

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 ·3H ₂ O (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. ^1H NMR spectrum of 2H-2e (CDCl_3).

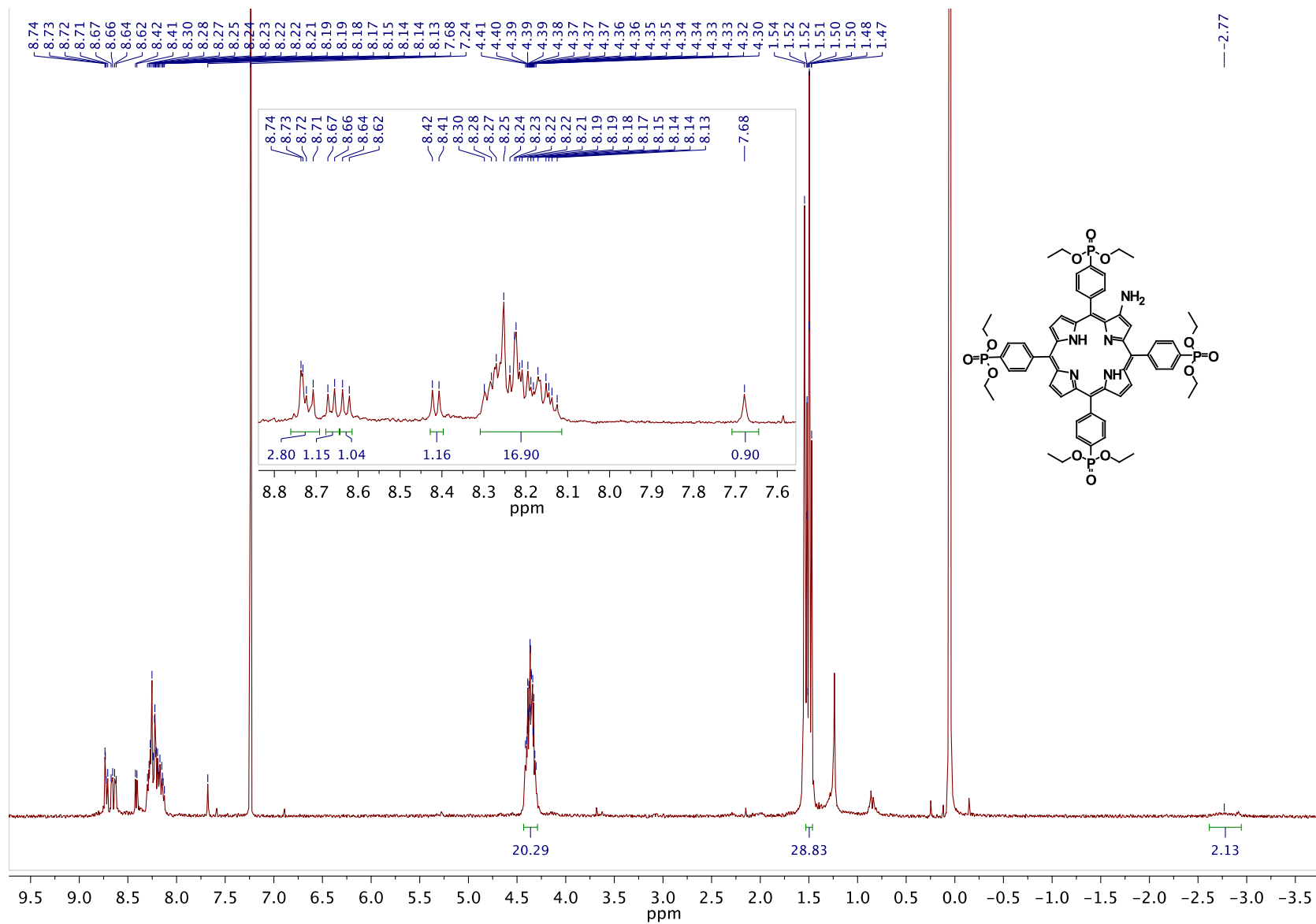


Figure S2. ^{31}P NMR spectrum of 2H-2e (CDCl_3).

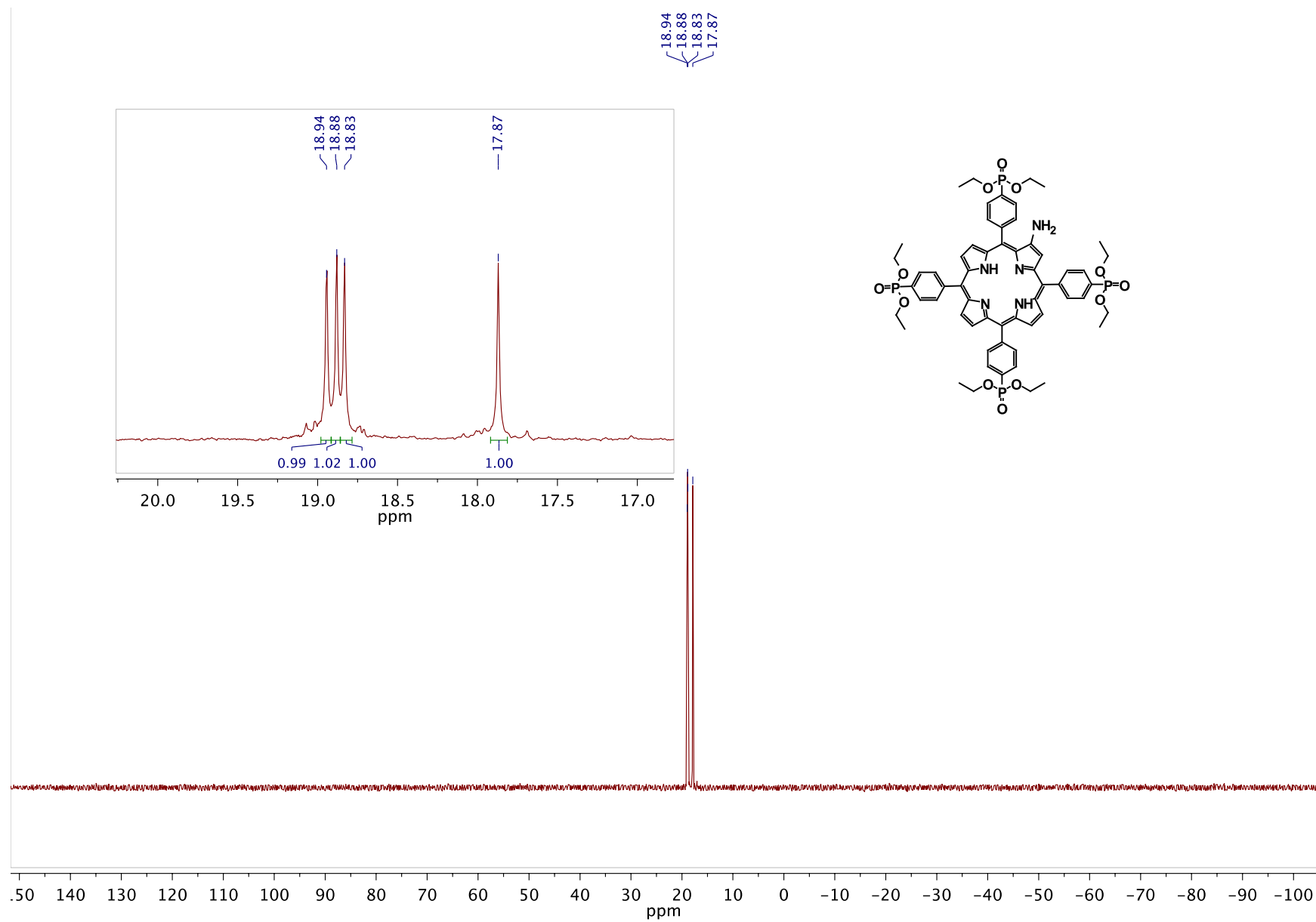
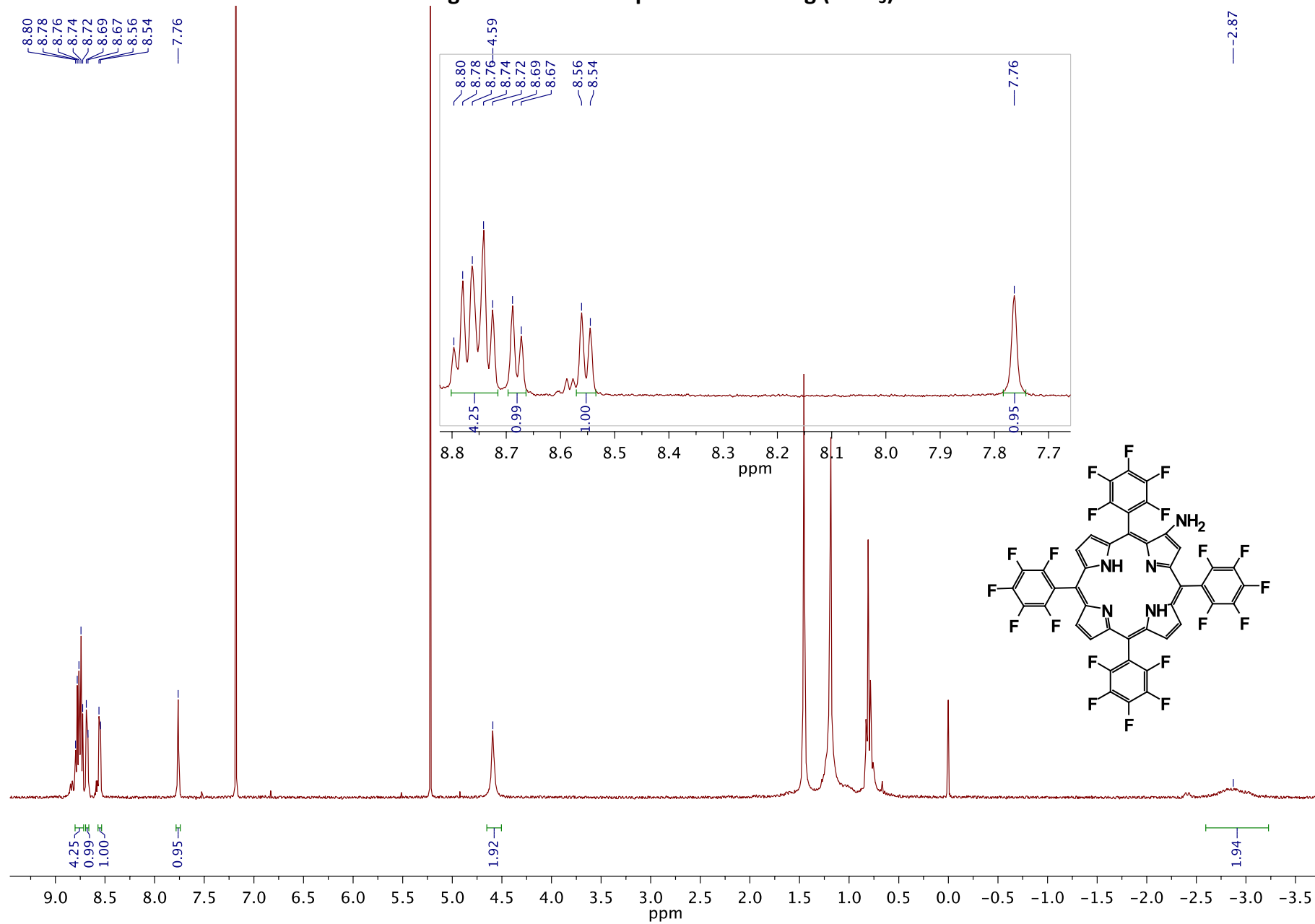


Figure S3. ^1H NMR spectrum of 2H-2g (CDCl_3).



3. NMR spectra of conjugated porphyrins M-3

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

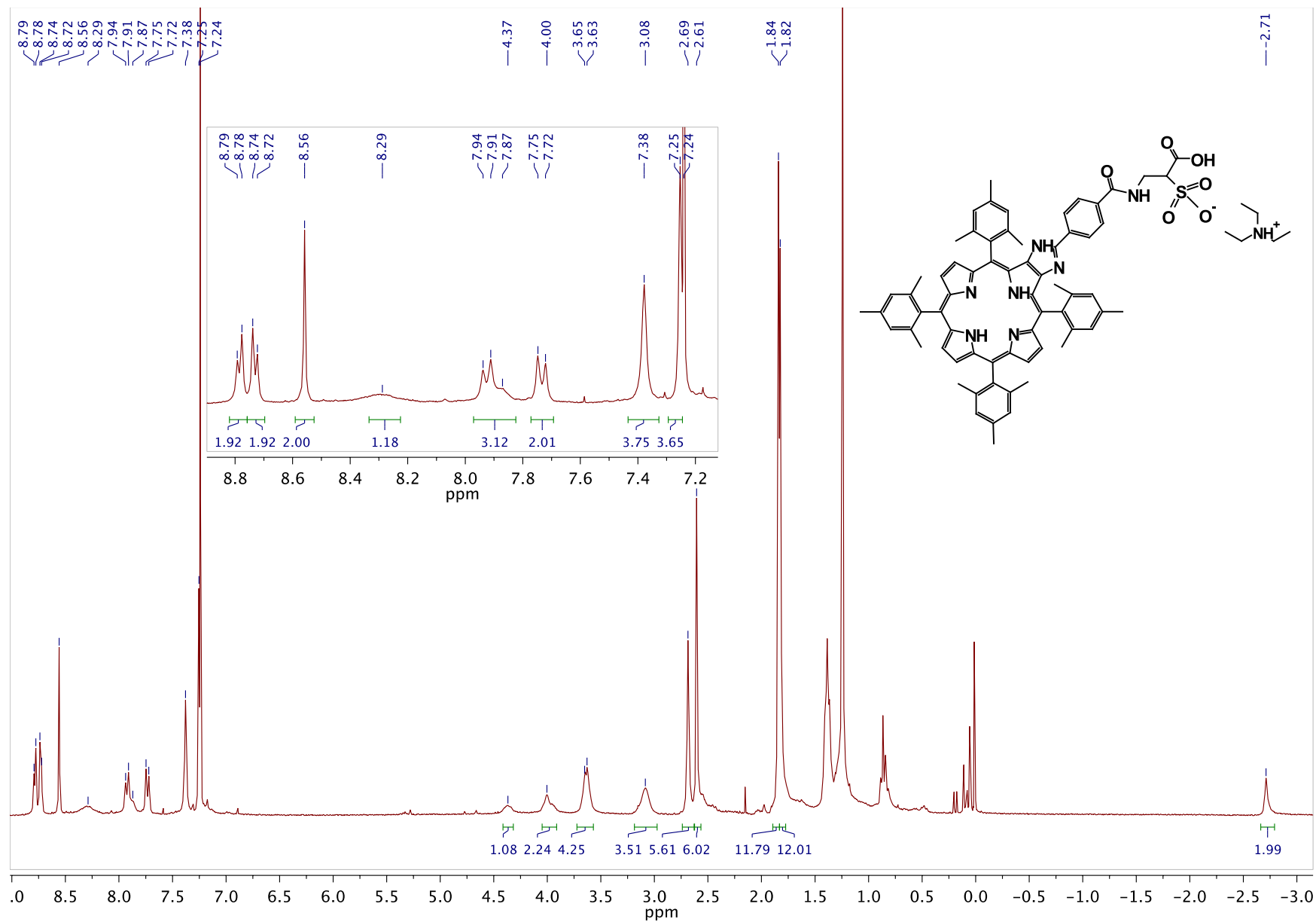


Figure S5. ^1H NMR spectrum of Zn-3e ($\text{CDCl}_3 + \text{MeOH-}d_4$).

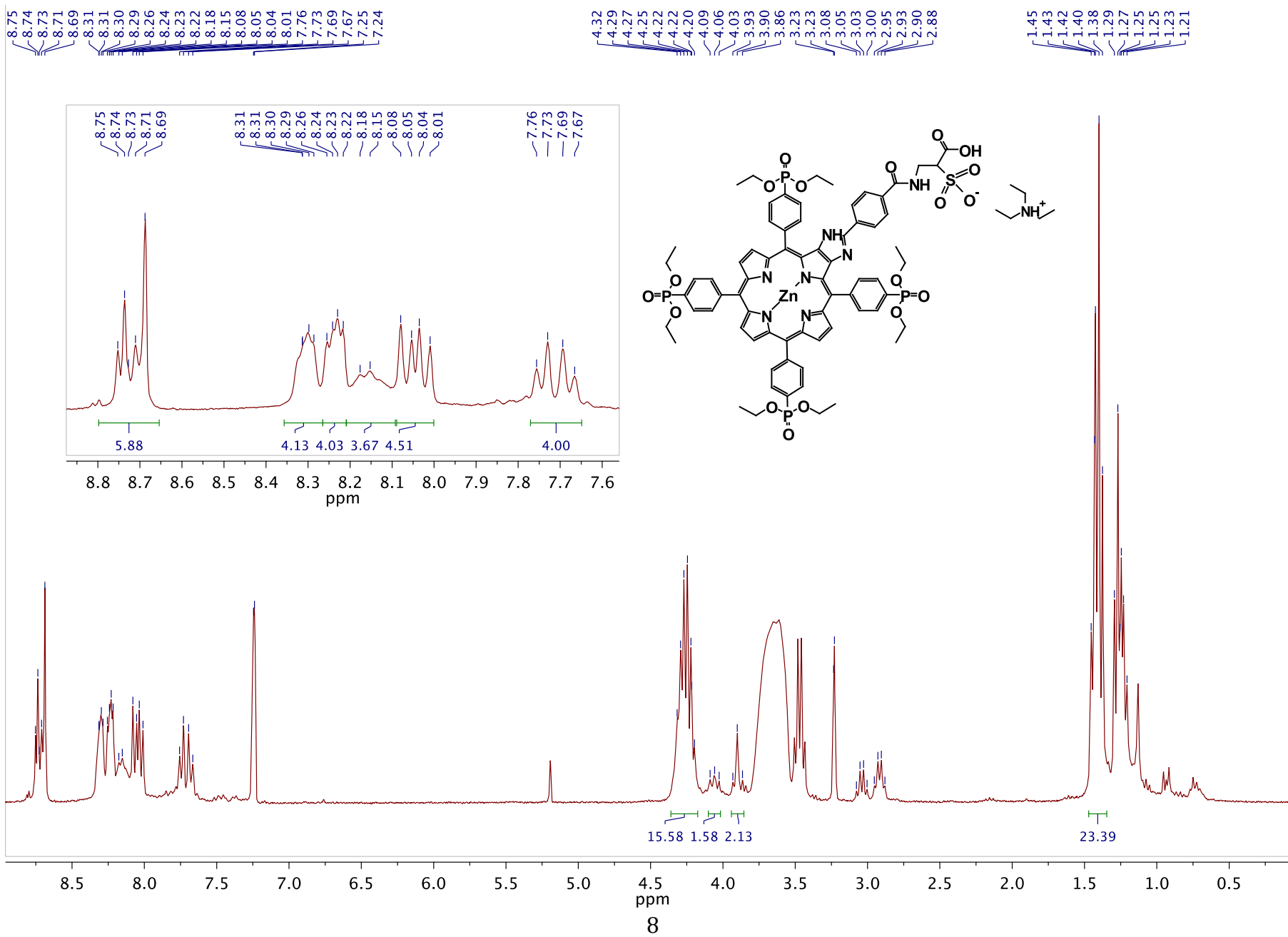
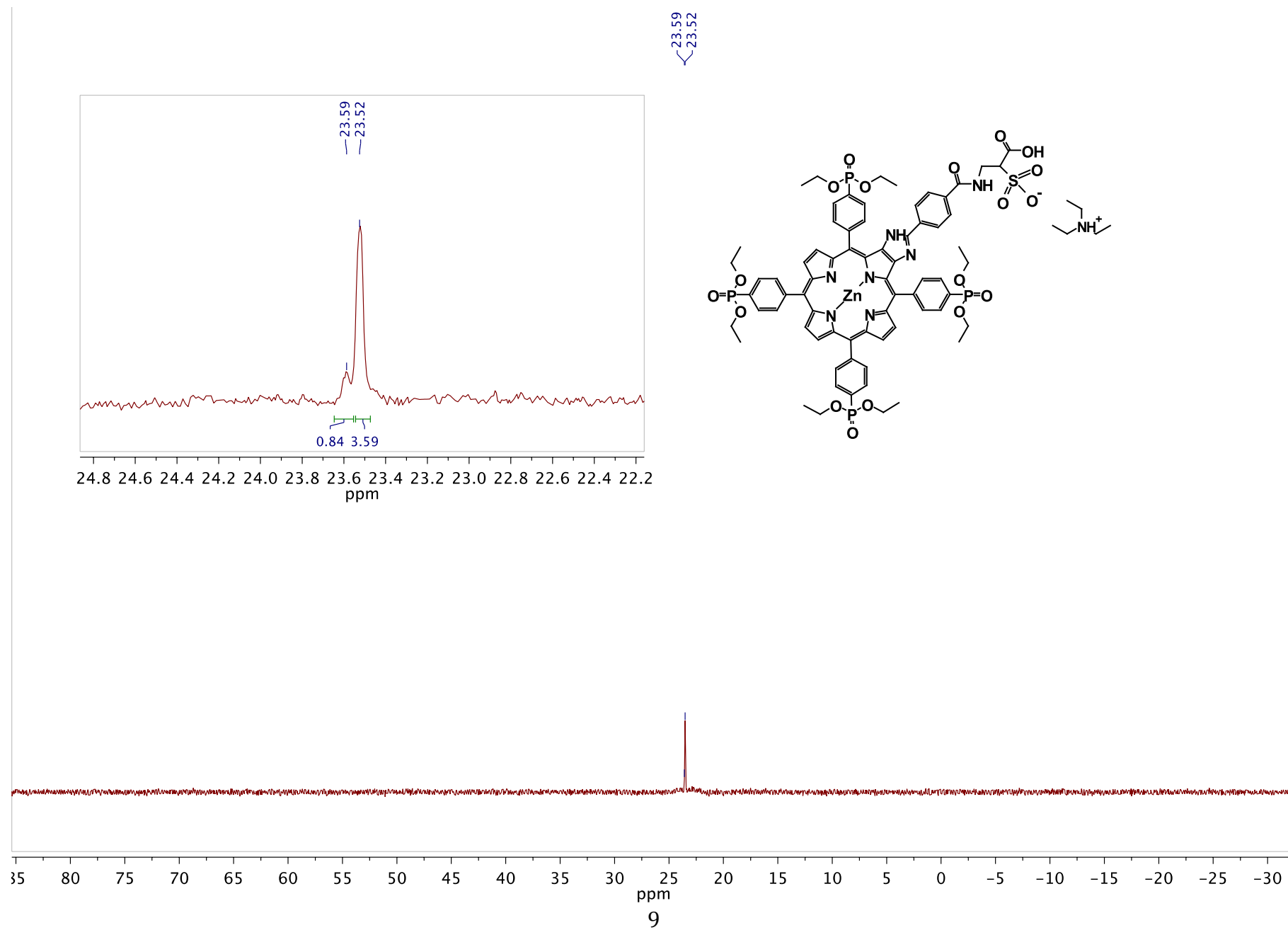


Figure S6. ^{31}P NMR spectrum of Zn-3e ($\text{CDCl}_3 + \text{MeOH-}d_4$).



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

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

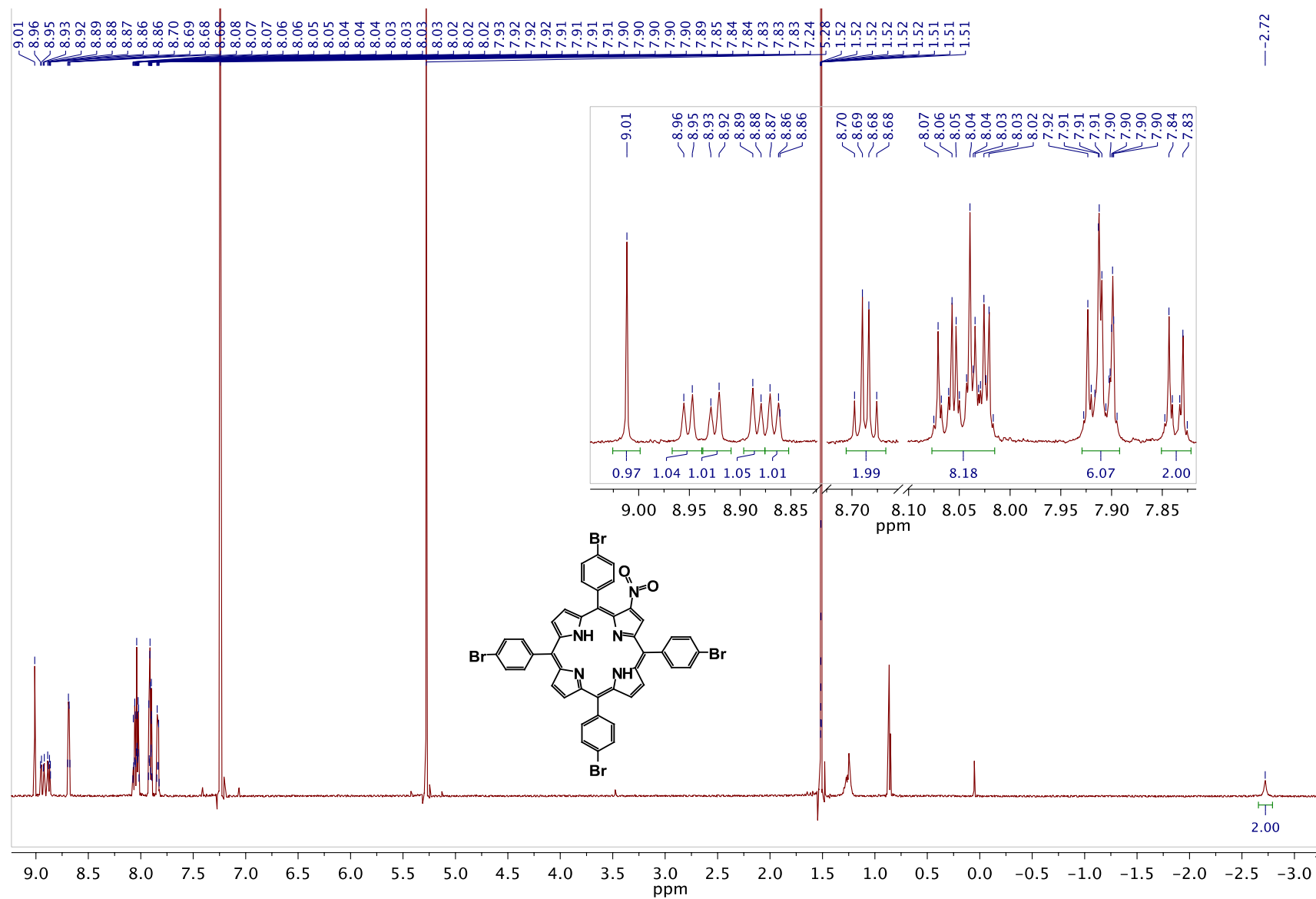
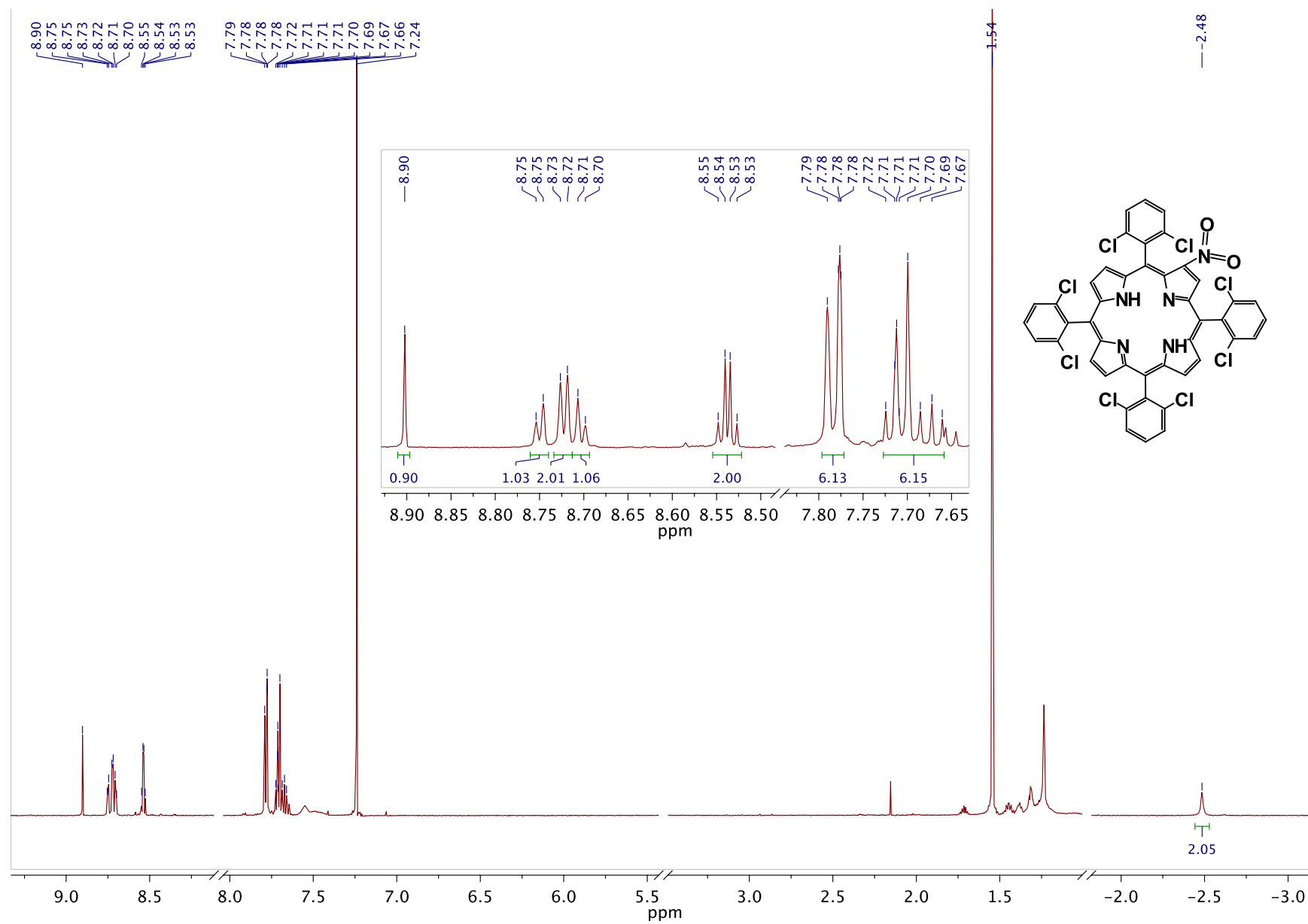


Figure S8. ^1H NMR spectrum of 2H-4f (CDCl_3).



5. NMR spectra of porphyrin 2H-5e

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

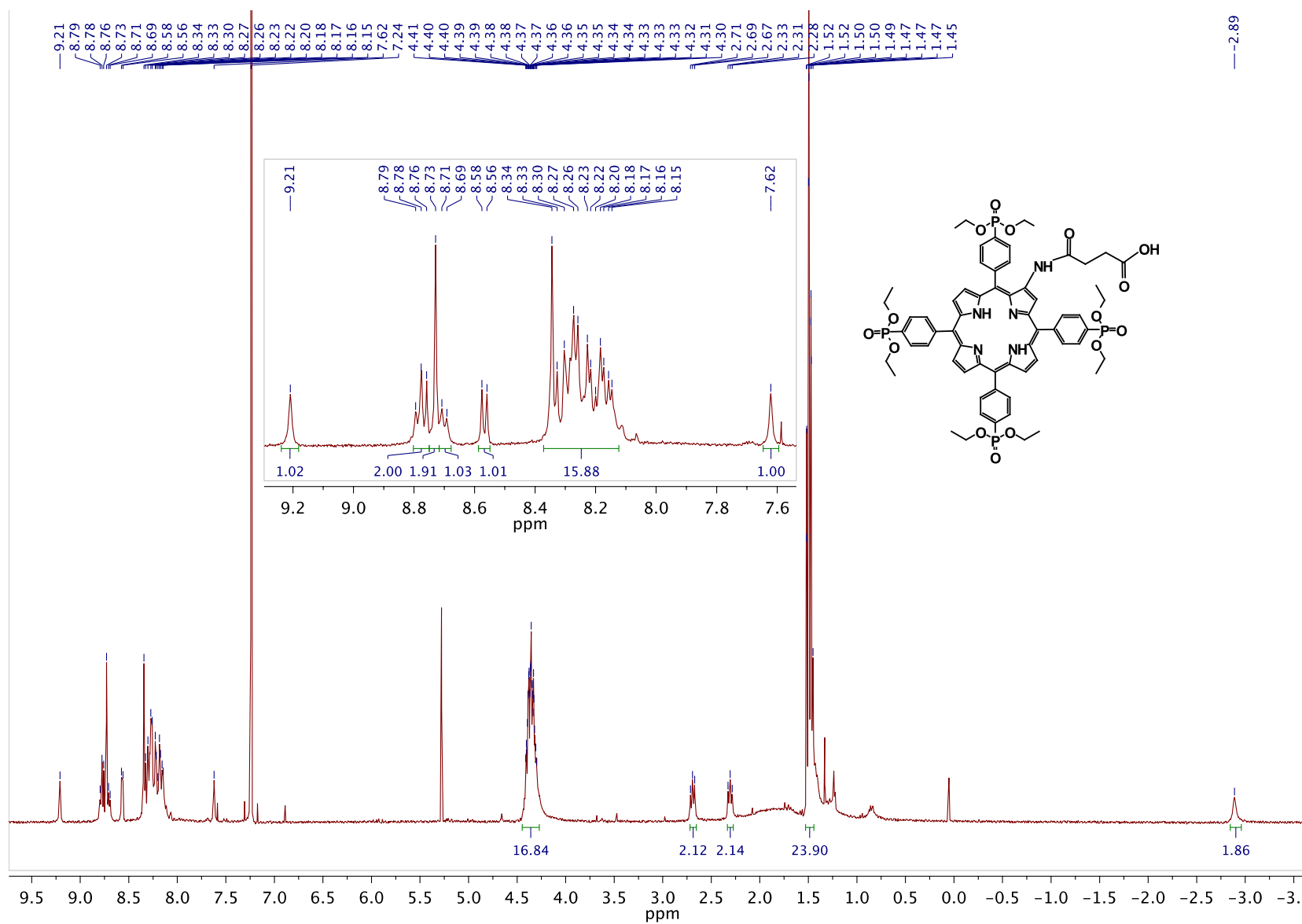
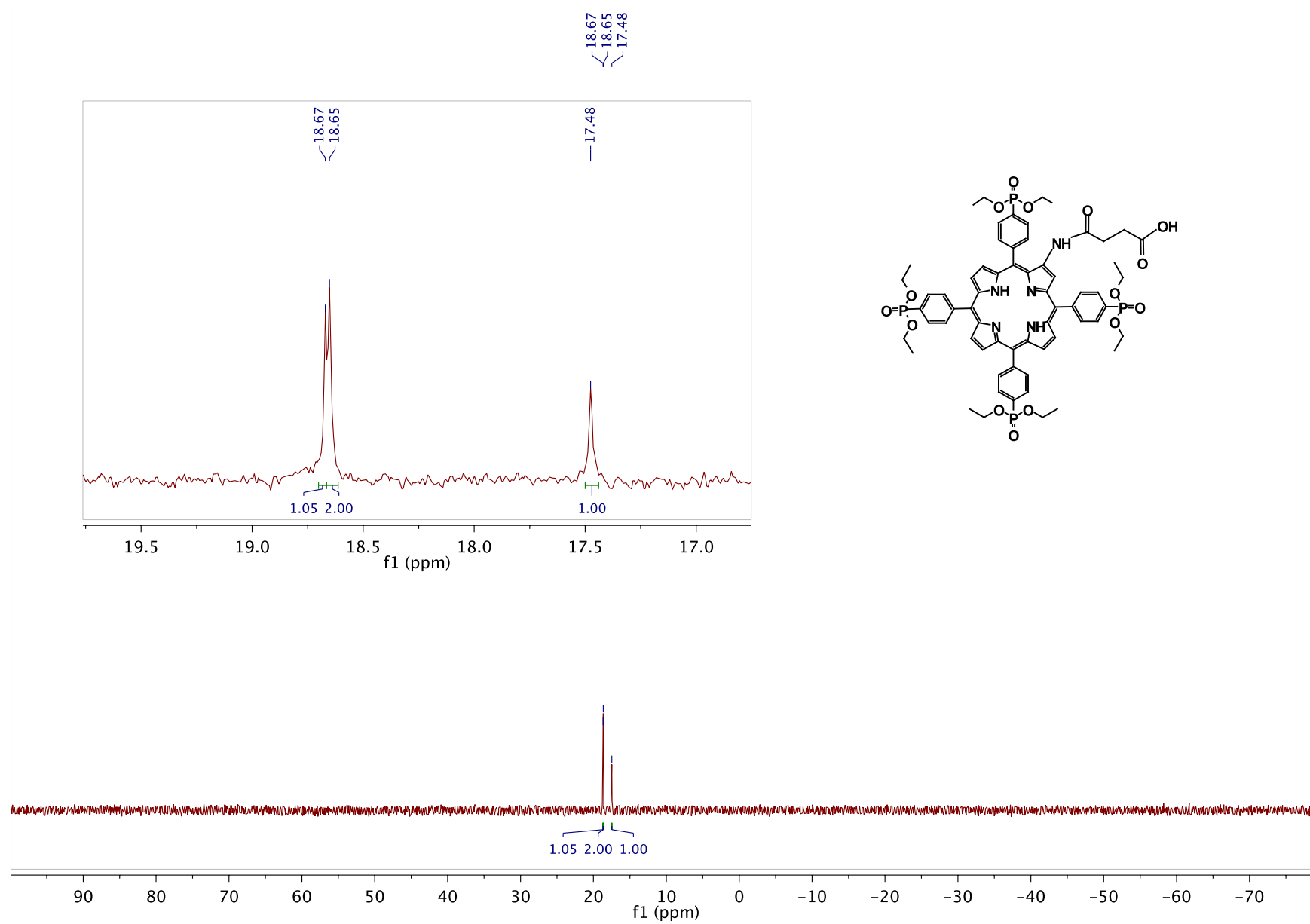


Figure S10. ^{31}P NMR spectrum of 2H-5e (CDCl_3).



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

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

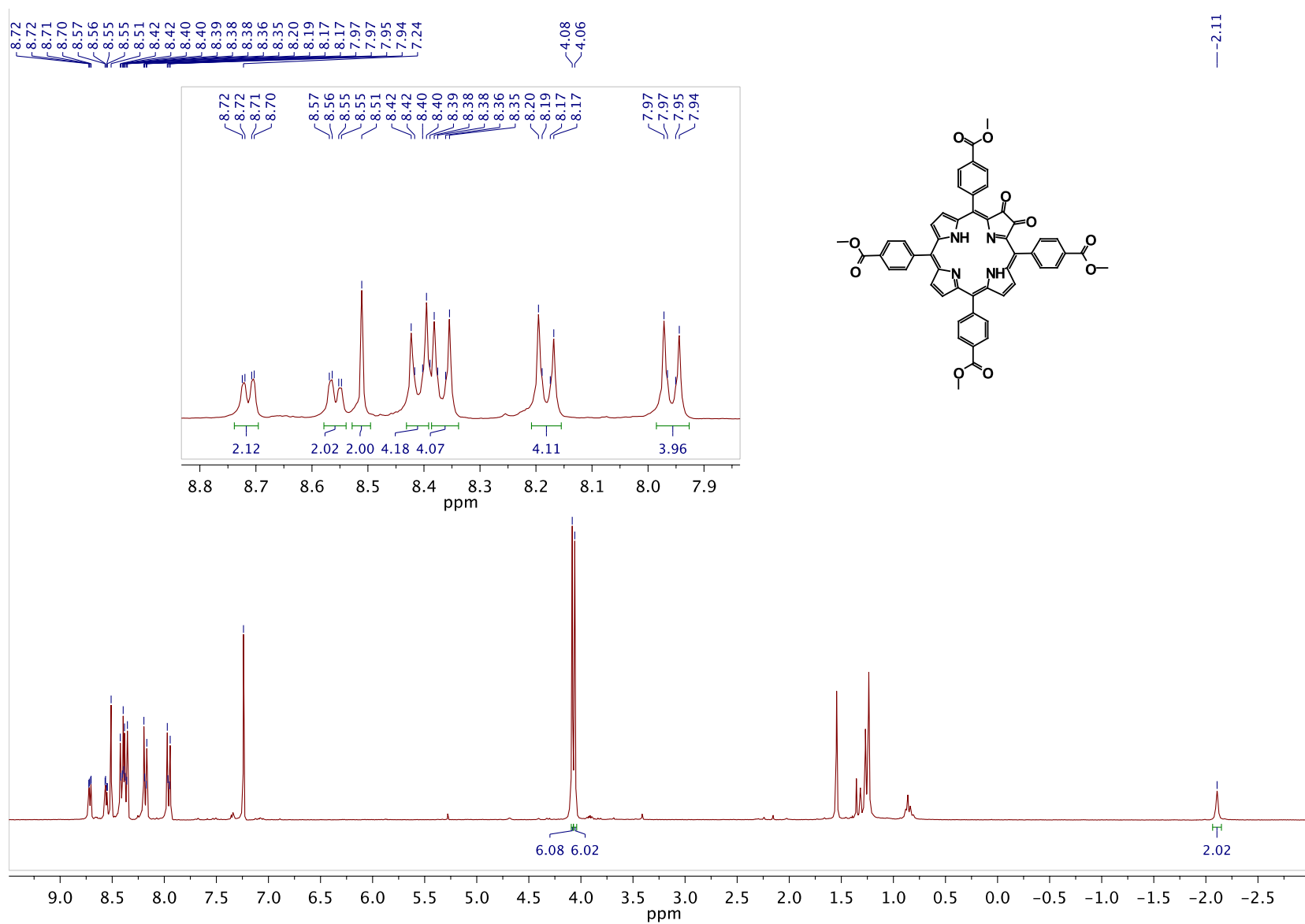


Figure S12. ^1H NMR spectrum of 2H-6e (CDCl_3).

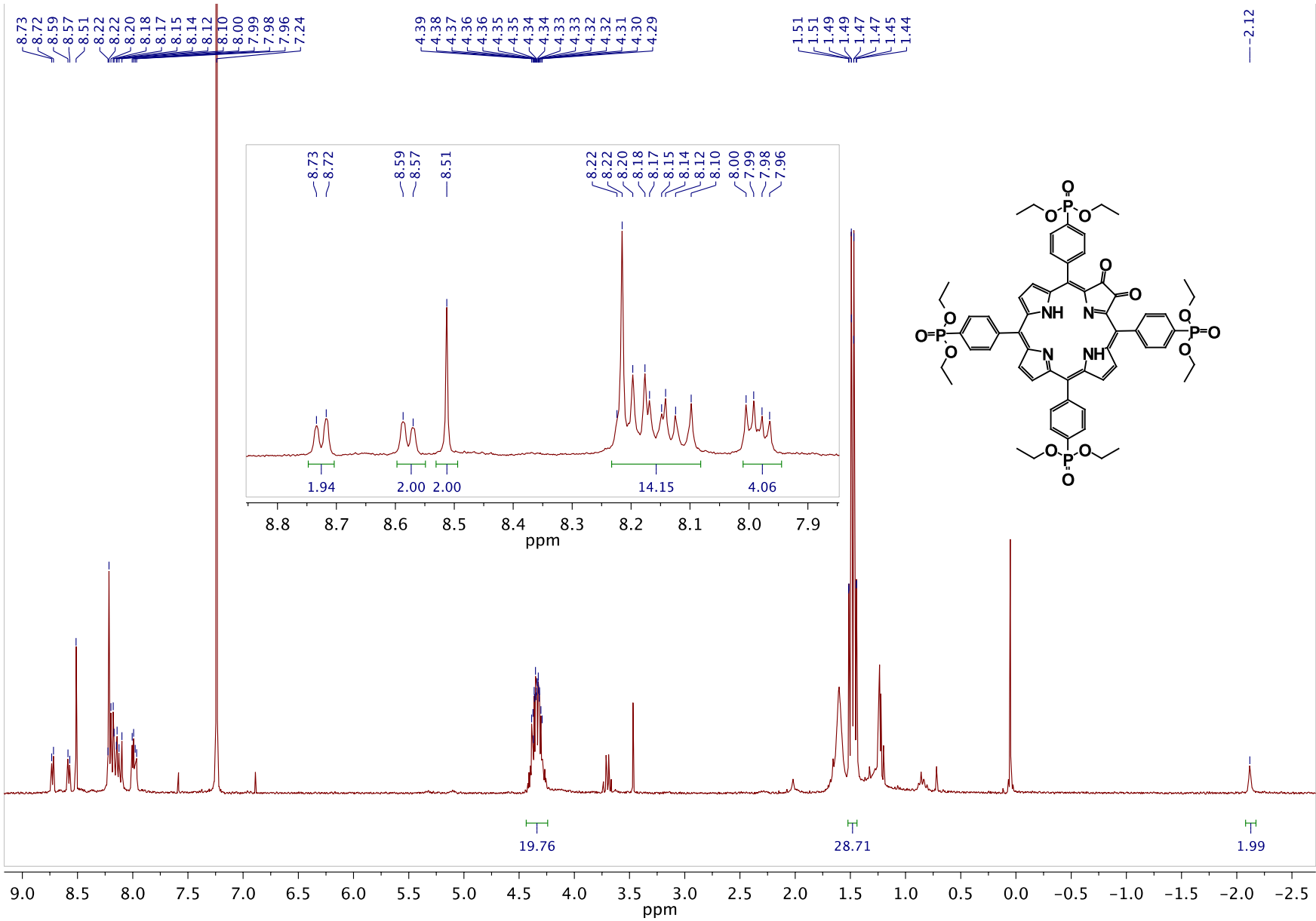


Figure S13. ^{31}P NMR spectrum of 2H-6e (CDCl_3).

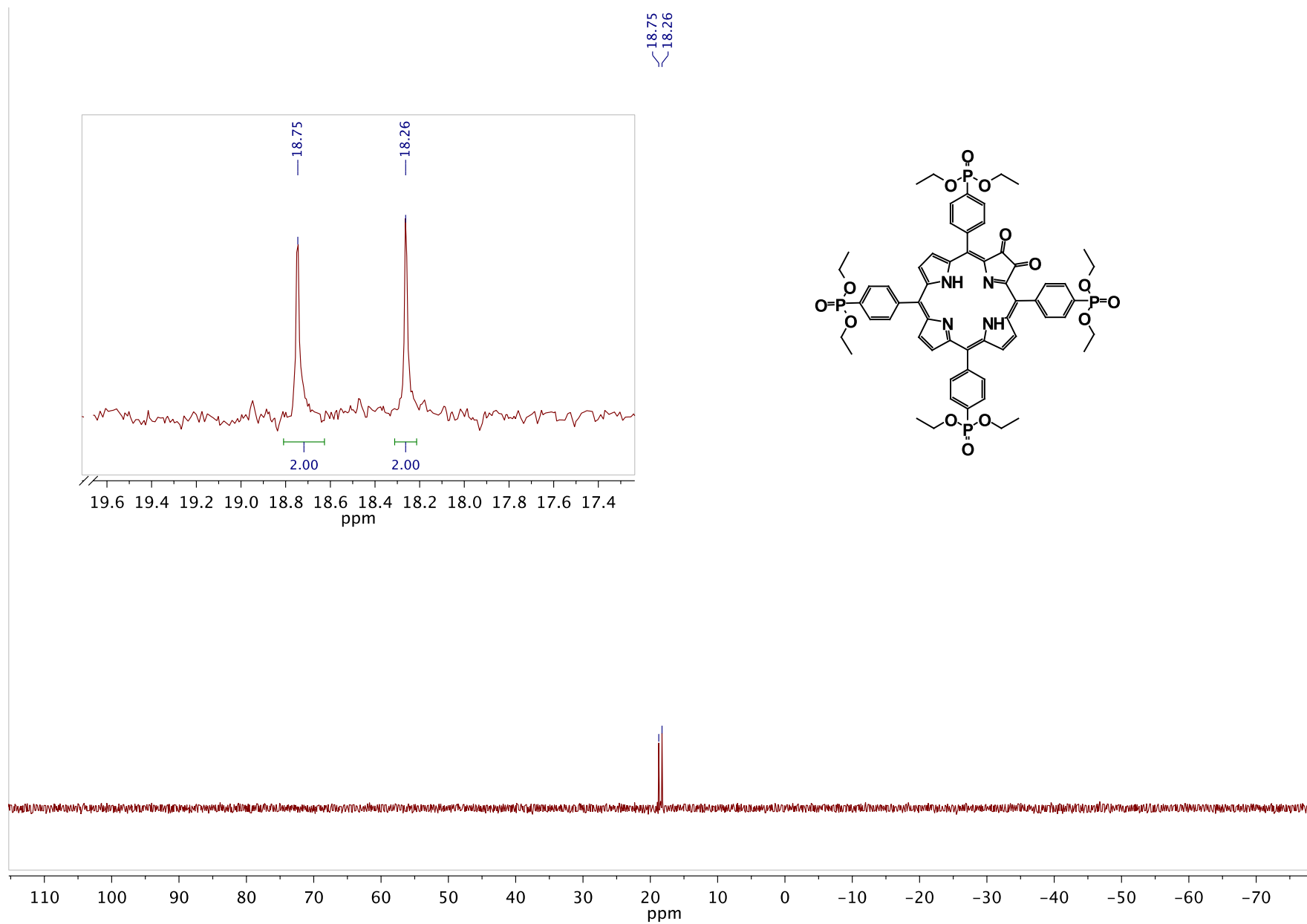
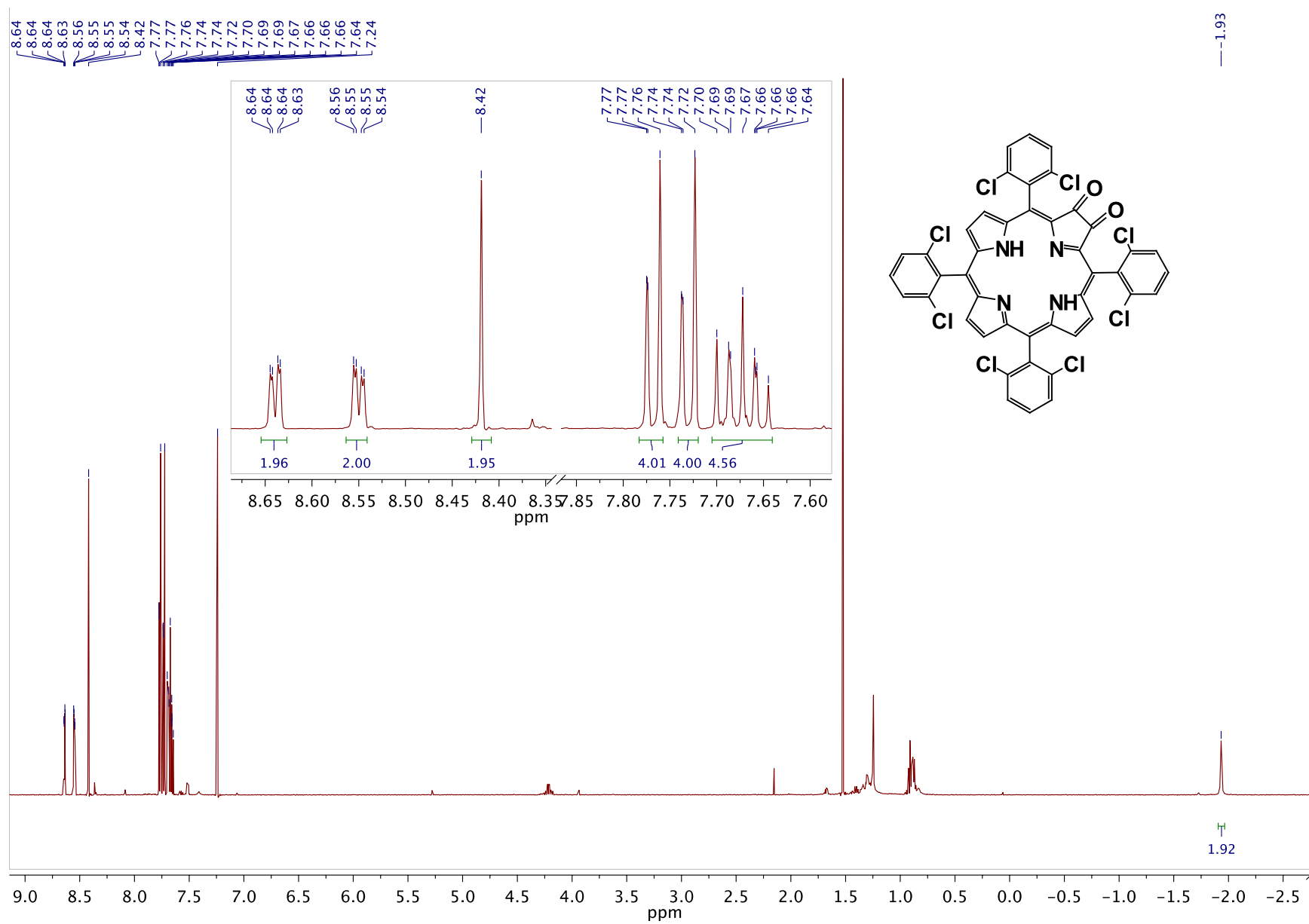


Figure S14. ^1H NMR spectrum of 2H-6f (CDCl_3).



7. NMR spectra of porphyrin 2H-7e

Figure S15. ^1H NMR spectrum of 2H-7e ($\text{CDCl}_3 + \text{MeOH-}d_4$).

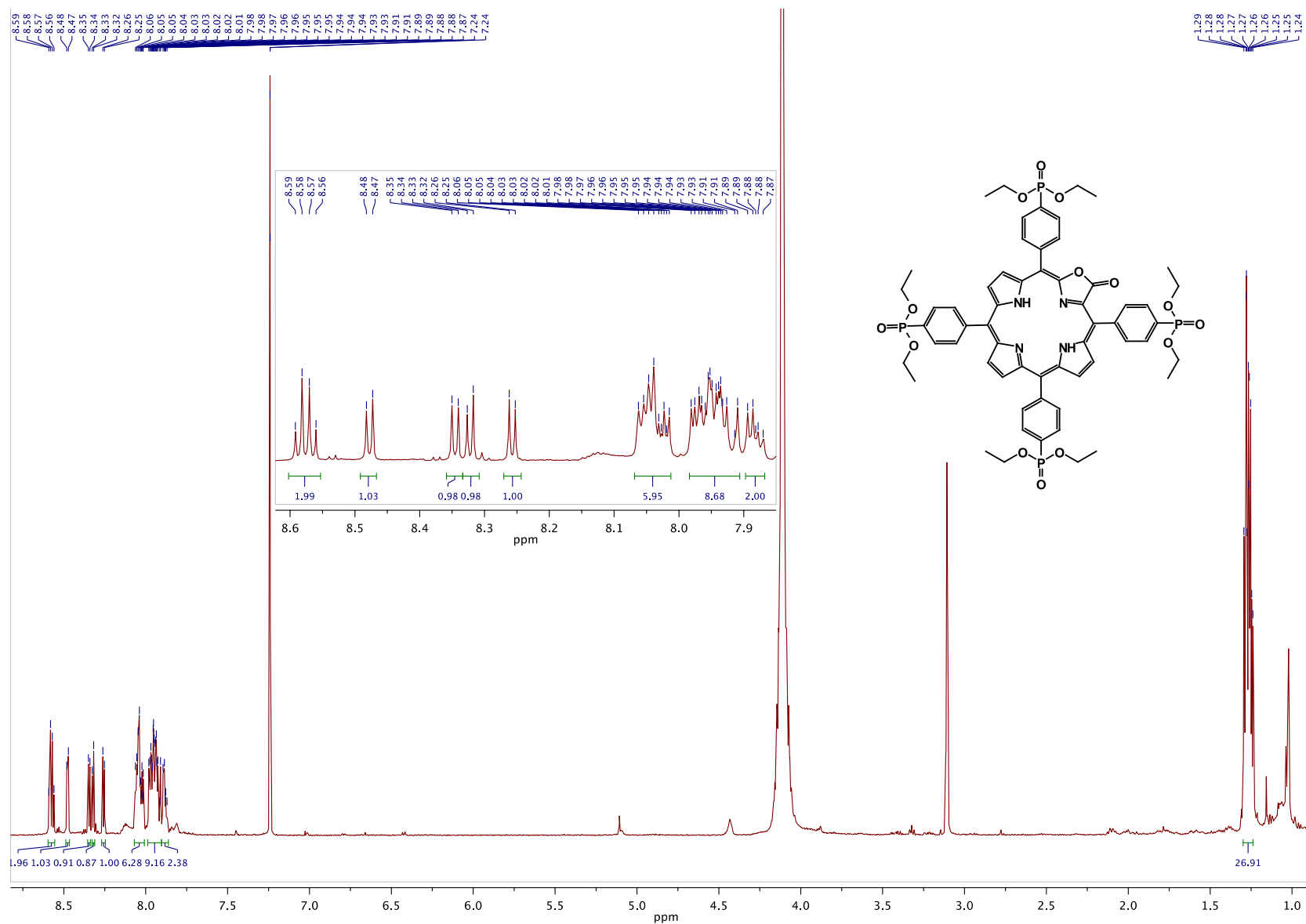
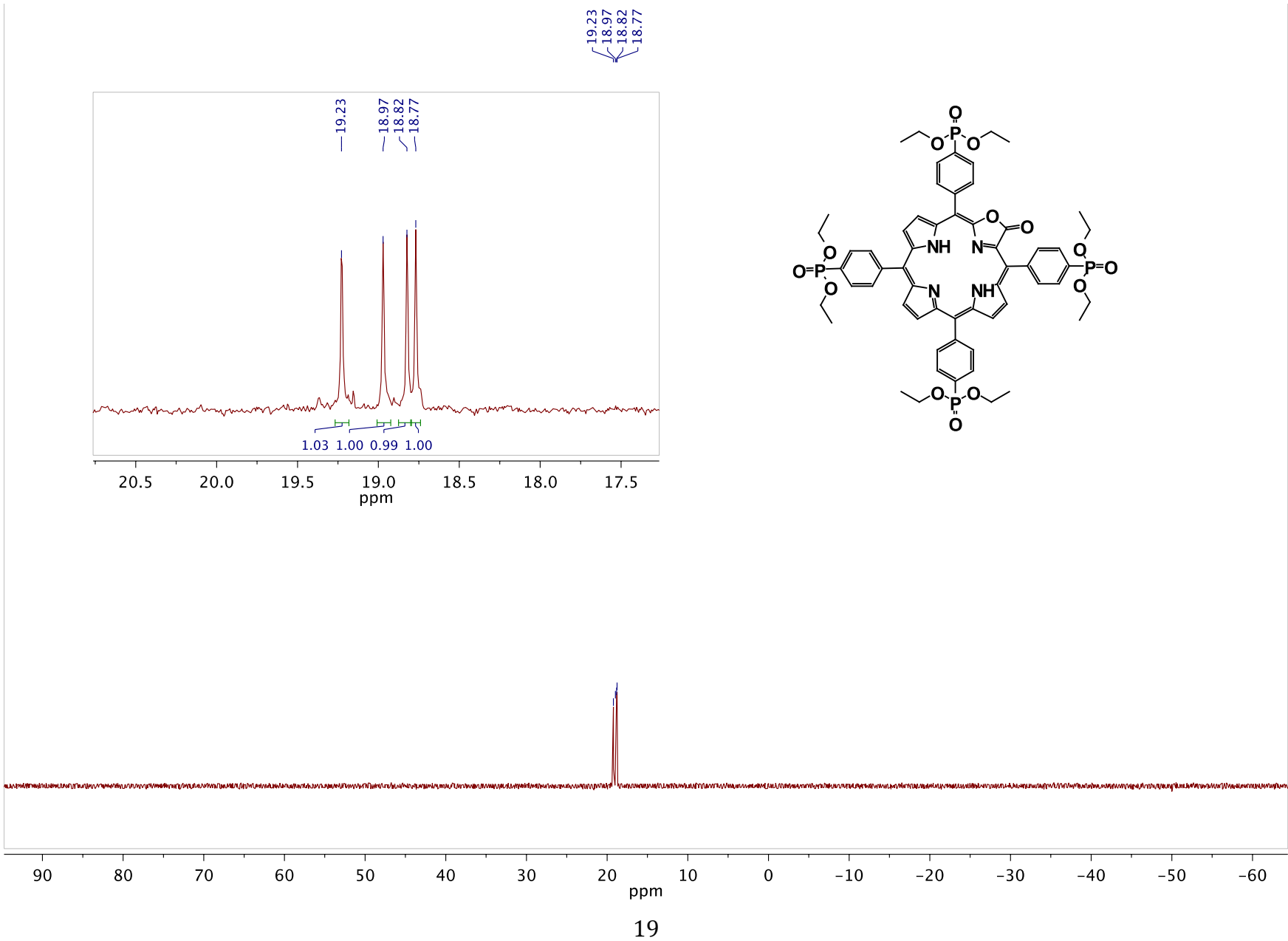


Figure S16. ^{31}P NMR spectrum of 2H-7e ($\text{CDCl}_3 + \text{MeOH-}d_4$).



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

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

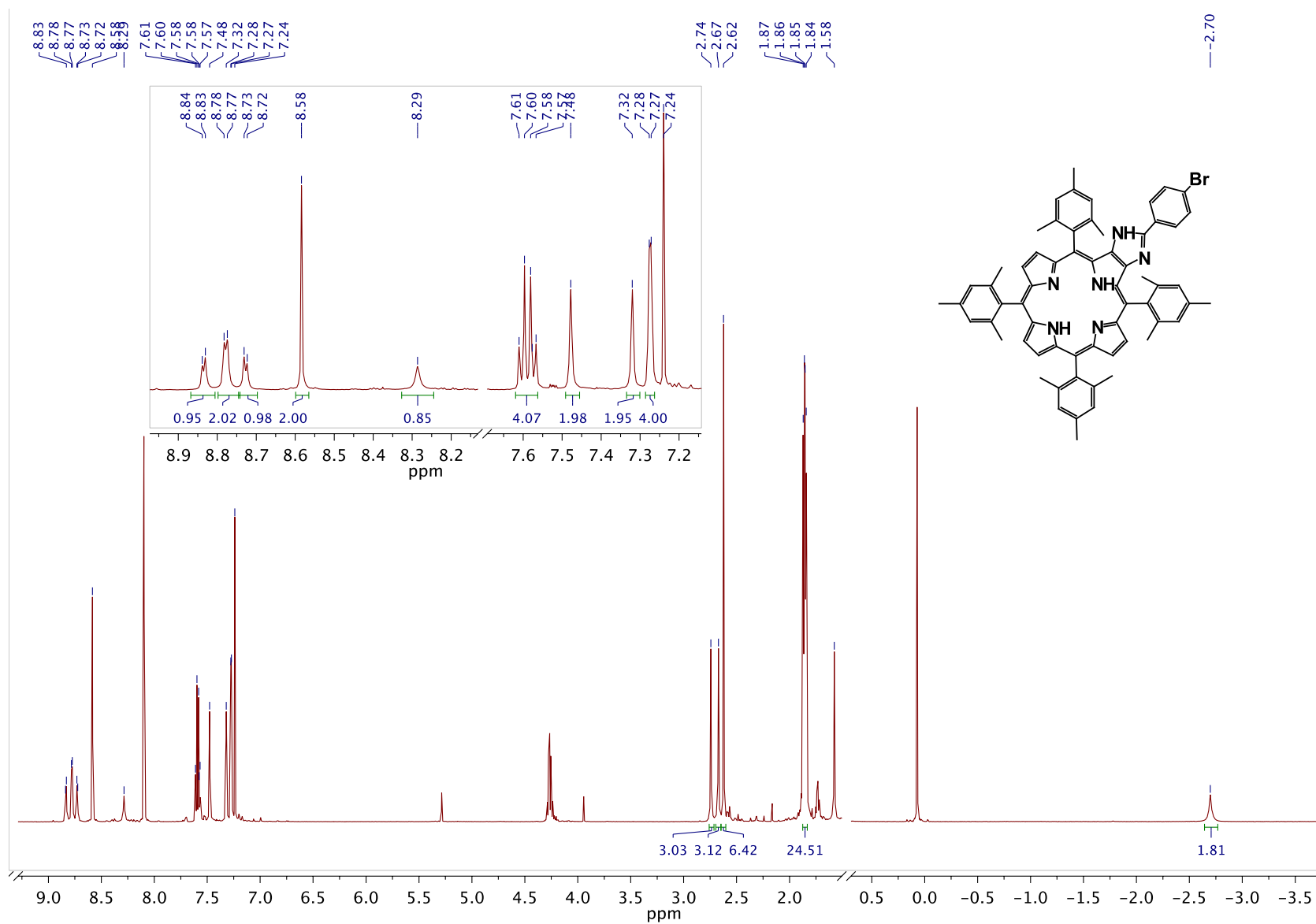


Figure S18. ^1H NMR spectrum of 2H-14f (CDCl_3).

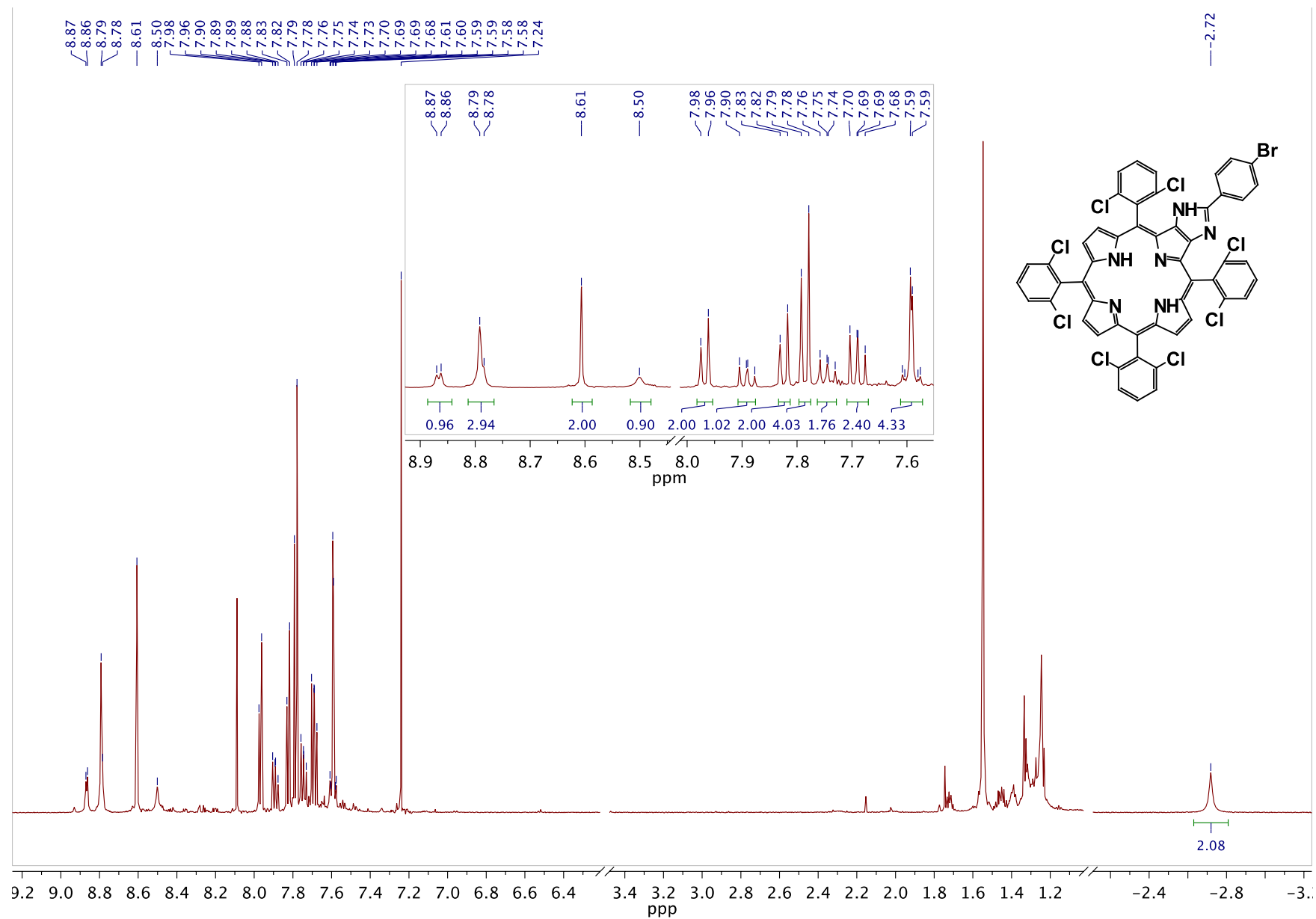


Figure S19. ¹H NMR spectrum of 2H-15a (CDCl₃).

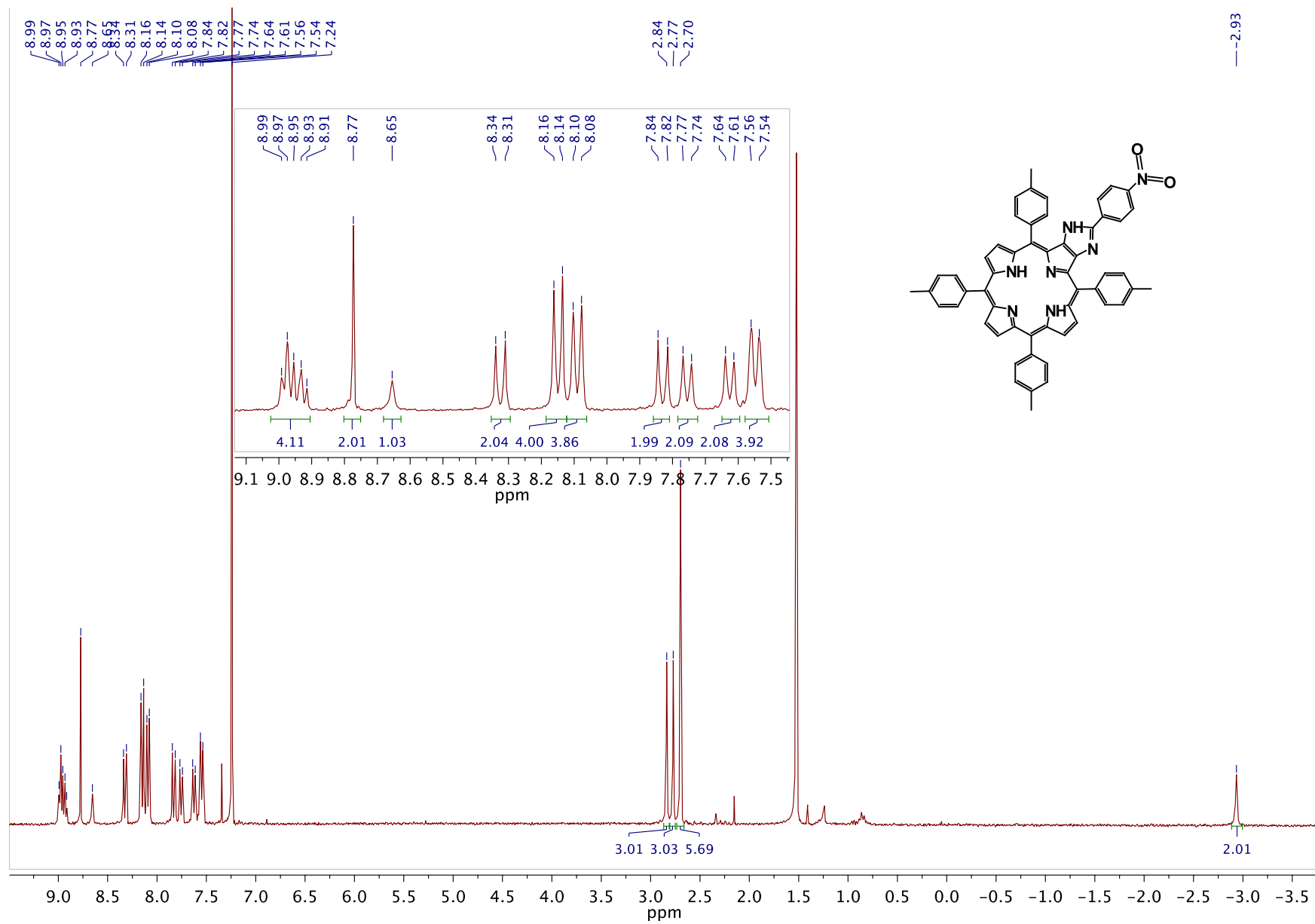


Figure S20. ^1H NMR spectrum of 2H-16e (CDCl_3).

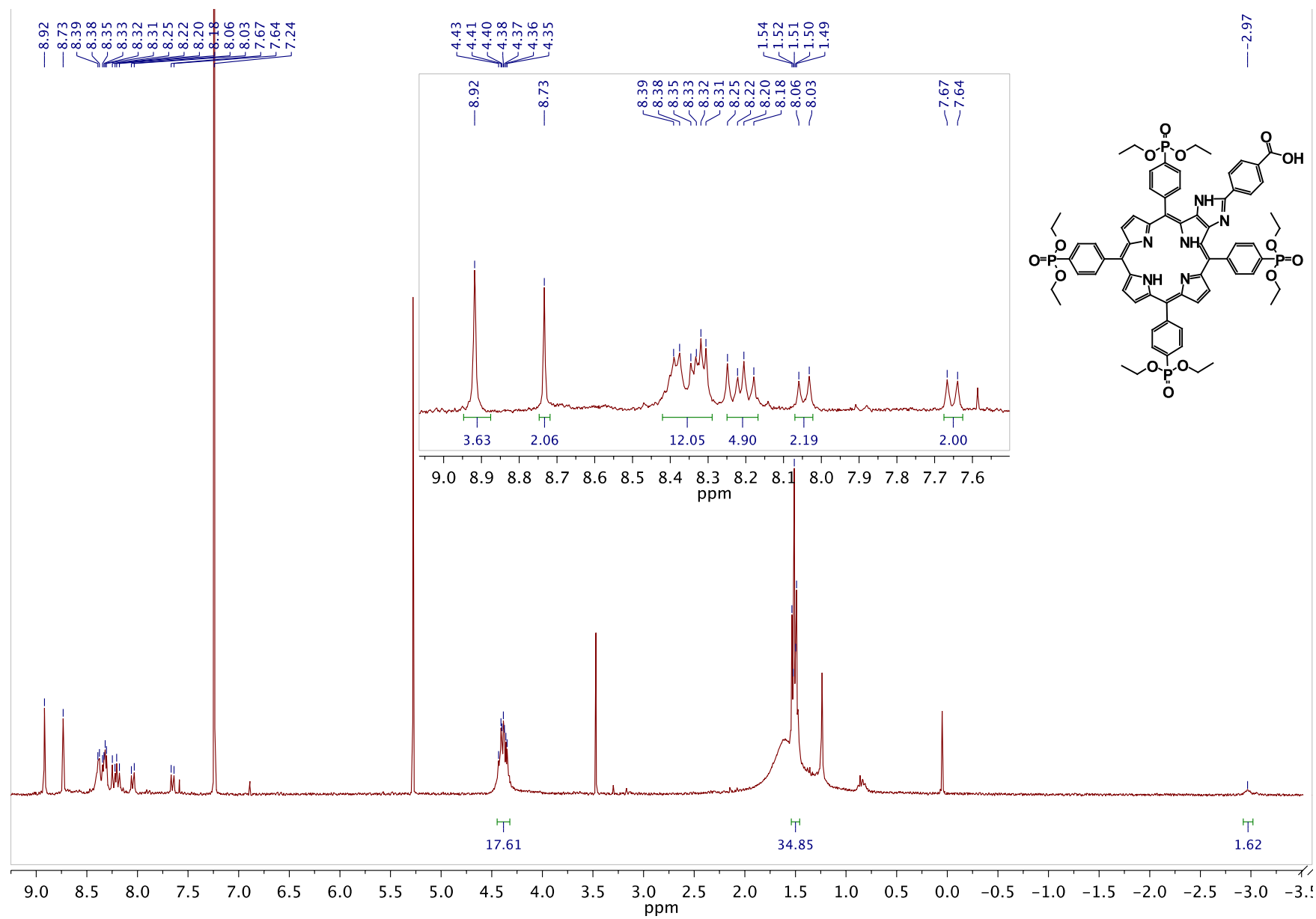


Figure S21. ^{31}P NMR spectrum of 2H-16e (CDCl_3).

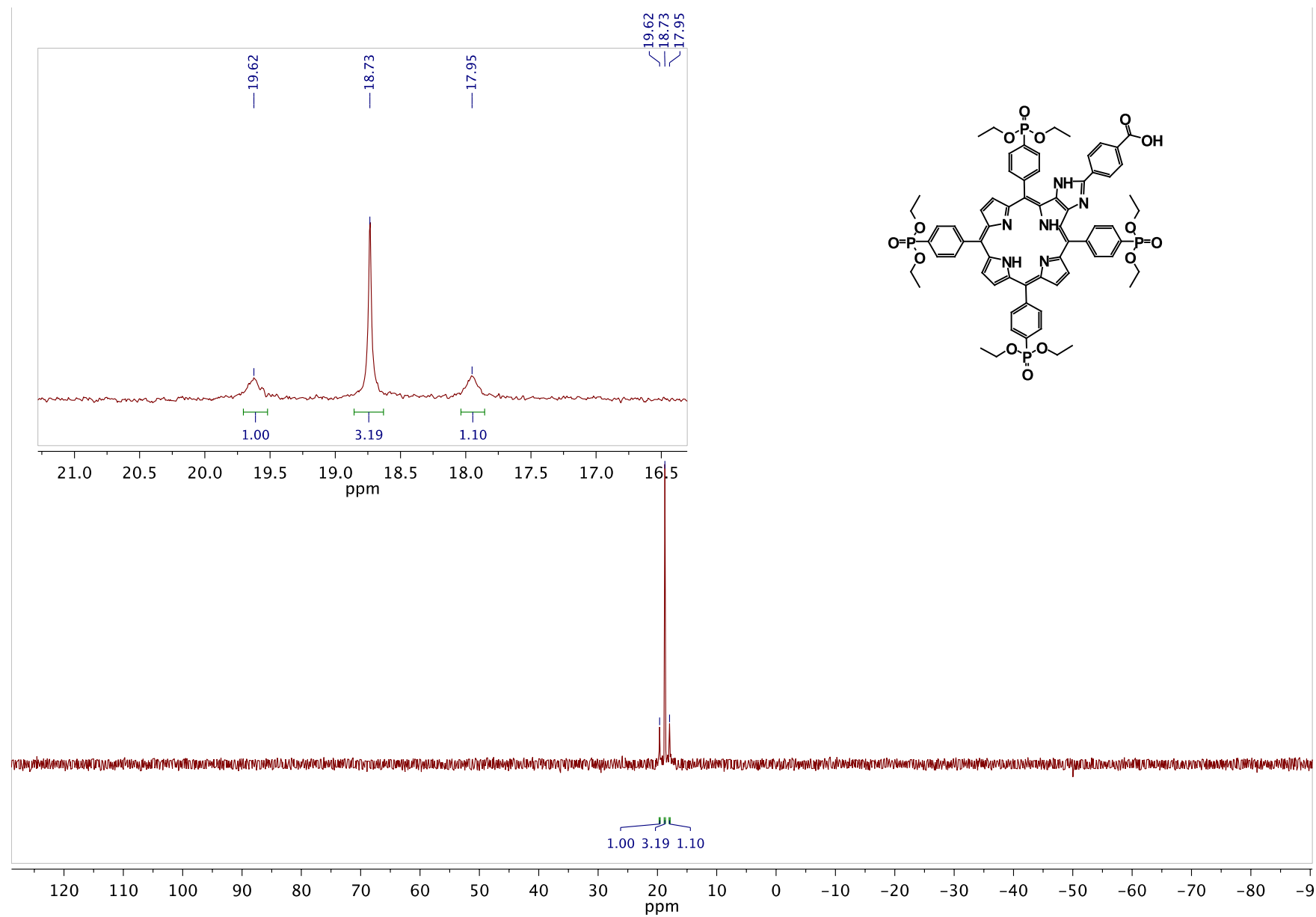
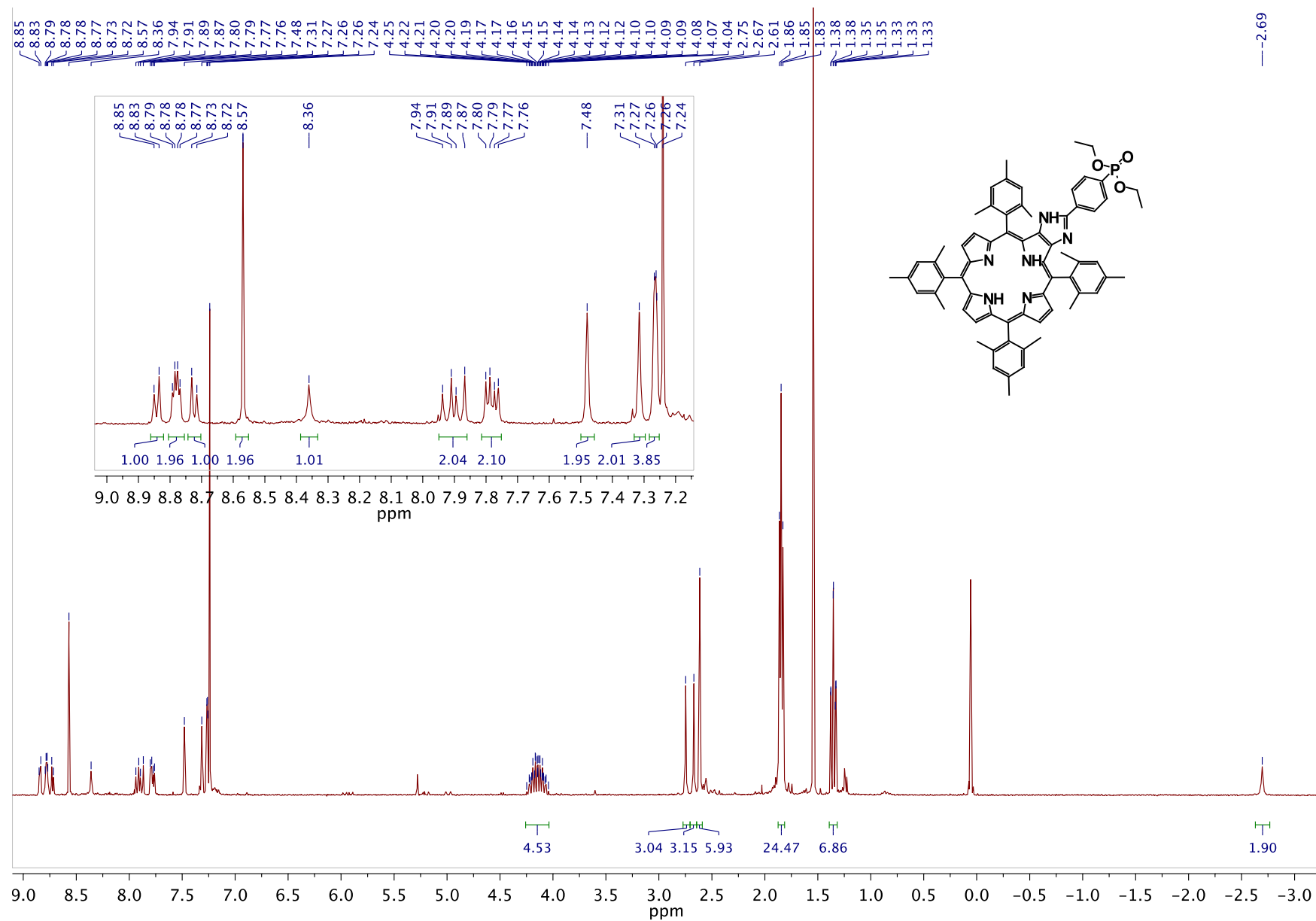


Figure S22. ^1H NMR spectrum of 2H-17b (CDCl_3).



The figure displays two NMR spectra of compound 1. The top spectrum is the ^1H NMR spectrum, showing a single sharp peak at $\delta = 18.31$ ppm with an integration value of 1.00. The x-axis ranges from 19.6 to 17.0 ppm. The bottom spectrum is the ^{13}C NMR spectrum, showing a single sharp peak at $\delta = 18.31$ ppm. The x-axis ranges from 30 to -50 ppm. The chemical structure of compound 1 is shown in the top right corner, featuring a central macrocyclic core with four methyl groups and a diethyl phosphonate group.

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

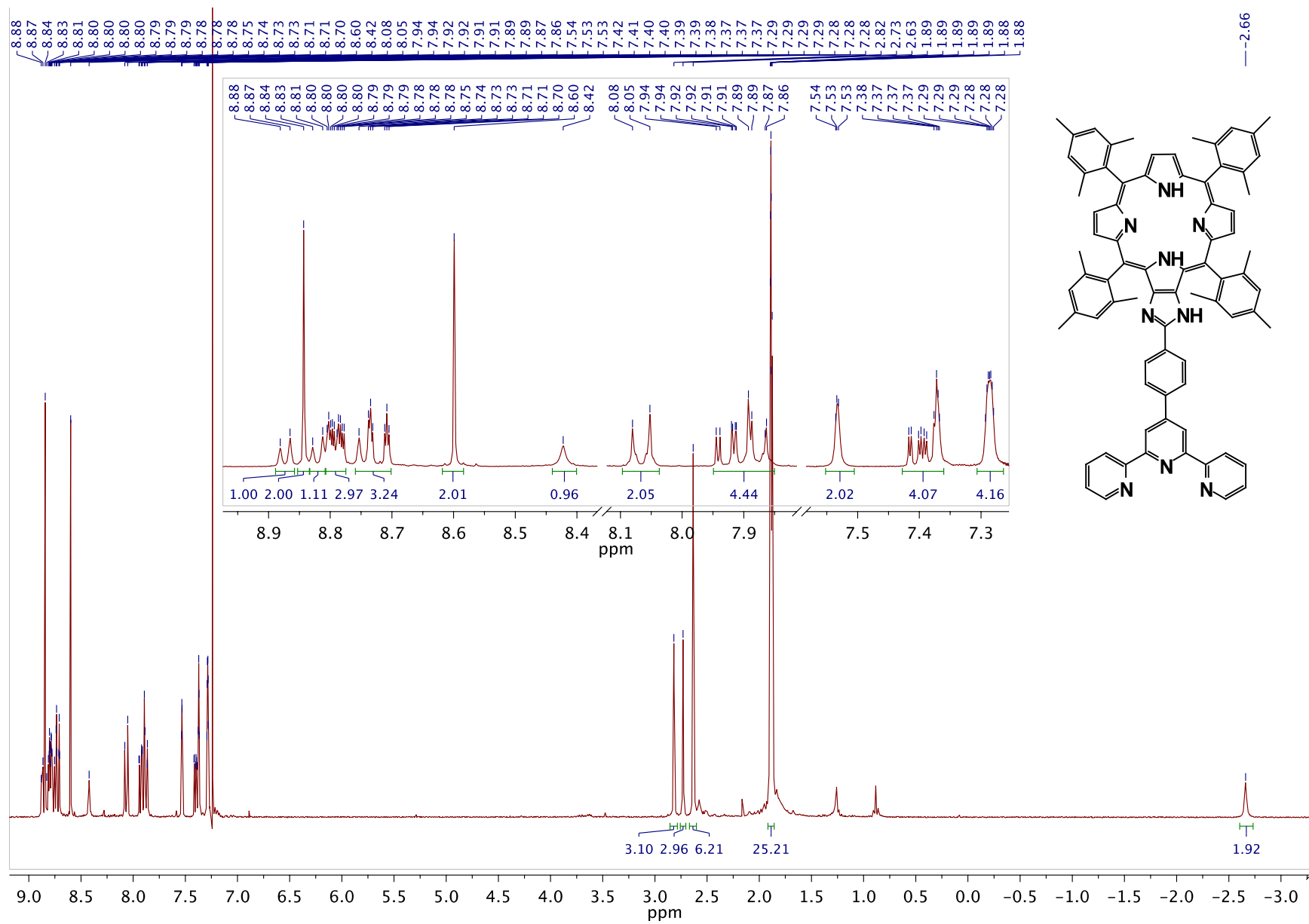
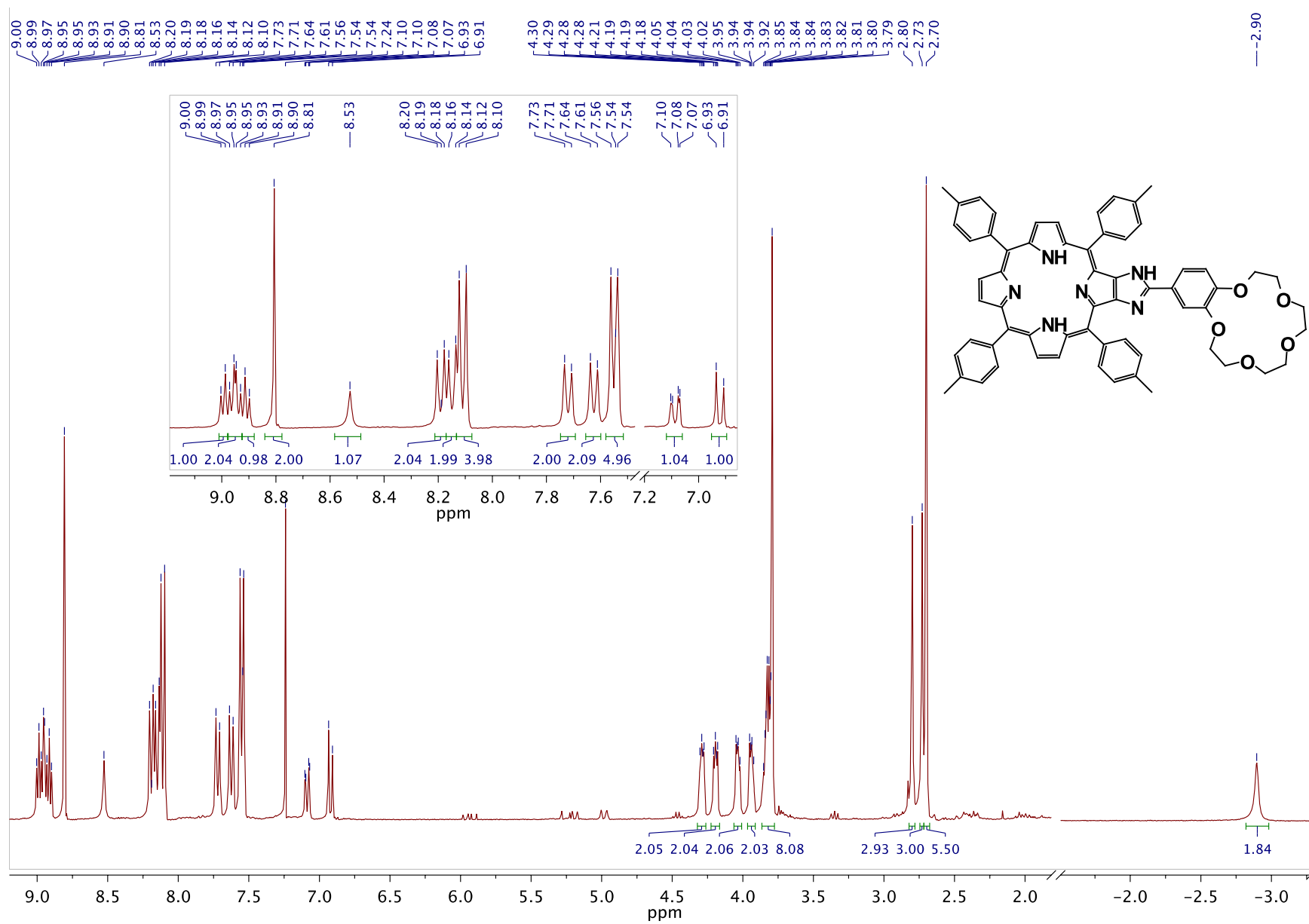


Figure S25. ^1H NMR spectrum of 2H-19a (CDCl_3).



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.

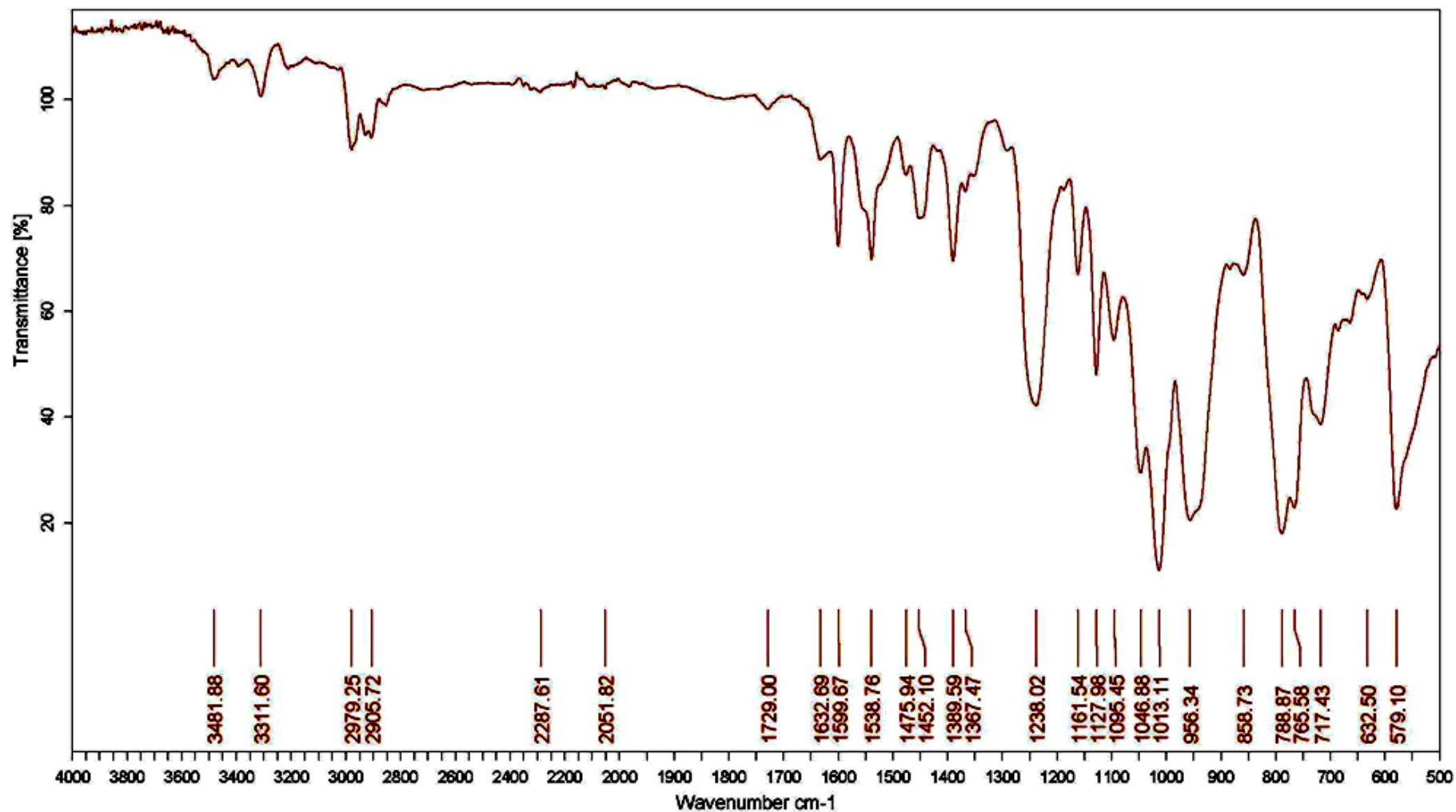


Figure S27. IR spectrum of free-base 2-nitroporphyrin 2H-4e.

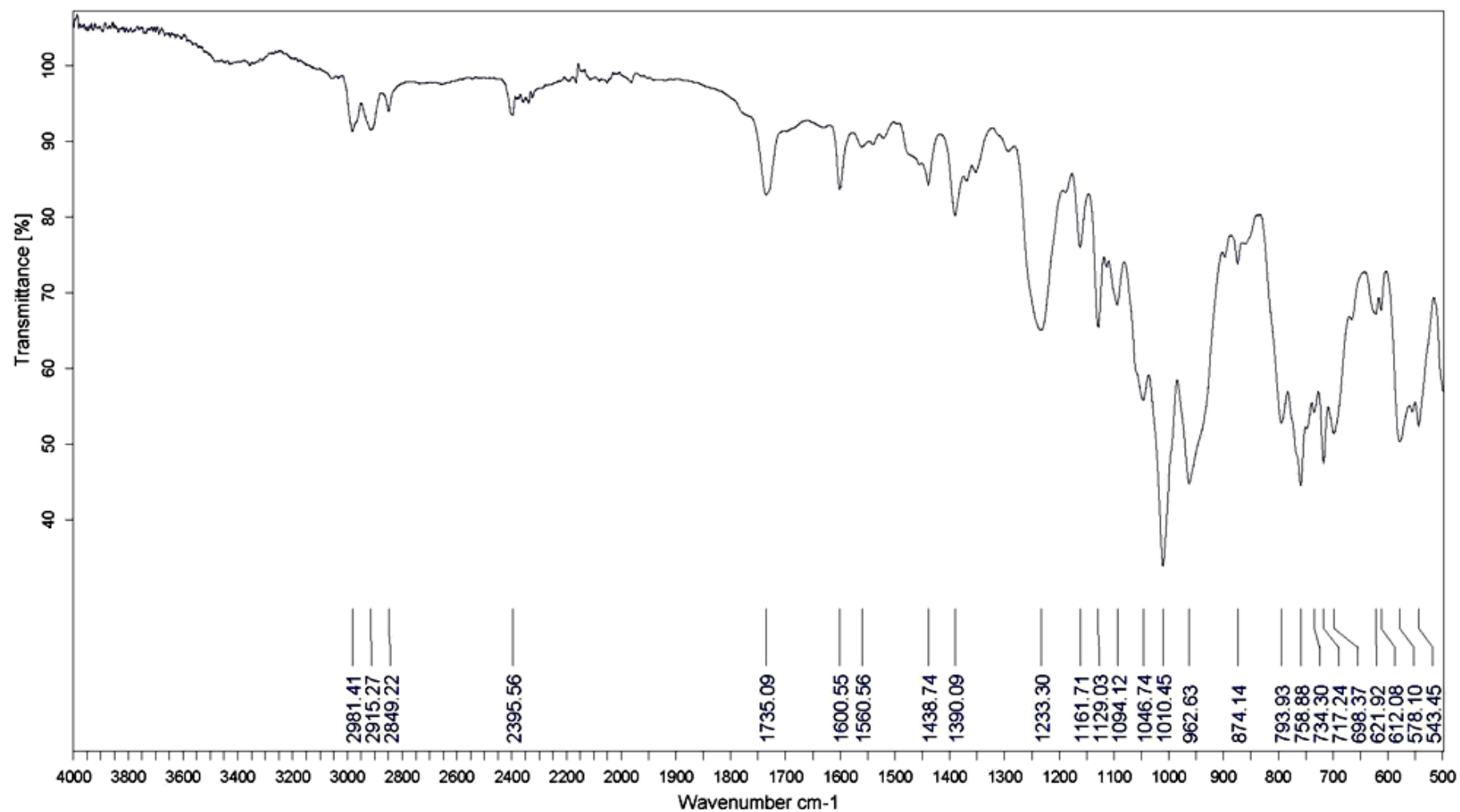


Figure S28. IR spectrum of copper(II) 2-nitroporphyrinate Cu-4e.

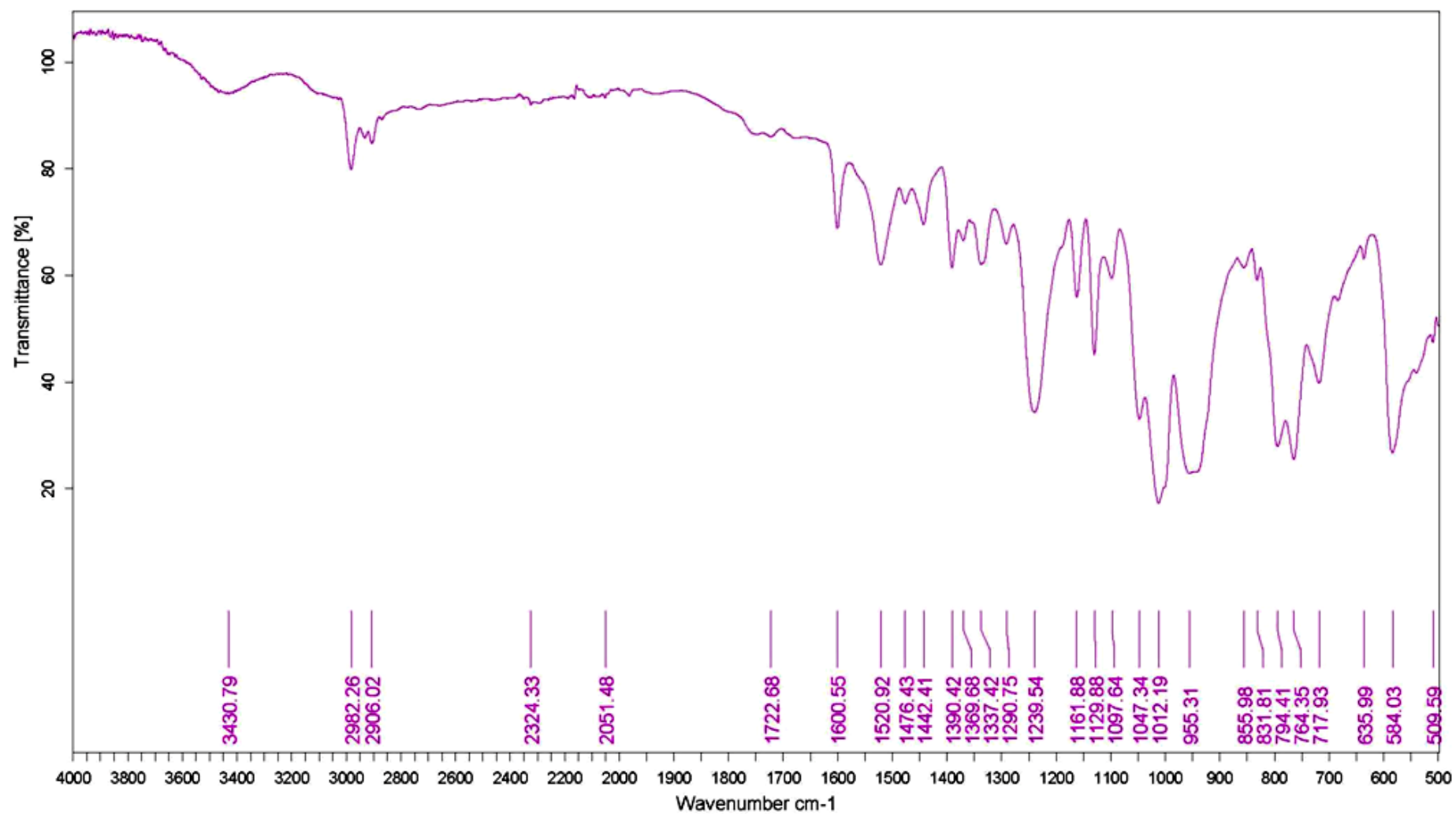


Figure S29. IR spectrum of 2,3-dioxochlorin 2H-6e.

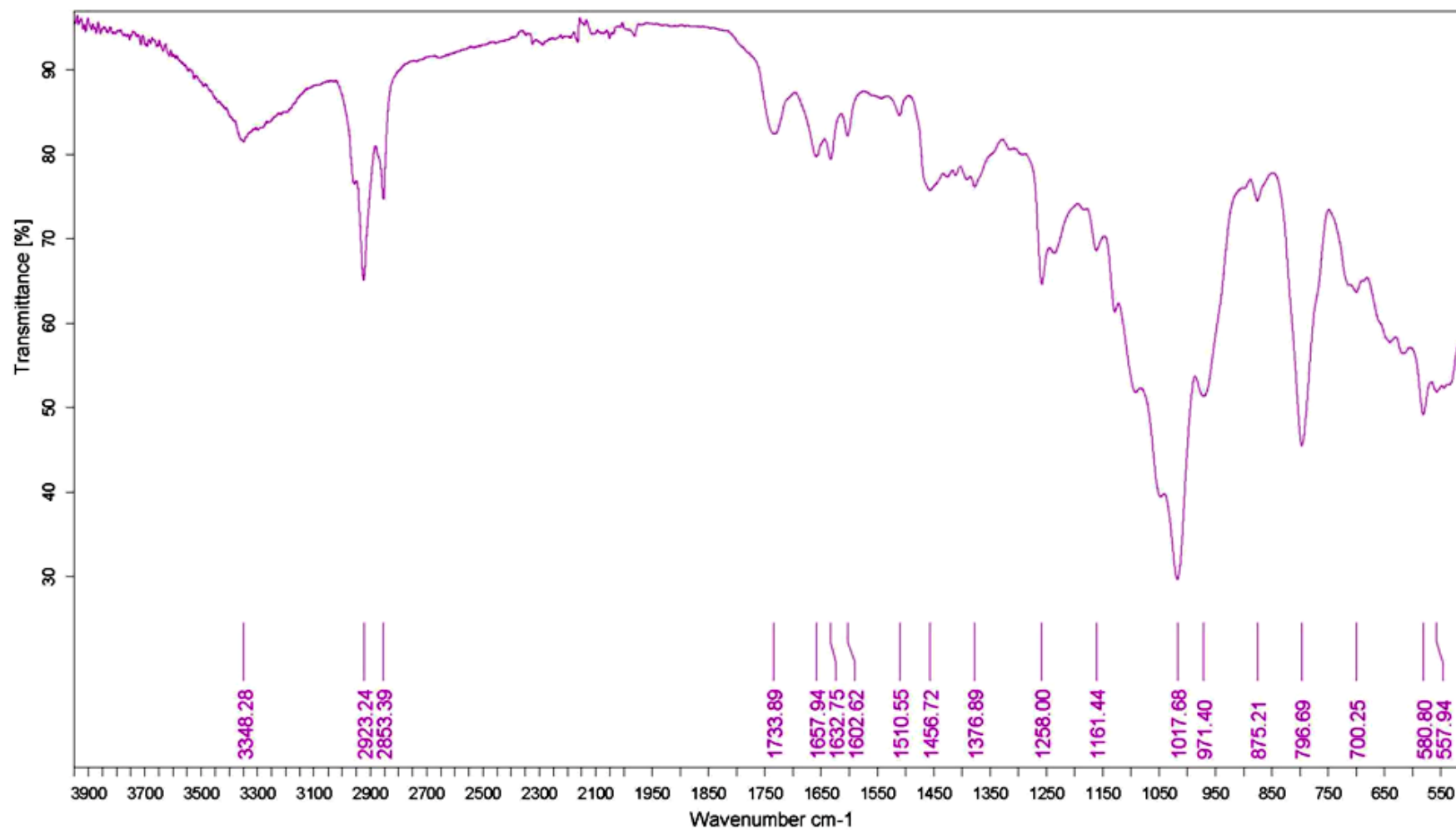
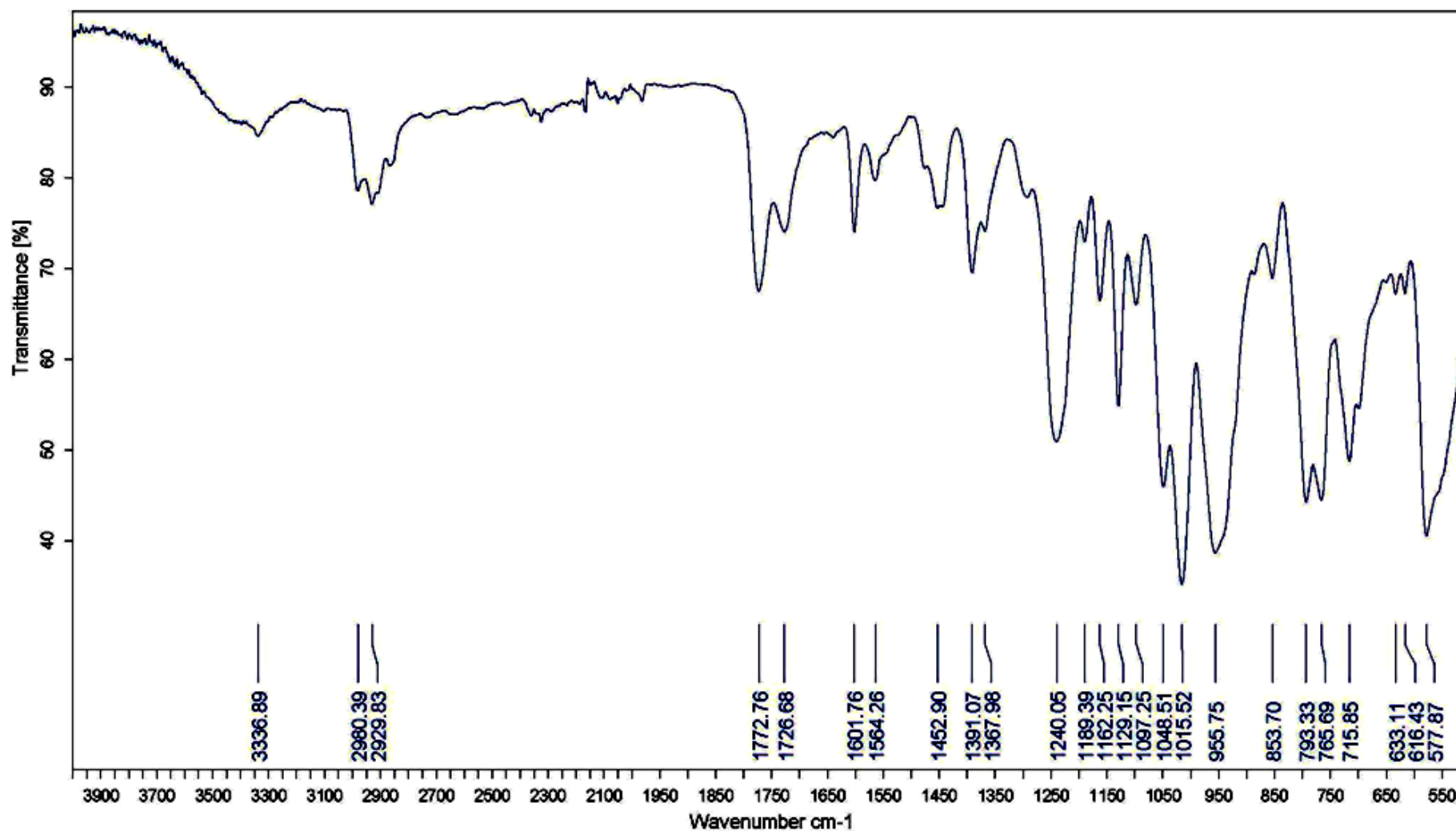


Figure S30. IR spectrum of 2-oxa-3oxochlorin 2H-7e.



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

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

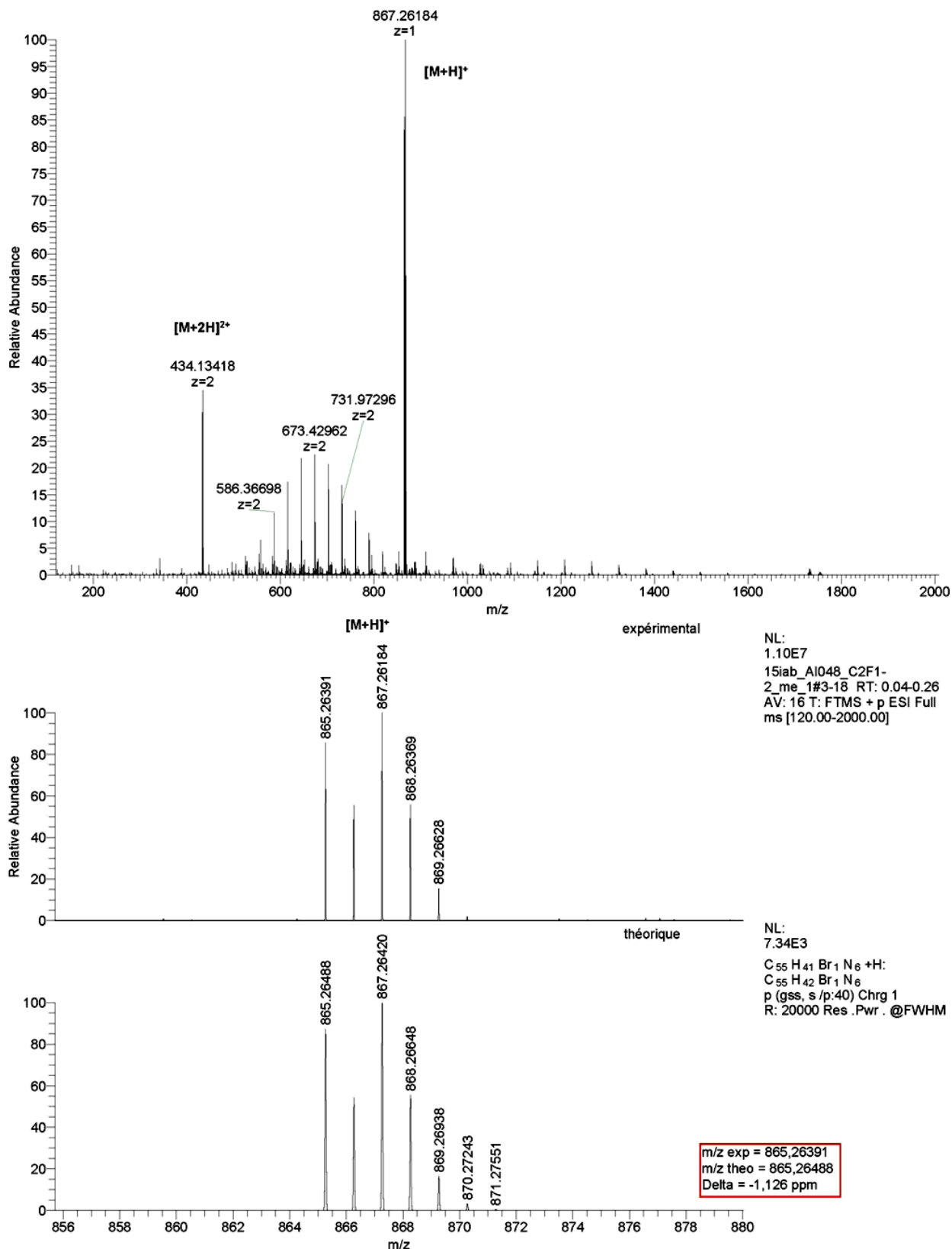


Figure S32. HR-ESI spectrum of imidazoporphyrin 2H-15a.

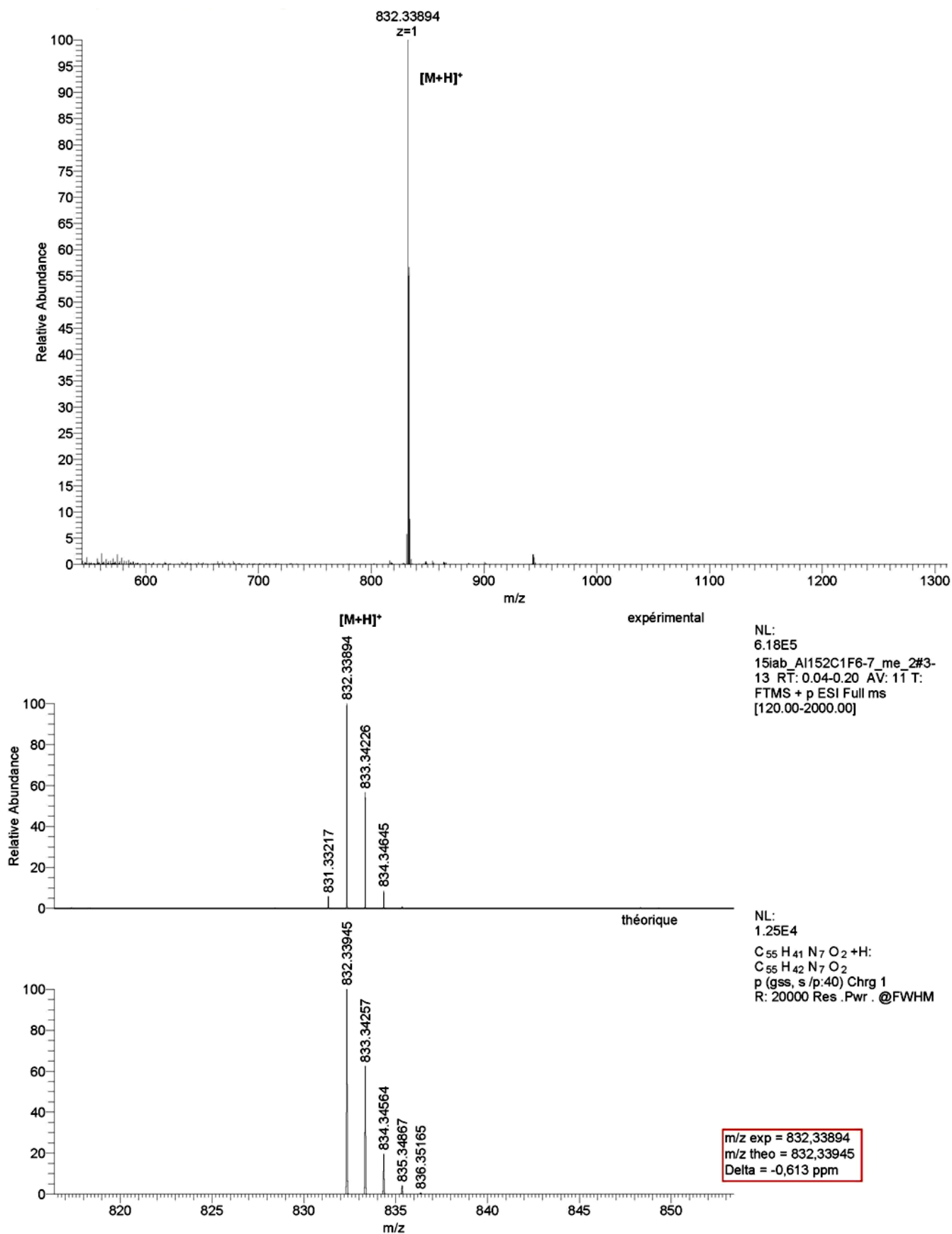
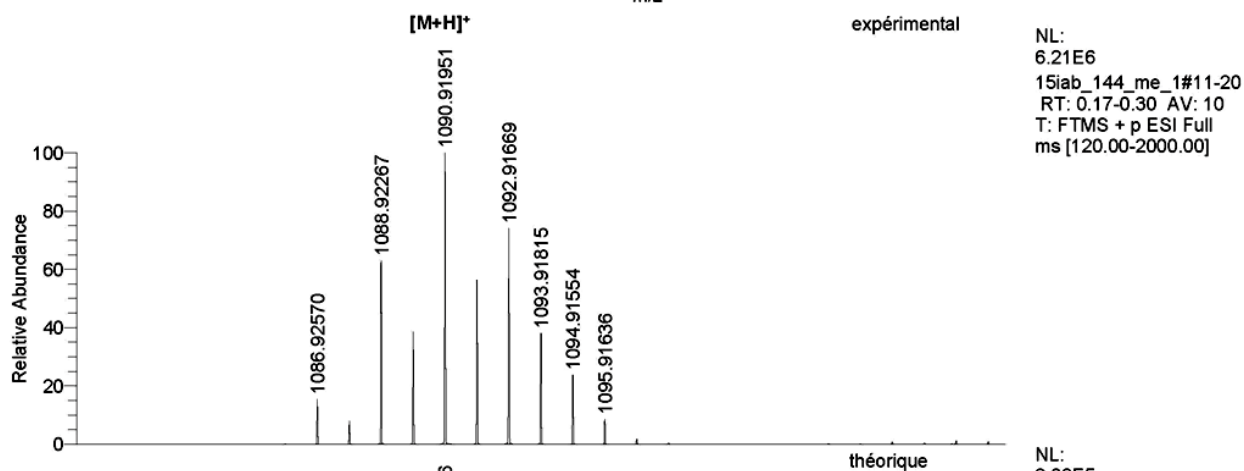
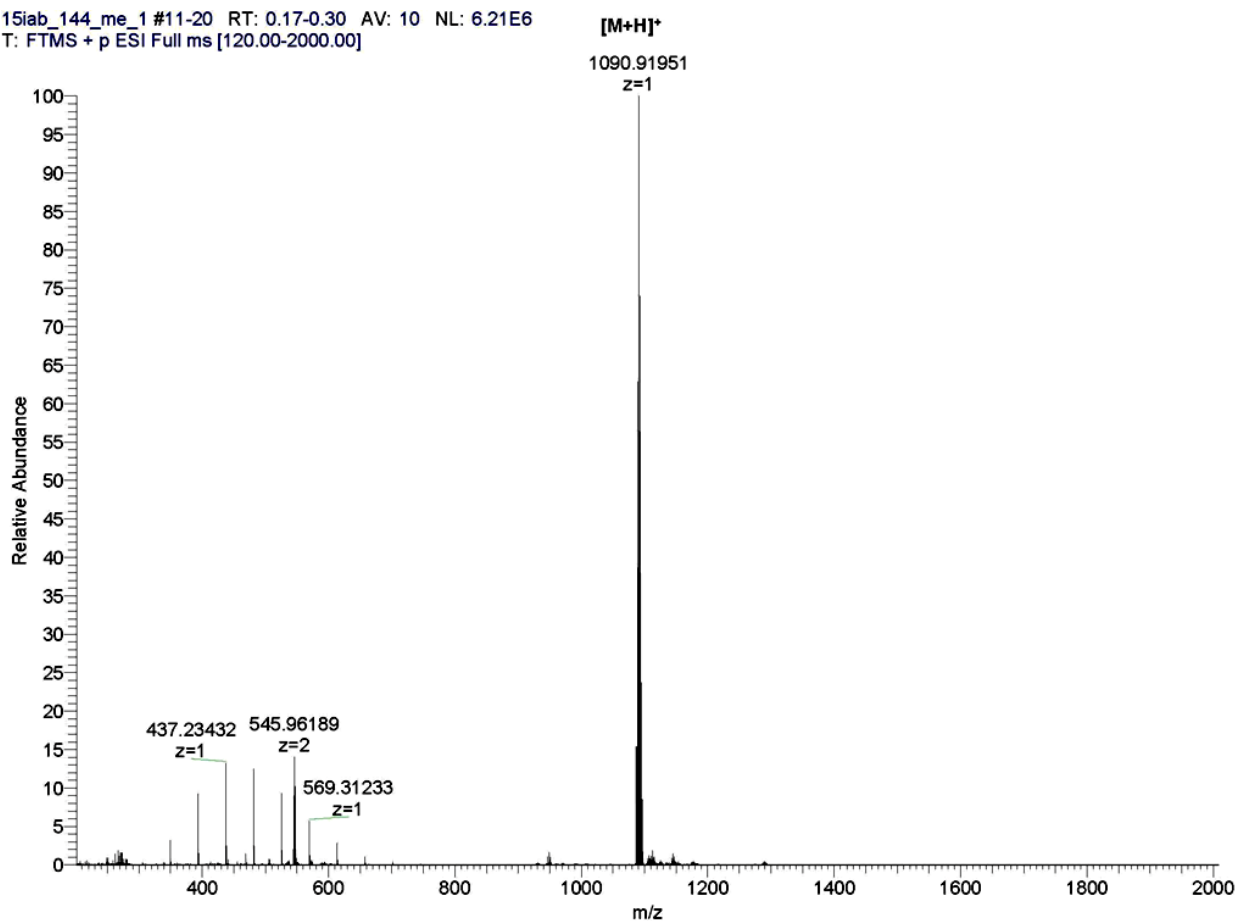


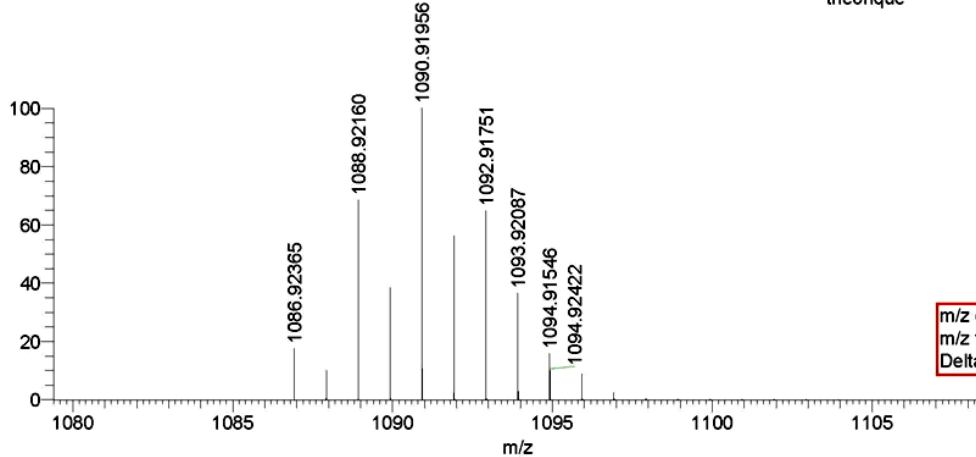
Figure S33. HR-ESI spectrum of imidazoporphyrin 2H-16c.

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T: FTMS + p ESI Full ms [120.00-2000.00]



NL:
6.21E6
15lab_144_me_1#11-20
RT: 0.17-0.30 AV: 10
T: FTMS + p ESI Full
ms [120.00-2000.00]

NL:
2.08E5
C₅₂H₃₀Br₄N₆O₂+H:
C₅₂H₃₁Br₄N₆O₂
pa Chrg 1



m/z exp = 1086.92570
m/z theo = 1086.92365
Delta = 1,885 ppm

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

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T: FTMS + p ESI Full ms [150.00-2000.00]

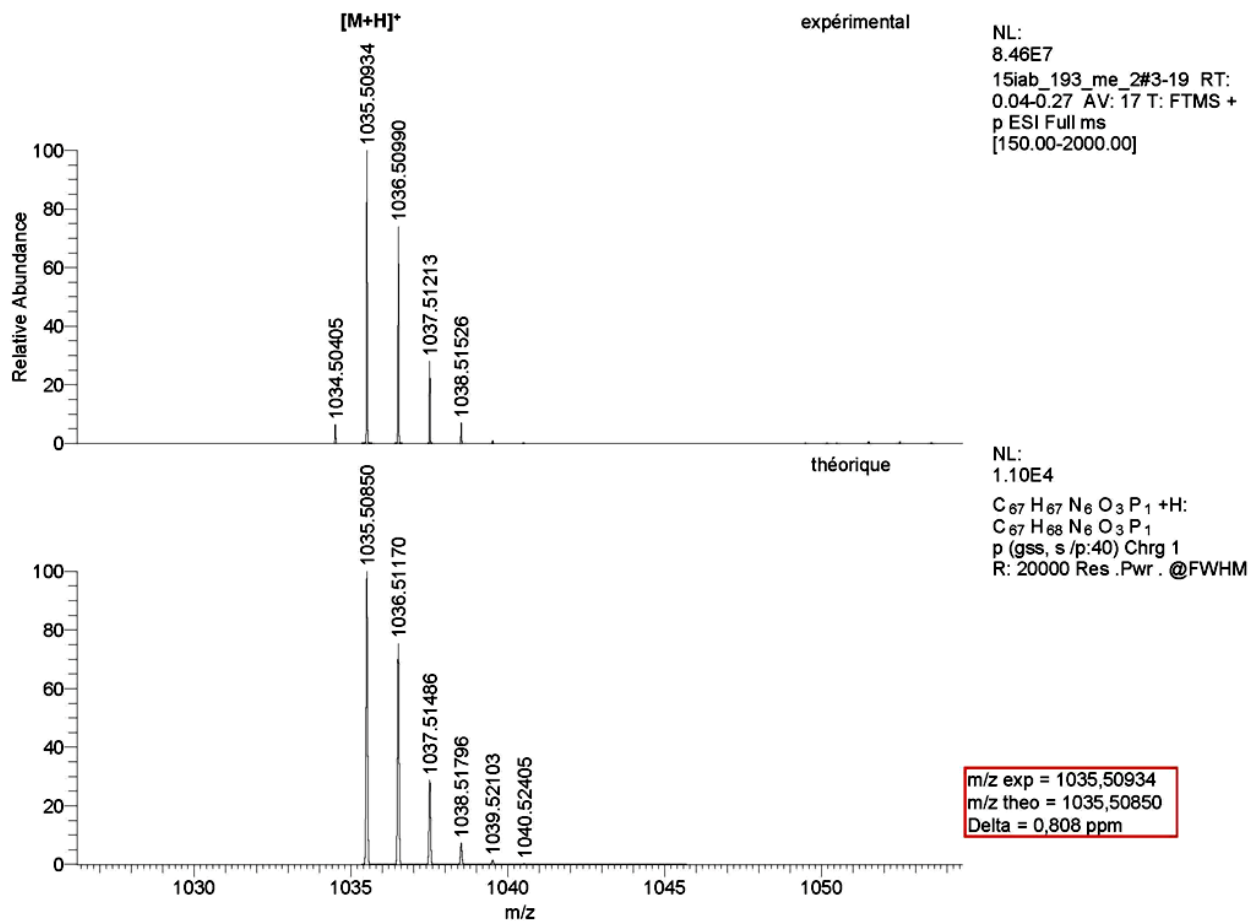
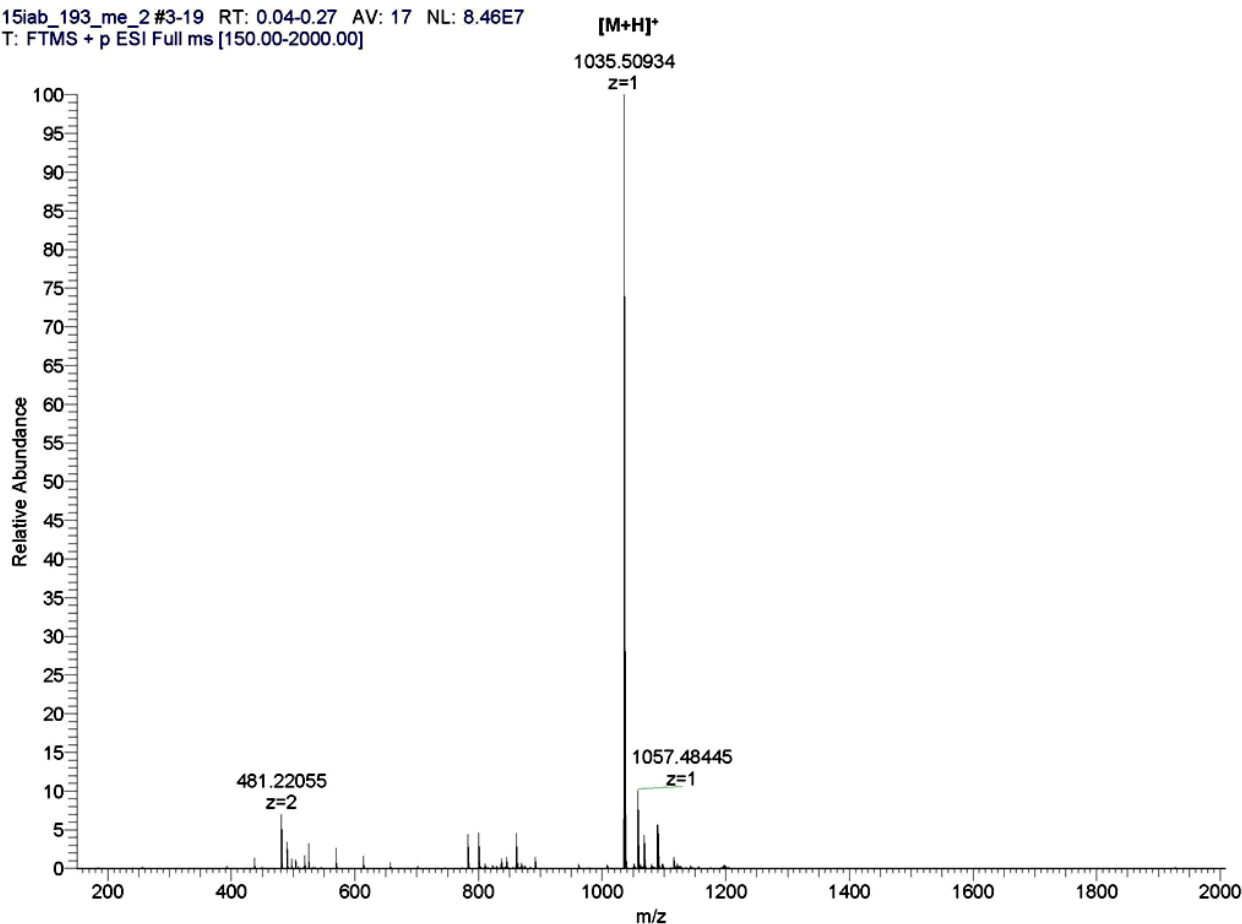
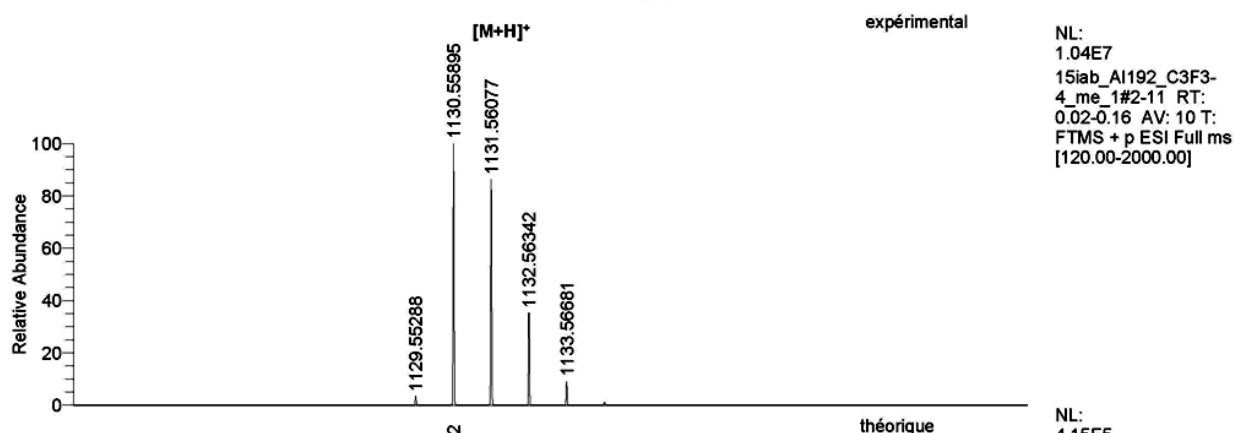
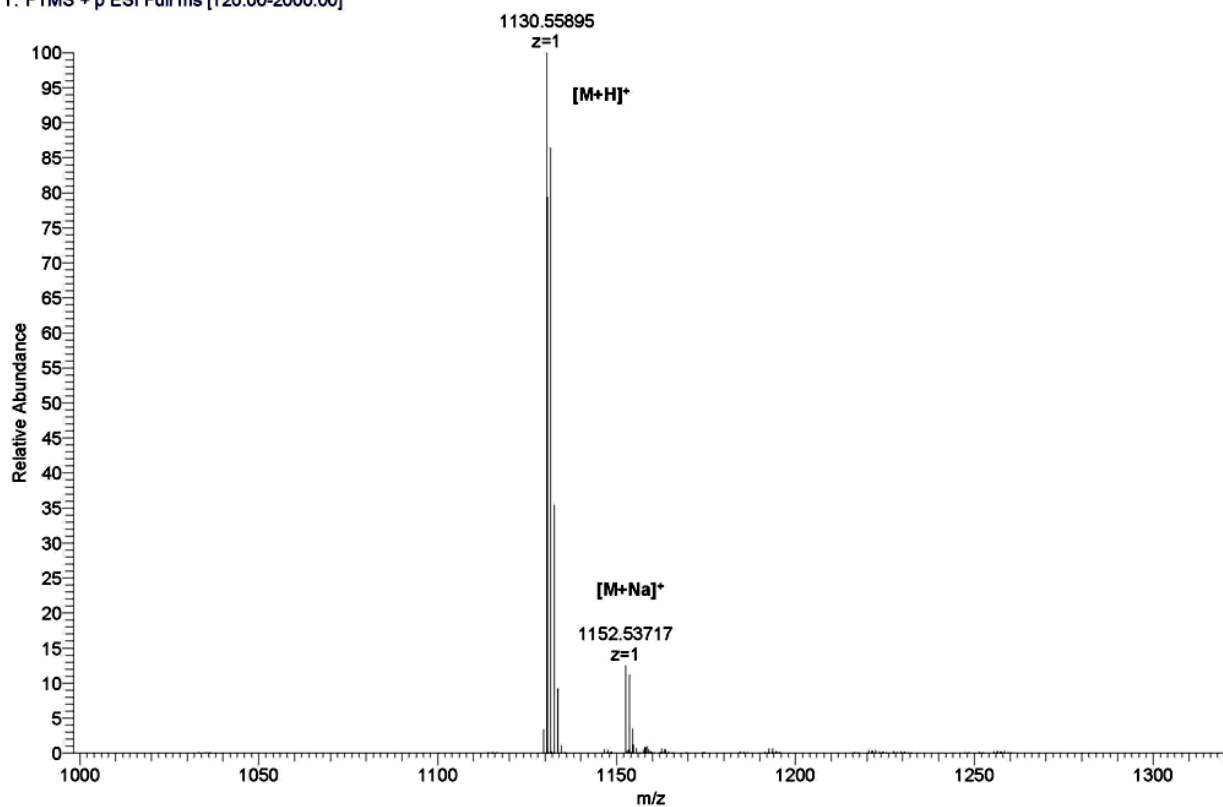


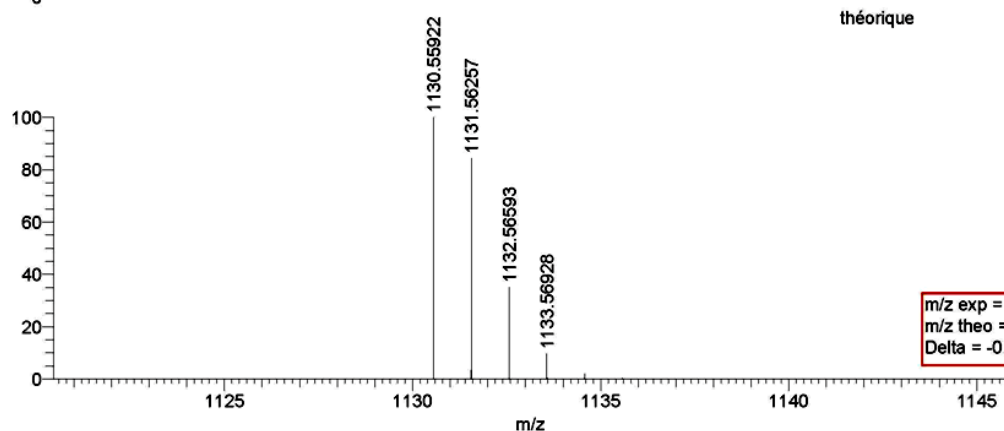
Figure S35. HR-ESI spectrum of imidazoporphyrin 2H-18b.

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T: FTMS + p ESI Full ms [120.00-2000.00]



NL:
1.04E7
15iab_AI192_C3F3-
4_me_1#2-11 RT:
0.02-0.16 AV: 10 T:
FTMS + p ESI Full ms
[120.00-2000.00]

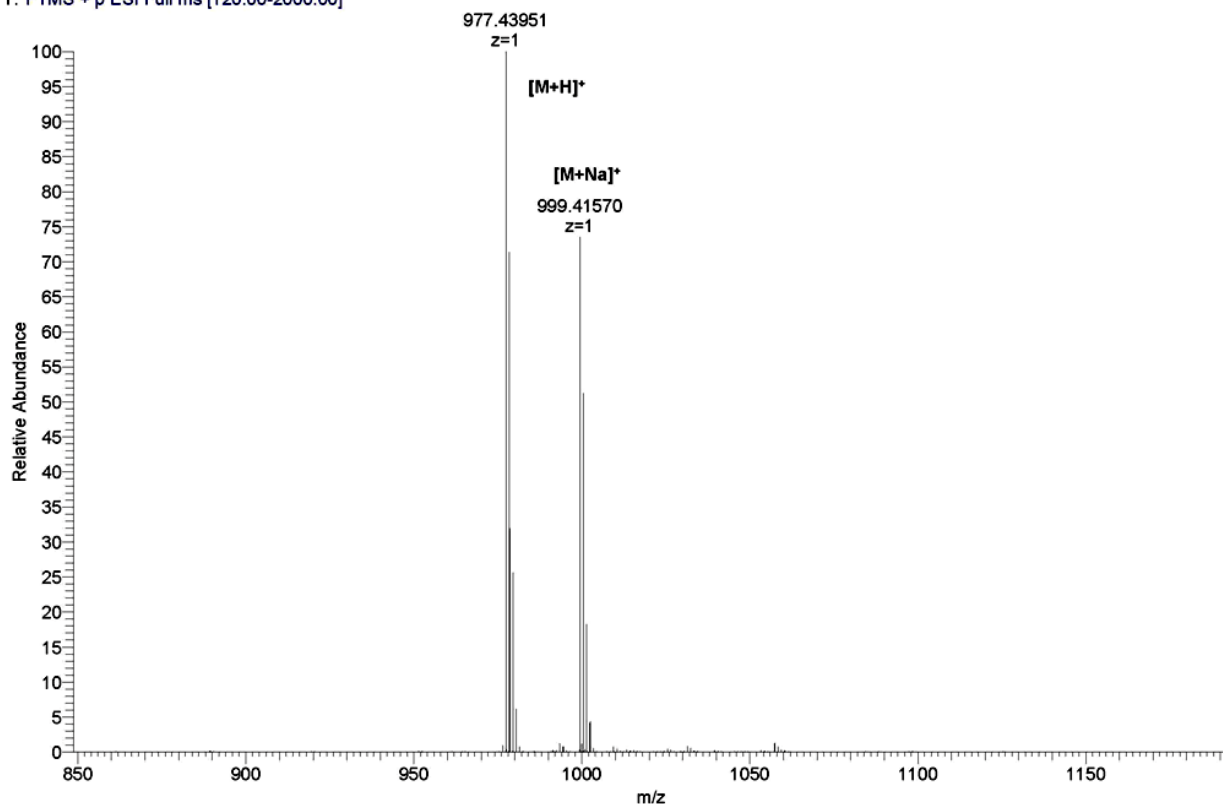
NL:
4.15E5
 $C_{78}H_{67}N_9 + H$:
 $C_{78}H_{68}N_9$
pa Chrg 1



m/z exp = 1130,55895
 m/z theo = 1130,55922
Delta = -0,167 ppm

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

15iab_AI095_C2F2-4_me_1 #4-6 RT: 0.04-0.07 AV: 3 NL: 4.78E7
T: FTMS + p ESI Full ms [120.00-2000.00]



C:\xcalibur\data\15iab_AI095_C2F2-4_me_1

3/25/2015 3:03:30 PM

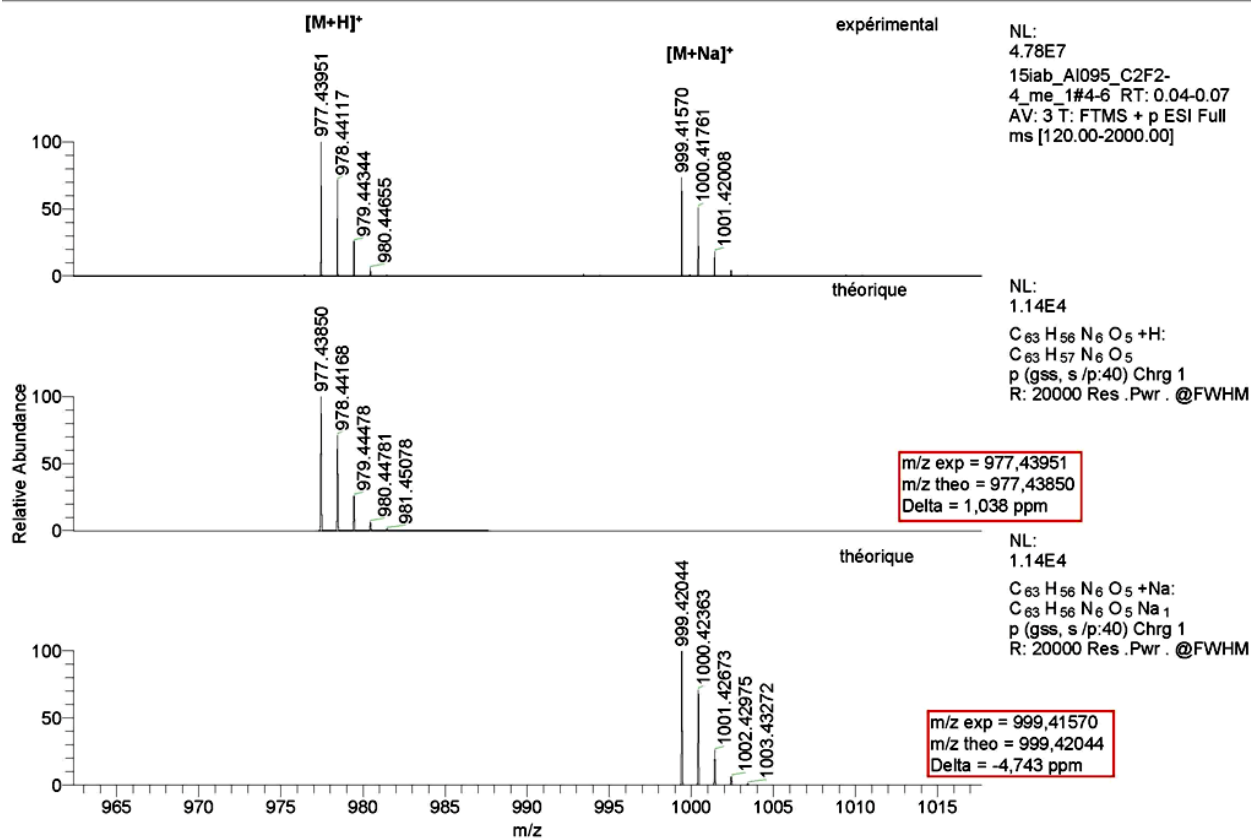
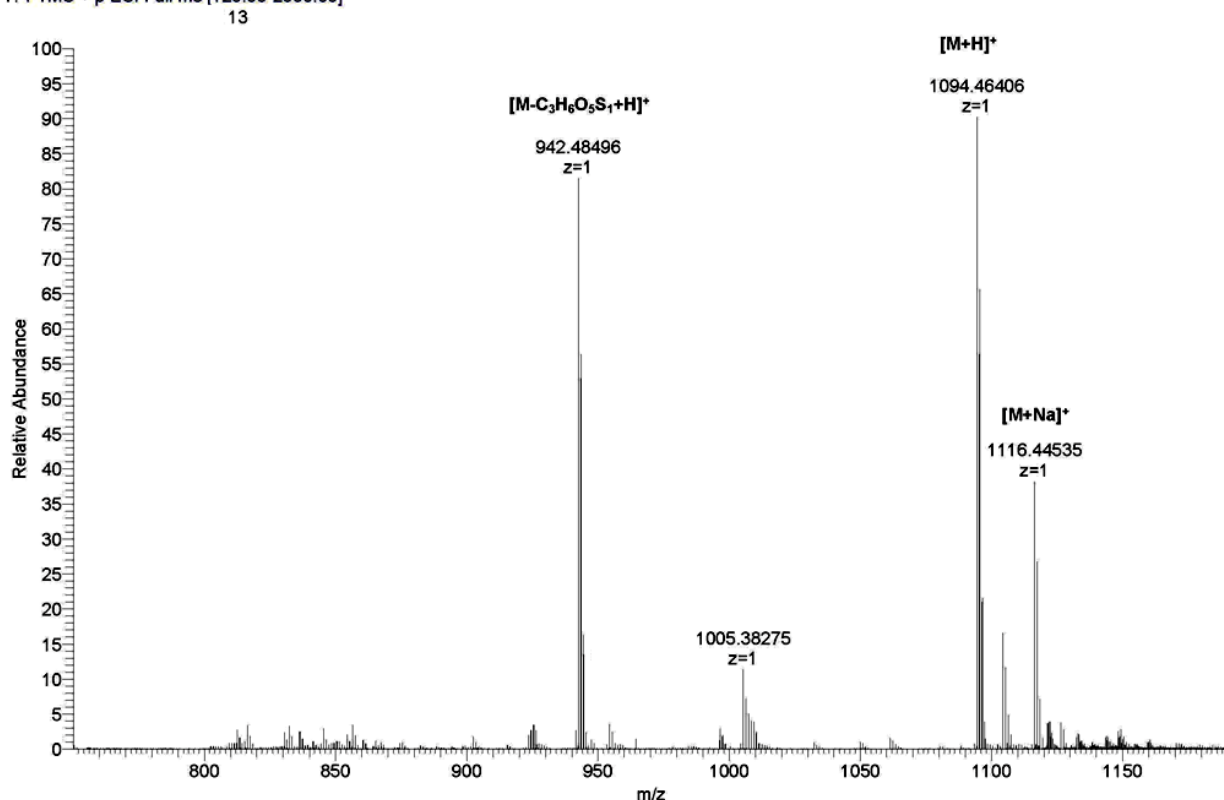


Figure S37. HR-ESI spectrum of imidazoporphyrin 2H-3b.

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3/25/2015 3:56:00 PM

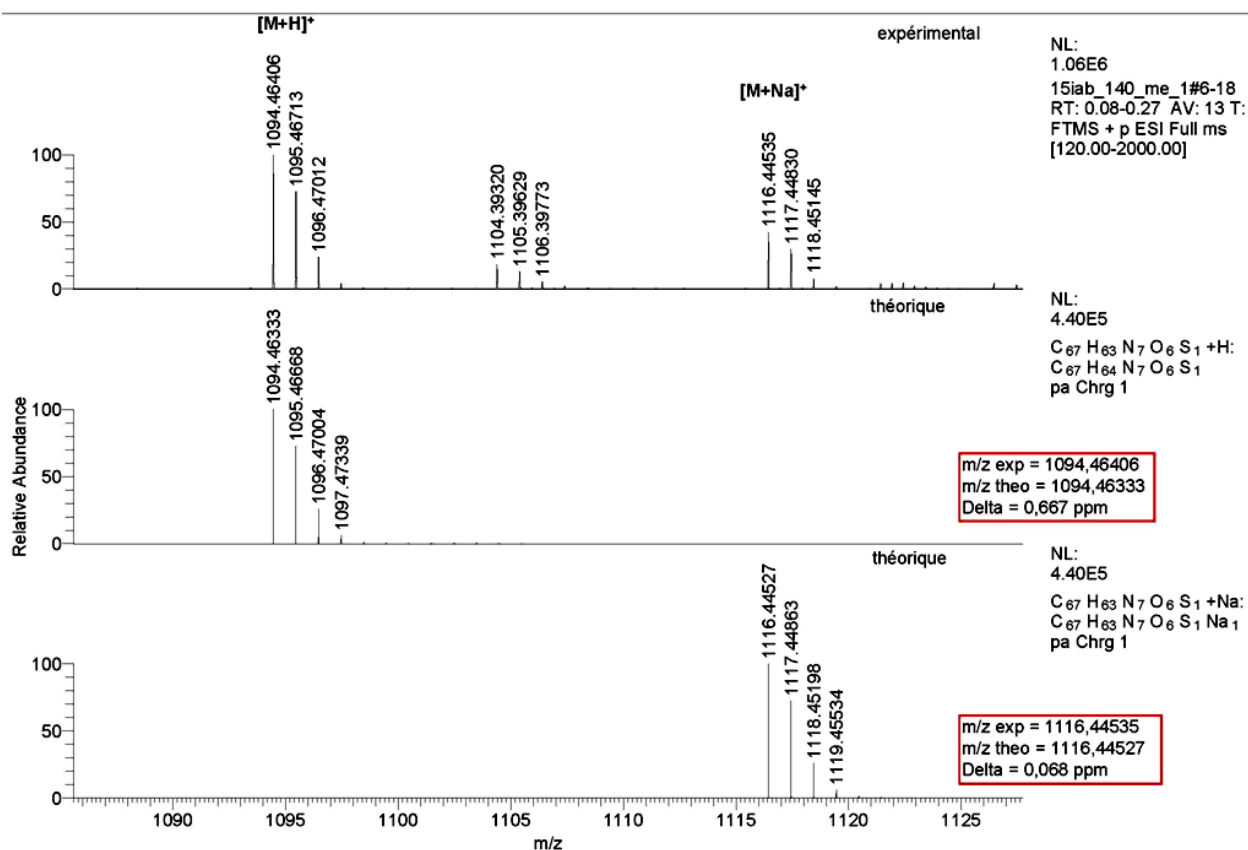
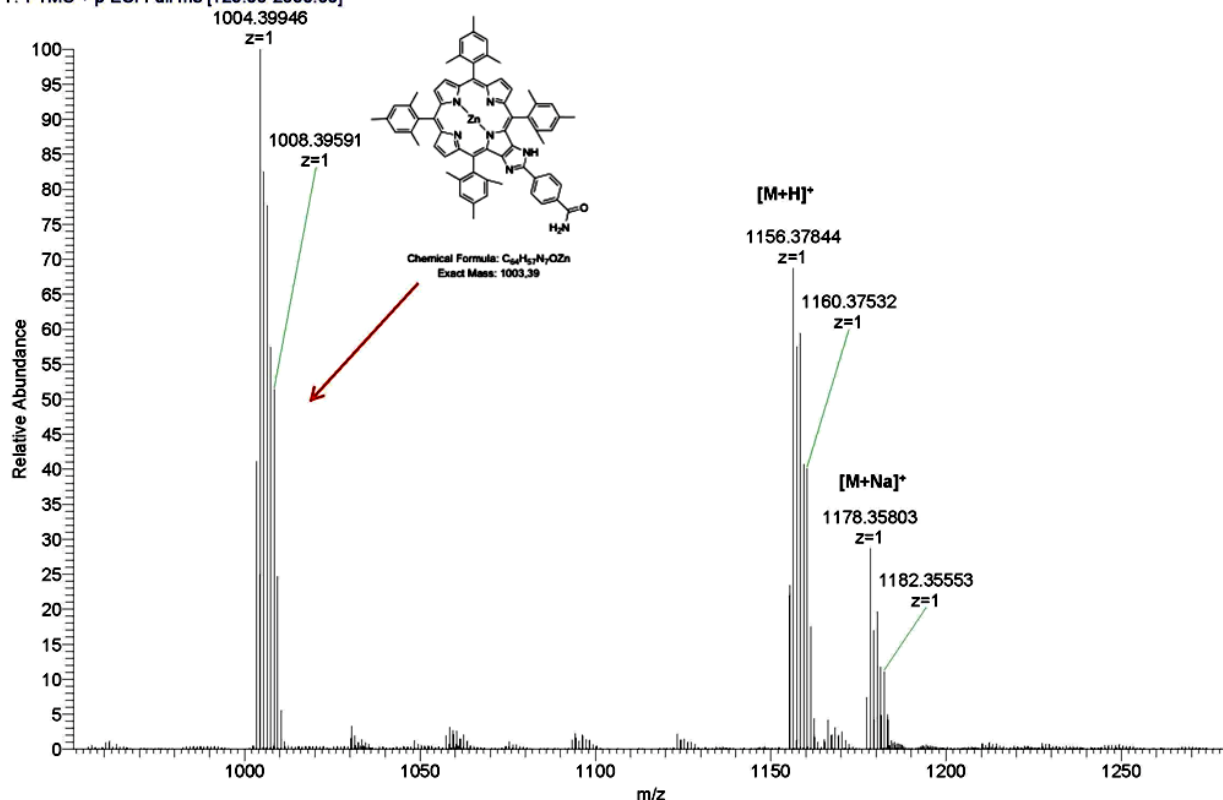


Figure S38. HR-ESI spectrum of imidazoporphyrin Zn-3b.

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T: FTMS + p ESI Full ms [120.00-2000.00]



15iab_152_me_150324143007

3/24/2015 2:30:08 PM

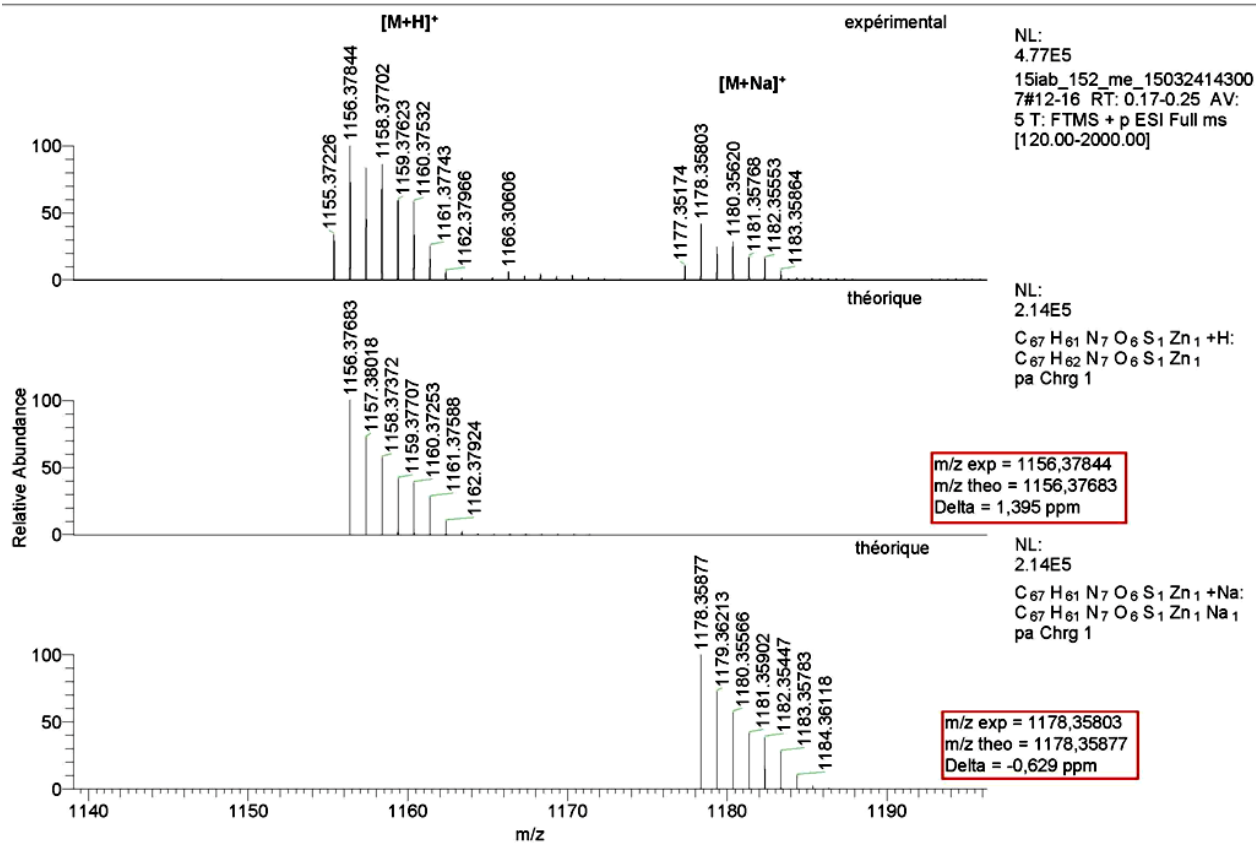
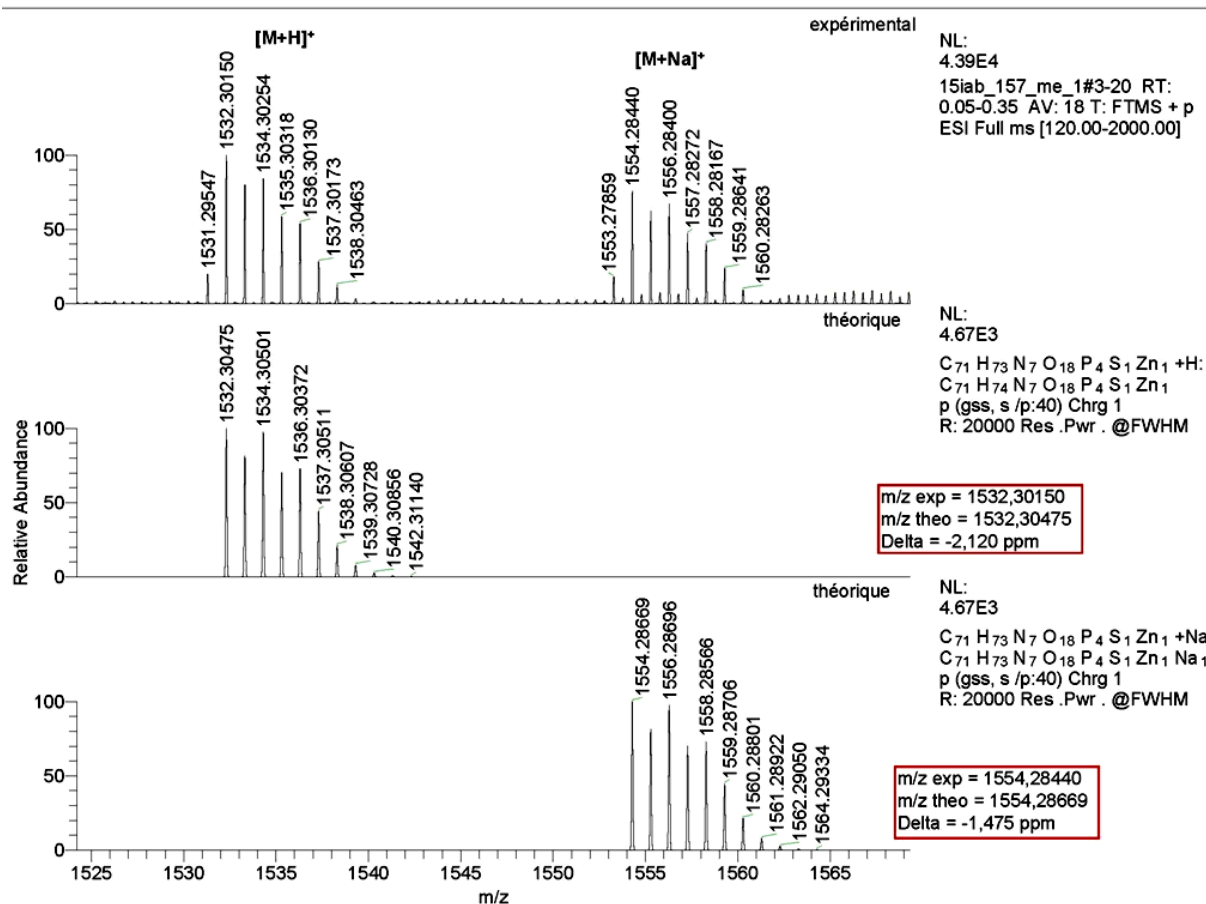
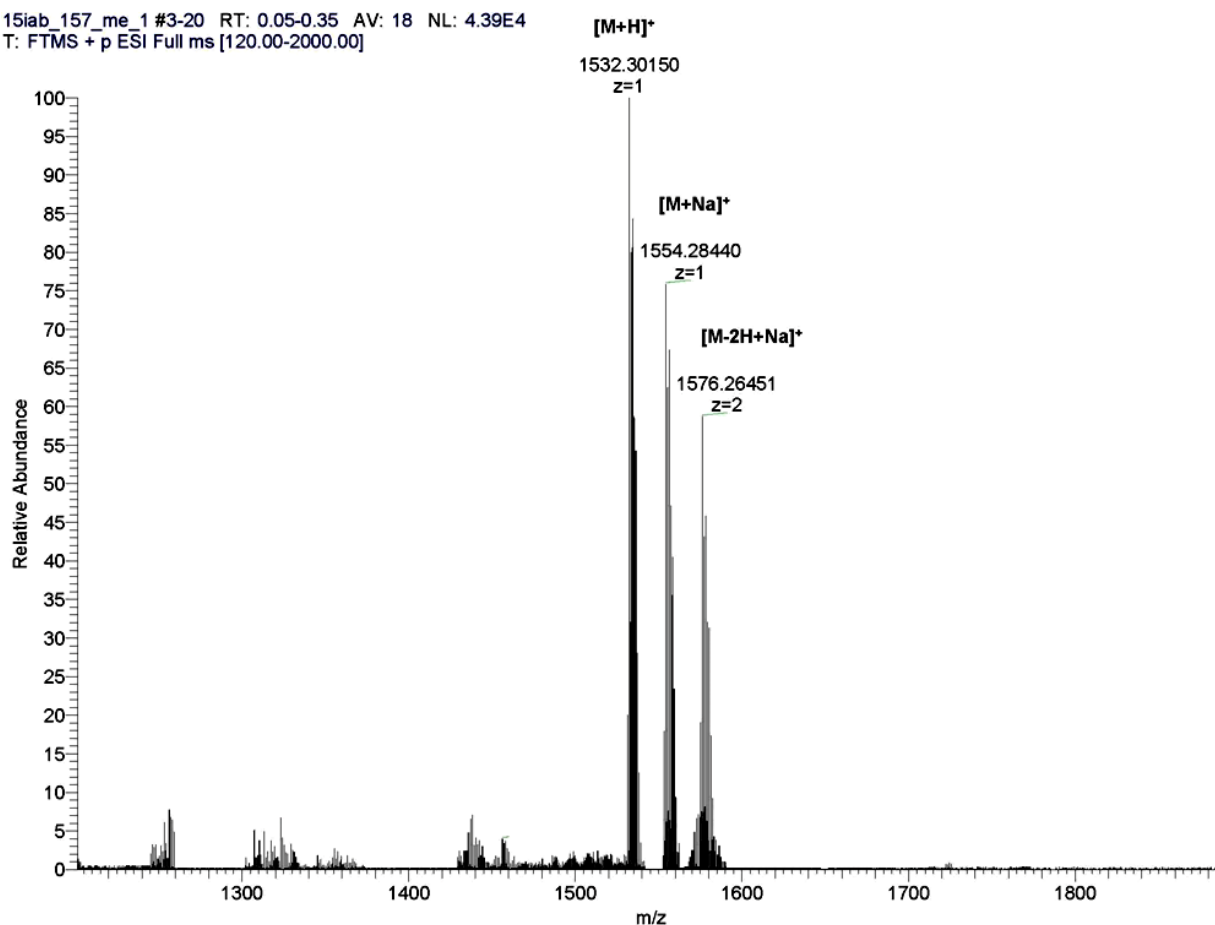


Figure S39. HR-ESI spectrum of imidazoporphyrin Zn-3e.

15iab_157_me_1 #3-20 RT: 0.05-0.35 AV: 18 NL: 4.39E4
T: FTMS + p ESI Full ms [120.00-2000.00]



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.

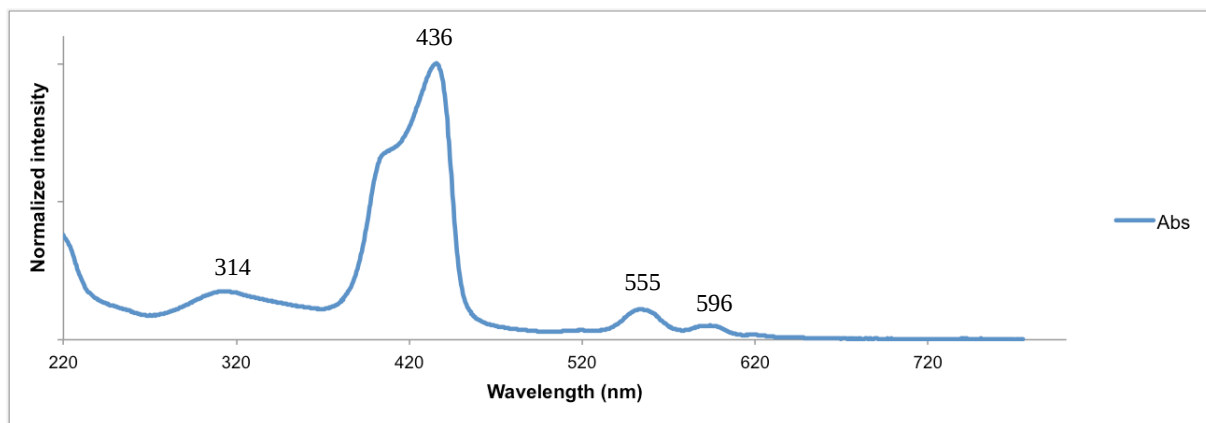
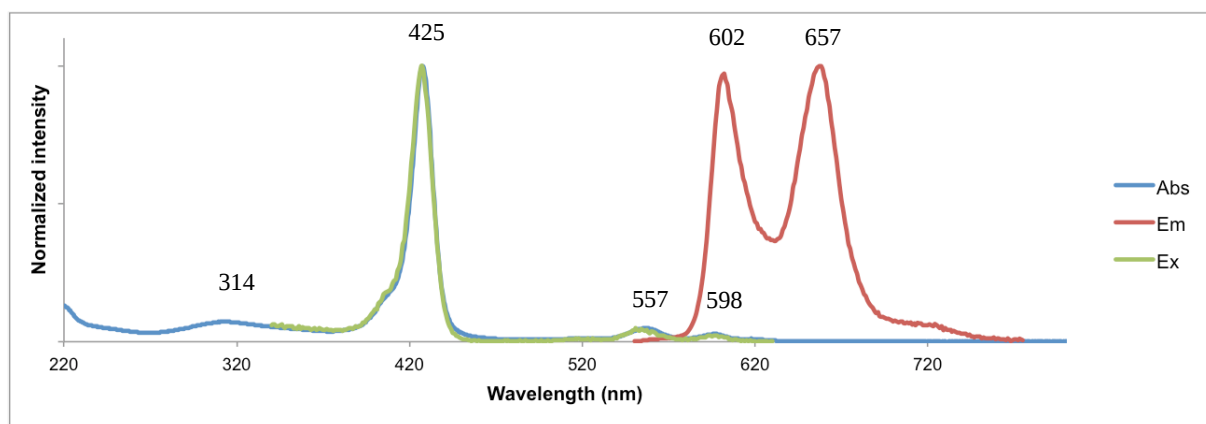


Figure S41. Normalized absorption (blue), excitation (green, $\lambda_{em} = 602, 657$ nm) and emission (red, $\lambda_{ex} = 427$ nm) spectra recorded in CH₃CN at 25 °C.



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

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

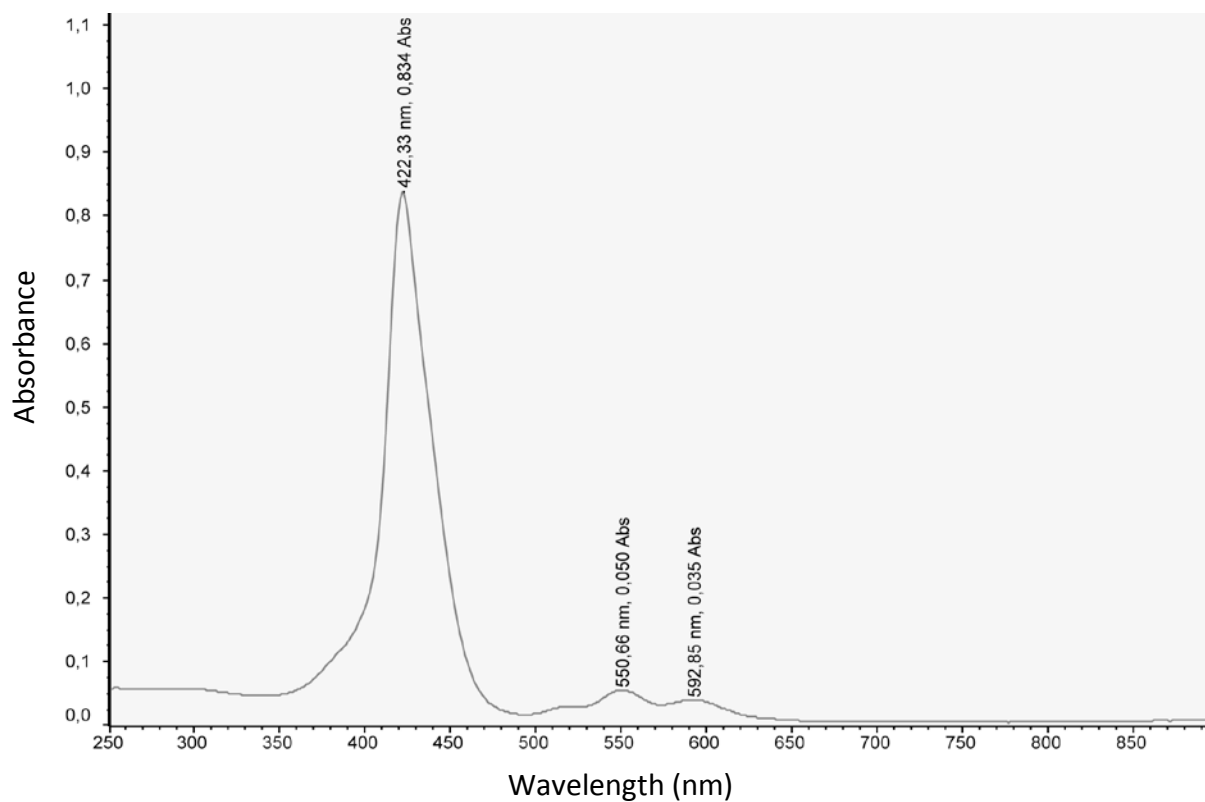


Figure S43. Absorption spectrum of 2H-6a (CHCl_3).

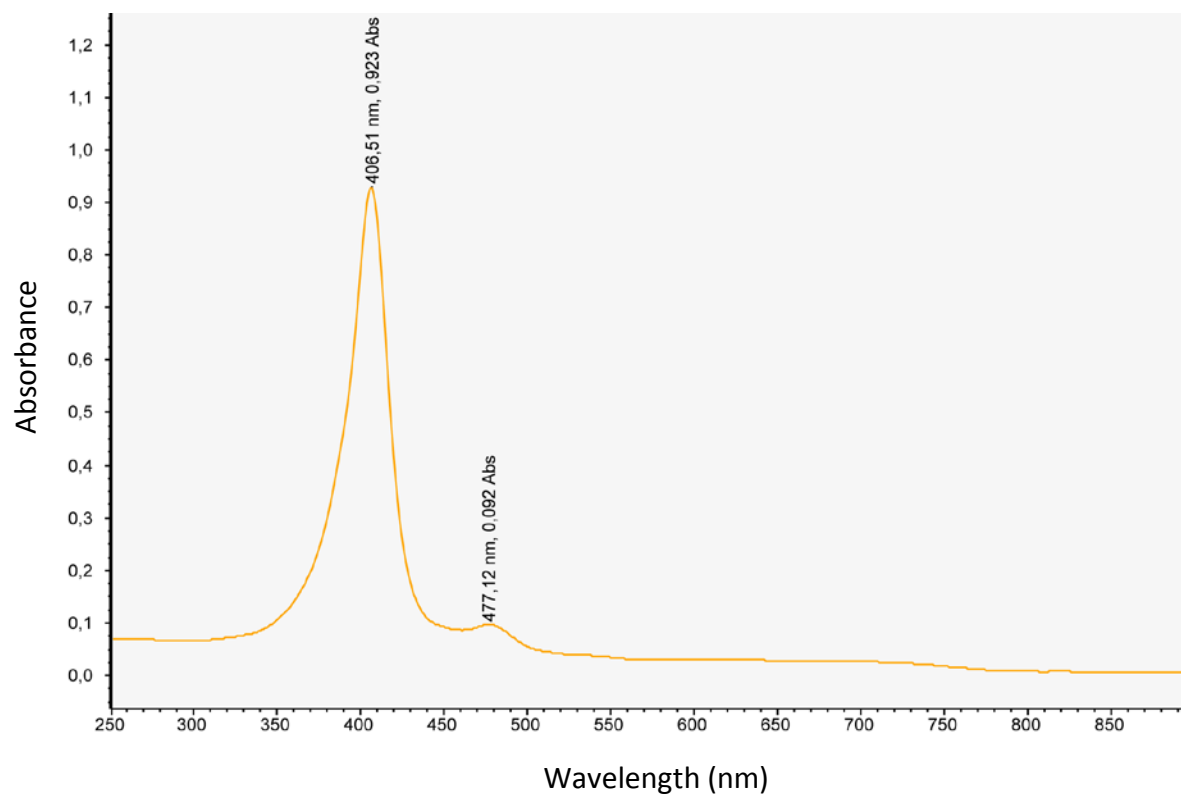


Figure S44. Absorption spectrum of 2H-14a (CHCl₃).

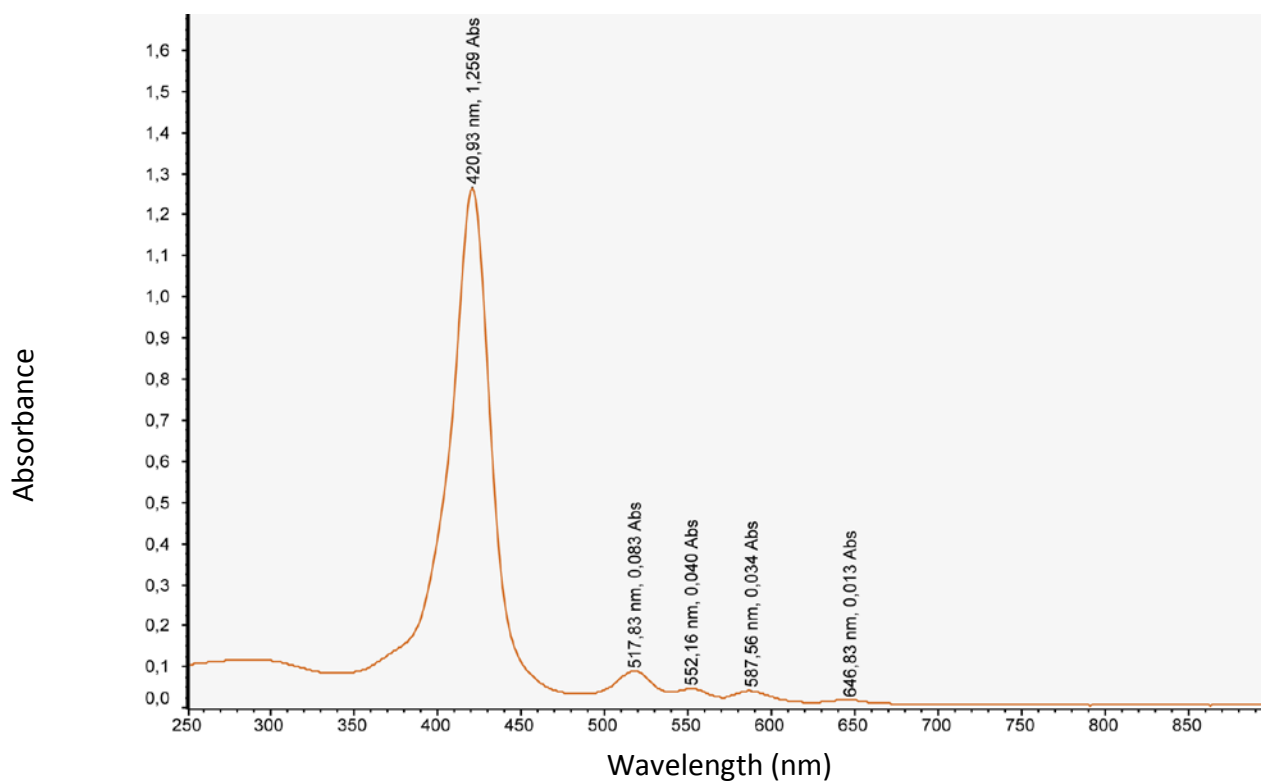


Figure S45. Absorption spectrum of 2H-15a (CHCl₃).

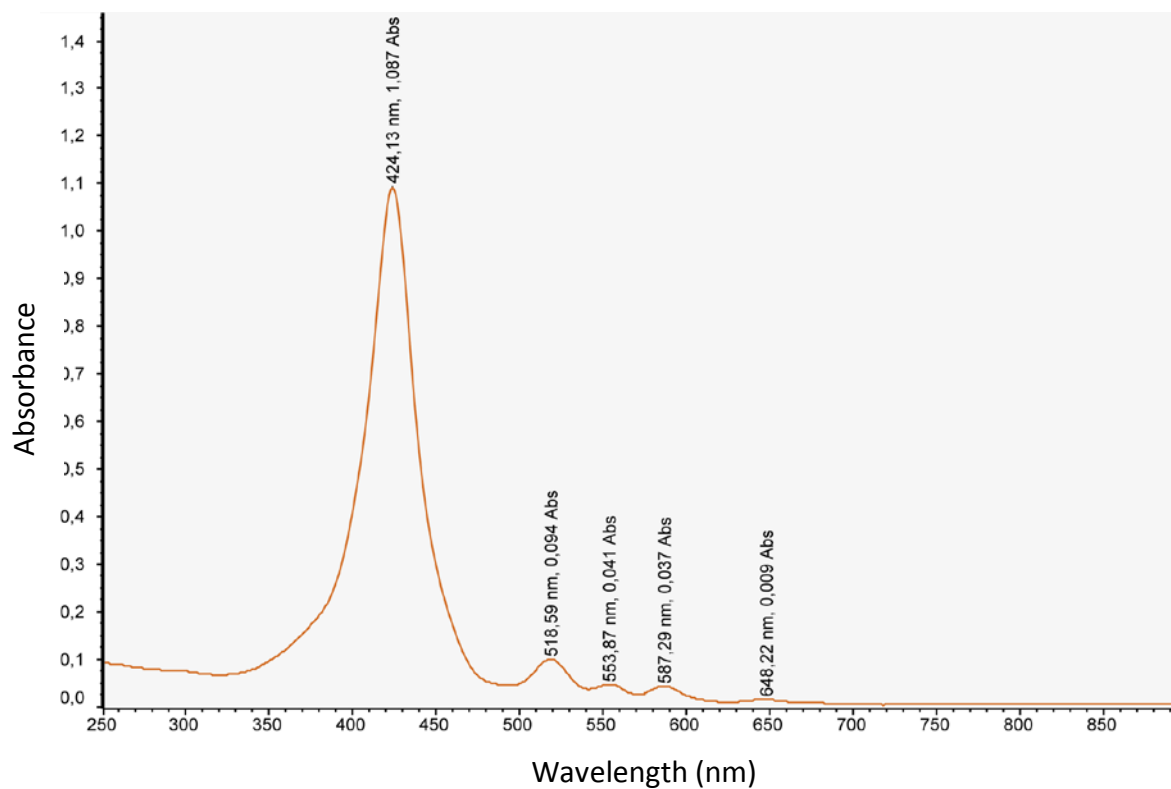


Figure S46. Absorption spectrum of 2H-19a (CHCl₃).

