Supporting Information

Synthesis, Structure, Spectral, Electrochemical and Fluoride Sensing Properties of *meso*-Pyrrolyl Boron Dipyrromethene

Booruga Umasekhar, Emandi Ganapathi, Tamal Chatterjee and Mangalampalli Ravikanth*

Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India.
E-mail: ravikanth@chem.iitb.ac.in

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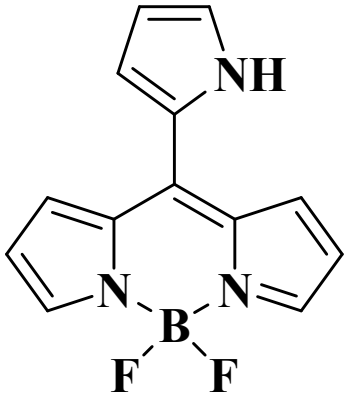

Calcd mol. wt. = 280.0830

Observed mol. Wt. = 280.0826

DEPARTMENT OF CHEMISTRY, I.I.T.(B)

Analysis Info

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Comment	C62H52FeN2O2S2		

Acquisition Parameter

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Scan End	1000 m/z	Set Collision Cell RF	900.0 Vpp	Set Divert Valve	Source

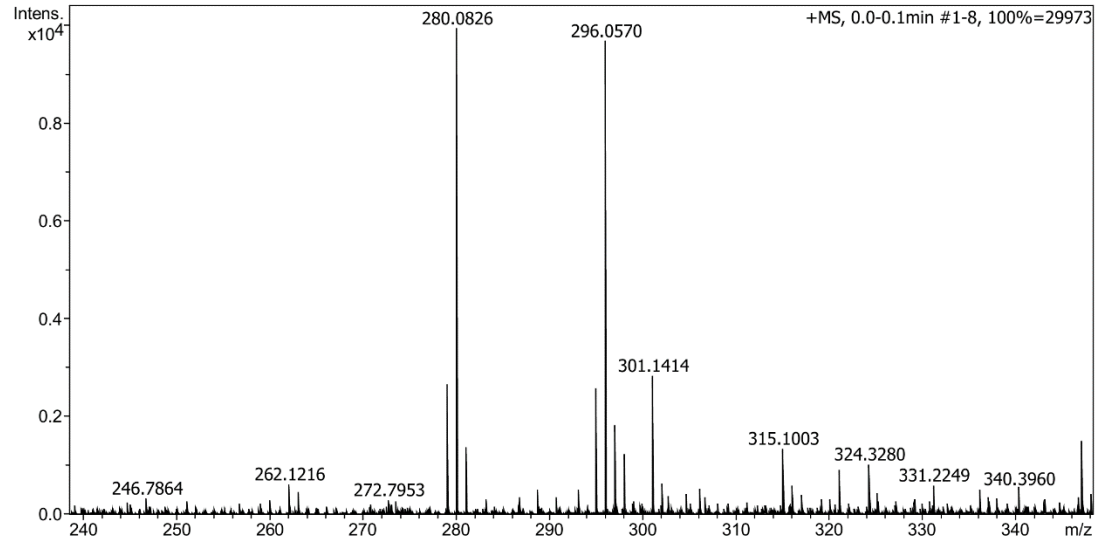

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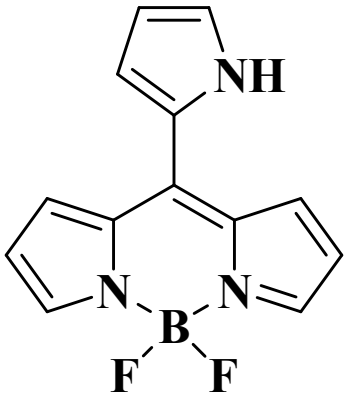
Figure S1: HRMS spectrum of compound **5**



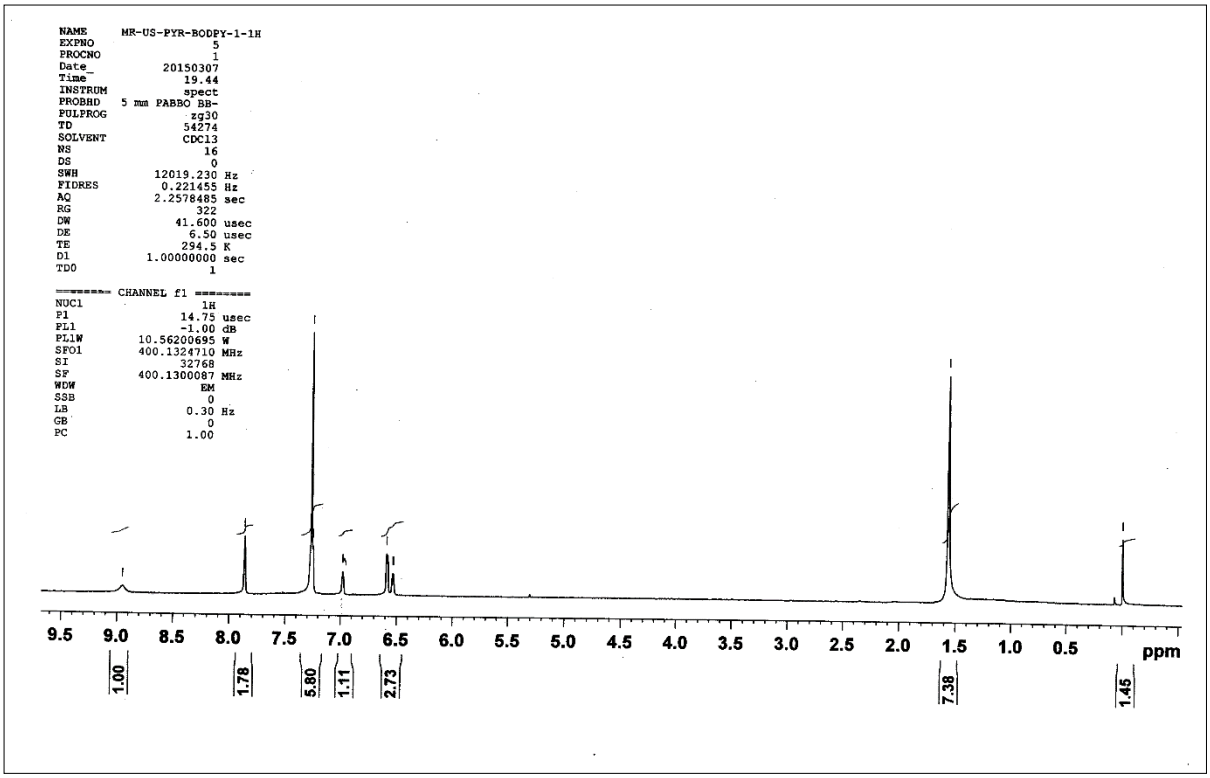


Figure S2: ^{1}H NMR spectrum of compound **5** recorded in $CDCl_3$.

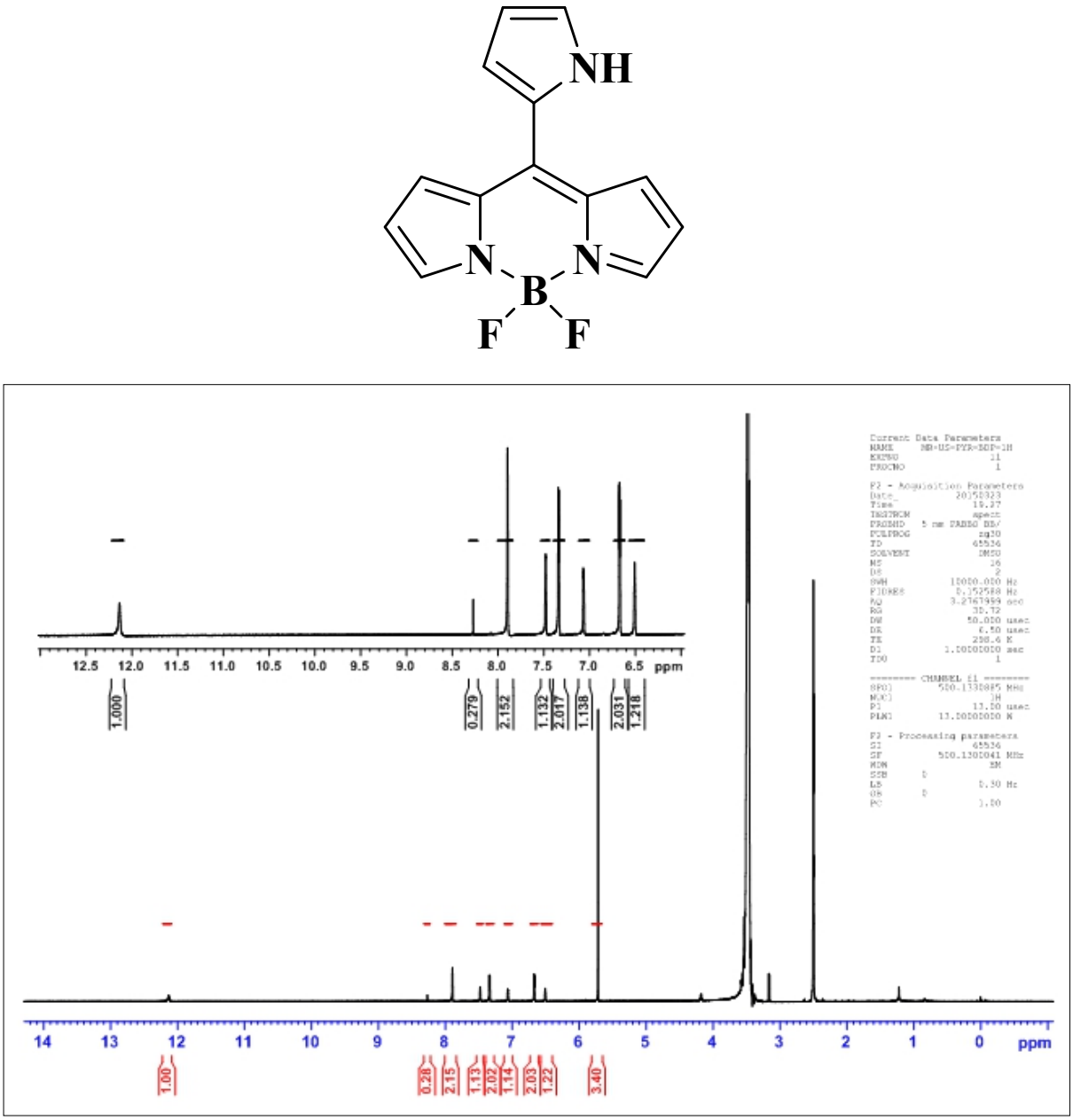


Figure S3: ^{1}H NMR spectrum of compound **5** recorded in DMSO-d_6. Inset shows the expansion.

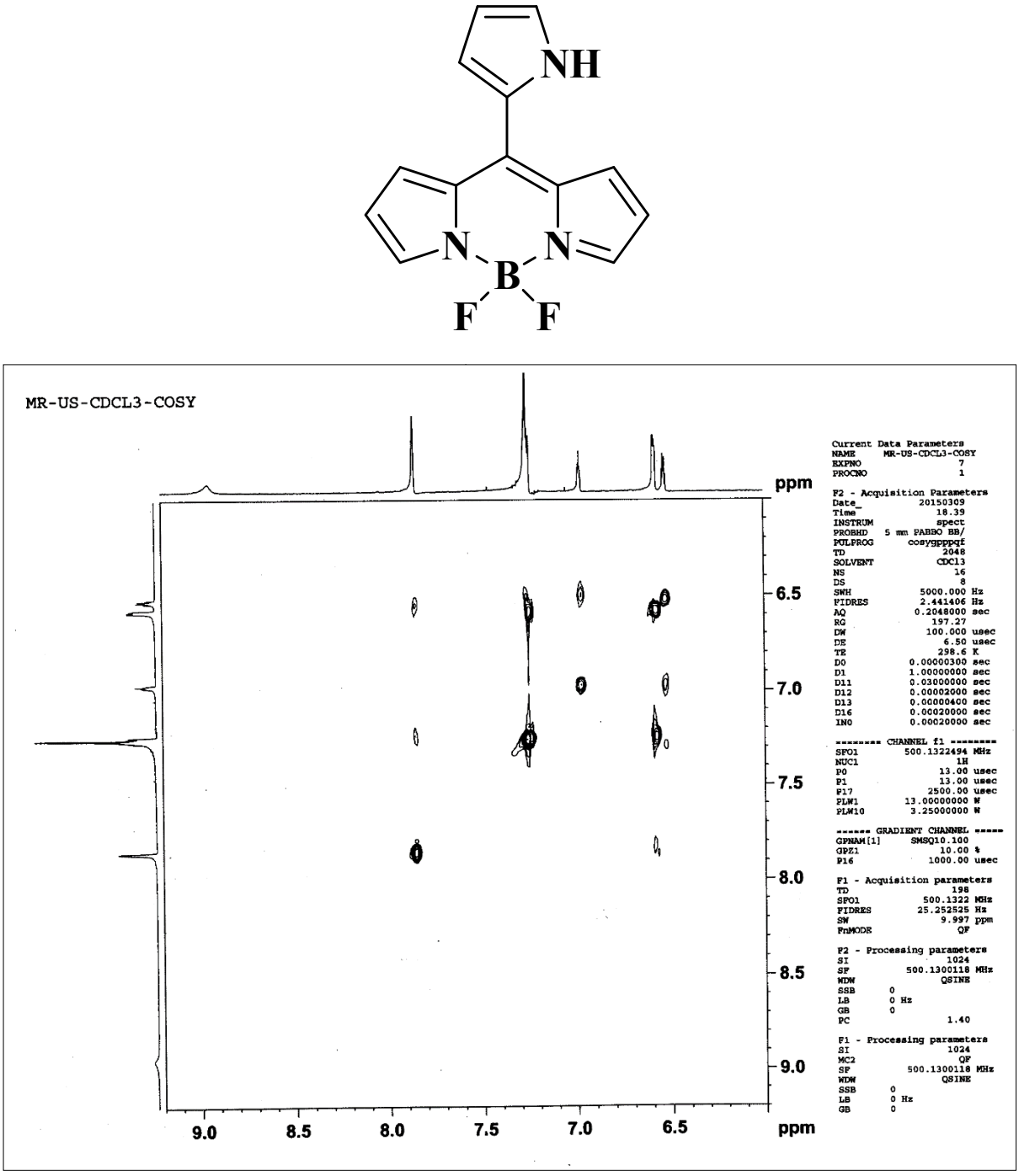
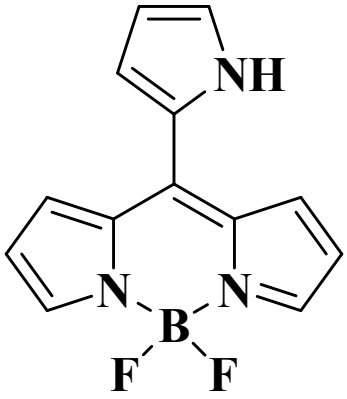


Figure S4: ^{1}H-^{1}HCOSY NMR spectrum of compound **5** recorded in $CDCl_3$.



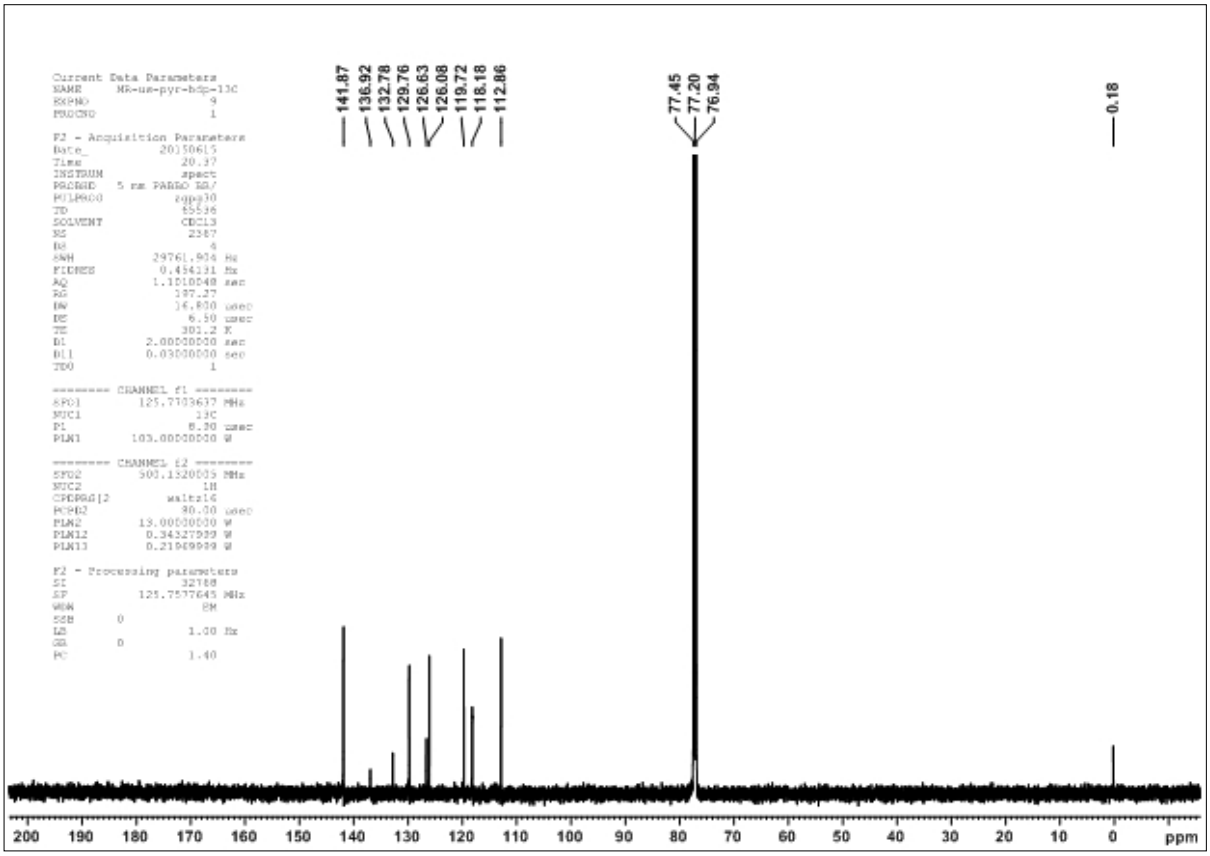
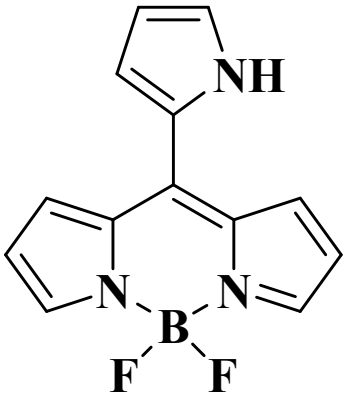


Figure S5: ^{13}C NMR spectrum of compound **5** recorded in $CDCl_3$.



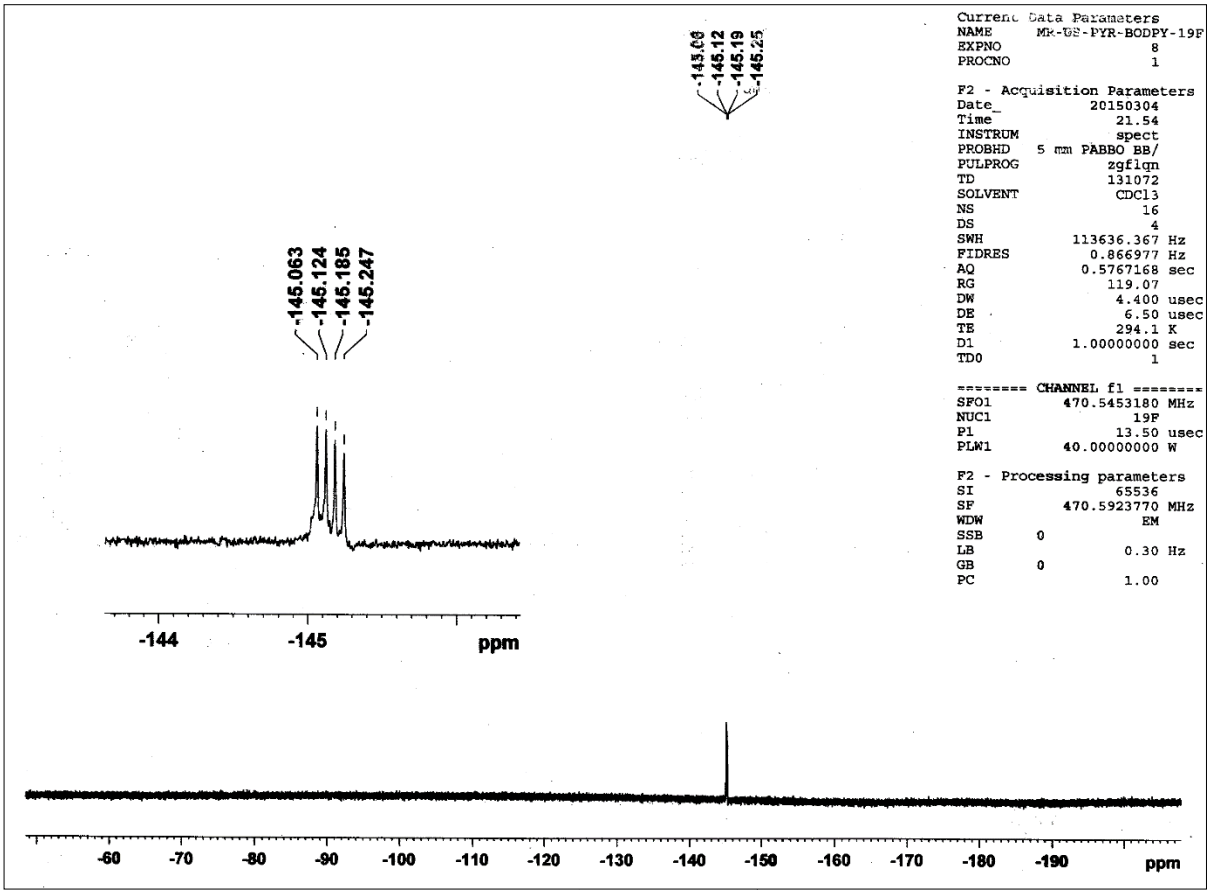
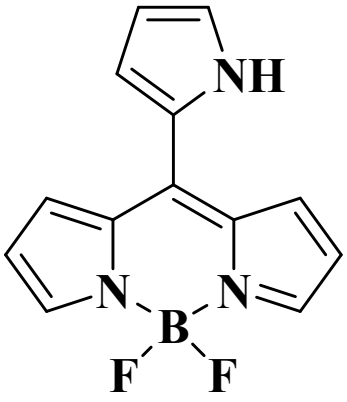


Figure S6: ^{19}F NMR spectrum of compound **5** recorded in $CDCl_3$. Inset shows the expansion.



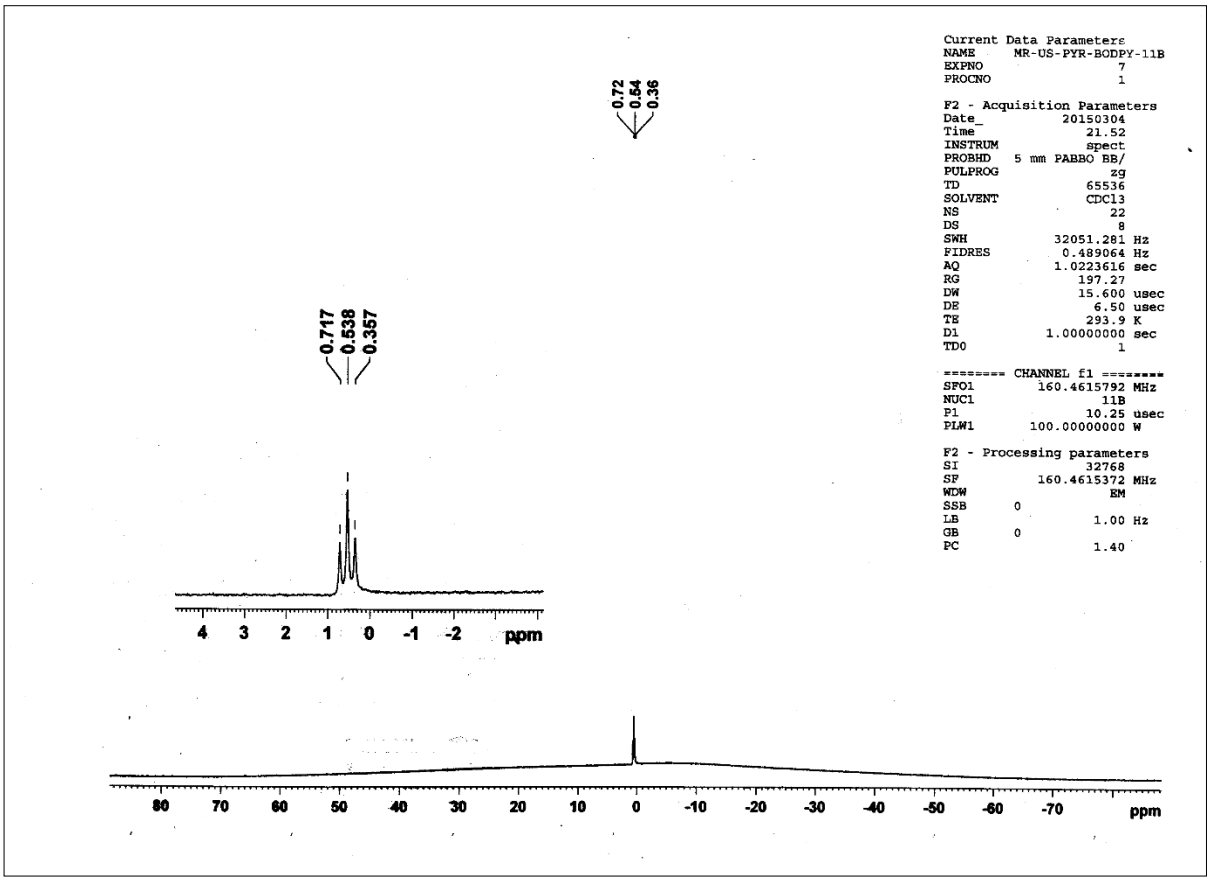
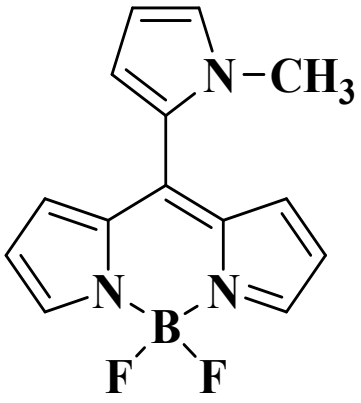


Figure S7: ^{11}B NMR spectrum of compound **5** recorded in $CDCl_3$. Inset shows the expansion.



Calcd mol. wt. = 294.0987

Observed mol. Wt. = 294.0960

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Analysis Info

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Comment	C14H12BF2N3		

Acquisition Parameter

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Scan End	1000 m/z	Set Collision Cell RF	1500.0 Vpp	Set Divert Valve	Source

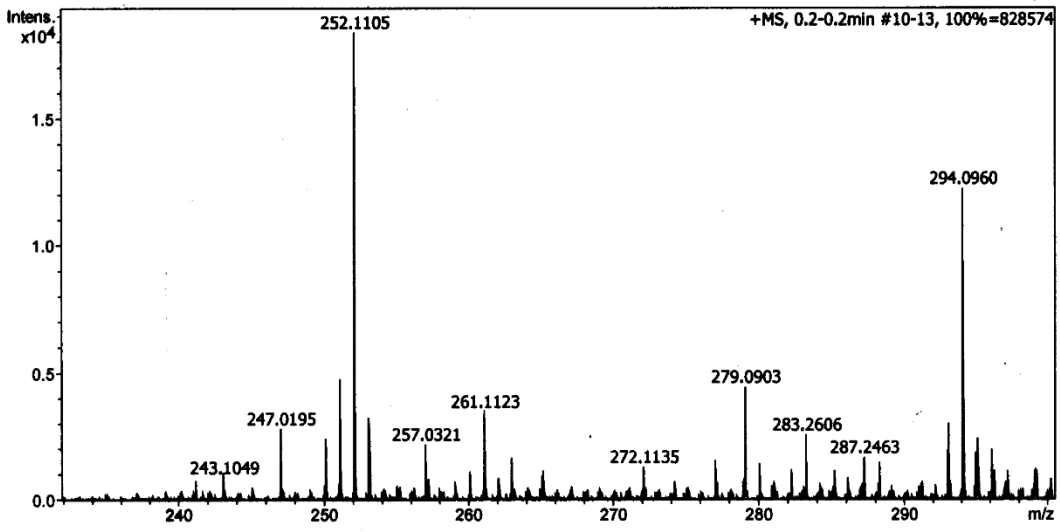

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Figure S8: HRMS spectrum of compound **6**

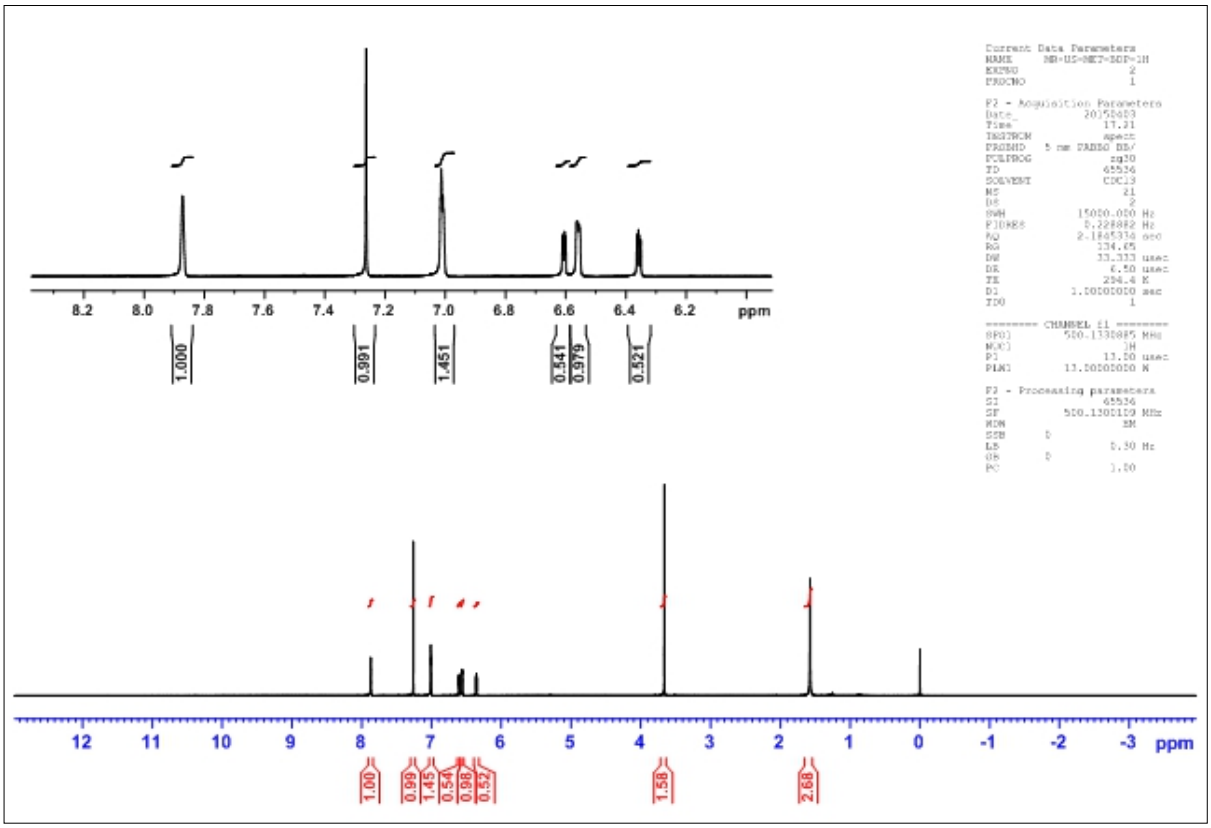
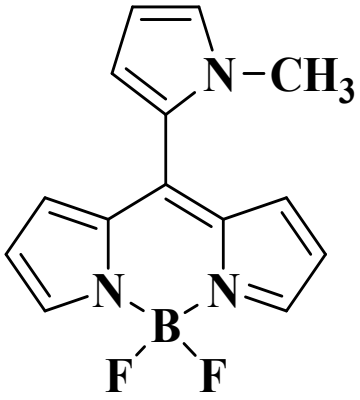


Figure S9: ^{1}H NMR spectrum of compound **6** recorded in $CDCl_3$. Inset shows the expansion.



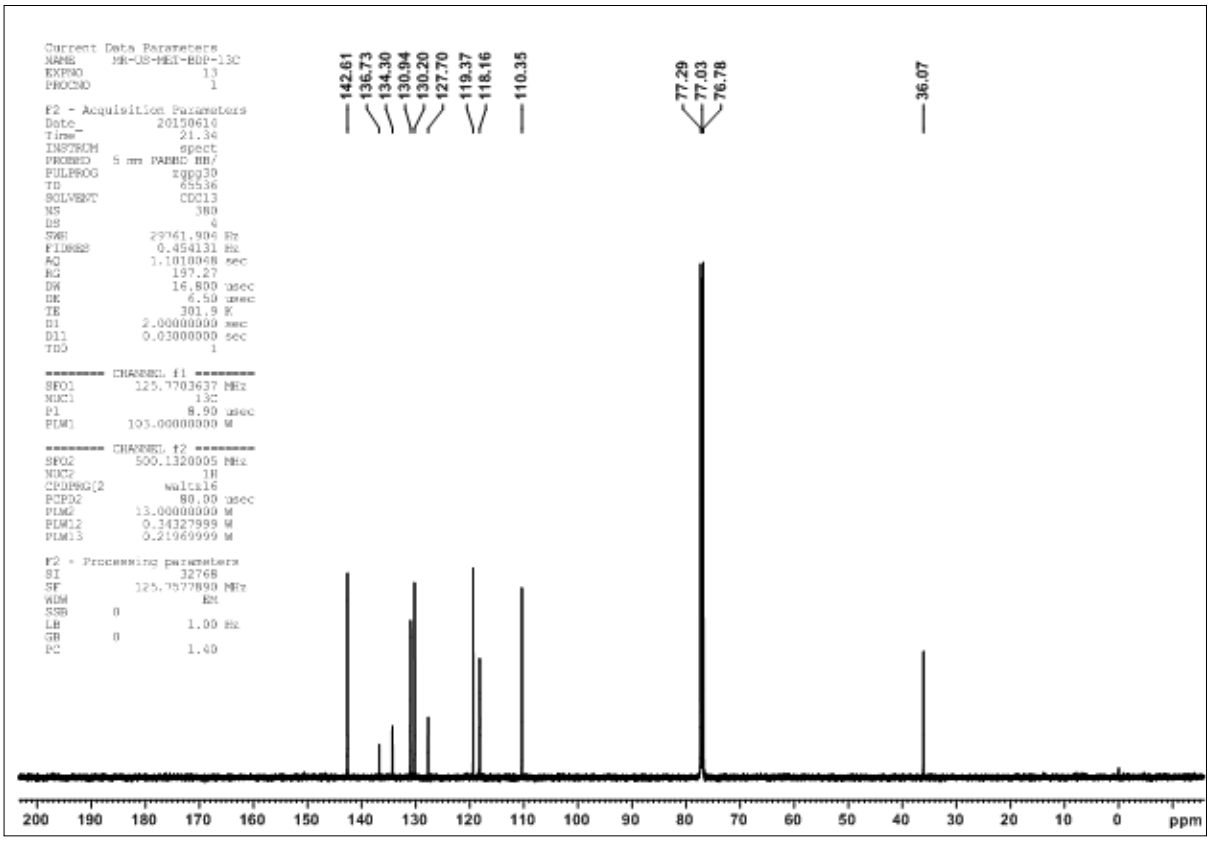
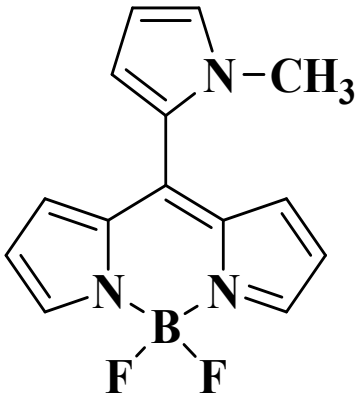


Figure S10: ^{13}C NMR spectrum of compound **6** recorded in $CDCl_3$.



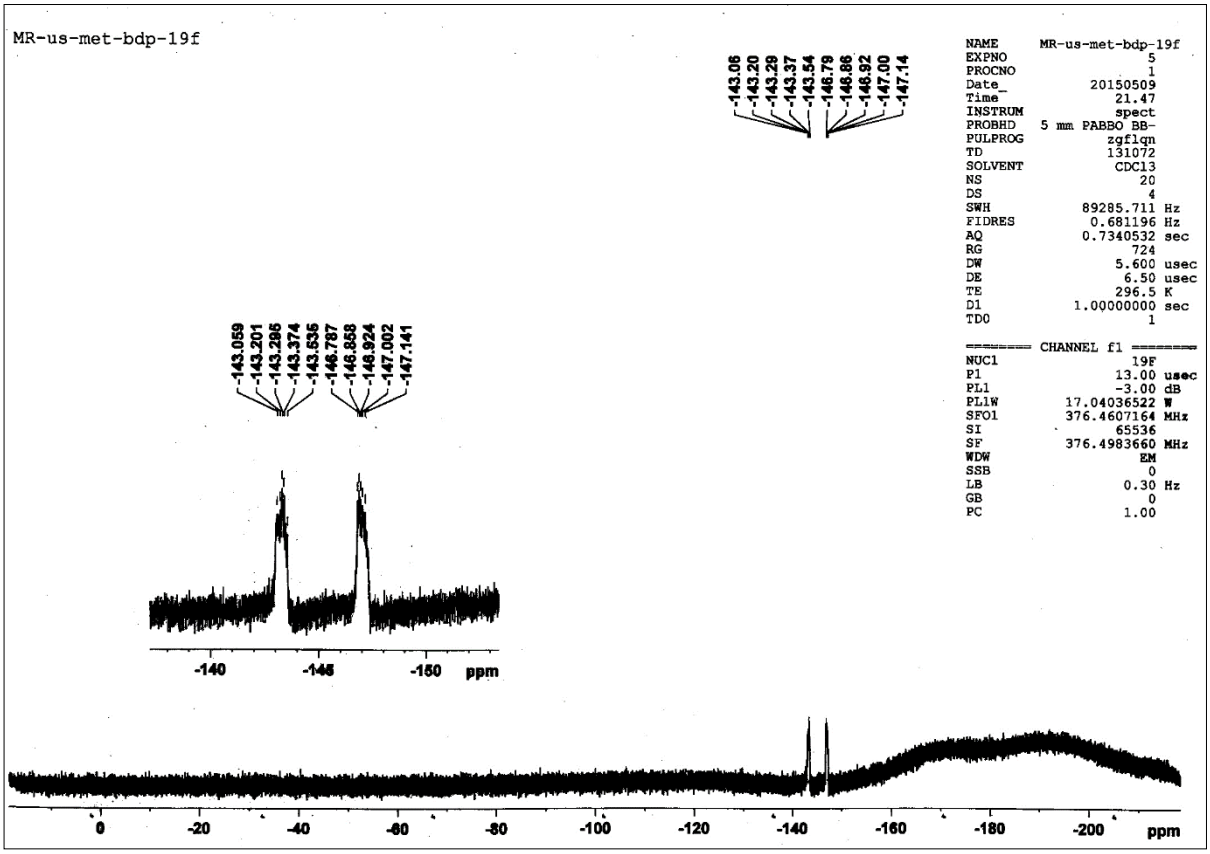


Figure S11: ^{19}F NMR spectrum of compound **6** recorded in $CDCl_3$. Inset shows the expansion.

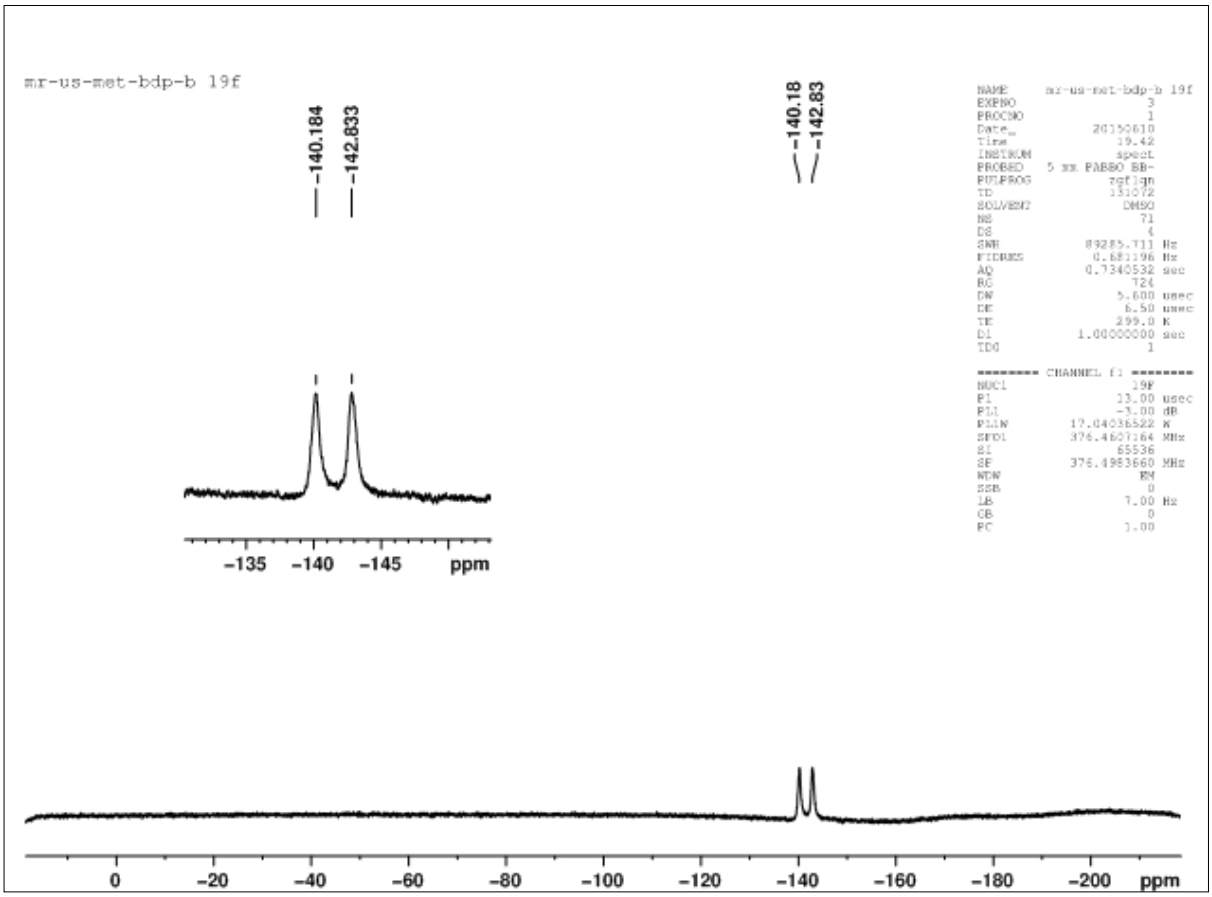


Figure S12: ^{19}F NMR spectrum of compound **6** recorded in DMSO-d6. Inset shows the expansion.

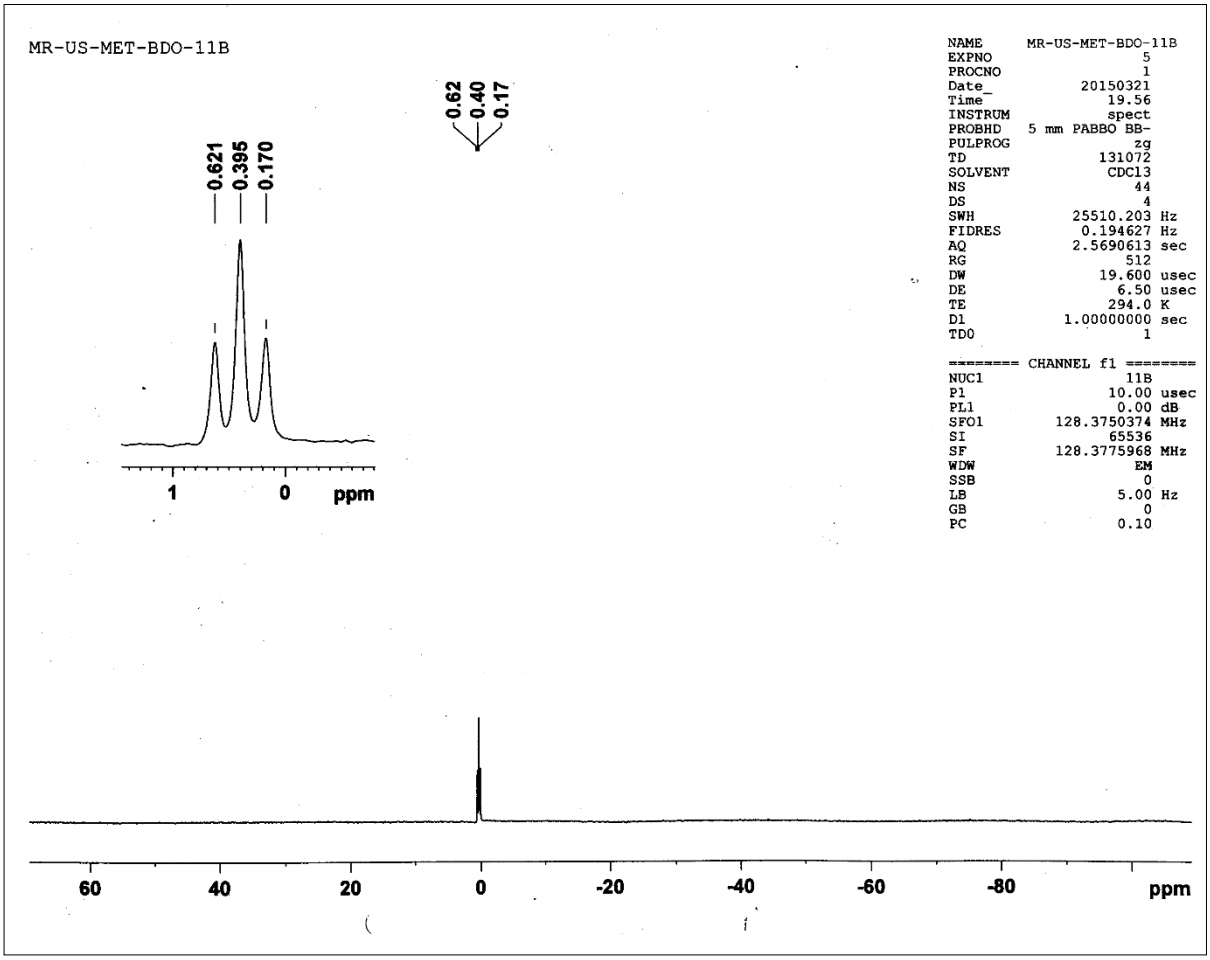
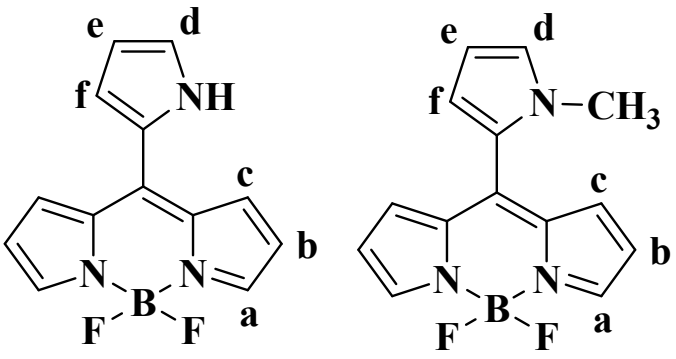


Figure S13: ^{19}B NMR spectrum of compound **6** recorded in $CDCl_3$. Inset shows the expansion.



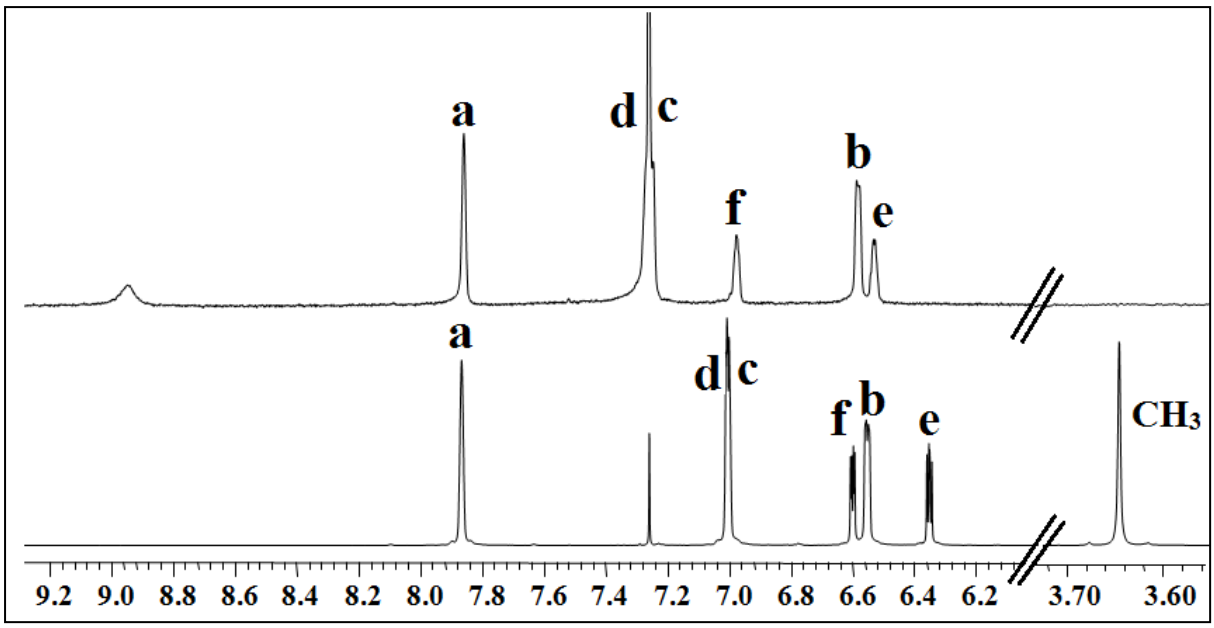
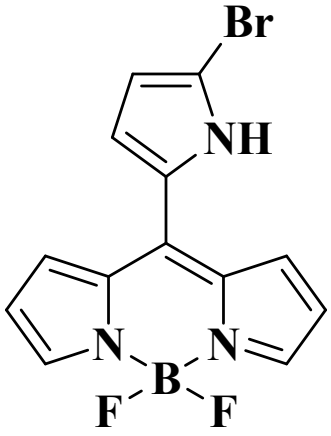


Figure S14: Comparison of ^{1}H NMR spectrum of compound **5** and **6** recorded in $CDCl_3$.



Calcd mol. wt. = 357.9936

Observed mol. Wt. = 357.9920

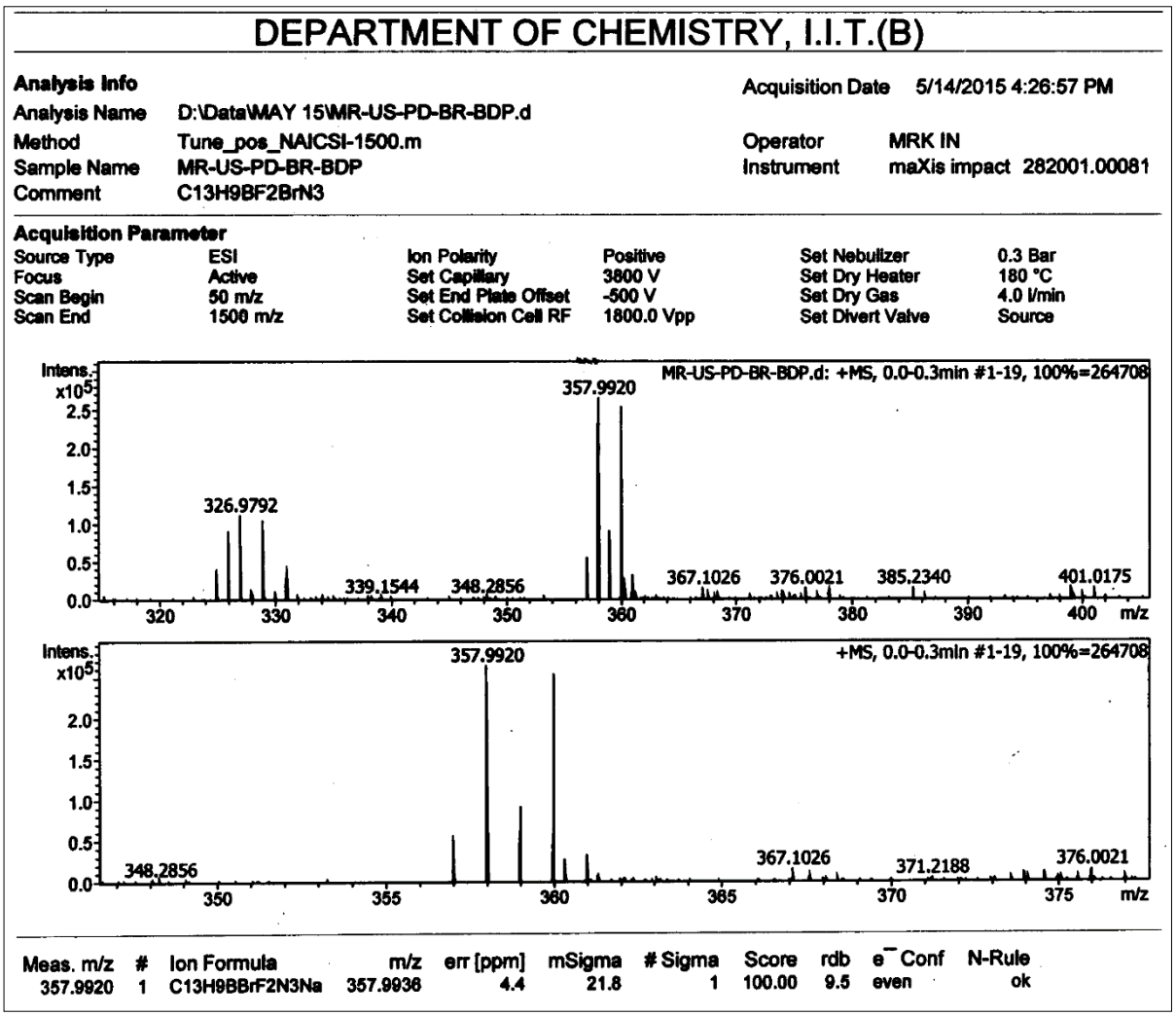
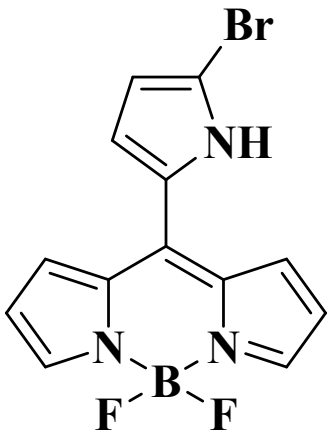


Figure S15: HRMS spectrum of compound **7**



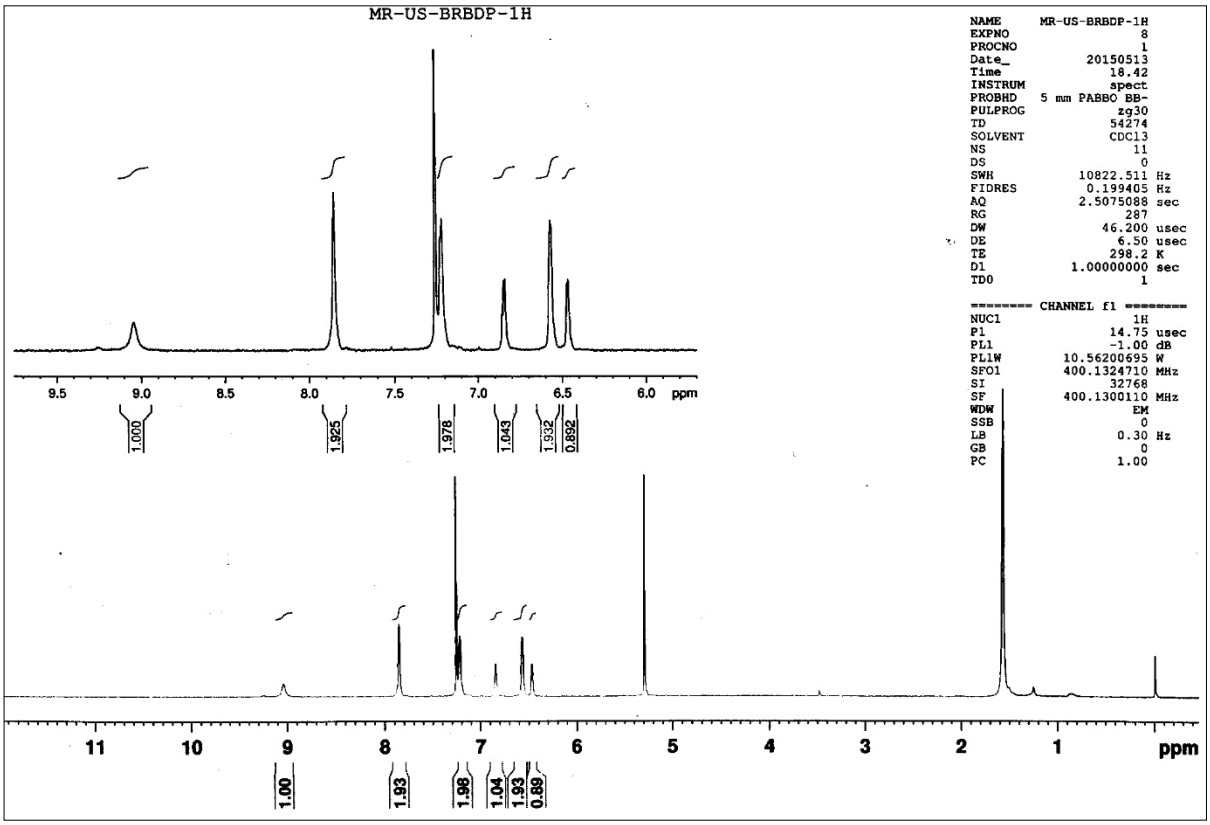
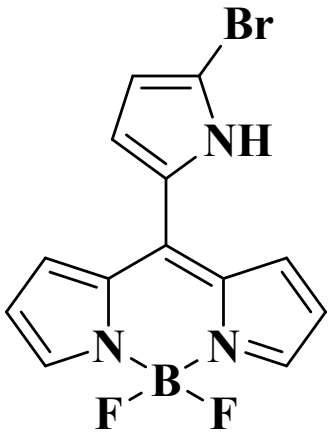


Figure S16: ^{1}H NMR spectrum of compound **7** recorded in $CDCl_3$. Inset shows the expansion.



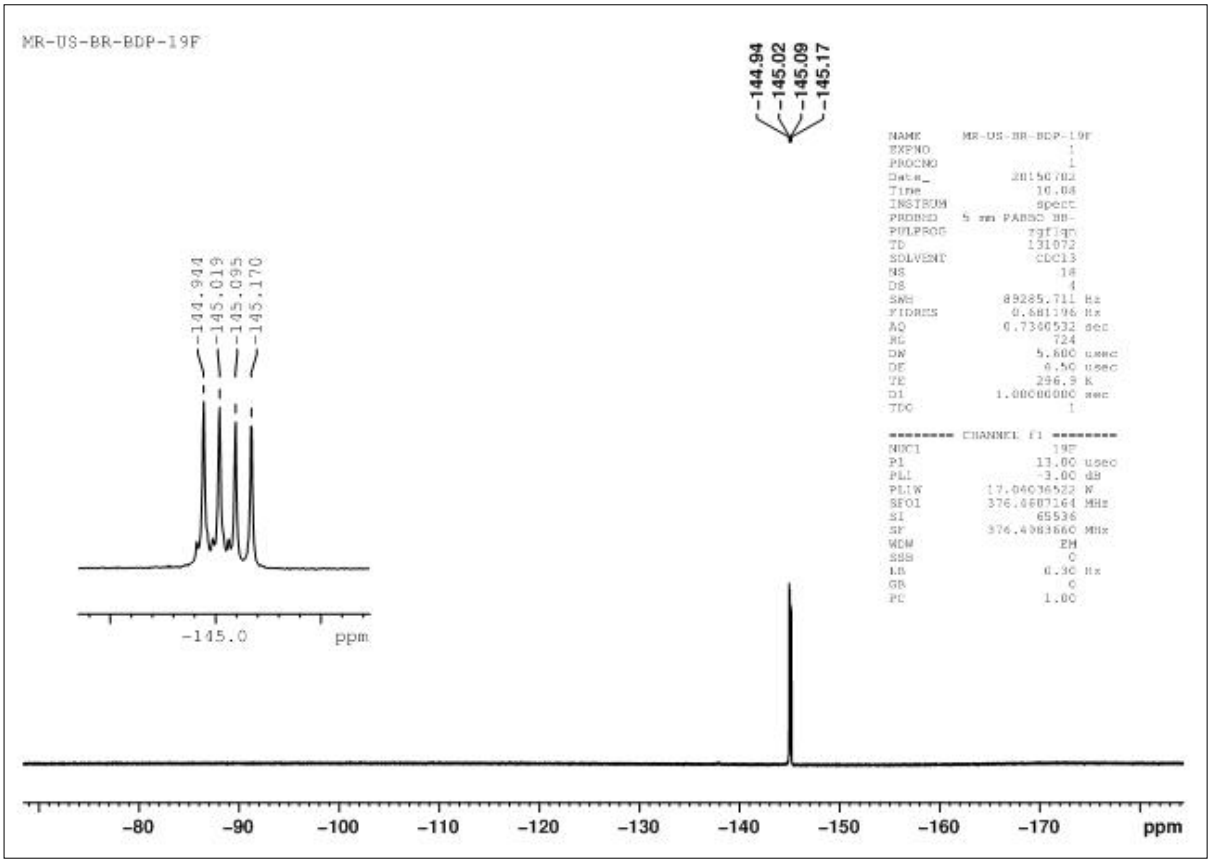
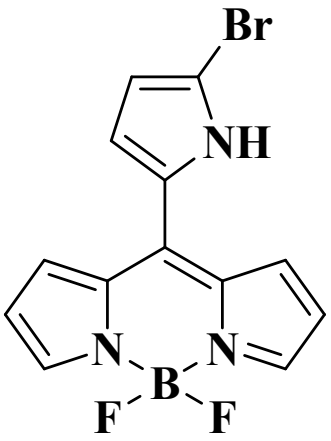


Figure S17: ^{19}F NMR spectrum of compound **7** recorded in $CDCl_3$. Inset shows the expansion



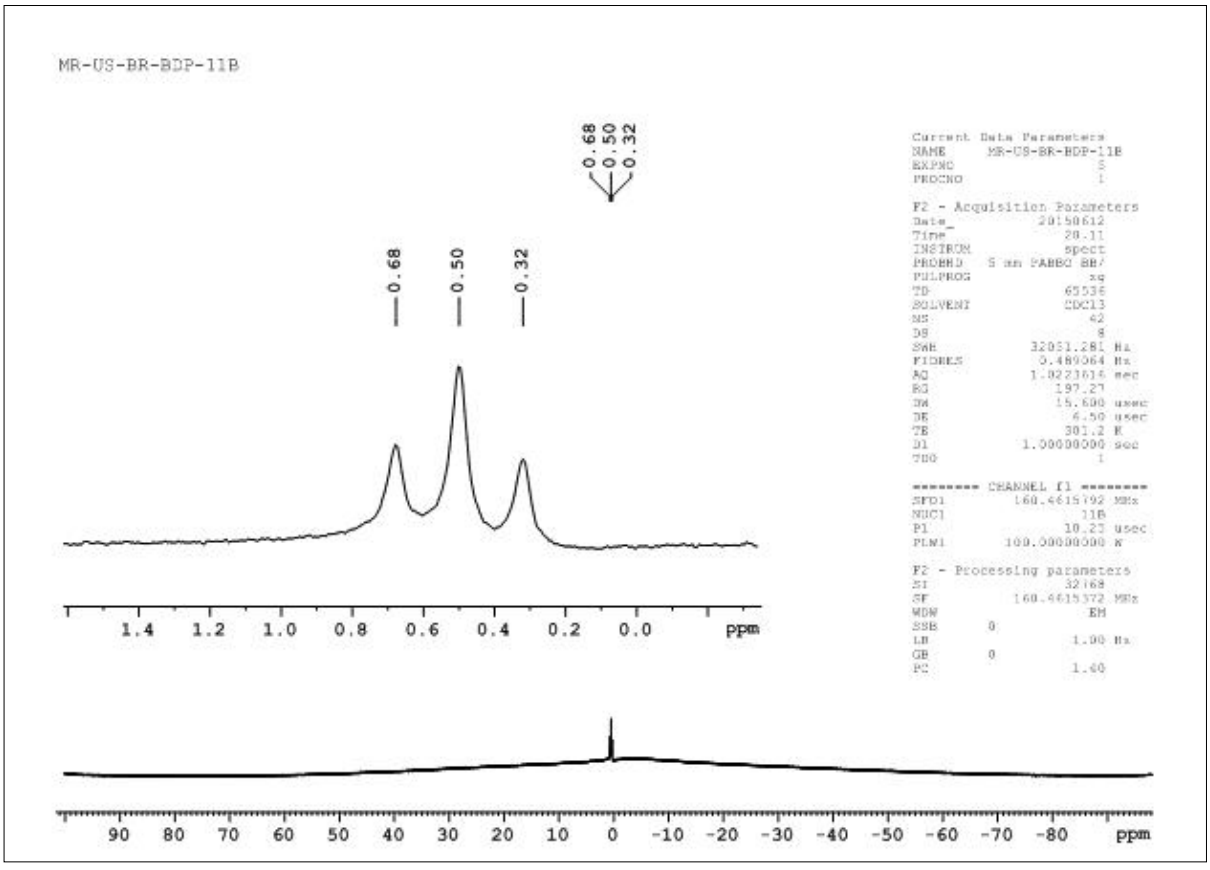
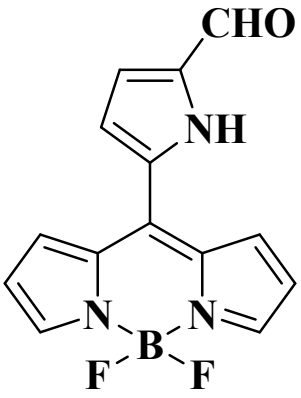


Figure S18: ^{11}B NMR spectrum of compound **7** recorded in $CDCl_3$.



Calcd mol. wt. = 308.0780

Observed mol. Wt. = 308.0779

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Analysis Info

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Sample Name	MR-US-FOR-BDP	Instrument	maXis impact 282001.00081
Comment	C14H10BF2N3O		

Acquisition Parameter

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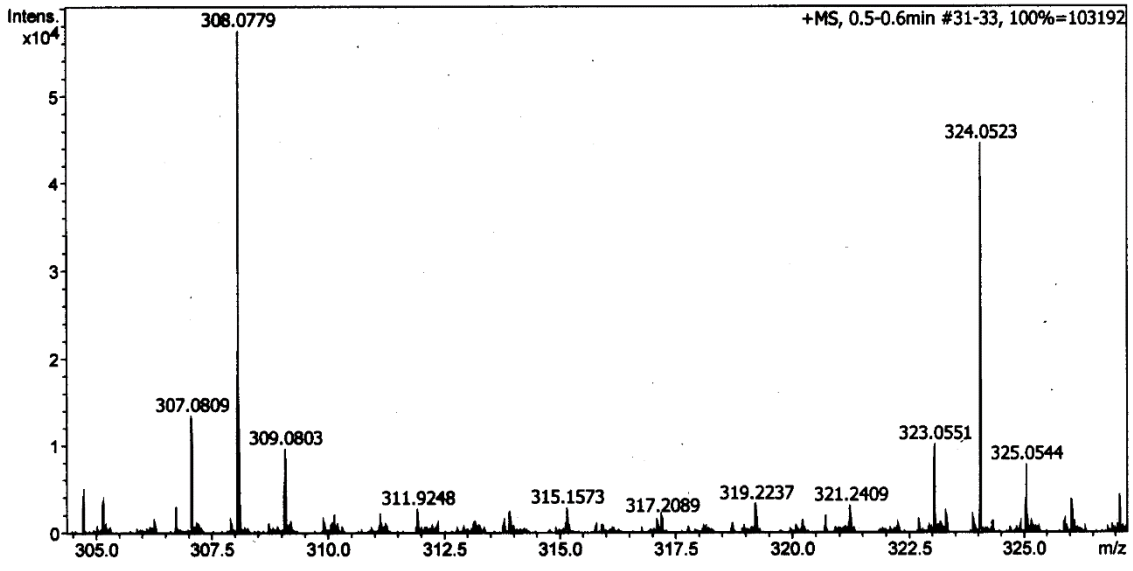
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	900.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
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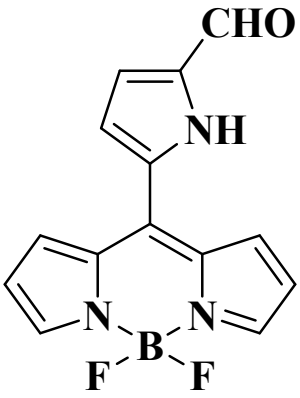
Figure S19: HRMS spectrum of compound **8**



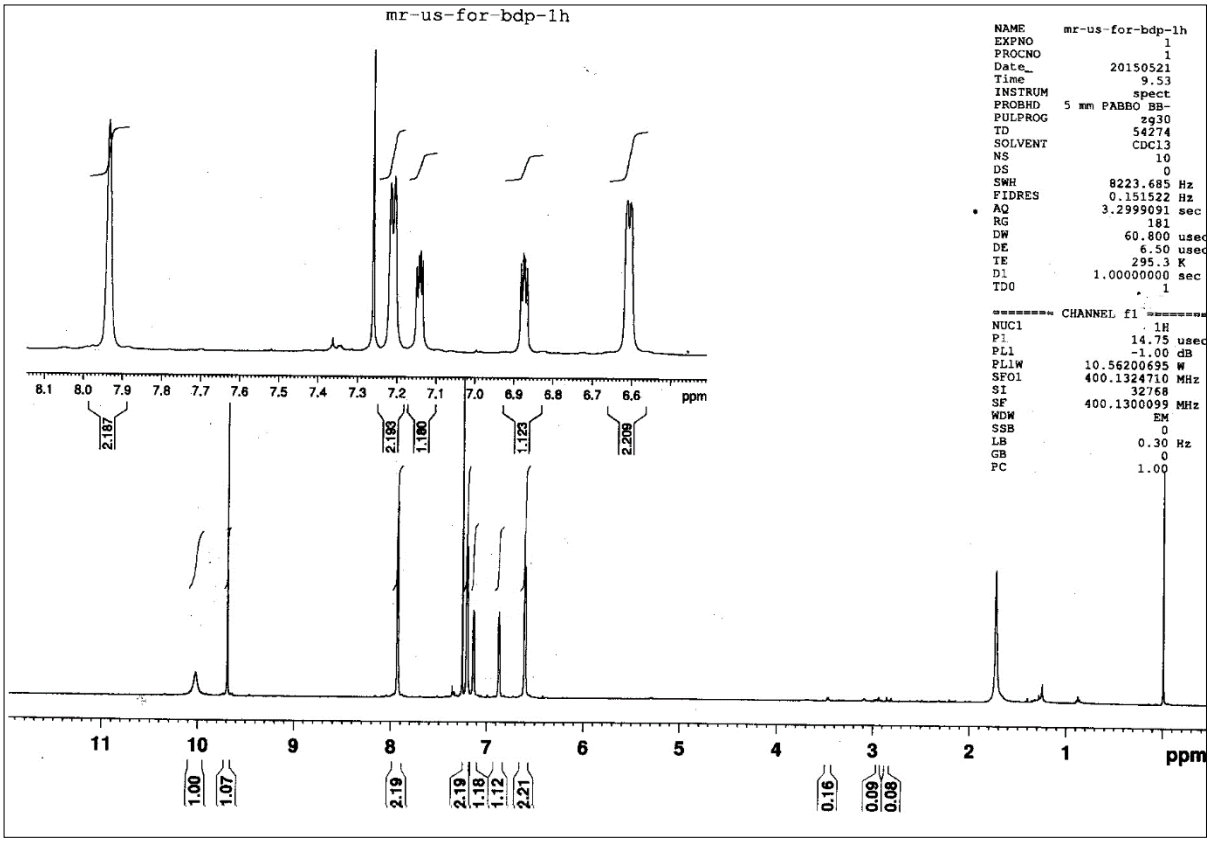
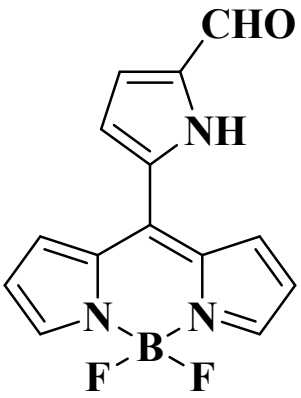


Figure S20: ^{1}H NMR spectrum of compound **8** recorded in $CDCl_3$. Inset shows the Expansion.



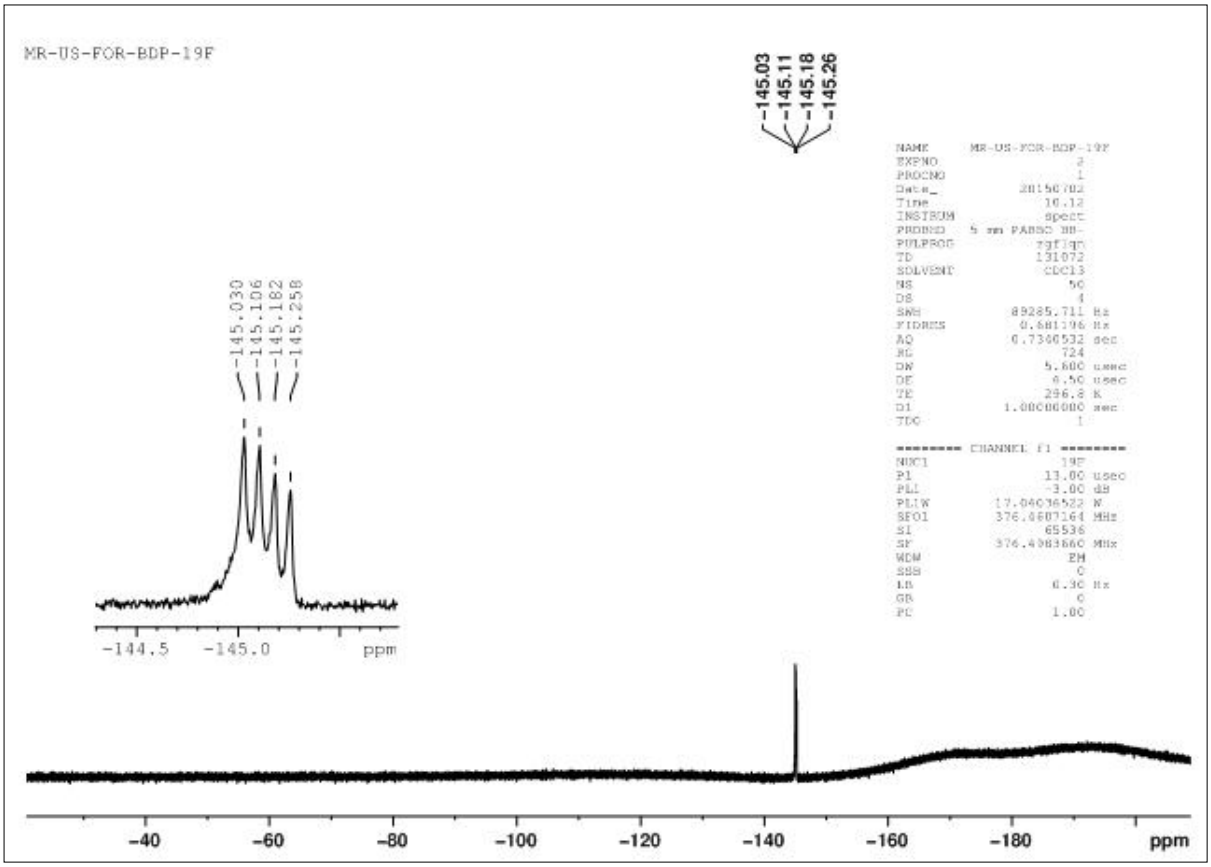
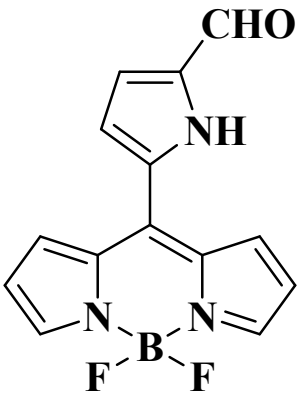


Figure S21: ^{1}H NMR spectrum of compound **8** recorded in $CDCl_3$. Inset shows the Expansion.



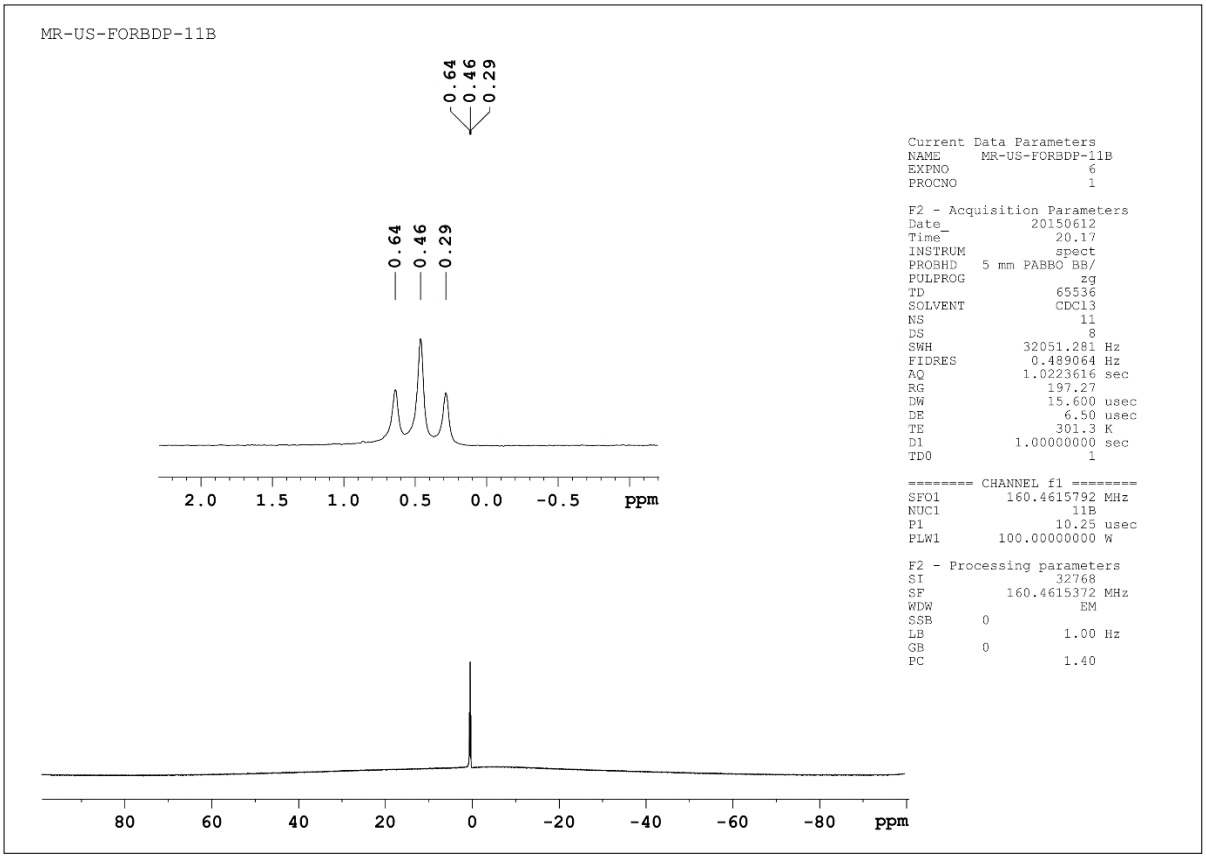


Figure S22: ^{11}B NMR spectrum of compound **8** recorded in $CDCl_3$. Inset shows the Expansion.

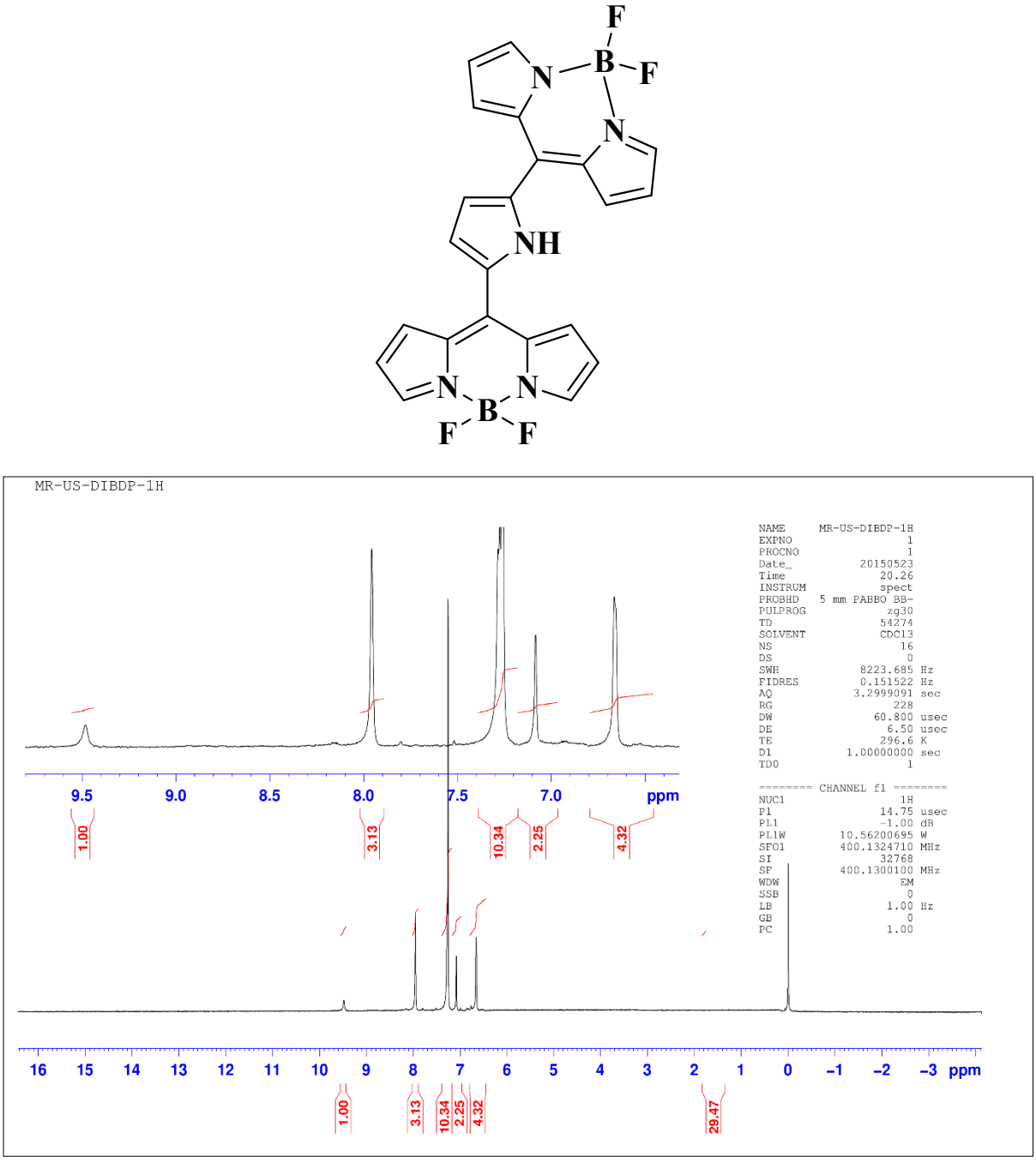


Figure S23: ^{1}H NMR spectrum of compound **9** recorded in $CDCl_3$. Inset shows the Expansion.

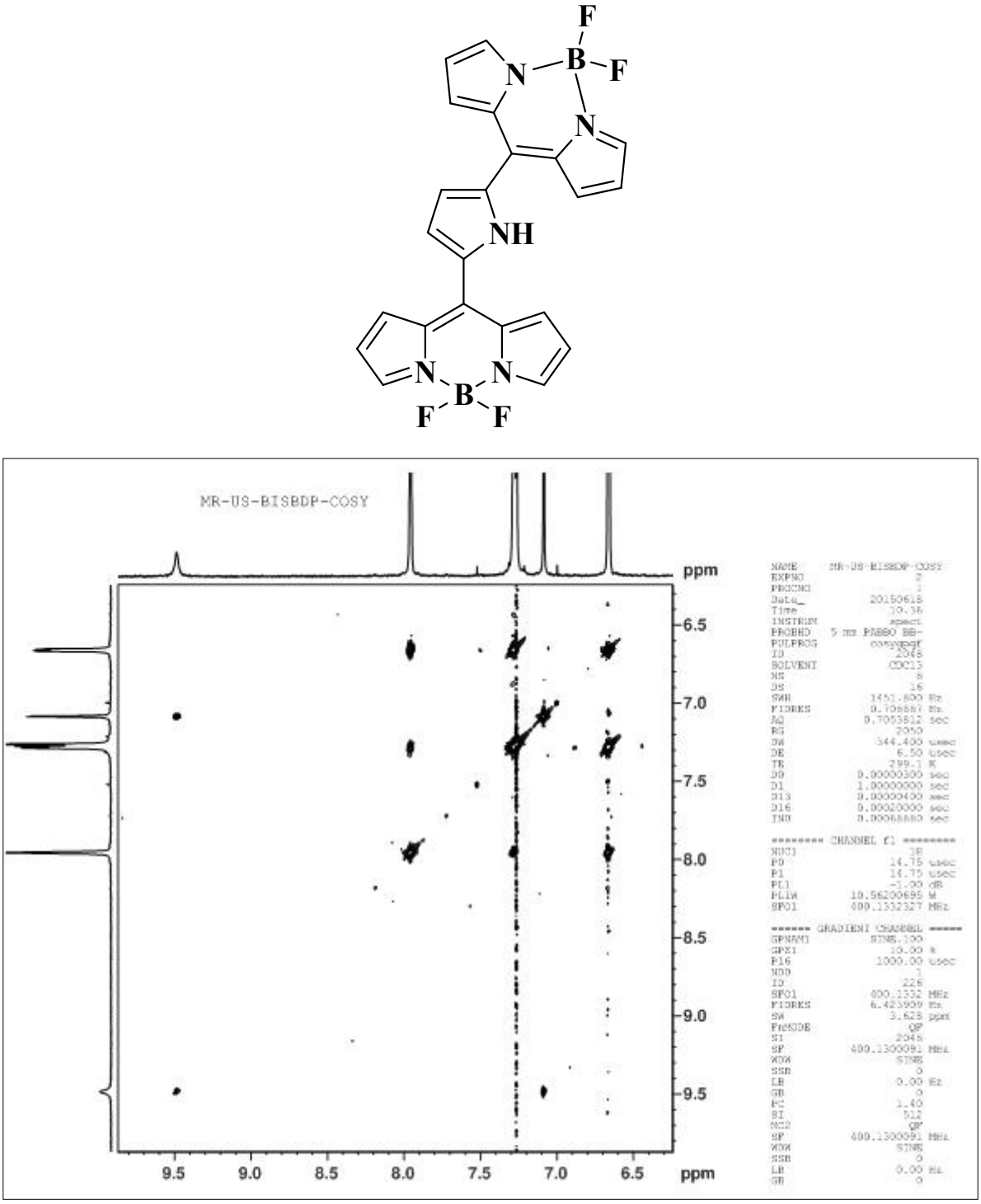


Figure S24: ^{1}H-^{1}H COSY spectrum of compound **9** recorded in $CDCl_3$

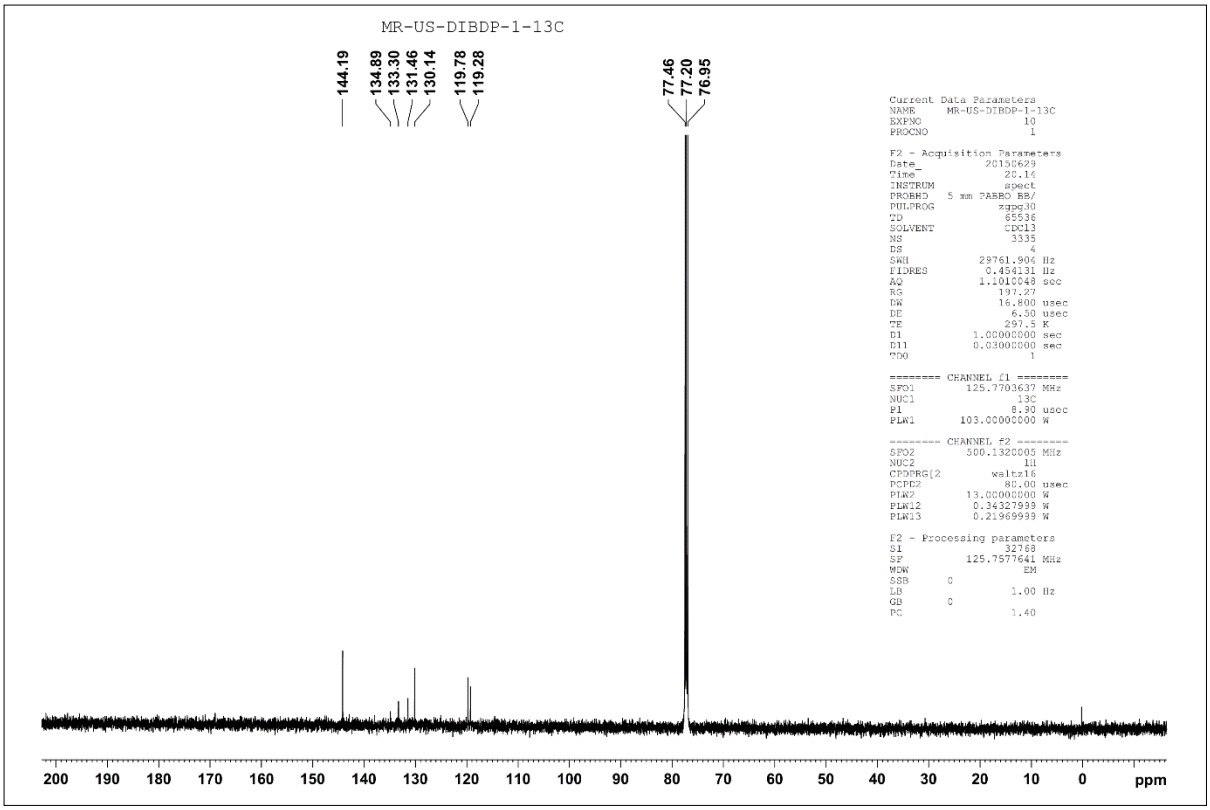


Figure S25: ^{13}C NMR spectrum of compound **9** recorded in $CDCl_3$.

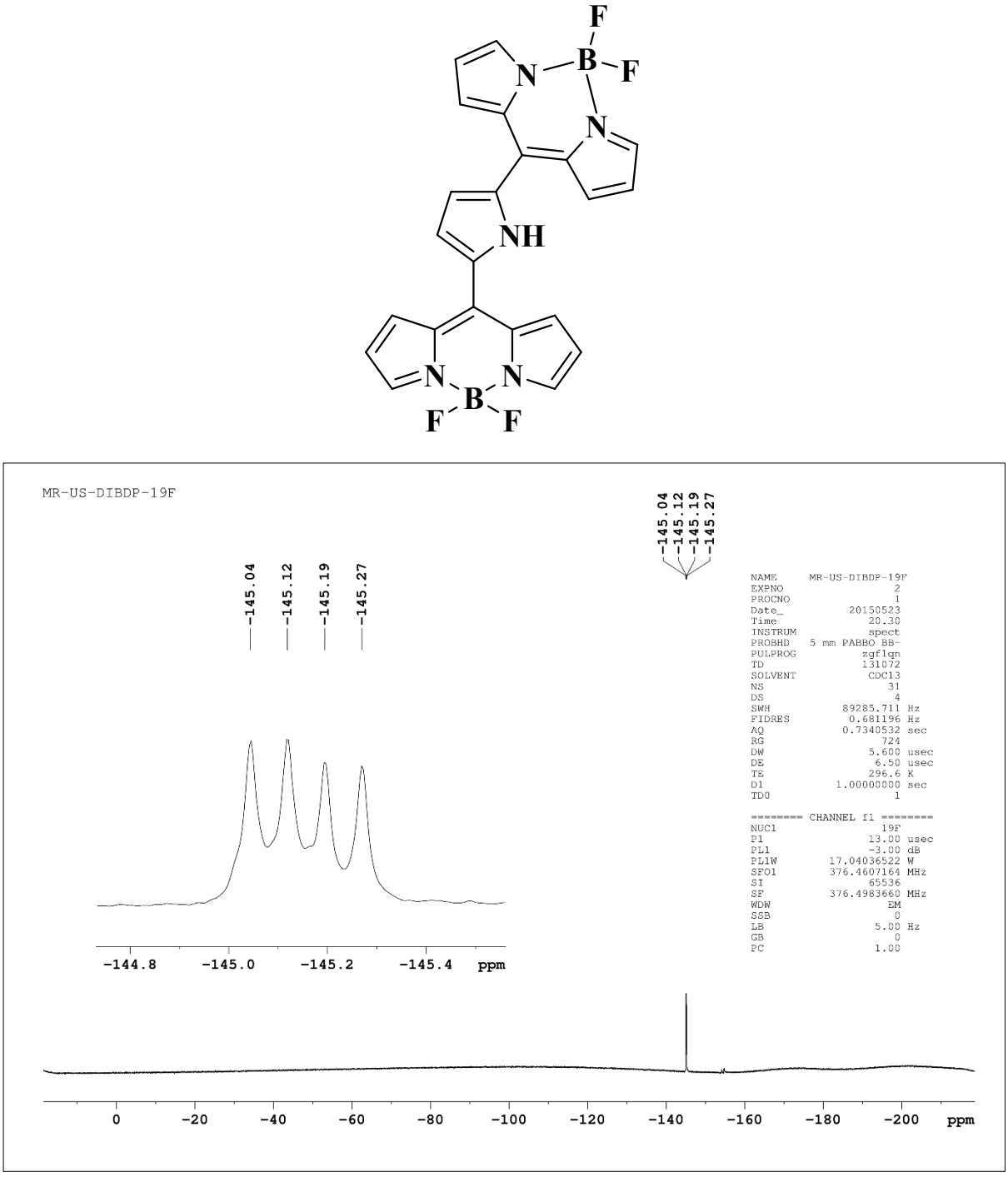


Figure S26: ^{19}F NMR spectrum of compound **9** recorded in $CDCl_3$. Inset shows the Expansion.

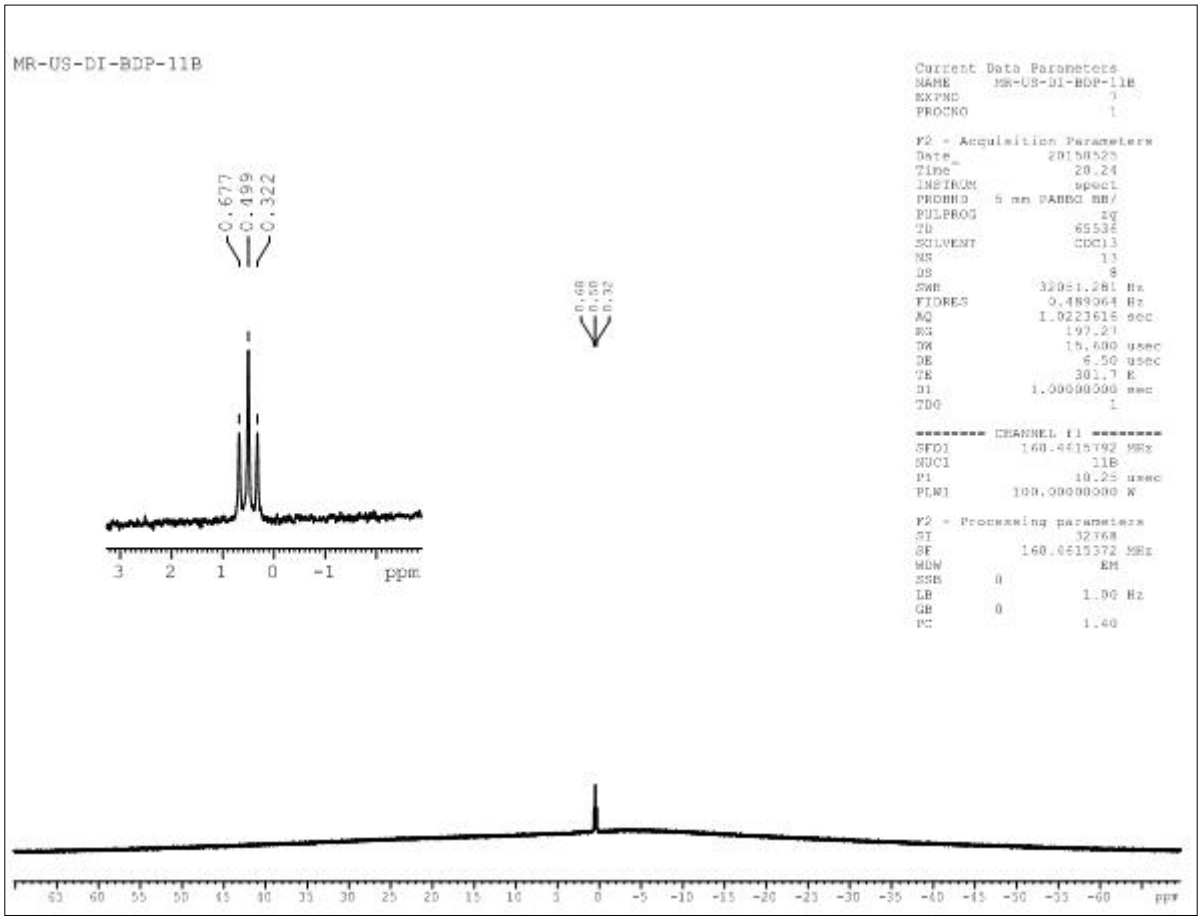
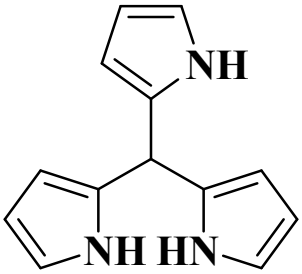


Figure S27: ^{11}B NMR spectrum of compound **9** recorded in $CDCl_3$. Inset shows the Expansion.



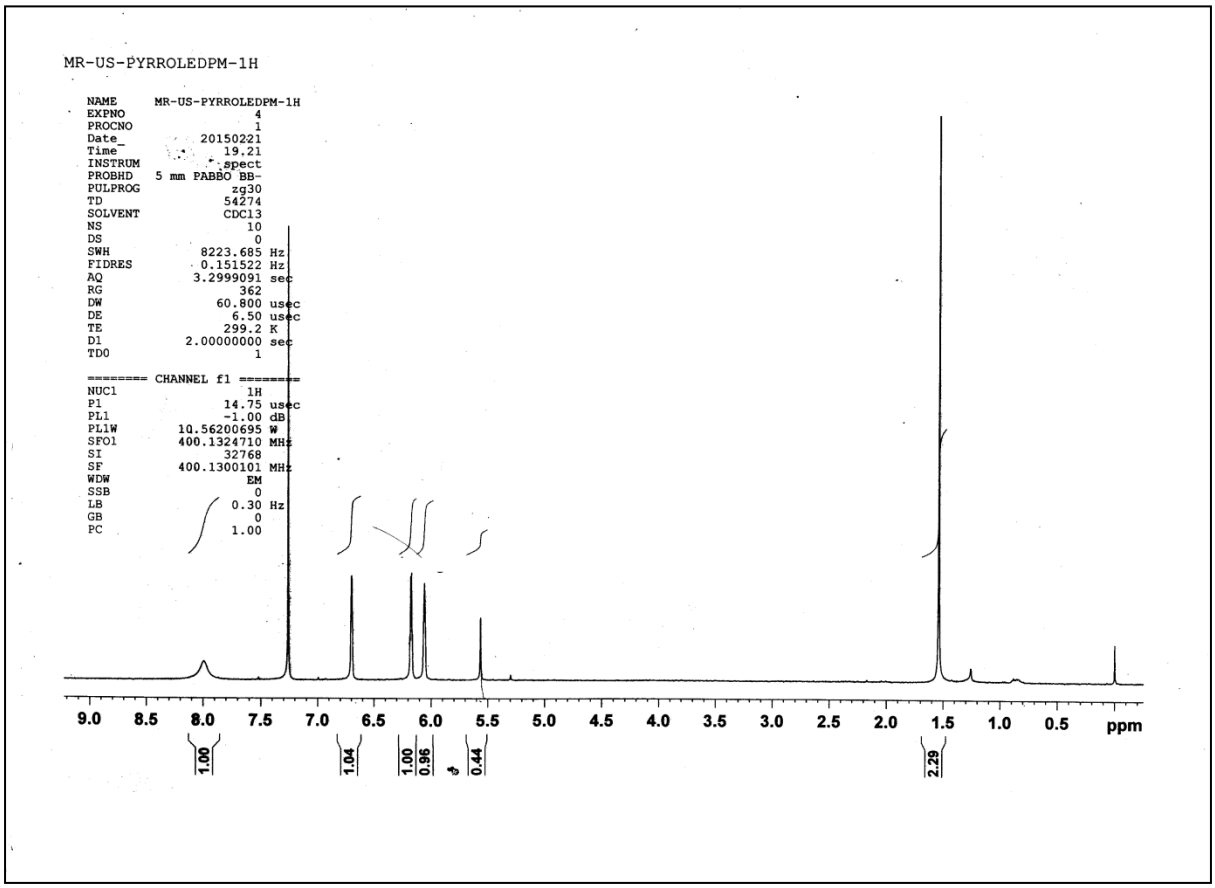


Figure S28: ^{1}H NMR spectrum of compound **11** recorded in $CDCl_3$.

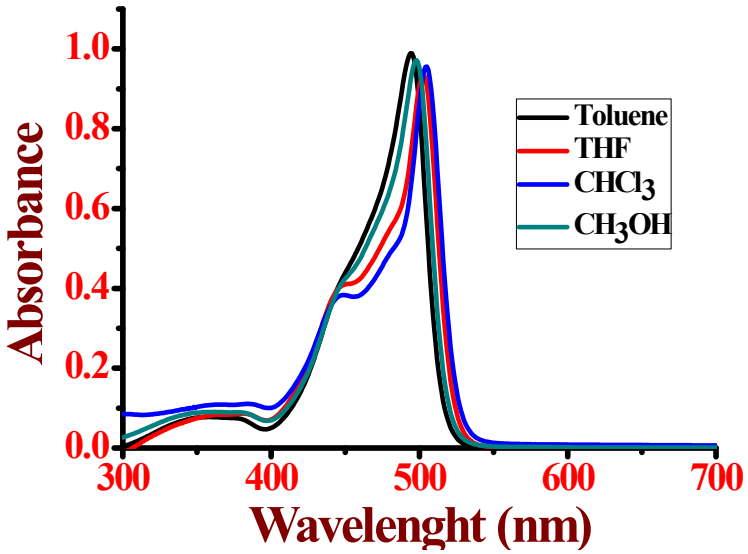


Figure S29: Comparison of absorption spectra of compound **5** (2×10^{-5}M) recorded in different solvents.

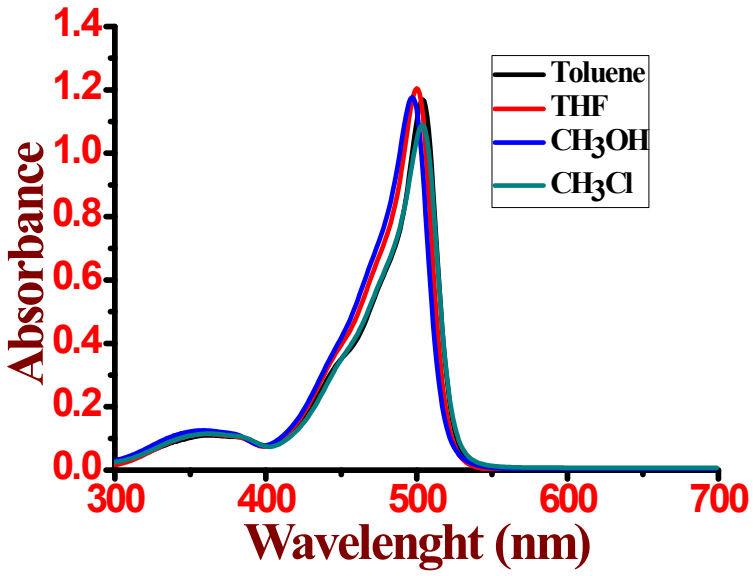


Figure S30: Comparison of absorption spectra of compound **6** (2×10^{-5}M) recorded in different solvents.

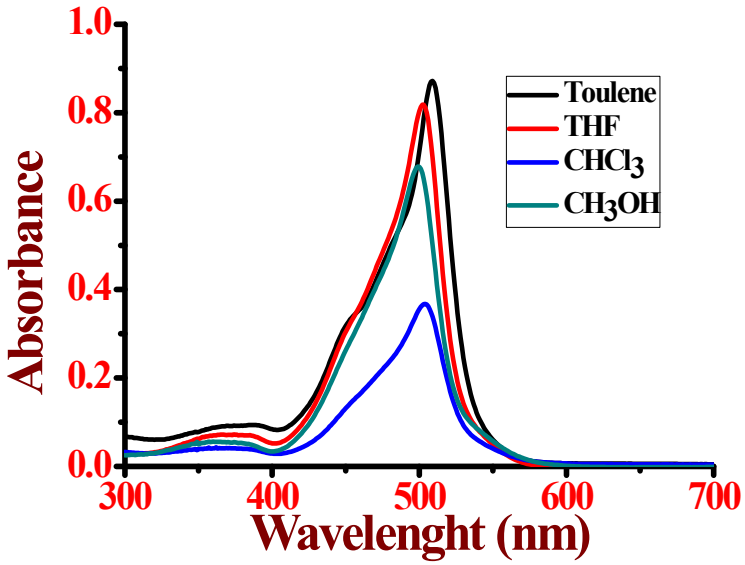


Figure S31: Comparison of absorption spectra of compound **7** (2×10^{-5}M) recorded in different solvents.

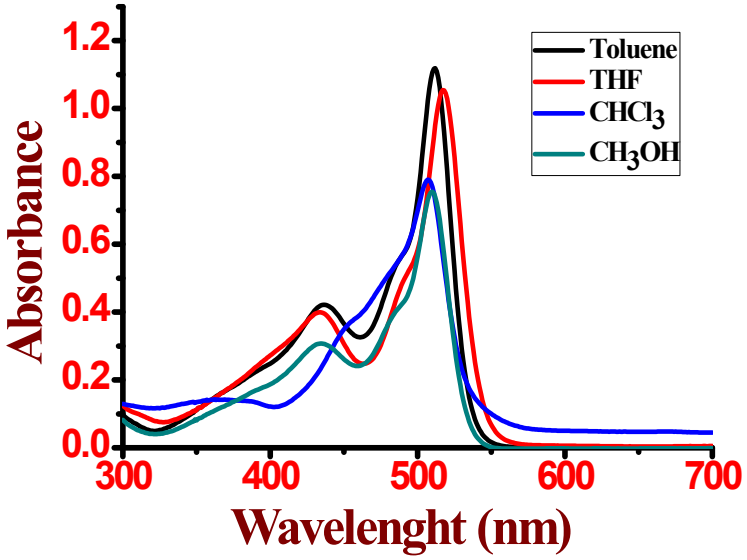


Figure S32: Comparison of absorption spectra of compound **8** (2×10^{-5}M) recorded in different solvents.

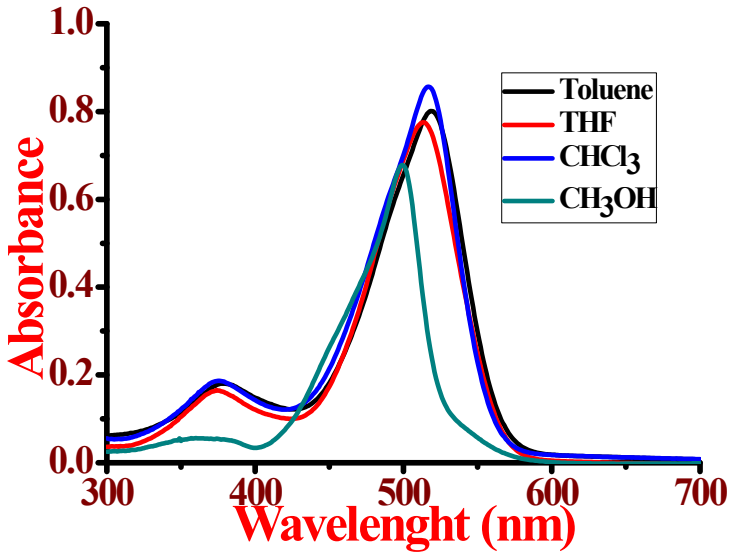


Figure S33: Comparison of absorption spectra of compound **9** (2×10^{-5}M) recorded in different solvents.

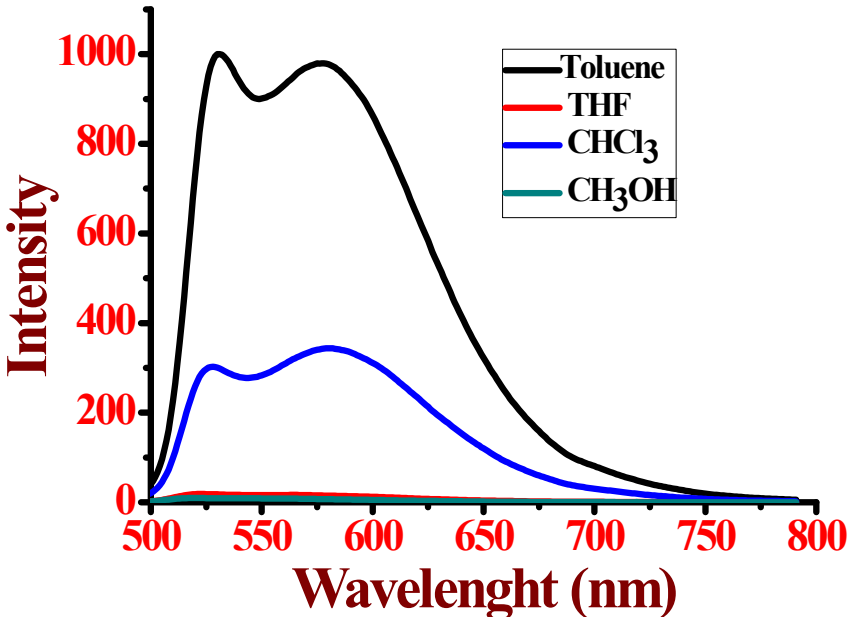


Figure S34: Comparison of emission spectrum of compound **5**(2×10^{-5}M) recorded in different solvents

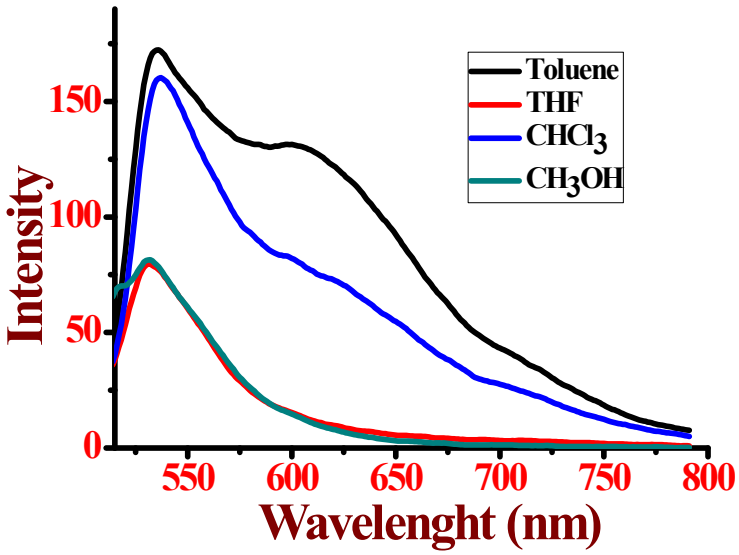


Figure S35: Comparison of emission spectrum of compound **6** (2×10^{-5}M) recorded in different solvents

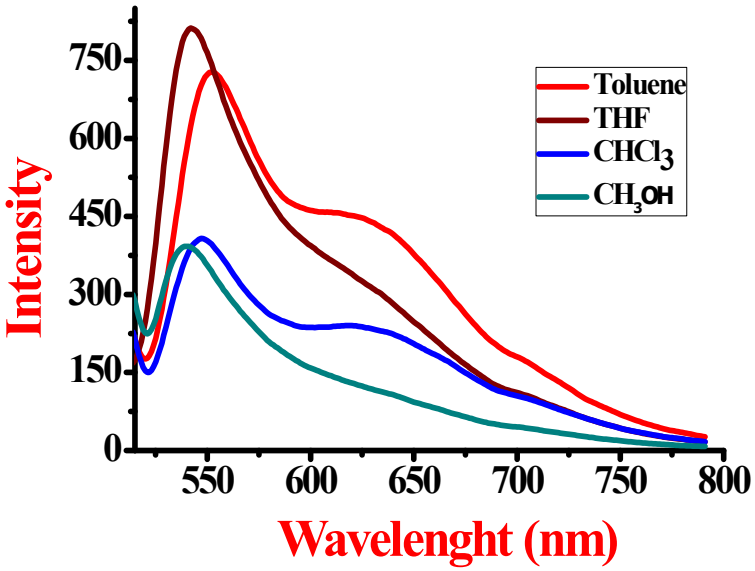


Figure S36: Comparison of emission spectrum of compound **8** (2×10^{-5}M) recorded in different solvents

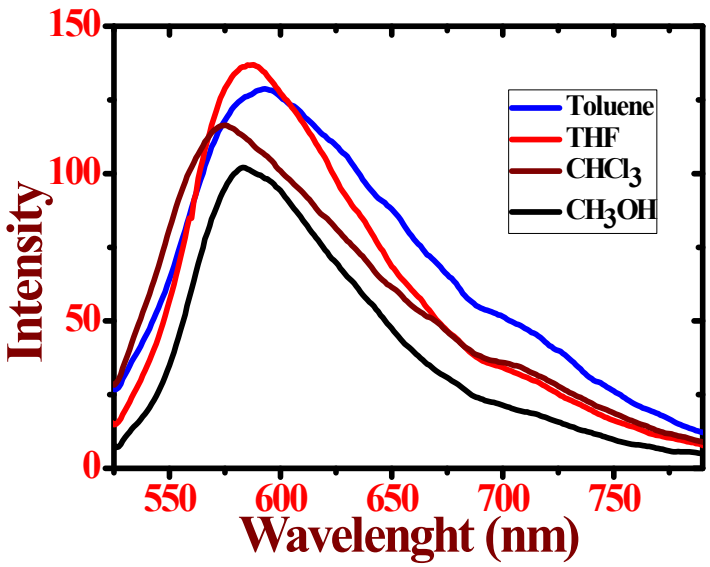


Figure S37: Comparison of emission spectrum of compound **9** (2×10^{-5}M) recorded in different solvents

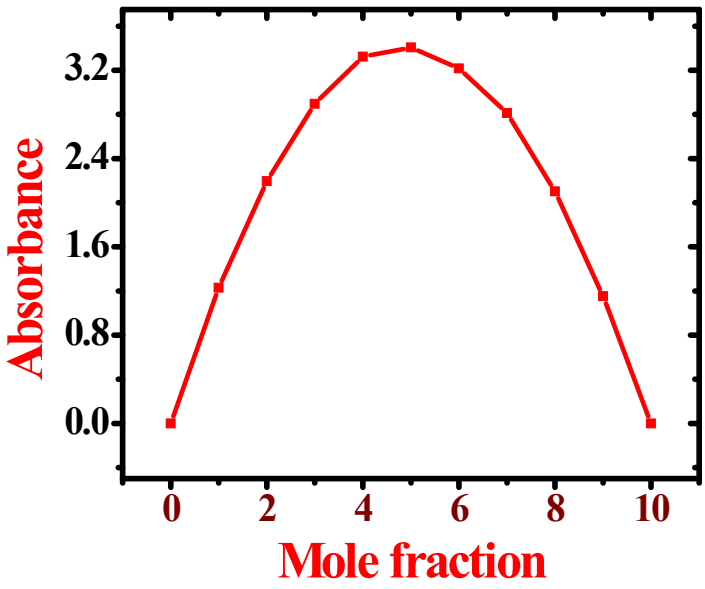


Figure S38. Job's plots of compound **5**

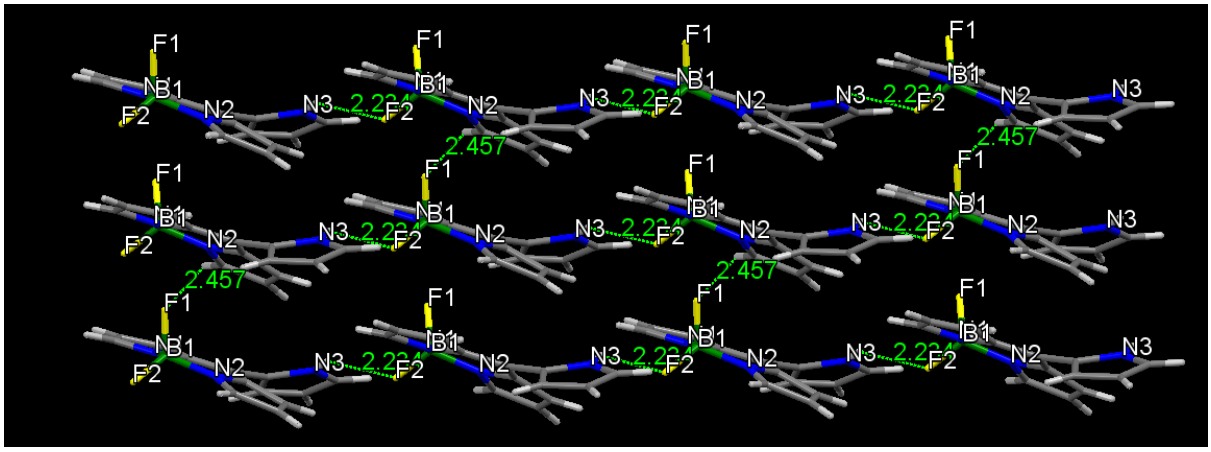


Figure 39. Supramolecular assembly through a weak intermolecular hydrogen bonding network in BODIPY **5**.

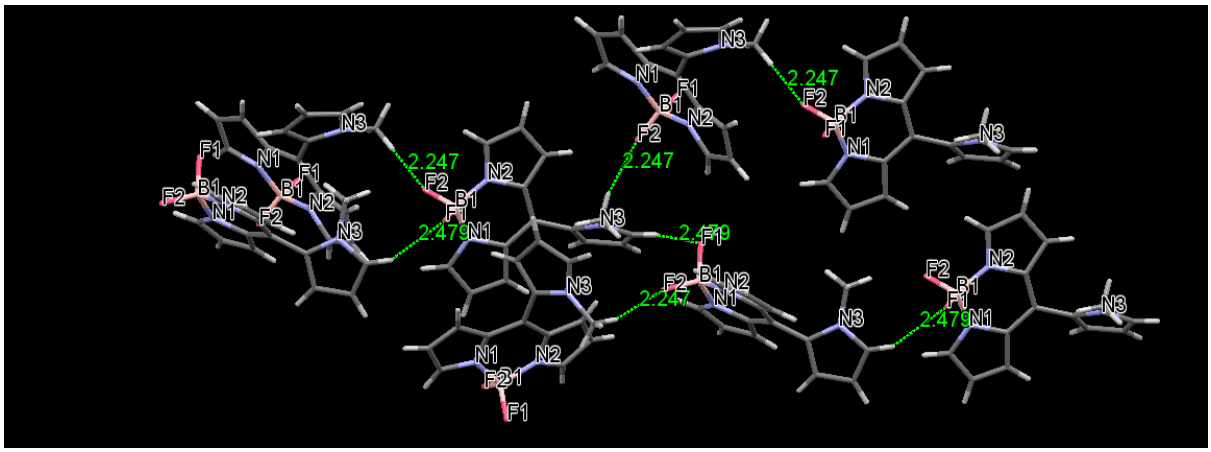


Figure 40. Supramolecular assembly through intermolecular-hydrogen bonding network (between Methyl-H and F (2.247 Å) which is attached to boron in Compound **6**.

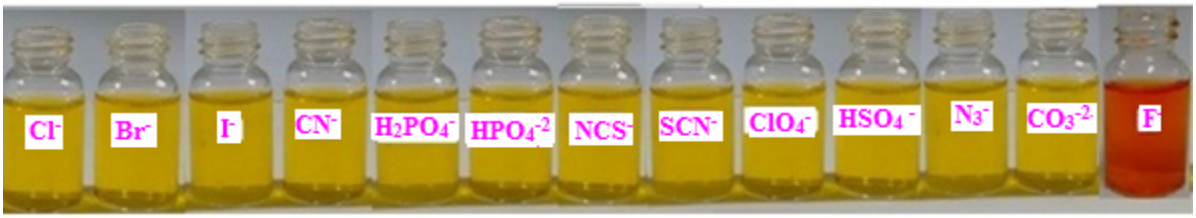


Figure 41. Optical response of BODIPY **5** after addition of different anions

Experimental section

General: THF and n-hexane was dried over sodium benzophenone ketyl, BF_3. Et_2O, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and TFA 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) or alumina. All the ^1H NMR spectra (δin ppm) were recorded using Bruker 400 and 500 MHz instruments. ^{13}C NMR spectra were recorded on Bruker operating at 100.6 and 125.7 MHz. TMS was used as an internal reference for ^1H and ^{13}C (δ 77.0 signal) in $CDCl_3$. For UV-vis, the stock solution of compound **5** (2×10^{-5} M) was prepared by using spectroscopic grade toluene.

Their corresponding UV-vis was recorded at 298 K. In ^1H NMR titration, the spectra were measured on 400 MHz NMR spectrometer. A solution of **5** in $CDCl_3$ was prepared (2×10^{-5} M), and a 0.4 mL portion of this solution was transferred to a 5-mm NMR tube. A small aliquot of Bu_4NF in $CDCl_3$ was added in an incremental fashion, and their corresponding spectra were recorded.

X-ray crystal structure analysis:

Single-crystal X-ray structure analysis was performed on a Rigaku Saturn 724 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,[33] SIR-92,[34] and WINGX.[35] All non-hydrogen atoms were refined anisotropically.

References:

(33) G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112-122.

(34) A. Altomare, G. Cascarano, C. Giacovazzo and A. Gualardi, *J. Appl. Crystallogr.,* 1993, **26**, 343-350.

(35) L. J. Farrugia, *J. Appl. Crystallogr.,* 1999, **32**, 837-838.

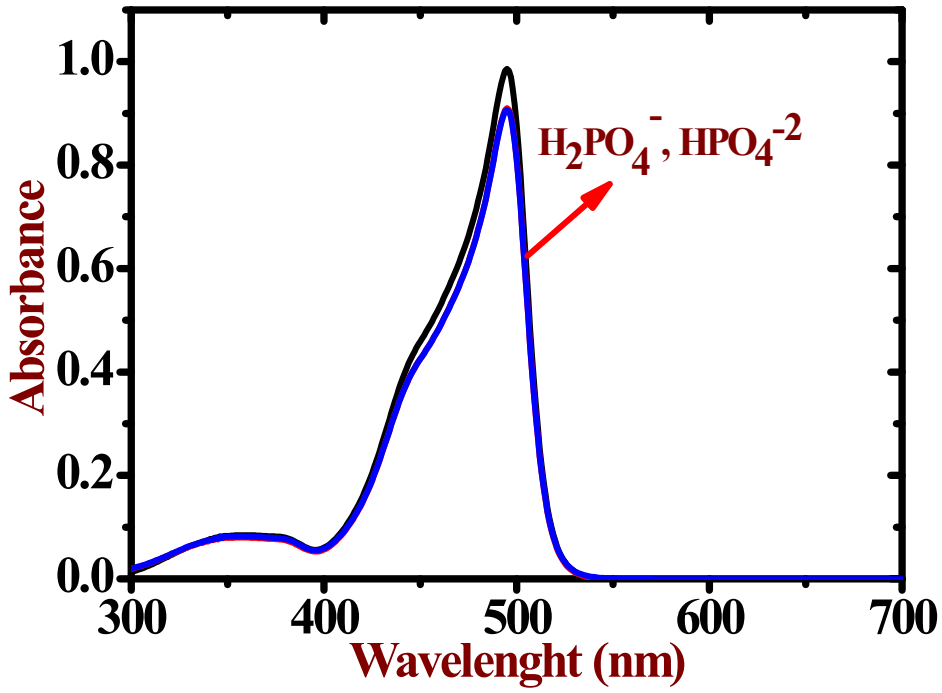


Figure 42. Absorption spectra of compound **5** (2×10^{-5}M) and after addition of HPO_4^{2-} $H_2PO_4^-$ recorded in Toluene

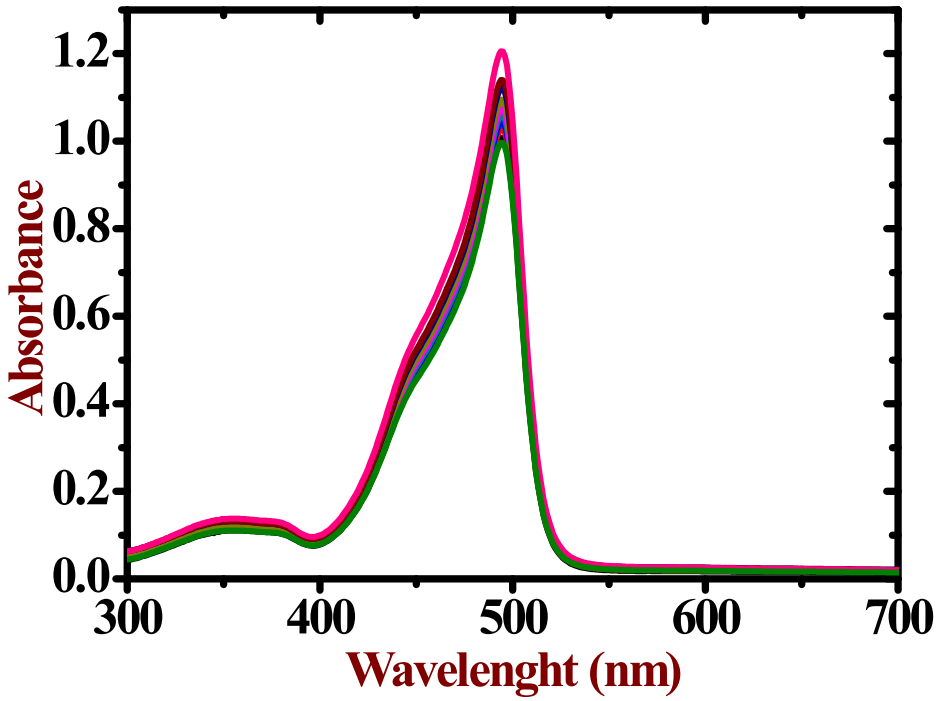


Figure 43. Absorption spectral change of compound **5** (2×10^{-5}M) and after addition of different equivalents of F^- (0-50 equiv.) recorded in CH_3OH.

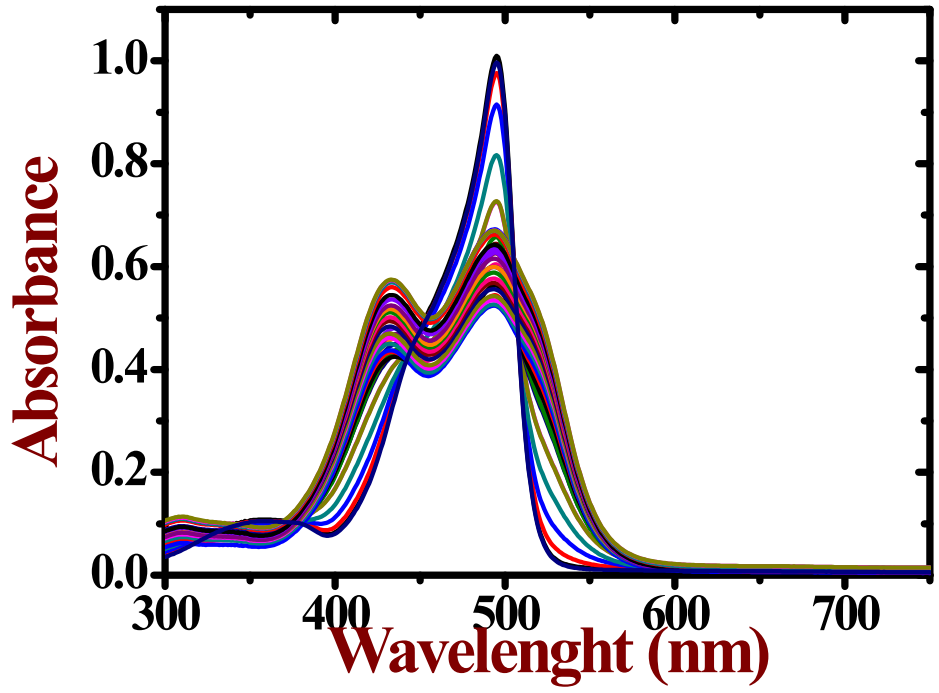


Figure 44. Absorption spectral changes of BODIPY **5** (2×10^{-5} M) upon addition of increasing equivalents of F^- ions (0−15 equiv) in CH_3CN.

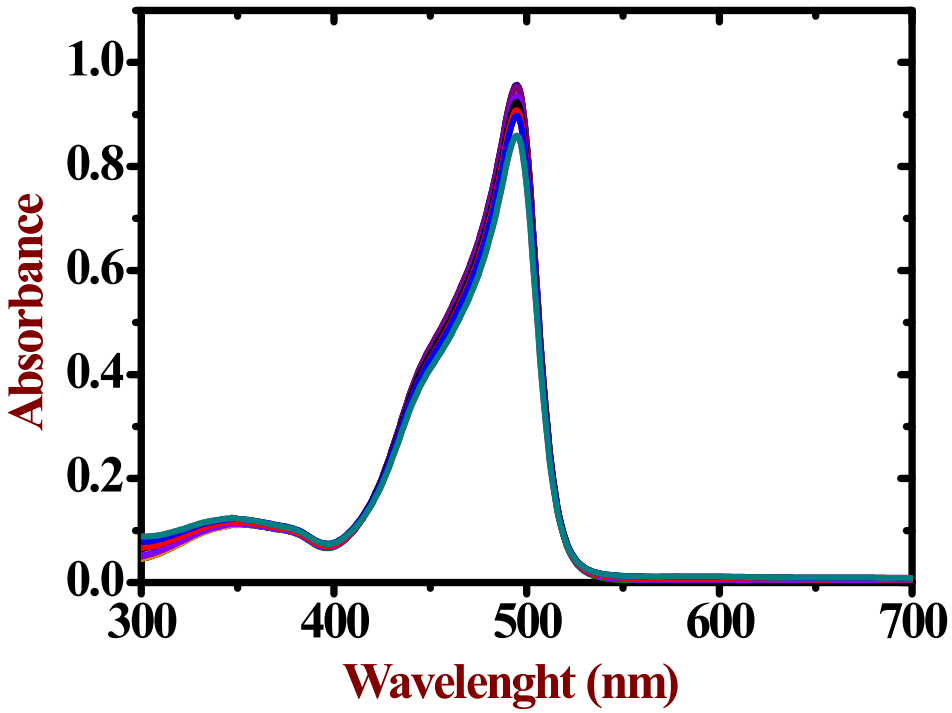


Figure 45. Absorption spectral changes of BODIPY **5** (2×10^{-5} M) upon addition of increasing equivalents of F^- ions (0−50 equiv) in $CH_3CN:H_2O$ (9:1).