Electronic Supplementary Material (ESI) for ChemComm.

Match-Mismatch Effects in Twofold Transfer of Chirality within a Möbius Metallo-Receptor

Bernard Boitrel* and Stéphane Le Gac*

SUPPORTING INFORMATION

Table of contents:

3. Selected UV-vis absorption and ECD spectra

1. Experimental part

General

All chemicals were commercial products used as received. All reactions were conducted under inert atmosphere. Anhydrous THF was obtained by distillation over Na/benzophenone according to standard procedures. ^{1}H and ^{19}F NMR spectra were recorded at 298 K (unless otherwise stated), at 500 MHz and 470 MHz, respectively. Residual traces of solvent were used as internal standard. Chemical shifts are expressed in parts per million (ppm; s = singlet [s_b = broad singlet, and so on], d = doublet, t = triplet) and coupling constants are given in Hz. The NMR experiments were conducted in 5 mm standard NMR tubes. The CD spectra were recorded in a quartz glass cuvette of 2 mm optical path length. The synthesis of [26]hexaphyrin **1** was previously reported.[1]

Synthesis and characterization of 2

In a sealed reactor, Pd(0)/C (30 wt. % loading, 12.5 mg) was added to [26]hexaphyrin **1** (250 mg, 190 µmol) in AcOEt (15 mL). The reaction was stirred under a pressure of H_2 (80 bar) for 24 h at room temperature, then filtered through a plug of celite. AcOEt was removed under reduced pressure affording the corresponding tris-(2-aminophenyl) [28]hexaphyrin as major compound. The crude mixture was dried under high vacuum, and used in the next step without purification. Under inert atmosphere, the crude residue was solubilized in anhydrous THF (10 mL) and, at 0°C, Et_3N (150 µL, 1.11 mmol) and acetyl chloride (54 µL, 757 µmol) were successively added. After 60 min of stirring, the excess of acyl chloride was quenched by addition of methanol. THF was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2/AcOEt 9:1) to afford [28]hexaphyrin **2** as a blue solid (60 mg, 23 % overall yield from **1**).

^{1}H NMR ($CDCl_3$, 330 K, broad spectrum due to fast equilibrium between Möbius conformers and atropisomers, see text and Figure S2): 8.42 (d_b, *J* = 7.8 Hz, HAr), 7.97 (broad signal, HAr), 7.61 (t_b, *J* = 7.6 Hz, HAr), 7.60 (broad signal), 7.55 (broad signal), 7.41 (t_b, *J* = 6.9 Hz, HAr), 7.40 (broad signal), 7.33 (t_b, *J* = 7.5 Hz), 7.15 (broad signal), 7.07 (broad signal), 1.68 (s_b, $COCH_3$). ^{19}F NMR ($CDCl_3$, 330 K, same remark as above, see Figure S3): -137.82 (broad signal, F_{ortho}), -138.54 (broad signal, F_{ortho}), -152.16 (broad signal, F_{para}), -153.42 (broad signal, F_{para}), -161.07 (broad signal, F_{meta}), -161.63 (broad signal, F_{meta}). UV-vis ($CHCl_3$, λ_{max} nm/ε $L{\cdot}mol^{-1}{\cdot}cm^{-1}$): 398 (30760), 444 (27200), 560 (49580), 601 (206540), 767 (14180), 857 (8480), 903 (7025), 1018 (3100). HRMS (ESI-TOF, positive ion mode): *m/z* calcd for $C_{72}H_{40}N_9O_3F_{15}$: 1363.30091 [$M^{+\cdot}$]; found: 1363.3007.

General procedure for NMR Zn(II) complexation experiments

Formation of ***2.Zn$_{OAc}^{NH2Bu}$***

The two following solutions were prepared:

- **S1**: 10.0 mg of $Zn(OTf)_2$ in 9:1 $CDCl_3/CD_3OD$ (500 µL).
- **S2**: 16.6 mg of Bu_4NOAc in 9:1 $CDCl_3/CD_3OD$ (500 µL).

[1] H. Ruffin, G. Nyame Mendendy Boussambe, T. Roisnel, V. Dorcet, B. Boitrel, S. Le Gac, *J. Am. Chem. Soc.,* 2017, **139**, 13847-13857.

In a NMR tube, hexaphyrin **2** (3.0 mg, 2.2 µmol) was dissolved in 9:1 $CDCl_3/CD_3OD$ (500 µL). To this solution, 2 µL of DIPEA (11.5 µmol, 5 equiv.), 60 µL of **S1** (1.5 equiv.), 60 µL of **S2** (3 equiv.) and 1 µL of $BuNH_2$ (10.1 µmol, 4.6 equiv.) were successively added at room temperature. A ^1H NMR spectrum recorded at 298 K showed **2.Zn**$_{OAc}^{NH2Bu}$ as major product(s) (mixture of isomers, see text/Figure 2d).

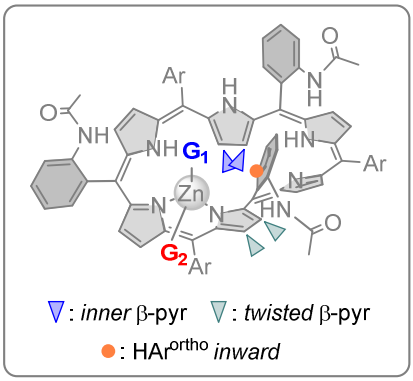
Formation of ***2.Zn***$_{(S)\text{-}BocProO}^{(R)\text{-}MBA}$

The following solution was prepared:

- **S3**: 29 mg of (*S*)-BocProOH in 9:1 $CDCl_3/CD_3OD$ (500 µL).

In a NMR tube, hexaphyrin **2** (3.0 mg, 2.2 µmol) was dissolved in 9:1 $CDCl_3/CD_3OD$ (500 µL). To this solution, 5 µL of DIPEA (28.7 µmol, 13 equiv.), 60 µL of **S1** (1.5 equiv.), 40 µL of **S3** (3 equiv.) and 1.4 µL of (*R*)-MBA (10.8 µmol, 4.9 equiv.) were successively added at room temperature. A ^1H NMR spectrum recorded at 298 K showed **2.Zn**$_{(S)\text{-}BocProO}^{(R)\text{-}MBA}$ as major product(s) (mixture of isomers, see text and Figure 3d). Note that an incomplete metalation is observed, even after heating (1h, 60 °C), which is likely due the steric hindrance of $BocProO^-$ larger than that of AcO^-.

Characterization of 2.Zn$_{G1}^{G2}$



^1H NMR ($CDCl_3/CD_3OD$ 9:1, 298 K, partial descriptions because of a strong overlapping and/or highly broaden signals; selected complexation induced shifts are displayed Figure S1):

2.Zn$_{OAc}$ [a]	**β-pyr *inner***	**β-pyr *twisted***
	M: -2.60 (s_b, 1H), -1.95 (d, *J* = 4.7 Hz, 1H) m: -2.81 (s_b, 1H), -1.79 (d, *J* = 4.5 Hz, 1H)	5.2 to 5.9: broad signals with strong overlapping
	HAr^{ortho} *inward*	**OAc**
	M: 4.17 (d, *J* = 7.1 Hz, 1H) m: 4.19 (d, *J* = 6.1 Hz, 1H)	-0.99 (s_b) -0.95 (s_b)

[a] "M" and "m" stand for major and minor.

2.Zn$_{OAc}^{NH2Bu}$ [a]	**β-pyr *inner***	**β-pyr *twisted***	
	A: -2.68 (d, *J* = 4.6 Hz, 1H), -1.66 (d, *J* = 4.8 Hz, 1H) **B**: -2.57 (d, *J* = 4.4 Hz, 1H), -1.51 (d, *J* = 4.4 Hz, 1H) **C**: -2.42 (d, *J* = 4.9 Hz, 1H), -1.60 (d, *J* = 4.7 Hz, 1H)	**A**: 4.84 (d, *J* = 4.3 Hz, 1H), 4.87 (d, *J* = 4.5 Hz, 1H) **B**: 4.89 (d, *J* = 4.4 Hz, 1H), 4.99 (d, *J* = 4.3 Hz, 1H) **C**: 4.95 (d, *J* = 4.5 Hz, 1H), 5.05 (d, *J* = 4.4 Hz, 1H)	
	HAr^{ortho} *inward*	**OAc**	**BuNH$_2$ (α-CH$_2$)** [b]
	A: 4.61 (d, *J* = 7.5 Hz, 1H) **B**: 4.62 (d, *J* = 7.2 Hz, 1H) **C**: 4.44 (d, *J* = 7.2 Hz, 1H)	**A:** -1.16 (s, 3H) **B:** -1.12 (s, 3H) **C:** -1.20 (s, 3H)	1.76/2.00

[a] At 278 K. The labeling "A", "B" and "C" corresponds to the three major species retaining the characteristic resonances of Zn(II) Möbius complexes (see text/Figure 2d). [b] Average values obtained from 2D ROESY experiment.

2.Zn$_{(S)\text{-BocProO}}^{NH2Bu}$ [a]	**β-pyr *inner***	**β-pyr *twisted***
	M: -2.61 (d, *J* = 4.7 Hz, 1H), -1.68 (d, *J* = 4.9 Hz, 1H) m: -2.58 (d, *J* = 4.6 Hz, 1H), -1.61 (d, *J* = 4.4 Hz, 1H)	M: 4.52 (d, *J* = 4.4 Hz, 1H), 4.70 (d, *J* = 4.6 Hz, 1H) m: 4.63 (d, *J* = 4.3 Hz, 1H), 4.74 (d, *J* = 4.3 Hz, 1H)
	HAr^{ortho} *inward*	**BuNH$_2$ (α-CH$_2$)** [b]
	M: 5.09 (d, *J* = 7.5 Hz, 1H) m: 5.04 (d, *J* = 7.6 Hz, 1H)	1.79/2.04

[a] "M" and "m" stand for major and minor. [b] Average values obtained from 2D ROESY experiment.

2.Zn$_{OOCEt}^{(R)\text{-MBA}}$ [a]	**β-pyr *inner***	**β-pyr *twisted***
	M: -2.68 (d, *J* = 4.5 Hz, 1H), -1.78 (d, *J* = 4.2 Hz, 1H) m: -2.60 (d, *J* = 4.3 Hz, 1H), -1.70 (d, *J* = 4.2 Hz, 1H)	M: 4.82 (d, *J* = 4.9 Hz, 1H), 4.84 (d, *J* = 4.4 Hz, 1H) m: 4.87 (d, *J* = 4.1 Hz, 1H), 4.94 (d, *J* = 4.4 Hz, 1H)
	HAr^{ortho} *inward*	
	M: 4.58 (d, *J* = 7.8 Hz, 1H) m: 4.54 (d, *J* = 7.8 Hz, 1H)	

[a] "M" and "m" stand for major and minor.

2.Zn$_{(S)\text{-BocProO}}^{(R)\text{-MBA}}$ [a]	**β-pyr *inner***	**β-pyr *twisted***
	M: -2.63 (d, *J* = 4.9 Hz, 1H), -1.72 (d, *J* = 4.7 Hz, 1H) m: -2.65 (d, *J* = 4.7 Hz, 1H), -1.71 (d, *J* = 4.1 Hz, 1H)	M: 4.44 (d, *J* = 4.5 Hz, 1H), 4.71 (d, *J* = 4.3 Hz, 1H) m: 4.53 (d, *J* = 4.5 Hz, 1H), 4.75 (d, *J* = 4.4 Hz, 1H)
	HAr^{ortho} *inward*	
	M: 5.15 (d, *J* = 7.6 Hz, 1H) m: 5.08 (d, *J* = 7.8 Hz, 1H)	

[a] "M" and "m" stand for major and minor.

General procedure for ECD spectroscopic measurements of 2.Zn$_{G1}^{G2}$

To ensure thermodynamic equilibria are reached, the NMR tube solutions of **2.Zn$_{G1}^{G2}$** were heated 1h at 60 °C and then allowed to stand overnight at room temperature. ^{1}H NMR spectra were then recorded, showing no evolution of the NMR patterns. 5 µL of the NMR solutions were added into 500 µL of a 9:1 $CHCl_3$/CH_3OH mixture, and ECD spectra were immediately recorded at 20 °C.

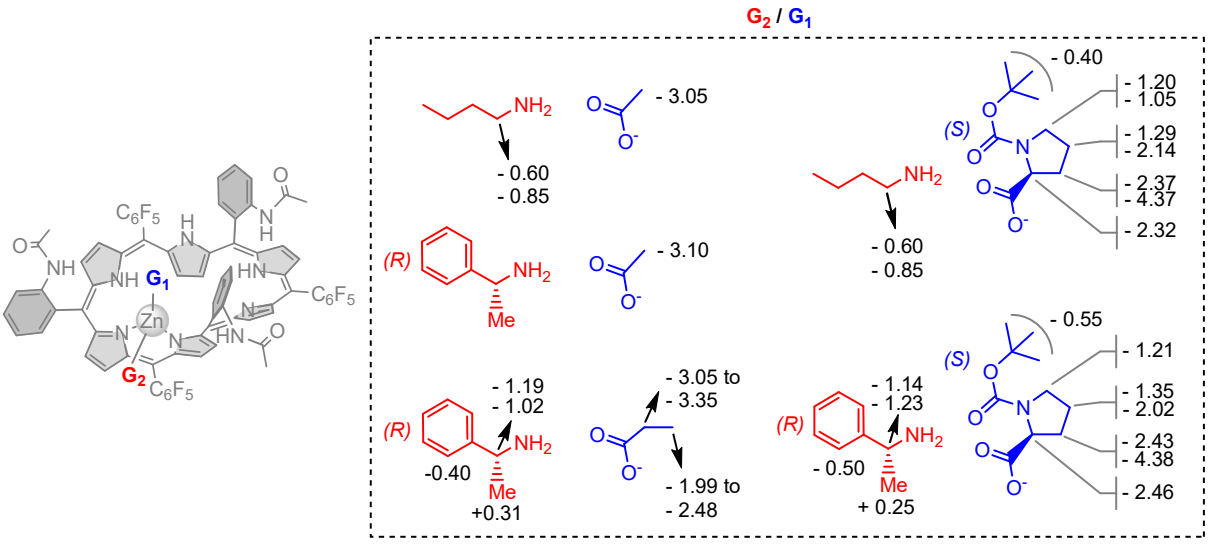


Figure S1. Selected ^{1}H NMR Complexation Induced Shift (CIS in ppm, $\Delta\delta = \delta_{bound} - \delta_{free}$) for **2.Zn$_{G1}^{G2}$** ($CDCl_3/CD_3OD$ 9:1, 298 K). Because of the presence of multiple species, the CISs are given for the major species as single values or, for complex spectra, as a range of values.

2. Selected NMR spectra

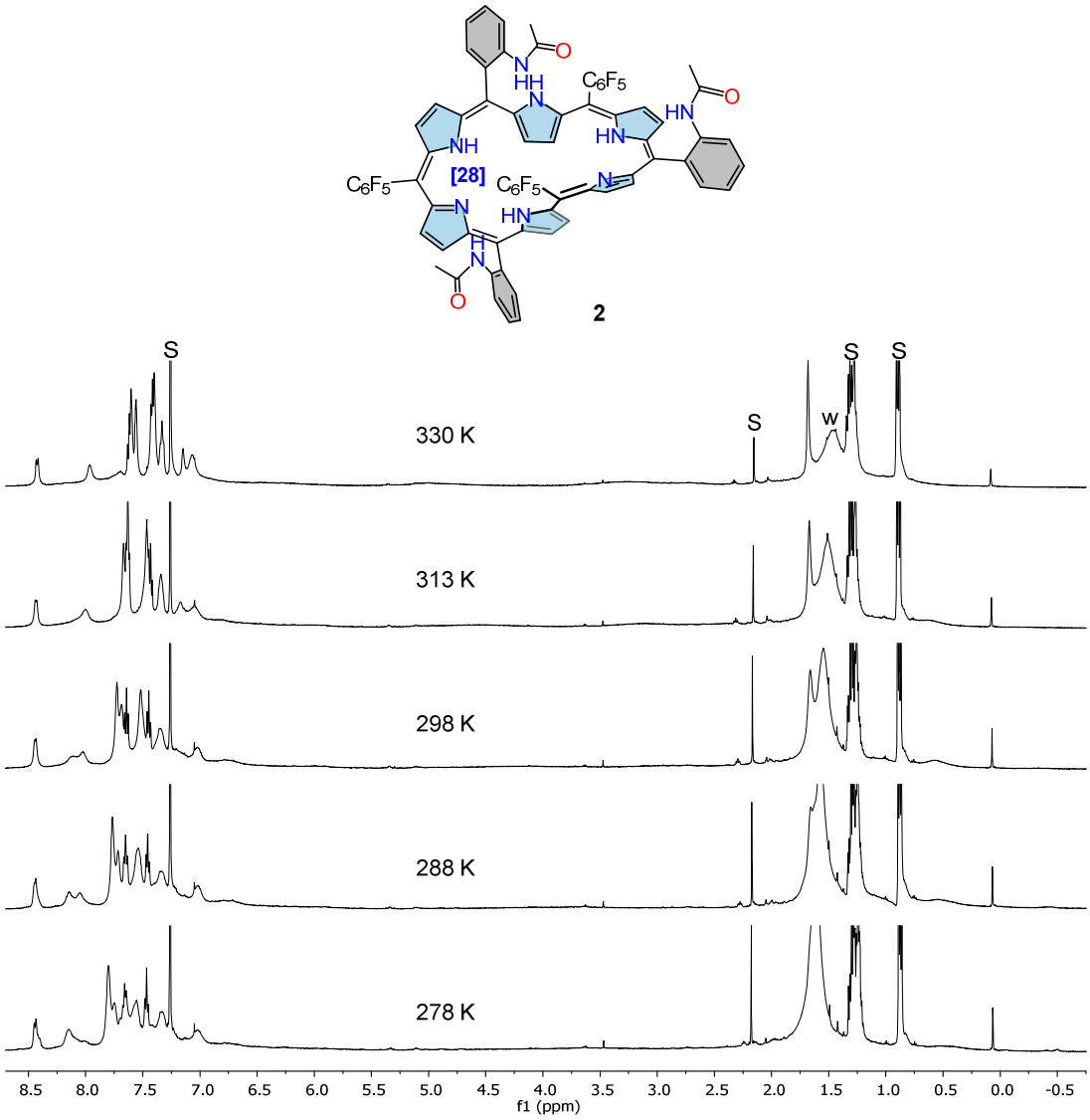


Figure S2(a). Variable temperature ^{1}H NMR spectra of **2** ($CDCl_3$, 500 MHz, 278-330 K). S = solvent; w = water.

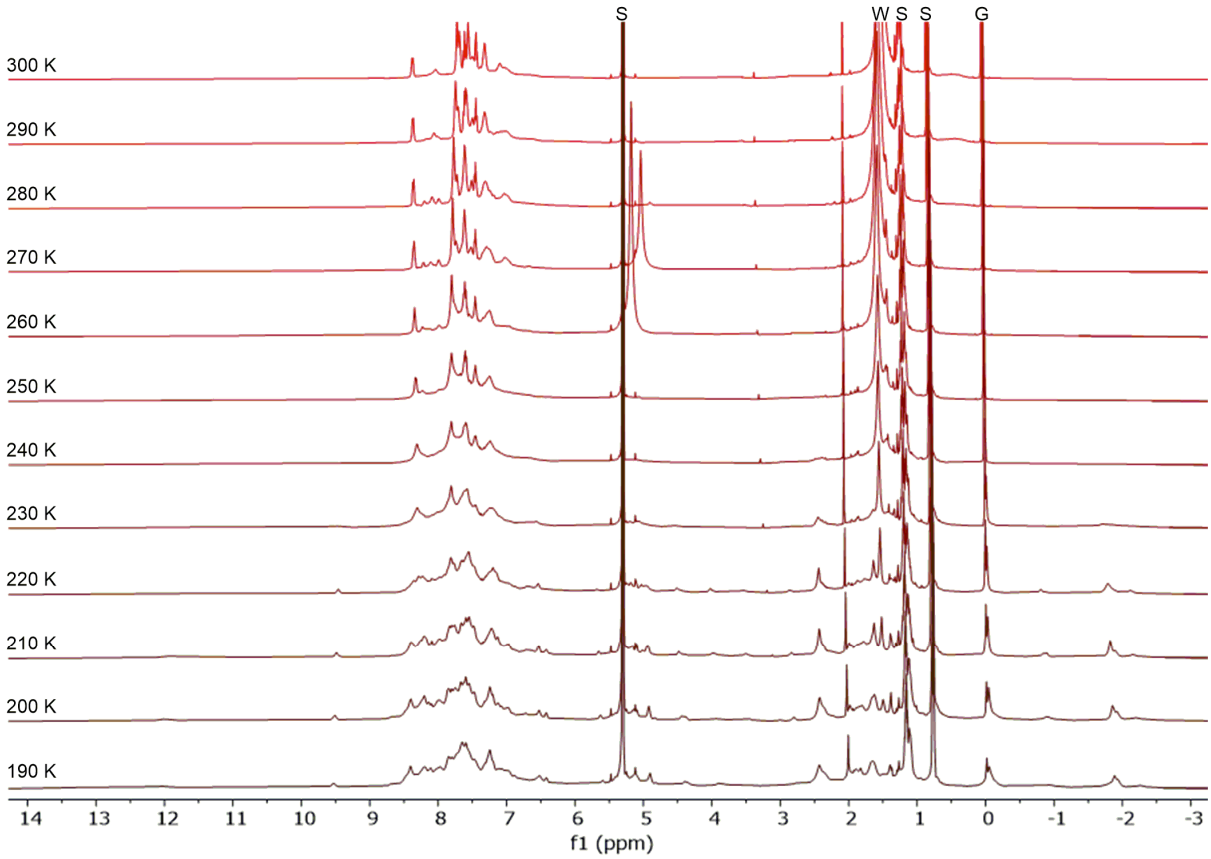
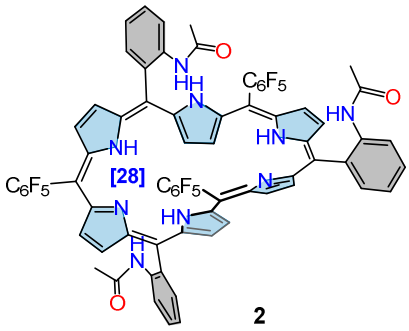


Figure S2(b). Variable temperature ^{1}H NMR spectra of **2** (CD_2Cl_2, 500 MHz, 190-300 K). S = solvent; w = water; G = grease.



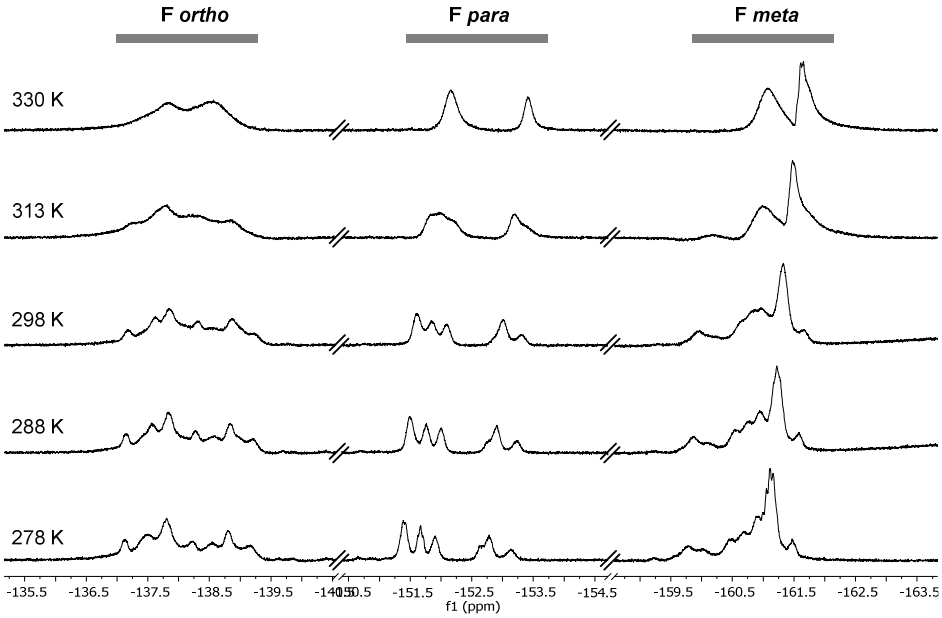


Figure S3(a). Variable temperature ^{19}F NMR spectrum of **2** ($CDCl_3$, 470 MHz, 278-330 K).

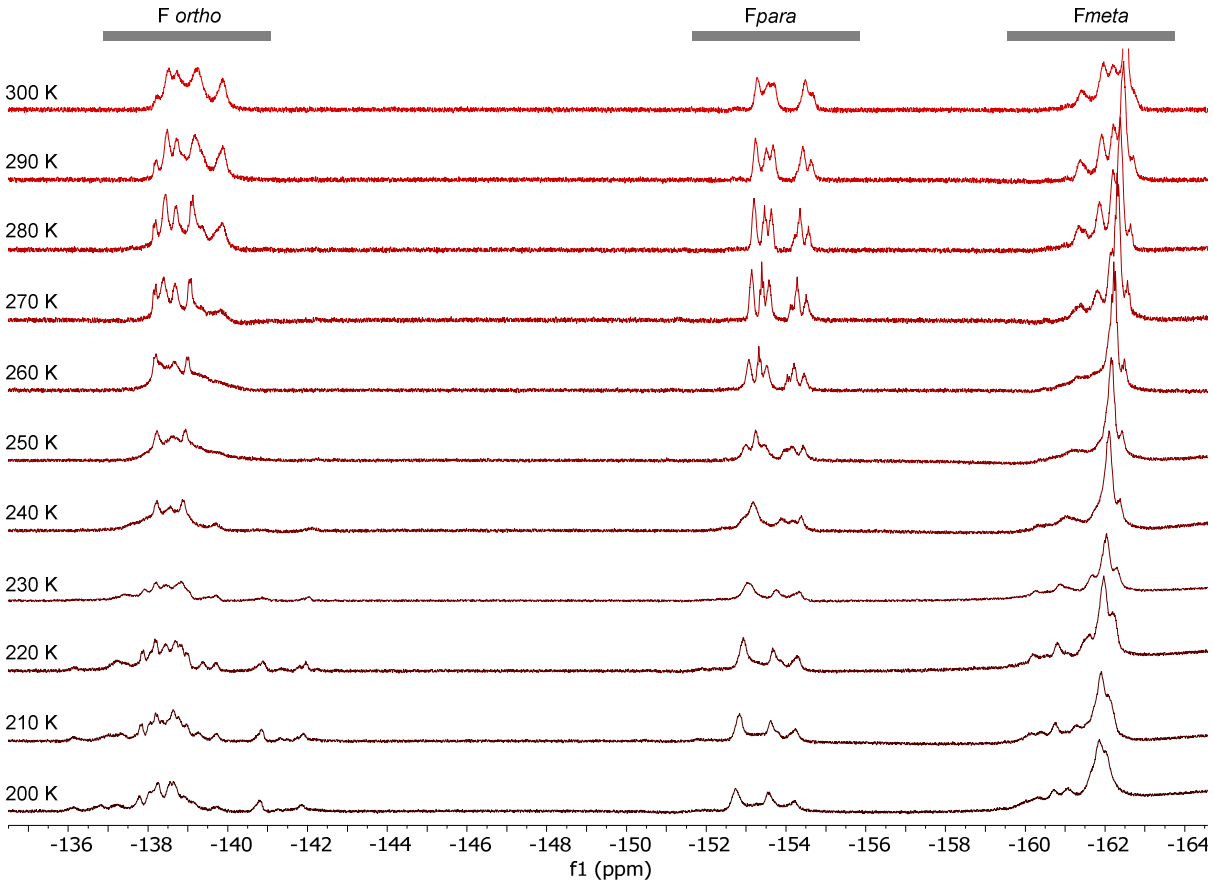


Figure S3(b). Variable temperature ^{19}F NMR spectrum of **2** (CD_2Cl_2, 470 MHz, 200-300 K).

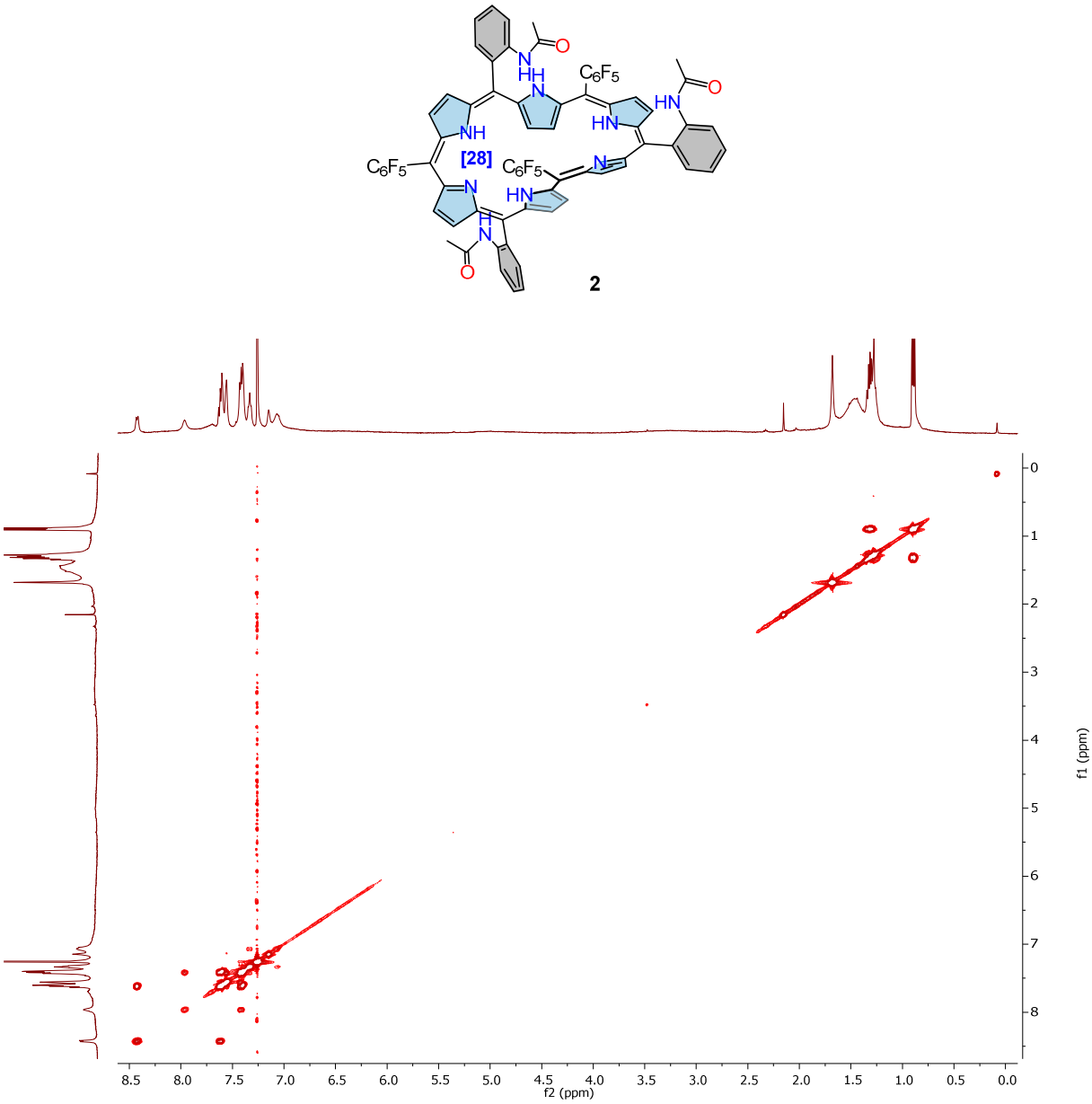


Figure S4. 2D COSY NMR spectrum of **2** ($CDCl_3$, 500 MHz, 330 K).

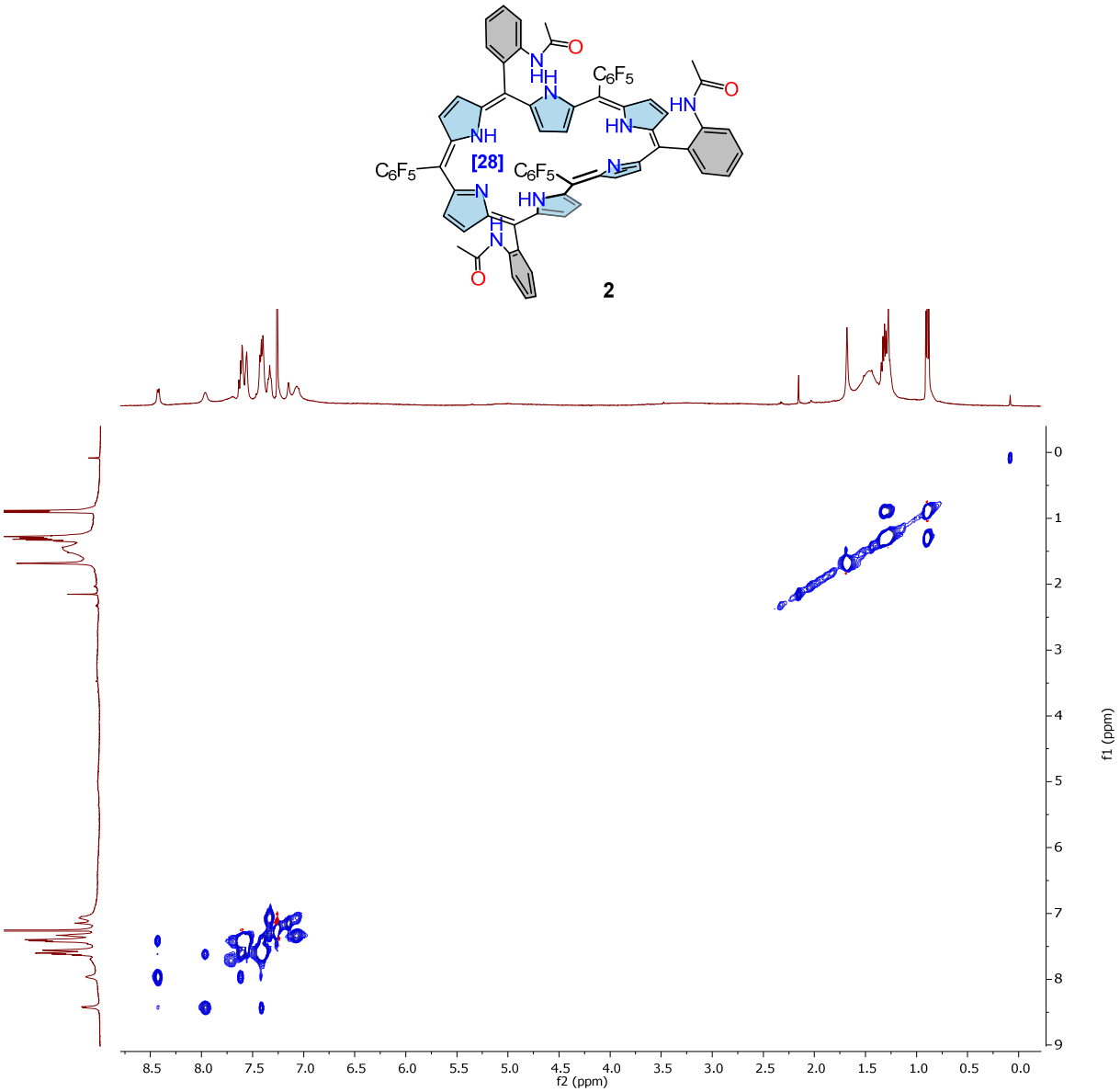


Figure S5. 2D TOCSY NMR spectrum of **2** ($CDCl_3$, 500 MHz, 330 K).

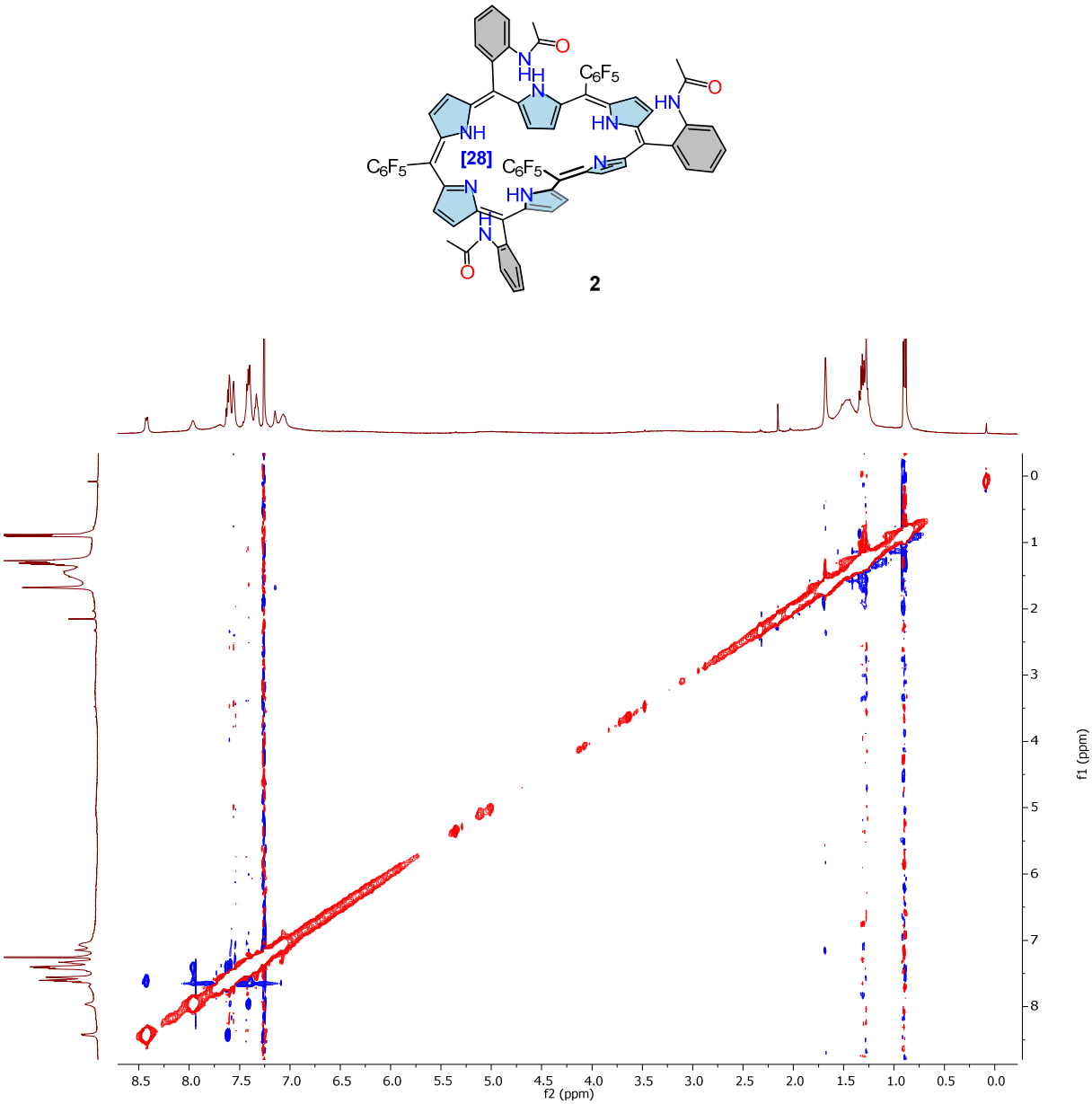


Figure S6. 2D ROESY NMR spectrum of **2** ($CDCl_3$, 500 MHz, 330 K).

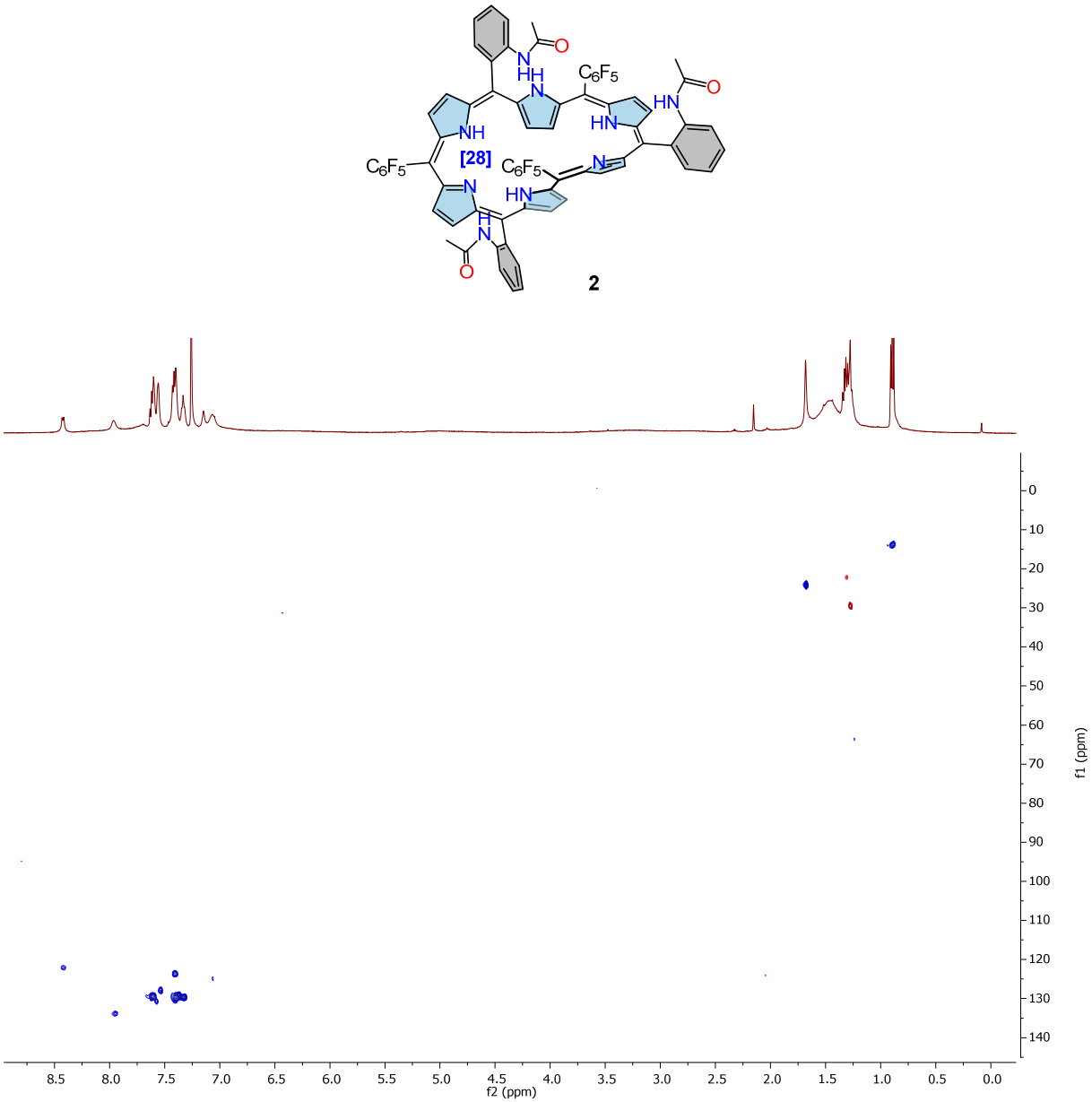


Figure S7. 2D HSQC NMR spectrum of **2** ($CDCl_3$, 500 MHz, 330 K).

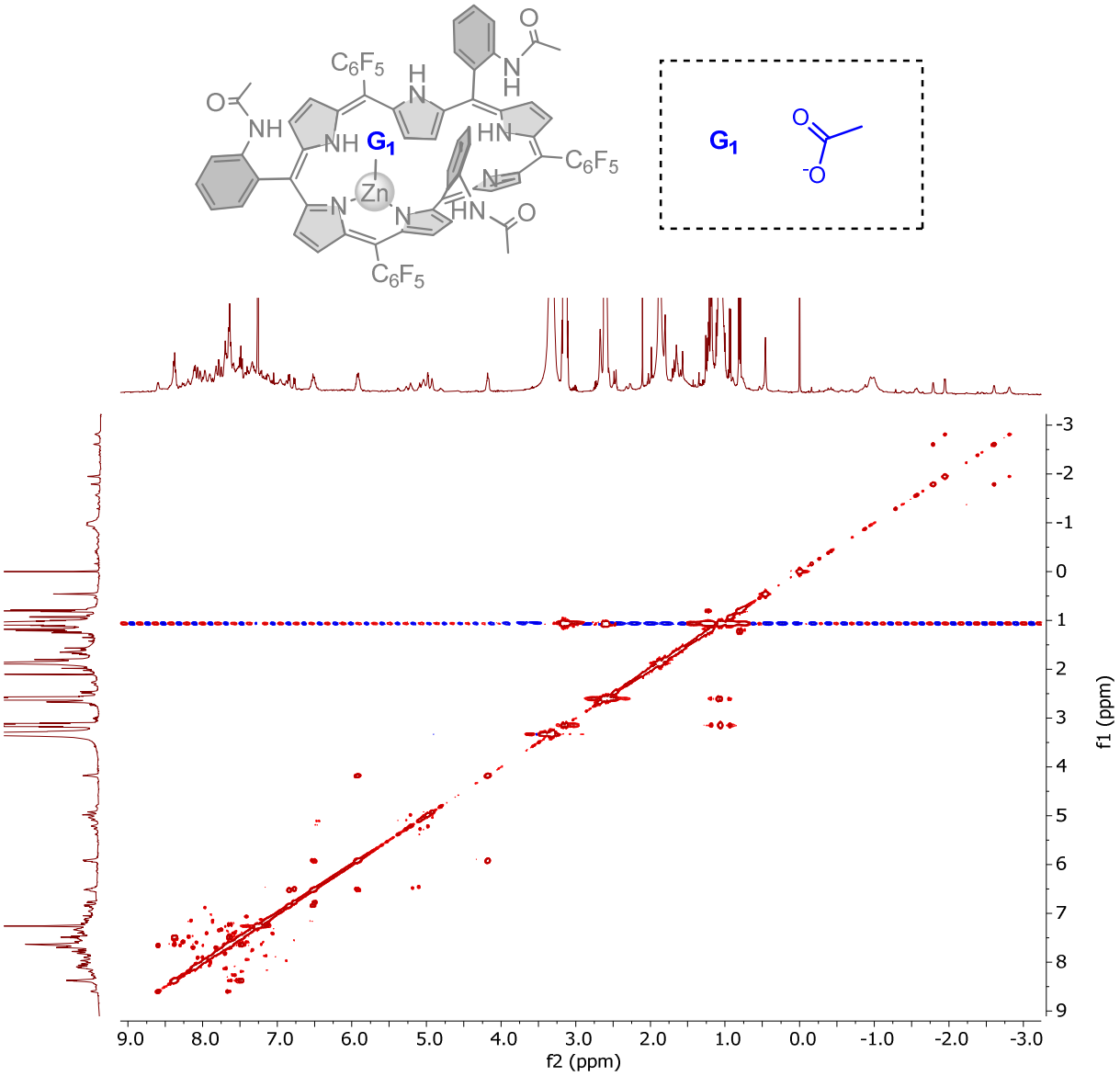


Figure S8. 2D COSY NMR spectrum of **2.Zn$_{OAc}$** ($CDCl_3$/CD_3OD 9:1, 500 MHz, 298 K).

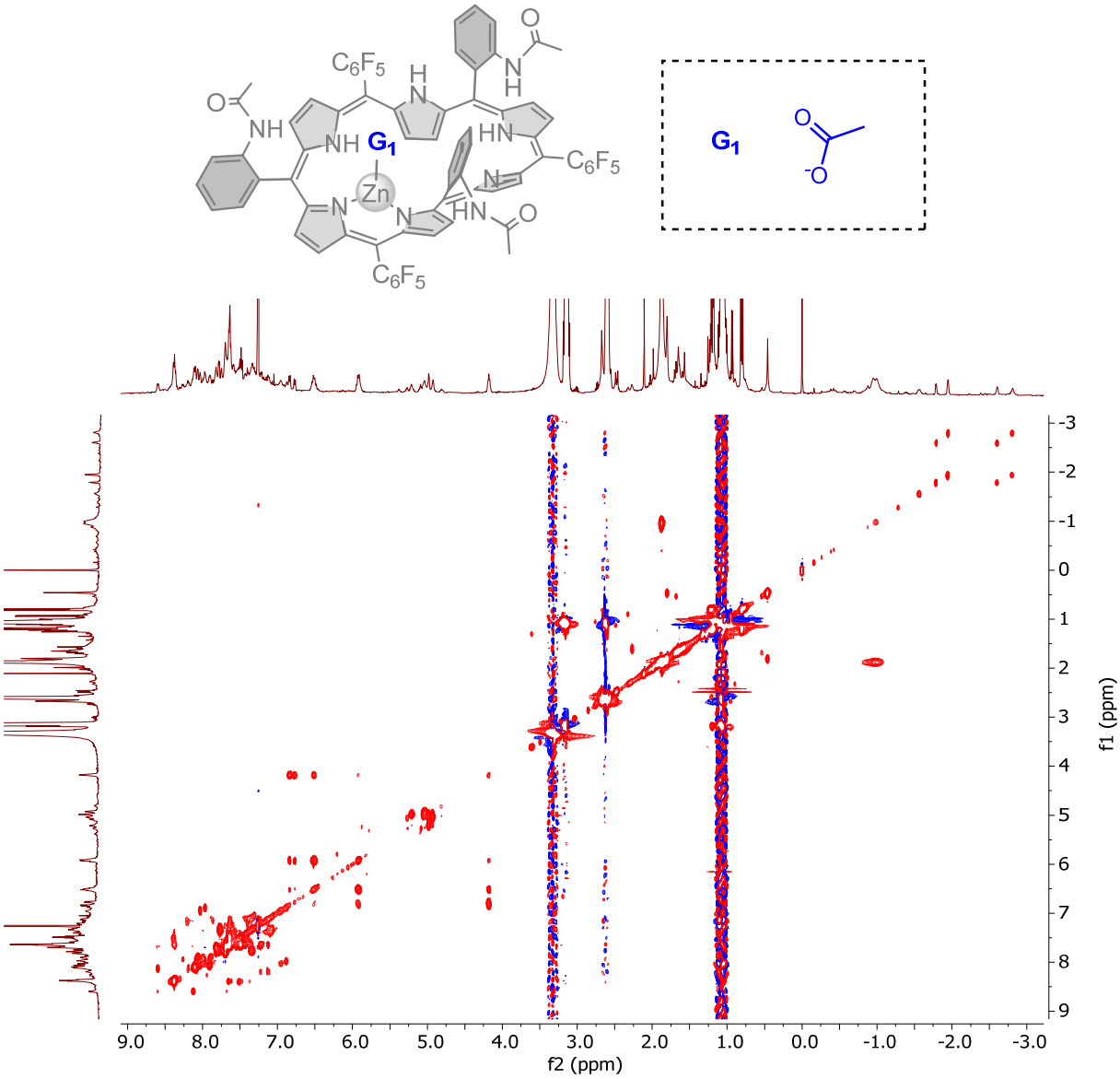


Figure S9. 2D TOCSY NMR spectrum of **2.Zn$_{OAc}$** ($CDCl_3$/CD_3OD 9:1, 500 MHz, 298 K).

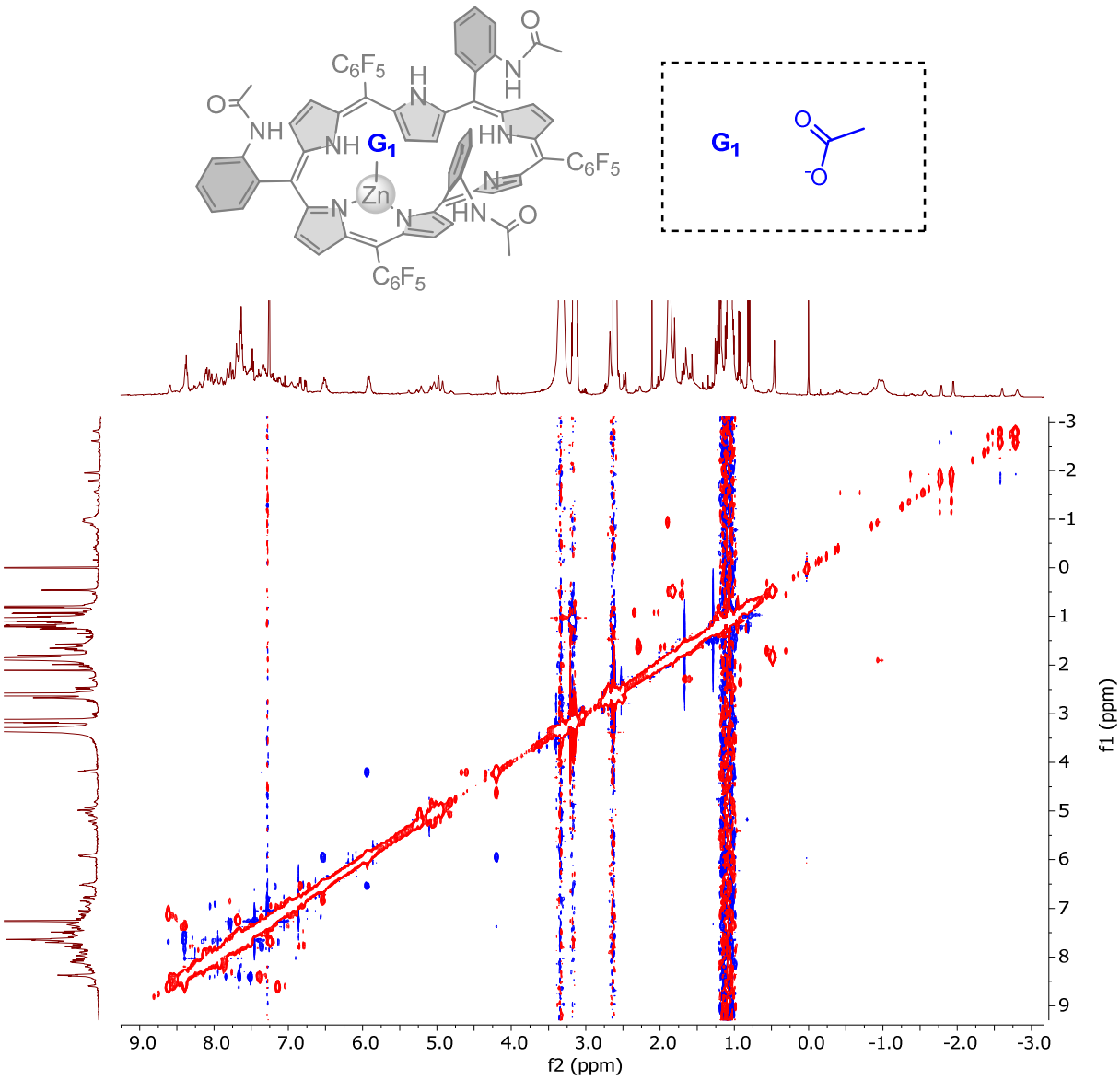
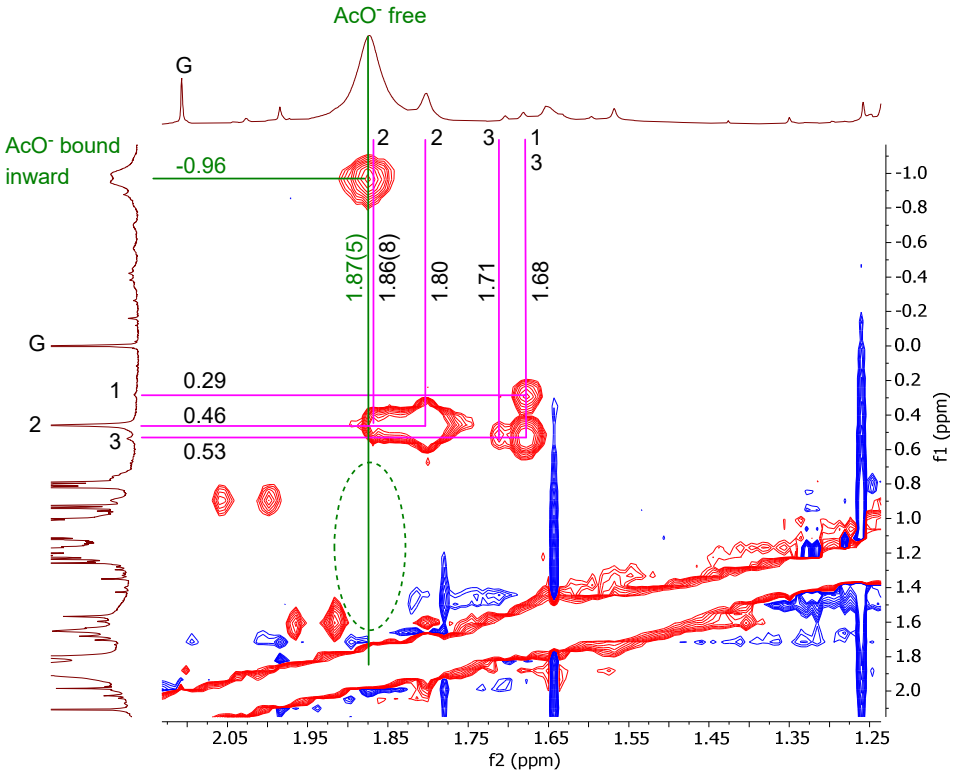


Figure S10. 2D ROESY NMR spectrum of **2.Zn$_{OAc}$** ($CDCl_3$/CD_3OD 9:1, 500 MHz, 298 K). Next page: selected expanded view showing exchange correlations involving the AcO^- ligand (highlighted in green), and those involving the *meso* 2-acetamidophenyl (atropisomerism phenomenon, highlighted in pink; CH_3 moieties in exchange labelled 1, 2 and 3). There are no observable exchange correlations involving the free AcO^-, in the expected region for a putative outward coordination (*i.e.* $\Delta\delta < 1$ ppm), represented by a dashed green circle. G = grease.


AcO⁻ free
G
AcO⁻ bound
inward
-0.96
2
2
3
1
3
1.87(5)
1.86(8)
1.80
1.71
1.68
G
1
2
3
0.29
0.46
0.53
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
f1 (ppm)
2.05
1.95
1.85
1.75
1.65
1.55
1.45
1.35
1.25
f2 (ppm)

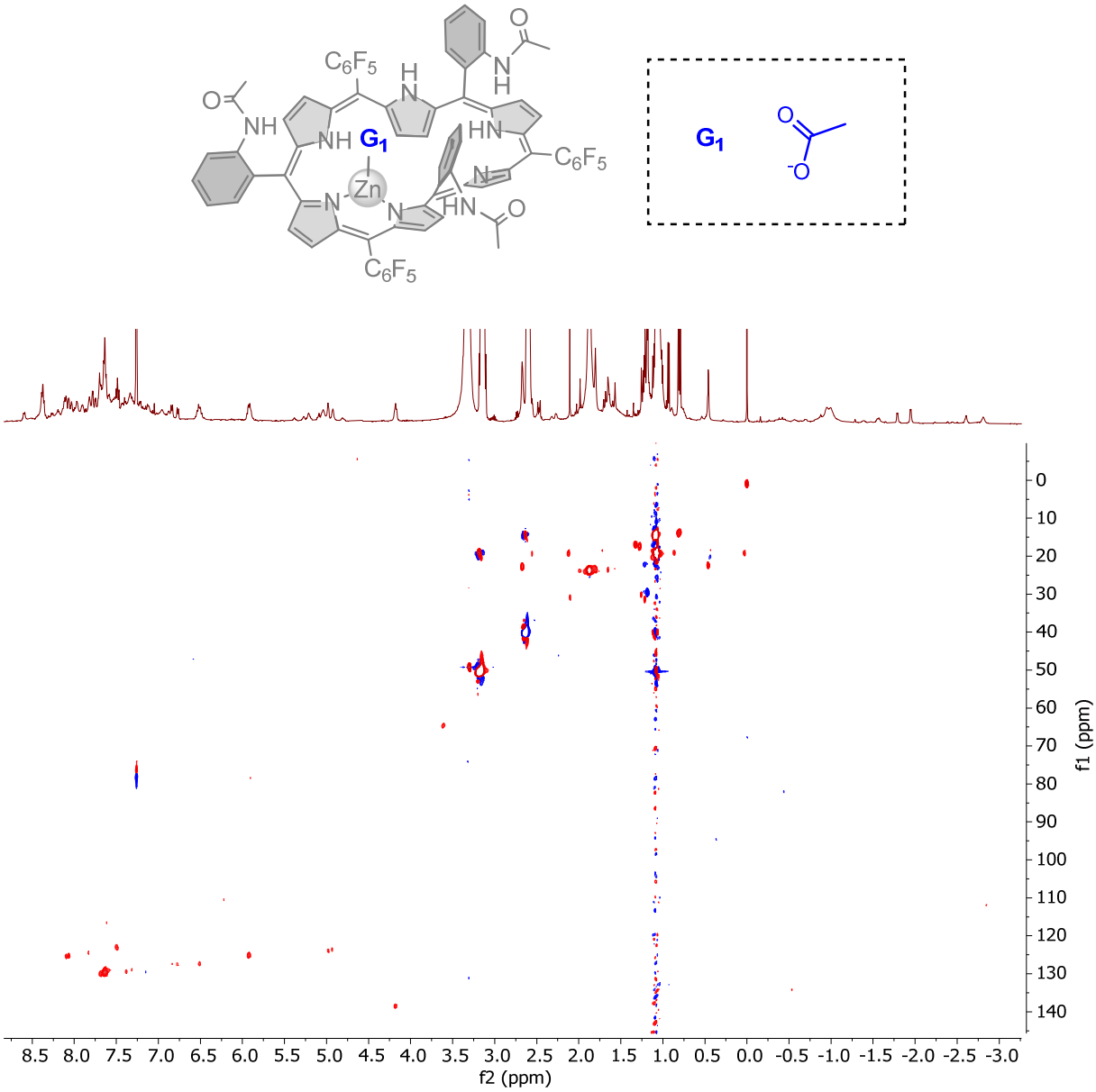


Figure S11. 2D HSQC NMR spectrum of **2.Zn$_{OAc}$** ($CDCl_3$/CD_3OD 9:1, 500 MHz, 298 K).

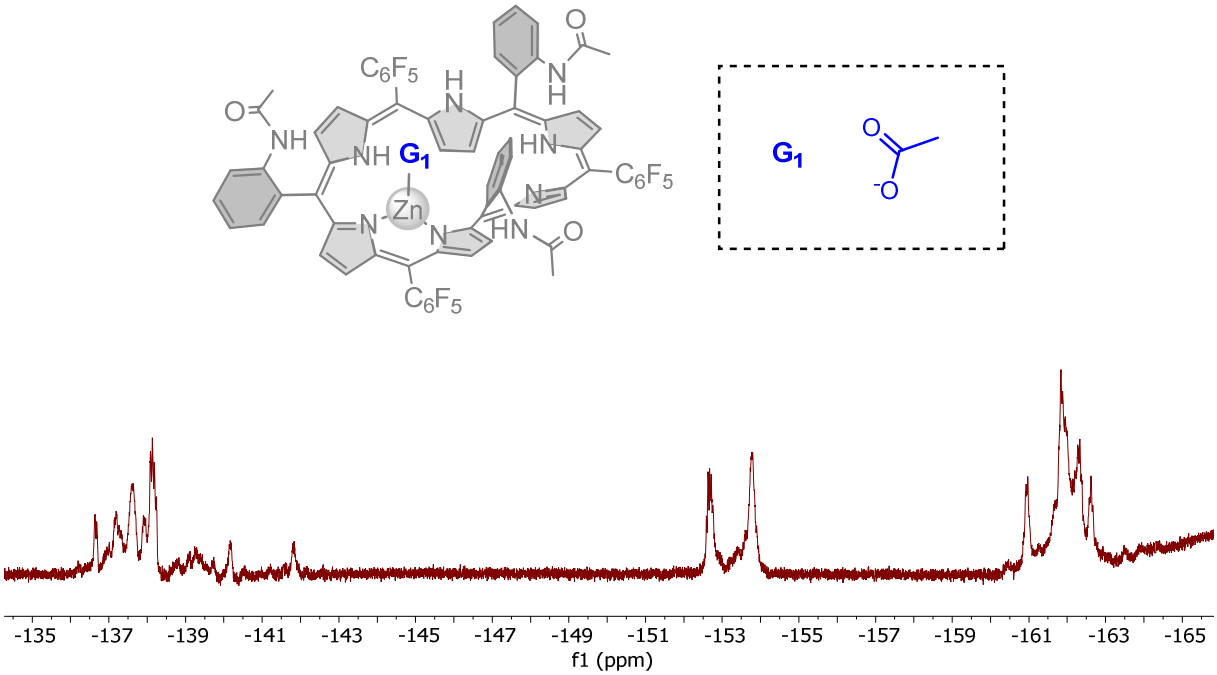


Figure S12. ^{19}F NMR spectrum of **2.Zn$_{OAc}$** ($CDCl_3$/CD_3OD 9:1, 470 MHz, 298 K).

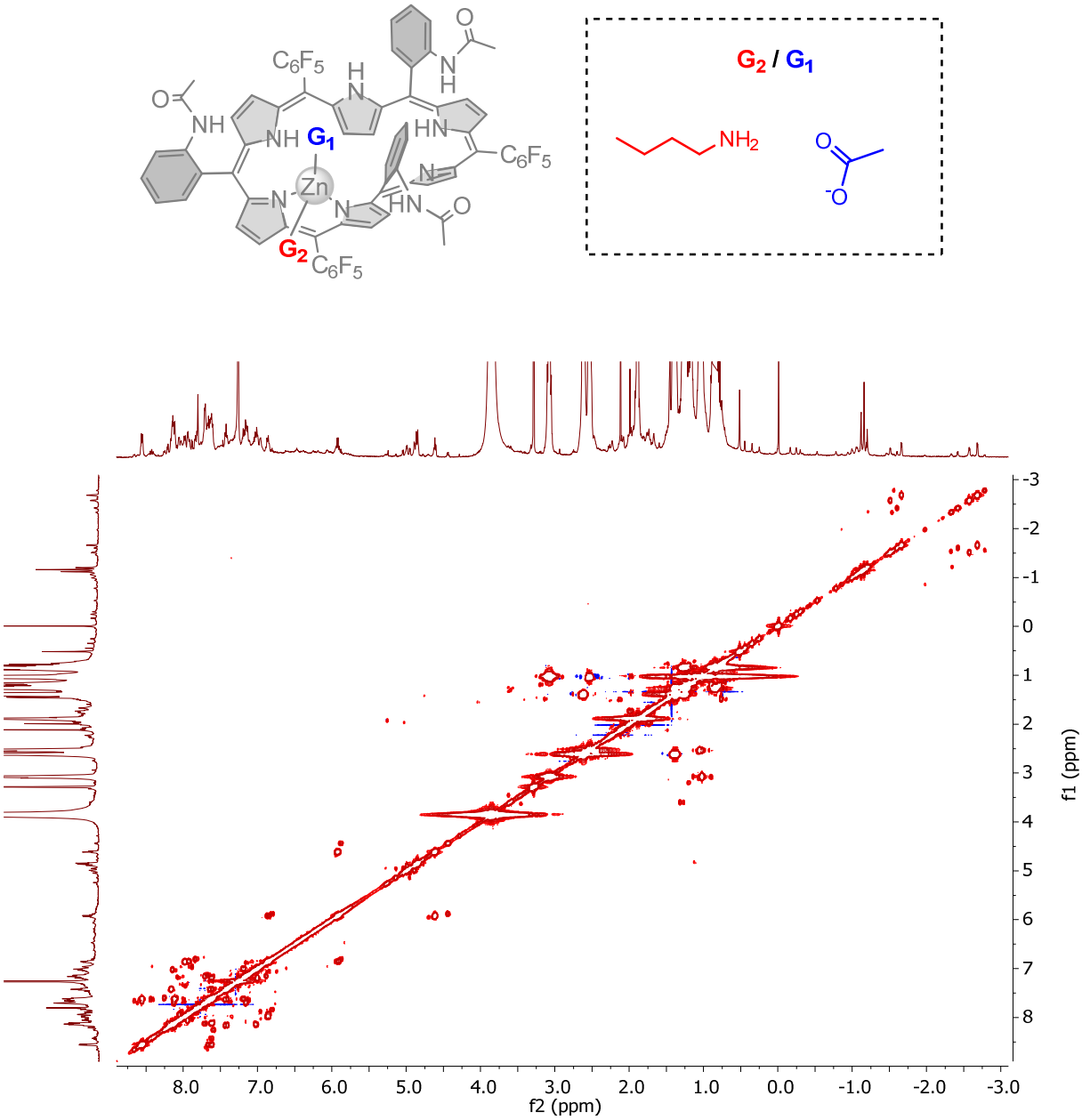


Figure S13. 2D COSY NMR spectrum of **2.Zn$_{OAc}^{NH2Bu}$** ($CDCl_3$/CD_3OD 9:1, 500 MHz, 278 K).

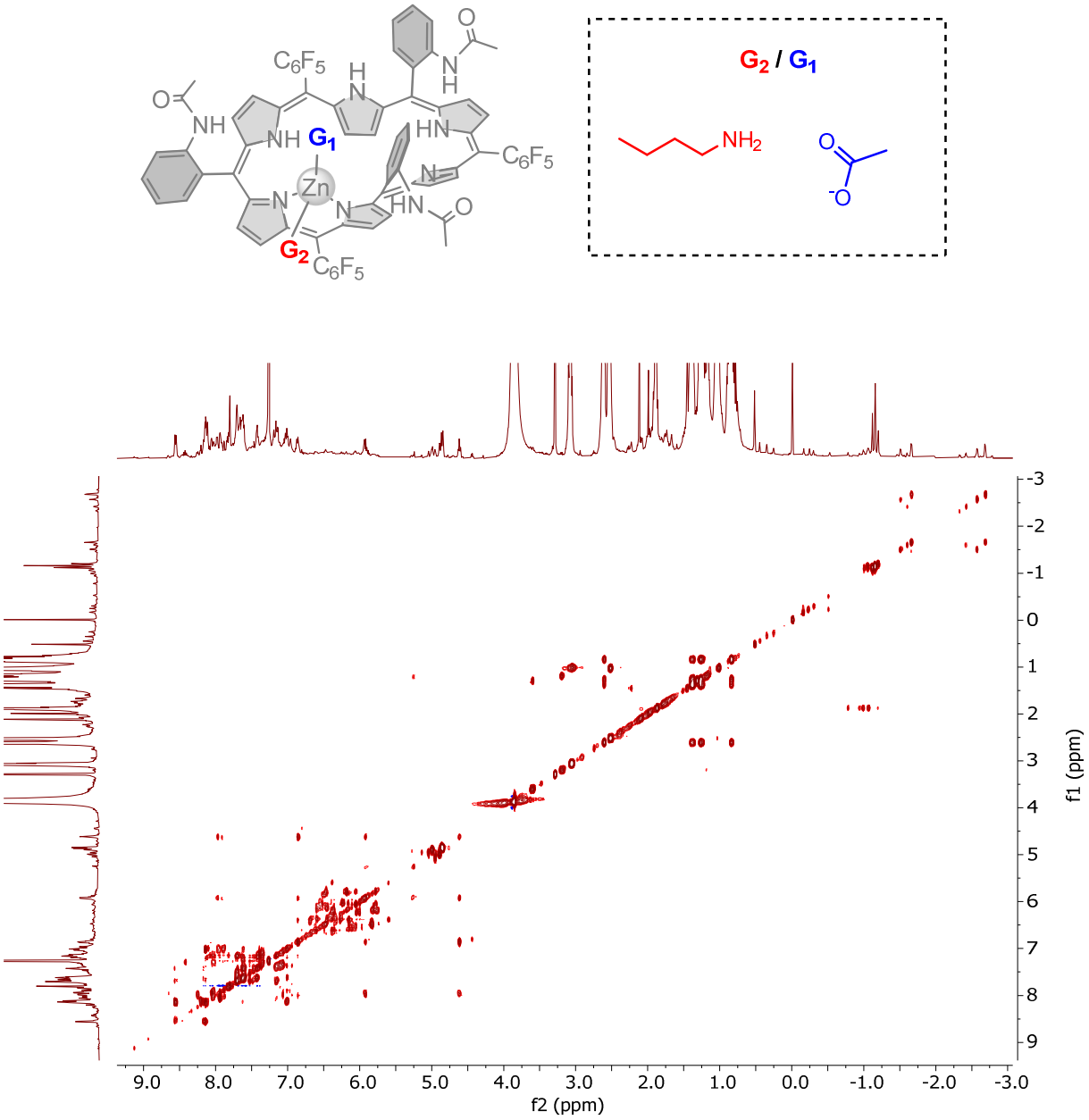


Figure S14. 2D TOCSY NMR spectrum of **2.Zn$_{OAc}^{NH2Bu}$** ($CDCl_3$/CD_3OD 9:1, 500 MHz, 278 K).

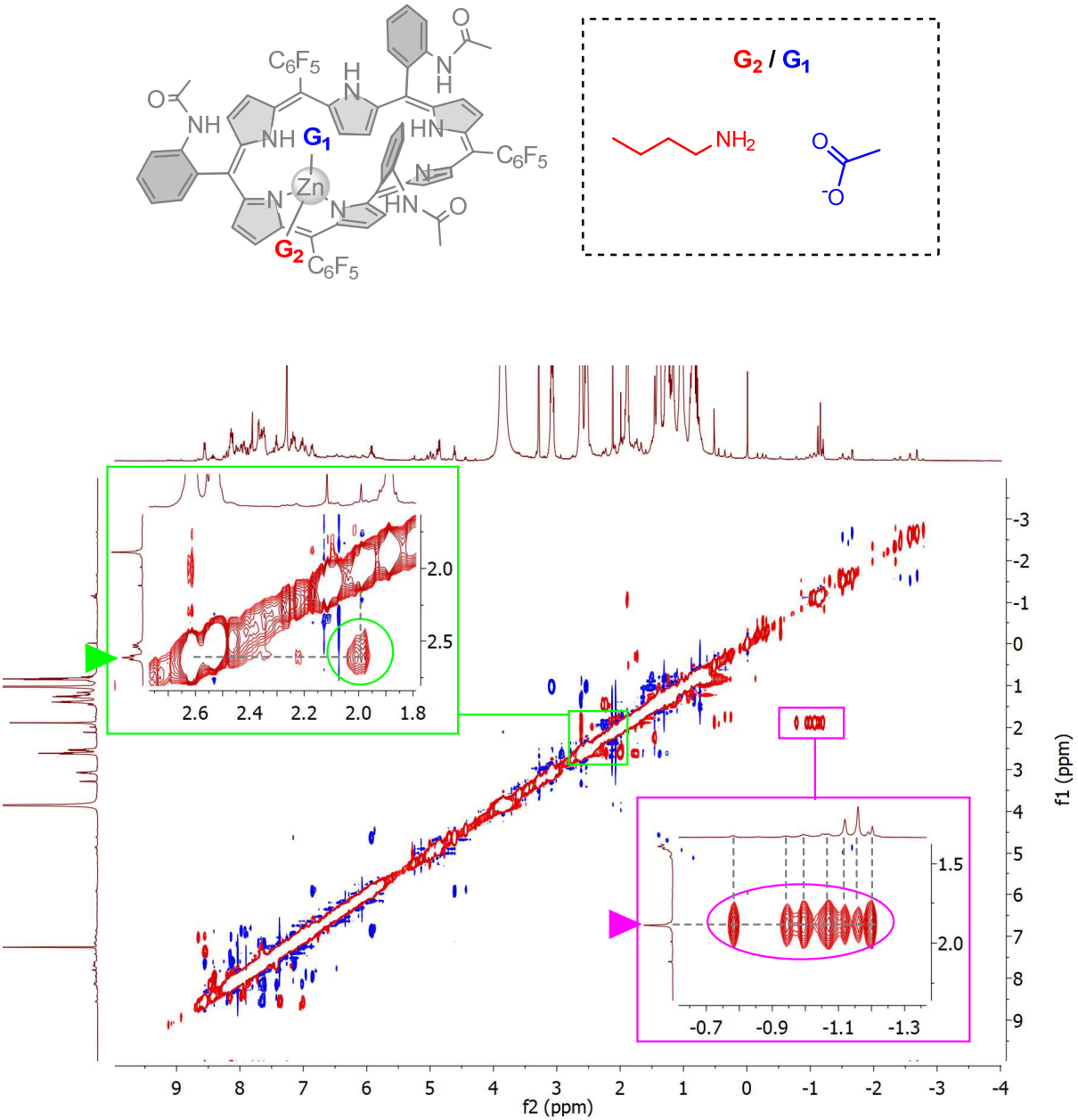


Figure S15. 2D ROESY NMR spectrum of **2.Zn$_{OAc}^{NH2Bu}$** ($CDCl_3$/CD_3OD 9:1, 500 MHz, 278 K). Pink and green frames correspond to expanded views on exchange correlations for respectively the acetato and butylamino (NC*H*$_2$) protons (pink and green triangles indicate signals of the free guests).

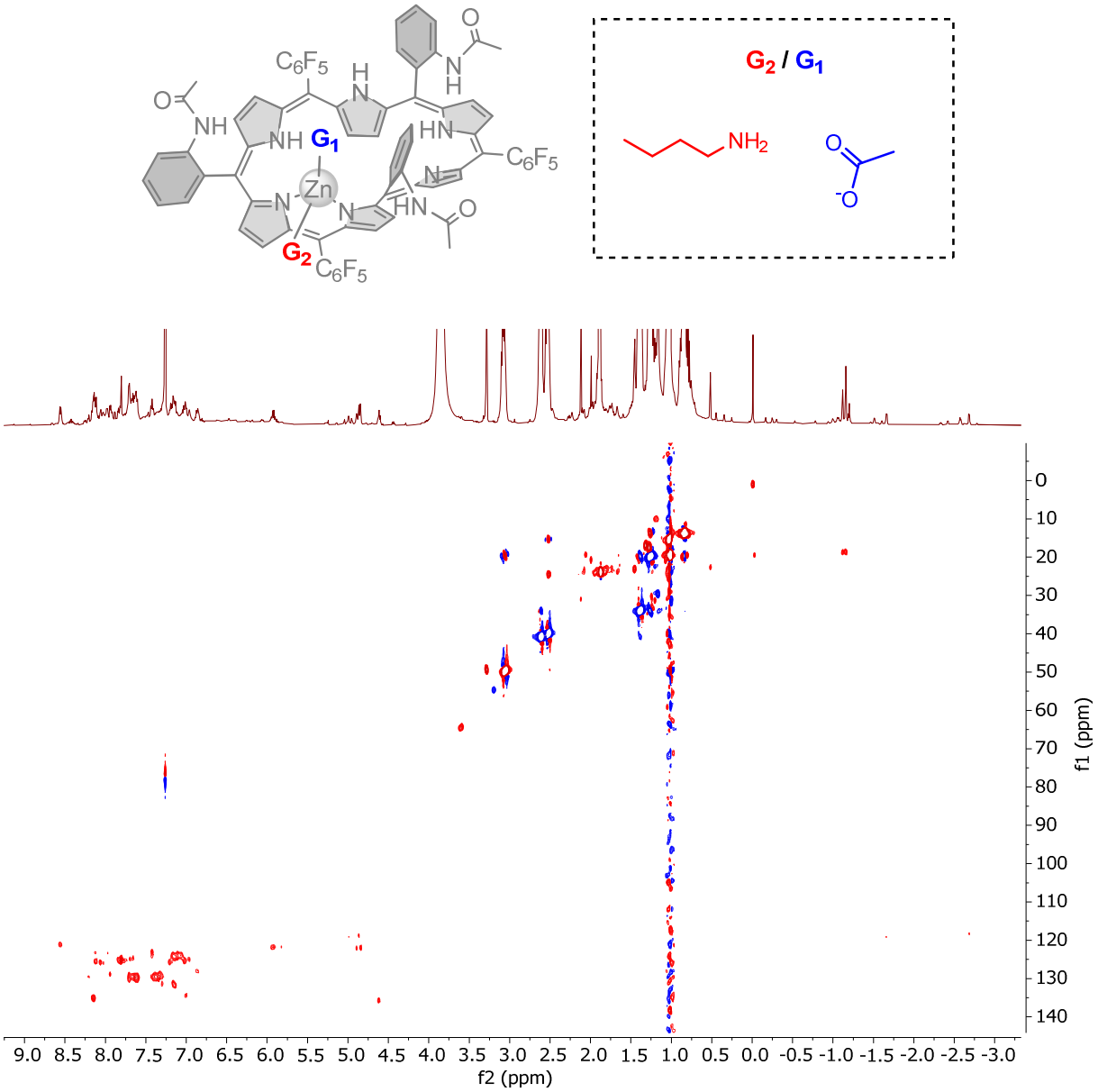


Figure S16. 2D HSQC NMR spectrum of **2.Zn$_{OAc}^{NH2Bu}$** ($CDCl_3$/CD_3OD 9:1, 500 MHz, 278 K).

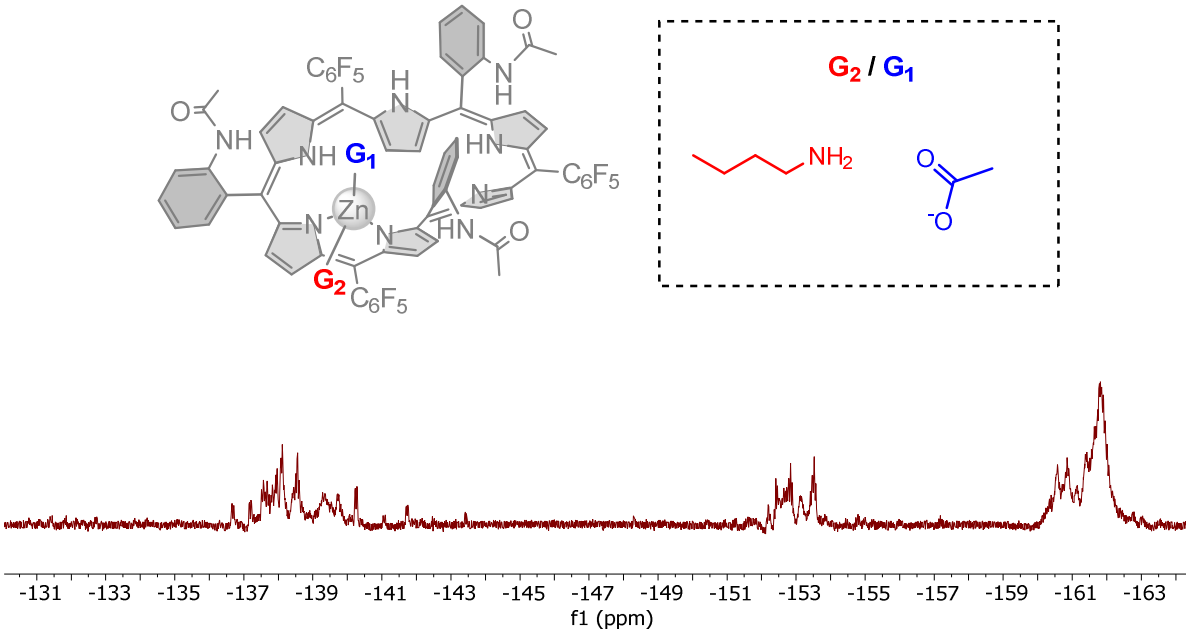


Figure S17. ^{19}F NMR spectrum of **2.Zn$_{OAc}^{NH2Bu}$** ($CDCl_3$/CD_3OD 9:1, 470 MHz, 278 K).

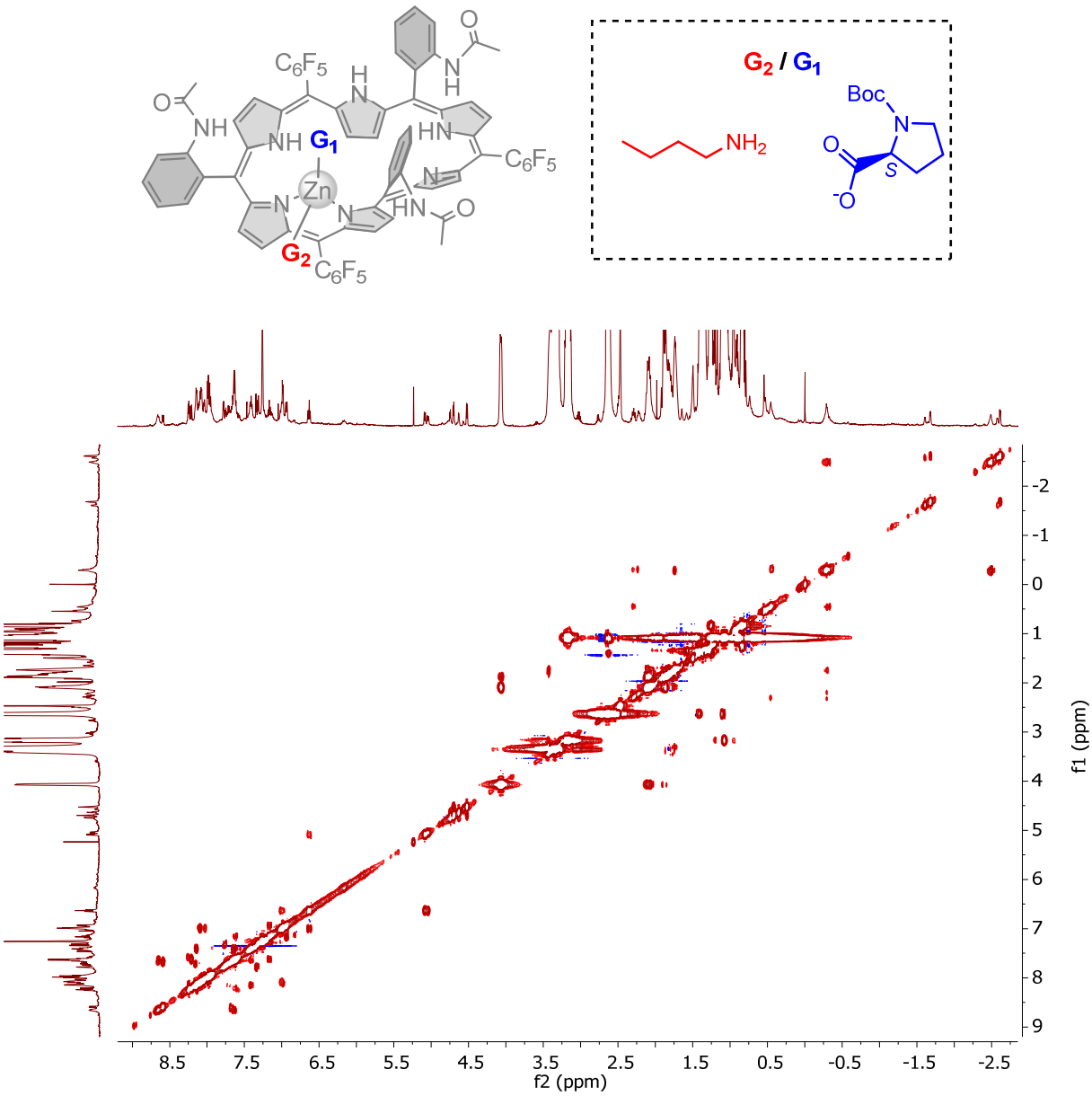


Figure S18. 2D COSY NMR spectrum of **2.Zn**$_{(S)\text{-BocProO}}^{NH2Bu}$ ($CDCl_3/CD_3OD$ 9:1, 500 MHz, 298 K).

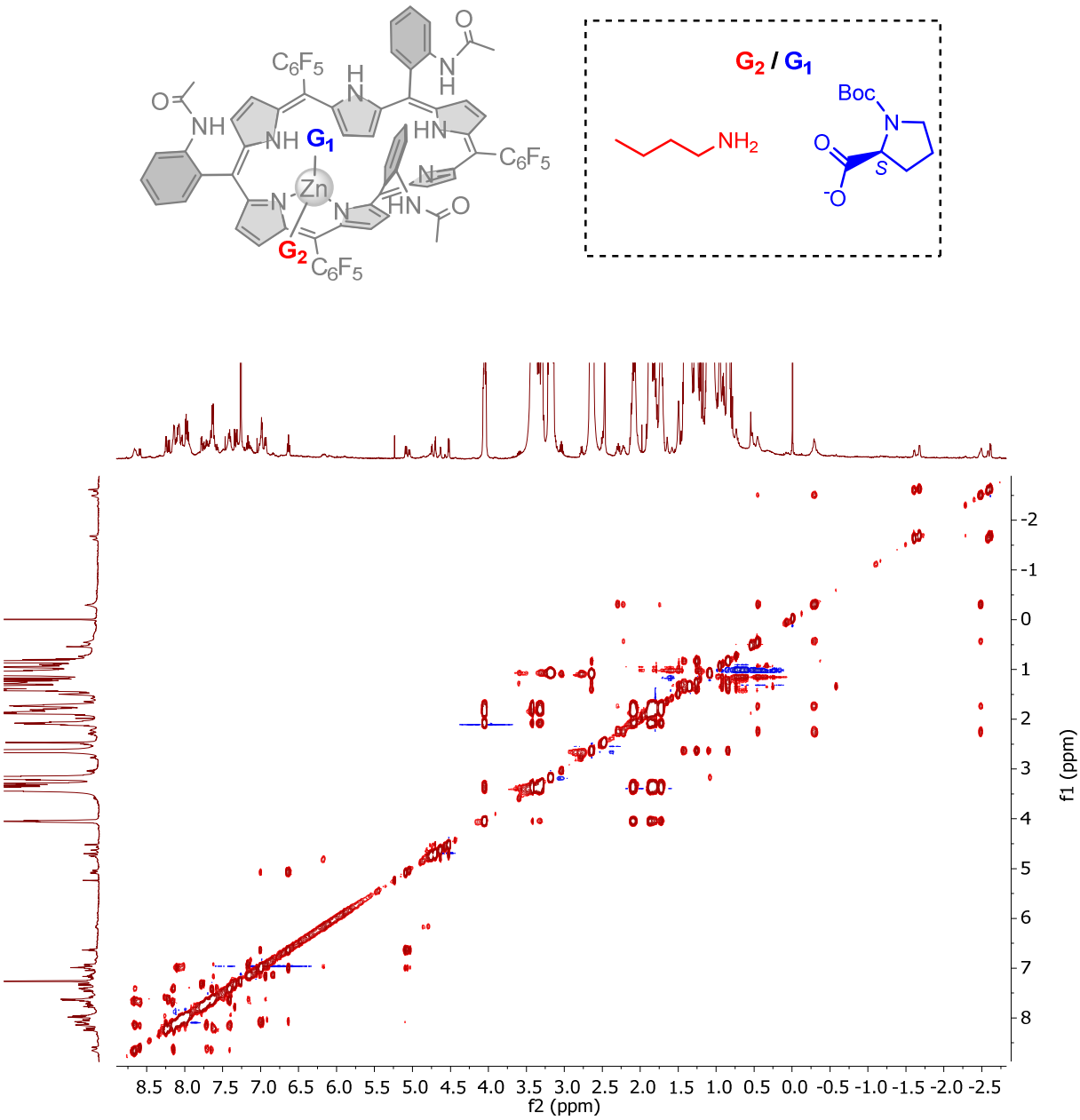


Figure S19. 2D TOCSY NMR spectrum of **2.Zn**$_{(S)\text{-BocProO}}^{NH2Bu}$ ($CDCl_3/CD_3OD$ 9:1, 500 MHz, 298 K).

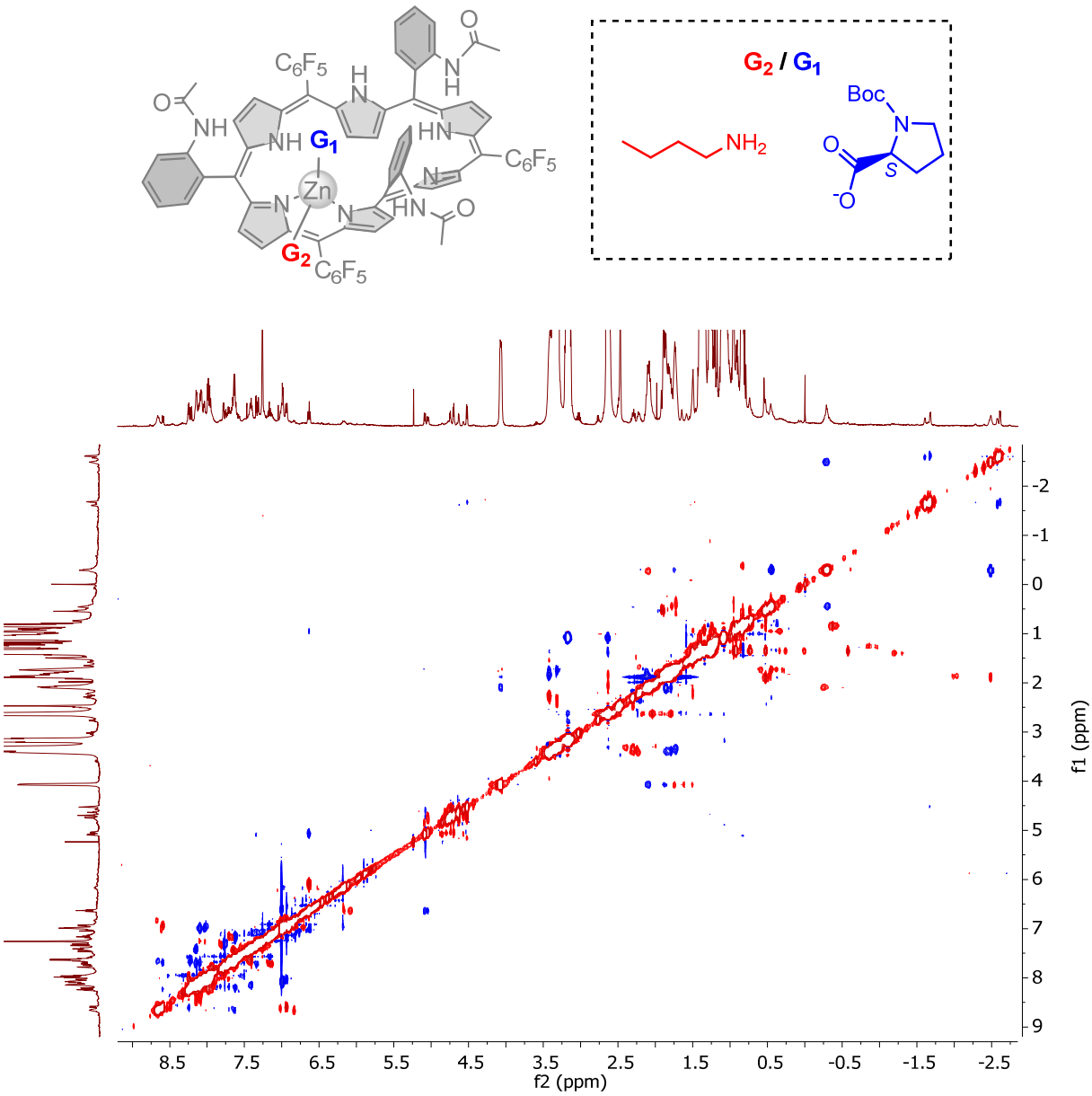
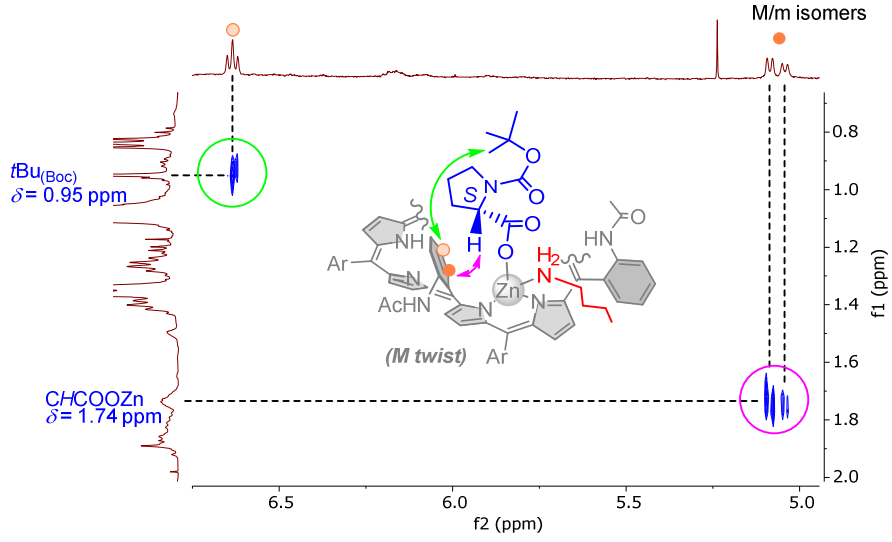


Figure S20. 2D ROESY NMR spectrum of **2.Zn**$_{(S)\text{-BocProO}}^{\text{NH2Bu}}$ ($CDCl_3/CD_3OD$ 9:1, 500 MHz, 298 K). Below: expanded view on selected NOE correlations (M/m stand for major/minor).



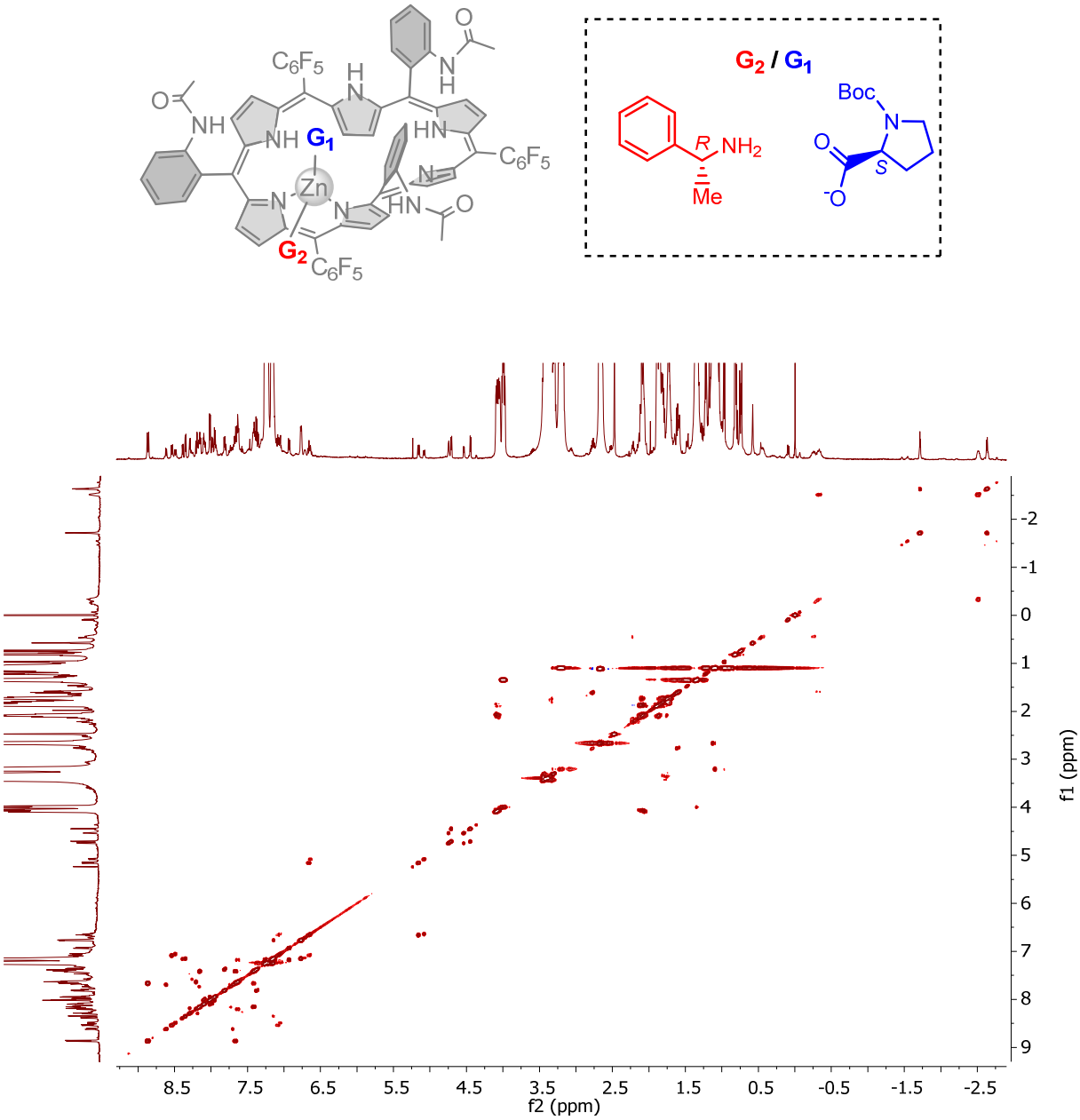


Figure S21. 2D COSY spectrum of **2.Zn**$_{(S)\text{-BocProO}}^{(R)\text{-MBA}}$ ($CDCl_3/CD_3OD$ 9:1, 500 MHz, 298 K).

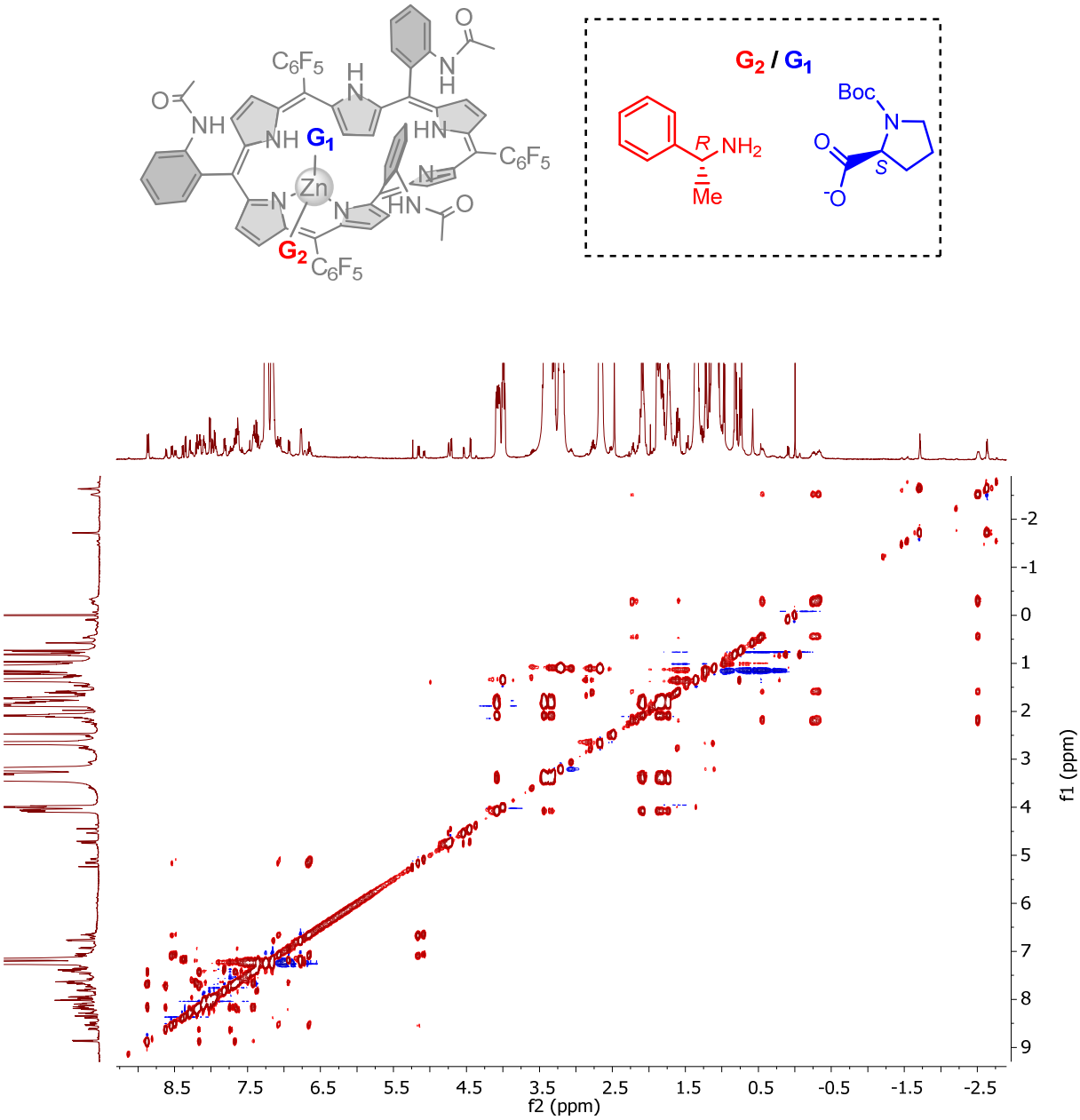


Figure S22. 2D TOCSY spectrum of **2.Zn**$_{(S)\text{-BocProO}}^{(R)\text{-MBA}}$ ($CDCl_3/CD_3OD$ 9:1, 500 MHz, 298 K).

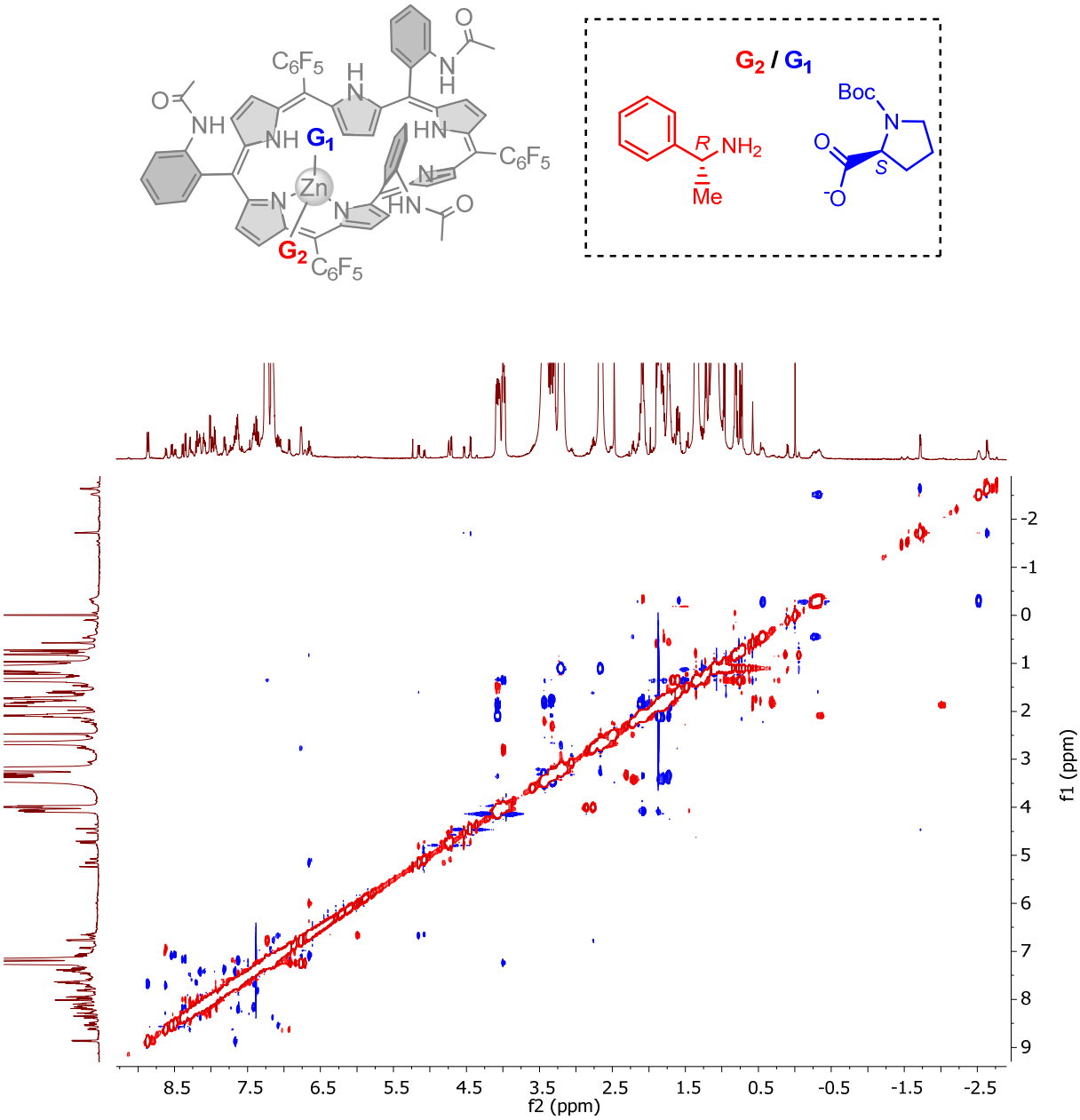


Figure S23. 2D ROESY spectrum of **2.Zn**$_{(S)\text{-BocProO}}^{(R)\text{-MBA}}$ ($CDCl_3/CD_3OD$ 9:1, 500 MHz, 298 K).

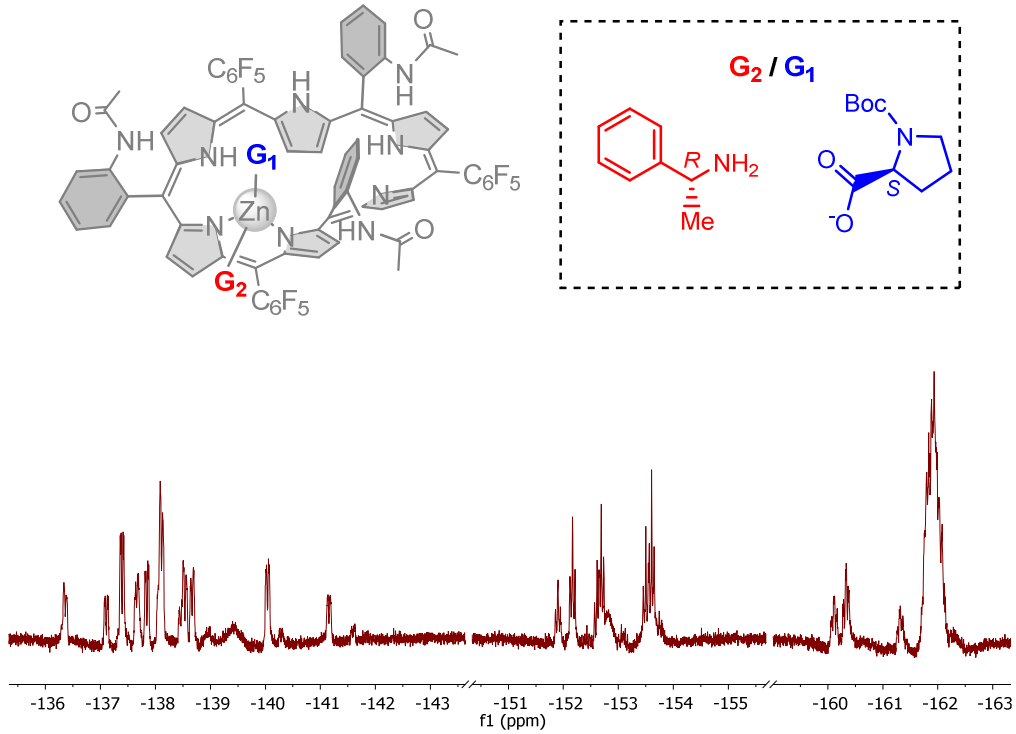


Figure S24. ^{19}F NMR spectrum of **2.Zn**$_{(S)\text{-BocProO}}^{(R)\text{-MBA}}$ ($CDCl_3/CD_3OD$ 9:1, 470 MHz, 298 K).

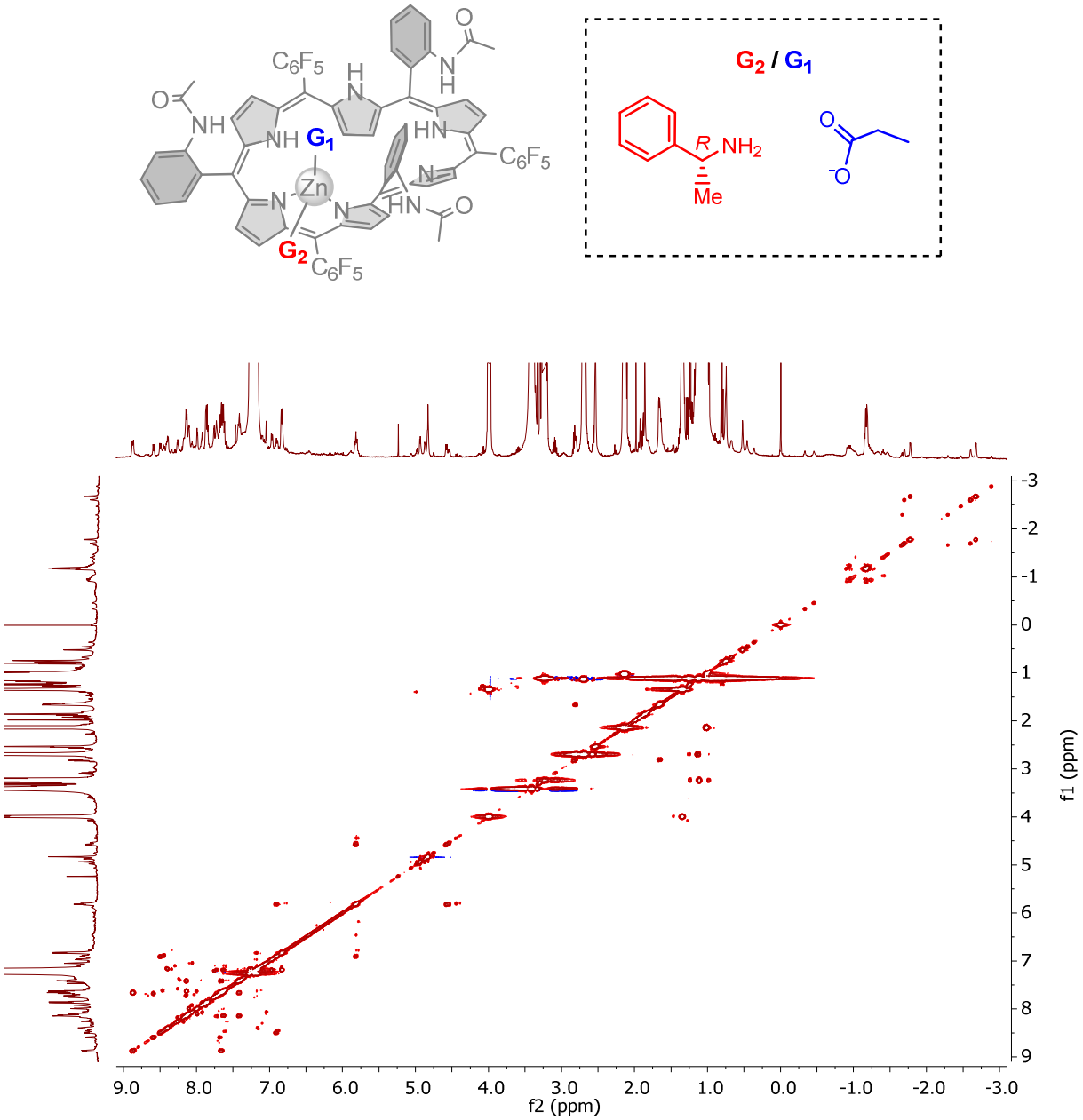


Figure S25. 2D COSY spectrum of **2.Zn$_{OOCEt}$**$^{(R)\text{-MBA}}$ ($CDCl_3$/CD_3OD 9:1, 500 MHz, 298 K).

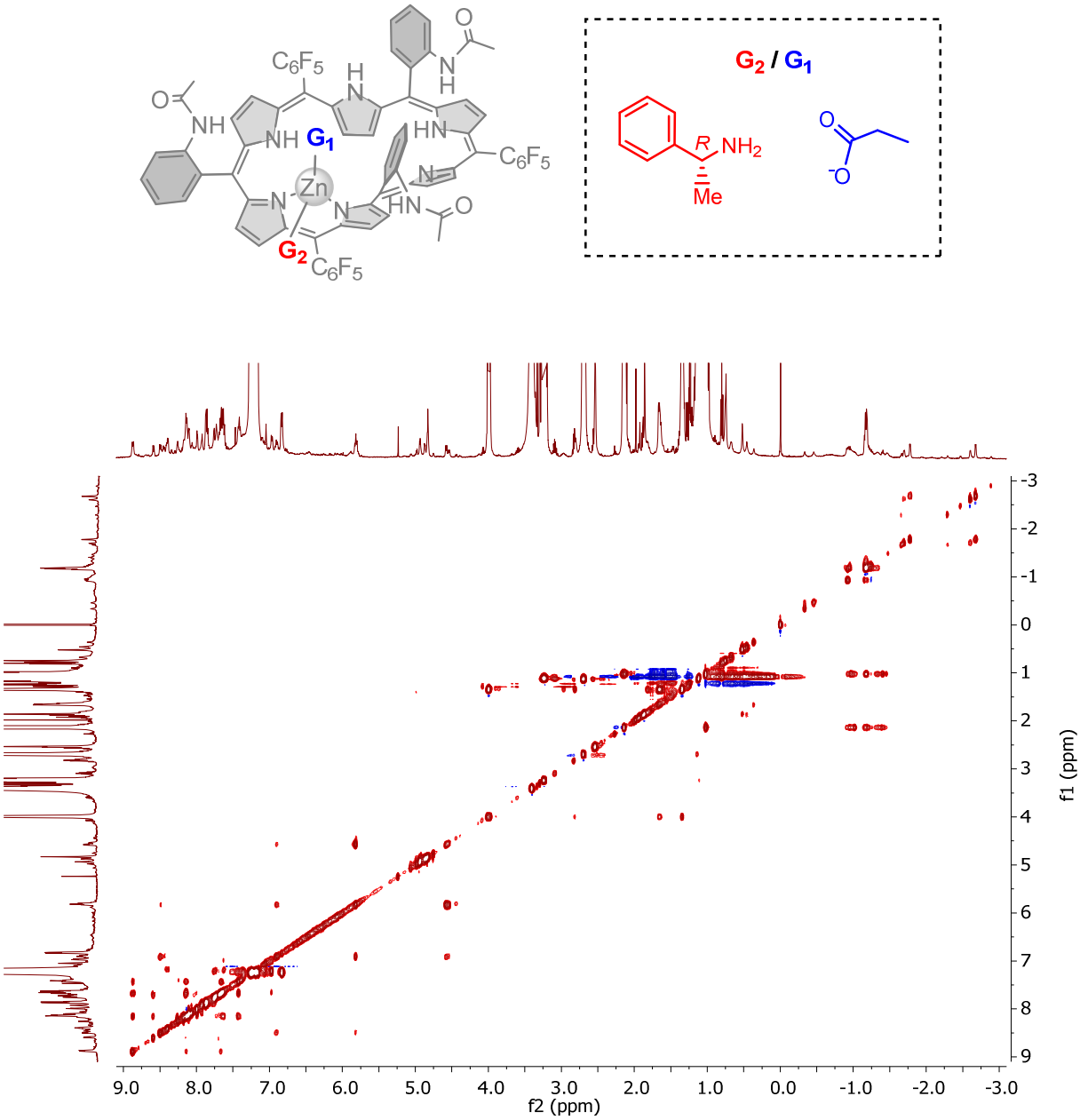


Figure S26. 2D TOCSY spectrum of **2.Zn$_{OOCEt}$**$^{(R)\text{-MBA}}$ ($CDCl_3$/CD_3OD 9:1, 500 MHz, 298 K).

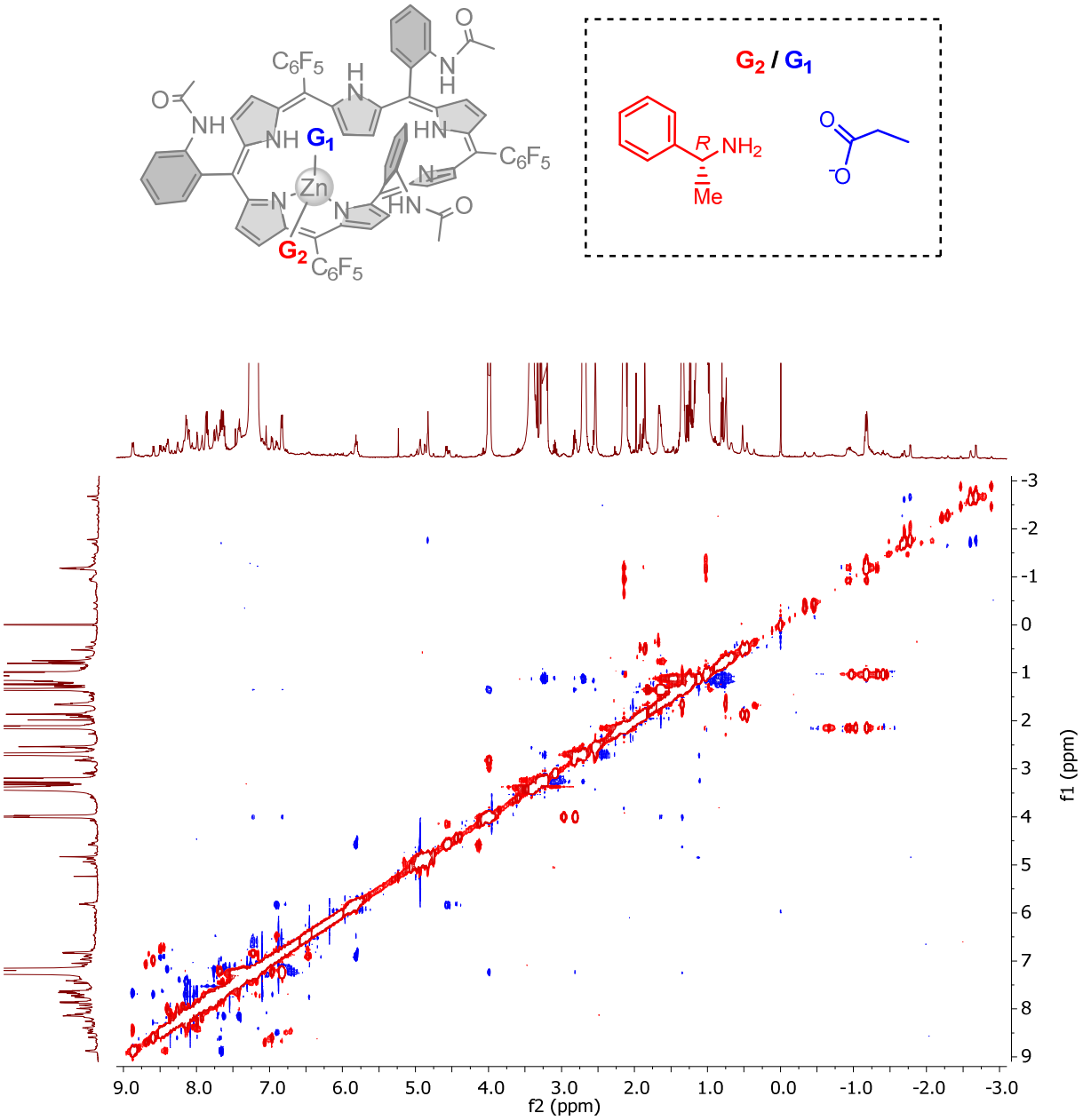


Figure S27. 2D ROESY spectrum of **2.Zn$_{OOCEt}$**$^{(R)\text{-MBA}}$ ($CDCl_3$/CD_3OD 9:1, 500 MHz, 298 K).

3. Selected UV-vis absorption and ECD spectra

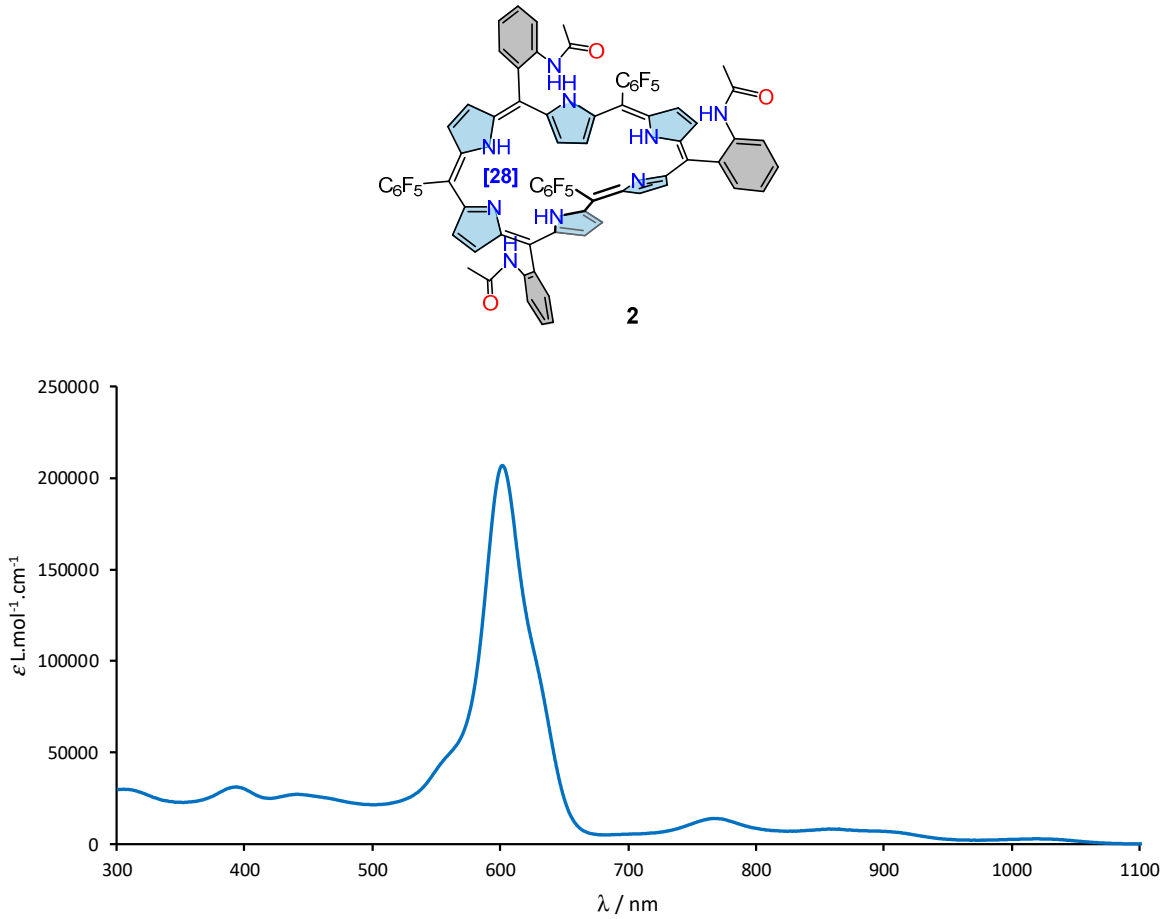


Figure S28. UV-vis-NIR absorption spectrum of **2** ($CHCl_3$).

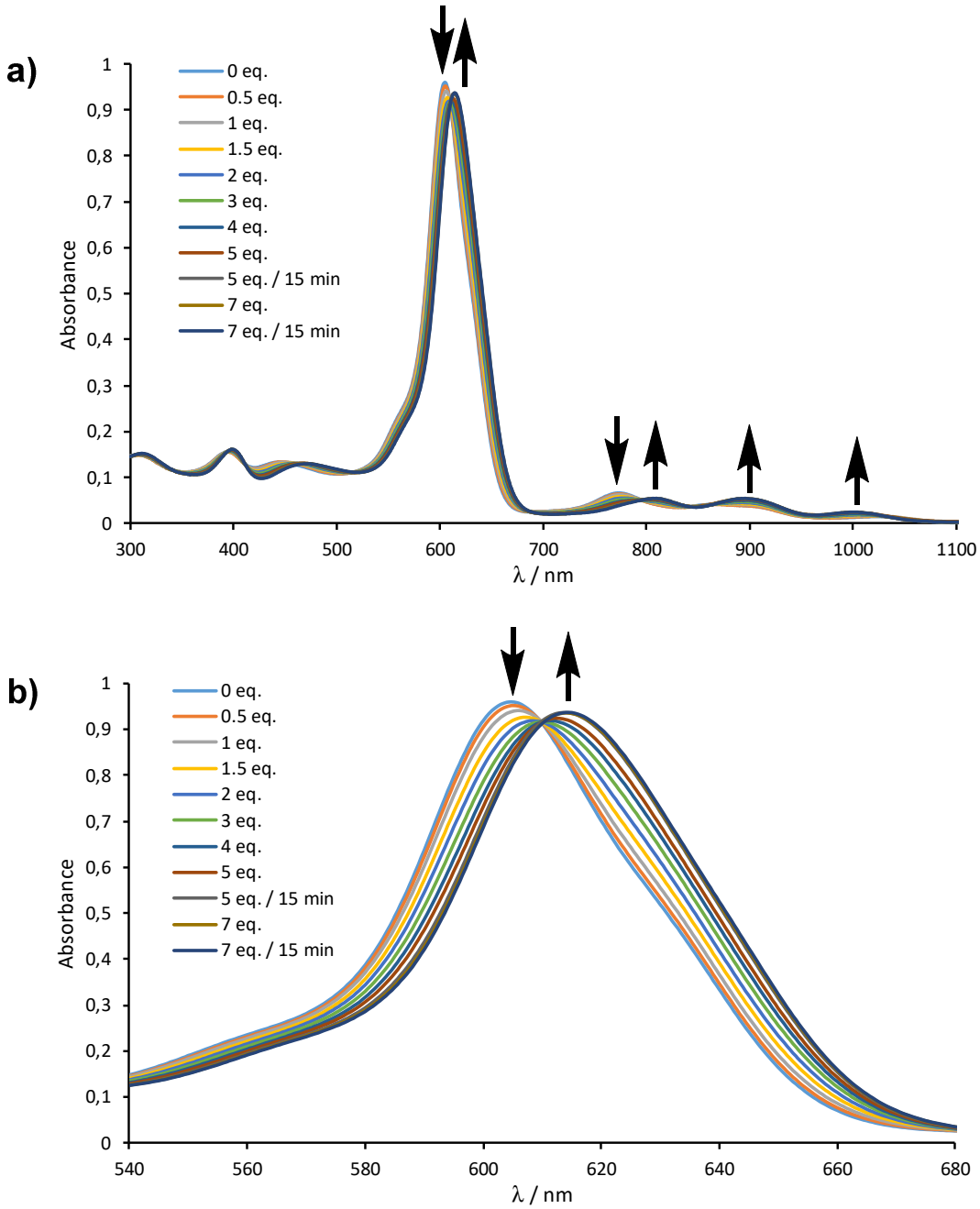


Figure S29. Titration of **2** by $Zn(OAc)_2$, monitored by UV-vis-NIR absorption spectroscopy ($CHCl_3$/MeOH 9:1, 5 µM, 20 eq. DIPEA): (a) full spectrum, (b) expanded view on the Soret-like band.

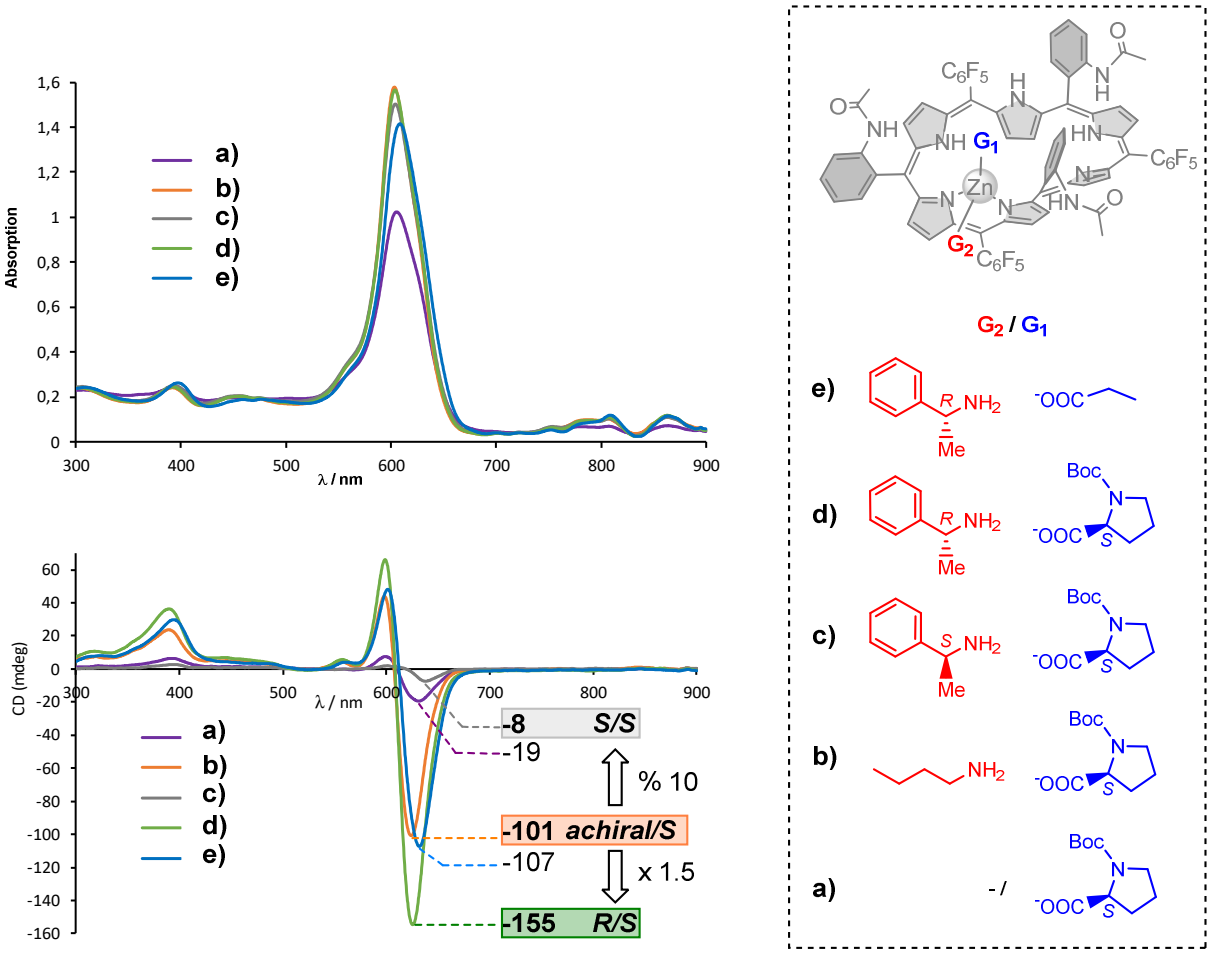


Figure S30. UV-vis absorption and ECD spectra for the metallation of **2** with $Zn(OTf)_2$/DIPEA ($CHCl_3$/MeOH 9:1), performed in the presence of different guest molecules: a) (*S*)-BocProO$^-$; b) $BuNH_2$ and (*S*)-BocProO$^-$; c) (*S*)-MBA and (*S*)-BocProO$^-$; d) (*R*)-MBA and (*S*)-BocProO$^-$; e) (*R*)-MBA and $EtCO_2^-$. ECD total concentration of **2**: 44 µM ($\Delta\varepsilon$ values and proportions of each species are not accessible).