Supporting Information

$Bu_4NI/tBuOOH$ Catalyzed, α-Regioselective Cross-Dehydrogenative Coupling of BODIPY with Allylic Alkenes and Ethers

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1. General information

Reagents and solvents were used as received from commercial suppliers (Energy Chemicals, Shanghai, China) unless noted otherwise. All reactions were performed in oven-dried or flame-dried glassware unless stated otherwise and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254). ^{1}H and ^{13}C NMR spectra were recorded on a 300 or 500 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to $CDCl_3$ (7.26 ppm for ^{1}H and 77 ppm for ^{13}C) or to internal TMS. High-resolution mass spectra (HRMS) were obtained using APCI-TOF in positive mode. Melting points reported were not corrected.

2. Synthesis and characterization

BODIPYs **2** were synthesized according to literature (*Eur J. Org. Chem.* **2011**, *28*, 5460).

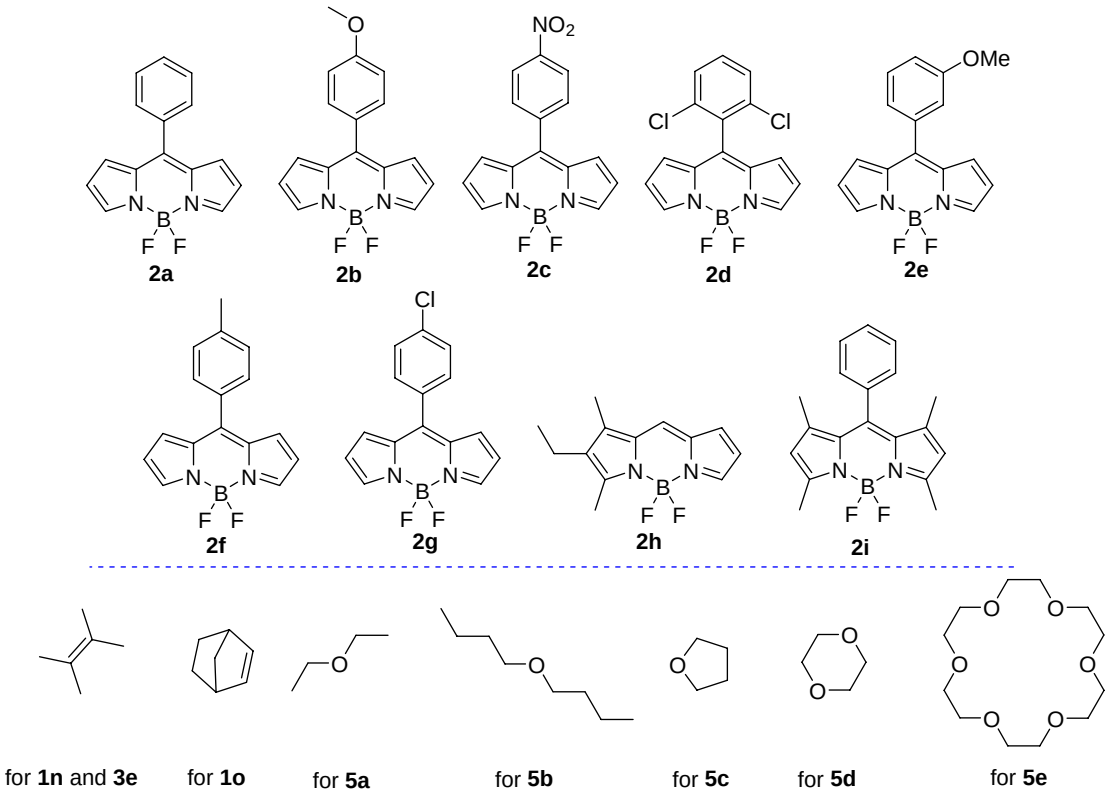


Figure S1. Chemical structure of BODIPYs **2a-i**, allylic alkenes and (poly)ethers.

General procedure for the synthesis of BODIPYs 1a-r

To BODIPY **2** (0.50 mmol) and Bu_4NI (0.10 mmol, 37 mg) in a Schlenk tube was added solvent (3.0 mL) and TBHP (70% aqueous solution, 0.36 mL, 2.5 mmol) via a syringe. The reaction mixture was stirred at 90 °C in an oil bath for 12 h. The organic solvent was removed under vacuum to yield the crude product, which was further purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1→9:1, v/v) as eluent to provide the corresponding product.

1a was obtained as orange oil in 63% yield (109 mg) from **2a** (134 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 70-73 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.62-7.48 (m, 5H), 6.89 (d, J = 4.2 Hz, 1H), 6.78 (s, 1H), 6.48 (s, 1H), 6.45 (s, 1H), 5.93 (d, J = 9.7 Hz, 1H), 5.71 (d, J = 9.9 Hz, 1H), 4.18 (s, 1H), 2.29-2.22 (m, 1H), 2.12 (s, 2H), 1.87-1.67 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 143.6, 139.5, 134.2, 132.8, 132.6, 131.7, 129.2, 129.1, 128.1, 127.5, 127.1, 125.7, 118.0, 115.9, 34.6, 28.4, 23.6, 19.8. HRMS calcd. for $C_{21}H_{19}BF_2N_2$ $[M-F]^+$: 329.1620, found 329.1606.

1b was obtained as orange oil in 60% yield (113 mg) from **2b** (150 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 75-77 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.51 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 4.4 Hz, 1H), 6.82 (d, J = 3.9 Hz, 1H), 6.49 (s, 1H), 6.44 (d, J = 4.4 Hz, 1H), 5.93 (d, J = 7.6 Hz, 1H), 5.72 (d, J = 10.1 Hz, 1H), 4.17 (s, 1H), 3.91 (s, 3H), 2.31-2.19 (m, 1H), 2.12 (s, 2H), 1.90-1.78 (m, 1H), 1.77-1.66 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 161.7, 145.0, 140.3, 135.4, 133.9, 132.8, 132.3, 129.3, 128.6, 127.1, 126.6, 119.0, 117.0, 114.0, 55.6, 35.9, 29.6, 24.9, 21.1. HRMS calcd. for $C_{22}H_{21}BF_2N_2O$ $[M-F]^+$: 359.1725, found 359.1710.

1c was obtained as red oil in 54% yield (106 mg) from **2c** (156 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 87-90 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, J = 8.6 Hz, 2H), 7.84 (s, 1H), 7.72 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 4.5 Hz, 1H), 6.68 (d, J = 4.0 Hz, 1H), 6.51 (d, J = 3.7 Hz, 1H), 6.49 (d, J = 4.5 Hz, 1H), 5.95 (d, J = 7.6 Hz, 1H), 5.69 (d, J = 10.0 Hz, 1H), 4.17 (s, 1H), 2.35-2.19 (m, 1H), 2.13 (s, 2H), 1.87-1.78 (m, 1H), 1.77-1.66 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 149.3,

142.2, 141.6, 140.6, 135.5, 133.6, 132.8, 131.6, 130.1, 128.6, 126.7, 124.0, 120.6, 118.2, 36.4, 29.7, 25.1, 21.3. HRMS calcd. for $C_{21}H_{18}BF_2N_3O_2$ $[M-F]^+$: 374.1471, found 374.1463.

1d was obtained as yellow oil in 56% yield (116 mg) from **2d** (168 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 72-74 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.55-7.43 (m, 2H), 7.42-7.37 (m, 1H), 6.64 (d, J = 4.5 Hz, 1H), 6.54 (d, J = 3.9 Hz, 1H), 6.44 (d, J = 2.3 Hz, 1H), 6.41 (d, J = 4.4 Hz, 1H), 5.94 (d, J = 7.6 Hz, 1H), 5.73 (d, J = 10.0 Hz, 1H), 4.17 (s, 1H), 2.31-2.24 (m, 1H), 2.11 (s, 2H), 1.90-1.77 (m, 1H), 1.76-1.68 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 141.9, 138.4, 135.8, 135.8, 133.6, 132.0, 131.6, 131.4, 130.0, 128.6, 127.2, 127.0, 120.3, 117.8, 36.4, 29.7, 25.2, 21.4. HRMS calcd. for $C_{21}H_{17}BCl_2F_2N_2$ $[M-F]^+$: 397.0840, found 397.0828.

1e was obtained as yellow oil in 39% yield (76 mg) from **2e** (150 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 90-93 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.40 (t, J = 8.1 Hz, 1H), 7.13-7.06 (m, 3H), 6.93 (d, J = 4.0 Hz, 1H), 6.81 (d, J = 2.7 Hz, 1H), 5.93 (d, J = 7.8 Hz, 1H), 5.71 (d, J = 10.0 Hz, 1H), 4.17 (s, 1H), 3.86 (s, 3H), 2.31-2.25 (m, 1H), 2.12 (s, 2H), 1.90-1.78 (m, 1H), 1.78-1.67 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 159.7, 144.9, 141.1, 135.8, 135.7, 134.1, 133.6, 133.3, 129.7, 129.0, 127.3, 123.3, 119.6, 117.5, 116.3, 116.2, 55.83, 36.22, 29.82, 25.17, 21.35. HRMS calcd. for $C_{22}H_{21}BF_2N_2O$ $[M-F]^+$: 359.1725, found 359.1719.

1f was obtained as yellow oil in 52% yield (94 mg) from **2f** (141 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 76-78 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.44 (d, J = 7.8 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 3.9 Hz, 1H), 6.79 (d, J = 2.8 Hz, 1H), 6.47 (s, 1H), 6.43 (d, J = 4.2 Hz, 1H), 5.92 (d, J = 8.1 Hz, 1H), 5.71 (d, J = 10.0 Hz, 1H), 4.17 (s, 1H), 2.46 (s, 3H), 2.33-2.23 (m, 1H), 2.11 (s, 2H), 1.85-1.76 (m, 1H), 1.76-1.68 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 145.5, 141.1, 140.8, 135.8, 134.2, 133.2, 131.7, 130.9, 129.6, 129.4, 128.9, 127.3, 119.4, 117.4, 36.2, 29.9, 25.2, 21.8, 21.4. HRMS calcd. for $C_{22}H_{21}BF_2N_2$ $[M-F]^+$: 343.1782, found 343.1799.

1g was obtained as yellow oil in 43% yield (94 mg) from **2g** (150 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 121-123 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.73-7.29 (m, 5H), 6.86 (d, J = 4.1 Hz, 1H), 6.74 (d, J = 3.0 Hz, 1H), 6.48 (s, 1H), 6.45 (d, J = 4.3 Hz, 1H), 5.94 (d, J = 8.4 Hz, 1H), 5.70 (d, J = 10.0 Hz, 1H), 4.16 (s, 1H), 2.34-2.26 (m, 1H), 2.11 (s, 2H), 1.85-1.75 (m, 1H), 1.76-1.66 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 143.6, 141.5, 137.0, 133.9, 132.9, 132.8, 131.9, 129.8, 129.1, 128.7, 127.1, 125.8, 119.9, 117.7, 36.3, 29.8, 25.2, 21.3. HRMS calcd. for $C_{21}H_{18}BClF_2N_2$ $[M\text{-}F]^+$: 363.1266, found 363.1269.

1h was obtained as yellow oil in 45% yield (74 mg) from **2e** (125 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 56-58 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.84 (d, J = 4.0 Hz, 1H), 6.26 (d, J = 3.9 Hz, 1H), 5.85 (d, J = 9.9 Hz, 1H), 5.72 (d, J = 10.0 Hz, 1H), 4.03 (s, 1H), 2.54 (s, 3H), 2.40 (q, J = 7.6 Hz, 2H), 2.17 (s, 4H), 2.08 (s, 2H), 1.84-1.74 (m, 1H), 1.74-1.62 (m, 2H), 1.07 (t, J = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7, 159.6, 139.4, 134.8, 133.9, 133.2, 128.7, 128.6, 127.5, 123.1, 116.1, 35.8, 30.2, 25.3, 21.4, 17.7, 14.7, 13.3, 9.8. HRMS calcd. for $C_{19}H_{23}BF_2N_2$ $[M\text{-}F]^+$: 309.1933, found 309.1914.

1i was obtained as orange oil in 60% yield (101 mg) from **2a** (134 mg, 0.5 mmol) and cyclopentene (3.0 mL). Melting point: 90-92 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.62-7.48 (m, 5H), 6.88 (d, J = 4.4 Hz, 1H), 6.77 (d, J = 3.9 Hz, 1H), 6.48 (d, J = 3.7 Hz, 1H), 6.36 (d, J = 4.4 Hz, 1H), 6.01 (d, J = 3.0 Hz, 1H), 5.80 (d, J = 3.3 Hz, 1H), 4.60 (s, 1H), 2.62-2.55 (m, 1H), 2.55-2.45 (m, 2H), 2.01-1.89 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 145.1, 141.0, 135.9, 134.4, 134.3, 133.6, 131.6, 130.8, 130.7, 129.9, 129.0, 128.7, 118.6, 117.5, 45.3, 32.9, 32.2. HRMS calcd. for $C_{20}H_{17}BF_2N_2$ $[M\text{-}F]^+$: 315.1463, found 315.1441.

1j was obtained as orange oil in 57% yield (104 mg) from **2b** (150 mg, 0.5 mmol) and cyclopentene (3.0 mL). Melting point: 93-95 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 4.1 Hz, 1H), 6.81 (d, J = 2.9 Hz, 1H), 6.48 (d, J = 1.3 Hz, 1H), 6.36 (d, J = 4.1 Hz, 1H), 6.00 (d, J = 2.9 Hz, 1H), 5.80 (d, J = 3.2 Hz, 1H), 4.59 (s, 1H), 3.90 (s, 3H), 2.64-2.56(m, 1H), 2.56-2.39 (m, 2H), 2.15-1.84 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 162.0,

145.2, 140.5, 135.8, 134.1, 133.4, 132.6, 131.8, 130.0, 128.8, 126.9, 118.2, 117.3, 114.3, 55.9, 45.2, 32.9, 32.3. HRMS calcd. for $C_{21}H_{19}BF_2N_2O$ $[M-F]^+$: 345.1569, found 345.1554.

1k was obtained as red oil in 40% yield (76 mg) from **2c** (156 mg, 0.5 mmol) and cyclopentene (3.0 mL). Melting point: 126-128 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, J = 8.4 Hz, 2H), 7.84 (s, 1H), 7.72 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 3.6 Hz, 1H), 6.67 (s, 1H), 6.51 (s, 1H), 6.41 (d, J = 3.8 Hz, 1H), 6.03 (s, 1H), 5.79 (d, J = 2.8 Hz, 1H), 4.60 (s, 1H), 2.78-2.44 (m, 3H), 2.04-1.85 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 149.3, 142.2, 141.5, 140.6, 135.6, 134.7, 133.6, 133.0, 131.6, 131.2, 128.5, 124.0, 119.6, 118.2, 45.4, 32.9, 32.2. HRMS calcd. for $C_{20}H_{16}BF_2N_3O_2$ $[M-F]^+$: 360.1319, found 360.1319.

1l was obtained as yellow oil in 52% yield (105 mg) from **2d** (168 mg, 0.5 mmol) and cyclopentene (3.0 mL). Melting point: 85-87 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.55-7.41 (m, 2H), 7.40-7.37 (m, 1H), 6.64 (d, J = 4.5 Hz, 1H), 6.54 (d, J = 3.4 Hz, 1H), 6.44 (d, J = 3.7 Hz, 1H), 6.34 (d, J = 4.6 Hz, 1H), 6.02 (d, J = 3.1 Hz, 1H), 5.81 (d, J = 2.5 Hz, 1H), 4.60 (s, 1H), 2.63-2.54 (m, 1H), 2.54-2.46 (m, 1H), 2.05-1.91 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 141.9, 138.5, 138.4, 135.8, 134.5, 133.6, 132.0, 131.8, 131.4, 128.9, 128.6, 127.3, 119.5, 117.8, 45.5, 32.9, 32.1. HRMS calcd. for $C_{20}H_{15}BCl_2F_2N_2$ $[M-F]^+$: 383.0684, found 383.0667.

1m was obtained as yellow oil in 40% yield (63 mg) from **2e** (125 mg, 0.5 mmol) and cyclopentene (3.0 mL). Melting point: 56-58 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.83 (d, J = 3.9 Hz, 1H), 6.18 (d, J = 3.9 Hz, 1H), 5.94 (d, J = 5.5 Hz, 1H), 5.80 (d, J = 5.5 Hz, 1H), 4.46 (s, 1H), 2.55 (s, 3H), 2.51-2.47 (m, 1H), 2.39 (t, J = 7.6 Hz, 2H), 2.17 (s, 3H), 1.91-1.85 (m, 1H), 1.25 (s, 2H), 1.07 (t, J = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7, 159.5, 139.5, 134.8, 133.9, 133.3, 133.1, 132.7, 127.8, 123.1, 114.9, 44.9, 32.7, 30.1, 17.7, 14.8, 13.3, 9.8. HRMS calcd. for $C_{18}H_{21}BF_2N_2$ $[M-F]^+$: 295.1776, found 295.1777.

1n was obtained as orange oil in 50% yield (88 mg) from **2a** (134 mg, 0.5 mmol) and 2,3-dimethyl-2-butene (3.0 mL). Melting point: 108-109 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.57-7.49 (m, 5H), 6.86 (d, J = 4.3 Hz, 1H), 6.76 (d, J = 3.9 Hz,

1H), 6.47 (s, 1H), 6.27 (d, J = 4.3 Hz, 1H), 3.84 (s, 2H), 1.75 (s, 3H), 1.74 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 144.7, 140.9, 136.2, 134.4, 134.2, 133.3, 130.8, 130.6, 128.9, 128.8, 128.7, 123.5, 120.1, 117.4, 34.5, 21.1, 21.0, 19.7. HRMS calcd. for $C_{21}H_{21}BF_2N_2$ [M-F]$^+$: 331.1776, found 331.1757.

1o was obtained as yellow oil in 53% yield (114 mg) from **2a** (134 mg, 0.5 mmol) and norbornene (3.0 mL). Melting point: 65-67 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.63-7.39 (m, 5H), 6.87 (s, 1H), 6.74 (s, 1H), 6.53 (d, J = 2.8 Hz, 1H), 6.45 (s, 1H), 4.40 (d, J = 5.6 Hz, 1H), 3.69 (s, 1H), 3.20 (d, J = 1.1 Hz, 1H), 2.72 (s, 1H), 2.38 (s, 1H), 2.02 (d, J = 8.1 Hz, 1H), 1.40 (s, 2H), 1.26 (s, 2H), 1.07(s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9, 144.2, 140.2, 135.4, 134.6, 133.9, 132.6, 130.8, 130.6, 128.7, 128.2, 121.3, 117.0, 88.6, 80.7, 47.5, 42.4, 40.1, 35.2, 30.4, 26.7, 23.6. HRMS calcd. for $C_{26}H_{29}BF_2N_2O$ [M-2F]$^+$: 395.2404, found 395.2404.

General procedure for the synthesis of BODIPYs 3a-e

To BODIPY **2** (0.50 mmol) and Bu_4NI (0.10 mmol, 37 mg) in a Schlenk tube was added solvent (3.0 mL) and TBHP (70% aqueous solution, 0.36 mL, 2.5 mmol) via a syringe. The reaction mixture was stirred at 90 °C in an oil bath for 24 h. The organic solvent was removed under vacuum to yield the crude product, which was further purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1→9:1, v/v) as eluent to provide the corresponding product.

3a was obtained as yellow oil in 35% yield (75 mg) from **2a** (134 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 72-74 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (s, 5H), 6.74 (d, J = 4.1 Hz, 2H), 6.36 (d, J = 4.2 Hz, 2H), 5.89 (d, J = 9.9 Hz, 2H), 5.71 (d, J = 9.6 Hz, 2H), 4.15 (s, 2H), 2.29-2.18 (m, 2H), 2.10 (s, 4H), 1.89-1.75 (m, 2H), 1.74-1.63 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 143.5, 134.7, 134.5, 130.8, 130.3, 129.2, 128.6, 128.0, 127.9, 118.0, 36.0, 30.1, 25.2, 21.4. HRMS calcd. for $C_{27}H_{27}BF_2N_2$ [M-F]$^+$: 409.2246，found 409.2259.

3b was obtained as yellow oil in 35% yield (80 mg) from **2b** (150 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 76-78 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 8.5 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 6.77 (d, J = 3.9 Hz, 2H), 6.35 (d, J = 4.1 Hz, 2H), 5.88 (d, J = 10.0 Hz, 2H), 5.71 (d, J = 9.9 Hz, 2H), 4.14 (s, 2H), 3.89 (s, 3H),

2.30-2.18 (m, 2H), 2.09 (s, 4H), 1.89-1.75 (m, 2H), 1.74-1.65 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 161.1, 143.1, 134.0, 132.0, 130.1, 128.6, 127.7, 126.7, 117.4, 113.6, 55.4, 35.5, 29.7, 24.8, 21.0. HRMS calcd. for $C_{28}H_{29}BF_2N_2O$ $[M-F]^+$: 439.2351，found 439.2359.

3c was obtained as red oil in 33% yield (78 mg) from **2c** (156 mg, 0.5 mmol) and cyclohexene (3.0 mL). Melting point: 106-108 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, J = 8.7 Hz, 1H), 7.69 (d, J = 8.7 Hz, 1H), 6.64 (d, J = 4.2 Hz, 1H), 6.40 (d, J = 4.2 Hz, 1H), 5.91 (d, J = 10.1 Hz, 1H), 5.70 (d, J = 9.9 Hz, 1H), 4.15 (s, 1H), 2.28-2.17 (m, 1H), 2.11 (s, 2H), 1.86-1.77 (m, 1H), 1.78-1.63 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 149.1, 141.0, 139.9, 134.0, 131.6, 130.2, 129.6, 127.5, 123.9, 118.9, 36.1, 30.0, 25.2, 21.4. HRMS calcd. for $C_{27}H_{26}BF_2N_3O_2$ $[M-F]^+$: 454.2097，found 454.2076.

3d was obtained as red oil in 35% yield (78 mg) from **2c** (156 mg, 0.5 mmol) and cyclopentene (3.0 mL). Melting point: 109-111 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, J = 8.7 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 4.0 Hz, 2H), 6.32 (d, J = 4.2 Hz, 2H), 5.99 (d, J = 5.5 Hz, 2H), 5.80 (d, J = 5.5 Hz, 2H), 4.58 (s, 2H), 2.68-2.54 (m, 2H), 2.53-2.43 (m, 4H), 1.99-1.89 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 149.1, 141.0, 139.8, 134.0, 131.9, 131.8, 131.6, 130.4, 123.9, 117.8, 45.2, 32.9, 32.5. HRMS calcd. for $C_{25}H_{22}BF_2N_3O_2$ $[M-F]^+$: 426.1784，found 426.1760.

3e was obtained as yellow oil in 40% yield (86 mg) from **2a** (134 mg, 0.5 mmol) and 2,3-dimethyl-2-butene (3.0 mL). Melting point: 121-123 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.43 (m, 5H), 6.69 (d, J = 4.2 Hz, 2H), 6.18 (d, J = 4.2 Hz, 2H), 3.83 (s, 4H), 1.75 (s, 12H), 1.73 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8, 142.7, 135.0, 134.6, 130.8, 130.6, 130.2, 128.5, 128.2, 124.0, 118.3, 34.2, 21.1, 21.0, 19.7. HRMS calcd. for $C_{27}H_{31}BF_2N_2$ $[M-F]^+$: 413.2559，found 413.2553.

General procedure for the synthesis of BODIPYs 5a-g

To BODIPY **2a** (0.50 mmol) and Bu_4NI (0.10 mmol, 37 mg) in a Schlenk tube was added solvent (3.0 mL) and TBHP (70% aqueous solution, 0.36 mL, 2.5 mmol) via a syringe. The reaction mixture was stirred at 90 °C (except for diethyl ether, reflux

temperature) in an oil bath for 12 h. The organic solvent was removed under vacuum to yield the crude product, which was further purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1→9:1, v/v) as eluent to provide the corresponding product.

5a was obtained as yellow oil in 50% yield (73 mg) from **2a** (134 mg, 0.5 mmol) and diethyl ether (3.0 mL) at refluxing temperature (40 °C oil bath). Melting point: 52-53 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.68-7.38 (m, 5H), 6.94 (d, J = 4.3 Hz, 1H), 6.82 (d, J = 3.4 Hz, 1H), 6.65 (d, J = 4.4 Hz, 1H), 6.50 (d, J = 2.1 Hz, 1H), 5.15-5.06 (m, 1H), 3.61-3.43 (m, 2H), 1.56 (d, J = 6.5 Hz, 3H), 1.33-1.12 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 145.7, 141.6, 135.0, 133.9, 133.8, 132.8, 130.4, 130.3, 129.6, 128.3, 117.6, 116.9, 71.2, 65.1, 22.2, 15.3. HRMS calcd. for $C_{19}H_{19}BF_2N_2O$ $[M\text{-}OC_2H_5]^+$: 295.1213, found 295.1229.

5b was obtained as yellow oil in 52% yield (102 mg) from **2a** (134 mg, 0.5 mmol) and dibutyl ether (3.0 mL). Melting point: 56-59 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.62-7.49 (m, 5H), 6.93 (d, J = 4.3 Hz, 1H), 6.81 (d, J = 3.8 Hz, 1H), 6.63 (d, J = 4.4 Hz, 1H), 6.49 (d, J = 2.1 Hz, 1H), 4.95 (t, J = 5.3 Hz, 1H), 3.49-3.44 (m, 2H), 1.93-1.73 (m, 2H), 1.75-1.63 (m, 2H), 1.57-1.50 (m, 2H), 1.43-1.37 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 145.5, 141.3, 135.1, 133.9, 133.8, 132.7, 130.4, 129.4, 128.7, 128.3, 117.7, 117.4, 75.1, 69.7, 38.4, 31.9, 29.6, 19.3, 18.9, 13.8. HRMS calcd. for $C_{23}H_{27}BF_2N_2O$ $[M\text{-}OC_4H_9]^+$: 323.1526, found 323.1554.

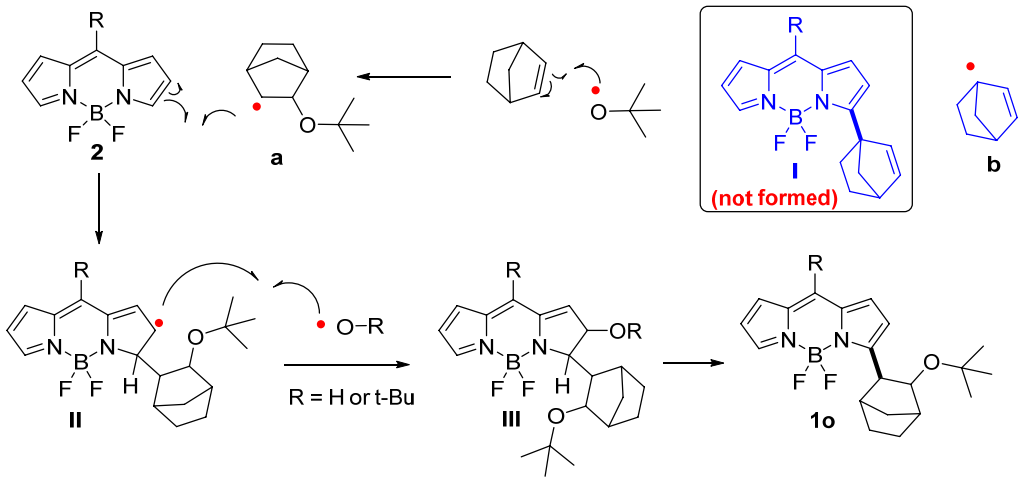
5c was obtained as yellow solid in 55% yield (93 mg) from **2a** (134 mg, 0.5 mmol) and tetrahydrofuran (3.0 mL). Melting point: 90-93 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.68-7.41 (m, 5H), 6.91 (d, J = 3.6 Hz, 1H), 6.82 (d, J = 3.0 Hz, 1H), 6.60 (d, J = 3.9 Hz, 1H), 6.49 (s, 1H), 5.49 (t, J = 6.4 Hz, 1H), 4.22-4.07 (m, 1H), 4.03-3.88 (m, 1H), 2.72-2.51 (m, 1H), 2.18-1.91 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 145.7, 141.6, 135.6, 133.9, 133.8, 132.7, 130.4, 129.5, 129.3, 128.3, 117.5, 117.1, 74.9, 69.3, 33.9, 26.3. HRMS calcd. for $C_{19}H_{17}BF_2N_2O$ $[M\text{-}BF_2]^+$: 289.1335, found 289.1336.

5d was obtained as yellow solid in 42% yield (74 mg) from **2a** (134 mg, 0.5 mmol)

and 1,4-dioxane (3.0 mL). Melting point: 131-134 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.73-7.43 (m, 5H), 6.92 (d, J = 3.9 Hz, 1H), 6.88 (d, J = 3.3 Hz, 1H), 6.67 (d, J = 3.9 Hz, 1H), 6.53 (s, 1H), 5.29 (d, J = 5.7 Hz, 1H), 4.25 (d, J = 11.4 Hz, 1H), 4.04-3.87 (m, 2H), 3.84-3.65 (m, 2H), 3.48 (t, J = 10.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 146.7, 143.3, 135.1, 134.4, 133.7, 132.1, 130.8, 130.6, 130.4, 128.4, 118.4, 117.6, 72.5, 70.7, 66.7, 66.3. HRMS calcd. for $C_{19}H_{17}BF_2N_2O_2$ $[M\text{-}BF_2]^+$: 305.1285, found 305.1297; $[M\text{-}BF_2+2H]^+$: 307.1447, found 307.1449.

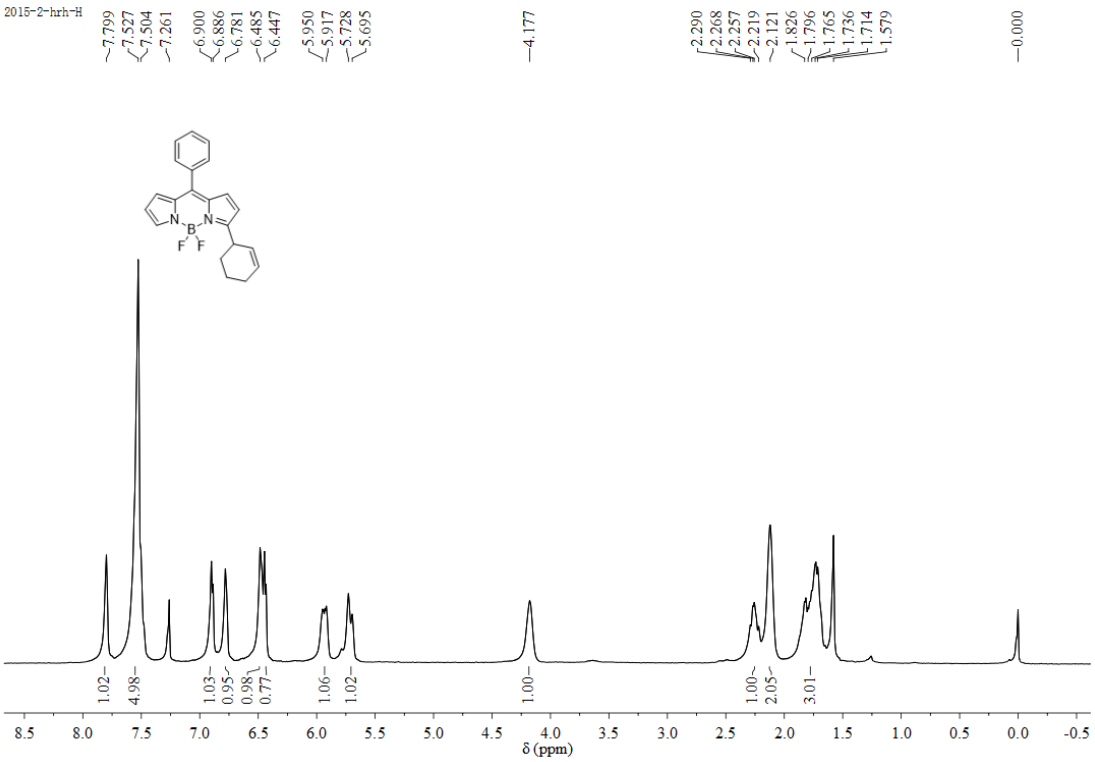
5e was obtained as yellow oil in 43% yield (114 mg) from **2a** (134 mg, 0.5 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane (3.0 mL). Melting point: 56-59 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.65-7.31 (m, 5H), 6.85 (d, J = 2.6 Hz, 1H), 6.78 (d, J = 4.2 Hz, 1H), 6.70 (d, J = 10.0 Hz, 1H), 6.45 (d, J = 4.3 Hz, 1H), 5.24 (s, 1H), 3.93-3.79 (m, 2H), 4.05-3.23 (m, 20H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.44, 146.08, 142.34, 135.29, 134.22, 133.74, 132.26, 130.47, 130.35, 130.15, 128.30, 119.02, 117.88, 75.34, 73.25, 70.86, 70.76, 70.74, 70.67, 70.62, 70.57, 70.40, 70.05, 69.51, 69.50. HRMS calcd. for $C_{27}H_{33}BF_2N_2O_6$ $[M\text{-}2HF+H]^+$: 491.2353, found 491.2365.

3. Scheme S1. Proposed reaction mechanism for the formation of BODIPY **1o**.

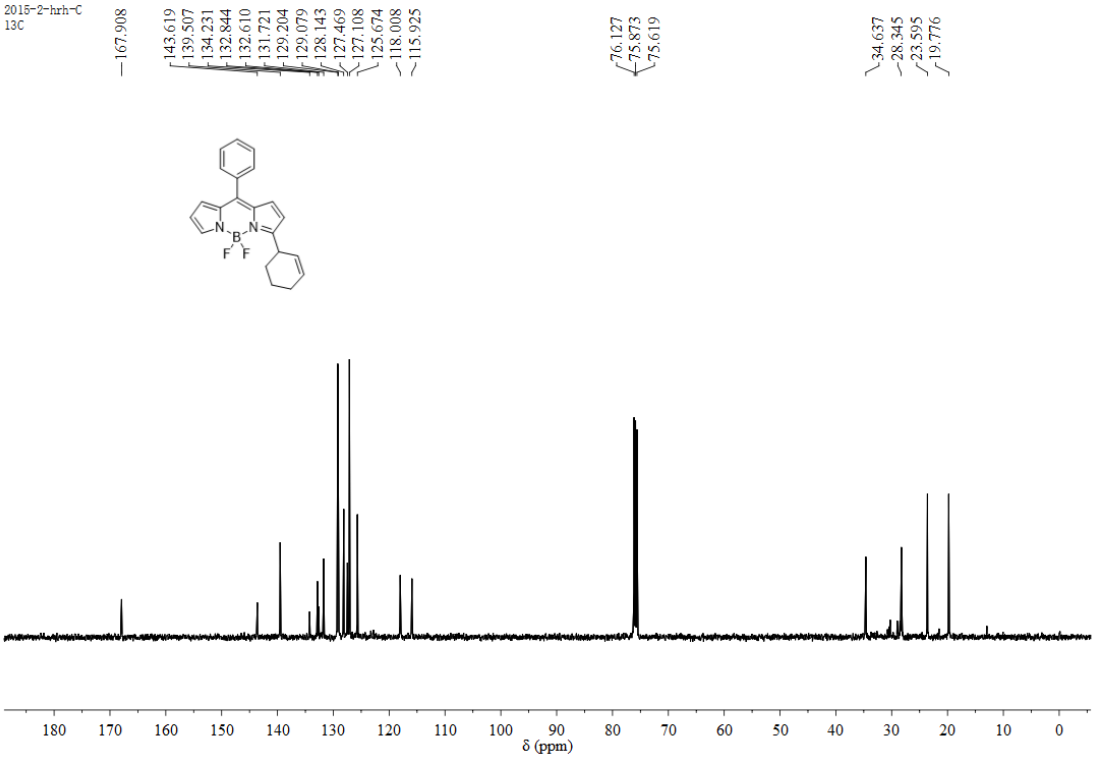


4. NMR and HRMS spectra for all new compounds

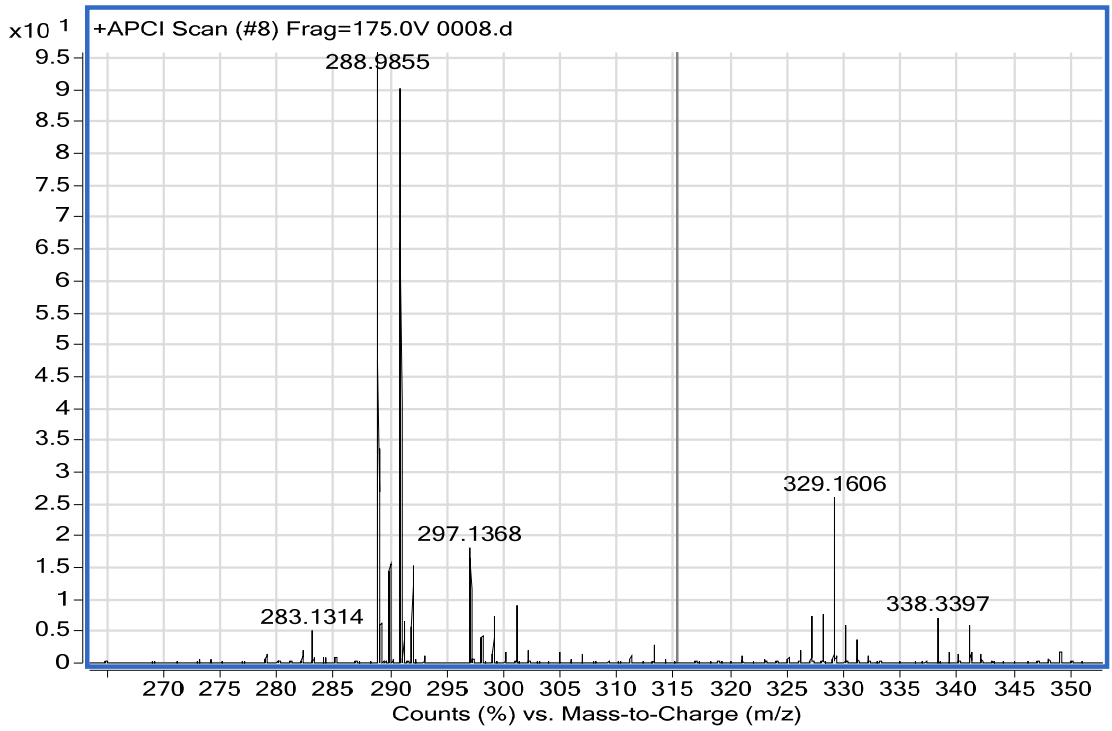
^{1}H NMR spectrum of **1a** in $CDCl_3$



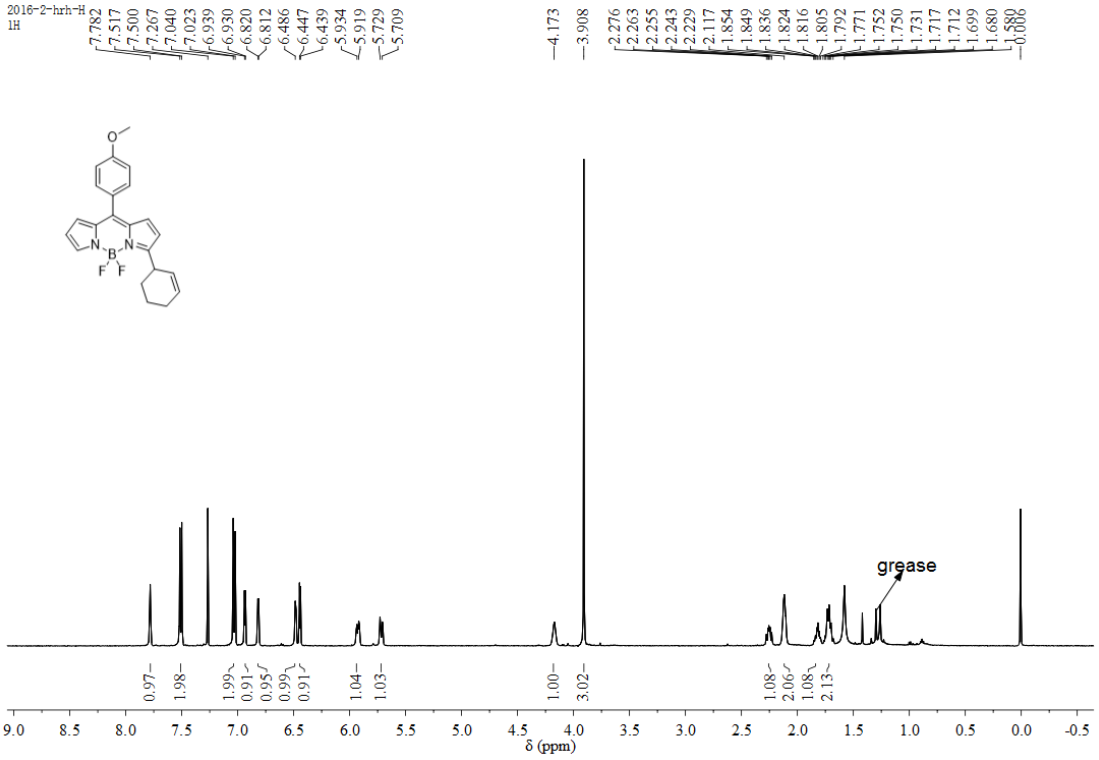
^{13}C NMR spectrum of **1a** in $CDCl_3$



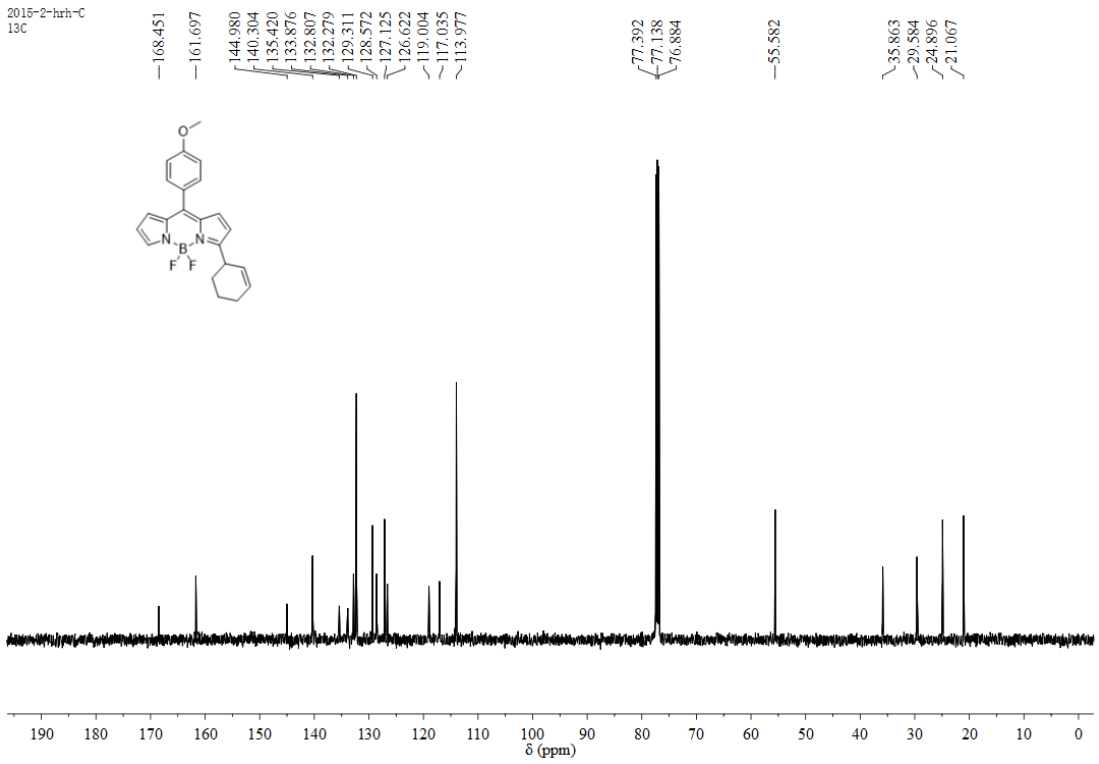
HRMS for **1a**


+APCI Scan (#8) Frag=175.0V 0008.d
x10 1
288.9855
329.1606
297.1368
338.3397
283.1314
Counts (%) vs. Mass-to-Charge (m/z)

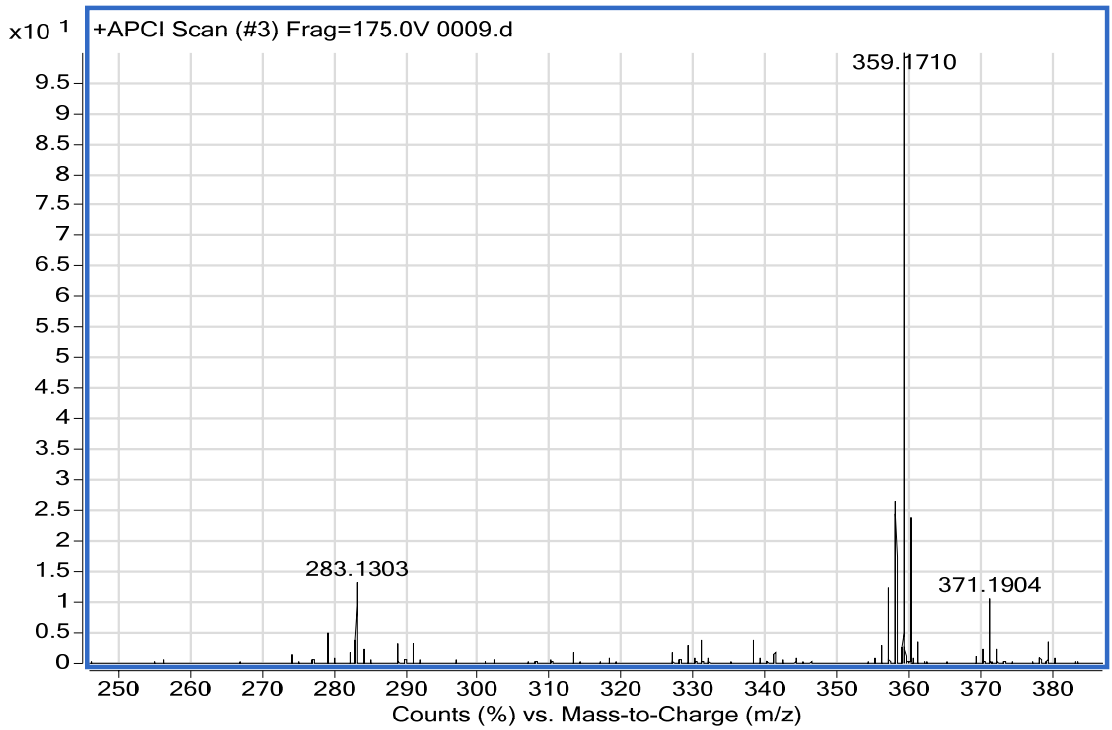
^{1}H NMR spectrum of **1b** in $CDCl_3$



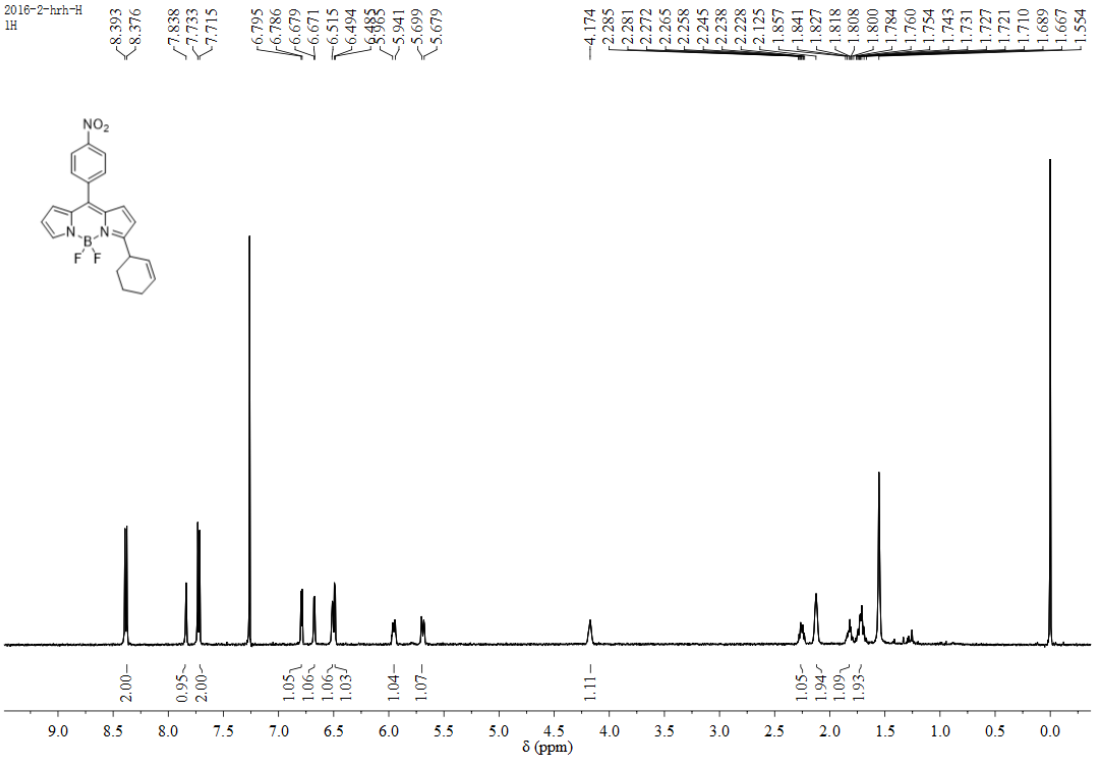
^{13}C NMR spectrum of **1b** in $CDCl_3$



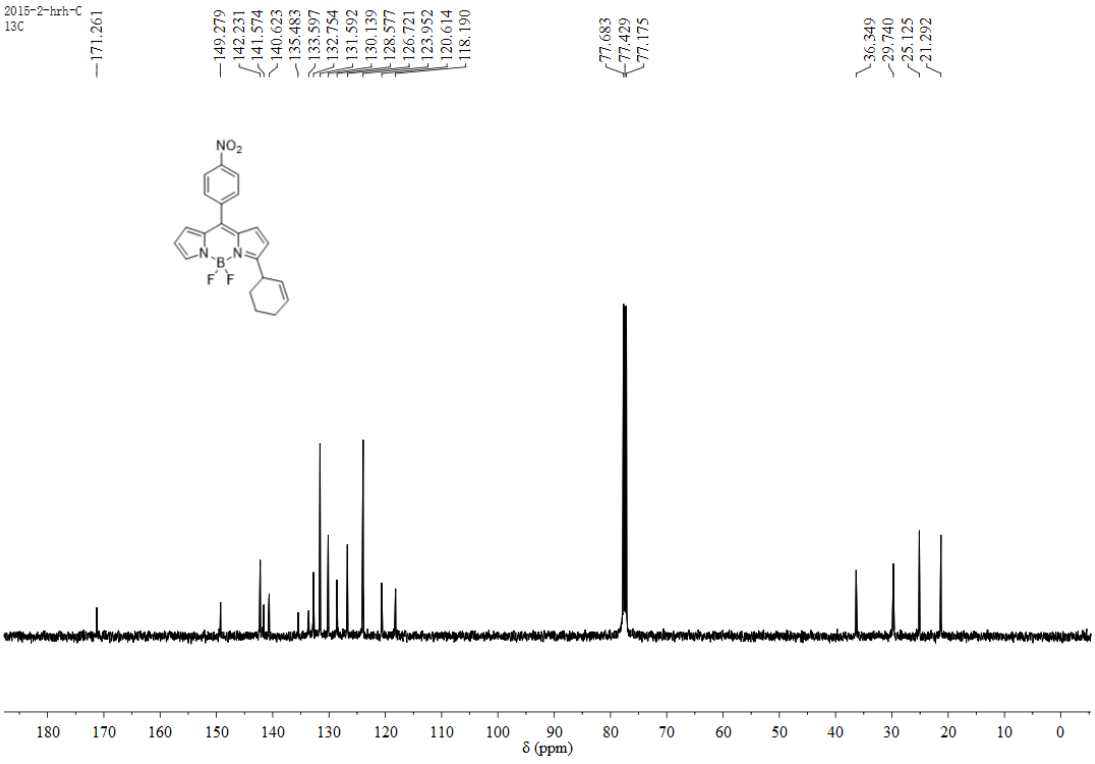
HRMS for **1b**


x10 1
+APCI Scan (#3) Frag=175.0V 0009.d
359.1710
283.1303
371.1904
Counts (%) vs. Mass-to-Charge (m/z)

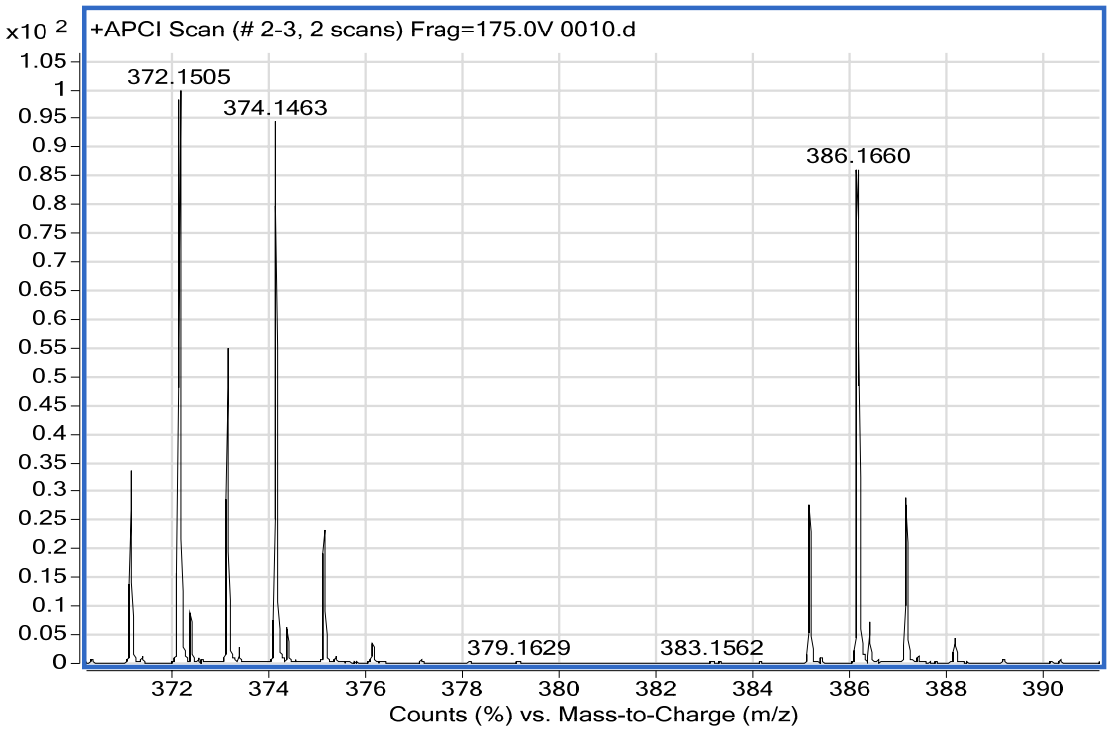
^{1}H NMR spectrum of **1c** in $CDCl_3$



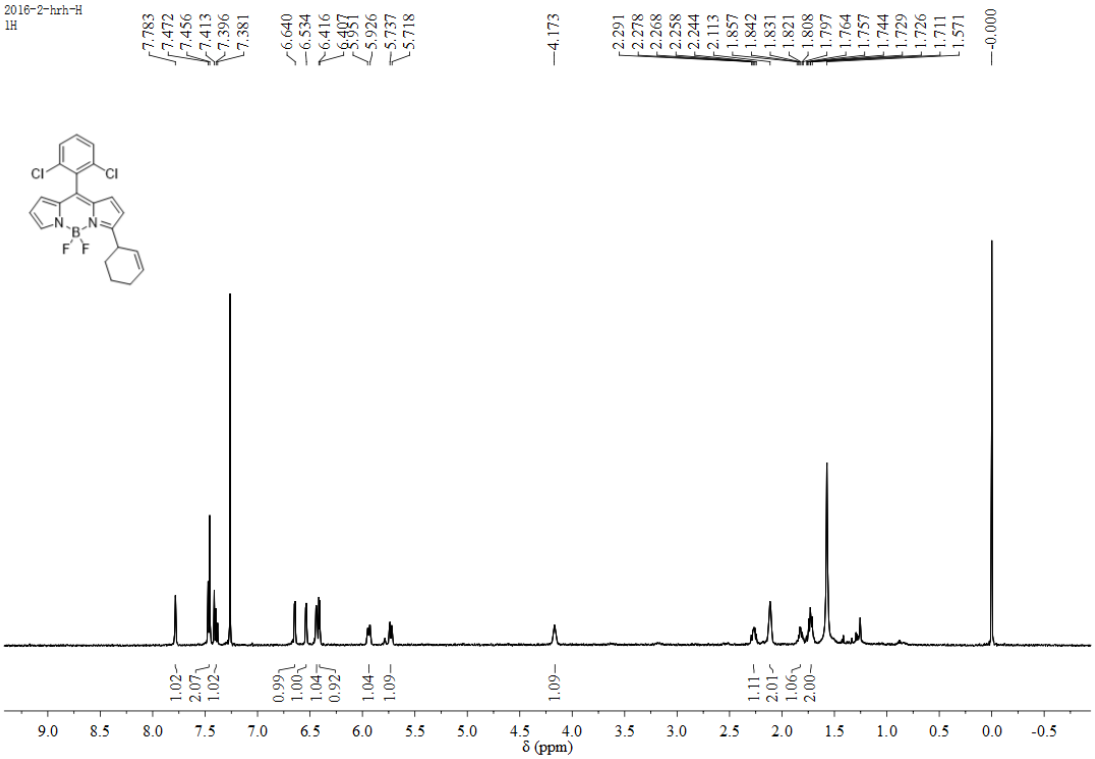
^{13}C NMR spectrum of **1c** in $CDCl_3$



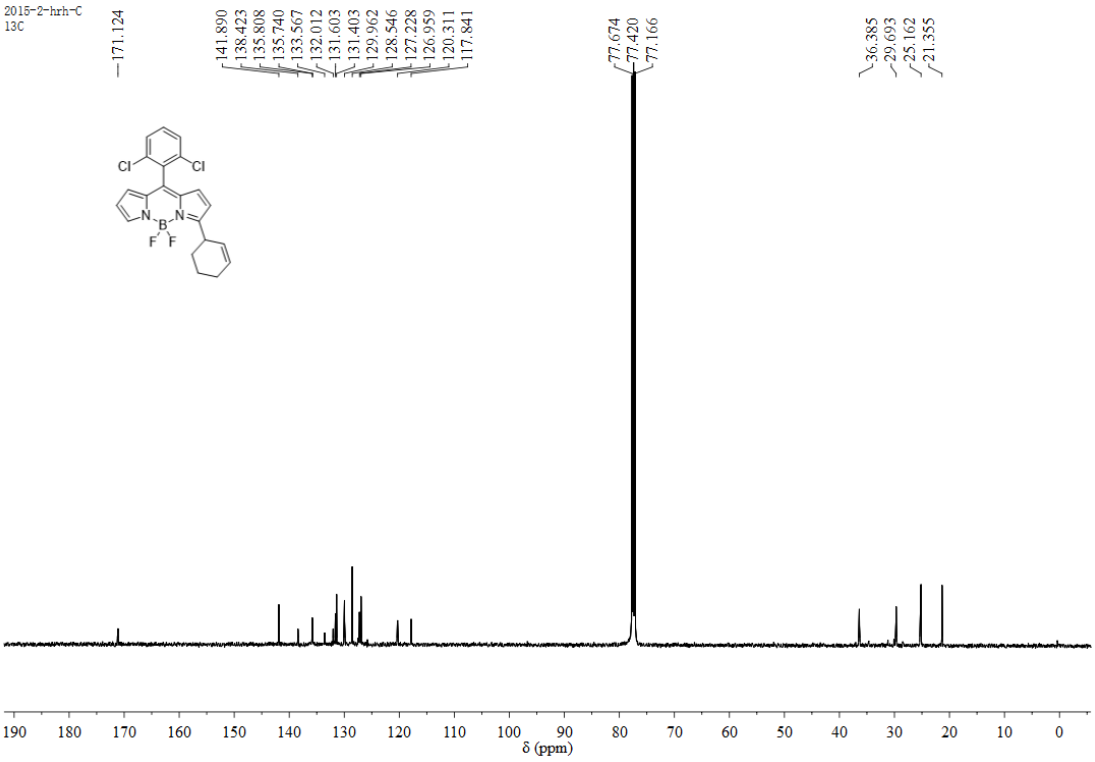
HRMS for **1c**


x10 2
+APCI Scan (# 2-3, 2 scans) Frag=175.0V 0010.d
372.1505
374.1463
386.1660
379.1629
383.1562
Counts (%) vs. Mass-to-Charge (m/z)

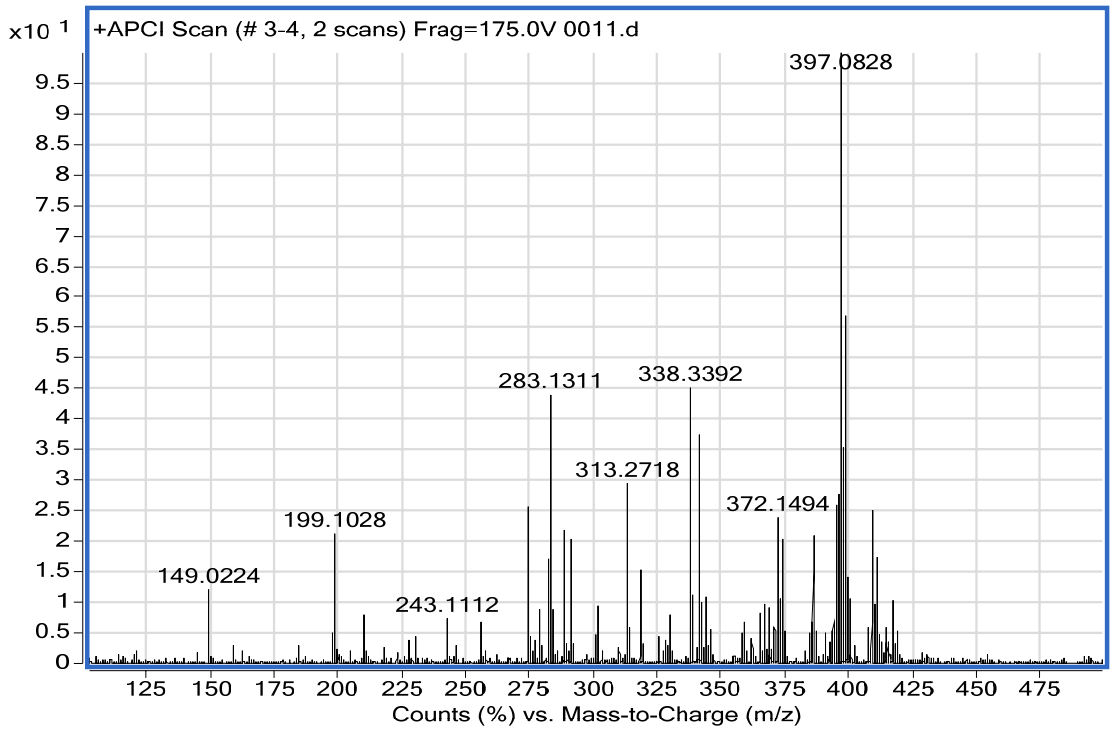
^{1}H NMR spectrum of **1d** in $CDCl_3$



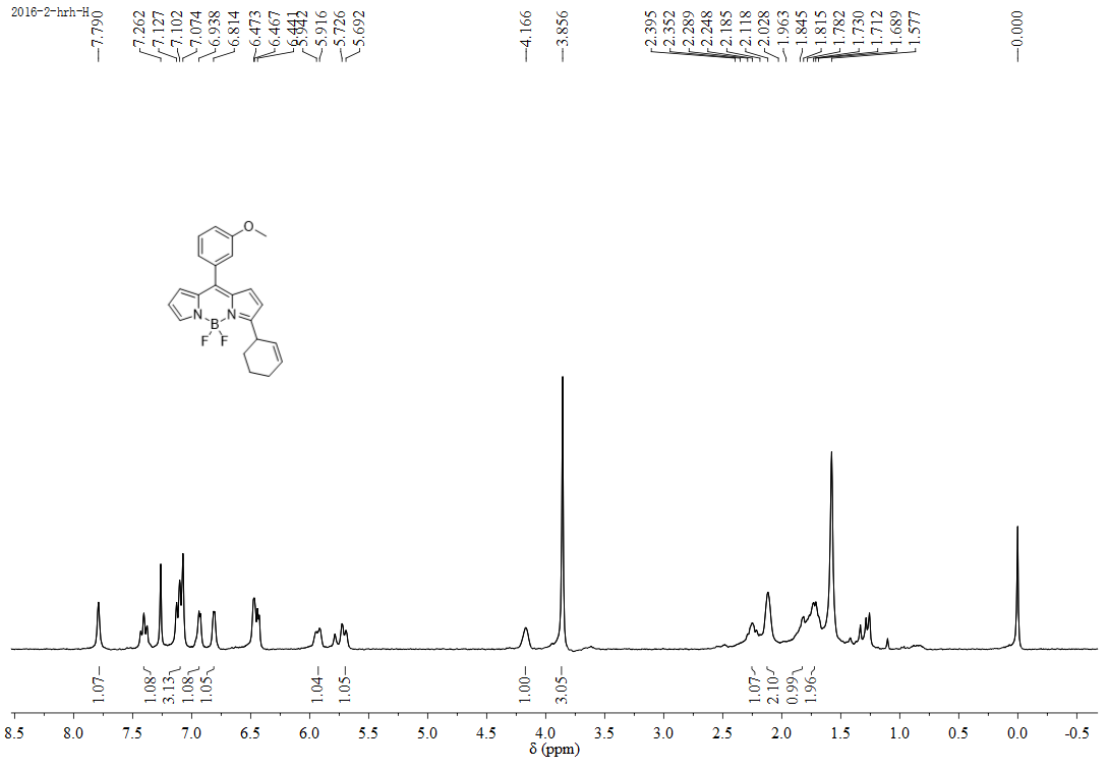
^{13}C NMR spectrum of **1d** in $CDCl_3$



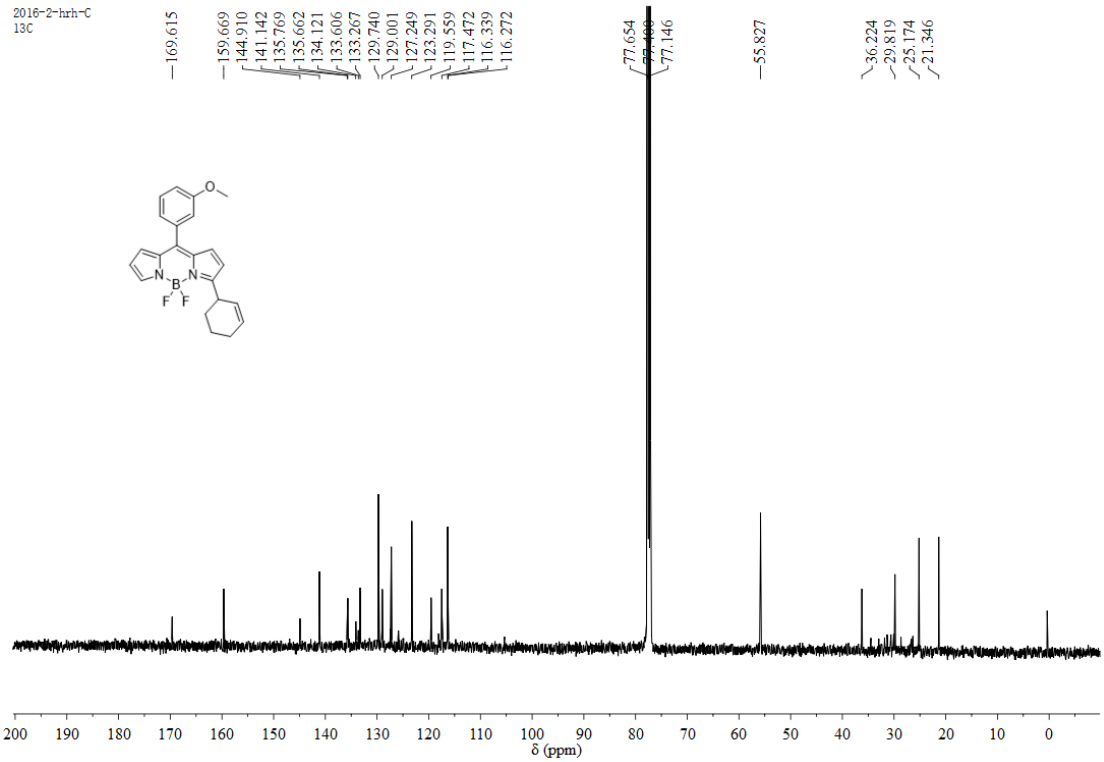
HRMS for **1d**


x10 1
+APCI Scan (# 3-4, 2 scans) Frag=175.0V 0011.d
397.0828
283.1311
338.3392
313.2718
372.1494
199.1028
149.0224
243.1112
Counts (%) vs. Mass-to-Charge (m/z)

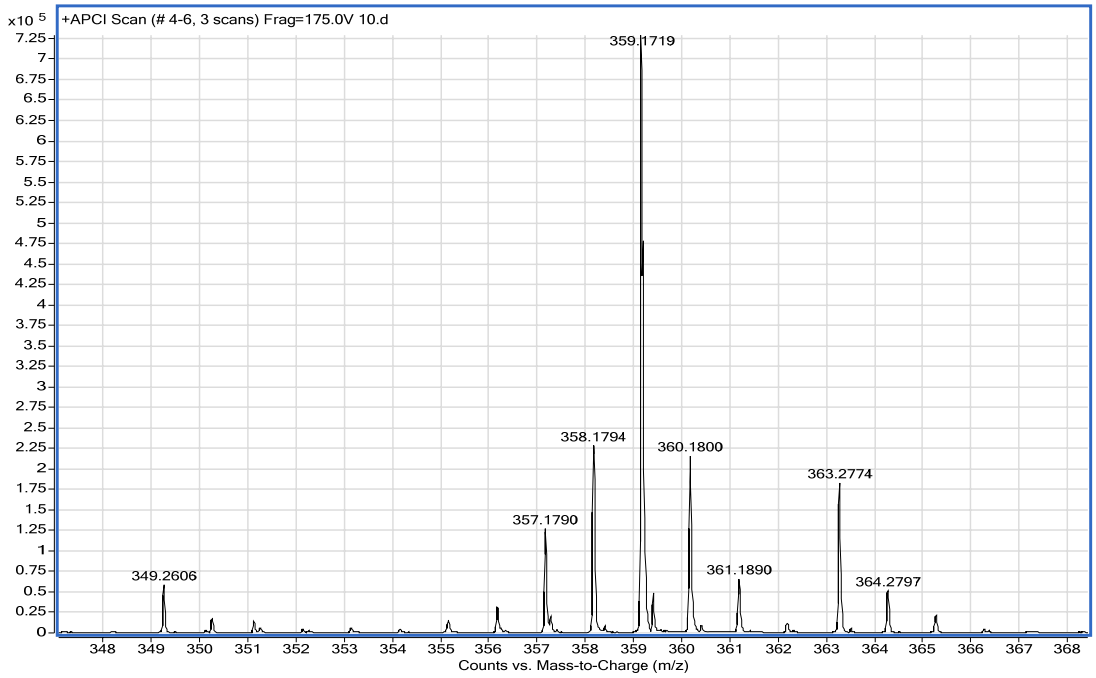
^{1}H NMR spectrum of **1e** in $CDCl_3$



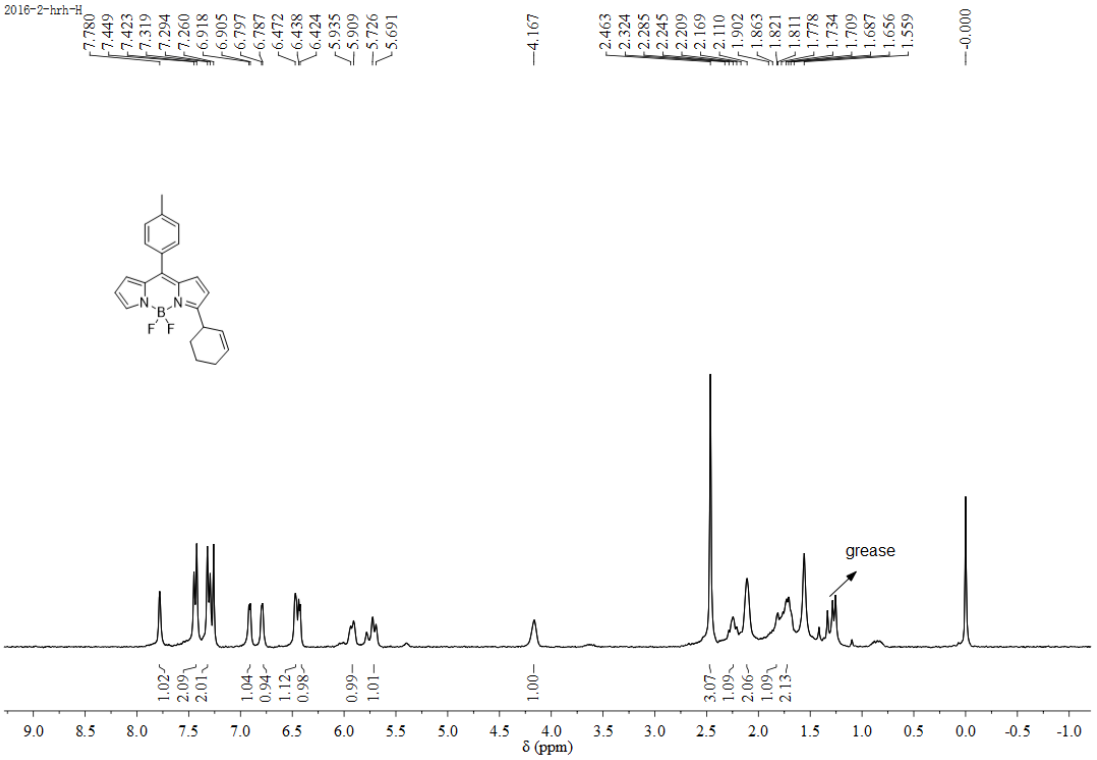
^{13}C NMR spectrum of **1e** in $CDCl_3$



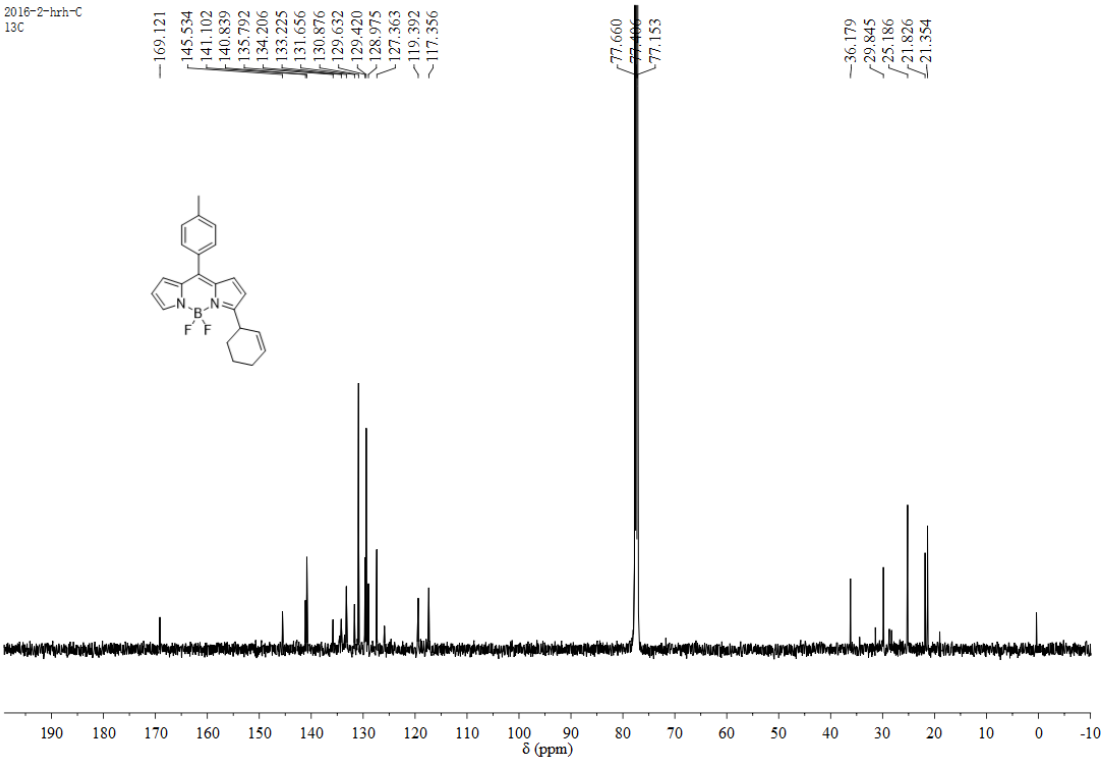
HRMS for **1e**


x10 5
+APCI Scan (# 4-6, 3 scans) Frag=175.0V 10.d
359.1719
358.1794
360.1800
363.2774
357.1790
361.1890
364.2797
349.2606
Counts vs. Mass-to-Charge (m/z)

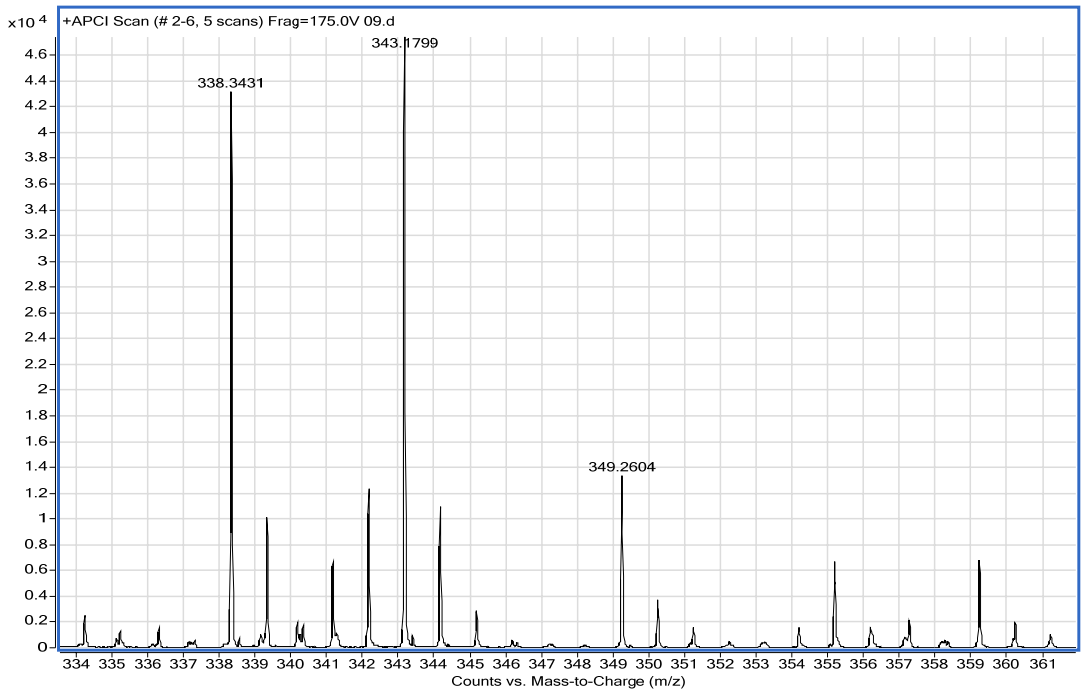
^{1}H NMR spectrum of **1f** in $CDCl_3$



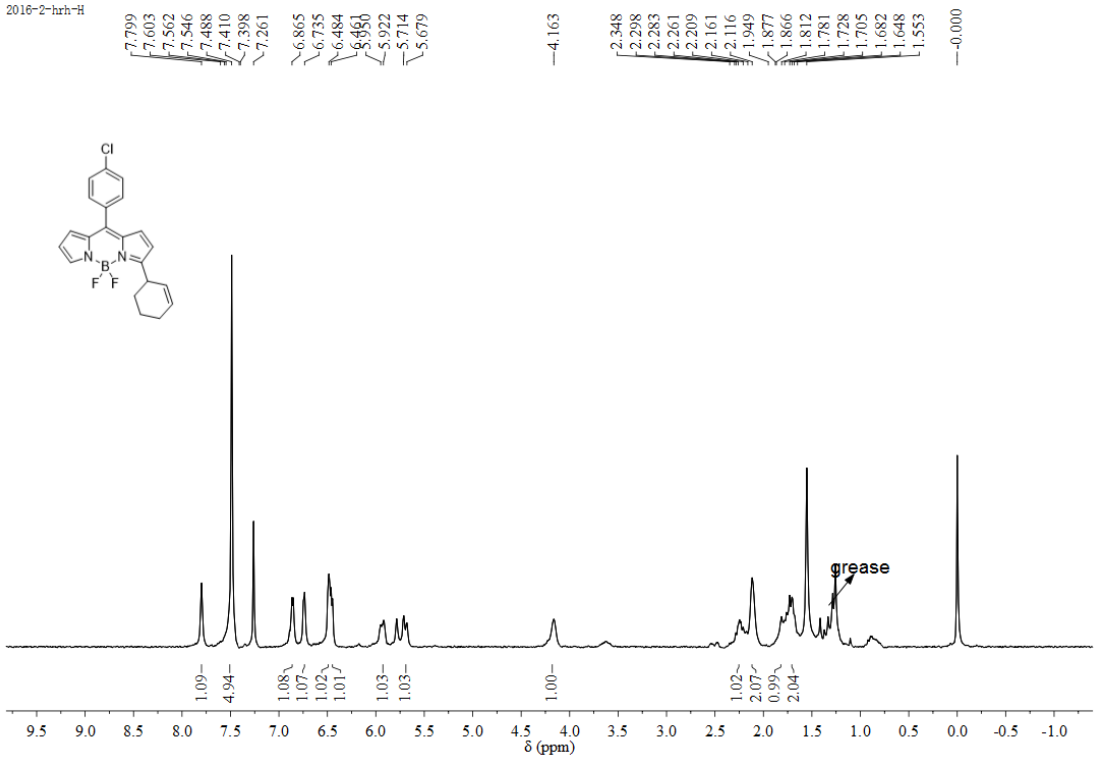
^{13}C NMR spectrum of **1f** in $CDCl_3$



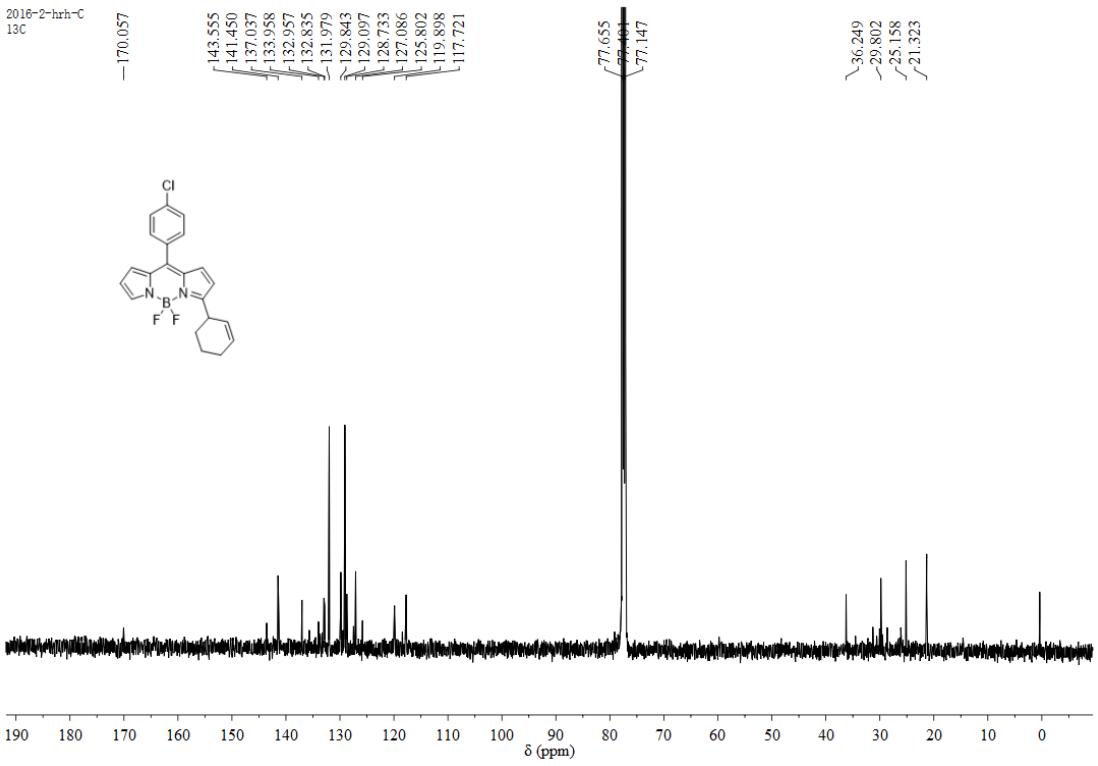
HRMS for **1f**


+APCI Scan (# 2-6, 5 scans) Frag=175.0V 09.d
x10 4
343.1799
338.3431
349.2604
Counts vs. Mass-to-Charge (m/z)

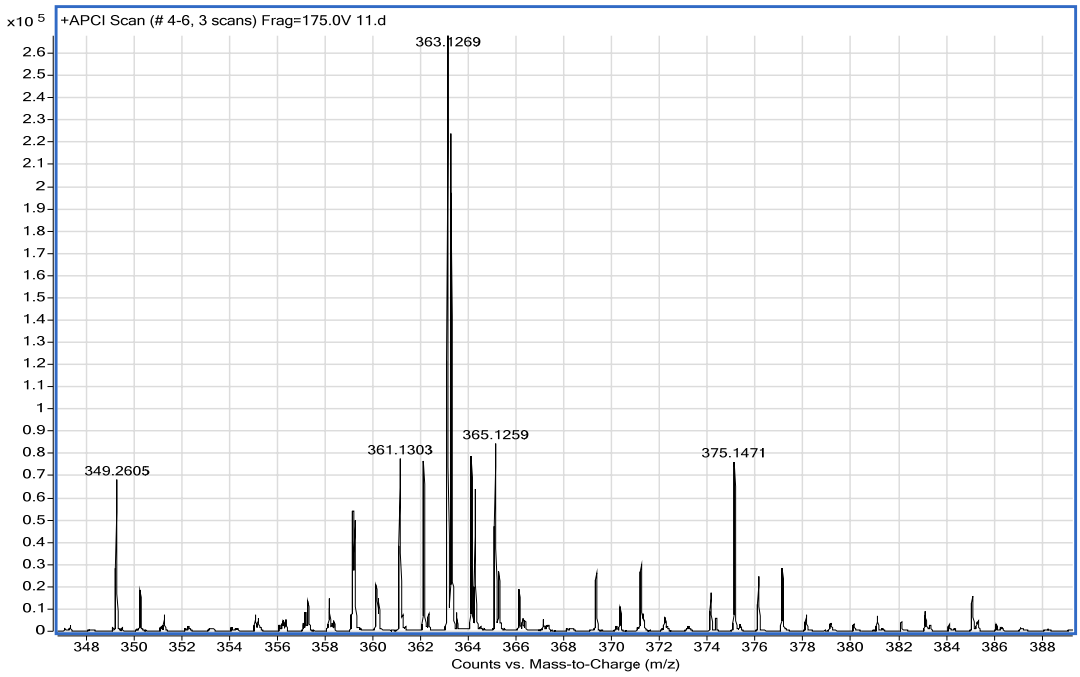
^{1}H NMR spectrum of **1g** in $CDCl_3$



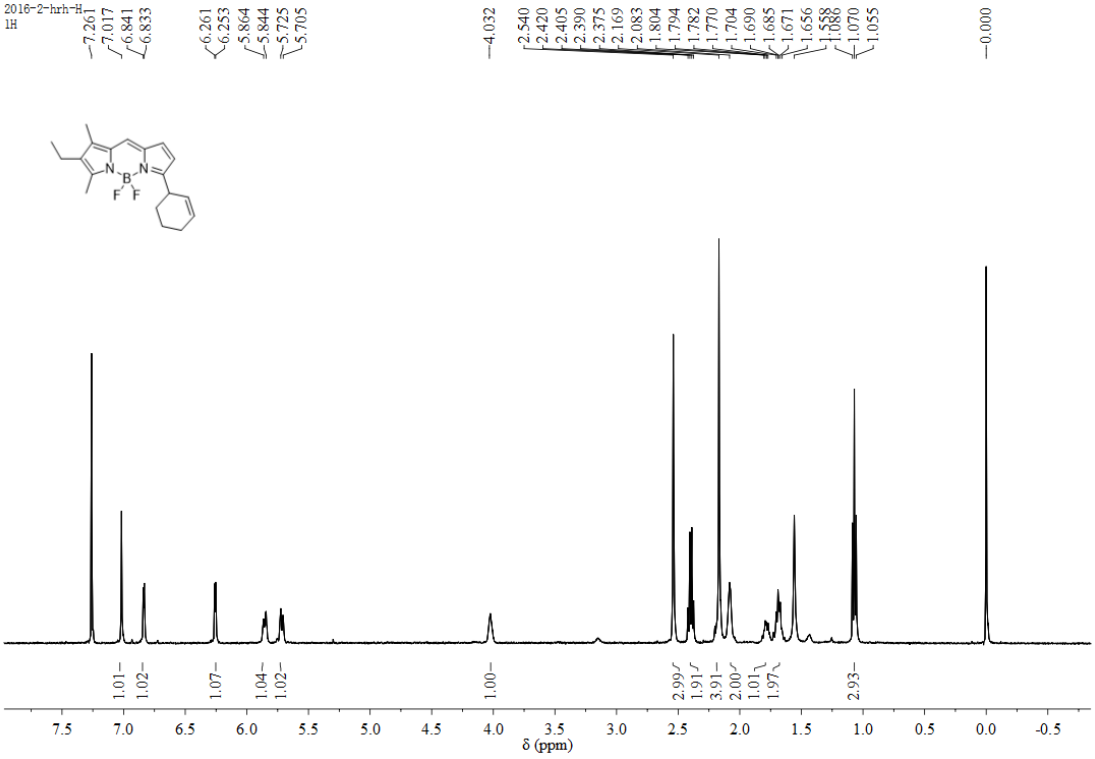
^{13}C NMR spectrum of **1g** in $CDCl_3$



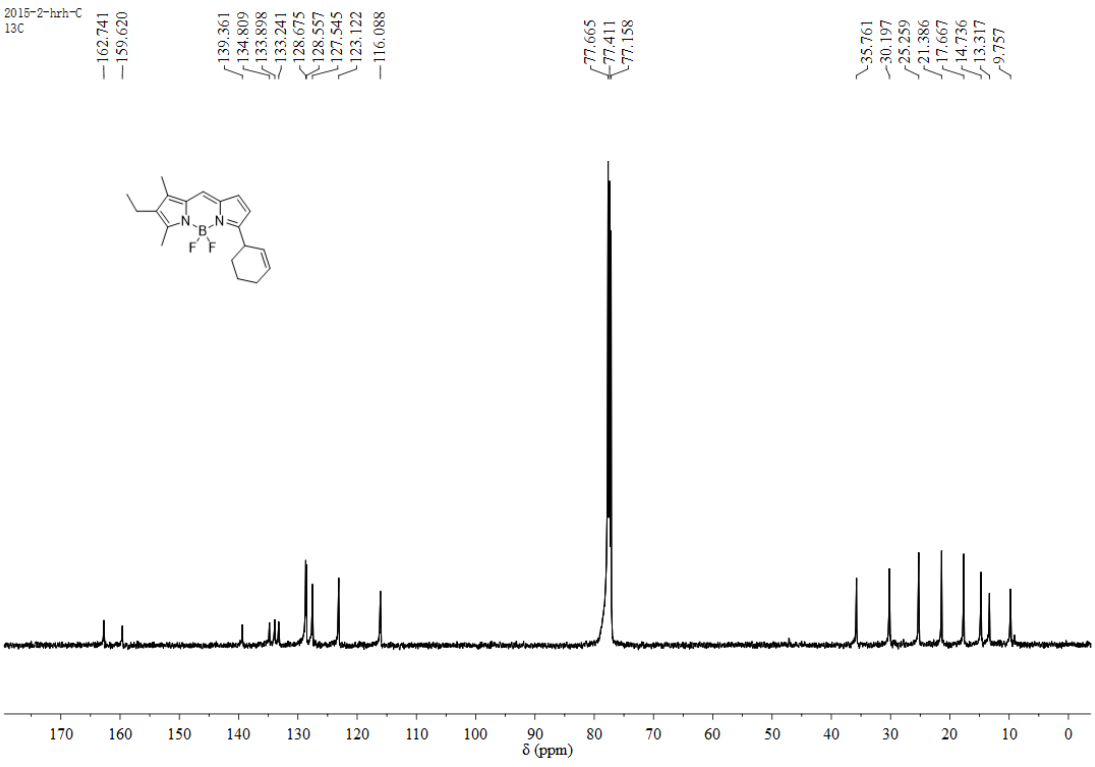
HRMS for **1g**


x10 5
+APCI Scan (# 4-6, 3 scans) Frag=175.0V 11.d
363.1269
365.1259
361.1303
375.1471
349.2605
Counts vs. Mass-to-Charge (m/z)

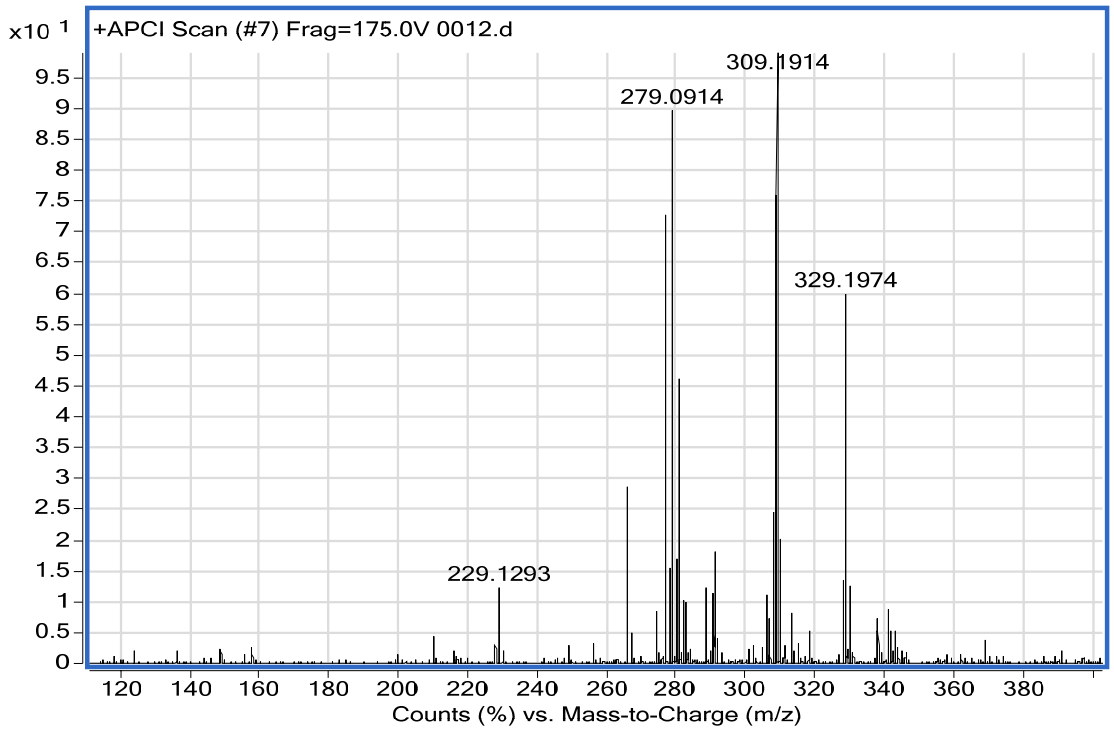
^{1}H NMR spectrum of **1h** in $CDCl_3$



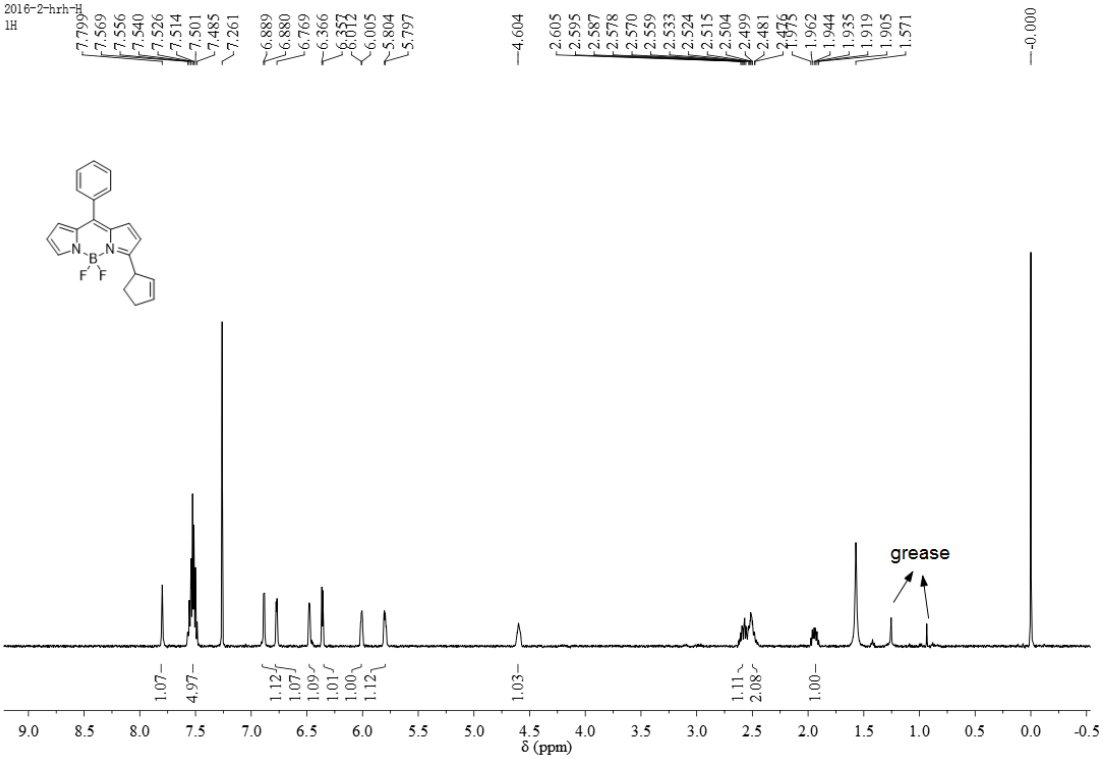
^{13}C NMR spectrum of **1h** in $CDCl_3$



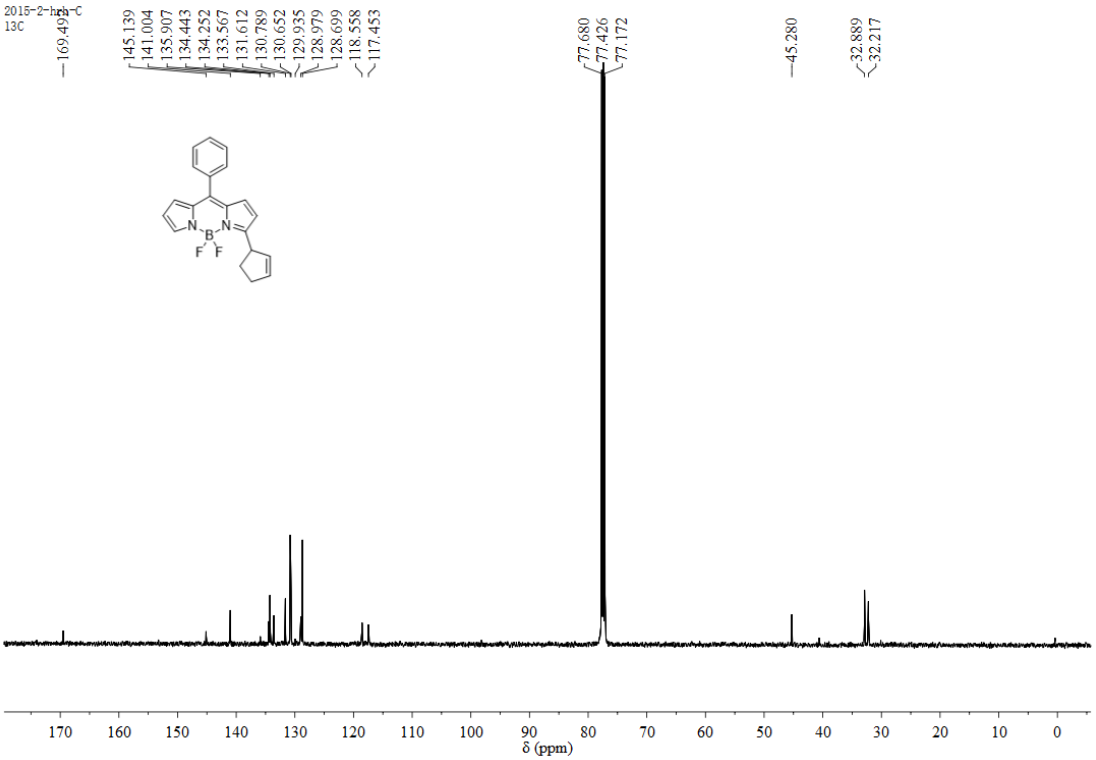
HRMS for **1h**


x10 1
+APCI Scan (#7) Frag=175.0V 0012.d
309.1914
279.0914
329.1974
229.1293
Counts (%) vs. Mass-to-Charge (m/z)

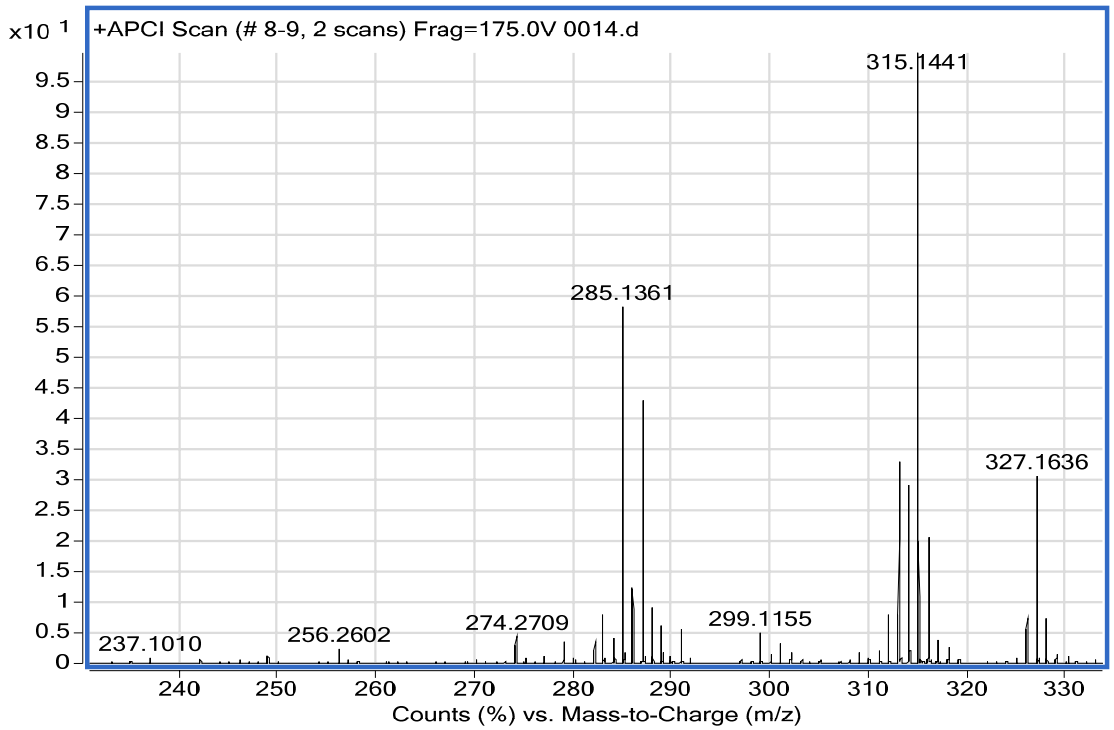
^{1}H NMR spectrum of **1i** in $CDCl_3$



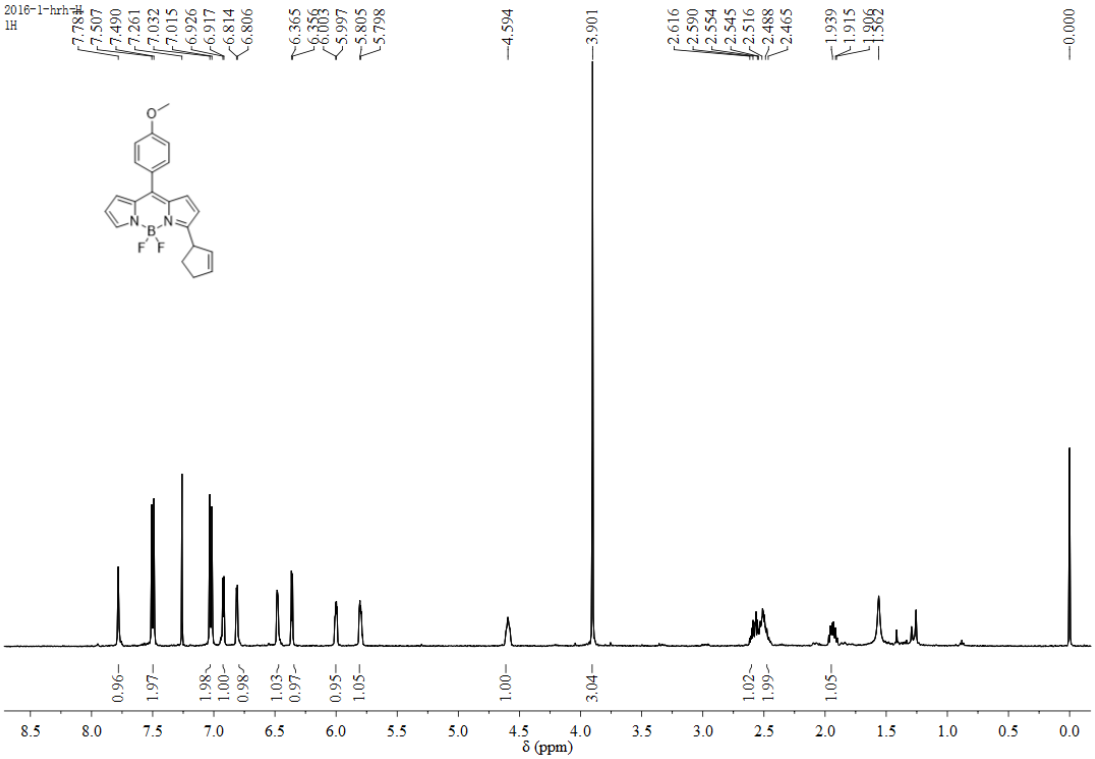
^{13}C NMR spectrum of **1i** in $CDCl_3$



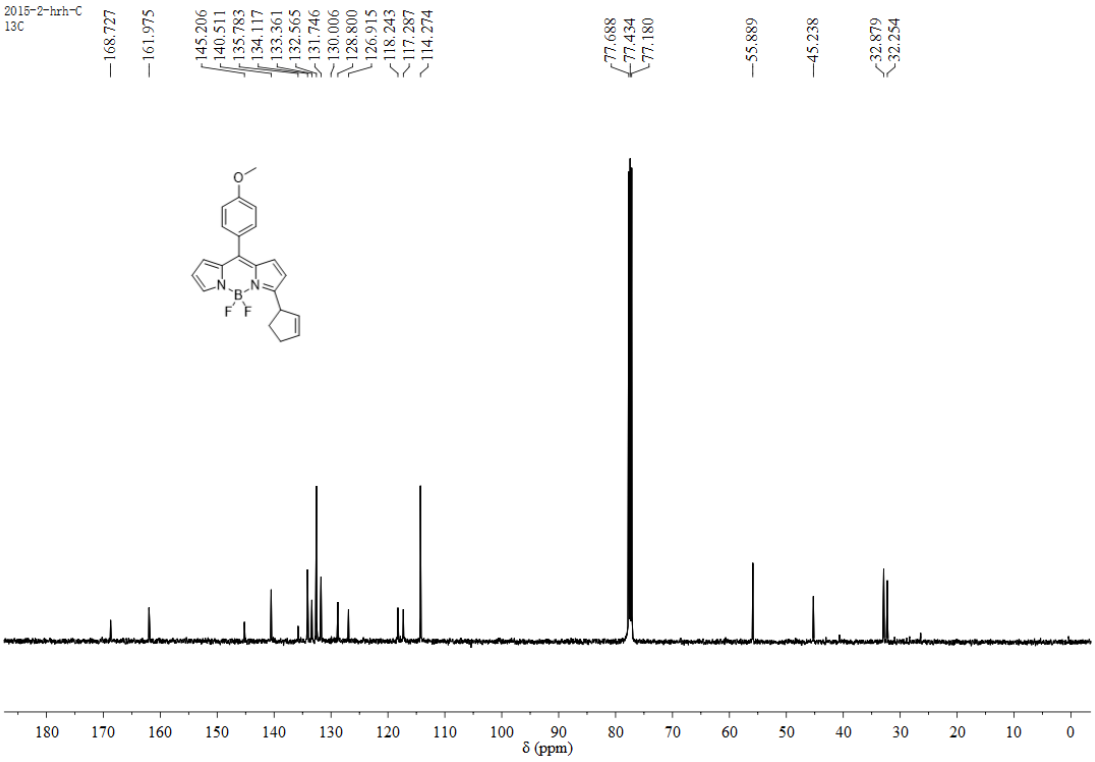
HRMS for **1i**


x10 1
+APCI Scan (# 8-9, 2 scans) Frag=175.0V 0014.d
315.1441
285.1361
327.1636
237.1010
256.2602
274.2709
299.1155
Counts (%) vs. Mass-to-Charge (m/z)

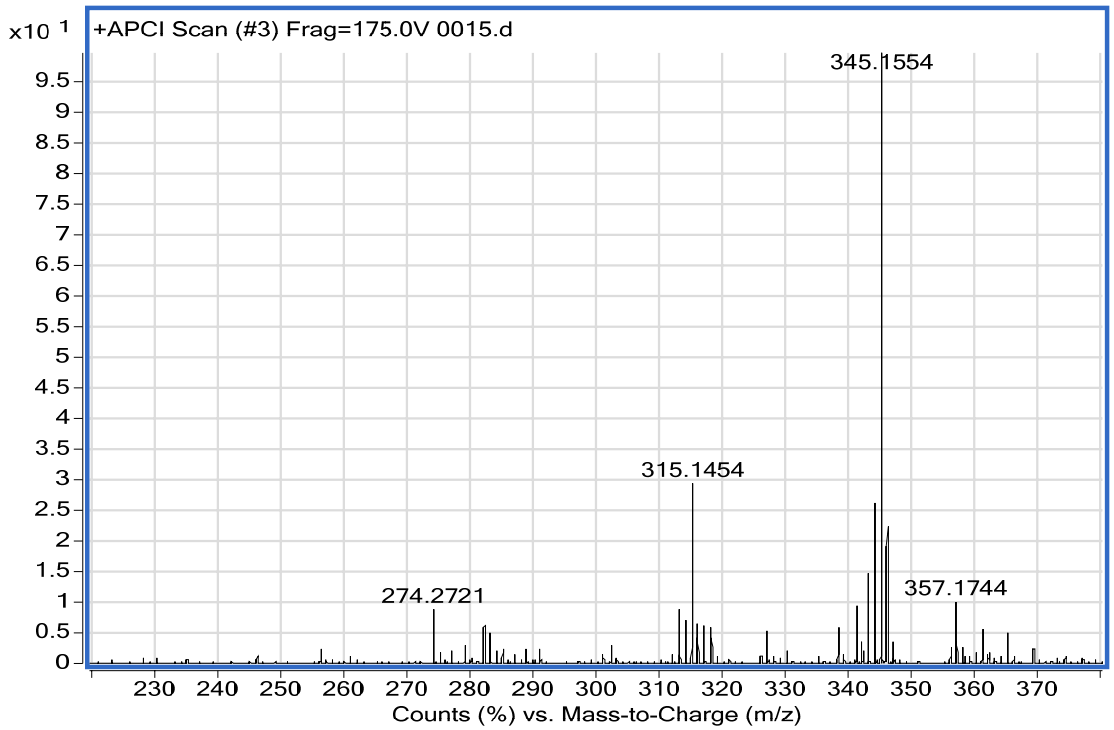
^{1}H NMR spectrum of **1j** in $CDCl_3$



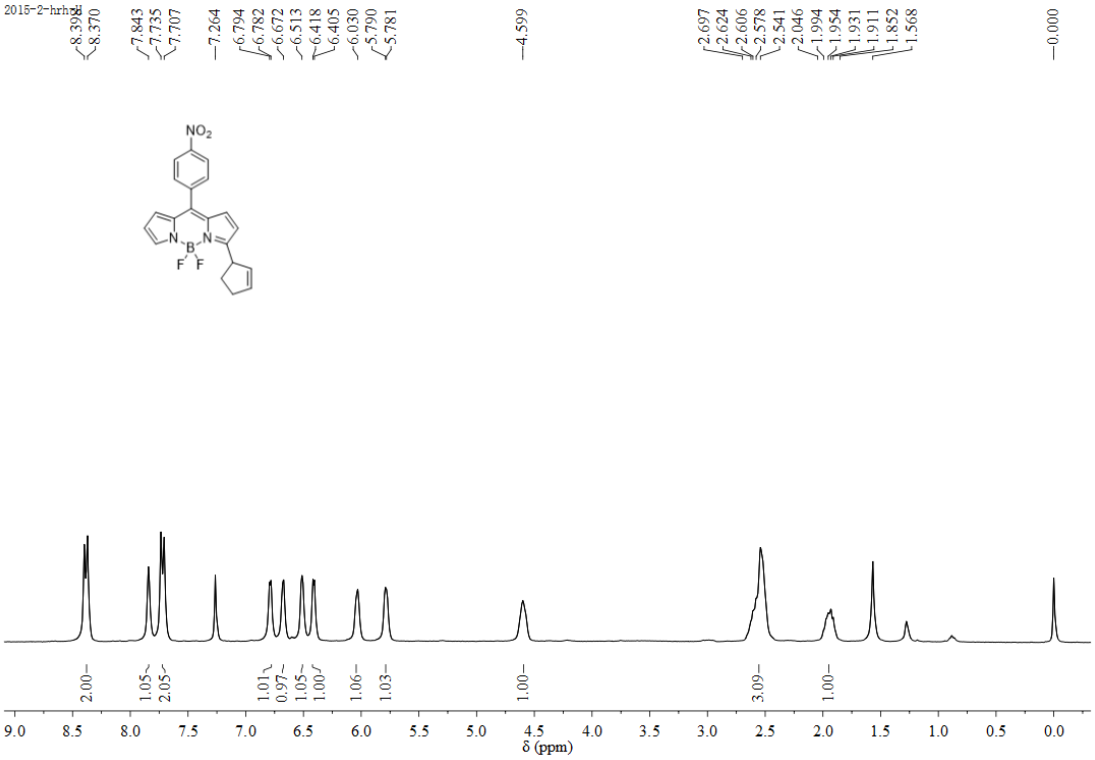
^{13}C NMR spectrum of **1j** in $CDCl_3$



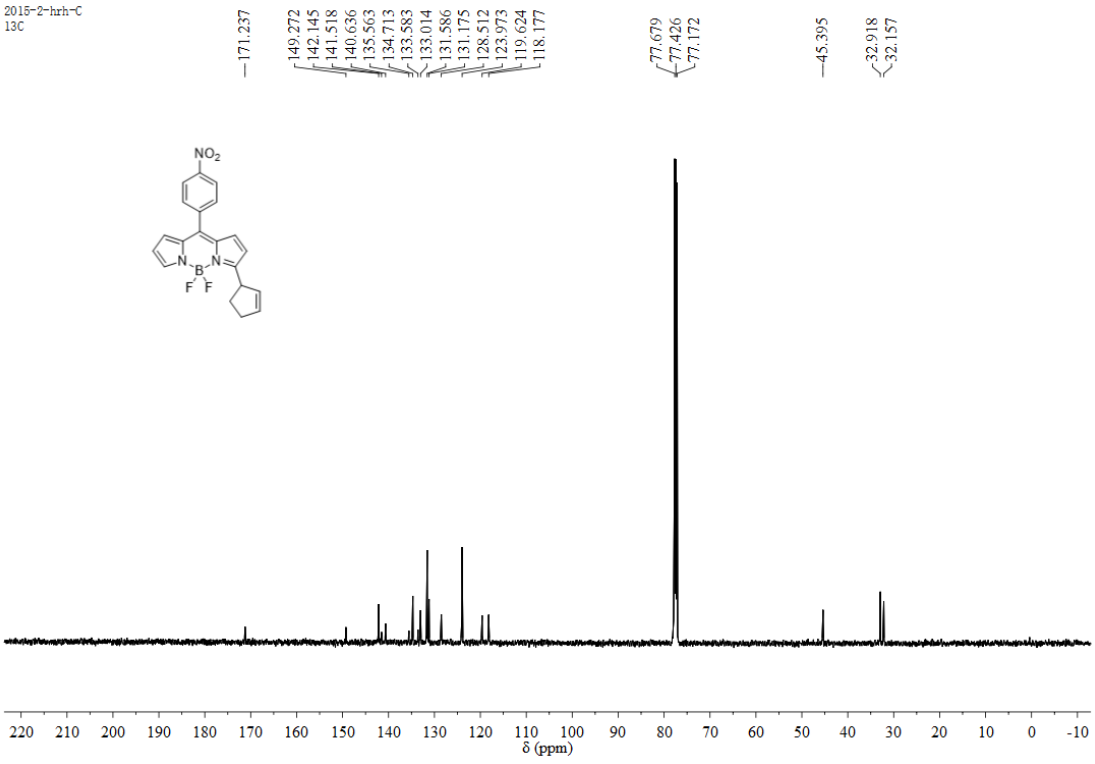
HRMS for **1j**


x10 1
+APCI Scan (#3) Frag=175.0V 0015.d
345.1554
315.1454
274.2721
357.1744
9.5
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
230 240 250 260 270 280 290 300 310 320 330 340 350 360 370
Counts (%) vs. Mass-to-Charge (m/z)

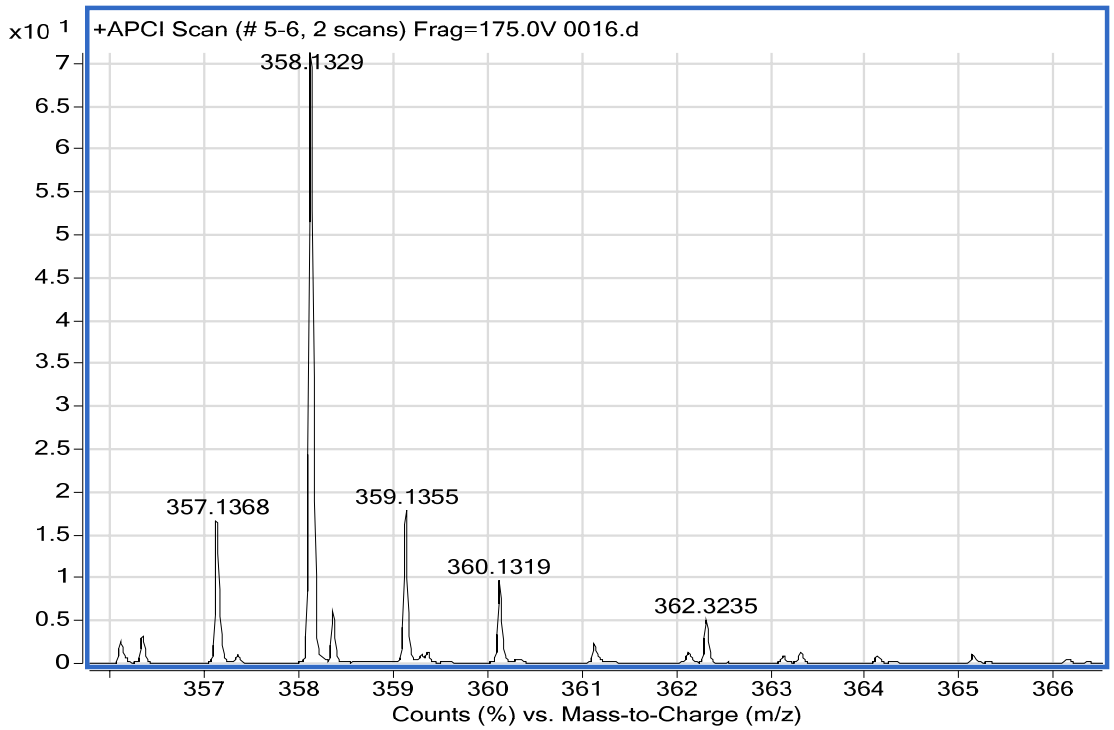
^{1}H NMR spectrum of **1k** in $CDCl_3$



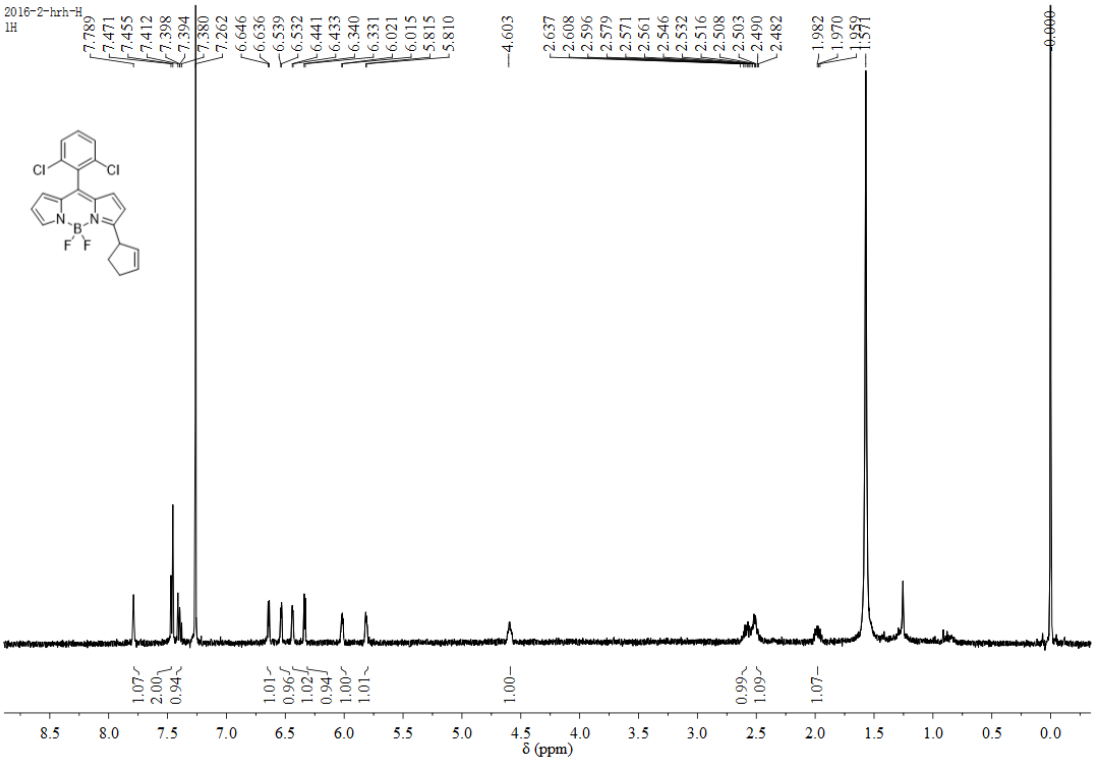
^{13}C NMR spectrum of **1k** in $CDCl_3$



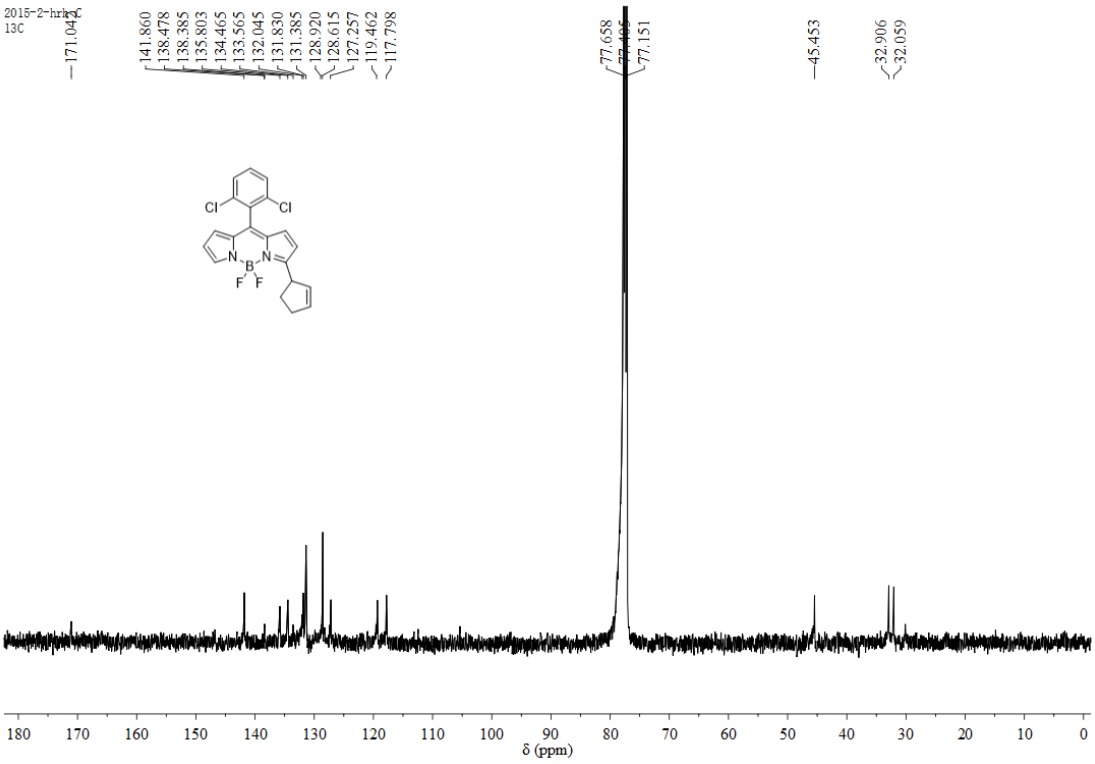
HRMS for **1k**


x10 1
+APCI Scan (# 5-6, 2 scans) Frag=175.0V 0016.d
358.1329
357.1368
359.1355
360.1319
362.3235
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
357
358
359
360
361
362
363
364
365
366
Counts (%) vs. Mass-to-Charge (m/z)

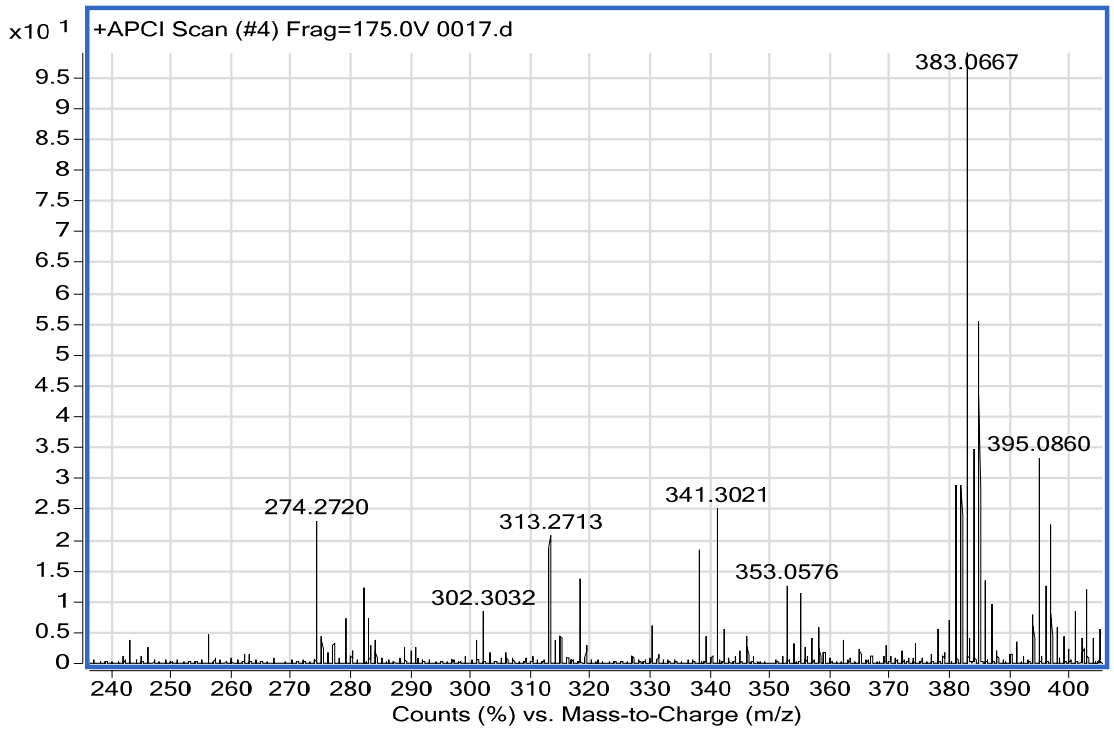
^{1}H NMR spectrum of **1l** in $CDCl_3$



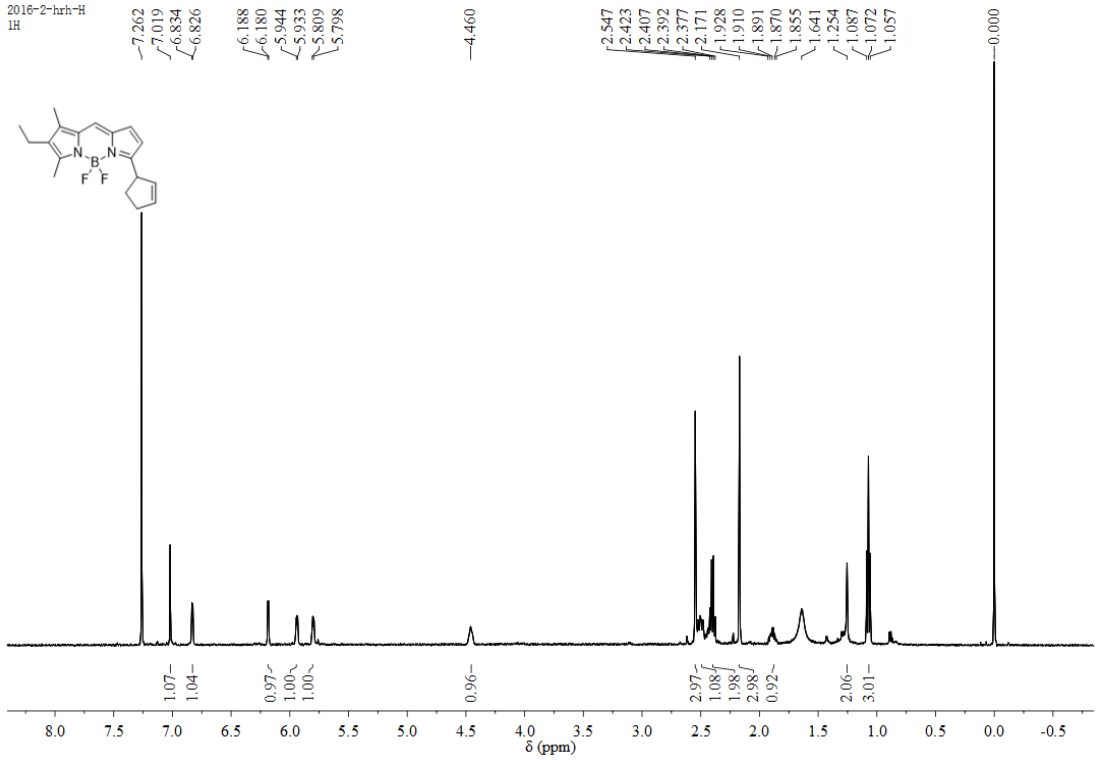
^{13}C NMR spectrum of **1l** in $CDCl_3$



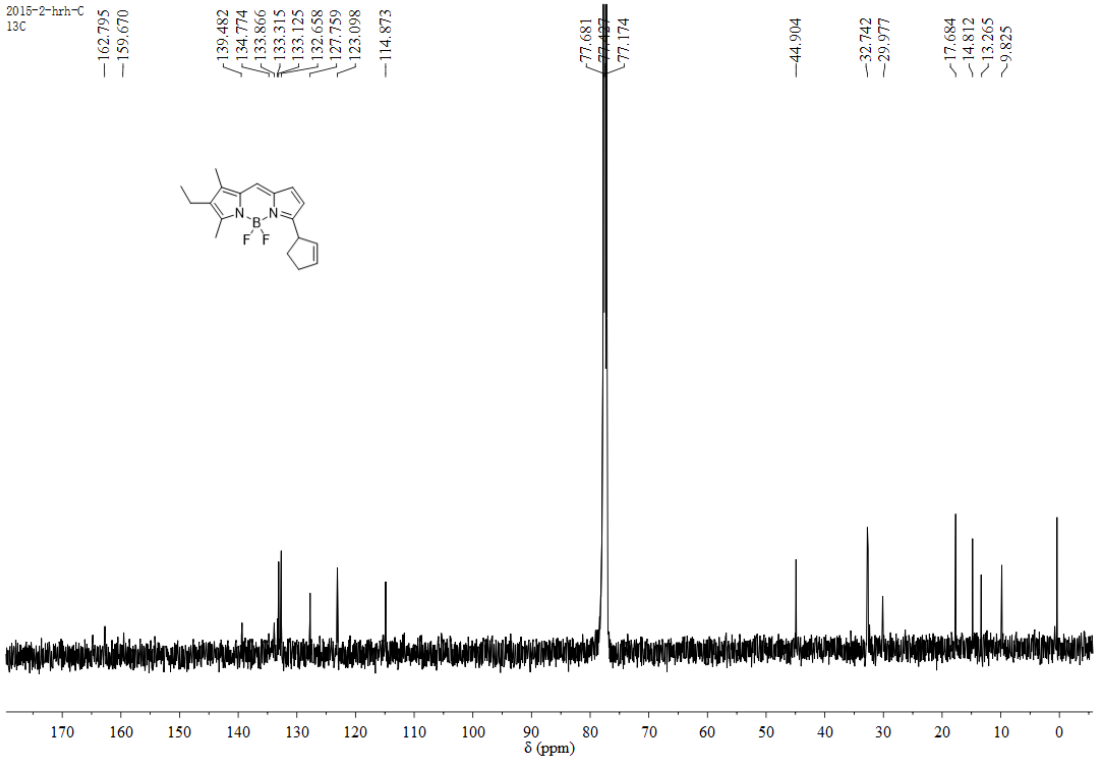
HRMS for **1l**


x10 1
+APCI Scan (#4) Frag=175.0V 0017.d
383.0667
395.0860
341.3021
274.2720
313.2713
353.0576
302.3032
Counts (%) vs. Mass-to-Charge (m/z)

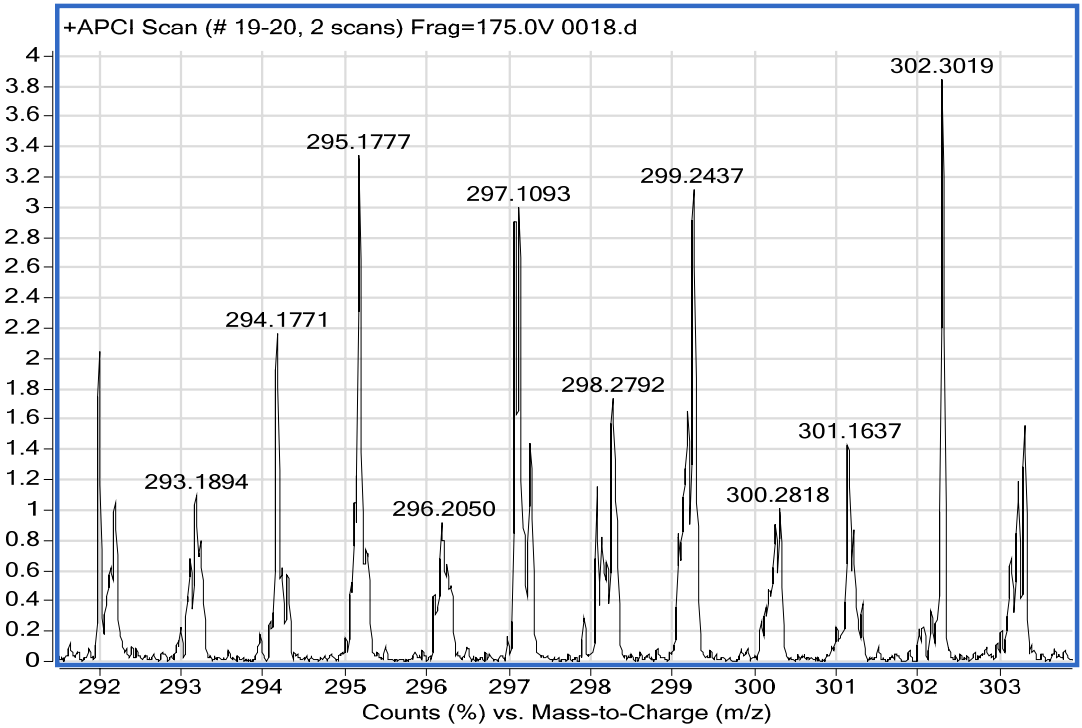
^{1}H NMR spectrum of **1m** in $CDCl_3$



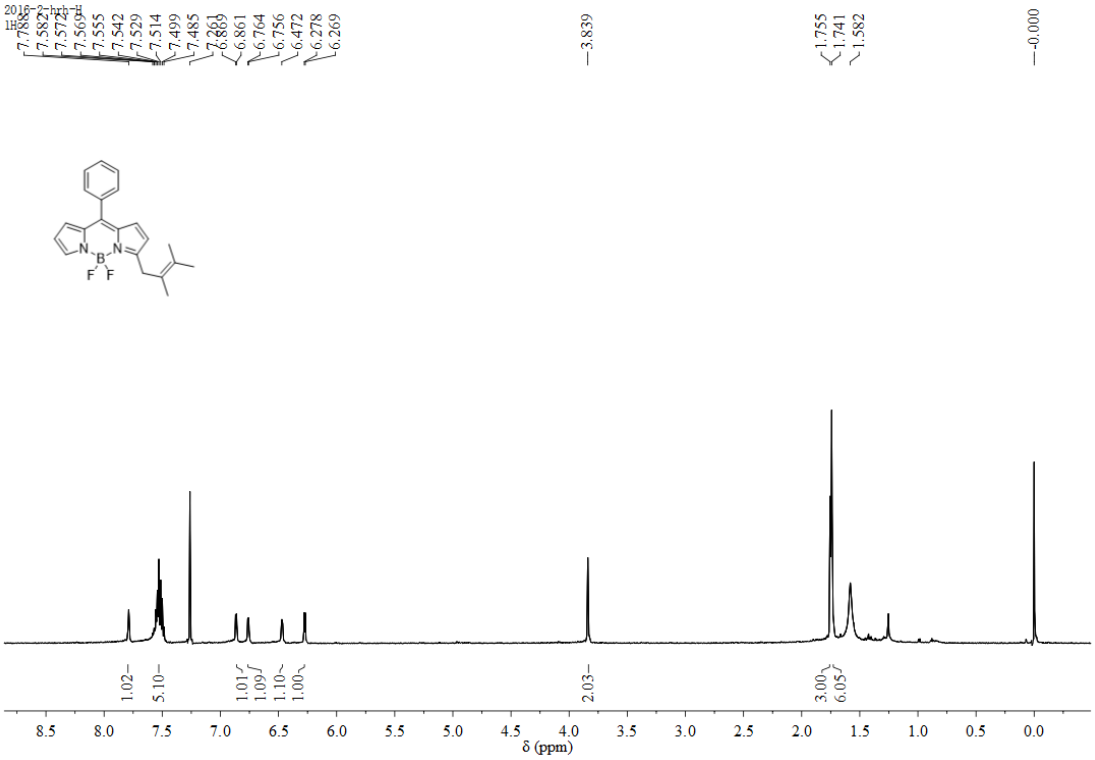
^{13}C NMR spectrum of **1m** in $CDCl_3$



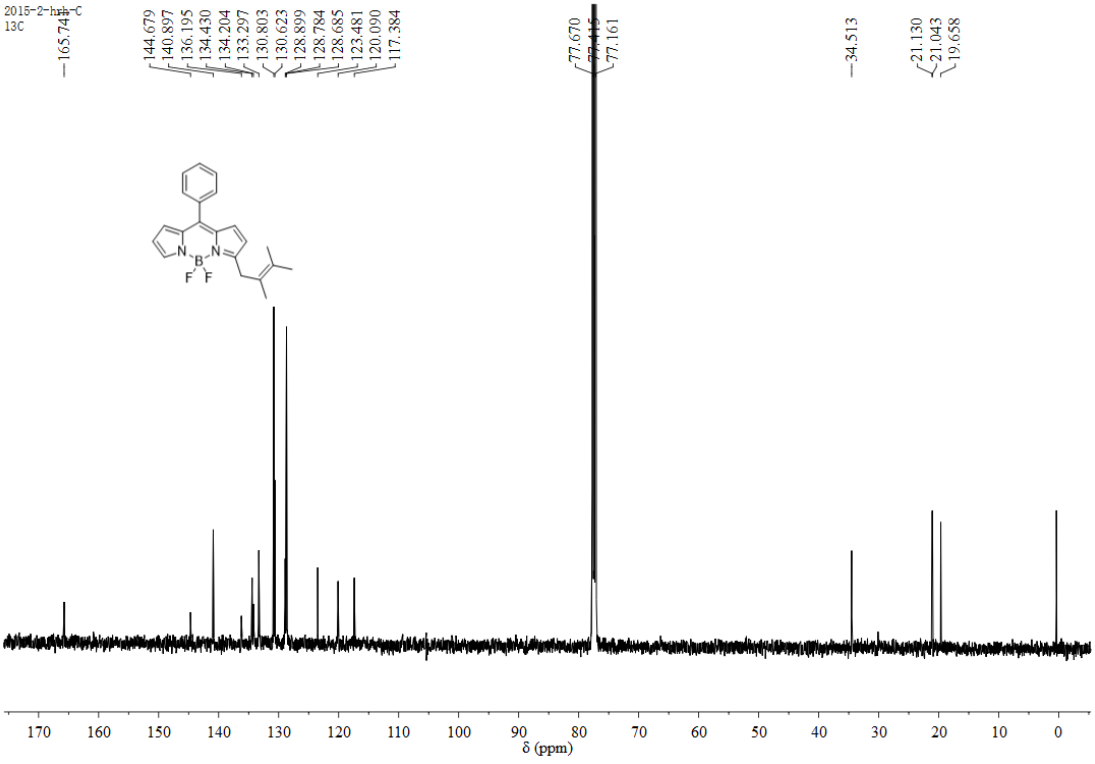
HRMS for **1m**


+APCI Scan (# 19-20, 2 scans) Frag=175.0V 0018.d
302.3019
295.1777
299.2437
297.1093
294.1771
298.2792
301.1637
293.1894
296.2050
300.2818
Counts (%) vs. Mass-to-Charge (m/z)

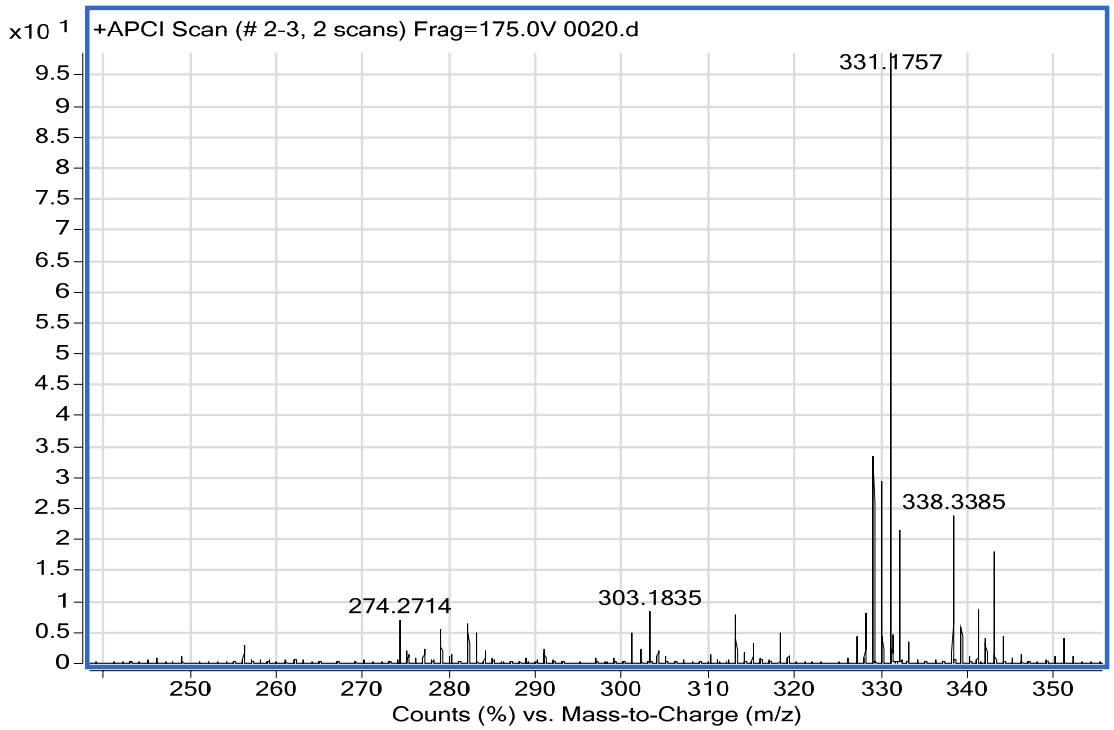
^{1}H NMR spectrum of **1n** in $CDCl_3$



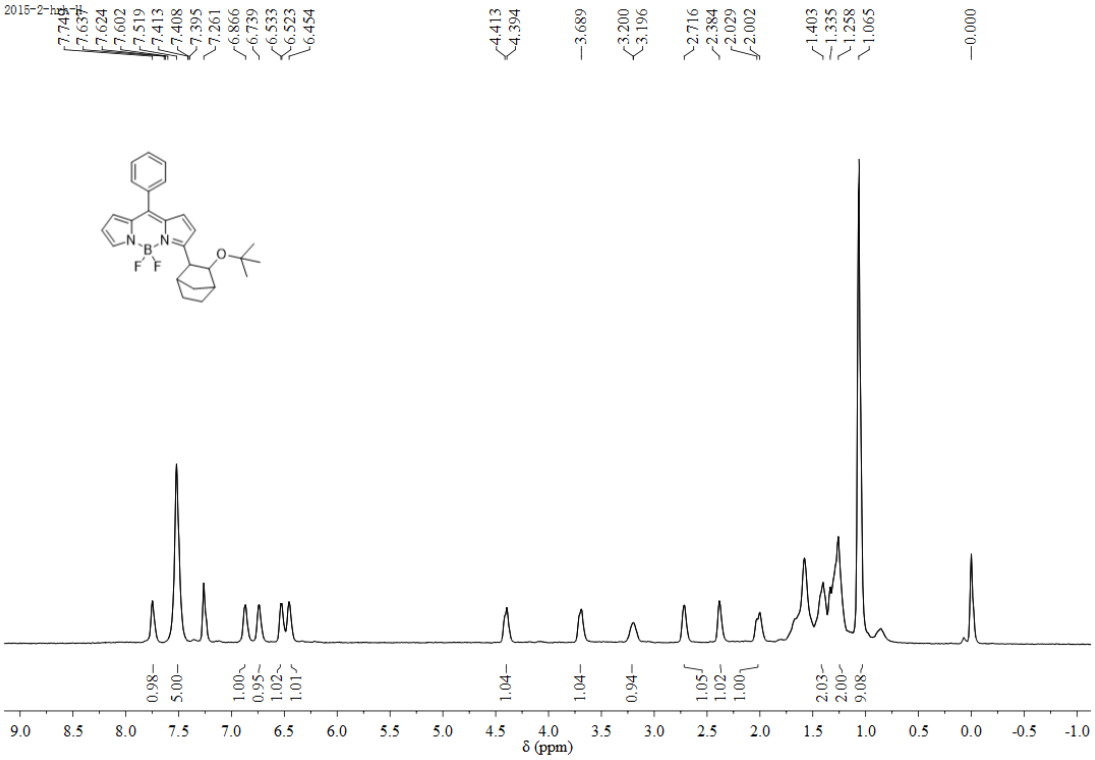
^{13}C NMR spectrum of **1n** in $CDCl_3$



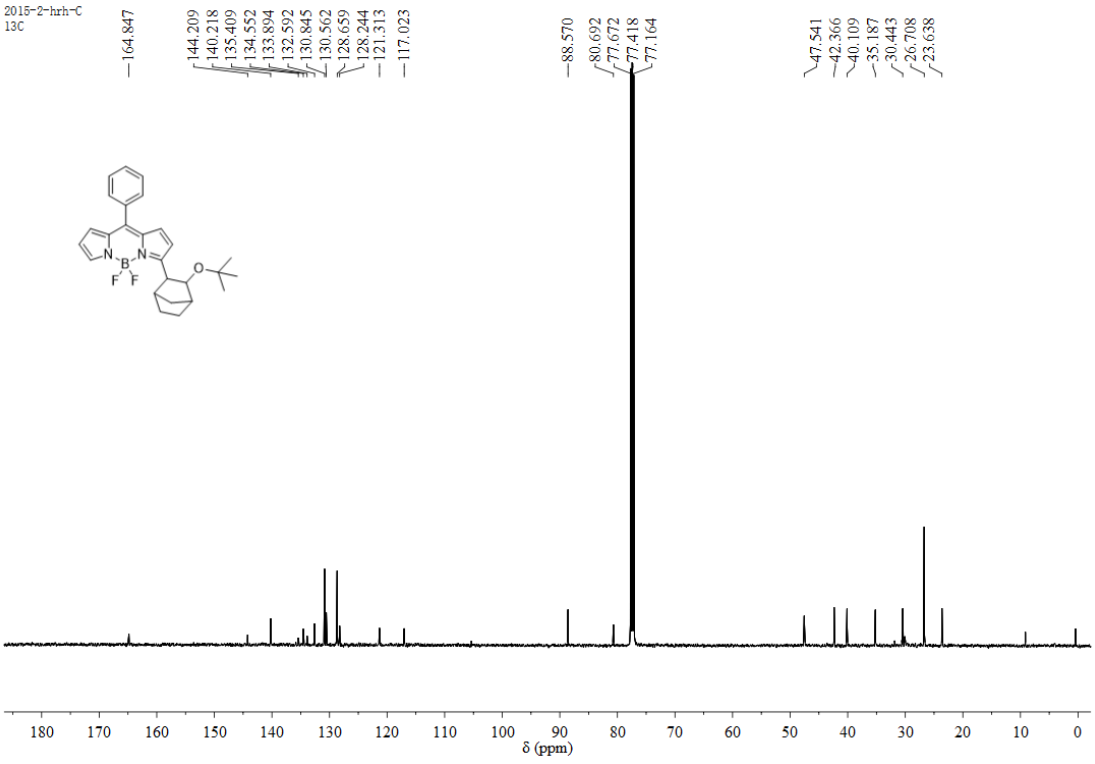
HRMS for **1n**


x10 1
+APCI Scan (# 2-3, 2 scans) Frag=175.0V 0020.d
331.1757
338.3385
303.1835
274.2714
Counts (%) vs. Mass-to-Charge (m/z)

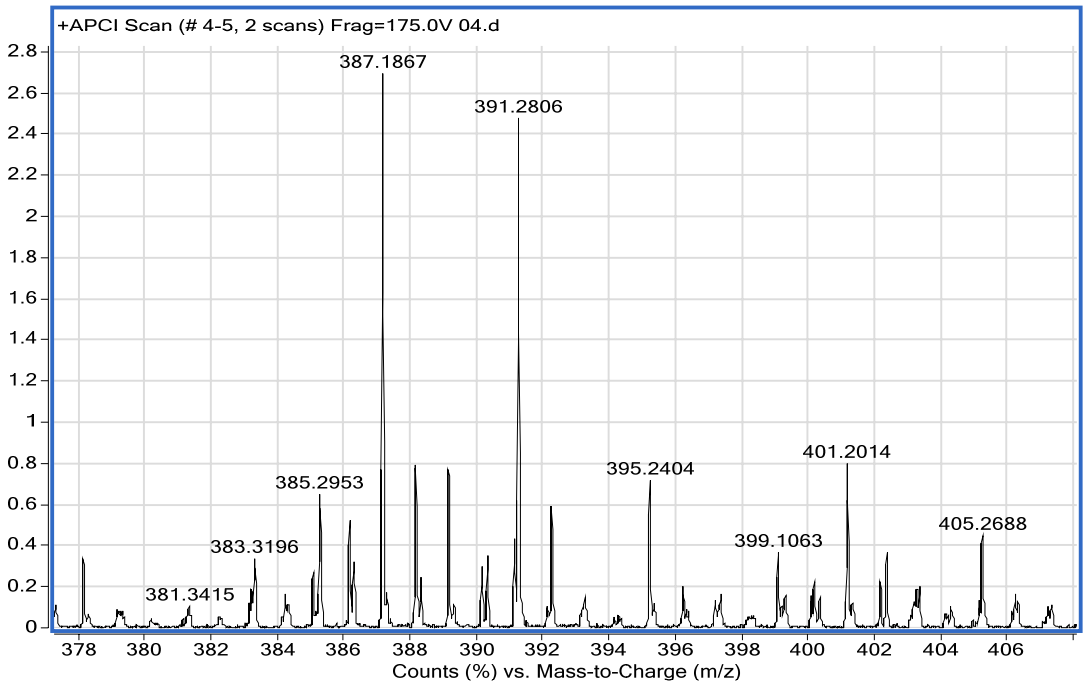
^{1}H NMR spectrum of **1o** in $CDCl_3$



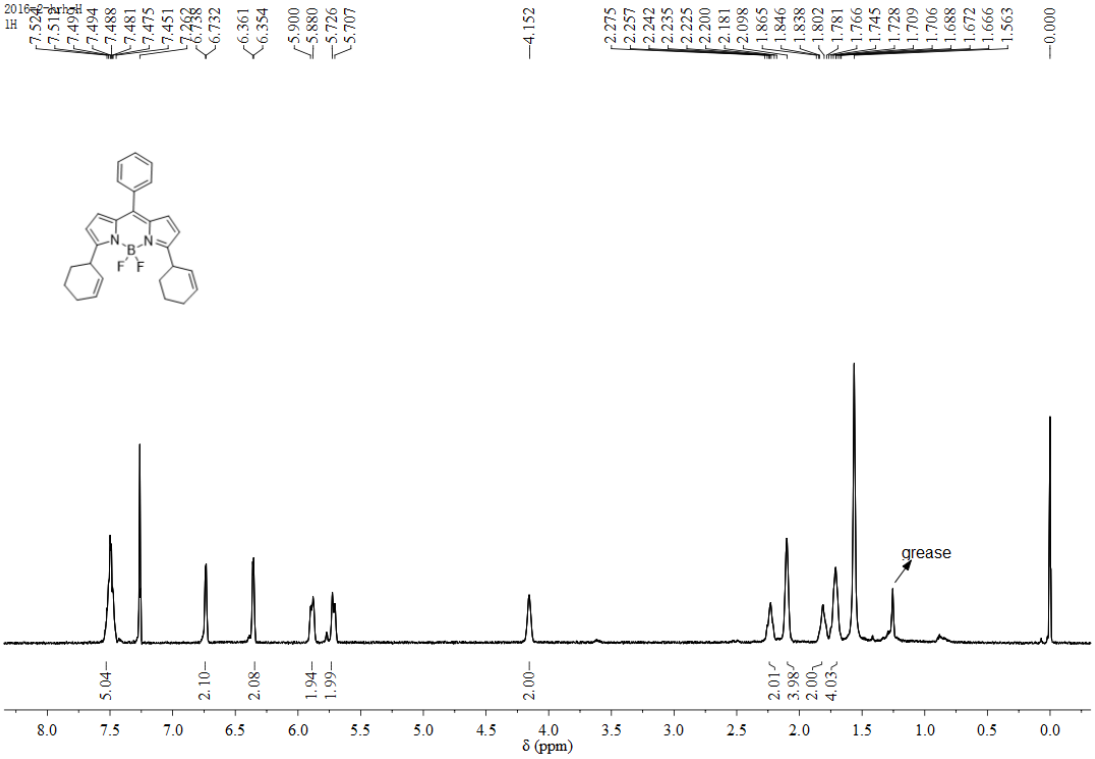
^{13}C NMR spectrum of **1o** in $CDCl_3$



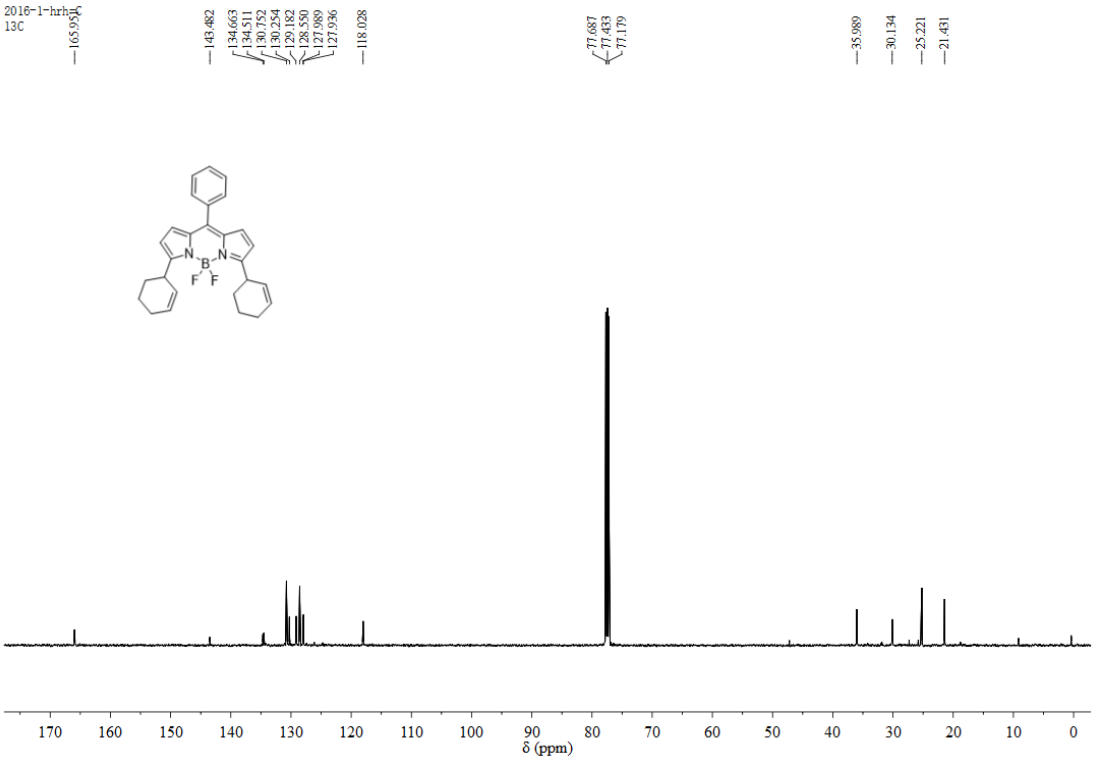
HRMS for **1o**


+APCI Scan (# 4-5, 2 scans) Frag=175.0V 04.d
387.1867
391.2806
385.2953
395.2404
401.2014
405.2688
383.3196
399.1063
381.3415
Counts (%) vs. Mass-to-Charge (m/z)

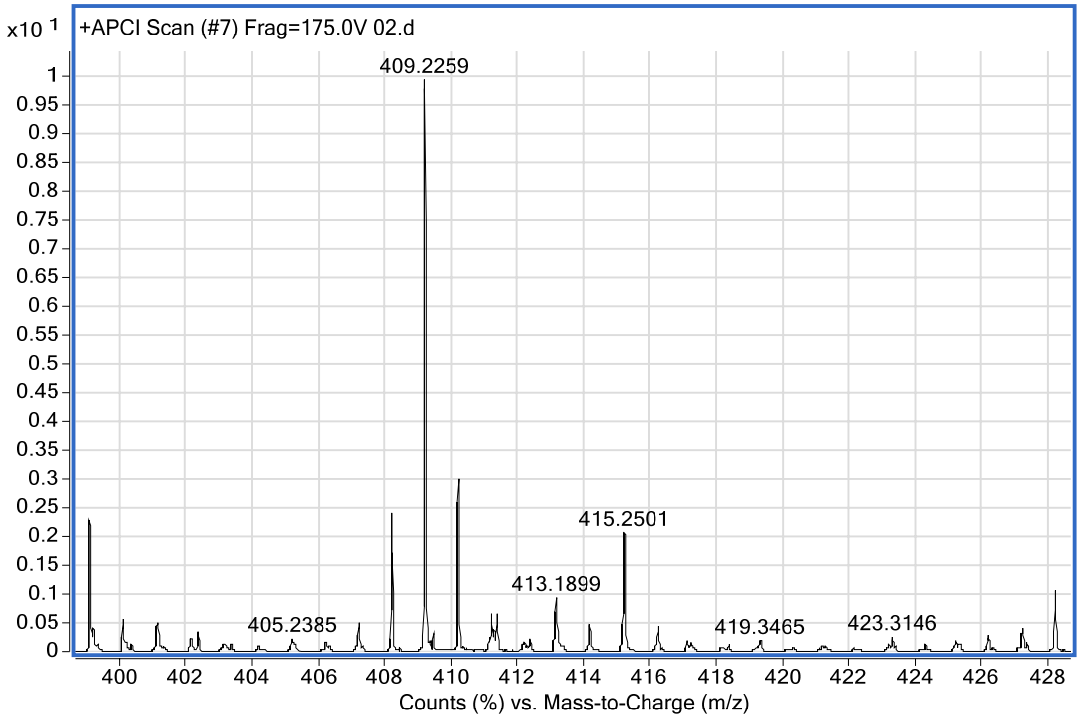
^{1}H NMR spectrum of **3a** in $CDCl_3$



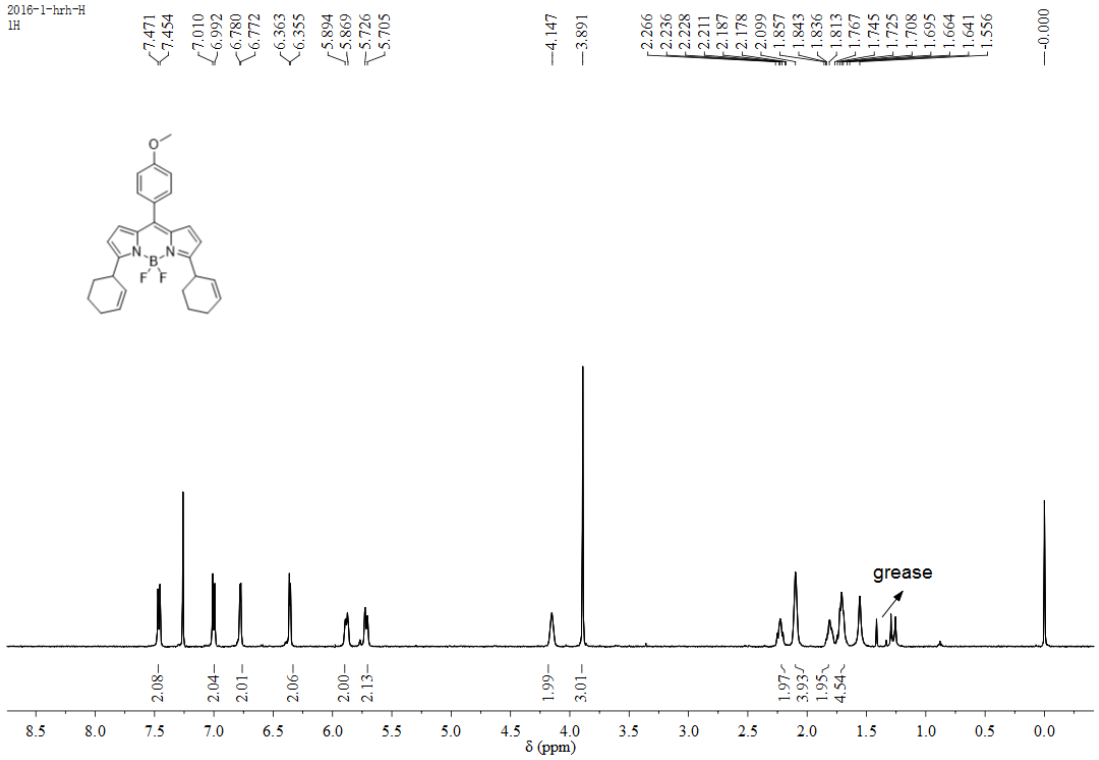
^{13}C NMR spectrum of **3a** in $CDCl_3$



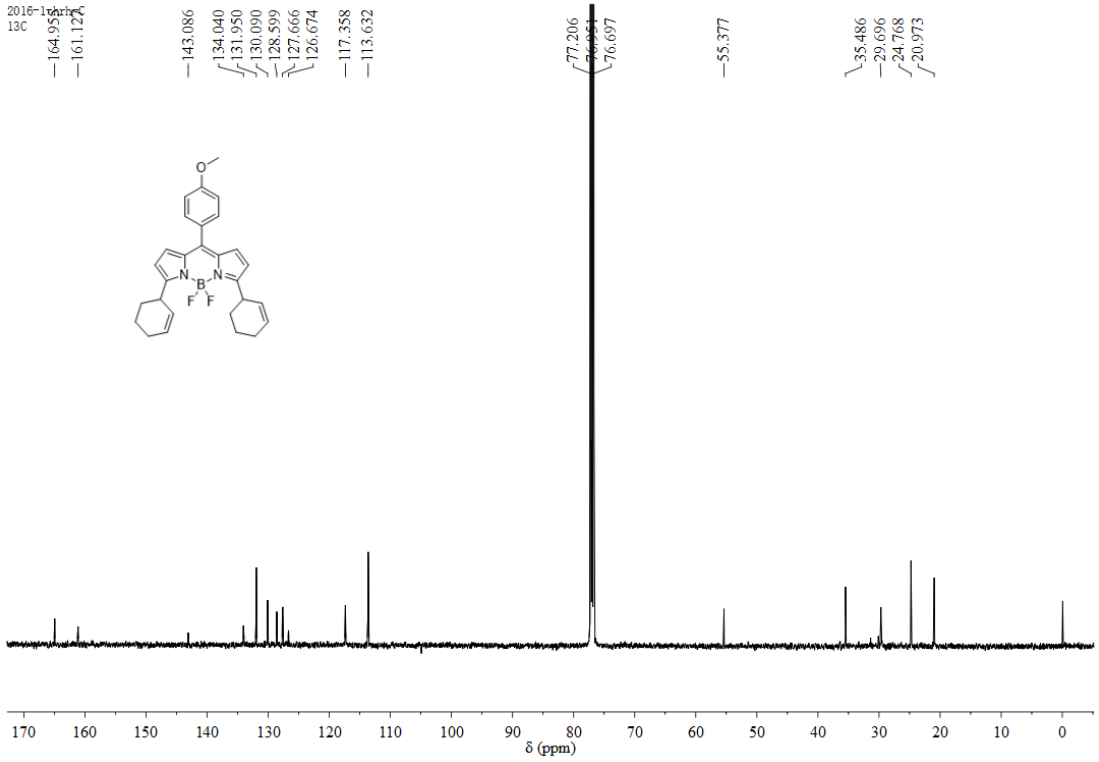
HRMS for **3a**


x10 1
+APCI Scan (#7) Frag=175.0V 02.d
409.2259
415.2501
413.1899
405.2385
419.3465
423.3146
Counts (%) vs. Mass-to-Charge (m/z)

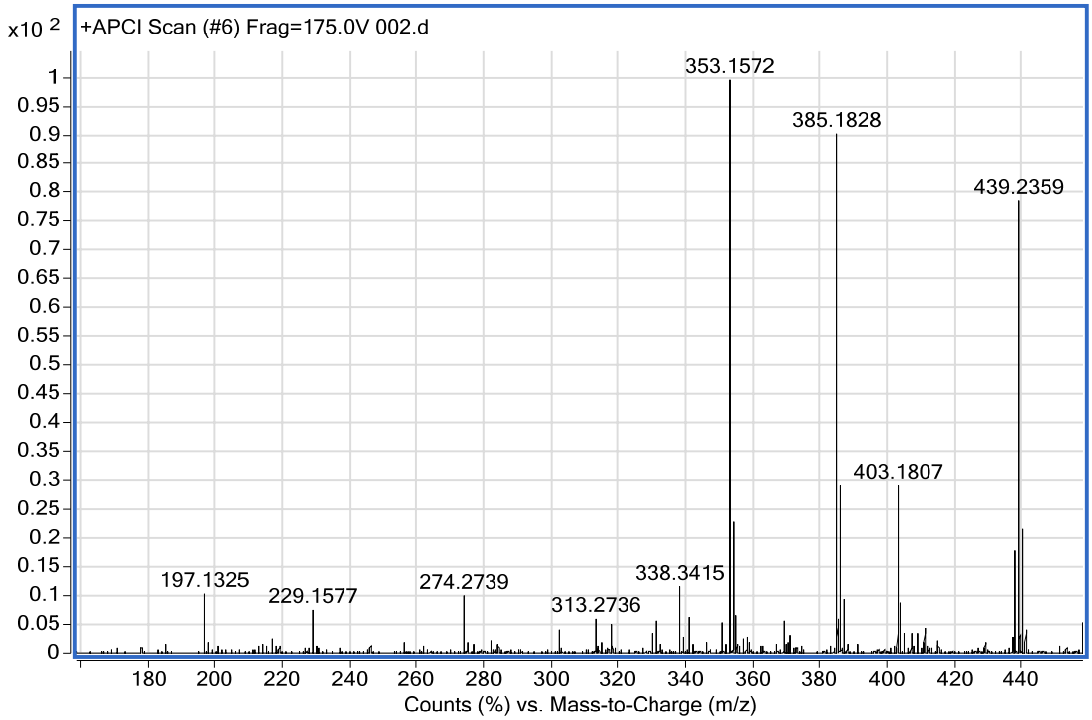
^{1}H NMR spectrum of **3b** in $CDCl_3$



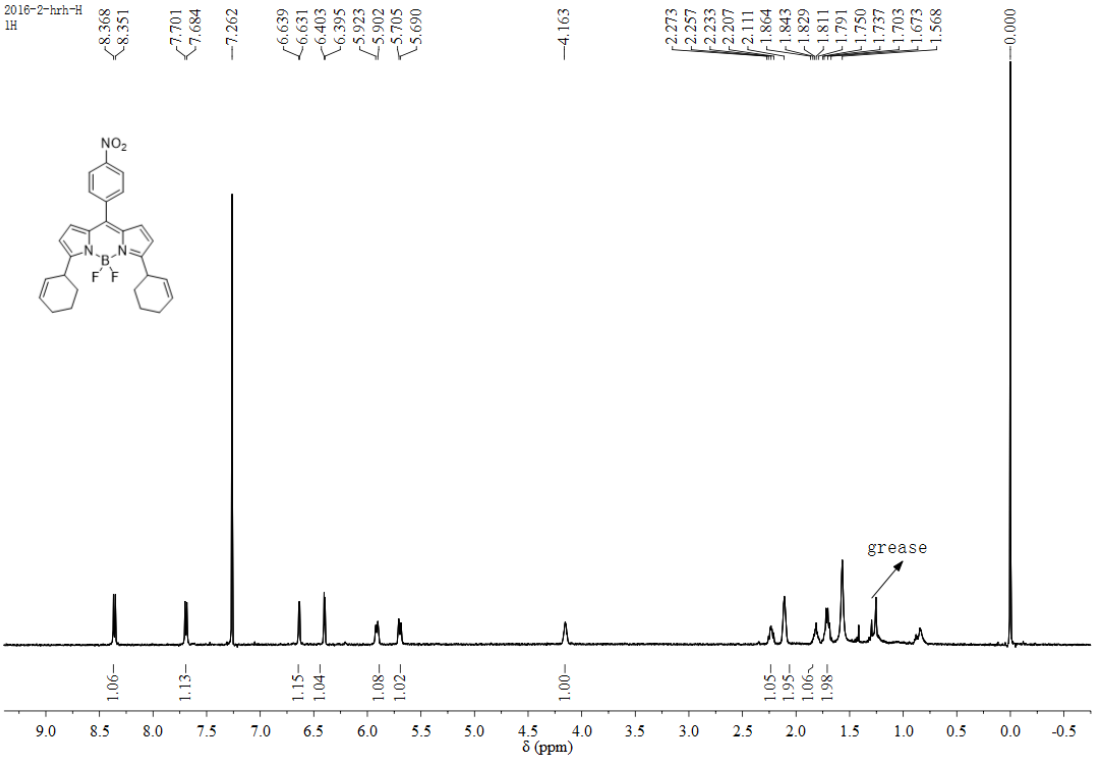
^{13}C NMR spectrum of **3b** in $CDCl_3$



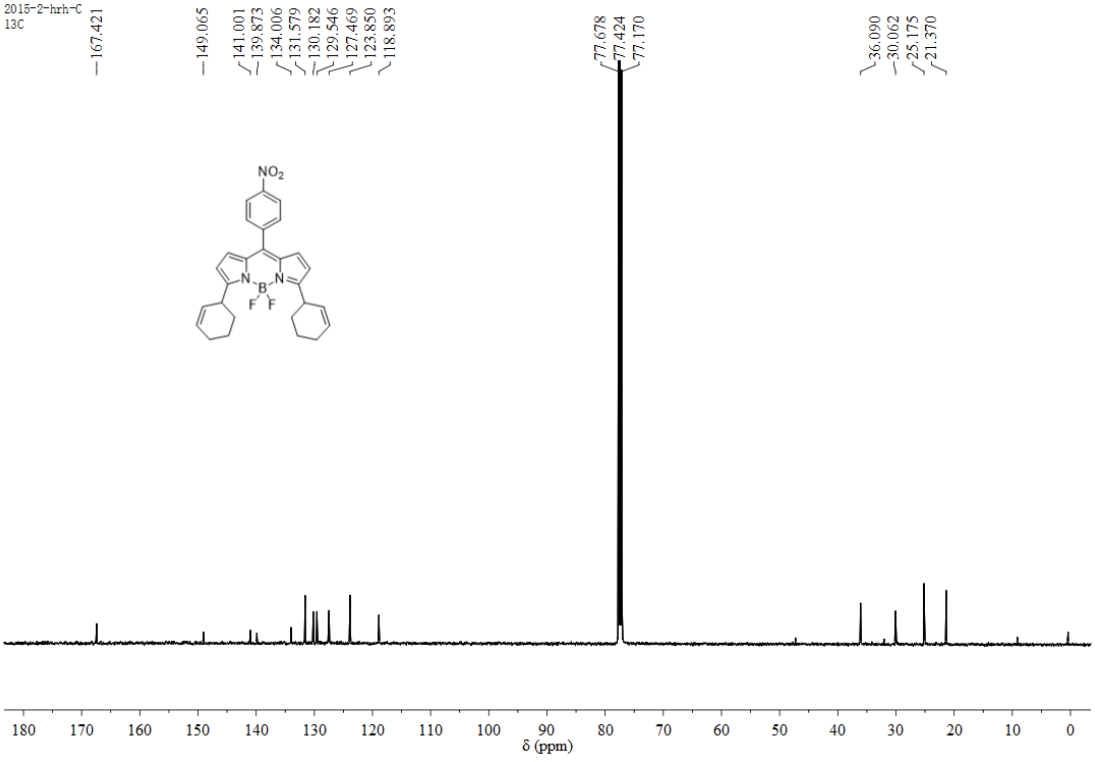
HRMS for **3b**


x10 2
+APCI Scan (#6) Frag=175.0V 002.d
353.1572
385.1828
439.2359
403.1807
197.1325
229.1577
274.2739
313.2736
338.3415
Counts (%) vs. Mass-to-Charge (m/z)

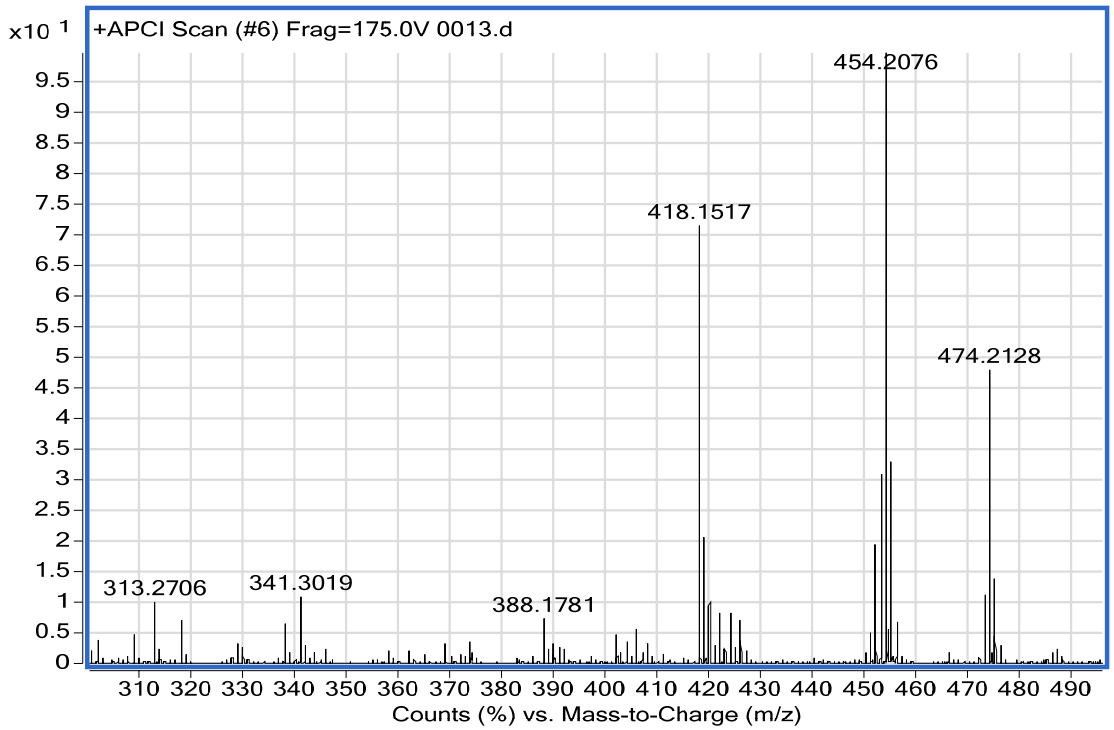
^{1}H NMR spectrum of **3c** in $CDCl_3$



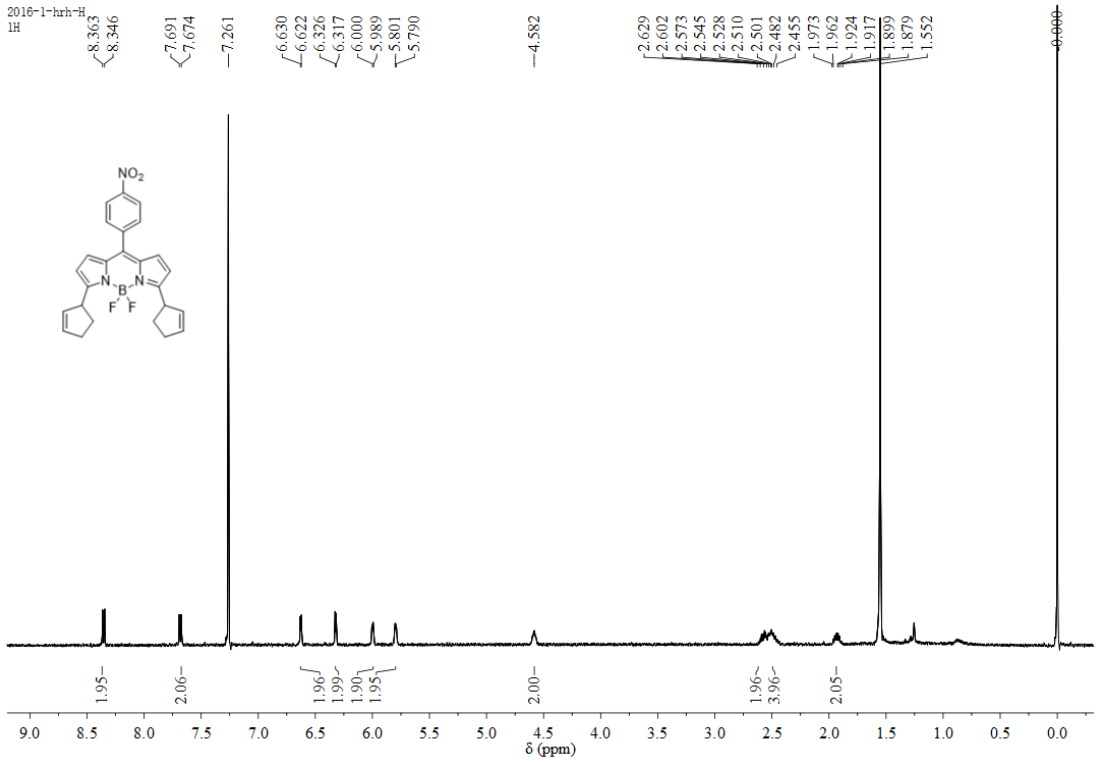
^{13}C NMR spectrum of **3c** in $CDCl_3$



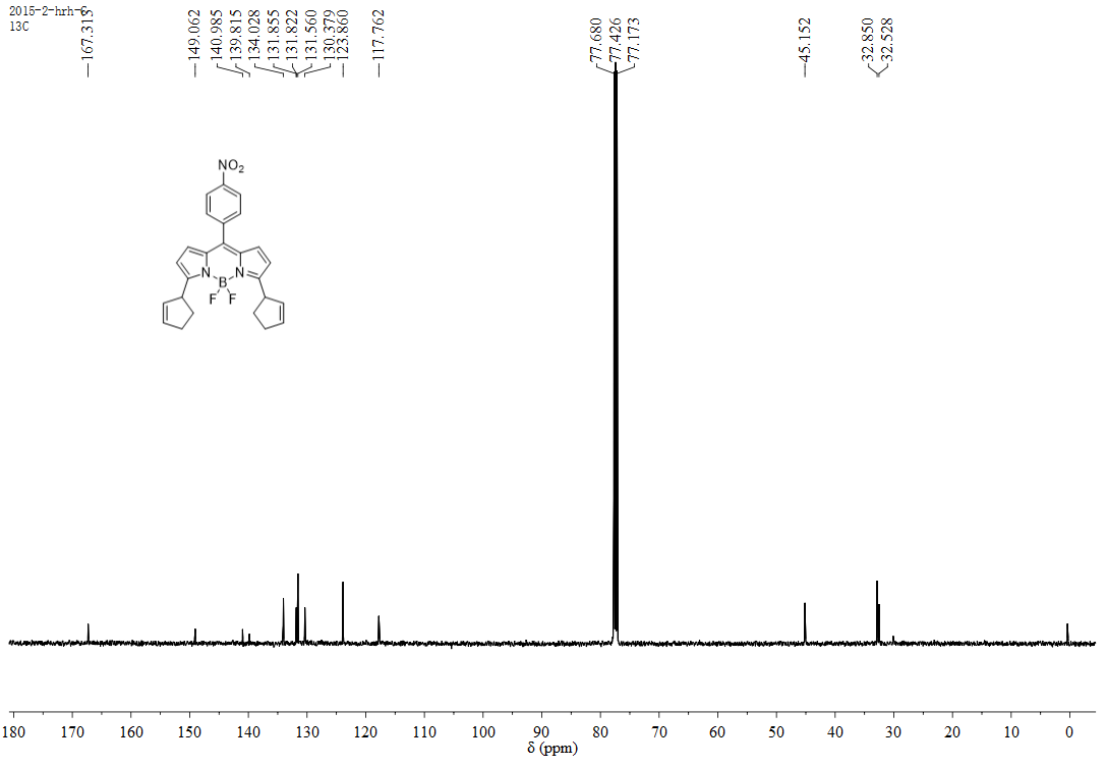
HRMS for **3c**


x10 1
+APCI Scan (#6) Frag=175.0V 0013.d
454.2076
418.1517
474.2128
313.2706
341.3019
388.1781
Counts (%) vs. Mass-to-Charge (m/z)

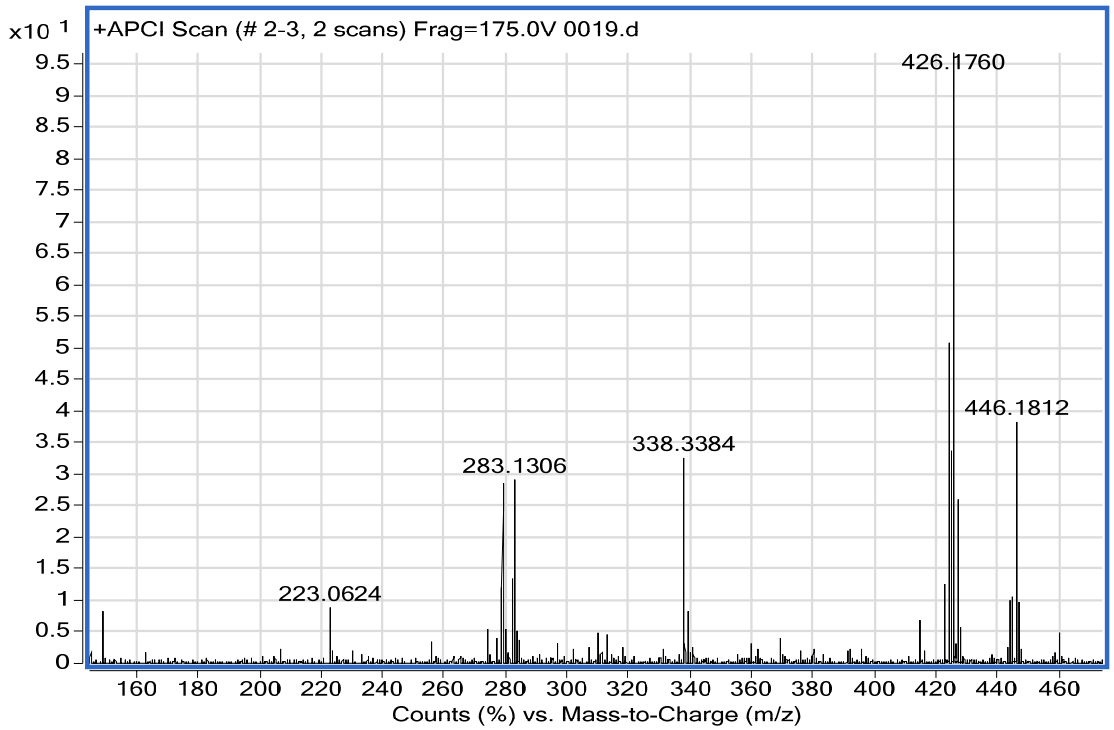
^{1}H NMR spectrum of **3d** in $CDCl_3$



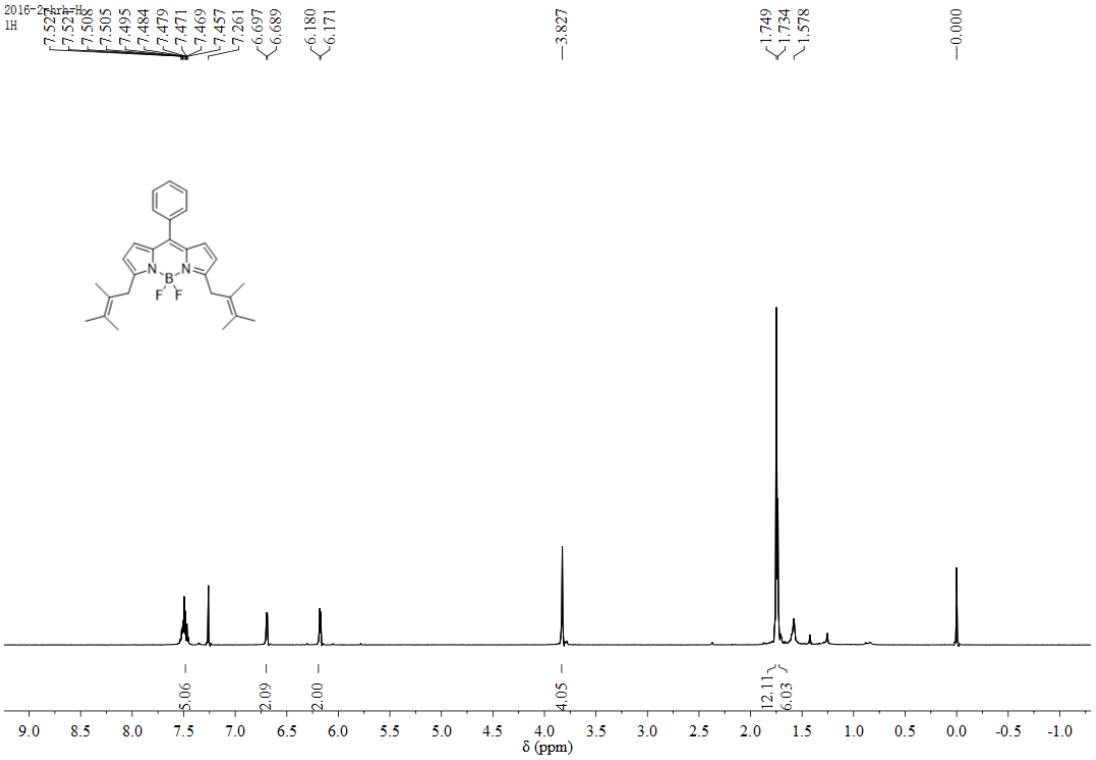
^{13}C NMR spectrum of **3d** in $CDCl_3$



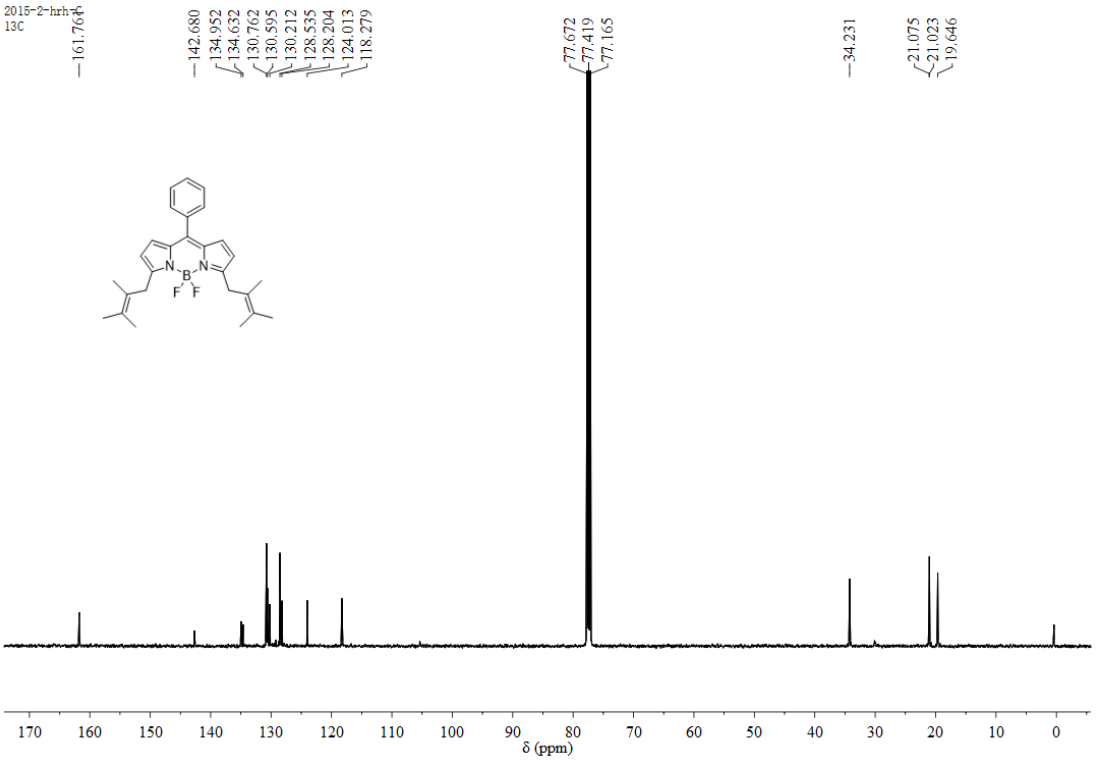
HRMS for **3d**


x10 1
+APCI Scan (# 2-3, 2 scans) Frag=175.0V 0019.d
426.1760
446.1812
338.3384
283.1306
223.0624
Counts (%) vs. Mass-to-Charge (m/z)

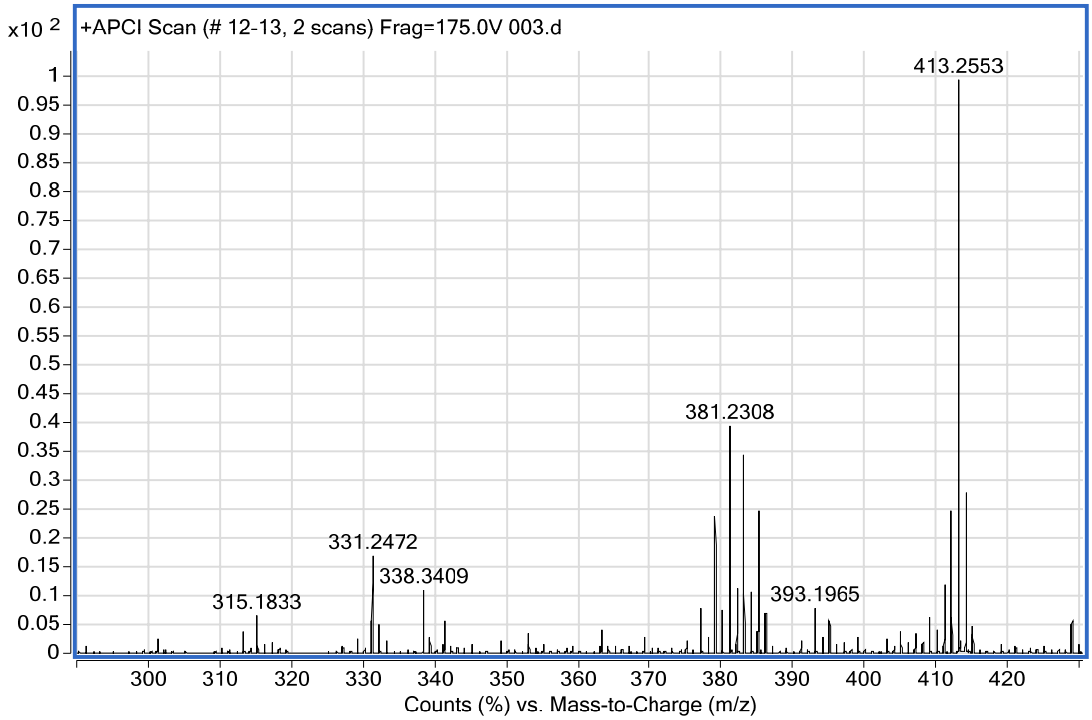
^{1}H NMR spectrum of **3e** in $CDCl_3$



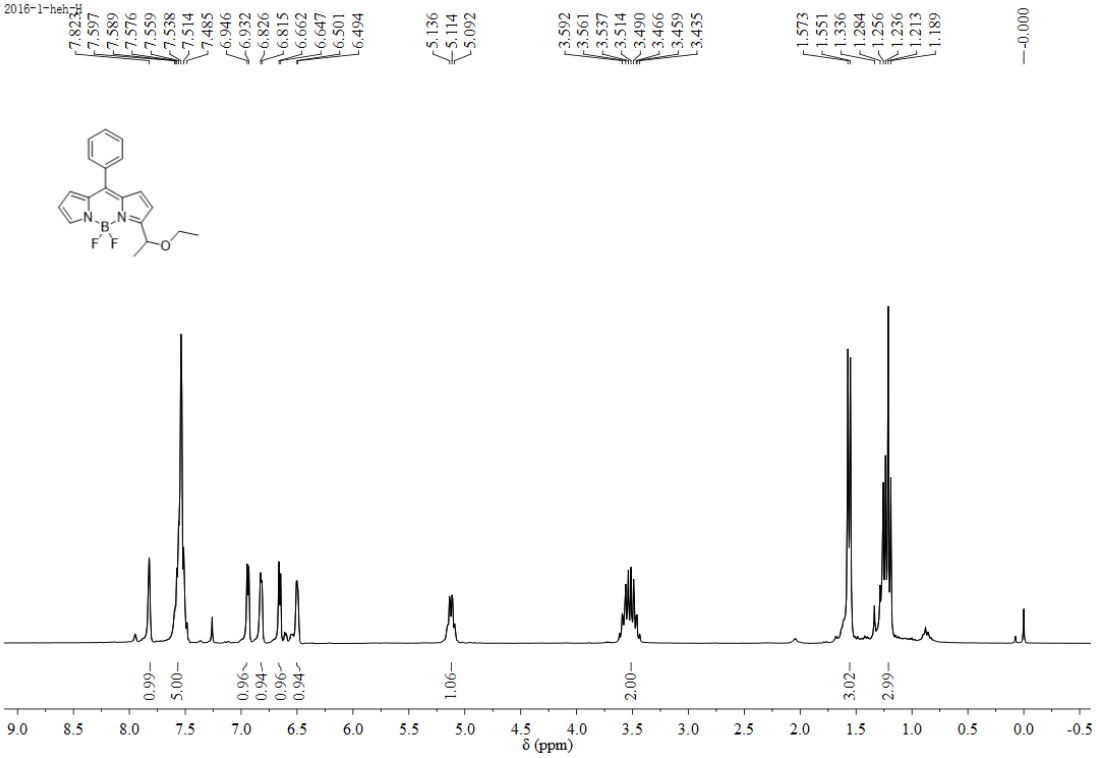
^{13}C NMR spectrum of **3e** in $CDCl_3$



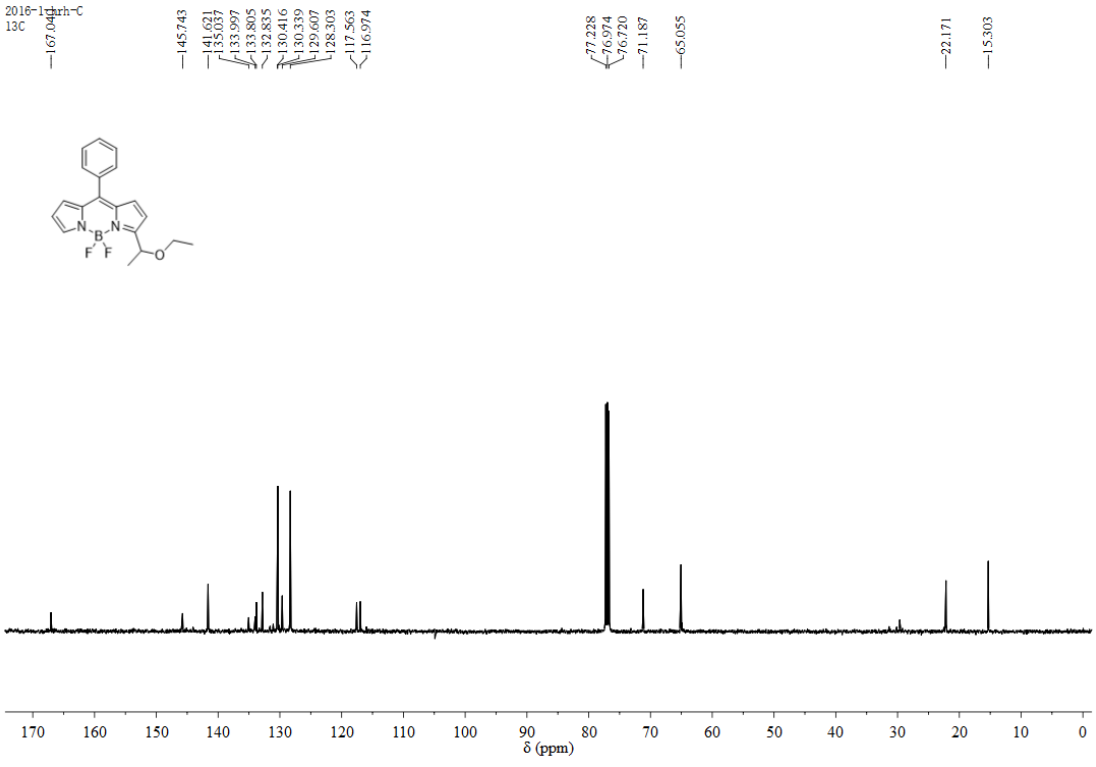
HRMS for **3e**


x10 2
+APCI Scan (# 12-13, 2 scans) Frag=175.0V 003.d
413.2553
381.2308
331.2472
338.3409
315.1833
393.1965
Counts (%) vs. Mass-to-Charge (m/z)

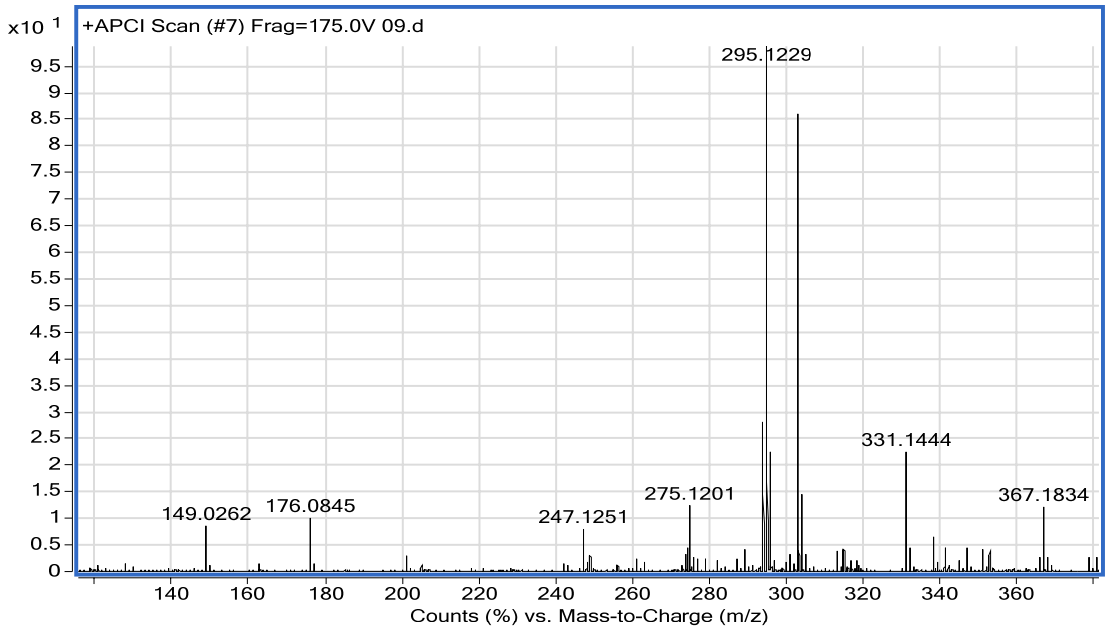
^{1}H NMR spectrum of **5a** in $CDCl_3$



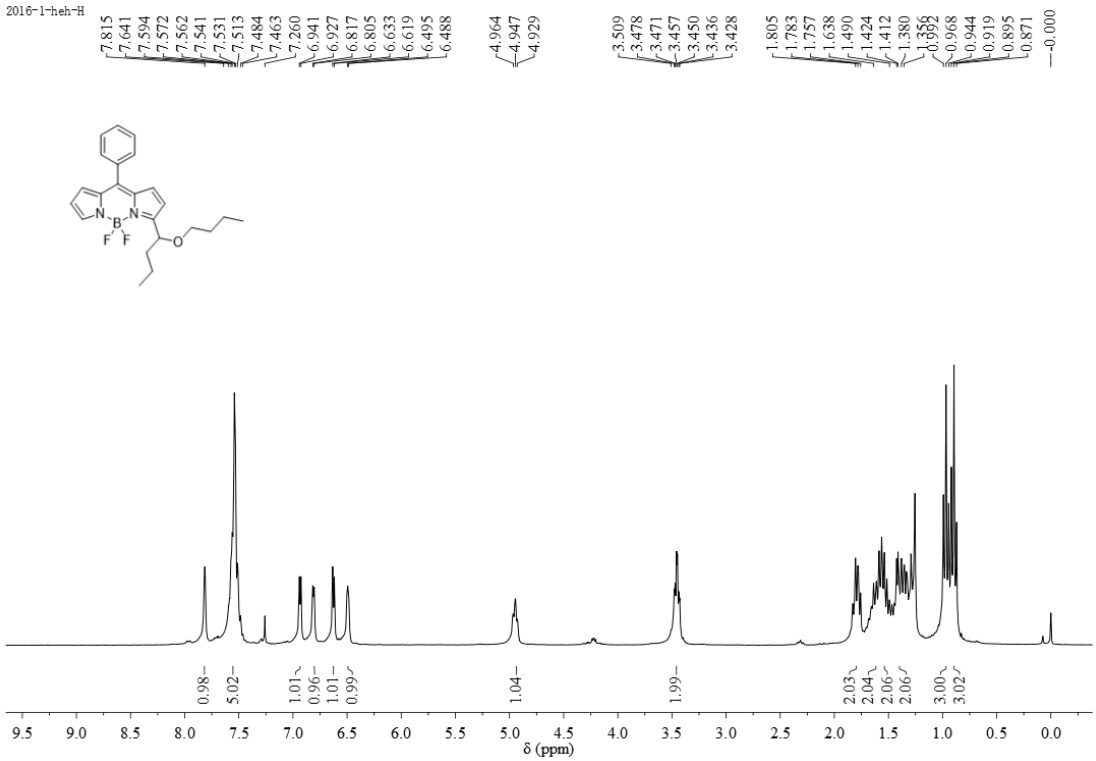
^{13}C NMR spectrum of **5a** in $CDCl_3$



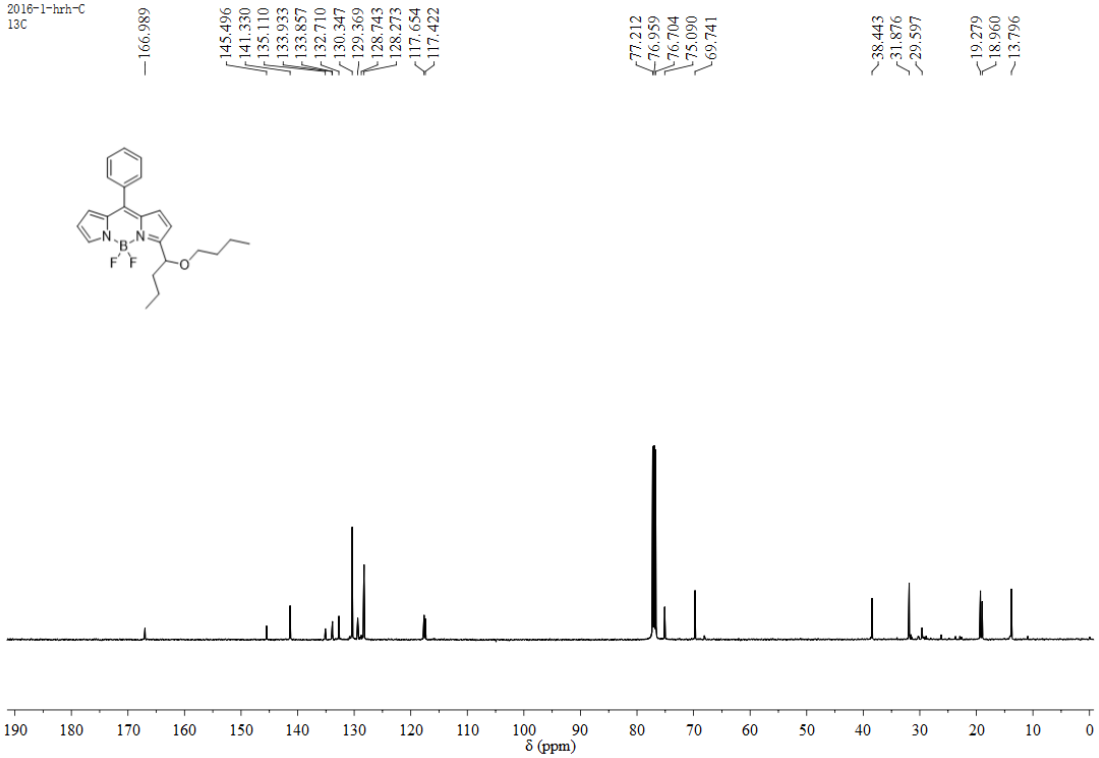
HRMS for **5a**


x10 1
+APCI Scan (#7) Frag=175.0V 09.d
295.1229
331.1444
275.1201
367.1834
149.0262
176.0845
247.1251
Counts (%) vs. Mass-to-Charge (m/z)

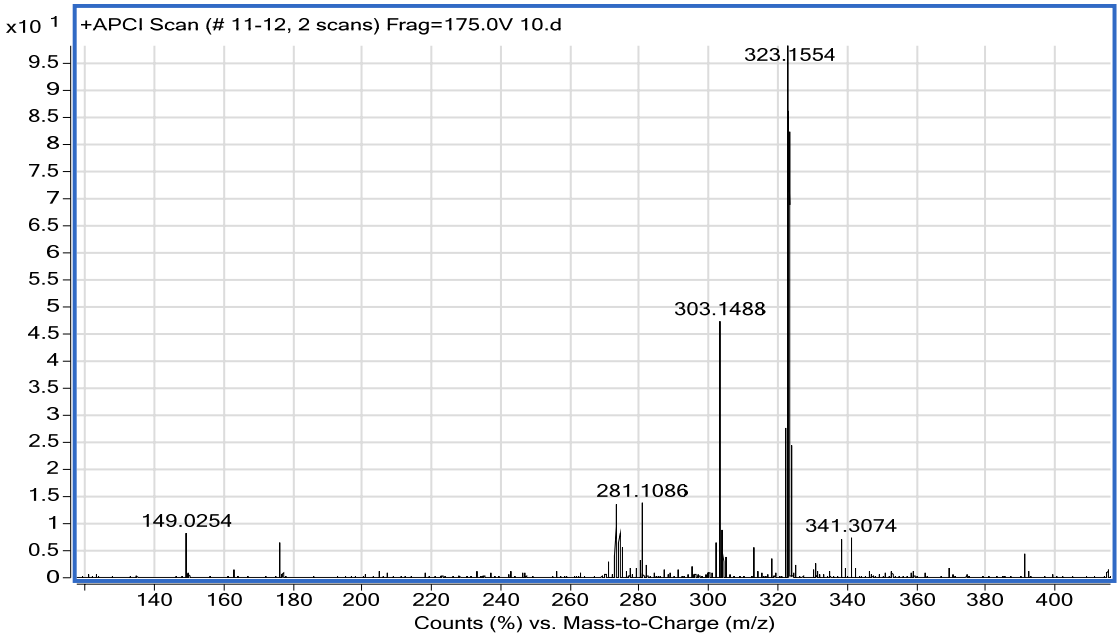
^{1}H NMR spectrum of **5b** in $CDCl_3$



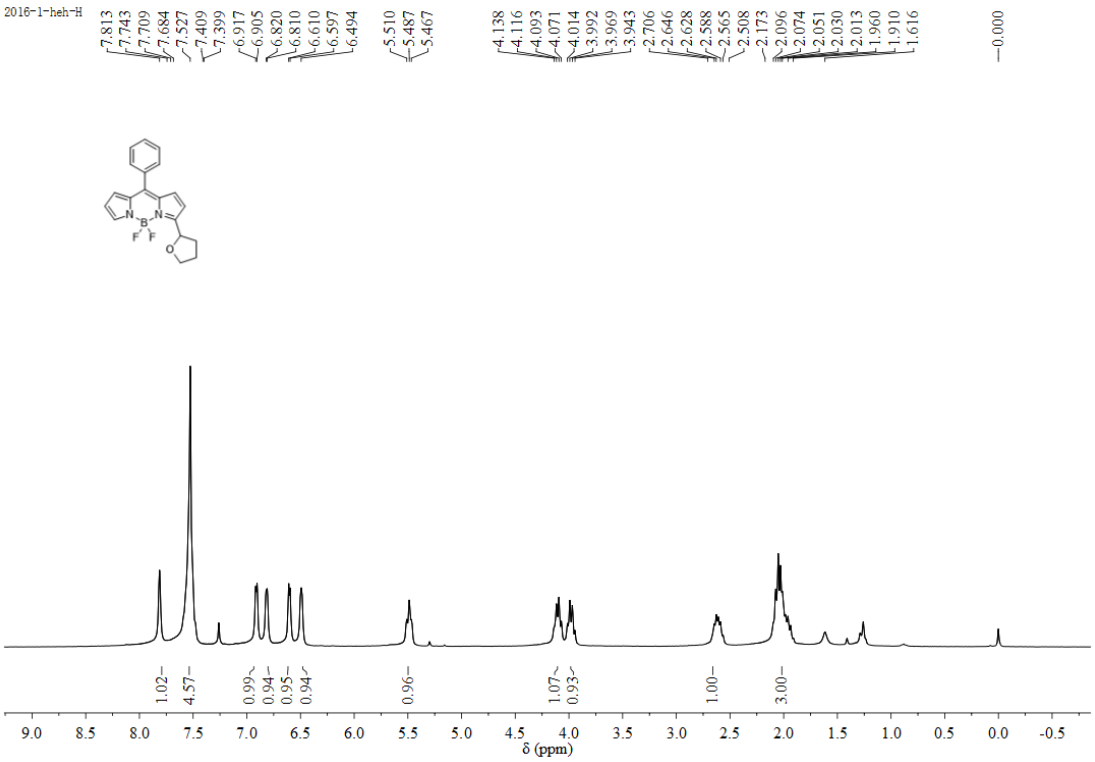
^{13}C NMR spectrum of **5b** in $CDCl_3$



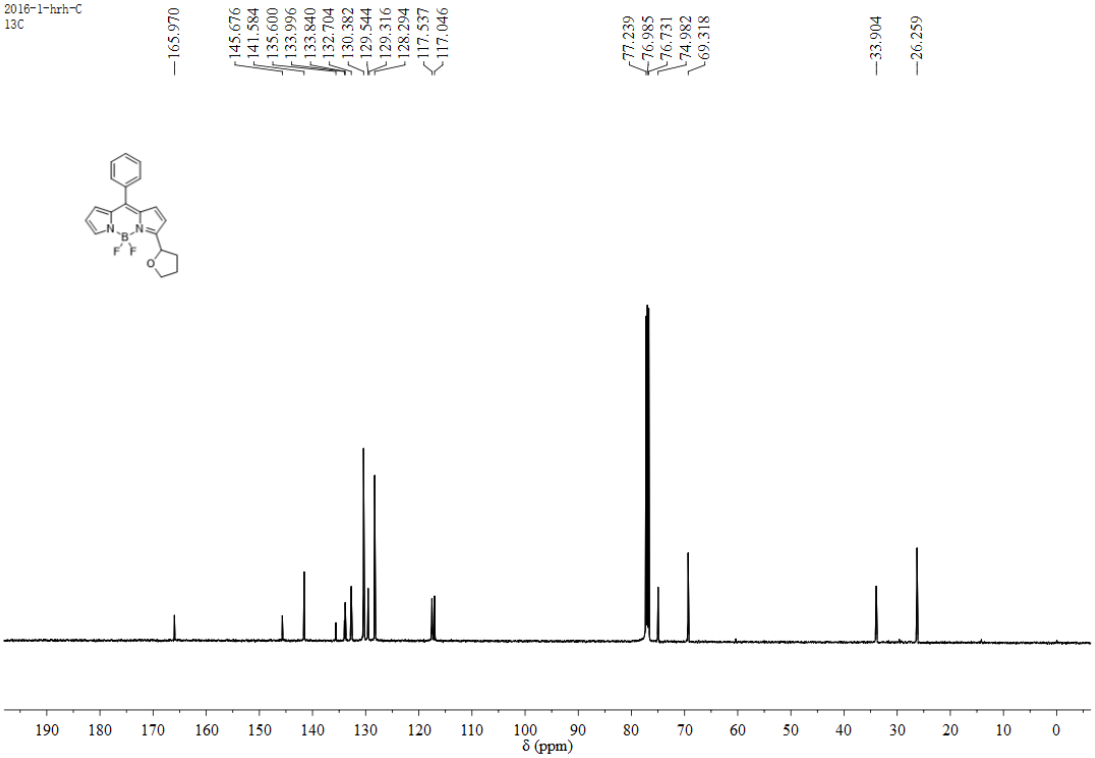
HRMS for **5b**


x10 1
+APCI Scan (# 11-12, 2 scans) Frag=175.0V 10.d
323.1554
303.1488
281.1086
149.0254
341.3074
Counts (%) vs. Mass-to-Charge (m/z)

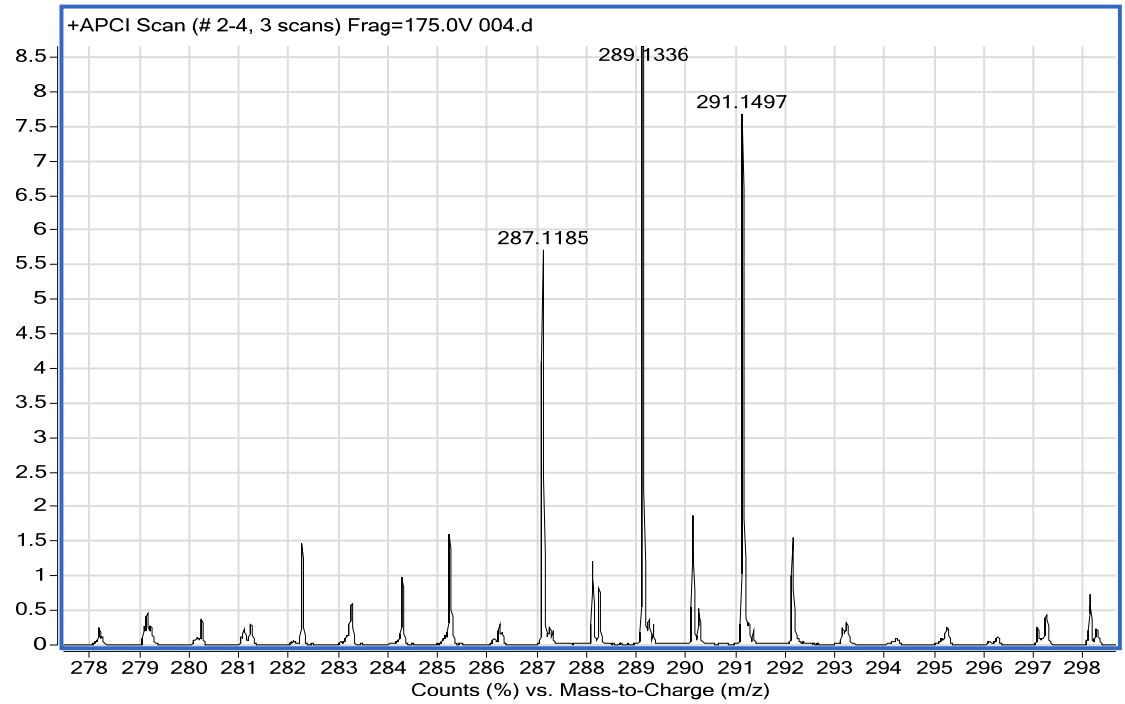
^{1}H NMR spectrum of **5c** in $CDCl_3$



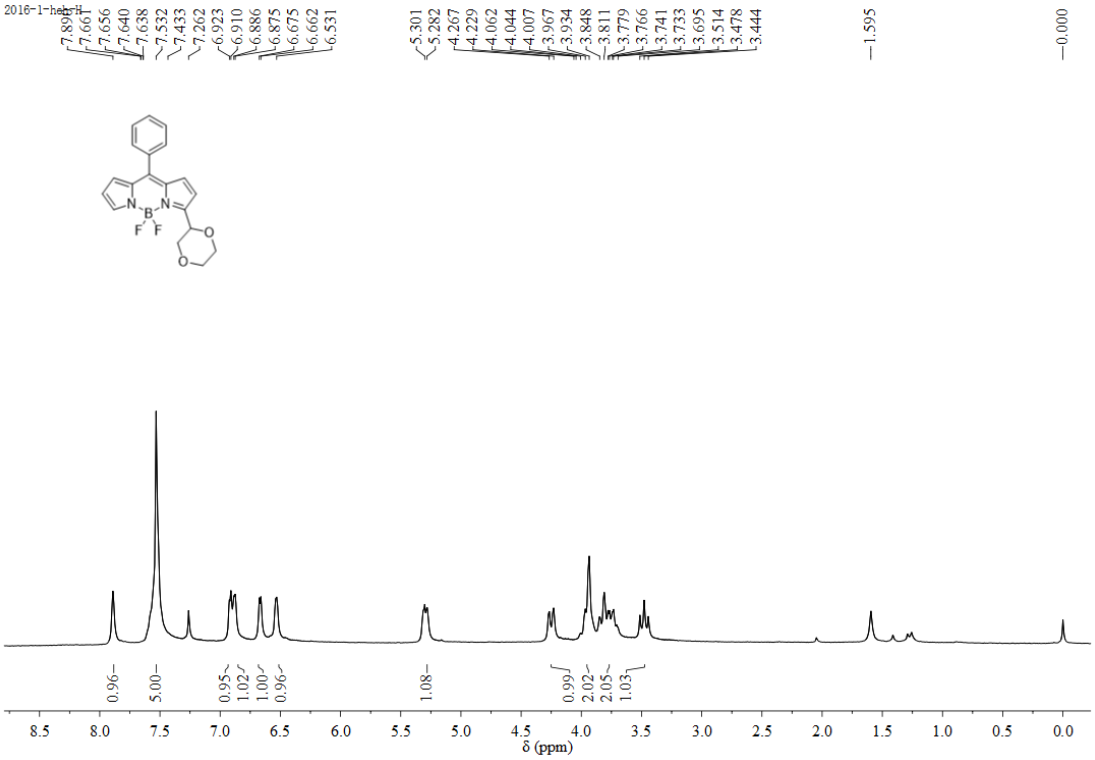
^{13}C NMR spectrum of **5c** in $CDCl_3$



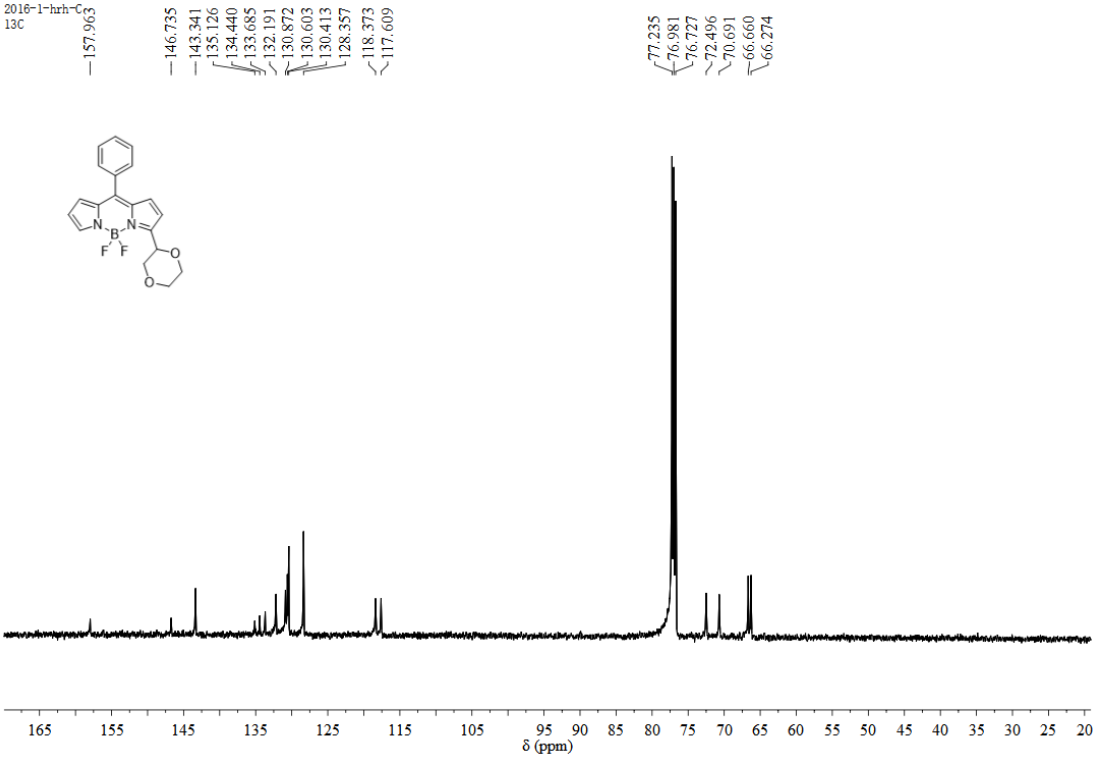
HRMS for **5c**


+APCI Scan (# 2-4, 3 scans) Frag=175.0V 004.d
289.1336
291.1497
287.1185
Counts (%) vs. Mass-to-Charge (m/z)

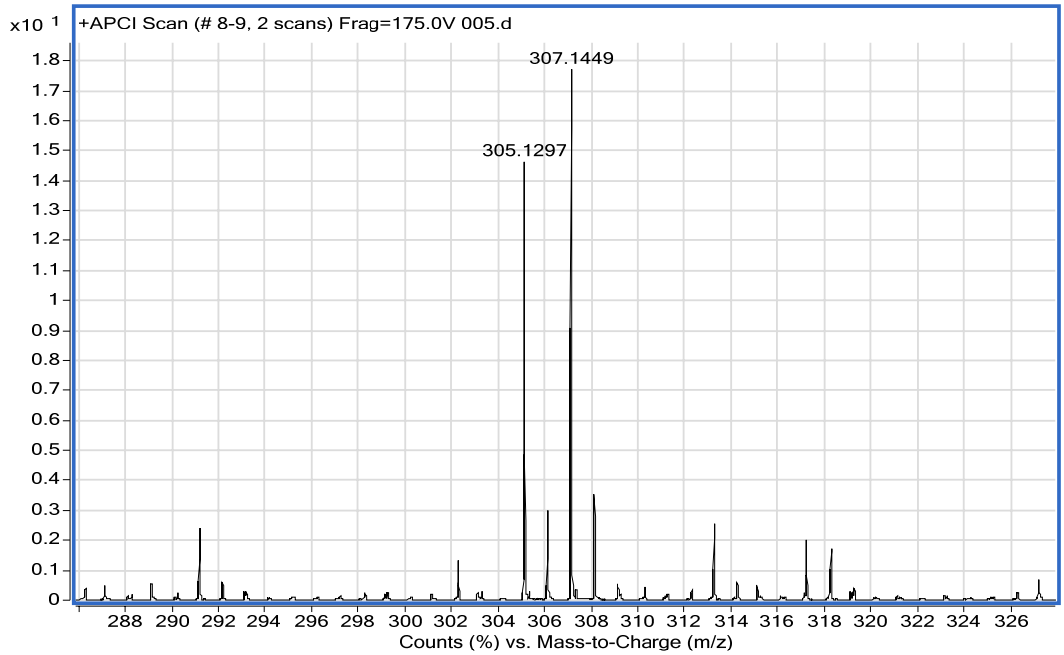
^{1}H NMR spectrum of **5d** in $CDCl_3$



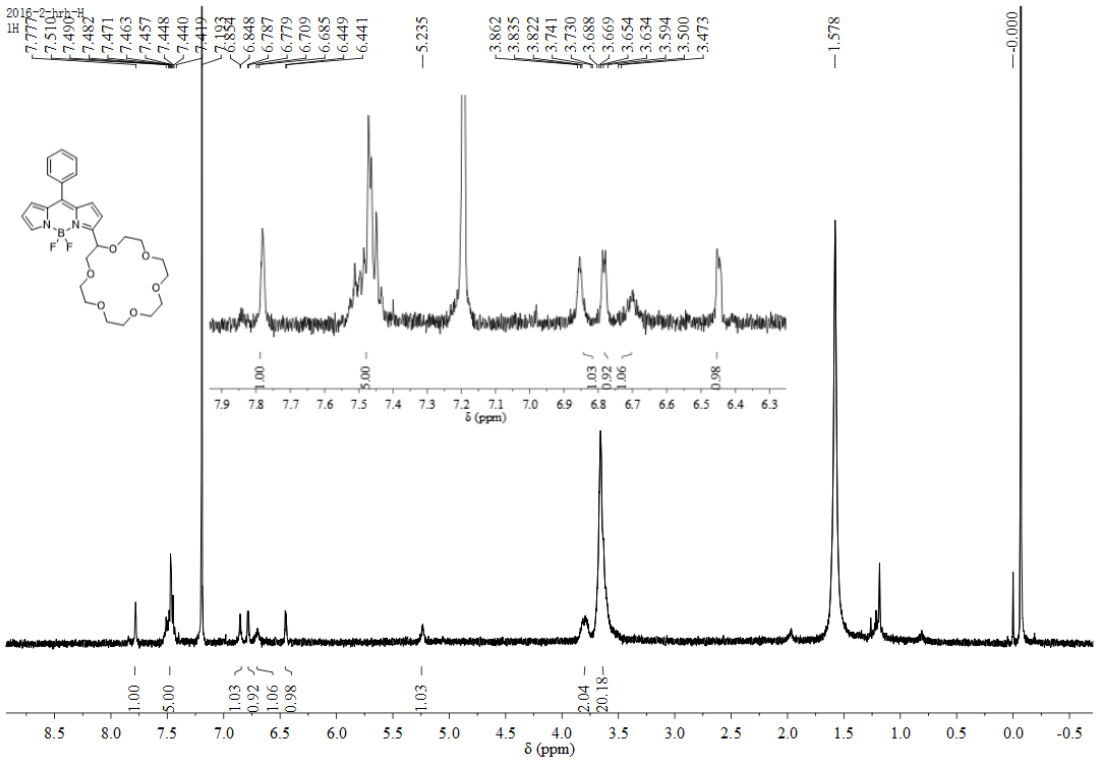
^{13}C NMR spectrum of **5d** in $CDCl_3$



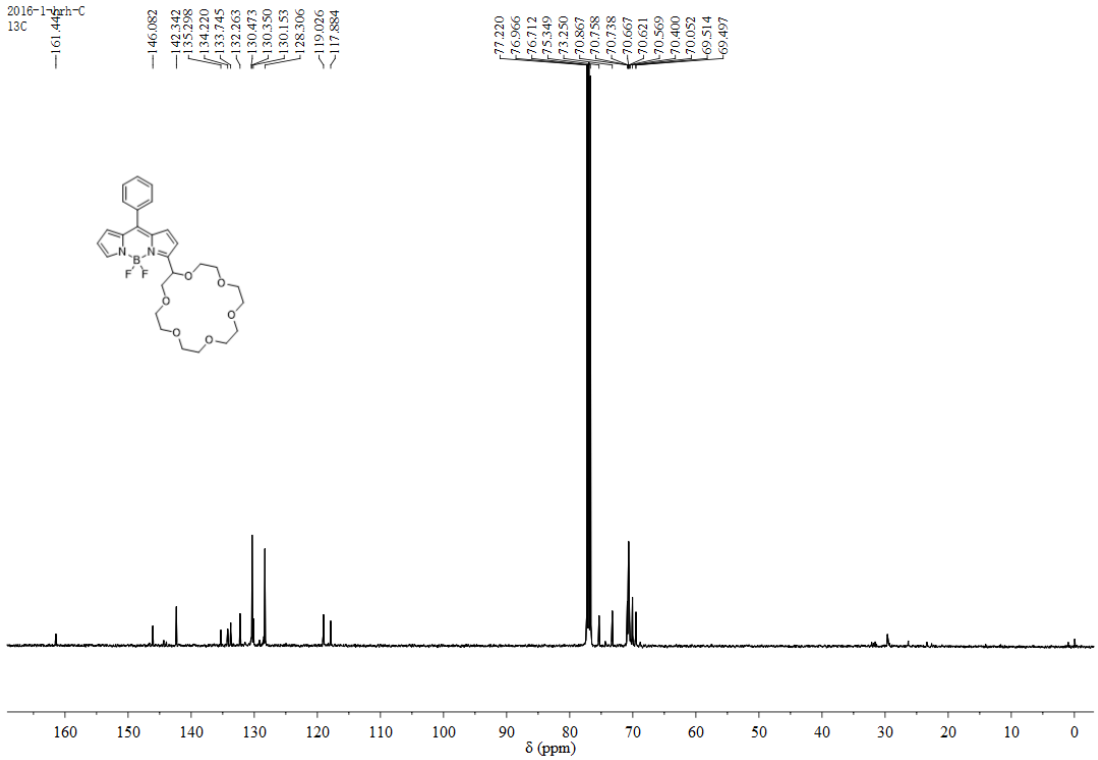
HRMS for **5d**


x10 1
+APCI Scan (# 8-9, 2 scans) Frag=175.0V 005.d
307.1449
305.1297
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
288 290 292 294 296 298 300 302 304 306 308 310 312 314 316 318 320 322 324 326
Counts (%) vs. Mass-to-Charge (m/z)

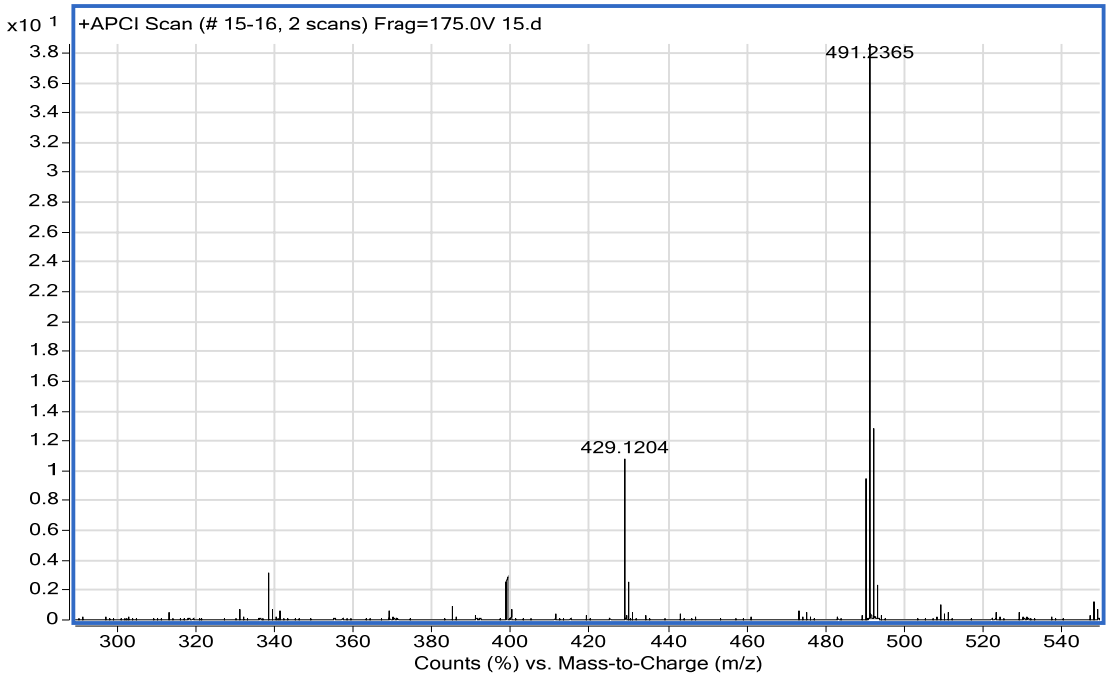
^{1}H NMR spectrum of **5e** in $CDCl_3$



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



HRMS for **5e**


x10 1
+APCI Scan (# 15-16, 2 scans) Frag=175.0V 15.d
491.2365
429.1204
Counts (%) vs. Mass-to-Charge (m/z)

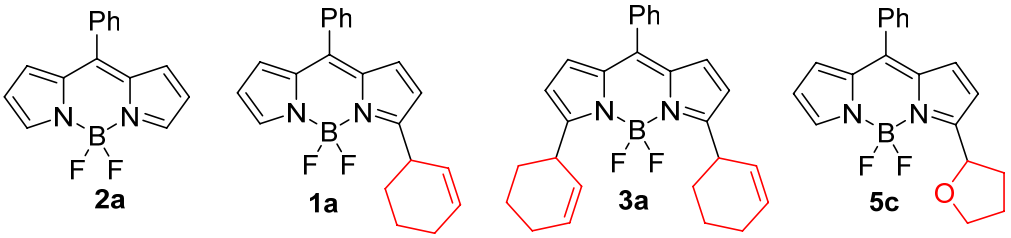
5. Photophysical properties of selected BODIPYs

UV-vis absorption and fluorescence emission spectra were recorded on commercial spectrophotometers (Shimadzu UV-2450 and Edinburgh FS5 spectrometers). All measurements were made at 25 ºC, using 5×10 mm cuvettes. Relative fluorescence quantum efficiencies of BODIPY derivatives were obtained by comparing the areas under the corrected emission spectrum of the test sample in various organic solvents with fluorescein (Φ_r = 0.90 in 0.1 N NaOH aqueous solution). Non-degassed, spectroscopic grade solvents and 10 mm optical path length quartz cuvettes were used. Dilute solutions ($0.01 < A(\lambda_{ex}) < 0.05$) were used to minimize the inner-filter effects. Quantum yields Φ_x were determined according to equation (S1):

$$\Phi_x = \Phi_r \times \frac{F_x}{F_r} \times \frac{1-10^{-A_r(\lambda_{ex})}}{1-10^{-A_x(\lambda_{ex})}} \times \frac{n_x^2}{n_r^2} \qquad \text{(S1)}$$

where the subscripts *x* and *r* refer respectively to the BODIPY sample *x* and reference (standard) fluorophore *r* with known quantum yield Φ_r in a specific solvent; *F* stands for the spectrally corrected, integrated fluorescence spectra; $A(\lambda_{ex})$ denotes the absorbance at the used excitation wavelength λ_{ex} and *n* represents the refractive index of the solvent (in principle at the average emission wavelength).

Table S1: Photophysical properties of selected BODIPYs in different solvents at room temperature



dyes	solvent	λ_{abs}(max) [nm]	log ε[a]	λ_{em}(max) [nm]	Φ[b]	Stokes-shift [cm^{-1}]
2a[c]	CH_2Cl_2	500	4.52	527	0.03	1025
1a	hexane	505	4.84	524	0.11 ± 0.01	718
	toluene	508	4.80	529	0.21 ± 0.02	781
	CH_2Cl_2	506	4.74	526	0.13 ± 0.01	751
	MeOH	503	4.79	522	0.07 ± 0.01	724
3a	hexane	516	4.46	530	0.91 ± 0.07	512
	toluene	518	4.49	533	0.93 ± 0.08	543
	CH_2Cl_2	516	4.47	533	0.64 ± 0.05	618
	MeOH	513	4.48	527	0.49 ± 0.05	518
5c	hexane	505	4.70	524	0.09 ± 0.01	718
	toluene	508	4.57	528	0.16 ± 0.02	746
	CH_2Cl_2	506	4.66	525	0.11 ± 0.01	715
	MeOH	503	4.63	522	0.07 ± 0.01	724

[a] Molar absorption coefficient at λ_{abs}(max). [b] Fluorescence quantum yield was calculated using fluorescein (Φ = 0.90 in 0.1 N NaOH aqueous solution) as standard. [c] Data from ref (*Eur J. Org. Chem.* **2011**, *28*, 5460–5468).

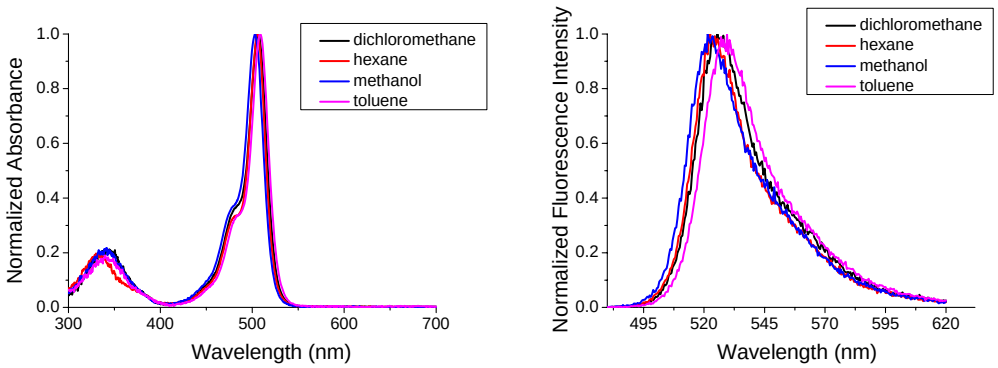


Figure S2. Absorption (left) and fluorescence emission (right) spectra of **1a** recorded in different solvents (excitation at 470 nm).

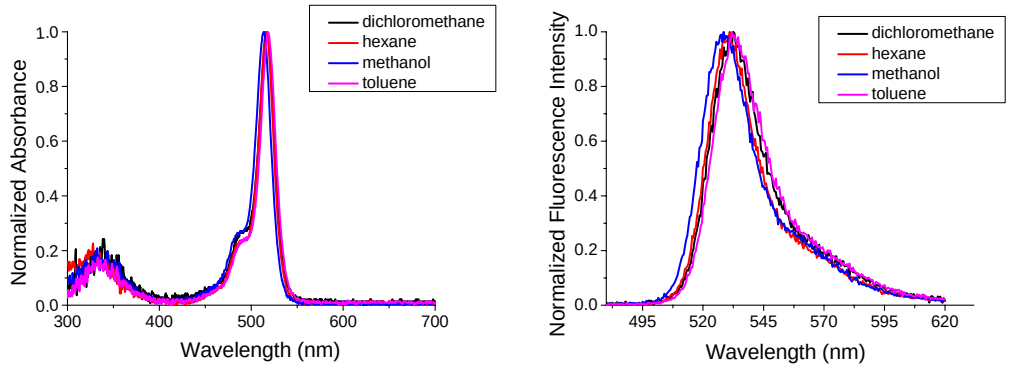


Figure S3. Absorption (left) and fluorescence emission (right) spectra of **3a** recorded in different solvents (excitation at 470 nm).

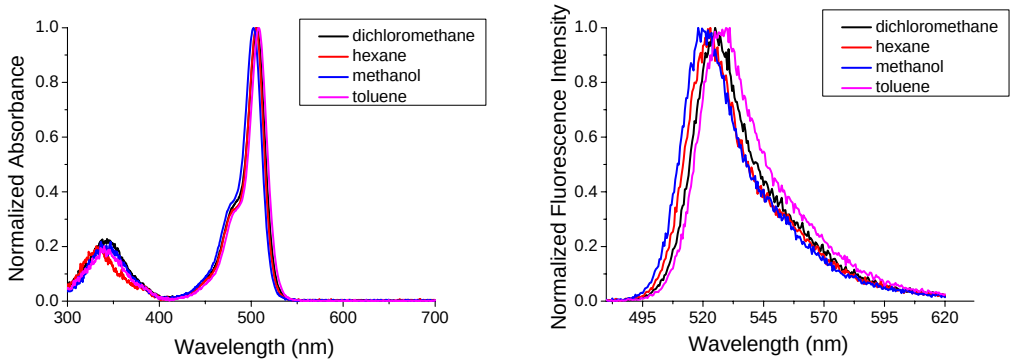


Figure S4. Absorption (left) and fluorescence emission (right) spectra of **5c** recorded in different solvents (excitation at 470 nm).