Electronic Supplementary Information for Synthesis of chiral carbazole-based BODIPYs showing circularly polarized luminescence

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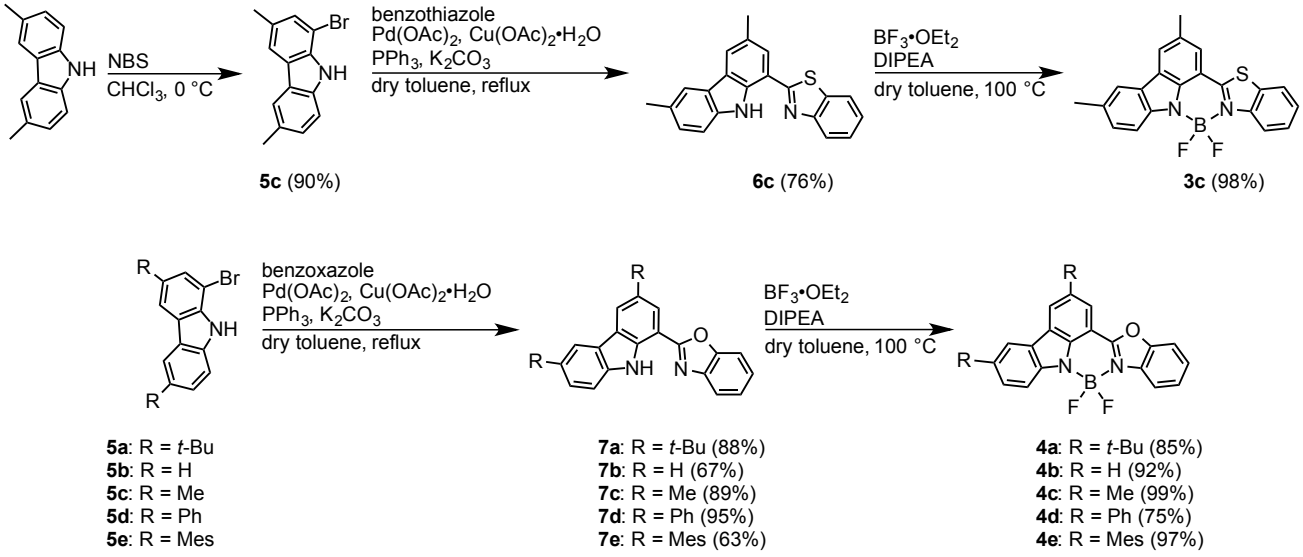
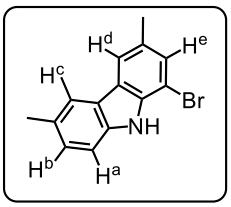
[A] Instrumentation and Materials

^{1}H and ^{13}C NMR spectra were taken on a JEOL ECA-400 spectrometer, and chemical shifts were reported as the delta scale in ppm using an internal reference (δ = 7.26 for ^{1}H NMR, 77.16 for ^{13}C NMR, for $CDCl_3$). UV/vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. CD spectra were recorded on a JASCO J-720 or a JASCO J-1500. Fluorescence spectra were recorded on a JASCO FP-750 or on a Hamamatsu Photonics C9920-02 spectrometer by the photon-counting method using an integration sphere. CPL spectra were measured on a JASCO CPL-200. HR mass spectra were taken on a Bruker microTOF. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Dry CH_2Cl_2 was distilled from CaH_2. **3a**–**b**,[S1] **3d**–**e**,[S1] **5a**,[S1] **5e**,[S2] **8**,[S3] and **10**[S4] were prepared by the literature method.

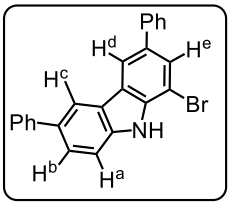
[B] Experimental Procedures and Compound Data



Scheme S1 Synthesis of **3** and **4**.

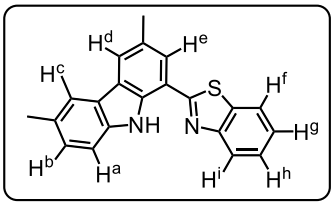


Synthesis of 5c. To a solution of 3,6-dimethylcarbazole (224 mg, 1.15 mmol) in $CHCl_3$ (20 mL) was added *N*-bromosuccinimide (225 mg, 1.26 mmol) at 0 °C, and the mixture was stirred at 0 °C for 3 h in the dark. The mixture was evaporated, and the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **5c** as a white solid (282 mg, 1.03 mmol, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.02 (s, 1H, NH), 7.81 (s, 1H, H^c), 7.76 (s, 1H, H^d), 7.39 (s, 1H, H^e), 7.35 (d, J = 8.4 Hz, 1H, H^a), 7.26 (dd, J = 1.4, 8.2 Hz, 1H, H^b), 2.53 (s, 3H, Me), and 2.51 ppm (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 137.85, 136.82, 130.22, 129.34, 129.03, 127.90, 124.70, 123.87, 120.76, 119.45, 110.80, 103.77, 21.57, and 21.31 ppm; HR-MS (APCI): m/z = 274.0228. calcd for $C_{14}H_{13}NBr$: 274.0226 $[M+H]^+$.



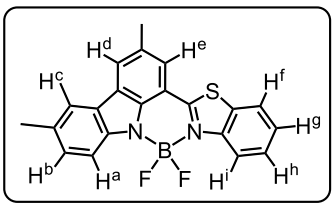
Synthesis of 5d. To a solution of 3,6-diphenylcarbazole (127 mg, 399 μmol) in $CHCl_3$ (10 mL) was added *N*-bromosuccinimide (71.7 mg, 403 μmol) at 0 °C, and the mixture was stirred at 0 °C for 1.5 h in the dark. The mixture was evaporated, and the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **5d** as a white solid (144 mg, 362 μmol, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.29 (d, J = 1.2 Hz, 1H, H^c), 8.24 (m, 2H, NH and H^d), 7.84 (d, J = 1.2 Hz, 1H, H^e), 7.74–7.68 (m, 5H, H^b and Ph), 7.54–7.48 (m, 5H, H^a and Ph), and 7.40–7.36 ppm (m, 2H, Ph); ^{13}C NMR ($CDCl_3$,

100 MHz) δ = 141.73, 140.78, 138.95, 137.87, 134.48, 133.62, 128.89, 128.86, 127.40, 127.28, 126.98, 126.72, 126.12, 125.07, 124.39, 119.17, 117.79, 111.36, and 104.41 ppm; HR-MS (APCI): *m*/*z* = 398.0356. calcd for $C_{24}H_{15}NBr$: 398.0374 $[M–H]^-$.



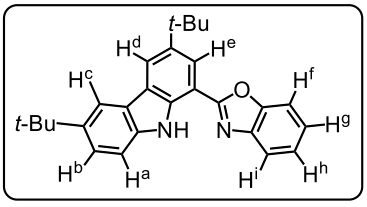
Synthesis of 6c. A flask containing **5c** (262 mg, 956 μmol), benzothiazole (0.31 mL, 2.9 mmol), $Pd(OAc)_2$ (12.3 mg, 54.8 μmol), $Cu(OAc)_2·H_2O$ (39.2 mg, 196 μmol), K_2CO_3 (274 mg, 1.98 mmol), and PPh_3 (148 mg, 564 μmol) was purged with N_2, charged with dry toluene (3 mL), and degassed. The mixture was heated at reflux for 15 h under N_2. After cooling to rt, the mixture was passed through a silica gel column with $CHCl_3$ and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **6c** as a green solid (239 mg, 728 μmol, 76%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 10.74 (s, 1H, NH), 8.15 (d, *J* = 8.4 Hz, 1H, H^f or H^i), 7.97 (s, 1H, H^d or H^e), 7.93 (d, *J* = 8.0 Hz, 1H, H^f or H^i), 7.88 (s, 1H, H^e), 7.73 (s, 1H, H^d or H^e), 7.53 (dt, *J* = 0.8, 8.0 Hz, 1H, H^g or H^h), 7.50 (d, *J* = 8.4 Hz, 1H, H^a), 7.41 (dt, *J* = 0.8, 7.2 Hz, 1H, H^g or H^h), 7.30 (dd, *J* = 0.8, 8.4 Hz, 1H, H^b), 2.61 (s, 3H, Me) and 2.56 ppm (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 168.13, 154.18, 138.53, 136.17, 133.84, 129.01, 128.21, 127.80, 126.40, 126.33, 125.20, 124.83, 123.59, 122.86, 122.79, 121.69, 120.48, 115.37, 111.12, 21.63, and 21.52 ppm; HR-MS (APCI): *m*/*z* = 329.1107. calcd for $C_{21}H_{17}N_2S$: 329.1107 $[M+H]^+$.



Synthesis of 3c. **6c** (227 mg, 691 μmol) was dissolved in dry toluene (4 mL). N,N-Diisopropylethylamine (1.0 mL, 5.8 mmol) and then $BF_3·OEt_2$ (0.30 mL, 2.4 mmol) were added, and the mixture was heated at 100 °C for 5 h under N_2. After the solvents were removed, the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **3c** as a yellow solid (254 mg, 675 μmol, 98%)

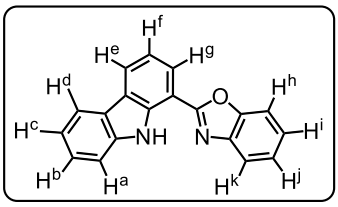
^{1}H NMR ($CDCl_3$) δ = 8.61 (d, *J* = 8.8 Hz, 1H, H^f or H^i), 8.10 (s, 1H, H^d or H^e), 7.93 (d, *J* = 8.4 Hz, 1H, H^f or H^i), 7.88 (s, 1H, H^e), 7.84 (d, *J* = 8.8 Hz, 1H, H^a), 7.71 (dt, *J* = 1.0, 7.9 Hz, 1H, H^g or H^h), 7.64 (s, 1H, H^d or H^e), 7.57 (dt, *J* = 0.8, 7.6 Hz, 1H, H^g or H^h), 7.37 (dd, *J* = 1.6, 6.8 Hz, 1H, H^b), 2.61 (s, 3H, Me), and 2.55 ppm (s, 3H, Me); ^{13}C NMR ($CDCl_3$) δ = 168.03, 144.31, 141.88, 139.00, 130.17, 129.33, 128.65, 128.58, 128.47, 128.42, 126.88, 125.52, 124.21, 123.03, 122.22, 120.94, 120.89, 113.89, 108.22, 21.67, and 21.54 ppm; HR-MS (APCI): *m*/*z* = 376.1019. calcd for $C_{21}H_{15}N_2SBF_2$: 376.1015 $[M]^+$.



Synthesis of 7a. A flask containing **5a** (366 mg, 1.01 mmol), benzoxazole (0.30 mL, 3.0 mmol), $Pd(OAc)_2$ (21.3 mg, 94.7 μmol), $Cu(OAc)_2·H_2O$ (54.6 mg, 273 μmol), K_2CO_3 (296 mg, 2.14 mmol), and PPh_3 (145 mg, 553 μmol) was purged with N_2, charged with dry toluene (3 mL), and degassed. The mixture was heated at reflux for 15 h under N_2. After cooling to rt, the mixture was passed through a silica gel column with $CHCl_3$ and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **7a** as a green solid (356 mg, 897 μmol, 88%).

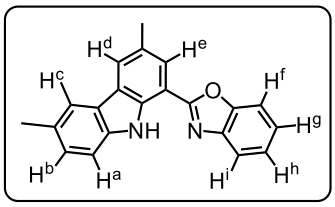
^{1}H NMR ($CDCl_3$) δ = 10.36 (s, 1H, NH), 8.30 (s, 2H, H^d and H^e), 8.14 (s, 1H, H^c), 7.86–7.84 (m, 1H, H^f or H^i), 7.68–7.66 (m, 1H, H^f or H^i), 7.58–7.53 (m, 2H, H^a and H^b), 7.42–7.37 (m, 2H, H^g and H^h), 1.55 (s, 9H, *t*-Bu), and 1.48 ppm (s, 9H, *t*-Bu); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 163.04, 150.10, 142.82, 142.33, 142.04, 138.42, 137.07,

124.99, 124.68, 124.57, 124.46, 122.82, 121.81, 120.52, 119.66, 116.52, 110.91, 110.69, 108.35, 35.05, 34.92, 32.22, and 32.19 ppm; HR-MS (APCI): *m*/*z* = 397.2277. calcd for $C_{27}H_{29}N_2O$: 397.2274 $[M+H]^+$.



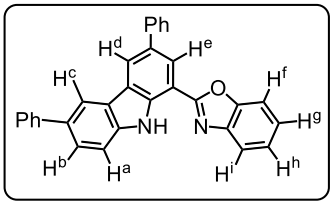
Synthesis of 7b. A flask containing **5b** (236 mg, 959 μmol), benzoxazole (0.29 mL, 2.9 mmol), $Pd(OAc)_2$ (10.8 mg, 48.1 μmol), $Cu(OAc)_2·H_2O$ (38.3 mg, 192 μmol), K_2CO_3 (265 mg, 1.92 mmol), and PPh_3 (145 mg, 481 μmol) was purged with N_2, charged with dry toluene (3 mL), and degassed. The mixture was heated at reflux for 15 h under N_2. After cooling to rt, the mixture was passed through a silica gel column with $CHCl_3$ and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **7b** as a green solid (183 mg, 644 μmol, 67%).

^{1}H NMR ($CDCl_3$) δ = 10.63 (s, 1H, NH), 8.26 (d, J = 7.6 Hz, 2H, H^e and H^g), 8.14 (d, J = 7.6 Hz, 1H, H^d), 7.88–7.86 (m, 1H, H^h or H^k), 7.66–7.64 (m, 2H, H^a, and H^h or H^k), 7.51 (dt, J = 1.2, 7.6 Hz, 1H, H^b), 7.43–7.39 (m, 2H, H^h and H^i), 7.37 (t, J = 7.6 Hz, 1H, H^f), and 7.31 ppm (dt, J = 0.8, 7.2 Hz, 1H, H^c); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.75, 150.23, 142.33, 140.05, 138.47, 126.71, 125.20, 124.81, 124.59, 124.50, 123.91, 123.09, 120.69, 120.13, 119.81, 119.11, 111.56, 110.76, and 109.25 ppm; HR-MS (APCI): *m*/*z* = 283.0878. calcd for $C_{19}H_{11}N_2O$: 283.0866 $[M–H]^–$.



Synthesis of 7c. A flask containing **5c** (343 mg, 1.25 mmol), benzoxazole (0.38 mL, 3.8 mmol), $Pd(OAc)_2$ (14.0 mg, 62.5 μmol), $Cu(OAc)_2·H_2O$ (49.9 mg, 250 μmol), K_2CO_3 (345 mg, 2.50 mmol), and PPh_3 (163 mg, 625 μmol) was purged with N_2, charged with dry toluene (3 mL), and degassed. The mixture was heated at reflux for 15 h under N_2. After cooling to rt, the mixture was passed through a silica gel column with $CHCl_3$ and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **7c** as a green solid (348 mg, 1.11 mmol, 89%).

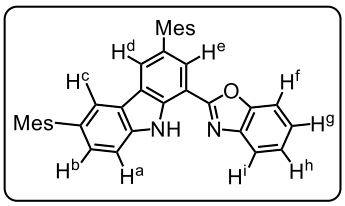
^{1}H NMR ($CDCl_3$) δ = 10.35 (s, 1H, NH), 8.05 (s, 1H, H^d or H^e), 8.02 (s, 1H, H^d or H^e), 7.89 (s, 1H, H^c), 7.85–7.83 (m, 1H, H^f or H^i), 7.65–7.63 (m, 1H, H^f or H^i), 7.50 (d, J = 8.4 Hz, 1H, H^a), 7.42–7.36 (m, 2H, H^g and H^h), 7.30 (d, J = 8.4 Hz, 1H, H^b), 2.63 (s, 3H, Me), and 2.55 ppm (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.79, 150.09, 142.29, 138.43, 137.02, 129.11, 128.19, 127.85, 125.18, 125.05, 124.71, 124.53, 124.21, 122.93, 120.49, 119.68, 111.10, 110.66, 108.56, 21.63, and 21.56 ppm; HR-MS (APCI): *m*/*z* = 311.1189. calcd for $C_{21}H_{15}N_2O$: 311.1190 $[M–H]^–$.



Synthesis of 7d. A flask containing **5d** (348 mg, 873 μmol), benzoxazole (0.29 mL, 2.9 mmol), $Pd(OAc)_2$ (15.1 mg, 67.2 μmol), $Cu(OAc)_2·H_2O$ (45.8 mg, 229 μmol), K_2CO_3 (295 mg, 2.13 mmol), and PPh_3 (141 mg, 538 μmol) was purged with N_2, charged with dry toluene (3 mL), and degassed. The mixture was heated at reflux for 15 h under N_2. After cooling to rt, the mixture was passed through a silica gel column with $CHCl_3$ and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **7d** as a green solid (360 mg, 825 μmol, 95%).

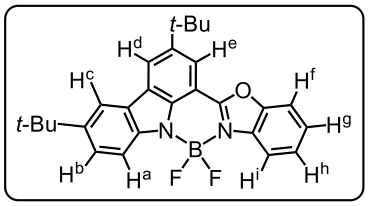
^{1}H NMR ($CDCl_3$) δ = 10.66 (s, 1H, NH), 8.52 (s, 2H, H^d and H^e), 8.40 (d, J = 1.6 Hz, 1H, H^c), 7.90–7.88 (m, 1H, H^f or H^i), 7.83 (dd, J = 1.2, 8.0 Hz, 2H, Ph), 7.79 (dd, J = 1.8, 8.0 Hz, 1H, H^b), 7.75 (dd, J = 1.6, 8.4 Hz, 2H, Ph),

7.72 (d, J = 8.4 Hz, 1H, H^a), 7.69–7.67 (m, 1H, H^f or H^i), 7.54 (t, J = 7.8 Hz, 2H, Ph), 7.50 (t, J = 8.0 Hz, 2H, Ph), and 7.46–7.35 ppm (m, 4H, H^g, H^h, and Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.41, 150.09, 142.14, 142.01, 141.37, 139.77, 138.15, 133.65, 132.84, 129.06, 128.95, 127.48, 127.45, 127.06, 126.76, 126.36, 125.27, 125.15, 124.83, 123.75, 123.65, 122.37, 119.78, 119.18, 111.82, 110.76, and 109.34 ppm; HR-MS (APCI): m/z = 435.1494. calcd for $C_{31}H_{19}N_2O$: 435.1503 [M–H]$^-$.



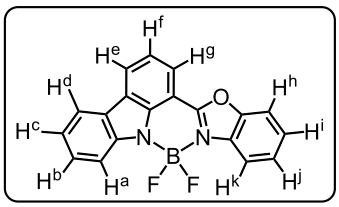
Synthesis of 7e. A flask containing **5e** (511 mg, 1.06 mmol), benzoxazole (0.32 mL, 3.2 mmol), $Pd(OAc)_2$ (23.4 mg, 104 μmol), $Cu(OAc)_2{\cdot}H_2O$ (49.7 mg, 249 μmol), K_2CO_3 (297 mg, 2.15 mmol), and PPh_3 (183 mg, 698 μmol) was purged with N_2, charged with dry toluene (3 mL), and degassed. The mixture was heated at reflux for 15 h under N_2. After cooling to rt, the mixture was passed through a silica gel column with $CHCl_3$ and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **7e** as a green solid (345 mg, 663 μmol, 63%).

^{1}H NMR ($CDCl_3$) δ = 10.65 (s, 1H, NH), 8.06 (d, J = 1.6 Hz, 1H, H^d or H^e), 7.97 (d, J = 1.2 Hz, 1H, H^d or H^e), 7.89 (dd, J = 1.4, 6.8 Hz, 1H, H^f or H^i), 7.84 (s, 1H, H^c), 7.70 (d, J = 8.4 Hz, 1H, H^a), 7.60 (dd, J = 1.0, 7.6 Hz, 1H, H^f or H^i), 7.42 (dt, J = 1.5, 7.2 Hz, 1H, H^g and H^h), 7.38 (dt, J = 1.7, 7.2 Hz, 1H, H^g and H^h), 7.28 (dd, J = 1.2, 8.0 Hz, 1H, H^b), 7.02 (s, 2H, Mes), 7.00 (s, 2H, Mes), 2.38 (s, 3H, Me), 2.37 (s, 3H, Me), 2.10 (s, 6H, Me), and 2.08 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.76, 150.23, 142.41, 139.69, 139.15, 138.98, 137.67, 136.89, 136.80, 136.57, 133.10, 132.21, 129.27, 128.64, 128.36, 128.25, 128.12, 125.83, 125.21, 124.93, 124.80, 124.71, 123.28, 121.23, 119.82, 111.48, 110.74, 109.26, 100.11, 21.20, 21.14, and 20.30 ppm; HR-MS (APCI): m/z = 519.2440. calcd for $C_{37}H_{31}N_2O$: 519.2442 [M–H]$^-$.



Synthesis of 4a. **7a** (84.4 mg, 254 μmol) was dissolved in dry toluene (4 mL). N,N-Diisopropylethylamine (1.0 mL, 5.8 mmol) and then $BF_3{\cdot}OEt_2$ (0.30 mL, 2.4 mmol) were added, and the mixture was heated at 100 °C for 5 h under N_2. After the solvents were removed, the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **4a** as a yellow solid (95.4 mg, 215 μmol, 85%).

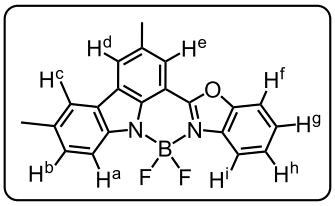
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.48 (d, J = 1.2 Hz, 1H, H^d), 8.15 (d, J = 1.6 Hz, 1H, H^c), 8.14 (d, J = 8.4 Hz, 1H, H^f or H^i), 8.12 (d, J = 1.6 Hz, 1H, H^e), 7.89 (d, J = 8.8 Hz, 1H, H^a), 7.75 (d, J = 8.0 Hz, 1H, H^f or H^i), 7.65 (dd, J = 2.0, 8.0 Hz, 1H, H^b), 7.59 (dt, J = 0.8, 7.6 Hz, 1H, H^g or H^h), 7.54 (dt, J = 1.6, 7.6 Hz, 1H, H^g or H^h), 1.54 (s, 9H, t-Bu), and 1.49 ppm (s, 9H, t-Bu); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.07, 149.34, 143.88, 142.42, 142.19, 141.79, 131.88, 127.26, 127.07, 125.78, 125.62, 125.45, 124.31, 118.39, 117.29, 117.04, 113.58, 111.68, 100.13, 35.23, 34.96, and 32.12 ppm; HR-MS (APCI): m/z = 444.2180. calcd for $C_{27}H_{27}N_2OBF_2$: 444.2195 [M]$^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 289 (13100), 310 (17400), and 429 nm (10300 $mol^{-1}dm^3cm^{-1}$).



Synthesis of 4b. **7b** (101 mg, 355 μmol) was dissolved in dry toluene (4 mL). N,N-Diisopropylethylamine (1.0 mL, 5.8 mmol) and then $BF_3{\cdot}OEt_2$ (0.30 mL, 2.4 mmol) were added, and the mixture was heated at 100 °C for 5 h under N_2. After the solvents were removed, the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **4b** as a yellow solid (108 mg, 325 μmol, 92%).

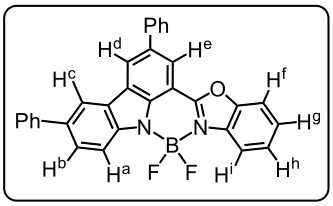
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.39 (d, J = 8.0 Hz, 1H, H^e), 8.19 (d, J = 7.6 Hz, 1H, H^h or H^k), 8.15–8.12 (m, 2H, H^a and H^g), 7.99 (d, J = 8.0 Hz, 1H, H^d), 7.78 (d, J = 8.0 Hz, 1H, H^h or H^k), 7.66–7.57 (m, 3H, H^c, H^i, and H^j), 7.38 (t, J = 7.8 Hz, 1H, H^f), and 7.35 ppm (t, J = 7.6 Hz, 1H, H^b); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 161.79, 149.34, 143.36, 142.91, 131.69, 128.05, 127.52, 127.37, 127.29, 125.34, 124.42, 121.99, 121.00, 119.02, 117.34, 114.27, 111.81, and 101.06 ppm; HR-MS (APCI): m/z = 332.0928. calcd for $C_{19}H_{11}N_2OBF_2$: 332.0941 [M]$^-$.

Synthesis of 4c. **7c** (143 mg, 458 μmol) was dissolved in dry toluene (4 mL). N,N-Diisopropylethylamine (1.0 mL, 5.8 mmol) and then BF_3·OEt_2 (0.30 mL, 2.4 mmol) were added, and the mixture was heated at 100 °C for 5 h under N_2. After the solvents were removed, the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **4c** as a yellow solid (164 mg, 455 μmol, 99%).



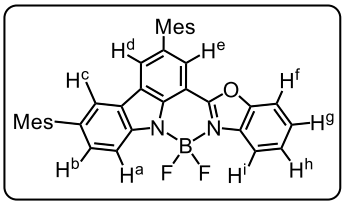
^{1}H NMR ($CDCl_3$) δ = 8.13 (d, J = 6.4 Hz, 1H, H^f or H^i), 8.12 (s, 1H, H^d), 7.87 (s, 1H, H^c), 7.85 (s, 1H, H^e), 7.82 (d, J = 8.4 Hz, 1H, H^a), 7.73 (d, J = 7.6 Hz, 1H, H^f or H^i), 7.60 (dt, J = 1.2, 7.6 Hz, 1H, H^g or H^h), 7.55 (dt, J = 1.4, 8.2 Hz, 1H, H^g or H^h), 7.37 (dd, J = 1.2, 8.4 Hz, 1H, H^b), 2.59 (s, 3H, Me), and 2.54 ppm (s, 3H, Me); ^{13}C NMR ($CDCl_3$) δ = 161.81, 149.34, 142.02, 141.81, 131.84, 130.19, 129.11, 128.77, 128.43, 127.29, 127.10, 125.44, 124.40, 121.85, 120.94, 117.32, 113.78, 111.73, 100.39, and 21.65 ppm; HR-MS (APCI): m/z = 360.1261. calcd for $C_{21}H_{15}N_2OBF_2$: 360.1255 [M]$^-$.

Synthesis of 4d. **7d** (153 mg, 351 μmol) was dissolved in dry toluene (4 mL). N,N-Diisopropylethylamine (1.0 mL, 5.8 mmol) and then BF_3·OEt_2 (0.30 mL, 2.4 mmol) were added, and the mixture was heated at 100 °C for 5 h under N_2. After the solvents were removed, the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **4d** as a yellow solid (128 mg, 264 μmol, 75%).



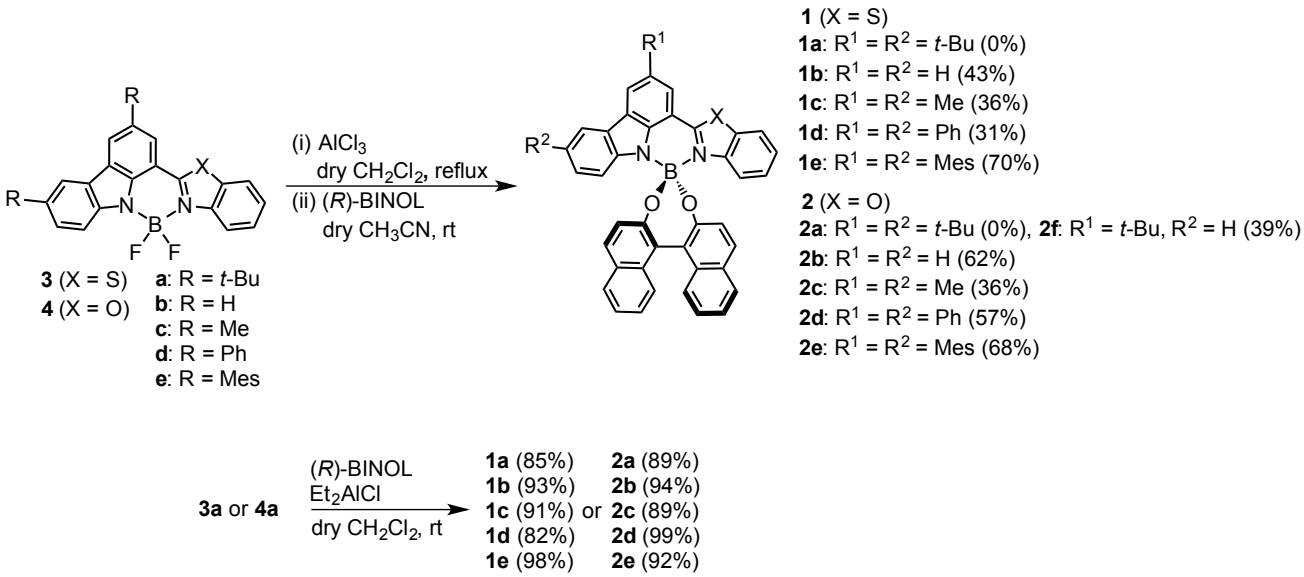
^{1}H NMR ($CDCl_3$) δ = 8.63 (d, J = 1.2 Hz, 1H, H^d), 8.36 (d, J = 2.0 Hz, 1H, H^c), 8.33 (d, J = 1.6 Hz, 1H, H^e), 8.19 (d, J = 8.0 Hz, 1H, H^f or H^i), 8.03 (d, J = 8.0 Hz, 1H, H^a), 7.83 (d, J = 1.6, 8.4 Hz, 1H, H^b), 7.79−7.73 (m, 5H, H^f or H^i, and Ph), 7.64 (dt, J = 1.2, 7.8 Hz, 1H, H^g or H^h), 7.59 (dt, J = 1.4, 7.8 Hz, 1H, H^g or H^h), 7.53 (t, J = 7.6 Hz, 2H, Ph), 7.49 (t, J = 7.8 Hz, 2H, Ph), 7.42 (t, J = 7.4 Hz, 1H, Ph), and 7.36 ppm (t, J = 7.4 Hz, 1H, Ph); ^{13}C NMR ($CDCl_3$) δ = 162.00, 149.66, 143.53, 142.15, 141.03, 134.87, 133.47, 132.02, 129.25, 128.97, 127.58, 127.51, 127.46, 127.39, 127.28, 126.91, 126.34, 125.27, 120.92, 119.69, 117.65, 114.68, 111.88, and 101.51 ppm; HR-MS (APCI): m/z = 484.1569. calcd for $C_{31}H_{19}N_2OBF_2$: 484.1569 [M]$^-$.

Synthesis of 4e. **7e** (204 mg, 392 μmol) was dissolved in dry toluene (4 mL). N,N-Diisopropylethylamine (1.0 mL, 5.8 mmol) and then BF_3·OEt_2 (0.30 mL, 2.4 mmol) were added, and the mixture was heated at 100 °C for 5 h under N_2. After the solvents were removed, the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **4e** as a yellow solid (216 mg, 380 μmol, 97%).

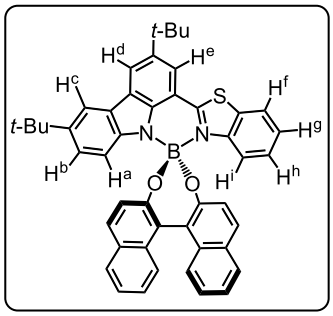


^{1}H NMR ($CDCl_3$) δ = 8.20 (d, J = 8.0 Hz, 1H, H^f or H^i), 8.11 (s, 1H, H^d), 8.04 (d, J = 8.4 Hz, 1H, H^a), 7.93 (d, J = 1.2 Hz, 1H, H^e), 7.85 (d, J = 1.2 Hz, 1H, H^c), 7.77 (d, J = 8.0 Hz, 1H, H^f or H^i), 7.65 (t, J = 7.6 Hz, 1H, H^g or H^h), 7.59 (dt, J = 0.8, 7.6 Hz, 1H, H^g or H^h), 7.37 (dd, J = 1.4, 8.2 Hz, 1H, H^b), 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 = 161.88, 149.44, 142.48, 142.40,

139.55, 138.18, 137.31, 136.75, 136.71, 136.63, 133.95, 132.26, 131.83, 129.44, 129.26, 128.44, 128.20, 127.46, 127.36, 125.90, 124.67, 122.63, 121.56, 117.46, 114.25, 111.85, 101.15, 21.24, and 21.18 ppm; HR-MS (APCI): m/z = 568.2514. calcd for $C_{37}H_{31}N_2OBF_2$: 568.2509 $[M]^-$.



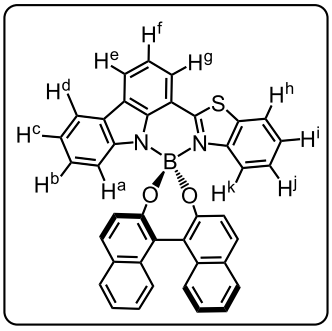
Scheme S2 Synthesis of **1** and **2**.



Synthesis of 1a. To a solution of **3a** (13.1 mg, 31.7 μmol) and (*R*)-BINOL (34.6 mg, 121 μmol) in dry CH_2Cl_2 (10 mL) was added dropwise Et_2AlCl (0.87 M in hexane, 50 μL, 44 μmol) under N_2, and the mixture was stirred at rt for 30 min. After the solvents were removed, and the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **1a** as a yellow solid (19.0 mg, 26.9 μmol, 85%).

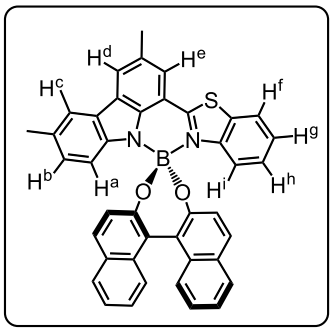
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.37 (d, J = 1.2 Hz, 1H, H^d), 7.96 (d, J = 2.0 Hz, 1H, H^c), 7.90 (d, J = 7.6 Hz, 1H, Np), 7.85 (d, J = 2.0 Hz, 1H, H^e), 7.84 (d, J = 8.0 Hz, 1H, Np), 7.74 (d, J = 6.8 Hz, 1H, H^f), 7.72 (d, J = 8.0 Hz, 1H, Np), 7.61 (d, J = 8.8 Hz, 1H, Np), 7.53–7.49 (m, 3H, H^i and Np), 7.43 (dt, J = 0.8, 7.2 Hz, 1H, Np), 7.39 (dt, J = 0.8, 8.0 Hz, 1H, Np), 7.30 (dt, J = 0.8, 7.2 Hz, 1H, Np), 7.29 (dt, J = 1.2, 7.2 Hz, 1H, Np), 7.17 (t, J = 7.6 Hz, 1H, H^g), 7.14 (d, J = 8.8 Hz, 1H, Np), 6.93 (d, J = 8.8 Hz, 1H, Np), 6.60 (dd, J = 2.2, 8.8 Hz, 1H, H^b), 6.52 (dt, J = 0.8, 7.6 Hz, 1H, H^h), 6.22 (d, J = 8.4 Hz, 1H, H^a), 1.54 (s, 9H, *t*-Bu), and 1.28 ppm (s, 9H, *t*-Bu); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.22, 155.86, 154.95, 145.50, 142.82, 142.72, 142.05, 139.61, 133.84, 133.77, 130.74, 130.25, 130.03, 129.65, 128.89, 128.22, 128.07, 127.43, 127.02, 125.99, 125.93, 125.67, 124.52, 124.44, 124.16, 123.79, 123.65, 122.32, 122.09, 121.64, 121.42, 119.22, 115.92, 115.03, 108.52, 35.08, 34.58, 32.15, and 31.89 ppm; HR-MS (APCI): m/z = 706.2851. calcd for $C_{47}H_{39}N_2O_2SB$: 706.2839 $[M]^-$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 228 (83600), 303 (21800), 326 (22400), and 466 nm (14100 $mol^{-1}dm^3cm^{-1}$).

Synthesis of 1b. A flask containing **3b** (54.5 mg, 157 μmol) and $AlCl_3$ (85.5 mg, 641 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, a solution of (*R*)-BINOL (232 mg, 810 μmol) in dry CH_3CN (5.0 mL) was added, and the mixture was stirred at rt for 6 h. The mixture was passed through basic alumina and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **1b** as a yellow solid (40.4 mg, 68.0 μmol, 43%).



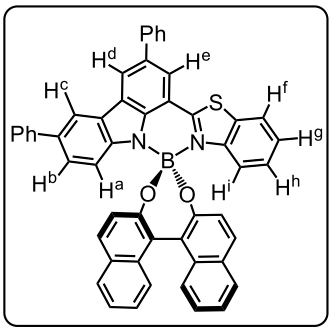
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.29 (dd, *J* = 0.8, 8.8 Hz, 1H, H^e), 7.97 (d, *J* = 8.0 Hz, 1H, H^d), 7.90 (d, *J* = 8.0 Hz, 2H, Np), 7.87 (d, *J* = 8.0 Hz, 1H, H^g), 7.76 (d, *J* = 8.0 Hz, 1H, H^h), 7.71 (d, *J* = 8.8 Hz, 1H, Np), 7.66 (d, *J* = 9.2 Hz, 1H, Np), 7.54–7.49 (m, 3H, Np and H^k), 7.43 (dt, *J* = 1.6, 6.4 Hz, 1H, Np), 7.42 (dt, *J* = 1.2, 6.8 Hz, 1H, Np), 7.33–7.28 (m, 3H, Np and H^f), 7.21 (dt, *J* = 1.2, 7.2 Hz, 1H, H^i), 7.09 (d, *J* = 8.4 Hz, 1H, Np), 7.00 (t, *J* = 7.6 Hz, 1H, H^c), 6.99 (d, *J* = 8.8 Hz, 1H, Np), 6.57 (dt, *J* = 1.0, 7.6 Hz, 1H, H^j), 6.53 (dt, *J* = 0.8, 8.0 Hz, 1H, H^b), and 6.32 ppm (d, *J* = 8.0 Hz, 1H, H^a); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.07, 155.85, 154.98, 145.38, 144.29, 140.46, 133.78, 133.73, 130.78, 130.30, 130.14, 129.82, 129.06, 128.25, 128.12, 127.49, 127.39, 127.19, 126.87, 126.29, 126.24, 125.78, 125.73, 124.09, 123.99, 123.91, 123.79, 123.64, 122.93, 122.50, 122.18, 121.53, 120.08, 120.05, 118.81, 115.74, and 109.44 ppm; HR-MS (APCI): *m*/*z* = 594.1581. calcd for $C_{39}H_{23}N_2O_2SB$: 594.1585 [*M*]$^-$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 225 (102000), 295 (22200), and 452 nm (14500 mol^{-1}dm^{3}cm^{-1}).

Synthesis of 1c. A flask containing **3c** (91.2 mg, 242 μmol) and $AlCl_3$ (124 mg, 930 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, a solution of (*R*)-BINOL (357 mg, 1.25 mmol) in dry CH_3CN (5.0 mL) was added, and the mixture was stirred at rt for 6 h. The mixture was passed through basic alumina and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **1c** as an orange solid (54.2 mg, 87.1 μmol, 36%).



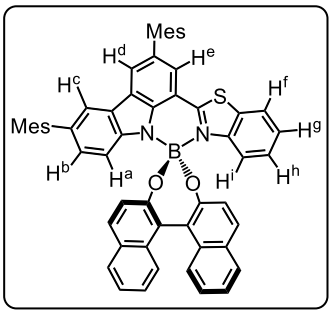
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.07 (s, 1H, H^d), 7.92 (d, *J* = 8.4 Hz, 1H, Np), 7.86 (d, *J* = 7.6 Hz, 1H, Np), 7.74 (d, *J* = 7.2 Hz, 1H, H^f), 7.73 (d, *J* = 9.2 Hz, 1H, Np), 7.73 (s, 1H, H^c), 7.67 (s, 1H, H^e), 7.64 (d, *J* = 8.8 Hz, 1H, Np), 7.52 (d, *J* = 8.4 Hz, 1H, Np), 7.50 (d, *J* = 8.0 Hz, 1H, Np), 7.47 (d, *J* = 8.8 Hz, 1H, H^i), 7.43 (dt, *J* = 1.2, 7.4 Hz, 1H, Np), 7.40 (dt, *J* = 1.6, 7.2 Hz, 1H, Np), 7.32–7.27 (m, 2H, Np), 7.18 (dt, *J* = 0.8, 7.8 Hz, 1H, H^g), 7.12 (d, *J* = 8.8 Hz, 1H, Np), 6.96 (d, *J* = 8.4 Hz, 1H, Np), 6.53 (dt, *J* = 1.0, 7.8 Hz, 1H, H^h), 6.35 (dd, *J* = 1.4, 8.8 Hz, 1H, H^b), 6.10 (d, *J* = 8.8 Hz, 1H, H^a), 2.62 (s, 3H, Me), and 2.31 ppm (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 168.86, 155.98, 155.05, 145.44, 142.74, 139.41, 133.75, 133.70, 130.73, 130.26, 130.12, 129.75, 129.19, 129.01, 128.25, 128.09, 128.05, 127.86, 127.63, 127.46, 127.41, 127.06, 126.02, 125.83, 125.71, 124.06, 123.84, 123.70, 123.67, 122.95, 122.42, 122.17, 121.55, 121.48, 120.01, 115.30, 108.85, 21.61, and 21.32 ppm; HR-MS (APCI): *m*/*z* = 623.1973. calcd for $C_{41}H_{28}N_2O_2SB$: 623.1966 [*M*+H]$^+$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 226 (95300), 304 (22600), 326 (23700), and 472 nm (14400 mol^{-1}dm^{3}cm^{-1}).

Synthesis of 1d. A flask containing **3d** (74.8 mg, 149 μmol) and $AlCl_3$ (78.5 mg, 589 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, a solution of (*R*)-BINOL (213 mg, 744 μmol) in dry CH_3CN (5.0 mL) was added, and the mixture was stirred at rt for 6 h. The mixture was passed through basic alumina and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **1d** as an orange solid (34.4 mg, 46.1 μmol, 31%).



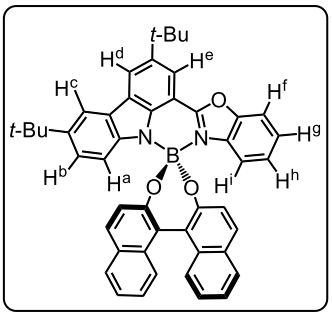
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.56 (d, *J* = 1.6 Hz, 1H, H^d), 8.23 (d, *J* = 2.0 Hz, 1H, H^c), 8.10 (d, *J* = 0.8 Hz, 1H, H^e), 7.91 (d, *J* = 8.0 Hz, 1H, Np), 7.88 (d, *J* = 8.0 Hz, 1H, Np), 7.80–7.76 (m, 3H, H^f and Ph), 7.73 (d, *J* = 8.8 Hz, 1H, Np), 7.68 (d, *J* = 8.8 Hz, 1H, Np), 7.57–7.53 (m, 7H, H^i, Np, and Ph), 7.47–7.28 (m, 8H, Np and Ph), 7.23 (t, *J* = 7.4 Hz, 1H, H^g), 7.15 (d, *J* = 8.8 Hz, 1H, Np), 7.01 (d, *J* = 8.8 Hz, 1H, Np), 6.81 (dd, *J* = 2.0, 8.8 Hz, 1H, H^b), 6.59 (dt, *J* = 0.8, 7.6 Hz, 1H, H^h), and 6.32 ppm (d, *J* = 8.8 Hz, 1H, H^a); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 168.92, 155.79, 154.89, 145.44, 144.26, 141.87, 141.17, 140.44, 133.76, 133.71, 133.50, 133.00, 130.82, 130.32, 130.29, 129.88, 129.21, 129.11, 128.76, 128.35, 128.14, 127.54, 127.49, 127.38, 127.35, 127.30, 126.60, 126.44, 126.36, 126.02, 126.00, 125.86, 125.83, 124.79, 124.01, 123.95, 123.83, 123.60, 122.54, 122.23, 121.91, 121.61, 121.58, 118.67, 115.98, and 109.70 ppm; HR-MS (APCI): *m*/*z* = 746.2249. calcd for $C_{51}H_{31}N_2O_2SB$: 746.2213 $[M]^-$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 223 (87600), 307 (40800), and 476 nm (14200 $mol^{-1}dm^3cm^{-1}$).

Synthesis of 1e. A flask containing **3e** (89.8 mg, 154 μmol) and $AlCl_3$ (79.2 mg, 594 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, a solution of (*R*)-BINOL (214 mg, 747 μmol) in dry CH_3CN (5.0 mL) was added, and the mixture was stirred at rt for 6 h. The mixture was passed through basic alumina and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **1e** as yellow solid (89.8 mg, 108 μmol, 70%).



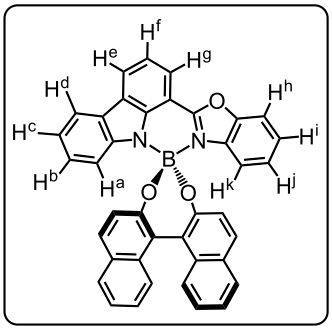
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.01 (d, *J* = 0.8 Hz, 1H, H^d), 7.91 (d, *J* = 8.0 Hz, 1H, Np), 7.82 (d, *J* = 8.4 Hz, 1H, Np), 7.80 (d, *J* = 7.6 Hz, 1H, H^f), 7.74 (d, *J* = 8.8 Hz, 1H, Np), 7.69 (d, *J* = 0.8 Hz, 1H, H^e), 7.65 (d, *J* = 1.2 Hz, 1H, H^c), 7.61 (d, *J* = 8.4 Hz, 1H, Np), 7.57 (d, *J* = 8.4 Hz, 2H, H^i and Np), 7.51 (d, *J* = 8.4 Hz, 1H, Np), 7.43 (dt, *J* = 0.8, 7.6 Hz, 1H, Np), 7.36 (dt, *J* = 1.4, 7.6 Hz, 1H, Np), 7.33–7.25 (m, 3H, Np and H^g), 7.11 (d, *J* = 8.8 Hz, 1H, Np), 7.06 (d, *J* = 8.4 Hz, 1H, Np), 7.05 (s, 2H, Mes), 6.93 (s, 1H, Mes), 6.87 (s, 1H, Mes), 6.70 (dt, *J* = 0.8, 8.0 Hz, 1H, H^h), 6.35 (d, *J* = 8.8 Hz, 1H, H^a), 6.20 (dd, *J* = 1.6, 8.8 Hz, 1H, H^b), 2.40 (s, 3H, Me), 2.31 (s, 3H, Me), 2.15 (s, 3H, Me), 2.11 (s, 3H, Me), 1.97 (s, 3H, Me), and 1.85 ppm (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 168.89, 155.73, 154.98, 145.35, 143.44, 139.77, 139.58, 138.47, 137.33, 136.97, 136.88, 136.73, 136.60, 136.39, 133.85, 133.78, 132.72, 131.80, 130.97, 130.23, 130.05, 129.82, 129.20, 128.46, 128.42, 128.21, 128.14, 128.07, 128.00, 127.95, 127.84, 127.59, 127.39, 127.25, 126.35, 126.15, 125.80, 125.78, 124.01, 123.83, 123.53, 122.57, 122.51, 121.64, 121.41, 120.25, 115.51, 109.54, 21.30, 21.25, 21.14, and 20.91 ppm; HR-MS (APCI): *m*/*z* = 830.3184. calcd for $C_{57}H_{43}N_2O_2SB$: 830.3153 $[M]^-$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 223 (102000), 303 (26300), 327 (23900), and 468 nm (14800 $mol^{-1}dm^3cm^{-1}$).

Synthesis of 2a. To a solution of **4a** (80.0 mg, 180 μmol) and (*R*)-BINOL (308 mg, 1.08 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise Et_2AlCl (0.87 M in hexane, 0.32 mL, 278 μmol) under N_2, and the mixture was stirred at rt for 30 min. After the solvents were removed, and the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **2a** as a yellow solid (111 mg, 161 μmol, 89%).



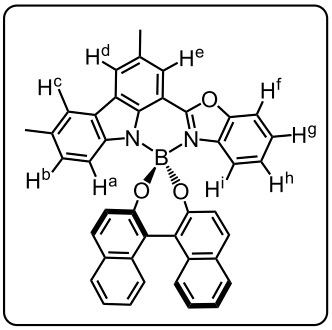
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.44 (d, J = 1.6 Hz, 1H, H^d), 8.15 (d, J = 2.0 Hz, 1H, H^e), 8.01 (d, J = 2.0 Hz, 1H, H^c), 7.95 (d, J = 8.4 Hz, 1H, Np), 7.87 (d, J = 8.4 Hz, 1H, Np), 7.79 (d, J = 8.4 Hz, 1H, Np), 7.66 (d, J = 8.8 Hz, 1H, Np), 7.61 (d, J = 8.4 Hz, 1H, H^f), 7.52 (d, J = 8.8 Hz, 1H, Np), 7.50 (d, J = 8.0 Hz, 1H, Np), 7.44 (dt, J = 0.8, 7.6 Hz, 1H, Np), 7.41 (t, J = 1.2, 8.0 Hz, 1H, Np), 7.31 (t, J = 7.8 Hz, 2H, Np), 7.22 (d, J = 8.8 Hz, 1H, H^g), 7.20 (d, J = 9.2 Hz, 1H, Np), 7.02 (d, J = 8.8 Hz, 1H, Np), 6.79 (dd, J = 2.0, 8.8 Hz, 1H, H^b), 6.64 (dt, J = 0.8, 8.0 Hz, 1H, H^h), 6.35 (d, J = 8.4 Hz, 1H, H^i), 6.23 (d, J = 8.8 Hz, 1H, H^a), 1.56 (s, 9H, *t*-Bu), and 1.31 ppm (s, 9H, *t*-Bu); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.34, 155.19, 154.86, 149.05, 142.97, 142.55, 142.45, 142.02, 133.52, 133.48, 132.72, 130.61, 130.44, 129.97, 129.68, 128.31, 128.17, 127.47, 127.43, 126.26, 126.09, 125.77, 125.64, 125.11, 124.76, 124.21, 124.04, 123.81, 123.76, 123.61, 122.40, 122.06, 118.95, 118.22, 116.19, 115.09, 110.89, 100.57, 35.19, 34.68, 32.17, and 31.96 ppm; HR-MS (APCI): m/z = 690.3069. calcd for $C_{47}H_{39}N_2O_3B$: 690.3067 [M]$^-$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 228 (73200), 290 (24300), 310 (25600), and 438 nm (12700 mol^{-1}dm^{3}cm^{-1}).

Synthesis of 2b. A flask containing **4b** (80.9 mg, 167 μmol) and $AlCl_3$ (89.1 mg, 668 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, a solution of (*R*)-BINOL (242 mg, 845 μmol) in dry CH_3CN (5.0 mL) was added, and the mixture was stirred at rt for 6 h. The mixture was passed through basic alumina and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **2b** as a yellow solid (60.2 mg, 104 μmol, 62%).



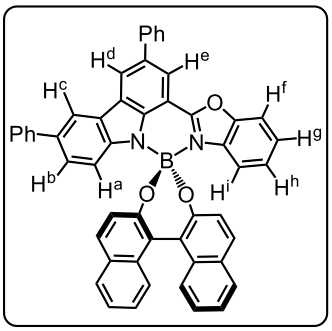
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.37 (dd, J = 1.0, 8.0 Hz, 1H, H^e), 8.15 (dd, J = 1.0, 8.0 Hz, 1H, H^g), 8.02 (d, J = 8.0 Hz, 1H, H^d), 7.94 (d, J = 8.0 Hz, 1H, Np), 7.91 (d, J = 8.0 Hz, 1H, Np), 7.76 (d, J = 8.4 Hz, 1H, Np), 7.71 (d, J = 8.8 Hz, 1H, Np), 7.63 (d, J = 8.4 Hz, 1H, H^h), 7.55 (d, J = 9.2 Hz, 1H, Np), 7.52 (d, J = 9.6 Hz, 1H, Np), 7.45 (dt, J = 1.2, 8.0 Hz, 1H, Np), 7.44 (dt, J = 1.2, 8.0 Hz, 1H, Np), 7.38 (t, J = 7.6 Hz, 1H, H^f), 7.34–7.25 (m, 3H, Np and H^i), 7.13 (d, J = 8.8 Hz, 1H, Np), 7.10 (d, J = 8.4 Hz, 1H, Np), 7.06 (t, J = 8.0 Hz, 1H, H^c), 6.70 (t, J = 8.0 Hz, 2H, H^b and H^j), 6.34 (d, J = 8.0 Hz, 1H, H^k), and 6.33 ppm (d, J = 8.4 Hz, 1H, H^a); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.07, 155.05, 154.81, 149.12, 144.01, 143.33, 133.47, 133.43, 132.51, 130.66, 130.45, 130.06, 129.79, 128.31, 128.21, 127.58, 127.47, 127.37, 126.59, 126.27, 125.87, 125.76, 125.51, 124.41, 123.94, 123.88, 123.84, 123.55, 122.34, 122.11, 121.87, 120.23, 120.21, 119.09, 118.74, 115.81, 111.06, and 101.59 ppm; HR-MS (APCI): m/z = 578.1816. calcd for $C_{39}H_{23}N_2O_3B$: 578.1814 [M]$^-$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 226 (83100), 286 (26500), 307 (26000), 338 (13400), and 424 nm (12700 mol^{-1}dm^{3}cm^{-1}).

Synthesis of 2c. A flask containing **4c** (79.2 mg, 220 μmol) and $AlCl_3$ (118 mg, 885 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, a solution of (*R*)-BINOL (312 mg, 1.09 mmol) in dry CH_3CN (5.0 mL) was added, and the mixture was stirred at rt for 6 h. The mixture was passed through basic alumina and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **2c** as a yellow solid (47.9 mg, 79.0 μmol, 36%).



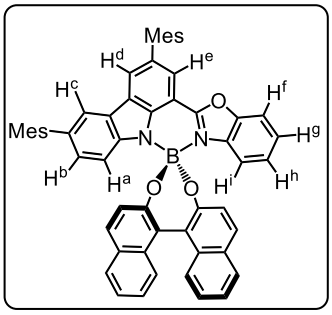
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.14 (d, J = 0.8 Hz, 1H, H^d), 7.94 (d, J = 8.8 Hz, 1H, Np), 7.93 (s, 1H, H^e), 7.89 (d, J = 8.0 Hz, 1H, Np), 7.78 (d, J = 9.2 Hz, 1H, Np), 7.77 (s, 1H, H^c), 7.70 (d, J = 8.8 Hz, 1H, Np), 7.60 (d, J = 8.4 Hz, 1H, H^f), 7.53 (d, J = 9.2 Hz, 1H, Np), 7.51 (d, J = 9.2 Hz, 1H, Np), 7.44 (dt, J = 1.0, 6.6 Hz, 1H, Np), 7.42 (dt, J = 1,6, 6.8 Hz, 1H, Np), 7.31 (dt, J = 1.6, 7.0 Hz, 2H, Np), 7.25 (dt, J = 1.2, 8.4 Hz, 1H, H^g), 7.15 (d, J = 8.4 Hz, 1H, Np), 7.07 (d, J = 8.8 Hz, 1H, Np), 6.68 (dt, J = 0.8, 7.6 Hz, 1H, H^h), 6.51 (dd, J = 1.6, 8.8 Hz, 1H, H^b), 6.31 (d, J = 8.0 Hz, 1H, H^i), 6.12 (d, J = 8.8 Hz, 1H, H^a), 2.65 (s, 3H, Me), and 2.35 ppm (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.07, 155.16, 154.85, 149.09, 142.44, 142.36, 133.45, 133.41, 132.60, 130.60, 130.40, 130.02, 129.72, 129.30, 128.55, 128.30, 128.19, 128.03, 127.89, 127.45, 127.38, 126.36, 126.14, 125.81, 125.69, 125.57, 124.38, 123.90, 123.86, 123.81, 123.59, 122.32, 122.13, 121.73, 120.20, 119.01, 115.32, 110.95, 100.89, 21.66, and 21.36 ppm; HR-MS (APCI): m/z = 606.2146. calcd for $C_{41}H_{27}N_2O_3B$: 606.2127 [M]$^-$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 226 (57200), 292 (21600), 312 (22500), and 443 nm (11400 mol^{-1}dm^{3}cm^{-1}).

Synthesis of 2d. A flask containing **4d** (80.8 mg, 167 μmol) and $AlCl_3$ (85.7 mg, 643 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, a solution of (*R*)-BINOL (239 mg, 835 μmol) in dry CH_3CN (5.0 mL) was added, and the mixture was stirred at rt for 6 h. The mixture was passed through basic alumina and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **2d** as a yellow solid (69.6 mg, 95.3 μmol, 57%).



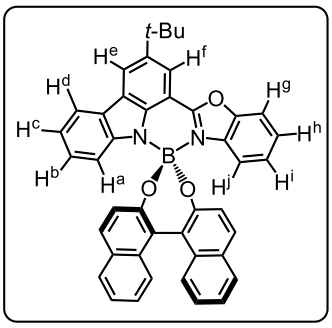
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.65 (d, J = 1.6 Hz, 1H, H^d), 8.39 (d, J = 1.2 Hz, 1H, H^e), 8.29 (d, J = 1.2 Hz, 1H, H^c), 7.97 (d, J = 8.4 Hz, 1H, Np), 7.92 (d, J = 8.0 Hz, 1H, Np), 7.82–7.80 (m, 3H, Np and Ph), 7.74 (d, J = 8.8 Hz, 1H, Np), 7.64 (d, J = 8.4 Hz, 1H, H^f), 7.59–7.53 (m, 6H, Np and Ph), 7.49–7.28 (m, 9H, Np, Ph, and H^g), 7.22 (d, J = 8.8 Hz, 1H, Np), 7.13 (d, J = 8.4 Hz, 1H, Np), 7.00 (dd, J = 1.6, 8.8 Hz, 1H, H^b), 6.72 (t, J = 7.8 Hz, 1H, H^h), 6.38 (d, J = 8.0 Hz, 1H, H^i), and 6.37 ppm (d, 1H, J = 8.8 Hz, H^a); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 161.93, 154.99, 154.71, 149.15, 143.96, 143.23, 141.80, 140.96, 133.62, 133.45, 133.40, 132.81, 132.49, 130.67, 130.46, 130.16, 129.83, 129.18, 128.76, 128.38, 128.22, 127.43, 127.37, 127.31, 126.68, 126.64, 126.57, 126.33, 126.18, 125.90, 125.83, 125.10, 123.97, 123.81, 123.49, 122.32, 122.17, 120.73, 119.08, 118.81, 116.01, 111.11, and 101.87 ppm; HR-MS (APCI): m/z = 730.2471. calcd for $C_{51}H_{31}N_2O_3B$: 730.2442 [M]$^-$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 225 (87100), 264 (53400), 299 (59300), and 448 nm (14600 mol^{-1}dm^{3}cm^{-1}).

Synthesis of 2e. A flask containing **4e** (86.5 mg, 152 μmol) and $AlCl_3$ (83.9 mg, 629 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, a solution of (*R*)-BINOL (221 mg, 772 μmol) in dry CH_3CN (5.0 mL) was added, and the mixture was stirred at rt for 6 h. The mixture was passed through basic alumina and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **2e** as a yellow solid (83.8 mg, 103 μmol, 68%).



^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.08 (d, *J* = 1.6 Hz, 1H, H^d), 7.95 (d, *J* = 1.2 Hz, 1H, H^e), 7.93 (d, *J* = 8.0 Hz, 1H, Np), 7.87 (d, *J* = 8.0 Hz, 1H, Np), 7.77 (d, *J* = 8.8 Hz, 1H, Np), 7.71 (s, 1H, H^c), 7.70 (d, *J* = 8.4 Hz, 1H,Np), 7.63 (d, *J* = 8.4 Hz, 1H, H^f), 7.58 (d, *J* = 8.4 Hz, 1H, Np), 7.52 (d, *J* = 8.8 Hz, 1H, Np), 7.45 (dt, *J* = 1.2, 8.0 Hz, 1H, Np), 7.39 (dt, *J* = 1.2, 7.2 Hz, 1H, Np), 7.35–7.27 (m, 3H, Np and H^g), 7.18 (d, *J* = 8.4 Hz, 1H, Np), 7.15 (d, *J* = 8.8 Hz, 1H, Np), 7.05 (s, 2H, Mes), 6.95 (s, 1H, Mes), 6.88 (s, 1H, Mes), 6.79 (dt, *J* = 1.0, 8.0 Hz, 1H, H^h), 6.47 (d, *J* = 8.4 Hz, 1H, H^i), 6.40 (dd, *J* = 1.8, 8.6 Hz, 1H, H^b), 6.33 (d, *J* = 8.4 Hz, 1H, H^a), 2.40 (s, 3H, Me), 2.31 (s, 3H, Me), 2.14 (s, 3H, Me), 2.11 (s, 3H, Me), 2.03 (s, 3H, Me), and 1.86 ppm (s, 3H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.04, 154.95, 154.77, 149.19, 143.12, 142.66, 139.52, 138.41, 137.21, 136.82, 136.78, 136.62, 136.40, 133.49, 132.89, 132.52, 131.83, 130.80, 130.40, 129.98, 129.76, 128.84, 128.42, 128.40, 128.23, 128.20, 128.06, 127.98, 127.51, 127.26, 126.63, 126.36, 125.94, 125.88, 125.77, 124.41, 123.93, 123.58, 122.46, 122.32, 122.27, 120.50, 119.09, 115.65, 111.12, 101.62, 21.26, 21.21, 21.14, 21.06, and 20.95 ppm; HR-MS (APCI): *m*/*z* = 814.3373. calcd for $C_{57}H_{43}N_2O_3B$: 814.3382 [*M*]$^-$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 226 (90300), 236 (90400), 293 (31600), 310 (27900), and 439 nm (12700 $mol^{-1}dm^3cm^{-1}$).

Synthesis of 2f. A flask containing **4a** (108 mg, 243 μmol) and $AlCl_3$ (145 mg, 1.09 mmol) was purged with N_2, charged with dry CH_2Cl_2 (10 mL), and heated at reflux for 10 min. After cooling to rt, a solution of (*R*)-BINOL (460 mg, 1.61 mmol) in dry CH_3CN (5.0 mL) was added, and the mixture was stirred at rt for 6 h. The mixture was passed through basic alumina and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **2f** as a yellow solid (59.7 mg, 94.1 μmol, 39%).



^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.45 (d, *J* = 1.2 Hz, 1H, H^e), 8.19 (d, *J* = 1.2 Hz, 1H, H^f), 8.02 (d, *J* = 8.0 Hz, 1H, H^d), 7.92 (d, *J* = 8.4 Hz, 1H, Np), 7.89 (d, *J* = 8.4 Hz, 1H, Np), 7.75 (d, *J* = 8.8 Hz, 1H, Np), 7.69 (d, *J* = 9.2 Hz, 1H, Np), 7.63 (d, *J* = 8.0 Hz, 1H, H^g), 7.54 (d, *J* = 9.2 Hz, 1H, Np), 7.51 (d, *J* = 10 Hz, 1H, Np), 7.44 (t, *J* = 7.4 Hz, 1H, Np), 7.43 (t, *J* = 7.2 Hz, 1H, Np), 7.33–7.23 (m, 3H, Np and H^h), 7.13 (d, *J* = 8.8 Hz, 1H, Np), 7.08 (d, *J* = 8.4 Hz, 1H, Np), 7.04 (t, *J* = 7.6 Hz, 1H, H^c), 6.69 (t, *J* = 7.8 Hz, 2H, H^b and H^i), 6.41 (d, *J* = 8.4 Hz, 1H, H^j), 6.35 (d, *J* = 8.0 Hz, 1H, H^a), and 1.57 ppm (s, 9H, *t*-Bu); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.25, 155.11, 154.84, 149.09, 144.38, 142.27, 142.12, 133.47, 133.44, 132.61, 130.64, 130.41, 130.00, 129.73, 128.29, 128.19, 127.46, 127.37, 126.43, 126.40, 126.19, 125.82, 125.70, 125.40, 125.27, 124.53, 123.88, 123.82, 123.59, 122.33, 122.15, 120.10, 119.96, 119.03, 118.56, 115.75, 110.96, 100.75, 35.18, and 32.14 ppm; HR-MS (APCI): *m*/*z* = 634.2421. calcd for $C_{43}H_{31}N_2O_3B$: 634.2440 [*M*]$^-$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 228 (69100), 288 (24000), 309 (24900), 338 (13500), and 432 nm (12700 $mol^{-1}dm^3cm^{-1}$).

Synthesis of 1b–e and 2b–e via the Et_2AlCl-mediated reaction

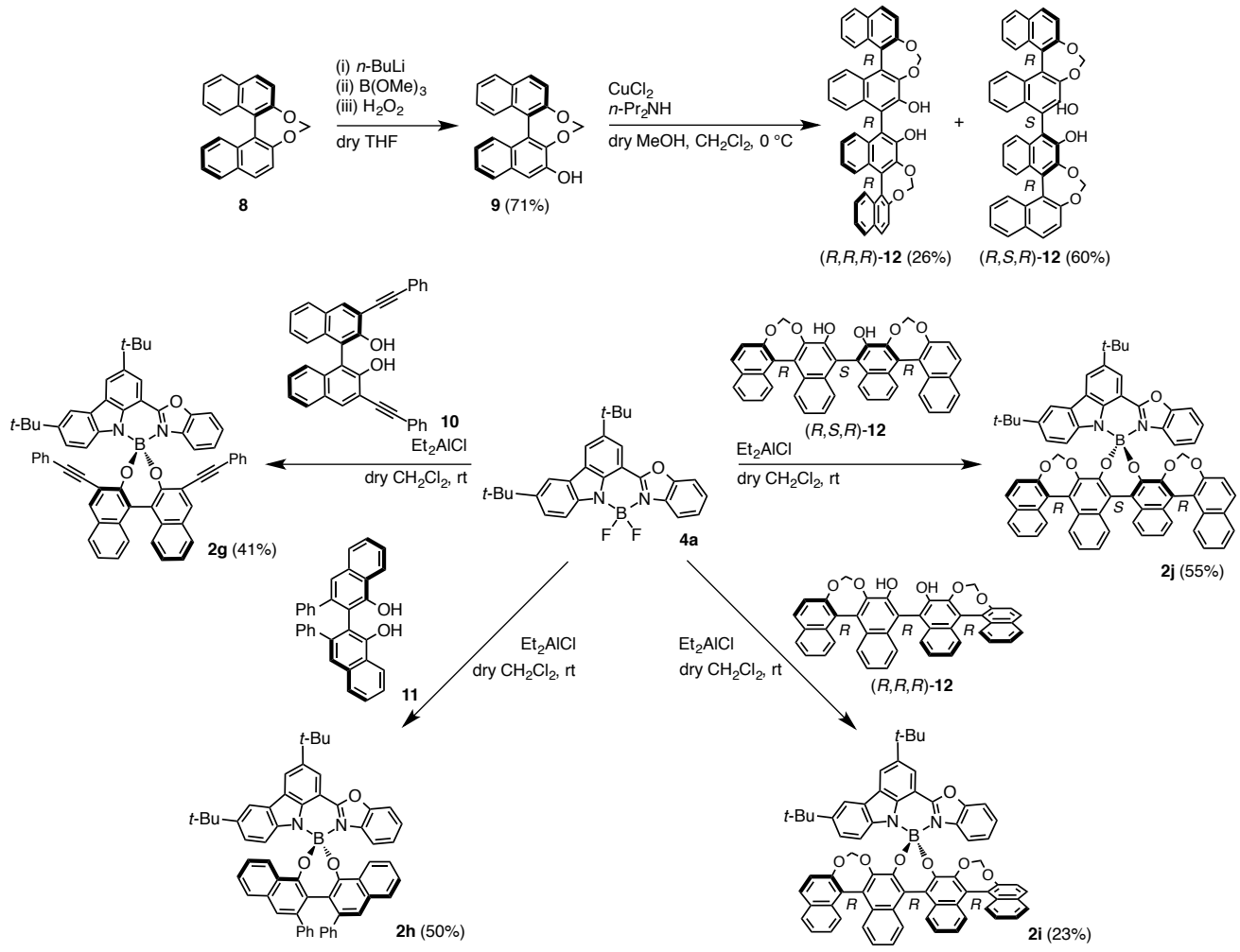
The reactions were performed via a method similar to the synthesis of **1a** and **2a**.

1b: yellow solid (16.0 mg, 26.9 μmol, 93%) **2b**: yellow solid (23.9 mg, 41.3 μmol, 95%)

1c: orange solid (15.1 mg, 24.3 μmol, 91%) **2c**: yellow solid (15.7 mg, 25.9 μmol, 89%)

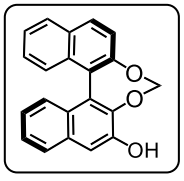
1d: orange solid (17.8 mg, 23.8 μmol, 82%) **2d**: yellow solid (20.9 mg, 28.6 μmol, 99%)

1e: yellow solid (24.2 mg, 29.1 μmol, 98%) **2e**: yellow solid (21.1 mg, 25.9 μmol, 92%)



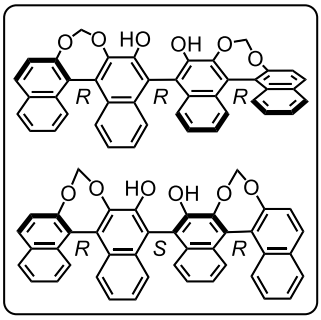
Scheme S3 Synthesis of **2g**–**j**.

Synthesis of 9. To a solution of **8** (1.52 g, 5.09 mmol) in dry THF (15 mL) was added dropwise *n*-BuLi (1.6 M in hexane, 4.85 mL, 7.76 mmol) at –78 °C under N_2. The solution was stirred at 0 °C for 1.5 h. $B(OMe)_3$ (1.20 mL, 10.8 mmol) was added to the solution at –78 °C, and the reaction mixture was stirred at rt for 18 h. H_2O_2 (30 wt% solution in water, 1.60 mL) was added at 0 °C, and the solution was heated at reflux for 6 h. The reaction mixture was poured into the mixed solvent of $CHCl_3$ and saturated aqueous Na_2SO_3. The organic layer was separated, washed successively with water and brine, dried over Na_2SO_4, and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$ to give **9** as a reddish brown solid (1.08 g, 3.44 mmol, 71%).



^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.00 (d, J = 8.8 Hz, 1H, Np), 7.95 (d, J = 8.0 Hz, 1H, Np), 7.81 (dd, J = 1.4, 8.6 Hz, 1H, Np), 7.54 (d, J = 8.8 Hz, 1H, Np), 7.50–7.39 (m, 5H, Np), 7.33 (dt, J = 1.2, 8.0 Hz, 1H, Np), 7.16 (dt, J = 1.4, 8.0 Hz, 1H, Np), 5.90 (s, 1H, OH), and 5.75 ppm (ABq, $\Delta\nu$ = 7.3 Hz, J = 3.2 Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 151.25, 147.01, 140.49, 132.57, 132.22, 132.04, 130.80, 128.55, 127.32, 127.13, 127.05, 126.92, 126.43, 126.32, 126.07, 125.80, 123.81, 120.71, 111.19, and 102.98 ppm; HR-MS (ESI): m/z = 313.0866. calcd for $C_{21}H_{13}O_3$: 313.0865 [M–H]$^-$.

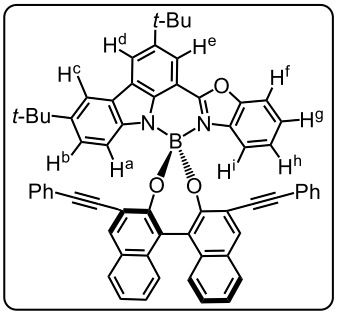
Synthesis of 12. A suspension of $CuCl_2$ (8.79 g, 65.4 mmol) in dry MeOH (120 mL) and n-Pr_2NH (12.5 mL, 91.4 mmol) was stirred at 0 °C under Ar. After 1 h, a solution of **9** (2.05 g, 6.52 mmol) in dry CH_2Cl_2 (120 mL) was added, and the reaction mixture was stirred at rt for 2.5 h. The reaction mixture was poured into a mixed solvent of 0.1 M HCl and $CHCl_3$. The aqueous layer was extracted with $CHCl_3$. The organic layer was combined, washed with water (twice) and brine, dried over Na_2SO_4, and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane/EtOAc to give (*R*,*R*,*R*)-**12** as a yellow solid (1.05 g, 1.68 mmol, 26%) and (*R*,*S*,*R*)-**12** as a yellow solid (2.43 g, 3.88 mmol, 60%). The synthetic methods for **12** were referred to [S5].



(*R*,*R*,*R*)-**12**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.06 (d, J = 8.8 Hz, 2H, Np), 7.99 (d, J = 8.4 Hz, 2H, Np), 7.74 (d, J = 8.8 Hz, 2H, Np), 7.60–7.55 (m, 4H, Np), 7.51 (dt, J = 1.6, 7.6 Hz, 2H, Np), 7.44 (d, J = 8.8 Hz, 2H, Np), 7.38 (dt, J = 1.2, 7.2 Hz, 2H, Np), 7.31 (dt, J = 1.2, 7.4 Hz, 2H, Np), 7.21 (dt, J = 1.0, 7.8 Hz, 2H, Np), 5.97 (s, 2H, OH), and 5.85 ppm (ABq, $\Delta\nu$ = 8.6 Hz, J = 3.2 Hz, 4H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 151.49, 145.45, 140.63, 132.38, 132.12, 131.80, 130.96, 128.57, 127.45, 127.36, 127.29, 127.15, 126.45, 126.35, 126.13, 125.65, 125.50, 124.14, 120.83, 115.94, and 103.26 ppm; HR-MS (ESI): m/z = 649.1604. calcd for $C_{42}H_{26}O_6Na$: 649.1622 [M+Na]$^+$.

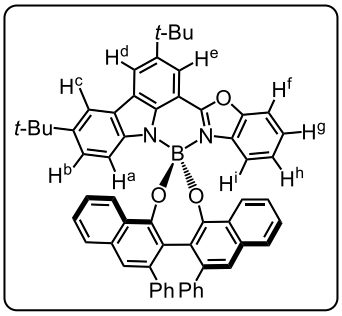
(*R*,*S*,*R*)-**12**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.06 (d, J = 8.4 Hz, 2H, Np), 8.00 (d, J = 8.4 Hz, 2H, Np), 7.76 (d, J = 8.0 Hz, 2H, Np), 7.59–7.42 (m, 10H, Np), 7.32 (t, J = 8.4 Hz, 2H, Np), 7.20 (t, J = 8.4 Hz, 2H, Np), 5.91 (s, 2H, OH), and 5.83 ppm (ABq, $\Delta\nu$ = 26.6 Hz, J = 3.2 Hz, 4H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 151.43, 145.75, 140.62, 132.31, 132.00, 131.85, 130.85, 128.58, 127.28, 127.22, 127.18, 127.00, 126.51, 126.19, 126.04, 125.48, 125.42, 124.07, 120.90, 116.21, and 103.02 ppm; HR-MS (ESI): m/z = 649.1609. calcd for $C_{42}H_{26}O_6Na$: 649.1622 [M+Na]$^+$.

Synthesis of 2g. To a solution of **4a** (92.9 mg, 209 μmol) and **10** (311 mg, 639 μmol) in dry CH_2Cl_2 (10 mL) was added dropwise Et_2AlCl (0.87 M in hexane, 0.36 mL, 313 μmol) under N_2, and the mixture was stirred at rt for 30 min. The solvents were removed, and the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **2g** as a yellow solid (76.8 mg, 86.2 μmol, 41%).



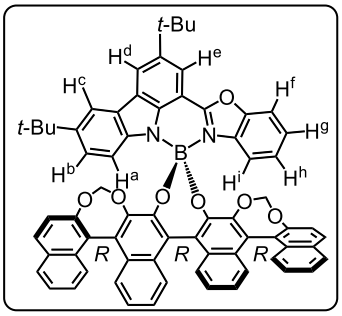
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.44 (d, J = 1.6 Hz, 1H, H^d), 8.13 (s, 1H, Np), 8.02 (d, J = 2.0 Hz, 1H, H^e), 7.95 (d, J = 2.0 Hz, 1H, H^e), 7.93 (d, J = 8.8 Hz, 1H, Np), 7.83 (s, 1H, Np), 7.78 (d, J = 8.4 Hz, 1H, Np), 7.54 (d, J = 8.0 Hz, 1H, H^f), 7.48–7.39 (m, 4H, Np and Ph), 7.31 (t, J = 7.2 Hz, 2H, Np), 7.21–7.14 (m, 2H, H^g and Np), 7.06–7.03 (m, 3H, Np and Ph), 6.97–6.92 (m, 3H, H^b and Ph), 6.83 (dd, J = 1.6, 7.6 Hz, 2H, Ph), 6.63–6.54 (m, 5H, H^a, H^h, H^i, and Ph), 1.52 (s, 9H, *t*-Bu), and 1.33 ppm (s, 9H, *t*-Bu); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.43, 154.89, 154.54, 148.90, 142.86, 142.74, 141.68, 133.62, 133.52, 133.45, 133.08, 132.94, 131.38, 129.96, 129.88, 128.17, 128.13, 128.04, 127.85, 127.76, 127.52, 127.44, 127.16, 126.52, 126.38, 125.97, 125.68, 125.03,

124.70, 124.41, 124.39, 124.12, 123.72, 123.32, 122.93, 122.20, 119.23, 118.71, 118.51, 117.89, 116.09, 115.02, 110.67, 100.52, 92.76, 92.63, 87.20, 86.63, 35.13, 34.68, 32.21, and 32.01 ppm; HR-MS (APCI): *m*/*z* = 890.3704. calcd for $C_{63}H_{47}N_2O_3B$: 890.3695 [*M*]$^-$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 234 (68400), 257 (61100), 277 (62900), 310 (51200), and 438 nm (12300 mol^{-1}dm^{3}cm^{-1}).



Synthesis of 2h. To a solution of **4a** (71.4 mg, 161 μmol) and (*R*)-VANOL (**11**) (281 mg, 641 μmol) in dry CH_2Cl_2 (10 mL) was added dropwise Et_2AlCl (0.87 M in hexane, 0.28 mL, 240 μmol) under N_2, and the mixture was stirred at rt for 30 min. The solvents were removed, and the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **2h** as a yellow solid (68.3 mg, 81.0 μmol, 50%).

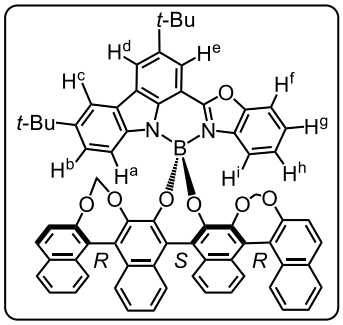
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.28 (d, *J* = 1.6 Hz, 1H, H^d), 8.00 (d, *J* = 8.4 Hz, 1H, Np), 7.95 (d, *J* = 1.6 Hz, 1H, H^c), 7.91 (s, 1H, Np), 7.85 (d, *J* = 8.0 Hz, 1H, Np), 7.70 (d, *J* = 1.2 Hz, 1H, H^e), 7.65 (s, 1H, Np), 7.56 (d, *J* = 8.4 Hz, 1H, Np), 7.50 (d, *J* = 8.4 Hz, 2H, H^f and Np), 7.46 (t, *J* = 7.6 Hz, 1H, Np), 7.40 (d, *J* = 7.4 Hz, 1H, Np), 7.32 (dt, *J* = 0.8, 8.4 Hz, 1H, Np), 7.30 (dt, *J* = 1.2, 8.2 Hz, 1H, Np), 7.25–7.21 (m, 3H, H^g and Ph), 6.97–6.81 (m, 9H, H^b and Ph), 6.65 (t, *J* = 7.8 Hz, 1H, H^h), 6.60 (d, *J* = 7.6 Hz, 1H, H^i), 6.53 (d, *J* = 8.8 Hz, 1H, H^a), 1.50 (s, 9H, *t*-Bu), and 1.36 ppm (s, 9H, *t*-Bu); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 161.64, 152.48, 152.25, 148.81, 142.73, 142.60, 142.43, 141.34, 138.88, 138.19, 136.02, 135.57, 133.59, 133.48, 132.77, 130.60, 130.28, 130.04, 129.67, 129.24, 128.34, 128.28, 127.44, 127.18, 127.05, 126.45, 126.16, 125.86, 125.67, 125.60, 125.55, 125.41, 124.54, 124.42, 124.16, 123.04, 123.87, 122.85, 118.46, 117.90, 115.85, 114.79, 110.48, 100.15, 35.03, 34.68, 32.13, and 32.02 ppm; HR-MS (APCI): *m*/*z* = 842.3685. calcd for $C_{59}H_{47}N_2O_3B$: 842.3695 [*M*]$^-$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 235 (54100), 256 (58500), 291 (20600), 313 (20200), and 438 nm (10200 mol^{-1}dm^{3}cm^{-1}).



Synthesis of 2i. To a solution of **4a** (90.0 mg, 203 μmol) and (*R*,*R*,*R*)-**12** (400 mg, 638 μmol) in dry CH_2Cl_2 (10 mL) was added dropwise Et_2AlCl (0.87 M in hexane, 0.35 mL, 305 μmol) under N_2, and the mixture was stirred at rt for 30 min. The solvents were removed, and the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **2i** as a yellow solid (48.7 mg, 47.2 μmol, 23%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.35 (d, *J* = 1.6 Hz, 1H, H^d), 8.05 (d, *J* = 1.6 Hz, 1H, H^e), 7.94–7.87 (m, 5H, Np and H^c), 7.84–7.81 (m, 1H, Np), 7.72–7.69 (m, 1H, Np), 7.67 (dd, *J* = 1.2, 8.4 Hz, 1H, Np), 7.64–7.62 (m, 1H, Np), 7.56 (dd, *J* = 1.6, 8.0 Hz, 1H, Np), 7.50–7.43 (m, 3H, Np), 7.41 (d, *J* = 8.8 Hz, 1H, Np), 7.40 (d, *J* = 8.4 Hz, 1H, H^f), 7.36–7.34 (m, 3H, Np), 7.30–7.23 (m, 4H, Np), 7.14–7.09 (m, 1H, H^g), 6.92 (dd, *J* = 1.8, 8.6 Hz, 1H, H^b), 6.88–6.86 (m, 2H, H^h and H^i), 6.69 (d, *J* = 8.8 Hz, 1H, H^a), 5.63 (d, *J* = 3.2 Hz, 1H, CH_2), 5.48 (d, *J* = 4.0 Hz, 1H, CH_2), 5.45 (d, *J* = 3.2 Hz, 1H, CH_2), 5.22 (d, *J* = 4.0 Hz, 1H, CH_2), 1.48 (s, 9H, *t*-Bu) and 1.17 ppm (s, 9H, *t*-Bu); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.44, 151.41, 148.95, 148.67, 148.58, 145.84, 145.57, 142.86, 142.71, 142.63, 141.79, 133.02, 132.64, 132.30, 131.97, 131.73, 130.92, 130.84, 130.26, 128.45, 128.33, 128.20, 128.04, 127.98, 127.69, 127.50, 127.19, 127.16, 126.72, 126.35, 126.18, 126.00, 125.70, 125.42, 125.14, 124.98, 124.91, 124.87, 124.68, 124.63, 124.42, 124.25, 123.95, 121.27, 121.21, 118.41, 118.15, 116.54, 114.47, 111.19, 102.93, 102.75, 100.65, 35.10, 34.56, 32.09, and 31.87 ppm; HR-MS (APCI): *m*/*z* = 1030.3775. calcd for $C_{69}H_{51}N_2O_7B$: 1030.3806 [*M*]$^-$;

UV/Vis (1,4-dioxane) λ_{max} (ε) = 223 (80600), 290 (23700), 324 (27300), 350 (30100), 364 (29000), and 438 nm (11100 $mol^{-1}dm^3cm^{-1}$).



Synthesis of 2j. To a solution of **4a** (79.1 mg, 178 μmol) and (*R*,*S*,*R*)-**12** (542 mg, 865 μmol) in dry CH_2Cl_2 (10 mL) was added dropwise Et_2AlCl (0.87 M in hexane, 0.31 mL, 270 μmol) under N_2, and the mixture was stirred at rt for 30 min. The solvents were removed, and the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **2j** as a yellow solid (101 mg, 98.0 μmol, 55%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.48 (d, J = 2.0 Hz, 1H, H^d), 8.17 (d, J = 1.6 Hz, 1H, H^e), 8.04 (d, J = 2.0 Hz, 1H, H^c), 7.93–7.87 (m, 4H, Np), 7.82 (d, J = 8.0 Hz, 1H, Np), 7.79–7.70 (m, 4H, Np and H^f), 7.56 (d, J = 8.0 Hz, 1H, Np), 7.54 (d, J = 6.8 Hz, 1H, Np), 7.50–7.38 (m, 6H, Np), 7.32 (dt, J = 1.6, 7.6 Hz, 1H, H^g), 7.31–7.25 (m, 3H, Np), 7.21 (d, J = 8.8 Hz, 1H, Np), 6.83 (t, J = 7.8 Hz, 1H, H^h), 6.79 (d, J = 6.8 Hz, 1H, H^i), 6.72 (dd, J = 2.0, 8.8 Hz, 1H, H^b), 6.51 (d, J = 9.2 Hz, 1H, H^a), 5.21 (d, J = 3.2 Hz, 1H, CH_2), 4.97 (d, J = 2.8 Hz, 1H, CH_2), 4.27 (d, J = 3.2 Hz, 1H, CH_2), 4.00 (d, J = 2.8 Hz, 1H, CH_2), 1.57 (s, 9H, *t*-Bu) and 1.26 ppm (s, 9H, *t*-Bu); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.33, 152.17, 151.79, 149.72, 149.51, 148.95, 146.08, 145.54, 143.45, 142.45, 142.37, 142.21, 132.63, 132.48, 132.44, 131.88, 131.70, 131.51, 131.44, 130.33, 130.11, 129.02, 128.50, 128.43, 128.11, 127.92, 127.82, 127.75, 127.39, 127.29, 126.94, 126.87, 126.57, 126.46, 126.31, 126.07, 125.69, 125.52, 125.37, 125.29, 125.16, 125.14, 124.88, 124.09, 124.03, 123.96, 123.79, 121.05, 120.85, 119.14, 118.11, 115.48, 111.20, 103.12, 102.87, 100.83, 35.22, 34.67, 32.16, and 31.81 ppm; HR-MS (APCI): m/z = 1030.3772. calcd for $C_{69}H_{51}N_2O_7B$: 1030.3806 [M]$^-$; UV/Vis (1,4-dioxane) λ_{max} (ε) = 223 (90100), 290 (24000), 325 (30300), 355 (28400), and 439 nm (12000 $mol^{-1}dm^3cm^{-1}$).

[C] References

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

[S2] C. Maeda, T. Todaka, T. Ueda and T. Ema, *Org. Biomol. Chem.*, 2017, **15**, 9283.

[S3] Y. Li, A. Urbas and Q. Li, *J. Am. Chem. Soc.*, 2012, **134**, 9573.

[S4] A. Bähr, B. Felber, K. Schneider and F. Diederich, *Helv. Chim. Acta*, 2000, **83**, 1346.

[S5] K. Takaishi, T. Yamamoto, S. Hinoide and T. Ema, *Chem. Eur. J.*, 2017, **23**, 9249.

[D] X-ray Crystal Structures

Single crystals of **1b** were obtained by slow diffusion of heptane vapor into a solution of **1b** in CH_2Cl_2, while those of **2b** and **4a** were obtained by slow diffusion of MeOH vapor into each CH_2Cl_2 solution. X-ray data at 93 K were taken on a Rigaku XtaLAB P200 with Cu-K_α radiation (λ = 1.54187 Å). The structures were solved by direct methods and refined with the full-matrix least square technique. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were calculated in ideal positions.

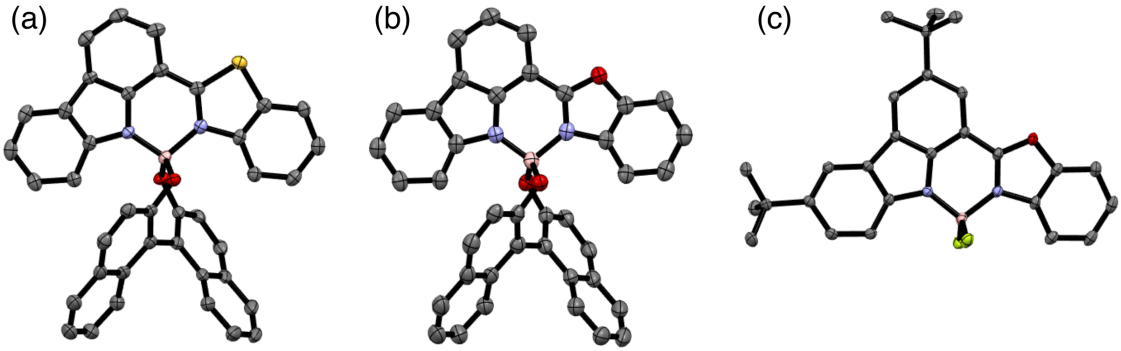


Fig. S1 X-ray crystal structures of (a) **1b**, (b) **2b**, and (c) **4a**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

Crystal data of 1b: $C_{39}H_{22}BN_2O_2S$, M_w = 593.45, monoclinic, space group $P2_1$, a = 12.978(2), b = 6.7317(11), c = 16.309(3) Å, β = 95.116(5)°, V = 1419.1(4) Å^3, Z = 2, ρ_{calcd} = 1.389 gcm^{-3}, T = –180 °C, 18311 measured reflections, 4918 unique reflections (R_{int} = 0.0435), R_1 = 0.0362 ($I > 2\sigma(I)$), wR_2 = 0.0949 (all data), GOF = 1.011.

Crystal data of 2b: $C_{39}H_{22}BN_2O_3$, M_w = 578.40, monoclinic, space group $P2_1/c$, a = 13.000(3), b = 6.5948(15), c = 16.243(4) Å, β = 93.955(6)°, V = 1389.3(5) Å^3, Z = 2, ρ_{calcd} = 1.383 gcm^{-3}, T = –180 °C, 18079 measured reflections, 4347 unique reflections (R_{int} = 0.0359), R_1 = 0.0542 ($I > 2\sigma(I)$), wR_2 = 0.1407 (all data), GOF = 1.063.

Crystal data of 4a: $C_{27}H_{27}N_3OBF_2$, M_w = 444.31, triclinic, space group $P2_1/c$, a = 9.496(2), b = 10.526(2), c = 11.5355(16) Å, α = 79.482(19), β = 77.43(3), γ = 89.68(2)°, V = 1105.8(4) Å^3, Z = 2, ρ_{calcd} = 1.334 gcm^{-3}, T = –180 °C, 14040 measured reflections, 3747 unique reflections (R_{int} = 0.0301), R_1 = 0.0349 ($I > 2\sigma(I)$), wR_2 = 0.0986 (all data), GOF = 1.062.

[E] Photophysical Properties

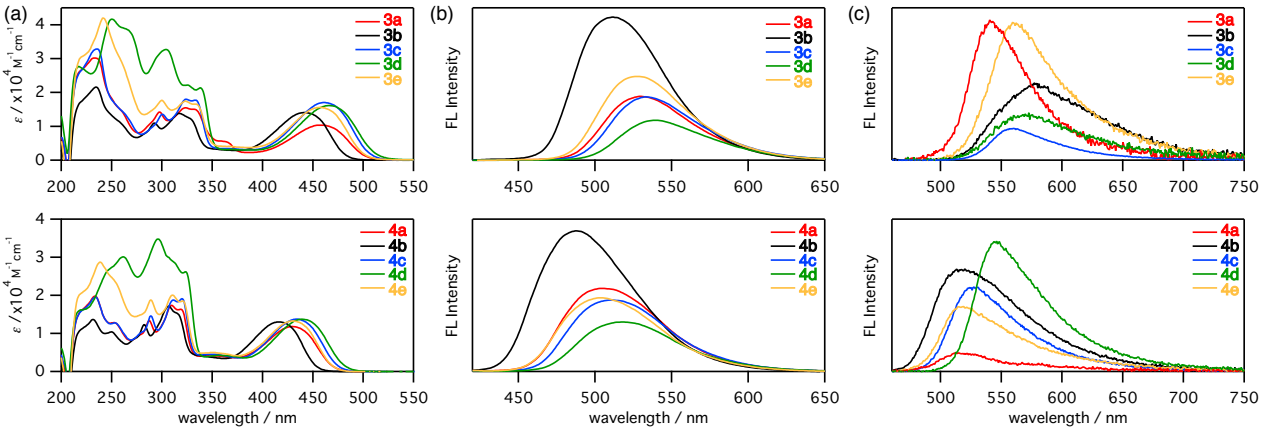


Fig. S2 (a) UV/vis spectra in 1,4-dioxane. (b) FL spectra in 1,4-dioxane. (c) FL spectra in the solid state.

Table S1 Photophysical properties of **3** and **4**.

Compd	1,4-dioxane				powder	
	λ_A (nm)	λ_F (nm)	$\Delta\nu_{St}$ (cm^{-1})[a]	Φ_F	λ_F (nm)	Φ_F
3a	458	529[b]	2930	0.376	542[b]	0.214
3b	442	511[c]	3050	0.474	575[c]	0.158
3c	461	533[b]	2930	0.304	560[b]	0.250
3d	466	539[b]	2910	0.275	573[b]	0.106
3e	457	528[b]	2940	0.422	560[b]	0.248
4a	430	504[d]	3410	0.413	518[d]	0.044
4b	416	488[e]	3550	0.495	519[e]	0.339
4c	434	510[d]	3430	0.311	525[d]	0.242
4d	439	517[d]	3440	0.285	546[d]	0.331
4e	430	503[d]	3380	0.436	519[d]	0.158

[a]Stokes shift. [b]Excited at 450 nm. [c]Excited at 430 nm. [d]Excited at 420 nm. [e]Excited at 400 nm.

Table S2 Photophysical properties of **2b** in several solvents.

	λ_A (nm)	λ_F (nm)[a]	$\Delta\nu_{St}$ (cm^{-1})[b]	Φ_F	g_{lum}[c,d]
CH_3CN	419	502	3950	0.008	-[e]
DMF	421	502	3830	0.015	-[e]
MeOH	422	498	3620	0.045	-5.1×10^{-4}
CH_2Cl_2	425	500	3530	0.076	-6.6×10^{-4}
1,4-dioxane	425	497	3410	0.245	-5.2×10^{-4}
toluene	432	497	3030	0.425	-5.6×10^{-4}

[a]Excited at 420 nm. [b]Stokes shift. [c]$g_{lum} = 2(I_L-I_R)/(I_L+I_R)$. Average value in the range of $\lambda_F \pm 10$ nm. [d]Excited at 320 nm. [e]The CPL signals were too weak to detect.

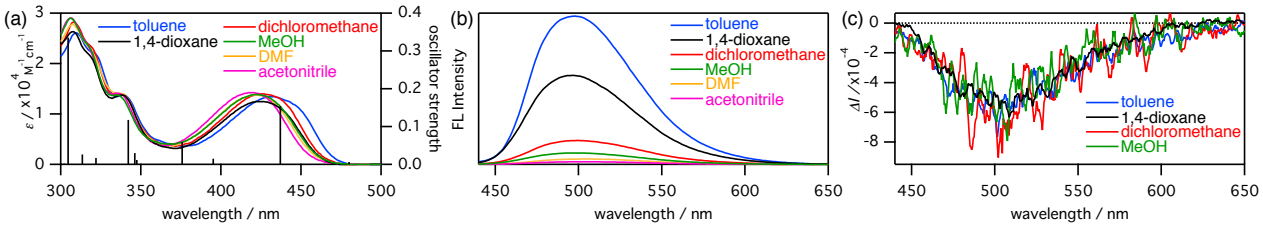


Fig. S3 (a) UV/vis, (b) FL, and (c) CPL spectra of **2b** in several solvents. The calculated oscillator strengths were inserted in the UV/vis spectra.

Table S3 Selected data of calculated electronic transitions in **2b**.

State	Transition energy (nm)	Oscillator strength	Composition of band and CI coefficiencies
1	480.00	0.0065	H → L (99%)
2	437.05	0.1541	H–1 → L (97%)
3	395.14	0.0151	H–2 → L (98%)
4	375.82	0.0594	H–3 → L (95%), H–6 → L (2%)
5	347.49	0.0118	H–4 → L (98%)
6	346.20	0.0299	H–5 → L (76%), H → L+1 (21%)
7	342.09	0.1175	H–5 → L (22%), H → L+1 (74%)
8	321.90	0.0174	H–2 → L+1 (14%), H–1 → L+1 (30%), H → L+2 (51%)
9	313.40	0.0261	H–2 → L+1 (4%), H–1 → L+1 (62%), H → L+2 (26%)
10	304.56	0.3356	H–6 → L (90%)

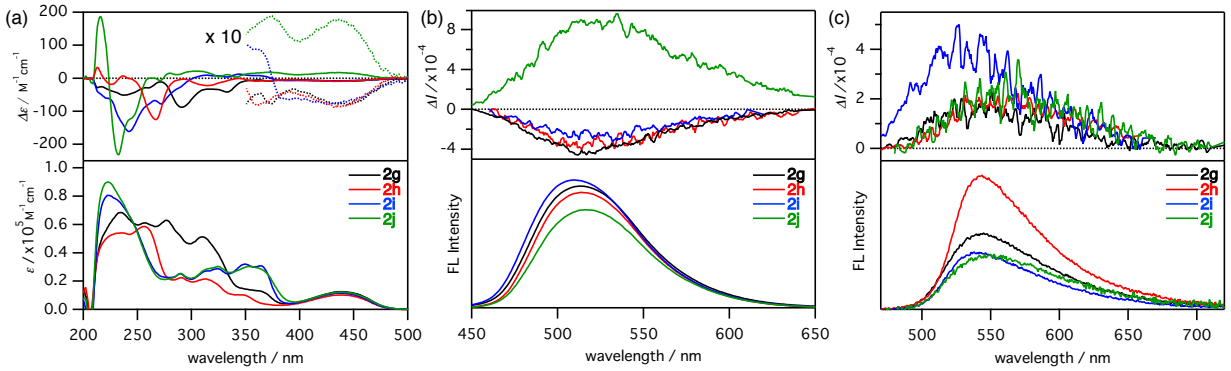
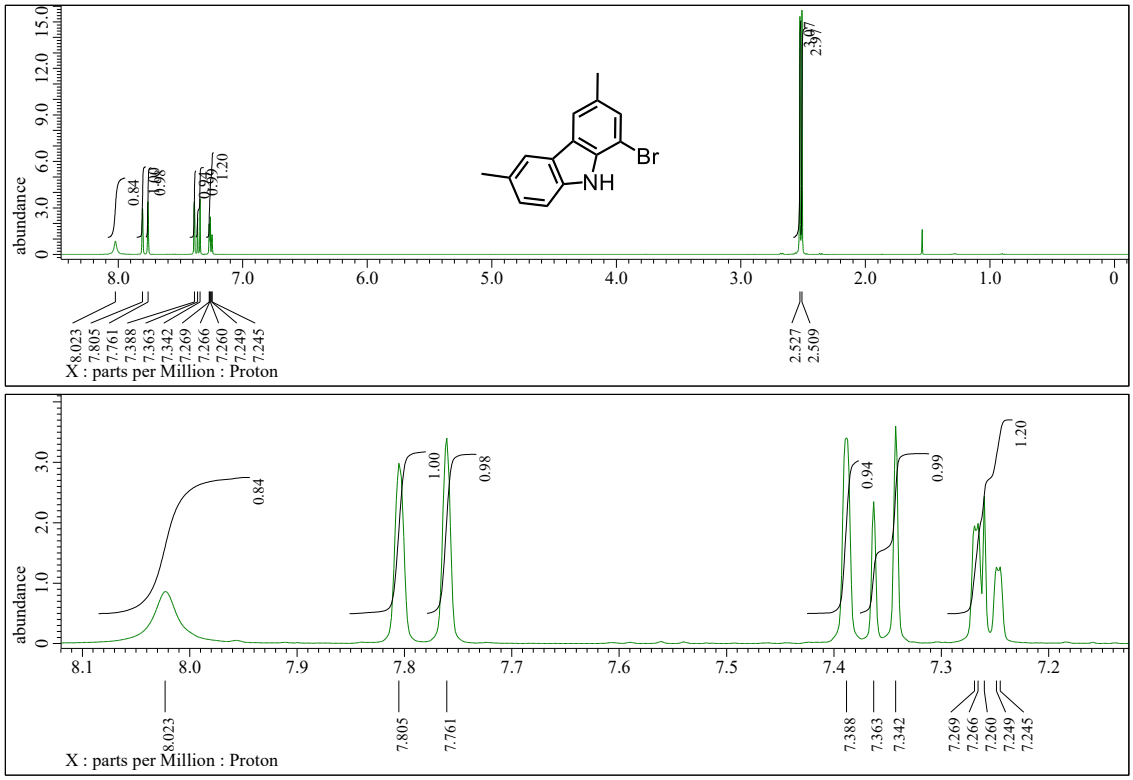
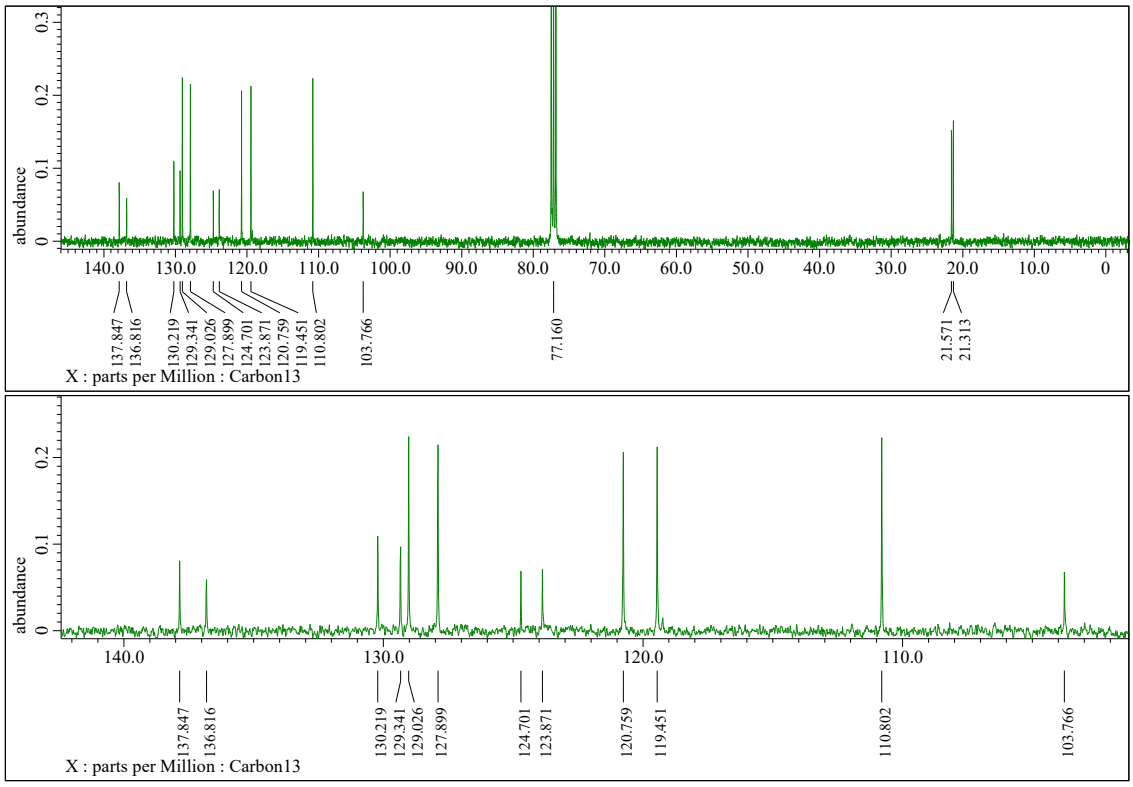


Fig. S4 (a) CD and UV/vis spectra of **2g–j** in 1,4-dioxane. (b) CPL and FL spectra of **2g–j** in 1,4-dioxane. (c) CPL and FL spectra of **2g–j** in the solid state.

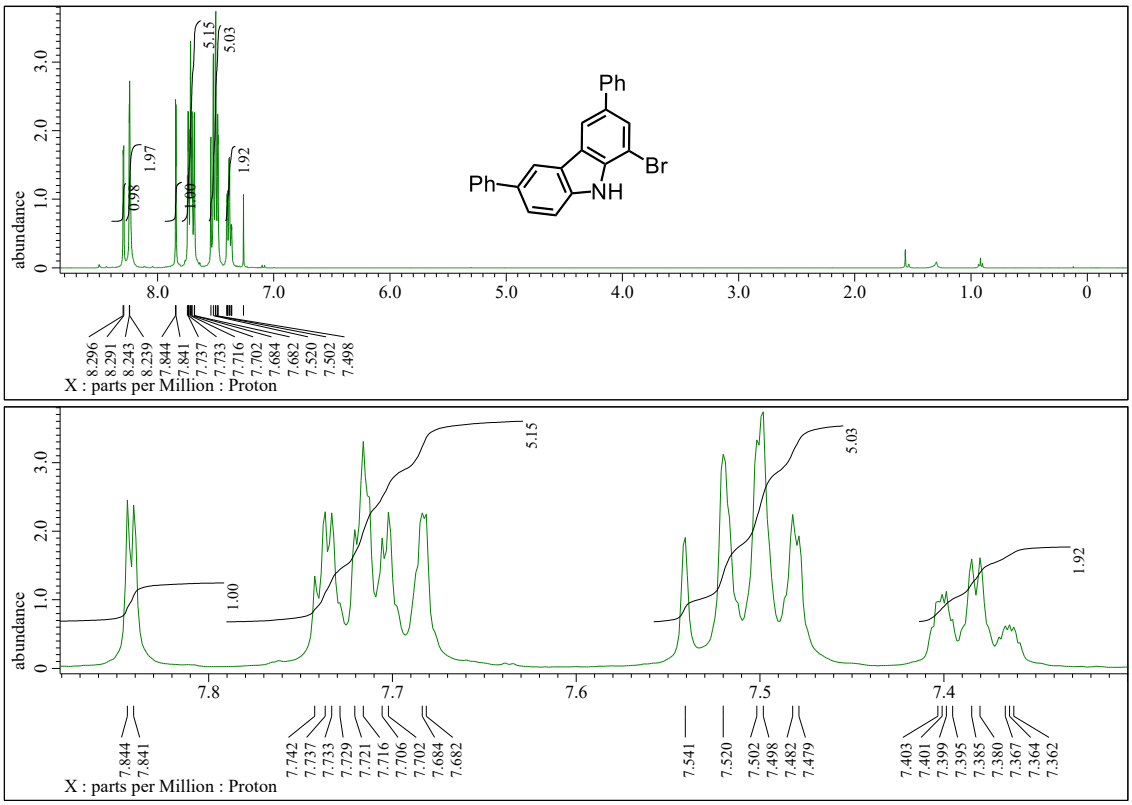
[F] NMR Spectra



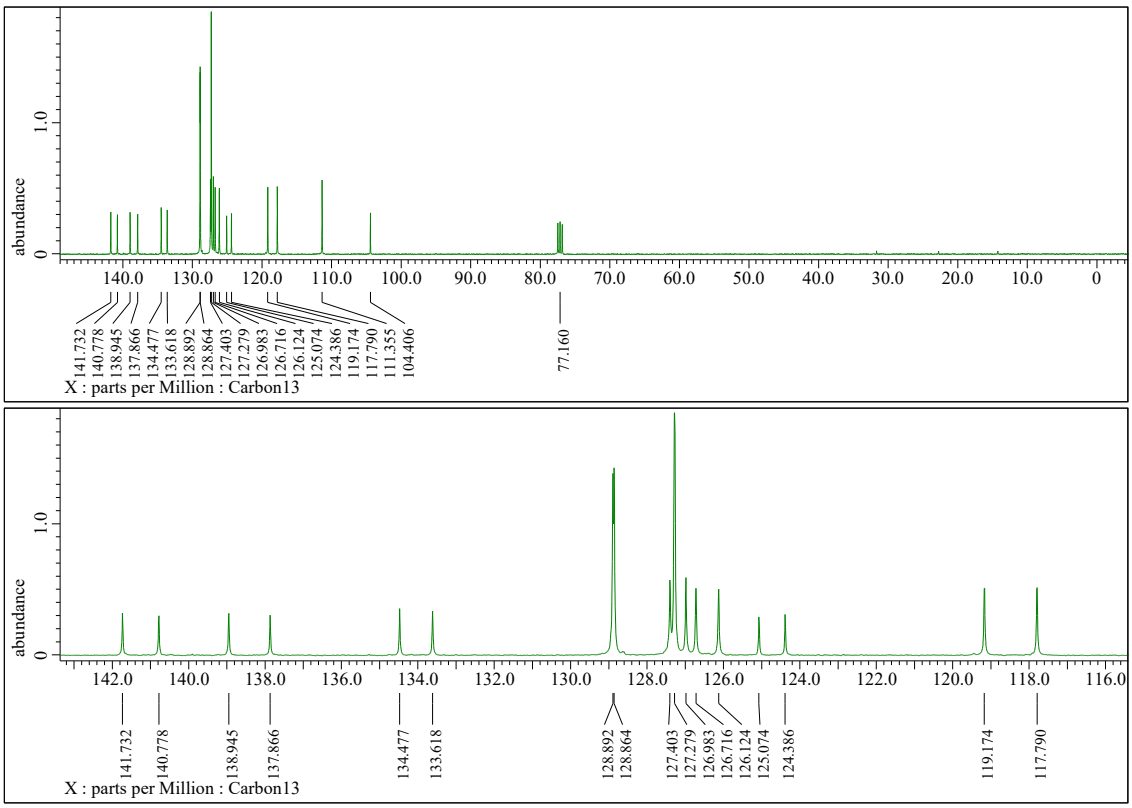
^{1}H NMR spectrum of **5c** in $CDCl_3$



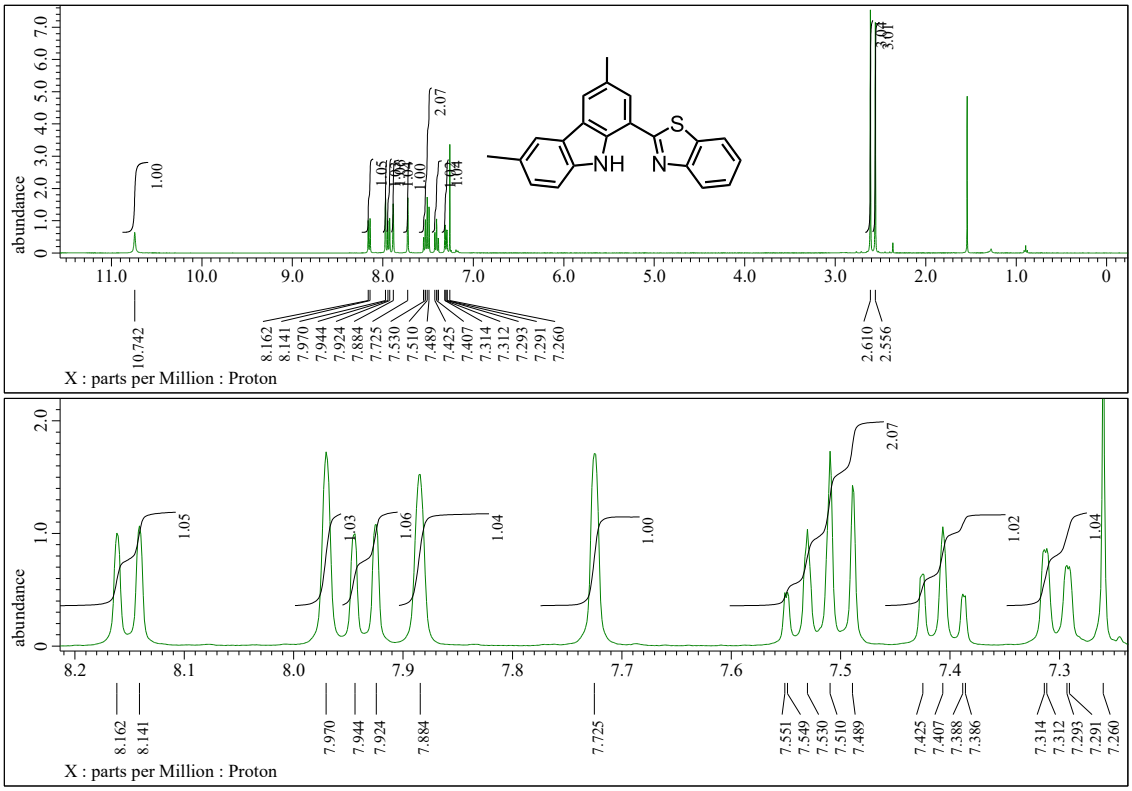
^{13}C NMR spectrum of **5c** in $CDCl_3$



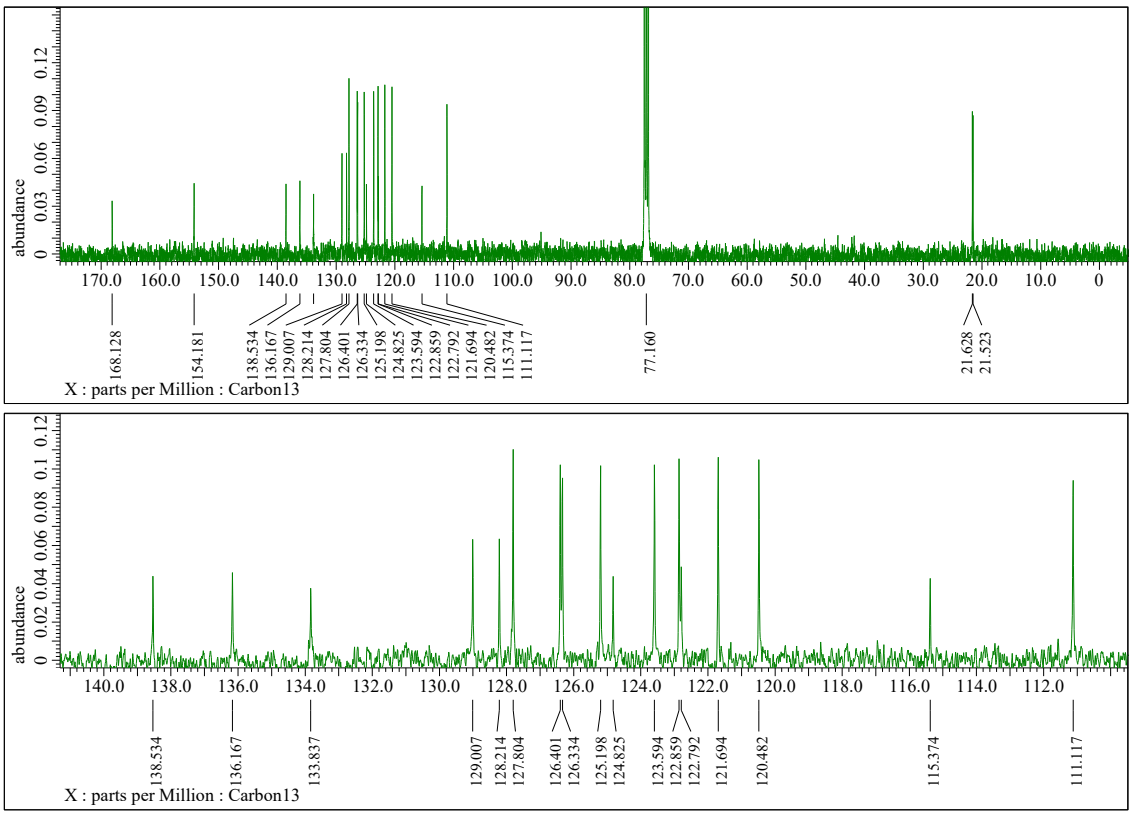
^{1}H NMR spectrum of **5d** in $CDCl_3$



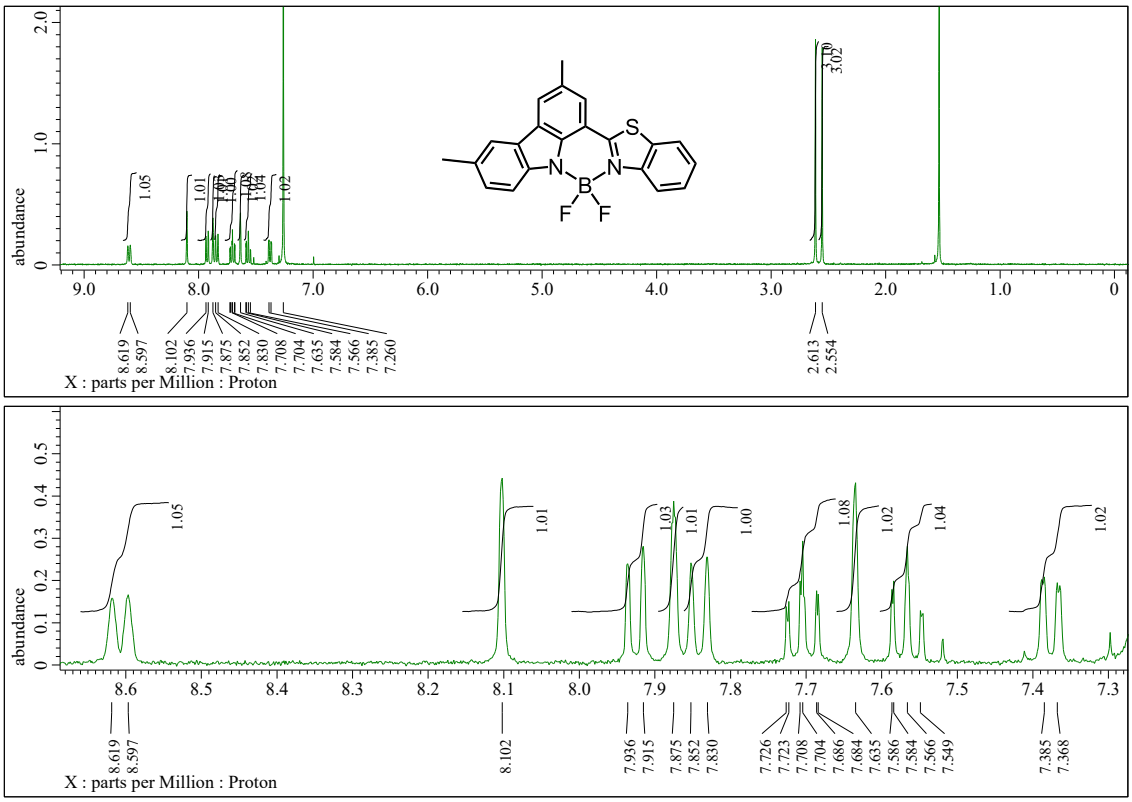
^{13}C NMR spectrum of **5d** in $CDCl_3$



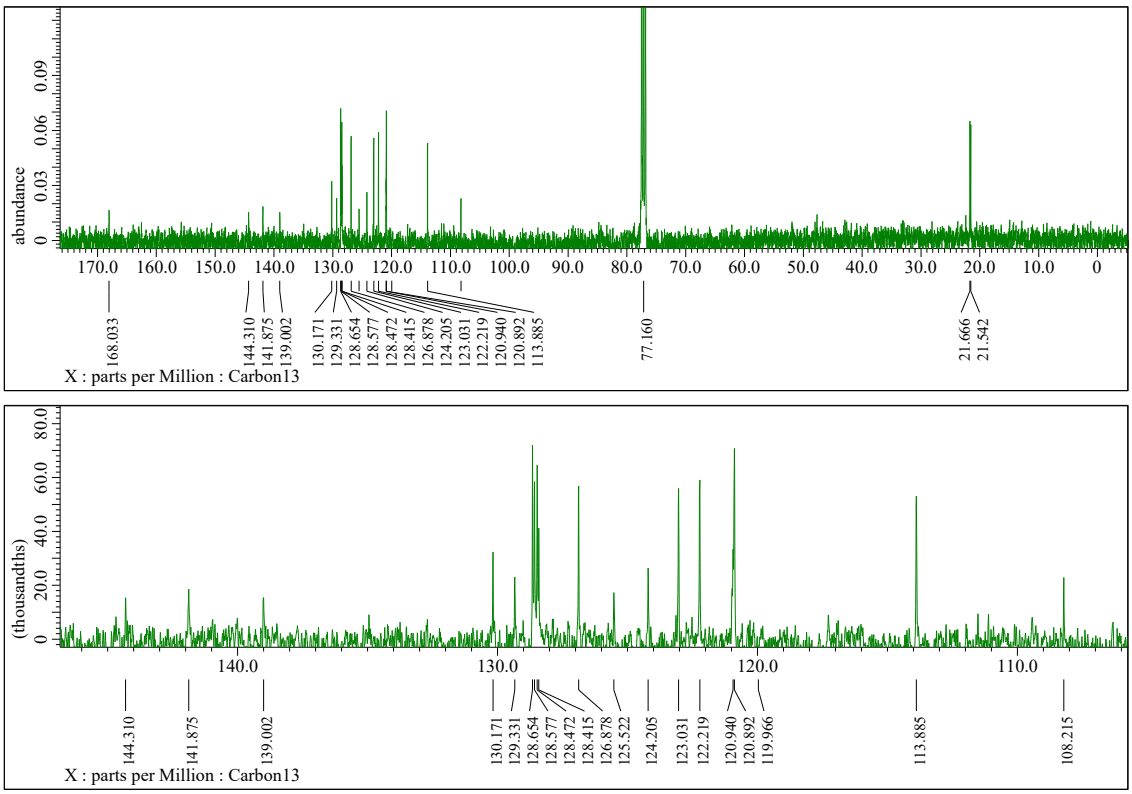
^{1}H NMR spectrum of **6c** in $CDCl_3$



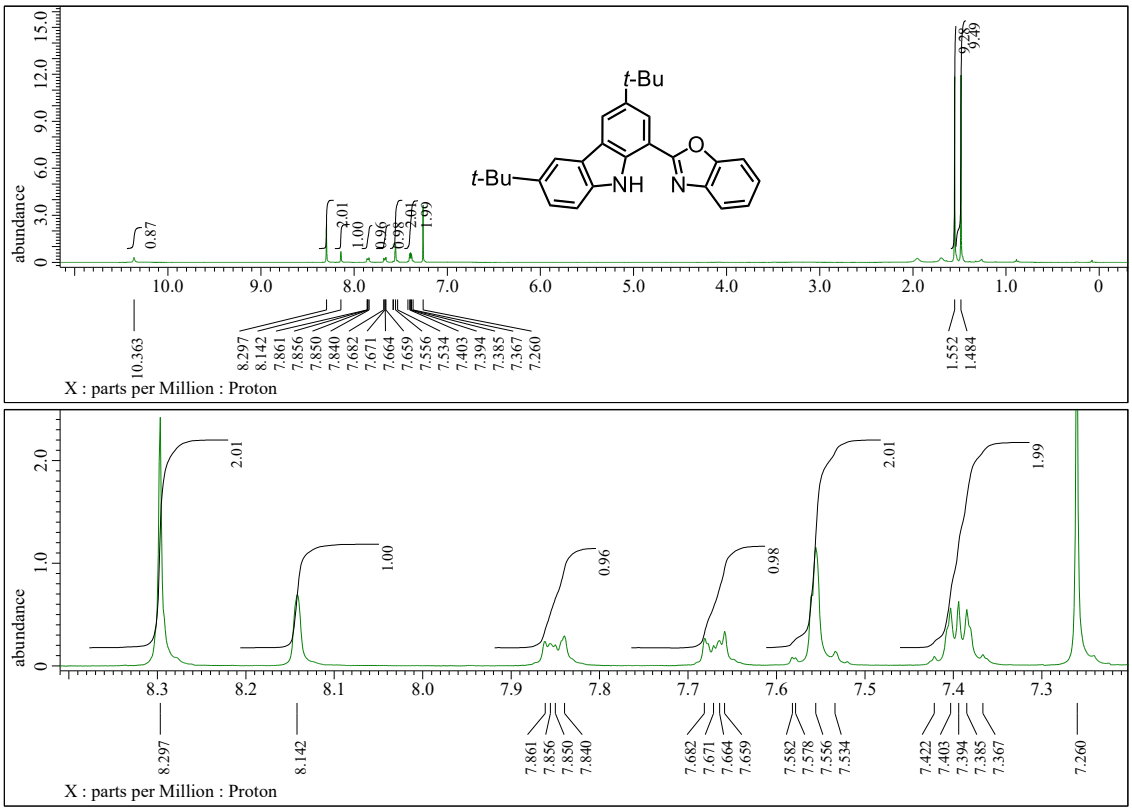
^{13}C NMR spectrum of **6c** in $CDCl_3$



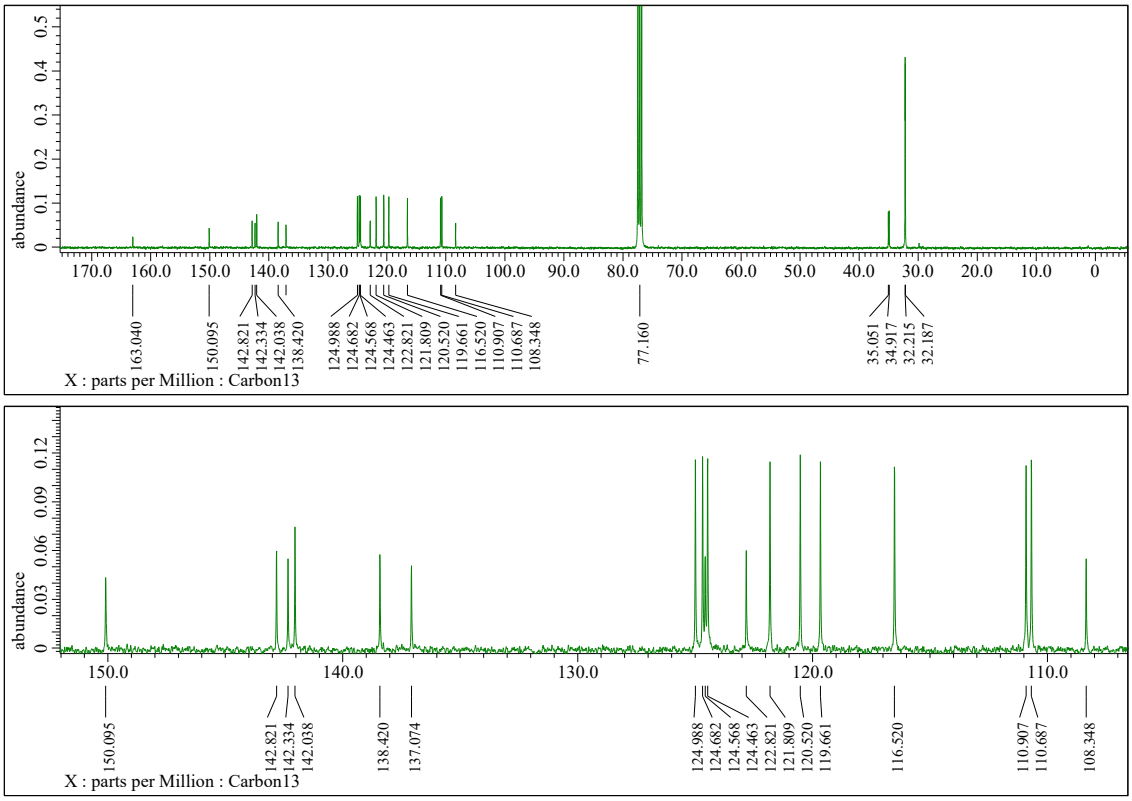
^{1}H NMR spectrum of **3c** in $CDCl_3$



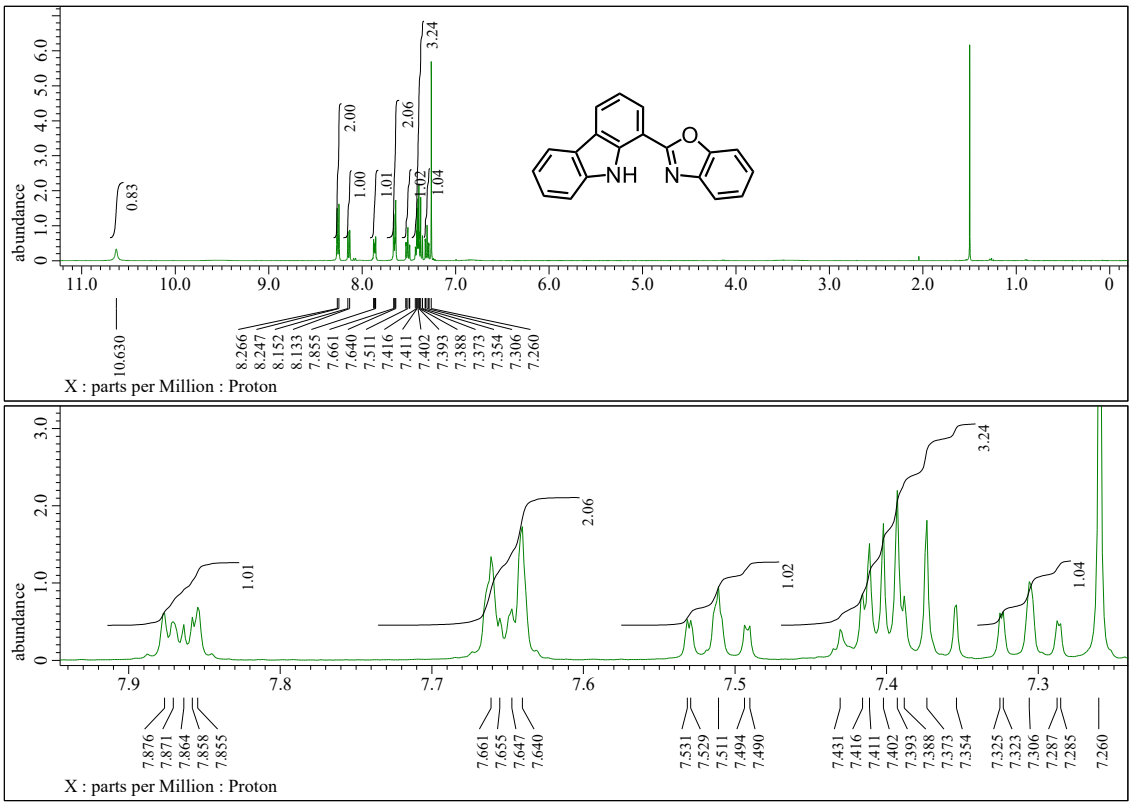
^{13}C NMR spectrum of **3c** in $CDCl_3$



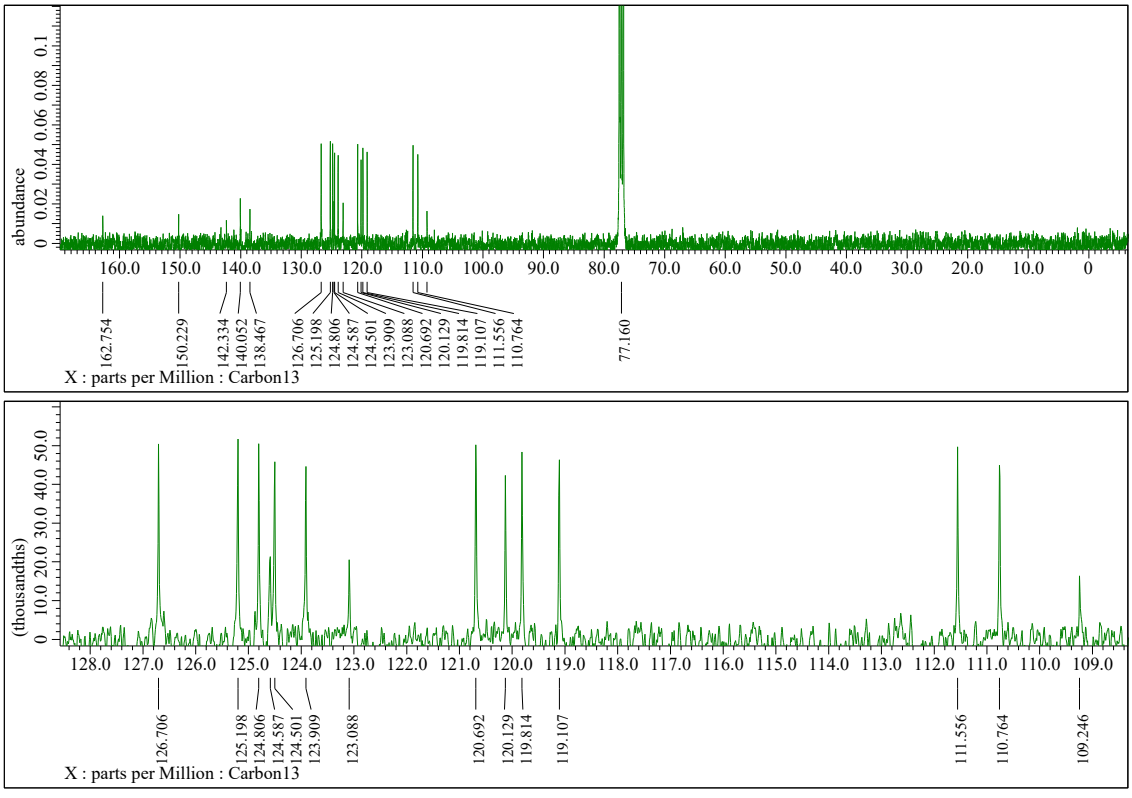
^{1}H NMR spectrum of **7a** in $CDCl_3$



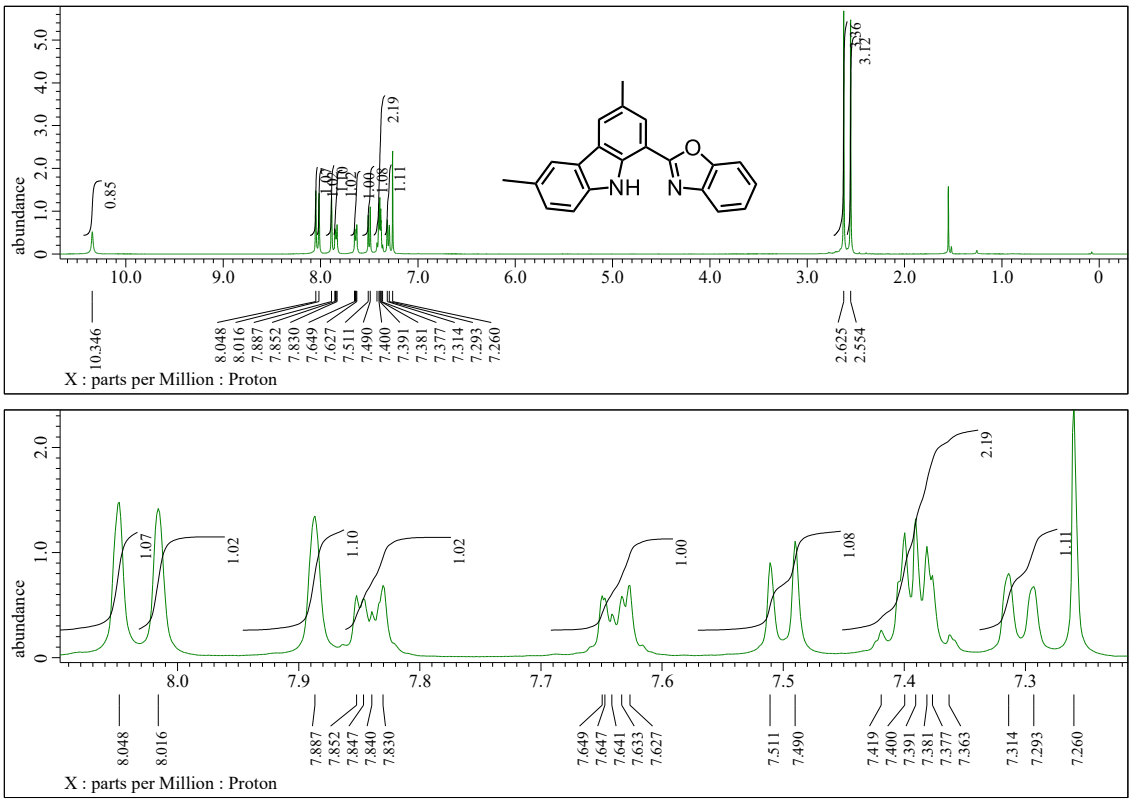
^{13}C NMR spectrum of **7a** in $CDCl_3$



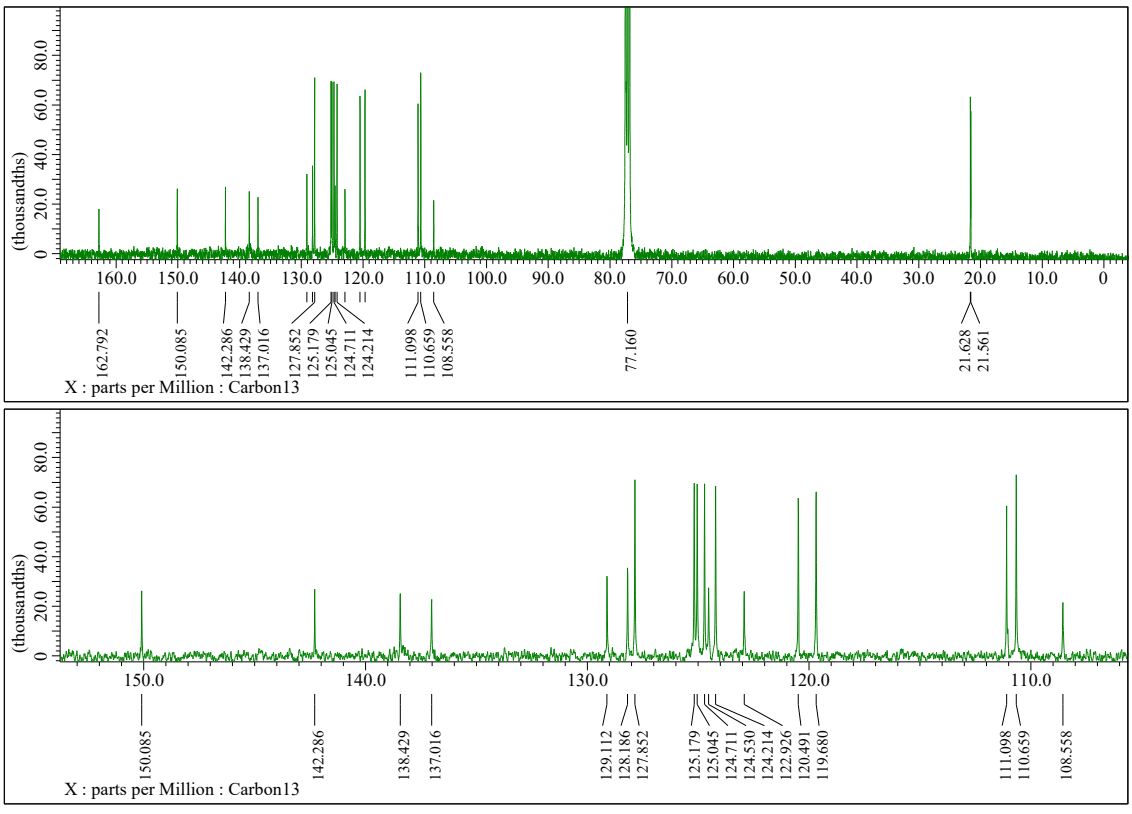
^{1}H NMR spectrum of **7b** in $CDCl_3$



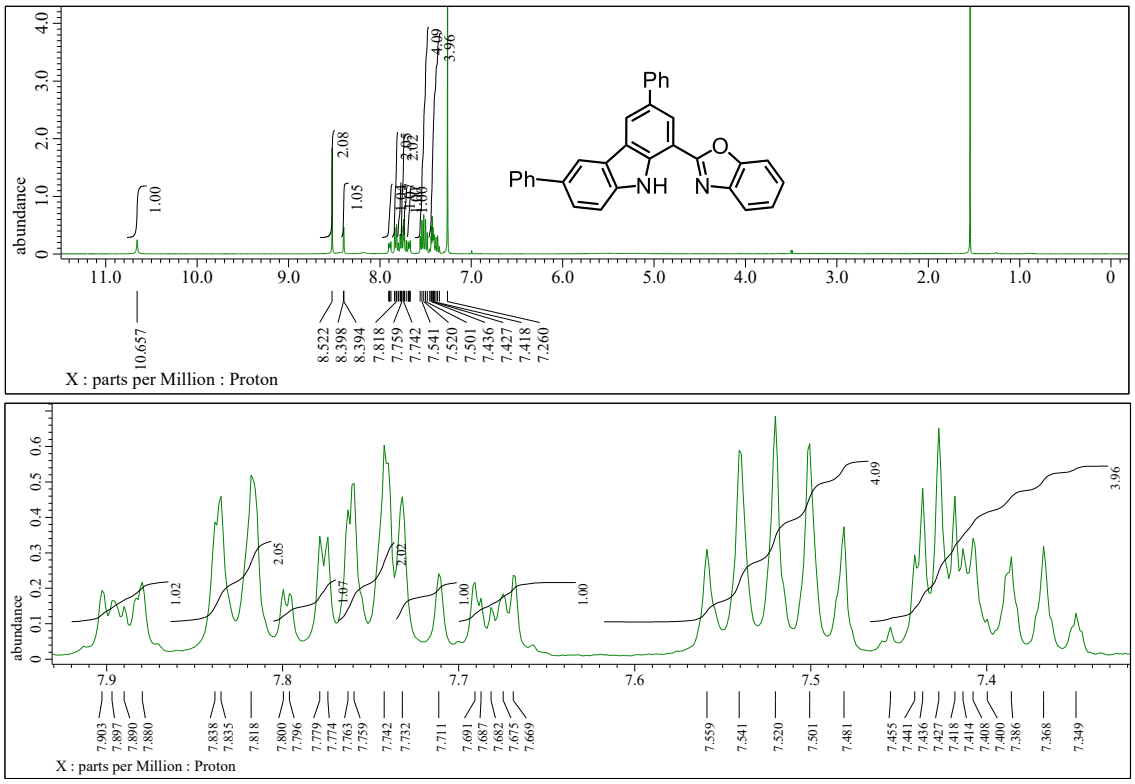
^{13}C NMR spectrum of **7b** in $CDCl_3$



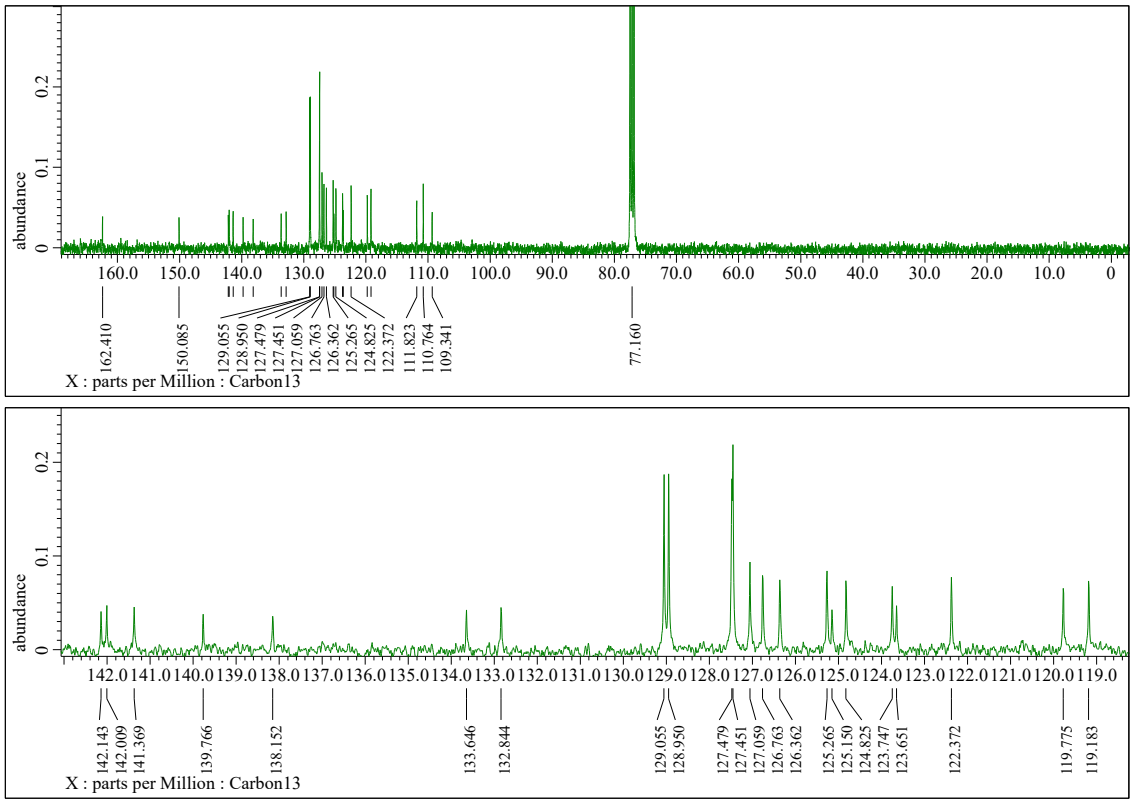
^{1}H NMR spectrum of **7c** in $CDCl_3$



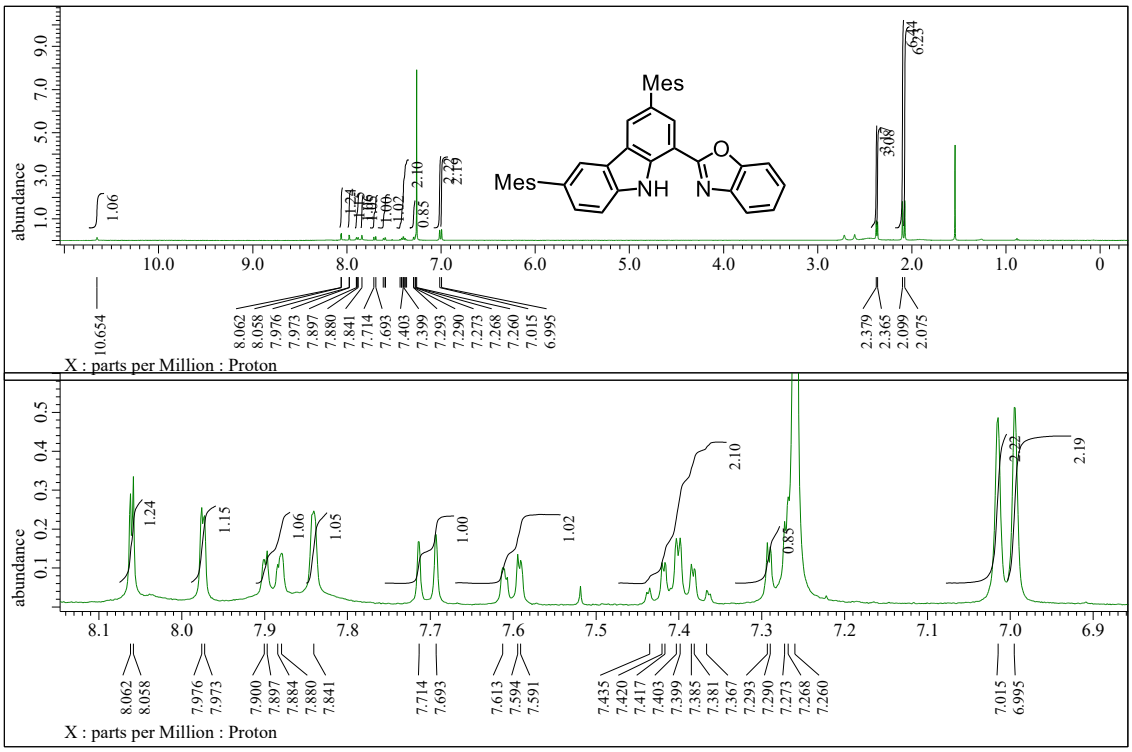
^{13}C NMR spectrum of **7c** in $CDCl_3$



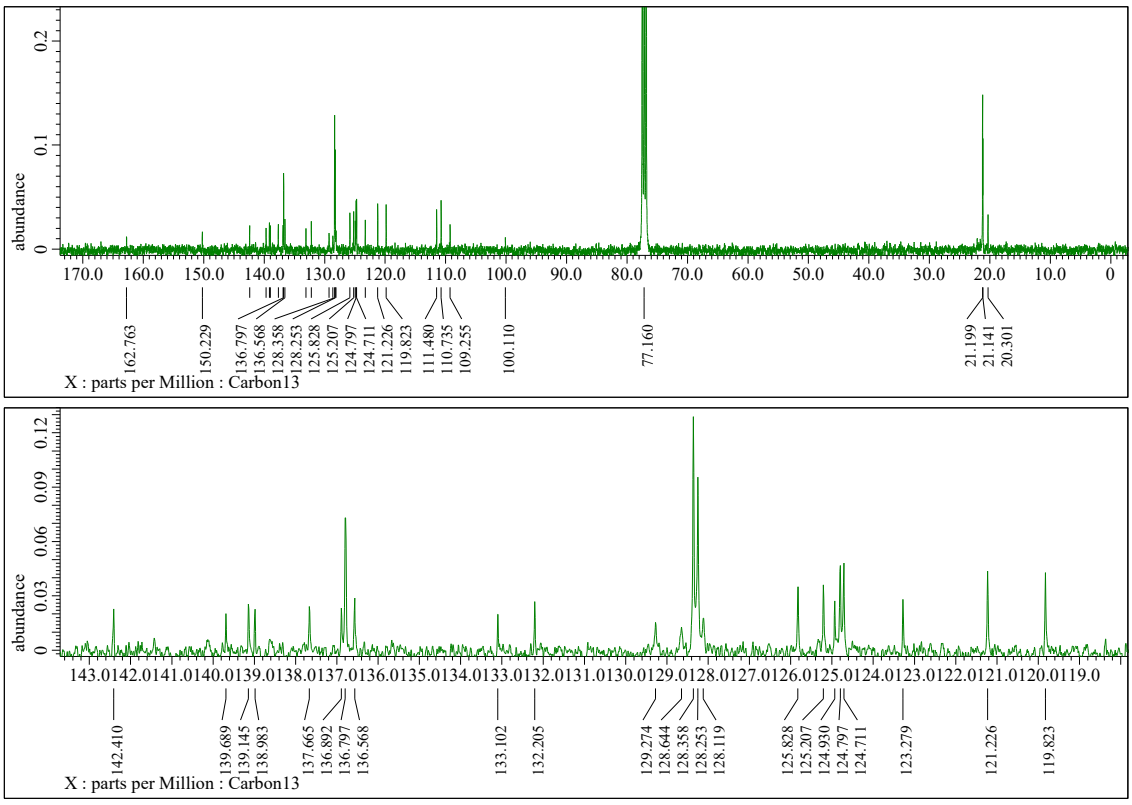
^{1}H NMR spectrum of **7d** in $CDCl_3$



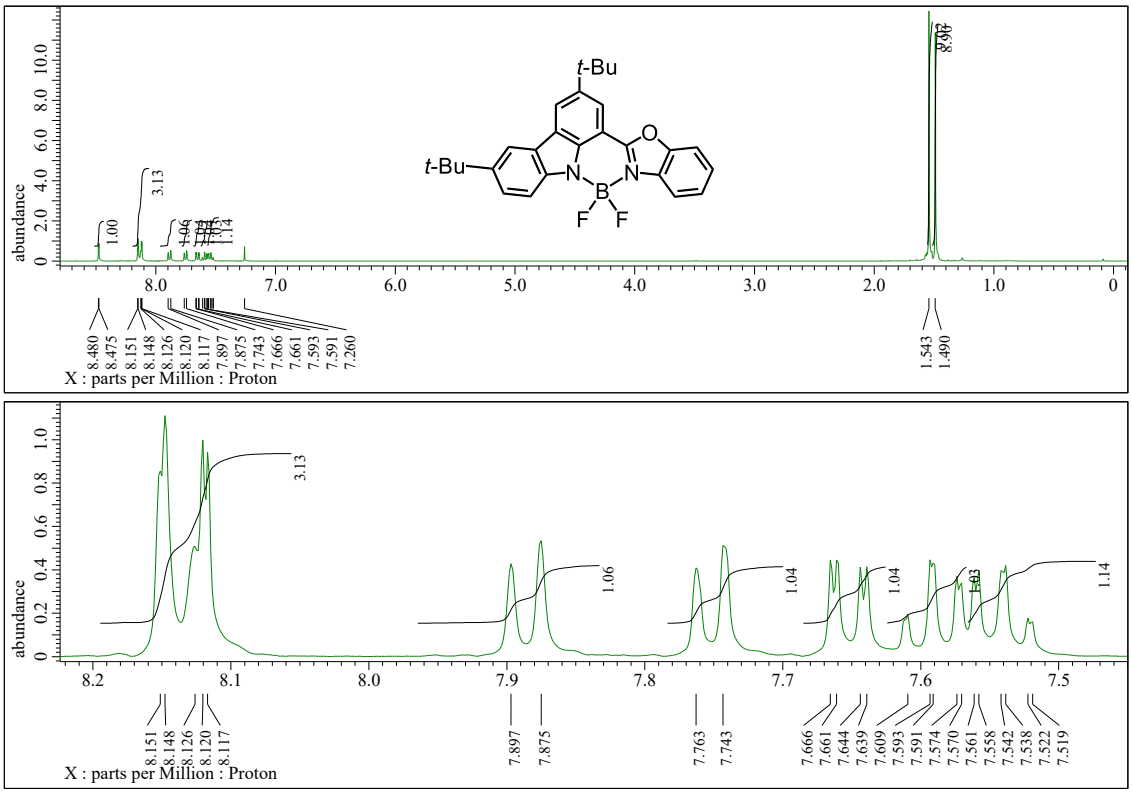
^{13}C NMR spectrum of **7d** in $CDCl_3$



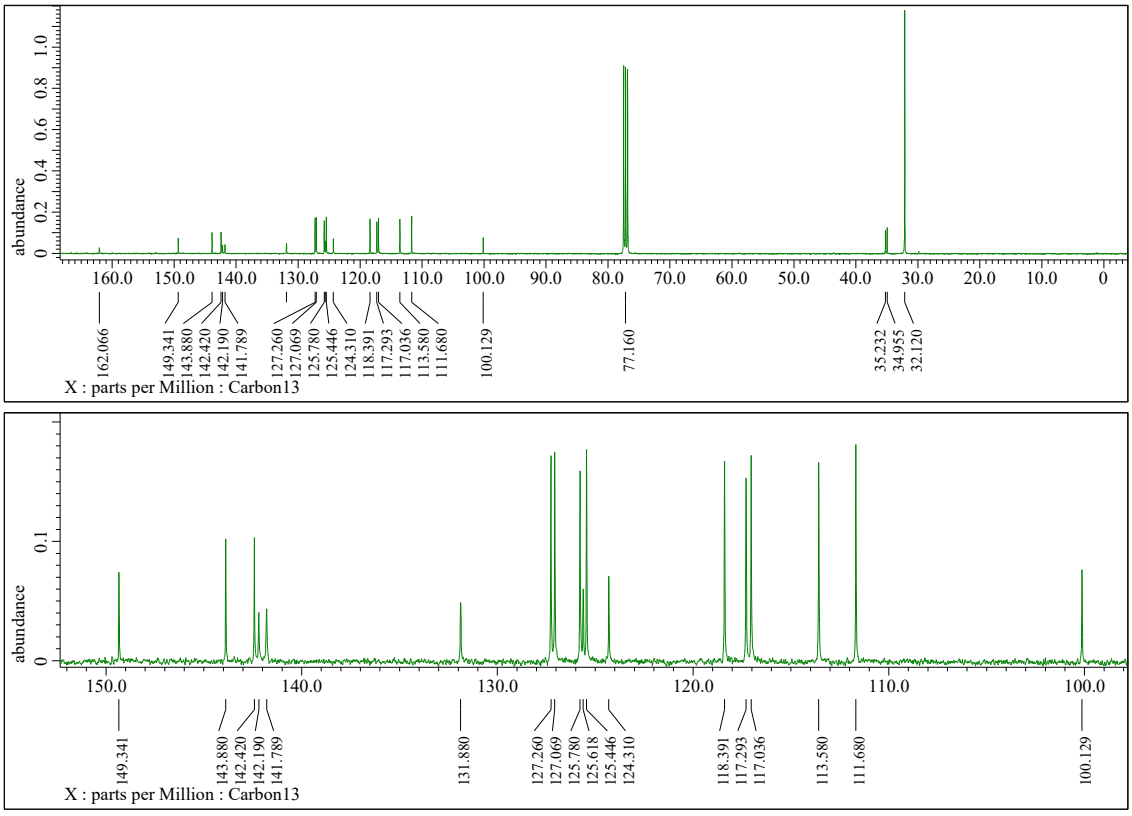
^{1}H NMR spectrum of **7e** in $CDCl_3$



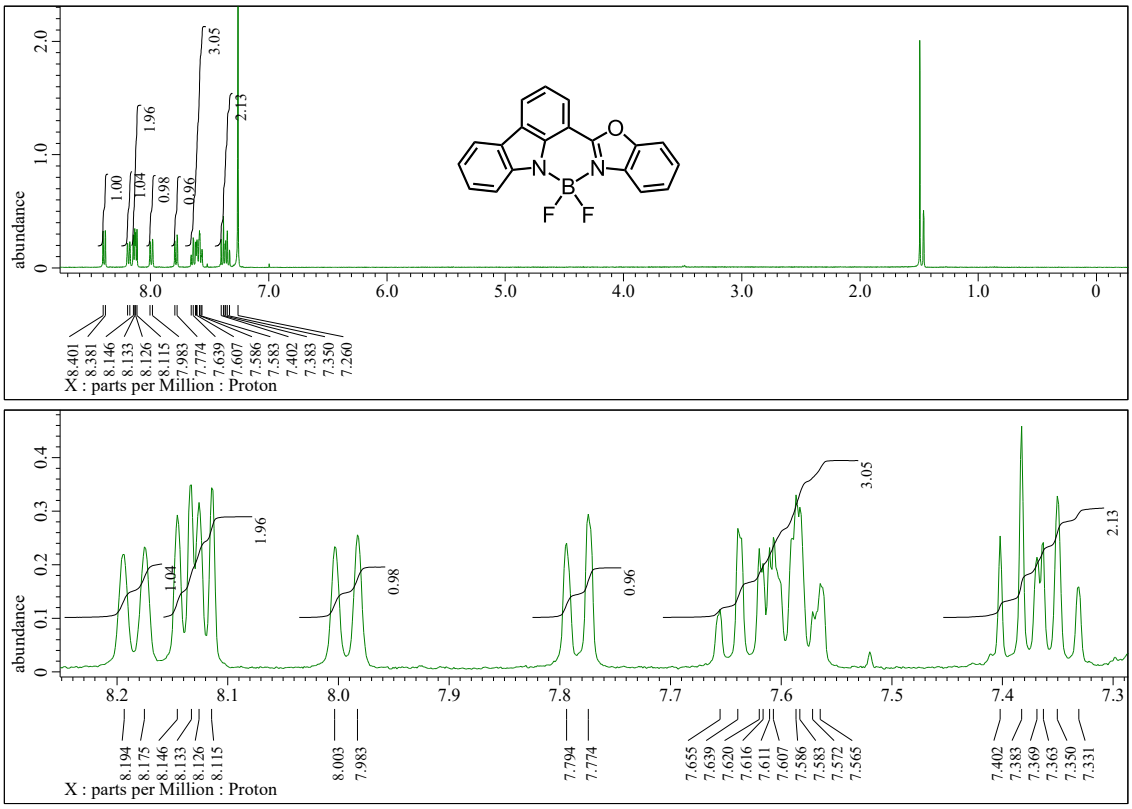
^{13}C NMR spectrum of **7e** in $CDCl_3$



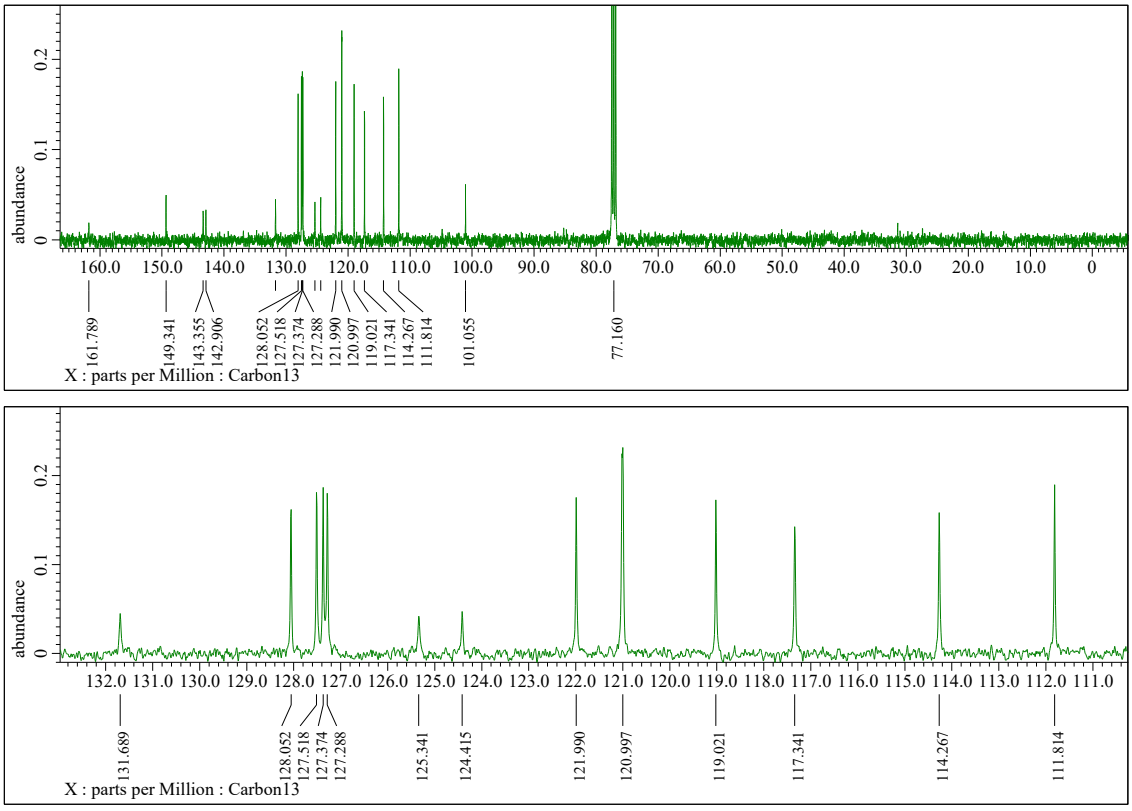
^{1}H NMR spectrum of **4a** in $CDCl_3$



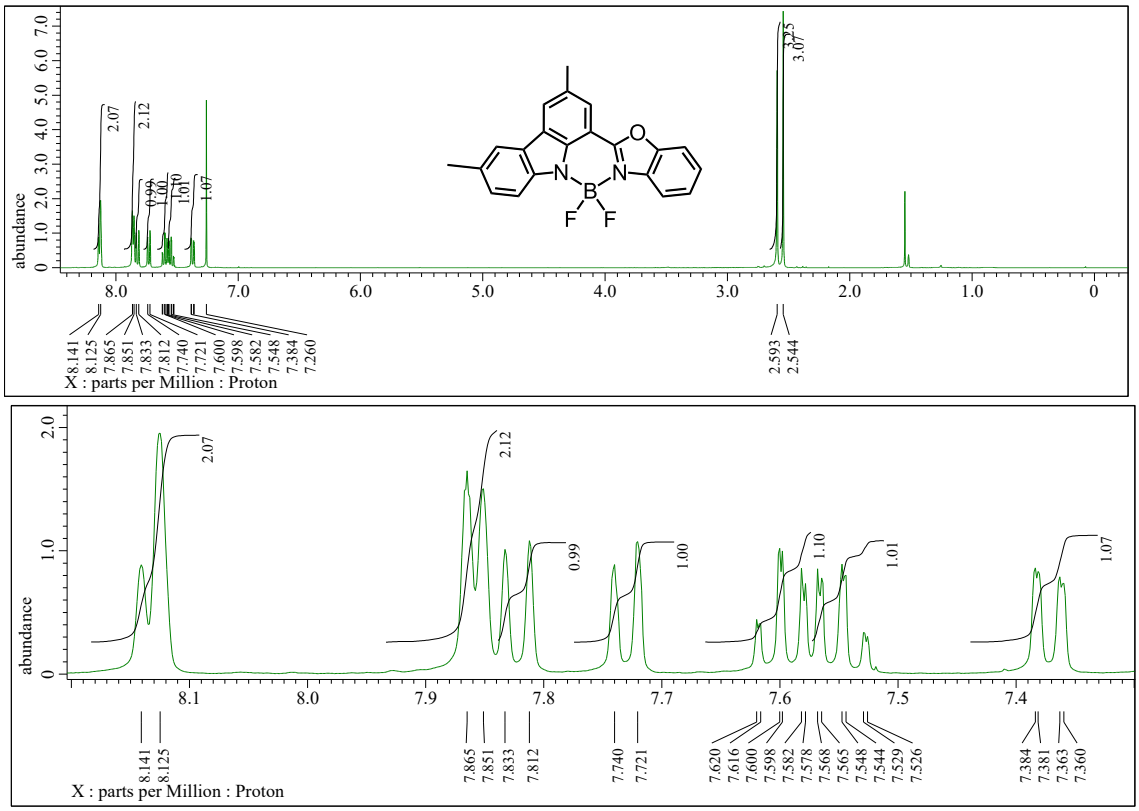
^{13}C NMR spectrum of **4a** in $CDCl_3$



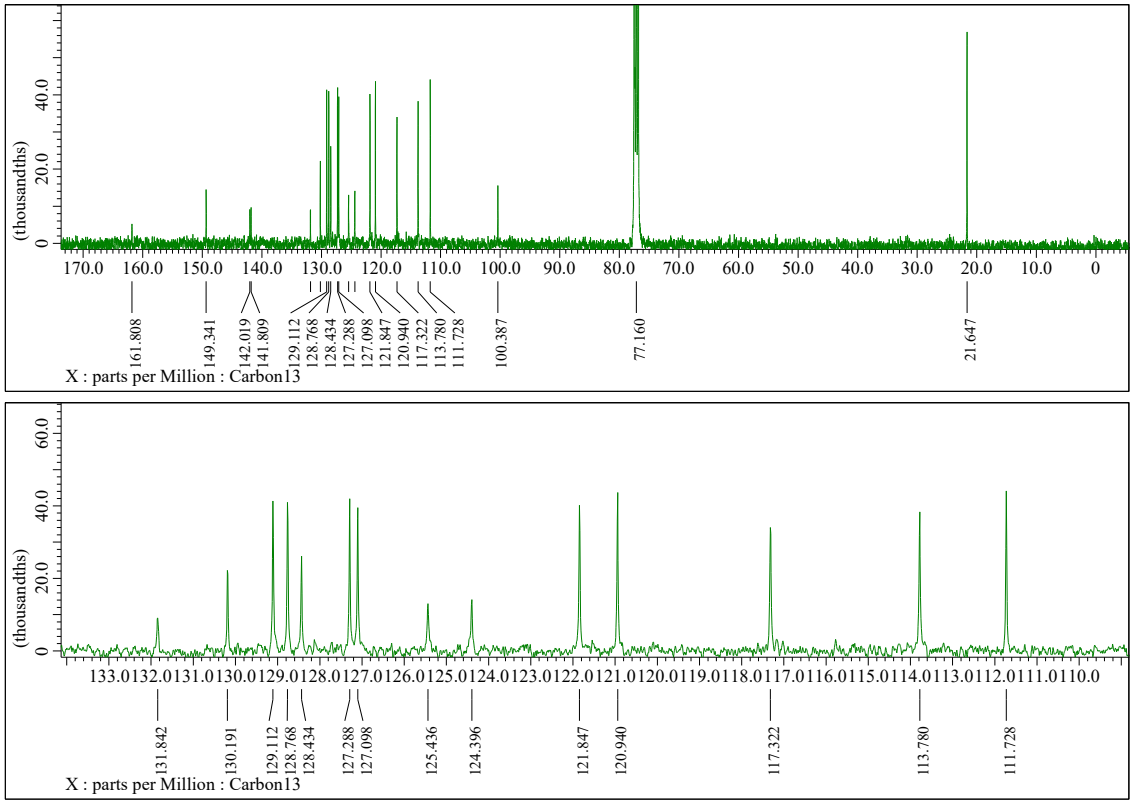
^{1}H NMR spectrum of **4b** in $CDCl_3$



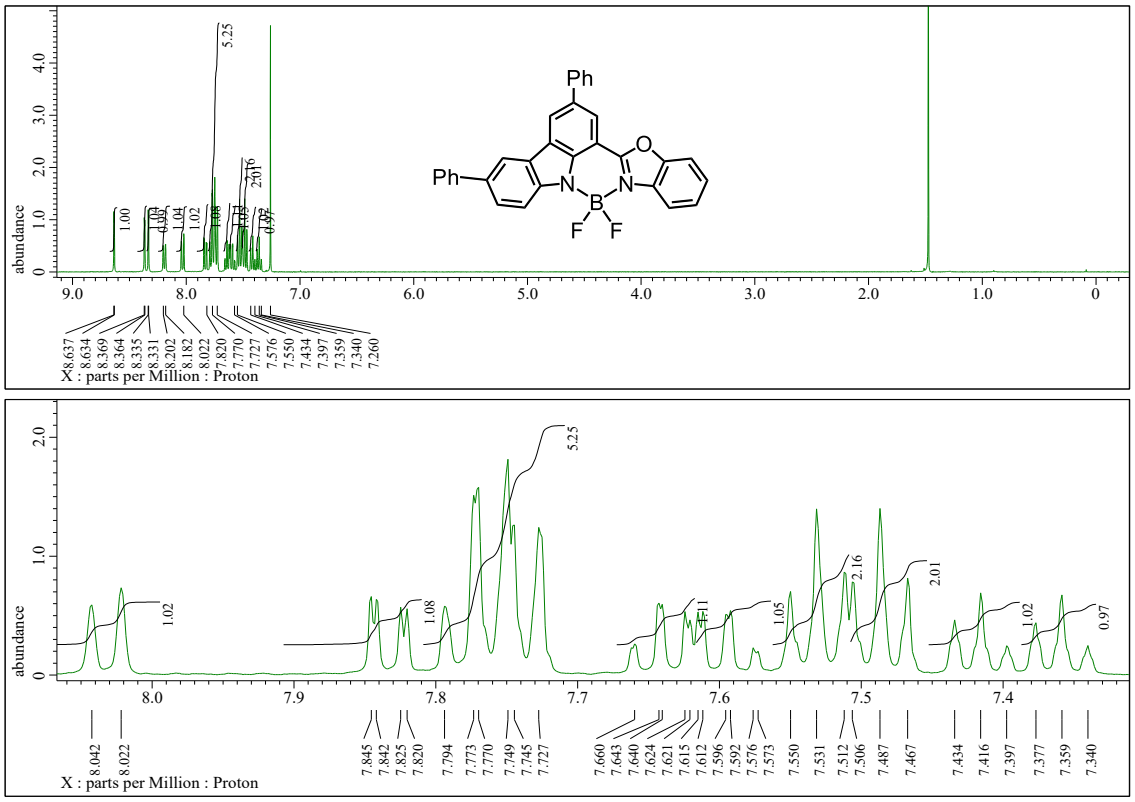
^{13}C NMR spectrum of **4b** in $CDCl_3$



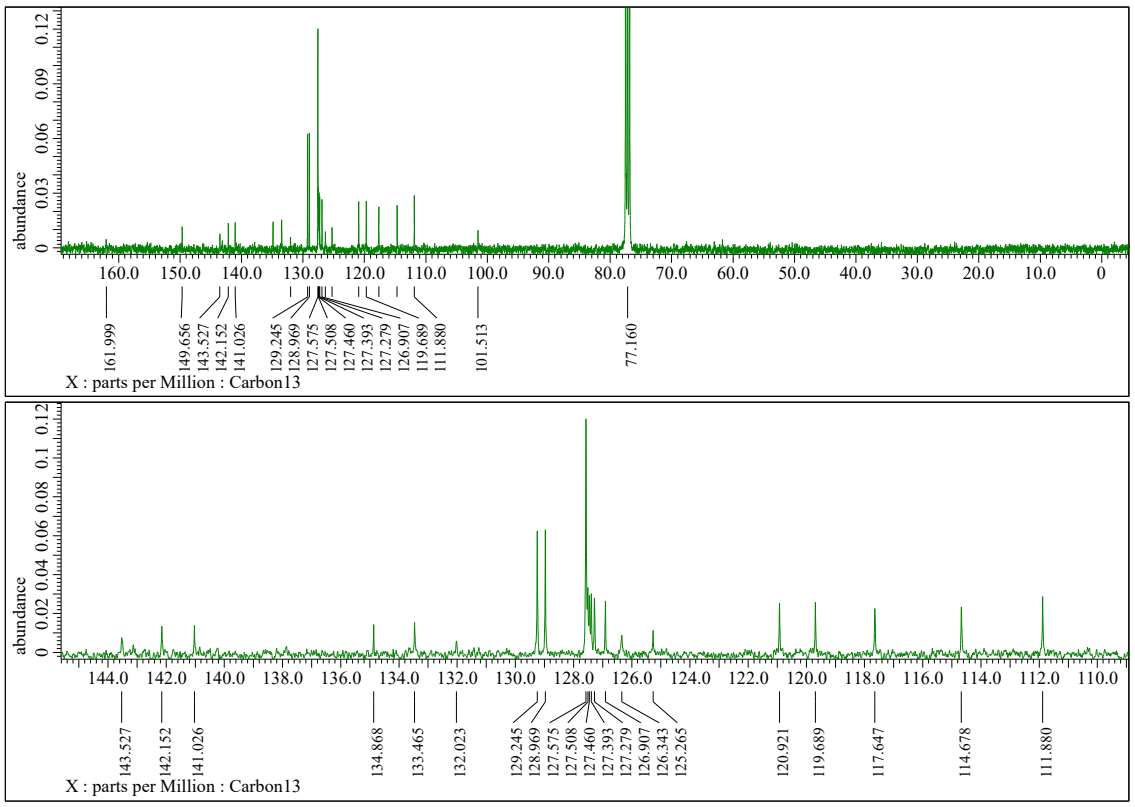
^{1}H NMR spectrum of **4c** in $CDCl_3$



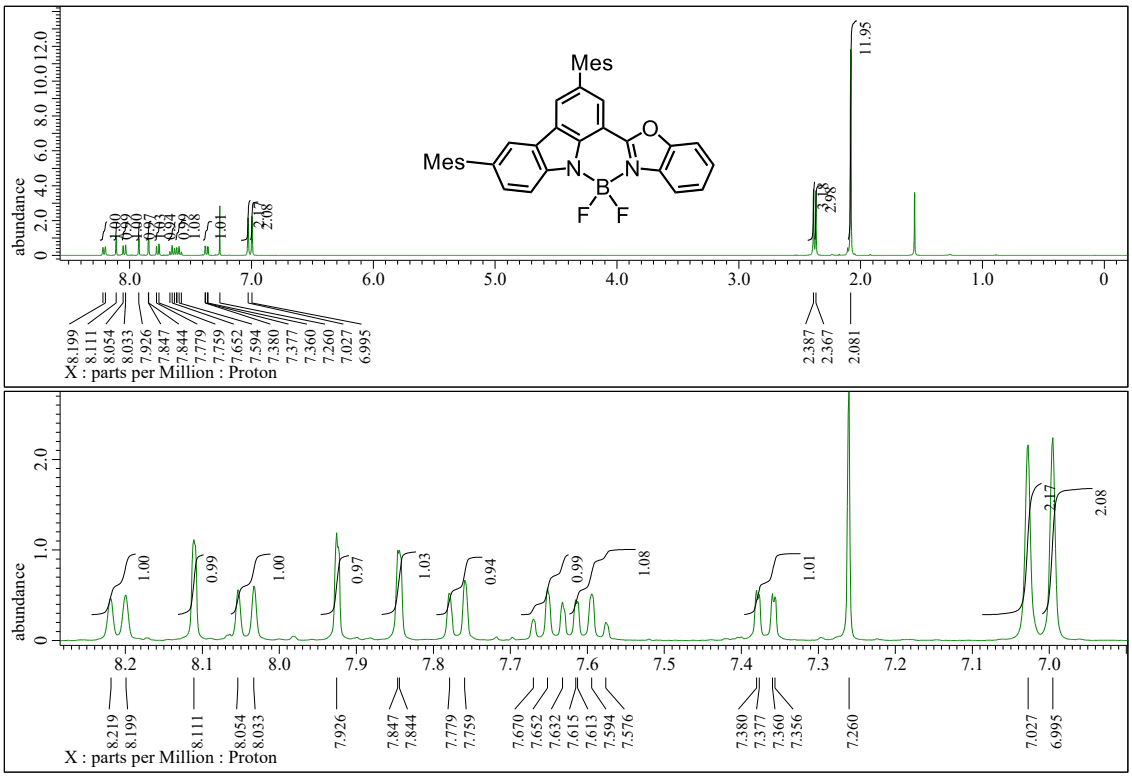
^{13}C NMR spectrum of **4c** in $CDCl_3$



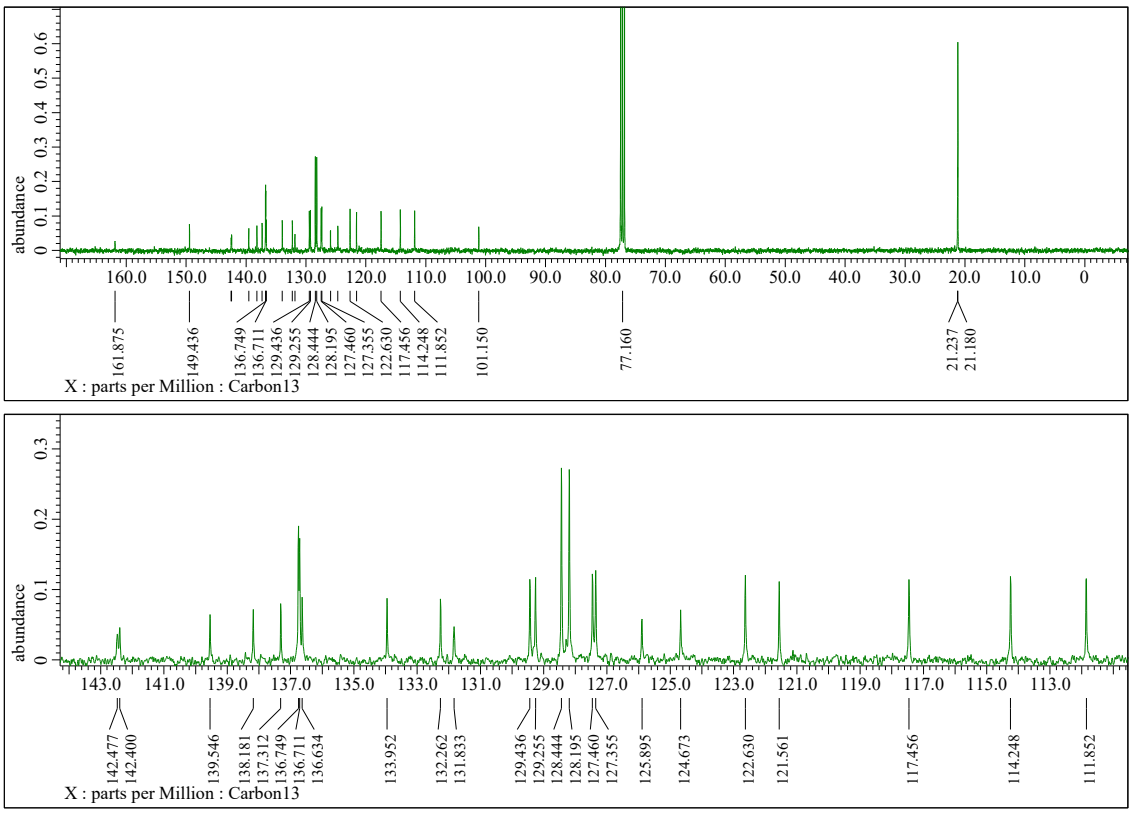
^{1}H NMR spectrum of **4d** in $CDCl_3$



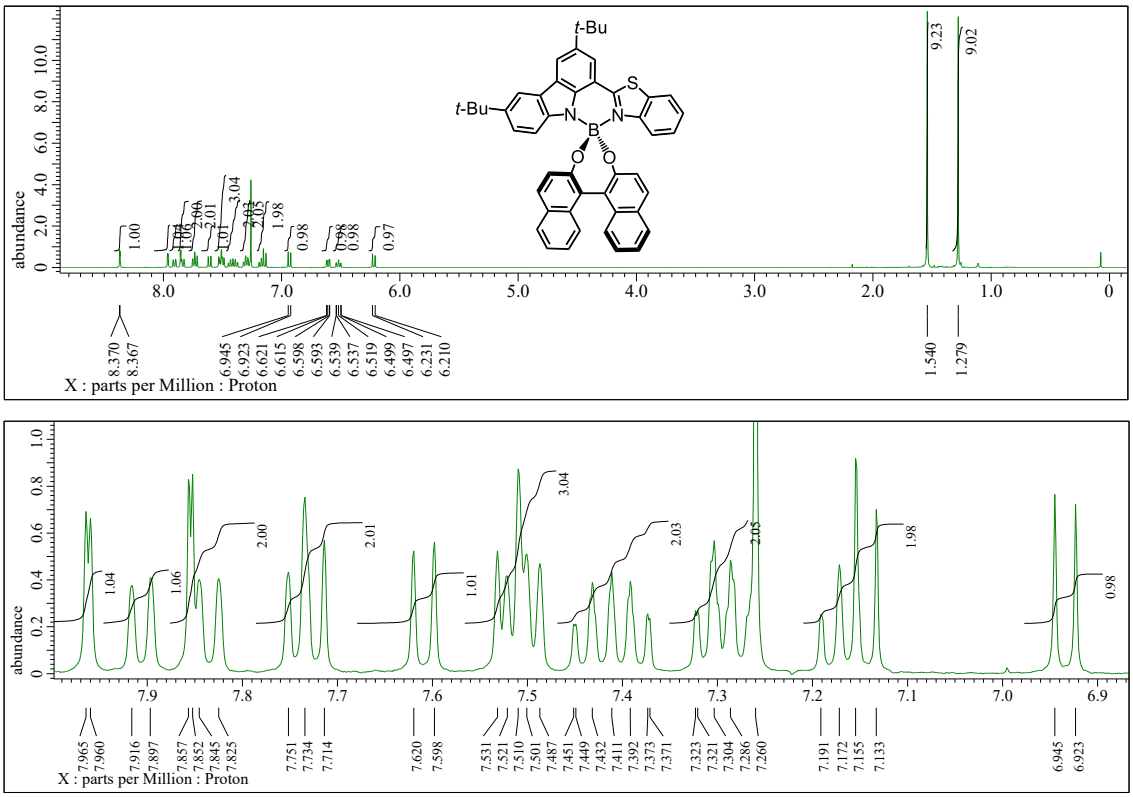
^{13}C NMR spectrum of **4d** in $CDCl_3$



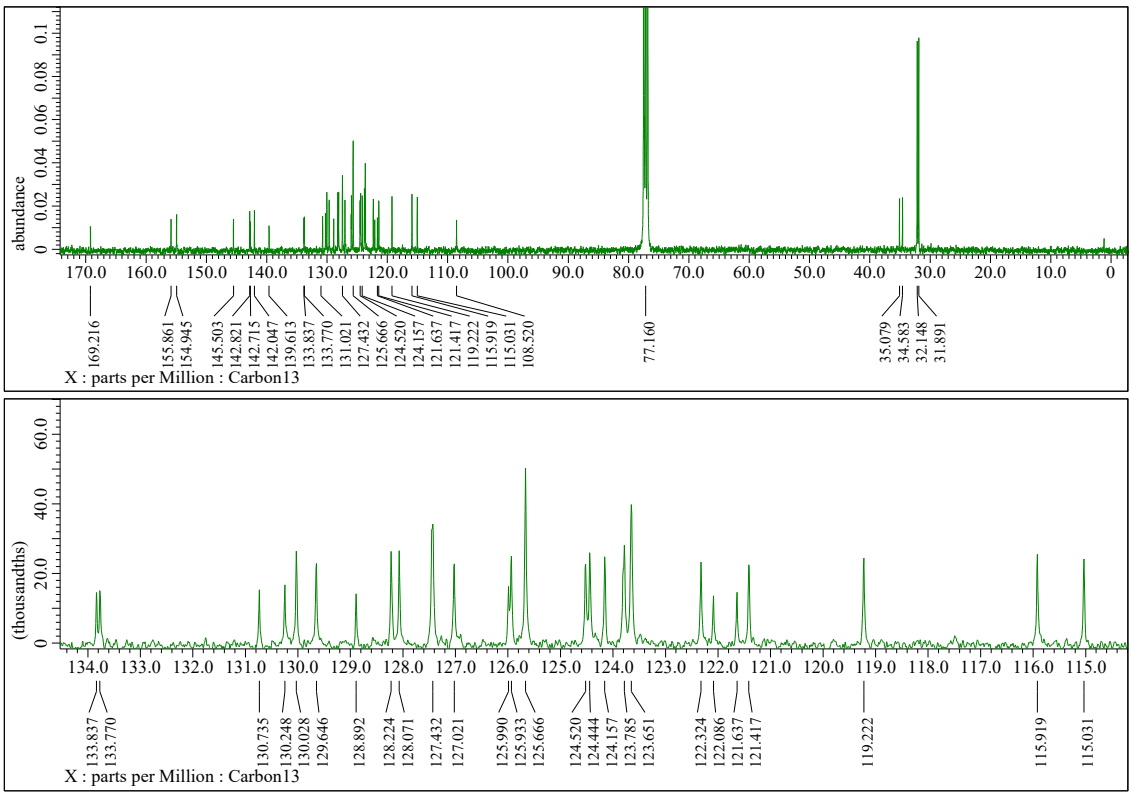
^{1}H NMR spectrum of **4e** in $CDCl_3$



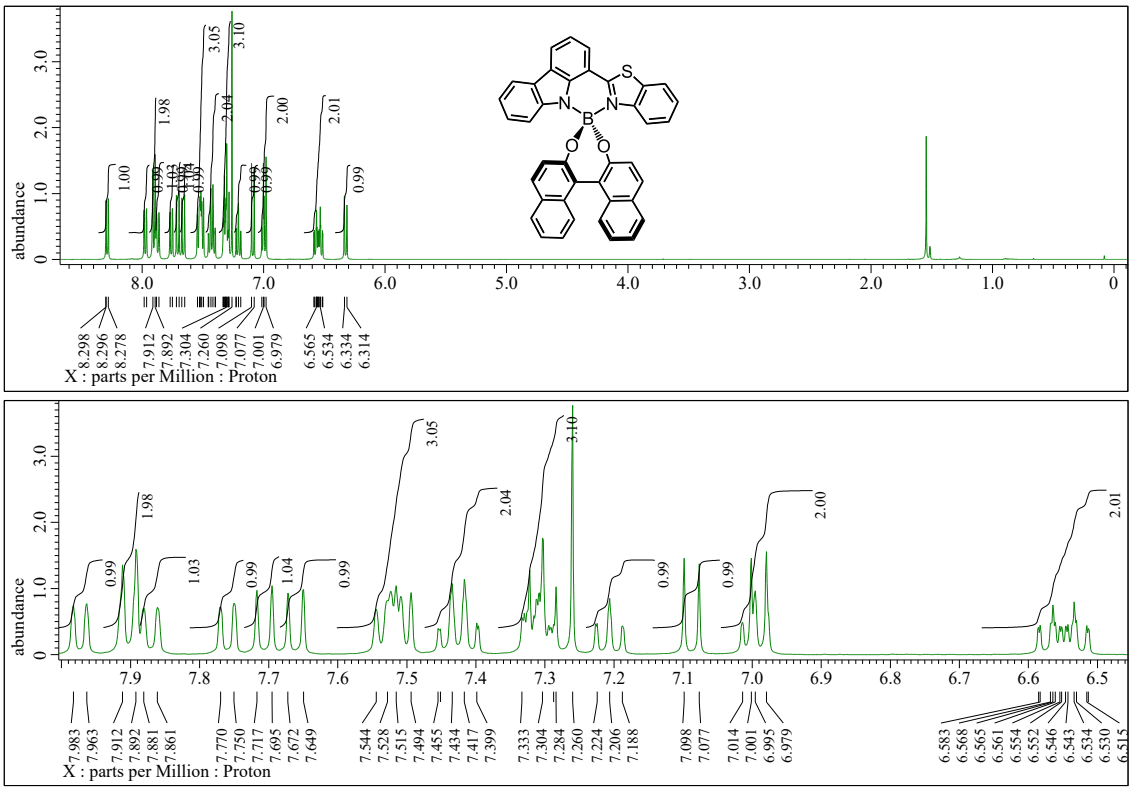
^{13}C NMR spectrum of **4e** in $CDCl_3$



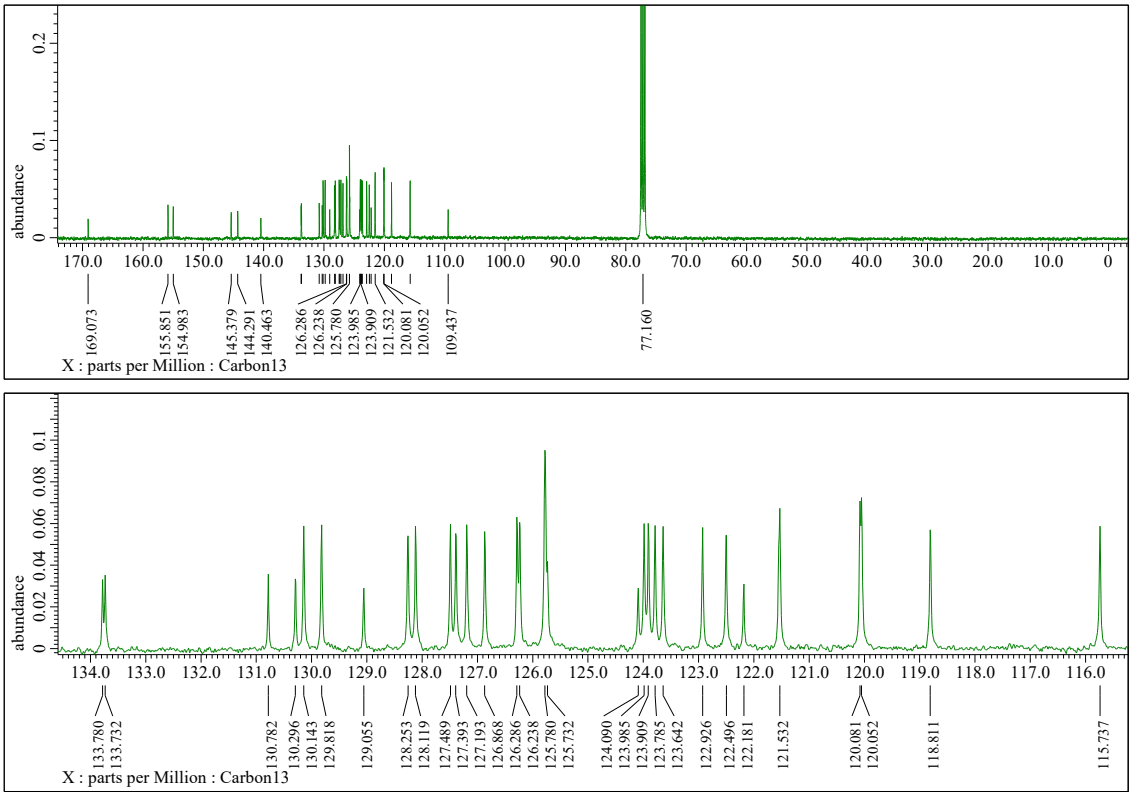
^{1}H NMR spectrum of **1a** in $CDCl_3$



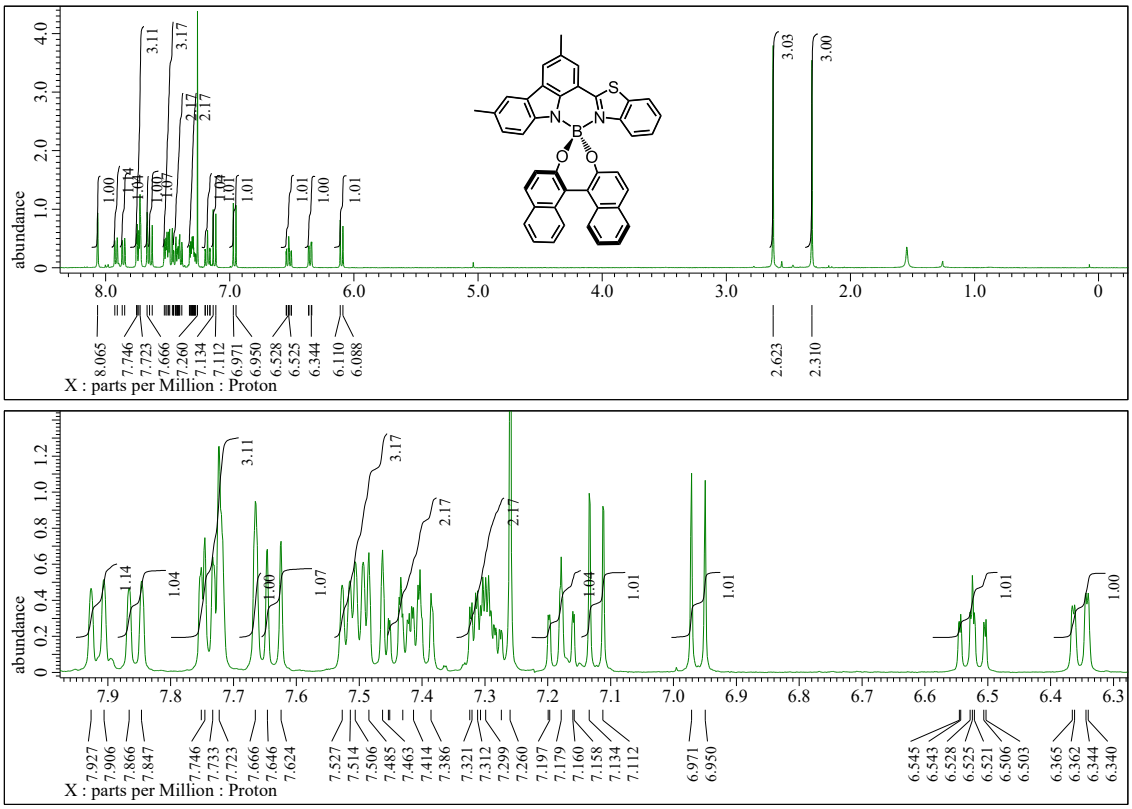
^{13}C NMR spectrum of **1a** in $CDCl_3$



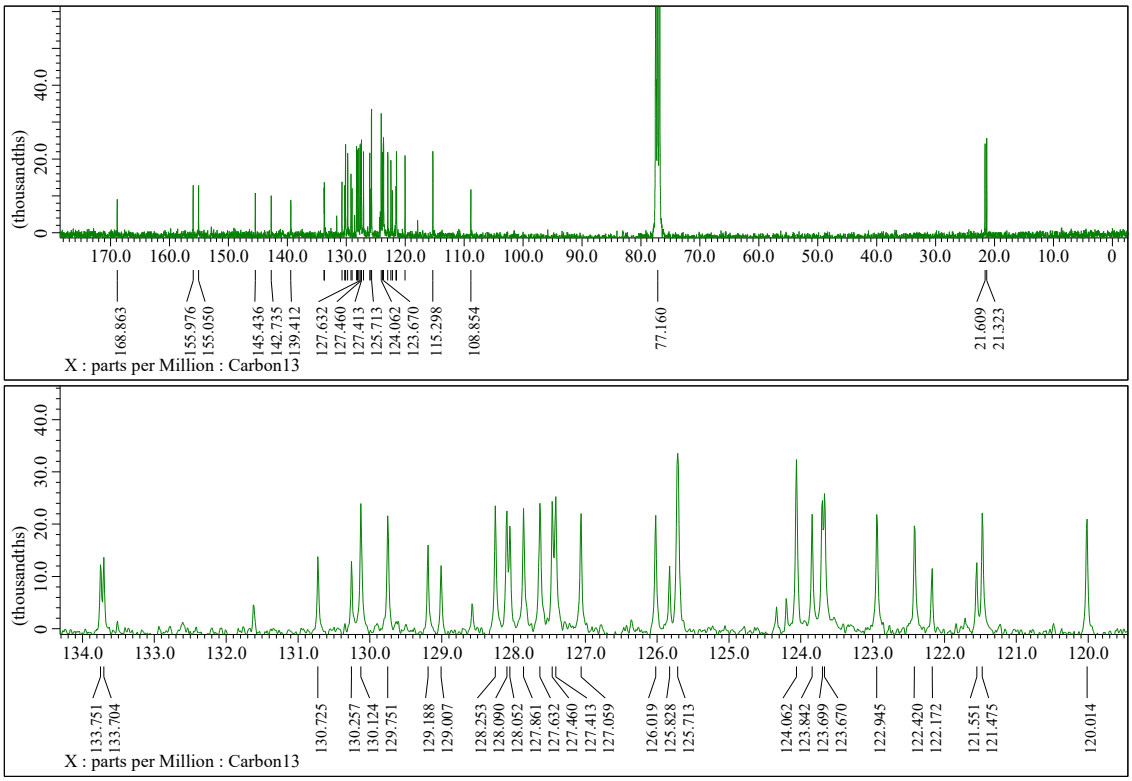
^{1}H NMR spectrum of **1b** in $CDCl_3$



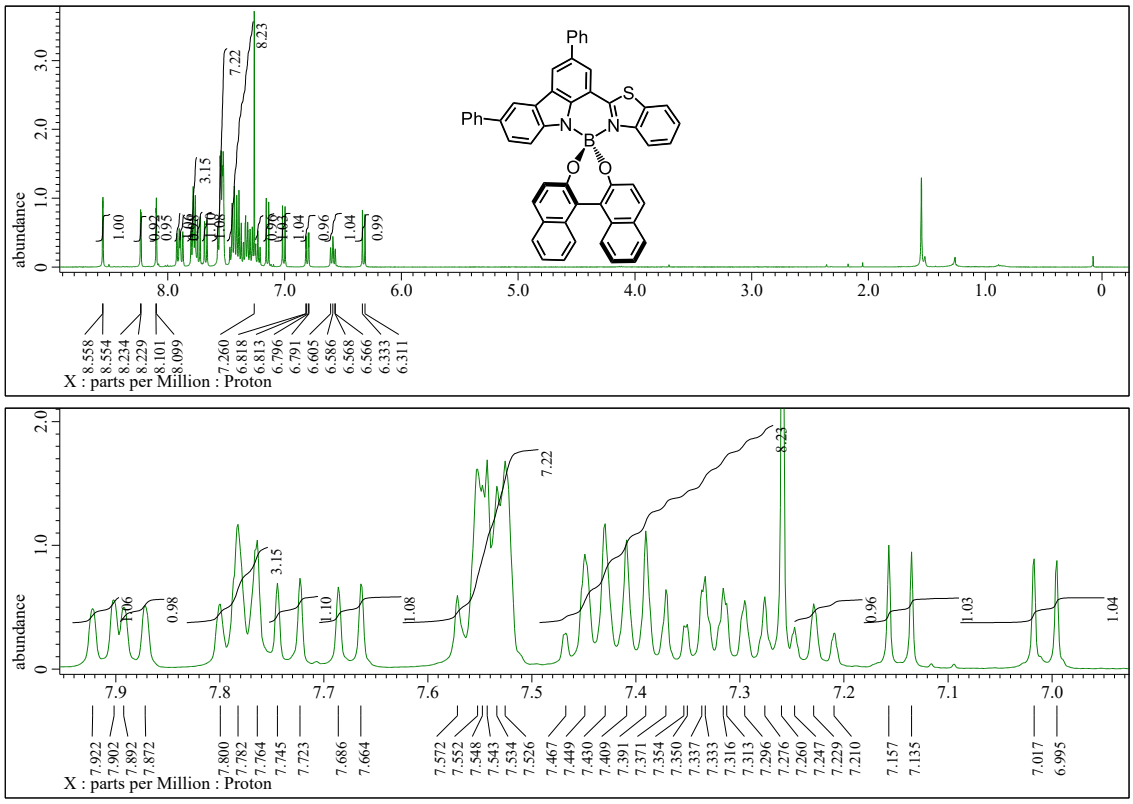
^{13}C NMR spectrum of **1b** in $CDCl_3$



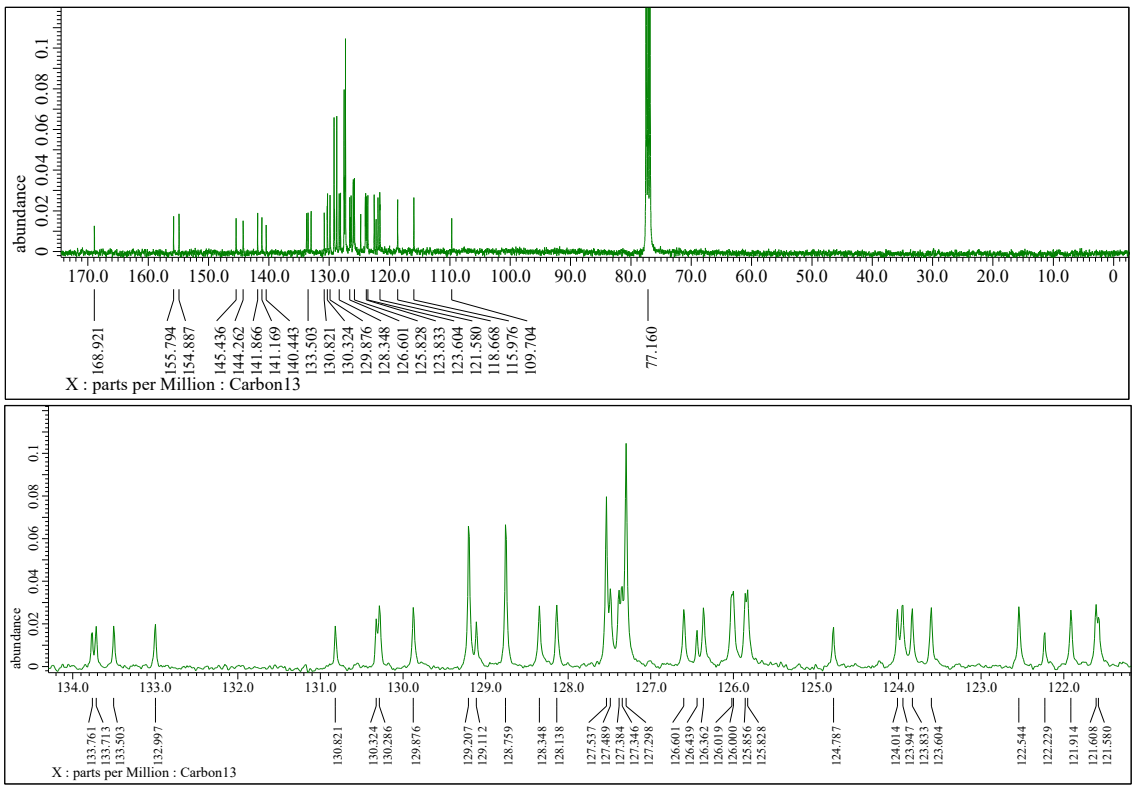
^{1}H NMR spectrum of **1c** in $CDCl_3$



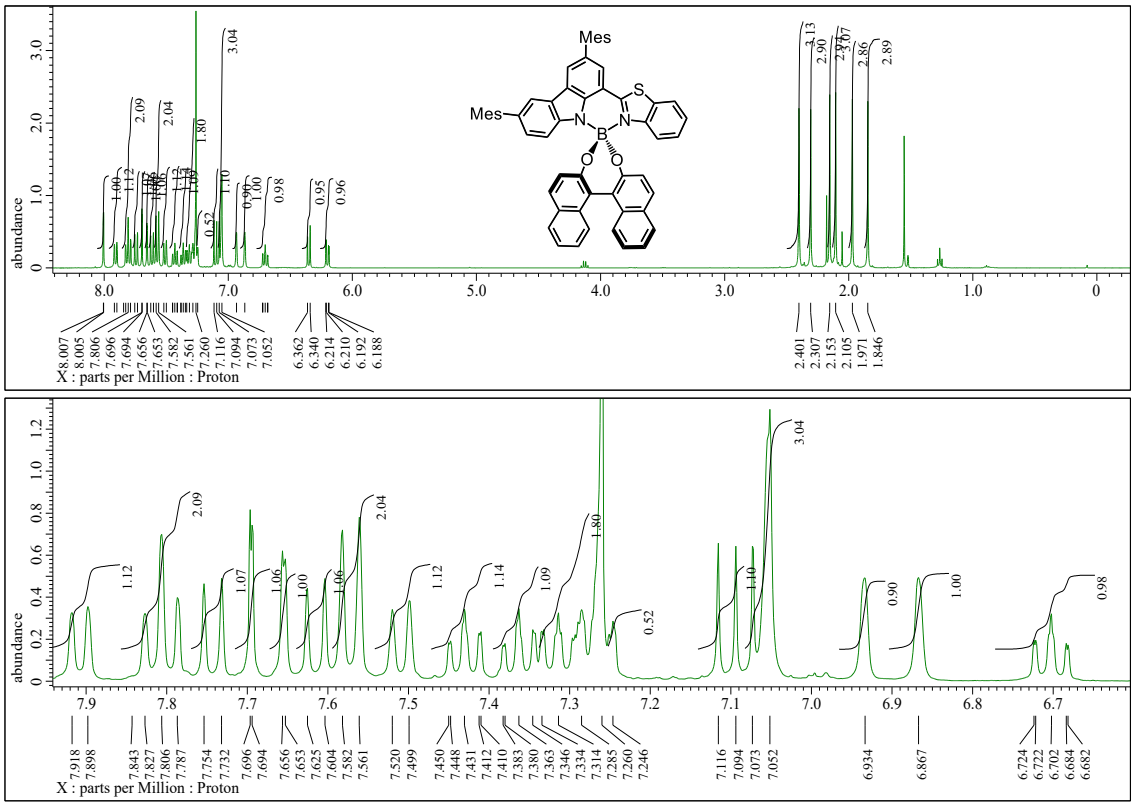
^{13}C NMR spectrum of **1c** in $CDCl_3$



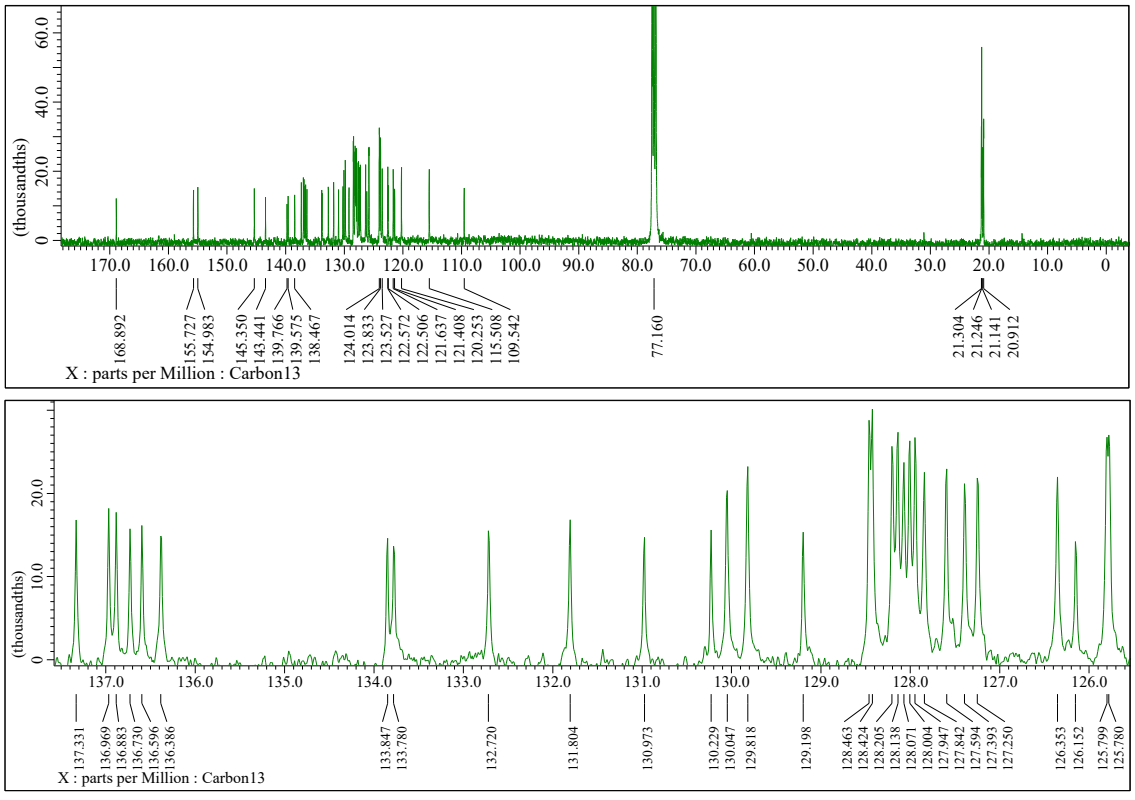
^{1}H NMR spectrum of **1d** in $CDCl_3$



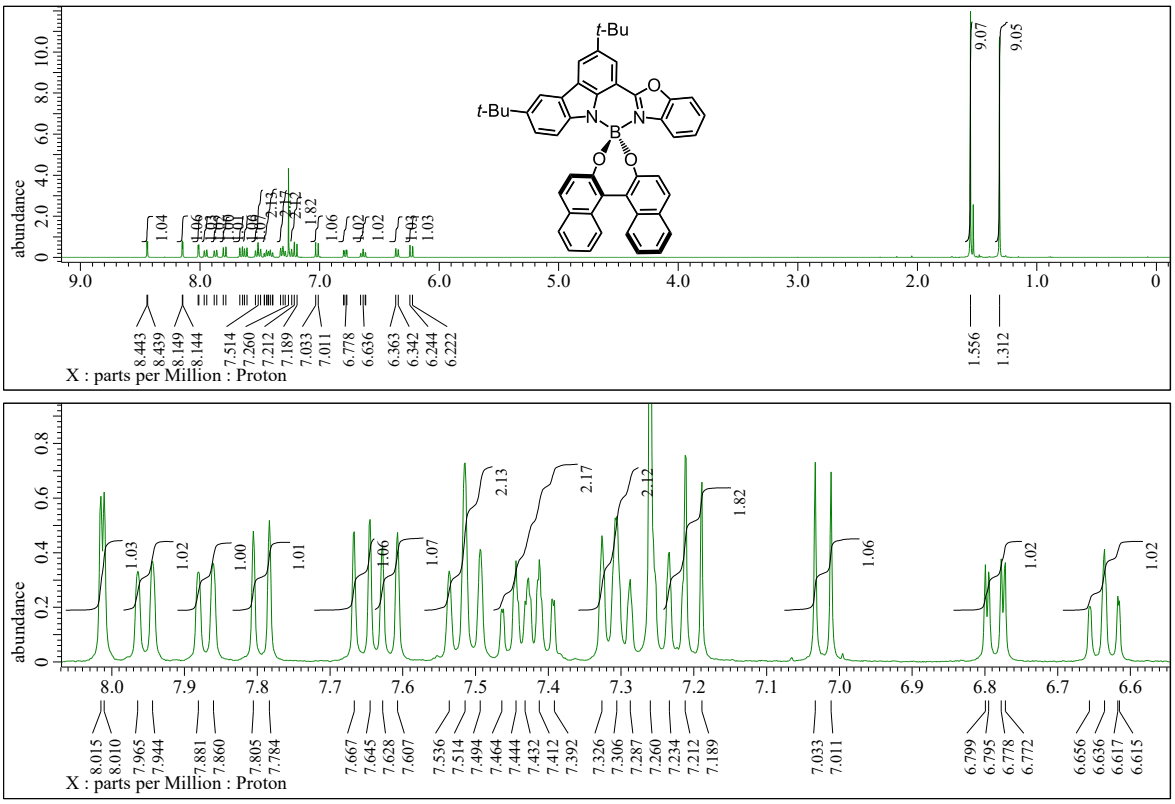
^{13}C NMR spectrum of **1d** in $CDCl_3$



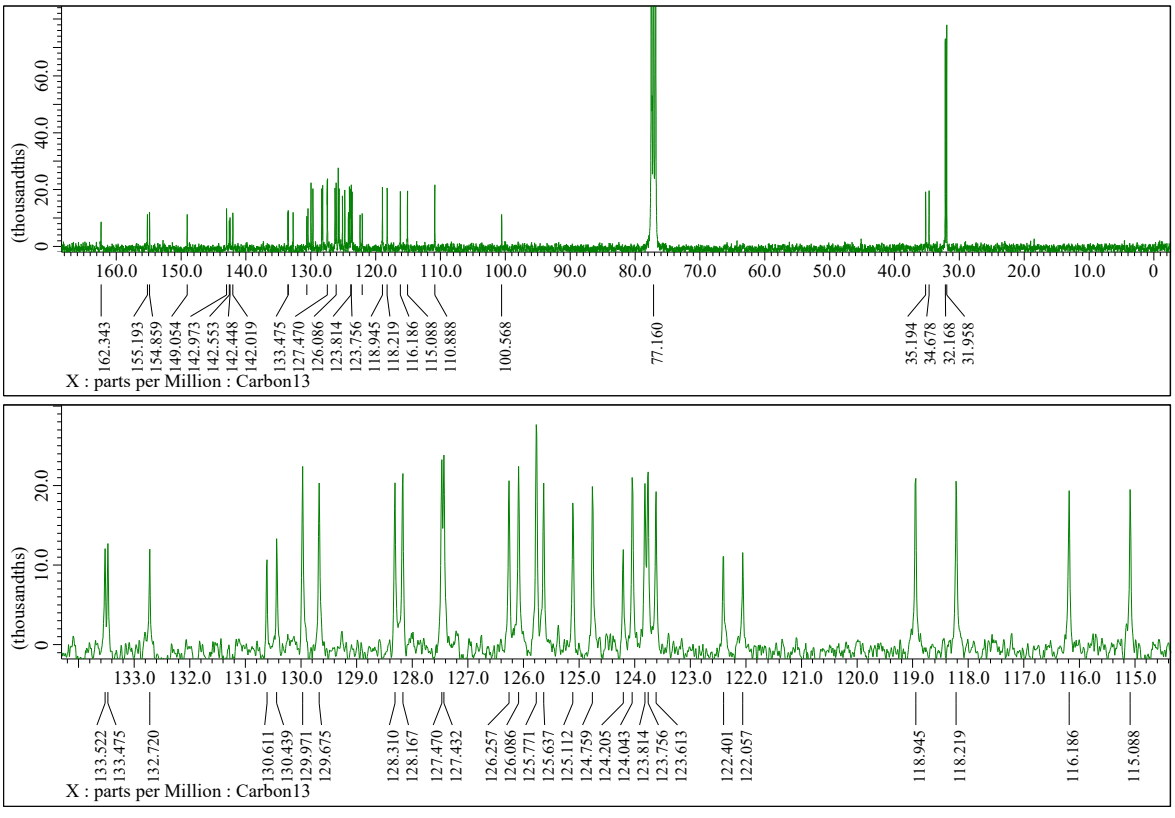
^{1}H NMR spectrum of **1e** in $CDCl_3$



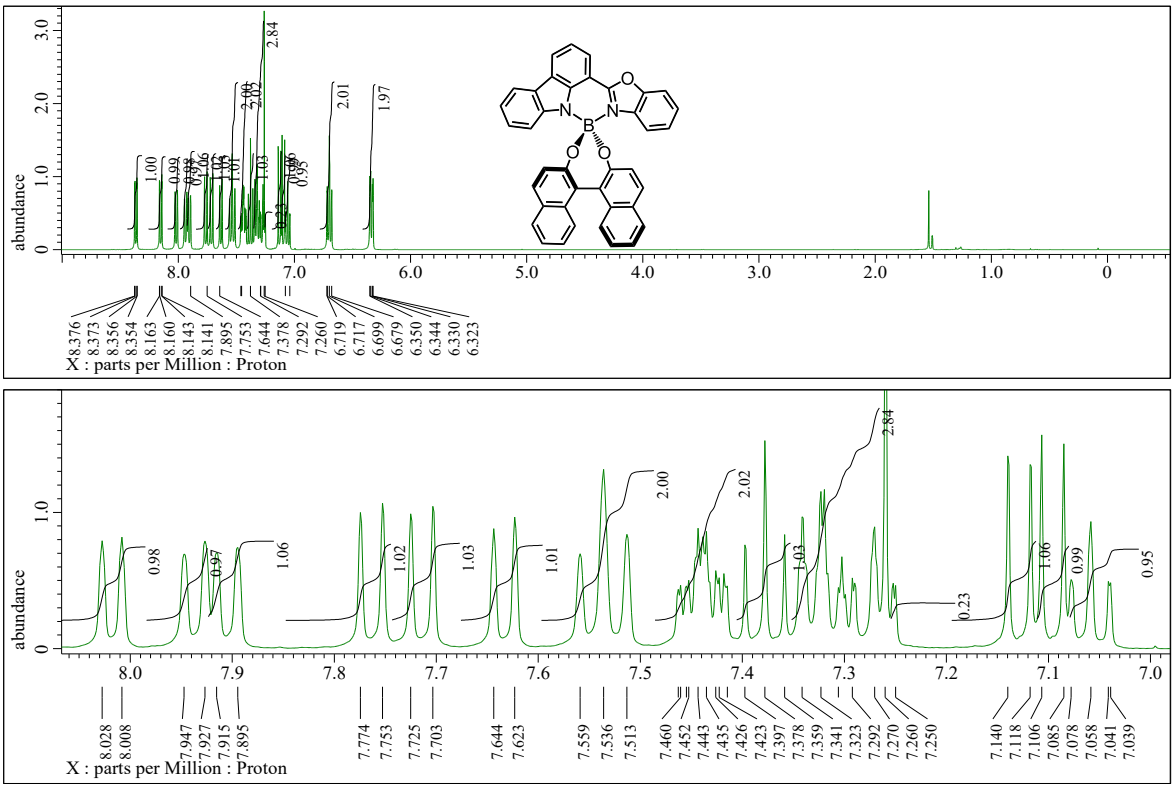
^{13}C NMR spectrum of **1e** in $CDCl_3$



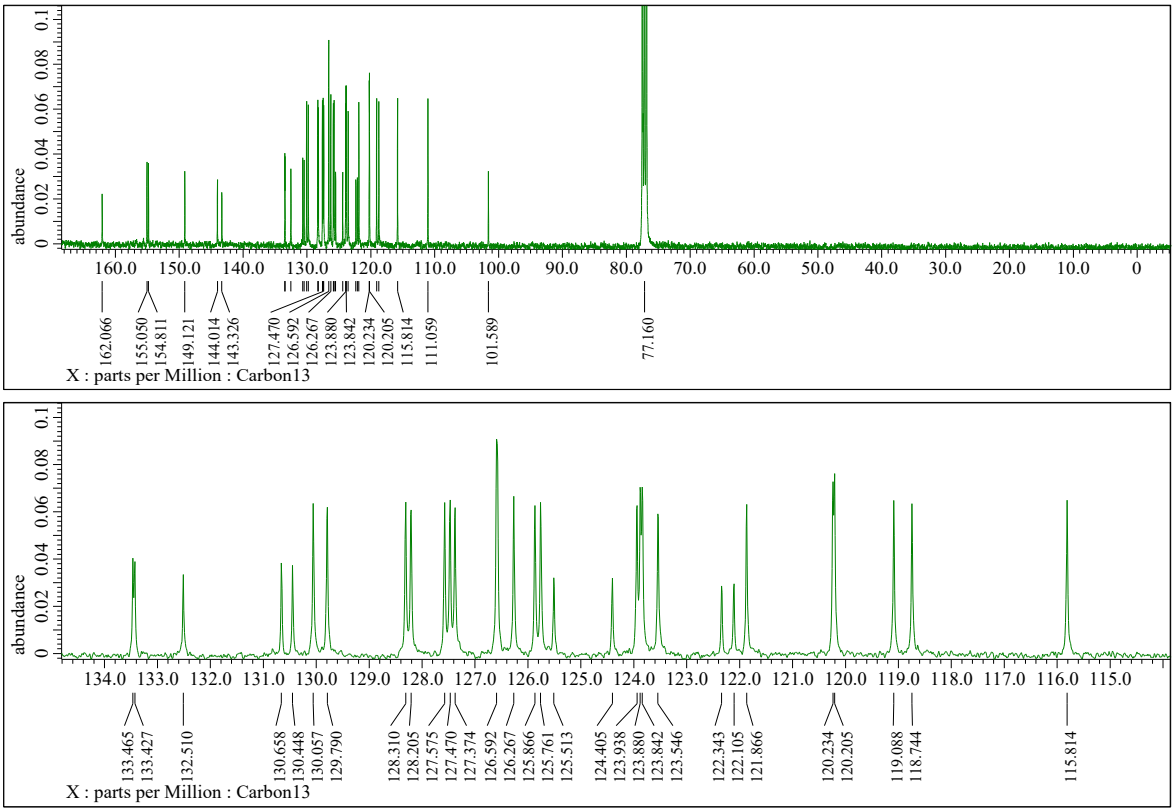
^{1}H NMR spectrum of **2a** in $CDCl_3$



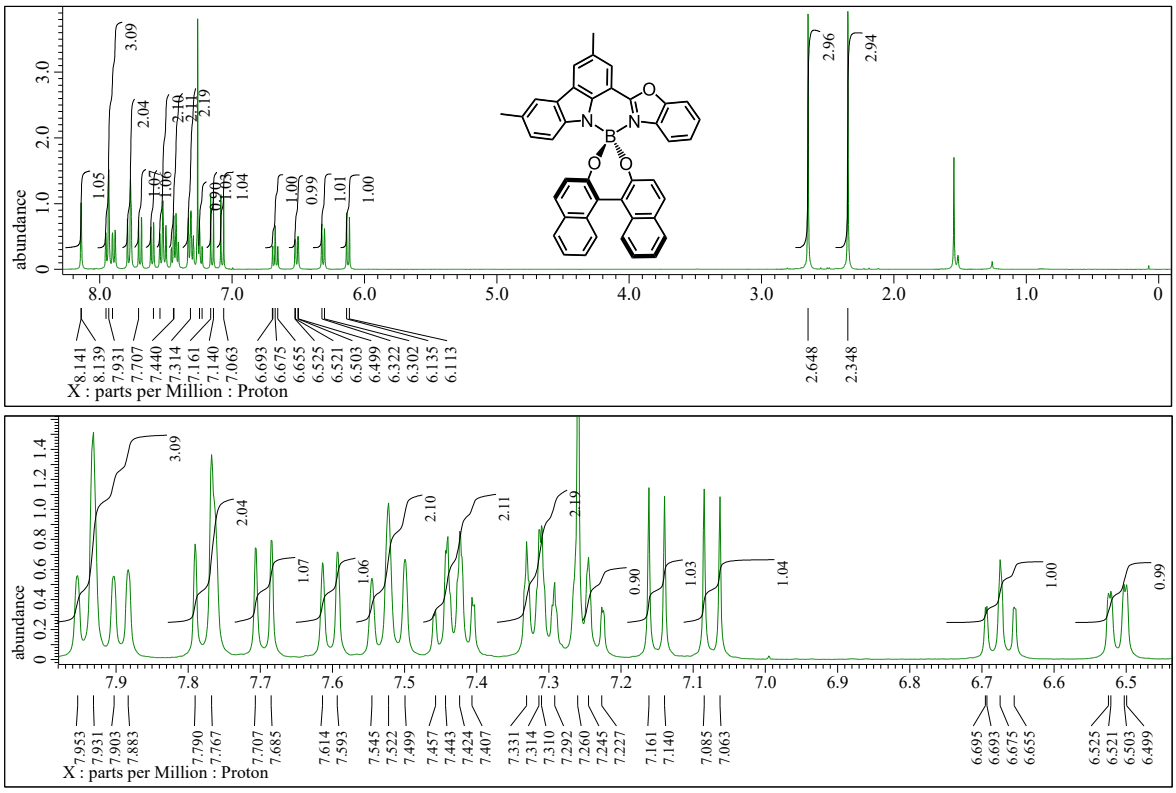
^{13}C NMR spectrum of **2a** in $CDCl_3$



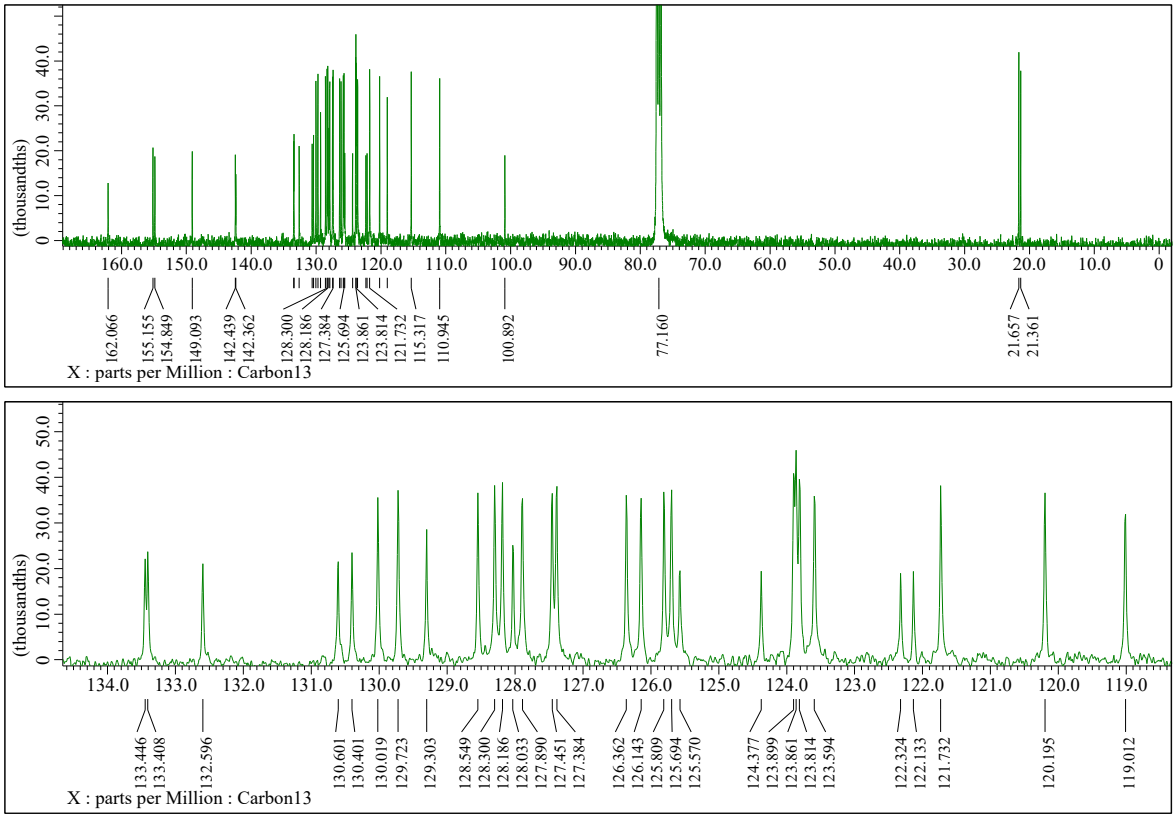
^{1}H NMR spectrum of **2b** in $CDCl_3$



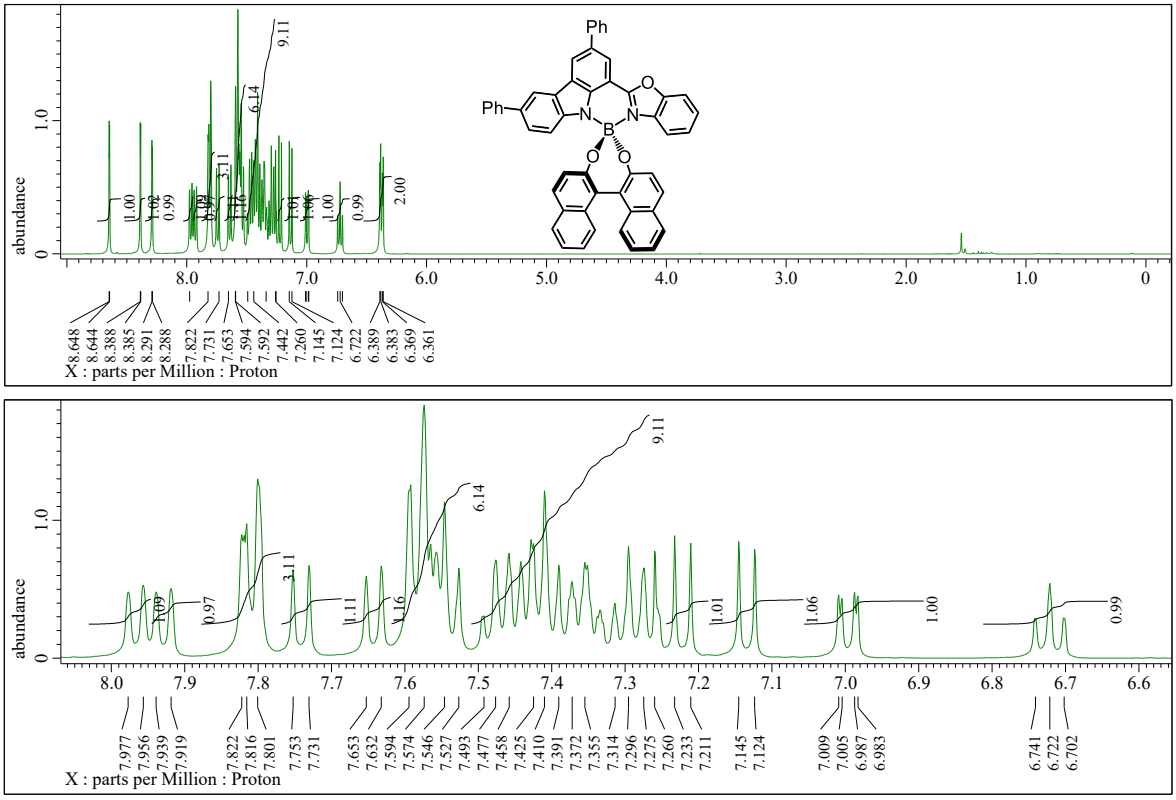
^{13}C NMR spectrum of **2b** in $CDCl_3$



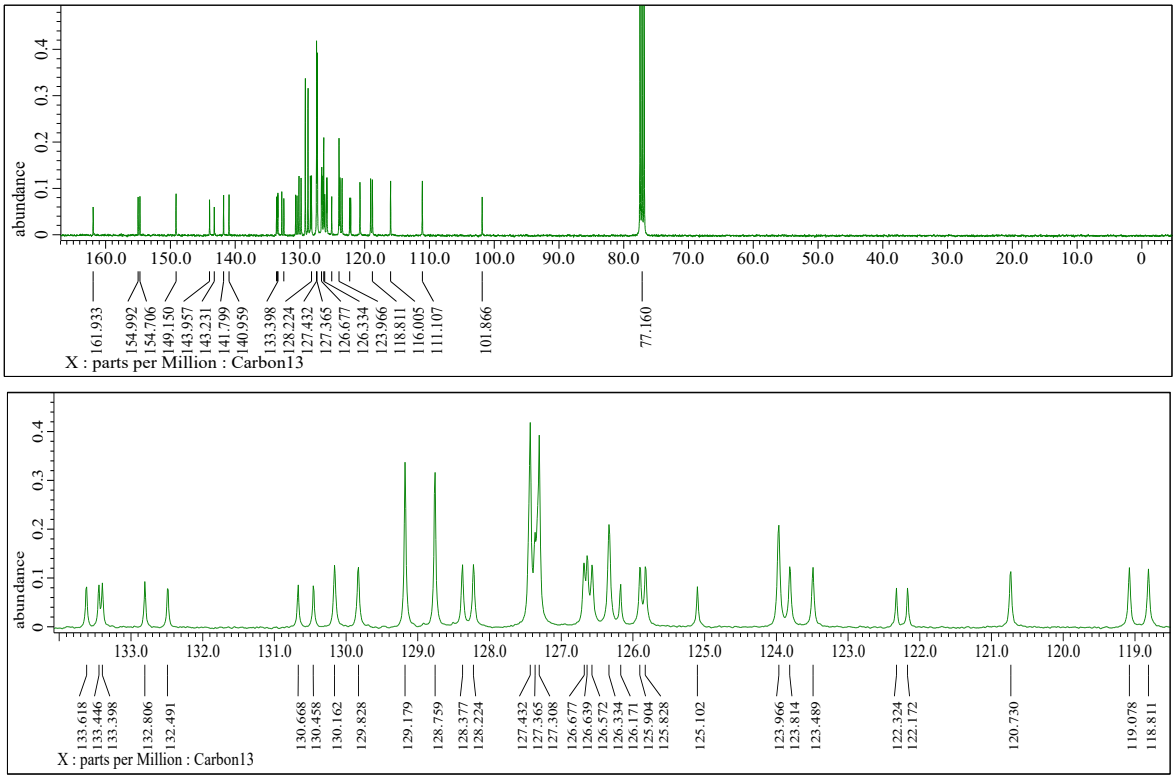
^{1}H NMR spectrum of **2c** in $CDCl_3$



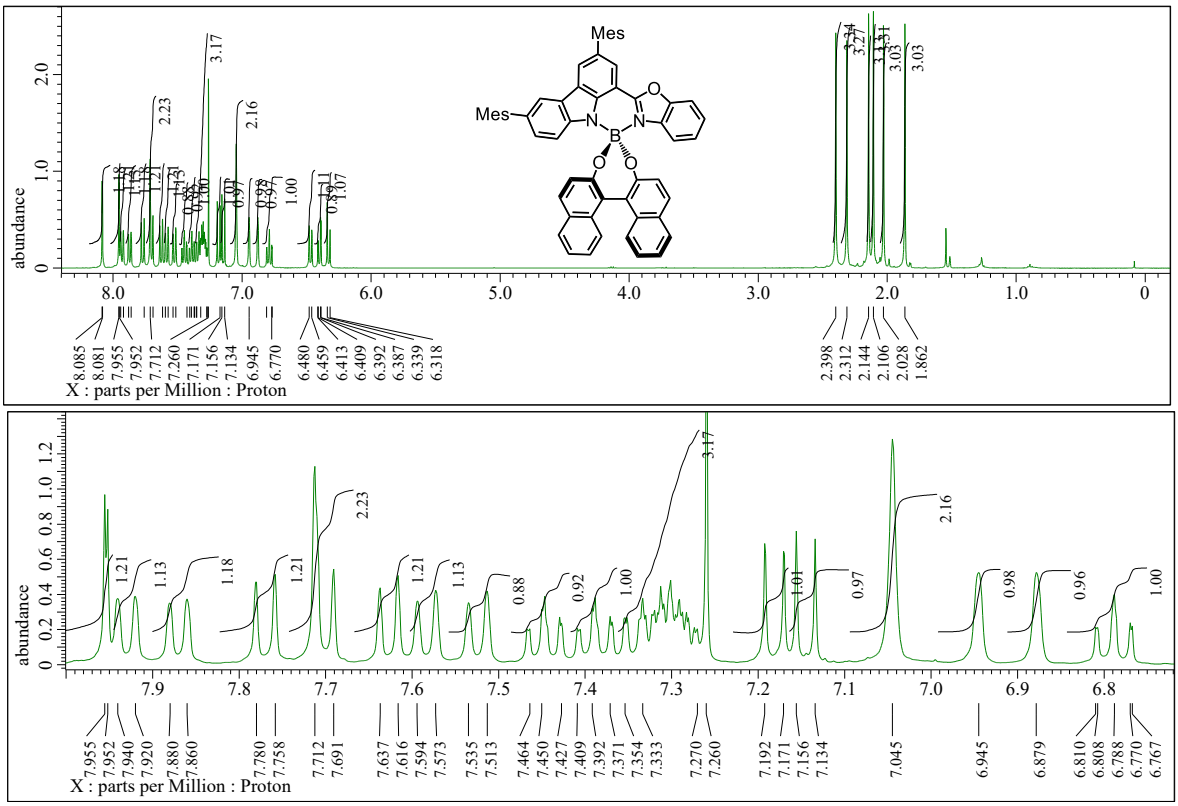
^{13}C NMR spectrum of **2c** in $CDCl_3$



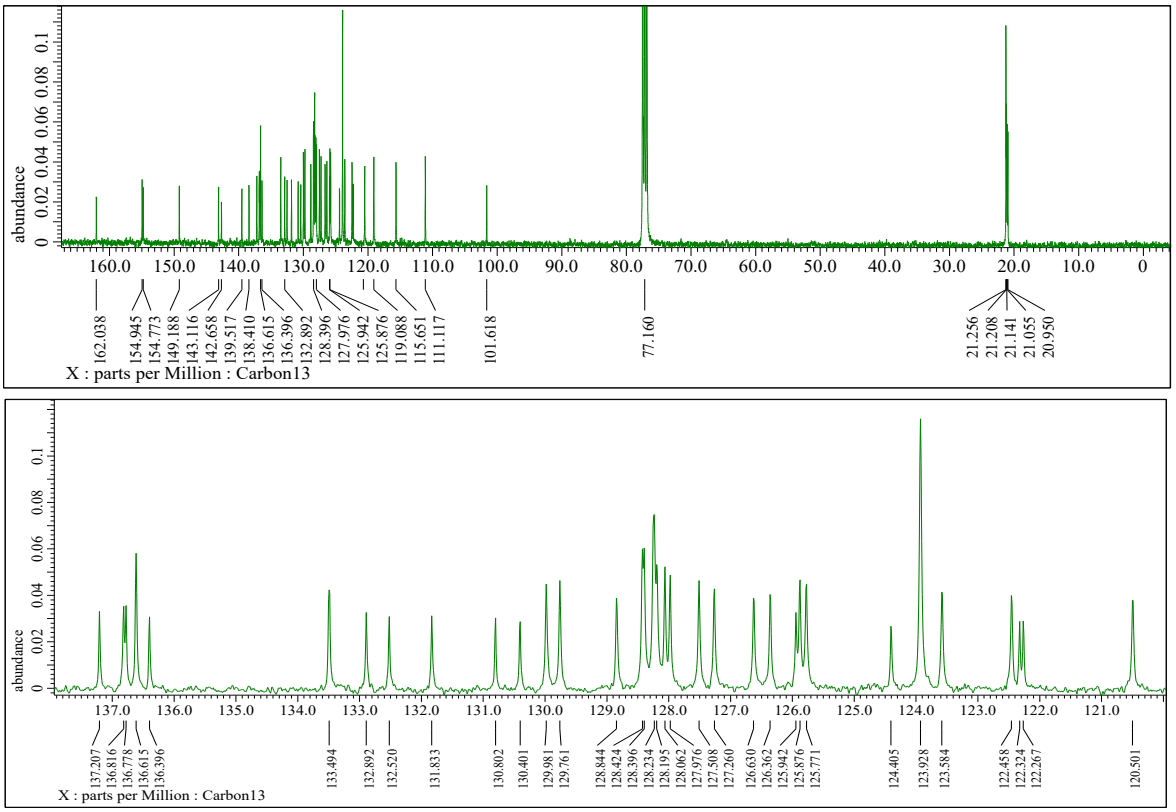
^{1}H NMR spectrum of **2d** in $CDCl_3$



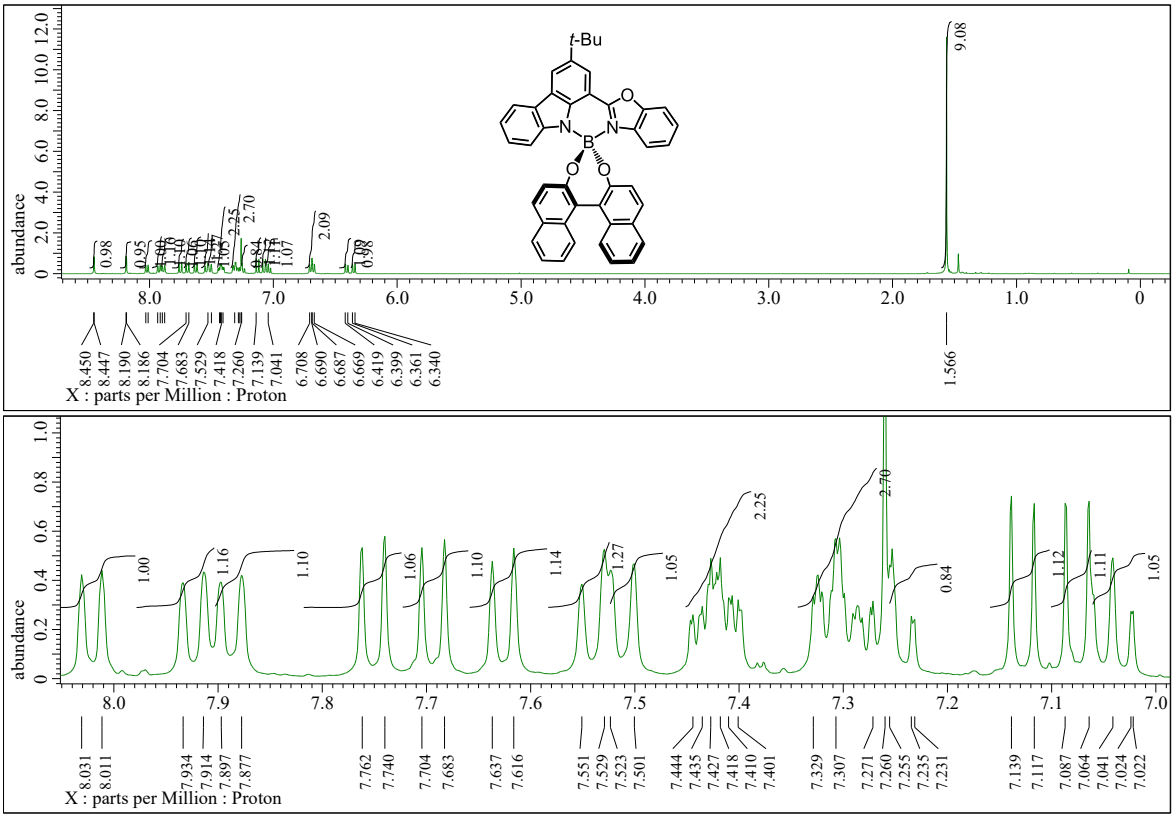
^{13}C NMR spectrum of **2d** in $CDCl_3$



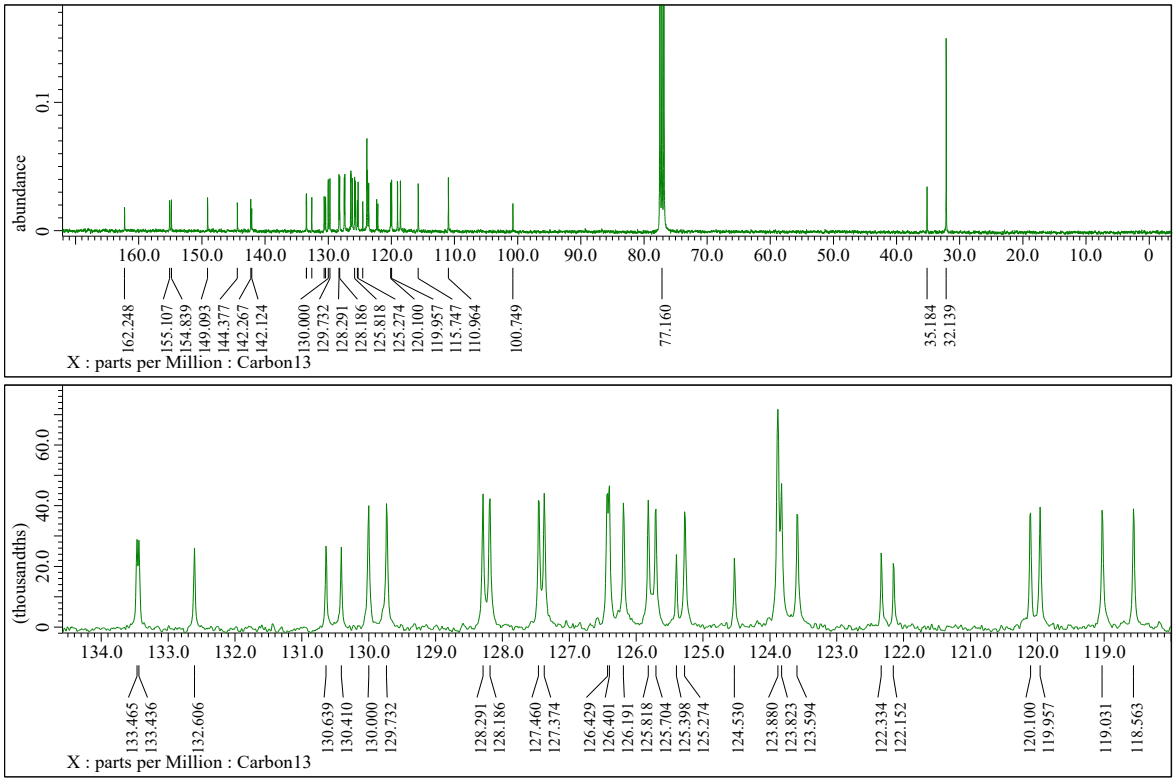
^{1}H NMR spectrum of **2e** in $CDCl_3$



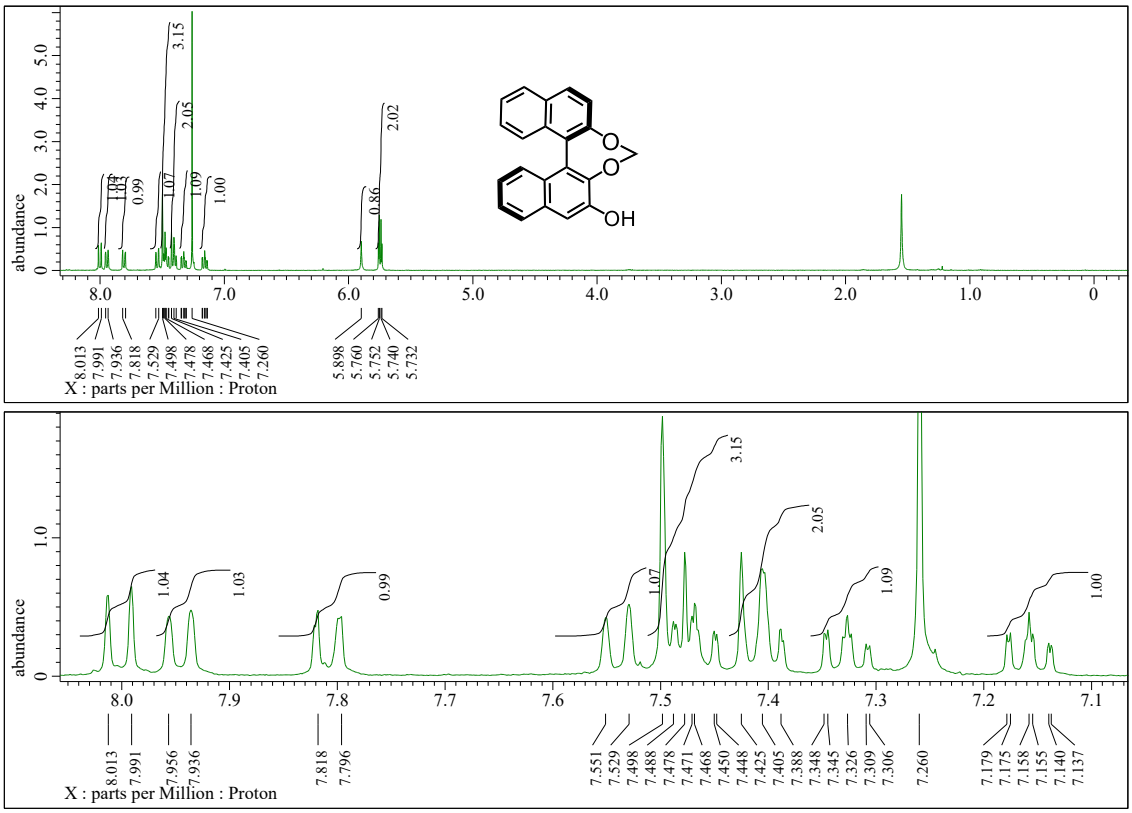
^{13}C NMR spectrum of **2e** in $CDCl_3$



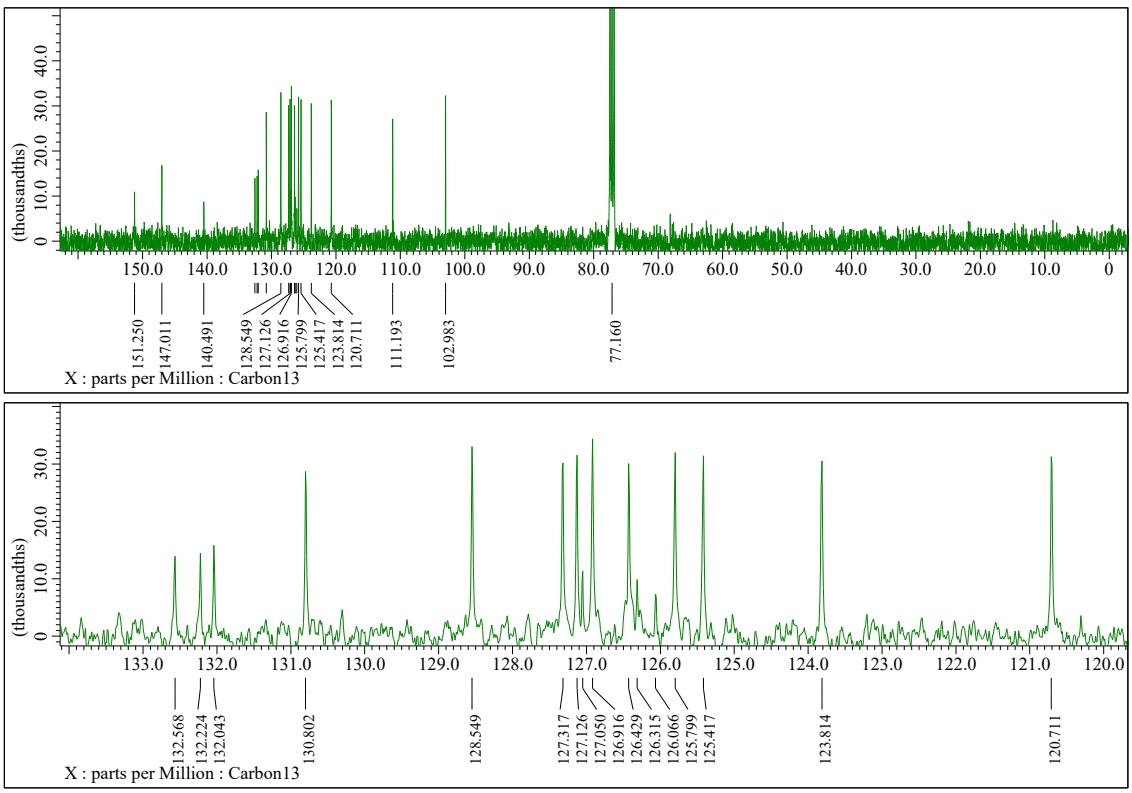
^{1}H NMR spectrum of **2f** in $CDCl_3$



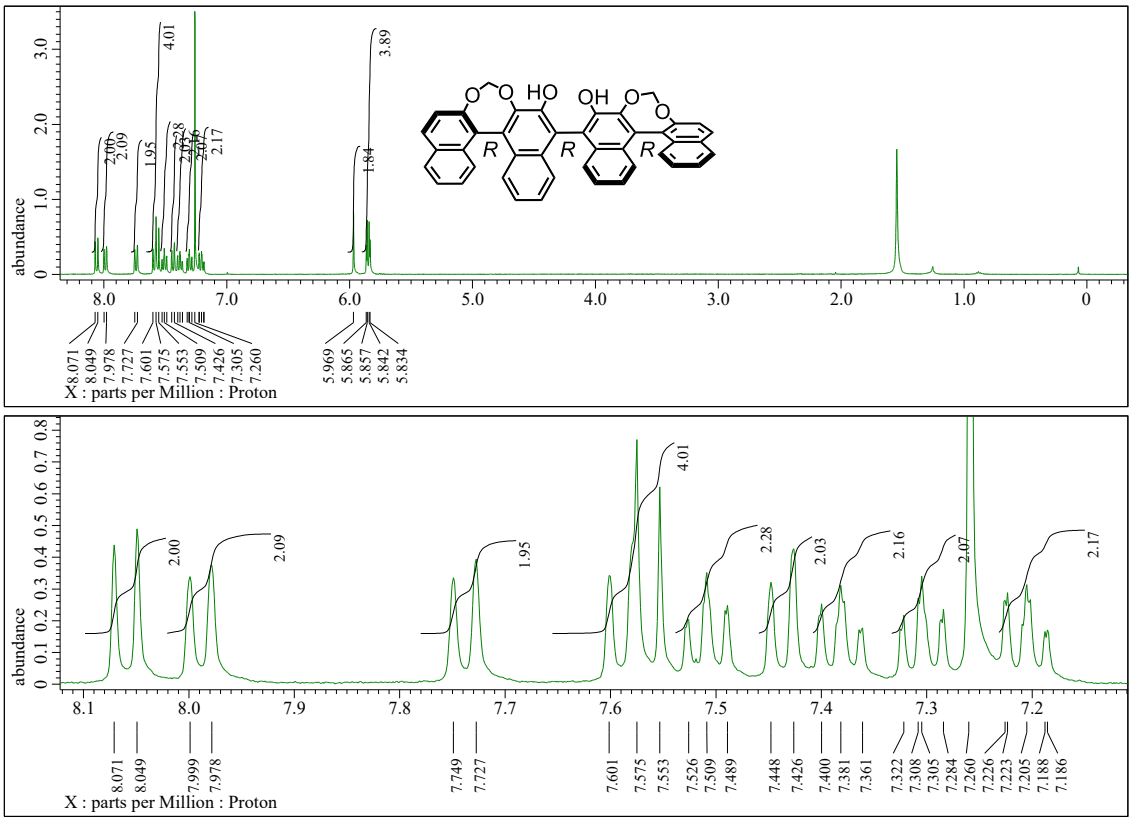
^{13}C NMR spectrum of **2f** in $CDCl_3$



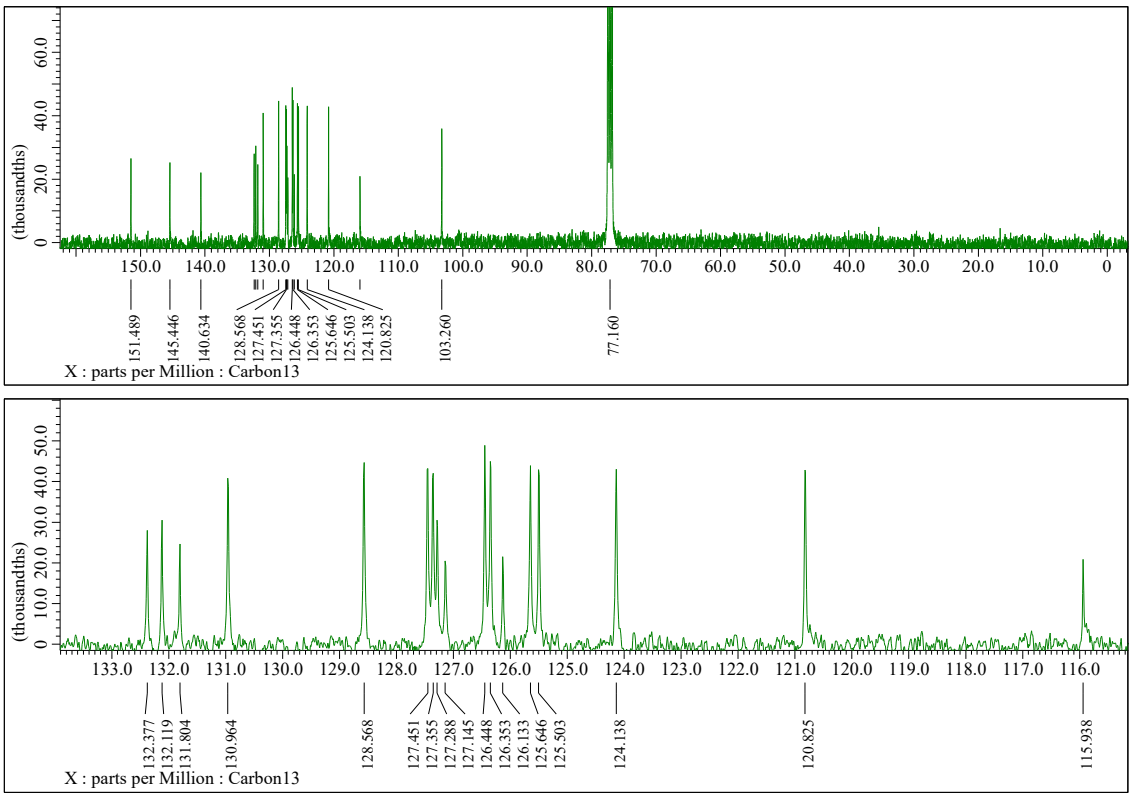
^{1}H NMR spectrum of **9** in $CDCl_3$



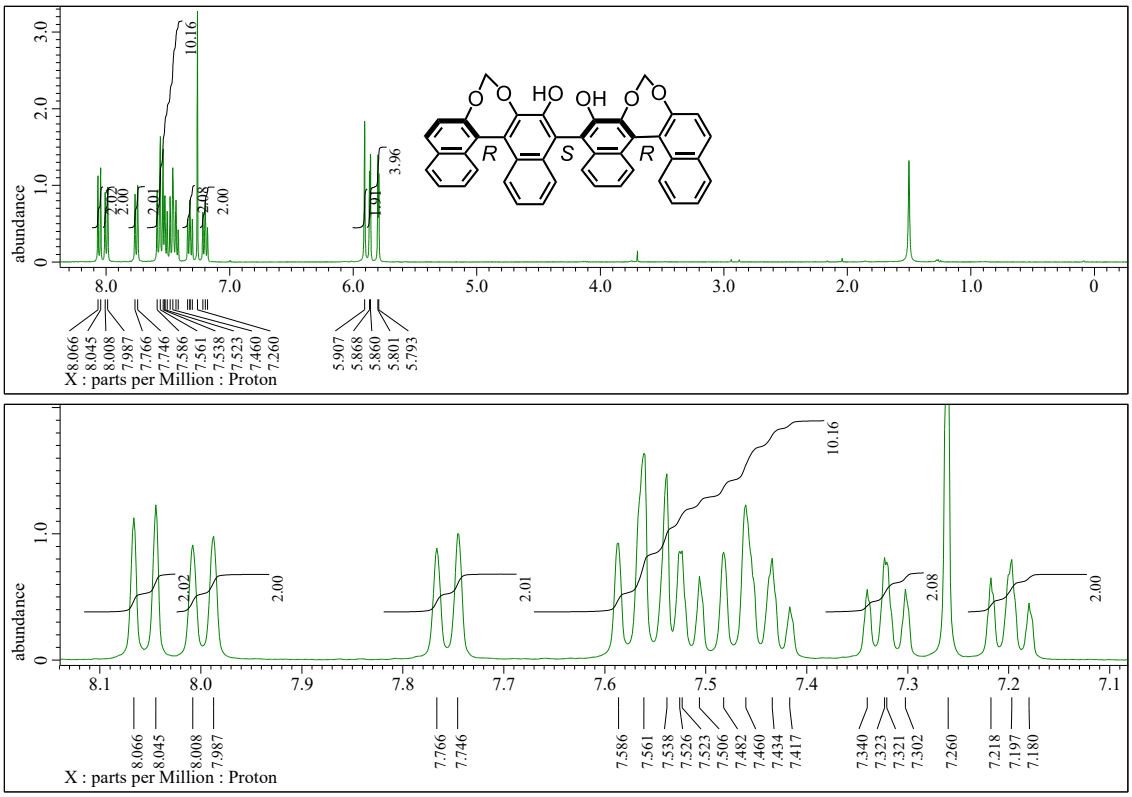
^{13}C NMR spectrum of **9** in $CDCl_3$



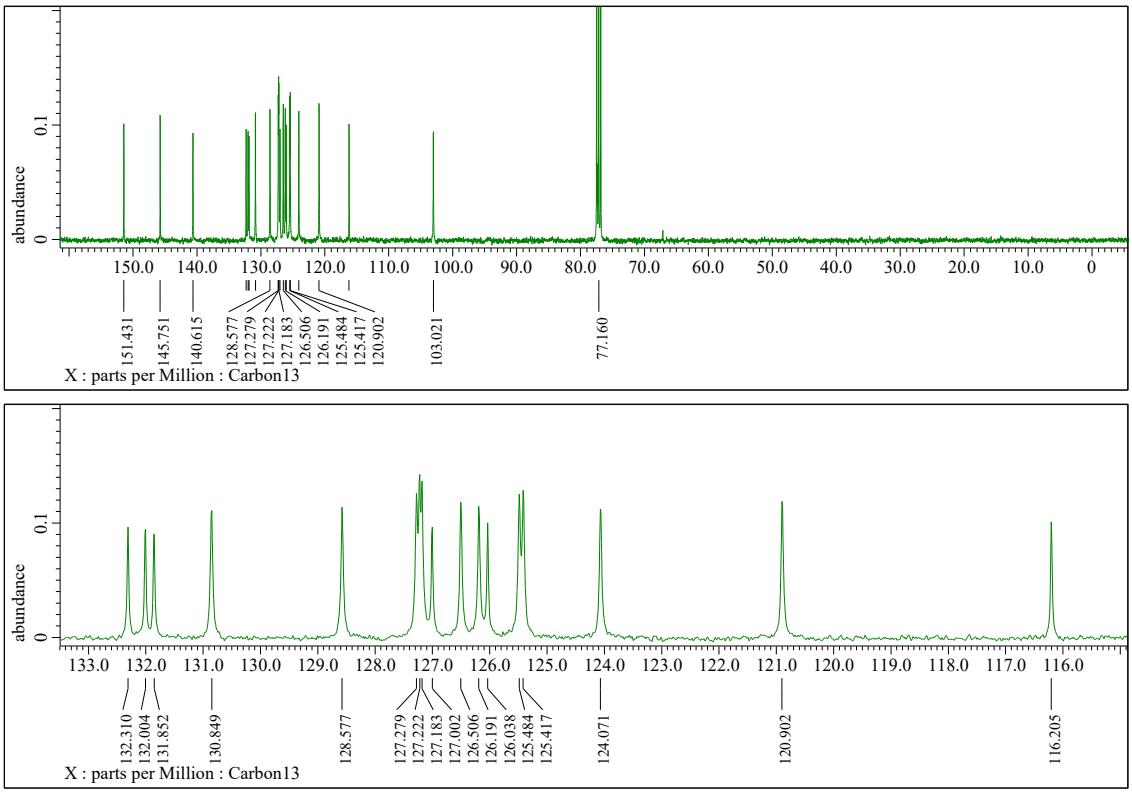
^{1}H NMR spectrum of (*R*,*R*,*R*)-**12** in $CDCl_3$



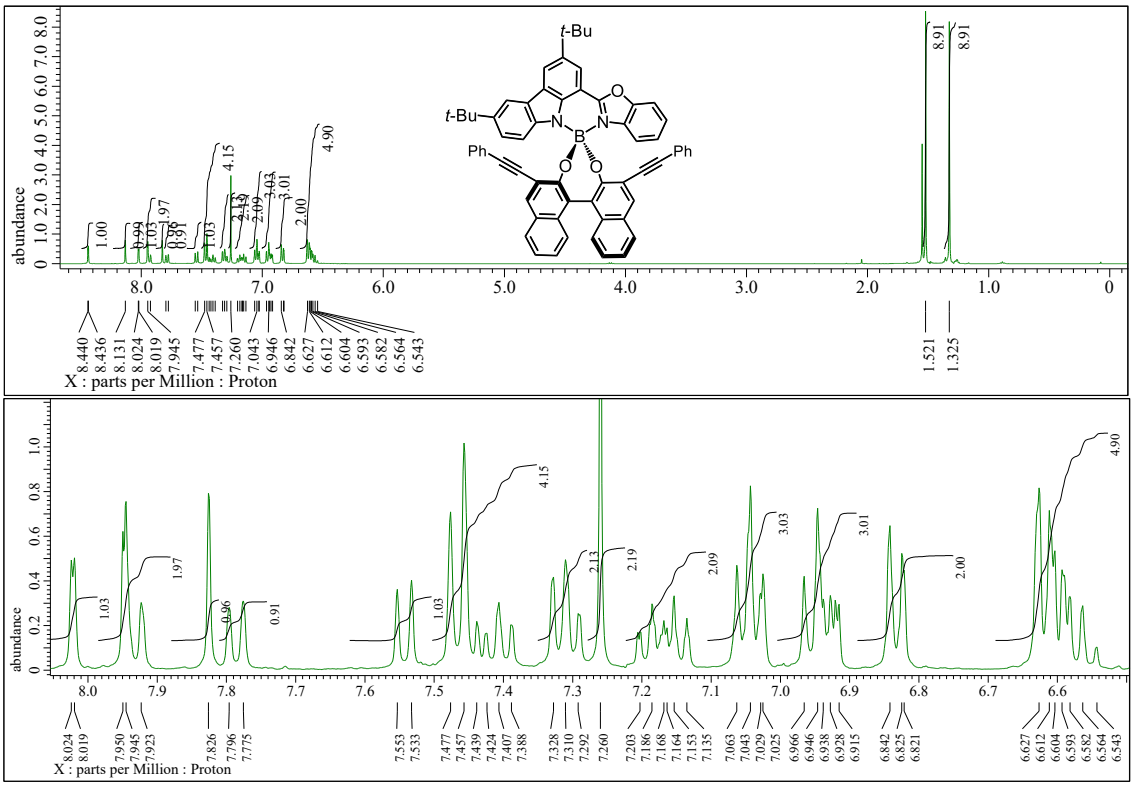
^{13}C NMR spectrum of (*R*,*R*,*R*)-**12** in $CDCl_3$



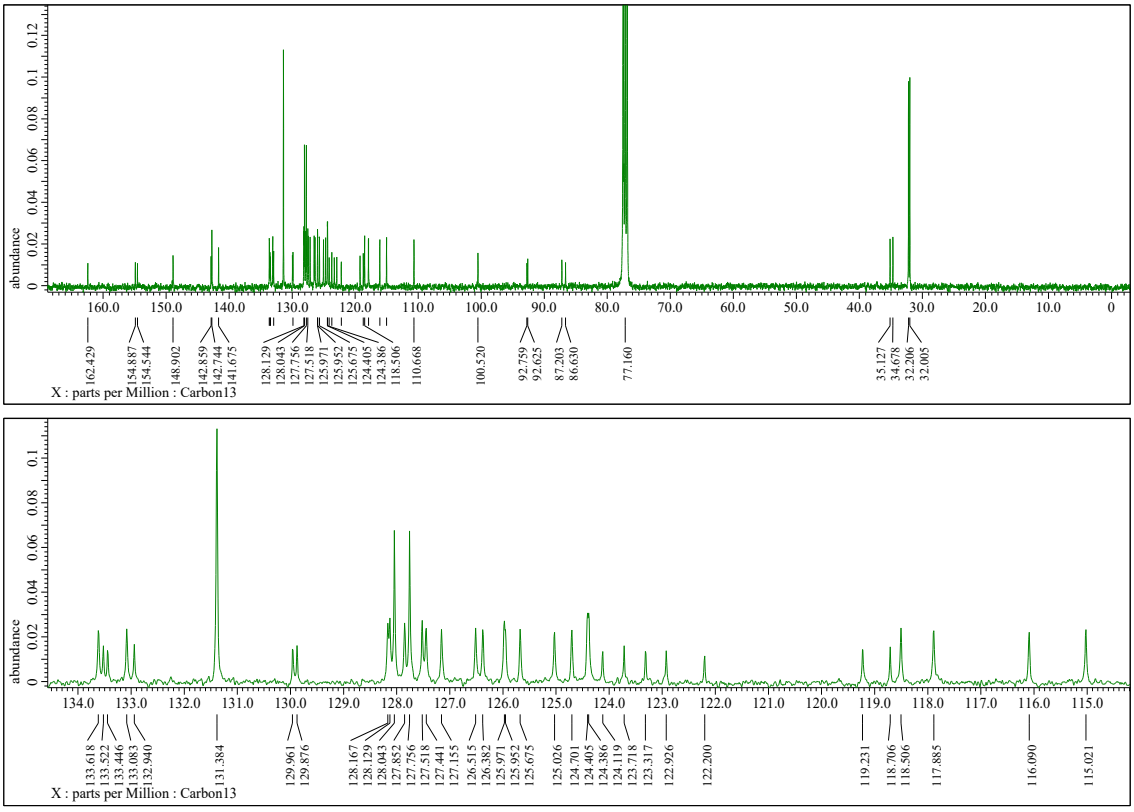
^{1}H NMR spectrum of (*R*,*S*,*R*)-**12** in $CDCl_3$



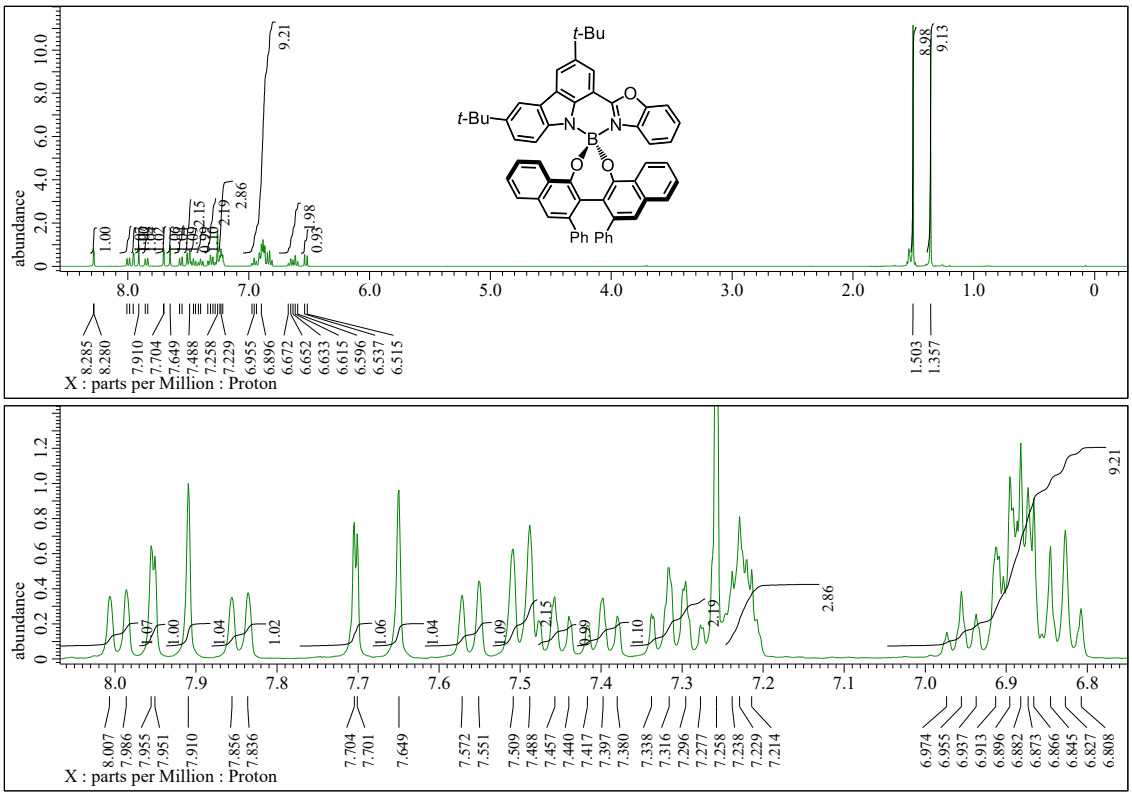
^{13}C NMR spectrum of (*R*,*S*,*R*)-**12** in $CDCl_3$



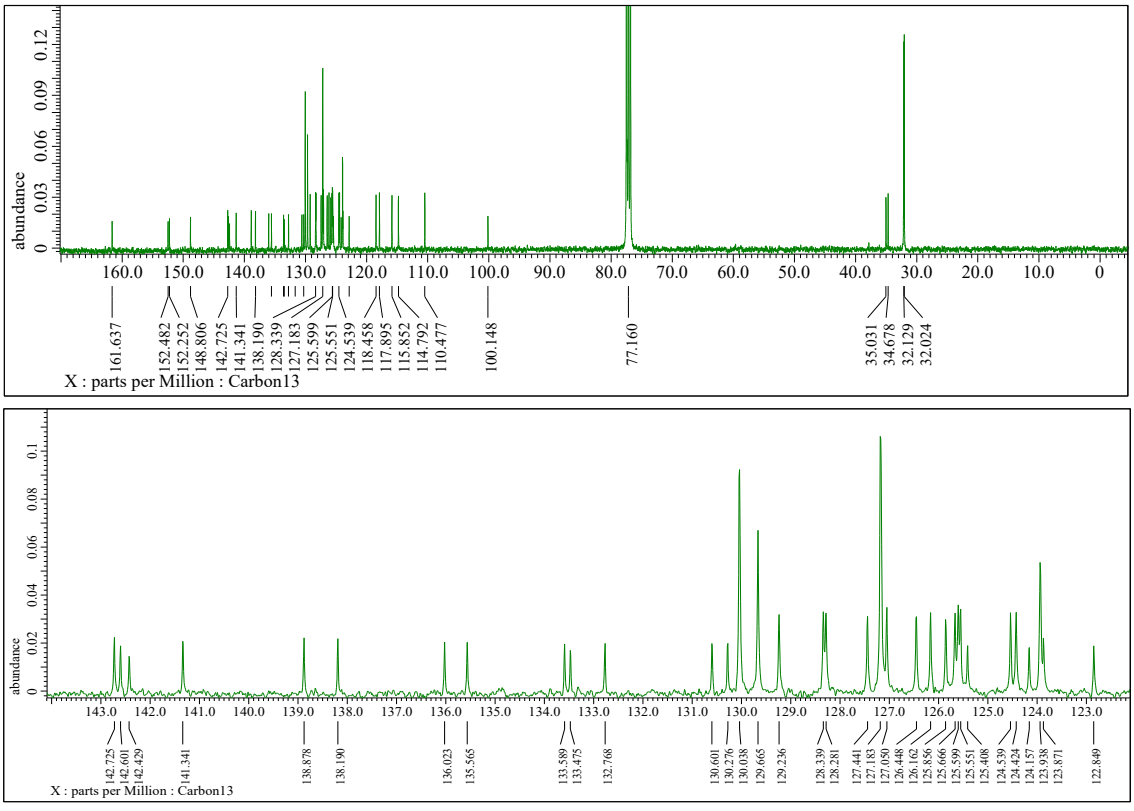
^{1}H NMR spectrum of **2g** in $CDCl_3$



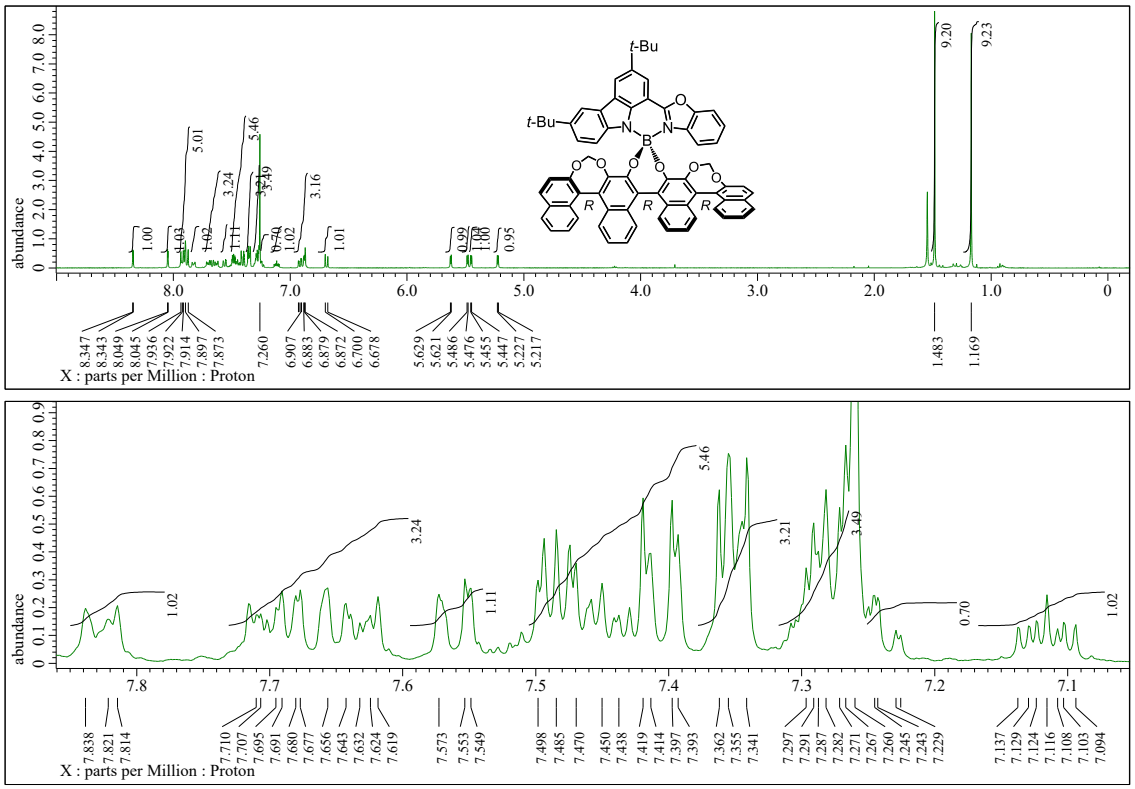
^{13}C NMR spectrum of **2g** in $CDCl_3$



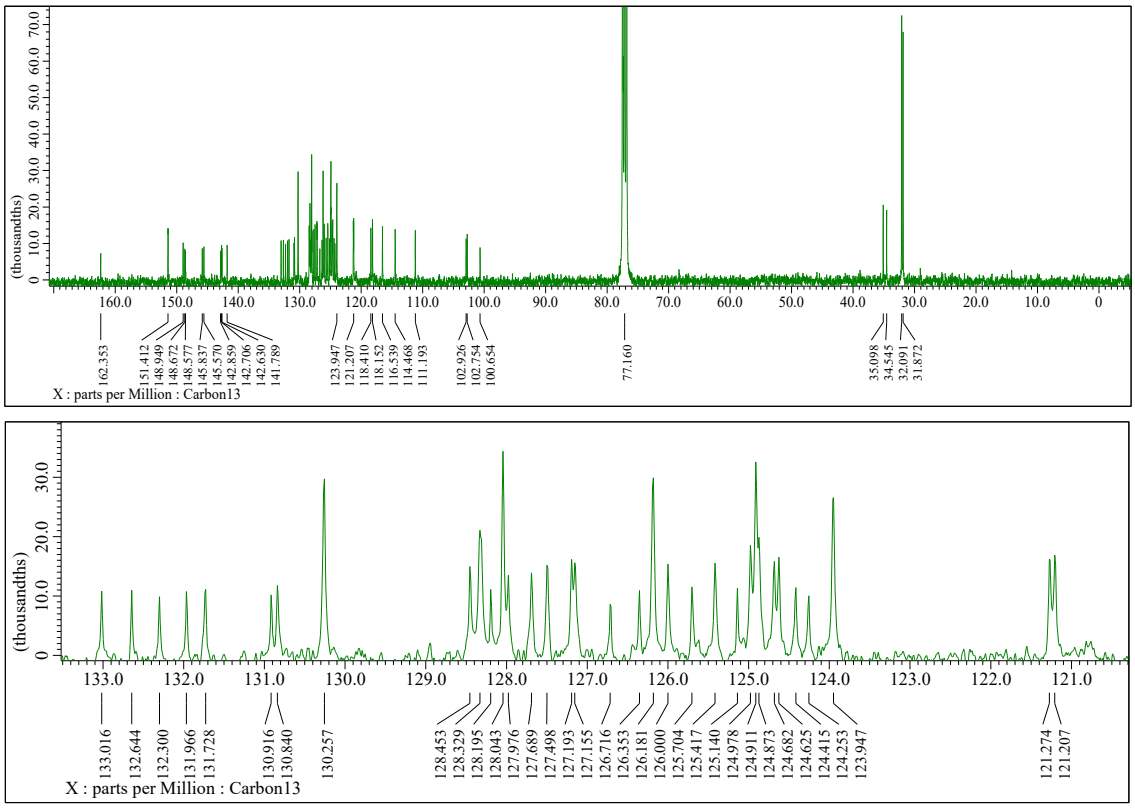
^{1}H NMR spectrum of **2h** in $CDCl_3$



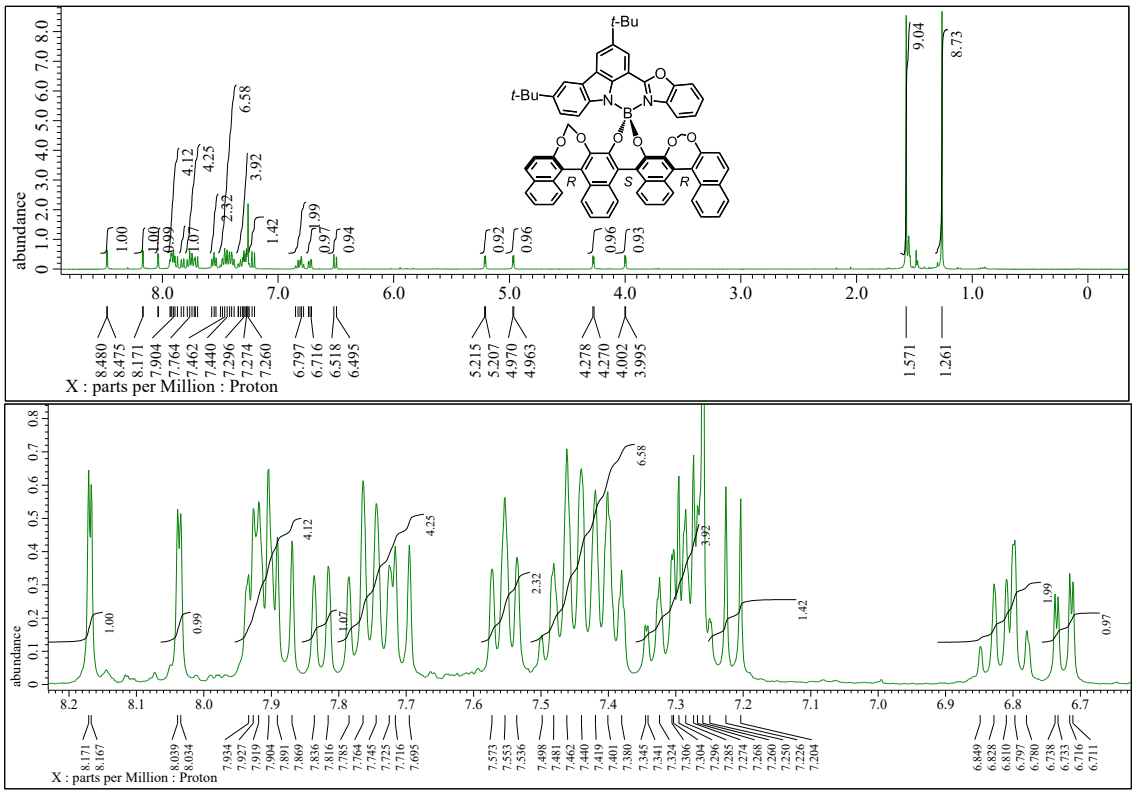
^{13}C NMR spectrum of **2h** in $CDCl_3$



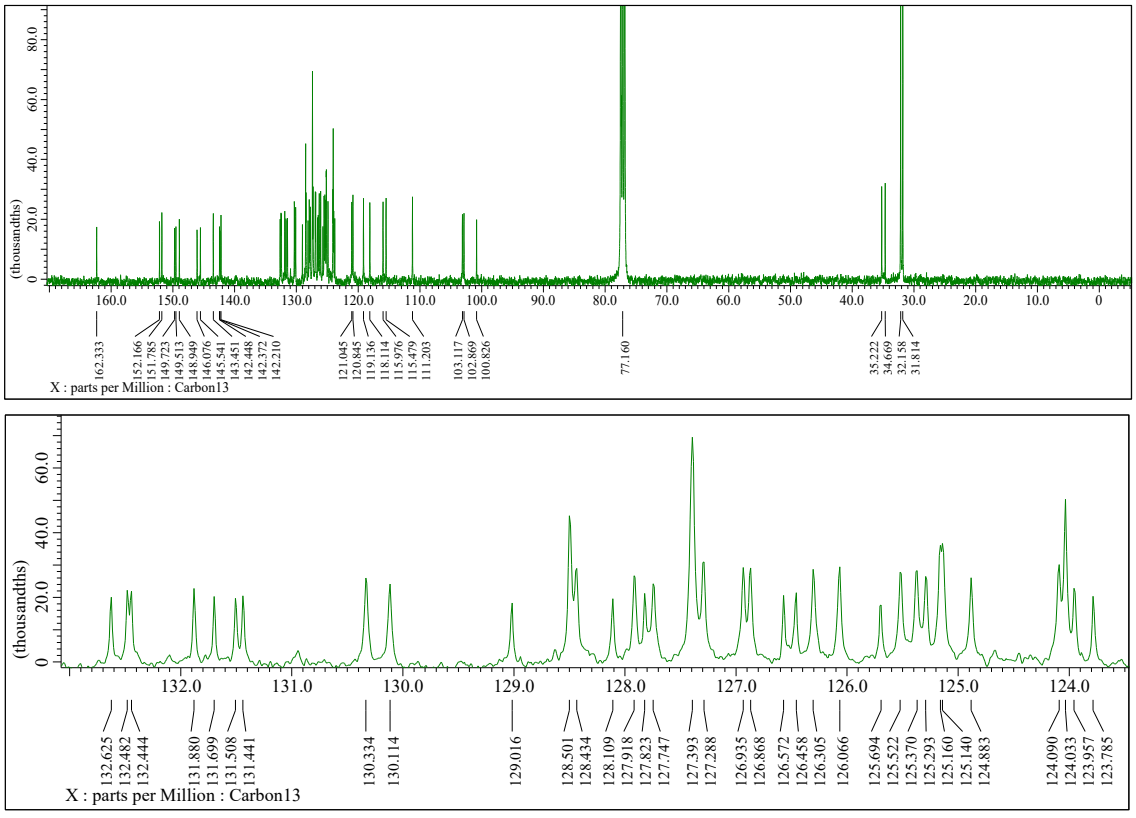
^{1}H NMR spectrum of **2i** in $CDCl_3$



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



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



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