.9, 135.3, 135.2, 133.7, 133.4, 132.6, 132.4, 131.9, 131.8, 131.6, 131.2, 131.10, 131.07, 130.6, 130.02, 129.99, 129.93, 129.5, 128.9, 128.2, 127.4, 127.3, 127.1, 126.6, 126.5, 126.4, 126.3, 123.2, 122.7, 122.6, 122.0, 121.81, 121.76, 106.2, 106.1, 21.1, 16.5, one signal for the carbon atom bound to the boron atom was not observed due to the quadrupolar relaxation and another two signals were not observed due to the overlap with other signals; ^{11}B{H} NMR were not obtained due to its poor solubility; HRMS (APCI) *m/z* calcd for $C_{52}H_{37}BO_2$ $[M]^+$ 704.2881, found: 704.2861.



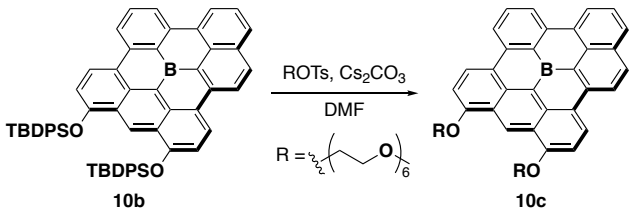
17 12

Compound 12. This compound was prepared according to the general procedure using compound **17** (73.3 mg, 0.100 mmol) in 19% yield (14.1 mg, 19.3 μmol) as a purple solid: Mp. >300 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 10.70 (s, 1H), 9.22 (d, J = 8.4 Hz, 1H), 9.14 (s, 1H), 8.93 (d, J = 8.4 Hz, 1H), 8.74 (d, J = 7.7 Hz, 1H), 8.64 (d, J = 8.4 Hz, 1H), 8.60 (d, J = 7.7 Hz, 1H), 8.11–8.08 (m, 2H), 8.00 (t, J = 7.7 Hz, 1H), 7.95–7.93 (m, 1H), 7.43–7.41 (m, 2H), 7.11 (s, 2H), 7.08 (s, 2H), 6.93 (d, J = 8.4 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H), 2.30 (s, 6H), 2.28 (s, 6H); ^{13}C{H} NMR and ^{11}B{H} NMR were not obtained due to its poor solubility; HRMS (APCI) *m/z* calcd for $C_{54}H_{37}BO_2$ $[M]^+$ 728.2881, found: 728.2854.



18 13

Compound 13. This compound was prepared according to the general procedure using compound **18** (68.3 mg, 0.100 mmol) in 44% yield as (29.9 mg, 44.1 μmol) a purple solid: Mp. >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.78 (s, 1H), 9.22 (d, J = 8.4 Hz, 2H), 9.09 (d, J = 8.4 Hz, 2H), 8.70 (d, J = 8.4 Hz, 2H), 8.44 (d, J = 8.4 Hz, 2H), 8.37 (d, J = 8.4 Hz, 2H), 7.08 (s, 4H), 6.94 (d, J = 8.4 Hz, 2H), 2.43 (s, 6H), 2.31 (s, 12H); ^{13}C{H} NMR (151 MHz, $CDCl_3$) δ 158.3, 149.0, 139.6, 135.4, 132.9, 132.1, 132.1, 131.2, 131.1, 130.8, 130.1, 129.8, 127.4, 127.3, 127.0, 126.8, 126.7, 122.9, 121.4, 106.4, 21.1, 16.5, two signals were not observed due to the overlap with other signals; ^{11}B{H} NMR (160 MHz, $CDCl_3$) δ 40.0; HRMS (APCI) *m/z* calcd for $C_{50}H_{35}BO_2$ $[M]^+$ 678.2725, found: 678.2706.



10b 10c

Compound 10c. A mixture of compound **10b** (44.8 mg, 50.0 μmol), 2,5,8,11,14,17-hexaoxanonadecan-19-yl 4-methylbenzenesulfonate (130 mg, 0.400 mmol) and Cs_2CO_3 (86.9 mg, 0.200 mmol) in DMF (1 mL) was stirred at 100 °C for 18 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite® and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (9/1 CH_2Cl_2/MeOH, R_f = 0.35) followed by preparative GPC ($CHCl_3$) to give 11.7 mg (12.0 μmol, 24%) of **10c** as a purple viscous solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.90 (dd, J = 7.7, 6.1 Hz, 2H), 8.76 (d, J = 8.4 Hz, 1H), 8.66 (dd, J = 10.7, 8.4 Hz, 2H), 8.52 (d, J = 7.7 Hz, 1H), 8.31 (d, J = 9.2 Hz, 1H), 8.11 (d, J = 7.7 Hz, 1H),

7.97 (t, J = 8.0 Hz, 1H), 7.83 (t, J = 7.7 Hz, 1H), 7.00 (t, J = 7.7 Hz, 2H), 4.47–4.45 (m, 4H), 4.12–4.09 (m, 4H), 3.91–3.88 (m, 4H), 3.78–3.75 (m, 4H), 3.70–3.68 (m, 4H), 3.64–3.61 (m, 4H), 3.59–3.50 (m, 22H), 3.47–3.45 (m, 4H), 3.33 (s, 6H); ^{13}C{H} NMR (151 MHz, $CDCl_3$) δ 159.0, 157.6, 140.2, 140.1, 140.0, 134.0, 133.1, 132.8, 132.1, 131.9, 131.7, 131.1, 130.5, 130.3, 129.3, 128.3, 127.8, 126.35, 126.29, 125.4, 125.2, 124.7, 123.0, 122.5, 121.9, 121.41, 121.37, 104.2, 72.0, 71.3, 70.9, 70.8, 70.7, 70.64, 70.62, 70.58, 70.55, 69.9, 69.8, 68.3, 68.2, 59.1, one signal for the carbon atom bound to the boron atom was not observed due to the quadrupolar relaxation and another 13 signals were not observed due to the overlap with other signals; ^{11}B{H} NMR (160 MHz, $CDCl_3$) δ45.2; HRMS (ESI) *m/z* calcd for $C_{56}H_{67}BNaO_{14}$ $[M+Na]^+$ 997.4522, found: 997.4521.

2. X-ray Crystallographic Analysis

Structural analysis of 10a. A single crystal of **10a** was obtained by slow diffusion of EtOH into a CH_2Cl_2 solution of **10a**. Intensity data were collected at 100 K on synchrotron radiation (λ = 0.4137 Å) at the BL40XU beamline in Spring-8 (JASRI). A total of 82231 reflections were measured at the maximum 2θ angle of 31.2°, of which 8423 were independent reflections (R_{int} = 0.0627). The structure was solved by direct methods (SHELXT–2018/2)[9] and refined by full-matrix least squares procedures on F^2 for all reflections (SHELXL–2018/1).[10] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{49}H_{37}BCl_2O_2$; FW = 739.49, crystal size 0.10 × 0.10 × 0.01 mm^3, *monoclinic*, $P2_1/n$, a = 9.02130(10) Å, b = 12.4023(2) Å, c = 32.9897(6) Å, β = 94.6850(10)°, V = 3678.72(10) Å^3, Z = 4, D_c = 1.335 g cm^{-3}, μ = 0.064 mm^{-1}, R_1 = 0.0681 ($I > 2\sigma(I)$), wR_2 = 0.1695 (all data), GOF = 1.163. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 2124573. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Structural analysis of 10b. A single crystal of **10b** was obtained by slow diffusion of EtOH into a CH_2Cl_2 solution of **10b**. Intensity data were collected at 123 K on a Rigaku Single Crystal X-ray diffractometer equipped with FR-X generator, Varimax optics, and PILATUS 200K photon counting detector with MoKα radiation (λ = 0.71073 Å). A total of 33495 reflections were measured at the maximum 2θ angle of 55.0°, of which 11130 were independent reflections (R_{int} = 0.0360). The structure was solved by direct methods (SHELXT–2014/5)[9] and refined by full-matrix least squares procedures on F^2 for all reflections (SHELXL–2018/1).[10] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{63}H_{53}BCl_2O_2Si_2$; FW = 979.94, crystal size 0.20 × 0.10 × 0.01 mm^3, *triclinic*, P–1, a = 9.1151(2) Å, b = 12.6682(2) Å, c = 21.4094(4) Å, α = 89.252(2)°, β = 84.010(2)°, γ = 84.665(2)°, V = 2448.02(8) Å^3, Z = 2, D_c = 1.329 g cm^{-3}, μ = 0.229 mm^{-1}, R_1 = 0.0580 ($I > 2\sigma(I)$), wR_2 = 0.1636 (all

data), GOF = 1.033. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 2124574. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Structural analysis of 12. A single crystal of **12** was obtained by slow cooling of a hot toluene solution of **12**. Intensity data were collected at 123 K on a Rigaku Single Crystal X-ray diffractometer equipped with FR-X generator, Varimax optics, and PILATUS 200K photon counting detector with MoKα radiation (λ = 0.71073 Å). A total of 49123 reflections were measured at the maximum 2θ angle of 55.0°, of which 8609 were independent reflections (R_{int} = 0.0817). The structure was solved by direct methods (SHELXT–2014/5)[9] and refined by full-matrix least squares procedures on F^2 for all reflections (SHELXL–2018/1).[10] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{54}H_{37}BO_2$; FW = 728.64, crystal size 0.10 × 0.10 × 0.01 mm^3, *monoclinic*, $P2_1/c$, a = 18.5697(8) Å, b = 12.0685(4) Å, c = 16.8103(7) Å, β = 95.339(4)°, V = 3751.0(3) Å^3, Z = 4, D_c = 1.290 g cm^{-3}, μ = 0.076 mm^{-1}, R_1 = 0.0613 ($I > 2\sigma(I)$), wR_2 = 0.1558 (all data), GOF = 1.008. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 2124575. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Structural analysis of 13. A single crystal of **13** was obtained by slow cooling of a hot toluene solution of **13**. Intensity data were collected at 123 K on a Rigaku Single Crystal X-ray diffractometer equipped with FR-X generator, Varimax optics, and PILATUS 200K photon counting detector with MoKα radiation (λ = 0.71073 Å). A total of 90543 reflections were measured at the maximum 2θ angle of 55.0°, of which 15631 were independent reflections (R_{int} = 0.1015). The structure was solved by direct methods (SHELXT–2014/5)[9] and refined by full-matrix least squares procedures on F^2 for all reflections (SHELXL–2018/1).[10] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{50}H_{35}BO_2$; FW = 678.59, crystal size 0.10 × 0.03 × 0.01 mm^3, *monoclinic*, $P2_1/c$, a = 12.1456(4) Å, b = 15.8222(5) Å, c = 35.8589(12) Å, β = 98.879(3)°, V = 6808.4(4) Å^3, Z = 8, D_c = 1.324 g cm^{-3}, μ = 0.079 mm^{-1}, R_1 = 0.0666 ($I > 2\sigma(I)$), wR_2 = 0.1682 (all data), GOF = 1.005. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 2124576. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

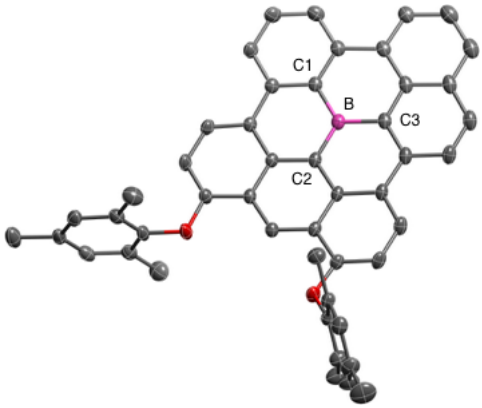


Figure S1. ORTEP of **10a** (50% probability for thermal ellipsoids). Hydrogen atoms and solvent molecules are omitted for clarify.

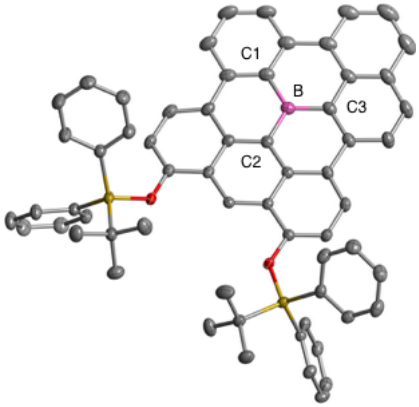


Figure S2. ORTEP of **10b** (50% probability for thermal ellipsoids). Hydrogen atoms and solvent molecules are omitted for clarify.

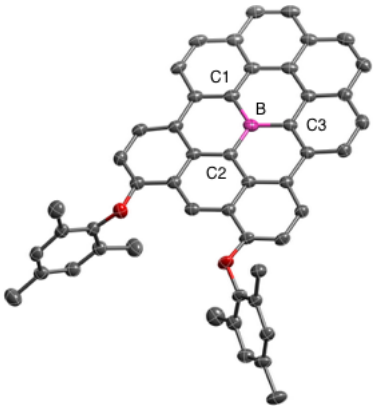


Figure S3. ORTEP of **13** (50% probability for thermal ellipsoids). The crystal structure contains crystallographically independent two molecules. One of the molecules is shown, while hydrogen atoms are omitted for clarify.

Table S1. Selected bond lengths (Å) and angles (°) in the crystal structures of **10a**, **10b**, **12**, and **13**

	10a	**10b**	**12**	**13**[a]
B–C1	1.515(3)	1.509(4)	1.519(3)	1.509(4)
B–C2	1.508(3)	1.515(3)	1.506(4)	1.497(4)
B–C3	1.512(3)	1.497(4)	1.498(3)	1.507(4)
C1–B–C2	120.06(17)	120.0(2)	120.8(2)	119.4(3)
C1–B–C3	120.29(18)	120.9(2)	120.7(2)	120.6(3)
C2–B–C3	119.64(18)	119.1(2)	118.5(2)	119.9(3)

[a] Single crystal of **13** contains crystallographically independent two molecules. Structural parameters for one of the molecules are shown.

3. Photophysical Properties

Methods. UV–vis absorption and fluorescence spectra were measured with a Shimadzu UV-3600 Plus spectrometer and a JASCO FP-8500 spectrofluorometer, respectively, using dilute sample solutions in a 1 cm square quartz cuvette. Absolute fluorescence quantum yields were determined with a Hamamatsu Absolute PL Quantum Yield spectrometer C11347 and C9920-02 calibrated integrating sphere system.

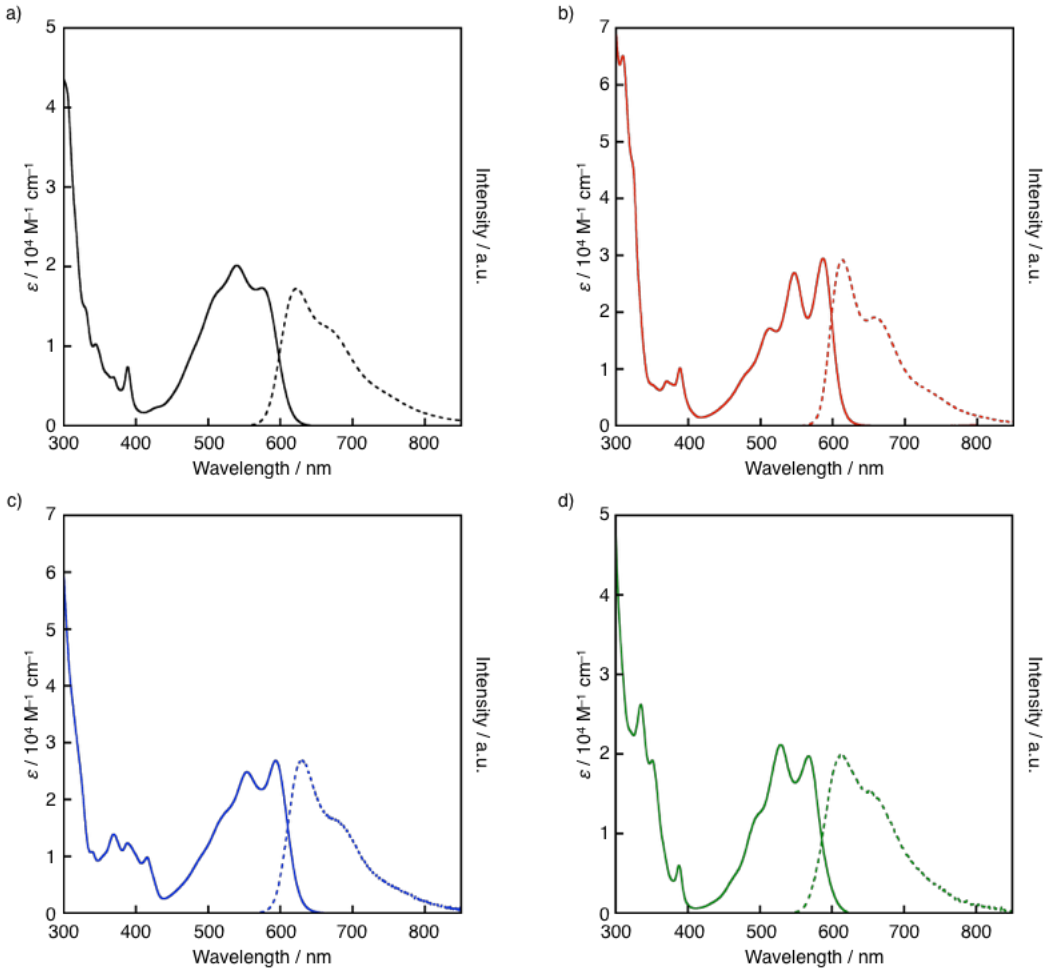


Figure S4. UV–vis absorption (solid lines) and fluorescence spectra (dashed lines) of a) **10a**, b) **11**, c) **12**, and d) **13** in CH_2Cl_2.

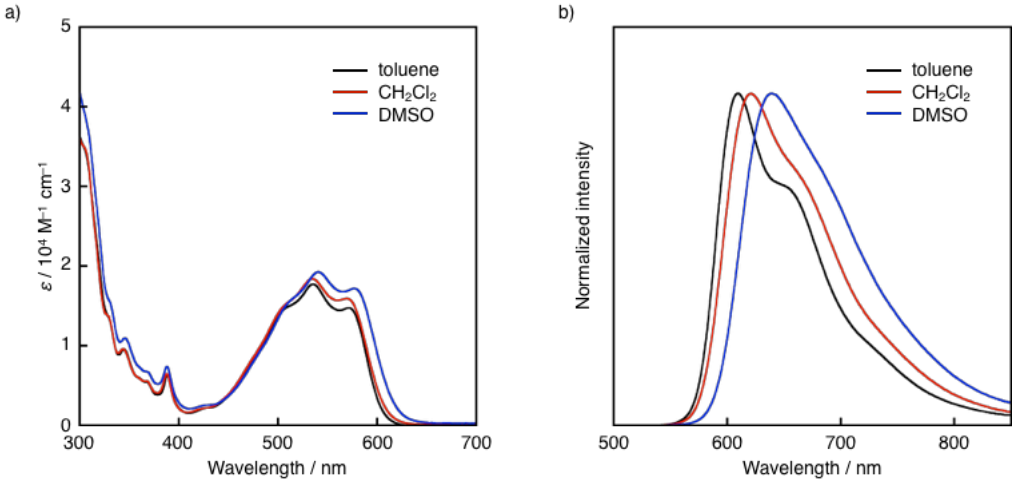


Figure S5. a) UV–vis absorption and b) fluorescence spectra of **10c** in various solvents.

Table S2. Photophysical properties of **10a**, **11**, **12**, **13**, and **10c**

Compound	Solvent	λ_{abs} / nm[a]	ε / 10^4 M^{-1} cm^{-1}	λ_{em} / nm	Stokes shift / cm^{-1}	Φ_F[b]
10a	toluene	577	1.41	606	829	0.41
	CH_2Cl_2	575	1.69	624	1370	0.29
11	toluene	586	2.90	599	370	0.52
	CH_2Cl_2	587	2.95	613	723	0.38
12	toluene	595	2.49	614	520	0.56
	CH_2Cl_2	594	2.68	629	937	0.39
13	toluene	565	1.96	600	1030	0.36
	CH_2Cl_2	568	1.97	612	1270	0.22
10c	toluene	571	1.47	611	1150	0.40
	CH_2Cl_2	569	1.59	621	1470	0.27
	DMSO	577	1.72	639	1680	0.33

[a] Only the longest absorption maximum wavelengths are shown. [b] Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within ±3% error.

Titration experiments. UV–vis absorption spectra were measured with a JASCO V-750 spectrometer equipped with a JASCO ETCR-762 temperature/stirring controller using dilute sample solutions in a 1 cm square quartz cuvette at 298 K.

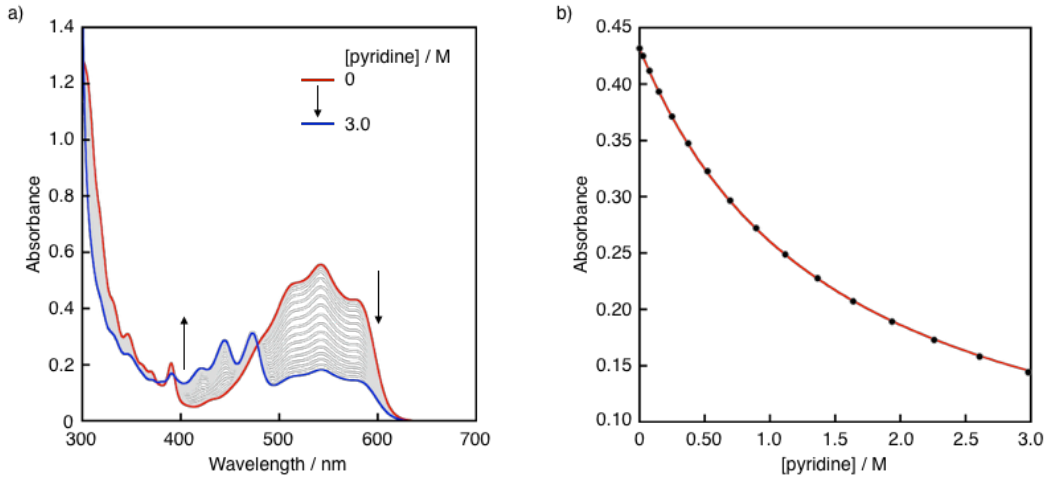


Figure S6. a) UV–vis absorption spectral changes upon addition of pyridine to a toluene solution of **10a** (3.19×10^{-5} M) and b) plots of the absorbance at 577 nm with a fitting curve for the binding constant toward pyridine. The binding constant was determined to be 0.660 (± 0.001) M^{-1} (R^2 = 0.99996).

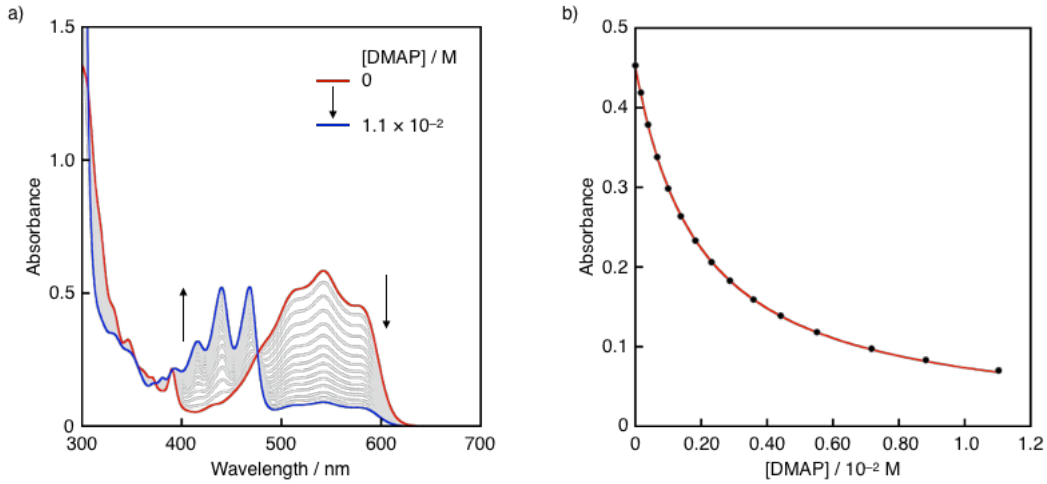


Figure S7. a) UV–vis absorption spectral changes upon addition of DMAP to a toluene solution of **10a** (3.19×10^{-5} M) and b) plots of the absorbance at 577 nm with a fitting curve for the binding constant toward DMAP. The binding constant was determined to be 5.16 (± 0.02) × 10^2 ($R^2 = 0.99990$).

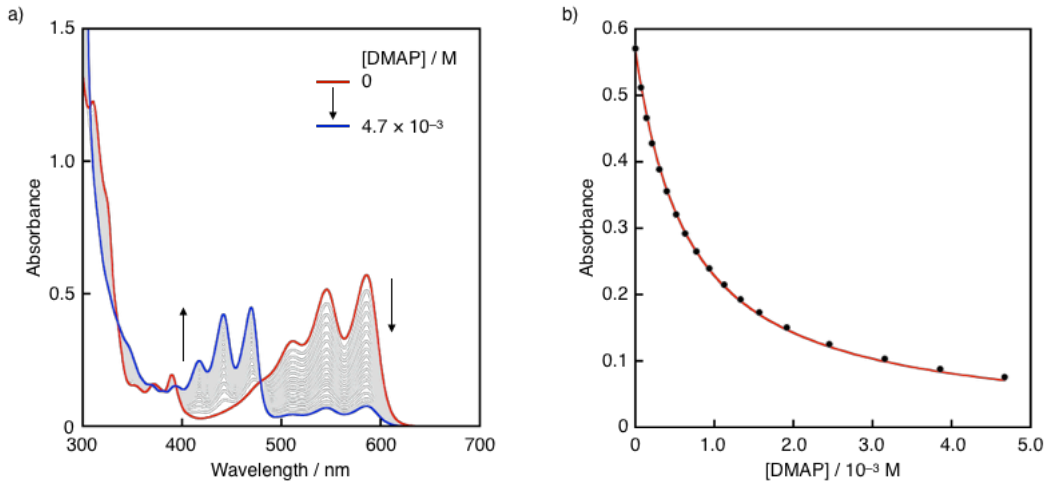


Figure S8. a) UV–vis absorption spectral changes upon addition of DMAP to a toluene solution of **11** (1.97×10^{-5} M) and b) plots of the absorbance at 586 nm with a fitting curve for the binding constant toward DMAP. The binding constant was determined to be 1.52 (± 0.01) × 10^3 M^{-1} ($R^2 = 0.99931$).

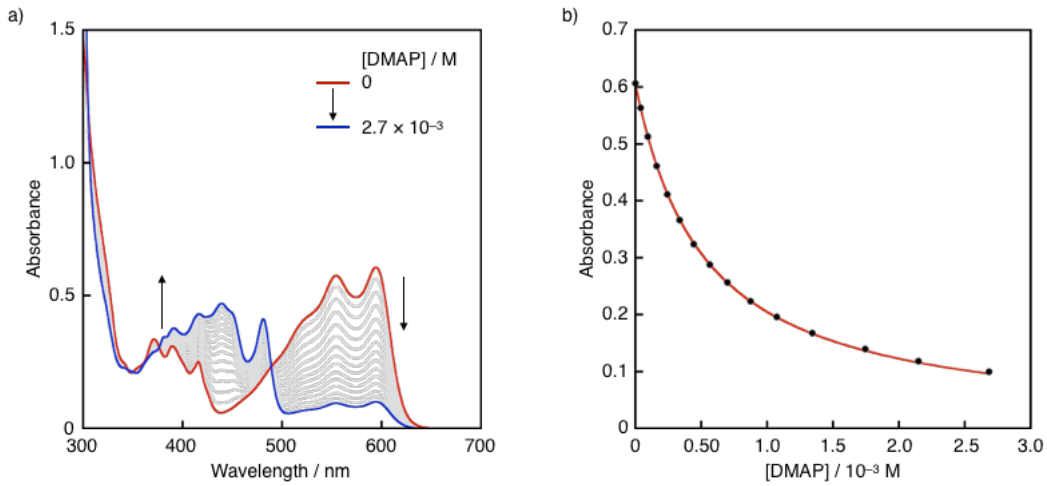


Figure S9. a) UV–vis absorption spectral changes upon addition of DMAP to a toluene solution of **12** (2.44×10^{-5} M) and b) plots of the absorbance at 595 nm with a fitting curve for the binding constant toward DMAP. The binding constant was determined to be 1.99 (± 0.01) × 10^3 M^{-1} (R^2 = 0.99988).

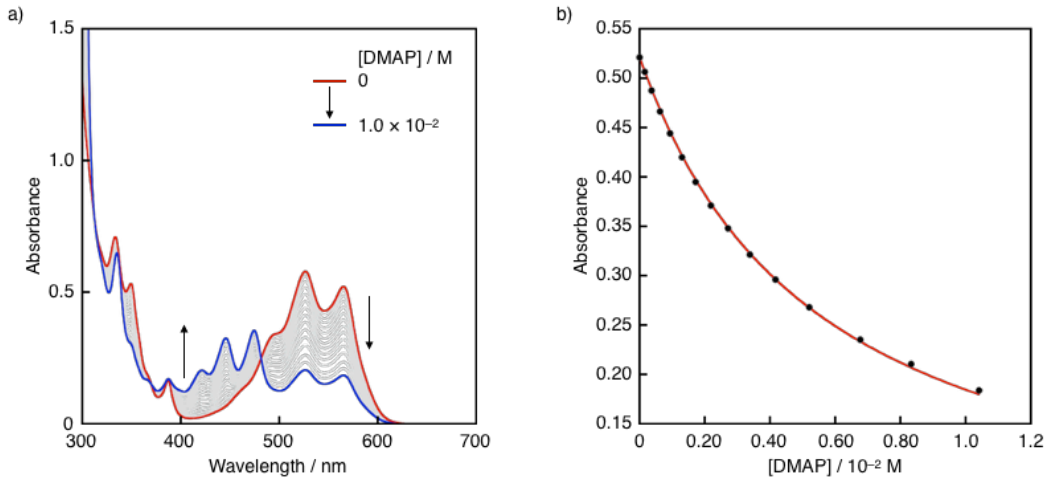


Figure S10. a) UV–vis absorption spectral changes upon addition of DMAP to a toluene solution of **13** (2.66×10^{-5} M) and b) plots of the absorbance at 565 nm with a fitting curve for the binding constant toward DMAP. The binding constant was determined to be 1.83 (± 0.01) × 10^2 M^{-1} (R^2 = 0.99963).

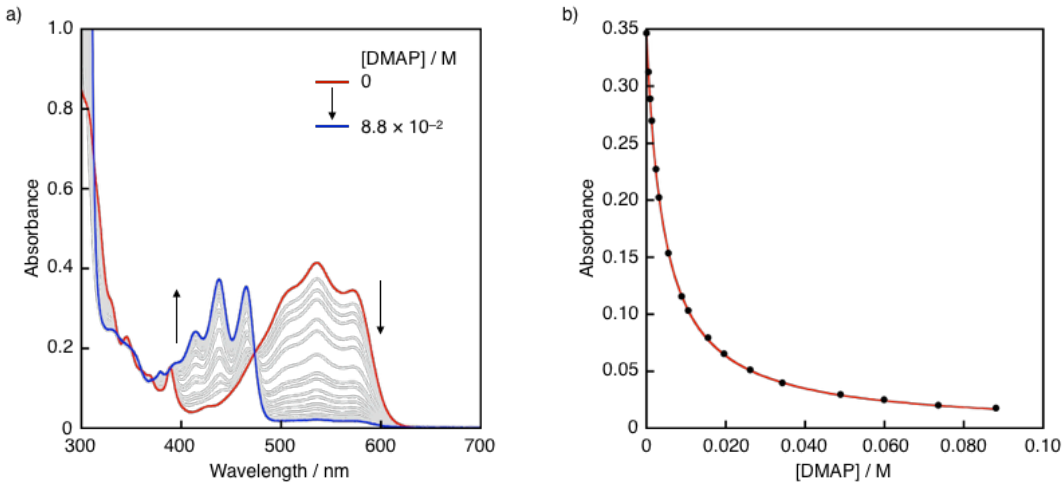


Figure S11. a) UV–vis absorption spectral changes upon addition of DMAP to a toluene solution of **10c** (2.28×10^{-5} M) and b) plots of the absorbance at 571 nm with a fitting curve for the binding constant toward DMAP. The binding constant was determined to be 2.24 (± 0.01) × 10^2 M^{-1} (R^2 = 0.99990).

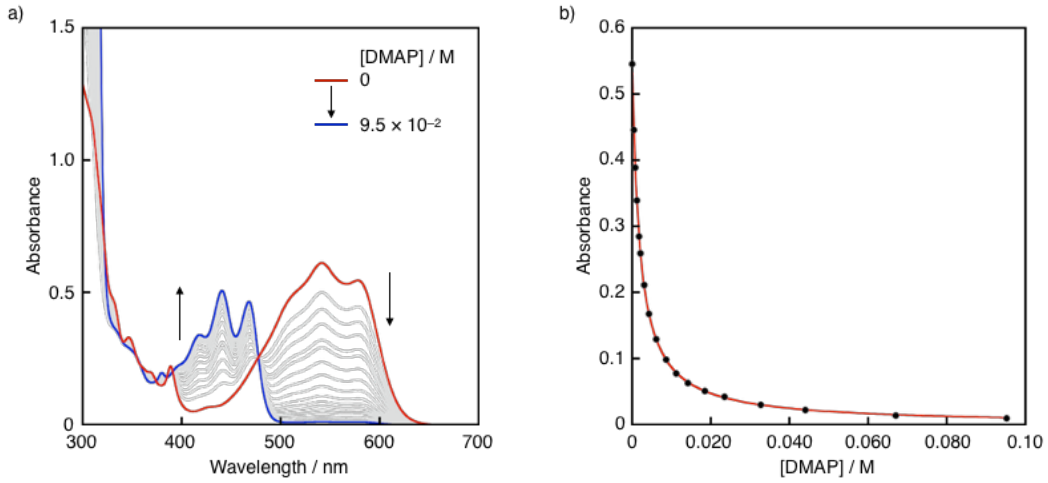


Figure S12. a) UV–vis absorption spectral changes upon addition of DMAP to a DMSO solution of **10c** (3.21×10^{-5} M) and b) plots of the absorbance at 578 nm with a fitting curve for the binding constant toward DMAP. The binding constant was determined to be 5.29 (± 0.02) × 10^2 M^{-1} (R^2 = 0.99996).

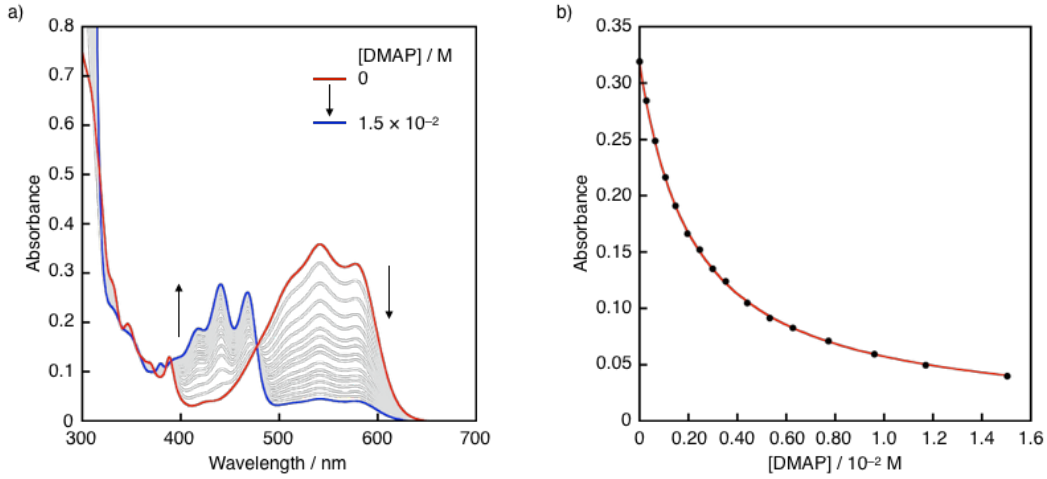


Figure S13. a) UV–vis absorption spectral changes upon addition of DMAP to a DMSO/H_2O (9:1) solution of **10c** (2.00×10^{-5} M) and b) plots of the absorbance at 577 nm with a fitting curve for the binding constant toward DMAP. The binding constant was determined to be 4.58 (± 0.02) × 10^2 (R^2 = 0.99981).

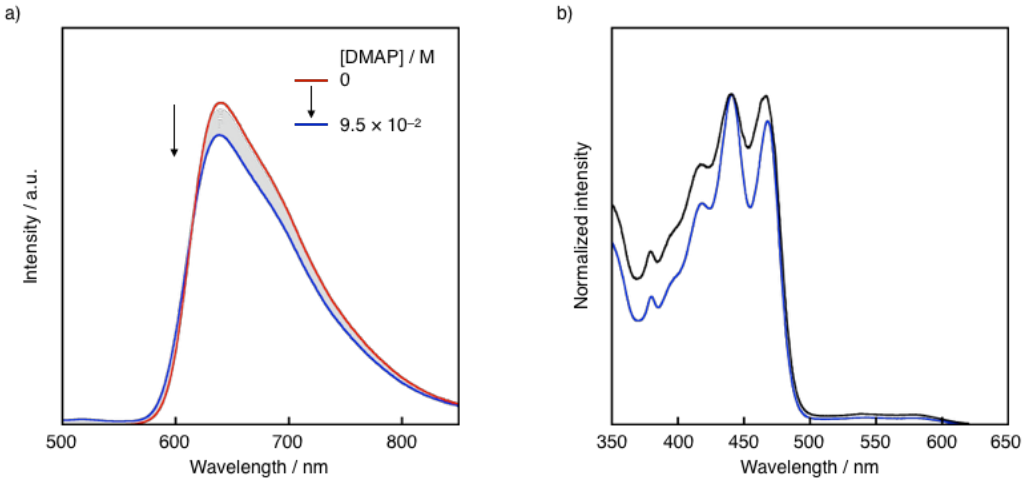


Figure S14. a) Fluorescence spectral changes upon addition of DMAP to a DMSO solution of **10c** (the same conditions as shown in Figure S12) with the excitation wavelength at λ_{ex} = 477 nm and b) UV–vis absorption spectrum (blue) and excitation spectrum with the fluorescence detection at 640 nm (black) of a DMSO solution of **10c**·DMAP ([**10c**] = 3.21×10^{-5} M, [DMAP] = 9.5×10^{-2} M).

4. Theoretical Calculations

Computational method. Geometry optimizations were performed using the Gaussian 16 program[12] at the B3LYP/6-31G(d) level of theory or the CAM-B3LYP/6-31G(d) level of theory including the effect of solvents by the PCM model. All the optimized structures have been confirmed as the energy minima by frequency analysis at the same level of theory, which showed only positive values. The optimized geometries were used for the TD-DFT calculations at the B3LYP/6-31G(d) level of theory or the CAM-B3LYP/6-31G(d) level of theory including the effect of solvents by the PCM model.

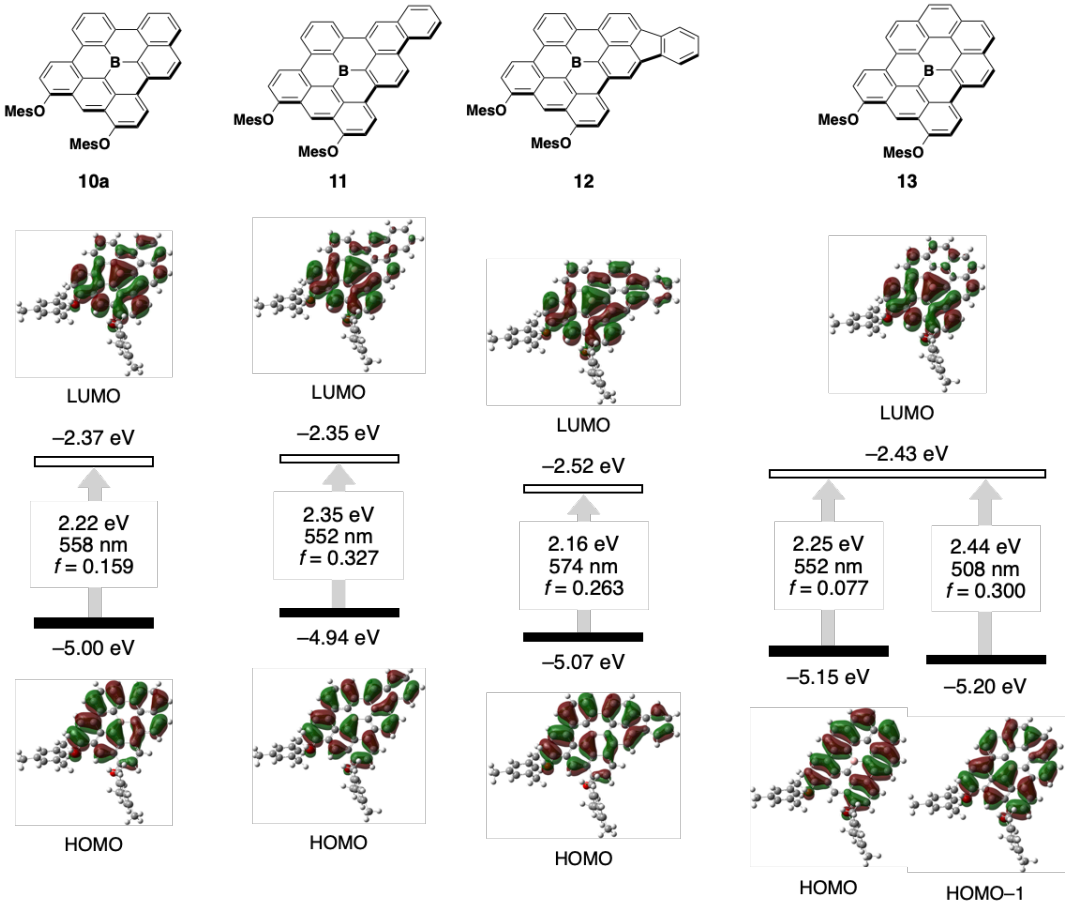


Figure S15. Kohn–Sham molecular orbitals for **10a**, **11**, **12**, and **13**, together with their corresponding $S_0 \rightarrow S_1$ excitation energies, wavelengths, and oscillator strengths obtained by the TD-DFT calculations at the B3LYP/6-31G(d) level of theory in the gas phase.

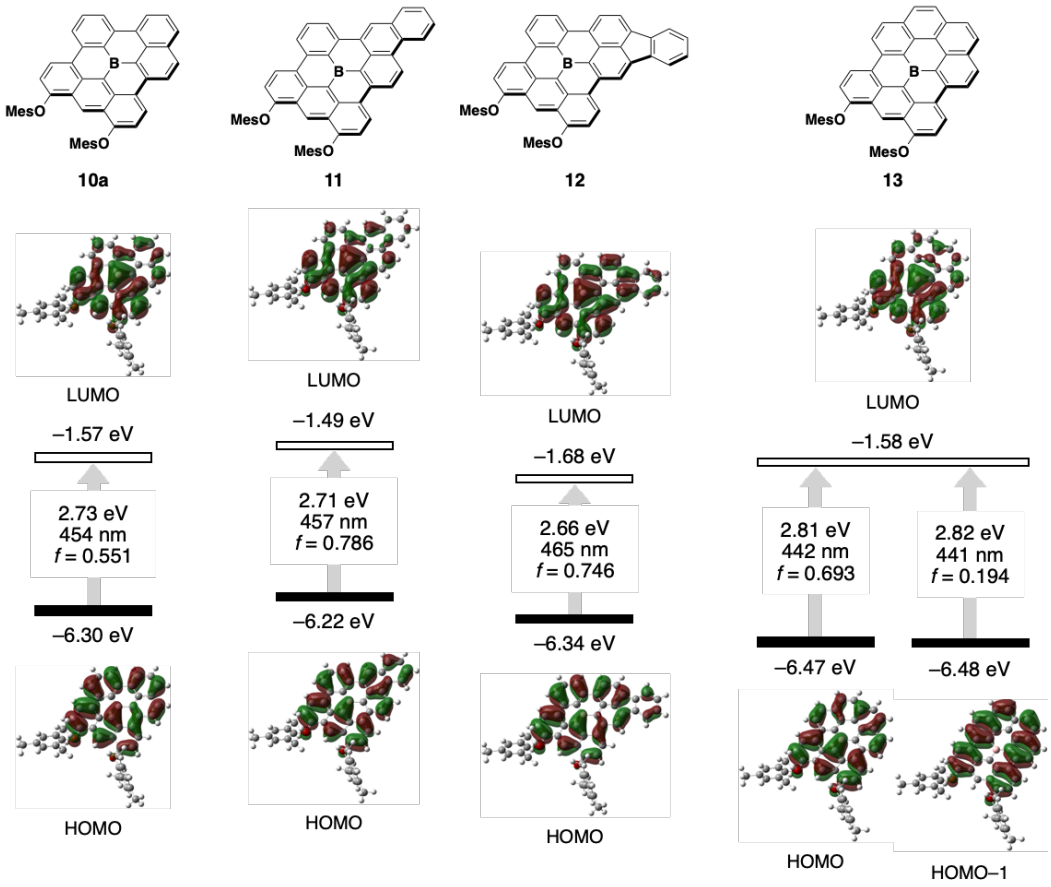


Figure S16. Kohn–Sham molecular orbitals for **10a**, **11**, **12**, and **13**, together with their corresponding $S_0 \rightarrow S_1$ excitation energies, wavelengths, and oscillator strengths obtained by the TD-DFT calculations at the CAM-B3LYP/6-31G(d) level of theory in toluene.

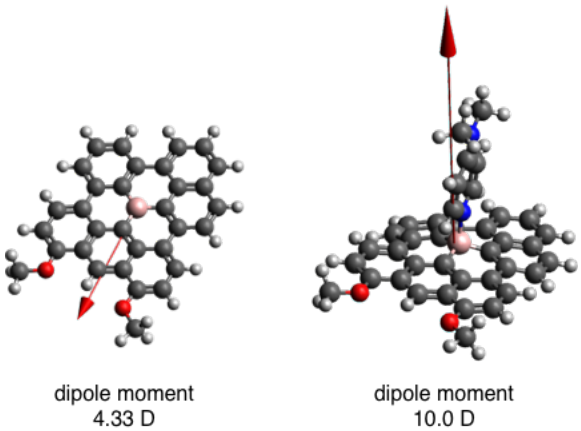


Figure S17. Optimized structures of **10d** and **10d**·DMAP in S_0 calculated at the M06-2X/6-311G(d) level of theory together with their dipole moments.

Table S3. Cartesian Coordinates (Å) for **10a** in the gas phase in S_0 calculated at B3LYP/6-31G(d)

atom	*x*	*y*	*z*	*atom*	*x*	*y*	*z*
B	-3.09968407	-0.48059207	-0.00008900	H	-5.16544997	-5.43615903	0.00003255
H	-0.78402633	-4.83386207	-0.00042080	O	2.86404038	-2.10553987	-0.00056306
C	-0.42288792	-3.81093314	-0.00038171	O	2.24184739	2.62309311	-0.00037719
C	-1.32713573	-2.75842690	-0.00026087	C	2.86170427	3.87769942	-0.00015436
C	1.52054145	-2.37348487	-0.00045233	C	4.24521452	6.29622960	0.00028430
C	-0.76667340	-1.42482119	-0.00025924	C	3.19986503	4.45622478	1.22902652
C	0.97958990	-3.63956034	-0.00047787	C	3.20019468	4.45642027	-1.22904337
C	0.65846213	-1.22793833	-0.00034837	C	3.89074797	5.67268057	-1.20083018
C	-1.60095960	-0.28575513	-0.00017882	C	3.89037635	5.67241773	1.20126195
H	1.62654759	-4.50970242	-0.00057186	H	4.16088372	6.14075653	-2.14532086
H	2.24565483	0.21719538	-0.00041103	H	4.16024669	6.14030577	2.14593740
C	-1.08760375	1.02755944	-0.00018862	C	3.78575485	-3.15744118	-0.00021249
C	-1.97234431	2.17414005	-0.00012372	C	5.74690890	-5.13761475	0.00052522
C	0.33937733	1.20469012	-0.00027049	C	4.26251459	-3.62988661	-1.22882083
C	1.17181054	0.07684549	-0.00034238	C	4.26187961	-3.62970676	1.22886381
C	-1.36930390	3.42585968	-0.00016168	C	5.24286908	-4.62645823	1.20140170
H	-1.98174454	4.32120077	-0.00013342	C	5.24358357	-4.62671775	-1.20060477
C	0.02837515	3.62047551	-0.00024561	H	5.62537594	-5.00937538	-2.14505978
H	0.43118167	4.62706259	-0.00028030	C	2.83350591	3.78274711	-2.52852007
C	0.87688873	2.53398039	-0.00028997	H	3.23966374	4.33599959	-3.38027553
C	-3.44481119	2.01778784	-0.00002406	H	1.74625808	3.71623611	-2.65559895
C	-4.00632990	0.72863048	-0.00000534	H	3.21993576	2.75810379	-2.56732788
C	-5.69680031	2.94224276	0.00015866	C	2.83275086	3.78228377	2.52824380
C	-5.41612015	0.51170305	0.00009699	H	3.23961448	4.33471921	3.38019320
C	-4.33635727	3.13162343	0.00006198	H	3.21813189	2.75723175	2.56646696
C	-6.28634303	1.64453729	0.00018152	H	1.74545231	3.71682936	2.65548848
C	-5.96806371	-0.82246115	0.00012122	C	5.02155986	7.59317218	0.00074716
H	-3.96026783	4.14956898	0.00005525	H	6.10432193	7.40958313	0.01167612
H	-8.34144024	2.33034132	0.00035180	H	4.78724050	8.20048234	0.88153144
H	-6.35822261	3.80628687	0.00022301	H	4.80330288	8.19140796	-0.89024045
C	-7.35724993	-0.93639997	0.00023238	C	3.73457006	-3.07362833	-2.52834282
H	-7.82090567	-1.91688218	0.00026111	H	3.84602541	-1.98423347	-2.56806393
C	-8.20920287	0.18402638	0.00031400	H	2.66632388	-3.28736158	-2.65393606
H	-9.28516653	0.03133665	0.00039855	H	4.26792787	-3.50527779	-3.38029235
C	-7.68796275	1.46092240	0.00028877	C	6.83168575	-6.19028646	0.00124653
C	-3.68215755	-1.87737386	-0.00006927	H	7.83045494	-5.73369868	0.01664474
C	-4.74666232	-4.43263848	0.00000166	H	6.77790811	-6.82200794	-0.89174060
C	-5.09450022	-2.03146540	0.00003719	H	6.75930620	-6.84011946	0.87991089
C	-2.79777366	-2.98958262	-0.00014422	H	5.62412893	-5.00893890	2.14616496
C	-3.36161565	-4.27600007	-0.00009532	C	3.73316155	-3.07316354	2.52794819
C	-5.61016029	-3.33726822	0.00006367	H	4.26647984	-3.50411238	3.38027735
H	-2.74360044	-5.16811983	-0.00012380	H	2.66499929	-3.28749063	2.65326911
H	-6.67840495	-3.52640320	0.00013491	H	3.84394184	-1.98368721	2.56719597

Table S4. Cartesian Coordinates (Å) for **11** in the gas phase in S_0 calculated at B3LYP/6-31G(d)

atom	*x*	*y*	*z*	*atom*	*x*	*y*	*z*
B	2.35306863	-0.79203085	0.00008038	H	-6.74011348	-4.53425062	-2.14603353
C	2.80408174	-2.23722826	0.00016104	C	-4.68570268	-2.77293069	-2.52807606
C	3.63458174	-4.87839941	0.00019296	H	-3.64088169	-3.08153601	-2.65353479
C	1.82383370	-3.26618029	0.00024286	H	-4.69902867	-1.67792961	-2.56736273
C	4.19497037	-2.51784407	0.00010775	H	-5.25538258	-3.15472534	-3.38031442
C	4.59186681	-3.86463666	0.00012321	C	-8.04714037	-5.60420562	-0.00072196
C	2.26965278	-4.59790279	0.00025160	H	-8.03981339	-6.24951674	0.88416229
H	5.63827140	-4.15002444	0.00006990	H	-8.04172917	-6.24665982	-0.88768020
H	1.57385947	-5.43063336	0.00028771	H	-9.00184133	-5.06126281	0.00122298
H	3.96221518	-5.91522409	0.00019517	C	-3.20235971	3.96615802	2.52800699
H	-0.34329855	-4.92520724	0.00056697	H	-2.12524021	3.80703787	2.65906464
C	-0.61274640	-3.87446595	0.00045293	H	-3.67467633	2.97799186	2.56240476
C	0.38064724	-2.90573409	0.00030069	H	-3.56337154	4.54998611	3.37970029
C	-2.42036323	-2.27122501	0.00035824	C	-5.00354236	7.97508305	0.00002398
C	-0.05740819	-1.52752134	0.00021210	H	-4.22881355	8.75362116	-0.00180397
C	-1.99436650	-3.58029383	0.00048191	H	-5.62499022	8.13878435	0.88683239
C	-1.46013243	-1.20654157	0.00023667	H	-5.62784005	8.13751909	-0.88502468
C	0.87511137	-0.46666810	0.00010215	C	-3.20343014	3.96573725	-2.52800617
H	-2.71582229	-4.38971948	0.00060313	H	-2.12651040	3.80509114	-2.65876393
H	-2.91557659	0.37087909	0.00016035	H	-3.56338360	4.55017437	-3.37972946
C	0.47559445	0.88633856	0.00001003	H	-3.67715864	2.97824532	-2.56268492
C	1.45487391	1.95125991	-0.00010737	C	-4.68745394	-2.77233002	2.52823044
C	-0.93058314	1.18783089	0.00002789	H	-3.64187846	-3.07849495	2.65325039
C	-1.85810514	0.13743415	0.00014246	H	-5.25607407	-3.15608487	3.38029584
C	0.96440588	3.25054183	-0.00022645	H	-4.70342322	-1.67737771	2.56835557
H	1.65297185	4.08870892	-0.00034616	C	2.90885010	1.66689850	-0.00011091
C	-0.41123358	3.56683904	-0.00020957	C	3.36632044	0.33346745	-0.00003769
H	-0.72437849	4.60484176	-0.00030468	C	5.23124360	2.38419142	-0.00018259
C	-1.35062222	2.55877469	-0.00007523	C	4.75215938	0.00472462	-0.00004504
O	-2.70337859	2.76510505	-0.00004052	C	3.88751431	2.69107155	-0.00017642
O	-3.73475810	-1.88525240	0.00039377	C	5.71715093	1.05156832	-0.00012191
C	-3.21222714	4.06844661	-0.00000799	C	5.17674322	-1.39311070	0.00003103
C	-4.39259985	6.59258394	0.00003807	H	3.60618004	3.73917260	-0.00021132
C	-3.50429238	4.67196219	1.22896195	H	7.89645313	2.78259709	-0.00028036
C	-3.50477372	4.67179496	-1.22896174	H	5.93821542	3.20712192	-0.00023058
C	-4.09544708	5.93949063	-1.20102238	C	6.52974626	-1.64283313	0.00003572
C	-4.09498392	5.93966764	1.20106172	H	6.89685816	-2.66389359	0.00010503
H	-4.33444168	6.42417338	-2.14553284	C	7.52455286	-0.62215015	-0.00004378
H	-4.33362566	6.42448258	2.14559163	C	8.90098919	-0.95959394	-0.00004163
C	-4.74589304	-2.85154181	0.00007460	C	7.13515657	0.74830261	-0.00012841
C	-6.87382106	-4.65124014	-0.00046674	C	9.87288359	0.01906786	-0.00012289
C	-5.26162396	-3.28021034	-1.22890164	H	9.17878100	-2.01121669	0.00002430
C	-5.26245397	-3.27999583	1.22879767	H	10.92515202	-0.25169918	-0.00012151
C	-6.32746608	-4.18648067	1.20068935	C	9.49217432	1.37596873	-0.00020924

C	-6.32667597	-4.18670198	-1.20132090	H	10.25354147	2.15144042	-0.00027462
H	-6.74150119	-4.53388797	2.14519474	C	8.15535114	1.72923003	-0.00021154

Table S5. Cartesian Coordinates (Å) for **12** in the gas phase in S_0 calculated at B3LYP/6-31G(d)

atom	*x*	*y*	*z*	*atom*	*x*	*y*	*z*
B	1.82669271	-1.62823024	-0.00010083	C	-2.48313009	5.10994079	1.22907856
H	-1.77869567	-4.97491939	-0.00036107	C	-2.73714520	6.48524293	1.20111540
C	-1.78207967	-3.89007183	-0.00030950	C	-2.73727571	6.48537686	-1.20100547
C	-0.58094251	-3.19440862	-0.00021294	H	-2.83886829	7.01581487	2.14571223
C	-3.14644277	-1.89204120	-0.00032472	H	-2.83910108	7.01604099	-2.14553302
C	-0.67661809	-1.75004674	-0.00019005	C	-5.54328001	-1.89003580	-0.00012367
C	-3.04997431	-3.26610000	-0.00036429	C	-8.04480930	-3.11792049	0.00046055
C	-1.95575172	-1.09379925	-0.00023592	C	-6.14769171	-2.18001296	1.22899050
C	0.48396883	-0.94811817	-0.00012940	C	-6.14824788	-2.17994499	-1.22888747
H	-3.94695133	-3.87530021	-0.00042871	C	-7.40180031	-2.80019076	-1.20068116
H	-2.97217178	0.79659388	-0.00023289	C	-7.40118588	-2.80022457	1.20137991
C	0.44300598	0.46330334	-0.00010553	H	-7.88682629	-3.03660951	2.14607906
C	1.65816551	1.25863151	-0.00005097	C	-2.35743196	4.35313598	2.52847001
C	-0.84700556	1.09951472	-0.00013514	H	-2.55775797	5.00939745	3.38034507
C	-2.00549464	0.30811952	-0.00019997	H	-1.35268214	3.93217072	2.65471671
C	1.49595913	2.63861800	-0.00002729	H	-3.05995717	3.51311177	2.56823186
H	2.36862626	3.28334805	0.00001530	C	-2.35776888	4.35337520	-2.52862936
C	0.23922432	3.28013591	-0.00005393	H	-2.55768627	5.00986393	-3.38042515
H	0.18844602	4.36312541	-0.00003140	H	-3.06070675	3.51370166	-2.56860894
C	-0.91894955	2.53191279	-0.00010703	H	-1.35321589	3.93193622	-2.65482817
C	3.00107146	0.62903161	-0.00001879	C	-3.17679325	8.67038618	0.00026330
C	3.06840201	-0.77870507	-0.00003835	H	-4.26002109	8.85141761	0.00487917
C	5.43498140	0.72628800	0.00005538	H	-2.76942312	9.16509129	-0.88782663
C	4.30699505	-1.47111025	-0.00000694	H	-2.76175642	9.16649991	0.88403852
C	4.22272556	1.38767342	0.00002830	C	-5.46583931	-1.82769424	2.52817884
C	5.46091066	-0.69562262	0.00003809	H	-5.21184745	-0.76245022	2.56696893
C	4.43786348	-2.90339487	-0.00001973	H	-4.52789571	-2.38174040	2.65453501
H	4.20189725	2.47346745	0.00003958	H	-6.11172909	-2.05852876	3.38029728
C	5.74695880	-3.40436507	0.00000563	C	-9.41465324	-3.75691886	0.00098179
H	5.90532827	-4.47854510	-0.00000976	H	-10.20856284	-2.99808220	0.01075689
C	6.90757712	-2.58799517	0.00004815	H	-9.56133990	-4.39031164	0.88234968
H	7.88332726	-3.06771476	0.00006457	H	-9.56878786	-4.37563590	-0.88942692
C	6.77307418	-1.20792814	0.00006693	H	-7.88790459	-3.03653630	-2.14513782
C	1.93520614	-3.14252298	-0.00011295	C	-5.46707029	-1.82757707	-2.52841739
C	2.09577528	-5.90896779	-0.00003797	H	-6.11329297	-2.05863402	-3.38022298
C	3.22021372	-3.76110800	-0.00005565	H	-4.52904954	-2.38140221	-2.65515446
C	0.73357441	-3.89858602	-0.00014230	H	-5.21335582	-0.76227277	-2.56741890
C	0.84180902	-5.30145754	-0.00009169	C	7.66768319	-0.03323783	0.00010725
C	3.27561548	-5.16140166	-0.00002357	C	8.84337968	2.49998598	0.00017270
H	-0.03665721	-5.93880317	-0.00007878	C	9.05401450	0.07659550	0.00014702

H	4.22523668	-5.68767301	0.00002263	C	6.85381673	1.14436830	0.00009997
H	2.15698160	-6.99458381	-0.00000051	C	7.44530016	2.40253343	0.00013268
O	-4.32705129	-1.19859533	-0.00039130	C	9.63752904	1.35076621	0.00017979
O	-2.17865282	3.06383875	-0.00013837	H	9.68137709	-0.81129405	0.00015287
C	-2.35315963	4.45265555	-0.00008274	H	6.83592747	3.30309178	0.00012745
C	-2.86804863	7.19073023	0.00007767	H	10.72022781	1.44464846	0.00021107
C	-2.48325976	5.11003900	-1.22913564	H	9.31333204	3.47980570	0.00019848

Table S6. Cartesian Coordinates (Å) for **13** in the gas phase in S_0 calculated at B3LYP/6-31G(d)

atom	*x*	*y*	*z*	*atom*	*x*	*y*	*z*
B	0.00000000	0.00000000	2.85290511	H	0.00000002	1.21979445	8.93316656
C	0.00001345	1.30966931	3.60294603	H	-0.00000252	3.37764924	7.73917573
C	-0.00000458	3.69878075	5.02342977	O	-0.00016326	-2.39111340	-2.83511647
C	0.00000470	1.26599243	5.02436425	O	0.00016326	2.39111340	-2.83511647
C	0.00001727	2.52312793	2.88813388	C	0.00043776	-3.55575462	-3.61081737
C	0.00000000	3.72837943	3.64286831	C	0.00142413	-5.76964246	-5.30280425
C	0.00000122	2.48329194	5.75770613	C	1.22963937	-4.08254056	-4.02473644
H	-0.00001787	4.69696900	3.15249294	C	-1.22834053	-4.08297218	-4.02569309
H	-0.00001584	4.63643311	5.57578457	C	-1.19990429	-5.19530073	-4.87337081
H	0.00013413	4.61862245	1.13835612	C	1.20216466	-5.19494766	-4.87248064
C	0.00008477	3.65206861	0.64515423	H	-2.14424284	-5.61807445	-5.21044449
C	0.00003628	2.48926627	1.40481318	H	2.14687628	-5.61741060	-5.20886509
C	0.00006889	2.47795323	-1.46973605	C	-0.00043776	3.55575462	-3.61081737
C	0.00001940	1.23854790	0.67148832	C	-0.00142413	5.76964246	-5.30280425
C	0.00010069	3.66391701	-0.76675284	C	-1.22963937	4.08254056	-4.02473644
C	0.00002942	1.22837210	-0.76625959	C	1.22834053	4.08297218	-4.02569309
C	0.00000000	0.00000000	1.34582466	C	1.19990429	5.19530073	-4.87337081
H	0.00014610	4.61030284	-1.29581530	C	-1.20216466	5.19494766	-4.87248064
H	0.00000000	0.00000000	-2.52745402	H	2.14424284	5.61807445	-5.21044449
C	-0.00001940	-1.23854790	0.67148832	H	-2.14687628	5.61741060	-5.20886509
C	-0.00003628	-2.48926627	1.40481318	C	-2.52855455	3.45722699	-3.57895253
C	-0.00002942	-1.22837210	-0.76625959	H	-2.65968964	3.53176312	-2.49271039
C	0.00000000	0.00000000	-1.44434939	H	-2.56285868	2.39101439	-3.82947428
C	-0.00008477	-3.65206861	0.64515423	H	-3.38031230	3.95039050	-4.05628395
C	-0.00010069	-3.66391701	-0.76675284	C	2.52772191	3.45789531	-3.58093337
H	-0.00014610	-4.61030284	-1.29581530	H	2.65820376	3.52951833	-2.49443386
C	-0.00006889	-2.47795323	-1.46973605	H	3.37916988	3.95330242	-4.05648936
C	-0.00001727	-2.52312793	2.88813388	H	2.56337071	2.39241060	-3.83443623
C	-0.00001345	-1.30966931	3.60294603	C	-0.00176047	6.98998325	-6.19459513
C	0.00000458	-3.69878075	5.02342977	H	0.00760899	7.91577159	-5.60371708
C	-0.00000470	-1.26599243	5.02436425	H	-0.89232483	7.02103479	-6.83122229
C	0.00000000	-3.72837943	3.64286831	H	0.87948030	7.01187896	-6.84452676
C	-0.00000122	-2.48329194	5.75770613	C	2.52855455	-3.45722699	-3.57895253
C	0.00000000	0.00000000	5.72221754	H	2.65968964	-3.53176312	-2.49271039
H	0.00000252	-3.37764924	7.73917573	H	2.56285868	-2.39101439	-3.82947428

H	0.00001584	-4.63643311	5.57578457	H	3.38031230	-3.95039050	-4.05628395
C	0.00000000	0.00000000	7.13952514	C	-2.52772191	-3.45789531	-3.58093337
C	0.00000007	-1.24402157	7.84581410	H	-2.65820376	-3.52951833	-2.49443386
H	-0.00000002	-1.21979445	8.93316656	H	-3.37916988	-3.95330242	-4.05648936
C	0.00000091	-2.44211306	7.18411150	H	-2.56337071	-2.39241060	-3.83443623
H	-0.00013413	-4.61862245	1.13835612	C	0.00176047	-6.98998325	-6.19459513
H	0.00001787	-4.69696900	3.15249294	H	-0.00760899	-7.91577159	-5.60371708
C	-0.00000007	1.24402157	7.84581410	H	0.89232483	-7.02103479	-6.83122229
C	-0.00000091	2.44211306	7.18411150	H	-0.87948030	-7.01187896	-6.84452676

Table S7. Cartesian Coordinates (Å) for **14** in the gas phase in S_0 calculated at B3LYP/6-31G(d)

atom	*x*	*y*	*z*	*atom*	*x*	*y*	*z*
B	3.76743561	0.00006183	-0.00002372	H	6.36760074	1.71815941	-4.51418715
H	1.94137711	-4.60964203	-0.24388262	O	-2.05160738	-2.35937111	-0.14813521
C	1.41955619	-3.65754786	-0.19535756	O	-2.05168108	2.35930595	0.14835808
H	3.21668489	-2.52199349	-0.11108834	C	-2.83941077	3.50837666	0.22080096
C	2.13194187	-2.49075403	-0.12392782	C	-4.56258169	5.69766848	0.36085670
C	-0.67903801	-2.46821424	-0.14241531	C	-3.27017234	4.10354329	-0.97165972
C	1.46616662	-1.22331194	-0.05293258	C	-3.25423228	3.95923340	1.48019565
C	-0.00273177	-3.66053283	-0.20760508	C	-4.11710227	5.05939742	1.52328518
C	0.02209934	-1.21366310	-0.06416957	C	-4.13254815	5.20050646	-0.87415890
C	2.18219726	0.00003592	0.00000868	H	-4.45338602	5.42108134	2.49310113
H	-0.54695669	-4.59650733	-0.26750011	H	-4.48103582	5.67324303	-1.79042442
H	-1.74890920	-0.00003149	0.00009575	C	-2.83930588	-3.50845514	-0.22068921
C	1.46612658	1.22335926	0.05297813	C	-4.56240084	-5.69779612	-0.36093089
C	2.13186159	2.49082448	0.12393911	C	-3.26997308	-4.10378209	0.97170307
C	0.02206024	1.21366138	0.06427791	C	-3.25420118	-3.95916336	-1.48013502
C	-0.66705678	-0.00001299	0.00007111	C	-4.11702074	-5.05934262	-1.52331749
C	1.41943949	3.65759449	0.19539821	C	-4.13232261	-5.20077869	0.87410772
H	3.21660301	2.52210058	0.11105535	H	-4.45337585	-5.42090222	-2.49315677
H	1.94123014	4.60970617	0.24390316	H	-4.48073466	-5.67363907	1.79033634
C	-0.00284793	3.66053176	0.20770735	C	-2.79153441	3.26459998	2.73716493
H	-0.54710294	4.59648720	0.26763329	H	-3.26763751	3.70109019	3.62022155
C	-0.67911648	2.46819061	0.14254649	H	-1.70501679	3.34403997	2.86267368
C	4.53055707	-0.49338969	1.27633941	H	-3.02877549	2.19517938	2.70955361
C	5.85802458	-1.37848277	3.61570655	C	-2.82443327	3.56146124	-2.30732505
C	5.82325838	-1.06033226	1.22100127	H	-3.31102342	4.09873622	-3.12680284
C	3.92401422	-0.40143963	2.54845745	H	-3.06303403	2.49622283	-2.40256597
C	4.58036491	-0.82001105	3.70392017	H	-1.73948560	3.65497960	-2.43641887
C	6.47525508	-1.50738052	2.36949145	C	-5.47064361	6.90369275	0.43750340
H	6.31415341	-1.17176377	0.25824497	H	-6.10191947	6.87410750	1.33205979
H	2.92272362	0.01372630	2.62519711	H	-6.12697913	6.96777341	-0.43705302
H	4.09439186	-0.72286770	4.67142798	H	-4.89308565	7.83712855	0.47858109
H	7.46363737	-1.95390553	2.29477143	C	-2.82415745	-3.56188996	2.30742049
H	6.36785183	-1.71799618	4.51400916	H	-3.06247492	-2.49659429	2.40270691

C	4.53048612	0.49352482	-1.27642581	H	-1.73923849	-3.65570587	2.43656209
C	5.85782355	1.37863818	-3.61585910	H	-3.31092536	-4.09908366	3.12684554
C	5.82317281	1.06050650	-1.22114954	C	-2.79160173	-3.26434001	-2.73703485
C	3.92388968	0.40154604	-2.54851593	H	-3.02845418	-2.19484596	-2.70905849
C	4.58017693	0.82012709	-3.70401125	H	-3.26808670	-3.70042344	-3.62008687
C	6.47510516	1.50756525	-2.36967234	H	-1.70514334	-3.34413123	-2.86285234
H	6.31410748	1.17196034	-0.25841594	C	-5.47039749	-6.90385923	-0.43774396
H	2.92260788	-0.01364995	-2.62520805	H	-6.12521348	-6.96929681	0.43784264
H	4.09416397	0.72296071	-4.67149670	H	-4.89275375	-7.83713617	-0.48117752
H	7.46347724	1.95412096	-2.29499953	H	-6.10321415	-6.87310715	-1.33117796

Table S8. Cartesian Coordinates (Å) for **15** in the gas phase in S_0 calculated at B3LYP/6-31G(d)

atom	*x*	*y*	*z*	*atom*	*x*	*y*	*z*
B	-3.79285443	0.00131105	0.00006887	O	1.96372917	2.35519255	0.16873627
H	-1.98221760	-4.61211964	0.08311671	C	2.74972113	3.51027167	0.23153254
C	-1.49378604	-3.64429704	0.06242988	C	4.46092987	5.70593947	0.36639981
C	-2.25132259	-2.48591824	0.16533241	C	3.10023611	4.01141405	1.49098150
C	0.59900508	-2.46174723	-0.08085303	C	3.23740463	4.05499247	-0.96243512
C	-1.55387244	-1.22891454	0.05849566	C	4.09310735	5.15749660	-0.86695128
C	-0.08913392	-3.65259689	-0.07150805	C	3.95905260	5.11482671	1.53092016
C	-0.11537070	-1.22038415	-0.01170532	H	4.48625137	5.59316582	-1.78335779
C	-2.25678865	0.00078080	0.00003559	H	4.24653567	5.51699588	2.50035051
H	0.44116846	-4.59515493	-0.14740872	C	2.74731583	-3.51213340	-0.23153640
H	1.64910652	-0.00055096	0.00000437	C	4.45698228	-5.70900219	-0.36640275
C	-1.55303595	1.22999573	-0.05844252	C	3.09749487	-4.01351198	-1.49098806
C	-2.24963274	2.48747228	-0.16528987	C	3.23460048	-4.05720593	0.96243018
C	-0.11453929	1.22048428	0.01173849	C	4.08953078	-5.16031268	0.86694595
C	0.56647370	-0.00018215	0.00001436	C	3.95553447	-5.11752528	-1.53092683
C	-1.49130100	3.64533466	-0.06242247	H	4.48235606	-5.59626732	1.78335299
H	-1.97906616	4.61349158	-0.08313449	H	4.24274556	-5.51988837	-2.50035778
C	-0.08664253	3.65267809	0.07150359	C	2.85946327	3.45807690	-2.29570269
H	0.44430295	4.59487604	0.14737716	H	3.38852794	3.96151001	-3.11011904
C	0.60068466	2.46135942	0.08086339	H	1.78301265	3.54627697	-2.48573067
C	-4.48095955	1.33288473	-0.41084549	H	3.10151203	2.39008444	-2.33578825
C	-5.67041564	3.78421233	-1.16397469	C	2.57653055	3.36788718	2.75135026
C	-5.82964793	1.41240682	-0.82355197	H	3.00614364	3.84403716	3.63754294
C	-3.70330920	2.52918584	-0.43969165	H	2.81881662	2.29966102	2.78221224
C	-4.32916839	3.73835282	-0.80816542	H	1.48490211	3.44680629	2.82018877
C	-6.42820233	2.60967214	-1.19246897	C	5.36319237	6.91644343	0.43854418
H	-6.41291847	0.50012273	-0.88528951	H	6.04892872	6.95676700	-0.41442223
H	-3.76017178	4.66045318	-0.85686642	H	5.96309072	6.91538751	1.35486525
H	-7.46730292	2.63173362	-1.51048655	H	4.78190001	7.84833150	0.43230599
H	-6.11764275	4.73327334	-1.44941613	C	2.57425366	-3.36960514	-2.75135576
C	-4.48187310	-1.32982573	0.41087698	H	2.81731754	-2.30155558	-2.78221931
C	-5.67299104	-3.78037920	1.16391035	H	1.48256795	-3.44772873	-2.82019084

C	-5.83063067	-1.40846024	0.82352723	H	3.00351740	-3.84606824	-3.63754946
C	-3.70502696	-2.52664987	0.43971751	C	2.85705684	-3.46004512	2.29570054
C	-4.33170132	-3.73540639	0.80814822	H	3.09975897	-2.39220089	2.33576900
C	-6.42999523	-2.60533452	1.19239895	H	3.38583127	-3.96379453	3.11010981
H	-6.41329345	-0.49578881	0.88527175	H	1.78055638	-3.54758564	2.48575466
H	-3.76331725	-4.65788529	0.85684784	C	5.35839310	-6.92013963	-0.43856057
H	-7.46912107	-2.62670908	1.51038078	H	5.95875570	-6.91917129	-1.35457981
H	-6.12086052	-4.72914741	1.44931791	H	4.77641396	-7.85160308	-0.43298561
O	1.96212053	-2.35651267	-0.16874355	H	6.04366790	-6.96129417	0.41473475

Table S9. Cartesian Coordinates (Å) for **10a** in toluene in S_0 calculated at CAM-B3LYP/6-31G(d)

atom	*x*	*y*	*z*	*atom*	*x*	*y*	*z*
B	3.07789663	-0.48312373	0.00010279	H	5.12872298	-5.42836272	0.00002478
H	0.76438092	-4.81715098	0.00009568	O	-2.86136633	-2.08567584	0.00004579
C	0.40641356	-3.79414924	0.00008640	O	-2.23240360	2.61414951	0.00014915
C	1.30546103	-2.75089791	0.00008018	C	-2.84545791	3.86602906	0.00006191
C	-1.52782268	-2.36043652	0.00006524	C	-4.19862968	6.28513085	-0.00017425
C	0.75167068	-1.41852500	0.00008451	C	-3.17418058	4.44477059	-1.22362622
C	-0.99540757	-3.62050893	0.00008143	C	-3.17435604	4.44485221	1.22355612
C	-0.66348737	-1.21974070	0.00007656	C	-3.85112581	5.66224911	1.19700426
C	1.58503763	-0.28654187	0.00009988	C	-3.85090541	5.66208872	-1.19731765
H	-1.64279182	-4.48901631	0.00009217	H	-4.11582716	6.13339604	2.14030856
H	-2.24597946	0.22317196	0.00008770	H	-4.11545029	6.13315955	-2.14071731
C	1.07663243	1.02184680	0.00011578	C	-3.77936227	-3.13359339	-0.00001418
C	1.95940732	2.16446046	0.00013636	C	-5.71595039	-5.11770238	-0.00021954
C	-0.34088172	1.20090150	0.00011362	C	-4.24798559	-3.60734661	1.22325091
C	-1.17290623	0.08049645	0.00008984	C	-4.24773288	-3.60744218	-1.22349319
C	1.36455308	3.40881349	0.00016140	C	-5.21801550	-4.60658871	-1.19733915
H	1.97790179	4.30231310	0.00018271	C	-5.21836461	-4.60658151	1.19688211
C	-0.03206995	3.60758297	0.00016545	H	-5.59652059	-4.99259649	2.14022935
H	-0.43088467	4.61462476	0.00019403	C	-2.80757067	3.76736736	2.51549902
C	-0.87584754	2.52863997	0.00014030	H	-3.20425873	4.32109118	3.36945928
C	3.43077911	2.00249071	0.00013331	H	-1.72138332	3.69410540	2.63411021
C	3.98521478	0.72235837	0.00011669	H	-3.20149659	2.74726068	2.55244593
C	5.67360166	2.92208717	0.00014193	C	-2.80715142	3.76710209	-2.51540302
C	5.39222097	0.50205827	0.00011172	H	-3.20384698	4.32059774	-3.36950750
C	4.32119540	3.11392637	0.00014593	H	-3.20089403	2.74692007	-2.55218804
C	6.25794272	1.62456769	0.00012461	H	-1.72093798	3.69400530	-2.63388571
C	5.93913851	-0.82816871	0.00009337	C	-4.96062858	7.58530490	-0.00055397
H	3.94595475	4.13074460	0.00015833	H	-6.04244286	7.40876200	-0.01048522
H	8.30958879	2.30770726	0.00012948	H	-4.72128572	8.18787565	-0.88117811
H	6.33771244	3.78256865	0.00015178	H	-4.73595795	8.17976320	0.88934398
C	7.31824909	-0.94753349	0.00008959	C	-3.71730463	-3.04872210	2.51509555
H	7.77864685	-1.92833081	0.00007663	H	-3.83229755	-1.96125668	2.55181036
C	8.17252882	0.16888820	0.00010237	H	-2.64935466	-3.26030806	2.63303439

H	9.24676652	0.01299010	0.00009853	H	-4.24405073	-3.48020774	3.36928810
C	7.65641500	1.43948984	0.00011959	C	-6.78968728	-6.17519819	-0.00069455
C	3.65765612	-1.88011611	0.00008611	H	-7.78855389	-5.72387503	-0.01468216
C	4.71220439	-4.42521408	0.00004307	H	-6.72953136	-6.80526139	0.89104976
C	5.06180826	-2.03584834	0.00007894	H	-6.71257155	-6.82171726	-0.87933440
C	2.77569201	-2.98391775	0.00007331	H	-5.59593214	-4.99269004	-2.14076706
C	3.33284754	-4.26646553	0.00005048	C	-3.71668295	-3.04878991	-2.51517375
C	5.57489211	-3.33508715	0.00005716	H	-4.24323019	-3.48021020	-3.36952155
H	2.71275162	-5.15563231	0.00003581	H	-2.64871251	-3.26042721	-2.63283550
H	6.64176557	-3.52518917	0.00004948	H	-3.83160481	-1.96131654	-2.55186131

Table S10. Cartesian Coordinates (Å) for **11** in toluene in S_0 calculated at CAM-B3LYP/6-31G(d)

atom	*x*	*y*	*z*	*atom*	*x*	*y*	*z*
B	-2.33527303	-0.79177212	-0.00008697	H	6.70975675	-4.51648818	2.14083186
C	-2.78390158	-2.23681321	-0.00018048	C	4.66337008	-2.74947667	2.51513320
C	-3.60606641	-4.86689023	-0.00035303	H	3.61862934	-3.05586936	2.63273883
C	-1.80722002	-3.25792003	-0.00026755	H	4.68048715	-1.65608210	2.55194241
C	-4.16663402	-2.51816041	-0.00017630	H	5.22640309	-3.13208014	3.36947081
C	-4.56184843	-3.85799182	-0.00026480	C	8.00645056	-5.58542184	0.00048963
C	-2.24697875	-4.58517634	-0.00035419	H	7.99528481	-6.22868906	-0.88379477
H	-5.60685934	-4.14395951	-0.00026711	H	7.99729521	-6.22596327	0.88676128
H	-1.54963950	-5.41499586	-0.00042224	H	8.96013734	-5.04495308	-0.00145903
H	-3.93177048	-5.90304397	-0.00042126	C	3.17617232	3.94769491	-2.51510967
H	0.35588425	-4.90674681	-0.00042111	H	2.10086032	3.78051969	-2.63752002
C	0.62260187	-3.85635375	-0.00034167	H	3.65688740	2.96535314	-2.54795889
C	-0.36450364	-2.89610759	-0.00026055	H	3.52680536	4.53188064	-3.36894883
C	2.42199545	-2.25850792	-0.00022939	C	4.93807731	7.96200861	-0.00005036
C	0.06741644	-1.51979301	-0.00016708	H	4.15511170	8.72925884	0.00144809
C	2.00361368	-3.56064037	-0.00032716	H	5.55663036	8.13010288	-0.88602165
C	1.46020217	-1.19852964	-0.00015420	H	5.55898583	8.12910083	0.88446969
C	-0.86300929	-0.46551479	-0.00008405	C	3.17657432	3.94767357	2.51519775
H	2.72501000	-4.36872109	-0.00038924	H	2.10132549	3.78007853	2.63756875
H	2.91214217	0.37503793	-0.00006075	H	3.52694296	4.53205422	3.36901206
C	-0.46708125	0.88197773	0.00000339	H	3.65768119	2.96552424	2.54814131
C	-1.44331674	1.94409249	0.00008621	C	4.66448083	-2.74915638	-2.51518295
C	0.92956547	1.18376638	0.00000770	H	3.61950459	-3.05470432	-2.63285350
C	1.85548257	0.14016138	-0.00006762	H	5.22731464	-3.13239337	-3.36936799
C	-0.95947274	3.23475981	0.00015971	H	4.68251286	-1.65577989	-2.55222937
H	-1.64821081	4.07146736	0.00022236	C	-2.89634633	1.65575558	0.00009278
C	0.41508166	3.55422255	0.00016012	C	-3.34874885	0.33100594	0.00000871
H	0.72501632	4.59206116	0.00021914	C	-5.20849986	2.36897151	0.00019309
C	1.34825577	2.55264803	0.00008771	C	-4.72966282	0.00104580	0.00001434
O	2.69324177	2.75398625	0.00009465	C	-3.87165343	2.67710895	0.00018530
O	3.72577310	-1.86649462	-0.00021728	C	-5.68839560	1.03860675	0.00011026
C	3.19538375	4.05405299	0.00004202	C	-5.15180415	-1.39526957	-0.00007629

C	4.34220162	6.57783365	-0.00004299	H	-3.59073307	3.72392007	0.00025363
C	3.47733215	4.65728986	-1.22346818	H	-7.86241333	2.76480570	0.00029362
C	3.47752194	4.65729589	1.22352151	H	-5.91690386	3.18915136	0.00026659
C	4.05273582	5.92575356	1.19712357	C	-6.49298601	-1.64748555	-0.00006461
C	4.05255640	5.92576097	-1.19715249	H	-6.85989835	-2.66749912	-0.00013001
H	4.28560048	6.41337536	2.14044509	C	-7.48914842	-0.62650322	0.00003402
H	4.28527881	6.41337923	-2.14050885	C	-8.85969813	-0.96715964	0.00004486
C	4.73352210	-2.82836781	-0.00001489	C	-7.10454779	0.73308340	0.00012338
C	6.84103139	-4.62990305	0.00034417	C	-9.82869004	0.00569642	0.00014266
C	5.24238730	-3.25823803	1.22344154	H	-9.13457195	-2.01833474	-0.00002465
C	5.24293005	-3.25811335	-1.22331310	H	-10.87951890	-0.26591763	0.00015095
C	6.29925633	-4.16589345	-1.19686591	C	-9.45075302	1.35927773	0.00023199
C	6.29874229	-4.16603032	1.19734734	H	-10.21252892	2.13268721	0.00030952
H	6.71067556	-4.51626261	-2.14021031	C	-8.12078587	1.71248239	0.00022245

Table S11. Cartesian Coordinates (Å) for **12** in toluene in S_0 calculated at CAM-B3LYP/6-31G(d)

atom	*x*	*y*	*z*	*atom*	*x*	*y*	*z*
B	-1.80609891	-1.62431710	0.00007779	C	2.45103620	5.09565415	-1.22366853
H	1.79459088	-4.94910514	0.00012525	C	2.68756475	6.46820580	-1.19721444
C	1.79362112	-3.86523362	0.00010580	C	2.68762604	6.46825523	1.19705744
C	0.59957652	-3.17813957	0.00009844	H	2.78165694	7.00006328	-2.14067080
C	3.14814183	-1.87214184	0.00006990	H	2.78176807	7.00012900	2.14049315
C	0.68772413	-1.73708597	0.00007247	C	5.52862884	-1.86057548	-0.00001518
C	3.05943352	-3.23779574	0.00009211	C	8.01050882	-3.09596029	-0.00023397
C	1.95600242	-1.08069155	0.00005764	C	6.12686933	-2.15331780	-1.22355540
C	-0.47060004	-0.94285121	0.00006081	C	6.12700078	-2.15338467	1.22335110
H	3.95695495	-3.84433373	0.00010514	C	7.37230053	-2.77729718	1.19690746
H	2.96656854	0.80701705	0.00002211	C	7.37209976	-2.77719410	-1.19733828
C	-0.43436401	0.46223069	0.00003577	H	7.85614893	-3.01708193	-2.14076707
C	-1.64723325	1.25293006	0.00002672	C	2.32894624	4.33506560	-2.51565788
C	0.84529151	1.09880385	0.00002117	H	2.51940935	4.98923187	-3.36948896
C	2.00187509	0.31566229	0.00003214	H	1.32840841	3.90596756	-2.63411920
C	-1.49227571	2.62350208	0.00000823	H	3.03878686	3.50324928	-2.55307726
H	-2.36615922	3.26495953	0.00000372	C	2.32906763	4.33513716	2.51559459
C	-0.23881579	3.27016478	-0.00000399	H	2.51950580	4.98935950	3.36938834
H	-0.19331412	4.35231332	-0.00001443	H	3.03896153	3.50336726	2.55304890
C	0.91336880	2.52891413	-0.00000007	H	1.32855881	3.90598399	2.63409771
C	-2.98621939	0.61687754	0.00003989	C	3.09920670	8.65009319	-0.00020288
C	-3.04856693	-0.77954476	0.00006630	H	4.17860671	8.84099838	-0.00444588
C	-5.40808443	0.70890940	0.00004180	H	2.68591260	9.13770796	0.88705300
C	-4.28155165	-1.47649541	0.00008288	H	2.67884253	9.13894496	-0.88347112
C	-4.20763288	1.37222982	0.00002671	C	5.44168645	-1.80056324	-2.51534989
C	-5.43083667	-0.70886425	0.00007037	H	5.19219448	-0.73586956	-2.55224068
C	-4.40884277	-2.90310081	0.00011121	H	4.50303239	-2.35211912	-2.63339279
H	-4.18967699	2.45685219	0.00000466	H	6.08112032	-2.03452612	-3.36954482

C	-5.70575071	-3.40725615	0.00012421	C	9.37265556	-3.74076447	-0.00056744
H	-5.86017156	-4.48095585	0.00014540	H	10.16707063	-2.98548632	-0.00896209
C	-6.86856220	-2.59565785	0.00011089	H	9.51496916	-4.37236122	-0.88189711
H	-7.84186162	-3.07768470	0.00012254	H	9.52136284	-4.35971952	0.88859317
C	-6.73652751	-1.22492646	0.00008341	H	7.85647294	-3.01722810	2.14025045
C	-1.91066944	-3.13800661	0.00010687	C	5.44204682	-1.80074926	2.51529991
C	-2.06195394	-5.89170370	0.00016615	H	6.08163399	-2.03478294	3.36936086
C	-3.18650199	-3.75722046	0.00012472	H	4.50341819	-2.35232217	2.63346647
C	-0.71316140	-3.88544466	0.00011761	H	5.19255600	-0.73606020	2.55233415
C	-0.81498525	-5.28263173	0.00014777	C	-7.63450590	-0.05092078	0.00006135
C	-3.24030612	-5.15011181	0.00015485	C	-8.81269348	2.46597382	0.00001020
H	0.06525239	-5.91544884	0.00015840	C	-9.01521501	0.05114347	0.00006168
H	-4.18789231	-5.67763293	0.00017058	C	-6.82971662	1.12109497	0.00003562
H	-2.11982217	-6.97629348	0.00019021	C	-7.41937111	2.37339657	0.00001005
O	4.31620674	-1.17378337	0.00006502	C	-9.60019077	1.31913153	0.00003589
O	2.16558527	3.05670358	-0.00001213	H	-9.63795583	-0.83860592	0.00008150
C	2.33171509	4.44091520	-0.00002403	H	-6.81190706	3.27385627	-0.00000990
C	2.80979419	7.17112686	-0.00007191	H	-10.68198333	1.40991259	0.0000358
C	2.45109035	5.09566504	1.22356314	H	-9.28532608	3.4432168	-0.00000977

Table S12. Cartesian Coordinates (Å) for **13** in toluene in S_0 calculated at CAM-B3LYP/6-31G(d)

atom	*x*	*y*	*z*	*atom*	*x*	*y*	*z*
B	0.00000000	0.00000000	2.83213268	H	0.00000046	1.21504654	8.89532927
C	0.00000106	1.30813879	3.58134988	H	0.00000063	3.36798629	7.70465263
C	0.00000000	3.68558200	4.99581221	O	-0.00006719	-2.37741098	-2.82925887
C	0.00000054	1.26417346	4.99898082	O	0.00006719	2.37741098	-2.82925887
C	0.00000107	2.51264734	2.87141166	C	0.00022548	-3.53926795	-3.59928388
C	-0.00000006	3.71579633	3.62227960	C	0.00070270	-5.75824403	-5.26060484
C	0.00000044	2.47218995	5.72655166	C	1.22386661	-4.06760837	-4.00399321
H	-0.00000117	4.68266463	3.13126231	C	-1.22325130	-4.06785515	-4.00444524
H	-0.00000055	4.62135249	5.54905466	C	-1.19659030	-5.18336478	-4.83836283
H	0.00000755	4.60154187	1.12775290	C	1.19767409	-5.18319657	-4.83796048
C	0.00000679	3.63581342	0.63522551	H	-2.13976284	-5.60993391	-5.17044047
C	0.00000364	2.48092303	1.38832535	H	2.14103210	-5.60960587	-5.16968422
C	0.00002046	2.46931100	-1.47276707	C	-0.00022548	3.53926795	-3.59928388
C	0.00000517	1.23293183	0.65925002	C	-0.00070270	5.75824403	-5.26060484
C	0.00001492	3.64881912	-0.77606246	C	-1.22386661	4.06760837	-4.00399321
C	0.00001028	1.22269815	-0.76925524	C	1.22325130	4.06785515	-4.00444524
C	0.00000000	0.00000000	1.33089102	C	1.19659030	5.18336478	-4.83836283
H	0.00001656	4.59493989	-1.30340540	C	-1.19767409	5.18319657	-4.83796048
H	0.00000000	0.00000000	-2.52787870	H	2.13976284	5.60993391	-5.17044047
C	-0.00000517	-1.23293183	0.65925002	H	-2.14103210	5.60960587	-5.16968422
C	-0.00000364	-2.48092303	1.38832535	C	-2.51544731	3.43890913	-3.55771265
C	-0.00001028	-1.22269815	-0.76925524	H	-2.63857264	3.50720541	-2.47170442
C	0.00000000	0.00000000	-1.44523344	H	-2.54771320	2.37608182	-3.81564637

C	-0.00000679	-3.63581342	0.63522551	H	-3.36929802	3.93342245	-4.02640864
C	-0.00001492	-3.64881912	-0.77606246	C	2.51505238	3.43929147	-3.55860915
H	-0.00001656	-4.59493989	-1.30340540	H	2.63797211	3.50648897	-2.47251494
C	-0.00002046	-2.46931100	-1.47276707	H	3.36874443	3.93468673	-4.02666313
C	-0.00000107	-2.51264734	2.87141166	H	2.54786076	2.37674896	-3.81766952
C	-0.00000106	-1.30813879	3.58134988	C	-0.00074819	6.98274601	-6.13899405
C	0.00000000	-3.68558200	4.99581221	H	0.00762598	7.89972265	-5.53834692
C	-0.00000054	-1.26417346	4.99898082	H	-0.89005051	7.01797910	-6.77435040
C	0.00000006	-3.71579633	3.62227960	H	0.88044629	7.00970441	-6.78600971
C	-0.00000044	-2.47218995	5.72655166	C	2.51544731	-3.43890913	-3.55771265
C	0.00000000	0.00000000	5.69613561	H	2.63857264	-3.50720541	-2.47170442
H	-0.00000063	-3.36798629	7.70465263	H	2.54771320	-2.37608182	-3.81564637
H	0.00000055	-4.62135249	5.54905466	H	3.36929802	-3.93342245	-4.02640864
C	0.00000000	0.00000000	7.10136955	C	-2.51505238	-3.43929147	-3.55860915
C	-0.00000036	-1.24159344	7.80921350	H	-2.63797211	-3.50648897	-2.47251494
H	-0.00000046	-1.21504654	8.89532927	H	-3.36874443	-3.93468673	-4.02666313
C	-0.00000049	-2.43252649	7.15181464	H	-2.54786076	-2.37674896	-3.81766952
H	-0.00000755	-4.60154187	1.12775290	C	0.00074819	-6.98274601	-6.13899405
H	0.00000117	-4.68266463	3.13126231	H	-0.00762598	-7.89972265	-5.53834692
C	0.00000036	1.24159344	7.80921350	H	0.89005051	-7.01797910	-6.77435040
C	0.00000049	2.43252649	7.15181464	H	-0.88044629	-7.00970441	-6.78600971

Table S13. Cartesian Coordinates (Å) for **10d** in the gas phase in S_0 calculated at M06-2X/6-311G(d)

atom	*x*	*y*	*z*	*atom*	*x*	*y*	*z*
B	-0.34416197	-0.98330727	0.00000000	C	-1.04337026	1.42674558	0.00000000
C	-1.79397438	-1.42225156	0.00000000	C	-3.06003292	3.38462091	0.00000000
C	-4.42902093	-2.21896797	0.00000000	C	-0.70540463	2.81402065	0.00000000
C	-2.08623323	-2.80422974	0.00000000	C	0.00000000	0.48563803	0.00000000
C	-2.80351573	-0.43417971	0.00000000	H	-3.87386463	4.09709890	0.00000000
C	-4.13508350	-0.86157574	0.00000000	H	0.88682242	4.24784607	0.00000000
C	-3.43019951	-3.18626960	0.00000000	C	1.35174553	0.86177080	0.00000000
H	-4.95985139	-0.15968755	0.00000000	C	2.40181809	-0.13159368	0.00000000
H	-3.72747511	-4.22718242	0.00000000	C	1.66980743	2.25340388	0.00000000
H	-5.46723285	-2.53362780	0.00000000	C	0.63860182	3.19451788	0.00000000
C	2.09578724	-1.58089136	0.00000000	C	3.69670296	0.33766498	0.00000000
C	0.76826292	-2.00662971	0.00000000	H	4.52574524	-0.35913889	0.00000000
C	2.78971989	-3.90400808	0.00000000	C	4.03394108	1.71084210	0.00000000
C	0.40811136	-3.38456663	0.00000000	H	5.07990119	1.98604747	0.00000000
C	3.11503617	-2.57737527	0.00000000	C	3.04531354	2.66244444	0.00000000
C	1.43973635	-4.35661469	0.00000000	O	-1.34340073	5.08064945	0.00000000
C	-0.97025582	-3.79642627	0.00000000	O	3.25483109	3.99327078	0.00000000
H	4.16380230	-2.30746168	0.00000000	C	4.59151840	4.45123508	0.00000000
C	-1.22524567	-5.15692499	0.00000000	H	5.12170407	4.11023936	0.89364286
H	-2.24514068	-5.51973596	0.00000000	H	4.53638505	5.53657523	0.00000000
C	-0.19786090	-6.11785765	0.00000000	H	5.12170407	4.11023936	-0.89364286

H	-0.45878442	-7.17010507	0.00000000	C	-2.33620786	6.08531156	0.00000000
C	1.11760272	-5.73055341	0.00000000	H	-2.96331518	6.01586197	0.89341526
H	-4.42501556	1.75066802	0.00000000	H	-2.96331518	6.01586197	-0.89341526
C	-3.37197249	2.00372003	0.00000000	H	-1.80457193	7.03320523	0.00000000
C	-2.42506715	1.00630184	0.00000000	H	1.91578464	-6.46617514	0.00000000
C	-1.75249439	3.79504607	0.00000000	H	3.57948817	-4.64956138	0.00000000

Table S14. Cartesian Coordinates (Å) for **10d**·DMAP in the gas phase in S_0 calculated at M06-2X/6-311G(d)

atom	*x*	*y*	*z*	*atom*	*x*	*y*	*z*
B	-0.68662511	0.01648140	-0.58548207	N	-0.98064627	-0.55498149	0.96648851
C	-1.20649737	-1.08956704	-1.58739327	C	-2.58677482	-1.35156382	2.55095325
C	-2.07812688	-3.01342441	-3.39118251	N	-1.89981574	-1.93009870	4.80013642
C	-2.50912573	-1.00963547	-2.10945915	C	-0.85015417	-2.04960857	5.79556553
C	-0.32173647	-2.10092282	-2.00309438	C	-3.26765716	-2.28537732	5.13259552
C	-0.77631752	-3.06410837	-2.90980507	H	-2.41277873	-3.75518171	-4.10855397
C	-2.93572082	-1.98907297	-3.01496548	H	-0.11089082	-3.83039023	-3.29052956
C	1.94175311	-3.13830297	-1.73490792	H	1.54934018	-4.08226610	-2.09515303
C	1.10371635	-2.06947649	-1.56335503	H	3.93177842	-3.96934436	-1.64110533
C	3.91330003	-1.91241639	-1.05466606	H	4.70080560	0.49020380	-0.13661494
C	1.68221999	-0.85037923	-1.03110852	H	0.56926074	4.55948820	0.84995940
C	3.33913103	-3.07930620	-1.47508293	H	2.95388974	4.70078685	1.24133466
C	3.09196433	-0.75779597	-0.81230470	H	-1.22780574	4.70337507	-0.03083853
C	0.86767903	0.23474660	-0.68747053	H	-6.58075217	1.26540992	-2.16681140
C	1.41432214	1.44533059	-0.24668988	H	0.53868926	-1.19210294	3.87552898
C	0.56116696	2.58366911	0.05095082	H	-2.98175240	-0.78987826	0.52608140
C	2.82855278	1.53351347	-0.04751202	H	0.97066355	-0.39749480	1.61181140
C	3.63689858	0.42921703	-0.32067358	H	-3.62207753	-1.60059098	2.73339058
C	1.16230037	3.69183842	0.58739521	H	-0.38066828	-1.08213511	5.99710554
C	2.56208211	3.78502867	0.81854500	H	-0.07520386	-2.75222615	5.47484078
C	3.38573765	2.74535082	0.48935184	H	-1.27851673	-2.41829289	6.72404686
C	-0.88357641	2.56227969	-0.30899714	H	-3.94019209	-1.42991718	5.01981216
C	-1.47788760	1.37665957	-0.71135885	H	-3.63265932	-3.10091443	4.50119600
C	-2.98942305	3.72305368	-0.65088135	H	-3.30931599	-2.61429076	6.16777378
C	-2.81591082	1.35321809	-1.19156167	H	-3.91499884	-1.93723473	-3.47568472
C	-1.66750295	3.75201526	-0.30630972	H	-5.19597287	-0.73033216	-2.46991476
C	-3.60978574	2.52743559	-1.10092005	C	6.08911819	-2.83401479	-1.04933981
C	-3.37996441	0.15894297	-1.77136363	H	6.04040113	-3.15390071	-2.09471005
C	-4.72673569	0.16319494	-2.07562789	H	5.83508465	-3.67824568	-0.40062085
C	-5.52840188	1.31244646	-1.90882594	H	7.09457867	-2.48944680	-0.82018316
C	-4.97732371	2.48371632	-1.46254137	C	5.33127779	3.90714544	1.15944972
O	4.73148978	2.74027253	0.64472676	H	5.13735217	4.76767867	0.51192170
O	5.23559550	-1.73757998	-0.81462525	H	6.39984203	3.70903601	1.19166394
C	-0.28779153	-1.12538785	3.18302803	H	4.96871564	4.12489533	2.16899004
C	-2.23657908	-0.89559026	1.30439729	H	-5.57794414	3.38384612	-1.37397947

C	-1.60034127	-1.48398052	3.55487697	H	-3.58223926	4.63211442	-0.61170910
C	-0.03237802	-0.67571030	1.90715186				

5. Analysis of Self-Assembly

Methods. UV–vis absorption spectra were recorded on JASCO V750 spectrophotometer equipped with a JASCO ETCR-762 cuvette holder for temperature control. Fluorescence spectra were measured on a JASCO FP-8500 spectrofluorometer. The measurement parameters for sensitivity, scanning rates, and ranges were chosen appropriately for each experiment. Quartz cuvettes with an optical path length of 5 mm were used for the experiments.

All self-assembly experiments were carried out in DMSO/H_2O mixed solvents, where a HEPES 1.0×10^{-2} or 0.1 M buffer solution with pH=7 was used as the water fraction. Spectroscopic samples were prepared with an appropriate amount of **10c**, DMAP, and solvents as described.

Preparation of self-assembled 10c. A stock solution of **10c** (concentrated) was prepared in DMSO. An appropriate volume of this stock solution was added to a 5 mm quartz cuvette. To prepare the final self-assembling solution of predetermined concentration and solvent ratio, an appropriate volume of a buffer solution (HEPES 0.1 M, pH 7) was added to the cuvette. This solution was utilized for the investigation of photophysical properties.

Preparation of tetracoordinate 10c with DMAP. For the disassembly study of **10c** in the presence of DMAP, various amounts (0–0.1 M) of DMAP were added to a stock solution of **10c** in DMSO. To prepare the final DMSO/H_2O (7:3, v/v) solution with a predetermined concentration of 2×10^{-5} M, an appropriate volume of a buffer solution (HEPES 0.1 M, pH 7) was added to the cuvette.

Acidification of a neutral solution of 10c·DMAP adduct. A DMSO/H_2O solution (7:3, v/v, HEPES 1.0×10^{-2} M) of **10c** (1.5 mL, 2×10^{-5} M) in the presence of DMAP (6.0×10^{-2} M) was acidified with incremental amounts of hydrogen ion by addition of a solution of TFA in H_2O (3 M). The resulting assembly process was monitored by UV–vis absorption and fluorescence spectroscopy.

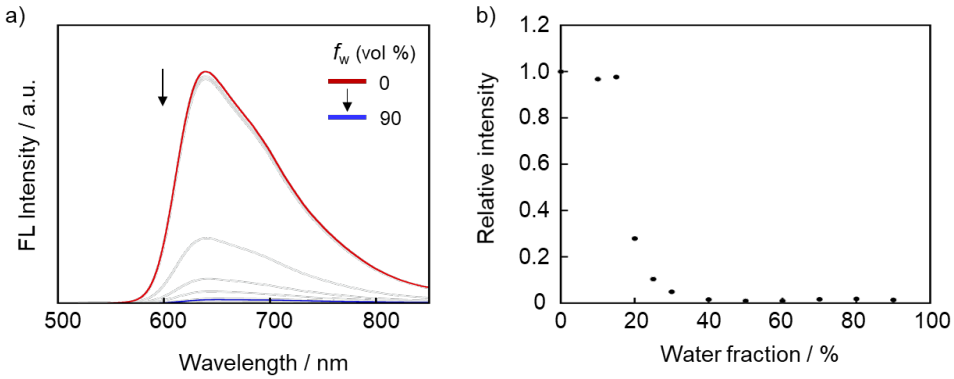


Figure S18. a) Fluorescence spectral changes of **10c** (2.0×10^{-5} M) in DMSO/H_2O mixtures with the excitation wavelength at λ_{ex} = 480 nm and b) plots of relative fluorescence intensity at 640 nm.

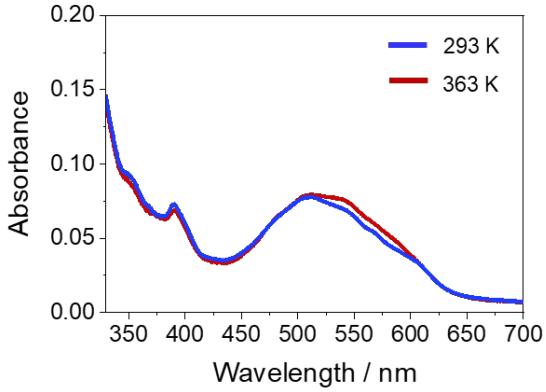


Figure S19. Temperature-dependent UV–vis absorption spectra of **10c** in DMSO/H_2O (5:5, v/v) at c_T = 2.0×10^{-5} M.

Thermodynamic parameters. Temperature-dependent aggregation process can be fitted by the nucleation-elongation model proposed by Meijer, Schenning et al.[12] In the elongation regime, the molar fraction of aggregates α_{agg} can be estimated by equation S1, in which the ΔH_e is the molecular enthalpy release during elongation, T is the absolute temperature, T_e is the critical elongation temperature, R is the ideal gas constant, and α_{sat} is a introduced parameter to ensure that $\alpha_{agg}/\alpha_{sat}$ does not exceed unity.

$$a_{agg} = a_{sat}\left[1 - exp\left(\frac{-\Delta H_e}{RT_e^2}(T - T_e)\right)\right] \quad \text{(eq. S1)}$$

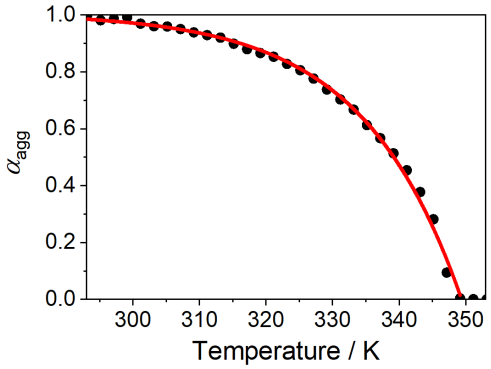


Figure S20. Plot of the variation of the degree of aggregation (α_{agg}) of **10c** (4×10^{-4} M) as a function of the temperature obtained through the cooling experiments in DMSO/H_2O (7:3, v/v) monitored at 577 nm. The cooling curve (1 K min^{-1}) was fitted with a nucleation-elongation model characteristic of a cooperative assembly,[12] giving the elongation enthalpies of $\Delta H_e = -68.4$ kJ mol^{-1} and $T_e = 349$ K.

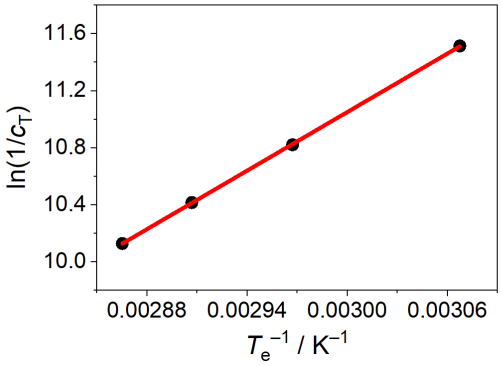


Figure S21. A van't Hoff plot for the aggregation processes at different total concentrations of **10c** upon cooling (correlation coefficient 0.999).

The standard enthalpy change ($\Delta H°$) and standard entropy change ($\Delta S°$) of the elongation process are determined from equation S2, in which R is the ideal gas constant. An elongation binding constant (K_e) for aggregation at 298 K was estimated according to equation S3:

$$\ln\left(\frac{1}{c_T(T_e)}\right) = \frac{-\Delta H°}{RT_e} + \frac{\Delta S°}{R} \qquad \text{(eq. S2)}$$

$$K_e = e^{-(\Delta H° - T\Delta S°)/(RT)} \qquad \text{(eq. S3)}$$

Table S15. Thermodynamic parameters for aggregates of **10c** (c_T = 2.0 × 10^{-5} M) in DMSO/H_2O (7:3, v/v)

	ΔH°[a]	ΔS°[b]	ΔG°[c]	K_e[d]
10c	–56.9 kJ mol^{-1}	–79.0 J mol^{-1} K^{-1}	–33.4 kJ mol^{-1}	7.2× 10^5 M^{-1}

[a] Standard enthalpy, [b] Entropy and [c] Gibbs free energy at 298 K. [d] Elongation binding constant at 298 K.

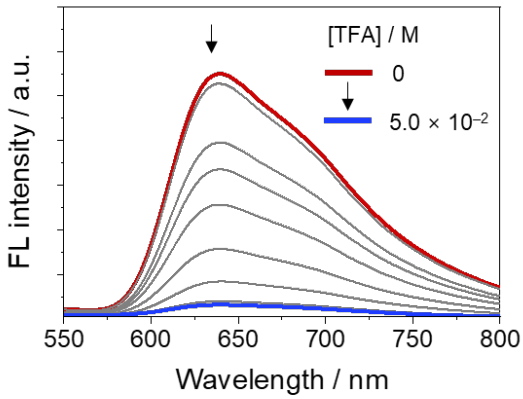


Figure S22. Fluorescence (λ_{ex} = 477 nm) spectral change of **10c** in the presence of DMAP (6.0 × 10^{-2} M) in DMSO/H_2O (7:3, v/v) with an increase in the concentration of TFA.

Preparation of the sample for X-ray powder diffraction analysis. A solution of **10c** in DMSO was diluted with distilled water to give a solution of **10c** in DMSO/H_2O (1:9, v/v) with a total concentration of 2 × 10^{-5} M. After the brief shaking, the solution was allowed to stand at 20 °C for 24 h. Then, the solvent was removed by freeze dry. The remained white powder was used for the measurement of X-ray powder diffraction analysis.

6. Microscopic Observation

Methods. The samples were drop-cast on a carbon-coated copper grid (400 mesh) for transmission electron microscopy (TEM) and a silicon wafer for atomic force microscopy (AFM). The solvent was removed with a filter paper, leaving some small patches of sample on the grid and wafer. After drying under vacuum for 2 h, the samples were examined using a JEOL JEM-1400EM transmission electron microscope operating with an acceleration voltage of 80 kV and a JEOL JSPM-5200V atomic force microscope, respectively.

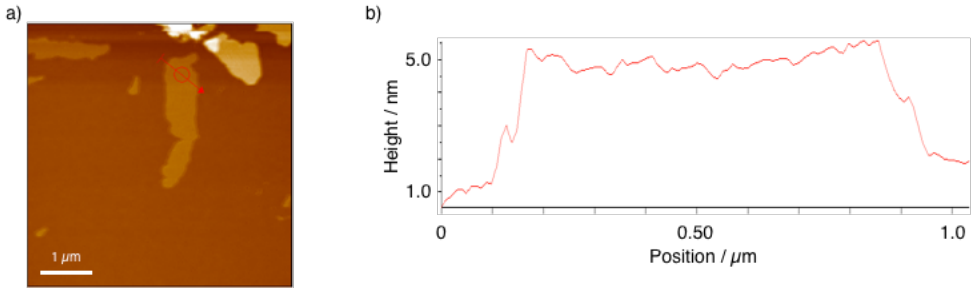


Figure S23. a) An AFM height image of aggregated **10c** and b) a cross-section analysis along the red arrow in the AFM image.

7. References

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8. NMR Spectra

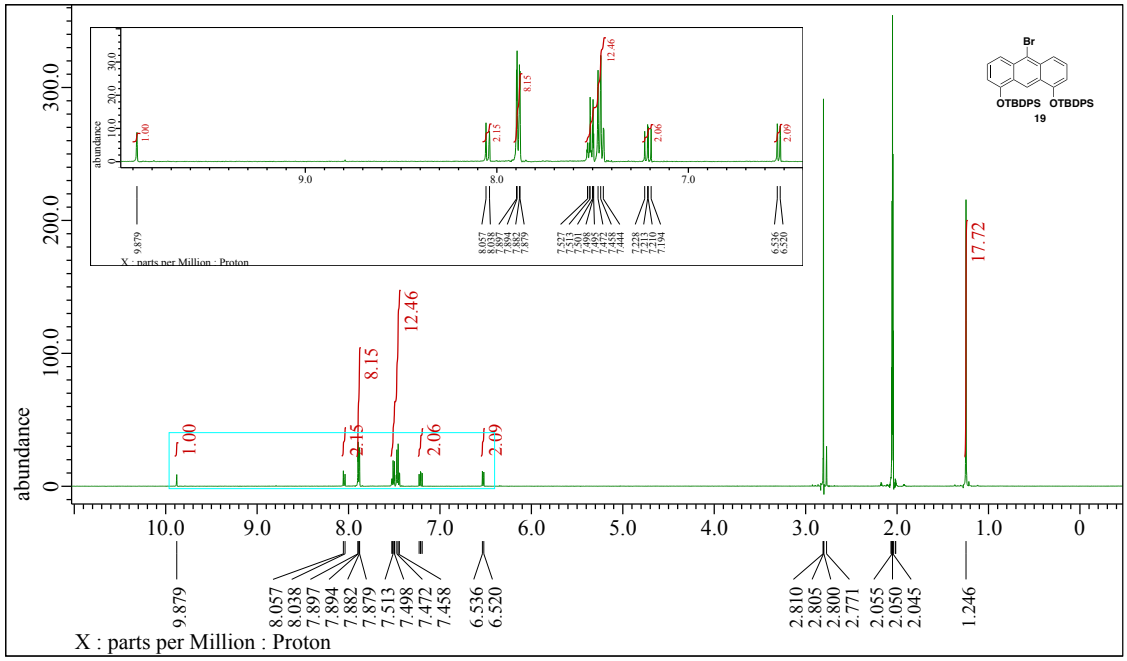

Figure S24. ^{1}H NMR spectrum of **19** (500 MHz, acetone-d_6).

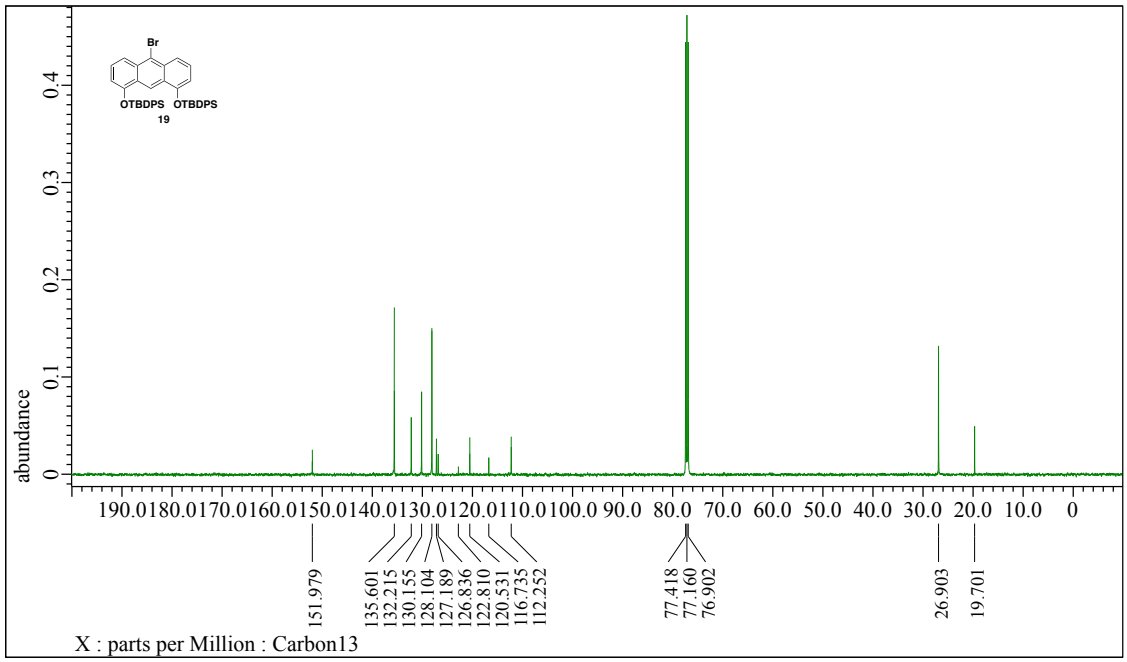

Figure S25. ^{13}C{^{1}H} NMR spectrum of **19** (126 MHz, $CDCl_3$).

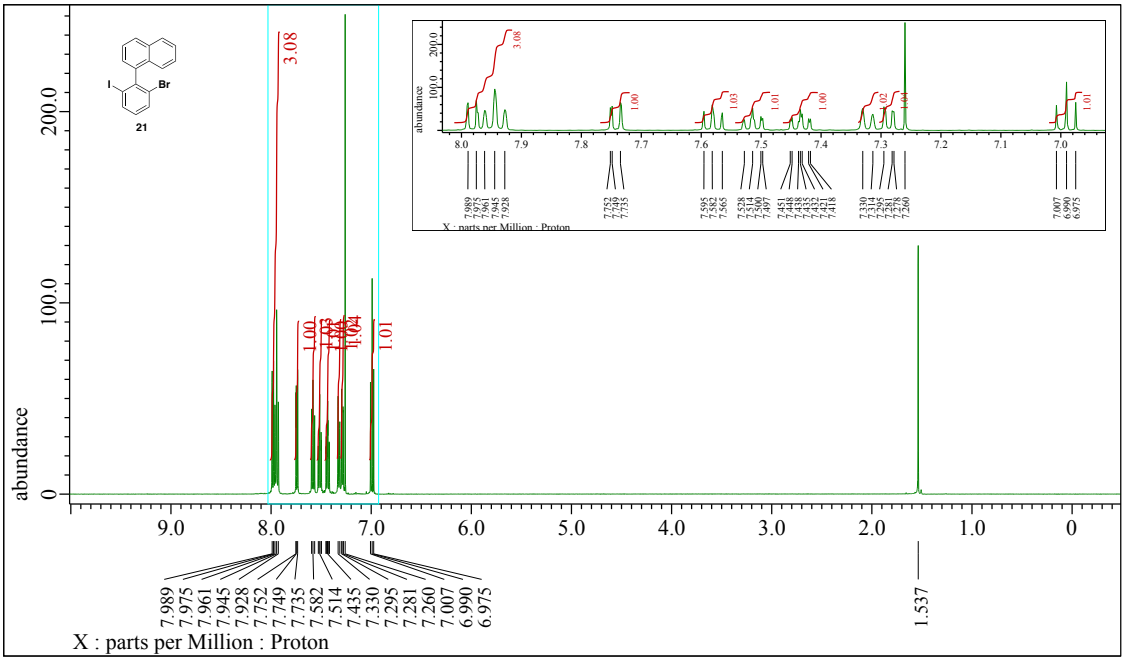

Figure S26. ^{1}H NMR spectrum of **21** (500 MHz, $CDCl_3$).

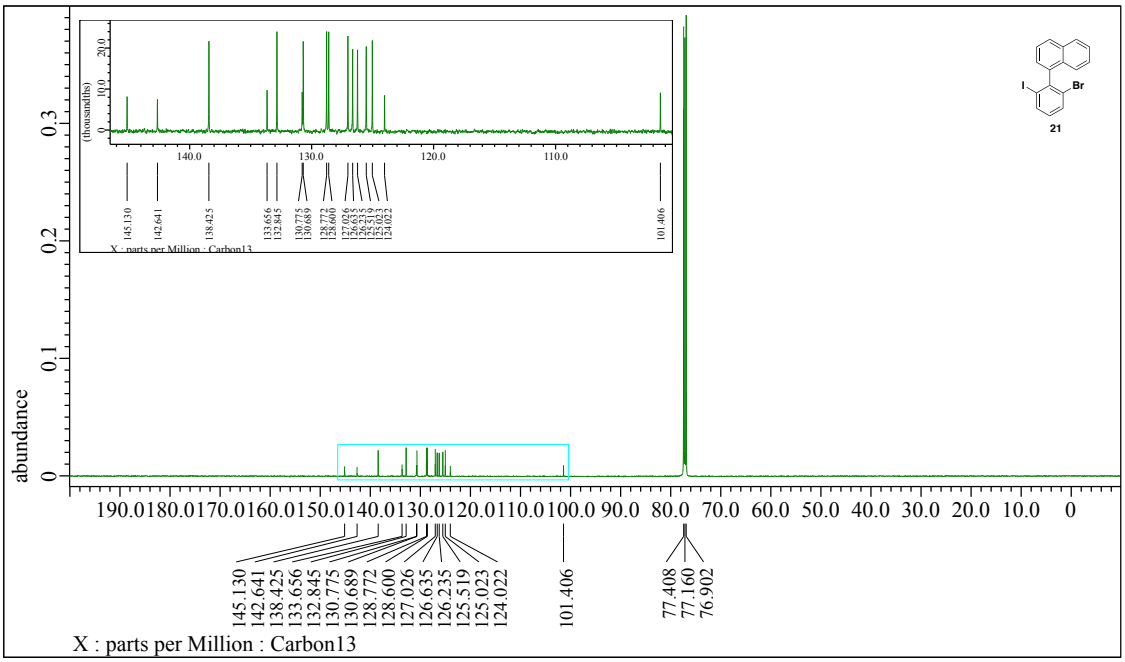

Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **21** (126 MHz, $CDCl_3$).

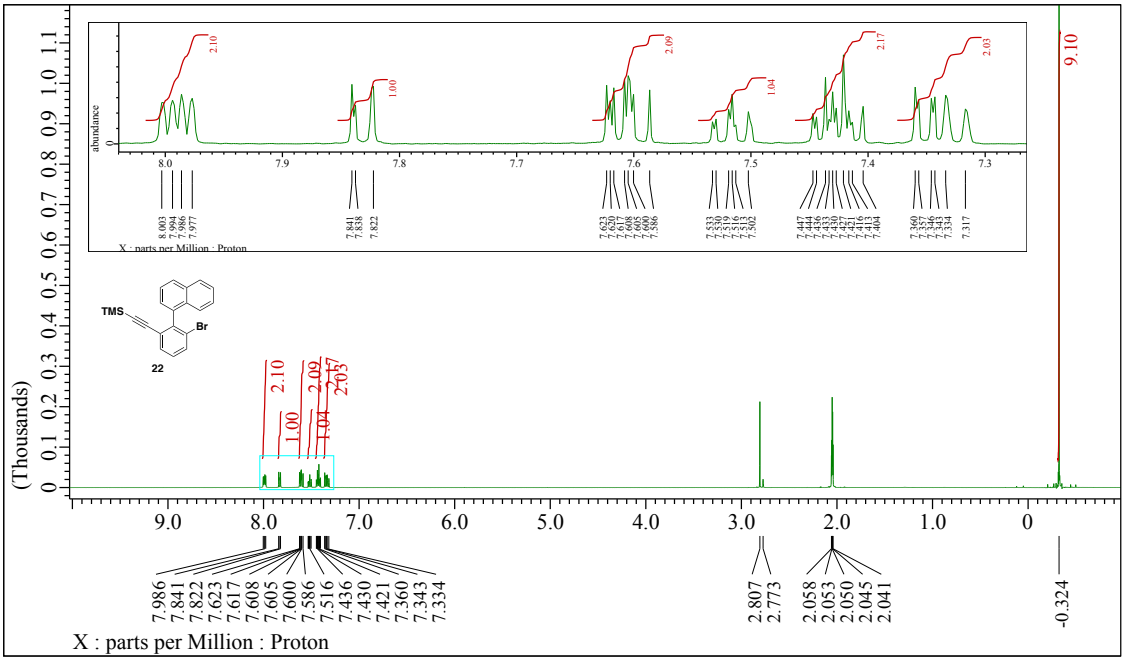

Figure S28. ^{1}H NMR spectrum of **22** (500 MHz, acetone-d_6).

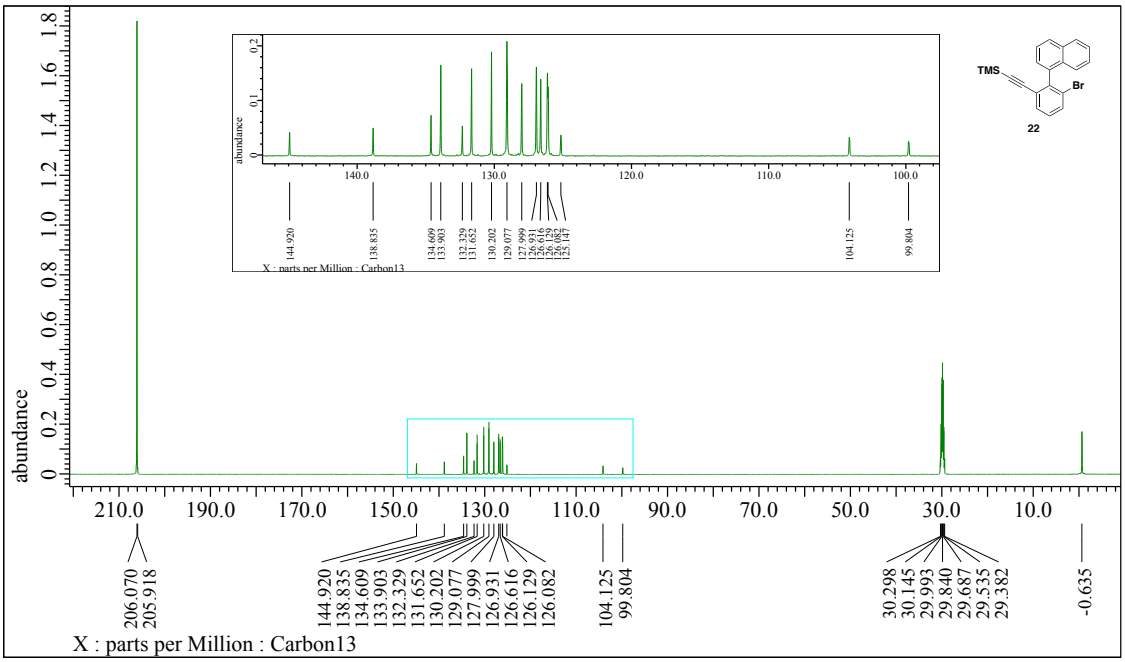

Figure S29. ^{13}C{^{1}H} NMR spectrum of **22** (126 MHz, acetone-d_6).

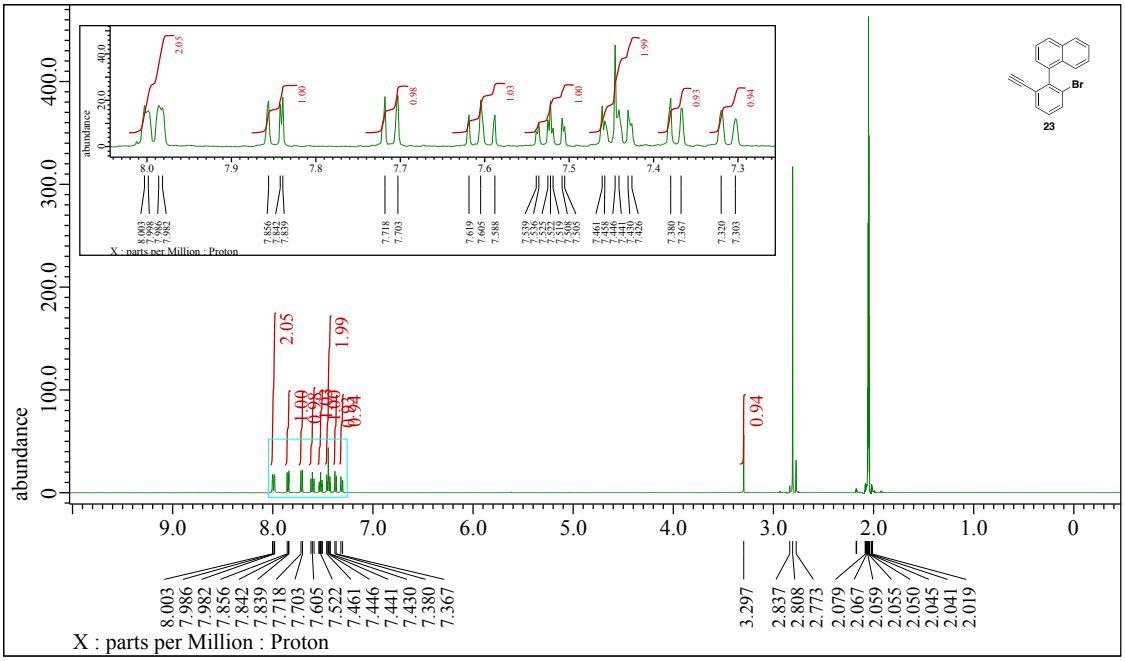

Figure S30. ^{1}H NMR spectrum of **23** (500 MHz, acetone-d_6).

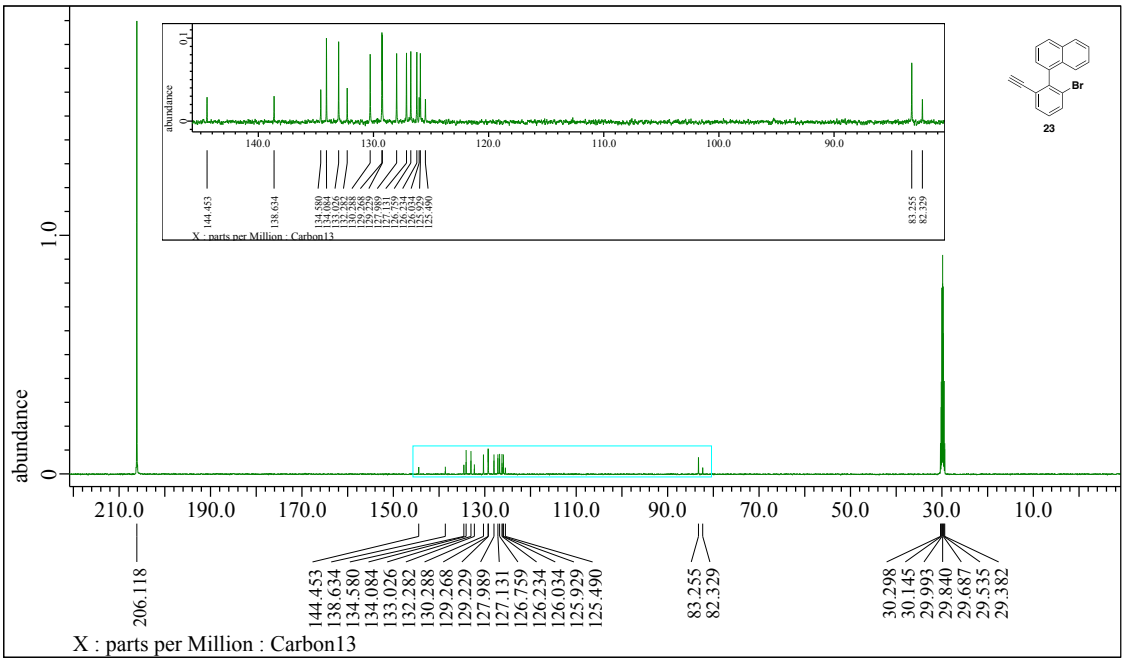

Figure S31. ^{13}C{^{1}H} NMR spectrum of **23** (126 MHz, acetone-d_6).

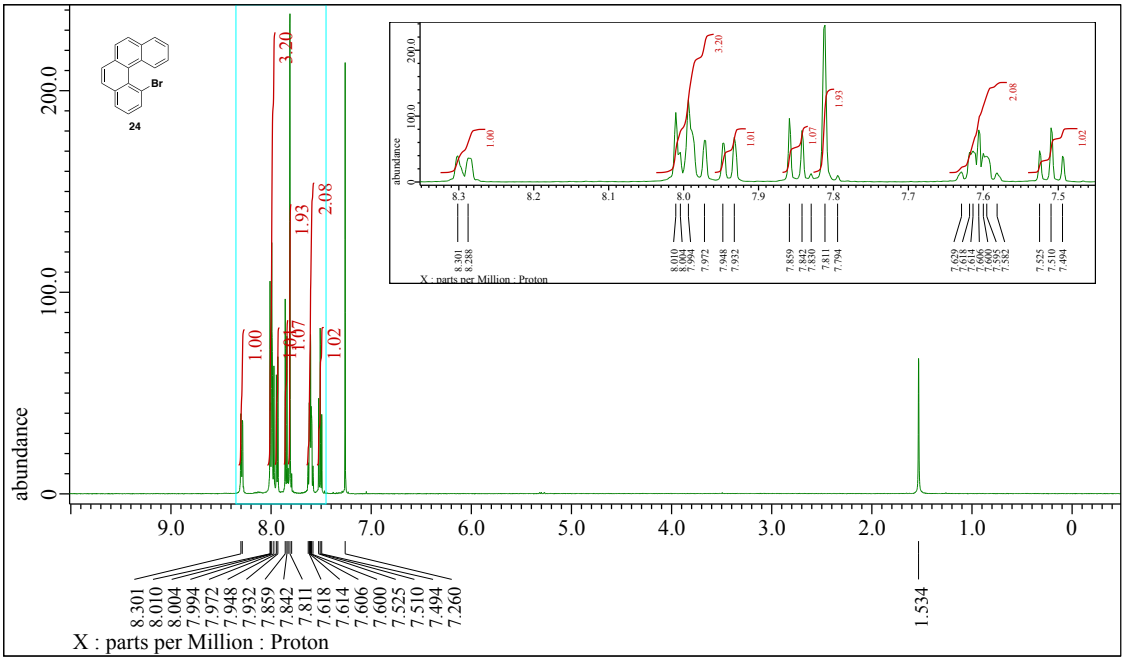

Figure S32. ^{1}H NMR spectrum of **24** (500 MHz, $CDCl_3$).

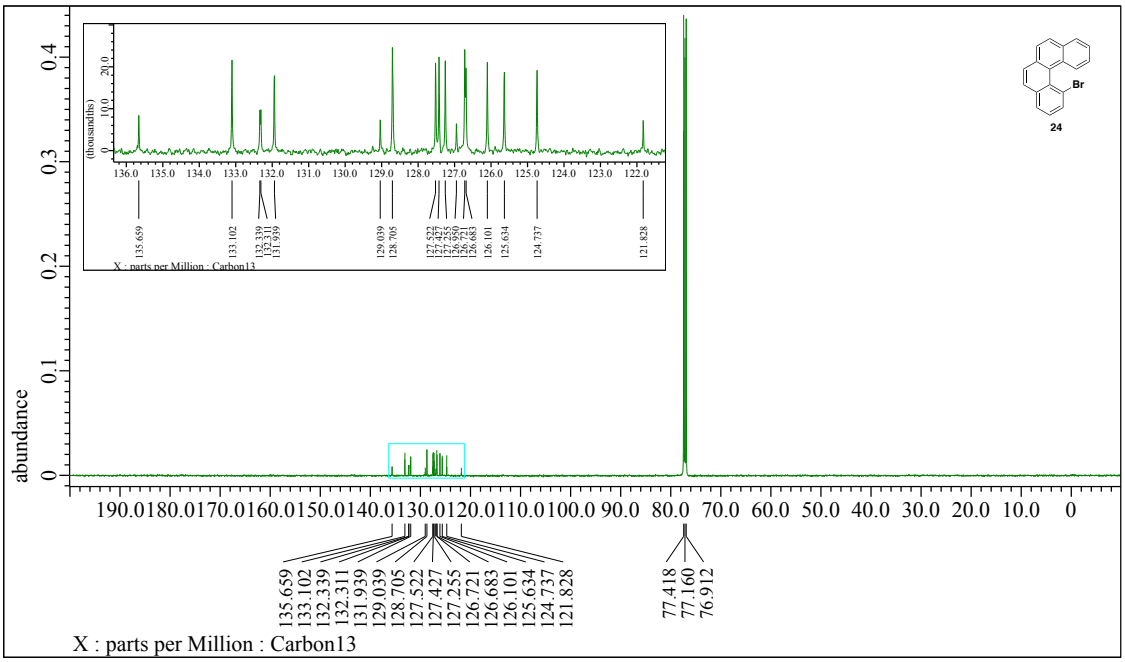

Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of **24** (126 MHz, $CDCl_3$).

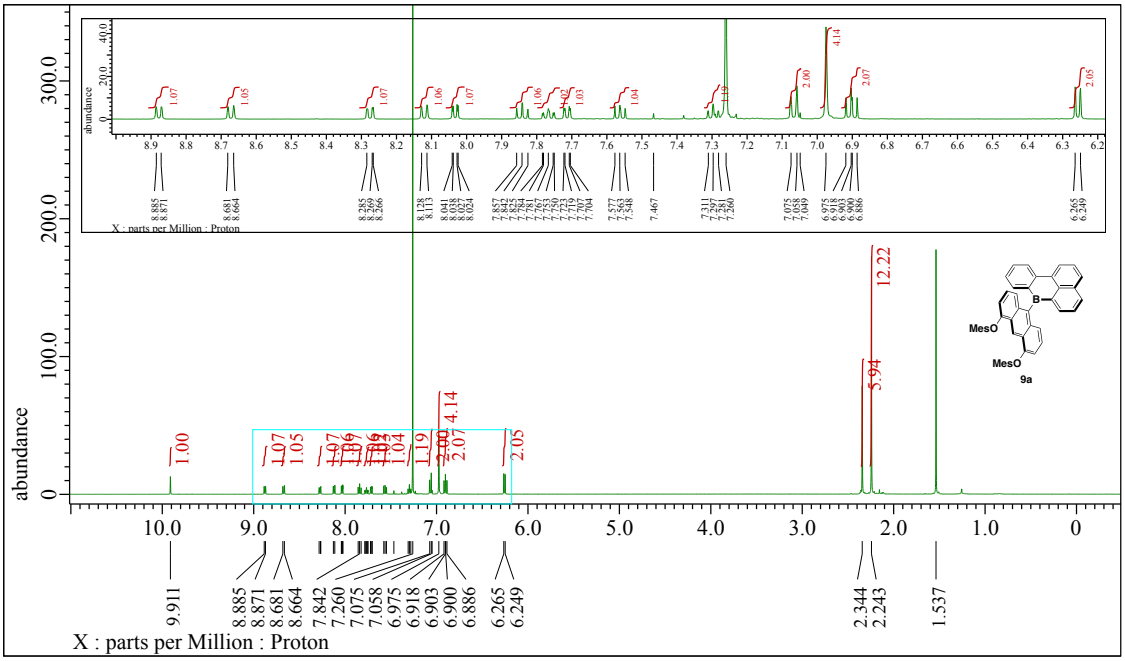

Figure S34. ^{1}H NMR spectrum of **9a** (500 MHz, $CDCl_3$).

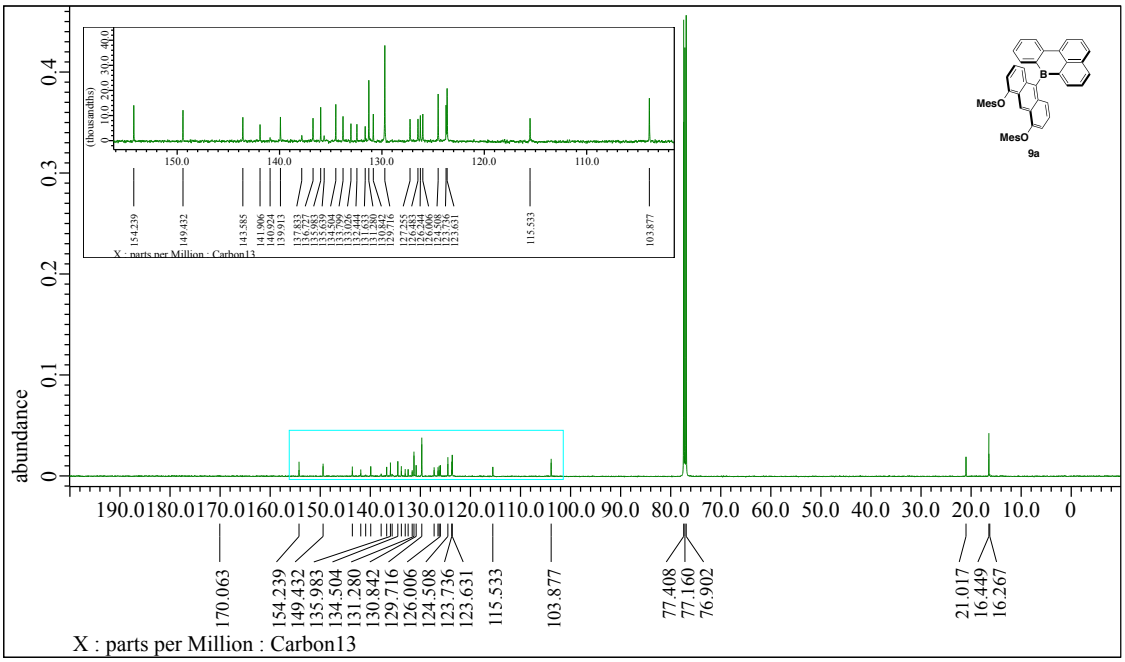

Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **9a** (126 MHz, $CDCl_3$).

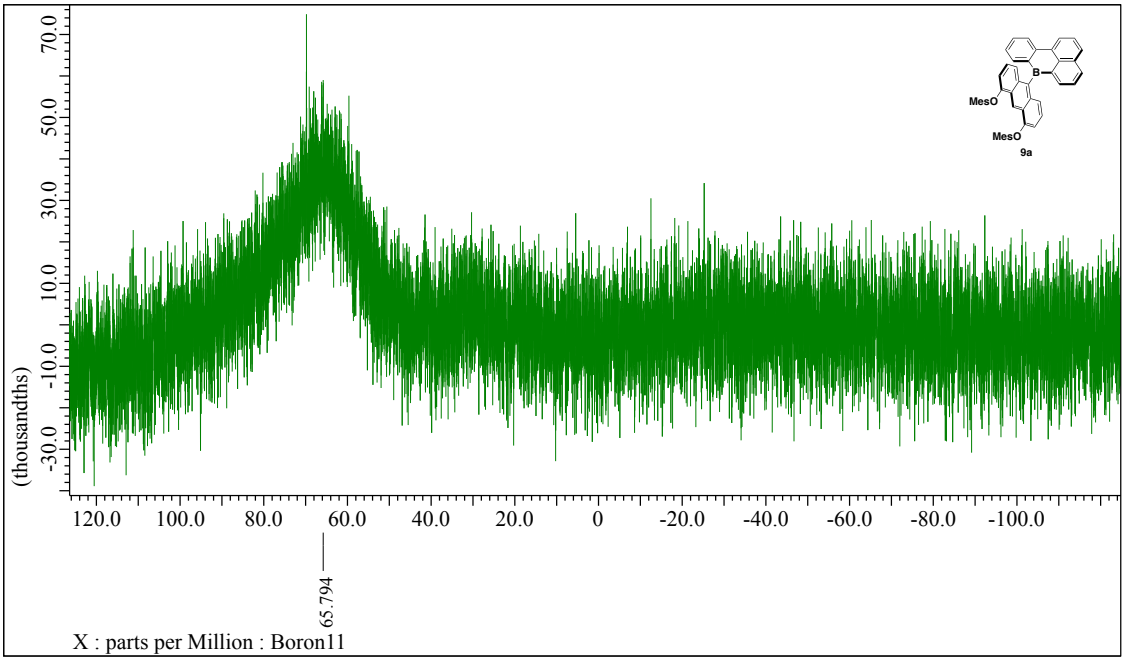

Figure S36. $^{11}B\{^{1}H\}$ NMR spectrum of **9a** (160 MHz, $CDCl_3$).

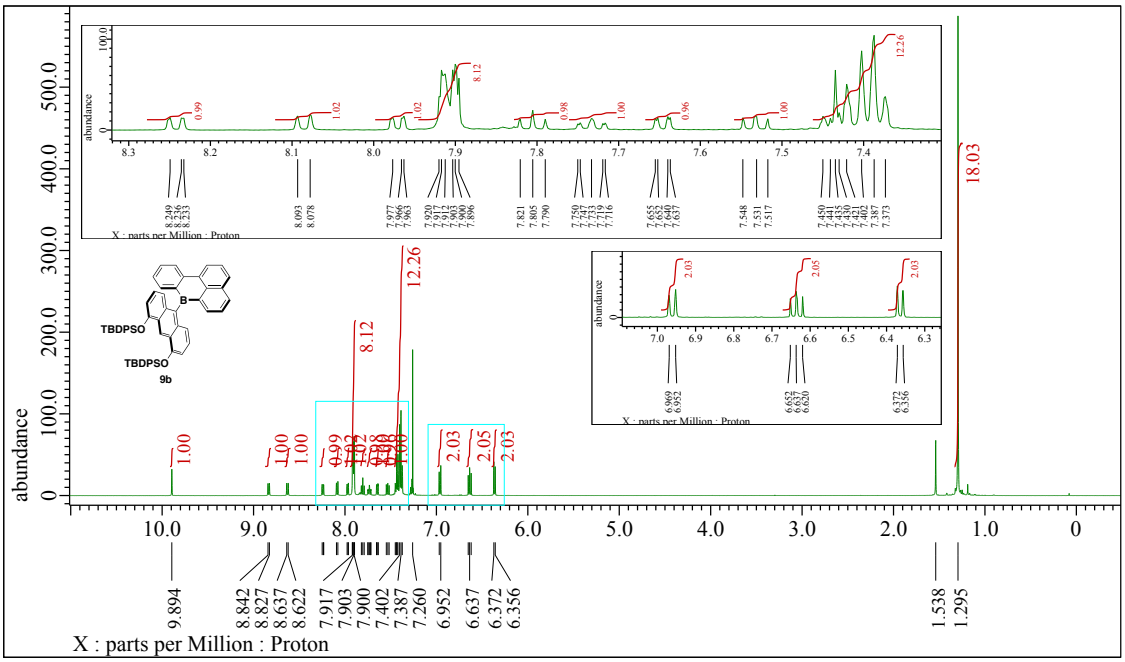

Figure S37. ^{1}H NMR spectrum of **9b** (500 MHz, $CDCl_3$).

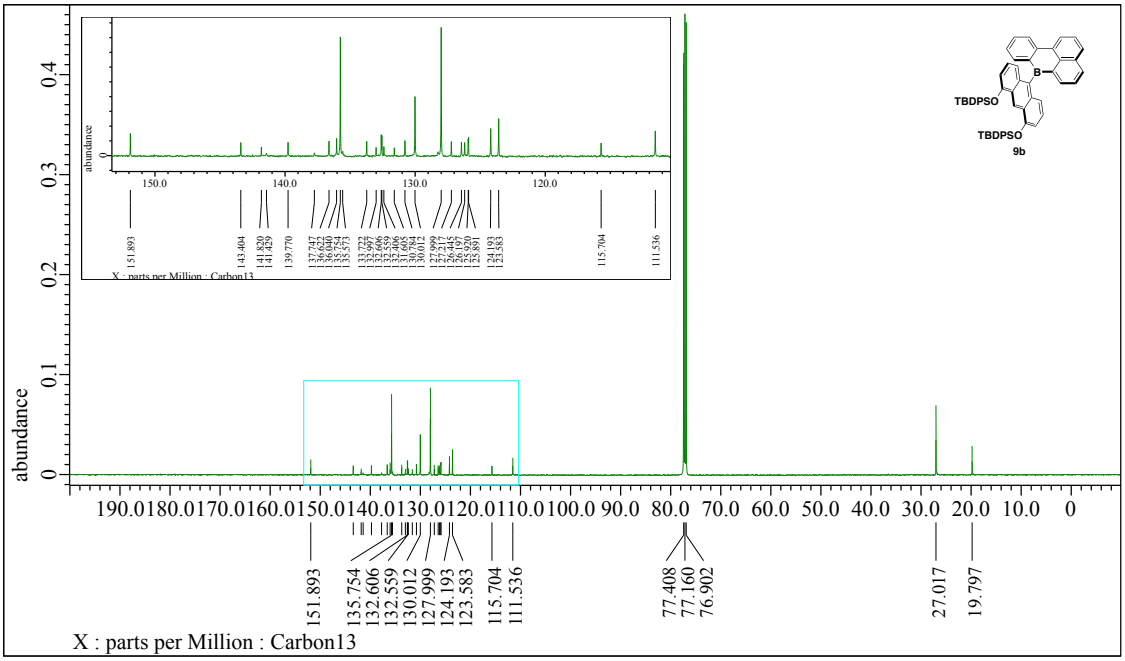

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of **9b** (126 MHz, $CDCl_3$).

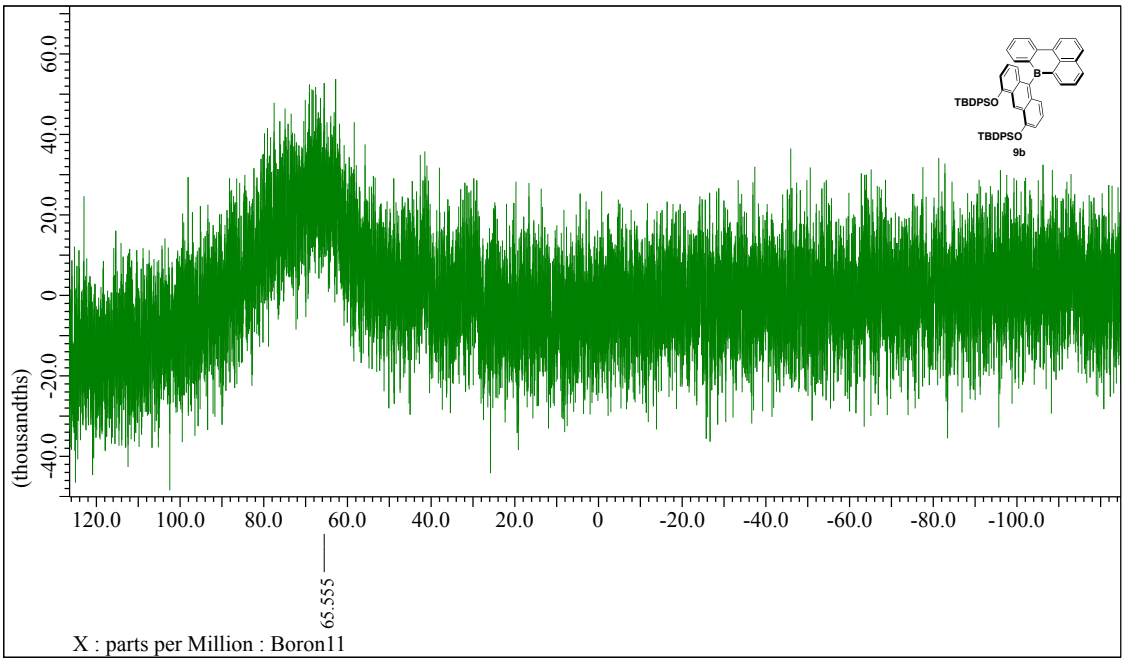

Figure S39. $^{11}B\{^{1}H\}$ NMR spectrum of **9b** (160 MHz, $CDCl_3$).

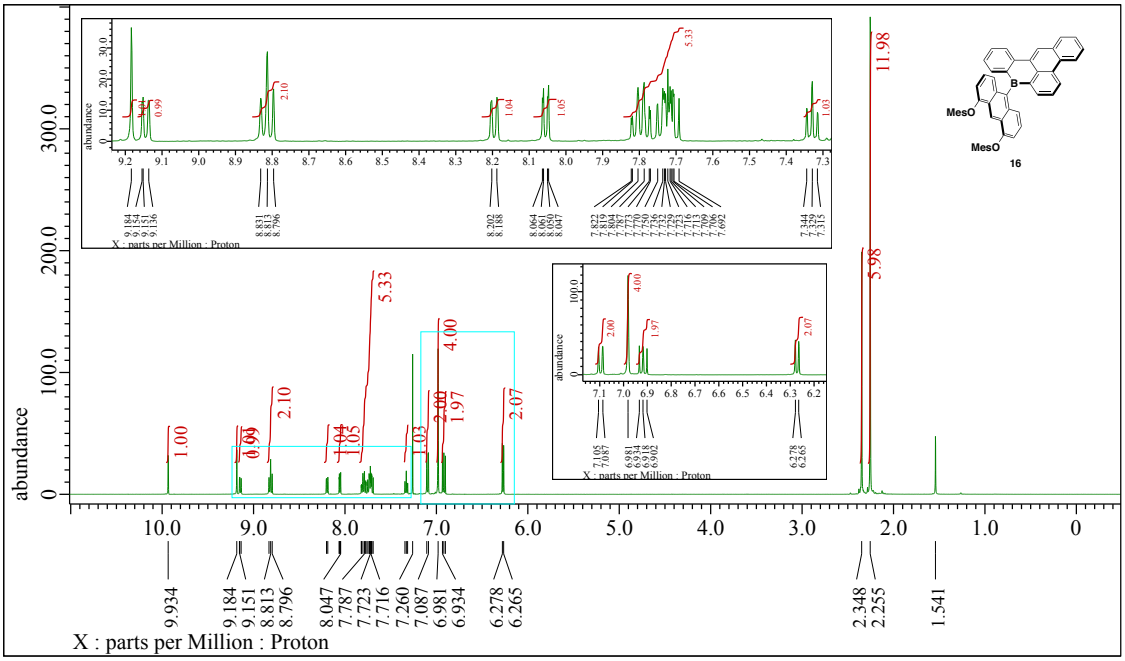

Figure S40. ^{1}H NMR spectrum of **16** (500 MHz, $CDCl_3$).

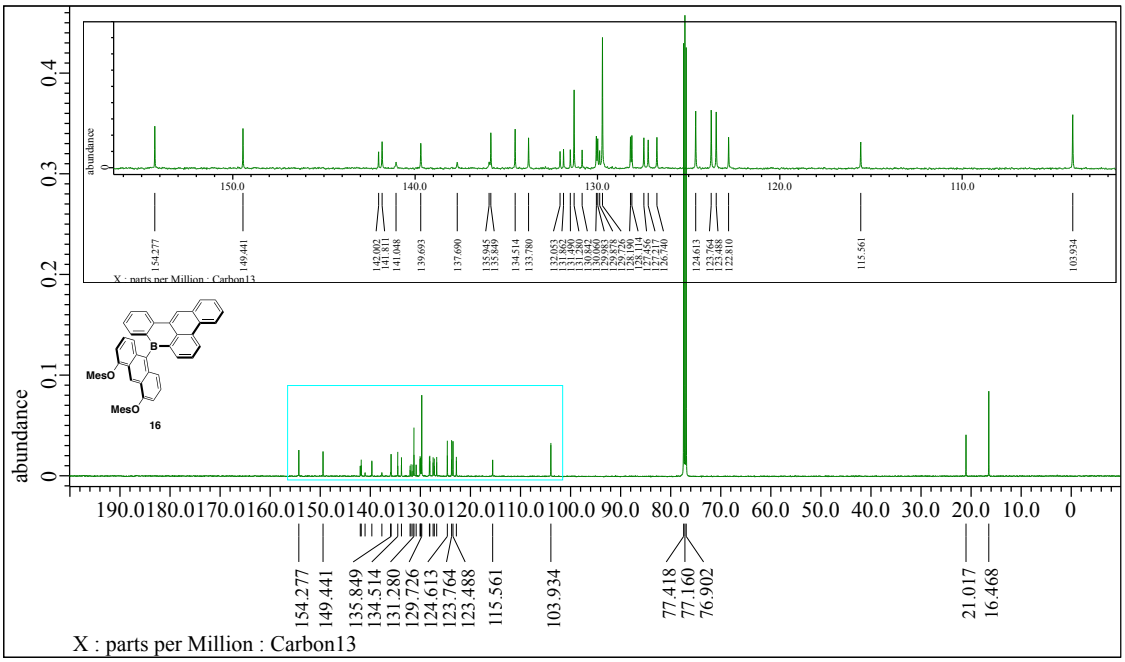

Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of **16** (126 MHz, $CDCl_3$).

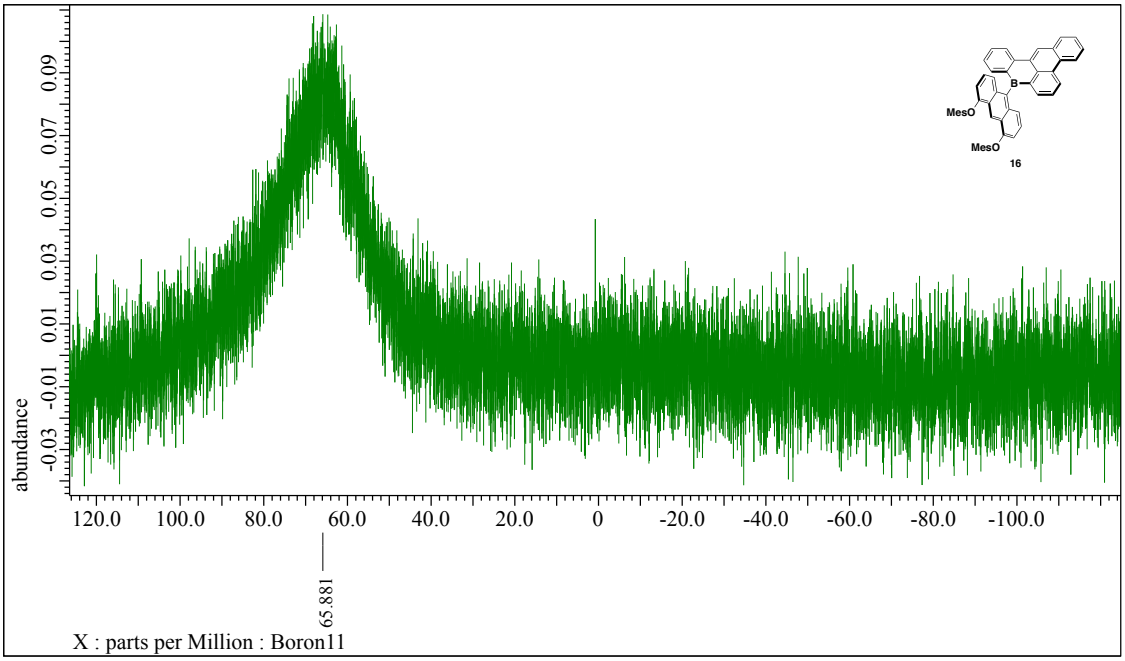

Figure S42. $^{11}B\{^{1}H\}$ NMR spectrum of **16** (160 MHz, $CDCl_3$).

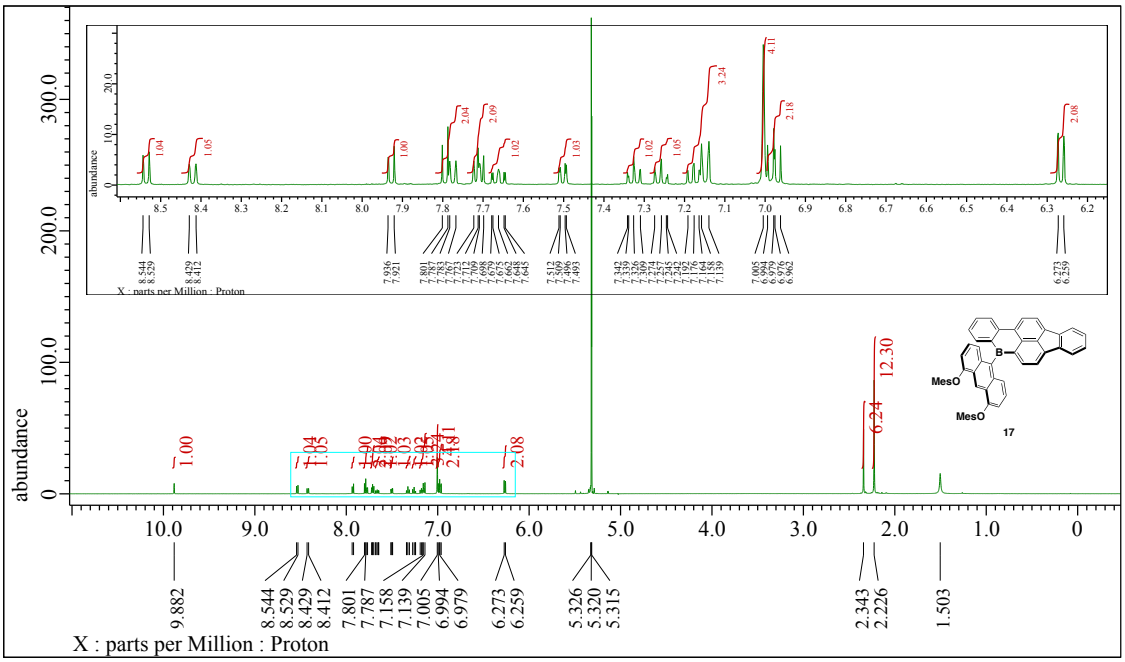

Figure S43. ^{1}H NMR spectrum of **17** (500 MHz, CD_2Cl_2).

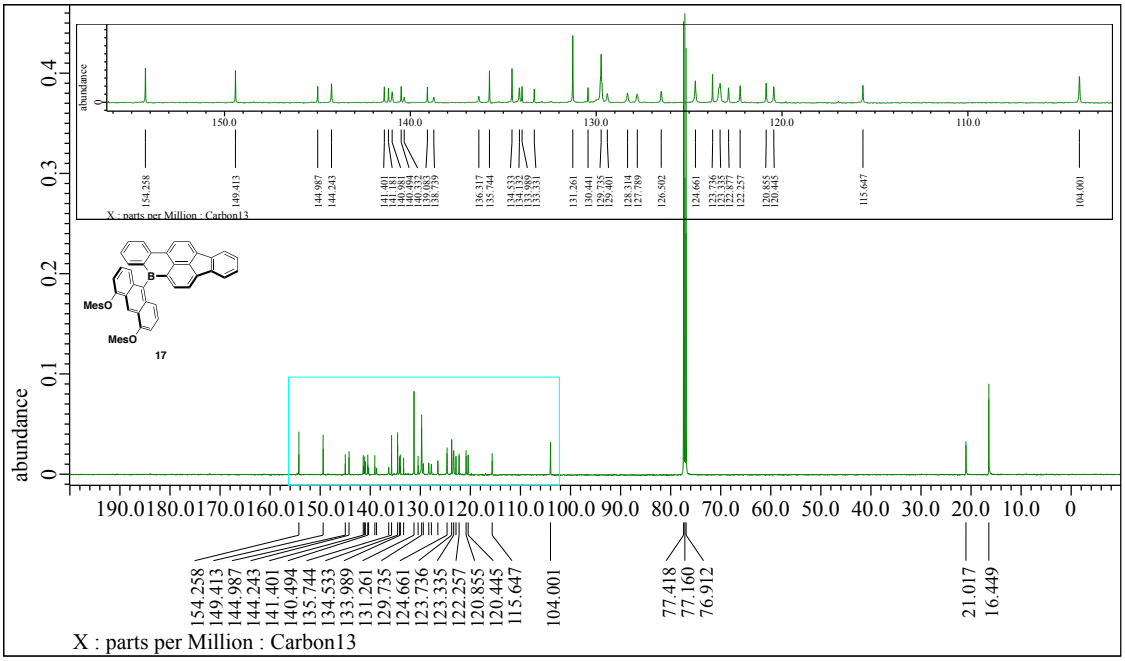

Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of **17** (126 MHz, $CDCl_3$).

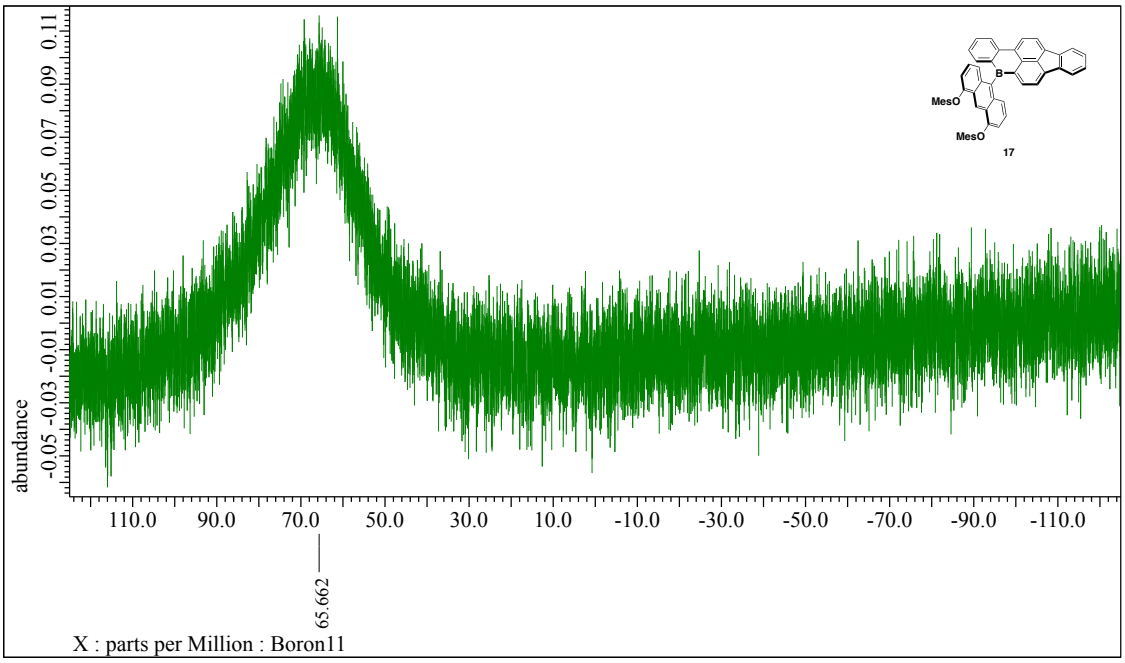

Figure S45. $^{11}B\{^{1}H\}$ NMR spectrum of **17** (160 MHz, $CDCl_3$).

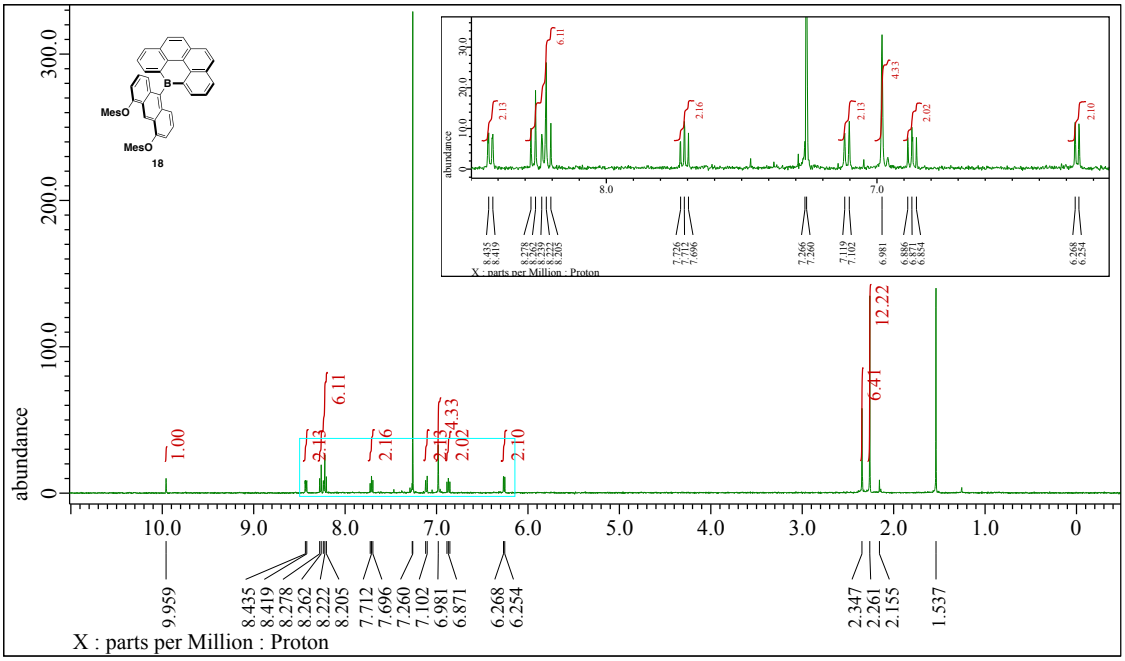

Figure S46. ^{1}H NMR spectrum of **18** (500 MHz, $CDCl_3$).

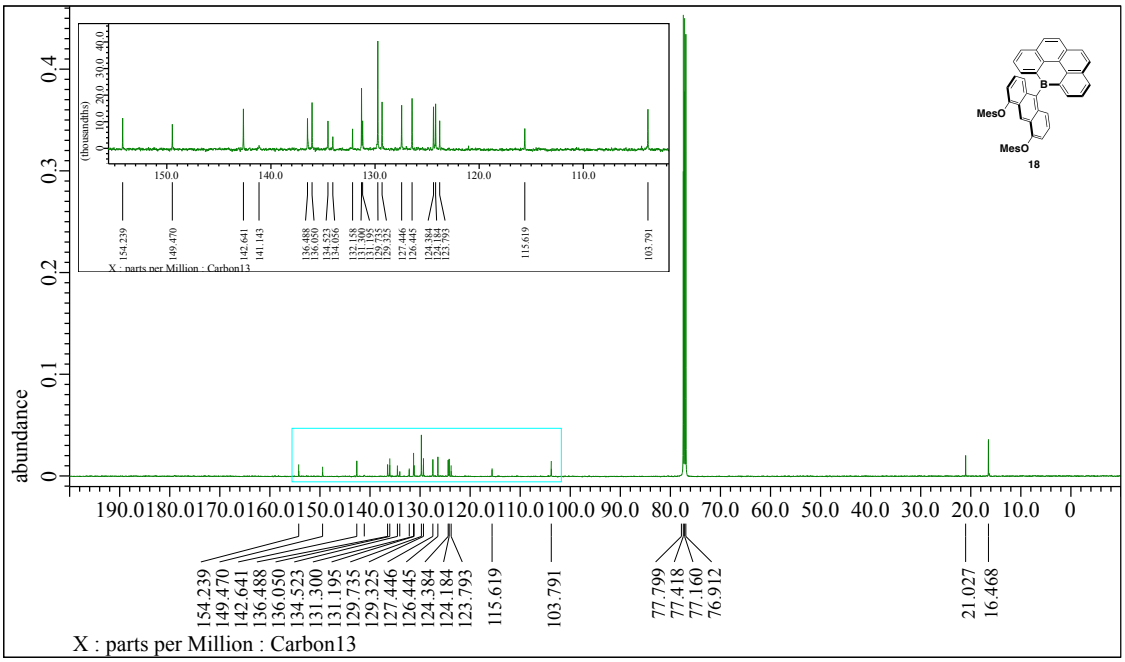

Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of **18** (126 MHz, $CDCl_3$).

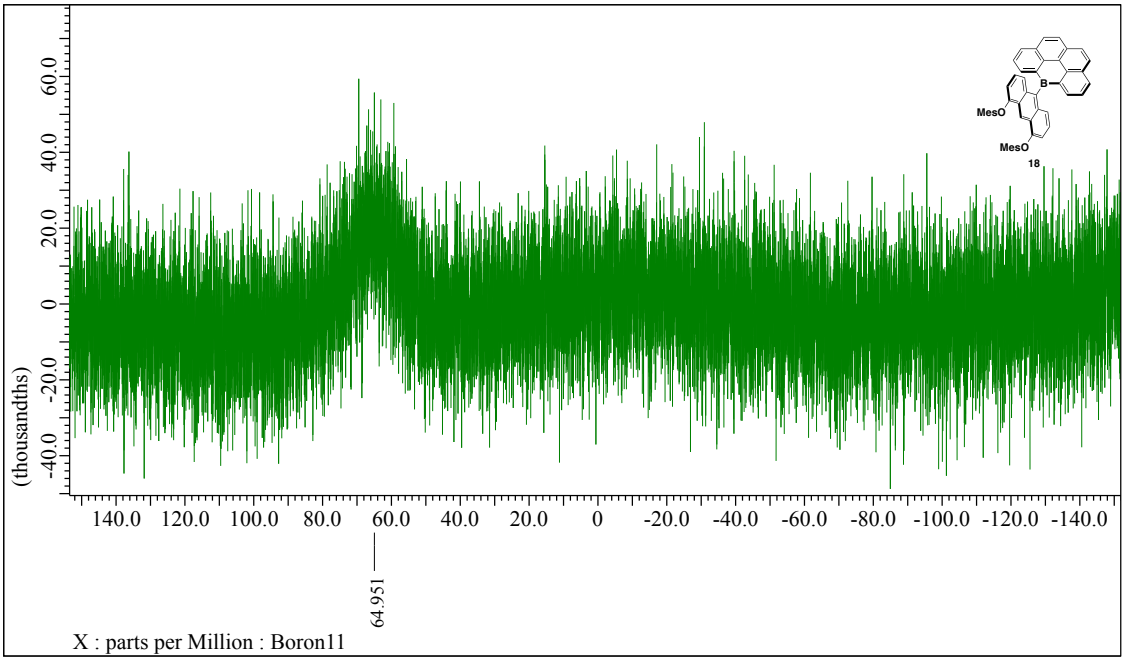

Figure S48. $^{11}B\{^{1}H\}$ NMR spectrum of **18** (160 MHz, $CDCl_3$).

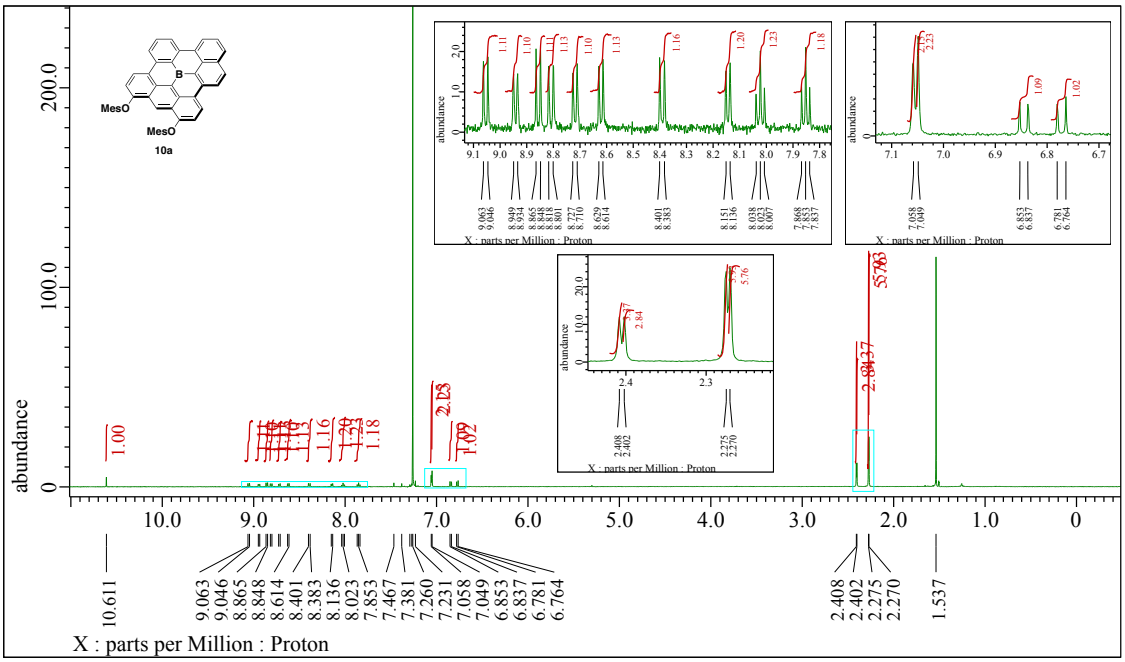

Figure S49. ^{1}H NMR spectrum of **10a** (500 MHz, $CDCl_3$).

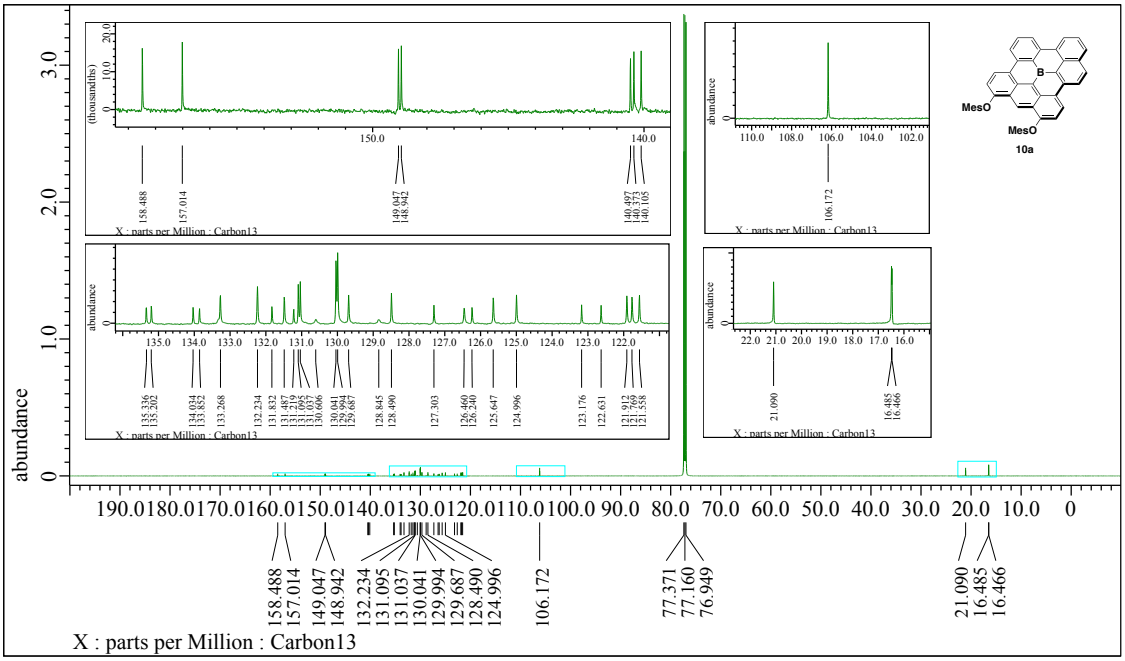

Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of **10a** (151 MHz, $CDCl_3$).

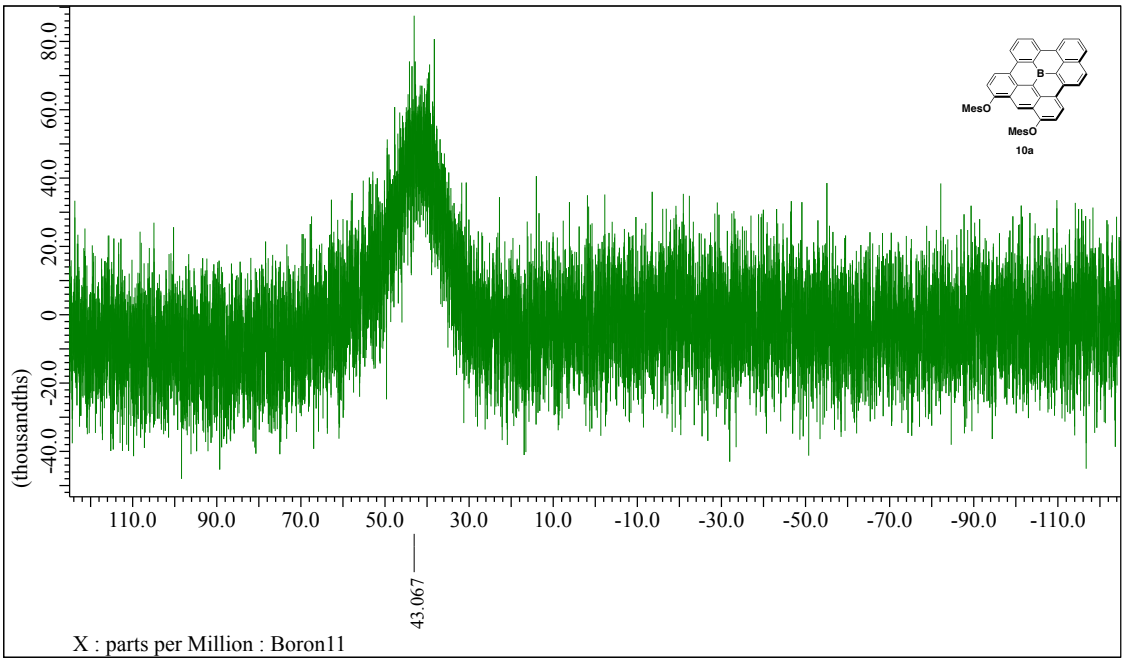

Figure S51. $^{11}B\{^{1}H\}$ NMR spectrum of **10a** (160 MHz, $CDCl_3$).

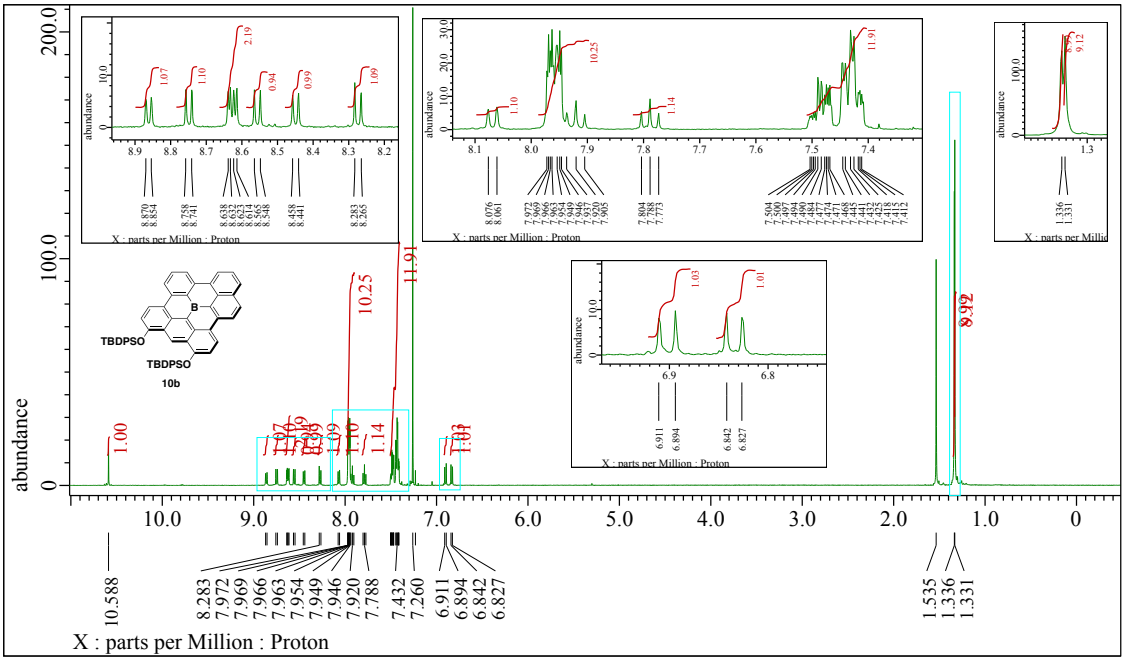

Figure S52. ^{1}H NMR spectrum of **10b** (500 MHz, $CDCl_3$).

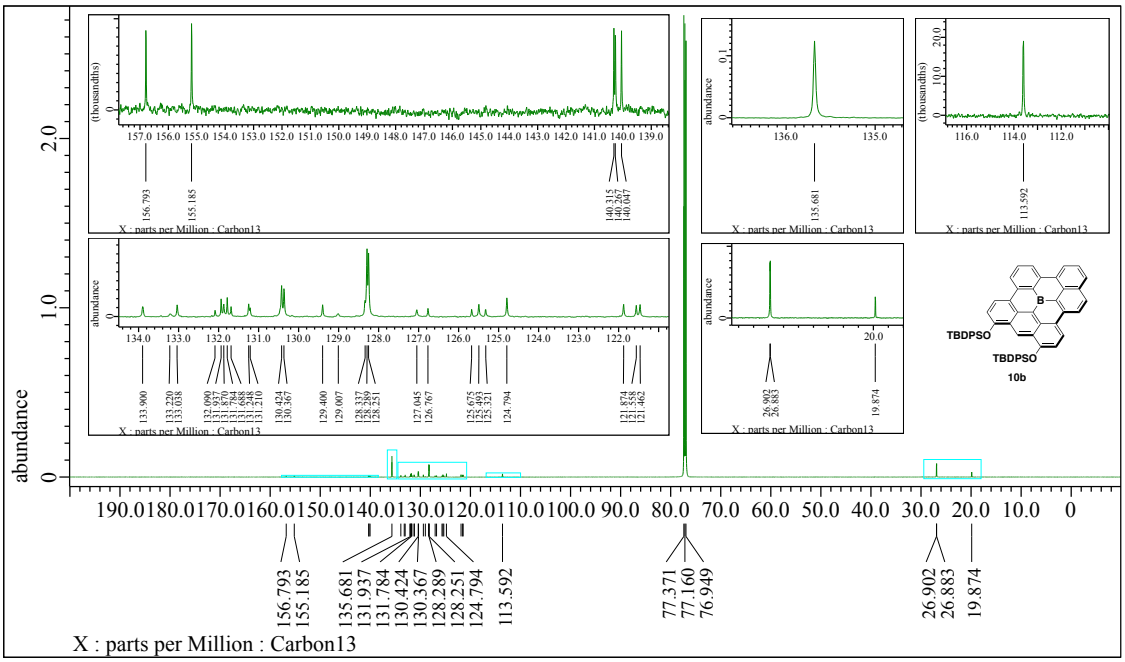

Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum of **10b** (151 MHz, $CDCl_3$).

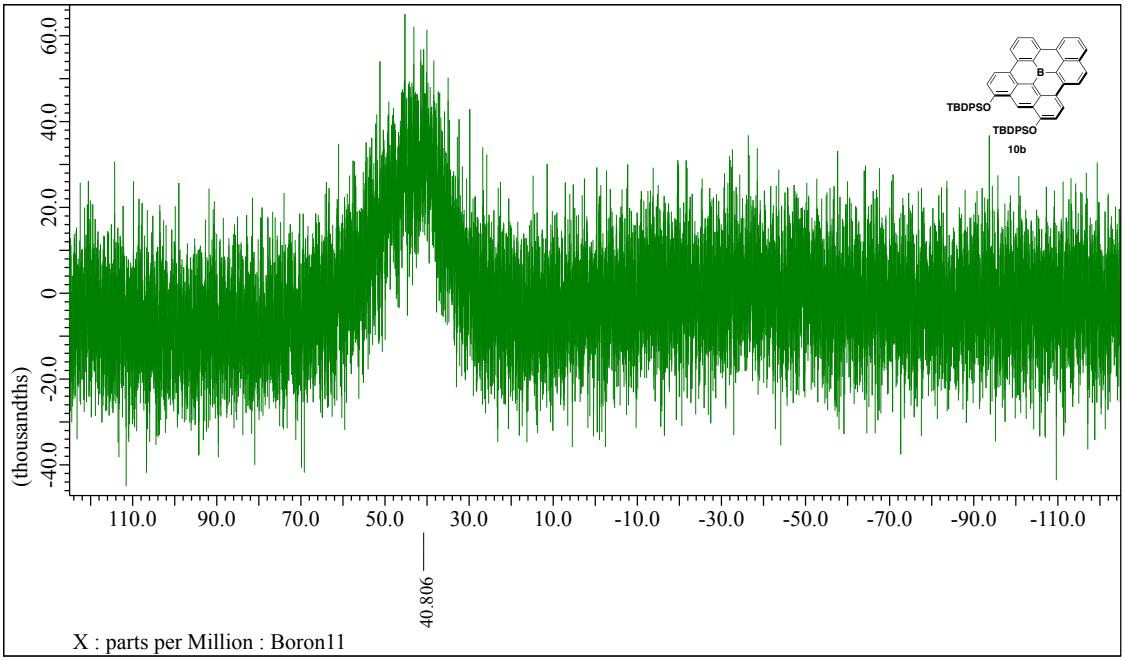

Figure S54. $^{11}B\{^{1}H\}$ NMR spectrum of **10b** (160 MHz, $CDCl_3$).

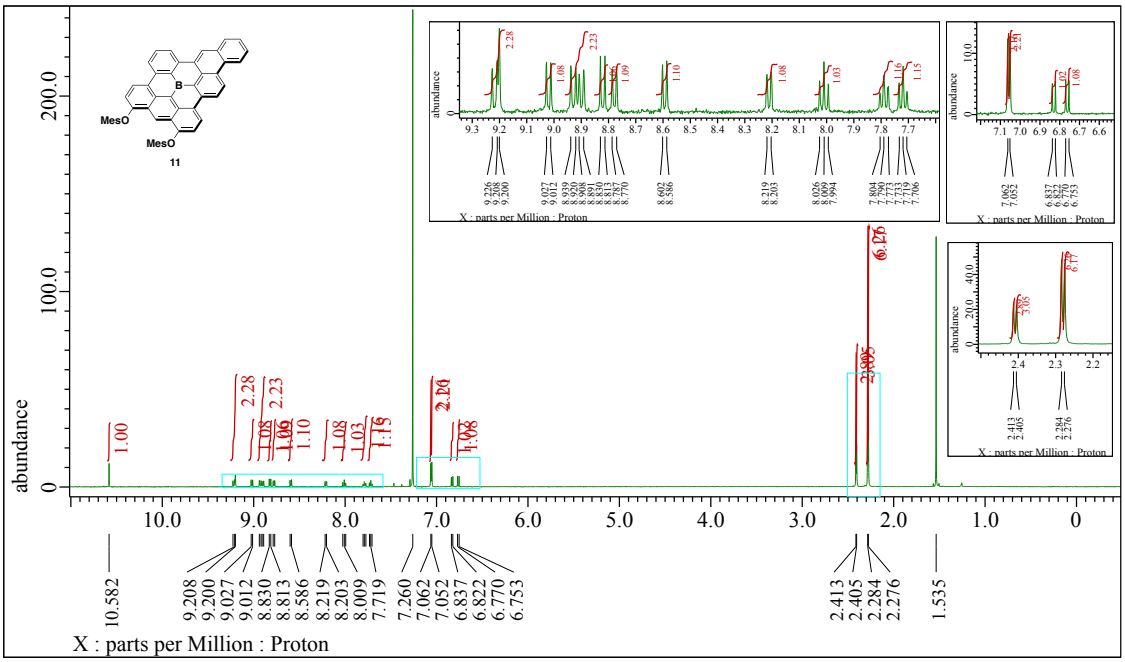

Figure S55. ^{1}H NMR spectrum of **11** (500 MHz, $CDCl_3$).

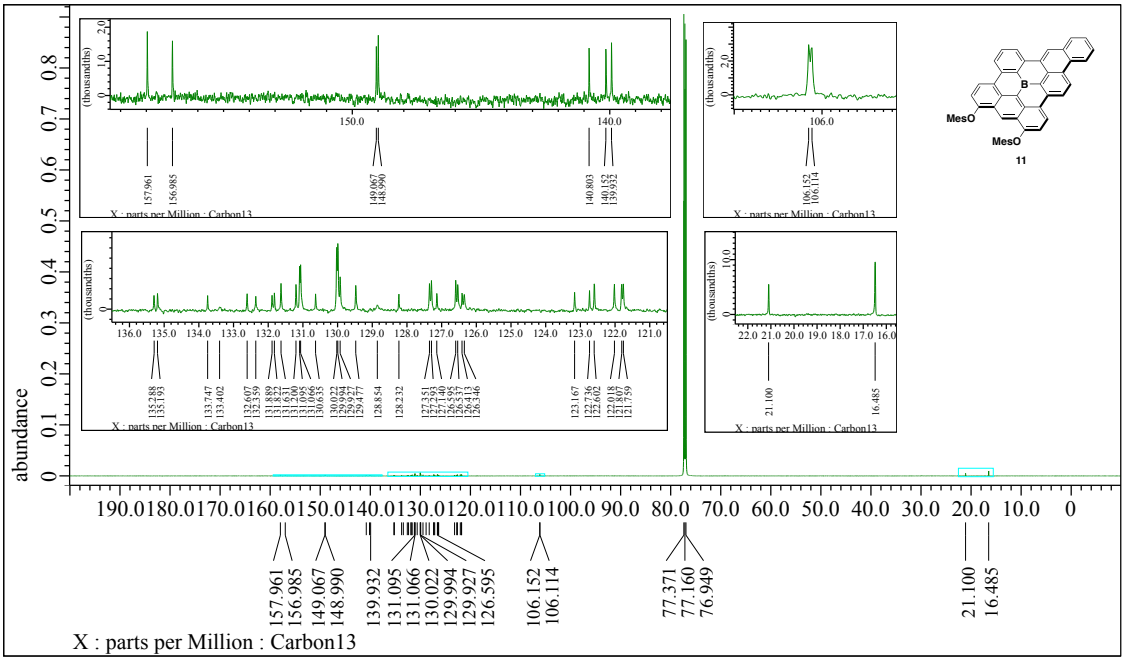

Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of **11** (151 MHz, $CDCl_3$).

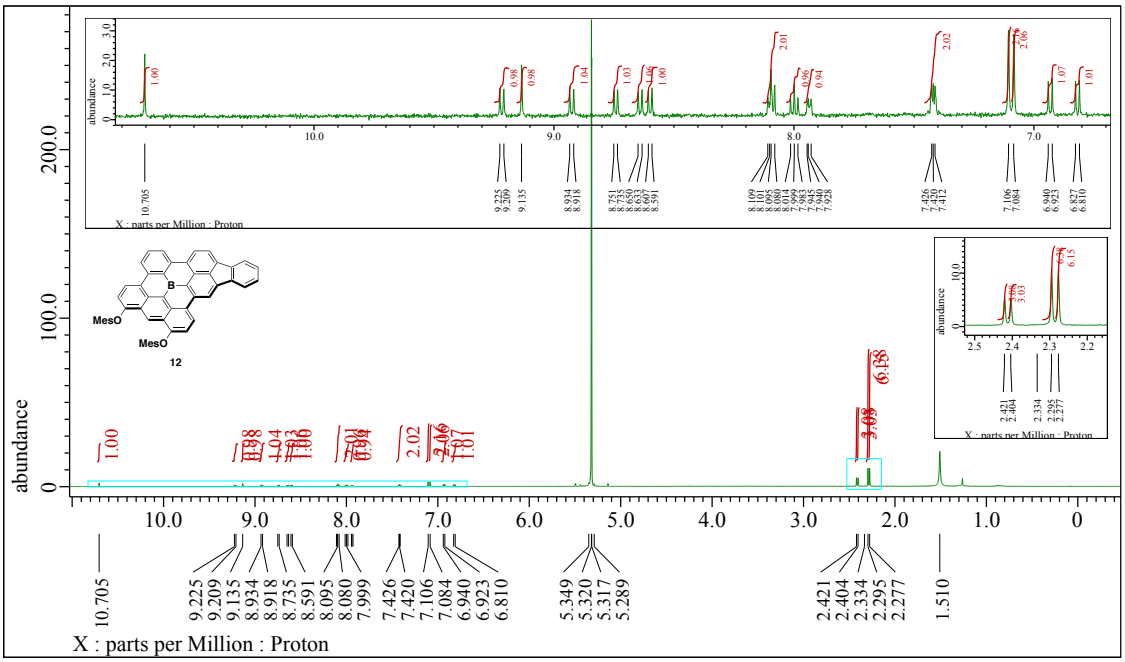

Figure S57. ^{1}H NMR spectrum of **12** (500 MHz, CD_2Cl_2).

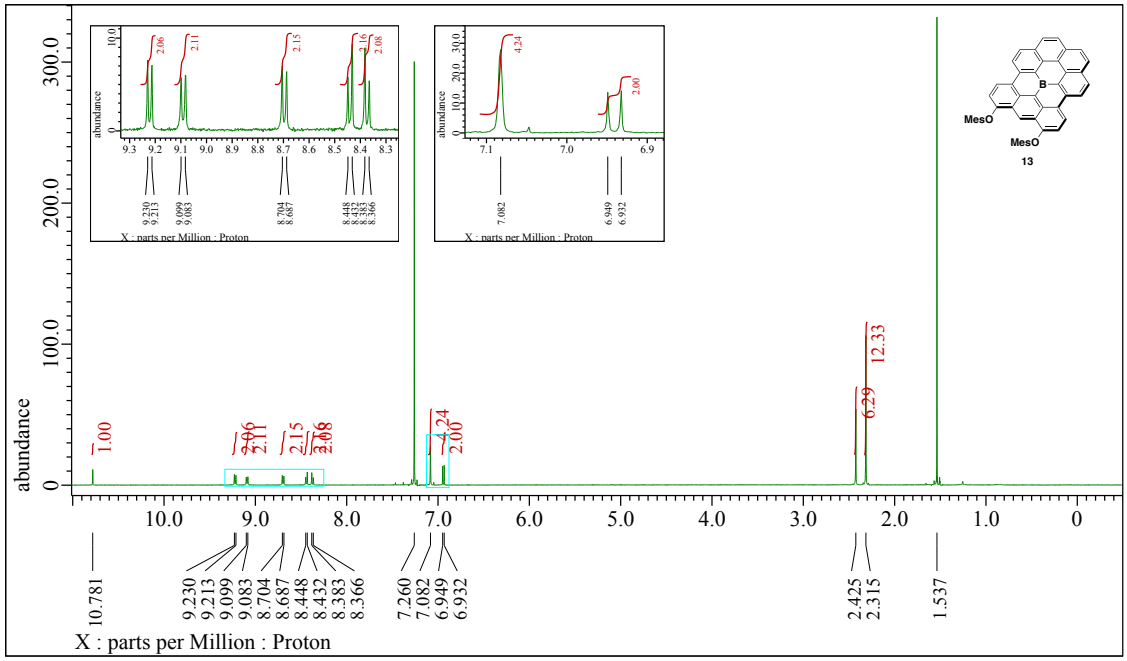

Figure S58. ^{1}H NMR spectrum of **13** (500 MHz, $CDCl_3$).

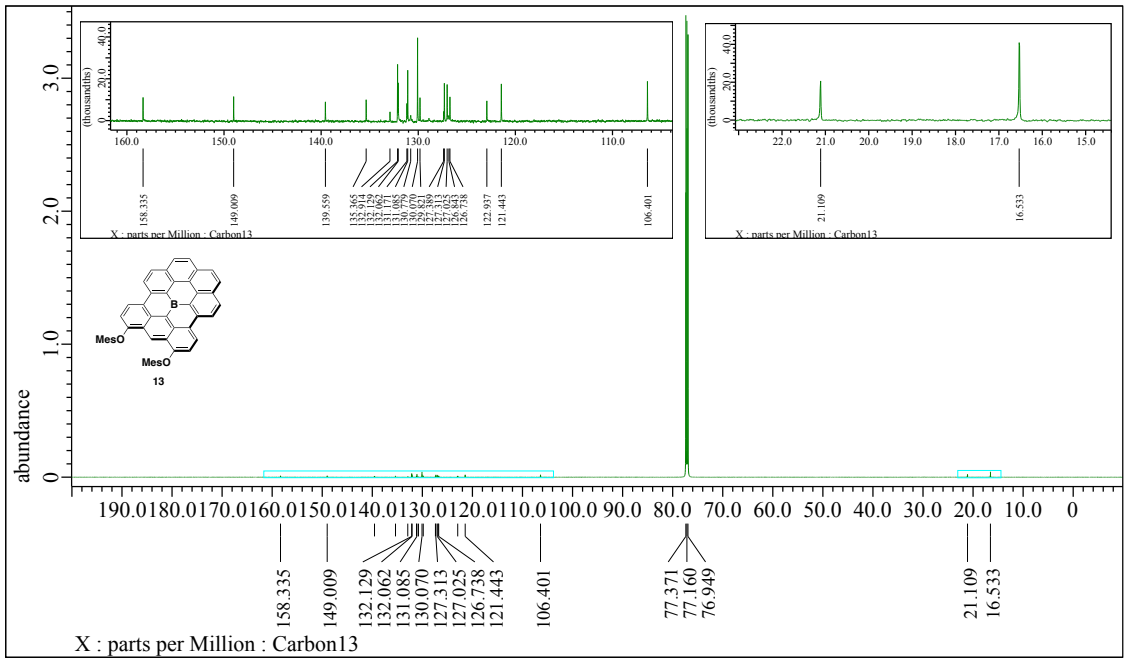

Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of **13** (151 MHz, $CDCl_3$).

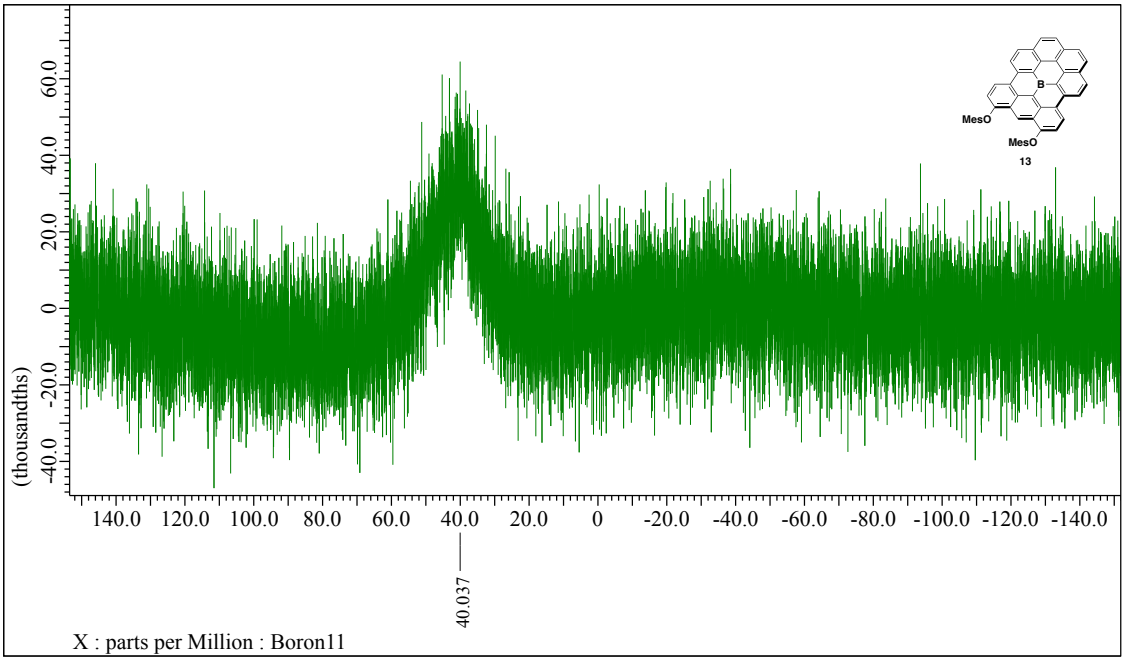

Figure S60. $^{11}B\{^{1}H\}$ NMR spectrum of **13** (160 MHz, $CDCl_3$).

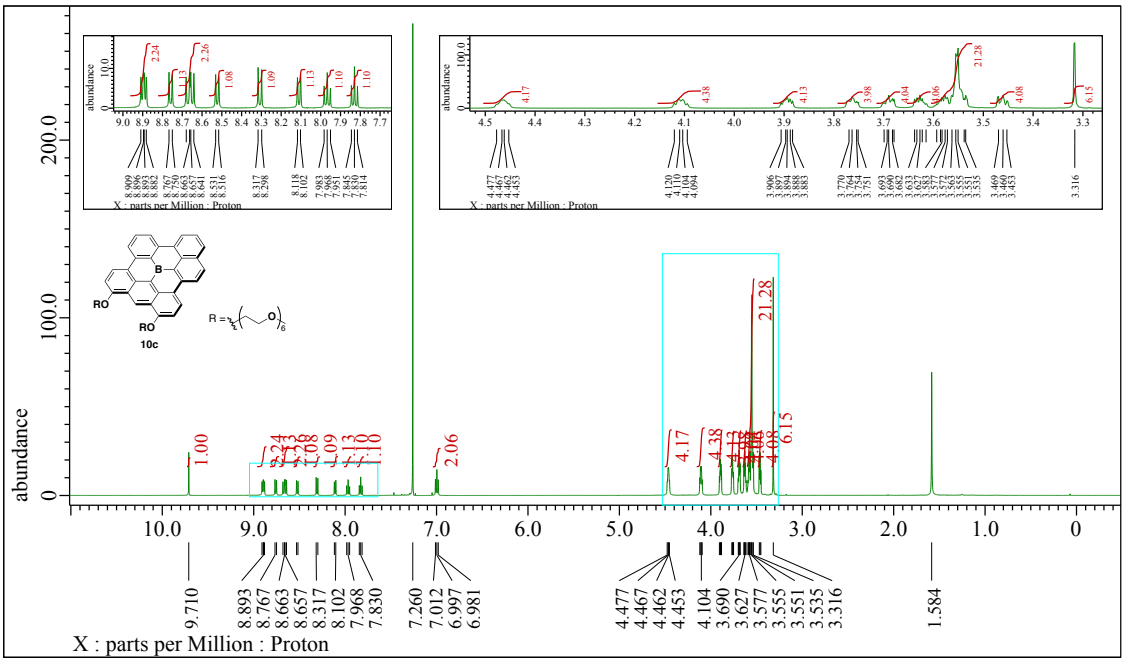

Figure S61. ^{1}H NMR spectrum of **10c** (500 MHz, $CDCl_3$).

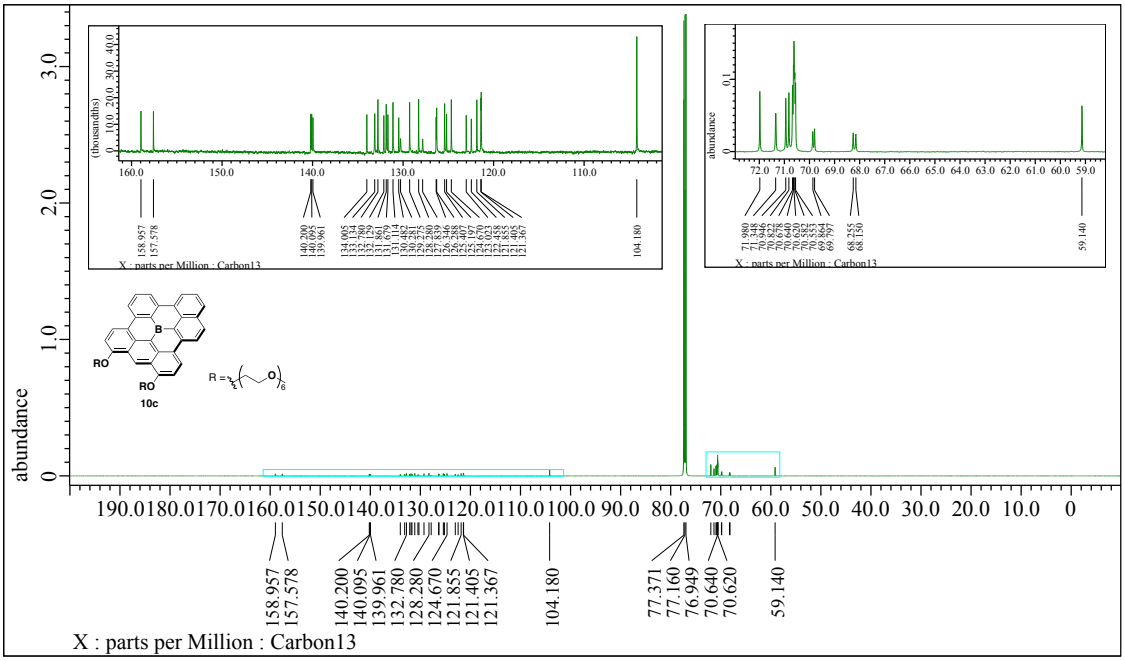

Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum of **10c** (151 MHz, $CDCl_3$).

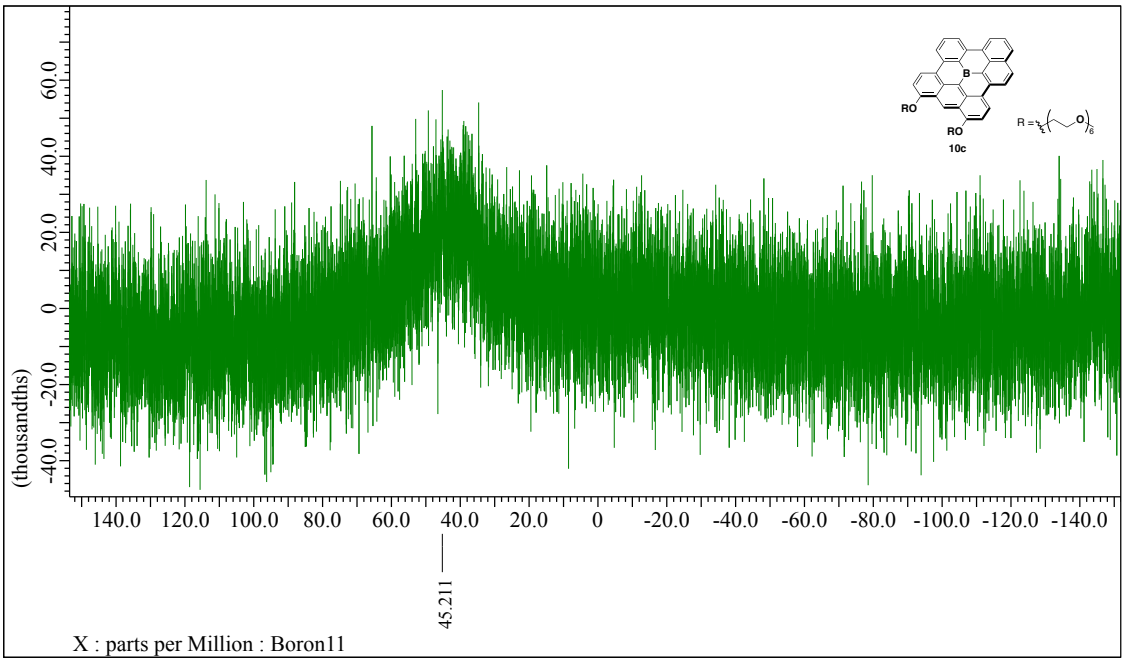

Figure S63. $^{11}B\{^{1}H\}$ NMR spectrum of **10c** (160 MHz, $CDCl_3$).