Supporting information

BOPAHY: A doubly chelated highly fluorescent pyrrole-acyl hydrazone –BF_2 chromophore

Pookkandam Parambil Shandev,[a] Flip de Jong,[b] Koen Veys,[c] Jianjun Huang,[a] Pulikkal Veettil Santhini,[a] Davy Verhaeghe,[b] Luc Van Meervelt,[d] Daniel Escudero,[c] Mark Van der Auweraer,[b] and Wim Dehaen*[a]

[a.] *Molecular Design and Synthesis, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium. E-mail: wim.dehaen@kuleuven.be*
[b.] *Molecular Imaging and Photonics, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium.*
[c.] *Quantum Chemistry and Physical Chemistry Section, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium.*
[d.] *Biochemistry, Molecular and Structural Biology, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium.*

Table of contents

1. General Methods

Chemicals received from commercial sources were used without further purification. Reaction dry solvents were used as received from commercial sources. TLC were carried out on Kieselgel 60 F254 plates (Merck) and visualized with UV lamp 254 nm. For column chromatography 70- 230 mesh silica 60 (E. M. Merck) was used as the stationary phase. NMR spectra were recorded on a Bruker 400 avance (400 MHz) or a Bruker 300, and chemical shifts (δ) are reported part per million (ppm) referenced to tetramethylsilane (^{1}H). Melting points were determined using a Reichert Thermovar apparatus.

Exact mass spectra were acquired with a quadrupole orthogonal acceleration time-of-flight mass spectrometer (Synapt G2 HDMS, Waters, Milford, MA). Samples were infused at 3uL/min

and spectra were obtained in positive (or: negative) ionization mode with a resolution of 15000 (FWHM) using leucine enkephalin as lock mass.

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of pentane into their dichloromethane solutions at room temperature. X-ray intensity data were collected at 293(2) K on an Agilent SuperNova diffractometer with Eos CCD detector using MoK_α radiation (λ = 0.71073 Å). Data frames were processed (unit cell determination, intensity data integration, correction for Lorentz and polarization effects, and empirical absorption correction) using CrysAlis PRO.[1] The structures were solved using Olex2[2] with the ShelXT[3] structure solution program using Intrinsic Phasing and refined with the ShelXL[4] refinement package using full-matrix least-squares minimization on F^2. Non-hydrogen atoms were refined anisotropically. Hydrogen atom H16 in **3e** was located from a difference electron density map and refined freely. The other hydrogen atoms were placed in idealized positions and included as riding contributions with isotropic temperature factors fixed at 1.2 times U_{eq} of the parent atoms (1.5 for methyl groups). The structure of **3a** was refined as a two-component twin (BASF = 0.516). CCDC 1982532-1982535 contain the supplementary crystallographic data for this paper and can be obtained free of charge via http://www.ccdc.cam.ac.uk/getstructures or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; deposit@ccdc.cam.ac.uk).

Dye solutions were prepared using commercially available toluene and acetonitrile of at least spectro or HPLC grade. UV-Vis absorption spectra were recorded on a PerkinElmer Lambda40 spectrophotometer using blank correction. Fluorescence spectra and excitation spectra were recorded on a HORIBA Jobin Yvon Fluorolog FL3-22 fluorimeter and corrections for the excitation beam intensity, the wavelength dependent sensitivity of the detector and the optical path were applied. Absolute fluorescence quantum yields were measured on the same machine using an integrating sphere and homemade cylindrical quartz cuvettes.[5-6] When recording the Rayleigh scatter, a neutral density filter of 0.3% was used.

The ground and excited state geometries were optimized with DFT [7]and TDDFT[8], respectively using the PBE0[9] in combination with the 6-31G*[10] basis set. All structures were verified to be local minima by computing the Hessian and checking for imaginary frequencies. Molecules 3a-c,e were optimized for 2 different conformers of the substituent ring to find the most stable structure (see Table S1). Single point algebraic diagrammatic construction through second order, ADC(2)[11] calculations using the Def2-TZVP [12]basis set were performed. Solvent effects were also included in the ADC(2) calculations using the conductor-like screening model (COSMO), which includes both linear-response terms and state-specific effects. Singlet electronic excitation energies were equilibrated to the ground state, while singlet electronic emission energies were equilibrated to S_1. $E_{0\text{-}0}$ energy differences were

calculated by using the singlet electronic energies from ADC(2), combined with the zero-point energies from (TD)DFT calculations. All the DFT calculations were performed with Gaussian 16, revision A.03.[13] while the Turbomole7.1 [14]package was used for the ADC(2) calculations.

Cyclic voltammetry measurements were carried out using an Autolab PGSTAT101 and a homebuilt three-electrode cell consisting of an HOPG working electrode with an area of 38.5 mm², a platinum wire counter electrode and an KCl-saturated Ag/AgCl reference electrode. Before each measurement the HOPG electrode was freshly cleaved using Scotch tape. For the electrochemical experiments, solutions of 10 mM of **3a-3e** in DCM were prepared, with 0.1 M of tetrabutylammonium hexafluorophosphate as supporting electrolyte. Prior to each measurement, the solutions were purged with argon. The scanning rate was 100 mV/s.

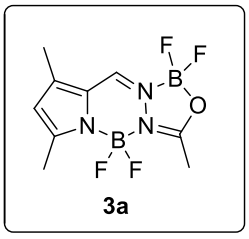
2. **Experimental Procedures**

2a General procedure for BOPAHY (3a-3e)

A mixture of 2-formyl pyrrole (1 mmol) and carbohydrazide (1.1 mmol) in 10 mL ethanol was refluxed after the addition of a few drops of glacial acetic acid. Reaction was monitored by TLC, after complete consumption of 2-formyl pyrrole, the solvent was completely evaporated under reduced pressure. The residue was dissolved in 8 mL dry toluene, triethylamine (2.5 mL) was added and the reaction mixture was stirred for 10 minutes at room temperature. After cooling to 0 °C, $BF_3.Et_2O$ (4 mL) was then added dropwise and refluxed under nitrogen for overnight. The cooled reaction mixture was quenched with water and extracted with DCM. The organic layer were washed with water, dried over magnesium sulphate and concentrated under reduced pressure. The residue was then purified by column chromatography (silica gel) using petroleum ether and dichloromethane as eluent to afford the corresponding BOPAHY as pure solids. The compound was then further purified by recrystallization from DCM-Pentane solvent mixture.

2b. **Synthesis and Characterisation of BOPAHY**

Synthesis of BOPAHY 3a



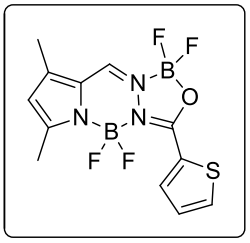
3a

The reaction was performed according to the general procedure with 3,5-dimethyl-1H-pyrrole-2-carbaldehyde (123 mg, 1 mmol) and acetohydrazide (81 mg, 1.1 mmol) to afford the desired product **3a** as a white solid (211 mg, 77%). The product was recrystallized from DCM/Pentane.

mp: 210-211 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 6.20 (s, 1H), 2.63 (s, 3H), 2.47 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.3, 152.9, 141.4, 132.5, 123.3, 119.2, 15.7, 14.3,

11.11; ^{11}B NMR (128 MHz, $CDCl_3$): δ 3.33 (s), 0.60 (t, *J* = 28.5 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -138.82 – -139.06 (m), -146.06 – -146.19 (m); HRMS (ESI, $[M-H]^+$) for $C_9H_{10}B_2F_4N_3O$ calcd 274.0946; found 274.0963.

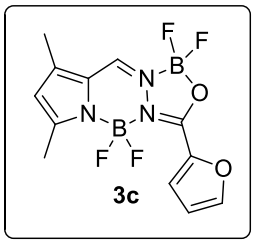
Synthesis of BOPAHY 3b



The reaction was performed according to the general procedure with 3,5-dimethyl-1H-pyrrole-2-carbaldehyde (123 mg, 1 mmol) and thiophene-2-carbohydrazide (156 mg, 1.1 mmol) to afford the desired product **3b** as a pale yellow solid (240 mg, 70%). The product was recrystallized from DCM/Pentane.

mp: 178- 179 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, *J* = 3.5 Hz, 1H), 7.93 (d, *J* = 4.3 Hz, 1H), 7.68 (s, 1H), 7.30 (t, *J* = 4.5 Hz, 1H), 6.23 (s, 1H), 2.52 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.3, 152.6, 140.8, 139.1 (t, *J* = 8.4 Hz), 138.2, 132.0, 129.7, 125.4, 123.2, 119.3, 14.4, 11.1; ^{11}B NMR (128 MHz, $CDCl_3$): δ 3.16 (bs), 1.14 (t, *J* = 28.2 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -137.11– -137.33 (m), -146.20 – -146.52 (m). HRMS (ESI, $[M-BF_2+H]^+$ for $C_{12}H_{13}B_1F_2N_4O$ calcd 296.0835; found：[M-BF_2 +H]: 296.0828

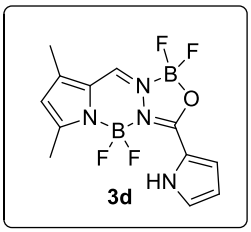
Synthesis of BOPAHY 3c



The reaction was performed according to the general procedure with 3,5-dimethyl-1H-pyrrole-2-carbaldehyde (123 mg, 1 mmol) and furan-2-carbohydrazide (139 mg, 1.1 mmol) to afford the desired product **3c** as a pale yellow solid (245 mg, 75%). The product was recrystallized from DCM/Pentane.

mp: 208-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 3.8 Hz, 1H), 7.92 – 7.85 (m, 1H), 7.69 (s, 1H), 6.75 (dd, *J* = 3.9, 1.6 Hz, 1H), 6.23 (s, 1H), 2.52 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 152.8, 150.5, 140.9, 138.6, 132.1, 126.4 (t, *J* = 6.9 Hz), 123.3, 119.3, 114.09, 77.16, 14.41, 11.12; ^{11}B NMR (128 MHz, $CDCl_3$): δ 3.36 (bs), 1.02 (t, *J* = 26.6 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -138.40 – -138.63 (m), -145.85 – -145.97 (m); GCMS (M^+) for $C_{12}H_{12}B_2F_4N_4O$ calcd 327.1205; found 327.1202; HRMS (ESI, $[M+H]^+$) for $C_{12}H_{121}B_2F_4N_3O_2$ calcd 328.1052; found 328.1054.

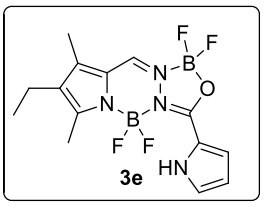
Synthesis of BOPAHY 3d



The reaction was performed according to the general procedure with 3,5-dimethyl-1H-pyrrole-2-carbaldehyde (123 mg, 1 mmol) and 1H-pyrole-2-carbohydrazide (137 mg, 1.1 mmol) to afford the desired product **3d** as an yellow solid (254 mg, 78%). The product was recrystallized from DCM/Pentane.

mp: 216-218 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.26 (s, 1H), 7.68 (s, 1H), 7.65 – 7.59 (m, 1H), 7.36 –7.30 (m, 1H), 6.48 (dt, *J* = 4.1, 2.2 Hz, 1H), 6.22 (s, 1H), 2.51 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.9, 150.7, 139.5, 131.4, 130.0, 125.3, 122.9, 118.9, 115.7, 113.0, 14.4, 11.1; ^{11}B NMR (128 MHz, $CDCl_3$): δ 3.21 (s), 1.16 (t, *J* = 31.8 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -136.18 (dd, *J* = 51.9, 33.8 Hz), -147.32 (d, *J* = 16.6 Hz); HRMS (ESI, $[M+H]^+$) for $C_{12}H_{12}B_2F_4N_4O$ calcd 327.1205; found 327.1202.

Synthesis of BOPAHY 3e



The reaction was performed according to the general procedure with 4-ethyl-3,5-dimethyl-1H-pyrrole-2-carbaldehyde (151 mg, 1 mmol) and 1H-pyrole-2-carbohydrazide (137 mg, 1.1 mmol) to afford the desired product **3e** as an yellow solid (194 mg, 55%). The product was recrystallized from DCM/Pentane.

Mp: 237-240 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.25 (s, 1H), 7.63 (s, 1H), 7.61 – 7.58 (m, 1H), 7.31 (dd, *J* = 3.9, 3.2 Hz, 1H), 6.47 (dt, *J* = 4.3, 2.3 Hz, 1H), 2.46 (q, *J* = 7.6 Hz, 2 H), 2.47 (s, 3H), 2.25 (s, 3H), 1.09 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7, 149.2, 136.2, 132.0, 130.6, 129.7, 125.0, 122.2, 115.8, 112.8, 17.3, 14.8, 12.3, 9.4; ^{11}B NMR (128 MHz, $CDCl_3$): δ 3.24 (s), 2.17 – 0.02 (m); ^{19}F NMR (377 MHz, $CDCl_3$): δ -138.40 – -138.63 (m), -145.96 – -148.63 (m): HRMS (ESI, $[M+H]^+$) for $C_{14}H_{16}B_2F_4N_4O$ calcd 355.1518; found 355.1517

3. **Crystal Diagrams and Selected Parameters**

3a. Crystallographic details

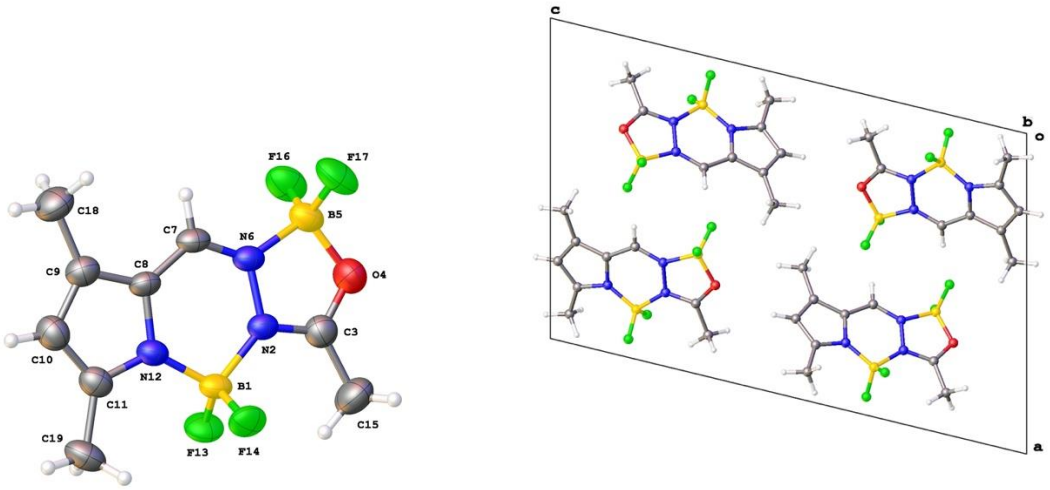


Fig. S1. Molecular structure of **3a**, with atom labels and displacement ellipsoids drawn at the 50% probability level, and crystal packing viewed along the b-axis.

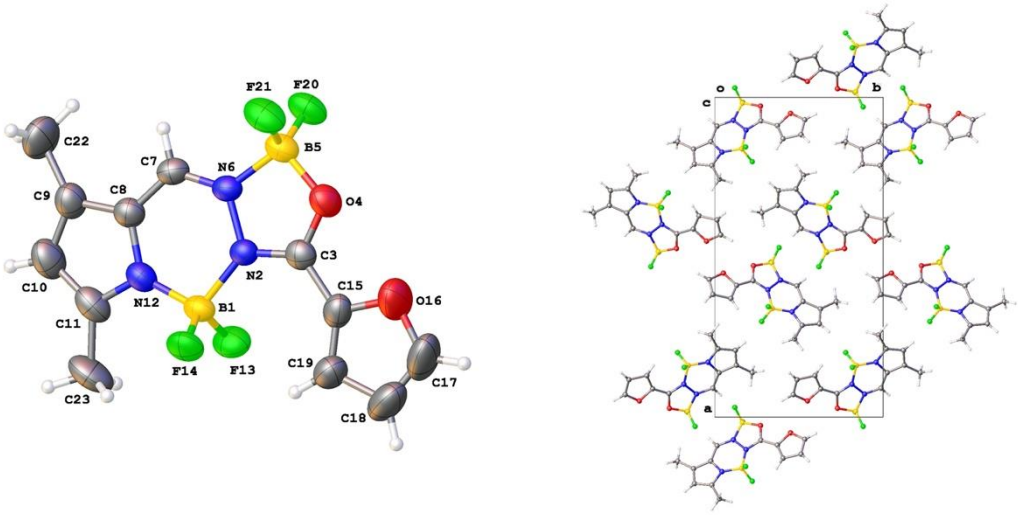


Fig. S2. Molecular structure of **3c**, with atom labels and displacement ellipsoids drawn at the 50% probability level, and crystal packing viewed along the c-axis.

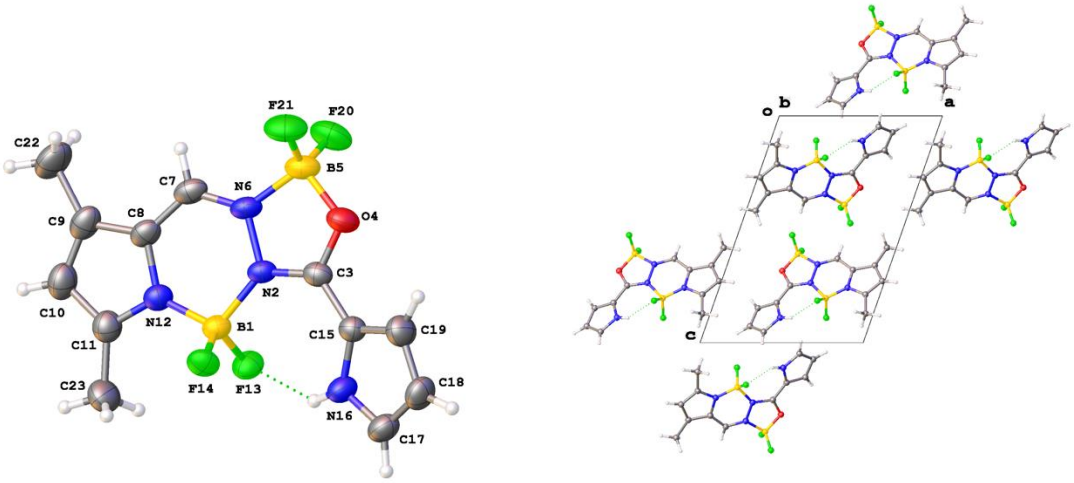


Fig. S3. Molecular structure of **3d**, with atom labels and displacement ellipsoids drawn at the 50% probability level, and crystal packing viewed along the b-axis.

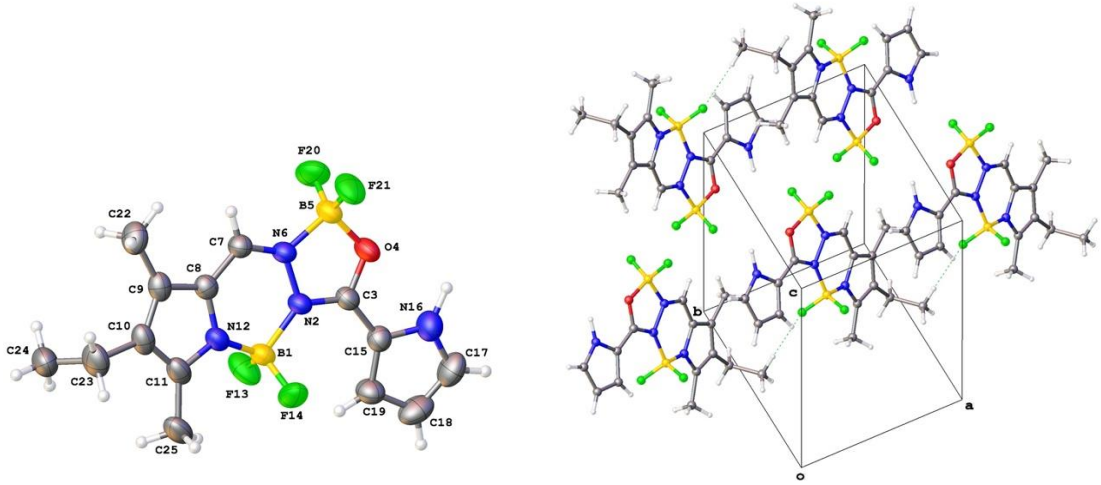


Fig. S4. Molecular structure of **3e**, with atom labels and displacement ellipsoids drawn at the 50% probability level, and crystal packing.

3b. Crystallographic Parameters

Crystal Data for **3a**.

$C_9H_{11}B_2F_4N_3O$, M =274.83, monoclinic, space group $P2_1/c$ (no. 14), a = 12.9329(11) Å, b = 4.8706(4) Å, c = 19.777(2) Å, β = 103.631(9)°, U = 1210.71(19) Å^3, Z = 4, T = 293(2) K, μ(MoKα) = 0.139 mm^{-1},*Dcalc* = 1.508 g/cm^3, 3570 reflections measured (5.912° ≤ 2Θ ≤ 52.736°), 3570 unique

(R_{int} = 0.0680, R_{sigma} = 0.0343) which were used in all calculations. The final R_1 was 0.0461 (I > 2σ(I)) and wR_2 was 0.1302 (all data).

Crystal Data for **3c**.
$C_{12}H_{11}B_2F_4N_3O_2$, M =326.86, orthorhombic, space group $Pna2_1$ (no. 33), a = 23.9330(10) Å, b = 12.5943(6) Å, c = 4.7440(2) Å, U = 1429.93(11) Å^3, Z = 4, T = 293(2) K, μ(MoKα) = 0.136 mm^{-1}, *Dcalc* = 1.518 g/cm^3, 8443 reflections measured (6.046° ≤ 2Θ ≤ 52.74°), 2817 unique (R_{int} = 0.0247, R_{sigma} = 0.0316) which were used in all calculations. The final R_1 was 0.0400 (I > 2σ(I)) and wR_2 was 0.0990 (all data).

Crystal Data for **3d**.
$C_{12}H_{12}B_2F_4N_4O$, M =325.88, monoclinic, space group $P2_1$ (no. 4), a = 10.2475(6) Å, b = 4.8212(2) Å, c = 15.1310(8) Å, β = 109.221(6)°, U = 705.88(7) Å^3, Z = 2, T = 293(2) K, μ(MoKα) = 0.135 mm^{-1}, *Dcalc* = 1.533 g/cm^3, 8064 reflections measured (5.702° ≤ 2Θ ≤ 52.736°), 2850 unique (R_{int} = 0.0216, R_{sigma} = 0.0265) which were used in all calculations. The final R_1 was 0.0363 (I > 2σ(I)) and wR_2 was 0.0857 (all data).

Crystal Data for **3e**.
$C_{14}H_{16}B_2F_4N_4O$, M =353.93, triclinic, space group P-1 (no. 2), a = 8.1042(6) Å, b = 9.7049(9) Å, c = 10.4691(10) Å, α = 80.218(8)°, β = 86.082(8)°, γ = 87.104(7)°, U = 808.89(12) Å^3, Z = 2, T = 293(2) K, μ(MoKα) = 0.124 mm^{-1}, *Dcalc* = 1.453 g/cm^3, 15627 reflections measured (5.042° ≤ 2Θ ≤ 52.744°), 3289 unique (R_{int} = 0.0518, R_{sigma} = 0.0436) which were used in all calculations. The final R_1 was 0.0508 (I > 2σ(I)) and wR_2 was 0.1332 (all data).

4. **Photophysical Properties and Quantum Chemical Calculations**

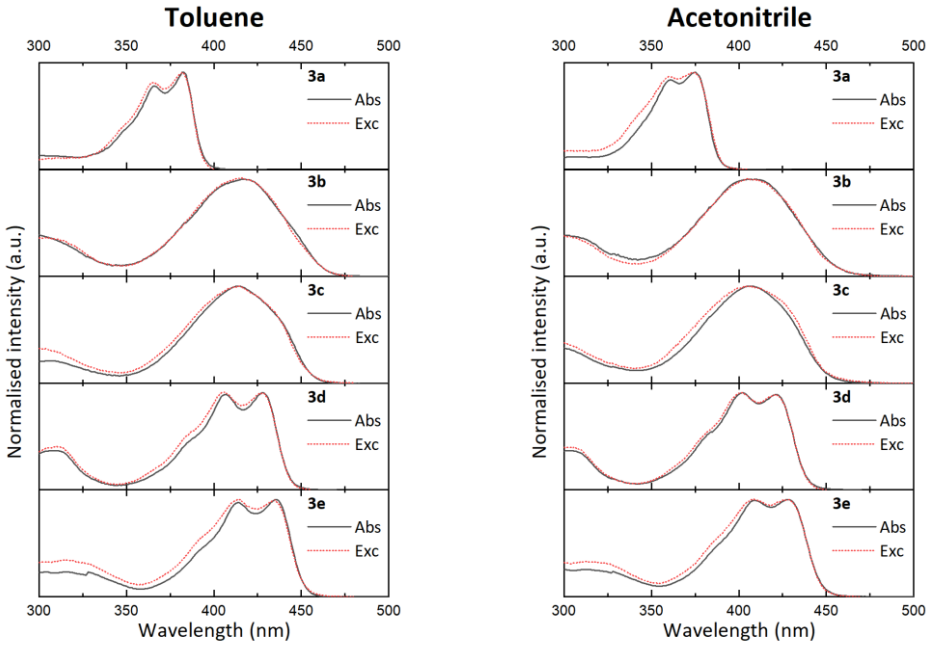


Fig S5. Normalised UV-Visible absorption (Abs) and excitation (Exc) spectra taken near $\lambda_{em,max}$ of 5×10^{-6} M solutions of **3a-e** in toluene (left) and acetonitrile (right).

Solvent	Molecule	$FWHM_{abs}$	$FWHM_{em}$	$\lambda_{abs,exp}$	$\lambda_{abs,ADC(2)}$ S0 → S1	$\lambda_{abs,ADC(2)}$ S0 → S2	$\lambda_{em,exp}$	$\lambda_{em,ADC(2)}$ S1 → S0	$\lambda_{em,ADC(2)}$ S2 → S0	f	$E_{0\text{-}0,exp}$	$E_{0\text{-}0,ADC(2)}$	$\bar{\nu}_{abs} - \bar{\nu}_{em}$	φ	ε
Toluene	**3a**	2540±50	3180±50	383	359	290	396	400	308	0.58	388	398	860±50	0.50	29600
	3b	3780±50	4450±50	418	402	300	505	530	333	0.47	454	463	4120±50	0.67	14300
	3c	3540±50	4190±50	414	399	298	492	509	327	0.49	448	453	3830±50	0.72	27900
	3d	3020±50	3310±50	428	391	293	442	475	305	0.59	435	438	740±50	0.85	32600
	3e	2970±50	3220±50	435	397	309	450	486	328	0.57	443	445	770±50	0.92	40600
MeCN	**3a**	2790±50	3150±50	375			388				382		890±50	0.05	30600
	3b	3930±50	4890±50	409			536				453		5790±50	0.12	24200
	3c	3700±50	4790±50	407			512				446		5040±50	0.23	29800
	3d	3240±50	3530±50	422			439				431		920±50	0.66	35500
	3e	3180±50	3620±50	428			452				439		1240±50	0.76	40100

Table S1. Full width at half maximum of the absorption ($FWHM_{abs}$) and emission ($FWHM_{em}$) band in cm^{-1}; experimental and calculated absorption and fluorescence maxima in nm (for first and second excited state); calculated oscillator strength (f) for emission; experimental and calculated 0-0 energy difference in nm; Stokes' shift in cm^{-1}; fluorescence quantum yield (φ) and extinction coefficient (ε in $M^{-1}cm^{-1}$) of **3a-e** in different solvents. For the presented experimental data, the used concentration was 5×10^{-6} M, except for the extinction coefficients, for which at least four concentrations were measured. The errors on the final values of extinction coefficient and quantum yield are estimated to be within approx. 10% of their value.

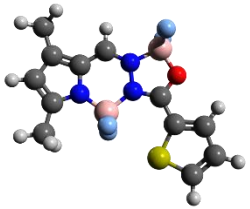
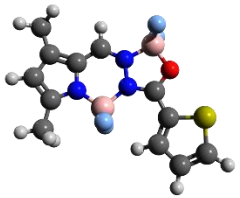
Molecule	ΔE (kcal/mol)	Example structure for E1	Example structure for E2
3b	-1.35		
3c	-1.08		
3d	2.40		
3e	1.82		

Table S2. Relative energy difference between the two conformers ΔE = E1 – E2, with E1: structure with heteroatom from the substituent ring X, pointing towards the Fluorine atom; and E2: structure with heteroatom pointing away from the Fluorine atom.

4a.

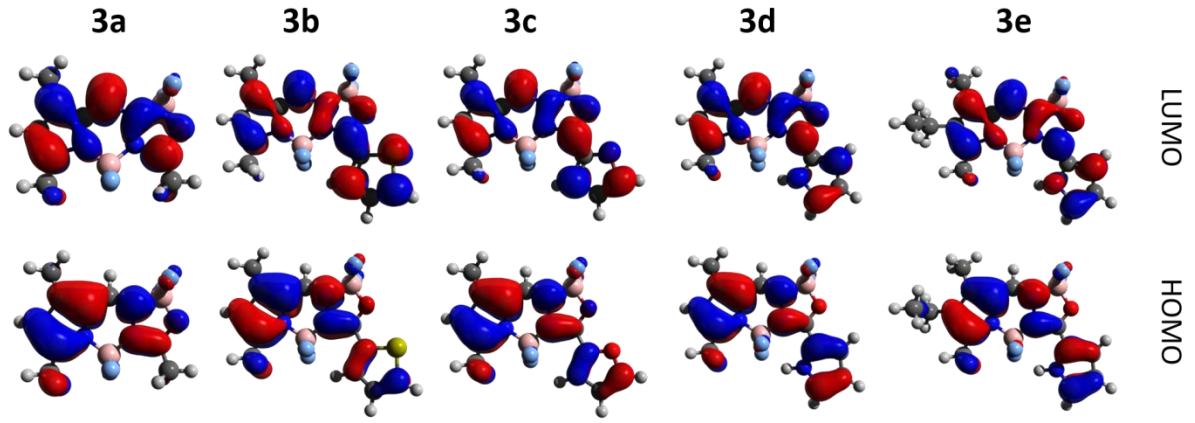


Fig. S6. Frontier molecular orbitals of 3a-e

4b. Coordinates of optimized ground state structures

3a

F	-2.9711485962	1.8396180630	-1.1466028866
F	-2.9433027517	1.8558799696	1.1373163240
F	0.4309144671	-2.1870698700	-1.1525539764
F	0.4086361543	-2.1907496148	1.1256845062
O	-3.1594815422	-0.2291956370	0.0115310665
N	1.5013302187	-0.3505196489	-0.0033302709
N	-1.0802920981	0.7944844245	-0.0178113873
N	-0.9749371546	-0.5802676855	-0.0173126744
C	-2.4630406737	-2.5365796683	0.0372511049
C	3.4012203486	-1.9422032241	0.0031024042
C	2.7728616046	3.1534823925	0.0250672297
C	2.8289668508	-0.5696349067	0.0024861901
C	3.4952338921	0.6669432821	0.0028797498
C	2.5402562328	1.6794919237	-0.0021493126
C	1.2910703547	1.0203399399	-0.0070487266
C	-0.0002543580	1.5351300106	-0.0142362957
C	-2.1967587924	-1.0799462173	0.0026611085
B	-2.6191607351	1.1960792516	-0.0042453164
B	0.3889871854	-1.4116440960	-0.0112755776
H	-2.3133479352	-2.9072273285	1.0569572036
H	-1.7631649265	-3.0636331985	-0.6139798615
H	-3.4939691427	-2.7197644874	-0.2674300916
H	4.4925509457	-1.9039029283	0.0190983662
H	3.0510532434	-2.5052634850	0.8750490509
H	3.0768661583	-2.4956384924	-0.8849270325
H	3.7678770443	3.3950123221	-0.3590895611
H	2.0415029410	3.6971615646	-0.5822423314
H	2.7109591480	3.5487836780	1.0466714592
H	4.5705009445	0.7935774042	0.0050842470
H	-0.1800412964	2.6051565577	-0.0153316024

3b

S	4.1523790000	0.2541470000	0.2613410000
F	0.3932500000	3.3859570000	1.0974120000
F	0.4547610000	3.4009180000	-1.1834370000
F	-0.1169080000	-1.8369410000	1.1003680000
F	-0.2205370000	-1.8805290000	-1.1758320000
O	1.7702490000	1.8036790000	-0.0224000000
N	-2.0520500000	-0.8873270000	0.0175630000
N	-0.5031720000	1.4560240000	-0.0752370000
N	0.1753420000	0.2547440000	-0.0840470000
C	-2.7787530000	-3.2589190000	0.1057150000
C	-5.0271220000	1.3560650000	0.0227910000
C	2.6197510000	-1.7536870000	-0.2850650000
C	3.9303270000	-2.2644840000	-0.1902230000
C	4.8543390000	-1.2930880000	0.1046140000
C	2.5697170000	-0.3925440000	-0.0553820000
C	-3.0445790000	-1.7961130000	0.0733490000
C	-4.2763570000	-1.1225130000	0.0942740000
C	-4.0288650000	0.2471370000	0.0492810000
C	-2.6237400000	0.3728070000	0.0023460000
C	-1.8110170000	1.4983740000	-0.0357350000
C	1.4776220000	0.5430910000	-0.0596980000
B	0.5264150000	2.6617250000	-0.0451760000
B	-0.5440580000	-1.1759610000	-0.0283280000
H	-3.7154670000	-3.8175600000	0.1634370000
H	-2.2327680000	-3.5714150000	-0.7911220000
H	-2.1542160000	-3.5192580000	0.9670320000
H	-5.9642230000	1.0451470000	0.4934140000
H	-4.6689000000	2.2454500000	0.5516890000
H	-5.2613210000	1.6575660000	-1.0058370000
H	1.7505610000	-2.3444950000	-0.5380580000

H 4.1836510000 -3.3079960000 -0.3374760000
H 5.9221220000 -1.4144790000 0.2368200000
H -5.2458050000 -1.6024430000 0.1405960000
H -2.2293610000 2.4993950000 -0.0273690000

3c

F -0.6674700000 3.3694830000 -1.1369770000
F -0.7212240000 3.3870470000 1.1445400000
F -0.0568230000 -1.8308050000 -1.1520790000
F -0.0188670000 -1.8931730000 1.1232420000
O -4.0011430000 0.0648270000 -0.1562890000
O -2.0182650000 1.7698990000 -0.0111880000
N 1.8413700000 -0.8720470000 -0.0094760000
N 0.2667010000 1.4570480000 0.0378000000
N -0.3937330000 0.2474480000 0.0425700000
C 2.5955900000 -3.2358680000 -0.0635290000
C 4.7907890000 1.4045810000 0.0313570000
C -2.8321470000 -1.8164320000 0.1894260000
C -4.2057620000 -2.1416710000 0.0998230000
C -4.8594450000 -0.9610730000 -0.1112560000
C -2.7534150000 -0.4546870000 0.0232250000
C 2.8451490000 -1.7700380000 -0.0355940000
C 4.0692250000 -1.0829130000 -0.0350700000
C 3.8054460000 0.2844280000 -0.0078100000
C 2.3986290000 0.3950450000 0.0067400000
C 1.5741830000 1.5136160000 0.0227470000
C -1.6994070000 0.5206420000 0.0184960000
B -0.7860360000 2.6458950000 0.0072440000
B 0.3361190000 -1.1756930000 -0.0060250000
H 3.5393170000 -3.7849500000 -0.0910340000
H 2.0278820000 -3.5476840000 0.8198640000
H 1.9985320000 -3.5093510000 -0.9402840000
H 5.7458610000 1.0955820000 -0.4029520000
H 4.4408270000 2.2804280000 -0.5250490000
H 4.9882290000 1.7270000000 1.0613590000
H -2.0047160000 -2.4830040000 0.3732160000
H -4.6525410000 -3.1219250000 0.1841370000
H -5.9002840000 -0.7054000000 -0.2452770000
H 5.0448800000 -1.5519690000 -0.0552360000
H 1.9829390000 2.5185640000 0.0188540000

3d

F -0.5929923283 3.3993283125 -1.1813314427
F -0.6101221914 3.4732788642 1.0991043425
F -0.0917373946 -1.6757034965 -1.3213508059
F -0.1517162296 -1.9514653652 0.9330801794
O -1.9778942001 1.8752459663 0.0002480315
N -2.7438616988 -1.6563394260 0.2725253357
N 1.7875646737 -0.8906015850 -0.0153861236
N 0.2936580772 1.4849418070 0.0291741765
N -0.4060565561 0.2971289040 0.0472142181
C 2.4629948364 -3.2812613154 -0.0935609668
C 4.8116826702 1.2774146934 0.1505557948
C -4.1503969963 0.0313272019 -0.1387232432
C -4.8892102322 -1.1528964705 -0.0450857388
C -3.9855170042 -2.1751786919 0.2188789728
C -2.8088263398 -0.3002134943 0.0606151076
C 2.7609577422 -1.8254644089 -0.0261244046
C 4.0047534953 -1.1827585965 0.0254473339
C 3.7880486868 0.1950702551 0.0625244832
C 2.3891494640 0.3556854715 0.0337174300
C 1.5998275389 1.5028254883 0.0357608123
C -1.7121194822 0.6090712084 0.0356533040
B -0.7220723921 2.7063327634 -0.0183971252
B 0.2813663935 -1.1241173850 -0.1172426263
H 3.3892334053 -3.8576806444 -0.1469224191
H 1.8955497814 -3.6051666735 0.7855955492
H 1.8520439534 -3.5108501814 -0.9735271143
H 5.7352613193 0.9804265056 -0.3552306739
H 4.4670148221 2.2094561932 -0.3087787090
H 5.0677491347 1.5002199626 1.1938932894
H -4.5140582262 1.0285985599 -0.3412535962
H -5.9586722107 -1.2649530729 -0.1544913137
H -4.1509687299 -3.2317855008 0.3768377016
H -1.8879337783 -2.1467889009 0.5150282258
H 4.9636820181 -1.6855502831 0.0304534343
H 2.0396975947 2.4944487169 0.0364430922

3e

F 1.6245833642 3.3261477614 1.2479582187
F 1.7637426875 3.4354277339 -1.0266386198
F 0.2834527106 -1.6098832394 1.2182673080
F 0.3982968968 -1.8257997855 -1.0403031713
O 2.7910619668 1.6114107782 0.0913890679
N 2.9683566414 -1.9917620720 -0.2515829550
N -1.3789496812 -0.4818284997 -0.1282913416
N 0.4903840474 1.6086183630 -0.0480081928
N 0.9823565154 0.3208751470 -0.0653602328
C -5.6850705545 -1.0238329223 1.0641670155
C -5.0538943493 -0.8508719233 -0.3200165771
C -2.4292972445 -2.7262400501 -0.1471709466
C -3.9913773613 2.1591991648 -0.3150717129
C 4.6158394031 -0.5759496154 0.2740949166
C 5.1496254327 -1.8655165988 0.1757519336
C 4.1015725564 -2.7139988583 -0.1599664611
C 3.2492053318 -0.6715828221 0.0056625700
C -2.4945511338 -1.2399250071 -0.1815321177

C -3.6246856764 -0.4047536748 -0.2660141504
C -3.1647007218 0.9188153399 -0.2511423277
C -1.7622692888 0.8465869955 -0.1645994678
C -0.7937918268 1.8447190296 -0.1072299003
C 2.3196569658 0.4087301346 0.0099661738
B 1.6912974810 2.6407013431 0.0749658797
B 0.0606926453 -0.9676567452 0.0211243474
H -5.6547133514 -0.0866263534 1.6303680278
H -5.1479962230 -1.7780478026 1.6495167919
H -6.7316513074 -1.3377087529 0.9836061039
H -5.6377641229 -0.1207475040 -0.8947564463
H -5.1295706378 -1.7944724577 -0.8745820467
H -3.4310574393 -3.1607798256 -0.1672298770
H -1.8607803411 -3.1118354213 -1.0003537158
H -1.9175995796 -3.0679298370 0.7595126163
H -4.5944849701 2.2858811880 0.5922528455
H -3.3788314430 3.0580728955 -0.4305807500
H -4.6876905182 2.1268613784 -1.1612467281
H 5.1310982348 0.3405709115 0.5237300259
H 6.1786202193 -2.1589640778 0.3285618799
H 4.0951739096 -3.7792589052 -0.3441005442
H 2.0554809717 -2.3243355379 -0.5482171048
H -1.0599626179 2.8961830298 -0.1002929957

4c. Coordinates of optimized ground state structures

3a

F -2.9303290623 1.8729101463 -1.1351227839
F -2.9216517414 1.8543808000 1.1495150070
F 0.4313682271 -2.1879516538 -1.1301764905
F 0.4001079931 -2.1577548655 1.1484570124
O -3.1771476153 -0.2042138372 -0.0079147033
N 1.4856909579 -0.3354124979 -0.0045062705
N -1.0717641639 0.7753300987 -0.0082089211
N -0.9762067830 -0.5646140099 -0.0256452036
C -2.4958797390 -2.5362230558 0.0104960231
C 3.3668136064 -1.9709665613 -0.0007963371
C 2.7880107257 3.1301858951 0.0025977271
C 2.8471020078 -0.5901629395 0.0005287766
C 3.5275503261 0.6322250344 0.0041696983
C 2.5909067204 1.6616478196 0.0014372776
C 1.3076265050 1.0110318928 -0.0025602086
C -0.0087574365 1.5660437599 -0.0013281394
C -2.2290694479 -1.0893474525 -0.0261119976
B -2.6244322397 1.1909247216 0.0005170135
B 0.3659373930 -1.3956820106 -0.0002517438
H -2.4372495132 -2.9244782939 1.0390298968
H -1.7562340915 -3.0796214994 -0.5841834011
H -3.5020413229 -2.7234264466 -0.3715776548
H 4.4586221192 -1.9760853824 0.0053786639
H 2.9959139837 -2.5270430166 0.8716802083
H 3.0051742144 -2.5216467108 -0.8805302314
H 3.8496425855 3.3895198119 -0.0022615386
H 2.3192734764 3.6019386184 -0.8746815215
H 2.3284680679 3.5998519033 0.8859047139
H 4.6047165268 0.7408365926 0.0068262767
H -0.2019493715 2.6296602459 0.0102770088

3b

S 4.2202060000 0.2926630000 0.1344630000
F 0.3274730000 3.3575870000 1.1178920000
F 0.4362780000 3.3536750000 -1.1642660000
F -0.2020590000 -1.7780150000 1.2182880000
F -0.2324050000 -1.9836030000 -1.0512780000
O 1.7729030000 1.8200810000 0.0421420000
N -2.0669930000 -0.8710690000 0.0000040000
N -0.5027390000 1.4066880000 -0.0552370000
N 0.1588900000 0.2221680000 -0.1120130000
C -2.7975670000 -3.2399740000 0.0674600000
C -5.0215830000 1.3899320000 -0.0301850000
C 2.6372850000 -1.7724870000 -0.1927210000
C 3.9397220000 -2.2652850000 -0.1400540000
C 4.8981300000 -1.2839300000 0.0327490000
C 2.5902080000 -0.3629280000 -0.0514680000
C -3.0682690000 -1.7895990000 0.0287060000
C -4.3085640000 -1.1042970000 0.0202070000
C -4.0565850000 0.2561410000 -0.0106580000
C -2.6326130000 0.3654790000 -0.0197000000
C -1.7853620000 1.5179790000 -0.0236670000
C 1.5376820000 0.5338950000 -0.0404300000
B 0.5556660000 2.6419180000 -0.0136080000
B -0.5339720000 -1.1694600000 0.0275600000
H -3.7261670000 -3.8123760000 0.1036090000
H -2.2107730000 -3.5418900000 -0.8092940000
H -2.1793170000 -3.4860780000 0.9407620000
H -6.0505750000 1.0220760000 -0.0237960000
H -4.8961540000 2.0445290000 0.8418180000
H -4.8954700000 2.0145130000 -0.9236690000
H 1.7606180000 -2.3802180000 -0.3597190000

H 4.1860740000 -3.3176040000 -0.2330810000
H 5.9704640000 -1.4123100000 0.1003220000
H -5.2787390000 -1.5843060000 0.0334040000
H -2.1775430000 2.5272620000 0.0149000000

3c

F -0.5794070000 3.3507130000 -1.1375790000
F -0.6900430000 3.3496620000 1.1443480000
F -0.0028530000 -1.7665940000 -1.2465290000
F -0.0064270000 -1.9893490000 1.0196490000
O -4.0584850000 0.1037210000 -0.0981640000
O -2.0162160000 1.8055200000 -0.0610620000
N 1.8454810000 -0.8625570000 0.0034970000
N 0.2702280000 1.4087100000 0.0404980000
N -0.3788670000 0.2219890000 0.0951650000
C 2.5872750000 -3.2283680000 -0.0497710000
C 4.7884270000 1.4128940000 0.0589730000
C -2.8611420000 -1.8060680000 0.1715880000
C -4.2264080000 -2.1251140000 0.1077600000
C -4.9038940000 -0.9439840000 -0.0546390000
C -2.7839030000 -0.4085980000 0.0375690000
C 2.8515270000 -1.7765560000 -0.0114820000
C 4.0878790000 -1.0856940000 0.0087120000
C 3.8293630000 0.2743200000 0.0322240000
C 2.4053740000 0.3782190000 0.0249420000
C 1.5542100000 1.5287520000 0.0180590000
C -1.7595660000 0.5250040000 0.0204800000
B -0.8055200000 2.6342000000 -0.0054050000
B 0.3162810000 -1.1657410000 -0.0469550000
H 3.5188830000 -3.7967640000 -0.0713370000
H 1.9895980000 -3.5312620000 0.8193620000
H 1.9830490000 -3.4804620000 -0.9313490000
H 5.8193500000 1.0503970000 0.0706330000
H 4.6731730000 2.0615580000 -0.8190550000
H 4.6456870000 2.0430970000 0.9461580000
H -2.0309440000 -2.4759290000 0.3241810000
H -4.6688440000 -3.1092600000 0.1783480000
H -5.9519960000 -0.7019550000 -0.1502450000
H 5.0604790000 -1.5611250000 0.0082320000
H 1.9411860000 2.5397680000 -0.0189450000

3d

F 0.4386059113 3.4145236202 1.1454098036
F 0.6480216302 3.3961948162 -1.1276333548
F 0.0389012548 -1.6442710265 1.3772179277
F 0.1377909123 -2.0023519610 -0.8660058675
O 1.9725779218 1.9075700787 0.1507216871
N 2.7745481400 -1.6330383988 -0.2710556598
N -1.7940722040 -0.8823046049 0.0065622192
N -0.2910582651 1.4304737028 -0.0458040077
N 0.3902602355 0.2758158834 -0.0655791798
C -2.4636278276 -3.2732327658 0.1180234569
C -4.8091814718 1.2853671262 -0.1995077716
C 4.2142281927 0.0559858040 0.1153820731
C 4.9364956448 -1.1282180003 -0.0221362062
C 4.0265982850 -2.1529772738 -0.2685230933
C 2.8409085018 -0.2649030222 -0.0464718716
C -2.7708848155 -1.8314774760 0.0230520904
C -4.0255931076 -1.1855863449 -0.0539933338
C -3.8140309808 0.1826117255 -0.1104764422
C -2.3950618022 0.3412922071 -0.0645791556
C -1.5885523389 1.5148118601 -0.0579325829
C 1.7713396243 0.6135921175 0.0187034351
B 0.7424660298 2.6920903768 0.0335802368
B -0.2714002695 -1.1156944555 0.1440496991
H -3.3803072018 -3.8654088806 0.1459793179
H -1.8475739142 -3.5949098169 -0.7312554106
H -1.8704373171 -3.4792035428 1.0187903609
H -5.8271634193 0.8886939170 -0.2275918014
H -4.7390787158 1.9650598959 0.6599839774
H -4.6611201707 1.8932097703 -1.1016134469
H 4.5900057497 1.0473072338 0.3221437827
H 6.0092346696 -1.2457107767 0.0505925905
H 4.1889442644 -3.2076064892 -0.4409190189
H 1.9222184976 -2.1210934950 -0.5183925763
H -4.9810731624 -1.6944789208 -0.0682442046
H -2.0030515438 2.5145199162 -0.0424005002

3e

F 1.4754531093 3.3633019600 1.2180339938
F 1.7721405234 3.3642595061 -1.0451395758
F 0.2422716894 -1.5787041447 1.2683100249
F 0.3724190587 -1.8729662550 -0.9816627059
O 2.7800749038 1.6470061688 0.2354642316
N 3.0019750101 -1.9693105171 -0.2474478622
N -1.3841792485 -0.4773823047 -0.1311806227
N 0.4782486572 1.5566249189 -0.0587459929
N 0.9612145842 0.3039931748 -0.0859980857
C -5.6706692084 -1.0765067348 1.0553542729
C -5.0592004304 -0.8702445135 -0.3357385182
C -2.4291746236 -2.7189690600 -0.1112140401
C -3.9728504386 2.1852039964 -0.3718471361
C 4.6833095977 -0.5516541266 0.2391845897
C 5.2050217402 -1.8369438342 0.0976810606
C 4.1500038388 -2.6905850529 -0.2116683967
C 3.2844311557 -0.6359755567 0.0153550847
C -2.4967819968 -1.2436036301 -0.1750801616

C -3.6438871889 -0.3964355663 -0.2836256124
C -3.1866242372 0.9209284185 -0.2904389796
C -1.7763648021 0.8378292132 -0.1894711369
C -0.7839936451 1.8572349067 -0.1186884030
C 2.3723957030 0.4065245377 0.0615614649
B 1.7023821136 2.6260208561 0.0969910178
B 0.0727409054 -0.9625803165 0.0469577401
H -5.6622733358 -0.1434035801 1.6279714265
H -5.1089428921 -1.8218920764 1.6282609606
H -6.7075636371 -1.4196498063 0.9751645315
H -5.6649644135 -0.1462185562 -0.8935107525
H -5.1151607614 -1.8090520201 -0.9006150465
H -3.4252111054 -3.1649613680 -0.1339060451
H -1.8359494626 -3.1140671520 -0.9456056187
H -1.9126890533 -3.0357832635 0.8042771874
H -5.0017783796 1.9907961437 -0.6871441722
H -4.0204936015 2.6987195226 0.5975836338
H -3.5355934969 2.8886090064 -1.0902484244
H 5.2089073720 0.3588016262 0.4870922154
H 6.2394002963 -2.1327224446 0.2094890143
H 4.1425956489 -3.7538239762 -0.4058828162
H 2.0940274408 -2.3017869796 -0.5486008324
H -1.0255903462 2.9118683820 -0.0882351173

5. Cyclic Voltammetry

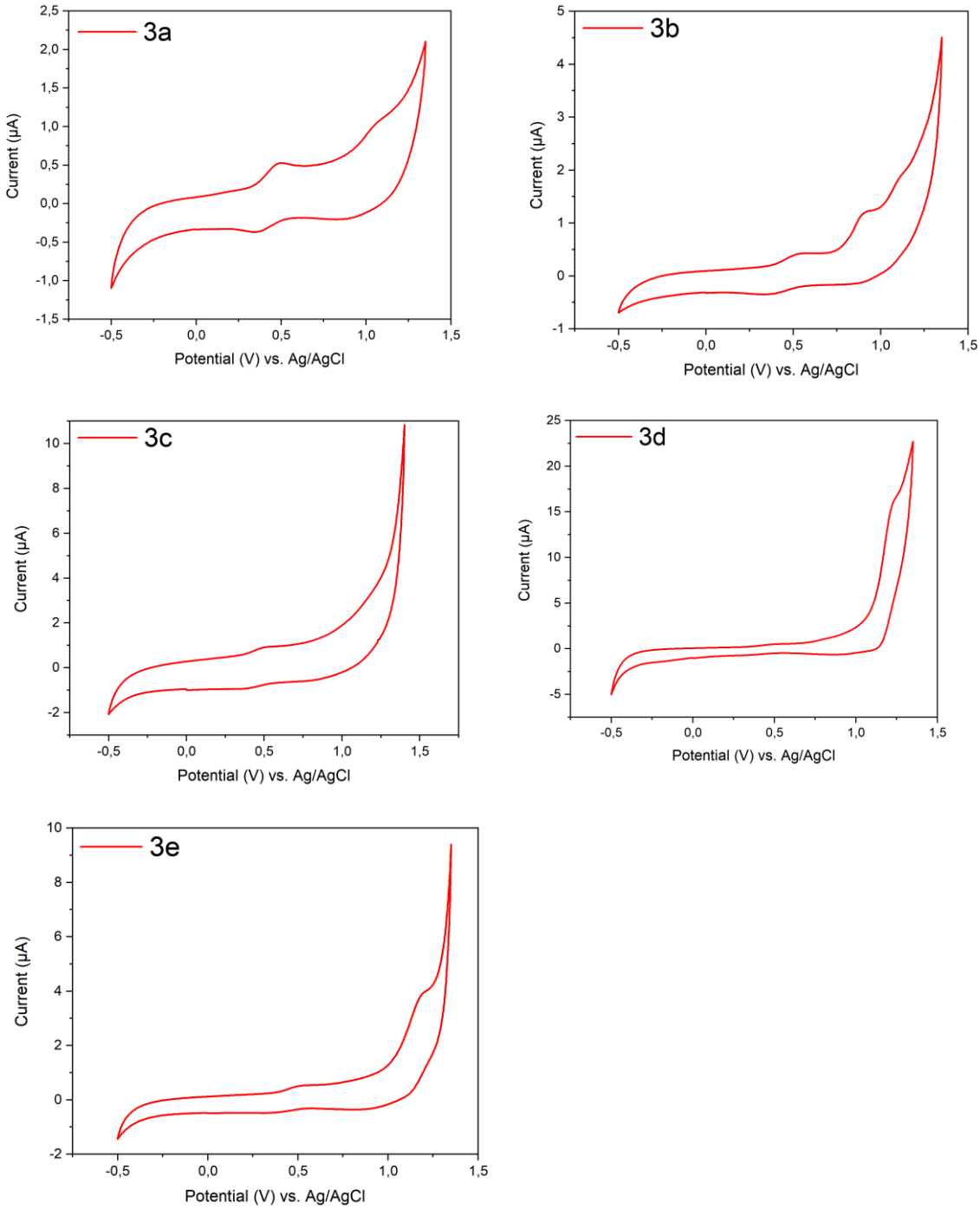


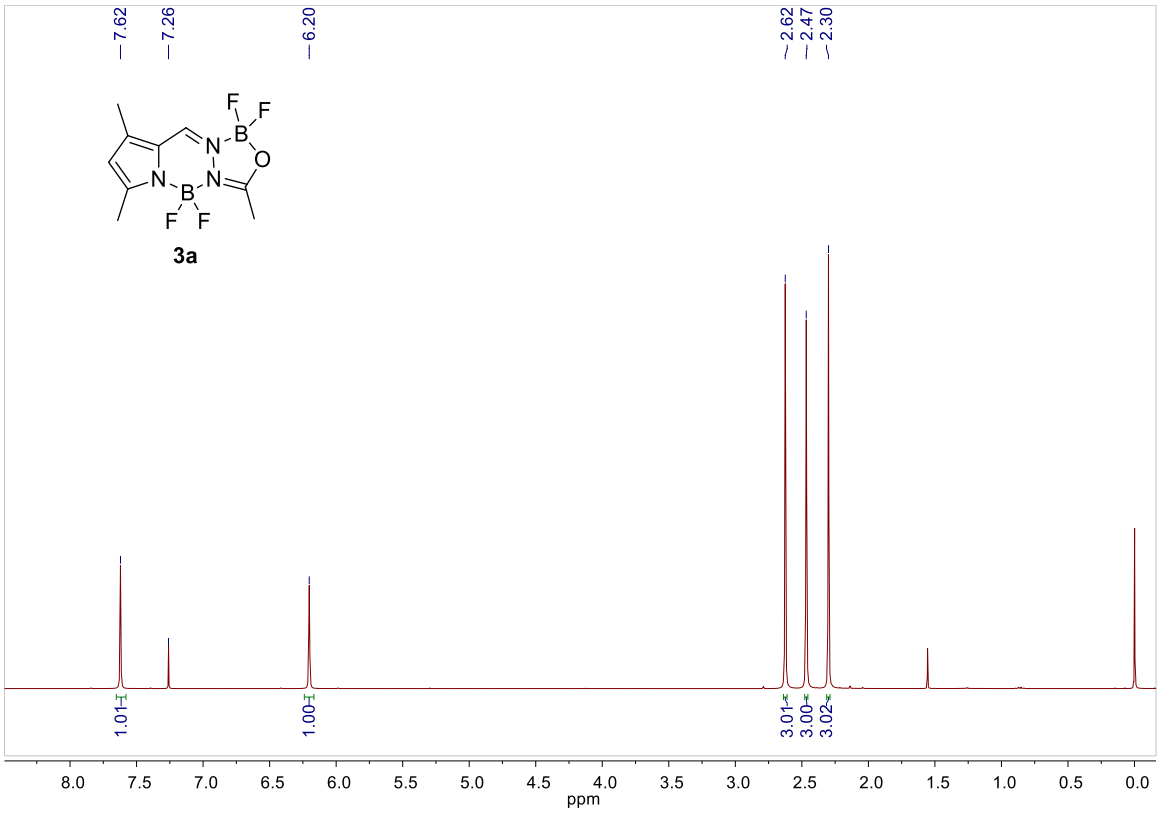
Fig. S7. Cyclic voltammograms of **3a-e** in DCM using 0.1 M $TBAPF_6$ as supporting electrolyte. The scanning rate was 100 mV/s.

	3a	3b	3c	3d	3e	Fc/Fc$^+$
$E_{1/2}$	0.42 V	0.45 V	0.44 V	0.41 V	0.44 V	0.51 V
$E_{onset,ox}$	0.33 V	0.40 V	0.38 V	0.34 V	0.38 V	0.46 V
E_{HOMO}	-4.92 eV	-4.99 eV	-4.97 eV	-4.93 eV	-4.97 eV	-5.1 eV

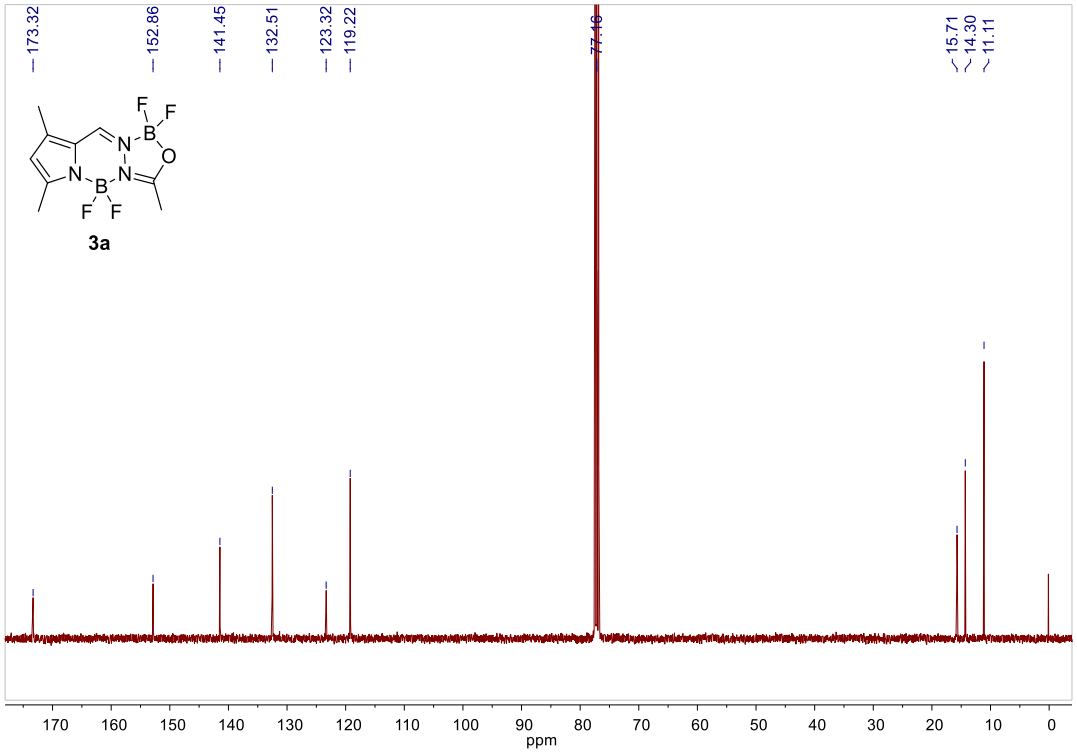
Table S3. Half-wave oxidation potentials are calculated from the mean of the peak potentials: $E_{1/2} = (E_{pc} + E_{pa})/2$. We used the ferrocene/ferrocenium redox couple as external standard. The $E_{1/2}$ of 0.51 V we obtained for Fc/Fc$^+$ is in agreement with literature.[15] The HOMO energies can be estimated using $E_{HOMO} = - e(E_{onset,ox} – 0.51\ V + 5.1\ V)$.[15]

6. ^{1}H , ^{13}C , ^{11}B, ^{19} FNMR spectra of products

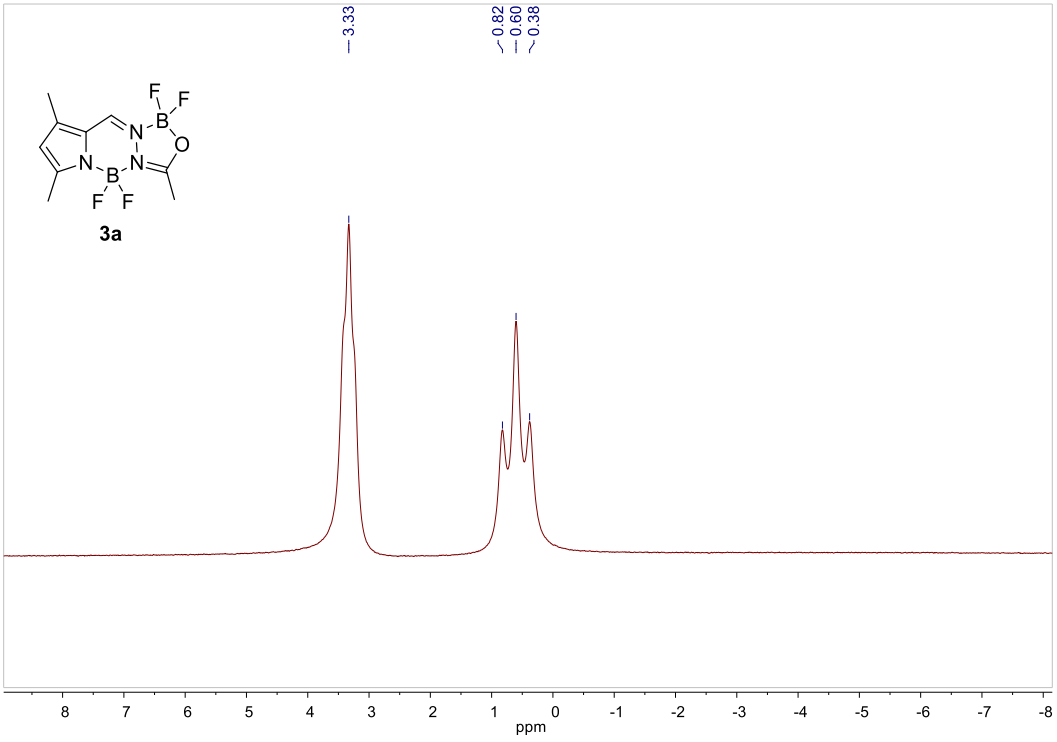
^{1}H NMR Spectra of 3a



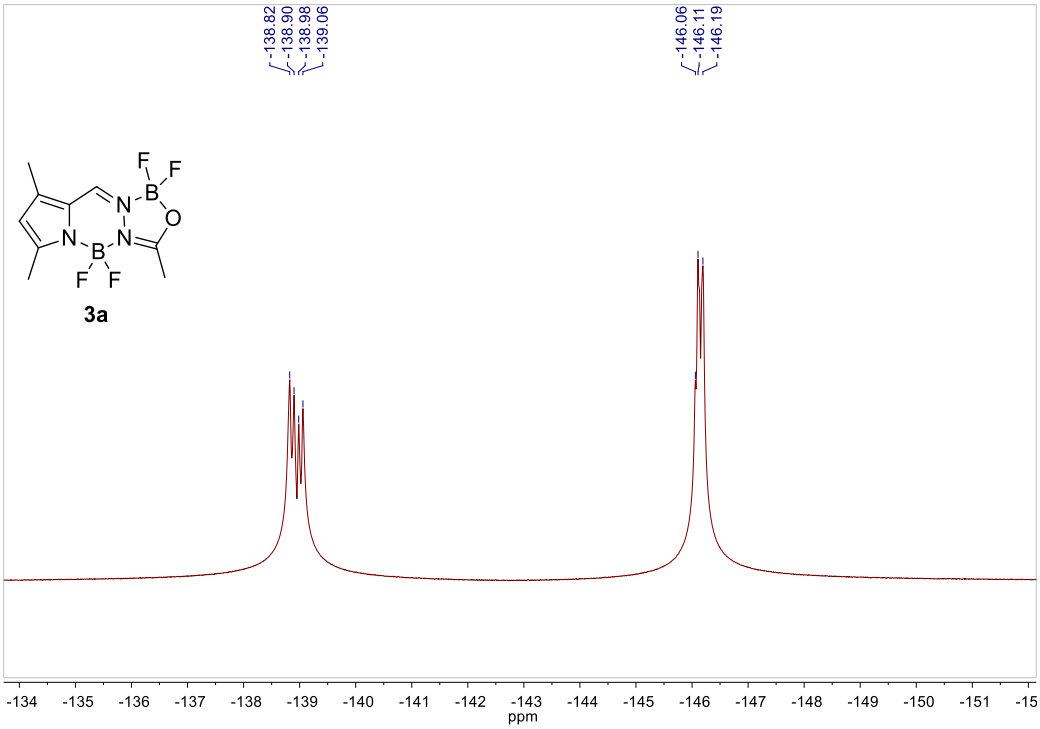
^{13}C NMR Spectra of 3a



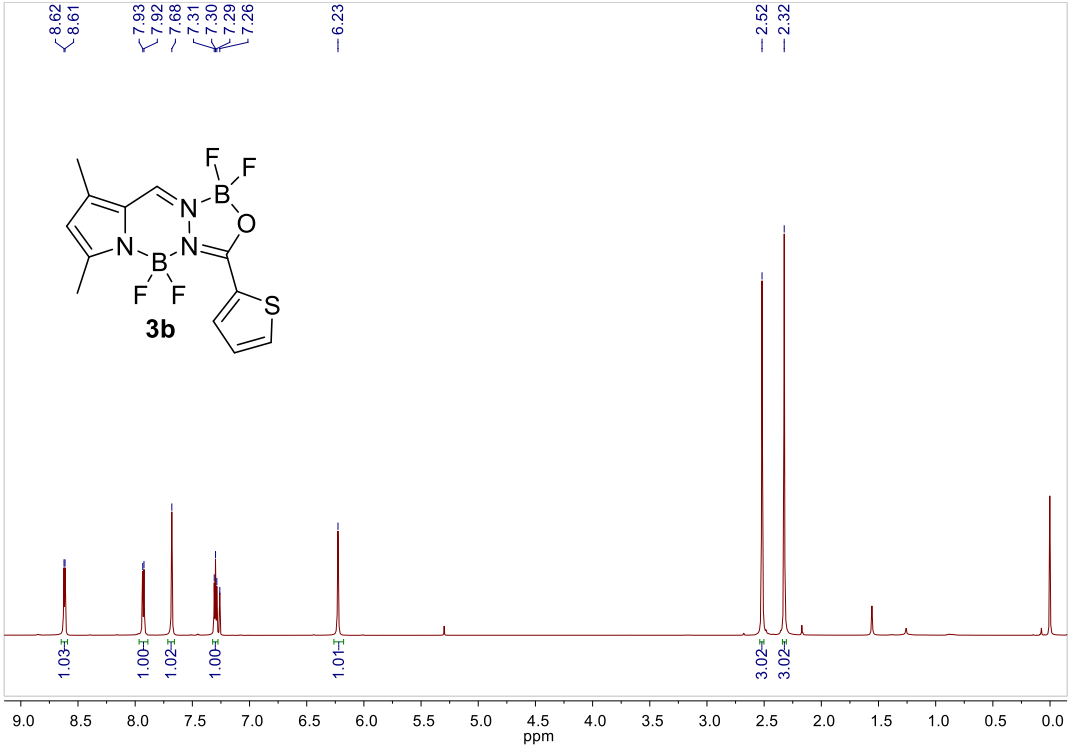
^{11}BNMR Spectra of 3a



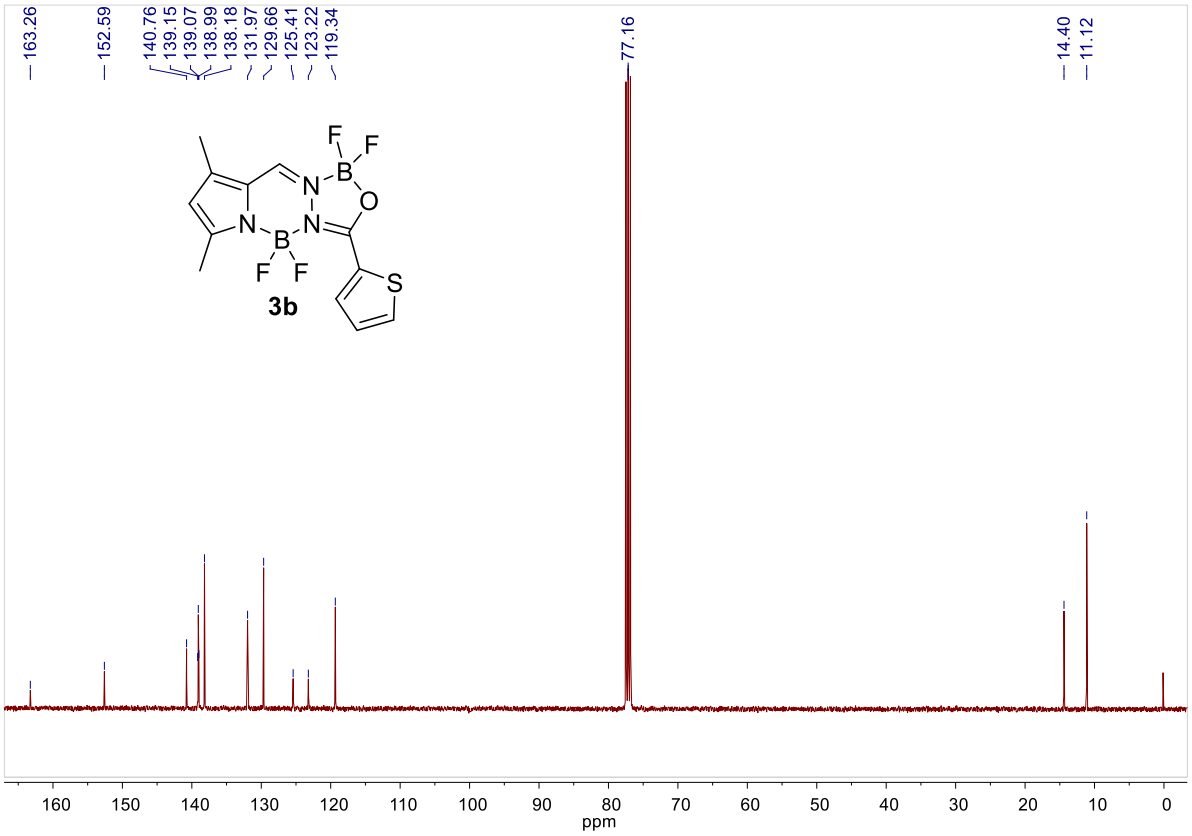
^{19}F NMR Spectra of 3a



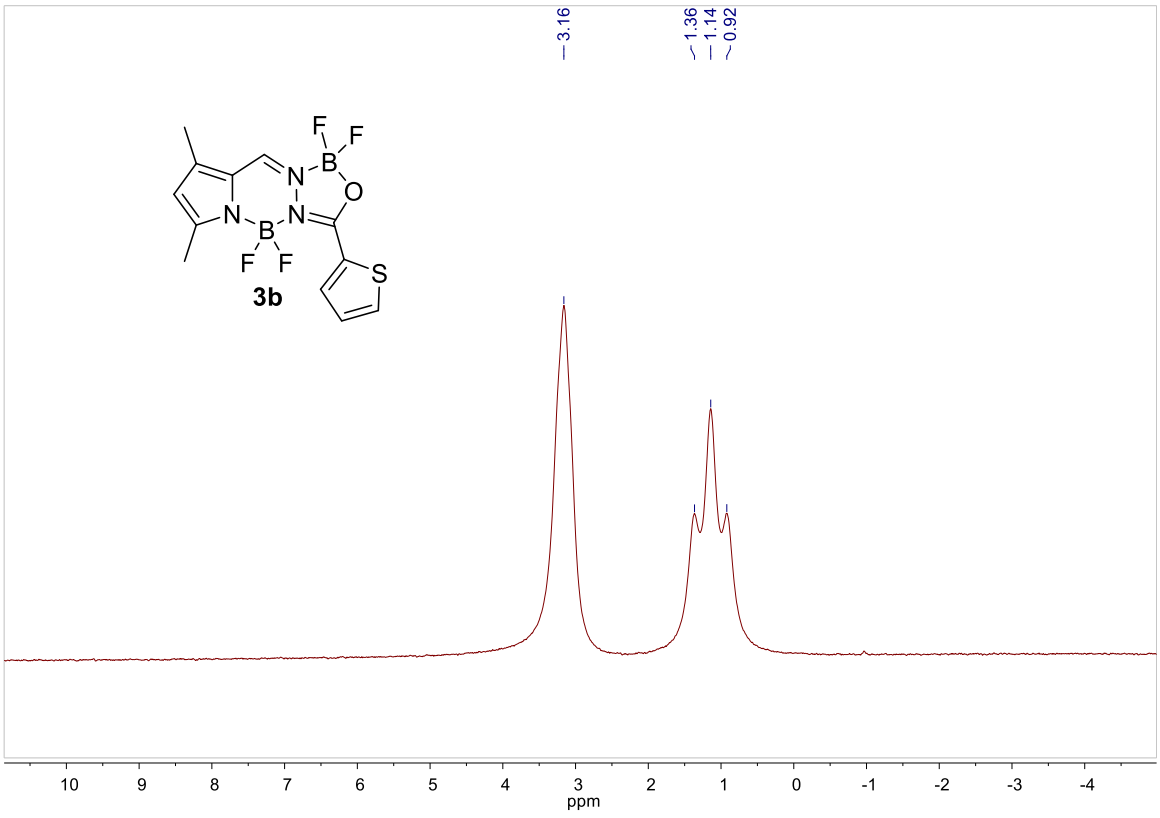
^{1}H NMR Spectra of 3b



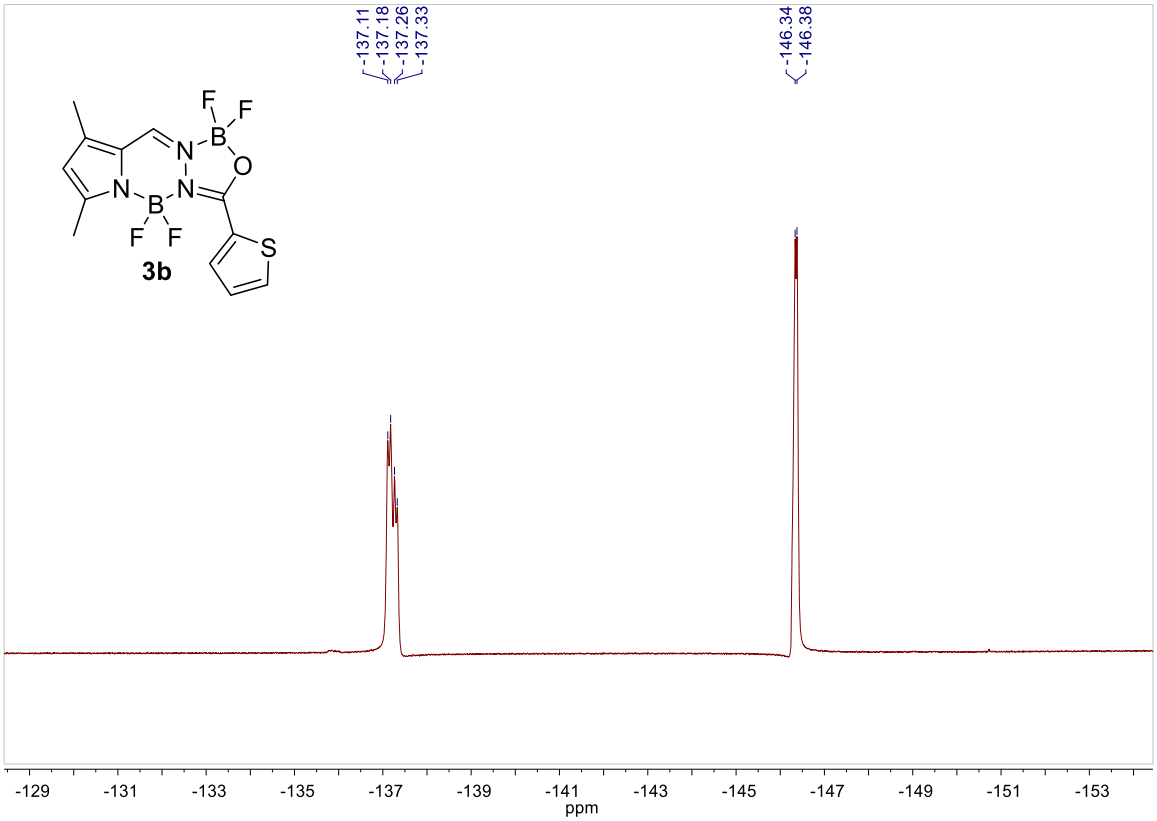
^{13}C NMR Spectra of 3b



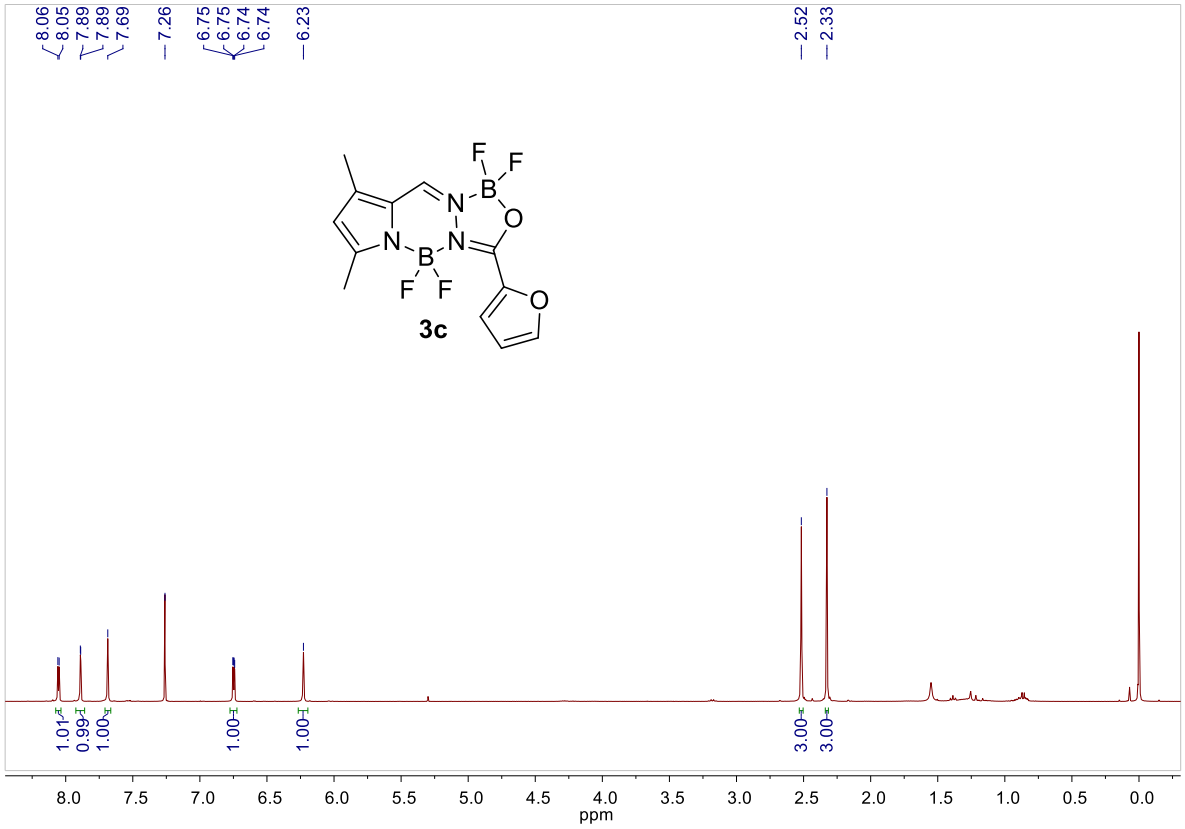
[11]BNMR Spectra of 3b



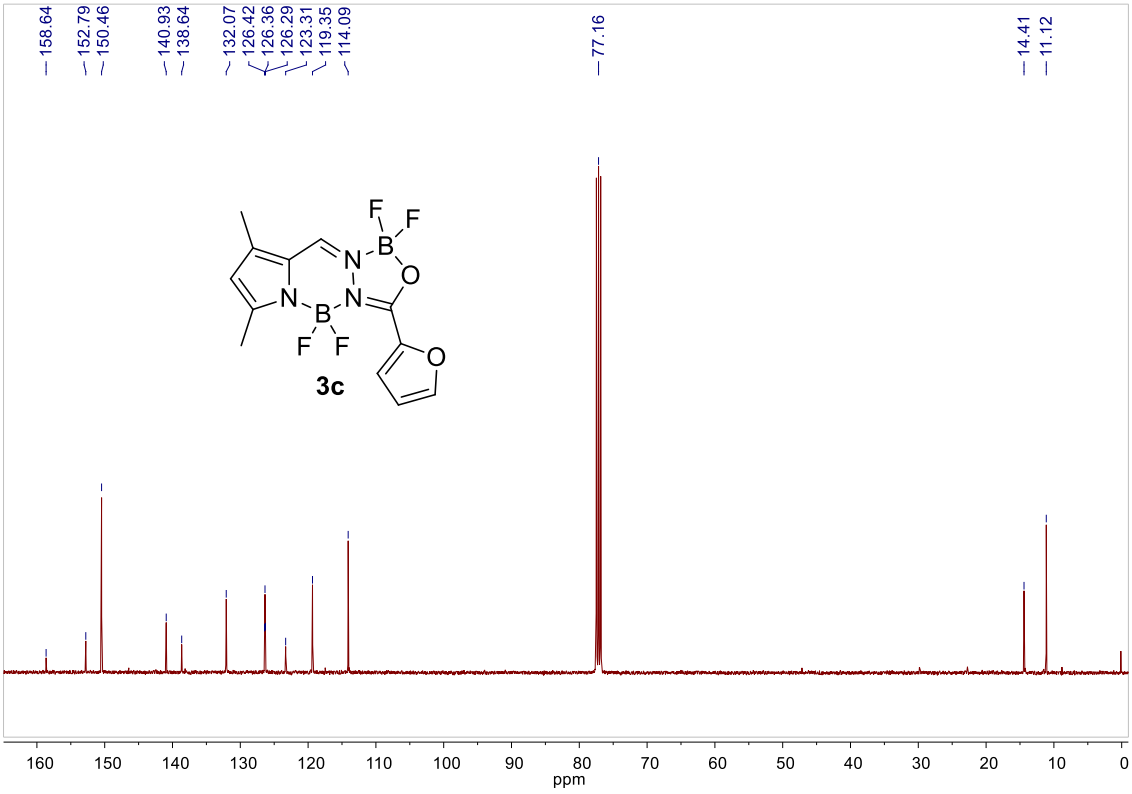
[19]F NMR Spectra of 3b



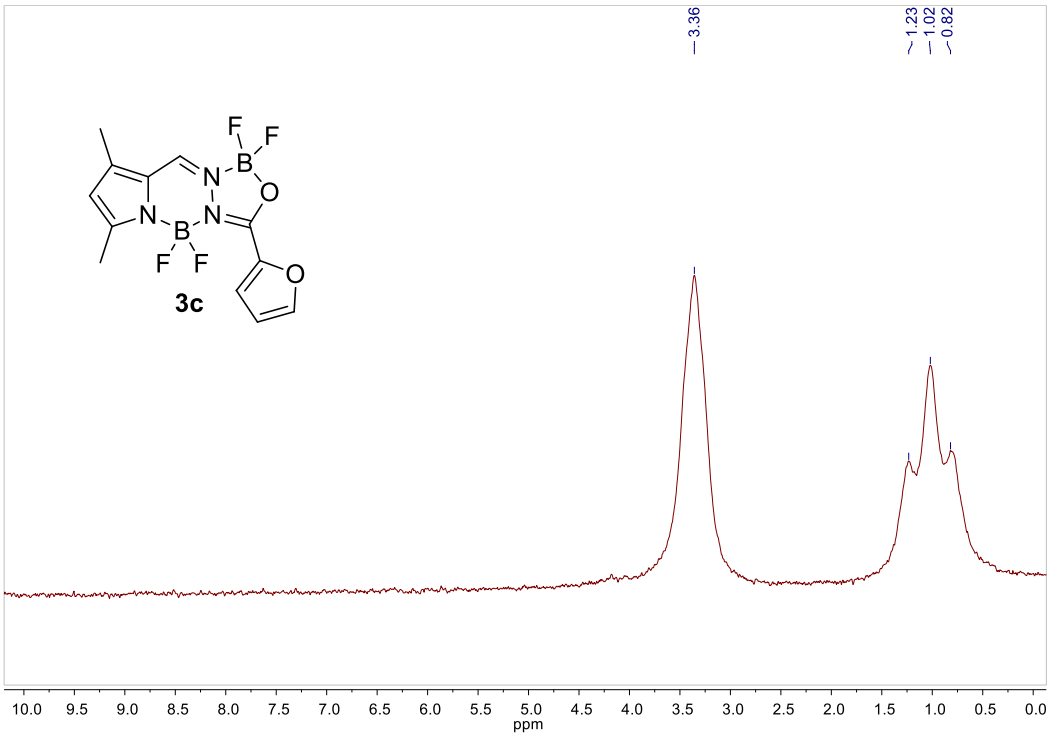
[1]H NMR Spectra of 3c



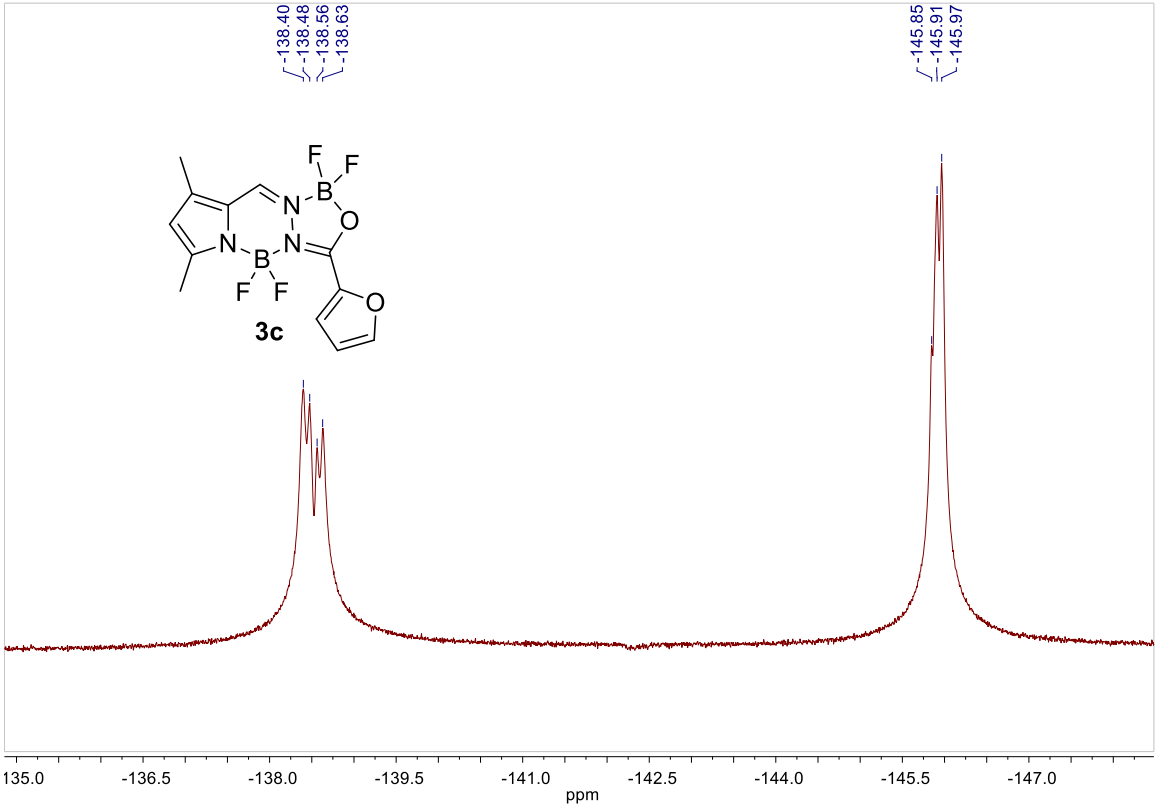
^{13}C NMR Spectra of 3c



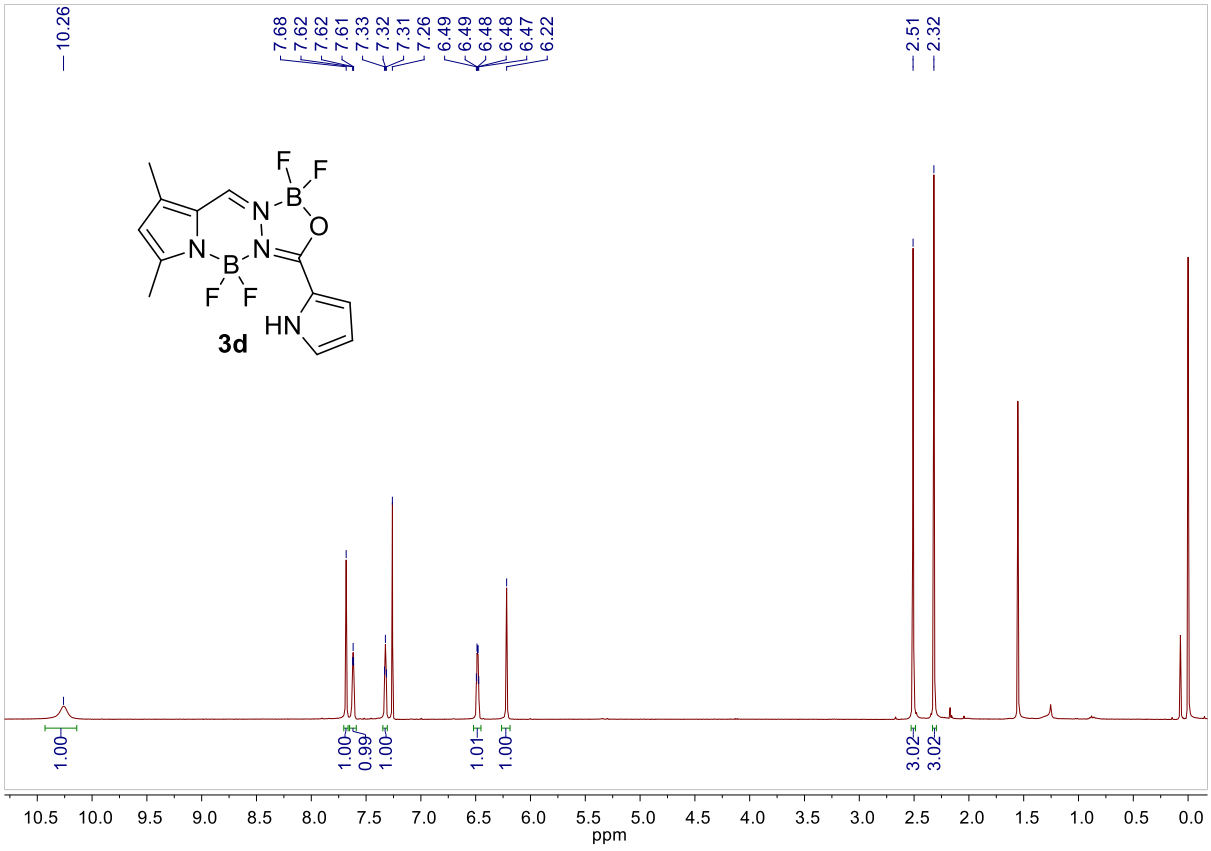
^{11}BNMR Spectra of 3c



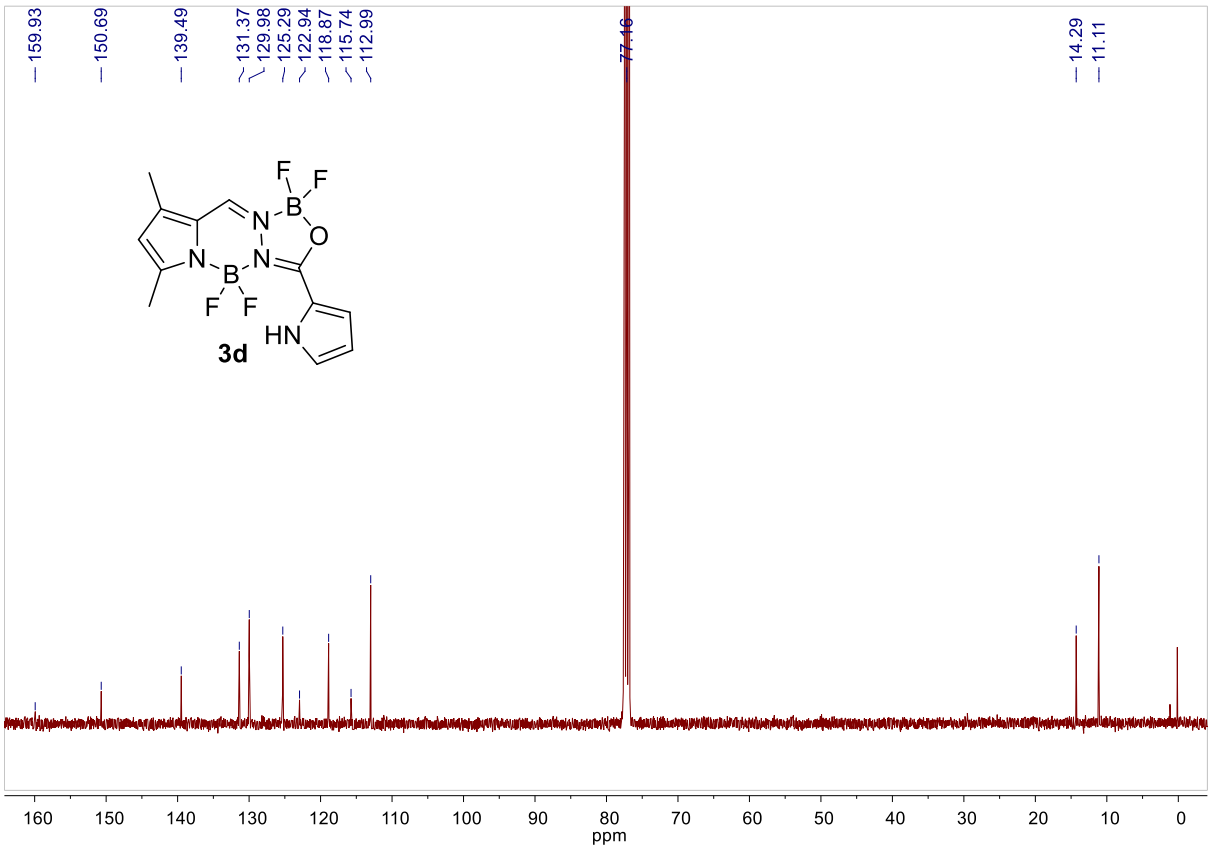
^{19}F NMR Spectra of 3c



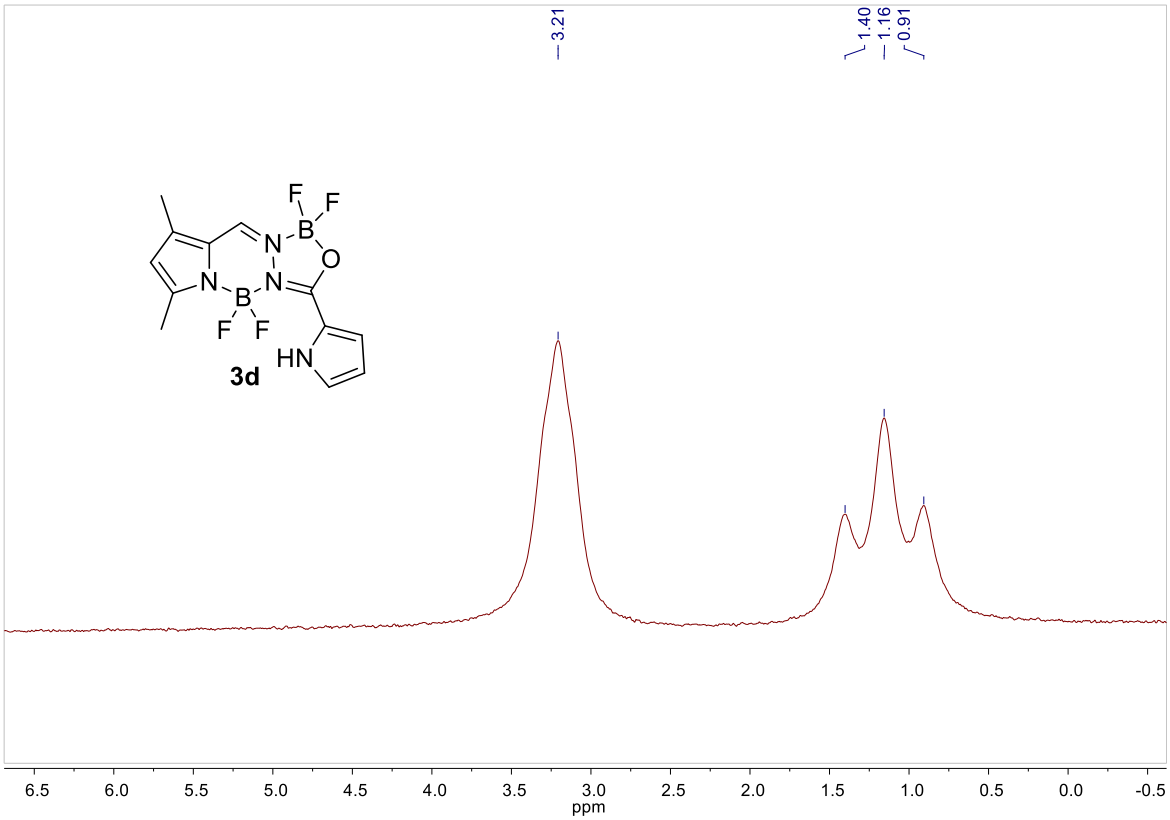
^{1}H NMR Spectra of 3d



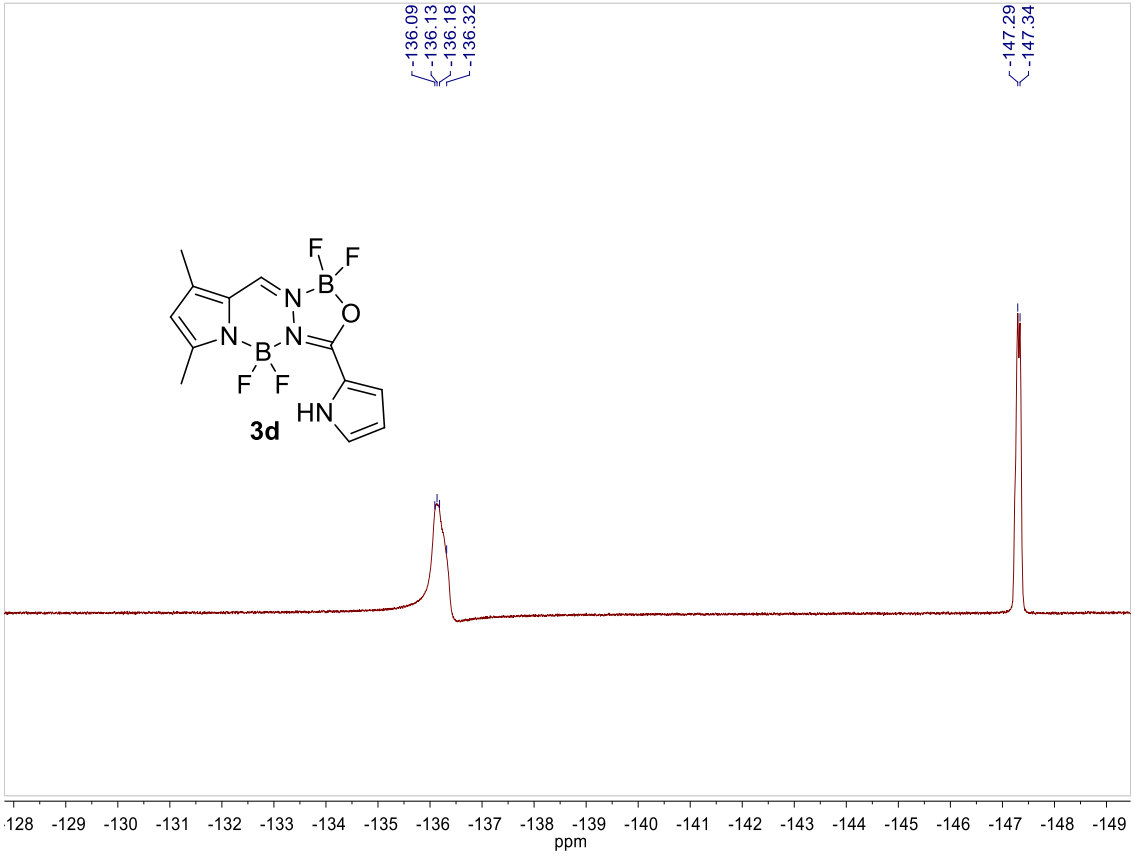
^{13}C NMR Spectra of 3d



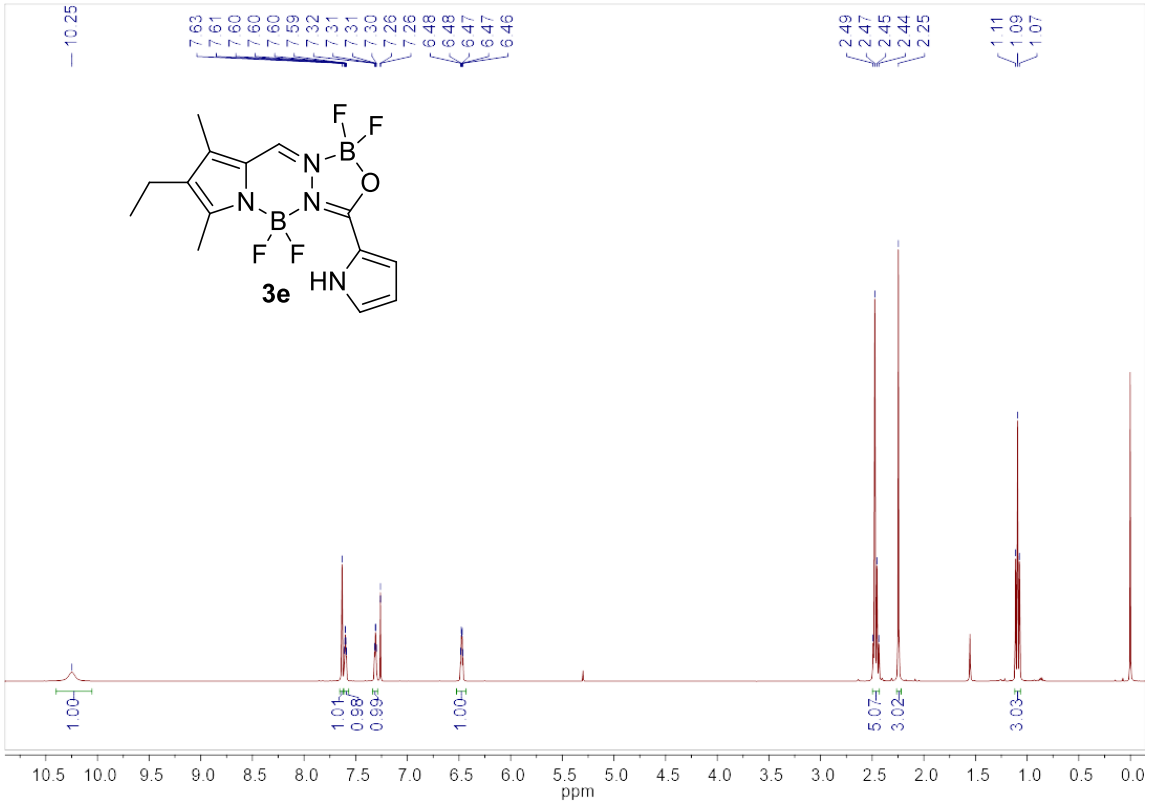
^{11}BNMR Spectra of 3d



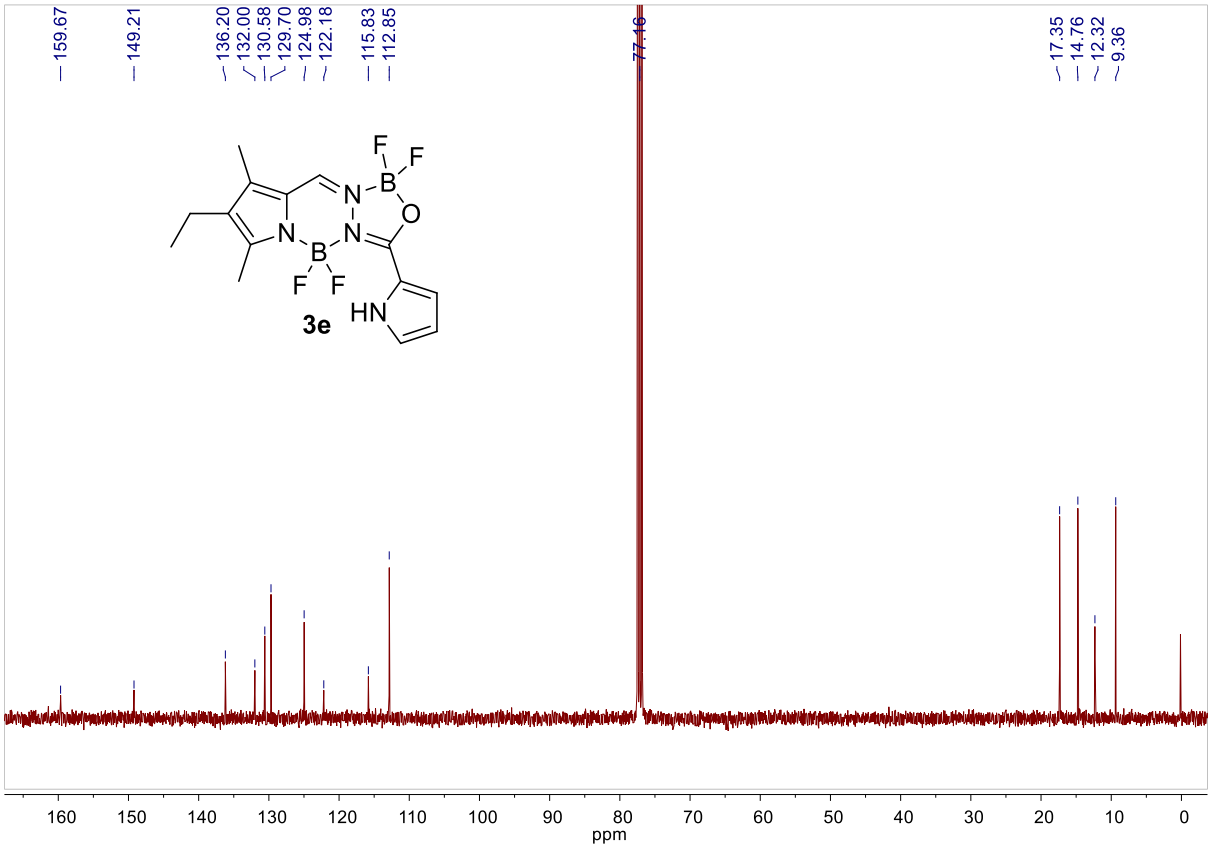
^{19}F NMR Spectra of 3d



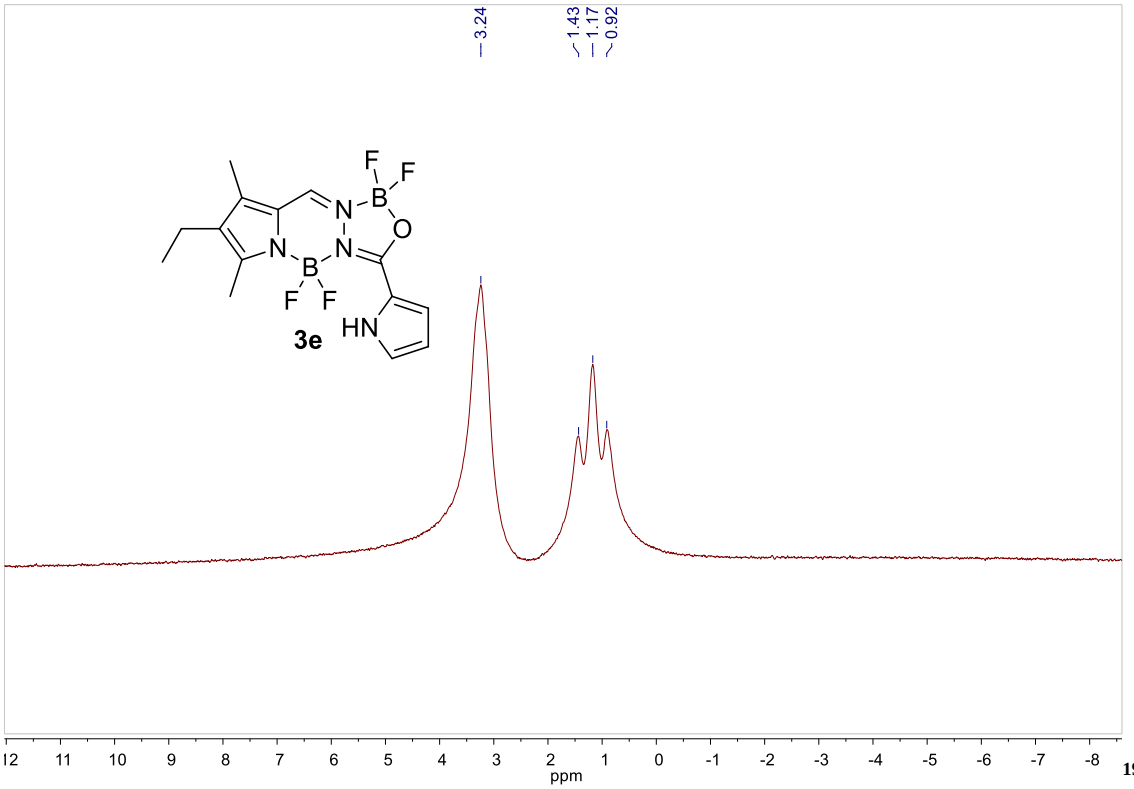
^{1}H NMR Spectra of 3e



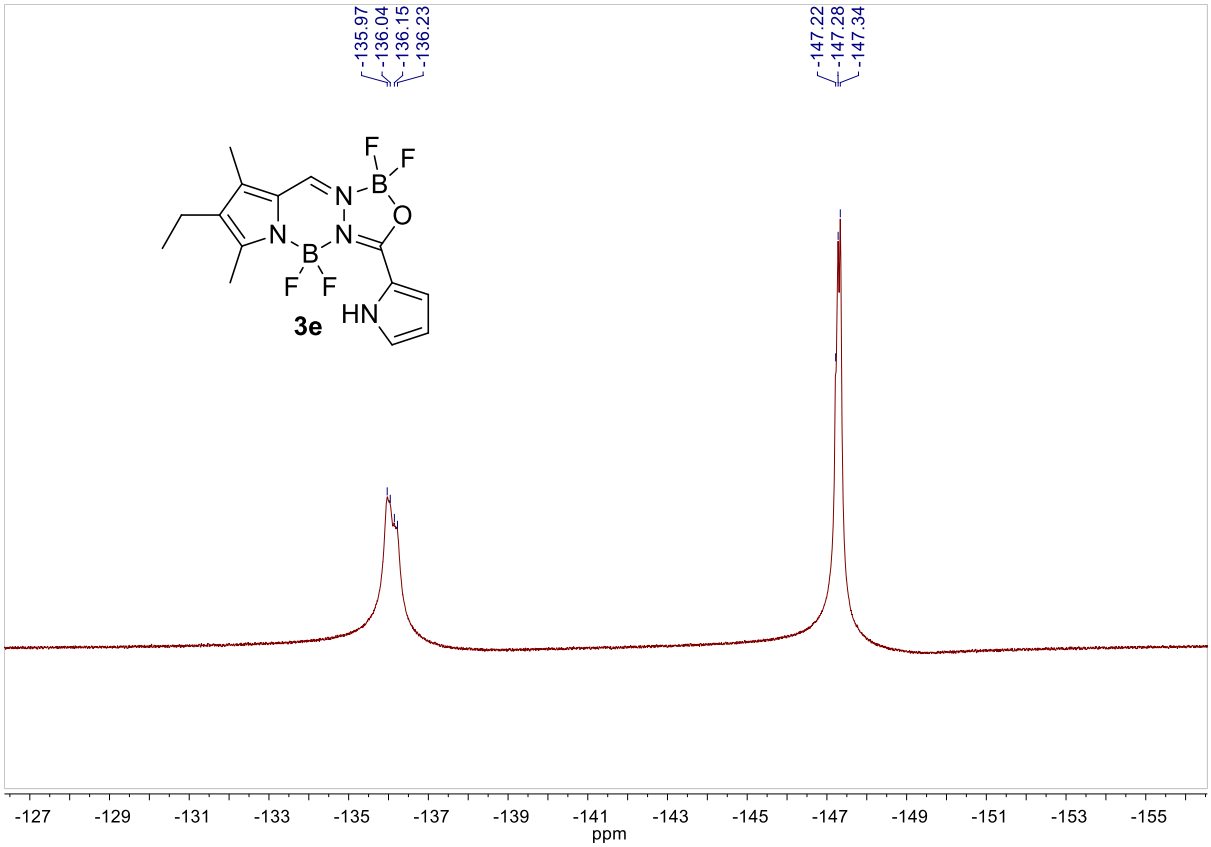
^{13}C NMR Spectra of 3e



^{11}B NMR Spectra of 3e



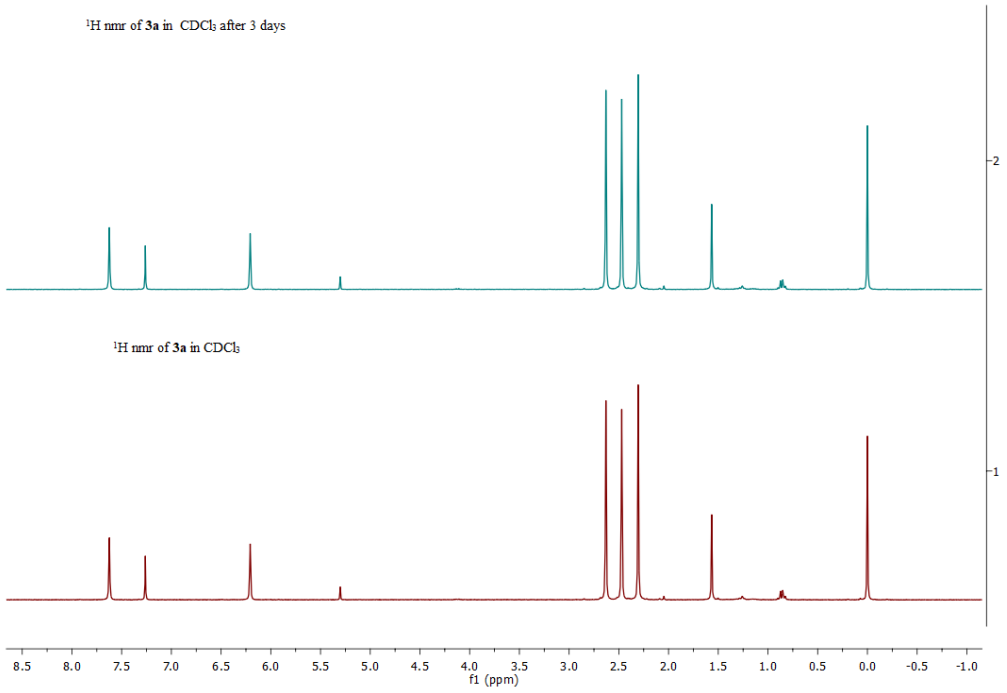
^{19}F NMR Spectra of 3e


-135.97
-136.04
-136.15
-136.23
-147.22
-147.28
-147.34
F
F
B
N
O
N
N
B
F
F
HN
3e
-127
-129
-131
-133
-135
-137
-139
-141
-143
-145
-147
-149
-151
-153
-155
ppm

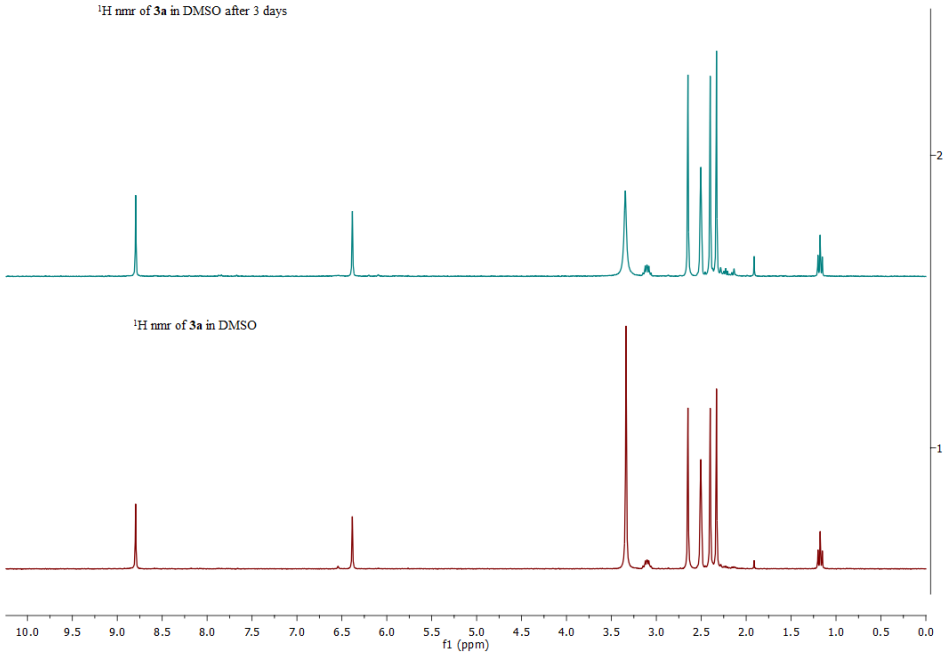
7. Chemical Stability Study of Compounds 3a and 3c

Chemical stability of the compound was determined by recording ^{1}H NMR of **3a** & **3c** in different deuteriated organic solvents such as $CDCl_3$, DMSO, toluene. We kept the compound in the same solution for 3 days and investigated the changes in ^{1}H nmr spectra. BOPAHY **3a** displayed good chemical stability in $CDCl_3$ and DMSO. The 1H NMR spectra remained unchanged even after 3 days. BOPAHY **3c** is stable in $CDCl_3$ and toluene, showed very poor stability in more polar DMSO.

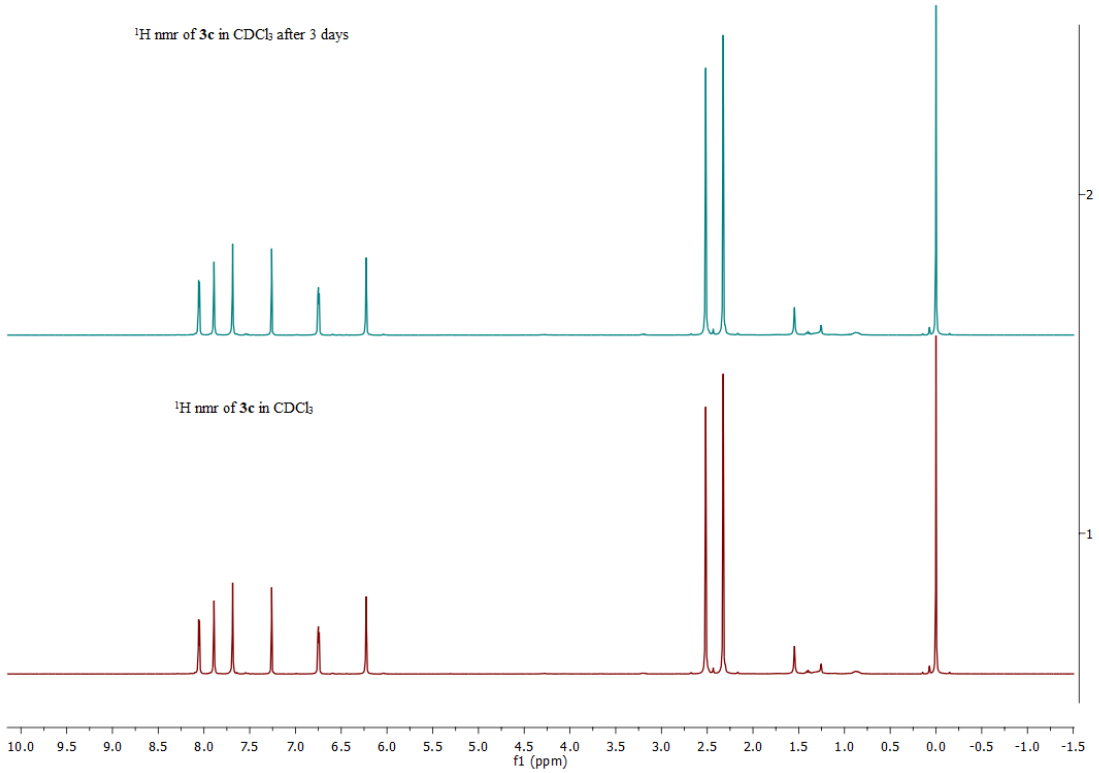
^{1}H nmr of **3a** in $CDCl_3$



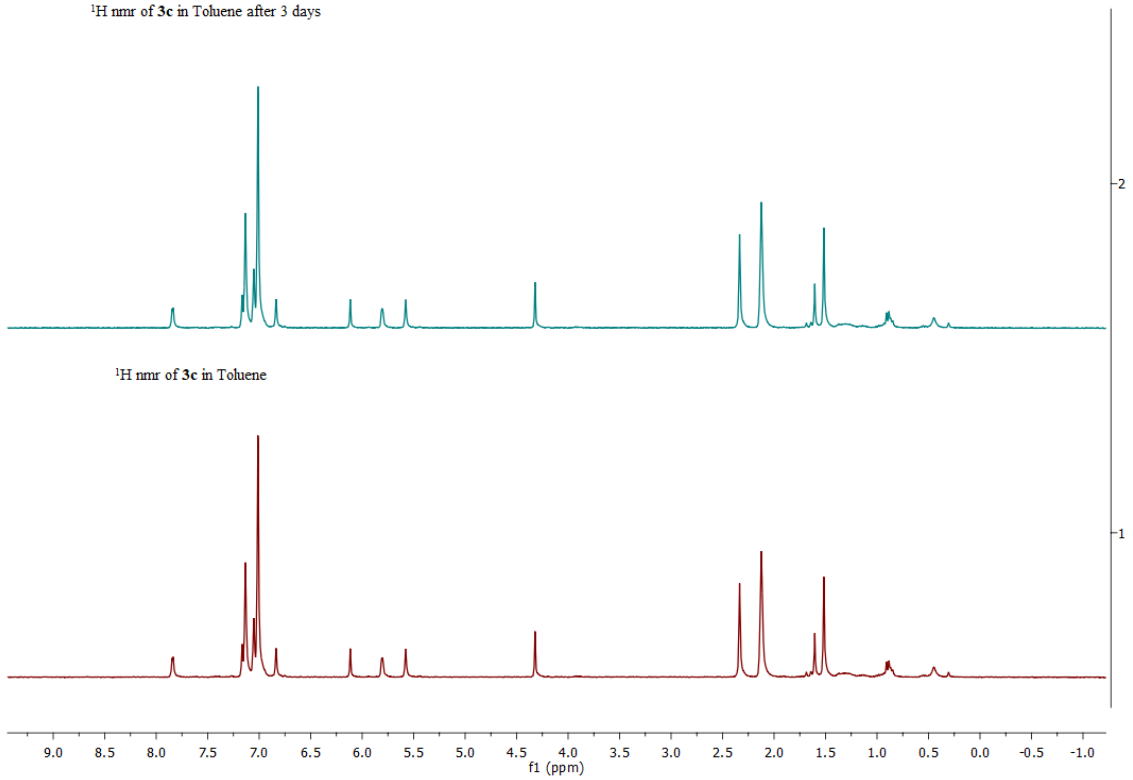
^{1}H nmr of **3a** in DMSO



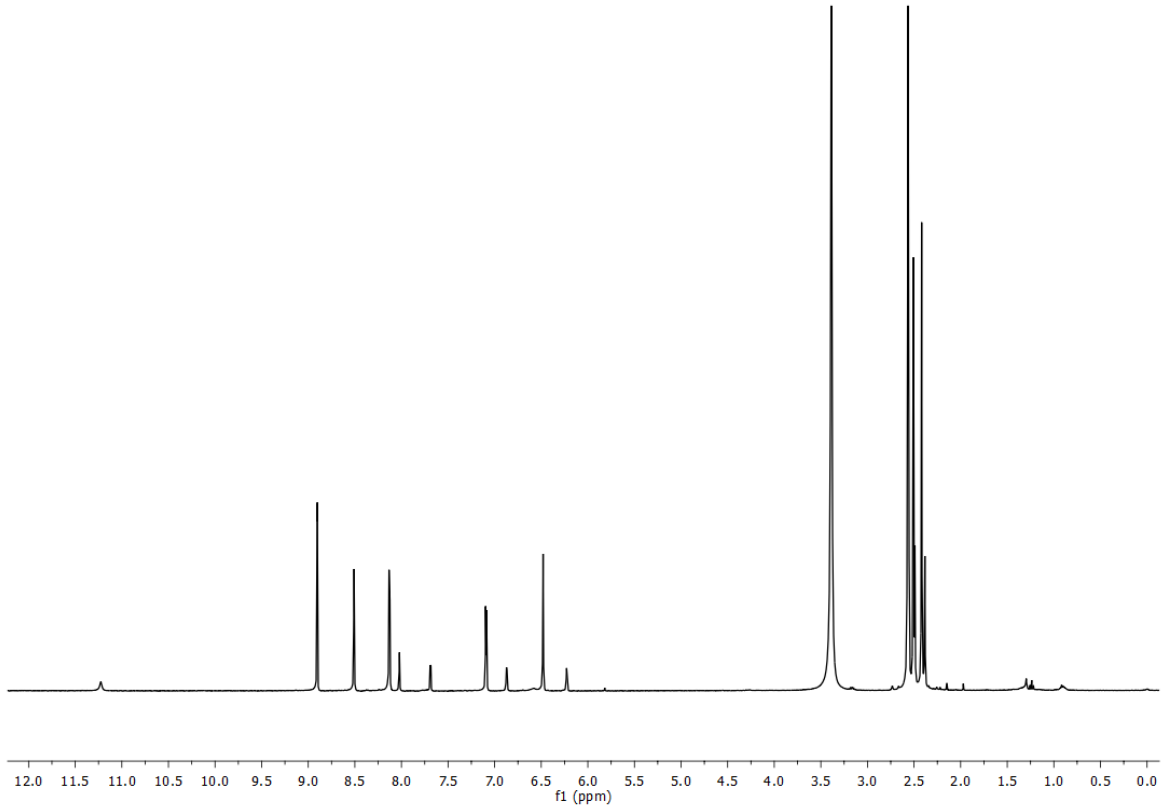
^{1}H nmr of **3c** in $CDCl_3$



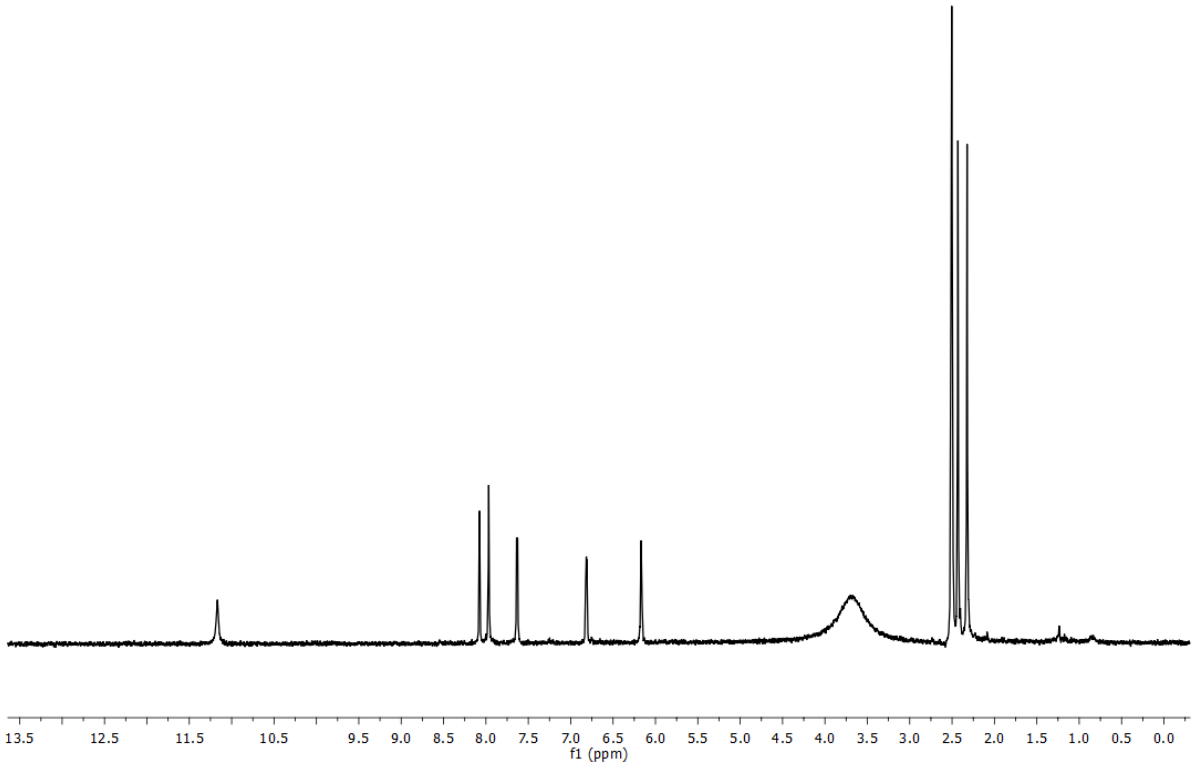
^{1}H nmr of **3c** in toluene



^{1}H nmr of **3c** in DMSO



^{1}H nmr of **3c** in DMSO after 3 days



8. References

1. Rigaku OD (2018). CrysAlis PRO. Rigaku Oxford Diffraction, Yarnton, UK.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
3. G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.
4. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.
5. J. C. de Mello, H. F. Wittmann and R. H. Friend, *Adv. Mater.*, 1997, **9 (3)**, 230–232.
6. L. Porrès, A. Holland, L.-O. Pålsson, A. P. Monkman, C. Kemp and A. Beeby, *J. Fluoresc.*, 2006, **16 (2)**, 267–273.
7. (a) P. Hohenberg and W. Kohn, *Phys. Rev.*,1964, **136**, B864-B71.; (b) W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, A1133-A38.; (c) R. G. Parr and W. Yang, Oxford Univ. Press, Oxford, 1989.; D. R. Salahub and M. C. Zerner, (ACS, Washington, D.C., 1989).
8. (a) E. Runge and E. K. U. Gross, *Phys. Rev. Lett.*, 1984, **52**, 997-1000.; (b) M. E. Casida, World Scientific: Singapore, 1995, **1**, 155−192.
9. (a) C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158-69.; (b) M. Ernzerhof and G. E. Scuseria, *J. Chem. Phys.*, 1999, **110**, 5029-36.
10. W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.
11. (a) J. Schirmer, *Phys. Rev. A.*,1981, **26**, 2395.; (b) A. B. Trofimov and J. Schirmer, *J. Phys. B.*,1995, **28**, 2299.; (c) C. Hättig and F. Weigend, *J. Chem. Phys.*, *2000*, **113**, 5154.; (d) C. Hättig and A. Köhn, *J. Chem. Phys.*, 2002,**117**, 6939.; (e) C. Hättig, A. Hellweg and A. Köhn, *Phys. Chem. Chem. Phys.*,2006, **8**, 1159.; (f) D. H. Friese, N. O. C. Winter, P. Balzerowski, R. Schwan and C. Hättig, *J. Chem. Phys.*,2012, **136**, 174106.
12. F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Letters.*, 1998, **294**, 143-152.
13. Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
14. TURBOMOLE V7.1 2016, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
15. C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, *Adv. Mater.*, 2011, **23**, 2367.