Electronic Supplementary Information
for
Carbazole-based BODIPYs with ethynyl substituents at the boron center: solid-state excimer fluorescence in the VIS/NIR region

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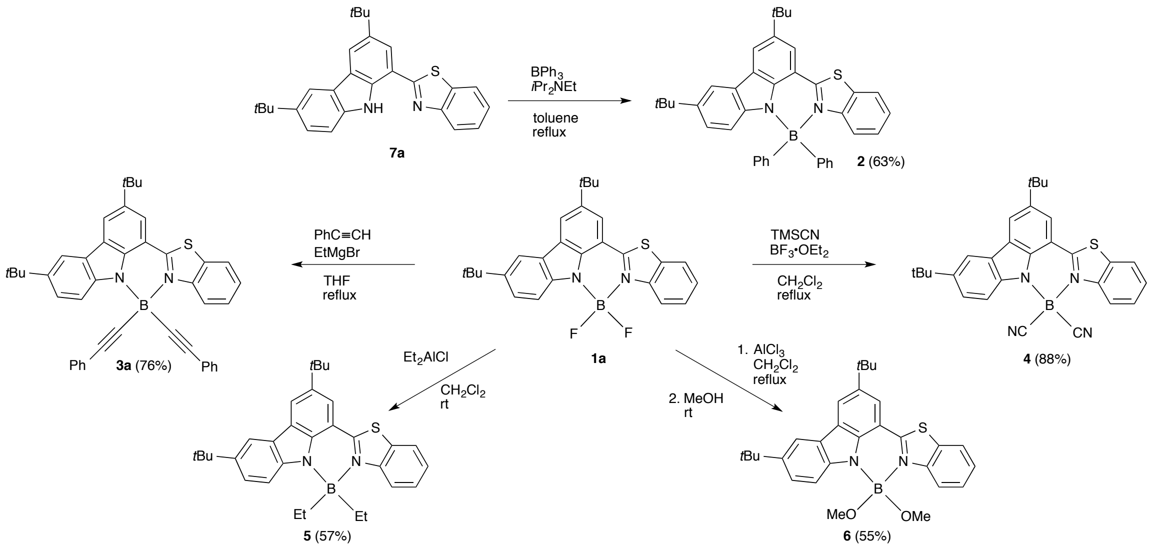
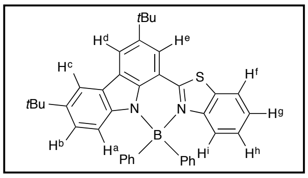
[A] Experimental Procedures and Compound Data

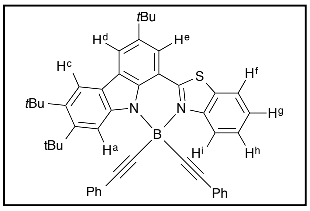


Scheme S1 Synthesis of **2–6**.



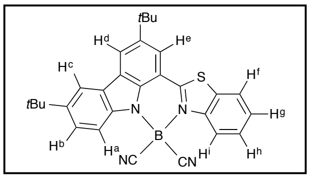
Synthesis of 2. A solution of **7a**[S1] (41.2 mg, 100 μmol), BPh_3 (93.0 mg, 384 μmol), and $i$$Pr_2NEt$ (0.33 mL, 1.9 mmol) in dry toluene (2.0 mL) was heated at reflux for 48 h under N_2. After cooling to rt, the mixture was evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **2** as an orange solid (36.2 mg, 62.8 μmol, 63%).

^{1}H NMR ($CDCl_3$) δ = 8.34 (d, J = 1.2 Hz, 1H, H^d), 8.05 (d, J = 2.0 Hz, 1H, H^c), 7.81 (dd, J = 0.8, 7.2 Hz, 1H, H^f), 7.73 (d, J = 2.0 Hz, 1H, H^e), 7.64 (d, J = 8.8 Hz, 1H, H^i), 7.46−7.43 (m, 4H, *o*Ph), 7.34 (t, J = 2.0 Hz, 1H, H^g), 7.25−7.16 (m, 8H, H^b, H^h, *m*Ph, *p*Ph), 6.78 (d, J = 8.8 Hz, 1H, H^a), 1.51 (s, 9H, *t*Bu), and 1.38 ppm (s, 9H, *t*Bu); ^{13}C NMR ($CDCl_3$) δ = 168.85, 146.55, 143.79, 141.82, 141.09, 140.35, 133.95, 130.22, 127.65, 127.34, 126.65, 125.90, 125.40, 124.63, 124.40, 123.99, 122.53, 122.02, 119.41, 116.43, 114.21, 109.46, 35.00, 34.72, 32.15, and 32.08 ppm; HR-MS (APCI): m/z = 576.2790. calcd for $C_{39}H_{37}N_2B_1S_1$: 576.2783 $[M]^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 310 (9470), 339 (9300), and 505 nm (7520 $mol^{-1}dm^3cm^{-1}$).



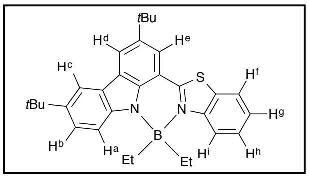
Synthesis of 3a. To a solution of phenylacetylene (0.20 mL 1.8 mmol) in dry THF (2.0 mL) was added EtMgBr (1 M in hexane, 2.0 mL, 2.0 mmol) under N_2, and the mixture was heated at 60 °C for 2 h. A solution of **1a**[S1] (54.8 mg, 119 μmol) in dry THF (5.0 mL) was added, and the mixture was heated at reflux for 24 h. After cooling to rt, water was added, and organic products were extracted with $CHCl_3$. The extracts were dried over Na_2SO_4 and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **3a** as an orange solid (56.3 mg, 90.1 μmol, 76%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 9.20 (d, J = 8.4 Hz, 1H, H^i), 8.34 (d, J = 1.2 Hz, 1H, H^d), 8.17 (d, J = 8.8 Hz, 1H, H^a), 8.14 (d, J = 2.0 Hz, 1H, H^c), 7.92 (d, J = 7.6 Hz, 1H, H^i), 7.73 (t, J = 8.0 Hz, 1H, H^h), 7.71 (d, J = 1.6 Hz, 1H, H^e), 7.65 (dd, J = 2.0, 8.8 Hz, 1H, H^b), 7.55 (t, J = 7.6 Hz, 1H, H^g), 7.33−7.30 (m, 4H, *o*Ph), 7.19−7.16 (m, 6H, *m*Ph, *p*Ph), 1.50 (s, 9H, *t*Bu), and 1.49 ppm (s, 9H, *t*Bu); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.48, 145.37, 142.58, 141.22, 138.49, 131.78, 129.83, 128.01, 127.65, 127.36, 126.64, 125.43, 125.05, 124.66, 123.98, 122.64, 121.90, 119.27, 116.62, 114.28, 108.08, 98.11, 35.02, 34.94, 32.24, and 32.15 ppm; HR-MS (APCI): m/z = 624.2755. calcd for $C_{43}H_{37}N_2B_1S_1$: 624.2783 $[M]^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) =307 (14700), 329 (13600), and 499 nm (12500 $mol^{-1}dm^3cm^{-1}$).



Synthesis of 4. To a solution of **1a** (50.4 mg 110 μmol) in dry CH_2Cl_2 (7.0 mL) was added trimethylsilyl cyanide (0.27 mL, 2.2 mmol) and $BF_3{\cdot}OEt_2$ (0.14 mL, 1.1 mmol) under N_2, and the mixture was heated at reflux for 2 h. After cooling to rt, water was added, and the organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$ to give **4** as an orange solid (45.7 mg, 96.4 μmol, 88%).

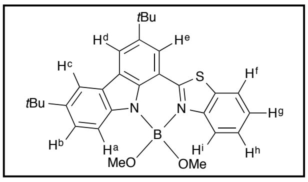
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.63 (d, J = 8.8 Hz, 1H, H^i), 8.42 (d, J = 2.0 Hz, 1H, H^d), 8.15 (d, J = 1.2 Hz, 1H, H^c), 8.02 (d, J = 8.0 Hz, 1H, H^f), 7.91 (d, J = 8.8 Hz, 1H, H^a), 7.87 (t, J = 8.4 Hz, 1H, H^h), 7.76 (d, J = 1.6 Hz, 1H, H^e), 7.74 (dd, J = 1.8, 8.6 Hz, 1H, H^b), 7.68 (t, J = 7.2 Hz, 1H, H^g), 1.51 (s, 9H, *t*Bu), and 1.49 ppm (s, 9H, *t*Bu); ^{13}C NMR ($CDCl_3$) δ = 169.37, 144.99, 143.75, 143.16, 140.94, 137.82, 129.65, 128.98, 127.98, 127.11, 126.11, 125.97, 124.39, 122.83, 119.76, 119.68, 117.44, 112.72, 107.17, 35.21, 35.04, 32.06, and 31.96 ppm; HR-MS (APCI): m/z = 474.2028. calcd for $C_{29}H_{27}N_4B_1S_1$: 474.2049 $[M]^+$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 304 (12200), 332 (14000), 343 (14000), and 490 nm (14600 $mol^{-1}dm^3cm^{-1}$).



Synthesis of 5. To a solution of **1a** (72.7 mg 163 μmol) in dry CH_2Cl_2 (10 mL) was added EtMgBr (1 M in hexane, 0.50 mL, 0.5 mmol) under N_2, and the mixture was stirred at rt for 30 min. Water was added, and organic products were extracted with $CHCl_3$. The extracts were dried over Na_2SO_4 and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **5** as a red solid (23.4 mg, 50.4 μmol, 31%).

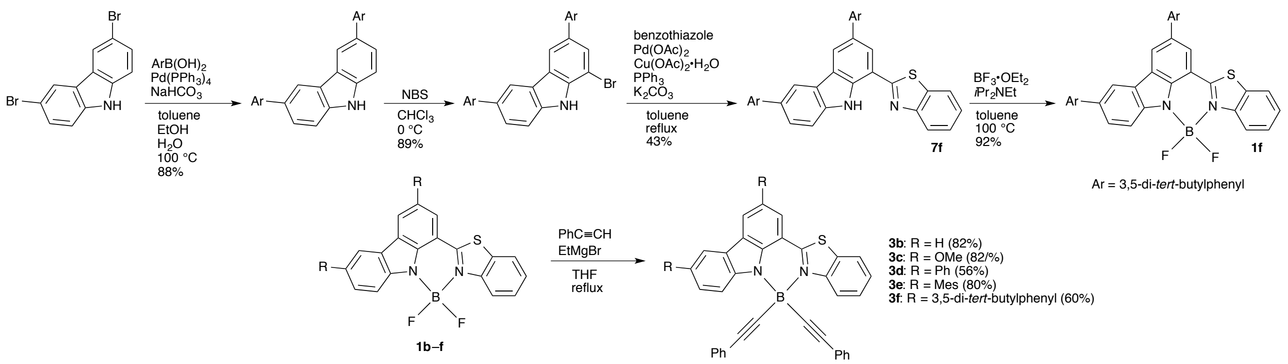
^{1}H NMR ($CDCl_3$) δ = 8.49 (d, J = 8.8 Hz, 1H, H^i), 8.26 (d, J = 2.0 Hz, 1H, H^d), 8.12 (d, J = 2.0 Hz, 1H, H^c), 7.89 (dd, J = 0.8, 8.0 Hz, 1H, H^f), 7.70 (d, J = 8.8 Hz, 1H, H^a), 7.60 (d, J = 1.6 Hz, 1H, H^e), 7.58 (t, J = 8.0 Hz, 1H, H^h), 7.51 (dd, J = 2.0, 8.8 Hz, 1H, H^b), 7.49 (t, J = 7.0 Hz, 1H, H^g), 1.50 (s, 9H, *t*Bu), 1.48 (s, 9H, *t*Bu), 1.30 (q, J = 7.6 Hz, 4H, CH_2), and 0.37 ppm (t, J = 7.8 Hz, 6H,

CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.16, 145.86, 142.30, 141.24, 140.73, 139.83, 130.05, 127.52, 126.13, 124.37, 124.28, 123.69, 122.31, 121.04, 119.35, 116.58, 113.59, 108.99, 34.87, 34.79, 32.21, 32.15, 14.83, and 9.65 ppm; HR-MS (APCI): m/z = 480.2760. calcd for $C_{31}H_{37}N_2B_1S_1$: 480.2782 $[M]^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 313 (22600), 331 (19500), and 515 nm (14100 $mol^{-1}dm^3cm^{-1}$).

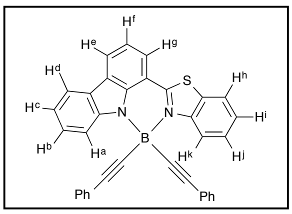


Synthesis of 6. A flask containing **1a** (52.0 mg, 113 µmol) and $AlCl_3$ (25.4 mg, 191 µmol) was purged with N_2, charged with dry CH_2Cl_2 (10 mL), and heated at reflux for 10 min. After cooling to rt, dry MeOH (3.0 mL, 74 mmol) was added, and the mixture was stirred at rt for 30 min. the mixture was passed through basic alumina and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$ to give **6** as a yellow solid (29.9 mg, 61.8 µmol, 55%).

^{1}H NMR ($CDCl_3$) δ = 8.91 (d, J = 8.4 Hz, 1H, H^i), 8.39 (d, J = 1.6 Hz, 1H, H^d), 8.14 (d, J = 2.0 Hz, 1H, H^c), 7.92 (d, J = 8.4 Hz, 1H, H^a), 7.91 (d, J = 7.6 Hz, 1H, H^f), 7.80 (d, J = 1.2 Hz, 1H, H^e), 7.64 (t, J = 7.2 Hz, 1H, H^h), 7.60 (dd, J = 2.0, 8.8 Hz, 1H, H^b), 7.53 (t, J = 7.6 Hz, 1H, H^g), 2.90 (s, 6H, OMe), 1.54 (s, 9H, *t*Bu), and 1.49 ppm (s, 9H, *t*Bu); ^{13}C NMR ($CDCl_3$) δ = 168.85, 145.63, 143.16, 142.45, 141.52, 140.43, 129.75, 128.24, 126.59, 125.55, 125.13, 124.21, 123.72, 122.28, 121.85, 119.34, 116.60, 114.01, 108.70, 50.09, 35.08, 34.95, and 32.19 ppm; HR-MS (APCI): m/z = 484.2352. calcd for $C_{29}H_{33}N_2O_2B_1S_1$: 484.2355 $[M]^+$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 301 (14000), 324 (16800), and 462 nm (14800 $mol^{-1}dm^3cm^{-1}$).

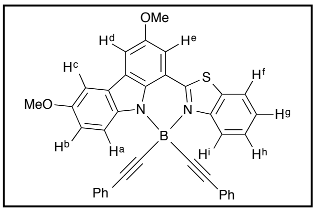


Scheme S2 Synthesis of **3b–f**.



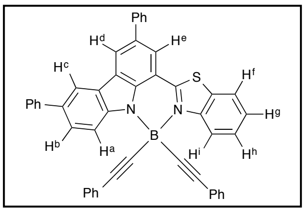
Synthesis of 3b. **3b** (Orange solid, 63.4 mg, 124 µmol, 82%) was synthesized from **1b**[S1] (53.0 mg, 152 µmol) via a method similar to the synthesis of **3a**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 9.23 (d, J = 8.8 Hz, 1H, H^k), 8.33 (d, J = 8.0 Hz, 1H, H^a), 8.27 (d, J = 7.2 Hz, 1H, H^e), 8.14 (d, J = 8.0 Hz, 1H, H^d), 7.94 (d, J = 8.4 Hz, 1H, H^h), 7.76 (t, J = 7.2 Hz, 1H, H^j^), 7.75 (d, J = 7.2 Hz, 1H, H^g), 7.61 (t, J = 8.0 Hz, 1H, H^b), 7.59 (t, J = 8.4 Hz, 1H, H^i), 7.36−7.31 (m, 5H, H^c, *o*Ph), and 7.23−7.17 ppm (m, 7H, H^f, *m*Ph, *p*Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.22, 145.23, 144.02, 139.33, 131.74, 129.92, 128.07, 127.75, 127.49, 126.84, 126.65, 125.15, 124.88, 124.25, 122.79, 122.65, 121.99, 120.65, 119.93, 118.01, 115.07, 108.98, and 98.37 ppm; HR-MS (APCI): *m*/*z* = 512.1525. calcd for $C_{35}H_{21}N_2B_1S_1$: 512.1530 $[M]^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 301 (17000), 324 (15900), and 482 nm (14400 $mol^{-1}dm^3cm^{-1}$).



Synthesis of 3c. **3c** (purple solid, 56.0 mg, 97.9 µmol, 82%) was synthesized from **1c**[S1] (48.6 mg, 119 µmol) via a method similar to the synthesis of **3a**.

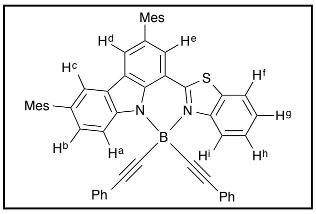
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 9.20 (d, J = 8.4 Hz, 1H, H^i), 8.19 (d, J = 8.8 Hz, 1H, H^a), 7.84 (d, J = 7.6 Hz, 1H, H^f), 7.79 (d, J = 2.4 Hz, 1H, H^d), 7.73 (t, J = 8.0 Hz, 1H, H^h), 7.54 (d, J = 2.0 Hz, 1H, H^c), 7.51 (t, J = 7.6 Hz, 1H, H^g), 7.35−7.33 (m, 4H, *o*Ph), 7.23 (dd, J = 2.2, 9.0 Hz, 1H, H^b), 7.21−7.18 (m, 7H, H^e, *m*Ph, *p*Ph), 3.92 (s, 3H, OMe), and 3.86 ppm (s, 3H, OMe); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.51, 154.00, 152.48, 145.26, 139.66, 135.79, 131.72, 129.93, 128.09, 127.71, 127.48, 126.74, 125.69, 124.92, 124.22, 122.54, 121.98, 116.14, 115.48, 114.25, 108.62, 108.27, 103.58, 98.29, 56.80, and 56.18 ppm; HR-MS (APCI): *m*/*z* = 572.1756. calcd for $C_{37}H_{25}N_2O_2B_1S_1$: 572.1742 $[M]^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 319 (16600), 348 (14400), and 534 nm (11600 $mol^{-1}dm^3cm^{-1}$).



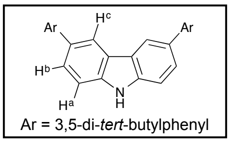
Synthesis of 3d. **3d** (red solid, 37.5 mg, 56.4 µmol, 56%) was synthesized from **1d**[S1] (50.4 mg, 101 µmol) via a method similar to the synthesis of **3a**.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 9.24 (d, J = 8.8 Hz, 1H, H^i), 8.49 (d, J = 1.2 Hz, 1H, H^d), 8.39 (d, J = 8.0 Hz, 1H, H^a), 8.34 (d, J = 1.6 Hz, 1H, H^c), 7.91 (d, J = 7.6 Hz, 1H, H^f), 7.88 (d, J = 1.6 Hz, 1H, H^e), 7.87 (dd, J = 1.6, 8.4 Hz, 1H, H^b), 7.78−7.74 (m, 3H, H^h, *o*Ph), 7.69 (d, J = 7.2 Hz, 2H, *o*Ph), 7.55 (t, J = 7.4 Hz, 1H, H^g), 7.51−7.46 (m, 4H, *m*Ph), 7.38−7.33 (m, 6H, *p*Ph, *o*Ph), and 7.23−7.18 ppm (m, 6H, *m*Ph, *p*Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.05, 145.26, 143.98, 142.40, 141.23, 139.29, 133.50, 132.19, 131.77, 129.94, 129.09, 128.86, 128.12, 127.85, 127.57, 127.54, 127.31, 127.10, 126.95, 126.61, 126.55, 126.50, 125.86, 124.96, 124.82, 122.66, 122.08, 121.81, 119.34, 115.19, 109.26, and 98.54 ppm; HR-MS (APCI): *m*/*z* = 665.2195. calcd for $C_{47}H_{30}N_2B_1S_1$: 665.2225 $[M+H]^+$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 255 (55100), 311 (32900), and 503 nm (12400 $mol^{-1}dm^3cm^{-1}$).

Synthesis of 3e. **3e** (Orange solid, 53.8 mg, 71.8 μmol, 80%) was synthesized from **1e**[S1] (52.8 mg, 90.3 μmol) via a method similar to the synthesis of **3a**.

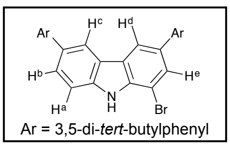


^{1}H NMR ($CDCl_3$, 400 MHz) δ = 9.25 (d, J = 8.8 Hz, 1H, H^i), 8.34 (d, J = 8.8 Hz, 1H, H^a), 7.98 (d, J = 0.8 Hz, 1H, H^d), 7.95 (d, J = 7.6 Hz, 1H, H^f), 7.84 (d, J = 0.8 Hz, 1H, H^c), 7.77 (t, J = 8.8 Hz, 1H, H^h), 7.59 (t, J = 8.4 Hz, 1H, H^g), 7.54 (d, J = 1.2 Hz, 1H, H^e), 7.38−7.35 (m, 5H, H^b, *o*Ph), 7.21−7.19 (m, 6H, *m*Ph, *p*Ph), 7.03 (s, 2H, Mes), 7.00 (s, 2H, Mes), 2.38 (s, 3H, Me), 2.37 (s, 3H, Me), 2.114 (s, 6H, Me), and 2.108 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.17, 145.34, 143.12, 140.02, 138.68, 138.59, 137.22, 136.94, 136.41, 132.75, 131.79, 130.97, 129.98, 128.63, 128.41, 128.14, 128.09, 127.82, 127.52, 126.93, 125.70, 124.90, 124.39, 123.41, 122.73, 122.01, 121.16, 114.88, 109.06, 98.44, 21.32, 21.25, and 21.22 ppm; HR-MS (APCI): m/z = 748.3103. calcd for $C_{53}H_{41}N_2B_1S_1$: 748.3087 $[M]^+$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 308 (17100), 330 (14600), and 496 nm (12900 mol^{-1}dm^{3}cm^{-1}).



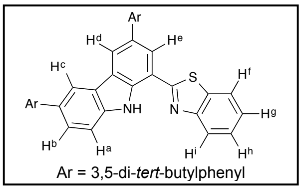
Synthesis of 3,6-bis(3,5-di-*tert*-butylphenyl)carbazole. A solution of 3,6-dibromocarbazole (825 mg, 2.54 mmol), 3,5-di-*tert*-butylphenylboronic acid (2.39 g, 10.2 mmol), $Pd(PPh_3)_4$ (194 mg, 168 μmol), and $NaHCO_3$ (2.12 g, 25.2 mmol) in toluene/EtOH/H_2O (18/12/12 mL) was degassed and heated at 100 °C for 12 h under N_2. After cooling to rt, organic products were extracted with EtOAc, and the extracts were passed through a silica gel column with EtOAc and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give the desired product as a white solid (1.21 g, 2.24 mmol, 88%).

^{1}H NMR ($CDCl_3$) δ = 8.43 (d, J = 1.2 Hz, 1H, H^c), 8.02 (s, 1H, NH), 7.77 (dd, J = 1.6, 8.4 Hz, 2H, H^b), 7.65 (d, J = 1.6 Hz, 4H, Ar), 7.55 (t, J = 1.6 Hz, 2H, Ar), 7.50 (d, J = 8.8 Hz, 1H, H^a), and 1.53 ppm (s, 36H, *t*Bu); ^{13}C NMR ($CDCl_3$) δ = 151.21, 141.74, 139.39, 134.68, 126.19, 124.01, 122.18, 120.90, 119.31, 110.95, 35.17, and 31.77 ppm. HR-MS (APCI): m/z = 544.3911. calcd for $C_{40}H_{50}N_1$: 544.3938 $[M\text{+H}]^+$.



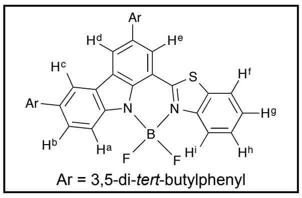
Synthesis of 3,6-bis(3,5-di-*tert*-butylphenyl)-1-bromocarbazole. To a solution of 3,6-bis(3,5-di-*tert*-butylphenyl)carbazole (1.10 g, 2.03 mmol) was added NBS (365 mg, 2.05 mmol) at 0 °C, and the mixture was stirred at 0 °C for 3 h in the dark. The mixture was evaporated, and the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give the desired product as a white solid (1.12 g, 1.80 mmol, 89%).

^{1}H NMR ($CDCl_3$) δ = 8.42 (d, J = 1.6 Hz, 1H, H^c), 8.37 (d, J = 0.8 Hz, 1H, H^d), 8.35 (s, 1H, NH), 7.94 (d, J = 1.2 Hz, 1H, H^e), 7.84 (dd, J = 1.4, 8.6 Hz, 1H, H^b), 7.66 (d, J = 1.6 Hz, 2H, Ar), 7.63 (d, J = 8.4 Hz, 1H, H^a), 7.62 (d, J = 1.6 Hz, 2H, Ar), 7.59 (t, J = 1.6 Hz, 1H, Ar), 7.58 (t, J = 1.6 Hz, 1H, Ar), 1.549 (s, 18H, *t*Bu), and 1.545 ppm (s, 18H, *t*Bu); ^{13}C NMR ($CDCl_3$) δ = 151.39, 151.27, 141.47, 140.62, 139.00, 137.92, 136.25, 135.34, 128.05, 126.92, 125.18, 124.45, 122.16, 121.34, 121.06, 119.78, 118.47, 111.37, 104.41, 35.18, and 31.77 ppm; HR-MS (APCI): *m*/*z* = 622.2889. calcd for $C_{40}H_{47}N_1Br_1$: 622.2880 [M–H]$^-$.



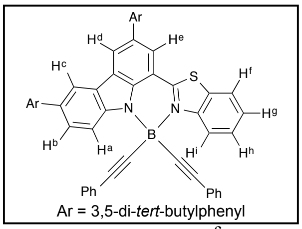
Synthesis of 7f. A suspension of 3,6-bis(3,5-di-*tert*-butylphenyl)-1-bromocarbazole (1.09 g, 1.75 mmol), benzothiazole (0.58 mL, 5.4 mmol), $Pd(OAc)_2$ (29.7 mg, 132 μmol), $Cu(OAc)_2 \cdot H_2O$ (73.2 mg, 366 μmol), PPh_3 (248 mg, 946 μmol), and K_2CO_3 (521 mg, 3.78 mmol) in dry toluene (3.0 mL) was degassed and heated at reflux for 15 h under N_2. After the solvent was removed, the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **7f** as a yellow solid (511 mg, 755 μmol, 43%).

^{1}H NMR ($CDCl_3$) δ = 11.05 (s, 1H, NH), 8.45 (d, J = 1.2 Hz, 1H, H^d or H^e), 8.38 (s, 1H, H^c), 8.23 (d, J = 8.0 Hz, 1H, H^f or H^i), 8.16 (d, J = 1.2 Hz, 1H, H^d or H^e), 7.97 (d, J = 7.6 Hz, 1H, H^f or H^i), 7.78 (dd, J = 1.6, 8.0 Hz, 1H, H^b), 7.73 (d, J = 8.0 Hz, 1H, H^a), 7.59 (d, J = 1.2 Hz, 2H, Ar), 7.57−7.55 (m, 3H, H^g or H^h, and Ar), 7.52 (t, J = 1.8 Hz, 1H, Ar), 7.47 (t, J = 1.6 Hz, 1H, Ar), 7.45 (t, J = 8.4 Hz, 1H, H^g or H^h), 1.47 (s, 18H, *t*Bu), and 1.45 ppm (s, 18H, *t*Bu); ^{13}C NMR ($CDCl_3$) δ = 168.04, 154.15, 151.50, 151.23, 141.64, 141.20, 139.76, 137.27, 135.05, 134.56, 133.90, 126.83, 126.53, 125.50, 125.42, 125.38, 123.43, 122.97, 122.43, 122.30, 122.19, 121.79, 121.38, 120.98, 119.52, 115.98, 111.71, 35.23, 35.18, and 31.78 ppm; HR-MS (APCI): *m*/*z* = 675.3801. calcd for $C_{47}H_{51}N_2S_1$: 675.3778 [M–H]$^-$.



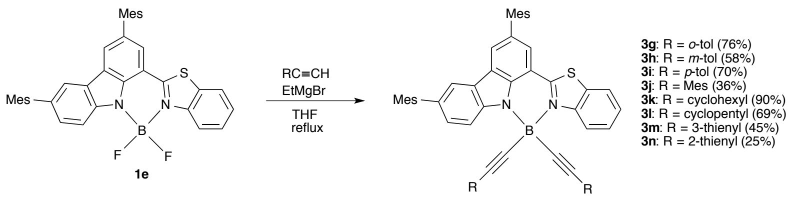
Synthesis of 1f. **7f** (536 mg, 792 μmol) was dissolved in dry toluene (10 mL). *i*Pr_2NEt (1.0 mL, 5.8 mmol) and then $BF_3 \cdot OEt_2$ (0.24 mL, 1.9 mmol) were added, and the mixture was heated at 100 °C for 1 h under N_2. After the solvents were removed, the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **1f** as a yellow solid (530 mg, 731 μmol, 92%).

^{1}H NMR ($CDCl_3$) δ = 8.66 (d, J = 8.0 Hz, 1H, H^i), 8.56 (s, 1H, H^d), 8.36 (s, 1H, H^c), 8.07 (d, J = 8.0 Hz, 1H, H^a), 8.03 (s, 1H, H^e), 7.94 (d, J = 8.0 Hz, 1H, H^f), 7.85 (dd, J = 1.4, 8.0 Hz, 1H, H^b), 7.74 (t, J = 7.6 Hz, 1H, H^h), 7.59 (t, J = 7.6 Hz, 1H, H^g), 7.57 (d, J = 2.0 Hz, 2H, Ar), 7.54−7.53 (m, 3H, Ar), 7.47 (s, 1H, Ar), 1.46 (s, 18H, *t*Bu), and 1.44 ppm (s, 18H, *t*Bu); ^{13}C NMR ($CDCl_3$) δ = 168.28, 151.70, 151.24, 144.36, 143.16, 141.60, 140.72, 139.99, 136.04, 134.80, 129.44, 128.84, 127.63, 127.28, 127.23, 126.10, 124.82, 122.45, 122.32, 122.24, 121.69, 121.06, 119.94, 114.46, 108.93, 35.24, 35.18, and 31.77 ppm; HR-MS (APCI): *m*/*z* = 725.3881. calcd for $C_{47}H_{52}N_2S_1B_1F_2$: 725.3915 [M+H]$^+$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 328 (21900), 341 (22100), and 470 nm (17400 $mol^{-1}dm^3cm^{-1}$).

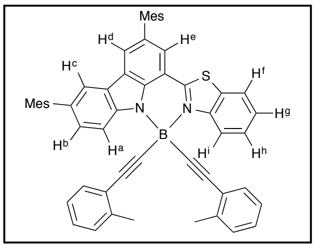


Synthesis of 3f. **3f** (red solid, 60.5 mg, 71.8 μmol, 60%) was synthesized from **1f** (82.0 mg, 113 μmol) via a method similar to the synthesis of **3a**.

^{1}H NMR ($CDCl_3$) δ = 9.26 (d, J = 8.0 Hz, 1H, H^i), 8.51 (d, J = 1.2 Hz, 1H, H^d), 8.39 (d, J = 8.8 Hz, 1H, H^a), 8.37 (d, J = 1.2 Hz, 1H, H^c), 7.96 (d, J = 8.4 Hz, 1H, H^f), 7.94 (d, J = 1.2 Hz, 1H, H^e), 7.86 (dd, J = 1.6, 8.8 Hz, 1H, H^b), 7.78 (t, J = 7.2 Hz, 1H, H^h), 7.60 (t, J = 7.6 Hz, 1H, H^g), 7.59 (d, J = 1.6 Hz, 2H, Ar), 7.53 (d, J = 2.0 Hz, 2H, Ar), 7.51 (t, J = 2.0 Hz, 1H, Ar), 7.44 (t, J = 2.0 Hz, 1H, Ar), 7.37−7.35 (m, 4H, *o*Ph), 7.20−7.19 (m, 6H, *m*Ph, *p*Ph), 1.45 (s, 18H, *t*Bu), and 1.44 ppm (s, 18H, *t*Bu); ^{13}C NMR ($CDCl_3$) δ = 167.20, 151.59, 151.11, 145.37, 143.87, 142.00, 141.07, 139.26, 134.97, 133.69, 131.80, 130.01, 128.08, 127.88, 127.51, 127.21, 127.01, 125.82, 124.90, 124.85, 122.74, 122.32, 122.13, 122.04, 121.45, 120.76, 119.57, 115.11, 109.14, 98.46, 35.23, 35.18, 31.79, and 31.77 ppm; HR-MS (APCI): m/z = 889.4740. calcd for $C_{63}H_{62}N_2B_1S_1$: 889.4732 $[M+H]^+$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 306 (33000), 345 (18000), and 507 nm (12700 $mol^{-1}dm^3cm^{-1}$).



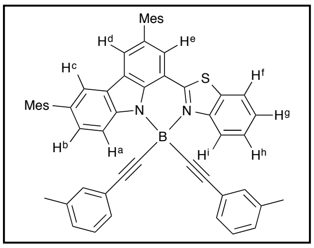
Scheme S3 Synthesis of **3g**–**n**.



Synthesis of 3g. **3g** (red solid, 47.3 mg, 72.5 μmol, 76%) was synthesized from **1e** (55.5 mg, 94.9 μmol) with 2-ethynyltoluene via a method similar to the synthesis of **3a**.

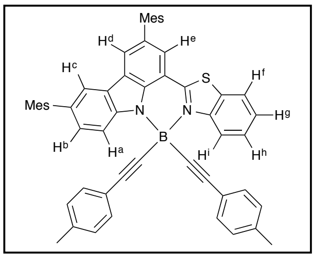
^{1}H NMR ($CDCl_3$) δ = 9.31 (d, J = 8.4 Hz, 1H, H^i), 8.41 (d, J = 8.0 Hz, 1H, H^a), 8.00 (s, 1H, H^d), 7.95 (d, J = 7.6 Hz, 1H, H^f), 7.86 (s, 1H, H^c), 7.75 (t, J = 7.8 Hz, 1H, H^h), 7.60 (t, J = 7.6 Hz, 1H, H^g), 7.55 (s, 1H, H^e), 7.36 (d, J = 8.4 Hz, 1H, H^b), 7.29 (d, J = 7.6 Hz, 2H, *o*-tolyl), 7.12−7.10 (m, 4H, *o*-tolyl), 7.04−7.01 (m, 6H, *o*-tolyl, Mes), 2.39 (s, 3H, Me), 2.38 (s, 9H, Me), 2.13 (s, 6H, Me), and 2.11 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$) δ = 167.23, 145.27, 143.05, 140.28, 140.04, 138.72, 138.60, 137.22, 136.98, 136.90, 136.42, 132.74, 131.92, 130.95, 129.96, 129.29, 128.67, 128.41, 128.21, 128.14, 127.69, 127.54, 126.95, 125.69, 125.30, 124.66, 124.38, 123.43, 122.92, 122.01, 121.11, 115.16, 109.06, 97.48, 21.28, 21.24, and 21.08 ppm; HR-MS (APCI): m/z = 776.3429. calcd for $C_{55}H_{45}N_2B_1S_1$: 776.3411 $[M]^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 308 (18600), 329 (15700), and 498 nm (12700 $mol^{-1}dm^3cm^{-1}$).

Synthesis of 3h. **3h** (Orange solid, 38.5 mg, 60.0 μmol, 58%) was synthesized from **1e** (60.4 mg, 103 μmol) with 3-ethynyltoluene via a method similar to the synthesis of **3a**.

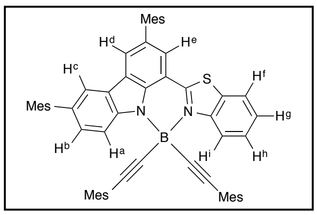


^{1}H NMR ($CDCl_3$) δ = 9.24 (d, J = 8.0 Hz, 1H, H^{i}), 8.34 (d, J = 8.8 Hz, 1H, H^{a}), 7.98 (d, J = 0.8 Hz, 1H, H^{d}), 7.94 (d, J = 8.0 Hz, 1H, H^{f}), 7.84 (d, J = 0.8 Hz, 1H, H^{c}), 7.77 (t, J = 7.6 Hz, 1H, H^{h}), 7.59 (t, J = 7.6 Hz, 1H, H^{g}), 7.53 (d, J = 0.8 Hz, 1H, H^{e}), 7.37 (dd, J = 1.6, 8.0 Hz, 1H, H^{b}), 7.20 (s, 2H, *m*-tolyl), 7.17 (d, J = 8.0 Hz, 2H, *m*-tolyl), 7.09 (t, J = 7.6 Hz, 2H, *m*-tolyl), 7.03 (s, 2H, Mes), 7.01 (d, J = 7.6 Hz, 2H, *m*-tolyl), 7.00 (s, 2H, Mes), 2.38 (s, 3H, Me), 2.37 (s, 3H, Me), 2.24 (s, 6H, Me), 2.113 (s, 6H, Me), and 2.110 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$) δ = 167.14, 145.38, 143.15, 140.07, 138.71, 138.63, 137.69, 137.21, 136.97, 136.40, 132.68, 132.42, 130.92, 129.97, 128.85, 128.60, 128.40, 128.14, 128.00, 127.84, 126.90, 125.71, 124.74, 124.38, 123.37, 122.79, 121.96, 121.11, 114.97, 109.07, 98.54, 21.32, and 21.26 ppm; HR-MS (APCI): m/z = 776.3424. calcd for $C_{55}H_{45}N_2B_1S_1$: 776.3411 $[M]^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 308 (19000), 329 (15900), and 496 nm (13500 $mol^{-1}dm^3cm^{-1}$).

Synthesis of 3i. **3i** (Orange solid, 54.7 mg, 70.4 μmol, 70%) was synthesized from **1e** (58.5 mg, 100 μmol) with 4-ethynyltoluene via a method similar to the synthesis of **3a**.

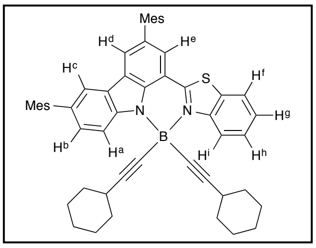


^{1}H NMR ($CDCl_3$) δ = 9.26 (d, J = 8.4 Hz, 1H, H^{i}), 8.35 (d, J = 8.4 Hz, 1H, H^{a}), 7.98 (d, J = 1.2 Hz, 1H, H^{d}), 7.93 (d, J = 7.6 Hz, 1H, H^{f}), 7.84 (d, J = 1.2 Hz, 1H, H^{c}), 7.76 (t, J = 7.2 Hz, 1H, H^{h}), 7.57 (t, J = 8.4 Hz, 1H, H^{g}), 7.53 (d, J = 1.2 Hz, 1H, H^{e}), 7.37 (dd, J = 1.6, 8.4 Hz, 1H, H^{b}), 7.26 (d, J = 8.0 Hz, 4H, *p*-tolyl), 7.03 (s, 2H, Mes), 7.01 (d, J = 8.0 Hz, 4H, *p*-tolyl), 7.00 (s, 2H, Mes), 2.39 (s, 3H, Me), 2.37 (s, 3H, Me), 2.28 (s, 6H, Me), and 2.12 ppm (s, 12H, Me); ^{13}C NMR ($CDCl_3$) δ = 167.08, 145.40, 143.16, 140.08, 138.70, 138.64, 137.43, 137.19, 136.96, 136.38, 132.65, 131.67, 130.88, 129.98, 128.84, 128.55, 128.40, 128.35, 128.13, 127.77, 126.87, 125.70, 124.37, 123.37, 122.84, 121.94, 121.90, 121.10, 114.97, 109.09, 98.51, 21.53, 21.33, 21.26, and 21.23 ppm; HR-MS (APCI): m/z = 776.3418. calcd for $C_{55}H_{45}N_2B_1S_1$: 776.3411 $[M]^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 308 (16500), 329 (16100), and 497 nm (13300 $mol^{-1}dm^3cm^{-1}$).



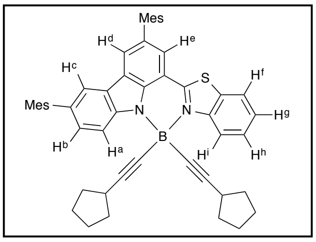
Synthesis of 3j. **3j** (Orange solid, 31.4 mg, 37.6 μmol, 36%) was synthesized from **1e** (60.9 mg, 104 μmol) with 2-ethynyl-1,3,5-trimethylbenzene via a method similar to the synthesis of **3a**.

^{1}H NMR ($CDCl_3$) δ = 9.36 (d, J = 8.0 Hz, 1H, H^{i}), 8.45 (d, J = 8.0 Hz, 1H, H^{a}), 7.98 (s, 1H, H^{d}), 7.94 (d, J = 7.6 Hz, 1H, H^{f}), 7.83 (s, 1H, H^{c}), 7.71 (t, J = 8.0 Hz, 1H, H^{h}), 7.58 (t, J = 7.8 Hz, 1H, H^g), 7.54 (s, 1H, H^e), 7.32 (d, J = 8.4 Hz, 1H, H^b), 7.03 (s, 2H, Mes), 7.00 (s, 2H, Mes), 6.74 (s, 4H, Mes), 2.39 (s, 3H, Me), 2.37 (s, 3H, Me), 2.23 (s, 12H, Me), 2.20 (s, 6H, Me), 2.13 (s, 6H, Me), and 2.08 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$) δ = 167.15, 145.24, 142.99, 140.11, 138.74, 138.67, 137.19, 137.03, 136.88, 136.76, 136.40, 132.63, 130.80, 129.90, 128.65, 128.39, 128.12, 127.92, 127.38, 126.95, 125.66, 124.27, 123.39, 123.33, 121.90, 121.63, 120.93, 115.64, 109.06, 96.46, 21.35, 21.30, 21.22, and 21.11 ppm; HR-MS (APCI): m/z = 832.4047. calcd for $C_{59}H_{53}N_2B_1S_1$: 832.4038 [M]$^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 308 (18400), 330 (15700), and 499 nm (12900 mol^{-1}dm^{3}cm^{-1}).



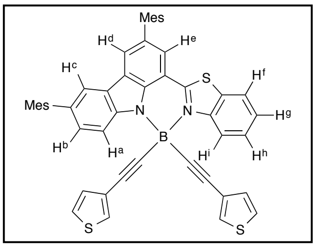
Synthesis of 3k. **3k** (Orange solid, 105 mg, 138 μmol, 90%) was synthesized from **1e** (89.5 mg, 153 μmol) with cyclohexylacetylene via a method similar to the synthesis of **3a**.

^{1}H NMR ($CDCl_3$) δ = 9.22 (d, J = 8.4 Hz, 1H, H^i), 8.26 (d, J = 8.4 Hz, 1H, H^a), 7.94 (d, J = 1.2 Hz, 1H, H^d), 7.87 (d, J = 7.6 Hz, 1H, H^f), 7.80 (d, J = 0.8 Hz, 1H, H^c), 7.68 (t, J = 8.0 Hz, 1H, H^h), 7.53 (t, J = 7.6 Hz, 1H, H^g), 7.47 (s, 1H, H^e), 7.31 (dd, J = 1.6, 8.0 Hz, 1H, H^b), 7.02 (s, 2H, Mes), 6.99 (s, 2H, Mes), 2.44−2.37 (m, 2H, *c*-hex), 2.38 (s, 3H, Me), 2.37 (s, 3H, Me), 2.11 (s, 12H, Me), 1.75−1.67 (m, 8H, *c*-hex), 1.49−1.41 (m, 6H, *c*-hex), and 1.38−1.24 ppm (m, 6H, *c*-hex); ^{13}C NMR ($CDCl_3$) δ = 166.72, 145.44, 143.14, 140.21, 138.78, 138.68, 137.09, 136.99, 136.94, 136.29, 132.24, 130.44, 130.01, 128.36, 128.26, 128.11, 127.88, 127.14, 126.65, 125.60, 124.27, 123.43, 123.16, 121.69, 120.89, 115.23, 109.12, 103.28, 32.96, 29.91, 26.27, 24.72, 21.25, and 21.22 ppm; HR-MS (APCI): m/z = 760.4030. calcd for $C_{53}H_{53}N_2B_1S_1$: 760.4037 [M]$^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 309 (16500), 340 (16100), and 497 nm (13300 mol^{-1}dm^{3}cm^{-1}).



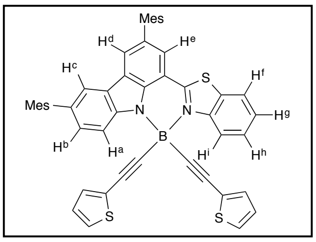
Synthesis of 3l. **3l** (Orange solid, 51.4 mg, 70.1 μmol, 69%) was synthesized from **1e** (59.2 mg, 101 μmol) with cyclopentylacetylene via a method similar to the synthesis of **3a**.

^{1}H NMR ($CDCl_3$) δ = 9.11 (d, J = 8.8 Hz, 1H, H^i), 8.19 (d, J = 8.0 Hz, 1H, H^a), 7.92 (d, J = 0.8 Hz, 1H, H^d), 7.89 (d, J = 8.4 Hz, 1H, H^f), 7.79 (d, J = 0.8 Hz, 1H, H^c), 7.69 (t, J = 7.4 Hz, 1H, H^h), 7.54 (t, J = 7.4 Hz, 1H, H^g), 7.47 (d, J = 0.8 Hz, 1H, H^e), 7.31 (dd, J = 1.4, 8.0 Hz, 1H, H^b), 7.02 (s, 2H, Mes), 6.99 (s, 2H, Mes), 2.60 (quin, J = 7.1 Hz, 2H, *c*-pent), 2.38 (s, 3H, Me), 2.36 (s, 3H, Me), 2.10 (s, 6H, Me), 2.09 (s, 6H, Me), 1.79−1.75 (m, 4H, *c*-pent), and 1.67−1.44 ppm (m, 12H, *c*-pent); ^{13}C NMR ($CDCl_3$) δ = 166.68, 145.47, 143.16, 140.21, 138.77, 138.66, 137.10, 137.00, 136.95, 136.30, 132.24, 130.44, 130.01, 128.36, 128.25, 128.12, 127.91, 127.17, 126.64, 125.57, 124.25, 123.27, 123.17, 121.69, 120.90, 115.10, 109.12, 103.48, 34.21, 34.17, 31.44, 24.95, 21.28, 21.25, and 21.22 ppm; HR-MS (APCI): m/z = 732.3740. calcd for $C_{51}H_{49}N_2B_1S_1$: 732.3724 $[M]^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 309 (16200), 338 (15900), and 496 nm (13600 $mol^{-1}dm^3cm^{-1}$).



Synthesis of 3m. **3m** (Orange solid, 35.8 mg, 47.1 μmol, 45%) was synthesized from **1e** (60.6 mg, 104 μmol) with 3-ethynylthiophene via a method similar to the synthesis of **3a**.

^{1}H NMR ($CDCl_3$) δ = 9.20 (d, J = 8.4 Hz, 1H, H^i), 8.30 (d, J = 8.4 Hz, 1H, H^a), 7.98 (s, 1H, H^d), 7.94 (d, J = 8.0 Hz, 1H, H^f), 7.84 (s, 1H, H^c), 7.76 (t, J = 7.6 Hz, 1H, H^h), 7.58 (t, J = 7.8 Hz, 1H, H^g), 7.54 (s, 1H, H^e), 7.36 (d, J = 8.4 Hz, 1H, H^b), 7.30 (d, J = 2.8 Hz, 2H, thiophene), 7.15 (dd, J = 3.2, 5.2 Hz, 2H, thiophene), 7.04 (d, J = 4.4 Hz, 2H, thiophene), 7.03 (s, 2H, Mes), 7.00 (s, 2H, Mes), 2.39 (s, 3H, Me), 2.37 (s, 3H, Me), and 2.08 ppm (s, 12H, Me); ^{13}C NMR ($CDCl_3$) δ = 167.14, 145.32, 143.08, 140.00, 138.65, 138.56, 137.23, 136.94, 136.42, 132.78, 131.00, 130.38, 129.97, 128.64, 128.41, 128.15, 127.93, 127.82, 126.92, 125.69, 124.74, 124.38, 124.00, 123.41, 122.67, 122.02, 121.16, 114.84, 109.04, 93.24, 21.33, and 21.24 ppm; HR-MS (APCI): m/z = 760.2244. calcd for $C_{49}H_{37}N_2B_1S_3$: 760.2226 $[M]^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 308 (19000), 329 (16500), and 496 nm (14000 $mol^{-1}dm^3cm^{-1}$).



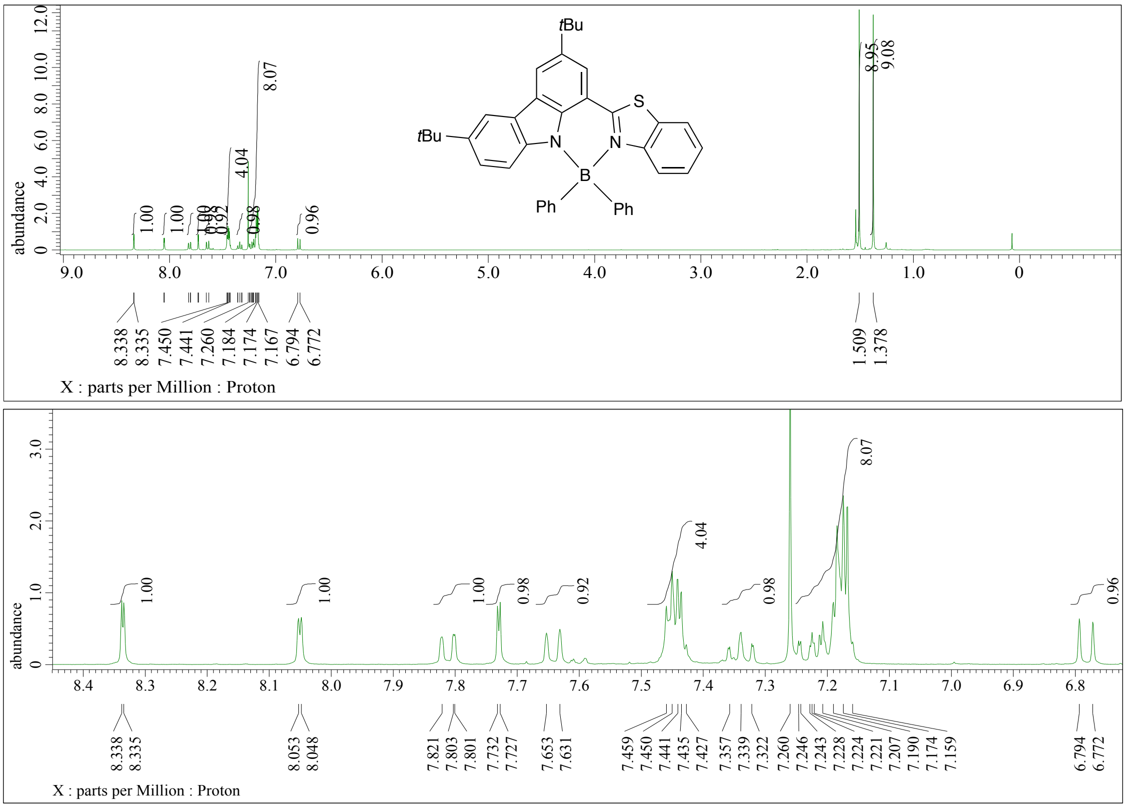
Synthesis of 3n. **3n** (red solid, 19.4 mg, 25.5 μmol, 25%) was synthesized from **1e** (59.0 mg, 101 μmol) with 2-ethynylthiophene via a method similar to the synthesis of **3a**.

^{1}H NMR ($CDCl_3$) δ = 9.12 (d, J = 8.8 Hz, 1H, H^i), 8.25 (d, J = 8.0 Hz, 1H, H^a), 7.98 (d, J = 0.8 Hz, 1H, H^d), 7.94 (d, J = 7.6 Hz, 1H, H^f), 7.83 (s, 1H, H^c), 7.77 (t, J = 7.4 Hz, 1H, H^h), 7.59 (t, J = 7.6 Hz, 1H, H^g), 7.54 (d, J = 0.8 Hz, 1H, H^e), 7.36 (dd, J = 1.6, 8.4 Hz, 1H, H^b), 7.12 (d, J = 5.2 Hz, 2H, thiophene), 7.09 (d, J = 3.6 Hz, 2H, thiophene), 7.03 (s, 2H, Mes), 6.99 (s, 2H, Mes), 6.87 (dd, J = 3.8, 5.0 Hz, 2H, thiophene), 2.38 (s, 3H, Me), 2.36 (s, 3H, Me), 2.11 (s, 6H, Me), and 2.10 ppm (s, 6H, Me); ^{13}C NMR couldn't detect peaks for **3n** because of the unstability; HR-MS (APCI): m/z = 760.2236. calcd for $C_{49}H_{37}N_2B_1S_3$: 760.2226 $[M]^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 331 (15100), 370 (4100), and 508 nm (9500 $mol^{-1}dm^3cm^{-1}$).

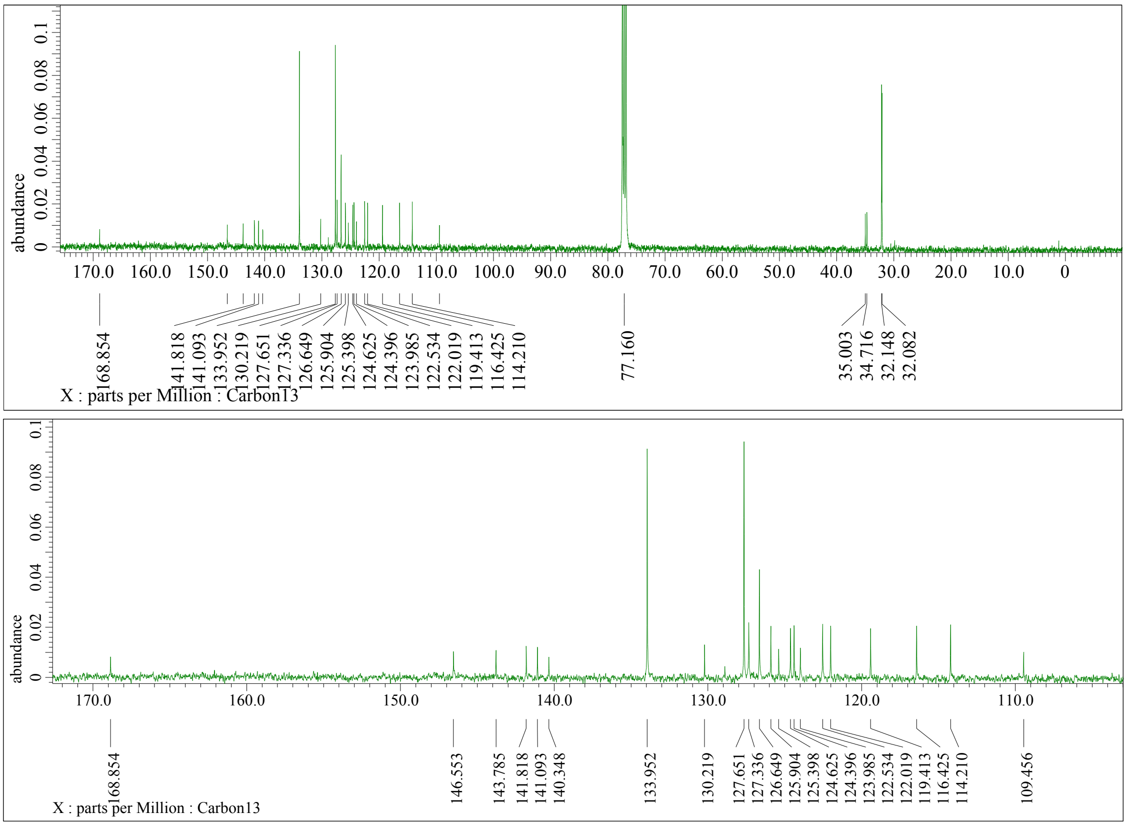
[B] Reference

[S1] C. Maeda, T. Todaka, T. Ueda and T. Ema, *Chem.–Eur. J.*, 2016, **22**, 7508.

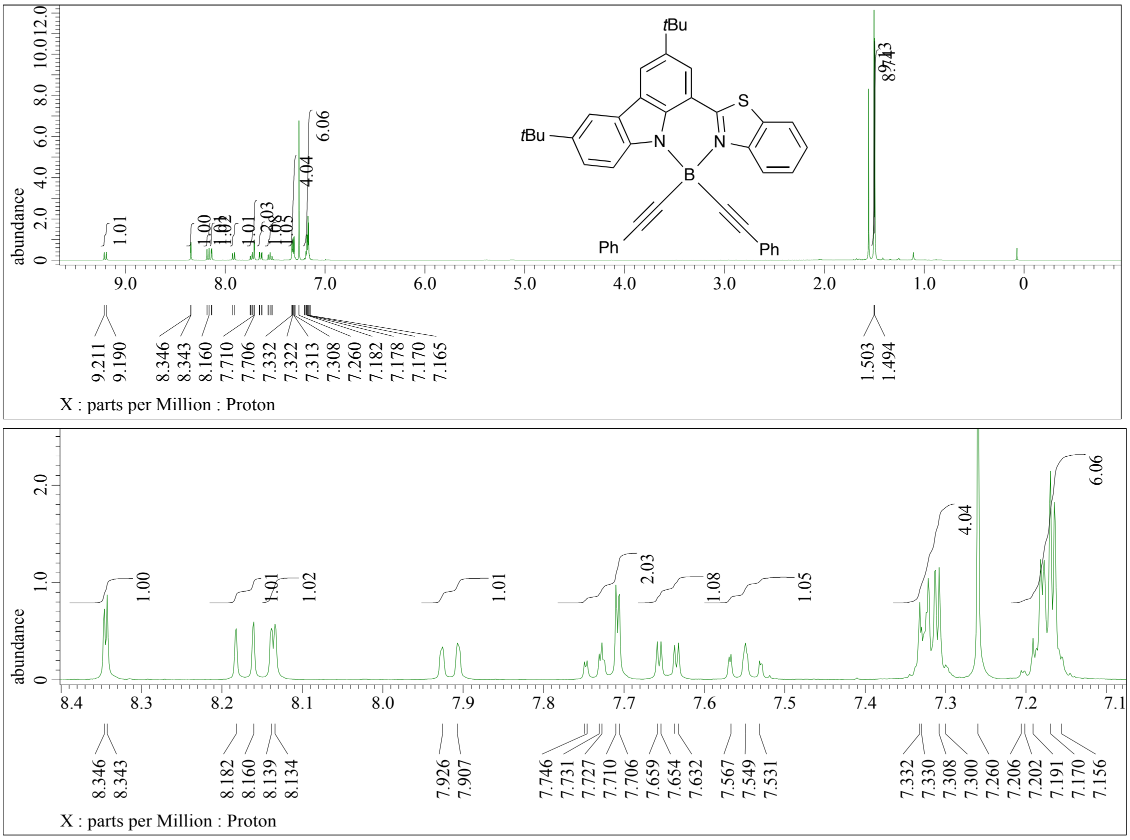
[C] NMR spectra



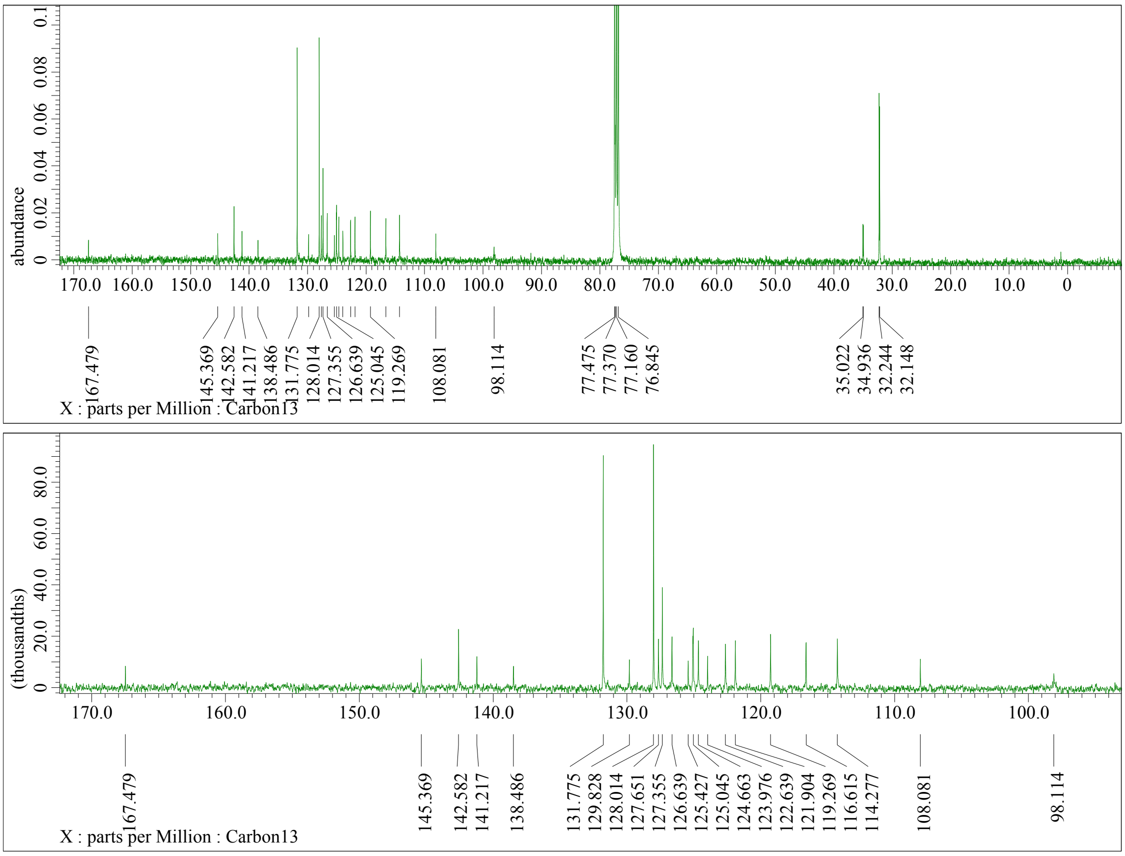
^{1}H NMR spectrum of **2** in $CDCl_3$



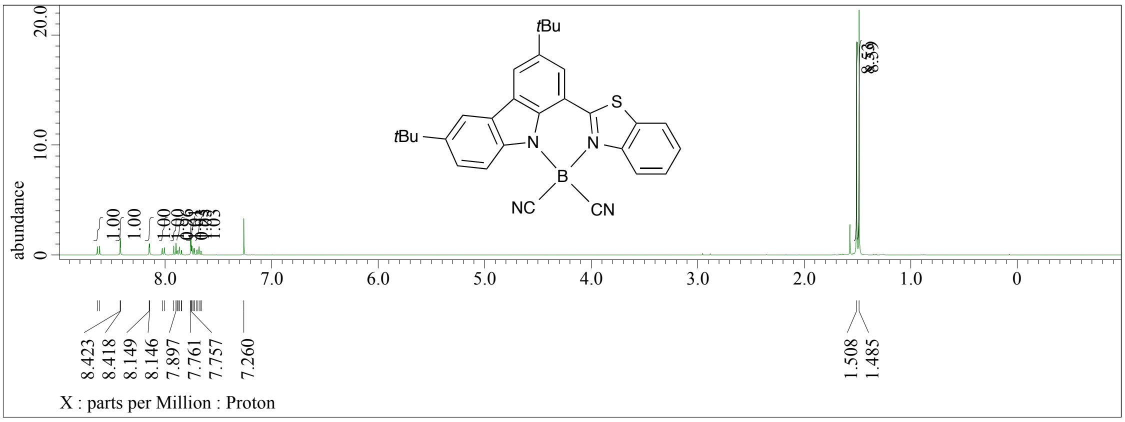
^{13}C NMR spectrum of **2** in $CDCl_3$

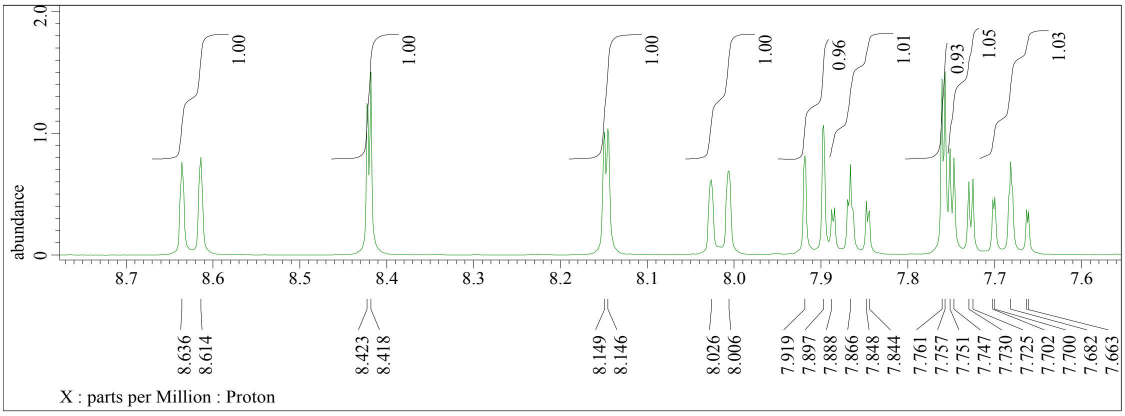


^{1}H NMR spectrum of **3a** in $CDCl_3$

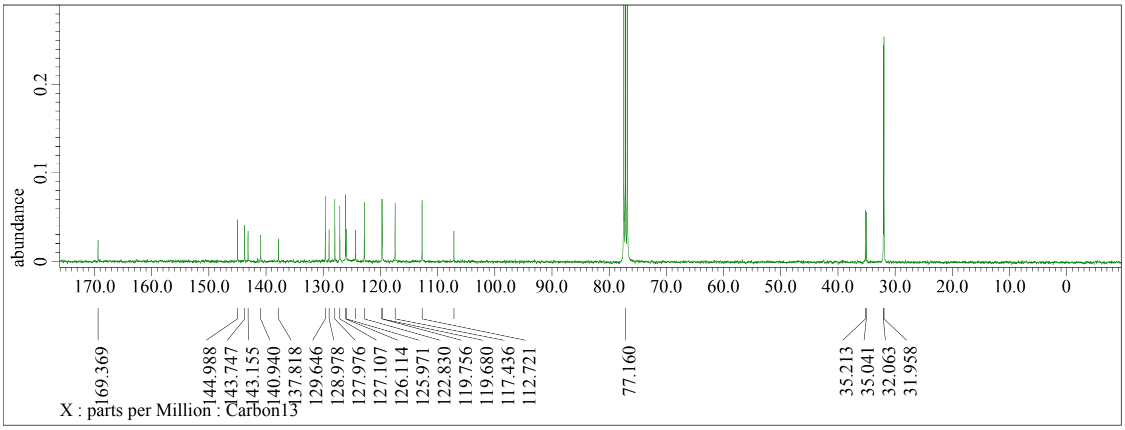


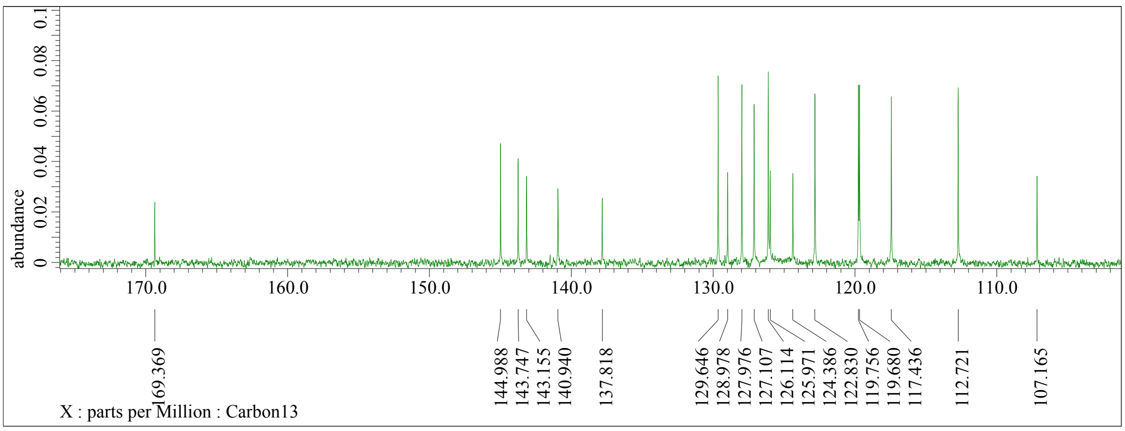
^{13}C NMR spectrum of **3a** in $CDCl_3$



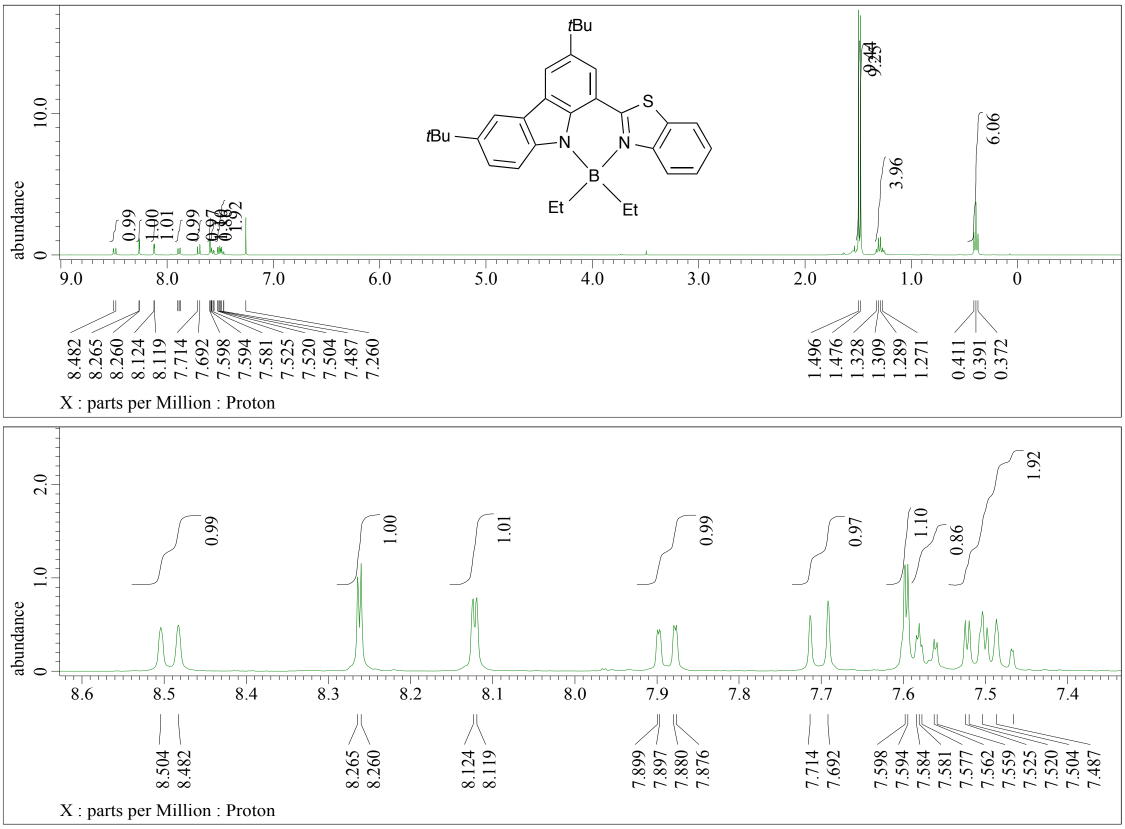


^{1}H NMR spectrum of **4** in $CDCl_3$

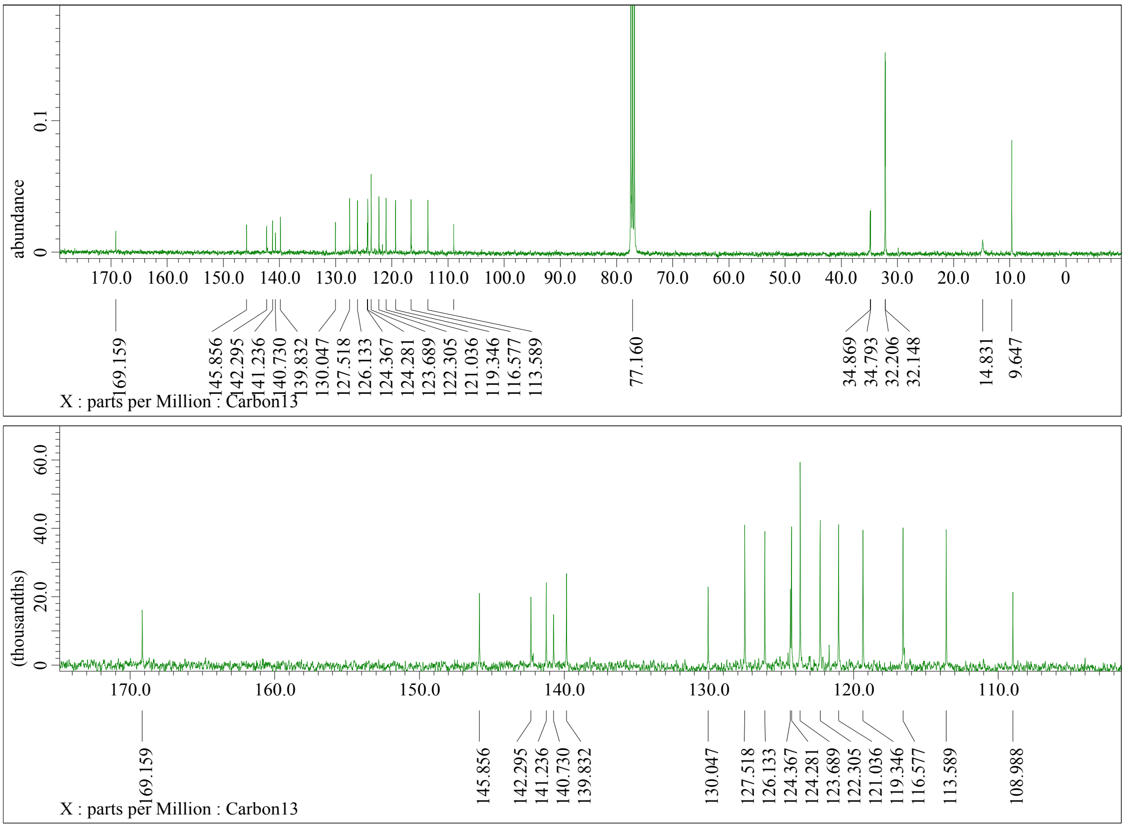




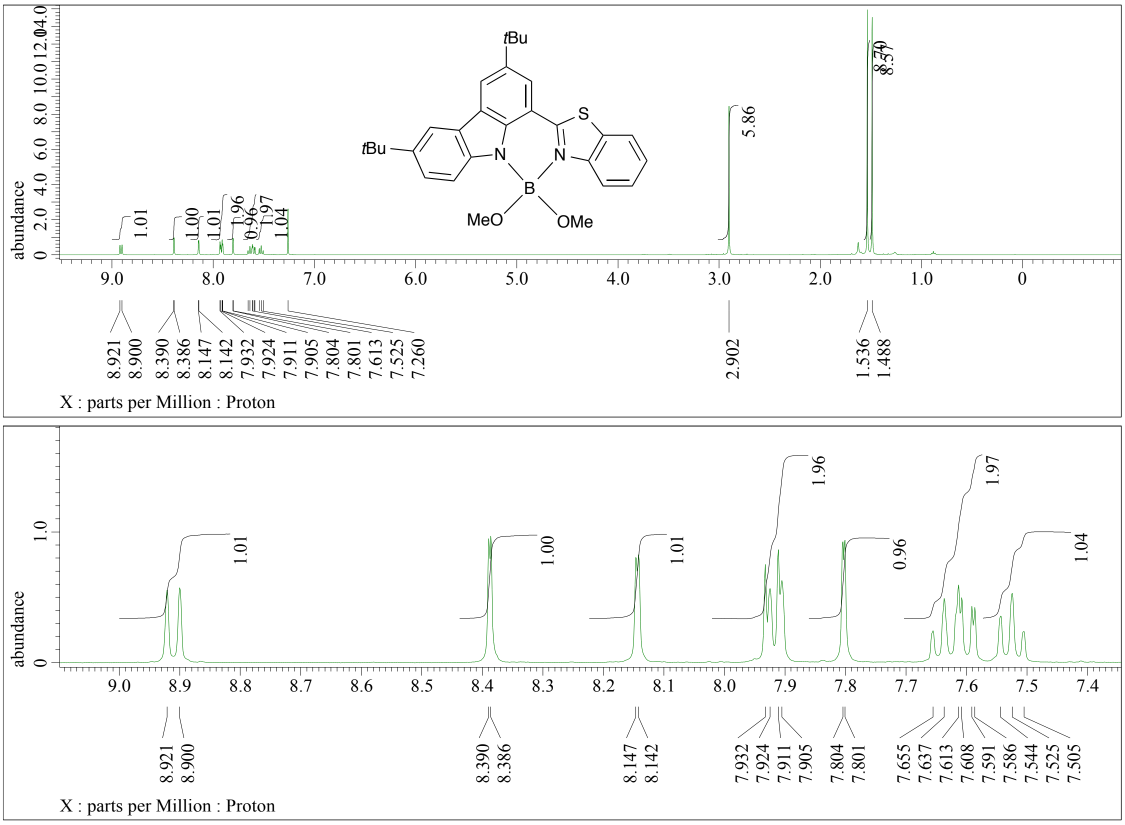
^{13}C NMR spectrum of **4** in $CDCl_3$



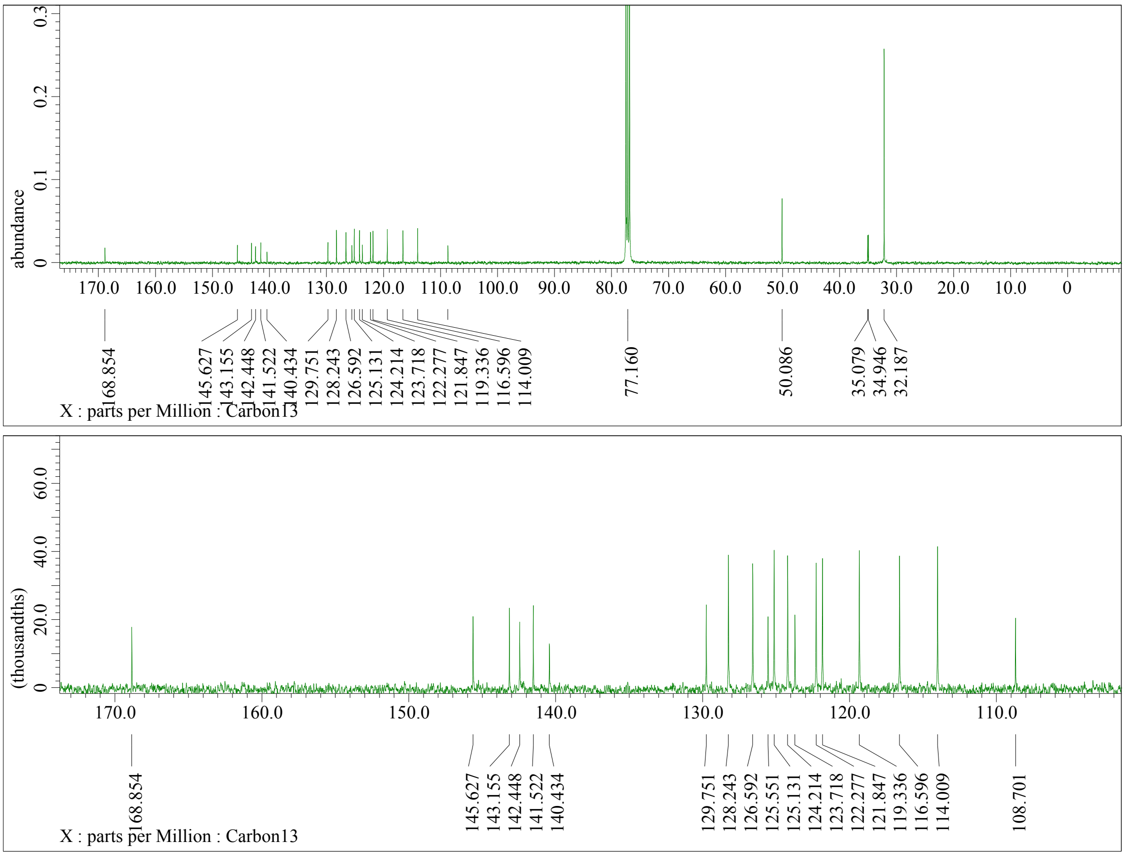
^{1}H NMR spectrum of **5** in $CDCl_3$



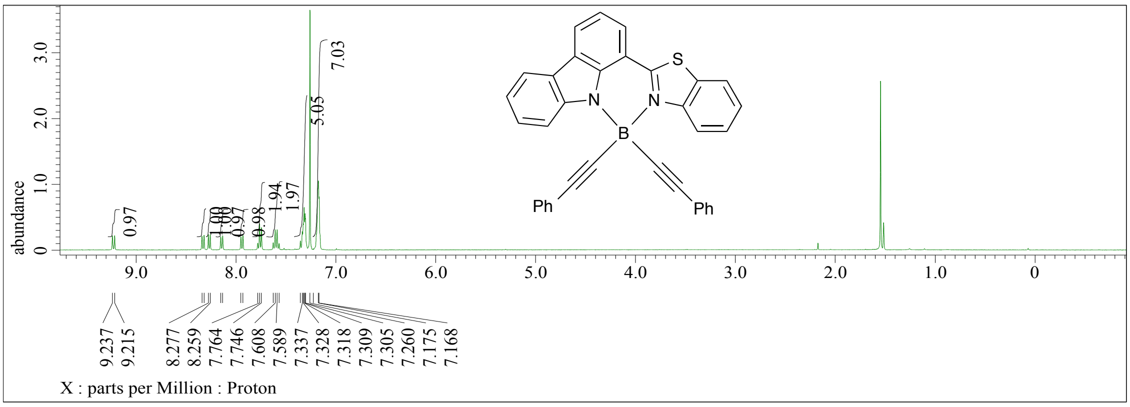
^{13}C NMR spectrum of **5** in $CDCl_3$

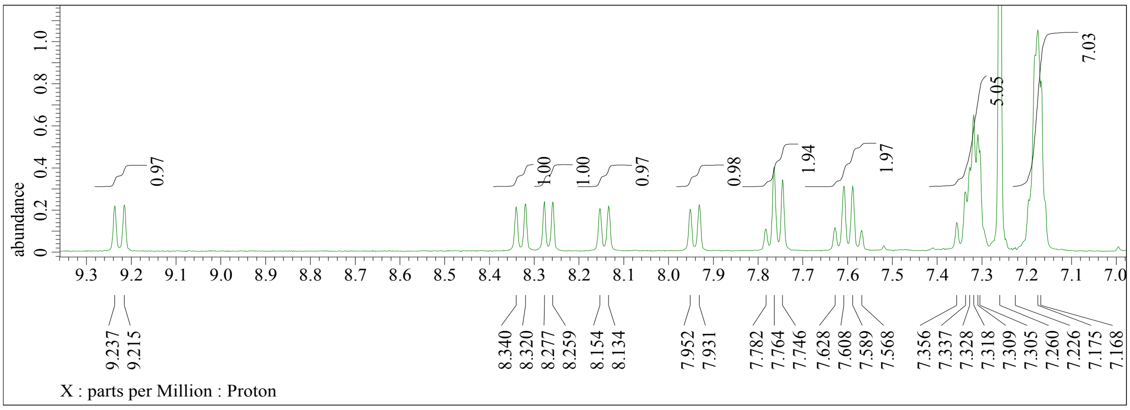


^{1}H NMR spectrum of **6** in $CDCl_3$

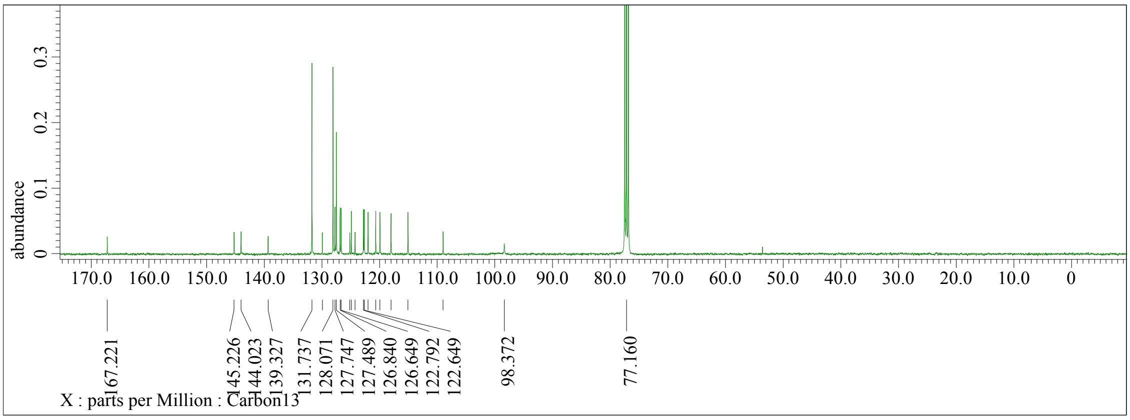


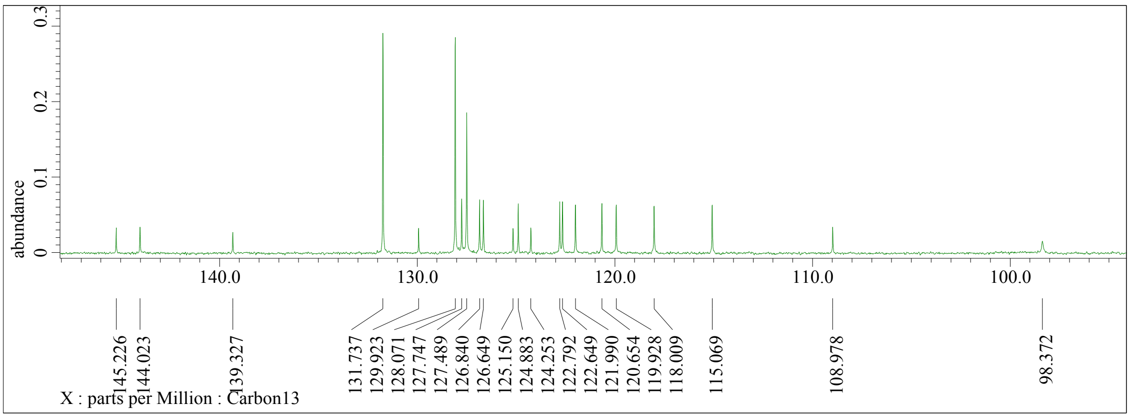
^{13}C NMR spectrum of **6** in $CDCl_3$



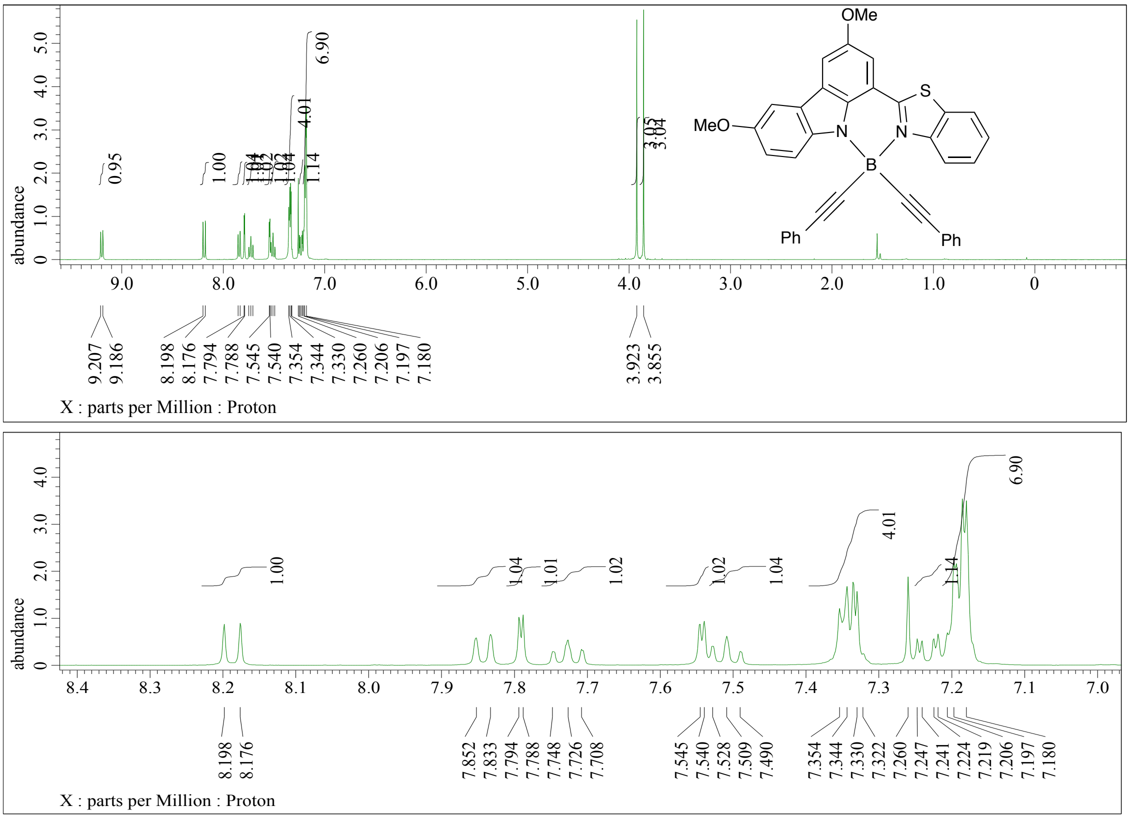


^{1}H NMR spectrum of **3b** in $CDCl_3$

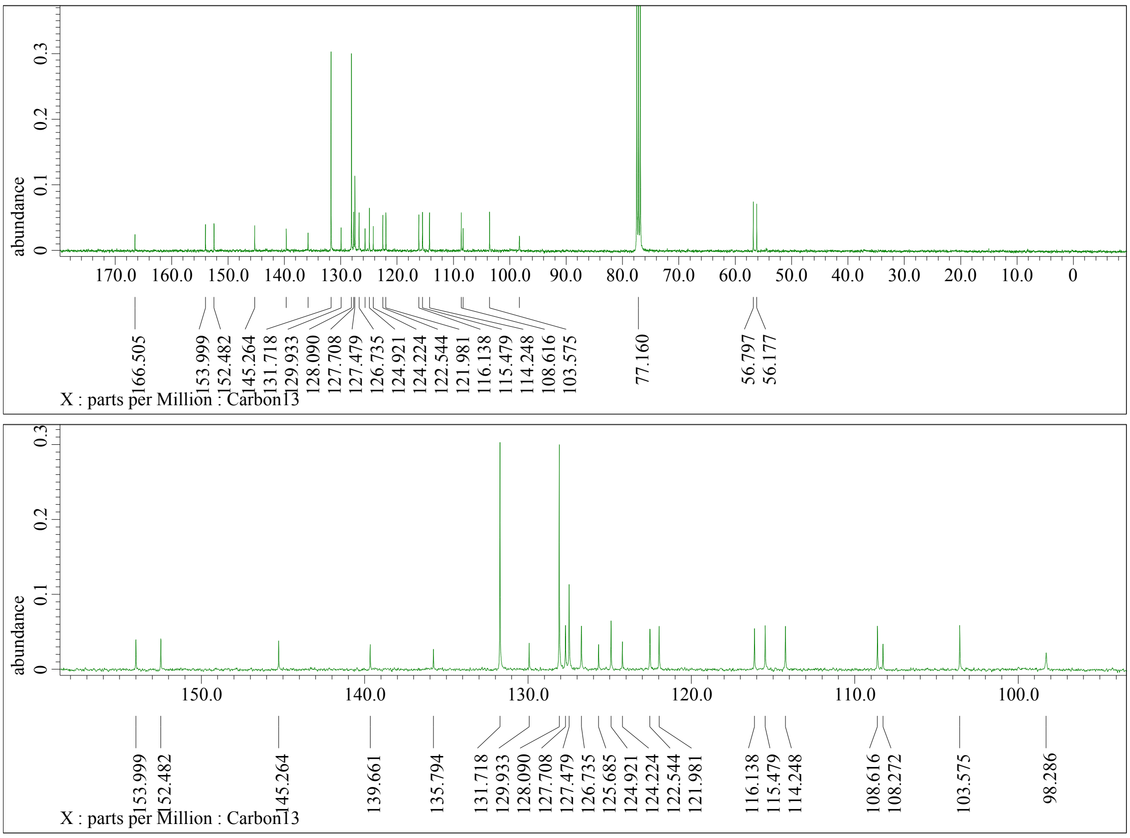




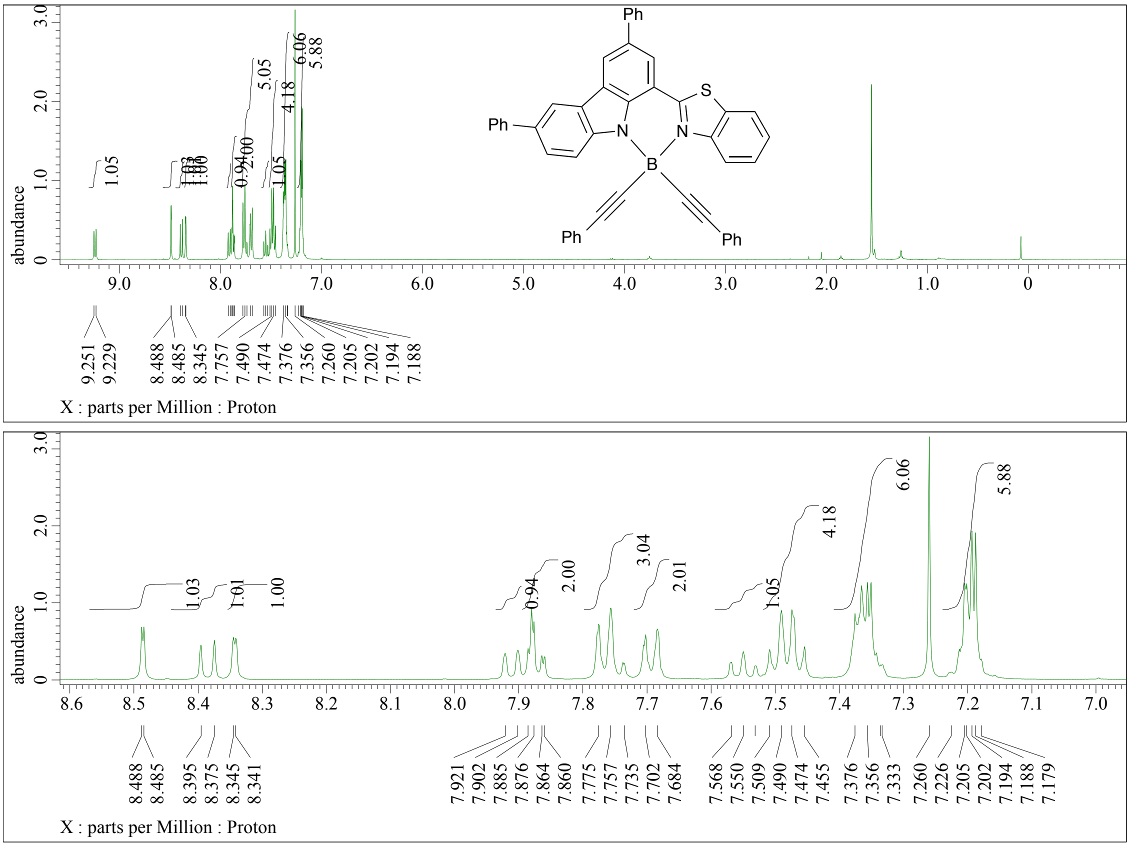
^{13}C NMR spectrum of **3b** in $CDCl_3$



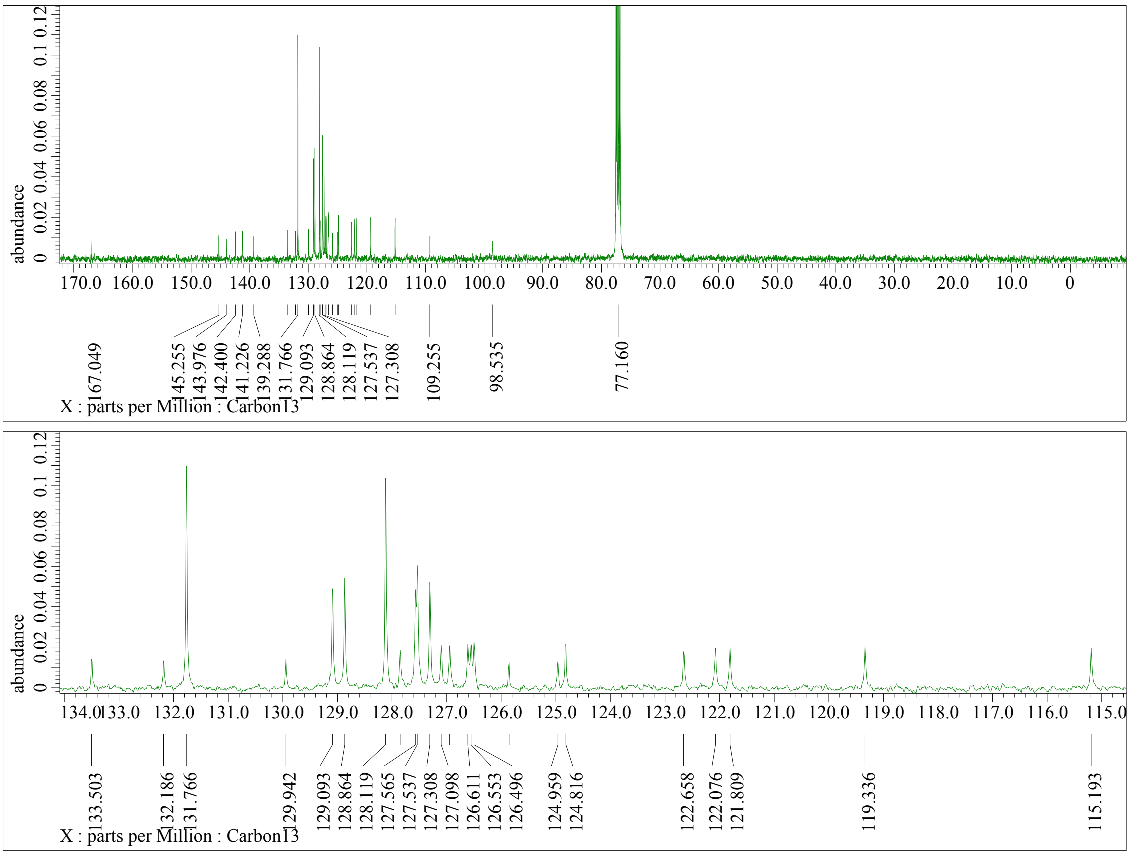
^{1}H NMR spectrum of **3c** in $CDCl_3$



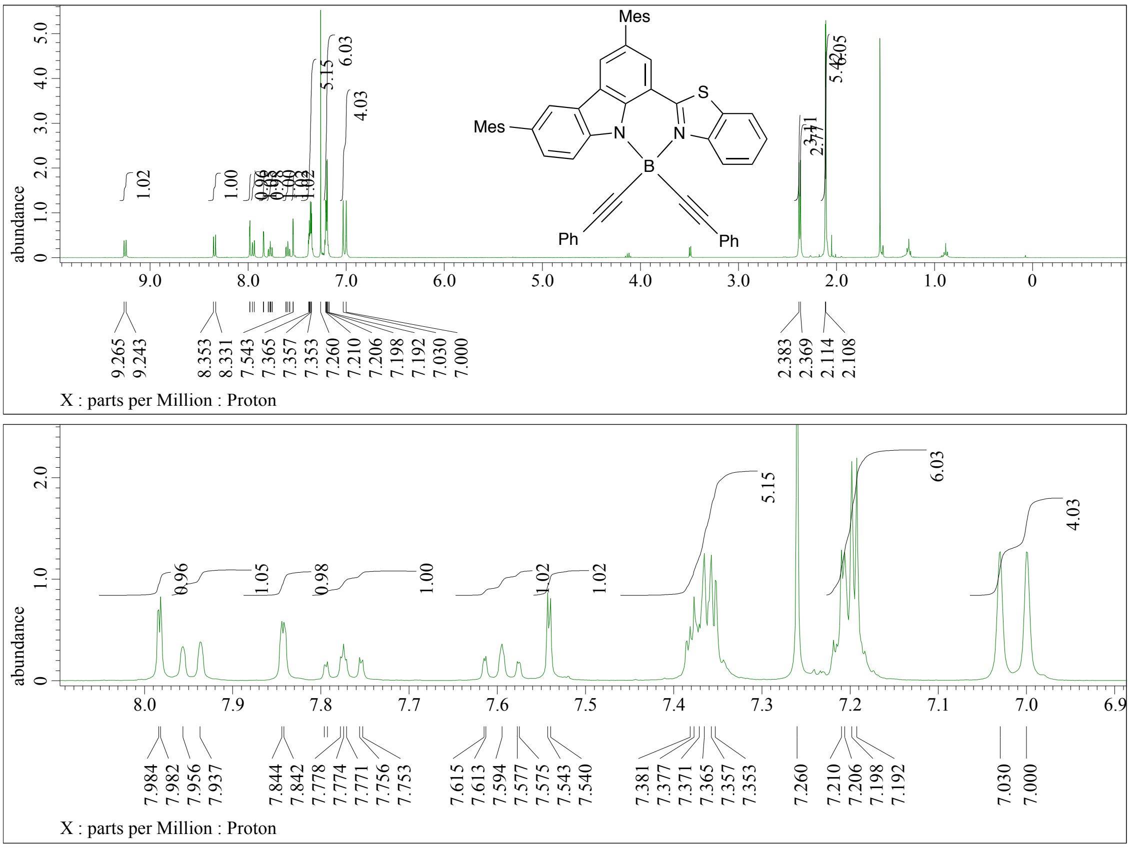
^{13}C NMR spectrum of **3c** in $CDCl_3$



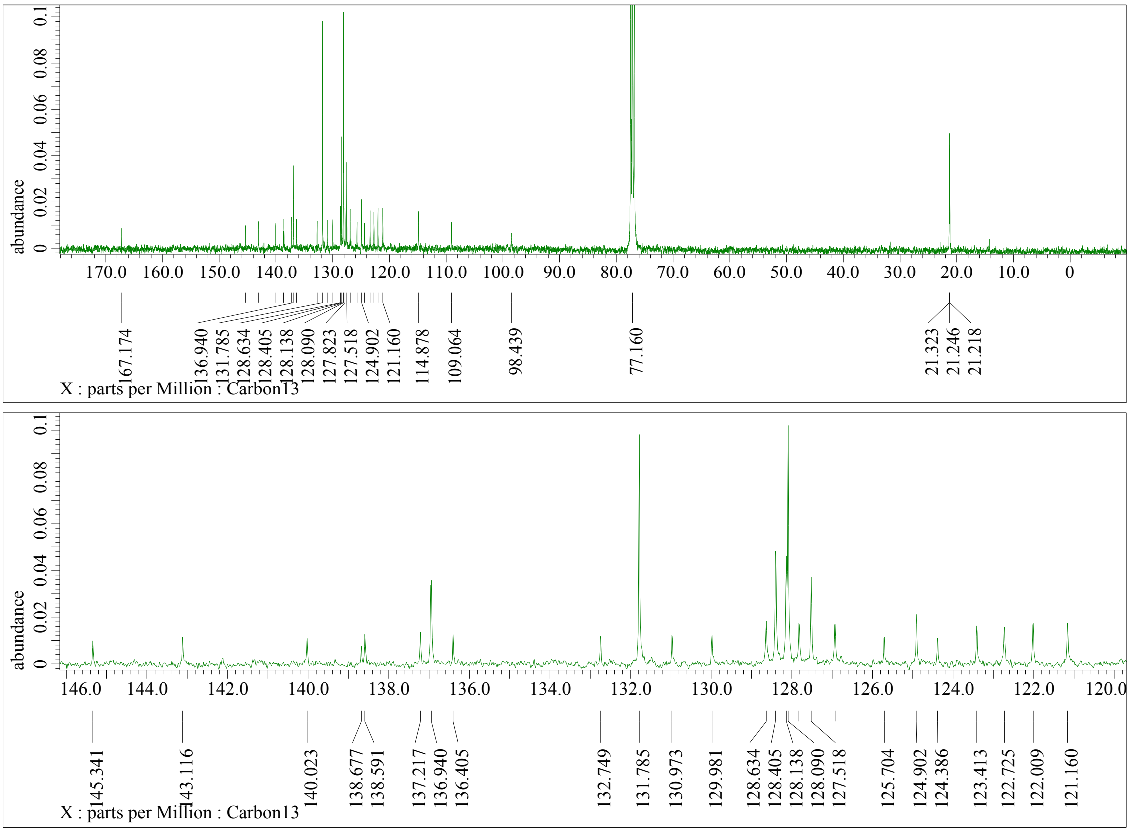
^{1}H NMR spectrum of **3d** in $CDCl_3$



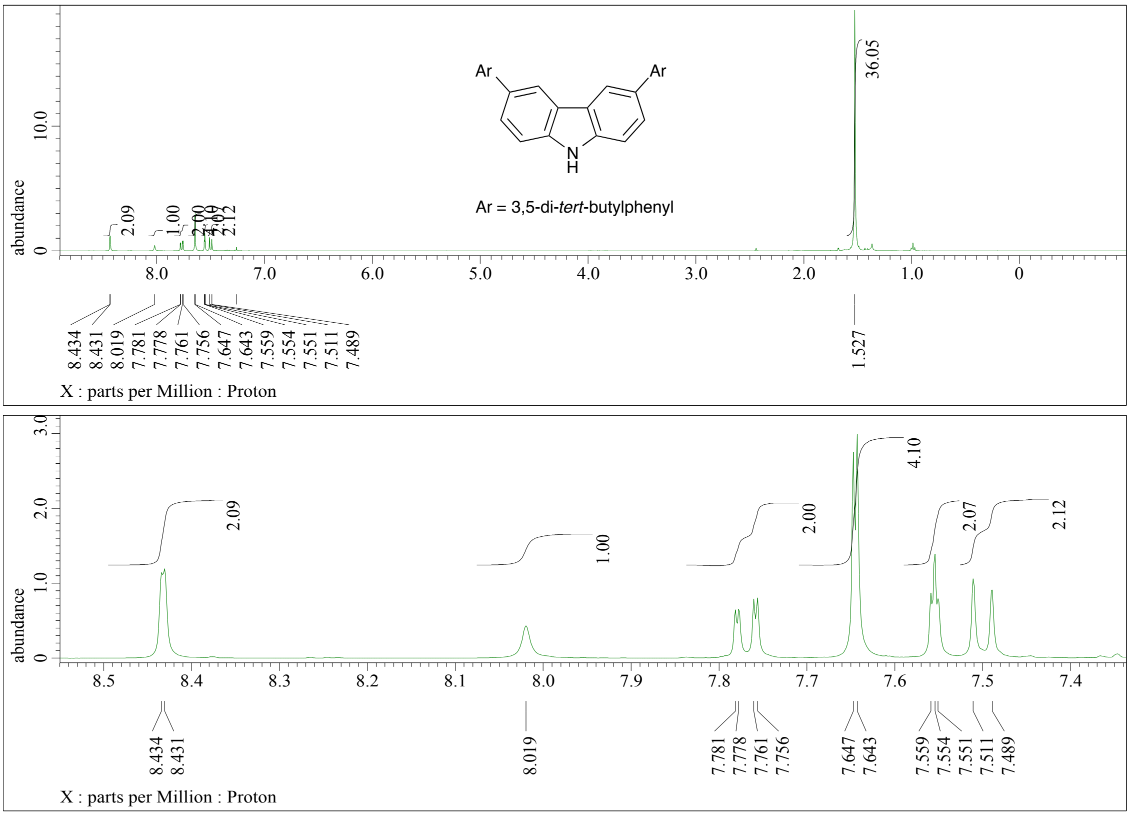
^{13}C NMR spectrum of **3d** in $CDCl_3$



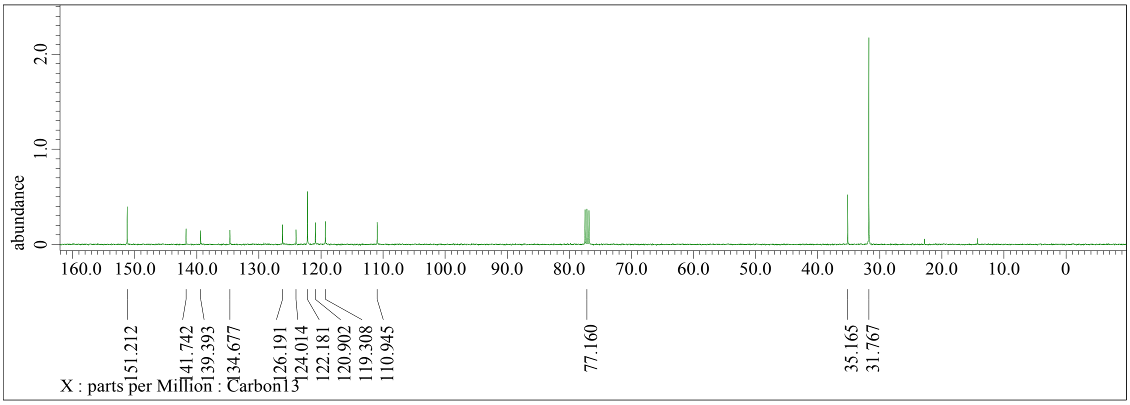
^{1}H NMR spectrum of **3e** in $CDCl_3$



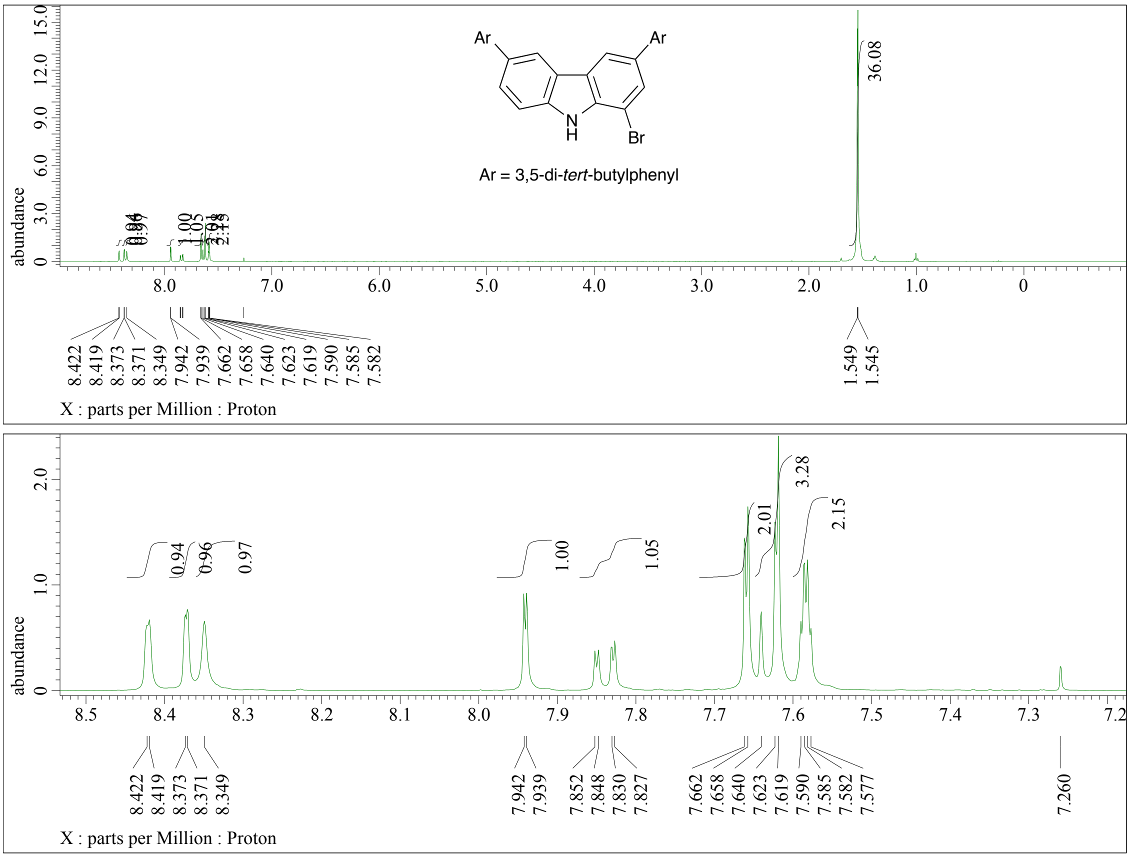
^{13}C NMR spectrum of **3e** in $CDCl_3$



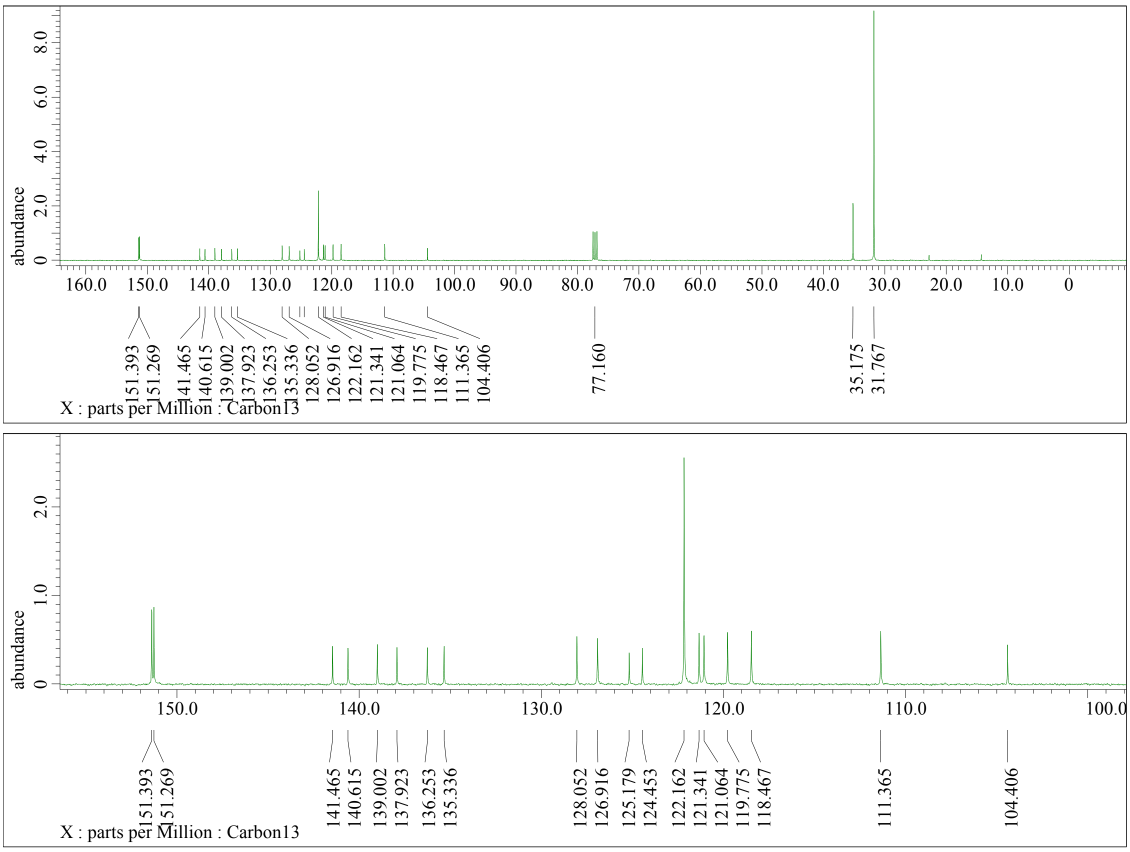
^{1}H NMR spectrum of 3,6-bis(3,5-di-*tert*-butylphenyl)carbazole in $CDCl_3$



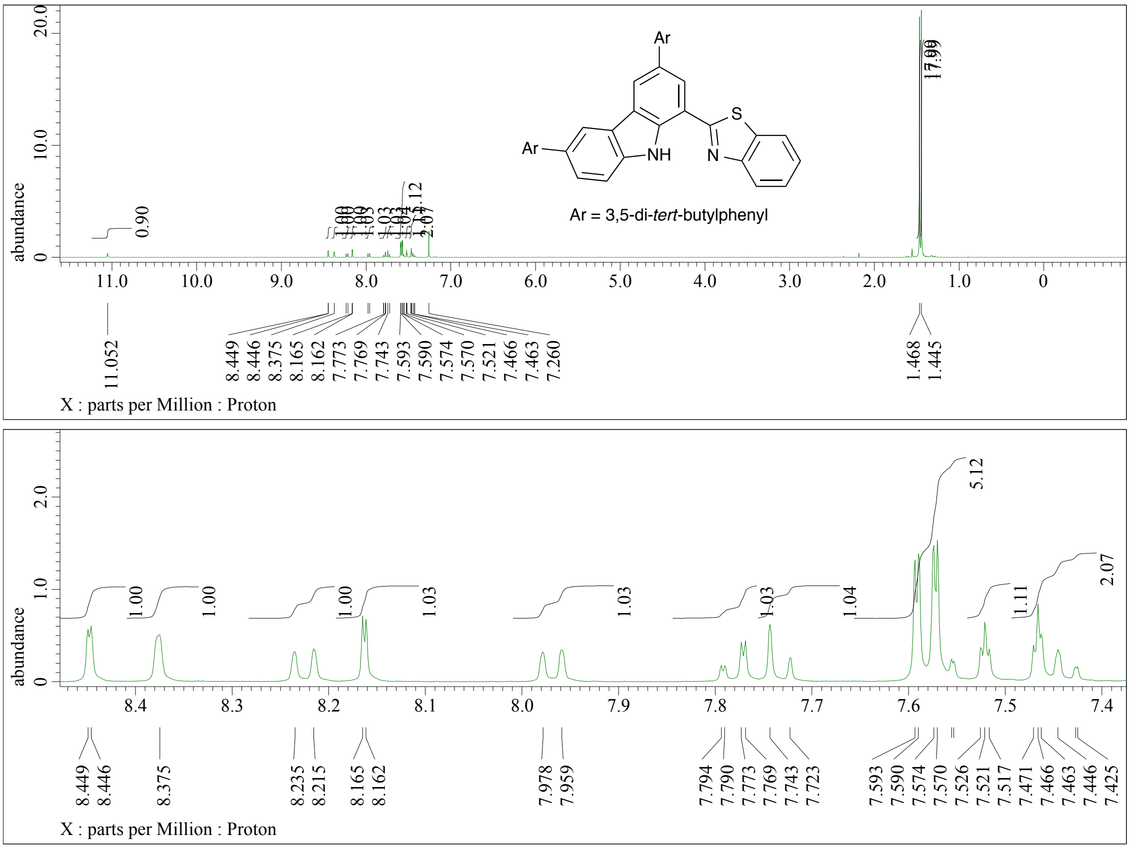
^{13}C NMR spectrum of 3,6-bis(3,5-di-*tert*-butylphenyl)carbazole in $CDCl_3$



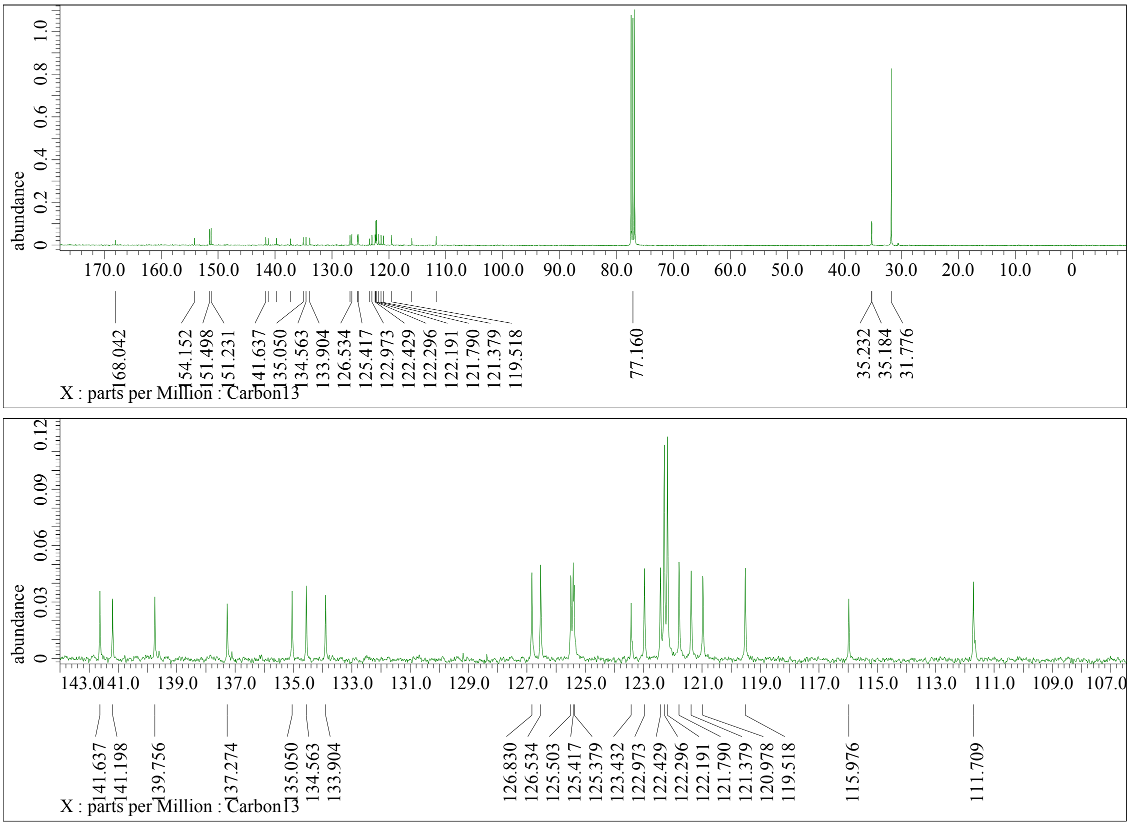
[1]H NMR spectrum of 3,6-bis(3,5-di-*tert*-butylphenyl)-1-bromocarbazole in $CDCl_3$



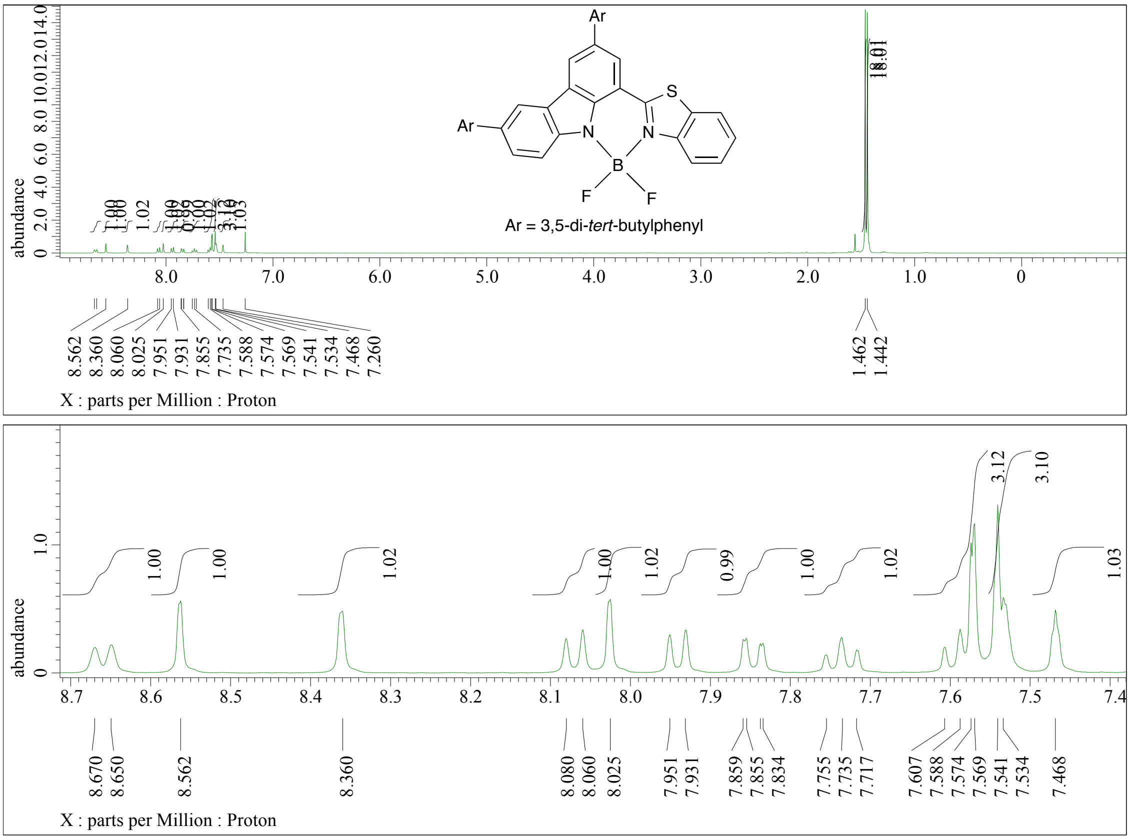
[13]C NMR spectrum of 3,6-bis(3,5-di-*tert*-butylphenyl)-1-bromocarbazole in $CDCl_3$



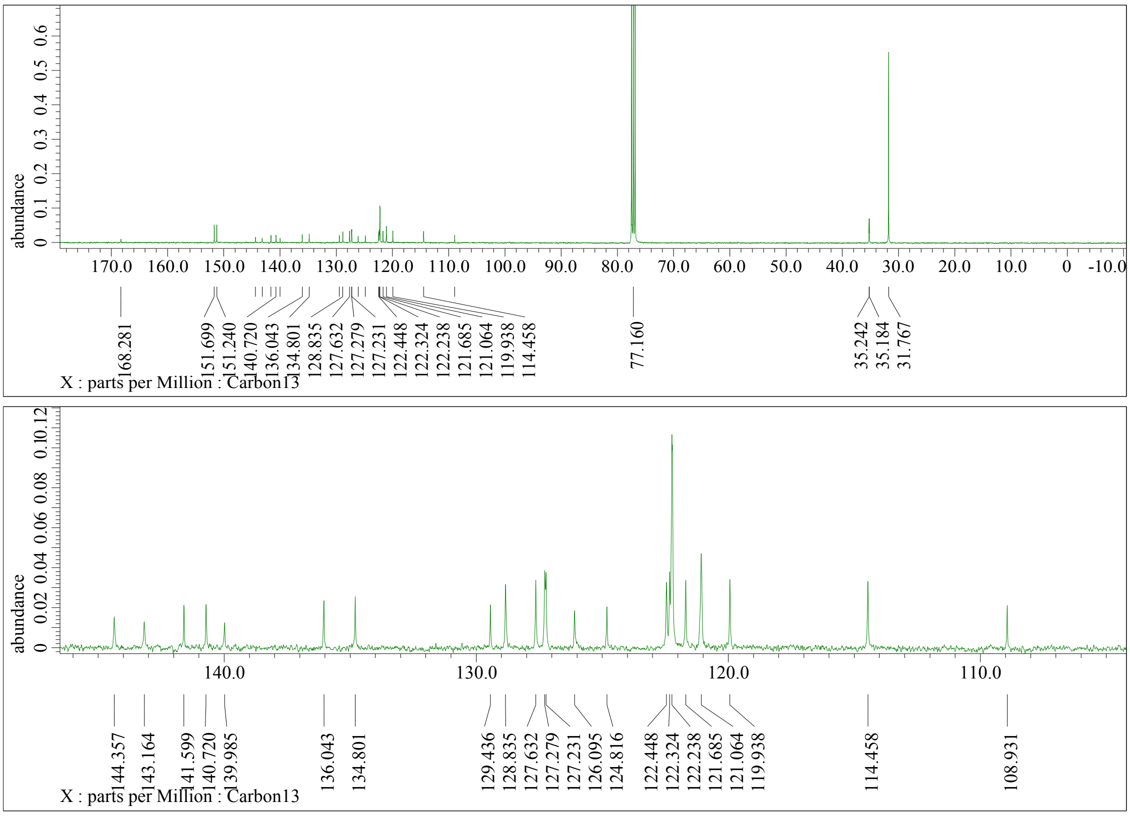
^{1}H NMR spectrum of **7f** in $CDCl_3$



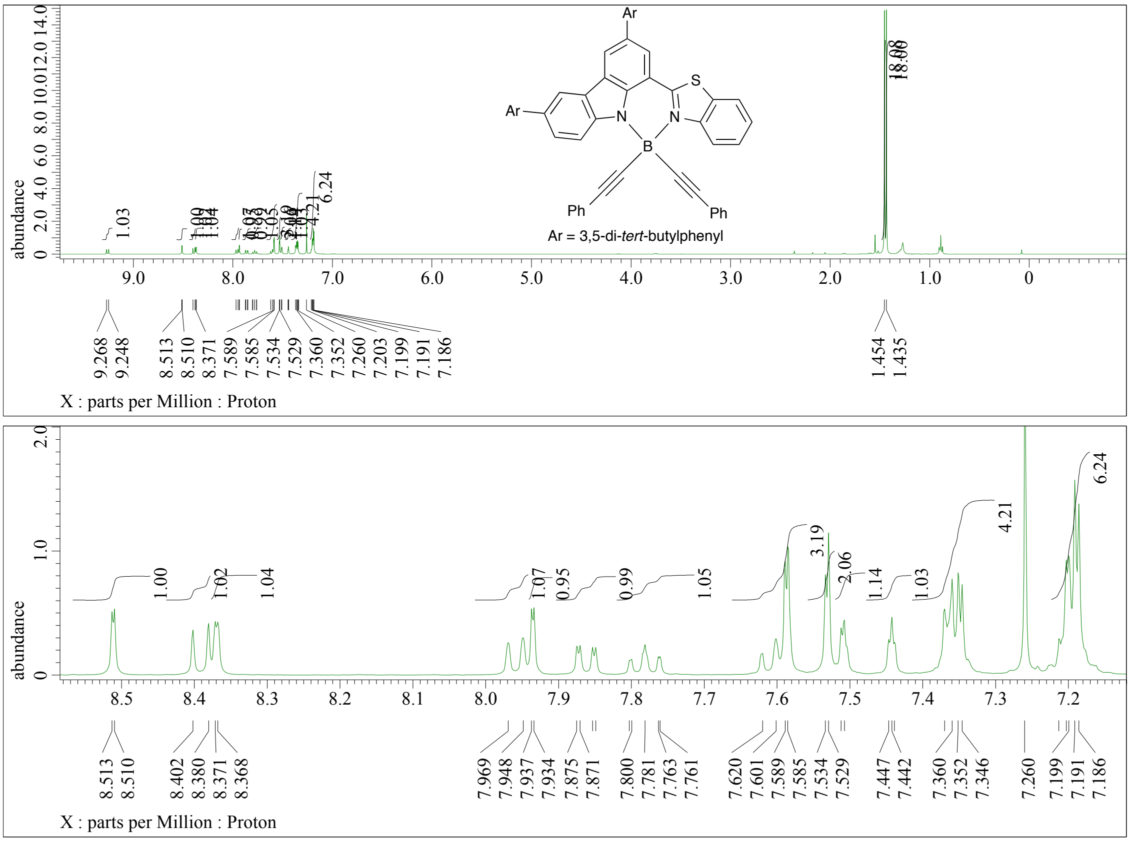
^{13}C NMR spectrum of **7f** in $CDCl_3$



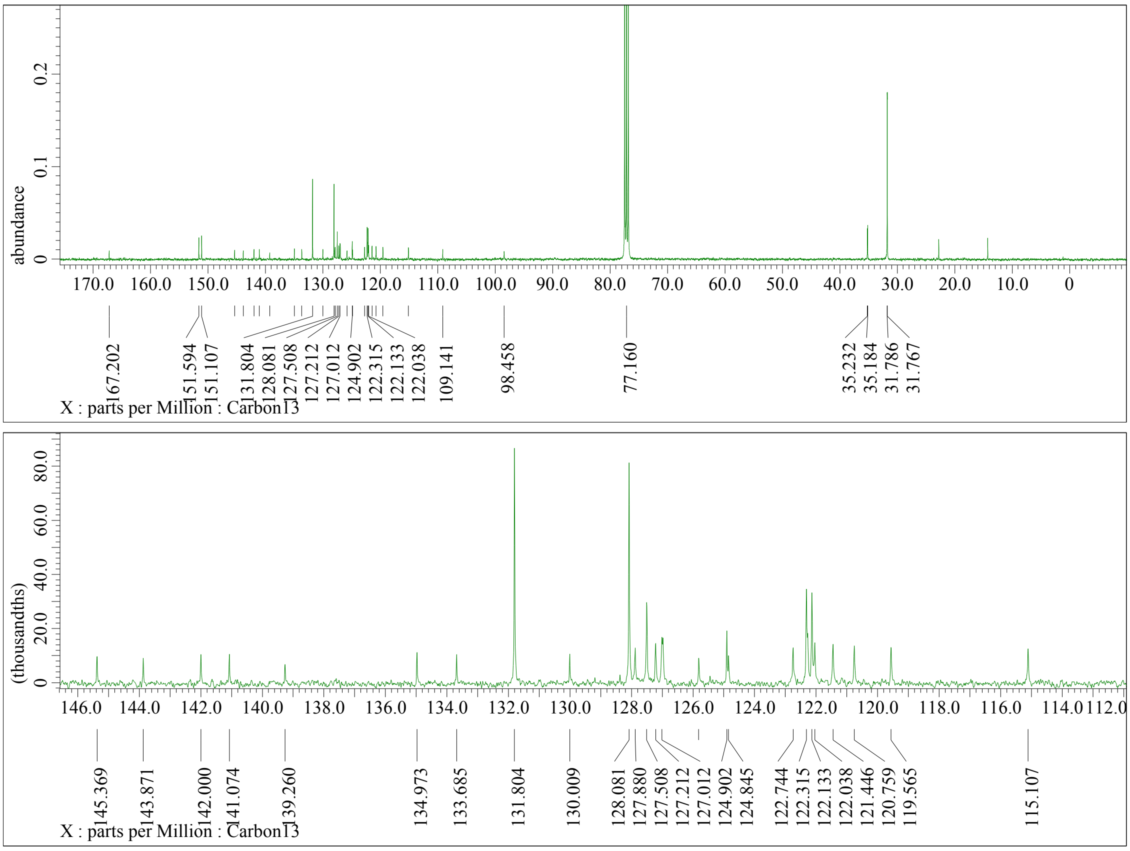
^{1}H NMR spectrum of **1f** in $CDCl_3$



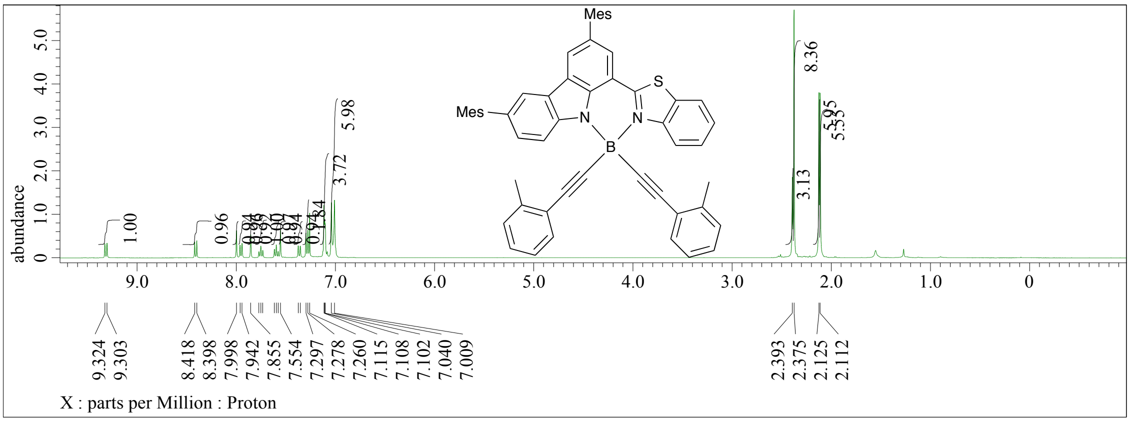
^{13}C NMR spectrum of **1f** in $CDCl_3$

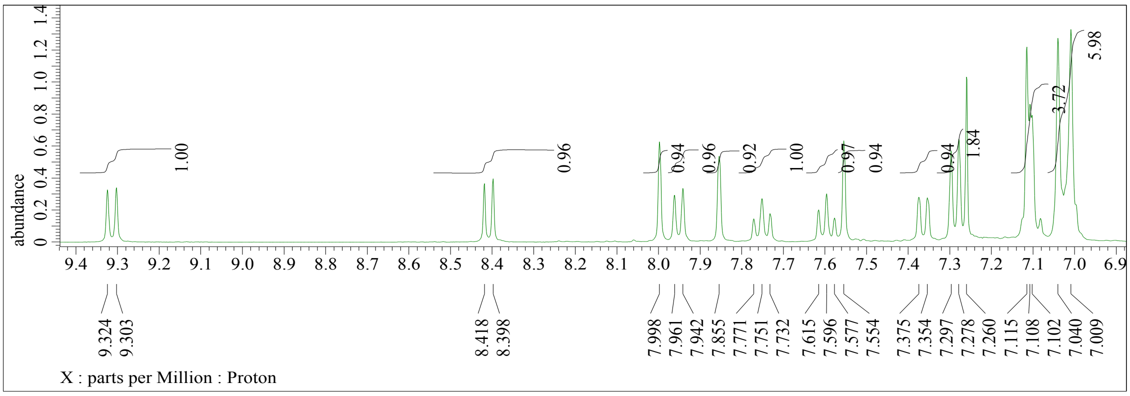


^{1}H NMR spectrum of **3f** in $CDCl_3$

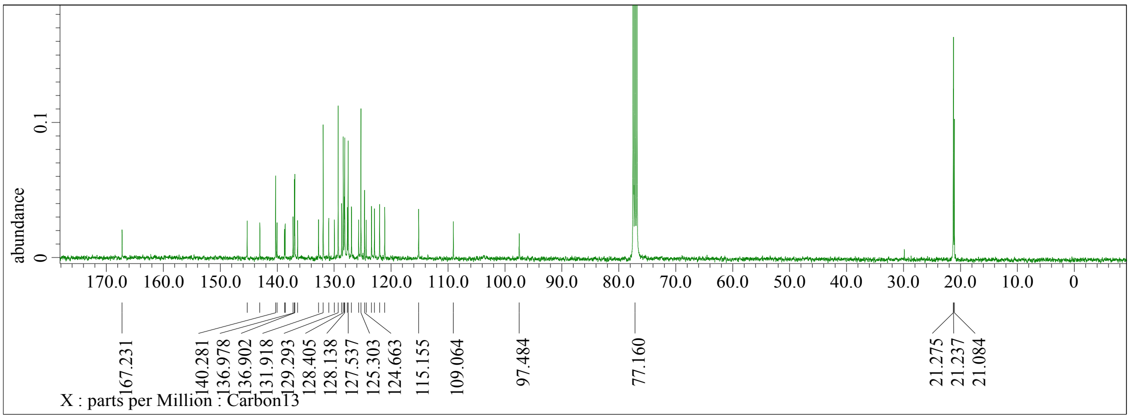


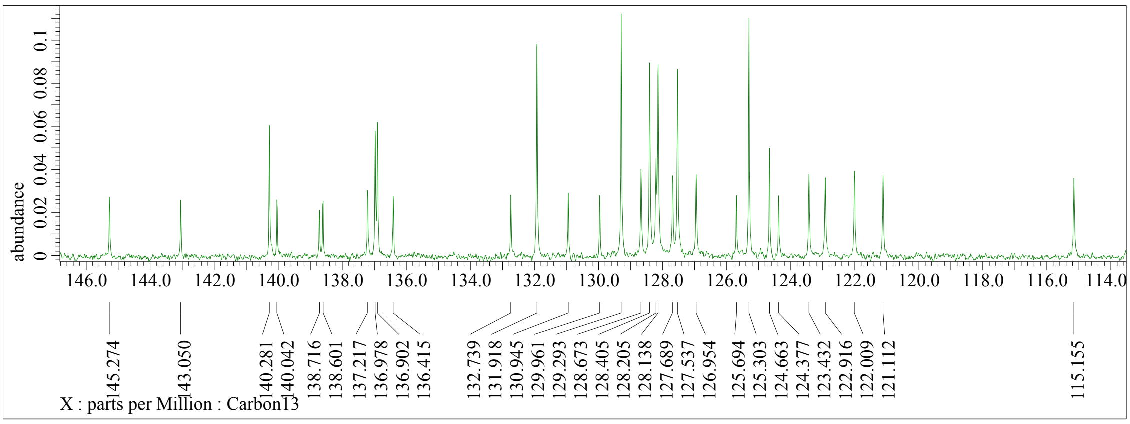
^{13}C NMR spectrum of **3f** in $CDCl_3$



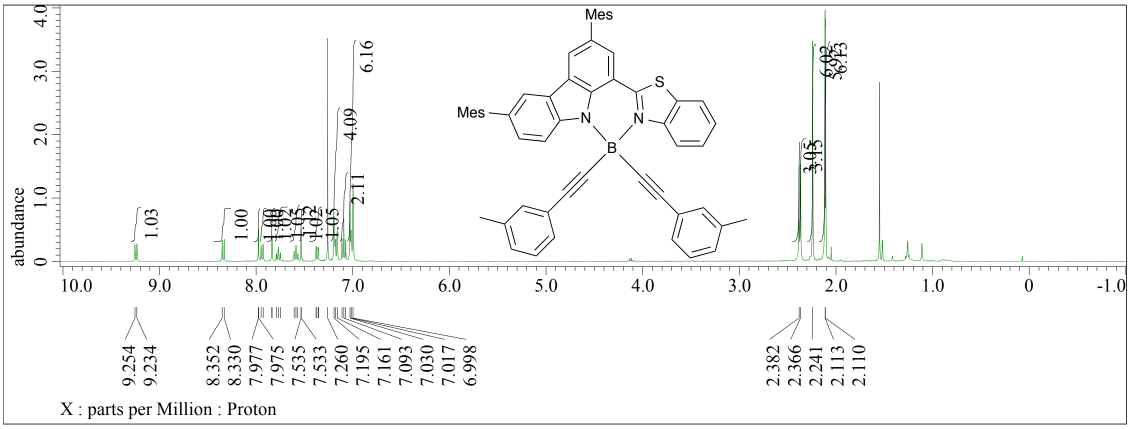


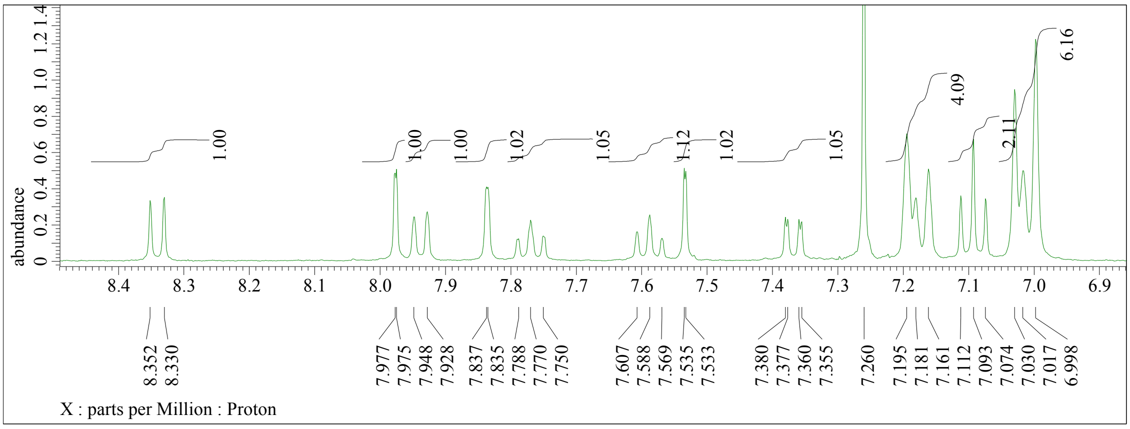
^{1}H NMR spectrum of **3g** in $CDCl_3$



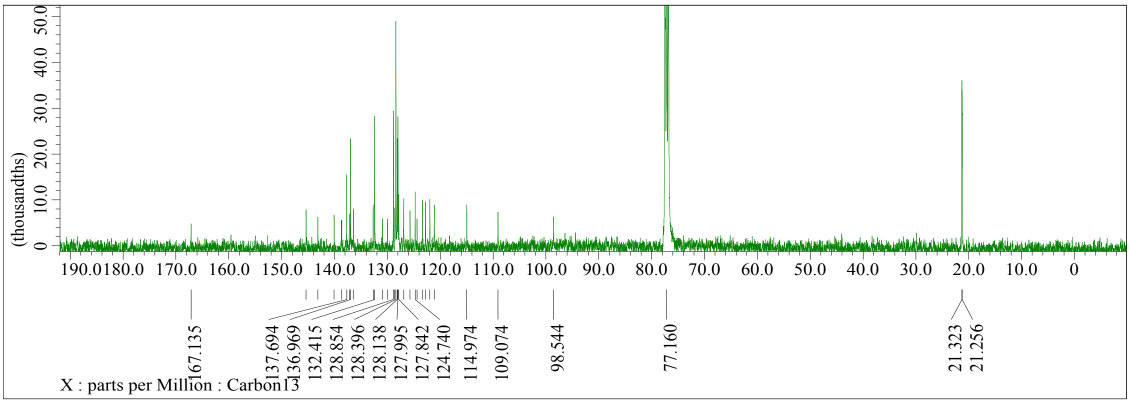


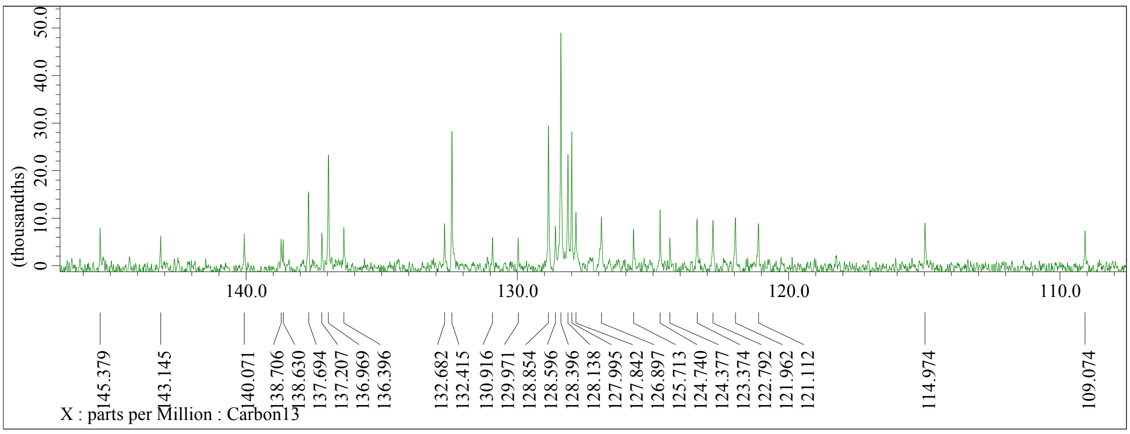
^{13}C NMR spectrum of **3g** in $CDCl_3$



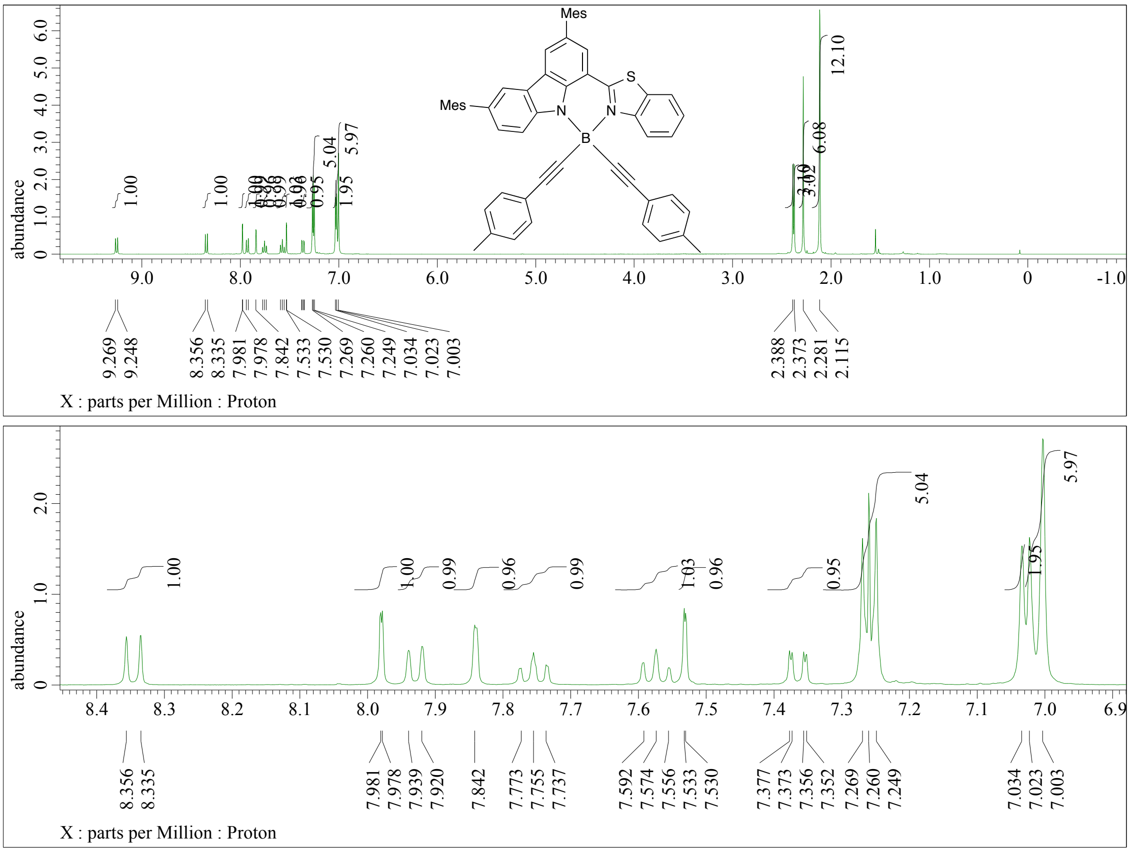


^{1}H NMR spectrum of **3h** in $CDCl_3$

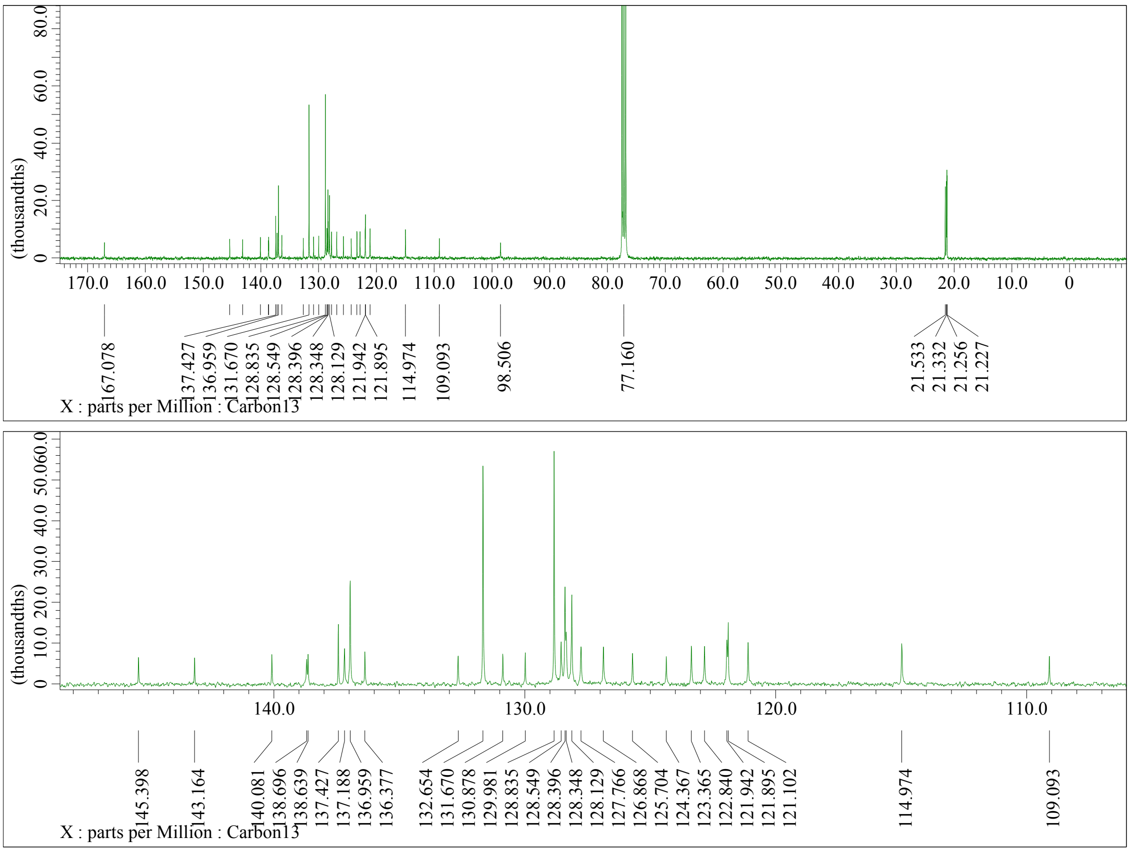




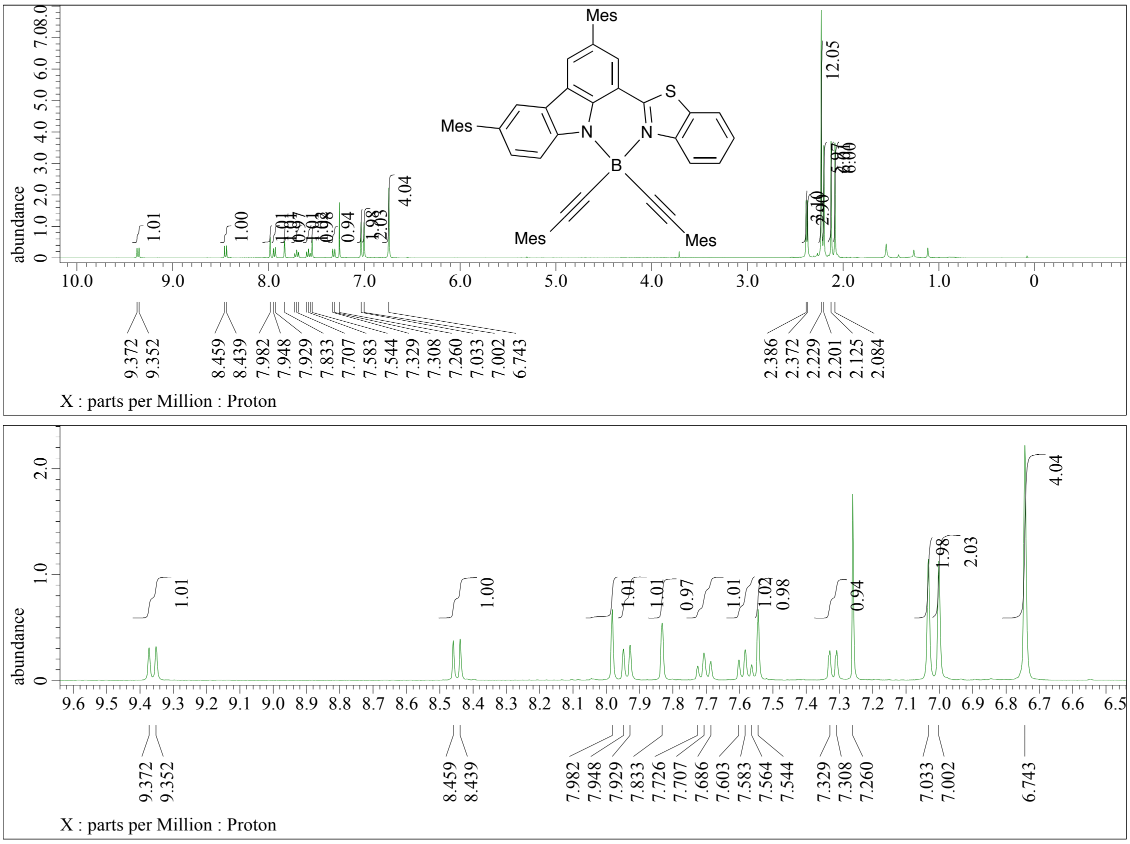
^{13}C NMR spectrum of **3h** in $CDCl_3$



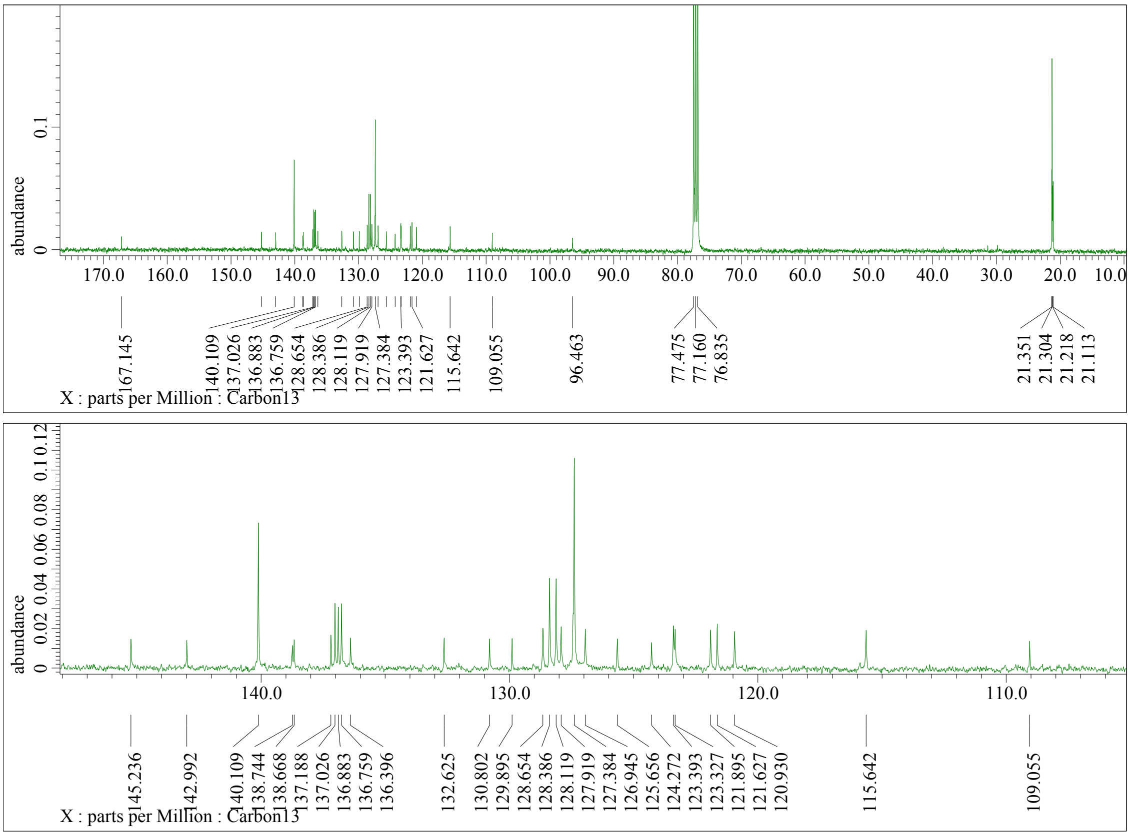
[1]H NMR spectrum of **3i** in $CDCl_3$



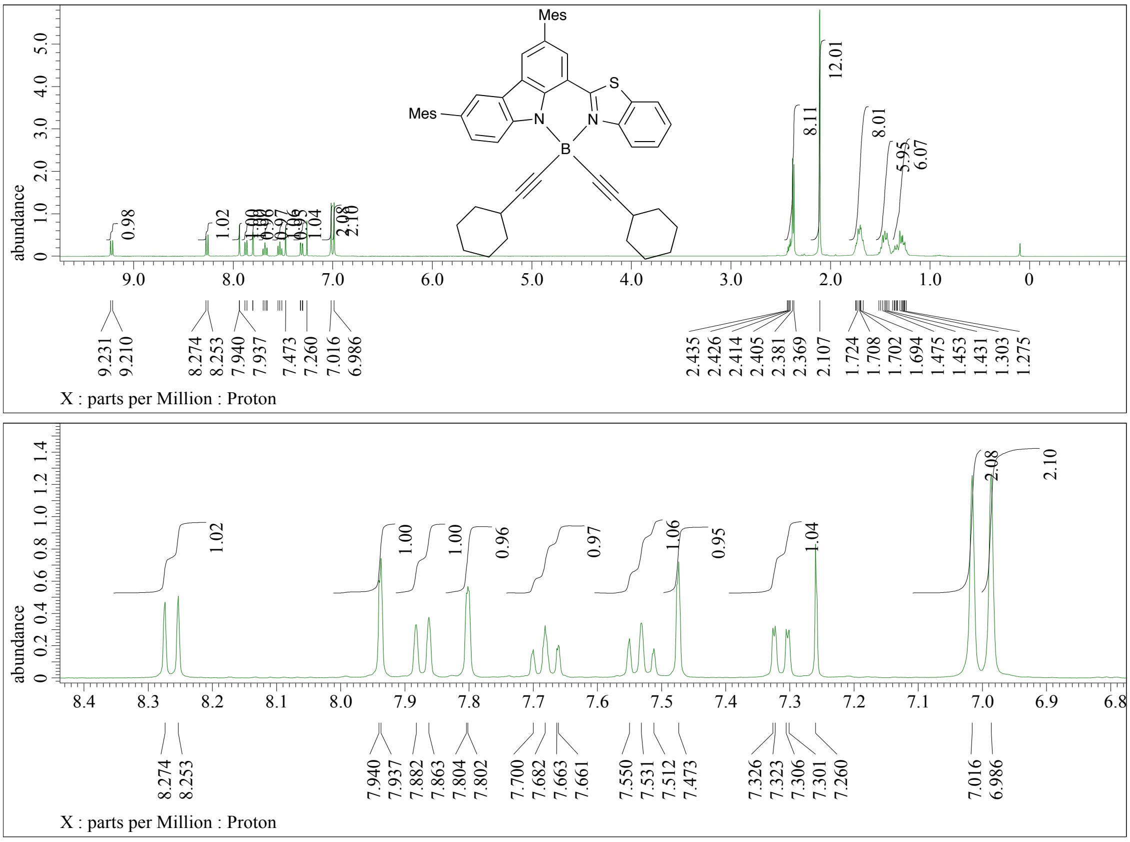
[13]C NMR spectrum of **3i** in $CDCl_3$



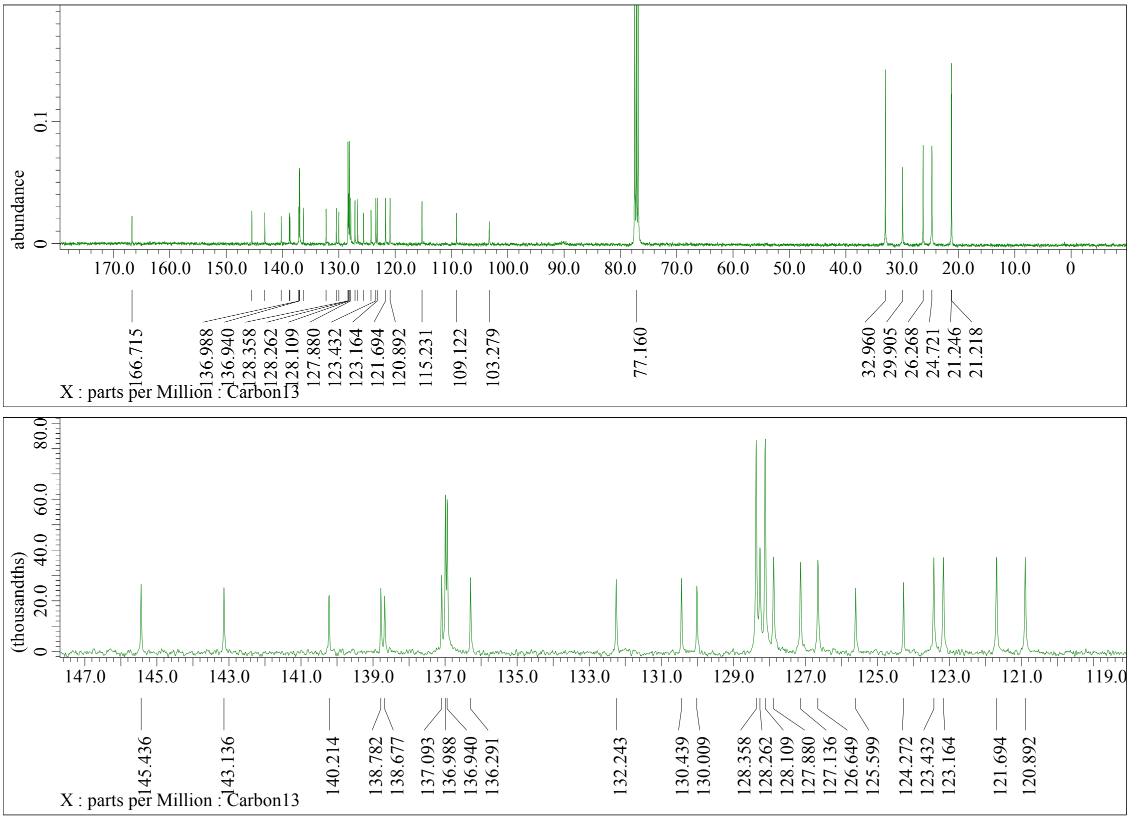
^{1}H NMR spectrum of **3j** in $CDCl_3$



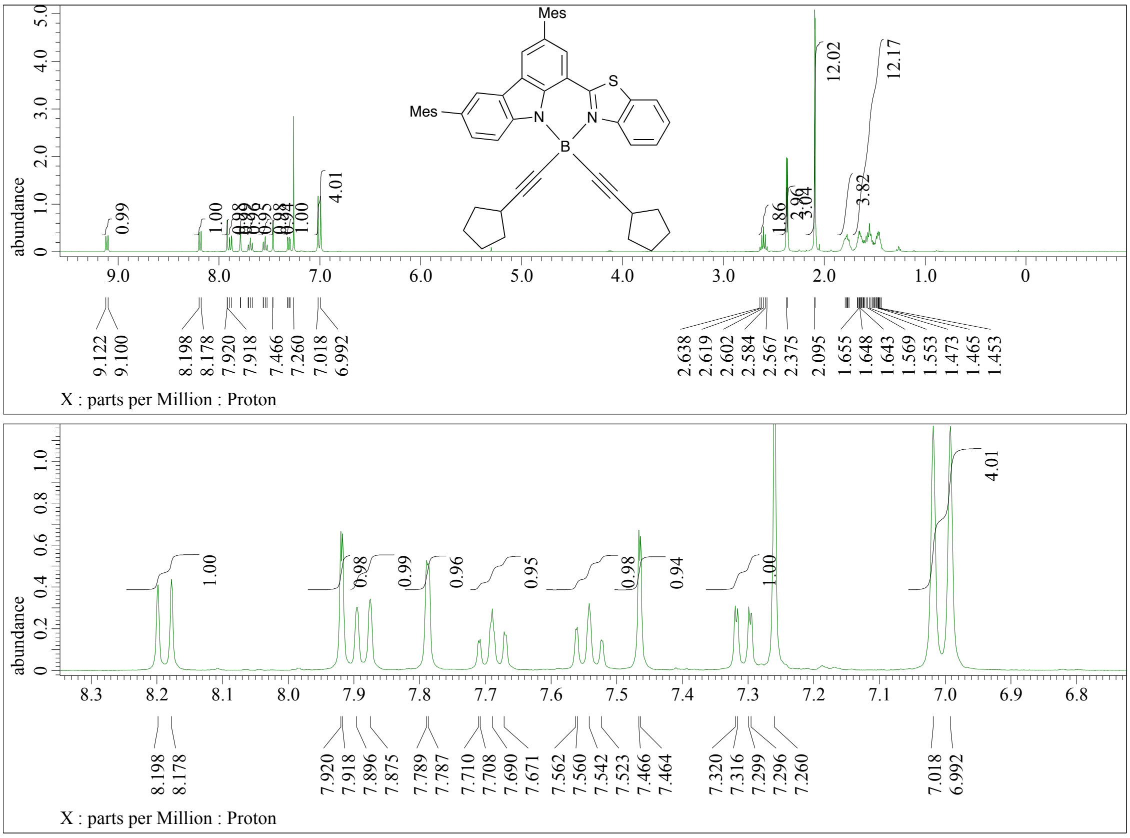
^{13}C NMR spectrum of **3j** in $CDCl_3$



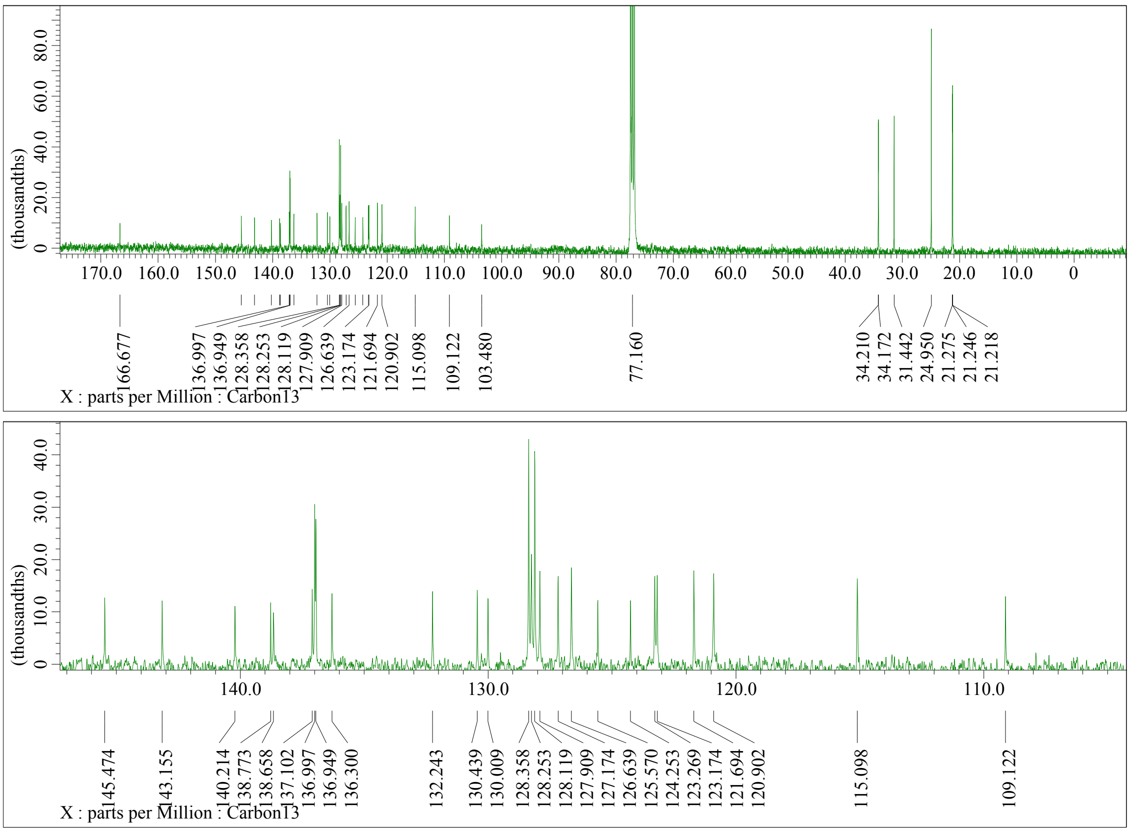
^{1}H NMR spectrum of **3k** in $CDCl_3$



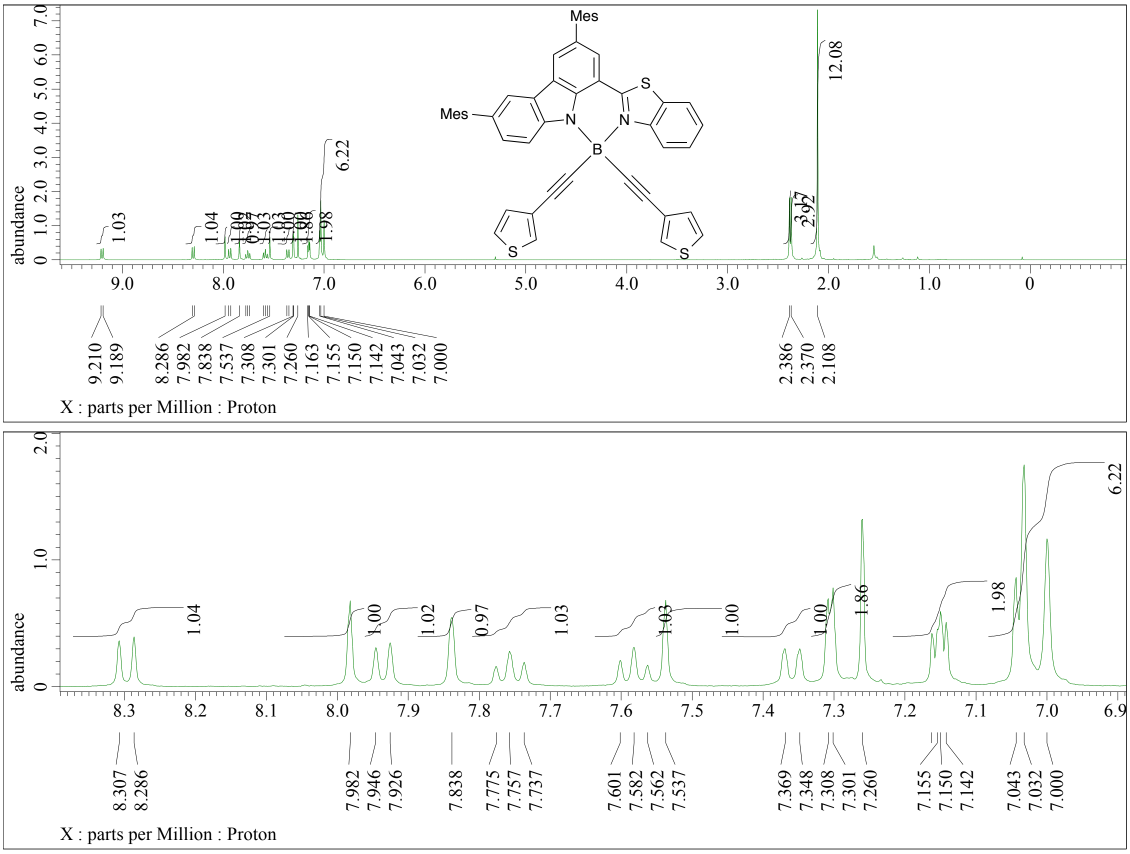
^{13}C NMR spectrum of **3k** in $CDCl_3$



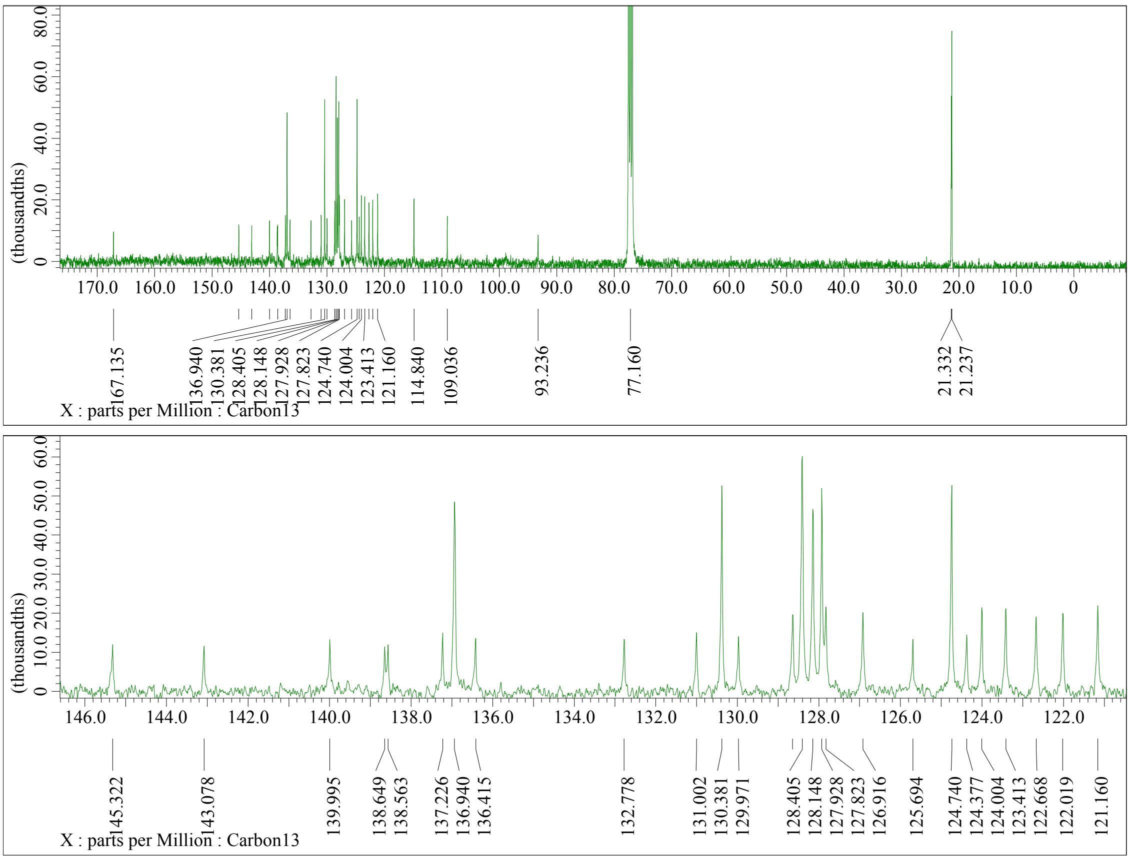
^{1}H NMR spectrum of **3l** in $CDCl_3$



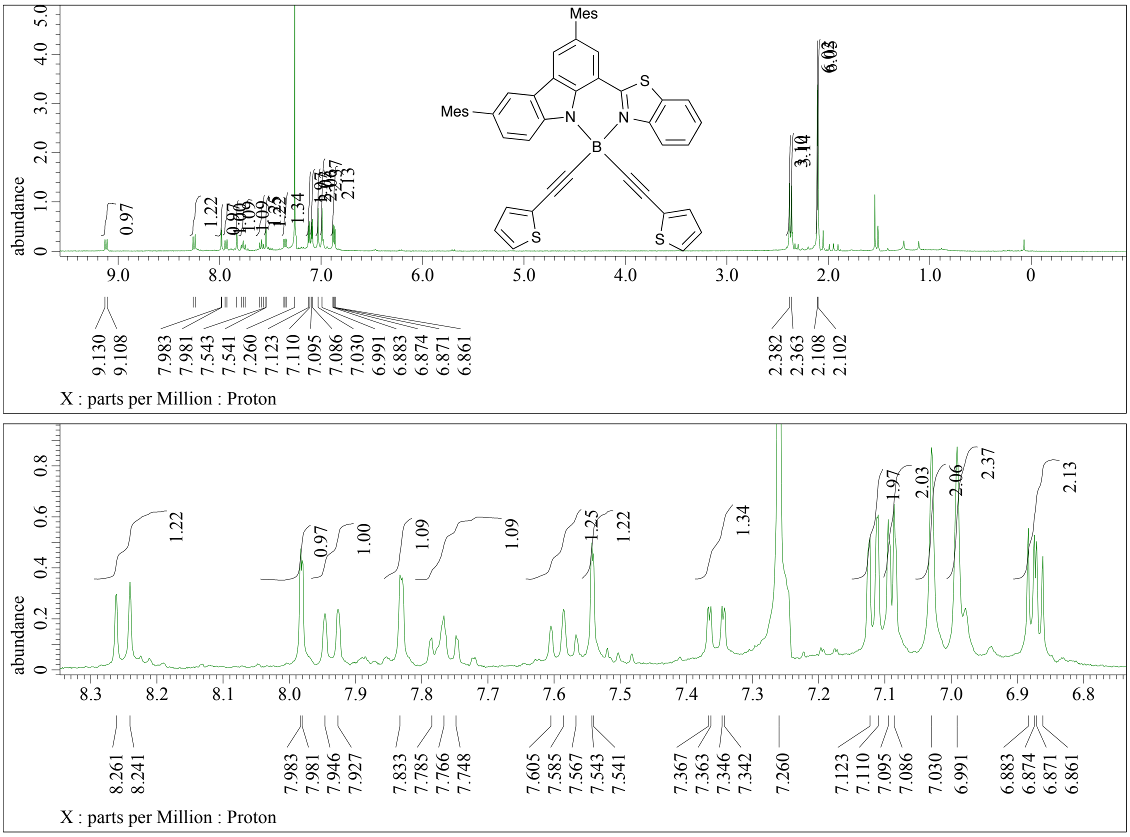
^{13}C NMR spectrum of **3l** in $CDCl_3$



^{1}H NMR spectrum of **3m** in $CDCl_3$



^{13}C NMR spectrum of **3m** in $CDCl_3$



^{1}H NMR spectrum of **3n** in $CDCl_3$

[D] UV/vis Absorption and Fluorescence Spectra

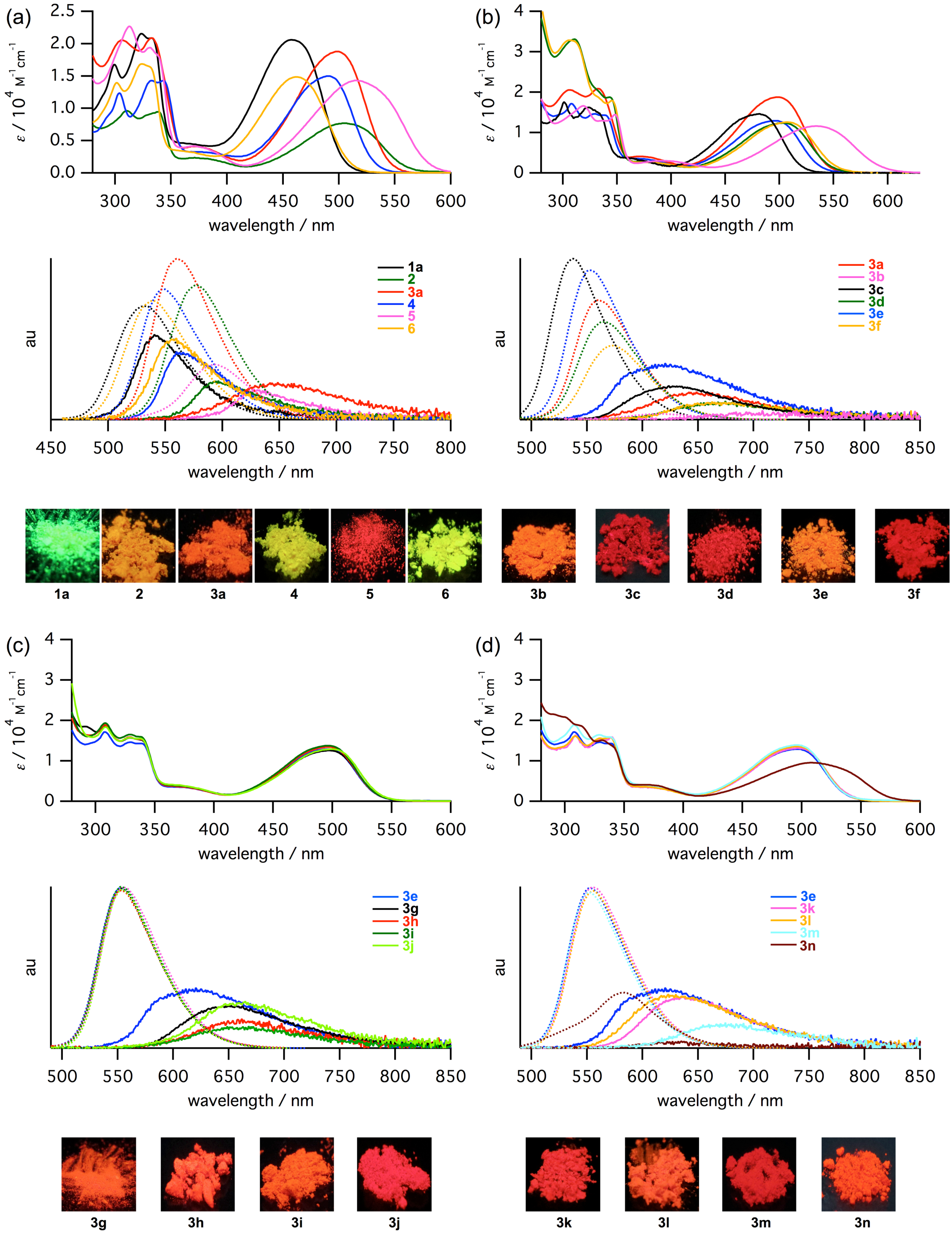
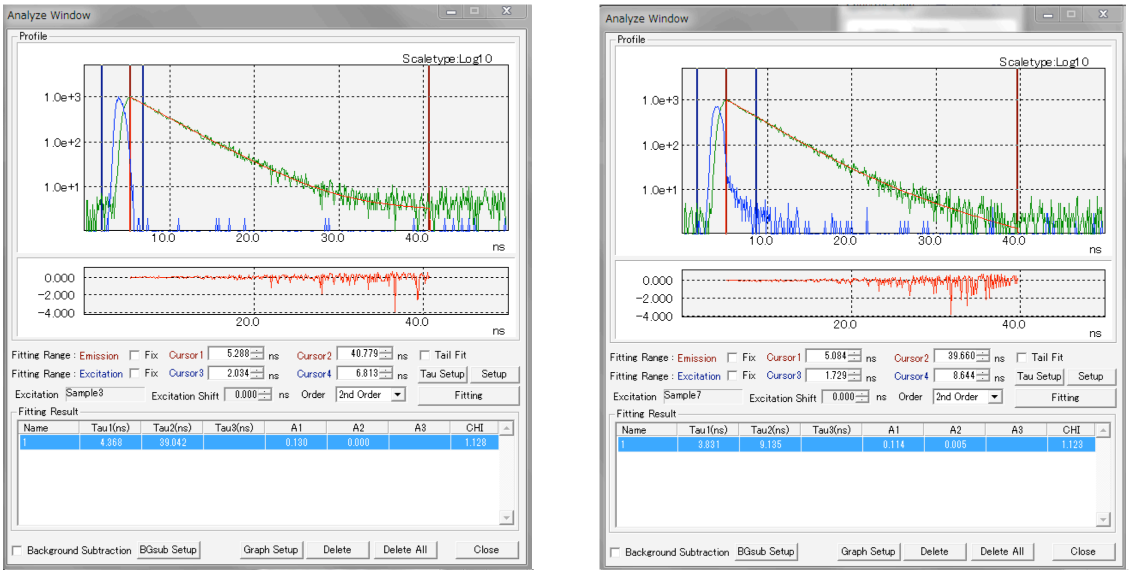


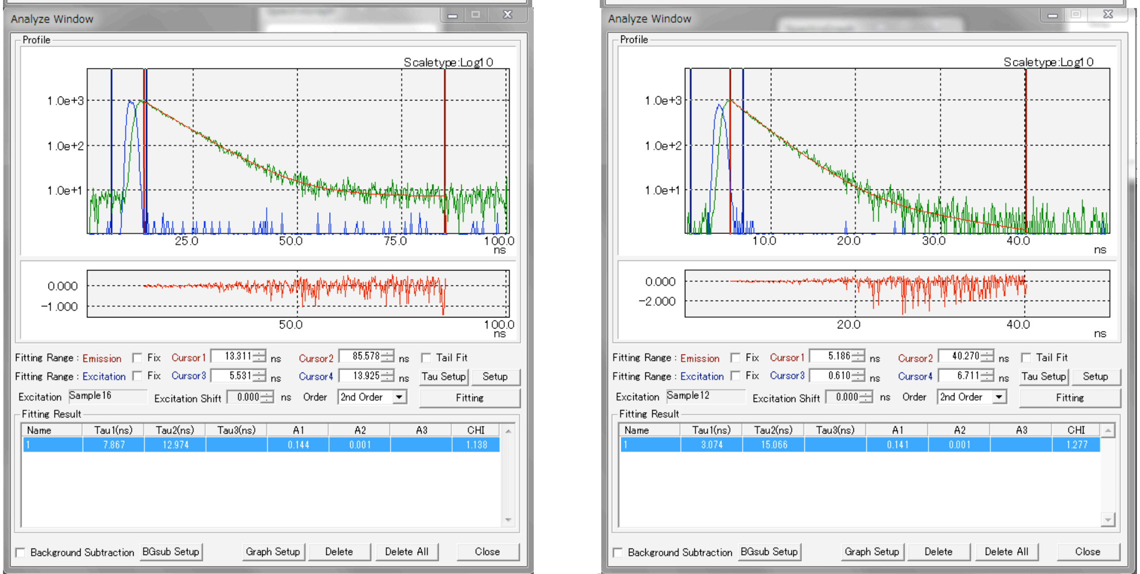
Fig. S1 UV/vis absorption (in CH_2Cl_2) and fluorescence (in CH_2Cl_2: dotted line, in the solid state: solid line) spectra of (a) **1**–**6**, (b) **3a**–**f**, (c) **3g**–**j** and (d) **3k**–**n**. Photographic images of the powdered compounds under black light (λ = 365 nm) are shown.

[E] Fluorescence Lifetime

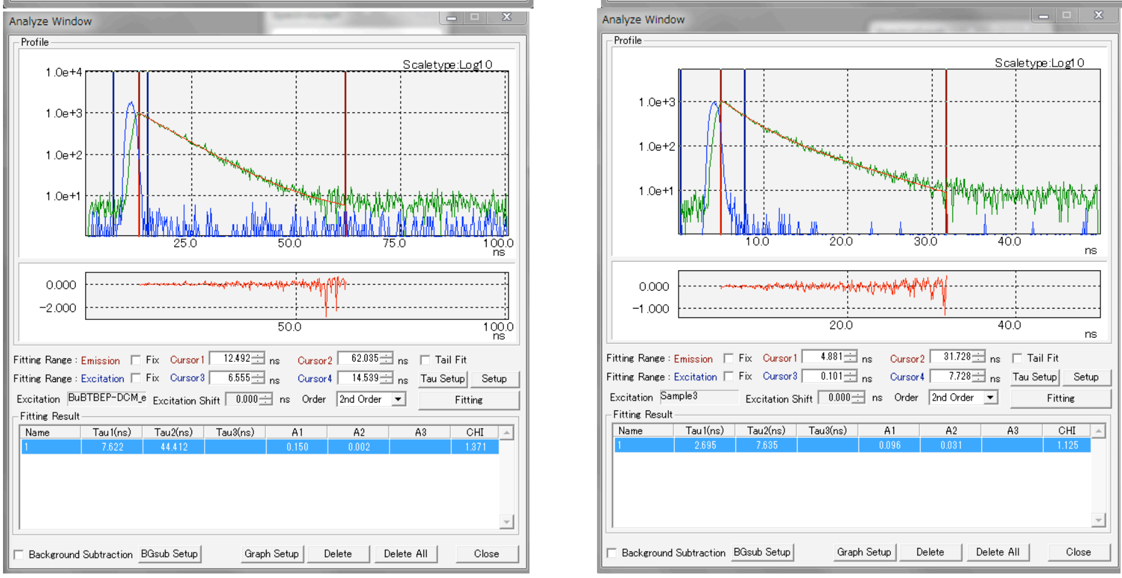
(a)



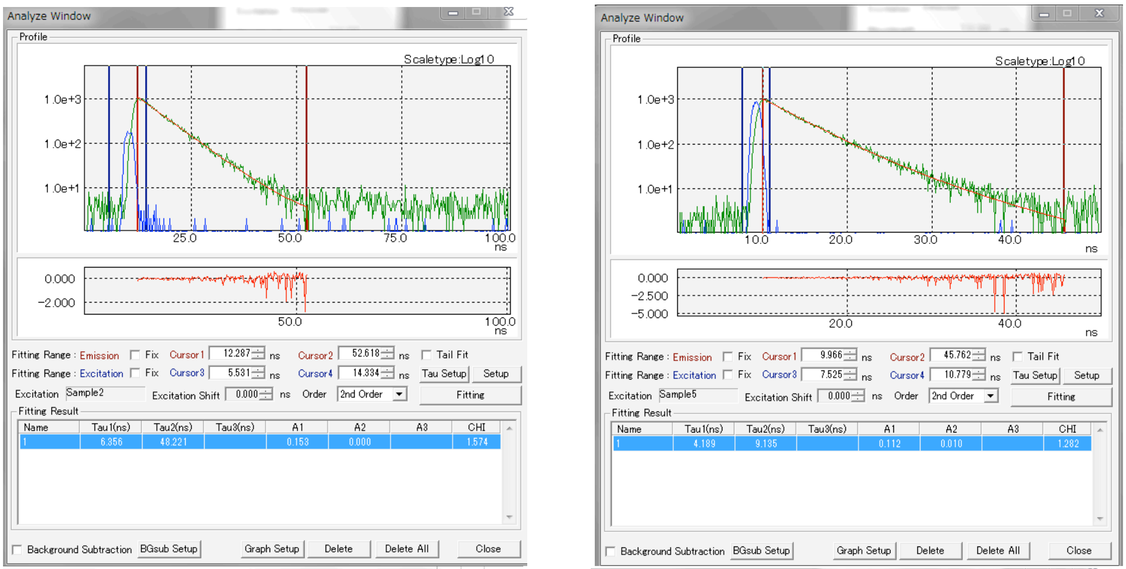
(b)



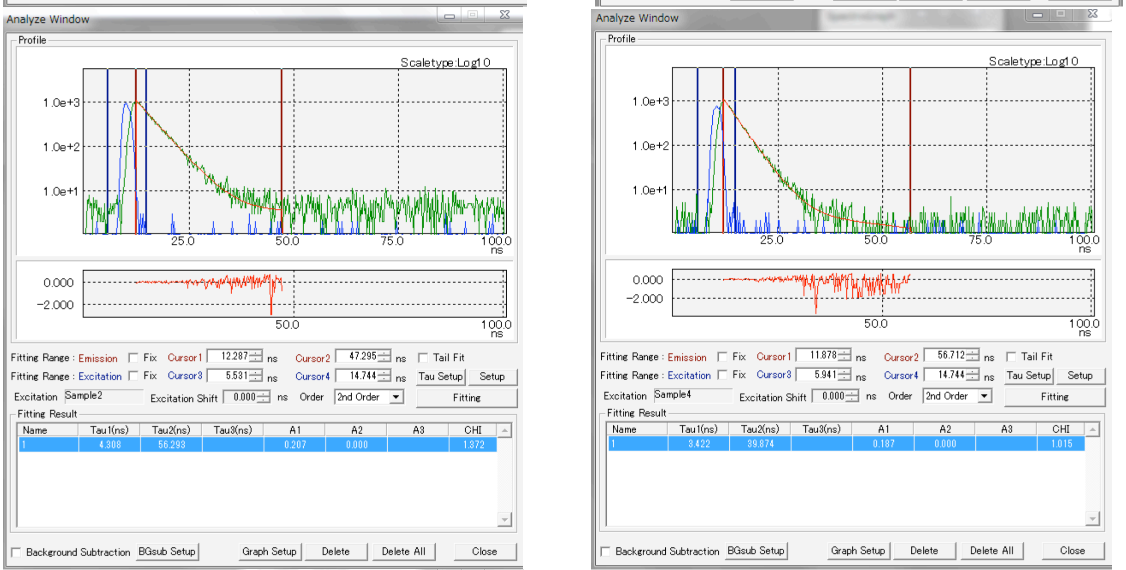
(c)



(d)



(e)



(f)

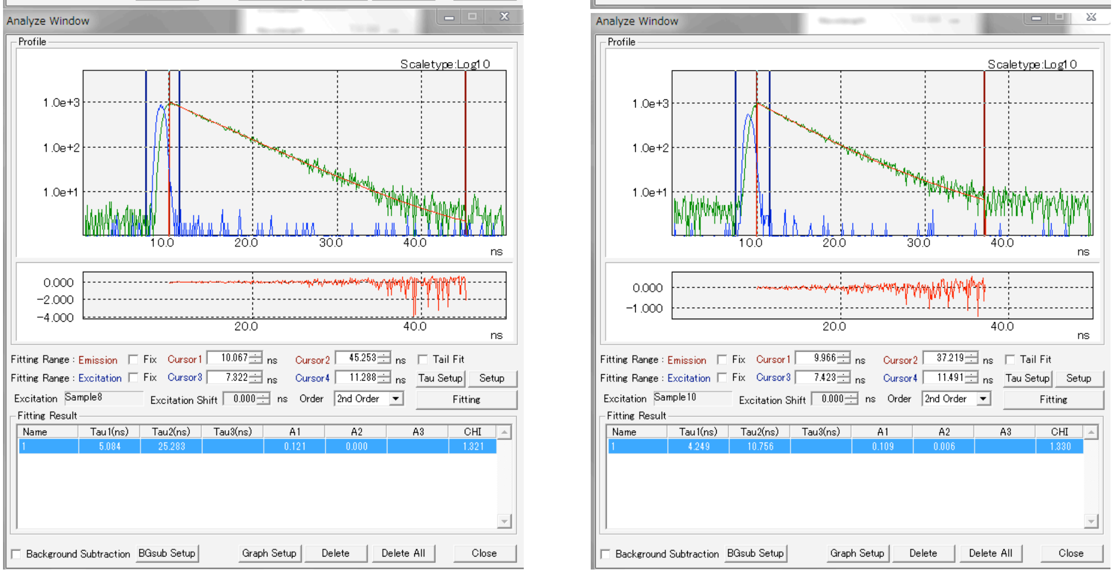


Fig. S2 Fluorescence decay analyses of (a) **1a**, (b) **2**, (c) **3a**, (d) **4**, (e) **5** and (f) **6** in CH_2Cl_2 (left) and in the solid state (right)

[F] X-ray Crystal Structures

Single crystals of **2**, **3a**, **4**, **3b**, **3e** and **3f** were obtained by the vapor diffusion method (CH_2Cl_2/hexane for **2** and **3b**, CH_2Cl_2/octane for **3a**, CH_2Cl_2/MeOH for **4** and **3e**, and $CHCl_3$/hexane for **3f**). X-ray data at 93 K were taken on a Rigaku-Raxis-RAPID imaging plate system with Cu-$K\alpha$ radiation (λ = 1.54187 Å), and structures were processed and refined by CrystalStructure and Yadokari. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were calculated in ideal positions.

Crystallographic data for 2: formula: $C_{39}H_{37}N_2S_1B_1 \cdot C_6H_{14}$, M_w = 662.74, monoclinic, space group $P2_1/a$, a = 10.337(2), b = 25.595(5), c = 14.097(3) Å, β = 97.574(5)°, V = 3697.2(13) Å^3, Z = 4, ρ_{calcd} = 1.191 gcm^{-3}, T = –180 °C, 23880 measured reflections, 6549 unique reflections (R_{int} = 0.0336), R_1 = 0.0568 ($I > 2\sigma(I)$), wR_2 = 0.1593 (all data), GOF = 1.048.
Crystallographic data for 3a: formula: $C_{43}H_{37}N_2S_1B_1 \cdot CH_2Cl_2$, M_w = 709.54, triclinic, space group P–1, a = 12.213(4), b = 13.215(7), c = 13.236(9) Å, α = 119.751(18), β = 96.382(14), γ = 91.1942(13)°, V = 1836.0(17) Å^3, Z = 2, ρ_{calcd} = 1.283 gcm^{-3}, T = –180 °C, 22400 measured reflections, 5715 unique reflections (R_{int} = 0.0695), R_1 = 0.0451 ($I > 2\sigma(I)$), wR_2 = 0.1261 (all data), GOF = 1.056.
Crystallographic data for 4: formula: $C_{29}H_{27}N_4S_1B_1$, M_w = 474.41, monoclinic, space group $P2_1/a$, a = 11.733(3), b = 9.921(2), c = 21.775(5) Å, β = 94.847(9)°, V = 2525.6(10) Å^3, Z = 4, ρ_{calcd} = 1.248 gcm^{-3}, T = –180 °C, 24175 measured reflections, 4480 unique reflections (R_{int} = 0.0465), R_1 = 0.0348 ($I > 2\sigma(I)$), wR_2 = 0.0997 (all data), GOF = 1.041.
Crystallographic data for 3b: formula: $C_{35}H_{21}N_2S_1B_1 \cdot CH_2Cl_2$, M_w = 597.33, triclinic, space group P–1, a = 10.523(3), b = 11.578(3), c = 12.402(6) Å, α = 97.230(11), β = 102.026(15), γ = 100.544(3)°, V = 1431.6(9) Å^3, Z = 2, ρ_{calcd} = 1.386 gcm^{-3}, T = –180 °C, 17192 measured reflections, 4602 unique reflections (R_{int} = 0.0406), R_1 = 0.0351 ($I > 2\sigma(I)$), wR_2 = 0.0929 (all data), GOF = 1.051.
Crystallographic data for 3e: formula: $C_{53}H_{41}N_2S_1B_1 \cdot CO$, M_w = 776.76, triclinic, space group P–1, a = 11.071(3), b = 12.310(4), c = 15.729(5) Å, α = 99.083(14), β = 96.913(9), γ = 99.963(9)°, V = 2060.7(11) Å^3, Z = 2, ρ_{calcd} = 1.252 gcm^{-3}, T = –180 °C, 26226 measured reflections, 6989 unique reflections (R_{int} = 0.0285), R_1 = 0.0649 ($I > 2\sigma(I)$), wR_2 = 0.1792 (all data), GOF = 1.074.
Crystallographic data for 3f: formula: $C_{63}H_{61}N_2S_1B_1 \cdot 2(CHCl_3)$, M_w = 1127.74, triclinic, space group P–1, a = 11.908(4), b = 13.971(6), c = 17.856(7) Å, α = 100.643(12), β = 92.2079(10), γ = 92.499(16)°, V = 2913(2) Å^3, Z = 2, ρ_{calcd} = 1.286 gcm^{-3}, T = –180 °C, 35282 measured reflections, 9820 unique reflections (R_{int} = 0.0702), R_1 = 0.0619 ($I > 2\sigma(I)$), wR_2 = 0.1859 (all data), GOF = 1.009.
CCDC 1536630 (**2**), 1536632 (**3a**), 1536633 (**4**), 1536631 (**3b**), 1536634 (**3e**) and 1536635 (**3f**) contains the supplementary crystallographic data for this paper.

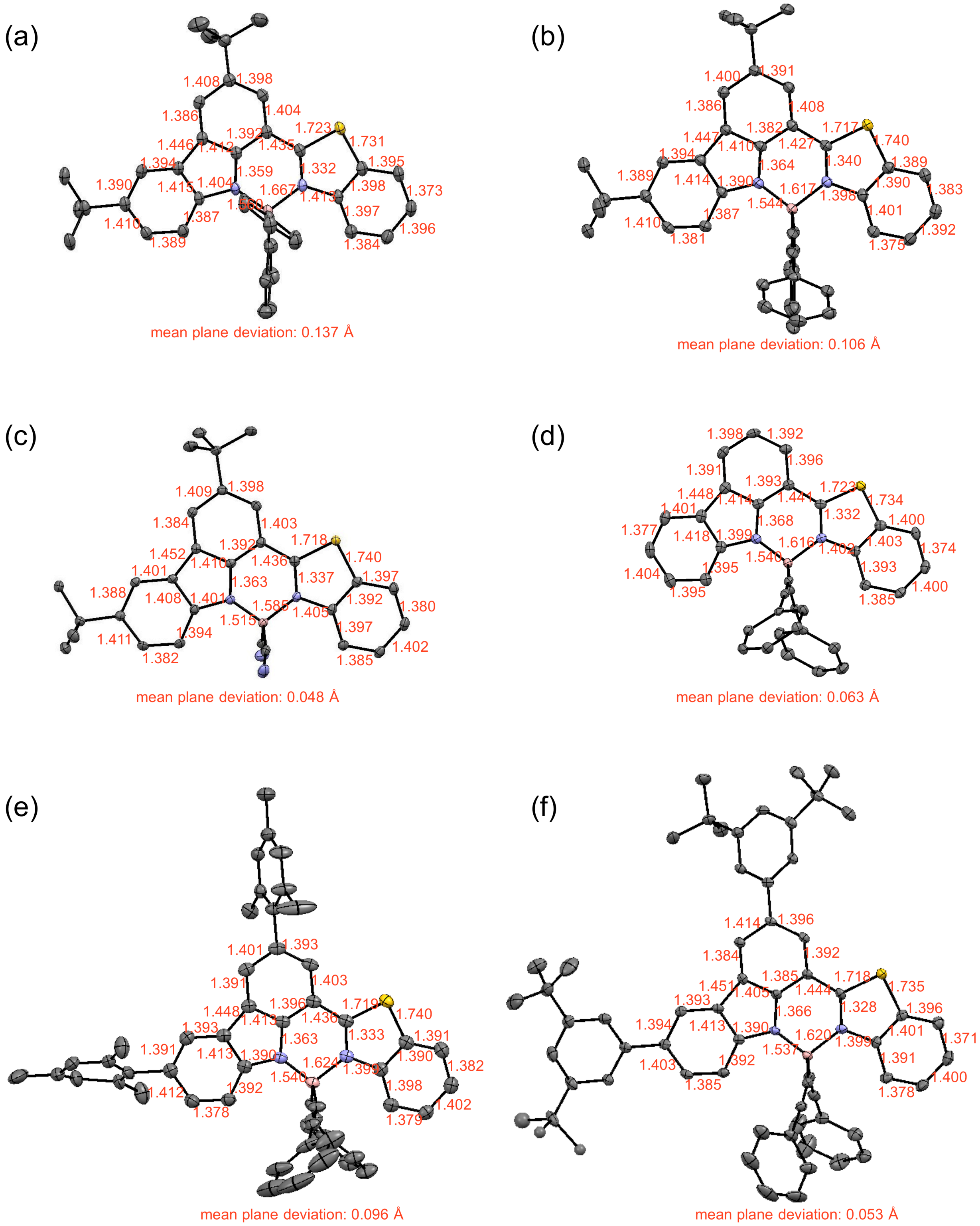


Fig. S3 Crystal structures of (a) **2**, (b) **3a**, (c) **4**, (d) **3b**, (e) **3e** and (f) **3f**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) are shown. Mean plane deviations are calculated for the atoms excluding the peripheral substituents.

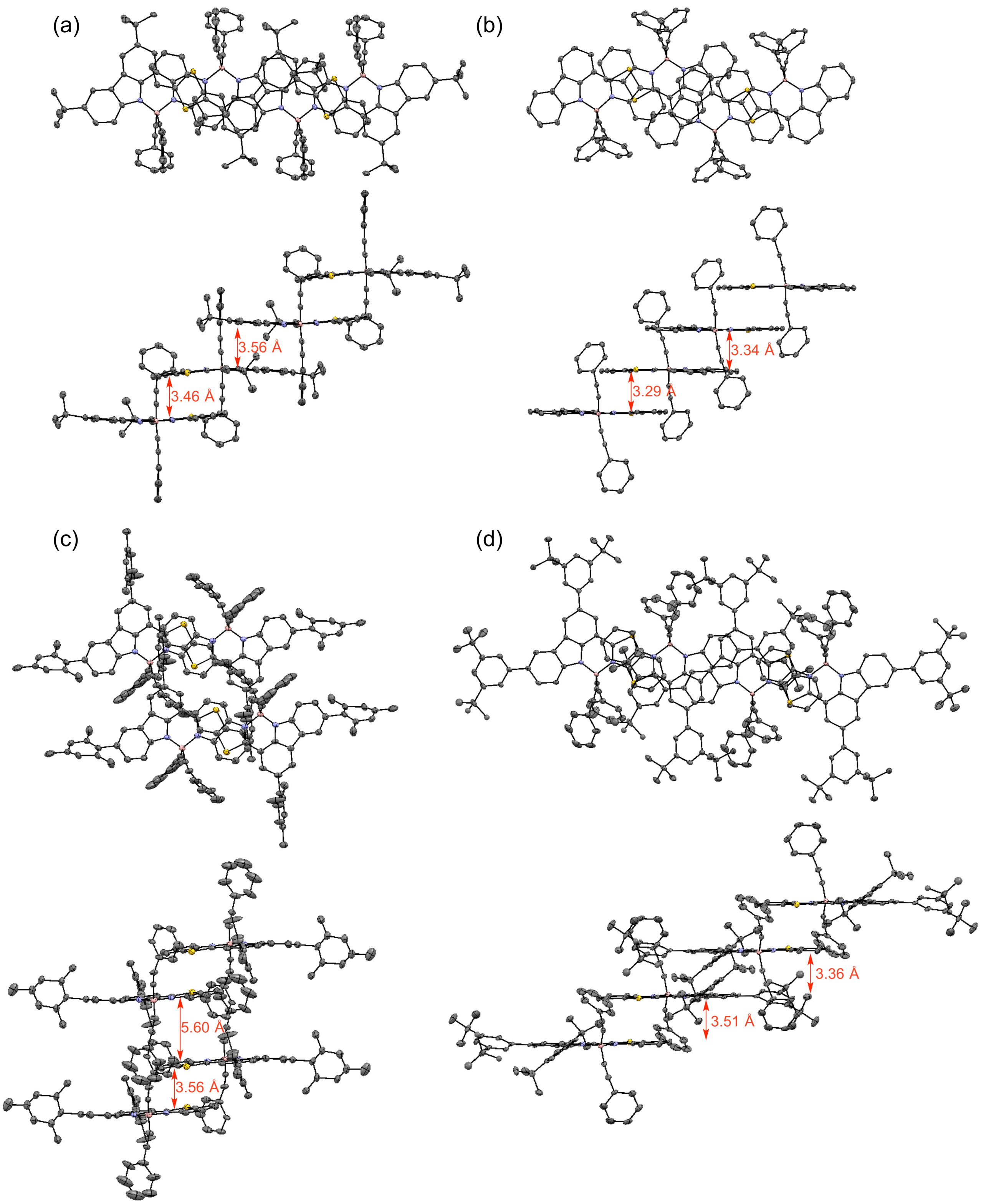


Fig. S4 Crystal packing of (a) **3a**, (b) **3b**, (c) **3e** and (d) **3f**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. Intermolecular distances are shown between the mean planes of the molecules, excluding the peripheral substituents.