Supporting information for

Synthesis and Functionalization of Asymmetrical Benzo-fused BODIPY Dyes

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1. General methods:

Reagents were purchased as reagent-grade and used without further purification unless otherwise stated. Solvents were used as received from commercial suppliers unless noted otherwise. THF was freshly distilled from sodium benzophenone ketyl. All reactions were performed in oven-dried or flame-dried glassware unless otherwise stated, and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254). ^{1}H- and ^{13}C-NMR are obtained on a 300 MHz spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to $CDCl_3$ 7.26 (^{1}H) and 77 ppm (^{13}C) or TMS. High-resolution mass spectra were obtained by using EI-TOF with positive mode. The isotope peaks were matched with the calculated patterns; only the most abundant peaks for each compound are listed.

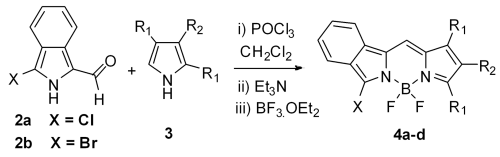
UV-visible absorption spectra were recorded on a commercial spectrophotometer (190-1100 nm scan range). Fluorescence emission spectra were recorded on a commercial spectrophotometer. The slit width was 2.5 nm for excitation and 5.0 nm emission. Relative quantum efficiencies of fluorescence of BODIPY derivatives were obtained by comparing the areas under the corrected emission spectrum of the test sample in various solvent with that of methylene blue (0.03 in MeOH)[1a] fluorescein (0.95 in 0.1 M NaOH aqueous solution)[1b] and Rhodamin B (0.49 in EtOH)[1c], respectively. Non-degassed, spectroscopic grade solvents and a 10 mm quartz cuvette were used. Dilute solutions ($0.01<A<0.05$) were used to minimize the reabsorption effects. Quantum yields were determined using the following equation[2]:

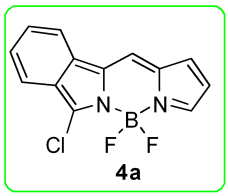
$$\Phi_X = \Phi_S (I_X/I_S) (A_S/A_X) (\eta_X/\eta_S)^2$$

Where Φ_S stands for the reported quantum yield of the standard, I stands for the integrated emission spectra, A stands for the absorbance at the excitation wavelength and η stands for the refractive index of the solvent being used ($\eta = 1$ when the same solvent was used for both the test sample and the standard). X subscript stands for the test sample, and S subscript stands for the standard.

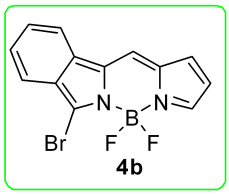
Fluorescence lifetimes were measured on a combined steady-state lifetime fluorescence spectrometer and the fluorescence lifetimes were obtained from deconvolution and distribution lifetime analysis[3]. The fluorescence lifetime was fitted in a single exponential and all fits had χ^2 values under 1.1. The radiative rate constant was calculated using equation $k_r = \Phi/\tau$, and the non-radiative rate constant was calculated using equation $k_{nr} = (1-\Phi)/\tau$.

2. Syntheses and Characterizations of Compounds



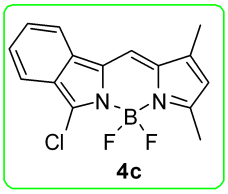


BODIPY **4a**: To compound **2a**[4] (895 mg, 5 mmol) in 10 mL CH_2Cl_2 was added pyrrole (138 μL, 2 mmol) in 1 mL CH_2Cl_2, and $POCl_3$ (470 μL, 5 mmol) in 1 mL CH_2Cl_2 rescpetively, at ice-cold condition under argon. The reaction mixture was stirred at this ice-cold condition for 30 min. To the reaction mixture was added Et_3N (7 mL), and the mixture was stirred for 10 min before addition of $BF_3{\cdot}OEt_2$ (7 mL) through syringe. The reaction mixture was left stirring for overnight, poured into 50 mL water and extracted with 30 mL CH_2Cl_2. Organic layers were combined, and solvent was removed under vacuum. The crude product was purified from chromatograph (silica gel, hexane/CH_2Cl_2 = 2/1, v/v), the desired compound **4a** was obtained as brown powder in 63% yield (348 mg): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (t, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 6.78 (brs, 1H), 6.32 (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.8, 137.5, 135.6, 132.3, 131.8, 130.0, 129.5, 127.3, 124.9, 122.4, 120.9, 119.5, 115.7. HRMS (EI) Calcd. for $C_{13}H_8BClF_2N_2$ $[M]^+$: 276.0437, found 276.0435.



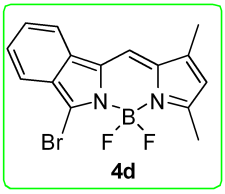
BODIPY **4b**: By reacting compound **2b**[4] (224 mg, 1 mmol) with pyrrole (28 μL, 0.4 mmol) and $POBr_3$ (29 mg, 0.1 mmol) using the same procedure described above, subsequently reacting with Et_3N (1.2 mL), complexation with $BF_3{\cdot}OEt_2$ (1.2 mL), and purification from chromatograph (silica gel, hexane/CH_2Cl_2 = 1/1, v/v), the desired compound **4b** was obtained as brown powder in 67% yield (86

mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (t, J = 7.2 Hz, 2H), 7.66 (q, J = 6.9 Hz, 2H), 7.47 (t, J = 6.3 Hz, 2H), 6.90 (d, J = 3.9 Hz, 1H), 6.43 (q, J = 2.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.9, 137.5, 135.6, 132.4, 131.8, 130.0, 129.5, 127.4, 124.9, 122.5, 121.0, 119.6, 115.8. HRMS (EI) Calcd. for $C_{13}H_8BF_2N_2{}^{79}Br$ $[M]^+$: 319.9932, found 319.9931; HRMS (EI) Calcd. for $C_{13}H_8BF_2N_2{}^{81}Br$ $[M]^+$: 321.9912, found 321.9922.



4c

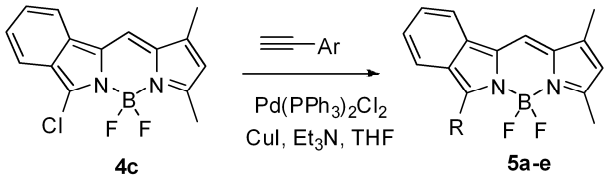
BODIPY **4c**: To compound **2a**[4] (895 mg, 5 mmol) in 10 mL CH_2Cl_2 was added 2,4-dimethylpyrrole (620 μL, 5 mmol) in 1 mL CH_2Cl_2 and $POCl_3$ (470 μL, 5 mmol) in 1 mL CH_2Cl_2, respectively at ice-cold condition under argon. The reaction mixture was stirred at this ice-cold condition for 30 min, Et_3N (7 mL) was added into the reaction mixture, the mixture was stirred for 10 min, $BF_3{\cdot}OEt_2$ (7 mL) was then added through syringe. The reaction mixture was left stirring for overnight, poured into 50 mL water and extracted with 30 mL CH_2Cl_2. Organic layers were combined, and solvent was removed under vacuum. The crude product was purified from chromatograph (silica gel, hexane/CH_2Cl_2 = 2/1, v/v) to give the desired compound **4c** as brown powder in 53% yield (800 mg): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, J = 7.7 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 7.3 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.10 (s, 1H), 5.88 (s, 1H), 2.39 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9, 140.3, 139.8, 134.3, 132.4, 130.6, 128.5, 126.8, 126.0, 121.7, 119.1, 118.3, 117.1, 14.6, 11.3. HRMS Calcd. for $C_{15}H_{12}BClF_2N_2$: $[M]^+$ 304.0750, found 304.0757.



4d

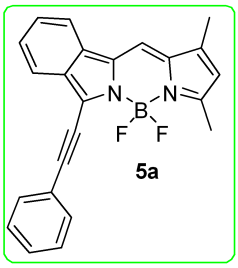
BODIPY **4d**: By reacting compound **2b**[4] (224 mg, 1 mmol) with 2,4-dimethylpyrrole (124 μL, 1 mmol) and $POBr_3$ (284 mg, 1 mmol) using the same procedure described above, subsequently reacting with Et_3N (1.2 mL), complexation with $BF_3{\cdot}OEt_2$ (1.2 mL) for 2 hours, and purification from

chromatograph (silica gel, hexane/CH_2Cl_2 = 1/1, v/v), the desired compound **4d** was obtained as brown powder in 45% yield (157 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78-7.65 (m, 2H), 7.50 (d, J = 7.0 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 7.31 (s, 1H), 6.02 (s, 1H), 2.55 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.6, 130.4, 125.9, 122.5, 121.6, 119.0, 118.9, 118.5, 118.3, 117.0, 116.8, 14.6, 11.3. HRMS (EI) Calcd. for $C_{15}H_{12}BBrF_2N_2$ [M]$^+$: 348.0245, found 348.0243.



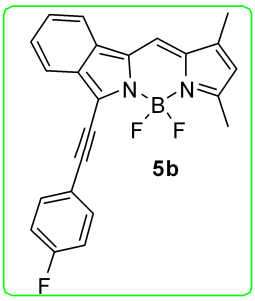
4c **5a-e**

General procedure for the preparation of BODIPYs **5a-e** using sonogashira coupling reaction was described in the following using compound **5a** arylacetylene as an example.



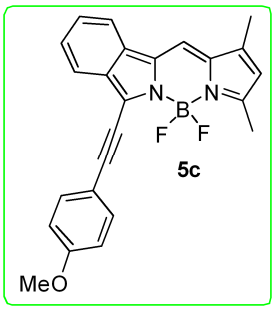
5a

BODIPY **5a**. To a 50 mL dry Schlank flask were added BODIPY **4c** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (22 mg, 3 mmol%) and CuI (13 mg, 7 mmol%) in 5 mL freshly distilled THF. After freeze-thaw for three times, Et_3N (0.4 mL) and phenylacetylene (110 μL, 1.0 mmol) in 1 mL THF were added through syringe into the mixture, respectively. The mixture was stirred at 65 °C for 3 h, cooled to room temperature, filtrated through Celite, and the cake was washed with CH_2Cl_2 (3 × 20 mL). Organic layers were combined, washed with brine, dried over anhydrous $MgSO_4$, and solvent was removed under vacuum. The crude product was purified from chromatograph (silica gel, hexane/CH_2Cl_2 = 5/2, v/v) to give the desired compound **5a** as dark blue solid in 55% yield (41 mg): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, J = 7.8 Hz, 1H), 8.05-8.00 (m, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.75-7.69 (m, 2H), 7.51-7.15 (m, 4H), 6.92 (s, 1H), 6.03 (s, 1H), 2.58 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.1, 138.3, 136.5, 129.6, 129.5, 129.0, 128.4, 127.7, 126.3, 125.3, 124.5, 123.9, 119.6(3), 119.5(8), 119.4, 118.8, 117.8, 116.1, 115.3, 14.6, 11.3. HRMS (EI) Calcd. for $C_{23}H_{17}BF_2N_2$ [M]$^+$: 370.1453, found 370.1451.



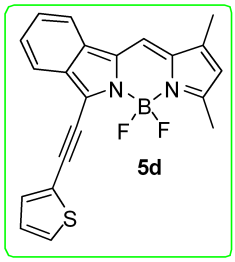
5b

BODIPY **5b.** By reacting BODIPY **4c** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (22 mg, 3 mmol%), CuI (13 mg, 7 mmol%), Et_3N (0.4 mL) and 4-florophenylacetylene (240 μL, 2.1 mmol) in 1 mL THF following the same procedure described above, BODIPY **5b** was obtained as dark blue solid in 55% yield (43 mg) after silica gel column separation (hexane/ CH_2Cl_2 = 2/3, v/v): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (d, J = 7.9 Hz, 1H), 7.90-7.65 (m, 3H), 7.50 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.31 (s, 1H), 7.14-7.09 (m, 2H), 6.02 (s, 1H), 2.57 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.1, 152.9, 150.1, 137.6, 135.8, 132.8, 132.6, 131.2, 129.4, 126.3, 125.3, 124.2, 123.7, 119.4, 117.8, 116.2, 115.9, 115.3, 14.6, 11.3. HRMS (EI) Calcd. for $C_{23}H_{18}BF_3N_2$ $[M+2H]^+$: 390.1515, found 390.1517.



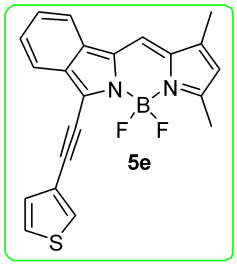
5c

BODIPY **5c.** By reacting BODIPY **4c** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (22 mg, 3 mmol%), CuI (13 mg, 7 mmol%), Et_3N (0.4 mL) and 4-methyloxyphenylacetylene (200 μL, 1.5 mmol) in 1 mL THF following the same procedure described above, BODIPY **5c** was obtained as dark blue solid in 61% yield (49 mg) after column separation (hexane/ CH_2Cl_2 = 2/1, v/v): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, J = 8.0 Hz, 1H), 7.91-7.64 (m, 4H), 7.51 (q, J = 7.4 Hz, 1H), 7.42 (q, J = 8.3 Hz, 1H), 6.97 (d, J = 7.5 Hz, 2H), 6.04 (d, J = 8.1 Hz, 1H), 3.87 (s, 3H), 2.60 (d, J = 8.3 Hz, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.0, 155.3, 151.7, 151.3, 139.2, 135.9, 129.4, 126.3, 125.9, 124.0, 122.6, 119.4, 119.1, 118.4, 117.3, 115.9, 114.6, 114.4, 114.2, 55.4, 14.6, 11.3. HRMS (EI) Calcd. for $C_{24}H_{19}BF_2N_2O$ $[M]^+$: 400.1559, found 400.1556.



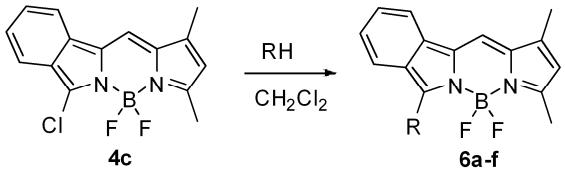
5d

BODIPY **5d**. By reacting BODIPY **4c** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (22 mg, 3 mmol%), CuI (13 mg, 7 mmol%), Et_3N (0.4 mL) and 2-ethylenethiophene (216 μL, 2.2 mmol) in 1 mL THF following the same procedure described above, BODIPY **5d** was obtained as dark blue solid in 53% yield (40 mg) after column separation (hexane/ CH_2Cl_2 = 2/1, v/v): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, J = 8.0 Hz, 1H), 7.82-7.75 (m, 2H), 7.53-7.34 (m, 4H), 7.09 (brs, 1H), 6.00 (s, 1H), 2.56 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.8, 149.9, 142.5, 137.4, 135.7, 132.6, 131.6, 131.0, 129.8, 129.5, 129.1, 128.2, 127.9, 126.3, 123.6, 119.4, 118.6, 117.7, 114.9, 14.6, 11.3. HRMS (EI) Calcd. for $C_{21}H_{17}BSF_2N_2$ $[M+2H]^+$: 378.1174, found 378.1176. HRMS (EI) Calcd. for $C_{21}H_{15}BF_2N_2S$ m/z: 376.1017, found 376.1047.

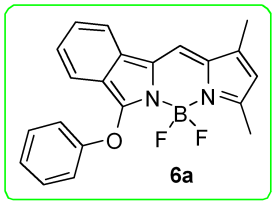


5e

BODIPY **5e**. By reacting BODIPY **4c** (61 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (22 mg, 3 mmol%), CuI (13 mg, 7 mmol%), NEt_3 (0.4 mL) and 3-ethylenethiophene (216 μL, 2.2 mmol) in 1 mL THF following the same procedure described above, BODIPY **5e** was obtained as dark blue solid in 64% yield (48 mg) after column separation (hexane/ CH_2Cl_2 = 2/1, v/v): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (d, J = 7.9 Hz, 1H), 7.82 (brs, 2H), 7.56-7.49 (m, 2H), 7.39 (brs, 2H), 7.31 (brs, 1H), 6.03 (s, 1H), 2.57 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.5, 150.8, 139.9, 133.0, 132.0, 129.4, 128.6, 128.5, 127.7, 126.8, 126.3, 125.5, 125.4, 123.8, 119.5, 117.6, 115.0, 111.0, 14.6, 11.3. HRMS (EI) Calcd. for $C_{21}H_{17}BF_2N_2S$ $[M+2H]^+$: 378.1174, found 378.1170.

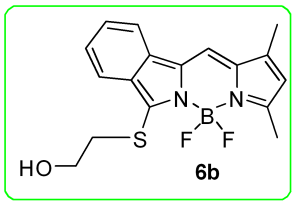


4c **6a-f**



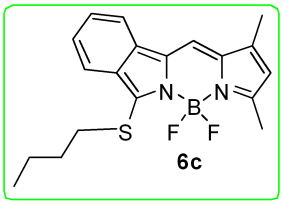
6a

BODIPY **6a**. To a 50 mL dry Schlank flask were added BODIPY **4c** (40 mg, 0.13 mmol) and phenol (61 mg, 0.65 mmol) in 10 mL CH_2Cl_2. Then K_2CO_3 (138 mg, 1 mmol) was added and the reaction mixture was stirred at room temperature for 10 min, poured into water and extracted with CH_2Cl_2 (3 × 20 mL). Organic layers were combined, solvent was removed under vacuum, the crude product was purified from chromatograph (silica gel, hexane/CH_2Cl_2 = 2/1, v/v), and the desired compound **6a** was obtained as powder in 85% yield (41 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 6.6 Hz, 2H), 7.28 (d, J = 7.8 Hz, 3H), 7.19 (s, 1H), 6.94 (t, J = 7.5 Hz, 2H), 6.50 (d, J = 8.1 Hz, 1H), 5.89 (s, 1H), 2.45 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.6, 149.1, 136.7, 134.7, 130.8, 130.2, 126.5, 125.4, 123.5, 123.2, 120.2, 120.0, 119.5, 116.2, 114.9, 14.2, 11.2. HRMS (EI) Calcd. for $C_{21}H_{17}BF_2N_2O$ $[M]^+$: 362.1402, found 362.1406.



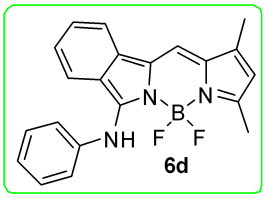
6b

Compound **6b**. To a 50 mL dry Schlank flask were added BODIPY 4**c** (40 mg, 0.13 mmol), and 100 equiv of 2-hydroxy-1-ethanethiol (0.9 mL, 13 mmol) in 10 mL CH_2Cl_2. Then 0.5 mL NEt_3 was added and the reaction mixture was stirred at room temperature for 24 h, poured into water and extracted CH_2Cl_2 (3 × 20 mL). Organic layers were combined, solvent was removed under vacuum, the crude product was purified from chromatograph (silica gel, hexane/ CH_2Cl_2 = 1/2, v/v), and the desired compound **6b** was obtained as powder in 60% yield (27 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (t, J = 8.8 Hz, 2H), 7.52 (t, J = 7.0 Hz, 1H), 7.38 (t, J = 7.8 Hz, 2H), 6.07 (s, 1H), 3.66 (s, 2H), 3.37 (s, 2H), 2.57 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.7, 147.6, 140.2, 134.6, 133.1, 129.8, 128.9, 125.8, 122.5, 119.4, 118.8, 117.0, 116.6, 61.2, 40.3, 14.8, 11.4. HRMS (EI) Calcd. for $C_{17}H_{17}BF_2N_2OS$ $[M\text{-}HF]^+$: 326.1064, found 326.1060.



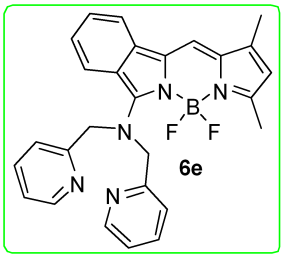
6c

BODIPY **6c**: To a 50 mL dry Schlank flask were added BODIPY **4c** (61 mg, 0.2 mmol) and butanethiol (214 μL, 2 mmol) in 10 mL CH_2Cl_2. Then 0.5 mL NEt_3 was added and the reaction mixture was stirred at room temperature for 6 h, poured into water and extracted with CH_2Cl_2 (3 × 20 mL). Organic layers were combined, solvent was removed under vacuum, the crude product was purified from chromatograph (silica gel, hexane/ CH_2Cl_2 = 2/1, v/v), and the desired compound **6c** was obtained as powder in 87% yield (62 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 7.3 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.26 (s, 1H), 6.01 (s, 1H), 3.39 (t, J = 7.4 Hz, 2H), 2.55 (s, 3H), 2.27 (s, 3H), 1.74 (t, J = 7.3 Hz, 2H), 1.52 (t, J = 7.3 Hz, 2H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.5, 151.7, 138.0, 134.8, 133.0, 132.2, 129.7, 129.5, 125.6, 123.0, 119.2, 117.8, 115.3, 35.4, 32.3, 21.8, 14.6, 13.6, 11.3. HRMS (EI) Calcd. for $C_{19}H_{21}BF_2N_2S$ $[M]^+$: 358.1487, found 358.1481.

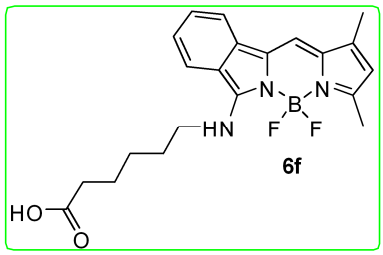


6d

BODIPY **6d**: By reacting BODIPY **4c** (40 mg, 0.13 mmol) and aniline (59 μL, 0.65 mmol) using the procedure described above for 10 min at room temperature and purified using chromatograph (silica gel, hexane/ CH_2Cl_2 = 2/1, v/v), the desired compound **6d** was obtained as powder in 91% yield (43 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (brs, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.47-7.44 (m, 6H), 7.04-7.00 (m, 2H), 6.79 (d, J = 8.2 Hz, 1H), 5.92 (s, 1H), 2.49 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.1, 129.8, 128.4, 128.1, 126.4, 125.6, 124.7, 119.6, 114.2, 108.4, 13.8, 11.0. HRMS (EI) Calcd. for $C_{21}H_{18}BF_2N_3$ $[M]^+$: 361.1562, found 361.1570.

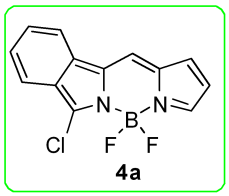


BODIPY **6e**: By reacting BODIPY **4c** (40 mg, 0.13 mmol) and di(2-pyridylmethyl)amine (DPA) (40 mg, 0.20 mmol) using the procedure described above for 10 min at room temperature and purified using chromatograph (silica gel, CH_2Cl_2), the desired compound **6e** was obtained as powder in 95% yield (58 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.53 (brs, 2H), 7.89 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 7.7 Hz, 1H), 7.71 (t, J = 7.2 Hz, 2H), 7.48 (d, J = 6.4 Hz, 3H), 7.21 (brs, 3H), 7.10 (s, 1H), 5.95 (s, 1H), 5.32 (s, 4H), 2.52 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.4, 156.5, 149.1, 144.1, 137.4, 137.3, 130.6, 129.3, 128.6, 128.2, 126.9, 125.9, 125.0, 122.7, 122.6, 119.2, 114.8, 109.9, 58.2, 14.1, 11.0. HRMS (EI) Calcd. for $C_{27}H_{24}BF_2N_5$ $[M]^+$: 467.2093, found 467.2099.



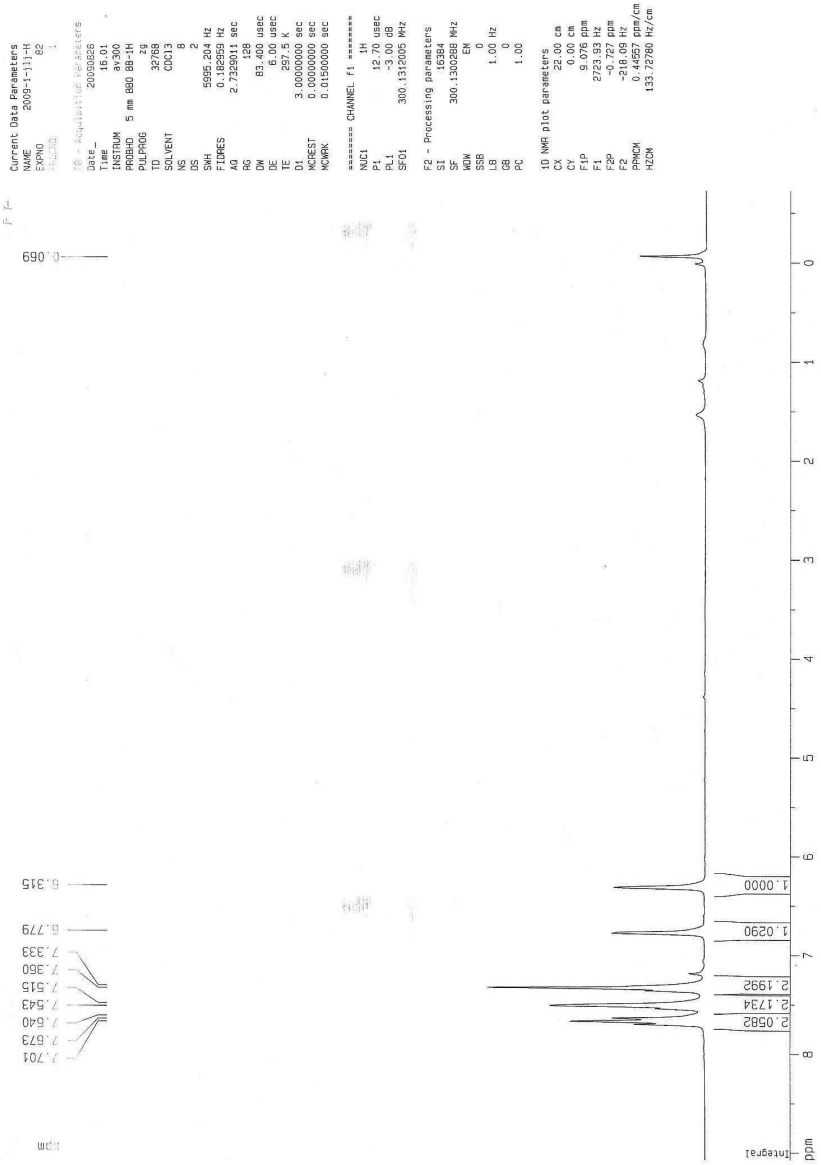
BODIPY **6f**: By reacting BODIPY **4c** (61 mg, 0.2 mmol) and 6-aminocaproic acid (132 mg, 1.0 mmol) using the procedure described above for 10 h at room temperature and purified using chromatograph (silica gel, hexane/EtOAc = 2/1, v/v), the desired compound **6f** was obtained as powder in 63% yield (50 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.0 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 6.87 (s, 1H), 6.81 (brs, 1H), 5.88 (s, 1H), 3.85 (d, J = 5.5 Hz, 2H), 2.45 (s, 3 H), 2.42 (s, 2H), 2.21 (s, 3H), 1.87 (d, J = 6.3 Hz, 2H), 1.74 (d, J= 6.8 Hz, 2H), 1.57 (s, 2H), 1.26 (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.0, 156.8, 140.5, 137.8, 131.3, 128.5, 127.3, 126.4, 126.1, 124.6, 123.9, 119.9, 113.6, 106.3, 44.4, 34.1, 29.6, 25.9, 24.2, 13.8, 11.0. HRMS (EI) Calcd. for $C_{21}H_{24}BF_2N_3O_2$ $[M- HF]^+$: 379.1867, found 379.1858.

3. Copies of ^{1}H NMR and ^{13}C NMR spectra for all new compounds

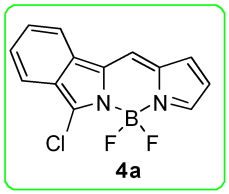


4a

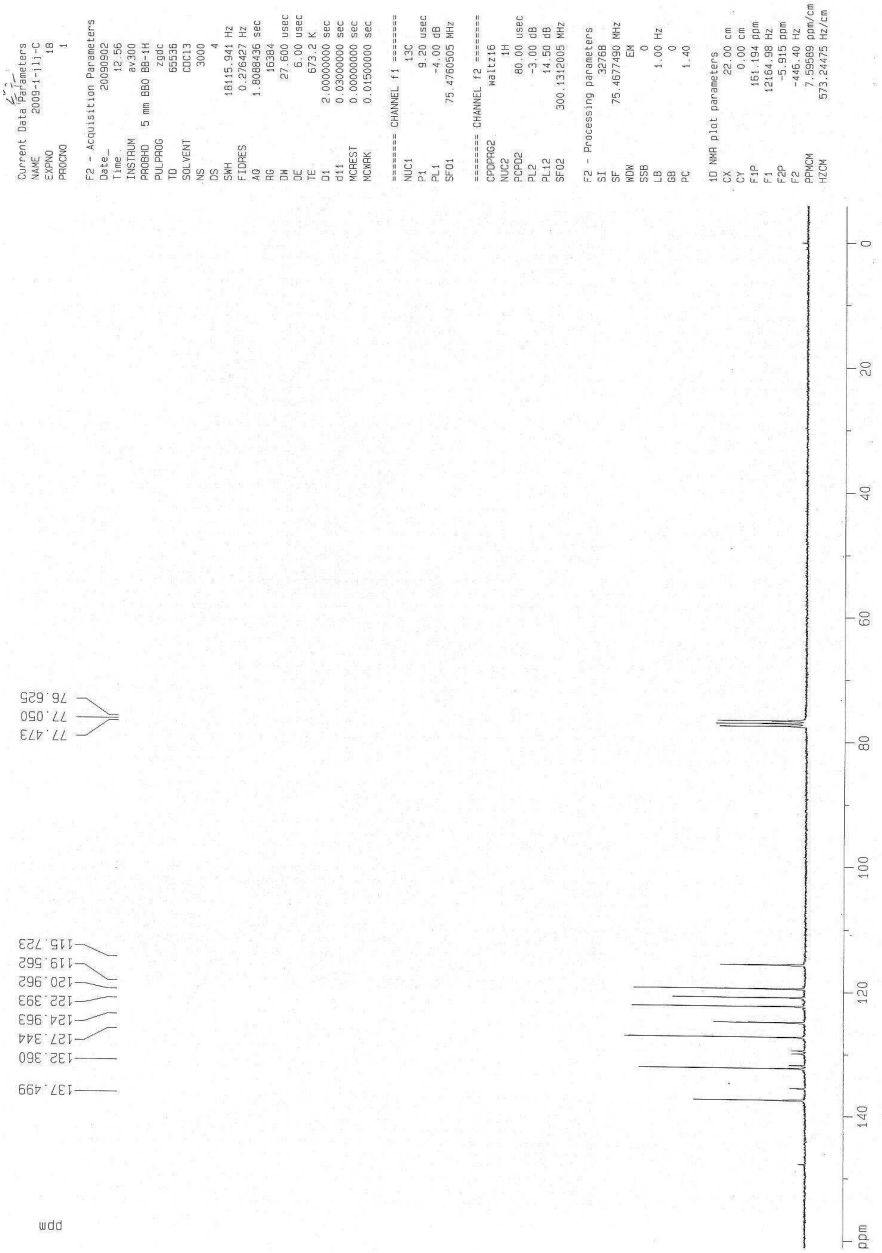
^{1}H NMR compound **4a** in $CDCl_3$

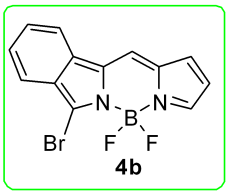


^{13}C NMR of compound **4a** in $CDCl_3$



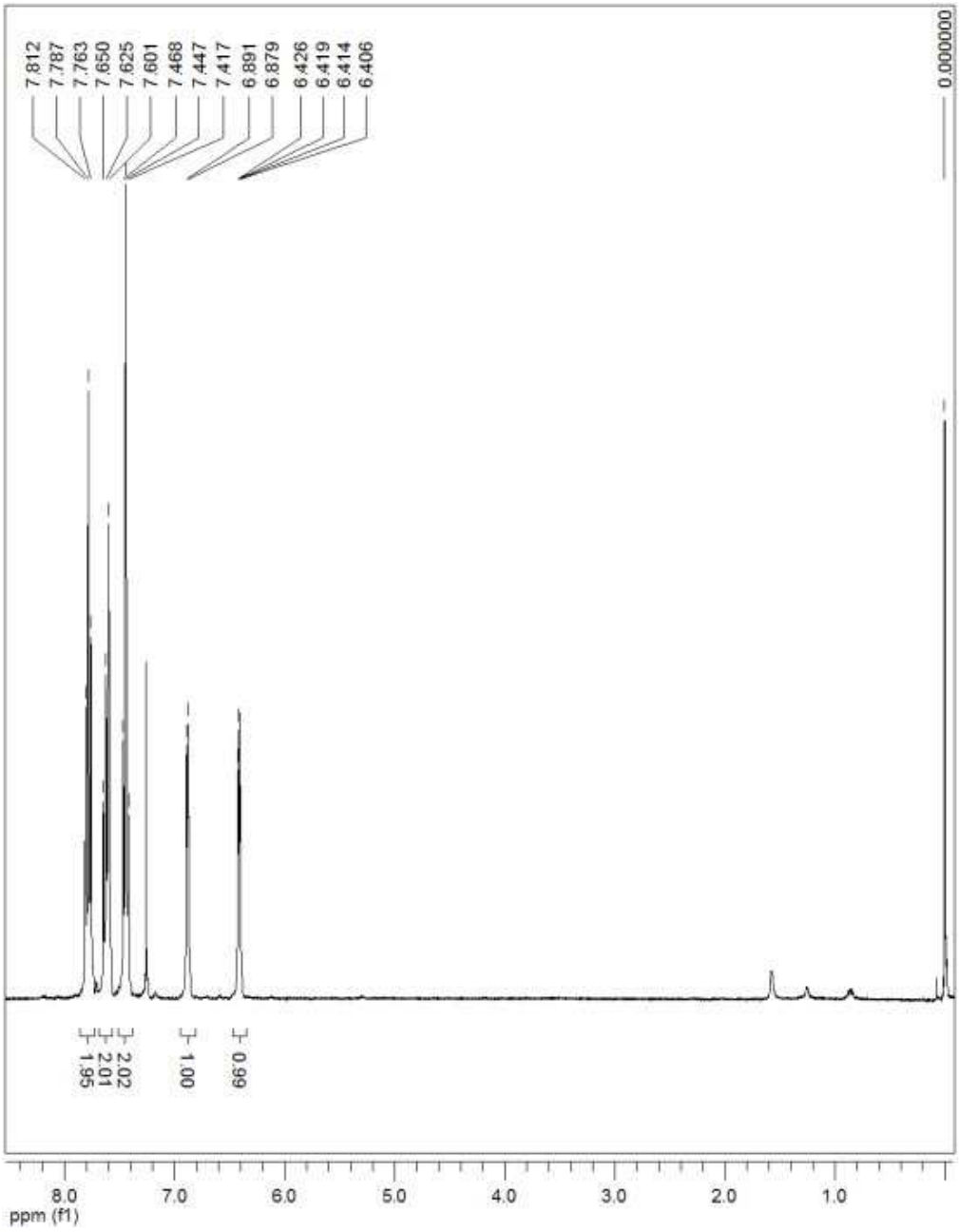
4a



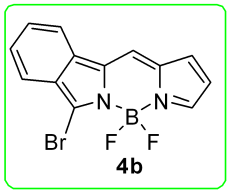


4b

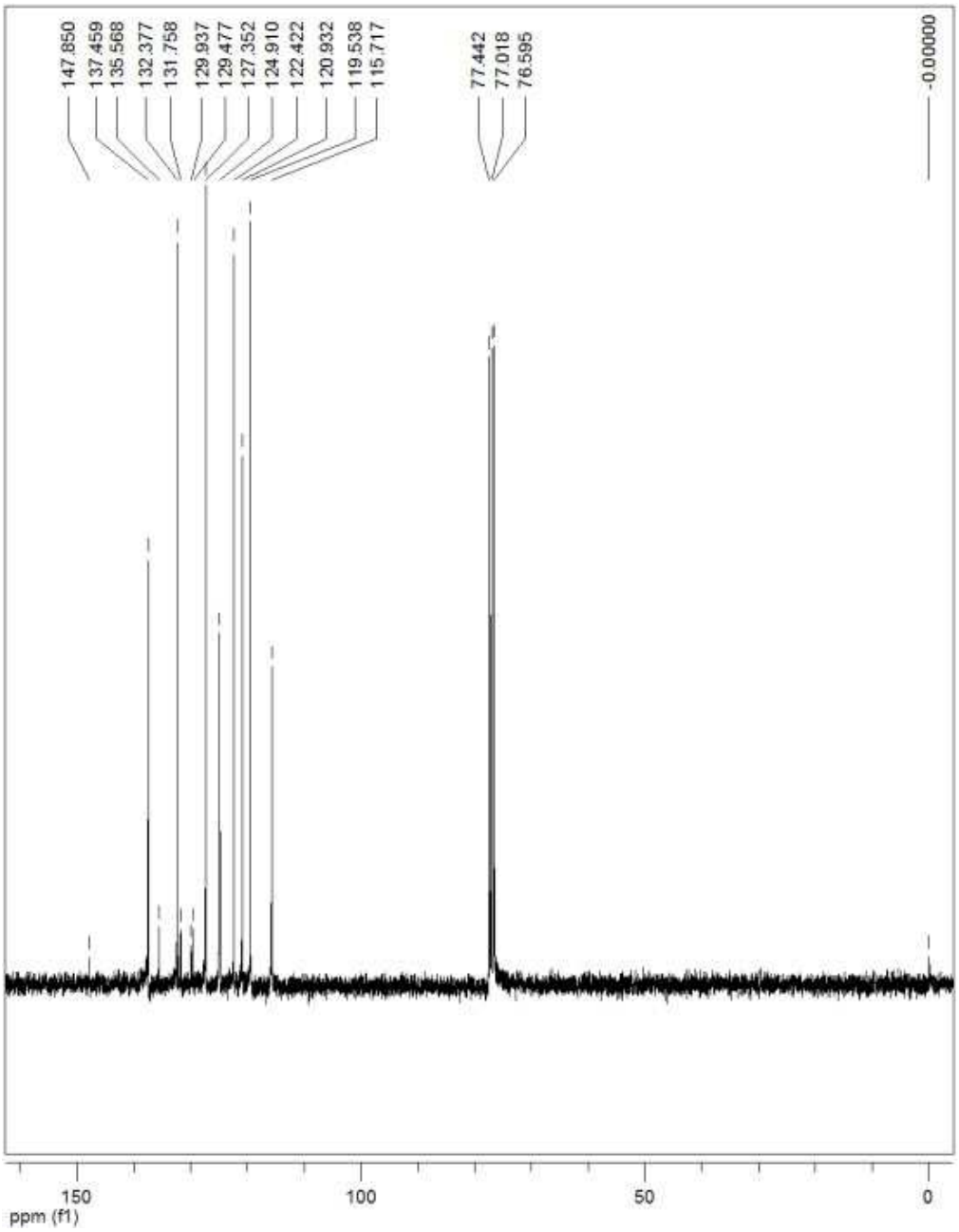
^{1}H NMR compound **4b** in $CDCl_3$

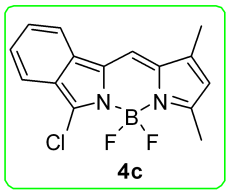


^{13}C NMR of compound **4b** in $CDCl_3$



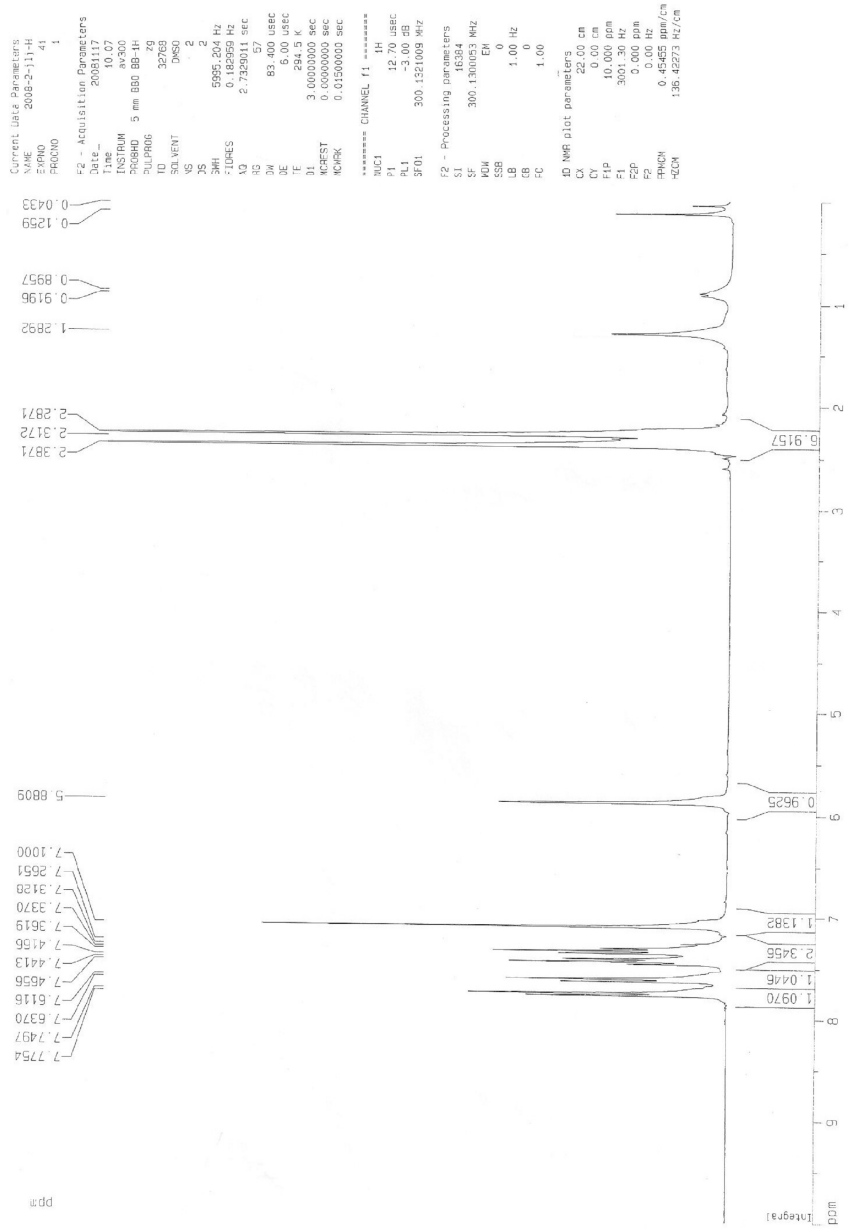
4b



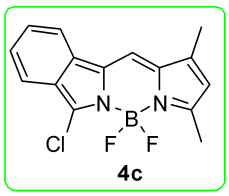


4c

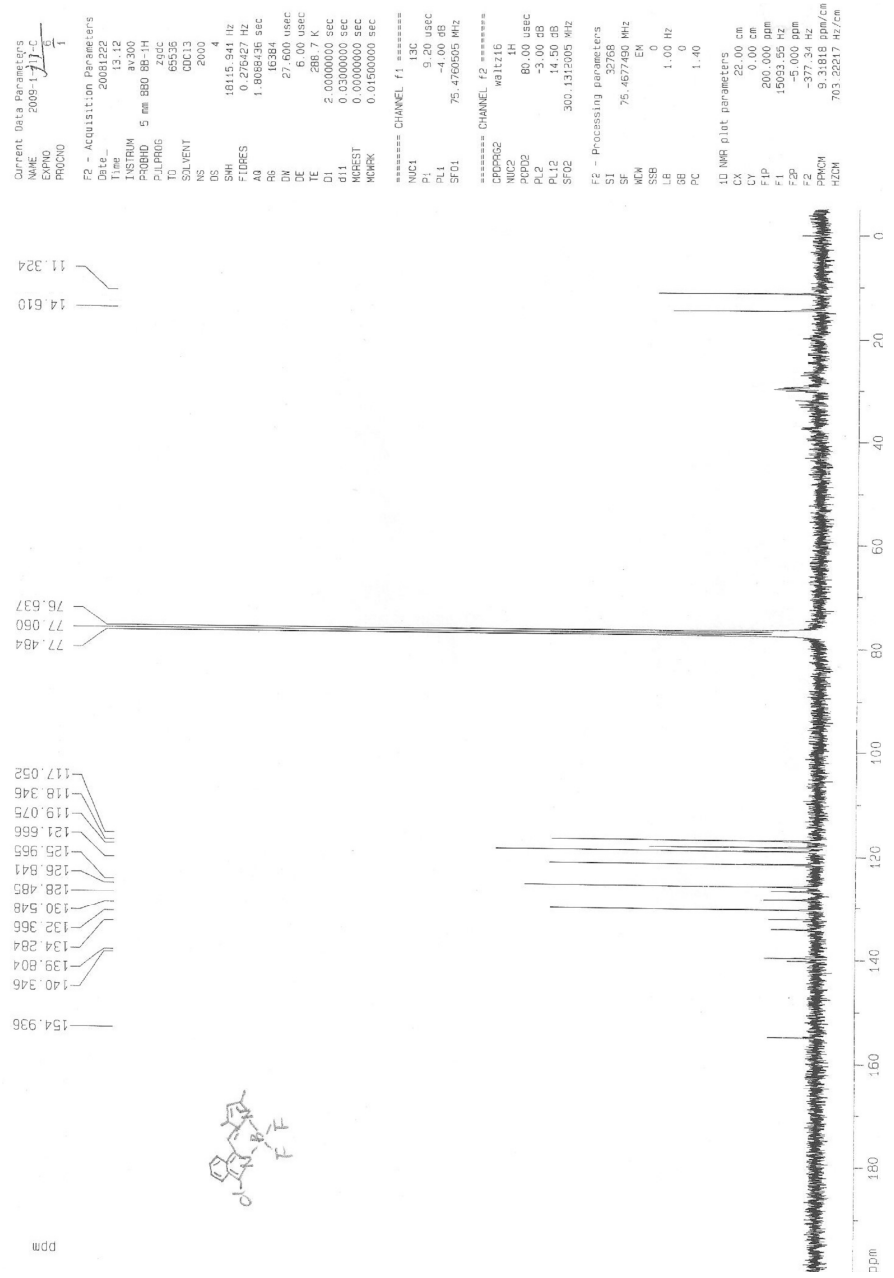
^{1}H NMR compound **4c** in $CDCl_3$

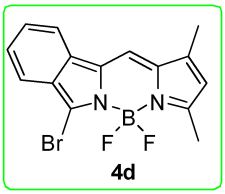


^{13}C NMR of compound **4c** in $CDCl_3$



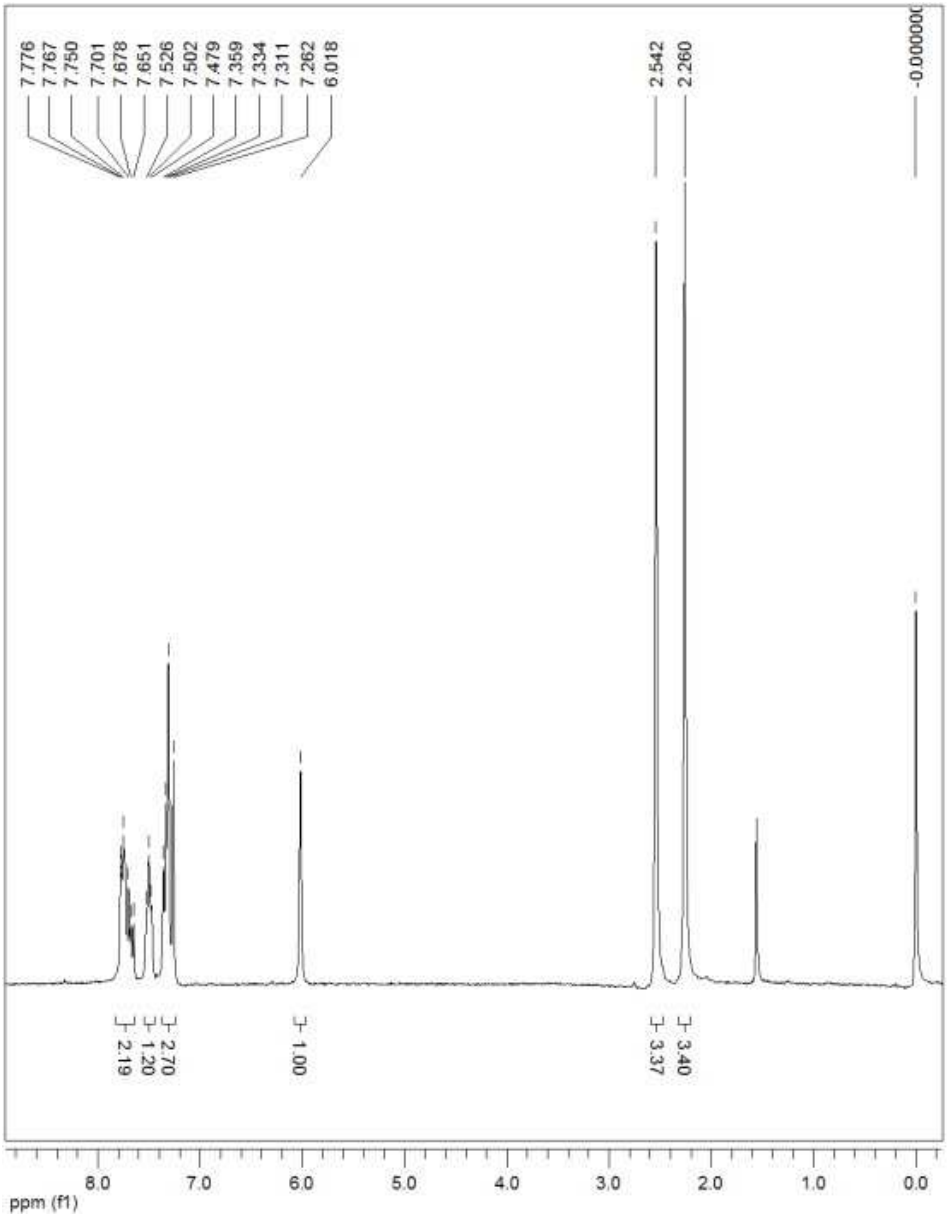
4c



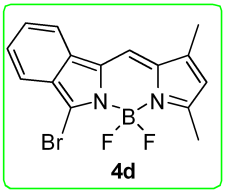


4d

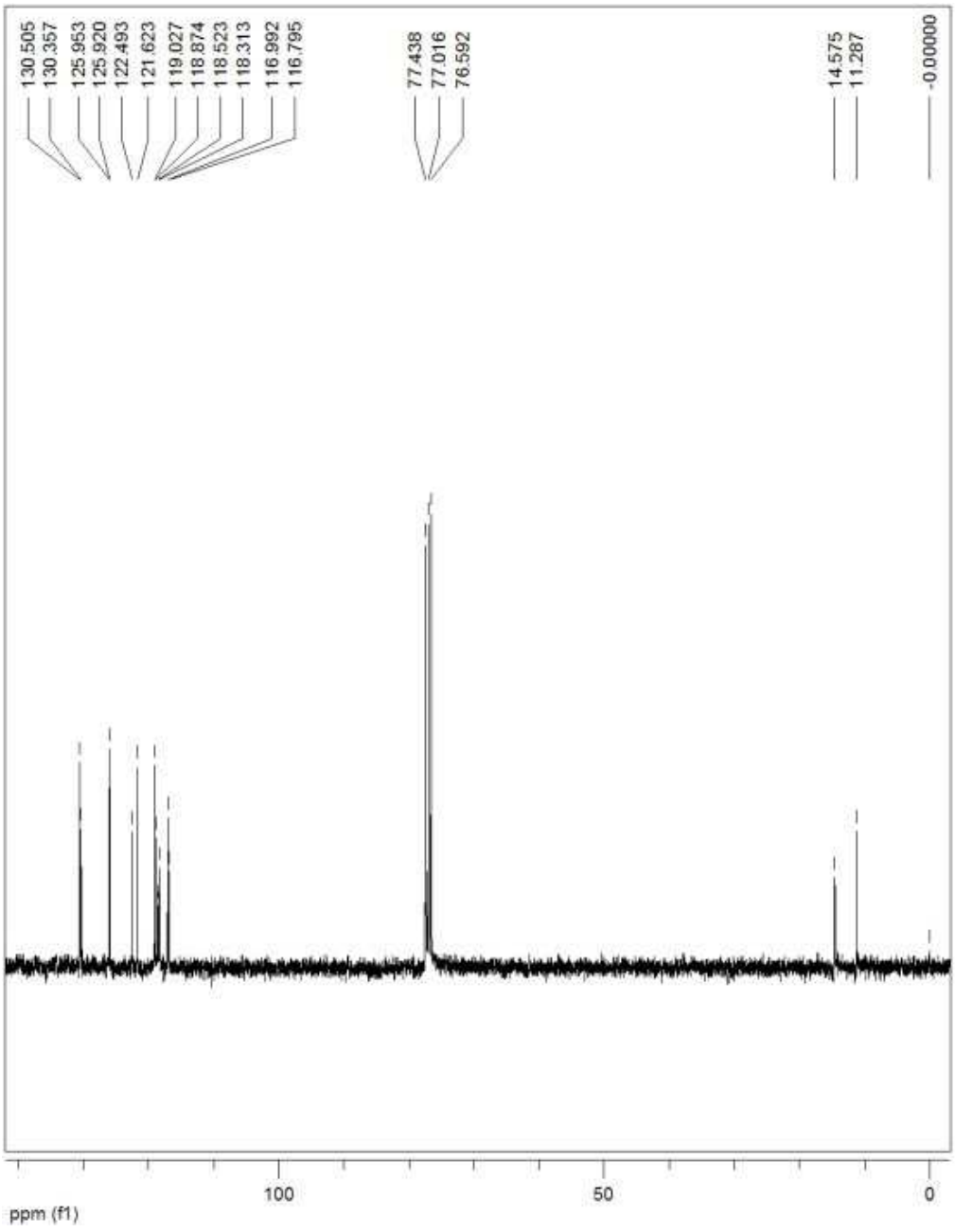
^{1}H NMR compound **4d** in $CDCl_3$

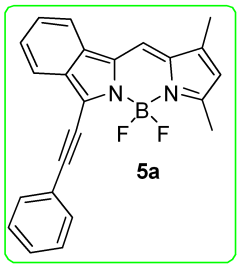


^{13}C NMR of compound **4d** in $CDCl_3$



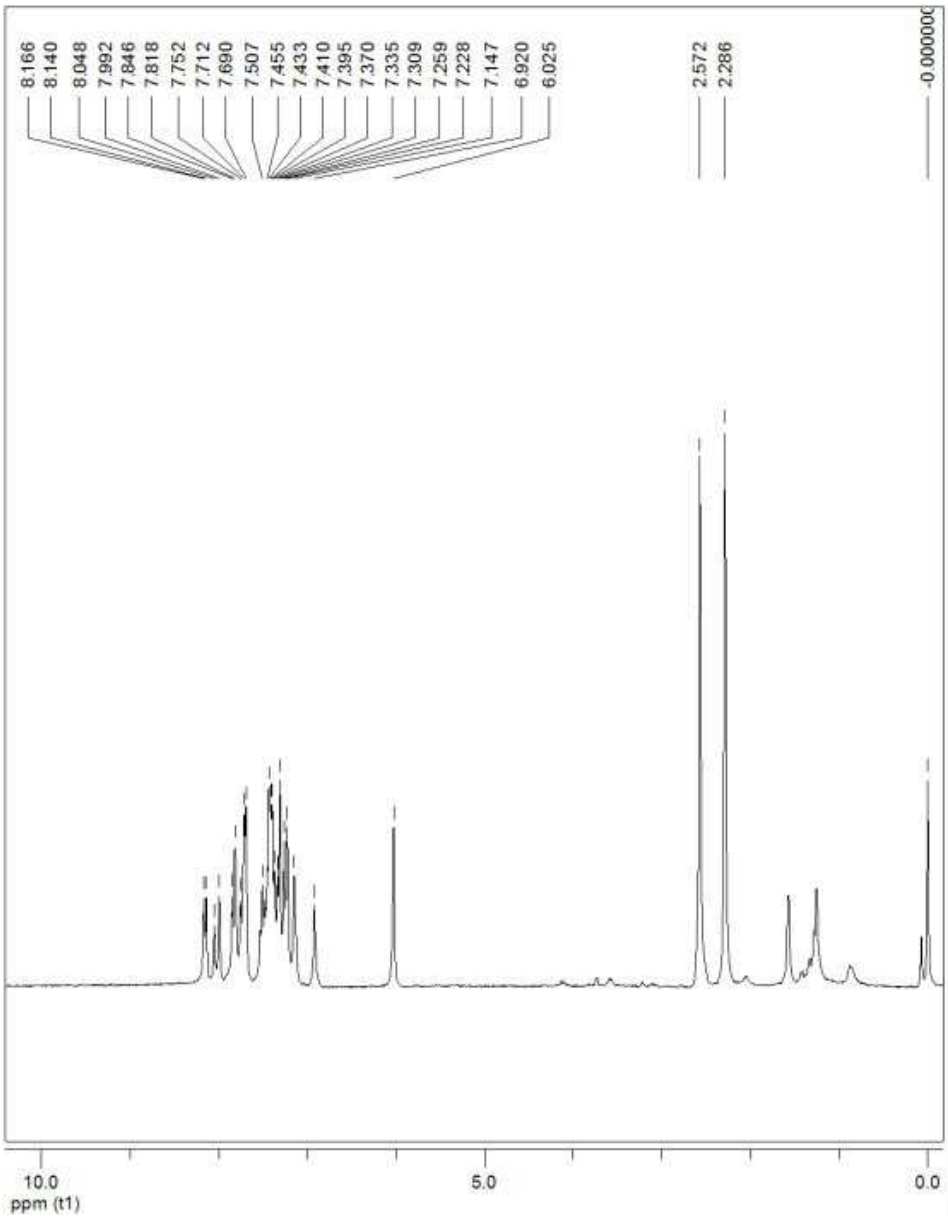
4d



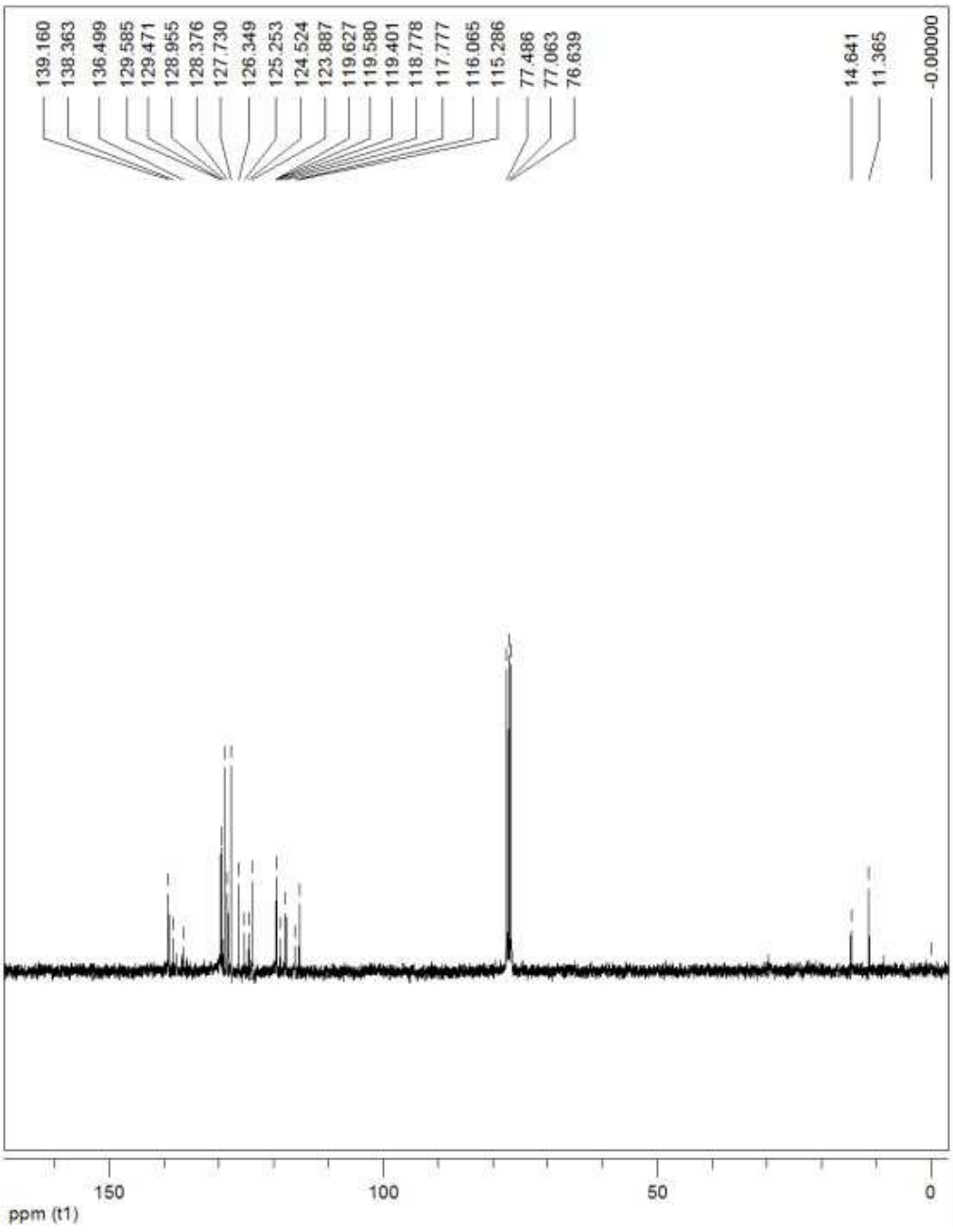


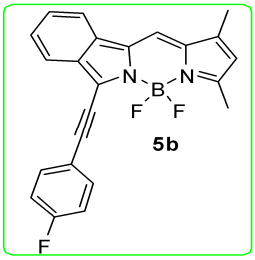
5a

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

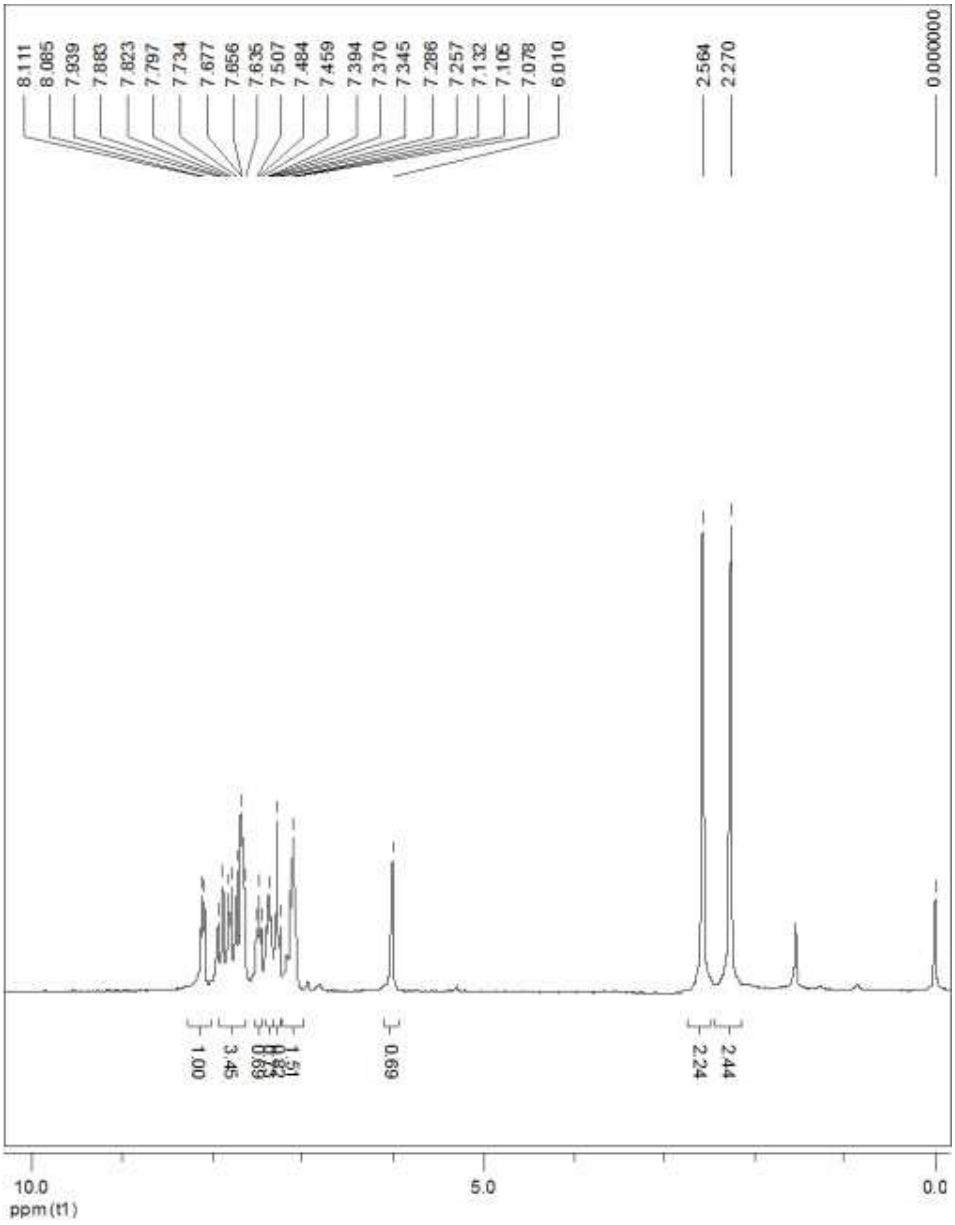


^{13}C NMR of compound **5a** in $CDCl_3$

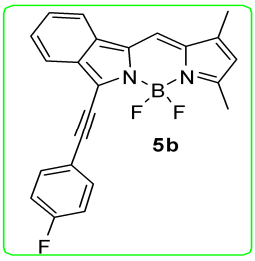


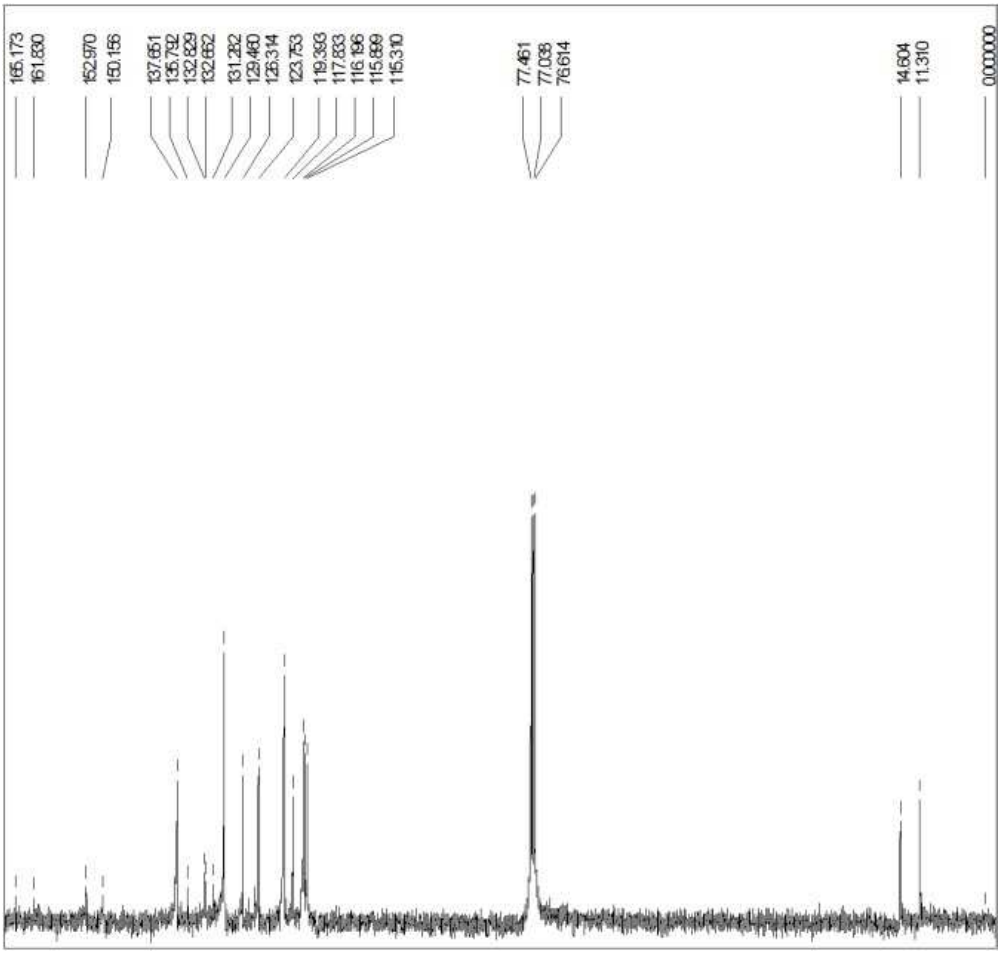


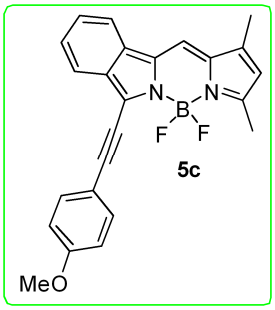
^{1}H NMR compound **5b** in $CDCl_3$



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

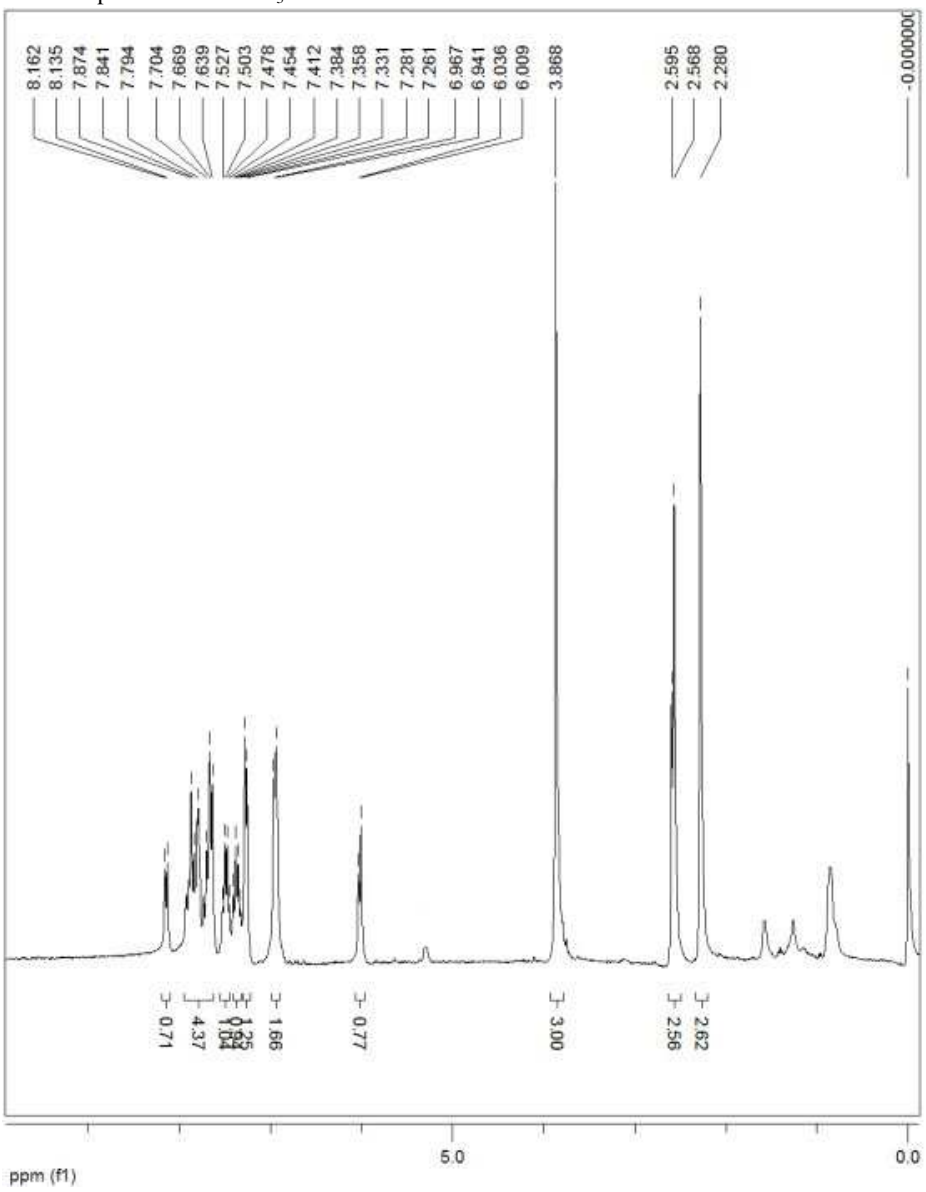




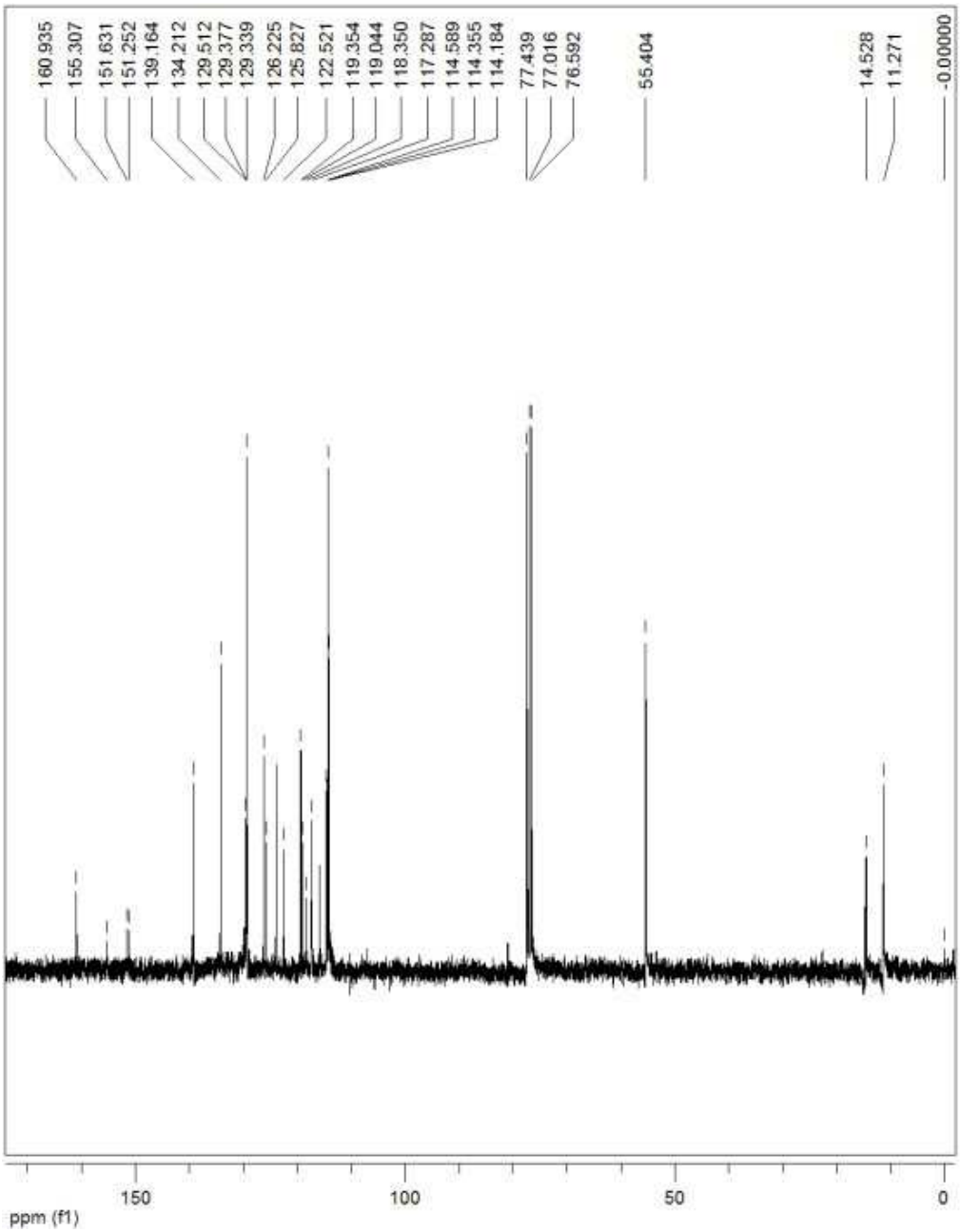


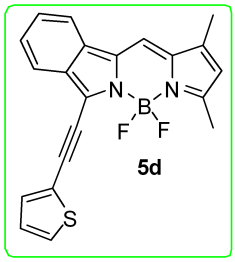
5c

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



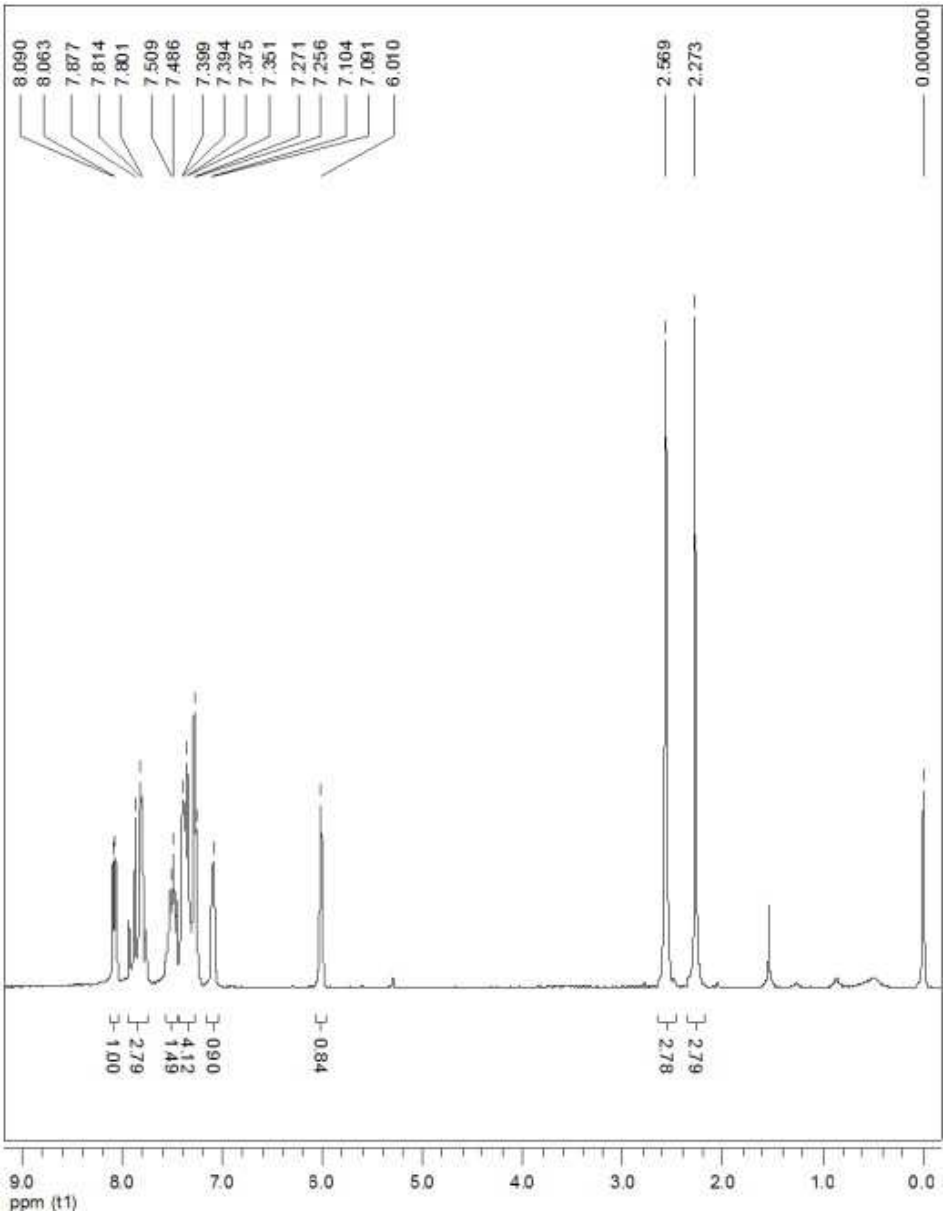
^{13}C NMR of compound **5c** in $CDCl_3$





5d

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



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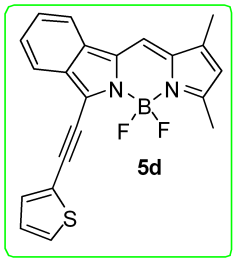
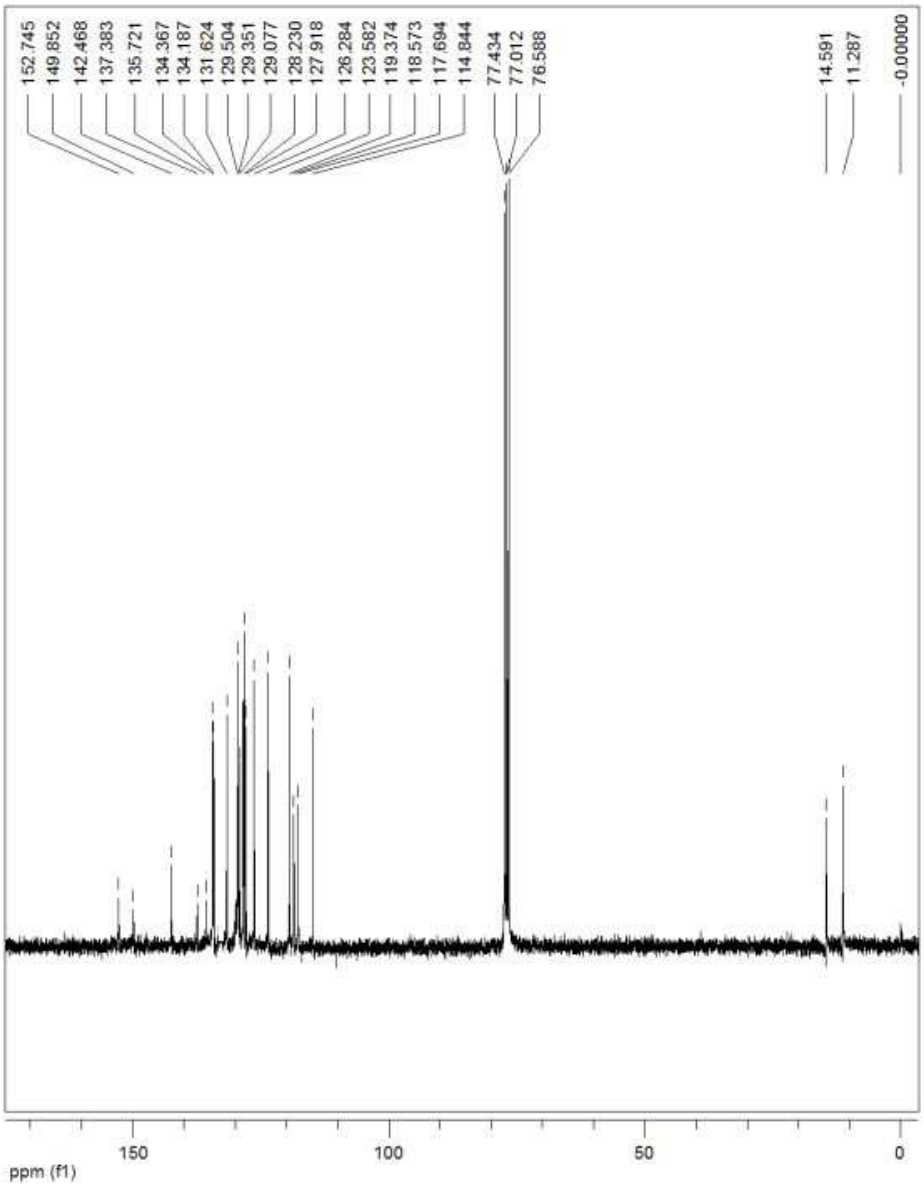
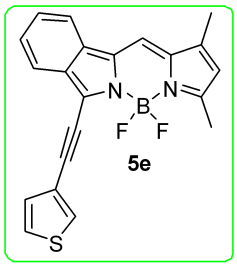


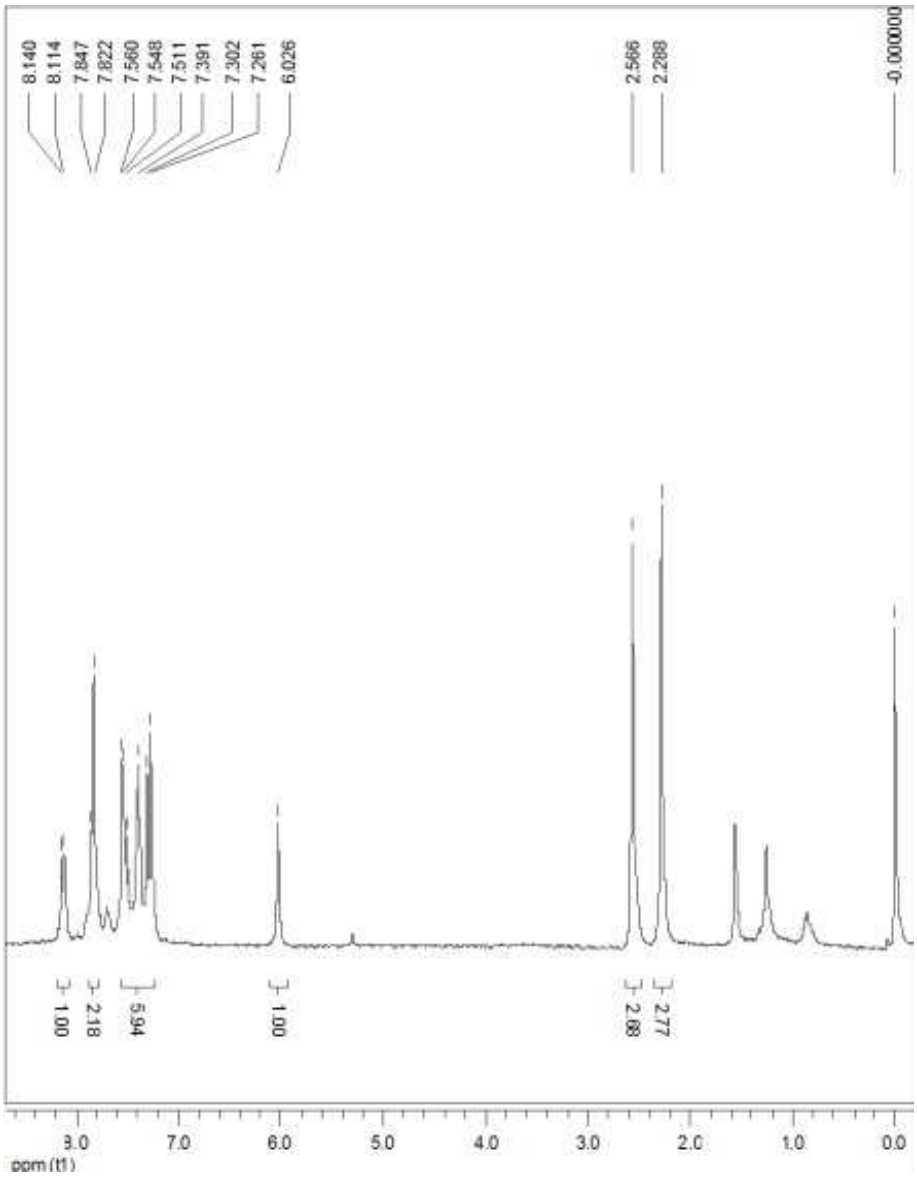
5d



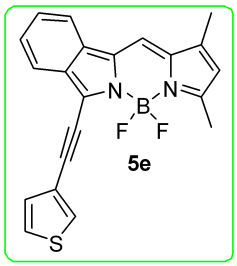


5e

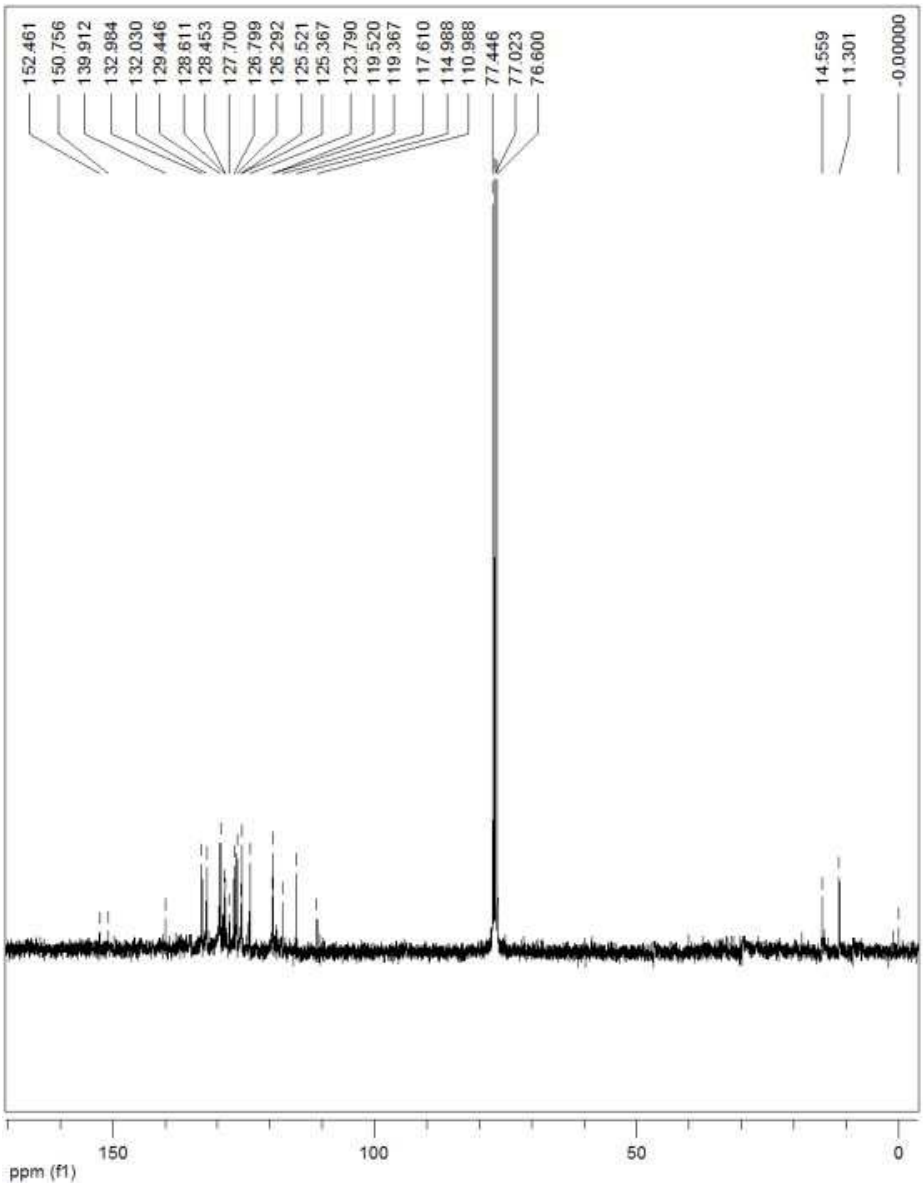
^{1}H NMR compound **5e** in $CDCl_3$

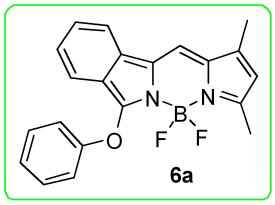


^{13}C NMR of compound **5e** in $CDCl_3$



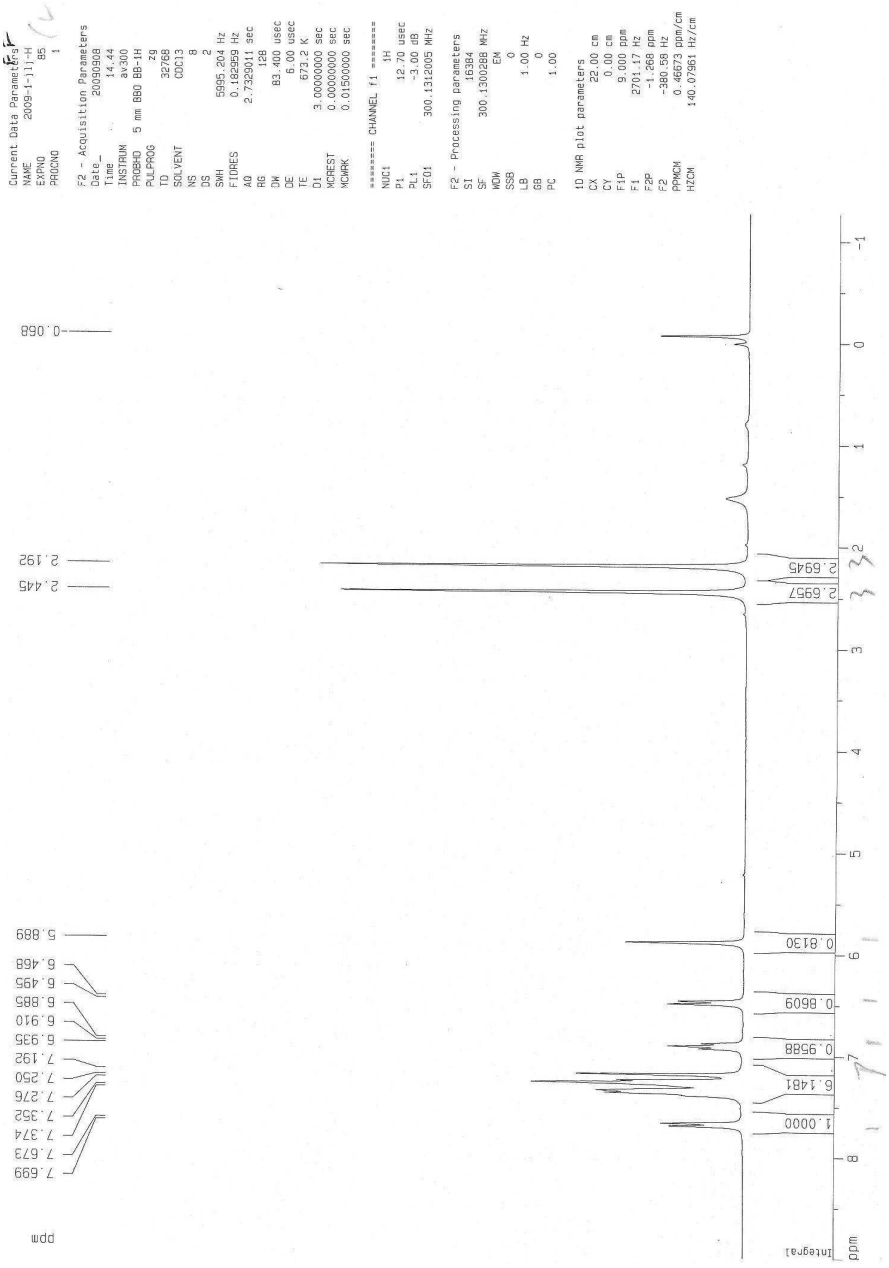
5e



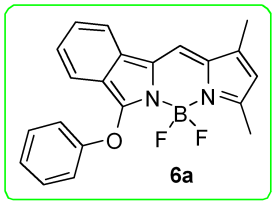


6a

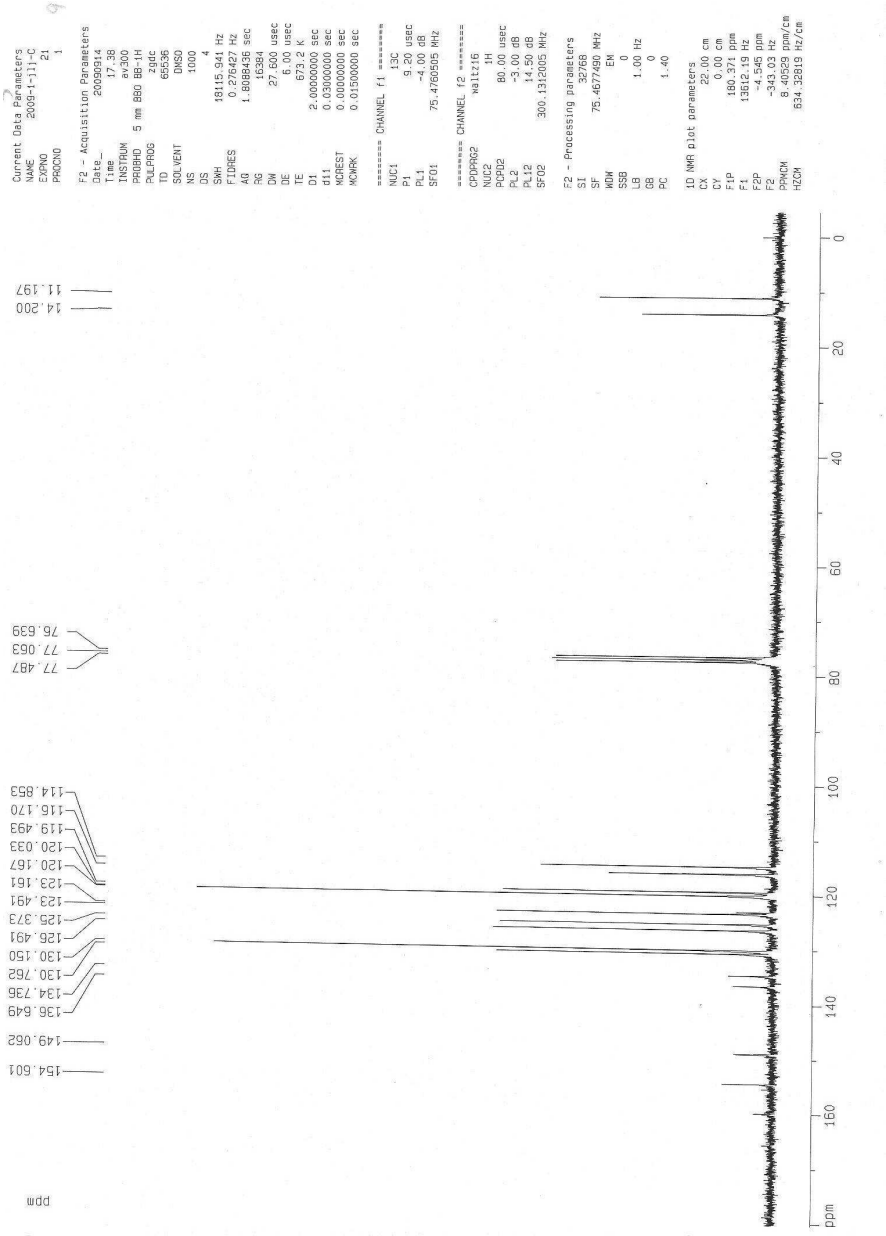
^{1}H NMR of compound **6a** in $CDCl_3$

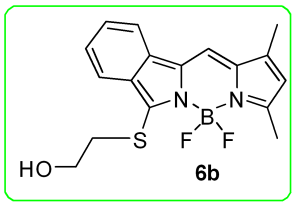


^{13}C NMR of compound **6a** in $CDCl_3$

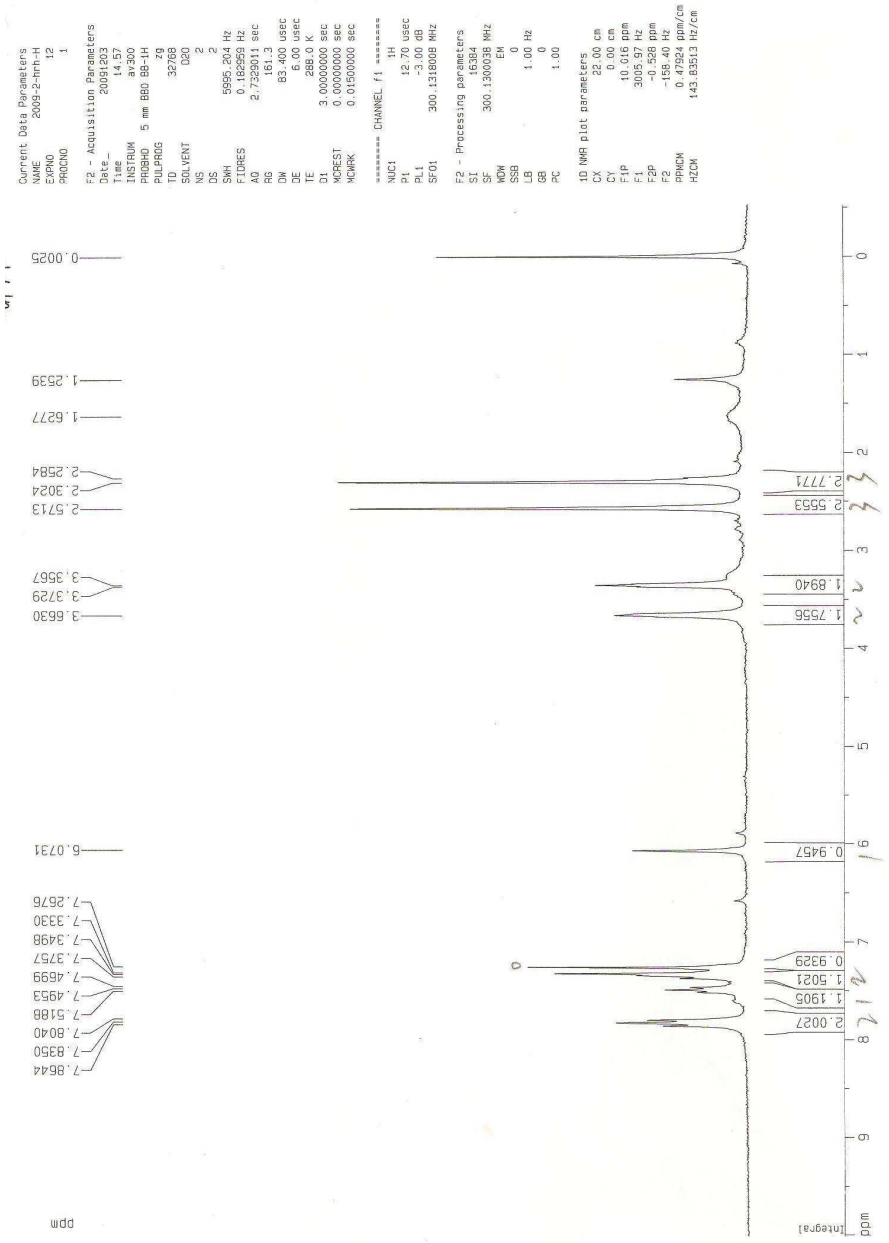


6a

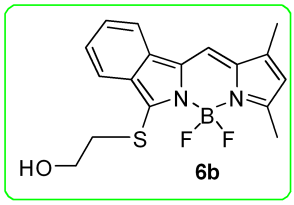




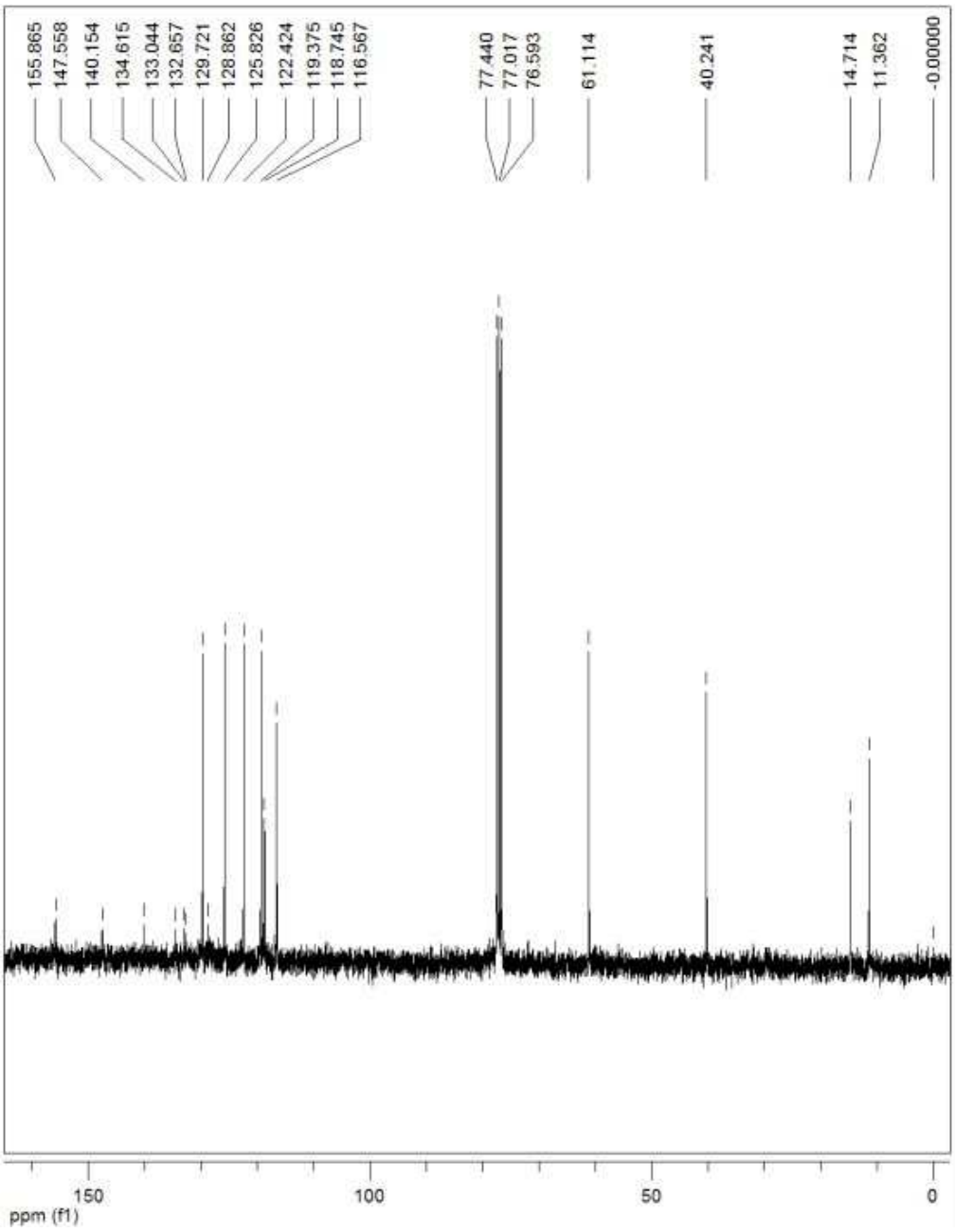
^{1}H NMR of compound **6b** in $CDCl_3$

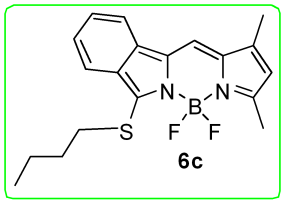


^{13}C NMR of compound **6b** in $CDCl_3$



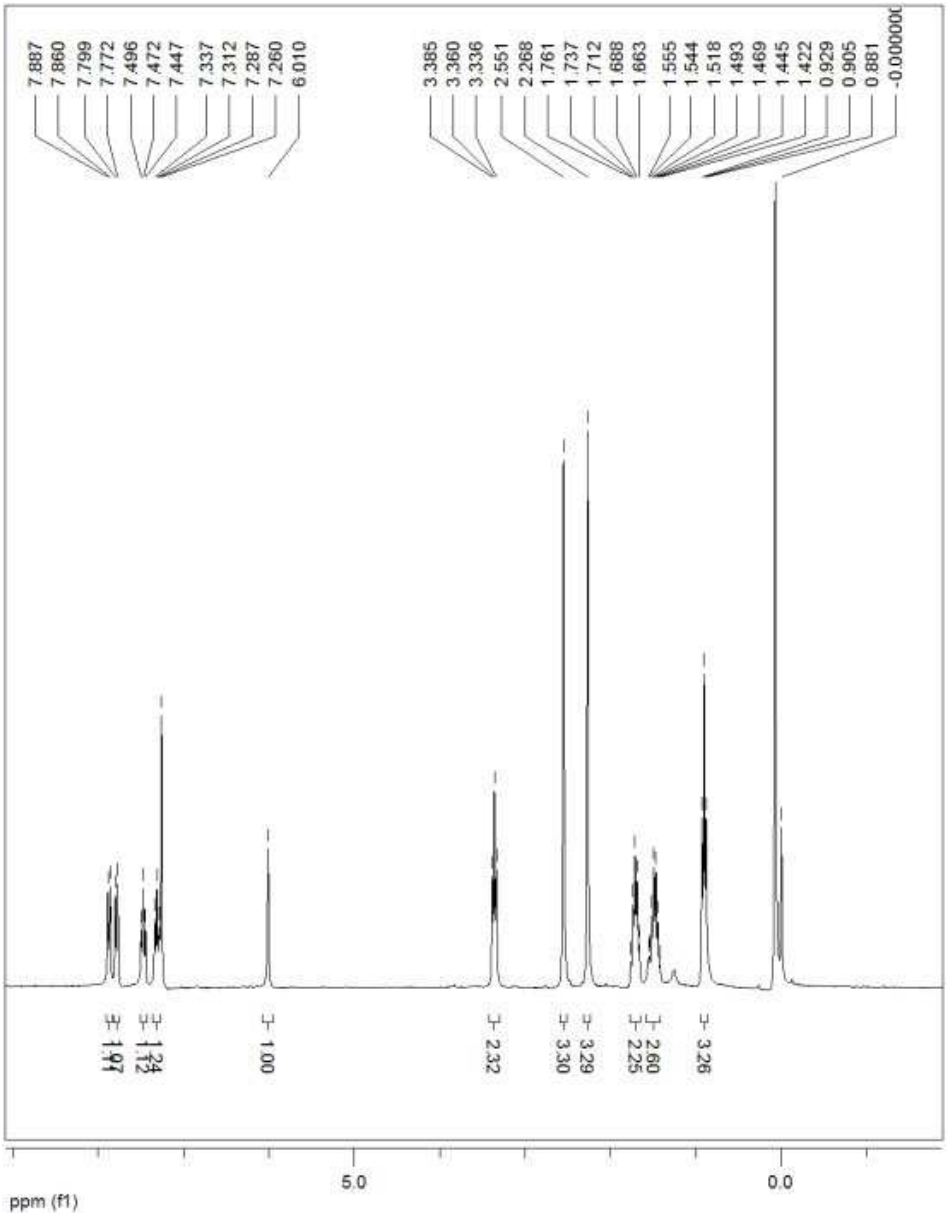
6b



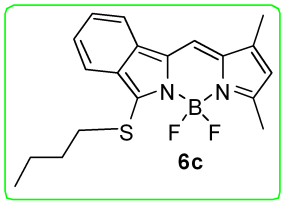


6c

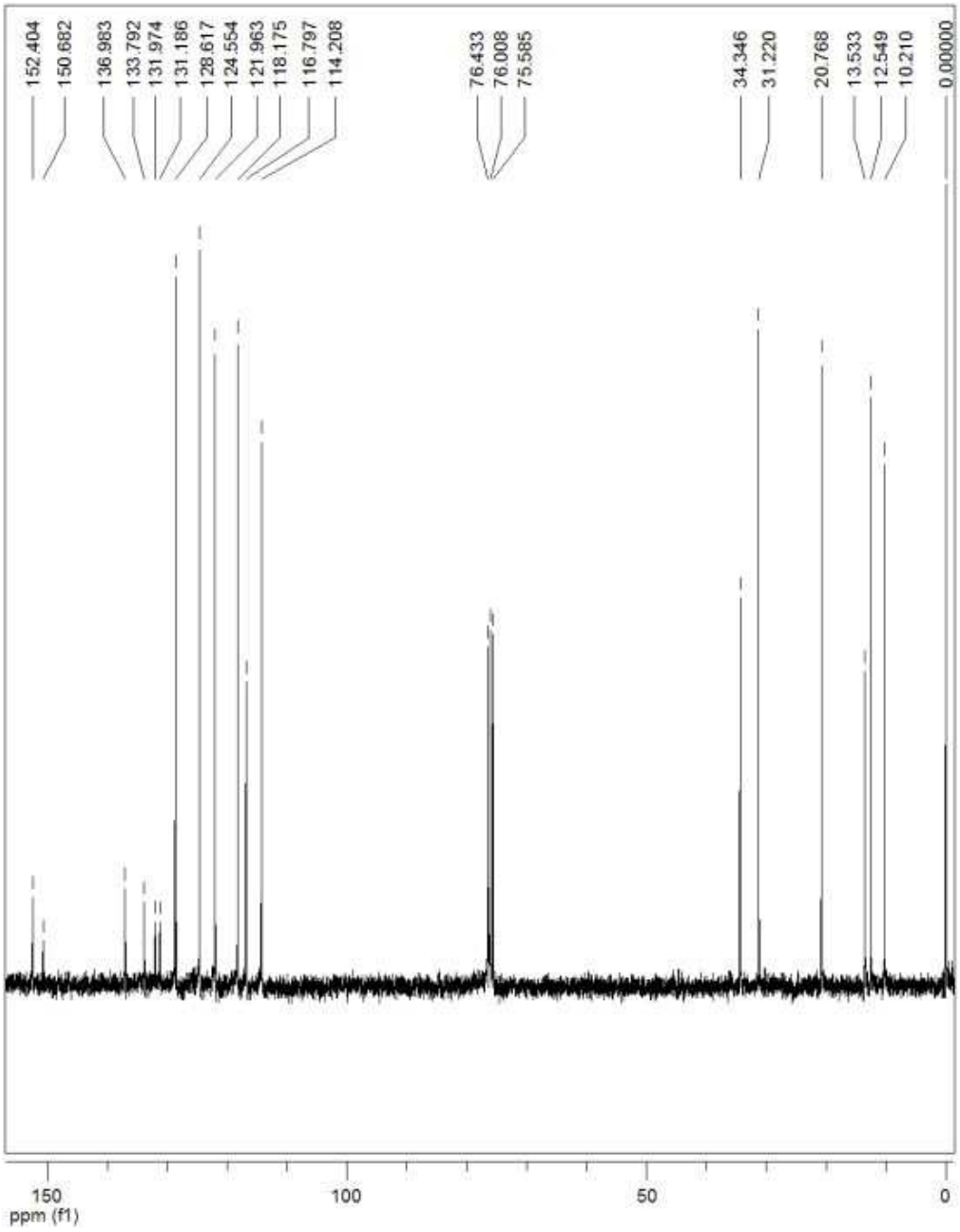
^{1}H NMR of compound **6c** in $CDCl_3$

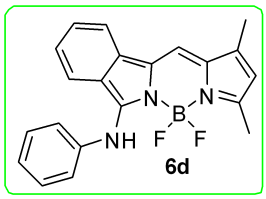


^{13}C NMR of compound **6c** in $CDCl_3$



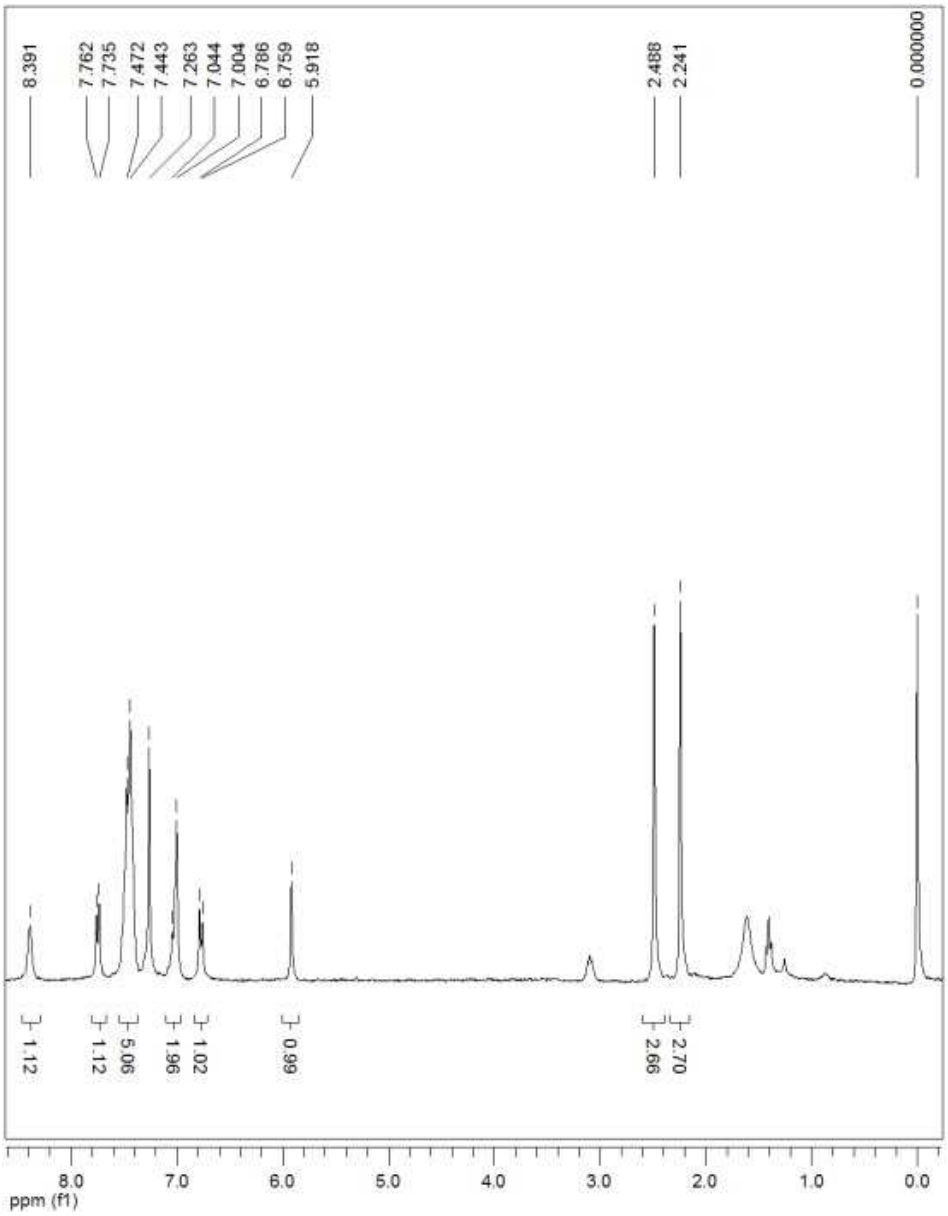
6c



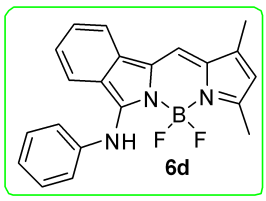


6d

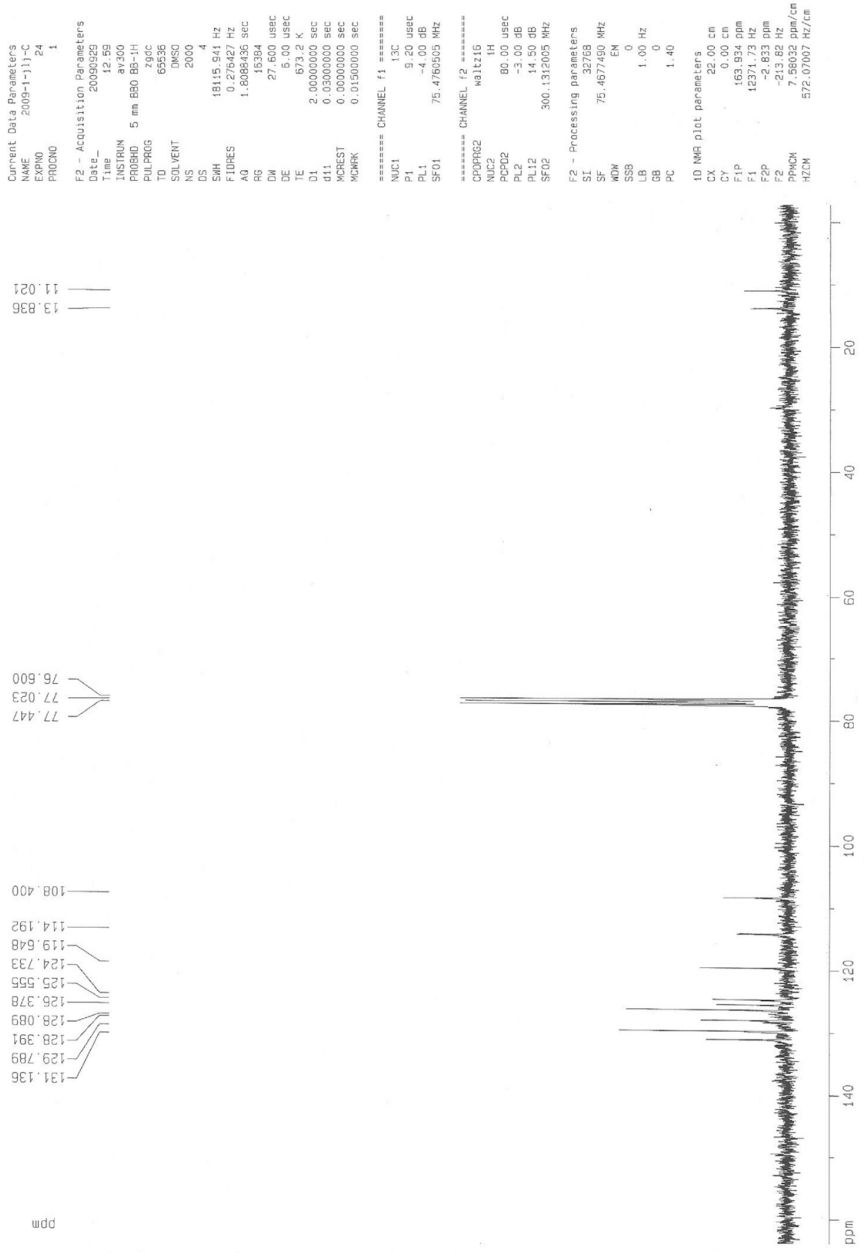
^{1}H NMR of compound **6d** in $CDCl_3$

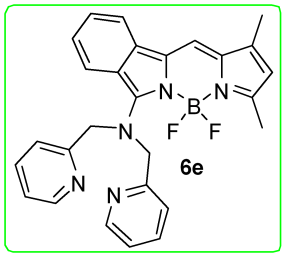


^{13}C NMR of compound **6d** in $CDCl_3$

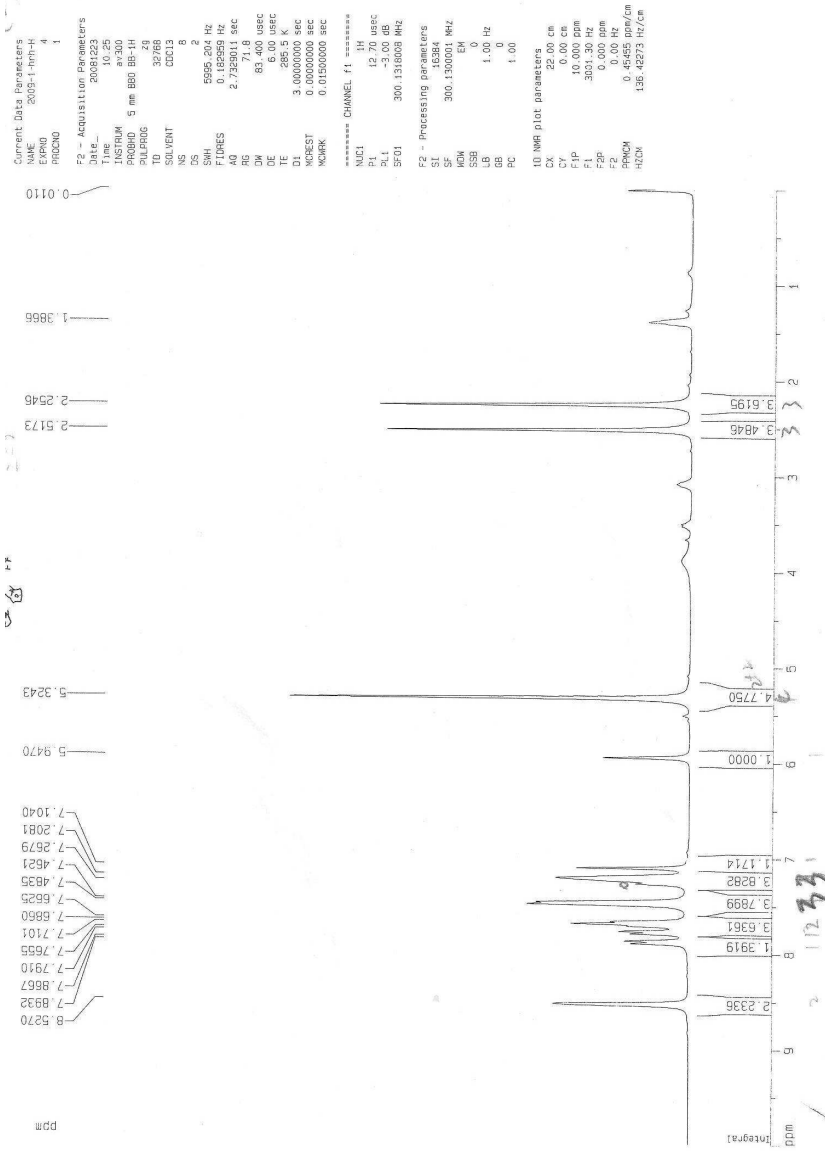


6d

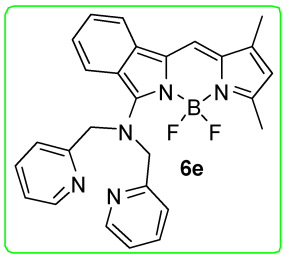


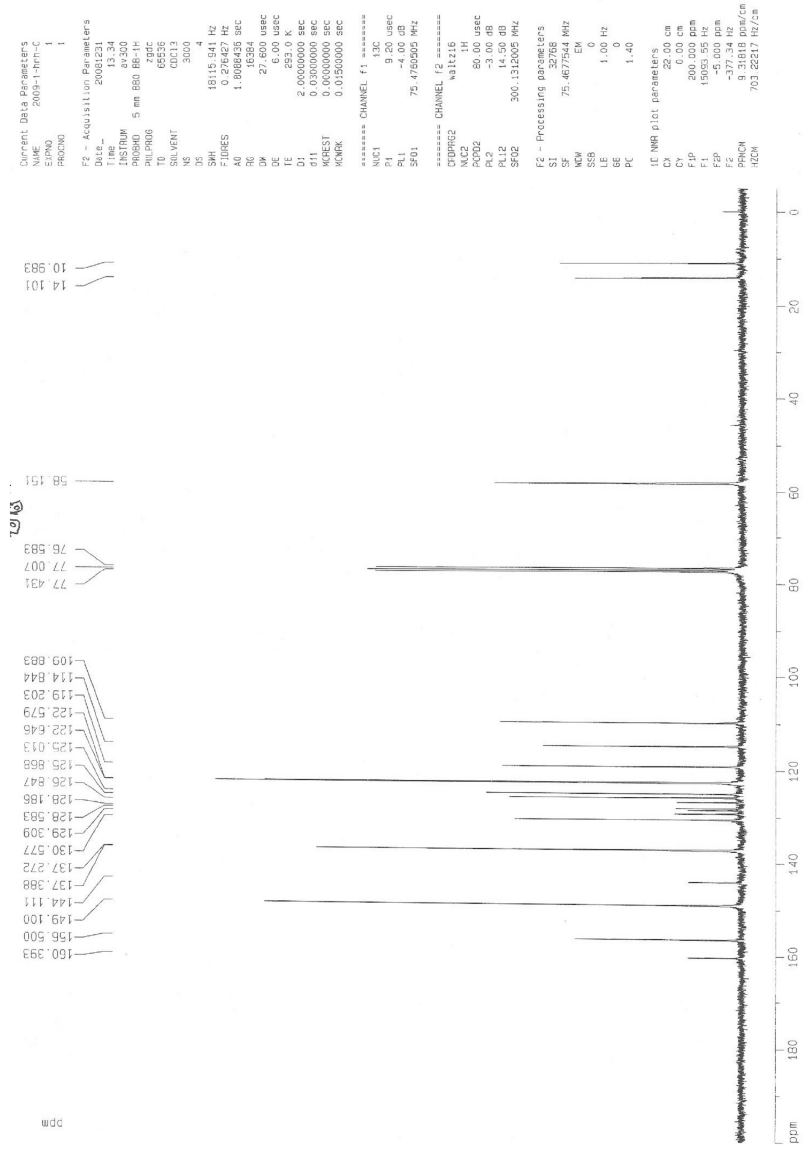


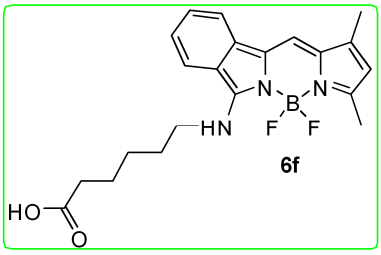
^{1}H NMR of compound **6e** in $CDCl_3$



^{13}C NMR of compound **6e** in $CDCl_3$

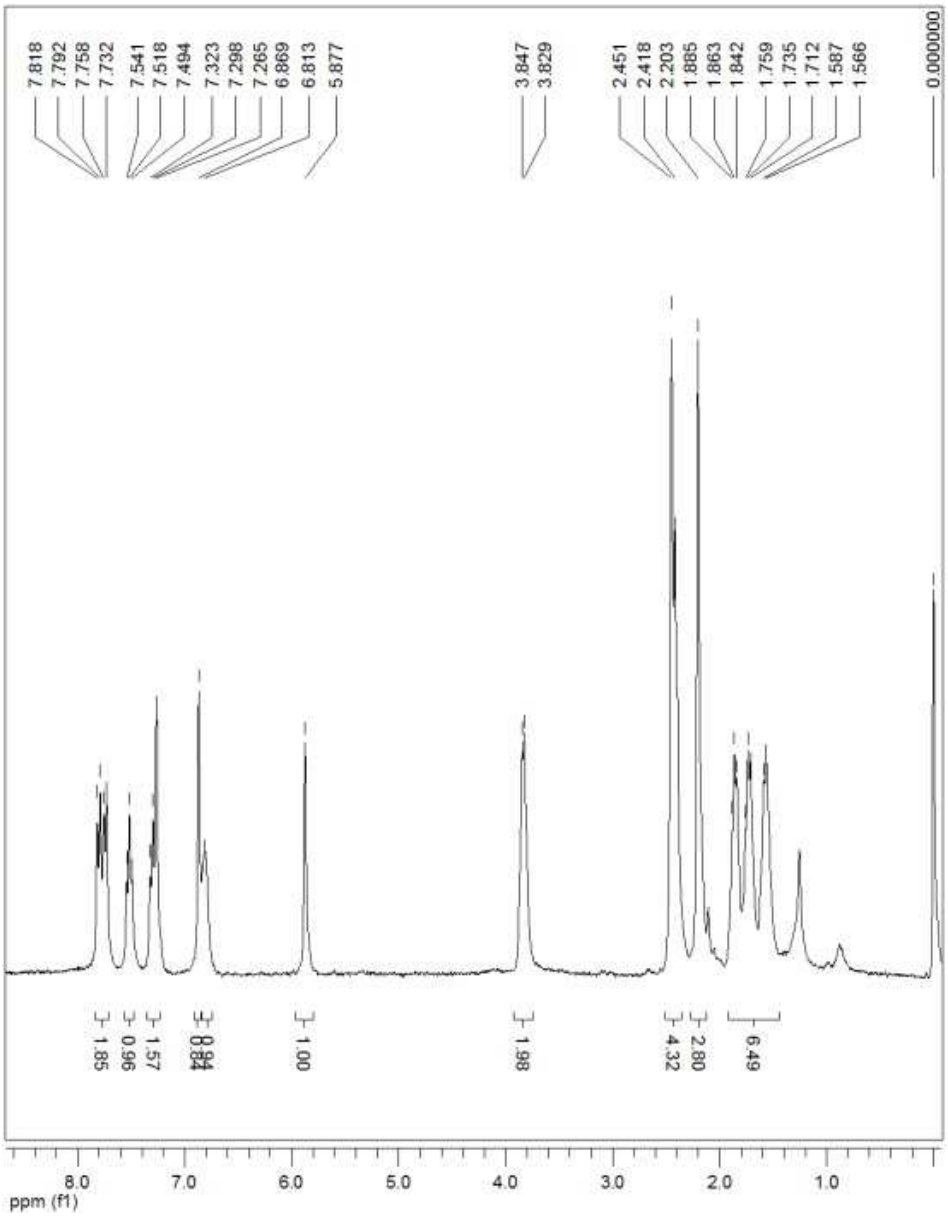




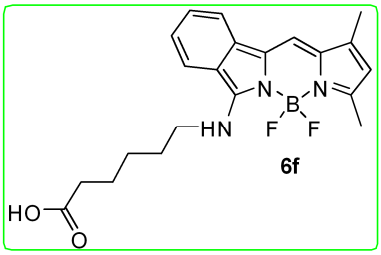


6f

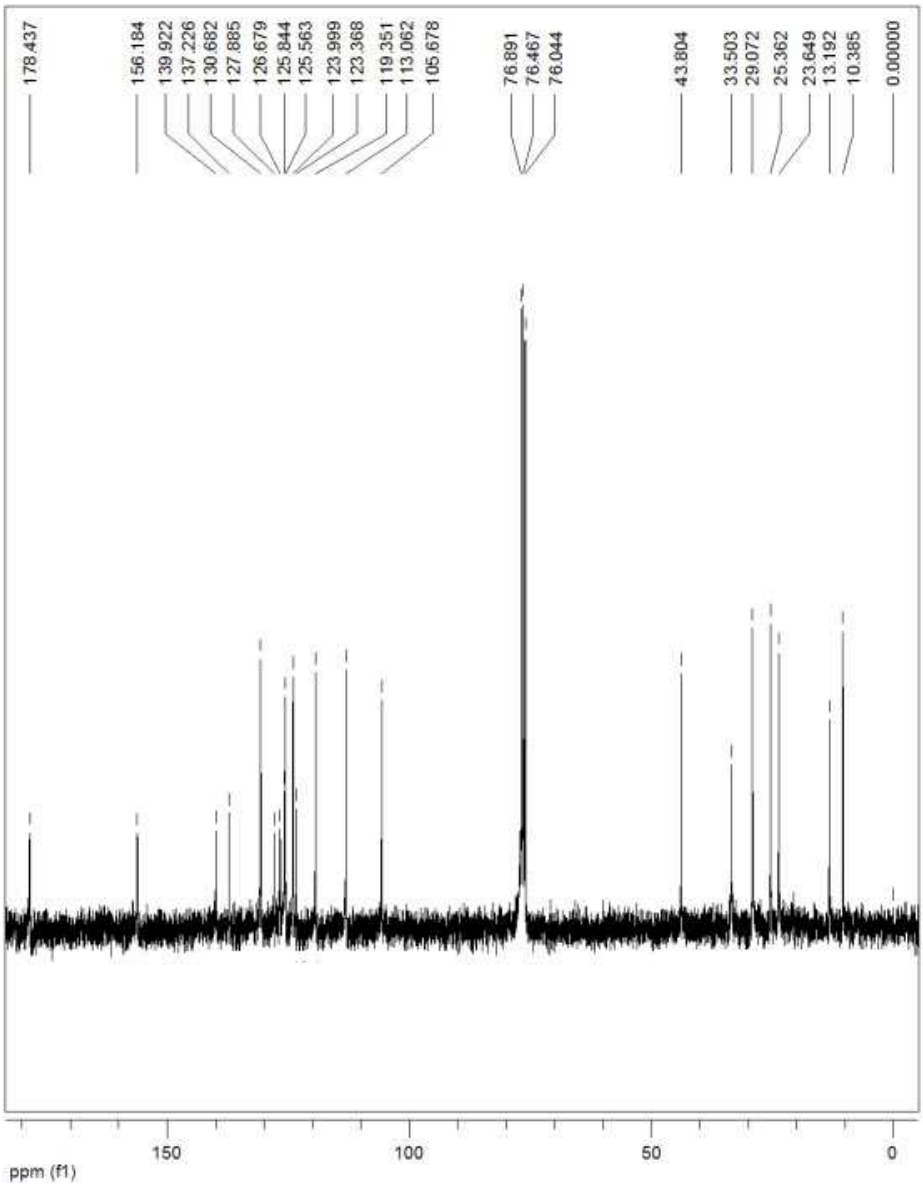
^{1}H NMR of compound **6f** in $CDCl_3$



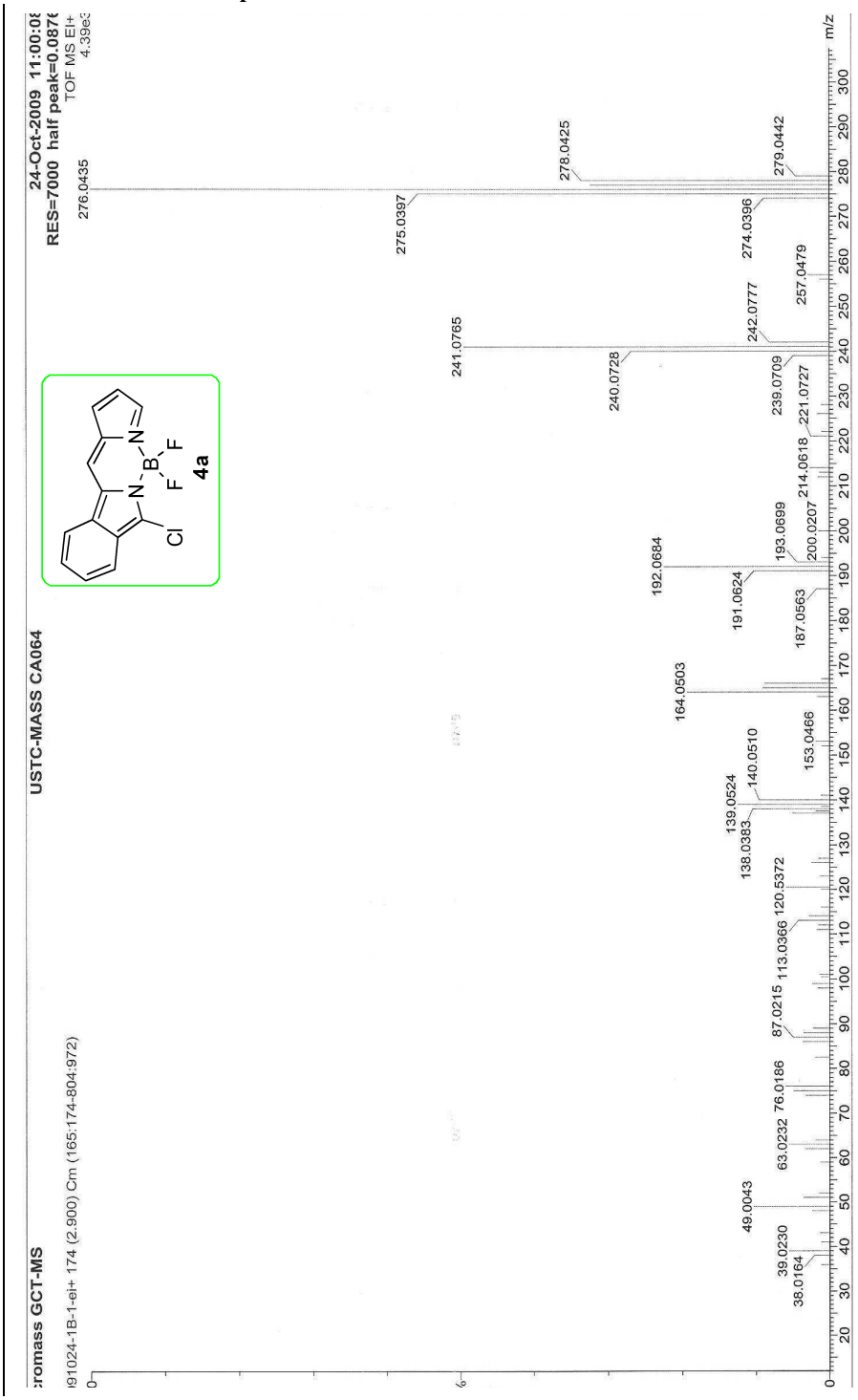
^{13}C NMR of compound **6f** in $CDCl_3$

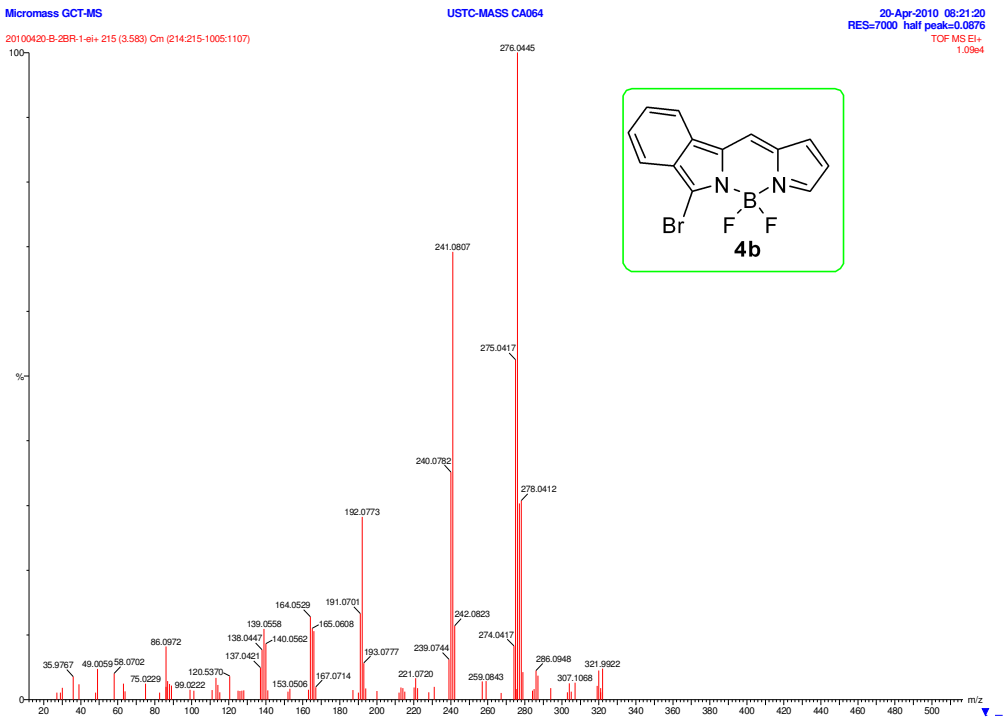


6f

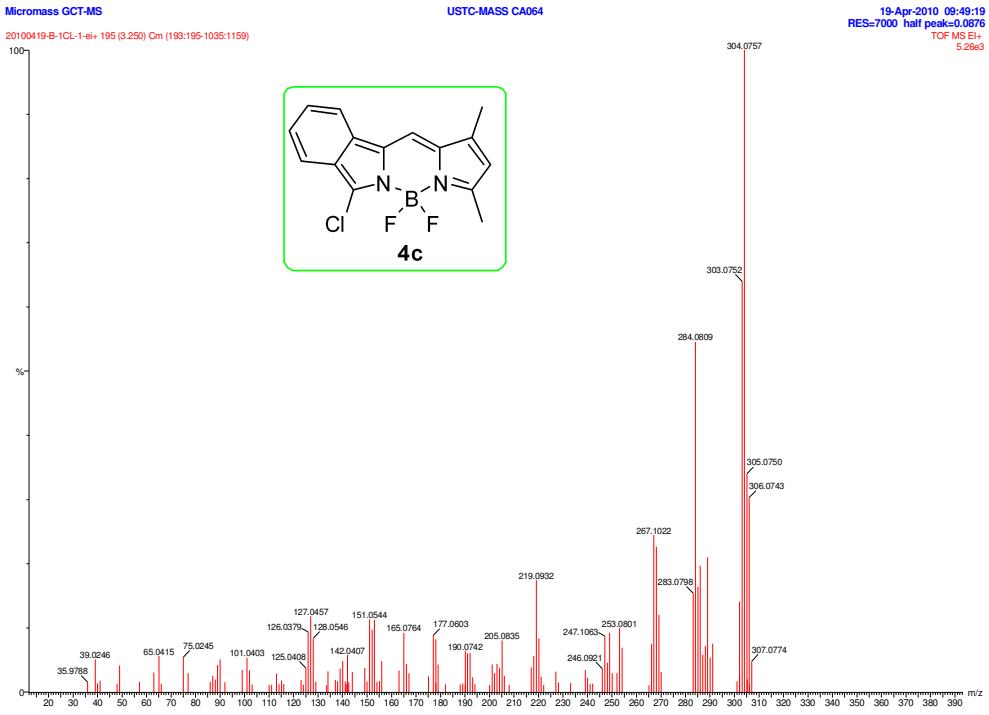


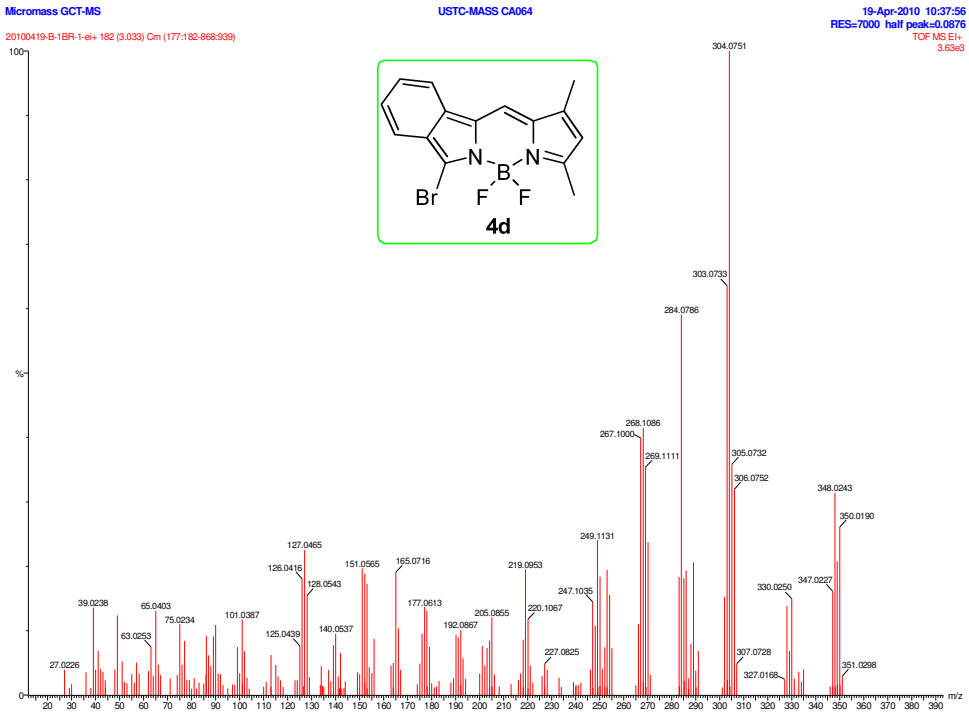
4. MS for all new compounds:

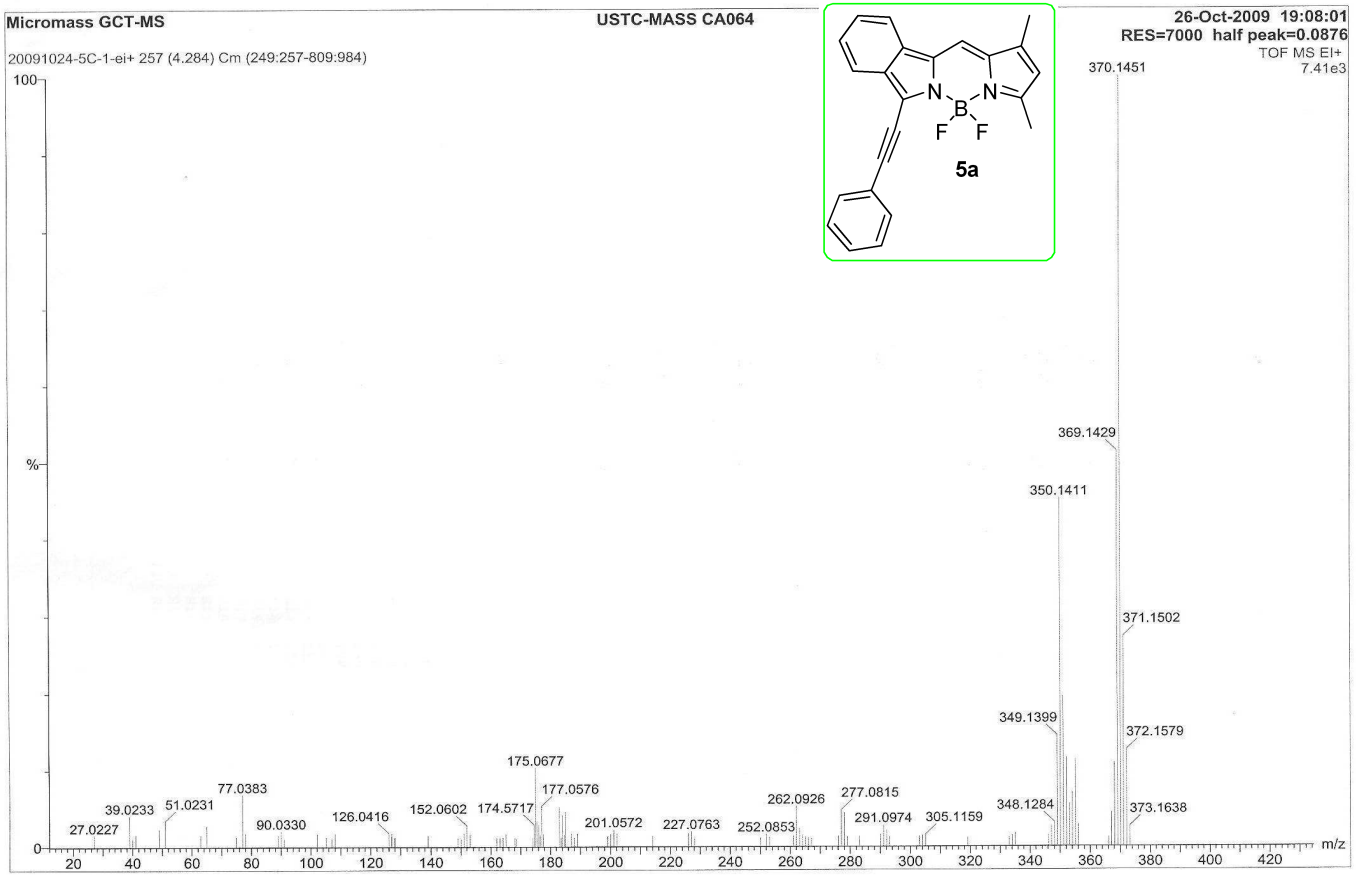


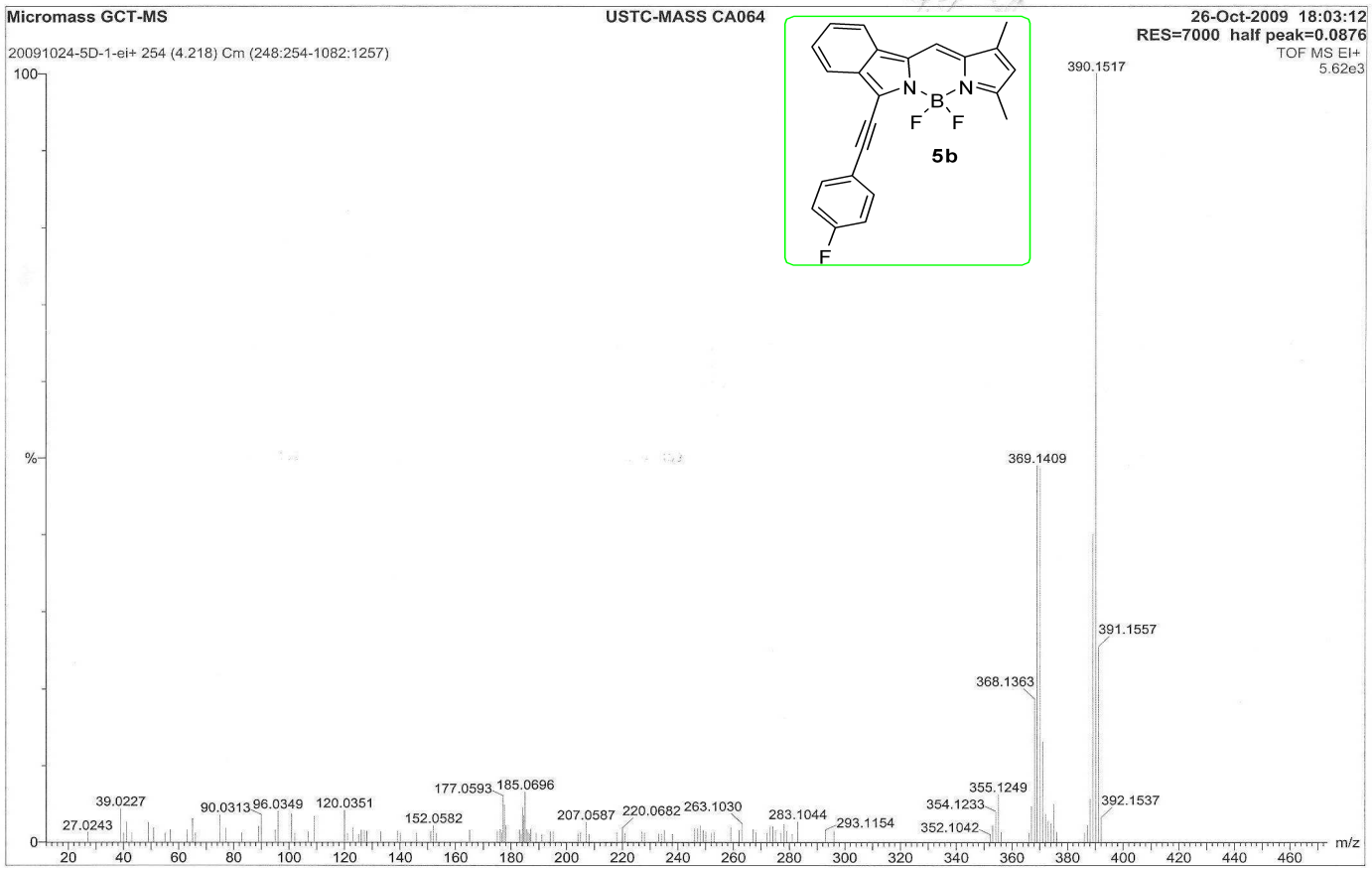

Micromass GCT-MS
USTC-MASS CA064
20-Apr-2010 08:21:20
RES=7000 half peak=0.0876
TOF MS EI+
1.09e4
20100420-B-2BR-1-ei+ 215 (3.583) Cm (214:215-1005:1107)
276.0445
241.0807
275.0417
240.0782
278.0412
192.0773
164.0529
191.0701
165.0608
242.0823
139.0558
138.0447
140.0562
274.0417
239.0744
193.0777
86.0972
137.0421
286.0948
321.9922
120.5370
221.0720
259.0843
307.1068
35.9767
49.0059
58.0702
75.0229
99.0222
153.0506
167.0714
%
m/z
Br
F
F
B
N
N
4b

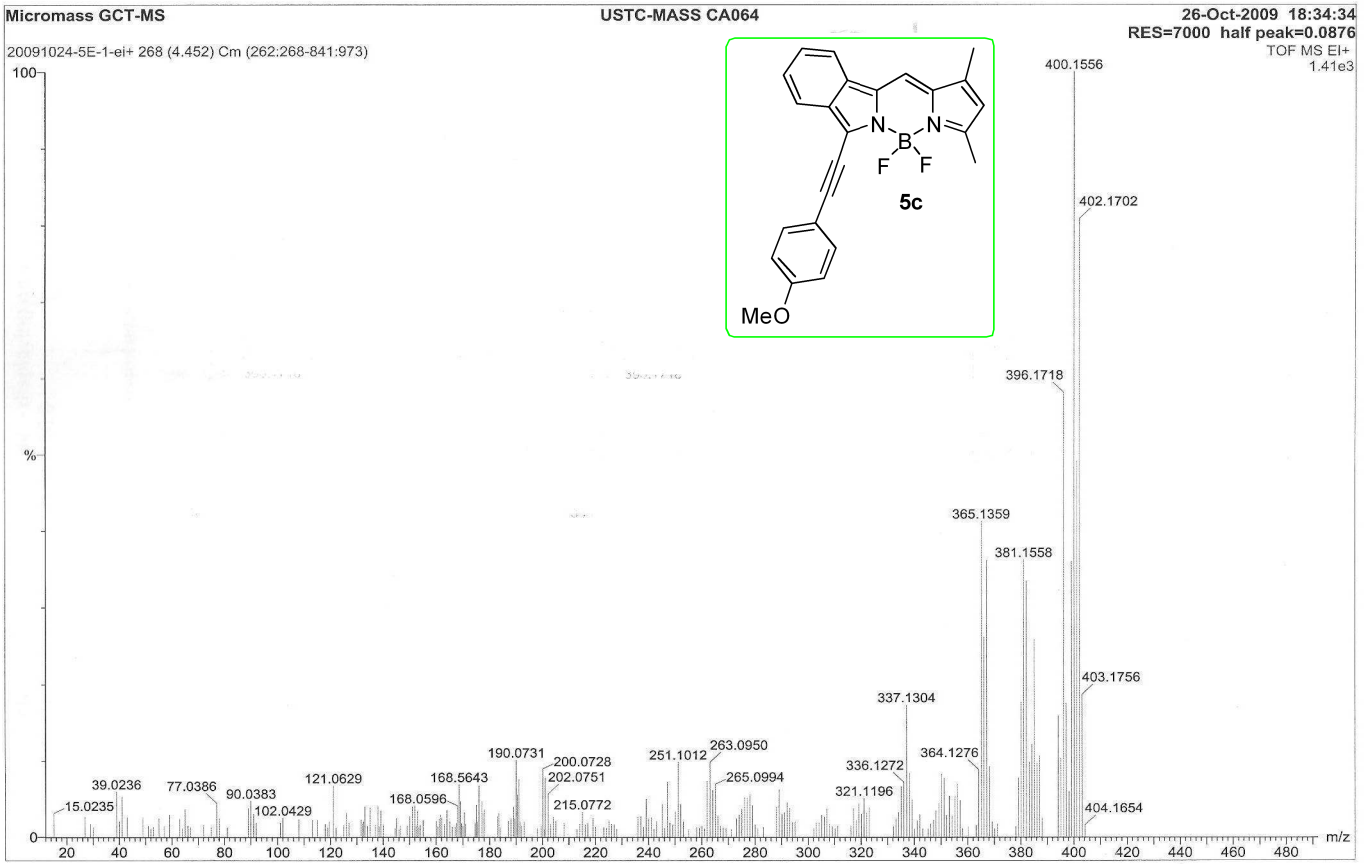
Deleted:

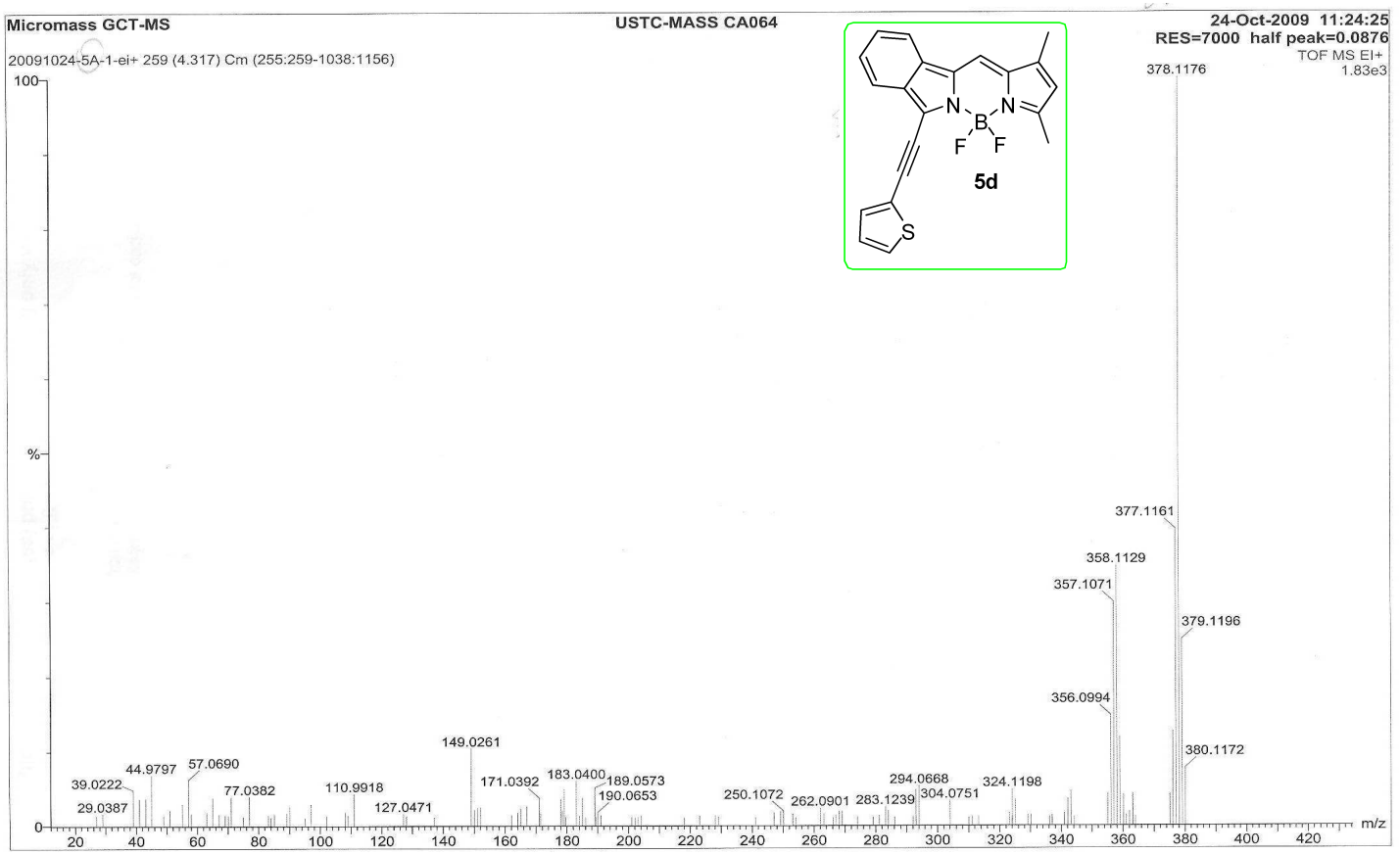

Micromass GCT-MS
USTC-MASS CA064
19-Apr-2010 09:49:19
RES=7000 half peak=0.0876
20100419-B-1CL-1-ei+ 195 (3.250) Cm (193:195-1035:1159)
TOF MS EI+
5.26e3
100
%
0
m/z
N
B
N
Cl
F
F
4c
304.0757
303.0752
284.0809
305.0750
306.0743
267.1022
283.0798
219.0932
127.0457
151.0544
126.0379
128.0546
165.0764
177.0603
205.0835
247.1063
253.0801
190.0742
39.0246
65.0415
75.0245
101.0403
125.0408
142.0407
246.0921
307.0774
35.9788

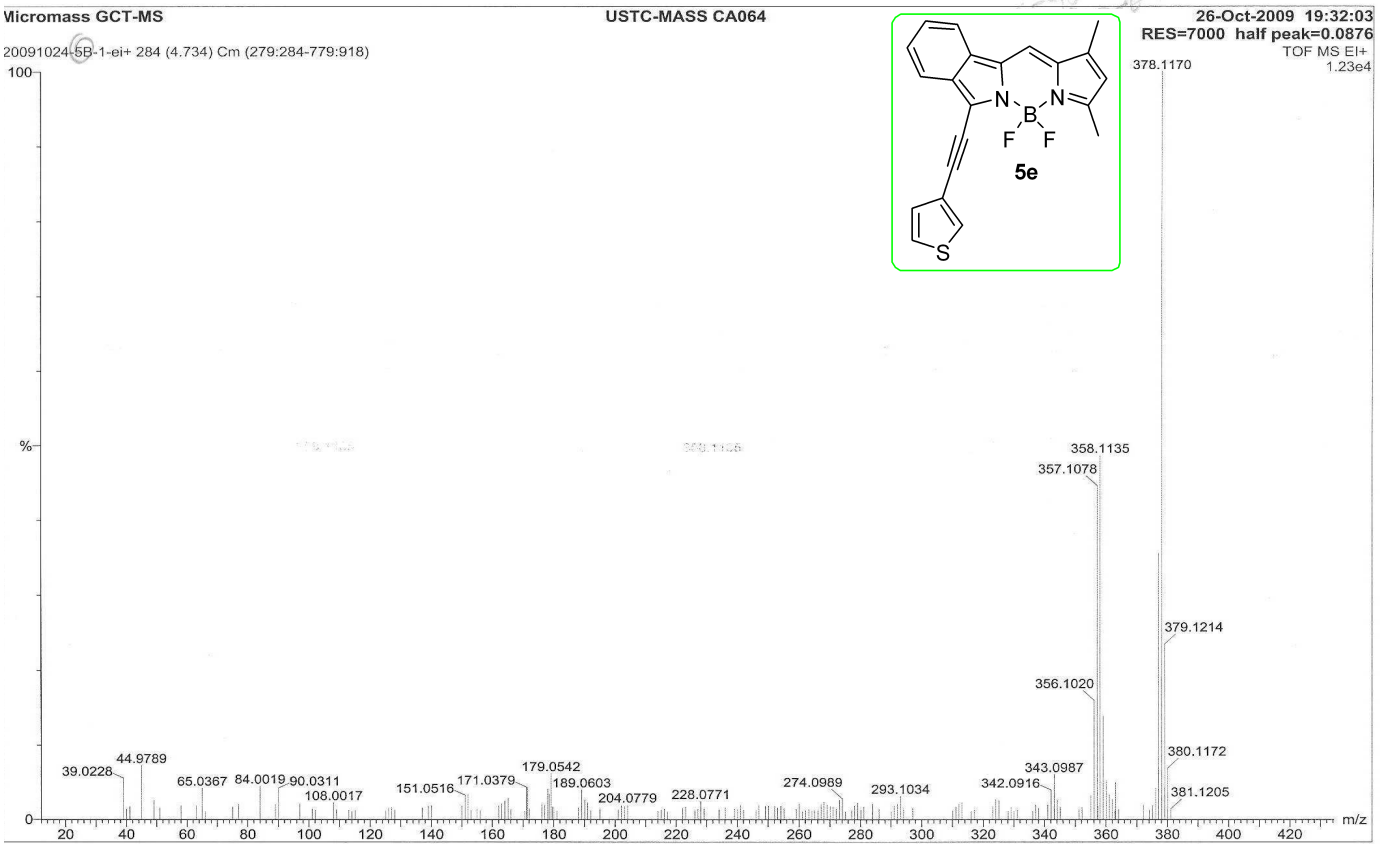

Micromass GCT-MS
USTC-MASS CA064
19-Apr-2010 10:37:56
RES=7000 half peak=0.0876
20100419-B-1BR-1-ei+ 182 (3.033) Cm (177:182-868:939)
TOF MS EI+
3.63e3
Br
N
B
N
F
F
4d
%
m/z
304.0751
303.0733
284.0786
268.1086
267.1000
269.1111
305.0732
306.0752
348.0243
350.0190
249.1131
127.0465
126.0416
128.0543
151.0565
165.0716
219.0953
247.1035
220.1067
177.0613
205.0855
192.0867
330.0250
347.0227
65.0403
39.0238
75.0234
63.0253
101.0387
125.0439
140.0537
227.0825
307.0728
327.0168
351.0298
27.0226

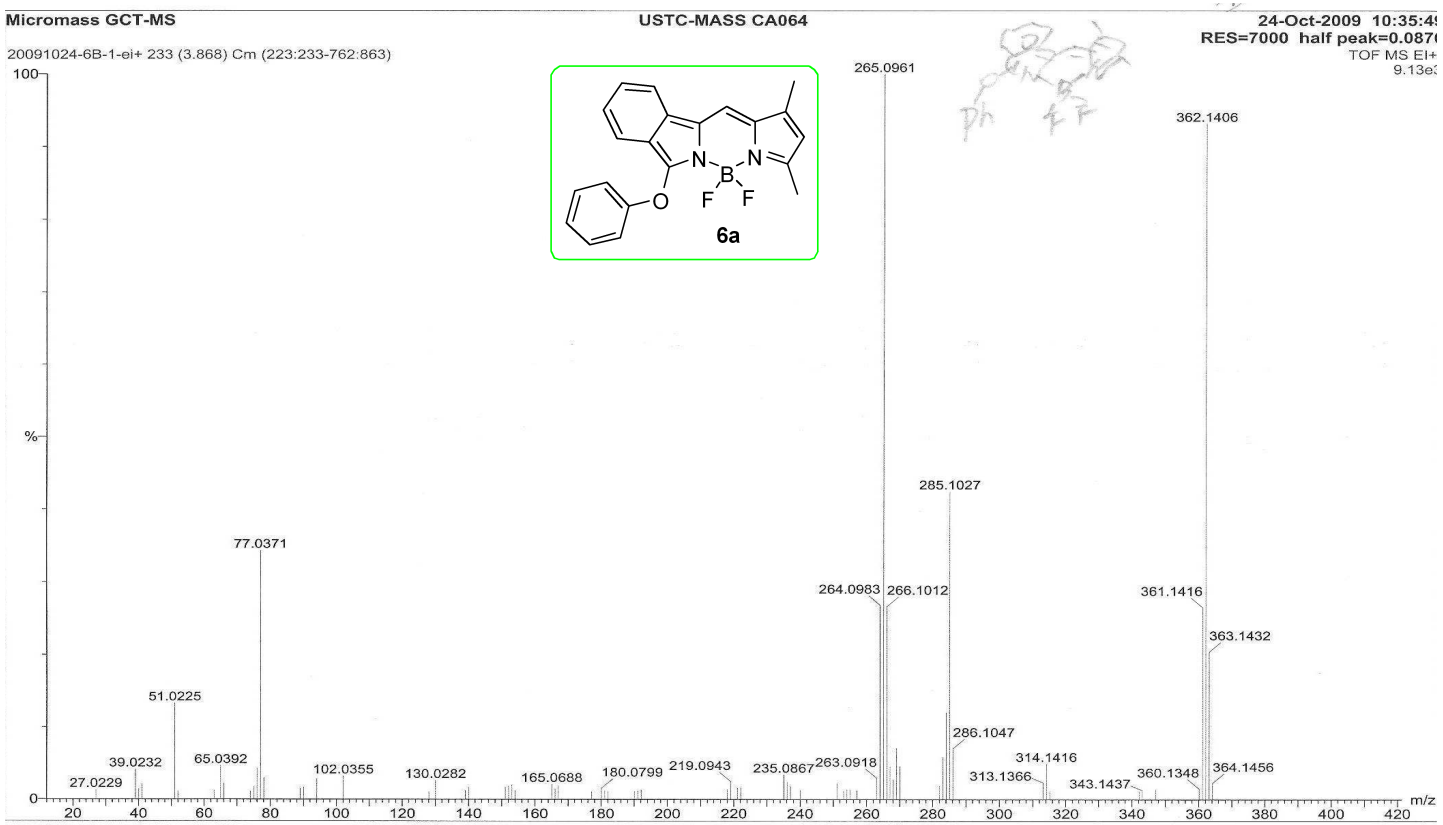

Micromass GCT-MS
USTC-MASS CA064
26-Oct-2009 19:08:01
RES=7000 half peak=0.0876
TOF MS EI+
7.41e3
20091024-5C-1-ei+ 257 (4.284) Cm (249:257-809:984)
5a
370.1451
369.1429
350.1411
371.1502
349.1399
372.1579
175.0677
177.0576
77.0383
39.0233
51.0231
27.0227
90.0330
126.0416
152.0602
174.5717
201.0572
227.0763
252.0853
262.0926
277.0815
291.0974
305.1159
348.1284
373.1638
100
%
0
m/z
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420

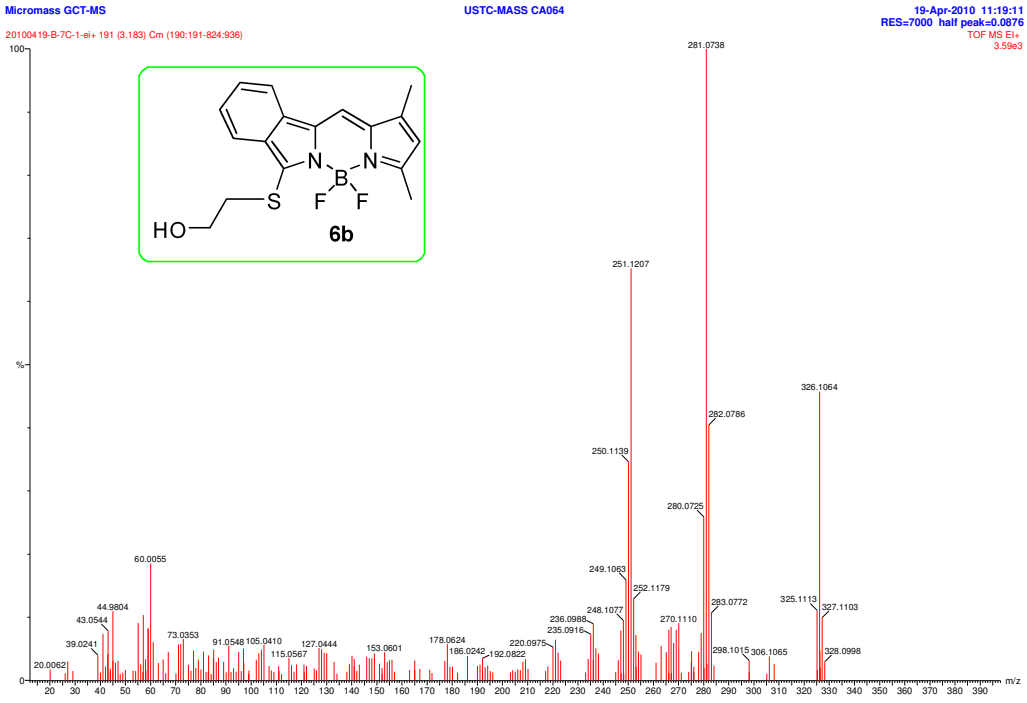

Micromass GCT-MS
USTC-MASS CA064
26-Oct-2009 18:03:12
RES=7000 half peak=0.0876
20091024-5D-1-ei+ 254 (4.218) Cm (248:254-1082:1257)
TOF MS EI+
5.62e3
5b
100
%
0
390.1517
369.1409
391.1557
368.1363
355.1249
392.1537
354.1233
352.1042
177.0593
185.0696
39.0227
90.0313
96.0349
120.0351
27.0243
152.0582
207.0587
220.0682
263.1030
283.1044
293.1154
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
m/z

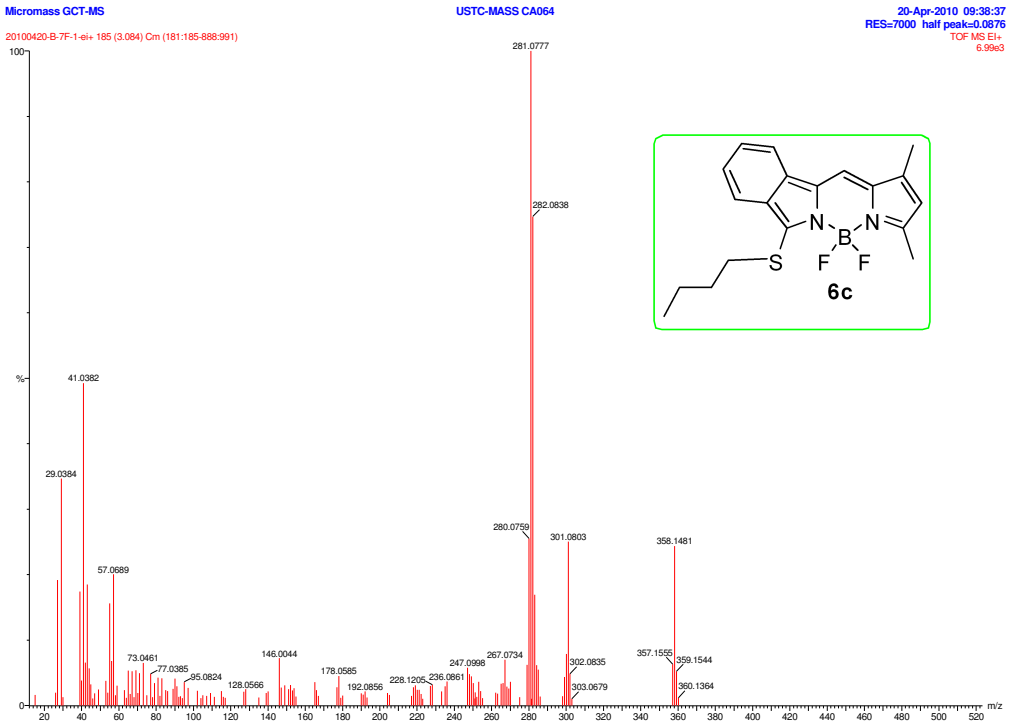

Micromass GCT-MS
USTC-MASS CA064
26-Oct-2009 18:34:34
RES=7000 half peak=0.0876
20091024-5E-1-ei+ 268 (4.452) Cm (262:268-841:973)
TOF MS EI+
1.41e3
5c
MeO
100
%
0
m/z
400.1556
402.1702
396.1718
365.1359
381.1558
403.1756
337.1304
364.1276
263.0950
251.1012
200.0728
190.0731
202.0751
265.0994
336.1272
321.1196
404.1654
215.0772
168.5643
168.0596
121.0629
39.0236
77.0386
90.0383
102.0429
15.0235
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480

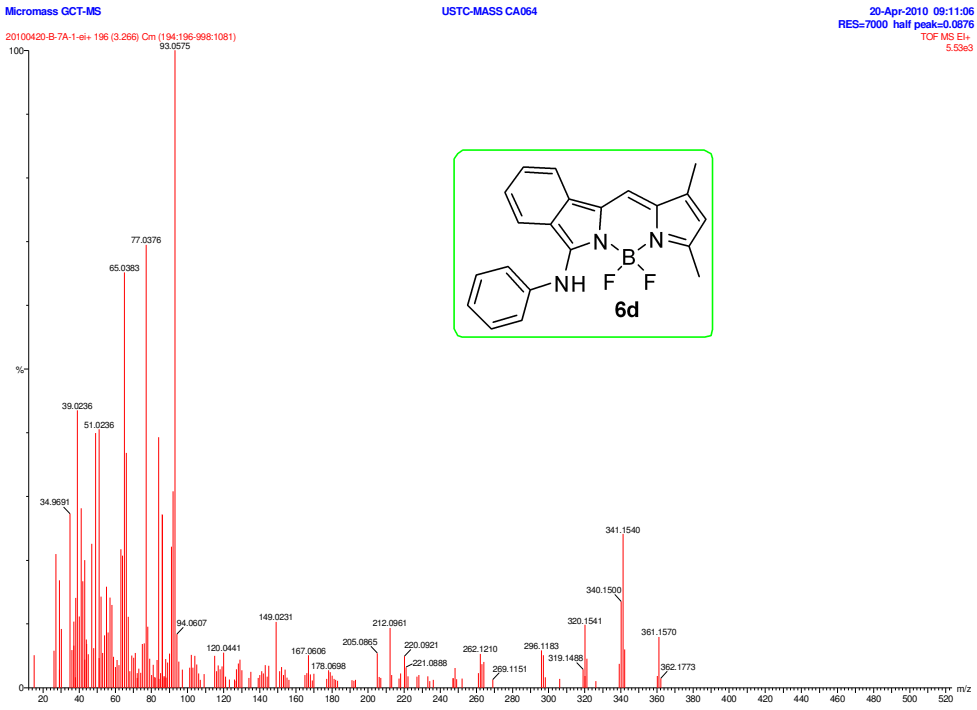

Micromass GCT-MS
USTC-MASS CA064
24-Oct-2009 11:24:25
RES=7000 half peak=0.0876
TOF MS EI+
1.83e3
20091024-5A-1-ei+ 259 (4.317) Cm (255:259-1038:1156)
5d
%
m/z
378.1176
377.1161
358.1129
357.1071
379.1196
356.0994
380.1172
149.0261
44.9797
57.0690
39.0222
77.0382
110.9918
171.0392
183.0400
189.0573
190.0653
29.0387
127.0471
250.1072
262.0901
283.1239
294.0668
304.0751
324.1198

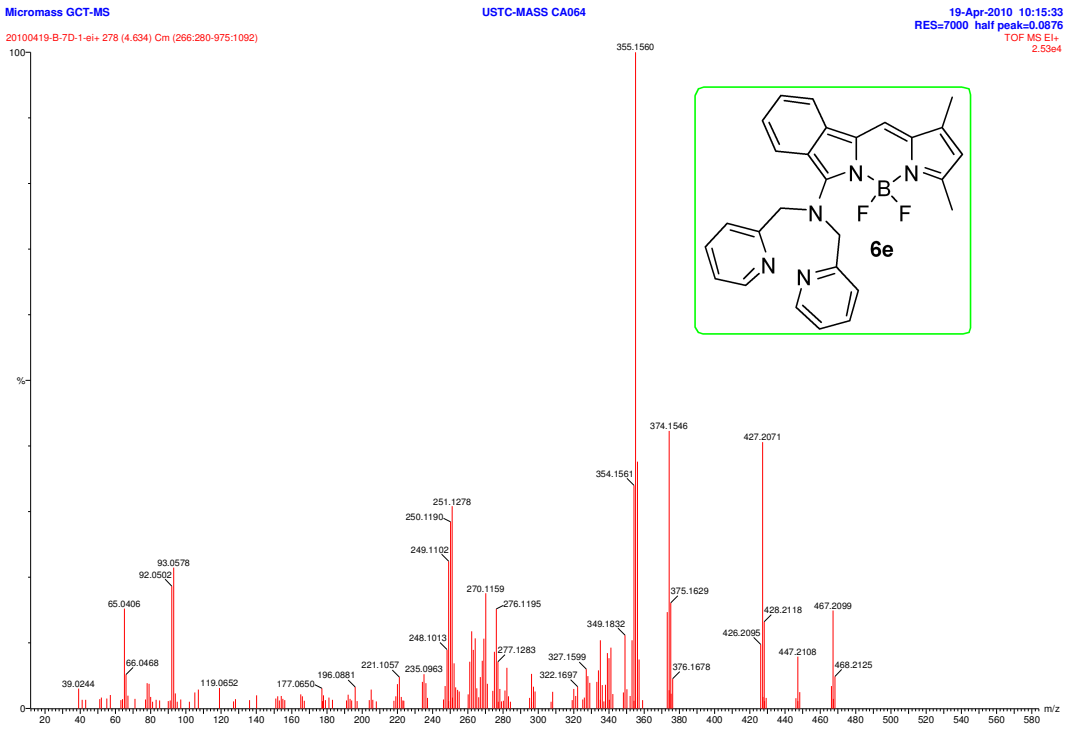

Micromass GCT-MS
USTC-MASS CA064
26-Oct-2009 19:32:03
RES=7000 half peak=0.0876
TOF MS EI+
1.23e4
20091024-5B-1-ei+ 284 (4.734) Cm (279:284-779:918)
5e
100
%
0
m/z
378.1170
358.1135
357.1078
379.1214
356.1020
380.1172
343.0987
381.1205
342.0916
44.9789
39.0228
65.0367
84.0019
90.0311
108.0017
151.0516
171.0379
179.0542
189.0603
204.0779
228.0771
274.0989
293.1034
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420

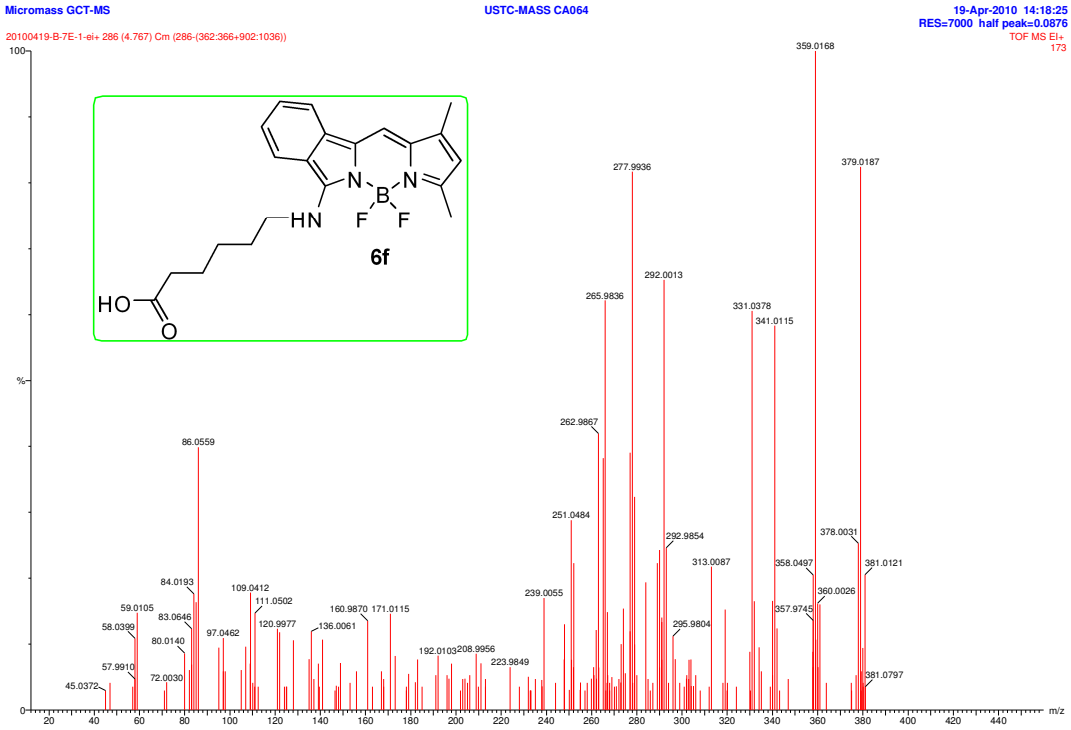

Micromass GCT-MS
USTC-MASS CA064
24-Oct-2009 10:35:45
RES=7000 half peak=0.087
TOF MS EI+
9.13e3
20091024-6B-1-ei+ 233 (3.868) Cm (223:233-762:863)
6a
100
%
0
265.0961
362.1406
285.1027
77.0371
264.0983
266.1012
361.1416
363.1432
51.0225
286.1047
314.1416
39.0232
65.0392
263.0918
313.1366
360.1348
364.1456
102.0355
219.0943
235.0867
343.1437
27.0229
130.0282
165.0688
180.0799
m/z
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420


Micromass GCT-MS
USTC-MASS CA064
19-Apr-2010 11:19:11
RES=7000 half peak=0.0676
20100419-B-7C-1-ei+ 191 (3.183) Cm (190:191-824:936)
TOF MS EI+
3.59e3
6b
281.0738
251.1207
326.1064
282.0786
250.1139
280.0725
60.0055
249.1063
252.1179
283.0772
325.1113
327.1103
44.9804
43.0544
248.1077
236.0988
270.1110
73.0353
235.0916
39.0241
91.0548
105.0410
115.0567
127.0444
220.0975
298.1015
306.1065
328.0998
153.0601
178.0624
186.0242
192.0822
20.0062
%
m/z


Micromass GCT-MS
USTC-MASS CA064
20-Apr-2010 09:38:37
RES=7000 half peak=0.0876
TOF MS EI+
6.99e3
20100420-B-7F-1-ei+ 185 (3.084) Cm (181:185-888:991)
100
%
0
m/z
281.0777
282.0838
41.0382
29.0384
280.0759
301.0803
358.1481
57.0689
73.0461
77.0385
95.0824
146.0044
128.0566
178.0585
192.0856
228.1205
236.0861
247.0998
267.0734
302.0835
303.0679
357.1555
359.1544
360.1364
N
B
N
S
F
F
6c


Micromass GCT-MS
USTC-MASS CA064
20-Apr-2010 09:11:06
RES=7000 half peak=0.0876
TOF MS EI+
5.53e3
20100420-B-7A-1-ei+ 196 (3.266) Cm (194:196-998:1081)
93.0575
77.0376
65.0383
39.0236
51.0236
34.9691
94.0607
120.0441
149.0231
167.0606
178.0698
205.0865
212.0961
220.0921
221.0888
262.1210
269.1151
296.1183
319.1488
320.1541
340.1500
341.1540
361.1570
362.1773
%
m/z
N
B
N
NH
F
F
6d


Micromass GCT-MS
USTC-MASS CA064
19-Apr-2010 10:15:33
RES=7000 half peak=0.0876
20100419-B-7D-1-ei+ 278 (4.634) Cm (266:280-975:1092)
TOF MS EI+
2.53e4
6e
355.1560
374.1546
427.2071
354.1561
251.1278
250.1190
249.1102
93.0578
92.0502
65.0406
270.1159
276.1195
375.1629
428.2118
467.2099
349.1832
426.2095
248.1013
277.1283
447.2108
66.0468
327.1599
376.1678
468.2125
221.1057
235.0963
322.1697
39.0244
119.0652
177.0650
196.0881
%
m/z


Micromass GCT-MS
USTC-MASS CA064
19-Apr-2010 14:18:25
RES=7000 half peak=0.0876
20100419-B-7E-1-ei+ 286 (4.767) Cm (286-(362:366+902:1036))
TOF MS EI+
173
6f
HO
O
HN
F
F
N
B
N
%
m/z
359.0168
379.0187
277.9936
292.0013
265.9836
331.0378
341.0115
262.9867
86.0559
251.0484
292.9854
378.0031
313.0087
358.0497
381.0121
84.0193
109.0412
111.0502
239.0055
360.0026
59.0105
83.0646
160.9870
171.0115
357.9745
58.0399
120.9977
136.0061
295.9804
80.0140
97.0462
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45.0372

5. UV-vis and Fluorescence data for all the new compounds

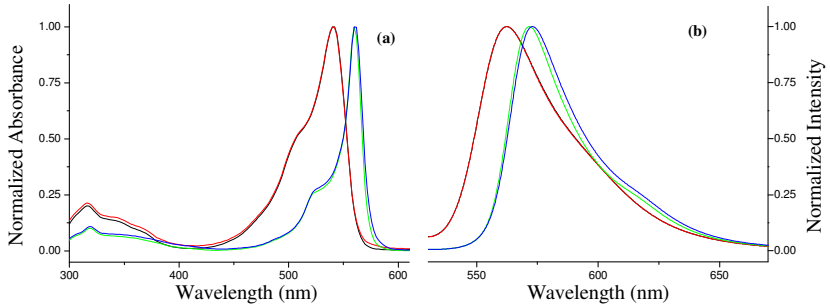

Figure S1. Normalized UV-vis (a) and Fluorescence (b, λ_{ex} = 520 nm) spectra of BODIPYs **4a** (black), **4b** (red), **4c** (green) and **4d** (blue) in dichloromethane at 25 ^{o}C.

Table S1. UV-vis and fluorescence properties of compounds **4a-d** in various solvent at room temperature.

BODIPYs		λ_{max} (nm)	Logε	λ_{em} (nm)	ϕ^{a}	Stokes shift (cm^{-1})
4a	MeOH	536	4.73	558	0.85	736
	DMSO	542	4.48	566	0.59	782
	Toluene	544	4.76	564	0.69	652
	MeCN	532	4.81	558	0.68	876
	Hexane	540	4.91	554	0.72	468
4b	MeOH	536	4.84	559	0.66	768
	DMSO	542	4.78	566	0.42	782
	Toluene	544	4.90	564	0.66	652
	MeCN	534	4.75	559	0.69	838
	Hexane	540	4.76	554	1.00	468
4c	MeOH	554	4.87	566	0.81	383
	DMSO	560	4.75	572	0.69	375
	Toluene	562	4.95	574	0.63	372
	MeCN	554	4.92	566	0.67	383
	Hexane	556	5.15	566	0.73	318
4d	MeOH	556	4.61	572	0.61	503
	DMSO	560	4.38	573	0.59	405
	Toluene	562	5.05	575	0.48	402
	MeCN	554	4.95	567	0.64	414
	Hexane	558	5.17	567	0.59	284

[a]Fluorescence quantum yields for BODIPYs **4a-d** (λ_{ex} = 520 nm) were calculated using Rhodamin B (0.49 in EtOH)[1c] as the reference.

Table S2. UV-vis and fluorescence properties of compounds **5a-e** in various solvent at room temperature.

BODIPYs		λ_{max} (nm)	Logε_{max}	λ_{em} (nm)	ϕ^a	Stokes shift (cm^{-1})
5a	DMSO	614	4.62	632	0.61	464
	MeOH	606	4.69	622	0.84	424
	Toluene	616	4.73	631	0.63	386
	MeCN	606	4.68	622	1.00	424
	Hexane	608	4.60	620	1.00	318
5b	DMSO	614	4.77	627	0.64	338
	MeOH	606	4.77	617	1.00	294
	Toluene	614	4.81	627	0.68	338
	MeCN	604	4.74	618	1.00	375
	Hexane	608	4.87	617	1.00	240
5c	DMSO	618	4.32	636	0.47	458
	MeOH	610	4.58	625	0.68	393
	Toluene	618	4.62	635	0.52	433
	MeCN	608	4.56	626	0.83	473
	Hexane	610	4.55	624	0.91	368
5d	DMSO	618	4.21	632	0.61	358
	MeOH	610	4.15	624	0.39	368
	Toluene	618	4.15	633	0.33	383
	MeCN	608	4.14	623	0.51	396
	Hexane	610	4.42	622	0.49	316
5e	DMSO	614	4.82	631	0.32	439
	MeOH	606	5.00	621	0.90	399
	Toluene	614	5.09	630	0.65	414
	MeCN	606	5.01	621	1.00	399
	Hexane	608	4.40	619	1.00	292

[a]Fluorescence quantum yields for BODIPYs **5a-e** (λ_{ex} = 580 nm) were calculated using methylene blue (0.03 in MeOH)[1a] as the reference.

Table S3. UV-vis and fluorescence properties of compounds **6a-f** in various solvent at room temperature.

BODIPYs		λ_{max} (nm)	Logε	λ_{em} (nm)	ϕ^a	Stokes shift (cm^{-1})
6a	DMSO	544	4.96	564	0.56	652
	MeOH	540	4.92	559	0.24	629
	Toluene	550	5.07	566	0.63	514
	MeCN	538	5.01	559	0.66	698
	Hexane	546	5.23	557	0.70	362
6b	DMSO	574	4.37	589	0.38	444
	MeOH	570	4.92	584	0.57	421
	Toluene	578	4.48	592	0.37	409
	MeCN	568	5.01	583	0.45	453
	Hexane	572	5.23	584	0.44	359
6c	DMSO	574	4.77	591	0.52	501
	MeOH	570	4.58	585	0.73	450
	Toluene	578	4.54	594	0.50	466
	MeCN	568	4.55	584	0.56	482
	Hexane	572	4.55	588	0.56	476
6d	DMSO	516	4.75	585	0.19	2286
	MeOH	518	4.53	576	0.51	1944
	Toluene	540	4.66	583	0.55	1366
	MeCN	512	4.49	578	0.57	2230
	Hexane	540	4.51	573	0.56	1067
6e	DMSO	534	4.49	586	0.56	1662
	MeOH	548	4.50	581	0.63	1036
	Toluene	558	4.61	587	0.54	1585
	MeCN	532	4.51	581	0.51	1585
	Hexane	558	4.75	579	0.61	650
6f	MeOH	510	4.28	551	0.24	1459
	Toluene	532	4.34	564	0.14	1066
	MeCN	504	4.28	554	0.20	1791
	Hexane	534	4.03	554	0.17	676

[a]Fluorescence quantum yields for BODIPYs **6a-e** (λ_{ex} = 520 nm) were calculated using Rhodamin B (0.49 in EtOH)[1c] as the reference, while fluorescein (0.95 in 0.1 M NaOH)[1b] was used as the standard for BODIPY **6f** (λ_{ex} = 490 nm).

References:

1. (a) Olmsted, J. *J. Phys. Chem.* **1979**, *83*, 2581. (b) Fery-Forgues, S.; Lavabre, D. *J. Chem. Educ.* **1999**, *76*, 1260. (c) Casey, K. G.; Quitevis, E. L. *J. Phys. Chem.* **1988**, *92*, 6590.
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4. Bonnett, R.; McManus, K. A. *J. Chem. Soc., Perkin Trans. 1***, 1996**, 2461.