Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supplementary Information
for
Synthesis of Carbazole-Based BODIPY Dimer Showing Red Fluorescence in the Solid State

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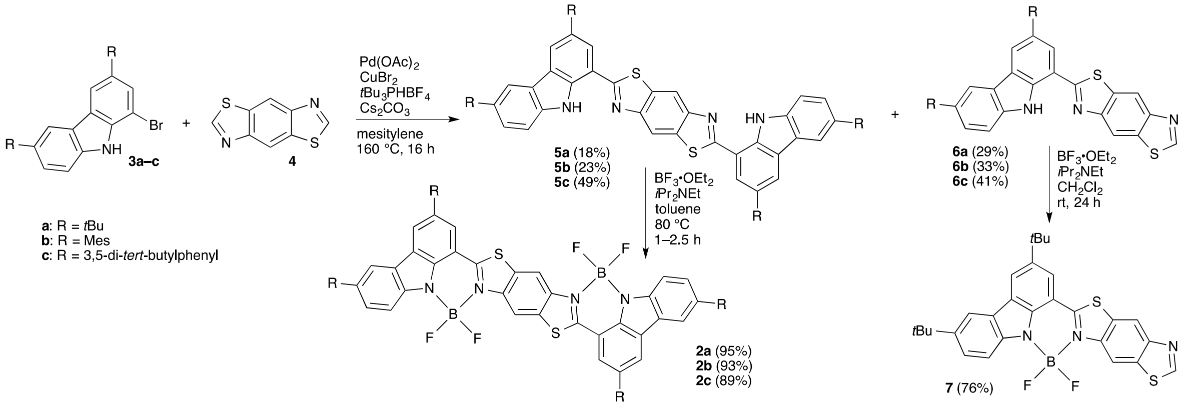
[A] Instrumentation and Materials

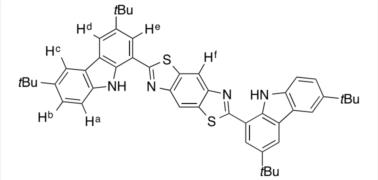
^{1}H and ^{13}C NMR spectra were taken on a JEOL ECS-400 spectrometer, and chemical shifts are reported as the delta scale in ppm using a solvent residual peak as an internal reference ($\delta = 7.260$ for ^{1}H NMR, 77.00 for ^{13}C NMR, in $CDCl_3$). UV/vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. 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. HR mass spectra were taken on a Bruker micrOTOF. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

[B] Experimental Procedures and Compound Data

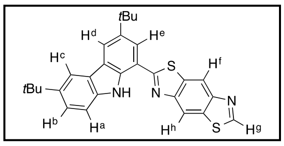


Scheme S1 Synthesis of **2a**–**c** and **7**

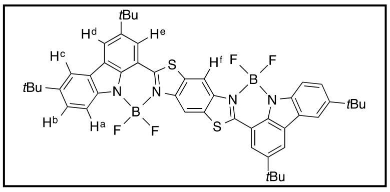
Synthesis of 5a and 6a. A flask containing 3,6-di-*tert*-butyl-1-bromocarbazole (**3a**)[S1] (359 mg, 1.00 mmol), benzobisthiazole (**4**)[S2] (48.1 mg, 251 μmol), $Pd(OAc)_2$ (22.5 mg, 100 μmol), $CuBr_2$ (22.3 mg, 100 μmol), $HP(t\text{-}Bu)_3BF_4$ (58.0 mg, 200 μmol), and Cs_2CO_3 (163 mg, 500 μmol) was purged with N_2, charged with mesitylene (4 mL), and degassed. The mixture was heated at 160 °C for 16 h under N_2. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, and evaporated. Excess mesitylene was removed by distillation. The residue was purified by silica gel chromatography with $CHCl_3$ and recrystallized from $CHCl_3$/MeOH to give **5a** as a yellow solid (34.5 mg, 46.2 μmol, 18%) and **6a** as a yellow solid (34.2 mg, 72.8 μmol, 29%).



Compound data for **5a**: ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 10.72$ (s, 2H, NH), 8.69 (s, 2H, H^f), 8.28 (d, $J = 1.6$ Hz, 2H, H^d), 8.15 (s, 2H, H^c), 8.01 (d, $J = 1.2$ Hz, 2H, H^e), 7.59 (dd, $J = 1.8, 8.6$ Hz, 1H, H^b), 7.56 (d, $J = 8.8$ Hz, 1H, H^a), 1.57 (s, 18H, *t*-Bu), and 1.50 ppm (s, 18H, *t*-Bu); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 169.21, 152.24, 142.91, 142.27, 138.52, 136.31, 133.17, 125.03, 124.40, 122.97, 122.72, 120.17, 116.45, 115.09, 114.77, 110.82, 34.85, 34.81, and 32.07 ppm; HR-MS (APCl): $m/z = 745.3426$. calcd for $C_{48}H_{49}N_4S_2$: 745.3404 $[M\text{–}H]^-$.

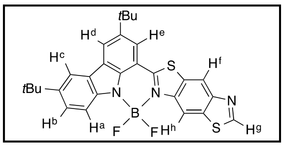


Compound data for **6a**: ^{1}H NMR (CDCl$_3$, 400 MHz) δ = 10.73 (s, 1H, NH), 9.08 (s, 1H, H^g), 8.72 (s, 1H, H^f or H^h), 8.67 (s, 1H, H^f or H^h), 8.28 (d, J = 2.0 Hz, 1H, H^d), 8.14 (s, 1H, H^c), 7.97 (d, J = 2.0 Hz, 1H, H^e), 7.58 (dd, J = 1.6, 8.4 Hz, 1H, H^b), 7.55 (d, J = 8.8 Hz, 1H, H^a), 1.54 (s, 9H, *t*-Bu), and 1.49 ppm (s, 9H, *t*-Bu); ^{13}C NMR (CDCl$_3$, 100 MHz) δ = 154.70, 152.70, 142.98, 142.32, 138.51, 136.33, 133.27, 125.09, 124.44, 123.11, 122.70, 120.39, 116.47, 115.94, 115.15, 114.93, 110.81, 34.84, 34.82, and 32.07 ppm; HR-MS (APCI): m/z = 470.1708. calcd for $C_{28}H_{28}N_3S_2$: 470.1719 [M+H]$^+$.



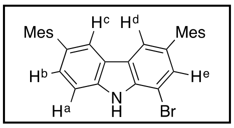
Synthesis of 2a. **5a** (25.8 mg, 34.5 μmol) was dissolved in dry toluene (4.0 mL). Diisopropylethylamine (0.66 mL, 3.8 mmol) and then $BF_3{\cdot}OEt_2$ (0.24 mL, 1.9 mmol) were added, and the mixture was heated at 80 °C for 2 h under N_2. After the solvents were removed, the residue was purified by silica gel chromatography with CHCl$_3$/hexane to give **2a** as an orange solid (27.7 mg, 32.9 μmol, 95%).

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 9.06 (s, 2H, H^f), 8.43 (d, J = 1.2 Hz, 2H, H^d), 8.14 (d, J = 1.6 Hz, 2H, H^c), 7.90 (d, J = 8.4 Hz, 2H, H^a), 7.78 (d, J = 1.6 Hz, 2H, H^e), 7.68 (dd, J = 1.8, 8.2 Hz, 2H, H^b), 1.51 (s, 18H, *t*-Bu), and 1.50 ppm (s, 18H, *t*-Bu); ^{13}C NMR (CDCl$_3$, 100 MHz) δ = 170.02, 144.37, 143.05, 142.38, 141.81, 139.64, 130.46, 126.33, 126.19, 125.52, 124.07, 119.62, 117.06, 113.87, 113.69, 107.72, 35.08, 34.91, 32.01, and 31.91 ppm; HR-MS (APCI): m/z = 842.3450. calcd for $C_{48}H_{48}N_4S_2B_2F_4$: 842.3464 [M]$^-$; UV/Vis (CH$_2$Cl$_2$) λ_{max} (ε) = 300 (17800), 342 (24000), 360 (23100), and 517 nm (54500 mol^{-1}dm^{3}cm^{-1}).



Synthesis of 7. **6a** (14.8 mg, 31.5 μmol) was dissolved in dry CH$_2$Cl$_2$ (6.0 mL). Diisopropylethylamine (0.66 mL, 3.8 mmol) and then $BF_3{\cdot}OEt_2$ (0.24 mL, 1.9 mmol) were added, and the mixture was stirred for 24 h under N_2. After the solvents were removed, the residue was passed through silica gel chromatography with CHCl$_3$ to give **7** as an orange solid (12.4 mg, 24.0 μmol, 76%).

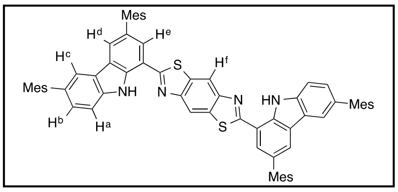
^{1}H NMR (CDCl$_3$, 400 MHz) δ = 9.19 (s, 2H, H^g, H^h), 8.64 (s, 1H, H^f), 8.44 (d, J = 1.6 Hz, 1H, H^d), 8.14 (d, J = 1.6 Hz, 1H, H^c), 7.89 (d, J = 8.4 Hz, 1H, H^a), 7.83 (d, J = 1.6 Hz, 1H, H^e), 7.66 (dd, J = 2.2, 8.6 Hz, 1H, H^b), 1.53 (s, 9H, *t*-Bu), and 1.49 ppm (s, 9H, *t*-Bu); ^{13}C NMR (CDCl$_3$, 100 MHz) δ = 169.52, 157.03, 151.89, 144.09, 142.69, 142.07, 141.81, 139.46, 135.38, 128.15, 125.96, 125.74, 125.39, 124.02, 119.44, 116.94, 116.58, 113.96, 113.63, 107.95, 35.06, 34.86, 31.99, and 31.97 ppm; HR-MS (APCI): m/z = 517.1628. calcd for $C_{28}H_{26}N_3S_2BF_2$: 517.1629 [M]$^+$; UV/Vis (CH$_2$Cl$_2$) λ_{max} (ε) = 293 (7400), 306 (7900), 336 (15500), and 417 nm (14100 mol^{-1}dm^{3}cm^{-1}).



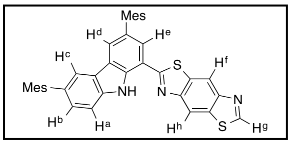
Synthesis of 3b. To a solution of 3,6-bis(2,4,6-trimethylphenyl)carbazole[S3] (807 mg, 2.00 mmol) in $CHCl_3$ (20 mL) was added *N*-bromosuccinimide (356 mg, 2.00 mmol) at 0 °C, and the mixture was stirred for 3 h in the dark. The mixture was passed through a pad of silica gel with $CHCl_3$ and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **3b** as a white solid (950 mg, 1.97 mmol, 98%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.31 (s, 1H, NH), 7.76 (d, *J* = 0.8 Hz, 1H, H^c), 7.72 (s, 1H, H^d), 7.57 (d, *J* = 8.0 Hz, 1H, H^a), 7.37 (d, *J* = 1.2 Hz, 1H, H^e), 7.24 (dd, *J* = 1.2, 8.4 Hz, 1H, H^b), 6.984 (s, 2H, *m*-Mes), 6.975 (s, 2H, *m*-Mes), 2.359 (s, 3H, *p*-Mes), 2.355 (s, 3H, *p*-Mes), 2.06 (s, 6H, *o*-Mes), and 2.05 ppm (s, 6H, *o*-Mes); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 139.29, 138.38, 138.34, 137.33, 136.58, 136.38, 136.29, 133.95, 133.23, 129.23, 128.19, 128.13, 128.08, 124.90, 124.05, 121.31, 120.05, 111.02, 104.02, 20.96, and 20.87 ppm; HR-MS (APCI): *m*/*z* = 482.1316. calcd for $C_{30}H_{27}NBr$: 482.1314 [*M*–H]$^-$.

Synthesis of 5b and 6b. A flask containing **3b** (483 mg, 1.00 mmol), **4** (48.8 mg, 254 μmol), $Pd(OAc)_2$ (23.4 mg, 104 μmol), $CuBr_2$ (23.2 mg, 10.4 μmol), $HP(t\text{-}Bu)_3BF_4$ (57.6 mg, 199 μmol), and Cs_2CO_3 (164 mg, 503 μmol) was purged with N_2, charged with mesitylene (4 mL), and degassed. The mixture was heated at 160 °C for 16 h under N_2. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, and evaporated. Excess mesitylene was removed by distillation. The residue was purified by silica gel chromatography with $CHCl_3$ and GPC with $CHCl_3$ to give **5b** as a brown solid (58.0 mg, 58.3 μmol, 23%) and **6b** as a brown solid (50.0 mg, 84.2 μmol, 33%).

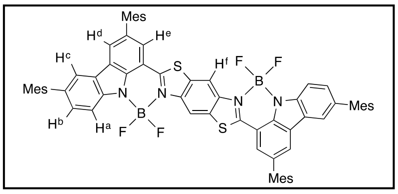


Compound data for **5b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 11.07 (s, 2H, NH), 8.76 (s, 2H, H^f), 7.97 (s, 2H, H^d), 7.86 (s, 2H, H^c), 7.79 (d, *J* = 0.8 Hz, 2H, H^e), 7.71 (d, *J* = 8.4 Hz, 2H, H^a), 7.30 (dd, *J* = 1.6, 8.4 Hz, 2H, H^b), 7.06 (s, 4H, *m*-Mes), 7.00 (s, 4H, *m*-Mes), 2.41 (s, 6H, *p*-Mes), 2.37 (s, 6H, *p*-Mes), 2.14 (s, 12H, *o*-Mes), and 2.09 ppm (s, 12H, *o*-Mes); ^{13}C NMR ($CDCl_3$) δ = 168.85, 152.23, 139.53, 139.04, 138.71, 136.93, 136.74, 136.62, 136.43, 133.30, 133.01, 132.17, 128.29, 128.10, 126.88, 125.17, 124.34, 122.95, 121.11, 115.76, 114.97, 111.35, 21.10, 21.03, and 20.99 ppm; HR-MS (APCl): *m*/*z* = 993.3994. calcd for $C_{68}H_{57}N_4S_2$: 993.4030 [*M*–H]$^-$.



Compound data for **6b**: ^{1}H NMR ($CDCl_3$) δ = 11.05 (s, 1H, NH), 9.09 (s, 1H, H^g), 8.79 (s, 1H, H^f or H^h), 8.67 (s, 1H, H^f or H^h), 7.96 (s, 1H, H^d), 7.85 (s, 1H, H^c), 7.74 (s, 1H, H^e), 7.71 (d, *J* = 8.0 Hz, 1H, H^a), 7.29 (dd, *J* = 1.0, 8.6 Hz, 1H, H^b), 7.05 (s, 2H, *m*-Mes), 7.00 (s, 2H, *m*-Mes), 2.40 (s, 3H, *p*-Mes), 2.37 (s, 3H, *p*-Mes), 2.13 (s, 6H, *o*-

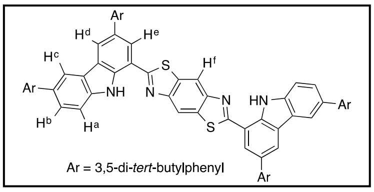
Mes), and 2.08 ppm (s, 6H, *o*-Mes); ^{13}C NMR ($CDCl_3$) δ = 168.76, 152.11, 139.46, 138.92, 138.64, 136.95, 136.78, 136.64, 136.45, 133.18, 132.84, 132.01, 128.24, 128.19, 128.05, 126.78, 125.03, 124.25, 122.81, 121.01, 115.67, 114.94, 111.36, 21.13, 21.09, and 21.04 ppm; HR-MS (APCl): *m*/*z* = 592.1911. calcd for $C_{38}H_{30}N_3S_2$: 592.1887 [*M*–H]$^-$.



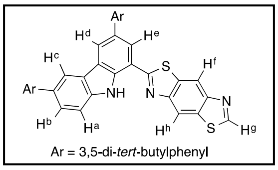
Synthesis of 2b. **5b** (33.6 mg, 33.8 μmol) was dissolved in dry toluene (4.0 mL). Diisopropylethylamine (0.66 mL, 3.8 mmol) and then $BF_3{\cdot}OEt_2$ (0.24 mL, 1.9 mmol) were added, and the mixture was heated at 80 °C for 2.5 h under N_2. After the solvents were removed, the residue was purified by silica gel chromatography with $CHCl_3$ and recrystallized from $CHCl_3$/MeOH to give **2b** as an orange solid (34.2 mg, 31.3 μmol, 93%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 9.17 (s, 2H, H^f), 8.12 (d, *J* = 0.8 Hz, 2H, H^d), 8.04 (d, *J* = 8.4 Hz, 2H, H^a), 7.86 (s, 2H, H^c), 7.73 (d, *J* = 0.8 Hz, 2H, H^e), 7.39 (dd, *J* = 1.8, 7.8 Hz, 2H, H^b), 7.05 (s, 4H, *m*-Mes), 7.00 (s, 4H, *m*-Mes), 2.40 (s, 6H, *p*-Mes), 2.37 (s, 6H, *p*-Mes), 2.11 (s, 12H, Me), and 2.09 ppm (s, 12H, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.12, 142.55, 142.40, 139.88, 139.32, 137.75, 137.45, 136.54, 134.44, 132.88, 130.75, 129.98, 129.36, 128.46, 128.12, 126.39, 124.39, 124.06, 121.63, 114.23, 114.13, 108.64, 21.06, and 20.98 ppm; HR-MS (APCI): *m*/*z* = 1090.4091. calcd for $C_{68}H_{56}N_4S_2B_2F_4$: 1090.4094 [*M*]$^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 302 (25800), 343 (28000), 362 (27100), and 516 nm (52300 mol^{-1}dm^{3}cm^{-1}).

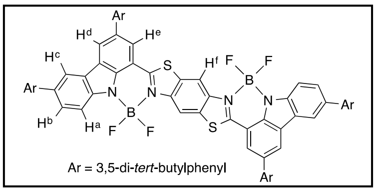
Synthesis of 5c and 6c. A flask containing 3,6-bis(3,5-di-*tert*-butylphenyl)-1-bromocarbaozle (**3c**)[S4] (624 mg, 1.00 mmol), **4** (48.9 mg, 255 μmol), $Pd(OAc)_2$ (22.2 mg, 98.7 μmol), $CuBr_2$ (22.3 mg, 100 μmol), $HP(t\text{-}Bu)_3BF_4$ (58.4 mg, 201 μmol), and Cs_2CO_3 (163 mg, 500 μmol) was purged with N_2, charged with mesitylene (4 mL), and degassed. The mixture was heated at 160 °C for 16 h under N_2. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, and evaporated. Excess mesitylene was removed by distillation. The residue was purified by silica gel chromatography with $CHCl_3$ and GPC with $CHCl_3$ to give **5c** as a yellow solid (160 mg, 125 μmol, 49%) and **6c** as a yellow solid (76.3 mg, 104 μmol, 41%).



Compound data for **5c**: ^{1}H NMR ($CDCl_3$) δ = 10.99 (s, 2H, NH), 8.74 (s, 2H, H^f), 8.45 (d, *J* = 1.2 Hz, 2H, H^d), 8.35 (s, 2H, H^c), 8.19 (d, *J* = 1.6 Hz, 2H, H^e), 7.78 (dd, *J* = 1.6, 8.4 Hz, 2H, H^b), 7.73 (d, *J* = 8.8 Hz, 2H, H^a), 7.61 (d, *J* = 2.0 Hz, 4H, *o*-Ar), 7.56 (d, *J* = 1.2 Hz, 4H, *o*-Ar), 7.54 (t, *J* = 1.6 Hz, 2H, *p*-Ar), 7.46 (t, *J* = 1.8 Hz, 2H, *p*-Ar), 1.49 (s, 36H, *t*-Bu), and 1.44 ppm (s, 36H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 168.73, 152.15, 151.48, 151.14, 141.53, 141.16, 139.63, 137.27, 135.14, 134.67, 133.27, 126.66, 125.49, 123.34, 122.63, 122.16, 121.97, 121.31, 120.82, 119.25, 115.71, 114.85, 111.47, 35.14, 35.04, 31.71, and 31.65 ppm; HR-MS (APCl): *m*/*z* = 1273.7152. calcd for $C_{88}H_{97}N_4S_2$: 1273.7160 [*M*−H]$^-$.

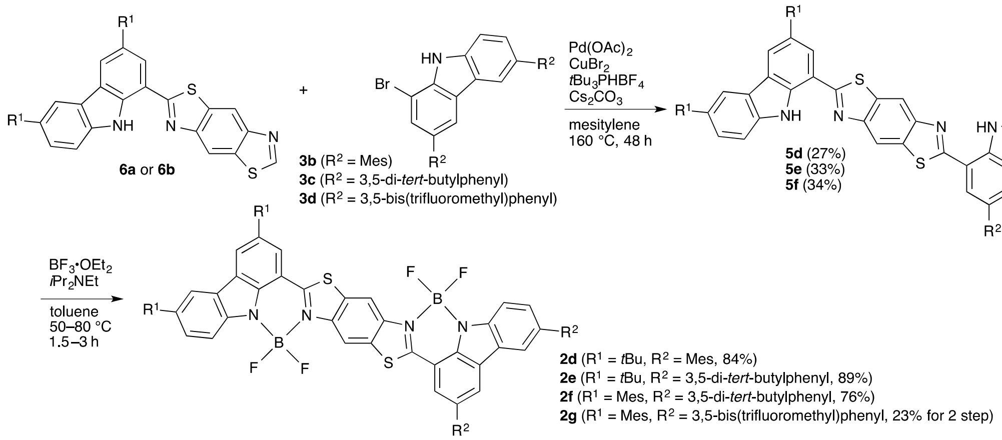


Compound data for **6c**: ^{1}H NMR ($CDCl_3$) δ = 11.02 (s, 1H, NH), 9.10 (s, 1H, H^g), 8.79 (s, 1H, H^f or H^h), 8.69 (s, 1H, H^f or H^h), 8.47 (s, 1H, H^d), 8.37 (s, 1H, H^c), 8.17 (s, 1H, H^e), 7.78 (d, *J* = 8.8 Hz, 1H, H^b), 7.73 (d, *J* = 8.4 Hz, 1H, H^a), 7.59 (d, *J* = 1.6 Hz, 2H, *o*-Ar), 7.56 (s, 2H, *o*-Ar), 7.52 (t, *J* = 1.2 Hz, 1H, *p*-Ar), 7.46 (t, *J* = 1.6 Hz, 1H, *p*-Ar), 1.46 (s, 18H, *t*-Bu), and 1.44 ppm (s, 18H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 168.90, 154.27, 152.10, 151.38, 151.11, 141.55, 140.92, 139.49, 137.08, 135.03, 134.38, 132.82, 126.56, 125.26, 123.27, 122.31, 121.95, 121.93, 121.17, 120.77, 119.19, 115.54, 115.38, 114.77, 111.32, 35.06, 35.02, and 31.68 ppm; HR-MS (APCl): *m*/*z* = 734.3594. calcd for $C_{48}H_{52}N_3S_2$: 734.3597 [*M*+H]$^+$.

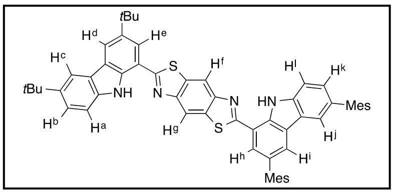


Synthesis of 2c. **5c** (51.0 mg, 40.0 μmol) was dissolved in dry toluene (4.0 mL). Diisopropylethylamine (0.66 mL, 3.8 mmol) and then $BF_3\cdot OEt_2$ (0.24 mL, 1.9 mmol) were added, and the mixture was heated at 80 °C for 1 h under N_2. After the solvents were removed, the residue was purified by silica gel chromatography with $CHCl_3$ to give **2c** as a red solid (49.0 mg, 35.7 μmol, 89%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 9.17 (s, 2H, H^f), 8.61 (d, *J* = 0.8 Hz, 2H, H^d), 8.38 (d, *J* = 1.2 Hz, 2H, H^c), 8.07−8.05 (m, 4H, H^a, H^e), 7.87 (dd, *J* = 1.6, 8.4 Hz, 2H, H^b), 7.58 (d, *J* = 1.2 Hz, 4H, *o*-Ar), 7.55 (s, 6H, *o*-Ar, *p*-Ar), 7.48 (t, *J* = 1.6 Hz, 2H, *p*-Ar), 1.48 (s, 36H, *t*-Bu), and 1.44 ppm (s, 36H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 170.06, 151.73, 151.20, 143.00, 142.45, 141.36, 140.28, 136.46, 135.30, 130.69, 128.36, 127.74, 126.41, 124.70, 122.64, 122.04, 121.77, 121.02, 119.94, 114.36, 114.02, 108.56, 35.14, 35.06, and 31.65 ppm; HR-MS (APCl): *m*/*z* = 1370.7176. calcd for $C_{88}H_{96}N_4S_2B_2F_4$: 1370.7229 [*M*]$^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 257 (88400), 351 (30000), 369 (32900), and 530 nm (48400 mol^{-1}dm^{3}cm^{-1}).

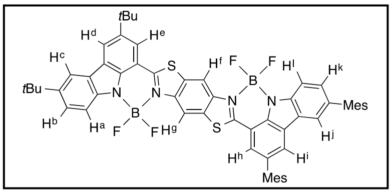


Scheme S2 Synthesis of **2d**–**g**



Synthesis of 5d. A flask containing **6a** (117 mg, 249 μmol), **3b** (256 mg, 531 μmol), $Pd(OAc)_2$ (11.0 mg, 48.9 μmol), $CuBr_2$ (12.2 mg, 54.7 μmol), $HP(t\text{-}Bu)_3BF_4$ (30.0 mg, 103 μmol), and Cs_2CO_3 (81.2 mg, 249 μmol) was purged with N_2, charged with mesitylene (2 mL), and degassed. The mixture was heated at 160 °C for 48 h under N_2. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, and evaporated. Excess mesitylene was removed by distillation. The residue was purified by silica gel chromatography with $CHCl_3$ and recrystallized from $CHCl_3$/MeOH. The crude product was purified by GPC with $CHCl_3$ to give **5d** as a yellow solid (58.5 mg, 67.2 μmol, 27%).

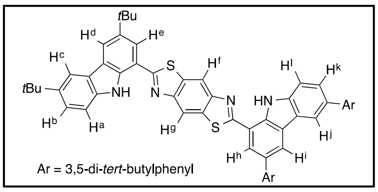
^{1}H NMR ($CDCl_3$) δ = 11.07 (s, 1H, NH), 10.76 (s, 1H, NH), 8.74 (s, 1H, H^f or H^g), 8.68 (s, 1H, H^f or H^g), 8.29 (d, J = 1.2 Hz, 1H, H^d), 8.15 (s, 1H, H^c), 8.00 (d, J = 2.0 Hz, 1H, H^e), 7.97 (s, 1H, H^i), 7.87 (s, 1H, H^j), 7.79 (d, J = 1.2 Hz, 1H, H^h), 7.73 (d, J = 8.4 Hz, 1H, H^l), 7.58 (dd, J = 1.6, 8.4 Hz, 1H, H^b), 7.56 (d, J = 8.4 Hz, 1H, H^a), 7.31 (dd, J = 1.4, 8.2 Hz, 1H, H^k), 7.06 (s, 2H, *m*-Mes), 7.01 (s, 2H, *m*-Mes), 2.41 (s, 3H, *p*-Mes), 2.38 (s, 3H, *p*-Mes), 2.15 (s, 6H, *o*-Mes), 2.10 (s, 6H, *o*-Mes), 1.56 (s, 9H, *t*-Bu), and 1.49 ppm (s, 9H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 169.19, 168.56, 152.15, 151.96, 142.72, 142.07, 139.48, 138.93, 138.67, 138.31, 136.94, 136.78, 136.66, 136.46, 136.12, 133.09, 133.04, 132.81, 131.99, 128.24, 128.17, 128.05, 126.77, 125.00, 124.80, 124.37, 124.19, 122.86, 122.47, 121.02, 120.21, 116.39 115.71, 114.83, 114.78, 111.36, 110.77, 34.79, 32.04, 21.15, and 21.06 ppm; HR-MS (APCl): m/z = 871.3834. calcd for $C_{58}H_{55}N_4S_2$: 871.3863 $[M\text{+H}]^+$.



Synthesis of 2d. **5d** (25.6 mg, 29.4 μmol) was dissolved in dry toluene (4.0 mL). Diisopropylethylamine (0.66 mL, 3.8 mmol) and then $BF_3{\cdot}OEt_2$ (0.24 mL, 1.9 mmol) were added, and the mixture was heated at 80 °C for 3 h under N_2. After the solvents were removed, the residue was purified by silica gel chromatography with $CHCl_3$ to give **2d** as a red solid (23.8 mg, 24.6 μmol, 84%).

^{1}H NMR ($CDCl_3$) δ = 9.14 (s, 1H, H^f or H^g), 9.12 (s, 1H, H^f or H^g), 8.48 (d, J = 1.6 Hz, 1H, H^d), 8.15 (d, J = 1.6 Hz, 1H, H^c), 8.11 (d, J = 0.8 Hz, 1H, H^i), 8.05 (d, J = 7.6 Hz, 1H, H^l), 7.89−7.86 (m, 3H, H^a, H^e, H^j), 7.72 (d, J = 1.2 Hz, 1H, H^h), 7.67 (dd, J = 1.6, 8.8 Hz, 1H, H^b), 7.40 (dd, J = 1.4, 8.2 Hz, 1H, H^k), 7.05 (s, 2H, *m*-Mes), 7.01 (s, 2H, *m*-Mes), 2.40 (s, 3H, *p*-Mes), 2.37 (s, 3H, *p*-Mes), 2.11 (s, 6H, *o*-Mes), 2.09 (s, 6H, *o*-Mes), 1.55 (s, 9H, *t*-Bu), and 1.49 ppm (s, 9H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 170.12, 169.88, 144.29, 143.00, 142.48, 142.24, 142.19, 141.56, 139.70, 139.59, 139.28, 137.71, 137.45, 136.58, 134.25, 132.71, 130.57, 130.47, 129.79, 129.25, 128.38, 128.07, 126.60, 126.21, 126.04, 125.53, 124.32, 123.98, 123.91, 121.56, 119.66, 117.08, 114.16, 113.95, 113.53, 108.60, 107.61, 35.09, 34.86, 31.94, 31.90, 21.11, and 21.04 ppm; HR-MS (APCl): m/z =

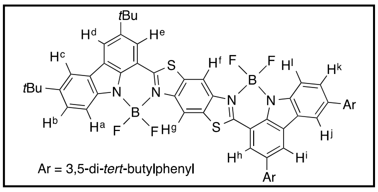
966.3815. calcd for $C_{58}H_{52}N_4S_2B_2F_4$: 966.3779 [*M*]$^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 306 (17100), 342 (24200), 361 (24600), and 517 nm (52600 mol^{-1}dm^{3}cm^{-1}).



Ar = 3,5-di-*tert*-butylphenyl

Synthesis of 5e. A flask containing **6a** (117 mg, 249 μmol), **3c** (311 mg, 499 μmol), Pd(OAc)$_2$ (11.2 mg, 49.8 μmol), CuBr$_2$ (11.1 mg, 49.8 μmol), HP(*t*-Bu)$_3$BF$_4$ (28.4 mg, 97.9 μmol), and Cs_2CO_3 (82.3 mg, 252 μmol) was purged with N_2, charged with mesitylene (2 mL), and degassed. The mixture was heated at 160 °C for 48 h under N_2. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, and evaporated. Excess mesitylene was removed by distillation. The residue was purified by silica gel chromatography with $CHCl_3$ and recrystallized from $CHCl_3$/MeOH. The crude product was purified by GPC with $CHCl_3$ to give **5e** as a yellow solid (82.4 mg, 81.5 μmol, 33%).

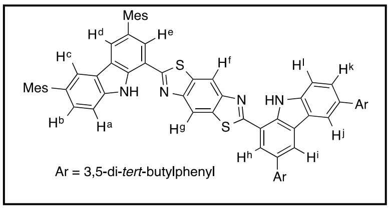
^{1}H NMR ($CDCl_3$) δ = 10.94 (s, 1H, NH), 10.58 (s, 1H, NH), 8.65 (s, 1H, H^f or H^g), 8.60 (s, 1H, H^f or H^g), 8.40 (d, *J* = 1.2 Hz, 1H, H^i), 8.24 (d, *J* = 1.6 Hz, 1H, H^d), 8.20 (s, 1H, H^j), 8.19 (d, *J* = 1.6 Hz, 1H, H^h), 8.05 (d, *J* = 1.6 Hz, 1H, H^c), 8.00 (d, *J* = 2.0 Hz, 1H, H^e), 7.72 (dd, *J* = 1.8, 8.2 Hz, 1H, H^k), 7.63−7.61 (m, 3H, H^l, *o*-Ar), 7.59−7.56 (m, 3H, H^b, *o*-Ar), 7.54 (t, *J* = 1.8 Hz, 1H, *p*-Ar), 7.51 (d, *J* = 8.8 Hz, 1H, H^a), 7.47 (t, *J* = 1.6 Hz, 1H, *p*-Ar), 1.49 (s, 18H, *t*-Bu), and 1.45 ppm (s, 36H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 168.85, 168.24, 151.94, 151.40, 151.02, 142.29, 141.71, 141.52, 141.01, 139.25, 137.95, 137.06, 135.91, 134.65, 133.92, 132.71, 132.63, 129.02, 128.21, 126.58, 125.28, 125.20, 125.02, 124.57, 123.93, 122.80, 122.58, 122.26, 122.02, 121.25, 120.79, 120.09, 119.07, 116.16, 115.42, 114.56, 114.39, 114.07, 110.79, 110.73, 35.13, 35.02, 34.78, 34.60, 32.13, 31.91, 31.68, and 31.66 ppm; HR-MS (APCl): *m*/*z* = 1011.5420. calcd for $C_{68}H_{75}N_4S_2$: 1011.5428 [*M*+H]$^+$.



Ar = 3,5-di-*tert*-butylphenyl

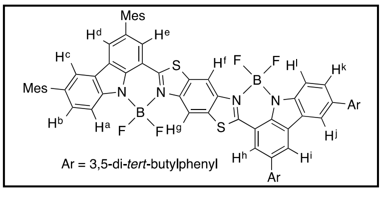
Synthesis of 2e. **5e** (51.7 mg, 51.1 μmol) was dissolved in dry toluene (4.0 mL). Diisopropylethylamine (0.66 mL, 3.8 mmol) and then $BF_3\cdot OEt_2$ (0.24 mL, 1.9 mmol) were added, and the mixture was heated at 80 °C for 1.5 h under N_2. After the solvents were removed, the residue was purified by silica gel chromatography with $CHCl_3$ to give **2e** as a red solid (50.4 mg, 45.5 μmol, 89%).

^{1}H NMR ($CDCl_3$) δ = 9.13 (s, 1H, H^f or H^g), 9.10 (s, 1H, H^f or H^g), 8.58 (s, 1H, H^i), 8.47 (d, *J* = 1.2 Hz, 1H, H^d), 8.35 (d, *J* = 1.6 Hz, 1H, H^j), 8.13 (d, *J* = 1.6 Hz, 1H, H^c), 8.06 (d, *J* = 1.6 Hz, 1H, H^h), 8.04 (d, *J* = 8.4 Hz, 1H, H^l), 7.88−7.84 (m, 3H, H^a, H^e, H^k), 7.66 (dd, *J* = 2.0, 8.8 Hz, 1H, H^b), 7.57 (d, *J* = 1.6 Hz, 2H, *o*-Ar), 7.54 (m, 3H, *o*-Ar, *p*-Ar), 7.48 (t, *J* = 1.8 Hz, 1H, *p*-Ar), 1.56 (s, 9H, *t*-Bu), 1.49 (s, 9H, *t*-Bu), 1.47 (s, 18H, Ar), and 1.44 ppm (s, 18H, Ar); ^{13}C NMR ($CDCl_3$) δ = 170.32, 170.08, 151.77, 151.27, 144.30, 143.02, 142.59, 142.30, 141.78, 141.53, 140.40, 140.35, 139.73, 137.72, 136.47, 135.32, 130.66, 130.52, 128.23, 127.65, 126.97, 126.41, 126.35, 126.25, 125.42, 124.75, 124.05, 122.58, 122.05, 121.74, 121.03, 119.90, 119.64, 116.99, 114.23, 113.80, 113.75, 113.69, 35.17, 35.10, 34.87, 32.00, 31.97, and 31.70 ppm; HR-MS (APCl): *m*/*z* = 1106.5320. calcd for $C_{68}H_{72}N_4S_2B_2F_4$: 1106.5347 [*M*]$^-$; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 345 (29400), 364 (29700), and 523 nm (54000 mol^{-1}dm^{3}cm^{-1}).



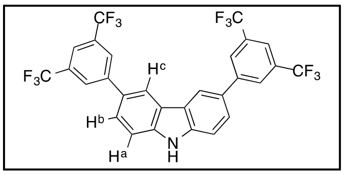
Synthesis of 5f. A flask containing **6b** (148 mg, 249 μmol), **3c** (311 mg, 499 μmol), $Pd(OAc)_2$ (11.3 mg, 50.2 μmol), $CuBr_2$ (10.7 mg, 48.0 μmol), HP(*t*-Bu)$_3$BF$_4$ (29.2 mg, 101 μmol), and Cs_2CO_3 (82.2 mg, 252 μmol) was purged with N_2, charged with mesitylene (2 mL), and degassed. The mixture was heated at 160 °C for 48 h under N_2. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, and evaporated. Excess mesitylene was removed by distillation. The residue was purified by silica gel chromatography with $CHCl_3$ and recrystallized from $CHCl_3$/MeOH. The crude product was purified by GPC with $CHCl_3$ to give **5f** as a yellow solid (95.2 mg, 83.8 μmol, 34%).

^{1}H NMR ($CDCl_3$) δ = 11.07 (s, 2H, NH), 8.77 (s, 1H, H^f or H^g), 8.76 (s, 1H, H^f or H^g), 8.47 (d, *J* = 1.2 Hz, 1H, H^i), 8.38 (s, 1H, H^j), 8.19 (d, *J* = 1.2 Hz, 1H, H^h), 7.97 (d, *J* = 1.2 Hz, 1H, H^d), 7.86 (s, 1H, H^c), 7.80 (d, *J* = 1.2 Hz, 1H, H^e), 7.79 (dd, *J* = 1.6, 7.2 Hz, 1H, H^k), 7.74 (d, *J* = 8.8 Hz, 2H, H^a, H^l), 7.60 (d, *J* = 2.0 Hz, 2H, *o*-Ar), 7.57 (d, *J* = 1.6 Hz, 2H, *o*-Ar), 7.53 (t, *J* = 1.6 Hz, 1H, *p*-Ar), 7.46 (t, *J* = 1.6 Hz, 1H, *p*-Ar), 7.31 (dd, *J* = 1.8, 8.2 Hz, 1H, H^b), 7.06 (s, 2H, *m*-Mes), 7.01 (s, 2H, *m*-Mes), 2.41 (s, 3H, *p*-Mes), 2.37 (s, 3H, *p*-Mes), 2.15 (s, 6H, *p*-Mes), 2.09 (s, 6H, *p*-Mes), 1.48 (s, 18H, *t*-Bu), and 1.44 ppm (s, 18H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 168.93, 168.85, 152.31, 152.24, 151.48, 151.21, 141.56, 141.09, 139.74, 139.57, 139.11, 138.75, 137.36, 136.91, 136.80, 136.74, 136.61, 136.42, 135.28, 134.79, 133.37, 133.10, 132.27, 128.33, 128.13, 126.96, 126.84, 125.53, 125.27, 124.41, 123.45, 123.03, 122.70, 122.14, 122.02, 121.32, 121.16, 120.89, 119.42, 115.85, 115.82, 115.00, 114.98, 111.54, 111.38, 35.13, 35.07, 31.68, 31.66, 21.09, 21.03, and 20.97 ppm; HR-MS (APCl): *m*/*z* = 1135.5737. calcd for $C_{78}H_{79}N_4S_2$: 1135.5741 [*M*+H]$^+$.



Synthesis of 2f. **5f** (26.0 mg, 22.9 μmol) was dissolved in dry toluene (2.0 mL). Diisopropylethylamine (0.66 mL, 3.8 mmol) and then $BF_3 \cdot OEt_2$ (0.24 mL, 1.9 mmol) were added, and the mixture was heated at 50 °C for 3 h under N_2. After the solvents were removed, the residue was passed through a pad of silica gel with $CHCl_3$/hexane and evaporated to dryness. The crude product was recrystallized from $CHCl_3$/MeOH to give **2f** as a red solid (21.6 mg, 17.5 μmol, 76%).

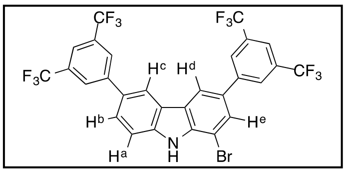
^{1}H NMR (CDCl$_3$) δ = 9.182 (s, 1H, H^f or H^g), 9.175 (s, 1H, H^f or H^g), 8.62 (d, J = 1.2 Hz, 1H, H^i), 8.37 (d, J = 1.6 Hz, 1H, H^j), 8.12 (d, J = 0.8 Hz, 1H, H^d), 8.08 (d, J = 1.6 Hz, 1H, H^h), 8.06 (d, J = 8.0 Hz, 2H, H^a, H^l), 7.87 (dd, J = 1.6, 8.8 Hz, 1H, H^k), 7.86 (d, J = 1.2 Hz, 1H, H^c), 7.73 (d, J = 1.2 Hz, 1H, H^e), 7.57 (d, J = 1.6 Hz, 2H, *o*-Ar), 7.54 (s, 3H, *o*-Ar, *p*-Ar), 7.47 (t, J = 1.8 Hz, 1H, *p*-Ar), 7.40 (dd, J = 1.4, 8.2 Hz, 1H, H^b), 7.06 (s, 2H, *m*-Mes), 7.00 (s, 2H, *m*-Mes), 2.40 (s, 3H, *p*-Mes), 2.37 (s, 3H, *p*-Mes), 2.12 (s, 6H, *p*-Mes), 2.09 (s, 6H, *p*-Mes), 1.47 (s, 18H, *t*-Bu), and 1.44 ppm (s, 18H, *t*-Bu); ^{13}C NMR (CDCl$_3$) δ = 169.99, 151.66, 151.12, 142.85, 142.36, 142.26, 141.27, 140.16, 139.75, 139.28, 137.71, 137.43, 136.57, 136.40, 135.16, 134.25, 132.72, 130.65, 130.60, 129.86, 129.26, 128.38, 128.06, 127.77, 126.25, 124.63, 124.29, 123.95, 122.68, 122.05, 121.74, 121.53, 121.01, 120.01, 114.30, 114.21, 114.06, 114.03, 108.58, 108.48, 35.11, 35.02, 31.62, 21.10, and 21.03 ppm; HR-MS (APCl): m/z = 1230.5693. calcd for $C_{78}H_{76}N_4S_2B_2F_4$: 1230.5662 [M]$^-$; UV/Vis (CH$_2$Cl$_2$) λ_{max} (ε) = 347 (27900), 366 (28300), and 523 nm (47600 mol^{-1}dm^3 cm^{-1}).



Synthesis of 3,6-bis[3,5-bis(trifluoromethyl)phenyl]carbazole. 3,6-Dibromocarbazole (1.29 g, 3.97 mmol), Pd(PPh$_3$)$_4$ (123 mg, 106 µmmol), and Cs$_2$CO$_3$ (5.02 g, 15.4 mmol) in toluene/EtOH/H$_2$O (17/8/8 mL) was degassed and then heated at 100 °C for 14 h under N$_2$. After cooling to rt, the organic layer was extracted with CH$_2$Cl$_2$ and evaporated. The residue was purified by silica gel chromatography with CH$_2$Cl$_2$/hexane. Recrystallization from CH$_2$Cl$_2$/hexane gave the product as a white solid (1.81 g, 3.06 mmol, 77%).

^{1}H NMR (CDCl$_3$) δ = 8.40 (d, J = 0.8 Hz, 2H, H^c), 8.37 (s, 1H, NH), 8.15 (s, 4H, *o*-Ar), 7.86 (s, 2H, *p*-Ar), 7.73 (dd, J = 1.8, 8.2 Hz, 2H, H^b), and 7.61 ppm (d, J = 8.4 Hz, 2H, H^a); ^{13}C NMR (CDCl$_3$) δ = 144.13, 140.47, 132.39 (q, J = 35 Hz), 130.73, 127.30, 125.96, 124.24, 123.63 (q, J = 271 Hz), 120.31 (sep, J = 3.8 Hz), 119.44, and 111.75 ppm; HR-MS (APCl): m/z = 590.0817 calcd for $C_{28}H_{12}NF_{12}$: 590.0784 [M−H]$^-$.

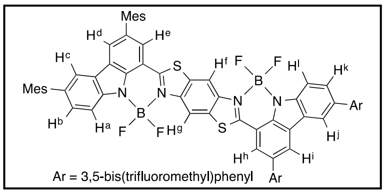
Synthesis of 3,6-bis[3,5-bis(trifluoromethyl)phenyl]-1-bromocarbazole (3d).



To a solution of 3,6-bis[3,5-bis(trifluoromethyl)phenyl]carbazole (57.7 mg, 97.6 µmol) in CHCl$_3$ (10 mL) was added *N*-bromosuccinimide (18.0 mg, 101 µmol) at 0 °C, and the mixture was stirred for 6 h in the dark. The mixture was passed through a pad of silica gel with CHCl$_3$, and evaporated to dryness. The residue was purified by silica gel chromatography with CHCl$_3$/hexane to give **3d** as a white solid (55.9 mg, 83.4 µmol, 85%).

^{1}H NMR (CDCl$_3$) δ = 8.51 (s, 1H, NH), 8.37 (d, J = 2.0 Hz, 1H, H^c), 8.33 (d, J = 1.2 Hz, 1H, H^d), 8.14 (s, 2H, *o*-Ar), 8.12 (s, 2H, *o*-Ar), 7.884−7.875 (m, 3H, H^e, *p*-Ar), 7.78 (dd, J = 1.8, 8.2 Hz, 1H,

H^b), and 7.68 ppm (d, *J* = 8.4 Hz, 1H, H^a); ^{13}C NMR ($CDCl_3$) δ = 143.81, 142.92, 140.02, 139.07, 132.58 (q, *J* = 35 Hz), 132.47 (q, *J* = 35 Hz), 132.15, 131.42, 127.91, 127.36, 126.68, 125.15, 124.62, 123.58 (q, *J* = 271 Hz), 123.51 (q, *J* = 271 Hz), 120.84 (sep, *J* = 3.8 Hz), 120.53 (sep, *J* = 3.8 Hz), 119.95, 118.53, 112.22, and 105.27 ppm; HR-MS (APCl): *m*/*z* = 669.9869 calcd for $C_{28}H_{11}NF_{12}Br$: 669.9870 [*M*–H]⁻.



Synthesis of 2g. A flask containing **6b** (148 mg, 249 μmol), **3d** (336 mg, 501 μmol), $Pd(OAc)_2$ (11.7 mg, 52.0 μmol), $CuBr_2$ (11.5 mg, 51.6 μmol), HP(*t*-Bu)$_3$BF$_4$ (28.6 mg, 98.6 μmol), and Cs_2CO_3 (81.0 mg, 248 μmol) was purged with N_2, charged with mesitylene (4 mL), and degassed. The mixture was heated at 160 °C for 48 h under N_2. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, and evaporated. Excess mesitylene was removed by distillation. The residue was purified by silica gel chromatography with $CHCl_3$, recrystallized from $CHCl_3$/MeOH, and then purified by GPC with $CHCl_3$ to give **5g** as a crude product. The crude product was dissolved in dry toluene (4.0 mL). Diisopropylethylamine (0.66 mL, 3.8 mmol) and then $BF_3{\cdot}OEt_2$ (0.24 mL, 1.9 mmol) were added, and the mixture was heated at 80 °C for 1.5 h under N_2. After the solvents were removed, the residue was purified by silica gel chromatography with $CHCl_3$/hexane to give **2g** as a red solid (73.6 mg, 57.5 μmol, 23%).

^1H NMR ($CDCl_3$) δ = 9.18 (s, 1H, H^f or H^g), 9.17 (s, 1H, H^f or H^g), 8.64 (d, *J* = 1.2 Hz, 1H, H^i), 8.46 (d, *J* = 1.6 Hz, 1H, H^j), 8.21 (s, 2H, *o*-Ar), 8.18 (s, 2H, *o*-Ar), 8.15 (d, *J* = 1.2 Hz, 1H, H^d or H^h), 8.14 (s, 1H, H^d or H^h), 8.13 (d, *J* = 7.6 Hz, 1H, H^e), 8.03 (d, *J* = 8.4 Hz, 1H, H^a), 7.97 (s, 1H, *p*-Ar), 7.91 (dd, *J* = 1.6, 8.4 Hz, 1H, H^k), 7.90 (s, 1H, *p*-Ar), 7.86 (s, 1H, H^c), 7.72 (d, *J* = 0.8 Hz, 1H, H^e), 7.40 (dd, *J* = 1.4, 8.6 Hz, 1H, H^b), 7.06 (s, 2H, *m*-Mes), 7.01 (s, 2H, *m*-Mes), 2.41 (s, 3H, *p*-Mes), 2.38 (s, 3H, *p*-Mes), 2.12 (s, 6H, *o*-Mes), and 2.10 ppm (s, 6H, *o*-Mes); ^{13}C NMR couldn’t detect peaks due to serious low solubility; HR-MS (APCl): *m*/*z* = 1278.2675. calcd for $C_{66}H_{40}N_4S_2B_2F_{16}$: 1278.2650 [*M*]⁻; UV/Vis (CH_2Cl_2) λ_{max} (ε) = 309 (42500), 343 (29600), 364 (30700), and 515 nm (56700 $mol^{-1}dm^3cm^{-1}$).

[C] References

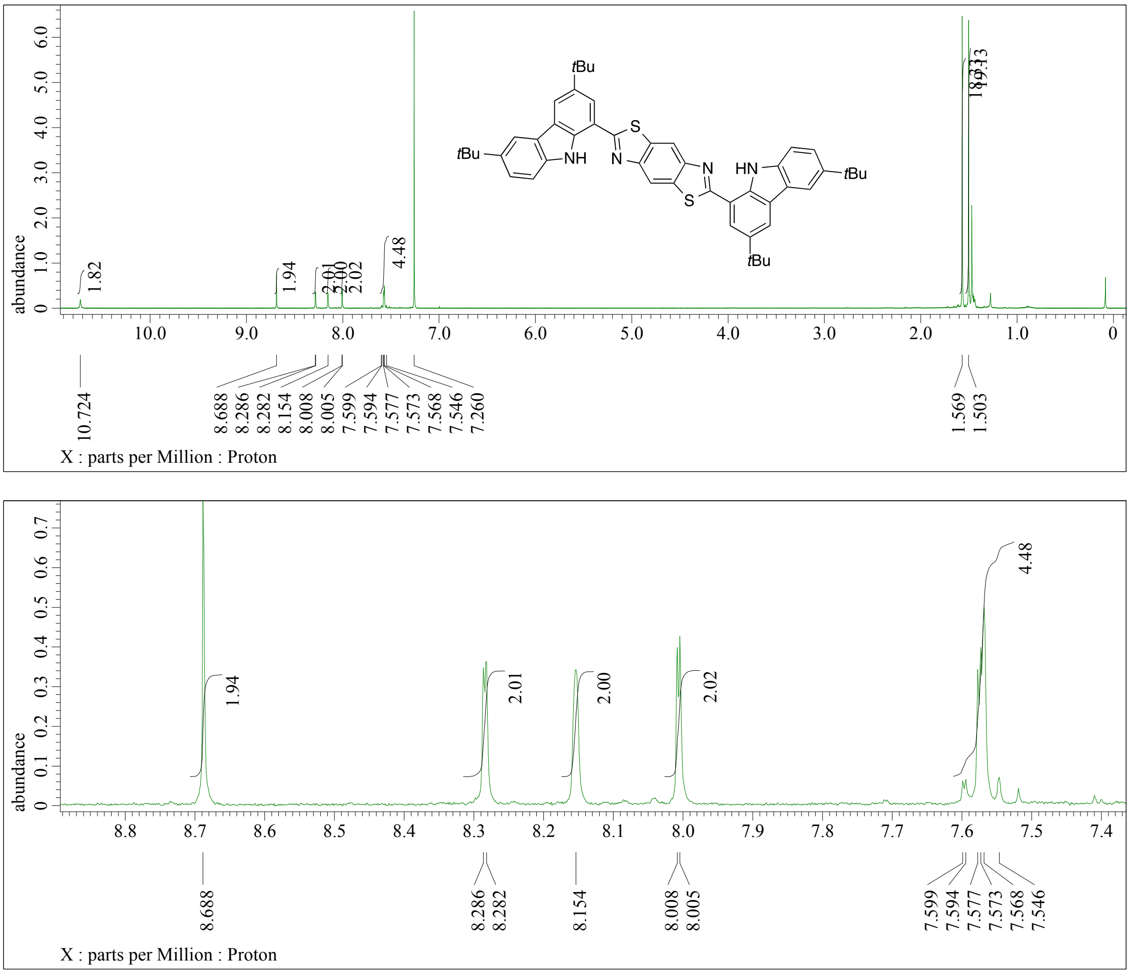
[S1] C. Maeda, T. Todaka, T. Ueda and T. Ema, *Chem.–Eur. J.,* 2016, **22**, 7508.

[S2] J. F. Mike, J. J. Inteman, A. Ellern and M. Jeffries-EL, *J. Org. Chem.,* 2010, **75**, 495.

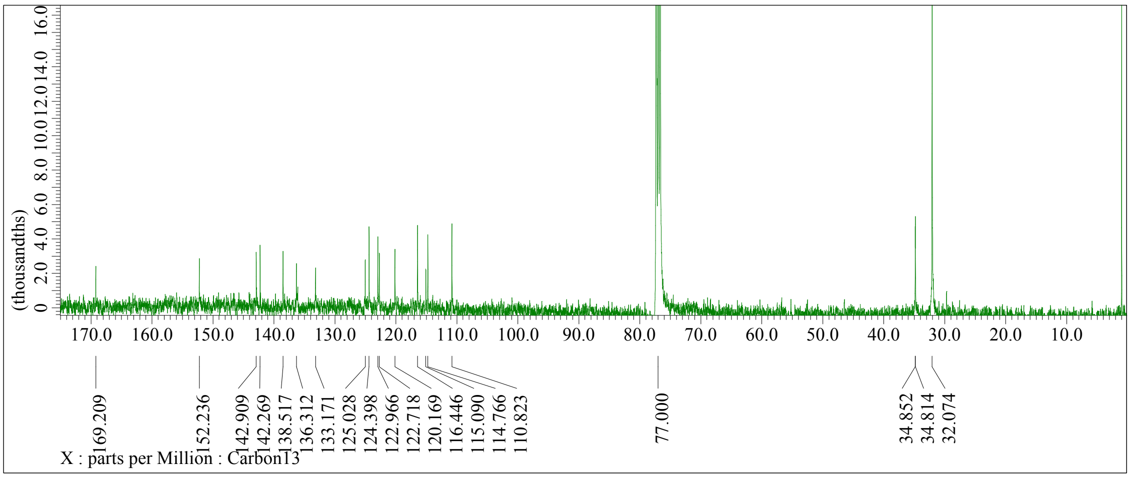
[S3] C. Maeda, T. Todaka and T. Ema, *Org. Lett.*, 2015, **17**, 3090.

[S4] C. Maeda, K. Nagahata and T. Ema, *Org. Biomol, Chem.*, 2017, **15**, 7783.

[D] NMR spectra

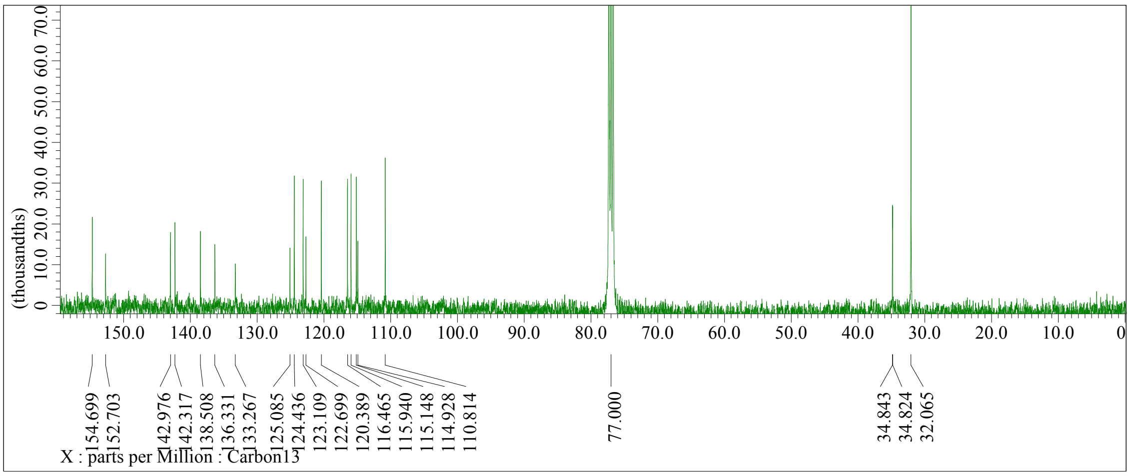


400 MHz ^1H NMR spectrum of **5a** in $CDCl_3$

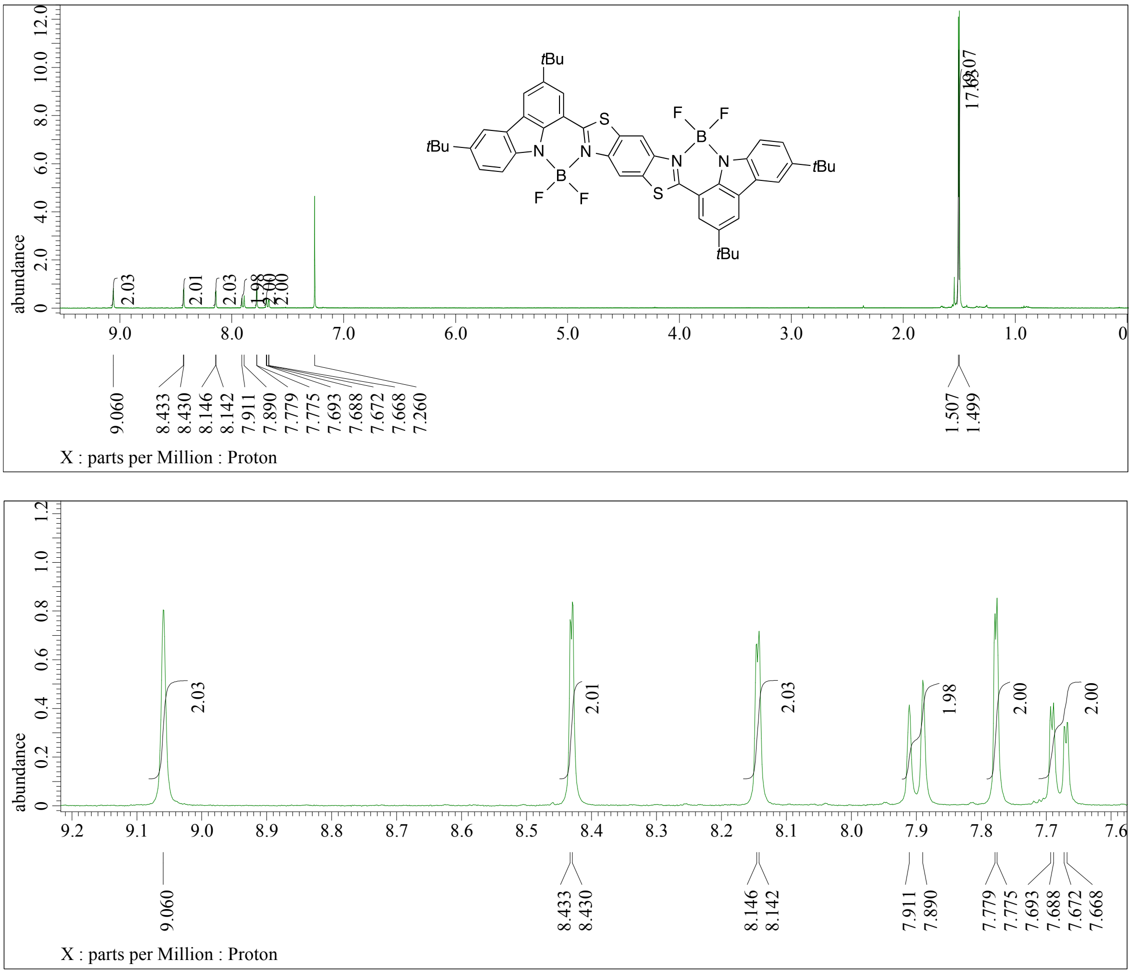


100 MHz ^{13}C NMR spectrum of **5a** in $CDCl_3$

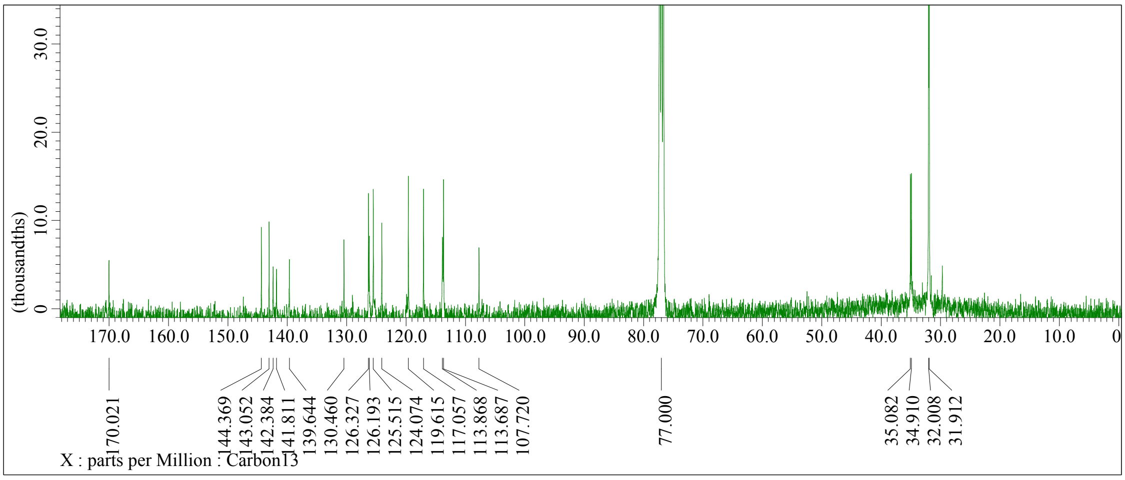
400 MHz ^{1}H NMR spectrum of **6a** in $CDCl_3$



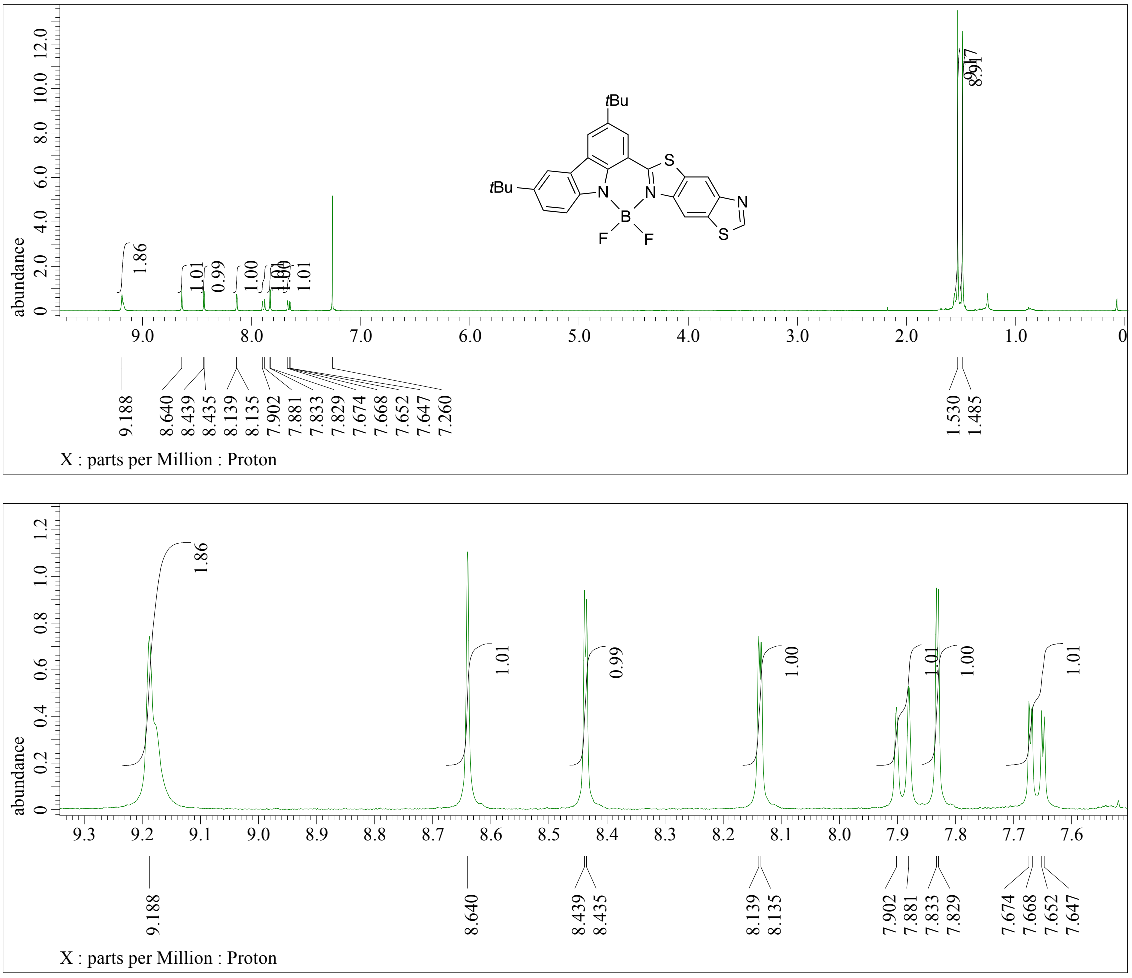
100 MHz ^{13}C NMR spectrum of **6a** in $CDCl_3$



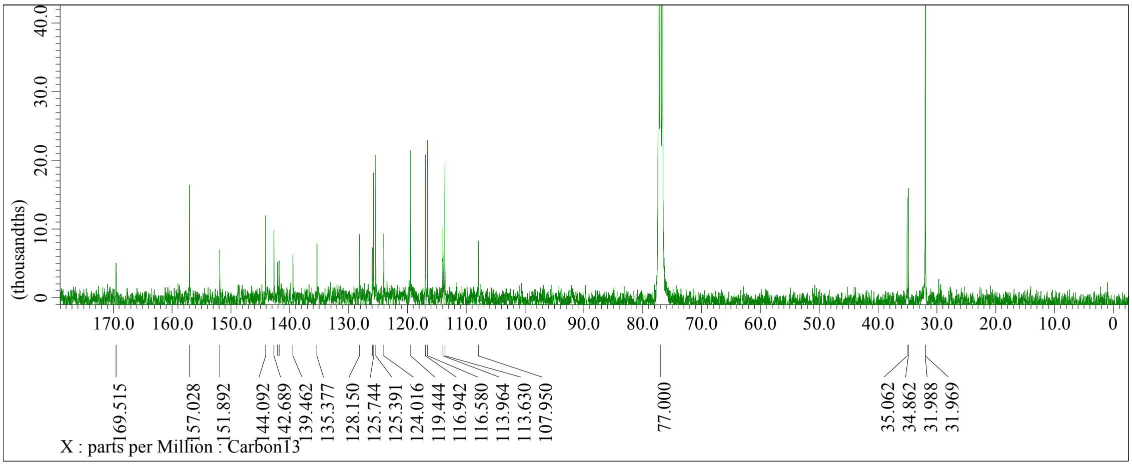
400 MHz ^{1}H NMR spectrum of **2a** in $CDCl_3$



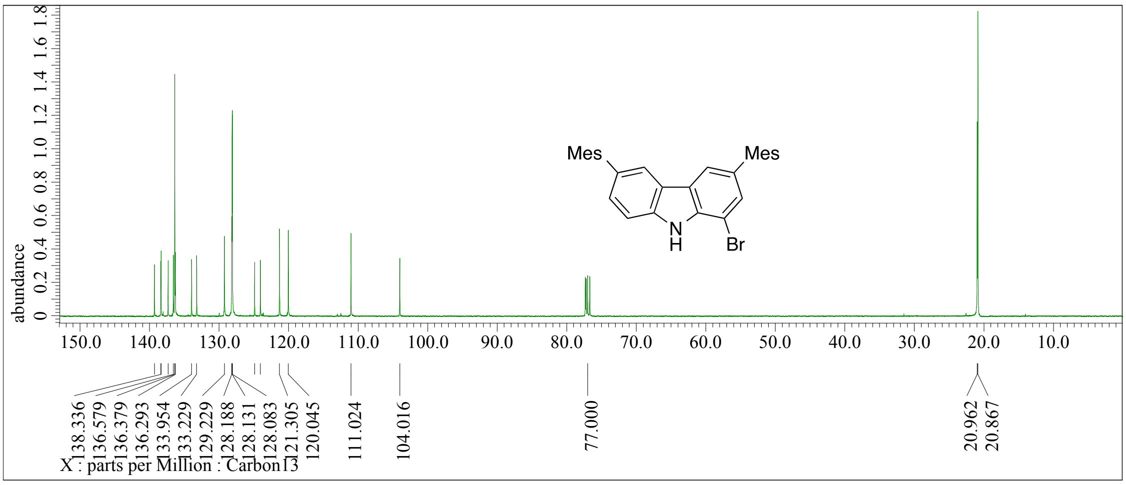
100 MHz ^{13}C NMR spectrum of **2a** in $CDCl_3$

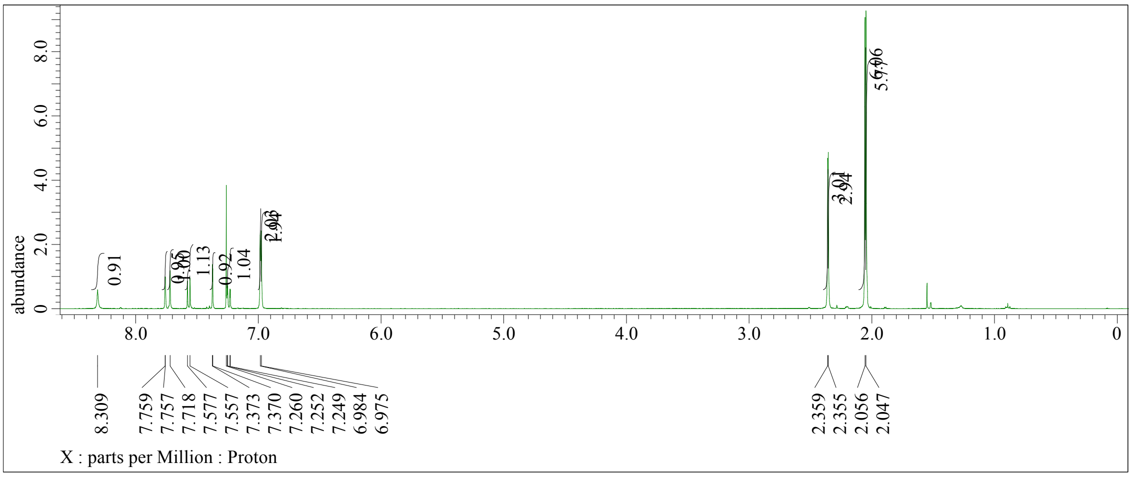


400 MHz ^{1}H NMR spectrum of **7** in CDCl$_3$

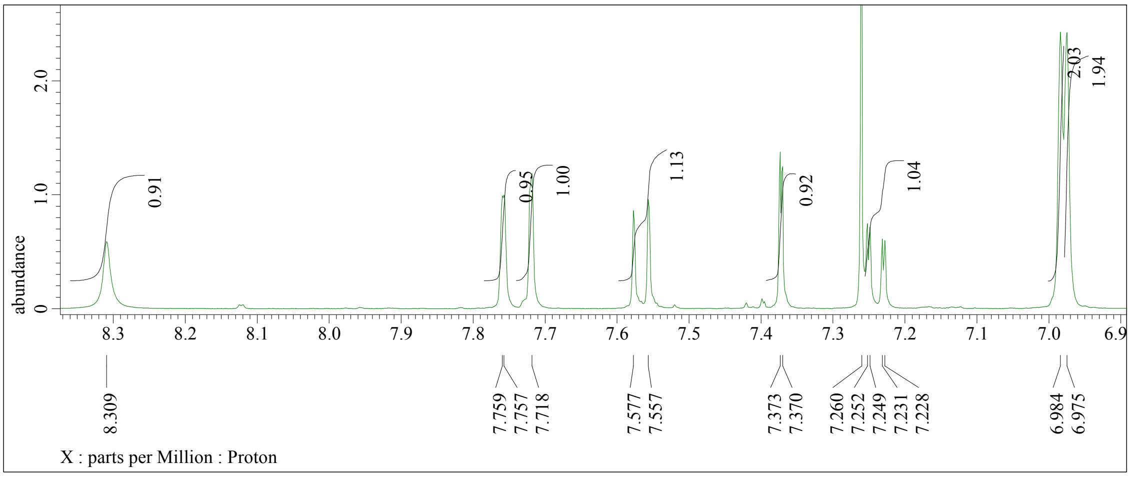


100 MHz ^{13}C NMR spectrum of **7** in CDCl$_3$

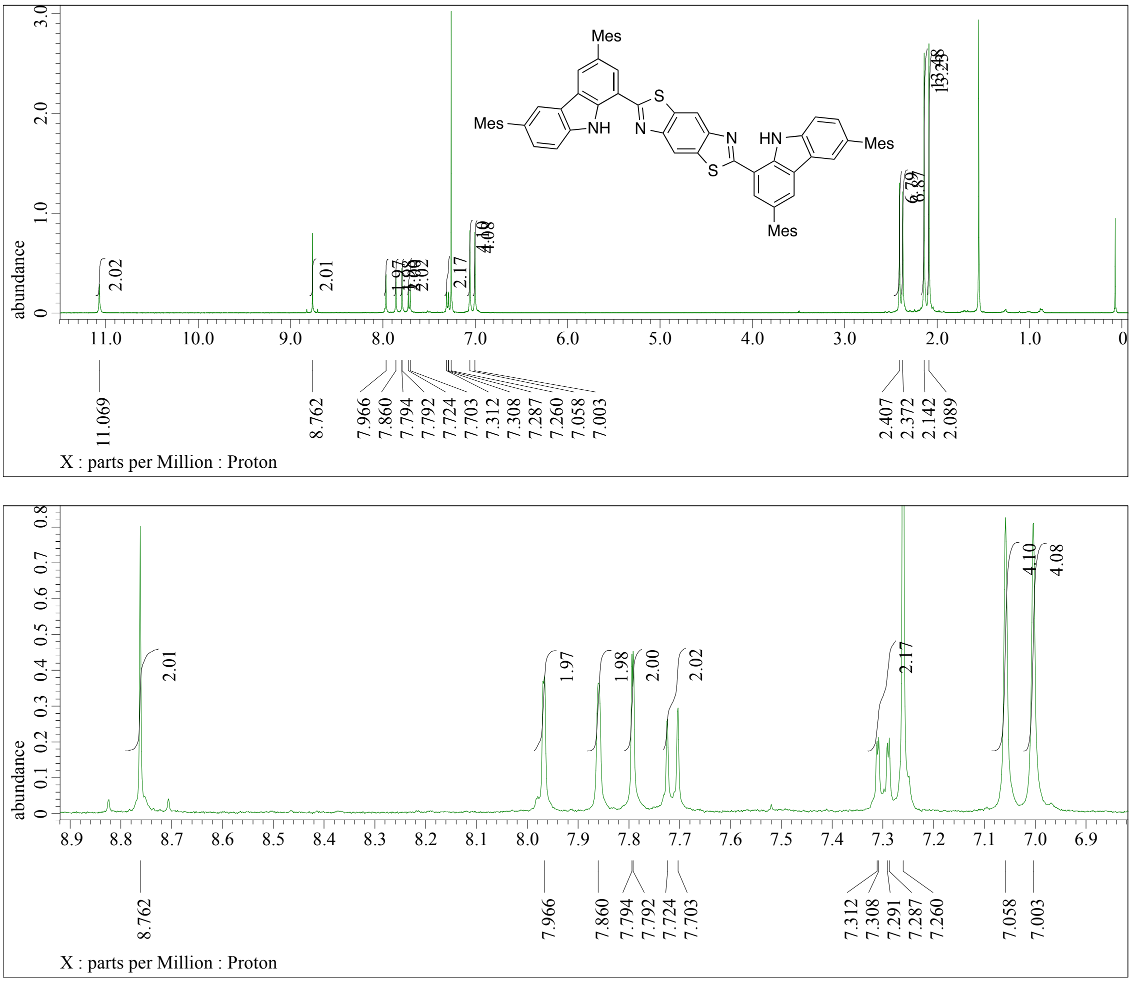




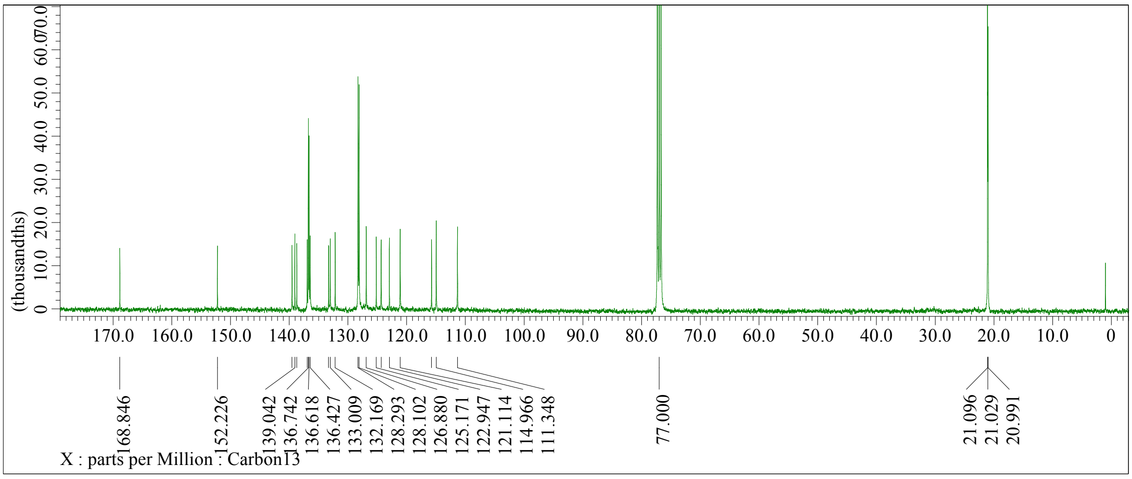
400 MHz ^{1}H NMR spectrum of **3b** in $CDCl_3$



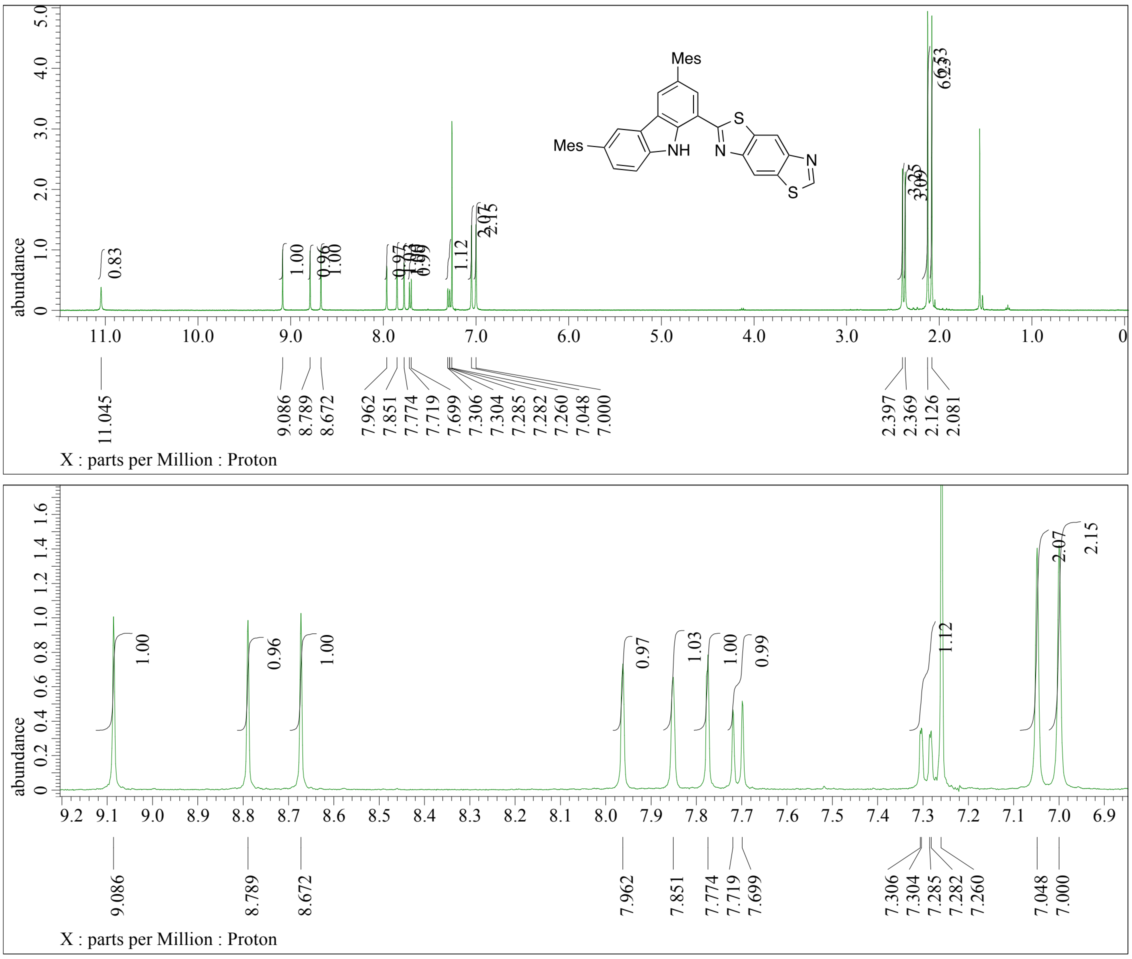
100 MHz ^{13}C NMR spectrum of **3b** in $CDCl_3$



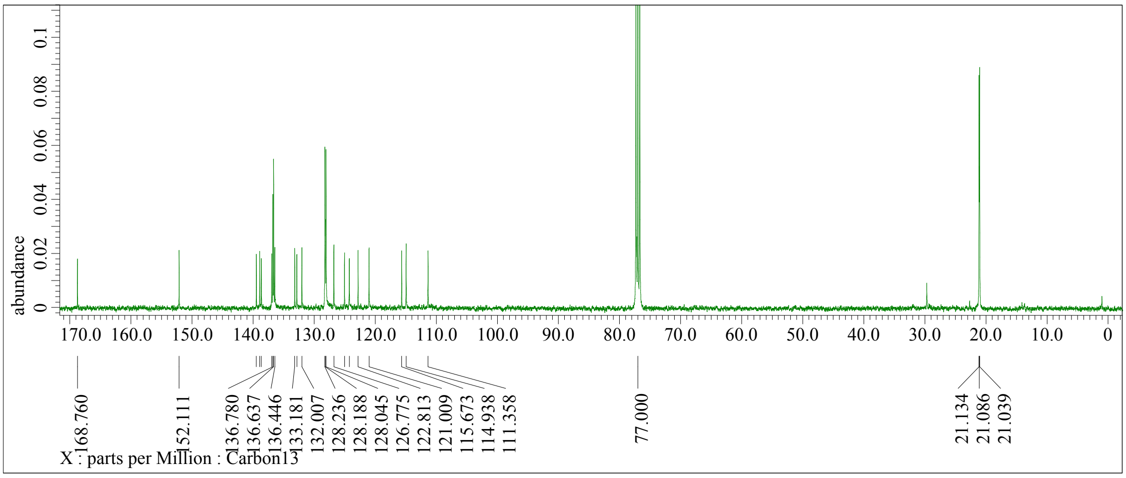
400 MHz ^{1}H NMR spectrum of **5b** in $CDCl_3$



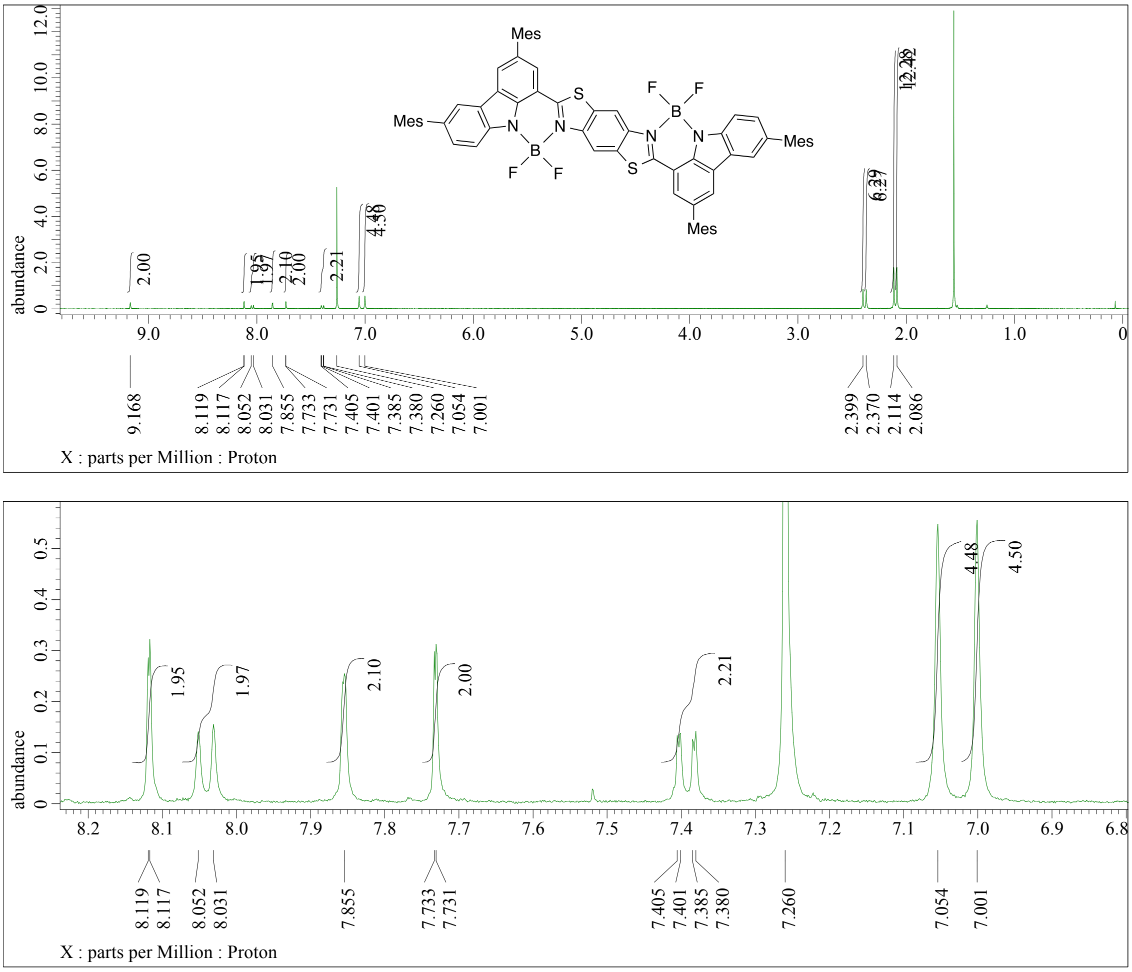
100 MHz ^{13}C NMR spectrum of **5b** in $CDCl_3$



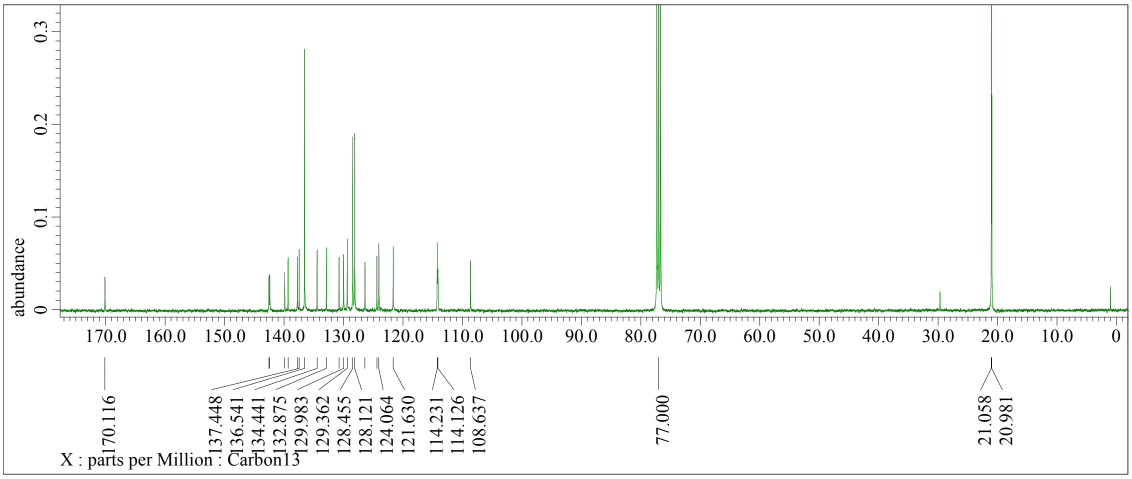
400 MHz ^{1}H NMR spectrum of **6b** in $CDCl_3$



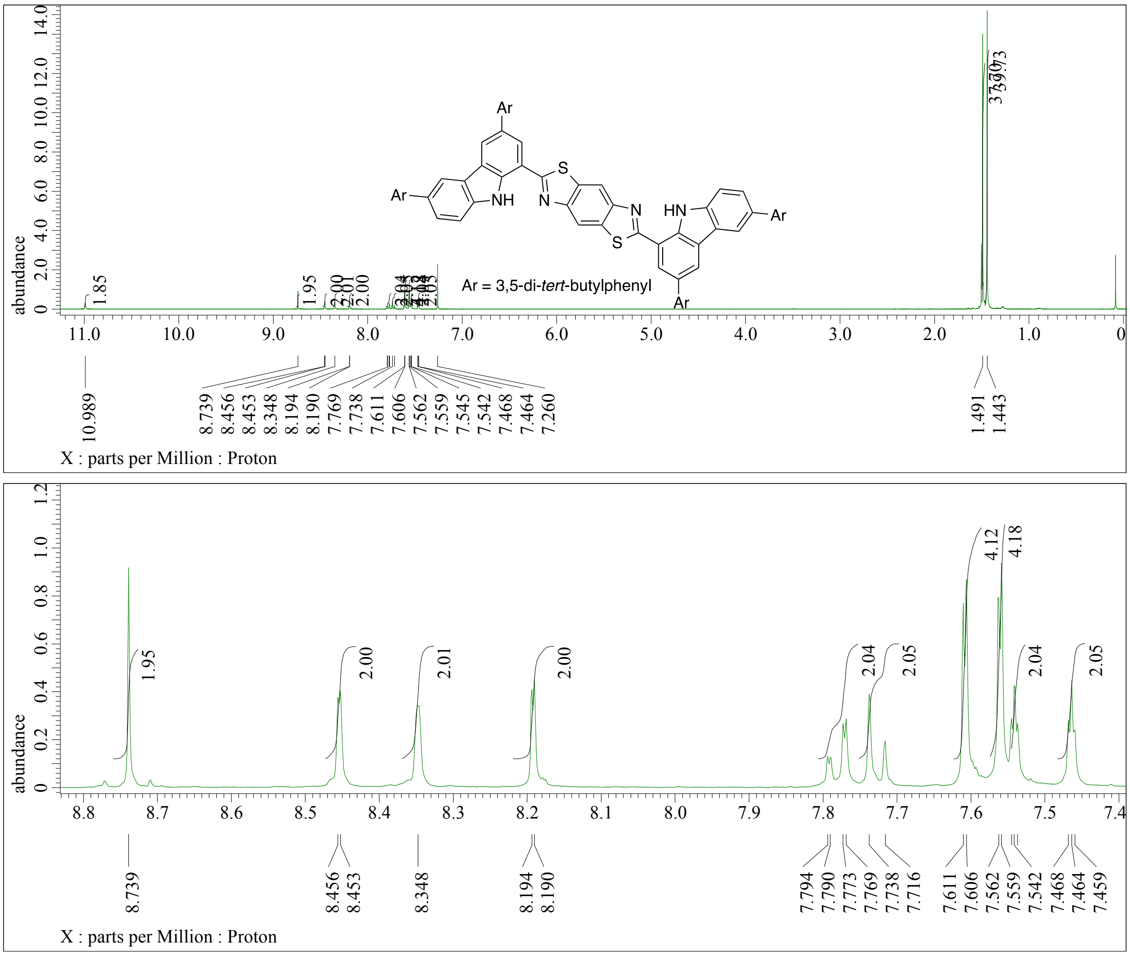
100 MHz ^{13}C NMR spectrum of **6b** in $CDCl_3$



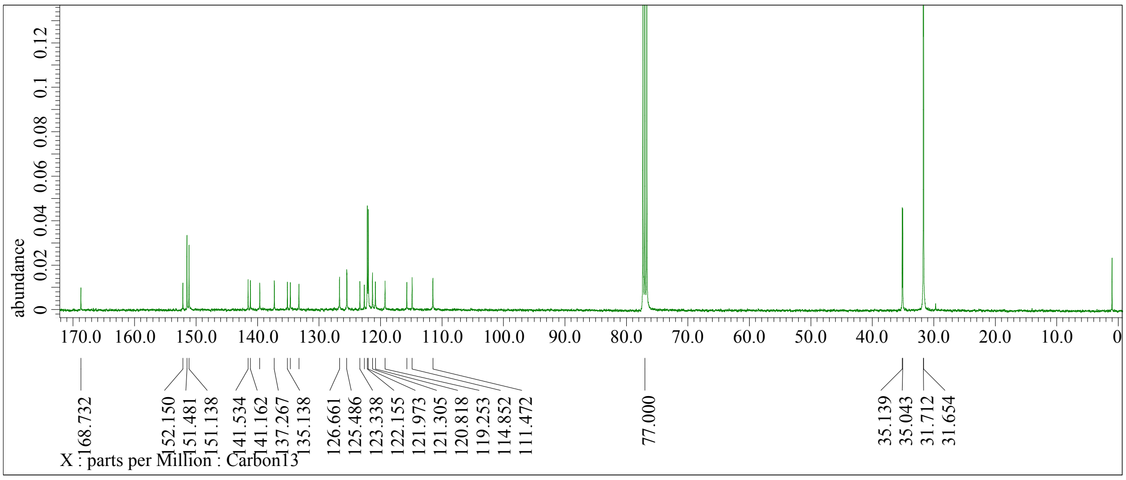
400 MHz ^{1}H NMR spectrum of **2b** in $CDCl_3$



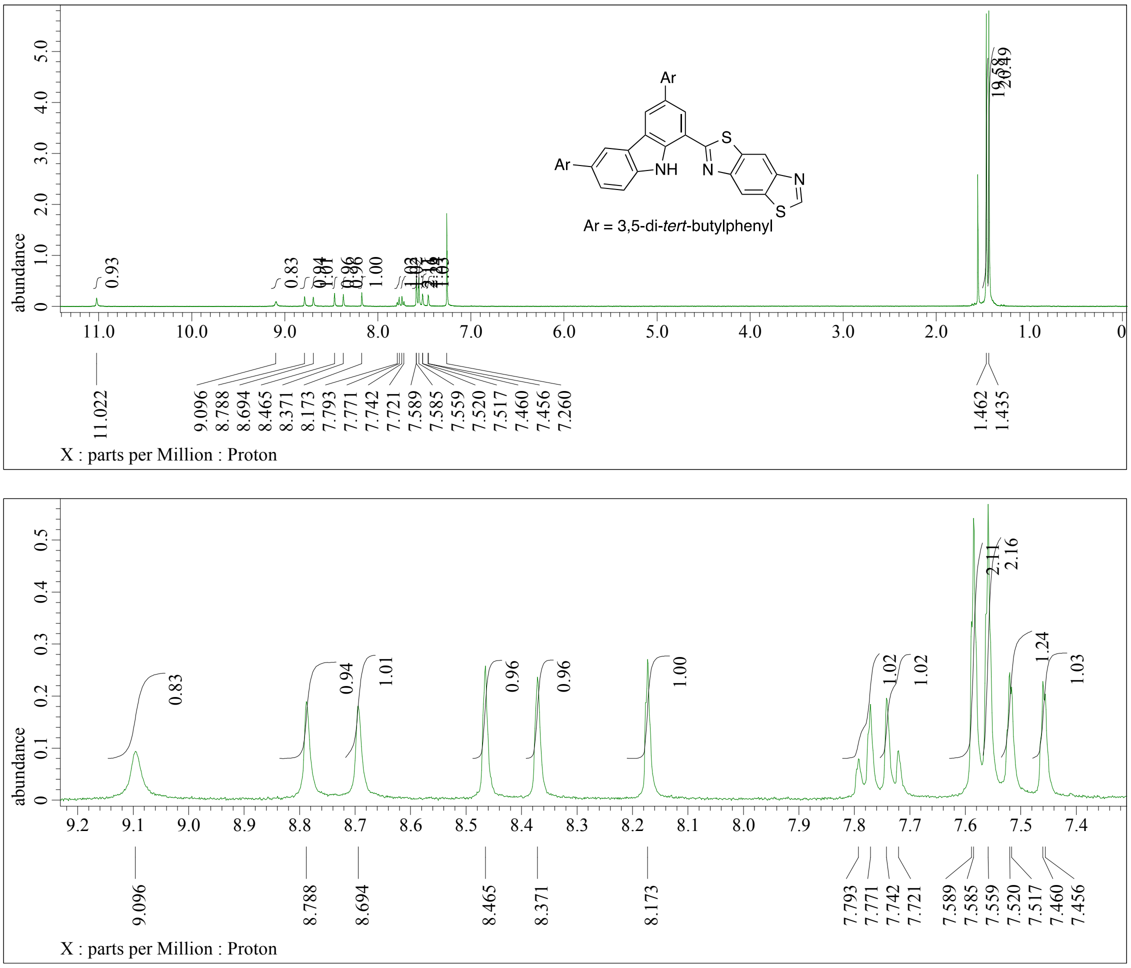
100 MHz ^{13}C NMR spectrum of **2b** in $CDCl_3$



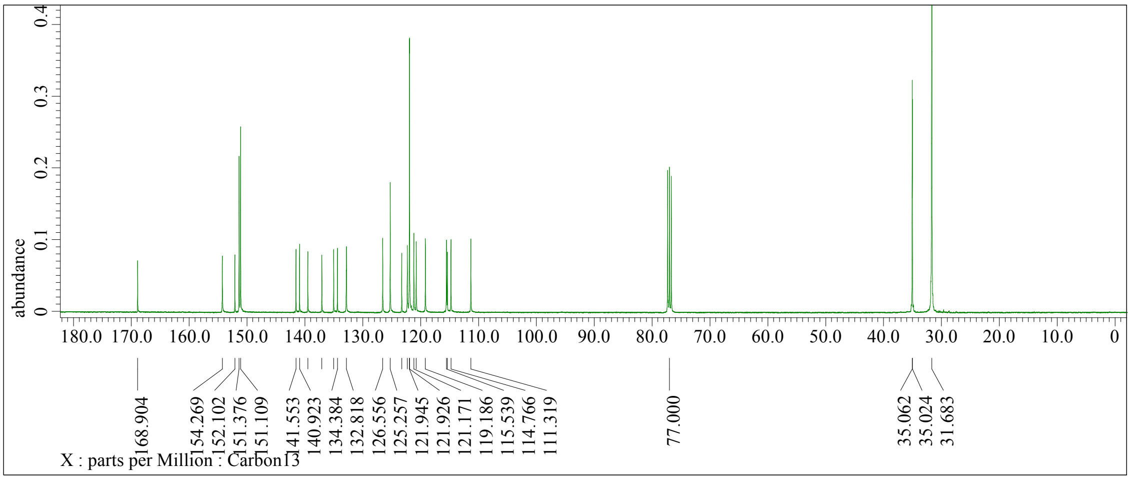
400 MHz ^{1}H NMR spectrum of **5c** in $CDCl_3$



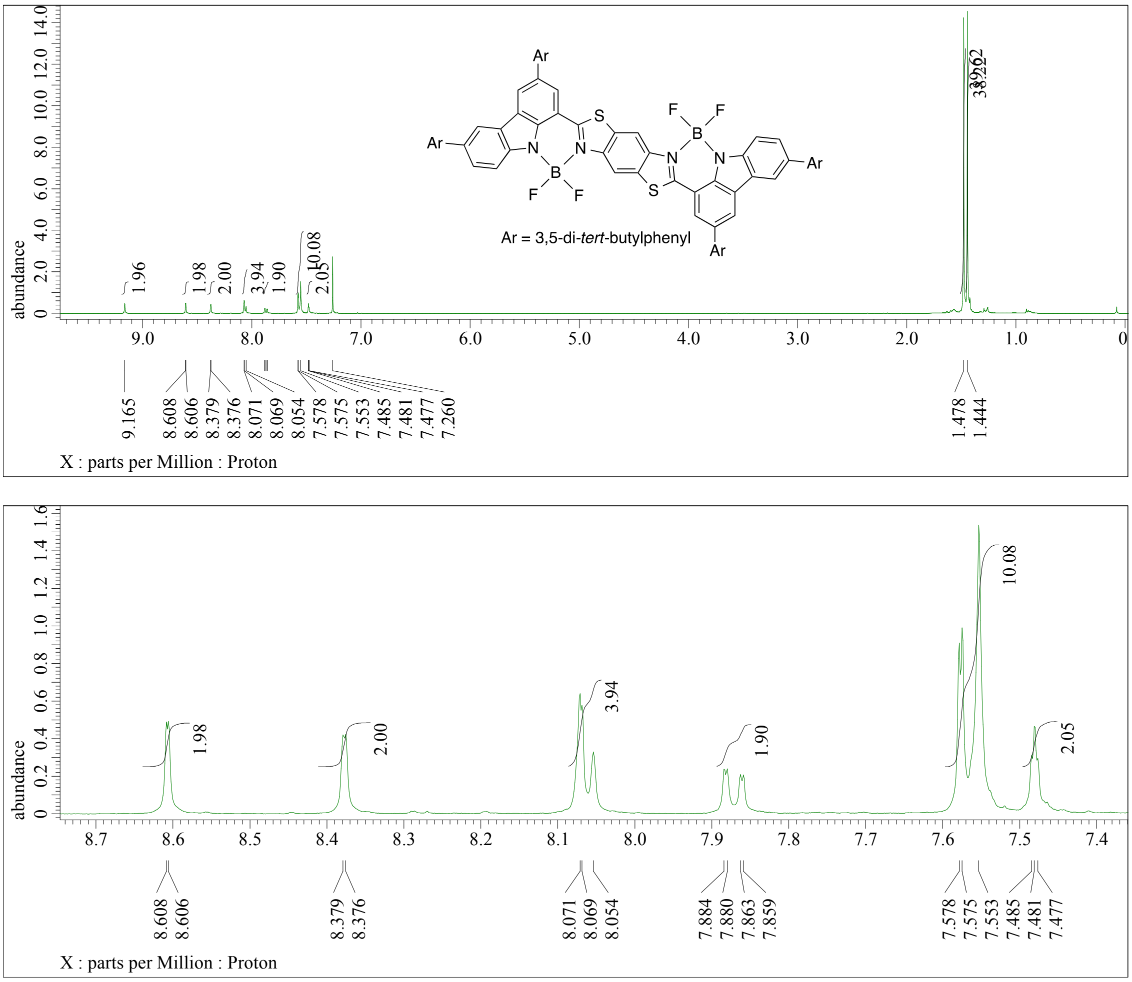
100 MHz ^{13}C NMR spectrum of **5c** in $CDCl_3$



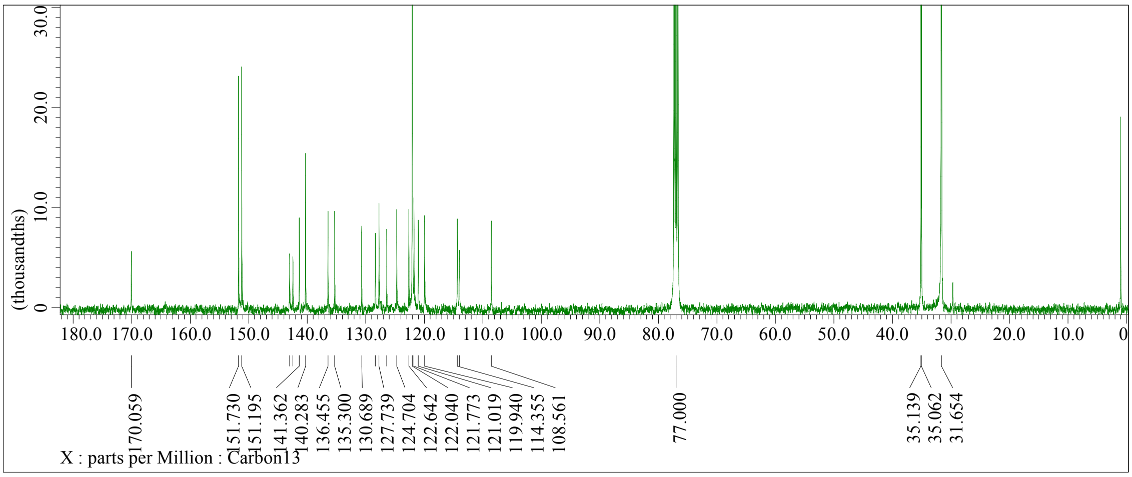
400 MHz ^{1}H NMR spectrum of **6c** in $CDCl_3$



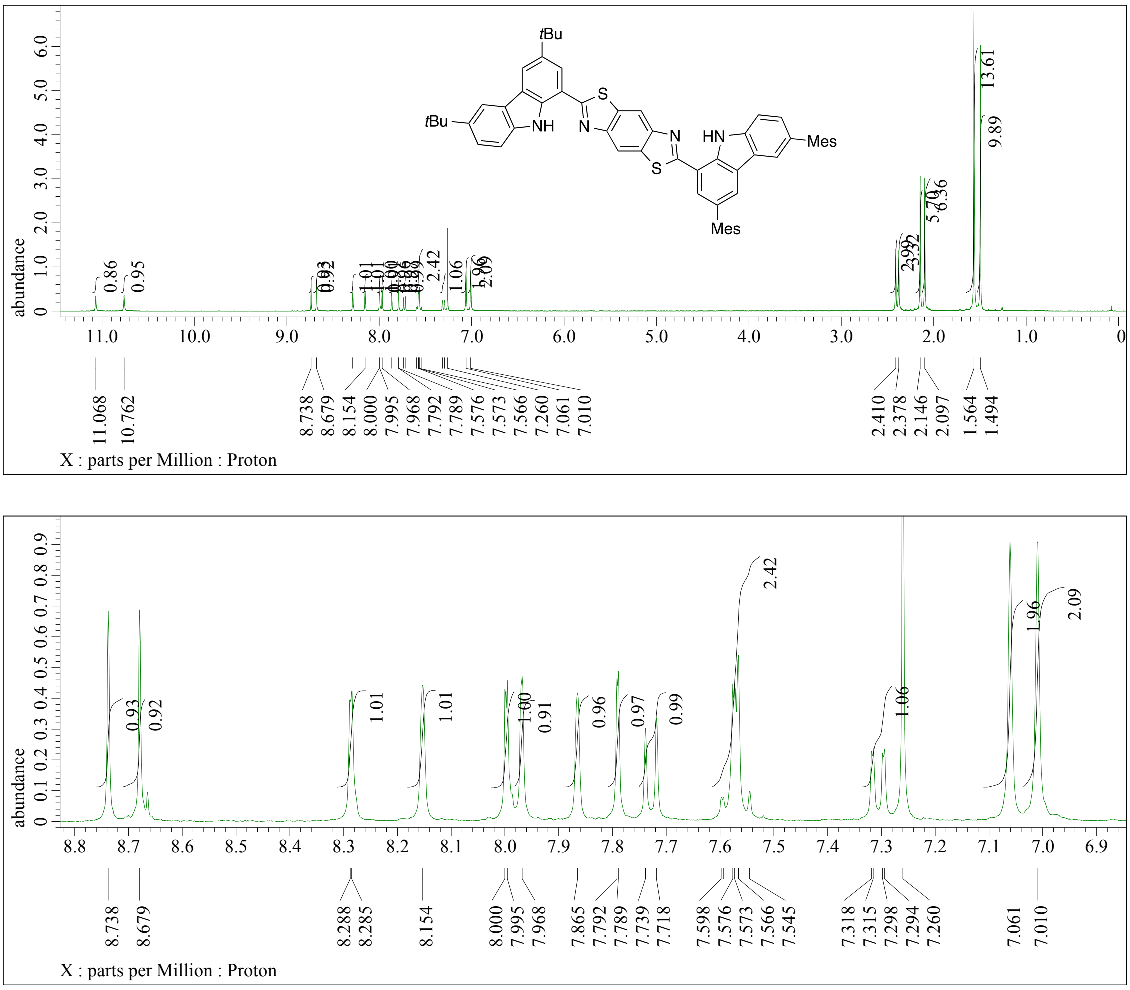
100 MHz ^{13}C NMR spectrum of **6c** in $CDCl_3$



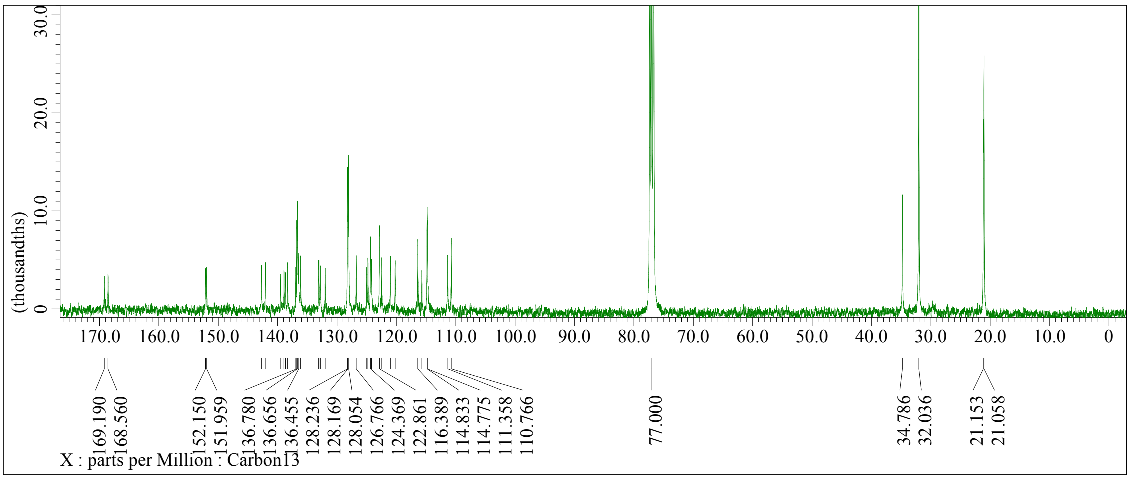
400 MHz ^{1}H NMR spectrum of **2c** in $CDCl_3$



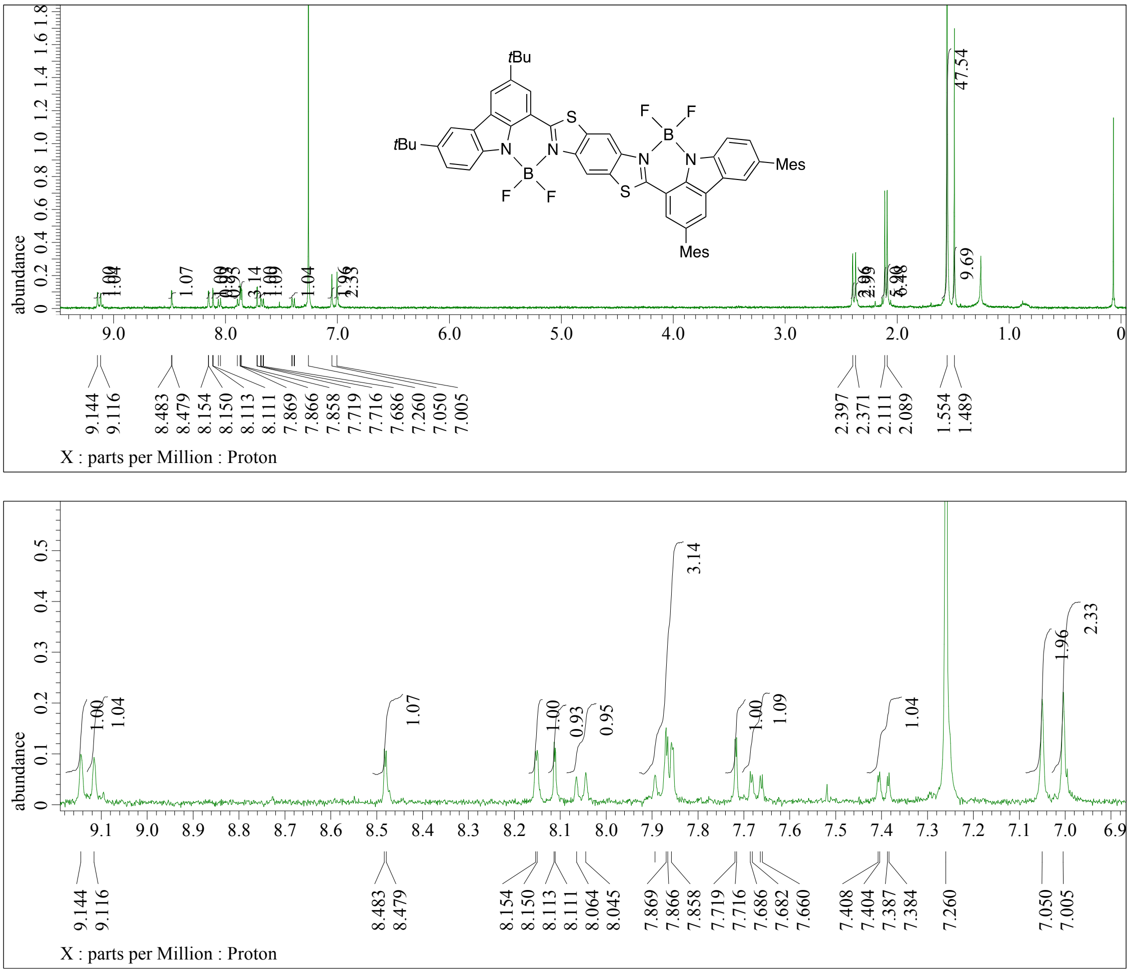
100 MHz ^{13}C NMR spectrum of **2c** in $CDCl_3$



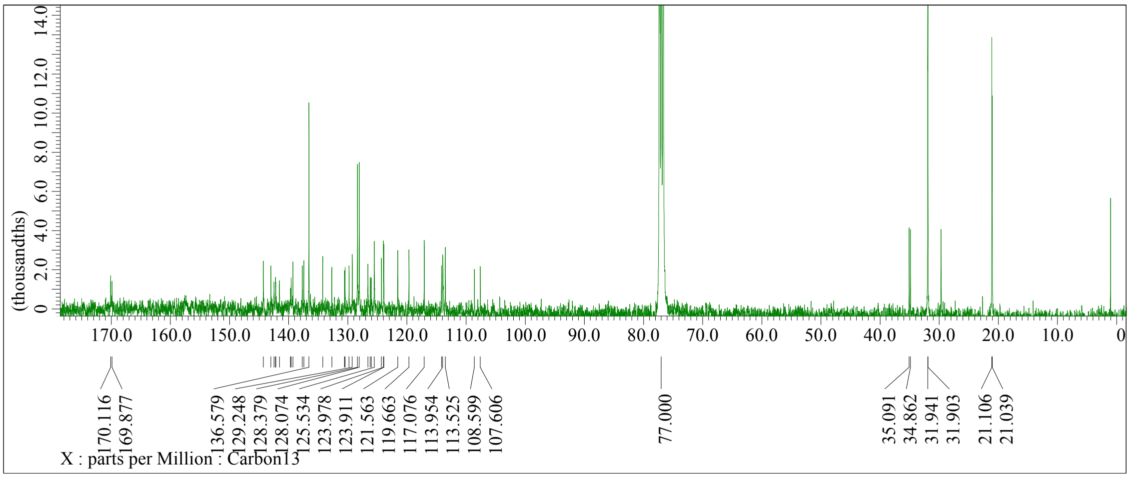
400 MHz ^{1}H NMR spectrum of **5d** in $CDCl_3$



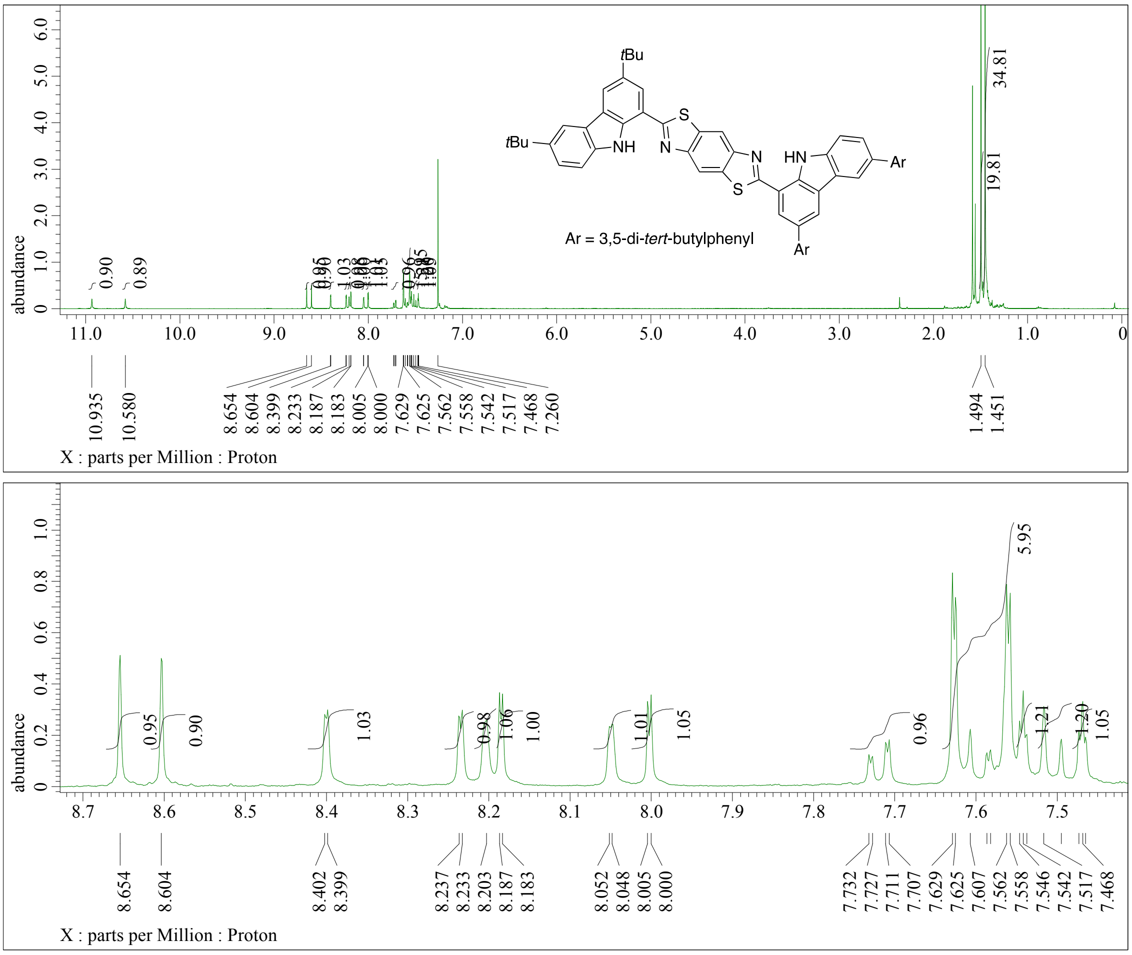
100 MHz ^{13}C NMR spectrum of **5d** in $CDCl_3$



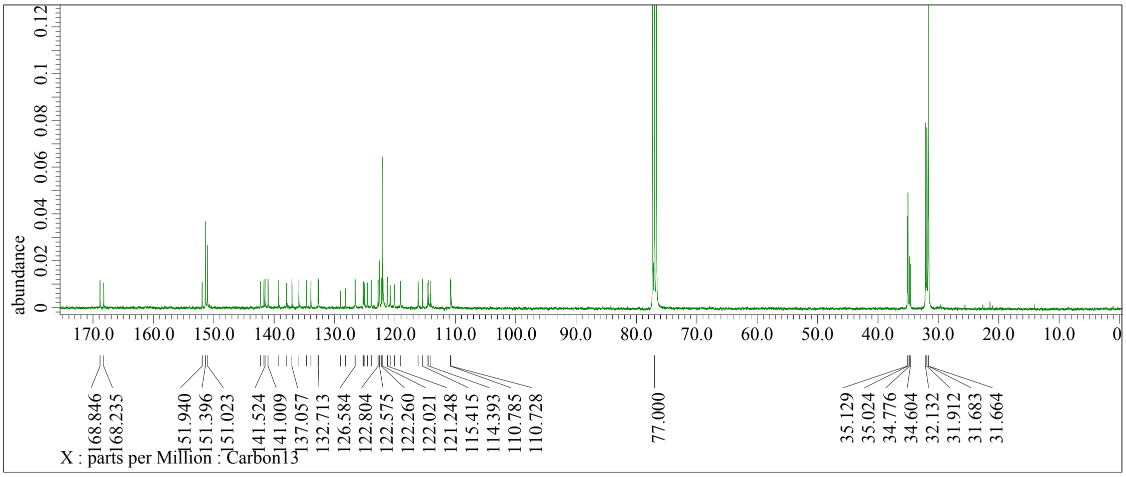
400 MHz ^{1}H NMR spectrum of **2d** in $CDCl_3$



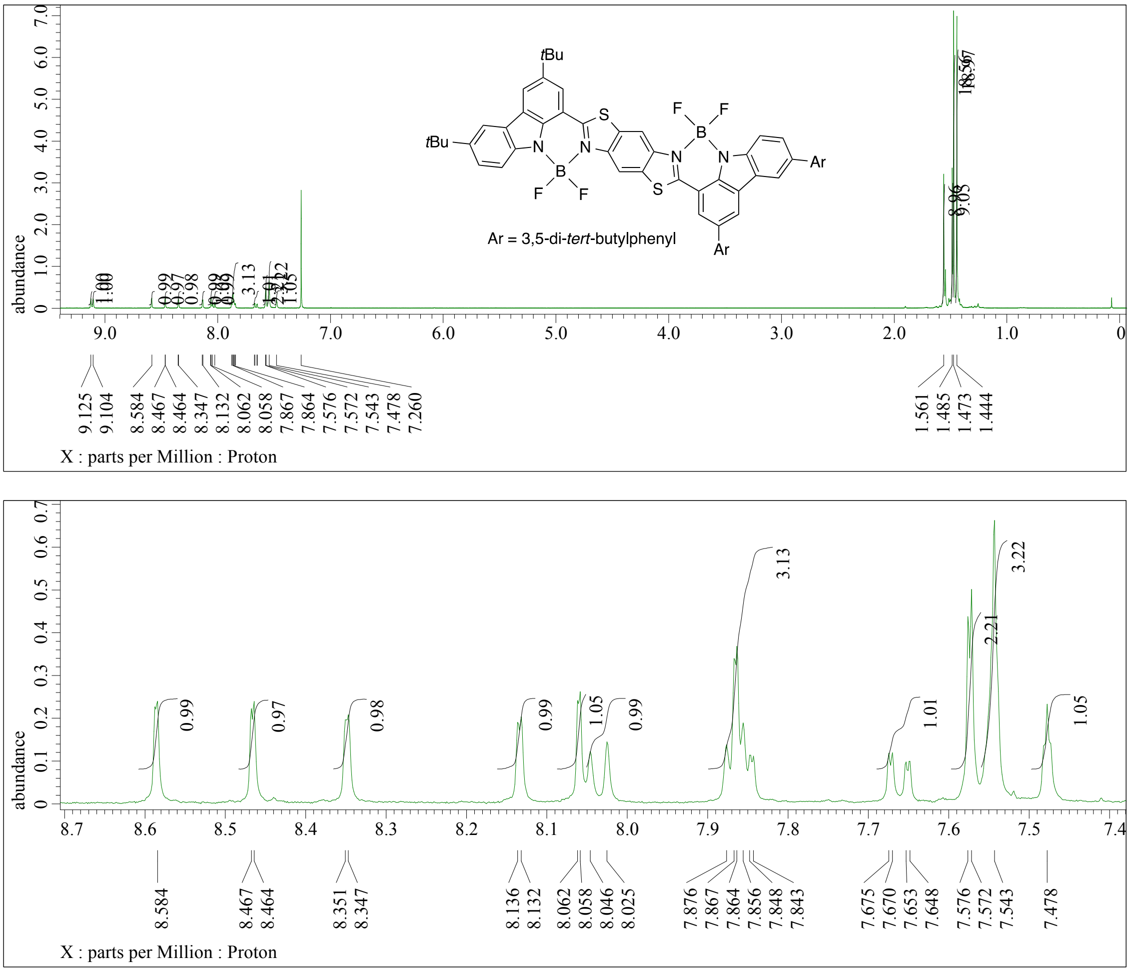
100 MHz ^{13}C NMR spectrum of **2d** in $CDCl_3$



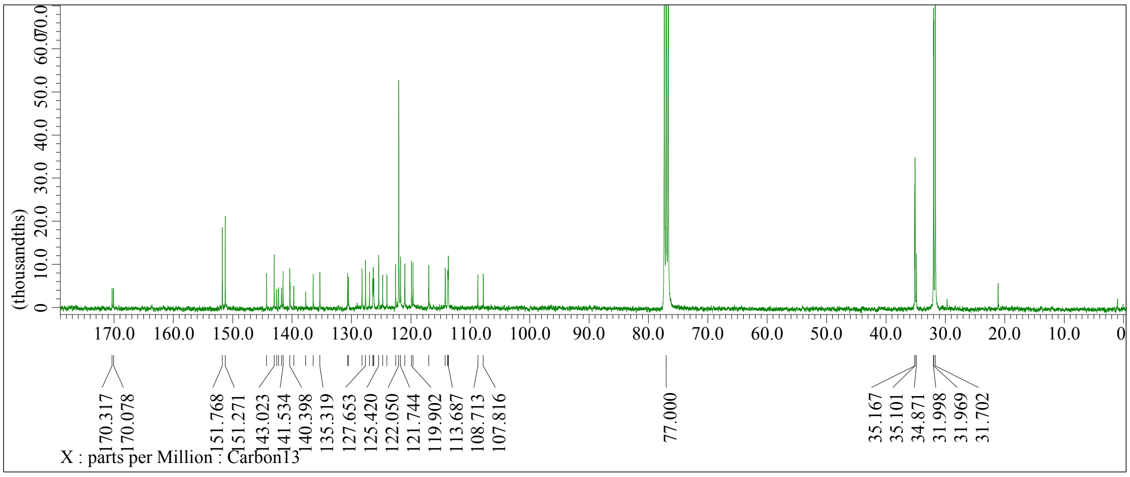
400 MHz ^{1}H NMR spectrum of **5e** in $CDCl_3$



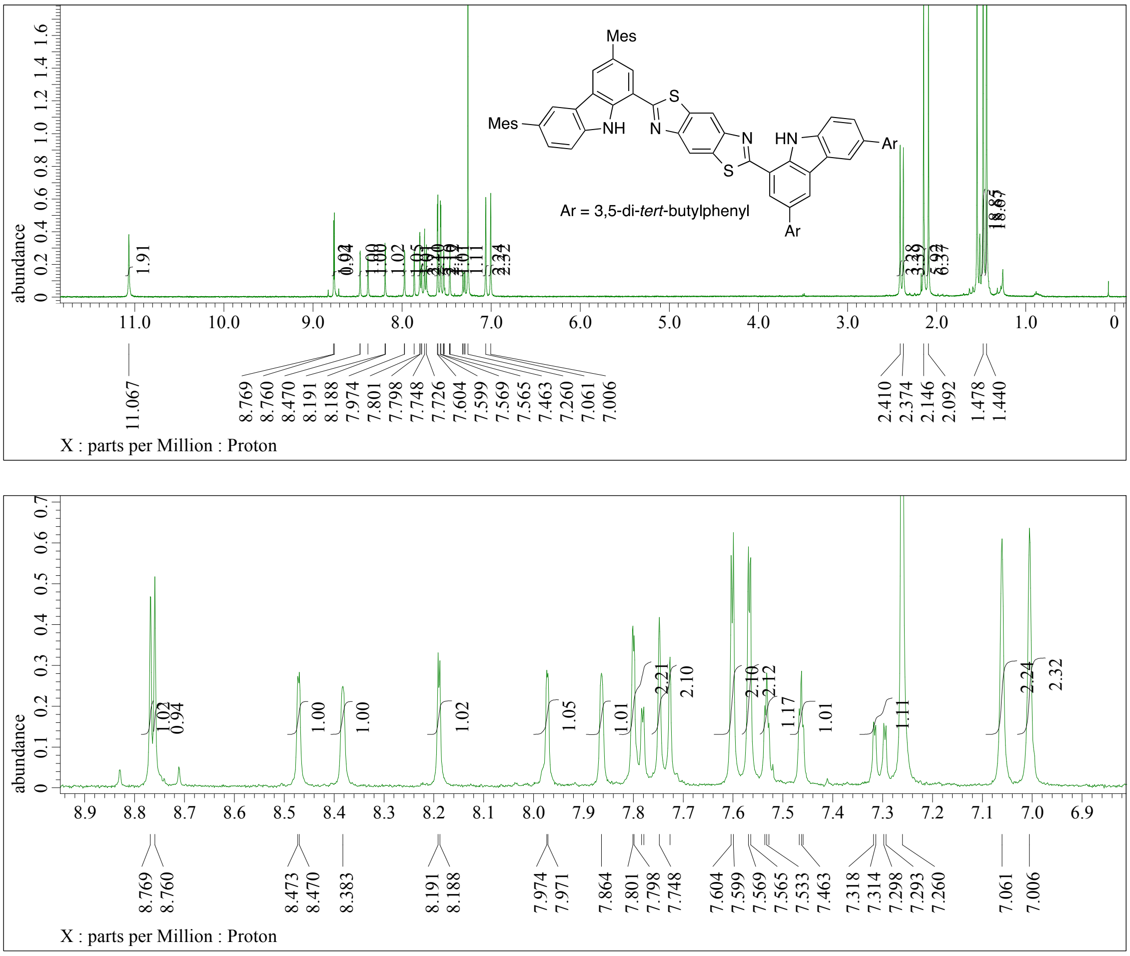
100 MHz ^{13}C NMR spectrum of **5e** in $CDCl_3$



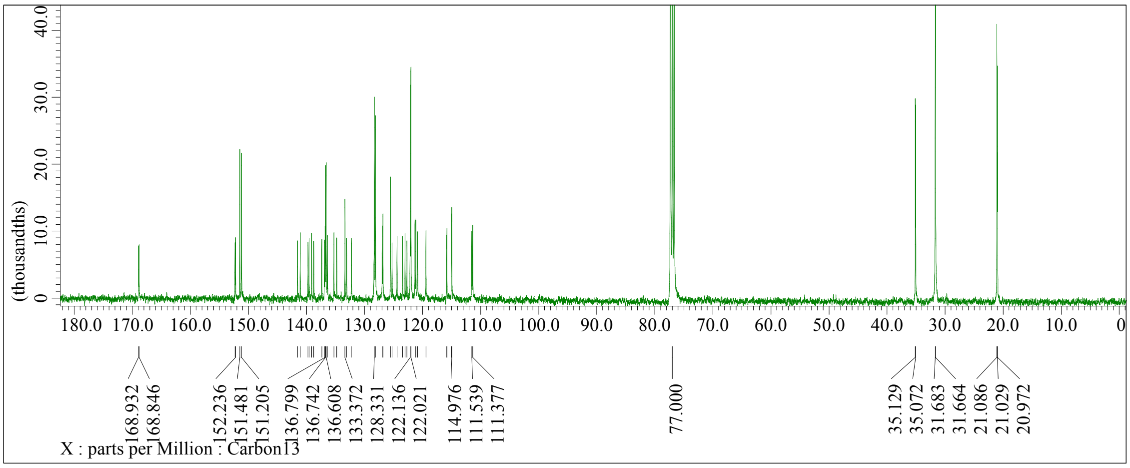
400 MHz ^{1}H NMR spectrum of **2e** in $CDCl_3$



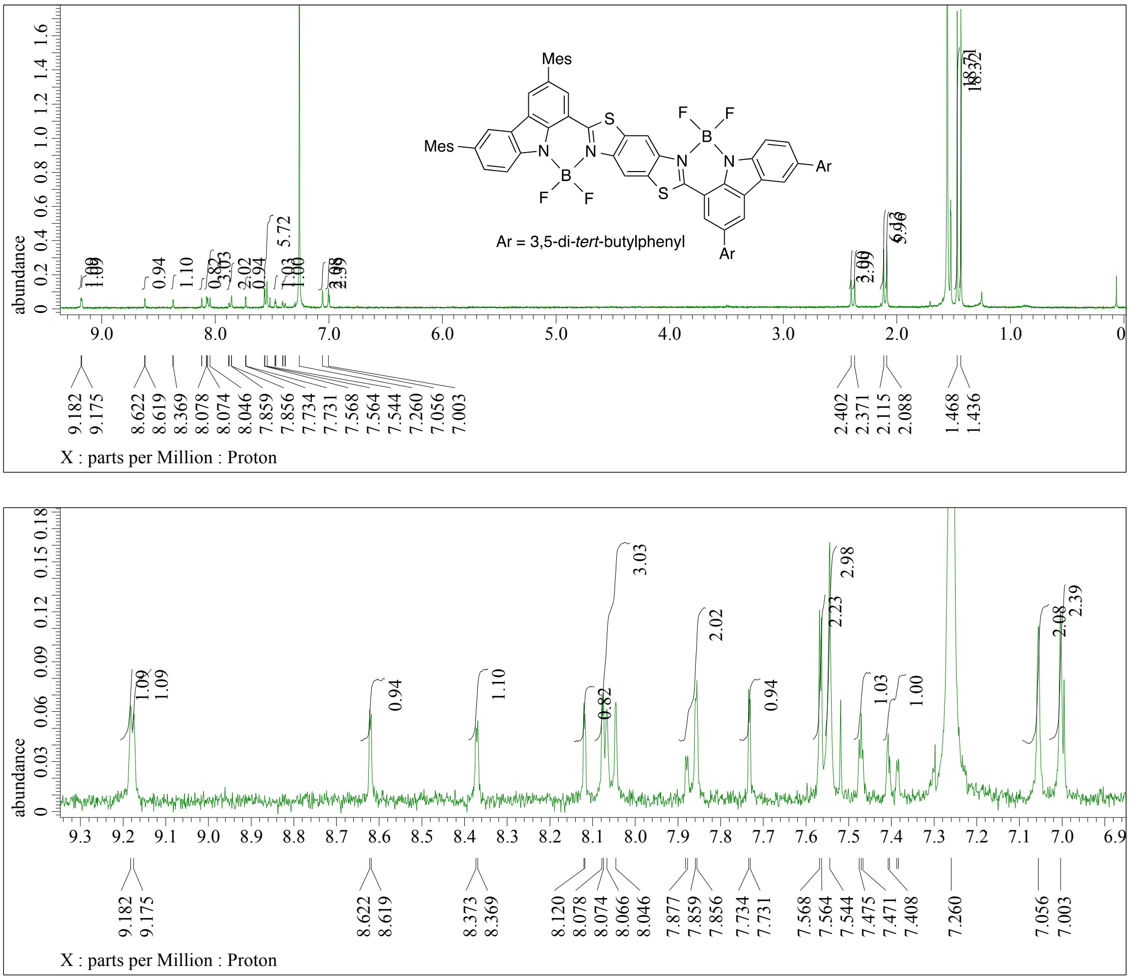
100 MHz ^{13}C NMR spectrum of **2e** in $CDCl_3$



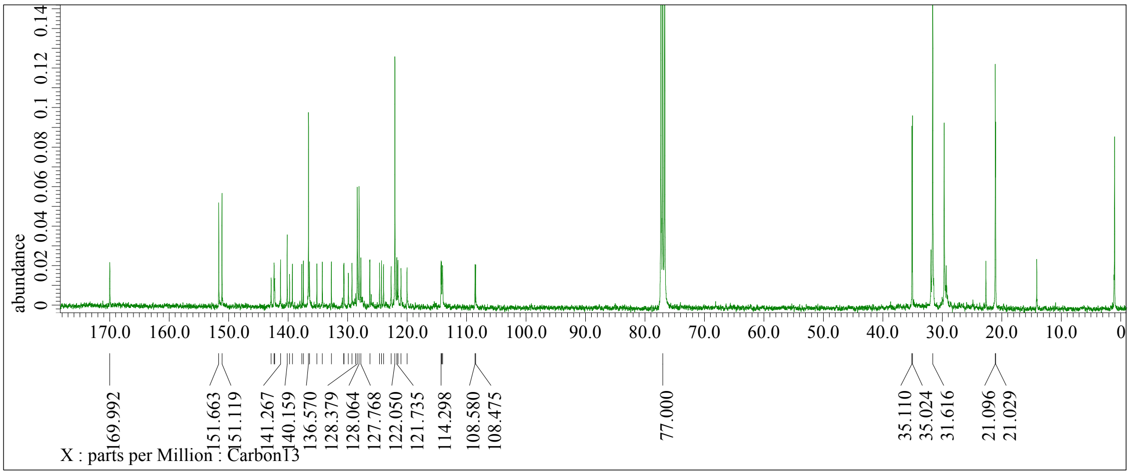
400 MHz ^{1}H NMR spectrum of **5f** in $CDCl_3$



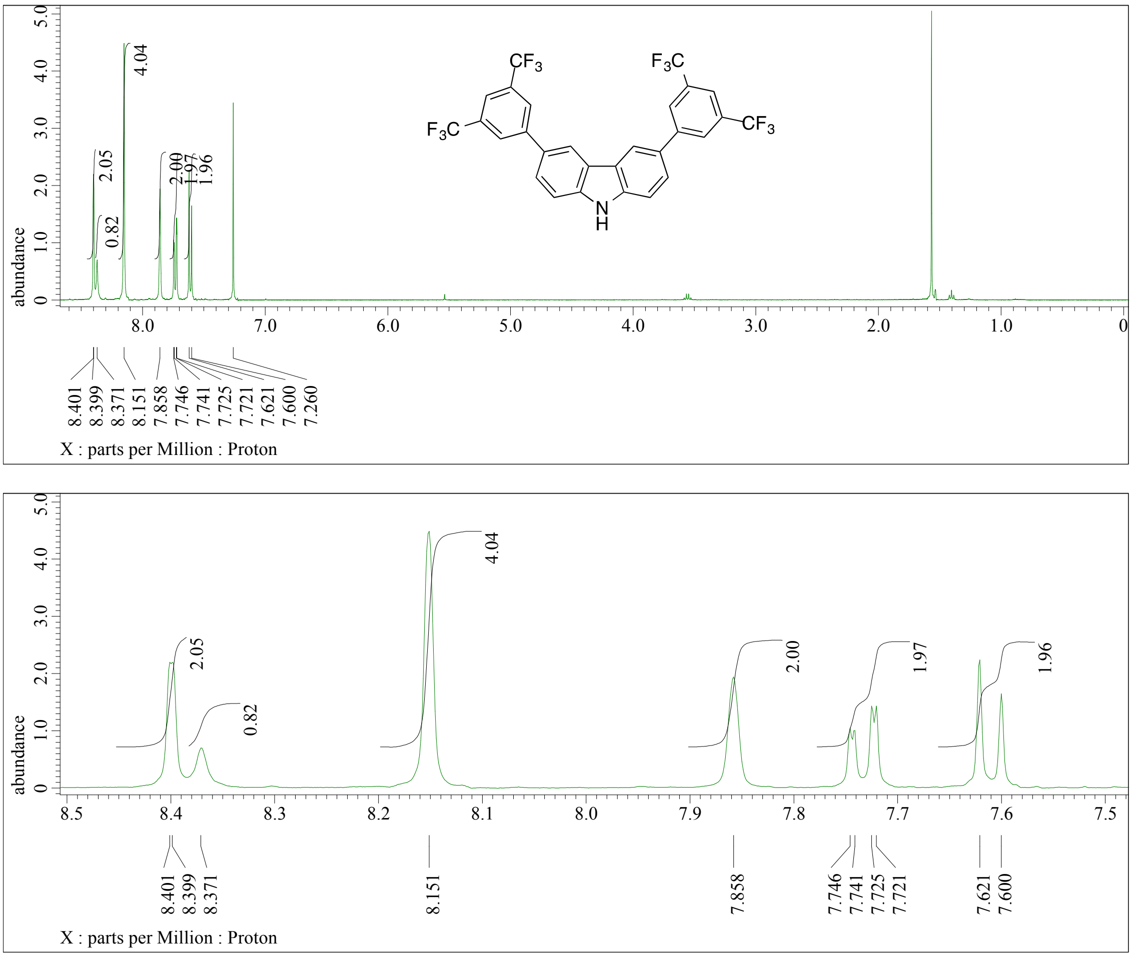
100 MHz ^{13}C NMR spectrum of **5f** in $CDCl_3$



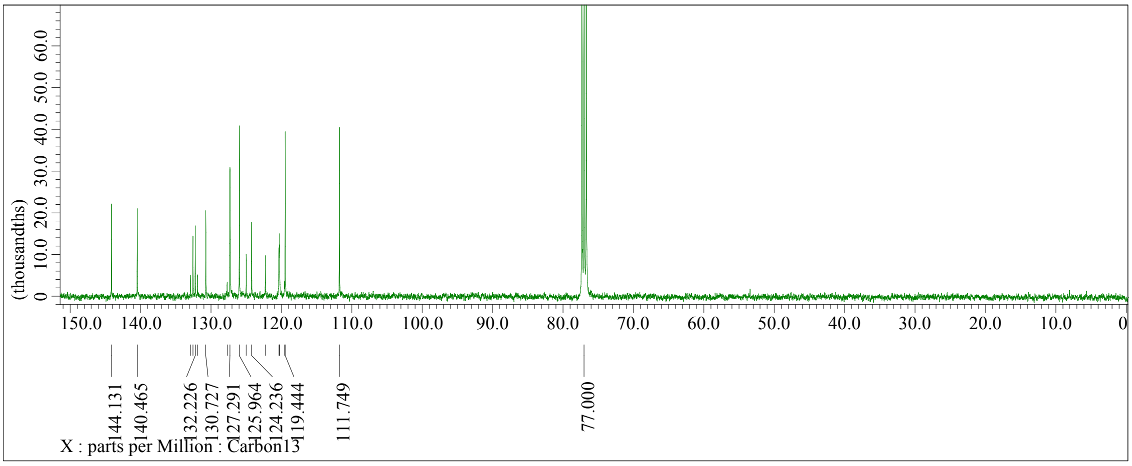
400 MHz ^{1}H NMR spectrum of **2f** in $CDCl_3$



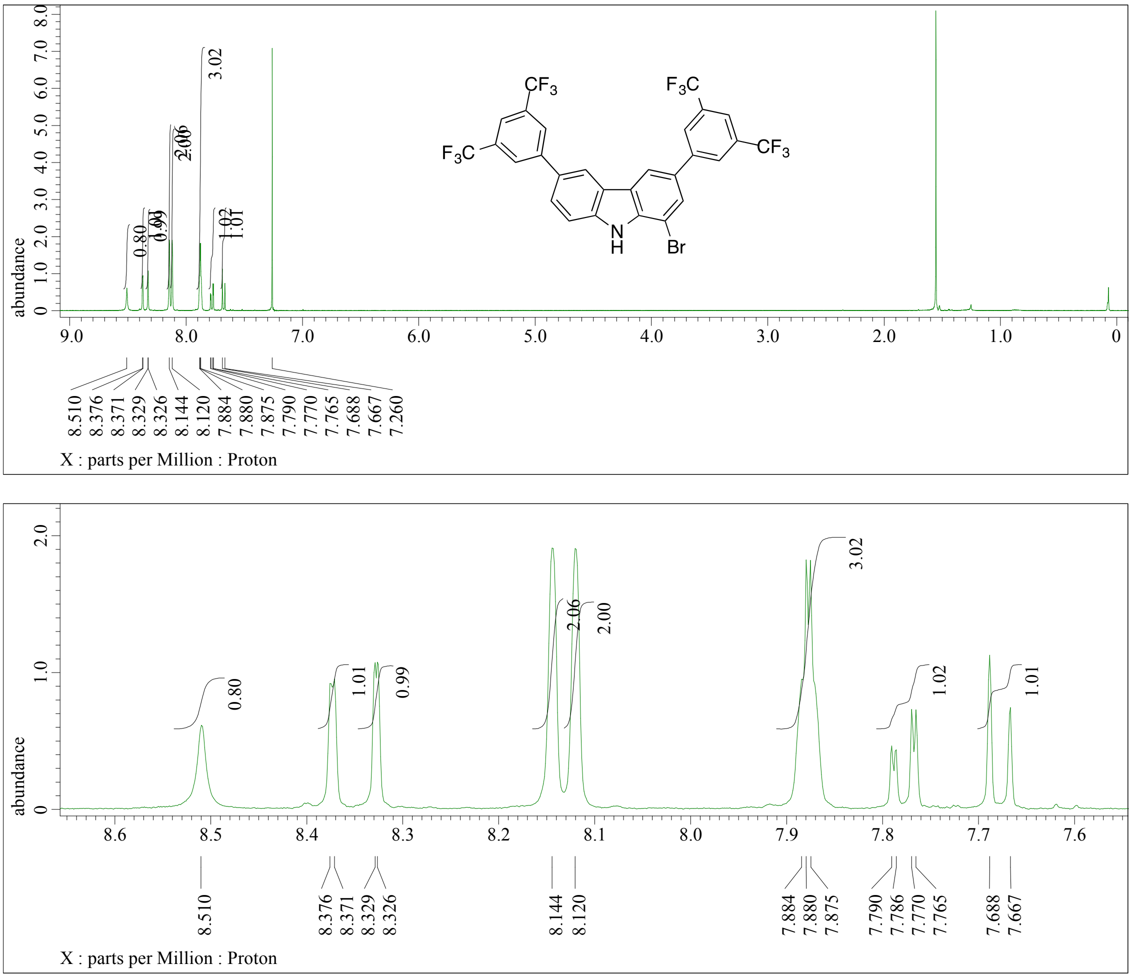
100 MHz ^{13}C NMR spectrum of **2f** in $CDCl_3$



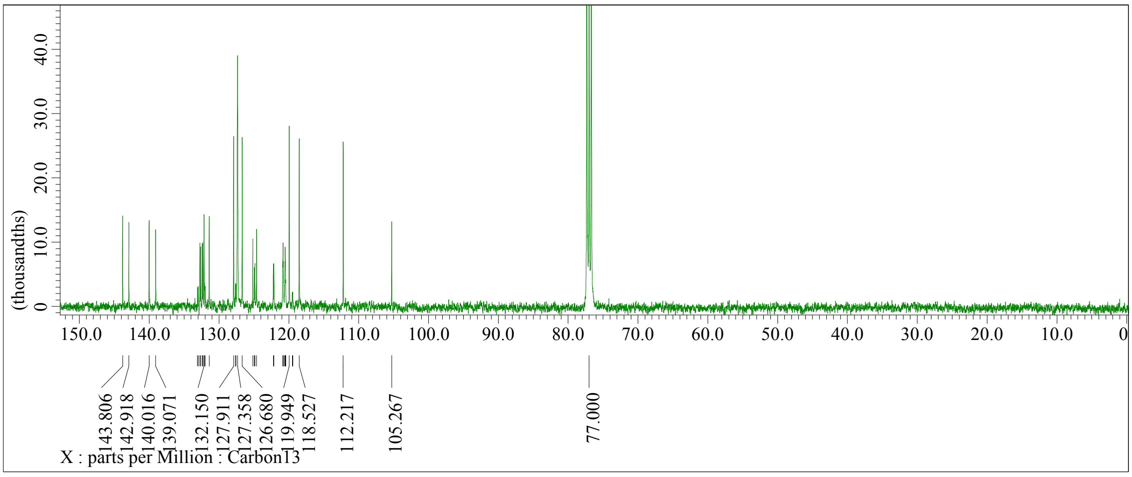
400 MHz ^{1}H NMR spectrum of 3,6-bis[3,5-bis(trifluoromethyl)phenyl]carbazole in $CDCl_3$



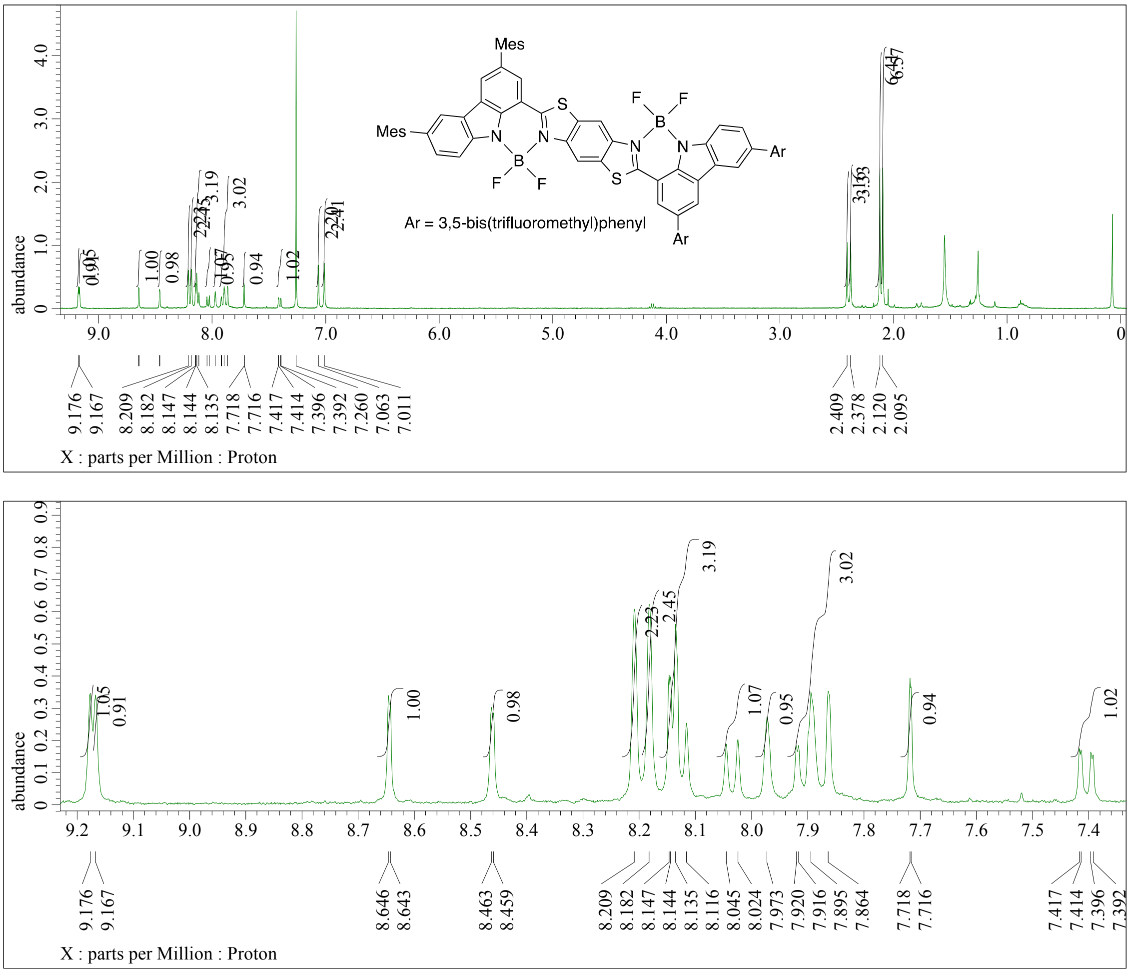
100 MHz ^{13}C NMR spectrum of 3,6-bis[3,5-bis(trifluoromethyl)phenyl]carbazole in $CDCl_3$



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



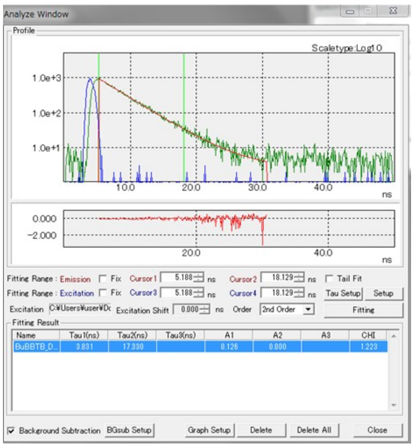
100 MHz ^{13}C NMR spectrum of **3d** in $CDCl_3$



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

[E] Fluorescence Lifetime

(a)



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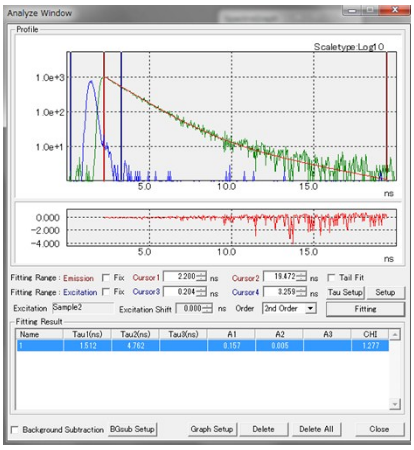
Fitting Range : Excitation ☐ Fix Cursor3 5.188 ns Cursor4 18.129 ns
Excitation C:¥Users¥user¥Dc Excitation Shift 0.000 ns Order 2nd Order

Fitting Result

Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
BuBBTB_D...	3.831	17.330		0.126	0.000		1.223

☑ Background Subtraction



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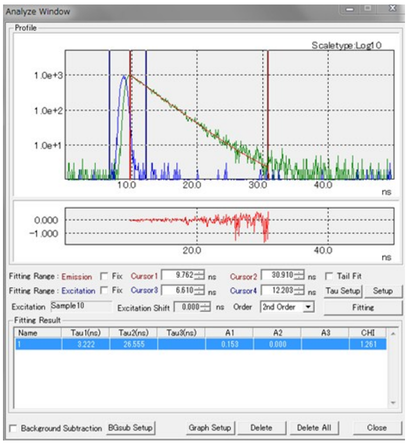
Fitting Range : Excitation ☐ Fix Cursor3 0.204 ns Cursor4 3.259 ns
Excitation Sample2 Excitation Shift 0.000 ns Order 2nd Order

Fitting Result

Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
1	1.512	4.762		0.157	0.005		1.277

☐ Background Subtraction

(b)



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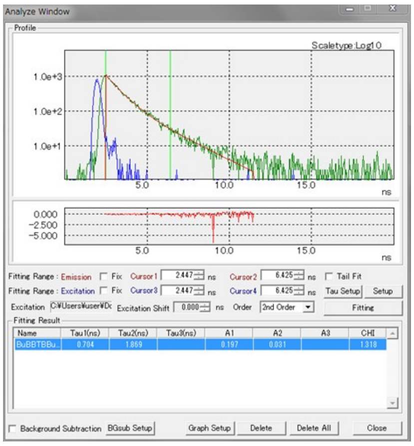
Fitting Range : Excitation ☐ Fix Cursor3 6.610 ns Cursor4 12.203 ns
Excitation Sample10 Excitation Shift 0.000 ns Order 2nd Order

Fitting Result

Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
1	3.222	26.555		0.153	0.000		1.261

☐ Background Subtraction



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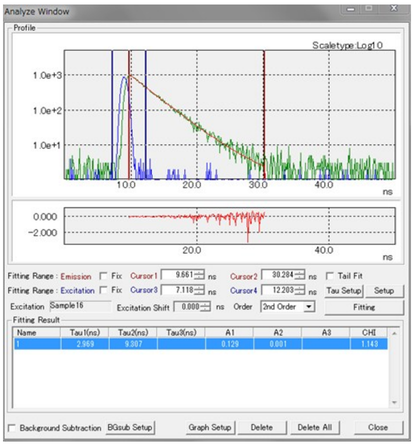
Fitting Range : Excitation ☐ Fix Cursor3 2.447 ns Cursor4 6.425 ns
Excitation C:¥Users¥user¥Dc Excitation Shift 0.000 ns Order 2nd Order

Fitting Result

Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
BuBBTBBu...	0.704	1.869		0.197	0.031		1.318

☐ Background Subtraction

(c)



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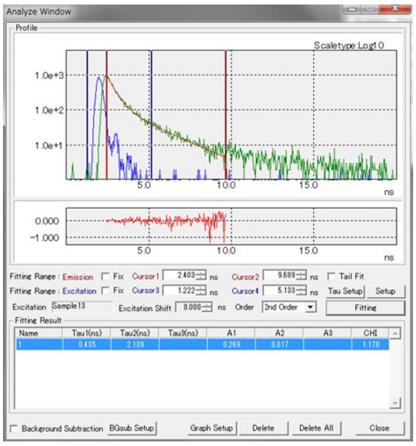
Fitting Range : Excitation ☐ Fix Cursor3 7.118 ns Cursor4 12.203 ns
Excitation Sample16 Excitation Shift 0.000 ns Order 2nd Order

Fitting Result

Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
1	2.969	9.307		0.129	0.001		1.143

☐ Background Subtraction



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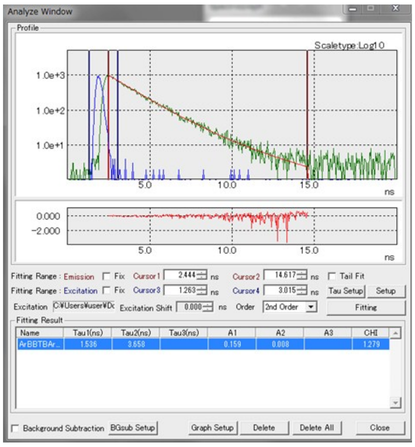
Fitting Range : Excitation ☐ Fix Cursor3 1.222 ns Cursor4 5.133 ns
Excitation Sample13 Excitation Shift 0.000 ns Order 2nd Order

Fitting Result

Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
1	0.435	2.139		0.269	0.017		1.178

☐ Background Subtraction

(d)



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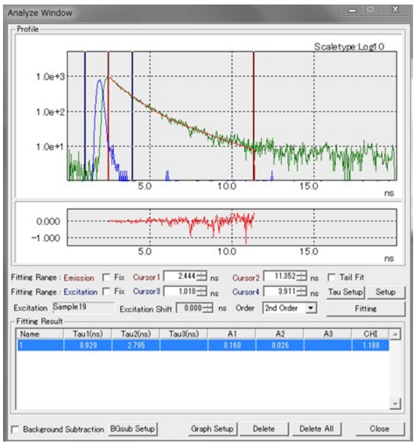
Fitting Range : Excitation ☐ Fix Cursor3 1.263 ns Cursor4 3.015 ns
Excitation C:¥Users¥user¥Dc Excitation Shift 0.000 ns Order 2nd Order

Fitting Result

Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
ArBBTBAr...	1.536	3.658		0.159	0.008		1.279

☐ Background Subtraction



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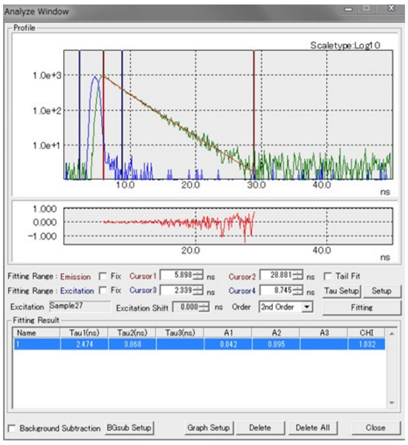
Fitting Range : Excitation ☐ Fix Cursor3 1.018 ns Cursor4 3.911 ns
Excitation Sample19 Excitation Shift 0.000 ns Order 2nd Order

Fitting Result

Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
1	0.929	2.795		0.160	0.026		1.188

☐ Background Subtraction

(e)



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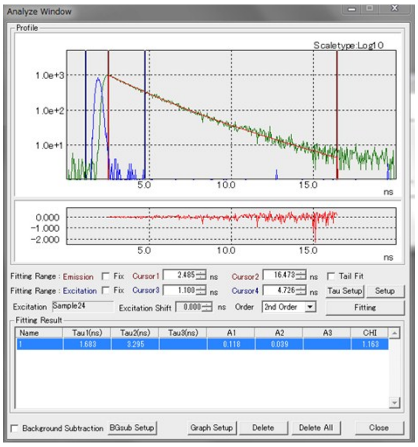
Fitting Range : Excitation ☐ Fix Cursor3 2.339 ns Cursor4 8.745 ns
Excitation Sample27 Excitation Shift 0.000 ns Order 2nd Order
Fitting Result

Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
1	2.474	3.868		0.042	0.095		1.032



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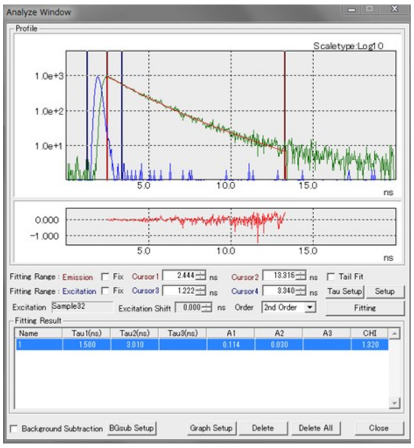
Fitting Range : Excitation ☐ Fix Cursor3 1.100 ns Cursor4 4.726 ns
Excitation Sample24 Excitation Shift 0.000 ns Order 2nd Order
Fitting Result

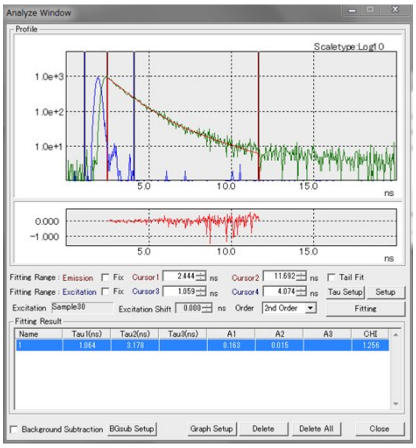
Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
1	1.683	3.295		0.118	0.039		1.163

(f)



Fitting Range : Emission ☐ Fix Cursor1 2.444 ns Cursor2 13.316 ns ☐ Tail Fit
Fitting Range : Excitation ☐ Fix Cursor3 1.222 ns Cursor4 3.340 ns
Excitation Sample32 Excitation Shift 0.000 ns Order 2nd Order
Fitting Result

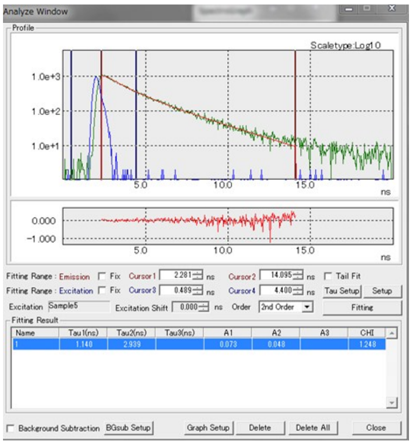
Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
1	1.500	3.010		0.114	0.030		1.320



Fitting Range : Emission ☐ Fix Cursor1 2.444 ns Cursor2 11.692 ns ☐ Tail Fit
Fitting Range : Excitation ☐ Fix Cursor3 1.059 ns Cursor4 4.074 ns
Excitation Sample30 Excitation Shift 0.000 ns Order 2nd Order
Fitting Result

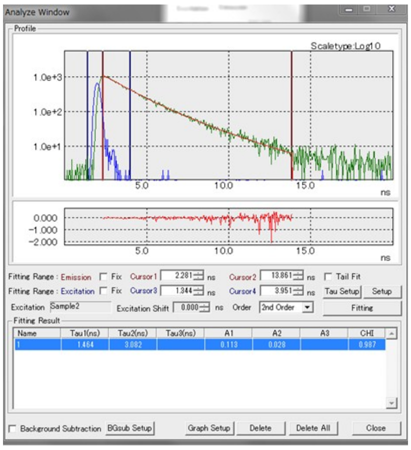
Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
1	1.064	3.178		0.163	0.015		1.256

(g)



Fitting Range : Emission ☐ Fix Cursor1 2.281 ns Cursor2 14.095 ns ☐ Tail Fit
Fitting Range : Excitation ☐ Fix Cursor3 0.489 ns Cursor4 4.400 ns
Excitation Sample5 Excitation Shift 0.000 ns Order 2nd Order
Fitting Result

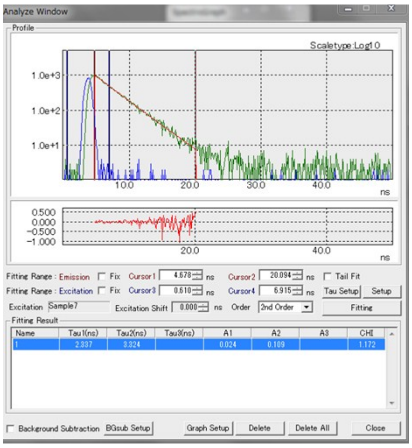
Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
1	1.140	2.939		0.073	0.048		1.248



Fitting Range : Emission ☐ Fix Cursor1 2.281 ns Cursor2 13.861 ns ☐ Tail Fit
Fitting Range : Excitation ☐ Fix Cursor3 1.344 ns Cursor4 3.951 ns
Excitation Sample2 Excitation Shift 0.000 ns Order 2nd Order
Fitting Result

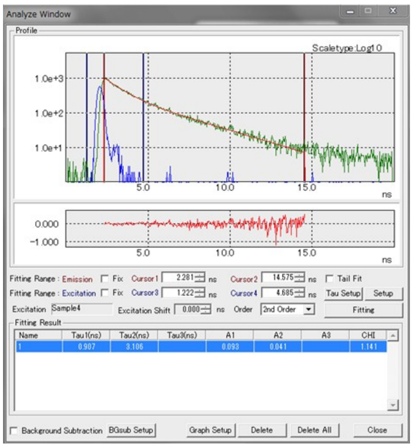
Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
1	1.464	3.082		0.113	0.028		0.987

(h)



Fitting Range : Emission ☐ Fix Cursor1 4.678 ns Cursor2 20.094 ns ☐ Tail Fit
Fitting Range : Excitation ☐ Fix Cursor3 0.610 ns Cursor4 6.915 ns
Excitation Sample7 Excitation Shift 0.000 ns Order 2nd Order
Fitting Result

Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
1	2.337	3.324		0.024	0.109		1.172



Fitting Range : Emission ☐ Fix Cursor1 2.281 ns Cursor2 14.575 ns ☐ Tail Fit
Fitting Range : Excitation ☐ Fix Cursor3 1.222 ns Cursor4 4.685 ns
Excitation Sample4 Excitation Shift 0.000 ns Order 2nd Order
Fitting Result

Name	Tau1(ns)	Tau2(ns)	Tau3(ns)	A1	A2	A3	CHI
1	0.907	3.106		0.093	0.041		1.141

Fig. S1 Fluorescence decay analyses of (a) **7**, (b) **2a**, (c) **2b**, (d) **2c**, (e) **2d**, (f) **2e**, (g) **2f** and (f) **2g** in CH_2Cl_2 (left) and in the solid state (right).

[F] X-ray Crystal Structures

Single crystals of **2a** and **7** were obtained by the vapor diffusion method (chlorobenzene/EtOH for **2a** and CH_2Cl_2/MeOH for **7**). X-ray data at 93 K were taken on a Rigaku-Raxis-RAPID imaging plate system with Cu-*K*α 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.

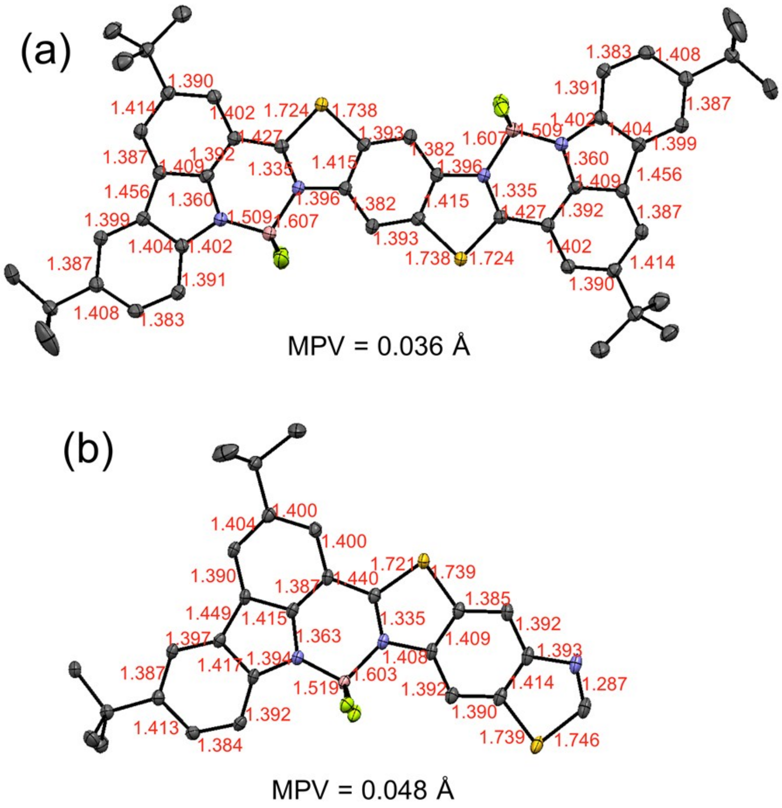


Fig. S2 Crystal structures of (a) **2a** and (b) **7**. Hydrogen atoms and solvent molecules are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) are shown. Mean plane deviations (MPV) are calculated for the atoms excluding the peripheral substituents.

Crystallographic data for 2a: formula: $C_{48}H_{46}N_4S_2B_2F_4 \cdot 3(C_6H_5Cl)$, M_w = 1078.28, Tricrinic, space group P–1 (2), a = 8.2634(10), b = 12.174(2), c = 15.232(3) Å, α = 88.77(3), β = 79.422(18), γ = 76.323(18), V = 1463.2(4) Å^3, Z = 1, ρ_{calcd} = 1.337, T = –180 °C, 18884 measured reflection, 5066 unique reflections (R_{int} = 0.0426), R_1 = 0.0487, wR_2 = 0.1387 (all data), GOF = 1.004
Crystallographic data for 7: formula: $2(C_{28}H_{26}N_3S_2BF_2) \cdot 0.615(CCl_2)$, M_w = 1085.71, Tricrinic, space group P–1 (2), a = 9.6199(15), b = 11.2244(19), c = 24.169(4) Å, α = 88.899(15), β = 85.634(13), γ = 83.446(12), V = 2585.0(7) Å^3, Z = 2, ρ_{calcd} = 1.395, T = –180 °C, 32248 measured reflection, 8710 unique reflections (R_{int} = 0.0258), R_1 = 0.0520, wR_2 = 0.1517 (all data), GOF = 1.024.