Supporting Information for

Copper-Catalyzed α–Benzylation of BODIPYs *via* Radical-Triggered Oxidative Cross-Coupling of Two C–H Bonds

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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.

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).[1] 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):[2]

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

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).

Crystals of compounds **3p**, **3r** and **4f** suitable for X-ray analysis were obtained *via* the slow diffusion of petroleum ether into their dichloromethane solutions. The vial containing this solution was placed, loosely capped, to promote the crystallization. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were collected using a diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. Cell parameters were retrieved using SMART[5] software and refined using SAINT on all observed reflections. The determination of unit cell parameters and data collections were performed with Mo Kα radiation (λ) at 0.71073 Å. Data reduction was performed using the SAINT software, which corrects for Lp and decay. The structure was solved by the direct method using the SHELXS-974 program and refined by least squares method on F^2, SHELXL-97,[7] incorporated in SHELXTL V5.10.[8] CCDC-1588356 (**3p**), CCDC-1588396 (**3r**), CCDC-1588355 (**4f**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

2. Figure S1

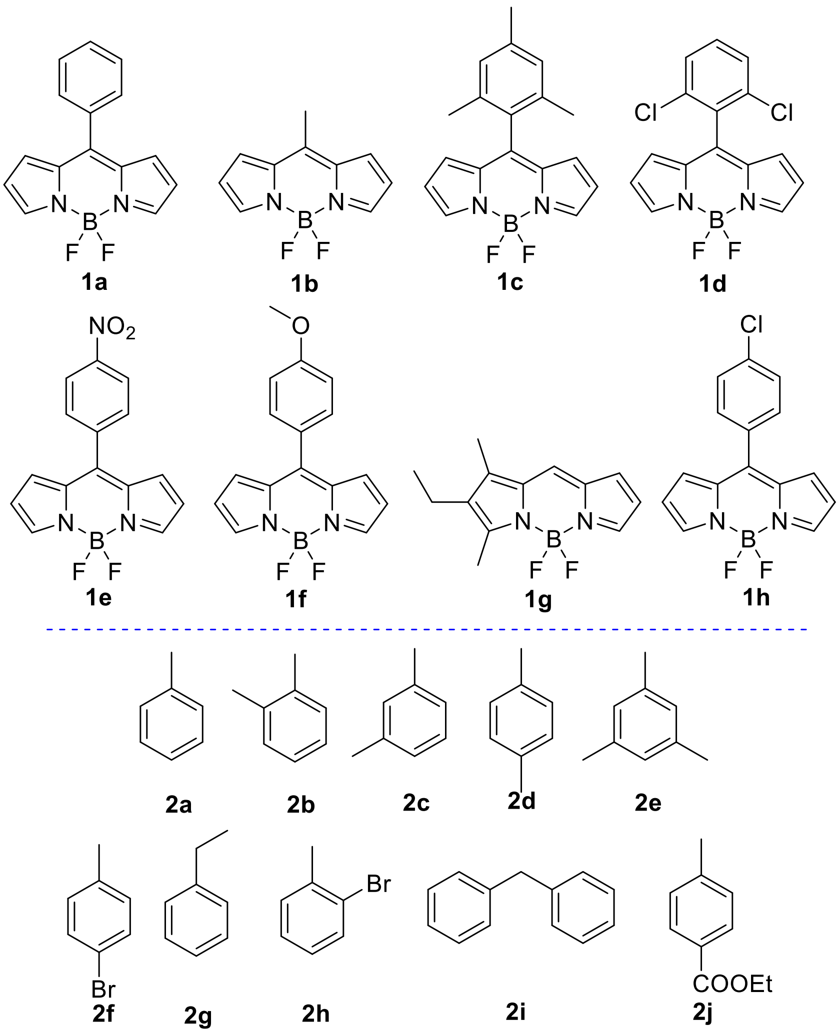
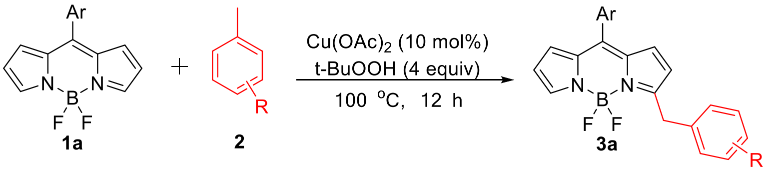


Figure S1. Chemical structure of BODIPYs **1a-h** and toluene derivatives **2a-j.**

3. Synthesis and characterization



General radical C–H monofunctionalization procedure: BODIPY **1a** (1 equiv, 0.2 mmol), $Cu(OAc)_2$ (0.02 mmol, 10 mol%), the oxidant *t*-BuOOH (*tert*-butyl hydroperoxide (TBHP), 4 equiv, 0.8 mmol) were dissolved in solvent (4 mL). The reaction mixture was heated at 100 °C and stirred for the indicated time. Upon completion, the reaction mixture was cooled to room temperature and was poured into dichloromethane (100 mL), washed three times with water (100 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by column chromatographically (silica; petroleum ether/ethyl acetate; 100:1-50:1 v/v).

3a Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1a** (54 mg, 0.2 mmol) and **2a** (4 mL). This reaction was completed after 12 h, providing an orange solid (46 mg, 65%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.56-7.49 (m, 5H), 7.35-7.28 (m, 5H), 6.83 (d, J = 7.4 Hz, 2H), 6.81(d, J = 4.3 Hz, 1H), 6.15 (d, J = 4.3 Hz, 1H), 4.42 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.83, 145.70, 141.68, 137.50, 135.88, 134.41, 134.32, 133.09, 130.80, 130.77, 129.92, 129.61, 129.15, 128.74, 127.29, 120.53, 117.82, 35.74; HRMS calcd. for $C_{22}H_{17}BF_2N_2$, $[M–F]^+$: 339.1463, found: 339.1474.

3b Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1a** (54 mg, 0.2 mmol) and **2b** (4 mL). This reaction was completed after 12 h, providing an orange solid (51 mg, 70%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.55-7.49 (m, 5H), 7.24-7.21 (m, 4H), 6.81 (d, J = 3.8 Hz, 2H), 6.51 (d, J = 2.0 Hz, 1H), 5.93 (d, J = 4.3 Hz, 1H), 4.43 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.46, 145.11, 141.24, 137.03, 135.63, 135.34, 134.00, 133.86, 132.54, 130.45, 130.35, 130.30, 129.52, 129.16, 128.27, 127.22, 126.19, 119.70, 117.36, 33.10, 19.34; HRMS calcd. for $C_{23}H_{19}BF_2N_2$, $[M–F]^+$: 353.1625, found: 353.1615.

3c Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1a** (54 mg, 0.2 mmol) and **2c** (4 mL). This reaction was completed after 12 h, providing an oily compound (50 mg, 68%). ^1H NMR (300 MHz, $CDCl_3$) δ

7.84 (s, 1H), 7.55-7.46 (m, 5H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 10.8 Hz, 2H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 3.9 Hz, 2H), 6.50 (d, *J* = 4.2 Hz, 1H), 6.15 (d, *J* = 4.3 Hz, 1H), 4.38 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.70, 145.14, 141.08, 138.35, 136.91, 135.44, 133.91, 132.62, 130.34, 130.28, 130.27, 130.23, 129.00, 128.56, 128.26, 127.58, 126.49, 120.18, 117.27, 35.22, 21.35; HRMS calcd. for $C_{23}H_{19}BF_2N_2$, [M–F]$^+$: 353.1625, found: 353.1618.

3d Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1a** (54 mg, 0.2 mmol) and **2d** (4 mL). This reaction was completed after 12 h, providing an oily compound (51 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.55-7.49 (m, 5H), 7.22 (s, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 4.1 Hz, 1H), 6.49 (d, *J* = 4.3 Hz, 1H), 6.15 (d, *J* = 4.4 Hz, 1H), 4.37 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.86, 145.11, 141.05, 136.41, 135.46, 133.92, 133.90,132.64, 130.34, 13027, 129.38, 129.34, 128.98, 128.44, 128,26, 120.13, 117.25, 34.96, 20.60; HRMS calcd. for $C_{23}H_{19}BF_2N_2$, [M–F]$^+$: 353.1625, found: 353.1607.

3e Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1a** (54 mg, 0.2 mmol) and **2e** (4 mL). This reaction was completed after 12 h, providing an oily compound (50 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.52 (s, 5H), 6.96 (s, 2H), 6.90 (s, 1H), 6.81 (d, *J* = 3.0 Hz, 1H), 6.80 (s, 1H), 6.50 (s, 1H), 6.17 (d, *J* = 3.7 Hz, 1H), 4.34 (s, 2H), 2.30 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.04, 145.09, 140.98, 138.27, 136.90, 136.84, 135.50, 133.98, 132.69, 130.40, 130.31, 128.93, 128.53, 128.31, 127.34, 120.33, 117.25, 35.20, 21.28; HRMS calcd. for $C_{24}H_{21}BF_2N_2$, [M–F]$^+$: 366.1813, 367.1776, found: 366.1810, 367.1752.

3f Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1a** (54 mg, 0.2 mmol) and **2f** (4 mL). This reaction was completed after 12 h, providing an orange solid (43 mg, 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.52-7.45 (m, 5H), 7.27-7.22 (m, 4H), 6.84 (d, *J* = 3.9 Hz, 2H), 6.51 (s, 1H), 6.13 (d, *J* = 4.2 Hz, 1H), 4.36 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.06, 145.64, 141.79, 136.23, 134.19, 133.88, 132.64, 131.86, 131.21, 130.45, 130.41, 129.66, 128.37, 122.24, 120.90, 119.78, 117.69, 34.69; HRMS calcd. for $C_{23}H_{20}BBrF_2N_2$, [M–F]$^+$: 432.0803, found: 432.0796.

3g Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1a** (54 mg, 0.2 mmol) and **2g** (4 mL). This reaction was completed after 12 h, providing an oily compound (44 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.55-7.49 (m, 5H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.36-7.23 (m, 3H), 6.85 (d, *J* = 4.3 Hz, 1H), 6.78 (d, *J* = 3.5 Hz, 1H), 6.49 (s, 1H), 6.36 (d, *J* = 4.4 Hz, 1H), 4.94 (q, *J* = 14.0 Hz, 1H), 1.74 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.56, 145.19, 142.59, 140.90, 134.86, 133.94, 133.83, 132.87, 130.29, 130.21, 128.81, 128.54, 128.23, 127.56, 126.75, 118.38, 117.19, 38.10, 19.95; HRMS calcd. for $C_{23}H_{19}BF_2N_2$, $[M–F]^+$: 353.1625, found: 353.1642.

3h Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1b** (41 mg, 0.2 mmol) and **2a** (4 mL). This reaction was completed after 12 h providing an orange solid (29 mg, 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.34-7.17 (m, 5H), 7.20 (d, *J* = 3.0 Hz, 1H), 7.18 (d, *J* = 3.0 Hz, 1H), 6.51 (s, 1H), 6.14 (d, *J* = 4.2 Hz, 1H), 4.37 (s, 2H), 2.56 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.58, 143.24, 140.44, 137.13, 135.92, 134.44, 129.42, 129.11, 128.64, 126.76, 125.51, 119.45, 116.69, 35.13, 15.66; HRMS calcd. for $C_{17}H_{15}BF_2N_2$, $[M–F]^+$: 277.1307, found: 277.1323.

3i Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1c** (60 mg, 0.2 mmol) and **2a** (4 mL). This reaction was completed after 12 h, providing a green solid (51 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.36-7.29 (m, 5H), 6.93 (s, 2H), 6.57-6.55 (m, 2H), 6.42 (s, 1H), 6.05 (d, *J* = 4.1 Hz, 1H), 4.41 (s, 2H), 2.33 (s, 3H), 2.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.43, 145.29, 141.21, 138.55 , 136.91, 136.41, 135.84, 134.19, 131.15, 129.78, 129.55, 128.68, 128.03, 127.69, 126.83, 119.93, 117.29, 35.34, 21.04, 19.92; HRMS calcd. for $C_{25}H_{23}BF_2N_2$, $[M–F]^+$: 381.1933, found: 381.1923.

3j Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1c** (60 mg, 0.2 mmol) and **2b** (4 mL). This reaction was completed after 12 h, providing an oily compound (56 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.24-7.17 (m, 4H), 6.93 (s, 2H), 6.55 (s, 2H), 6.43 (s, 1H), 5.85 (d, *J* = 4.2 Hz, 1H), 4.42 (s, 2H), 2.34 (s, 3H), 2.30 (s, 3H), 2.10 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.54, 145.20, 141.27, 138.62, 137.09, 136.47, 136.07, 135.36, 134.29, 131.17, 130.51, 130.45, 129.85, 128.10, 127.75, 127.28, 126.26, 119.69, 117.36, 33.37, 21.12, 20.01, 19.58; HRMS calcd. for $C_{26}H_{25}BF_2N_2$, $[M–F]^+$: 395.2089, found: 395.2091.

3k Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1c** (60 mg, 0.2 mmol) and **2h** (4 mL). This reaction was completed after 12 h, providing a green solid (47 mg, 50%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.39 (d, J = 6.8 Hz, 1H), 7.30 (d, J = 7.3 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.93 (s, 2H), 6.57 (d, J = 3.6 Hz, 2H), 6.43 (s, 1H), 6.00 (d, J = 4.0 Hz, 1H), 4.59 (s, 2H), 2.35 (s, 3H), 2.11 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.81, 145.41, 141.55, 138.64, 136.90, 136.47, 135.94, 134.37, 133.04, 131.79, 131.17, 129.81, 128.76, 128.10, 128.00, 127.81, 124.94, 119.76, 117.50, 35.63, 21.12, 20.02; HRMS calcd. for $C_{25}H_{22}BBrF_2N_2$, $[M–F]^+$: 459.1153, found: 459.1163.

3l Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1c** (60 mg, 0.2 mmol) and **2e** (4 mL). This reaction was completed after 12 h, providing a green solid (57 mg, 67%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (s, 1H), 6.98 (s, 2H), 6.92 (d, J = 5.1 Hz, 3H), 6.56 (d, J = 6.0 Hz, 2H), 6.42 (s, 1H), 6.07 (d, J = 4.0 Hz, 1H), 4.33 (s, 2H), 2.35 (s, 3H), 2.31 (s, 6H), 2.10 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.11, 145.14, 140.99, 138.59, 138.27, 136.70, 136.51, 135.95, 134.19, 131.23, 129.91, 128.56, 128.10, 127.47, 126.91, 120.16, 117.21, 35.29, 21.28, 21.12, 20.00; HRMS calcd. for $C_{27}H_{27}BF_2N_2$, $[M–F]^+$: 409.2246, found: 409.2242.

3m Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1c** (60 mg, 0.2 mmol) and **2i** (4 mL). This reaction was completed after 12 h, providing a green solid (57 mg, 60%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.34-7.31 (m, 4H), 7.27-7.23 (m, 6H), 6.93 (s, 2H), 6.62 (d, J = 4.3 Hz, 1H), 6.55 (d, J = 3.9 Hz, 1H), 6.39 (d, J = 2.2 Hz, 1H), 6.25 (d, J = 4.3 Hz, 1H), 6.23 (s, 1H), 2.35 (s, 3H), 2.10 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.46, 145.94, 141.91, 141.43, 138.66, 136.51, 135.44, 134.45, 130.77, 129.86, 129.09, 128.55, 128.11, 126.89, 120.42, 120.40, 117.59, 50.32, 21.13, 20.10; HRMS calcd. for $C_{31}H_{27}BF_2N_2$, $[M–F]^+$: 457.2246, found: 457.2255.

3n Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1c** (60 mg, 0.2 mmol) and **2j** (4 mL). This reaction was completed after 12 h. providing an oily compound (45 mg, 48%). ^1H NMR (300 MHz, $CDCl_3$) δ

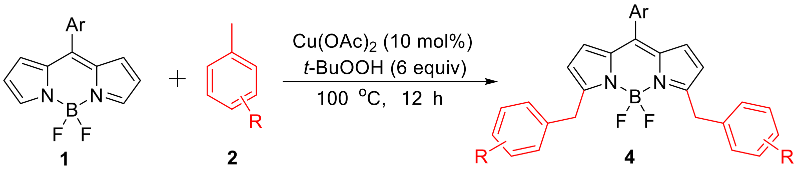
8.02 (d, *J* = 8.0 Hz, 2H), 7.82 (s, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 6.93 (s, 2H), 6.58 (s, 2H), 6.44 (s, 1H), 6.01 (d, *J* = 3.7 Hz, 1H), 4.45 (s, 2H), 4.37 (q, *J* = 9.0 Hz, 2H), 2.35 (s, 3H), 2.10 (s, 6H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.83, 162.10, 146.19, 142.61, 142.28, 139.09, 136.83, 136.21, 134.86, 131.52, 130.41, 130.13, 129.95, 129.65, 128.68, 128.51, 120.02, 118.07, 61.31, 35.69, 21.49, 20.37, 14.72; HRMS calcd. for $C_{28}H_{27}BF_2N_2O_2$, [M+H]$^+$: 473.2212, found: 473.2208.

3o Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1d** (62 mg, 0.2 mmol) and **2b** (6 mL). This reaction was completed after 12 h, providing a green solid (55 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.46-7.36 (m, 3H), 7.20 (s, 4H), 6.56 (s, 2H), 6.47 (s, 1H), 5.91 (d, *J* = 3.9 Hz, 1H), 4.43 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.13, 142.20, 138.39, 137.11, 135.65, 135.33, 135.07, 133.52, 131.51, 131.06, 130.94, 130.54, 130.47, 128.18, 127.43, 127.37, 126.30, 120.44, 117.80 , 33.52, 19.59; HRMS calcd. for $C_{23}H_{17}BClF_2N_2$, [M–F]$^+$: 421.0846, found: 421.0839.

3p Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1e** (60 mg, 0.2 mmol) and **2a** (4 mL). This reaction was completed after 12 h, providing a red solid (38 mg, 48%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.0 Hz, 2H), 7.89 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.34 (s, 5H), 6.72 (s, 2H), 6.54 (s, 1H), 6.19 (s, 1H), 4.42 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.54, 149.33, 142.86, 142.08, 140.46, 137.01, 135.52, 133.82, 132.54, 131.59, 129.90, 129.25, 129.13, 127.48, 123.99, 121.53, 118.55, 35.84; HRMS calcd. for $C_{22}H_{16}BF_2N_3O$, [M–F]$^+$: 384.1314, found: 384.1334.

3q Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1f** (60 mg, 0.2 mmol) and **2a** (4 mL). This reaction was completed after 12 h providing an orange solid (49 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.35-7.28 (m, 5H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 4.3 Hz, 1H), 6.84 (d, *J* = 3.8 Hz, 1H), 6.51 (d, *J* = 2.1 Hz, 1H), 6.14 (d, *J* = 4.3 Hz, 1H), 4.41 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.63, 161.63, 145.30, 140.69, 137.20, 135.31, 133.91, 132.39, 132.13, 129.46, 128.93, 128.65, 126.76, 126.36, 119.77, 117.15, 113.86, 55.42, 35.23; HRMS calcd. for $C_{23}H_{19}BF_2N_2O$, [M–F]$^+$: 369.1569, found: 369.1563.

3r Prepared according to the general radical C–H monofunctionalization procedure using BODIPY **1g** (50 mg, 0.2 mmol) and **2a** (4 mL). This reaction was completed after 12 h, providing an orange solid (31 mg, 46%).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.32-7.22 (m, 5H), 6.99 (d, J = 3.8 Hz, 1H), 6.07 (d, J = 3.8 Hz, 1H), 4.19 (s, 2H), 2.49 (s, 3H), 2.40 (q, J = 7.5 Hz, 2H), 2.20 (s, 3H), 1.04 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, DMSO) δ 160.29, 156.15, 141.14, 139.05, 134.97, 134.34, 133.26, 129.86, 129.30, 128.44, 127.25, 125.39, 117.44, 34.82, 17.42, 14.98, 13.57, 9.92; HRMS calcd. for $C_{31}H_{27}BF_2N_2$, $[M+H]^+$: 339.1844, found: 339.1838.



General radical C–H difunctionalization procedure: BODIPY **1a** (1 equiv, 0.2 mmol), $Cu(OAc)_2$ (0.02 mmol, 10 mol%), the oxidant TBHP (6 equiv, 1.2 mmol) were dissolved in solvent (4 mL). The reaction mixture was heated at 100 °C and stirred for the indicated time. Upon completion, the reaction mixture was cooled to room temperature. Subsequently, the crude mixture was poured into dichloromethane (100 mL), washed three times with water (100 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by column chromatographically (silica; petroleum ether/ethyl acetate; 100:1-50:1 v/v).

4a Prepared according to the general radical C–H difunctionalization procedure using BODIPY **1a** (54 mg, 0.2 mmol) and **2b** (4 mL). This reaction was completed after 12 h, providing an orange solid (38 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.46 (m, 2.5H), 7.26-7.19 (m, 4H), 6.67 (d, J = 3.9 Hz, 1H), 5.86 (d, J = 3.9 Hz, 1H), 4.45 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.61, 143.62, 137.08, 135.94, 134.79, 134.06, 133.75, 130.45, 130.38, 130.03, 128.54, 128.22, 127.13, 126.20, 118.58, 33.22, 19.54; HRMS calcd. for $C_{31}H_{27}BF_2N_2$, $[M+H]^+$: 477.2314, found: 477.2315.

4b Prepared according to the general radical C–H difunctionalization procedure using BODIPY **1a** (54 mg, 0.2 mmol) and **2g** (4 mL). This reaction was completed after 12 h, providing a green solid (37 mg, 32%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.44 (m, 5H), 7.36-7.20 (m, 2.5H), 6.69 (s, 1H), 6.26 (d, J = 14.7 Hz, 1H), 4.96 (q, J = 12.3 Hz, 1H), 1.75 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.72, 143.78, 143.38, 134.10, 133.70, 130.52, 130.29, 129.88, 128.52, 128.14, 127.60, 126.61, 117.09, 38.30, 20.84; HRMS calcd. for $C_{31}H_{27}BF_2N_2$, [M–F]$^+$: 457.2282, found: 457.2285.

4c Prepared according to the general radical C–H difunctionalization procedure using BODIPY **1h** (60 mg, 0.2 mmol) and **2a** (4 mL). This reaction was completed after 12 h, providing an orange solid (34 mg, 36%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.42 (m, 2H), 7.35-7.33 (m, 4H), 7.29-7.28 (m, 1H), 6.67 (d, *J* = 4.2 Hz, 1H), 6.09 (d, *J* = 4.2 Hz, 1H), 4.43 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.98, 142.18, 137.55, 136.38, 134.26, 132.41, 131.52, 130.19, 129.47, 128.69, 128.62, 126.76, 119.16, 35.15. HRMS calcd. for $C_{29}H_{22}BClF_2N_2$, [M+H]$^+$: 483.1611 found: 483.1610.

4d Prepared according to the general radical C–H difunctionalization procedure using BODIPY **1c** (60 mg, 0.2 mmol) and **2a** (4 mL). This reaction was completed after 12 h, providing an orange solid (34 mg, 35%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.33 (m, 4H), 7.28 (d, *J* = 6.7 Hz, 1H), 6.91 (s, 1H), 6.45 (d, *J* = 3.9 Hz, 1H), 5.98 (d, *J* = 4.0 Hz, 1H), 4.43 (s, 2H), 2.33 (s, 1.5H), 2.10 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.51, 143.69, 138.41, 137.59, 136.60, 134.73, 129.97, 129.60, 129.05, 128.66, 128.02, 126.73, 118.73, 35.21, 21.10, 20.02; HRMS calcd. for $C_{32}H_{29}BF_2N_2$, [M+H]$^+$: 491.2470 found: 491.2458.

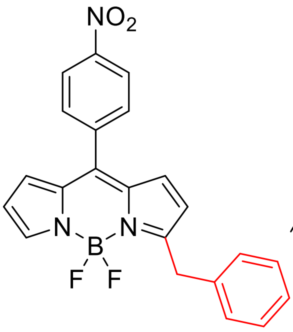
4e Prepared according to the general radical C–H difunctionalization procedure using BODIPY **1c** (60 mg, 0.2 mmol) and **2b** (4 mL). This reaction was completed after 12 h, providing an orange solid (39 mg, 38%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24-7.15 (m, 4H), 6.91 (s, 1H), 6.42 (d, *J* = 4.1 Hz, 1H), 5.78 (d, *J* = 4.1 Hz, 1H), 4.44 (s, 2H), 2.32 (s, 4.5H), 2.12 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.49, 143.42, 138.40, 137.08, 136.61, 135.90, 134.96, 130.44, 130.21, 129.98, 129.00, 128.03, 127.12, 126.19, 118.41, 33.19, 21.12, 20.03, 19.59; HRMS calcd. for $C_{35}H_{34}BF_2N_2$, [M+H]$^+$: 519.2783 found: 519.2788.

4f Prepared according to the general radical C–H difunctionalization procedure using BODIPY **1c** (60 mg, 0.2 mmol) and **2i** (4 mL). This reaction was completed after 12 h, providing an orange solid (43 mg, 34%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.22 (m, 10H), 6.91 (s, 1H), 6.51 (d, *J* = 3.9 Hz, 1H), 6.25 (s, 2H), 6.22 (d, *J* = 3.4 Hz, 1H), 2.33 (s, 1.5H), 2.10 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.05, 144.42, 141.96, 138.47, 136.70, 134.31, 130.05, 129.16, 128.90, 128.44, 128.04, 126.69, 119.57, 49.93, 21.11, 20.20; HRMS calcd. for $C_{44}H_{37}BF_2N_2$, [M–F]$^+$: 623.3028, found: 623.3026.

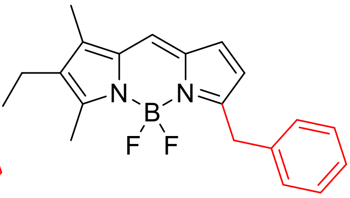
4g Prepared according to the general radical C–H difunctionalization procedure using **4** BODIPY **1d** (62 mg, 0.2 mmol) and **2h** (4 mL). This reaction was completed after 12 h, providing a red solid (36 mg, 35%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 1H), 7.38-7.34 (m, 0.5H), 7.25 (s,1H), 7.23 – 7.18 (m, 3H), 6.44 (d, *J* = 4.2 Hz, 1H), 5.83 (d, *J* = 4.2 Hz, 1H), 4.45 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.79, 144.96, 137.11, 136.78, 135.67, 135.50, 134.37, 131.70, 130.88, 130.46, 128.69, 128.11, 127.19, 126.22, 119.04, 33.31, 29.71, 19.61; HRMS calcd. for $C_{31}H_{25}BCl_2F_2N_2$, [M–F]$^+$: 525.1581, found: 525.1570.

4. Crystal data

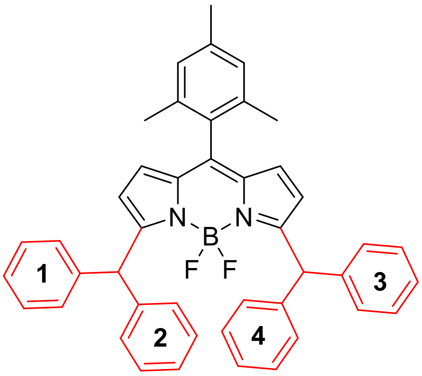
Table S1. Selected Geometrical Parameters of 3p, 3r, and 4f obtained from crystallography



3p



3r



4f

	3p	**3r**	**4f**
B-N bond distances (Å)	1.5455(24) 1.5613(26)	1.5514(24) 1.5437(22)	1.5525(24) 1.5524(27)
dihedral angles between dipyyrin core and phenyl ring at 3- and/or 5- positions (deg)	72.960(64)	84.384(88)	87.373(83) (**1**) 80.386(61) (**2**) 79.063(69) (**3**) 79.894(54) (**4**)
dihedral angles between *meso*-mesityl group and dipyyrin core (deg)	59.457(58)	/	77.573(39)
dihedral angles of two pyrrole rings in dipyyrin core (deg)	4.200(71)	4.758(55)	4.514(81)

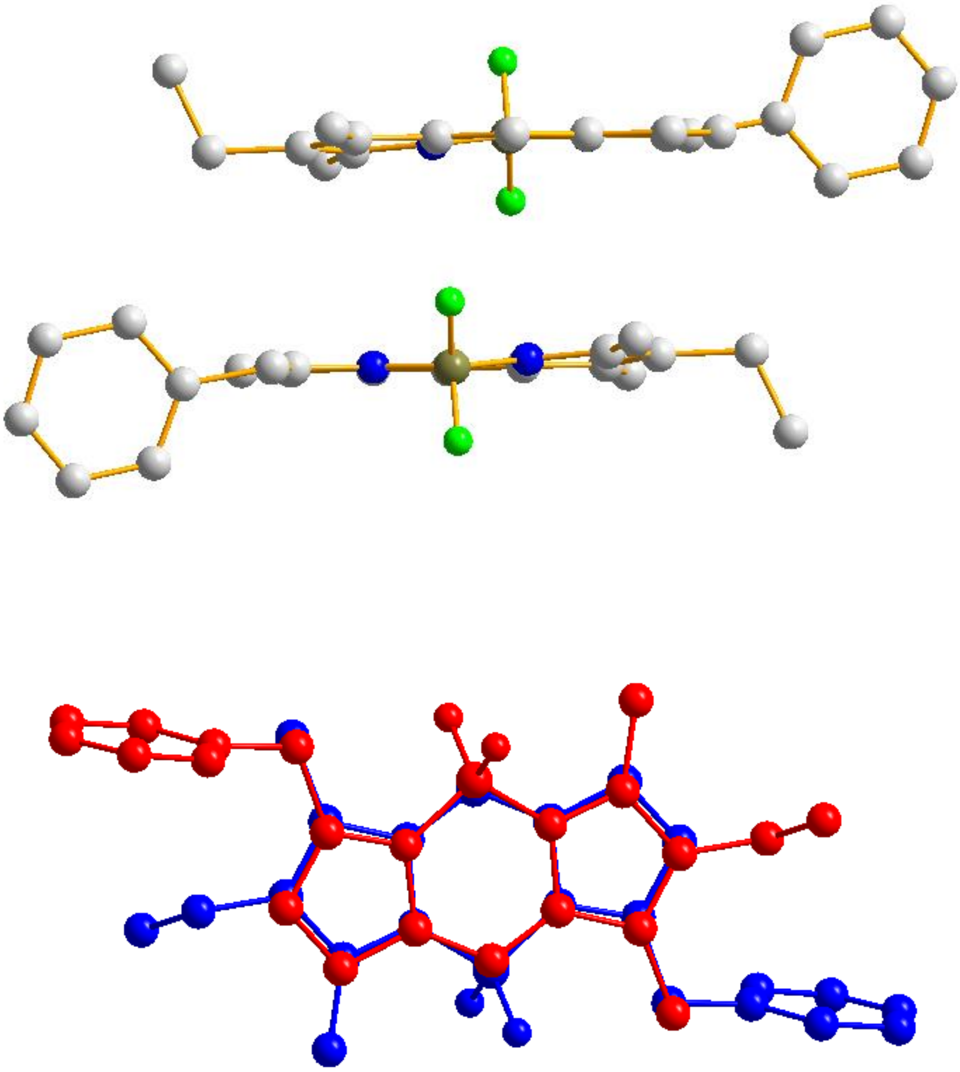


Figure S2. Crystal-packing pattern of BOPPY **3r** between the adjacent interlayered crystals. Dihedral angle between the adjacent molecules is 0.0°. The interlayer distance is 3.67 Å

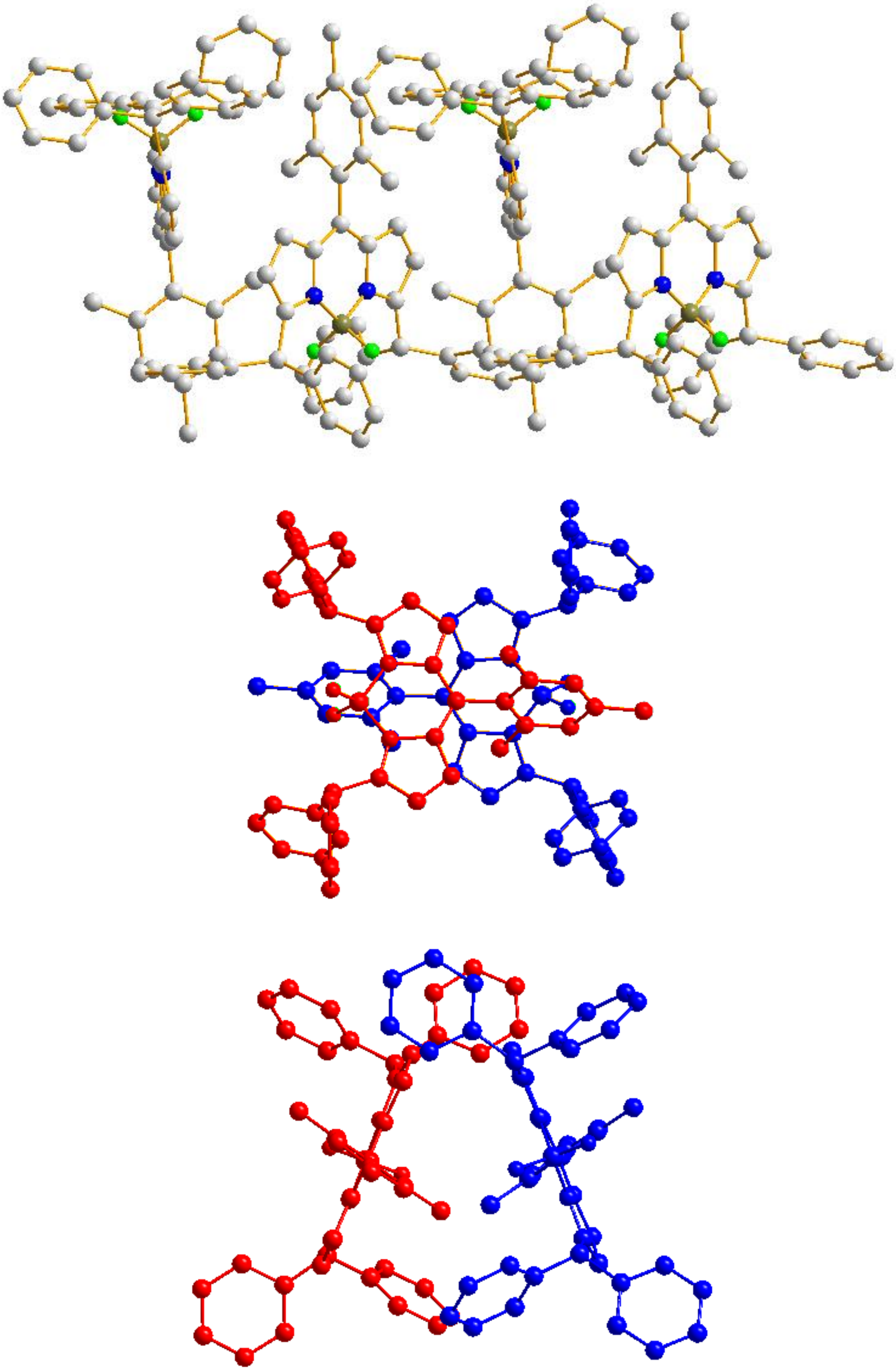


Figure S3. Crystal-packing pattern of BOPPY **4f** between the adjacent interlayered crystals. Dihedral angle between the adjacent molecules is 46.5°.

5. Table S2: Spectroscopic and photophysical properties of BODIPYs in CH_2Cl_2.

dye~~s~~	λ_{abs}^{max} (nm)	ε_{abs}^{max} [b]	λ_{em}^{max} (nm)	Φ[a]	Stokes shift (cm^{-1}) [c]
3a	507	49900	527	0.10	750
3b	506	44500	526	0.10	750
3c	507	48400	525	0.10	680
3d	506	54900	523	0.10	640
3e	507	48900	525	0.10	680
3f	507	50800	517	0.11	380
3g	507	49400	527	0.11	750
3h	501	43200	514	0.71	510
3i	506	64500	522	0.92	610
3j	506	61300	521	0.91	570
3k	507	66600	522	0.94	570
3l	507	66800	523	0.94	600
3m	510	63700	524	0.90	520
3n	507	49300	523	0.94	600
3o	517	50800	532	0.77	550
3p	515	45900	546	0.01	1100
3q	504	44900	521	0.13	650
3r	521	48300	531	0.86	360
4a	517	93500	534	0.55	620
4b	517	86400	535	0.48	650
4c	518	68200	535	0.32	610
4d	516	60600	528	0.95	440
4e	518	83800	531	0.99	470
4f	523	72600	537	0.92	500
4g	529	96400	543	0.93	490

[a] Fluorescence quantum yield was calculated using fluorescein (Φ = 0.90 in 0.1 N NaOH aqueous solution) as reference at room temperature. Standard uncertainties on Φ are less than 10%. [b] Standard uncertainties on ε_{abs}^{max} are less than 1000 M^{-1} cm^{-1}. [c] The Stokes shift values of are rounded to the nearest 10 cm^{-1}.

6. UV-Vis absorption and fluorescence emission spectra in CH_2Cl_2.

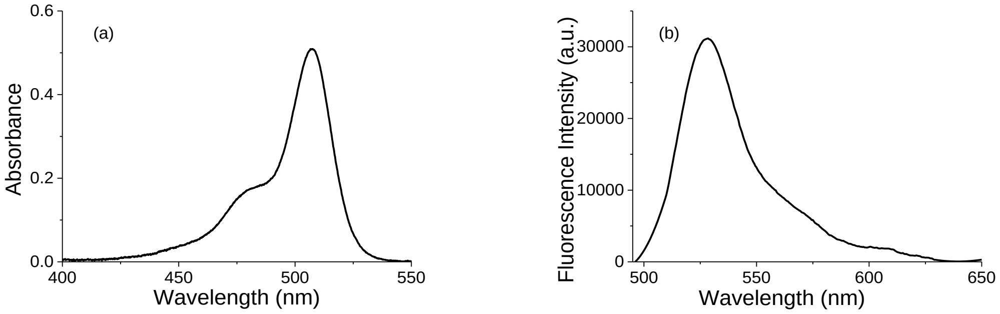


Figure S4. Absorption (a) and fluorescence emission (b) spectra of **3a** recorded in CH_2Cl_2 (excitation at 480 nm).

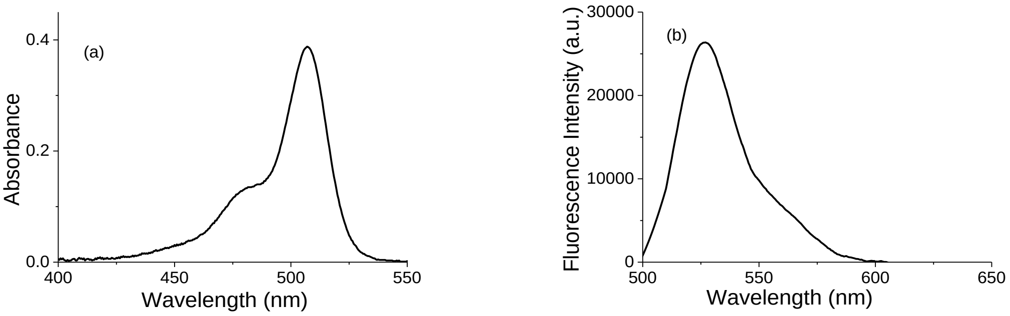


Figure S5. Absorption (a) and fluorescence emission (b) spectra of **3b** recorded in CH_2Cl_2 (2 (excitation at 480 nm).

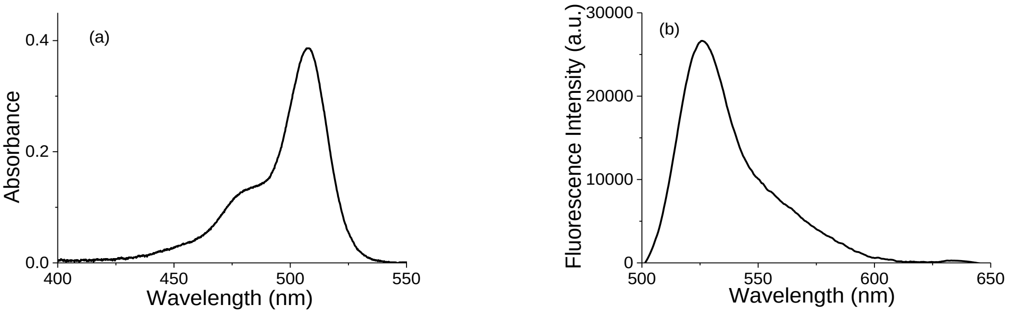


Figure S6. Absorption (a) and fluorescence emission (b) spectra of **3c** recorded in CH_2Cl_2 (excitation at 480 nm).

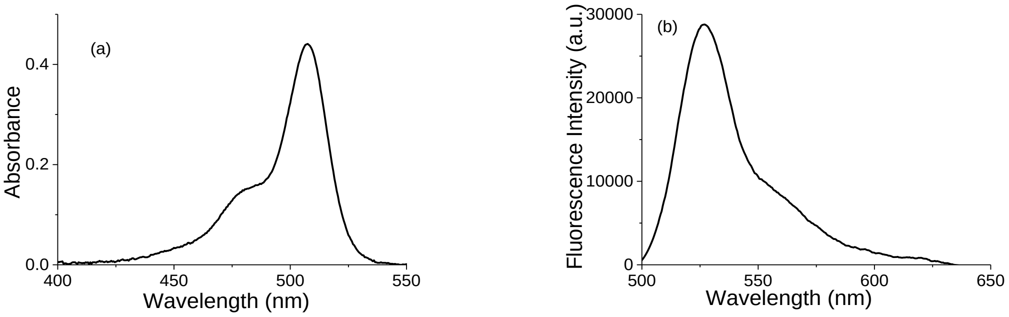


Figure S7. Absorption (a) and fluorescence emission (b) spectra of **3d** recorded in CH_2Cl_2 (excitation at 480 nm).

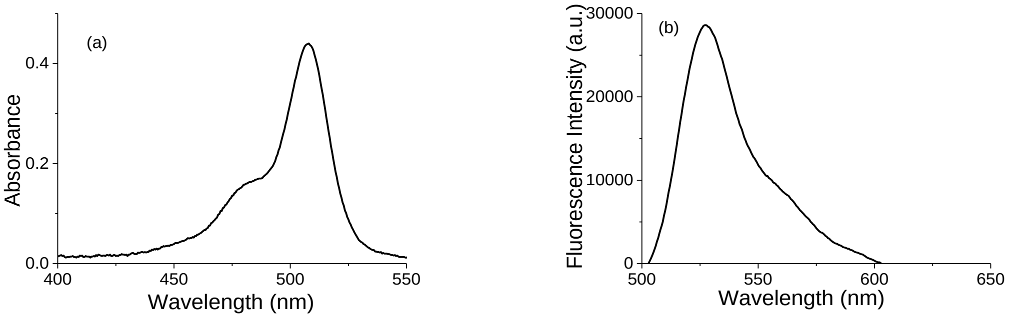


Figure S8. Absorption (a) and fluorescence emission (b) spectra of **3e** recorded in CH_2Cl_2 (excitation at 480 nm).

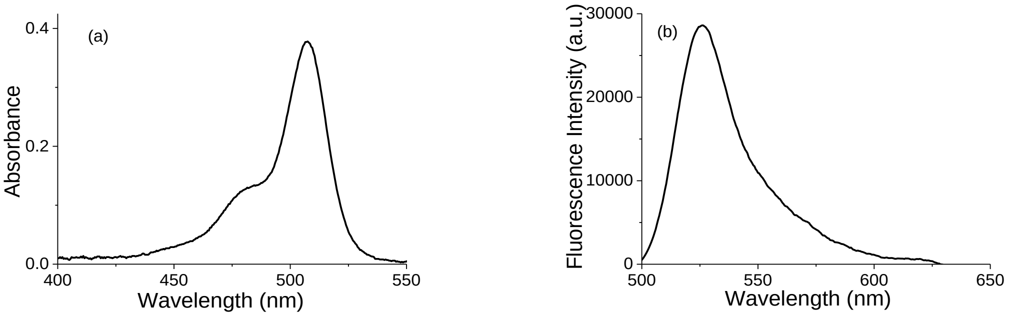


Figure S9. Absorption (a) and fluorescence emission (b) spectra of 3**f** recorded in CH_2Cl_2 (excitation at 480 nm).

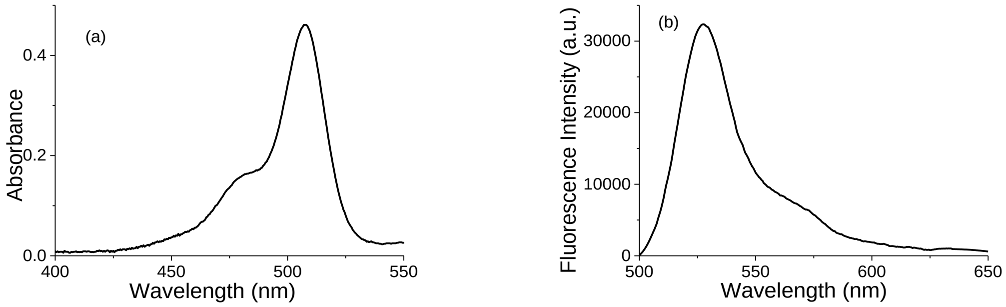


Figure S10. Absorption (a) and fluorescence emission (b) spectra of 3**g** recorded in CH_2Cl_2 (excitation at 480 nm).

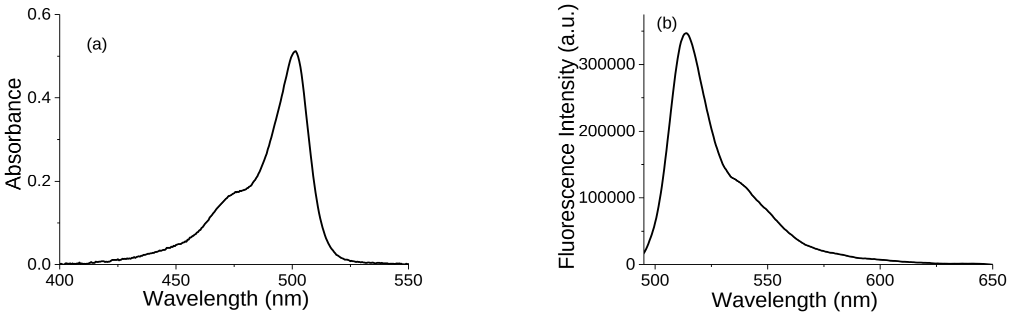


Figure S11. Absorption (a) and fluorescence emission (b) spectra of 3**h** recorded in CH_2Cl_2 (excitation at 480 nm).

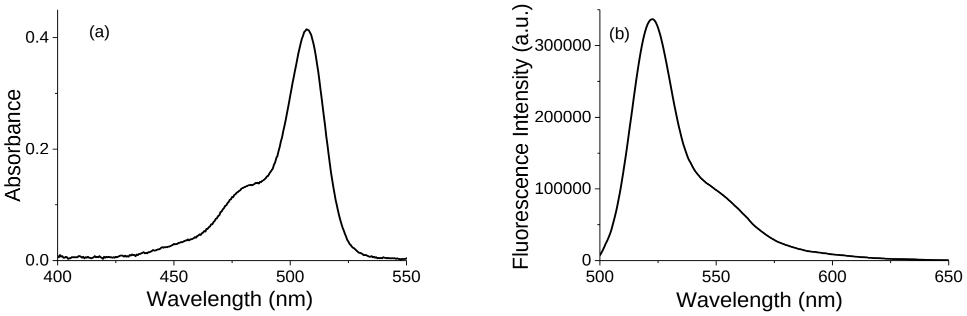


Figure S12. Absorption (a) and fluorescence emission (b) spectra of **3i** recorded in CH_2Cl_2 (excitation at 480 nm).

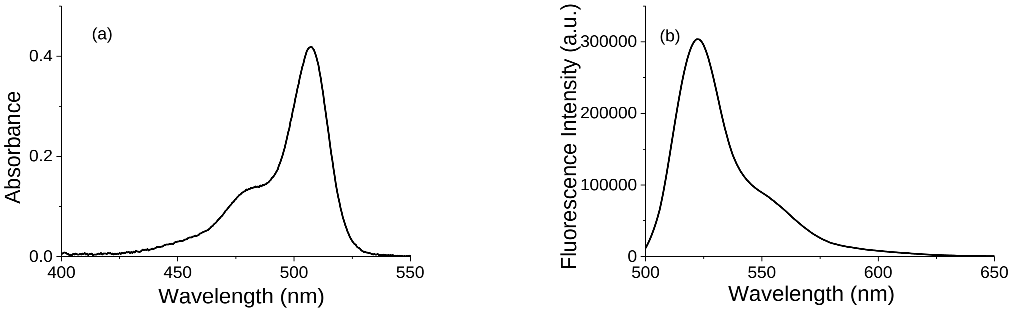


Figure S13. Absorption (a) and fluorescence emission (b) spectra of **3j** recorded in CH_2Cl_2 (excitation at 480 nm).

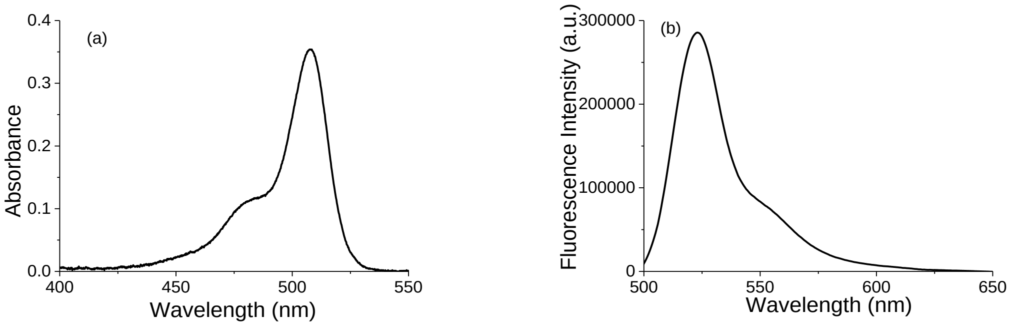


Figure S14. Absorption (a) and fluorescence emission (b) spectra of **3k** recorded in CH_2Cl_2 (excitation at 480 nm).

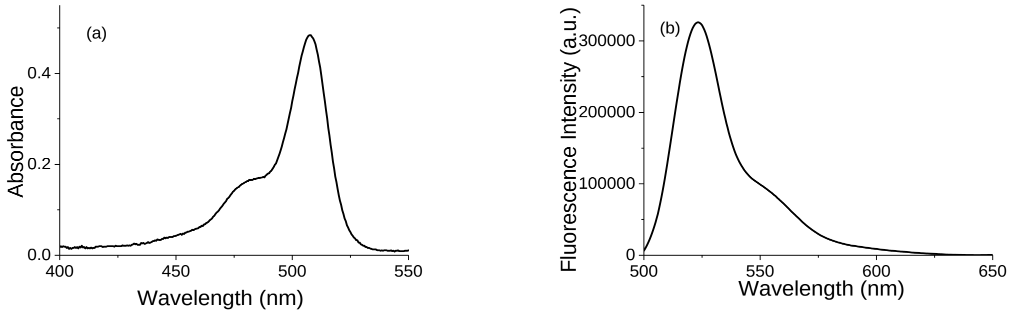


Figure S15. Absorption (a) and fluorescence emission (b) spectra of **3l** recorded in CH_2Cl_2 (excitation at 480 nm).

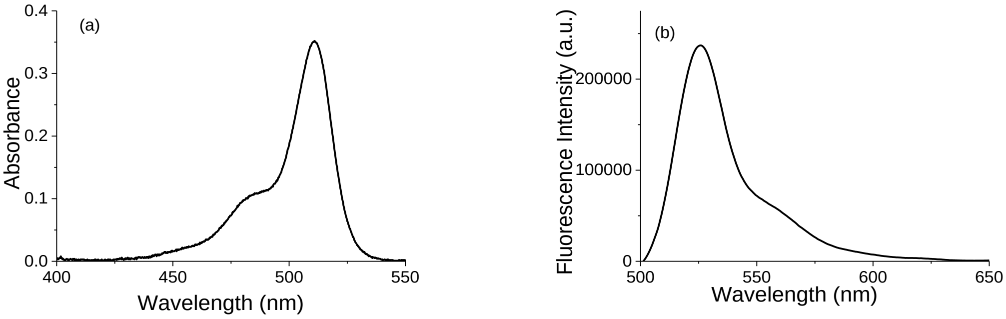


Figure S16. Absorption (a) and fluorescence emission (b) spectra of **3m** recorded in CH_2Cl_2 (excitation at 480 nm).

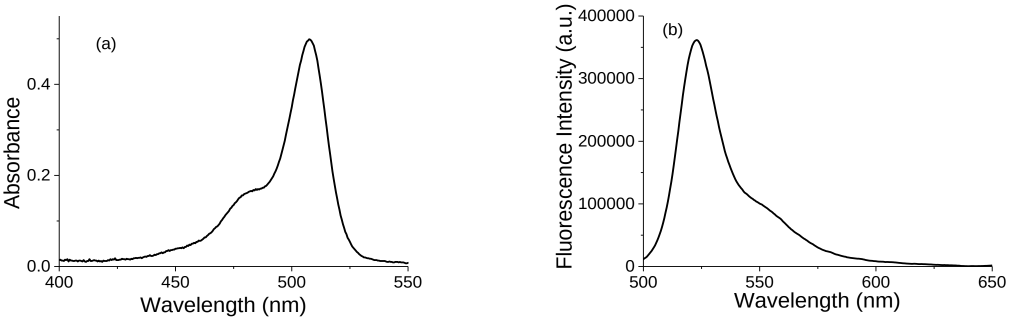


Figure S17. Absorption (a) and fluorescence emission (b) spectra of **3n** recorded in CH_2Cl_2 (excitation at 480 nm).

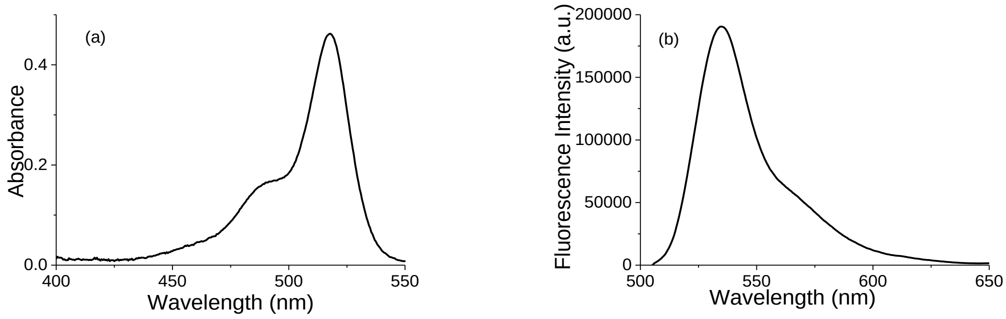


Figure S18. Absorption (a) and fluorescence emission (b) spectra of **3o** recorded in CH_2Cl_2 (excitation at 480 nm).

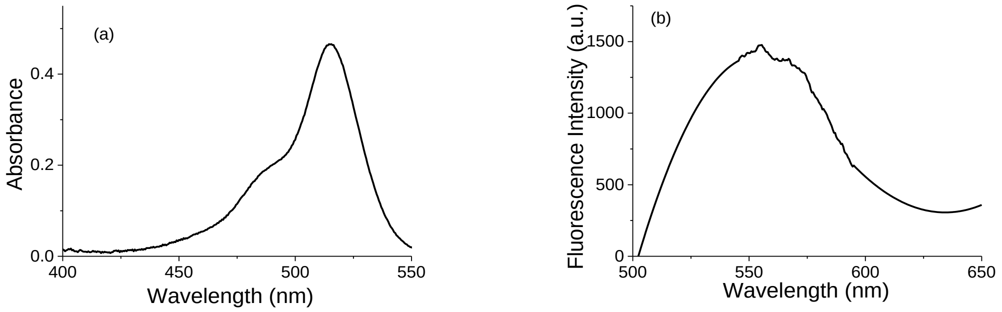


Figure S19. Absorption (a) and fluorescence emission (b) spectra of **3p** recorded in CH_2Cl_2 (excitation at 480 nm).

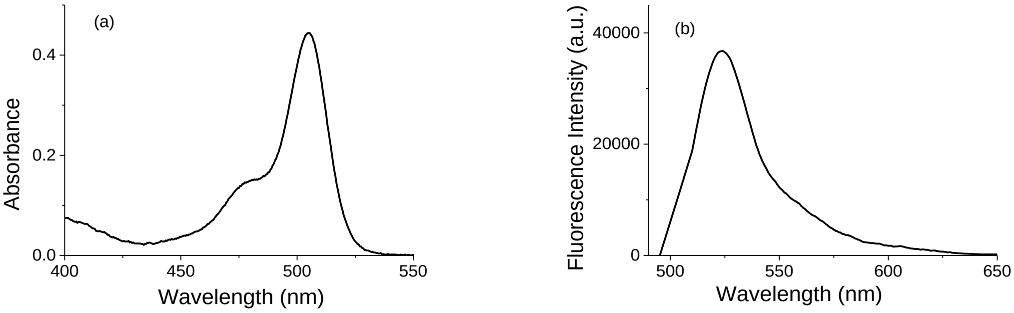


Figure S20. Absorption (a) and fluorescence emission (b) spectra of **3q** recorded in CH_2Cl_2 (excitation at 480 nm).

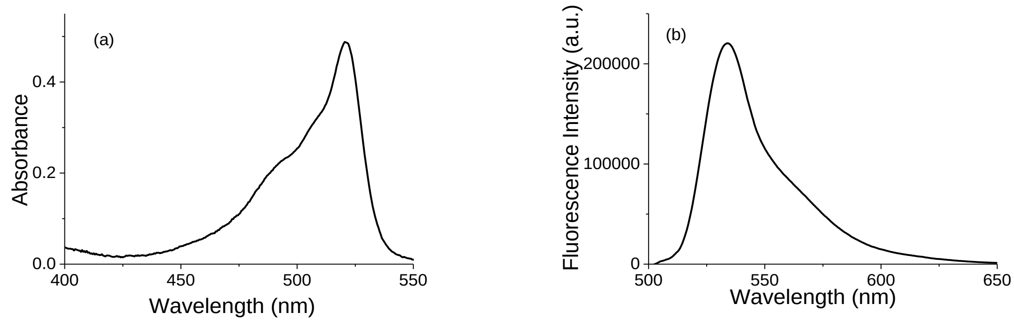


Figure S21. Absorption (a) and fluorescence emission (b) spectra of **3r** recorded in CH_2Cl_2 (excitation at 480 nm).

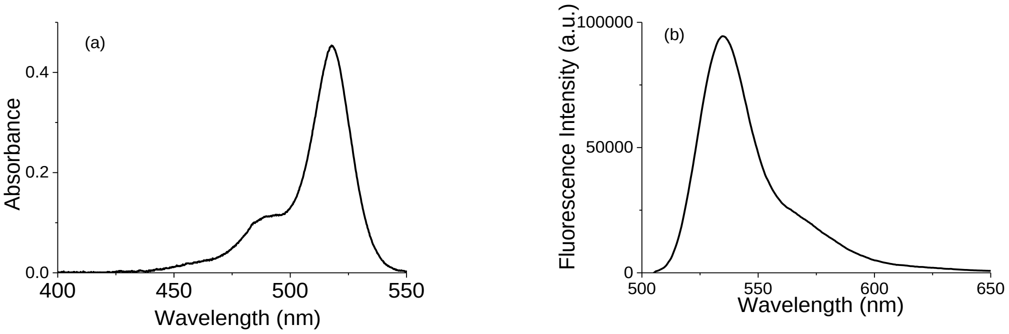


Figure S22. Absorption (a) and fluorescence emission (b) spectra of **4a** recorded in CH_2Cl_2 (excitation at 480 nm).

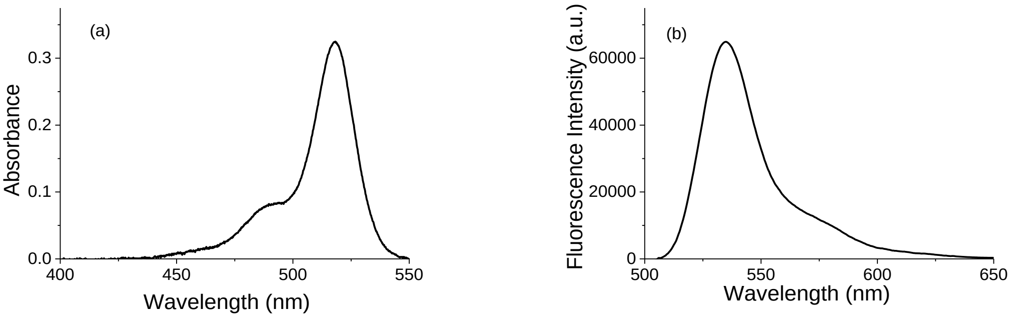


Figure S23. Absorption (a) and fluorescence emission (b) spectra of **4b** recorded in CH_2Cl_2 (excitation at 480 nm).

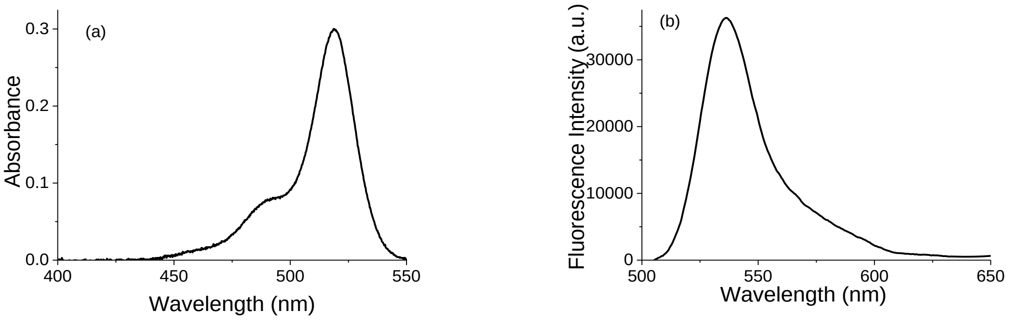


Figure S24. Absorption (a) and fluorescence emission (b) spectra of **4c** recorded in CH_2Cl_2 (excitation at 480 nm).

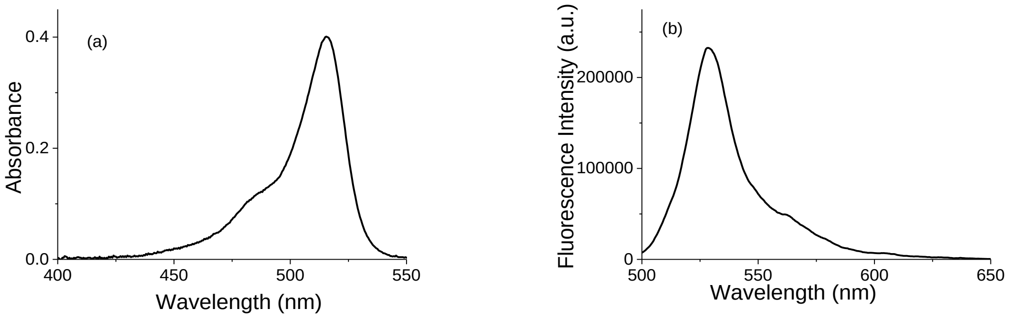


Figure S25. Absorption (a) and fluorescence emission (b) spectra of **4d** recorded in CH_2Cl_2 (excitation at 480 nm).

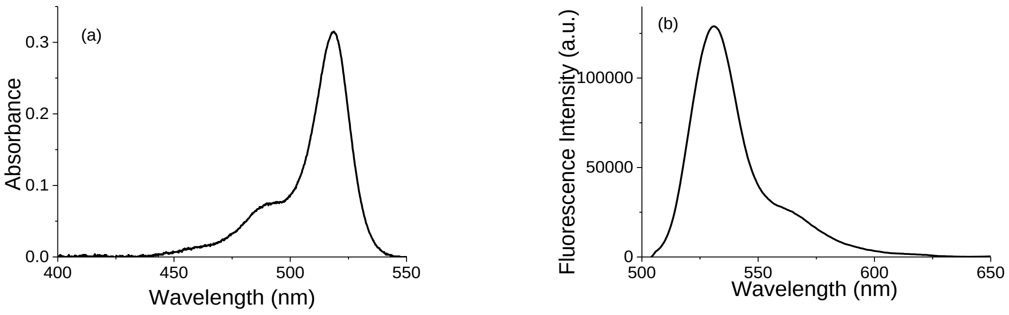


Figure S26. Absorption (a) and fluorescence emission (b) spectra of **4e** recorded in CH_2Cl_2 (excitation at 480 nm).

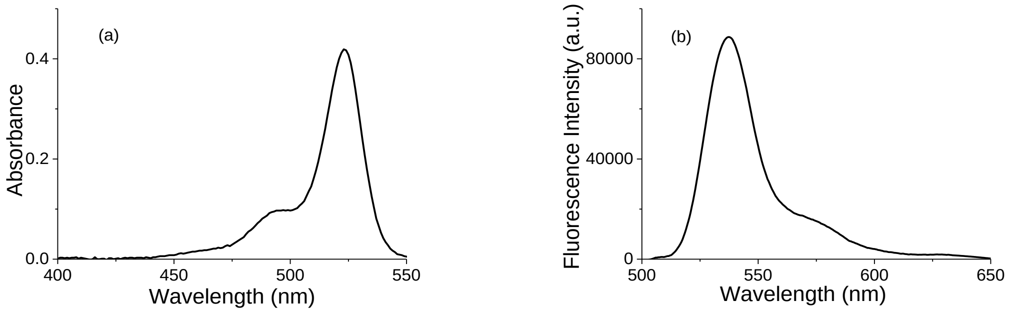


Figure S27. Absorption (a) and fluorescence emission (b) spectra of **4f** recorded in CH_2Cl_2 (excitation at 480 nm).

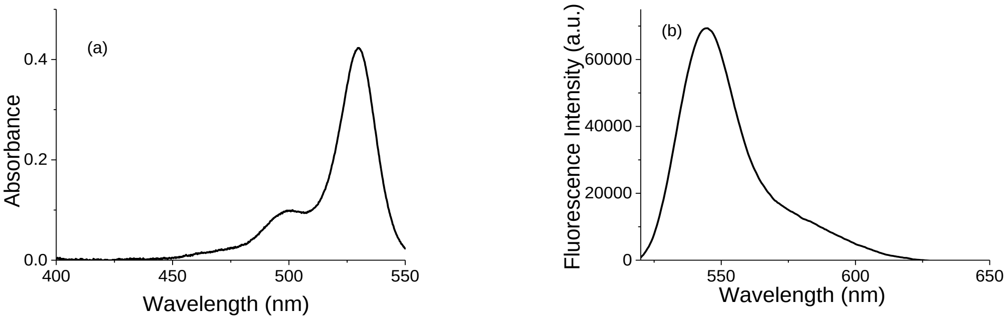


Figure S28. Absorption (a) and fluorescence emission (b) spectra of **4g** recorded in CH_2Cl_2 (excitation at 480 nm).

7. Solid-state fluorescence of selected dyes

Absolute fluorescence quantum yields Φ of these dyes in powdered solid state were measured using Edinburgh FLS 920 fluorescence spectrometer with an integrating sphere[4] according to the definition of fluorescence efficiency.

Table S3: **Solid-state fluorescence emission maxima and fluorescence quantum yields Φ of selected BODIPYs in powdered solid state**.

dyes	**3a**	**3b**	**3i**	**3m**	**3o**	**4a**	**4d**	**4f**
λ_{em}^{max} (nm)	626	602	628	610	625	648	600	622
Φ	0.12	0.10	0.11	0.17	0.14	0.13	0.12	0.16

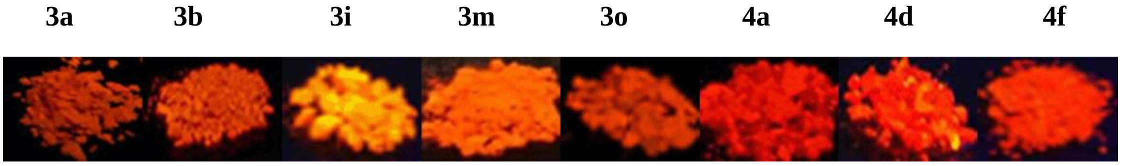


Figure S29. Photo of solid fluorescence of BODIPYs in powdered solid state under 365 nm handhold UV-light irradiation.

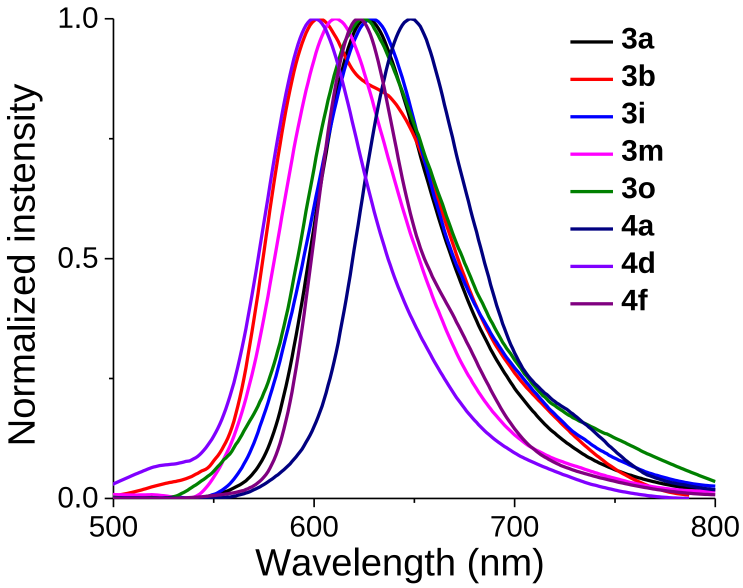
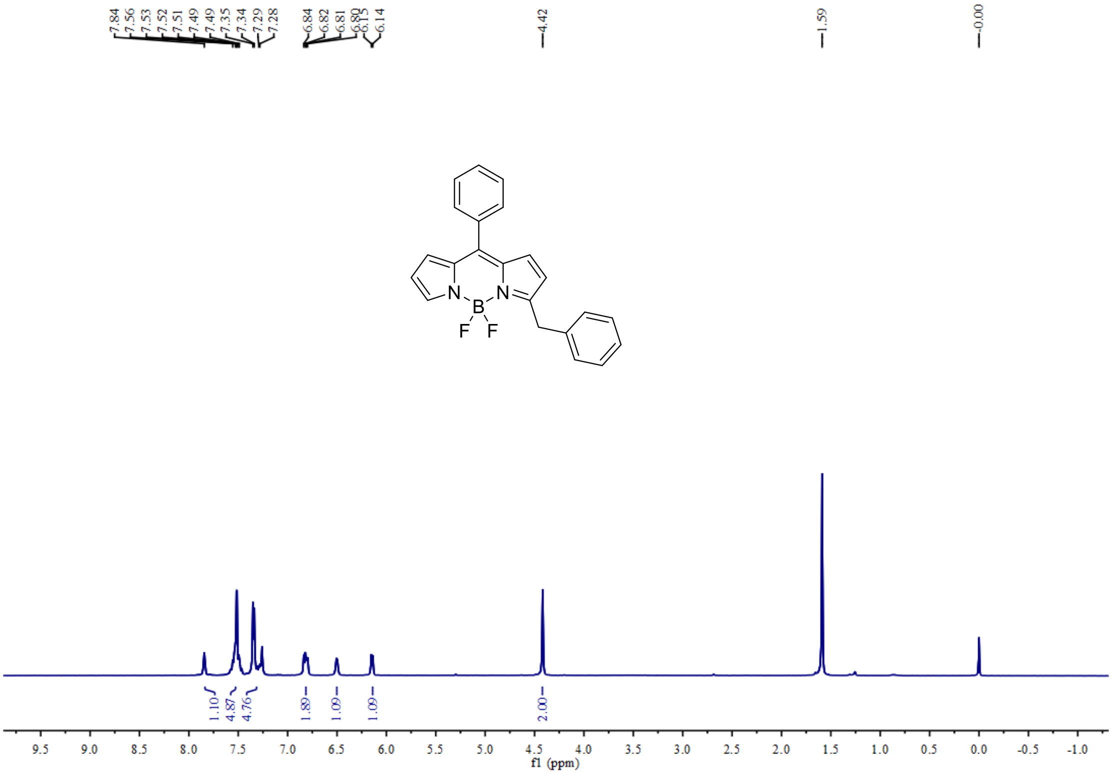


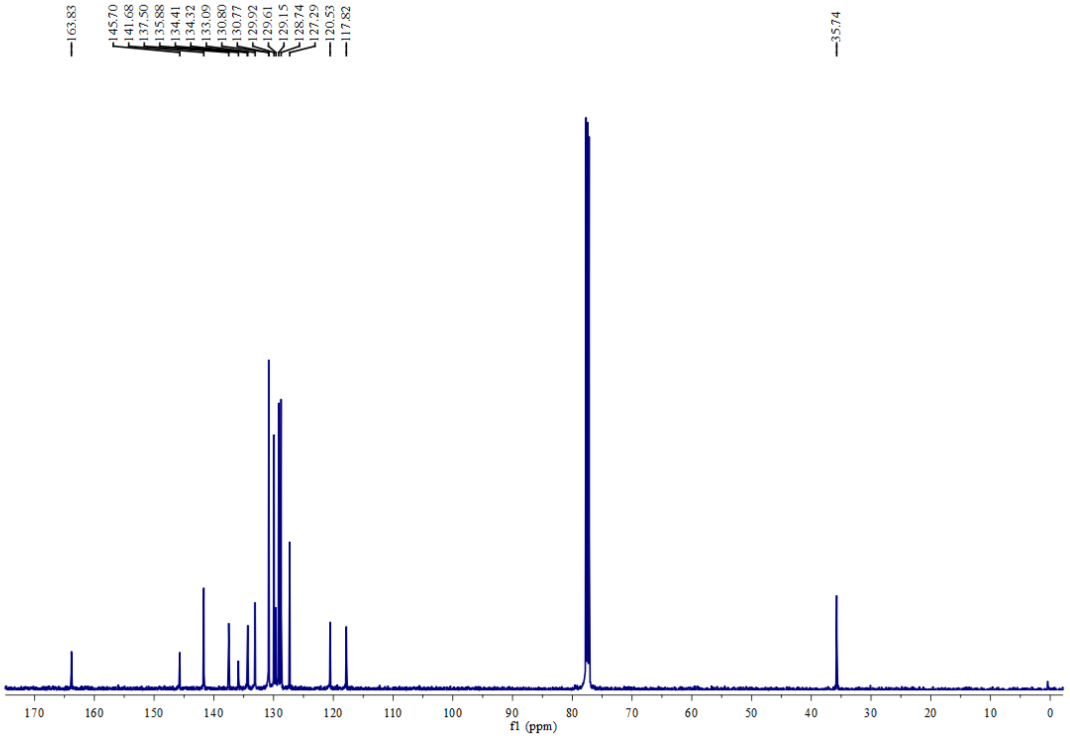
Figure S30. Normalized fluorescence emission spectra of selected BODIPYs in powdered solid state.

8. NMR-spectra of all new compounds

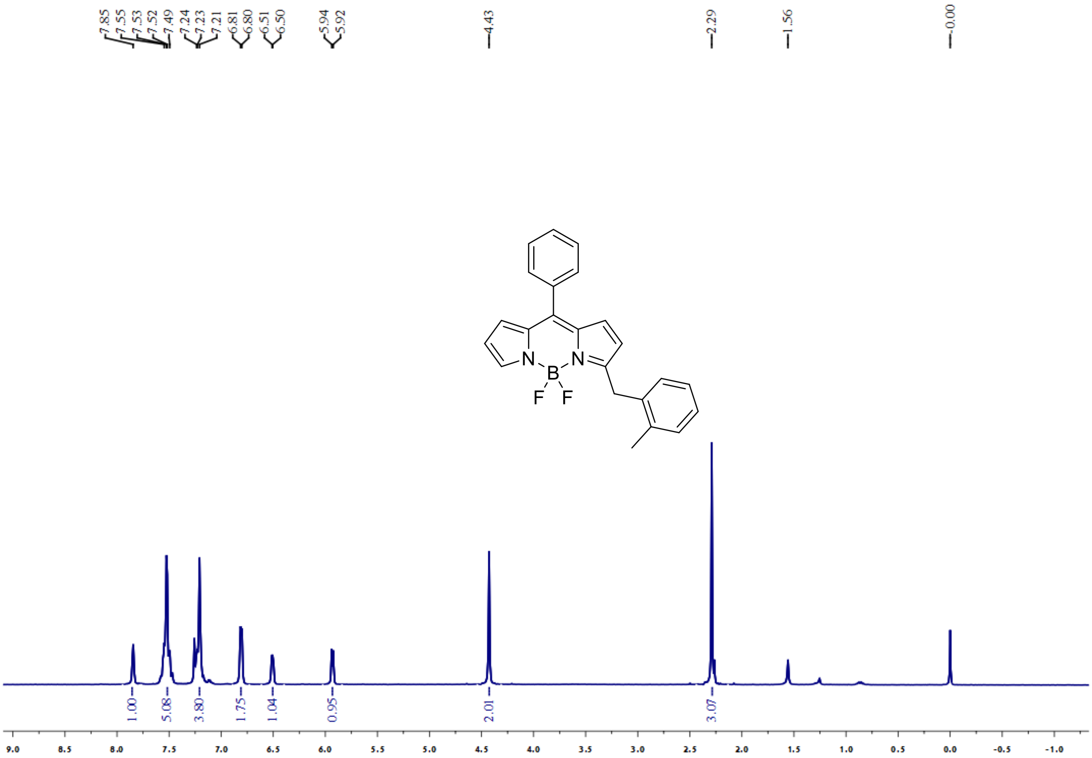
3a, ^{1}H, 300 MHz, CDCl$_3$



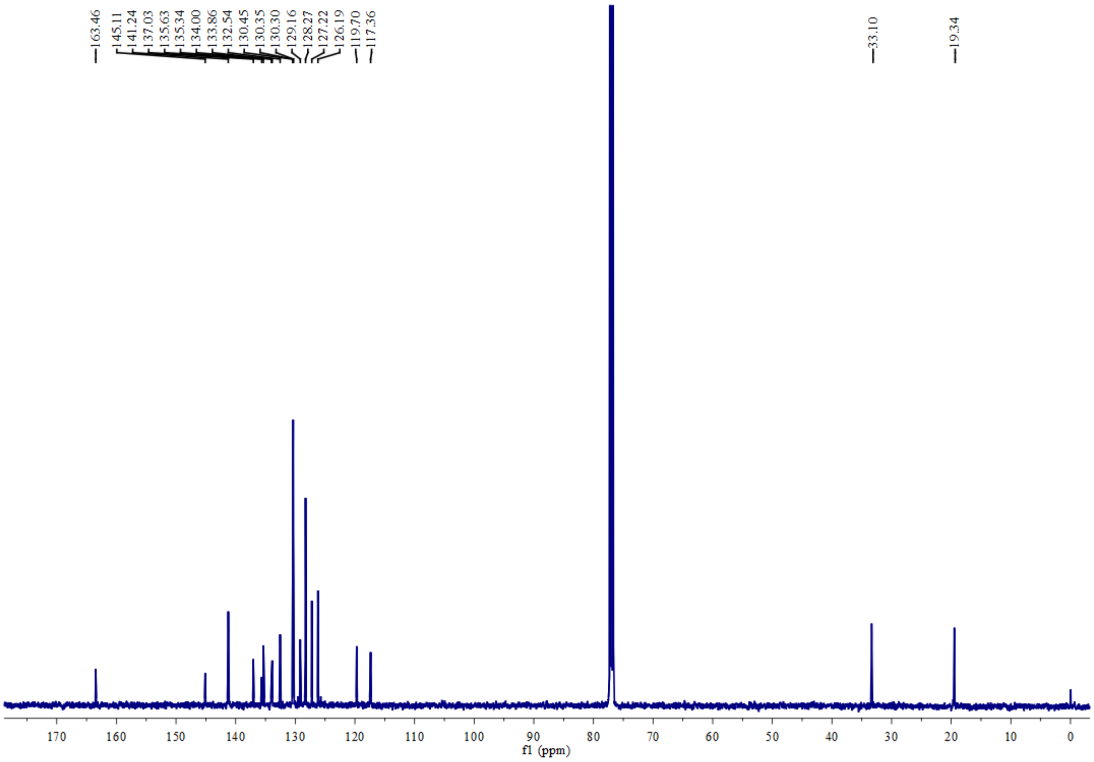
3a, ^{13}C, 126 MHz, CDCl$_3$



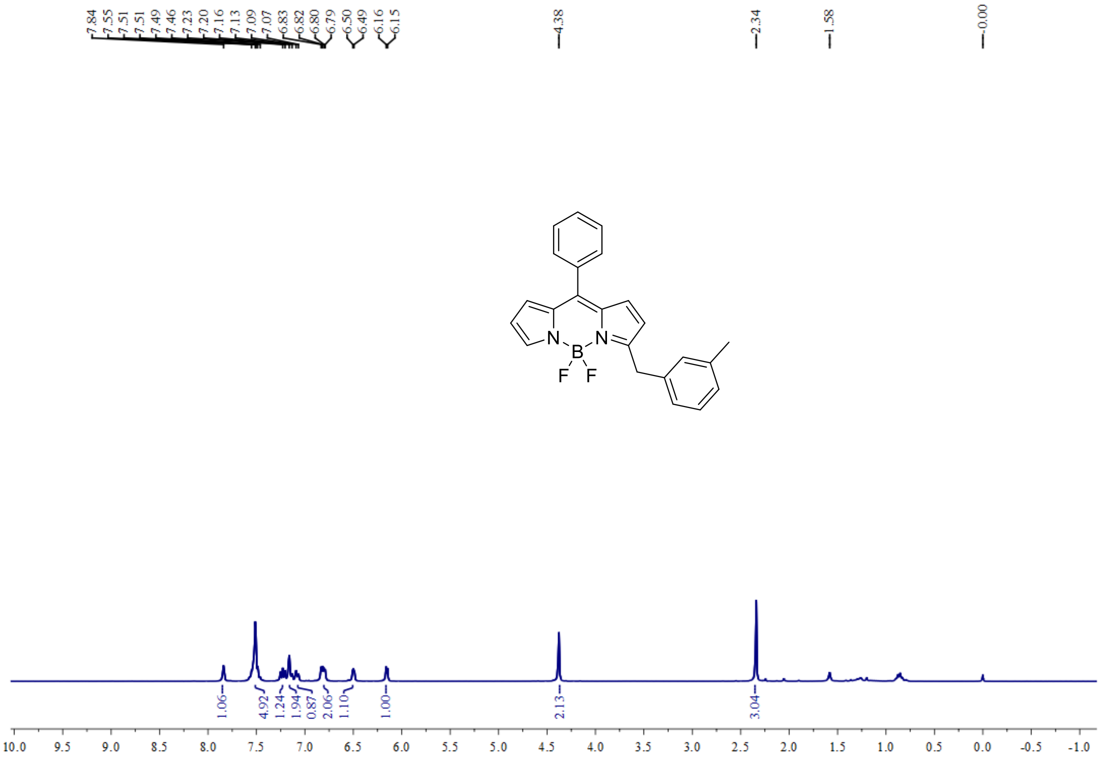
3b, ^{1}H, 300 MHz, CDCl$_3$



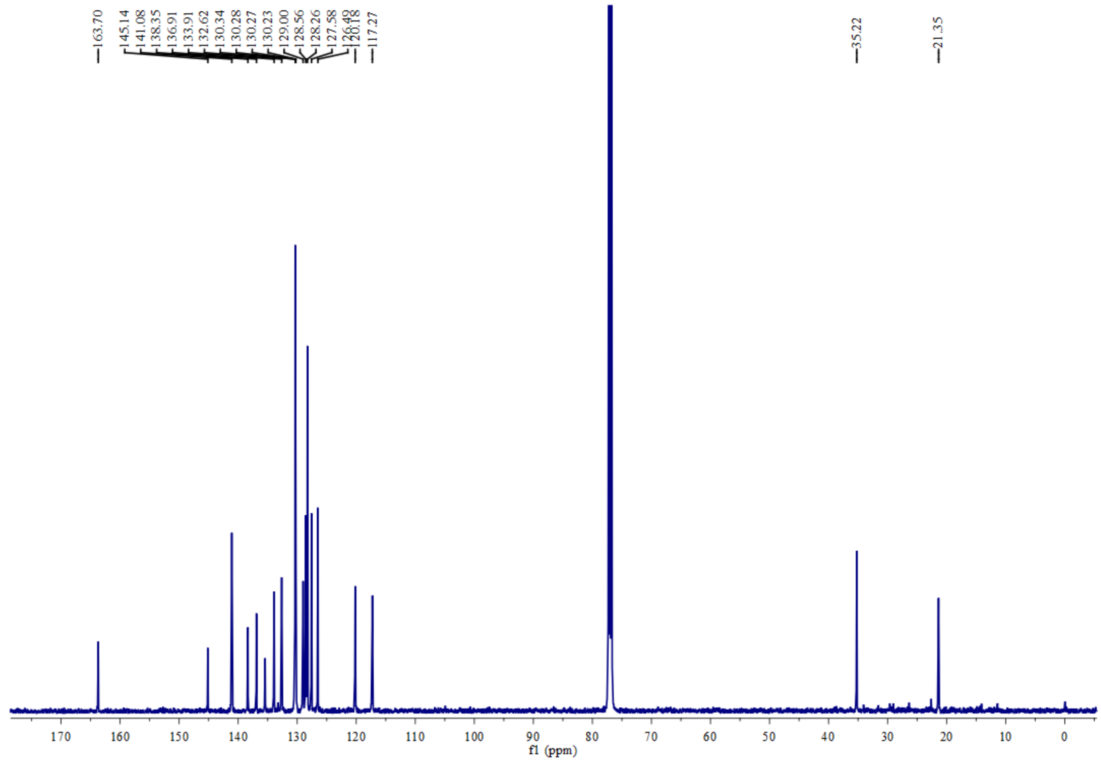
3b, ^{13}C, 126 MHz, CDCl$_3$



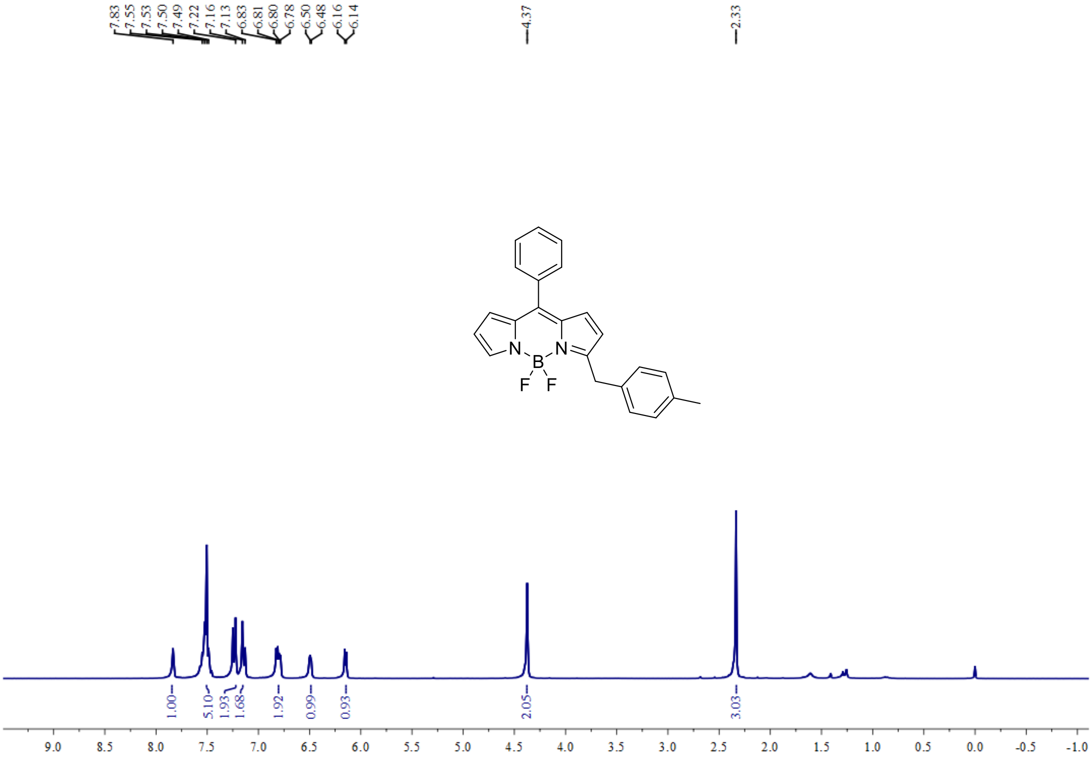
3c, ^{1}H, 300 MHz, CDCl$_3$



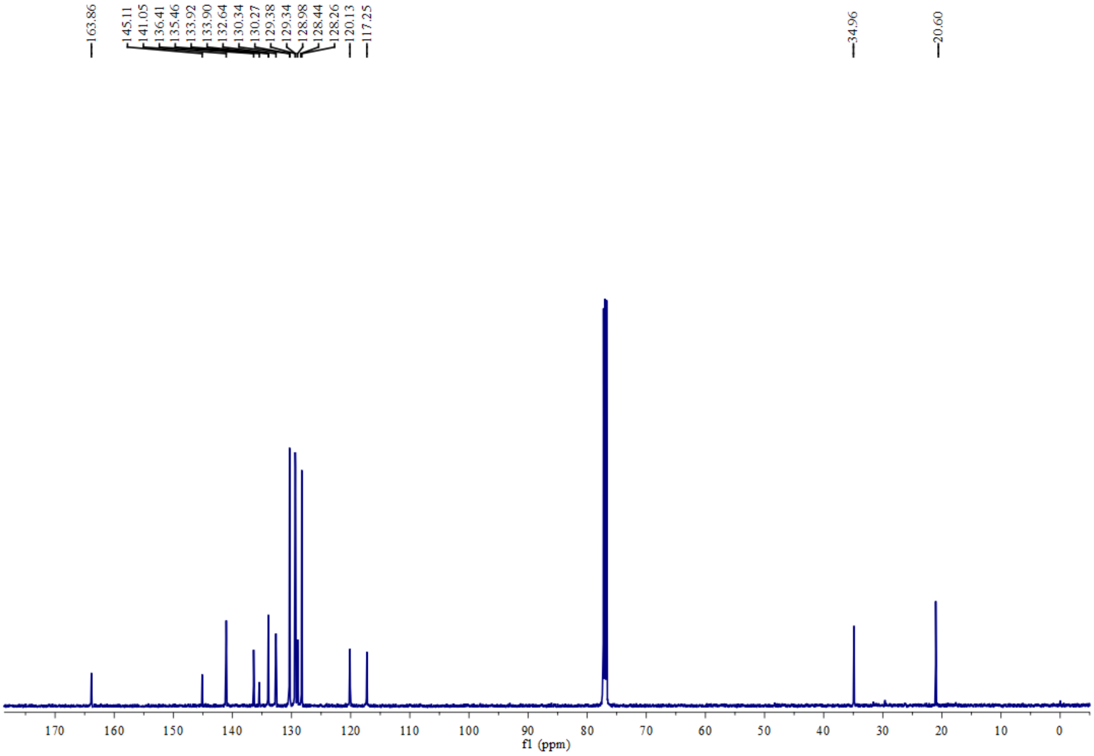
3c, ^{13}C, 126 MHz, CDCl$_3$



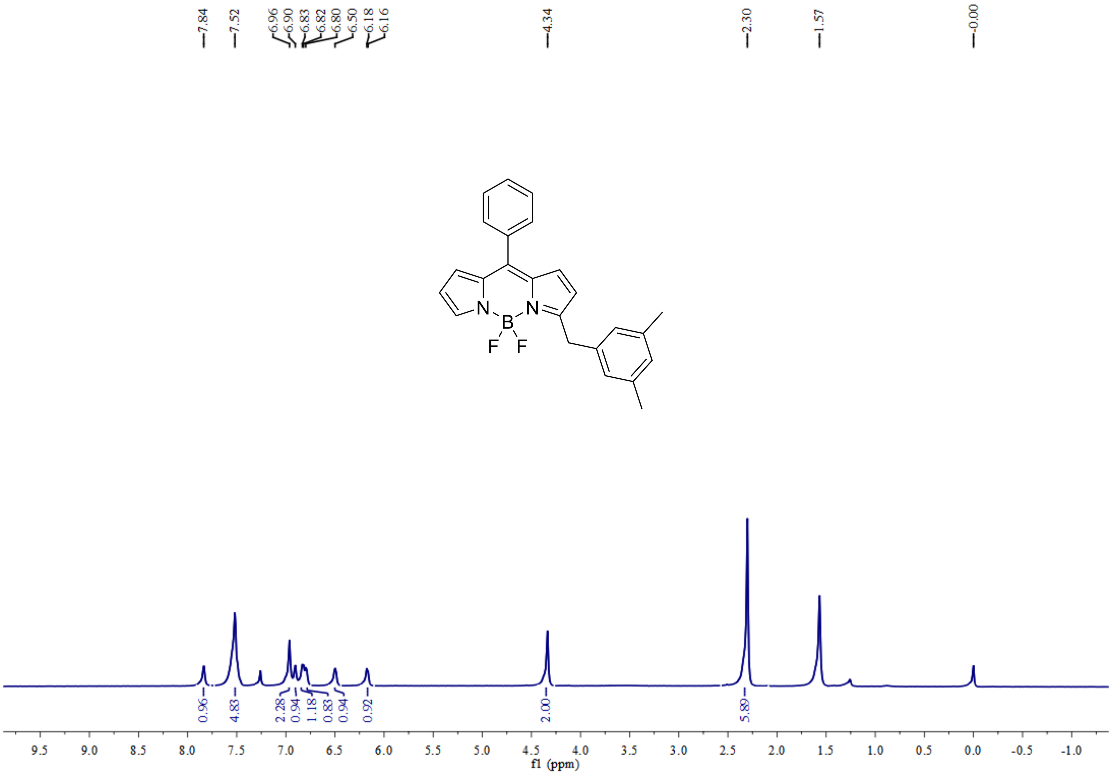
3d, ^{1}H, 300 MHz, CDCl$_3$



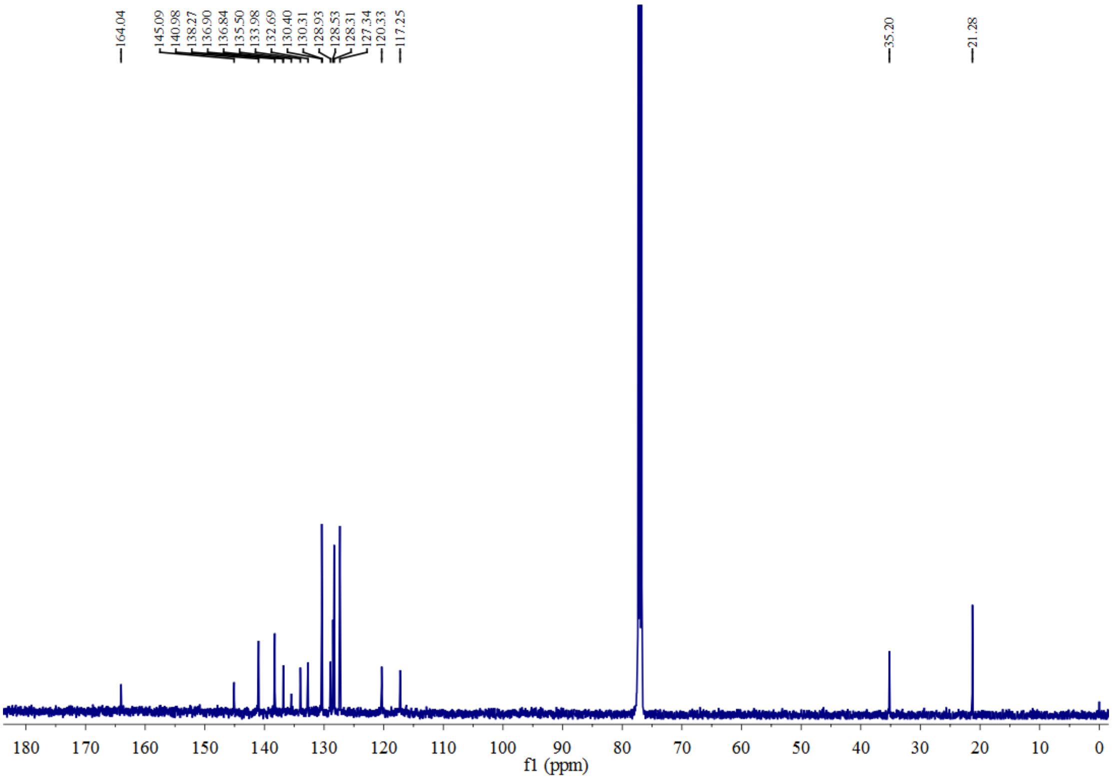
3d, ^{13}C, 126 MHz, CDCl$_3$



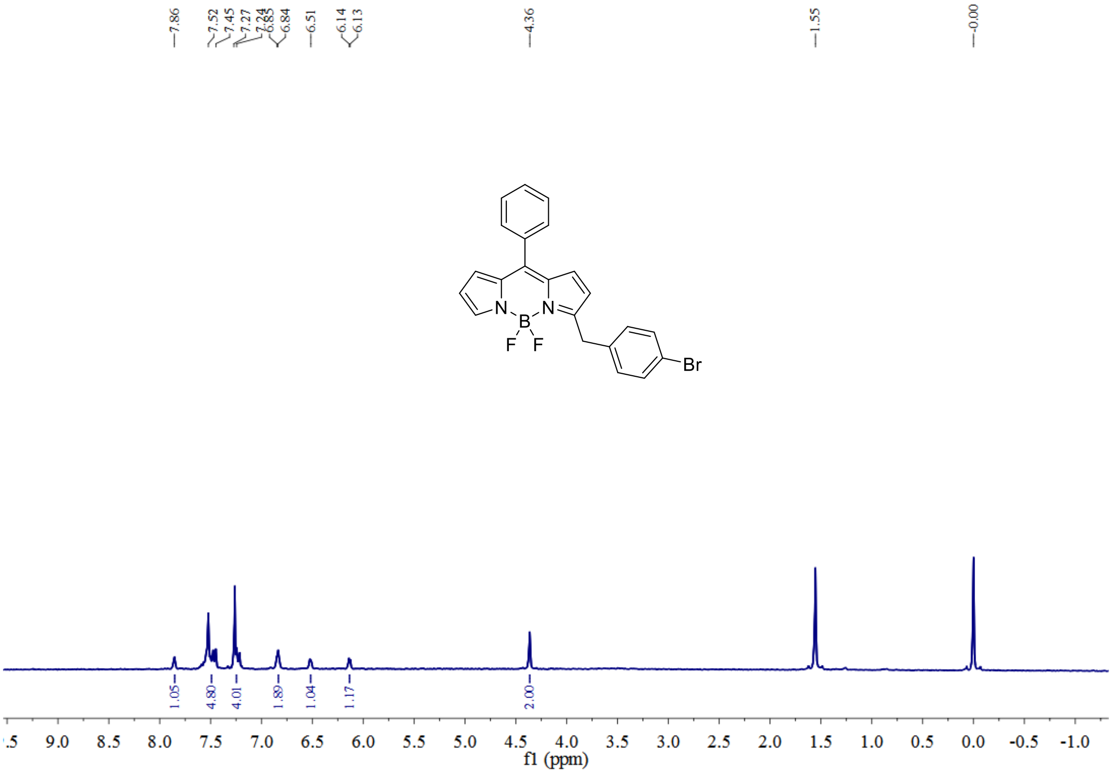
3e, ^{1}H, 300 MHz, CDCl$_3$



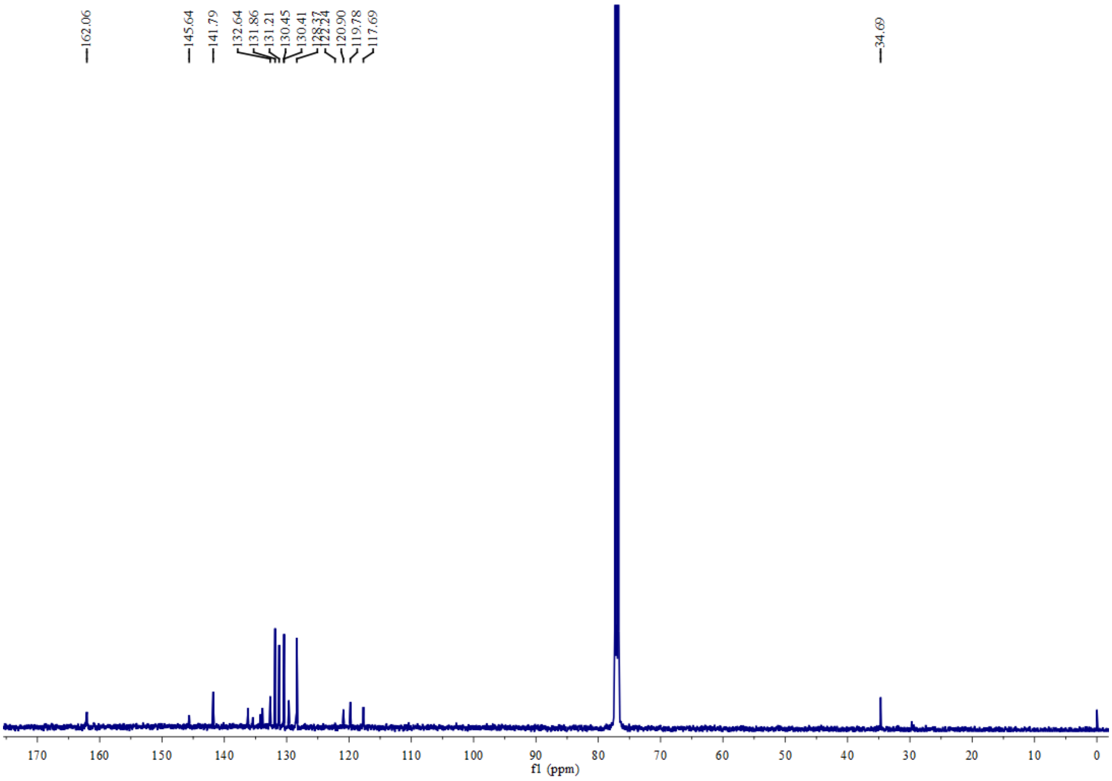
3e, ^{13}C, 126 MHz, CDCl$_3$



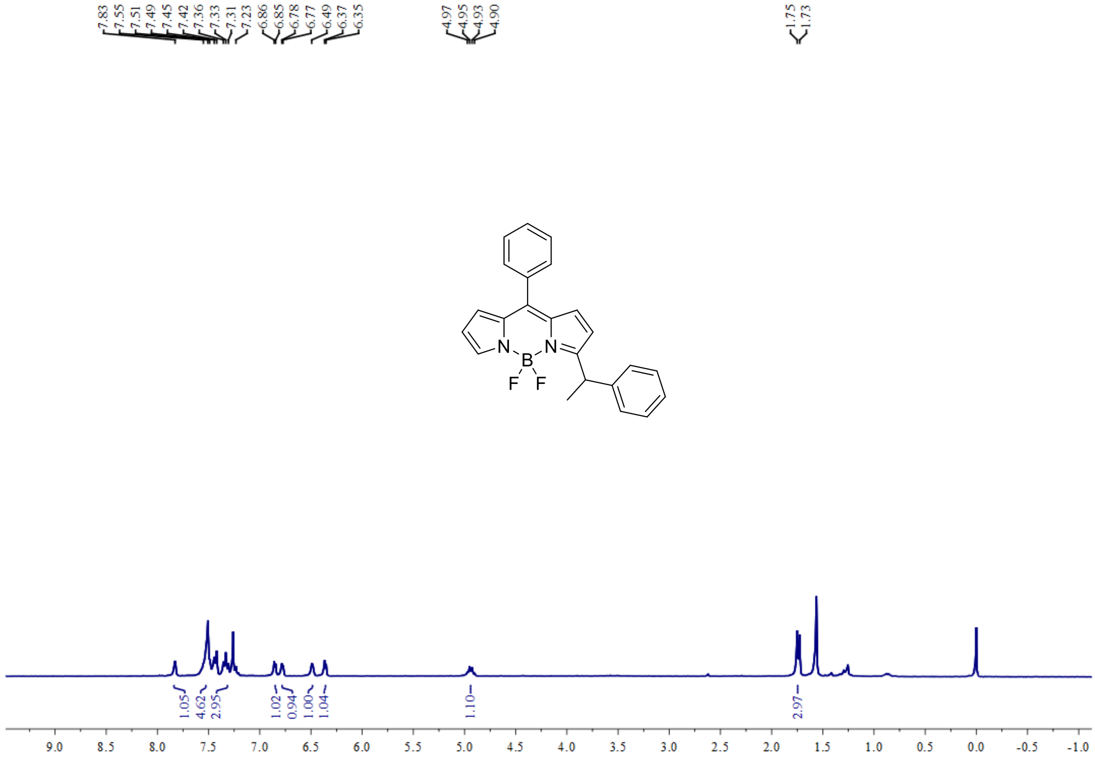
3f, ^{1}H, 300 MHz, $CDCl_3$



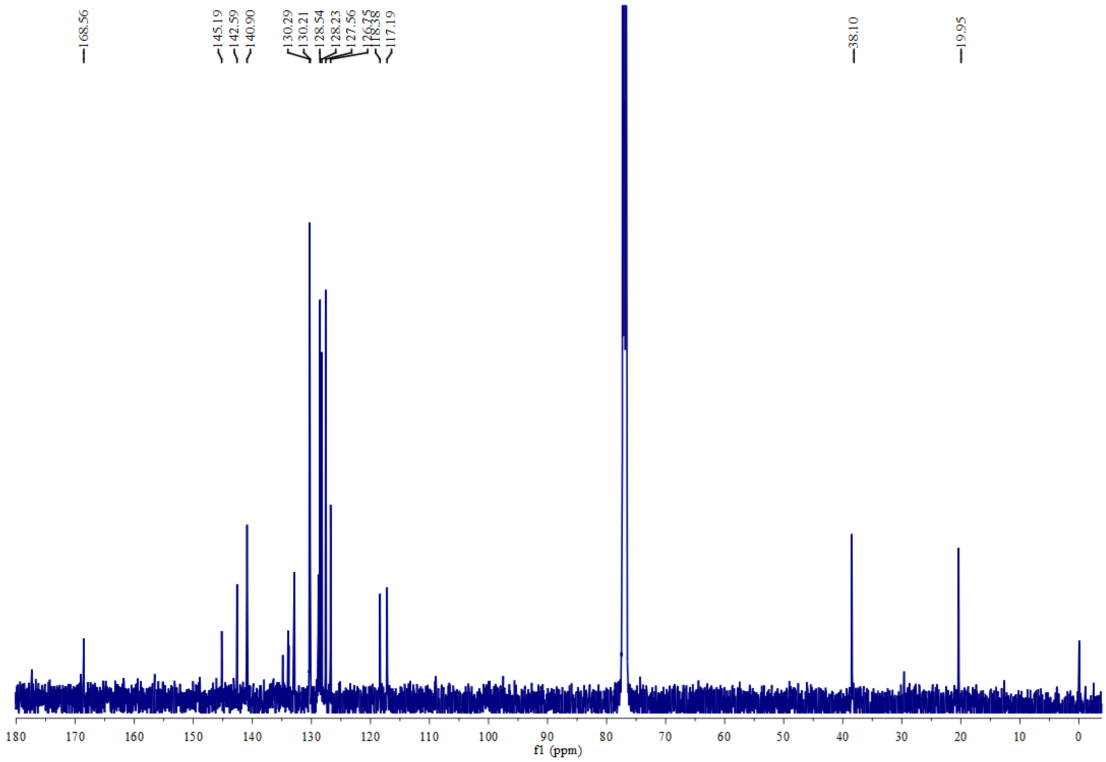
3f, ^{13}C, 126 MHz, $CDCl_3$



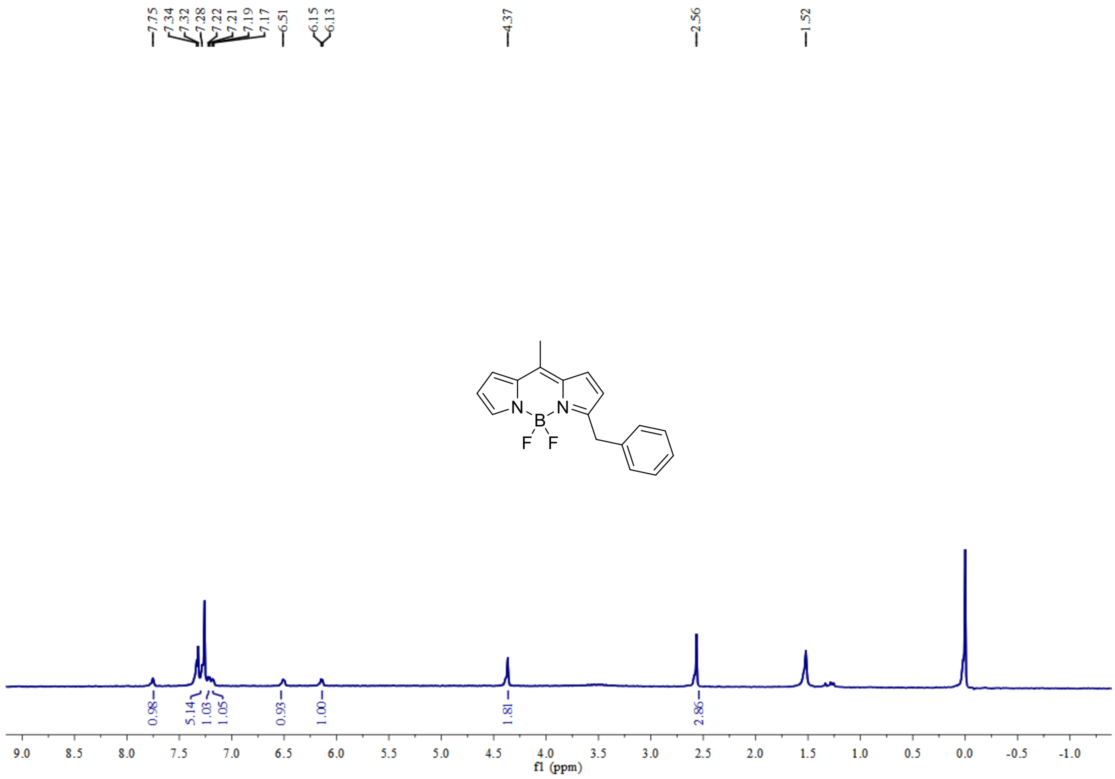
3g, ^{1}H, 300 MHz, CDCl$_3$



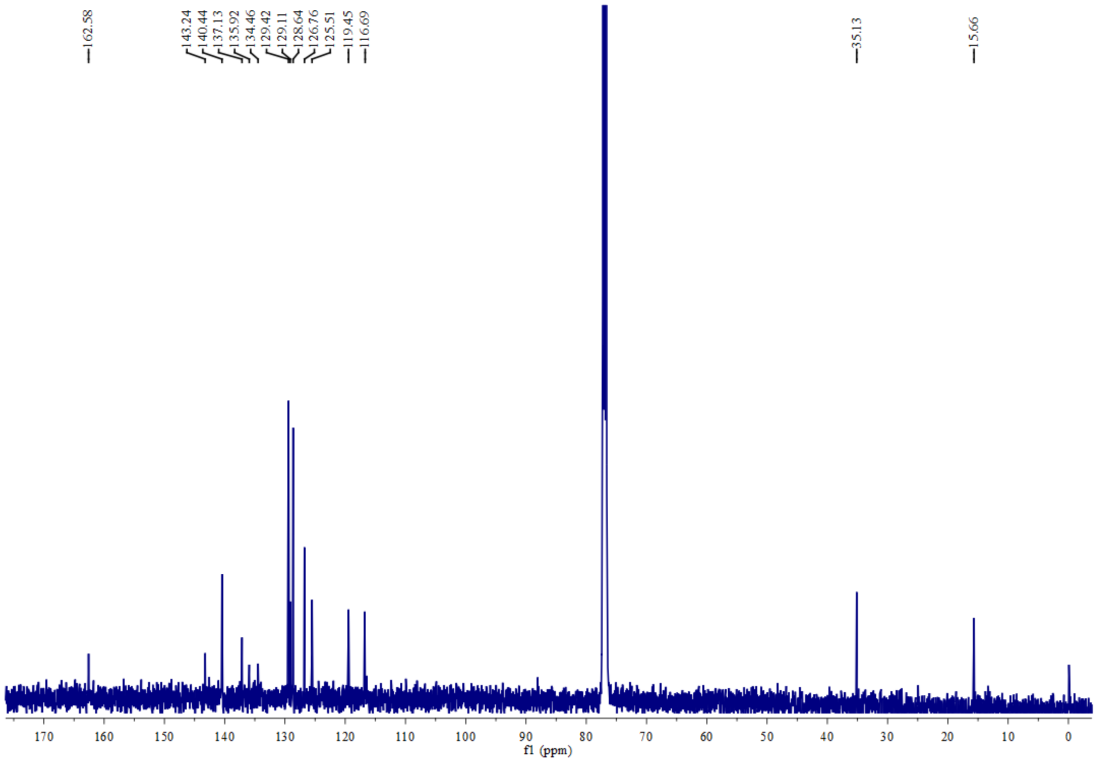
3g, ^{13}C, 126 MHz, CDCl$_3$



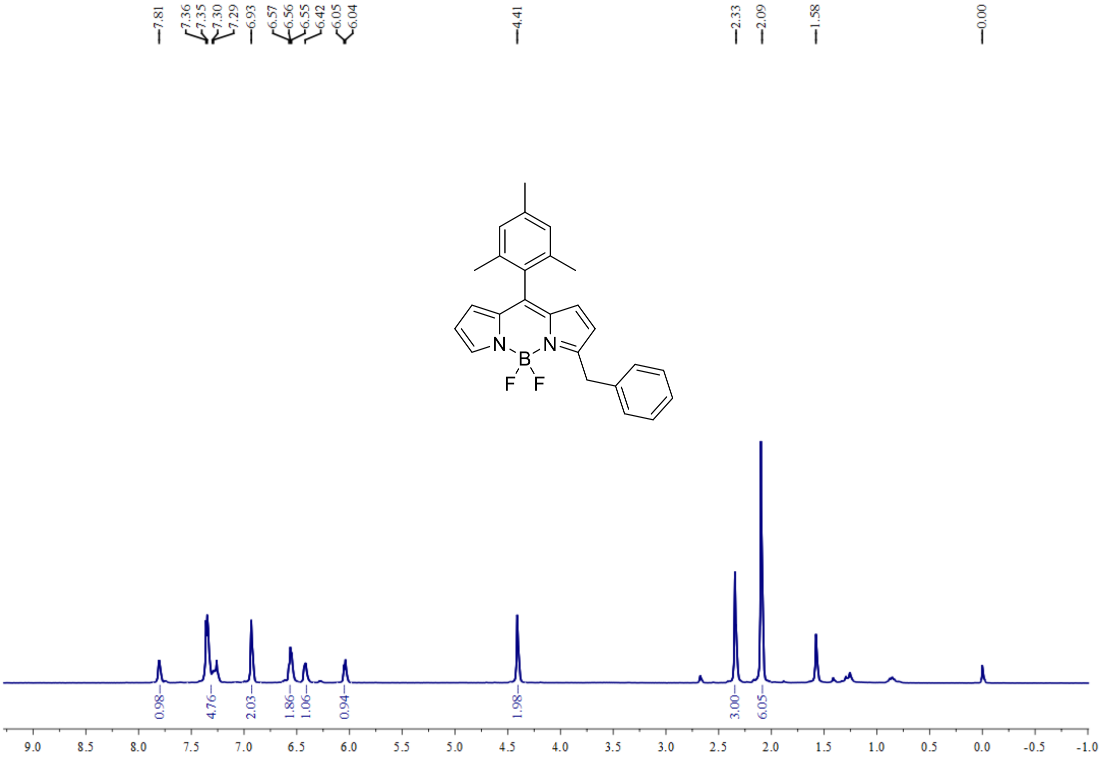
3h, ^{1}H, 300 MHz, CDCl$_3$



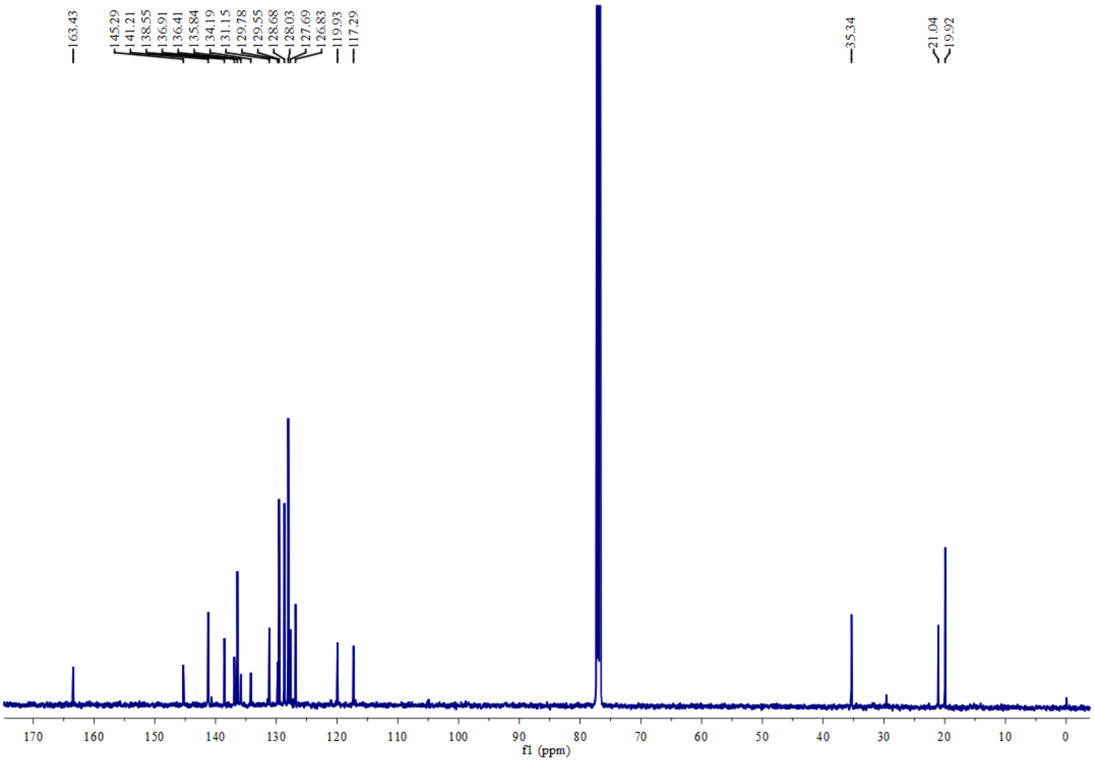
3h, ^{13}C, 126 MHz, CDCl$_3$



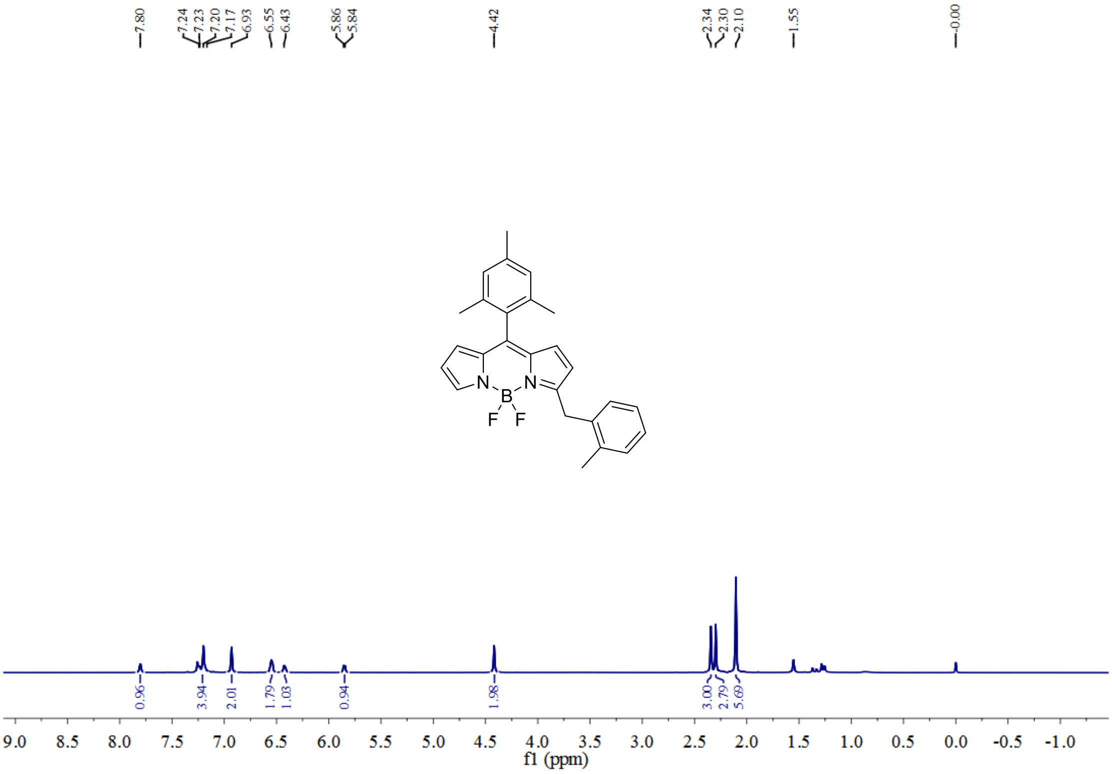
3i, ^{1}H, 300 MHz, CDCl$_3$



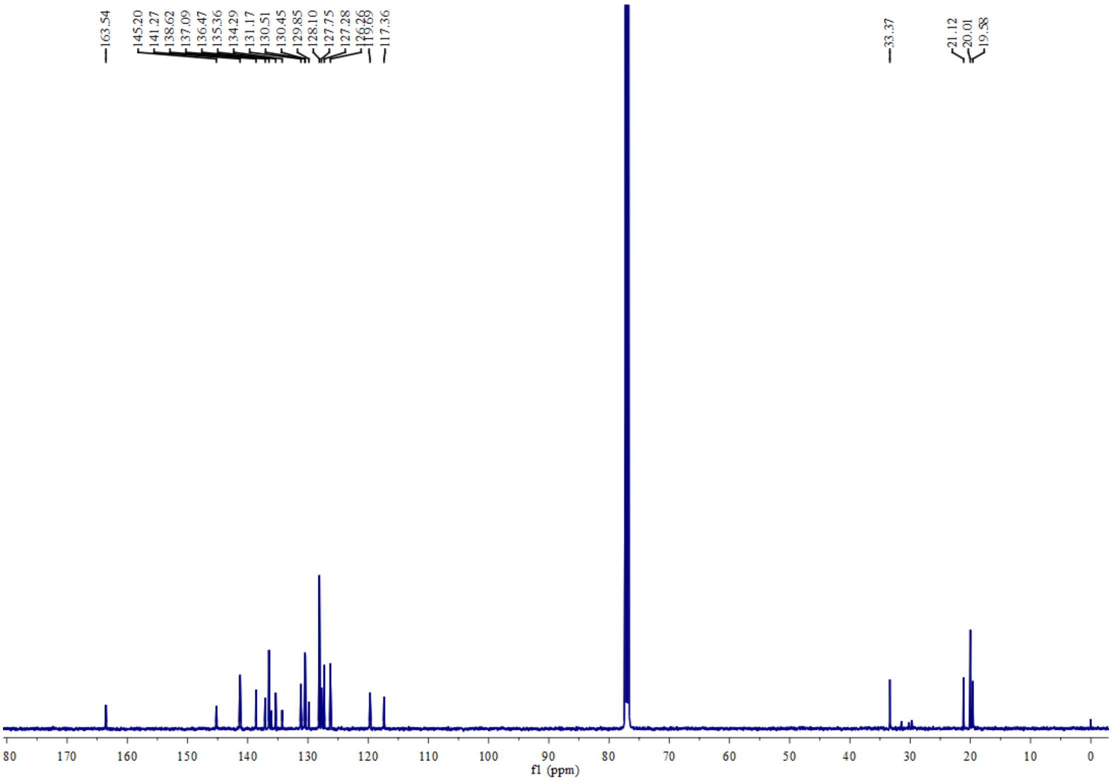
3i, **^{13}**C, 126 MHz, CDCl$_3$



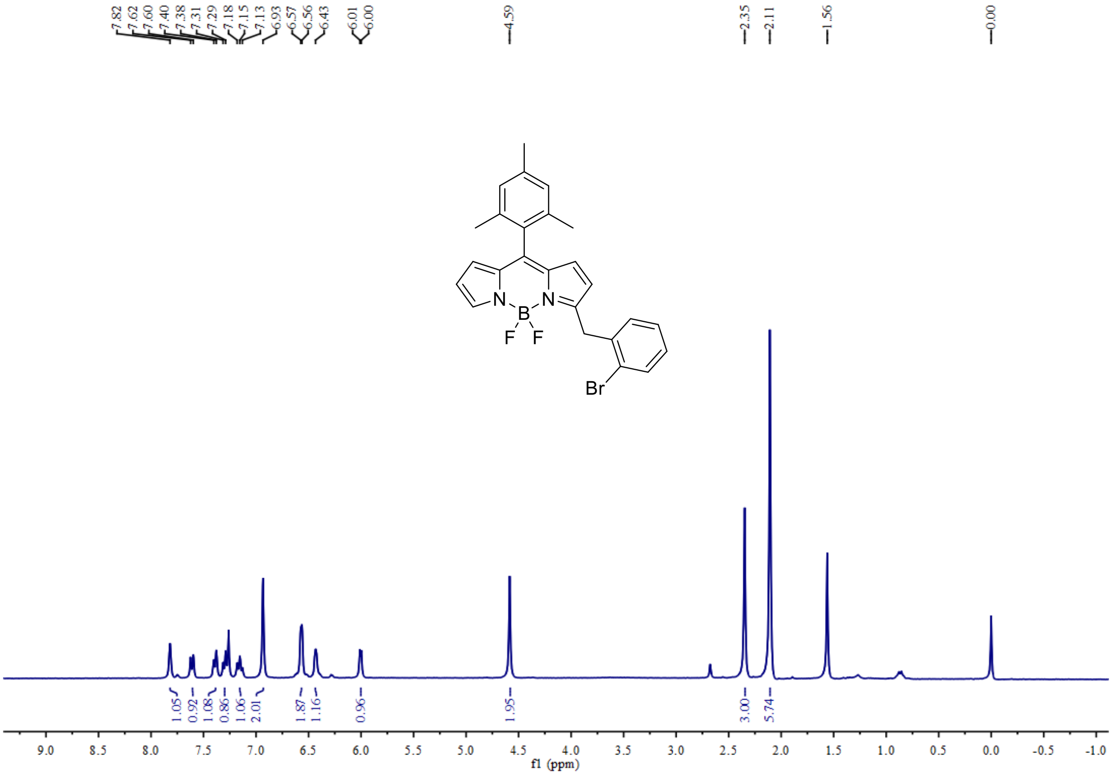
3j, ^{1}H, 300 MHz, CDCl$_3$



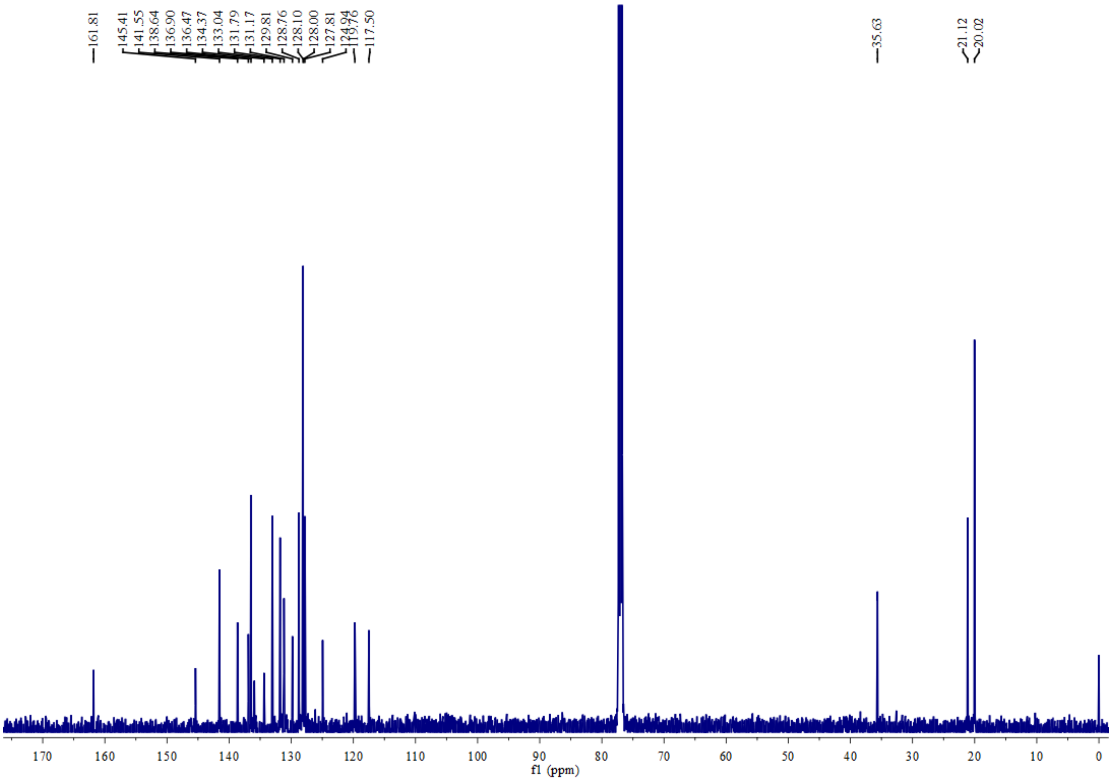
3j, ^{13}C, 126 MHz, CDCl$_3$



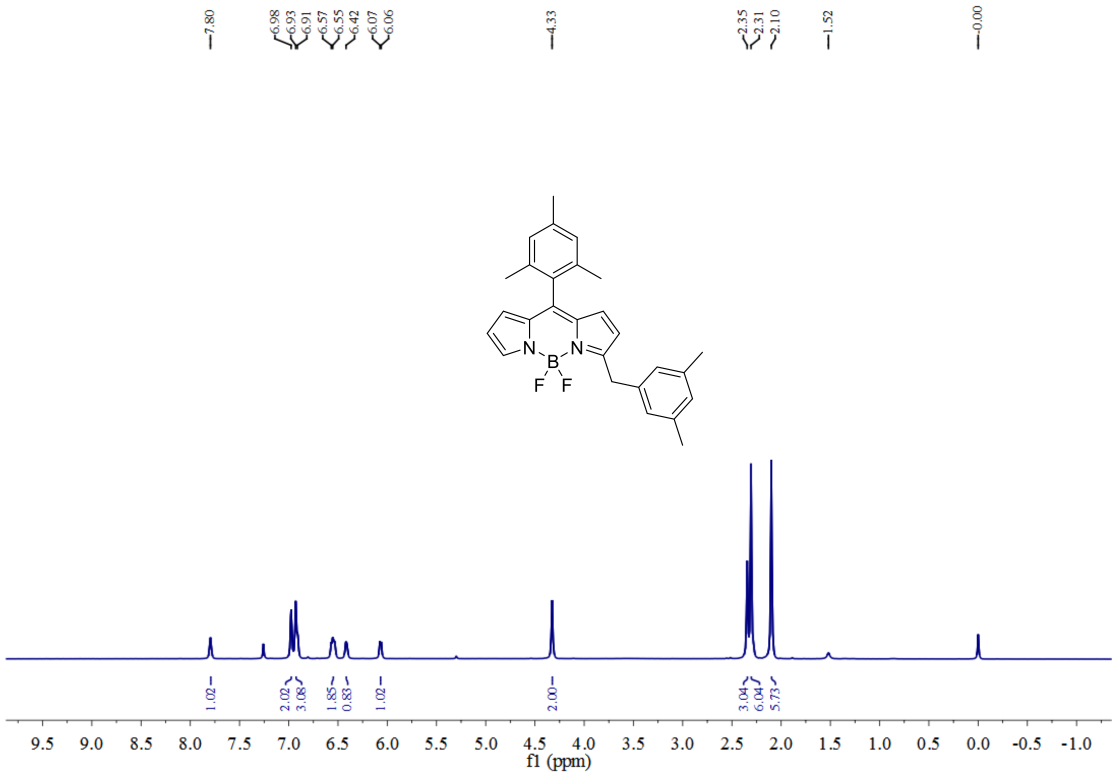
3k, ^{1}H, 300 MHz, CDCl$_3$



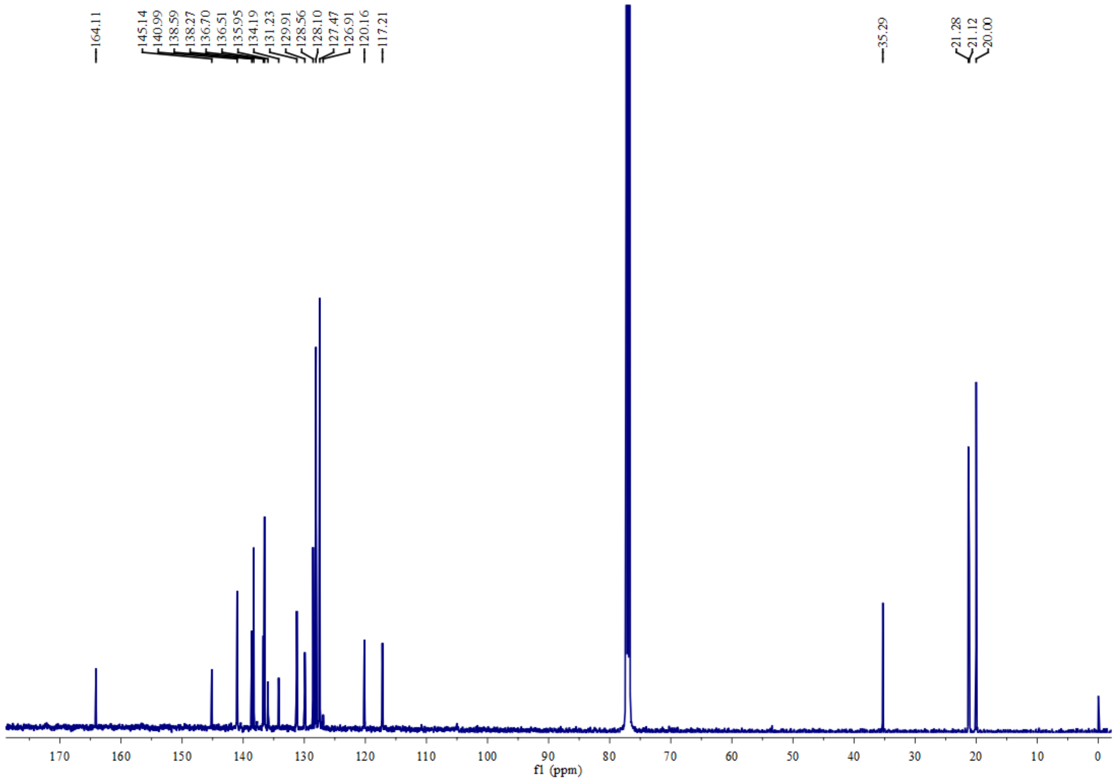
3k, ^{13}C, 126 MHz, CDCl$_3$



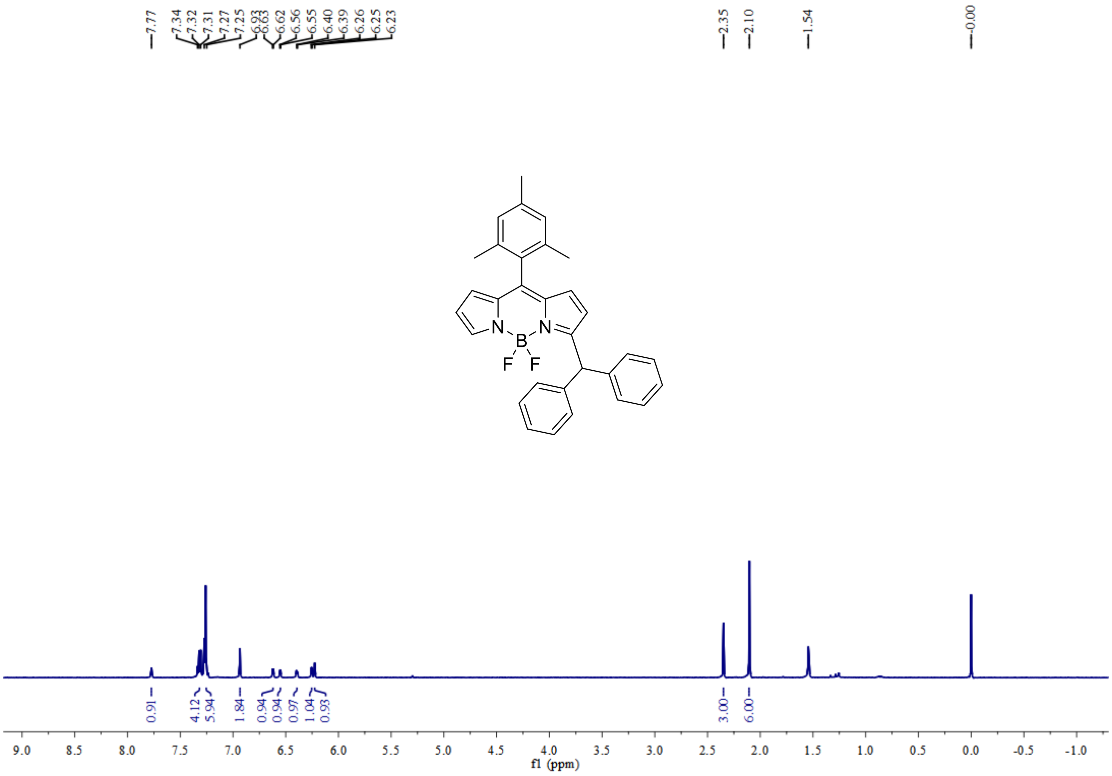
3l, ^{1}H, 300 MHz, $CDCl_3$



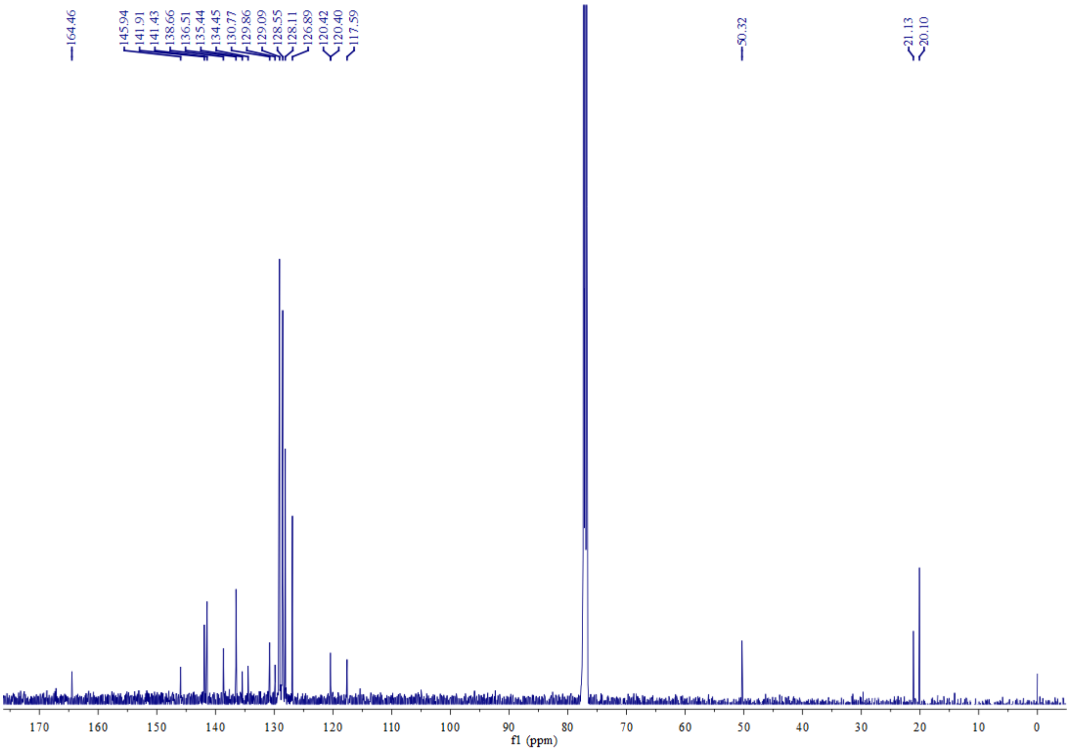
3l, ^{13}C, 126 MHz, $CDCl_3$



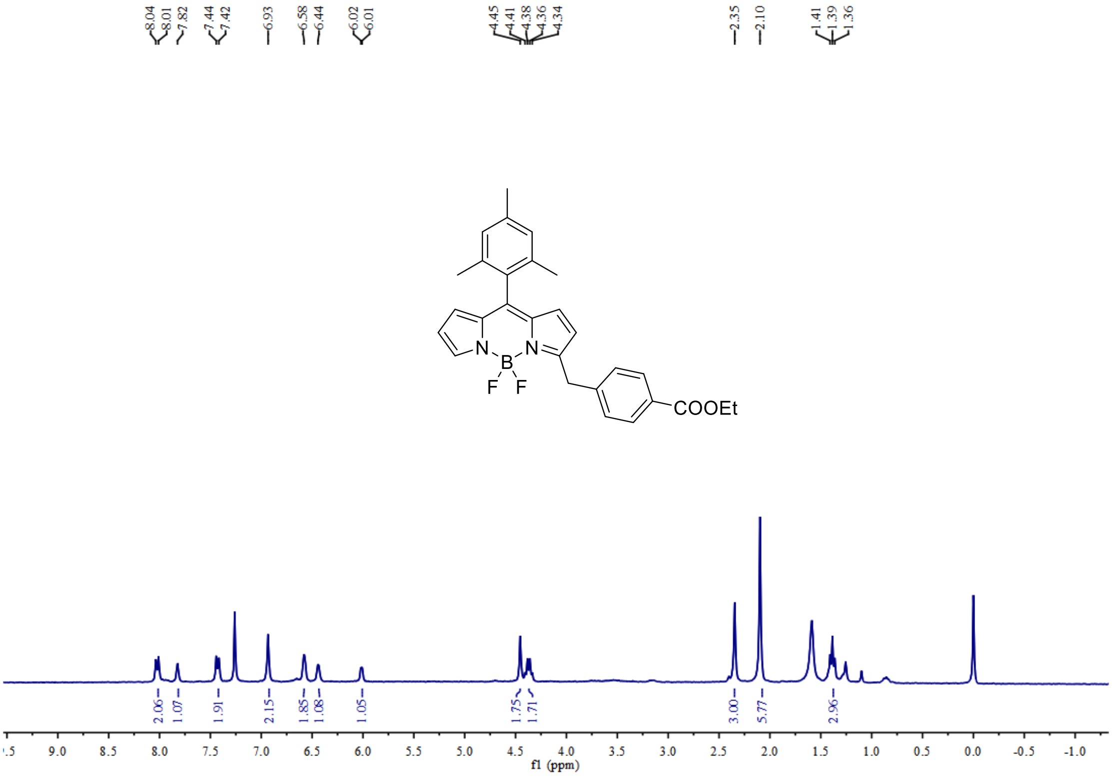
3m, ^{1}H, 300 MHz, CDCl$_3$



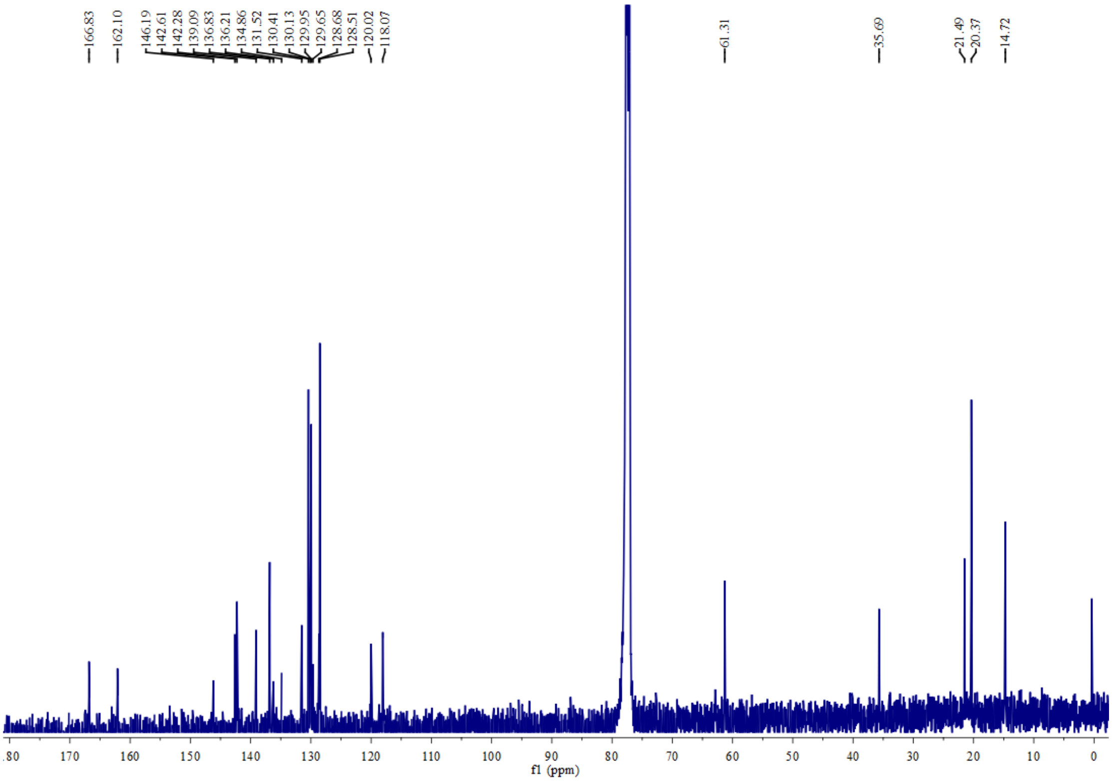
3m, ^{13}C, 126 MHz, CDCl$_3$



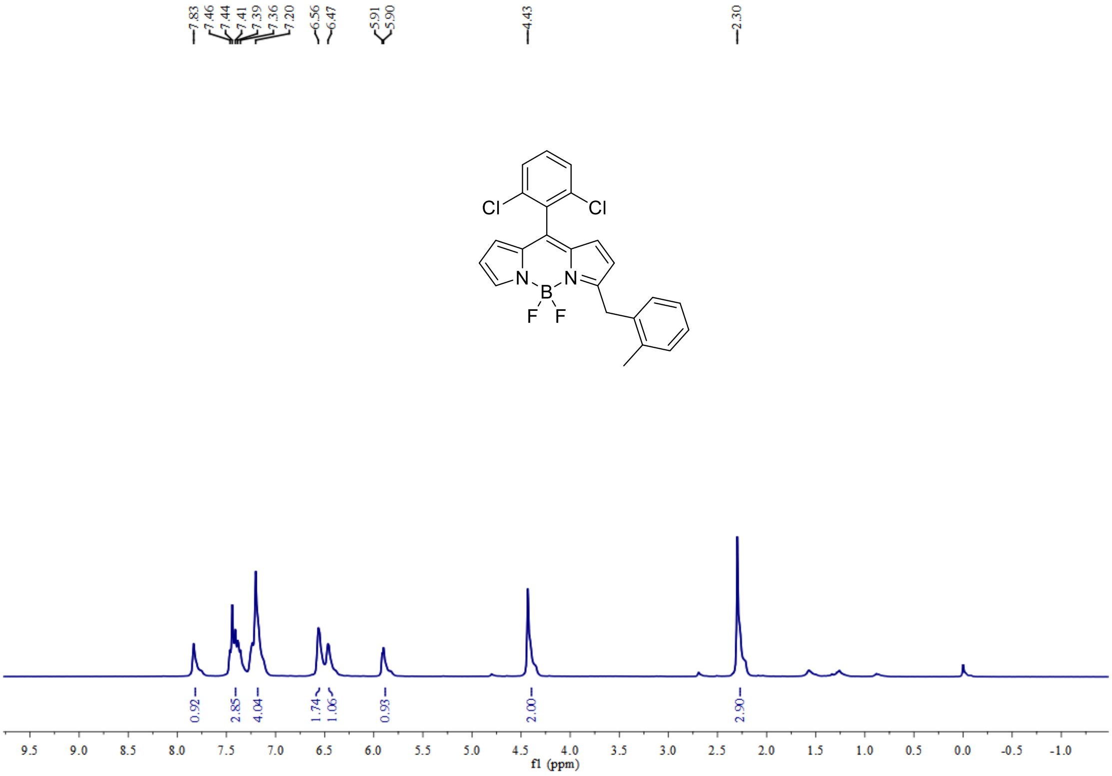
3n, ^{1}H, 300 MHz, CDCl$_3$



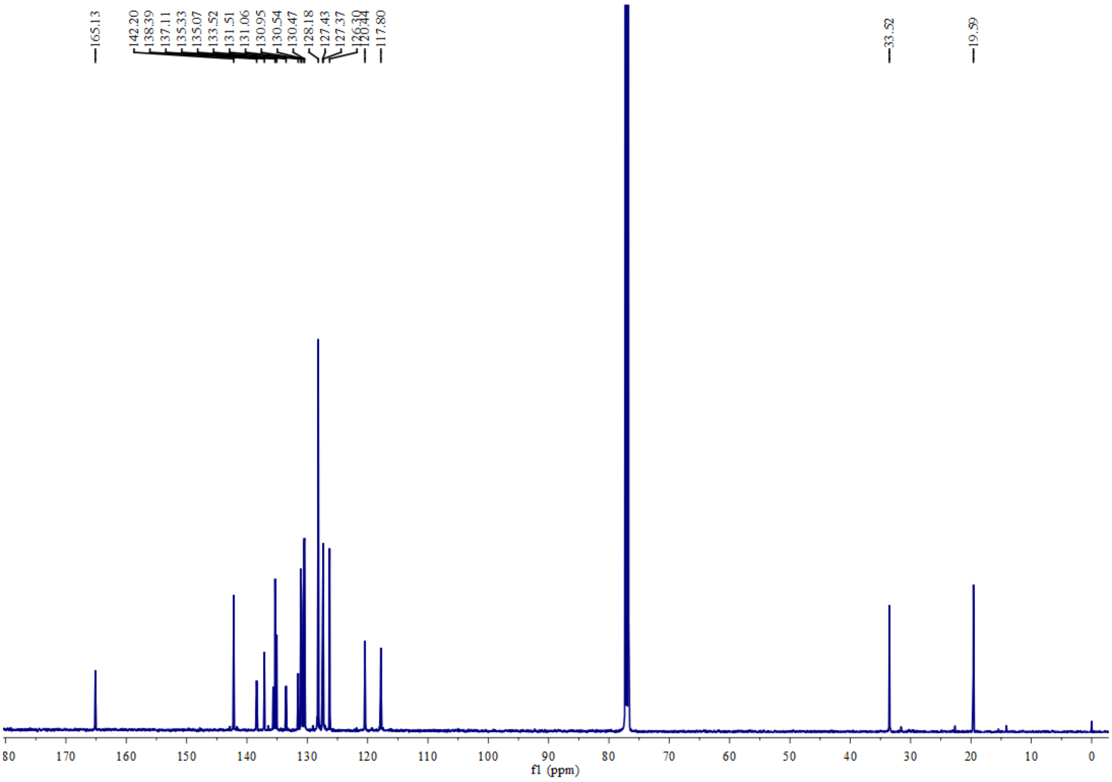
3n, ^{13}C, 126 MHz, CDCl$_3$



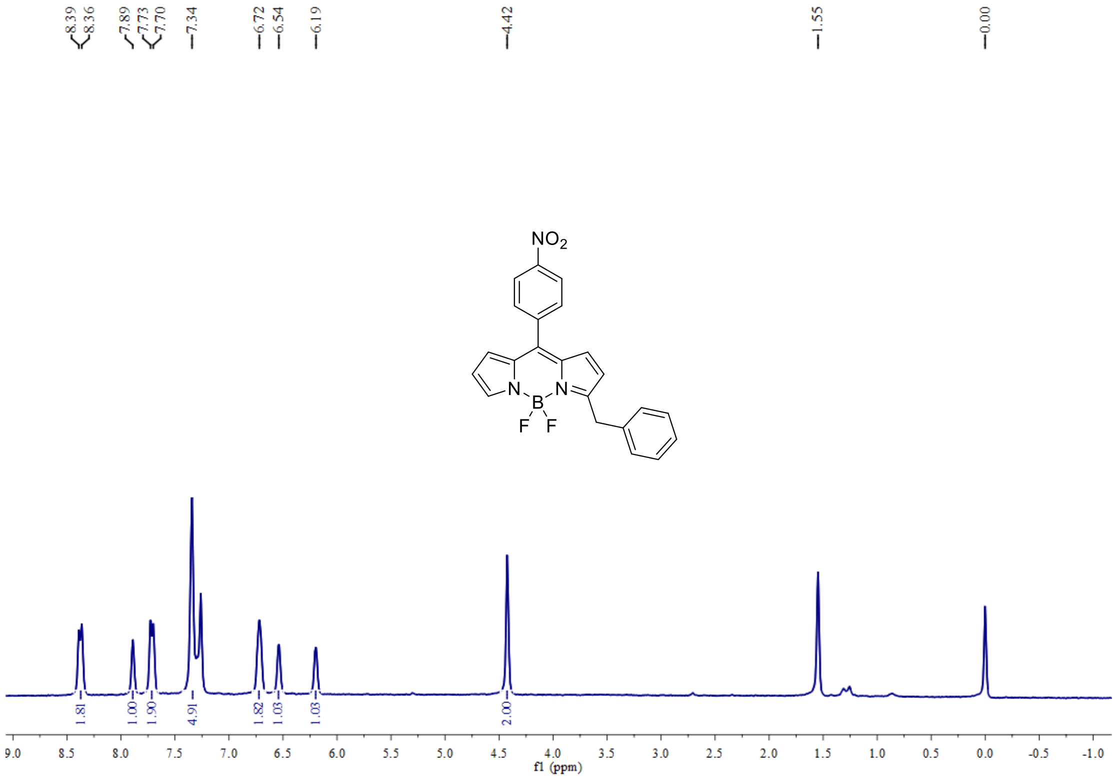
3o, ^{1}H, 300 MHz, CDCl$_3$



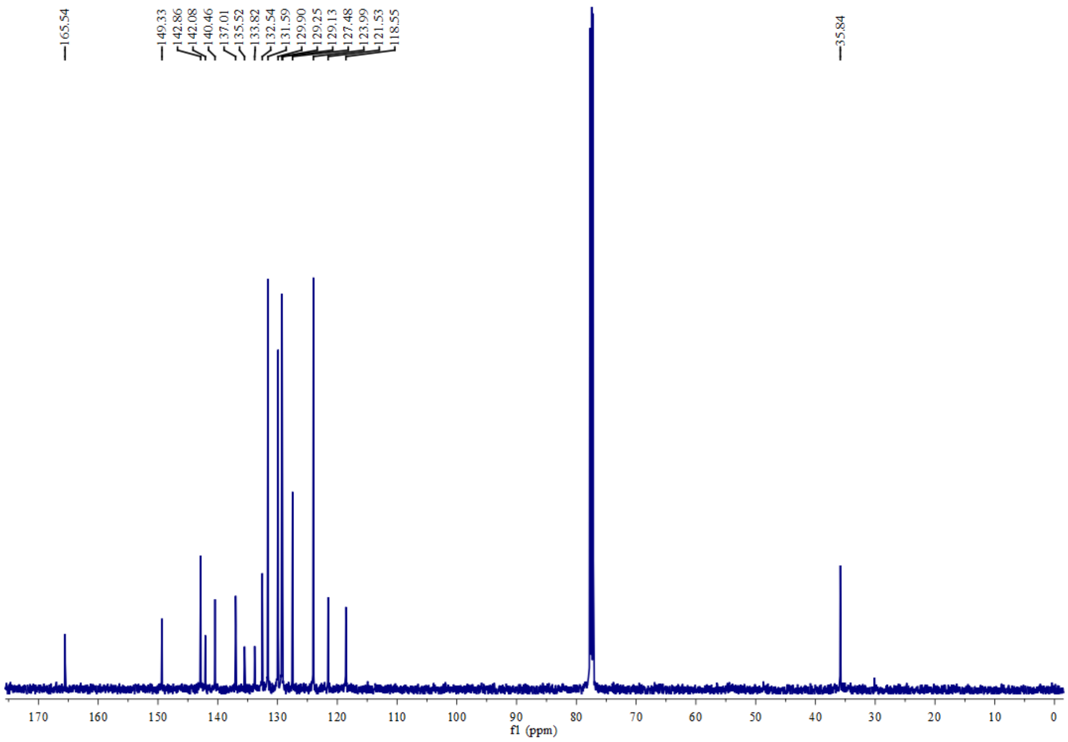
3o, ^{13}C, 126 MHz, CDCl$_3$



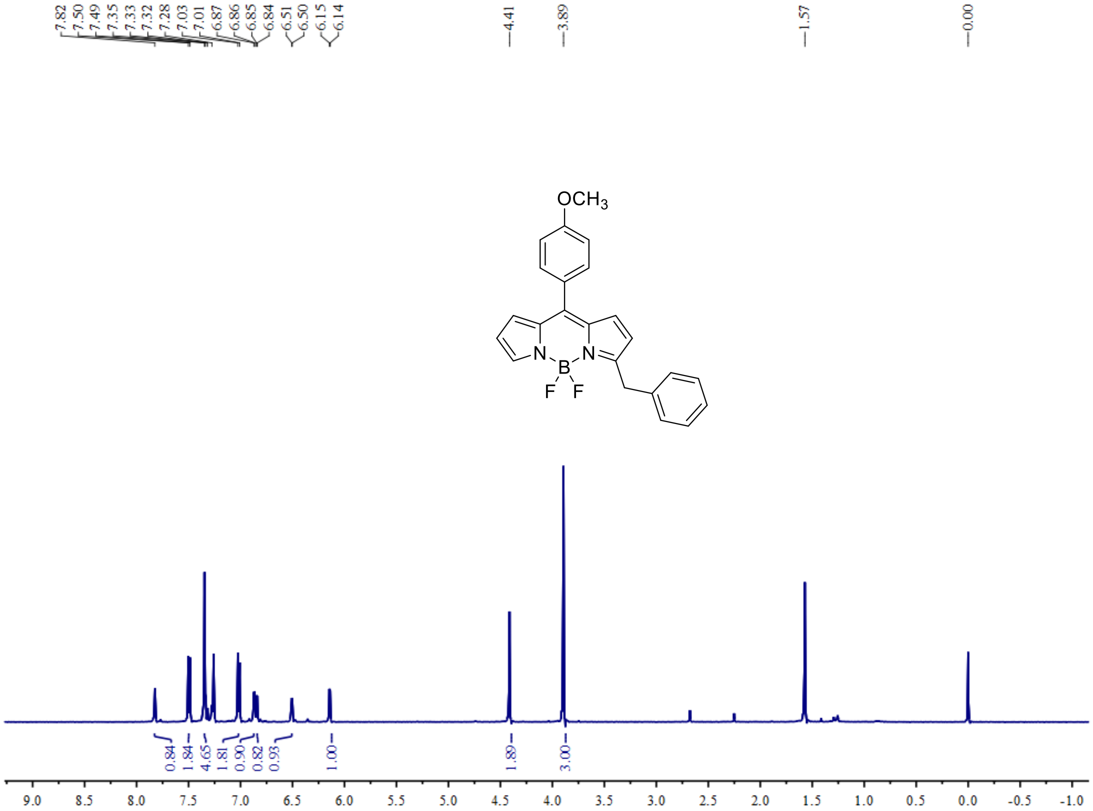
3p, ^{1}H, 300 MHz, CDCl$_3$



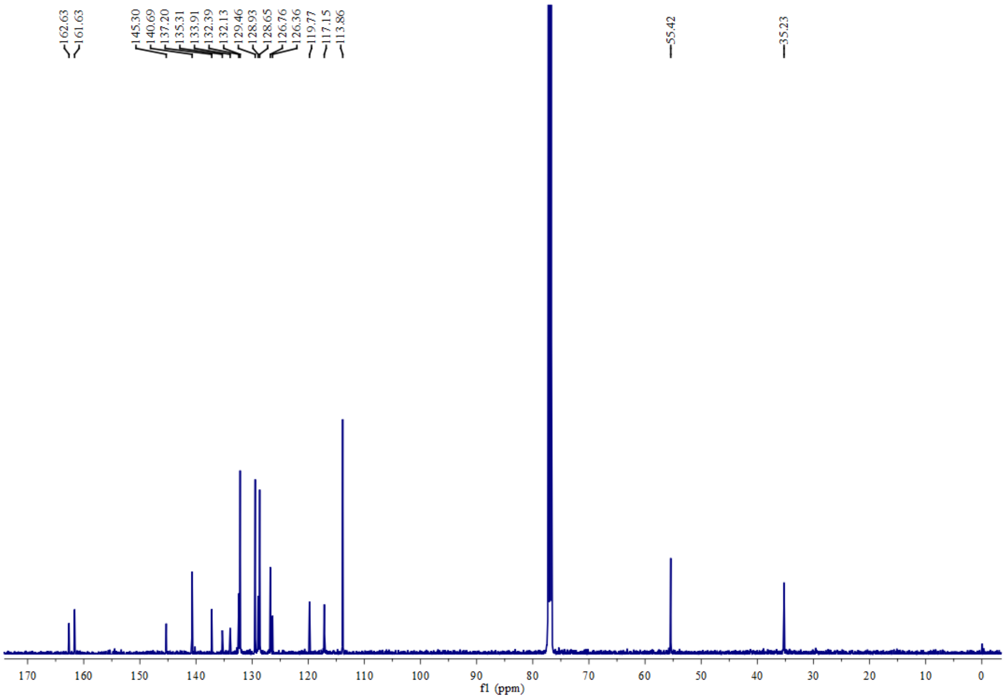
3p, ^{13}C, 126 MHz, CDCl$_3$



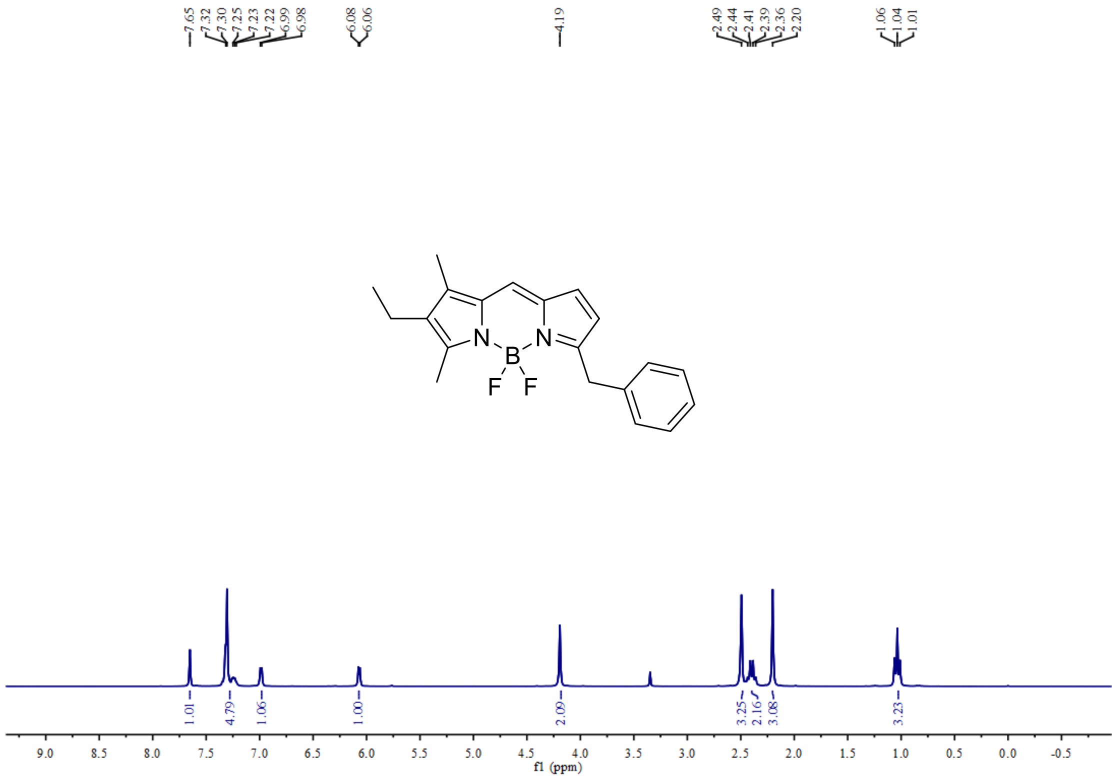
3q, ^{1}H, 300 MHz, CDCl$_3$



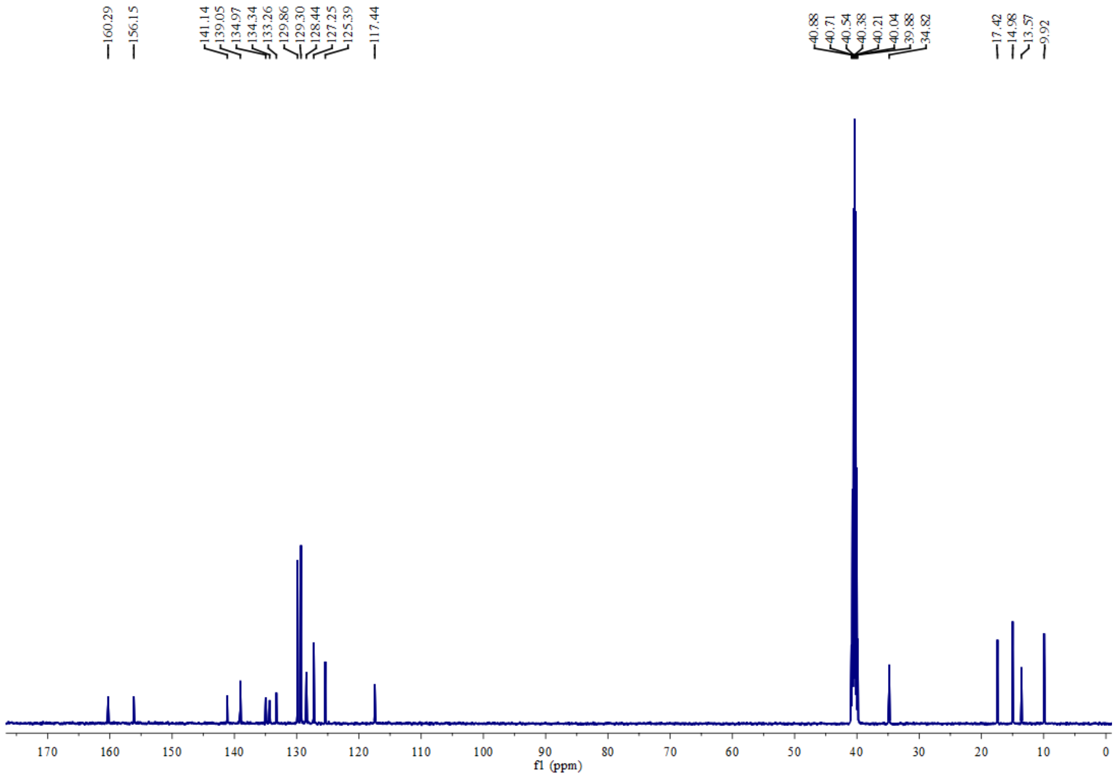
3q, ^{13}C, 126 MHz, CDCl$_3$



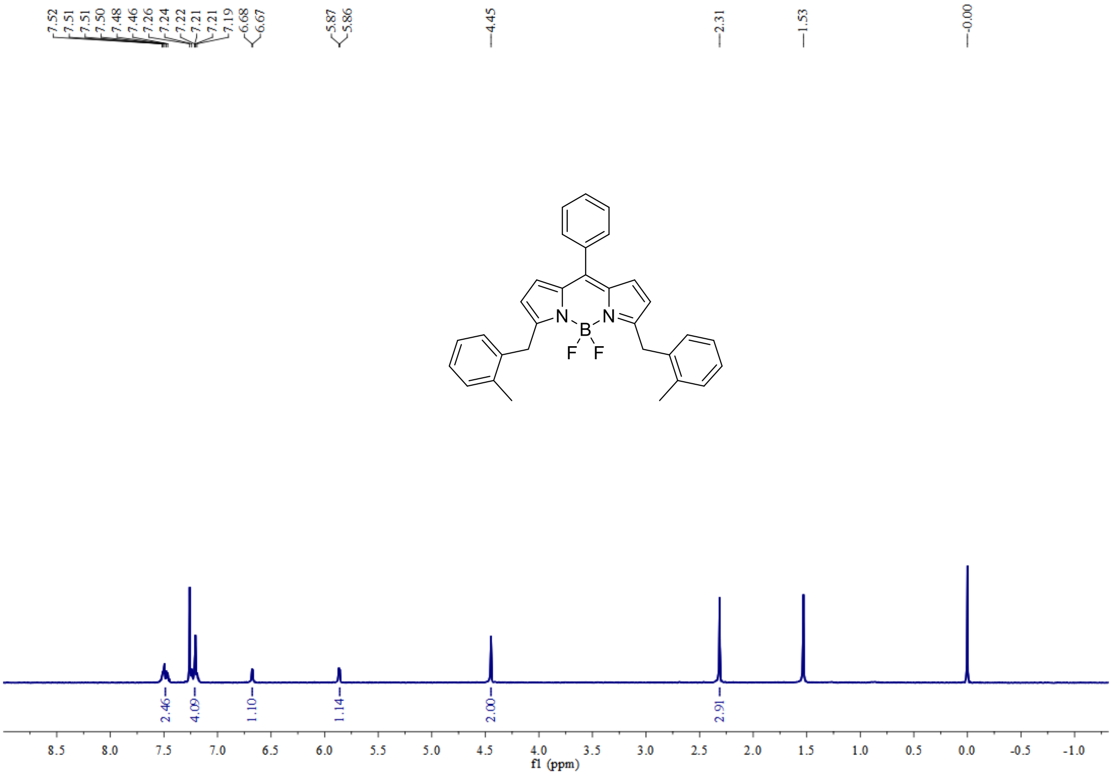
3r, ^{1}H, 300 MHz, CDCl$_3$



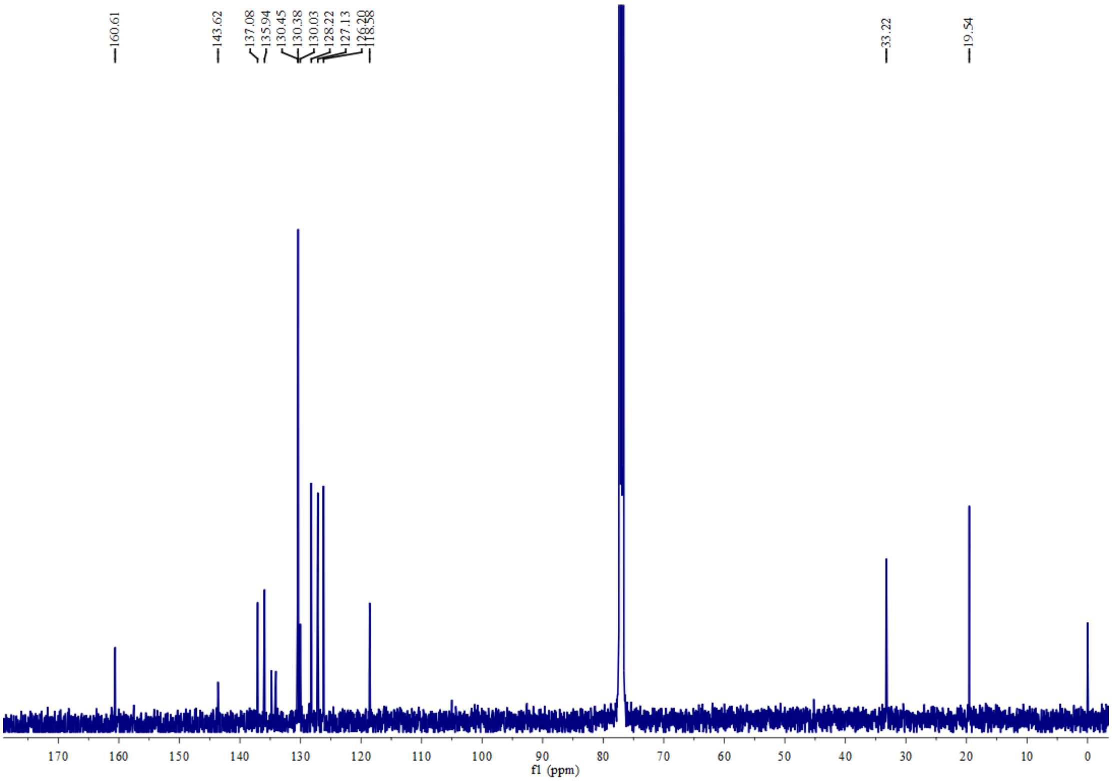
3r, ^{13}C, 126 MHz, DMSO



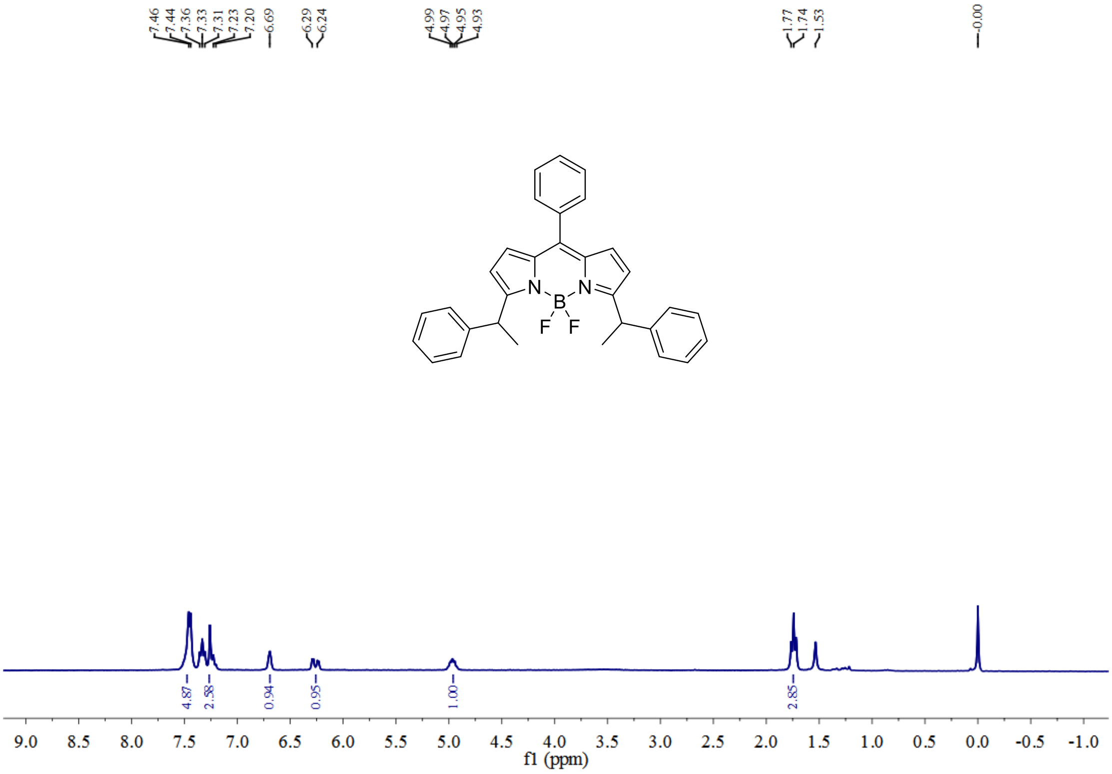
4a, ^{1}H, 300 MHz, CDCl$_3$



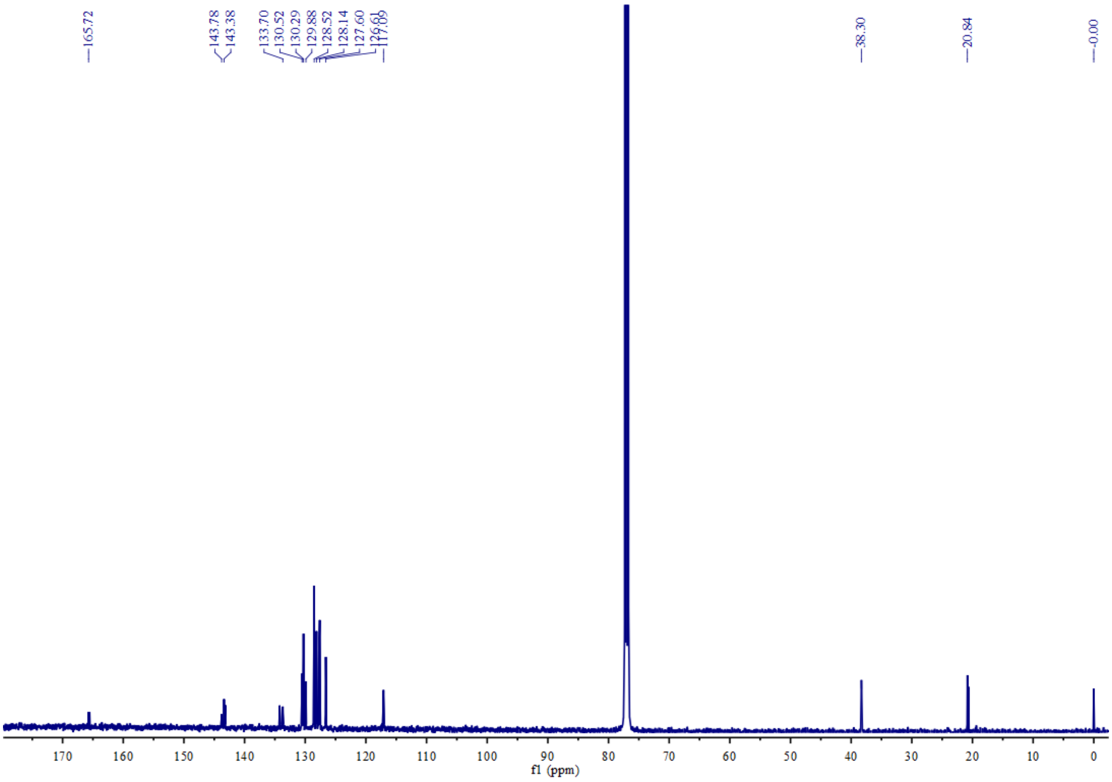
4a, ^{13}C, 126 MHz, CDCl$_3$



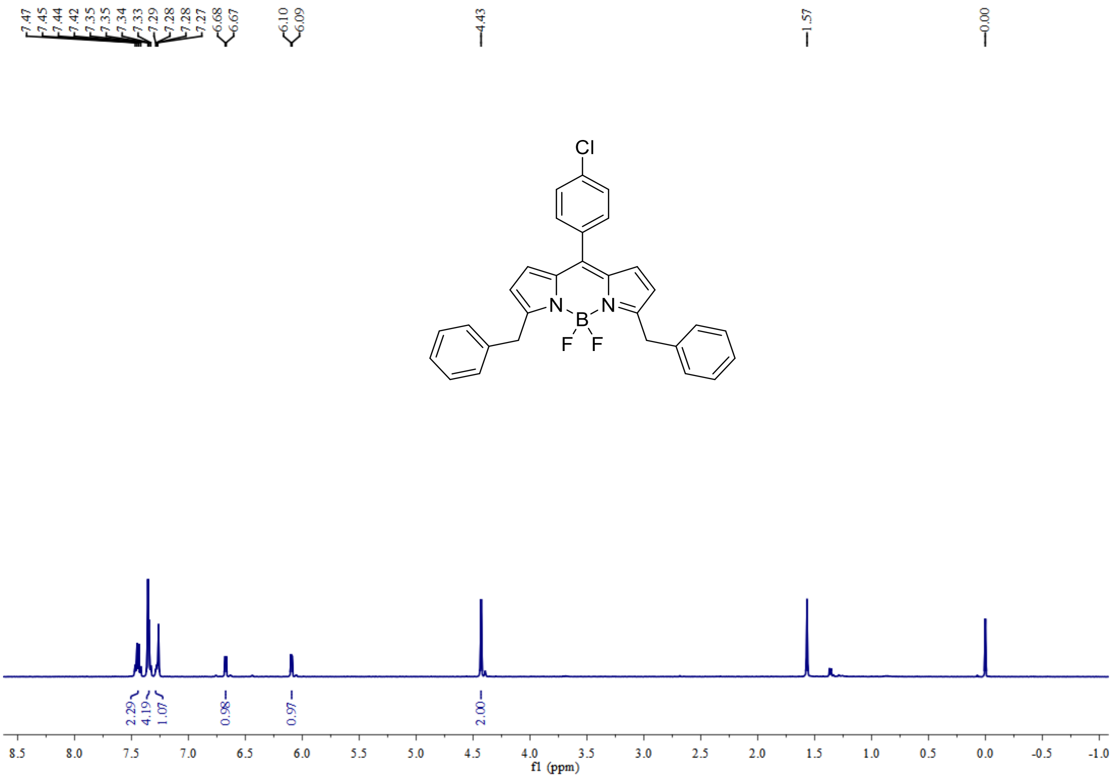
4b, ^{1}H, 300 MHz, $CDCl_3$



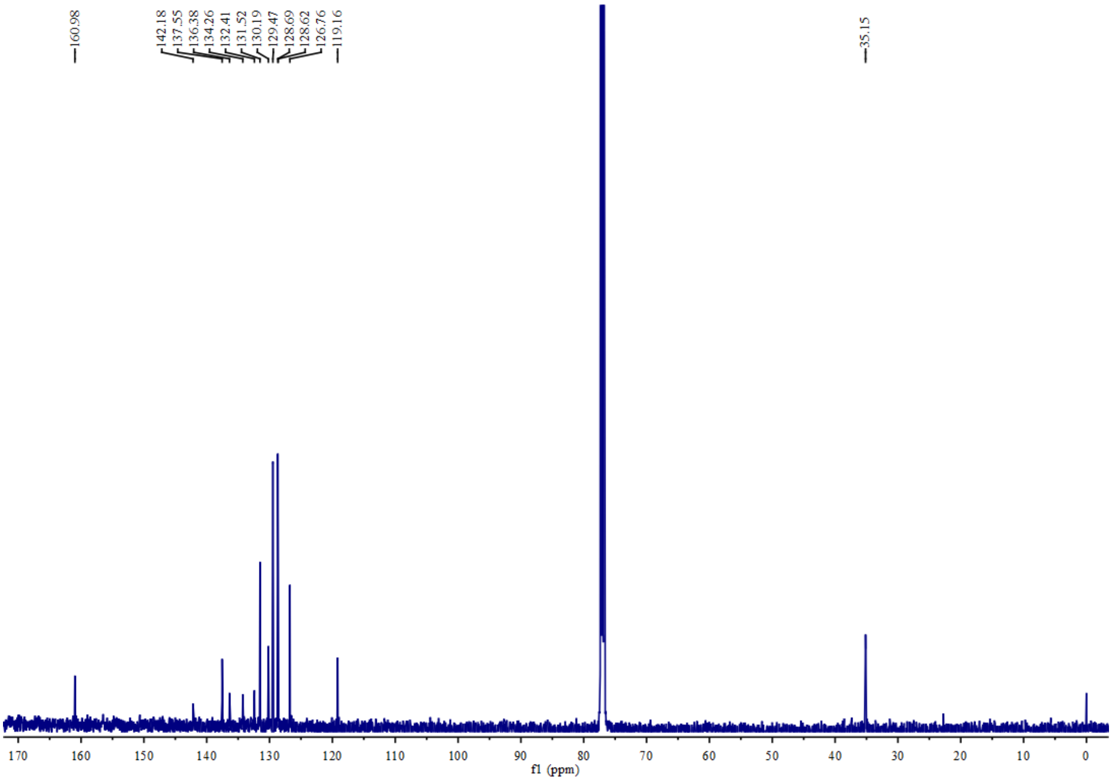
4b, ^{13}C, 126 MHz, $CDCl_3$



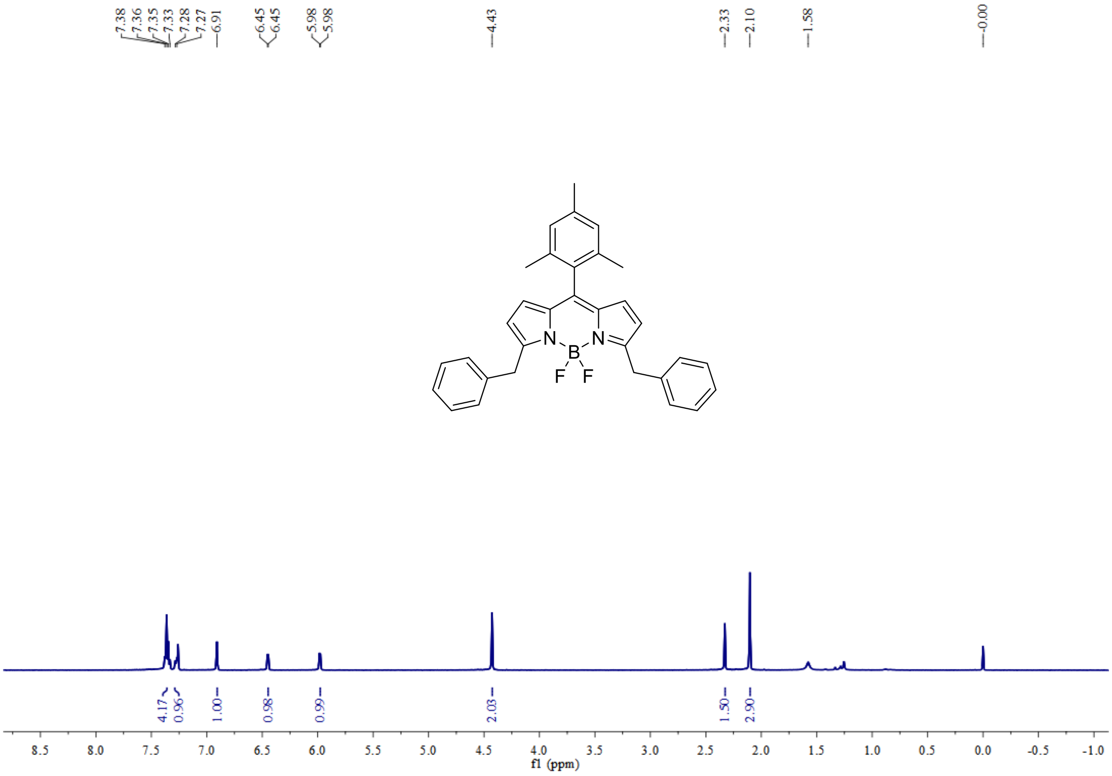
4c, ^{1}H, 300 MHz, CDCl$_3$



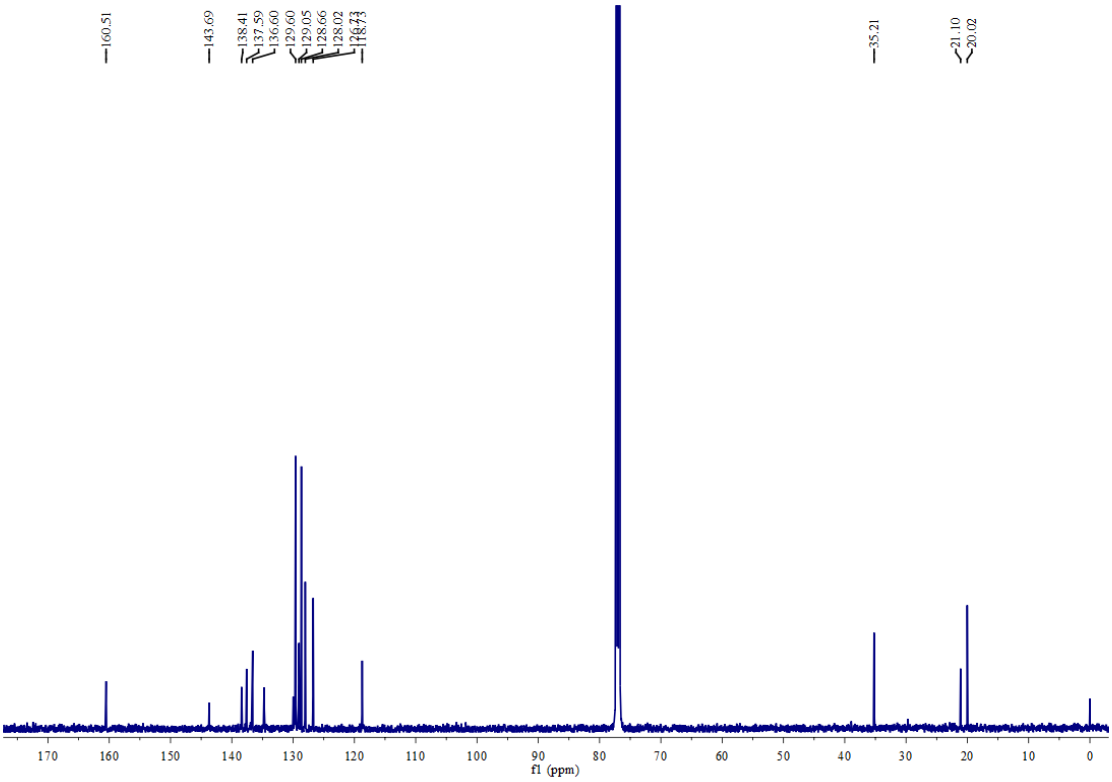
4c, ^{13}C, 126 MHz, CDCl$_3$



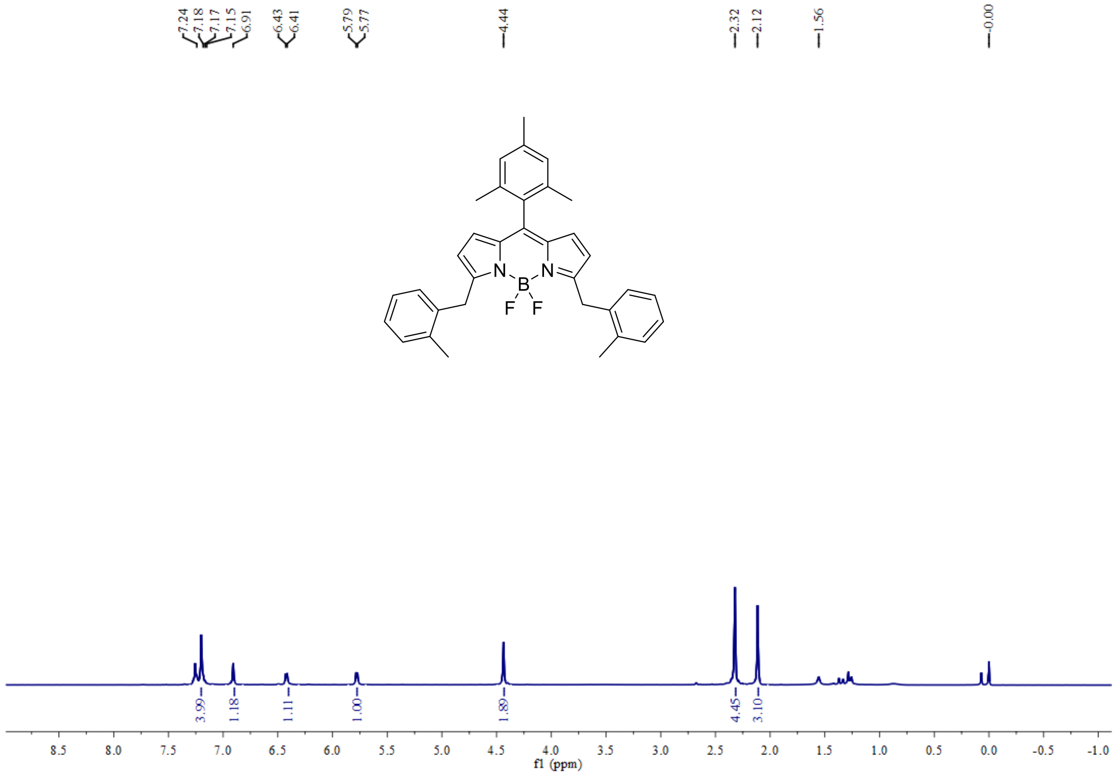
4d, ^{1}H, 300 MHz, $CDCl_3$



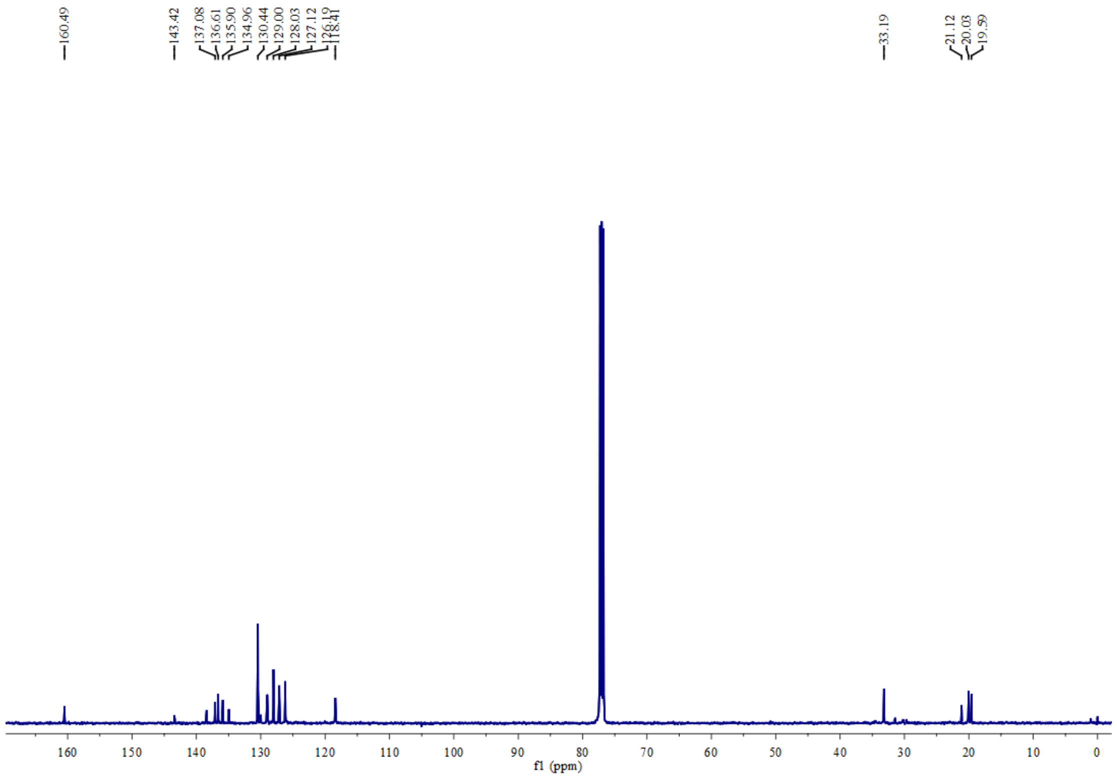
4d, ^{13}C, 126 MHz, $CDCl_3$



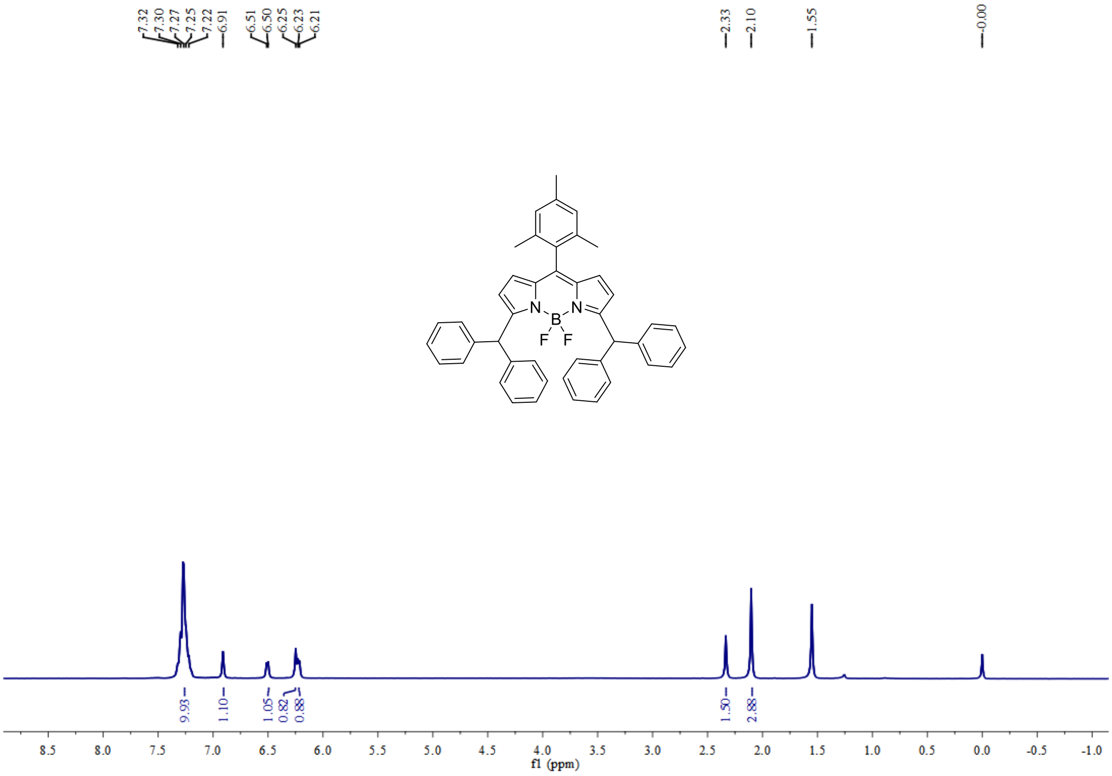
4e, ^{1}H, 300 MHz, CDCl$_3$



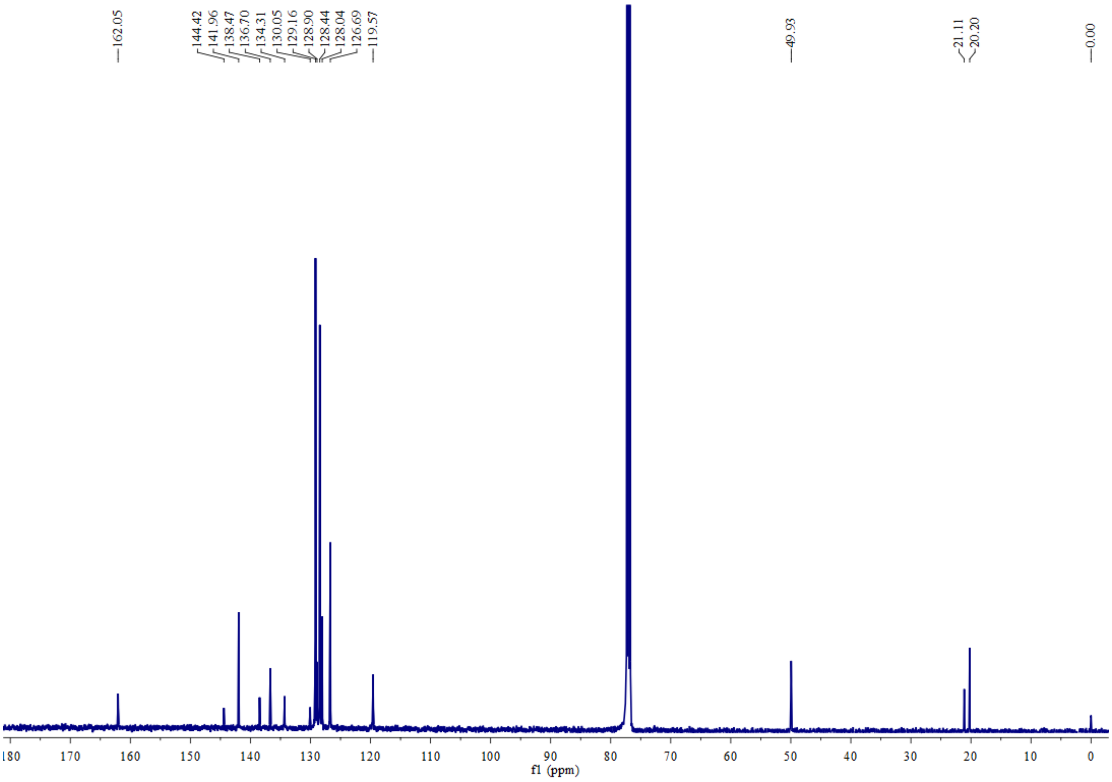
4e, ^{13}C, 126 MHz, CDCl$_3$



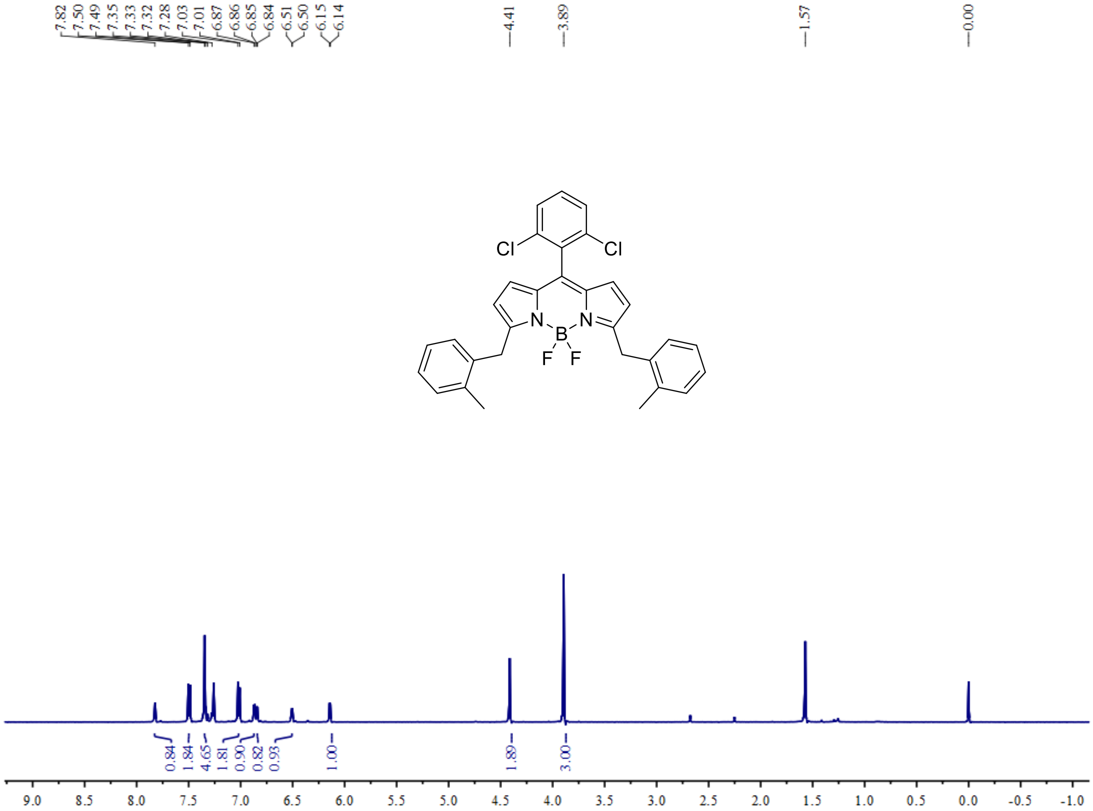
4f, ^{1}H, 300 MHz, CDCl$_3$



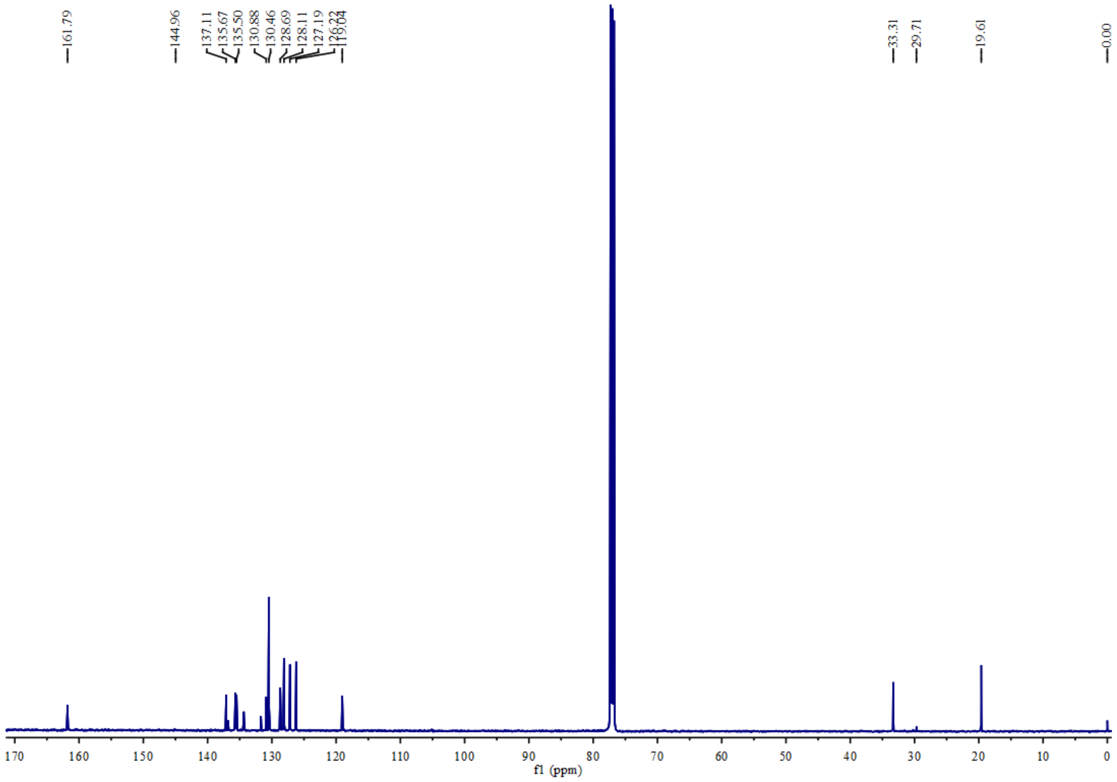
4f, ^{13}C, 126 MHz, CDCl$_3$



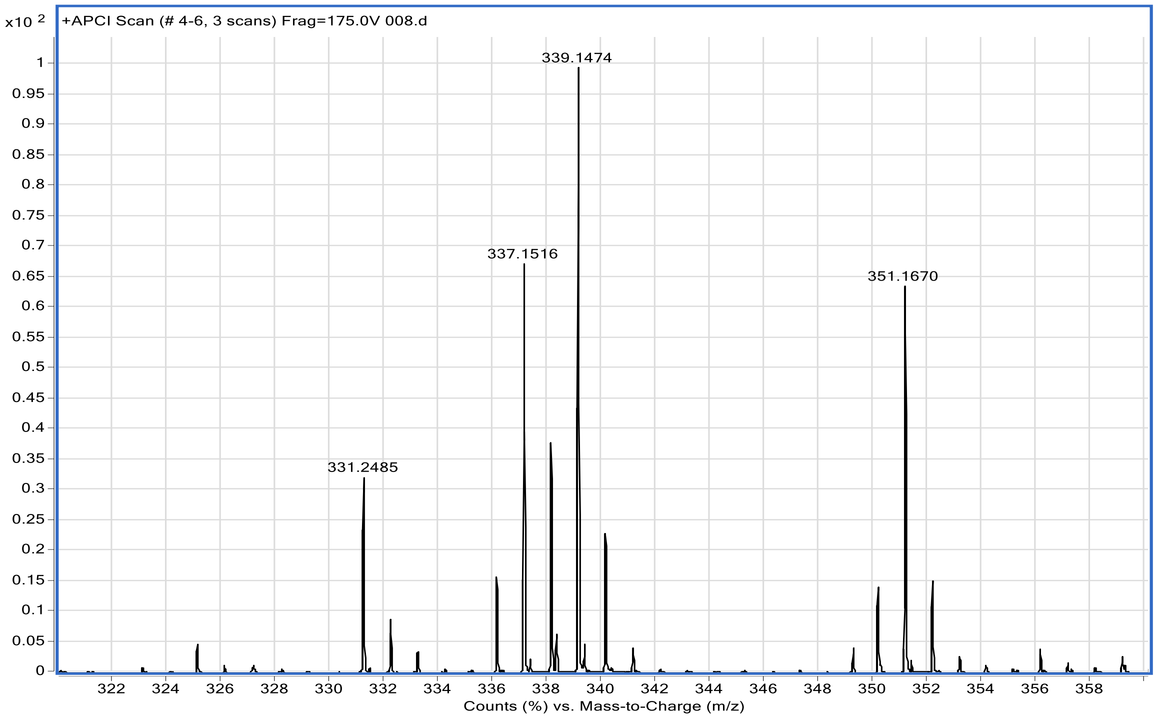
4g, ^{1}H, 300 MHz, CDCl$_3$



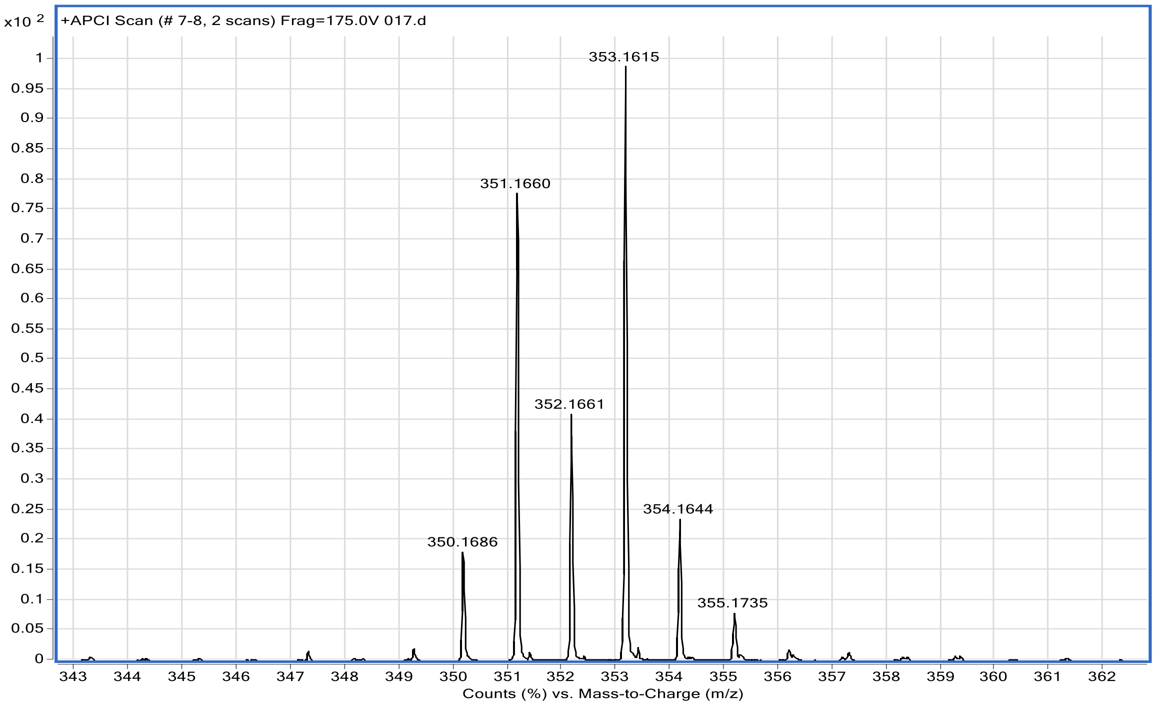
4g, ^{13}C, 126 MHz, CDCl$_3$



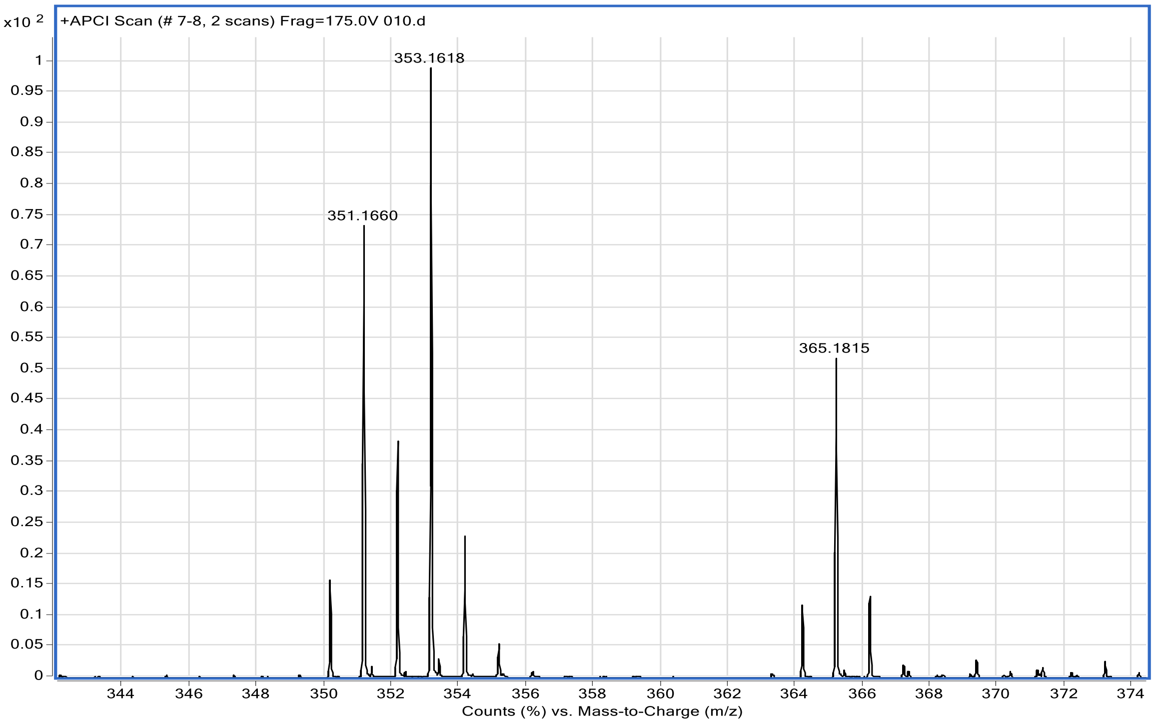
HRMS for **3a**



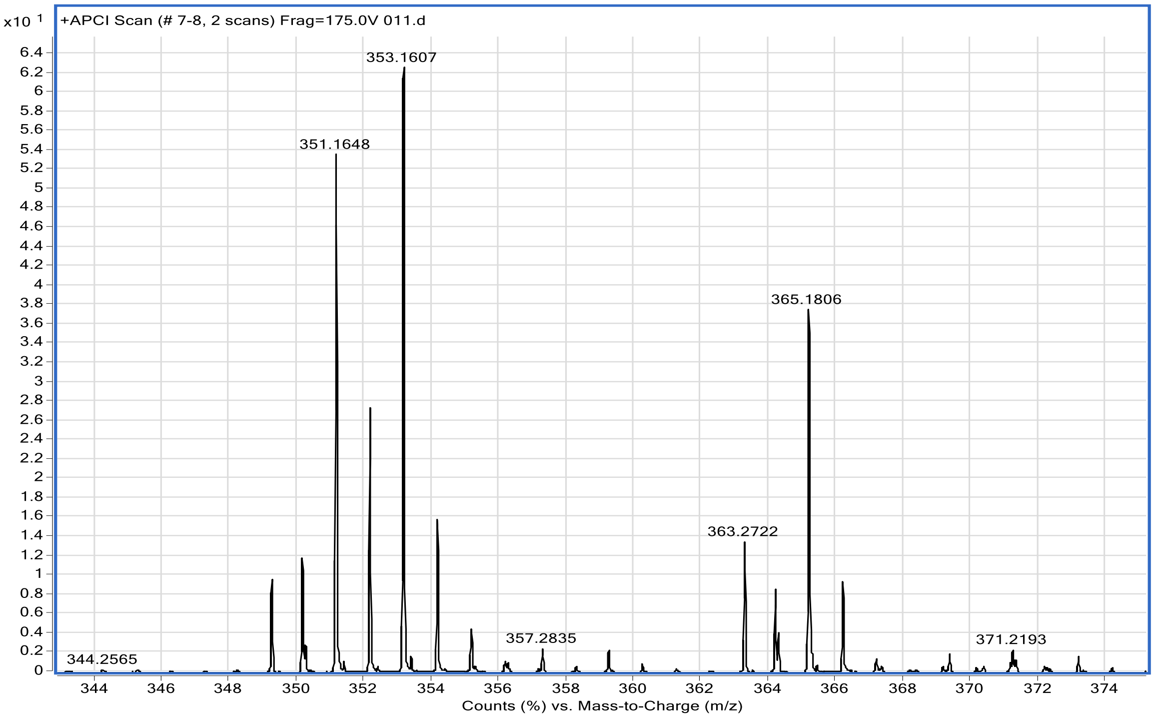
HRMS for **3b**



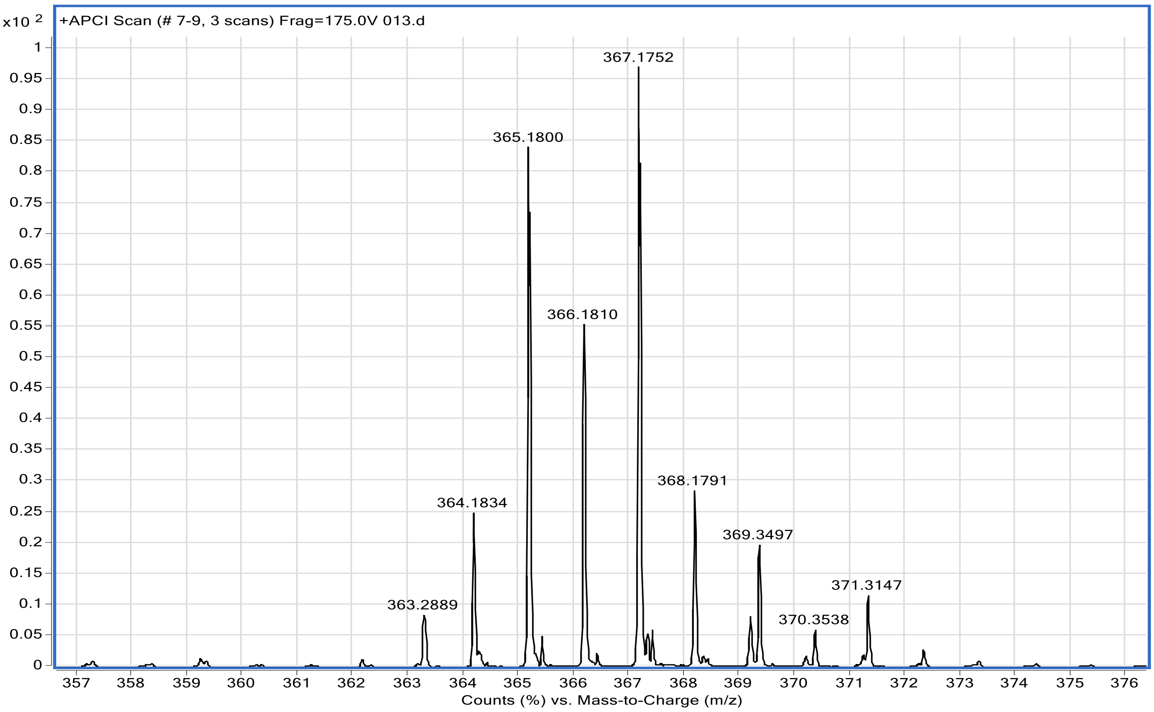
HRMS for **3c**



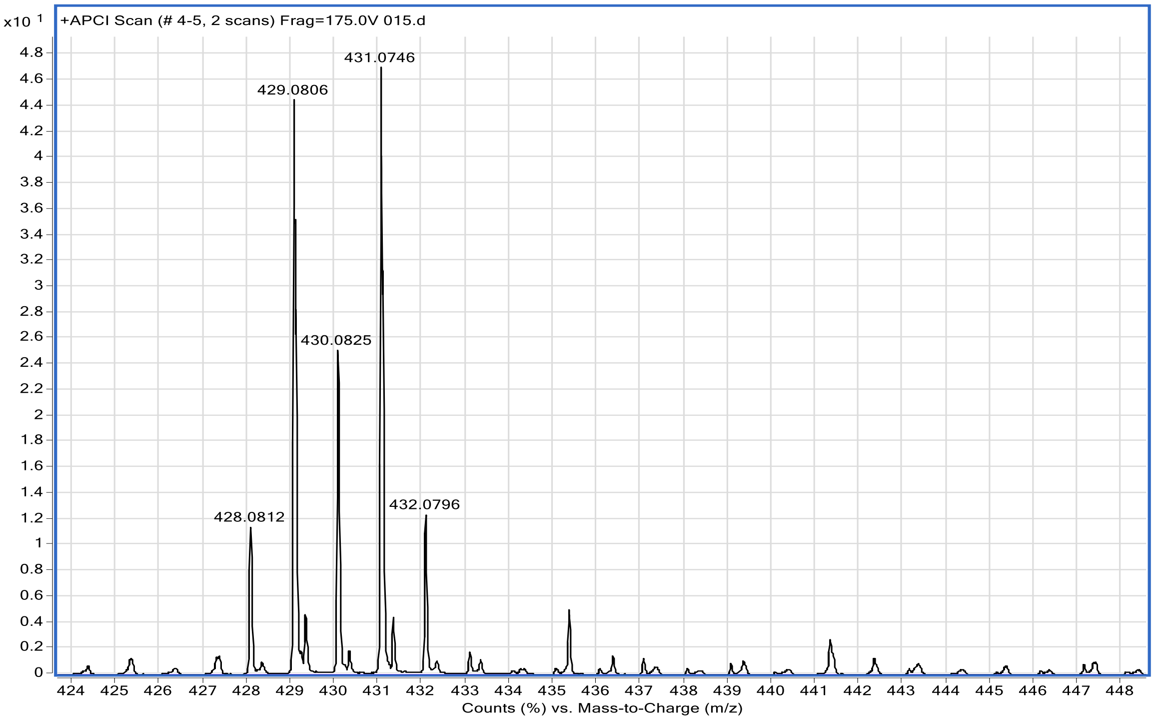
HRMS for **3d**



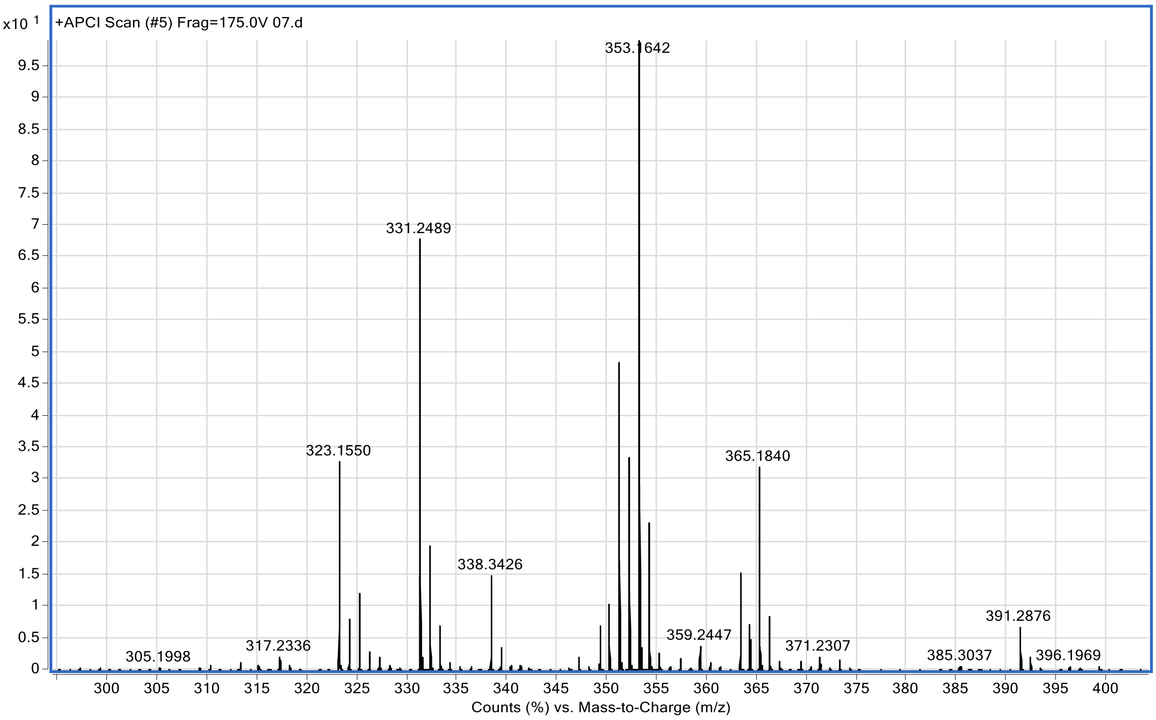
HRMS for **3e**



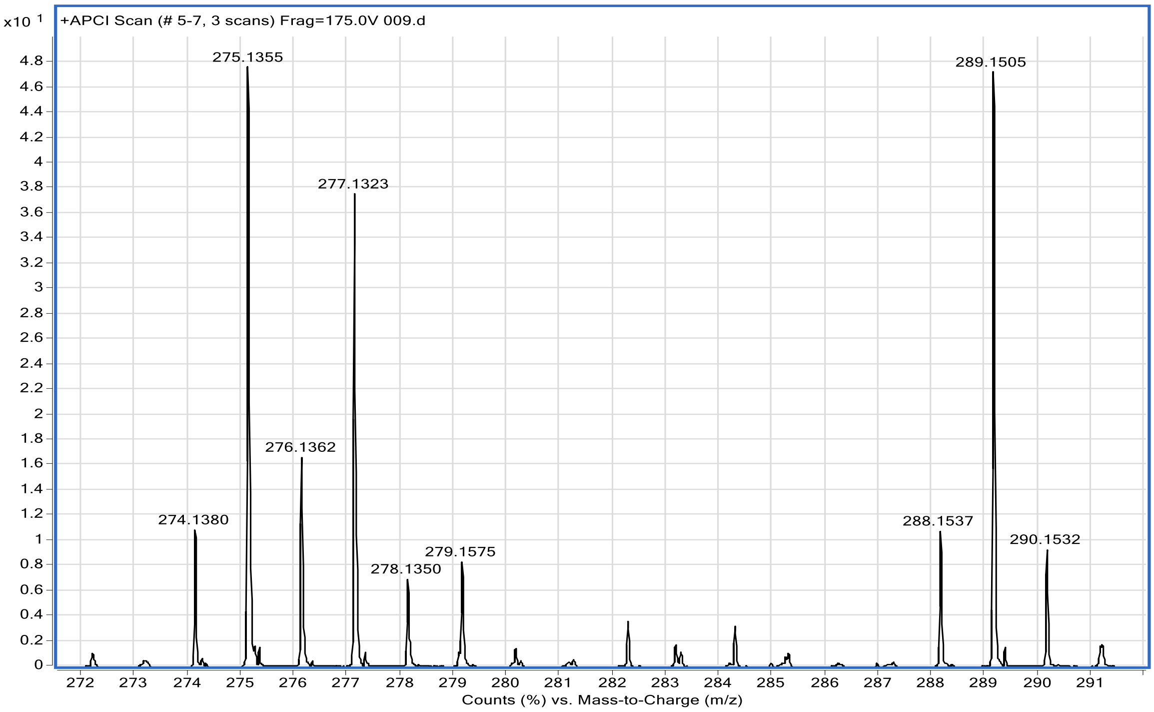
HRMS for **3f**



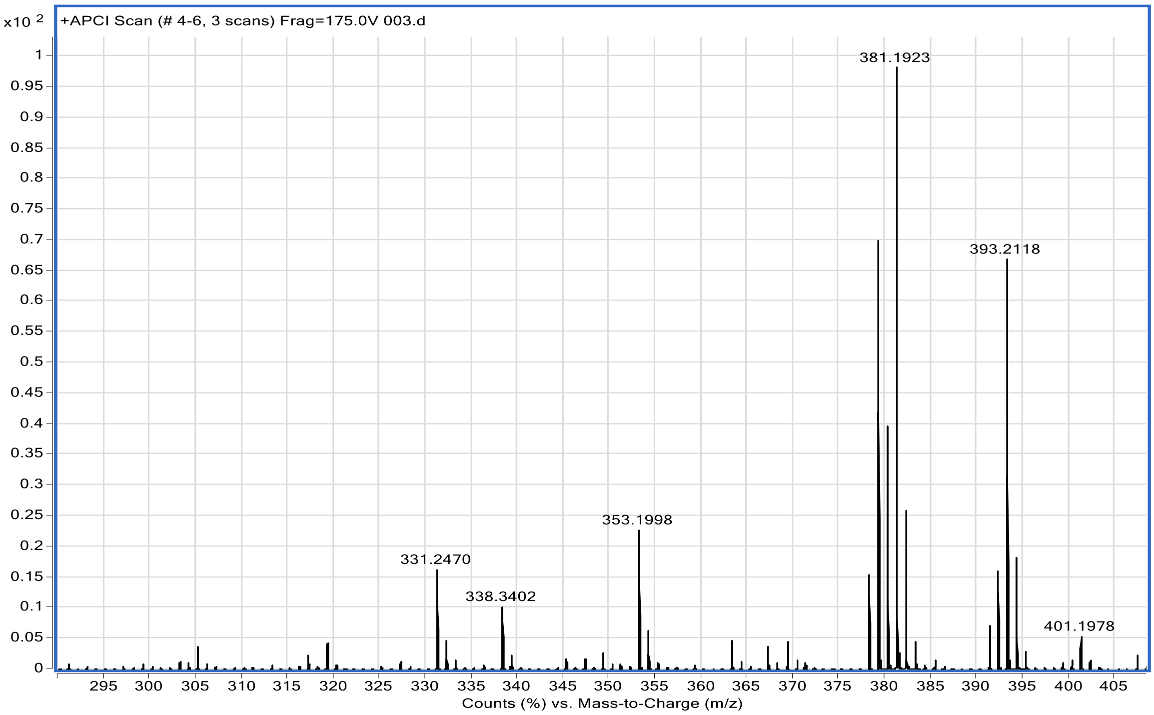
HRMS for **3g**



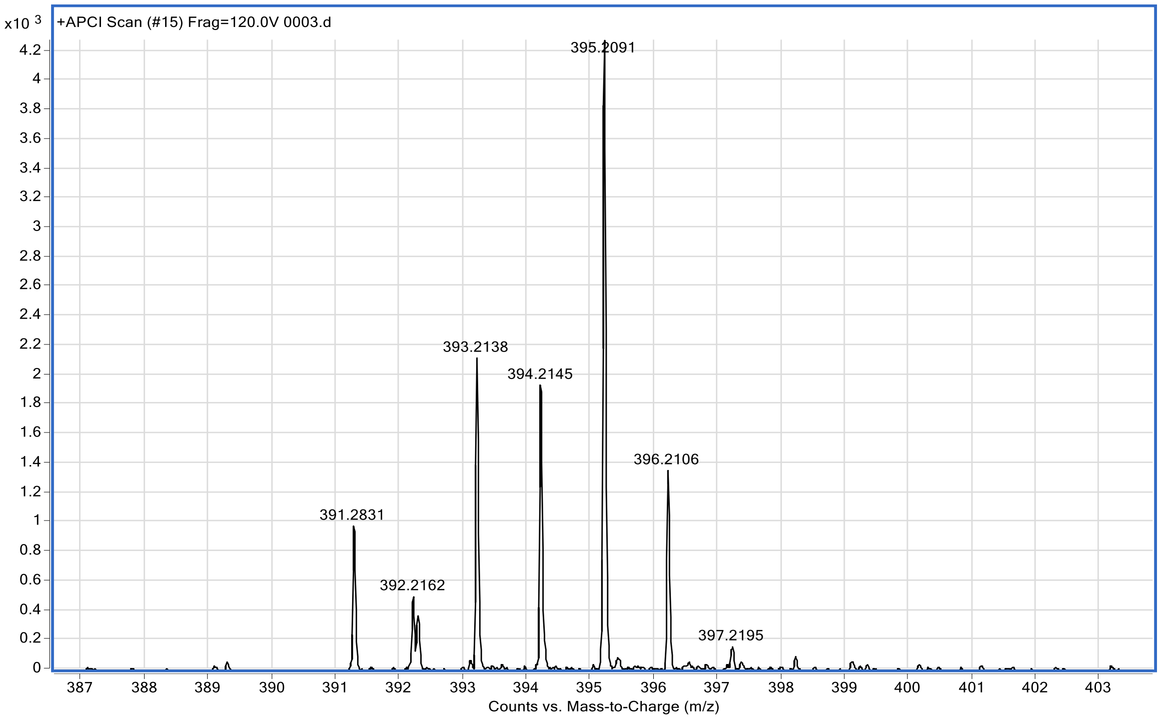
HRMS for **3h**



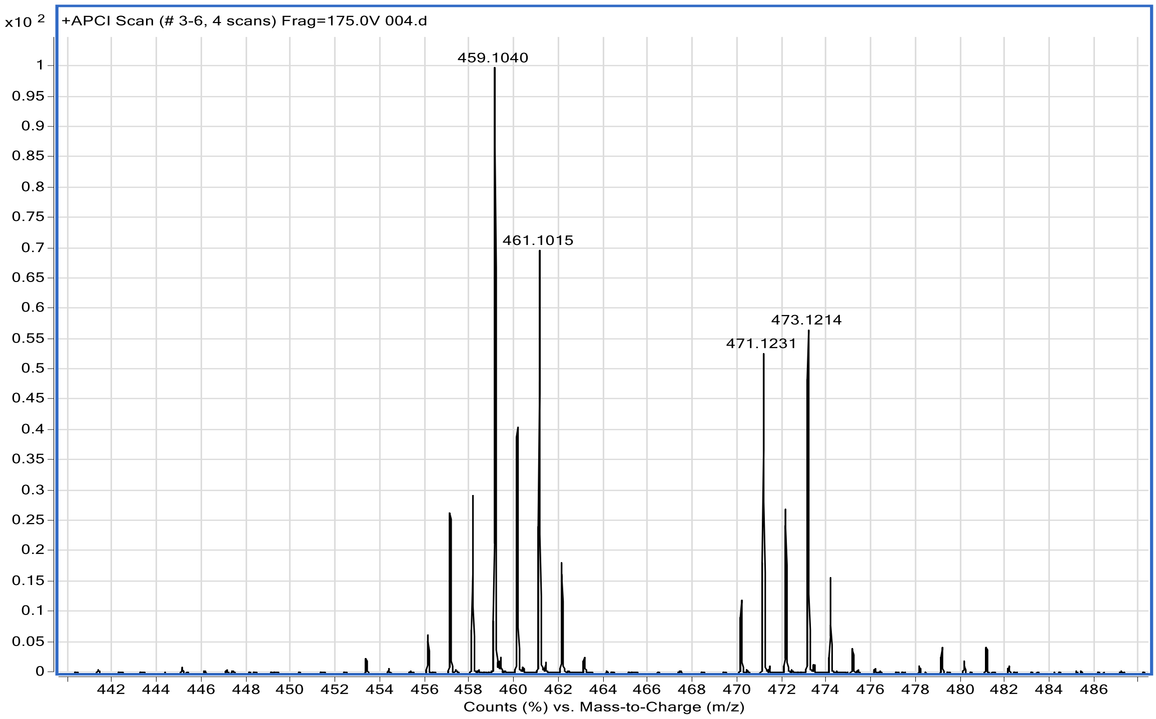
HRMS for **3i**



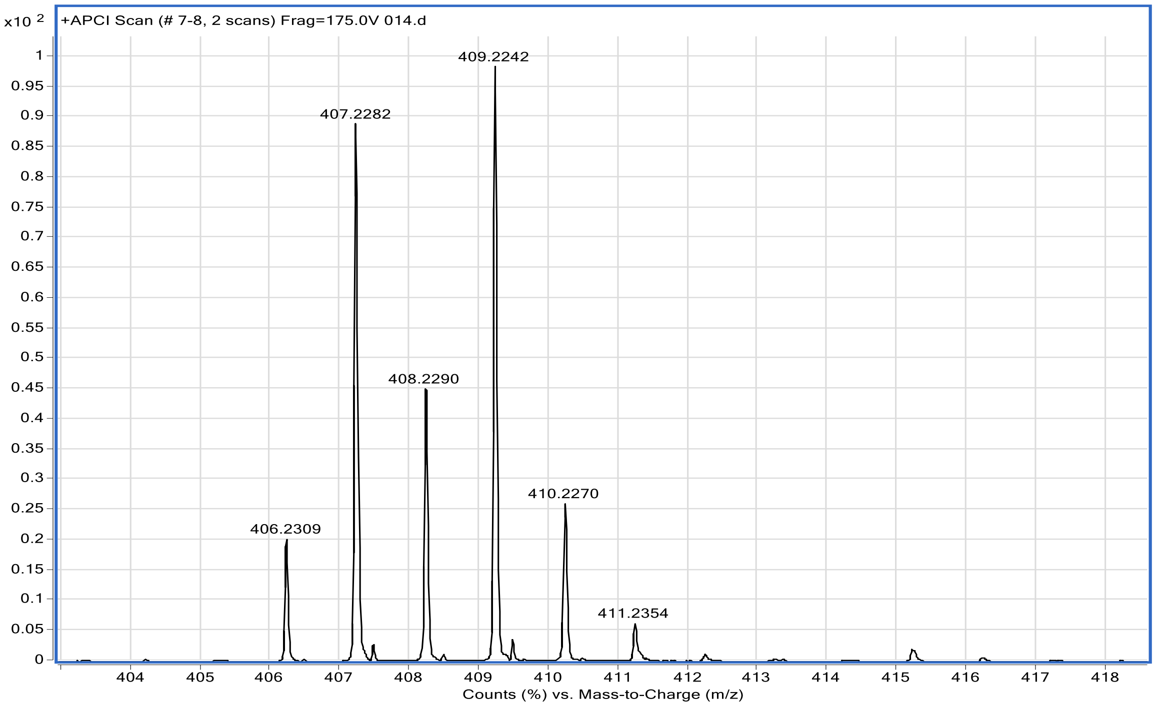
HRMS for **3j**



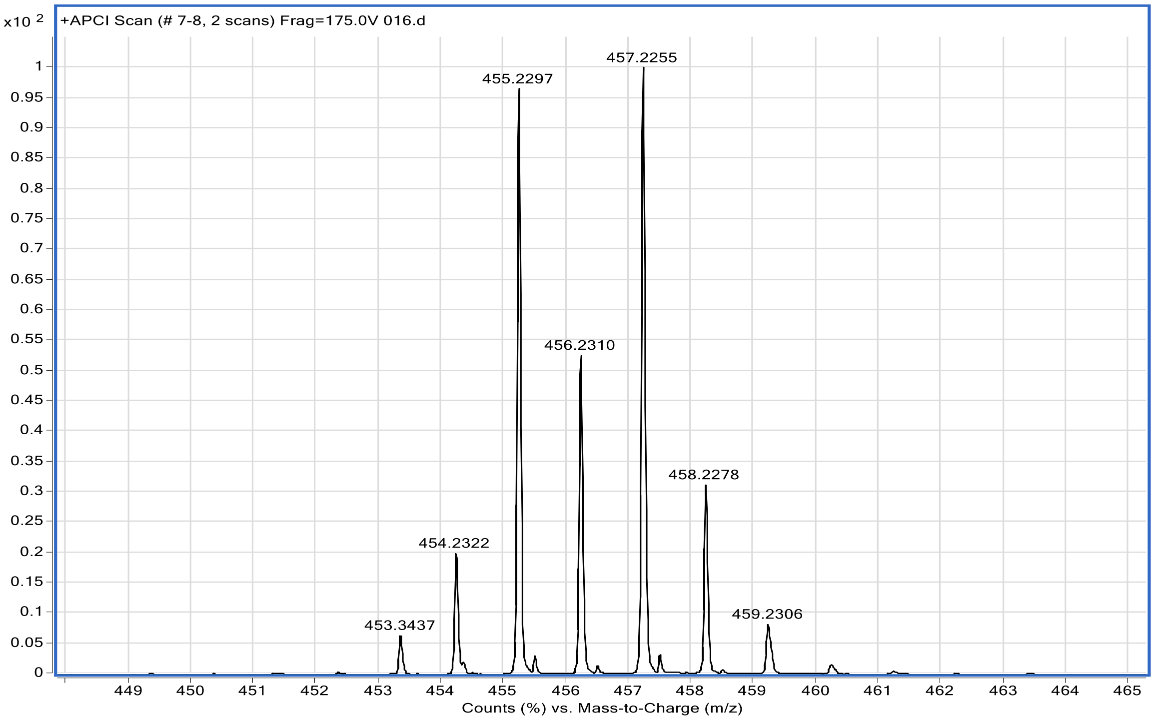
HRMS for **3k**



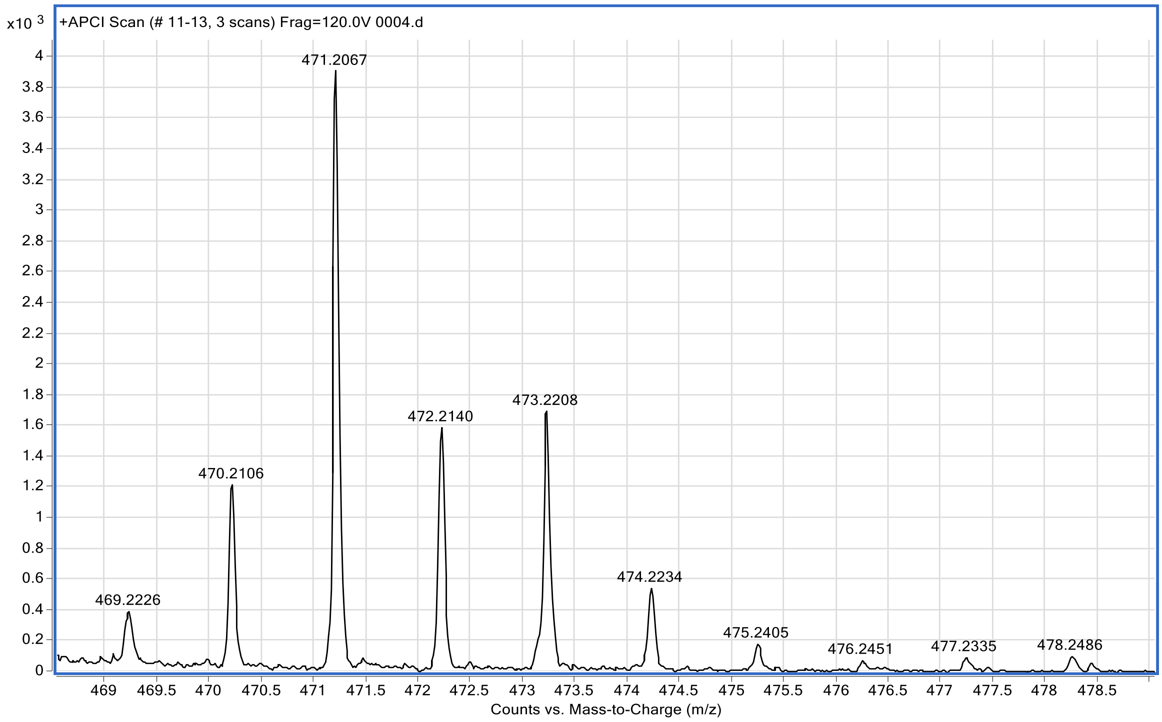
HRMS for **3l**



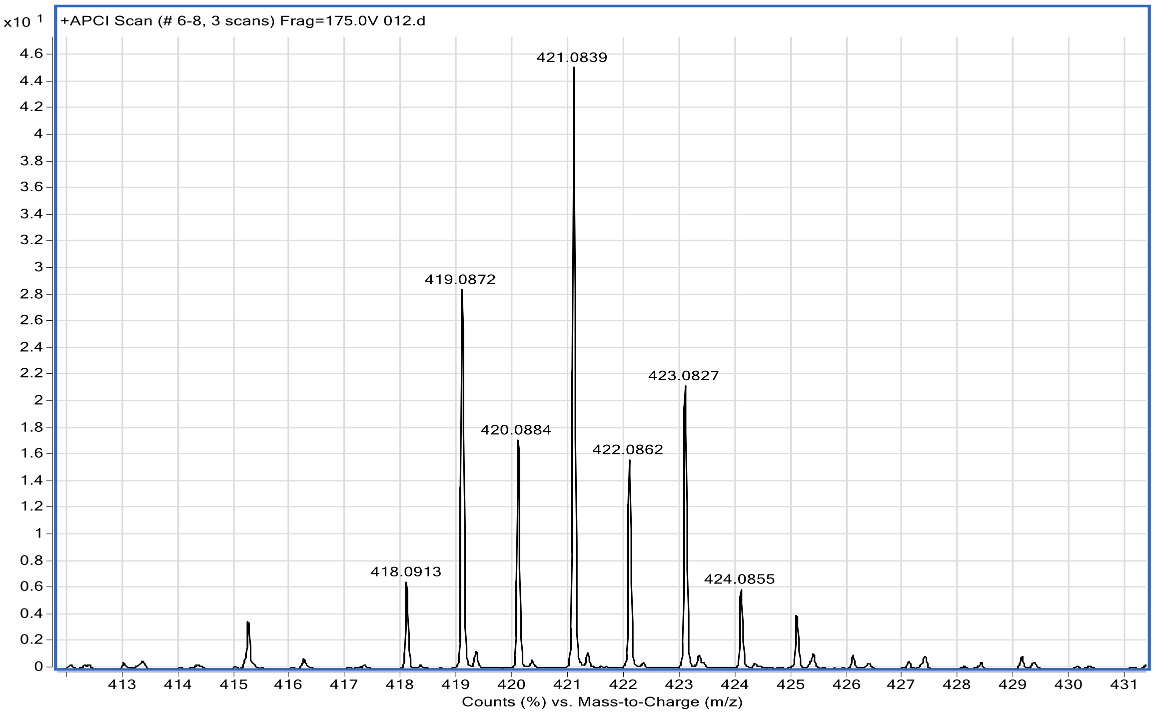
HRMS for **3m**



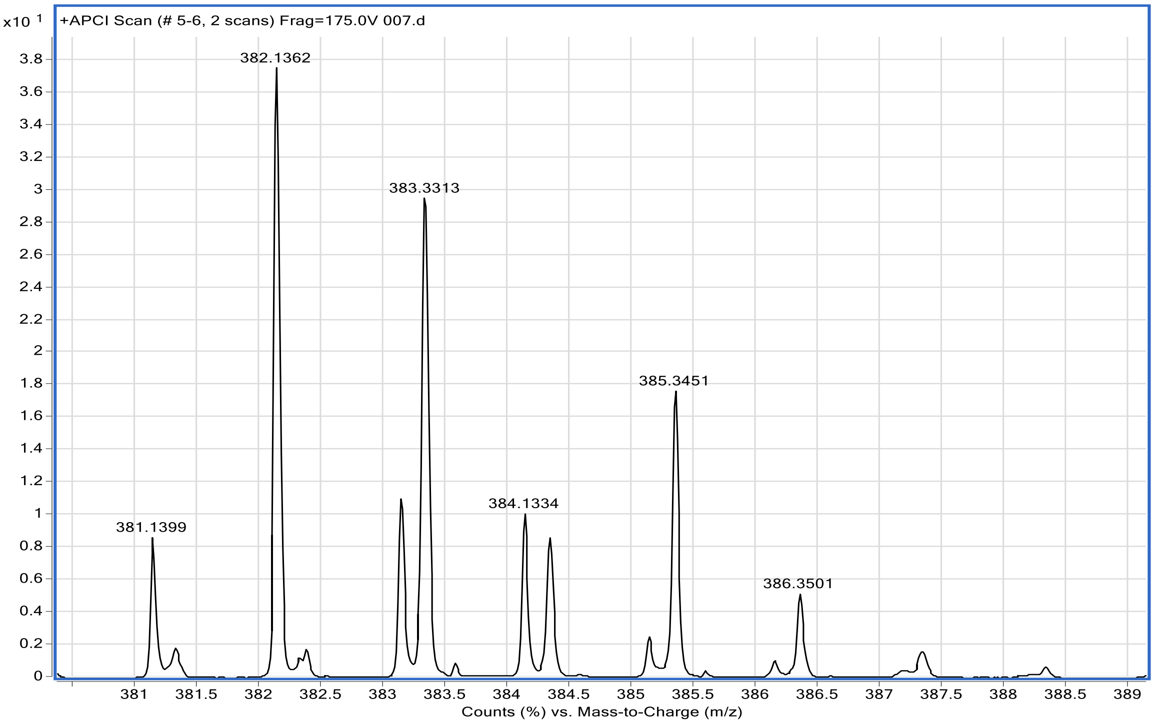
HRMS for **3n**



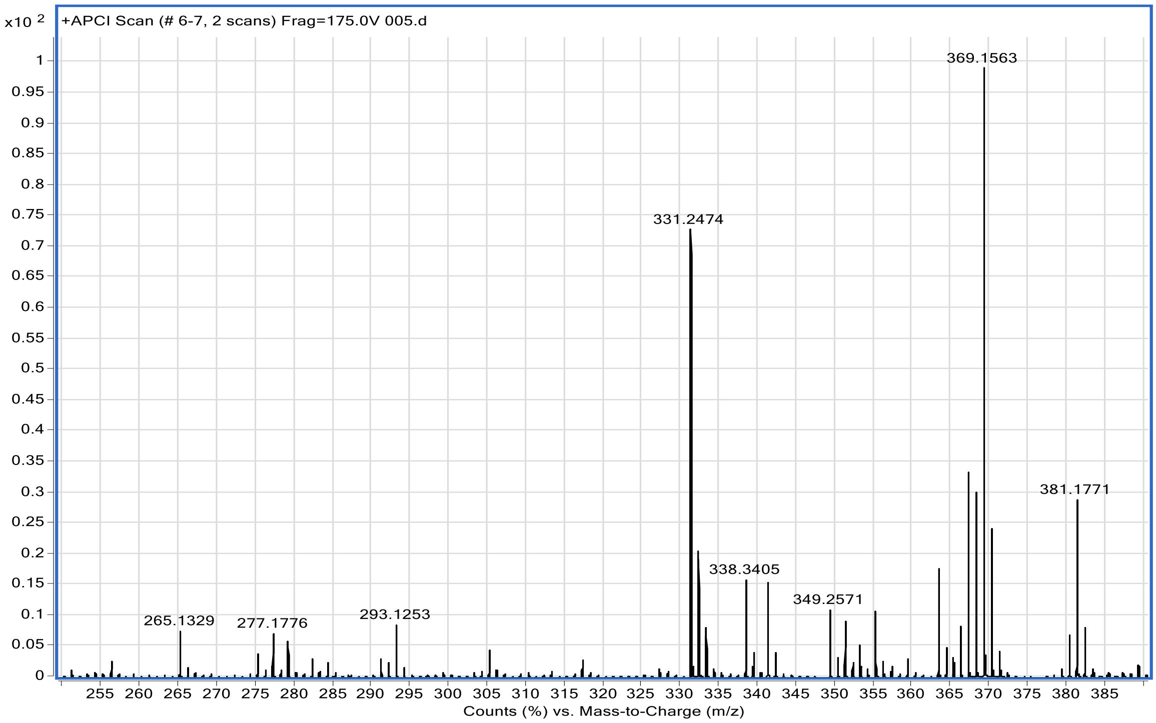
HRMS for **3o**



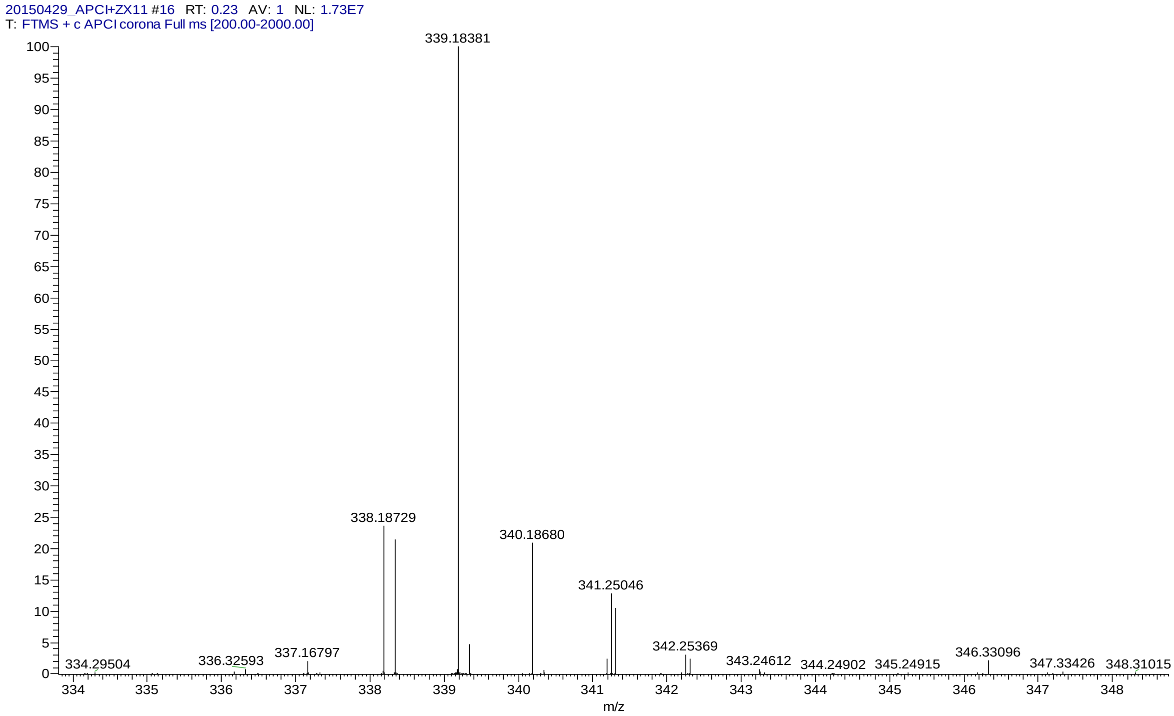
HRMS for **3p**



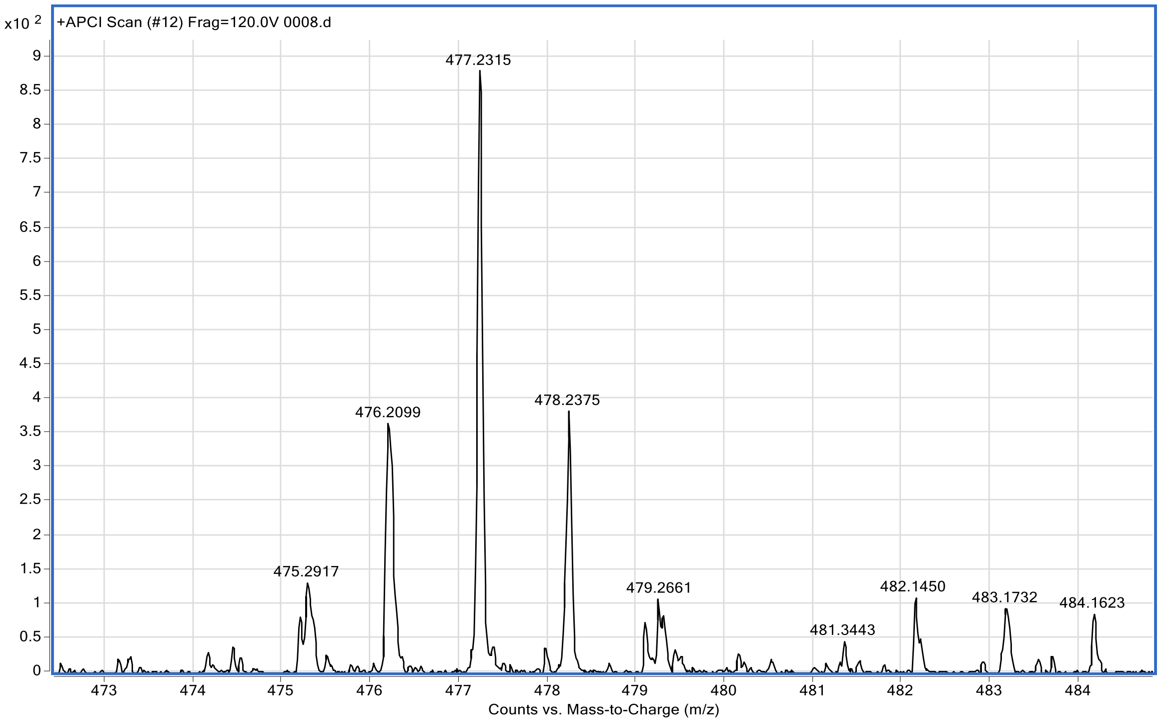
HRMS for **3q**



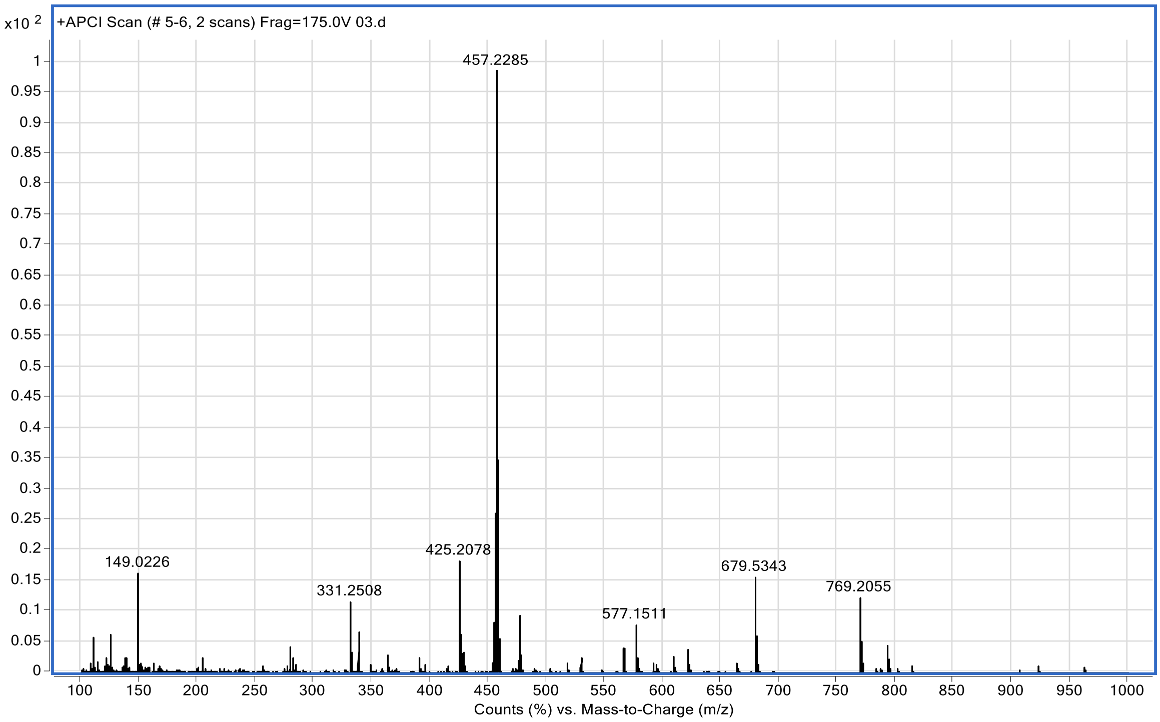
HRMS for **3r**



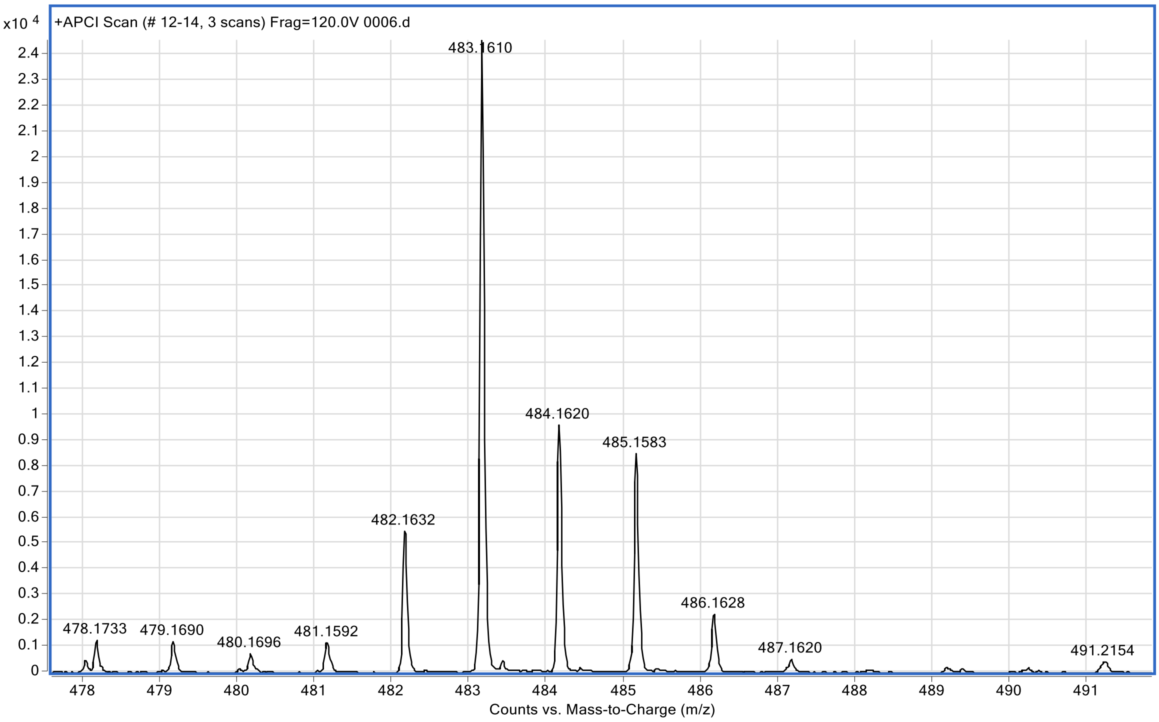
HRMS for **4a**



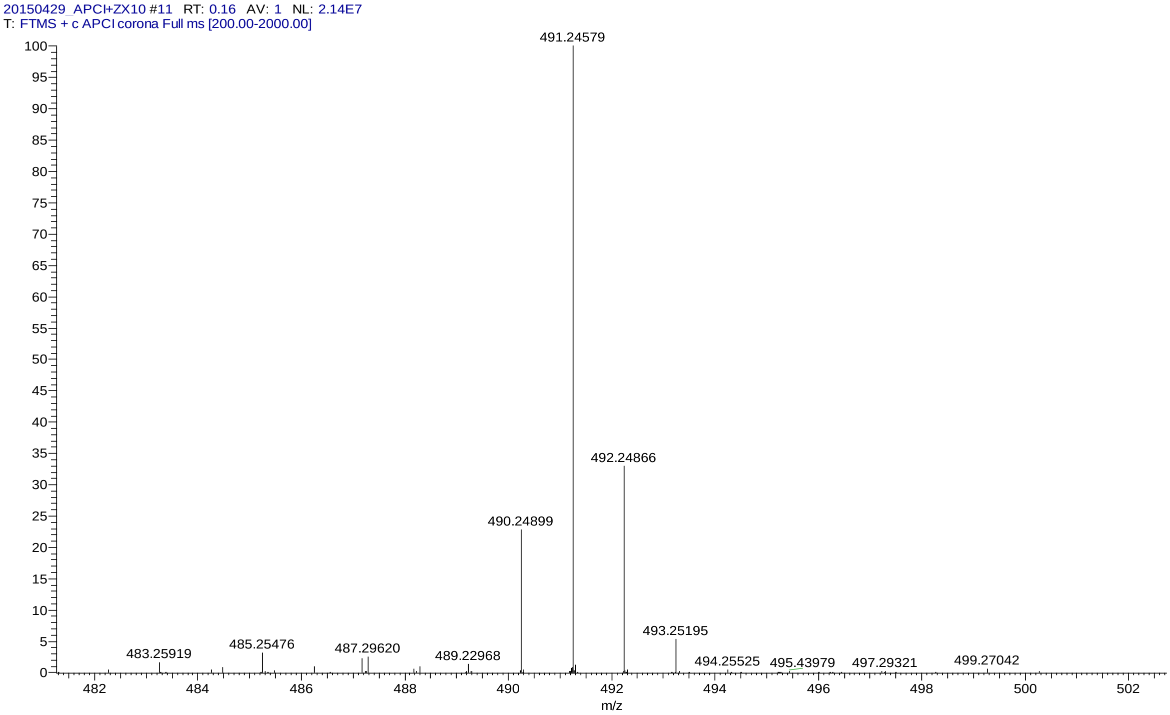
HRMS for **4b**



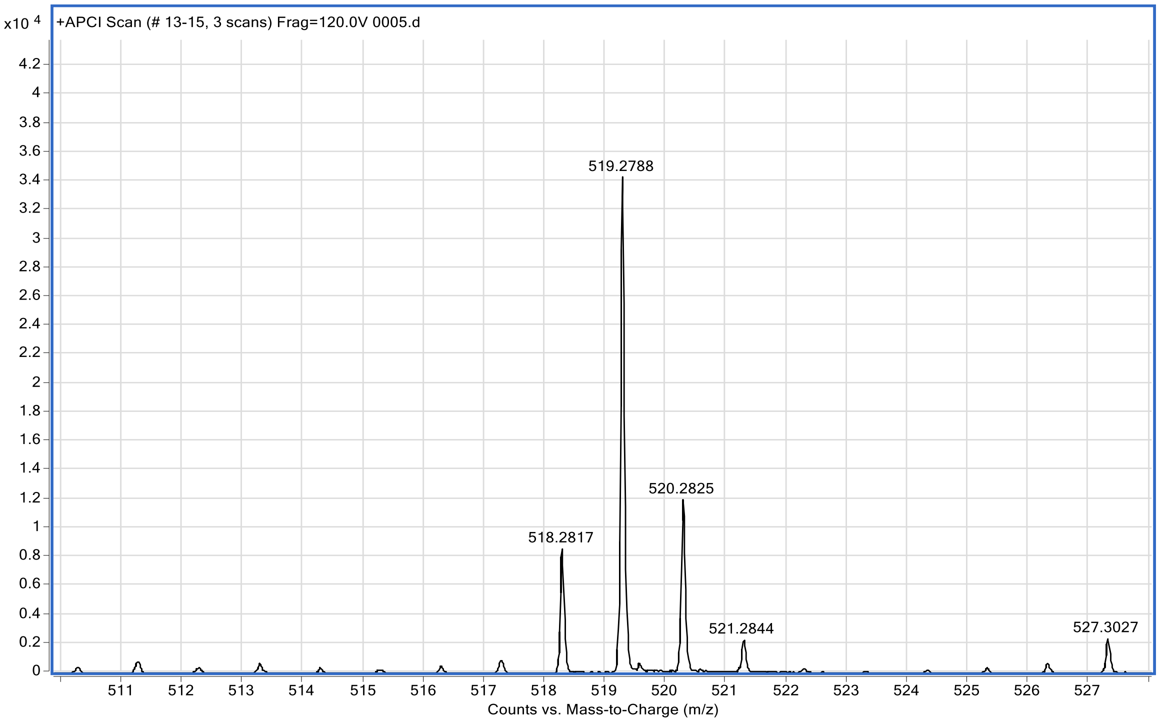
HRMS for **4c**



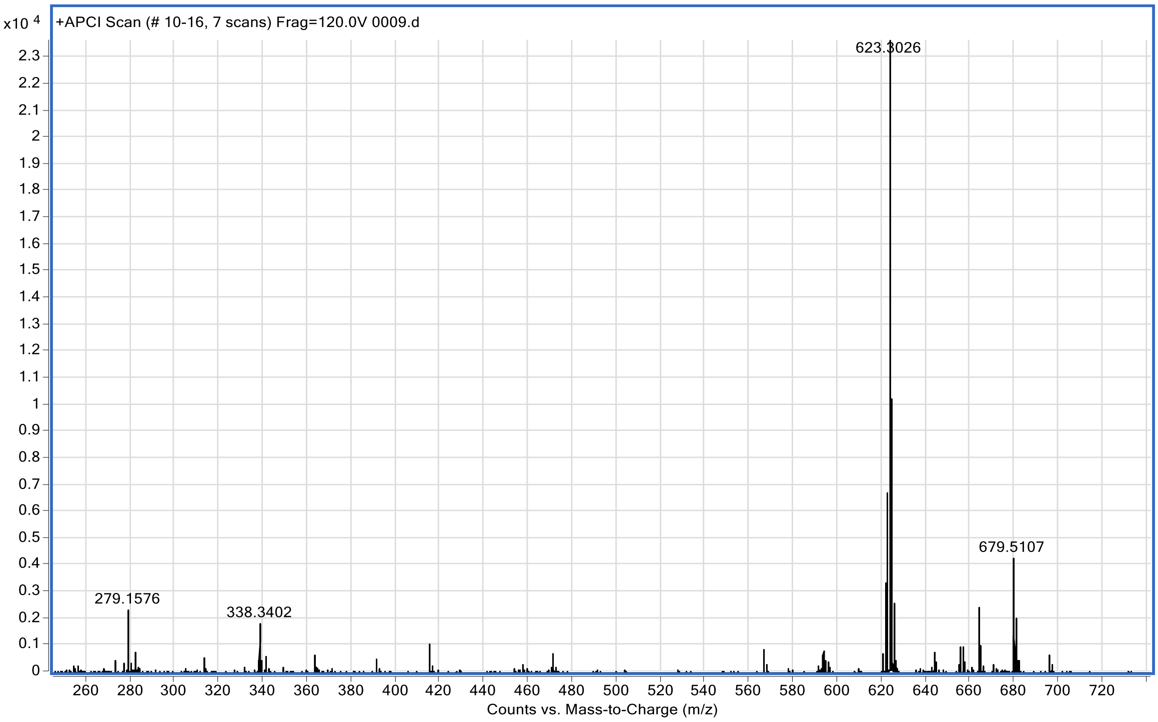
HRMS for **4d**



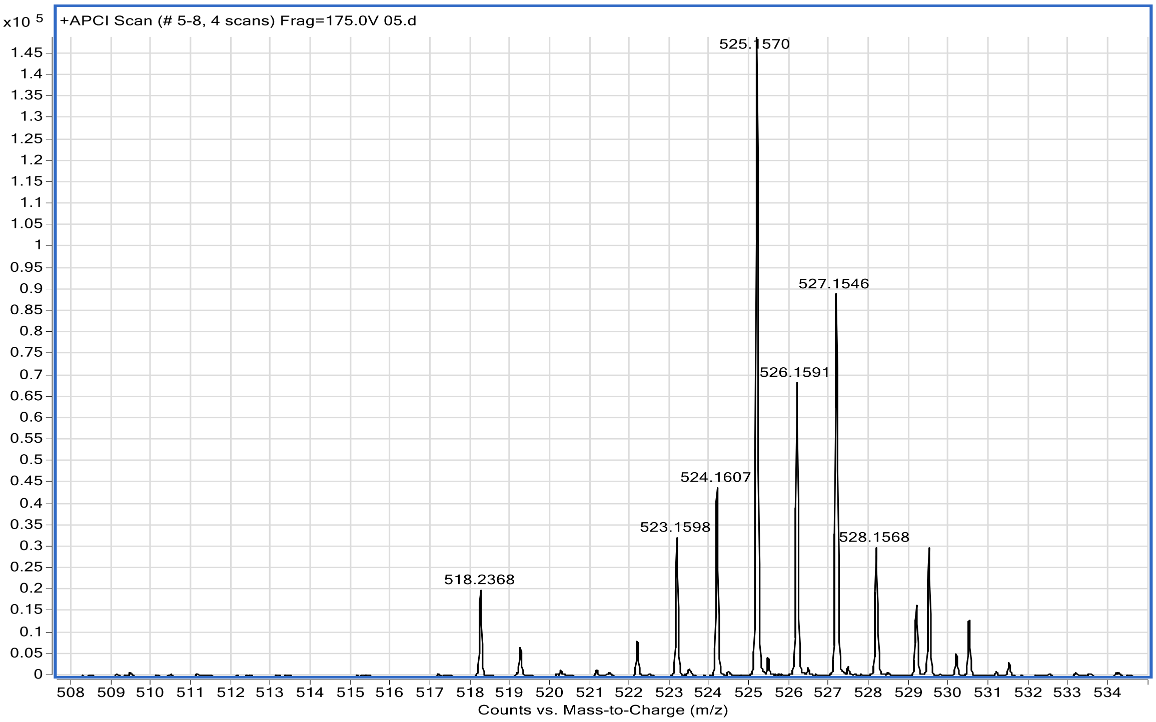
HRMS for **4e**



HRMS for **4f**



HRMS for **4g**



x10 5
+APCI Scan (# 5-8, 4 scans) Frag=175.0V 05.d
525.1570
527.1546
526.1591
524.1607
523.1598
528.1568
518.2368
1.45
1.4
1.35
1.3
1.25
1.2
1.15
1.1
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
508 509 510 511 512 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 528 529 530 531 532 533 534
Counts vs. Mass-to-Charge (m/z)

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