Supplementary Material (ESI) for New Journal of Chemistry

On the synthesis of functionalized porphyrins and porphyrin conjugates *via* β–aminoporphyrins

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1. Table S1. Synthesis of β-nitroporphyrinate M-4a-g

Entry	Porphyrin (mmol)	$Cu(NO_3)_2 \cdot 3H_2O$ (equiv.)	Anhydride	$CHCl_3$/AcOH (mL/mL)	T	Time (h)	Yield (%)
1	**2H-1a** (0.5)	2.75	Acetic anhydride 31 mL	500/5	r.t.	16	68
2	**2H-1b** (0.5)	2.45	Acetic anhydride 15 mL	325/7.5	40 °C	0.5	90
3	**2H-1c** (0.47)	7	Acetic anhydride 42 mL	305/7	reflux	2	70
4	**2H-1d** (0.2)	5	Succinic anhydride 50 equiv.	130/3	r.t.	10	79
5	**2H-1e** (0.26)	4	Acetic anhydride 70 mL	-	r.t.-120°C	Heating to 120°C (15 min) and stirring (5 min)	82
6	**2H-1f** (1.0)	5	Succinic anhydride 50 equiv.	695/15	reflux	0.5	75
7	**Ni-1g** (0.65)	5	Succinic anhydride 50 equiv.	115/6	reflux	24	88

2. NMR spectra of β-aminoporphyrins 2H-2

Figure S1. ^{1}H NMR spectrum of 2H-2e ($CDCl_3$).

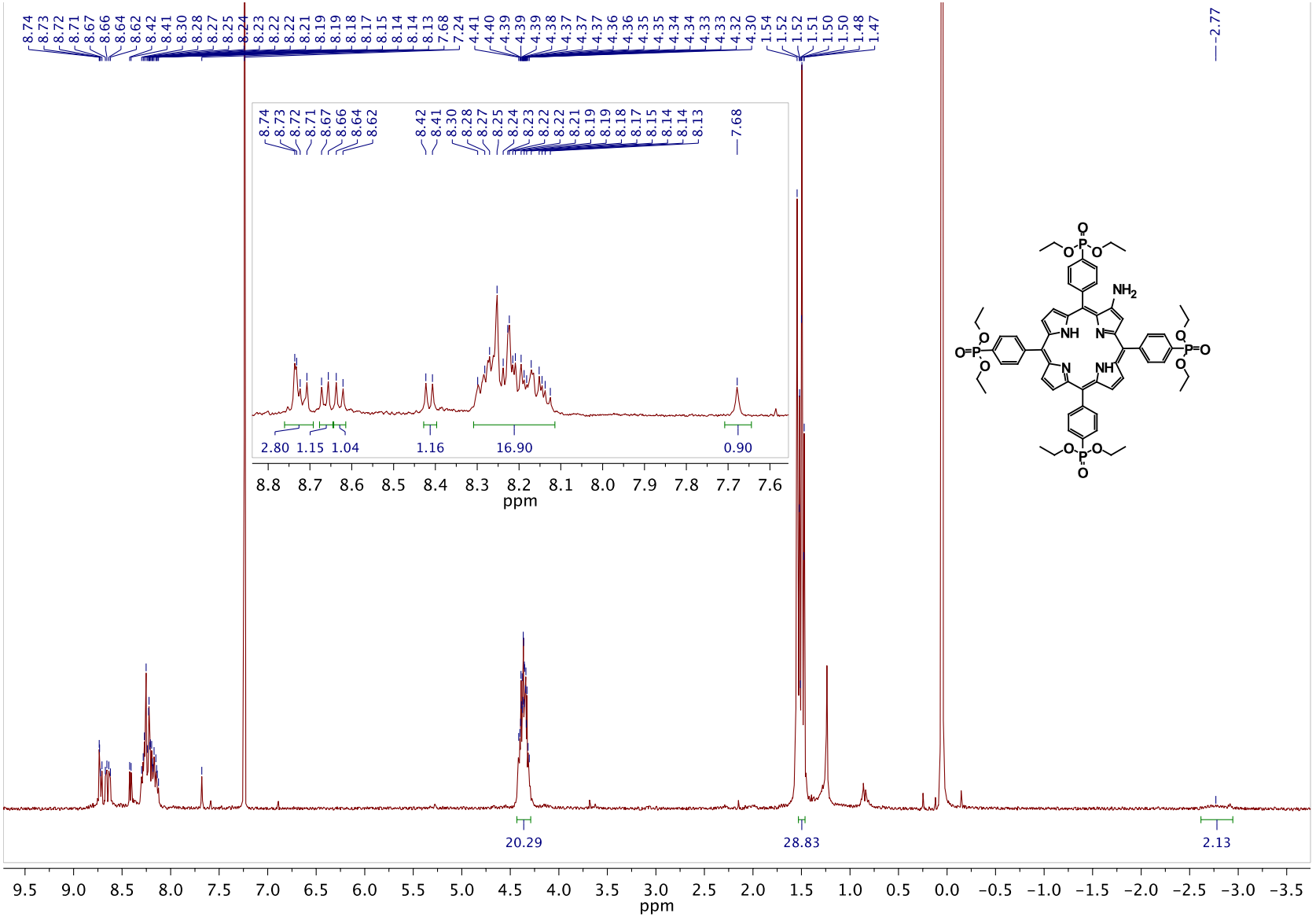


Figure S2. ^{31}P NMR spectrum of 2H-2e ($CDCl_3$).

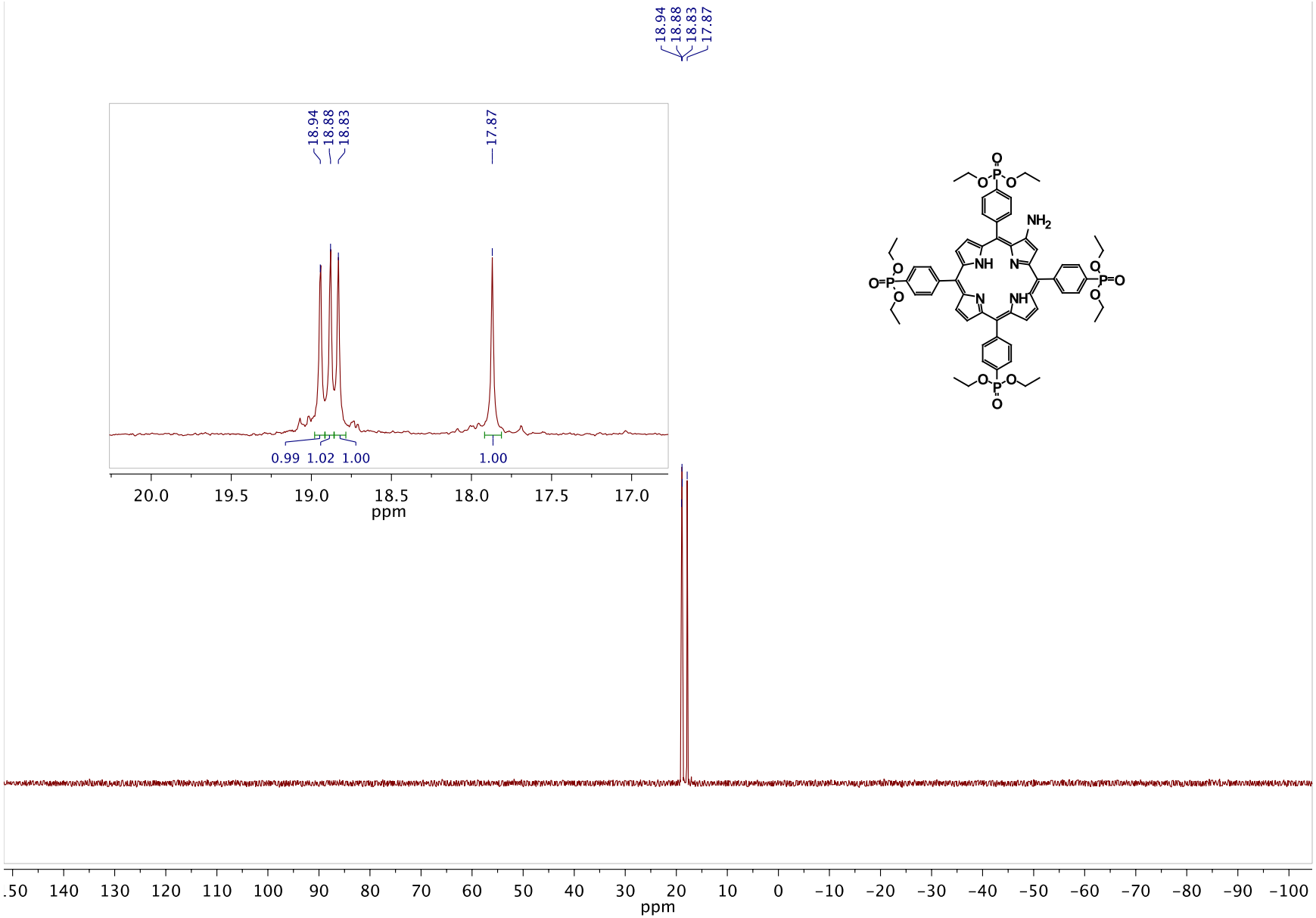
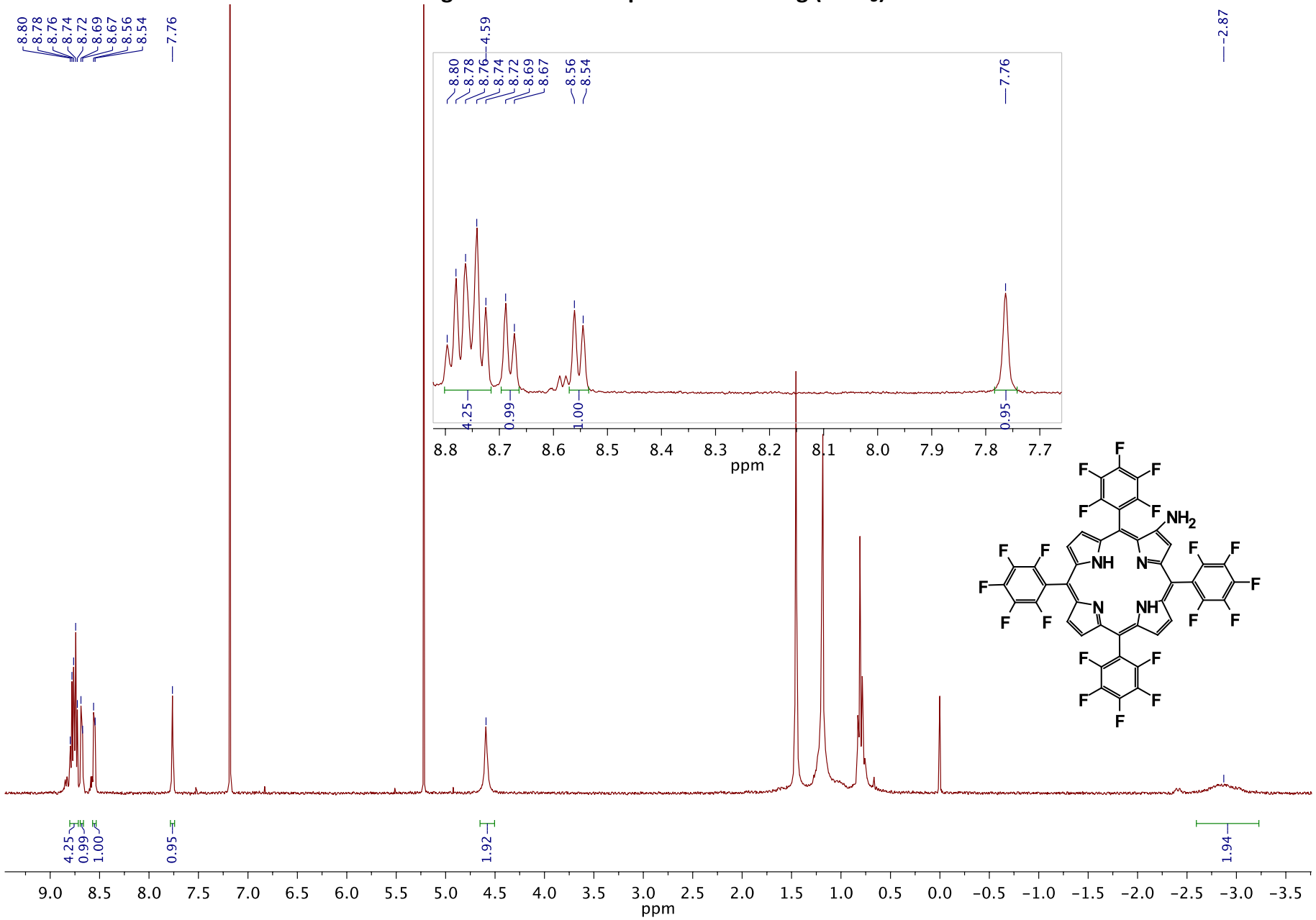


Figure S3. ^{1}H NMR spectrum of 2H-2g ($CDCl_3$).



3. **NMR spectra of conjugated porphyrins M-3**

Figure S4. ^{1}H NMR spectrum of 2H-3b ($CDCl_3$).

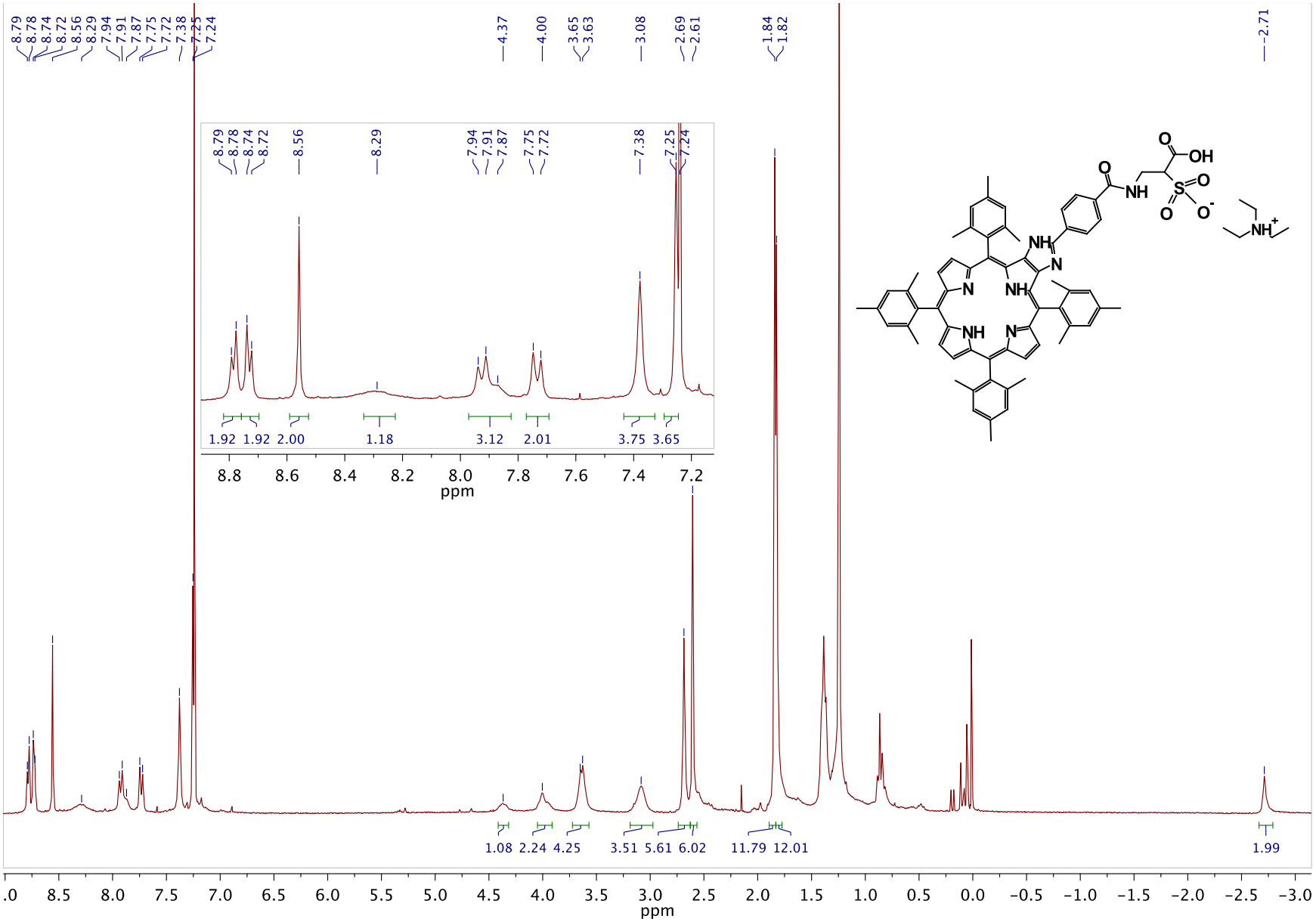


Figure S5. ^{1}H NMR spectrum of Zn-3e ($CDCl_3$+ MeOH-*d4*).

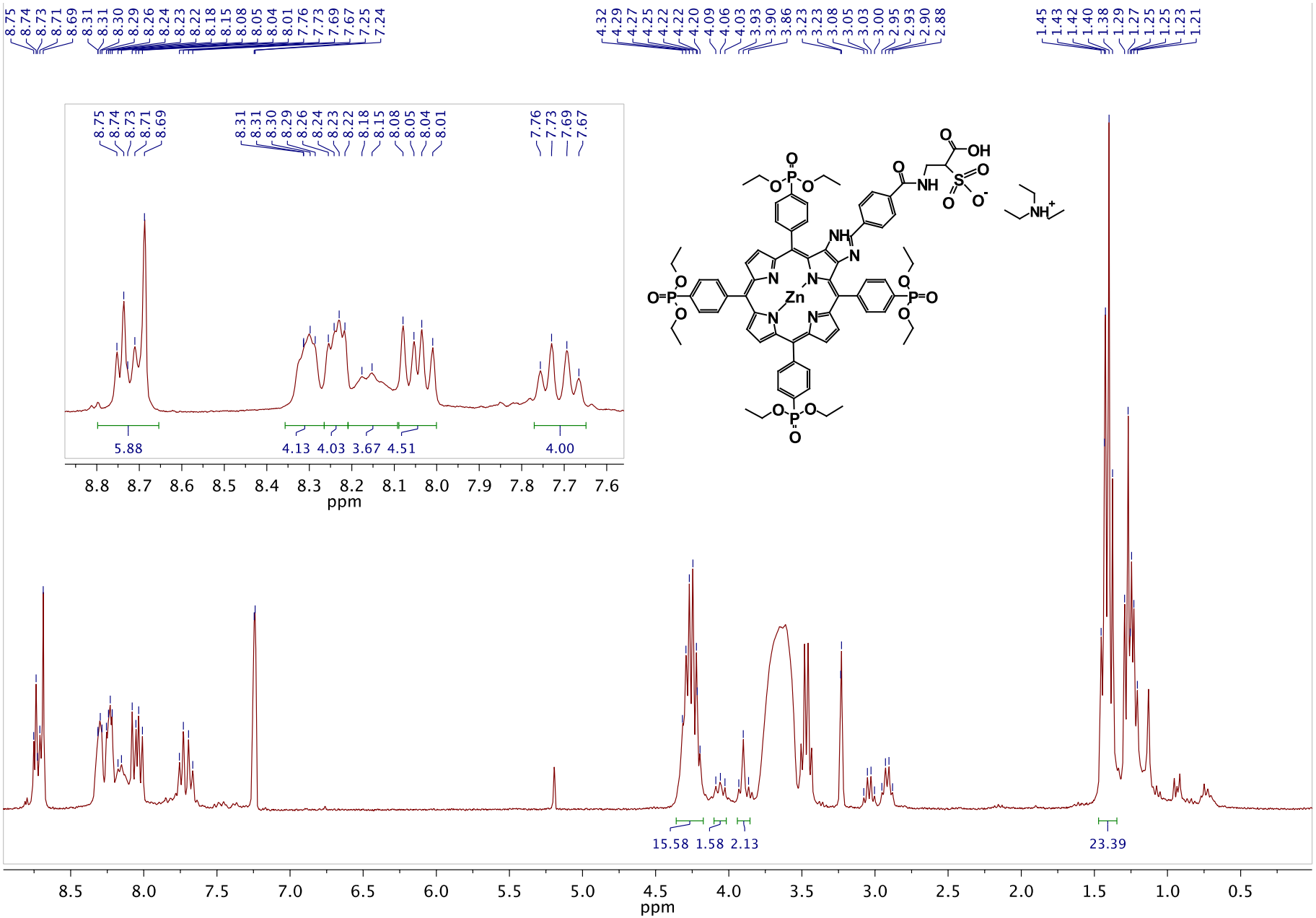
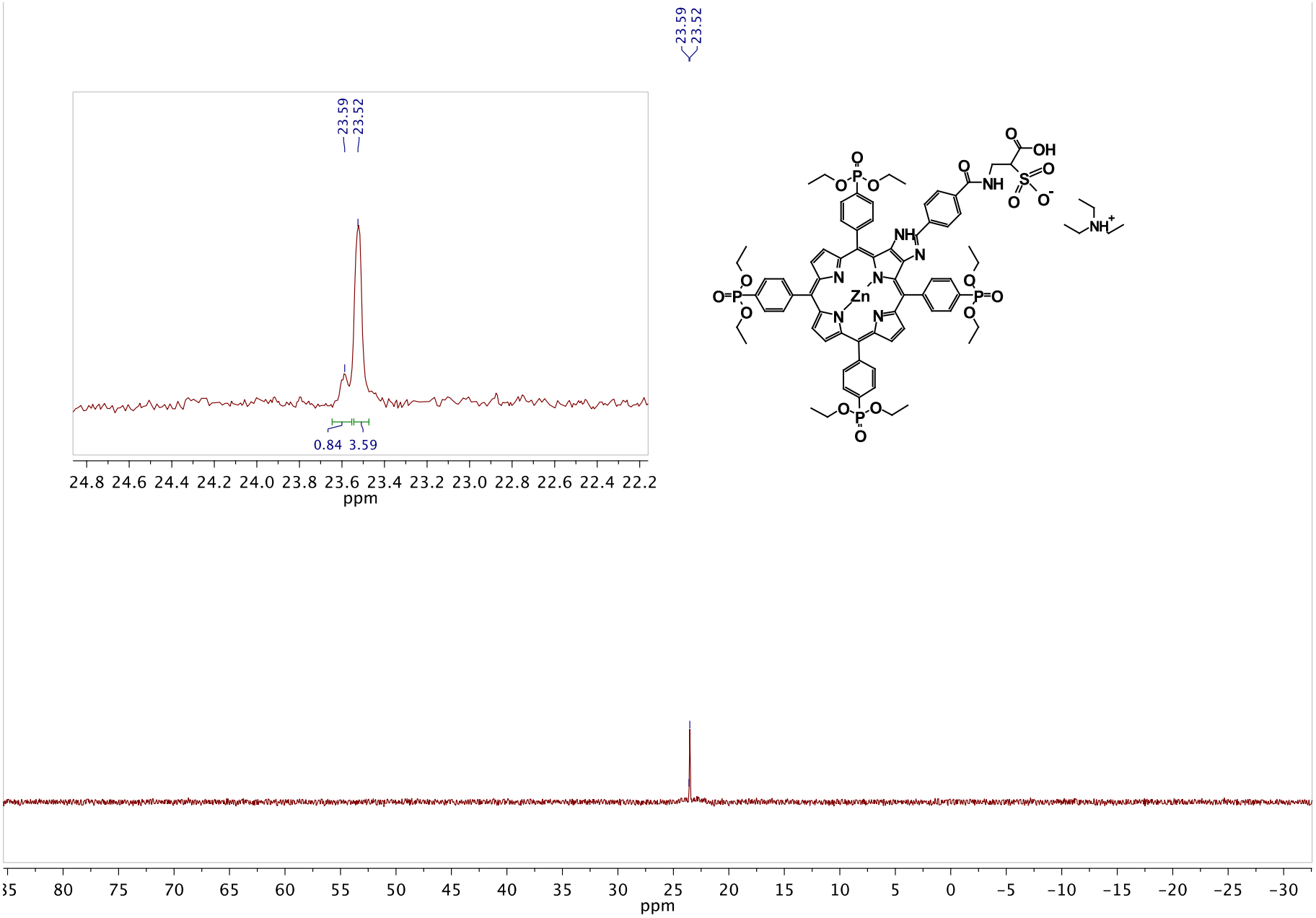


Figure S6. ^{31}P NMR spectrum of Zn-3e ($CDCl_3$+ MeOH-*d4*).



4. NMR spectra of β-nitroporphyrins 2H-4

Figure S7. ^{1}H NMR spectrum of 2H-4c ($CDCl_3$).

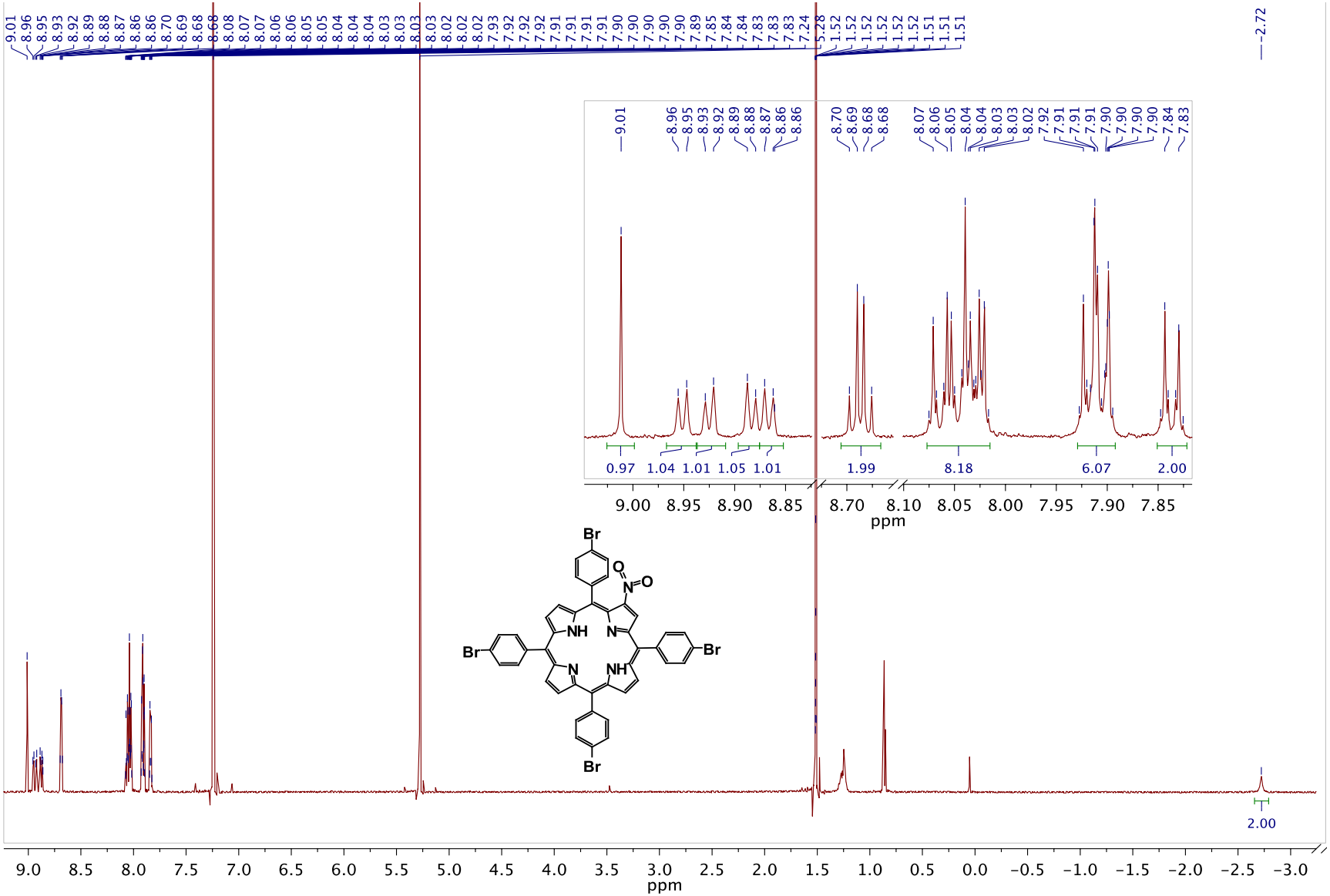
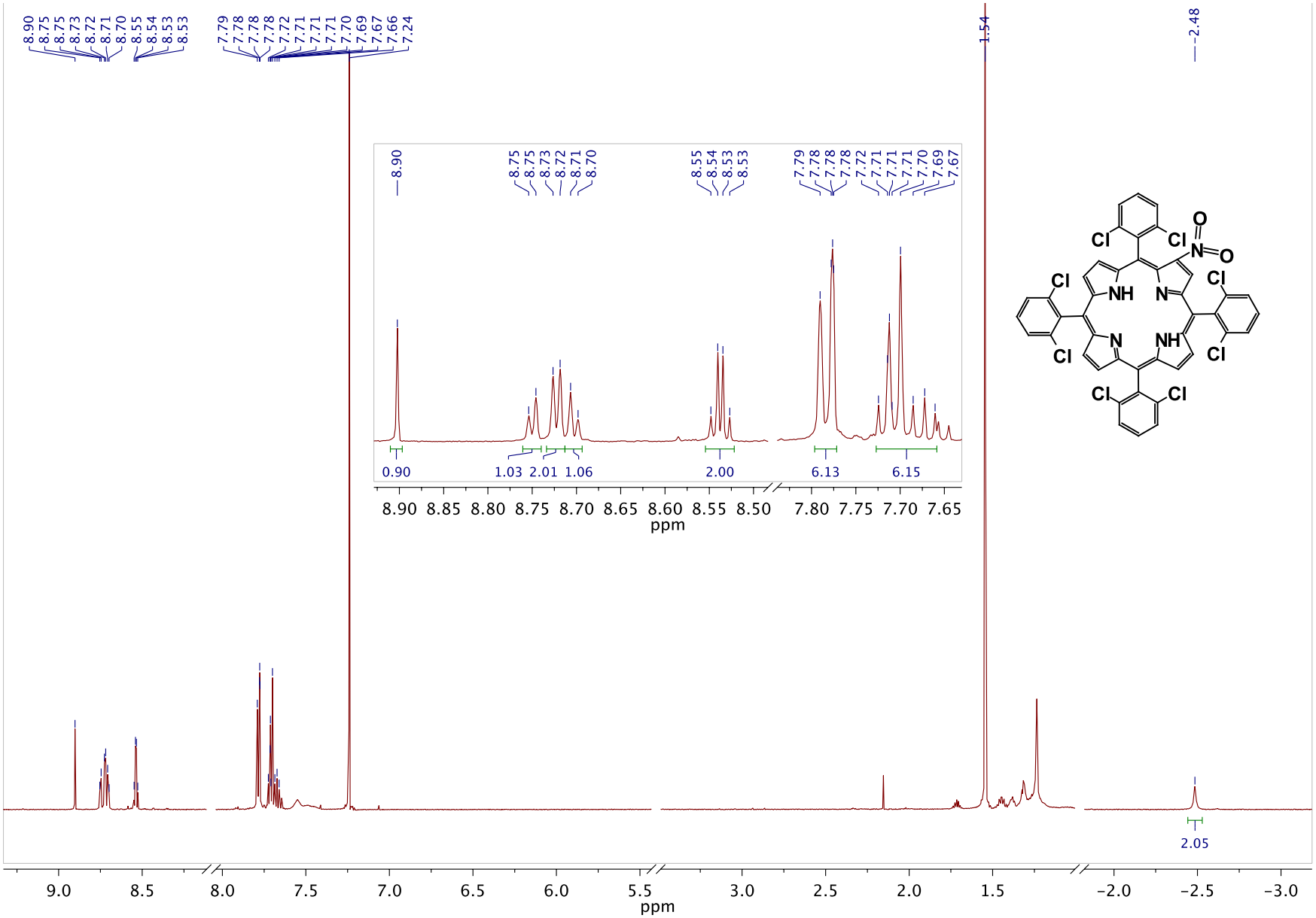


Figure S8. ^{1}H NMR spectrum of 2H-4f ($CDCl_3$).



5. **NMR spectra of porphyrin 2H-5e**

Figure S9. ^{1}H NMR spectrum of 2H-5e ($CDCl_3$).

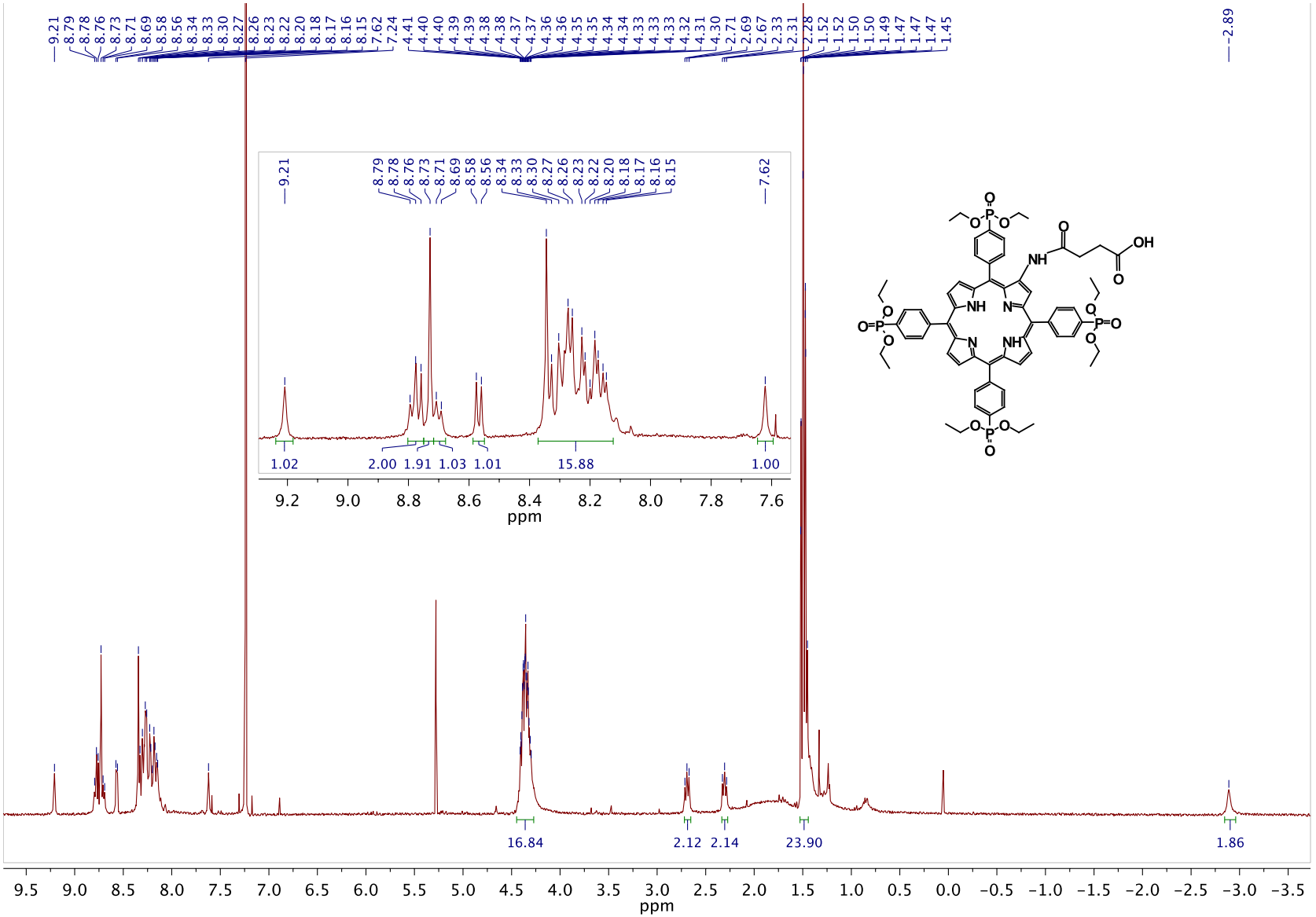
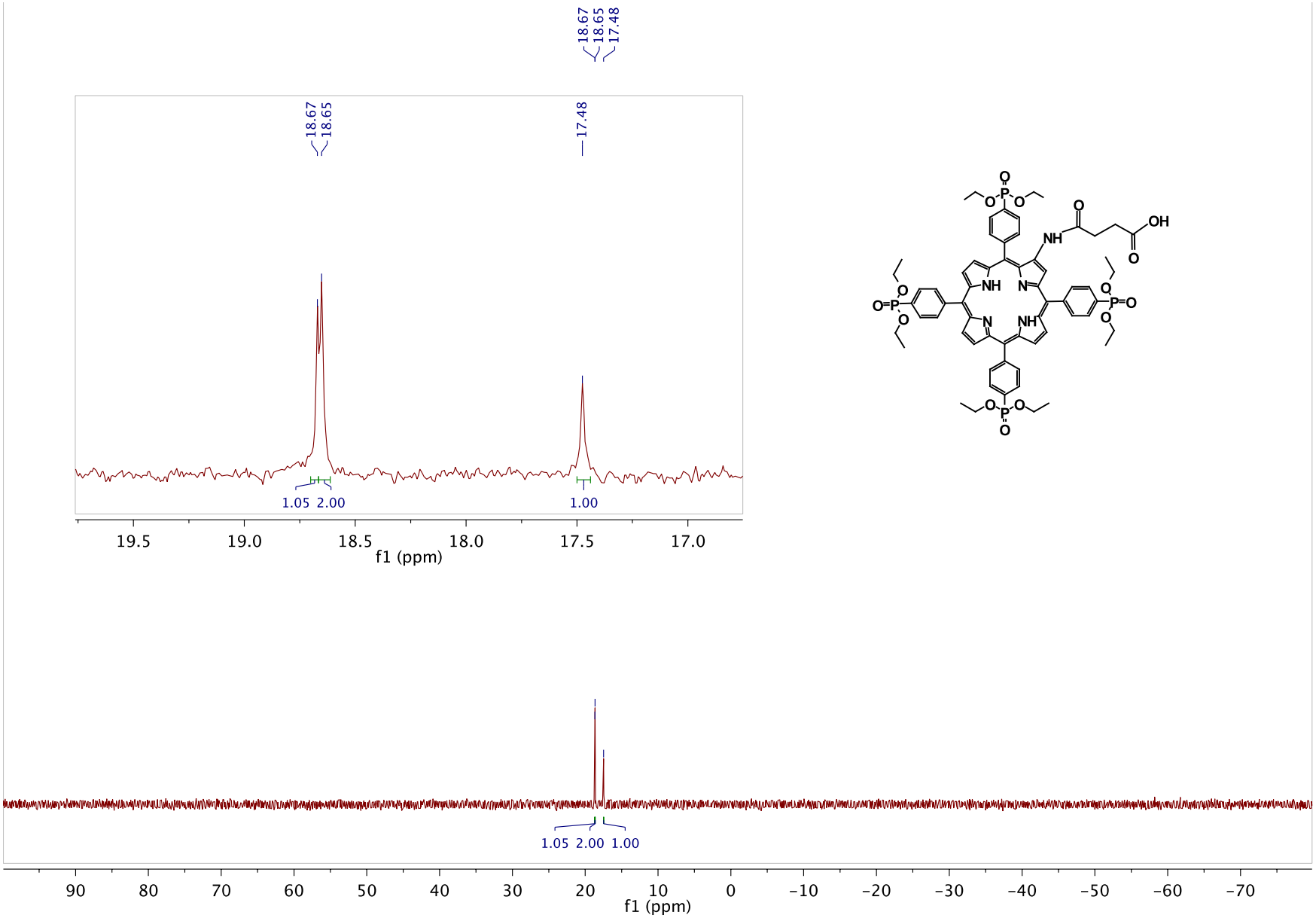


Figure S10. ^{31}P NMR spectrum of 2H-5e ($CDCl_3$).



6. **NMR spectra of 2,3-dioxochlorins 2H-6**

Figure S11. ^{1}H NMR spectrum of 2H-6d ($CDCl_3$).

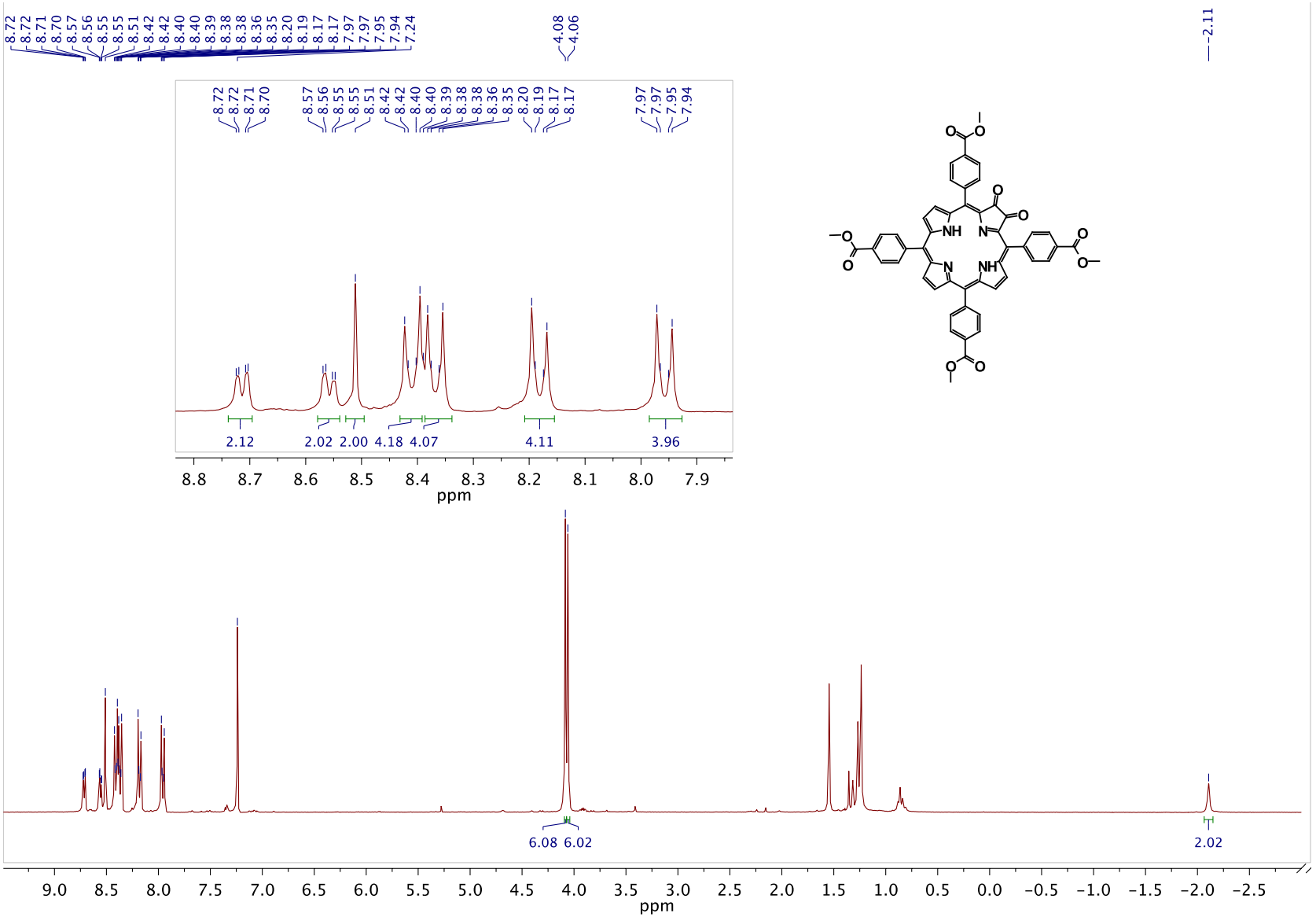


Figure S12. ^{1}H NMR spectrum of 2H-6e ($CDCl_3$).

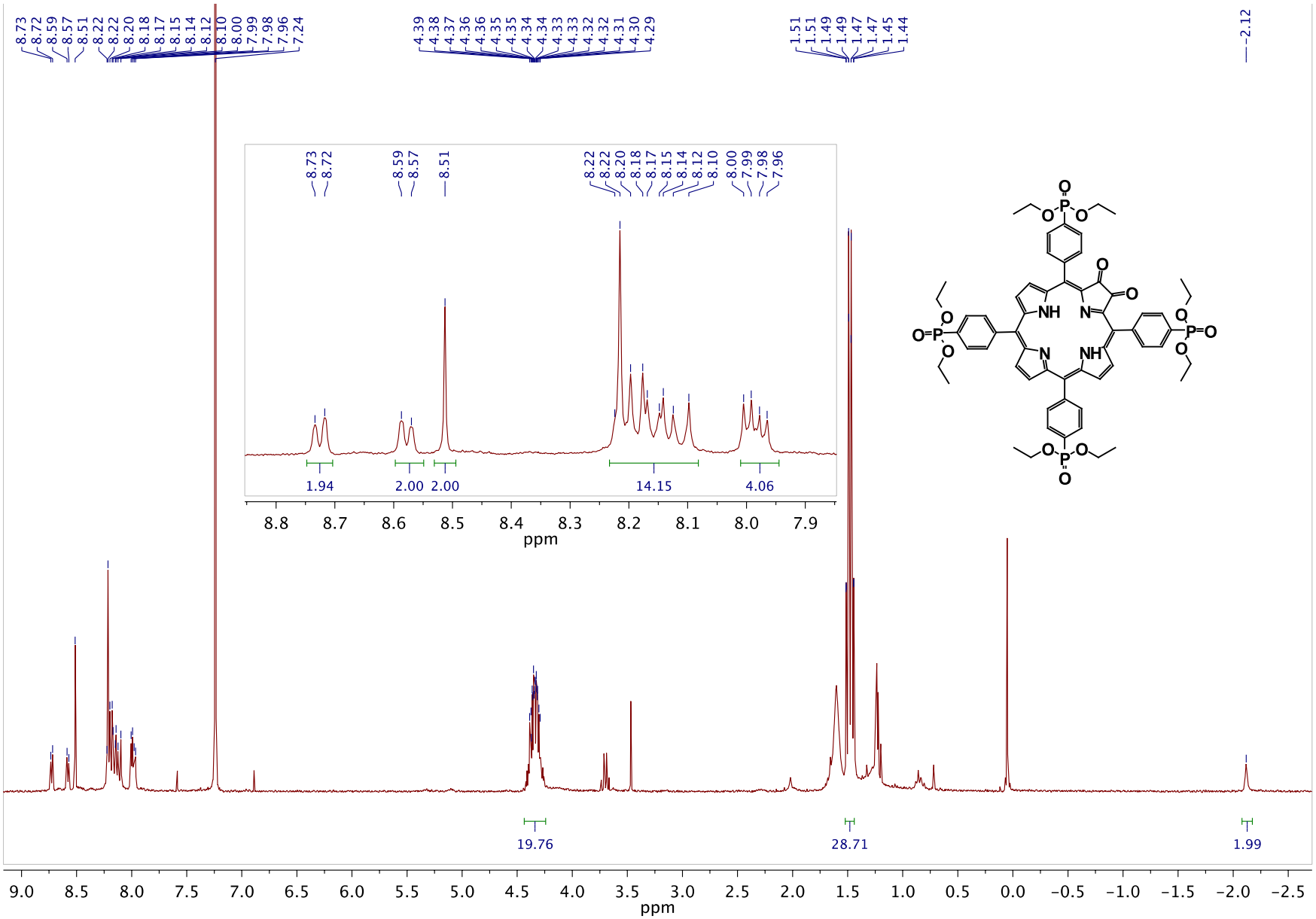


Figure S13. ^{31}P NMR spectrum of 2H-6e ($CDCl_3$).

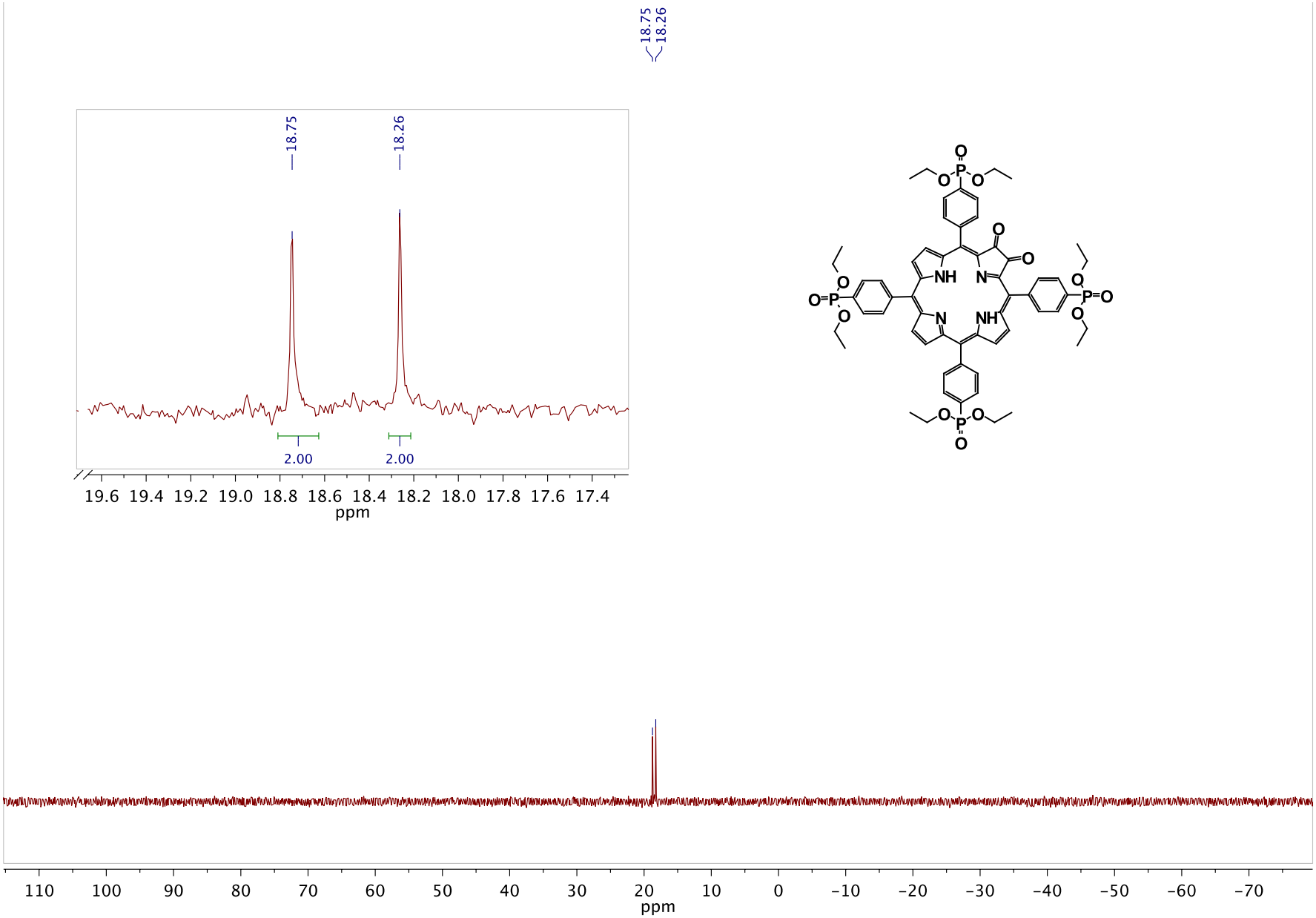
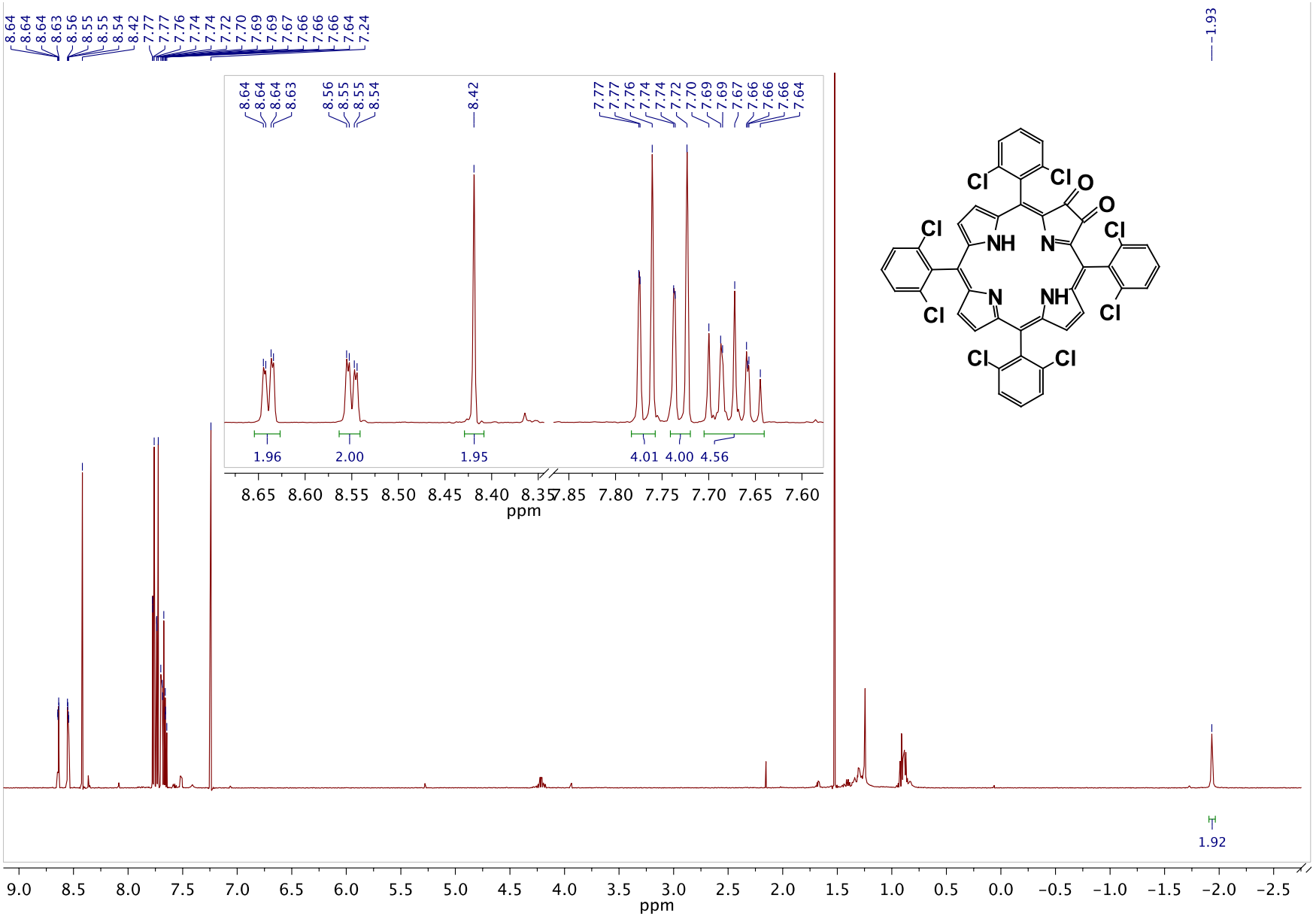


Figure S14. ^{1}H NMR spectrum of 2H-6f ($CDCl_3$).



7. **NMR spectra of porphyrin 2H-7e**

Figure S15. ^{1}H NMR spectrum of 2H-7e ($CDCl_3$ + MeOH-*d4*).

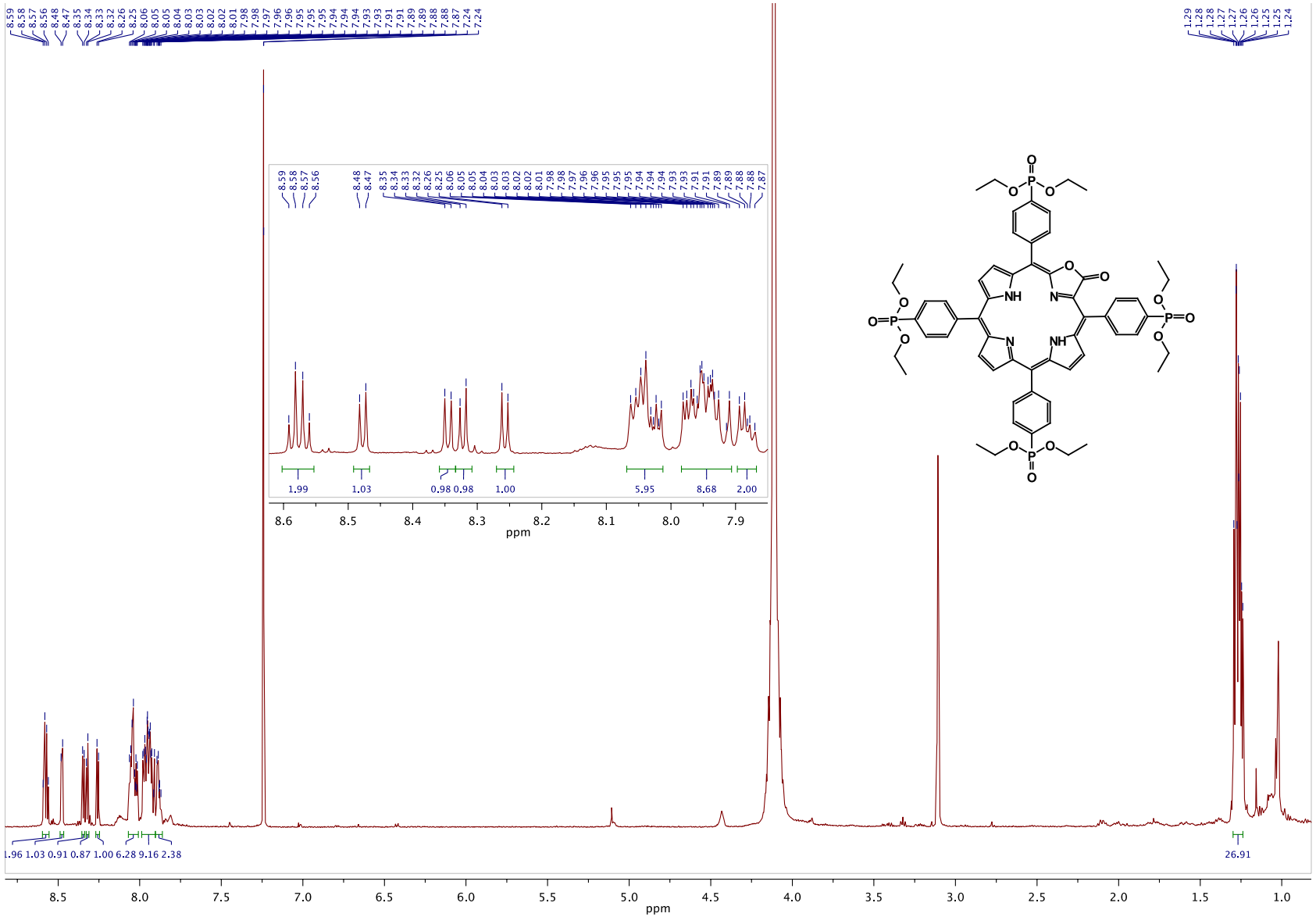
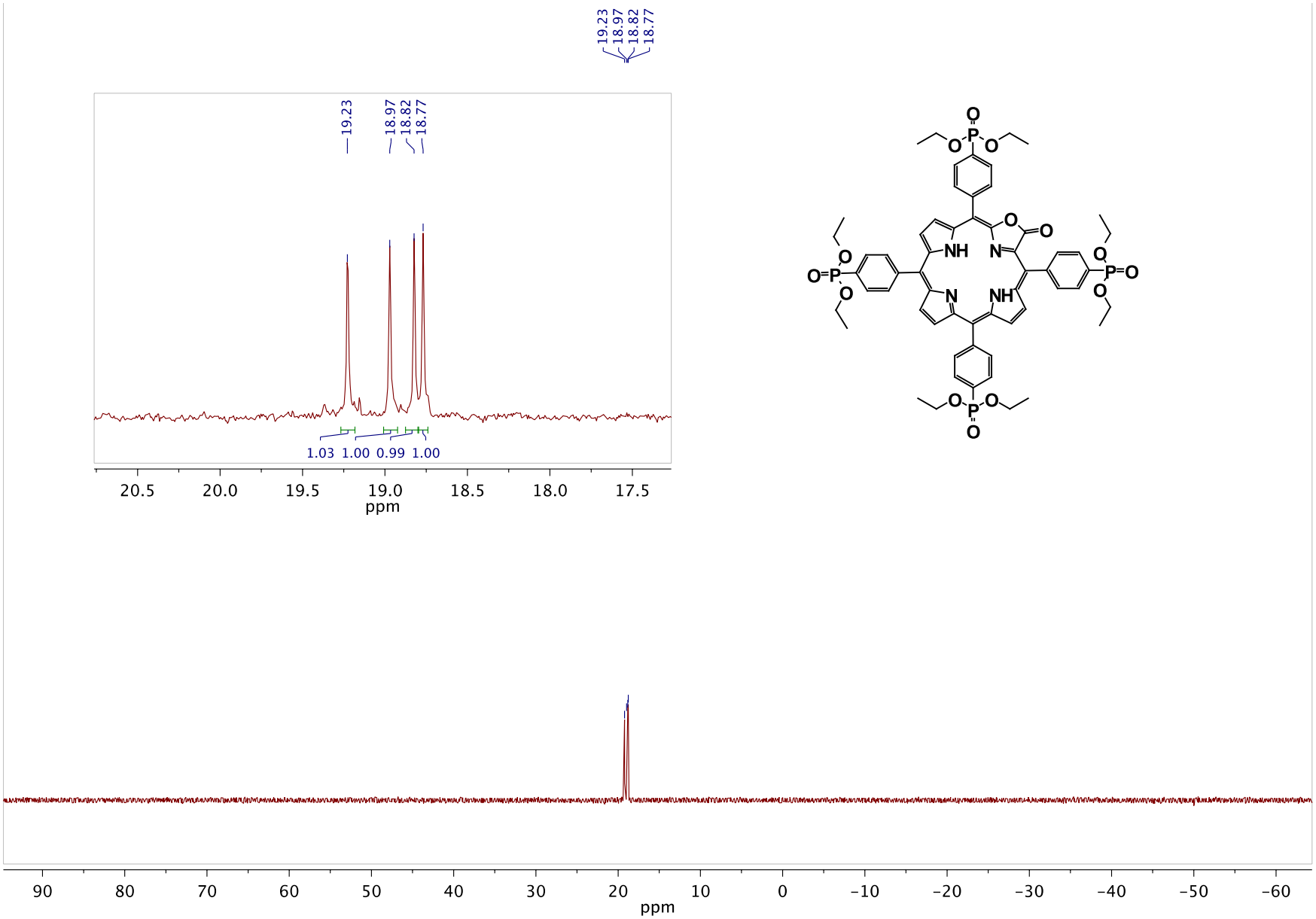


Figure S16. ^{31}P NMR spectrum of 2H-7e ($CDCl_3$ + MeOH-*d4*).



8. **NMR spectra of imidazoporphyrins 2H-14-19**

Figure S17. ^{1}H NMR spectrum of 2H-14b ($CDCl_3$).

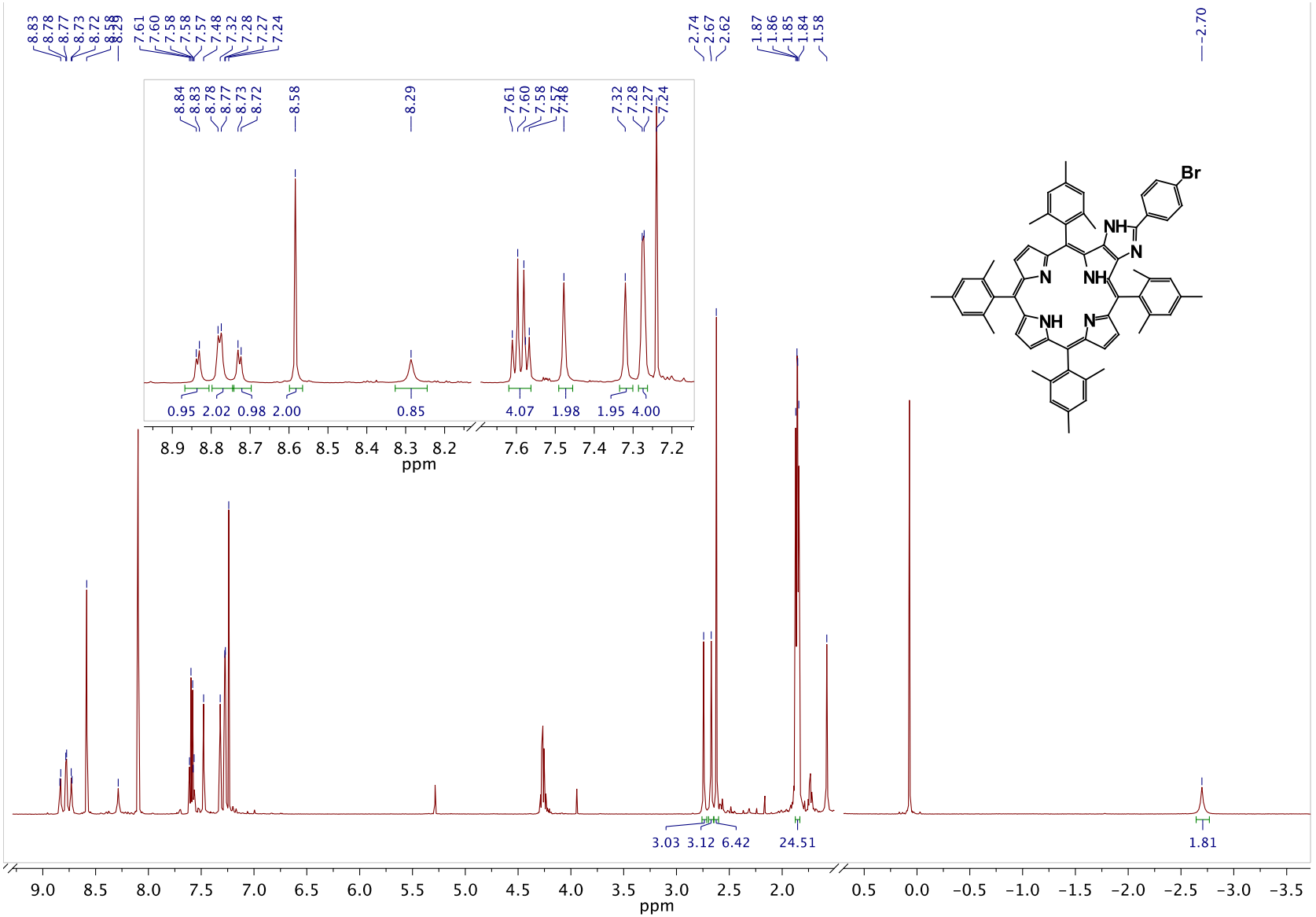


Figure S18. ^{1}H NMR spectrum of 2H-14f ($CDCl_3$).

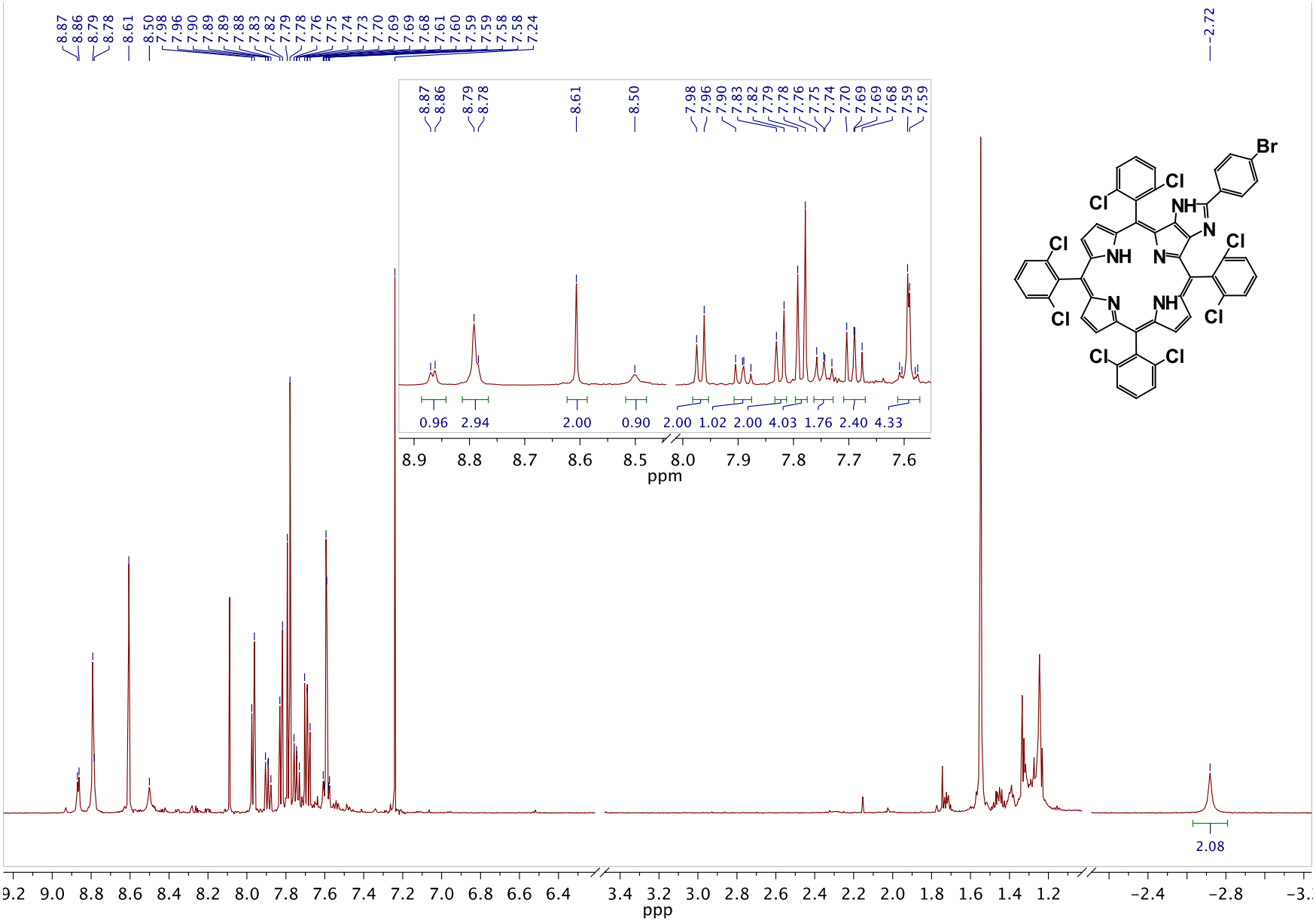


Figure S19. 1H NMR spectrum of 2H-15a (CDCl3).

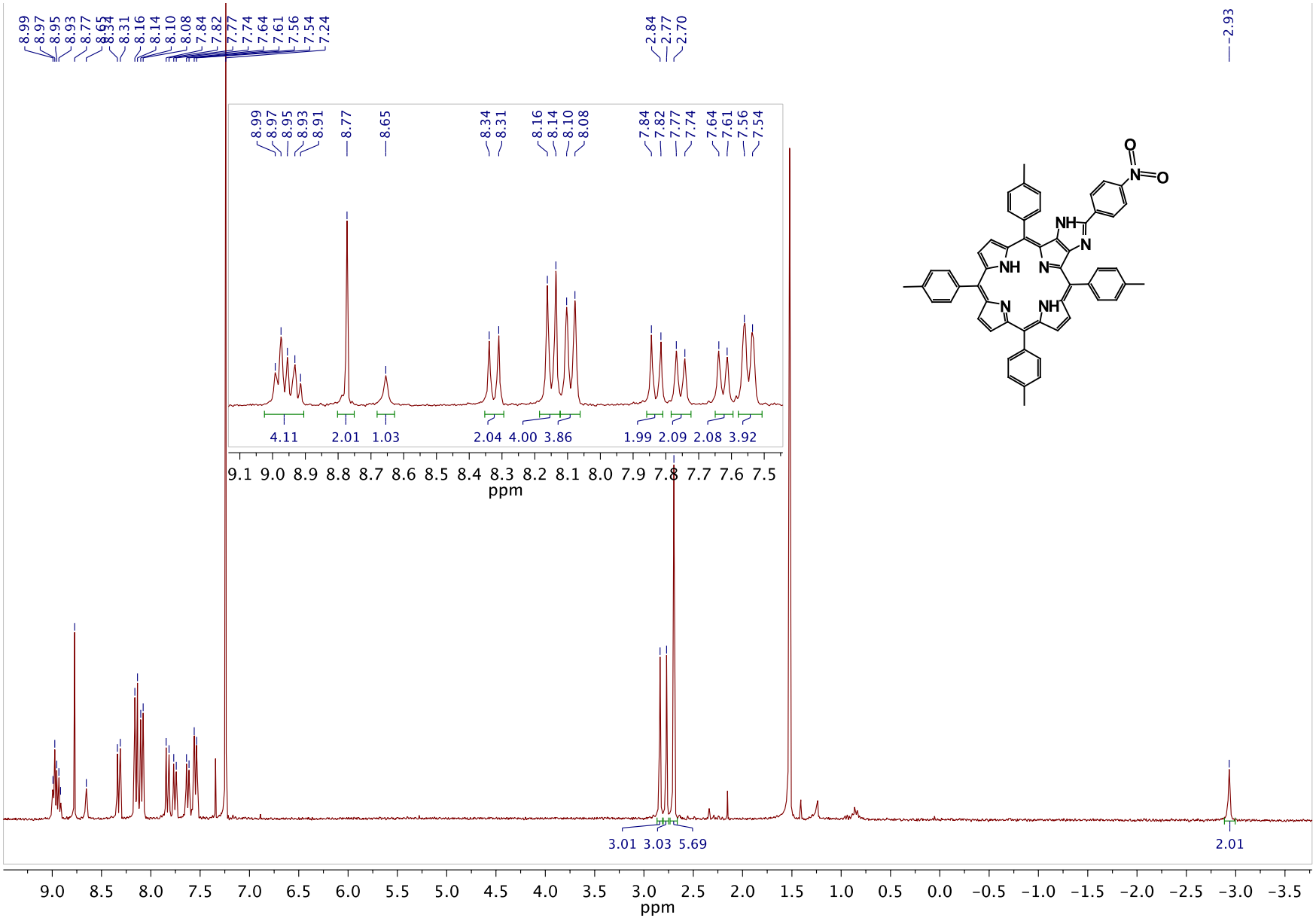


Figure S20. ^{1}H NMR spectrum of 2H-16e ($CDCl_3$).

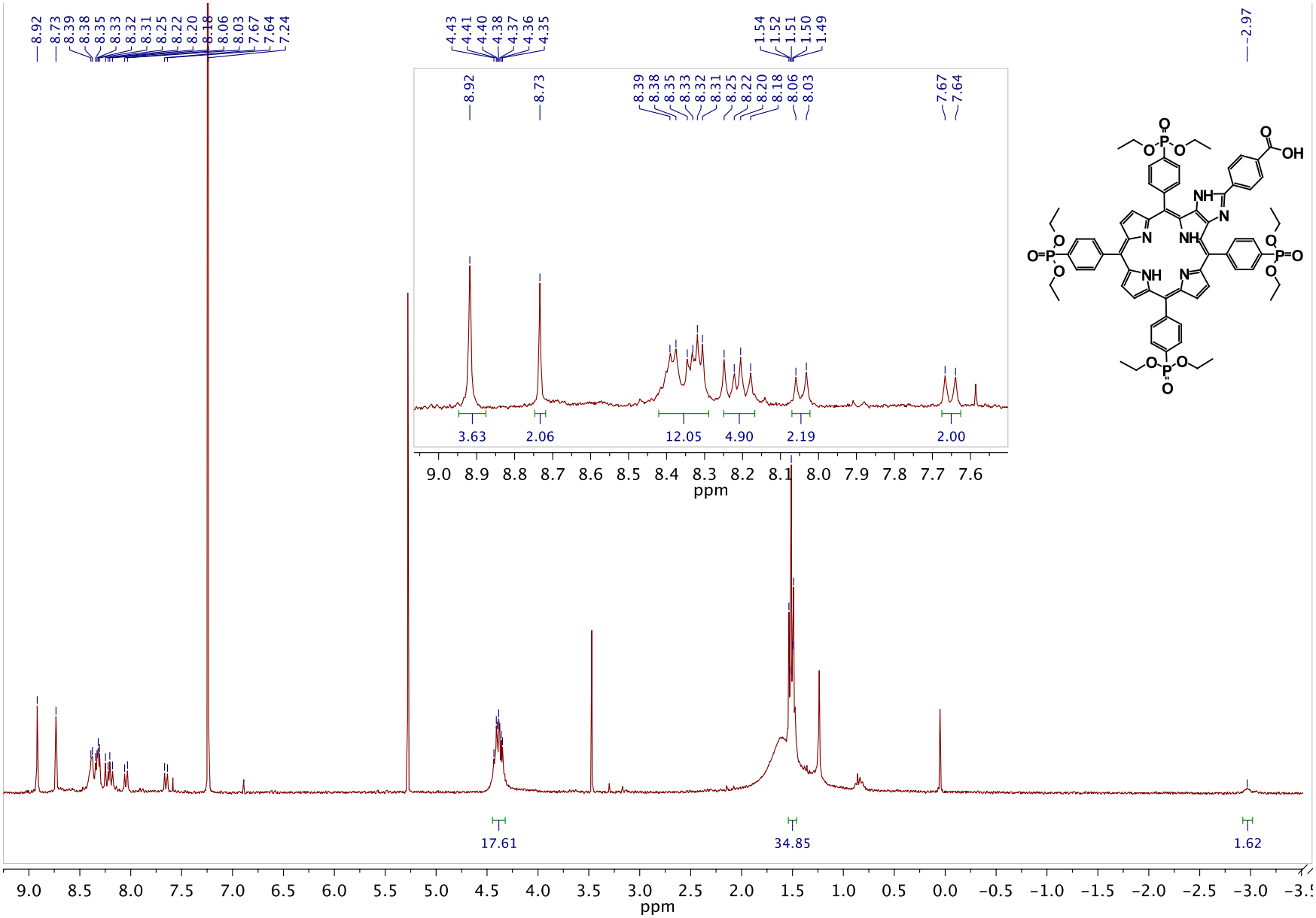


Figure S21. ^{31}P NMR spectrum of 2H-16e ($CDCl_3$).

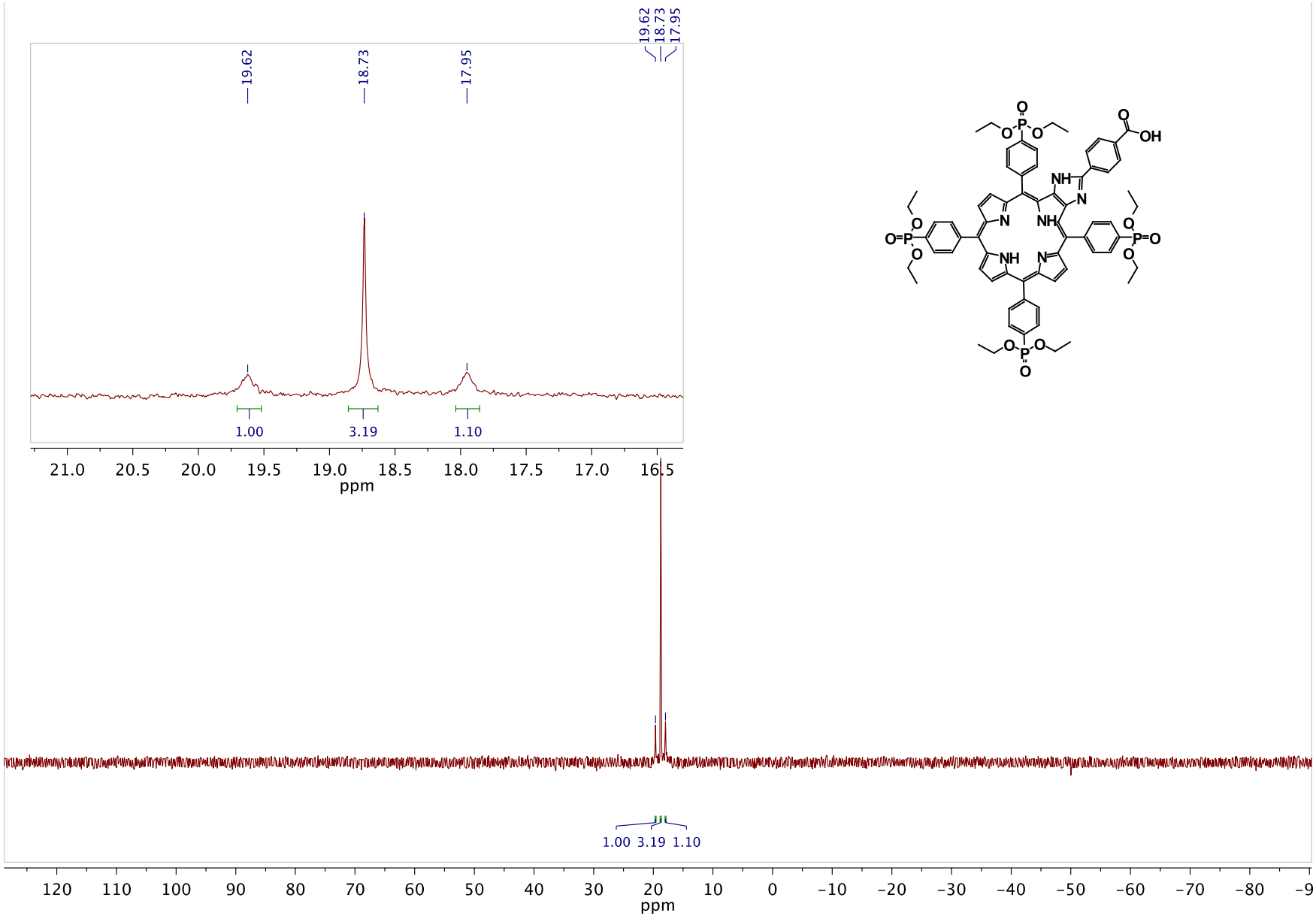


Figure S22. ^{1}H NMR spectrum of 2H-17b ($CDCl_3$).

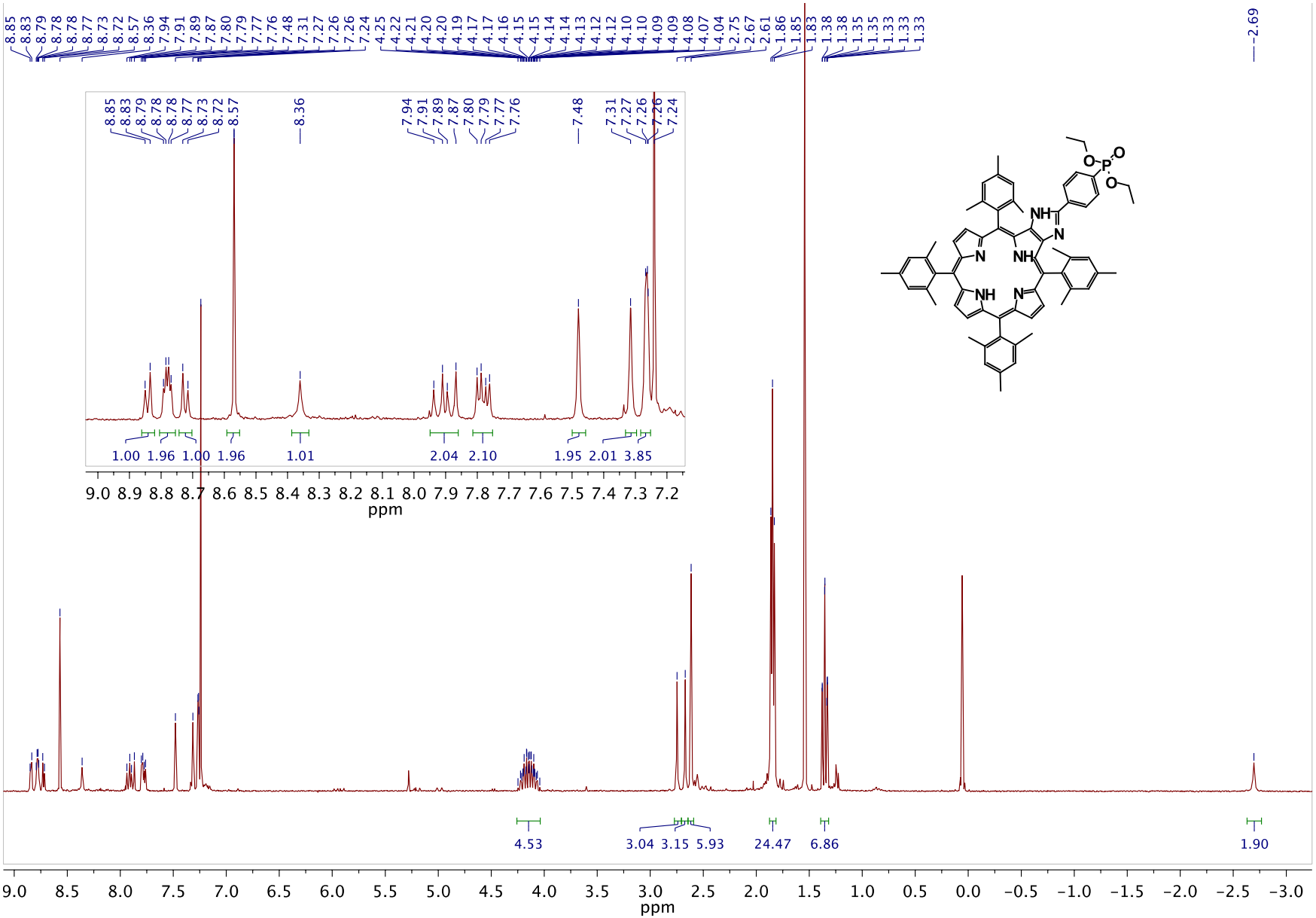


Figure S23. ^{31}P NMR spectrum of 2H-17b ($CDCl_3$).

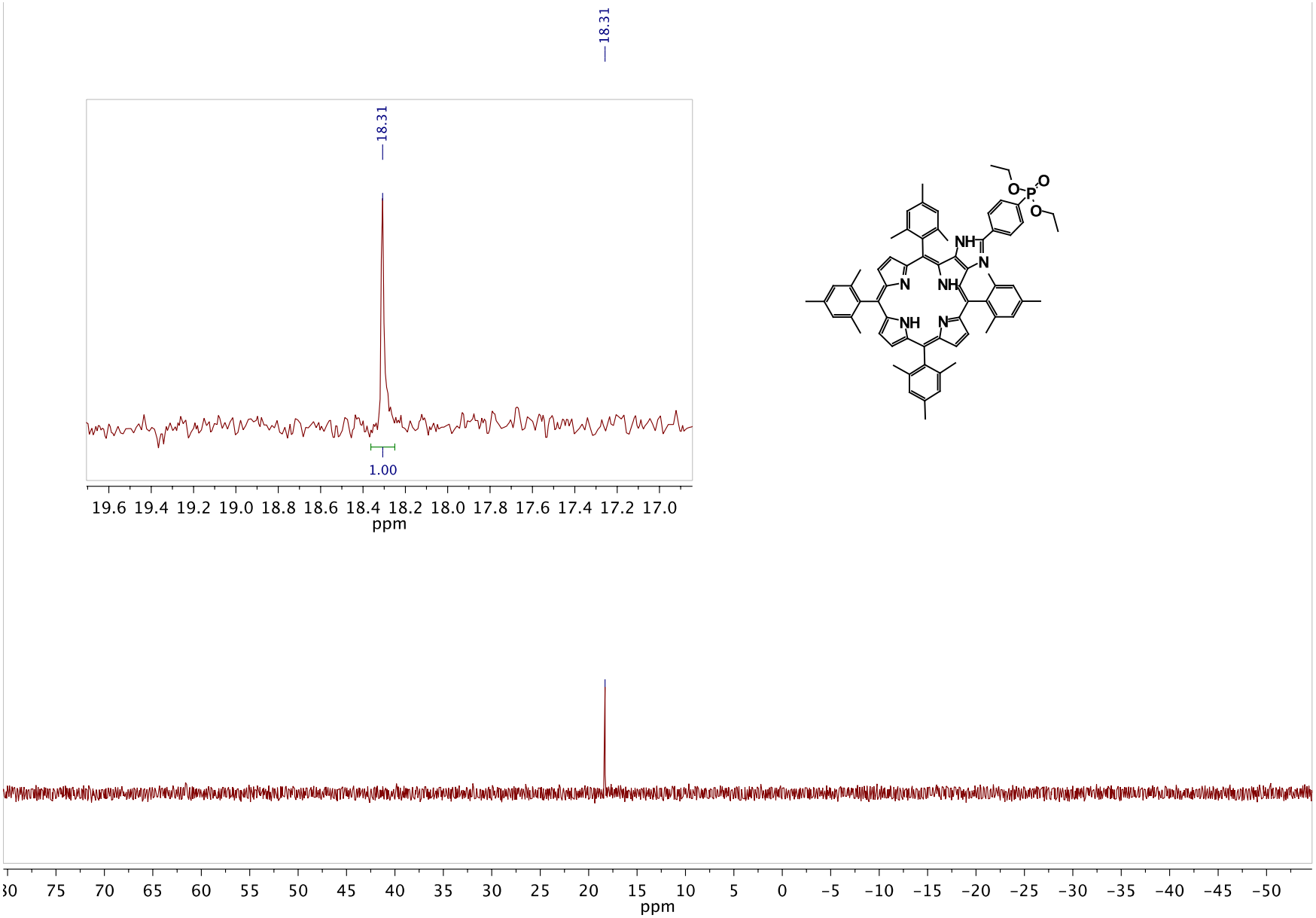


Figure S24. ^{1}H NMR spectrum of 2H-18b ($CDCl_3$).

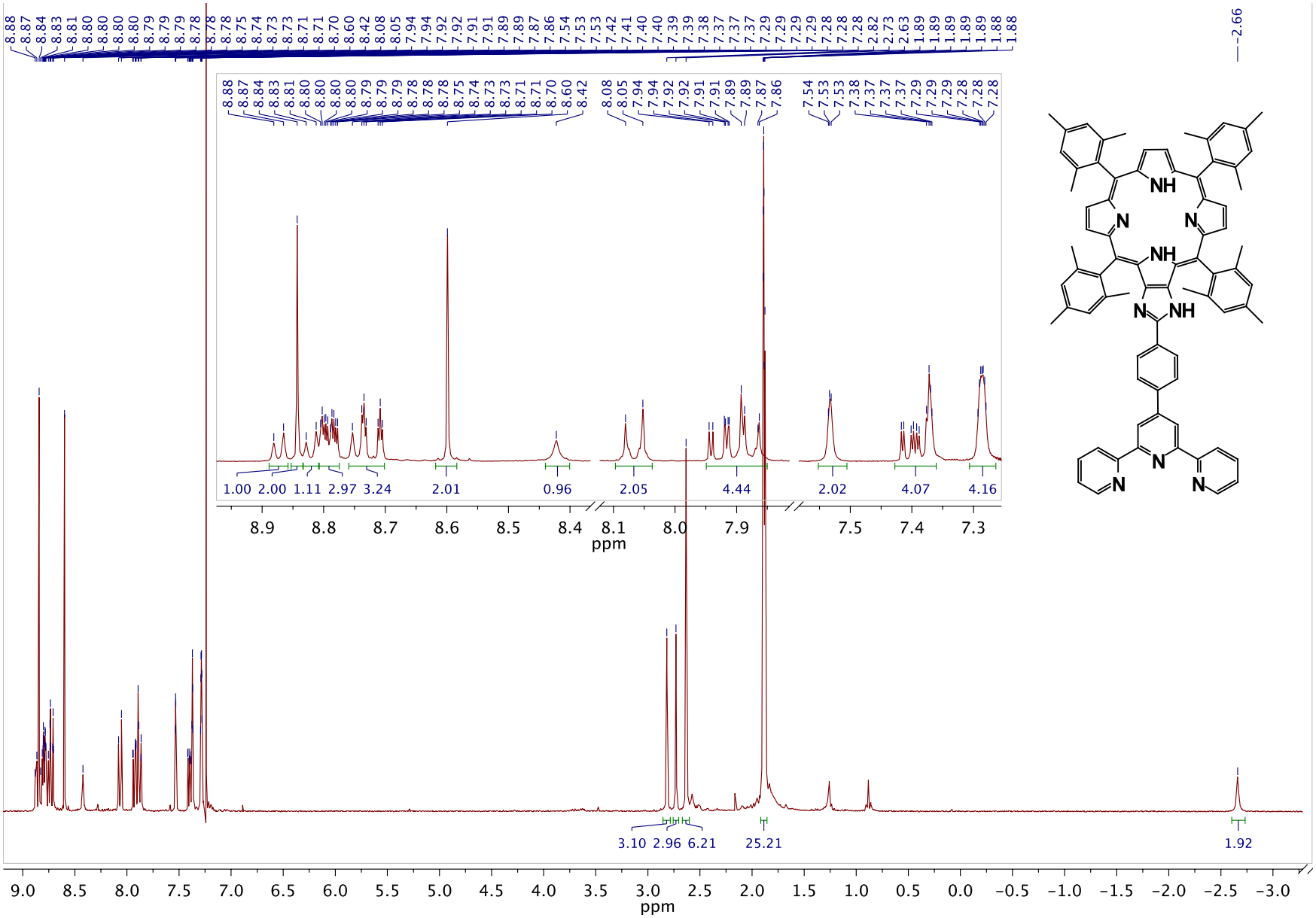
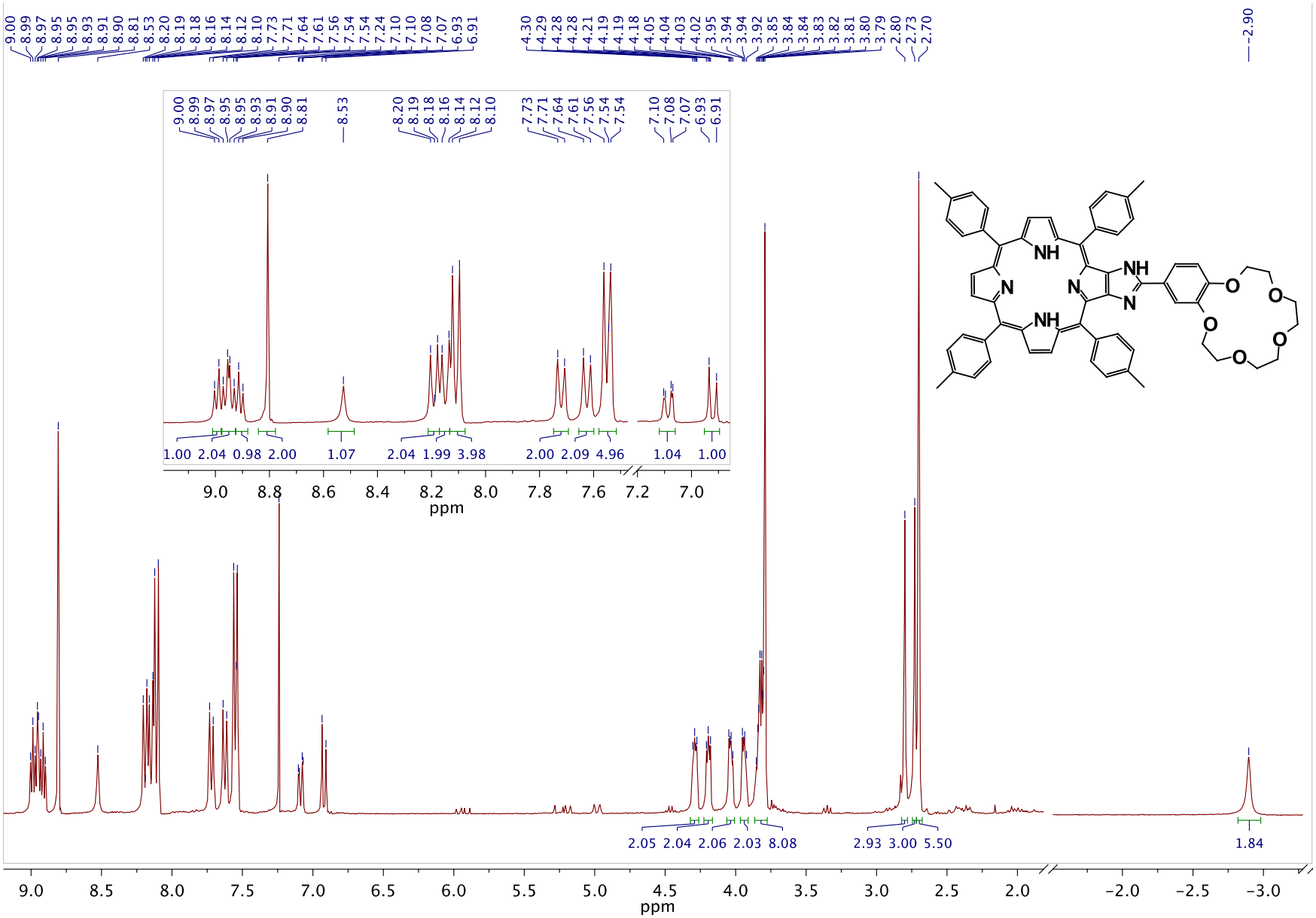


Figure S25. ^{1}H NMR spectrum of 2H-19a ($CDCl_3$).



9. IR spectra of diethoxyphosphoryl substituted porphyrins Cu-4e, 2H-4e, 2H-2e, 2,3-dioxochlorin 2H-6e and 2-oxa-3-oxochlorin 2H-7[e]

Figure S26. IR spectrum of free-base 2-aminoporphyrin 2H-2e.

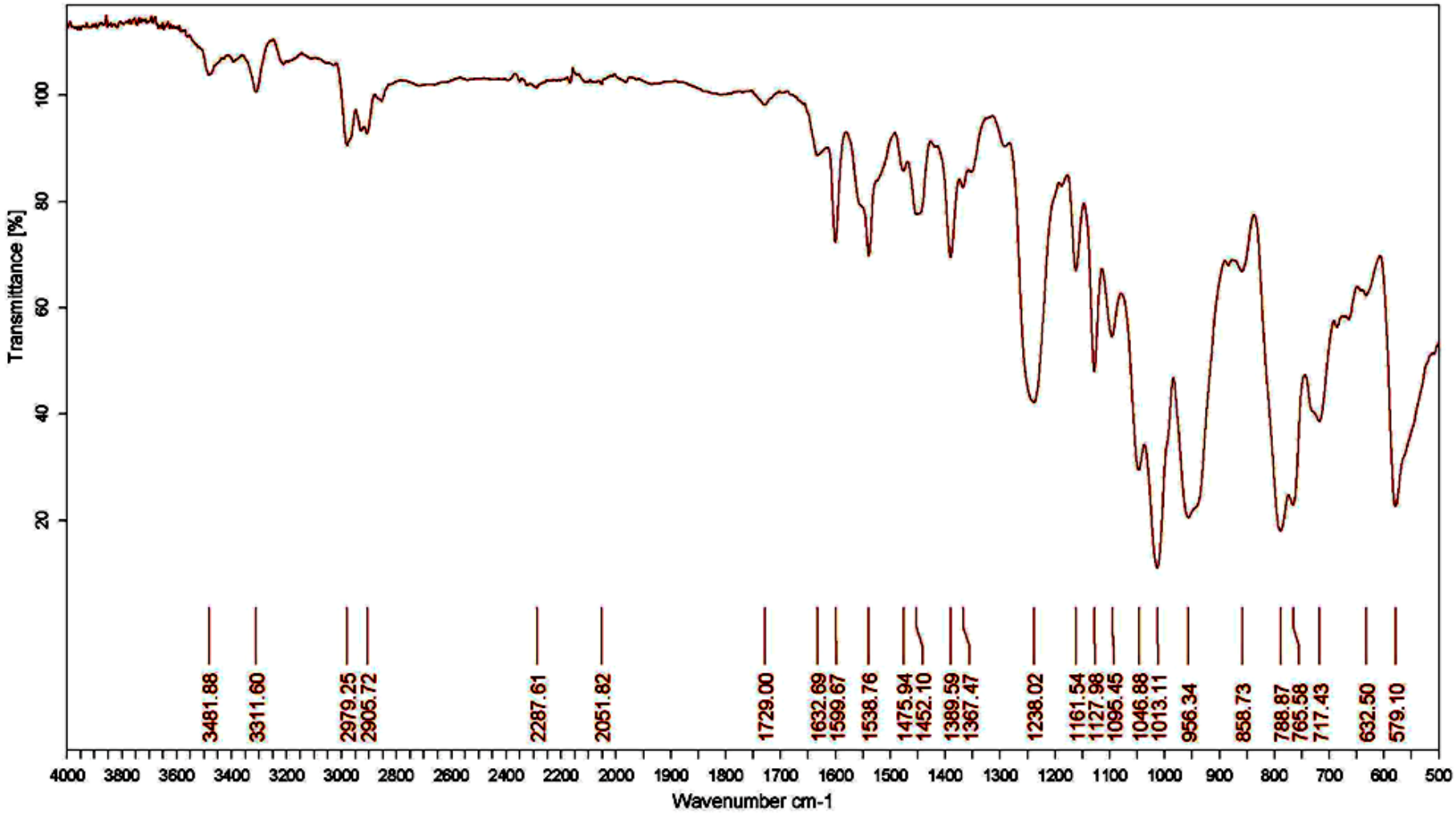


Figure S27. IR spectrum of free-base 2-nitroporphyrin 2H-4e.

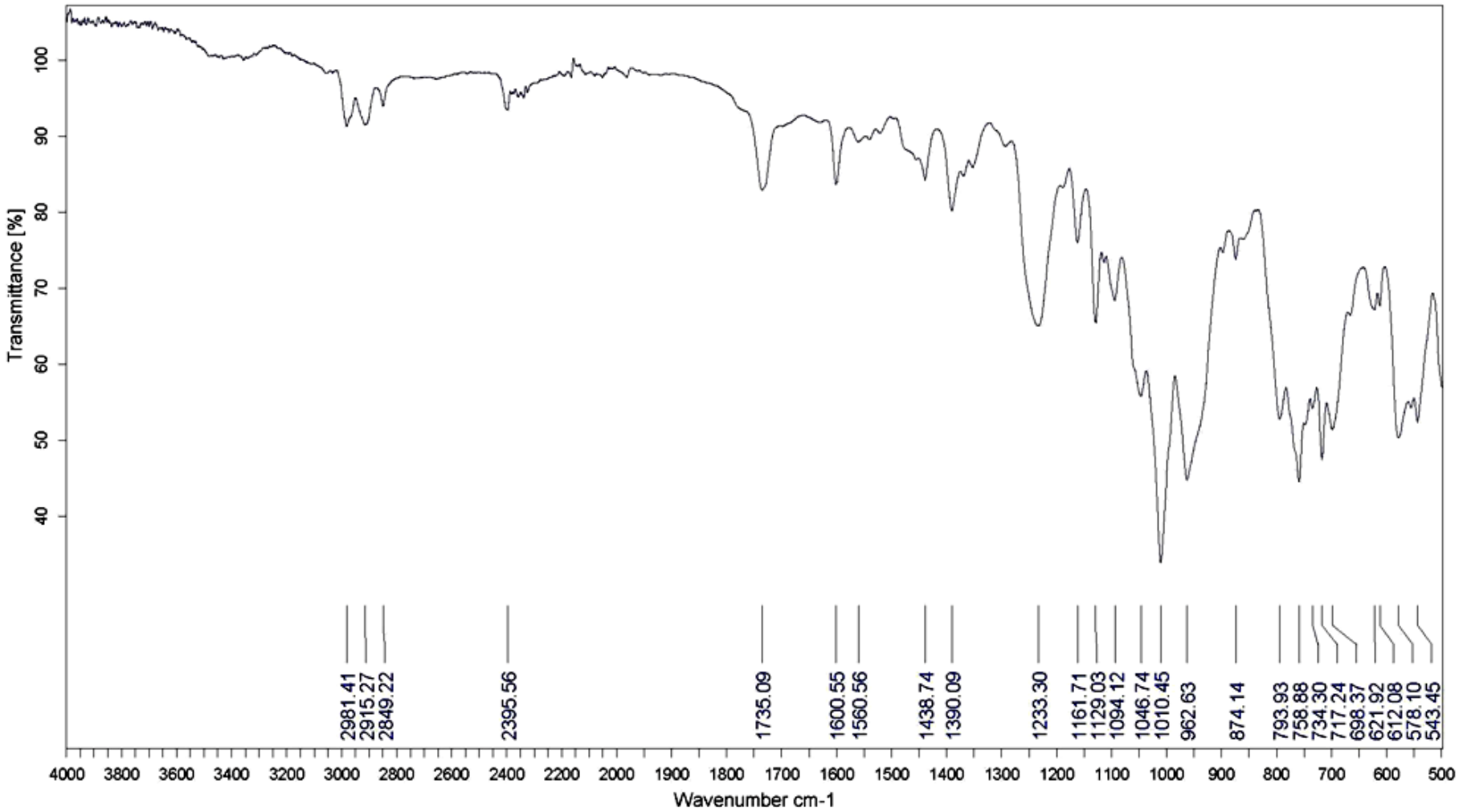


Figure S28. IR spectrum of copper(II) 2-nitroporphyrinate Cu-4e.

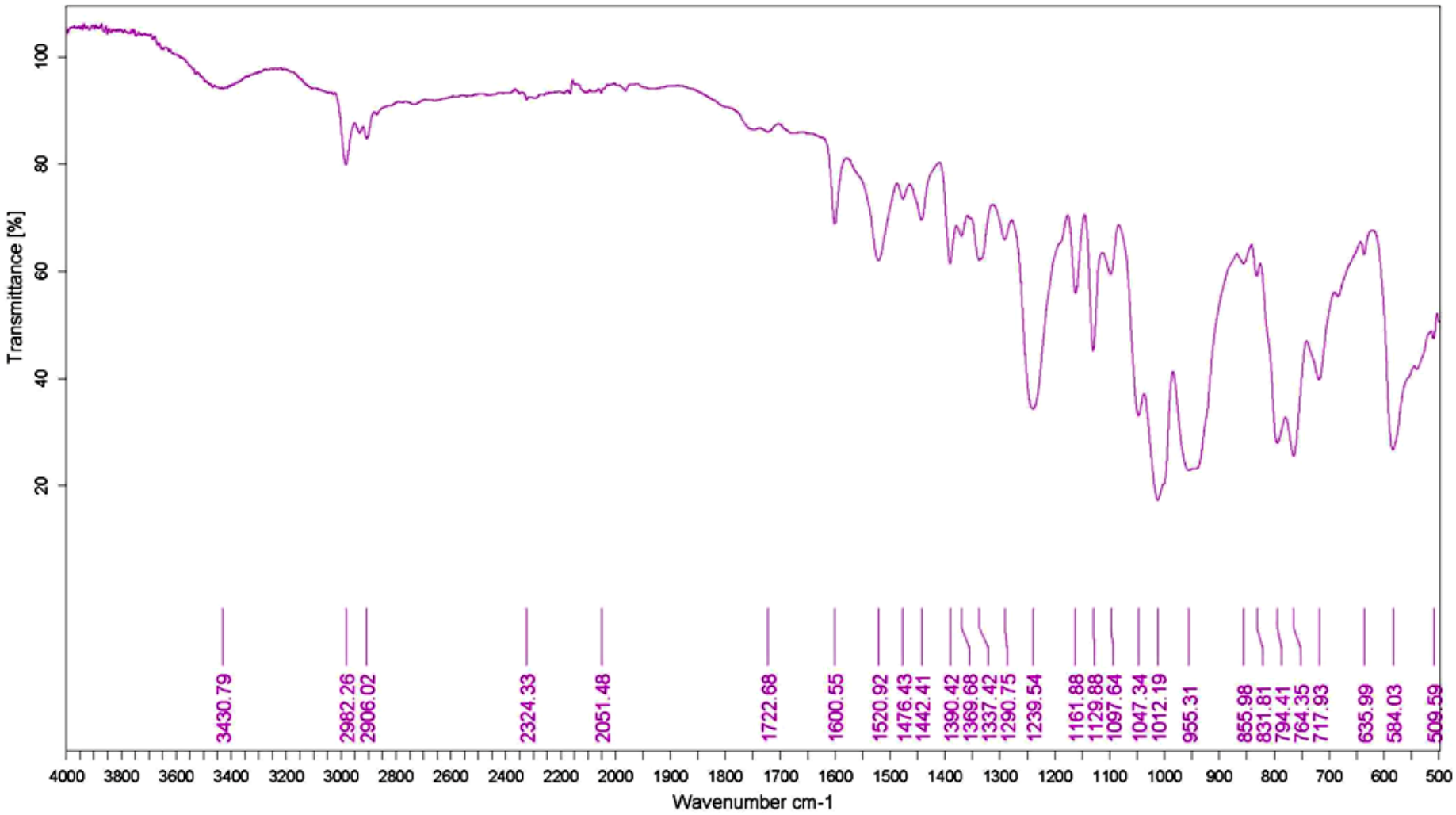


Figure S29. IR spectrum of 2,3-dioxochlorin 2H-6e.

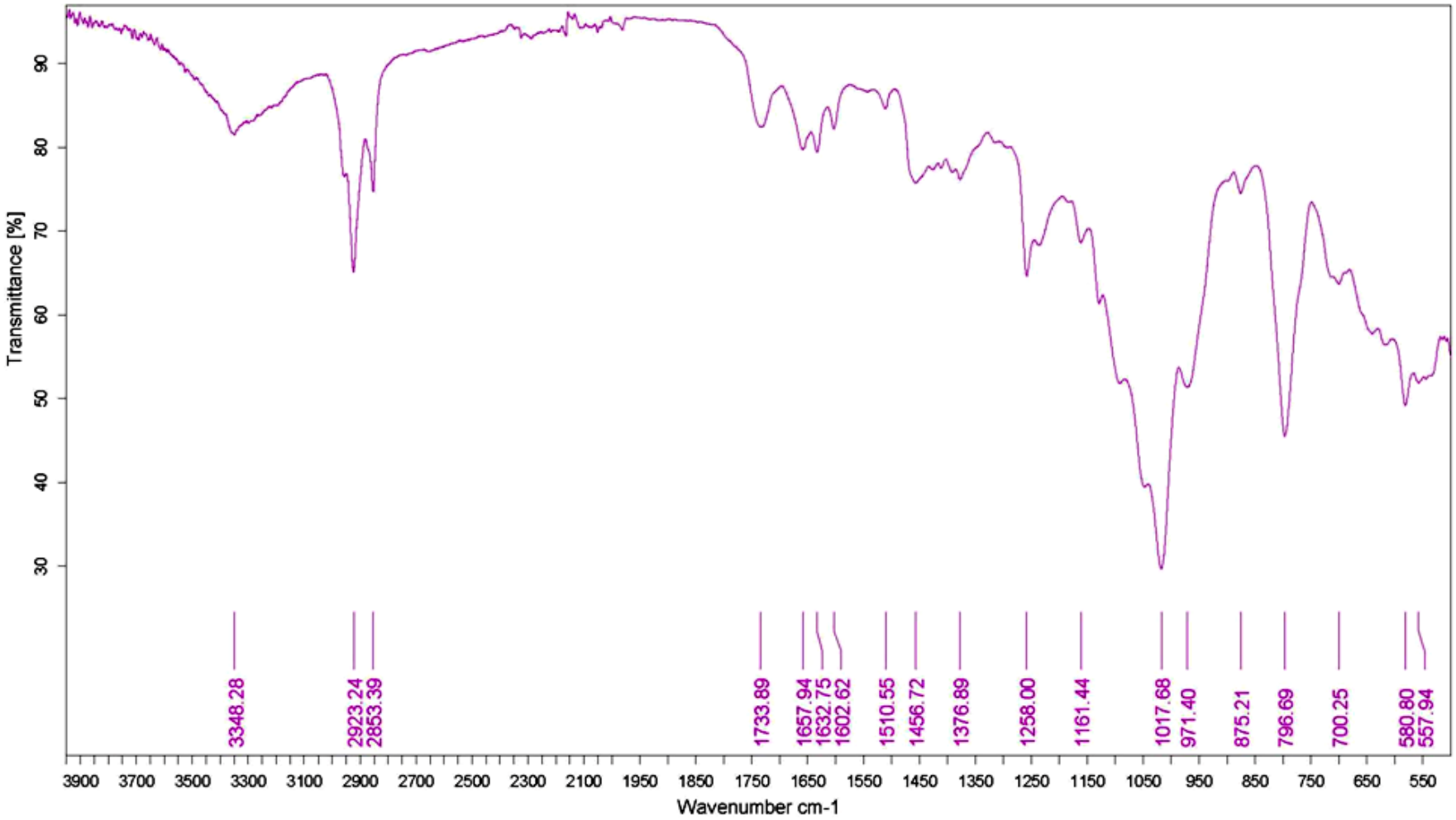
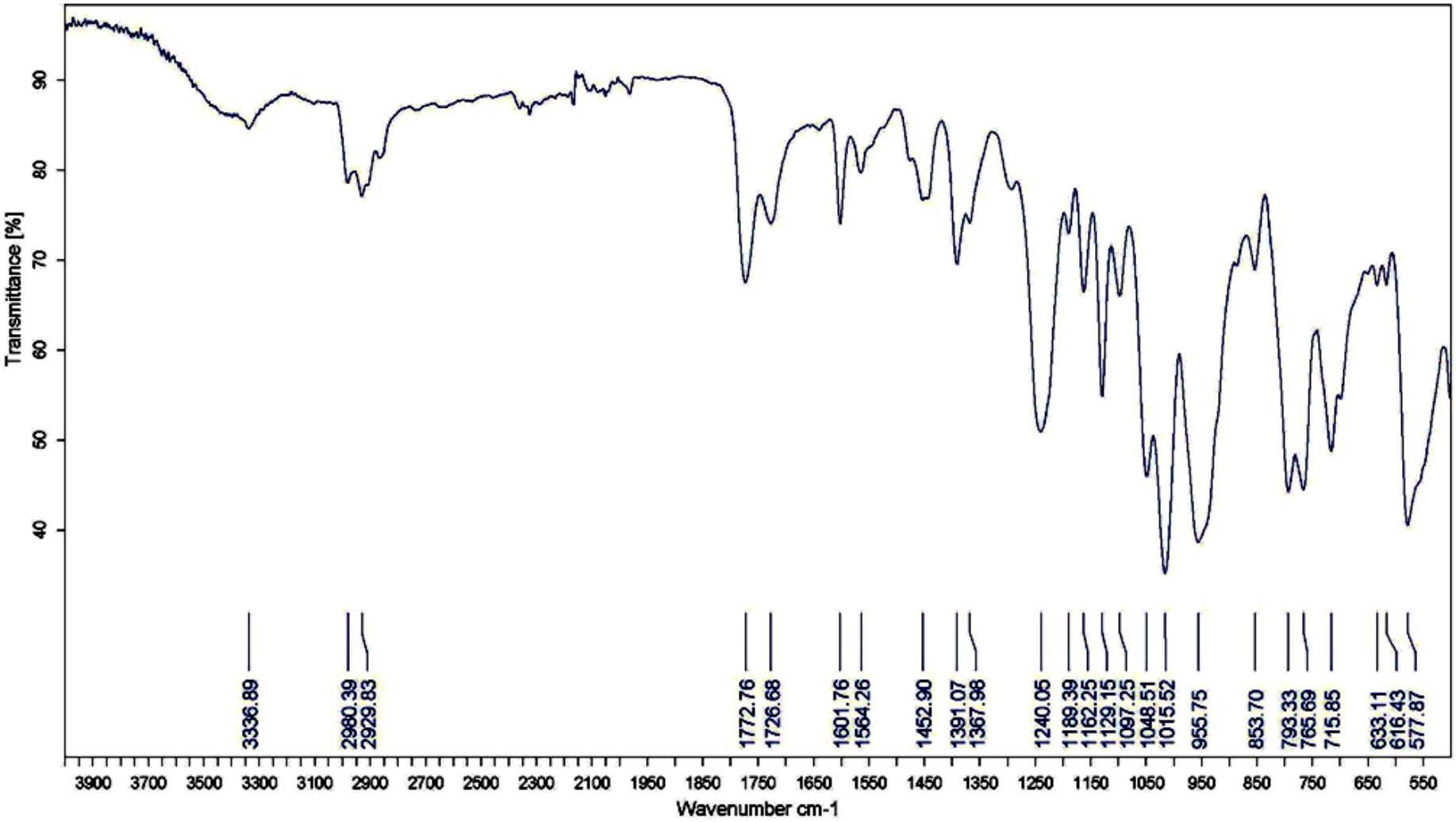


Figure S30. IR spectrum of 2-oxa-3oxochlorin 2H-7e.



10. ESI-HR mass spectra of imidazoporphyrins 2H-14-19 and porphyrin conjugates M-3

Figure S31. HR-ESI spectrum of imidazoporphyrin 2H-14a.

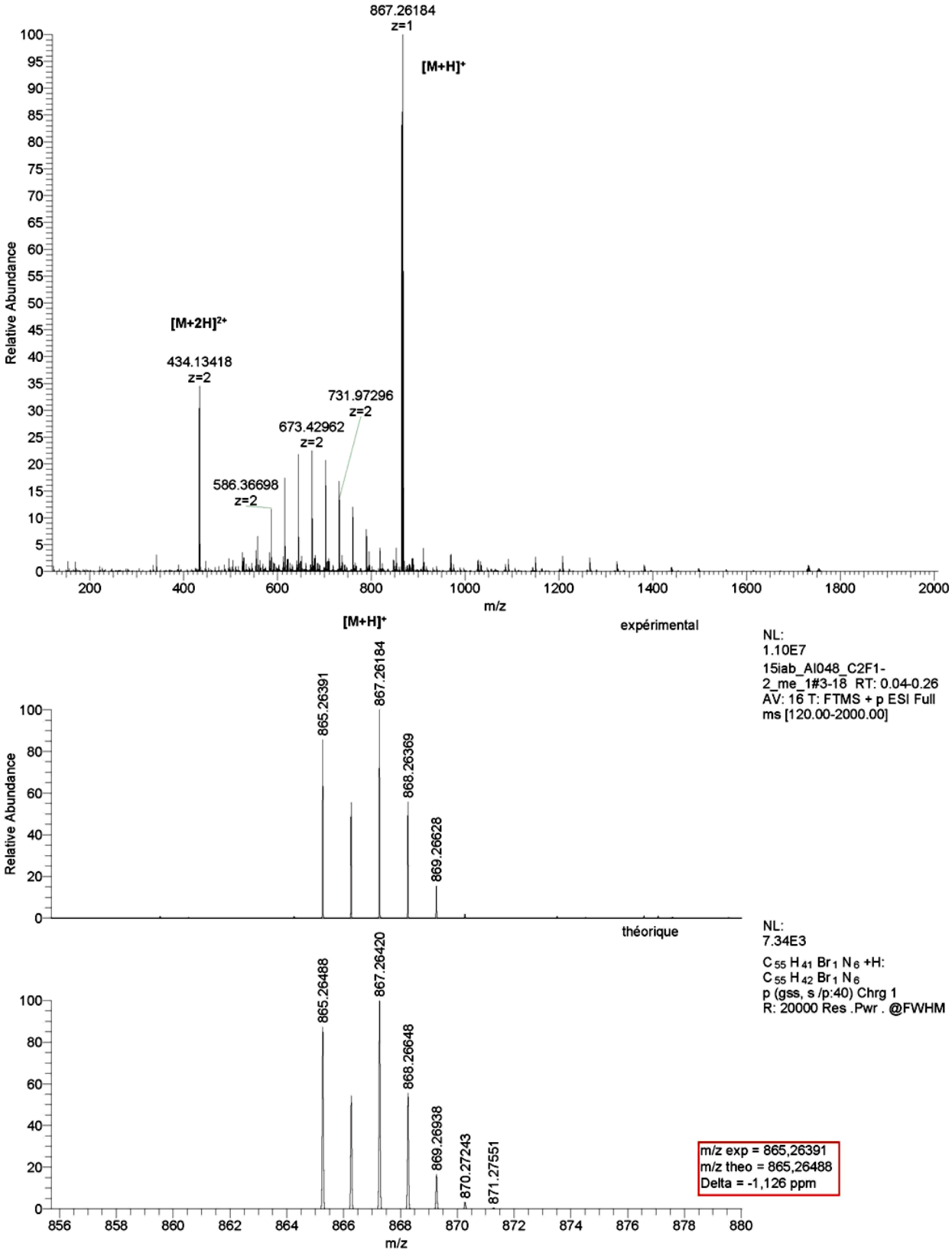


Figure S32. HR-ESI spectrum of imidazoporphyrin 2H-15a.

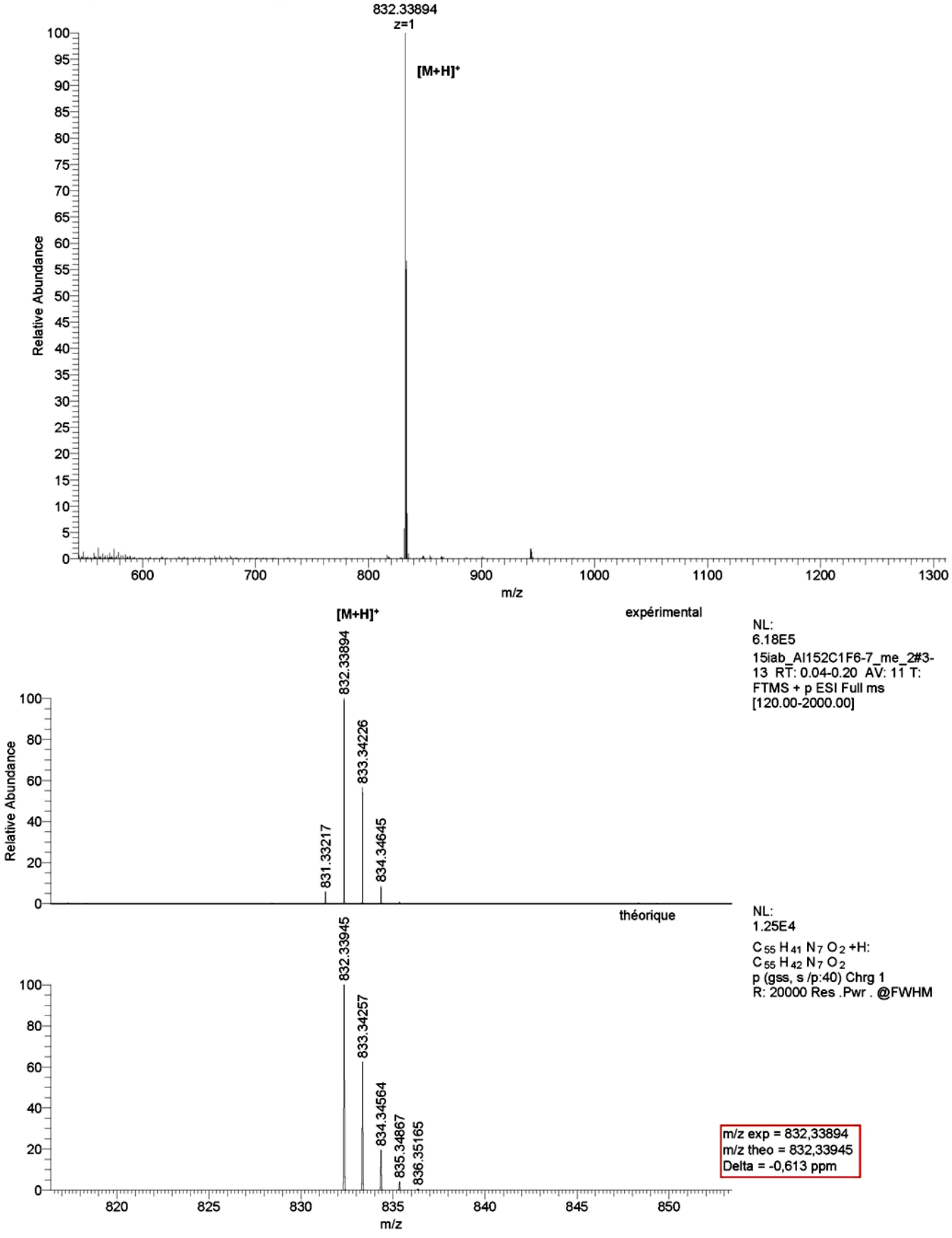


Figure S33. HR-ESI spectrum of imidazoporphyrin 2H-16c.

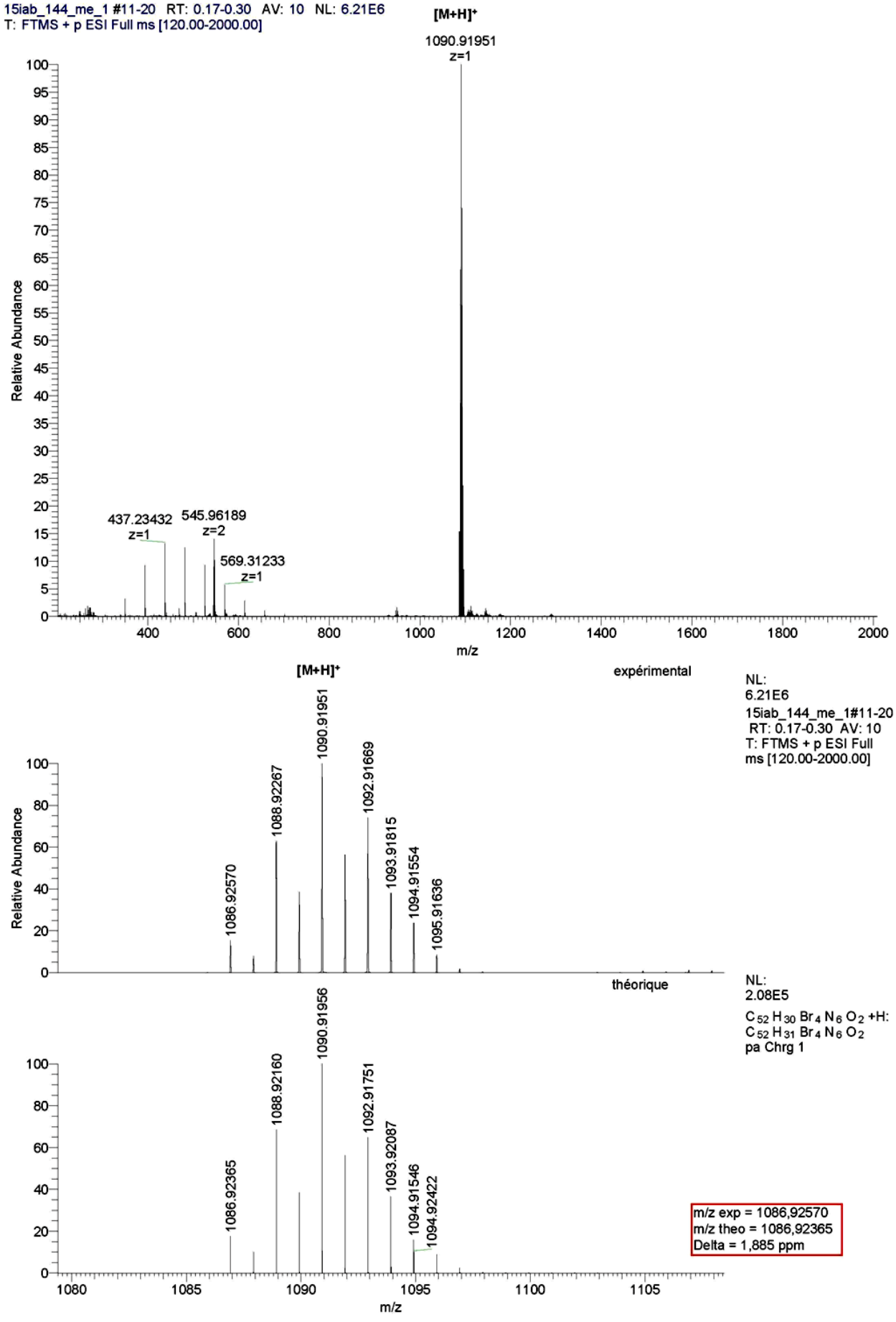


Figure S34. HR-ESI spectrum of imidazoporphyrin 2H-17b.

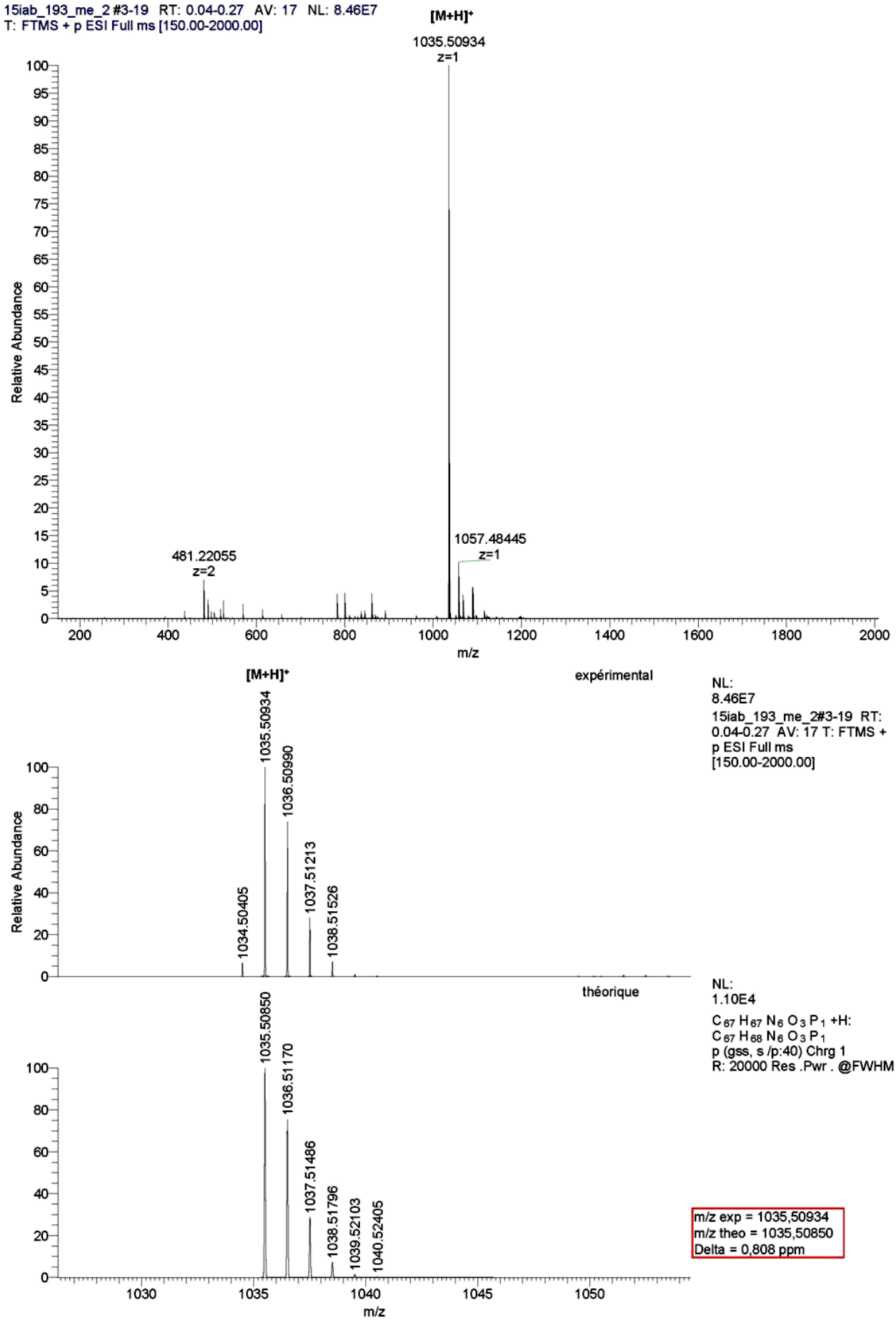


Figure S35. HR-ESI spectrum of imidazoporphyrin 2H-18b.

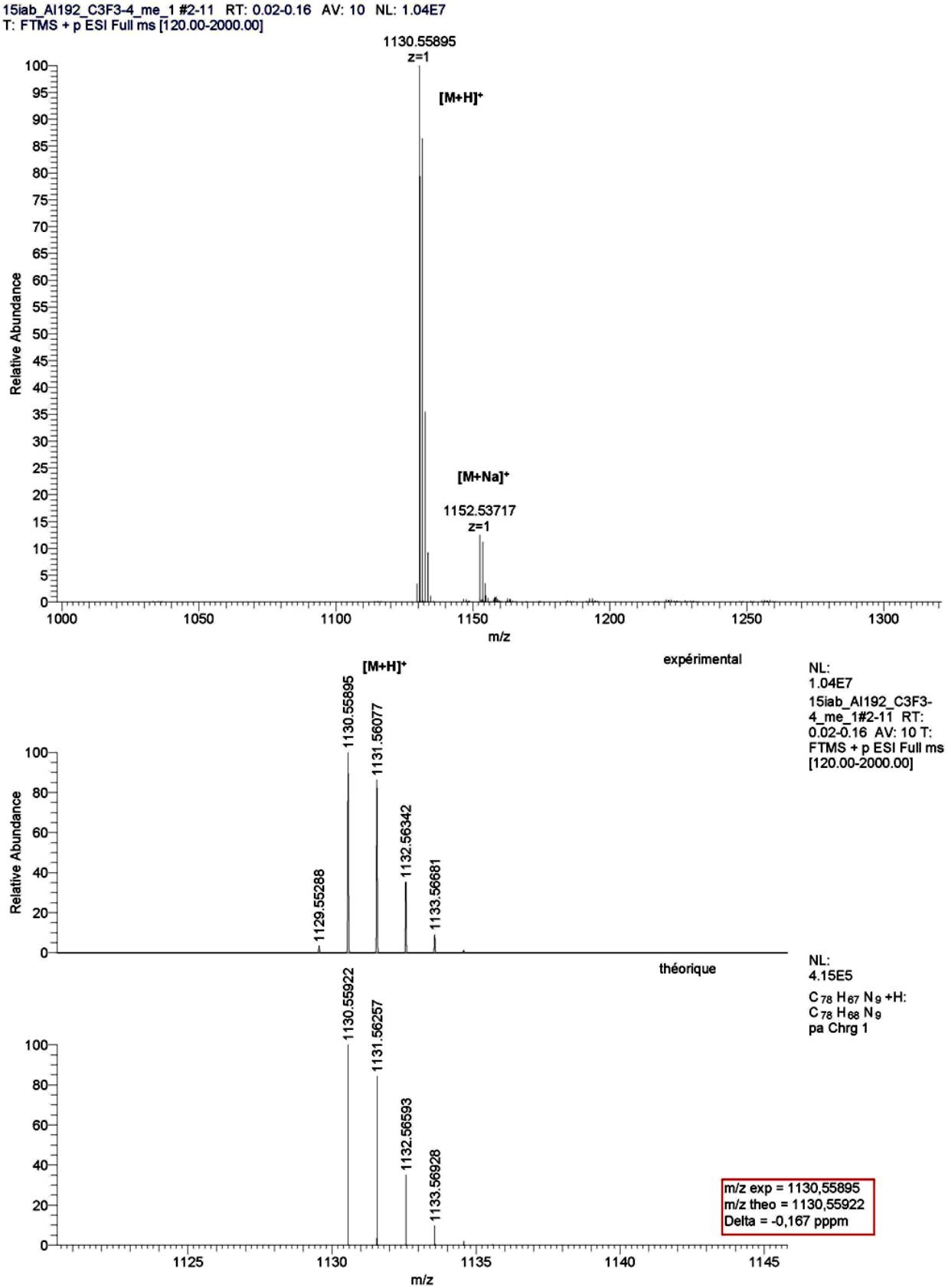


Figure S36. HR-ESI spectrum of imidazoporphyrin 2H-19a.

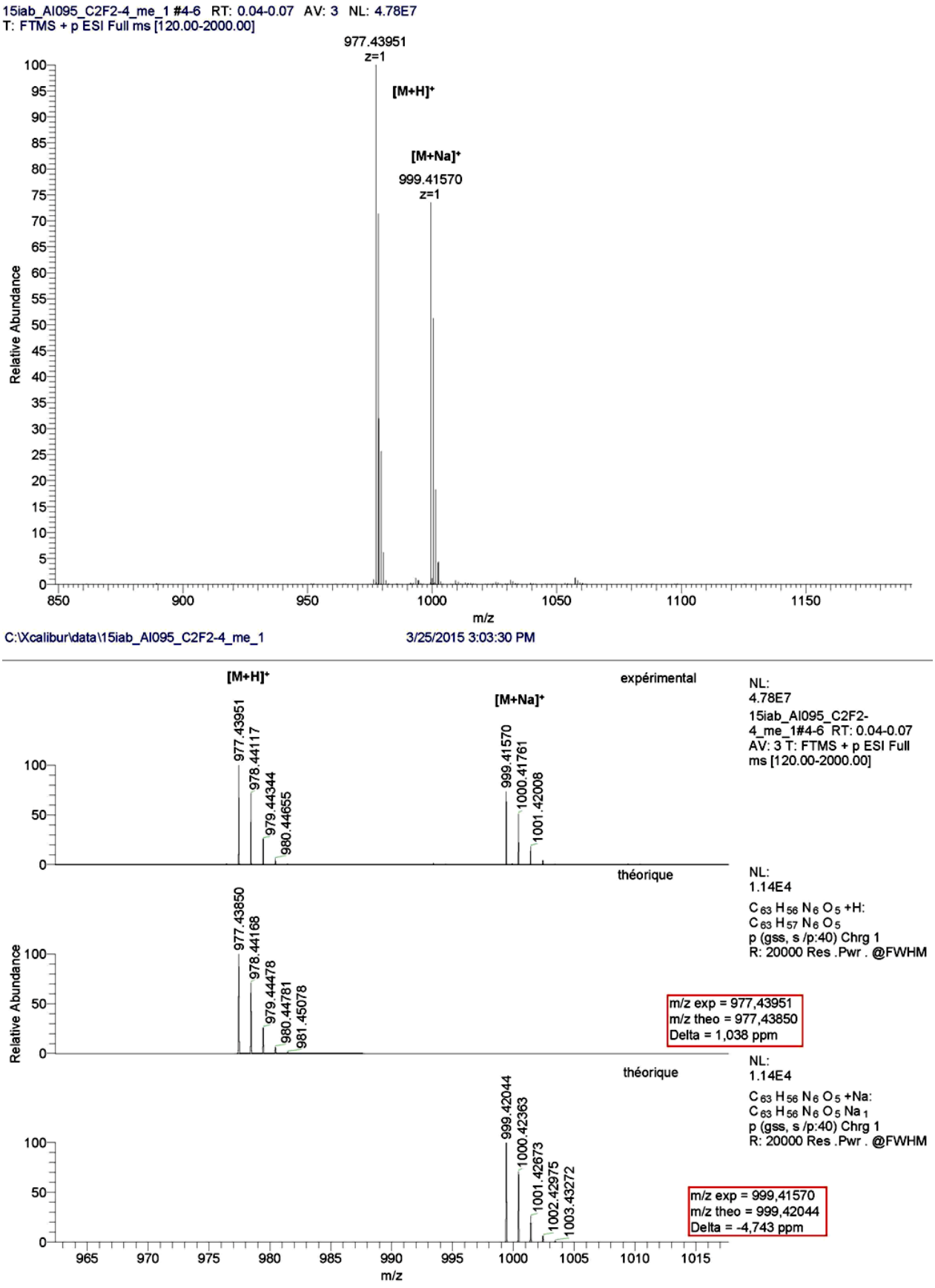


Figure S37. HR-ESI spectrum of imidazoporphyrin 2H-3b.

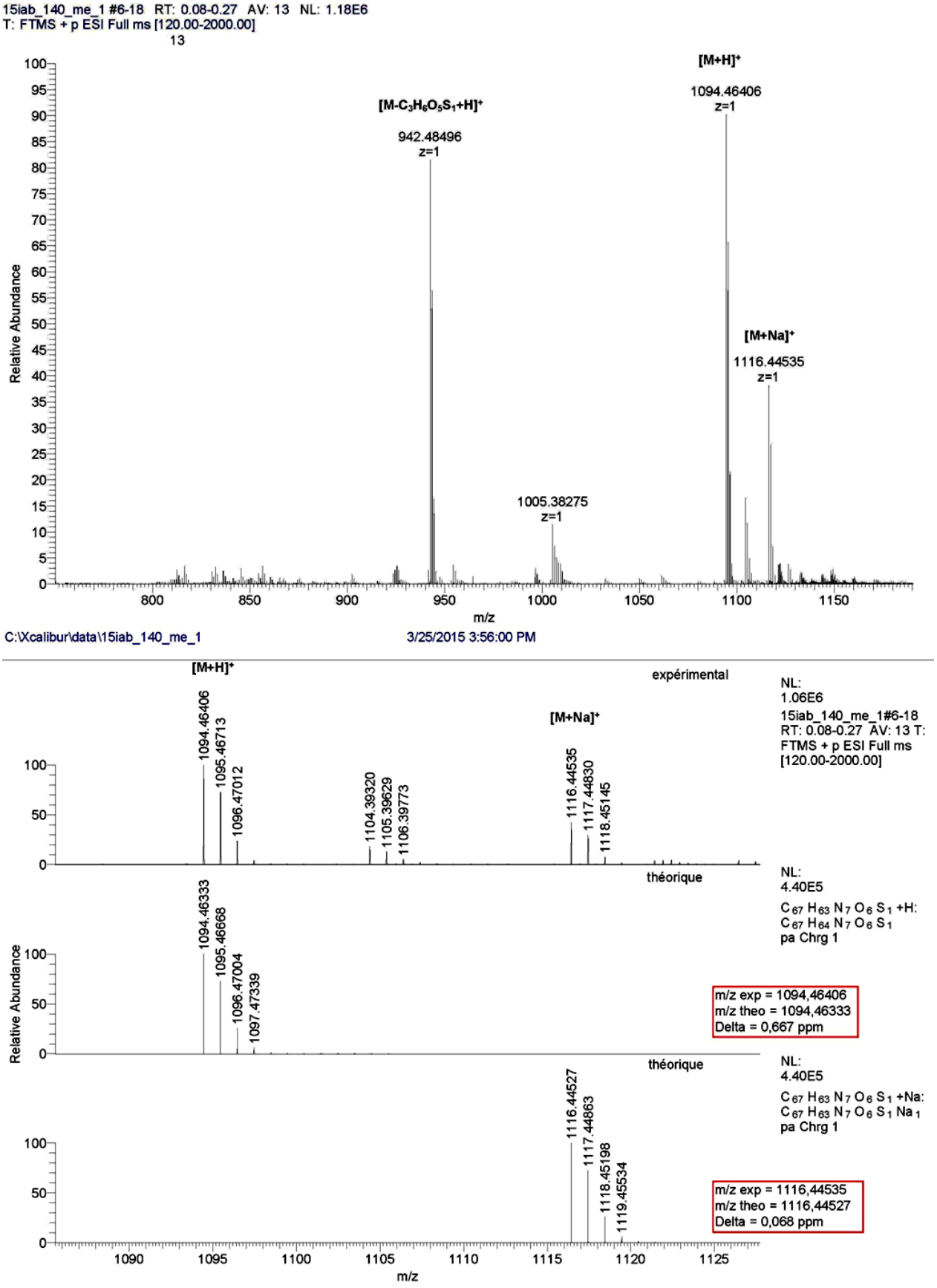


Figure S38. HR-ESI spectrum of imidazoporphyrin Zn-3b.

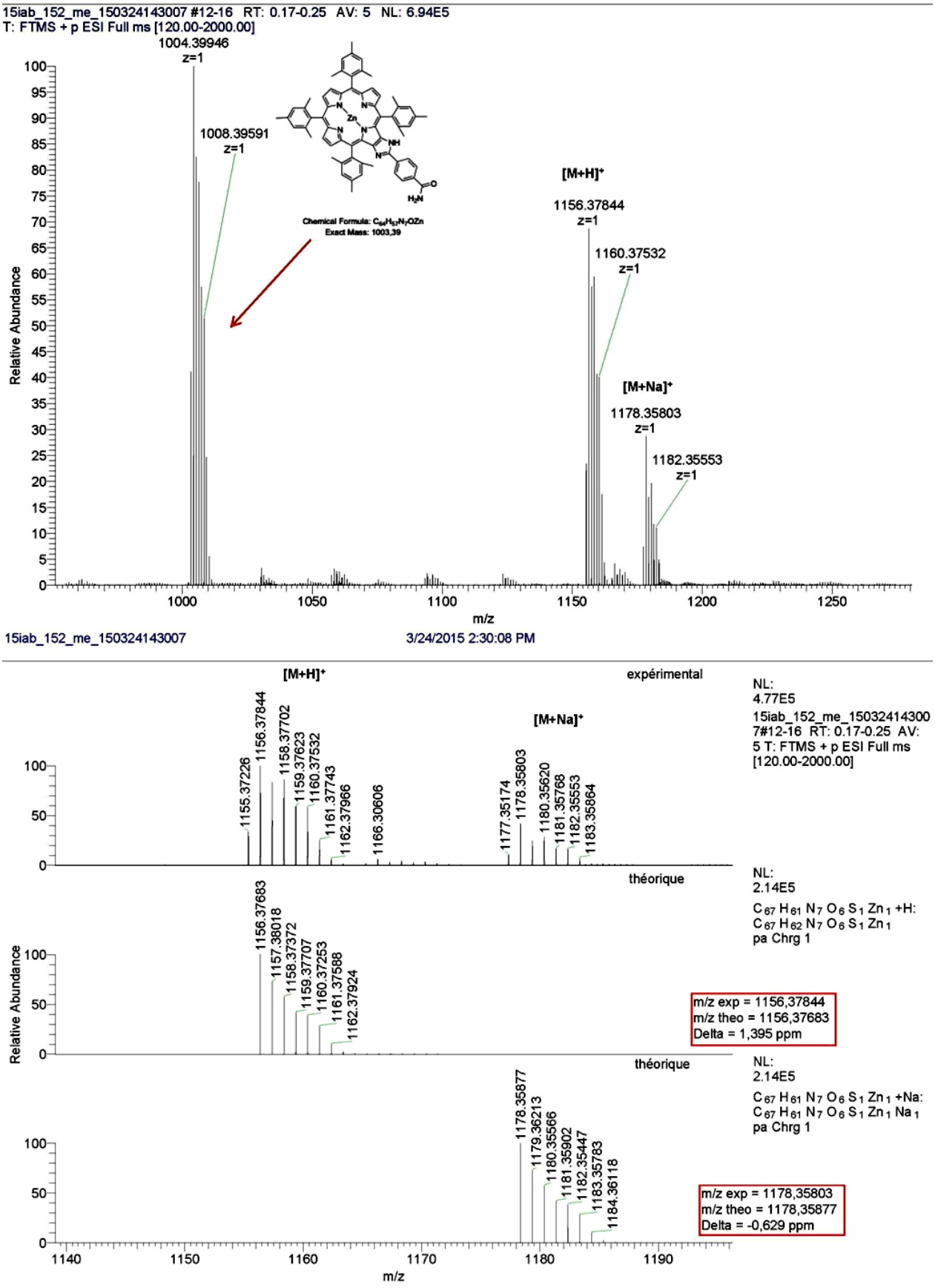
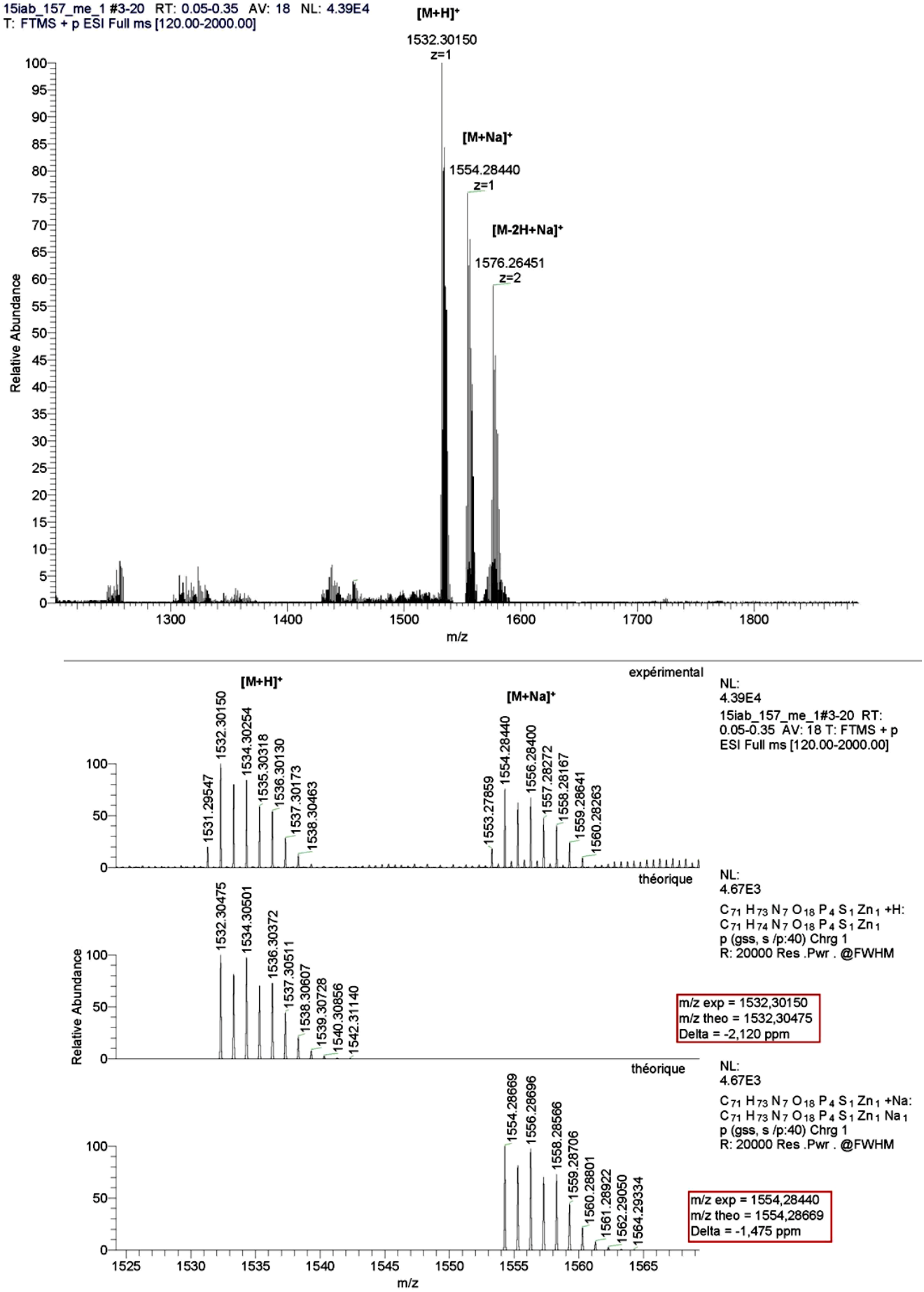


Figure S39. HR-ESI spectrum of imidazoporphyrin Zn-3e.



11. Absorption and emission spectra of Zn-3b

Figure S40. Normalized absorption spectrum recorded in PBS (100 mM phosphate + 150 mM NaCl, pH 7.5) at 25 °C.

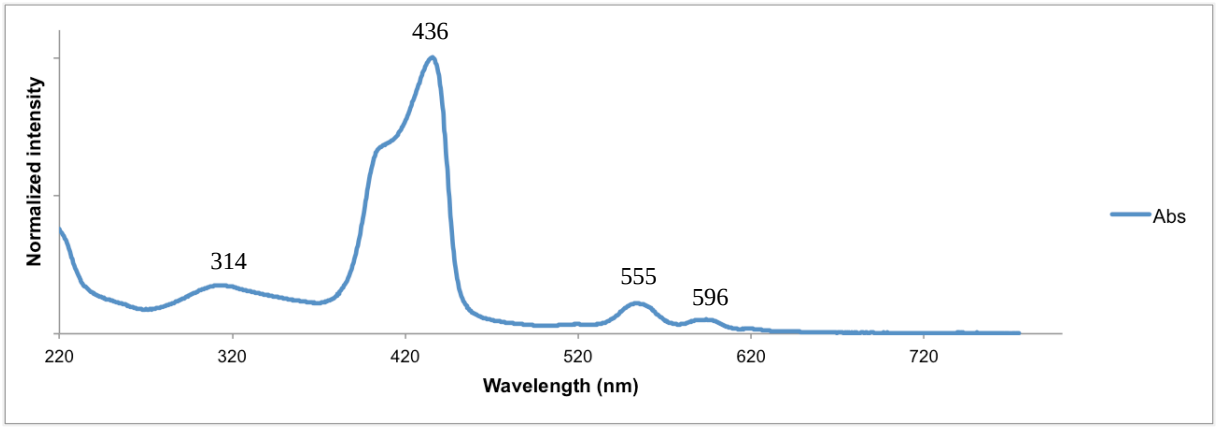
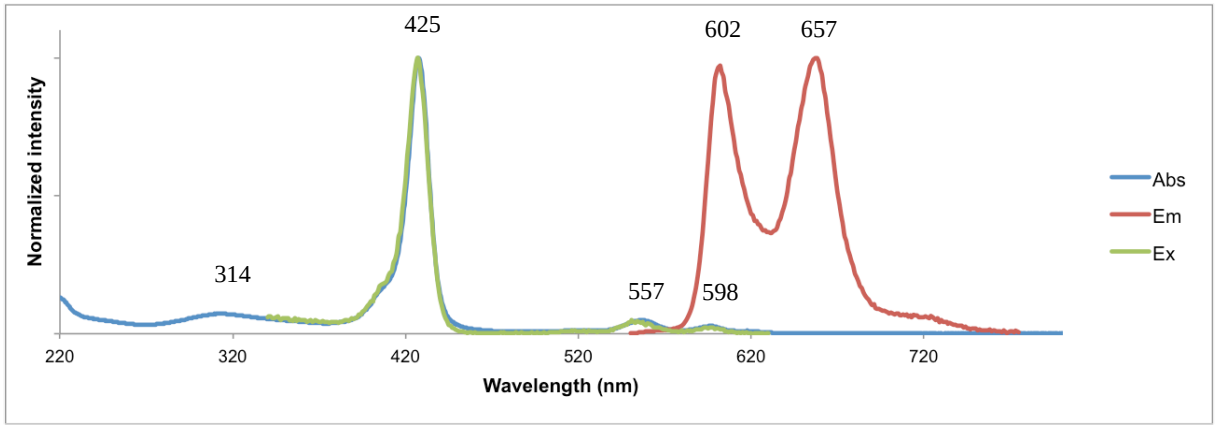


Figure S41. Normalized absorption (blue), excitation (green, λ_{em} = 602, 657 nm) and emission (red, λ_{ex} = 427 nm) spectra recorded in CH_3CN at 25 °C.



12. Absorption spectra of the derivatives of tetratolylporphyrin (2H-1a)

Figure S42. Absorption spectrum of Cu-4a ($CHCl_3$).

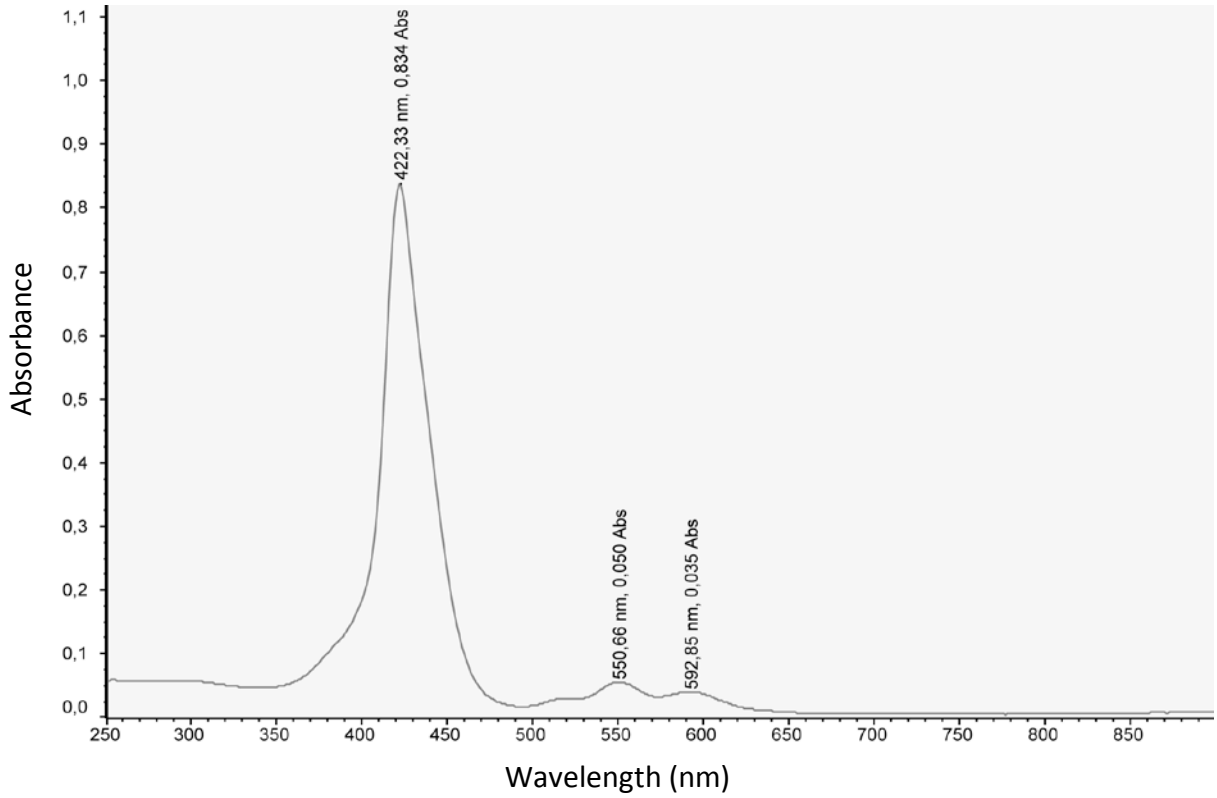


Figure S43. Absorption spectrum of 2H-6a ($CHCl_3$).

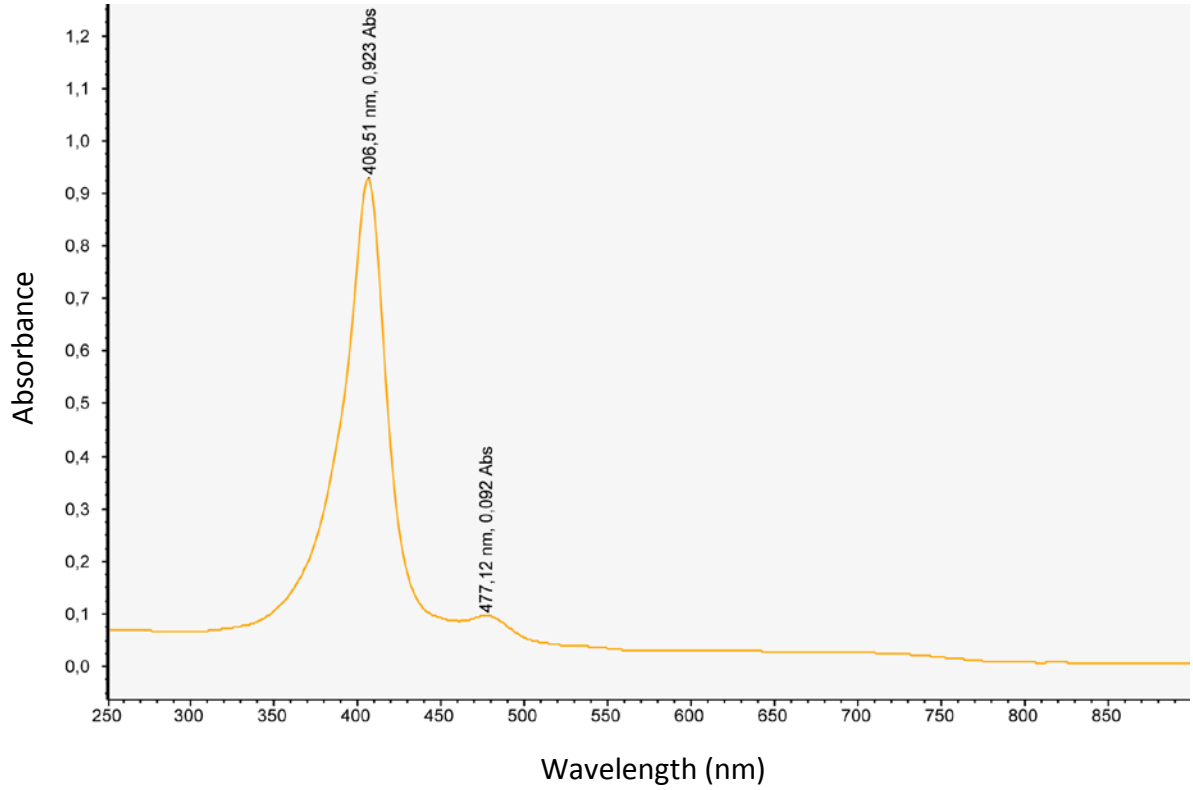


Figure S44. Absorption spectrum of 2H-14a ($CHCl_3$).

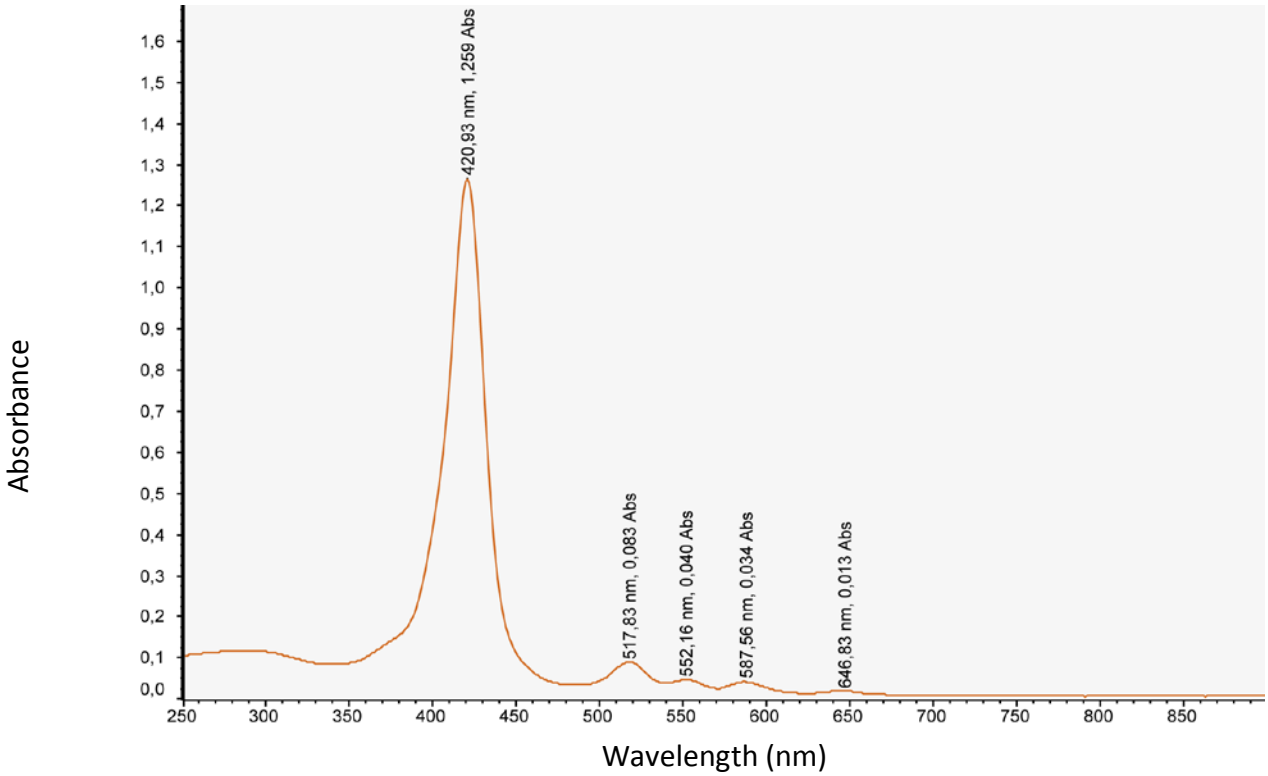


Figure S45. Absorption spectrum of 2H-15a ($CHCl_3$).

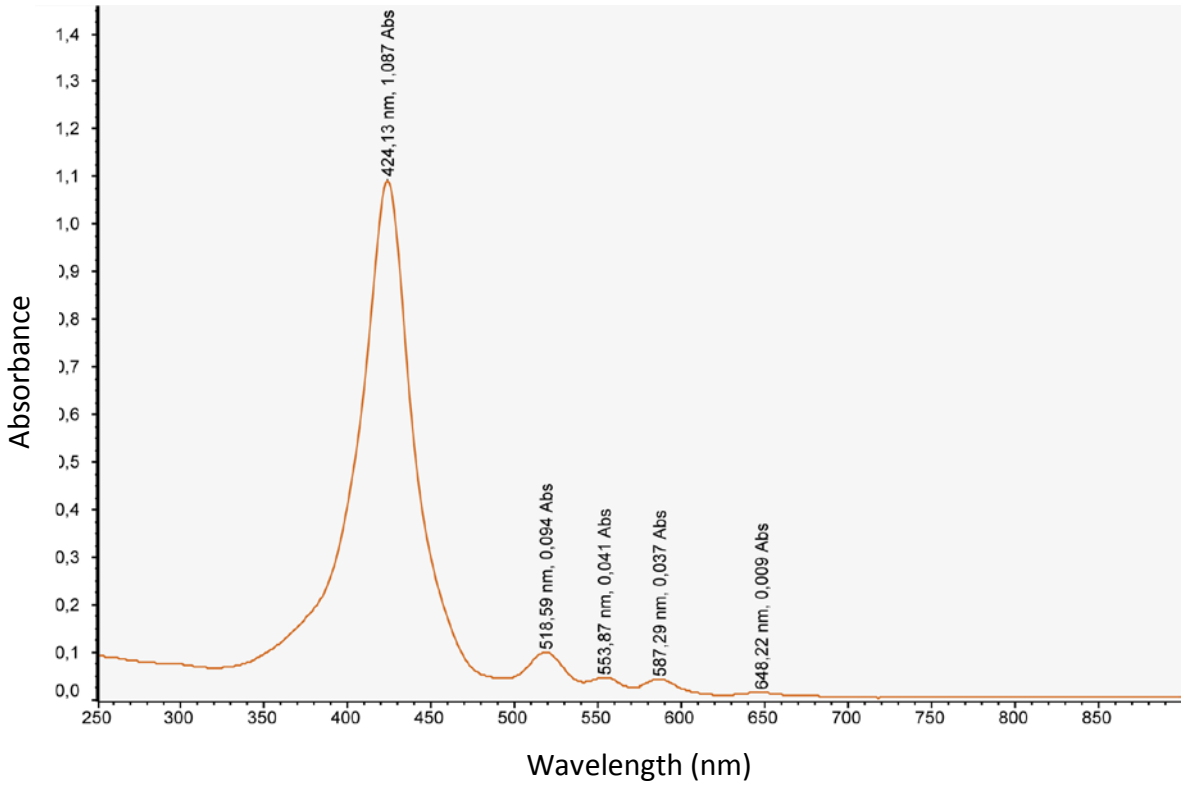


Figure S46. Absorption spectrum of 2H-19a ($CHCl_3$).