Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Effect of Five Membered Aromatic Heterocycle at *Meso*-Position on the Electronic Properties of 3-Pyrrolyl BODIPY

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General Experimental Section

Chemicals: $BF_3.(OEt)_2$ and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) obtained from Spectrochem (India) were used as obtained. All other chemicals used for the synthesis were reagent grade unless otherwise specified. Column chromatography was performed on silica (60-120 mesh).

Instrumentation: The ^1H, ^{13}C and ^{11}B NMR spectra were recorded on 400 MHz and 500 MHz instruments in $CDCl_3$. TMS was used as an internal reference for recording ^1H (of residual proton; δ 7.26) and ^{13}C (δ 77.0 signal) in $CDCl_3$. ^1H-^1H COSY and NOESY experiments were performed on 400 MHz and 500 MHz instruments. Absorption and steady-state fluorescence spectra were obtained with Varian and PC1 Photon Counting Spectrofluorometer manufactured by ISS, USA instruments respectively. Fluorescence spectra were recorded at 25 ˚C in a 1 cm quartz fluorescence cuvette. The fluorescence quantum yields (ϕ_f) were estimated from the emission and absorption spectra by comparative method at the excitation wavelength of 488 nm using Rhodamine 6G (ϕ_f = 0.88in ethanol) as standard.[1] The time-resolved fluorescence decay measurements were carried out at the magic angle using a picosecond-diode-laser-based, time-correlated, single-photon-counting (TCSPC) fluorescence spectrometer from IBH, UK.

Cyclic voltammetric (CV) studies were carried out with electrochemical system utilizing the three electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxillary electrode) and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte (TBAP). Half wave potentials were measured using DPV and also calculated manually by taking the average of the cathodic and anodic peak potentials. All potentials were calibrated versus saturated calomel electrode by the addition of ferrocene as

an internal standard, taking $E_{1/2}$ (Fc/Fc^+) = 0.51 V, vs SCE. The HRMS spectra were recorded with Bruker maxis imapact 282001.00081 using eletron spray ionization method and TOF analyser.

X-ray crystal structure analysis:

Single-crystal X-ray structure analysis was performed on a Rigaku Saturn724 diffractometer that was equipped with a low-temperature attachment. Data were collected at 100 K using graphite-monochromated Mo-K_α radiation (λ_α= 0.71073 Å) with the ω-scan technique. The data were reduced by using CrystalClear-SM Expert 2.1 b24 software. The structures were solved by direct methods and refined by least-squares against F^2 utilizing the software packages SHELXL-97[2], WINGX[3] and CRYSTAL ISSUE 10[4]. All non-hydrogen atoms were refined anisotropic displacement factors. The hydrogen atoms were placed in ideal positions and fixed with relative isotropic displacement parameters.

Reference

1. J. Olmested, III, *J. Phys. Chem.*, 1979, **83**, 2581-2584.
2. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
3. A. Altomare, G. Cascarano, C. Giacovazzo and A. Gualardi, *J. Appl. Cryst.*, 1993, **26**, 343.
4. D.J. Watkin, C. K. Prout, R. J. Carruthers and P.W. Betteridge CRYSTAL ISSSUE 10. Chemical Crystallography Laboratory, Oxford, UK, 1996.

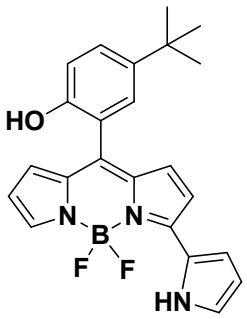
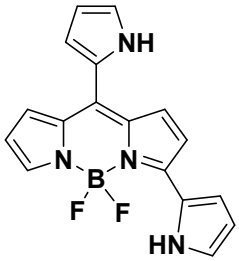


Chart S1: Molecular structure of compound **8**.



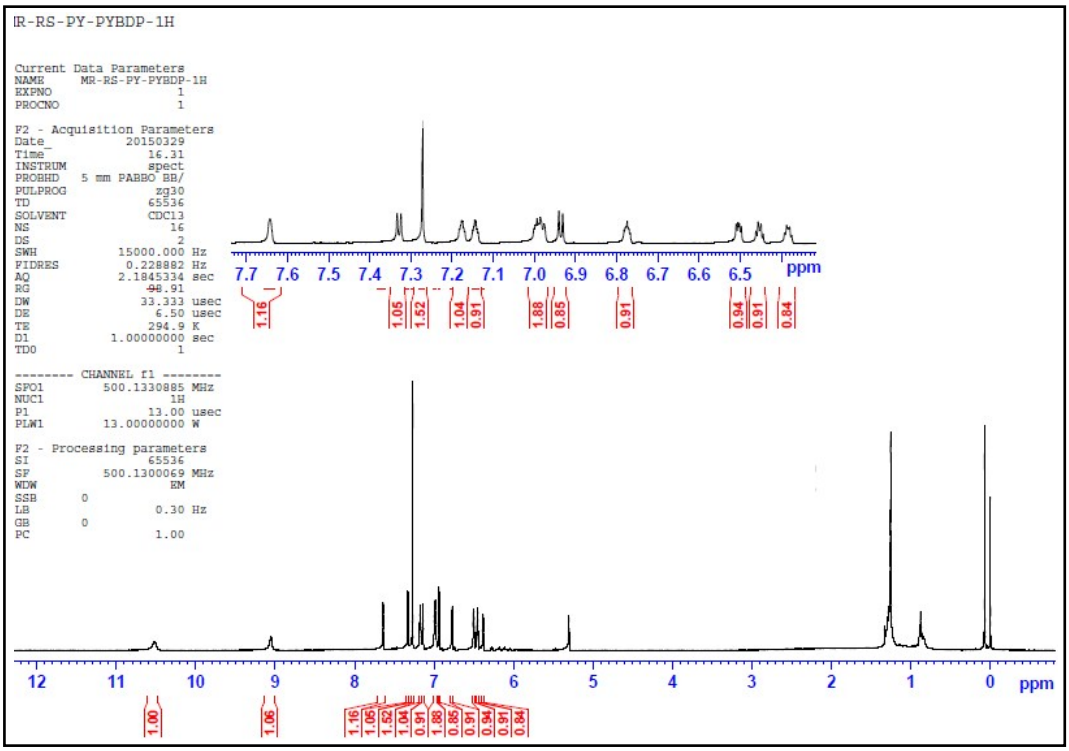
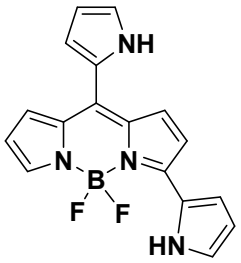


Figure S1: ^{1}H NMR spectrum of compound **2** recorded in $CDCl_3$.



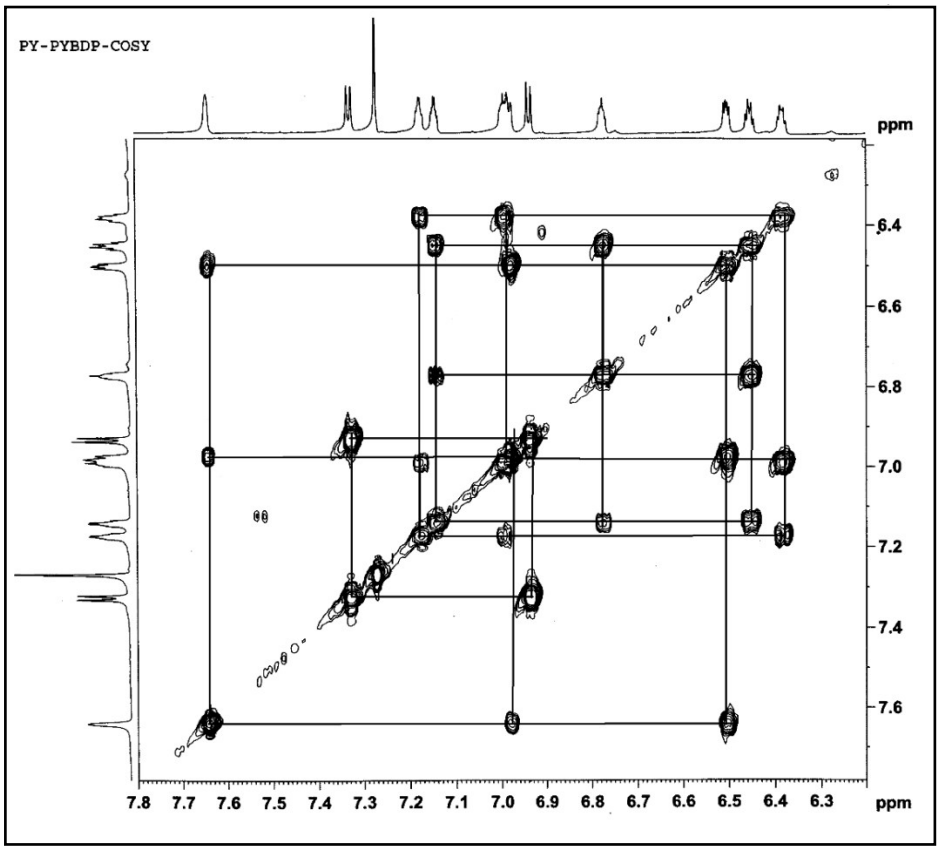


Figure S2: Partial ^{1}H-^{1}H correlation spectrum of compound **2** recorded in $CDCl_3$.

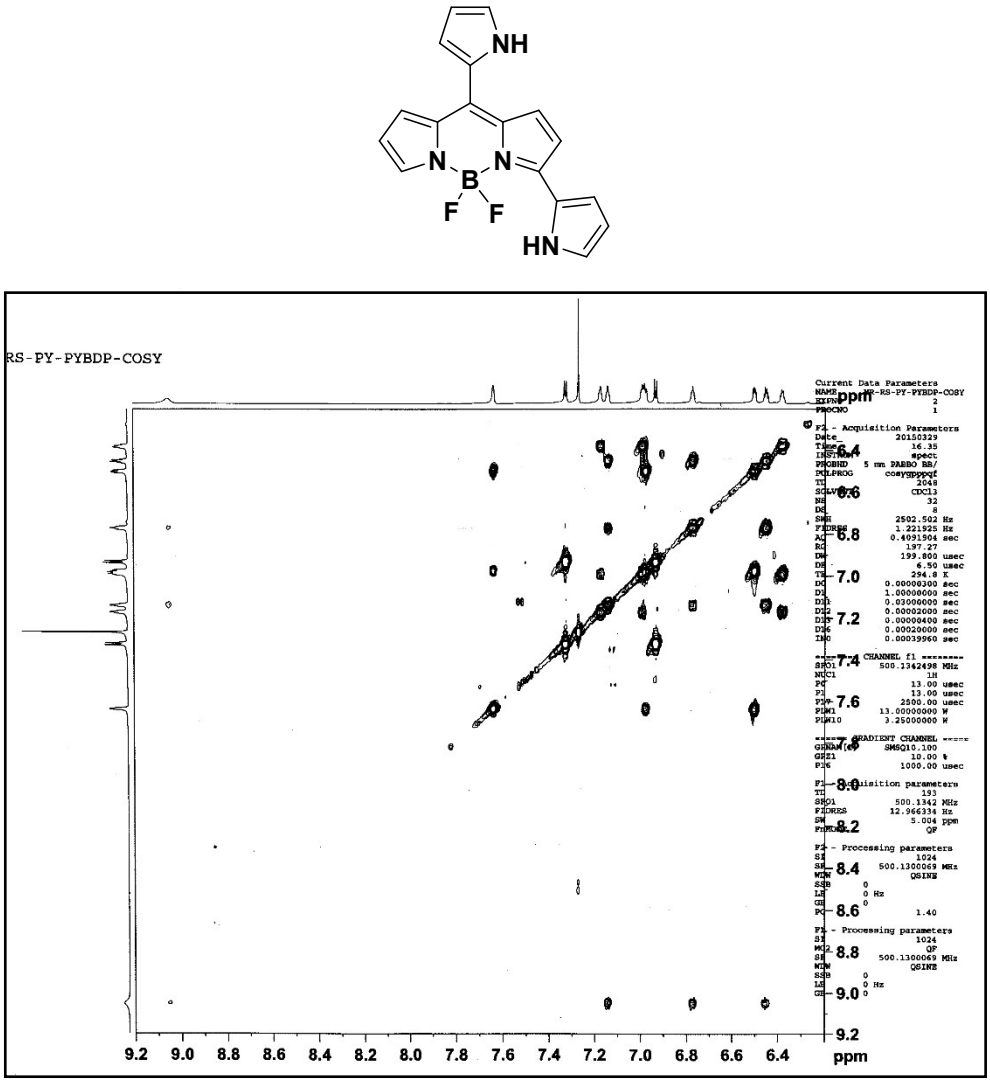
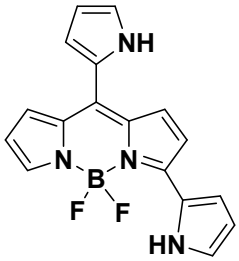


Figure S3: ^{1}H-^{1}H correlation spectrum of compound **2** recorded in $CDCl_3$.



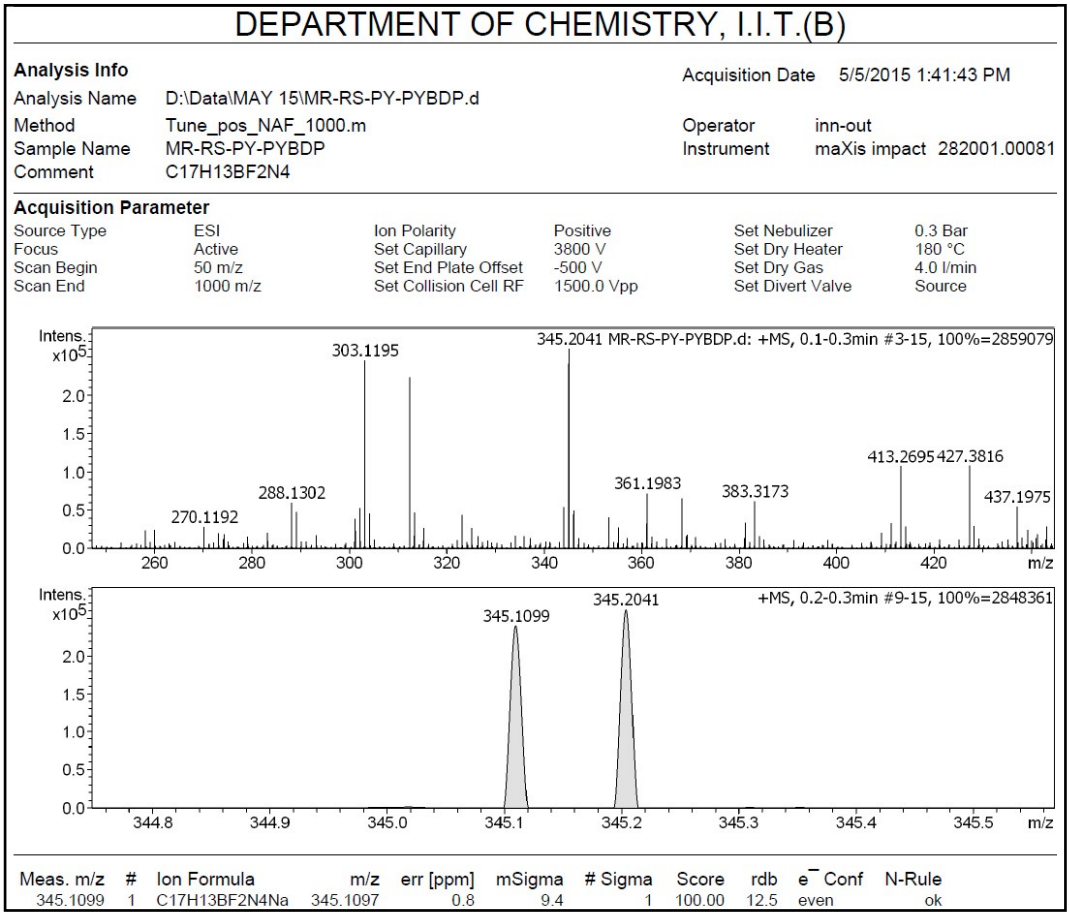
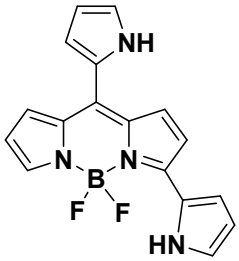


Figure S4: HRMS of compound **2**.



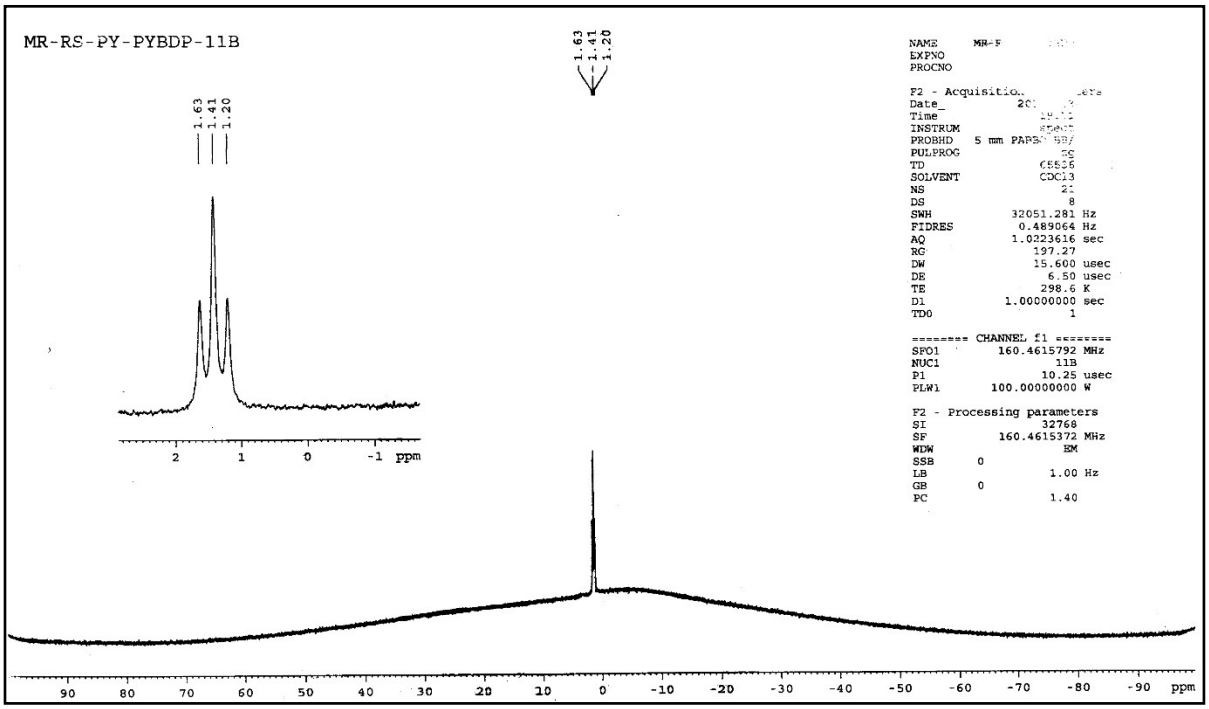


Figure S5: ^{11}B NMR spectrum of compound **2** recorded in $CDCl_3$.

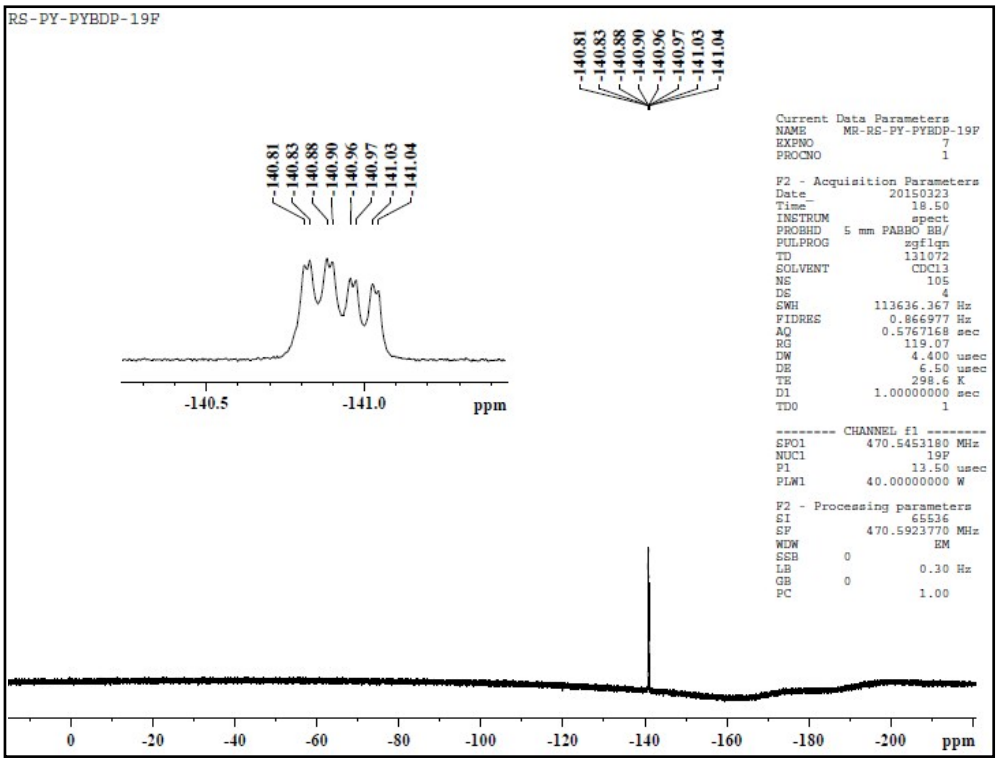
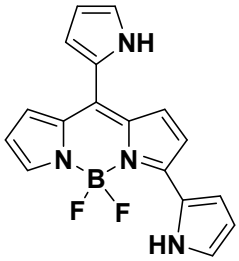


Figure S6: ^{19}F NMR spectrum of compound **2** recorded in $CDCl_3$.



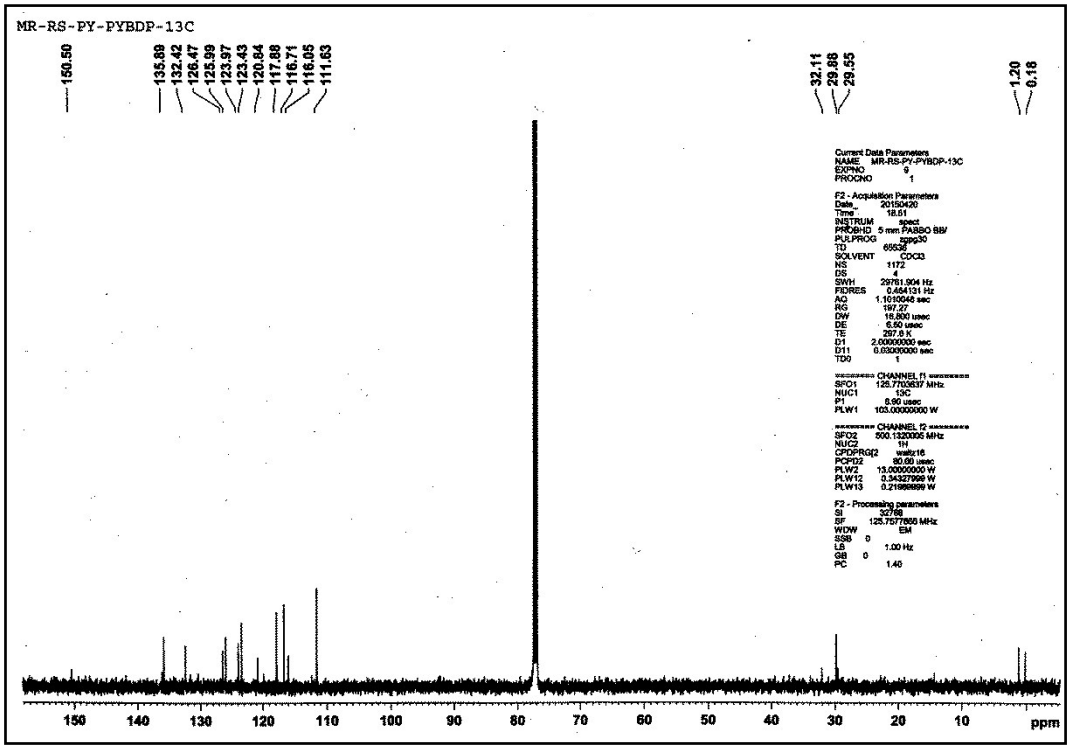
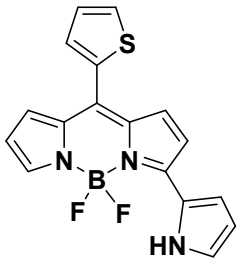


Figure S7: ^{13}C NMR spectrum of compound **2** recorded in $CDCl_3$.



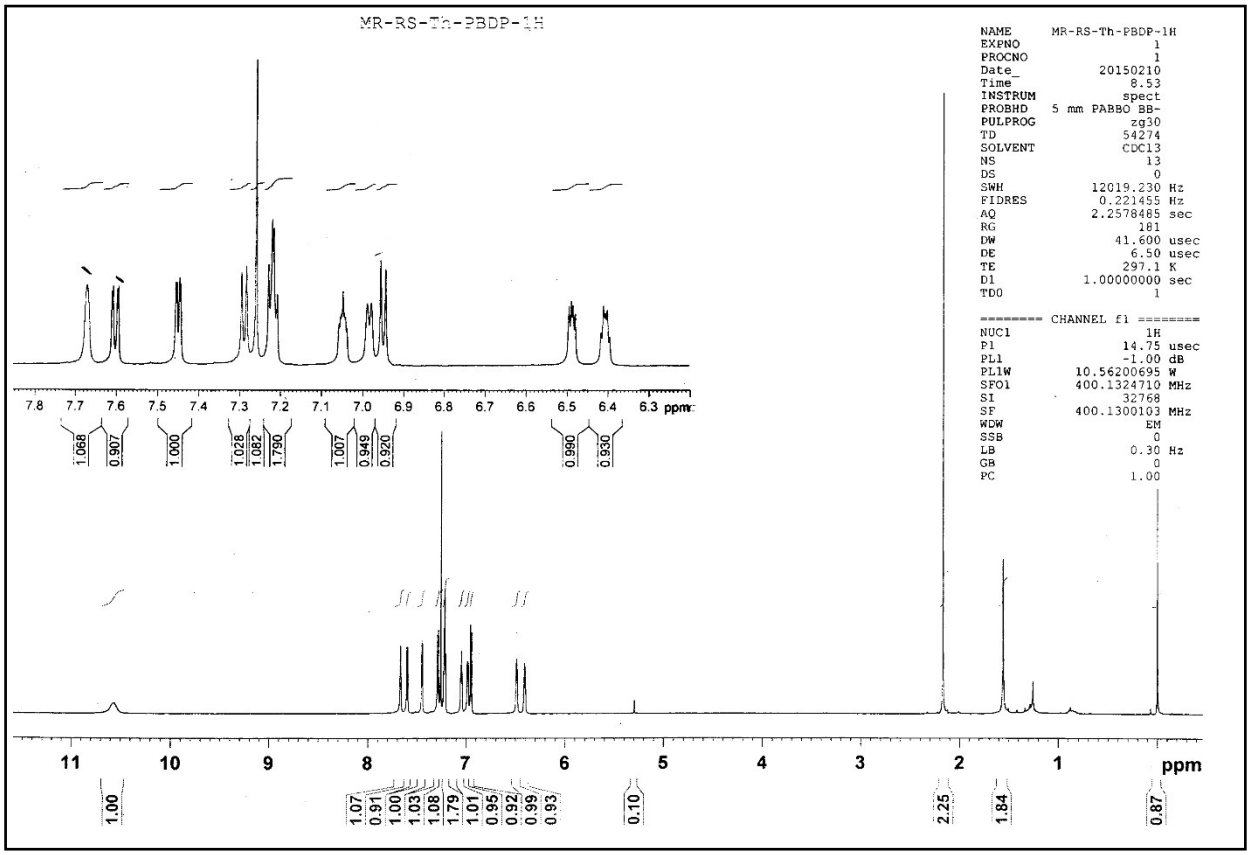
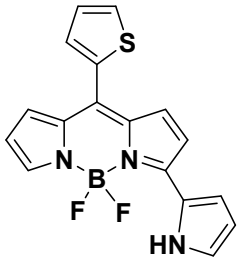


Figure S8: ^{1}H NMR spectrum of compound **3** recorded in $CDCl_3$.



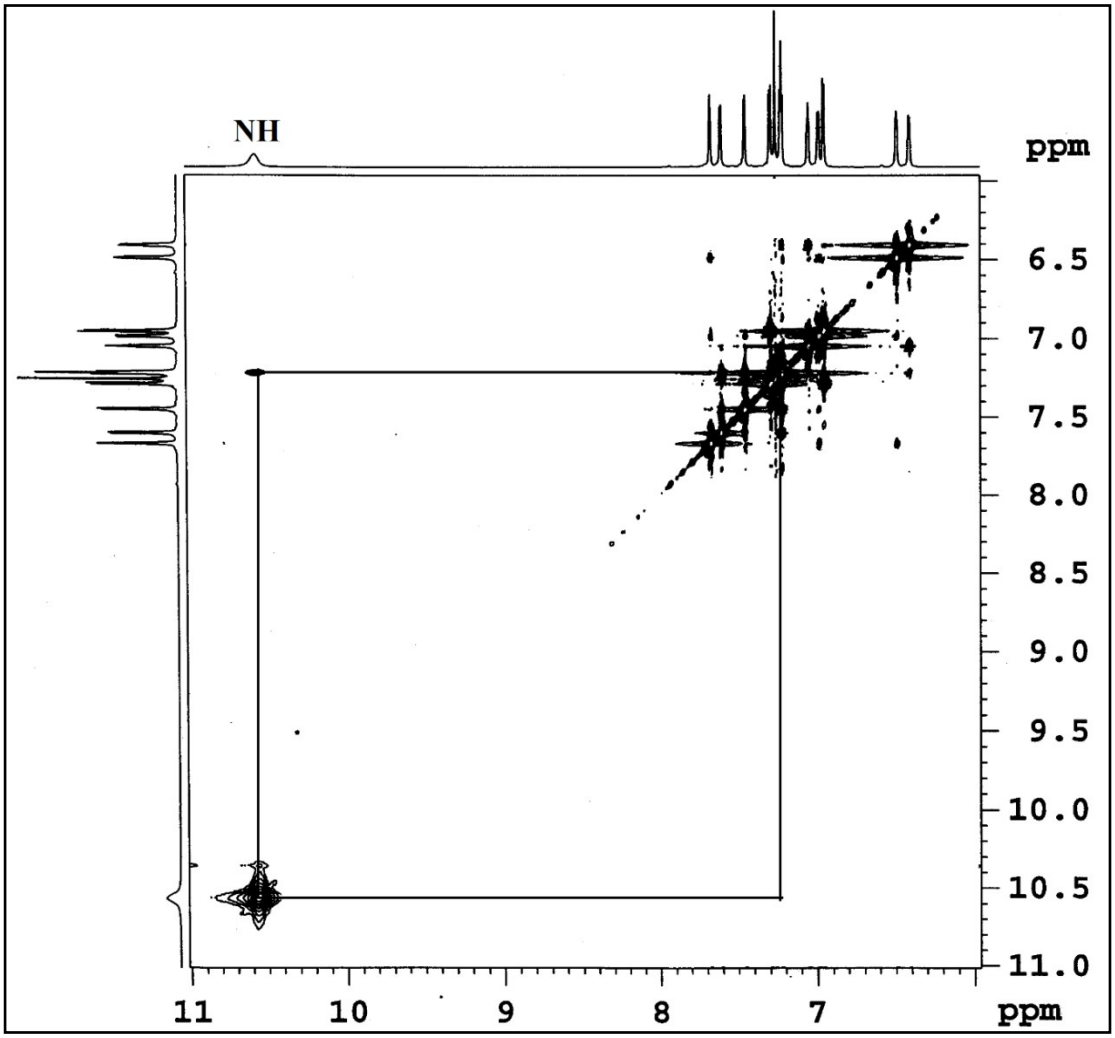
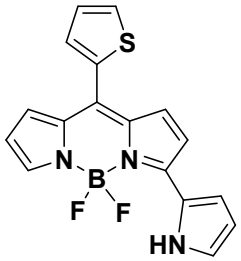


Figure S9: Partial ^{1}H-^{1}H correlation spectrum of compound **3** recorded in $CDCl_3$.



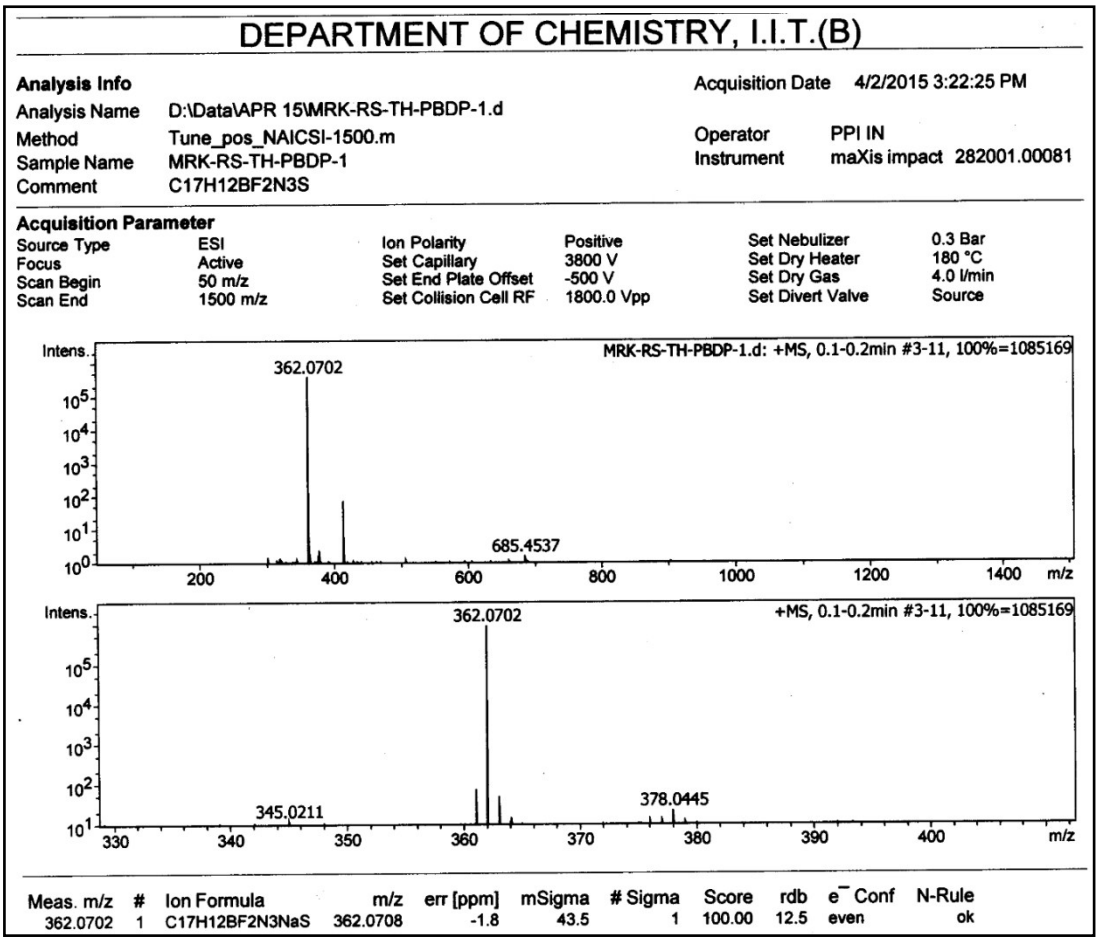


Figure S10: HRMS of compound **3**.

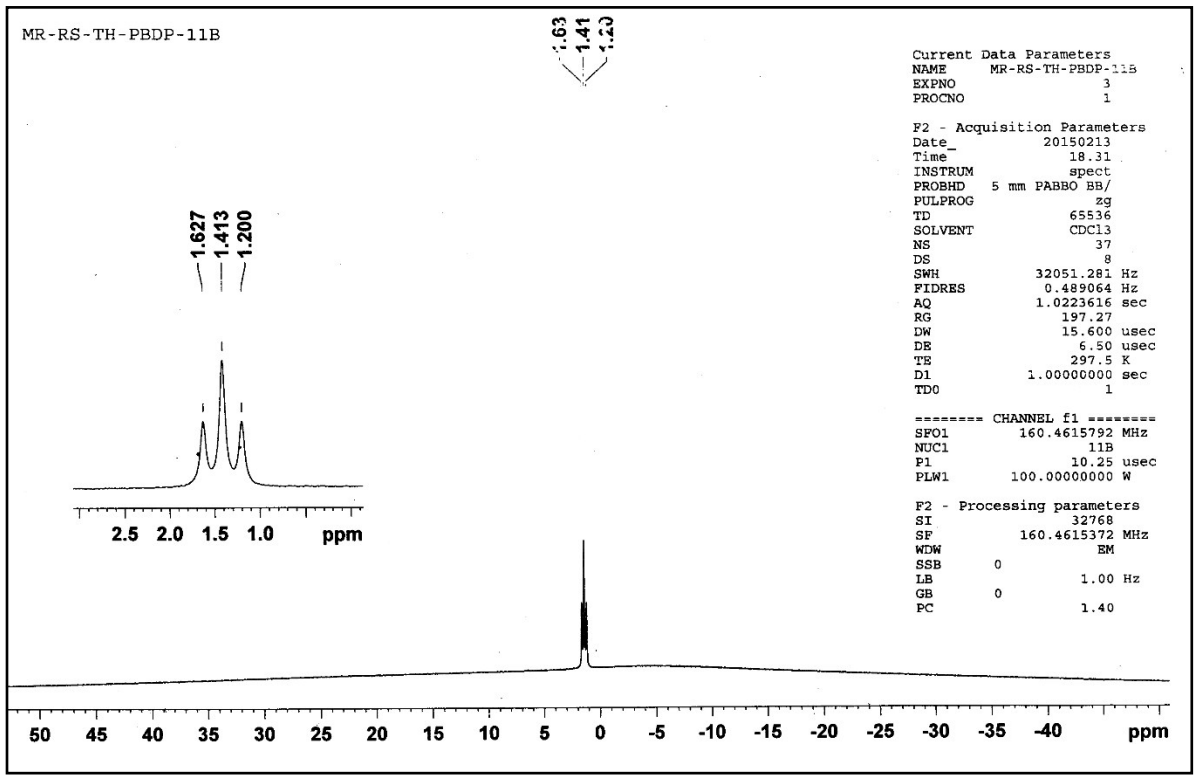


Figure S11: ^{11}B NMR spectrum of compound **3** recorded in $CDCl_3$.

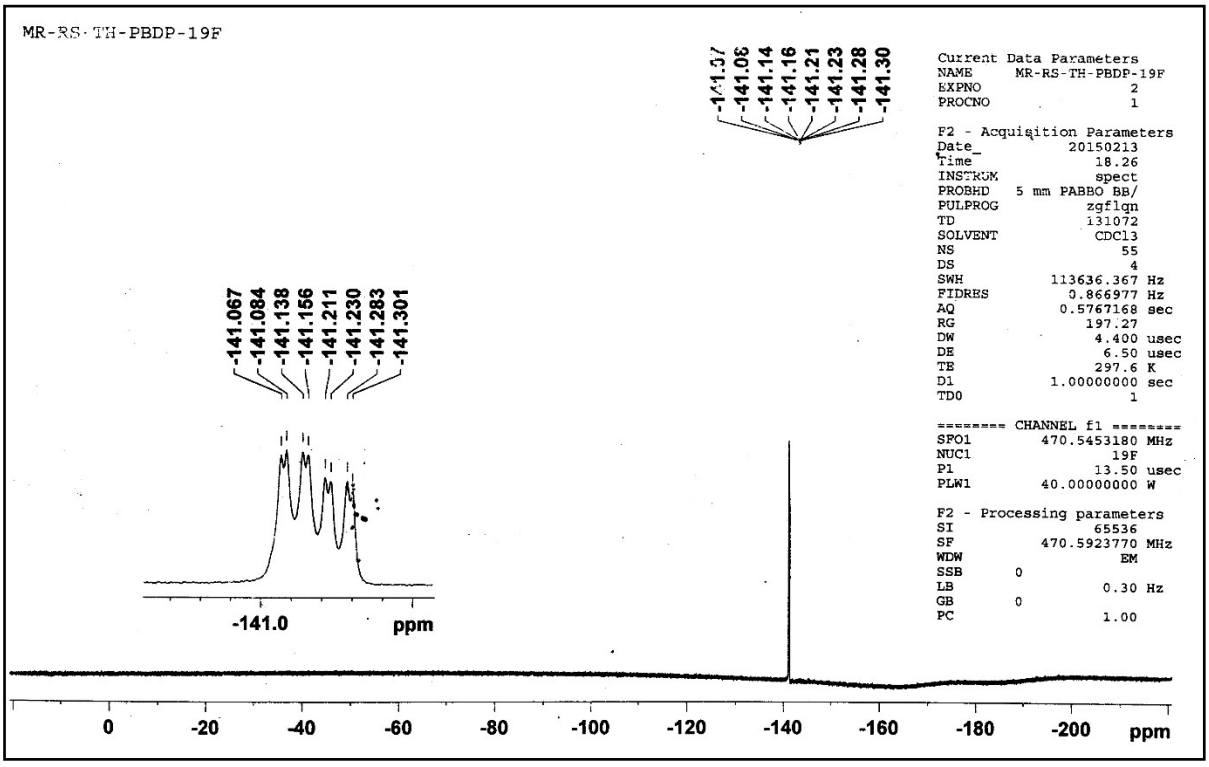


Figure S12: ^{19}F NMR spectrum of compound **3** recorded in $CDCl_3$.

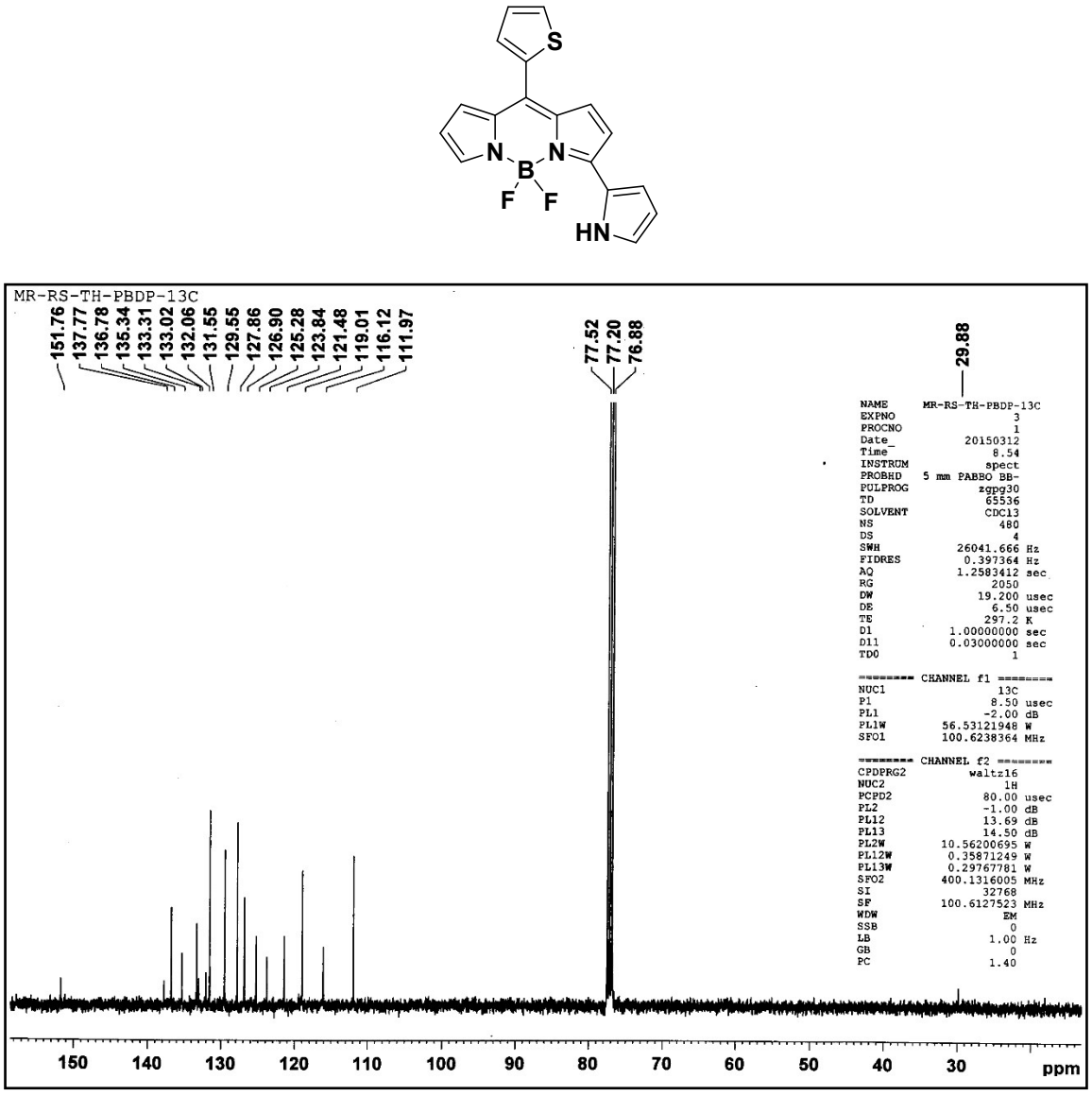
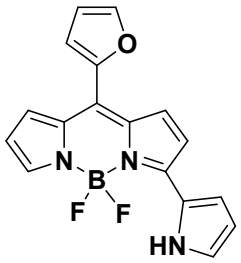


Figure S13: ^{13}C NMR spectrum of compound **3** recorded in $CDCl_3$.



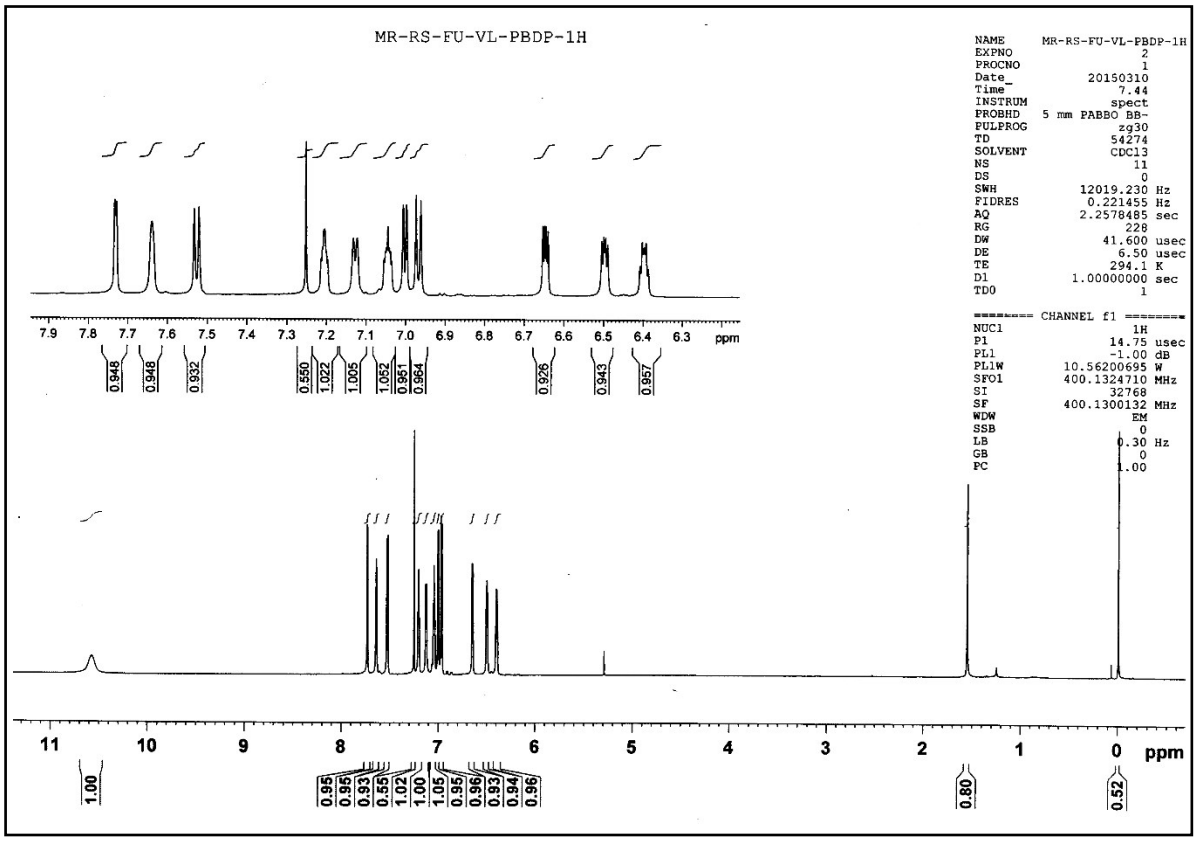


Figure S14: ^{1}H NMR spectrum of compound **4** recorded in $CDCl_3$.

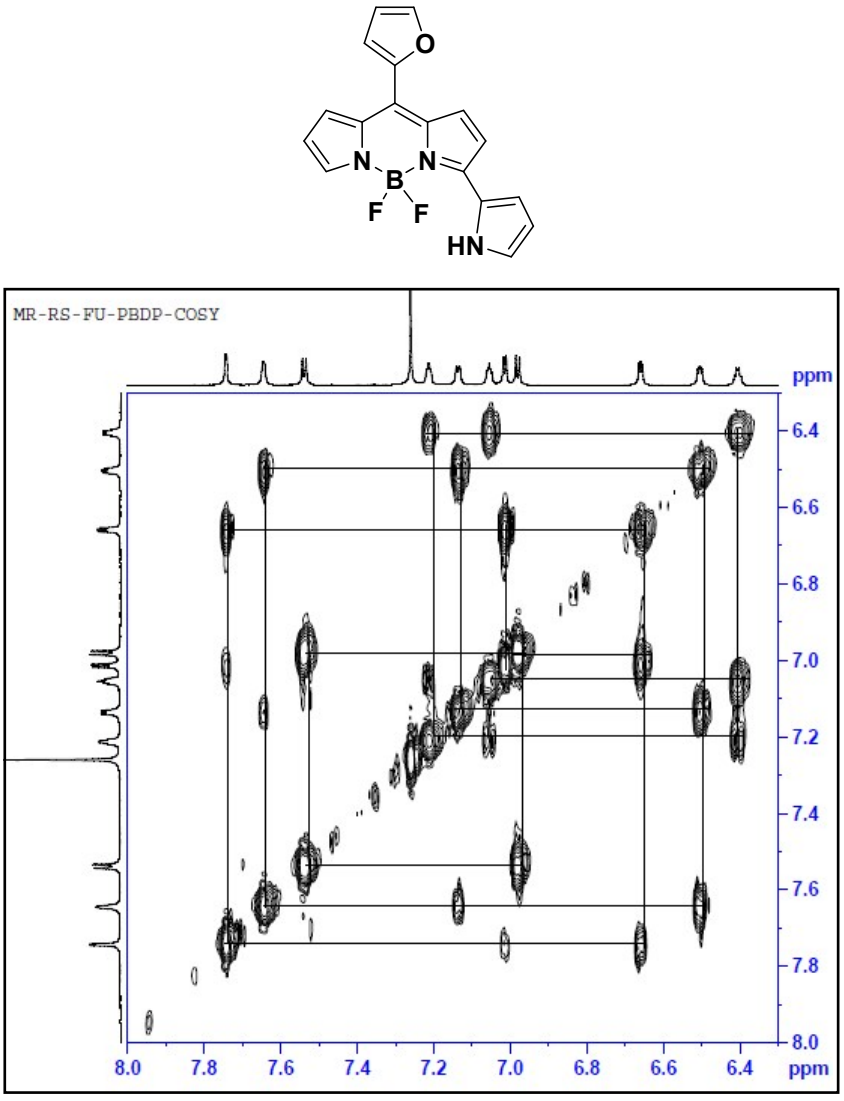
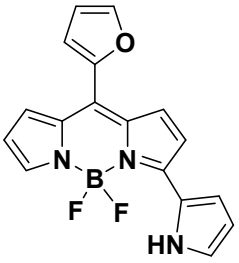


Figure S15: Partial ^{1}H-^{1}H correlation spectrum of compound **4** recorded in $CDCl_3$.



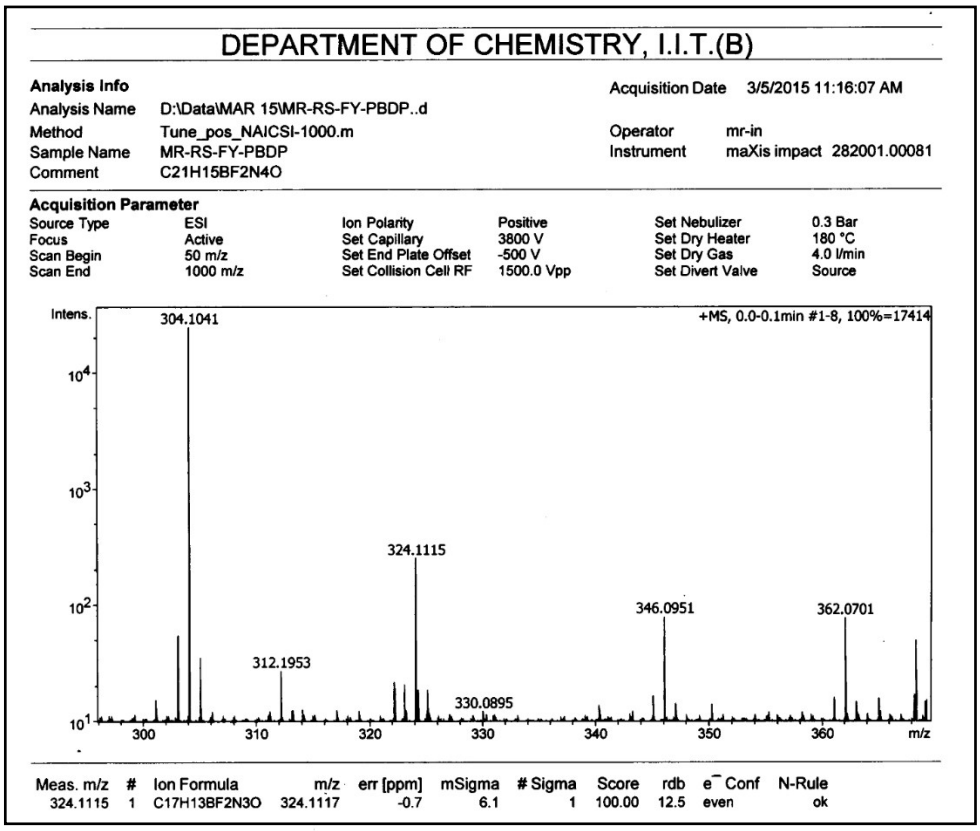


Figure S16: HRMS of compound **4**.

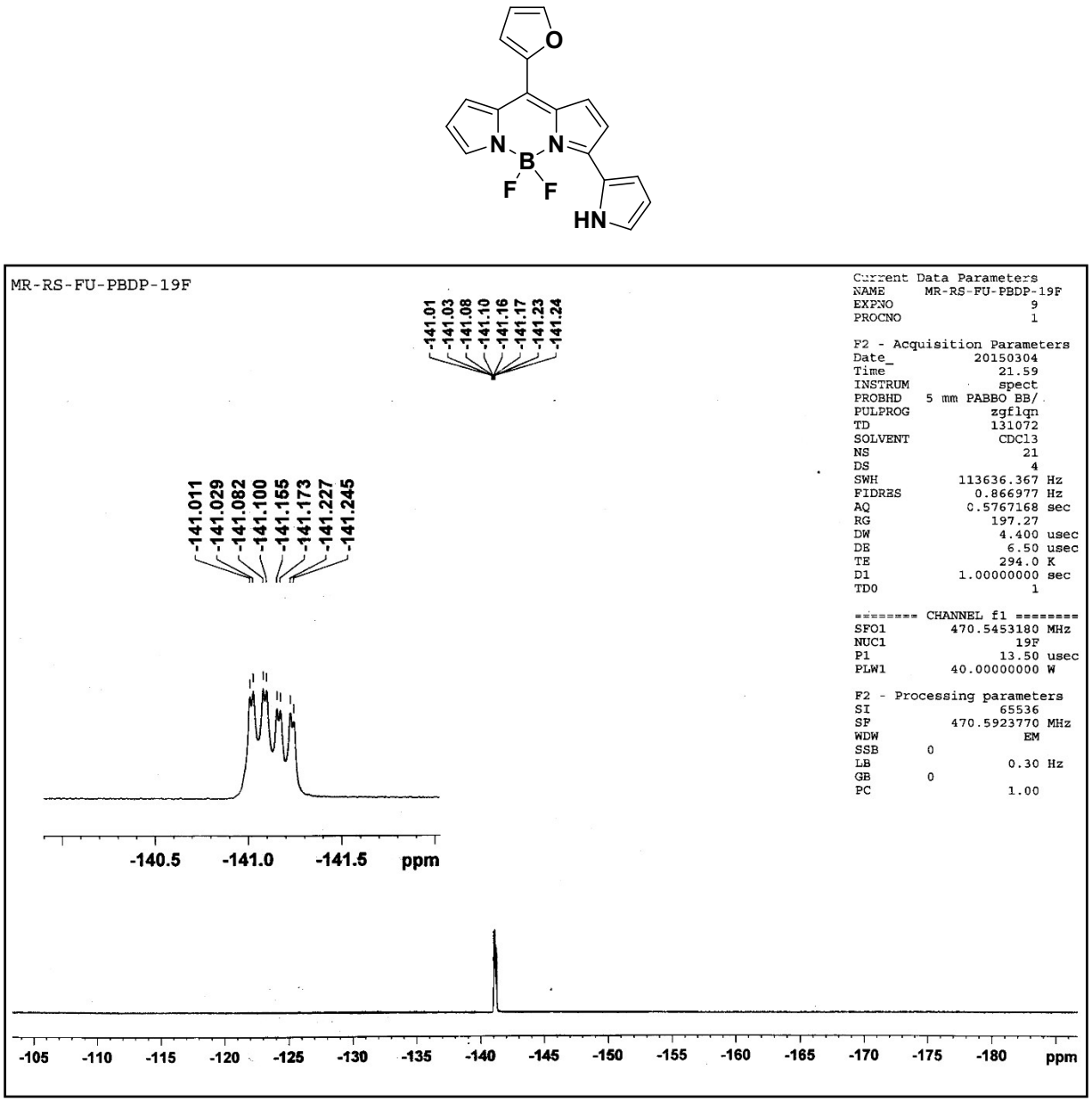
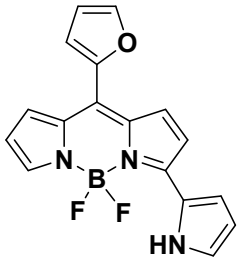


Figure S17: ^{19}F NMR spectrum of compound **4** recorded in $CDCl_3$.



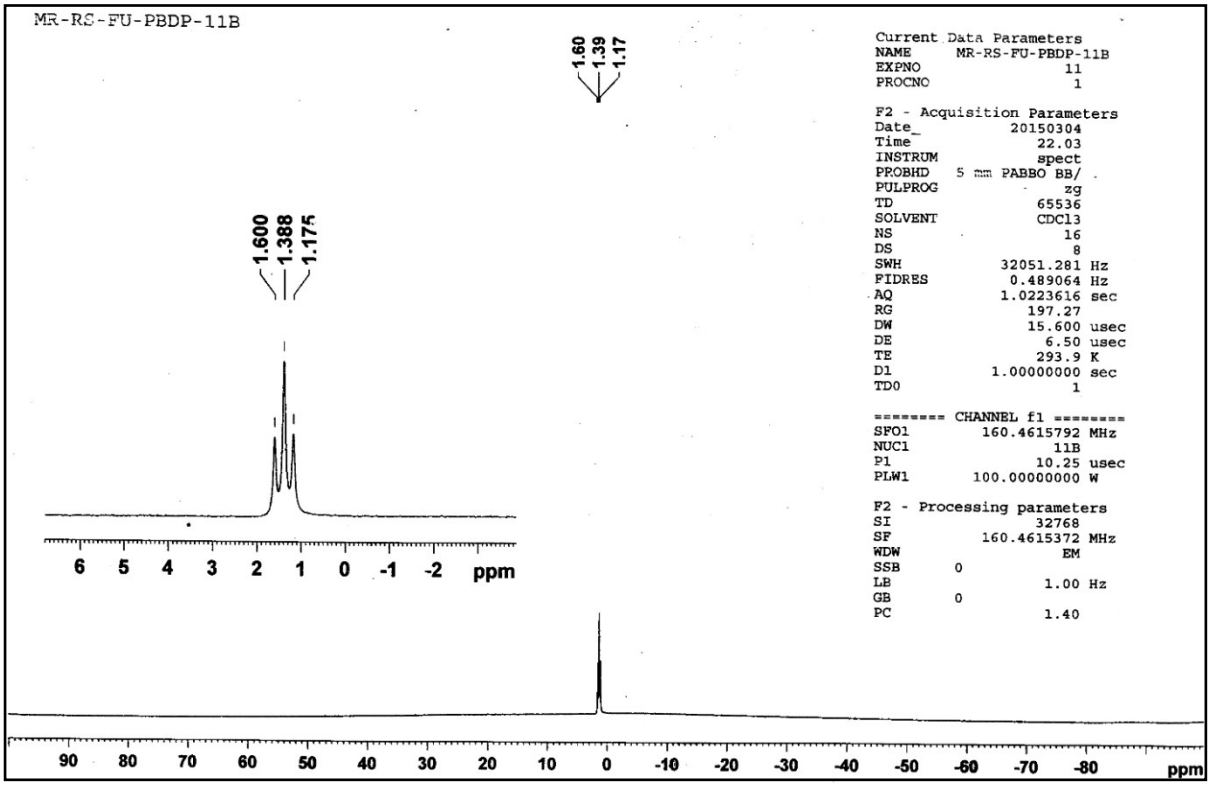


Figure S18: ^{11}B NMR spectrum of compound **4** recorded in $CDCl_3$.

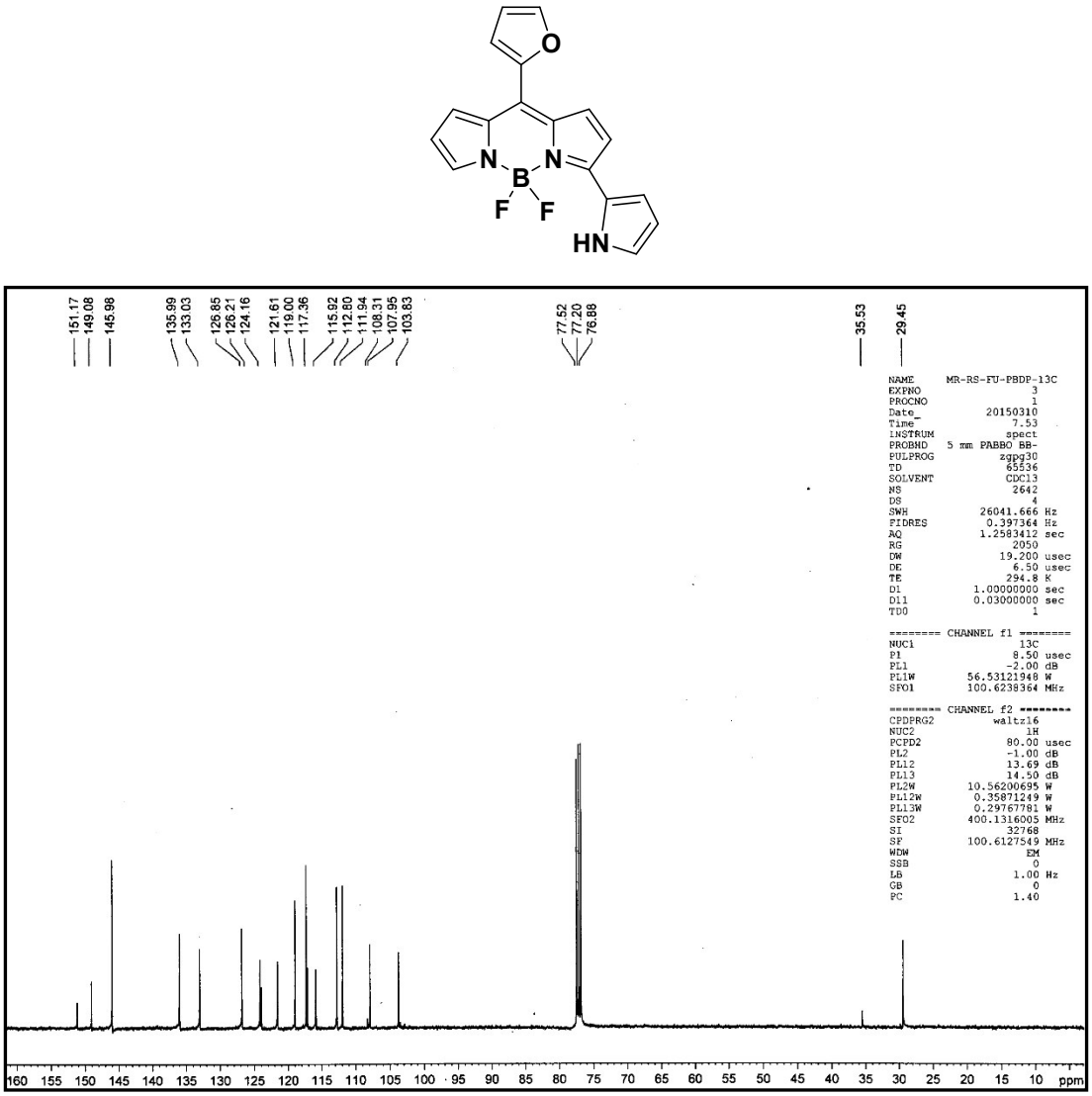


Figure S19: ^{13}C NMR spectrum of compound **4** recorded in $CDCl_3$.

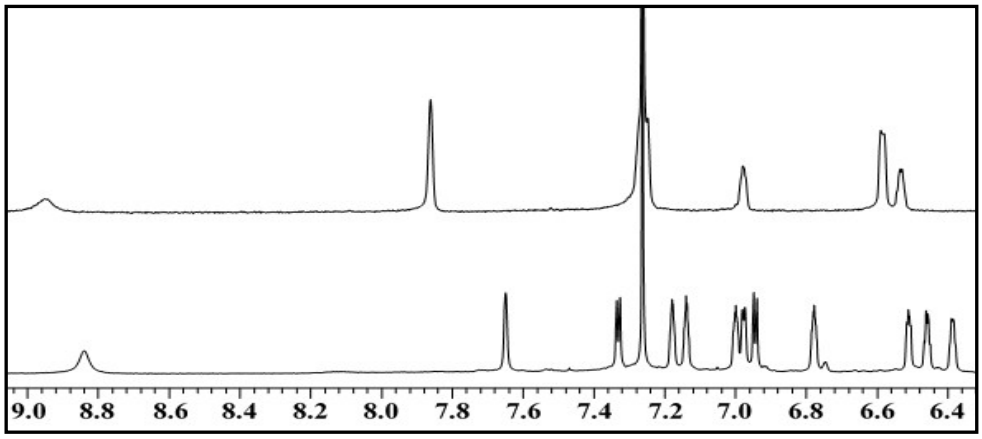


Figure S20: Comparison of ^{1}H NMR of compounds **2** and **5**.

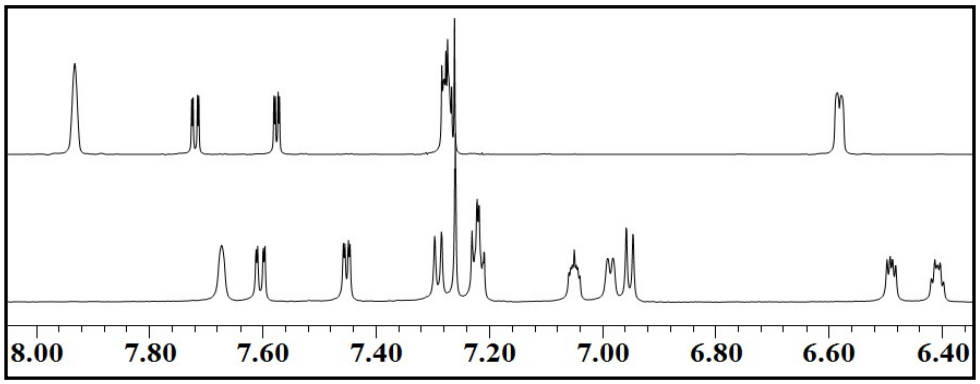


Figure S21: Comparison of ^{1}H NMR of compounds **3** and **6**.

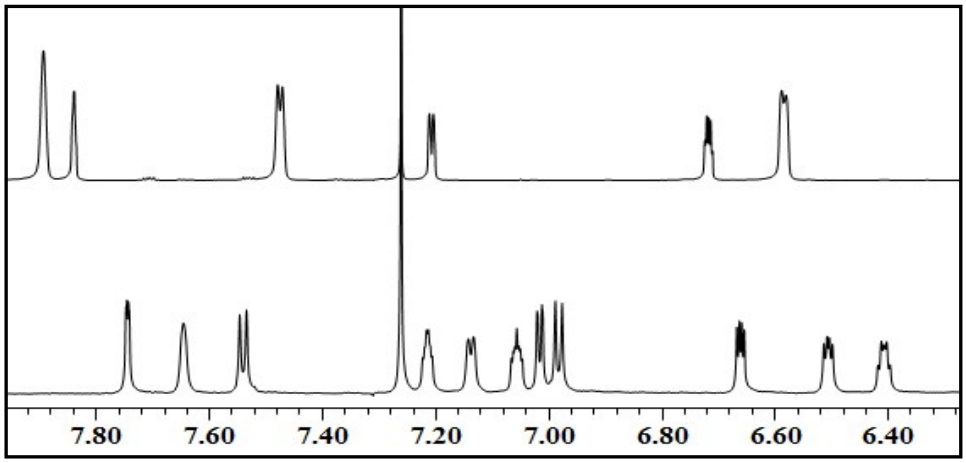


Figure S22: Comparison of ^{1}H NMR of compounds **4** and **7**.

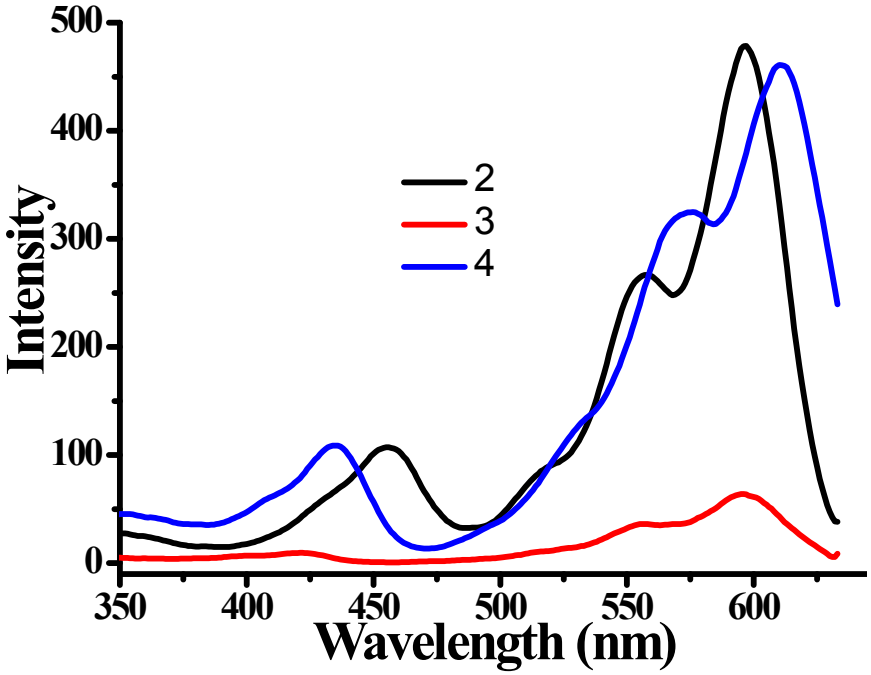


Figure S23: Excitation spectra of compounds **2-4**.

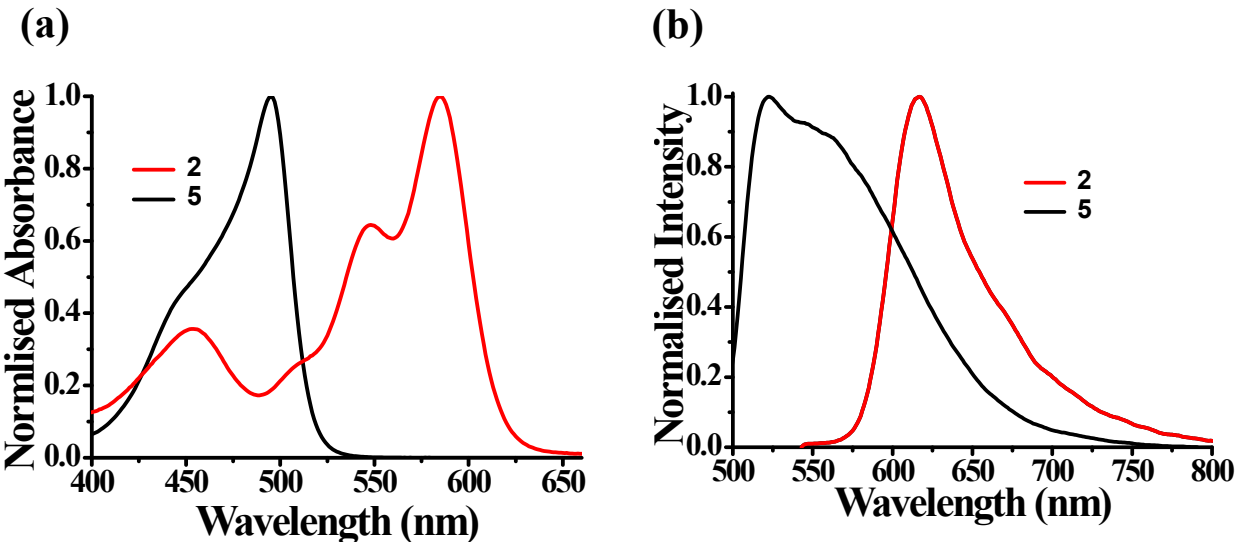


Figure S24: (a) Absorption and (b) emission spectra of compounds **2** and **5**.

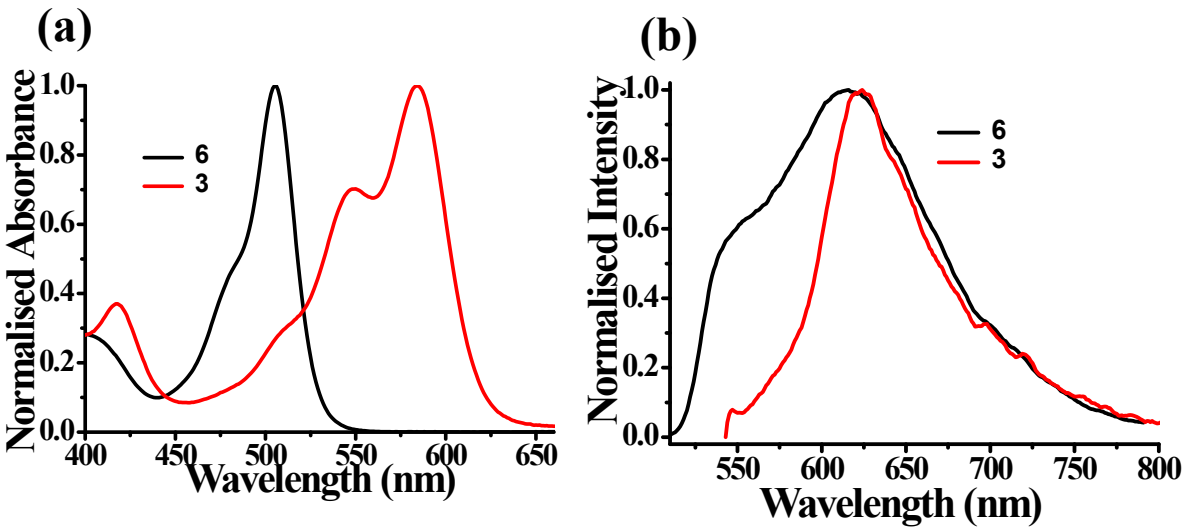


Figure S25: (a) Absorption and (b) emission spectra of compounds **3** and **6**.

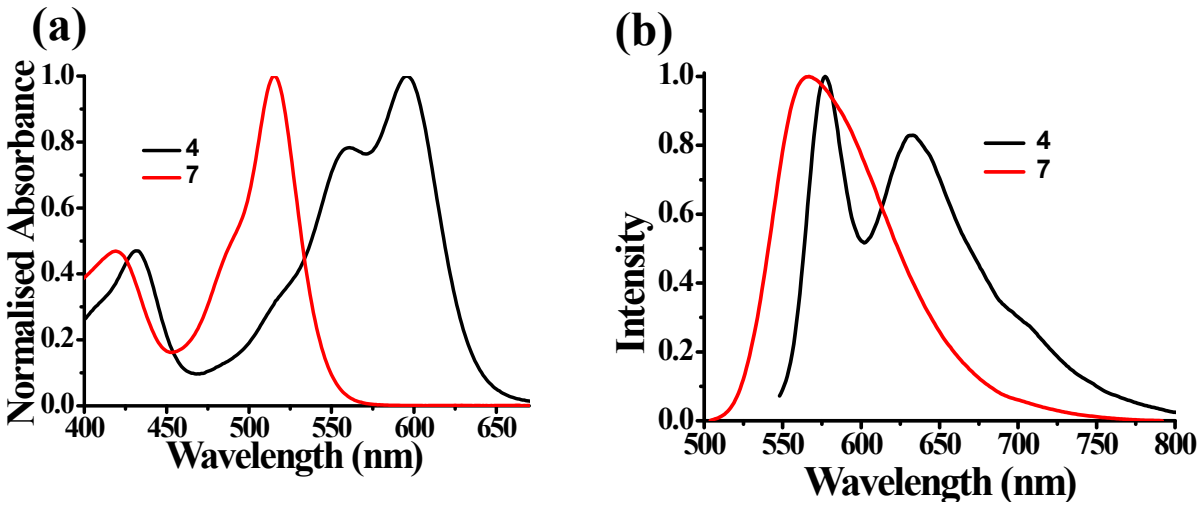


Figure S26: (a) Absorption and (b) emission spectra of compounds **4** and **7**.

Table 1: Crystal data and structure refinement parameters for compound **4**.

Parameters	data
Molecular formula	$C_{17}H_{12}BF_2N_3O$
fw	323.01
Crystal system	Orthorhombic
Space group	Pna21
a (Å)	20.469(4)
b (Å)	10.079(2)
c (Å)	6.7220(13)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	1386.8(5)
Z	4
θ (°)	3.0–29.1
μ (mm^{-1})	0.116
R_{int}	0.070
D_{calcd} (Mg m^{-3})	1.547
F(000)	616
R1, wR2 [I > 2σ(I)]	0.0557, 0.1459
R1, WR2 (all data)	0.0517, 0.1406
GOF	0.99
largest diff. peak/hole, (e/ Å$^{3)}$	0.25, -0.19

Table 2: Comparison of some selected bond lengths (Å) bond angles (°) obtained from X-ray crystal structure of compounds **4** and **8***.

Bond length/ Bond angle	Compound **4**	Compound **8**
C5-C14	1.455 (4)	1.479 (4)
B-F2	1.410 (4)	1.390 (4)
C9-C10	1.433 (4)	1.427 (4)
C5-C6	1.390 (4)	1.377 (4)
C5-C4	1.421 (4)	1.408 (4)
C1-N1	1.359 (3)	1.345 (4)
C9-N2	1.360 (3)	1.356 (4)
N2-B	1.550 (4)	1.552 (4)
B-F1	1.402 (4)	1.394 (4)
C4C5C14	119.9 (2)	118.2 (3)
C3C4C5	132.7 (3)	131.4 (3)
C5C6C7	130.6 (2)	107.4 (2)
F1BF2	107.5 (2)	109.0 (2)
N1BN2	107.8 (2)	107.6 (2)

*data was taken from the M. R. Rao, M. D. Tiwari, J. R. Bellare and M. Ravikanth, *J. Org. Chem.*, 2011, **76**, 7263.