Supporting Information

Rhodium-catalyzed regioselective alkynylations of 8-pyrrole-appended BODIPYs

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1. Instruments and materials

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were taken on a Bruker AVANCE-500 spectrometer and Quantum-I Plus 500 MHz, and chemical shifts were reported as the delta scale in ppm. The residual peak of $CDCl_3$ was used as internal reference for ^{1}H NMR (δ = 7.26 ppm) and the solvent $CDCl_3$ was used as internal reference for ^{13}C NMR (δ = 77.0 ppm). UV/vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Measurement of photoluminescence spectra and the fluorescent quantum yields were measured in CH_2Cl_2 using an integrating sphere by an Edinburgh FLS1000 machine. The MALDI-TOF mass spectra were obtained with a Bruker ultrafle Xtreme MALDI-TOF/TOF spectrometer with matrix. X-Ray data were taken on a Bruker SMART APEX X-Ray diffractometer equipped with a large area CCD detector. BODIPYs **1a-1e** and brominated alkynes **2a-2l** were prepared according to the literature procedures.[S1-S8] Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. General procedure for syntheses and spectral data

2.1. Synthesis of alkynylated BODIPYs 3aa-3aj, 3ba-bb, 3bd, 3bg-h, 3bj, and 3ca

A mixture of **1** (0.1 mmol), alkyne (0.15 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), Na_2CO_3 (0.20 mmol), AgOAc (0.12 mmol) in *o*-xylene was stirred at 70 ^{o}C for about 12 h. After cooling to room temperature, the mixture was passed through a short silica-gel column (CH_2Cl_2 as an eluent). After removal of solvents in *vacuo*, the crude product was purified by silica-gel (CH_2Cl_2/*n*-hexane as an eluent) and recrystallized from CH_2Cl_2/*n*-hexane to afford **3** as red solids.

3aa: yield: 78%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.38 (br, 1H), 7.56 (d, J = 2.5 Hz, 1H), 7.29 (d, J = 9.0 Hz, 2H), 7.25 (d, J = 9.0 Hz, 2H), 6.99 (td, J = 2.5, 1.5 Hz, 1H), 6.56 (d, J = 2.5 Hz, 1H), 6.44 (ddd, J = 3.5, 2.5, 1.5 Hz, 1H), 6.38 (td, J = 3.5, 2.5 Hz, 1H), 6.15 (s, 1H), 2.60 (s, 3H), 1.68 (s, 3H) and 1.30 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 162.8, 151.6, 148.4, 137.1, 135.6, 134.0, 133.1, 131.8, 125.1, 123.8, 122.1, 121.3, 120.8, 120.2, 120.2, 112.7, 110.2, 98.0, 83.2, 34.8, 31.2, 15.2 and 14.0 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{27}H_{26}BF_2N_3$ 441.2188; Found: 441.2189.

3ab: yield: 74%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.34 (br, 1H), 7.58 (br, 1H), 7.34-7.30 (m, 2H), 7.28-7.26 (m, 3H), 6.99 (td, J = 3.0, 1.5 Hz, 1H), 6.58 (d, J = 2.5 Hz, 1H), 6.45 (ddd, J = 4.0,

3.0, 1.5 Hz, 1H), 6.37 (dt, *J* = 4.0, 3.0 Hz, 1H), 6.17 (s, 1H), 2.61 (s, 3H) and 1.70 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 163.2, 148.6, 136.9, 135.7, 134.1, 133.1, 132.0, 128.2, 128.1, 123.9, 123.3, 121.6, 121.2, 120.9, 120.2, 112.7, 110.2, 97.5, 83.7, 15.3 and 14.1 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{23}H_{18}BF_2N_3$ 385.1562; Found: 385.1561.

3ac: yield: 73%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.38 (br, 1H), 7.56 (br, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.95-6.94 (m, 1H), 6.55 (d, *J* = 2.5 Hz, 1H), 6.44-6.43 (m, 1H), 6.34-6.33 (m, 1H), 6.14 (s, 1H), 2.59 (s, 3H), 2.33 (s, 3H) and 1.67 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 162.8, 148.4, 138.4, 137.0, 135.6, 134.0, 133.0, 131.9, 128.8, 123.8, 121.9, 121.2, 120.7, 120.1, 112.6, 110.2, 97.9, 83.1, 21.5, 15.2 and 14.0 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{24}H_{20}BF_2N_3$ 399.1718, Found: 399.1719.

3ad: yield: 55%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.42 (br, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 2.5 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.98 (td, *J* = 2.5, 1.5 Hz, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 6.45 (td, *J* = 3.0, 2.5, 1.5 Hz, 1H), 6.39-6.33 (m, 1H), 6.18 (s, 1H), 2.61 (s, 3H), 2.58 (s, 3H) and 1.69 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 197.4, 164.1, 149.0, 136.6, 136.0, 135.9, 134.3, 132.8, 132.0, 128.3, 127.9, 124.2, 121.2, 120.9, 120.4, 120.2, 112.7, 110.3, 96.3, 87.0, 26.6, 15.4 and 14.0 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{25}H_{20}BF_2N_3O$ 427.1667, Found: 427.1673.

3ae: yield: 73%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.38 (br, 1H), 7.56 (d, *J* = 2.5 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.94 (dd, *J* = 4.0, 2.0 Hz, 1H), 6.56 (d, *J* = 2.5 Hz, 1H), 6.42 (dt, *J* = 4.0, 2.0 Hz, 1H), 6.33 (dt, *J* = 4.0, 2.5 Hz, 1H), 6.16 (s, 1H), 2.60 (s, 3H) and 1.67 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 163.7, 148.8, 136.8, 135.9, 134.1, 133.4, 132.9, 131.3, 124.1, 122.4, 122.2, 121.2, 120.9, 120.7, 120.1, 112.6, 110.2, 96.2, 84.8, 15.4 and 14.0 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{23}H_{17}BF_2N_3Br$ 463.0667, Found: 463.0662.

3af: yield: 71%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.39 (br, 1H), 7.57-7.55 (m, 1H), 7.23 (br, 4H), 6.94 (td, *J* = 3.0, 1.5 Hz, 1H), 6.56 (d, *J* = 2.5 Hz, 1H), 6.42 (ddd, *J* = 4.0, 2.5, 1.5 Hz, 1H), 6.33 (dt, *J* = 4.0, 2.5 Hz, 1H), 6.15 (s, 1H), 2.60 (s, 3H) and 1.67 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 163.7, 148.8, 136.8, 135.9, 134.1, 133.4, 132.9, 131.3, 124.1, 122.4, 122.2, 121.2, 120.9, 120.7, 120.1, 112.6, 110.2, 96.2, 84.8, 15.4 and 14.0 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{23}H_{17}BClF_2N_3$ 419.1172, Found: 419.1185.

3ag: yield: 41%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.32 (br, 1H), 7.56 (br, 1H), 7.24 (d, *J* =

5.0 Hz, 1H), 7.11 (d, J = 3.5 Hz, 1H), 7.04 (dd, J = 4.5, 3.0 Hz, 1H), 6.94 (dd, J = 5.0, 3.5 Hz, 1H), 6.55 (d, J = 2.5 Hz, 1H), 6.45-6.39 (m, 2H), 6.17 (s, 1H), 2.61 (s, 3H) and 1.72 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 163.3, 148.6, 137.1, 135.8, 135.3, 134.4, 134.1, 133.0, 129.4, 127.9, 127.0, 124.0, 123.6, 121.2, 120.4, 112.7, 110.5, 90.6, 87.6, 15.4 and 14.2 ppm; HRMS (MALDI-TOF) m/z: $[M-F]^+$ Calcd for $C_{21}H_{16}BFN_3S$ 372.1142, Found: 372.1138.

3ah: yield: 71%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.27 (br, 1H), 7.55 (br, 1H), 6.94 (td, J = 3.0, 1.5 Hz, 1H), 6.54 (d, J = 2.5 Hz, 1H), 6.38 (td, J = 3.0, 2.5, 1.5 Hz, 1H), 6.26 (dt, J = 4.0, 2.5 Hz, 1H), 6.15 (s, 1H), 2.59 (s, 3H), 1.66 (s, 3H) and 1.02 (br, 21H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 163.0, 148.6, 136.6, 135.7, 133.9, 133.3, 123.8, 122.4, 121.7, 121.3, 120.2, 113.1, 110.3, 100.3, 100.1, 18.8, 15.3, 14.1 and 11.4 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{26}H_{34}BF_2N_3Si$ 465.2583, Found: 465.2588.

3ai: yield: 75%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.26 (br, 1H), 7.50 (br, 1H), 6.96-6.94 (m, 1H), 6.51 (d, J = 2.5 Hz, 1H), 6.36-6.34 (m, 1H), 6.29-6.26 (m, 1H), 6.15 (s, 1H), 2.59 (s, 3H), 1.70 (s, 3H), 0.93 (t, J = 8.0 Hz, 9H) and 0.55 (d, J = 8.0 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 163.2, 148.7, 136.6, 135.7, 134.5, 133.1, 123.9, 121.7, 121.3, 119.9, 112.7, 110.0, 100.5, 98.9, 15.3, 14.2, 7.5 and 4.5 ppm; HRMS (MALDI-TOF) m/z: $[M-F]^+$ Calcd for $C_{23}H_{28}BF_2N_3Si$ 423.2114, Found: 423.2122.

3aj: yield: 46%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.24 (br, 1H), 7.53 (d, J = 2.5 Hz, 1H), 6.96 (td, J = 3.0, 1.5 Hz, 1H), 6.42 (d, J = 2.5 Hz, 1H), 6.34 (td, J = 3.0, 2.5, 1.5 Hz, 1H), 6.32-6.27 (m, 1H), 6.14 (s, 1H), 2.59 (s, 3H), 2.16 (t, J = 7.0 Hz, 2H), 1.70 (s, 3H), 1.47-1.35 (m, 2H), 1.28 (dt, J = 7.0, 3.0 Hz, 4H) and 0.89 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 162.3, 148.2, 137.4, 135.4, 134.2, 133.3, 123.6, 123.2, 121.4, 120.5, 119.8, 112.3, 109.9, 99.8, 74.1, 31.3, 28.4, 22.3, 20.2, 15.3, 14.2 and 14.1.ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{22}H_{24}BF_2N_3$ 379.2031, Found: 379.2045.

3ba: yield: 22%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 9.21 (br, 1H), 7.89 (br, 1H), 7.78 (br, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.25 (m, 3H), 7.22–7.19 (m, 1H), 6.97 (d, J = 3.5 Hz, 1H), 6.72 (d, J = 2.0 Hz, 1H), 6.61-6.57 (m, 1H), 6.54-6.52 (m, 1H) and 1.31 (s, 9H) ppm; UV/vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 520 (60424), 447 (16990) nm; HRMS (MALDI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}BF_2N_3$ 414.1952, Found: 414.1947.

3bb: yield: 24%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 9.20 (br, 1H), 7.90 (br, 1H), 7.78 (d, J =

2.5 Hz, 1H), 7.33-7.28 (m, 5H), 7.25 (br, 1H), 7.20 (td, *J* = 2.5, 1.5 Hz, 1H), 6.97 (ddd, *J* = 4.0, 2.5, 1.5 Hz, 1H), 6.72 (d, *J* = 2.5 Hz, 1H), 6.59 (dd, *J* = 4.5, 2.0 Hz, 1H) and 6.52 (dt, *J* = 4.0, 2.5 Hz, 1H) ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{21}H_{14}BF_2N_3$ 357.1249, Found: 357.1251.

3bd: yield: 8%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 9.09 (br, 1H), 7.94 (br, 1H), 7.90-7.85 (m, 2H), 7.79 (d, *J* = 2.5 Hz, 1H), 7.40-7.37 (m, 2H), 7.29 (d, *J* = 4.0 Hz, 1H), 7.20 (td, *J* = 3.0, 1.5 Hz, 1H), 6.98 (ddd, *J* = 4.0, 2.5, 1.5 Hz, 1H), 6.79-6.73 (m, 1H), 6.66-6.61 (m, 1H), 6.53 (dt, *J* = 4.0, 2.5 Hz, 1H) and 2.60 (s, 3H) ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{23}H_{16}BF_2N_3O$ 399.1354, Found: 399.1364.

3bg: yield: 20%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 9.12 (br, 1H), 7.90 (br, 1H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.30 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.26-7.24 (m, 2H), 7.15 (dd, *J* = 4.0, 1.5 Hz, 1H), 6.97 (dd, *J* = 5.0, 4.0 Hz, 1H), 6.94 (ddd, *J* = 4.0, 2.5, 1.5 Hz, 1H), 6.70 (d, *J* = 2.5 Hz, 1H), 6.59 (dd, *J* = 4.0, 2.0 Hz, 1H) and 6.54 (dt, *J* = 4.0, 2.5 Hz, 1H) ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{19}H_{12}BF_2N_3S$ 363.0813, Found: 363.0840.

3bh: yield: 23%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 9.31 (br, 1H), 7.86 (br, 1H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.24 (d, *J* = 4.5 Hz, 1H), 7.20 (dd, *J* = 4.5 Hz, 3.0 Hz, 1H), 6.96-6.95 (m, 1H), 6.71 (d, *J* = 2.5 Hz, 1H), 6.57 (dd, *J* = 4.5, 2.0 Hz, 1H), 6.47-6.44 (m, 1H) and 1.04-1.03 (br, 21H) ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{24}H_{30}BF_2N_3Si$ 437.2270, Found: 437.2281.

3bj: yield: 15%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 9.10 (br, 1H), 7.86 (br, 1H), 7.75 (br, 1H), 7.23 (d, *J* = 4.5 Hz, 1H), 7.17 (dd, *J* = 4.5, 3.0 Hz, 1H), 6.90-6.84 (td, *J* = 4.0, 1.5 Hz, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 6.56 (dd, *J* = 4.5, 2.0 Hz, 1H), 6.46 (dd, *J* = 4.5, 3.0 Hz, 1H), 2.27 (t, *J* = 7.0 Hz, 2H), 1.45-1.42 (m, 2H), 1.28-1.26 (m, 4H) and 0.89 (t, *J* = 7.0 Hz, 3H) ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{20}H_{20}BF_2N_3$ 351.1718, Found: 351.1710.

3ca: yield: 38%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.70 (br, 1H), 7.98 (br, 1H), 7.86 (d, *J* = 2.5 Hz, 1H), 7.78-7.77 (m, 1H), 7.35-7.34 (m, 1H), 7.2 -7.26 (m, 2H), 7.25-7.24(m, 1H) 7.05 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 2.5 Hz, 1H), 6.61 (dd, *J* = 4.5, 2.0 Hz, 1H), 6.34 (d, *J* = 8.5 Hz, 2H) and 1.23 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 152.1, 145.0, 142.0, 137.7, 136.0, 135.9, 133.3, 132.7, 131.5, 131.3, 128.9, 128.1, 125.8, 125.0, 124.9, 122.3, 121.9, 121.1, 119.3, 118.8, 112.2, 109.5, 101.4, 83.1, 34.7 and 31.0 ppm; HRMS (MALDI-TOF) m/z: $[M-F]^+$ Calcd for $C_{29}H_{24}BFN_3$ 444.2047, Found: 444.2047.

2.2. Synthesis of BODIPY dimer 3ak and trimer 3al

A mixture of **1a** (0.1 mmol), 1,4-bis(bromoethynyl)benzene **2k** (0.06 mmol), $[Cp^*RhCl_2]_2$ (0.006 mmol), Na_2CO_3 (0.20 mmol), AgOAc (0.12 mmol) in *o*-xylene was stirred at 70 ℃ for about 16 h. After cooling to room temperature, the mixture was passed through a short silica-gel column (CH_2Cl_2 as an eluent). After removal of solvents in *vacuo*, the crude product was purified by silica-gel (CH_2Cl_2/*n*-hexane as an eluent) and recrystallized from CH_2Cl_2/*n*-hexane to afford BODIPY dimer **3ak**.

3ak: red solids, yield: 55%, ^{1}H NMR (500 MHz, Acetone-d_6, 298 K) δ = 10.57 (br, 2H), 7.61 (br, 2H), 7.34 (br, 4H), 7.21 (td, J = 3.0, 1.5 Hz, 2H), 6.64 (d, J = 2.5 Hz, 2H), 6.48-6.45 (m, 2H), 6.42 (s, 2H), 6.40 (dt, J = 4.0, 2.5 Hz, 2H), 2.61 (s, 6H) and 1.73 (s, 6H) ppm; ^{13}C NMR (126 MHz, Acetone-d_6, 298 K) δ = 163.5, 149.0, 136.3, 135.9, 134.1, 131.6, 124.0, 123.2, 121.1, 120.7, 120.4, 112.1, 109.5, 96.7, 86.0, 14.3 and 13.1 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{40}H_{30}B_2F_4N_6$ 692.2654, Found: 692.2657.

A mixture of **1a** (0.1 mmol), 1,3,5-tris(bromoethynyl)benzene **2l** (0.04 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), Na_2CO_3 (0.30 mmol), AgOAc (0.18 mmol) in *o*-xylene was stirred at 70 ℃ for about 16 h. After cooling to room temperature, the mixture was passed through a short silica-gel column (CH_2Cl_2 as an eluent). After removal of solvents in *vacuo*, the crude product was purified by silica-gel (CH_2Cl_2/*n*-hexane as an eluent) and recrystallized from CH_2Cl_2/*n*-hexane to afford BODIPY trimer **3al**.

3al: purple solids, yield: 42%, ^{1}H NMR (500 MHz, Acetone-d_6, 298 K) δ = 10.60 (br, 3H), 7.59-7.58 (m, 3H), 7.25 (s, 3H), 7.19 (td, J = 3.0, 1.5 Hz, 3H), 6.71 (d, J = 2.5 Hz, 3H), 6.52-6.50 (m, 3H), 6.41 (s, 3H), 6.40-6.35 (m, 3H), 2.60 (s, 9H) and 1.72 (s, 9H) ppm; ^{13}C NMR (126 MHz, Acetone-d_6, 298 K) δ = 163.8, 149.2, 136.1, 134.2, 124.1, 123.8, 121.1, 120.8, 120.5, 112.1, 109.6, 94.9, 84.9, 54.6, 14.4 and 13.1 ppm; HRMS (MALDI-TOF) m/z: $[M-F]^+$ Calcd for $C_{57}H_{42}B_3F_5N_9$ 980.3762, Found: 980.3762.

2.3. Synthesis of di-alkynylated BODIPYs 4ba-4bj and 4ca-4ea

A mixture of **1** (0.1 mmol), alkyne (0.3 mmol), $[Cp^*RhCl_2]_2$ (0.01 mmol), Na_2CO_3 (0.40 mmol), AgOAc (0.12 mmol) in *o*-xylene was stirred at 70 ℃ for about 16 h. After cooling to room temperature, the mixture was passed through a short silica-gel column (CH_2Cl_2 as an eluent). After removal of solvents in *vacuo*, the crude product was purified by silica-gel (CH_2Cl_2/*n*-hexane as an

eluent) and recrystallized from CH_2Cl_2/*n*-hexane to afford **4** as purple solids.

4ba: yield: 72%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.99 (br, 1H), 7.80 (d, J = 2.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 8H), 7.18-7.17 (m, 1H), 7.11-7.09 (m, 1H), 6.70 (d, J = 2.5 Hz, 2H), 6.52 (dd, J = 6.0 Hz, 3.0 Hz, 1H) and 1.31 (s, 18H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 152.3, 141.6, 135.6, 134.2, 131.6, 126.4, 125.2, 124.1, 122.9, 121.6, 119.7, 119.2, 111.6, 100.1, 84.0, 34.9 and 31.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 453 (14450), 545 (46652) nm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{37}H_{34}BF_2N_3$ 569.2814, Found: 569.2810.

4bb: yield: 61%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.96 (br, 1H), 7.82 (d, J = 2.0 Hz, 2H), 7.37-7.35 (m, 4H), 7.32-7.27 (m, 6H), 7.16 (td, J = 3.0, 1.5 Hz, 1H), 7.11 (ddd, J = 4.0, 2.5, 1.5 Hz, 1H), 6.73 (d, J = 2.5 Hz, 2H) and 6.49 (dt, J = 4.0, 2.5 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 141.7, 135.8, 134.3, 131.8, 128.8, 128.2, 126.1, 124.1, 123.1, 122.7, 121.6, 119.1, 111.6, 99.7 and 84.3 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{29}H_{18}BF_2N_3$ 457.1562, Found: 457.1558.

4bc: yield: 62%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.95 (br, 1H), 7.81 (d, J = 2.5 Hz, 2H), 7.26-7.25 (m, 4H), 7.15 (td, J = 3.0, 1.5 Hz, 1H), 7.12-7.08 (m, 5H), 6.71 (d, J = 2.5 Hz, 2H), 6.48 (dt, J = 4.0, 2.5 Hz, 1H) and 2.35 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 141.6, 139.2, 134.2, 131.8, 129.0, 126.3, 124.0, 122.9, 121.6, 119.7, 119.1, 111.5, 100.1, 83.9 and 21.6 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{31}H_{22}BF_2N_3$ 485.1875, Found: 485.1867.

4bd: yield: 25%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.89 (s, 1H), 7.88 (d, J = 8.5 Hz, 4H), 7.86 (d, J = 2.0 Hz, 2H), 7.42 (d, J = 8.5 Hz, 4H), 7.15 (td, J = 3.0, 1.5 Hz, 1H), 7.09 (ddd, J = 4.0, 2.5, 1.5 Hz, 1H), 6.78 (d, J = 2.0 Hz, 2H), 6.47 (dt, J = 3.0, 2.5 Hz, 1H) and 2.60 (s, 6H) ppm; ^{3}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 197.2, 142.3, 136.6, 136.0, 134.7, 132.0, 128.2, 127.6, 125.8, 124.1, 123.6, 121.6, 118.9, 111.7, 98.8, 87.1 and 26.7 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{33}H_{22}BF_2N_3O_2$ 541.1773, Found: 541.1771.

4be: yield: 76%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.84 (br, 1H), 7.83 (br, 2H), 7.43 (d, J = 8.5 Hz, 4H), 7.20 (d, J = 8.5 Hz, 4H), 7.12 (td, J = 3.0, 1.5 Hz, 1H), 7.05 (tt, J = 2.5, 1.5 Hz, 1H), 6.73 (d, J = 2.5 Hz, 2H) and 6.44 (dt, J = 4.0, 2.5 Hz, 1H) ppm;^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 142.2, 135.7, 134.5, 133.2, 131.6, 126.0, 123.8, 123.3, 123.27, 121.7, 121.5, 118.6, 111.5, 98.7 and 85.3 ppm; HRMS (MALDI-TOF) m/z: $[M-F]^+$ Calcd for $C_{29}H_{16}BBr_2FN_3$ 593.9788, Found: 593.9783.

4bf: yield: 72%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.86 (br, 1H), 7.83 (d, *J* = 2.0 Hz, 2H), 7.27 - 7.26 (m, 8H), 7.13 - 7.11 (m, 1H), 7.06 - 7.04 (m, 1H), 6.73 (d, *J* = 2.5 Hz, 2H) and 6.45 (dd, *J* = 6.0, 2.5 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 142.0, 135.6, 135.0, 134.4, 128.6, 126.0, 123.7, 123.22, 123.2, 121.4, 121.1, 118.5, 111.4, 98.6 and 85.0 ppm; HRMS (MALDI-TOF) m/z: $[M-F]^+$ Calcd for $C_{29}H_{16}BCl_2FN_3$ 506.0798, Found: 506.0790.

4bg: yield: 55%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.83 (br, 1H), 7.81 (d, *J* = 2.5 Hz, 2H), 7.31 (d, *J* = 5.0 Hz, 2H), 7.25-7.23 (m, 1H), 7.19 (d, *J* = 4.0 Hz, 2H), 7.01 (dt, *J* = 4.0, 2.0 Hz, 1H), 6.98 (dd, *J* = 5.0, 4.0 Hz, 2H), 6.70 (d, *J* = 2.5 Hz, 2H) and 6.59-6.57 (m, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 141.9, 135.4, 134.6, 133.5, 128.7, 127.3, 125.9, 124.0, 122.9, 122.4, 121.4, 118.4, 111.9, 93.2 and 88.4 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{25}H_{14}BF_2N_3S_2$ 469.0690, Found: 469.0682.

4bh: yield: 79%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 10.26 (br, 1H), 7.67 (d, *J* = 2.0 Hz, 2H), 7.31 (ddd, *J* = 4.0, 2.5, 1.5 Hz, 1H), 7.22 (td, *J* = 2.5, 1.5 Hz, 1H), 6.68 (d, *J* = 2.0 Hz, 2H), 6.38 (dt, *J* = 4.0, 2.5 Hz, 1H) and 1.17-1.05 (m, 42H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 138.7, 137.0, 133.4, 128.1, 127.0, 125.0, 123.7, 123.1, 113.1, 101.9, 100.9, 18.6 and 11.4 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{35}H_{50}BF_2N_3Si_2$ 617.3604, Found: 617.3601.

4bi: yield: 79%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 9.49 (br, 1H), 7.71 (br, 2H), 7.19 (br, 1H), 7.15 (br, 1H), 6.88 (br, 2H), 6.42-6.35 (m, 1H), 0.99 (t, *J* = 8.0 Hz, 18H) and 0.63 (q, *J* = 8.0 Hz, 12H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 140.0, 136.5, 134.0, 126.0, 124.4, 123.7, 123.4, 123.39, 122.4, 112.1, 102.4, 100.2, 7.4 and 4.3 ppm; HRMS (MALDI-TOF) m/z: $[M-F]^+$ Calcd for $C_{29}H_{38}BFN_3Si_2$ 514.2681, Found: 514.2688.

4bj: yield: 43%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.75 (br, 1H), 7.74 (d, *J* = 2.0 Hz, 2H), 7.07 (td, *J* = 3.5, 1.5 Hz, 1H), 6.89 (td, *J* = 2.5, 1.5 Hz, 1H), 6.55 (d, *J* = 2.0 Hz, 2H), 6.34 (dt, *J* = 3.5, 2.5 Hz, 1H), 2.23 (t, *J* = 7.0 Hz, 4H), 1.43 (p, *J* = 7.0 Hz, 4H), 1.31-1.26 (m, 8H) and 0.90 (t, *J* = 7.0 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 141.4, 135.8, 134.2, 127.1, 122.9, 122.5, 121.3, 118.2, 110.5, 101.9, 75.0, 31.1, 28.0, 22.2, 20.1 and 14.0 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{27}H_{30}BF_2N_3$ 445.2501, Found: 445.249.

4ca: yield: 14%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.40 (br, 1H), 7.94 (br, 2H), 7.73 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.40 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.28 (dd, 7.5, 1.5 Hz, 1H), 7.25 (dd, 7.5, 1.5 Hz, 1H), 7.03 (dd, *J* = 2.0, 1.0 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 4H), 6.70 (d, *J* = 2.5 Hz, 2H), 6.25 (d, *J* =

8.5 Hz, 4H) and 1.19 (s, 18H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 152.2, 145.1, 142.1, 137.8, 132.7, 131.4, 129.0, 128.2, 125.0, 124.96, 122.3, 122.0, 121.2, 119.4, 118.9, 112.3, 109.6, 101.4, 83.7, 34.8, and 31.1 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{41}H_{36}BF_2N_3$ 619.2970, Found: 619.2971.

4da: yield: 52%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.55 (br, 1H), 7.33 (br, 8H), 7.09 (td, *J* = 3.0, 1.5 Hz, 1H), 6.78 (ddd, *J* = 4.0, 2.5, 1.5 Hz, 1H), 6.54-6.45 (m, 3H), 2.64 (s, 6H) and 1.34 (s, 18H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 156.2, 152.0, 135.0, 131.9, 131.4, 126.1, 125.1, 124.0, 121.2, 121.1, 120.0, 115.5, 110.7, 100.0, 83.3, 34.9, 31.2 and 14.8 ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{39}H_{38}BF_2N_3$ 597.3127, Found: 597.3149.

4ea: yield: 66%,^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 9.03 (br, 1H), 7.88 (d, *J* = 2.5 Hz, 1H), 7.81 (s, 1H), 7.38 (d, *J* = 7.0 Hz, 2H), 7.35 (d, *J* = 7.0 Hz, 4H), 7.27 (td, *J* = 3.0, 1.5 Hz, 1H), 7.20 (ddd, *J* = 4.0, 2.5, 1.5 Hz, 1H), 6.78 (d, *J* = 2.5 Hz, 1H), 6.60 (dt, *J* = 4.0, 2.5 Hz, 1H), 1.35 (s, 9H) and 1.348 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 152.6, 152.6, 142.7, 140.1, 135.3, 134.2, 133.46, 131.8, 131.6, 127.5, 125.3, 125.3, 124.8, 123.3, 121.5, 120.0, 119.5, 119.5, 111.8, 111.1, 103.6, 100.8, 83.9, 82.6, 34.9 and 31.1 ppm; HRMS (MALDI-TOF) m/z: $[M-F]^+$ Calcd for $C_{37}H_{33}BBrFN_3$ 628.1935, Found: 628.1929.

2.4. Synthesis of di-alkynylated BODIPYs 5 and 6

A mixture of **4ba** (0.1 mmol), alkyne **2d** (0.15 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), Na_2CO_3 (0.20 mmol), AgOAc (0.12 mmol) in *o*-xylene was stirred at 70 °C for about 12 h. After cooling to room temperature, the mixture was passed through a short silica-gel column (CH_2Cl_2 as an eluent). After removal of solvents in *vacuo*, the crude product was purified by silica-gel (CH_2Cl_2/*n*-hexane as an eluent) and recrystallized from CH_2Cl_2/*n*-hexane to afford **5**.

5: purple solids, yield: 42%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 9.00 (br, 1H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.85 (br, 1H), 7.81 (br, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.34–7.29 (m, 4H), 7.10 (m, 1H), 7.17 (td, *J* = 3.0, 1.5 Hz, 1H), 6.79 (dd, *J* = 5.0, 2.5 Hz, 2H), 6.49 (dt, *J* = 5.0, 2.5 Hz, 1H), 2.60 (s, 3H), and 1.31 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298K) δ = 197.2, 152.6, 142.7, 141.1, 136.4, 135.7, 134.4, 131.8, 131.7, 131.6, 128.2, 128.1, 127.7, 127.2, 125.3, 125.2, 124.8, 124.1, 123.3, 123.1, 121.6, 119.5, 119.1, 111.6, 100.9, 98.0, 87.4, 83.9, 34.9, 31.1, 31.1, 29.7 and 26.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 447 (12617), 545 (48440) nm; HRMS (MALDI-TOF) m/z: $[M-F]^+$ Calcd for $C_{35}H_{28}BFN_3O$ 536.2310, Found: 536.2309.

A mixture of **4ba** (0.1 mmol), alkyne **2h** (0.15 mmol), $[Cp^*RhCl_2]_2$ (0.005 mmol), Na_2CO_3 (0.20 mmol), AgOAc (0.12 mmol) in *o*-xylene was stirred at 70 ℃ for about 12 h. After cooling to room temperature, the mixture was passed through a short silica-gel column (CH_2Cl_2 as an eluent). After removal of solvents in *vacuo*, the crude product was purified by silica-gel (CH_2Cl_2/*n*-hexane as an eluent) and recrystallized from CH_2Cl_2/*n*-hexane to afford **6**.

6: purple solids, yield: 75%, ^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ = 9.27 (br, 1H), 7.78 (s, 1H), 7.74 (s, 1H), 7.3 (q, *J* = 8.5 Hz, 4H), 7.17–7.16 (m, 2H), 6.71–6.69 (m, 2H), 6.45–6.43 (m, 1H), 1.31 (s, 9H), 1.26 (s, 3H) and 1.05 (s, 18H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298K) δ = 152.3, 141.1, 140.3, 136.1, 134.0, 133.7, 131.5, 128.8, 126.0, 125.31, 125.28, 125.0, 124.4, 122.8, 122.6, 121.6, 119.7, 112.1, 102.3, 101.2, 99.4, 84.1, 34.9, 31.1, 18.6 and 11.4 ppm; HRMS (MALDI-TOF) m/z: $[M-F]^+$ Calcd for $C_{36}H_{42}BFN_3Si$ 574.3226, Found: 574.3244.

2.5. Synthesis of multi-fused compounds 7-9

Under green light, a mixture of corresponding alkynylated BODIPY (0.035 mmol), Cs_2CO_3 (0.035 mmol) in CH_2Cl_2/Acetone (volume ratio is 9:1, 10 mL) was stirred at room temperature for about 6 h. After cooling to room temperature, the mixture was passed through a short silica-gel column (CH_2Cl_2 as an eluent). After removal of solvents in *vacuo*, the crude product was purified by silica-gel (CH_2Cl_2/*n*-hexane as an eluent) and recrystallized from CH_2Cl_2/*n*-hexane to afford multi-fused compounds **7-9**.

7: orange solids, yield: 34%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.47 (br, 1H), 8.42 (s, 1H), 8.13 (d, *J* = 10.0 Hz, 1H), 8.02 (d, *J* = 5.0 Hz, 1H), 7.98-7.96 (m, 2H), 7.88 (d, *J* = 5.0 Hz, 1H), 7.69 (br, 1H), 7.32 (br, 1H), 7.11 (br, 1H), 6.54 (br, 1H) and 1.58 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 152.9, 136.4, 135.2, 133.8, 130.9, 128.7, 128.5, 127.6, 126.8, 126.6, 123.2, 122.9, 122.7, 121.7, 118.9, 118.7, 114.9, 112.3, 105.0, 35.7 and 31.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 483 (13152), 500 (17085), 534 (72227) nm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{25}H_{20}BF_2N_3$ 411.1718; Found: 411.1719.

8: orange solids, yield: 20%, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 9.65 (d, *J* = 5.0 Hz, 1H), 8.60 (br, 1H), 8.51 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.97-7.94 (m, 3H), 7.59 (d, *J* = 9.0 Hz, 2H), 7.54 (br, 1H), 7.52 (d, *J* = 9.0 Hz, 2H), 7.24 (d, *J* = 2.5 Hz, 1H), 6.80 (dd, *J* = 4.5, 2.5 Hz, 1H), 1.56 (s, 9H) and 1.42 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ = 152.7, 151.8, 137.2, 134.5, 132.2, 131.2, 130.9, 129.1, 129.0, 127.6, 127.3, 126.9, 126.1, 125.7, 124.4, 123.1, 122.8, 122.3,

120.6, 120.4, 118.8, 114.9, 113.1, 111.6, 105.2, 95.5, 88.0, 35.7, 35.0, 31.3 and 31.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 490 (18004), 555 (47092) nm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{37}H_{32}BF_2N_3$ 567.2657; Found: 567.2651;

9: orange solids, yield: 15%, ^1H NMR (500 MHz, $CDCl_3$) δ = 9.73 (br, 1H), 8.60 (br, 1H), 8.54 (s, 1H), 8.24-8.14 (m, 1H), 8.06 (s, 1H), 7.96-7.79 (m, 3H), 7.69-7.62 (m, 3H), 7.51-7.44 (m, 3H), 7.32 (br, 1H), 6.76 (s, 1H) ppm; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{29}H_{16}BF_2N_3$ 455.1405; Found: 455.1425.

3. NMR spectra

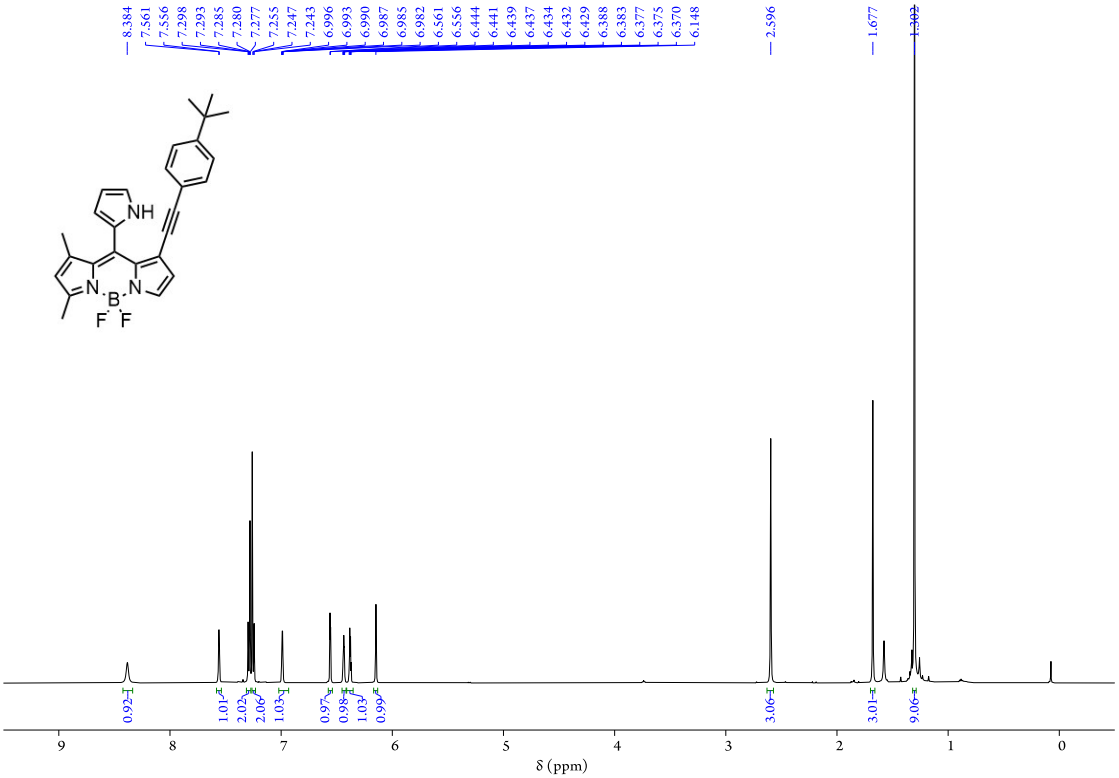


Figure S1 ^{1}H NMR spectrum of **3aa** in $CDCl_3$ at 298 K

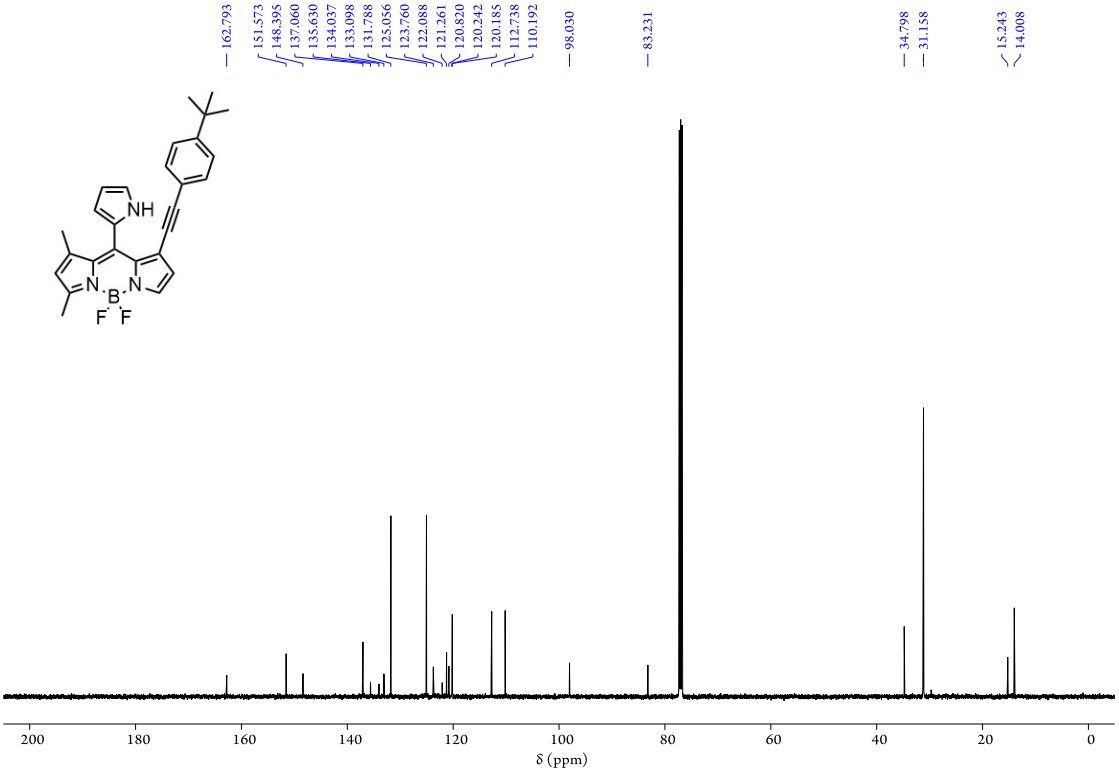


Figure S2. ^{13}C NMR spectrum of **3aa** in $CDCl_3$ at 298 K

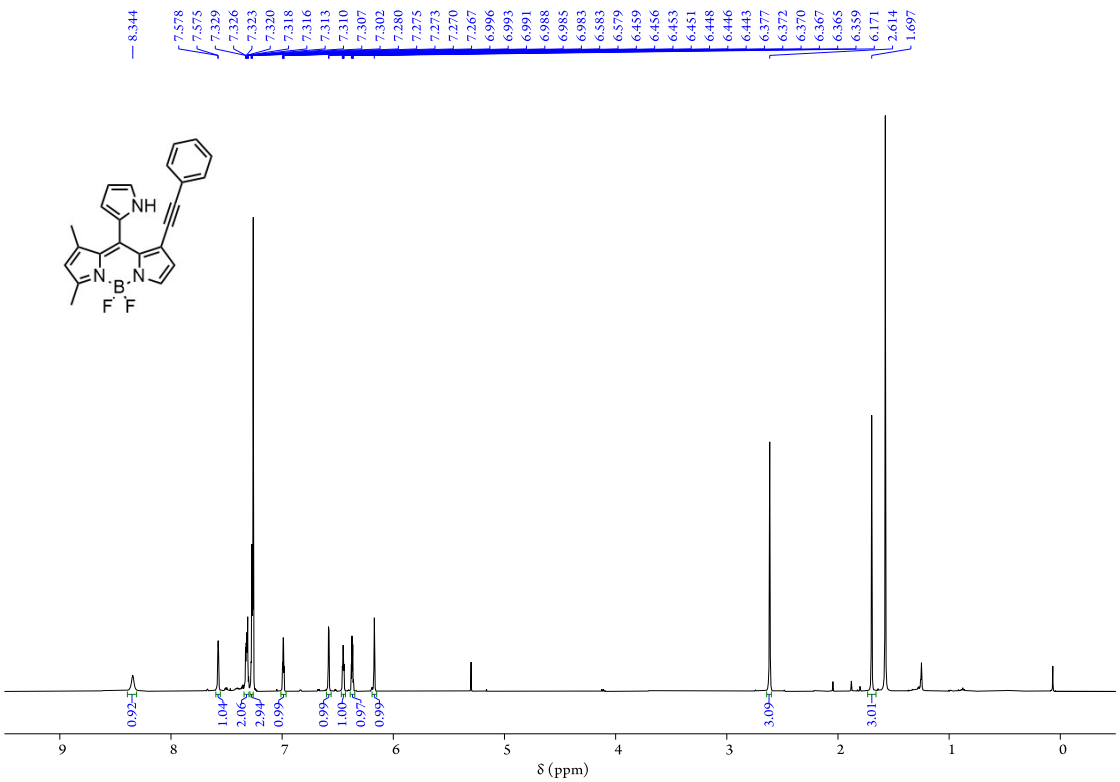


Figure S3. ^{1}H NMR spectrum of **3ab** in $CDCl_3$ at 298 K

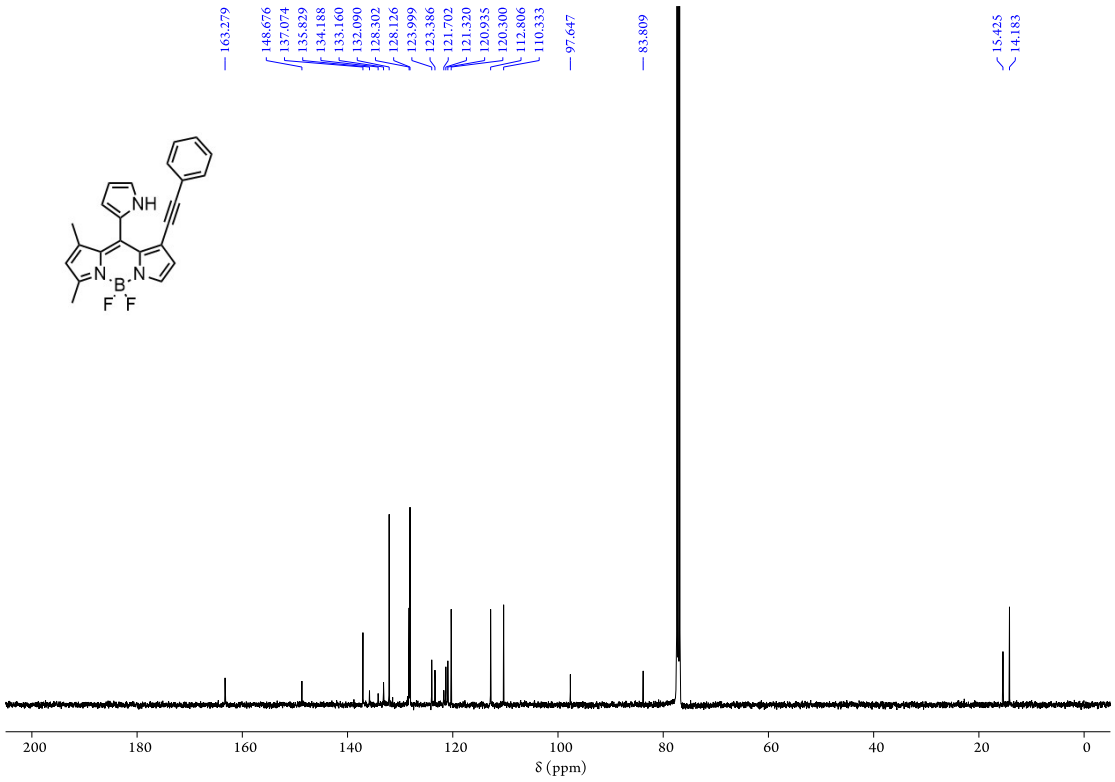


Figure S4. ^{13}C NMR spectrum of **3ab** in $CDCl_3$ at 298 K

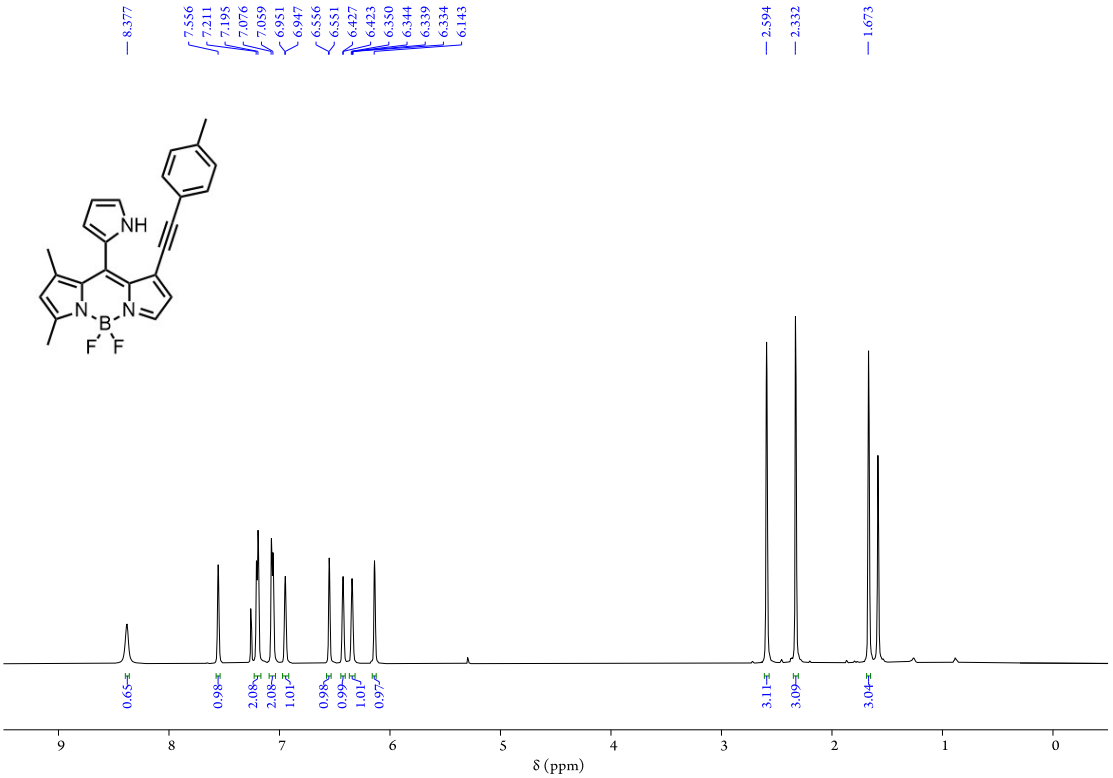


Figure S5. ^{1}H NMR spectrum of **3ac** in $CDCl_3$ at 298 K

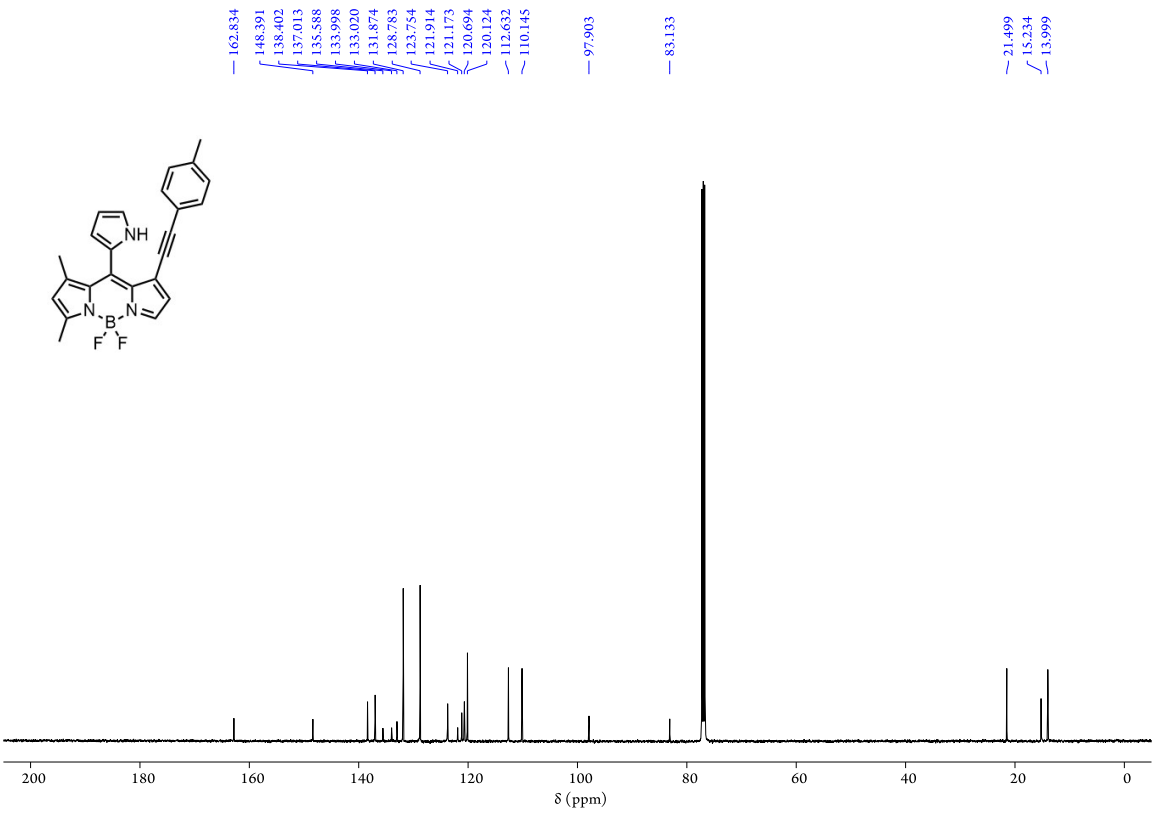


Figure S6. ^{13}C NMR spectrum of **3ac** in $CDCl_3$ at 298 K

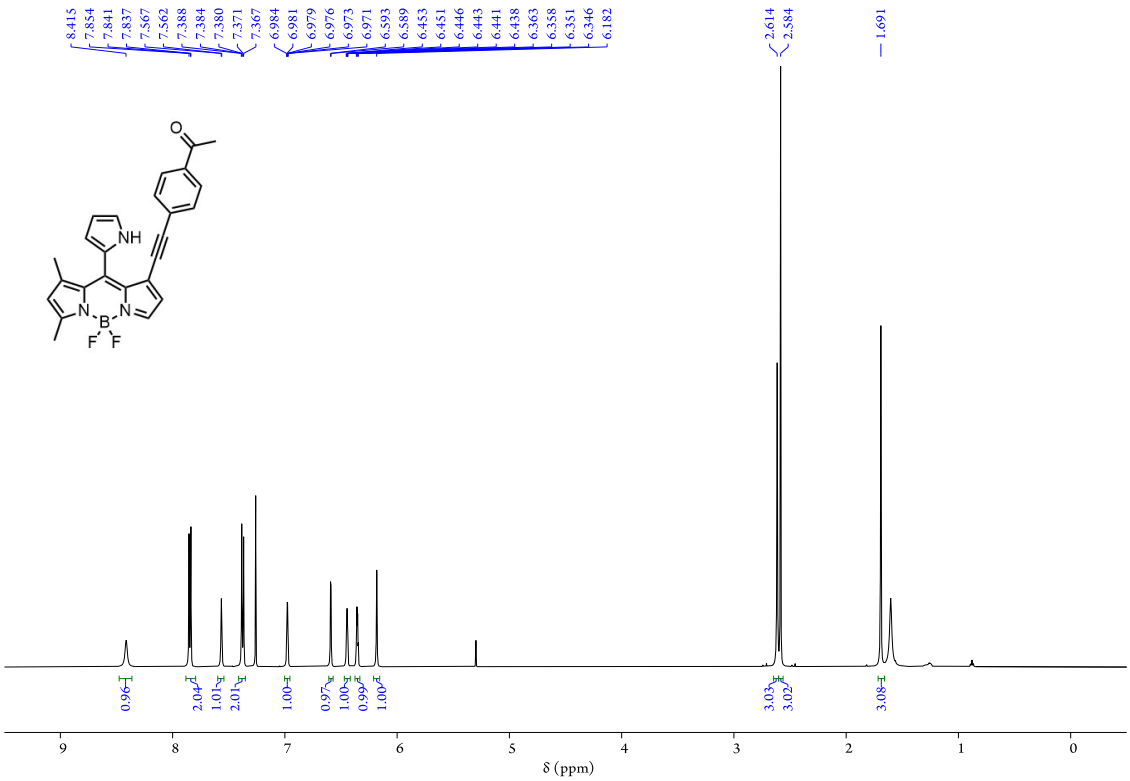


Figure S7. ^{1}H NMR spectrum of **3ad** in $CDCl_3$ at 298 K

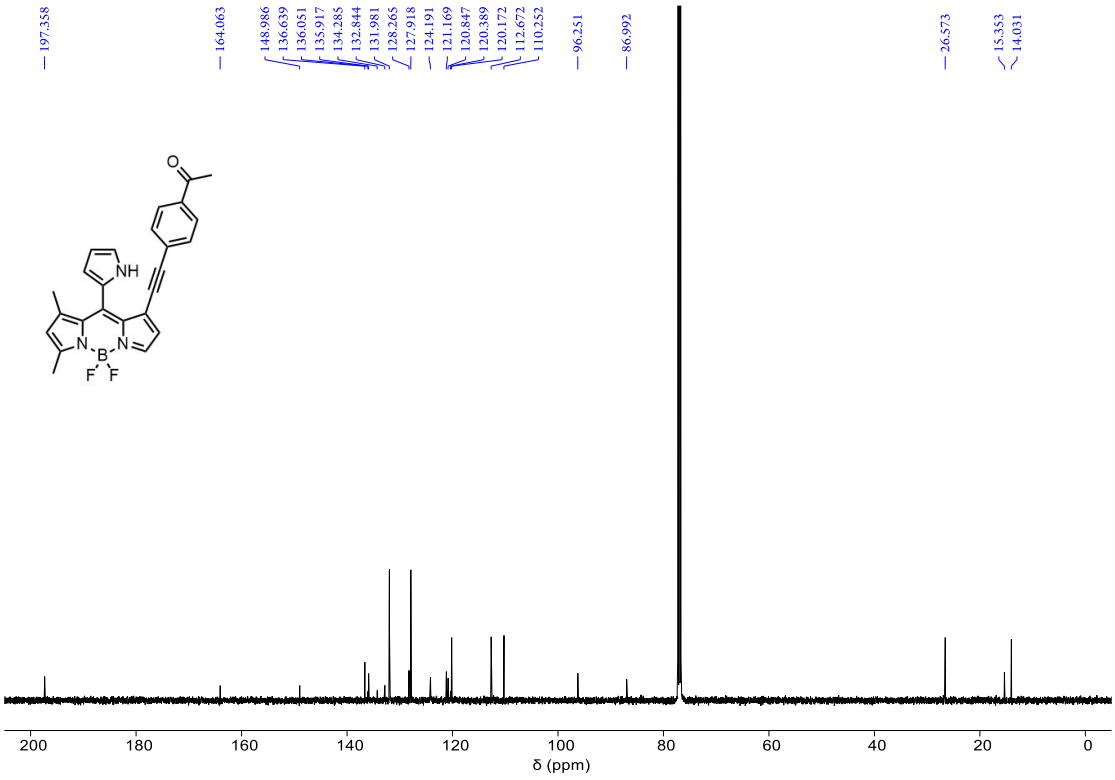


Figure S8. ^{13}C NMR spectrum of **3ad** in $CDCl_3$ at 298 K

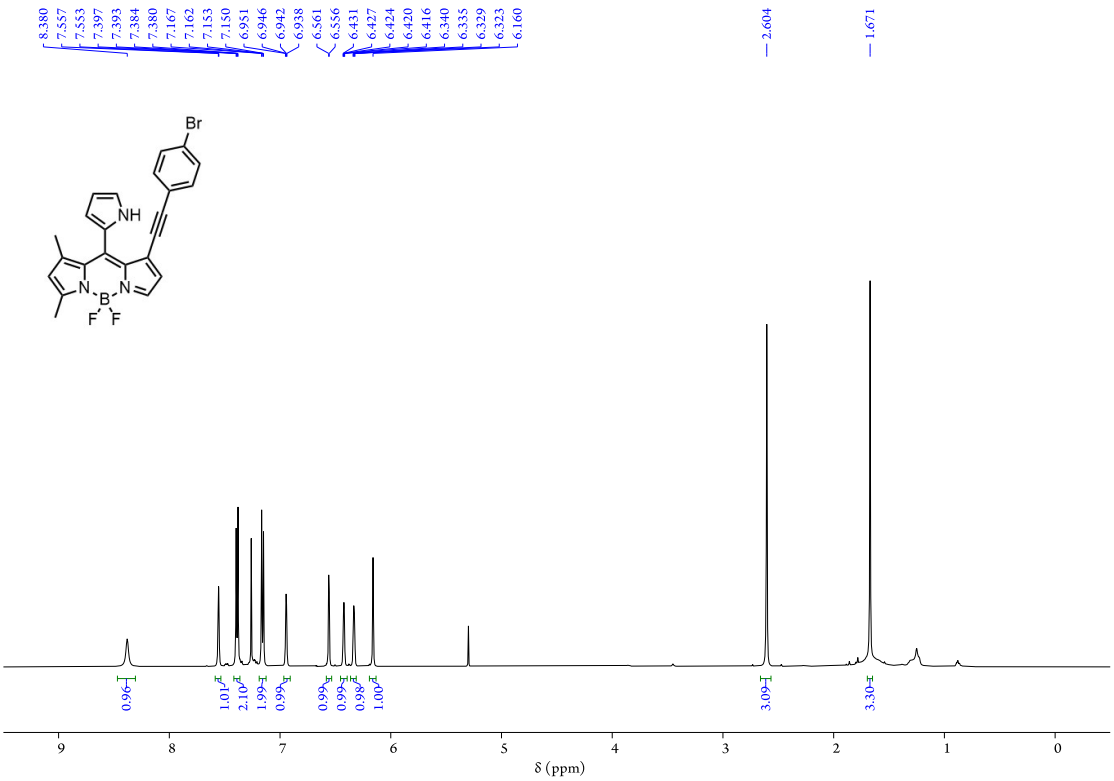


Figure S9. ^{1}H NMR spectrum of **3ae** in $CDCl_3$ at 298 K

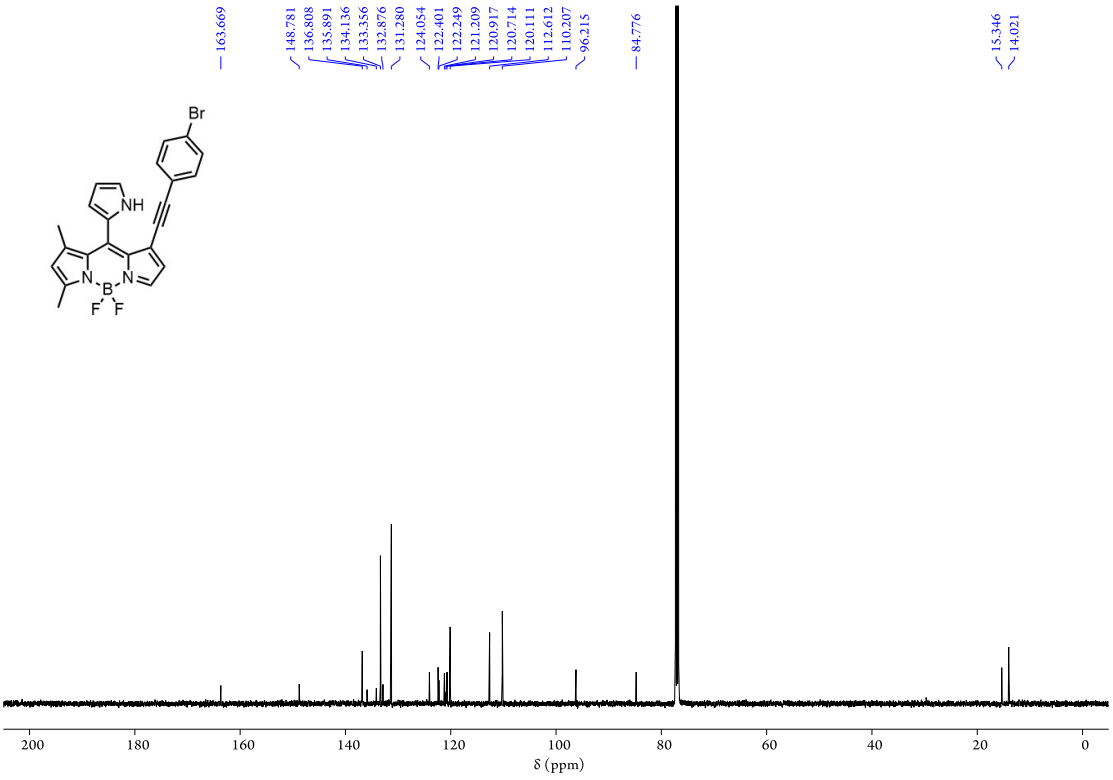


Figure S10. ^{13}C NMR spectrum of **3ae** in $CDCl_3$ at 298 K

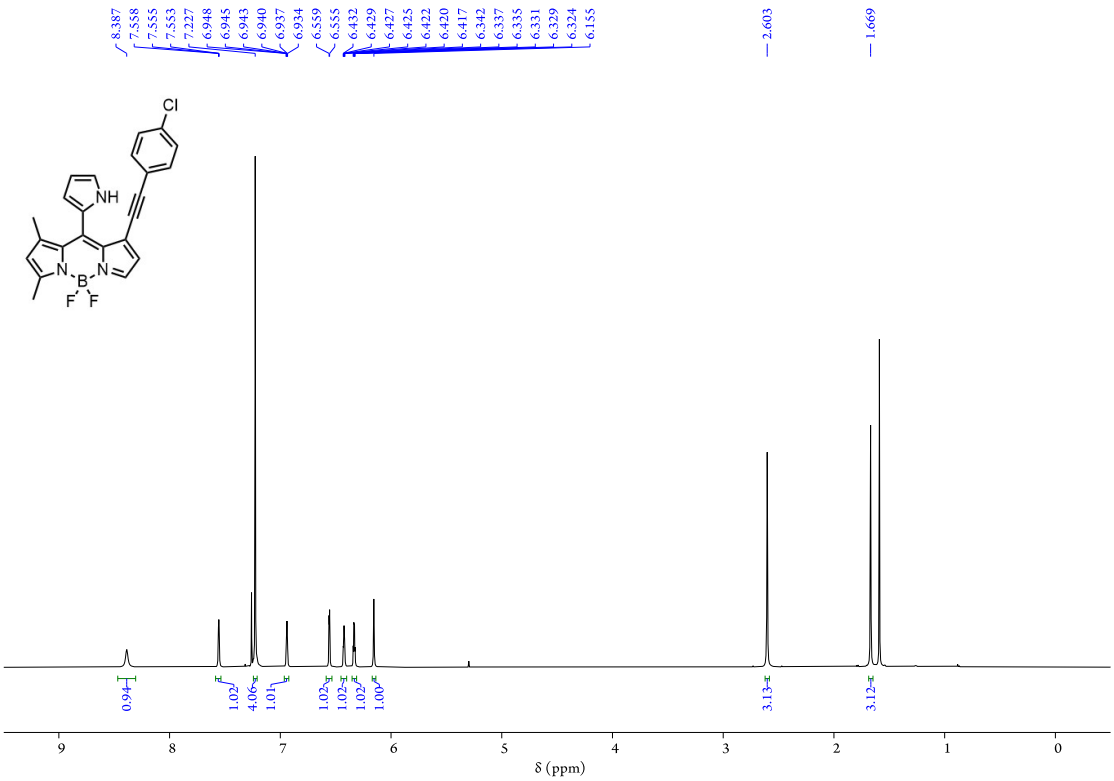


Figure S11. ^{1}H NMR spectrum of **3af** in $CDCl_3$ at 298 K

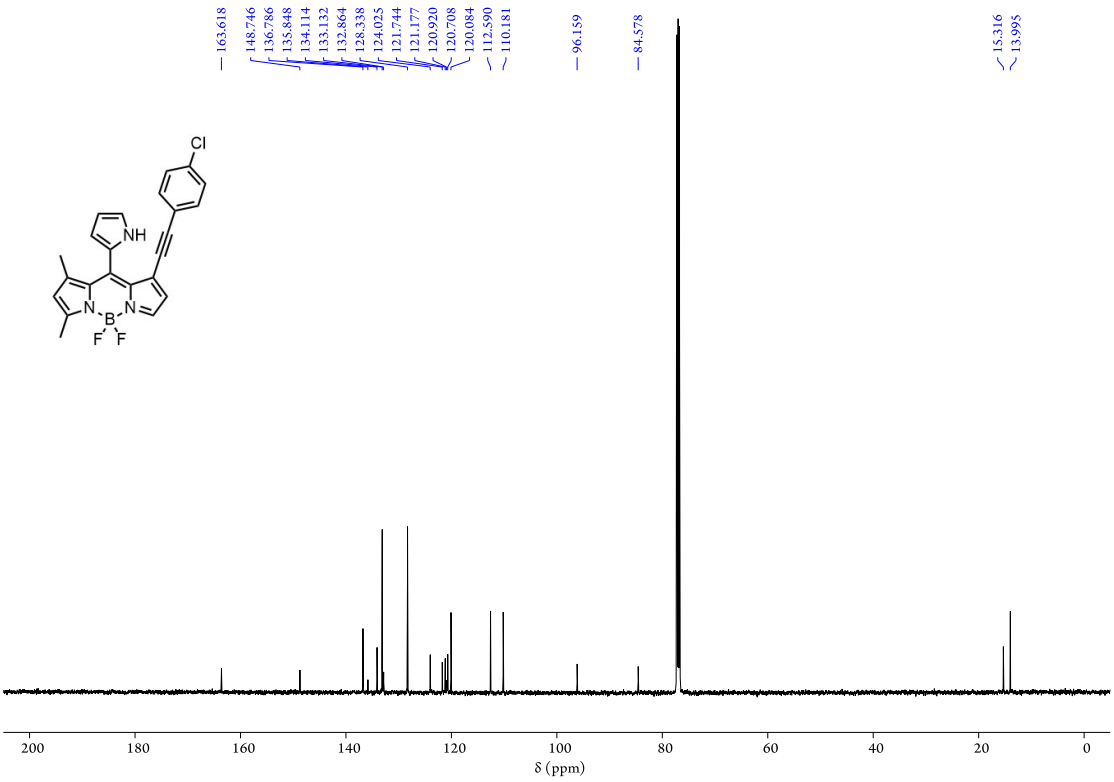


Figure S12. ^{13}C NMR spectrum of **3af** in $CDCl_3$ at 298 K

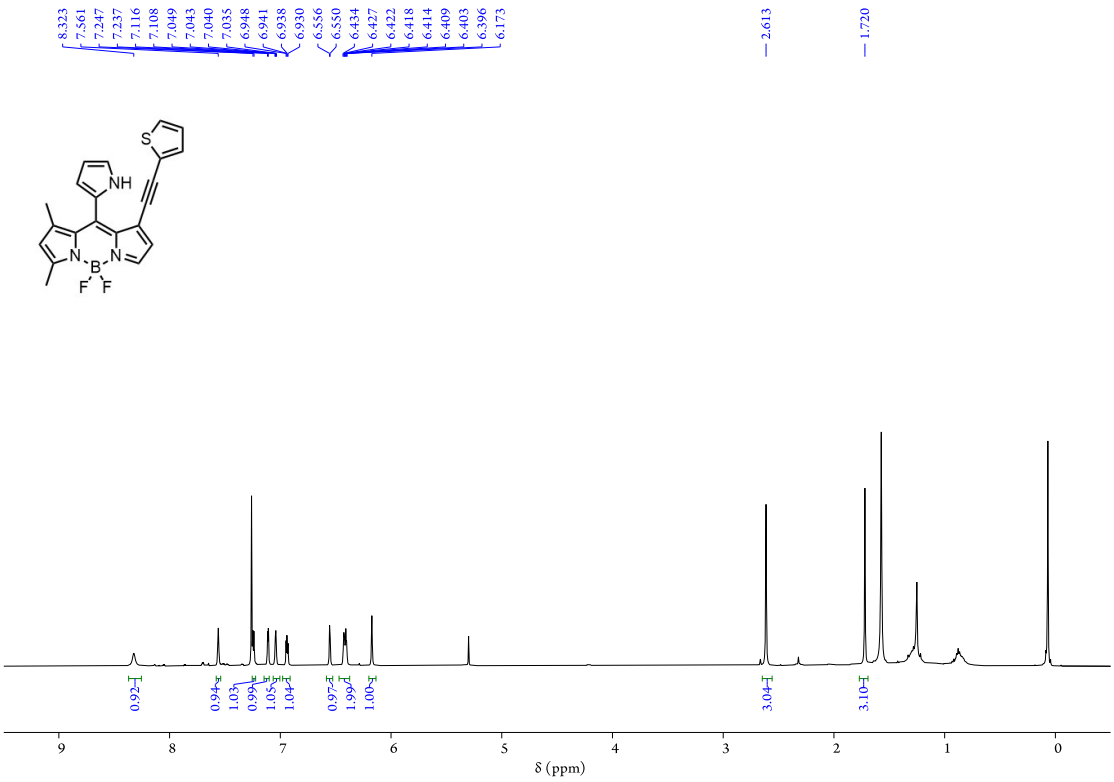


Figure S13. ^{1}H NMR spectrum of **3ag** in $CDCl_3$ at 298 K

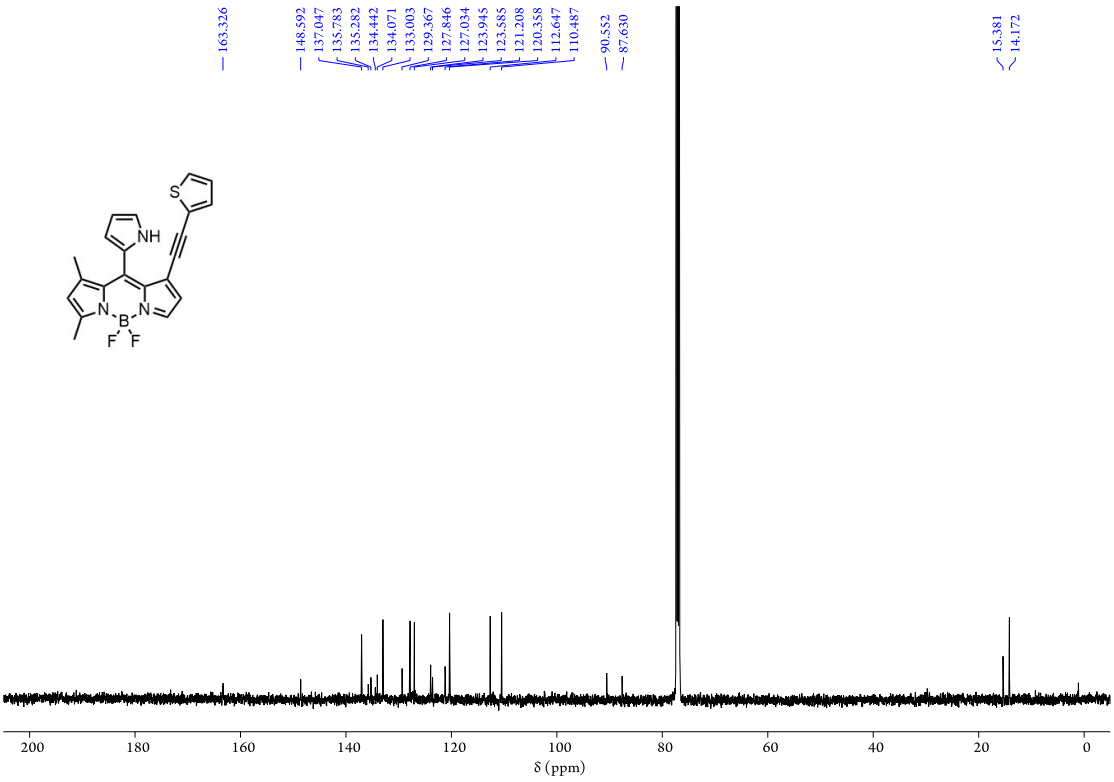


Figure S14. ^{13}C NMR spectrum of **3ag** in $CDCl_3$ at 298 K

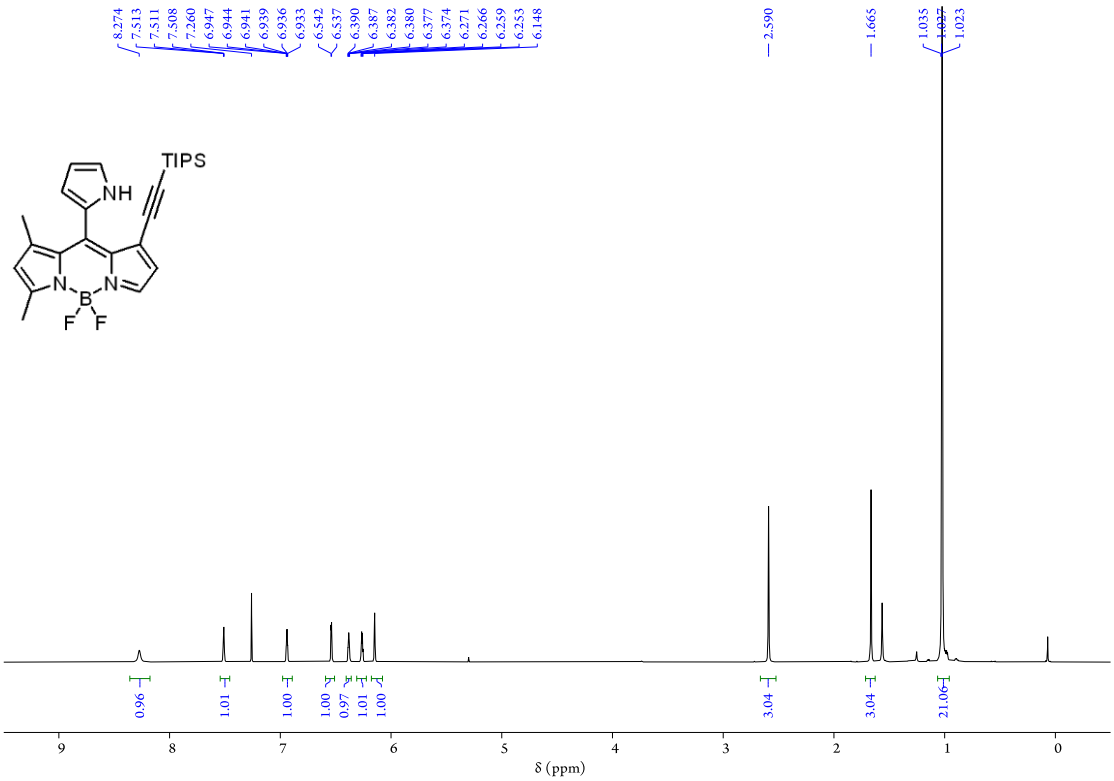


Figure S15. ^{1}H NMR spectrum of **3ah** in $CDCl_3$ at 298 K

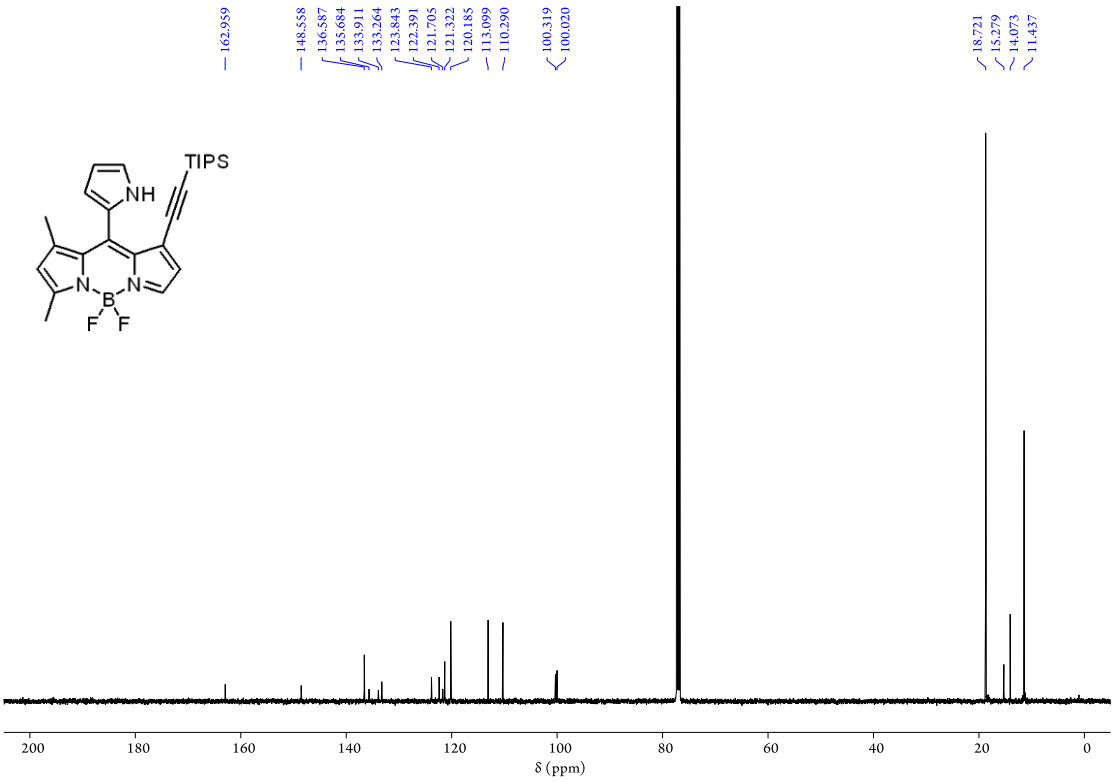


Figure S16. ^{13}C NMR spectrum of **3ah** in $CDCl_3$ at 298 K

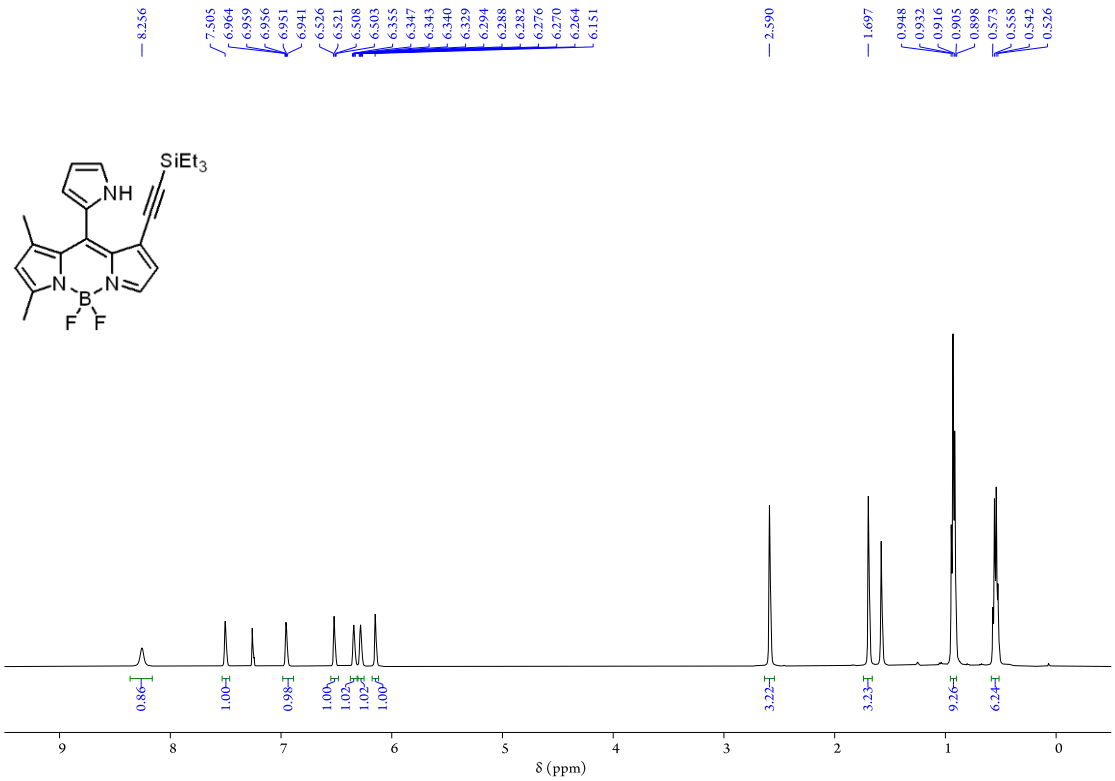


Figure S17. ^{1}H NMR spectrum of **3ai** in $CDCl_3$ at 298 K

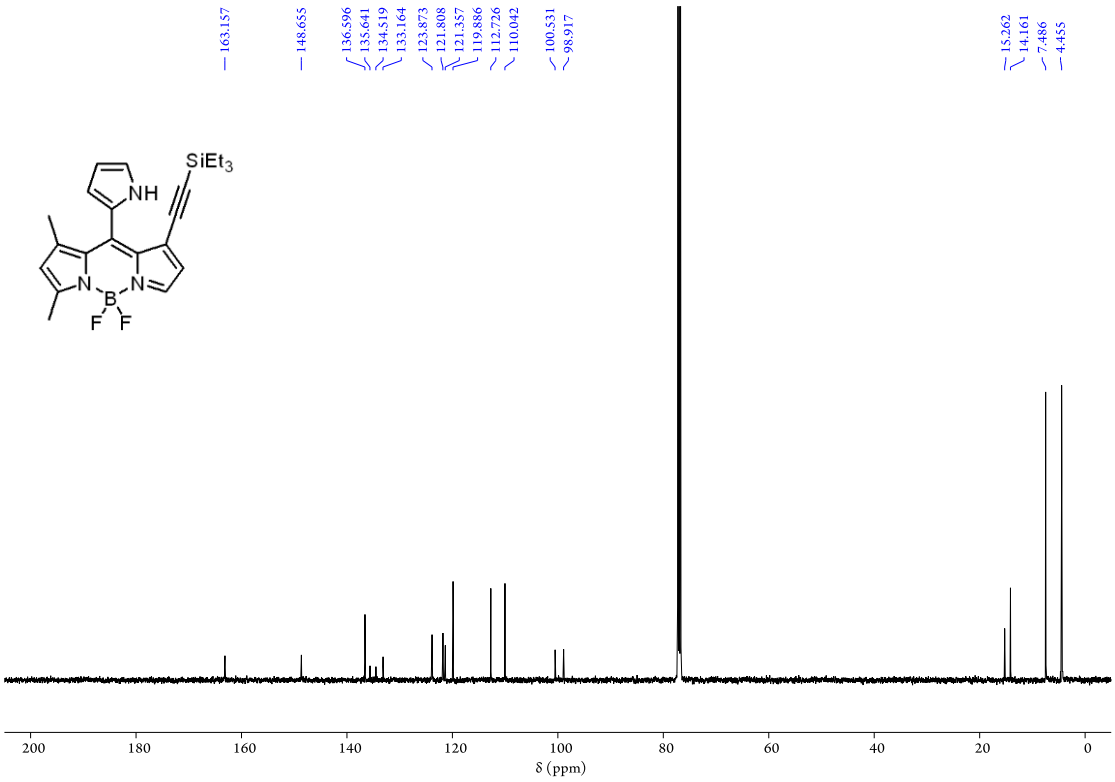


Figure S18. ^{13}C NMR spectrum of **3ai** in $CDCl_3$ at 298 K

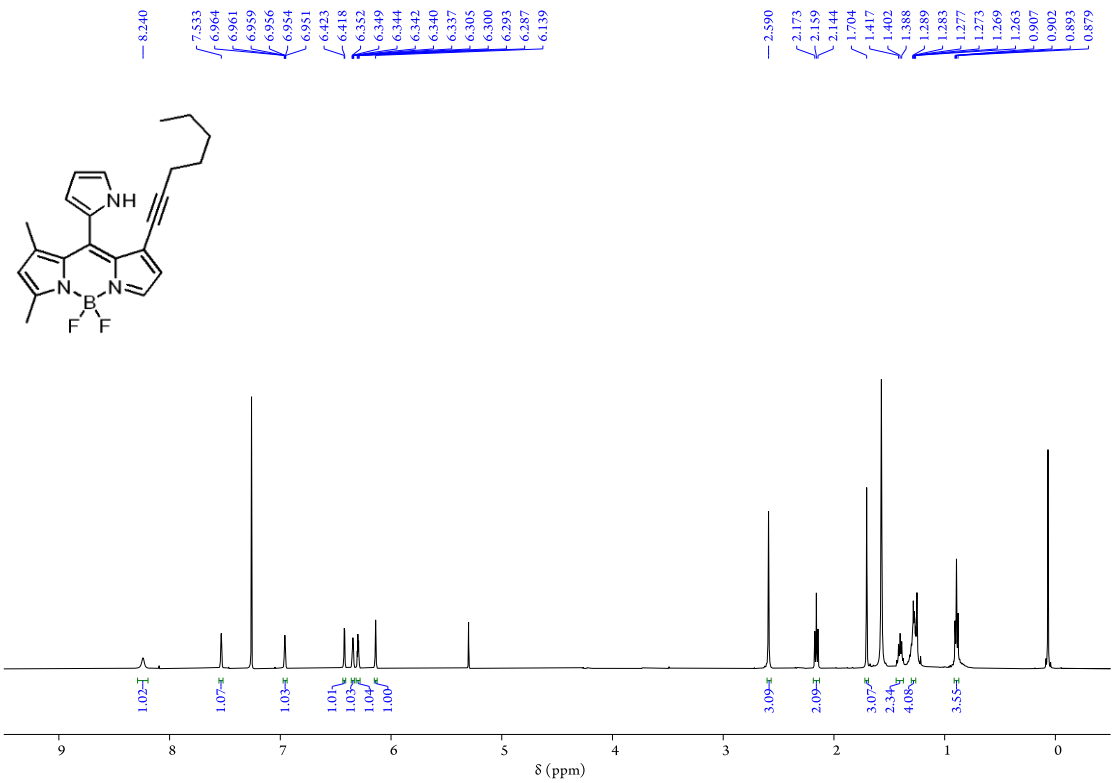


Figure S19. ^{1}H NMR spectrum of **3aj** in $CDCl_3$ at 298 K

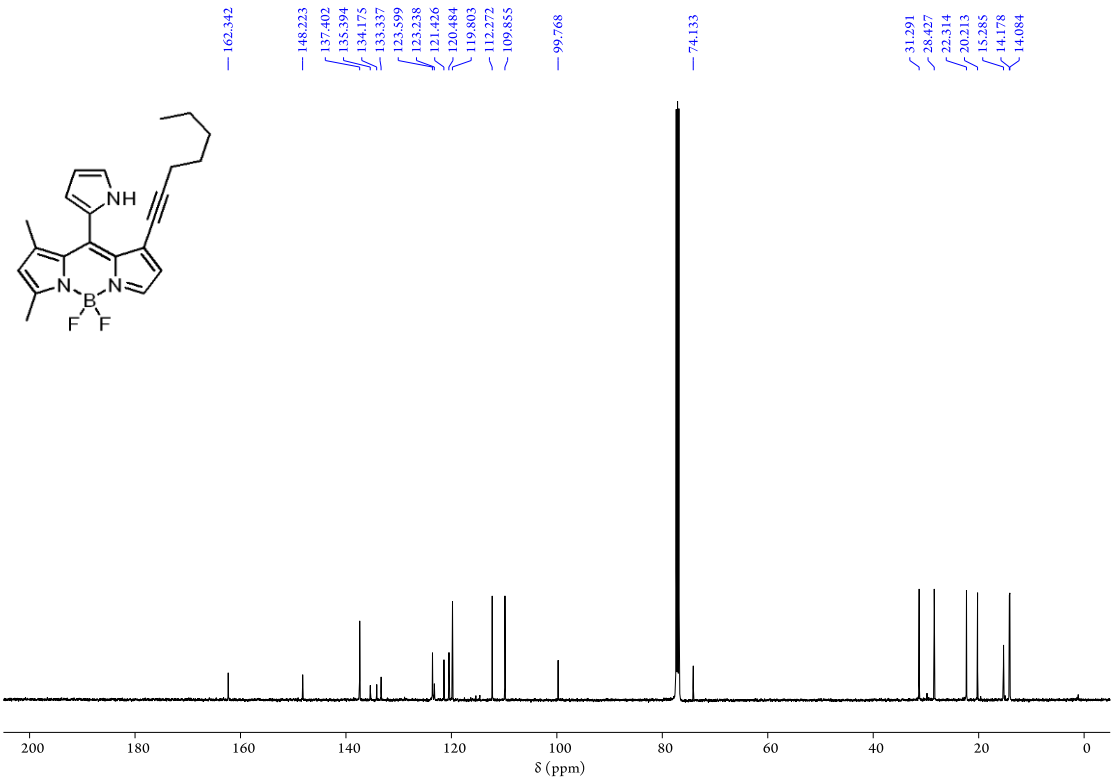


Figure S20. ^{13}C NMR spectrum of **3aj** in $CDCl_3$ at 298 K

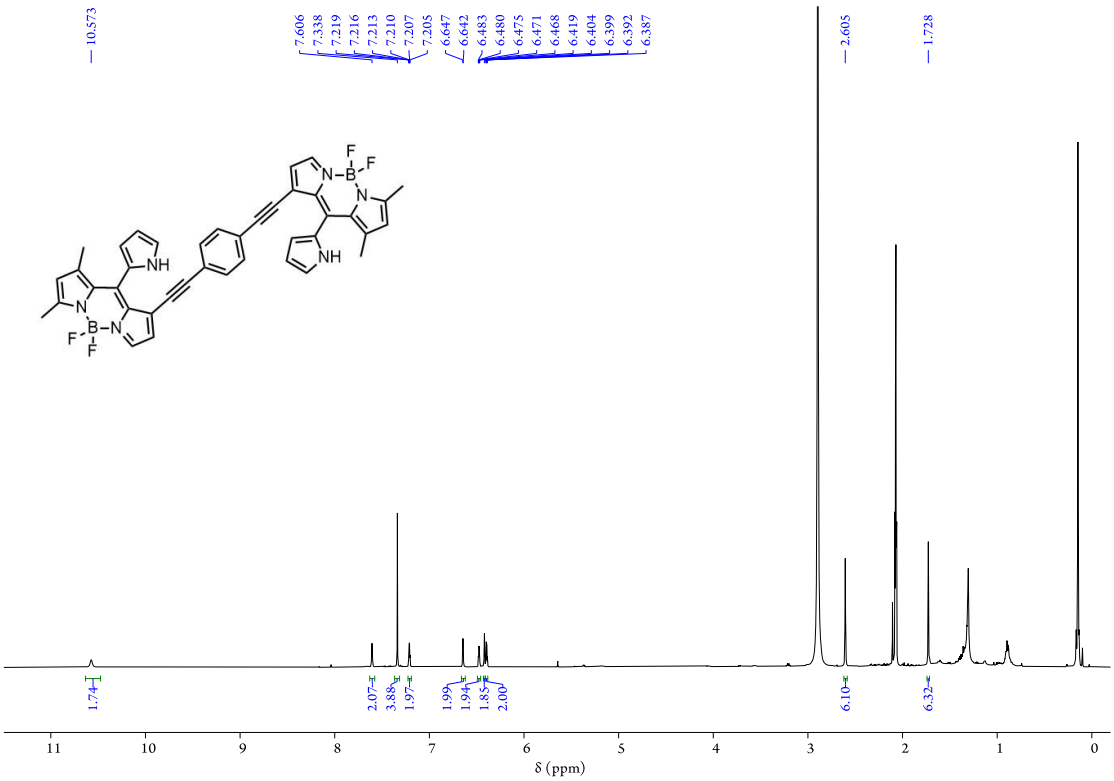


Figure S21. [1]H NMR spectrum of **3ak** in acetone-d_6 at 298 K

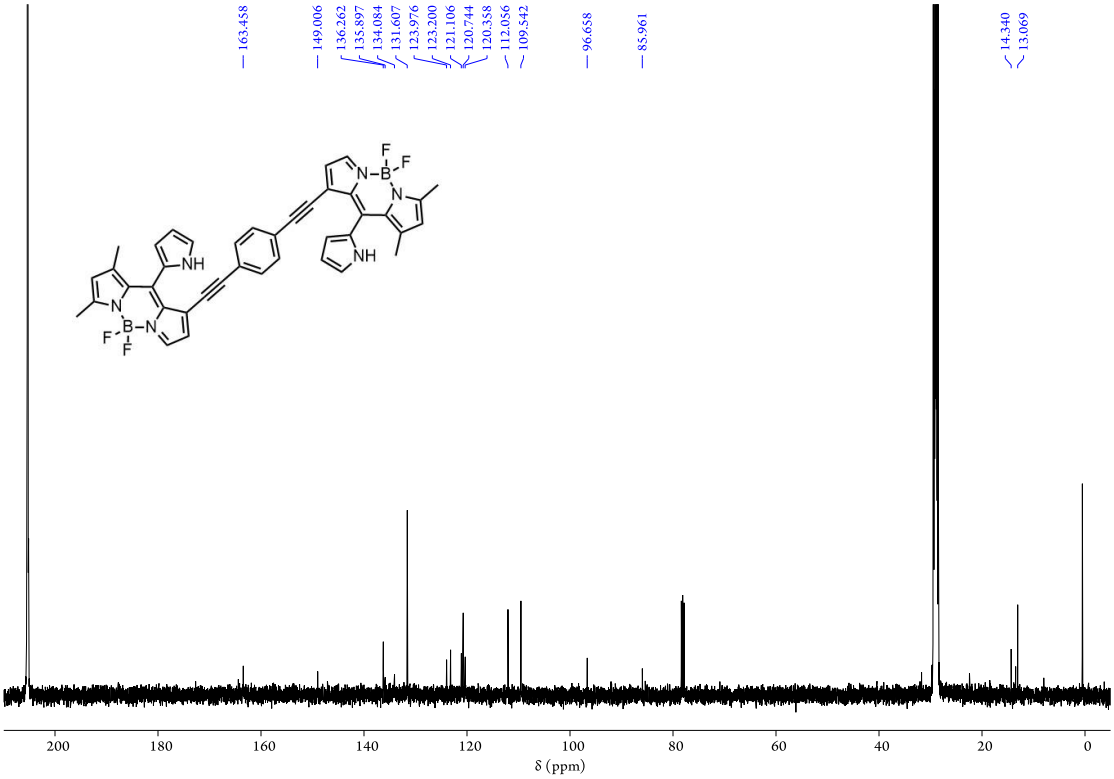


Figure S22. [13]C NMR spectrum of **3ak** in acetone-d_6 at 298 K

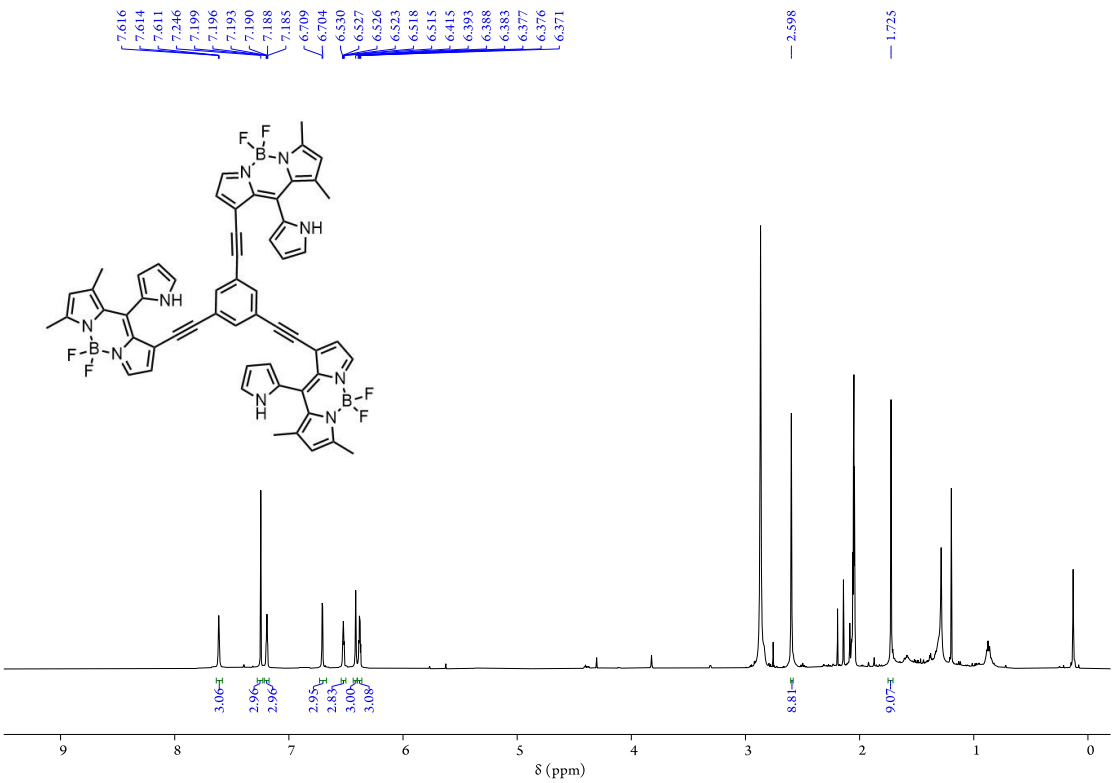


Figure S23. ^{1}H NMR spectrum of **3al** in acetone-d_6 at 298 K

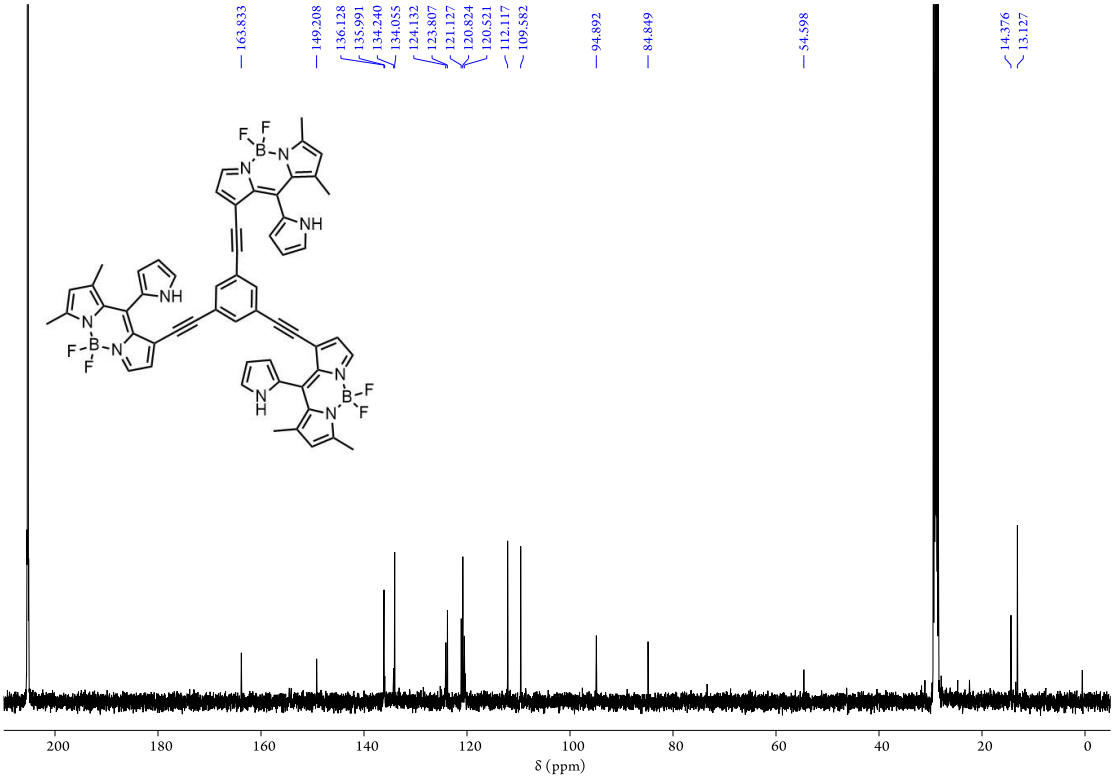


Figure S24. ^{13}C NMR spectrum of **3al** in acetone-d_6 at 298 K

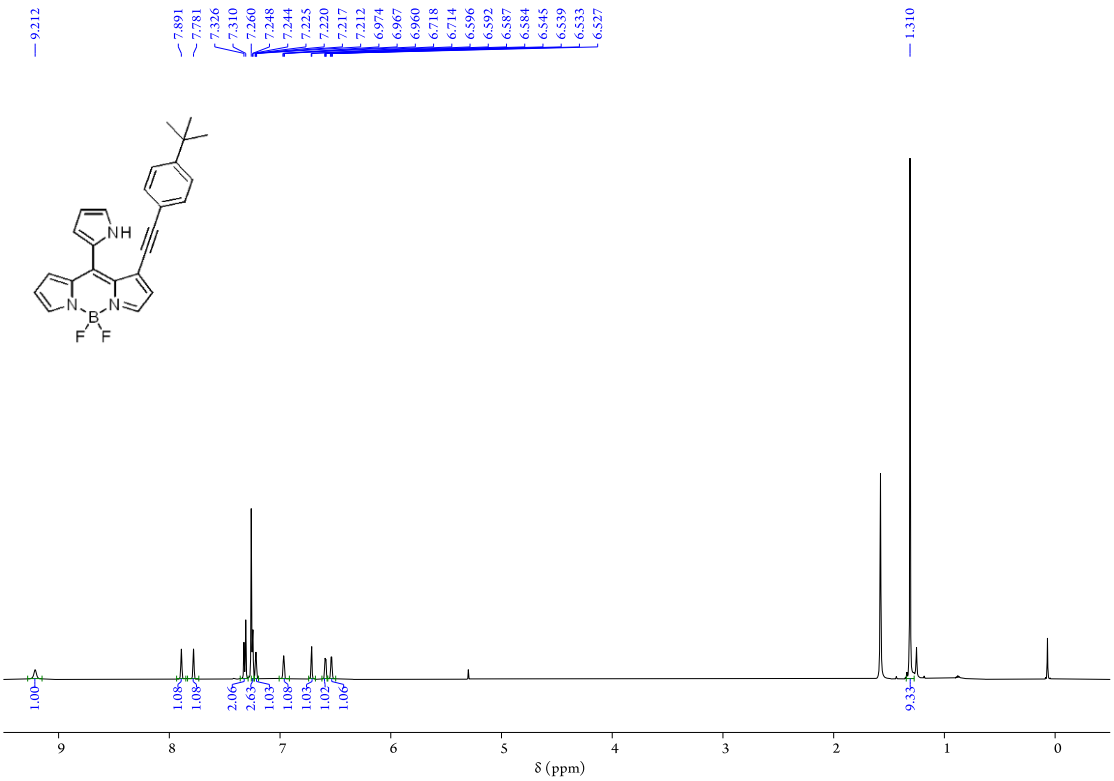


Figure S25. ^{1}H NMR spectrum of **3ba** in $CDCl_3$ at 298 K

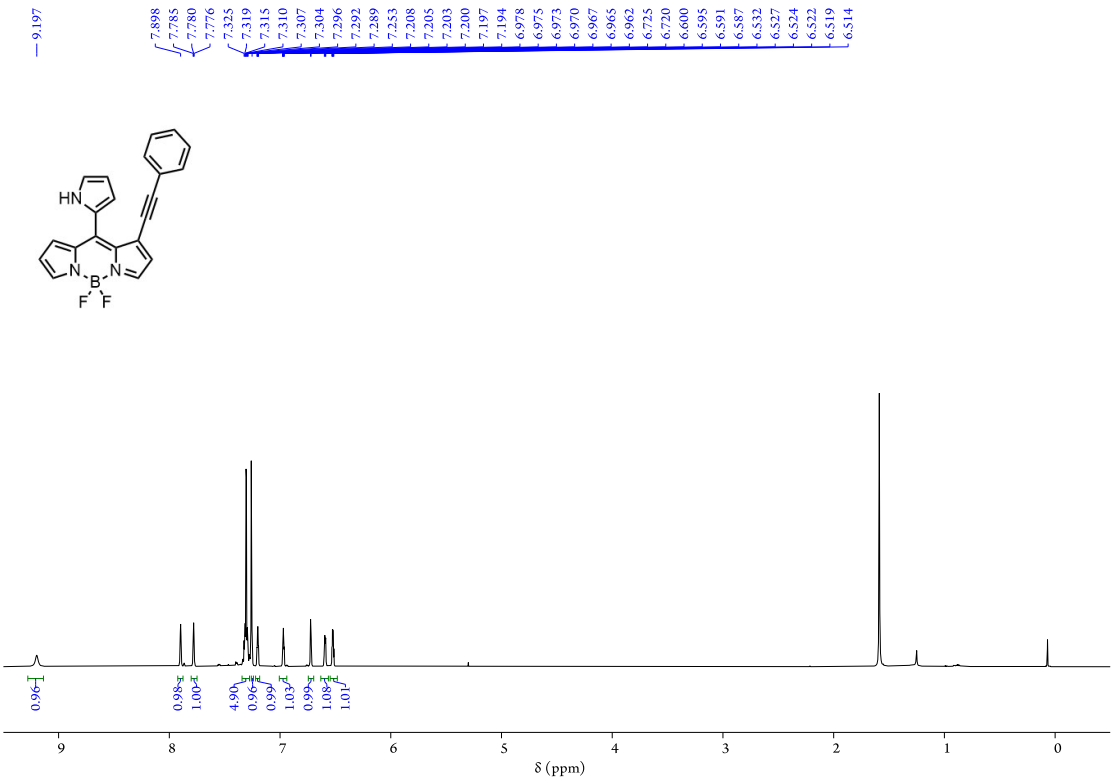


Figure S26. ^{1}H NMR spectrum of **3bb** in $CDCl_3$ at 298 K

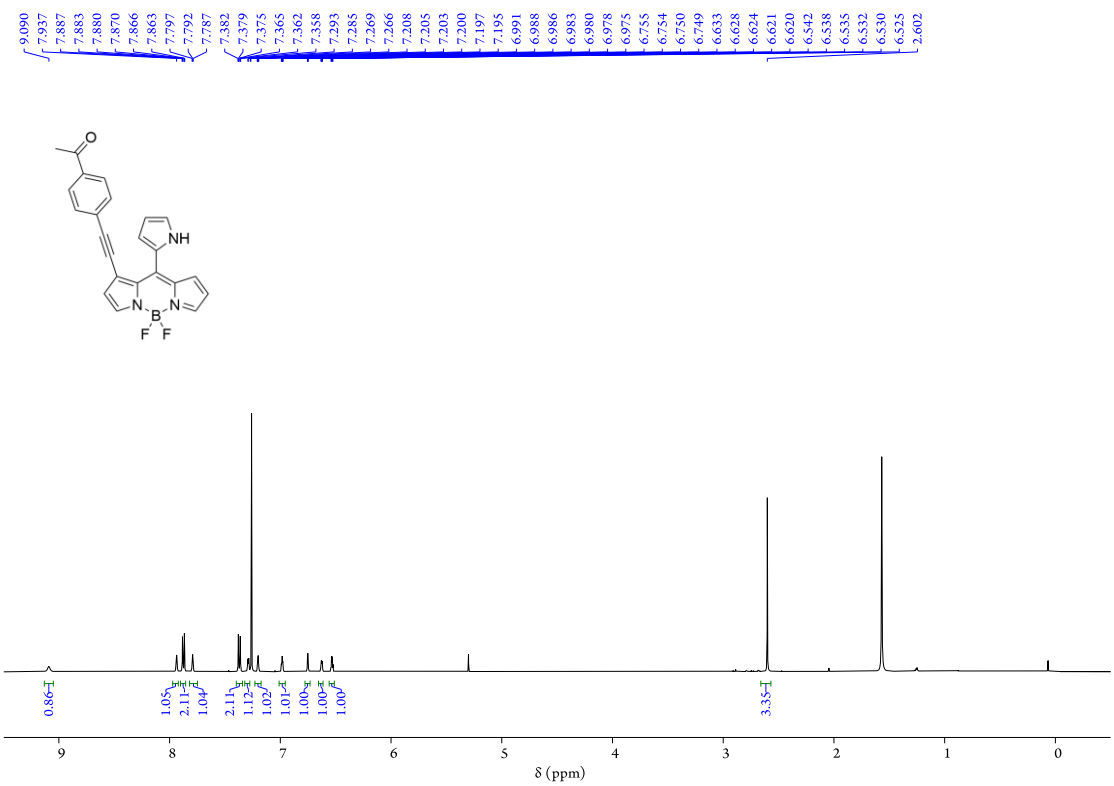


Figure S27. ^{1}H NMR spectrum of **3bd** in $CDCl_3$ at 298 K

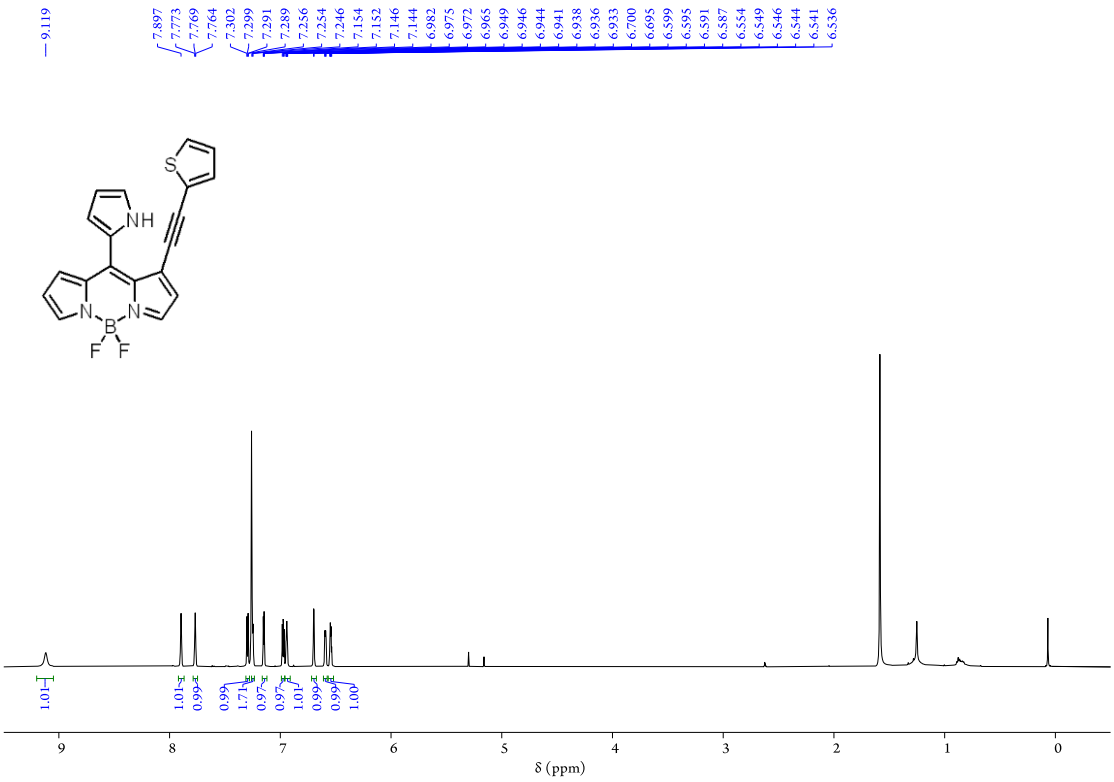


Figure S28. ^{1}H NMR spectrum of **3bg** in $CDCl_3$ at 298 K

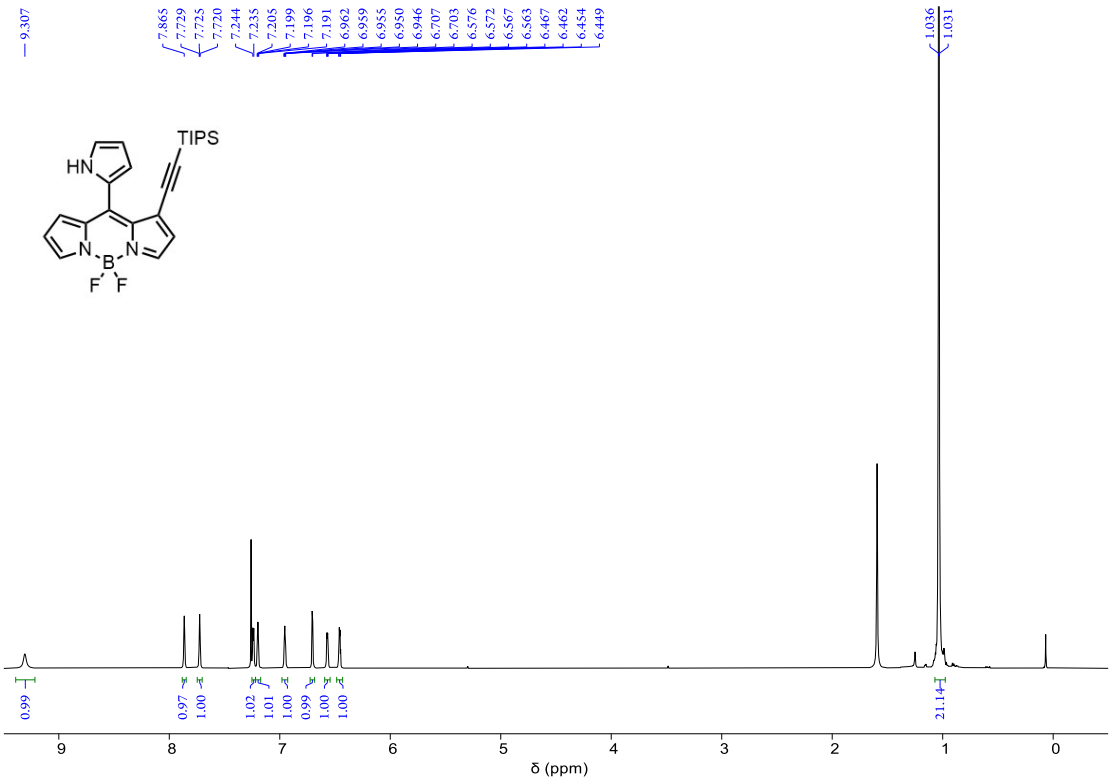


Figure S29. ^{1}H NMR spectrum of **3bh** in $CDCl_3$ at 298 K

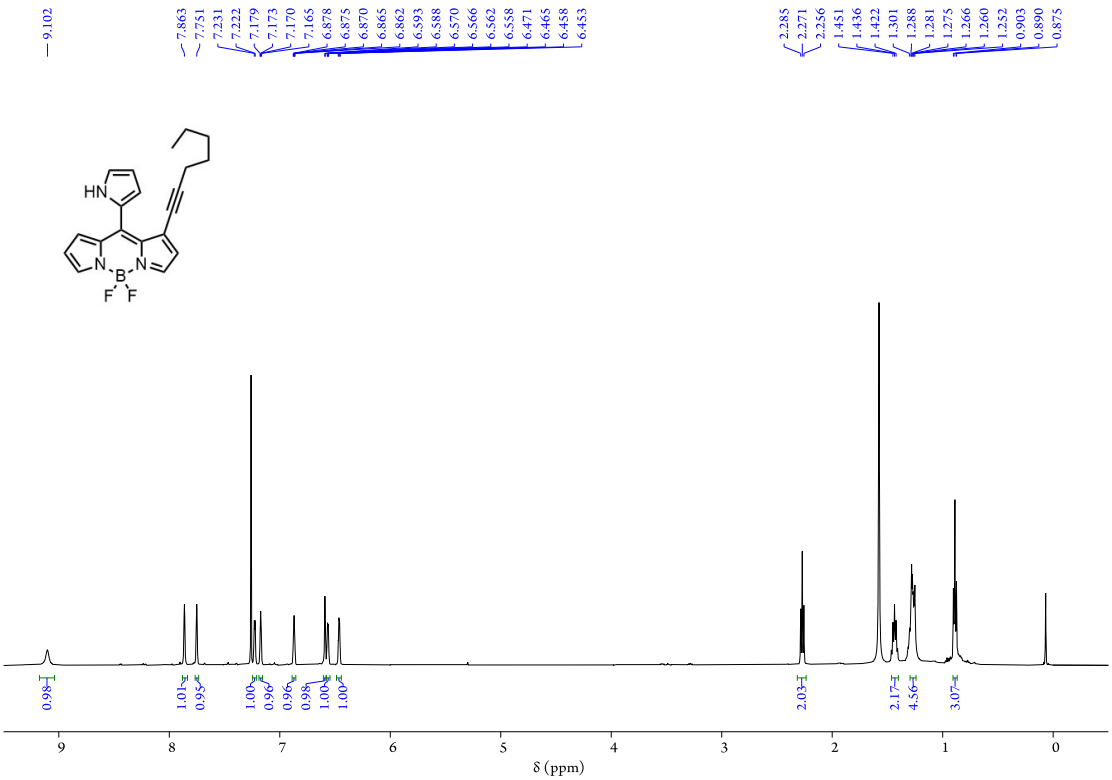


Figure S30 ^{1}H NMR spectrum of **3bj** in $CDCl_3$ at 298 K

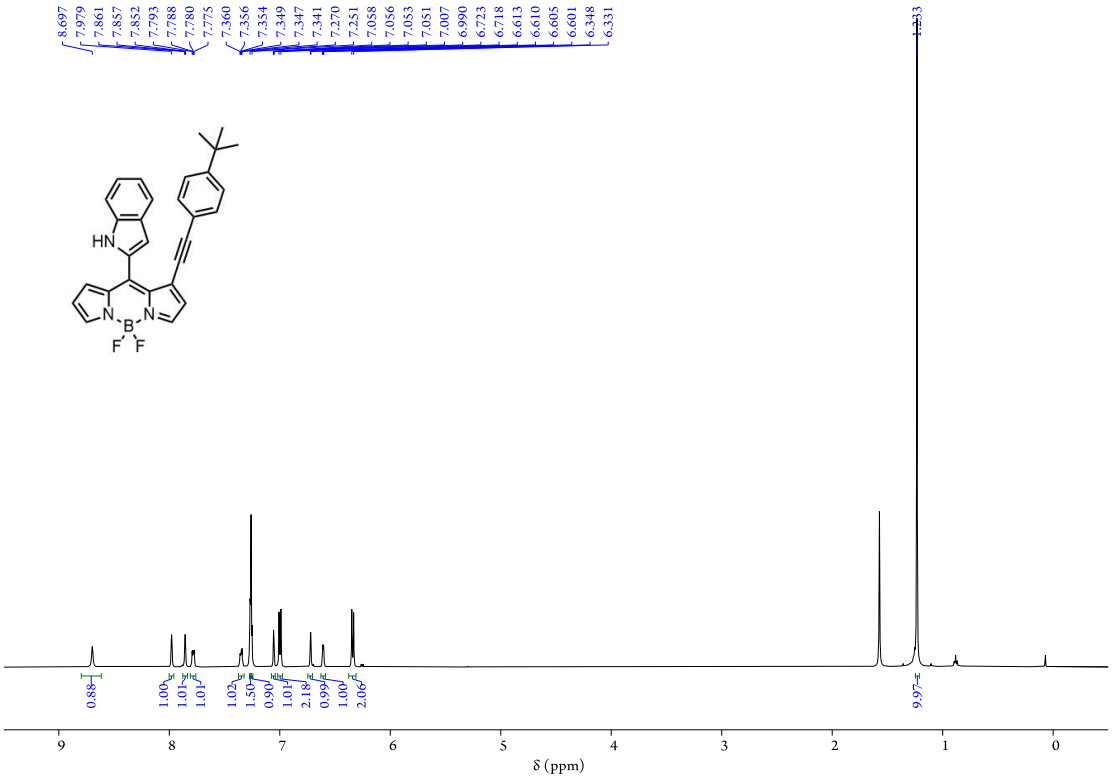


Figure S31 ^{1}H NMR spectrum of **3ca** in $CDCl_3$ at 298 K

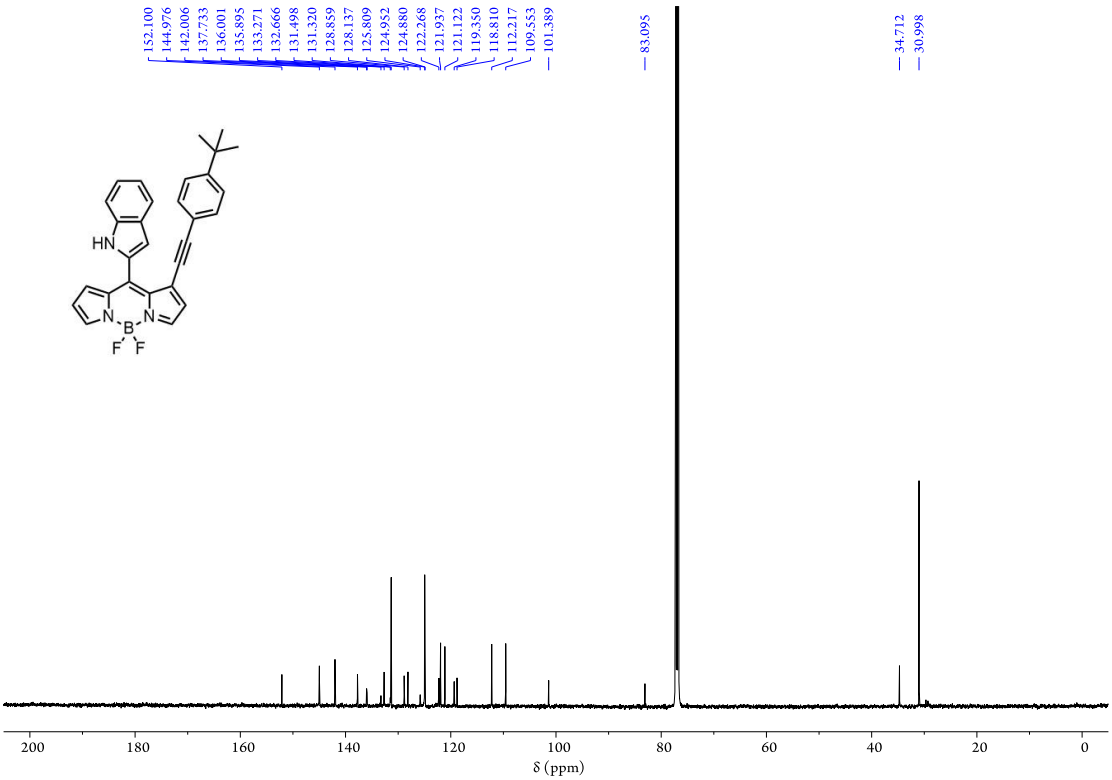


Figure S32 ^{13}C NMR spectrum of **3ca** in $CDCl_3$ at 298 K

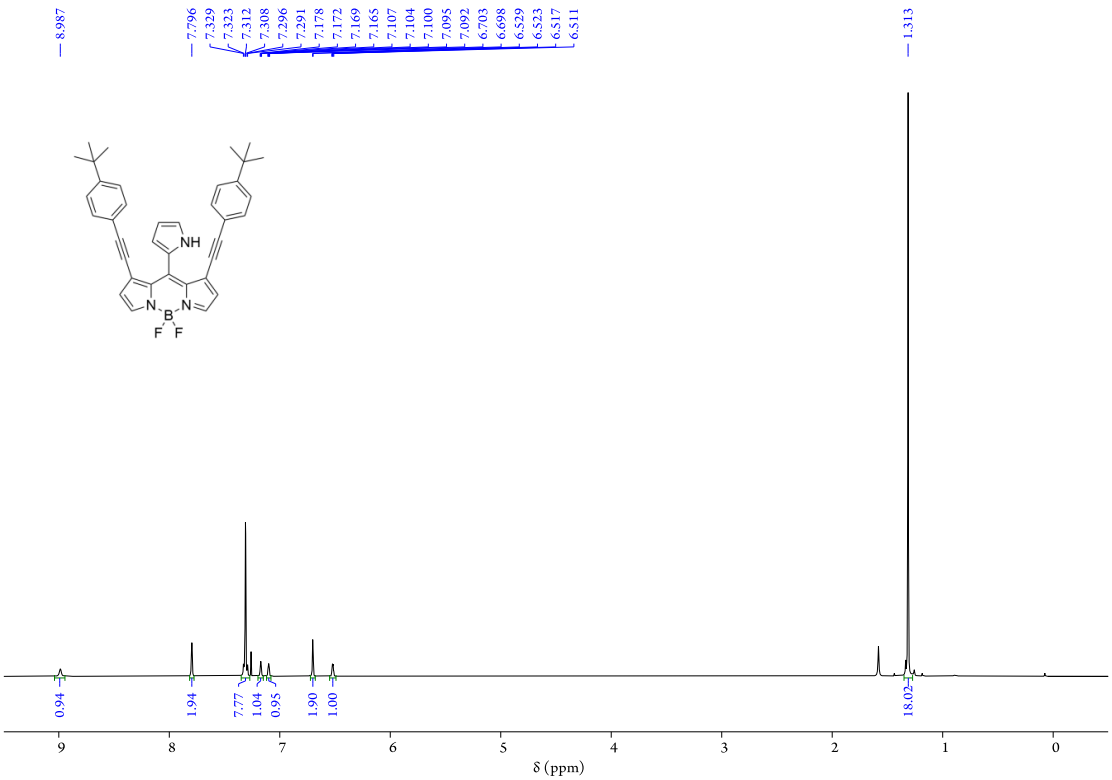


Figure S33. ^{1}H NMR spectrum of **4ba** in $CDCl_3$ at 298 K

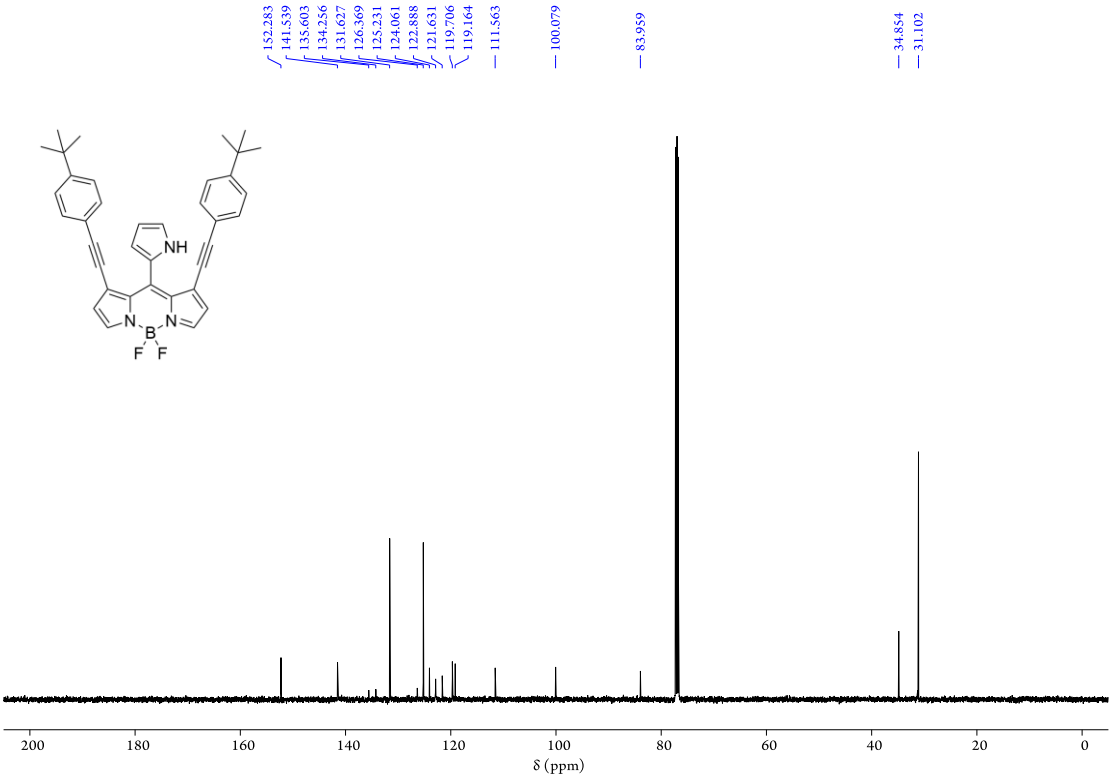


Figure S34. ^{13}C NMR spectrum of **4ba** in $CDCl_3$ at 298 K

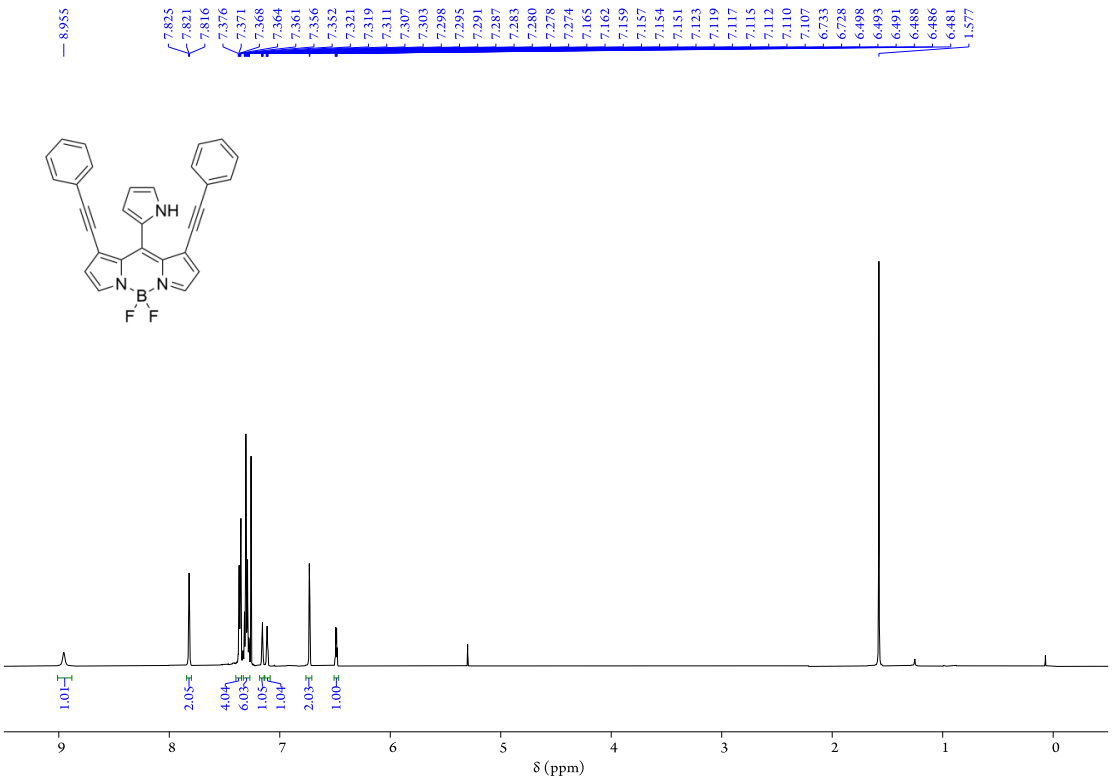


Figure S35. ^{1}H NMR spectrum of **4bb** in $CDCl_3$ at 298 K

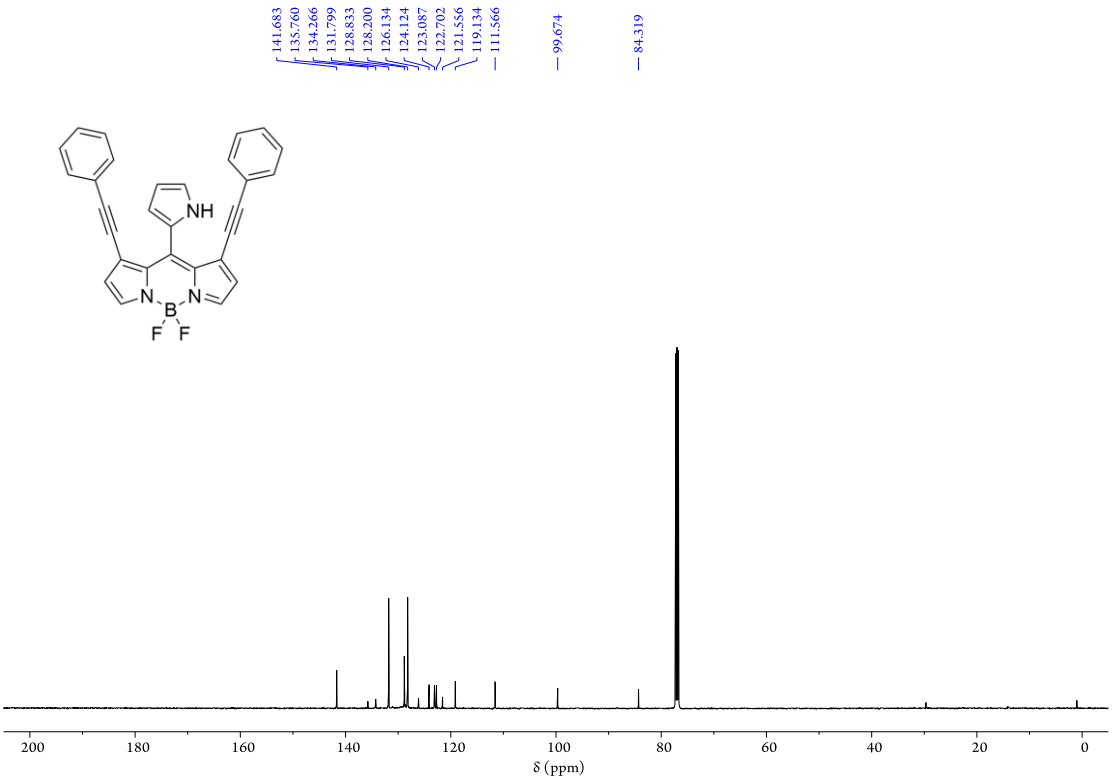


Figure S36. ^{13}C NMR spectrum of **4bb** in $CDCl_3$ at 298 K

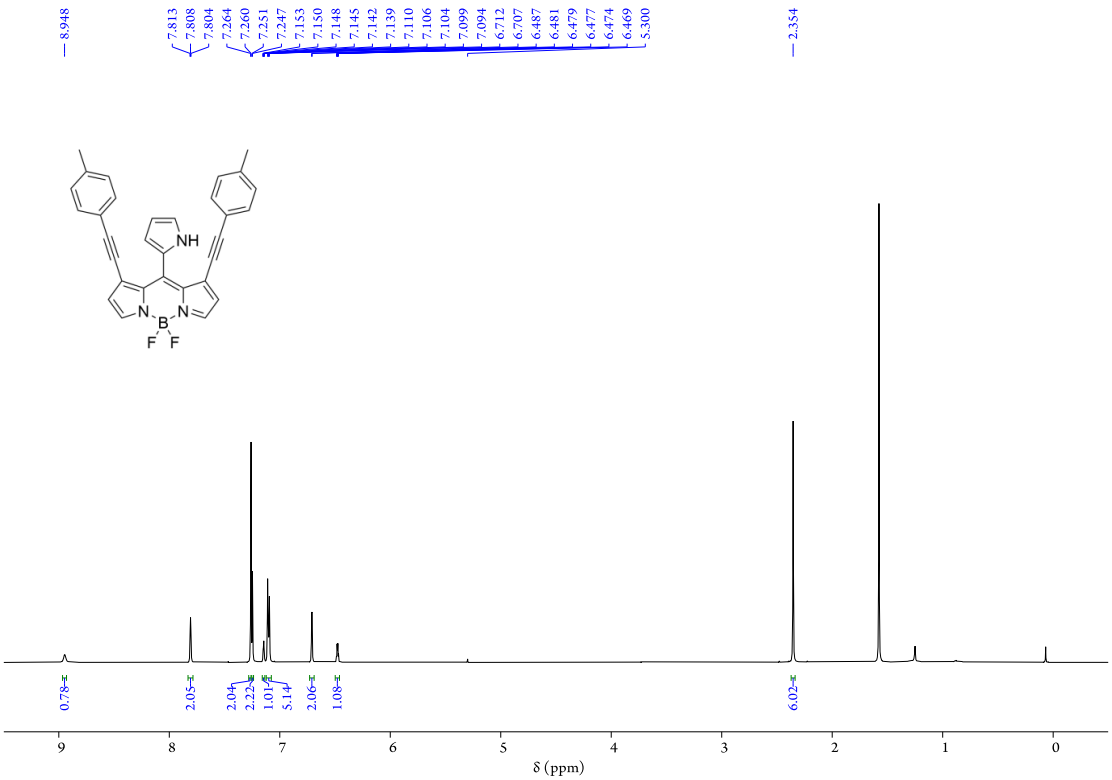


Figure S37. ^{1}H NMR spectrum of **4bc** in $CDCl_3$ at 298 K

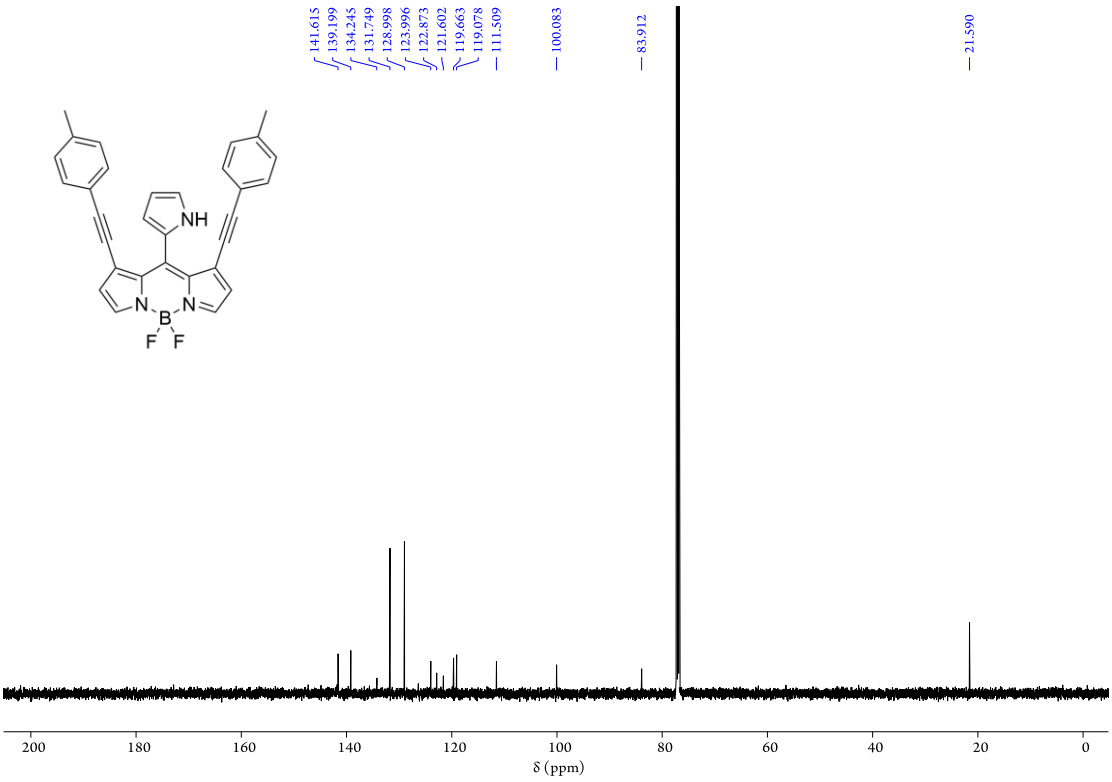


Figure S38. ^{13}C NMR spectrum of **4bc** in $CDCl_3$ at 298 K

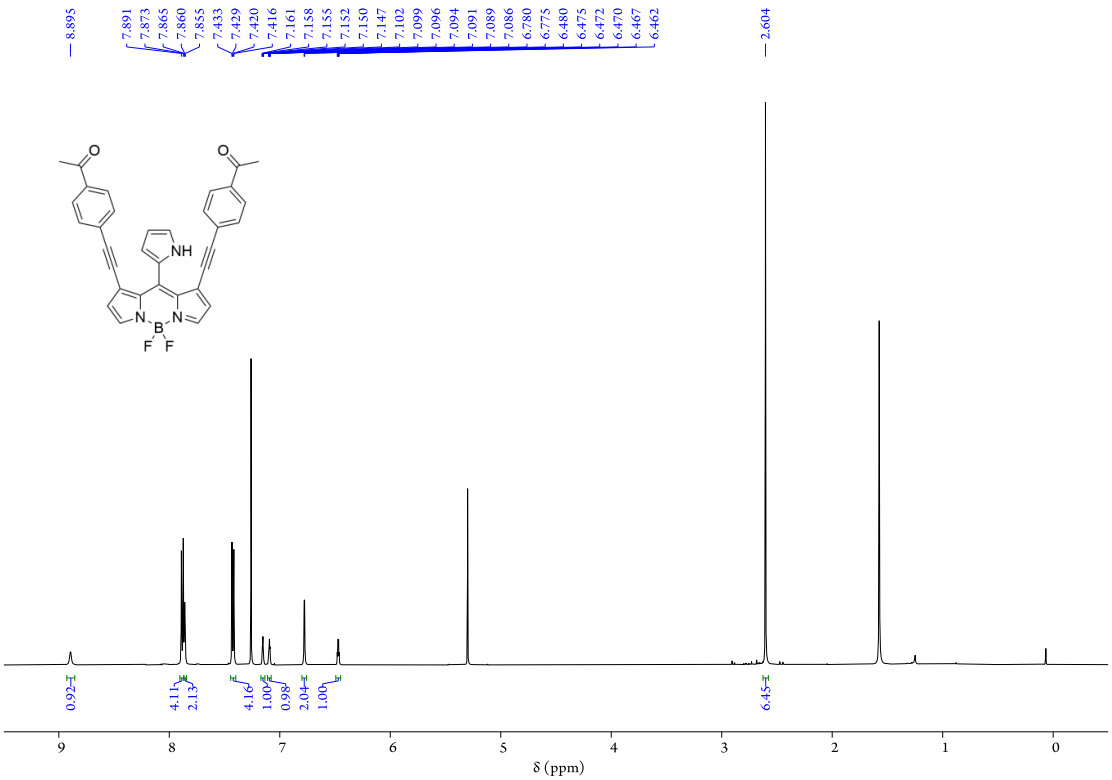


Figure S39. ^{1}H NMR spectrum of **4bd**in $CDCl_3$ at 298 K

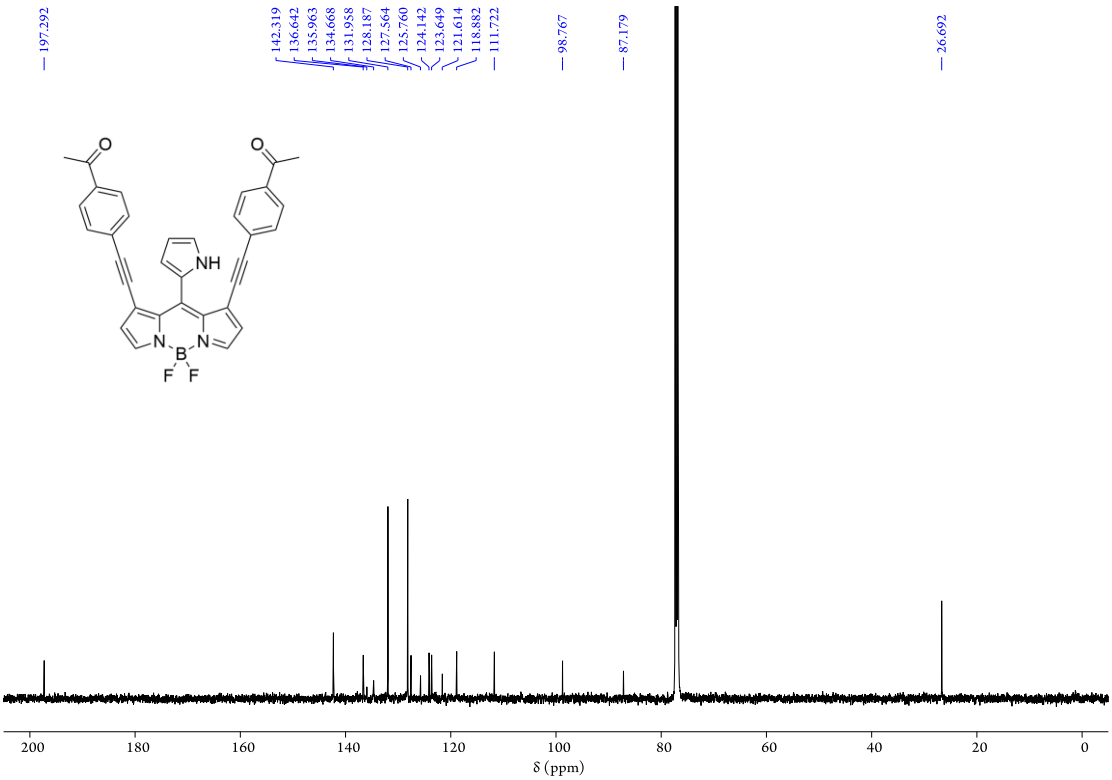


Figure S40. ^{13}C NMR spectrum of **4bd** in $CDCl_3$ at 298 K

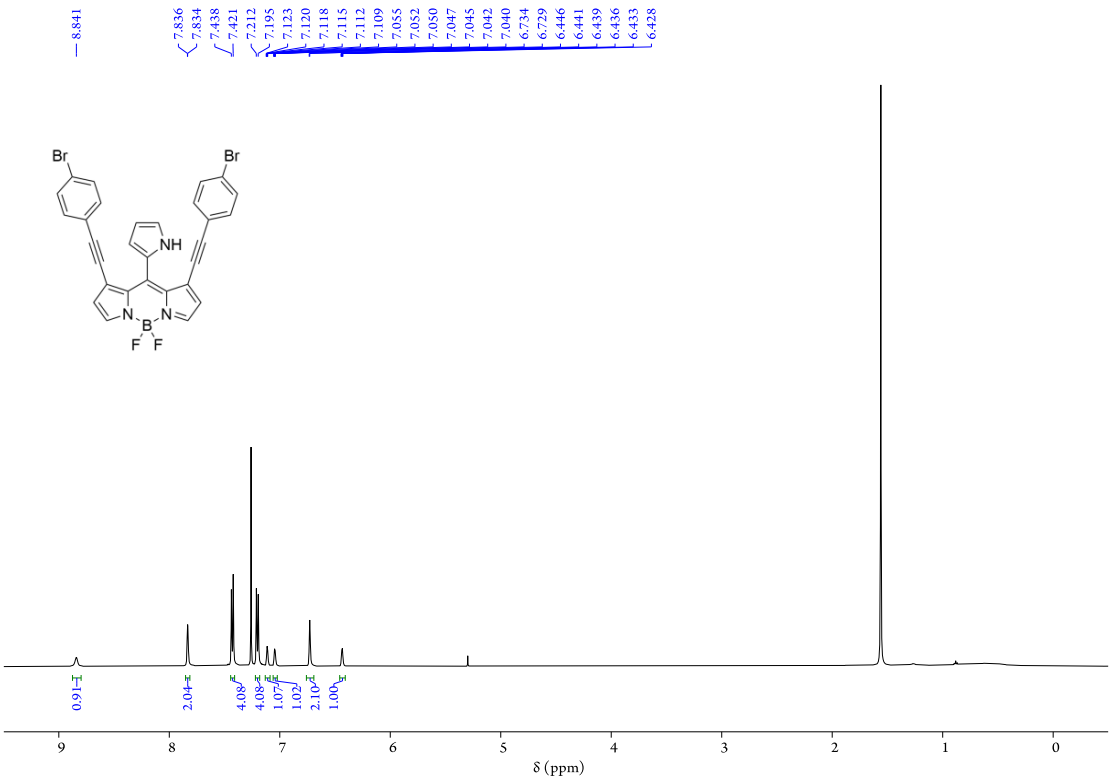


Figure S41. ^{1}H NMR spectrum of **4be** in $CDCl_3$ at 298 K

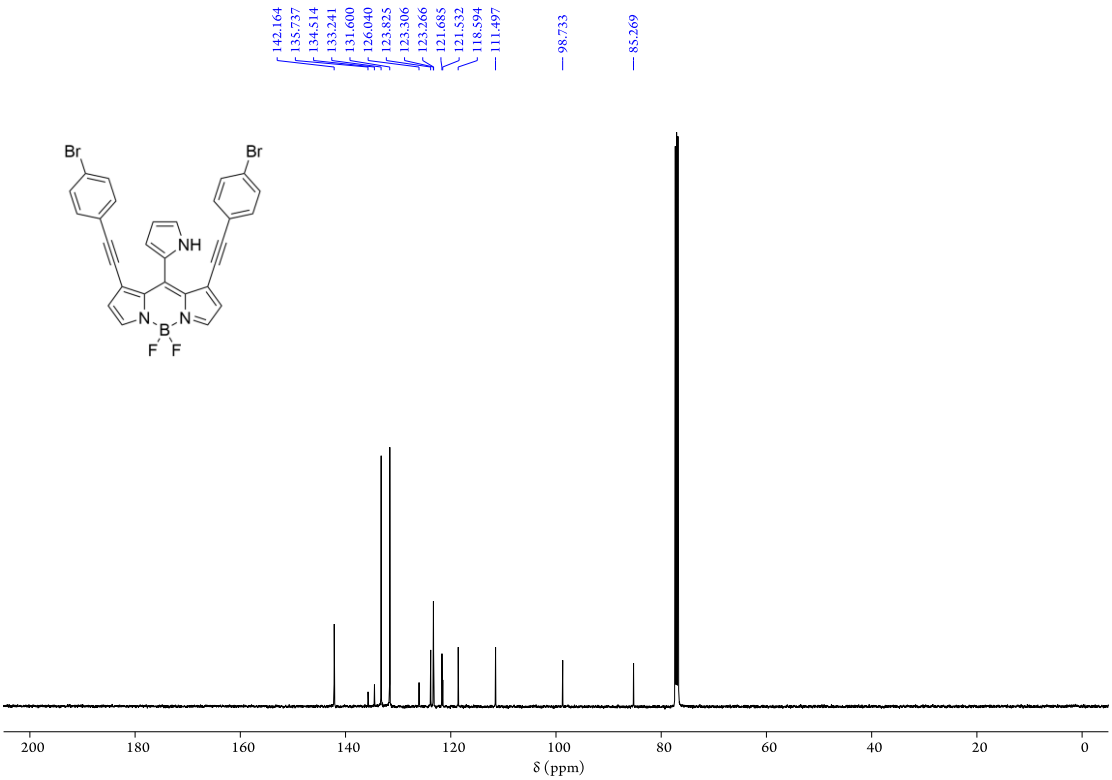


Figure S42. ^{13}C NMR spectrum of **4be** in $CDCl_3$ at 298 K

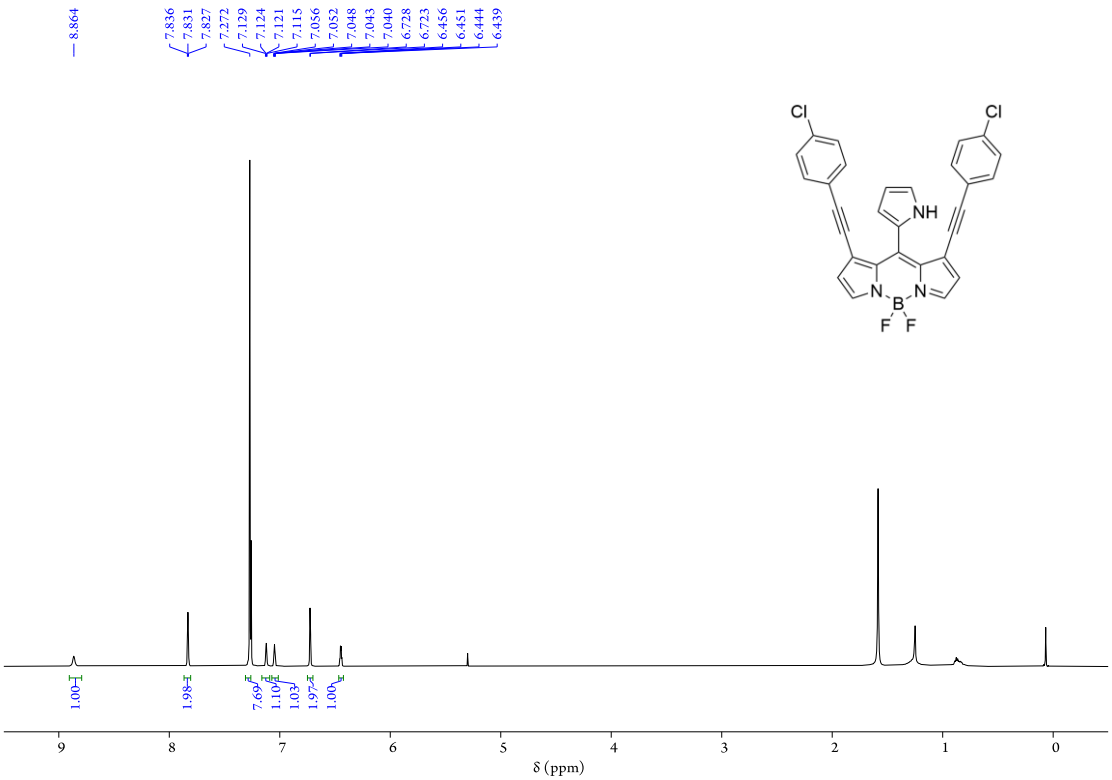


Figure S43. ^{1}H NMR spectrum of **4bf** in $CDCl_3$ at 298 K

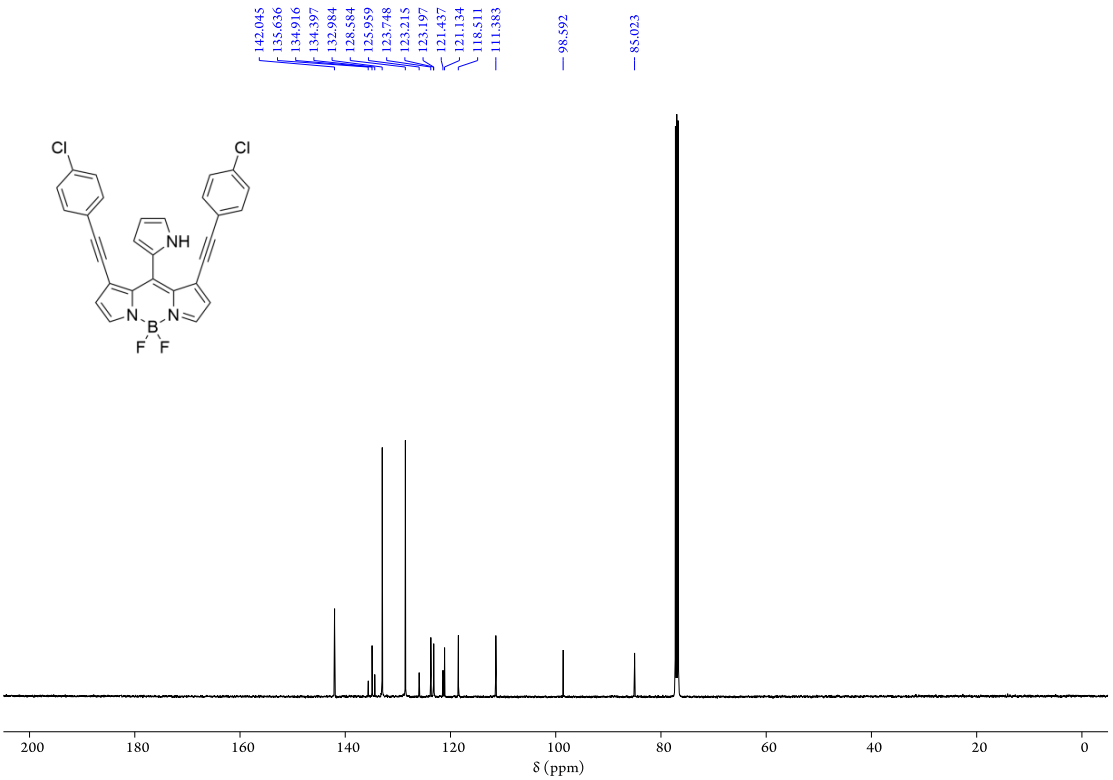


Figure S44. ^{13}C NMR spectrum of **4bf** in $CDCl_3$ at 298 K

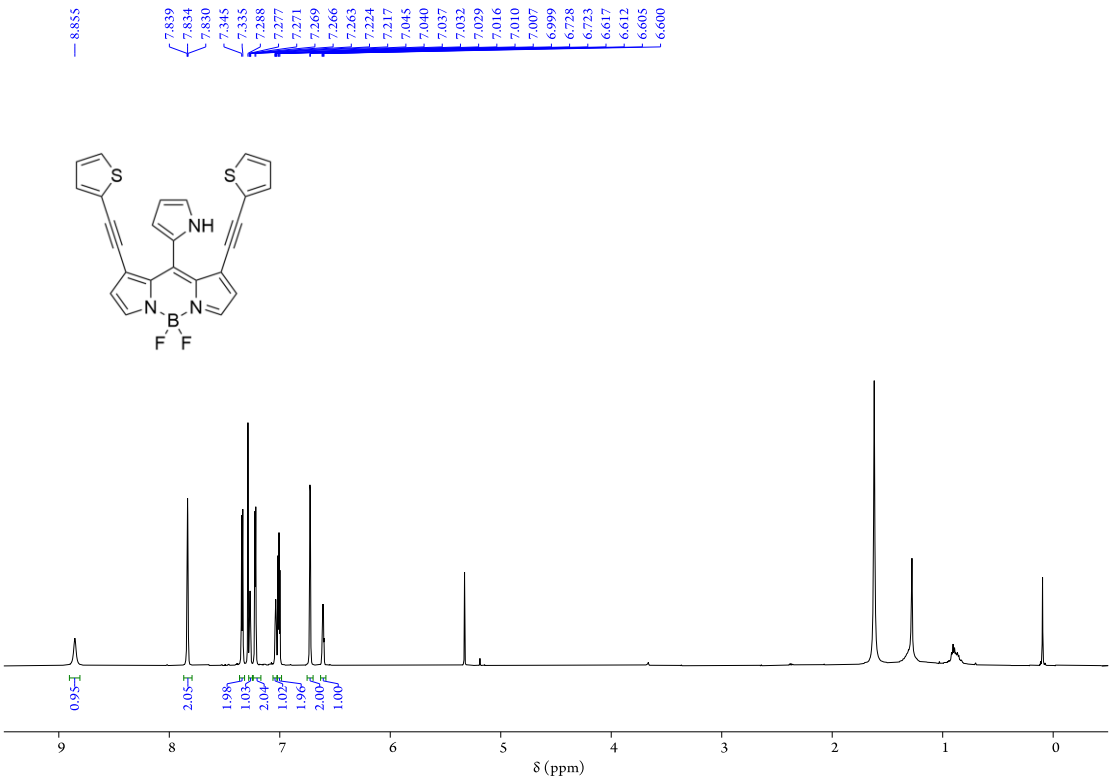


Figure S45. ^{1}H NMR spectrum of **4bg** in $CDCl_3$ at 298 K

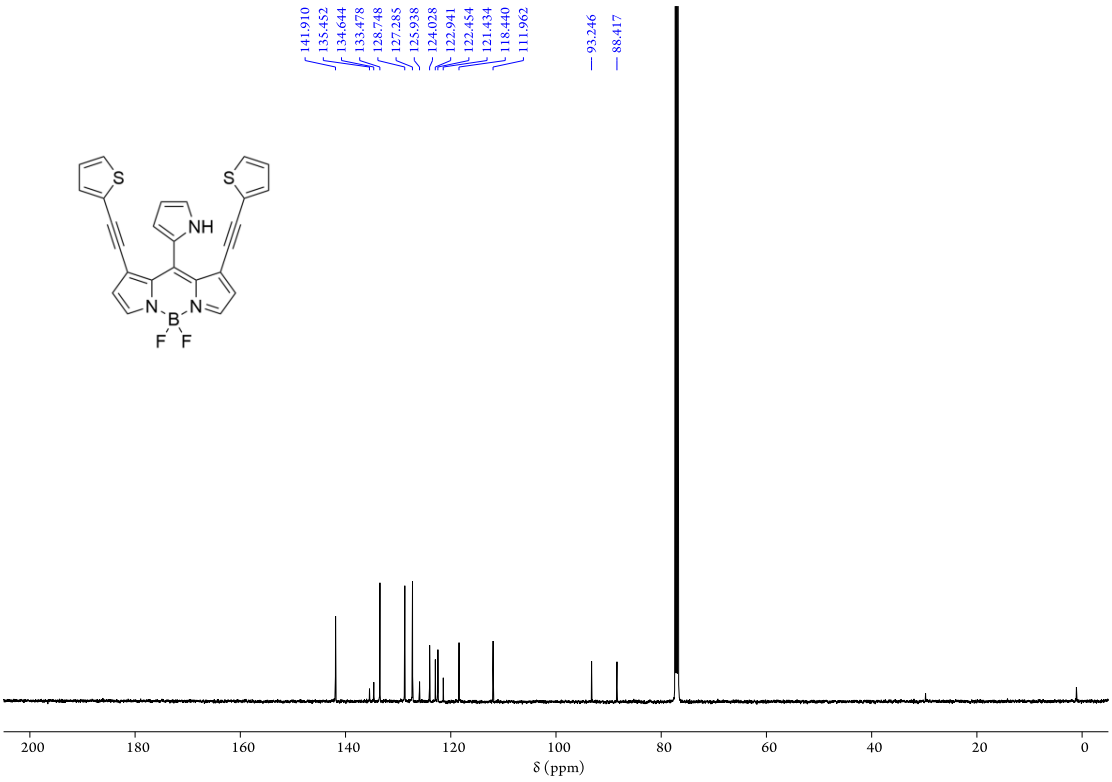


Figure S46. ^{13}C NMR spectrum of **4bg** in $CDCl_3$ at 298 K

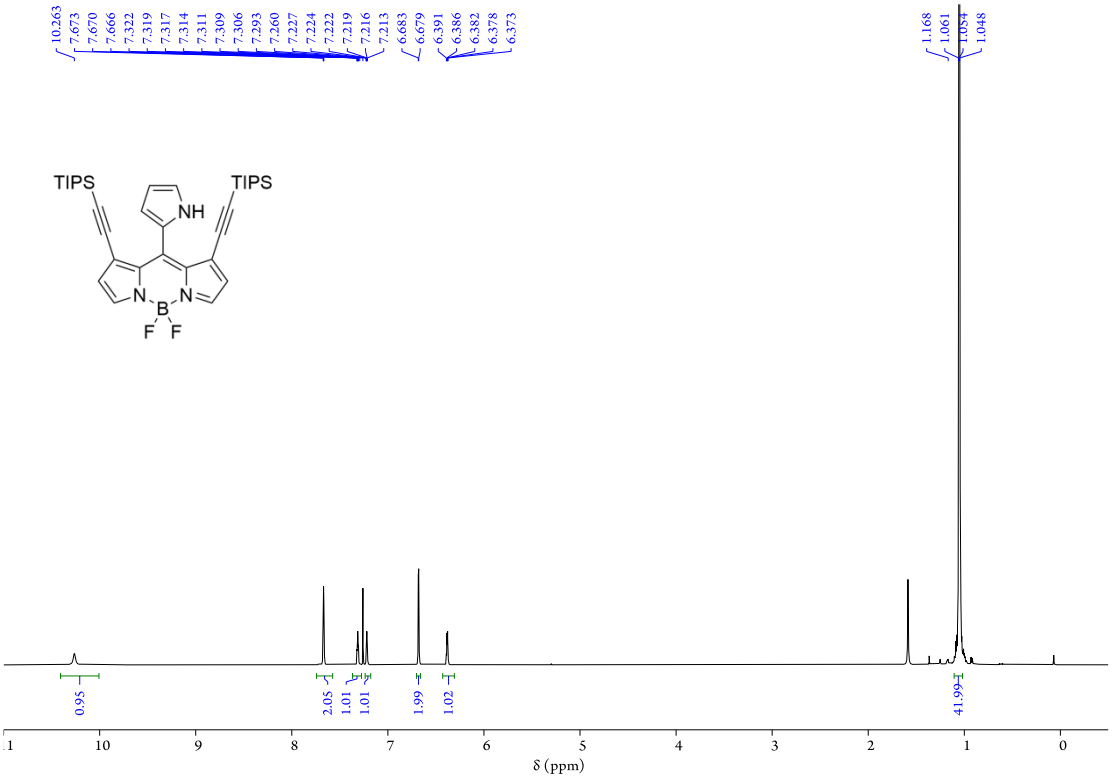


Figure S47. ^{1}H NMR spectrum of **4bh** in $CDCl_3$ at 298 K

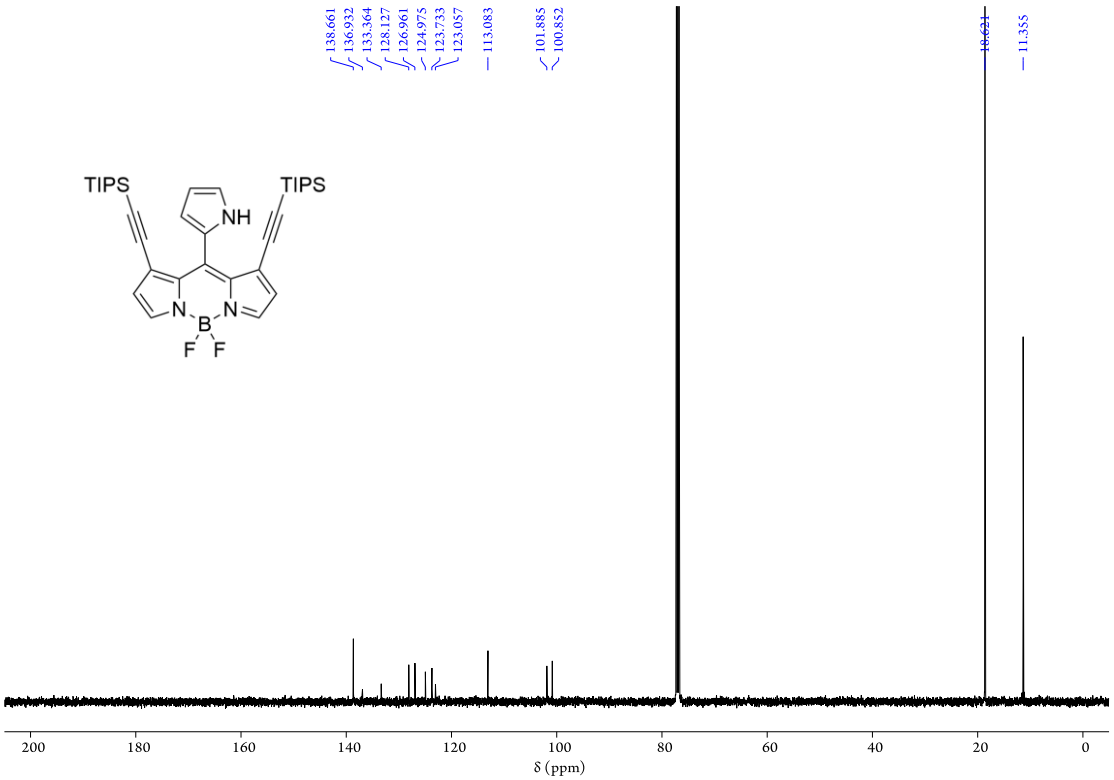


Figure S48. ^{13}C NMR spectrum of **4bh** in $CDCl_3$ at 298 K

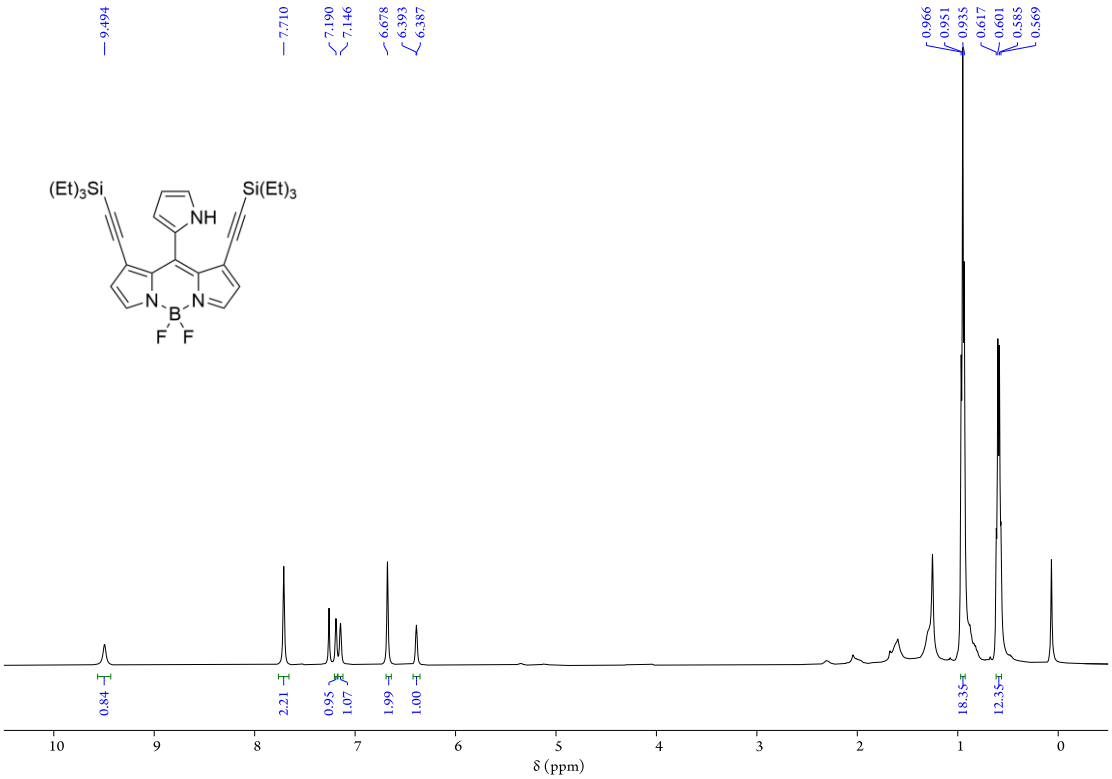


Figure S49. ^{1}H NMR spectrum of **4bi** in $CDCl_3$ at 298 K

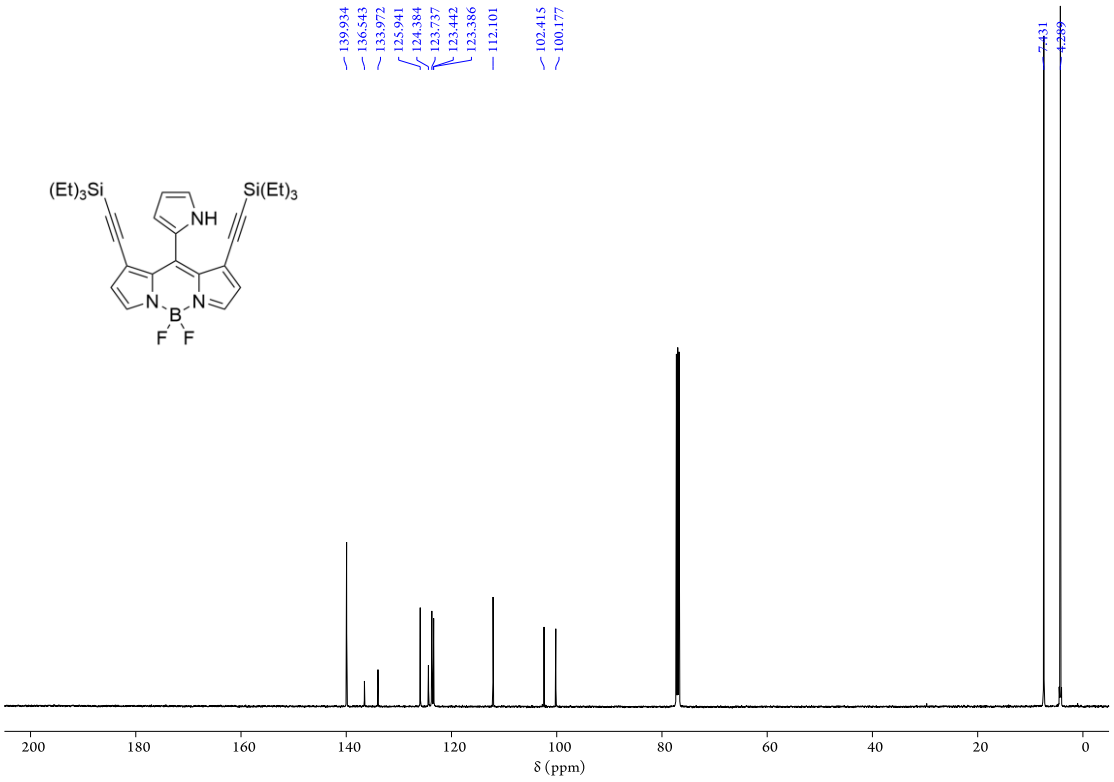


Figure S50. ^{13}C NMR spectrum of **4bi** in $CDCl_3$ at 298 K

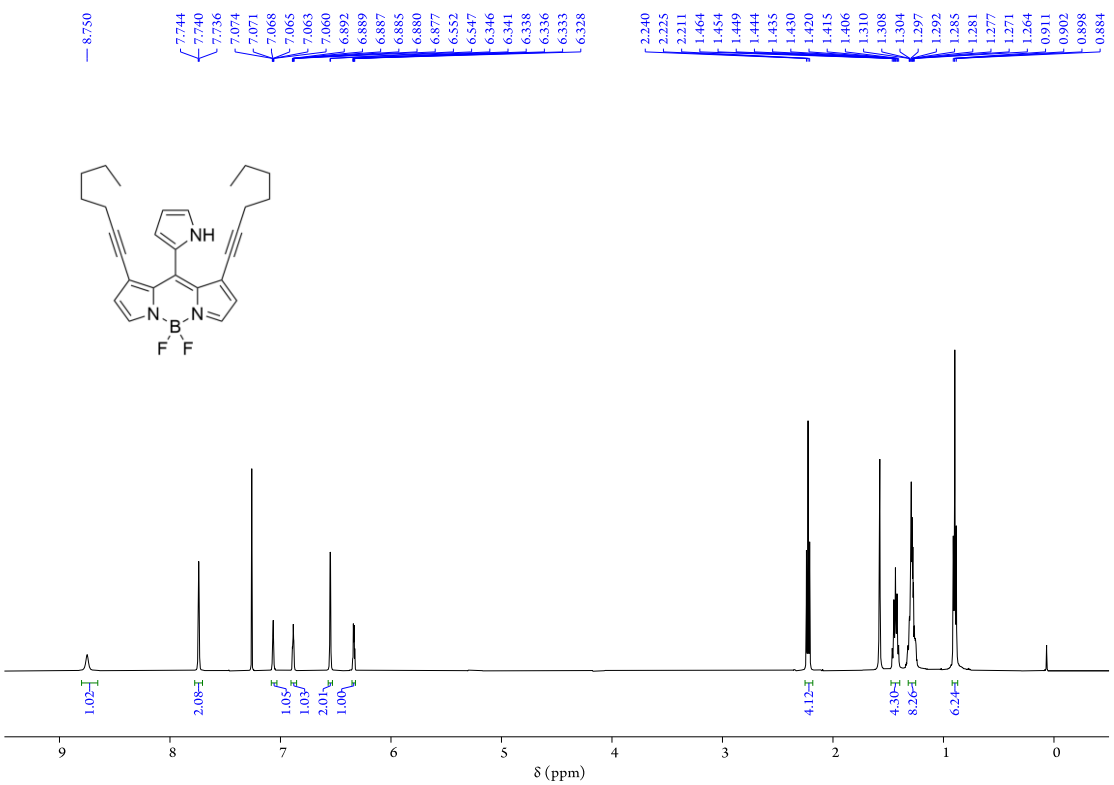


Figure S51. ^{1}H NMR spectrum of **4bj** in $CDCl_3$ at 298 K

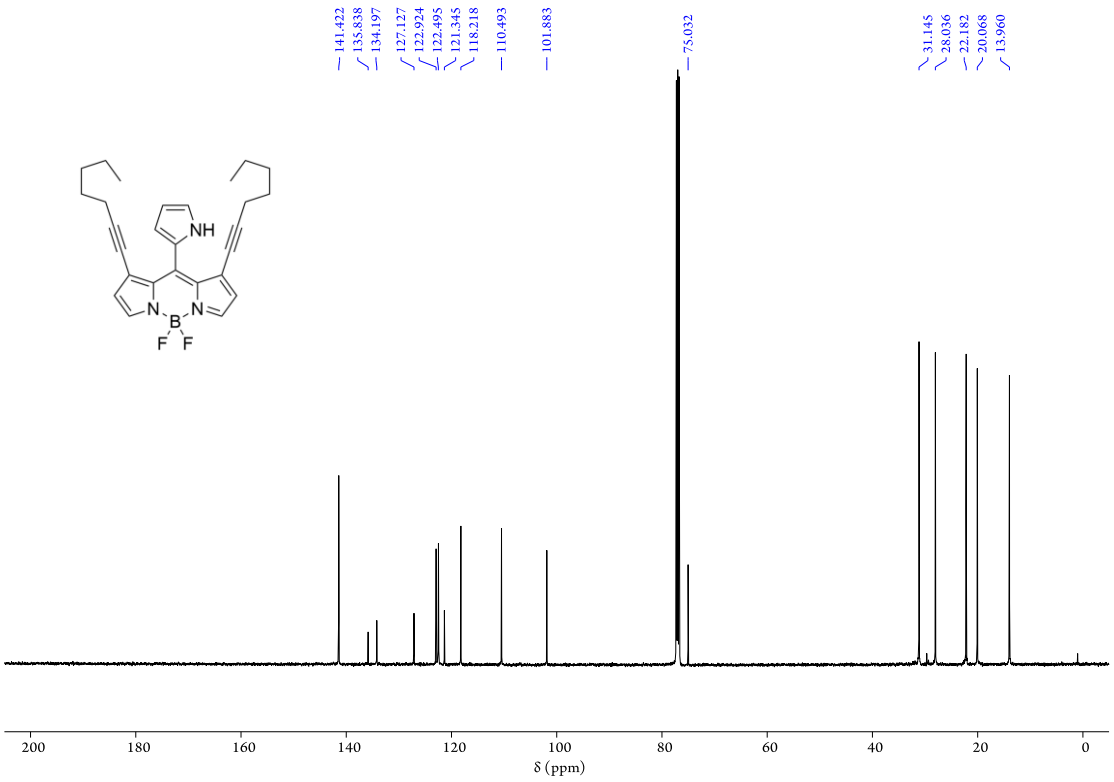


Figure S52. ^{13}C NMR spectrum of **4bj** in $CDCl_3$ at 298 K

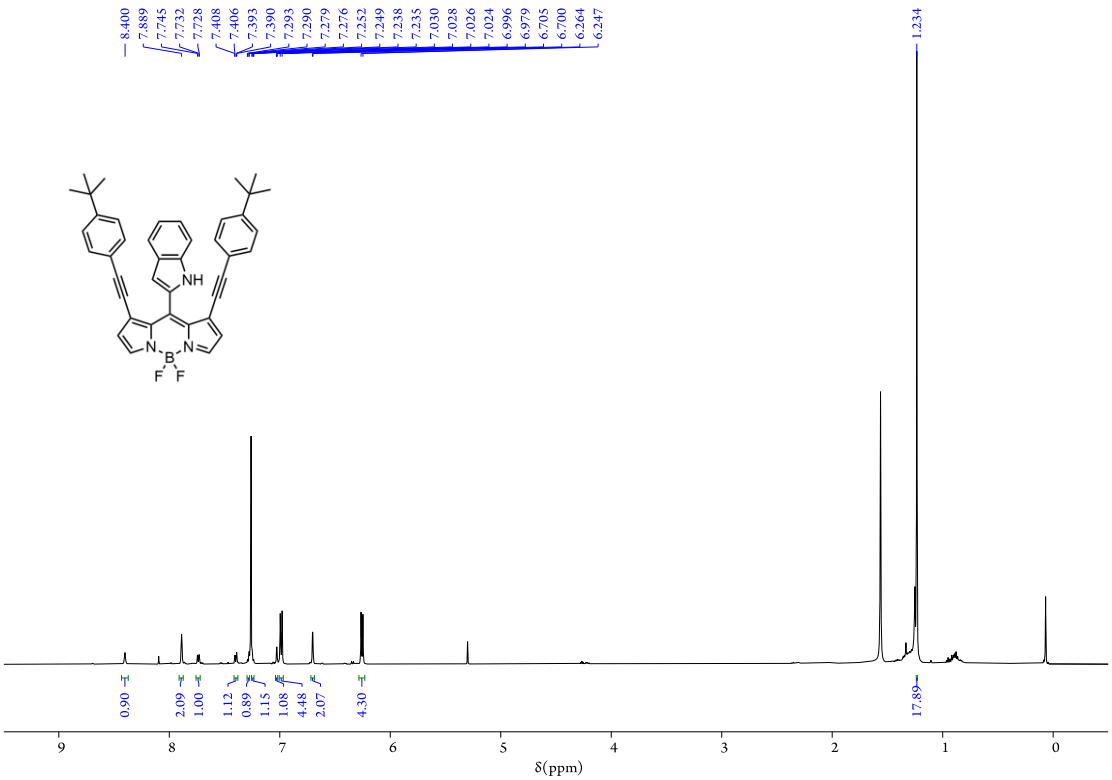


Figure S53. ^{1}H NMR spectrum of **4ca** in $CDCl_3$ at 298 K

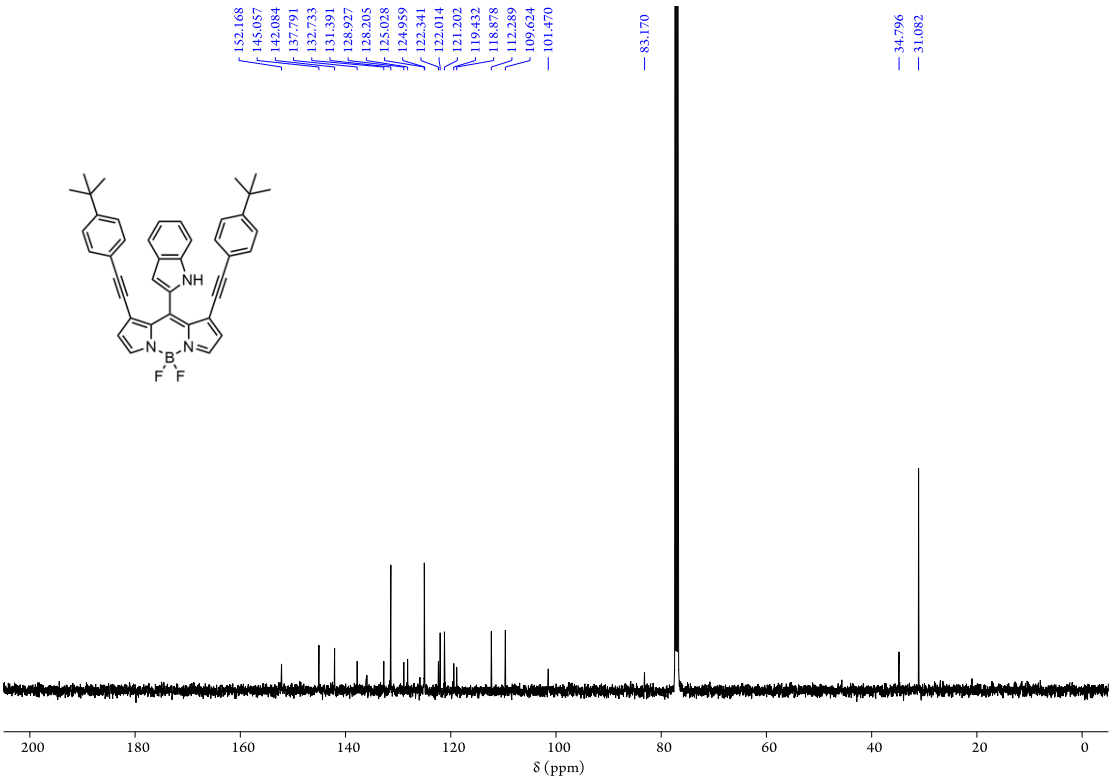


Figure S54. ^{13}C NMR spectrum of **4ca** in $CDCl_3$ at 298 K.

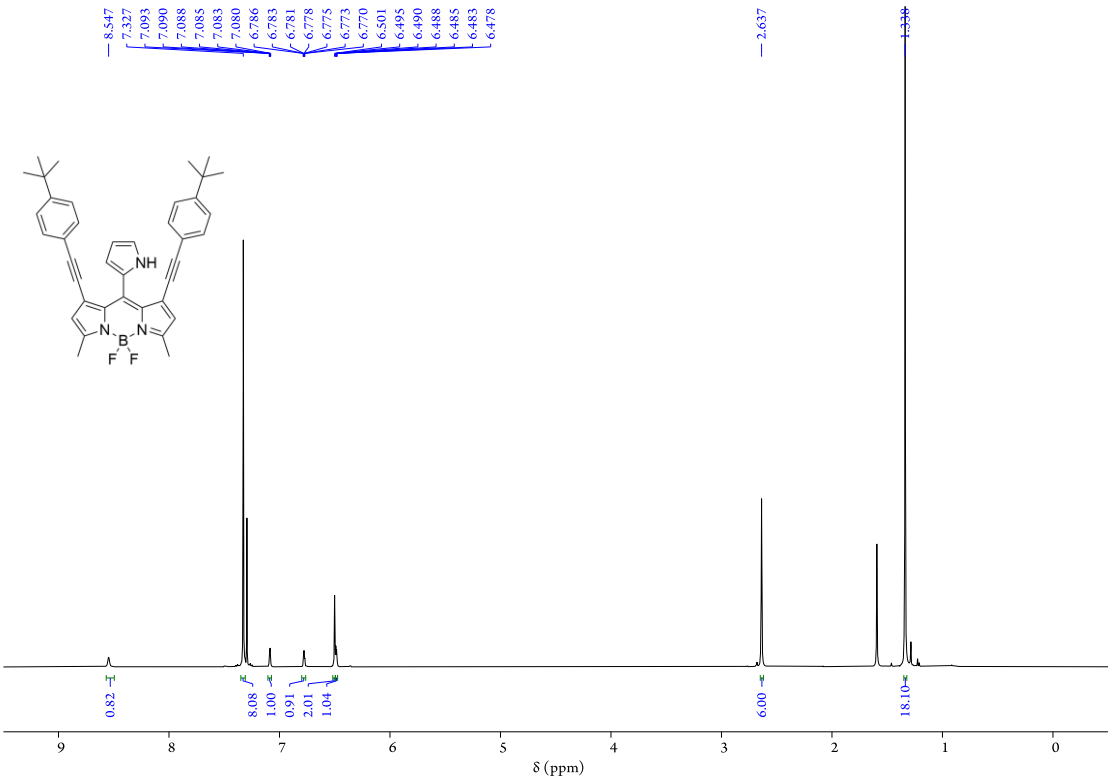


Figure S55. ^{1}H NMR spectrum of **4da** in $CDCl_3$ at 298 K

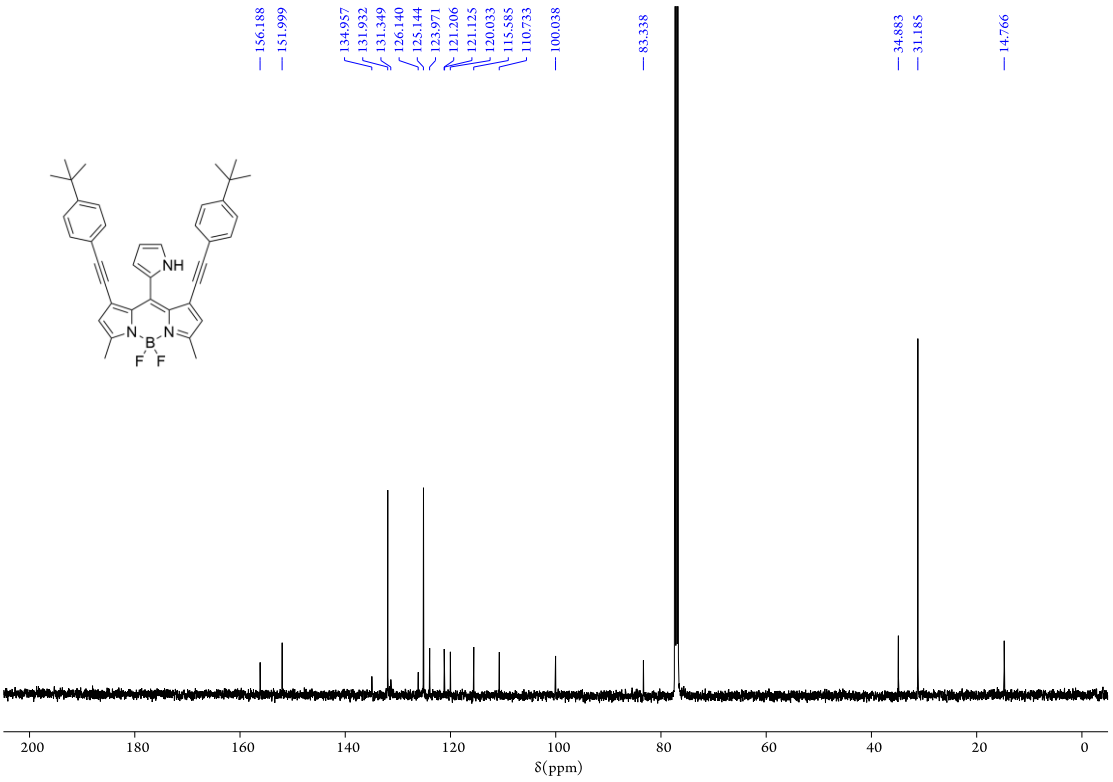


Figure S56. ^{13}C NMR spectrum of **4da** in $CDCl_3$ at 298 K

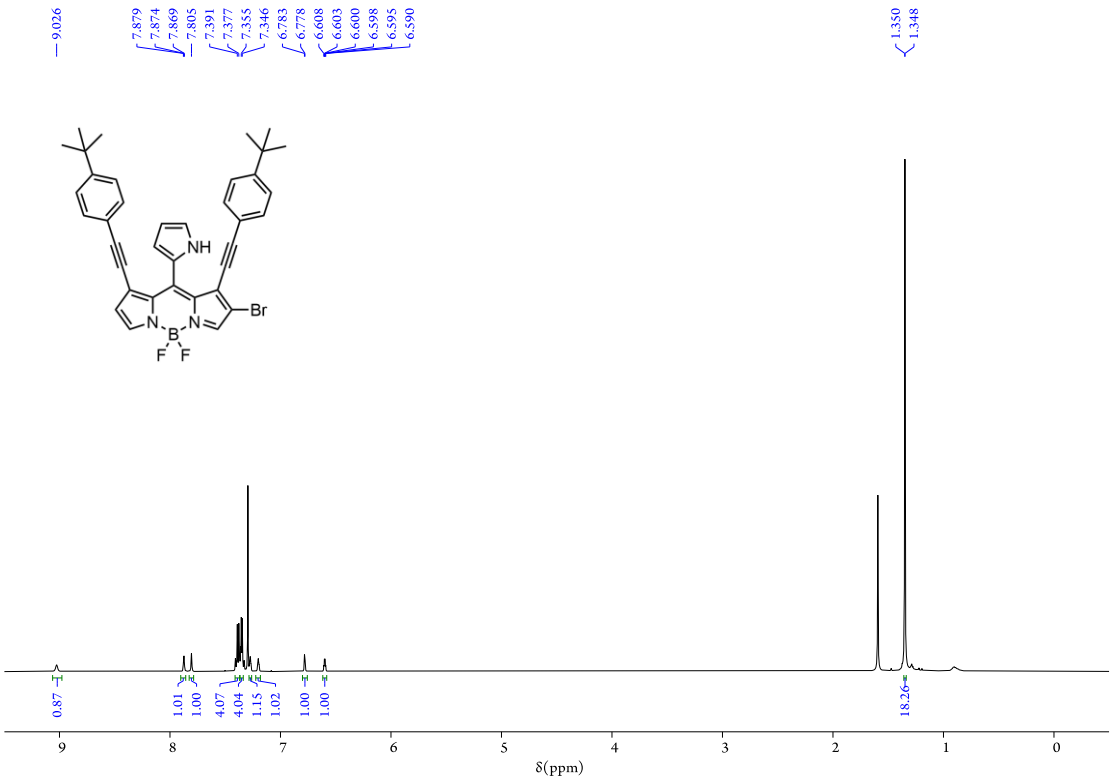


Figure S57. ^{1}H NMR spectrum of **4ea** in $CDCl_3$ at 298 K

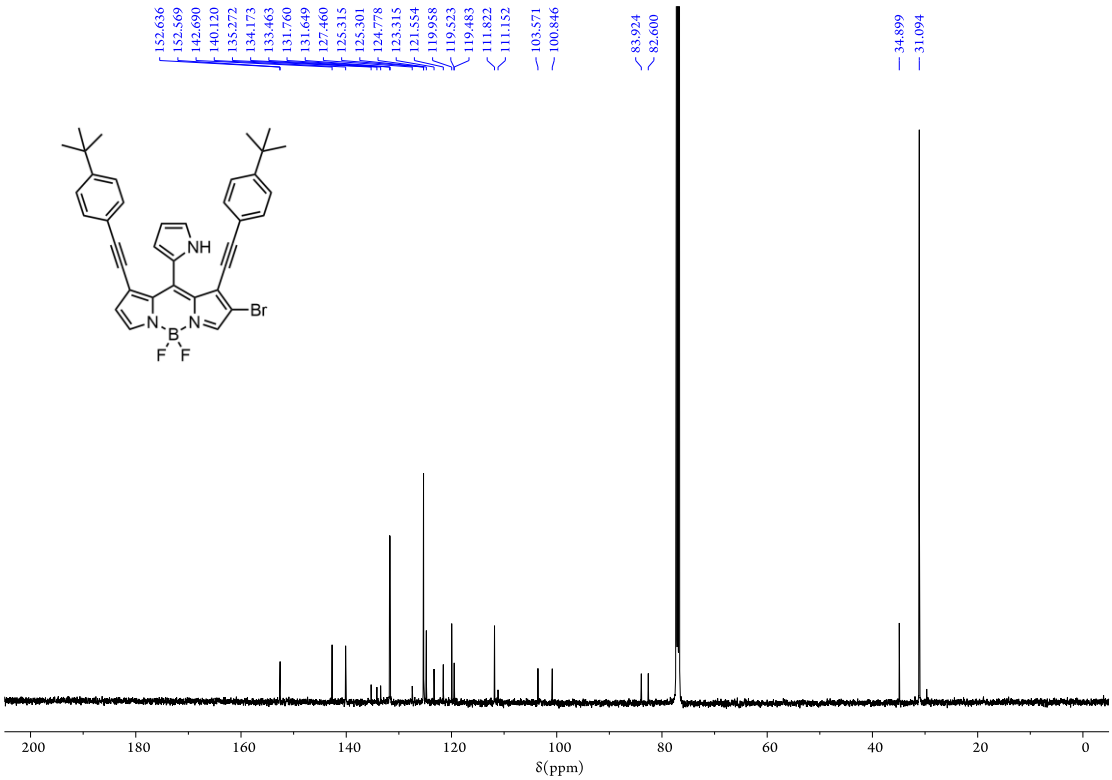


Figure S58. ^{13}C NMR spectrum of **4ea** in $CDCl_3$ at 298 K.

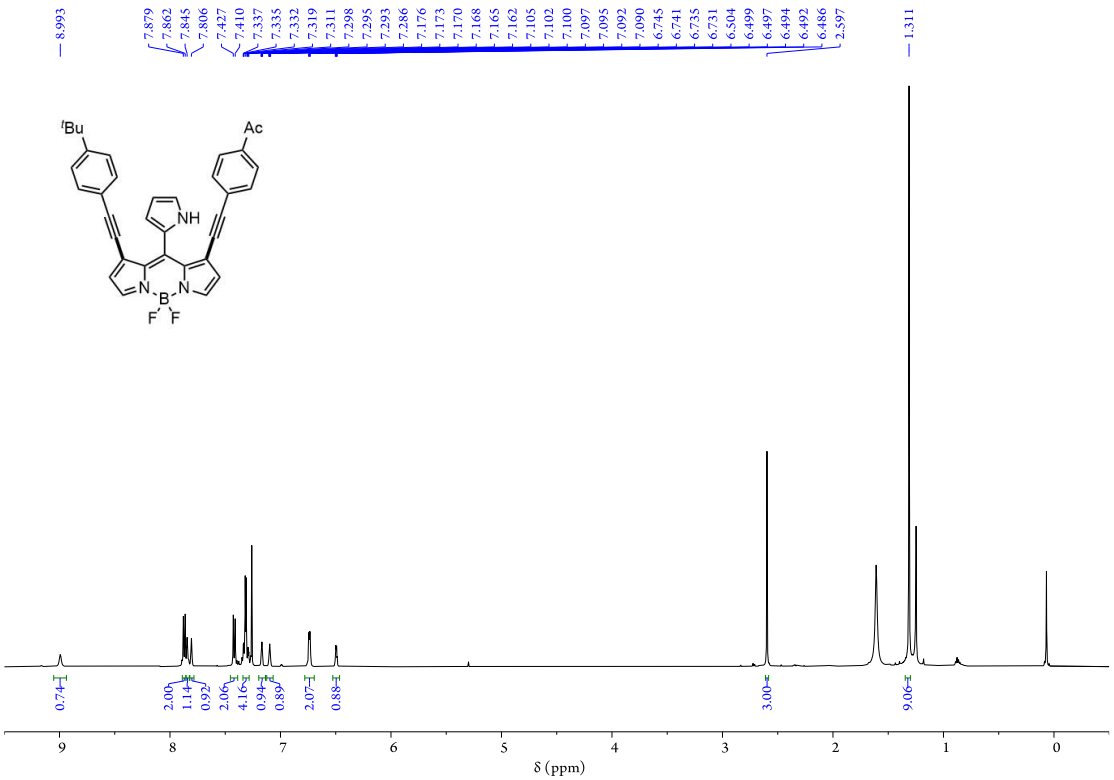


Figure S59. ^{1}H NMR spectrum of **5** in $CDCl_3$ at 298 K

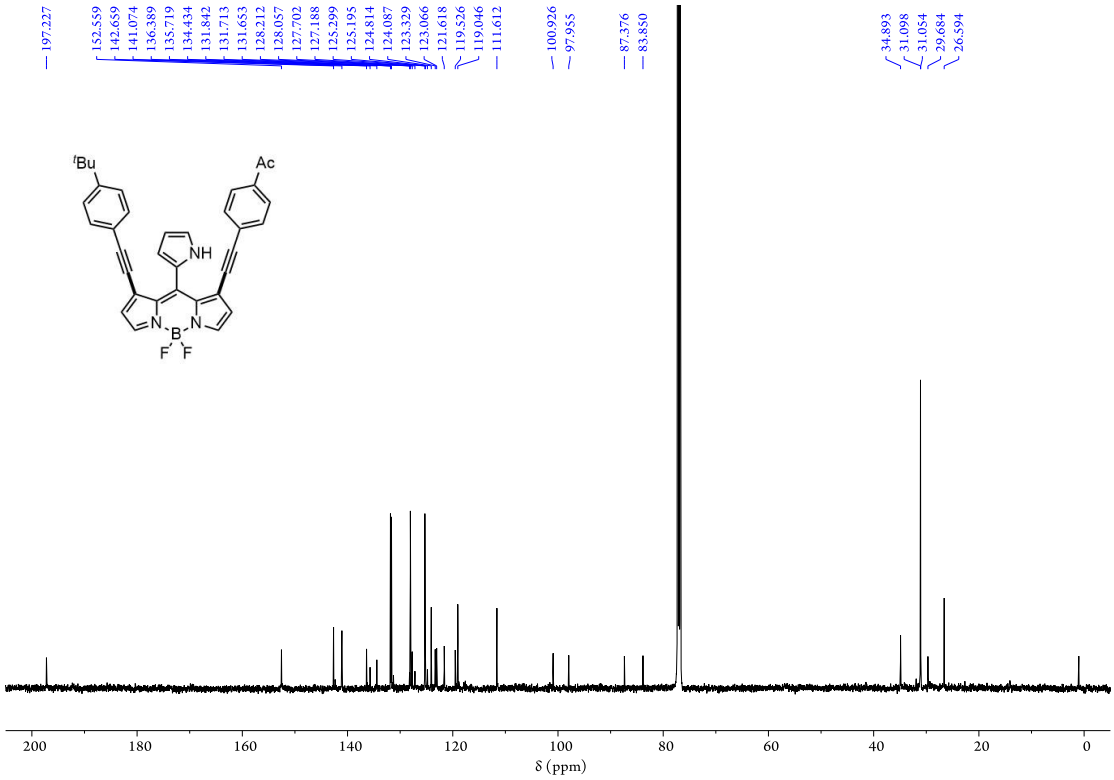


Figure S60. ^{13}C NMR spectrum of **5** in $CDCl_3$ at 298 K

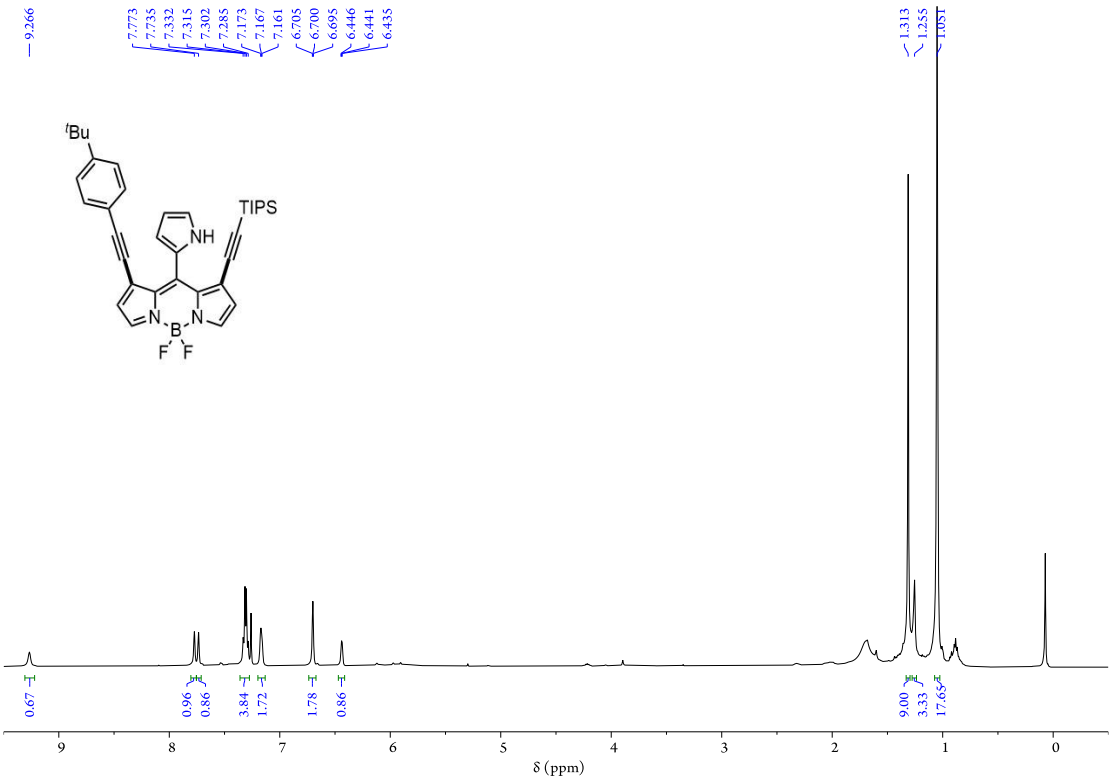


Figure S61. ^{1}H NMR spectrum of **6** in $CDCl_3$ at 298 K

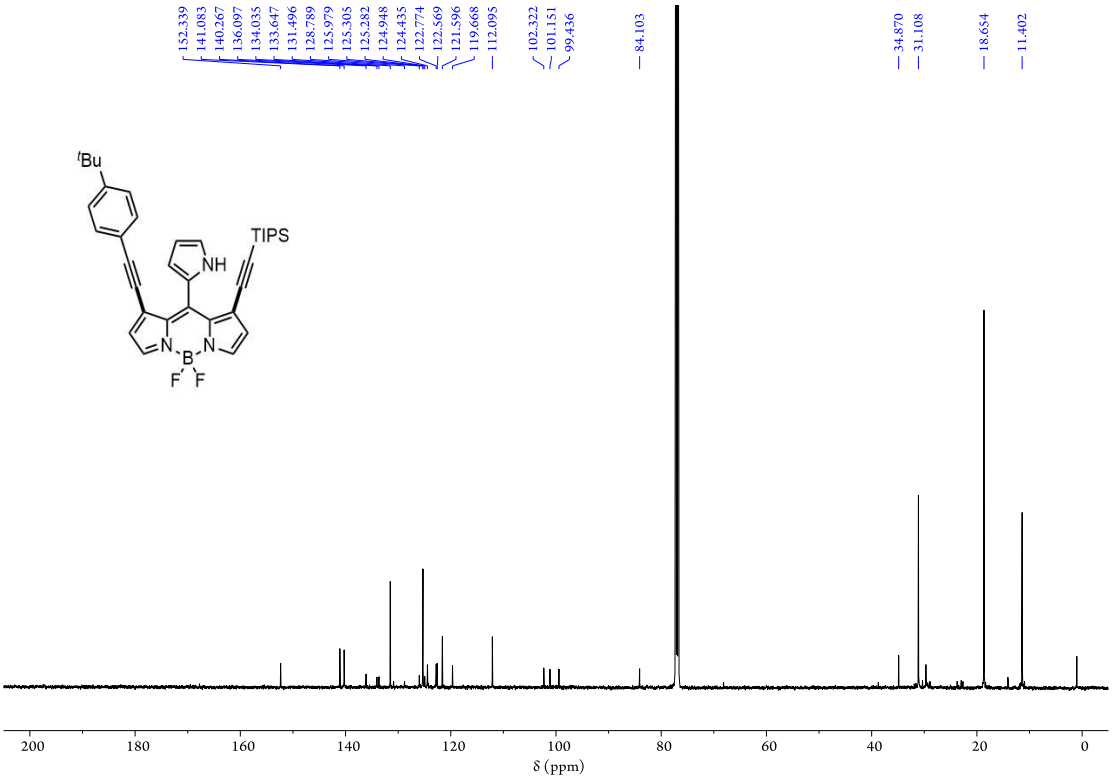


Figure S62. ^{13}C NMR spectrum of **6** in $CDCl_3$ at 298 K

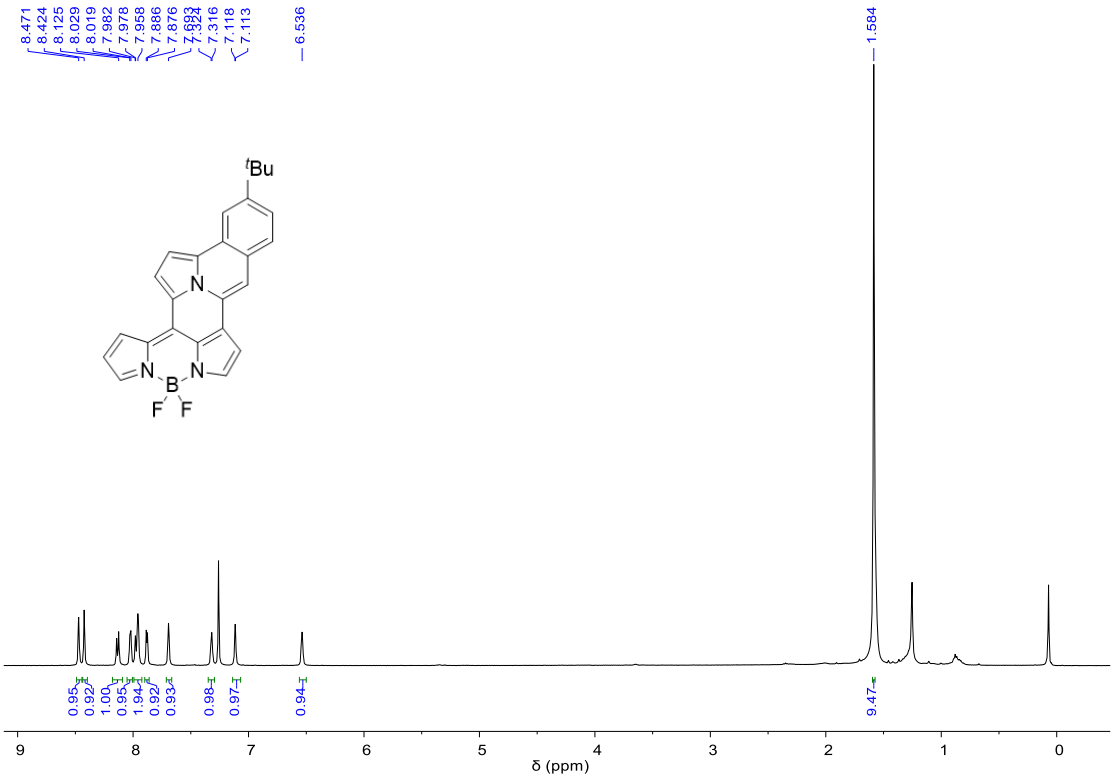


Figure S63. ^{1}H NMR spectrum of **7** in $CDCl_3$ at 298 K.

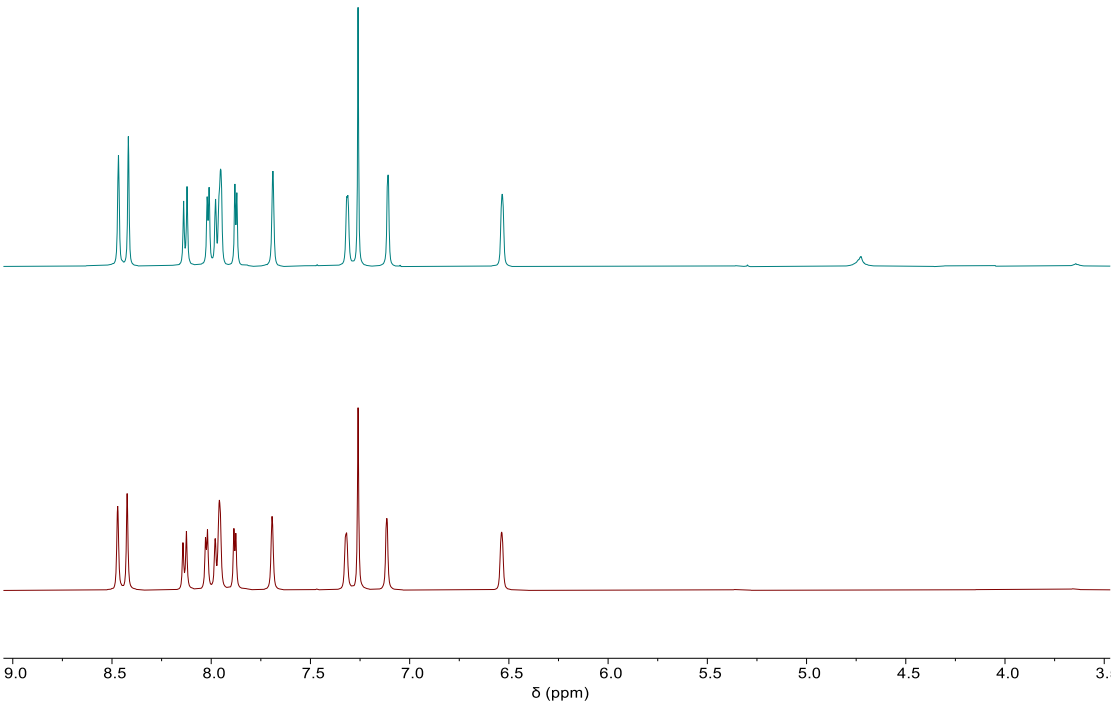


Figure 64. ^{1}H NMR spectra of **7** with D_2O (top) and **7** (bottom) in $CDCl_3$ at 298 K

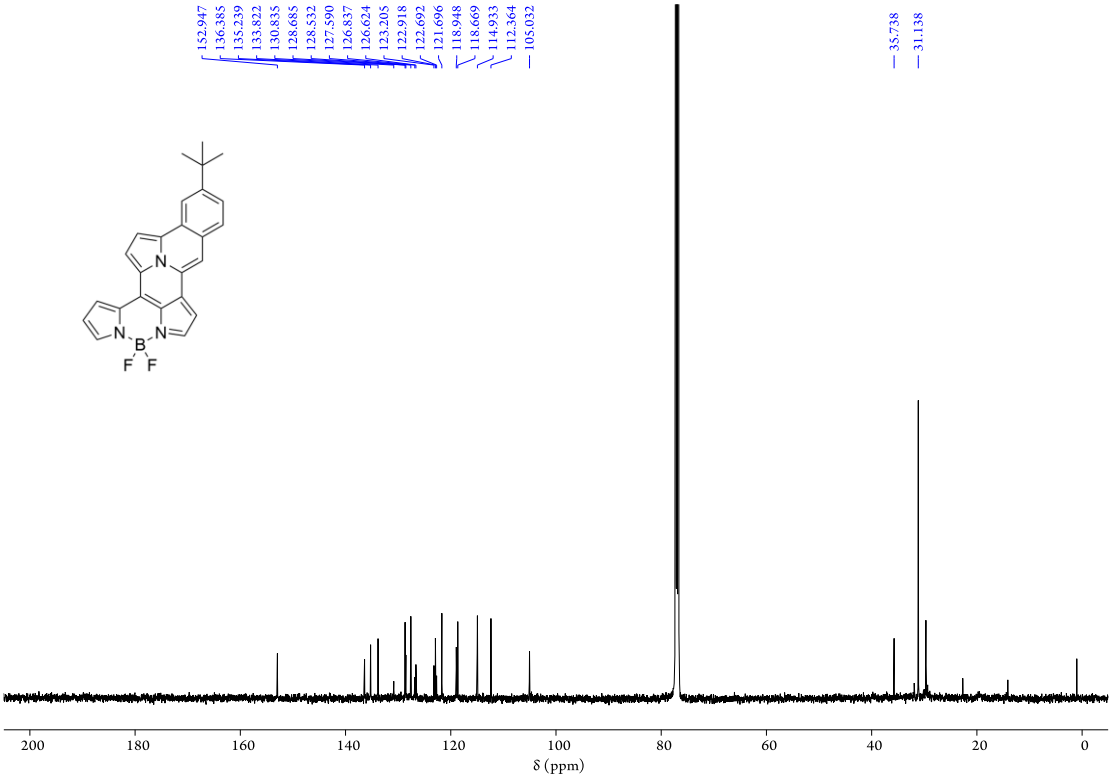


Figure S65. ^{13}C NMR spectrum of **7** in $CDCl_3$ at 298 K.

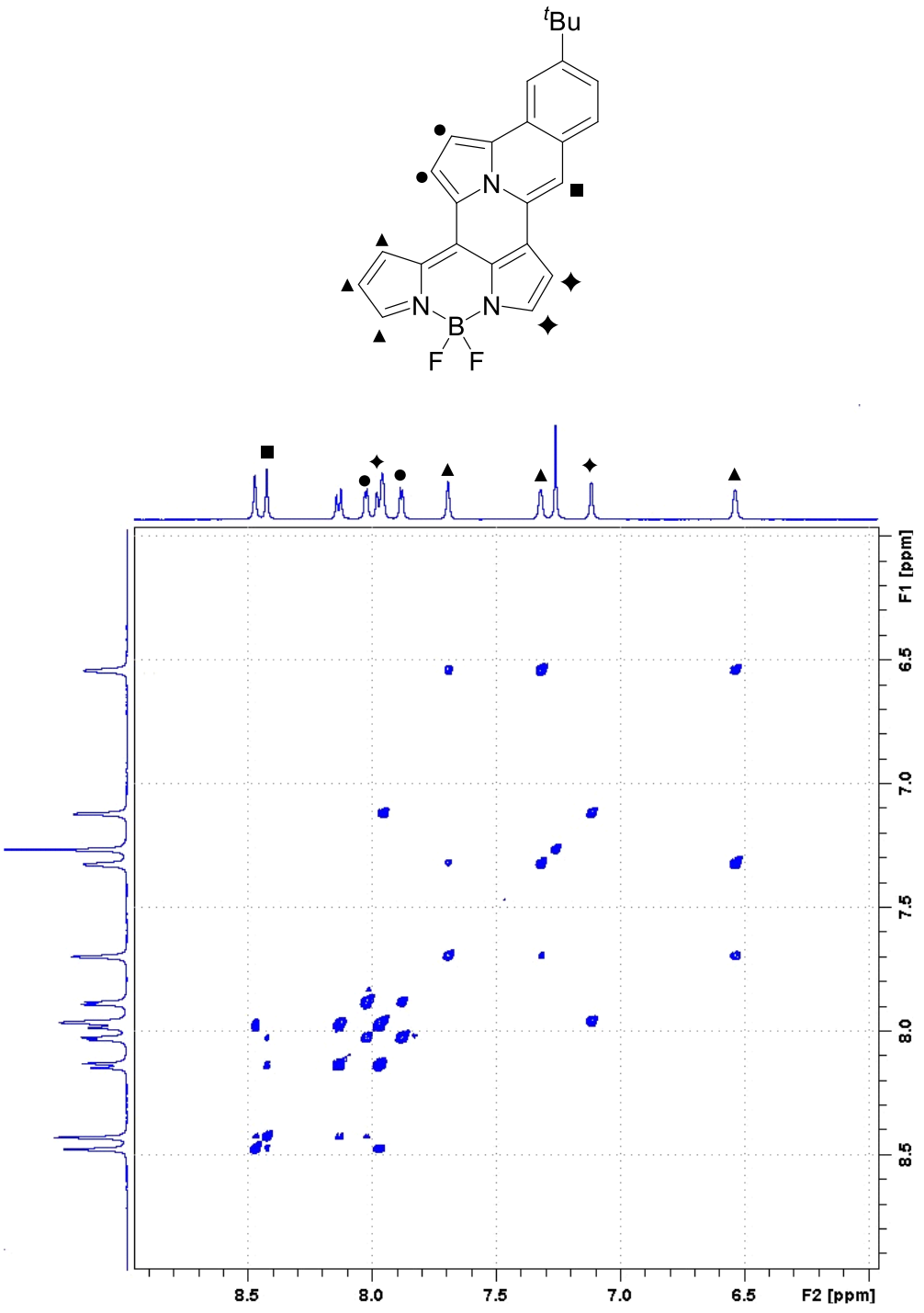


Figure S66. ^{1}H-^{1}H COSY spectrum of **7** in $CDCl_3$ at 298 K

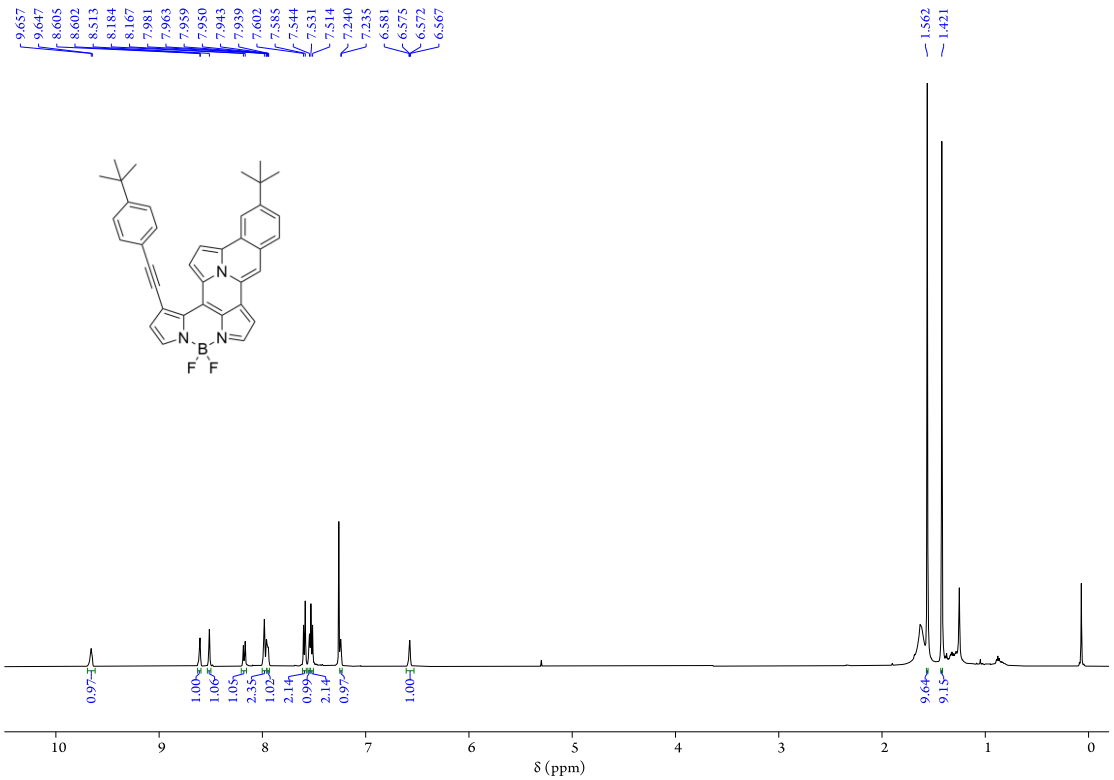


Figure S67. ^{1}H NMR spectrum of **8** in $CDCl_3$ at 298 K.

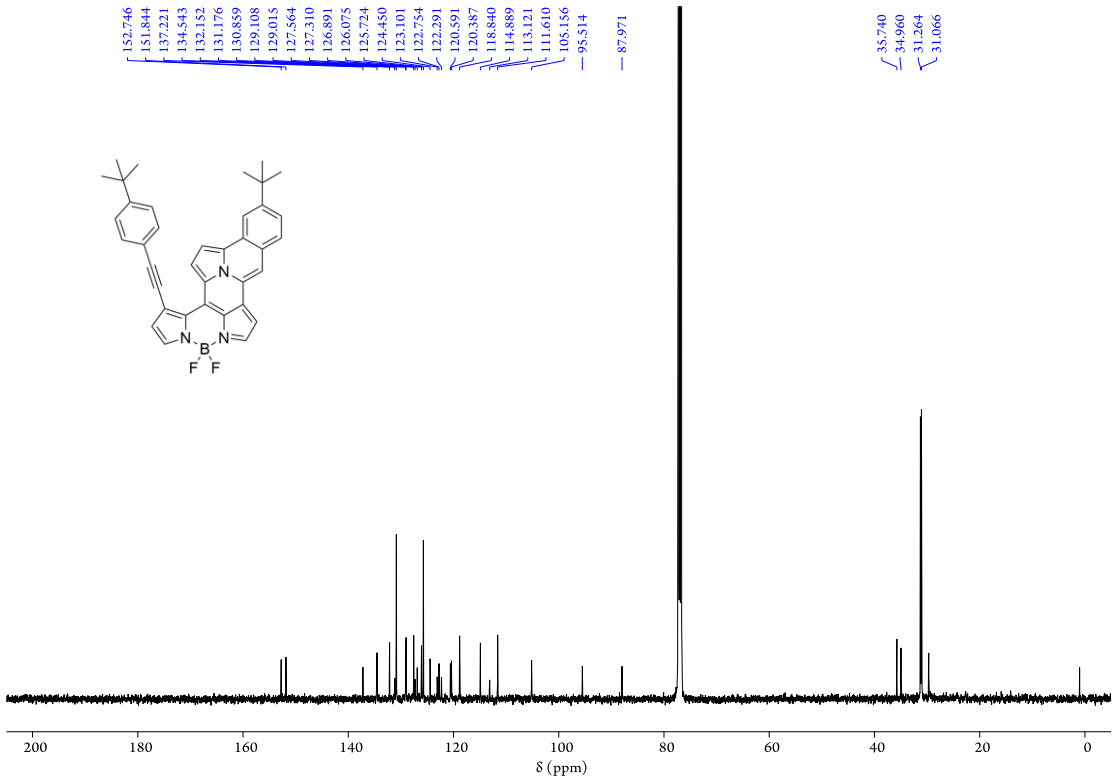


Figure S68. ^{13}C NMR spectrum of **8** in $CDCl_3$ at 298 K.

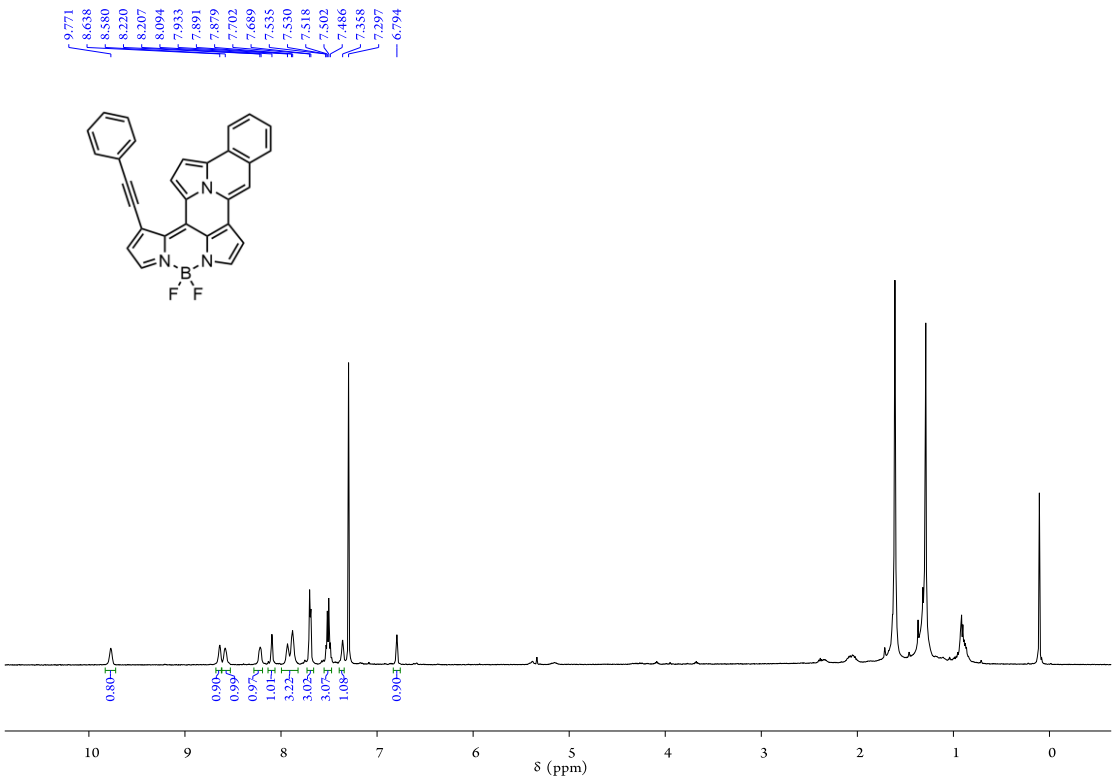


Figure S69. ^{1}H NMR spectrum of **9** in $CDCl_3$ at 298 K.

4. UV/vis absorption and fluorescence spectra and data

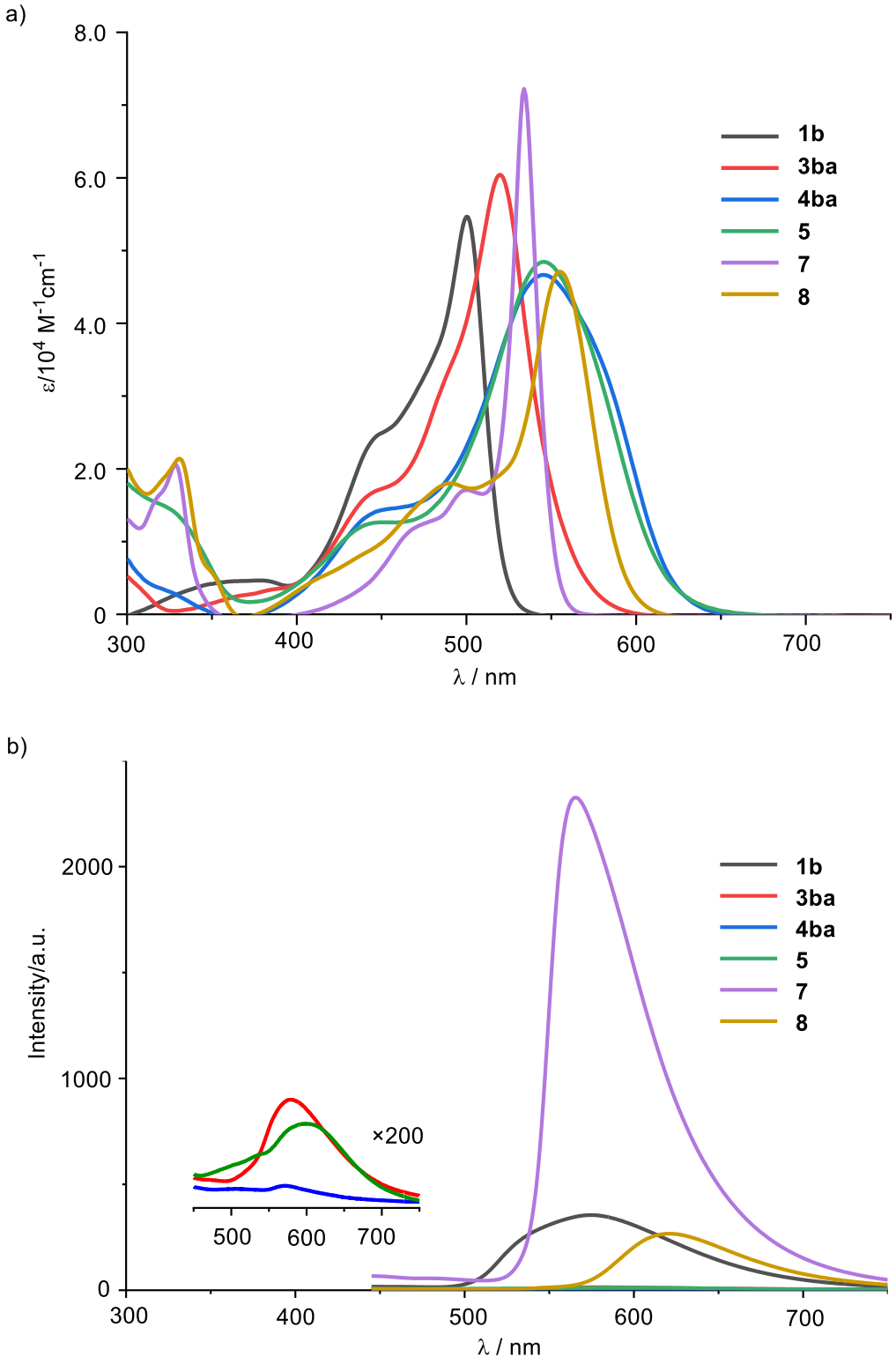


Figure S70. Absorption and fluorescence spectra in CH_2Cl_2.

Table S1. UV/vis absorption and fluorescence spectra data

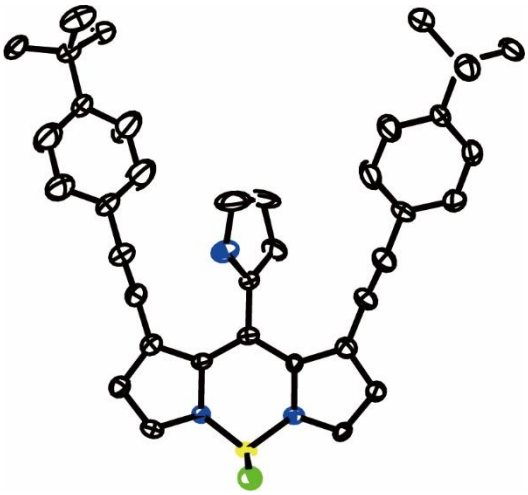
Compound	λ_{abs} /nm ($\varepsilon/10^4 \cdot M^{-1} \cdot cm^{-1}$)	λ_{em} /nm	Φ_F
1b	500 (5.48), 447 (2.45)	575	0.04
3ba	520 (6.04), 447 (1.70)	580	
4ba	545 (4.67), 453 (1.44)	572	
5	545 (4.84), 447 (1.26)	600	
7	534 (7.22), 500 (1.71), 483 (1.31)	566	0.77
8	555 (4.71), 490 (1.80)	621	0.047

Fluorescence quantum yield was obtained by $\Phi_F = S_F/S_R \cdot A_R/A_F \cdot \Phi_R$ (λ_{ex} = 425 nm), here S is the measured integrated emission intensity; A is the optical density; F means sample and R means reference; **1b** was used as the reference (Φ = 0.04 in CH_2Cl_2).[S6, S9]

5. X-ray crystal data

Single crystals of **4ba**, **5**, and **9** was obtained by diffusion of methanol into toluene solution. A suitable crystal was selected and measured on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. The crystal was kept at 100.01(10) K during data collection. Using Olex[S10], the structure was solved with the olex2.solve[S11] structure solution program using Charge Flipping and refined with the ShelXL[S12] refinement package using Least Squares minimization.

a)



b)

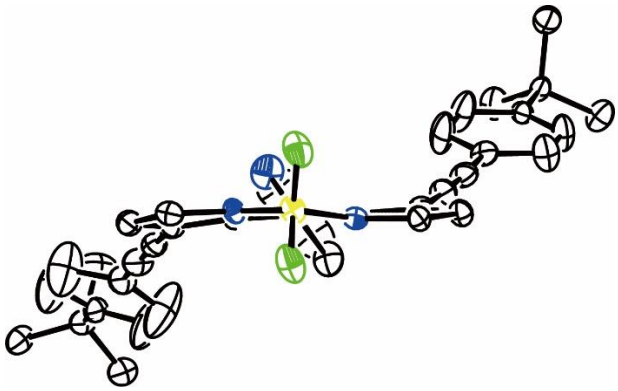


Figure S71. X-ray crystal structure of **4ba**: a) top view, b) side view. The thermal ellipsoids are 50% probability level. H atom and solvent molecules are omitted for clarity.

Table S2. X-ray Crystal Data for **4ba**.

Identification code	exp_2153_sq	
Empirical formula	$C_{37}H_{34}BF_2N_3$	
Formula weight	569.48	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$Pca2_1$	
Unit cell dimensions	a = 38.5907(19) Å	α = 90°.
	b = 6.1918(3) Å	β = 90°.
	c = 29.5351(13) Å	γ = 90°.
Volume	7057.3(6) $Å^3$	
Z	4	
Density (calculated)	1.072 Mg/m^3	
Absorption coefficient	0.556 mm^{-1}	
F(000)	2400	
Crystal size	0.3 x 0.1 x 0.05 mm^3	
Theta range for data collection	2.735 to 71.982°.	
Index ranges	-46<=h<=47, -7<=k<=6, -18<=l<=36	
Reflections collected	16481	
Independent reflections	9240 [R(int) = 0.0422]	
Completeness to theta = 67.684°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.47230	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9240 / 1 / 787	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0620, wR2 = 0.1613	
R indices (all data)	R1 = 0.0775, wR2 = 0.1784	
Absolute structure parameter	0.3(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.281 and -0.266 $e.Å^{-3}$	
CCDC	2374385	

Table S3. bond lengths (Å) and angles (°) for **4ba**

F(1)-B(1)	1.376(7)	C(12)-C(13)	1.418(8)
F(2)-B(1)	1.388(6)	C(13)-C(14)	1.392(8)
N(1)-C(22)	1.381(6)	C(13)-C(16)	1.417(7)
N(1)-C(25)	1.347(6)	C(14)-H(14)	0.9500
N(1)-B(1)	1.561(7)	C(14)-C(15)	1.415(8)
N(2)-C(15)	1.349(6)	C(15)-H(15)	0.9500
N(2)-C(16)	1.398(6)	C(16)-C(17)	1.405(7)
N(2)-B(1)	1.523(7)	C(17)-C(18)	1.458(7)
N(3)-H(3)	0.8800	C(17)-C(22)	1.417(7)
N(3)-C(18)	1.360(7)	C(18)-C(19)	1.394(8)
N(3)-C(21)	1.367(9)	C(19)-H(19)	0.9500
C(1)-H(1A)	0.9800	C(19)-C(20)	1.467(11)
C(1)-H(1B)	0.9800	C(20)-H(20)	0.9500
C(1)-H(1C)	0.9800	C(20)-C(21)	1.303(13)
C(1)-C(4)	1.531(8)	C(21)-H(21)	0.9500
C(2)-H(2A)	0.9800	C(22)-C(23)	1.424(7)
C(2)-H(2B)	0.9800	C(23)-C(24)	1.401(8)
C(2)-H(2C)	0.9800	C(23)-C(26)	1.430(7)
C(2)-C(4)	1.491(8)	C(24)-H(24)	0.9500
C(3)-H(3A)	0.9800	C(24)-C(25)	1.387(7)
C(3)-H(3B)	0.9800	C(25)-H(25)	0.9500
C(3)-H(3C)	0.9800	C(26)-C(27)	1.190(8)
C(3)-C(4)	1.523(9)	C(27)-C(28)	1.437(7)
C(4)-C(5)	1.529(8)	C(28)-C(29)	1.371(9)
C(5)-C(6)	1.352(11)	C(28)-C(30)	1.374(8)
C(5)-C(9)	1.342(10)	C(29)-H(29)	0.9500
C(6)-H(6)	0.9500	C(29)-C(33)	1.392(8)
C(6)-C(7)	1.430(11)	C(30)-H(30)	0.9500
C(7)-H(7)	0.9500	C(30)-C(31)	1.395(8)
C(7)-C(10)	1.363(11)	C(31)-H(31)	0.9500
C(8)-H(8)	0.9500	C(31)-C(32)	1.356(8)
C(8)-C(9)	1.384(11)	C(32)-C(33)	1.370(8)
C(8)-C(10)	1.333(11)	C(32)-C(34)	1.538(7)
C(9)-H(9)	0.9500	C(33)-H(33)	0.9500
C(10)-C(11)	1.447(8)	C(34)-C(35)	1.521(9)
C(11)-C(12)	1.197(8)	C(34)-C(36)	1.551(8)
		C(34)-C(37)	1.537(7)
		C(35)-H(35A)	0.9800

C(35)-H(35B)	0.9800	C(45)-H(45)	0.9500
C(35)-H(35C)	0.9800	C(45)-C(47)	1.368(8)
C(36)-H(36A)	0.9800	C(46)-H(46)	0.9500
C(36)-H(36B)	0.9800	C(46)-C(47)	1.393(8)
C(36)-H(36C)	0.9800	C(47)-C(48)	1.445(7)
C(37)-H(37A)	0.9800	C(48)-C(49)	1.192(7)
C(37)-H(37B)	0.9800	C(49)-C(50)	1.431(7)
C(37)-H(37C)	0.9800	C(50)-C(51)	1.402(7)
F(3)-B(2)	1.375(6)	C(50)-C(53)	1.427(7)
F(4)-B(2)	1.400(7)	C(51)-H(51)	0.9500
N(4)-H(4)	0.8800	C(51)-C(52)	1.389(7)
N(4)-C(55)	1.366(7)	C(52)-H(52)	0.9500
N(4)-C(58)	1.359(9)	C(53)-C(54)	1.388(7)
N(5)-C(60)	1.394(6)	C(54)-C(55)	1.477(7)
N(5)-C(63)	1.356(6)	C(54)-C(60)	1.418(7)
N(5)-B(2)	1.538(7)	C(55)-C(59)	1.375(8)
N(6)-C(52)	1.338(6)	C(56)-H(56A)	0.9800
N(6)-C(53)	1.383(6)	C(56)-H(56B)	0.9800
N(6)-B(2)	1.539(7)	C(56)-H(56C)	0.9800
C(38)-H(38A)	0.9800	C(56)-C(72)	1.534(7)
C(38)-H(38B)	0.9800	C(57)-H(57)	0.9500
C(38)-H(38C)	0.9800	C(57)-C(58)	1.380(13)
C(38)-C(40)	1.534(8)	C(57)-C(59)	1.414(10)
C(39)-H(39A)	0.9800	C(58)-H(58)	0.9500
C(39)-H(39B)	0.9800	C(59)-H(59)	0.9500
C(39)-H(39C)	0.9800	C(60)-C(61)	1.423(7)
C(39)-C(40)	1.512(10)	C(61)-C(62)	1.423(7)
C(40)-C(41)	1.548(9)	C(61)-C(64)	1.408(7)
C(40)-C(42)	1.534(7)	C(62)-H(62)	0.9500
C(41)-H(41A)	0.9800	C(62)-C(63)	1.388(7)
C(41)-H(41B)	0.9800	C(63)-H(63)	0.9500
C(41)-H(41C)	0.9800	C(64)-C(65)	1.203(8)
C(42)-C(43)	1.384(8)	C(65)-C(66)	1.431(8)
C(42)-C(44)	1.394(8)	C(66)-C(67)	1.378(9)
C(43)-H(43)	0.9500	C(66)-C(71)	1.403(8)
C(43)-C(46)	1.382(8)	C(67)-H(67)	0.9500
C(44)-H(44)	0.9500	C(67)-C(68)	1.388(8)
C(44)-C(45)	1.397(8)	C(68)-H(68)	0.9500

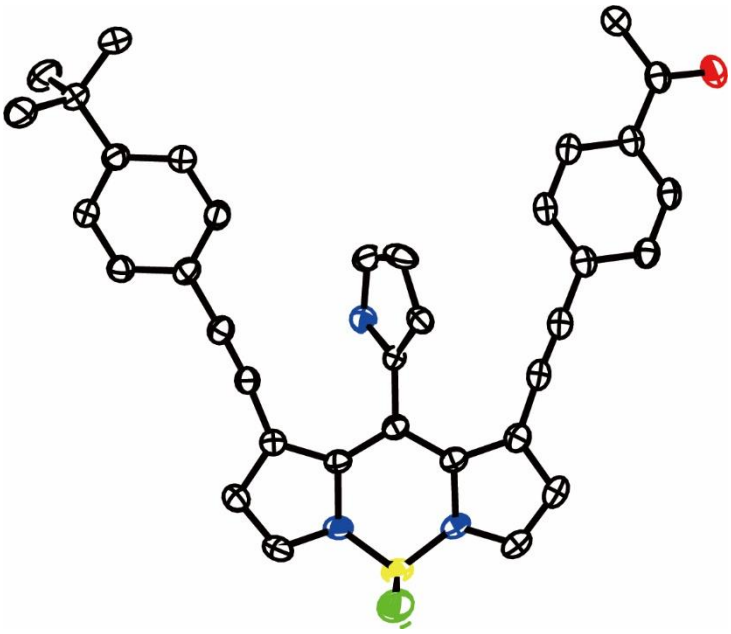
C(68)-C(69)	1.417(7)	C(4)-C(3)-H(3A)	109.5
C(69)-C(70)	1.386(8)	C(4)-C(3)-H(3B)	109.5
C(69)-C(72)	1.537(7)	C(4)-C(3)-H(3C)	109.5
C(70)-H(70)	0.9500	C(2)-C(4)-C(1)	108.1(5)
C(70)-C(71)	1.385(8)	C(2)-C(4)-C(3)	110.5(5)
C(71)-H(71)	0.9500	C(2)-C(4)-C(5)	111.5(5)
C(72)-C(73)	1.521(7)	C(3)-C(4)-C(1)	107.6(6)
C(72)-C(74)	1.544(7)	C(3)-C(4)-C(5)	108.4(5)
C(73)-H(73A)	0.9800	C(5)-C(4)-C(1)	110.7(5)
C(73)-H(73B)	0.9800	C(6)-C(5)-C(4)	122.0(6)
C(73)-H(73C)	0.9800	C(9)-C(5)-C(4)	124.4(6)
C(74)-H(74A)	0.9800	C(9)-C(5)-C(6)	113.5(7)
C(74)-H(74B)	0.9800	C(5)-C(6)-H(6)	118.3
C(74)-H(74C)	0.9800	C(5)-C(6)-C(7)	123.4(8)
C(22)-N(1)-B(1)	125.5(4)	C(7)-C(6)-H(6)	118.3
C(25)-N(1)-C(22)	108.2(4)	C(6)-C(7)-H(7)	120.7
C(25)-N(1)-B(1)	125.2(4)	C(10)-C(7)-C(6)	118.7(8)
C(15)-N(2)-C(16)	107.2(4)	C(10)-C(7)-H(7)	120.7
C(15)-N(2)-B(1)	124.9(4)	C(9)-C(8)-H(8)	119.8
C(16)-N(2)-B(1)	127.5(4)	C(10)-C(8)-H(8)	119.8
C(18)-N(3)-H(3)	125.5	C(10)-C(8)-C(9)	120.4(8)
C(18)-N(3)-C(21)	108.9(6)	C(5)-C(9)-C(8)	125.1(8)
C(21)-N(3)-H(3)	125.5	C(5)-C(9)-H(9)	117.5
H(1A)-C(1)-H(1B)	109.5	C(8)-C(9)-H(9)	117.5
H(1A)-C(1)-H(1C)	109.5	C(7)-C(10)-C(11)	120.6(6)
H(1B)-C(1)-H(1C)	109.5	C(8)-C(10)-C(7)	118.3(7)
C(4)-C(1)-H(1A)	109.5	C(8)-C(10)-C(11)	121.1(6)
C(4)-C(1)-H(1B)	109.5	C(12)-C(11)-C(10)	176.2(7)
C(4)-C(1)-H(1C)	109.5	C(11)-C(12)-C(13)	176.0(6)
H(2A)-C(2)-H(2B)	109.5	C(14)-C(13)-C(12)	125.6(5)
H(2A)-C(2)-H(2C)	109.5	C(14)-C(13)-C(16)	107.8(5)
H(2B)-C(2)-H(2C)	109.5	C(16)-C(13)-C(12)	126.3(5)
C(4)-C(2)-H(2A)	109.5	C(13)-C(14)-H(14)	127.1
C(4)-C(2)-H(2B)	109.5	C(13)-C(14)-C(15)	105.8(5)
C(4)-C(2)-H(2C)	109.5	C(15)-C(14)-H(14)	127.1
H(3A)-C(3)-H(3B)	109.5	N(2)-C(15)-C(14)	111.0(4)
H(3A)-C(3)-H(3C)	109.5	N(2)-C(15)-H(15)	124.5
H(3B)-C(3)-H(3C)	109.5	C(14)-C(15)-H(15)	124.5

N(2)-C(16)-C(13)	108.1(4)	C(28)-C(30)-H(30)	119.8
N(2)-C(16)-C(17)	119.3(4)	C(28)-C(30)-C(31)	120.4(6)
C(17)-C(16)-C(13)	132.6(5)	C(31)-C(30)-H(30)	119.8
C(16)-C(17)-C(18)	120.0(5)	C(30)-C(31)-H(31)	118.7
C(16)-C(17)-C(22)	120.1(4)	C(32)-C(31)-C(30)	122.7(6)
C(22)-C(17)-C(18)	119.9(5)	C(32)-C(31)-H(31)	118.7
N(3)-C(18)-C(17)	124.1(5)	C(31)-C(32)-C(33)	116.3(5)
N(3)-C(18)-C(19)	109.7(5)	C(31)-C(32)-C(34)	123.5(5)
C(19)-C(18)-C(17)	126.2(5)	C(33)-C(32)-C(34)	120.2(5)
C(18)-C(19)-H(19)	128.8	C(29)-C(33)-H(33)	118.8
C(18)-C(19)-C(20)	102.4(7)	C(32)-C(33)-C(29)	122.3(6)
C(20)-C(19)-H(19)	128.8	C(32)-C(33)-H(33)	118.8
C(19)-C(20)-H(20)	124.9	C(32)-C(34)-C(36)	107.4(5)
C(21)-C(20)-C(19)	110.2(7)	C(35)-C(34)-C(32)	112.7(5)
C(21)-C(20)-H(20)	124.9	C(35)-C(34)-C(36)	109.3(5)
N(3)-C(21)-H(21)	125.6	C(35)-C(34)-C(37)	108.3(5)
C(20)-C(21)-N(3)	108.8(7)	C(37)-C(34)-C(32)	110.4(4)
C(20)-C(21)-H(21)	125.6	C(37)-C(34)-C(36)	108.8(5)
N(1)-C(22)-C(17)	120.3(4)	C(34)-C(35)-H(35A)	109.5
N(1)-C(22)-C(23)	107.5(4)	C(34)-C(35)-H(35B)	109.5
C(17)-C(22)-C(23)	132.2(5)	C(34)-C(35)-H(35C)	109.5
C(22)-C(23)-C(26)	128.4(5)	H(35A)-C(35)-H(35B)	109.5
C(24)-C(23)-C(22)	107.0(4)	H(35A)-C(35)-H(35C)	109.5
C(24)-C(23)-C(26)	124.2(5)	H(35B)-C(35)-H(35C)	109.5
C(23)-C(24)-H(24)	126.8	C(34)-C(36)-H(36A)	109.5
C(25)-C(24)-C(23)	106.4(5)	C(34)-C(36)-H(36B)	109.5
C(25)-C(24)-H(24)	126.8	C(34)-C(36)-H(36C)	109.5
N(1)-C(25)-C(24)	110.8(4)	H(36A)-C(36)-H(36B)	109.5
N(1)-C(25)-H(25)	124.6	H(36A)-C(36)-H(36C)	109.5
C(24)-C(25)-H(25)	124.6	H(36B)-C(36)-H(36C)	109.5
C(27)-C(26)-C(23)	173.7(7)	C(34)-C(37)-H(37A)	109.5
C(26)-C(27)-C(28)	176.2(7)	C(34)-C(37)-H(37B)	109.5
C(29)-C(28)-C(27)	120.9(5)	C(34)-C(37)-H(37C)	109.5
C(29)-C(28)-C(30)	117.6(5)	H(37A)-C(37)-H(37B)	109.5
C(30)-C(28)-C(27)	121.5(5)	H(37A)-C(37)-H(37C)	109.5
C(28)-C(29)-H(29)	119.7	H(37B)-C(37)-H(37C)	109.5
C(28)-C(29)-C(33)	120.6(6)	F(1)-B(1)-F(2)	110.2(5)
C(33)-C(29)-H(29)	119.7	F(1)-B(1)-N(1)	109.3(4)

F(1)-B(1)-N(2)	112.3(5)	C(43)-C(42)-C(44)	117.0(5)
F(2)-B(1)-N(1)	108.4(4)	C(44)-C(42)-C(40)	120.2(5)
F(2)-B(1)-N(2)	110.9(5)	C(42)-C(43)-H(43)	119.0
N(2)-B(1)-N(1)	105.5(4)	C(46)-C(43)-C(42)	122.1(6)
C(55)-N(4)-H(4)	125.5	C(46)-C(43)-H(43)	119.0
C(58)-N(4)-H(4)	125.5	C(42)-C(44)-H(44)	119.5
C(58)-N(4)-C(55)	109.0(6)	C(42)-C(44)-C(45)	121.1(6)
C(60)-N(5)-B(2)	125.9(4)	C(45)-C(44)-H(44)	119.5
C(63)-N(5)-C(60)	107.7(4)	C(44)-C(45)-H(45)	119.5
C(63)-N(5)-B(2)	126.2(4)	C(47)-C(45)-C(44)	121.0(5)
C(52)-N(6)-C(53)	109.0(4)	C(47)-C(45)-H(45)	119.5
C(52)-N(6)-B(2)	124.9(4)	C(43)-C(46)-H(46)	119.8
C(53)-N(6)-B(2)	124.8(4)	C(43)-C(46)-C(47)	120.4(6)
H(38A)-C(38)-H(38B)	109.5	C(47)-C(46)-H(46)	119.8
H(38A)-C(38)-H(38C)	109.5	C(45)-C(47)-C(46)	118.4(5)
H(38B)-C(38)-H(38C)	109.5	C(45)-C(47)-C(48)	120.7(5)
C(40)-C(38)-H(38A)	109.5	C(46)-C(47)-C(48)	120.9(5)
C(40)-C(38)-H(38B)	109.5	C(49)-C(48)-C(47)	177.9(6)
C(40)-C(38)-H(38C)	109.5	C(48)-C(49)-C(50)	173.3(6)
H(39A)-C(39)-H(39B)	109.5	C(51)-C(50)-C(49)	123.8(5)
H(39A)-C(39)-H(39C)	109.5	C(51)-C(50)-C(53)	106.7(4)
H(39B)-C(39)-H(39C)	109.5	C(53)-C(50)-C(49)	129.1(5)
C(40)-C(39)-H(39A)	109.5	C(50)-C(51)-H(51)	126.6
C(40)-C(39)-H(39B)	109.5	C(52)-C(51)-C(50)	106.8(5)
C(40)-C(39)-H(39C)	109.5	C(52)-C(51)-H(51)	126.6
C(38)-C(40)-C(41)	106.8(6)	N(6)-C(52)-C(51)	110.3(4)
C(39)-C(40)-C(38)	109.1(5)	N(6)-C(52)-H(52)	124.8
C(39)-C(40)-C(41)	111.3(6)	C(51)-C(52)-H(52)	124.8
C(39)-C(40)-C(42)	108.4(5)	N(6)-C(53)-C(50)	107.1(4)
C(42)-C(40)-C(38)	110.6(5)	N(6)-C(53)-C(54)	121.0(4)
C(42)-C(40)-C(41)	110.7(5)	C(54)-C(53)-C(50)	132.0(5)
C(40)-C(41)-H(41A)	109.5	C(53)-C(54)-C(55)	120.5(5)
C(40)-C(41)-H(41B)	109.5	C(53)-C(54)-C(60)	120.3(4)
C(40)-C(41)-H(41C)	109.5	C(60)-C(54)-C(55)	119.2(4)
H(41A)-C(41)-H(41B)	109.5	N(4)-C(55)-C(54)	124.4(5)
H(41A)-C(41)-H(41C)	109.5	N(4)-C(55)-C(59)	109.0(5)
H(41B)-C(41)-H(41C)	109.5	C(59)-C(55)-C(54)	126.6(5)
C(43)-C(42)-C(40)	122.7(5)	H(56A)-C(56)-H(56B)	109.5

H(56A)-C(56)-H(56C)	109.5	C(70)-C(69)-C(68)	117.2(5)
H(56B)-C(56)-H(56C)	109.5	C(70)-C(69)-C(72)	123.8(5)
C(72)-C(56)-H(56A)	109.5	C(69)-C(70)-H(70)	119.1
C(72)-C(56)-H(56B)	109.5	C(71)-C(70)-C(69)	121.9(5)
C(72)-C(56)-H(56C)	109.5	C(71)-C(70)-H(70)	119.1
C(58)-C(57)-H(57)	126.2	C(66)-C(71)-H(71)	119.8
C(58)-C(57)-C(59)	107.7(6)	C(70)-C(71)-C(66)	120.5(5)
C(59)-C(57)-H(57)	126.2	C(70)-C(71)-H(71)	119.8
N(4)-C(58)-C(57)	108.1(7)	C(56)-C(72)-C(69)	112.5(4)
N(4)-C(58)-H(58)	126.0	C(56)-C(72)-C(74)	107.4(4)
C(57)-C(58)-H(58)	126.0	C(69)-C(72)-C(74)	109.1(4)
C(55)-C(59)-C(57)	106.3(6)	C(73)-C(72)-C(56)	108.6(4)
C(55)-C(59)-H(59)	126.9	C(73)-C(72)-C(69)	109.0(4)
C(57)-C(59)-H(59)	126.9	C(73)-C(72)-C(74)	110.2(4)
N(5)-C(60)-C(54)	119.5(4)	C(72)-C(73)-H(73A)	109.5
N(5)-C(60)-C(61)	108.2(4)	C(72)-C(73)-H(73B)	109.5
C(54)-C(60)-C(61)	132.3(5)	C(72)-C(73)-H(73C)	109.5
C(62)-C(61)-C(60)	106.4(4)	H(73A)-C(73)-H(73B)	109.5
C(64)-C(61)-C(60)	128.4(5)	H(73A)-C(73)-H(73C)	109.5
C(64)-C(61)-C(62)	125.0(5)	H(73B)-C(73)-H(73C)	109.5
C(61)-C(62)-H(62)	126.7	C(72)-C(74)-H(74A)	109.5
C(63)-C(62)-C(61)	106.5(4)	C(72)-C(74)-H(74B)	109.5
C(63)-C(62)-H(62)	126.7	C(72)-C(74)-H(74C)	109.5
N(5)-C(63)-C(62)	111.0(4)	H(74A)-C(74)-H(74B)	109.5
N(5)-C(63)-H(63)	124.5	H(74A)-C(74)-H(74C)	109.5
C(62)-C(63)-H(63)	124.5	H(74B)-C(74)-H(74C)	109.5
C(65)-C(64)-C(61)	177.3(6)	F(3)-B(2)-F(4)	109.0(4)
C(64)-C(65)-C(66)	177.4(6)	F(3)-B(2)-N(5)	110.0(4)
C(67)-C(66)-C(65)	119.5(5)	F(3)-B(2)-N(6)	111.7(4)
C(67)-C(66)-C(71)	118.4(5)	F(4)-B(2)-N(5)	110.1(4)
C(71)-C(66)-C(65)	122.1(5)	F(4)-B(2)-N(6)	109.4(4)
C(66)-C(67)-H(67)	119.4	N(5)-B(2)-N(6)	106.5(4)
C(66)-C(67)-C(68)	121.2(5)		
C(68)-C(67)-H(67)	119.4		
C(67)-C(68)-H(68)	119.6		
C(67)-C(68)-C(69)	120.8(5)		
C(69)-C(68)-H(68)	119.6		
C(68)-C(69)-C(72)	119.1(5)		

a)



b)

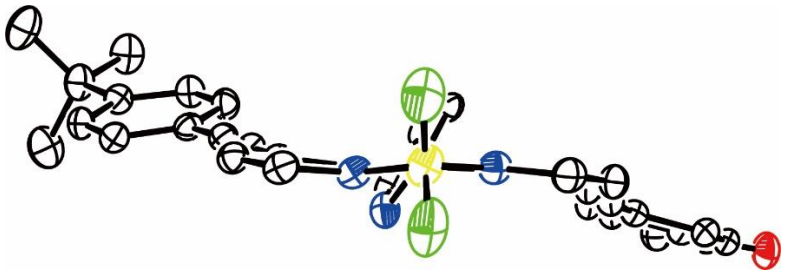


Figure S72. X-ray crystal structure of **5**: a) top view, b) side view. The thermal ellipsoids are 50% probability level. H atom and solvent molecules are omitted for clarity.

Table S4. X-ray Crystal Data for **5**.

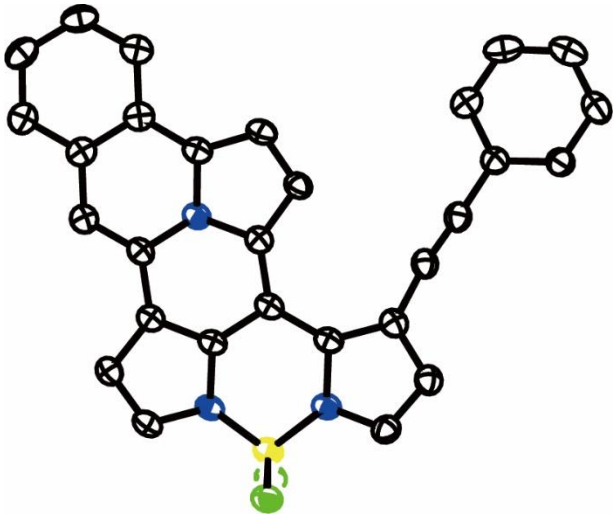
Identification code	exp_3434	
Empirical formula	$C_{35}H_{28}BF_2N_3O$	
Formula weight	555.41	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9099(2) Å	α= 69.706(2)°.
	b = 11.4408(3) Å	β= 87.070(2)°.
	c = 13.8879(3) Å	γ = 78.071(2)°.
Volume	1444.57(6) $Å^3$	
Z	2	
Density (calculated)	1.277 Mg/m^3	
Absorption coefficient	0.696 mm^{-1}	
F(000)	580	
Crystal size	0.3 x 0.1 x 0.1 mm^3	
Theta range for data collection	3.394 to 66.571°.	
Index ranges	-11<=h<=11, -13<=k<=13, -16<=l<=16	
Reflections collected	18263	
Independent reflections	5097 [R(int) = 0.0180]	
Completeness to theta = 66.571°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.83801	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5097 / 12 / 383	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.1017	
R indices (all data)	R1 = 0.0433, wR2 = 0.1038	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.342 and -0.296 $e.Å^{-3}$	
CCDC	2374386	

Table S5. bond lengths (Å) and angles (°) for **5**

F(1)-B(015)	1.379(2)	C(2)-C(1)	1.383(2)
F(2)-B(015)	1.385(2)	C(10)-C(9)	1.400(2)
O(1)-C(34)	1.2231(18)	C(10)-C(11)	1.393(2)
N(2)-C(4)	1.3915(17)	C(10)-C(13)	1.532(2)
N(2)-C(1)	1.344(2)	C(34)-C(35)	1.498(2)
N(2)-B(015)	1.539(2)	C(12)-C(11)	1.388(2)
N(1)-C(22)	1.3915(18)	C(24)-C(23)	1.378(2)
N(1)-C(23)	1.344(2)	C(13)-C(14)	1.532(2)
N(1)-B(015)	1.545(2)	C(13)-C(16)	1.537(2)
N(3)-C(18)	1.3754(19)	C(13)-C(15)	1.530(2)
N(3)-C(20)	1.357(2)	C(20)-C(19)	1.356(3)
C(0AA)-C(4)	1.426(2)	C(4)-N(2)-B(015)	125.98(13)
C(0AA)-C(5)	1.4197(19)	C(1)-N(2)-C(4)	108.31(12)
C(0AA)-C(2)	1.401(2)	C(1)-N(2)-B(015)	124.21(13)
C(17)-C(4)	1.407(2)	C(22)-N(1)-B(015)	125.92(13)
C(17)-C(18)	1.4606(19)	C(23)-N(1)-C(22)	108.16(13)
C(17)-C(22)	1.404(2)	C(23)-N(1)-B(015)	125.72(13)
C(18)-C(21)	1.374(2)	C(20)-N(3)-C(18)	109.15(14)
C(22)-C(25)	1.428(2)	C(5)-C(0AA)-C(4)	129.24(13)
C(5)-C(6)	1.200(2)	C(2)-C(0AA)-C(4)	106.91(12)
C(21)-C(19)	1.424(2)	C(2)-C(0AA)-C(5)	123.83(13)
C(28)-C(33)	1.405(2)	C(4)-C(17)-C(18)	120.05(12)
C(28)-C(26)	1.430(2)	C(22)-C(17)-C(4)	119.95(13)
C(28)-C(29)	1.392(2)	C(22)-C(17)-C(18)	119.97(13)
C(32)-C(31)	1.392(2)	N(2)-C(4)-C(0AA)	107.15(12)
C(32)-C(33)	1.376(2)	N(2)-C(4)-C(17)	120.40(13)
C(27)-C(26)	1.202(2)	C(17)-C(4)-C(0AA)	132.28(13)
C(27)-C(25)	1.414(2)	N(3)-C(18)-C(17)	124.28(13)
C(31)-C(30)	1.398(2)	C(21)-C(18)-N(3)	108.59(13)
C(31)-C(34)	1.490(2)	C(21)-C(18)-C(17)	126.95(13)
C(6)-C(7)	1.432(2)	N(1)-C(22)-C(17)	120.76(13)
C(30)-C(29)	1.380(2)	N(1)-C(22)-C(25)	107.31(12)
C(7)-C(8)	1.402(2)	C(17)-C(22)-C(25)	131.70(13)
C(7)-C(12)	1.395(2)	C(6)-C(5)-C(0AA)	174.60(15)
C(8)-C(9)	1.381(2)	C(18)-C(21)-C(19)	105.54(14)
C(25)-C(24)	1.398(2)	C(33)-C(28)-C(26)	120.47(14)
		C(29)-C(28)-C(33)	118.92(14)
		C(29)-C(28)-C(26)	120.61(13)

C(33)-C(32)-C(31)	120.95(13)	F(1)-B(015)-F(2)	109.77(14)
C(26)-C(27)-C(25)	174.98(16)	F(1)-B(015)-N(2)	110.25(15)
C(32)-C(31)-C(30)	118.81(14)	F(1)-B(015)-N(1)	110.54(14)
C(32)-C(31)-C(34)	119.61(13)	F(2)-B(015)-N(2)	109.72(14)
C(30)-C(31)-C(34)	121.56(14)	F(2)-B(015)-N(1)	110.39(15)
C(32)-C(33)-C(28)	120.19(14)	N(2)-B(015)-N(1)	106.12(12)
C(5)-C(6)-C(7)	178.00(16)	F(001)-B(00U)-N(005)	111.3(5)
C(27)-C(26)-C(28)	177.42(16)	F(002)-B(00U)-F(001)	109.4(5)
C(29)-C(30)-C(31)	120.56(14)	F(002)-B(00U)-N(004)	110.2(5)
C(8)-C(7)-C(6)	119.77(13)	F(002)-B(00U)-N(005)	111.5(5)
C(12)-C(7)-C(6)	121.93(14)	N(005)-B(00U)-N(004)	104.9(5)
C(12)-C(7)-C(8)	118.27(13)	C(2)-C(1)-C(6)	109.3(12)
C(9)-C(8)-C(7)	120.49(14)	C(2)-C(1)-C(9)	114.0(14)
C(27)-C(25)-C(22)	128.27(14)	C(2)-C(1)-C(0AA)	108.2(13)
C(24)-C(25)-C(22)	106.50(13)	C(9)-C(1)-C(6)	102.9(12)
C(24)-C(25)-C(27)	124.98(14)	C(0AA)-C(1)-C(6)	109.1(13)
C(1)-C(2)-C(0AA)	106.87(13)	C(0AA)-C(1)-C(9)	113.1(14)
N(2)-C(1)-C(2)	110.75(13)	C(7)-C(8)-C(6)	120.0
C(9)-C(10)-C(13)	119.64(13)	C(00Z)-C(7)-C(8)	120.0
C(11)-C(10)-C(9)	117.19(13)	C(7)-C(00Z)-C(00T)	120.3(6)
C(11)-C(10)-C(13)	123.16(13)	C(7)-C(00Z)-C(00Y)	120.0
O(1)-C(34)-C(31)	119.98(14)	C(00Y)-C(00Z)-C(00T)	119.6(6)
O(1)-C(34)-C(35)	120.62(14)	C(00Z)-C(00Y)-C(011)	120.0
C(31)-C(34)-C(35)	119.38(13)	C(6)-C(011)-C(00Y)	120.0
C(11)-C(12)-C(7)	120.50(14)	C(8)-C(6)-C(1)	123.4(9)
C(8)-C(9)-C(10)	121.74(14)	C(011)-C(6)-C(1)	116.5(9)
C(30)-C(29)-C(28)	120.56(14)	C(011)-C(6)-C(8)	120.0
C(12)-C(11)-C(10)	121.74(14)		
C(23)-C(24)-C(25)	107.35(14)		
N(1)-C(23)-C(24)	110.67(13)		
C(10)-C(13)-C(16)	109.15(13)		
C(14)-C(13)-C(10)	111.89(13)		
C(14)-C(13)-C(16)	108.05(14)		
C(15)-C(13)-C(10)	109.36(14)		
C(15)-C(13)-C(14)	108.80(14)		
C(15)-C(13)-C(16)	109.56(15)		
C(19)-C(20)-N(3)	108.01(14)		
C(20)-C(19)-C(21)	108.67(14)		

a)



b)

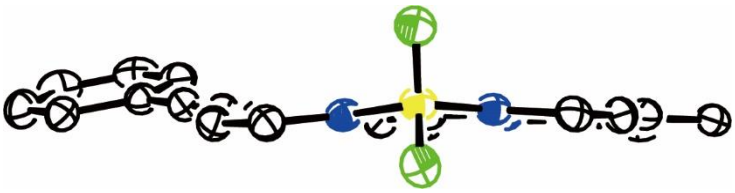


Figure S73. X-ray crystal structure of **9**: a) top view, b) side view. The thermal ellipsoids are 50% probability level. H atom and solvent molecules are omitted for clarity.

Table S6. X-ray Crystal Data for **9**.

Identification code	exp_1730	
Empirical formula	$C_{37}H_{32}BF_2N_3$	
Formula weight	567.26	
Temperature	100.3(8) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 14.2196(5) Å	α = 90°.
	b = 7.5050(2) Å	β = 109.003(4)°.
	c = 20.4147(7) Å	γ = 90°.
Volume	2059.89(12) $Å^3$	
Z	4	
Density (calculated)	1.468 Mg/m^3	
Absorption coefficient	0.811 mm^{-1}	
F(000)	936	
Crystal size	0.3 x 0.2 x 0.1 mm^3	
Theta range for data collection	3.287 to 66.576°.	
Index ranges	-11<=h<=16, -8<=k<=8, -24<=l<=19	
Reflections collected	7016	
Independent reflections	3627 [R(int) = 0.0308]	
Completeness to theta = 66.576°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.76303	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3627 / 0 / 316	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0481, wR2 = 0.1189	
R indices (all data)	R1 = 0.0631, wR2 = 0.1301	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.302 and -0.252 $e.Å^{-3}$	
CCDC	2374387	

Table S7. bond lengths (Å) and angles (°) for **9**

F(2)-B(1)	1.385(3)	C(20)-C(19)	1.365(3)
F(1)-B(1)	1.391(3)	C(23)-H(23)	0.9300
N(2)-C(4)	1.369(2)	C(23)-C(24)	1.364(3)
N(2)-C(1)	1.358(3)	C(8)-H(8)	0.9300
N(2)-B(1)	1.537(3)	C(8)-C(9)	1.369(3)
N(3)-C(18)	1.405(3)	C(9)-H(9)	0.9300
N(3)-C(21)	1.379(3)	C(2)-H(2)	0.9300
N(3)-C(29)	1.396(3)	C(19)-H(19)	0.9300
N(1)-C(6)	1.393(2)	C(13)-H(13)	0.9300
N(1)-C(9)	1.348(3)	C(13)-C(14)	1.385(3)
N(1)-B(1)	1.554(3)	C(17)-H(17)	0.9300
C(4)-C(0AA)	1.400(3)	C(17)-C(16)	1.381(3)
C(4)-C(5)	1.421(3)	C(26)-H(26)	0.9300
C(0AA)-C(29)	1.424(3)	C(26)-C(25)	1.369(3)
C(0AA)-C(2)	1.414(3)	C(25)-H(25)	0.9300
C(6)-C(5)	1.440(3)	C(25)-C(24)	1.418(3)
C(6)-C(7)	1.420(3)	C(24)-H(24)	0.9300
C(18)-C(5)	1.415(3)	C(14)-H(14)	0.9300
C(18)-C(19)	1.410(3)	C(14)-C(15)	1.382(4)
C(21)-C(22)	1.421(3)	C(16)-H(16)	0.9300
C(21)-C(20)	1.408(3)	C(16)-C(15)	1.379(4)
C(29)-C(28)	1.371(3)	C(15)-H(15)	0.9300
C(22)-C(27)	1.426(3)		
C(22)-C(23)	1.407(3)	C(4)-N(2)-B(1)	123.99(17)
C(27)-C(28)	1.414(3)	C(1)-N(2)-C(4)	107.06(17)
C(27)-C(26)	1.417(3)	C(1)-N(2)-B(1)	128.95(17)
C(12)-C(11)	1.432(3)	C(21)-N(3)-C(18)	110.15(17)
C(12)-C(13)	1.403(3)	C(21)-N(3)-C(29)	122.89(18)
C(12)-C(17)	1.395(3)	C(29)-N(3)-C(18)	126.91(17)
C(1)-H(1)	0.9300	C(6)-N(1)-B(1)	128.76(17)
C(1)-C(2)	1.367(3)	C(9)-N(1)-C(6)	109.04(17)
C(10)-C(7)	1.414(3)	C(9)-N(1)-B(1)	121.95(17)
C(10)-C(11)	1.208(3)	N(2)-C(4)-C(0AA)	108.89(17)
C(7)-C(8)	1.406(3)	N(2)-C(4)-C(5)	125.07(19)
C(28)-H(28)	0.9300	C(0AA)-C(4)-C(5)	125.97(19)
C(20)-H(20)	0.9300	C(4)-C(0AA)-C(29)	120.02(18)
		C(4)-C(0AA)-C(2)	106.72(18)
		C(2)-C(0AA)-C(29)	133.23(19)

N(1)-C(6)-C(5)	117.83(17)	C(22)-C(23)-H(23)	119.8
N(1)-C(6)-C(7)	106.55(17)	C(24)-C(23)-C(22)	120.4(2)
C(7)-C(6)-C(5)	135.45(18)	C(24)-C(23)-H(23)	119.8
N(3)-C(18)-C(5)	119.76(18)	C(7)-C(8)-H(8)	126.2
N(3)-C(18)-C(19)	104.93(17)	C(9)-C(8)-C(7)	107.63(19)
C(19)-C(18)-C(5)	135.3(2)	C(9)-C(8)-H(8)	126.2
C(4)-C(5)-C(6)	117.60(18)	N(1)-C(9)-C(8)	109.92(19)
C(18)-C(5)-C(4)	113.67(18)	N(1)-C(9)-H(9)	125.0
C(18)-C(5)-C(6)	128.64(18)	C(8)-C(9)-H(9)	125.0
N(3)-C(21)-C(22)	119.58(18)	C(0AA)-C(2)-H(2)	127.0
N(3)-C(21)-C(20)	106.90(18)	C(1)-C(2)-C(0AA)	105.97(19)
C(20)-C(21)-C(22)	133.52(19)	C(1)-C(2)-H(2)	127.0
N(3)-C(29)-C(0AA)	113.59(18)	C(18)-C(19)-H(19)	125.0
C(28)-C(29)-N(3)	118.00(18)	C(20)-C(19)-C(18)	109.96(19)
C(28)-C(29)-C(0AA)	128.40(19)	C(20)-C(19)-H(19)	125.0
C(21)-C(22)-C(27)	118.13(19)	C(12)-C(13)-H(13)	120.1
C(23)-C(22)-C(21)	122.3(2)	C(14)-C(13)-C(12)	119.9(2)
C(23)-C(22)-C(27)	119.5(2)	C(14)-C(13)-H(13)	120.1
C(28)-C(27)-C(22)	119.4(2)	C(12)-C(17)-H(17)	119.6
C(28)-C(27)-C(26)	121.9(2)	C(16)-C(17)-C(12)	120.7(2)
C(26)-C(27)-C(22)	118.7(2)	C(16)-C(17)-H(17)	119.6
C(13)-C(12)-C(11)	121.0(2)	C(27)-C(26)-H(26)	119.7
C(17)-C(12)-C(11)	120.24(19)	C(25)-C(26)-C(27)	120.6(2)
C(17)-C(12)-C(13)	118.8(2)	C(25)-C(26)-H(26)	119.7
N(2)-C(1)-H(1)	124.3	C(26)-C(25)-H(25)	120.0
N(2)-C(1)-C(2)	111.34(18)	C(26)-C(25)-C(24)	120.0(2)
C(2)-C(1)-H(1)	124.3	C(24)-C(25)-H(25)	120.0
C(11)-C(10)-C(7)	172.4(2)	C(23)-C(24)-C(25)	120.7(2)
C(10)-C(7)-C(6)	132.03(19)	C(23)-C(24)-H(24)	119.6
C(8)-C(7)-C(6)	106.84(18)	C(25)-C(24)-H(24)	119.6
C(8)-C(7)-C(10)	121.11(19)	C(13)-C(14)-H(14)	119.8
C(29)-C(28)-C(27)	122.0(2)	C(15)-C(14)-C(13)	120.5(2)
C(29)-C(28)-H(28)	119.0	C(15)-C(14)-H(14)	119.8
C(27)-C(28)-H(28)	119.0	C(17)-C(16)-H(16)	120.0
C(10)-C(11)-C(12)	178.1(2)	C(15)-C(16)-C(17)	120.0(2)
C(21)-C(20)-H(20)	126.0	C(15)-C(16)-H(16)	120.0
C(19)-C(20)-C(21)	108.06(18)	C(14)-C(15)-H(15)	119.9
C(19)-C(20)-H(20)	126.0	C(16)-C(15)-C(14)	120.1(2)

C(16)-C(15)-H(15)	119.9
F(2)-B(1)-F(1)	109.16(17)
F(2)-B(1)-N(2)	111.12(18)
F(2)-B(1)-N(1)	110.88(18)
F(1)-B(1)-N(2)	110.14(18)
F(1)-B(1)-N(1)	110.07(18)
N(2)-B(1)-N(1)	105.43(16)

6. HR-MALDI-TOF mass data

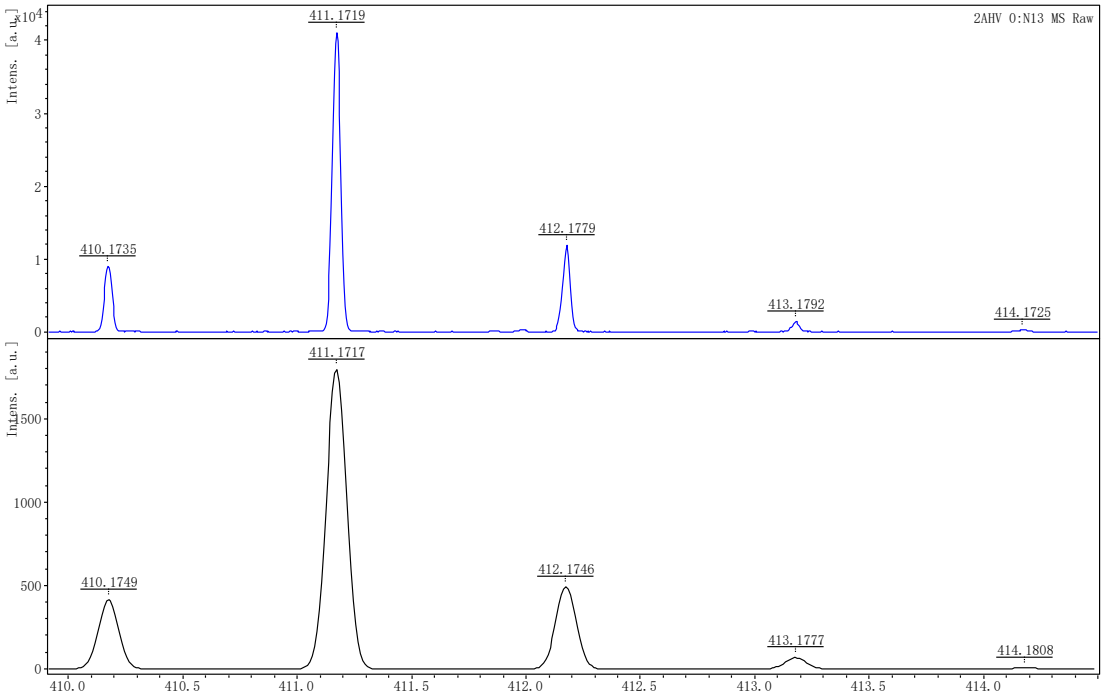


Figure S74. Observed (top) and simulated (bottom) HR-MALDI-TOF mass spectra of **7**.

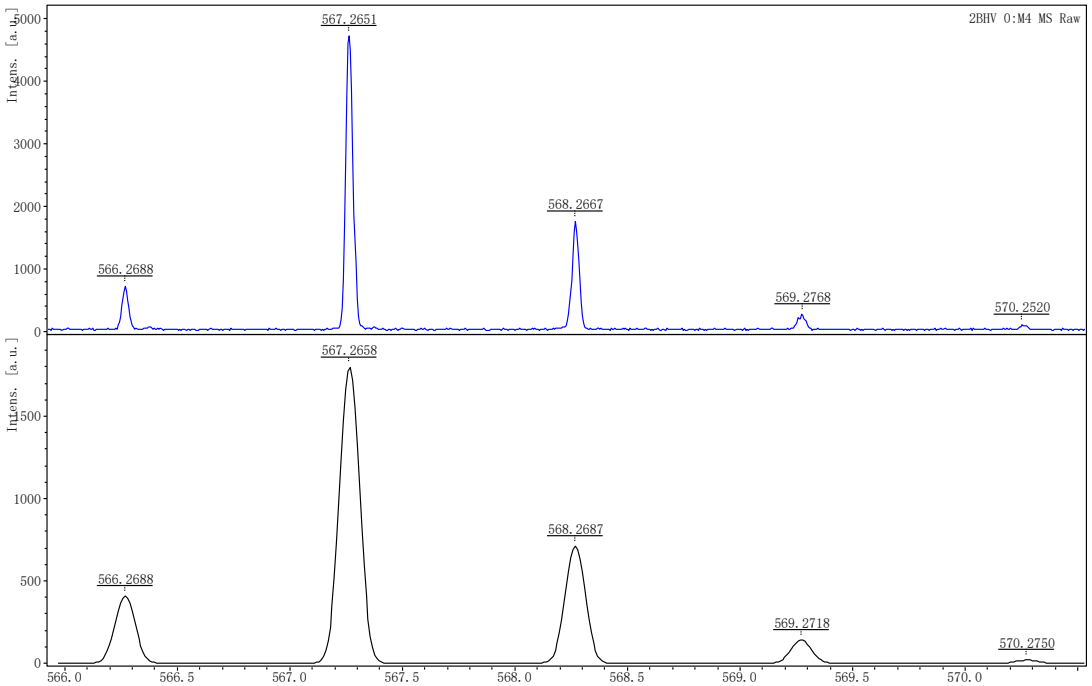


Figure S75 Observed (top) and simulated (bottom) HR-MALDI-TOF mass spectra of **8**.

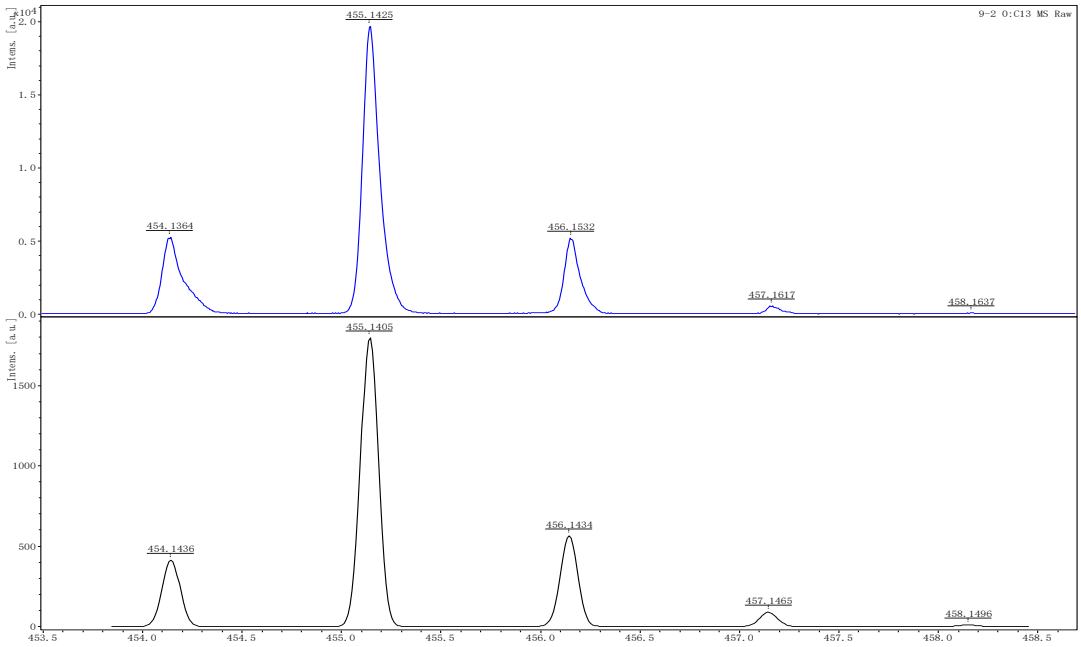


Figure S76. Observed (top) and simulated (bottom) HR-MALDI-TOF mass spectra of **9**.

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