Electronic Supplementary Material (ESI) for Dalton Transactions.

Effect of the substituents on the $^1O_2$ production and biological activity of (N^N^N)Pt(py) complexes.

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Supporting Information

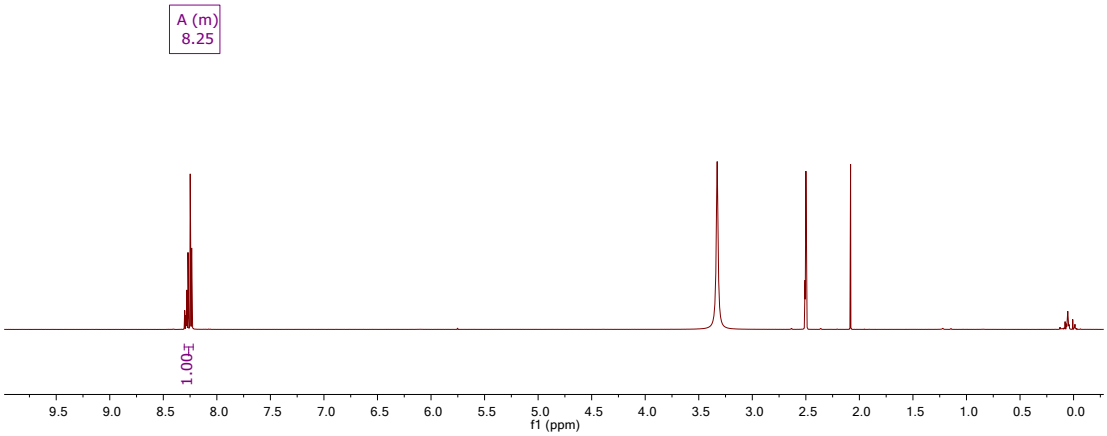

Figure S1. ^{1}H NMR spectrum of ligand $\mathbf{H_2L^3}$ in DMSO-d^6.

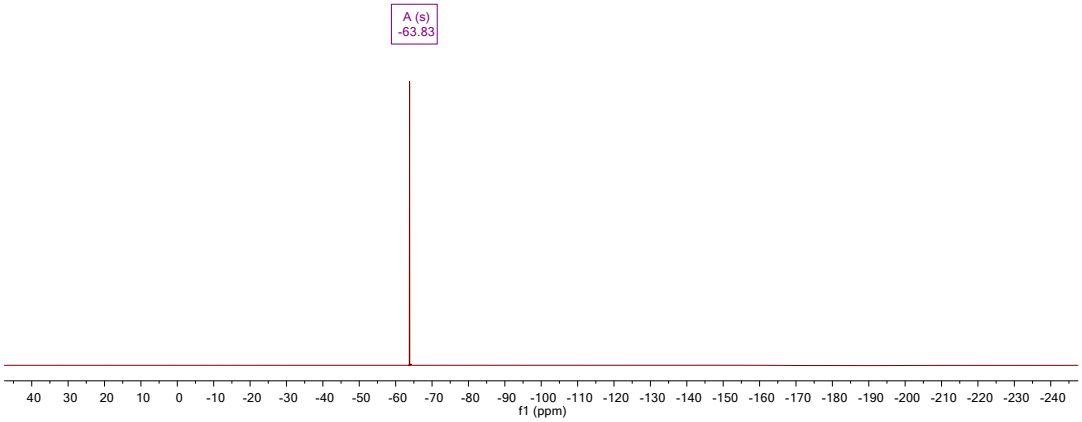

Figure S2. ^{19}F NMR spectrum of complex $\mathbf{H_2L^3}$ in DMSO-d^6.

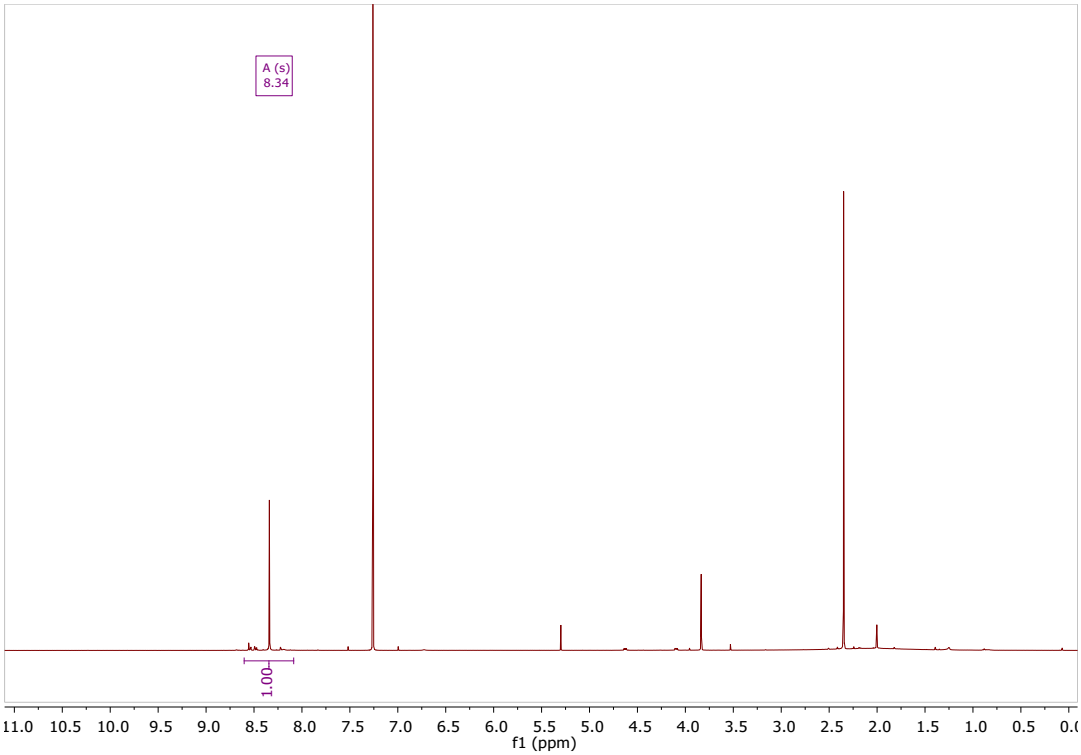

Figure S3. ^{1}H NMR spectrum of ligand $\mathbf{H_2L^4}$ in $CDCl_3$.

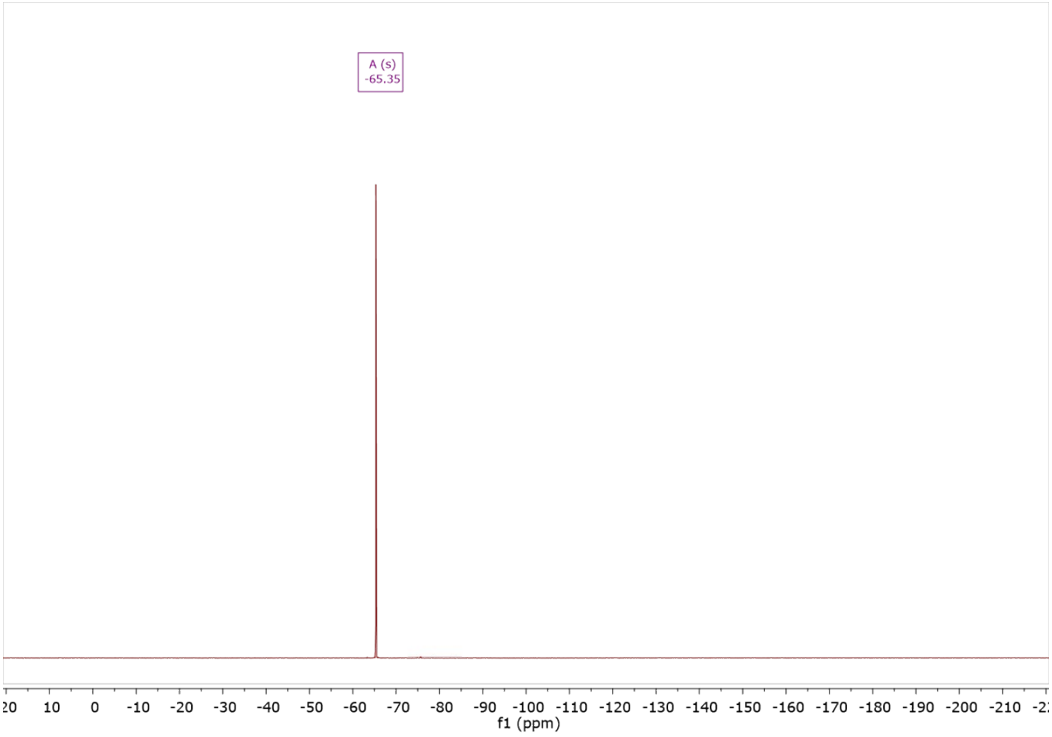

Figure S4. ^{19}F NMR spectrum of complex $\mathbf{H_2L^4}$ in $CDCl_3$.

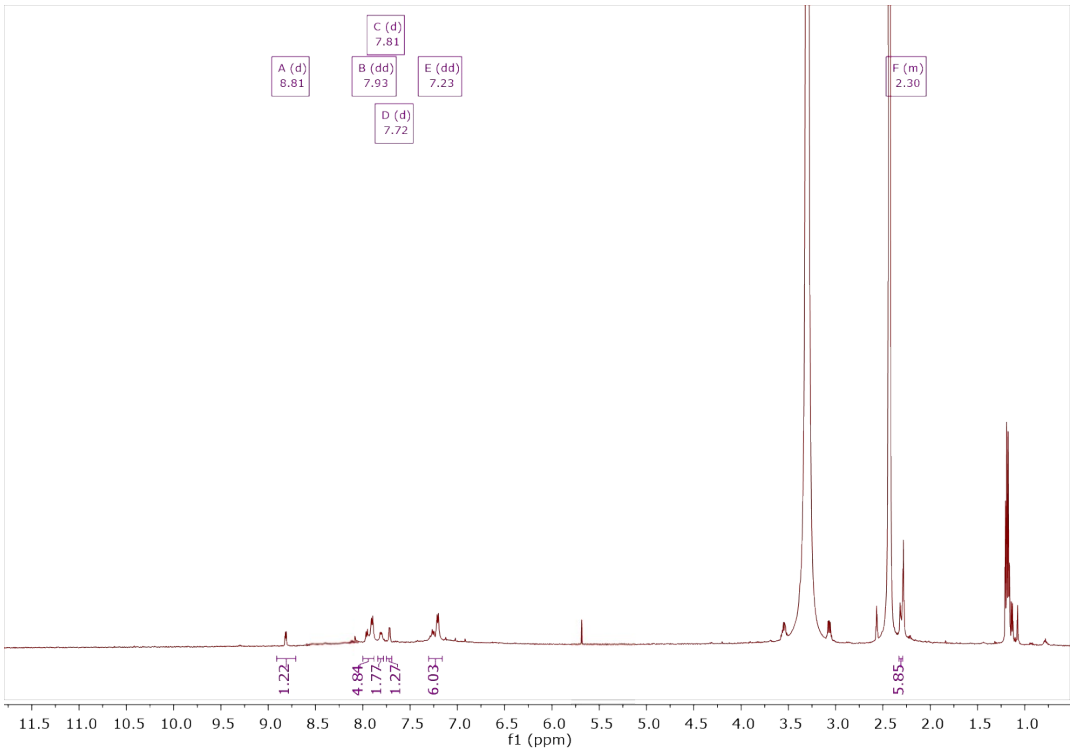

Figure S5. ^{1}H NMR spectrum of complex **1-CF$_3$** in DMSO-*d*^{6}.

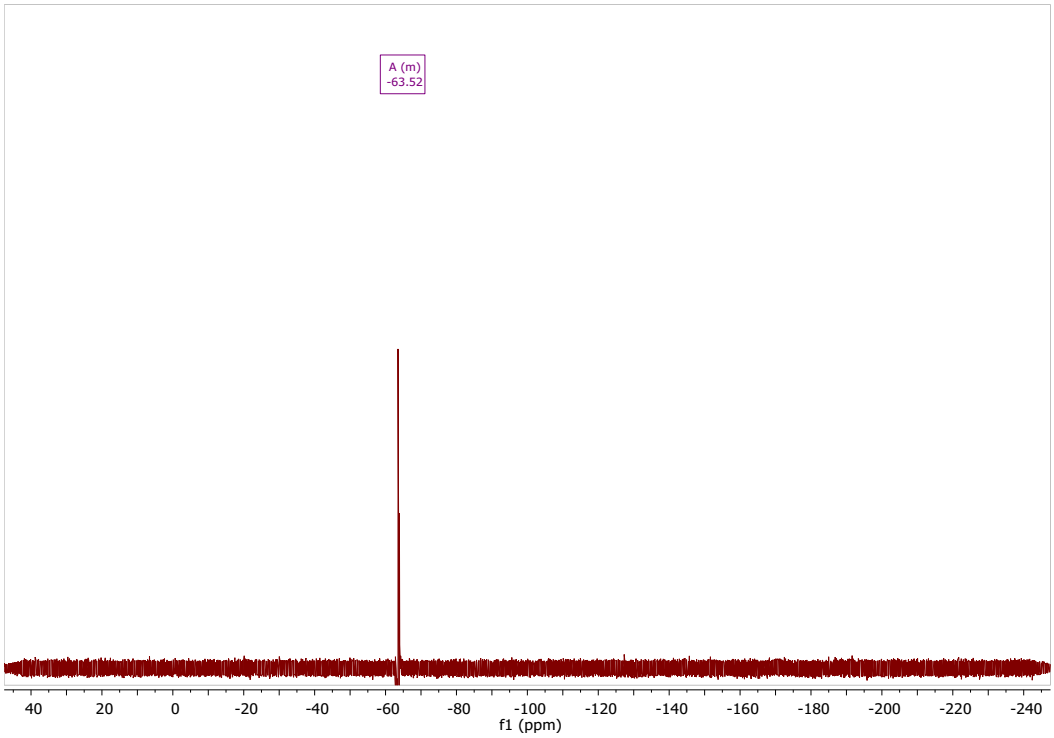

Figure S6. ^{19}F NMR spectrum of complex **1-CF$_3$** in DMSO-*d*^{6}.

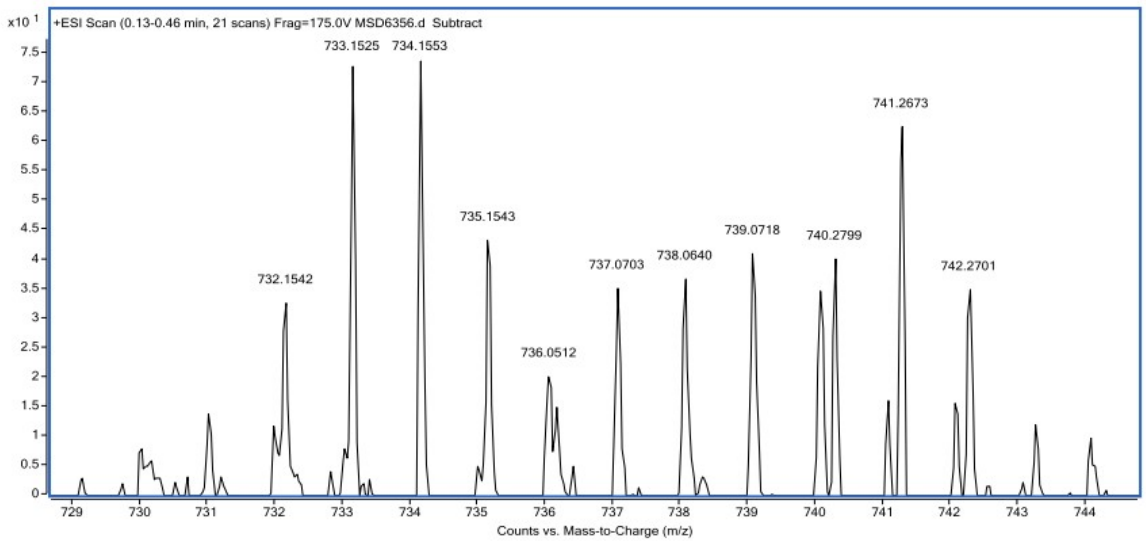

Figure S7. ESI-TOF(+) of complex **1-CF_3.**

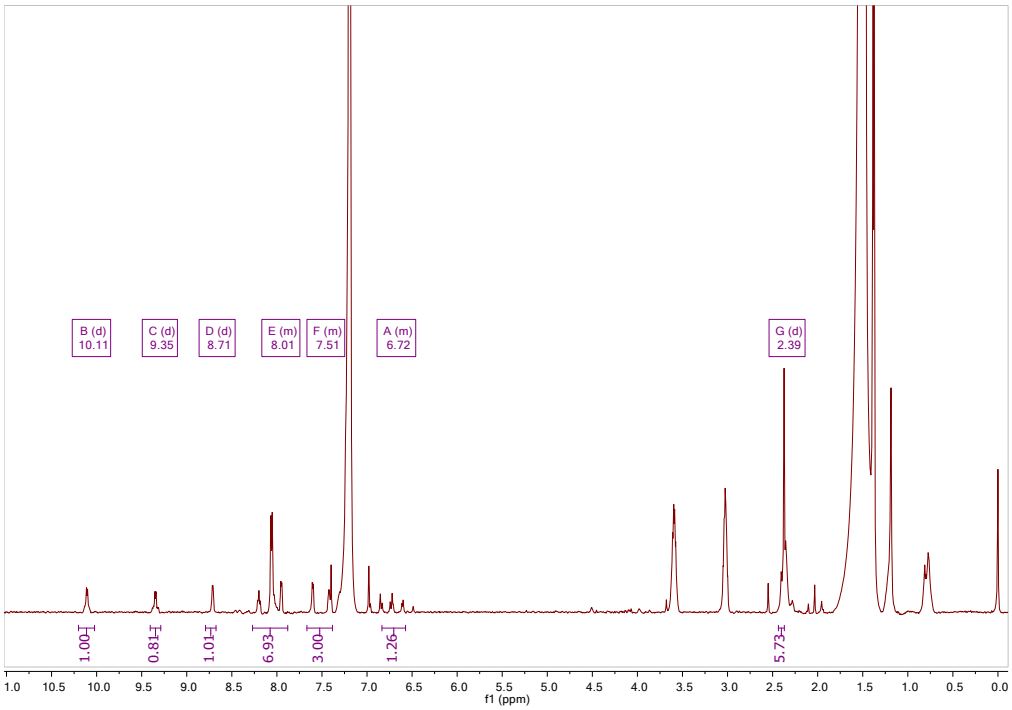

Figure S8. ^{1}H NMR spectrum of complex **1-CHF_2** in $CDCl_3$.

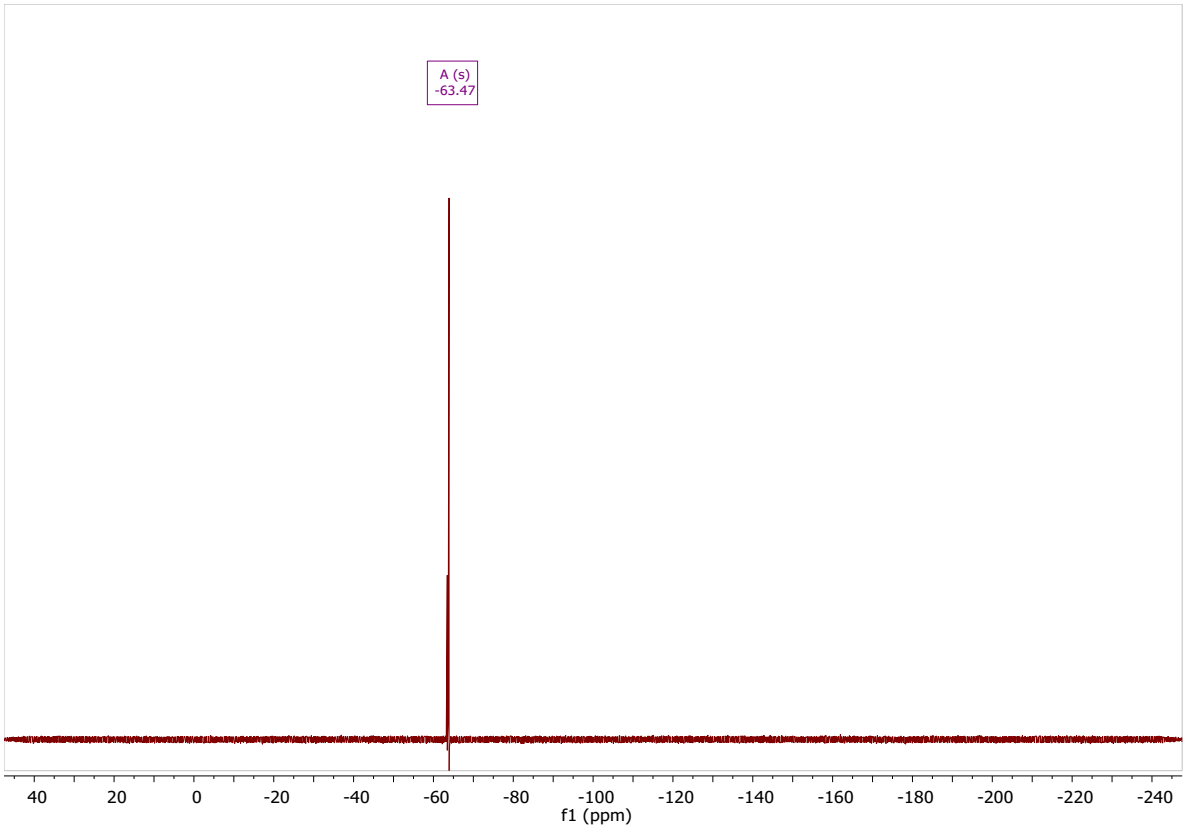

Figure S9. ^{19}F NMR spectrum of complex **1-CHF$_2$** in $CDCl_3$.

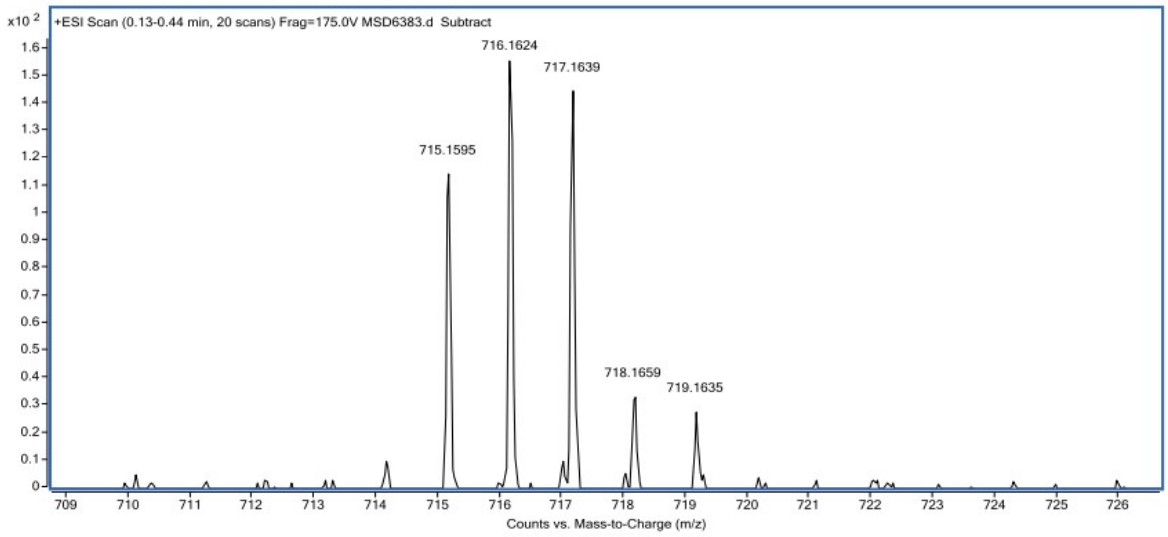

Figure S10. ESI-TOF(+) of complex **1-CHF$_2$.**

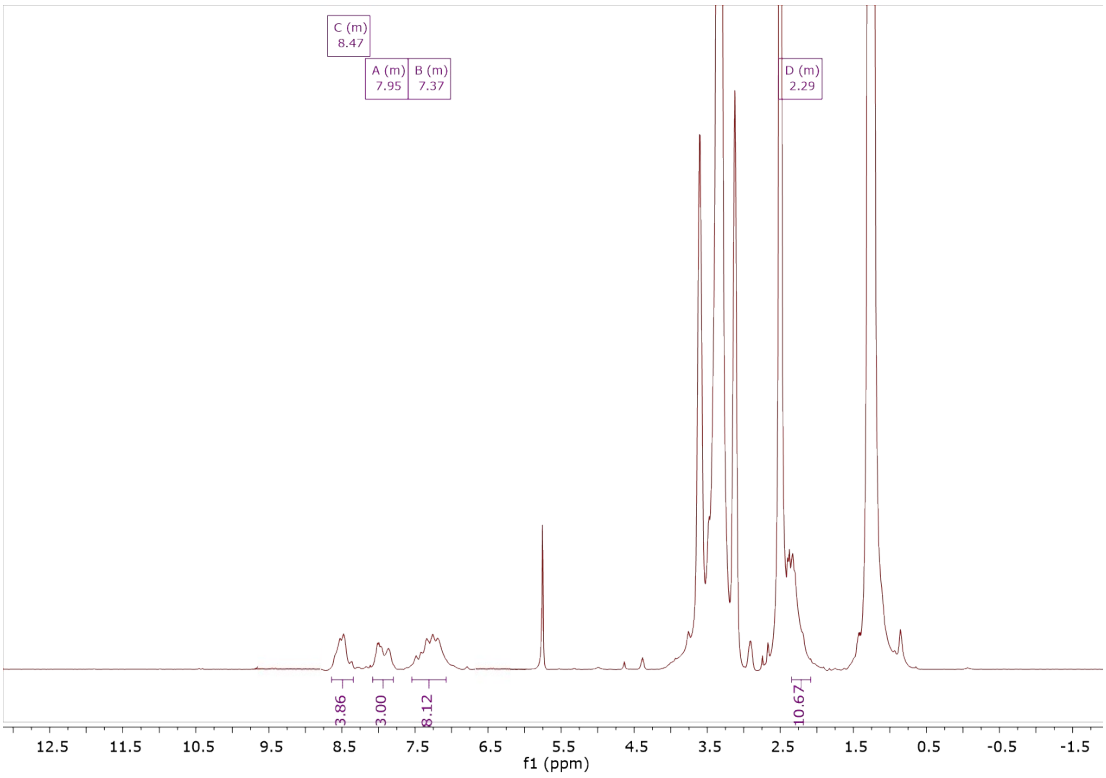

Figure S11. ^{1}H NMR spectrum of complex **1-CH$_3$** in DMSO-*d*^{6}.

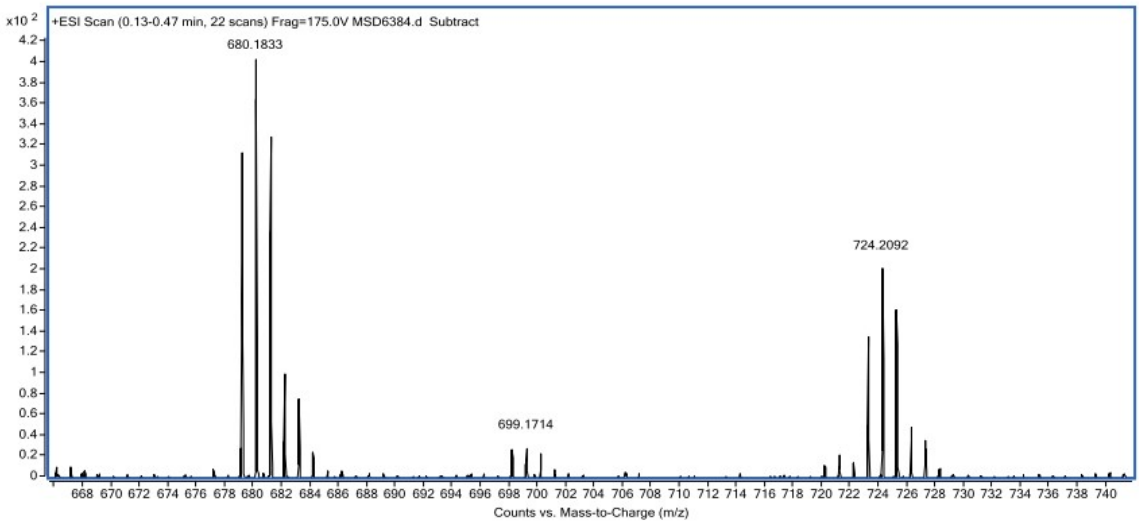

Figure S12. ESI-TOF(+) of complex **1-CH$_3$.**

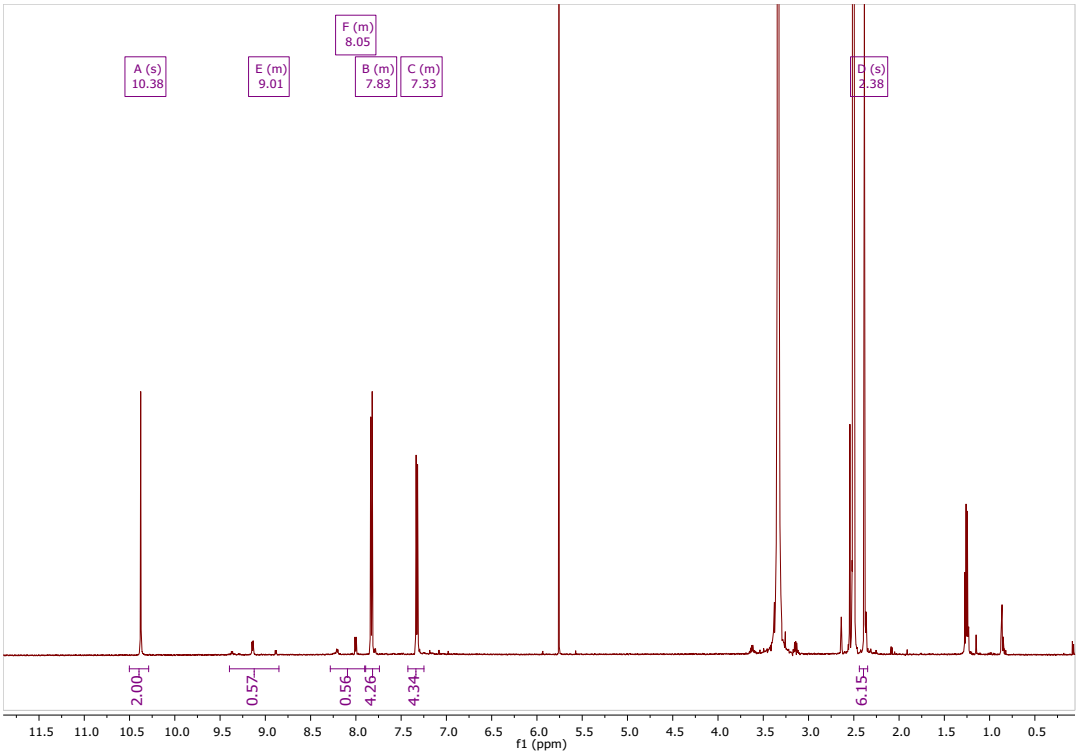

Figure S13. ^{1}H NMR spectrum of complex **2-CF$_3$** in DMSO-*d*^{6}.

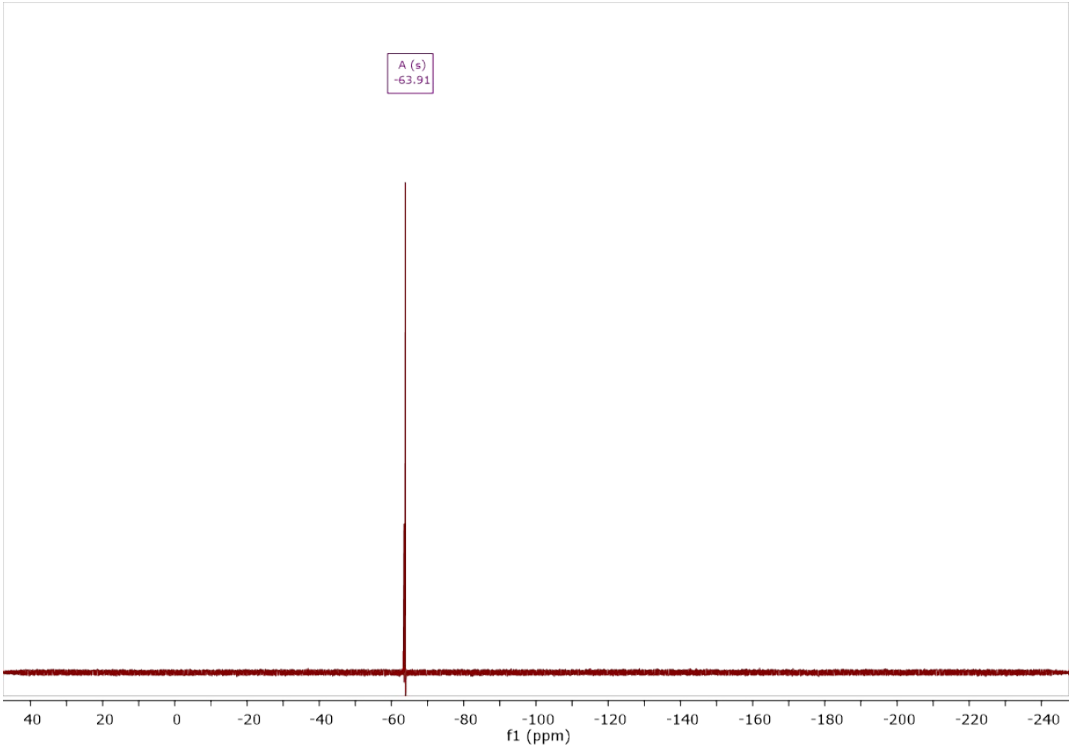

Figure S14. ^{19}F NMR spectrum of complex **2-CF$_3$** in DMSO-*d*^{6}.

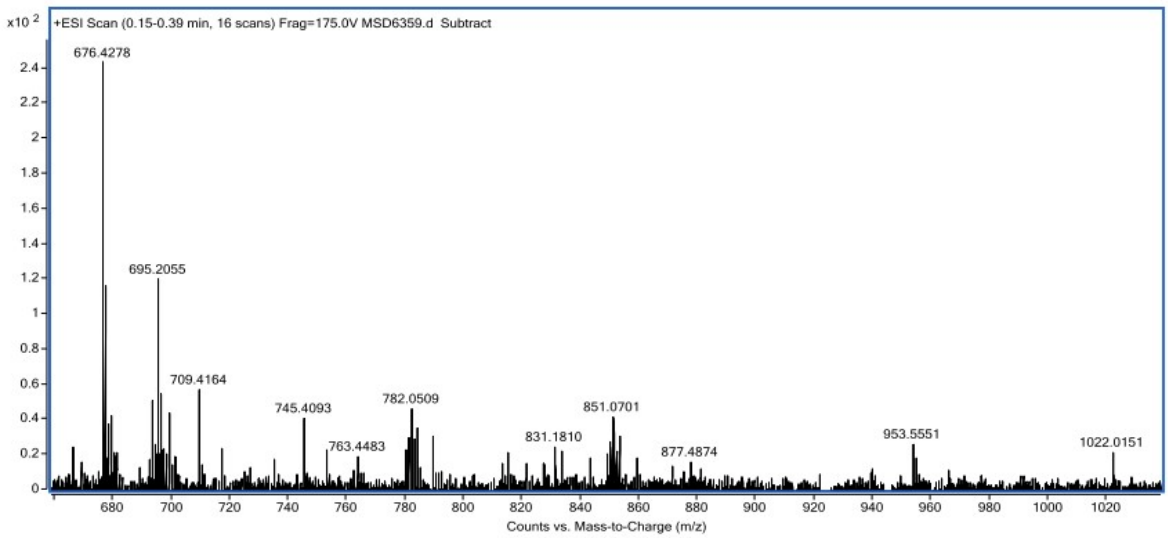

Figure S15. ESI-TOF(+) of complex **2-CF_3.**

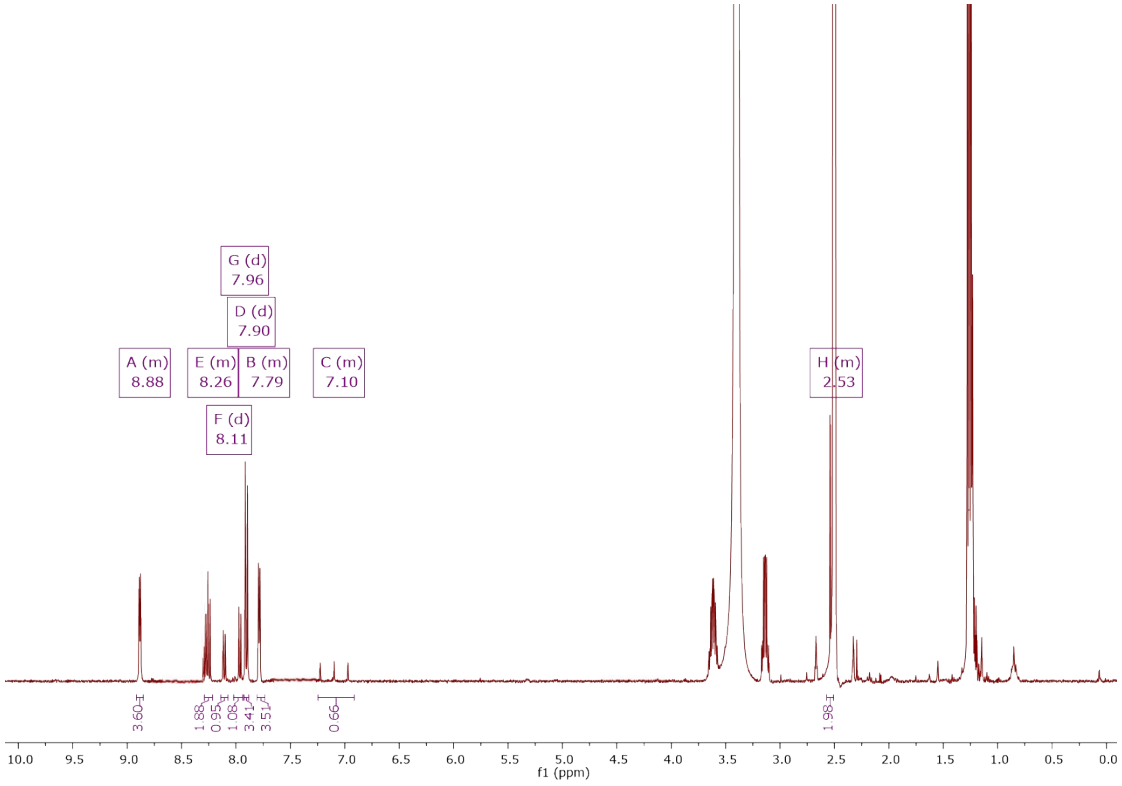

Figure S16. ^{1}H NMR spectrum of complex **2-CHF_2** in DMSO-d^6.

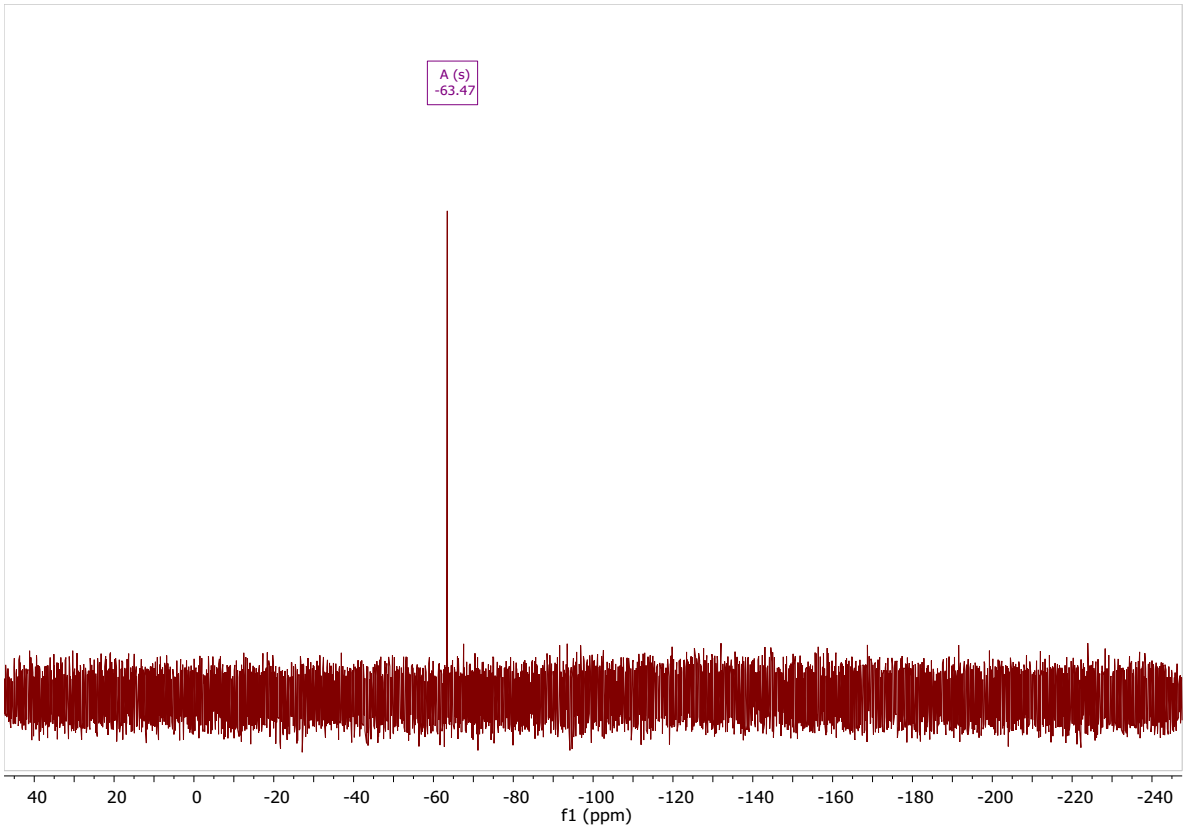

Figure S17. ^{19}F NMR spectrum of complex **2-CHF$_2$** in DMSO-d^6.

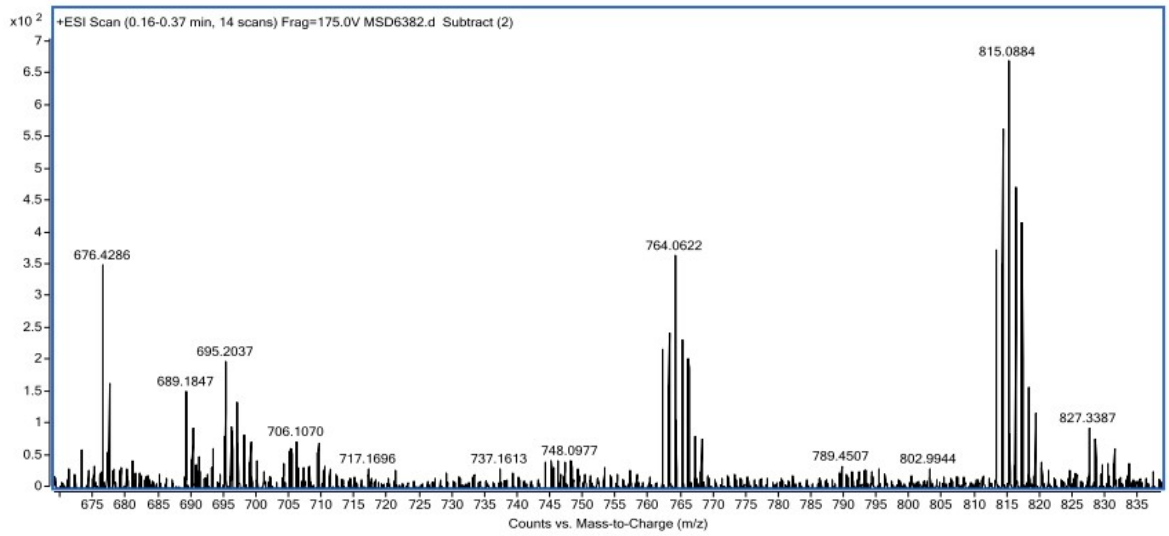

Figure S18. ESI-TOF(+) of complex **2-CHF$_2$.**

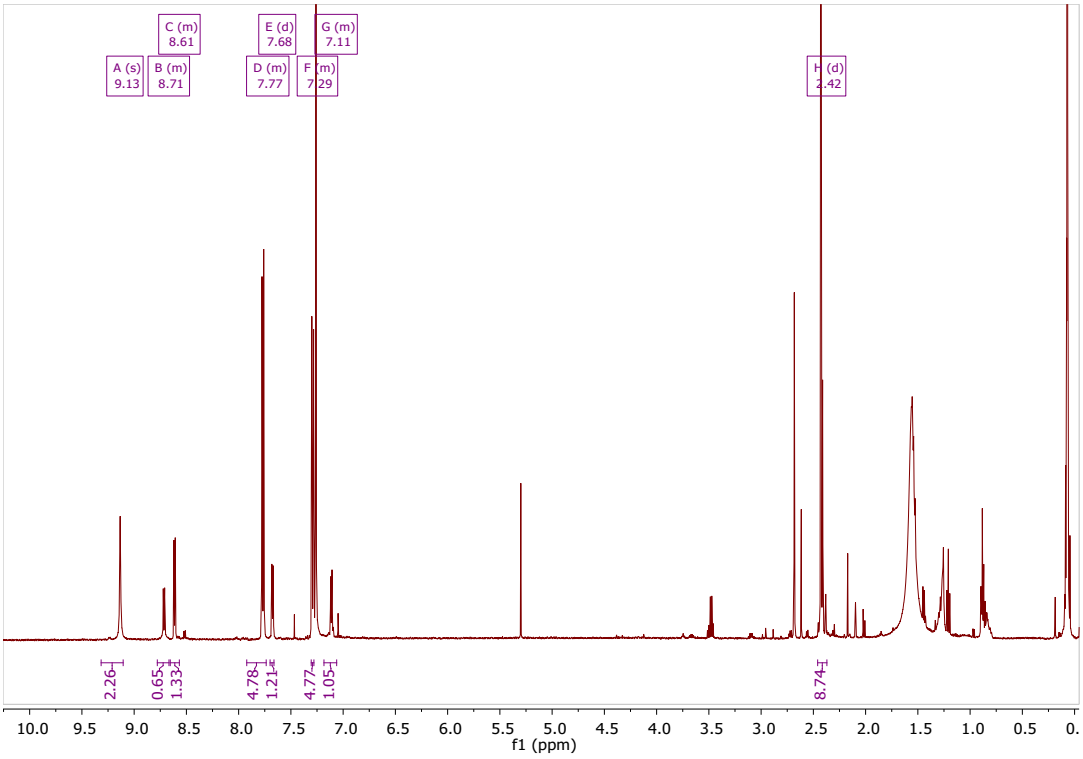

Figure S19. ^{1}H NMR spectrum of complex **2-CH$_3$** in $CDCl_3$.

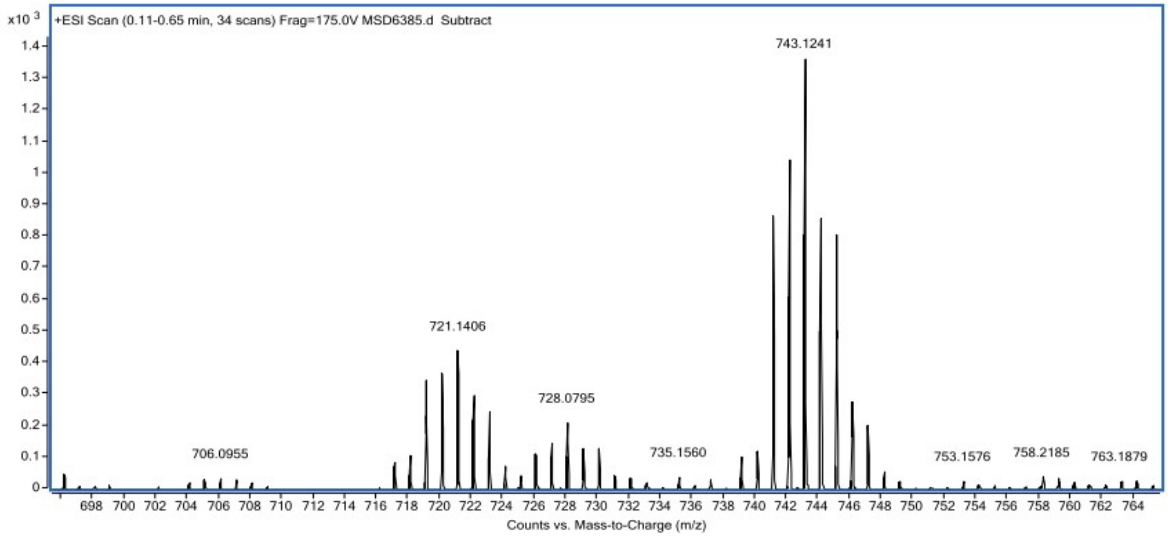

Figure S20. ESI-TOF(+) of complex **2-CH$_3$.**

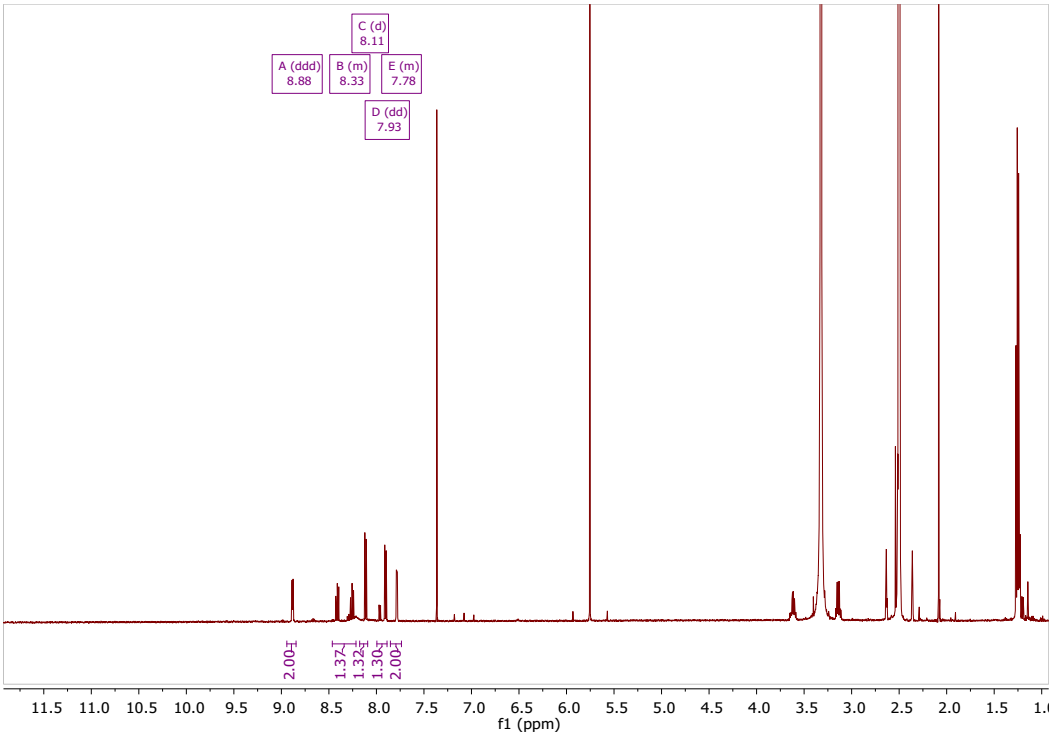

Figure S21. ^{1}H NMR spectrum of complex **3-CF$_3$** in DMSO-*d*^{6}.

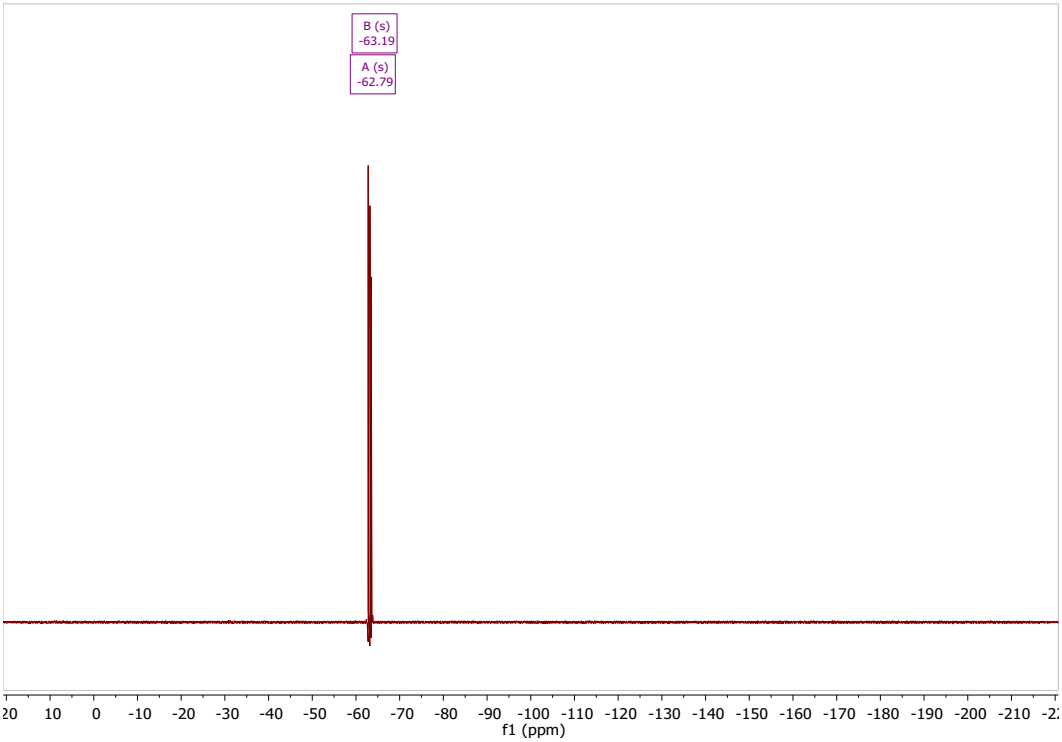

Figure S22. ^{19}F NMR spectrum of complex **3-CF$_3$** in DMSO-*d*^{6}.

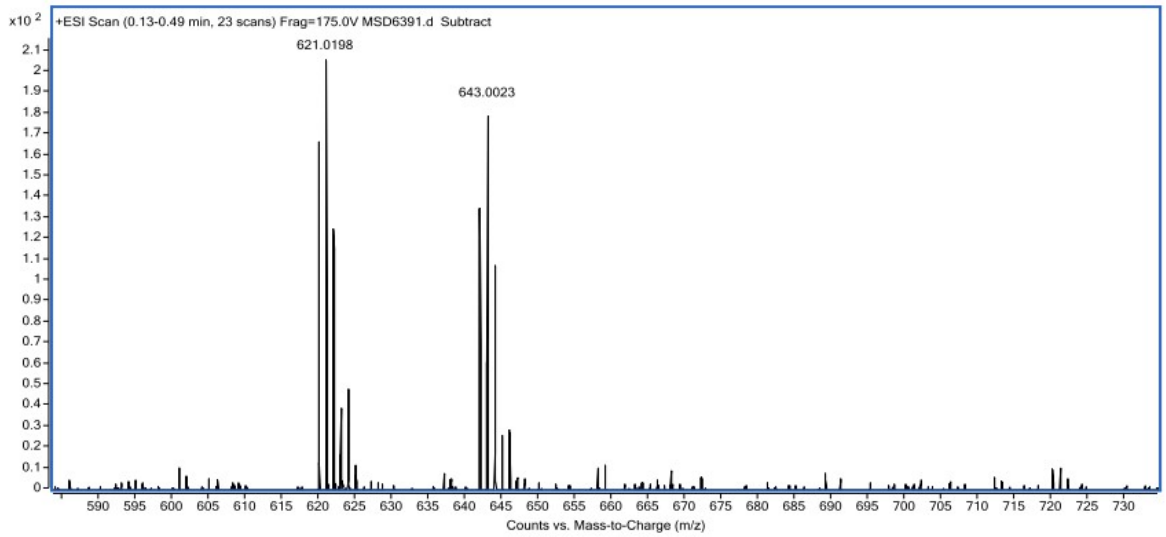

Figure S23. ESI-TOF(+) of complex **3-CF_3.**

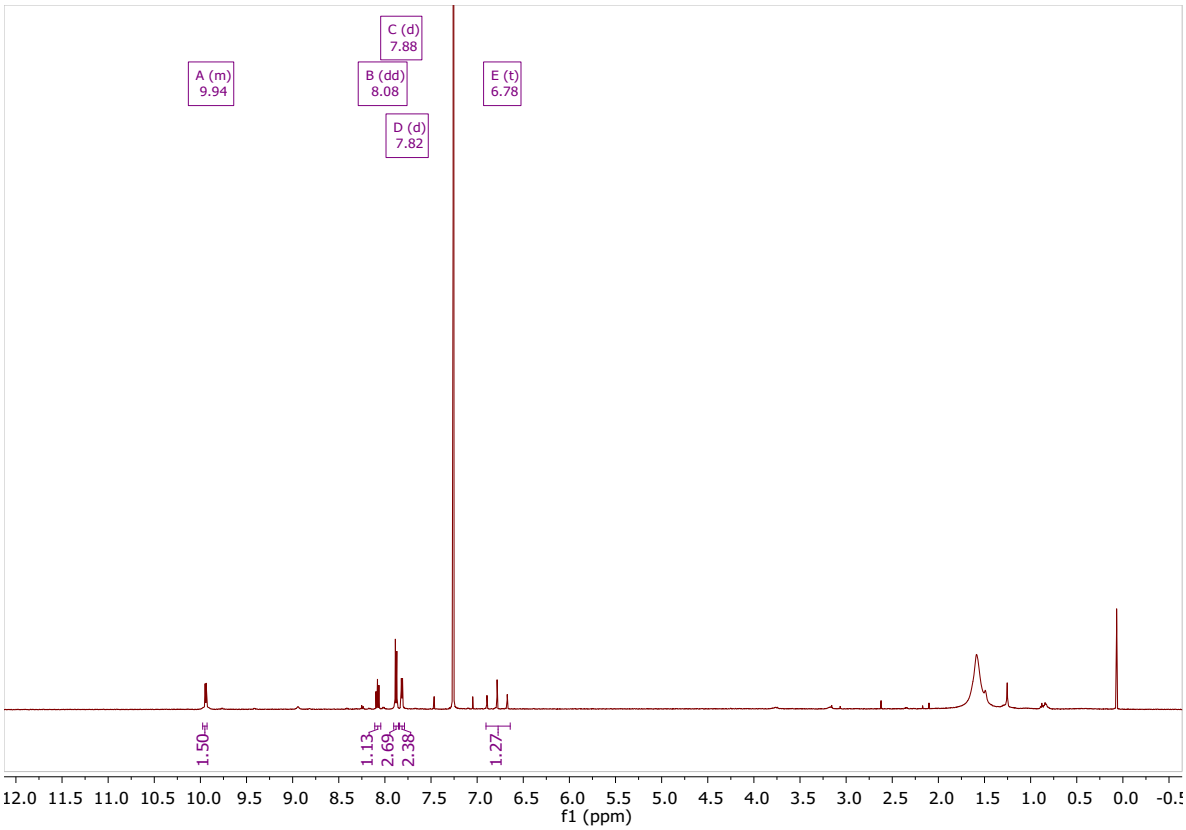

Figure S24. ^{1}H NMR spectrum of complex **3-CHF_2** in $CDCl_3$.

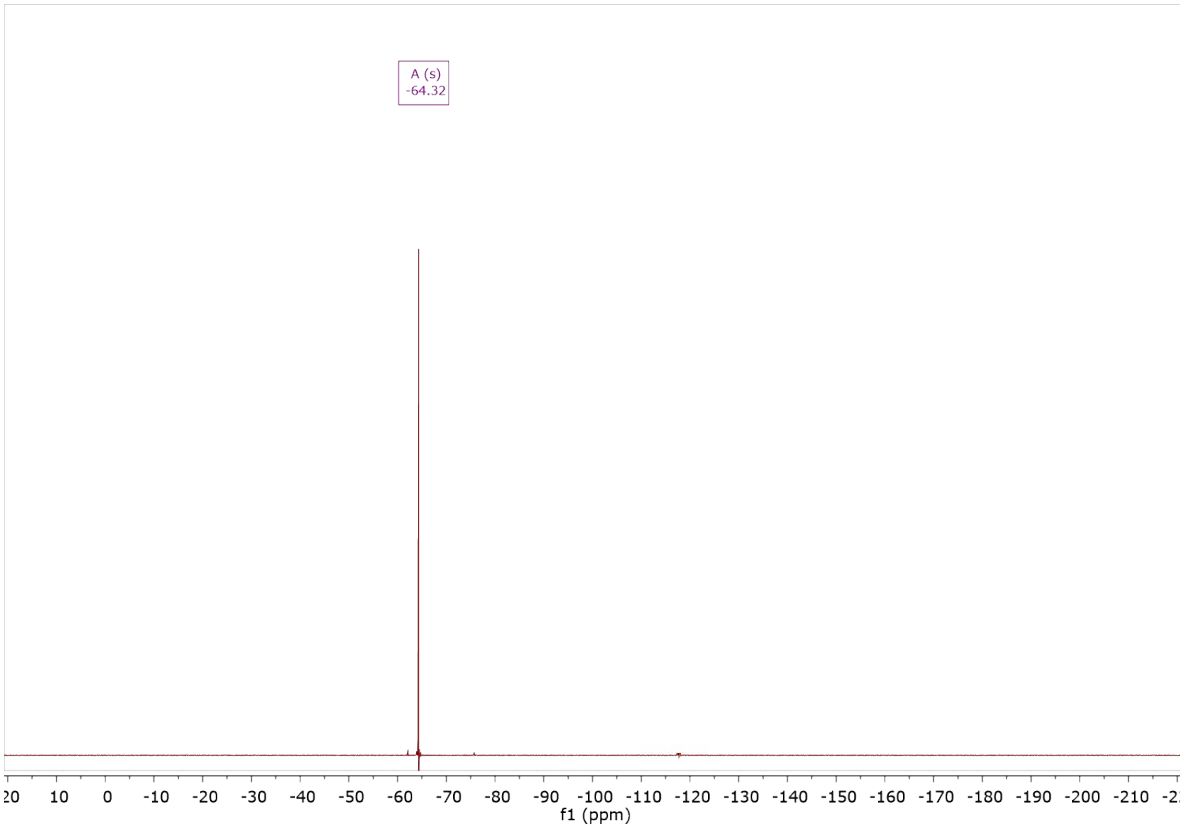

Figure S25. ^{19}F NMR spectrum of complex **3-CHF_2** in $CDCl_3$.

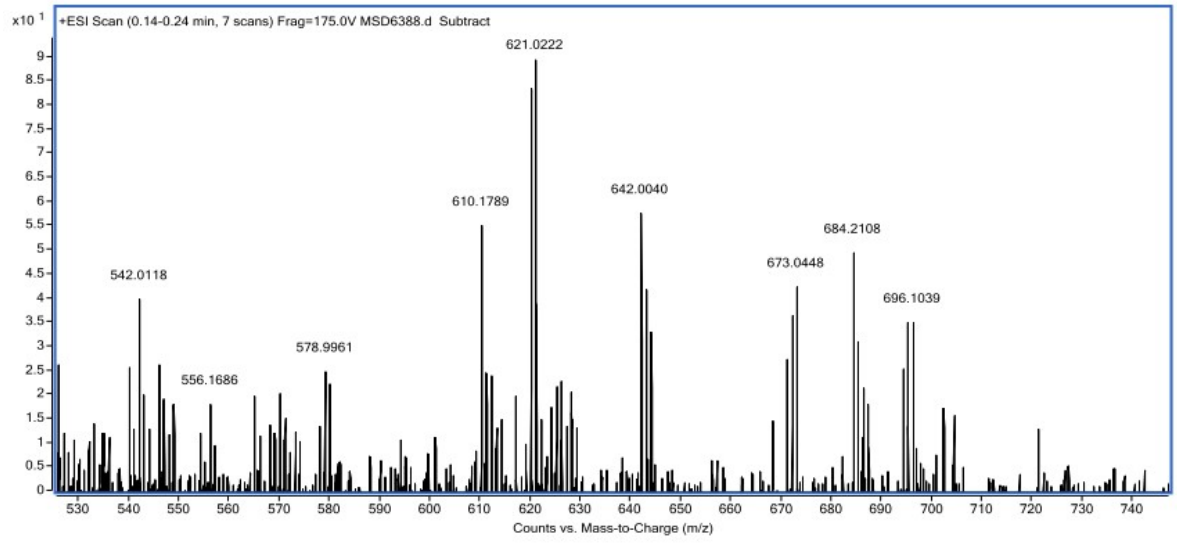

Figure S26. ESI-TOF(+) of complex **3-CHF_2.**

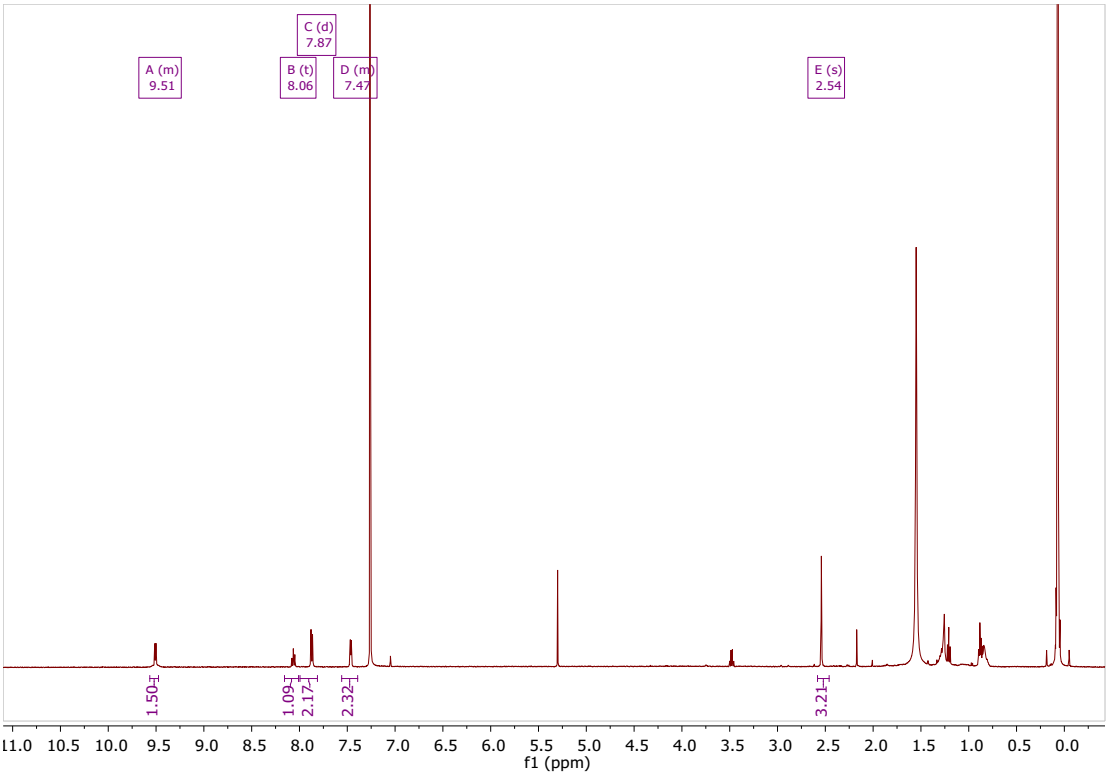

Figure S27. ^{1}H NMR spectrum of complex **3-CH$_3$** in $CDCl_3$.

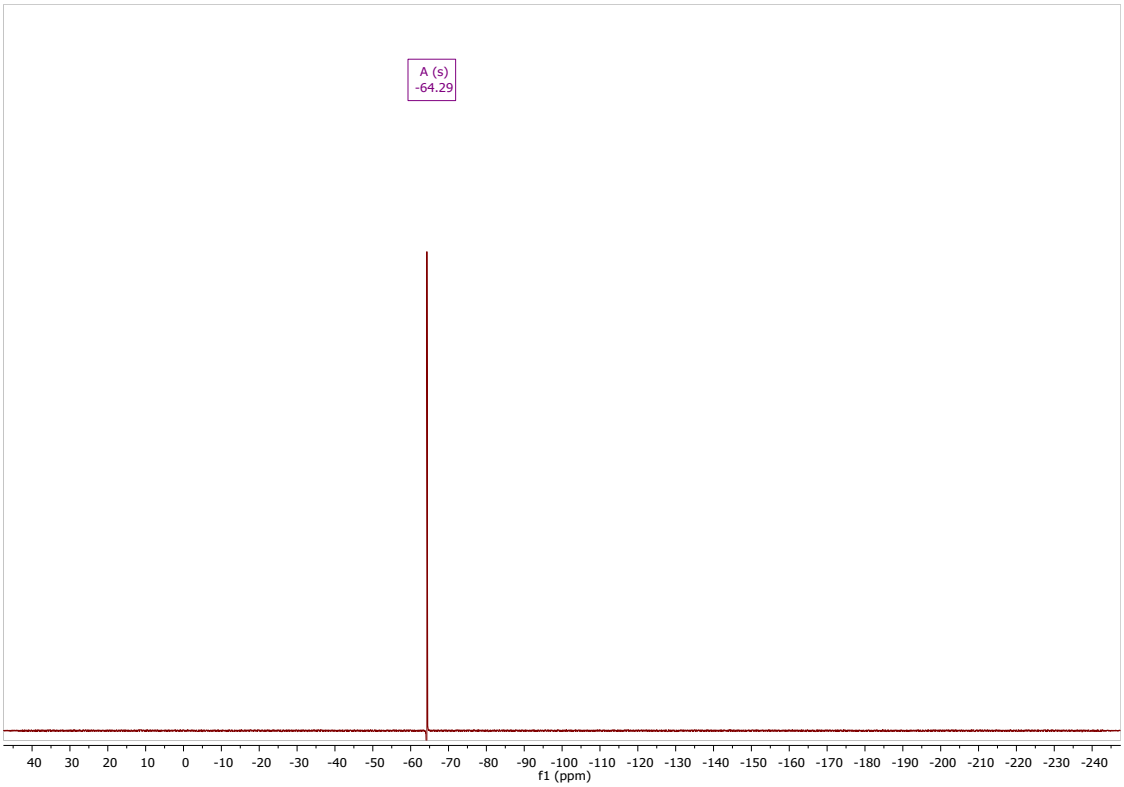

Figure S28. ^{19}F NMR spectrum of complex **3-CH$_3$** in $CDCl_3$.

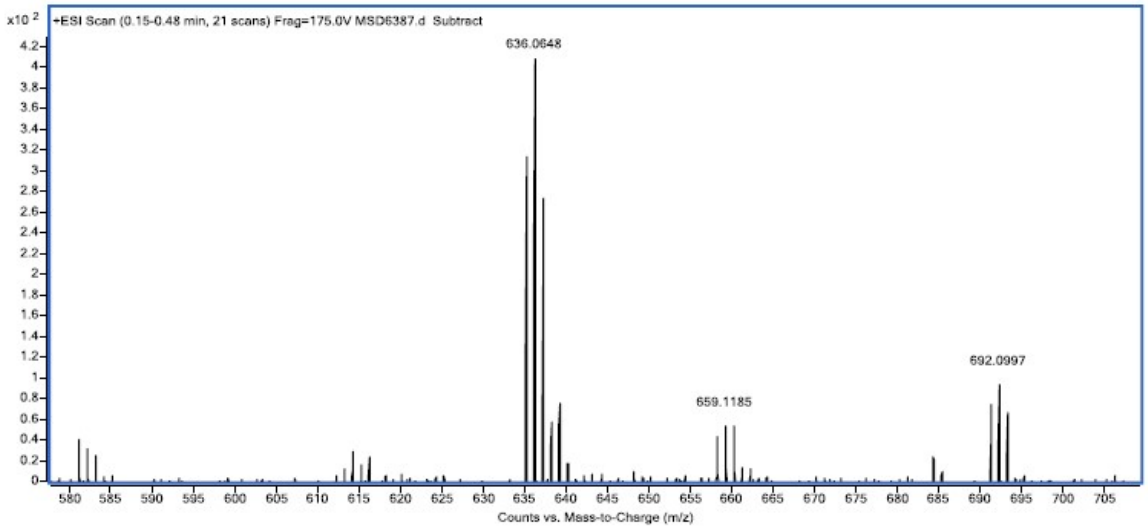

Figure S29. ESI-TOF(+) of complex **3-CH_3.**

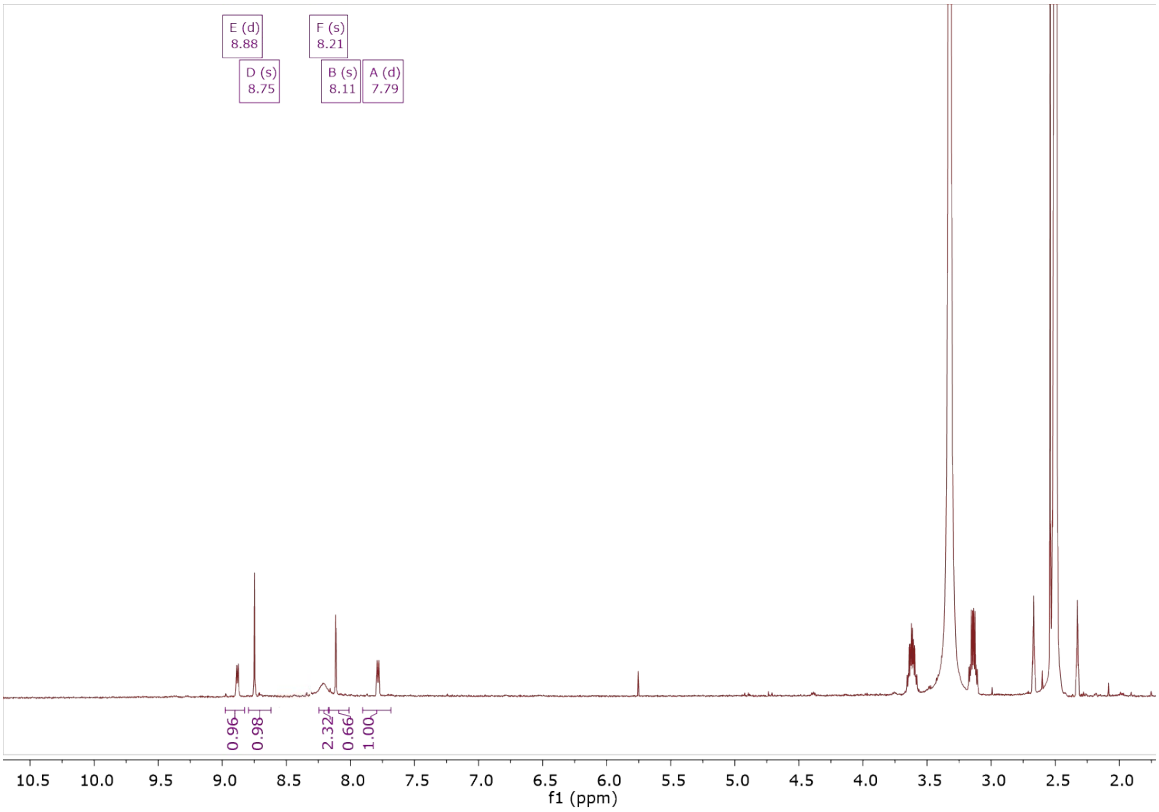

Figure S30. ^{1}H NMR spectrum of complex **4-CF_3** in DMSO-d^6.

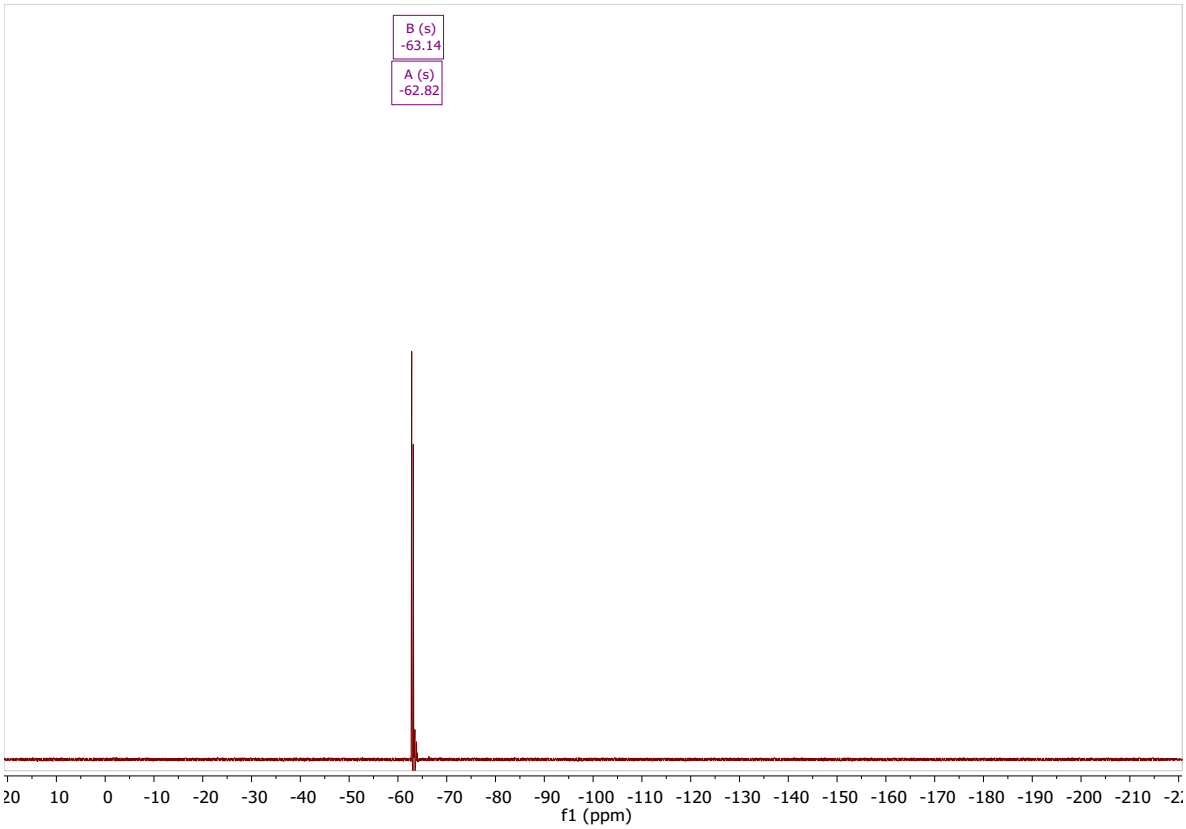

Figure S31. ^{19}F NMR spectrum of complex **4-CF$_3$** in DMSO-*d*^{6}.

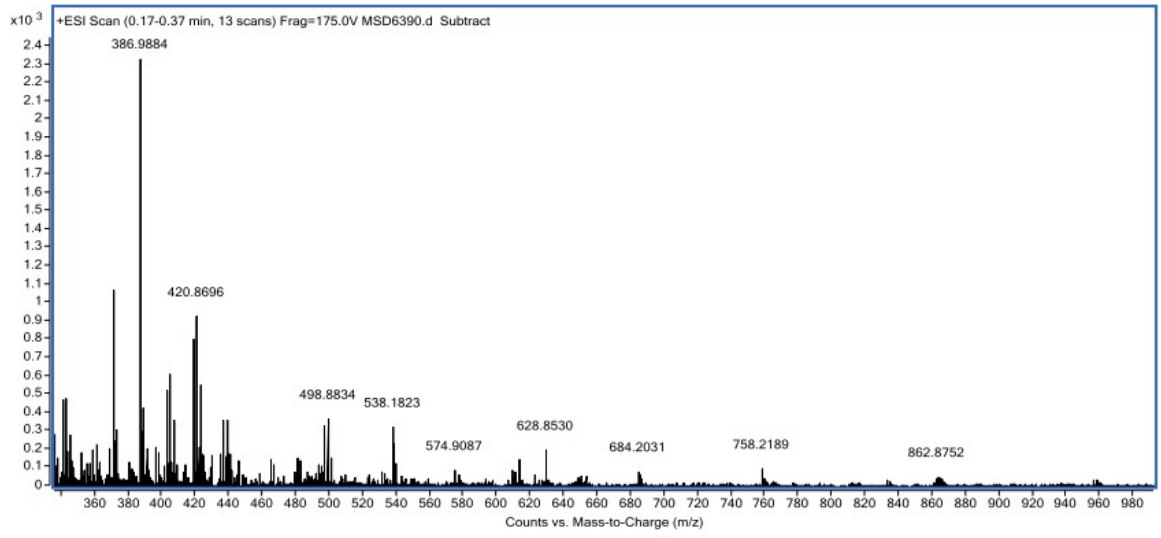

Figure S32. ESI-TOF(+) of complex **4-CF$_3$.**

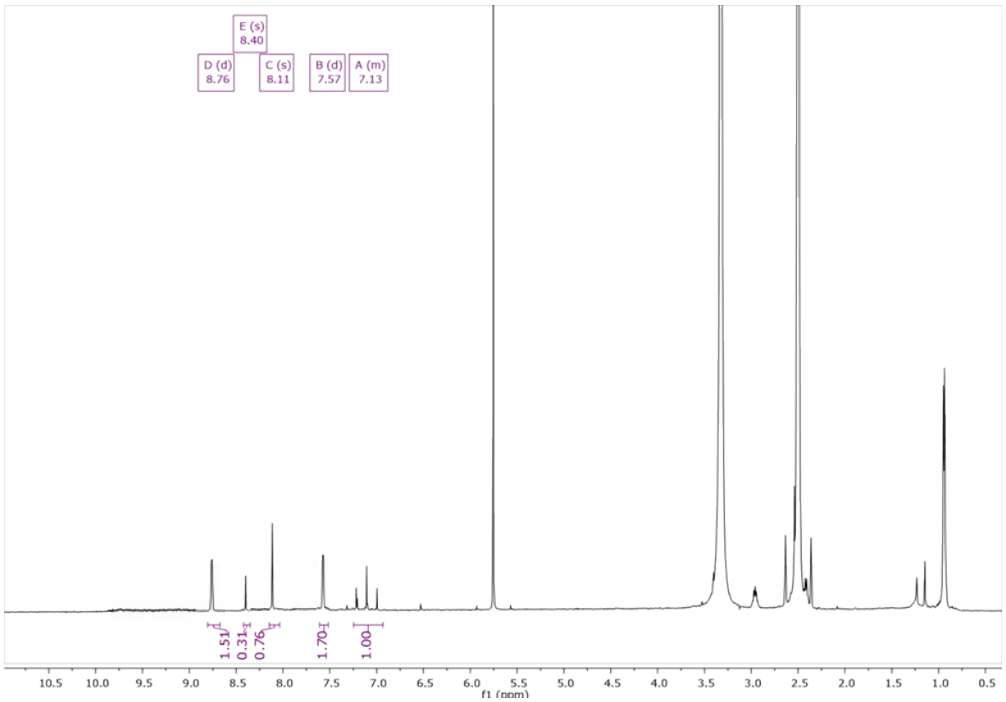

Figure S33. ^{1}H NMR spectrum of complex **4-CHF$_2$** in DMSO-d^6.

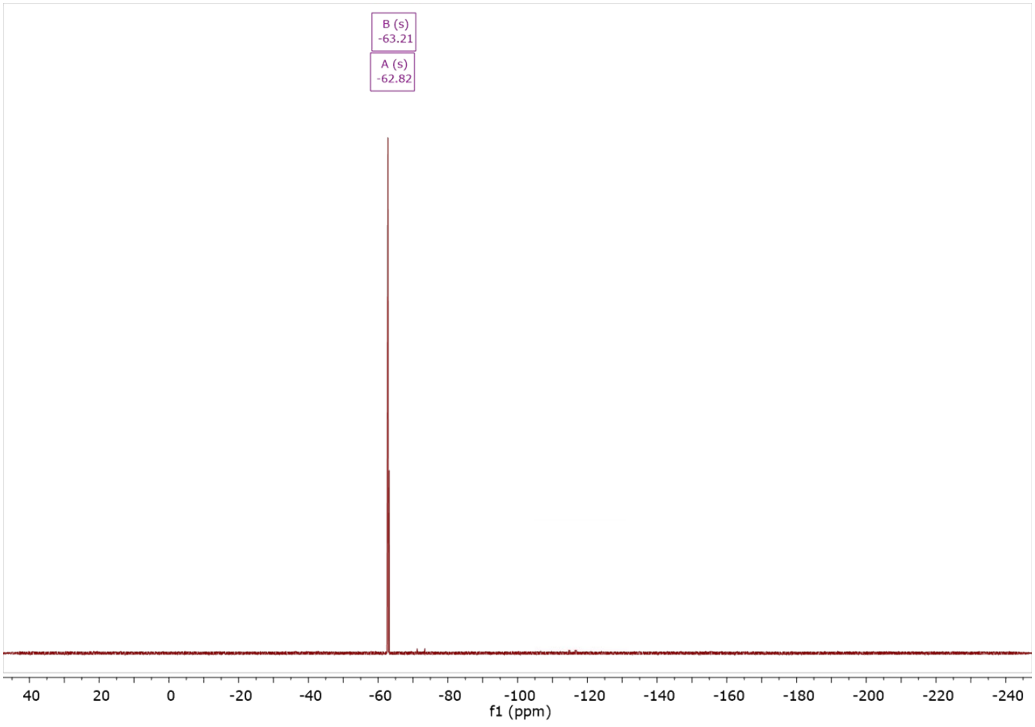

Figure S34. ^{19}F NMR spectrum of complex **4-CHF$_2$** in DMSO-d^6.

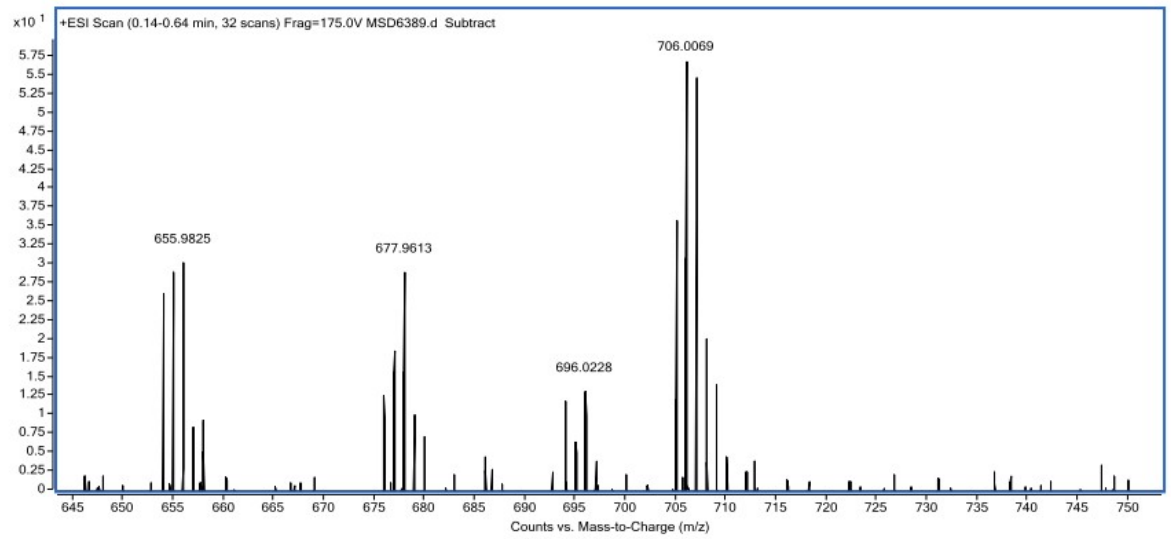

Figure S35. ESI-TOF(+) of complex **4-CHF_2.**

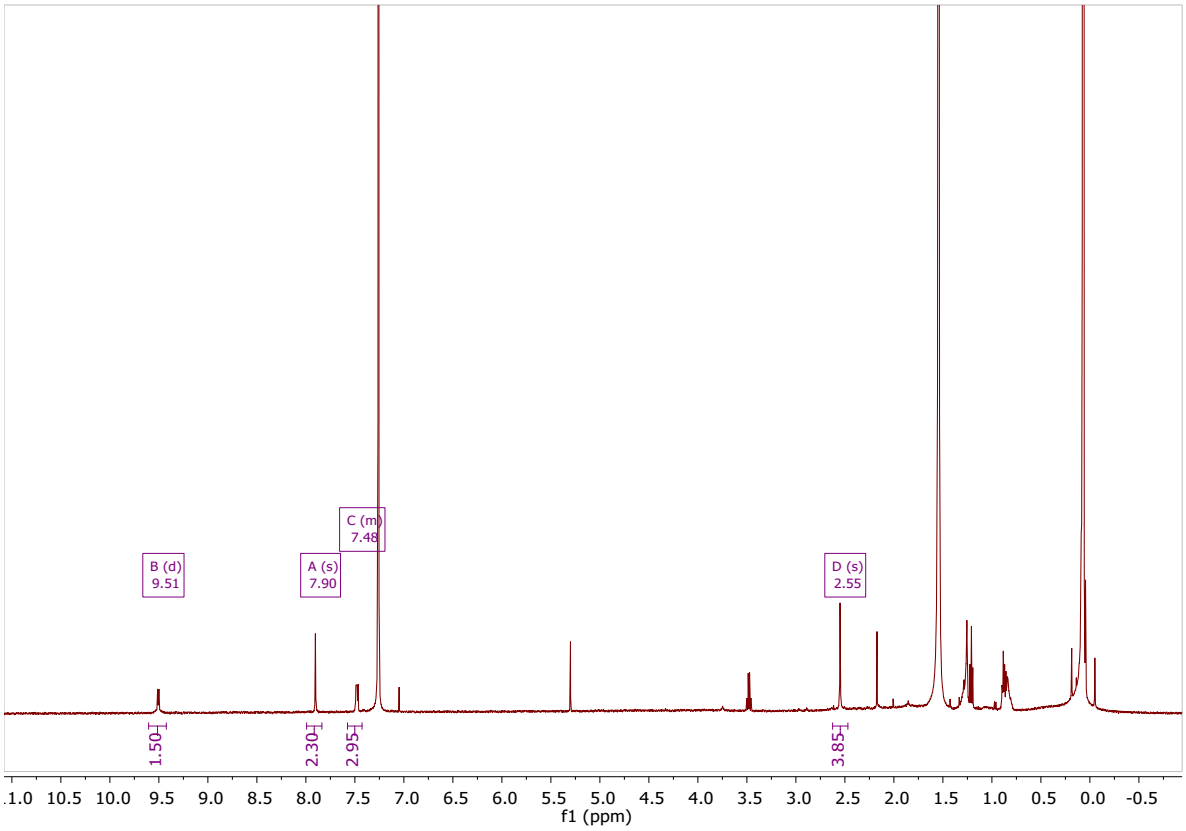

Figure S36. ^{1}H NMR spectrum of complex **4-CH_3** in $CDCl_3$.

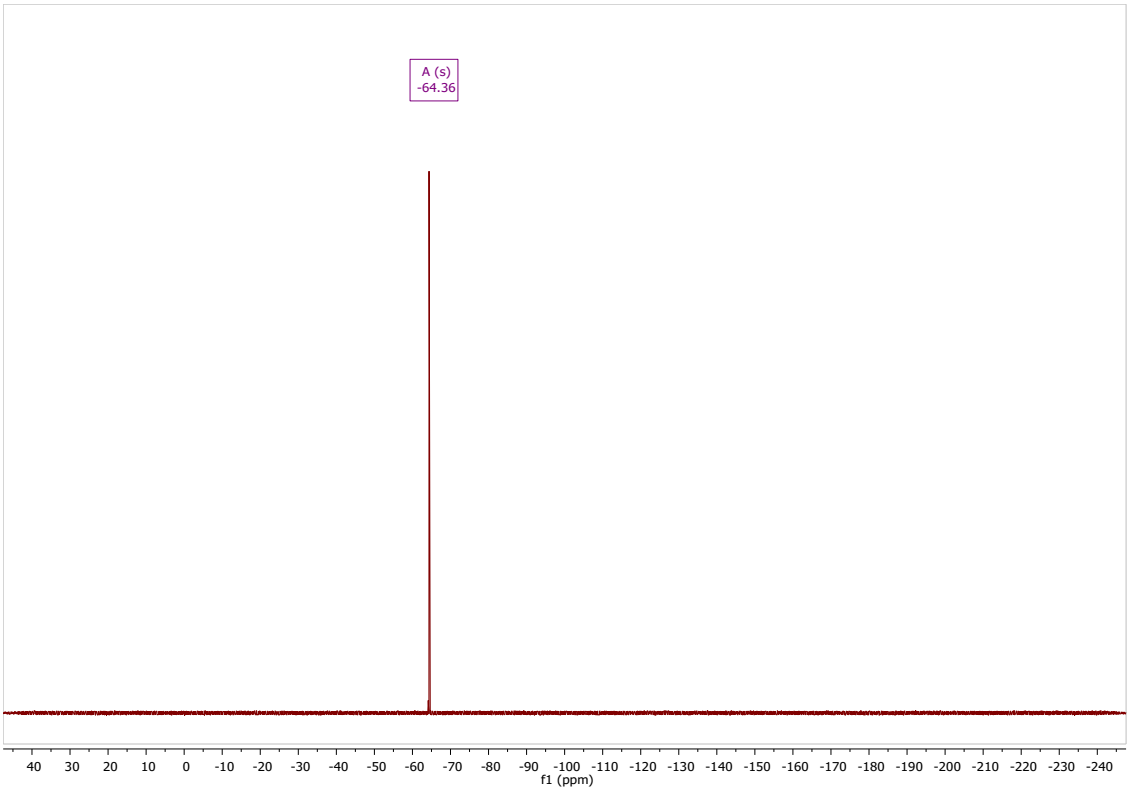

Figure S37. ^{19}F NMR spectrum of complex **4-CH$_3$** in $CDCl_3$.

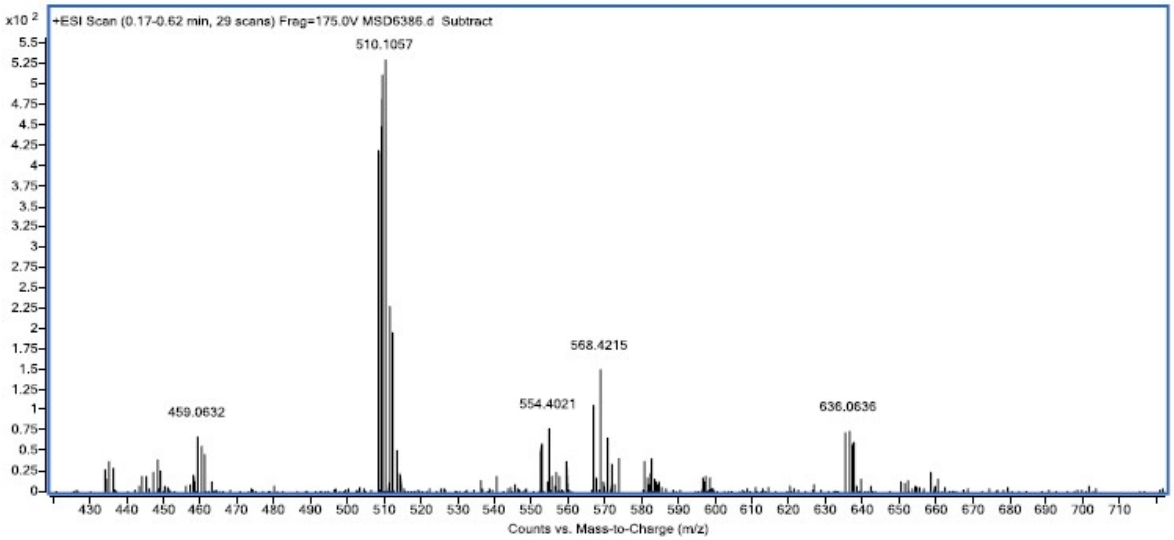

Figure S38. ESI-TOF(+) of complex **4-CH$_3$.**

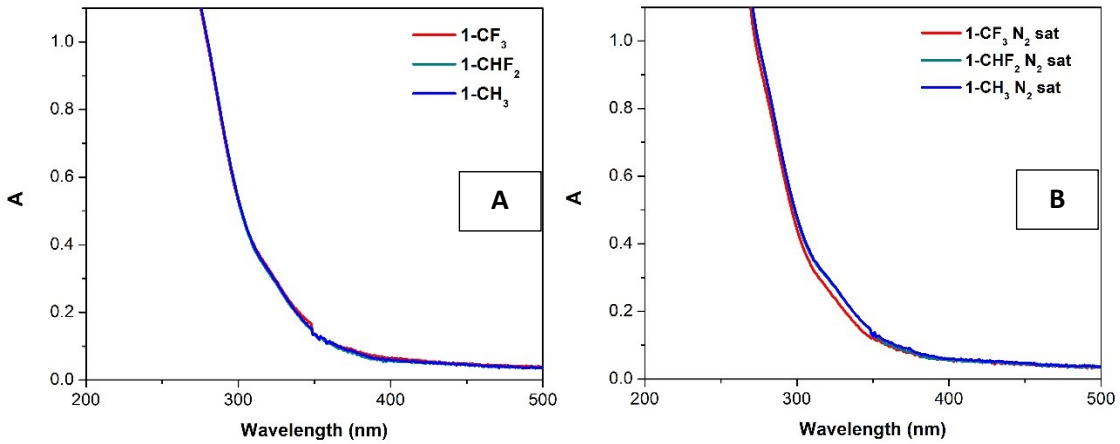

Figure S39. Absorption spectra of 10^{-5} M DMSO air-equilibrated (A) and N_2 saturated solutions of compounds **1-CF$_3$**, **1-CHF$_2$**, and **1-CH$_3$**.

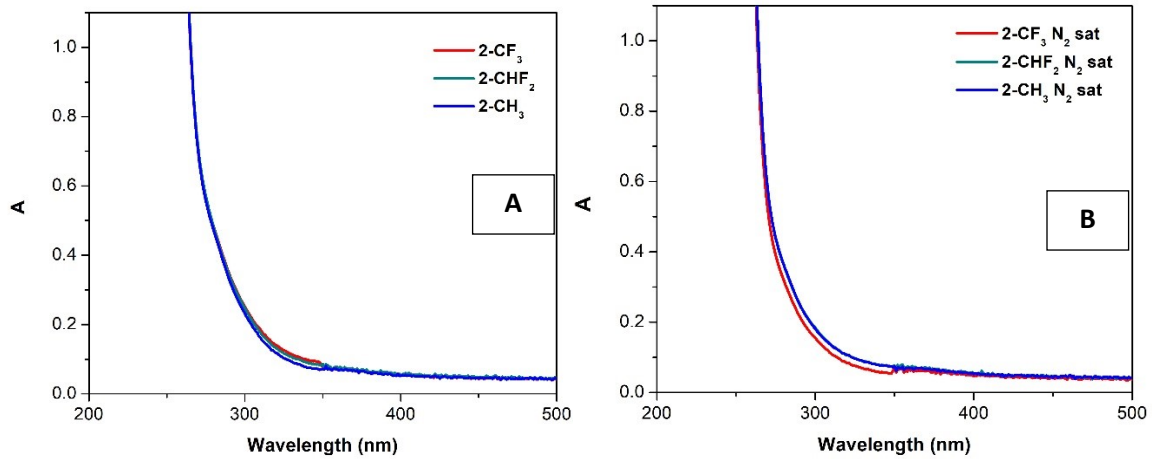

Figure S40. Absorption spectra of 10^{-5} M DMSO air-equilibrated (A) and N_2 saturated solutions of compounds **2-CF$_3$**, **2-CHF$_2$**, and **2-CH$_3$**.

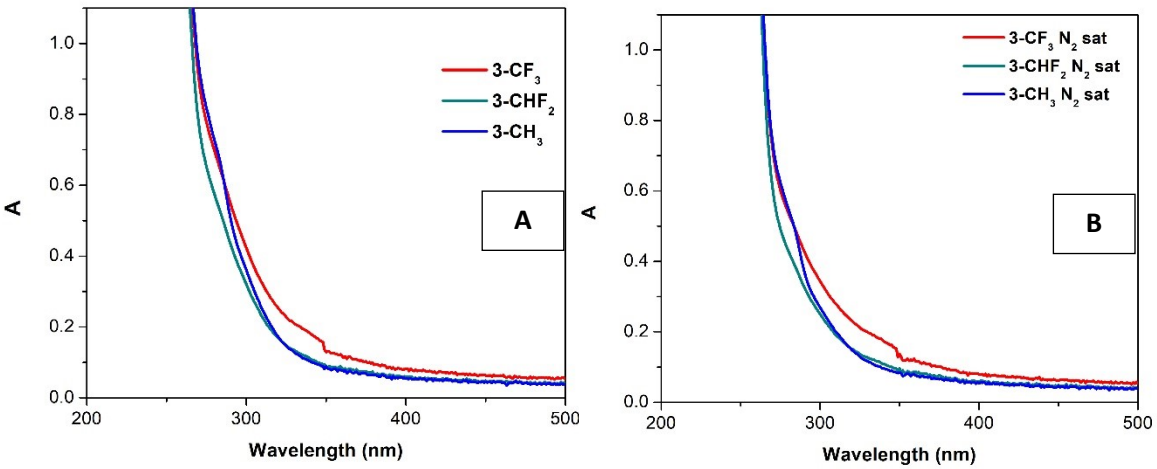

Figure S41. Absorption spectra of 10^{-5} M DMSO air-equilibrated (A) and N_2 saturated solutions of compounds **3-CF$_3$**, **3-CHF$_2$**, and **3-CH$_3$**.

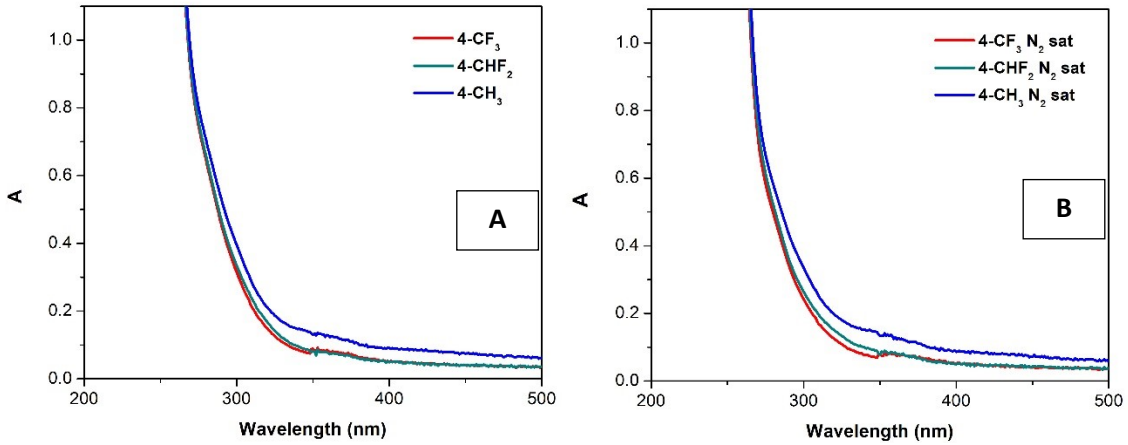

Figure S42. Absorption spectra of 10^{-5} M DMSO air-equilibrated (A) and N_2 saturated solutions of compounds **4-CF_3**, **4-CHF_2**, and **4-CH_3**.

Table S1. Calculated wavelengths of absorption, transition energies, and oscillator strength computed at the CAM-B3LYP/def2-TZVP level

Complex	*Wavelength (nm)*	*Energy (eV)*	*Oscillator strength*	*Transitions*
1-CF_3	376	3.298	0.0170	$S_0 \rightarrow S_1$
	305	4.060	0.0160	$S_0 \rightarrow S_2$
1-CHF_2	375	3.308	0.0184	$S_0 \rightarrow S_1$
	305	4.062	0.0158	$S_0 \rightarrow S_2$
1-CH_3	373	3.327	0.0204	$S_0 \rightarrow S_1$
	304	4.084	0.0159	$S_0 \rightarrow S_2$
2-CF_3	382	3.244	0.0184	$S_0 \rightarrow S_1$
2-CHF_2	381	3.256	0.0201	$S_0 \rightarrow S_1$
2-CH_3	379	3.271	0.0220	$S_0 \rightarrow S_1$
3-CF_3	338	3.670	0.0098	$S_0 \rightarrow S_1$
3-CHF_2	337	3.674	0.0100	$S_0 \rightarrow S_1$
3-CH_3	337	3.682	0.0100	$S_0 \rightarrow S_1$
4-CF_3	341	3.633	0.0079	$S_0 \rightarrow S_1$
4-CHF_2	341	3.637	0.0080	$S_0 \rightarrow S_1$
	316	3.930	0.0002	$S_0 \rightarrow S_2$
4-CH_3	341	3.639	0.0079	$S_0 \rightarrow S_1$
	314	3.941	0.0000	$S_0 \rightarrow S_2$

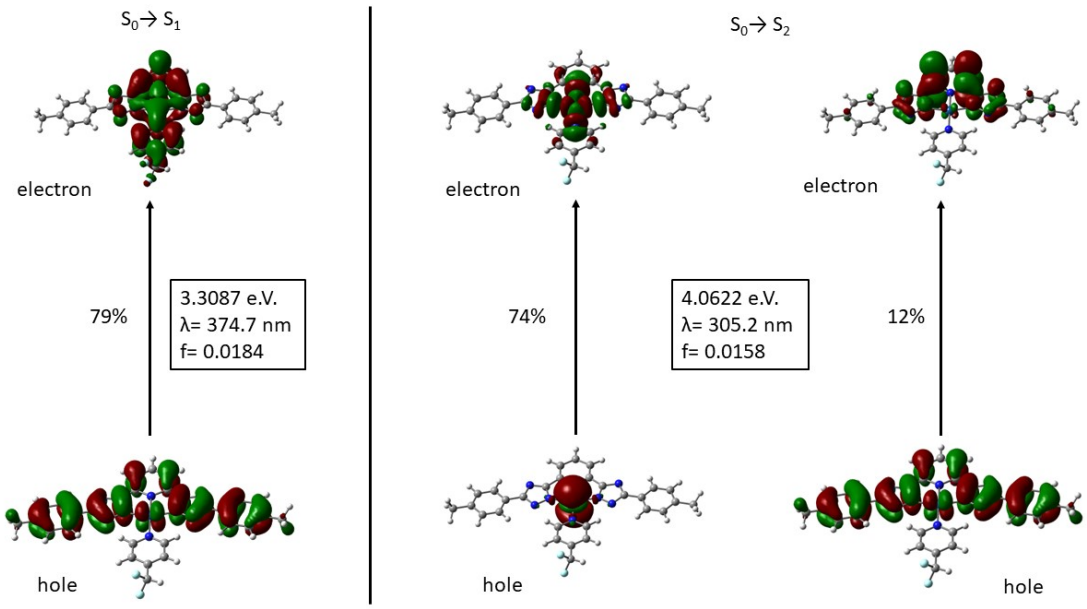

Figure S34. Representation of the NTOs involved in the $S_0 \rightarrow S_1$ (left) $S_0 \rightarrow S_2$ (right) excitation of compound **1-CHF$_2$**, with indication of the theoretical λ_{exc}, oscillator strength and relative contribution of each NTO pair.

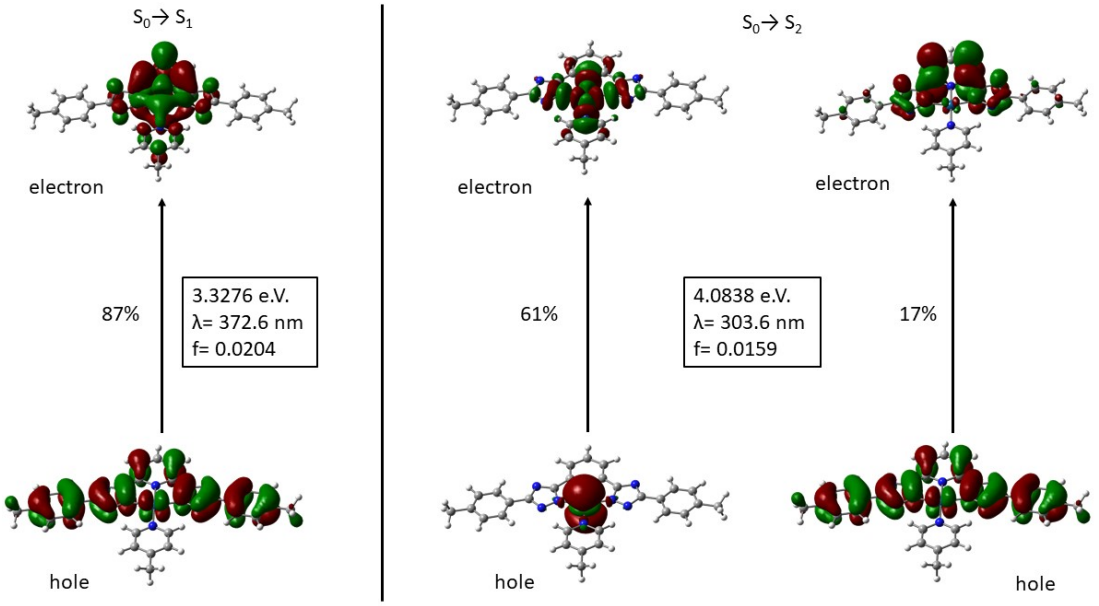

Figure S44. Representation of the NTOs involved in the $S_0 \rightarrow S_1$ (left) $S_0 \rightarrow S_2$ (right) excitation of compound **1-CH$_3$**, with indication of the theoretical λ_{exc}, oscillator strength and relative contribution of each NTO pair.

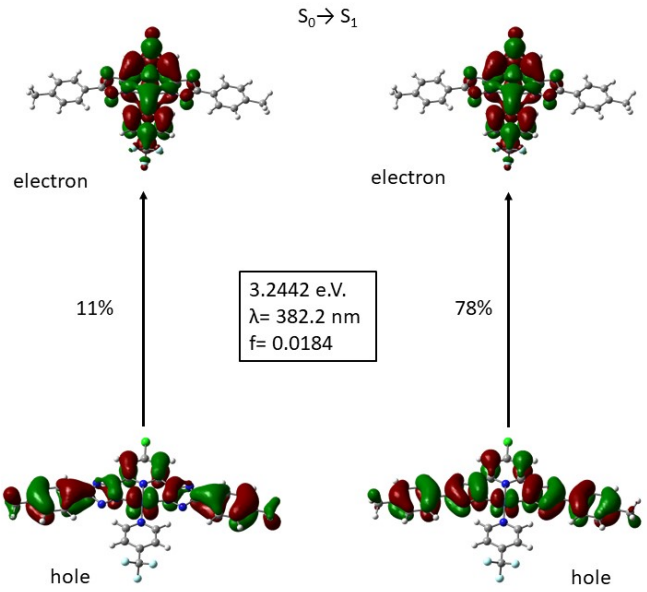

Figure S45. Representation of the NTOs involved in the $S_0 \rightarrow S_1$ excitation of compound **2-CF_3**, with indication of the theoretical λ_{exc}, oscillator strength and relative contribution of each NTO pair.

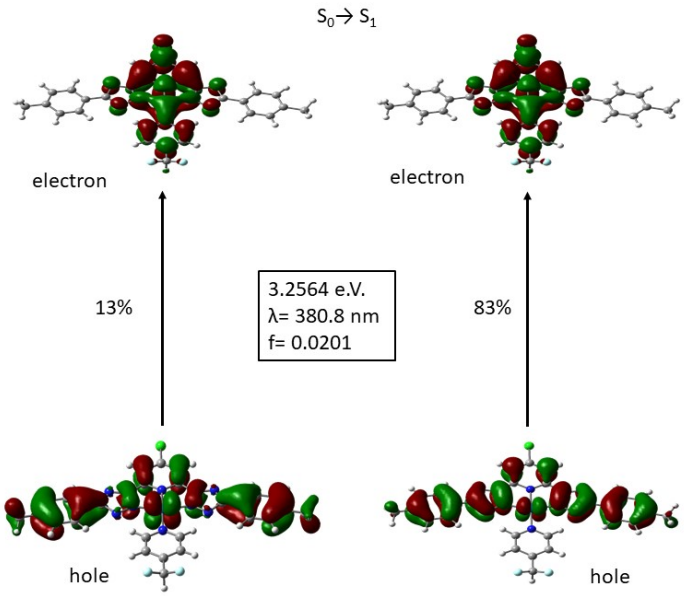

Figure S46. Representation of the NTOs involved in the $S_0 \rightarrow S_1$ excitation of compound **2-CHF_2**, with indication of the theoretical λ_{exc}, oscillator strength and relative contribution of each NTO pair.

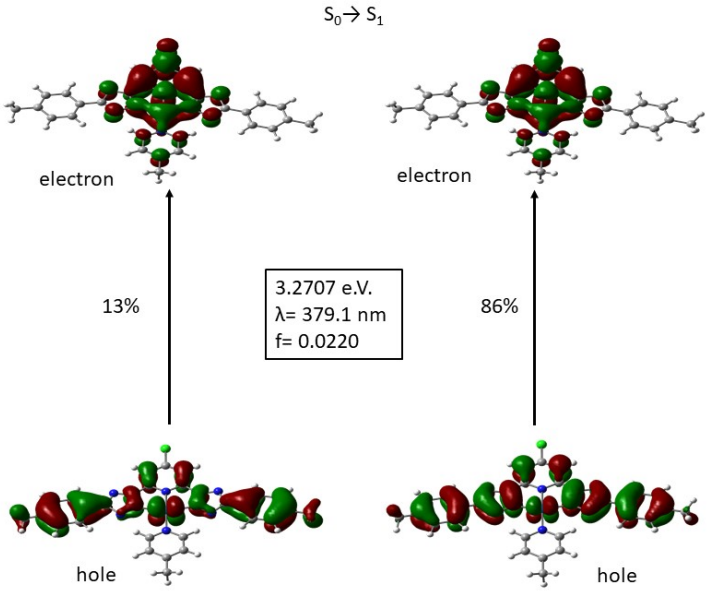

Figure S47. Representation of the NTOs involved in the $S_0 \rightarrow S_1$ (left) excitation of compound **2-CH$_3$**, with indication of the theoretical λ_{exc}, oscillator strength and relative contribution of each NTO pair.

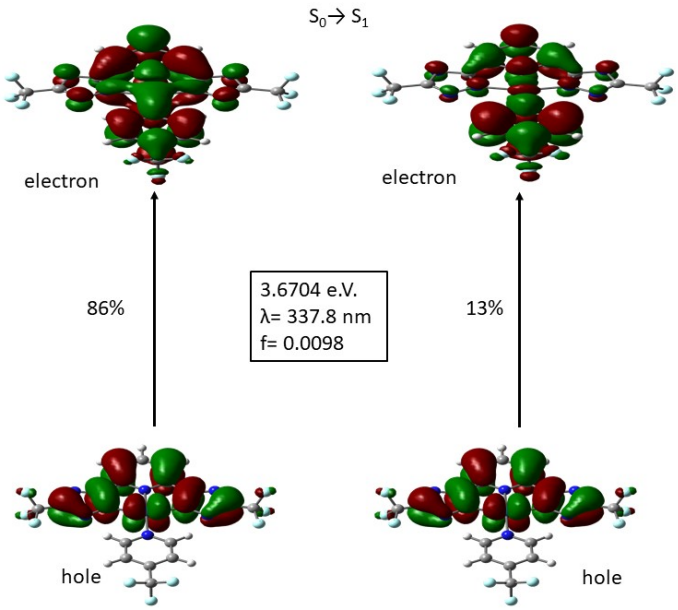

Figure S48. Representation of the NTOs involved in the $S_0 \rightarrow S_1$ excitation of compound **3-CF$_3$**, with indication of the theoretical λ_{exc}, oscillator strength and relative contribution of each NTO pair.

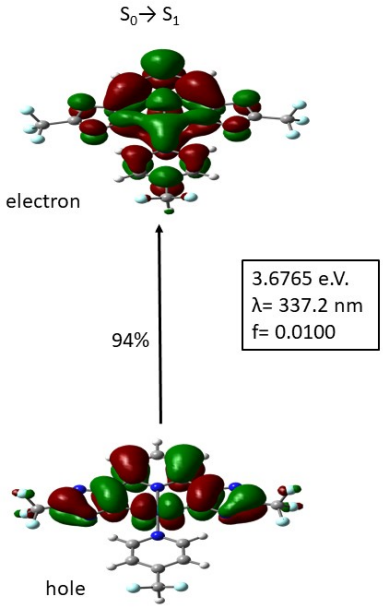

Figure S49. Representation of the NTOs involved in the $S_0 \rightarrow S_1$ excitation of compound **3-CHF_2**, with indication of the theoretical λ_{exc}, oscillator strength and relative contribution of each NTO pair.

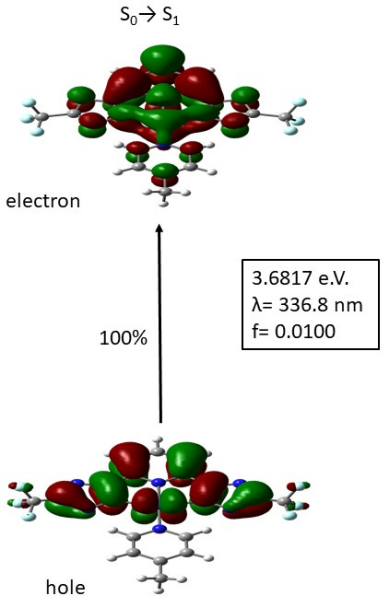

Figure S50. Representation of the NTOs involved in the $S_0 \rightarrow S_1$ excitation of compound **3-CH_3**, with indication of the theoretical λ_{exc}, oscillator strength and relative contribution of each NTO pair.

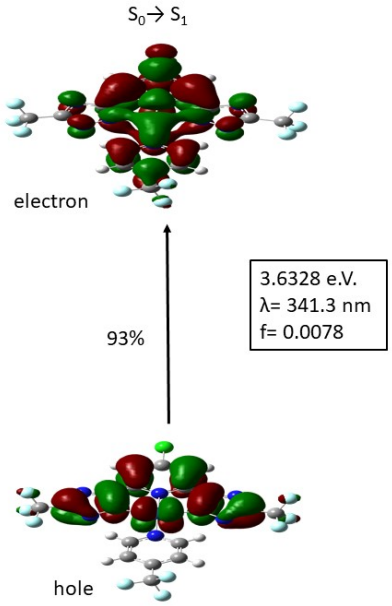

Figure S51. Representation of the NTOs involved in the $S_0 \rightarrow S_1$ excitation of compound **4-CF_3**, with indication of the theoretical λ_{exc}, oscillator strength and relative contribution of each NTO pair.

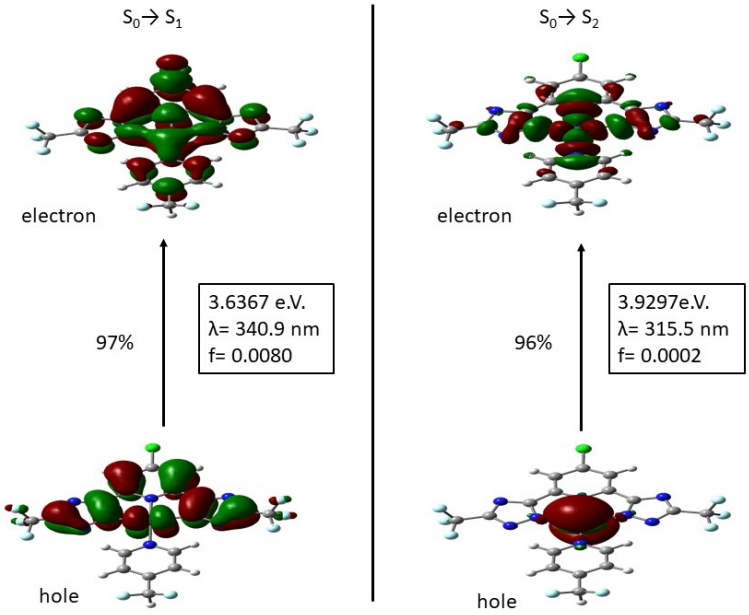

Figure S52. Representation of the NTOs involved in the $S_0 \rightarrow S_1$ (left) $S_0 \rightarrow S_2$ (right) excitation of compound **4-CHF_2**, with indication of the theoretical λ_{exc}, oscillator strength and relative contribution of each NTO pair.

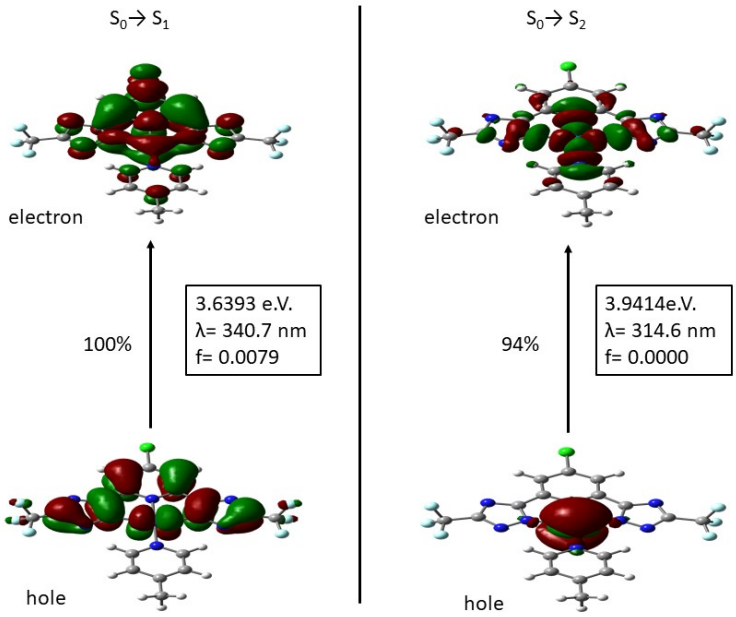

Figure S53. Representation of the NTOs involved in the $S_0 \rightarrow S_1$ (left) $S_0 \rightarrow S_2$ (right) excitation of compound **4-CH$_3$**, with indication of the theoretical λ_{exc}, oscillator strength and relative contribution of each NTO pair.

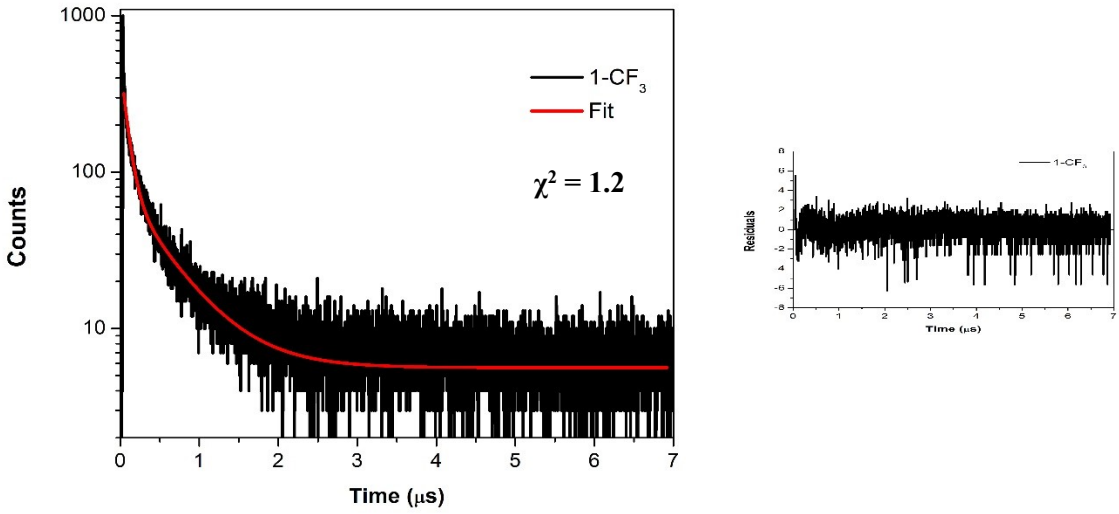

Figure S54. Phosphorescence lifetime and residuals of **1-CF_3** in solid state.

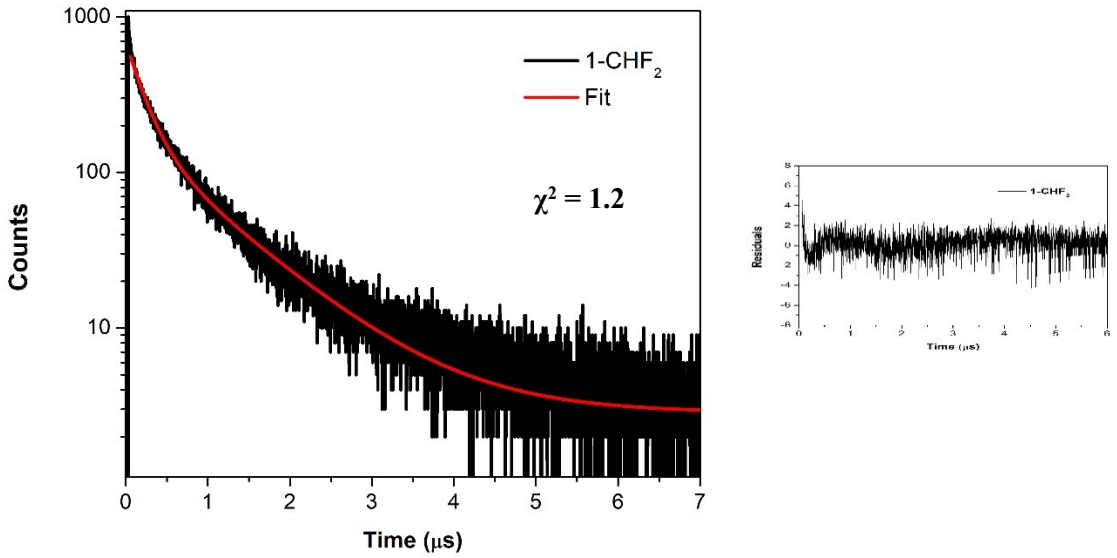

Figure S55. Phosphorescence lifetime and residuals of **1-CHF_2** in solid state.

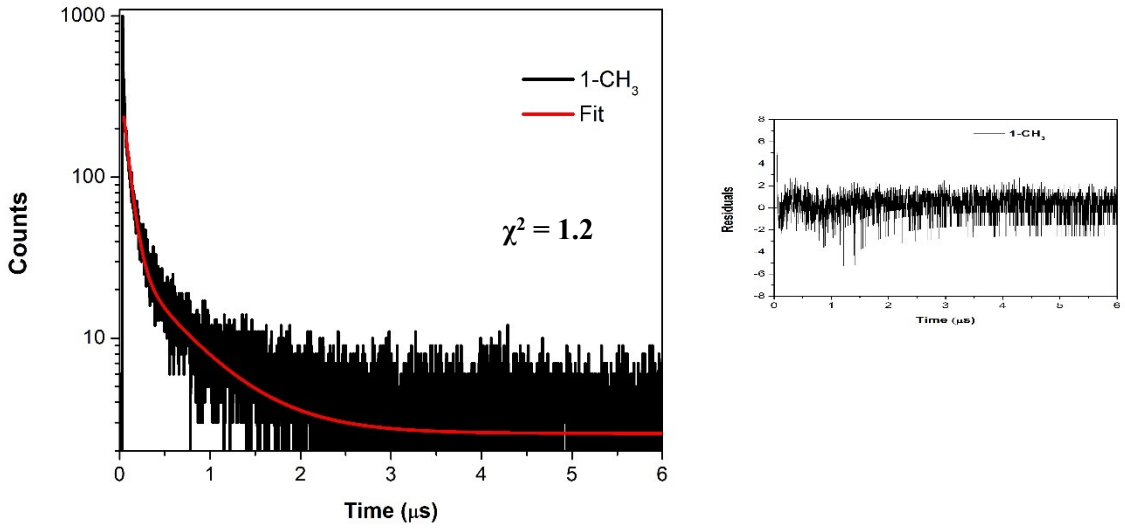

Figure S56. Phosphorescence lifetime and residuals of **1-CH$_3$** in solid state.

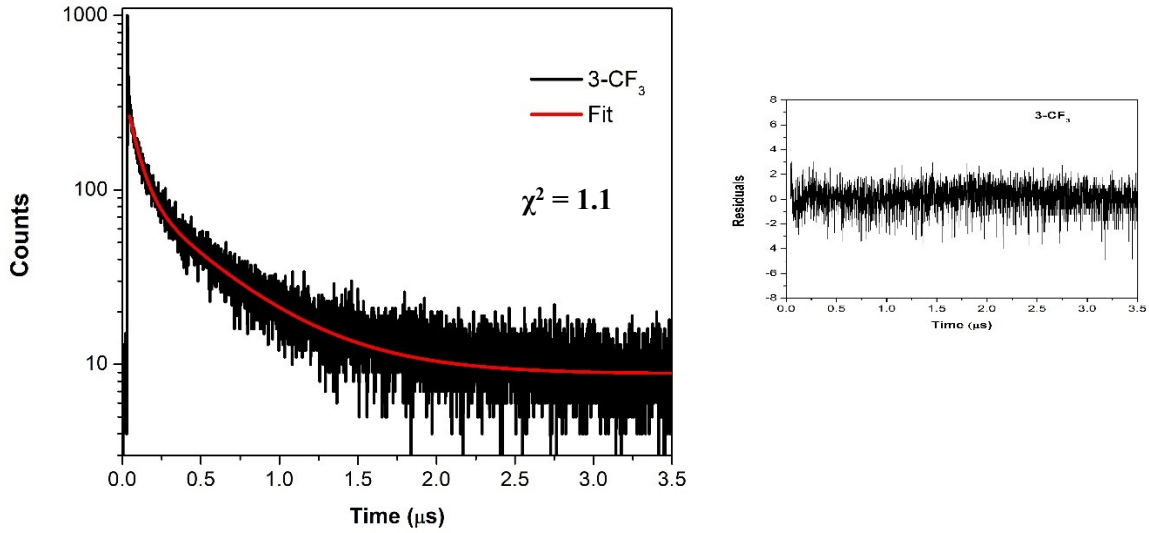

Figure S57. Phosphorescence lifetime and residuals of **3-CF$_3$** in solid state.

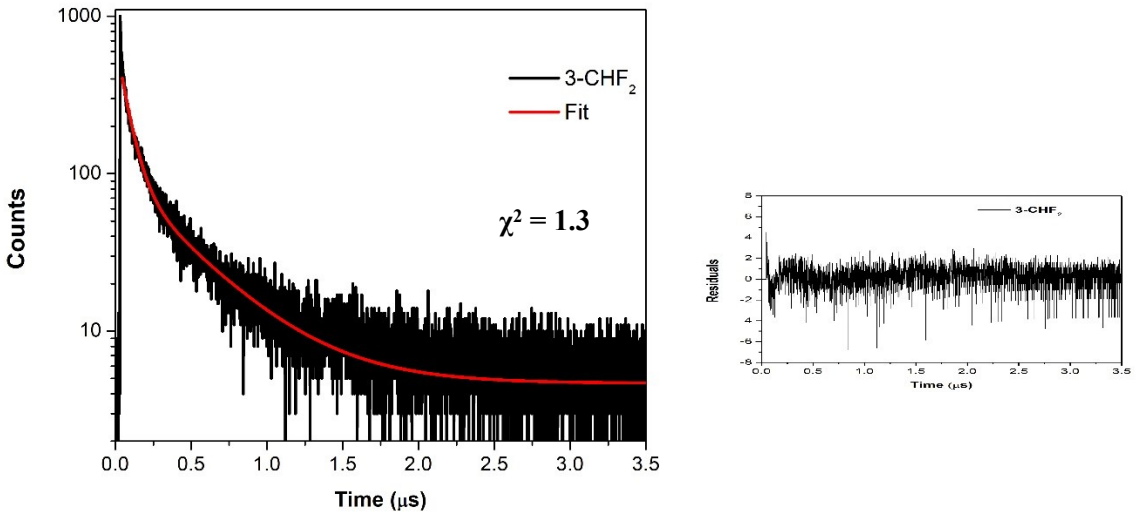

Figure S58. Phosphorescence lifetime and residuals of **3-CHF$_2$** in solid state.

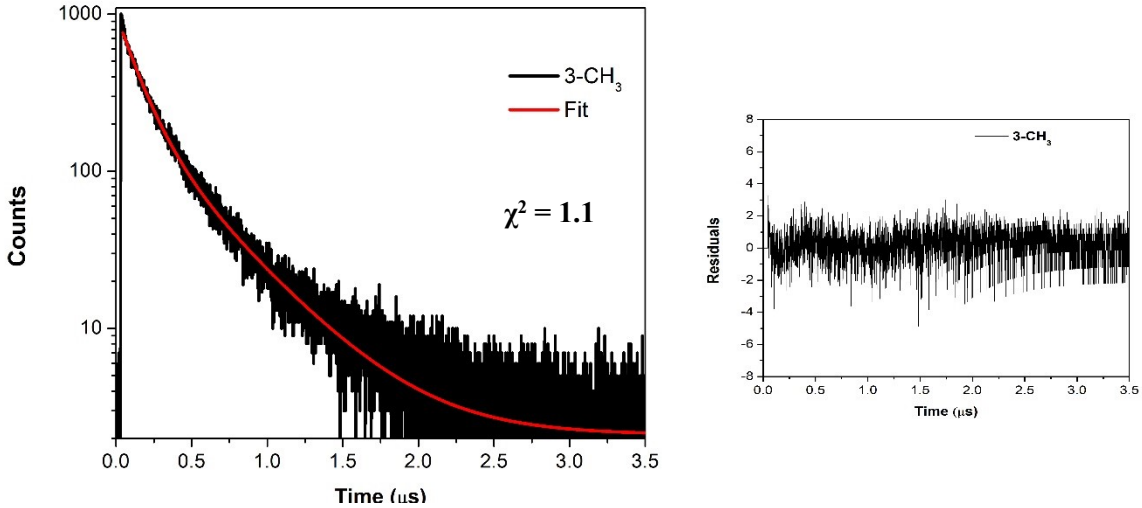

Figure S59. Phosphorescence lifetime and residuals of **3-CH$_3$** in solid state.

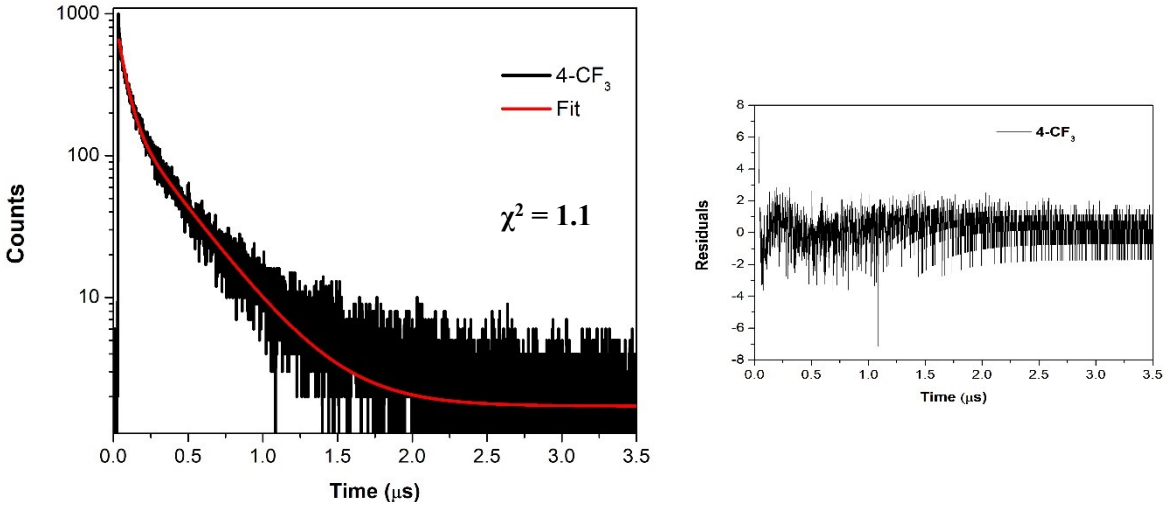

Figure S60. Phosphorescence lifetime and residuals of **4-CF_3** in solid state.

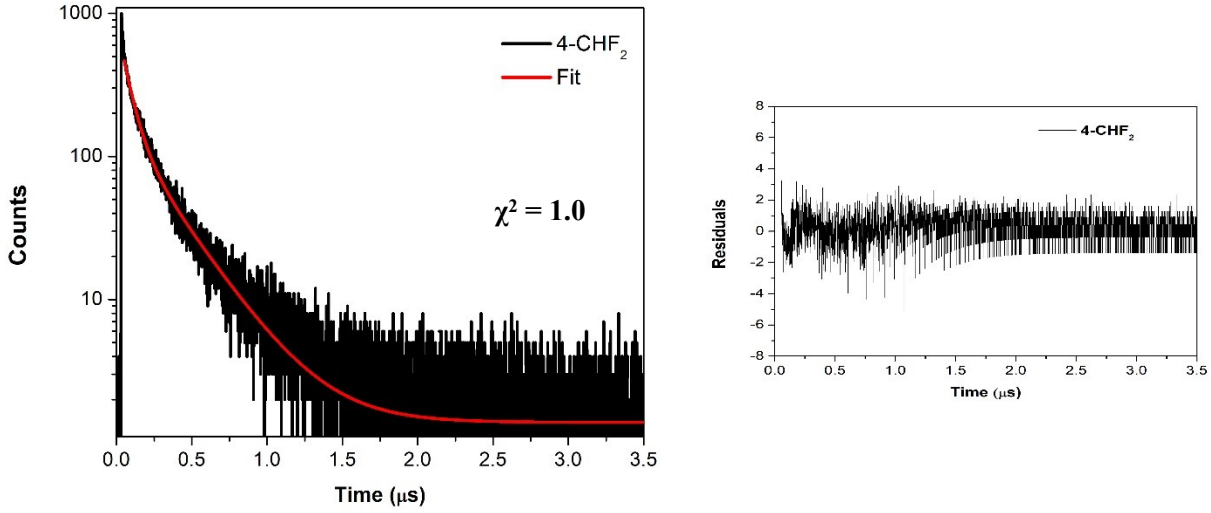

Figure S61. Phosphorescence lifetime and residuals of **4-CHF_2** in solid state.

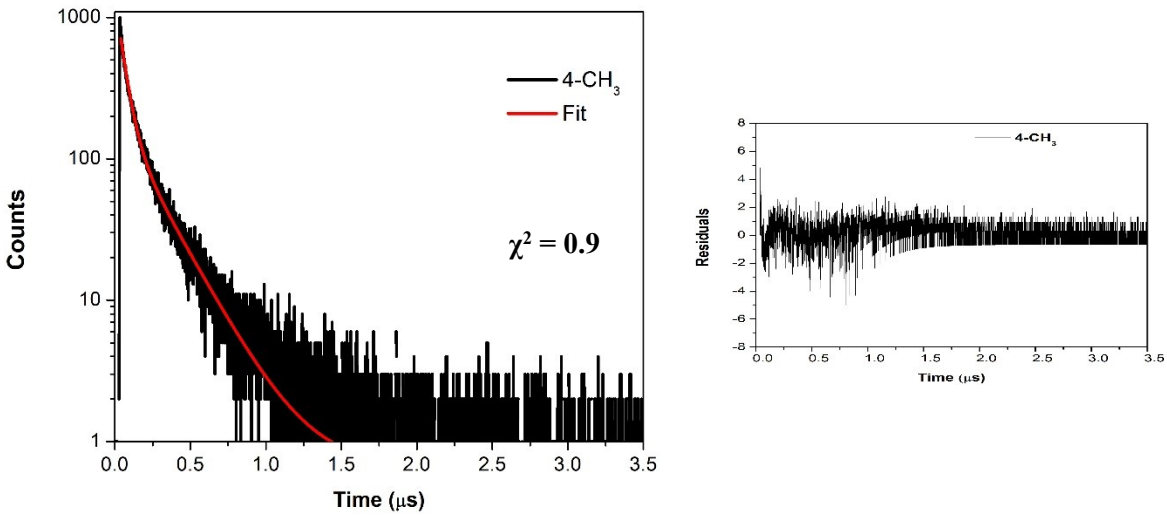

Figure S62. Phosphorescence lifetime and residuals of **4-CH_3** in solid state.

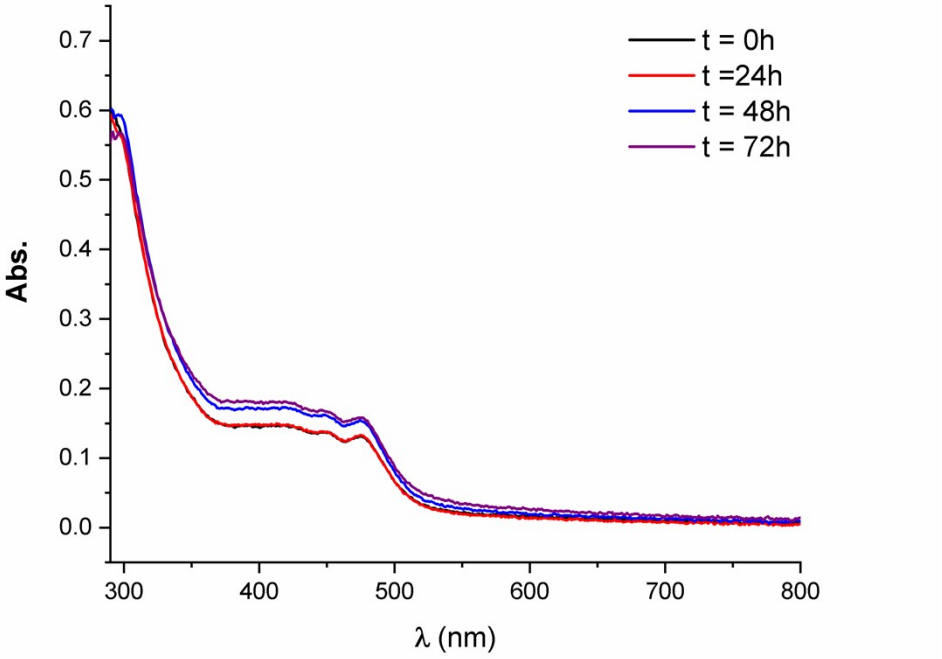

Figure S63. Stability of **1-CHF_2** in PBS and DMSO (5%) at 37 ºC measured by UV-Vis.

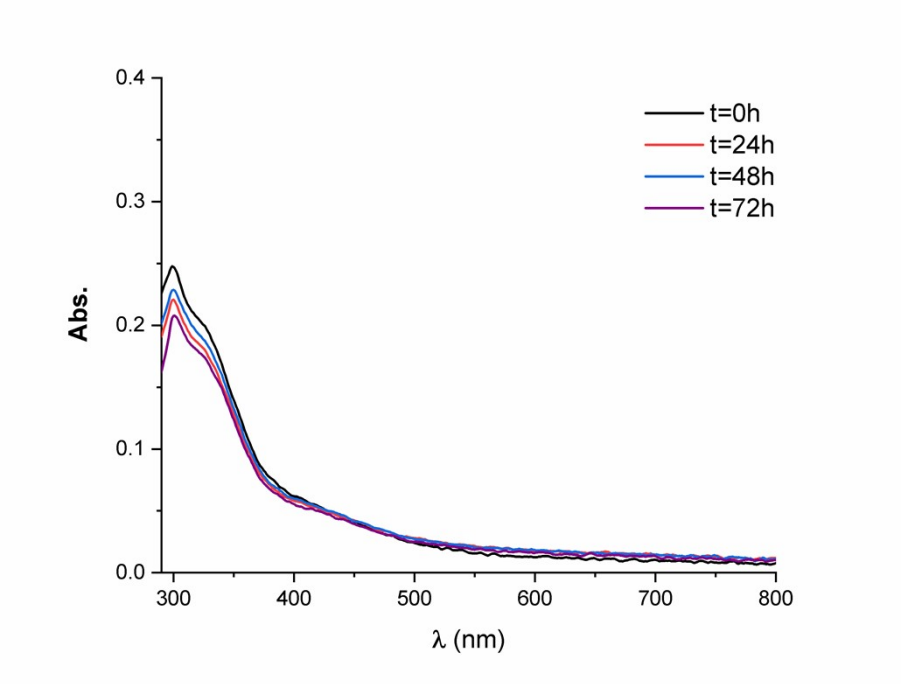

Figure S64. Stability of **1-CH$_3$** in PBS and DMSO (5%) at 37 ºC measured by UV-Vis.

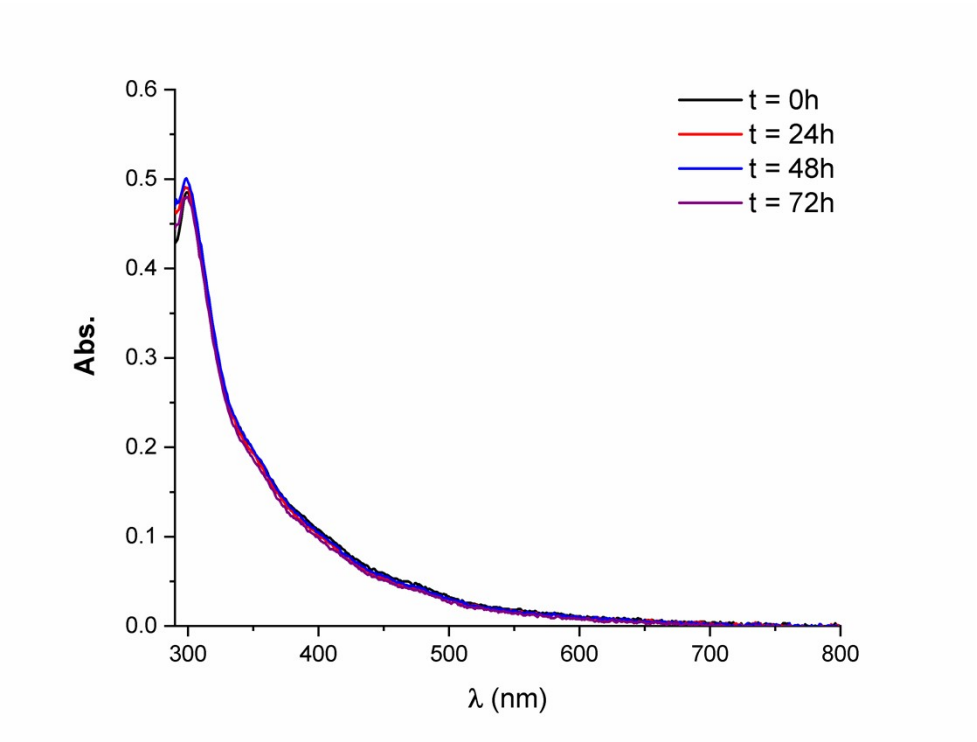

Figure S65. Stability of **2-CH$_3$** in PBS and DMSO (5%) at 37 ºC measured by UV-Vis.

Figure S66. Stability of **3-CF_3** in PBS and DMSO (5%) at 37 ºC measured by UV-Vis.

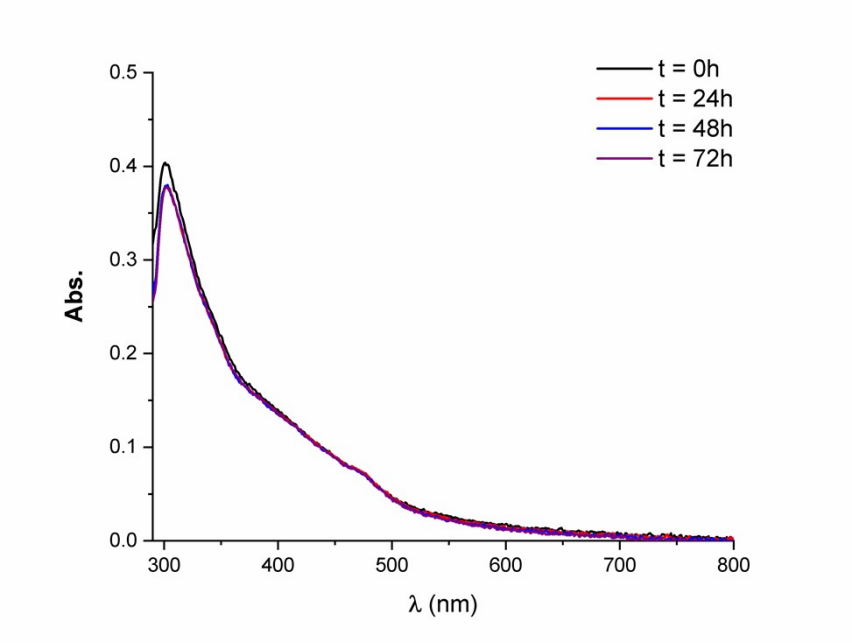

Figure S67. Stability of **3-CH_3** in PBS and DMSO (5%) at 37 ºC measured by UV-Vis.

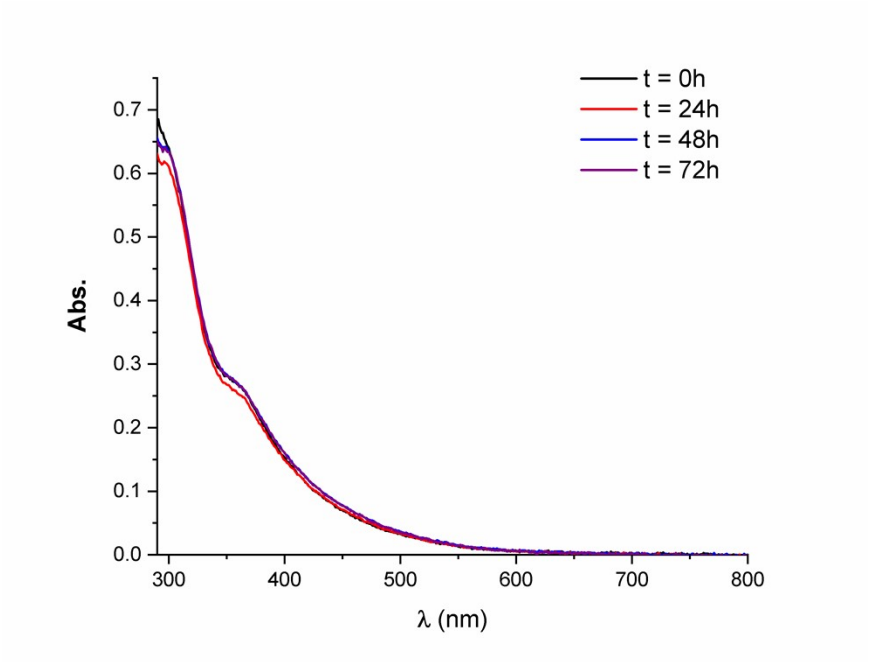

Figure S68. Stability of **4-CF_3** in PBS and DMSO (5%) at 37 ºC measured by UV-Vis.

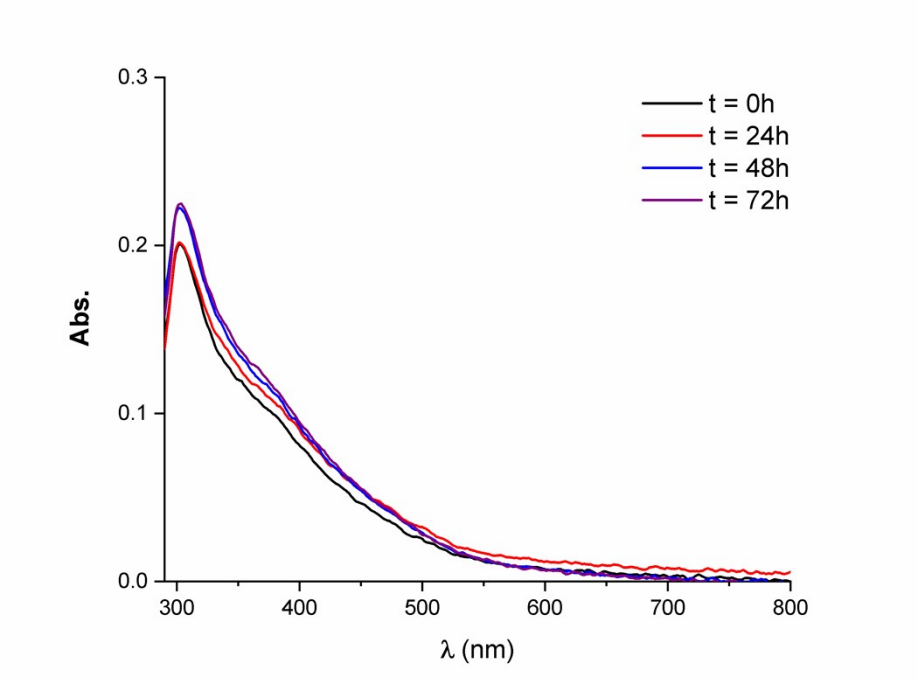

Figure S69. Stability of **4-CH_3** in PBS and DMSO (5%) at 37 ºC measured by UV-Vis.