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Supporting information for

Synthesis and coordination studies of 5-(4′-carboxyphenyl)-10,15,20-tris(pentafluorophenyl)porphyrin and its pyrrolidine-fused chlorin derivative

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Contents

NMR spectra of porphyrin 1a

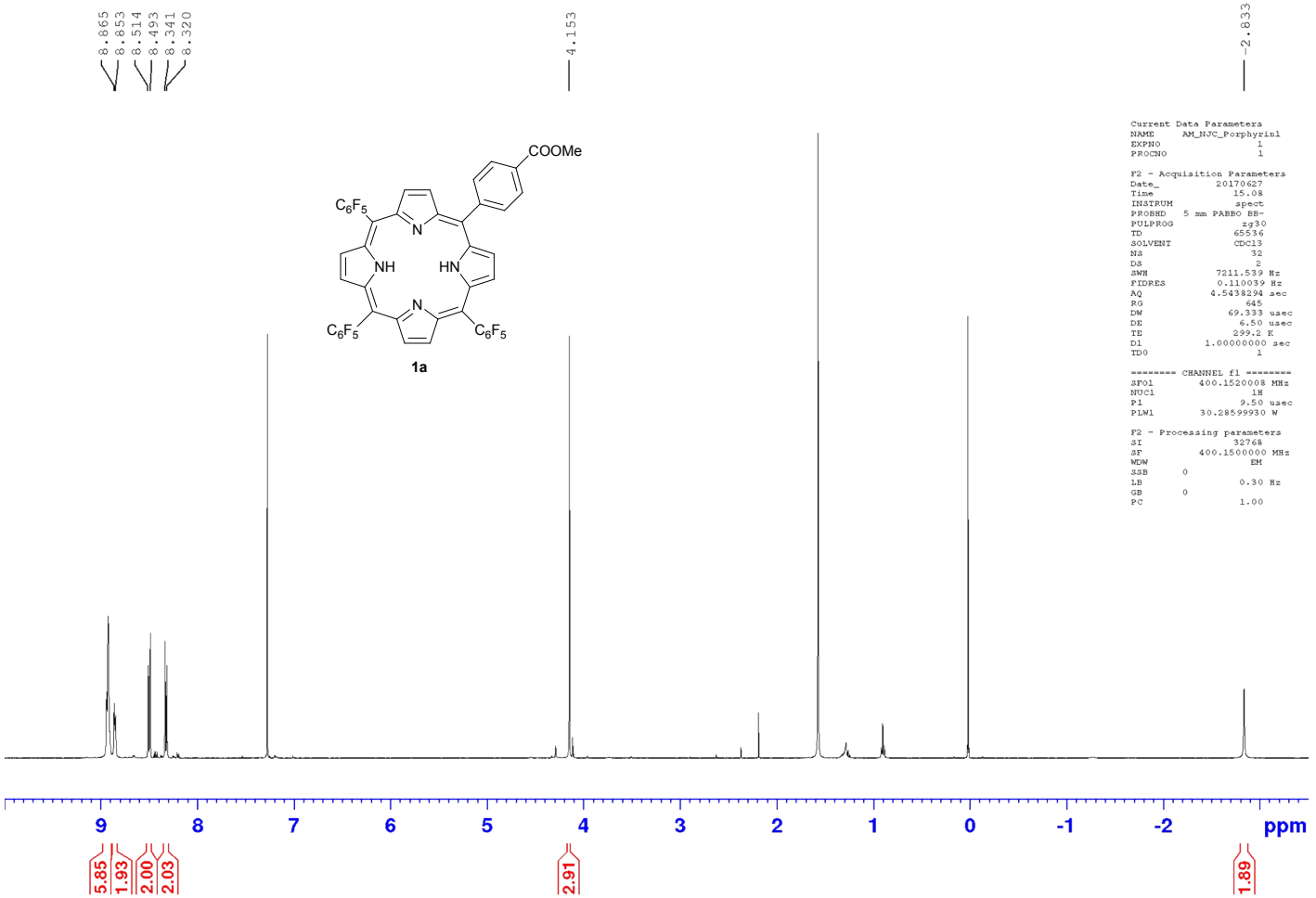

Figure S1. ^{1}H NMR spectrum of porphyrin **1a** ($CDCl_3$, 400.15 MHz).

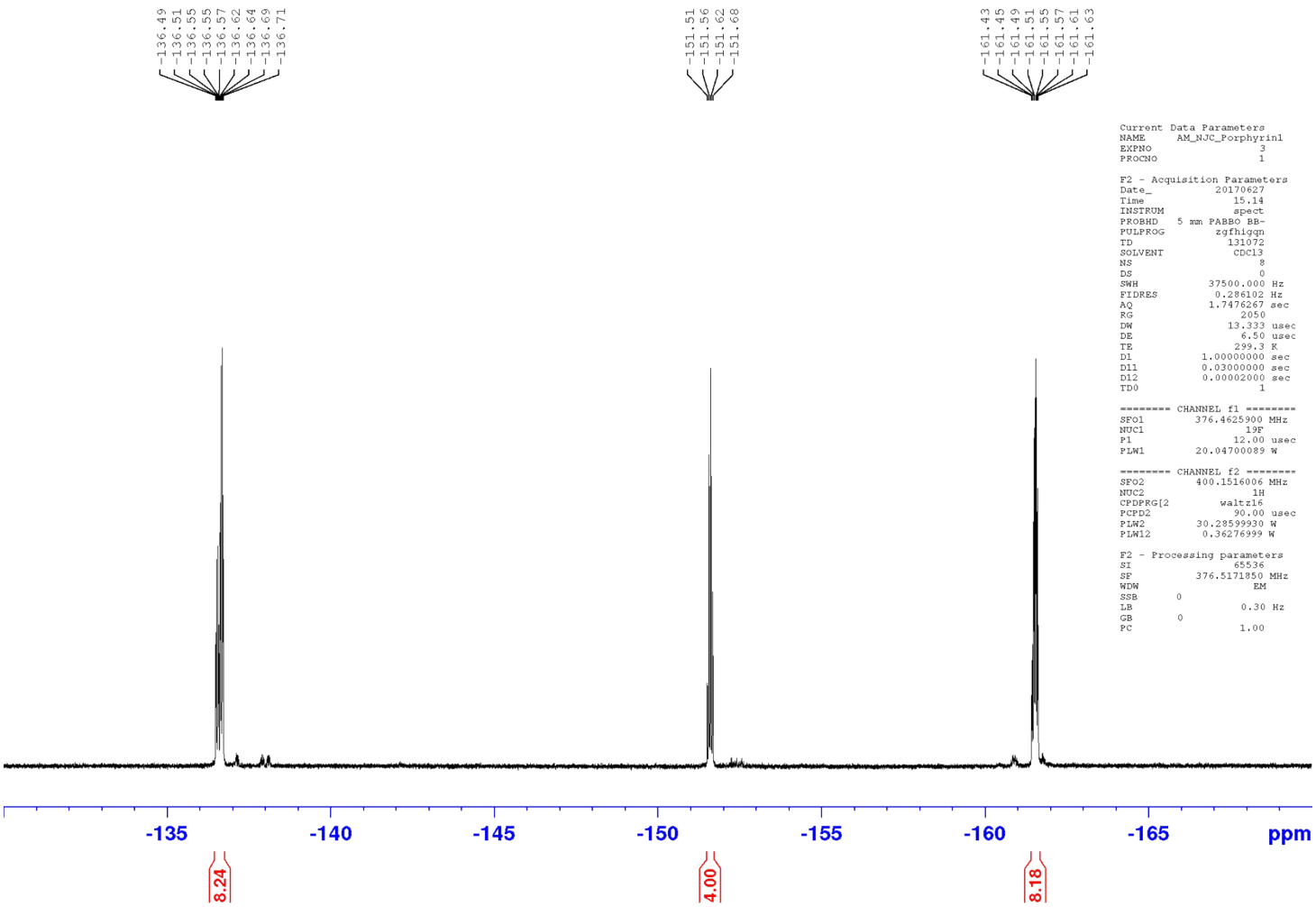

Figure S2. ^{19}F NMR spectrum of porphyrin **1a** ($CDCl_3$, 376.46 MHz).

NMR spectra of chlorins 2a,b

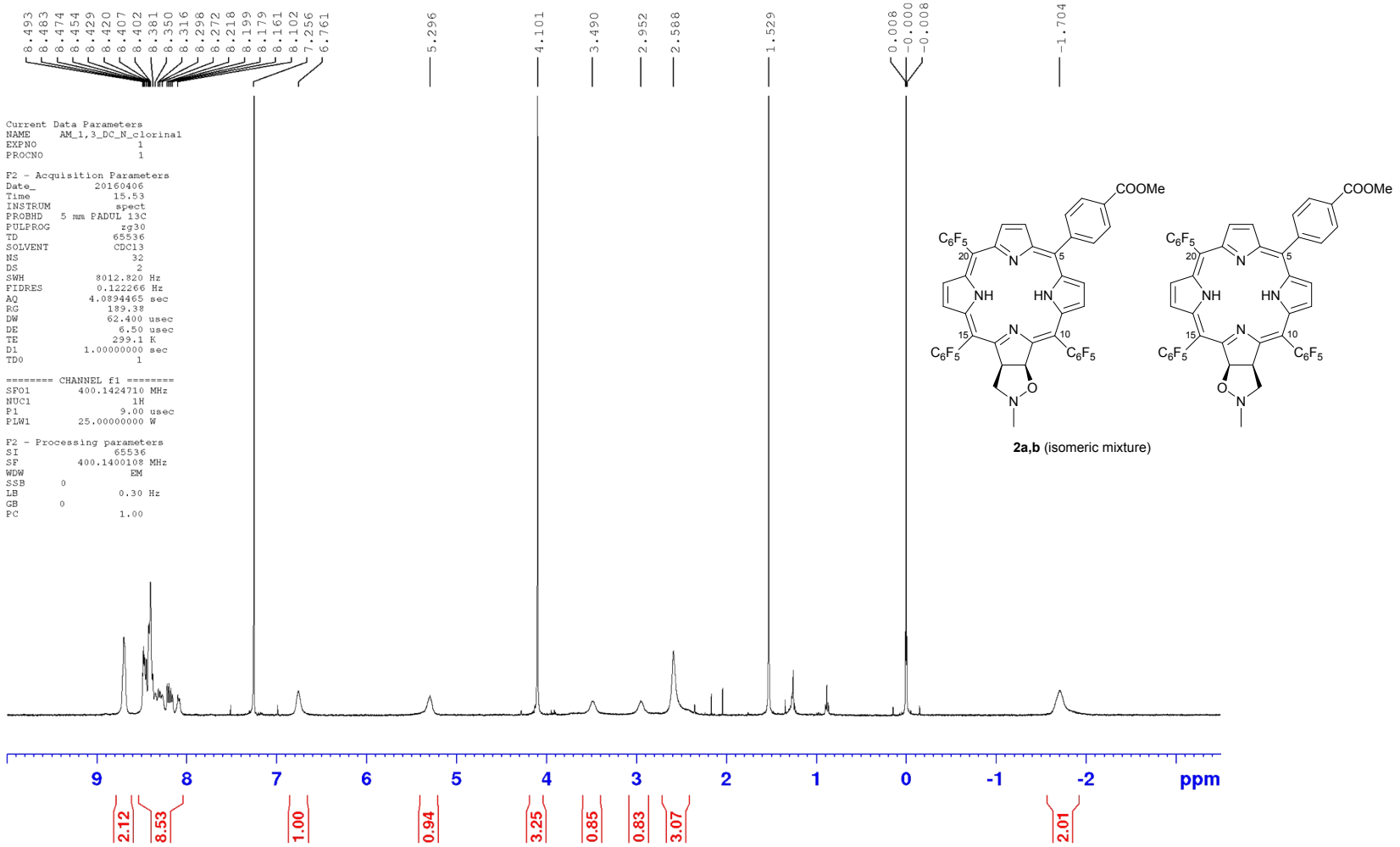

Figure S3. ^{1}H NMR spectrum of chlorins **2a,b** ($CDCl_3$, 400.15 MHz).

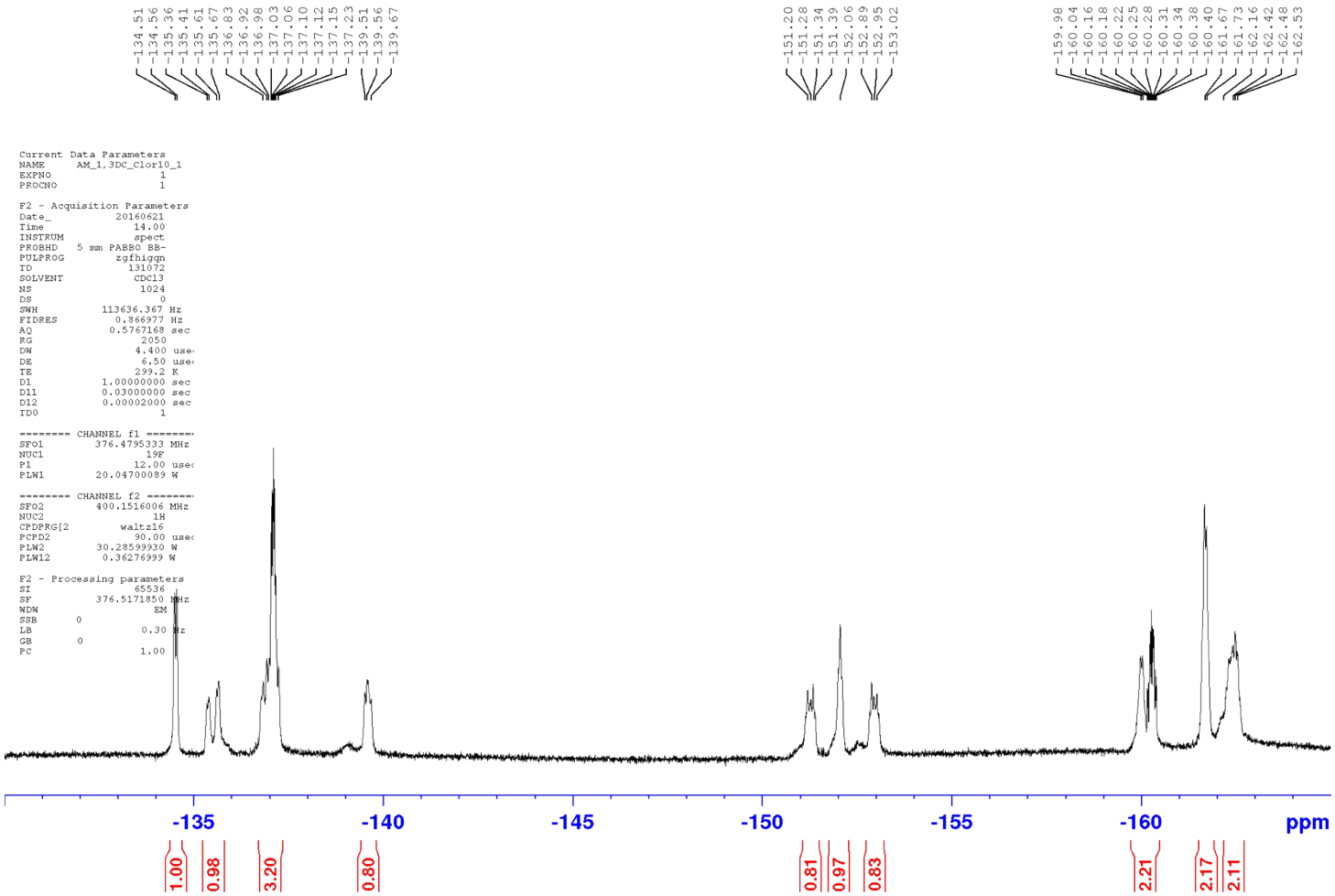

Figure S4. ^{19}F NMR spectrum of chlorins **2a,b** ($CDCl_3$, 376.46 MHz).

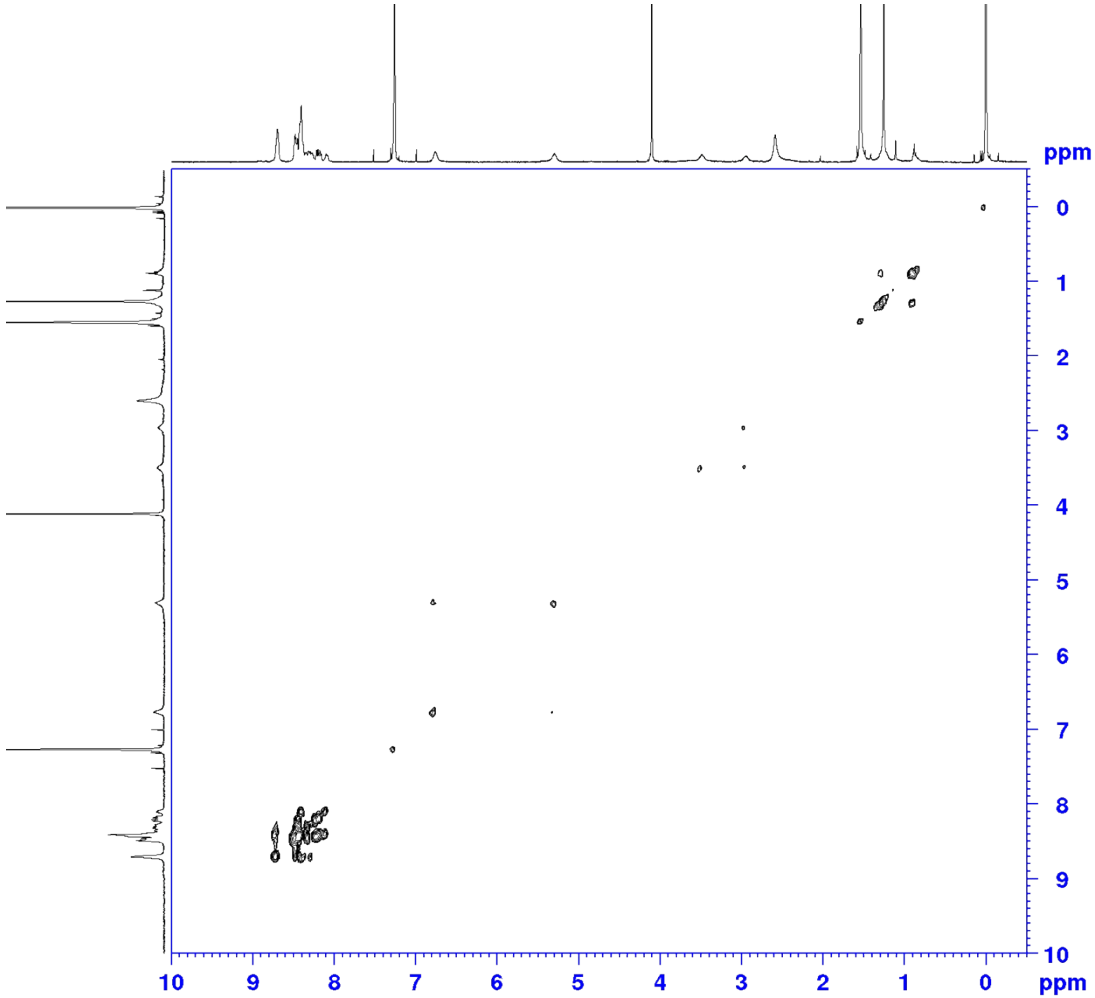


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Figure S5. COSY spectrum of chlorins **2a,b**.

NMR spectra of chlorin 2c

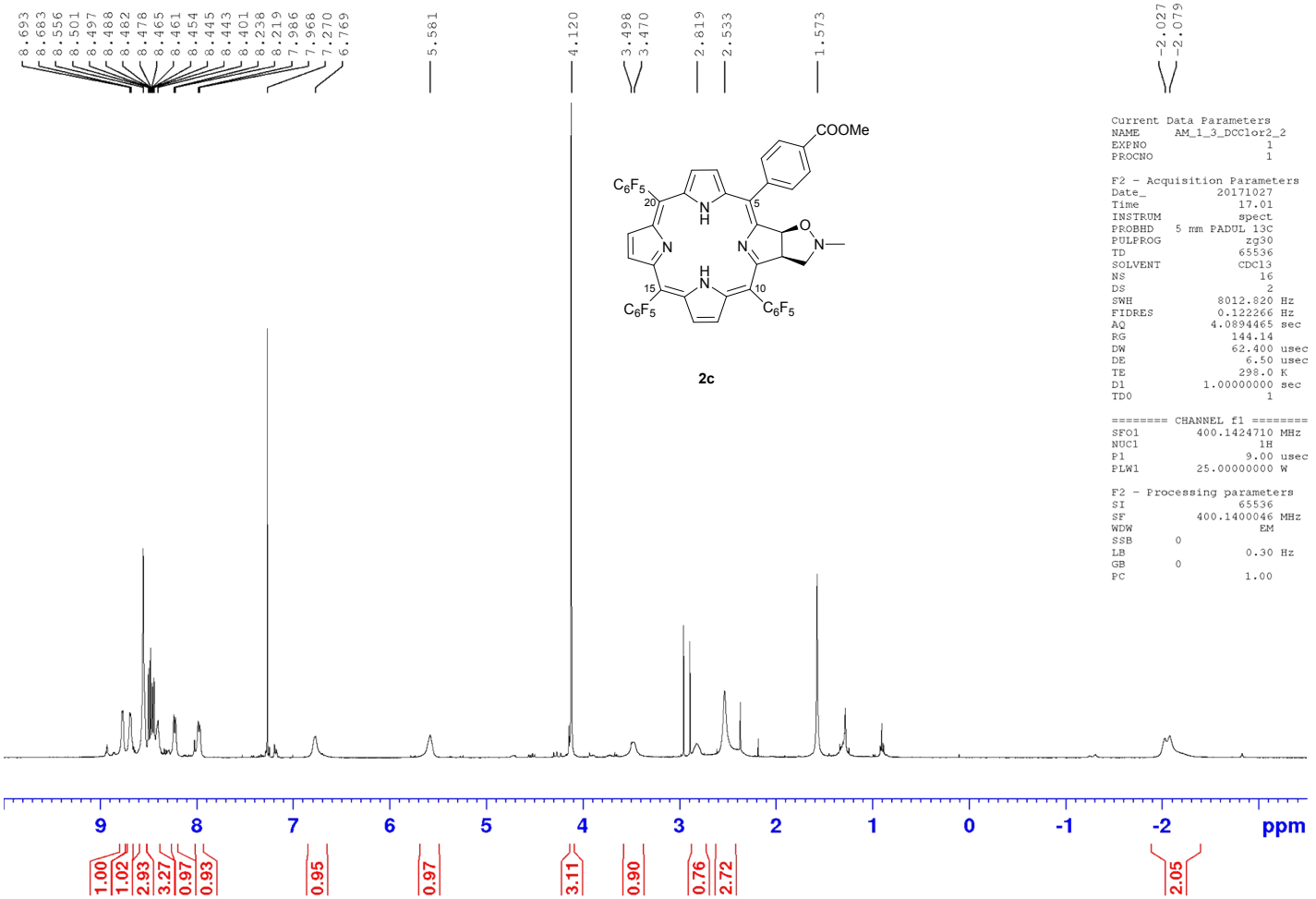

Figure S6. ^{1}H NMR spectrum of chlorin **2c** ($CDCl_3$, 400.15 MHz).

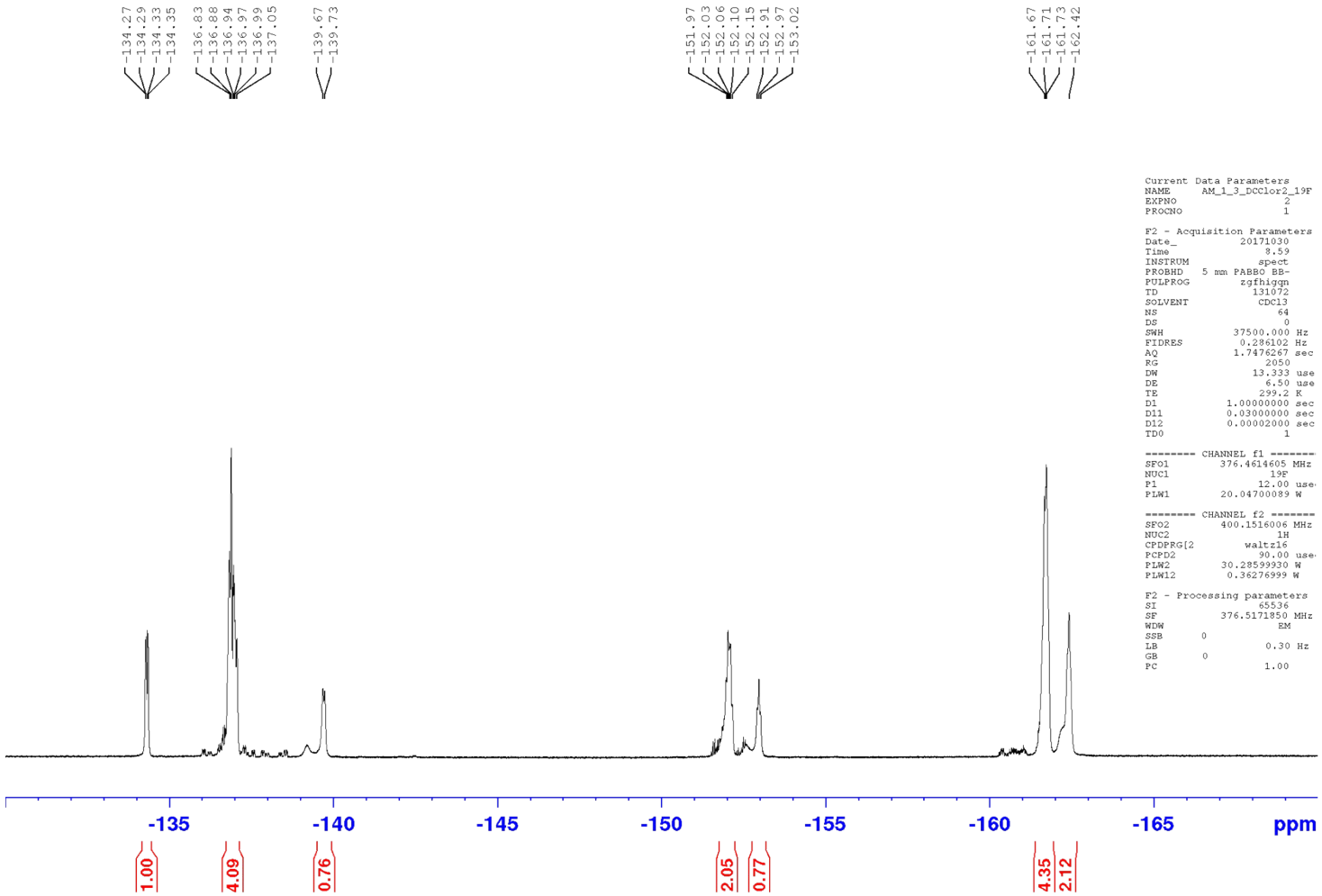

Figure S7. ^{19}F NMR spectrum of chlorin **2c** $CDCl_3$, 376.46 MHz).

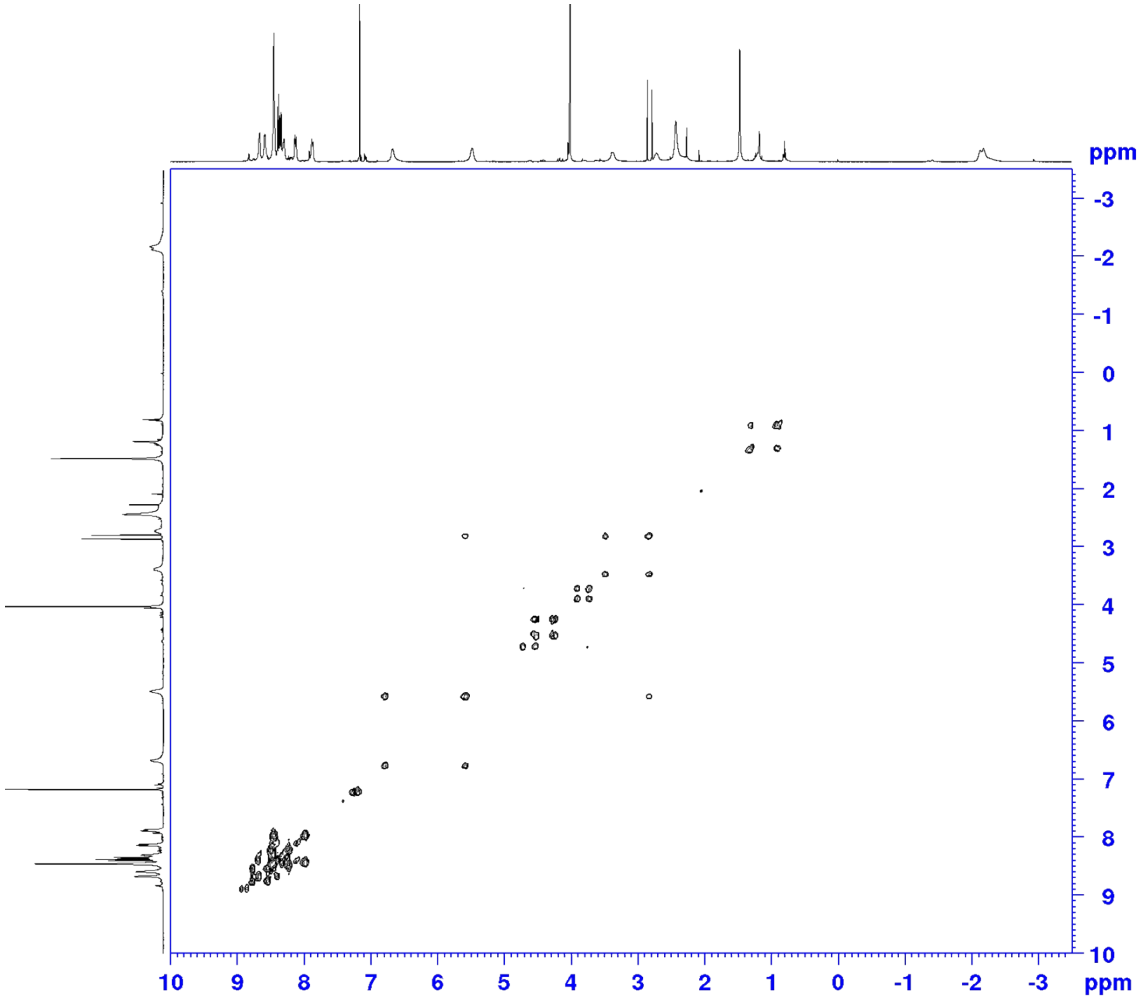


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Figure S8. COSY spectrum of chlorin **2c**

NMR spectra of chlorin 2d

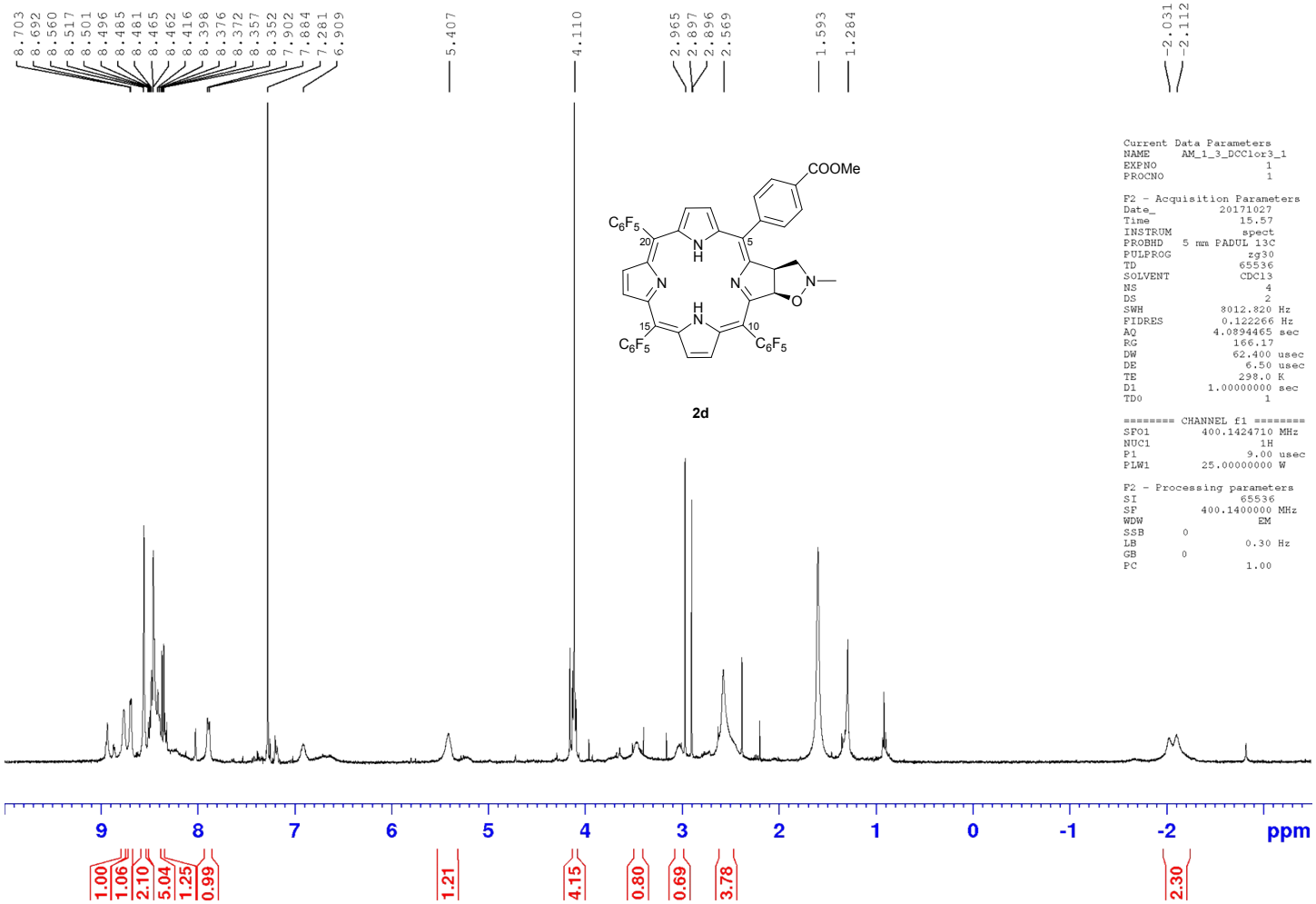


Figure S9. ^{1}H NMR spectrum of chlorin **2d** ($CDCl_3$, 400.15 MHz).

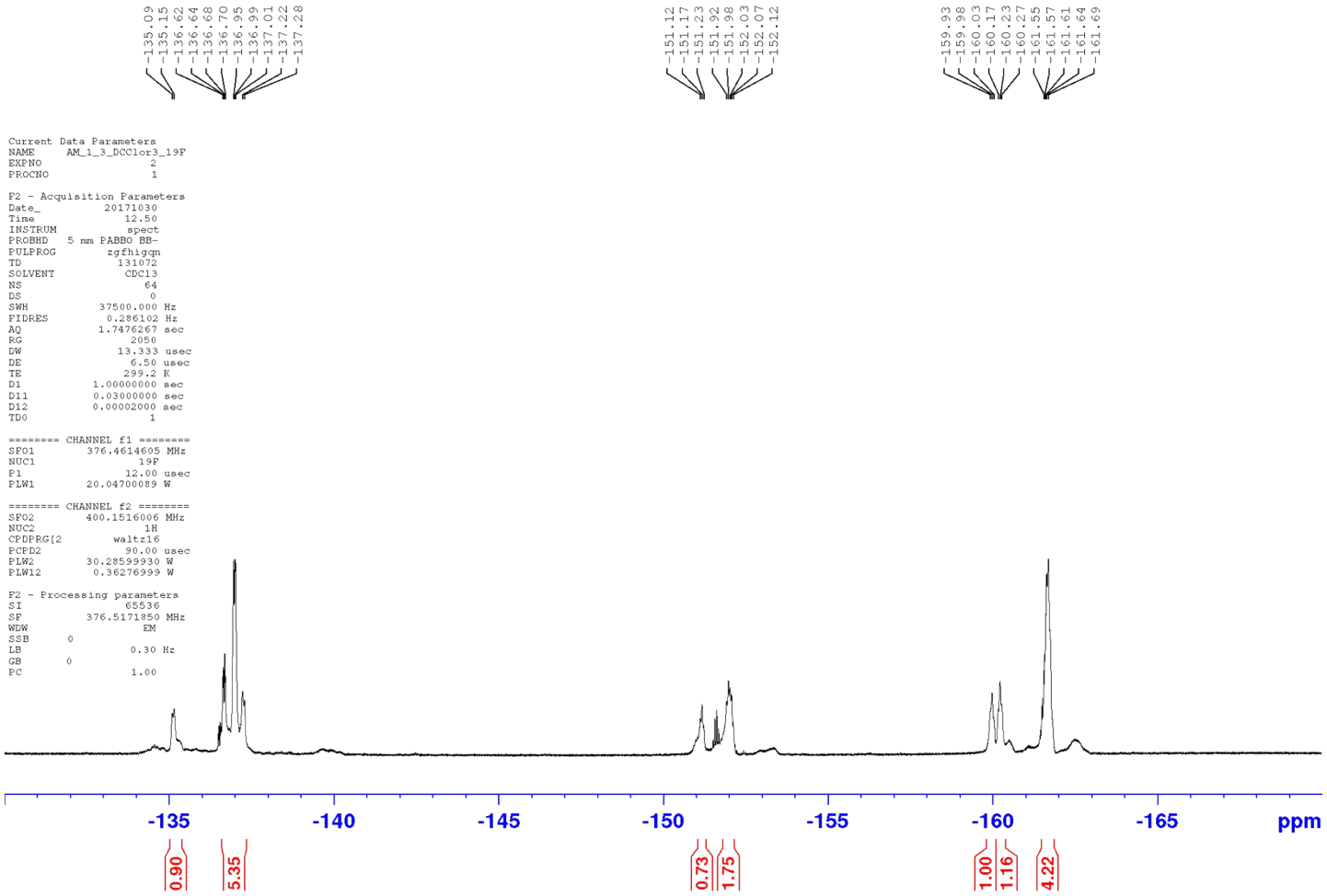
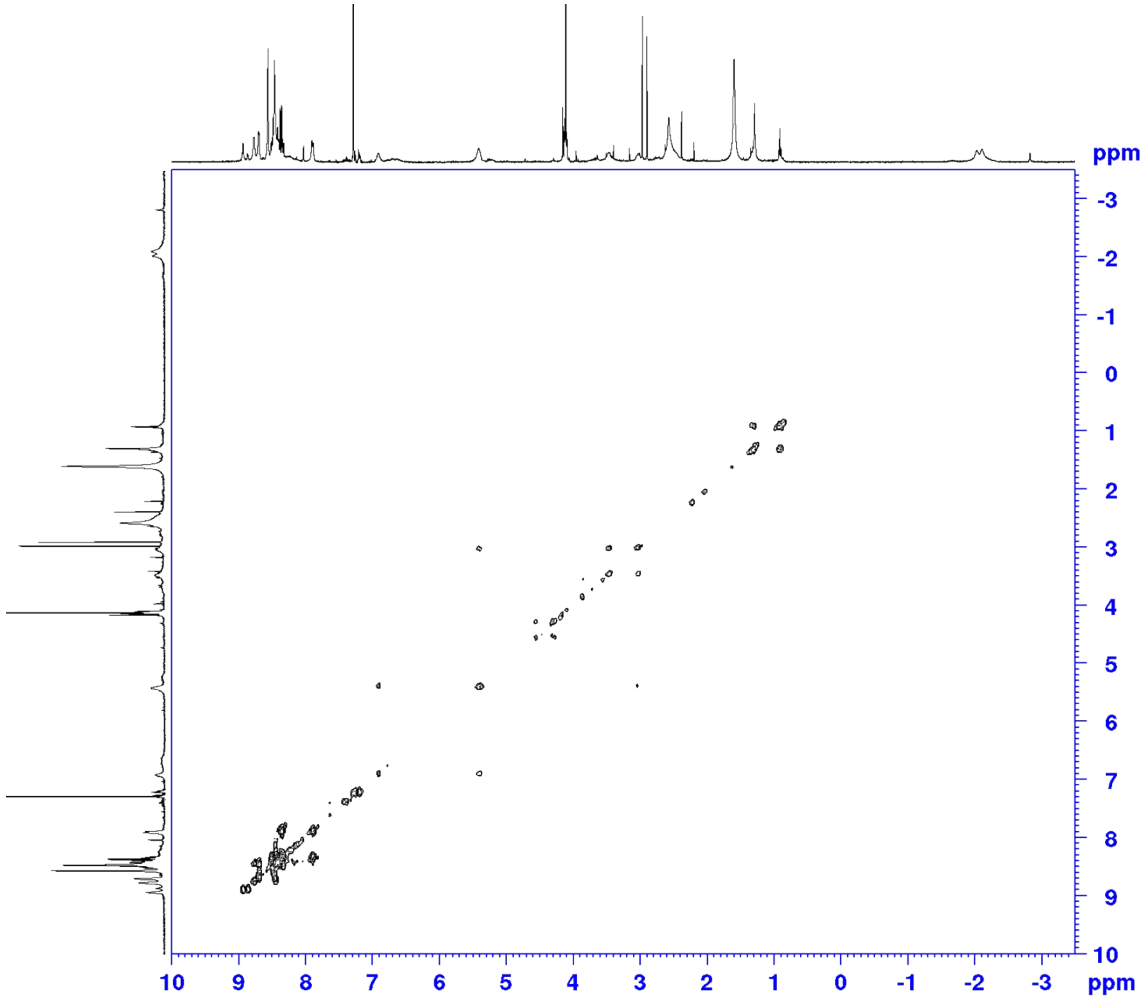


Figure S10. ^{19}F NMR spectrum of chlorin **2d** ($CDCl_3$, 376.46 MHz).

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TD               2048
SOLVENT          CDCl3
NS                  8
DS                  8
SWH           8012.820 Hz
FIDRES        3.912510 Hz
AQ            0.1277952 sec
RG              212.73
DW               62.400 usec
DE                6.50 usec
TE              298.0 K
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D1           1.50000000 sec
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D16          0.00020000 sec
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F1 - Processing parameters
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MC2                QF
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Figure S11. COSY spectrum of chlorin **2d**.

NMR spectra of chlorin 3a

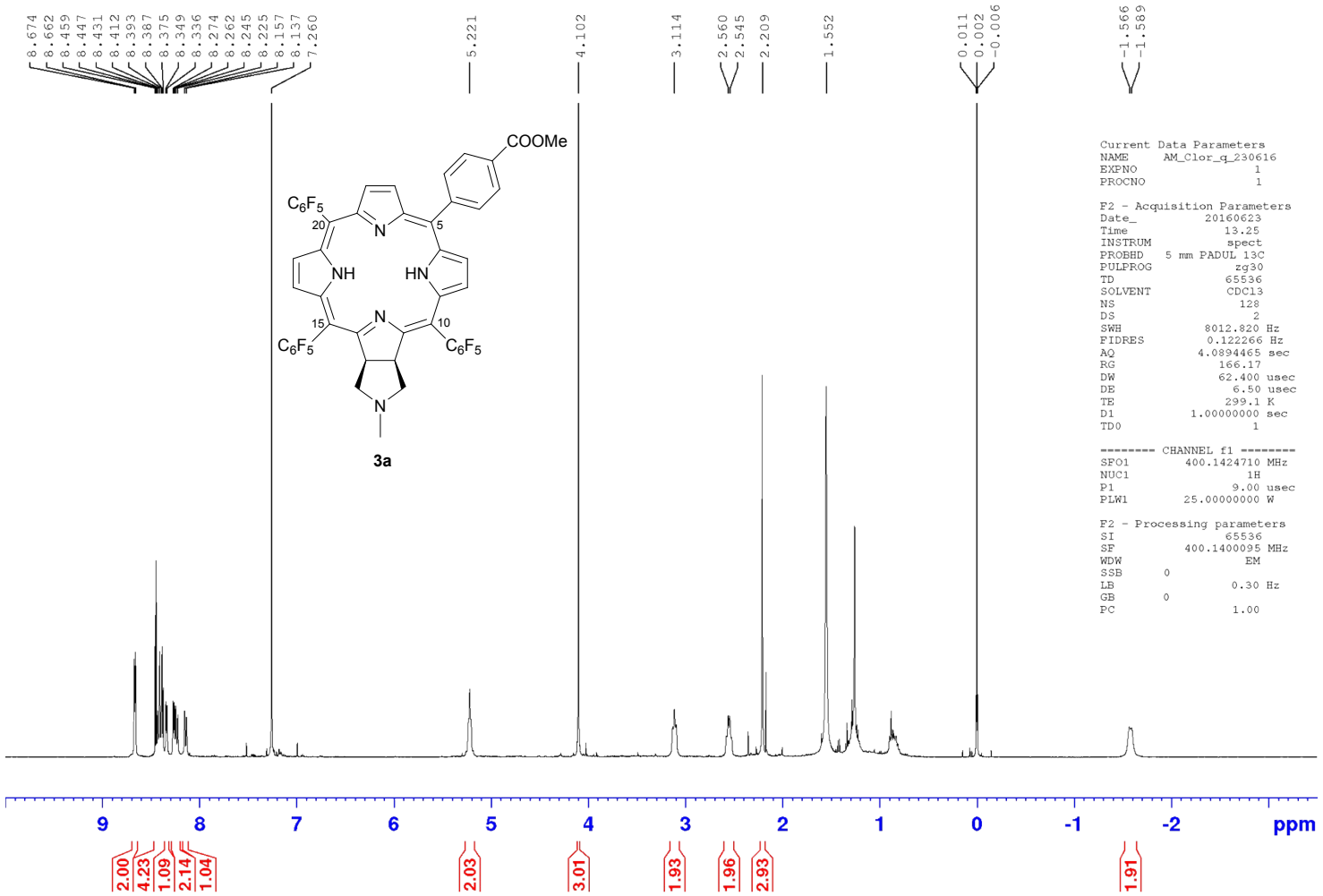


Figure S12. ^{1}H NMR spectrum of chlorin **3a** ($CDCl_3$, 400.15 MHz).

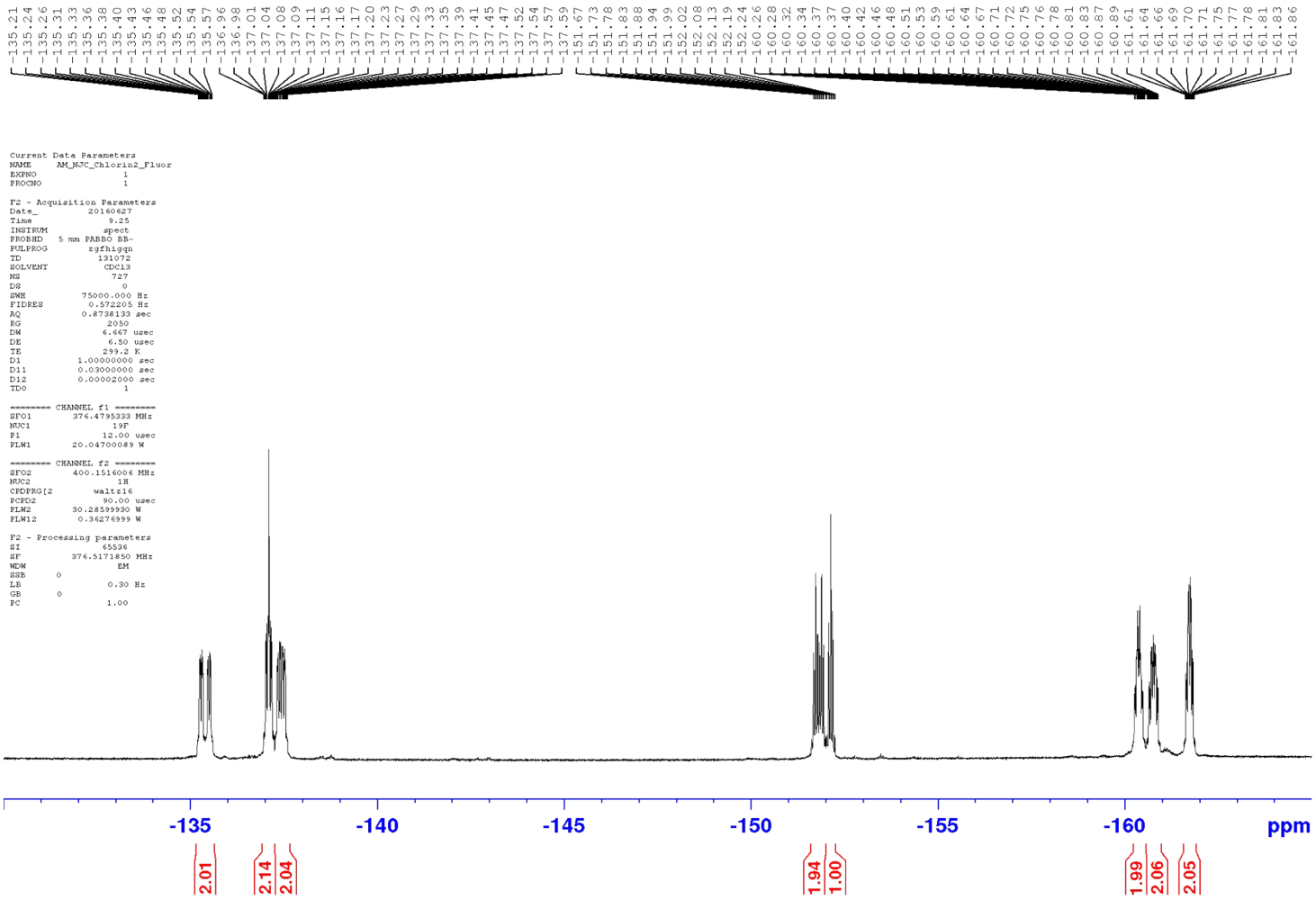
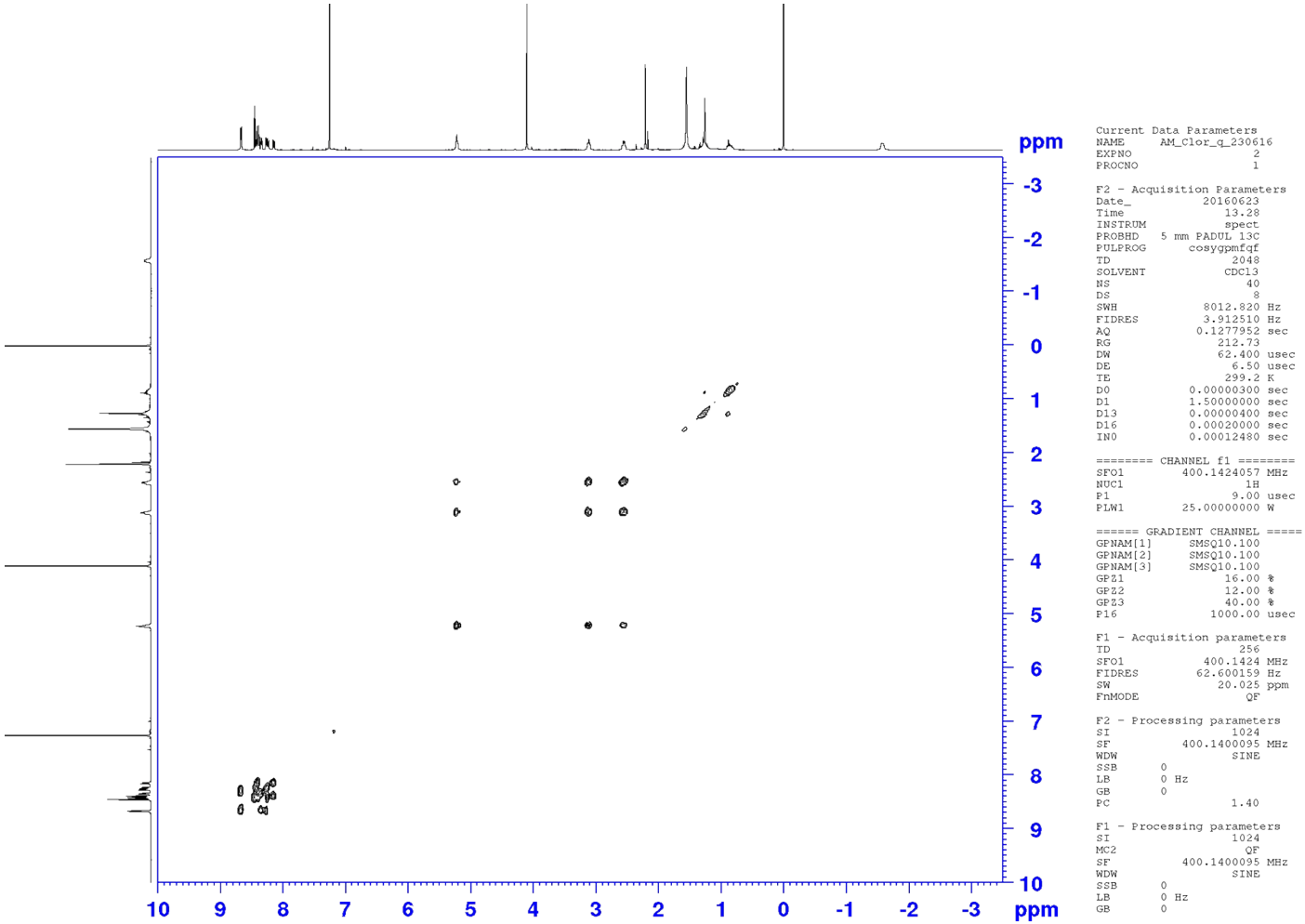


Figure S13. ^{19}F NMR spectrum of chlorin **3a** ($CDCl_3$, 376.46 MHz).

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RG              212.73
DW              62.400 usec
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TE              299.2 K
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SW              20.025 ppm
FnMODE             QF

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PC                1.40

F1 - Processing parameters
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MC2                QF
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Figure S14. COSY spectrum of chlorin **3a**.

NMR spectra of chlorin 3b

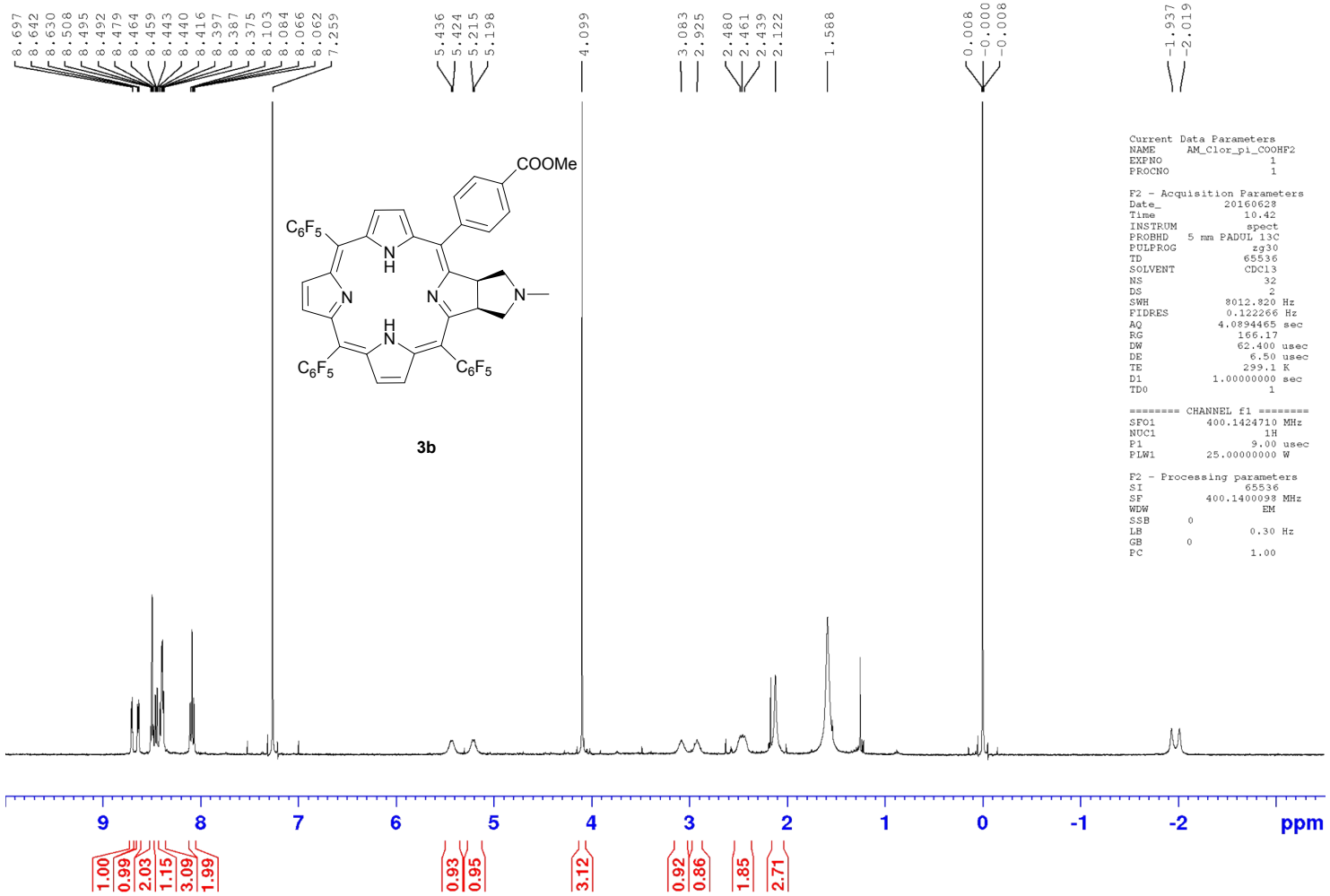


Figure S15. ^{1}H NMR spectrum of chlorin **3b** ($CDCl_3$, 400.15 MHz).

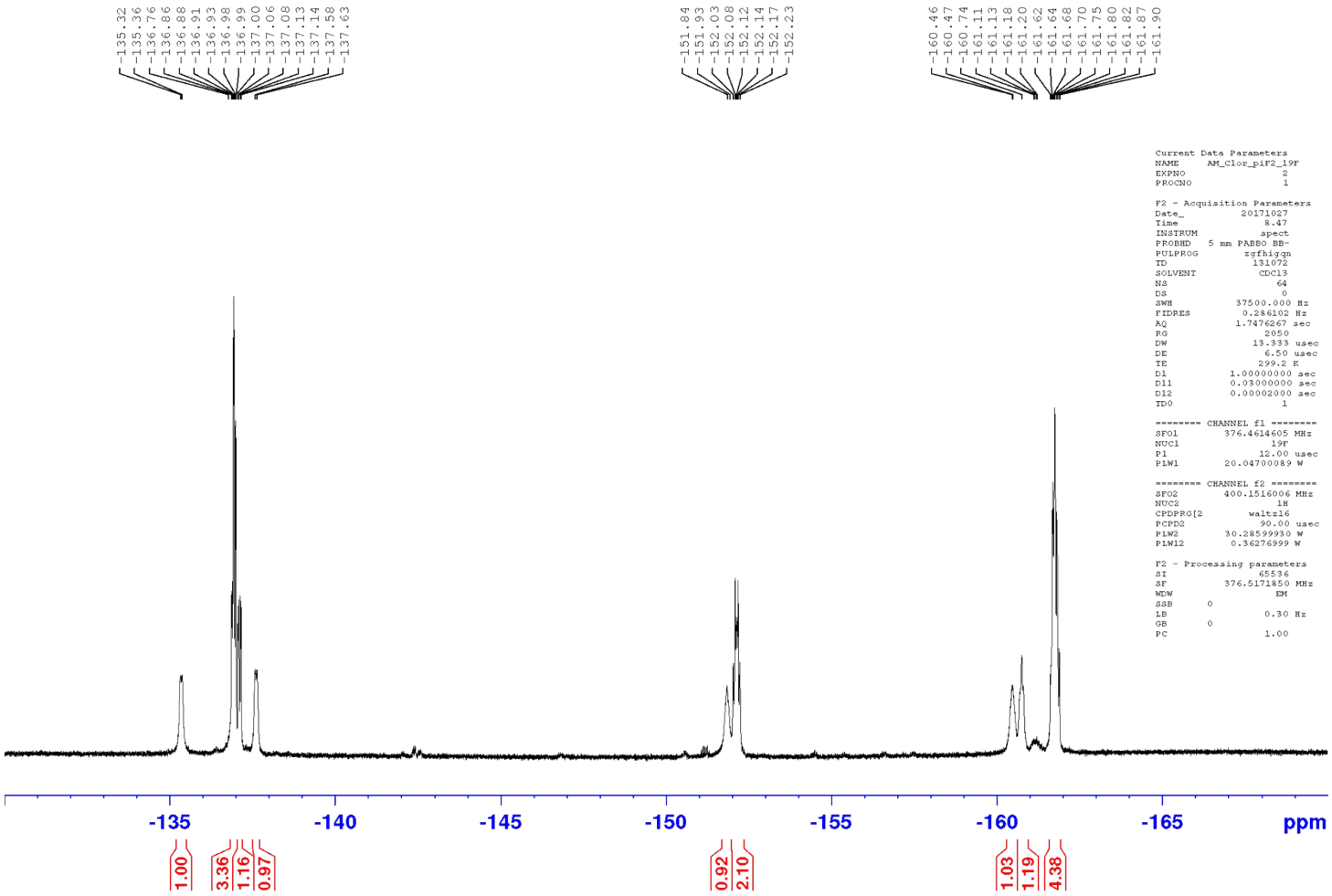
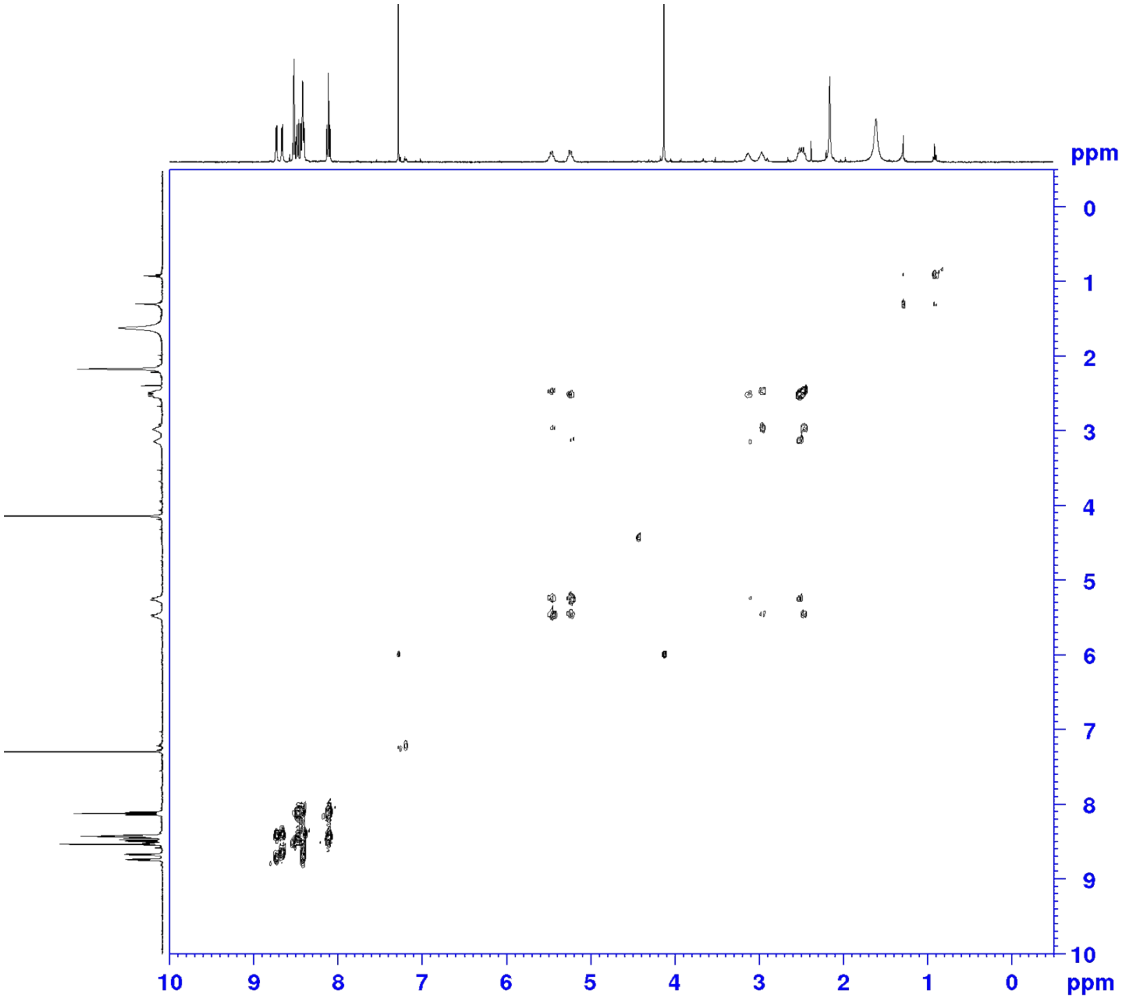


Figure S16. ^{19}F NMR spectrum of chlorin **3b** ($CDCl_3$, 376.46 MHz).

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F1 - Processing parameters
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Figure S17. COSY spectrum of chlorin **3b**.

NMR spectra of iBC 4a

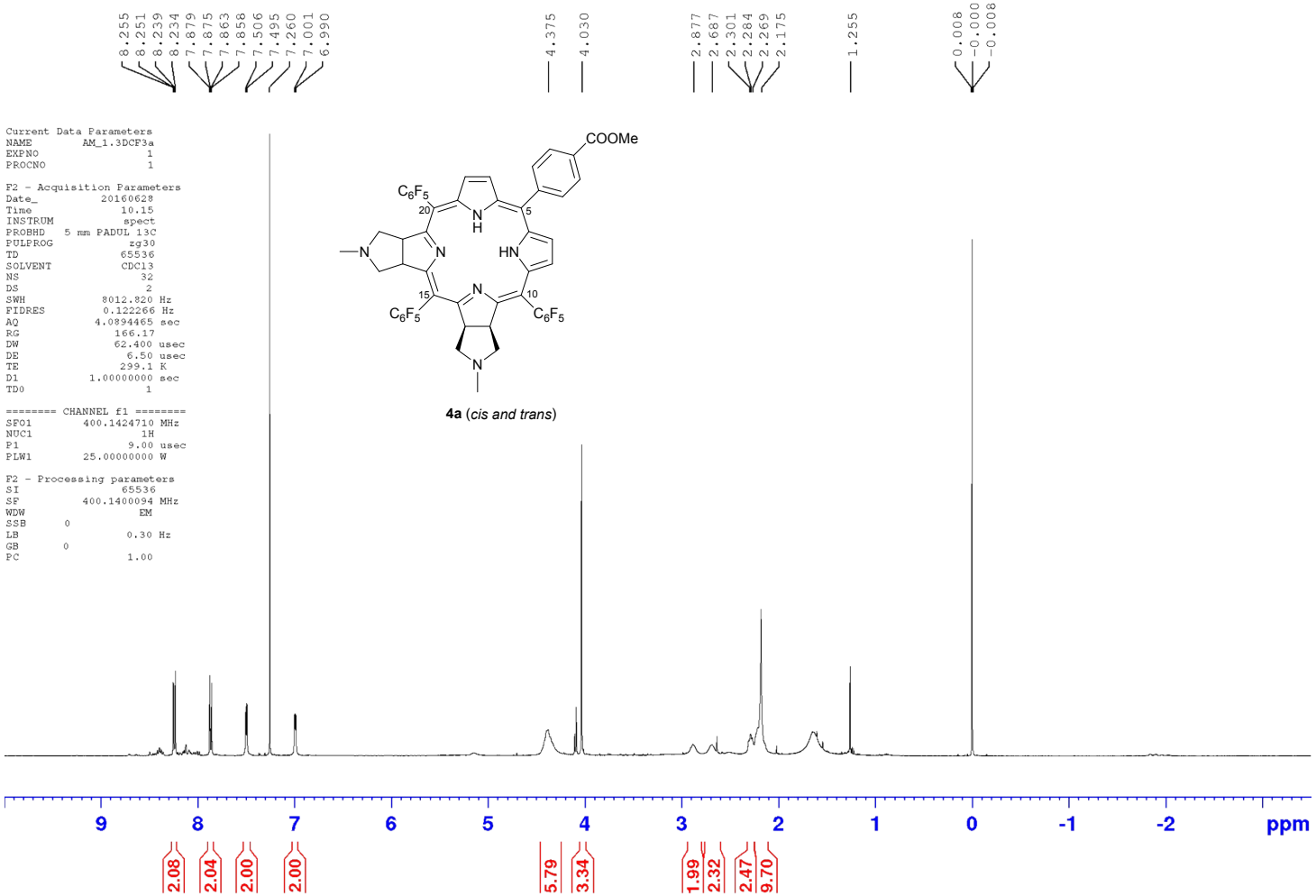


Figure S18. ^{1}H NMR spectra of iBC **4a** ($CDCl_3$, 400.15 MHz).

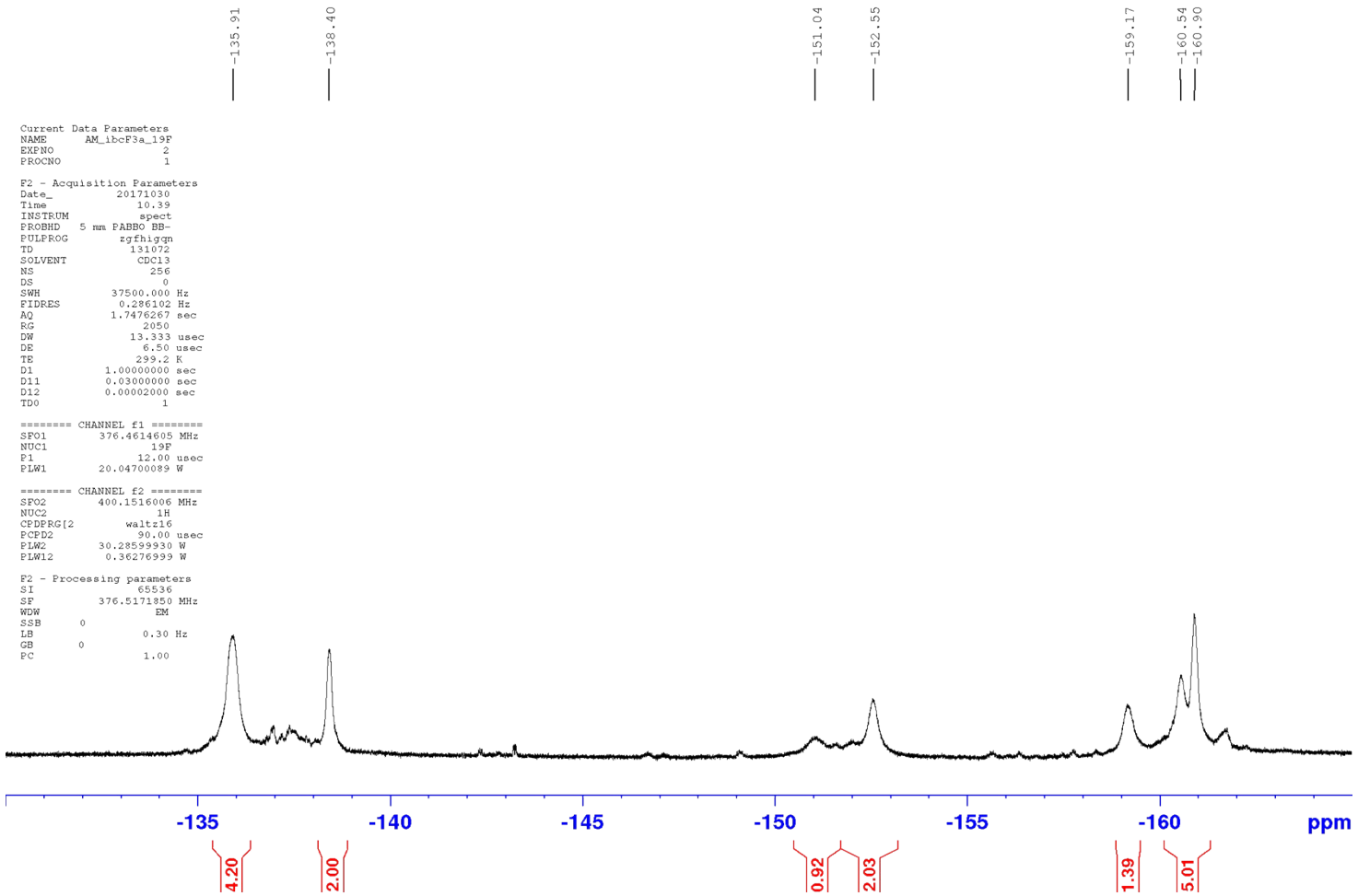
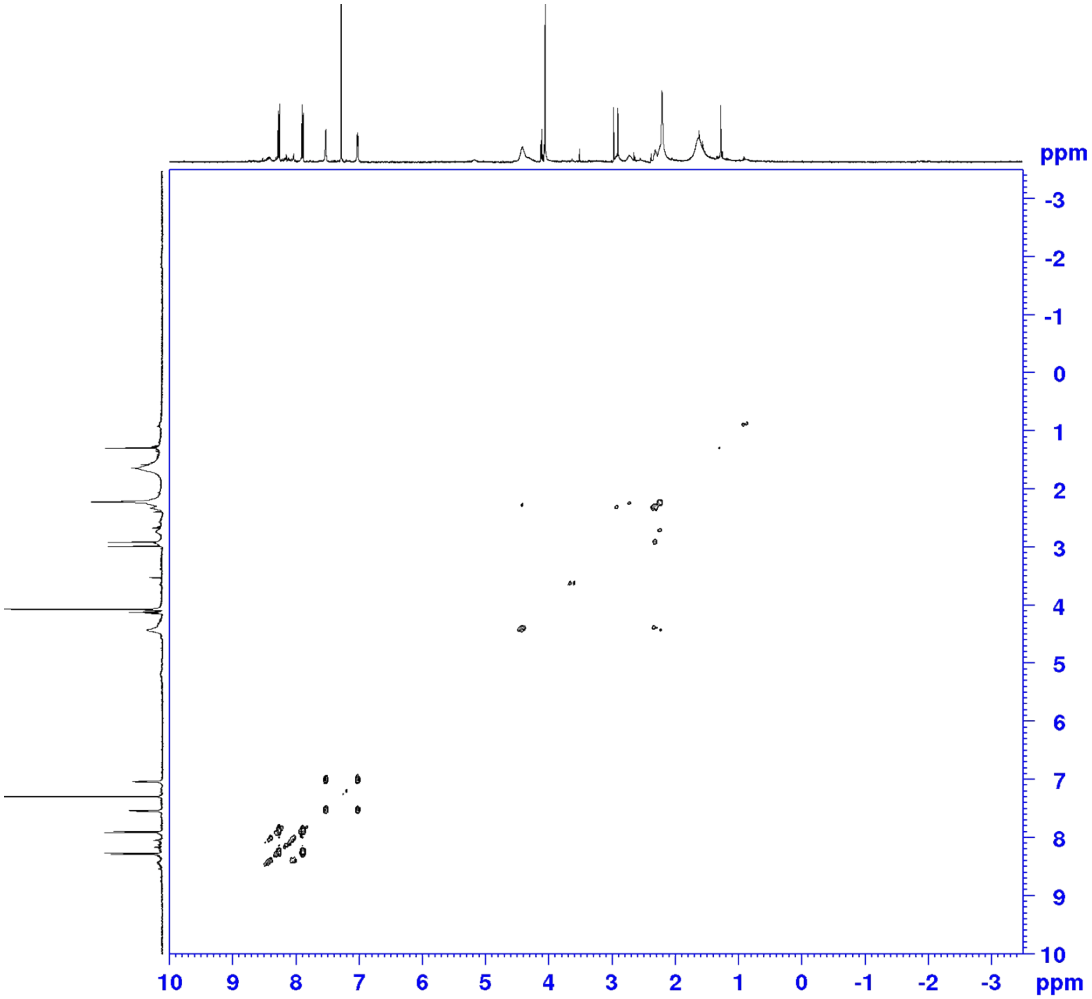


Figure S19. ^{19}F NMR spectrum of iBC **4a** ($CDCl_3$, 376.46 MHz).

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RG                212.73
DW                62.400 usec
DE                 6.50 usec
TE                298.0 K
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D13           0.00000400 sec
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GB        0
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F1 - Processing parameters
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Figure S20. COSY spectrum of iBC **4a**.

NMR spectrum of porphyrin 1

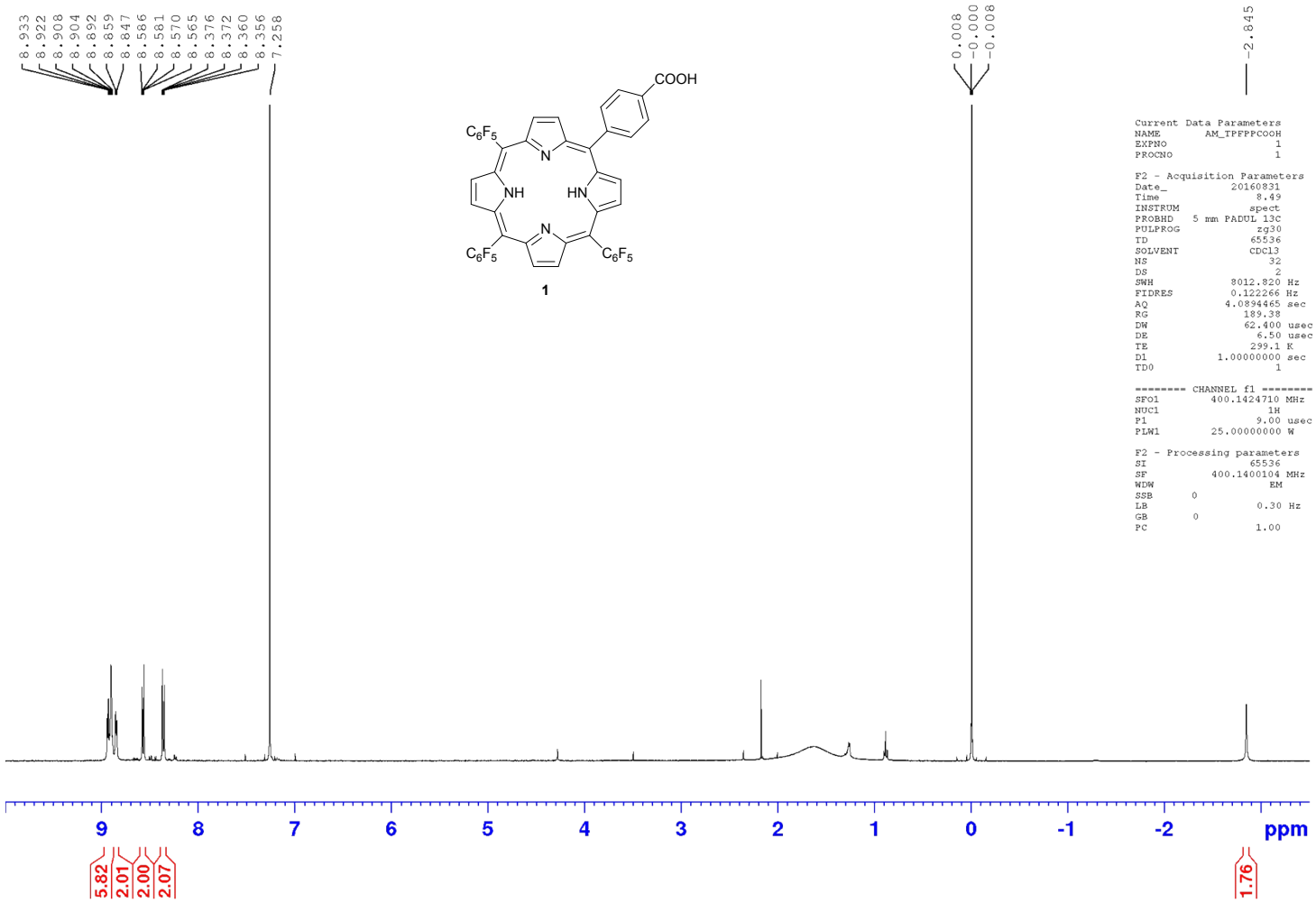


Figure S21. ^{1}H NMR spectrum of porphyrin **1** ($CDCl_3$, 400.15 MHz).

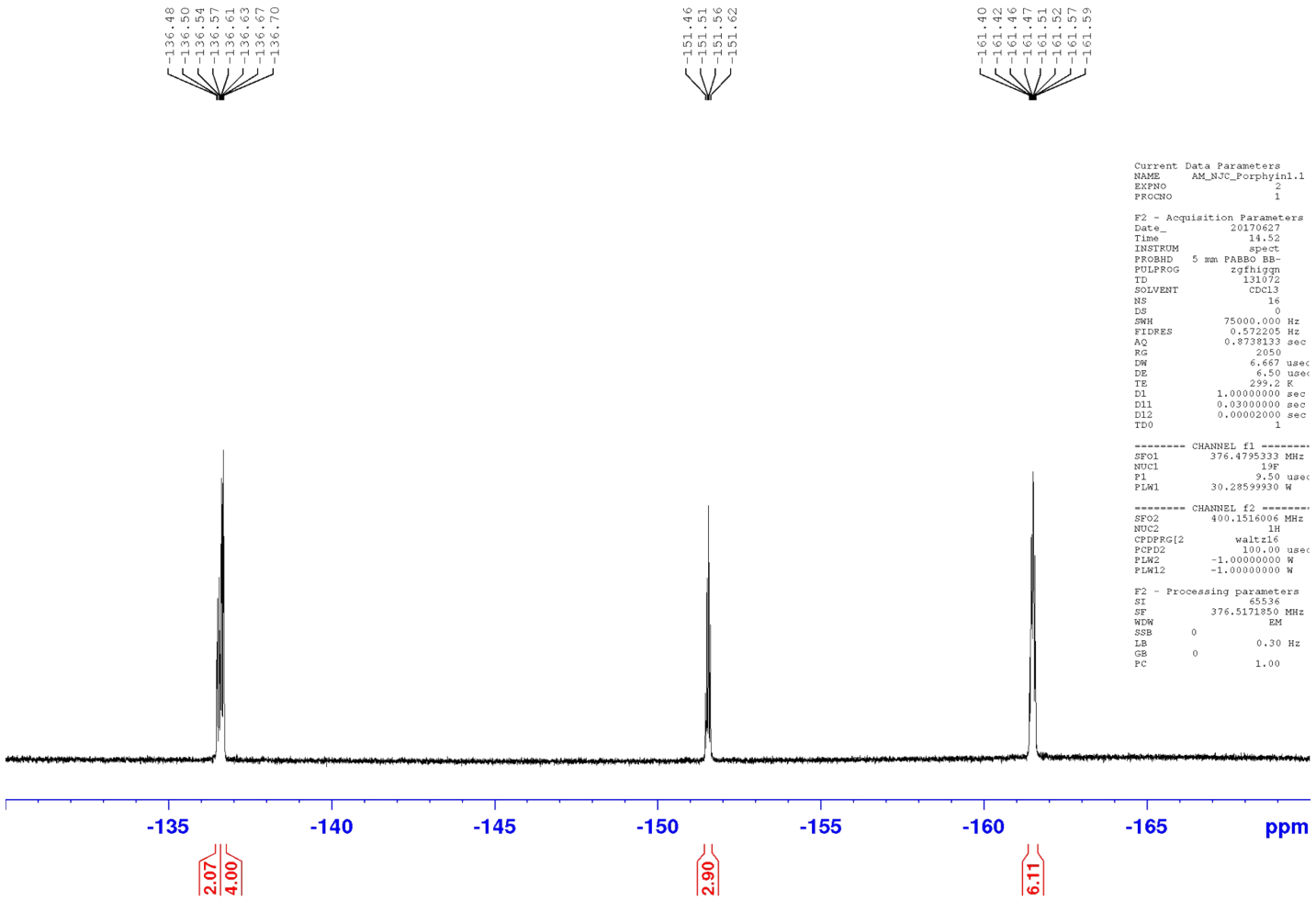


Figure S22. ^{19}F NMR spectrum of porphyrin **1** ($CDCl_3$, 376.46 MHz).

NMR spectra of chlorin 2

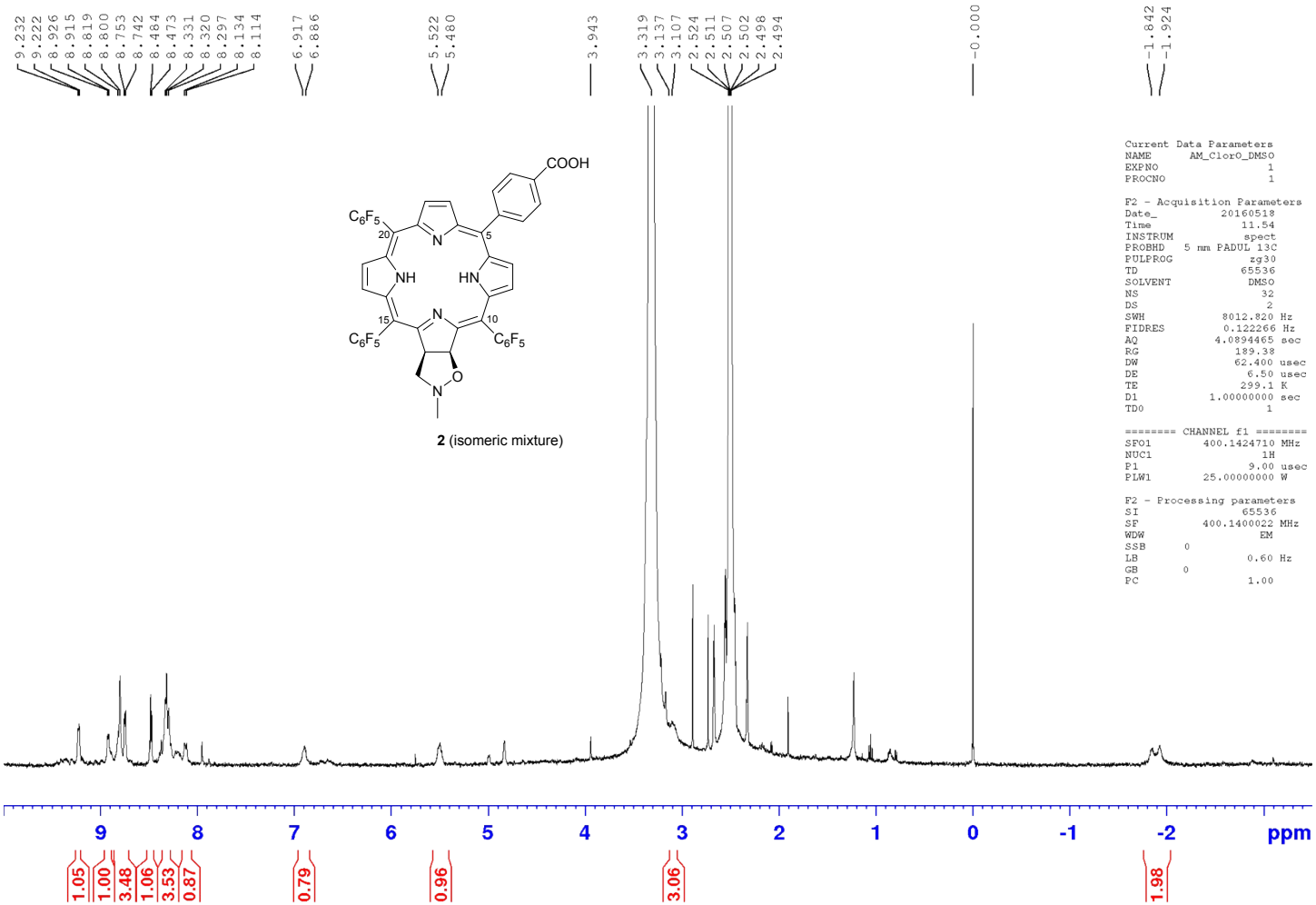


Figure S23. ^{1}H NMR spectrum of chlorin **2** (DMSO-d_6, 400.15 MHz).

NMR spectra of chlorin 3

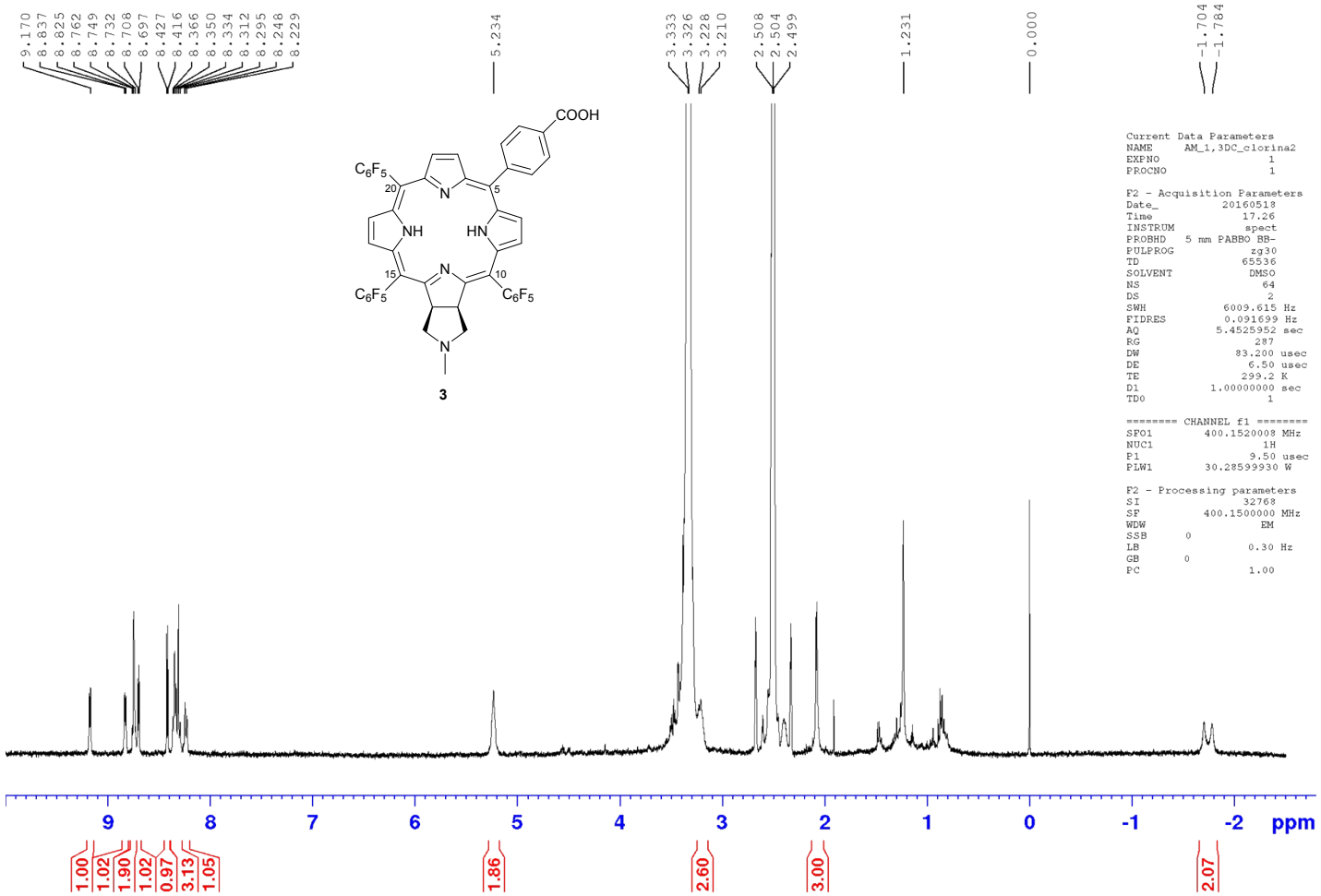


Figure S24. ^{1}H NMR spectrum of chlorin **3** (DMSO-d_6, 400.15 MHz).

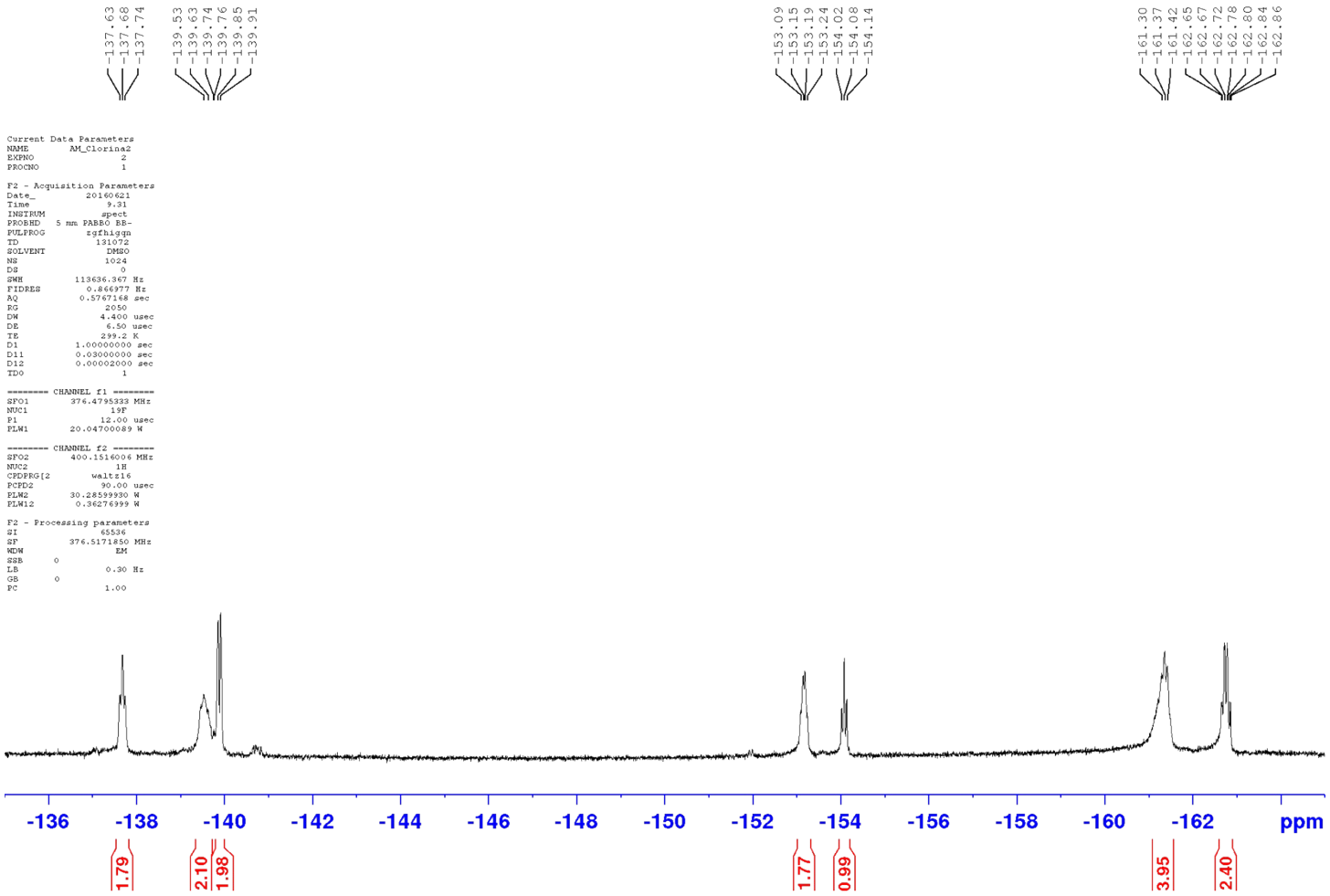
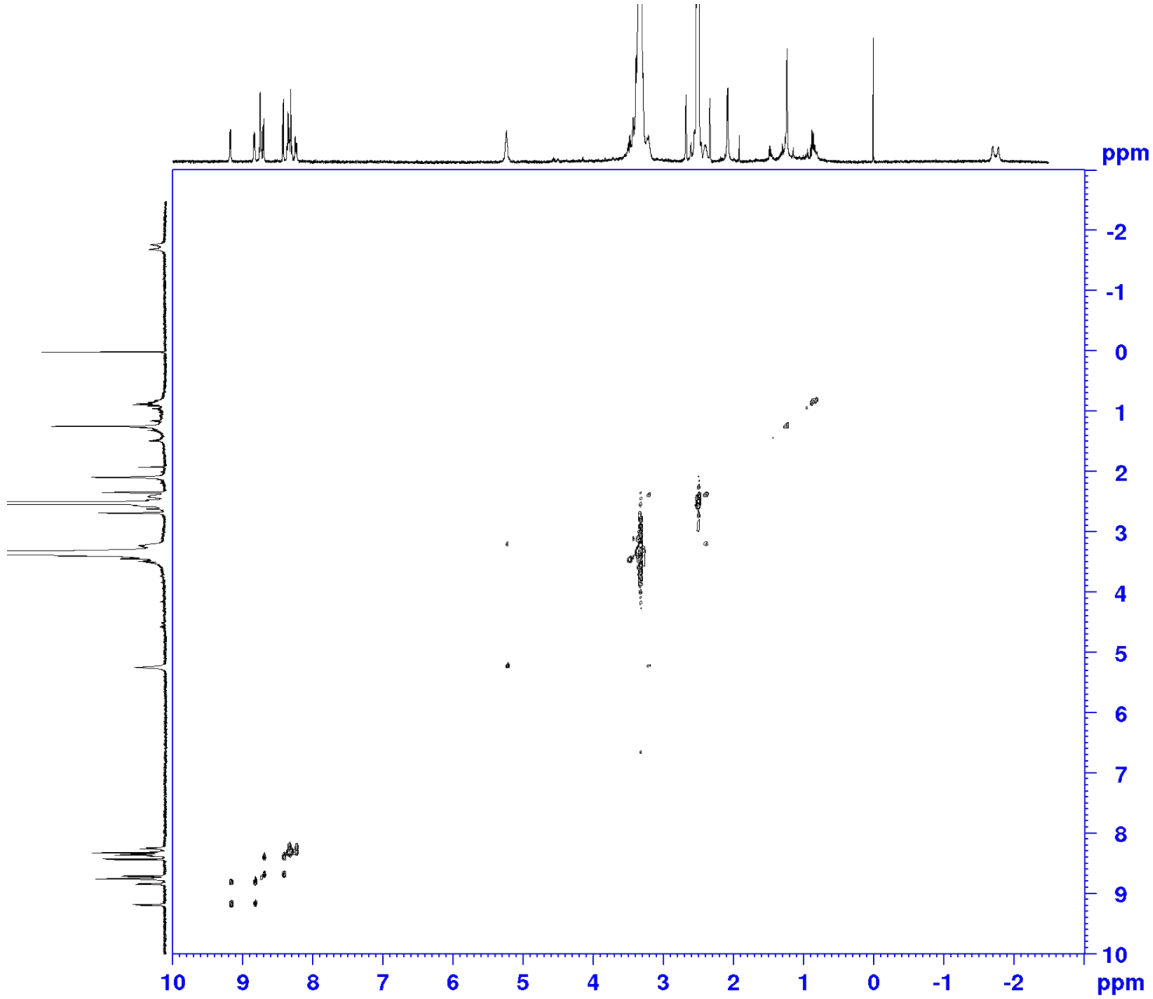


Figure S25. ^{19}F NMR spectrum of chlorin **3** (DMSO-d_6, 376.46 MHz).

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DW                    78.000 usec
DE                     6.50 usec
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P16                 1000.00 usec

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SW                    16.020 ppm
FnMODE                    QF

F2 - Processing parameters
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SF              400.1500000 MHz
WDW                      SINE
SSB          0
LB           0 Hz
GB           0
PC                       1.00

F1 - Processing parameters
SI                       1024
MC2                       QF
SF              400.1500000 MHz
WDW                      SINE
SSB          0
LB           0 Hz
GB           0
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Figure S26. COSY spectrum of chlorin **3**.

NMR spectra of metalloporphyrin 1Zn

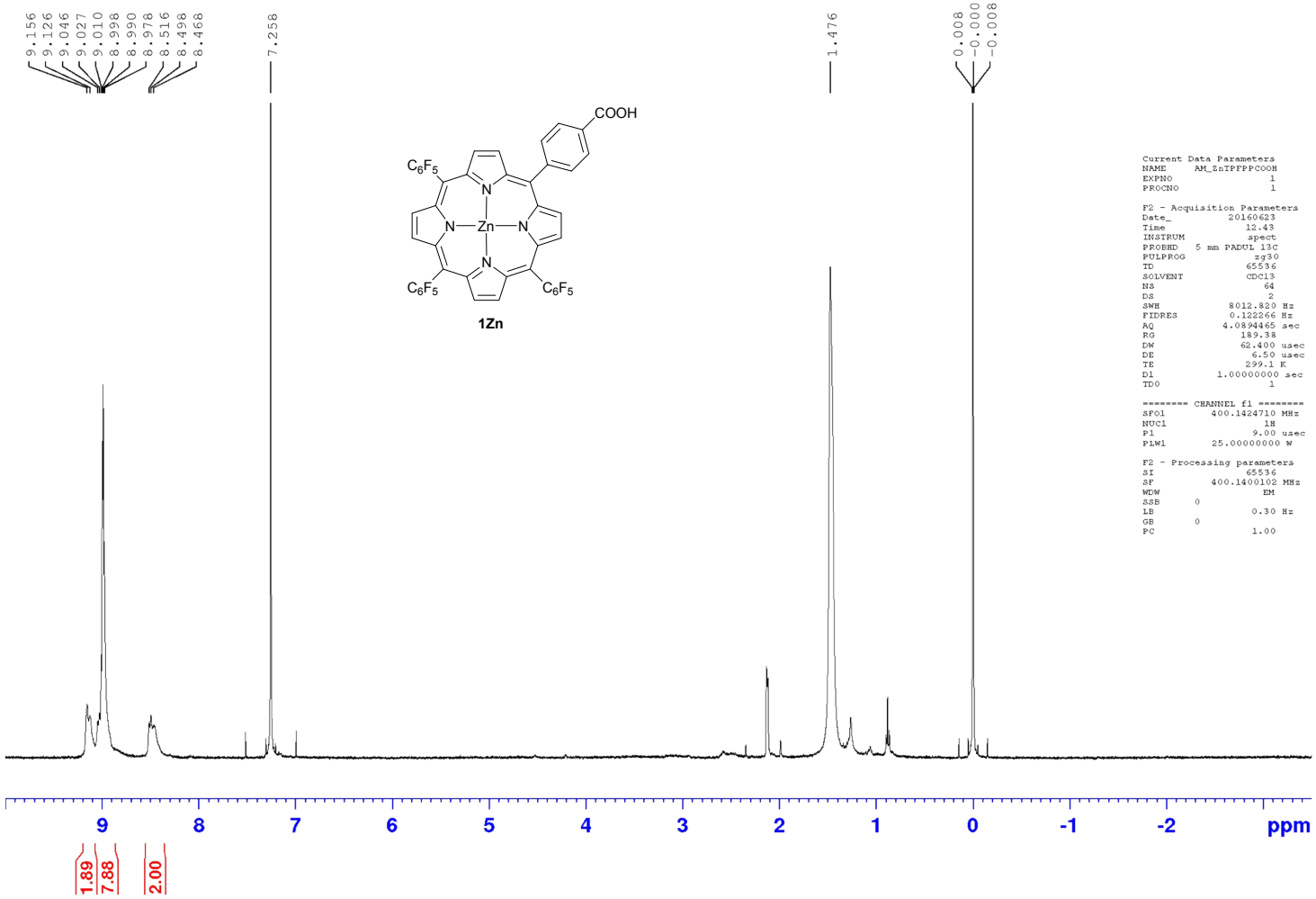


Figure S27. ^{1}H NMR spectra of metalloporphyrin **1Zn** ($CDCl_3$, 400.15 MHz).

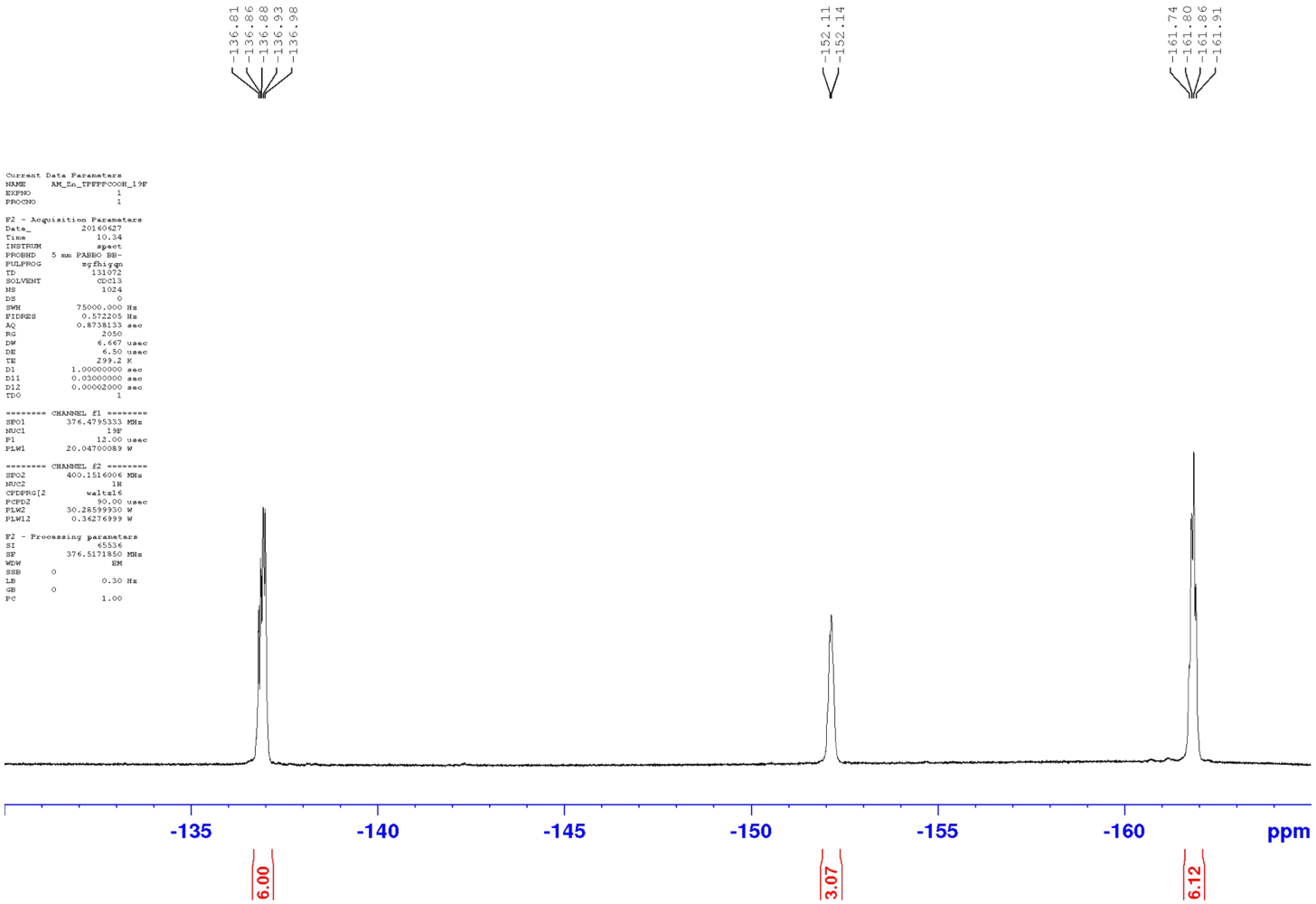


Figure S28. ^{19}F NMR spectra of metalloporphyrin **1Zn** ($CDCl_3$, 376.46 MHz).

NMR spectra of metallochlorin 3Zn

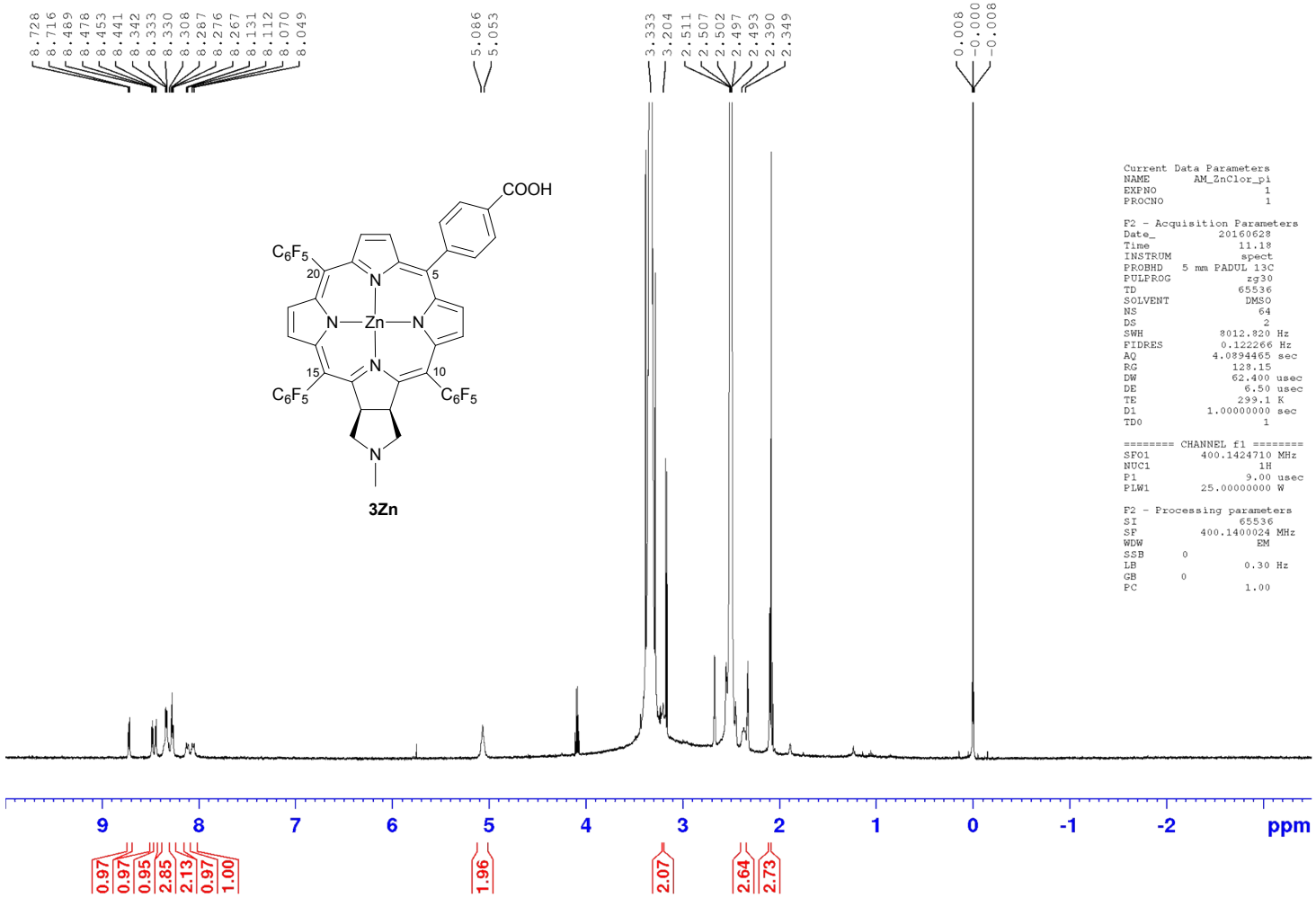


Figure S29. ^{1}H NMR spectra of metallochlorin **3Zn** (DMSO-d_6, 400.15 MHz).

MS-ESI spectra

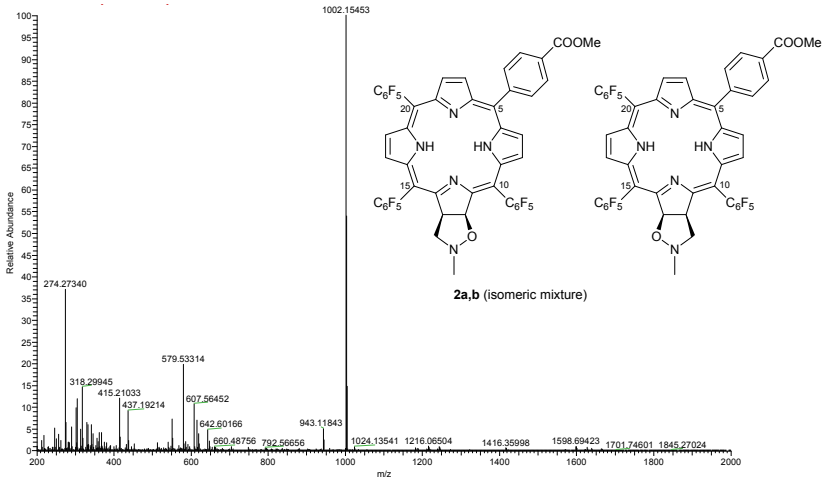


Figure S30. MS spectrum of chlorins **2a,b**.

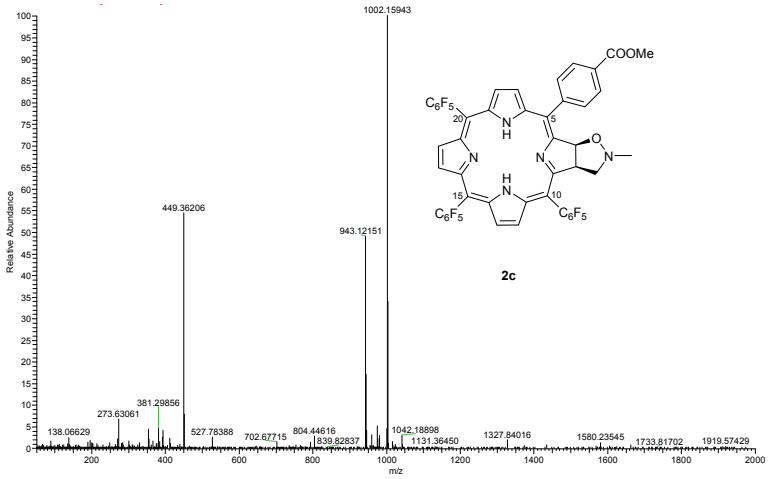


Figure S31. MS spectrum of chlorin **2c**.

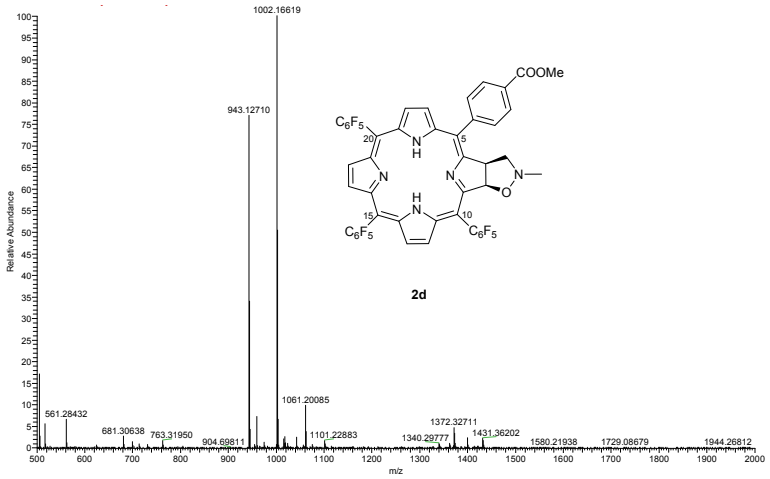


Figure S32. MS spectrum of chlorin **2d**.

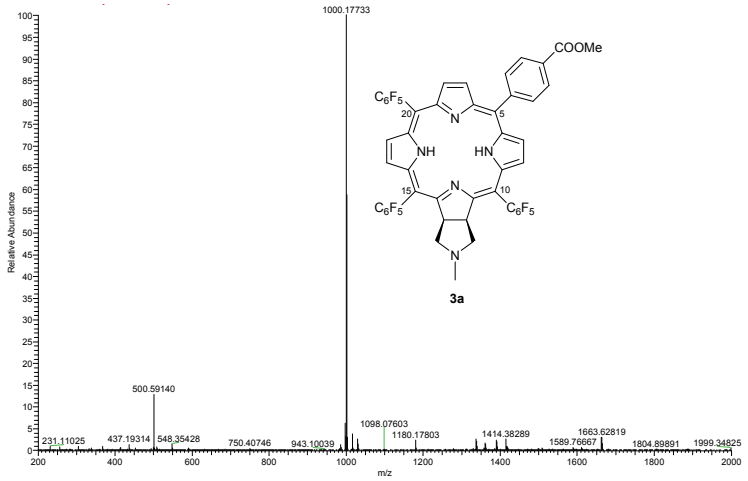


Figure S33. MS spectrum of chlorin **3a**.

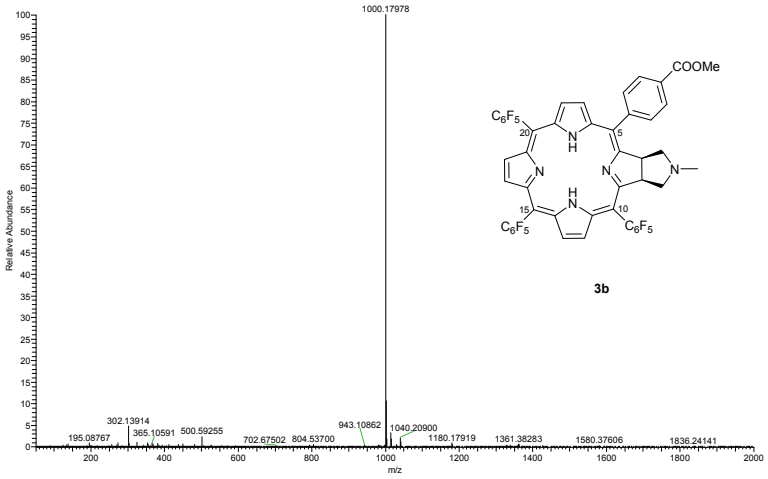


Figure S34. MS spectrum of chlorin **3b**.

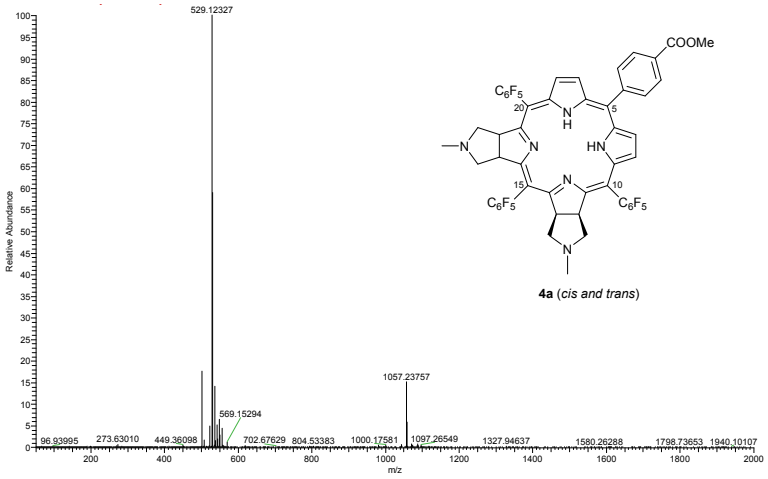


Figure S35. MS spectrum of iBC **4a**

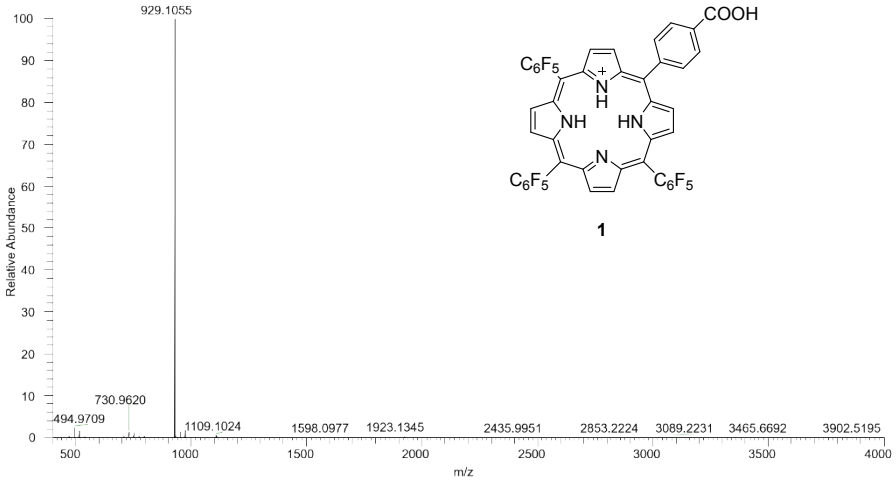


Figure S36. MS spectrum of porphyrin **1**.

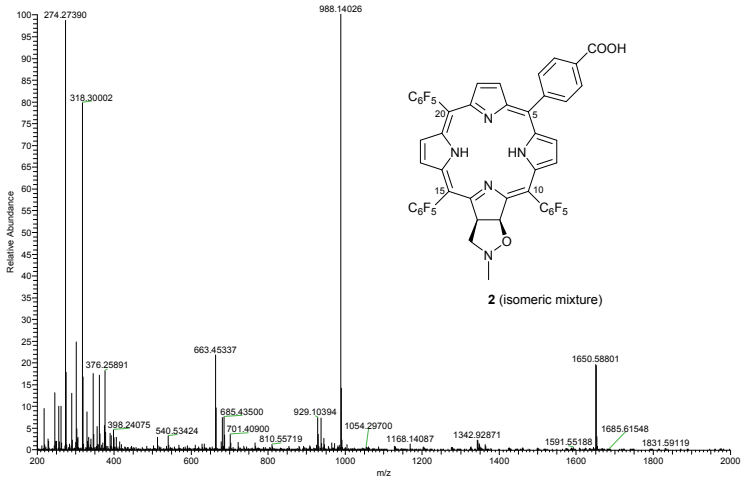


Figure S37. MS spectrum of chlorin **2**.

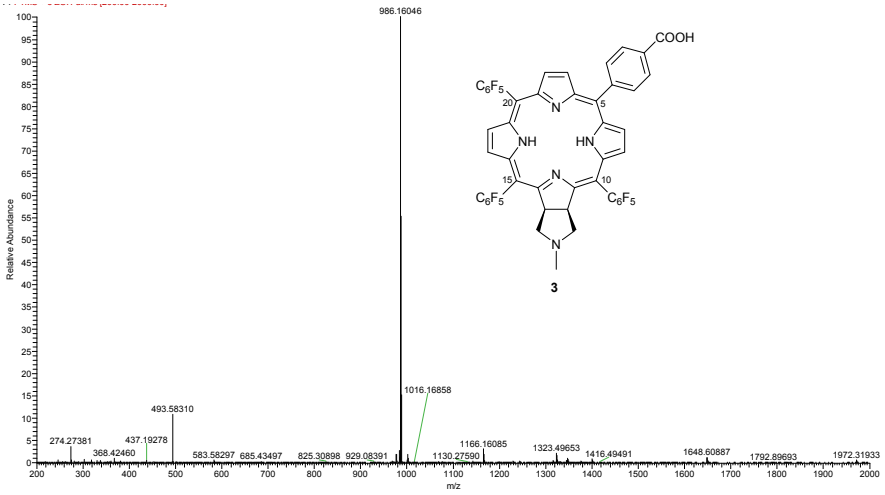


Figure S38. MS spectrum of chlorin **3**.

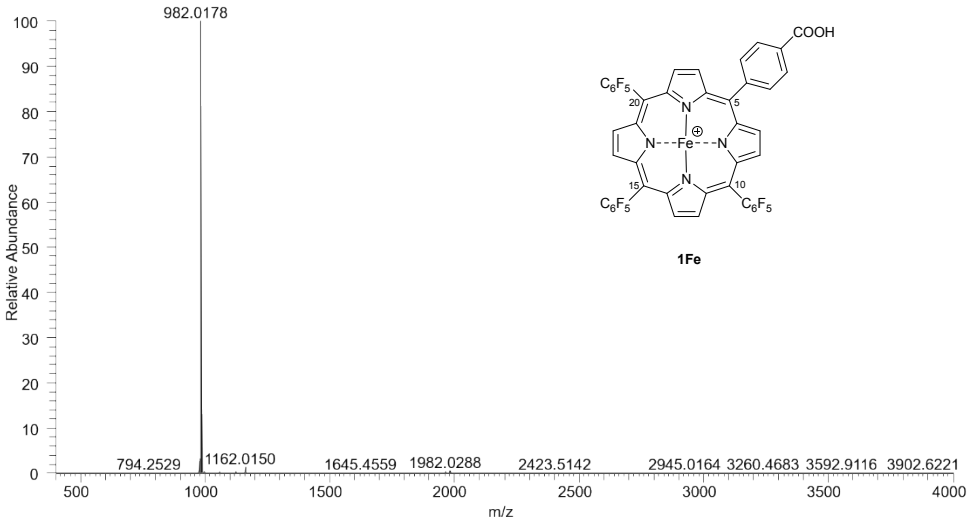
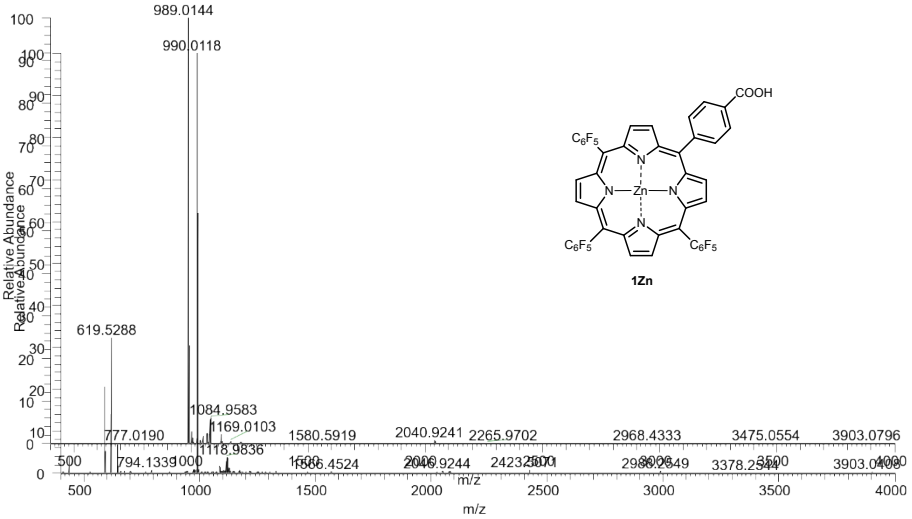


Figure S39. MS spectrum of **1Fe**.

Figure S40. MS spectrum of **1Cu**.

Figure S41. MS spectrum of **1Zn**.



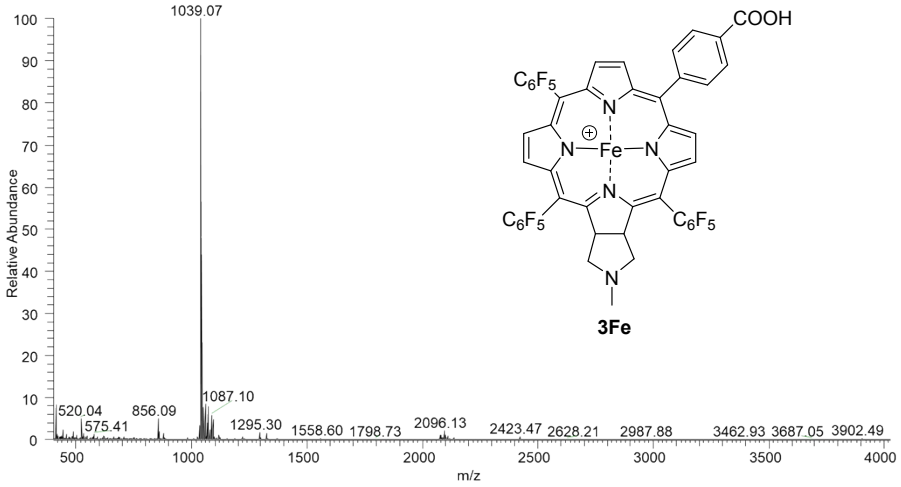


Figure S42. MS spectrum of **3Fe**.

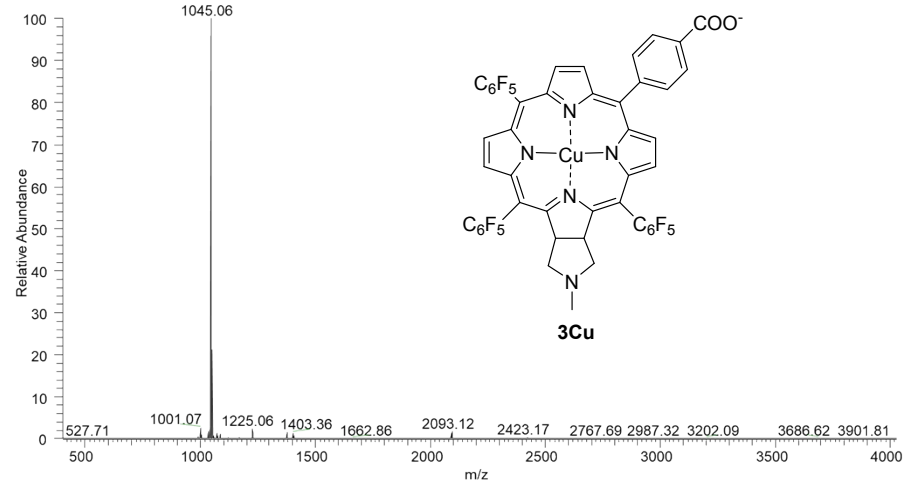


Figure S43. MS spectrum of **3Cu**.

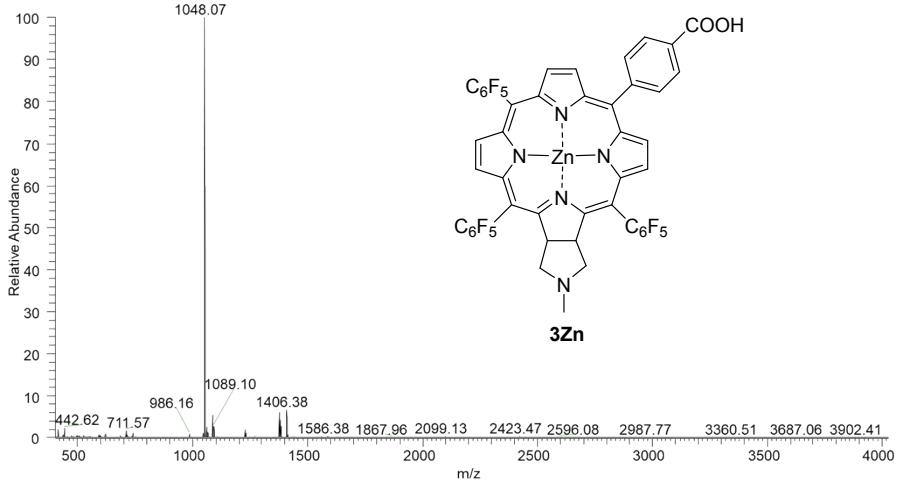


Figure S44. MS spectrum of **3Zn**.

SC-XRD data

Table S1. Crystal and structure refinement details for porphyrin **1**.

Formula	$C_{54}H_{36}F_{15}N_4O_2$
Fw / g mol^{-1}	1057.87
Crystal type	red prism
Crystal size / mm^3	0.35 × 0.26 × 0.12
Crystal system	Monoclinic
Space group	*C*2/c
a / Å	16.7872(9)
b / Å	24.9663(13)
c / Å	26.3075(13)
α / º	90
β / º	91.737(2)
γ / º	90
Volume / Å^3	11020.8(10)
Z	8
Temparature / K	150(2)
D_c / g cm^{-3}	1.275
μ / mm^{-1}	0.113
θ range	3.691 – 25.027
Index ranges	−19 ≤ h ≤ 19 −29 ≤ k ≤ 29 −30 ≤ l ≤ 30
Collected reflection	71076
Independent reflections	9700 (R_{int} = 0.0265)
Data completeness	to θ = 25.03º, 99.6%
Final *R* indices	*R*1 = 0.0626
[I>2σ(I)]	*wR*2 = 0.2499
Final *R* indices	*R*1 = 0.0758
(all data)	*wR*2 = 0.2696
$(\Delta\rho)_{max,min}$ / e Å^{-3}	0.462 and −0.437

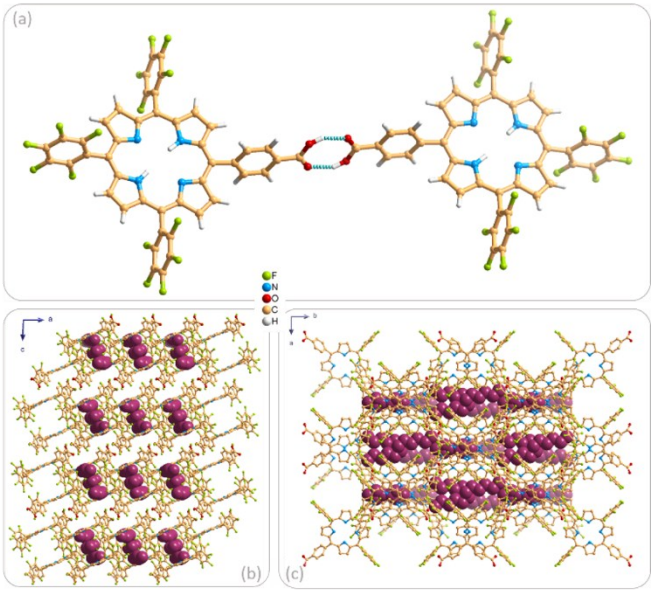


Figure S45. Structural details fo porphyrin **1**: dimer (a) and extended packing arrangements viewed in the ac (ab) and ab (c) planes of the unit cell; *n*-hexane atoms represented in purple.

Photophysical data

Table S2. Absorption and emission spectra data for synthesized compounds **1**, **1Fe**, **1Cu**, **1Zn**, **3**, **3Fe**, **3Cu** and **3Zn**, in methanol.

		Absorption λ_{max}[nm] (ε_{max} [M^{-1} cm^{-1}])			Emission	
Entry	Compound	B(0,0)	Q(1,0)	Q(0,0)	λ_{max}[nm]	ϕ_F
1	**1**	409 (173x10^3)	505 (12x10^3)[a]	536 (0.8 x10^3)[a]	642, 708	0.051
			582 (4x10^3)[a]	653 (2x10^3)[a]		
2	**1Fe**	404 (65x10^3)	583 (35x10^3)		N.O.[c]	0.008
3	**1Cu**	408 (139x10^3)	536 (57x10^3)	569 (19x10^3)	N.O.[c]	0.01
4	**1Zn**	418 (346x10^3)	551 (5x10^3)	583 (0.48x10^3)	599, 645	0.033
5	**3**	400 (115x10^3)	503 (12x10^3)[a]	530 (5.5x10^3)[a]	648, 714	0.157
			594 (7.2x10^3)[a]	647 (35x10^3)[a]		
6	**3Fe**	404 (65x10^3)	535 (6.7x10^3)	651 (9.9x10^3)	N.O.[c]	0.007
7	**3Cu**	407 (171x10^3)	567 (6.8x10^3)	611 (34x10^3)	N.O.[c]	0.008
8	**3Zn**	412 (305x10^3)	579[b]	615 (50x10^3)	620, 672	0.079

[a]The Q(1,0) and Q(0,0) bands are each split into $Q_y(1,0)$ and $Q_x(1,0)$ and $Q_y(0,0)$ and $Q_x(0,0)$, respectively. In compound **3**, the Q(1,0) and Q(0,0) bands are each split into the $Q_x(1,0)$ and $Q_y(1,0)$ and $Q_x(0,0)$ and $Q_y(0,0)$ bands, respectively. The $Q_y(0,0)$ band corresponds to the Q band with maximum absorbance.

[b]The determination of ε wasn't possible without a significant experimental error.

[c]The emission spectra was not observable, or too low in intensity to be observed.

EPR spectra

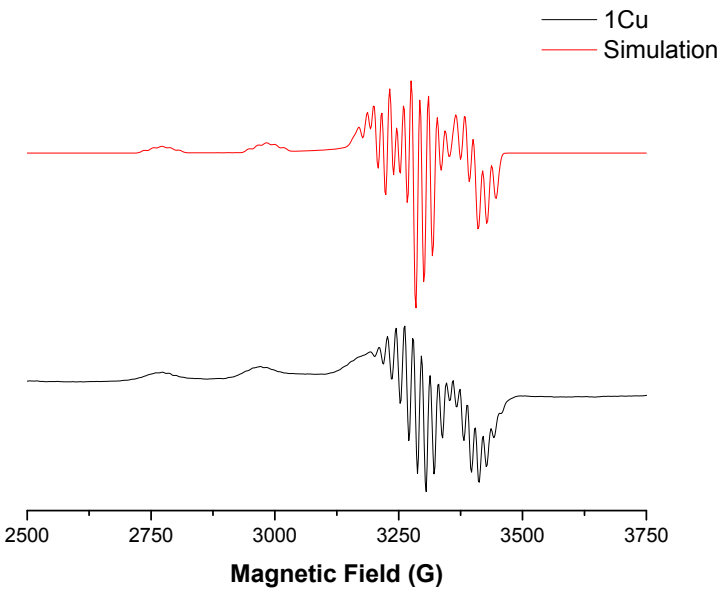


Figure S46. EPR spectrum of **1Cu** (black line) and EPR spectrum of **1Cu** obtained by computer simulation (red line).

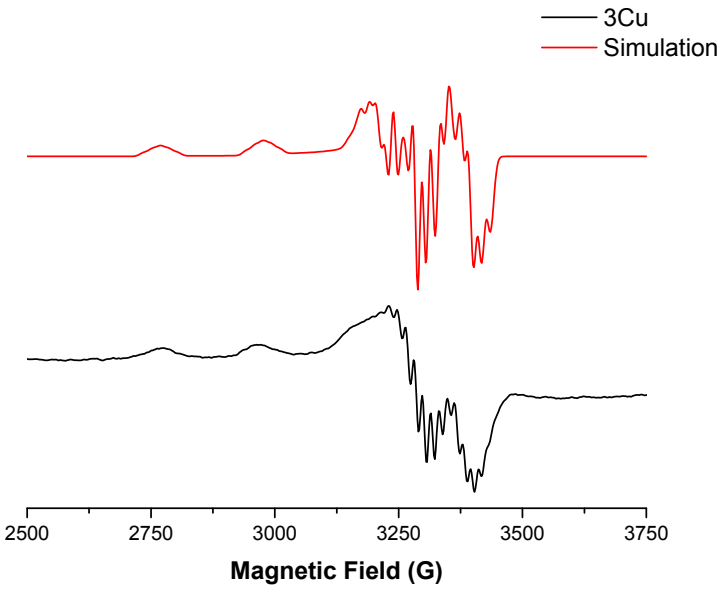


Figure S47. EPR spectrum of **3Cu** (black line) and EPR spectrum of **3Cu** obtained by computer simulation (red line).

Table S3. Spin-Hamiltonian parameters for **1Cu**, **3Cu** and for **1Zn** and **3Zn** after addition of a copper(II) solution ten times more concentrated (**1Zn/3Zn + Cu(II)**).

	g_x	g_y	g_z		A_x (Gauss)	A_y (Gauss)	A_z (Gauss)
1Cu	2.066	2.066	2.184	Cu	35	35	212
				$^{14}N_{1,3}$	20	15	15
				$^{14}N_{2,4}$	15	15	20
3Cu	2.064	2.060	2.190	Cu	35	35	208
				$^{14}N_{1,3}$	19	15	15
				$^{14}N_{2,4}$	15	15	19
1Zn + Cu(II)	2.076	2.076	2.362	Cu	10	10	136
3Zn + Cu(II)	2.076	2.076	2.360	Cu	10	10	140

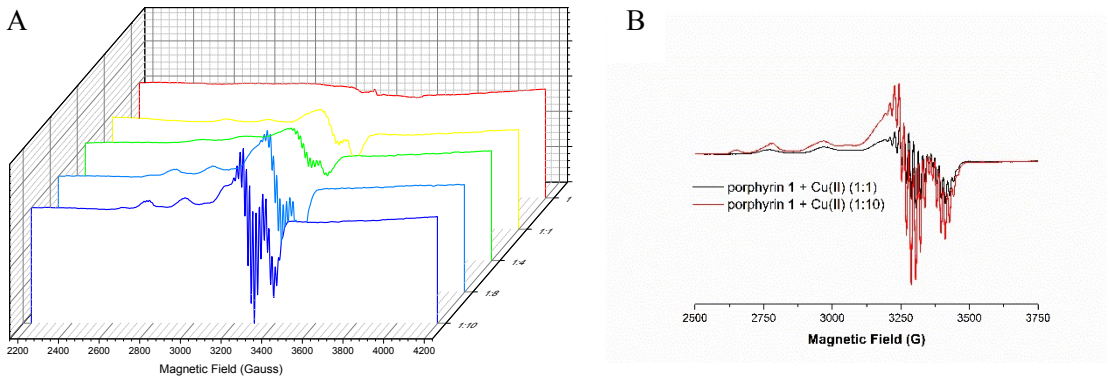


Figure S48. A) EPR spectra of porphyrin **1** obtained in a DMSO/toluene frozen matrix after addition of different concentrations of copper(II) solutions. Porphyrin **1** without any addition (red line); porphyrin **1**:copper(II) (1:1) (yellow line); porphyrin **1**:copper(II) (1:4) (green line); porphyrin **1**:copper(II) (1:8) (light blue line); porphyrin **1**:copper (II) (1:10) (dark blue line), B) EPR spectra of porphyrin **1** after addition of an equimolar solution of Cu(II) (black line) and after addition of a ten time more concentrated solution of Cu(II) (red line).

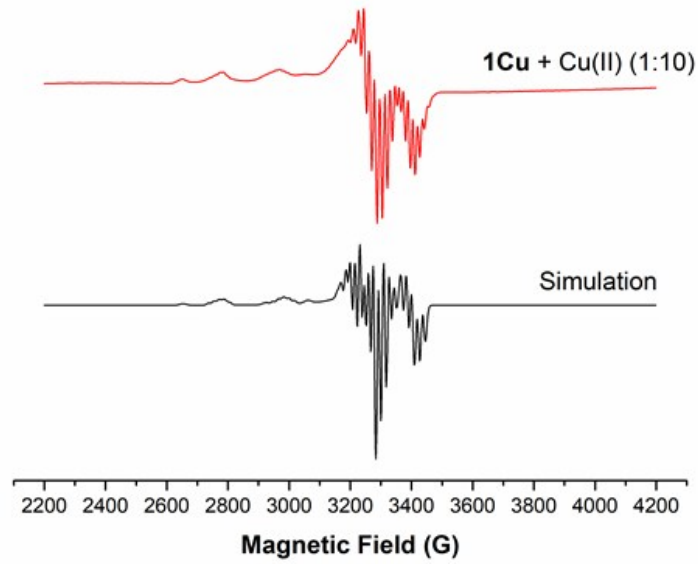


Figure S49. EPR spectra of **1Cu** after addition of a ten time more concentrated solution of Cu(II) (red line), and EPR simulation of the same solution (black line). The simulation was obtained by considering the sum of the Spin-Hamiltonian parameters of the **1Cu** and **1Zn** spectra.