

Supporting information for

Microwave-assisted synthesis and spectral properties of pyrrolidine-fused chlorin derivatives

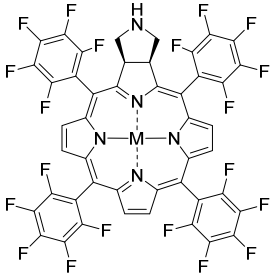
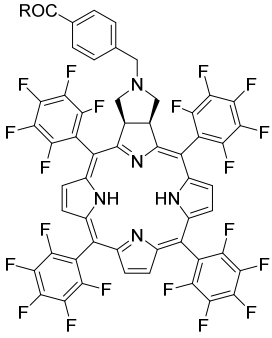
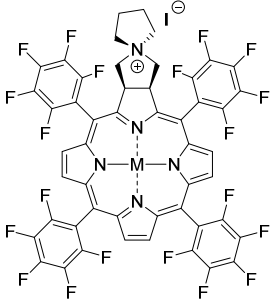
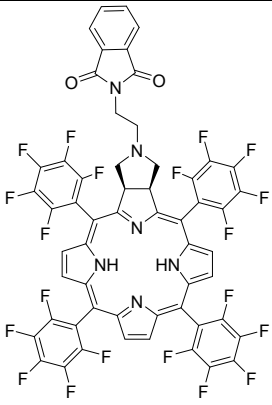
José Almeida, Augusto C. Tomé, Maria Rangel, Ana M. G. Silva*

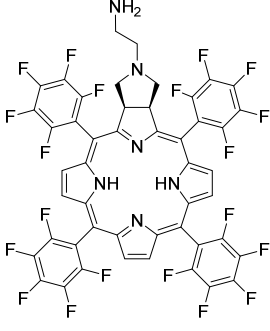
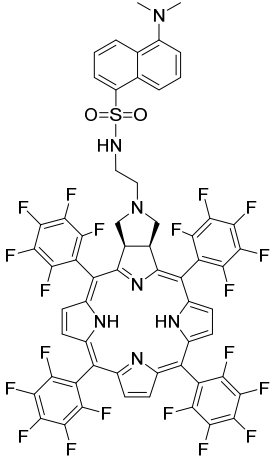
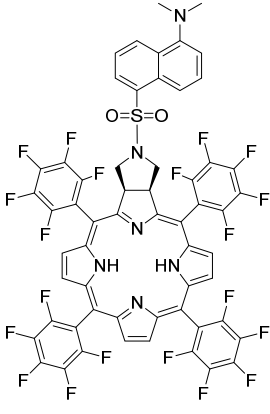
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Structures and corresponding numbers of the *N*-alkylated chlorins

Table S1. Structure, number, molecular formula and weight of *N*-alkylated chlorins synthesized.

Structure	M	Number	Molecular form.	MW
	2H	1	C ₄₆ H ₁₅ F ₂₀ N ₅	1017.63
	Zn(II)	Zn-1	C ₄₆ H ₁₃ F ₂₀ N ₅ Zn	1080.99
	2H	2a, R = OCH₃	C ₅₅ H ₂₃ F ₂₀ N ₅ O ₂	1199.63
		2b, R = OH	C ₅₄ H ₂₁ F ₂₀ N ₅ O ₂	1151.76
		2c, R = NHC₆H₅	C ₆₀ H ₂₆ F ₂₀ N ₆ O	1226.87
	2H	3	C ₅₀ H ₂₂ F ₂₀ IN ₅	1199.63
	Zn(II)	Zn-3	C ₅₀ H ₂₀ F ₂₀ IN ₅ Zn	1262.99
	2H	4	C ₅₆ H ₂₂ F ₂₀ N ₆ O ₂	1190.80

	2H	5	$C_{48}H_{20}F_{20}N_6$	1060.70
	2H	6	$C_{60}H_{31}F_{20}N_7O_2S$	1293.98
	2H	7	$C_{58}H_{26}F_{20}N_6O_2S$	1250.91

NMR spectra

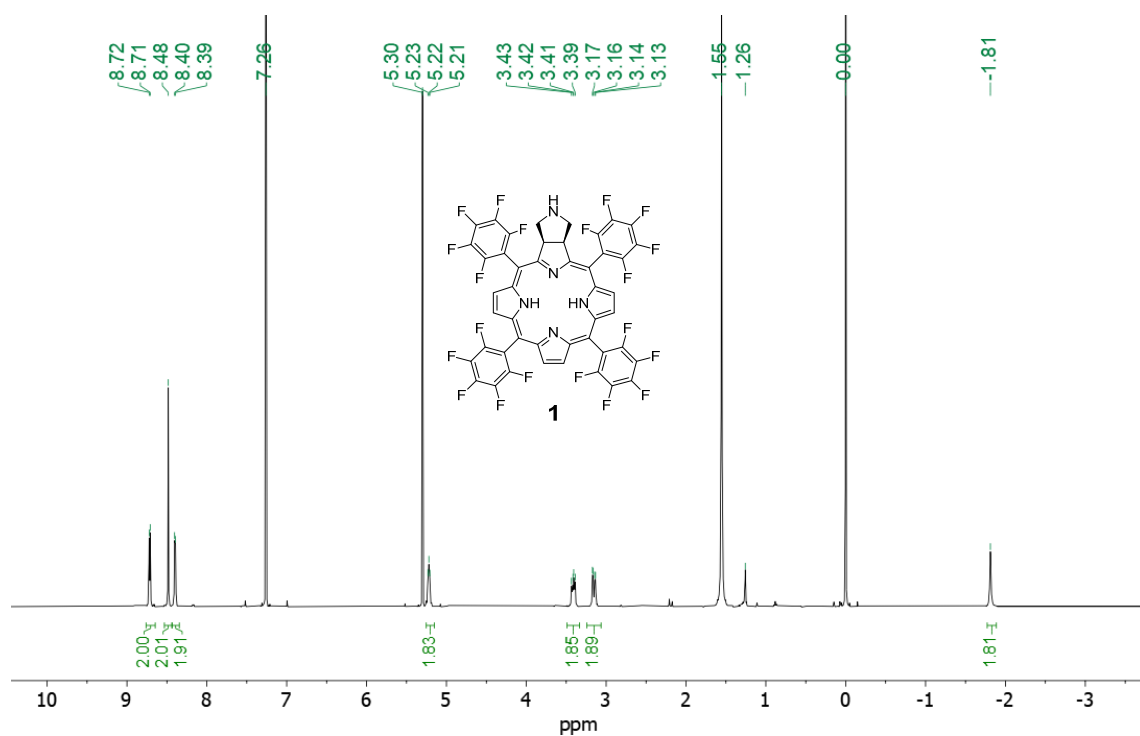


Figure S 1. ^1H NMR spectrum (400.14 MHz, CDCl_3) of **1** (*dichloromethane).

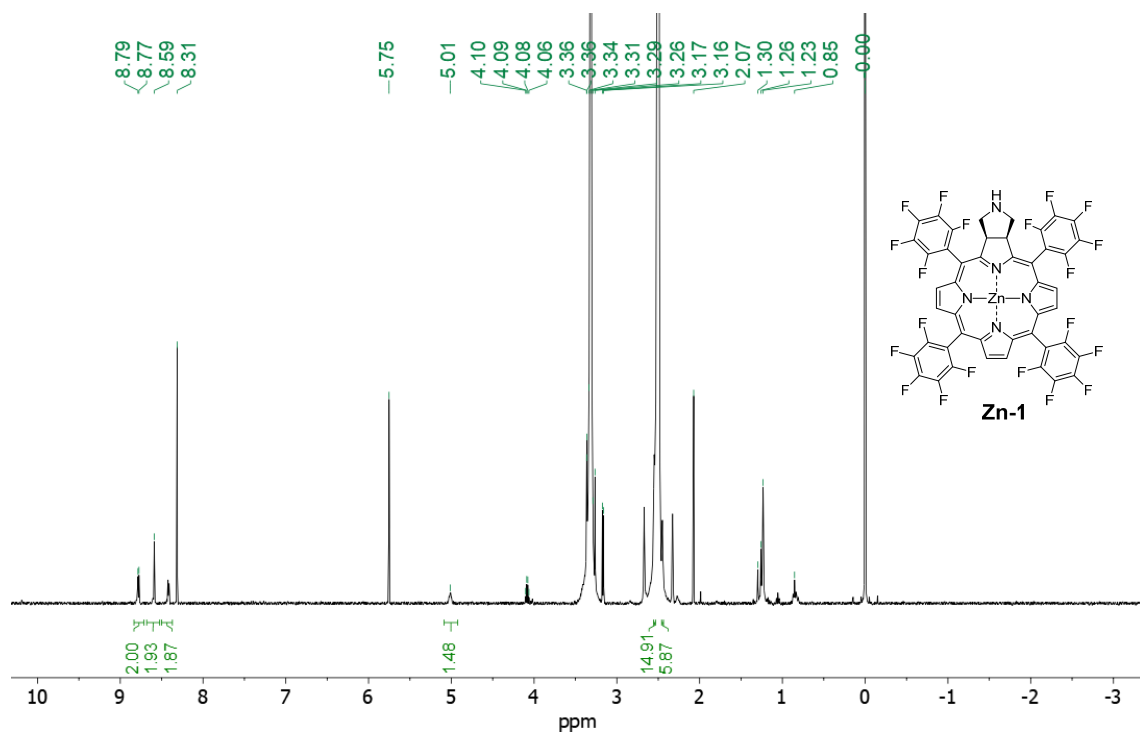


Figure S 2. ^1H NMR spectrum (400.14 MHz, DMSO-d_6) of **Zn-1**.

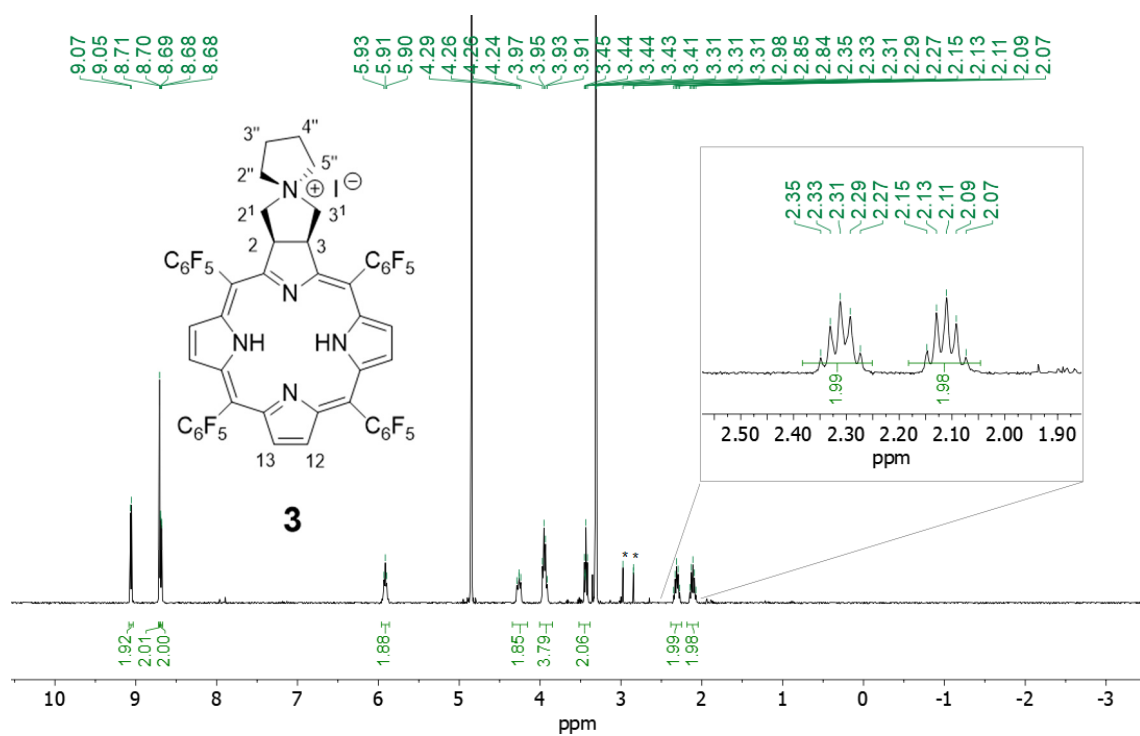


Figure S 3. ¹H NMR spectrum (400.14 MHz, CD₃OD) of **3** (*solvent impurities).

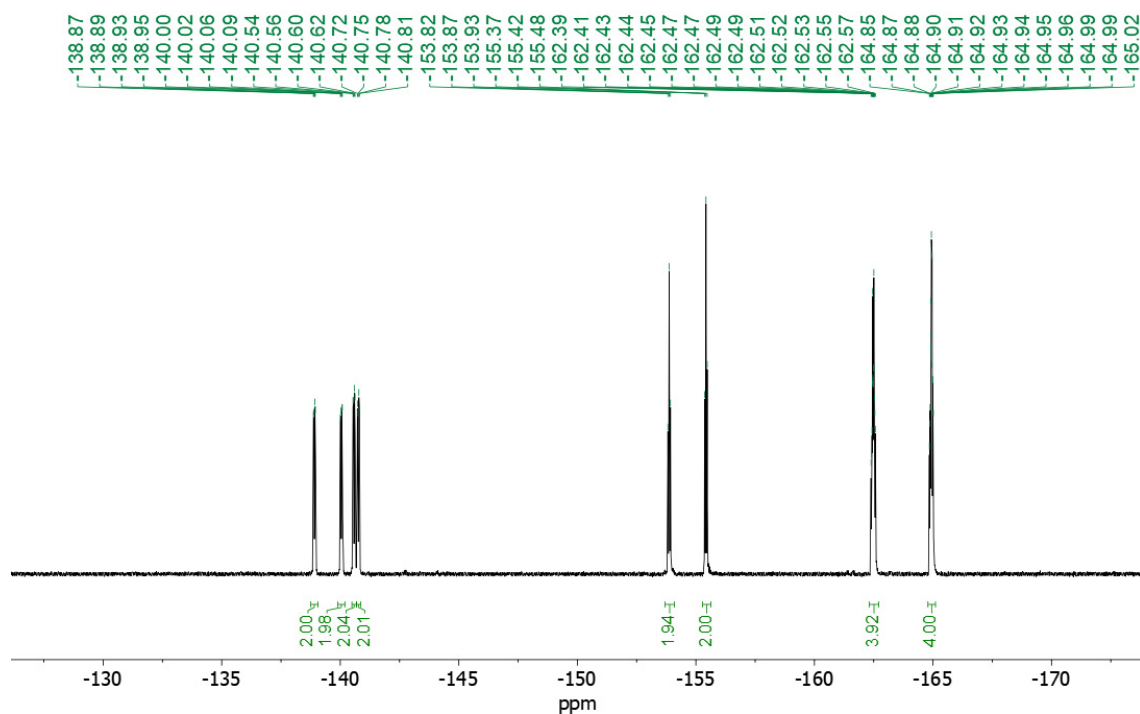


Figure S 4. ¹⁹F NMR spectrum (376.48 MHz, CDCl₃) of **3**.

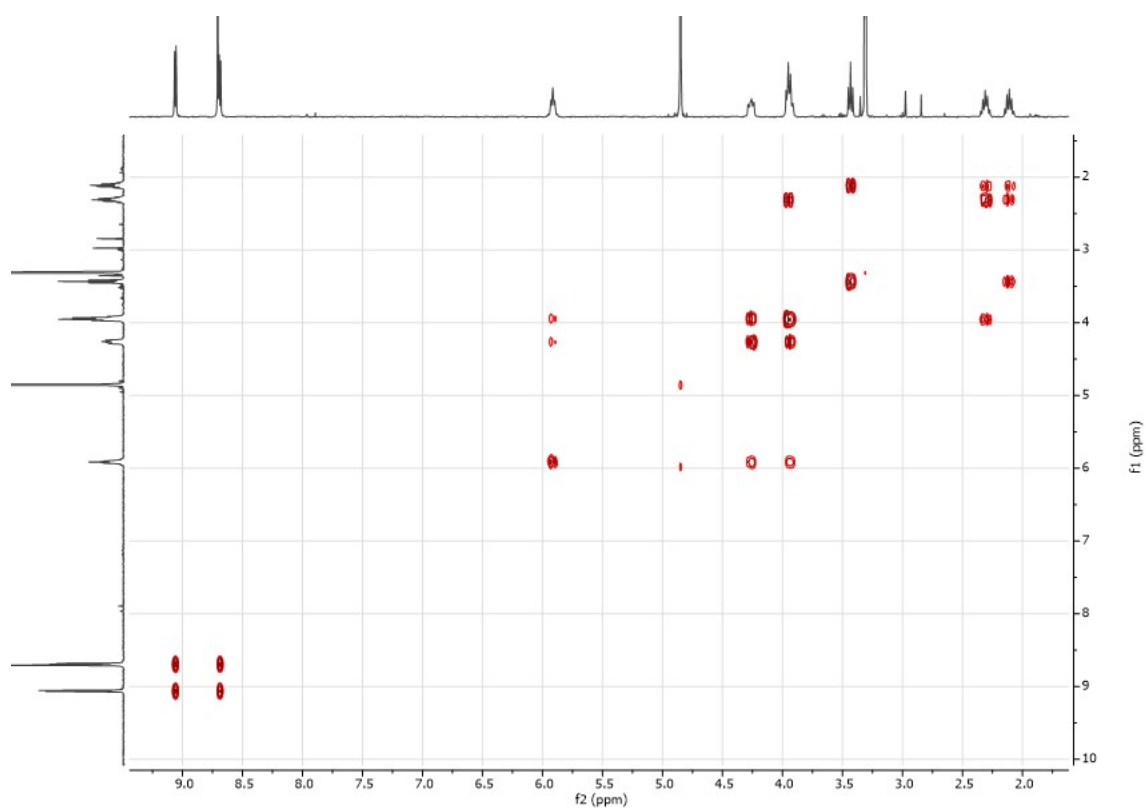


Figure S 5. COSY spectrum of **3**.

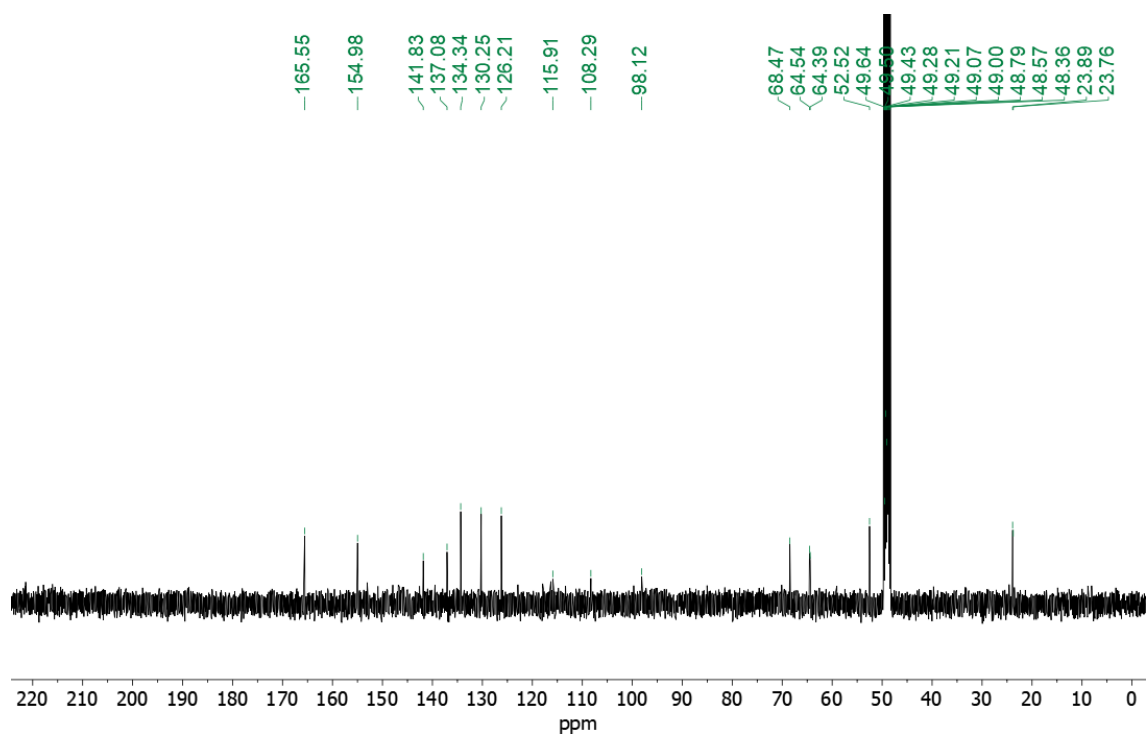


Figure S 6. ^{13}C NMR spectrum (100.62 MHz, CD_3OD) of **3**.

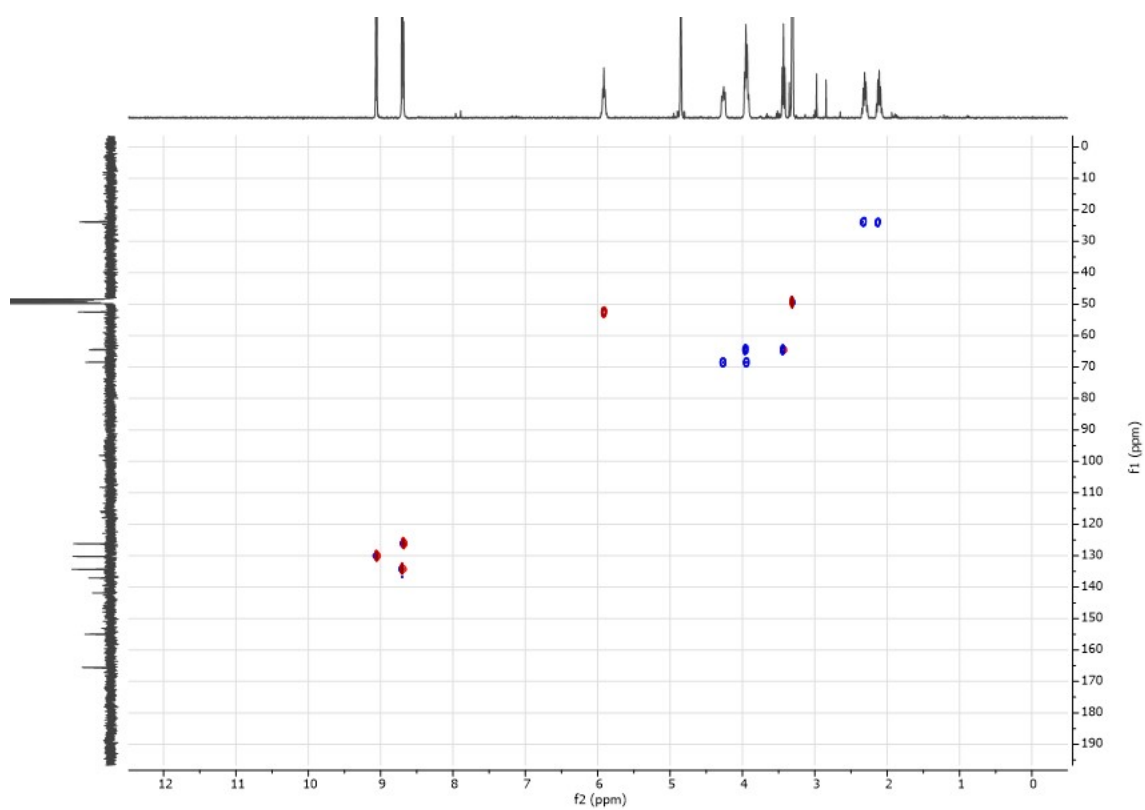


Figure S 7. HSQC spectrum of **3**.

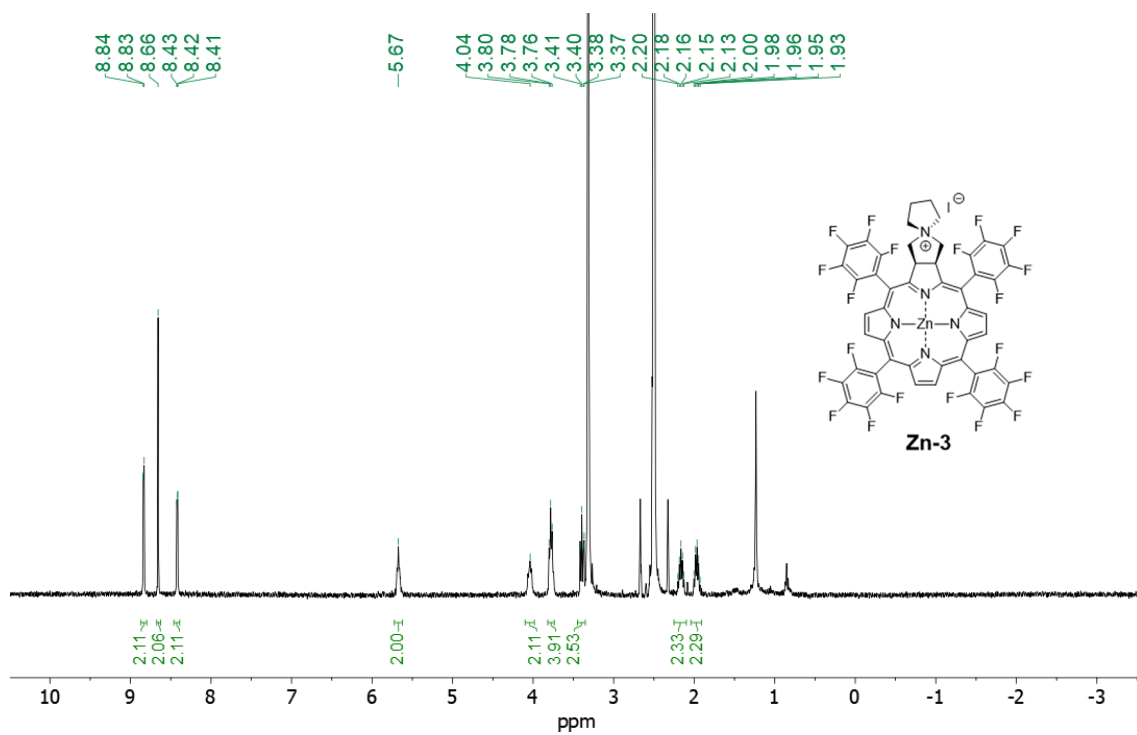


Figure S 8. ^1H NMR spectrum (400.14 MHz, CD_3OD) of **Zn-3**.

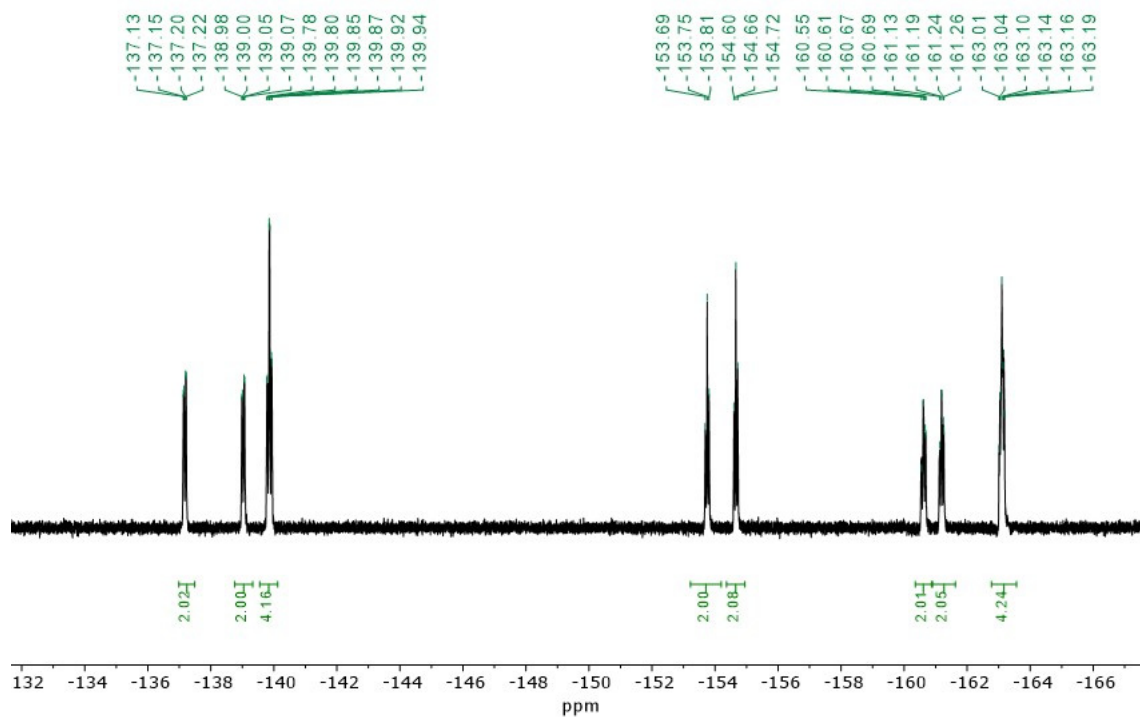


Figure S 9. ^{19}F NMR spectrum (376.48 MHz, CD_3OD) of **Zn-3**.

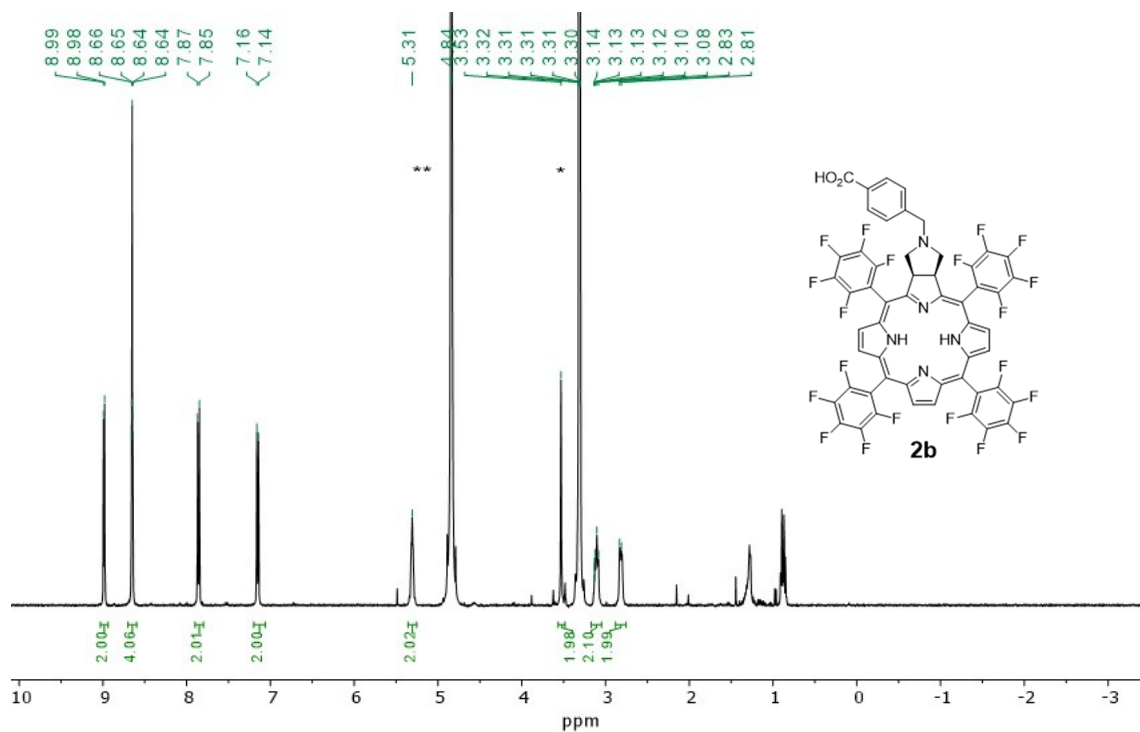


Figure S 10. ^1H NMR spectrum (400.14 MHz, CD_3OD) of **2b** (* CD_3OD ; **water).

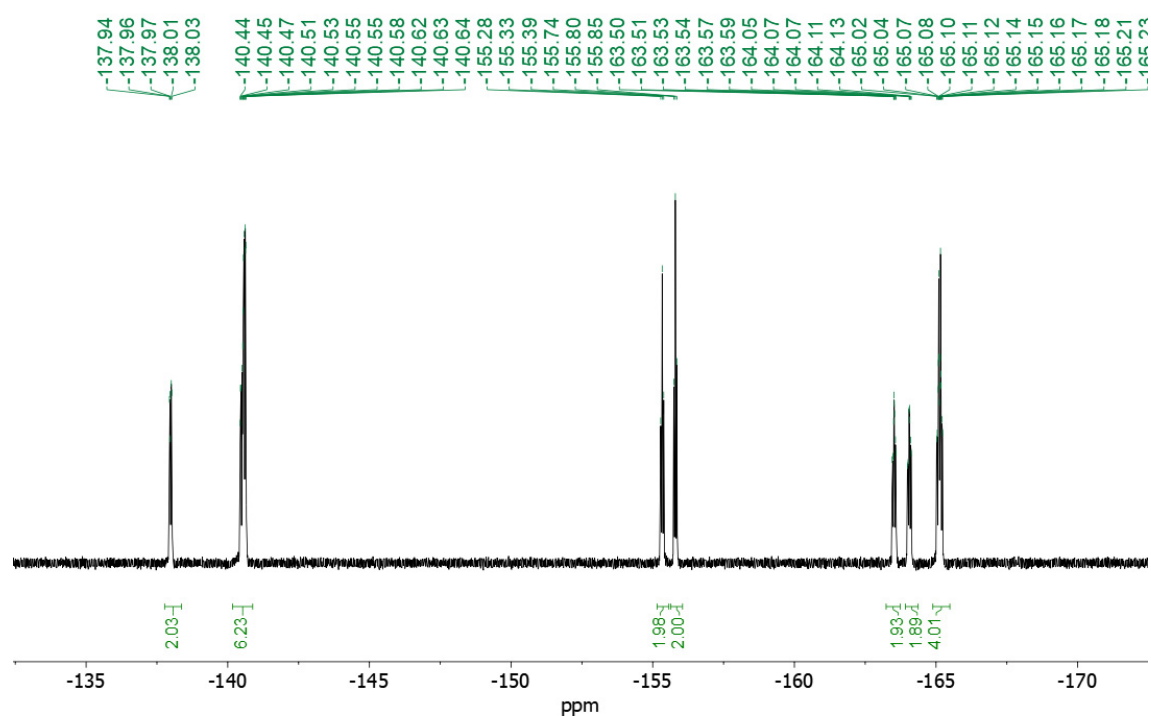


Figure S 11. ¹⁹F NMR spectrum (376.48 MHz, CD₃OD) of **2b**.

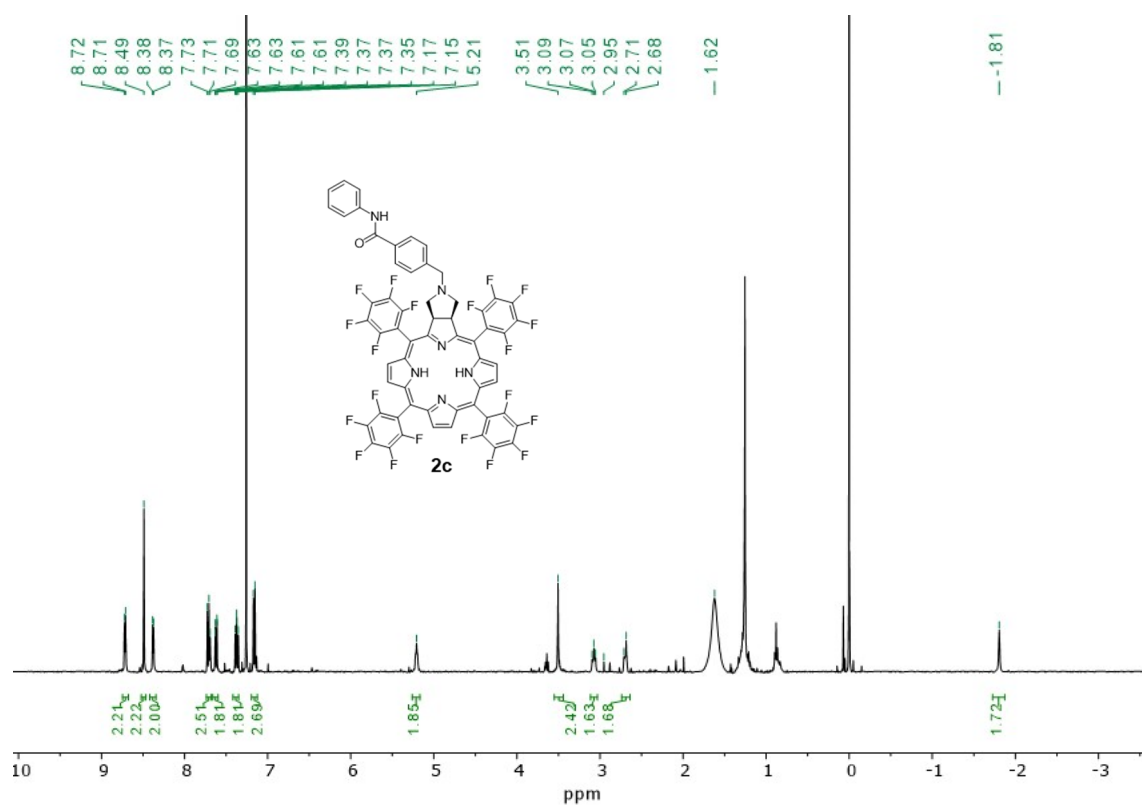


Figure S 12. ¹H NMR spectrum (400.14 MHz, CDCl₃) of **2c**.

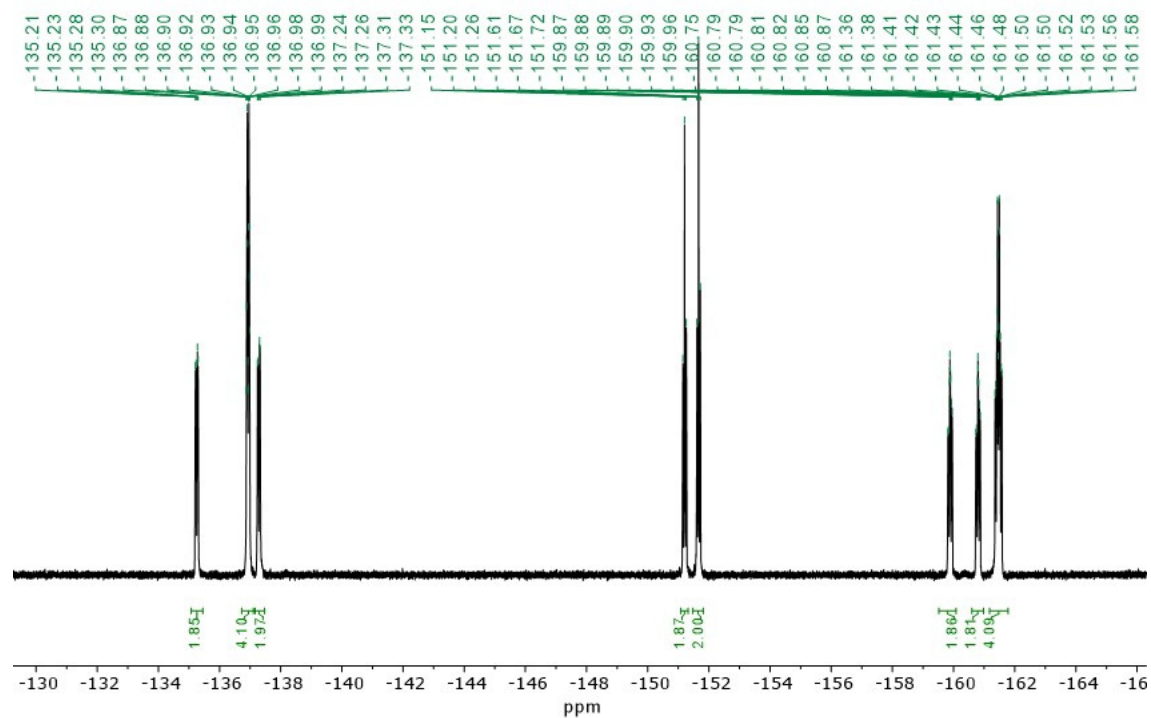


Figure S 13. ¹⁹F NMR spectrum (376.48 MHz, CDCl₃) of **2c**.

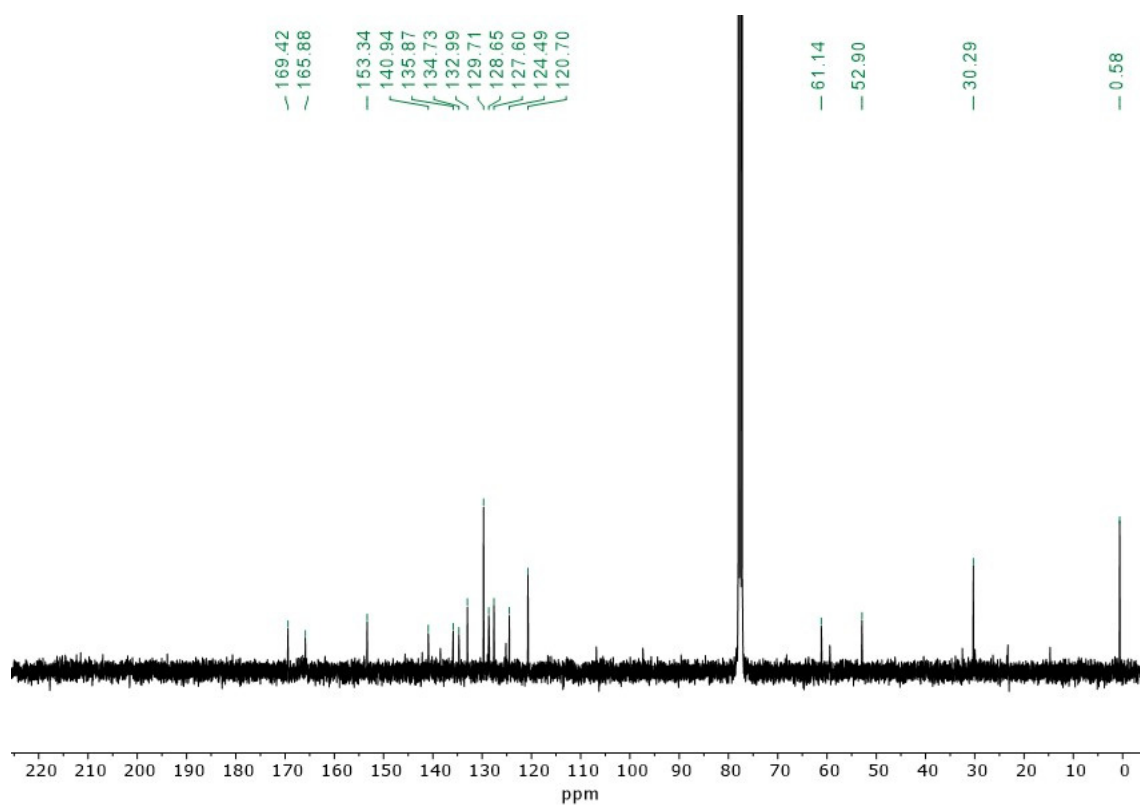


Figure S 14. ^{13}C NMR spectrum (100.62 MHz, CDCl_3) of **2c**.

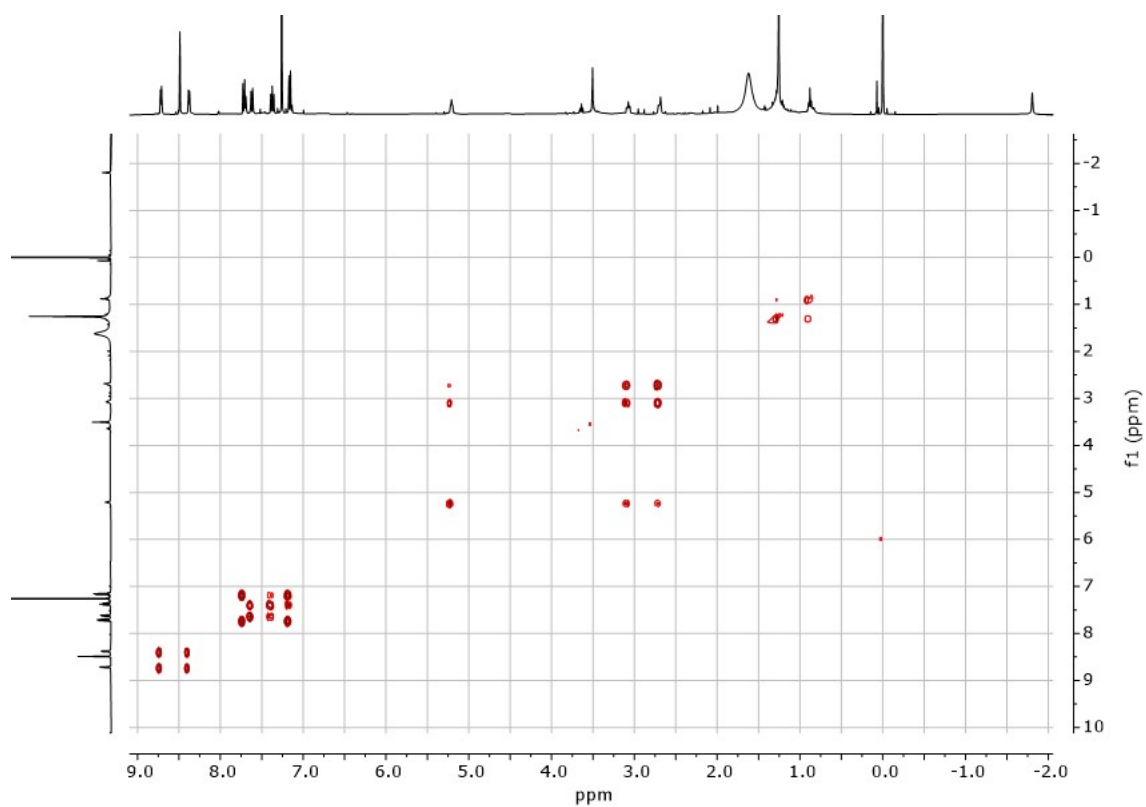


Figure S 15. COSY spectrum of **2c**.

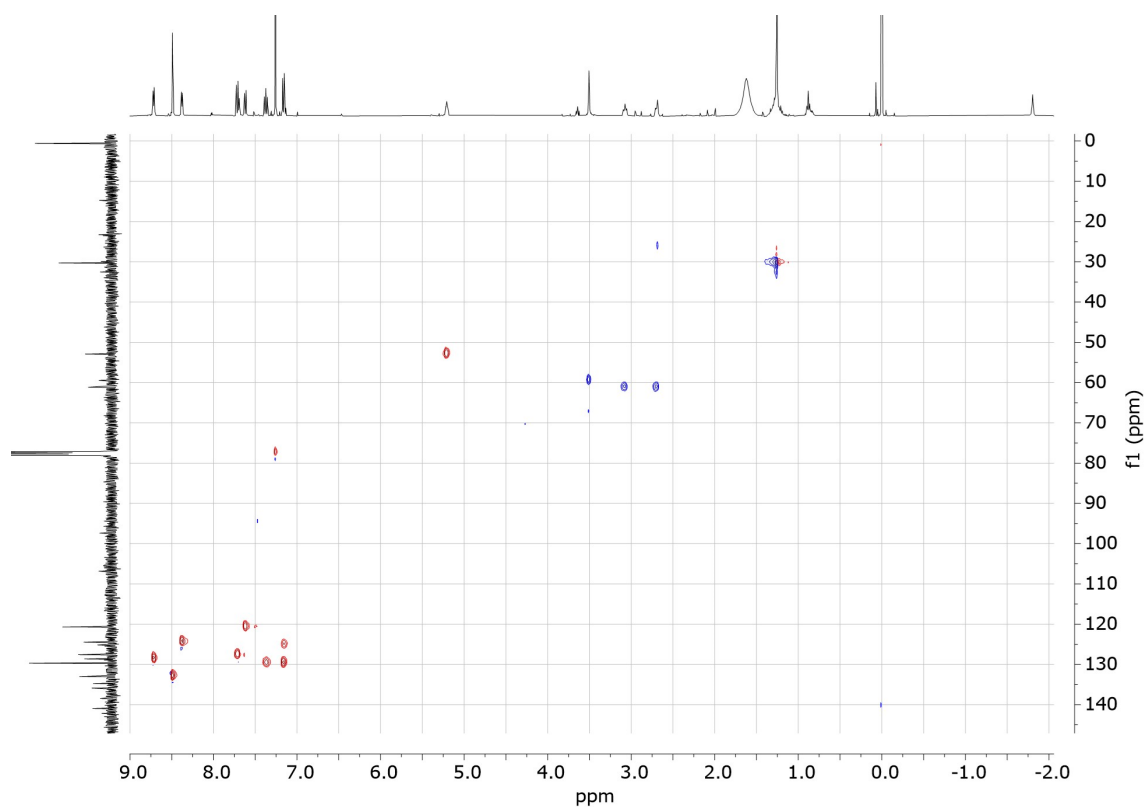


Figure S 16. HSQC spectrum of **2c**.

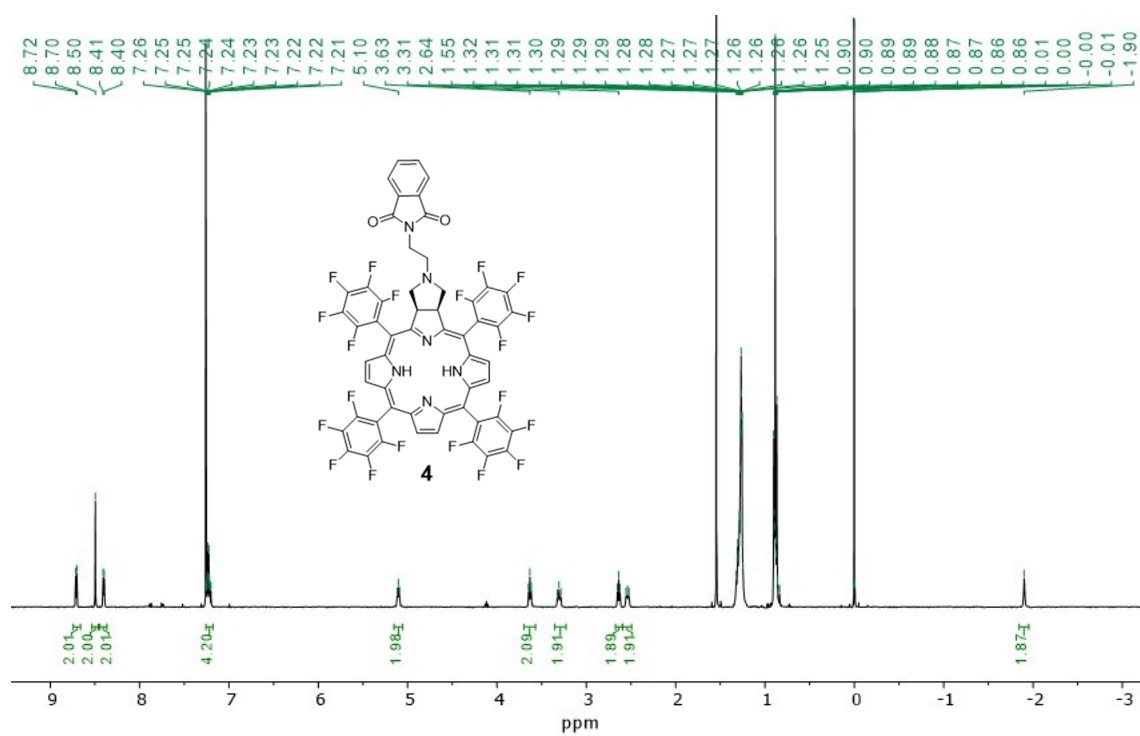


Figure S 17. ^1H NMR (400.14 MHz, CDCl_3) spectrum of **4**.

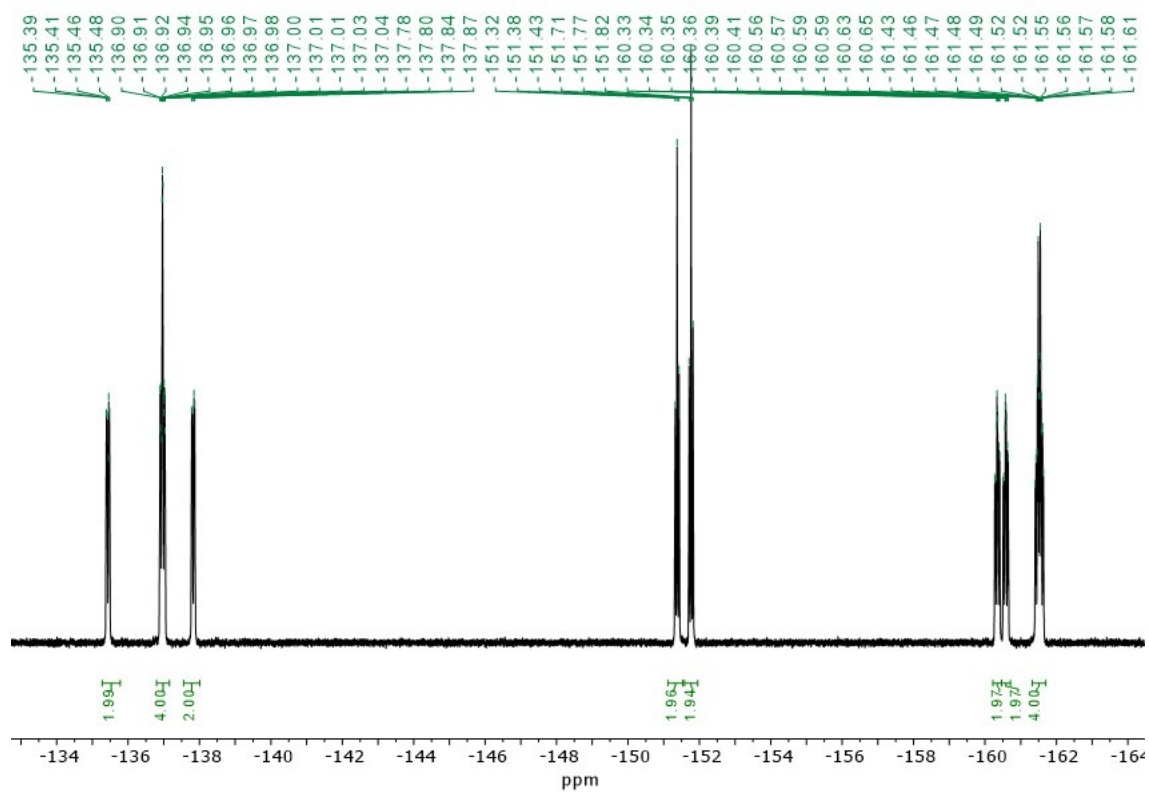


Figure S 18. ¹⁹F NMR (376.48 MHz, CD₃Cl) spectrum of 4.

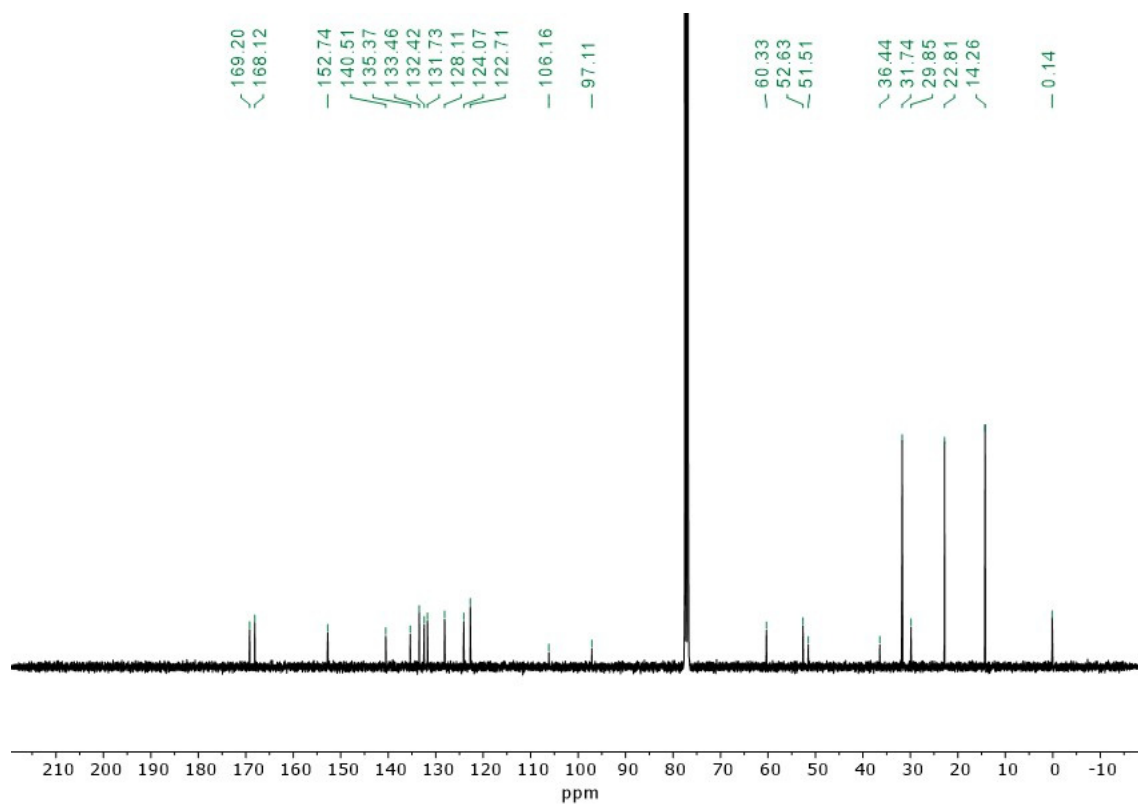


Figure S 19. ¹³C NMR spectrum (100.62 MHz, CDCl₃) of 4.

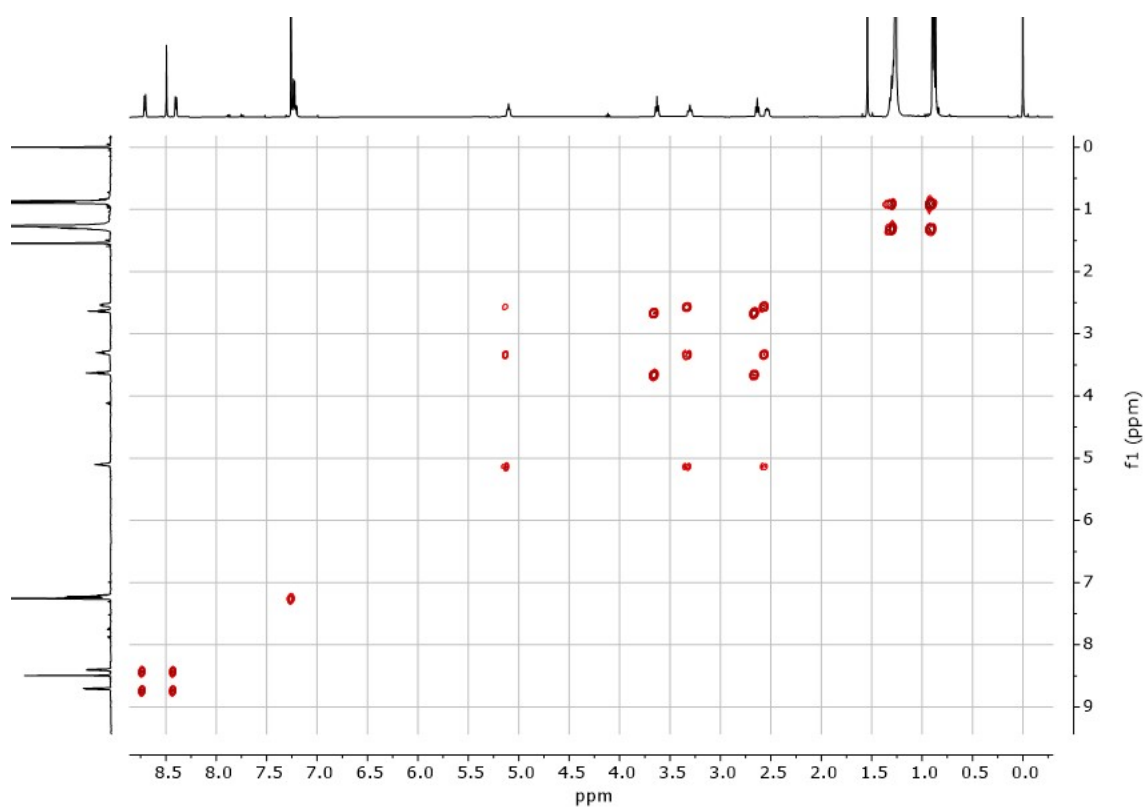


Figure S 20. COSY spectrum of 4.

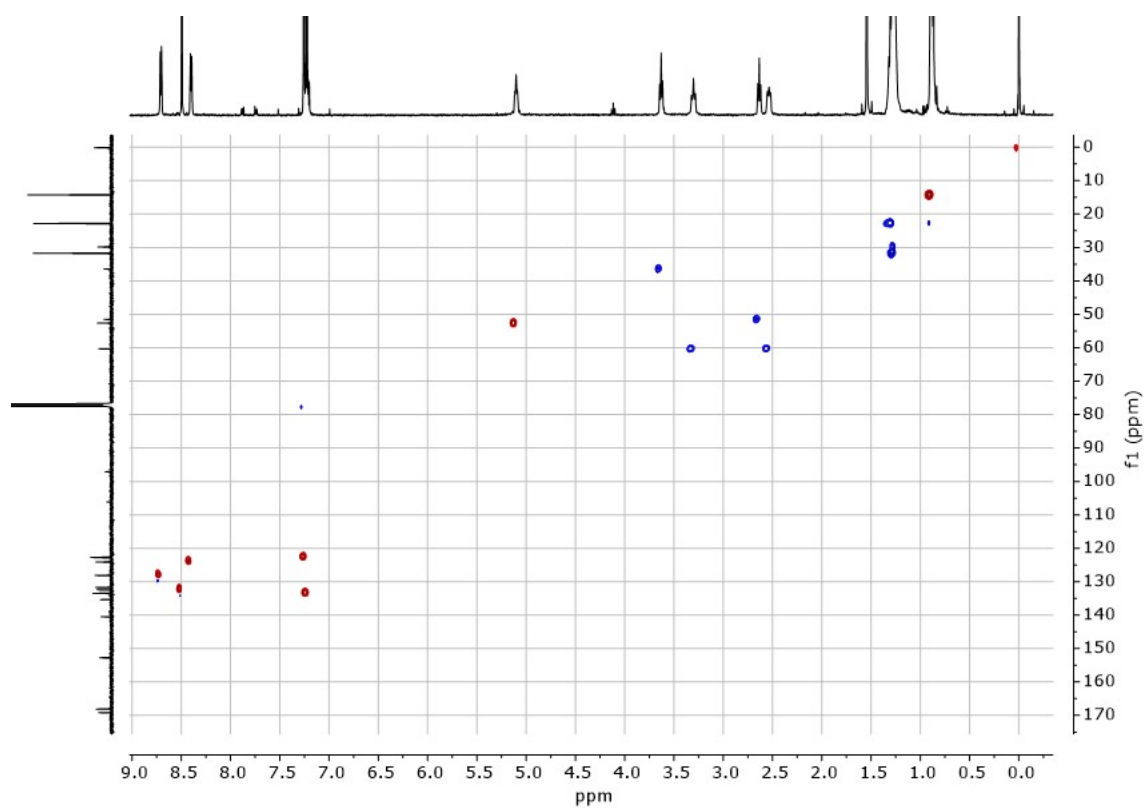


Figure S 21. HSQC spectrum of 4.

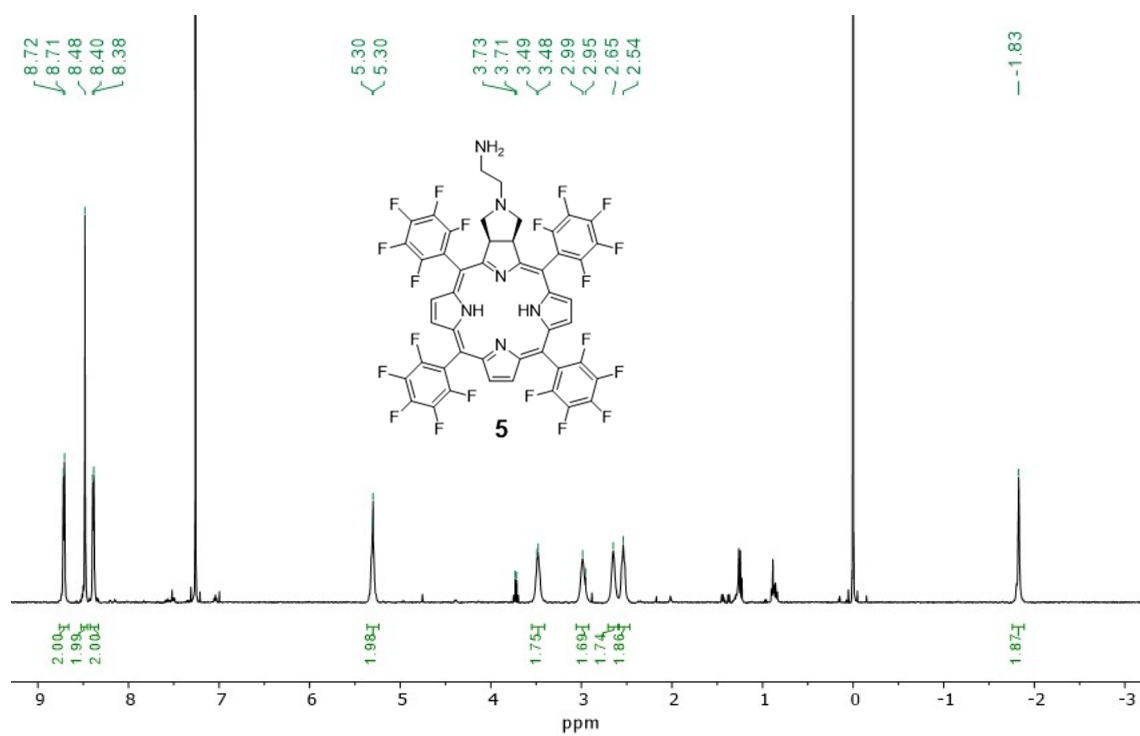


Figure S 22. ¹H NMR spectrum (400.14 MHz, CDCl₃) of **5**.

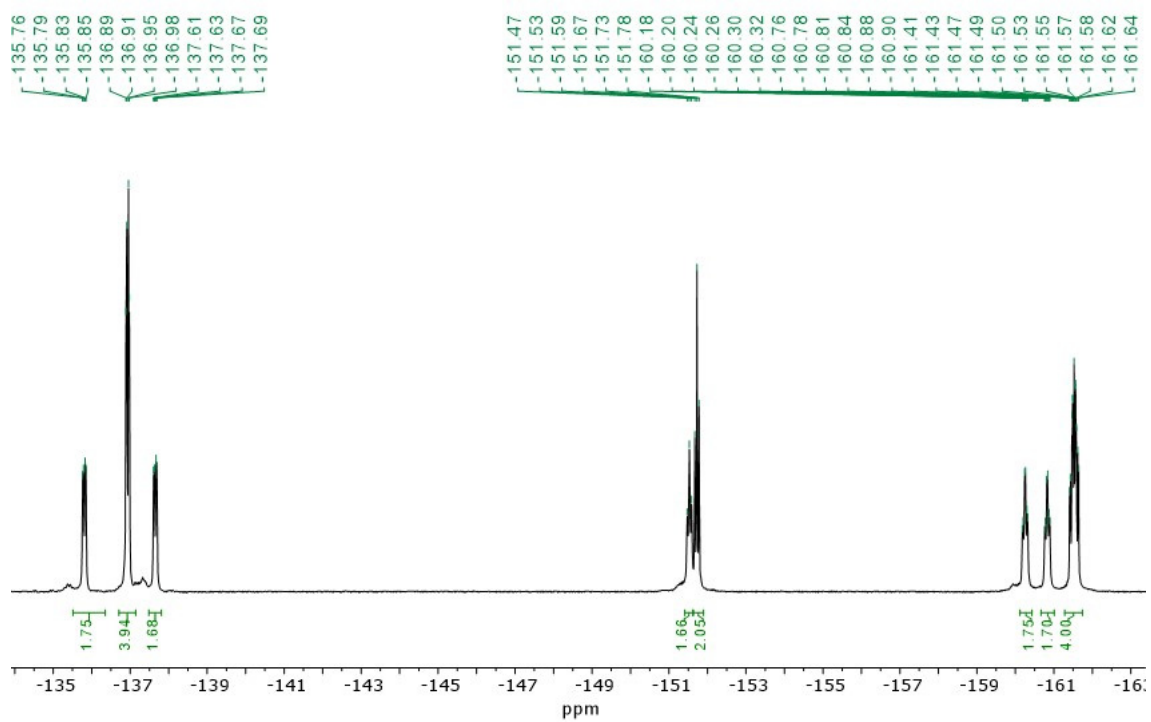


Figure S 23. ¹⁹F NMR spectrum (376.48 MHz, CDCl₃) of **5**.

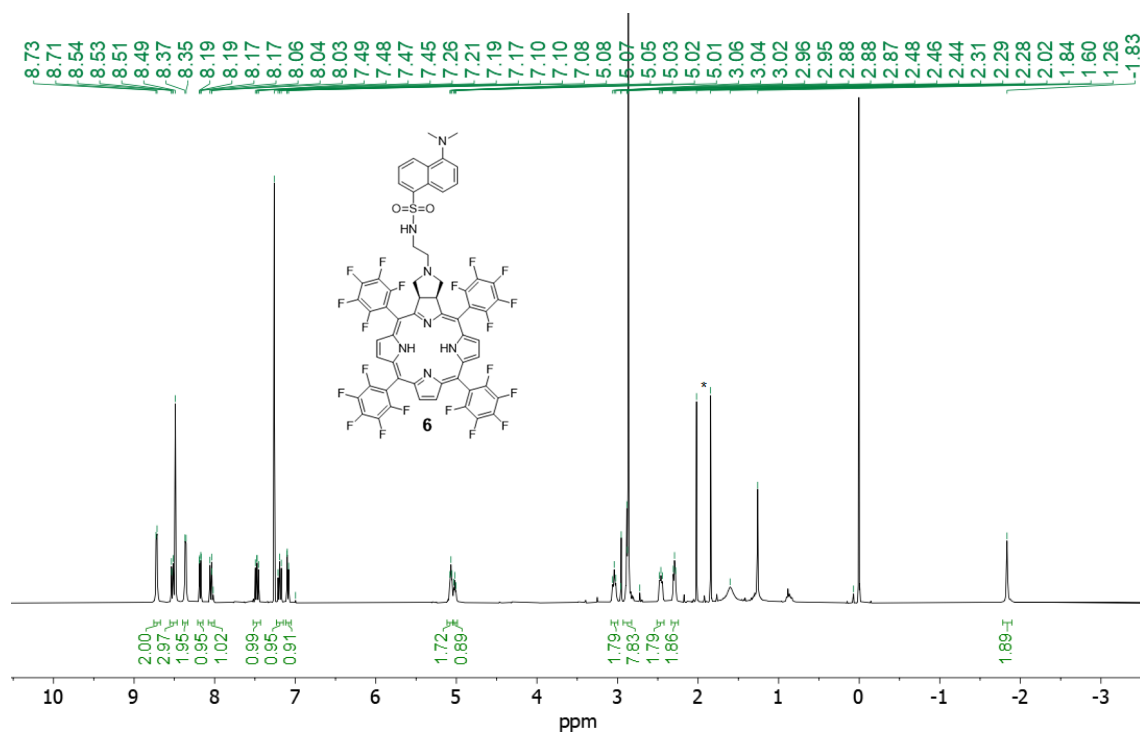


Figure S 24. ¹H NMR spectrum (400.14 MHz, CDCl₃) of **6** (*impurities).

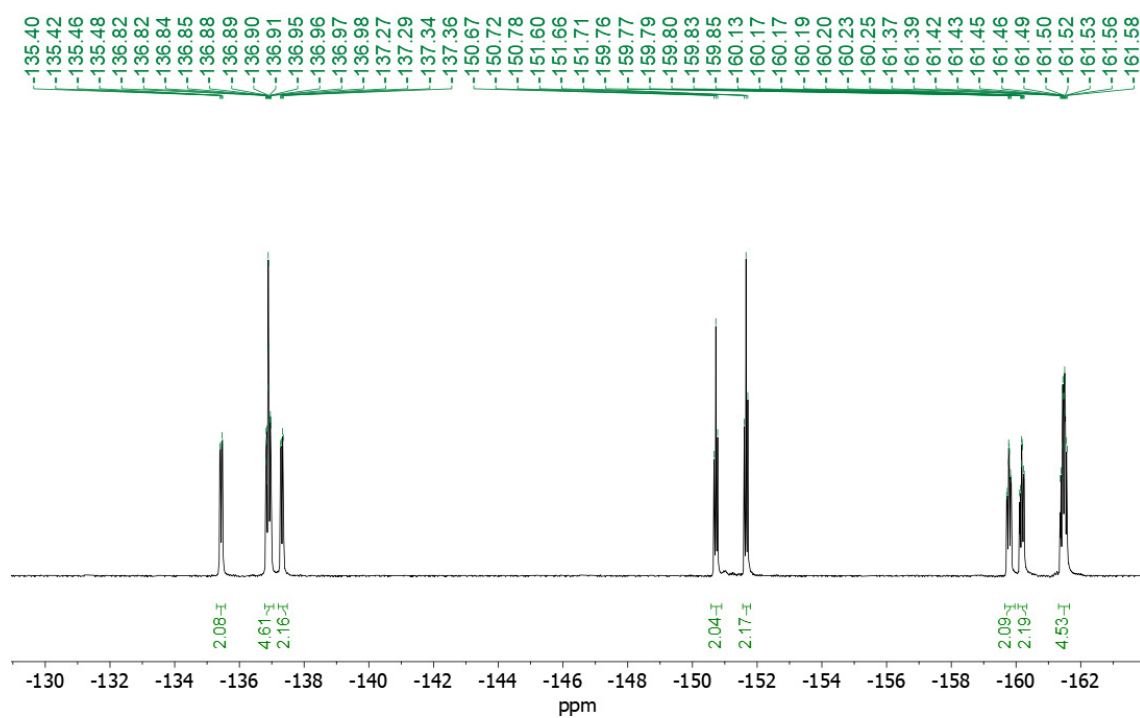


Figure S 25. ¹⁹F NMR spectrum (376.48 MHz, CDCl₃) of **6**.

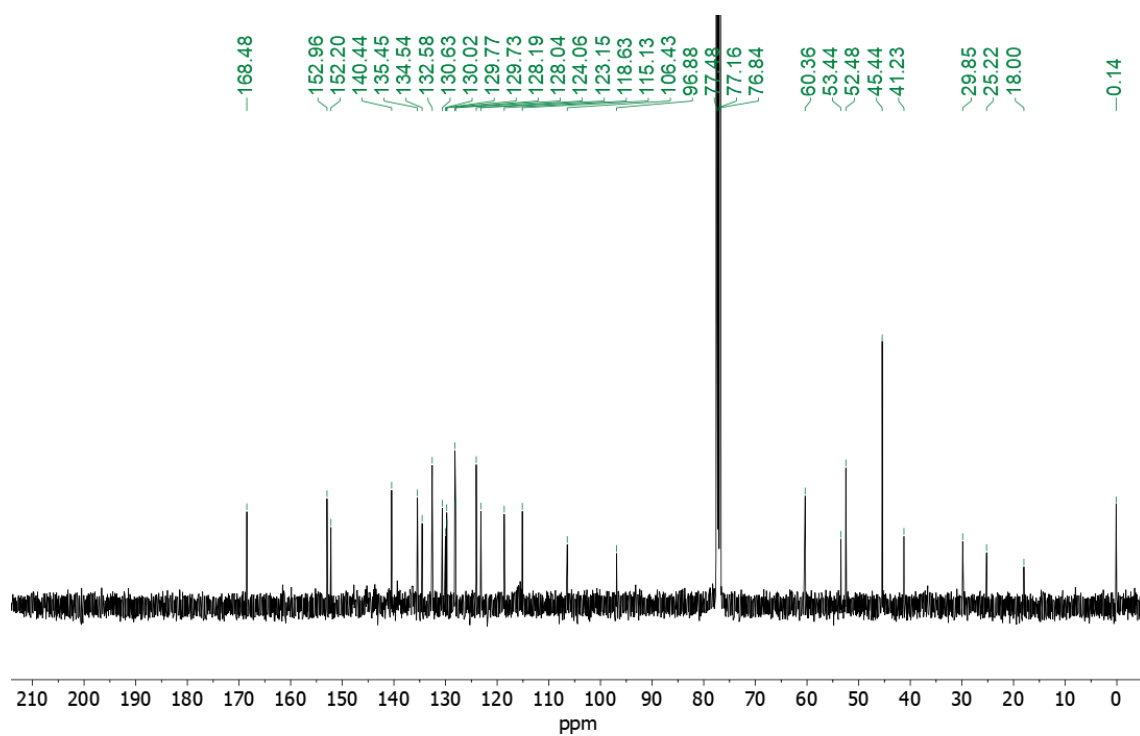


Figure S 26. ^{13}C NMR spectrum (100.62 MHz, CDCl_3) of **6**.

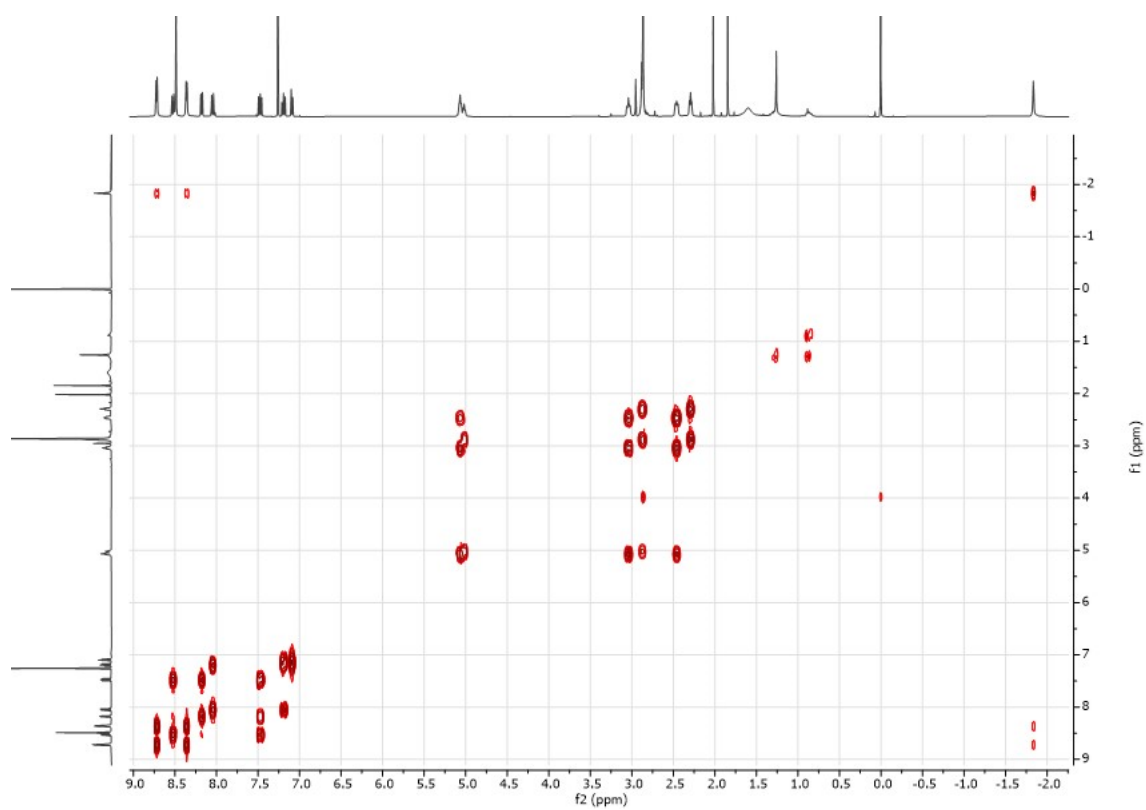


Figure S 27. COSY spectrum of **6**.

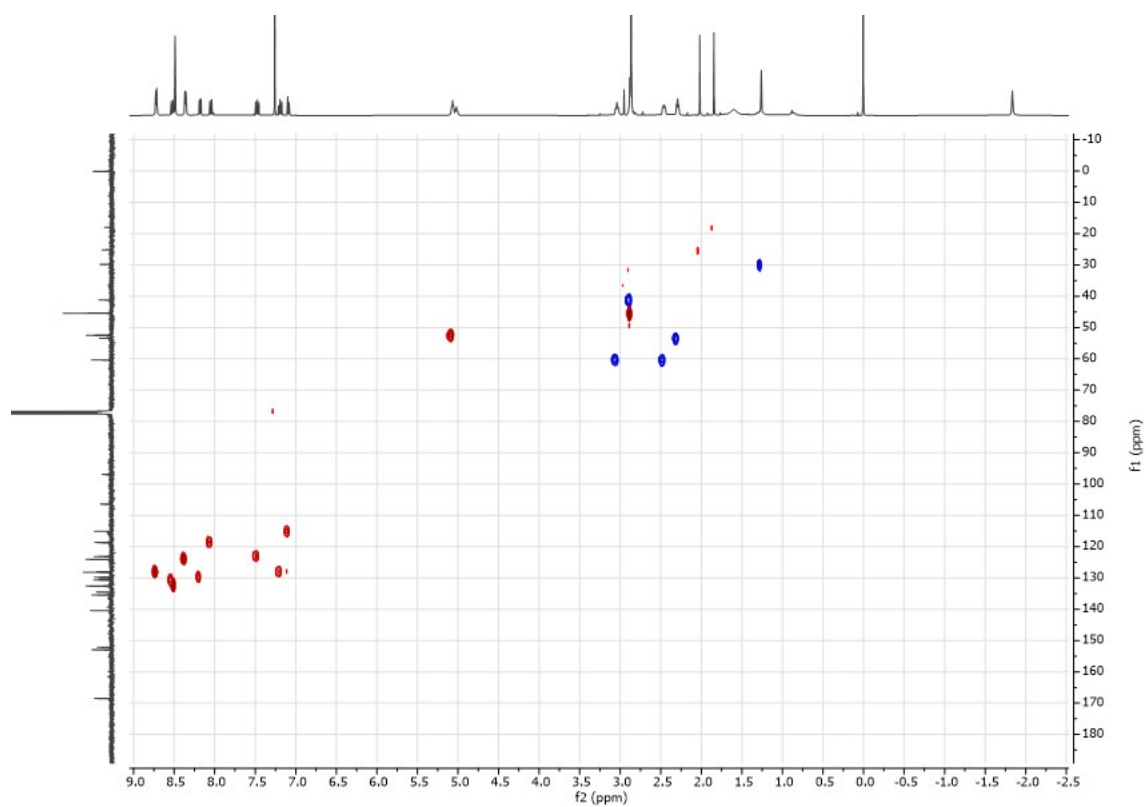


Figure S 28. HSQC spectrum of 6.

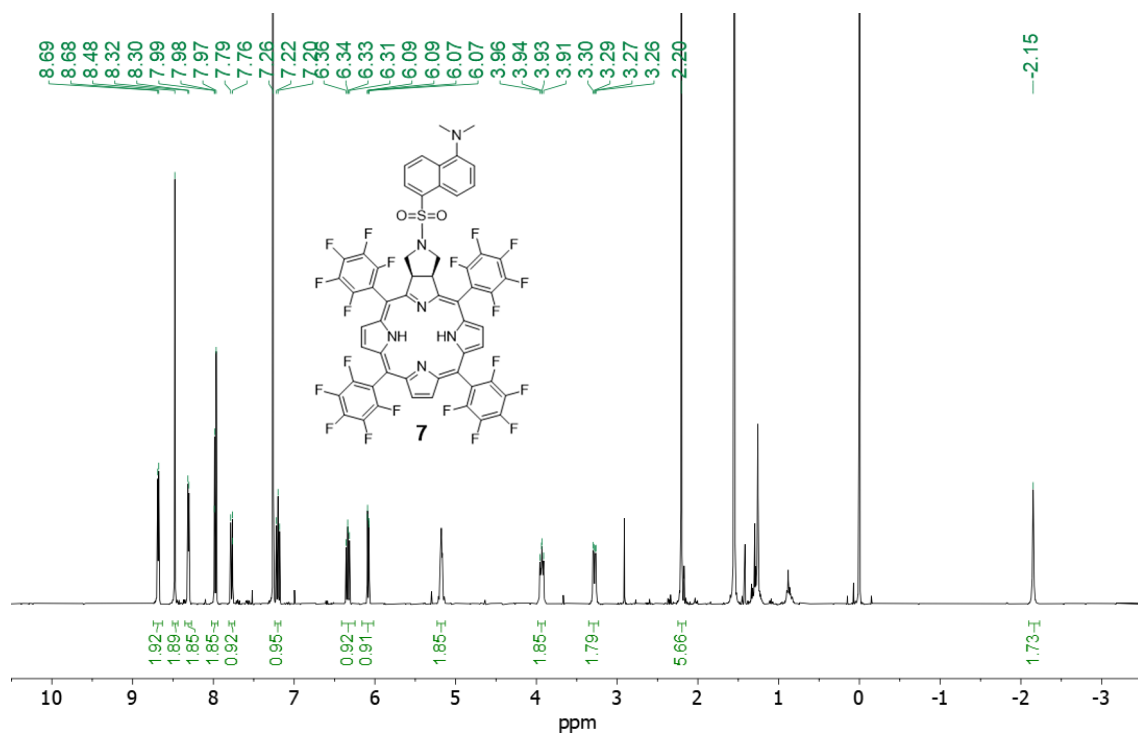


Figure S 29. ^1H NMR spectrum (400.14 MHz, CDCl_3) of 7.

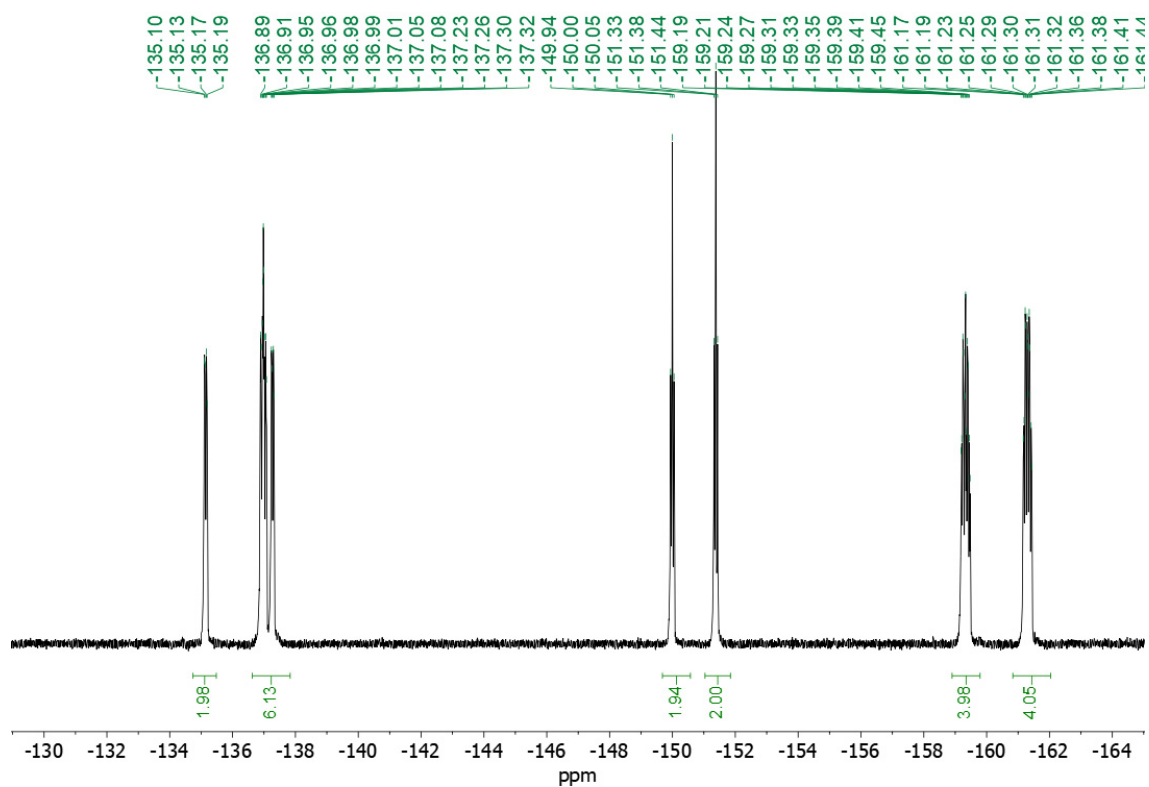


Figure S 30. ¹⁹F NMR spectrum (376.48 MHz, CD₃Cl) of 7.

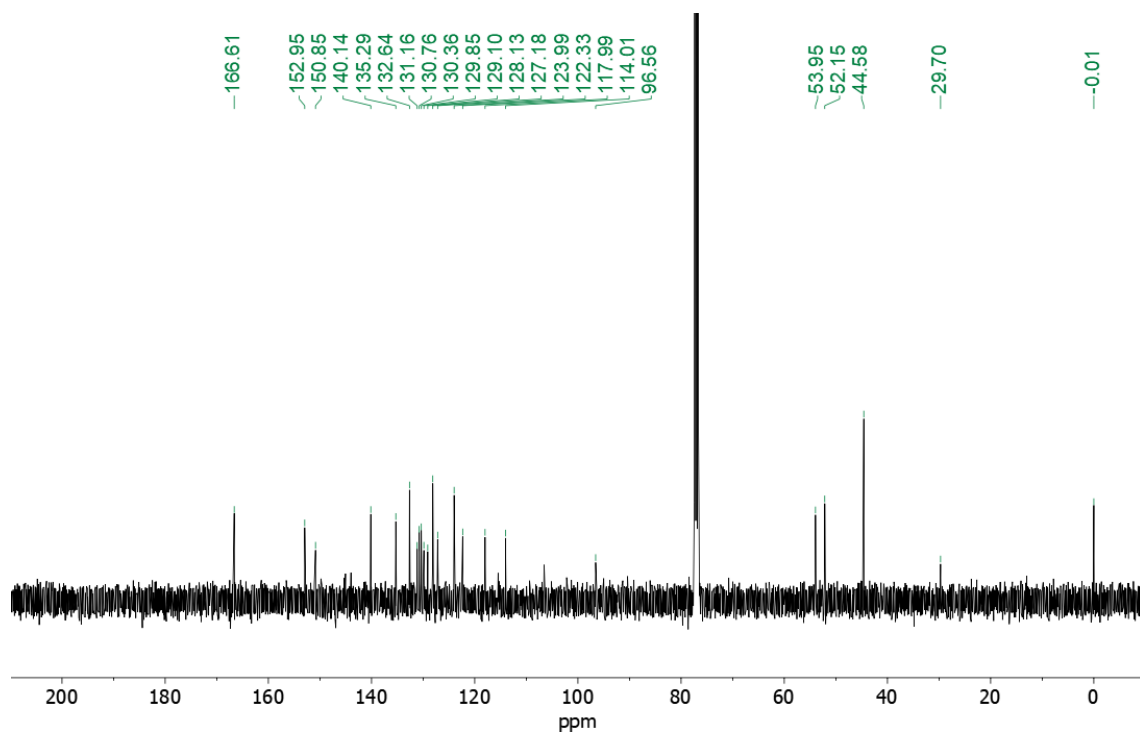


Figure S 31. ¹³C NMR spectrum (101 MHz, CDCl₃) of 7.

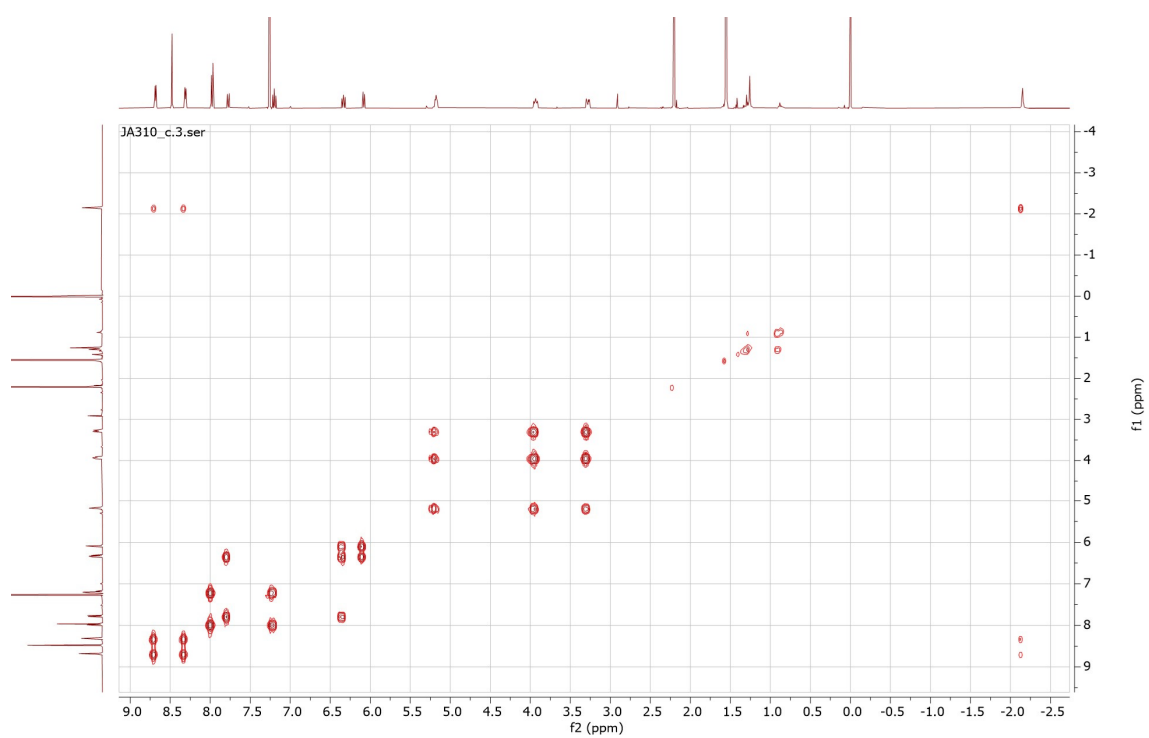


Figure S 32. COSY spectrum of 7.

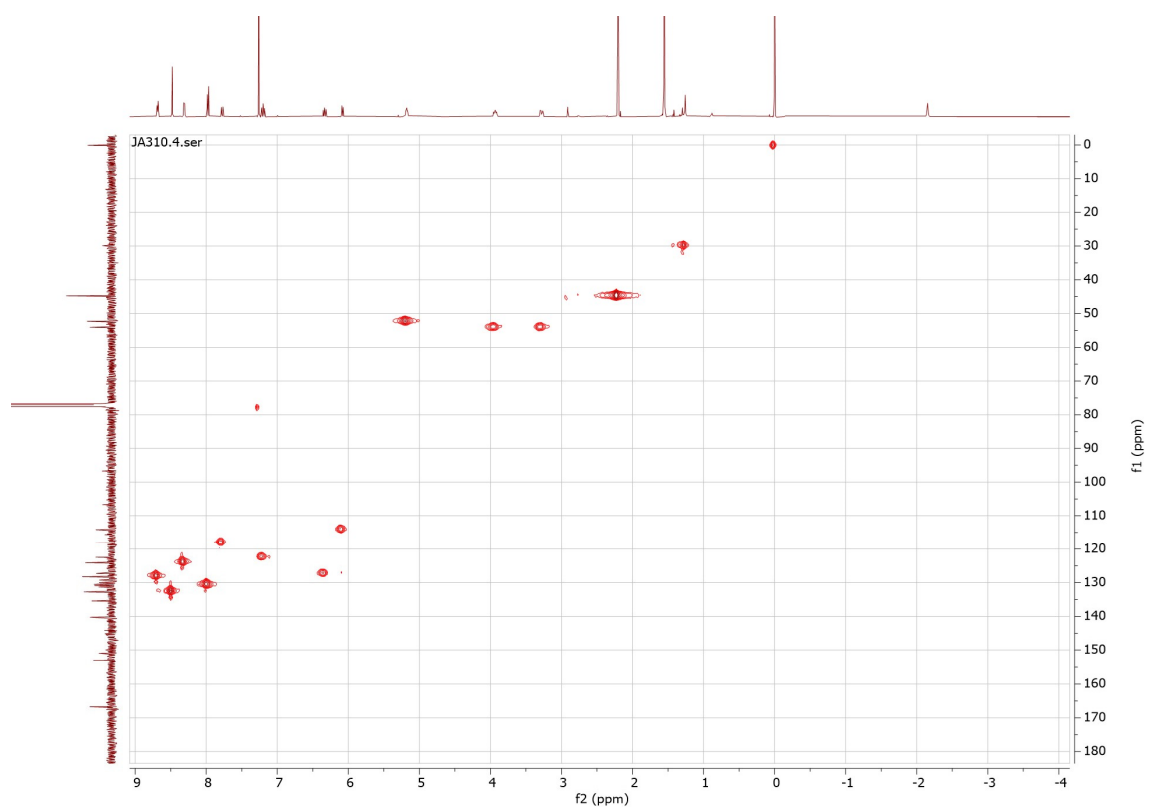


Figure S 33. HSQC spectrum of 7.

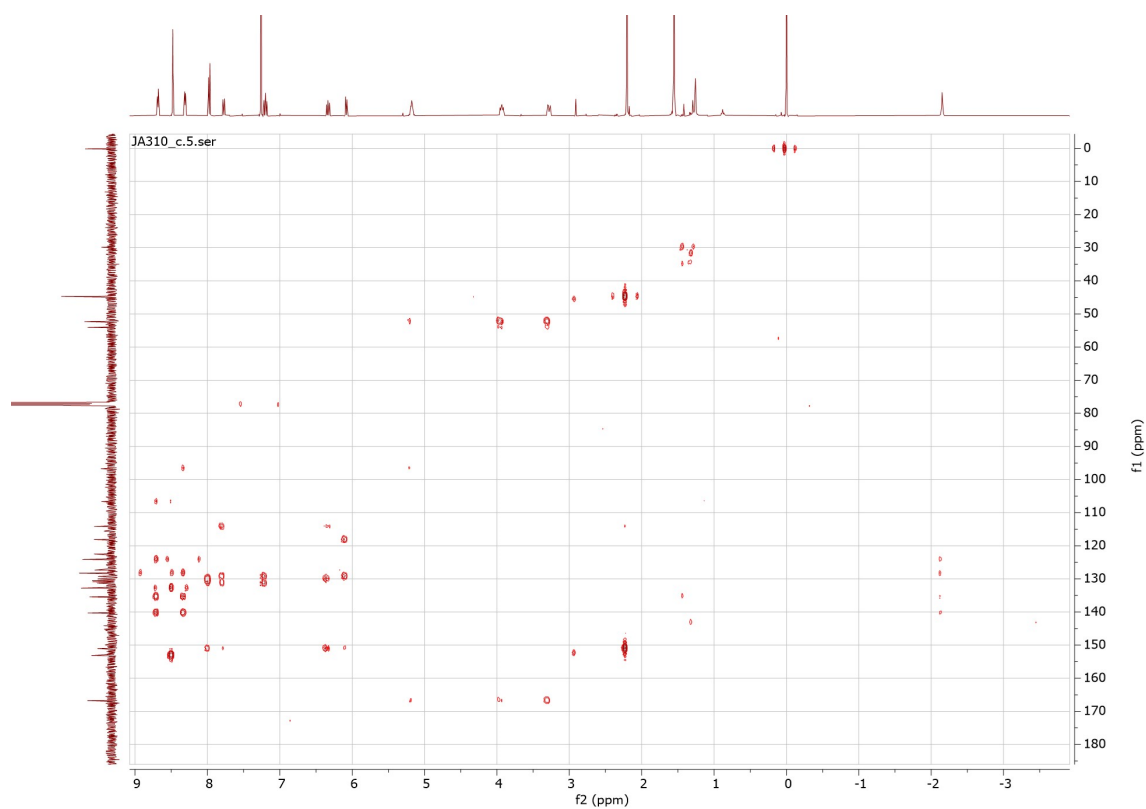


Figure S 34. HMBC spectrum of **7**.

Mass spectrometry

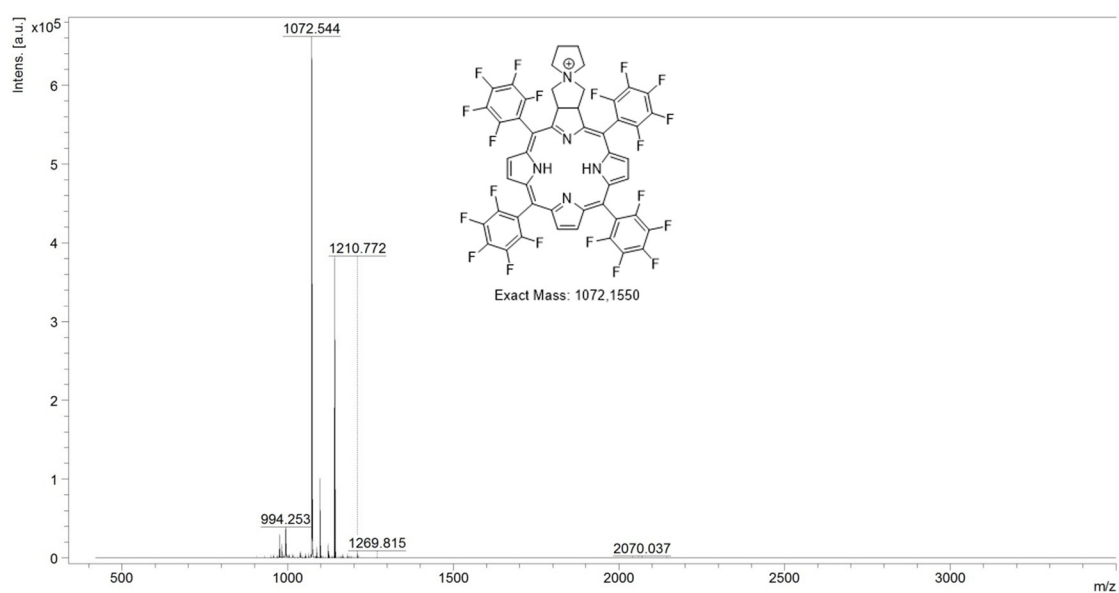


Figure S 35. MALDI-TOF spectrum of **3**.

CN-BenzCOOH 1#1-70 RT: 0.00-1.00 AV: 70 NL: 5.67E7
F: FTMS + p ESI Full ms [100.00-2000.00]

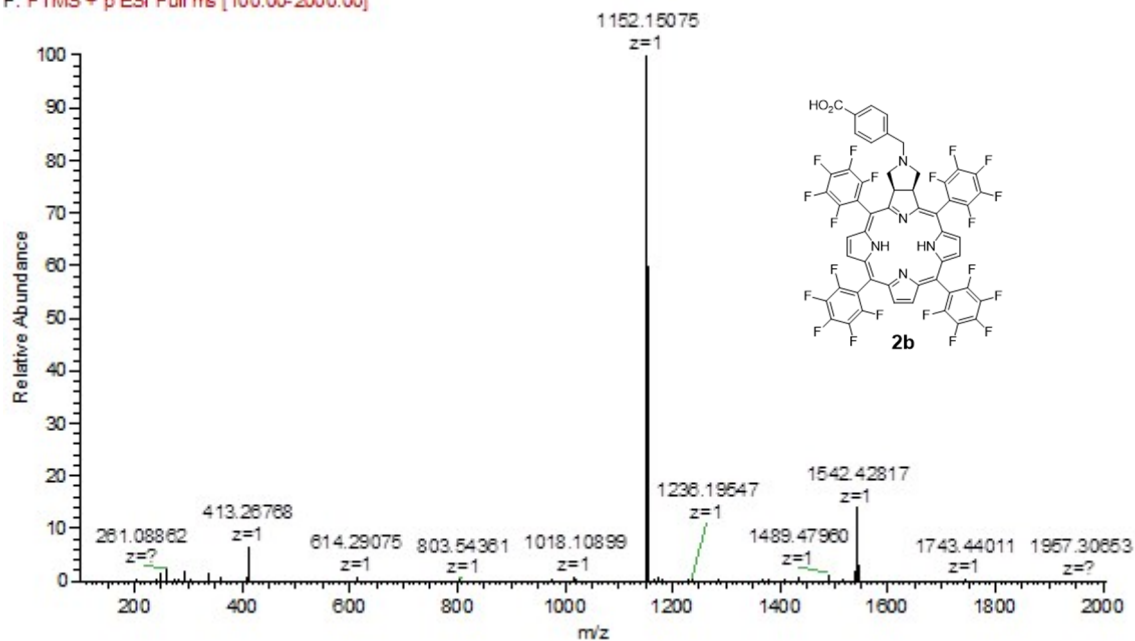


Figure S 36. ESI-MS spectrum of **2b**.

CN-BzAc7-A 496-99 RT: 2.082.11 AV: 2 NL: 3.03E5
F: FTMS + p ESI Full ms [200.00-2000.00]

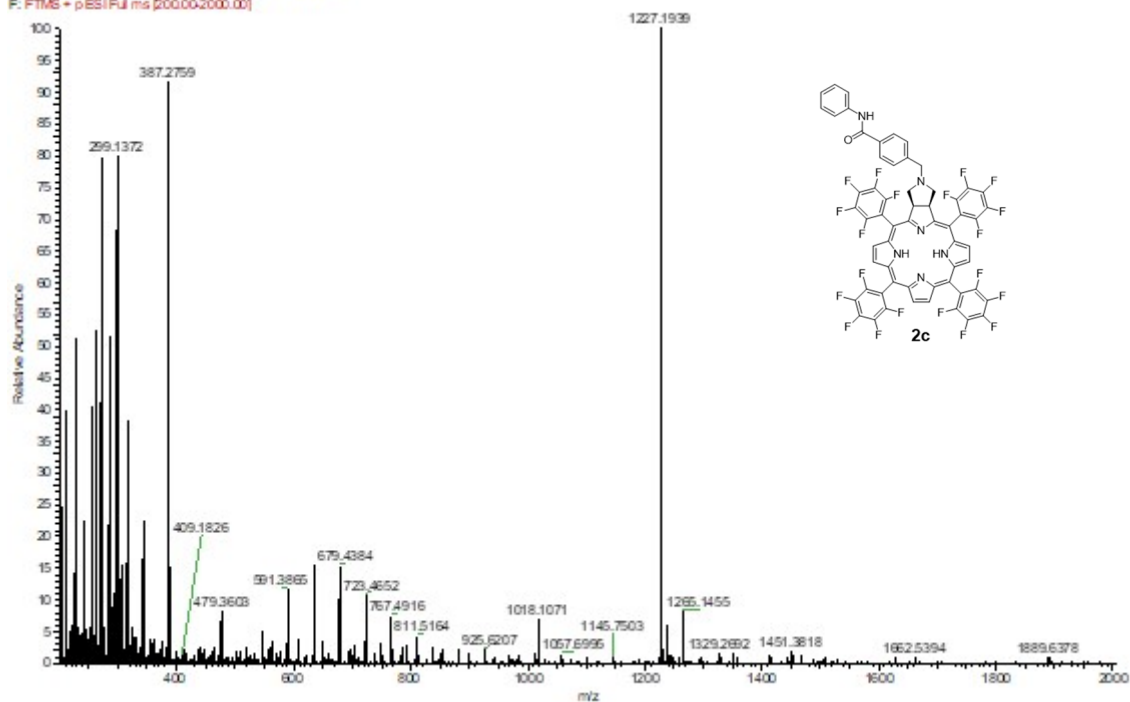


Figure S 37. ESI-MS full spectrum of **2c**.

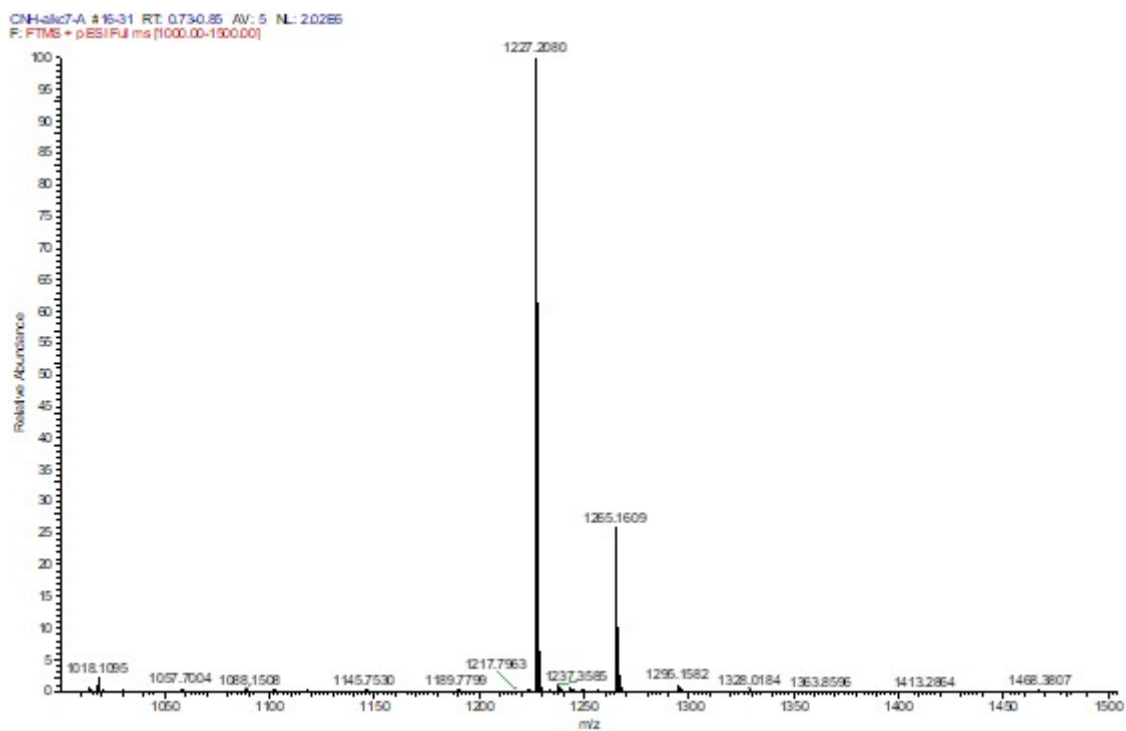


Figure S 38. ESI-MS spectrum of chlorin **2c** (1000.00-1500.00 Da).

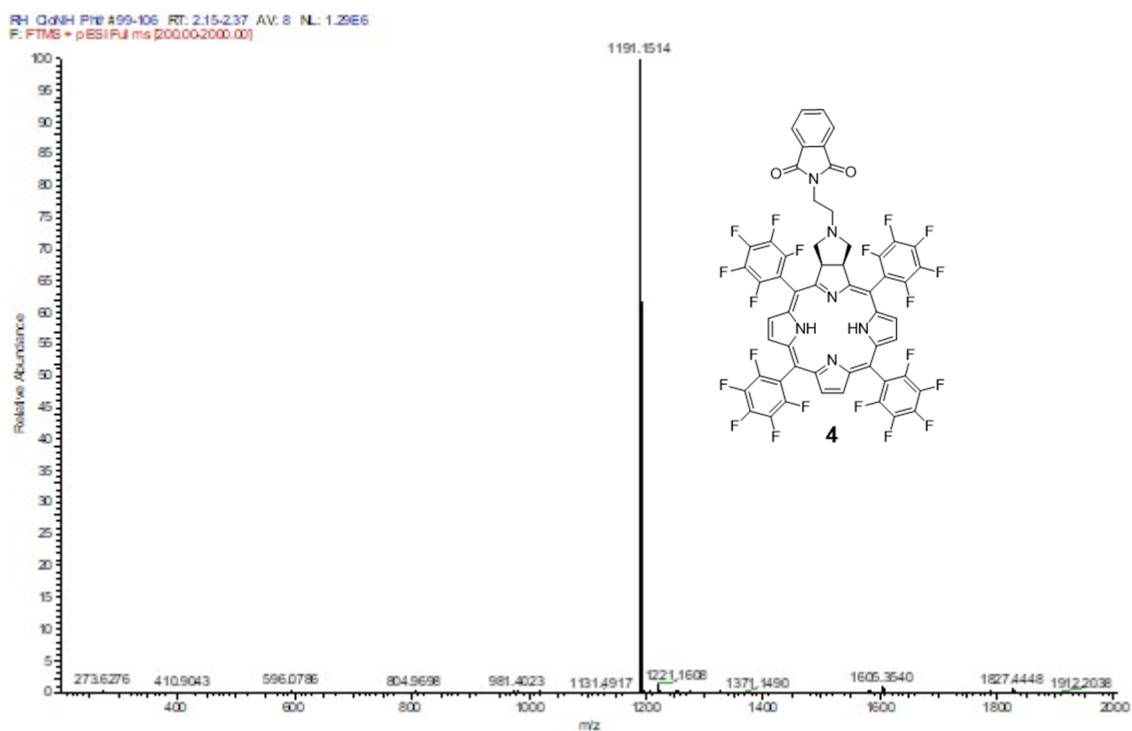


Figure S 39. ESI-MS spectrum of chlorin **4**.

200915_JA106_1 #1-120 RT: 0.00-1.99 AV: 120 NL: 1.68E8
T: FTMS + p ESI Full ms [100.00-2000.00]

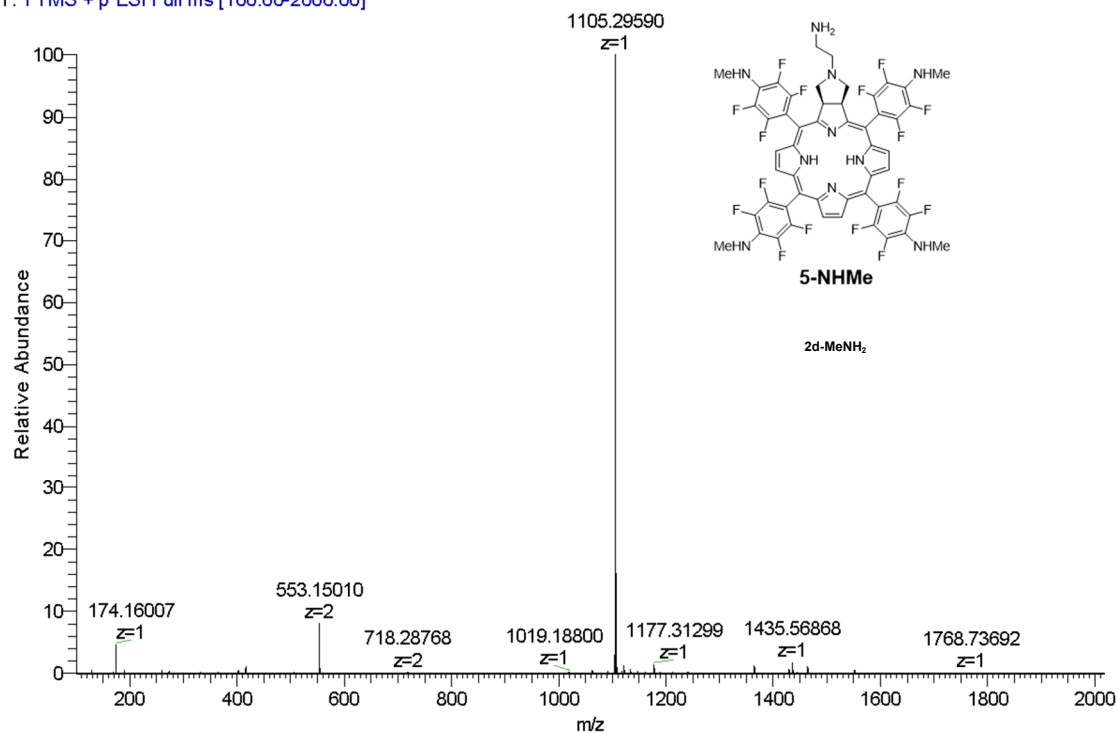


Figure S 40. ESI-MS spectrum of methylamine tetrasubstituted chlorin **5-MeNH₂**

200915_JA83_1 #1-74 RT: 0.02-2.00 AV: 74 NL: 8.67E7
T: FTMS + p ESI Full ms [100.00-2000.00]

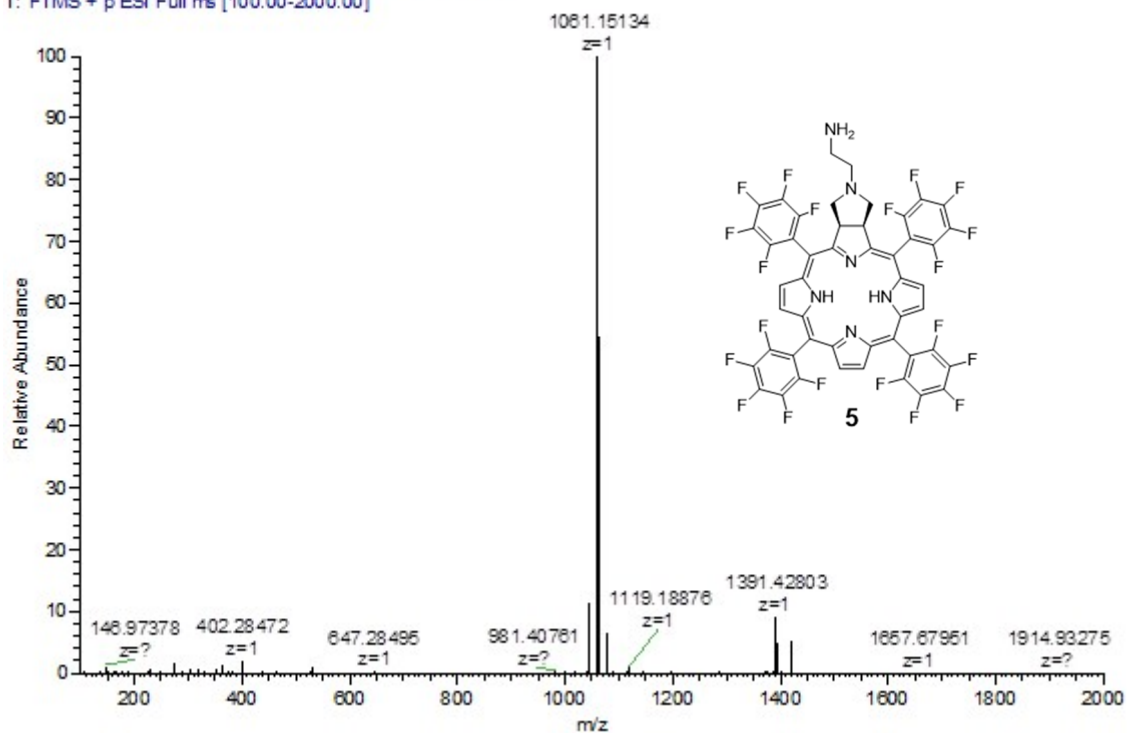


Figure S 41. ESI-MS spectrum of **5**.

JA140 1#1-25 RT: 0.00-1.99 AV: 25 NL: 7.19E6
T: FTMS + p ESI Full ms [150.00-2000.00]

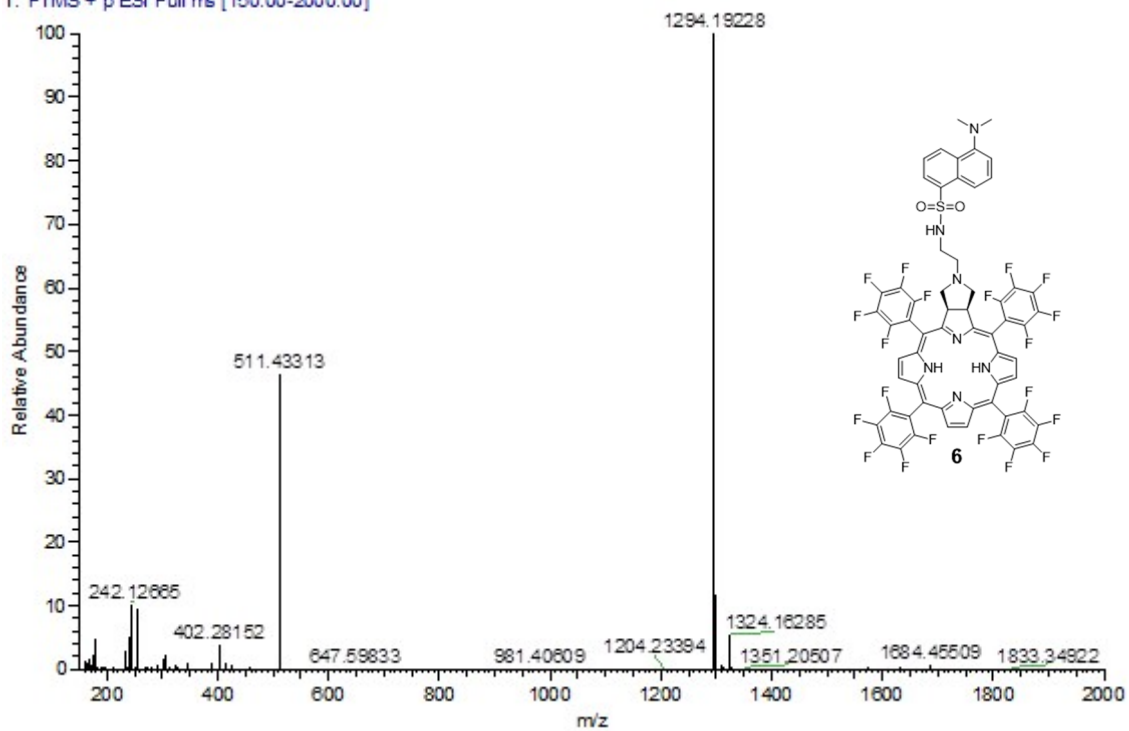


Figure S 42. ESI-MS spectrum of **6**.

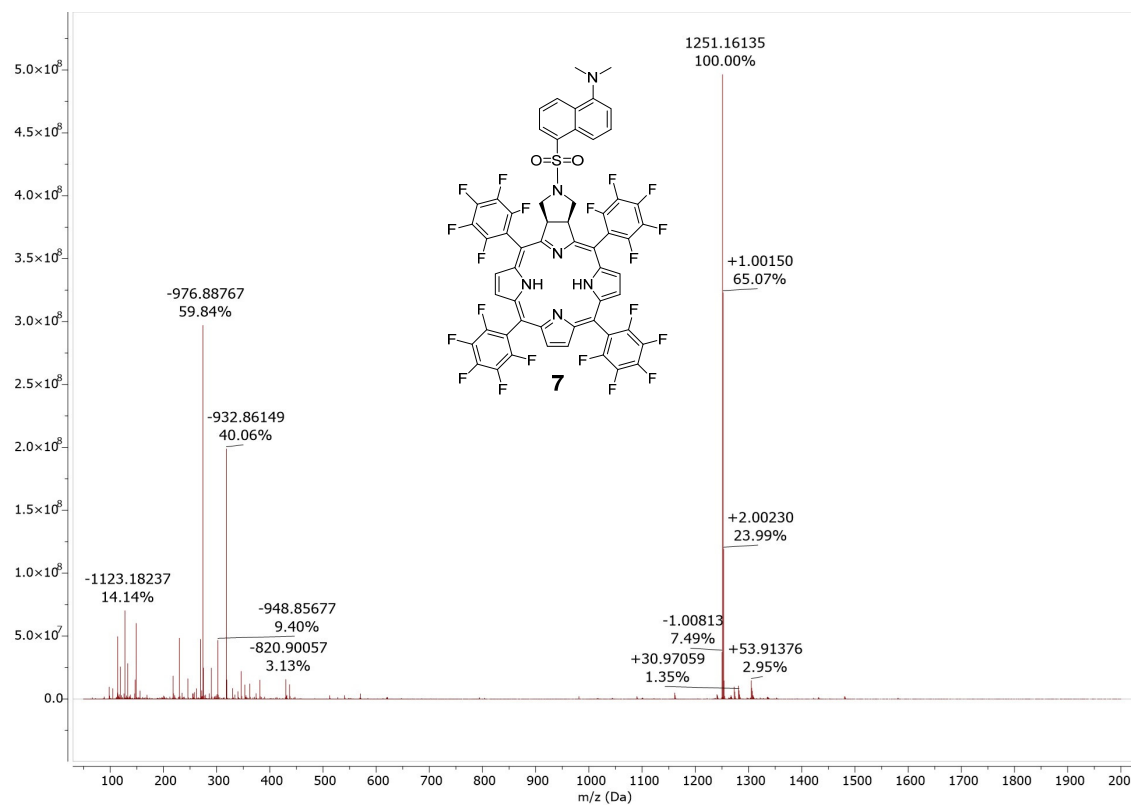


Figure S 43. ESI-MS spectrum of **7**.

UV-Vis and fluorescence spectroscopy

Table S 2. Spectral data for dansyl-ethylamine **dansylNH(CH₂)₂NH₂**, chlorin ethylamine **5** and chlorin–dansyl conjugates **6** and **7** in DMF

	Absorption			Emission
	ϵ at λ_{max} ($\times 10^3$ / $\text{M}^{-1} \cdot \text{cm}^{-1}$)			$\lambda_{\text{max, nm}}$ (ϕ_F)
	338 nm	405 nm	650 nm	
dansylNH(CH₂)₂NH₂	7.64	-	-	512 (n.d.)
5	19.1	153	43	655 (0.147)
6	20.3	144	37	655 (0.188)
7	18.2	130	34	655 (0.123)

n.d. = not determined

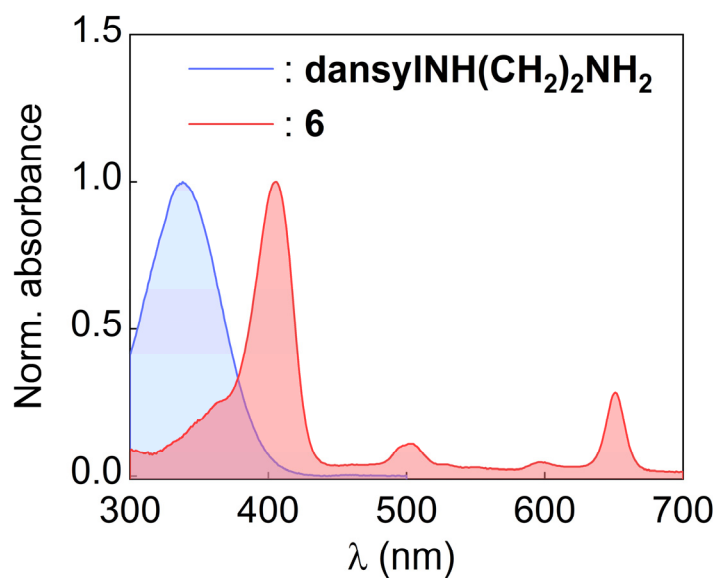


Figure S 44. Absorption spectrum of ethylamine functionalized dansyl (**dansylNH(CH₂)₂NH₂**) and chlorin–dansyl dyad **6**, in DMF.

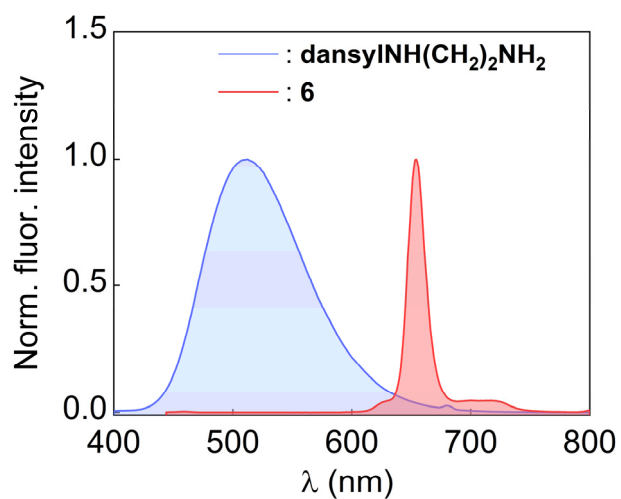


Figure S 45. Emission spectrum of ethylamine functionalized dansyl (**dansylNH(CH₂)₂NH₂**) and chlorin–dansyl dyad **6**, in DMF.

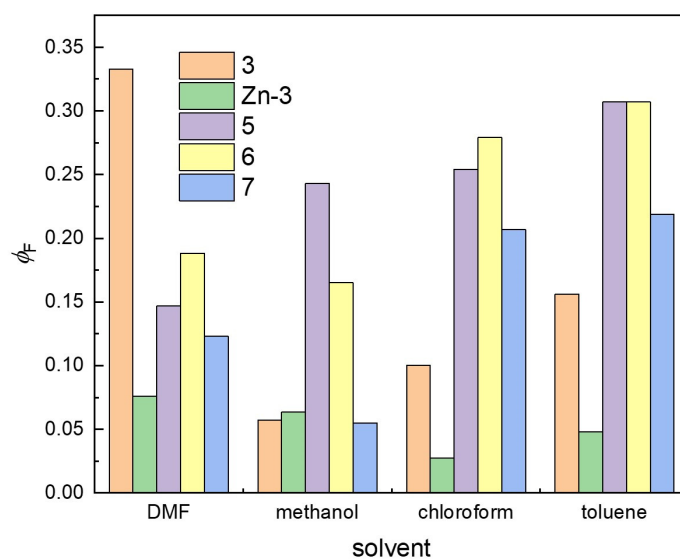


Figure S 46. Fluorescence quantum yield values for chlorins **3**, **Zn-3**, **5**, and chlorin–dyads **6** and **7** in DMF, methanol, chloroform, and toluene.