Supporting Information for

Dipyrrolylquinoxaline Difluoroborates with Intense Red Solid-State Fluorescence

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1. Experimental

General procedure for the synthesis of Dipyrrolediketone 7-9: This was synthesized as the reported procedure[6] published. Oxalyl chloride (1.48 ml, 17.5 mmol) and freshly distilled dichloromethane (30 ml) were placed together under an argon atmosphere and stirred. Upon cooling to -78 °C in an acetone/ethanol bath, dry pyridine (3.5 g, 42 mmol) was added, resulting in the formation of a yellow precipitate. To this cooled suspension was added a solution of freshly distilled pyrrole (2.8 ml, 40 mmol) in dichloromethane (25 ml) by drop and drop. The mixture was continued to be stirred for an additional 30 min at -60 °C, and hydrochloric acid (5 M, 35 ml) was added to quench the reaction. The organic phase was extracted, dried, filtered, and evaporated to dryness. The crude mixture was purified by silica gel column (hexane/ EtOAc = 3:1, v/v) to afford a yellow powder.

Dipyrrolediketone 7 was obtained using oxalyl chloride (1.48 ml, 17.5 mmol) and pyrrole (2.8 ml, 40 mmol) as starting materials, giving a yellow powder in 35% yield (1.1 g). ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.29 (s, 2H), 7.30 (s, 2H), 6.89 (s, 2H), 6.25 (s, 2H).

Dipyrrolediketone 8 was obtained using oxalyl chloride (0.74 ml, 8.7 mmol) and 2, 4-methylpyrrole (2 ml, 20 mmol) as starting materials, giving a yellow powder in 42% yield (0.89 g). ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.65 (s, 2H), 5.83 (s, *2*H), 2.19 (s, 6H), 1.96 (s, 6H).

Dipyrrolediketone 9 was obtained using oxalyl chloride (0.74 ml, 8.7 mmol) and 3-ethyl-2, 4-methylpyrrole (2.6 ml, 20 mmol) as starting materials, giving a yellow powder in 45% yield (1.17 g). ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.60 (s, 2H), 2.29-2.24 (m, 4H), 2.16 (s, 6H), 1.97-1.87 (m, 6H), 0.94 (t, J = 7.2 Hz, 6H).

2. Photophysical spectra

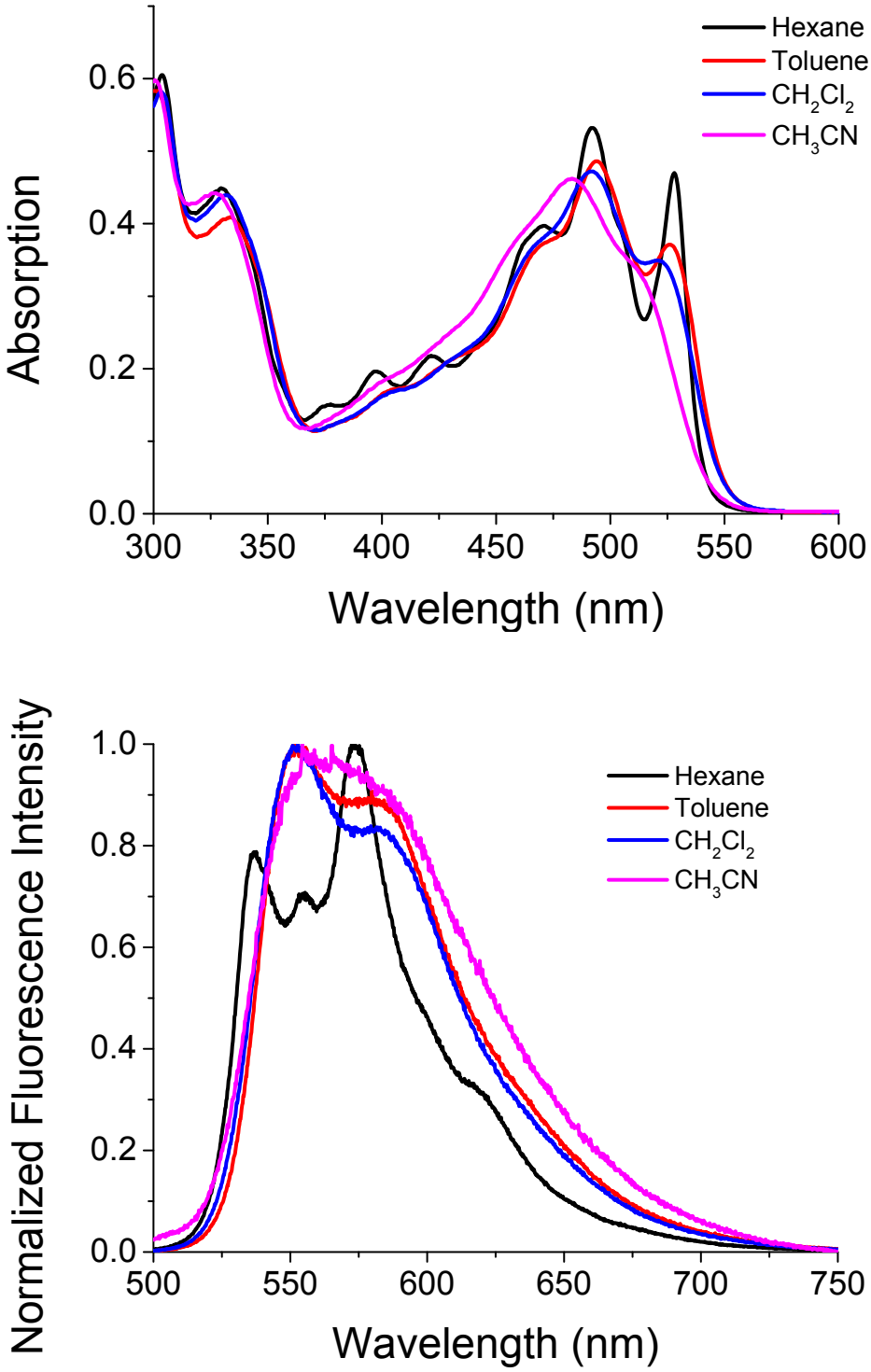


Figure S1. Absorption (top) (2.8×10^{-5} M) and emission (bottom) spectra of **1** recorded in different solvents, excited at 400 nm.

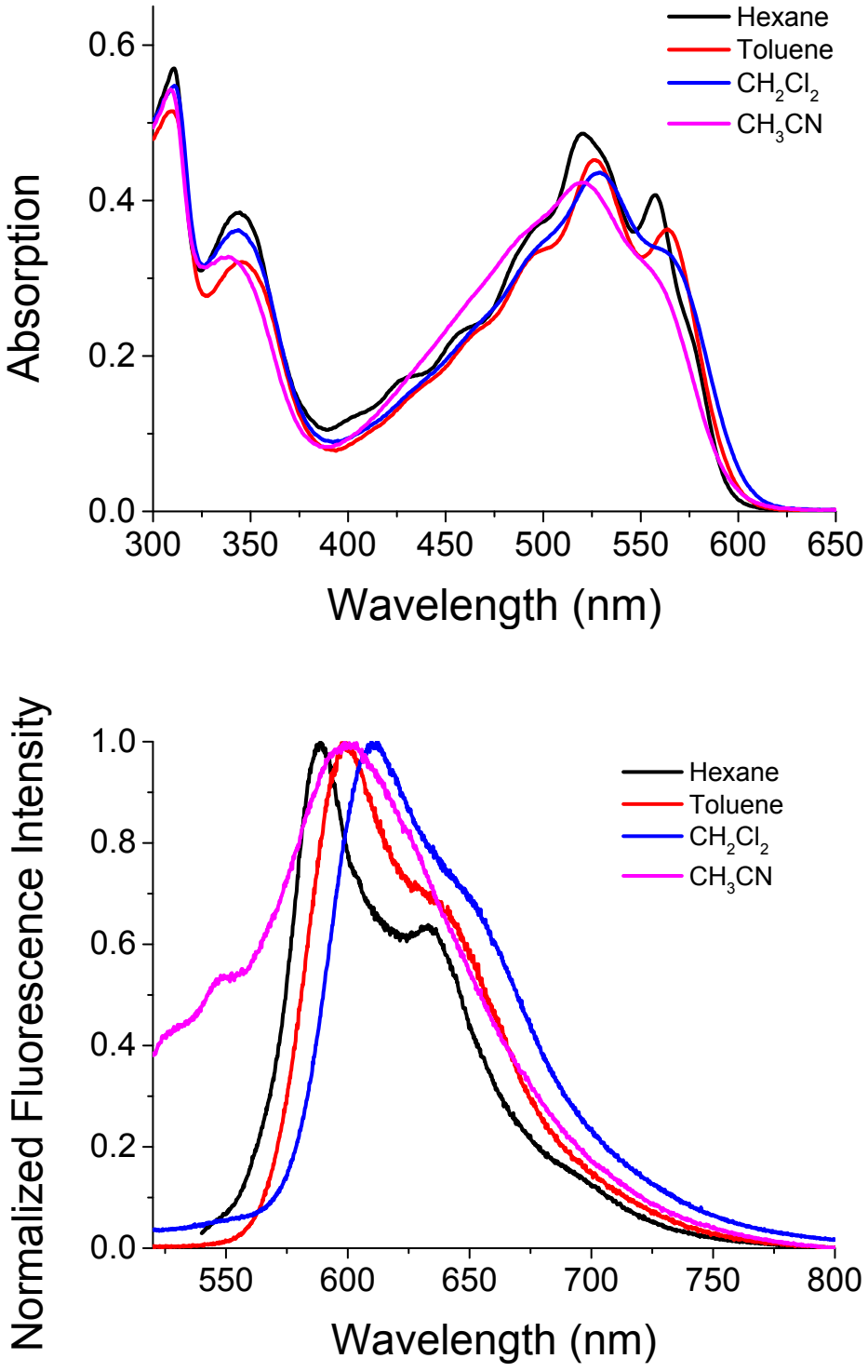


Figure S2. Absorption (top) (9.9×10^{-6} M) and emission (bottom) spectra of **2** recorded in different solvents, excited at 500 nm.

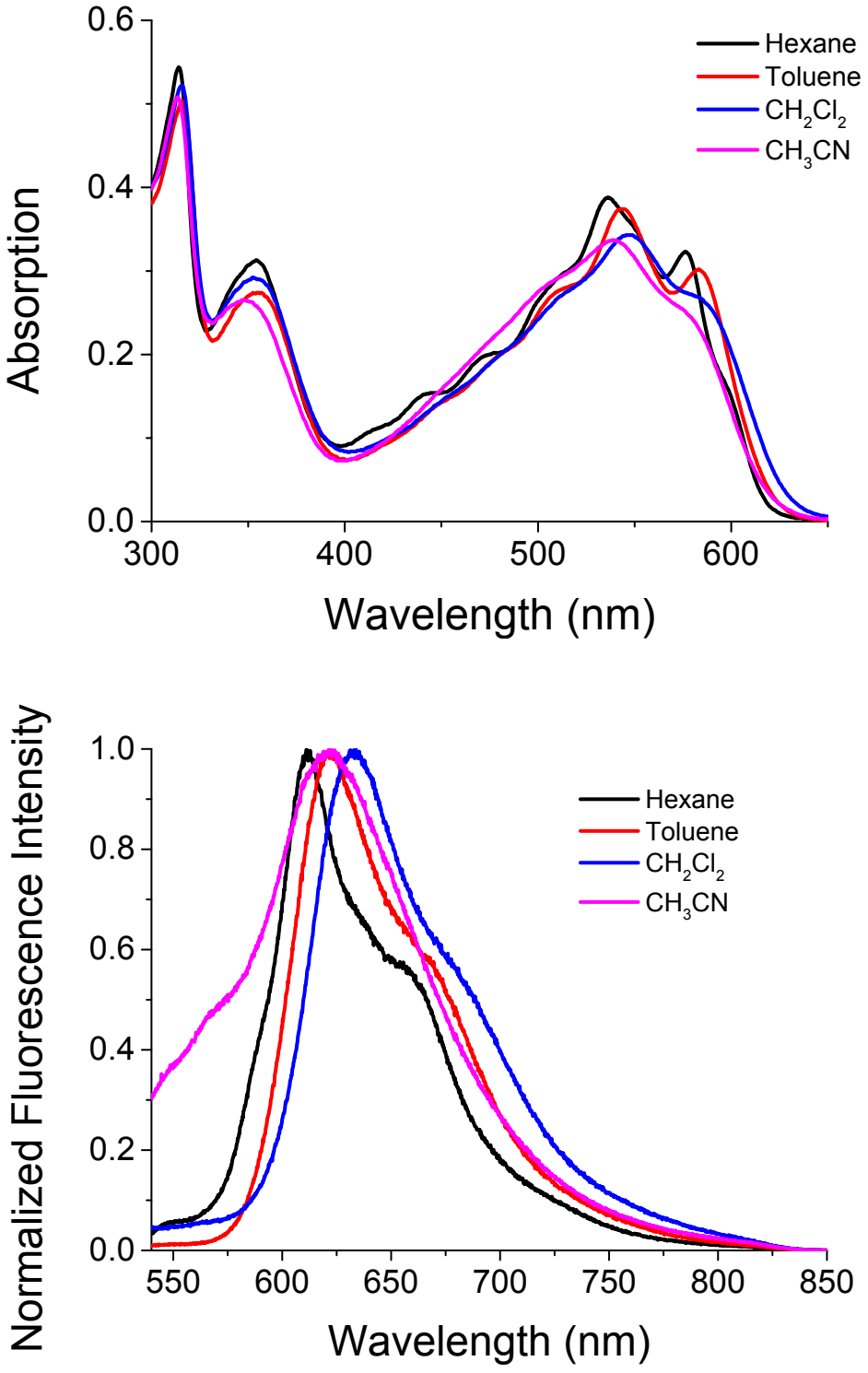


Figure S3. Absorption (top) (1.4×10^{-5} M) and emission (bottom) spectra of **3** recorded in different solvents, excited at 520 nm.

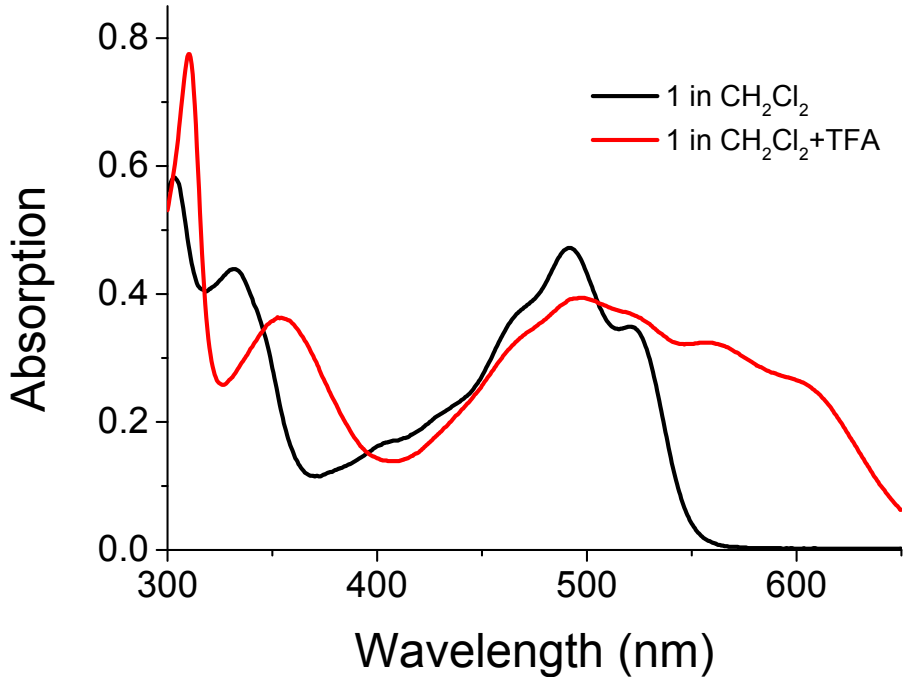


Figure S4. Absorption spectra changes of **1** in dichloromethane (2.8×10^{-5} M) after adding TFA. (TFA: trifluoroacetic acid).

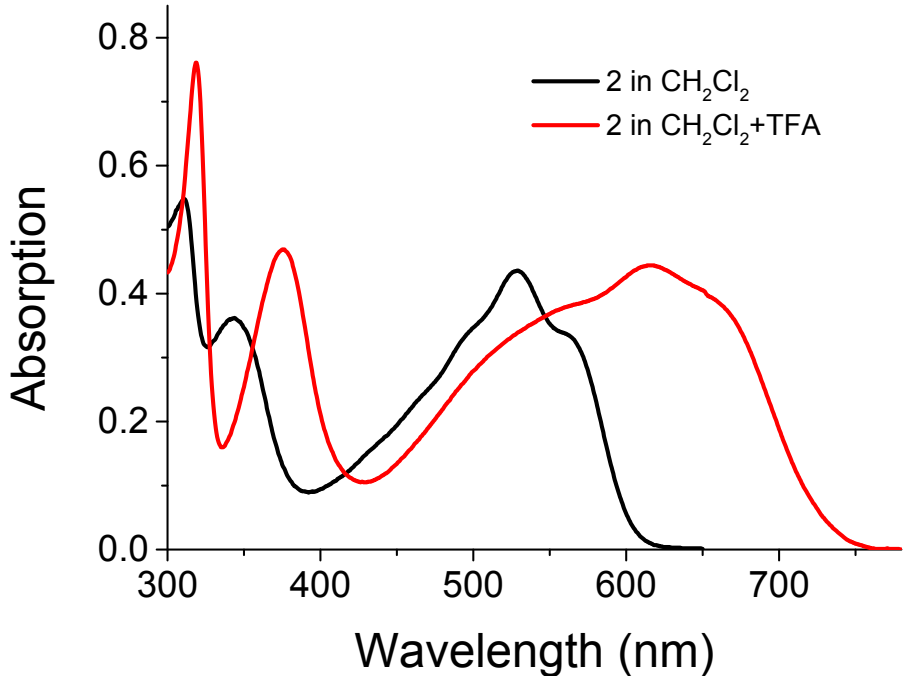


Figure S5. Absorption spectra changes of **2** in dichloromethane (9.9×10^{-6} M) after adding TFA.

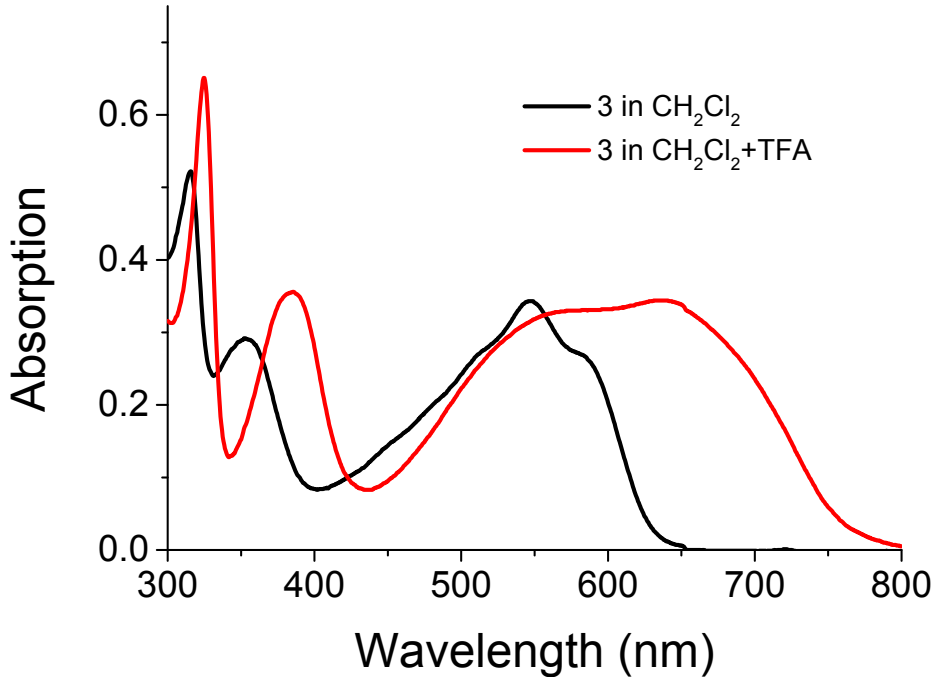


Figure S6. Absorption spectra changes of **3** in dichloromethane (1.4×10^{-5} M) after adding TFA.

3. Crystal packings

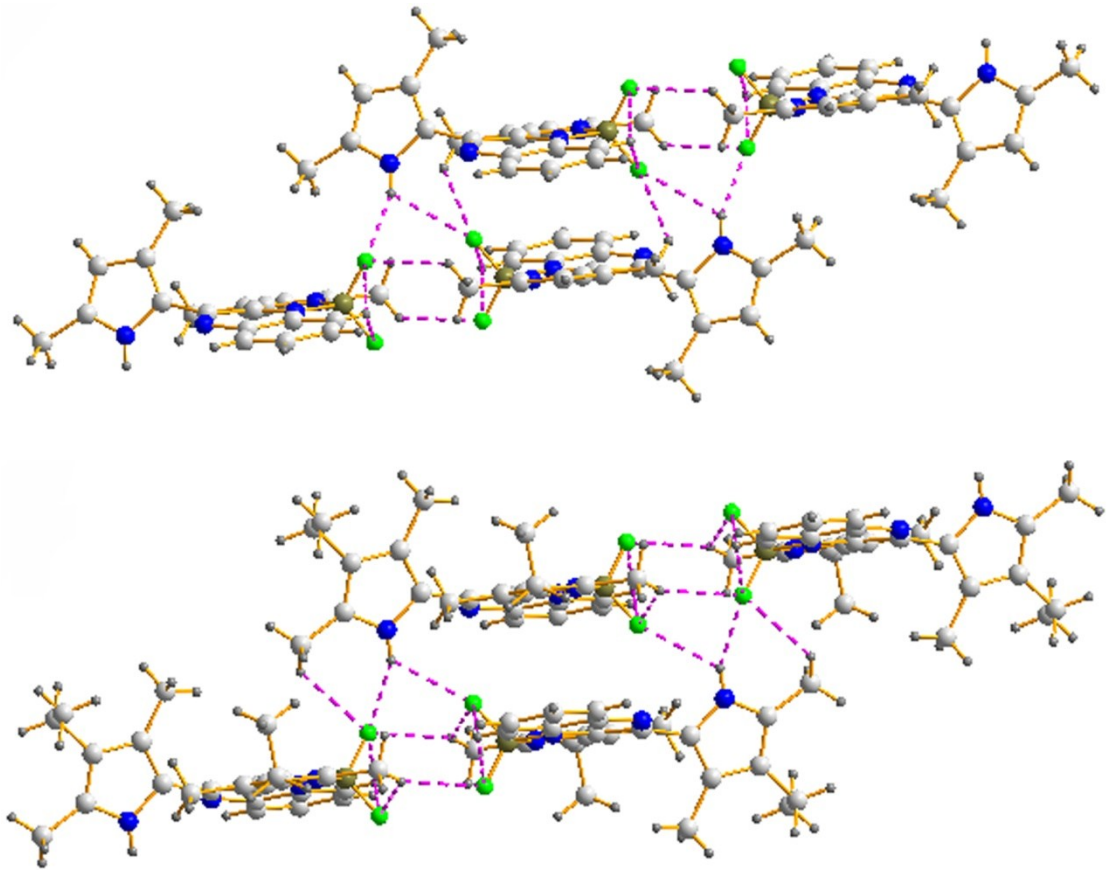
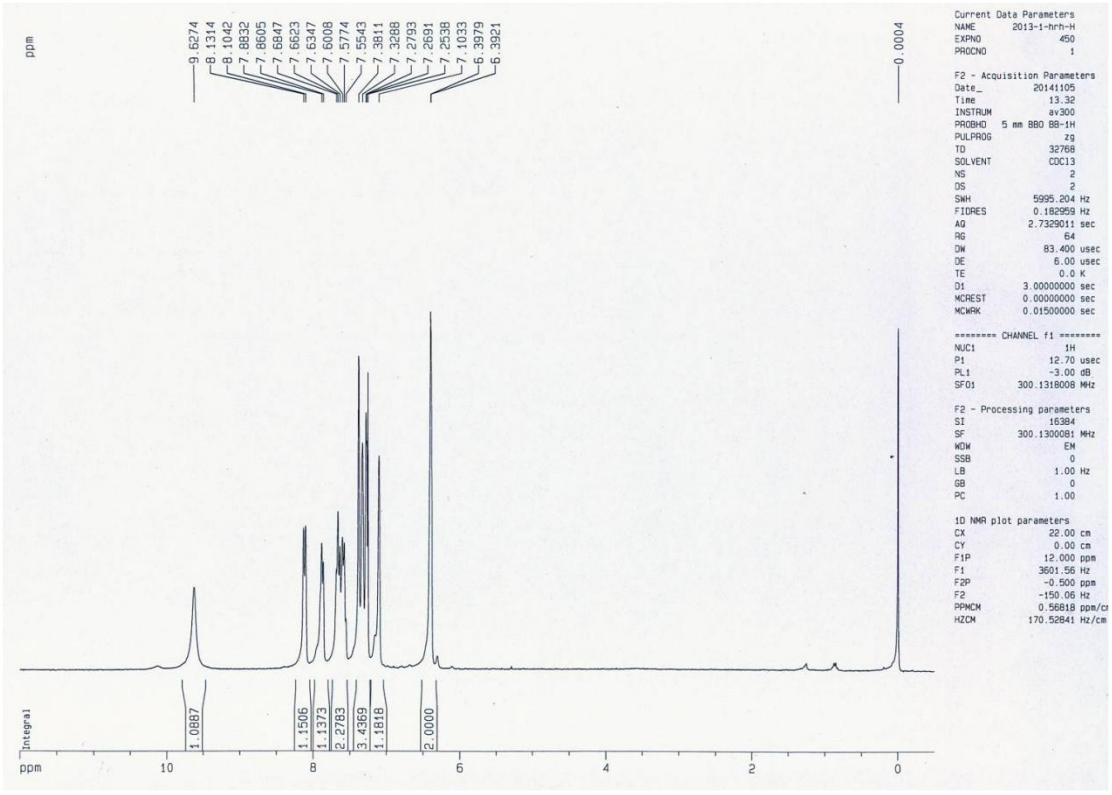


Figure S7. Crystal packings of **2** (top) and **3** (botton).

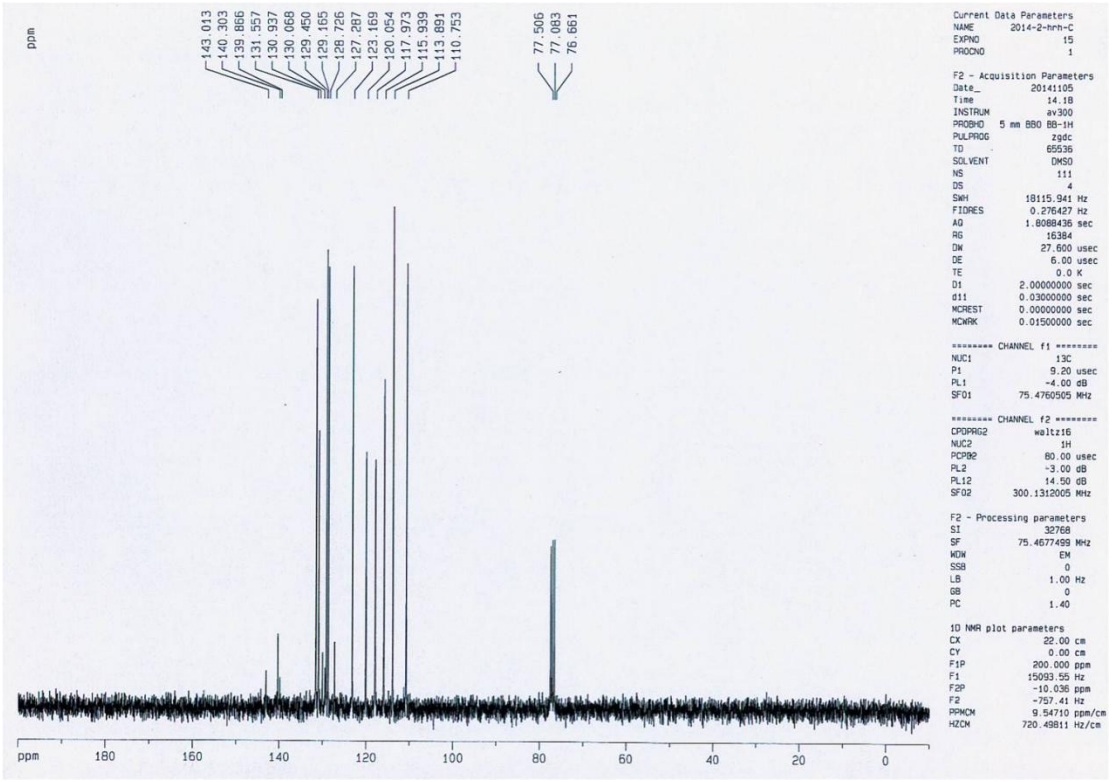
Table S1. Selected geometrical parameters for BPQs **2-3** and PQs **4-5** obtained from crystallography

	2	**3**	**4**	**5**
the B-N bond distances (Å)	1.527(2), 1.607(2)	1.507(5), 1.593(5)		
dihedral angles between the free pyrrole plane and BN_2C_2 plane (deg)	70.64(5)	72.82(4)		
dihedral angles between pyrrole and pyrazine plane (deg)	66.09(2), 10.08(4)	68.6(2), 6.3(2)	86.11(1), 5.61(2)	35.6(1), 40.6(2)
dihedral angles of two pyrrole planes (deg)	74.09(5)	73.8(2)	88.43(5)	66.6(2)

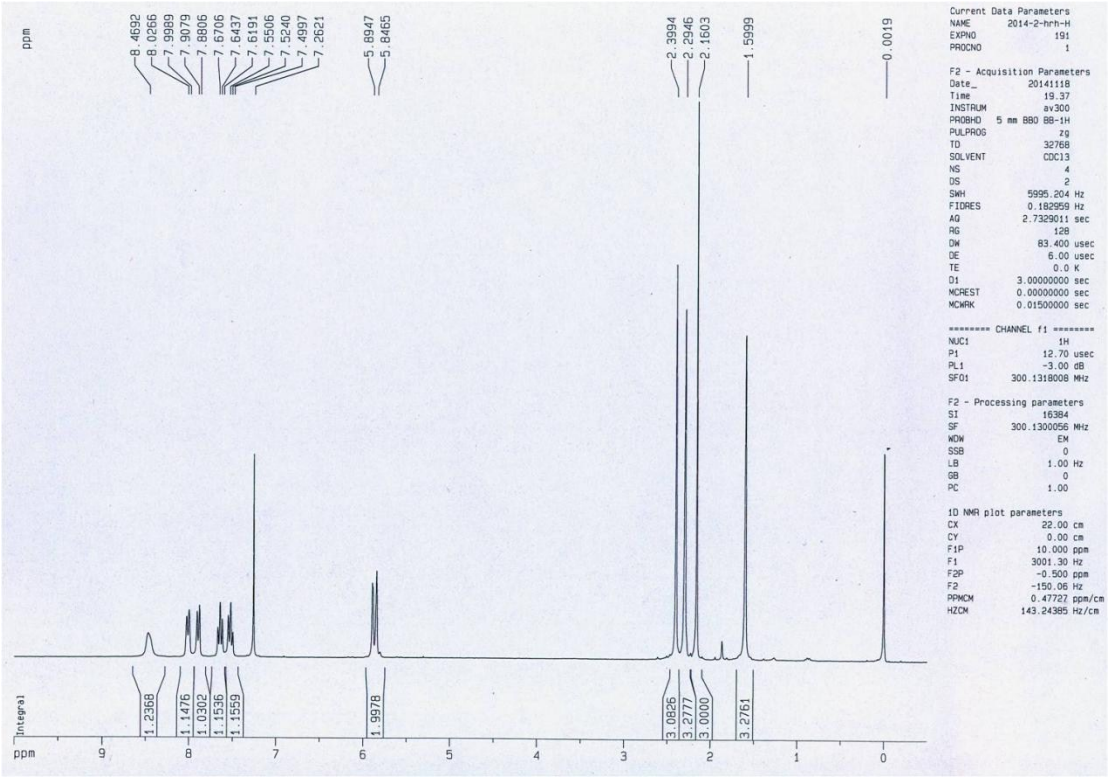
4. Copies of NMR spectra for all compounds



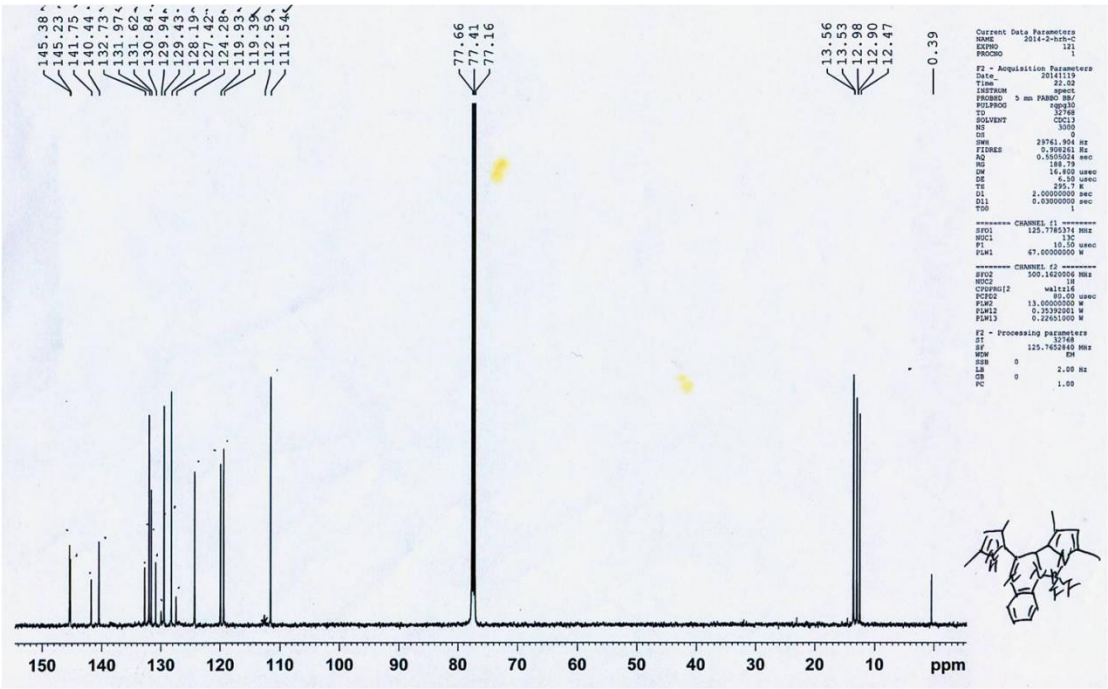
^{1}H NMR spectrum of **1** in $CDCl_3$



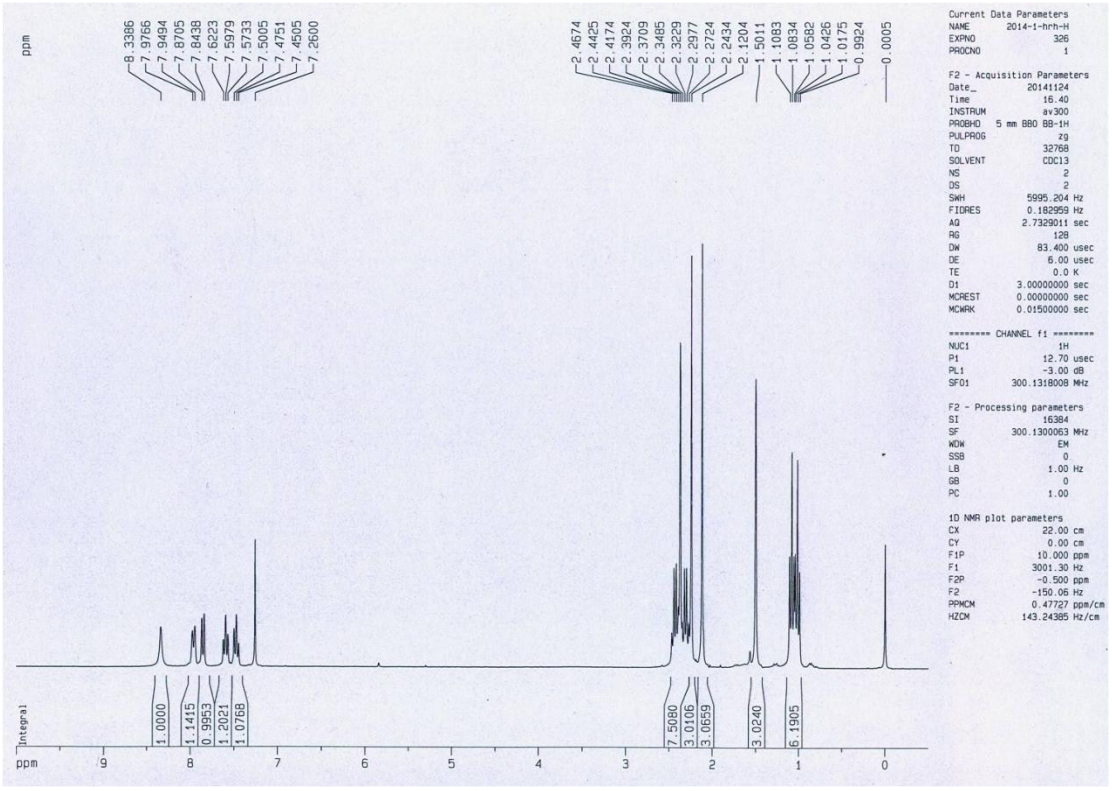
^{13}C NMR spectrum of **1** in $CDCl_3$



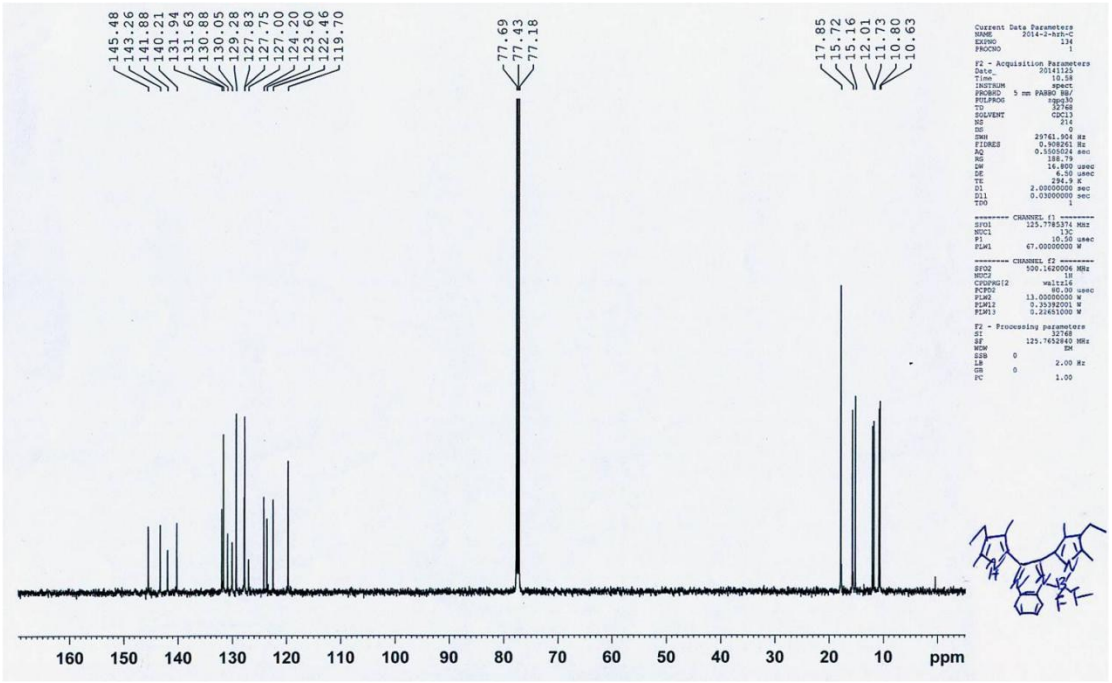
^{1}H NMR spectrum of **2** in $CDCl_3$



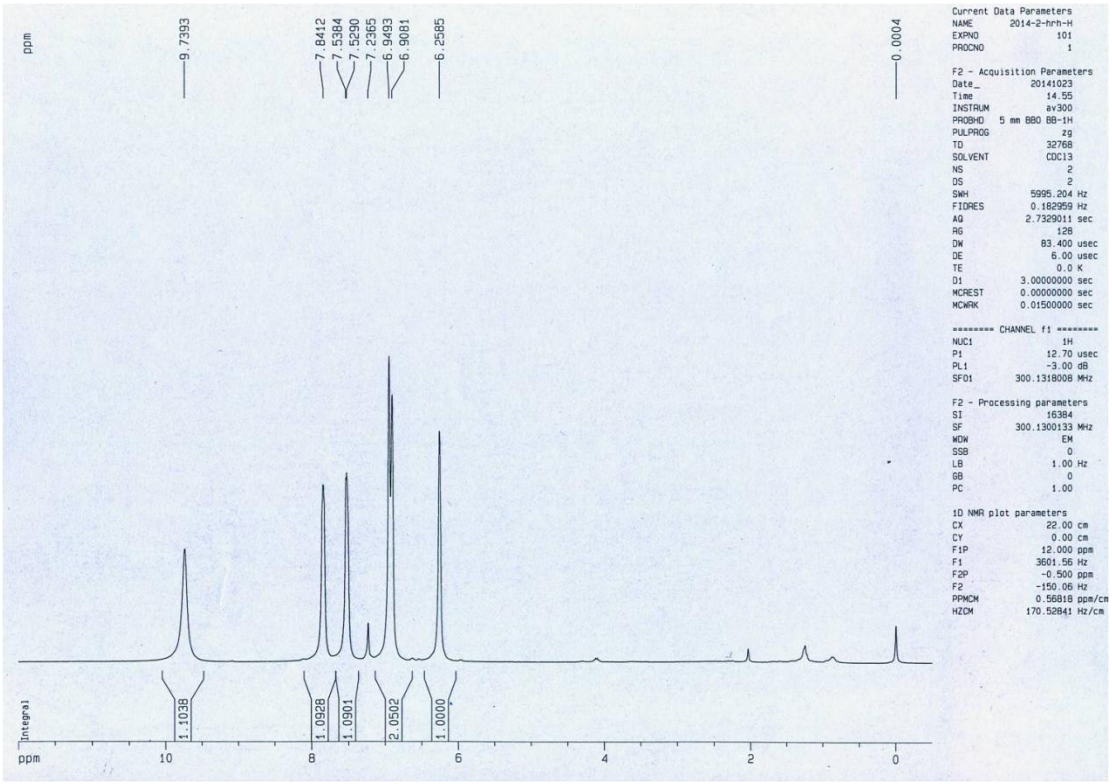
^{13}C NMR spectrum of **2** in $CDCl_3$



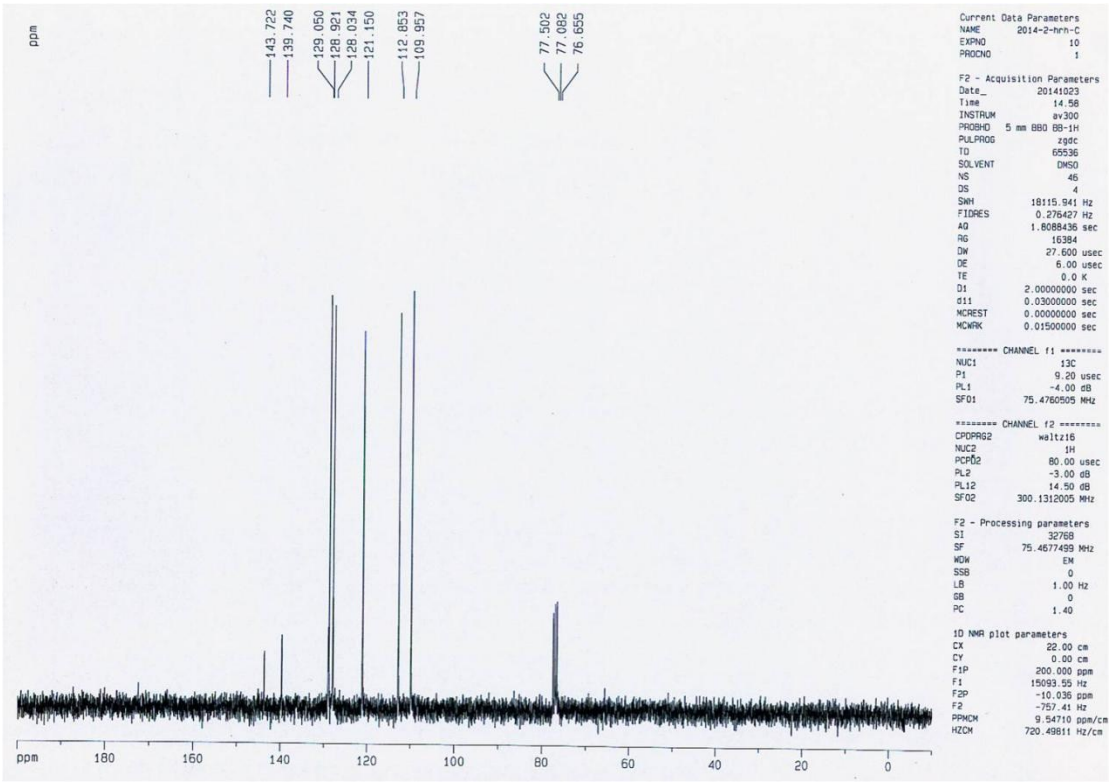
^{1}H NMR spectrum of **3** in $CDCl_3$



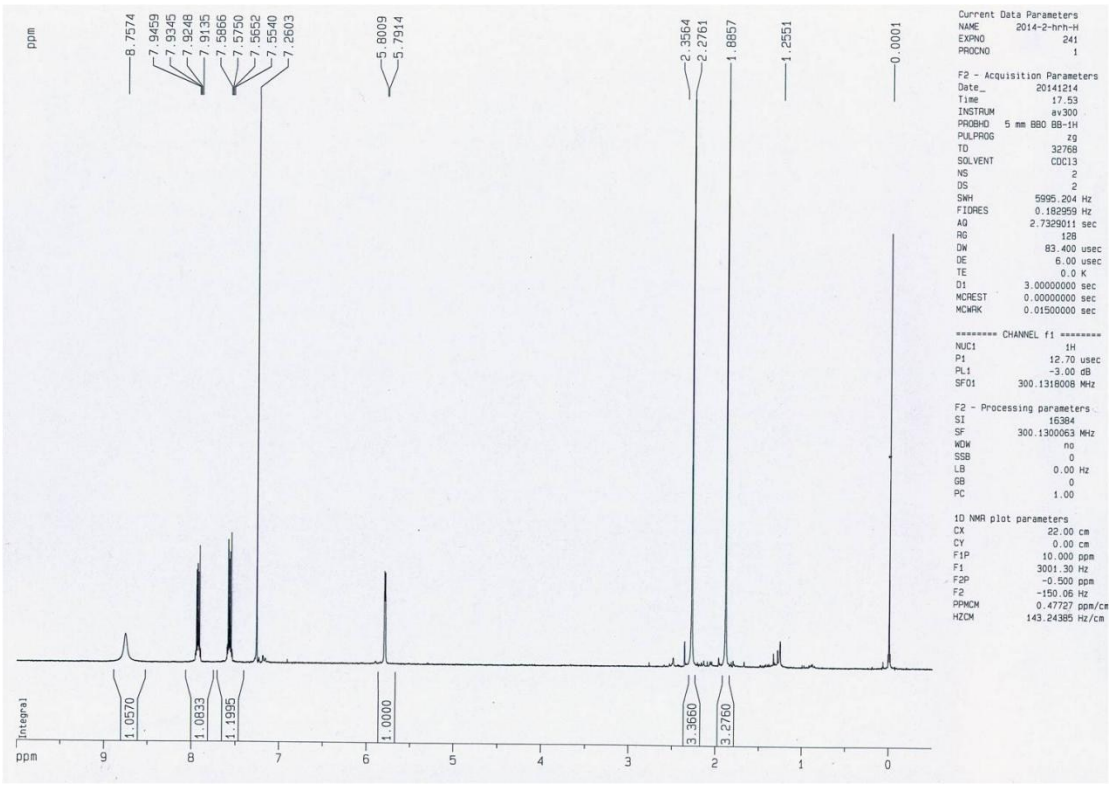
^{13}C NMR spectrum of **3** in $CDCl_3$



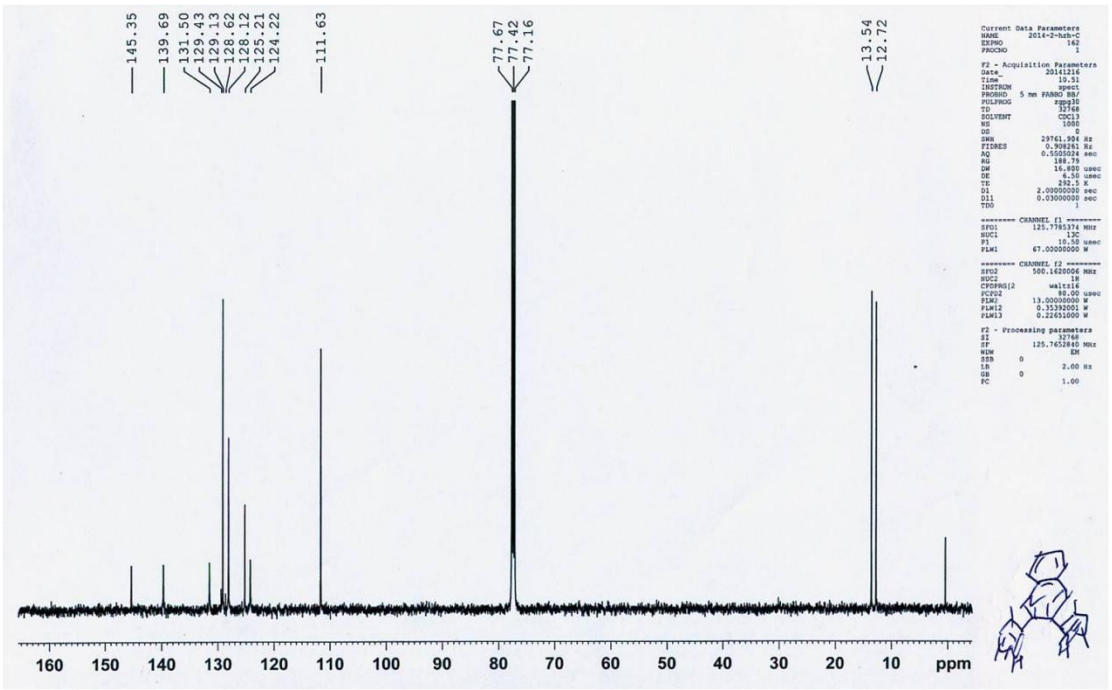
^{1}H NMR spectrum of **4** in $CDCl_3$



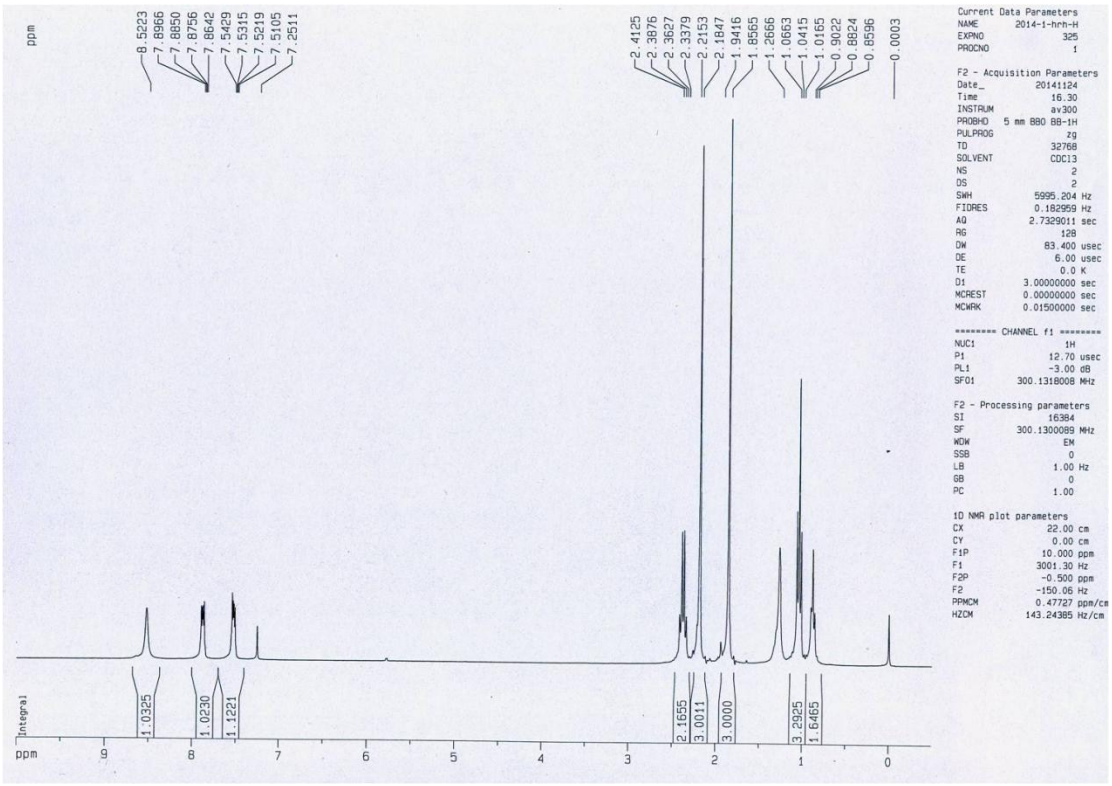
^{13}C NMR spectrum of **4** in $CDCl_3$



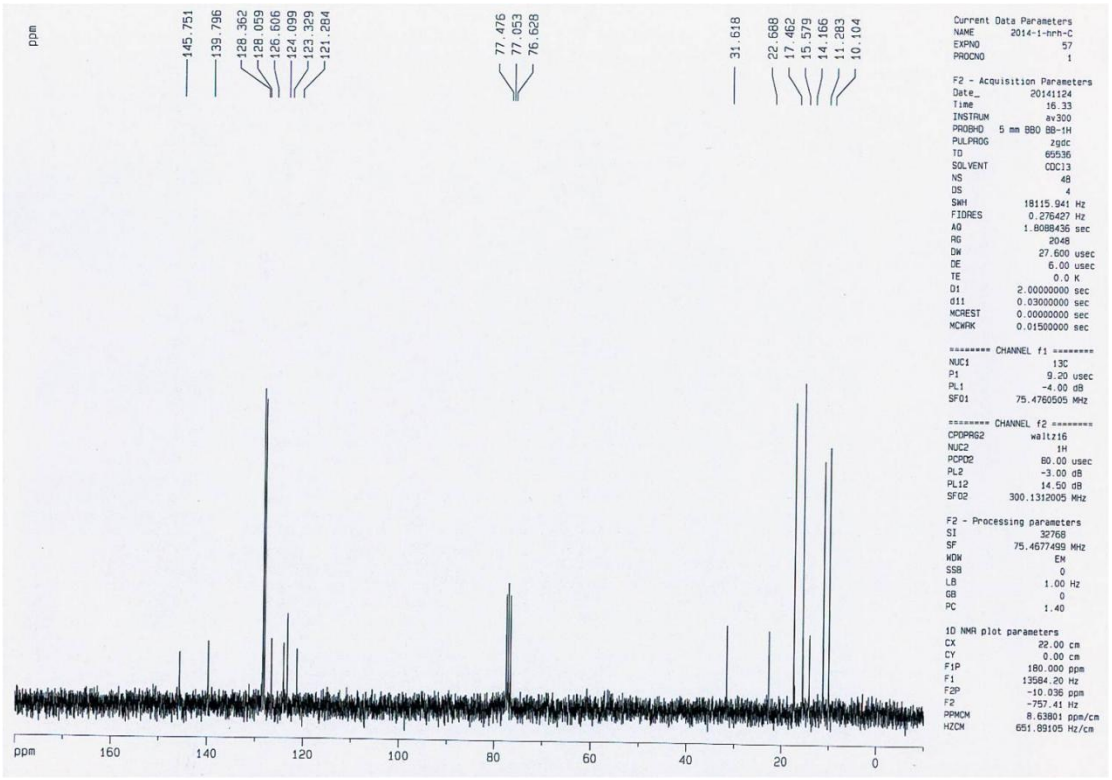
^{1}H NMR spectrum of **5** in $CDCl_3$



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



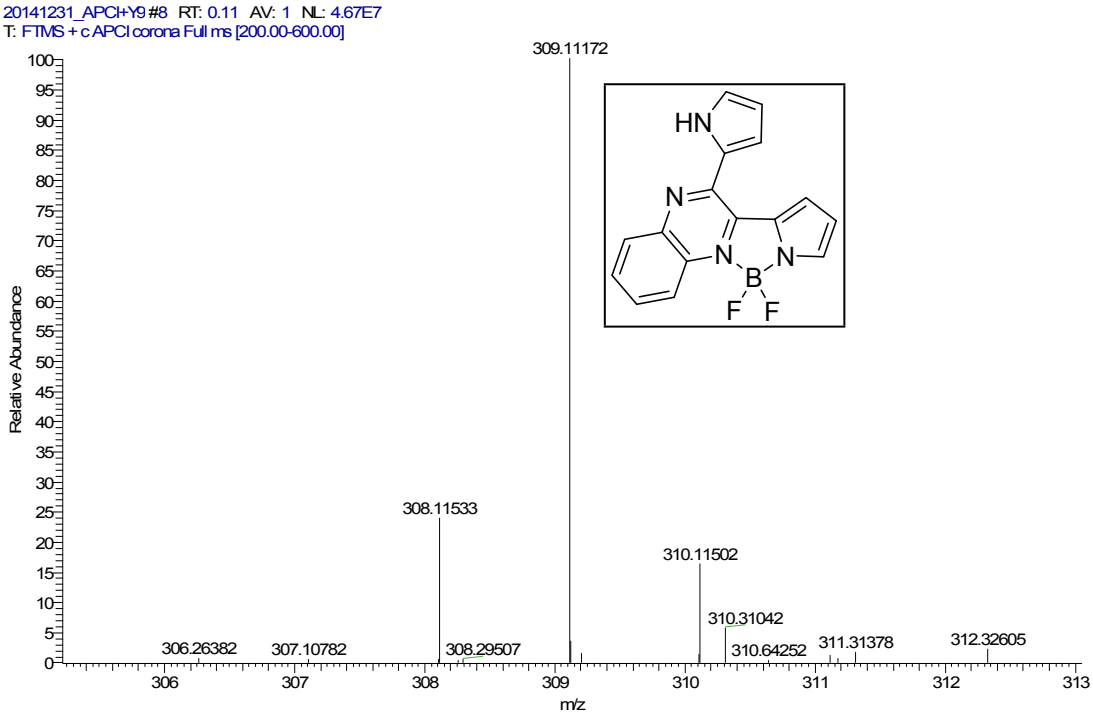
^{1}H NMR spectrum of **6** in $CDCl_3$



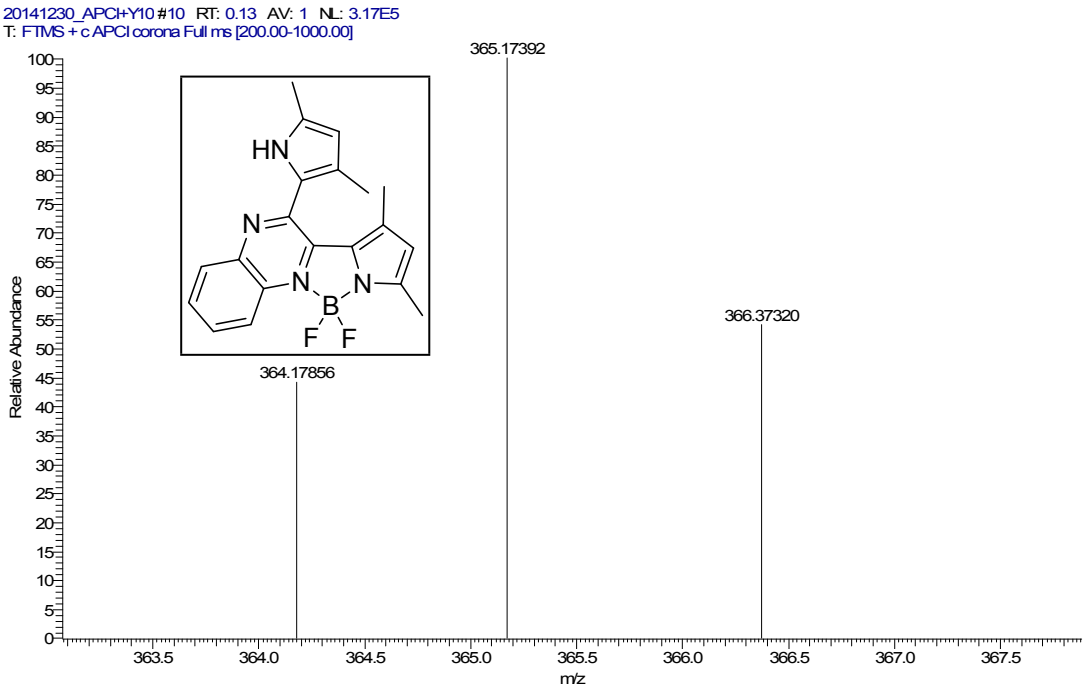
^{13}C NMR spectrum of **6** in $CDCl_3$

5. Copies of high resolution mass spectra for all compounds

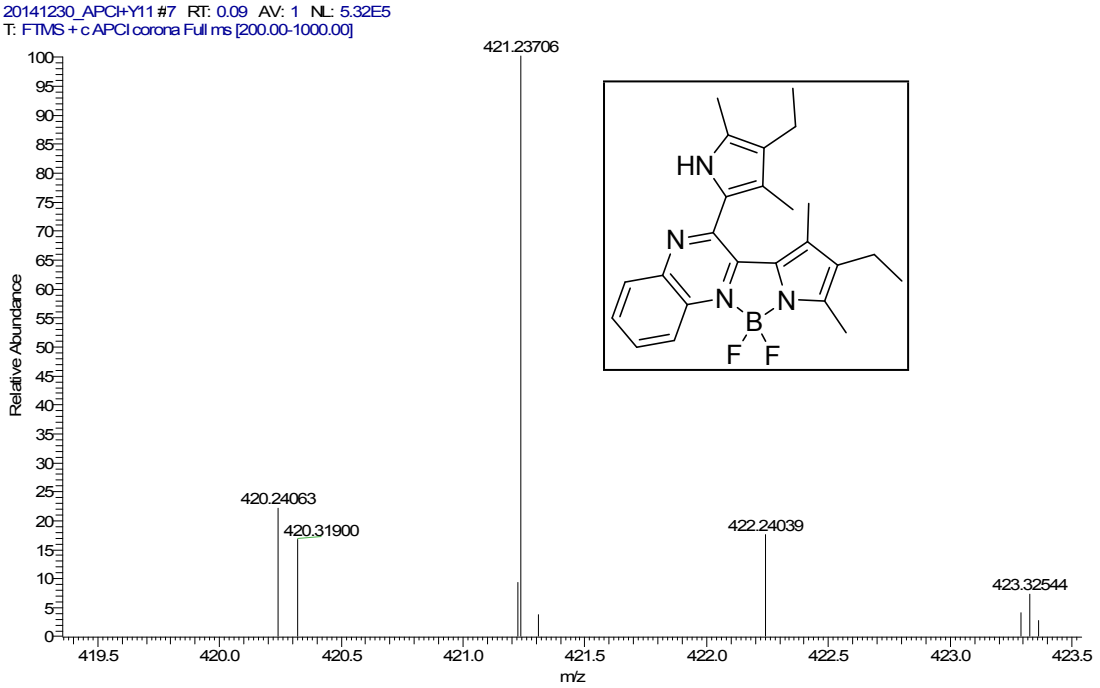
HRMS for **1**



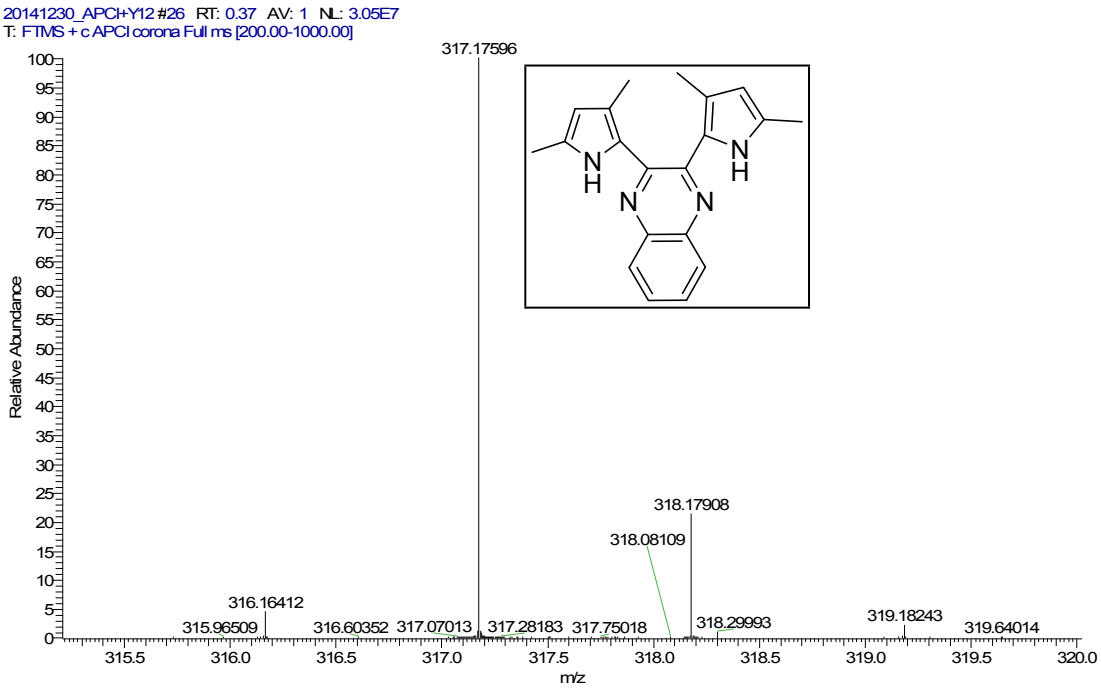
HRMS for **2**



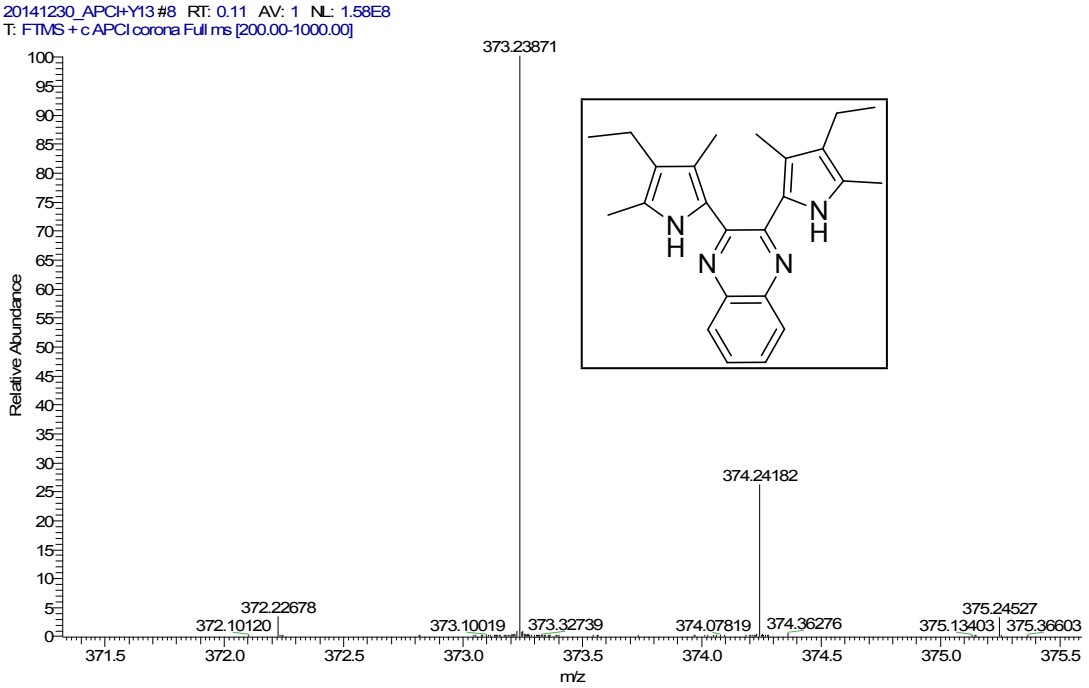
HRMS for **3**



HRMS for **5**



HRMS for **6**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H