Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Borondifluoride complexes of hemicurcuminoids as bio-inspired push-pull dyes for bioimaging

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Supporting information

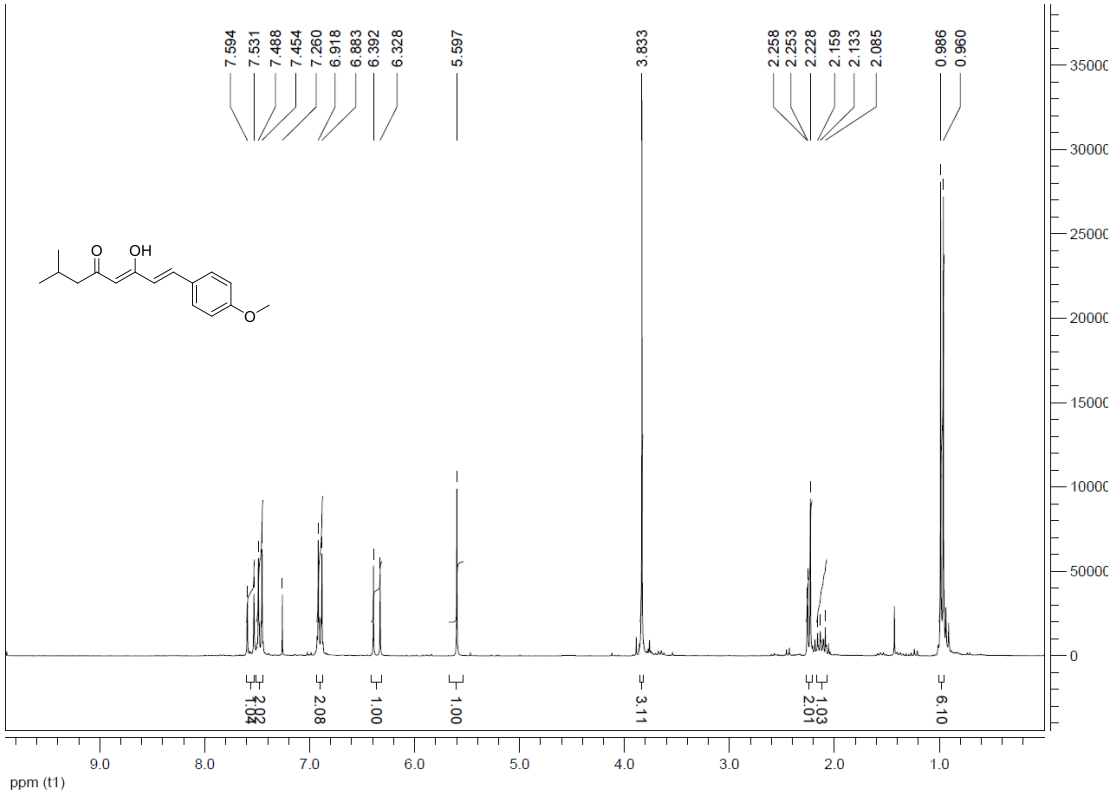


Figure NMR1. [1]H NMR spectrum of **Lig(1-iPr)** ((1E,4Z)-5-hydroxy-1-(4-methoxyphenyl)-7-methylocta-1,4-dien-3-one)

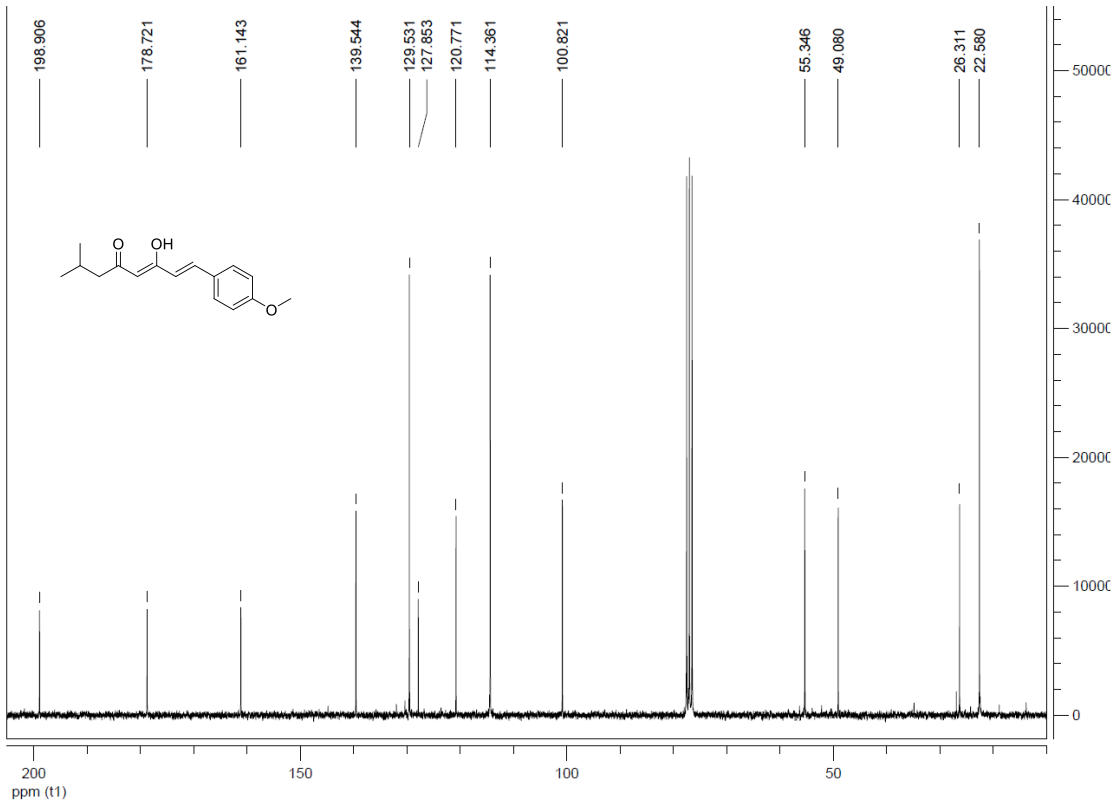


Figure NMR2. [13]C NMR spectrum of **Lig(1-iPr)** ((1E,4Z)-5-hydroxy-1-(4-methoxyphenyl)-7-methylocta-1,4-dien-3-one)

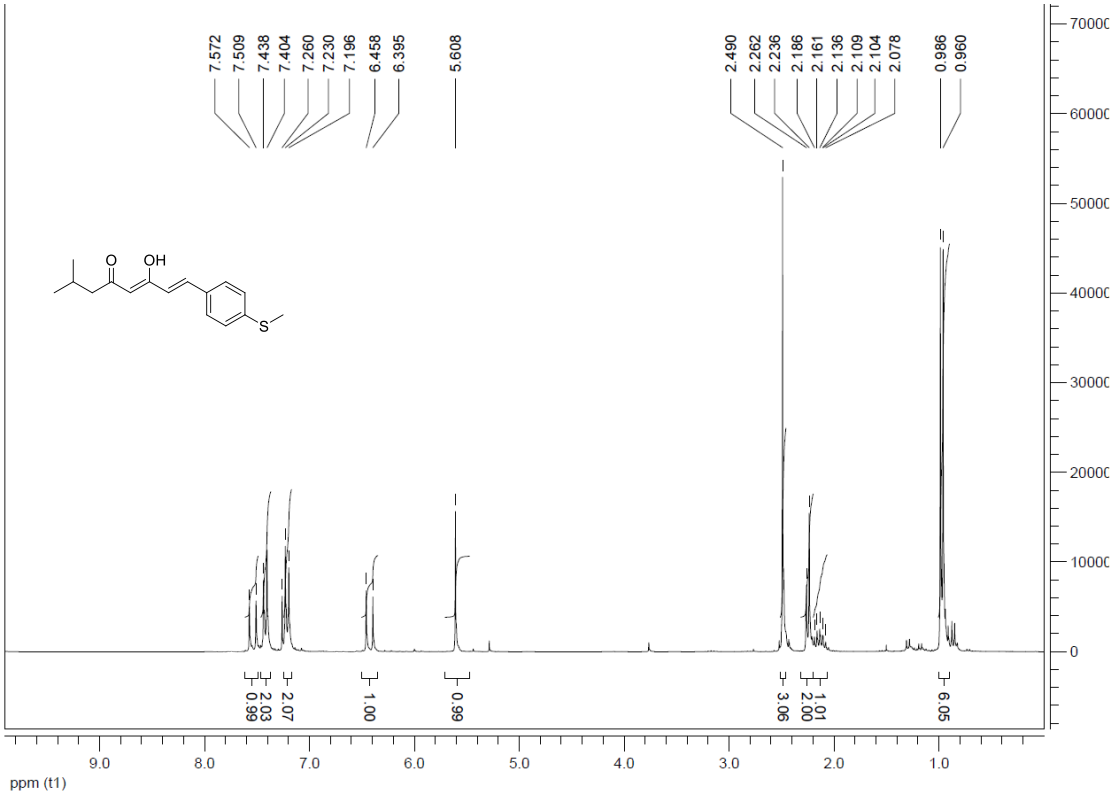


Figure NMR3. ^{1}H NMR spectrum of **Lig(2-iPr)** ((1E,4Z)-5-hydroxy-7-methyl-1-(4-(methylthio)phenyl)octa-1,4-dien-3-one)

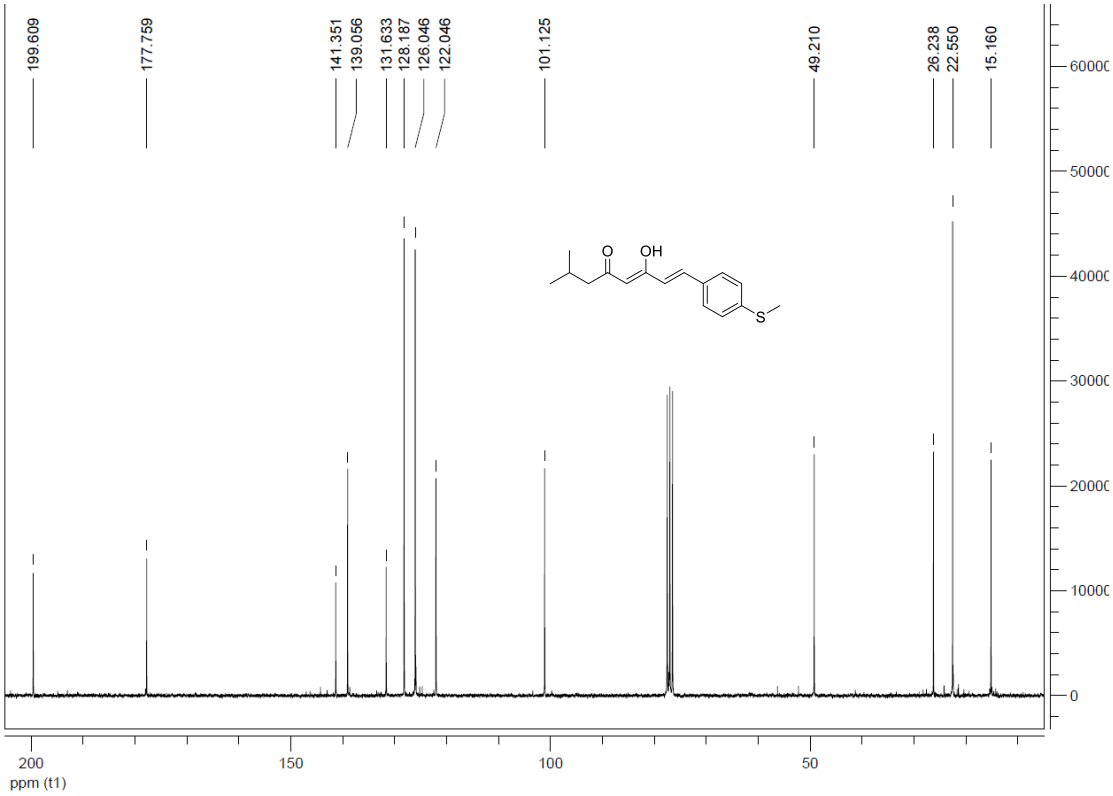


Figure NMR4. ^{13}C NMR spectrum of **Lig(2-iPr)** ((1E,4Z)-5-hydroxy-7-methyl-1-(4-(methylthio)phenyl)octa-1,4-dien-3-one)

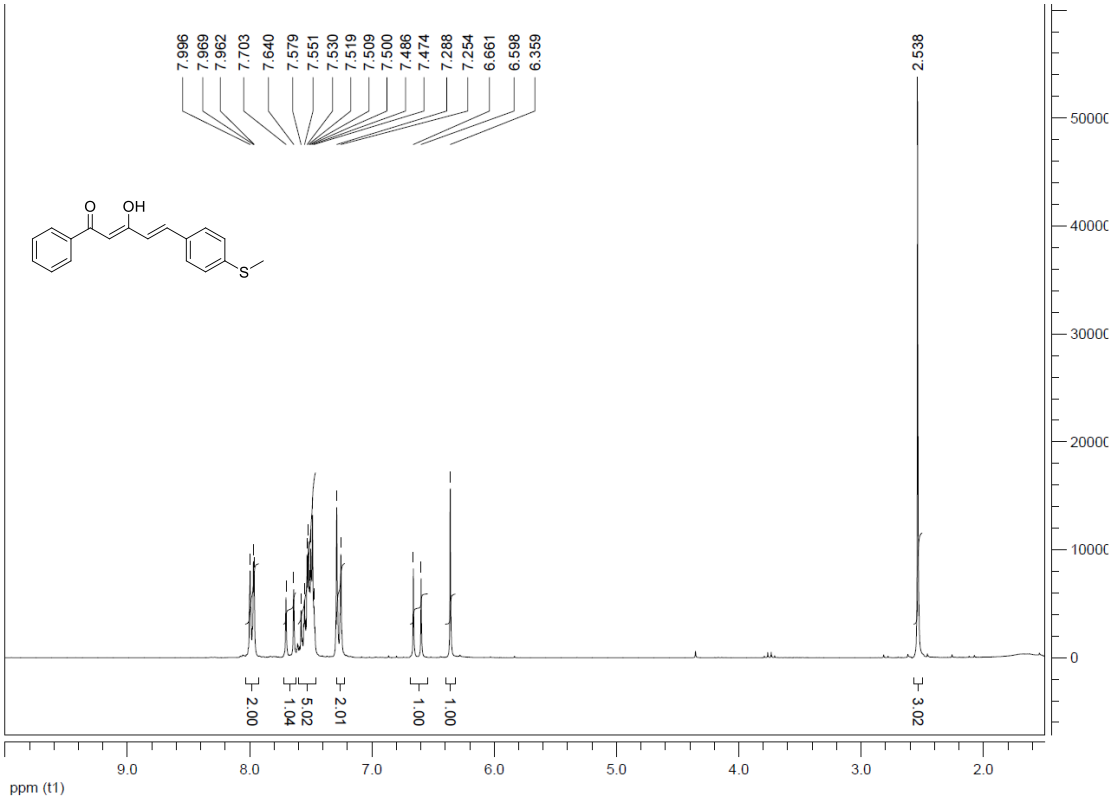


Figure NMR5. ^{1}H NMR spectrum of **Lig(2-Ph)** ((1Z,4E)-1-hydroxy-5-(4-(methylthio)phenyl)-1-phenylpenta-1,4-dien-3-one)

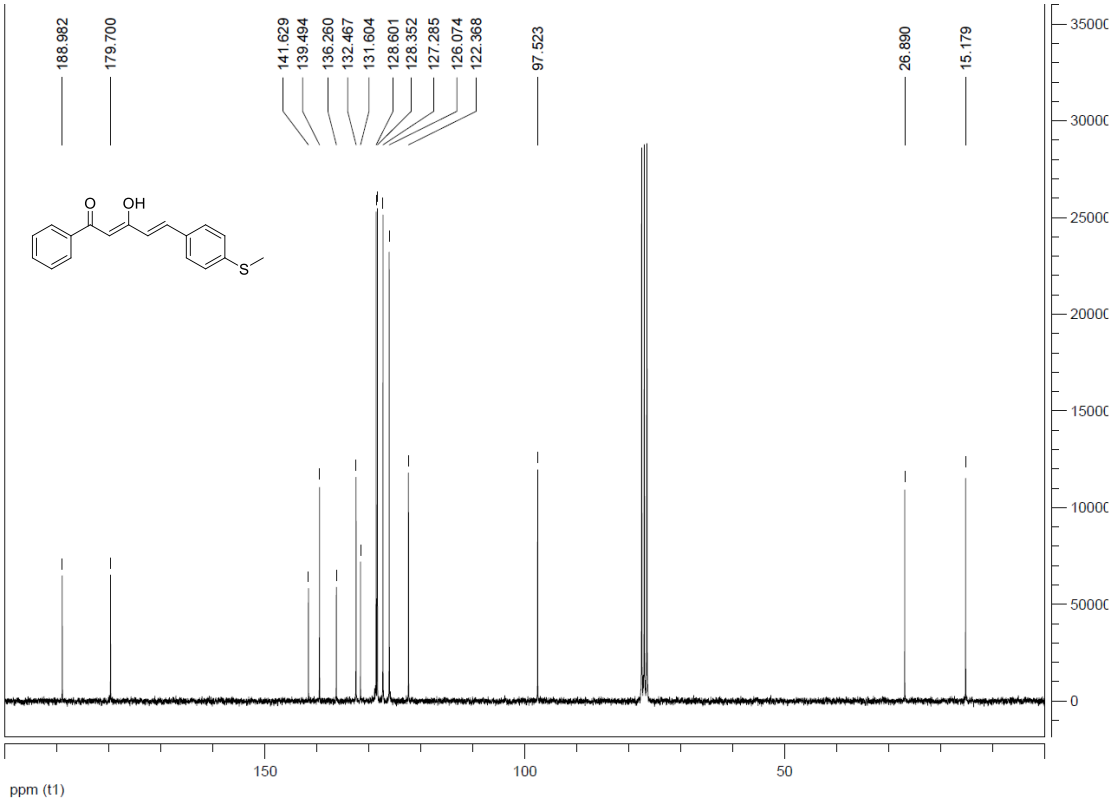


Figure NMR6. ^{13}C NMR spectrum of **Lig(2-Ph)** ((1Z,4E)-1-hydroxy-5-(4-(methylthio)phenyl)-1-phenylpenta-1,4-dien-3-one)

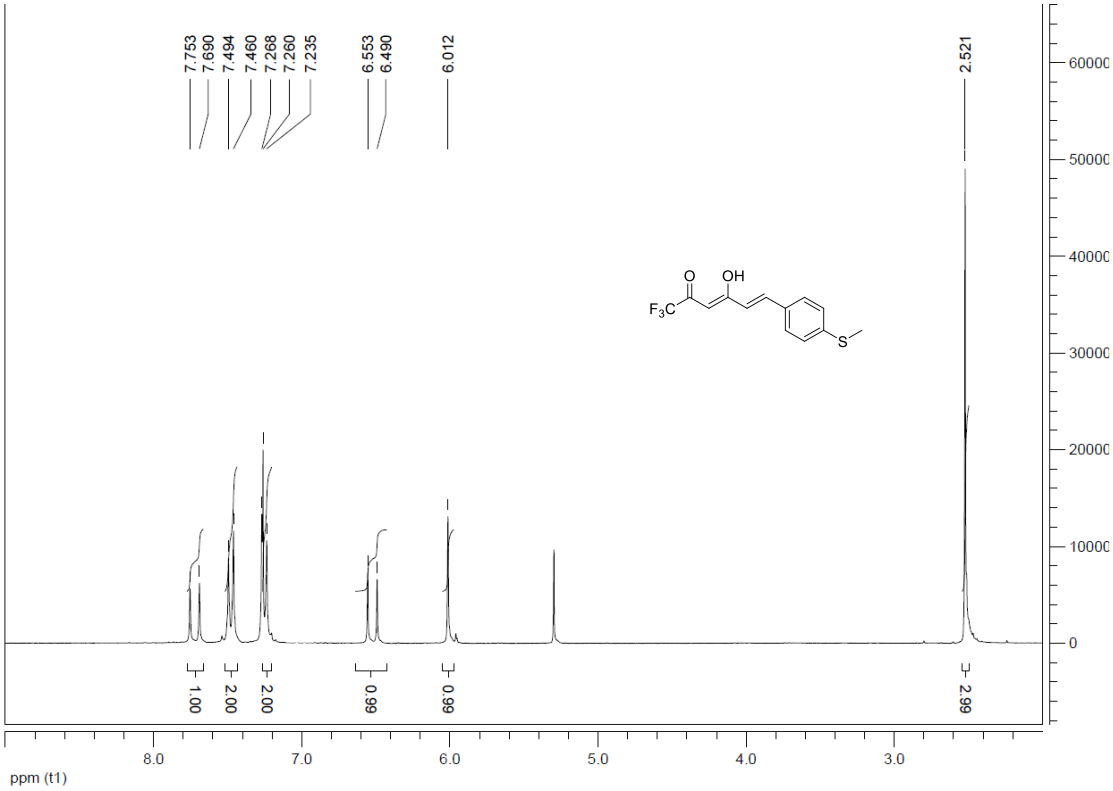


Figure NMR7. ^{1}H NMR spectrum of **Lig(2-CF$_3$)** ((1E,4Z)-6,6,6-trifluoro-5-hydroxy-1-(4-(methylthio)phenyl)hexa-1,4-dien-3-one)

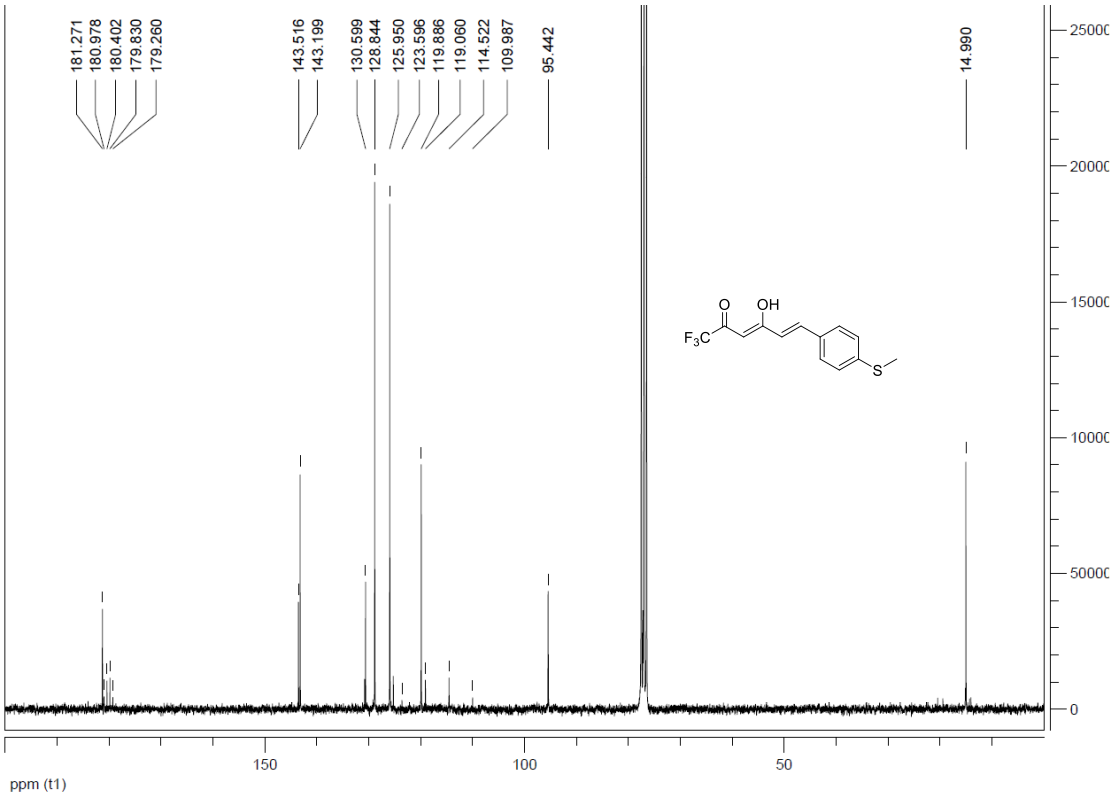


Figure NMR8. ^{13}C NMR spectrum of **Lig(2-CF$_3$)** ((1E,4Z)-6,6,6-trifluoro-5-hydroxy-1-(4-(methylthio)phenyl)hexa-1,4-dien-3-one)

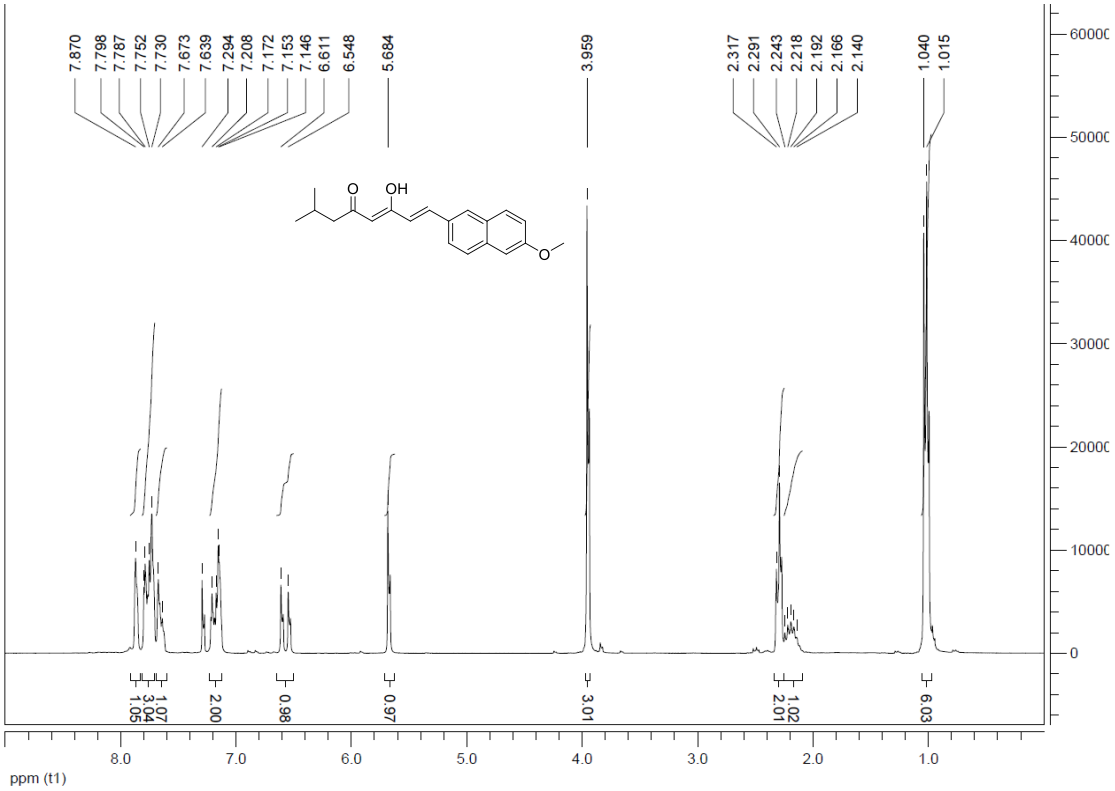


Figure NMR9. ^{1}H NMR spectrum of **Lig(3-iPr)** ((1E,4Z)-5-hydroxy-1-(6-methoxynaphthalen-2-yl)-7-methylocta-1,4-dien-3-one)

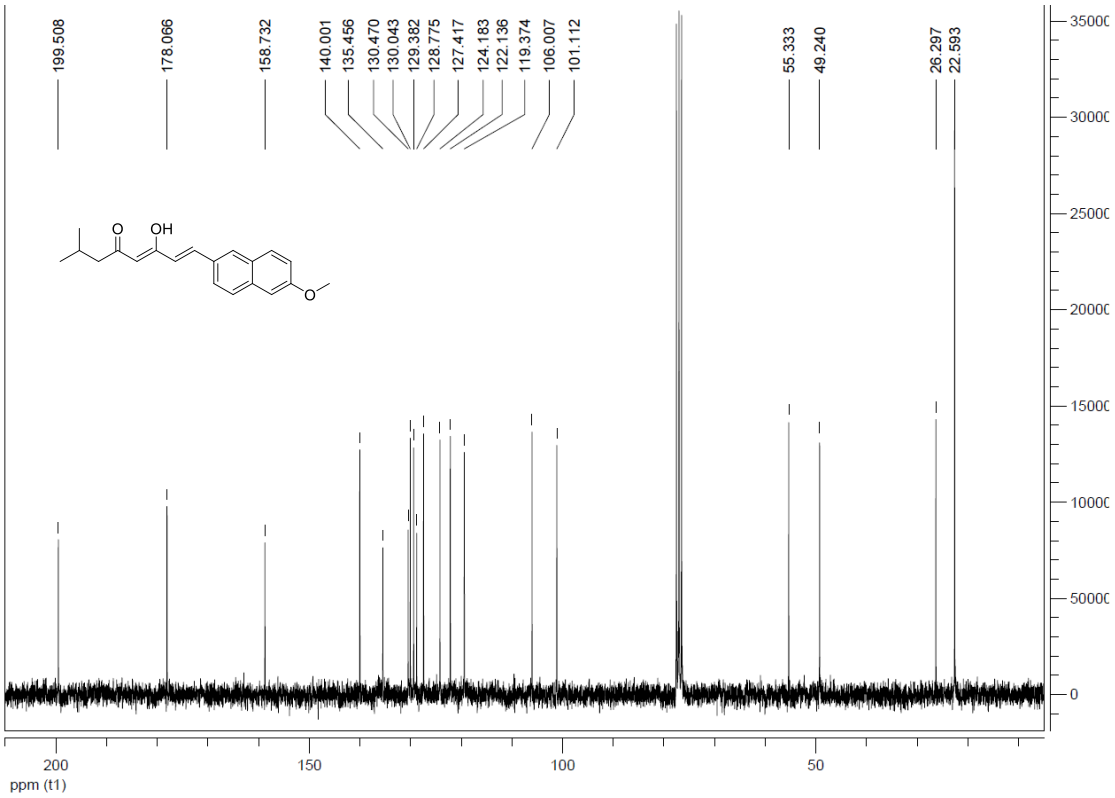


Figure NMR10. ^{13}C NMR spectrum of **Lig(3-iPr)** ((1E,4Z)-5-hydroxy-1-(6-methoxynaphthalen-2-yl)-7-methylocta-1,4-dien-3-one)

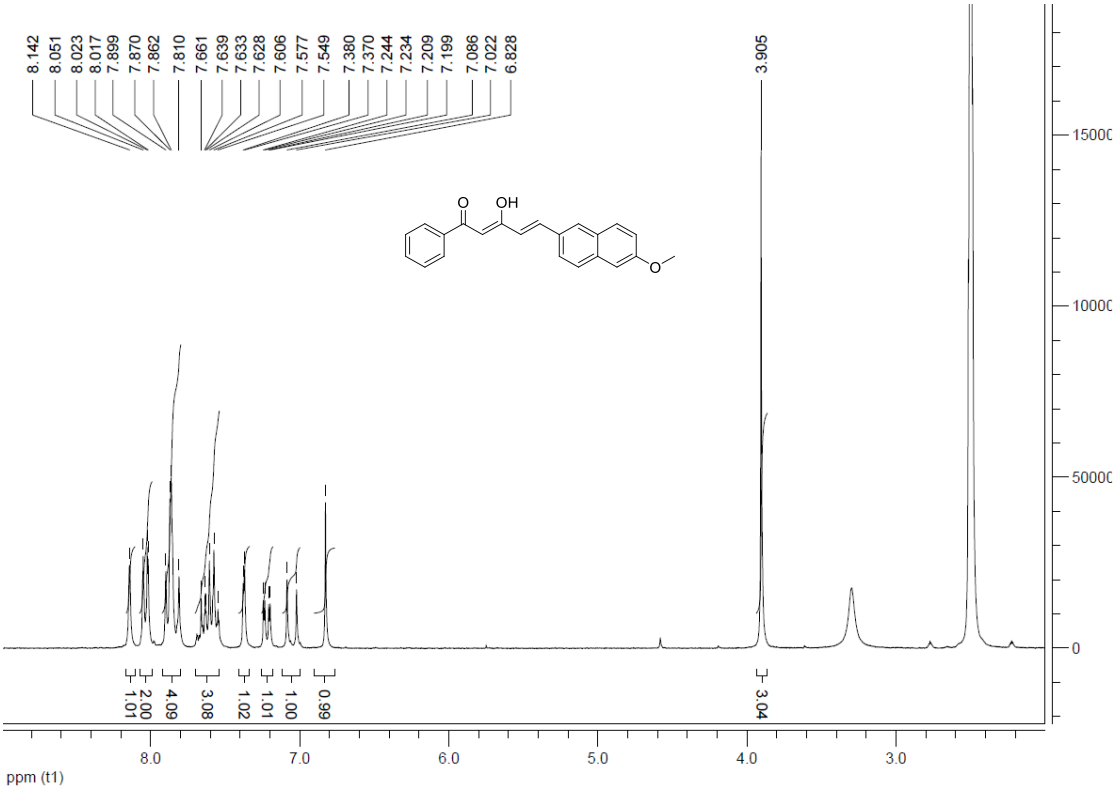


Figure NMR11. ^{1}H NMR spectrum of **Lig(3-Ph)** ((1Z,4E)-1-hydroxy-5-(6-methoxynaphthalen-2-yl)-1-phenylpenta-1,4-dien-3-one)

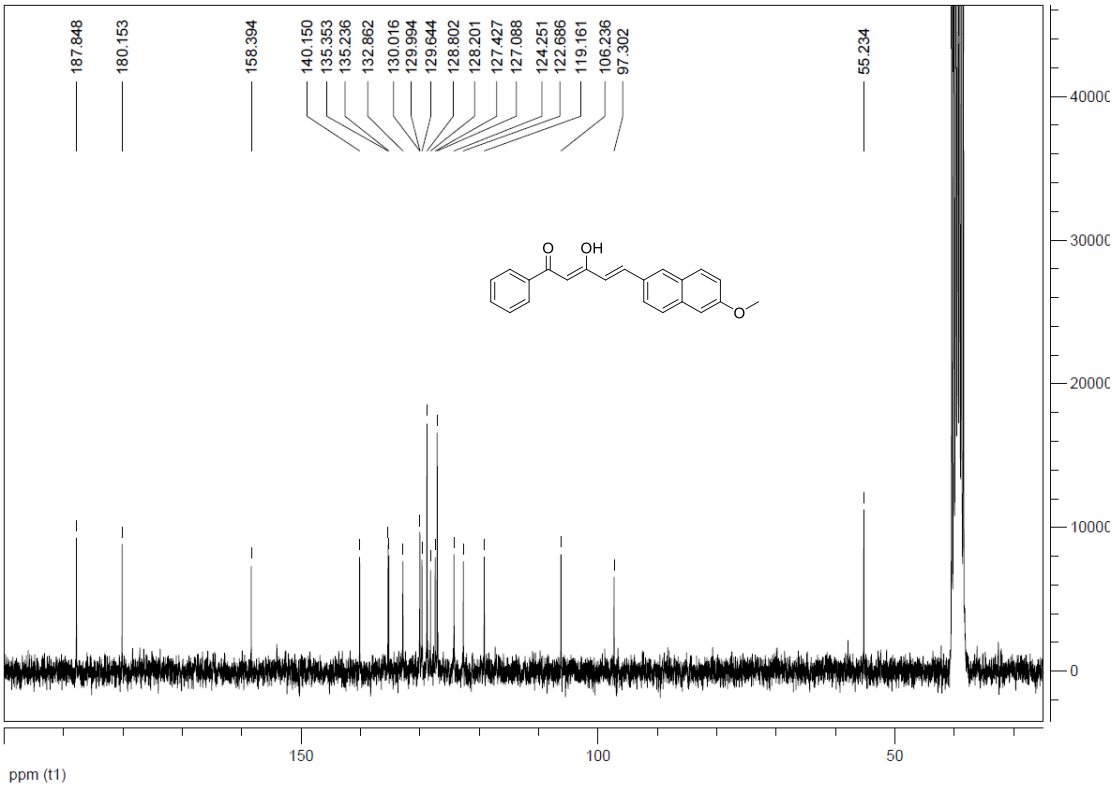


Figure NMR12. ^{13}C NMR spectrum of **Lig(3-Ph)** ((1Z,4E)-1-hydroxy-5-(6-methoxynaphthalen-2-yl)-1-phenylpenta-1,4-dien-3-one)

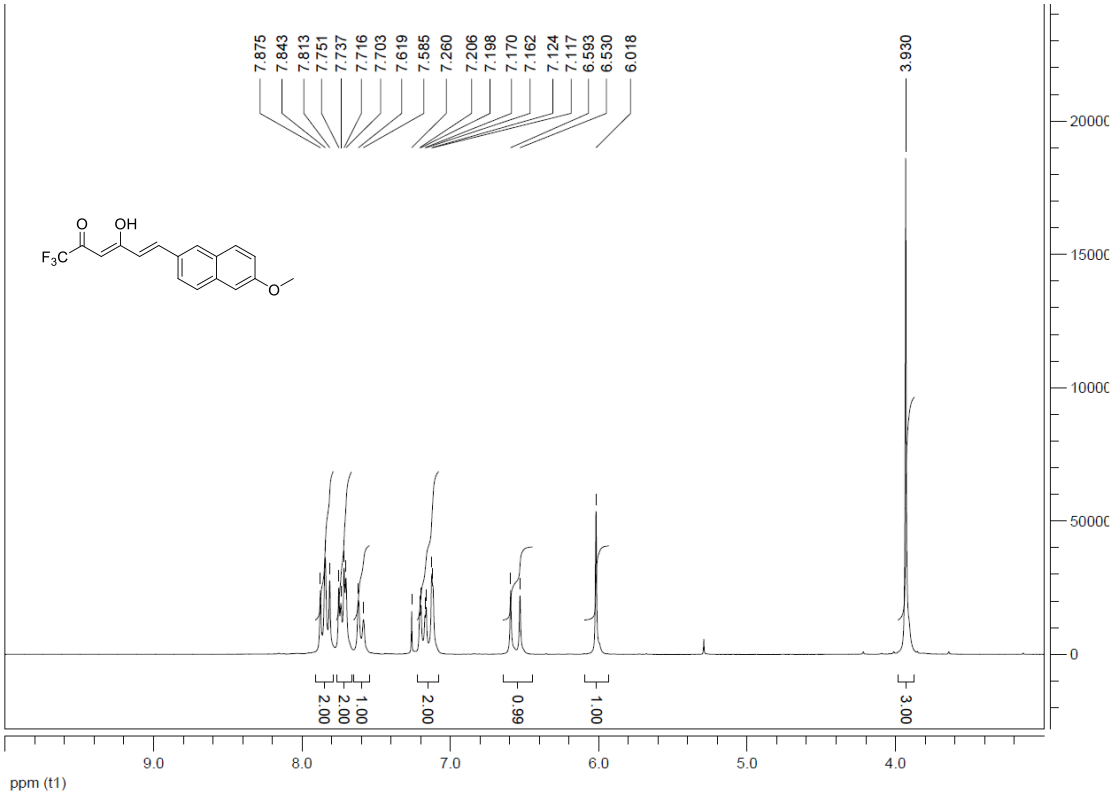


Figure NMR13. ^{1}H NMR spectrum of **Lig(3-CF$_3$)** ((1E,4Z)-6,6,6-trifluoro-5-hydroxy-1-(6-methoxynaphthalen-2-yl)hexa-1,4-dien-3-one)

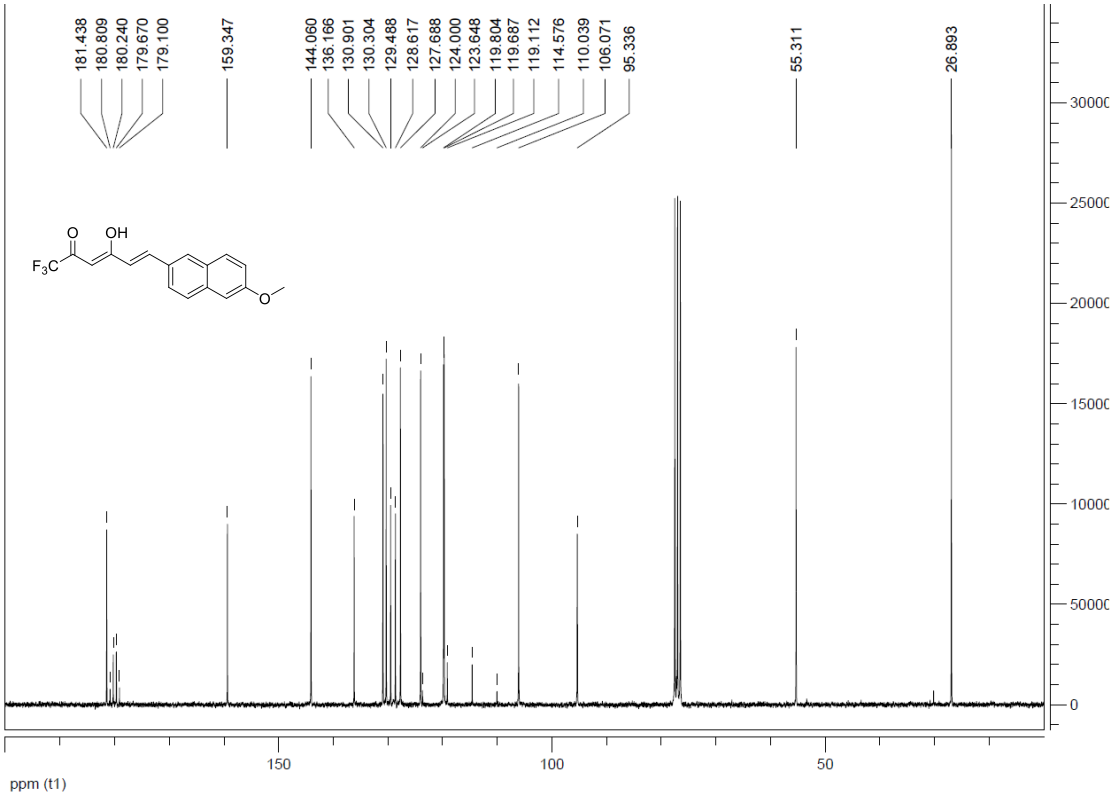


Figure NMR14. ^{13}C NMR spectrum of **Lig(3-CF$_3$)** ((1E,4Z)-6,6,6-trifluoro-5-hydroxy-1-(6-methoxynaphthalen-2-yl)hexa-1,4-dien-3-one)

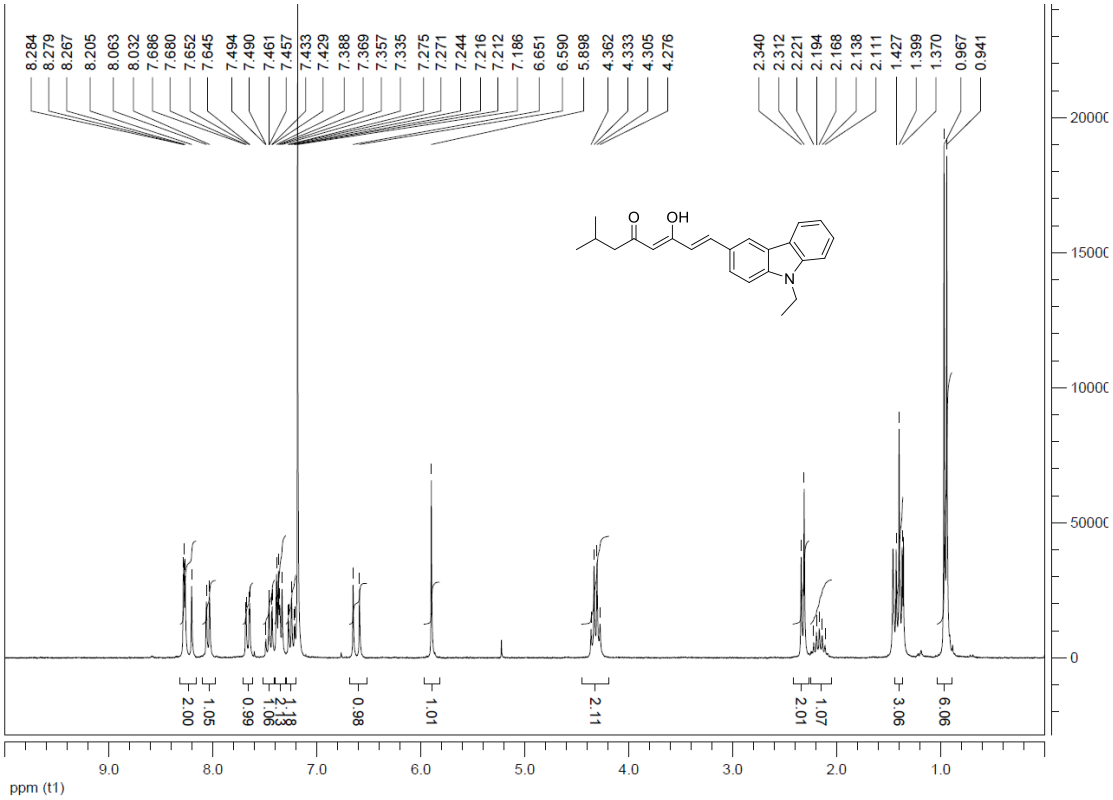


Figure NMR15. ^{1}H NMR spectrum of **Lig(4-iPr)** ((1E,4Z)-1-(9-ethyl-9H-carbazol-3-yl)-5-hydroxy-7-methylocta-1,4-dien-3-one)

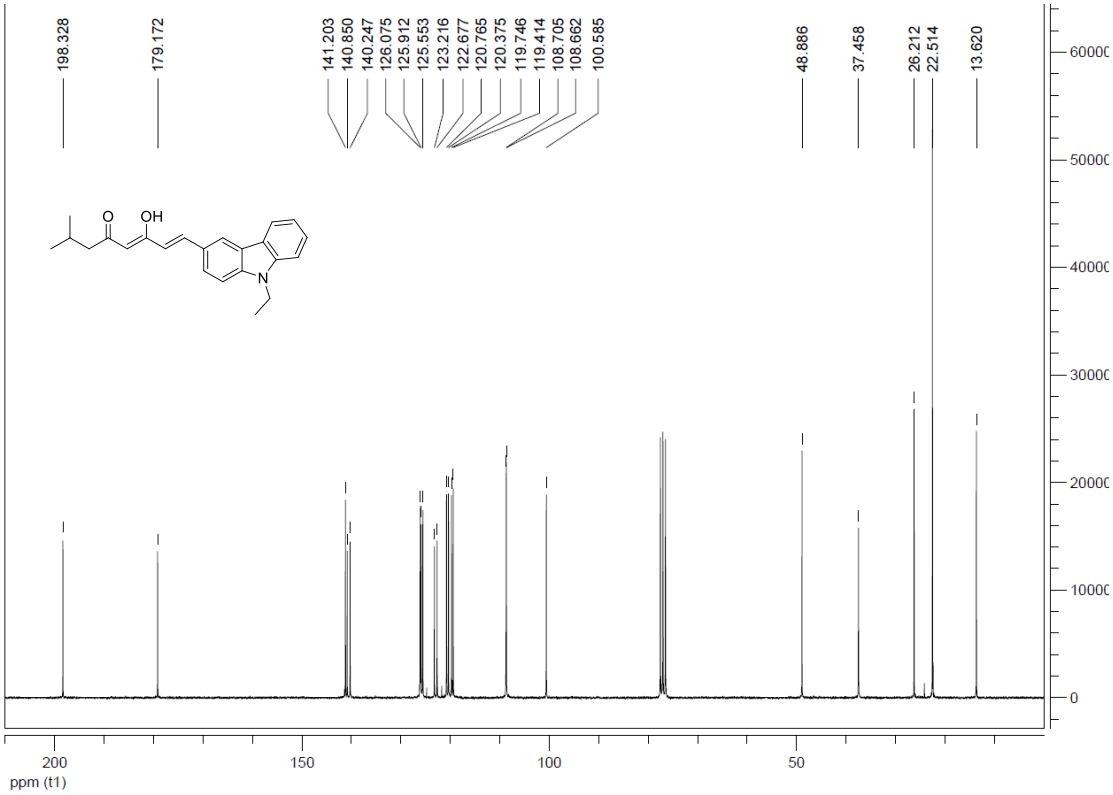


Figure NMR16. ^{13}C NMR spectrum of **Lig(4-iPr)** ((1E,4Z)-1-(9-ethyl-9H-carbazol-3-yl)-5-hydroxy-7-methylocta-1,4-dien-3-one)

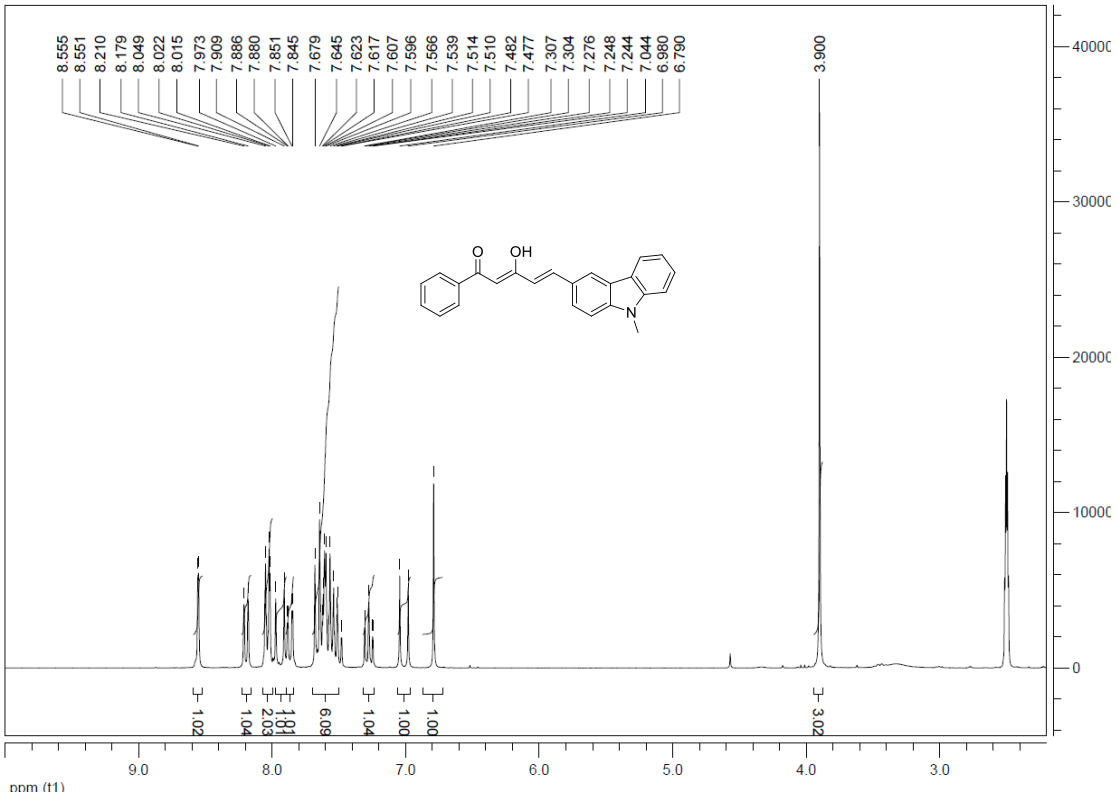


Figure NMR17. ^{1}H NMR spectrum of **Lig(4-Ph)** ((1Z,4E)-1-hydroxy-5-(9-methyl-9H-carbazol-3-yl)-1-phenylpenta-1,4-dien-3-one)

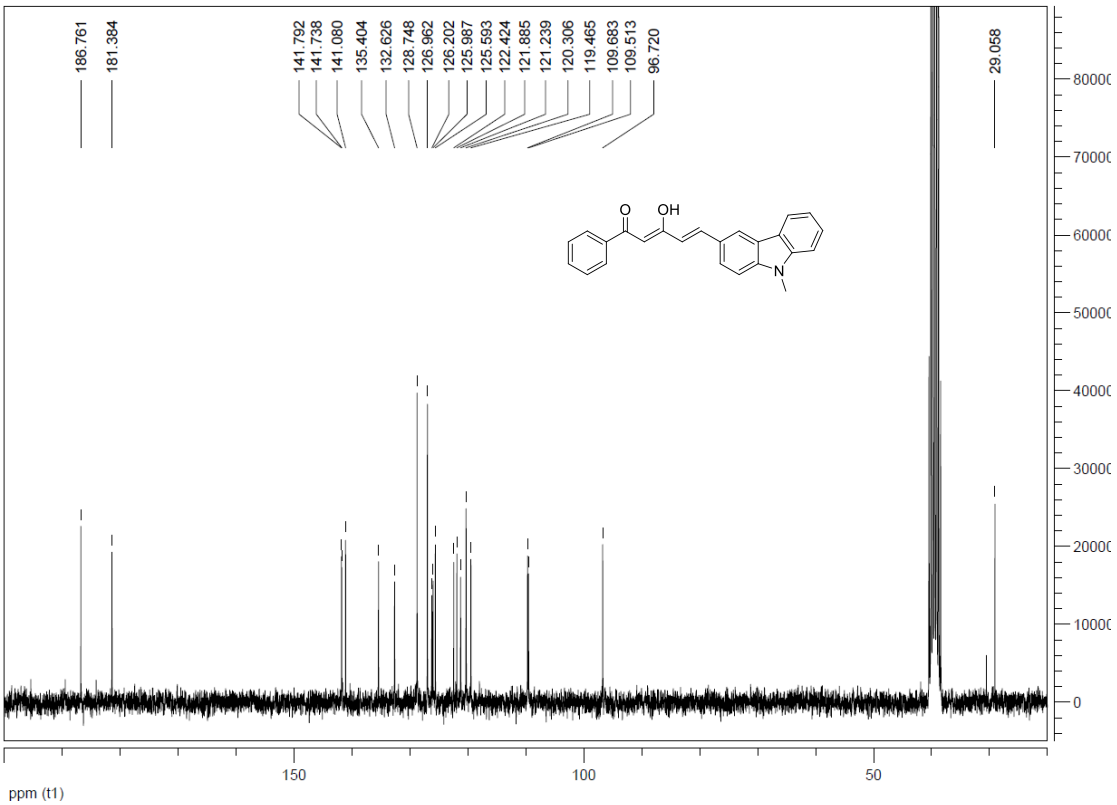


Figure NMR18. ^{13}C NMR spectrum of **Lig(4-Ph)** ((1Z,4E)-1-hydroxy-5-(9-methyl-9H-carbazol-3-yl)-1-phenylpenta-1,4-dien-3-one)

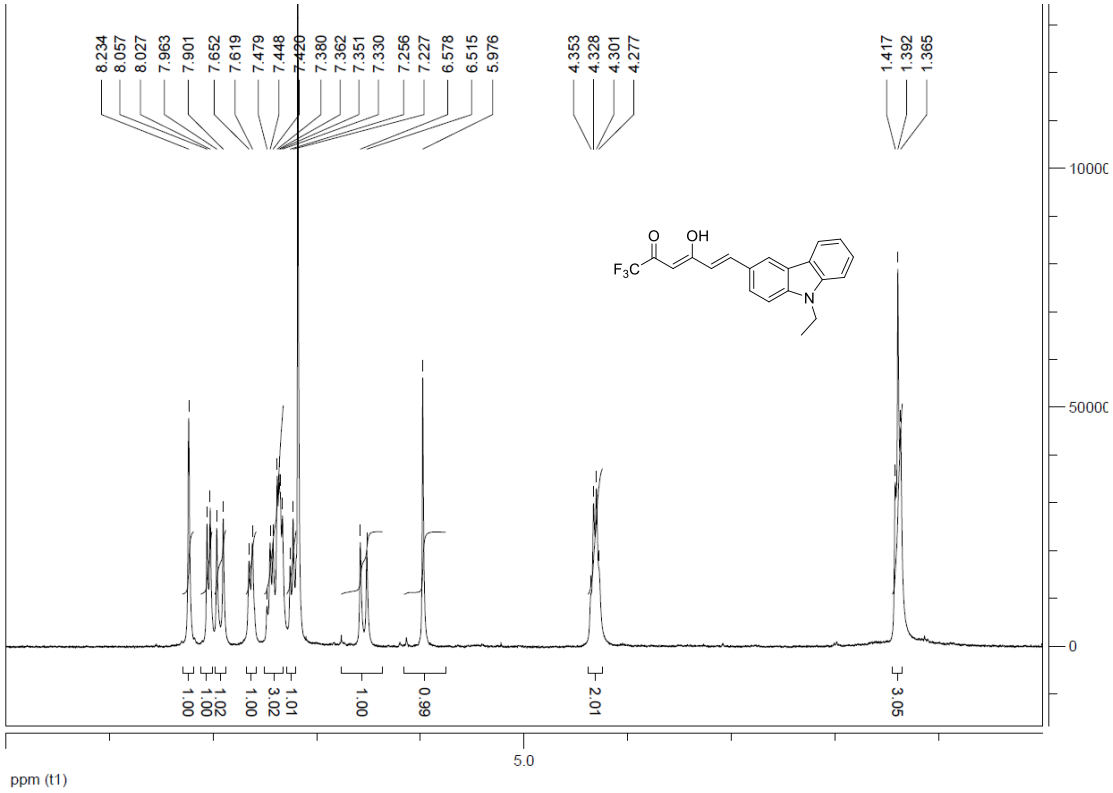


Figure NMR19. ^{1}H NMR spectrum of **Lig(4-CF$_3$)** ((1E,4Z)-1-(9-ethyl-9H-carbazol-3-yl)-6,6,6-trifluoro-5-hydroxyhexa-1,4-dien-3-one)

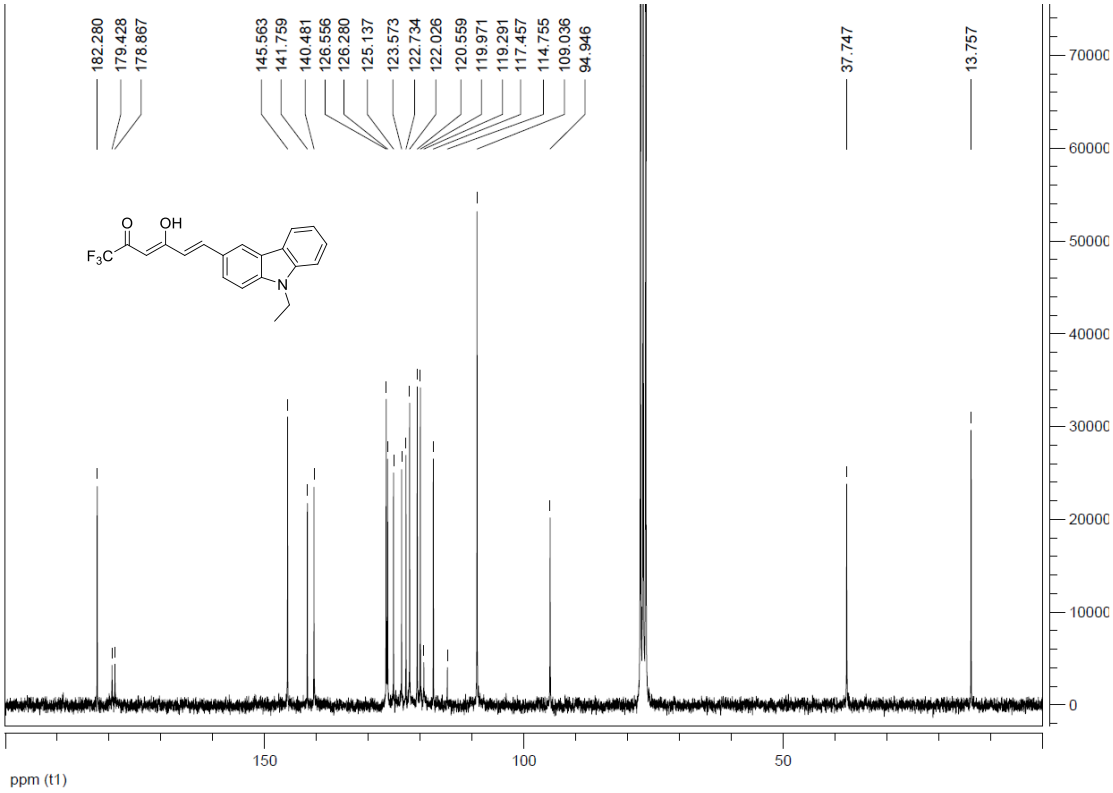


Figure NMR20. ^{13}C NMR spectrum of **Lig(4-CF$_3$)** ((1E,4Z)-1-(9-ethyl-9H-carbazol-3-yl)-6,6,6-trifluoro-5-hydroxyhexa-1,4-dien-3-one)

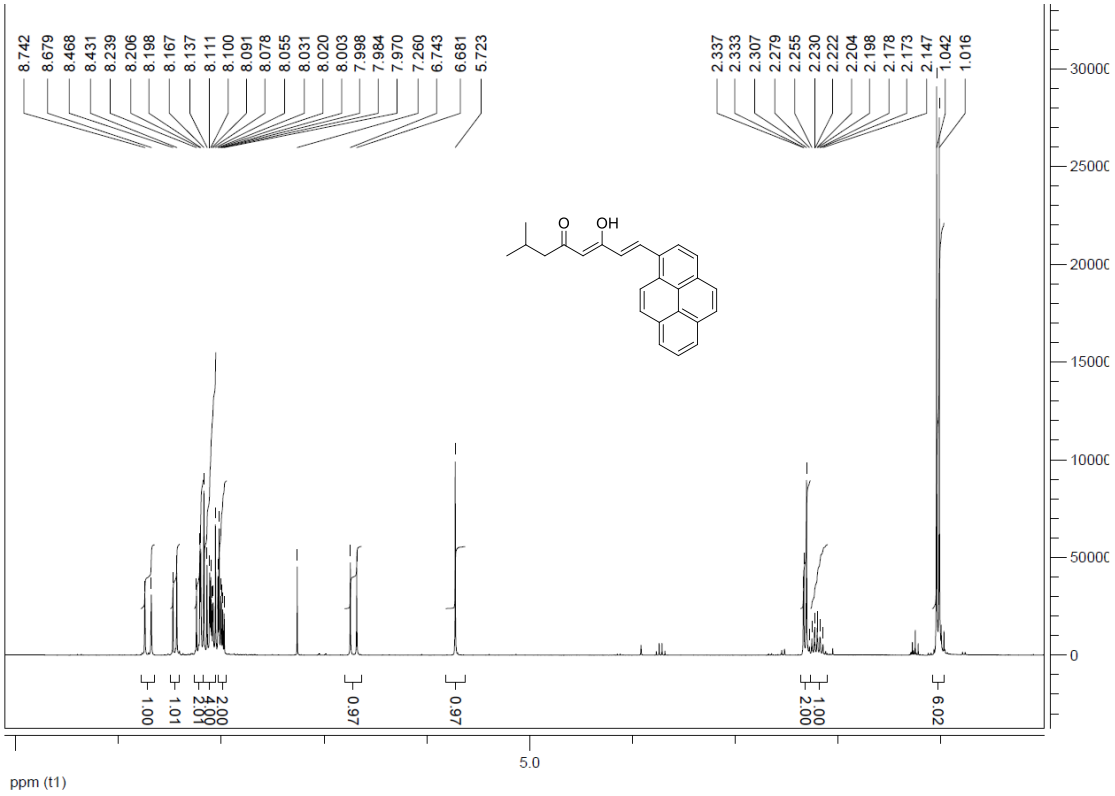


Figure NMR21. ^{1}H NMR spectrum of **Lig(5-iPr)** ((1E,4Z)-5-hydroxy-7-methyl-1-(pyren-1-yl)octa-1,4-dien-3-one)

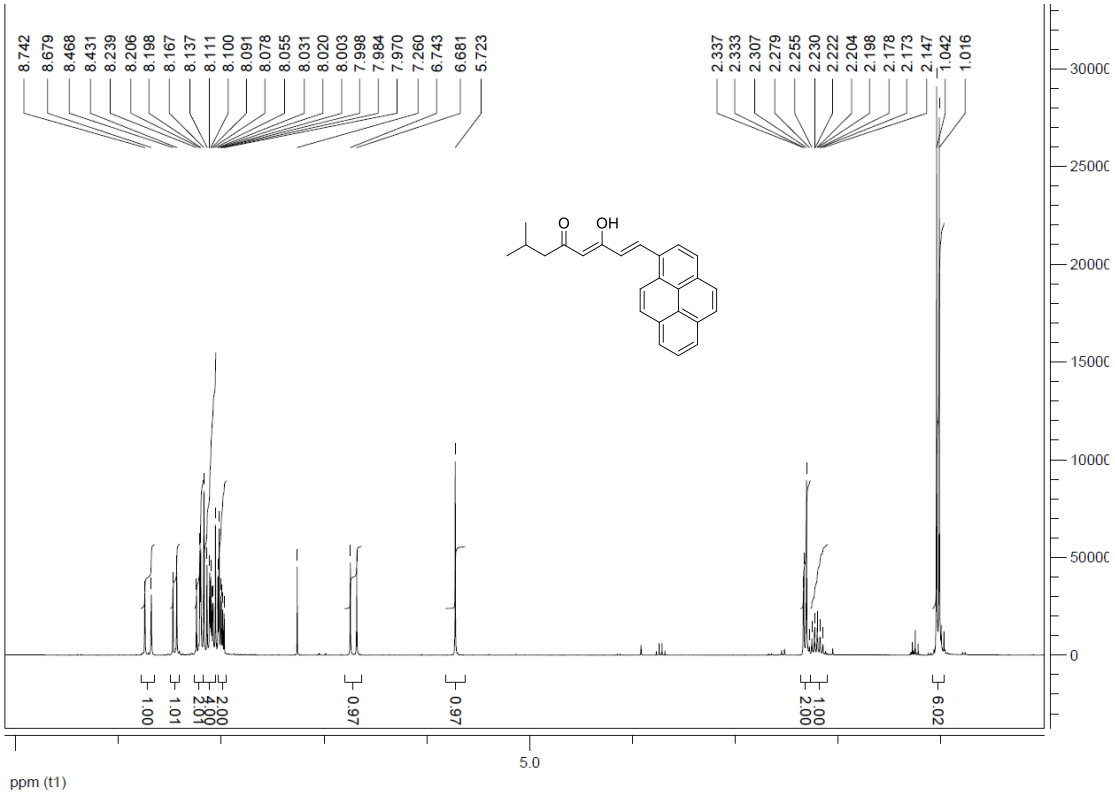
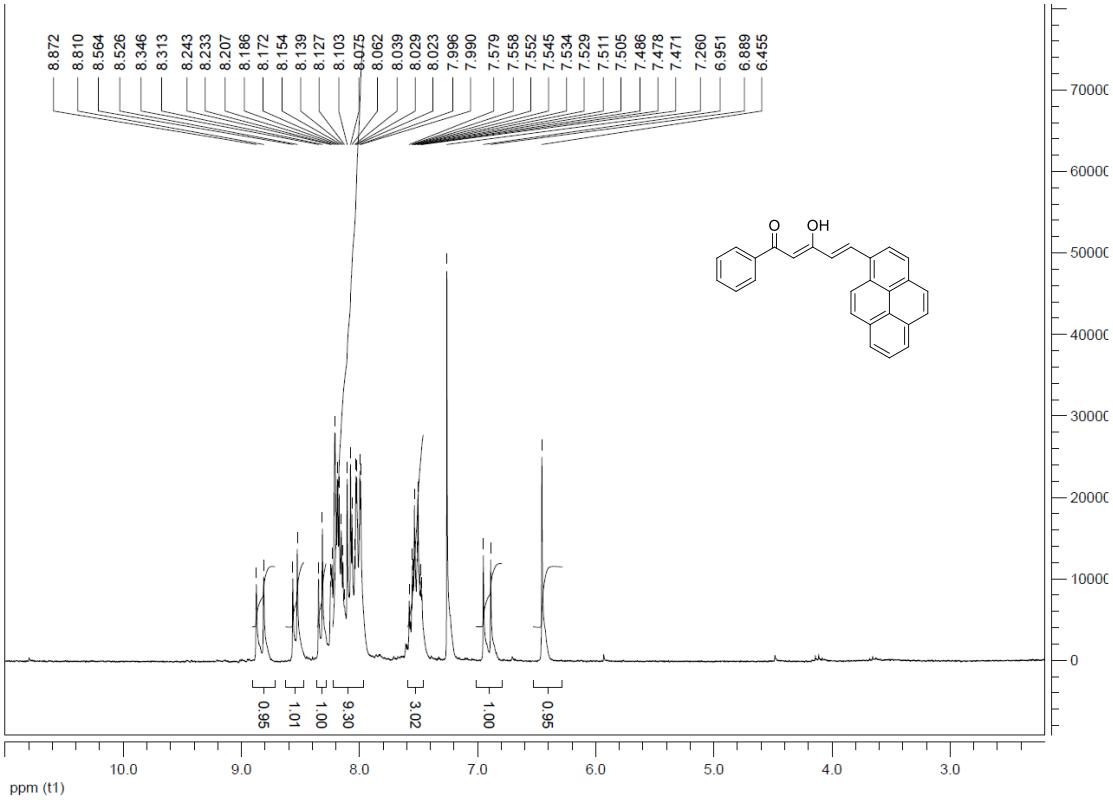


Figure NMR22. ^{13}C NMR spectrum of **Lig(5-iPr)** ((1E,4Z)-5-hydroxy-7-methyl-1-(pyren-1-yl)octa-1,4-dien-3-one)



FigureNMR23. [1]H NMR spectrum of **Lig(5-Ph)** ((1Z,4E)-1-hydroxy-1-phenyl-5-(pyren-1-yl)penta-1,4-dien-3-one)

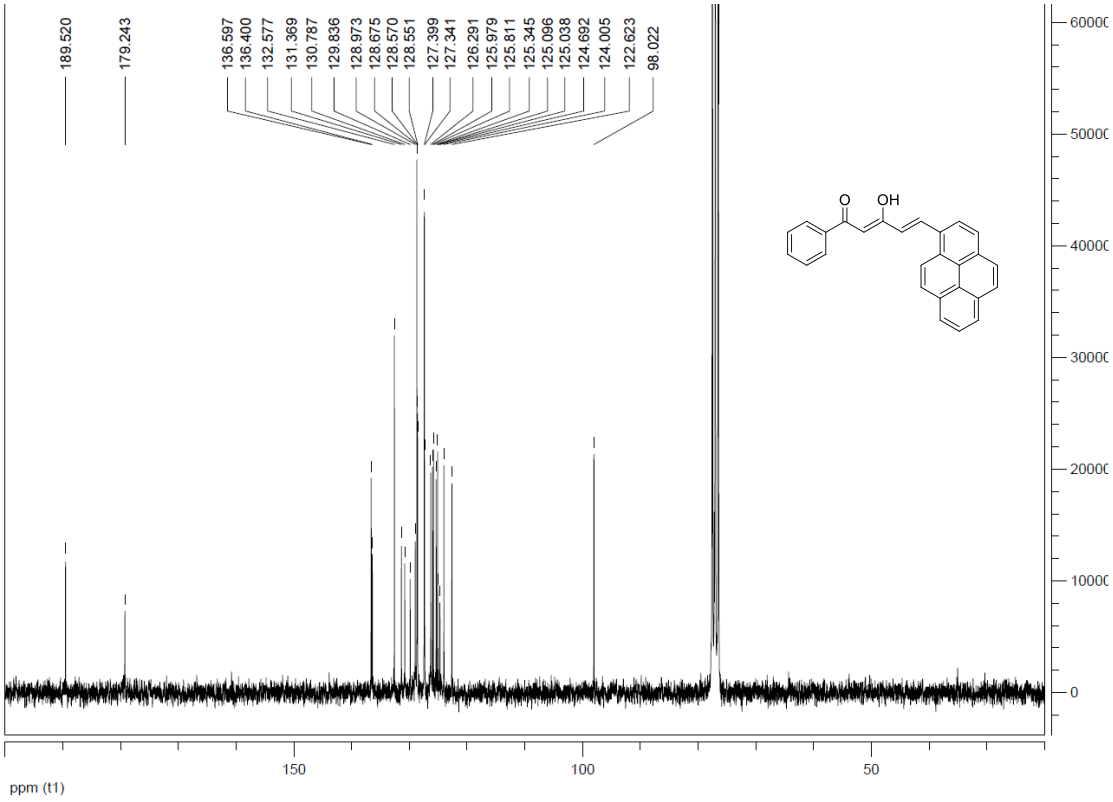


Figure NMR24. [13]C NMR spectrum of **Lig(5-Ph)** ((1Z,4E)-1-hydroxy-1-phenyl-5-(pyren-1-yl)penta-1,4-dien-3-one)

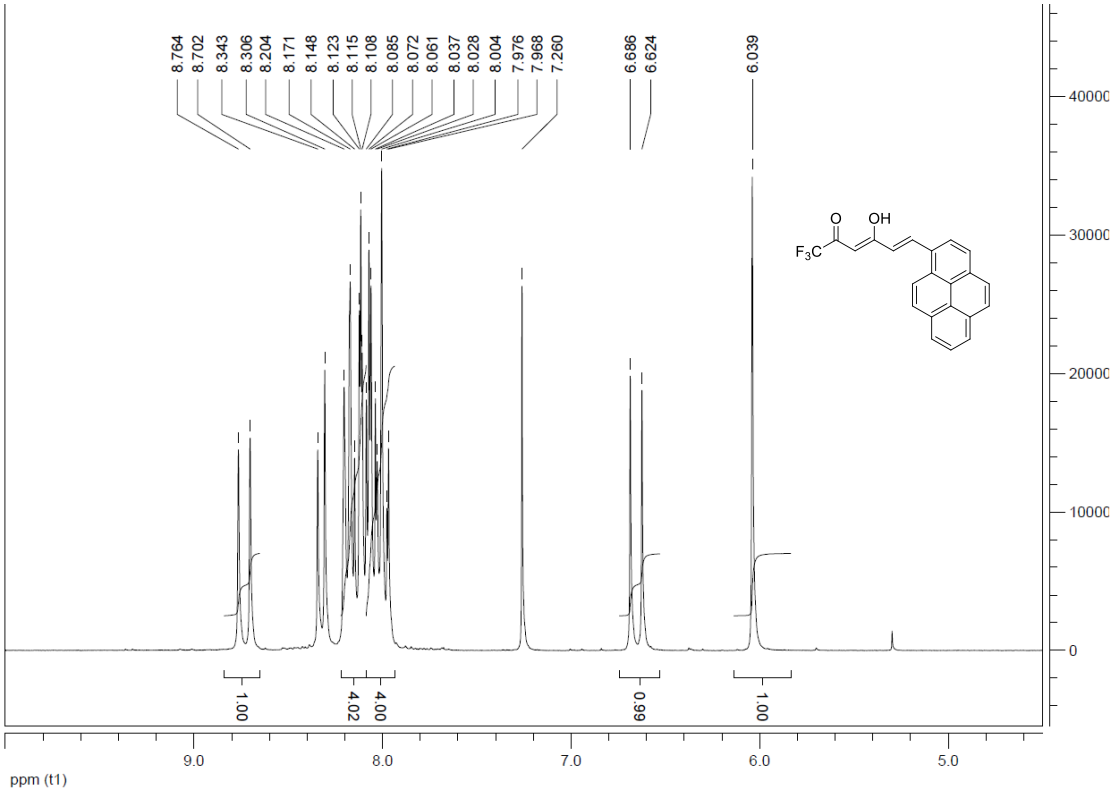


Figure NMR25. ^{1}H NMR spectrum of **Lig(5-CF$_3$)** ((1E,4Z)-6,6,6-trifluoro-5-hydroxy-1-(pyren-1-yl)hexa-1,4-dien-3-one)

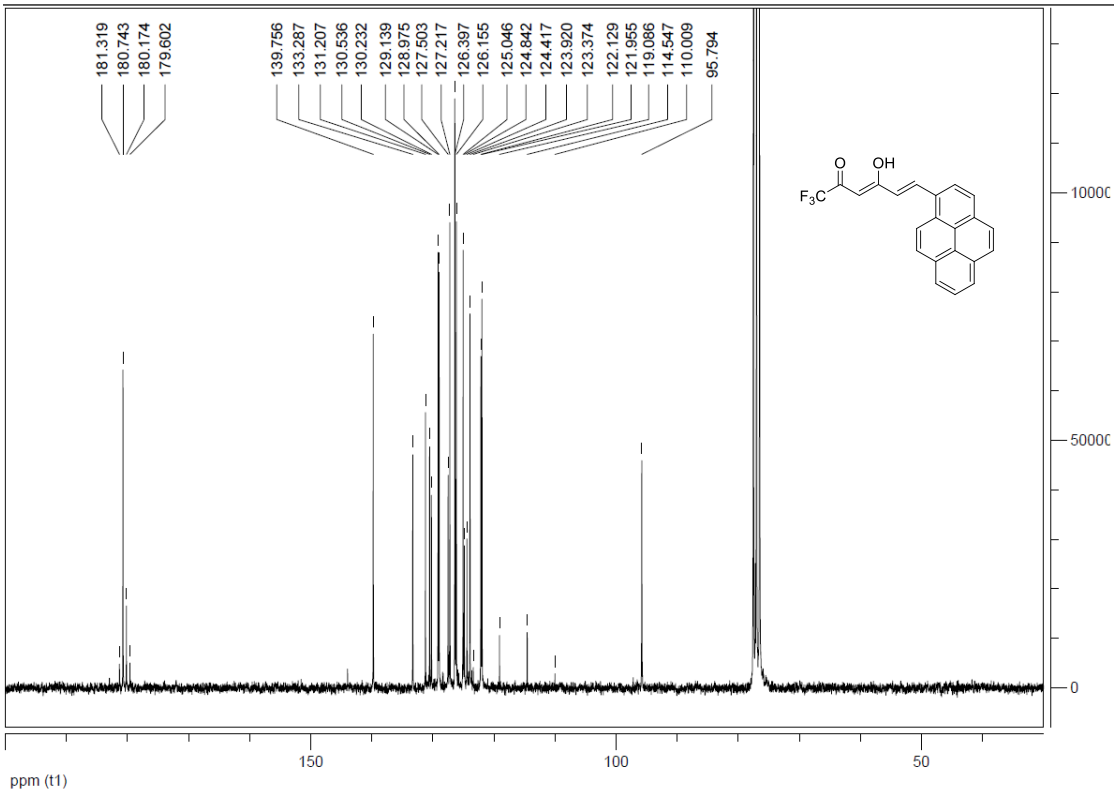


Figure NMR26. ^{13}C NMR spectrum of **Lig(5-CF$_3$)** ((1E,4Z)-6,6,6-trifluoro-5-hydroxy-1-(pyren-1-yl)hexa-1,4-dien-3-one)

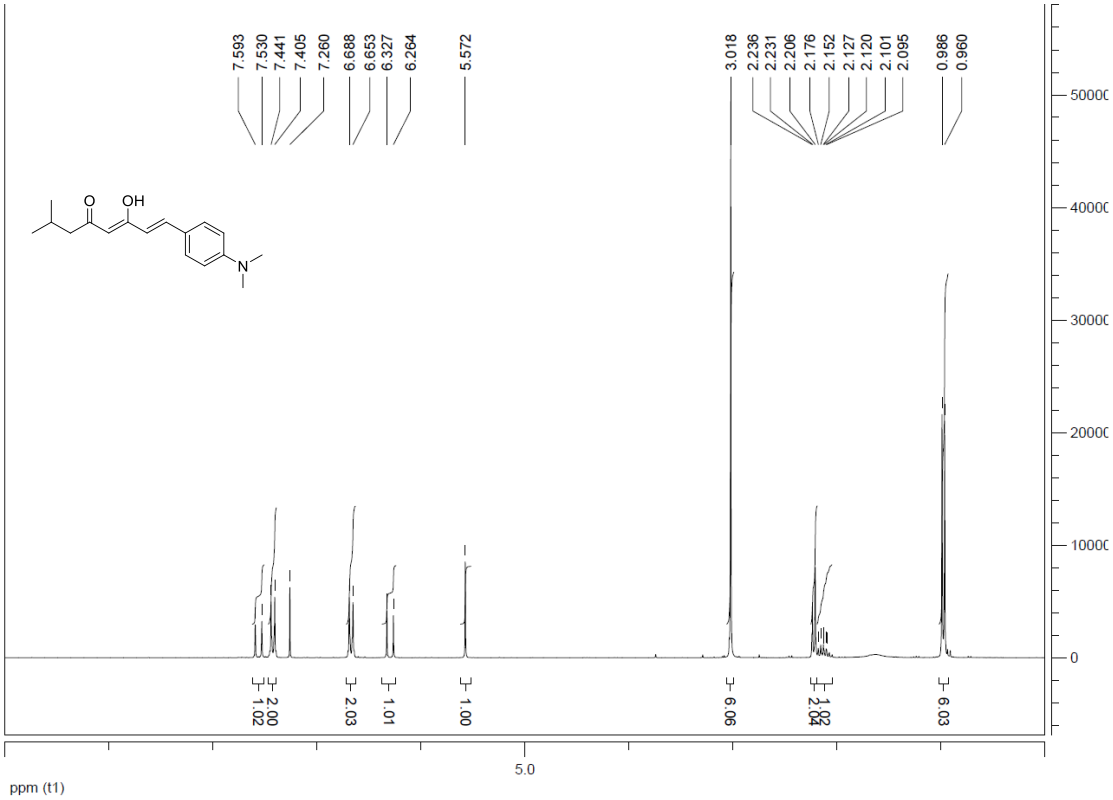


Figure NMR27. ^{1}H NMR spectrum of **Lig(6-iPr)** ((1E,4Z)-1-(4-(dimethylamino)phenyl)-5-hydroxy-7-methylocta-1,4-dien-3-one)

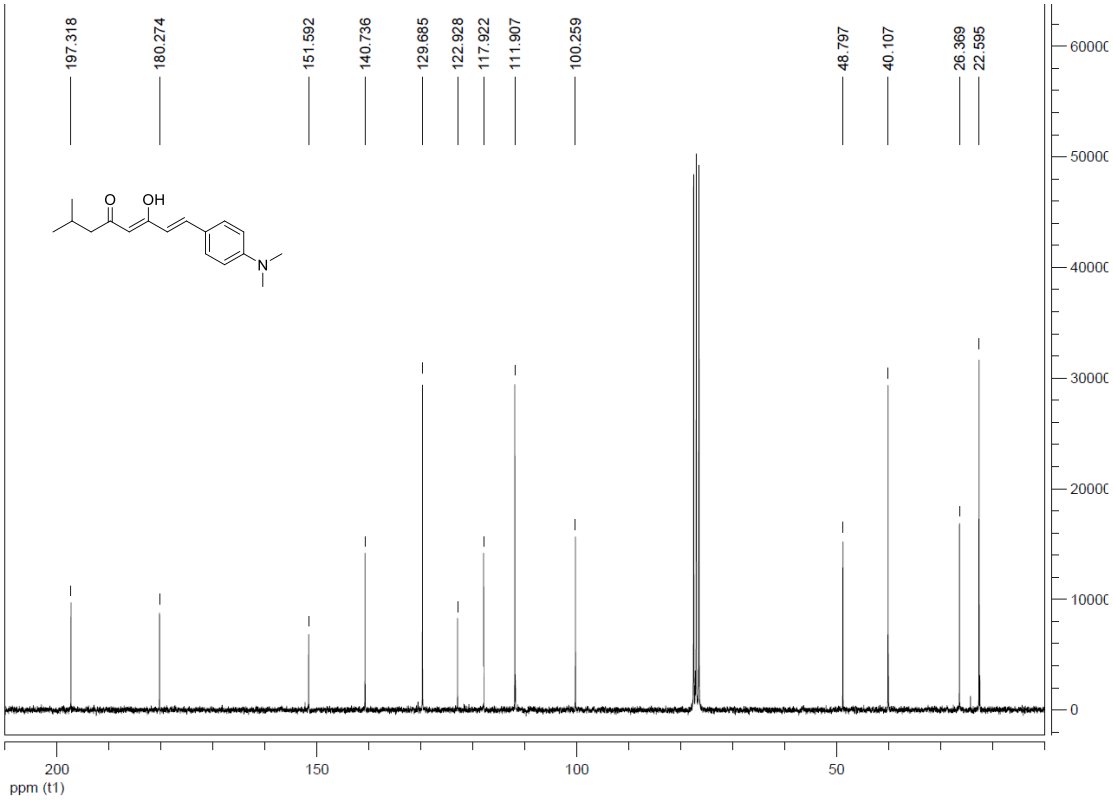


Figure NMR28. ^{13}C NMR spectrum of **Lig(6-iPr)** ((1E,4Z)-1-(4-(dimethylamino)phenyl)-5-hydroxy-7-methylocta-1,4-dien-3-one)

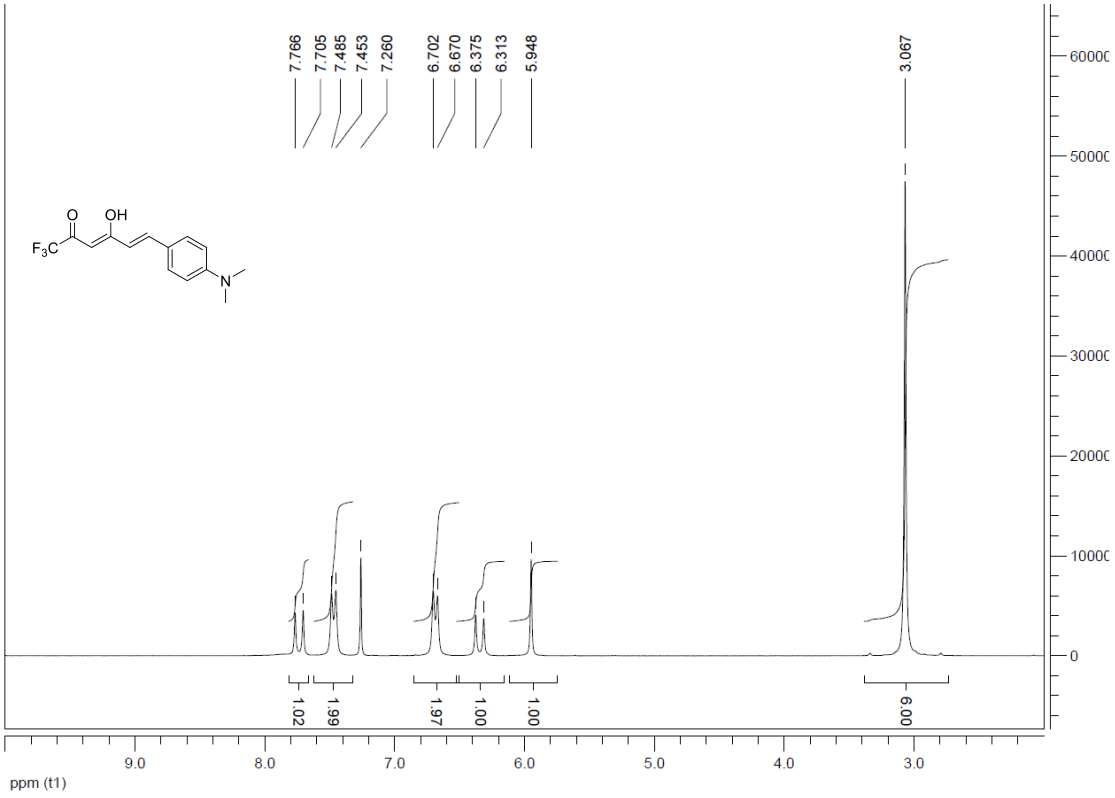


Figure NMR29. ^{1}H NMR spectrum of **Lig(6-CF$_3$)** ((1E,4Z)-1-(4-(dimethylamino)phenyl)-6,6,6-trifluoro-5-hydroxyhexa-1,4-dien-3-one)

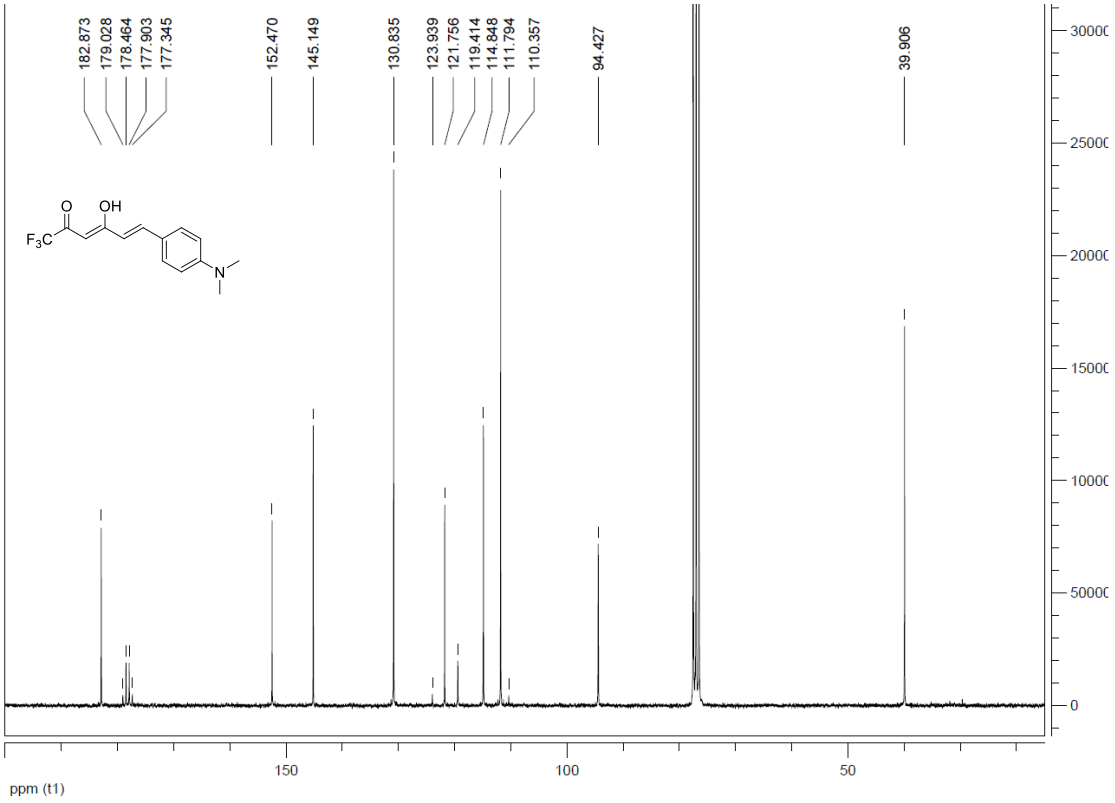


Figure NMR30. ^{13}C NMR spectrum of **Lig(6-CF$_3$)** ((1E,4Z)-1-(4-(dimethylamino)phenyl)-6,6,6-trifluoro-5-hydroxyhexa-1,4-dien-3-one)

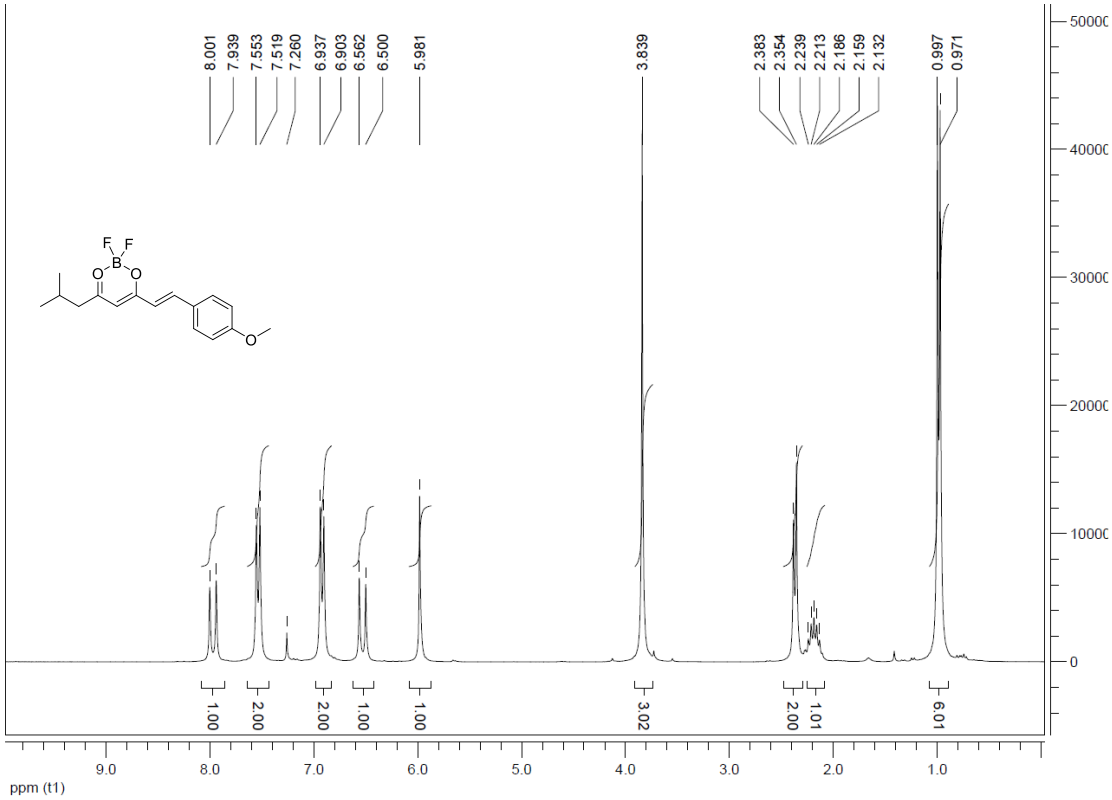


Figure NMR31. ^{1}H NMR spectrum of **1-iPr** ((E)-2,2-difluoro-4-isobutyl-6-(4-methoxystyryl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

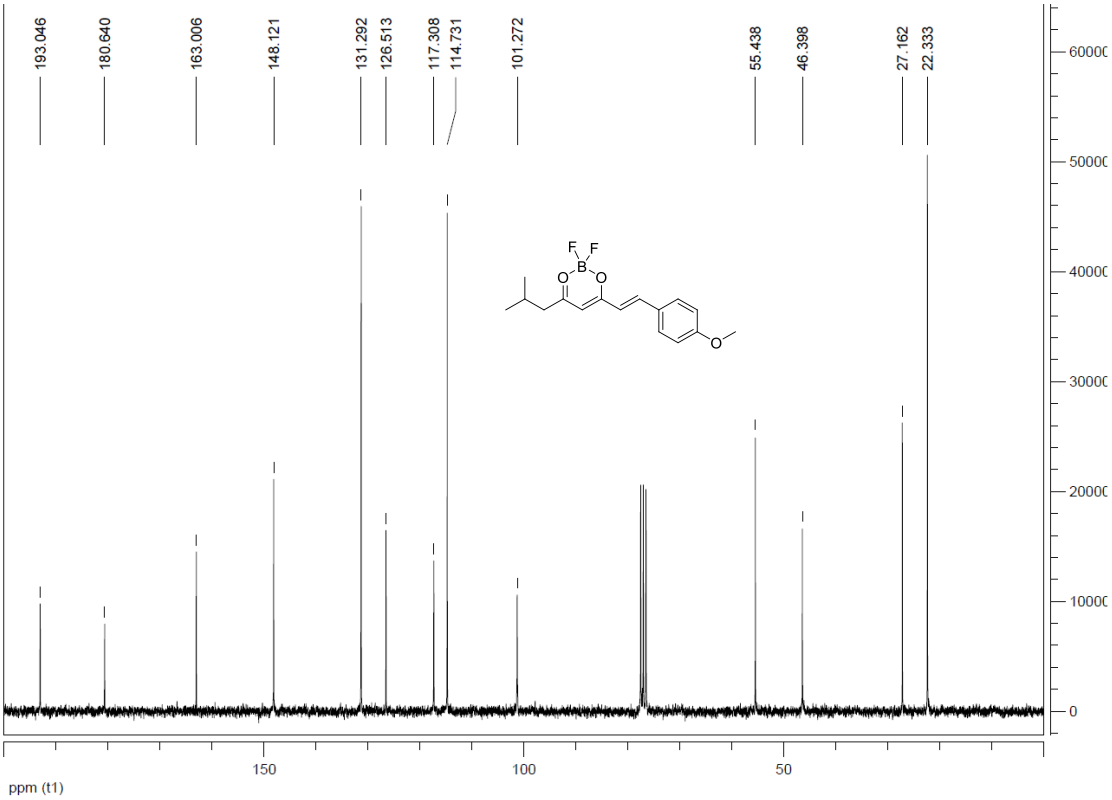


Figure NMR32. ^{13}C NMR spectrum of **1-iPr** ((E)-2,2-difluoro-4-isobutyl-6-(4-methoxystyryl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

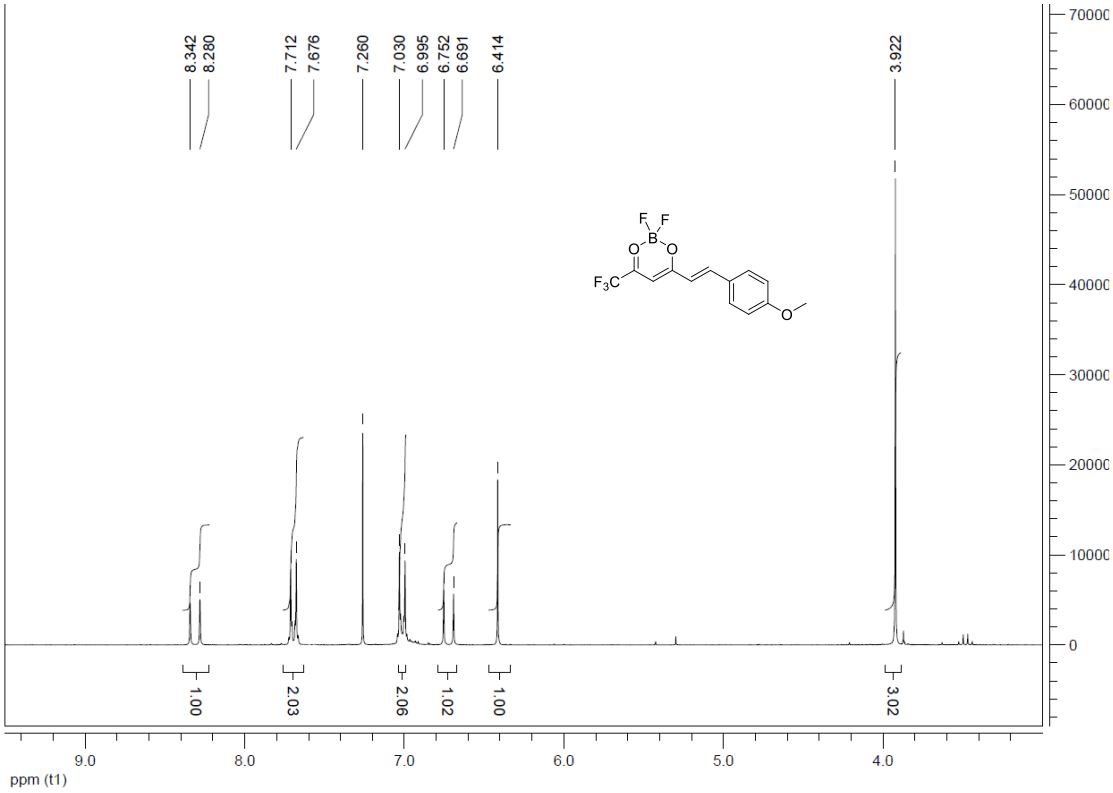


Figure NMR33. ^{1}H NMR spectrum of **1-CF$_3$** ((E)-2,2-difluoro-6-(4-methoxystyryl)-4-(trifluoromethyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

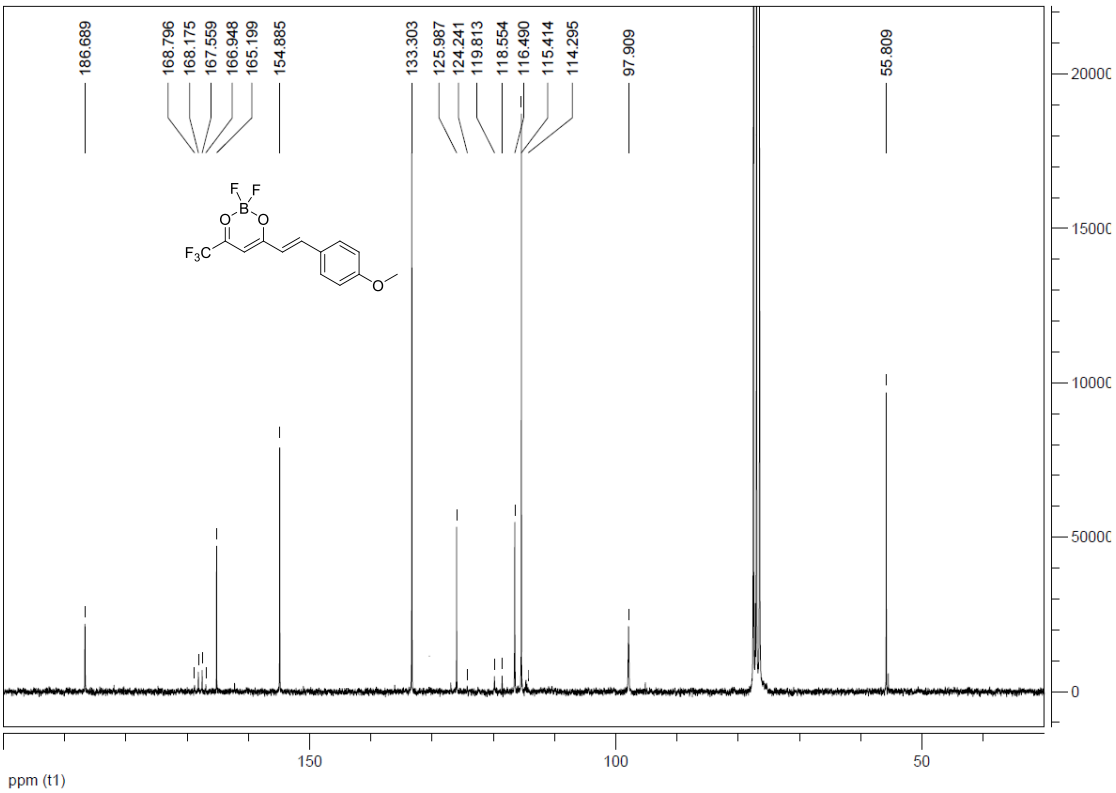


Figure NMR34. ^{13}C NMR spectrum of **1-CF$_3$** ((E)-2,2-difluoro-6-(4-methoxystyryl)-4-(trifluoromethyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

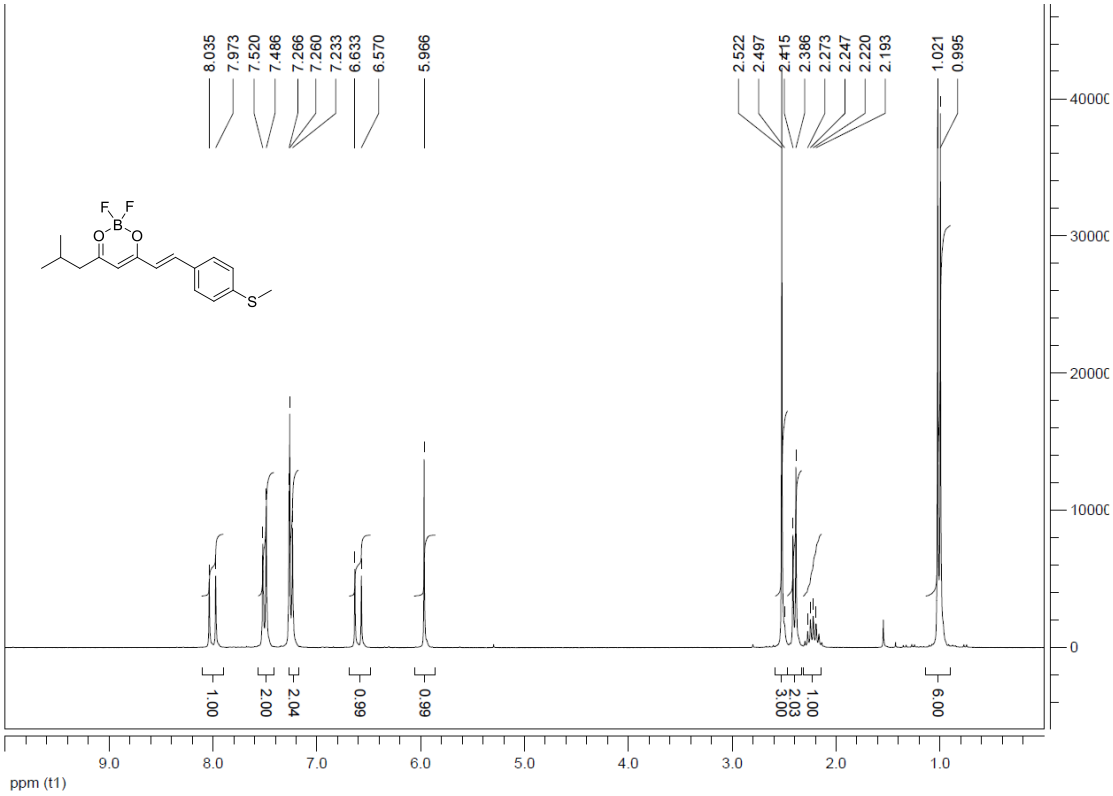


Figure NMR35. ^{1}H NMR spectrum of **2-iPr** ((E)-2,2-difluoro-4-isobutyl-6-(4-(methylthio)styryl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

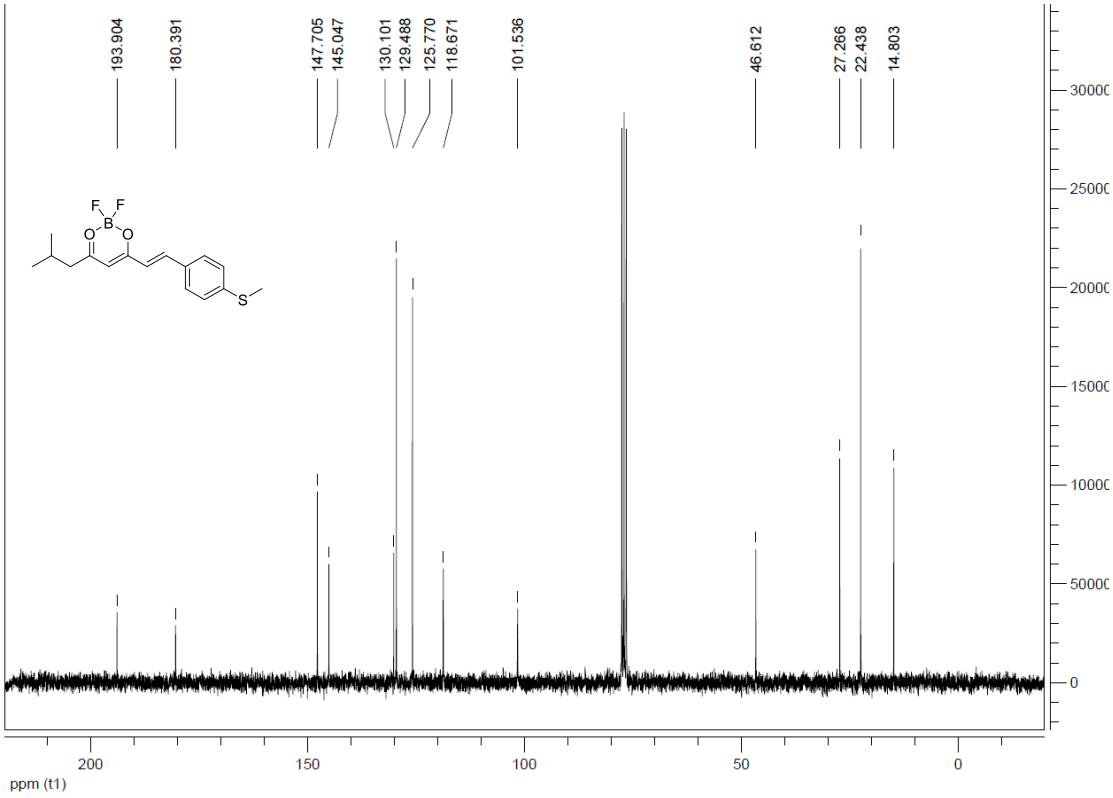


Figure NMR36. ^{13}C NMR spectrum of **2-iPr** ((E)-2,2-difluoro-4-isobutyl-6-(4-(methylthio)styryl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

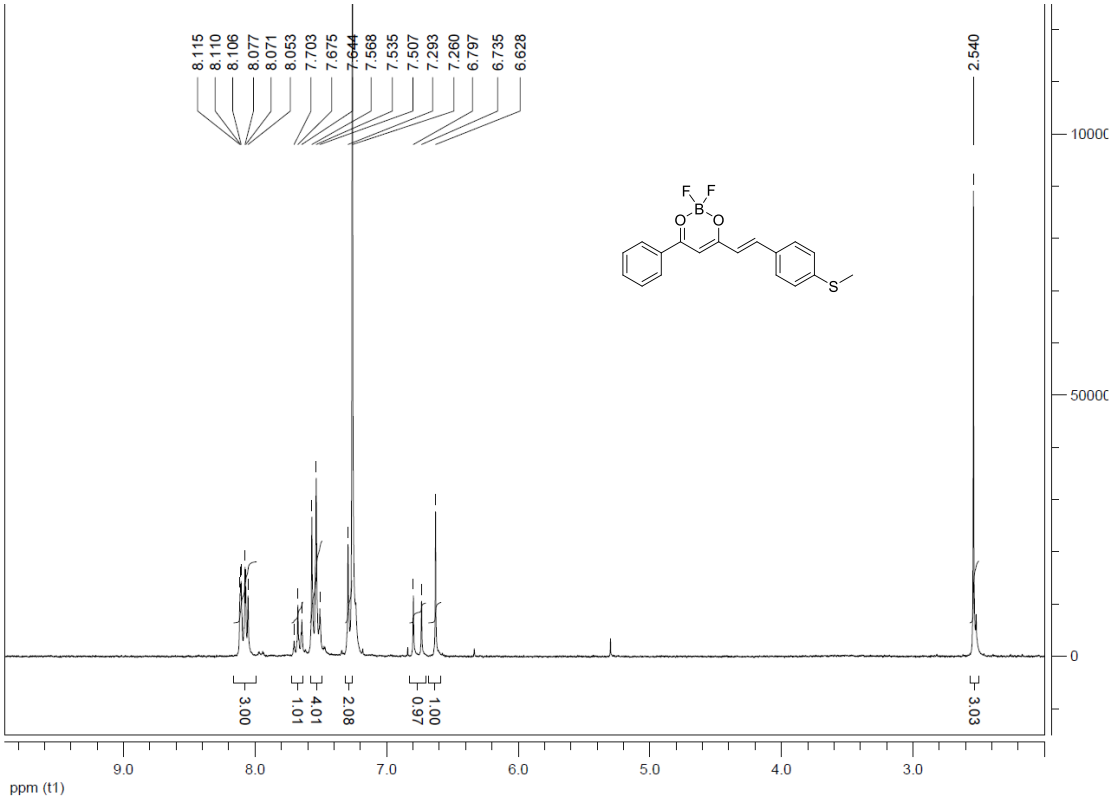


Figure NMR37. ^{1}H NMR spectrum of **2-Ph** ((E)-2,2-difluoro-6-(4-(methylthio)styryl)-4-phenyl-2H-1,3,2-dioxaborinin-1-ium-2-uide)

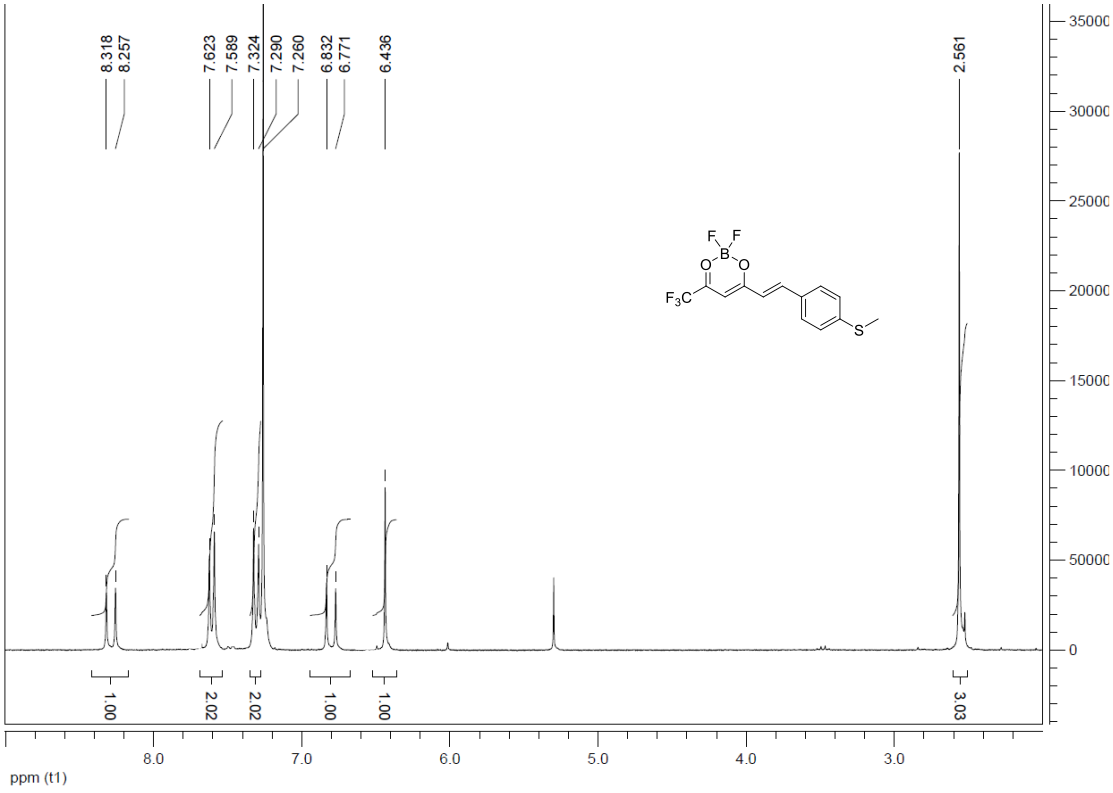


Figure NMR38. ^{1}H NMR spectrum of **2-CF$_3$** ((E)-2,2-difluoro-6-(4-(methylthio)styryl)-4-(trifluoromethyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

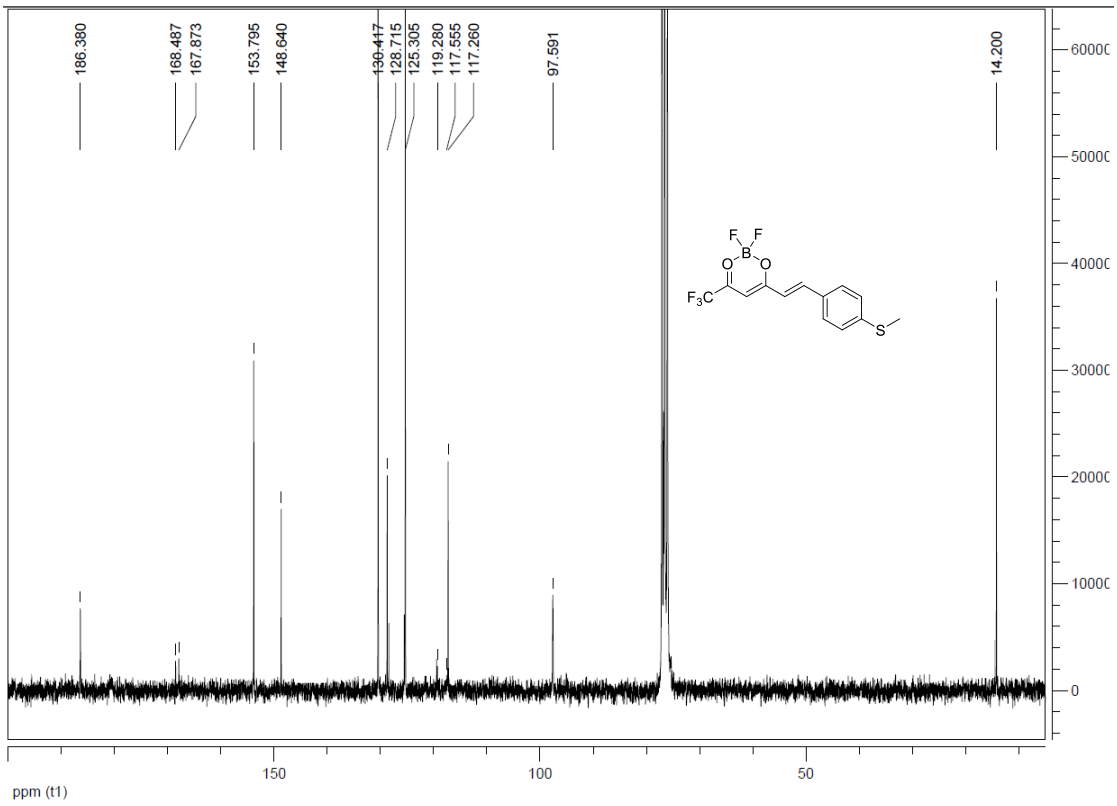


Figure NMR39. ^{13}C NMR spectrum of **2-CF$_3$** ((E)-2,2-difluoro-6-(4-(methylthio)styryl)-4-(trifluoromethyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

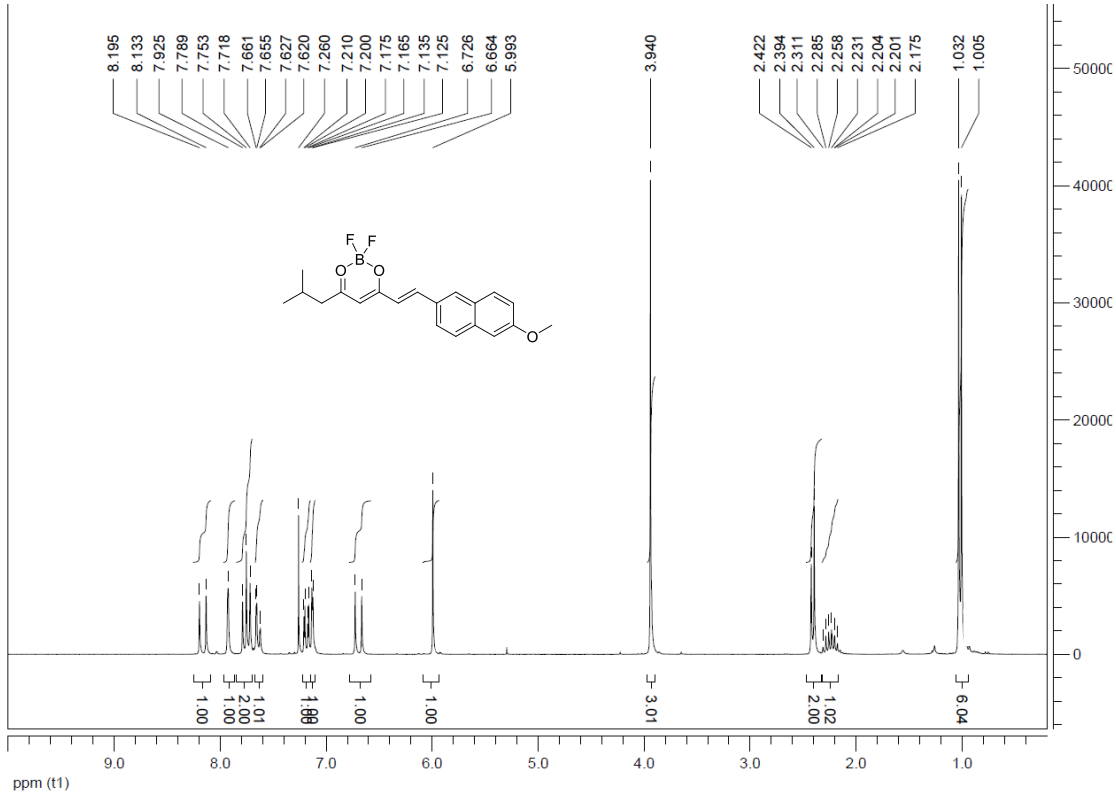


Figure NMR40. ^{1}H NMR spectrum of **3-iPr** ((E)-2,2-difluoro-4-isobutyl-6-(2-(6-methoxynaphthalen-2-yl)vinyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

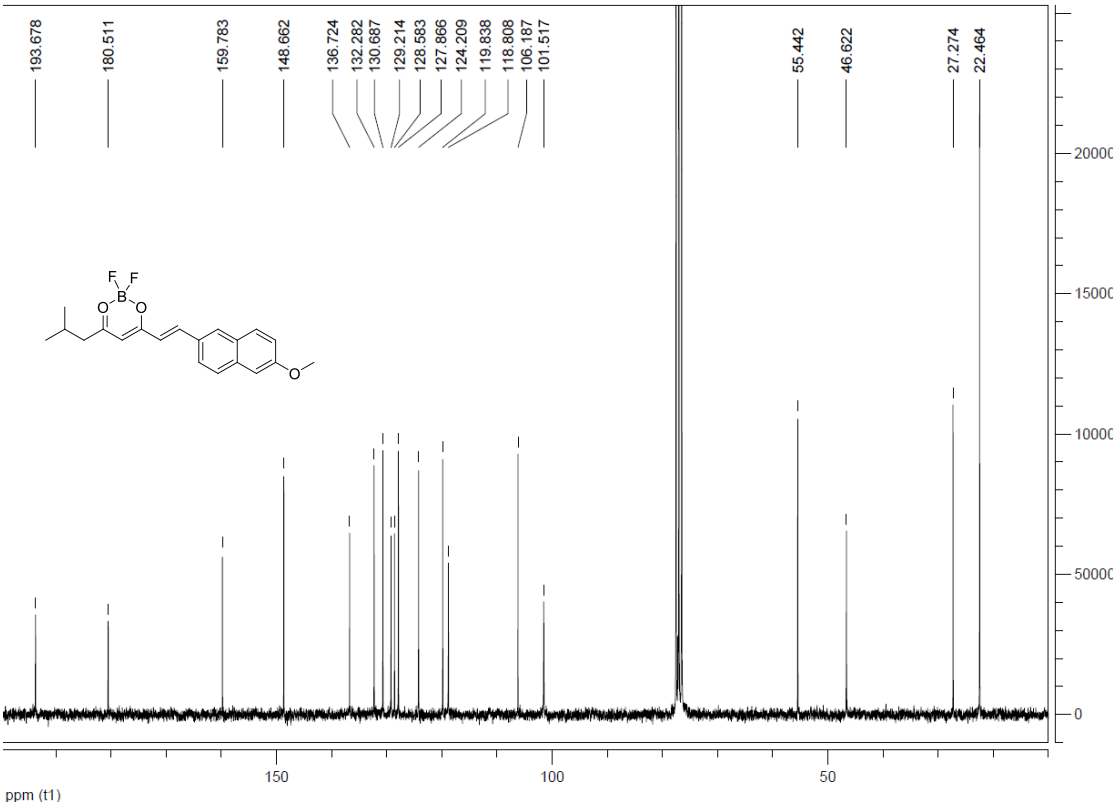


Figure NMR41. ^{13}C NMR spectrum of **3-iPr** ((E)-2,2-difluoro-4-isobutyl-6-(2-(6-methoxynaphthalen-2-yl)vinyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

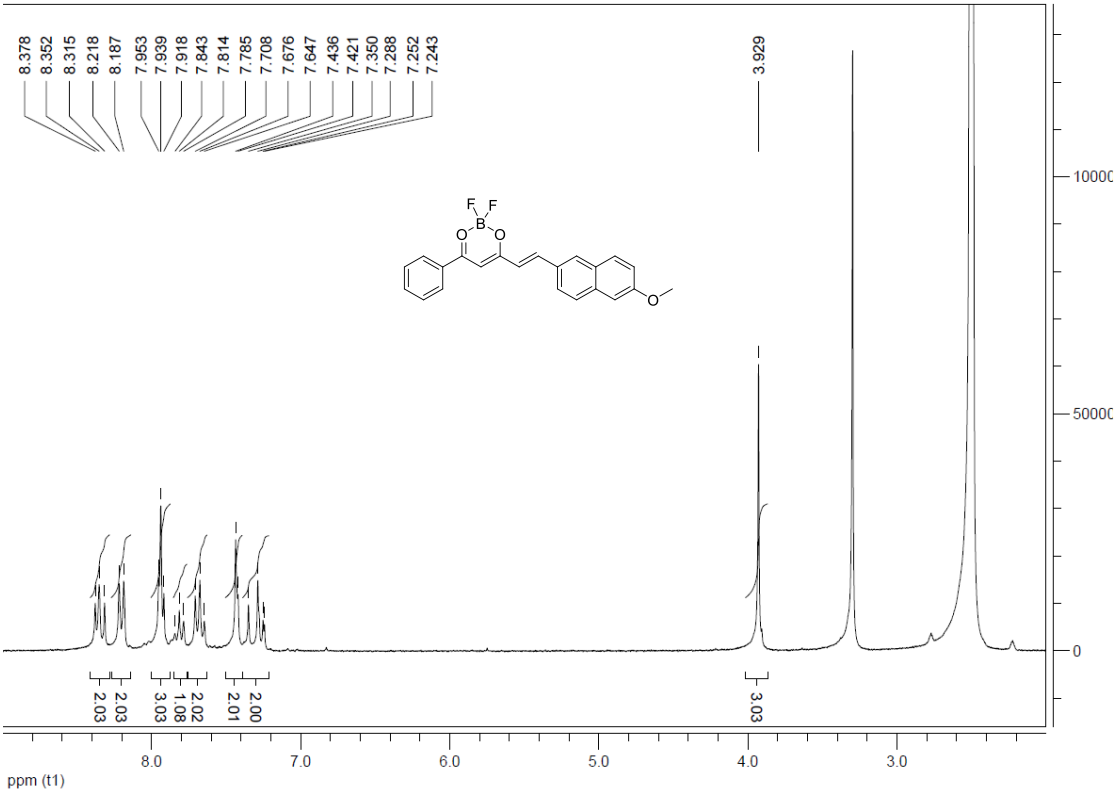


Figure NMR42. ^{1}H NMR spectrum of **3-Ph** ((E)-2,2-difluoro-6-(2-(6-methoxynaphthalen-2-yl)vinyl)-4-phenyl-2H-1,3,2-dioxaborinin-1-ium-2-uide)

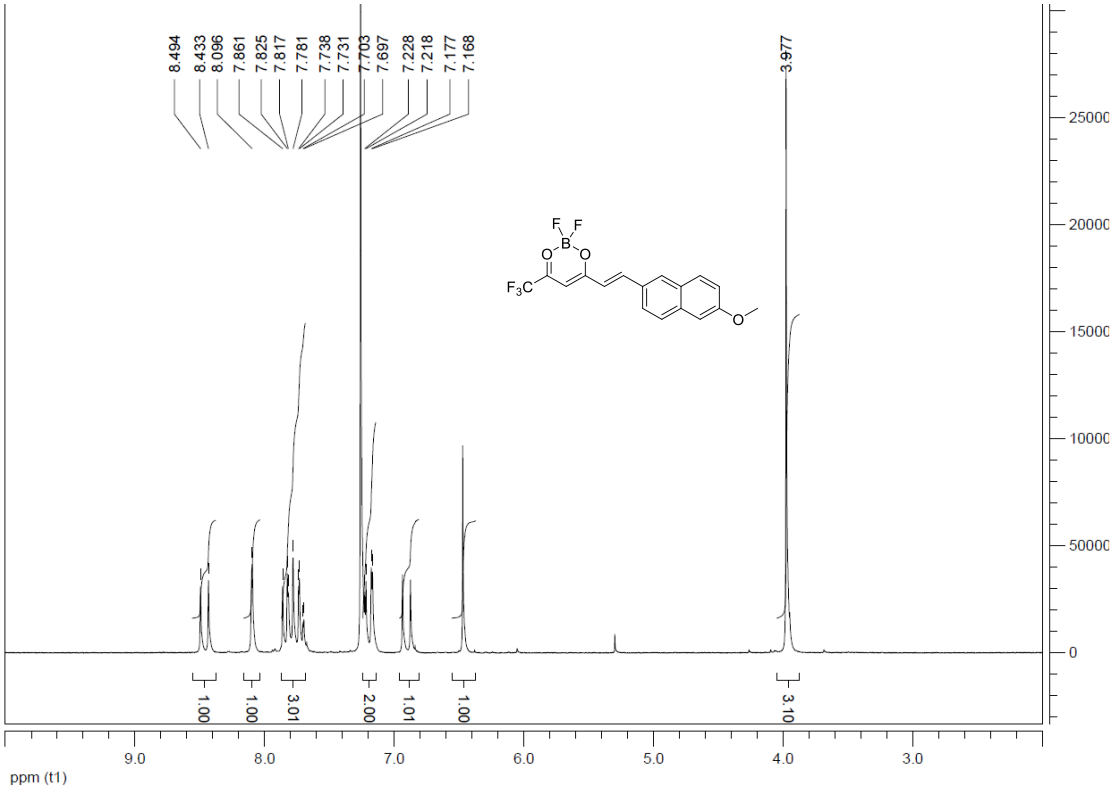


Figure NMR43. [1]H NMR spectrum of **3-CF$_3$** ((E)-2,2-difluoro-6-(2-(6-methoxynaphthalen-2-yl)vinyl)-4-(trifluoromethyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

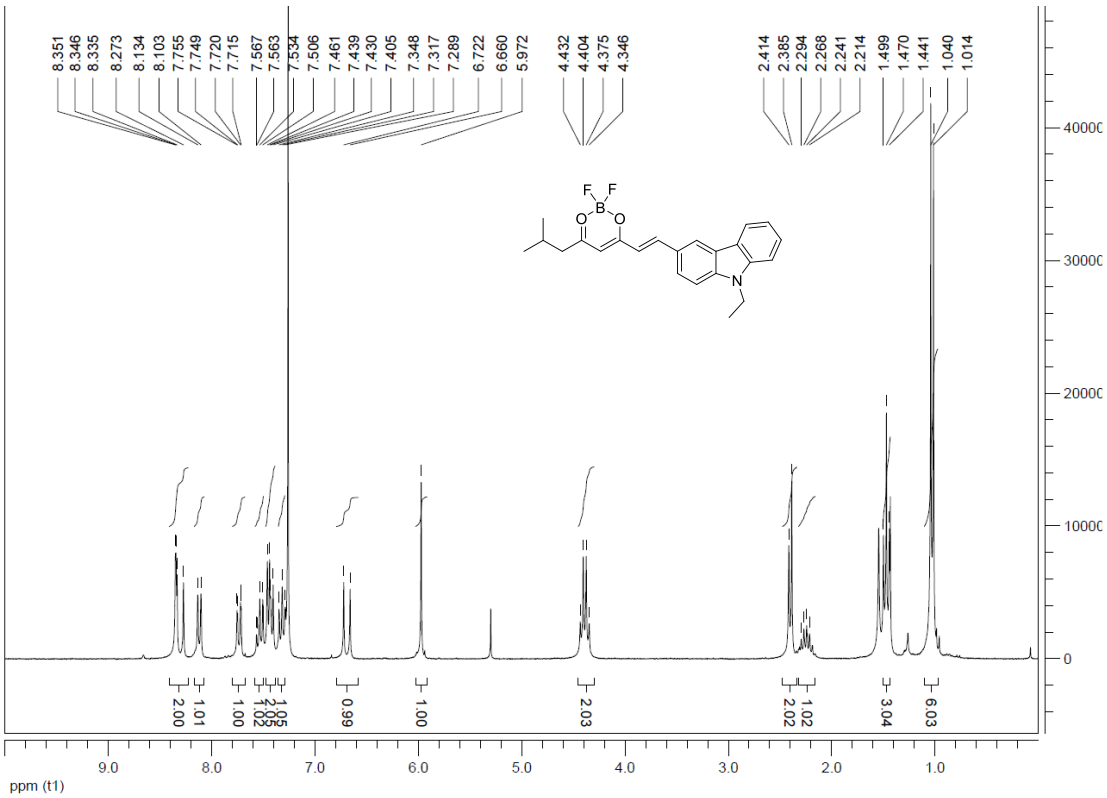


Figure NMR44. [1]H NMR spectrum of **4-iPr** ((E)-6-(2-(9-ethyl-9H-carbazol-3-yl)vinyl)-2,2-difluoro-4-isobutyl-2H-1,3,2-dioxaborinin-1-ium-2-uide)

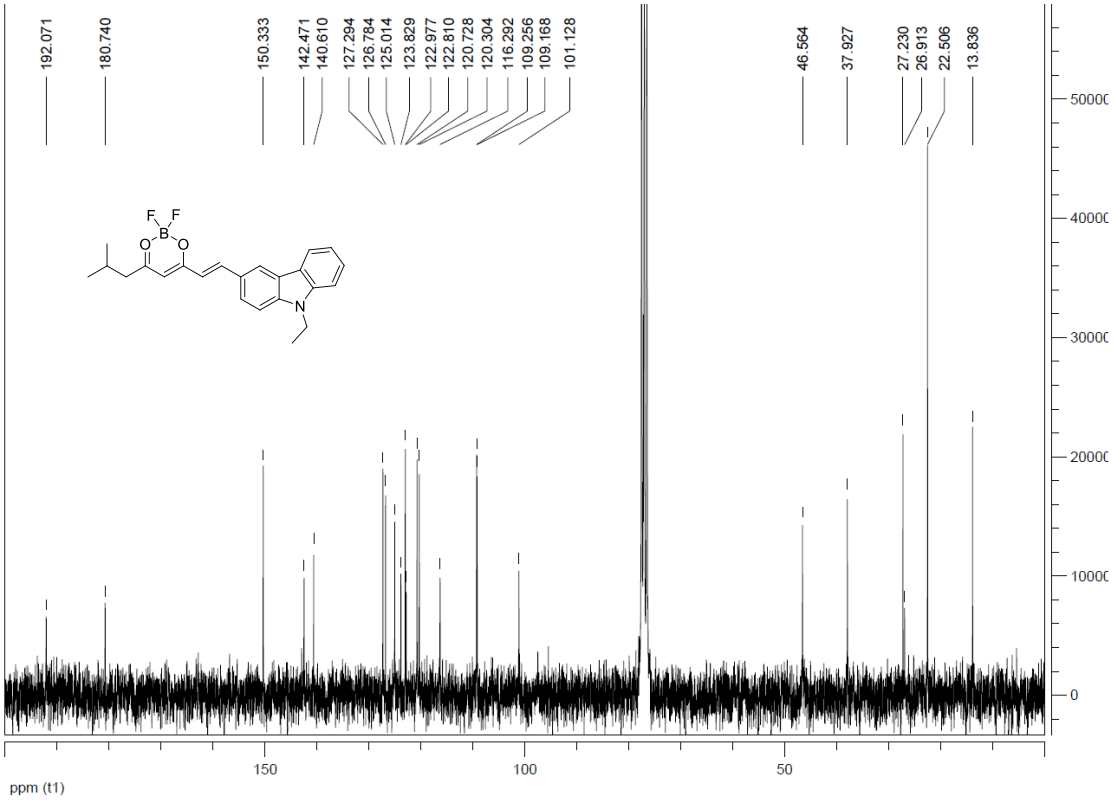


Figure NMR45. ^{13}C NMR spectrum of **4-iPr** ((E)-6-(2-(9-ethyl-9H-carbazol-3-yl)vinyl)-2,2-difluoro-4-isobutyl-2H-1,3,2-dioxaborinin-1-ium-2-uide)

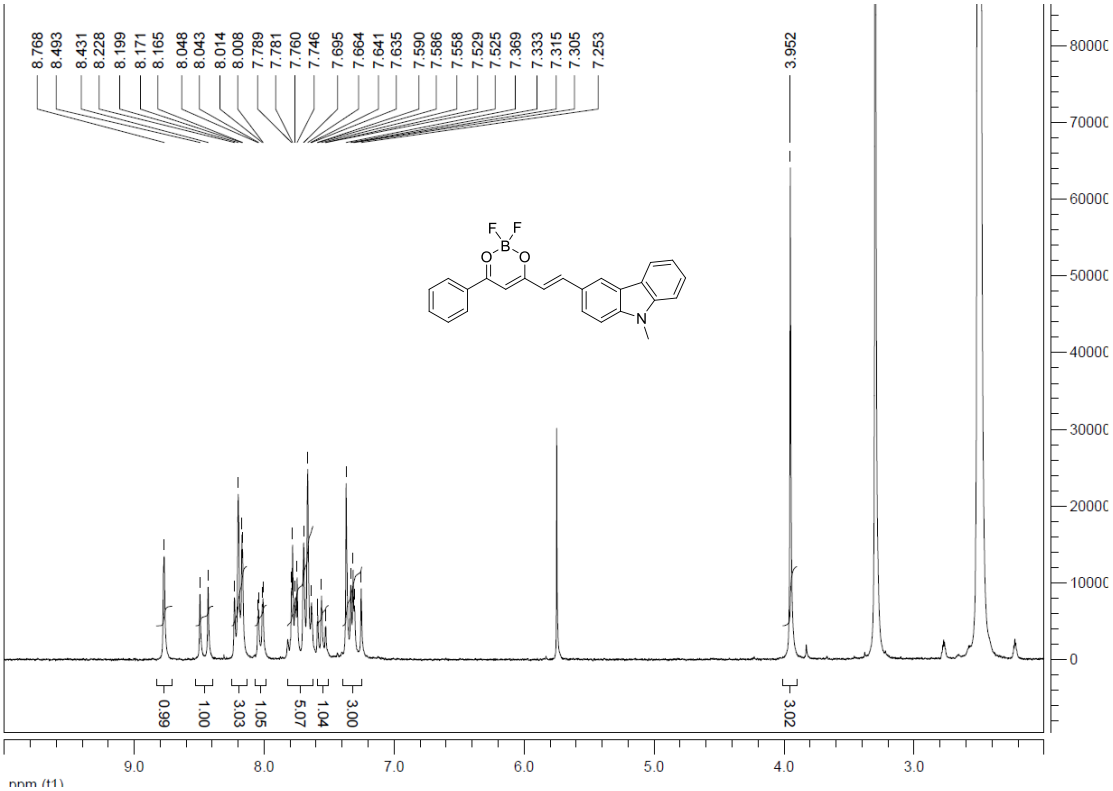


Figure NMR46. ^{1}H NMR spectrum of **4-Ph** ((E)-2,2-difluoro-6-(2-(9-methyl-9H-carbazol-3-yl)vinyl)-4-phenyl-2H-1,3,2-dioxaborinin-1-ium-2-uide)

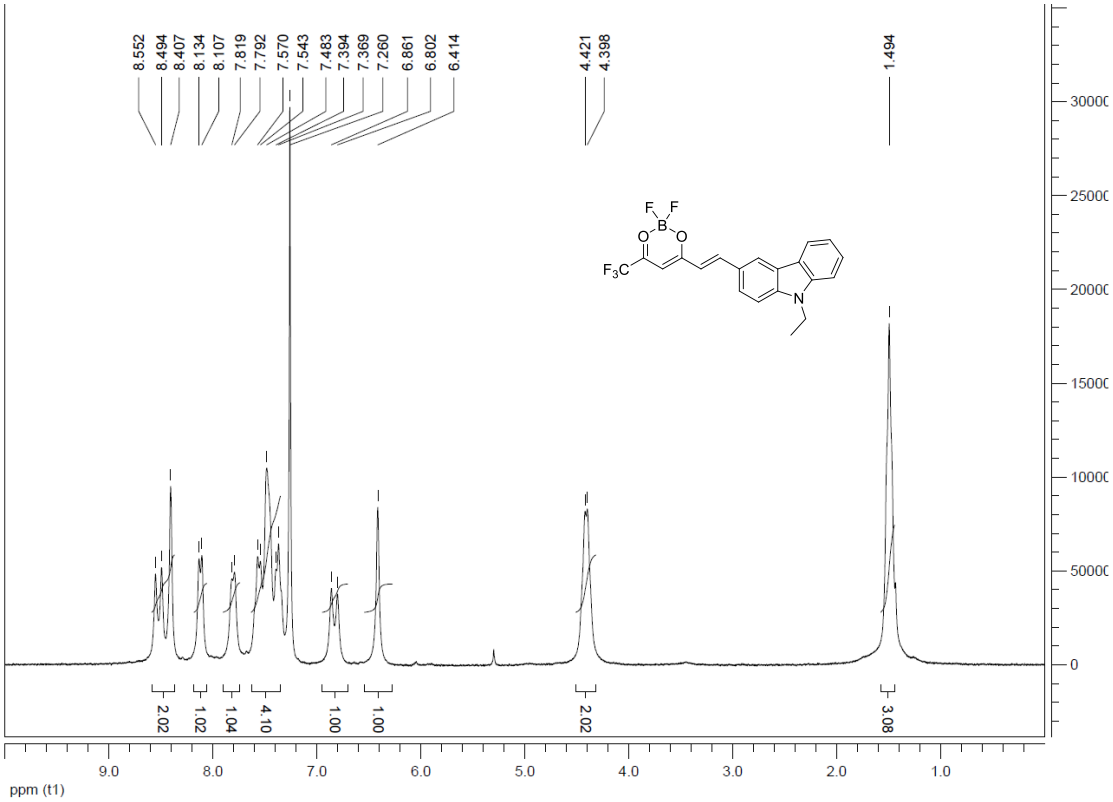


Figure NMR47. ^{1}H NMR spectrum of **4-CF$_3$** ((E)-6-(2-(9-ethyl-9H-carbazol-3-yl)vinyl)-2,2-difluoro-4-(trifluoromethyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

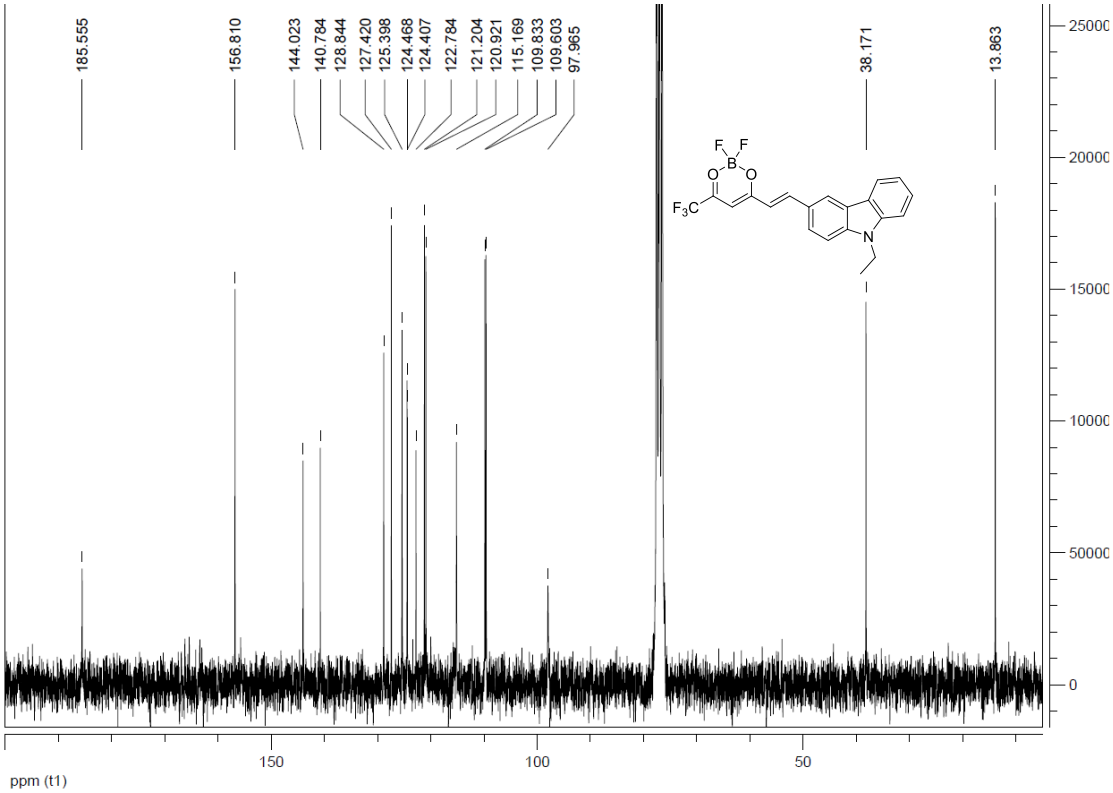


Figure NMR48. ^{13}C NMR spectrum of **4-CF$_3$** ((E)-6-(2-(9-ethyl-9H-carbazol-3-yl)vinyl)-2,2-difluoro-4-(trifluoromethyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

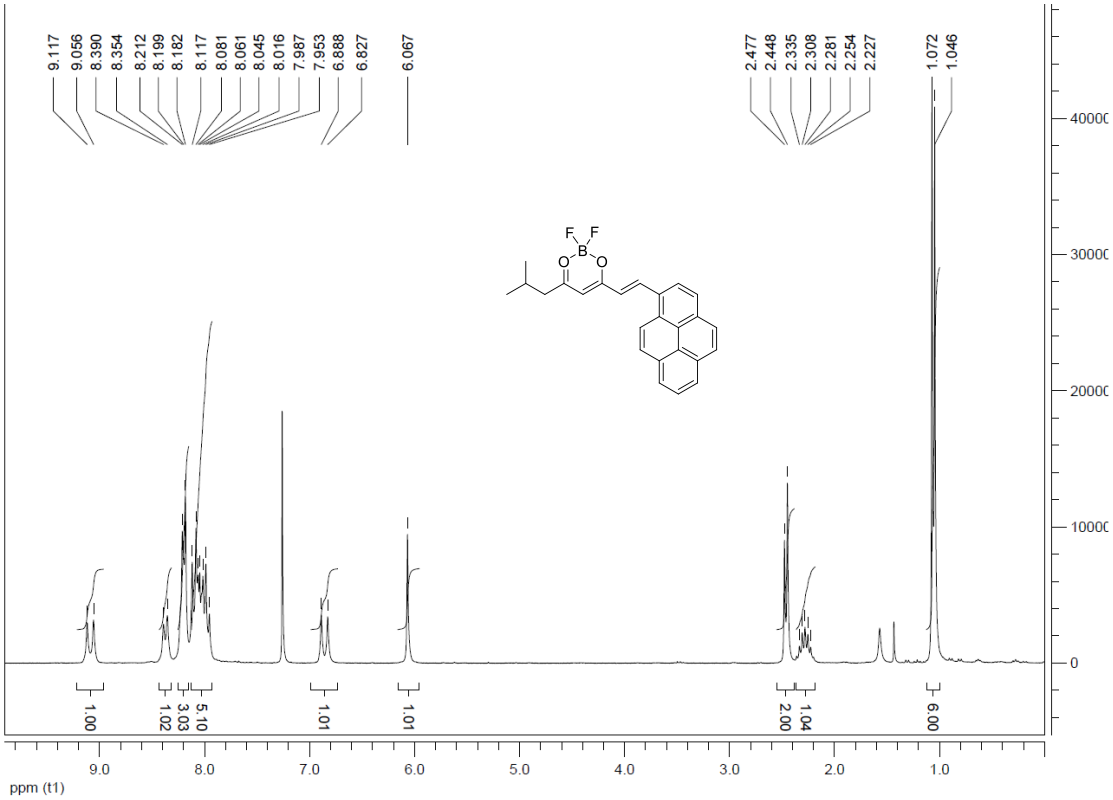


Figure NMR49. ^{1}H NMR spectrum of **5-iPr** ((E)-2,2-difluoro-4-isobutyl-6-(2-(pyren-1-yl)vinyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

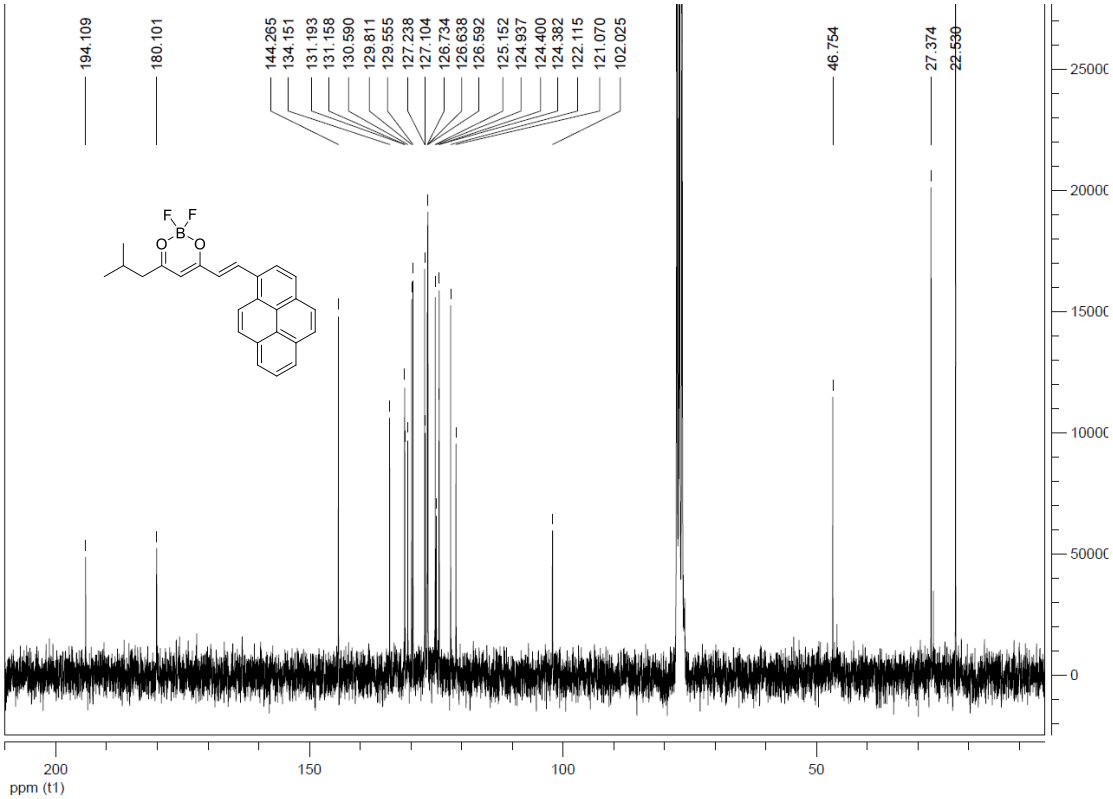


Figure NMR50. ^{13}C NMR spectrum of **5-iPr** ((E)-2,2-difluoro-4-isobutyl-6-(2-(pyren-1-yl)vinyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

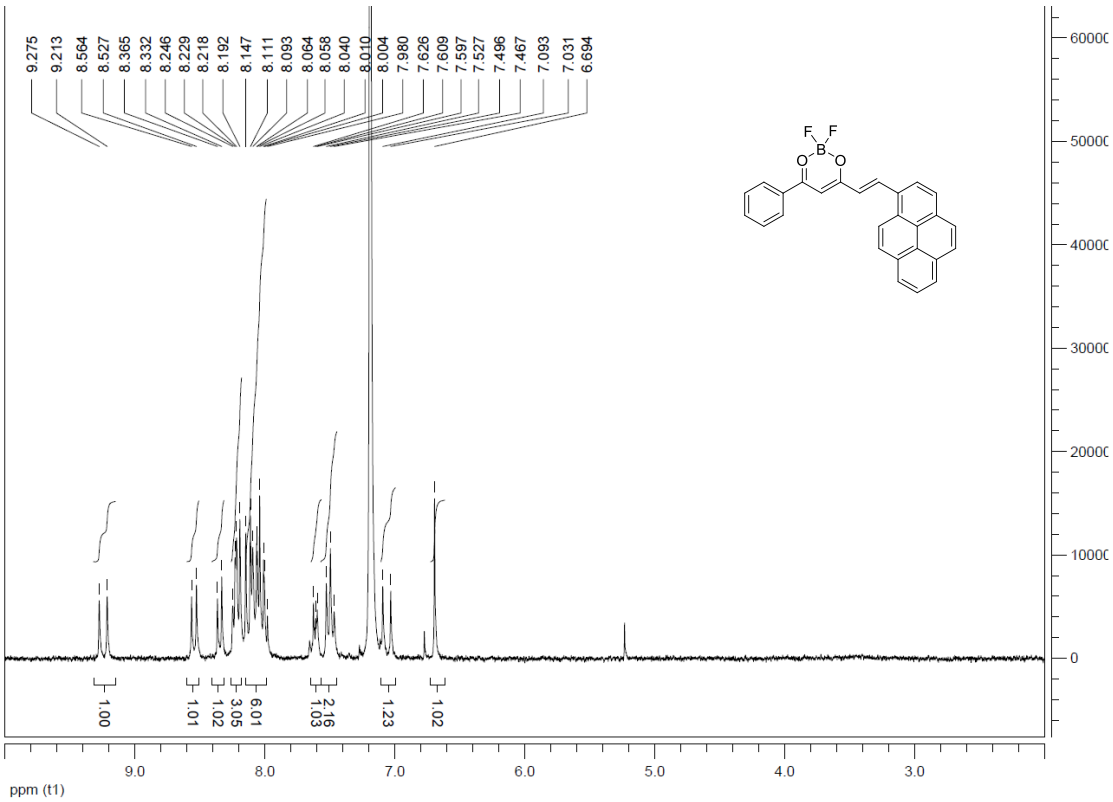


Figure NMR51. ^{1}H NMR spectrum of **5-Ph** ((E)-2,2-difluoro-4-phenyl-6-(2-(pyren-1-yl)vinyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

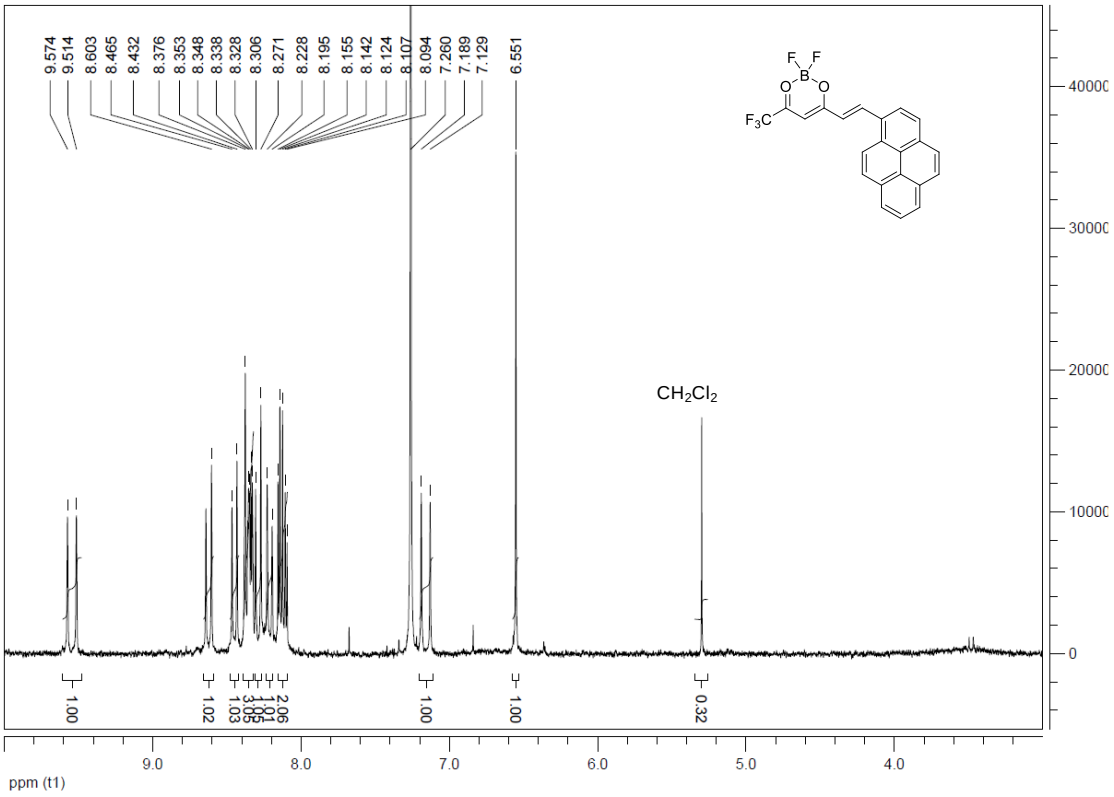


Figure NMR52. ^{1}H NMR spectrum of **5-CF$_3$** ((E)-2,2-difluoro-6-(2-(pyren-1-yl)vinyl)-4-(trifluoromethyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

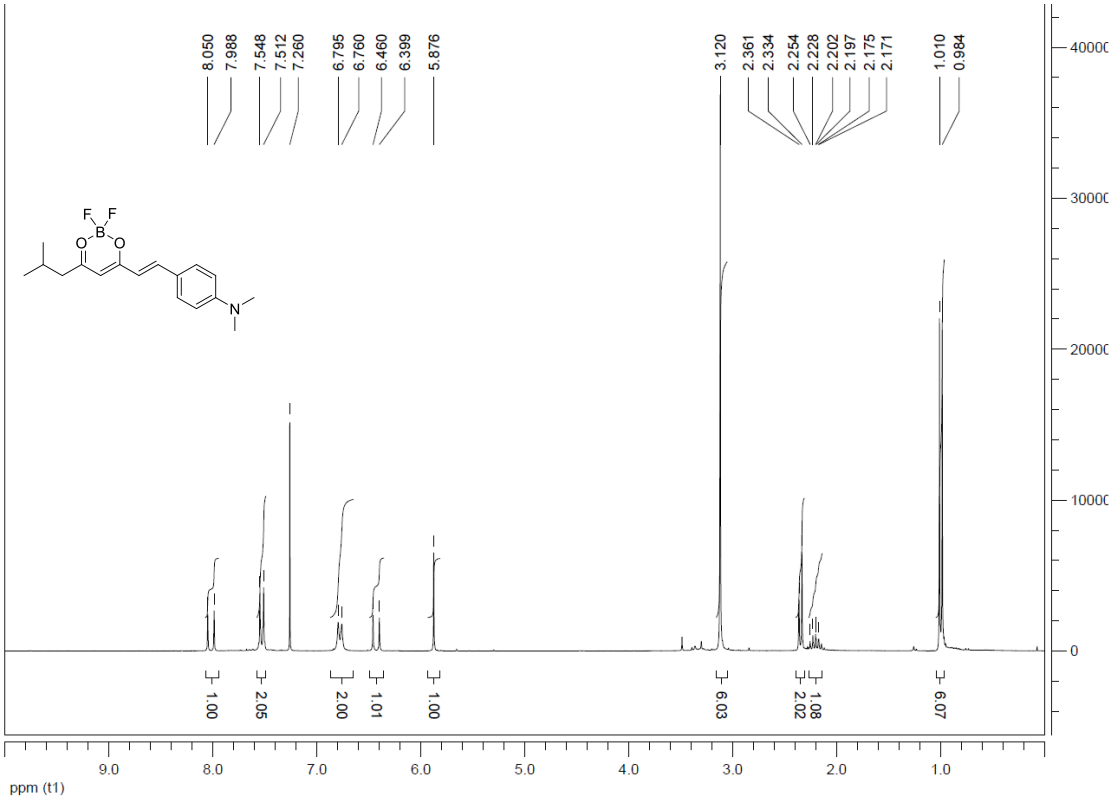


Figure NMR53. ^{1}H NMR spectrum of **6-iPr** ((E)-6-(4-(dimethylamino)styryl)-2,2-difluoro-4-isobutyl-2H-1,3,2-dioxaborinin-1-ium-2-uide)

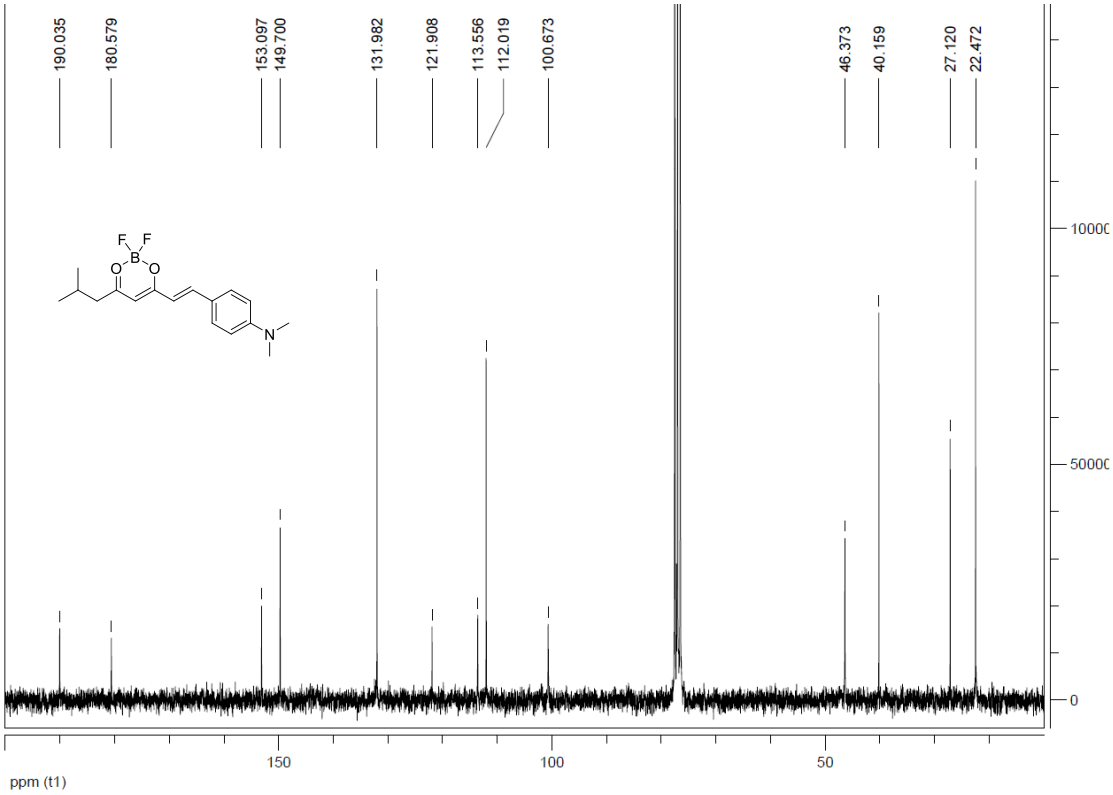


Figure NMR54. ^{13}C NMR spectrum of **6-iPr** ((E)-6-(4-(dimethylamino)styryl)-2,2-difluoro-4-isobutyl-2H-1,3,2-dioxaborinin-1-ium-2-uide)

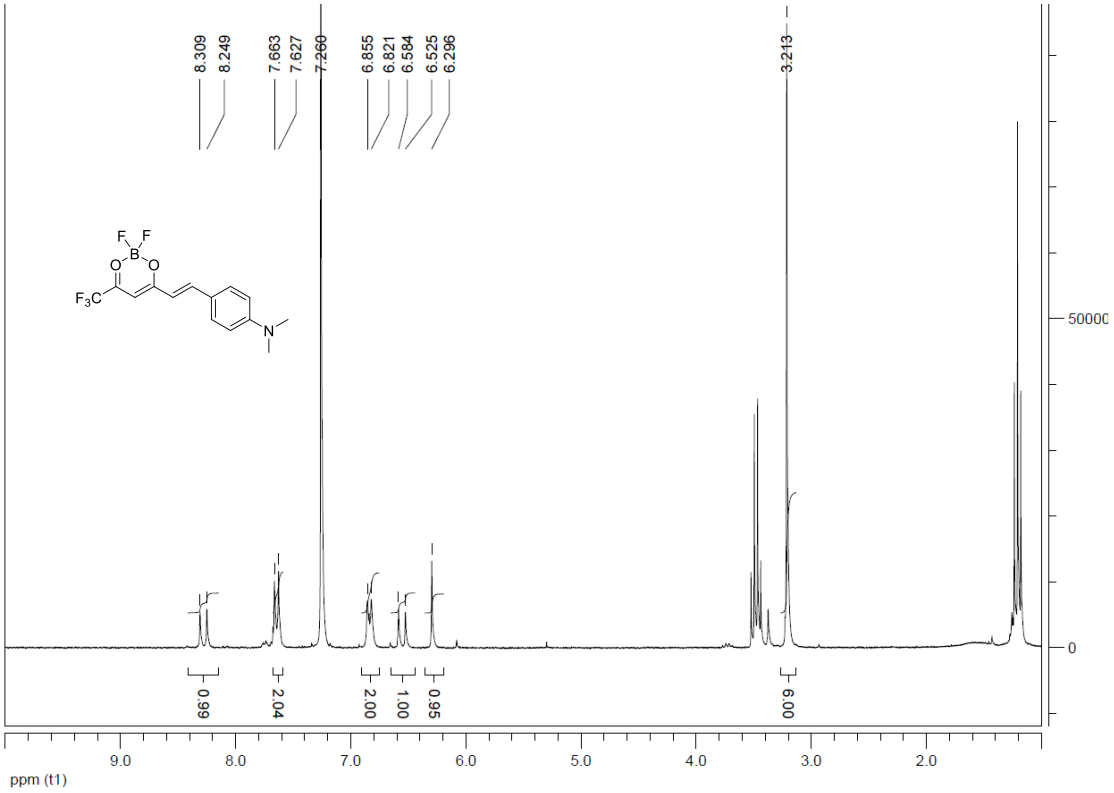


Figure NMR55. ^{1}H NMR spectrum of **6-CF$_3$** ((E)-6-(4-(dimethylamino)styryl)-2,2-difluoro-4-(trifluoromethyl)-2H-1,3,2-dioxaborinin-1-ium-2-uide)

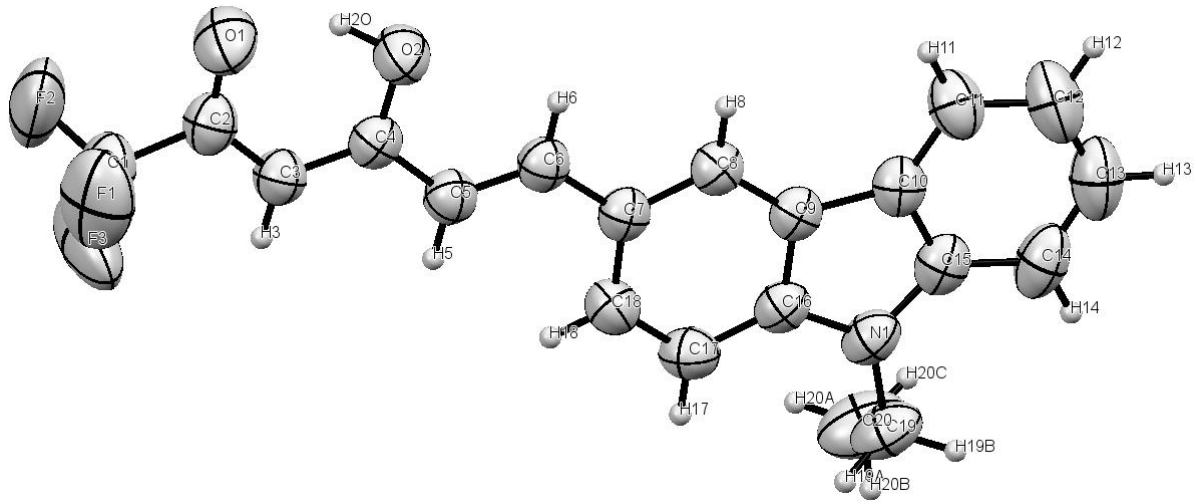


Figure S1. The molecular structure (ORTEP) of compound **Lig(4-CF$_3$)** with displacement ellipsoids drawn at the 50% probability level.

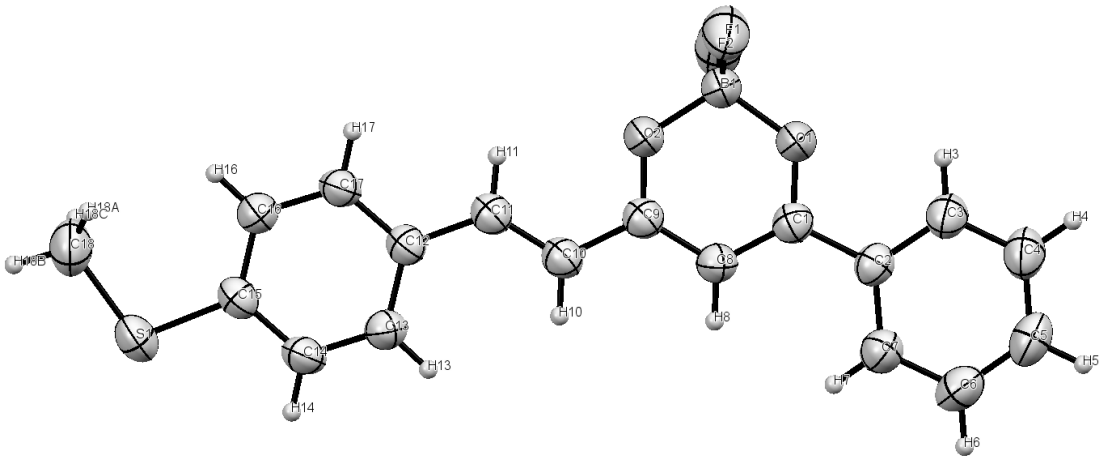


Figure S2. The molecular structure (ORTEP) of compound **2-Ph** with displacement ellipsoids drawn at the 50% probability level.

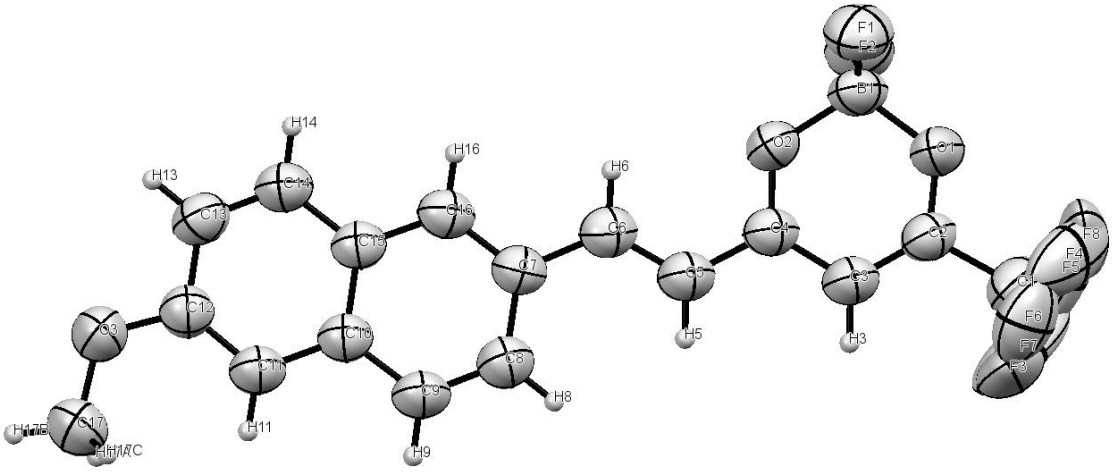


Figure S3. The molecular structure (ORTEP) of compound **3-CF$_3$** with displacement ellipsoids drawn at the 50% probability level.

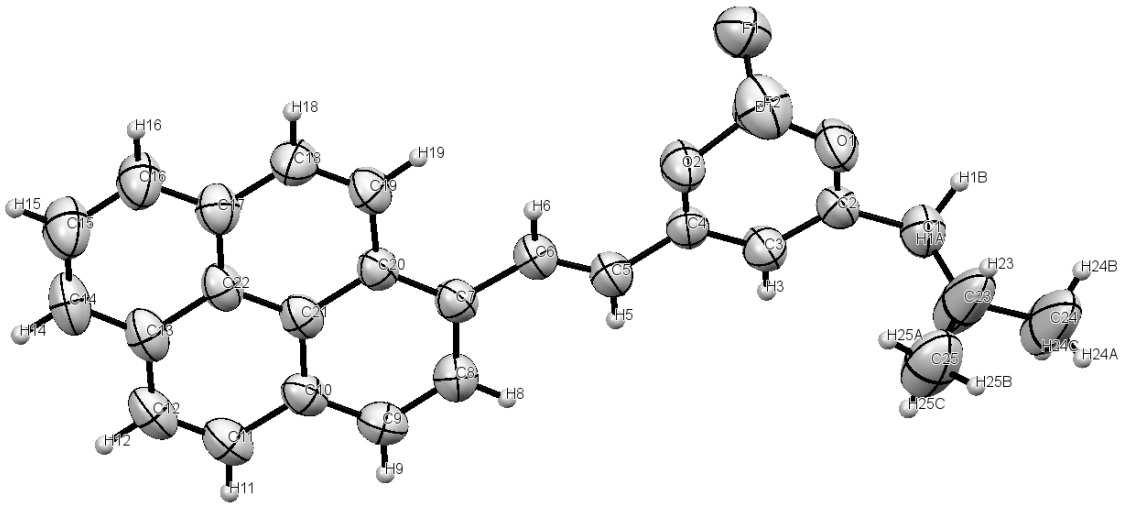


Figure S4. The molecular structure (ORTEP) of compound **5-iPr** with displacement ellipsoids drawn at the 50% probability level.

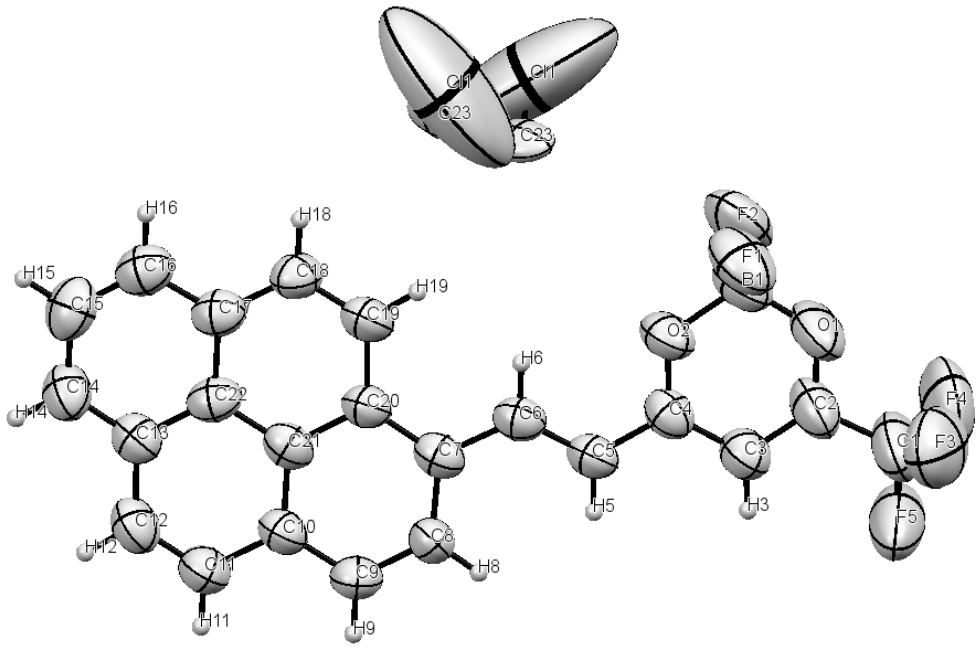


Figure S5. The molecular structure (ORTEP) of compound **5-CF$_3$** with displacement ellipsoids drawn at the 50% probability level.

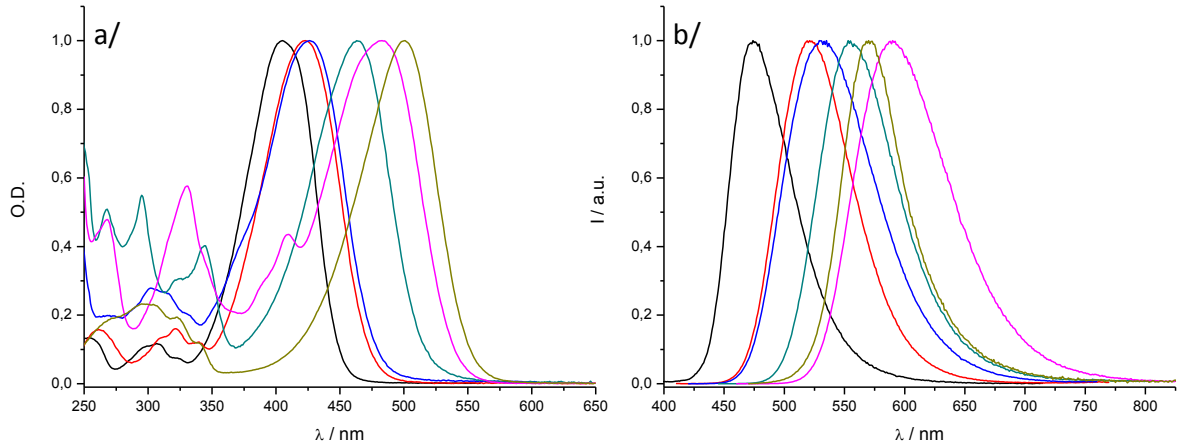


Figure S6. a/ UV/visible electronic absorption spectra and b/ fluorescence spectra of **1-iPr** (—), **2-iPr** (—), **3-iPr** (—), **4-iPr** (—), **5-iPr** (—) and **6-iPr** (—) exciting in the lowest transition in energy in dichloromethane solution.

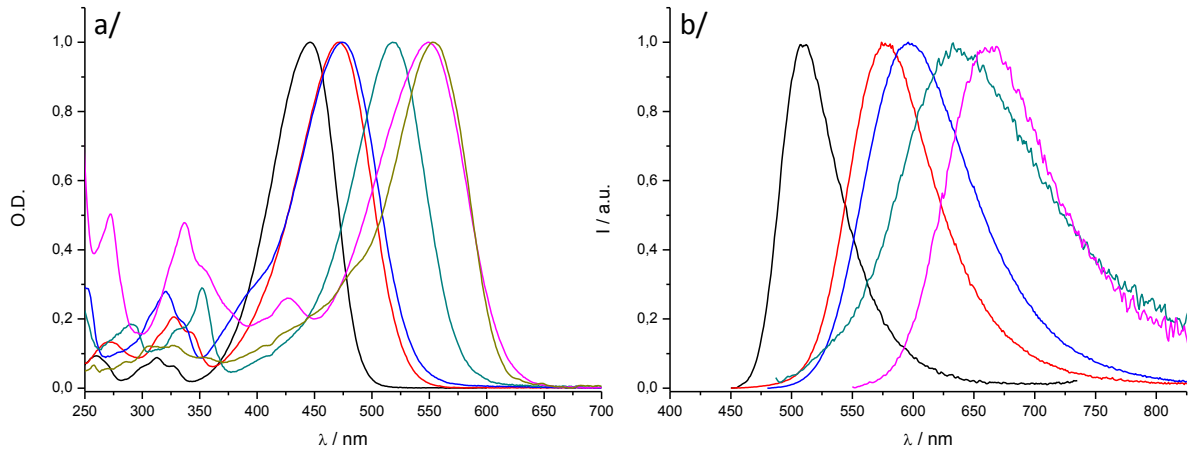


Figure S7. a/ UV/visible electronic absorption spectra and b/ fluorescence spectra of **1-CF$_3$** (—), **2-CF$_3$** (—), **3-CF$_3$** (—), **4-CF$_3$** (—), **5-CF$_3$** (—) and **6-CF$_3$** (—) exciting in the lowest transition in energy in dichloromethane solution. Note than **6-CF$_3$** is not emissive.

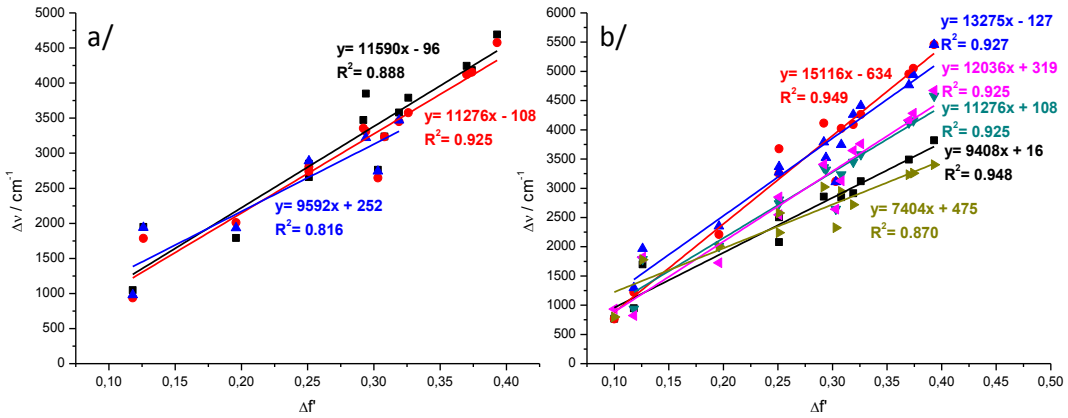
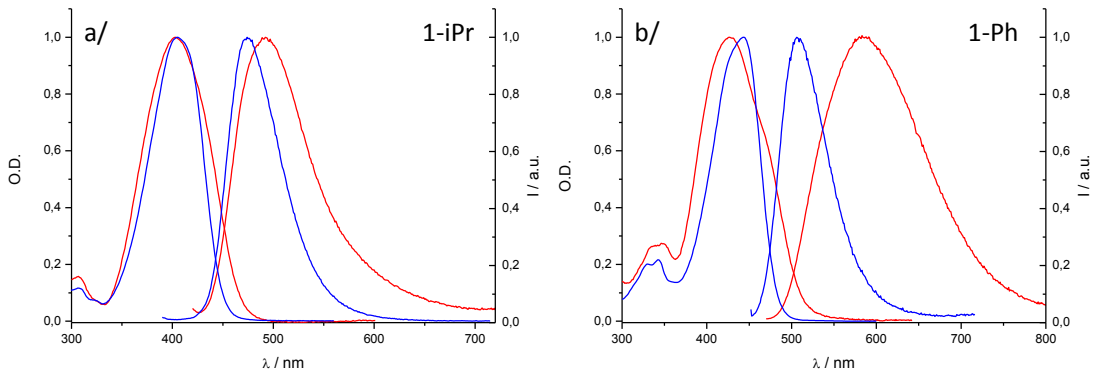


Figure S8. Lippert-Mataga slopes for a/ **4-iPr** (—), **4-Ph** (—) and **4-CF$_3$** (—); b/ **1-Ph** (—), **2-Ph** (—), **3-Ph** (—), **4-Ph** (—), **5-Ph** (—) and **6-Ph** (—).



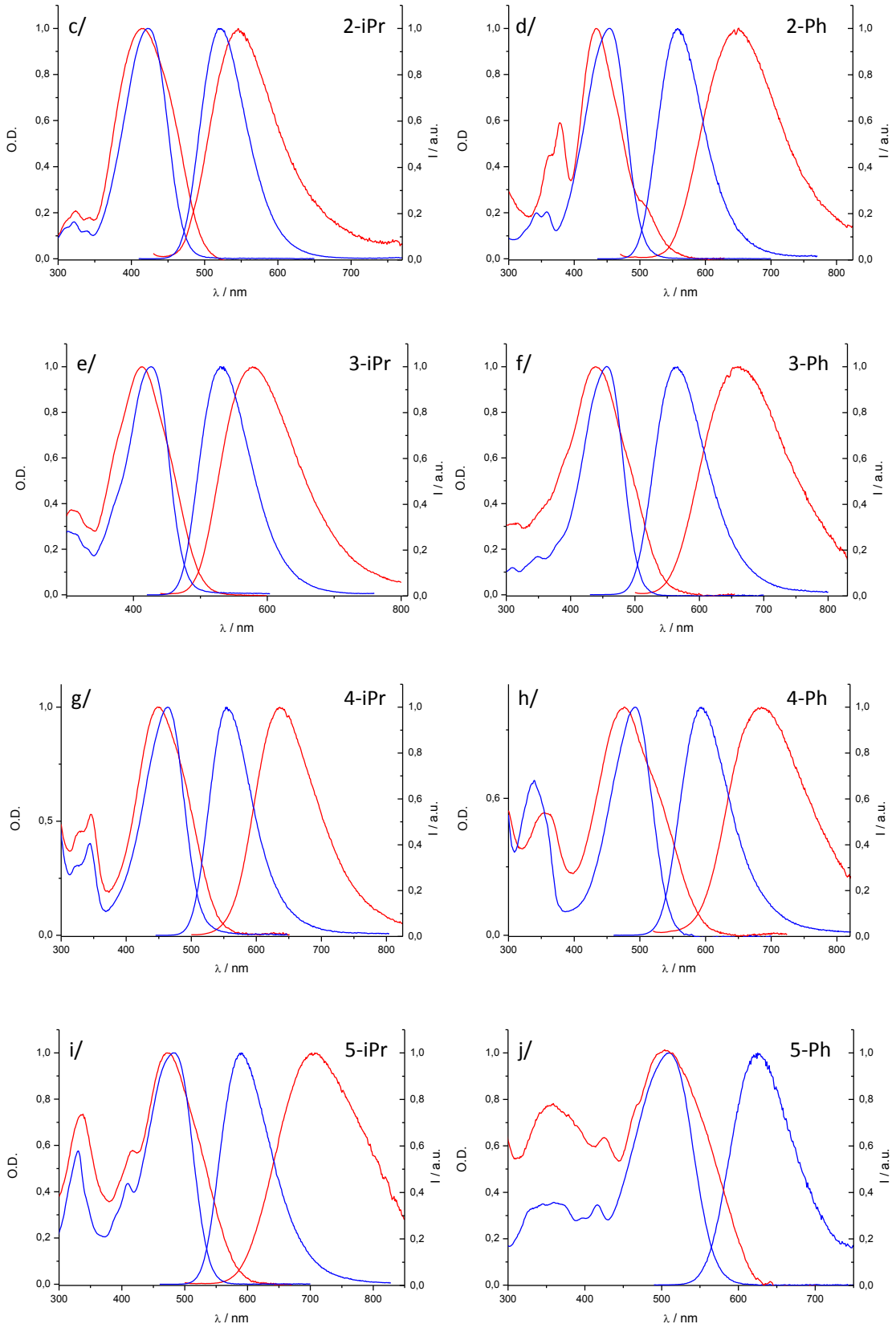


Figure S9. UV/visible absorption spectra of particles in water (—) and in DCM (—) and emission spectra of particles in water (—) and in DCM (—). Note that no emission was recorded for the particles of **5-Ph**.

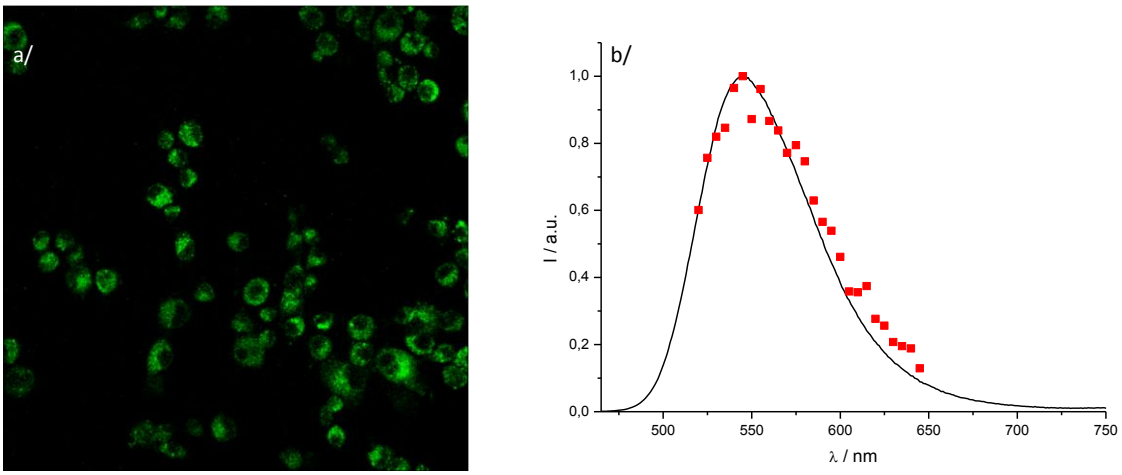


Figure S10. a/ One-photon (λ^{exc}= 500nm; 525 < λ^{det} < 700nm); b/ Fluorescence spectrum of **4-Ph** in dibutylether solution (▬, black solid line) and fluorescence spectrum measured into cells (■, red squares).

Table S1. Selected crystal data for compounds of **Lig(4-CF_3)**, **2-Ph**, **3-CF_3**, **5-iPr** and **5-CF_3**.

	Lig(4-CF_3)	**2-Ph**	**3-CF_3**	**5-iPr**	**5-CF_3**
Formula	$C_{20}H_{16}F_3NO_2$	$C_{18}H_{15}BF_2O_2S$	$C_{17}H_{12}BF_5O_3$	$C_{25}H_{21}BF_2O_2$	$4C_{22}H_{12}BF_5O_2.3CH_2Cl_2$
M / g	359.34	344.17	370.08	402.23	428.92
Size / mm^3	0.2x0.2x0.18	0.4x0.2x0.18	0.2x0.18x0.12	0.3x0.18x0.04	0.26x0.14x0.04
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	C2/c	$P2_1/c$	C2/c
a / Å	7.2632(2)	8.0580(2)	22.4771(8)	11.5387(4)	21.523(1)
b / Å	14.5322(4)	11.8497(3)	12.8997(8)	9.8453(4)	13.3264(9)
c / Å	16.5698(6)	17.4330(5)	15.6366(8)	19.8519(9)	14.604(1)
β / deg	91.431(1)	104.565(1)	132.732(5)	117.760(1)	95.233(7)
V / $Å^3$	1748.4	1611.09	3330.24	1995.65(14)	41.7132
Z	4	4	8	4	8
λ(Mo/$K\alpha$) / Å	0.71073	0.71073	0.71073	0.71073	0.71073
T / K	293(2)	293(2)	293(2)	293(2)	293(2)
Dc / $g.cm^{-3}$	1.365	1.419	1.476	1.339	1.366
θ range / deg	1.86-29.02	3.106-29.013	3.18-26.37	2.246-29.022	2.333-28.589
hkl ranges	$0 < h < 9$ $0 < k < 19$ $-22 < l < 22$	$0 < h < 10$ $-16 < k < 0$ $-23 < l < 22$	$0 < h < 28$ $0 < k < 16$ $-19 < l < 14$	$0 < h < 15$ $0 < k < 12$ $-24 < l < 23$	$0 < h < 28$ $0 < k < 17$ $-18 < l < 18$
Variable	238	217	264	271	289
Refln measured	16427	15748	15681	19127	19024
Refln $I > 2\sigma(I)$	4436	4145	3394	5138	5015
R1 $I > 2\sigma(I)$	0.0676	0.0501	0.0612	0.0796	0.111
R1 all data	0.1311	0.0964	0.1608	0.2017	0.2664
*w*R2 $I > 2\sigma(I)$	0.1843	0.1161	0.1417	0.2015	0.2749
*w*R2 all data	0.2309	0.1385	0.1897	0.2477	0.3379
$\Delta\rho$ (+/-) / e. $Å^{-3}$	0.341 / -0.281	0.174 / -0.243	0.155 / -0.156	0.434 / -0.47	0.26 / -0.354

Table S2. Half-life ($t_{1/2}$) and kinetic rates (k_{obs}) for solvolysis of the hemicurcuminoide borondifluoride complexes with [BF_2]= 7.5 x 10^{-6} M in presence of 5% ethanol in DCM or in pure ethanol

	5% EtOH		100% EtOH	
	$t_{1/2}$ / min	k_{obs} / s^{-1}	$t_{1/2}$ / min	k_{obs} / s^{-1}
1-iPr	-[a]	-[a]	521.5	2.2 x 10^{-5}
2-iPr	-[a]	-[a]	350	3.3 x 10^{-5}
3-iPr	-[a]	-[a]	355	3.25 x 10^{-5}
4-iPr	-[a]	-[a]	927	1.25 x 10^{-5}
5-iPr	-[a]	-[a]	167	6.9 x 10^{-5}
6-iPr	-[a]	-[a]	3071	3.8 x 10^{-6}
1-Ph	-[a]	-[a]	1260	9.2 x 10^{-6}
2-Ph	-[a]	-[a]	567.5	2.0 x 10^{-5}
3-Ph	-[a]	-[a]	823.5	1.4 x 10^{-5}
4-Ph	-[a]	-[a]	1996	5.8 x 10^{-6}
5-Ph	-[a]	-[a]	518	2.2 x 10^{-5}
6-Ph	-[a]	-[a]	5700	2.0 x 10^{-6}
1-CF_3	5.95	1.9 x 10^{-3}	-[b]	-[b]
2-CF_3	2.35	4.9 x 10^{-3}	-[b]	-[b]
3-CF_3	2.95	3.9 x 10^{-3}	-[b]	-[b]
4-CF_3	22.65	5.1 x 10^{-4}	-[b]	-[b]
5-CF_3	1.95	5.9 x 10^{-3}	-[b]	-[b]
6-CF_3	243.6	4.7 x 10^{-5}	-[b]	-[b]

a- No solvolysis is observed; b- Solvolysis was too fast to be observed.

Table S3. Photophysical properties of compounds **4-iPr**, **4-Ph** and **4-CF_3** in solvents of different polarity at room temperature

	4-iPr				**4-Ph**				**4-CF_3**			
Solvent	Φ_f	τ_f	k_f	k_{nr}	Φ_f	τ_f	k_f	k_{nr}	Φ_f	τ_f	k_f	k_{nr}
CCl_4	0.033	<0.6	-	-	0.161	0.93	1.7	9.0	0.235	2.00	1.2	3.8
Bu_2O	0.054	<0.6	-	-	0.352	1.83	1.9	3.5	0.378	3.24	1.2	1.9
Et_2O	0.090	0.70	1.3	13.0	0.536	2.42	2.2	1.9	0.342	2.87	1.2	2.3
DCM	0.331	2.40	1.4	2.8	0.570	3.08	1.9	1.4	0.009	0.12	0.8	82.6
Acetone	0.355	2.47	1.4	2.6	0.233	1.28	1.8	6.0	-	-	-	-
ACN	0.133	0.85	1.6	10.2	0.045	<0.6	-	-	-	-	-	-

Fluorescence quantum yields Φ_f, fluorescence lifetimes τ_f (ns), radiative k_f (10^8 s^{-1}) and nonradiative k_{nr} = (1 - Φ_f)/τ_f (10^8 s^{-1}) rate constants; Bu_2O: n-dibutyl ether, Et_2O: ethylic ether, DCM: dichloromethane, ACN: acetonitrile.

Table S4. Photophysical properties of compounds **5-iPr**, **5-Ph** and **5-CF$_3$** in solvents of different polarity at room temperature

	5-iPr				**5-Ph**				**5-CF$_3$**			
Solvent	Φ_f	τ_f	k_f	k_{nr}	Φ_f	τ_f	k_f	k_{nr}	Φ_f	τ_f	k_f	k_{nr}
CCl_4	0.058	0.61	1.0	15.4	0.210	1.40	1.5	5.8	0.326	2.80	1.2	2.4
Bu_2O	0.109	0.97	1.1	9.2	0.345	2.02	1.7	3.2	0.402	2,70	1.5	2.2
Et_2O	0.134	1.21	1.1	7.2	0.356	2.52	1.4	2.6	0.479	3,21	1.5	1.6
DCM	0.293	2.30	1.3	3.1	0.600	3.27	1.8	2.2	0.010	0.090	1.1	110
Acetone	0.351	2.85	1.2	2.3	0.460	3.11	1.5	1.7	-	-	-	-
ACN	0.281	2.30	1.2	3.1	0.199	1.32	1.5	6.1	-	-	-	-

Fluorescence quantum yields Φ_f, fluorescence lifetimes τ_f (ns), radiative k_f (10^8 s^{-1}) and nonradiative k_{nr} = $(1 - \Phi_f)/\tau_f$ (10^8 s^{-1}) rate constants; Bu_2O: n-dibutyl ether, Et_2O: ethylic ether, DCM: dichloromethane, ACN: acetonitrile.

Table S5. Theoretical electronic absorption data obtained for hemi-curcuminoids in DCM solution.

		λ_{max}		*f*	Assignment (%)	
		(nm)	(cm^{-1})			
1-Ph	I	440	22 727	1.422	HOMO→LUMO	(98.49)
	II	281	35 587	0.190	HOMO→LUMO+1	(94.84)
	III	338	29 586	0.116	HOMO-1→LUMO	(95.96)
1-iPr	I	395	25 316	1.328	HOMO→LUMO	(99.53)
	II	300	33 333	0.066	HOMO-1→LUMO	(91.13)
	III	241	41 494	0.065	HOMO-4→LUMO	(89.06)
1-CF$_3$	I	432	23 148	1.114	HOMO→LUMO	(100)
	II	304	32 895	0.162	HOMO-2→LUMO	(92.79)
	III	208	48 077	0.105	HOMO-1→LUMO+1	(84.96)
2-iPr	I	479	20 877	1.453	HOMO→LUMO	(100)
	II	312	32 051	0.279	HOMO-1→LUMO	(75.15)
	III	280	35 714	0.029	HOMO-2→LUMO	(83.97)
3-iPr	I	443	22 573	0.977	HOMO→LUMO	(98.76)
	II	357	28 011	0.576	HOMO-1→LUMO	(93.66)
	III	241	41 494	0.435	HOMO-1→LUMO+1 HOMO→LUMO+2	(50.80) (25.58)
4-iPr	I	441	22 676	1.071	HOMO→LUMO	(99.04)
	II	332	30 120	0.567	HOMO-2→LUMO HOMO→LUMO+1	(76.89) (16.72)
	III	255	39 216	0.290	HOMO→LUMO+2	(73.40)
5-iPr	I	506	19 763	0.887	HOMO→LUMO	(99.10)
	II	327	30 581	0.467	HOMO→LUMO+1 HOMO-2→LUMO	(43.36) (37.15)
	III	374	26 738	0.270	HOMO-1→LUMO	(84.84)

6-iPr	I	419	23 866	1.190	HOMO→LUMO	(99.30)
	II	316	31 646	0.251	HOMO-1→LUMO	(95.78)
	III	253	39 526	0.061	HOMO→LUMO+1 HOMO→LUMO+2	(67.57) (22.77)

Table S6. Spectroscopic data and photophysical properties of all compounds in their particles form at room temperature.

	Particles in water			
Compound	$\lambda^{abs\ a}$ / nm	$\lambda^{em\ a}$ / nm	ϕ^{em} (solid)^{a,b}	FWHM / cm^{-1}
1-Ph	427	583	0.015	4159
1-iPr	403	492	0.005	3452
1-CF_3	-	-	-	-
2-Ph	433	648	0.02	3185
2-iPr	415	532	0.01	3838
2-CF_3	-	-	-	-
3-Ph	438	663	0.04	3470
3-iPr	413	580	0.04	3814
3-CF_3	-	-	-	-
4-Ph	477	685	0.04	2953
4-iPr	449	636	0.07	2663
4-CF_3	-	-	-	-
5-Ph	506	-[c]	-[c]	-[c]
5-iPr	472	708	0.015	3307
5-CF_3	-	-	-	-
6-Ph	-	-[c]	-[c]	-[c]
6-iPr	-	-[c]	-[c]	-[c]
6-CF_3	-	-	-	-

a: determined on particles, b: determined using an integration sphere, c: no emission was observed.