Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Synthesis and Characterization of Pyrrolyldipyrrin *F*-BODIPYs

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Supporting Information

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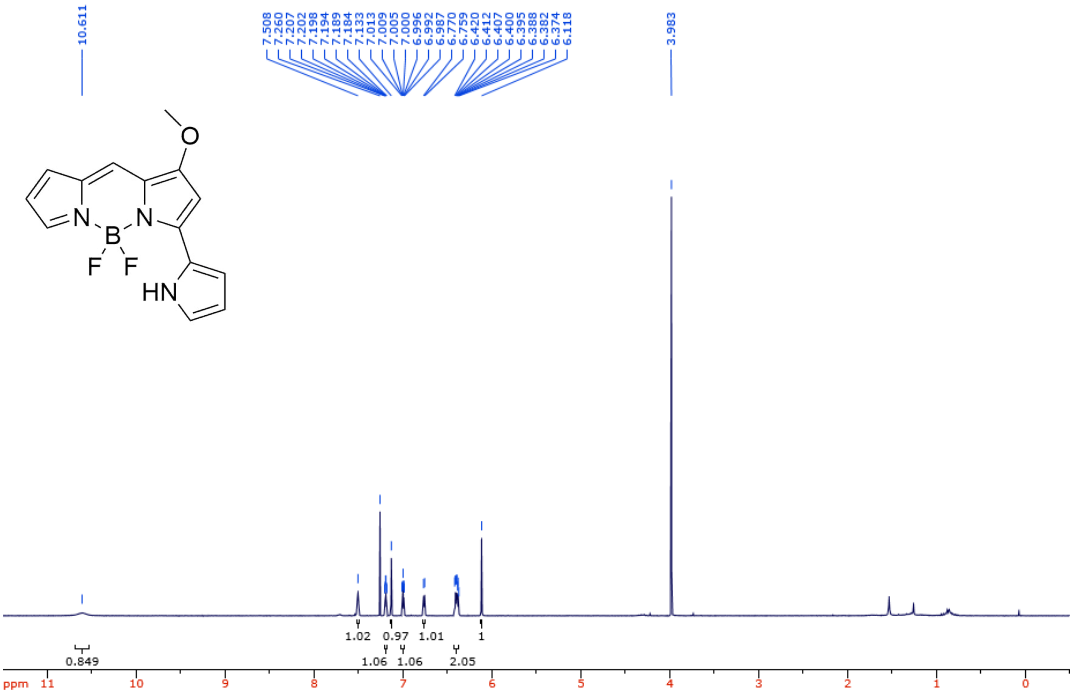
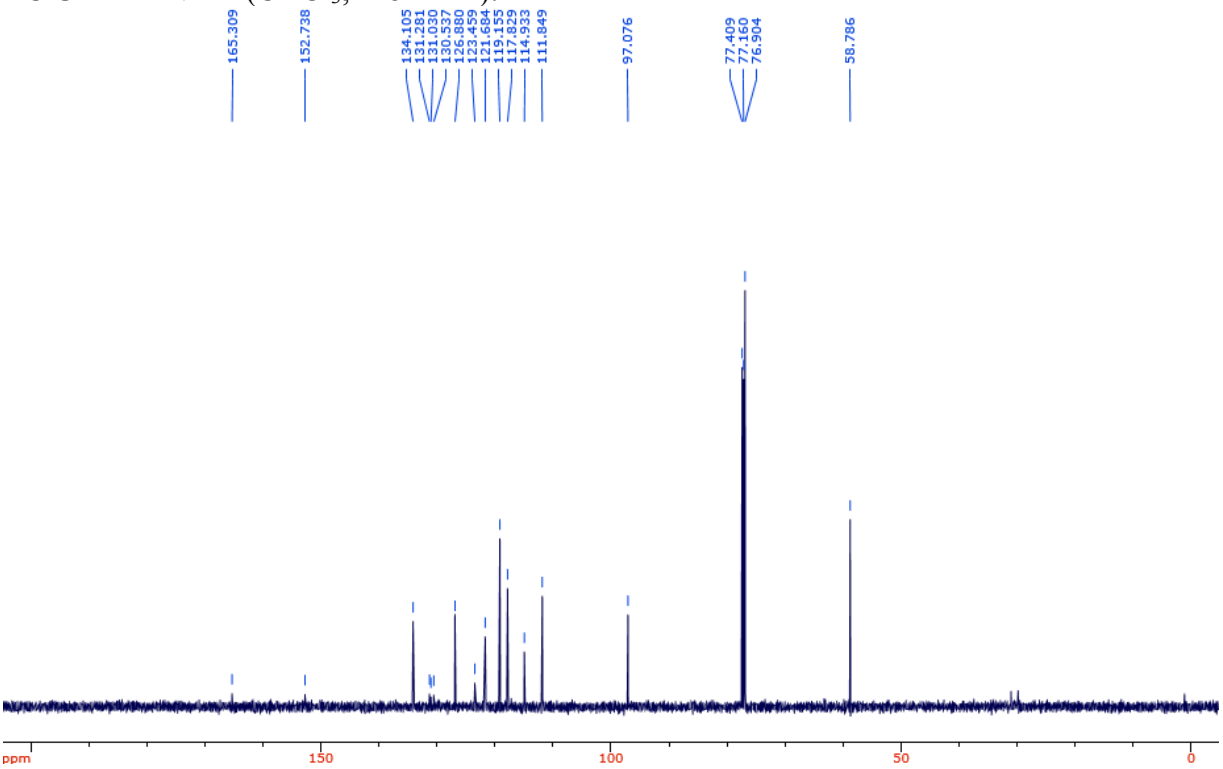
^{1}H, ^{13}C, ^{11}B and ^{19}F NMR Spectra

Boron, difluoro[[(2H-pyrrol-2-ylidene)methyl]-4-methoxy-1H, 1'H-2,2'-bipyrrole] (2a)

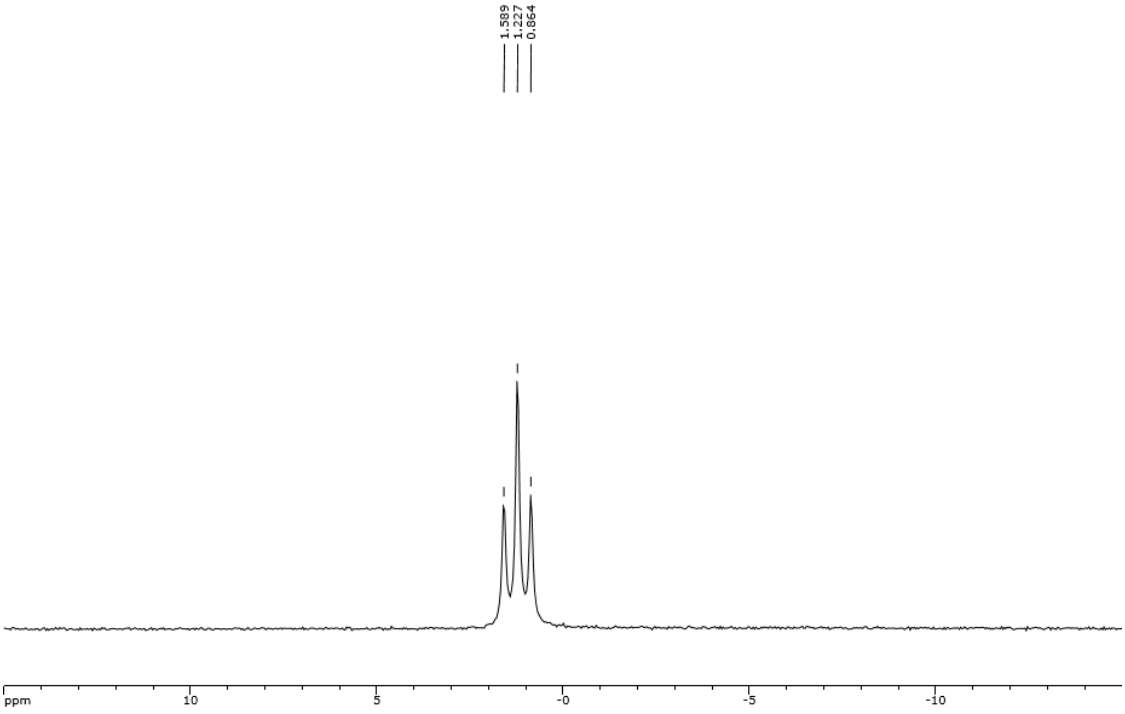
^{1}H NMR ($CDCl_3$, 500 MHz):



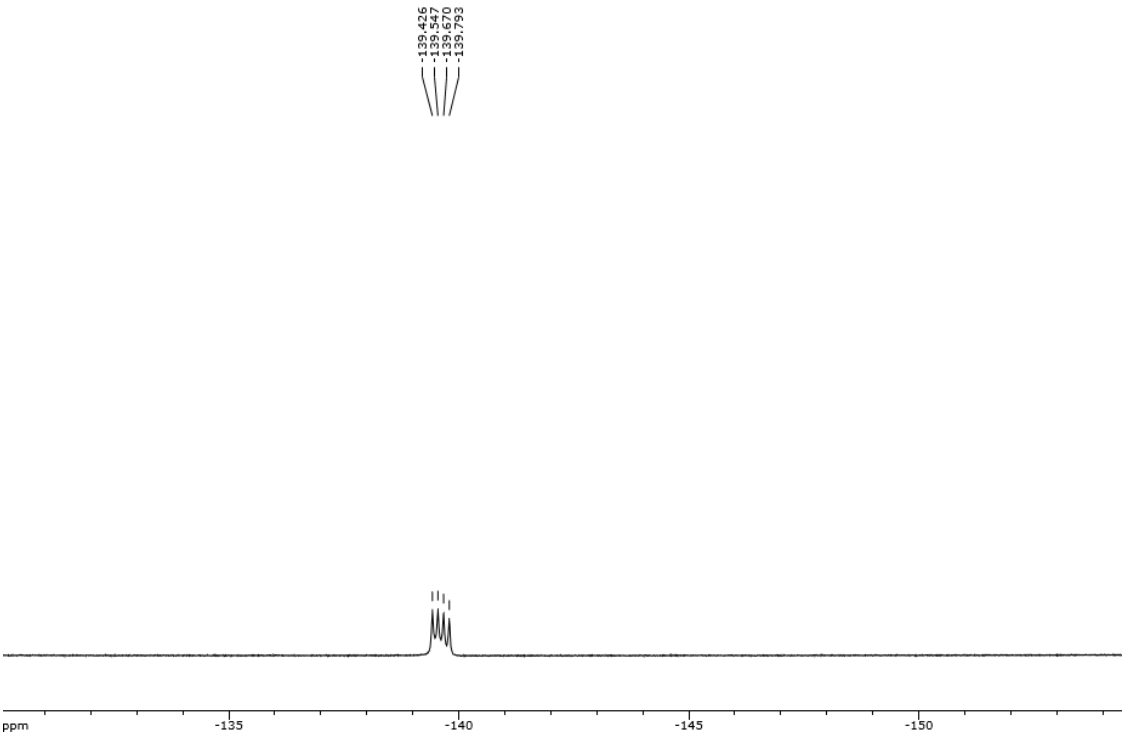
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

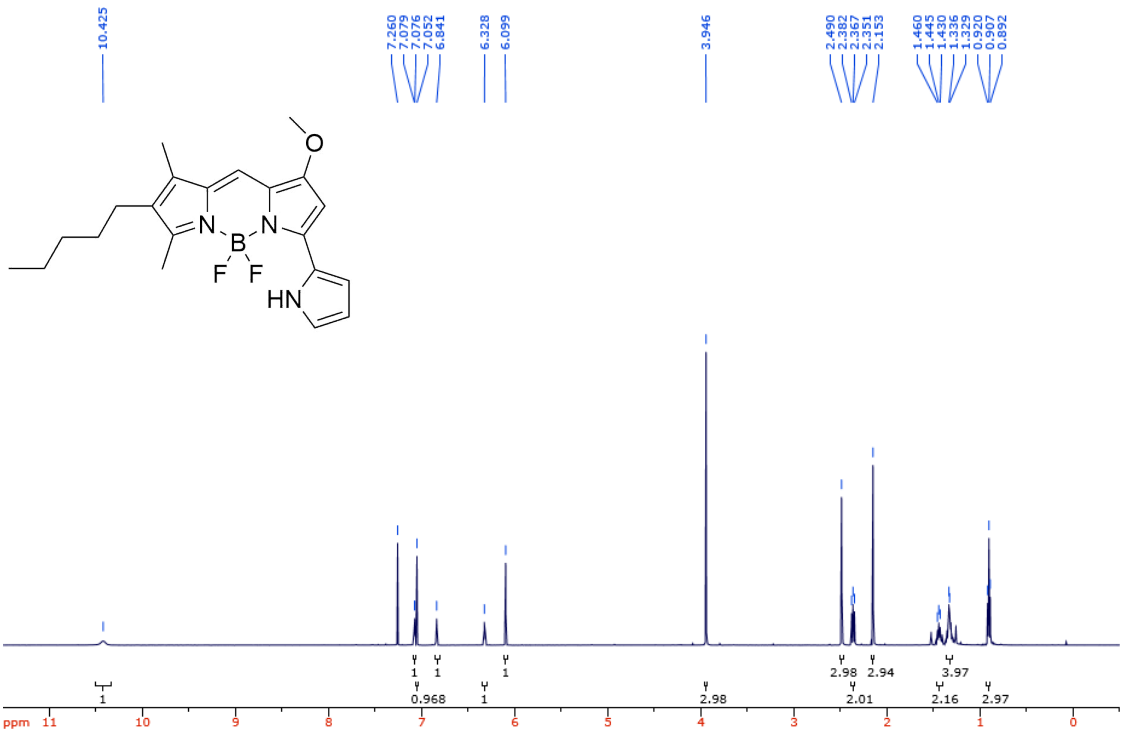


^{19}F NMR (CDCl3, 235 MHz)

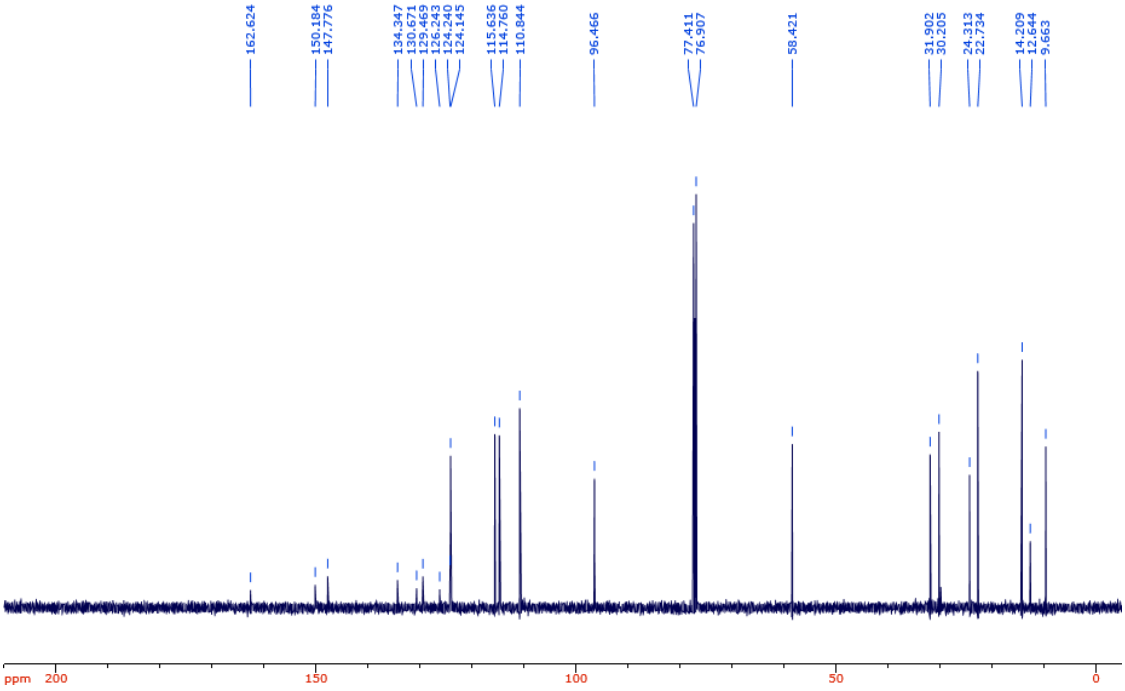


Boron, difluoro[5-[(3,5-dimethyl-4-pentyl-2*H*-pyrrol-2ylidene)methyl]-4-methoxy-1*H*,1'*H*-2,2'-bipyrrole] (2b)

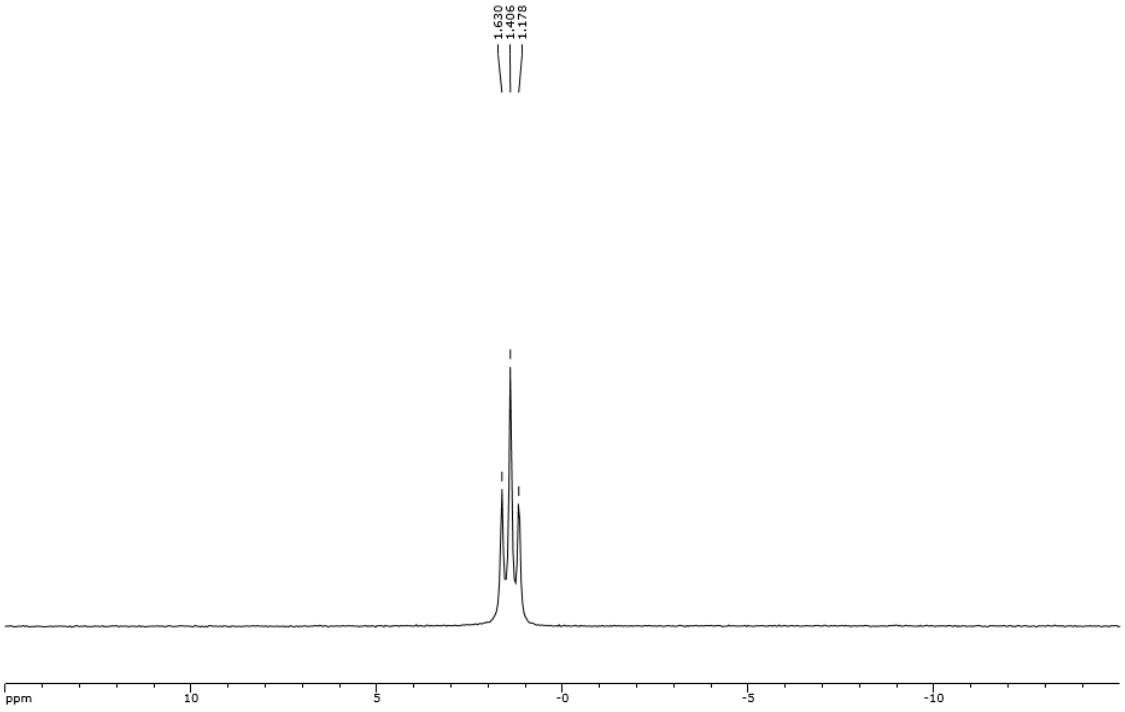
^{1}H NMR ($CDCl_3$, 500 MHz):



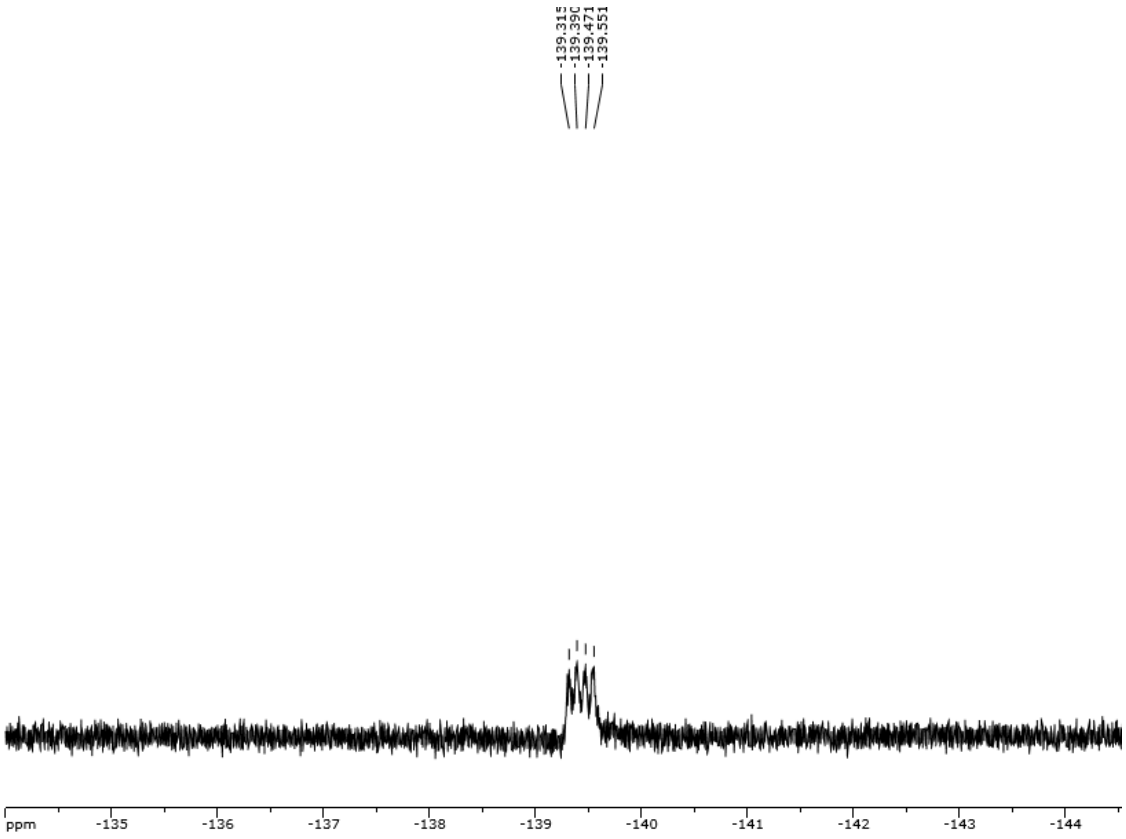
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

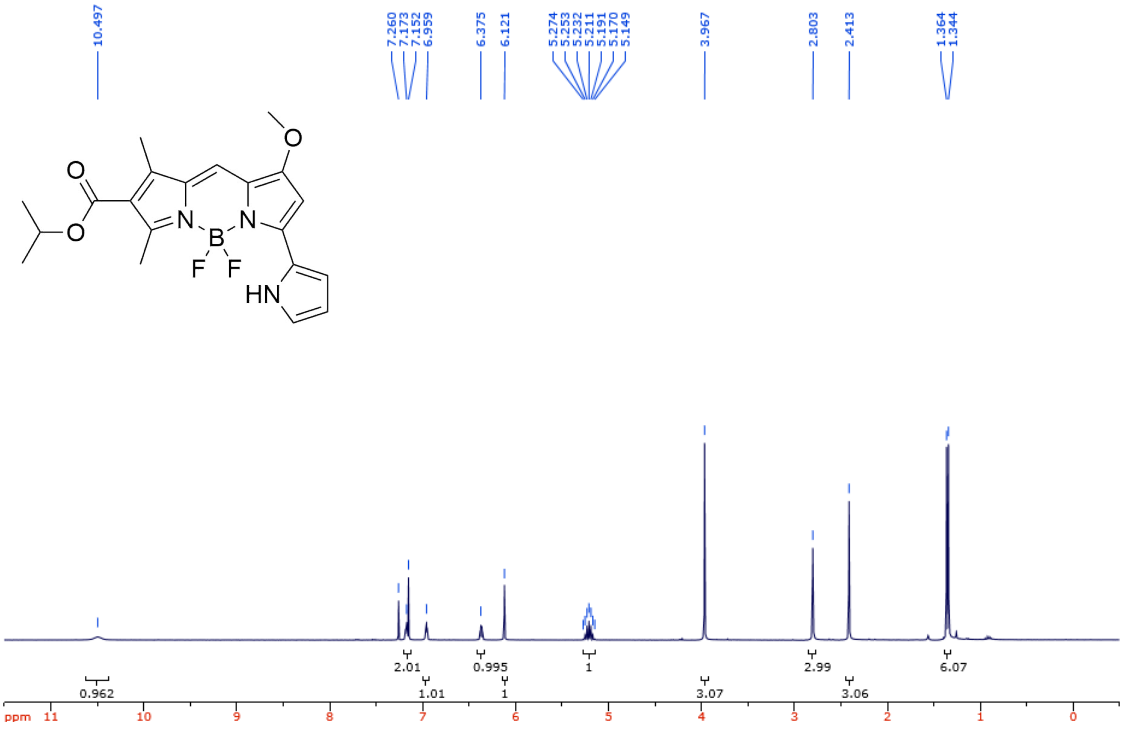


^{19}F NMR (CDCl3, 235 MHz)

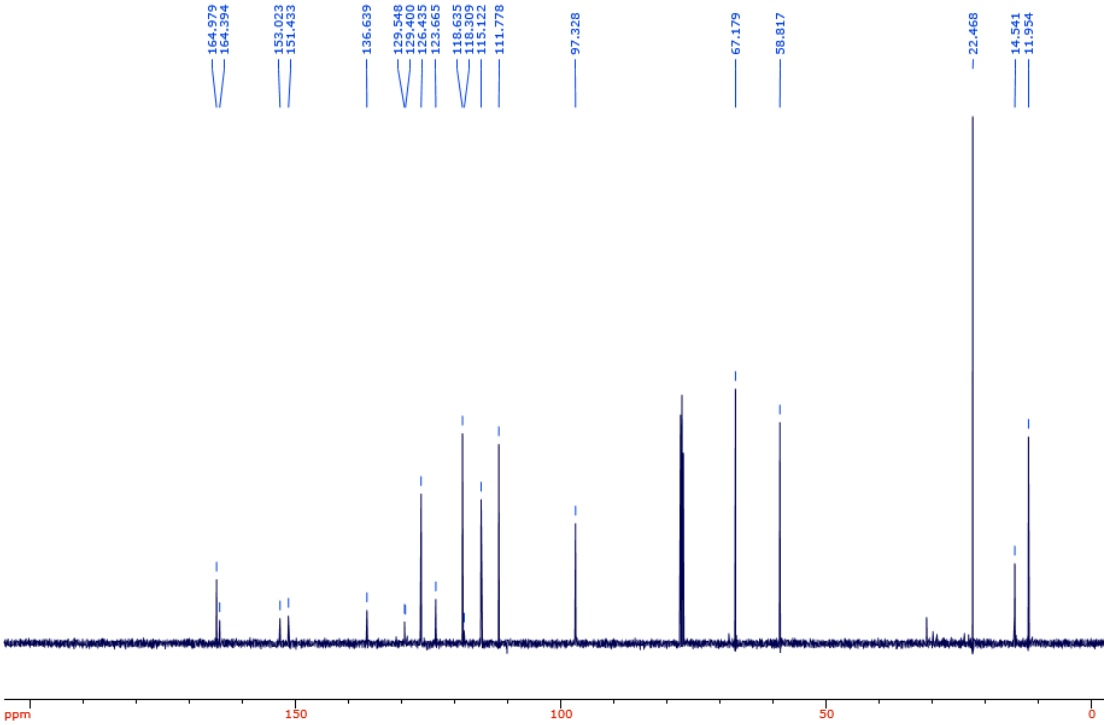


Boron, difluoro[isopropyl 2-[(4-methoxy-1H,1'H-2,2'-bipyrrol-5-yl)-methylene]-3,5-dimethyl-2*H*-pyrrole-4-carboxylate] (2d)

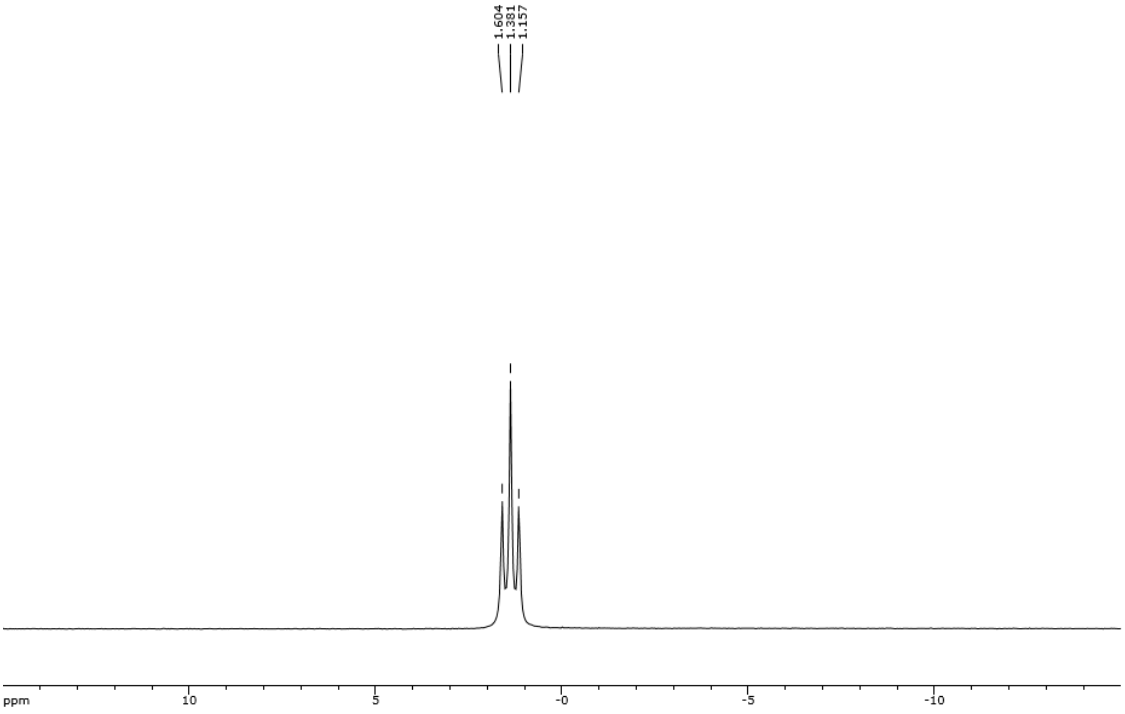
^{1}H NMR ($CDCl_3$, 300 MHz):



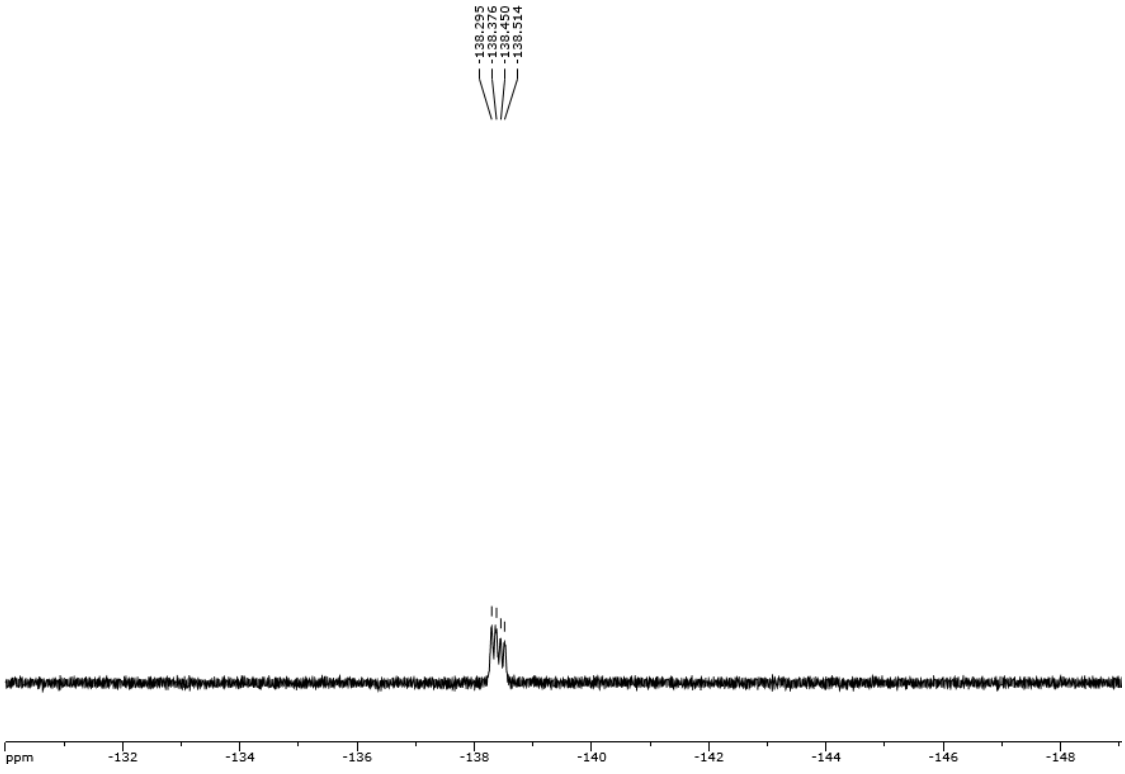
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

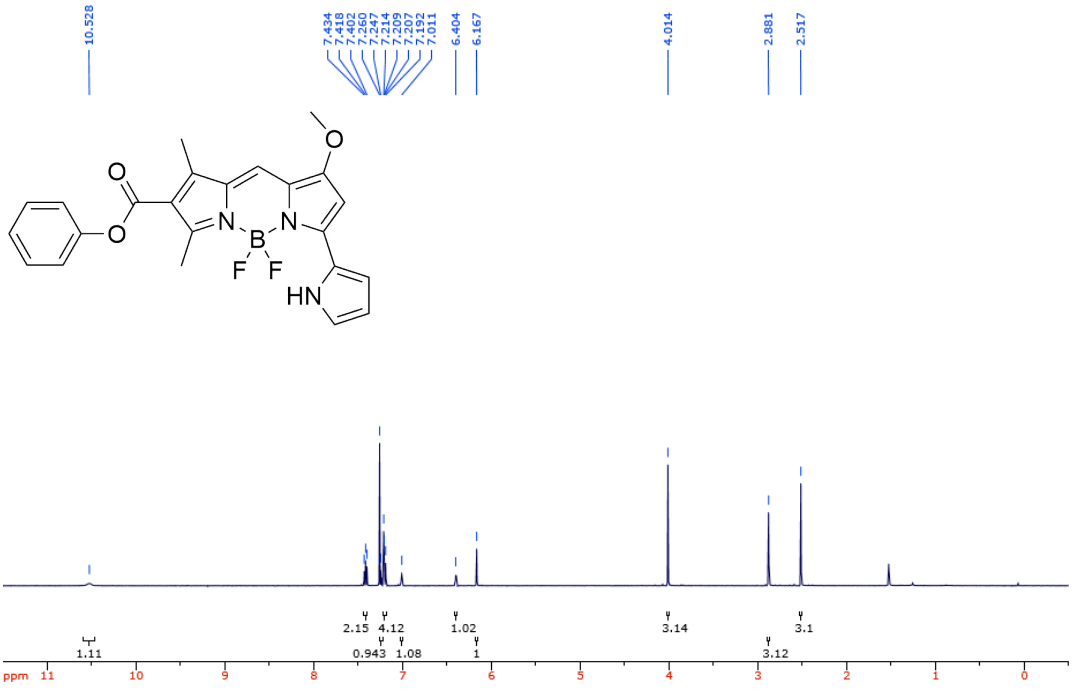


^{19}F NMR (CDCl3, 235 MHz)

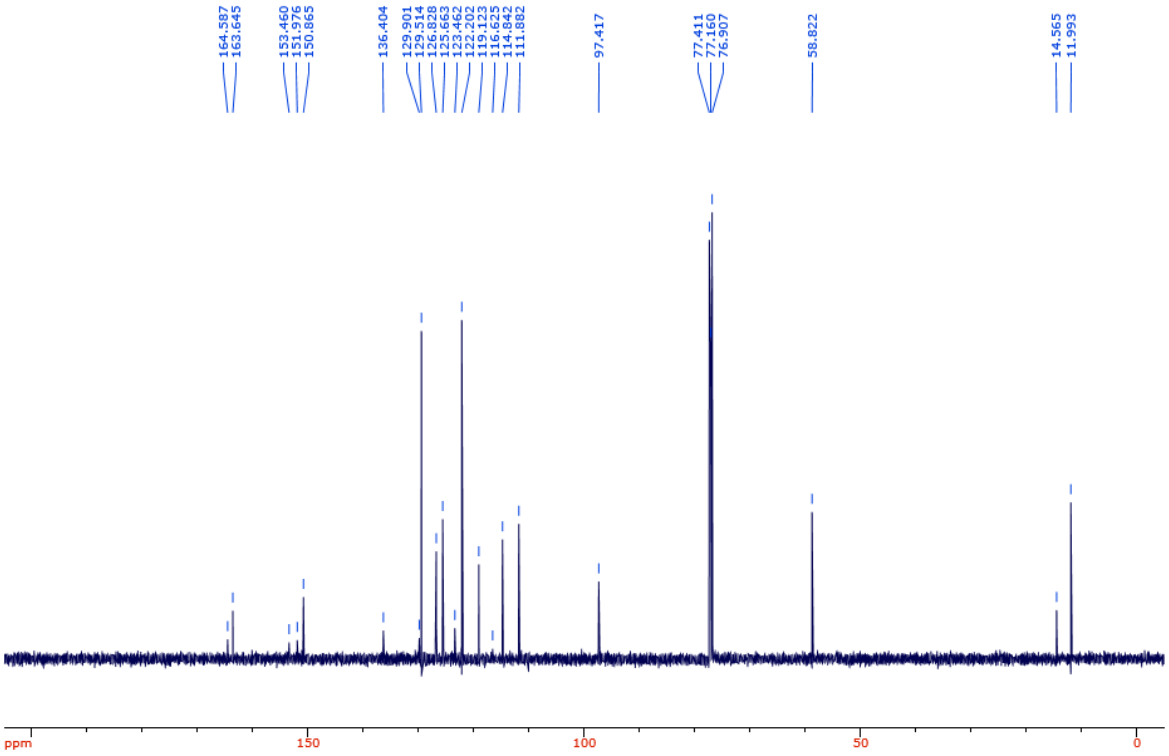


Boron, difluoro[phenyl 2-[(4-methoxy-1H,1'H-2,2'-bipyrrol-5-yl)-methylene]-3,5-dimethyl-2*H*-pyrrole-4-carboxylate] (2e)

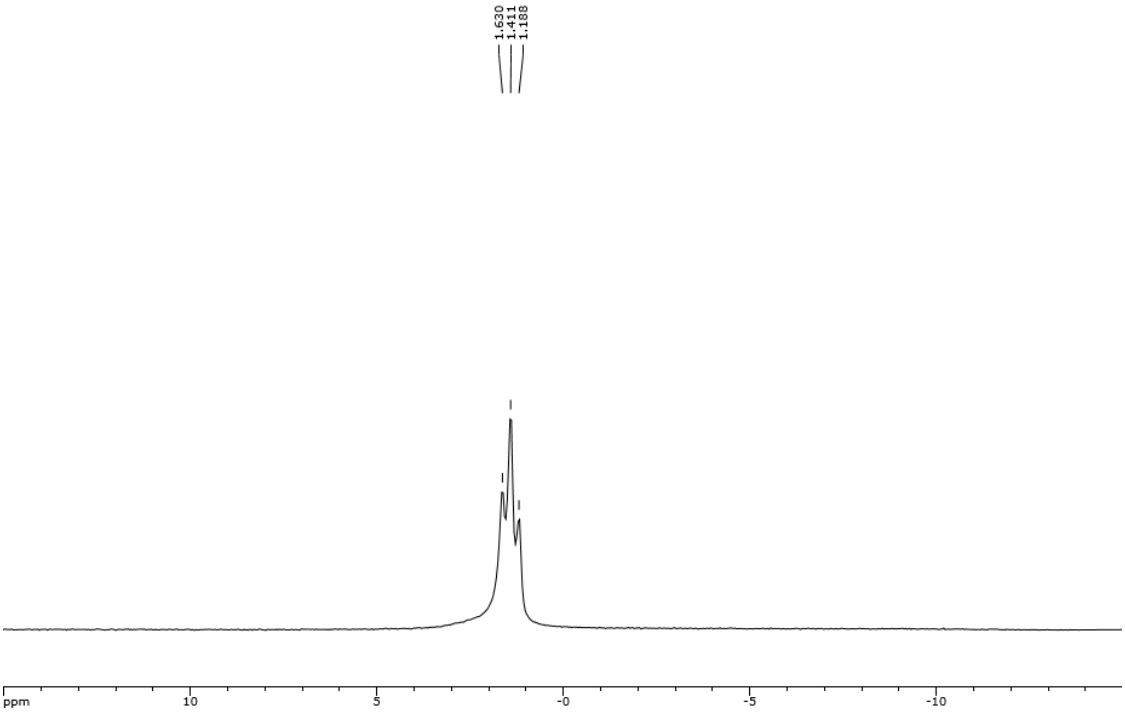
^{1}H NMR ($CDCl_3$, 500 MHz):



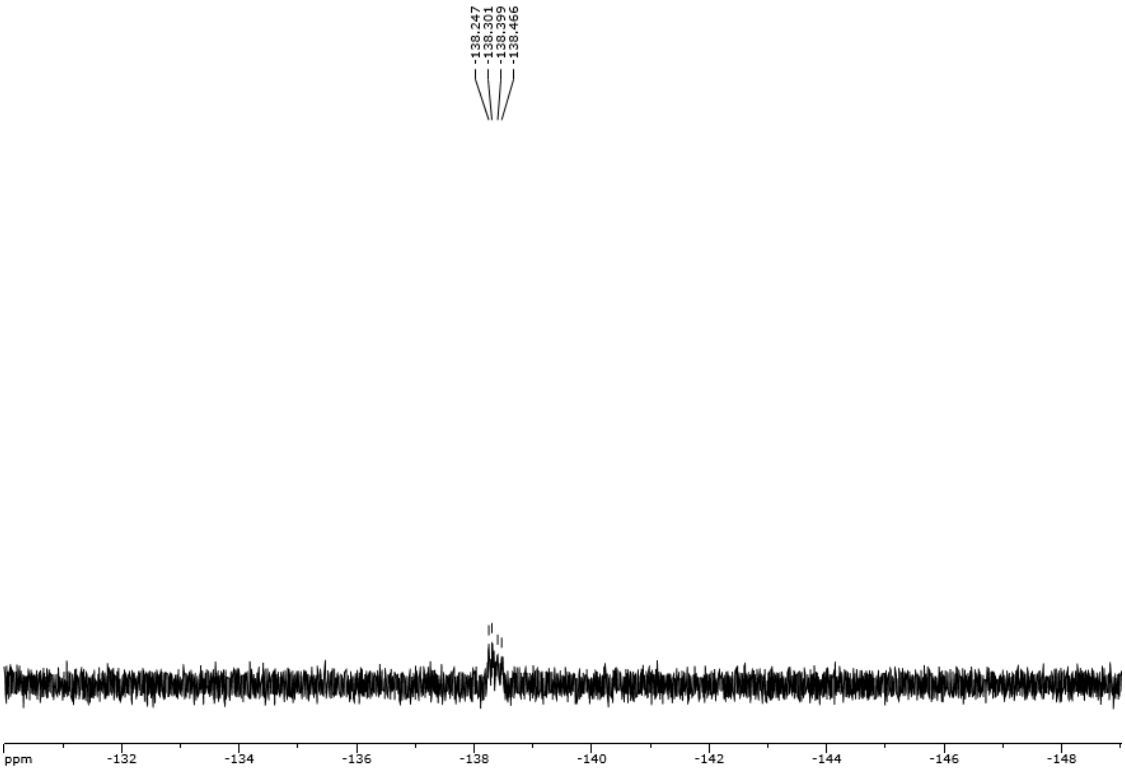
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

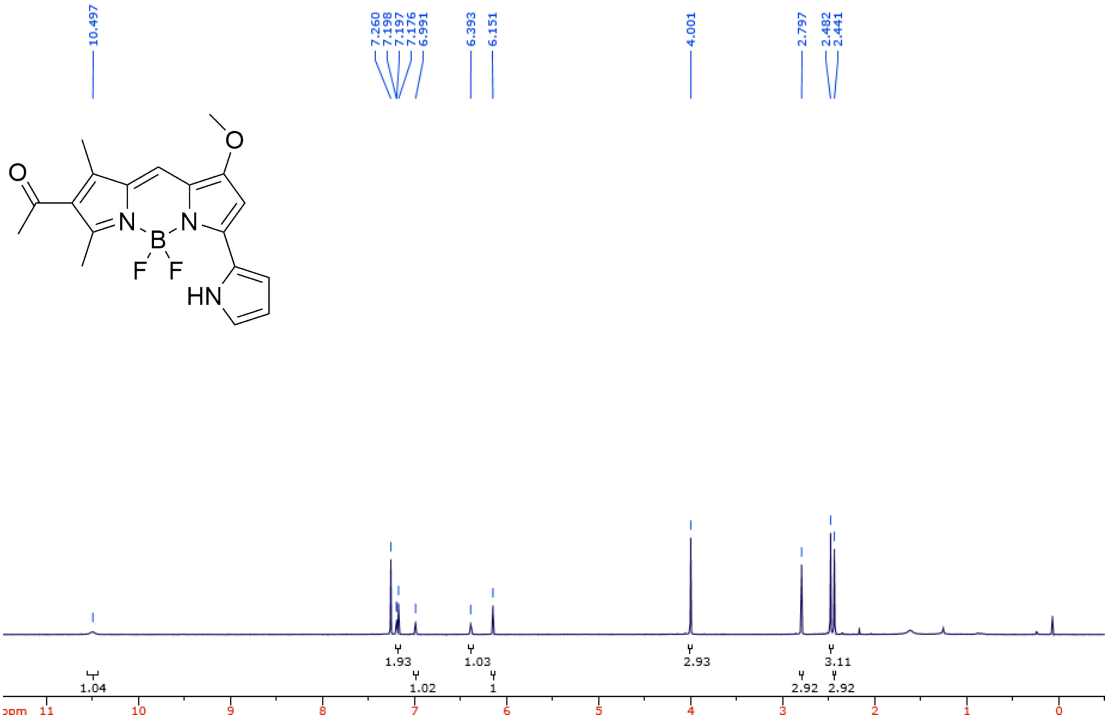


^{19}F NMR (CDCl3, 235 MHz)

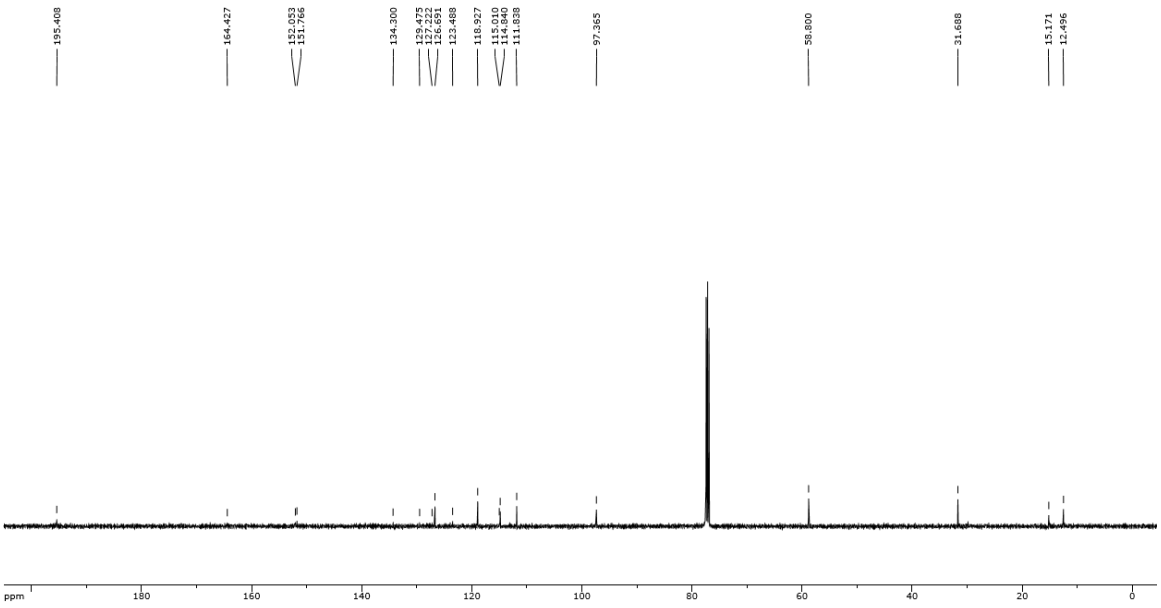


Boron, difluoro[1-[2-[(4-methoxy-1H,1'H-2,2'-bipyrrol-5-yl)methylene]-3,5-dimethyl-2*H*-pyrrol-4-yl]ethanone] (2g)

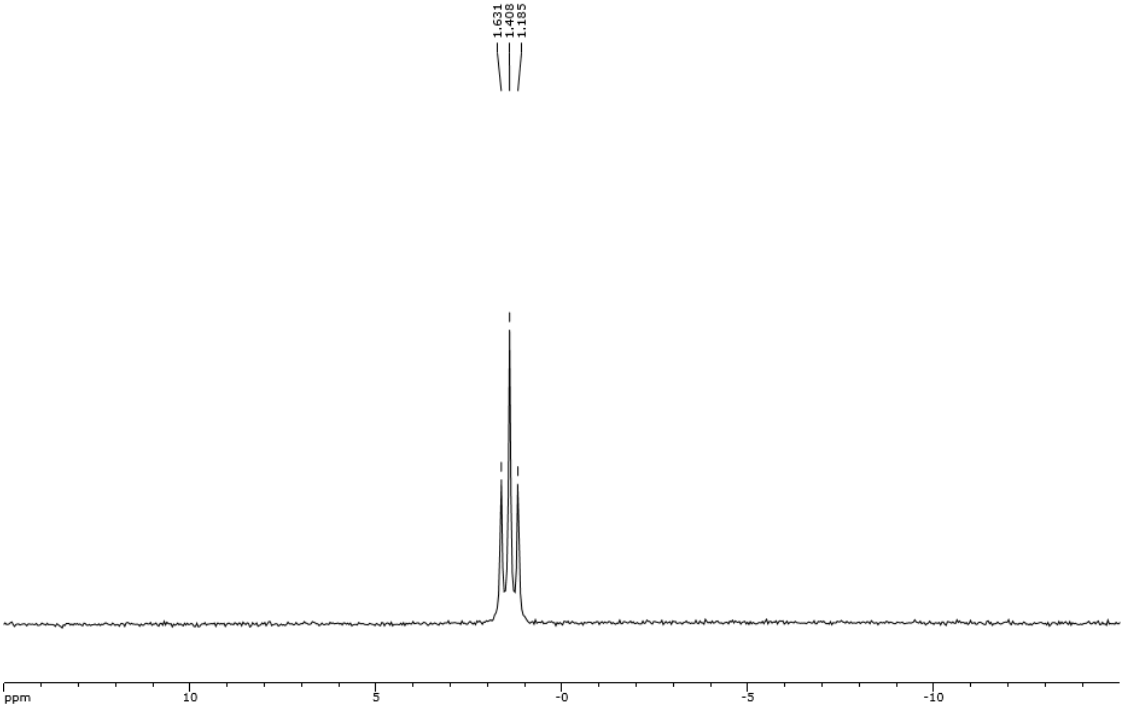
^{1}H NMR ($CDCl_3$, 500 MHz):



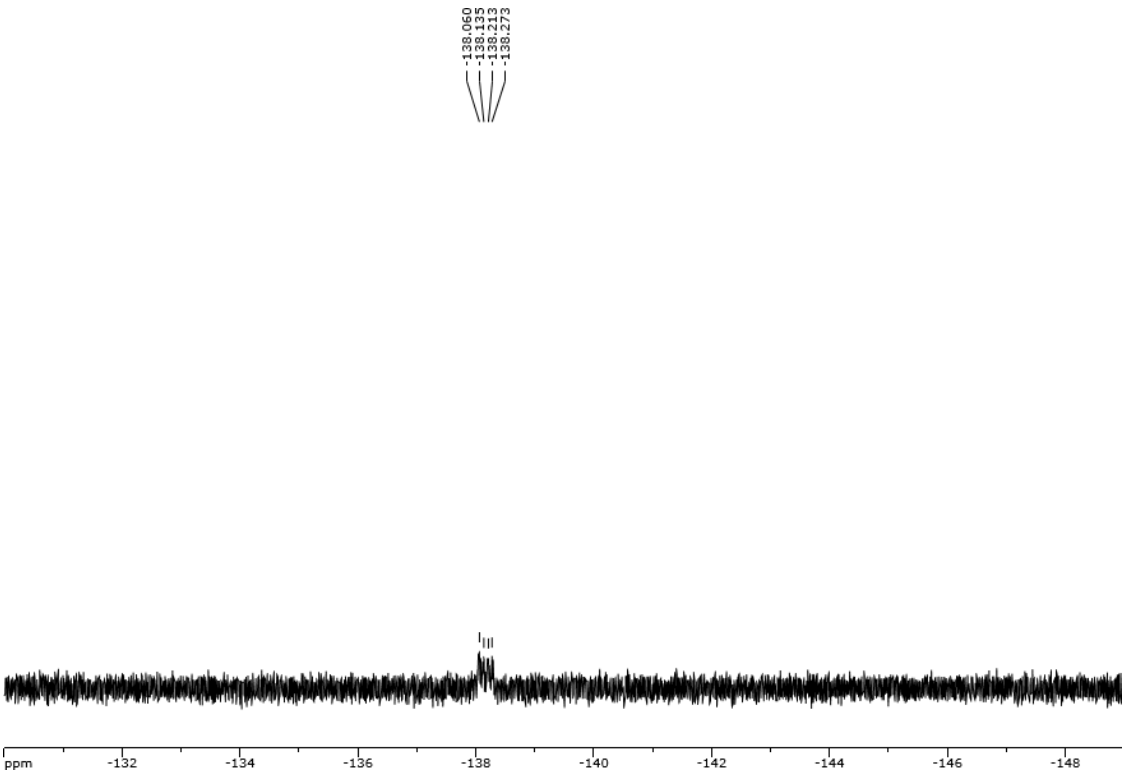
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

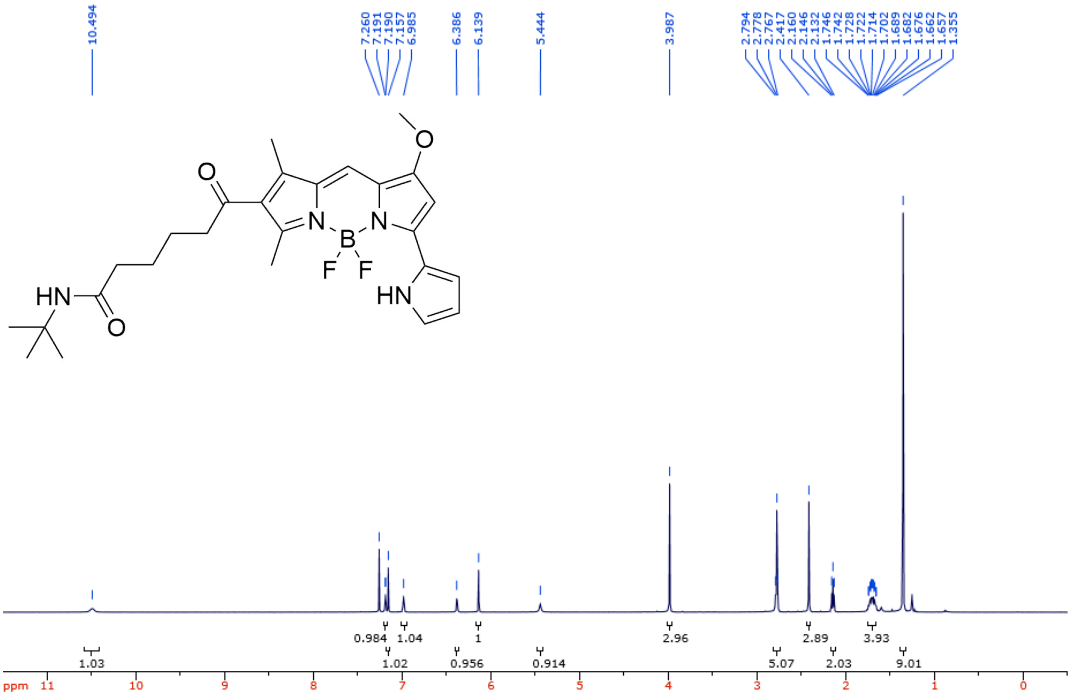


^{19}F NMR (CDCl3, 235 MHz)

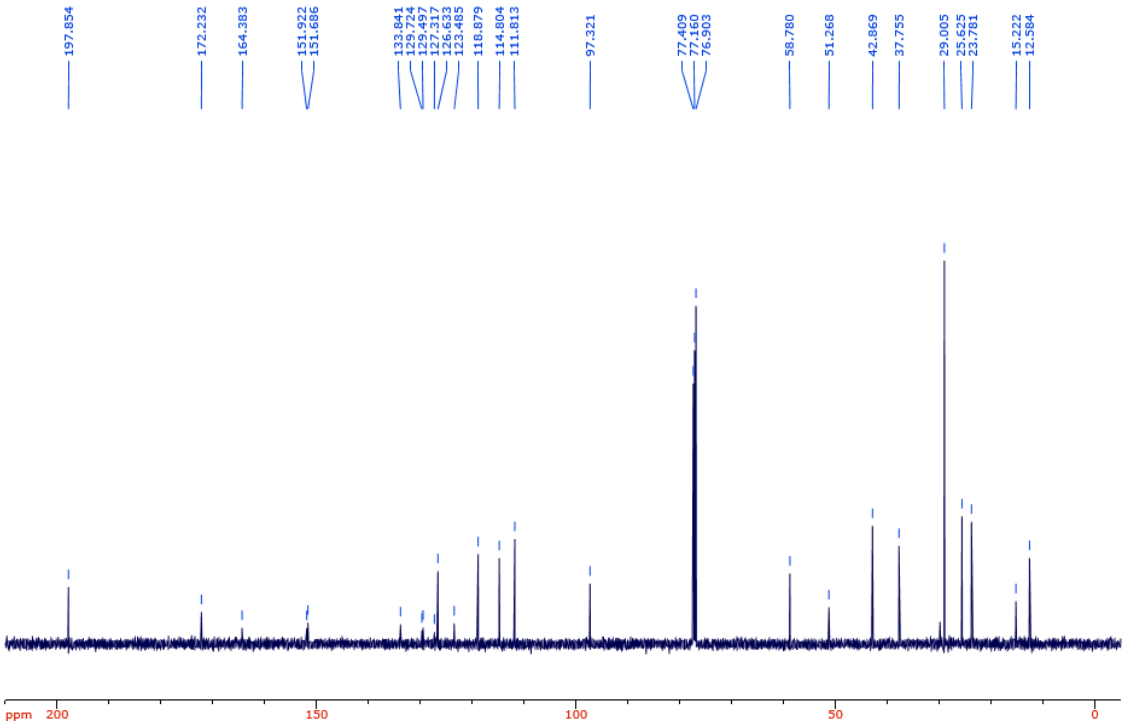


Boron, difluoro[N-tert-butyl-6-[2-[(4-methoxy-1H,1'H-2,2'-bipyrrol-5-yl)methylene]-3,5-dimethyl-2H-pyrrol-4-yl]-6-oxohexanamide] (2h)

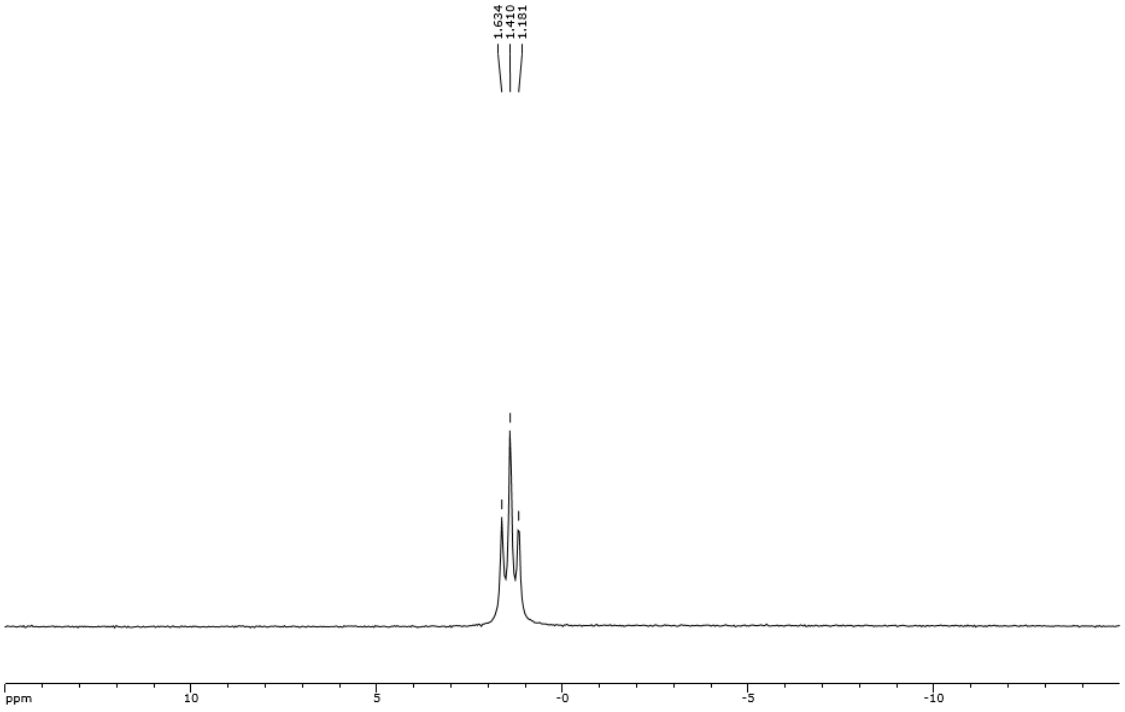
^{1}H NMR ($CDCl_3$, 500 MHz):



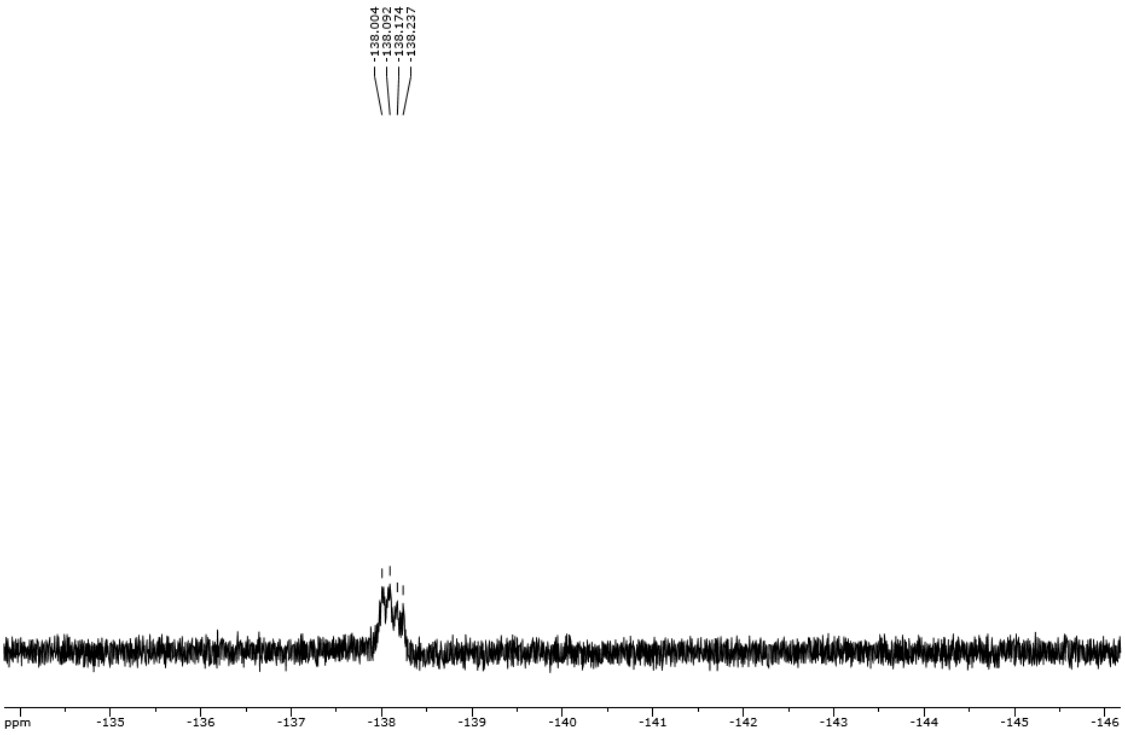
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

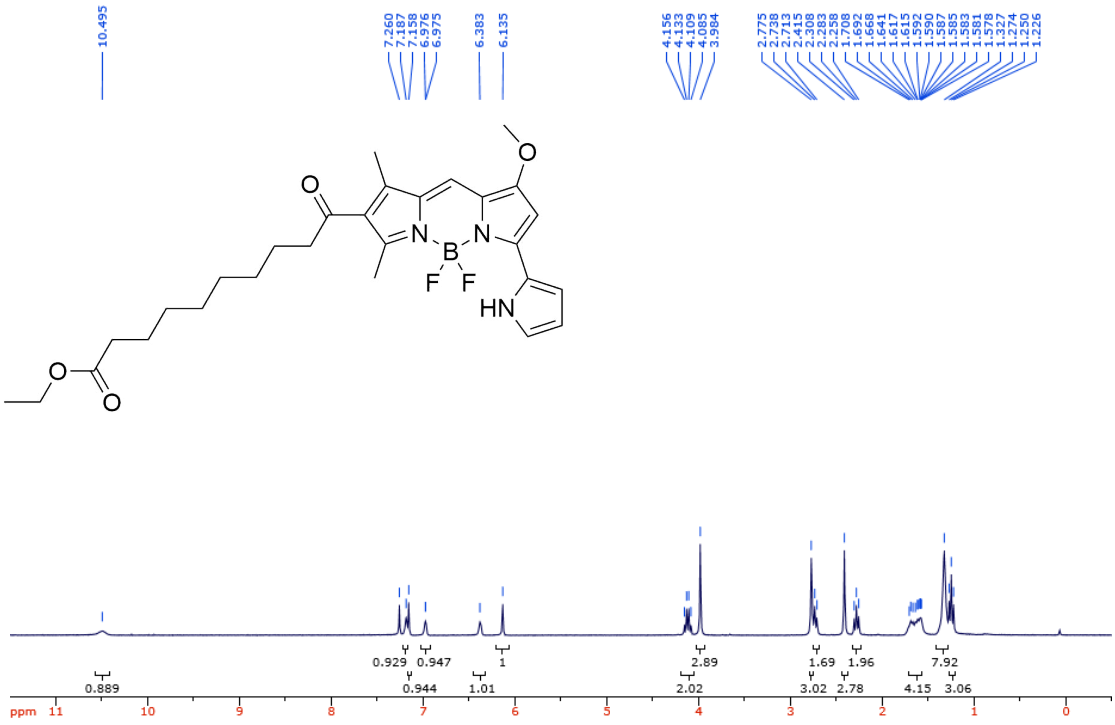


^{19}F NMR (CDCl3, 235 MHz)

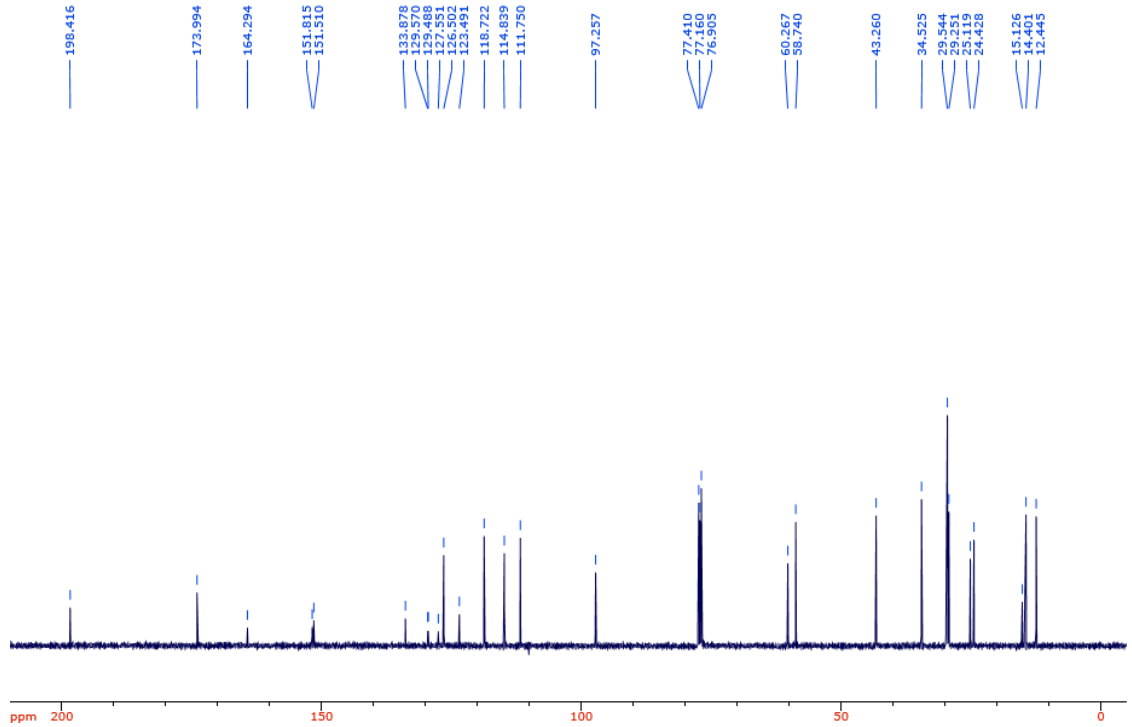


BODIPY Boron, difluoro[ethyl 10-[2-[(4-methoxy-1H,1'H-2,2'-bipyrrol-5-yl)methylene]-3,5-dimethyl-2*H*-pyrrol-4-yl]-10-oxodecanoate] (2i)

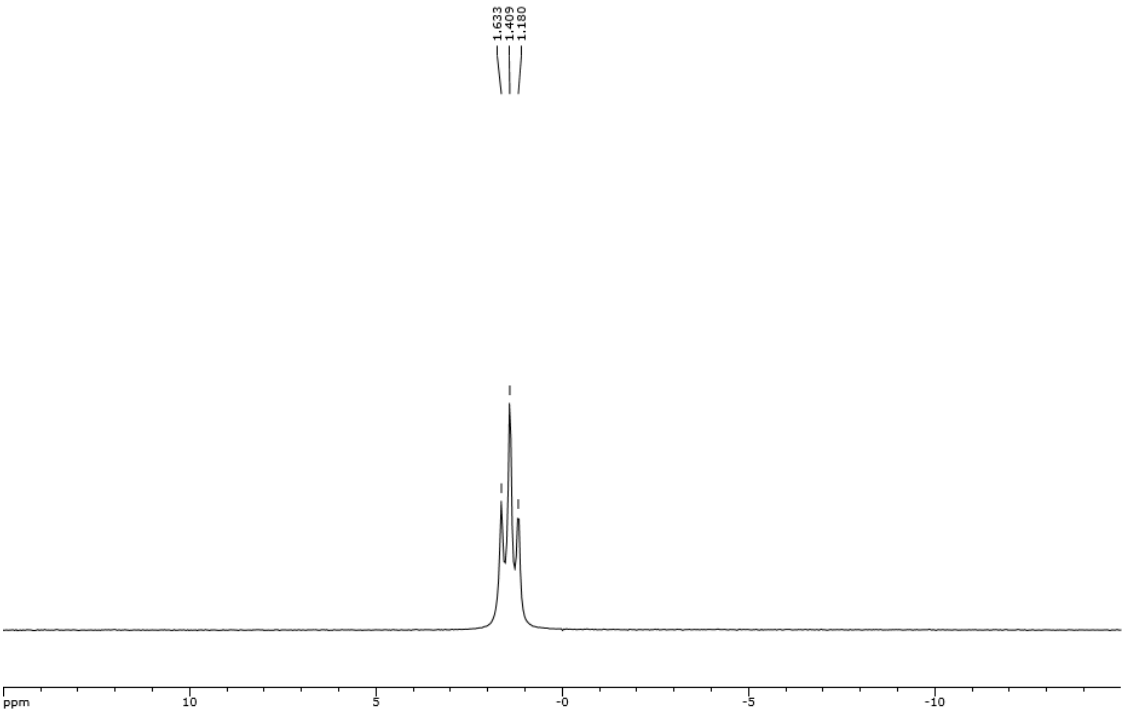
^{1}H NMR ($CDCl_3$, 500 MHz):



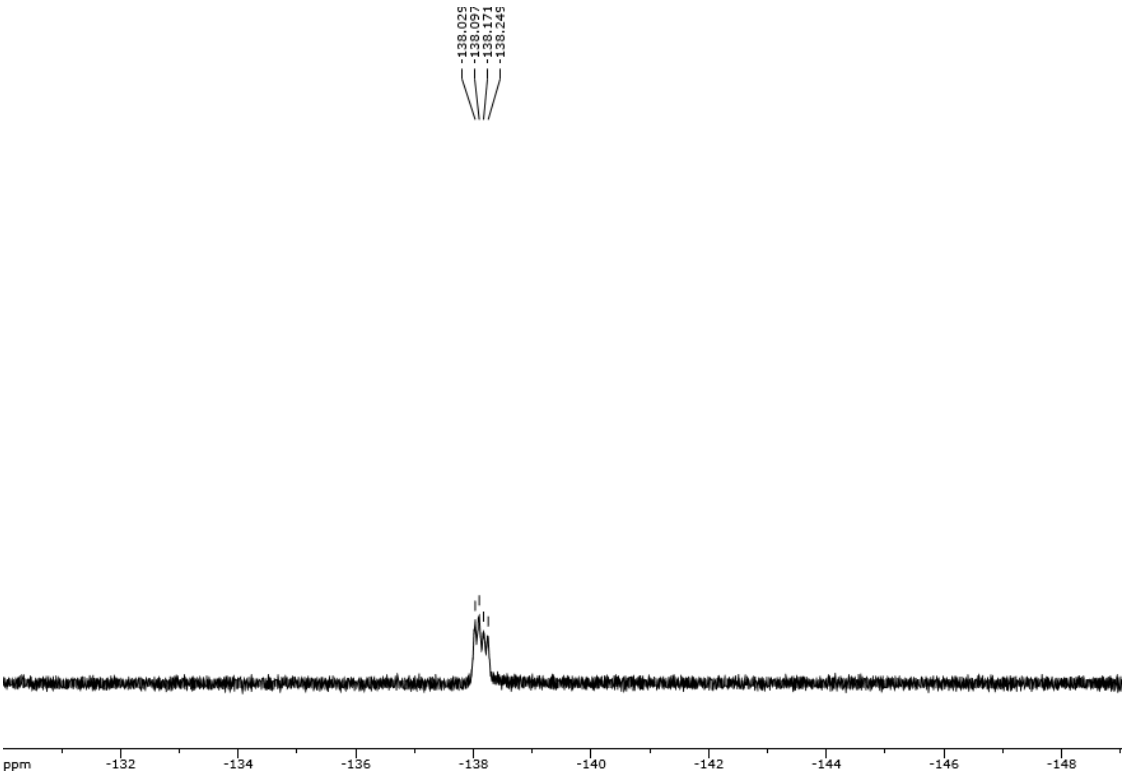
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

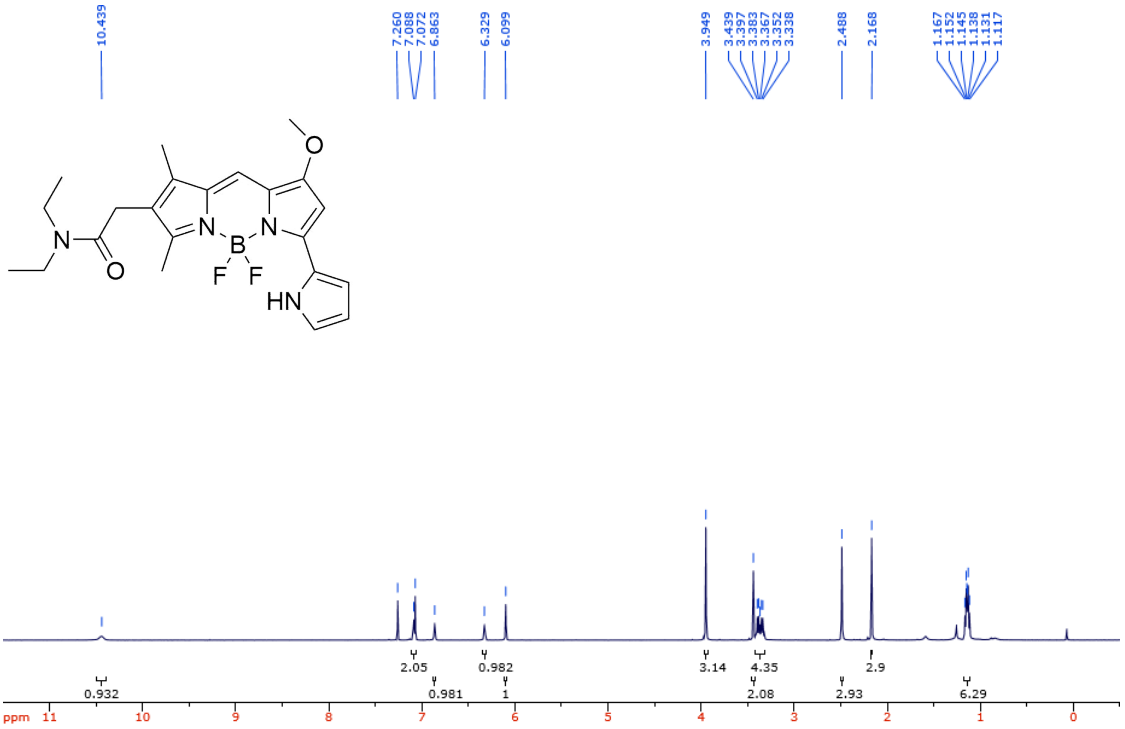


^{19}F NMR (CDCl3, 235 MHz)

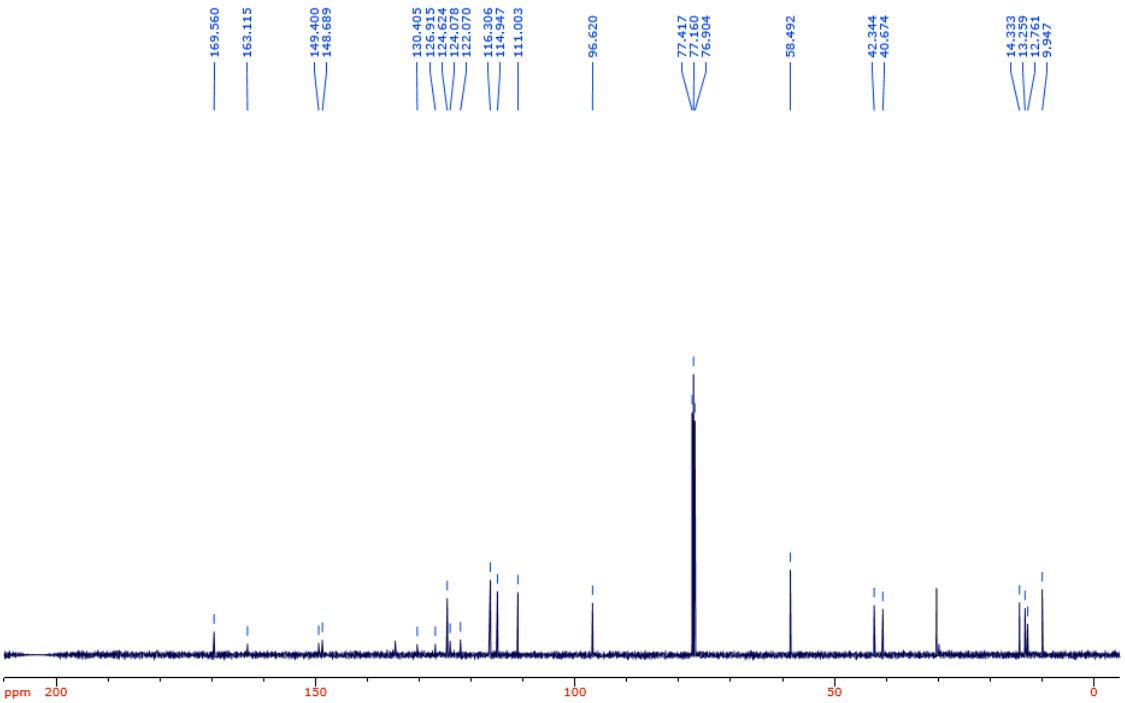


Boron, difluoro[N,N-diethyl-2-[2-[(4-methoxy-1H,1'H-2,2'-bipyrrol-5-yl)methylene]-3,5-dimethyl-2*H*-pyrrol-4-yl]acetamide (2j)

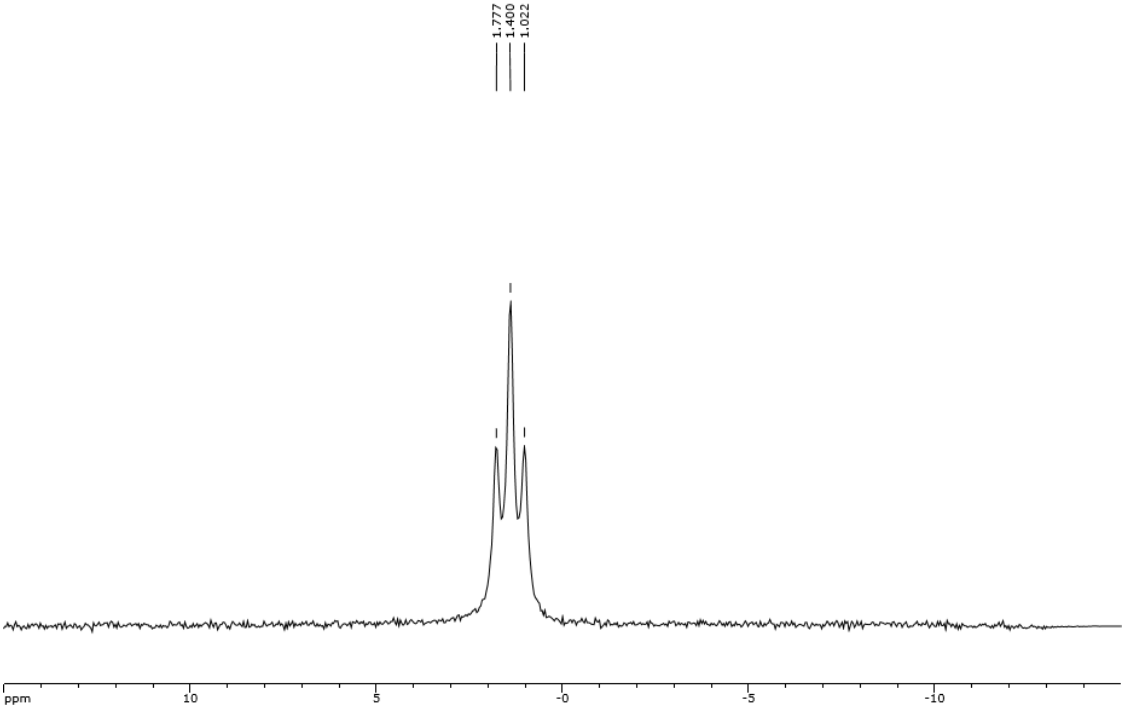
^{1}H NMR ($CDCl_3$, 500 MHz):



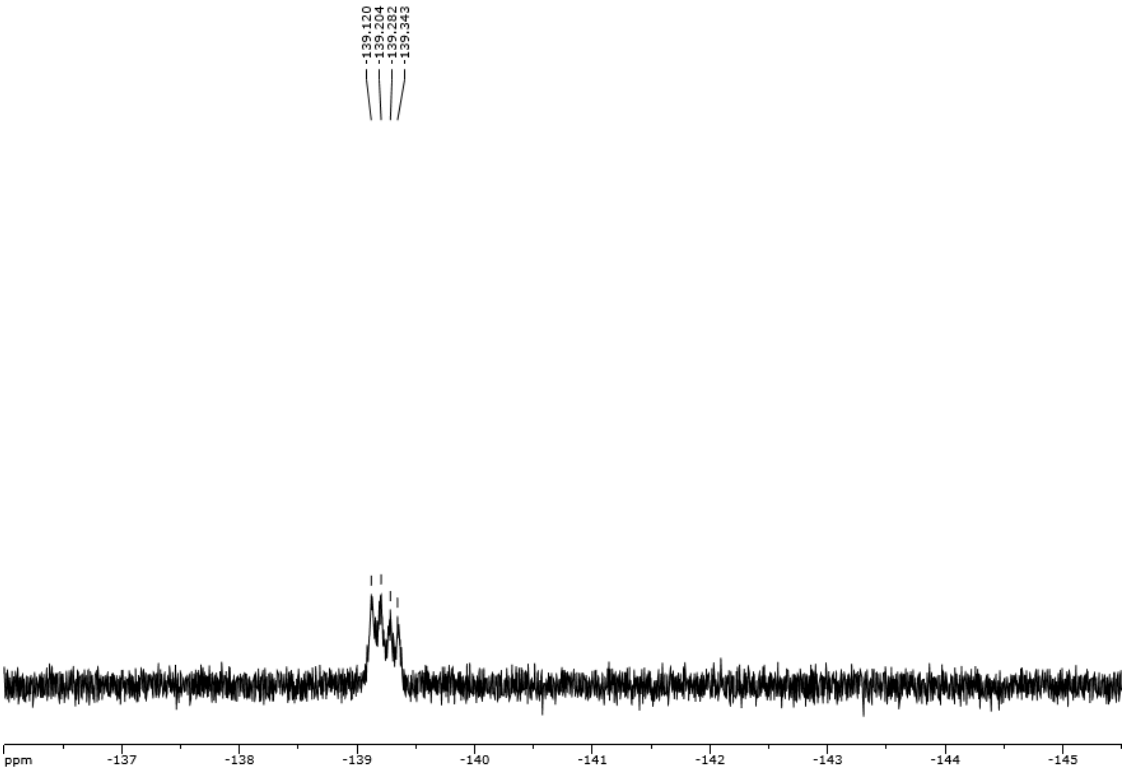
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

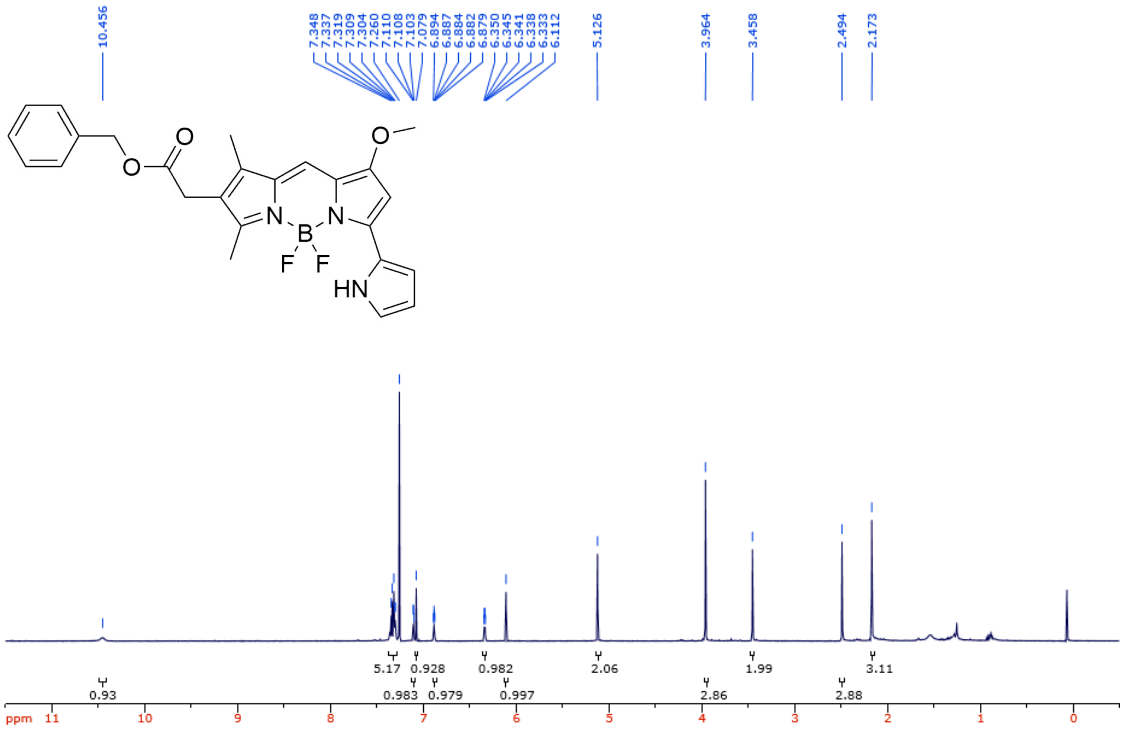


^{19}F NMR (CDCl3, 235 MHz)

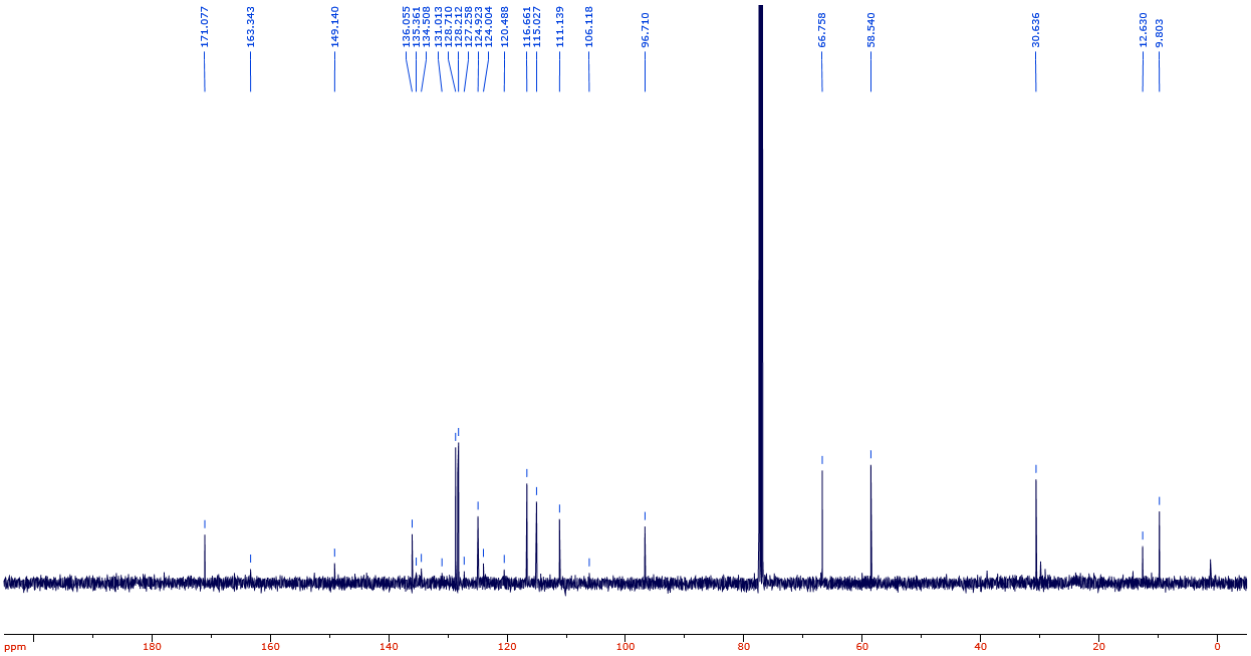


Boron, difluoro[benzyl 2-[2-[(4-methoxy-1H,1'H-2,2'-bipyrrol-5-yl)methylene]-3,5-dimethyl-2*H*-pyrrol-4-yl]acetate] (2k)

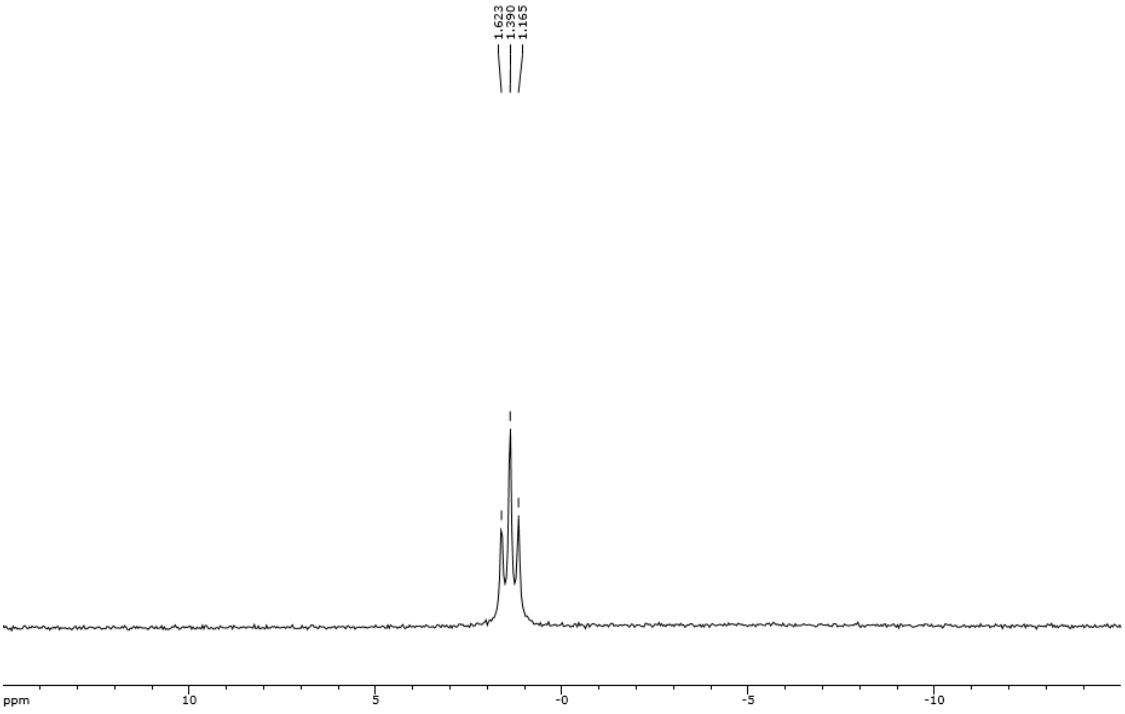
^{1}H NMR ($CDCl_3$, 300 MHz):



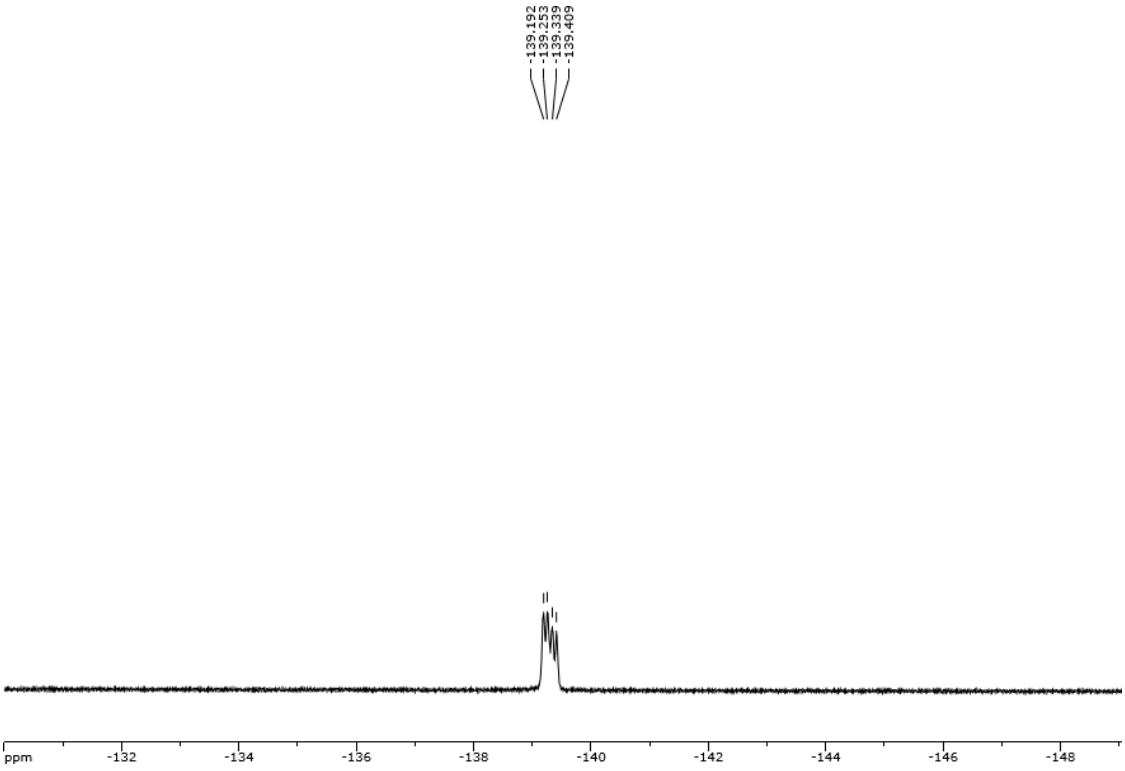
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

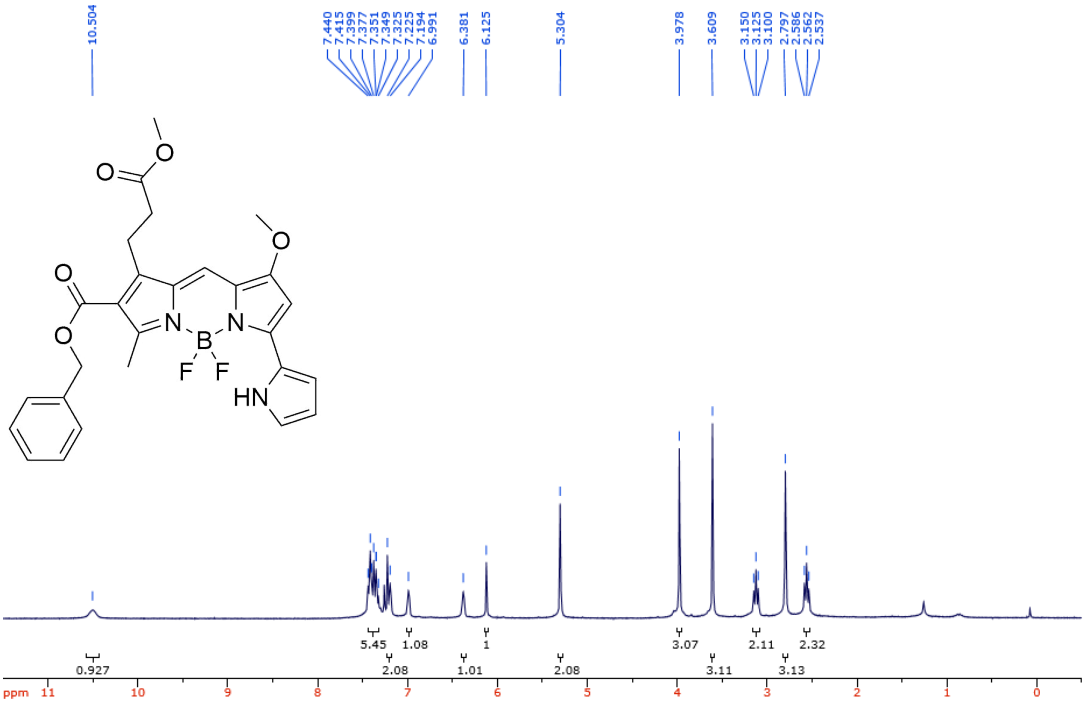


^{19}F NMR (CDCl3, 235 MHz)

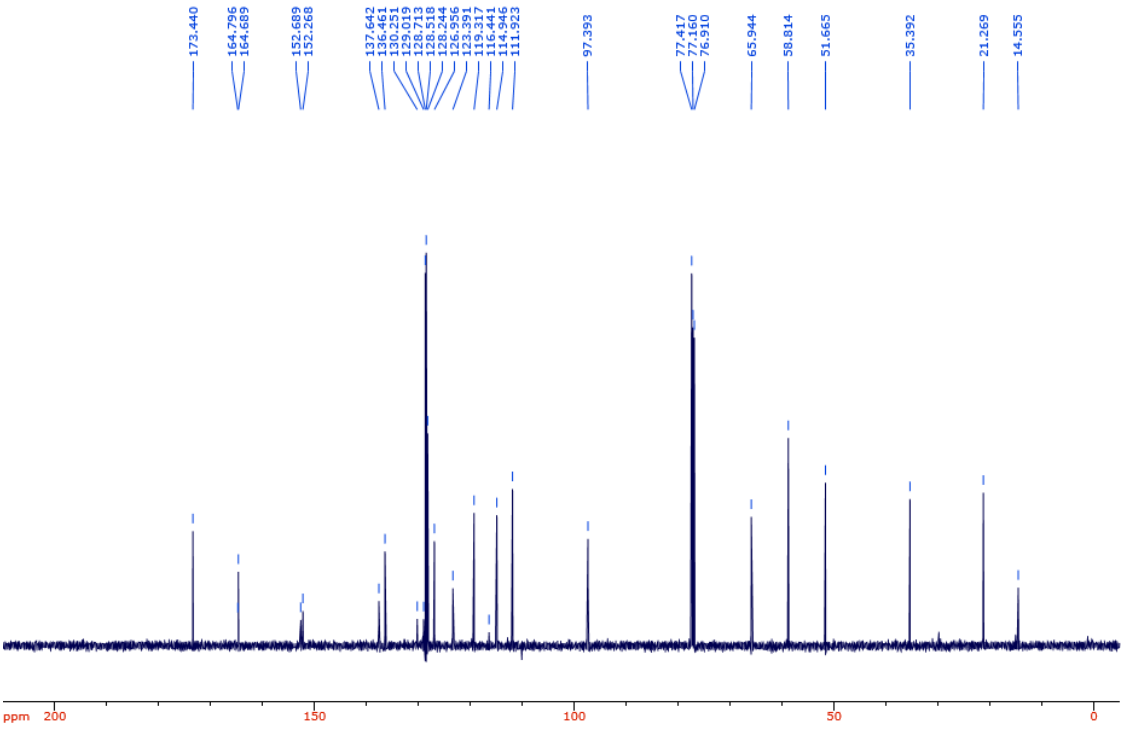


Boron, difluoro[benzyl 2[(4-methoxy-1H,1'H-2,2'-bipyrrol-5-yl)methylene]-3-(3-methoxy-3-oxopropyl)-5-methyl-2H-pyrrole-4-carboxylate] (2l)

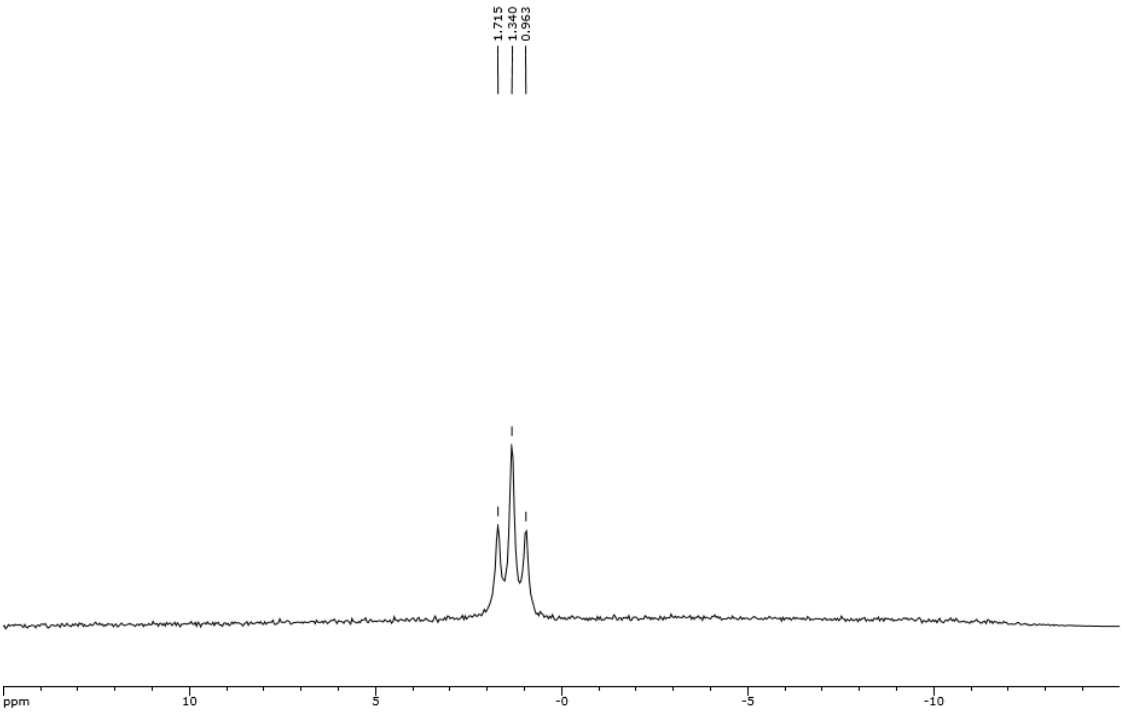
^{1}H NMR ($CDCl_3$, 300 MHz):



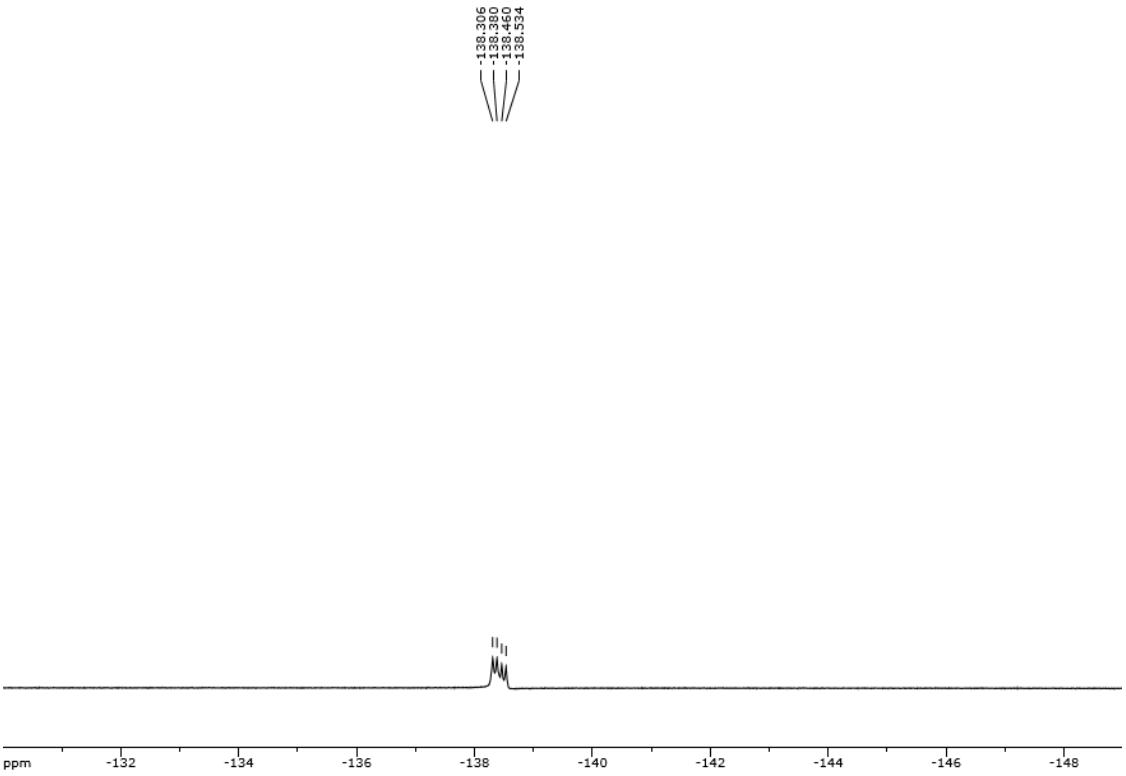
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

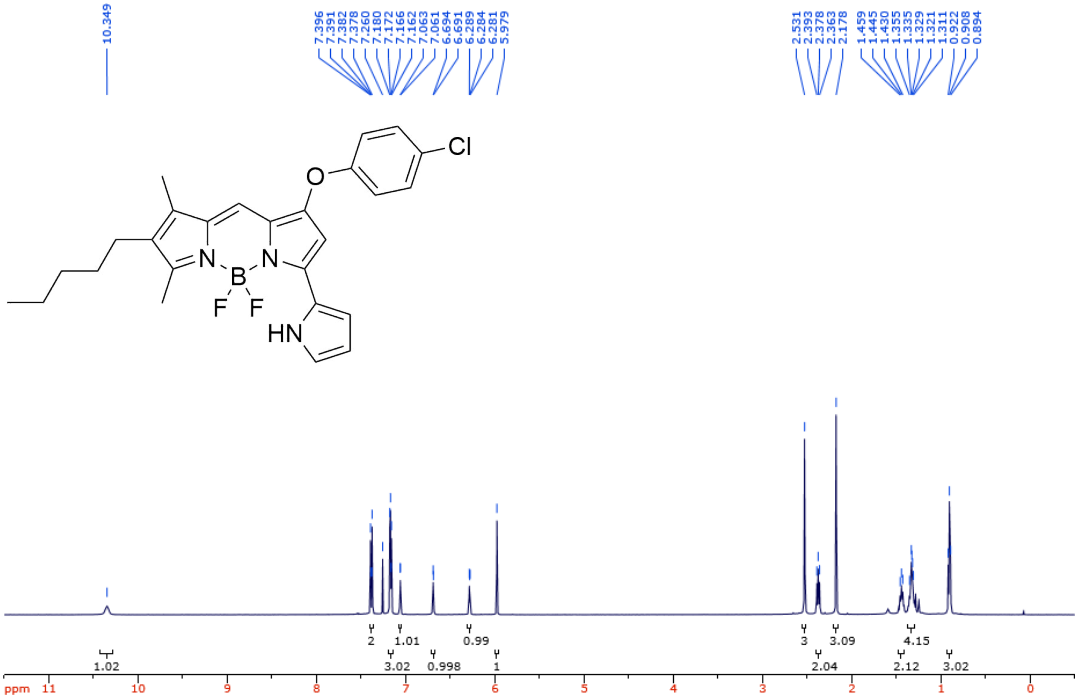


^{19}F NMR (CDCl3, 235 MHz)

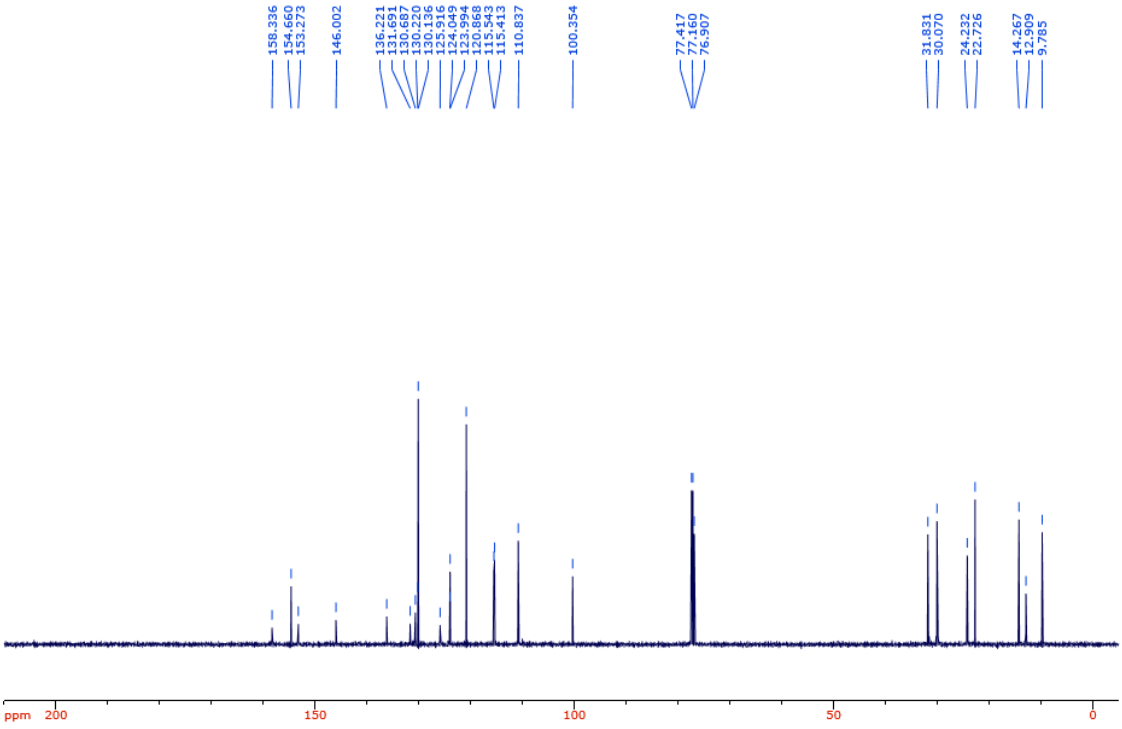


Boron, difluoro[4-(4-chlorophenoxy)-5-[(3,5-dimethyl-4-pentyl-2*H*-pyrrol-2-ylidene)methyl]-1H,1'H-2,2'-bipyrrole] (3m)

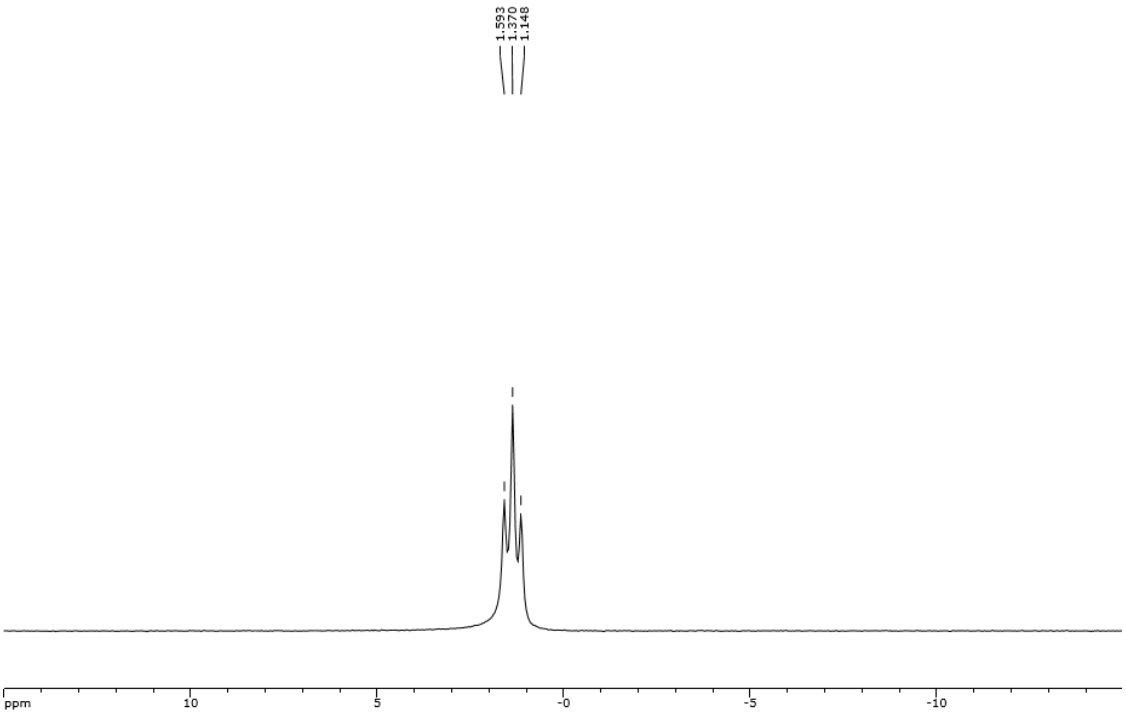
^{1}H NMR ($CDCl_3$, 500 MHz):



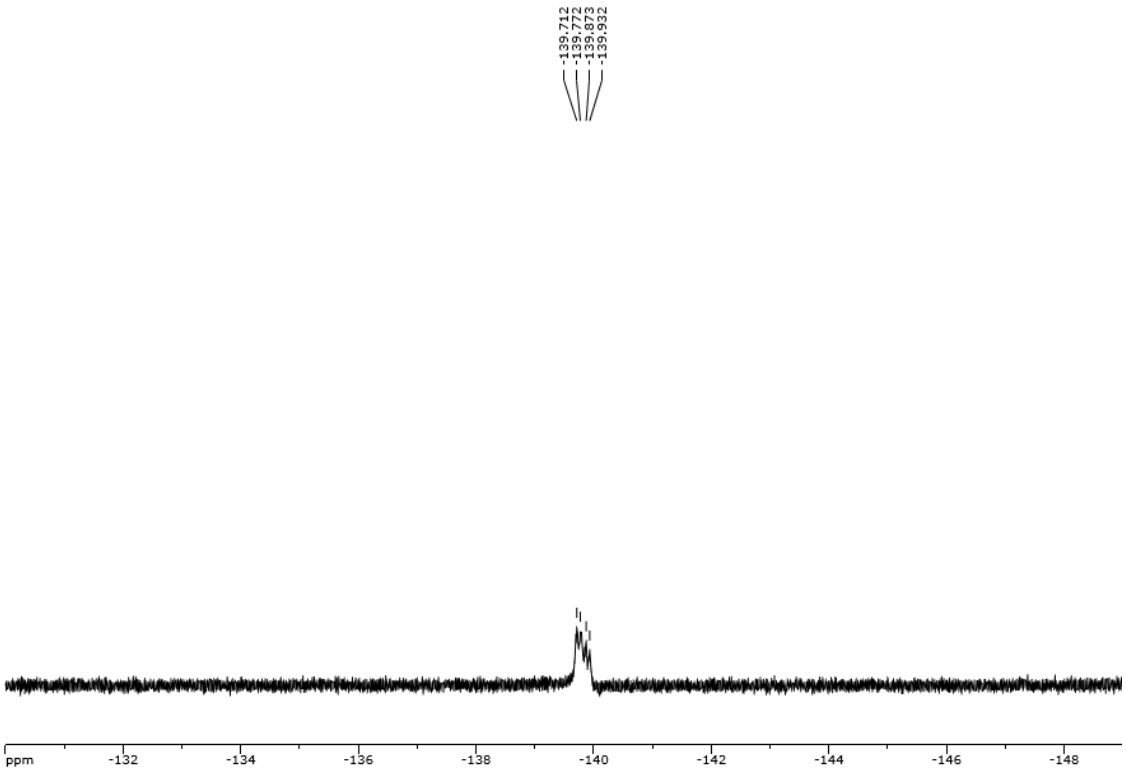
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

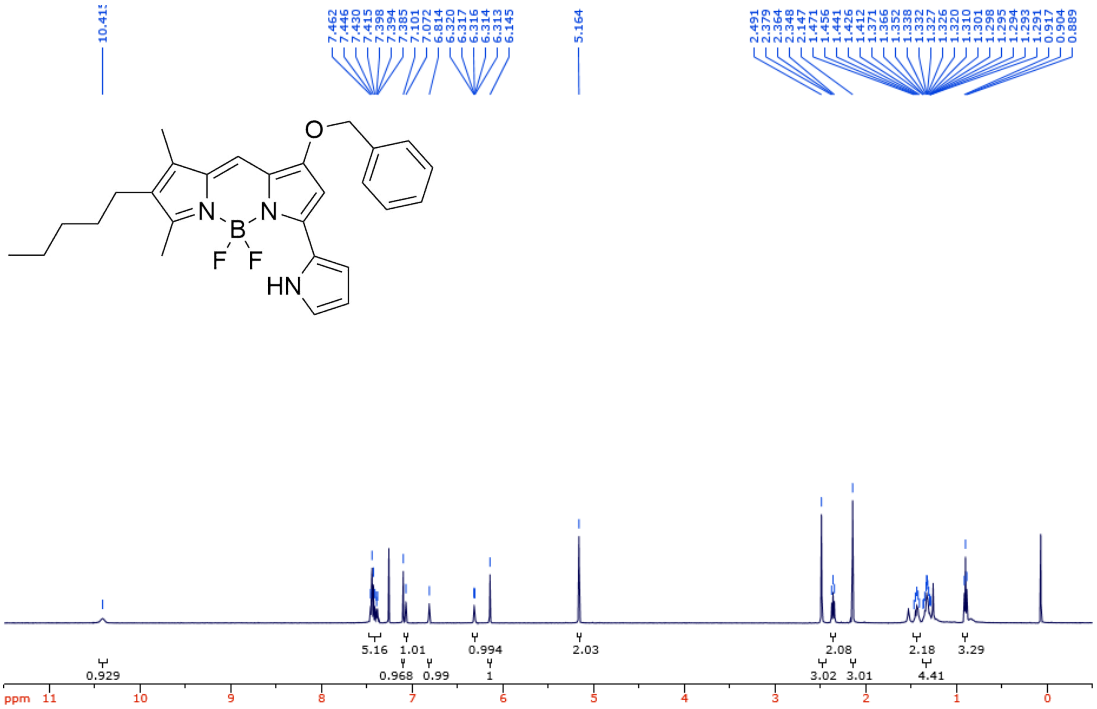


^{19}F NMR (CDCl3, 235 MHz)

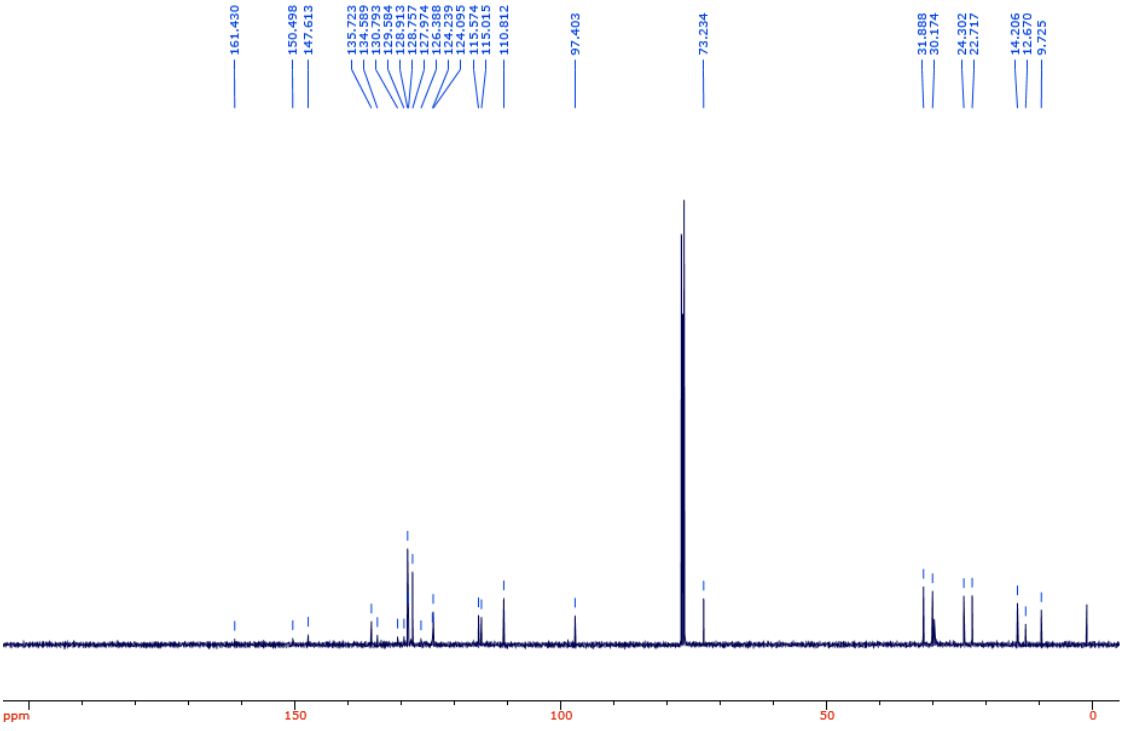


Boron, difluoro[4-(benzyloxy)-5-[(3,5-dimethyl-4-pentyl-2H-pyrrol-2-ylidene)methyl]-1H,1'H-2,2'-bipyrrole] (3n)

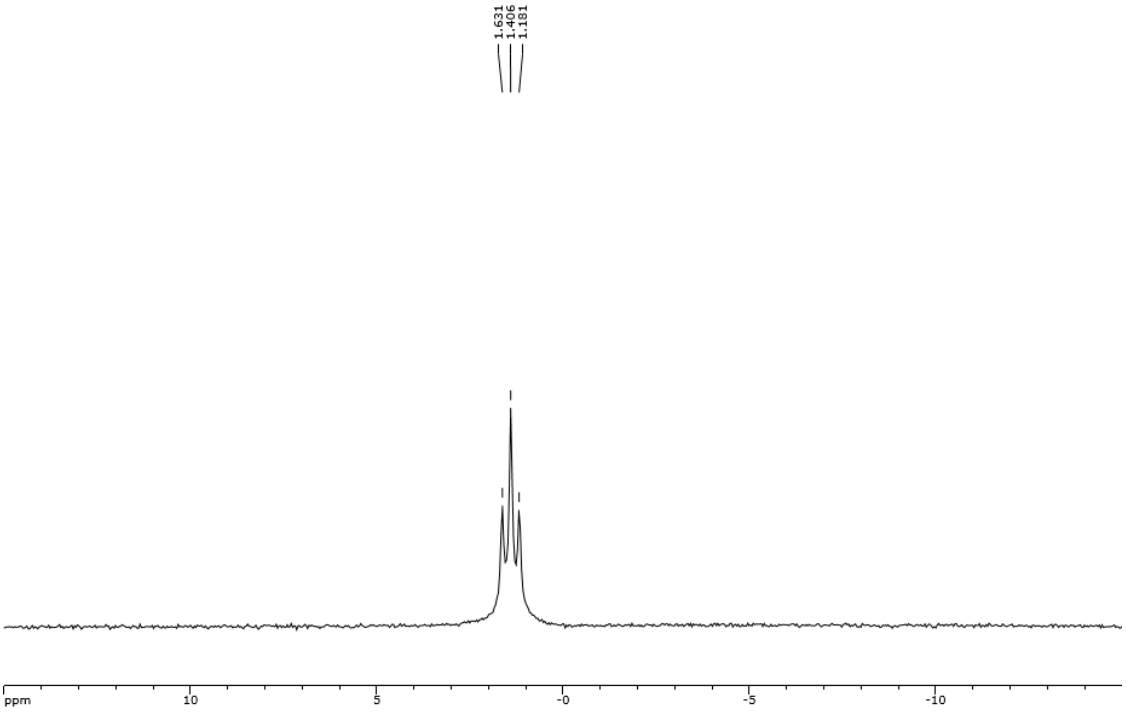
^{1}H NMR ($CDCl_3$, 500 MHz):



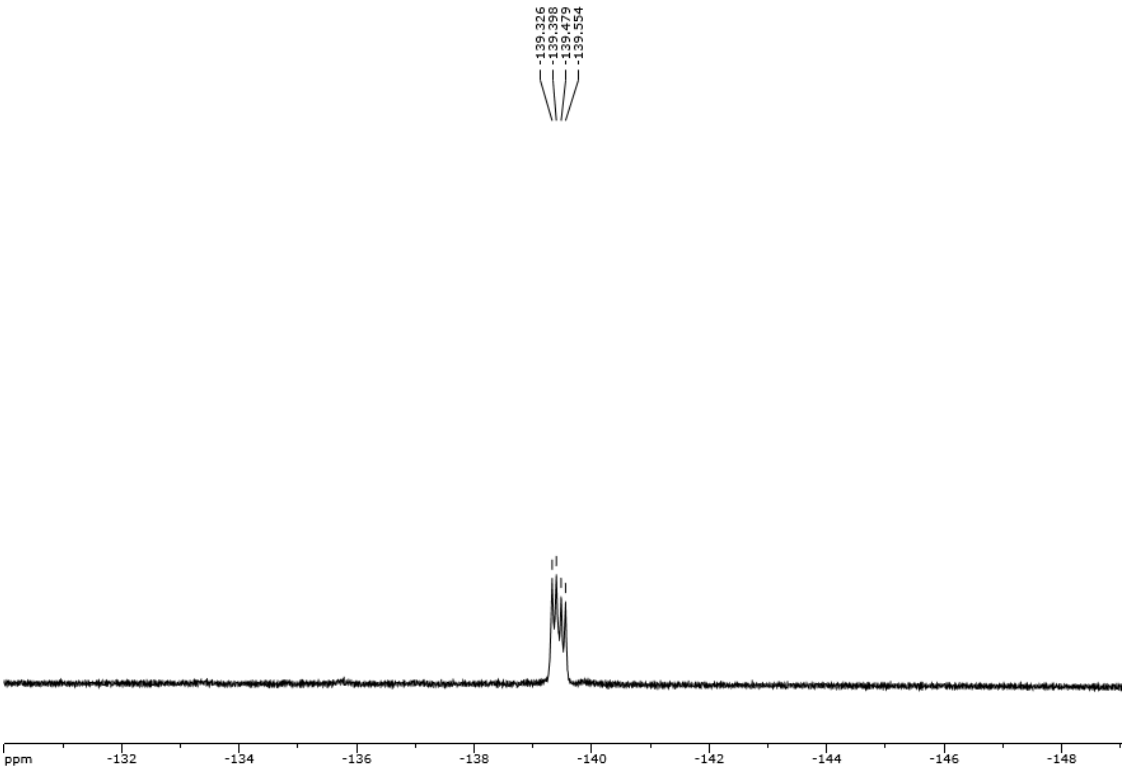
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

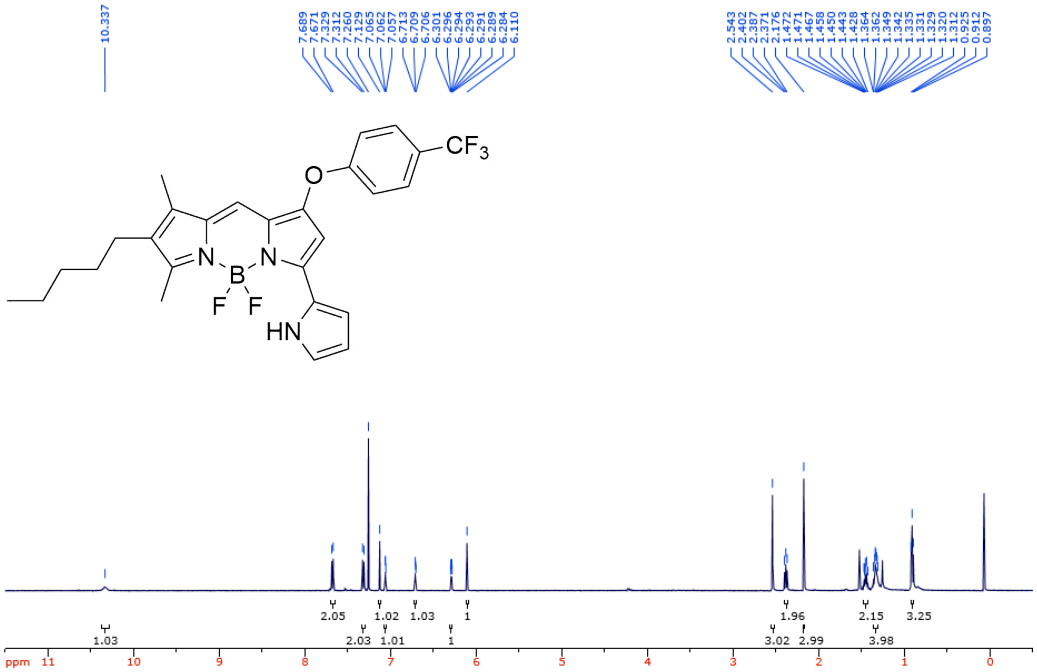


^{19}F NMR (CDCl3, 235 MHz)

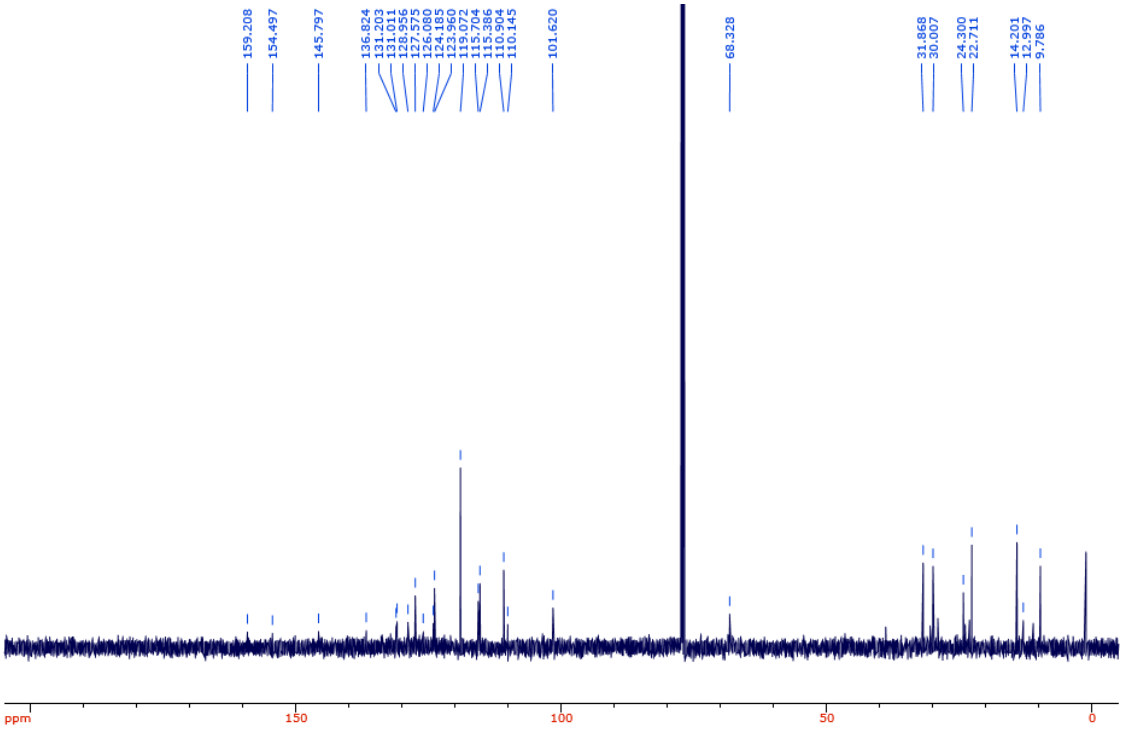


Boron, difluoro[5-[(3,5-dimethyl-4-pentyl-2*H*-pyrrol-2-ylidene)methyl]-4-[4-(trifluoromethyl)phenoxy]-1H,1'H-2,2'-bipyrrole] (3o)

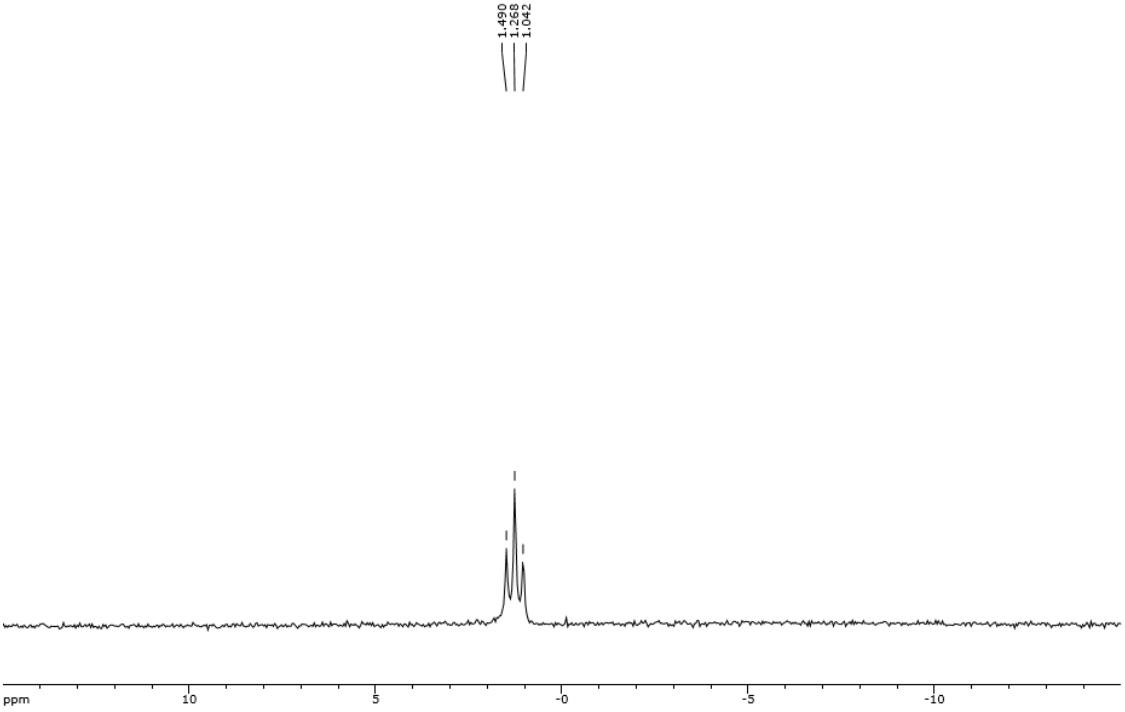
^{1}H NMR ($CDCl_3$, 500 MHz):



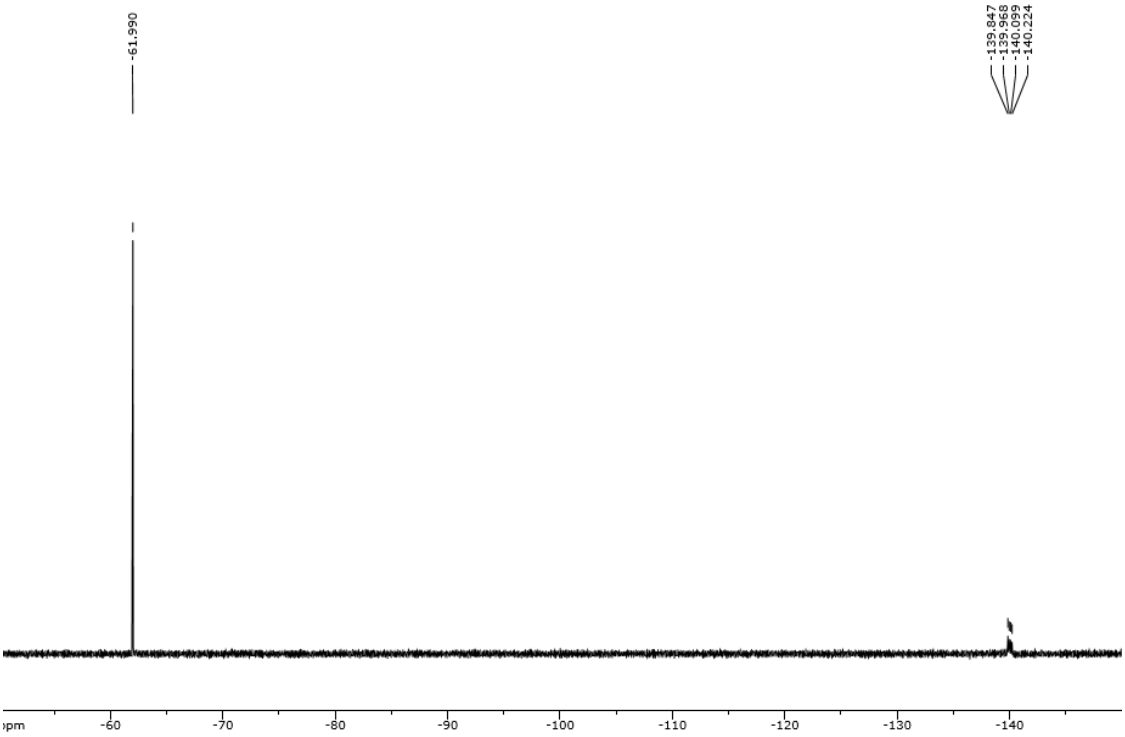
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

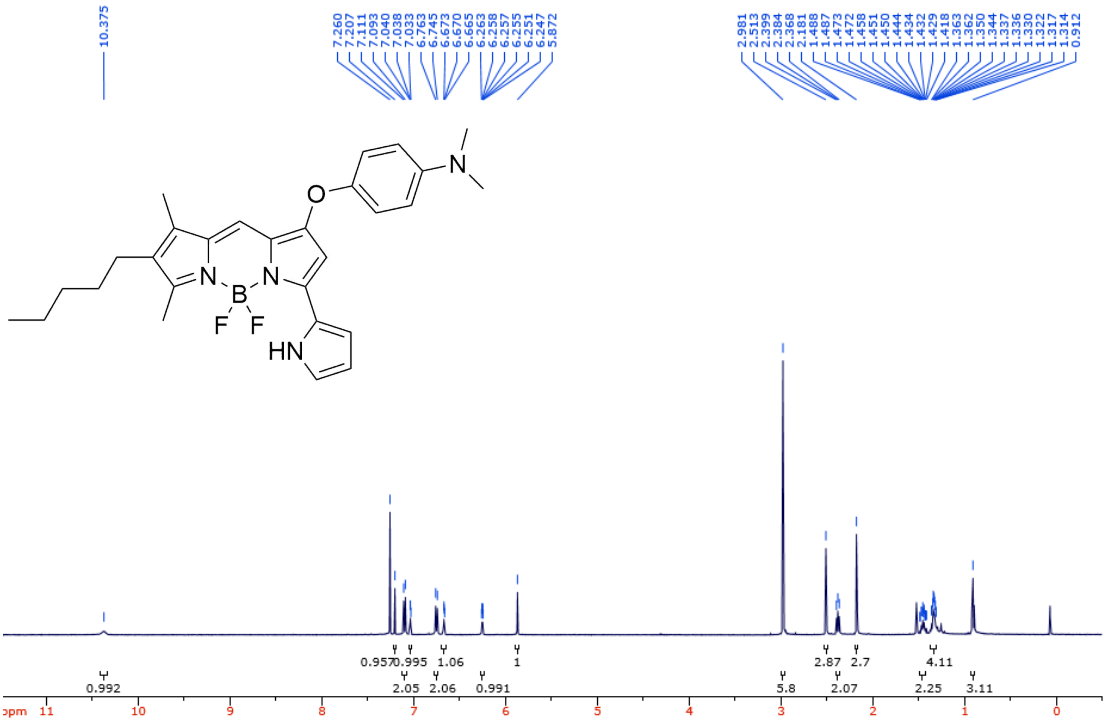


^{19}F NMR (CDCl3, 235 MHz)

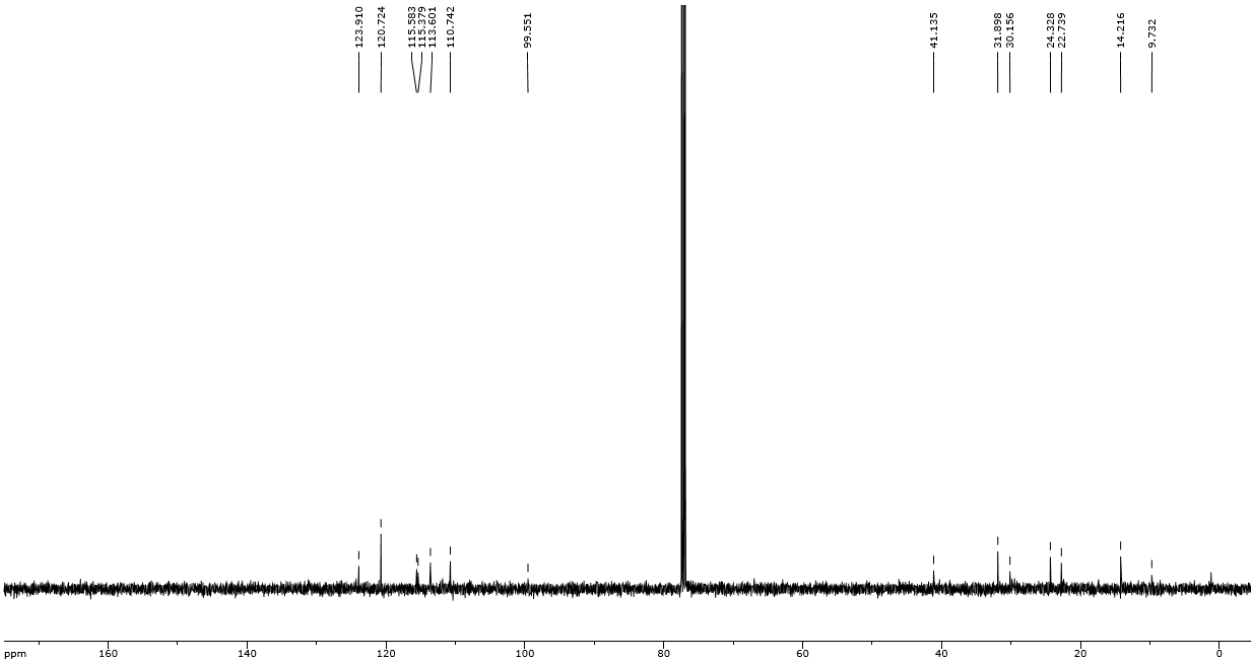


Boron, difluoro[4-[5-((3,5-dimethyl-4-pentyl-2*H*-pyrrol-2-ylidene)methyl)-1H,1'H-2,2'-bipyrrol4-yloxy]-*N*,*N*-dimethylaniline] (3p)

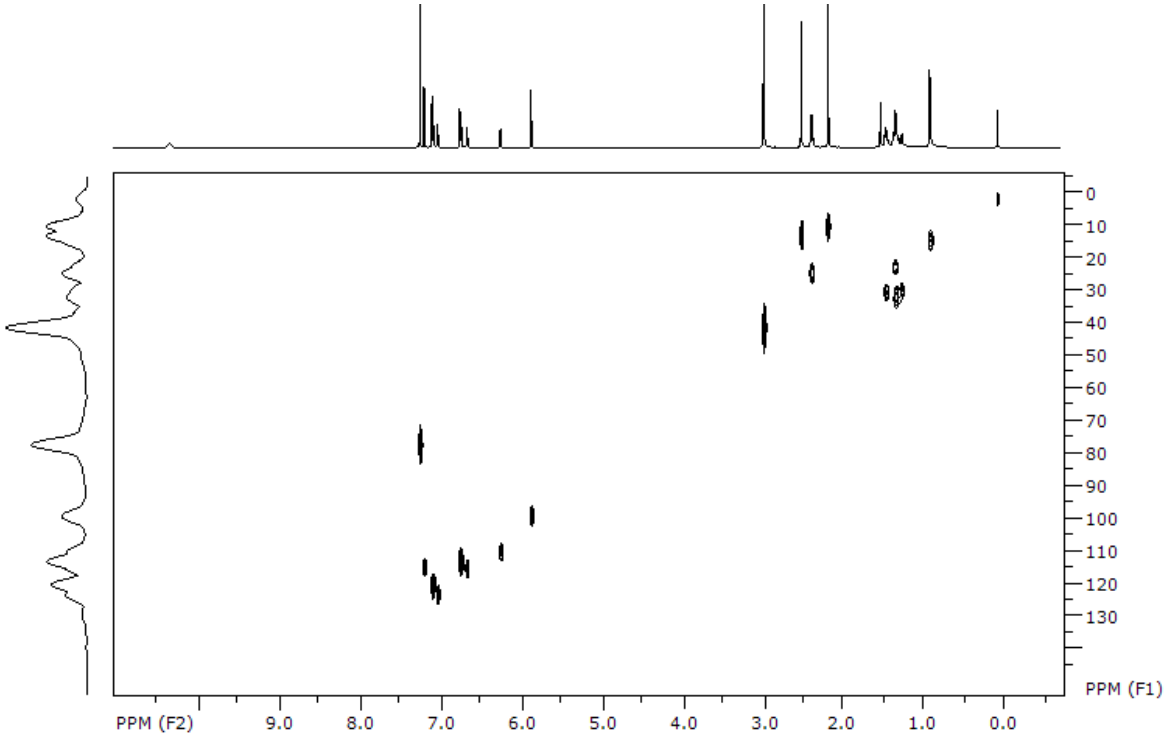
^{1}H NMR ($CDCl_3$, 500 MHz):



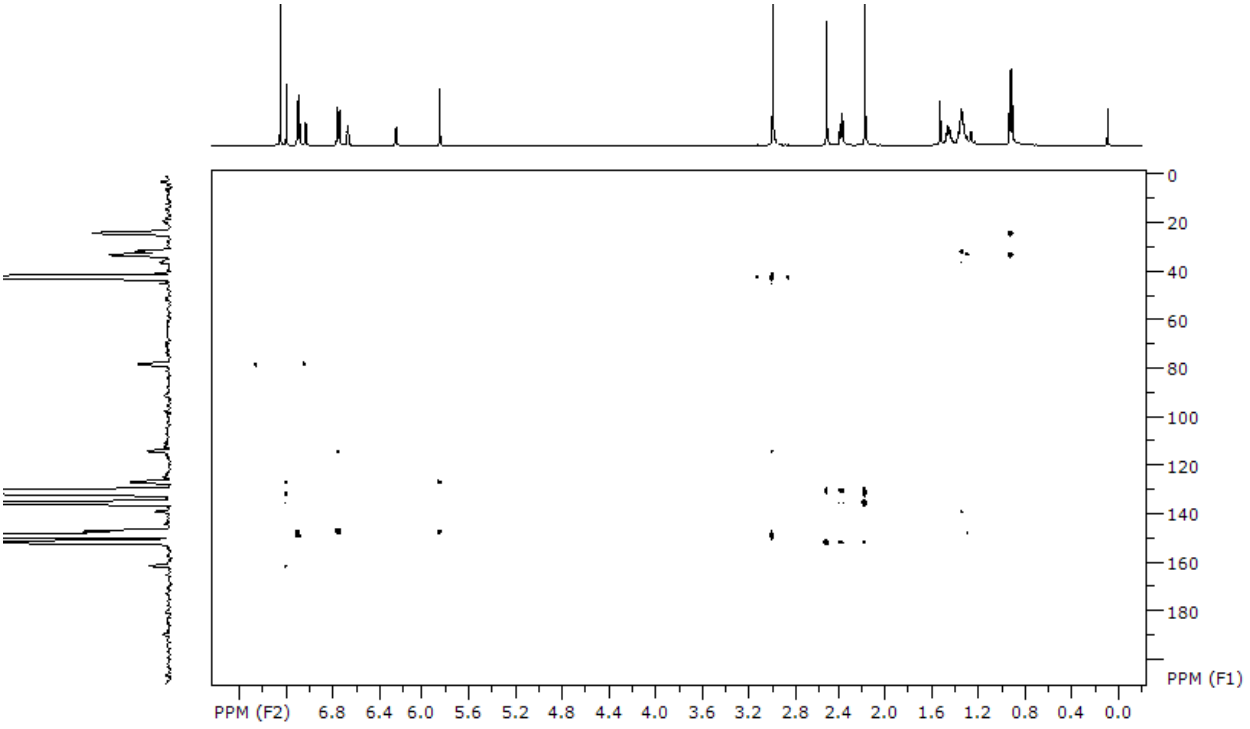
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



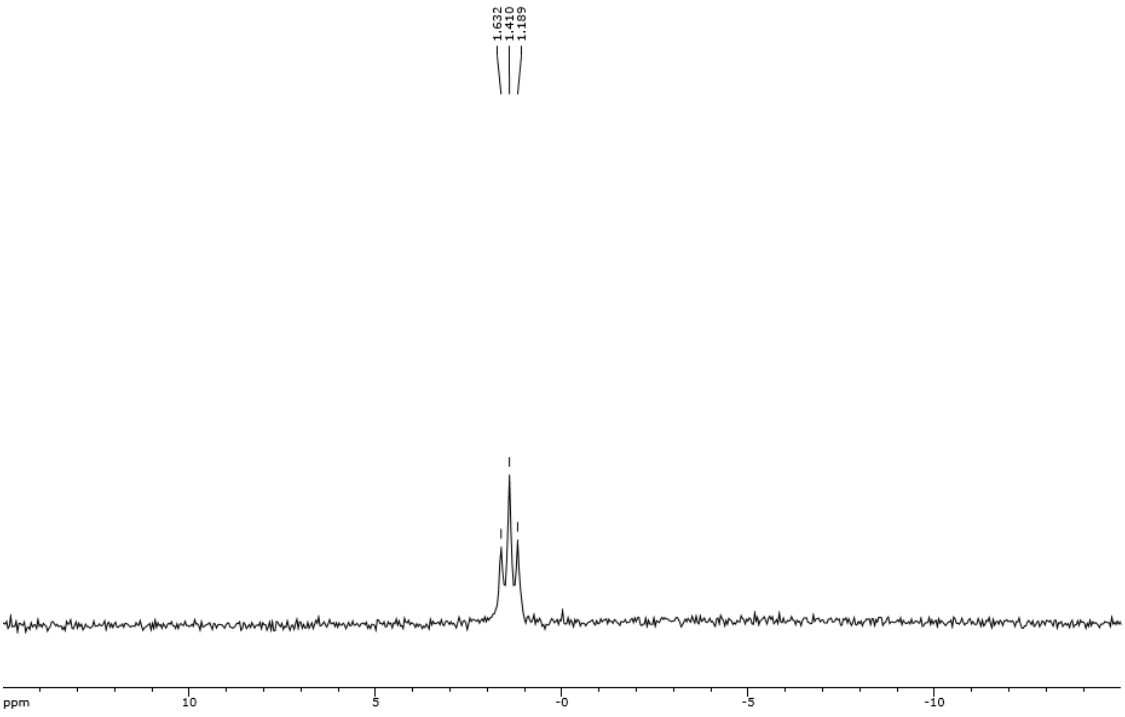
^{1}H-^{13}C HSQC NMR ($CDCl_3$):



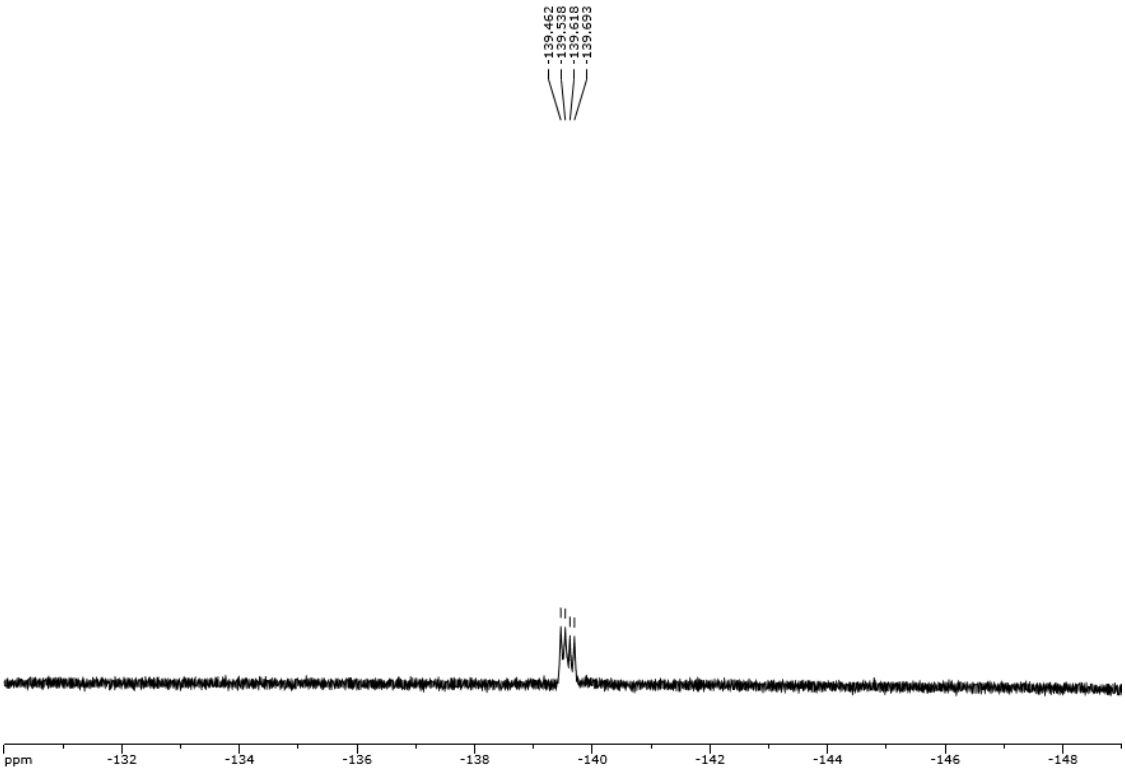
^{1}H-^{13}C HMBC NMR ($CDCl_3$):



^{11}B NMR ($CDCl_3$, 160 MHz)

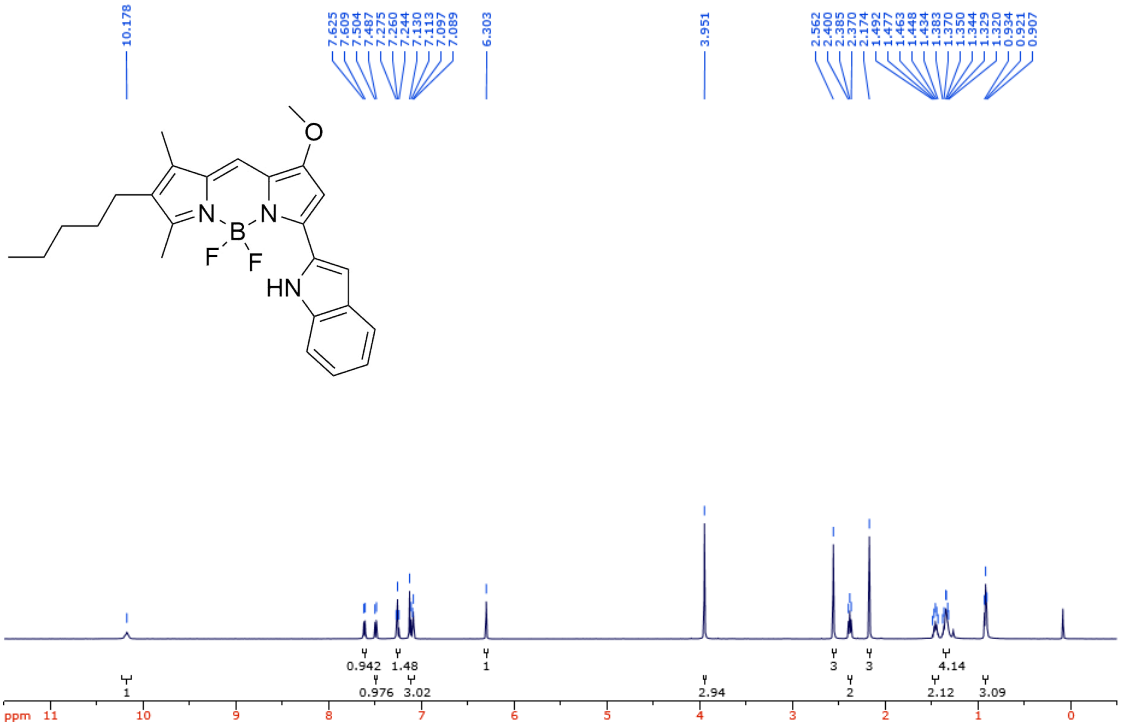


^{19}F NMR (CDCl3, 235 MHz)

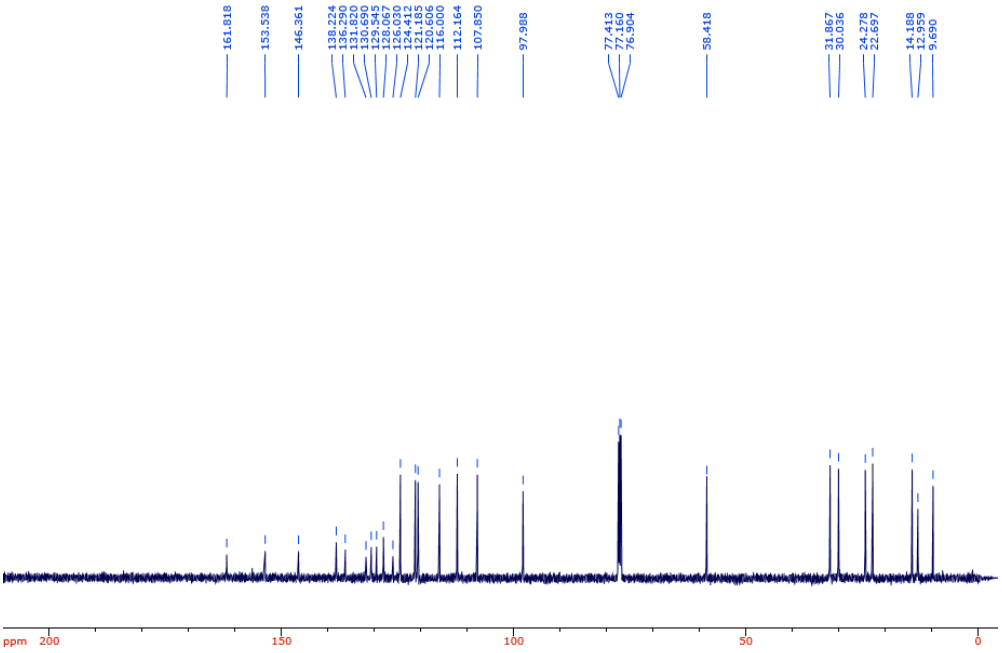


Boron, difluoro[2-[5-((3,5-dimethyl-4-pentyl-2*H*-pyrrol-2-ylidene)methyl)-4-methoxy-1H-pyrrol-2-yl]-1H-indole] (4q)

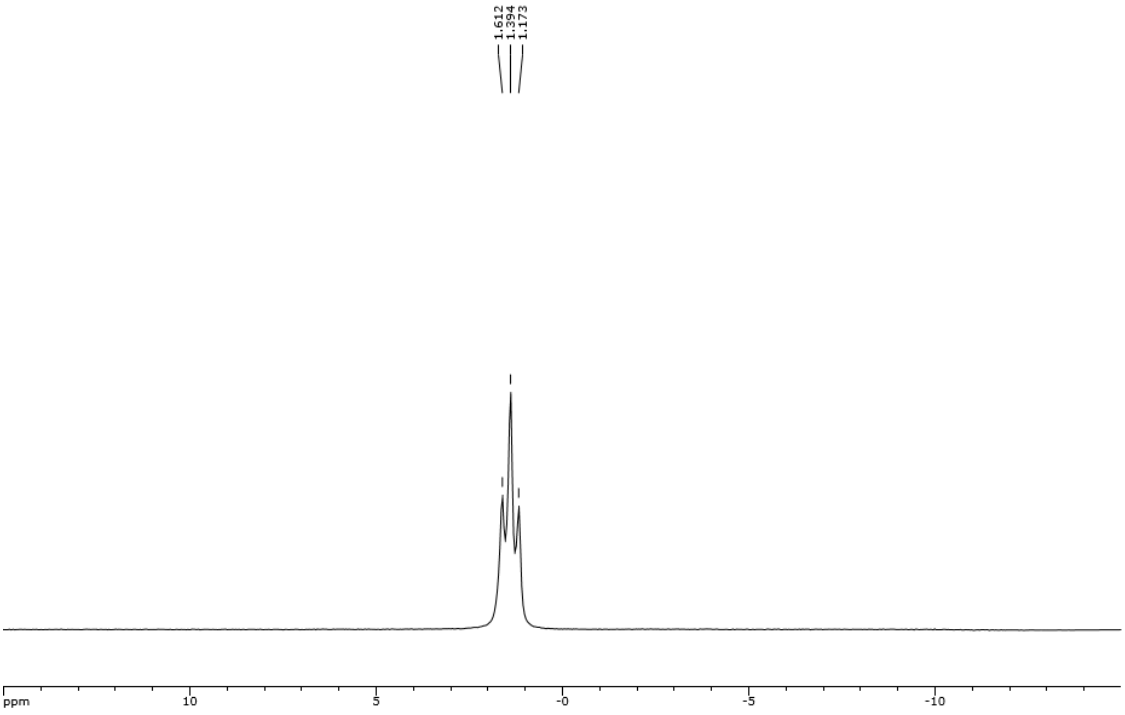
^{1}H NMR ($CDCl_3$, 500 MHz):



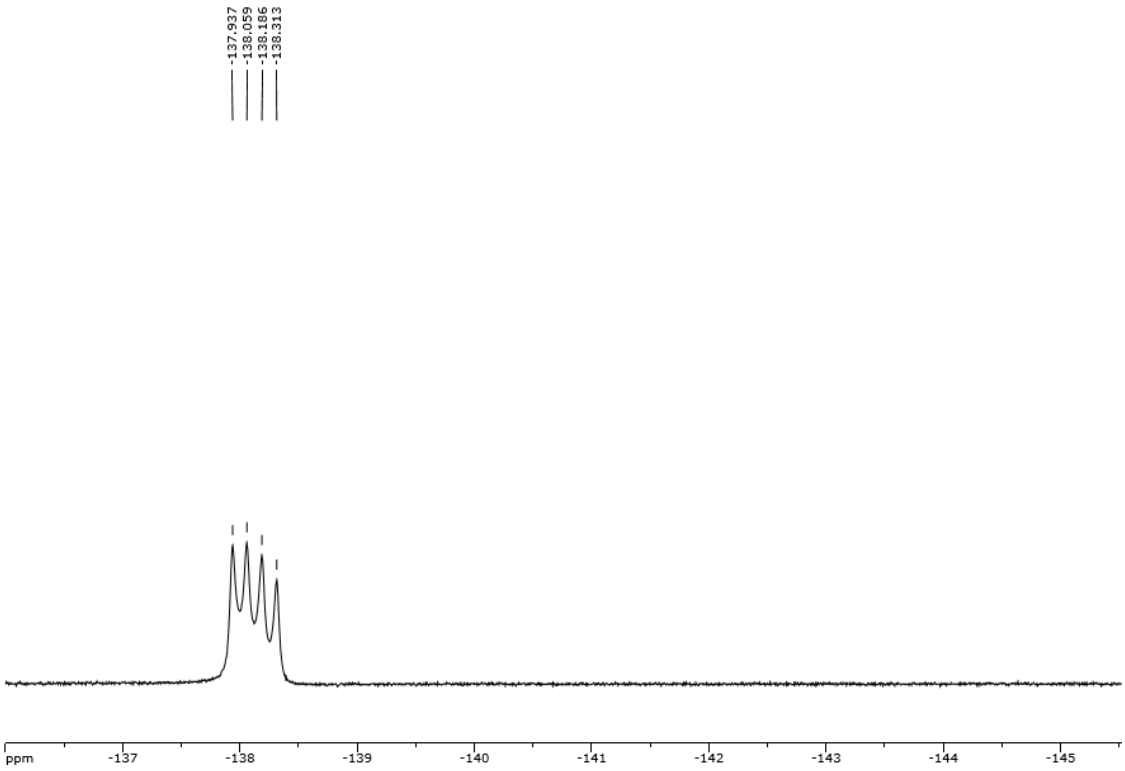
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

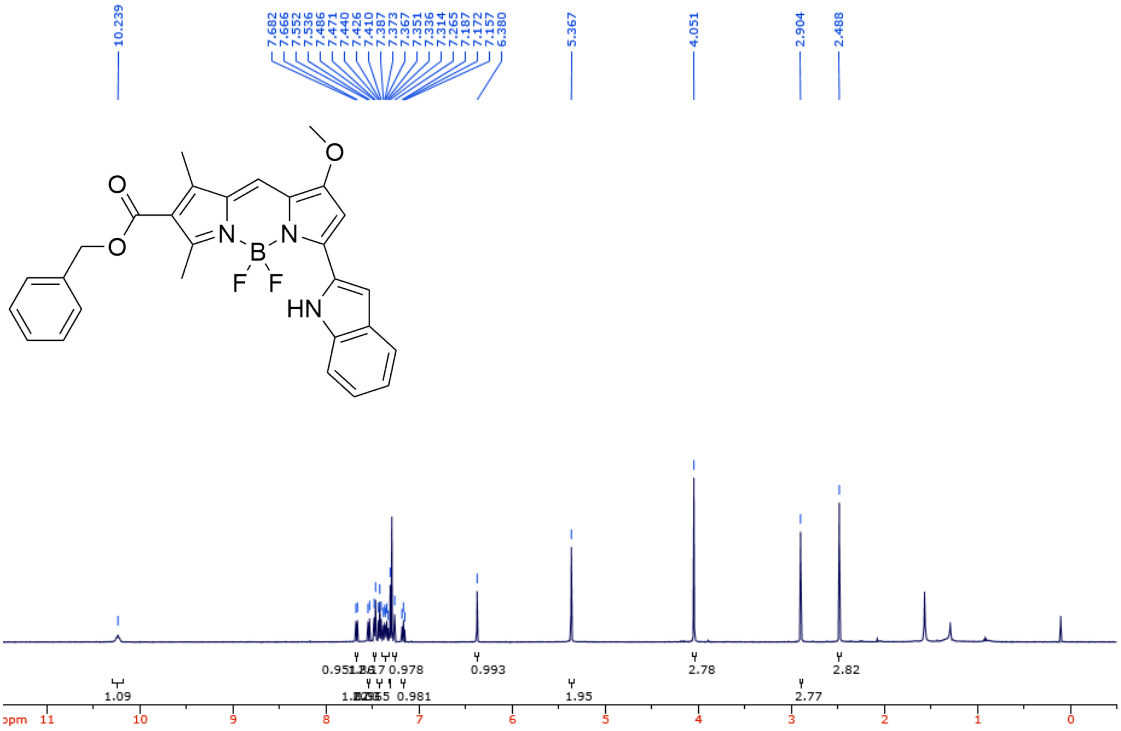


^{19}F NMR (CDCl3, 235 MHz)

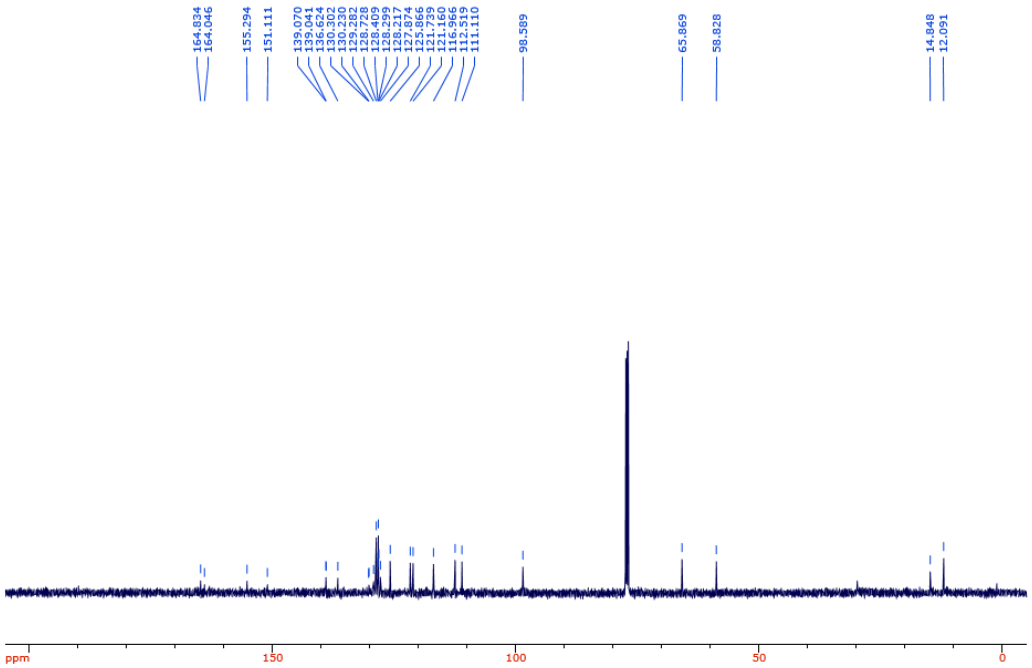


Boron, difluoro[benzyl 2-[(5-(1H-indol-2-yl)-3-methoxy-1H-pyrrol-2-yl)methylene]-3,5-dimethyl-4-pentyl-2H-pyrrol-4-carboxylate] (4r)

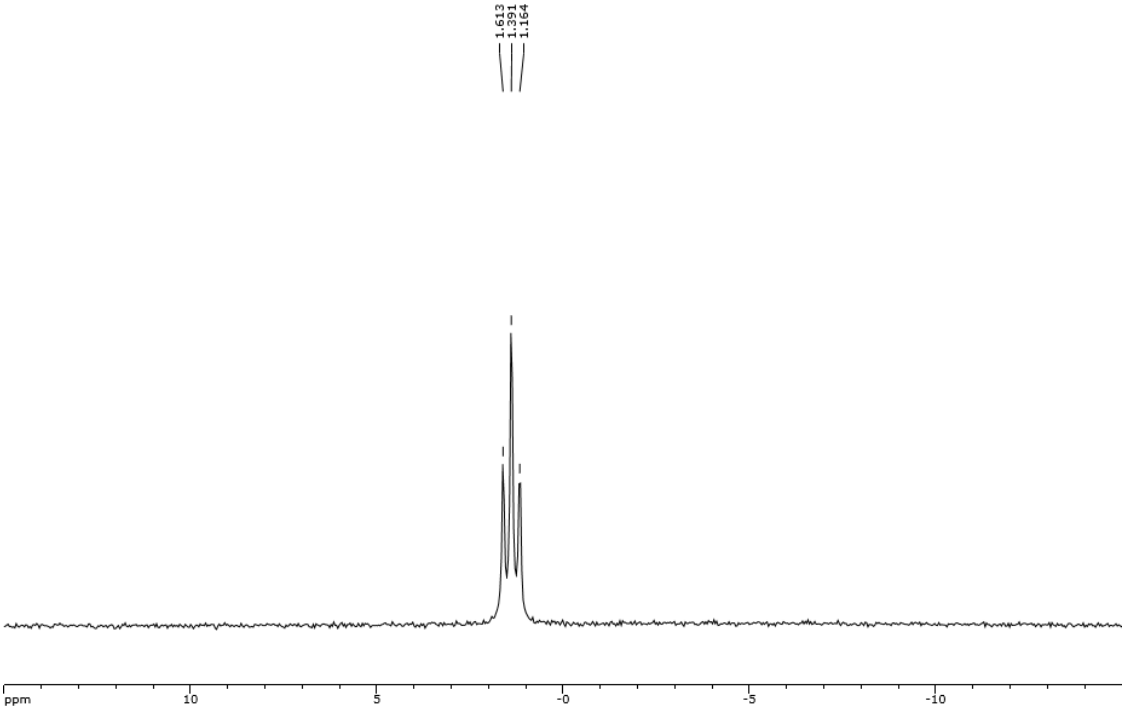
^{1}H NMR ($CDCl_3$, 500 MHz):



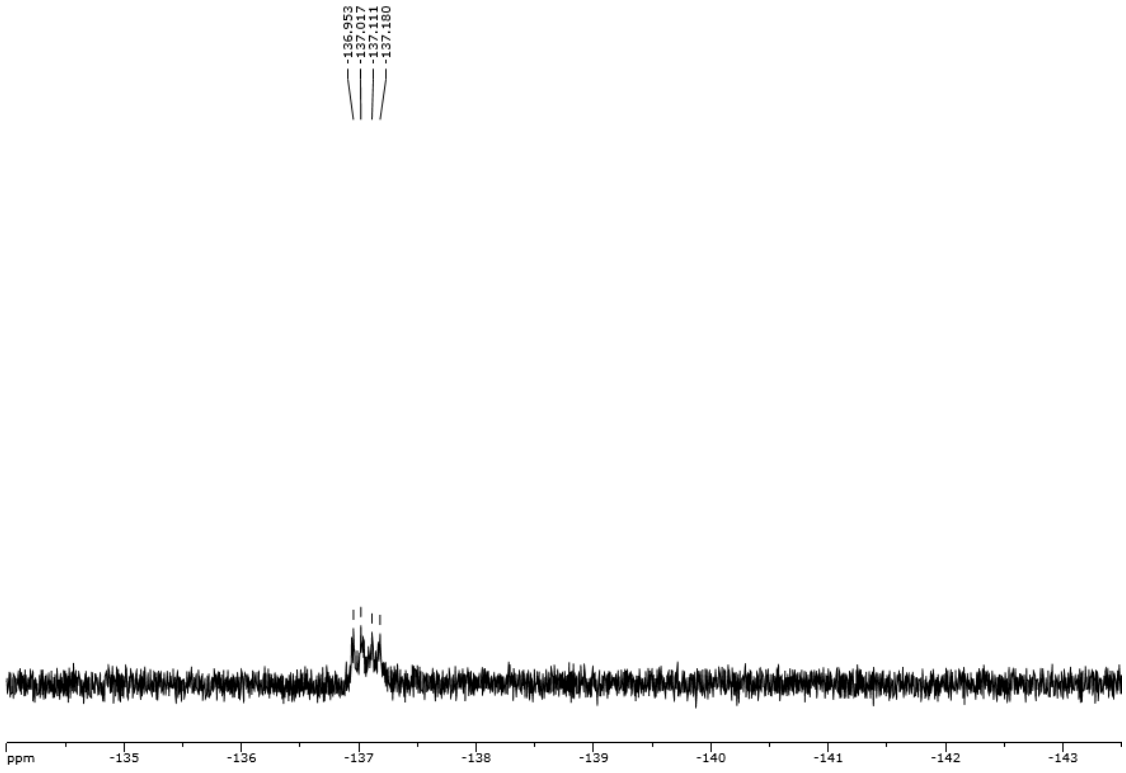
^{13}C UDEFT NMR ($CDCl_3$, 125 MHz):



^{11}B NMR ($CDCl_3$, 160 MHz)

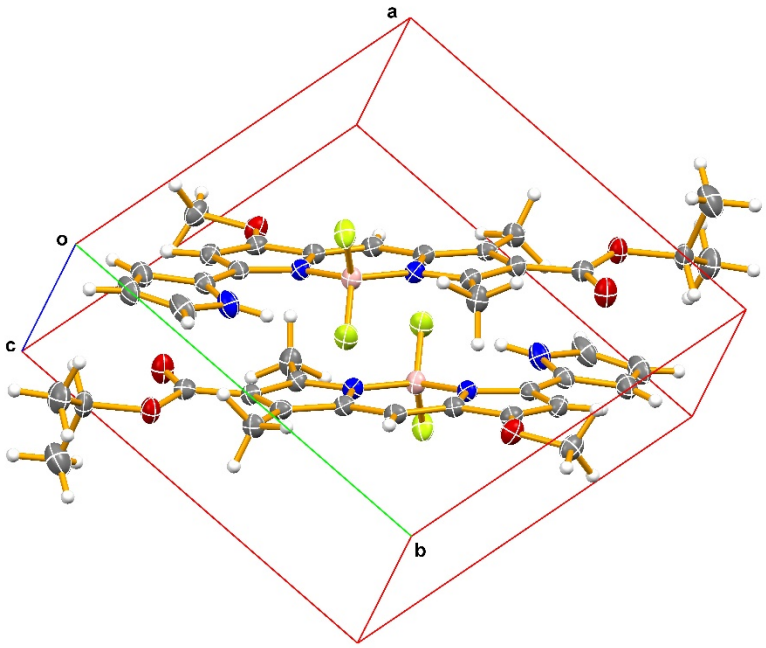


^{19}F NMR (CDCl3, 235 MHz)



Crystal data for *F*-BODIPY 2d

C_{20} H_{22} B F_2 N_3 O_3, MM = 401.21 g/mol. Clear red irregular, thin plate-like crystal, dimensions 0.03 x 0.25 x 0.30 mm; triclinic space group, P-1; a = 9.9279(4) Å, b = 10.1181(4) Å, c = 11.2898(4) Å, α = 69.506(2)°, β = 73.657(2)°, γ = 68.8943(19)°, V = 975.26(8) $Å^3$; d = 1.366 Mg/m^3, 17503 reflections (4711 unique, R_{int} = 0.0292), R = 0. 0.0412, R_w = 0.0931, GOF = 1.048. CCDC 1573487.



Absorbance and Emission Spectra

Absorbance spectra and calibration curve of 2a

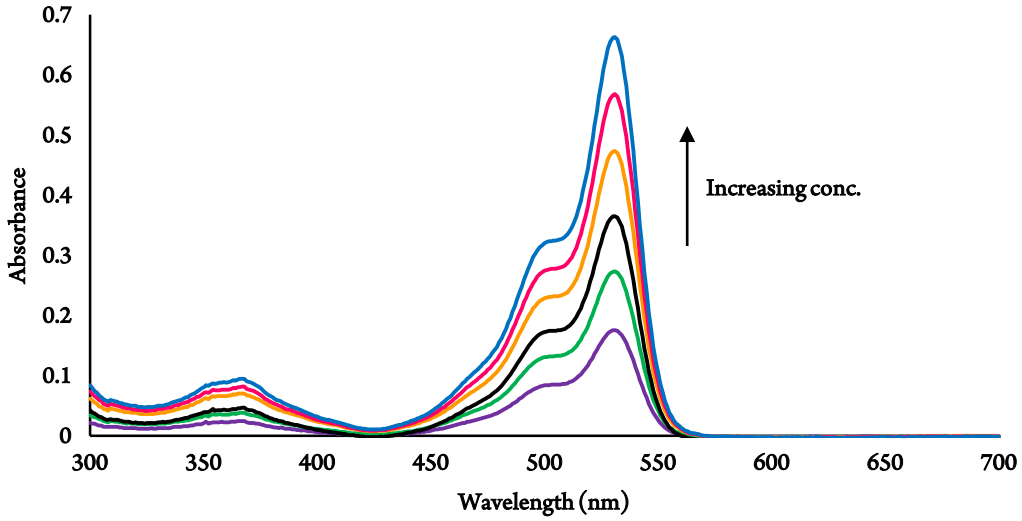


Figure S1. Absorbance spectra of **2a** over varying concentration (5-18 μM)

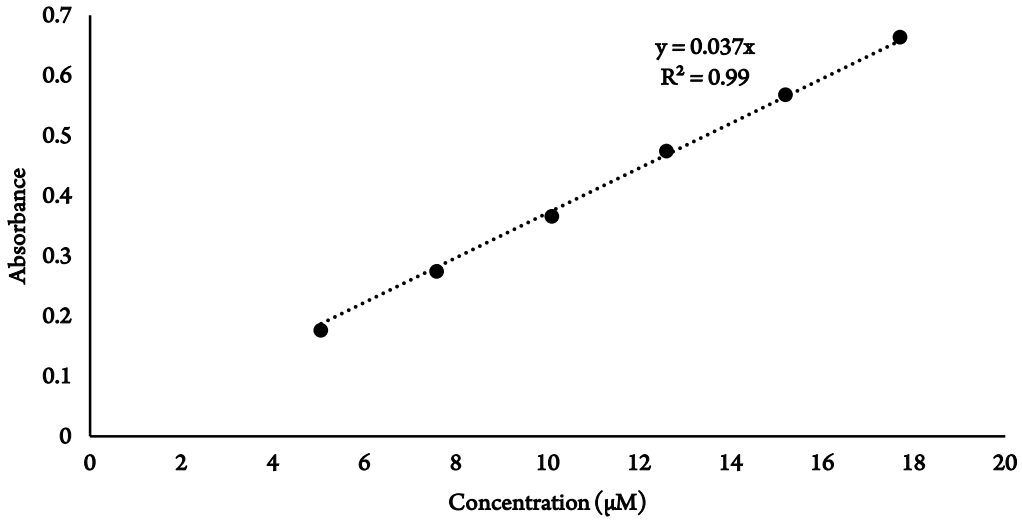


Figure S2. Calibration curve of **2a** over varying concentration (5-18 μM)

Absorbance and emission spectra of *F*-BODIPYs 2a-2l

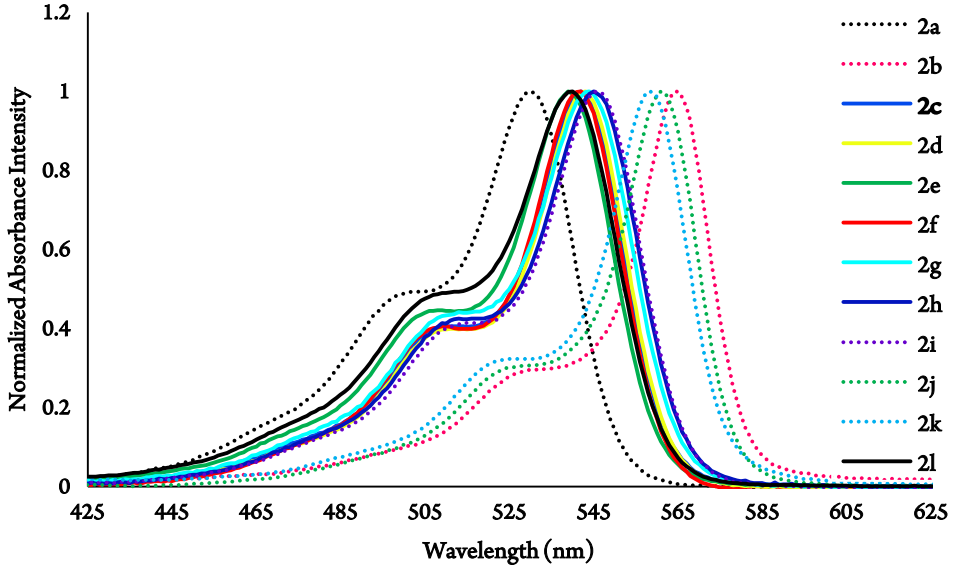


Figure S3. Normalized absorbance spectra of **2a**-**2l**

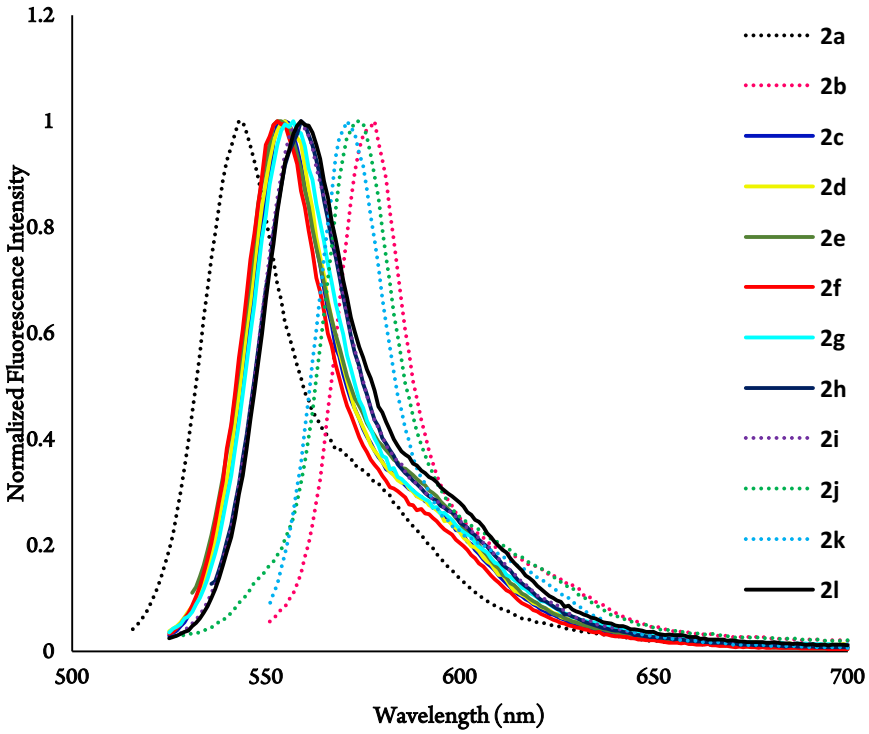


Figure S4. Normalized emission spectra of **2a-2l**

Absorbance and emission spectra of *F*-BODIPYs 3m-3p

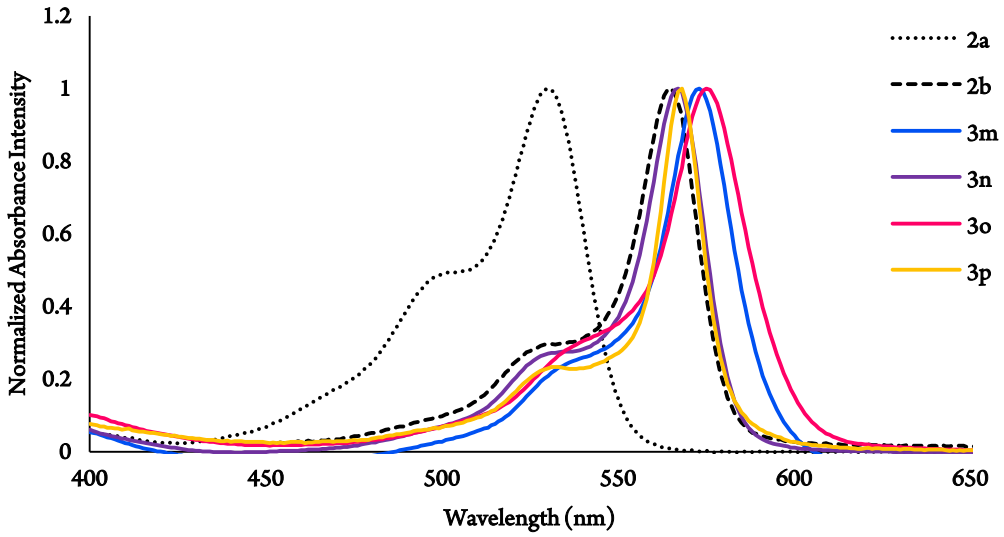


Figure S5. Absorbance spectra of **2a**, **2b** and **3m-3p**

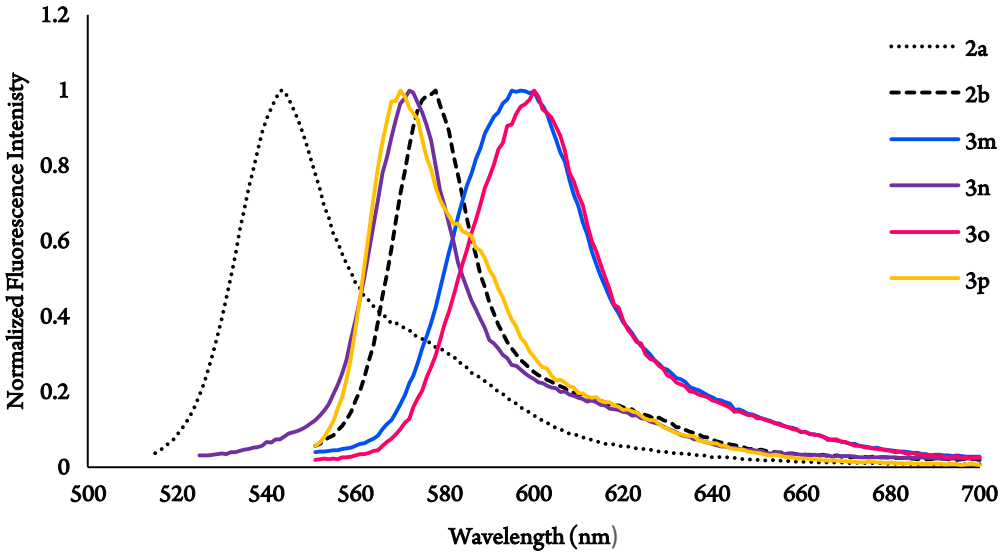


Figure S6. Emission spectra of **2a**, **2b** and **3m-3p**

Absorbance and emission spectra of *F*-BODIPYs 4q and 4r

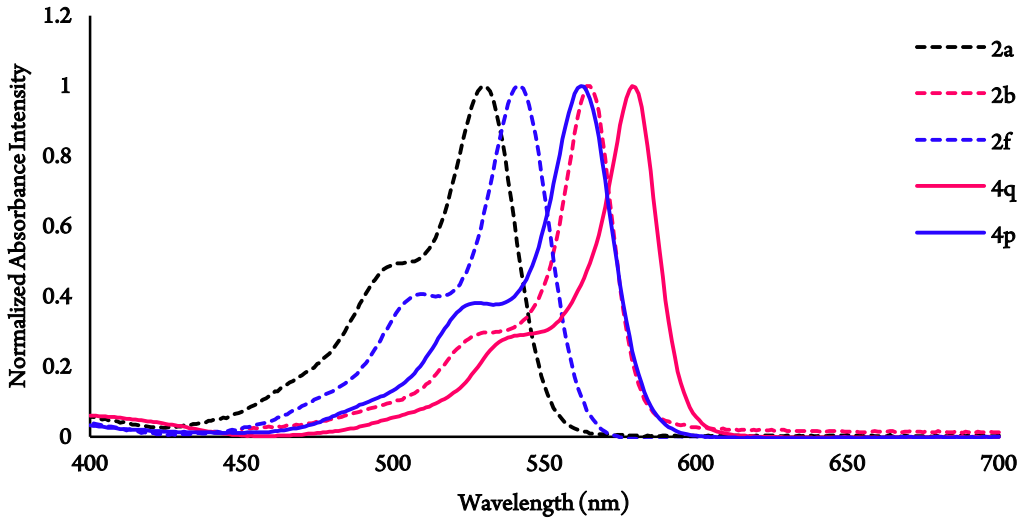


Figure S7. Normalized absorbance spectra of **2a**, **2b**, **2f**, **4q** and **4r**

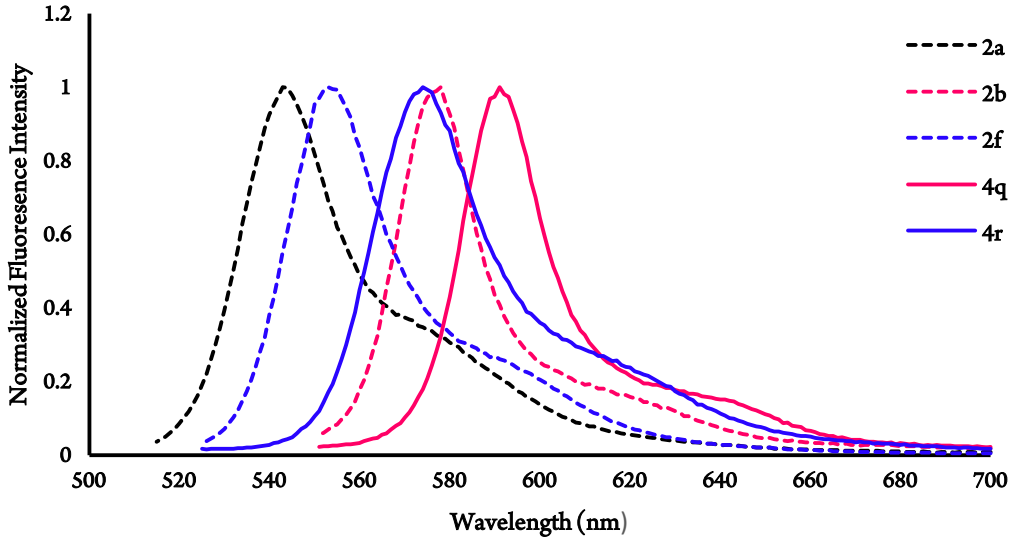


Figure S8. Normalized emission spectra of **2a**, **2b**, **2f**, **2q** and **2r**

Absorbance and emission spectra of 3p

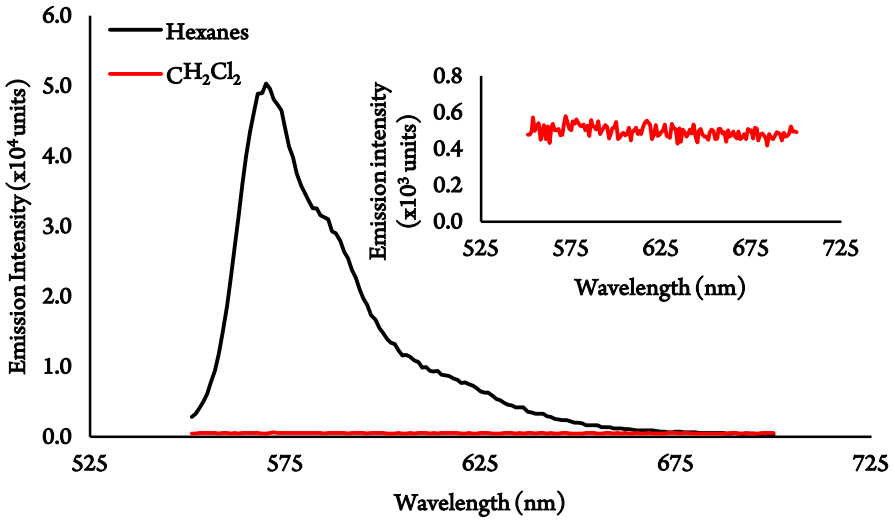


Figure S9. Emission spectra of **3p** in hexanes and CH_2Cl_2

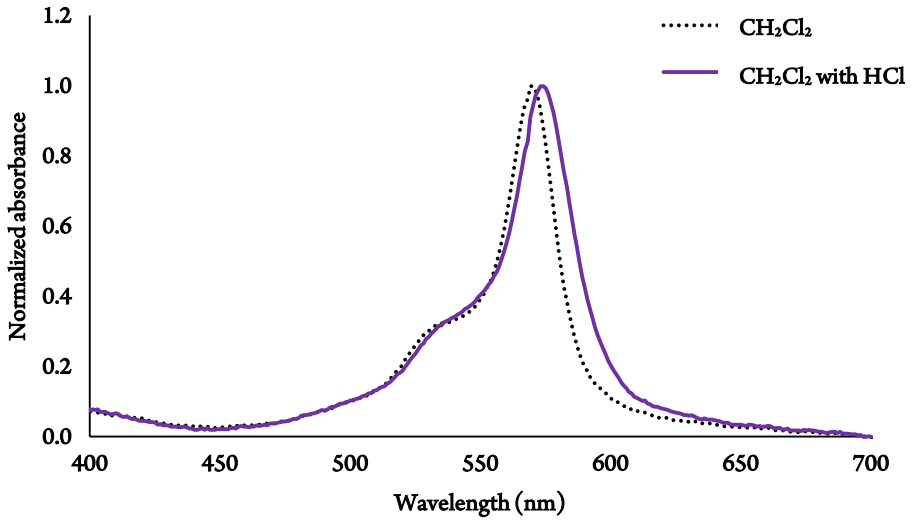


Figure S10. Absorbance spectra of **3p** in CH_2Cl_2 with and without the addition of 1M HCl

Absorbance and emission spectra of 2b **in various solvents**

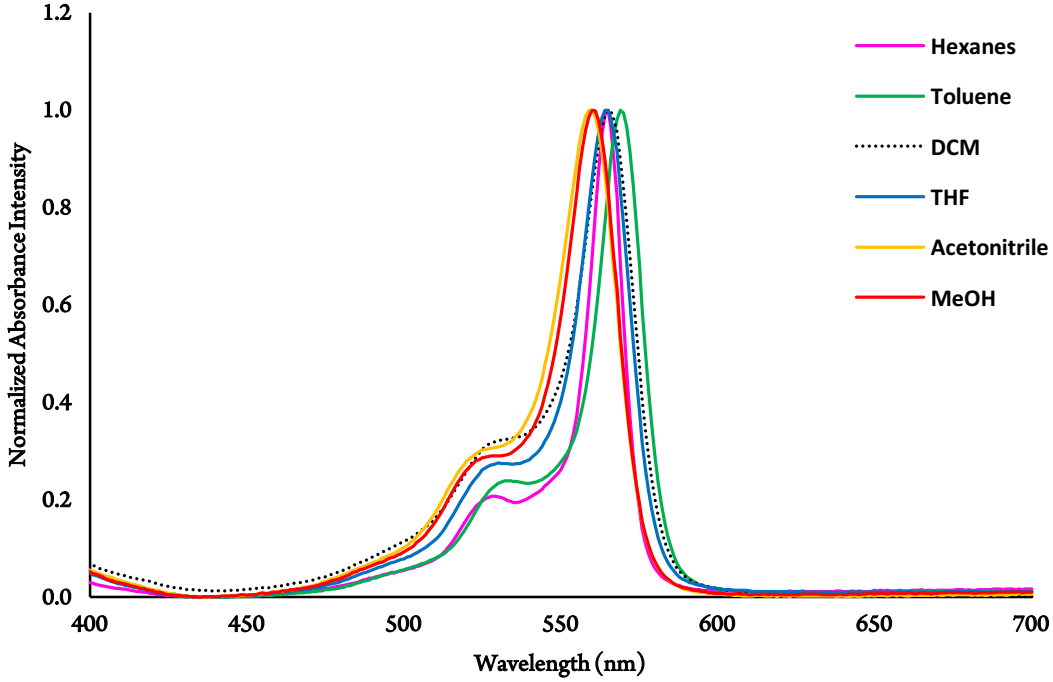


Figure S11. Absorption spectra of **2b** in various solvents

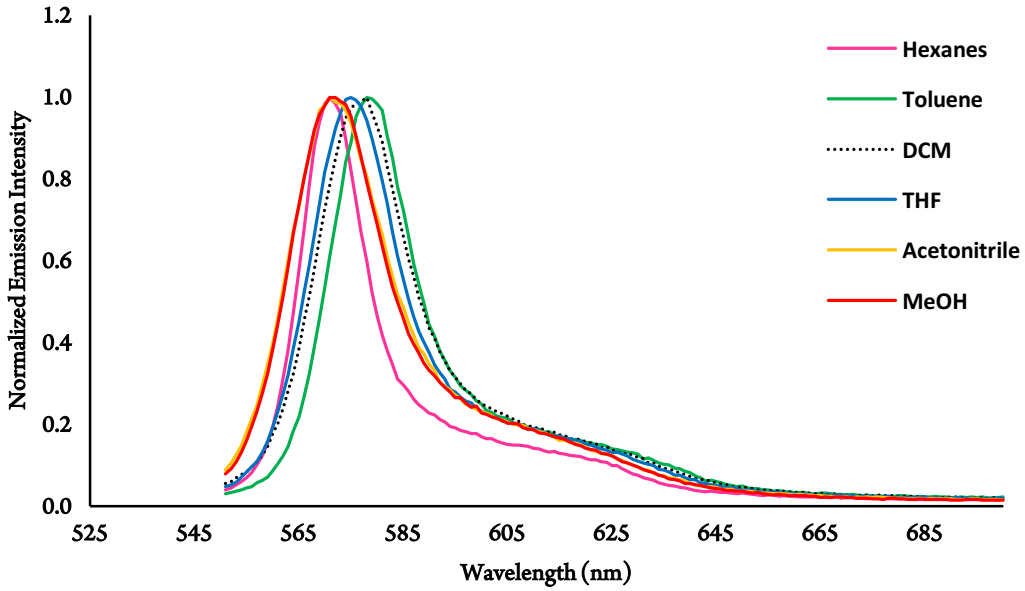


Figure S12. Emission spectra of **2b** in various solvents

Solvatochromatic photophysical data of 2b and 3m-3p

Table S1. Maximum absorption/emission wavelengths and relative quantum yield of **2b** and **3m**-**3p** in various solvents

Compound	Solvent	λ_{abs}(nm)	λ_{em} (nm)	Stokes' shift (nm)	Φ_F
2b	Hexanes	565	571	6	0.90
	Toluene	569	578	9	0.92
	CH_2Cl_2	565	578	13	0.84
	Tetrahydrofuran	565	575	10	0.95
	Acetonitrile	559	571	12	0.82
	Methanol	560	572	12	0.96
3m	Hexanes	572	589	17	0.99
	Toluene	577	594	17	0.79
	CH_2Cl_2	573	597	24	0.89
	Tetrahydrofuran	572	595	23	0.82
	Acetonitrile	567	586	19	0.81
	Methanol	568	590	22	0.78
3n	Hexanes	565	567	2	1.00
	Toluene	570	574	4	0.75
	CH_2Cl_2	566	572	6	0.98
	Tetrahydrofuran	565	570	5	0.82
	Acetonitrile	560	566	6	0.92
	Methanol	561	566	5	0.93
3o	Hexanes	575	589	14	0.78
	Toluene	581	597	16	0.60
	CH_2Cl_2	575	600	25	0.89
	Tetrahydrofuran	576	596	20	0.53
	Acetonitrile	569	592	23	0.68
	Methanol	570	592	22	0.52
3p	Hexanes	567	570	3	0.55
	Toluene	573	580	7	0.28
	CH_2Cl_2	569	-	-	-
	Tetrahydrofuran	569	591	22	0.27
	Acetonitrile	564	587	23	0.30
	Methanol	565	590	25	0.22

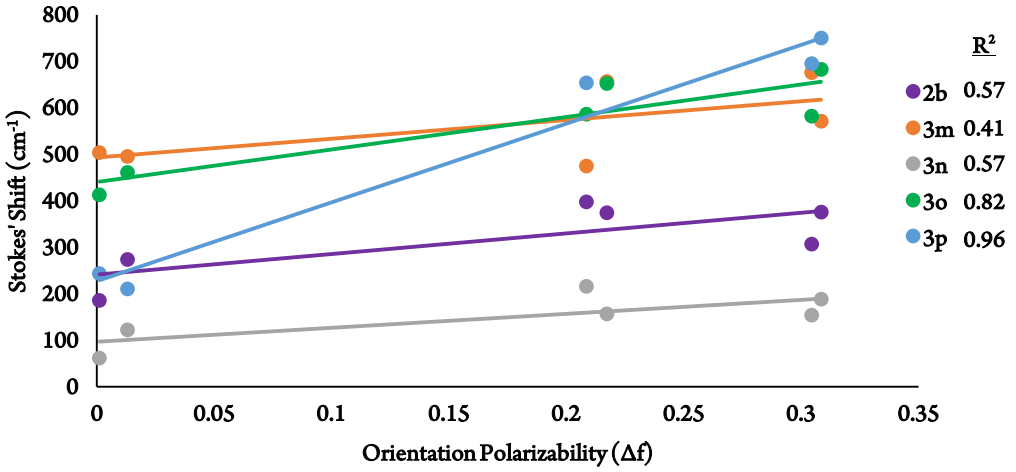


Figure S13. Lippert-Mataga Plot illustrating Stokes' Shift as a function of solvent orientation polarizability (Δf) for **2b** and **3m**-**3p**. Solvents from left-right: hexane, toluene, tetrahydrofuran, dichloromethane, acetonitrile and methanol. Dichloromethane is not represented on the plot for **3p**, as there was no measurable emission maximum for the compound in this solvent.