Electronic Supplementary Information: 6-Oxopyriphlorins

Alexandra M. Young and Timothy D. Lash

Department of Chemistry, Illinois State University, Normal, Illinois 61790-6160, U.S.A.

Table of Contents

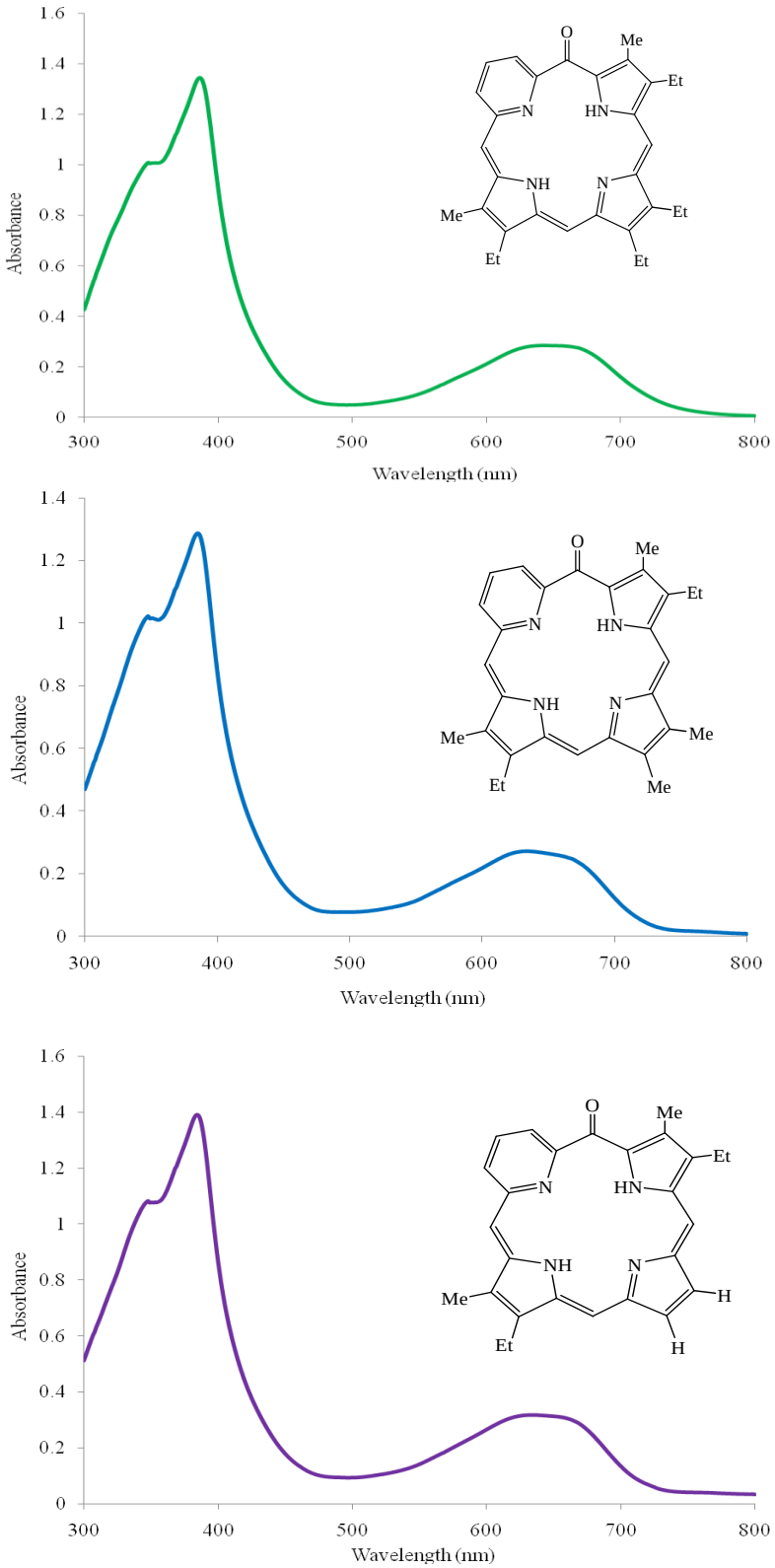


Figure S1. UV-Visible Spectra of free base oxopyriphlorins **6a-c** in chloroform.

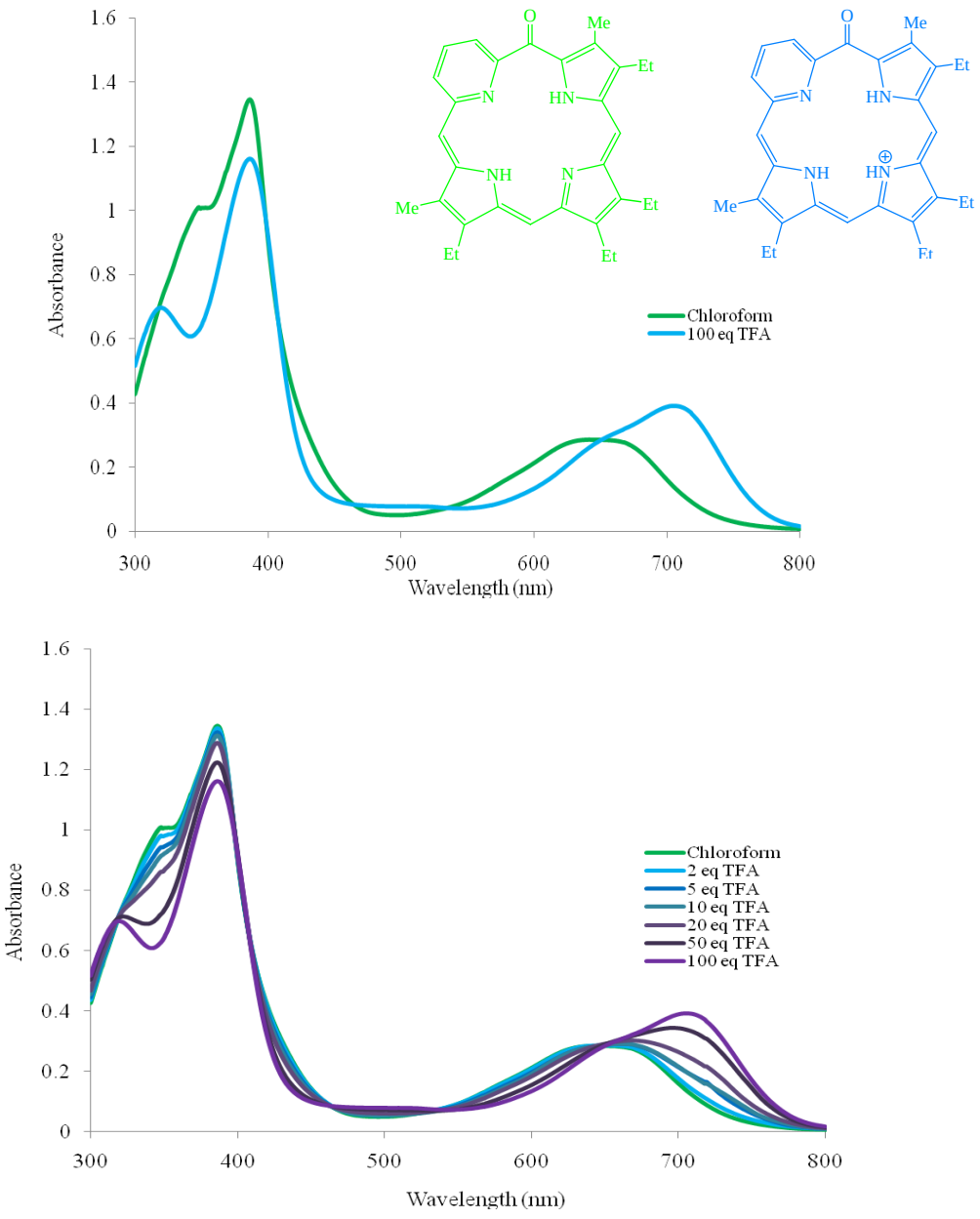


Figure S2. UV-Visible Spectra of 6-oxopyriphlorin **6a** in chloroform with 0-100 equiv. TFA.

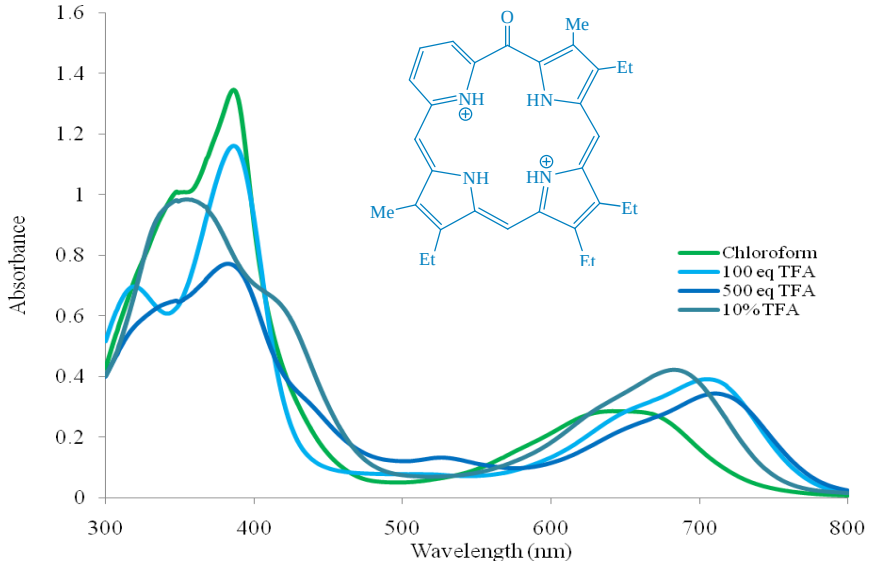


Figure S3. UV-Visible Spectra of **6a** free base in chloroform and progressively protonated forms in TFA-chloroform.

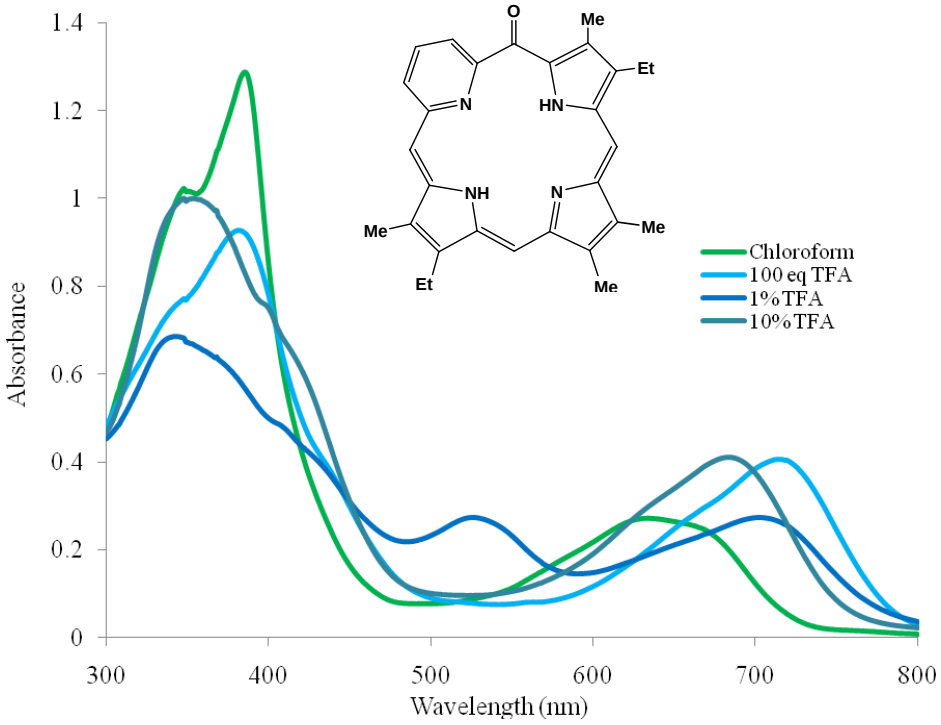


Figure S4. UV-Visible Spectra of **6b** free base in chloroform and progressively protonated forms in TFA-chloroform.

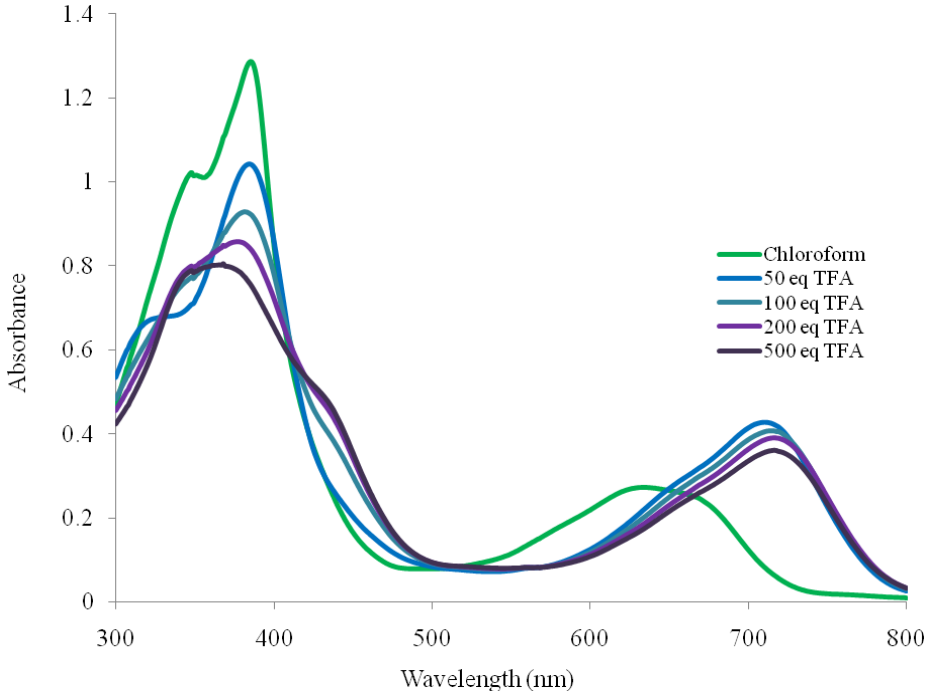


Figure S5. UV-Visible Spectra of **6a** free base in chloroform and the formation of a monoprotonated species with 50-500 equiv TFA.

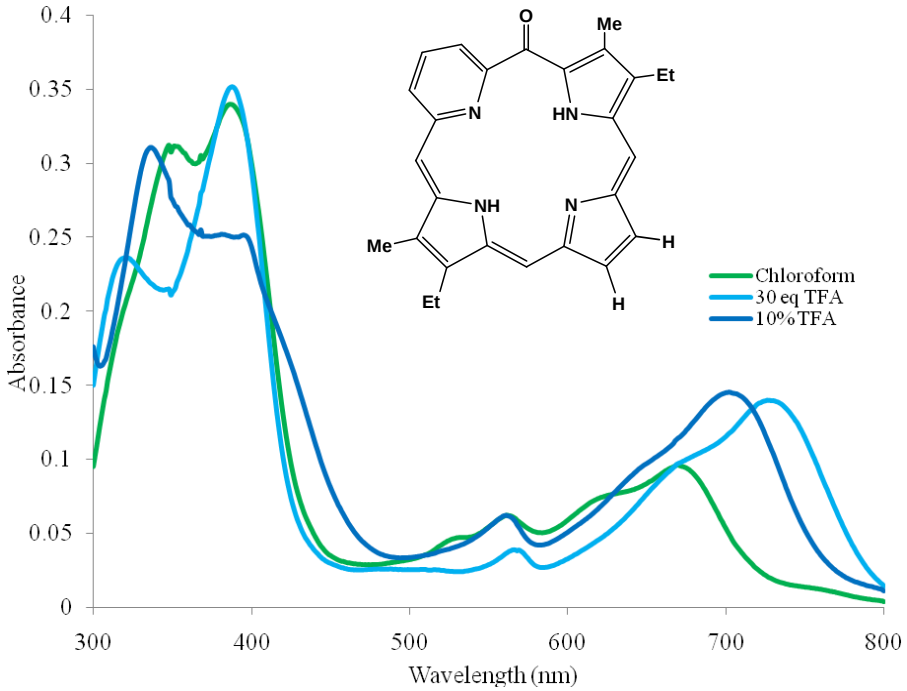


Figure S6. UV-Visible Spectra of **6b** in chloroform free base), chloroform with 30 equiv. TFA and 10% TFA-chloroform.

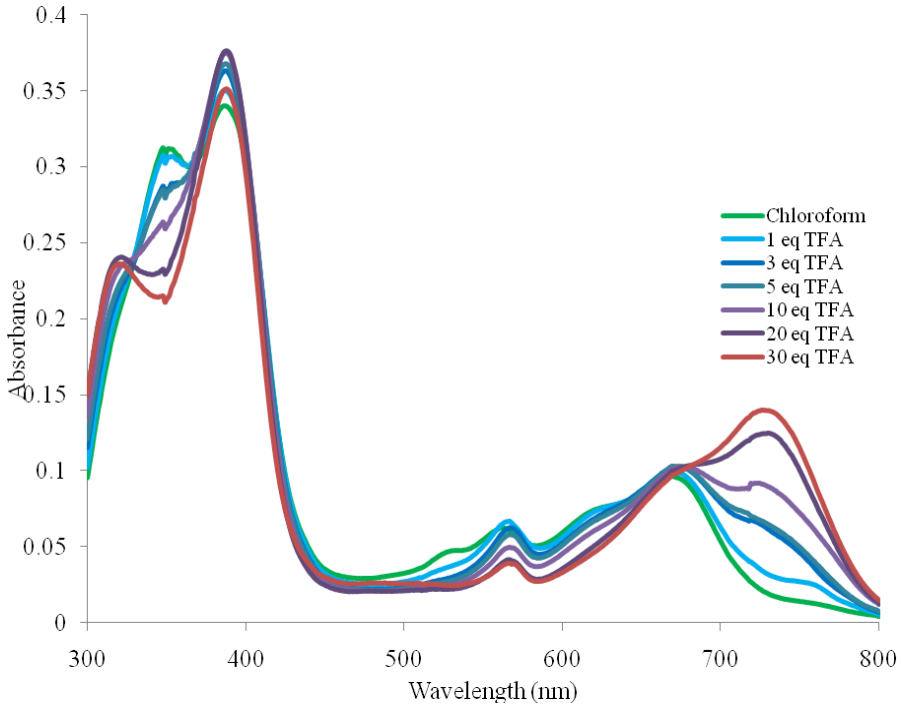


Figure S7. UV-visible spectra of **6c** in chloroform with 0-30 equiv. of TFA showing the formation of a monoprotonated species.

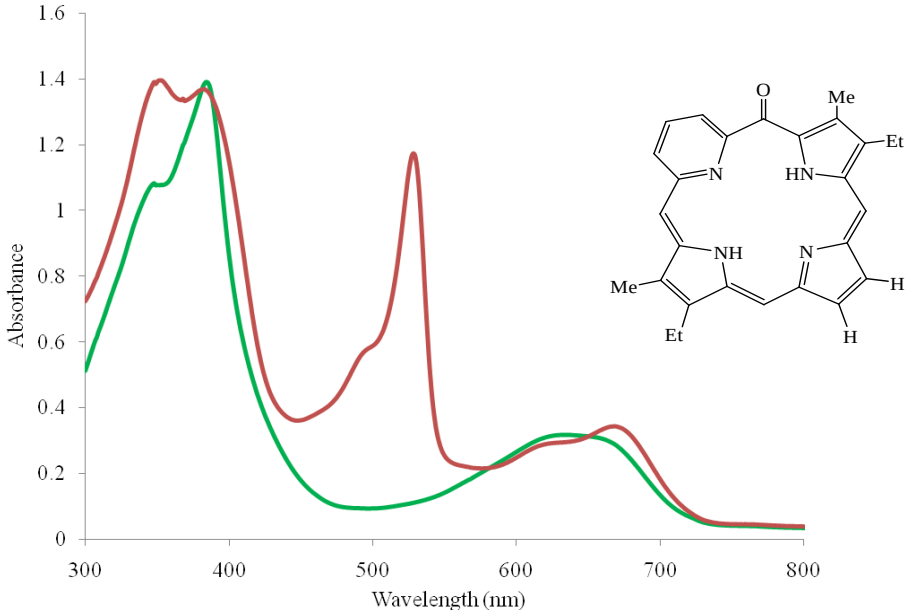


Figure S8. UV-vis spectrum of 6-oxopyriphlorin **6c** (green line) and the red decomposition product (red line).

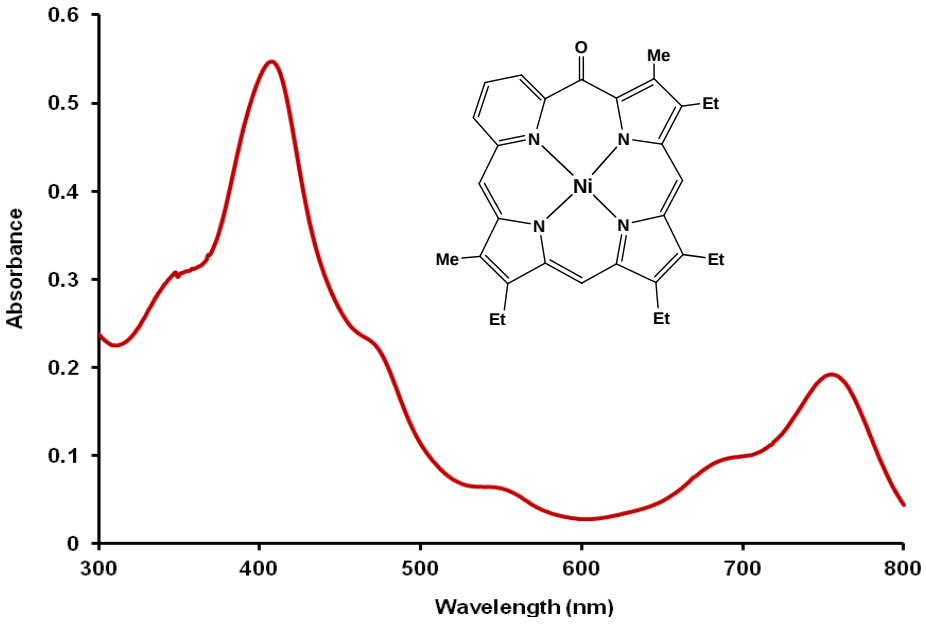


Figure S9. UV-Visible Spectrum of nickel(II) complex **28a** in chloroform.

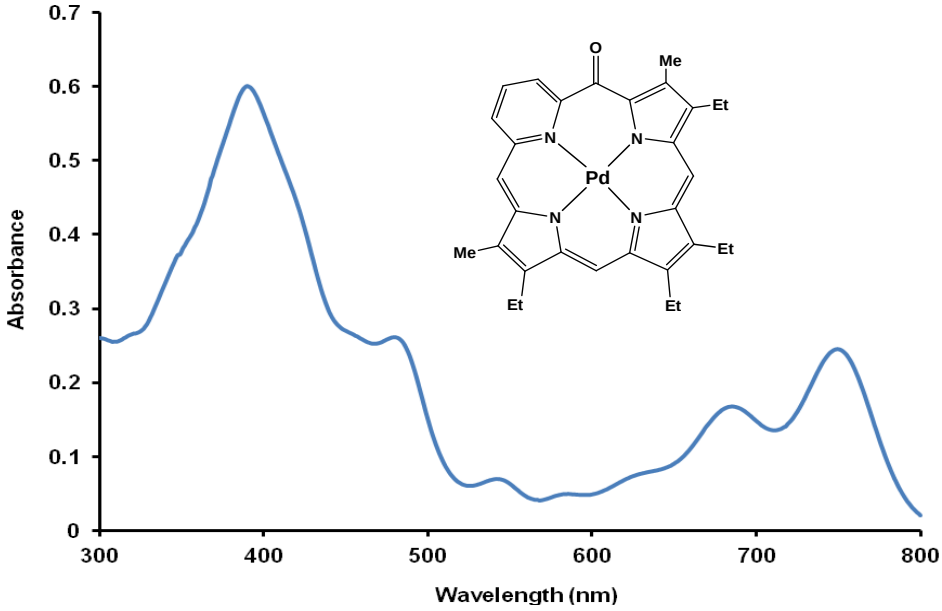


Figure S10. UV-Visible Spectrum of palladium(II) complex **28b** in chloroform.

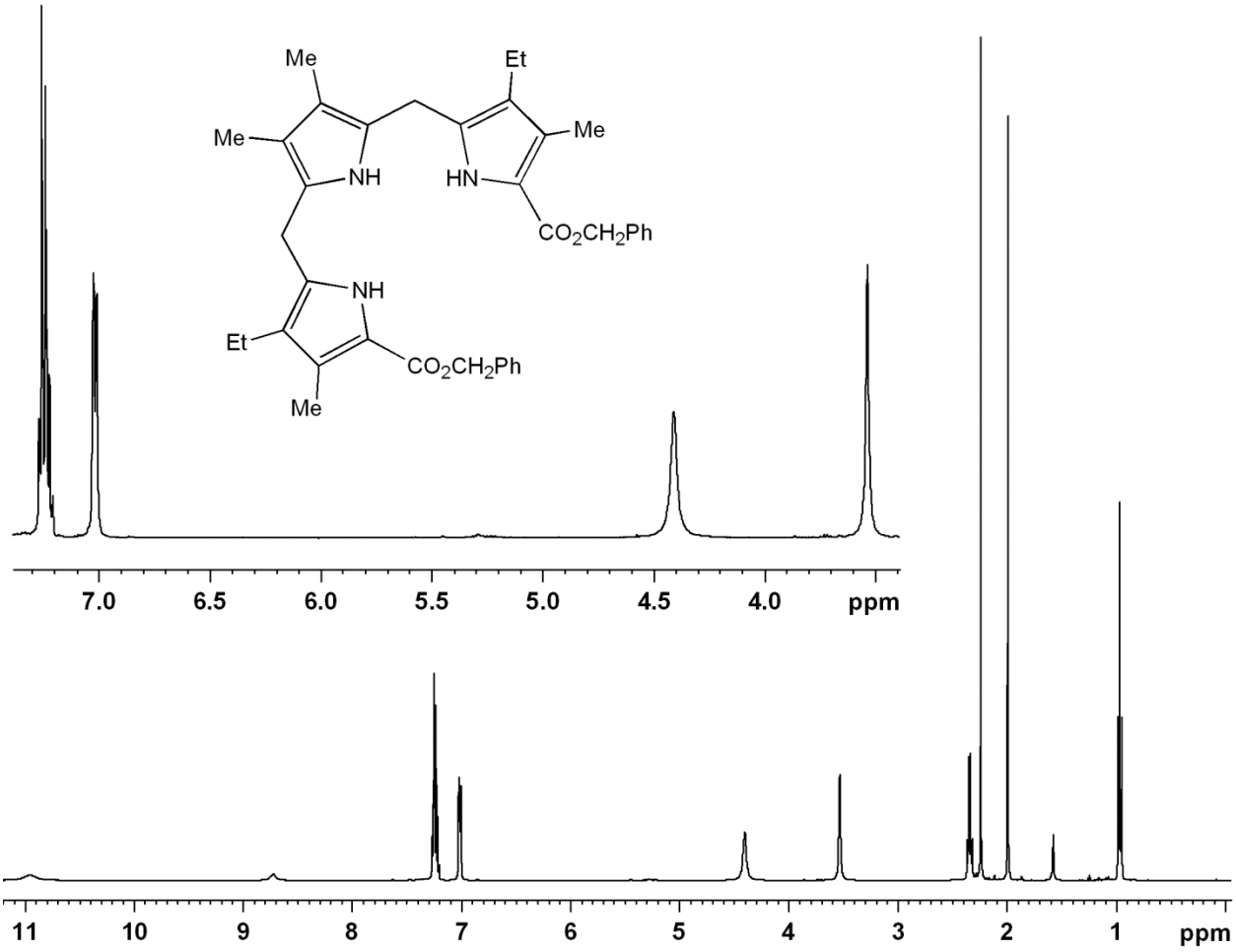


Figure S11. 500 MHz proton NMR spectrum of tripyrrane **20b** in $CDCl_3$.

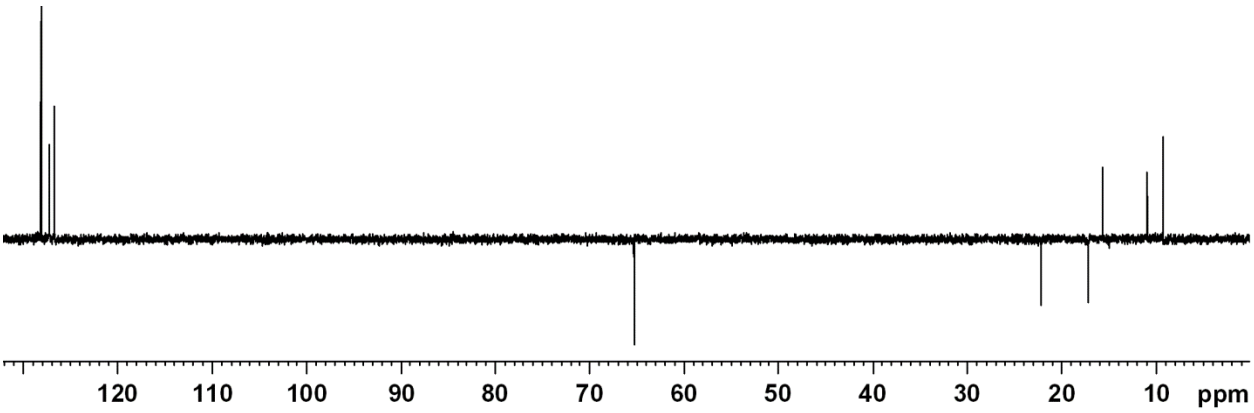


Figure S12. DEPT-135 NMR spectrum of tripyrrane **20b** in $CDCl_3$.

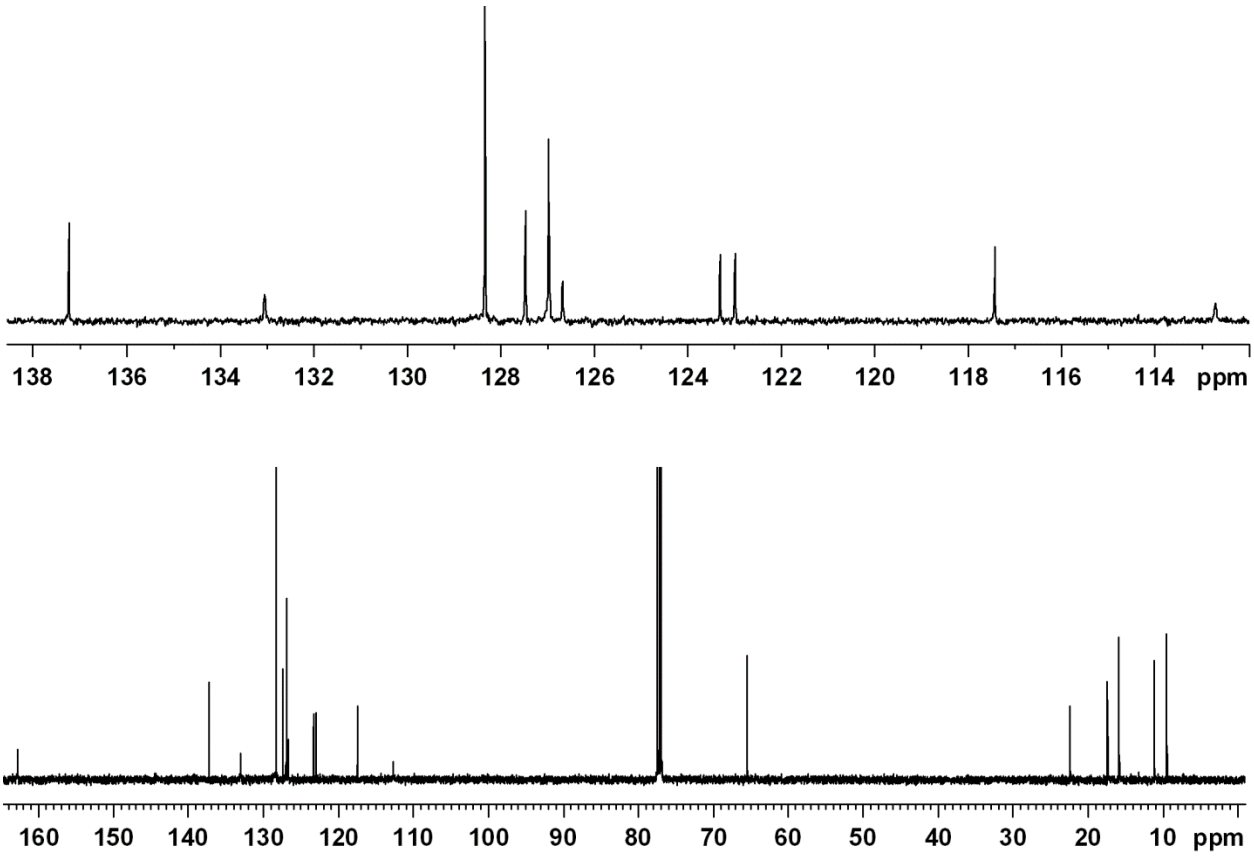


Figure S13. 125 MHz carbon-13 NMR spectrum of tripyrrane **20b** in $CDCl_3$.

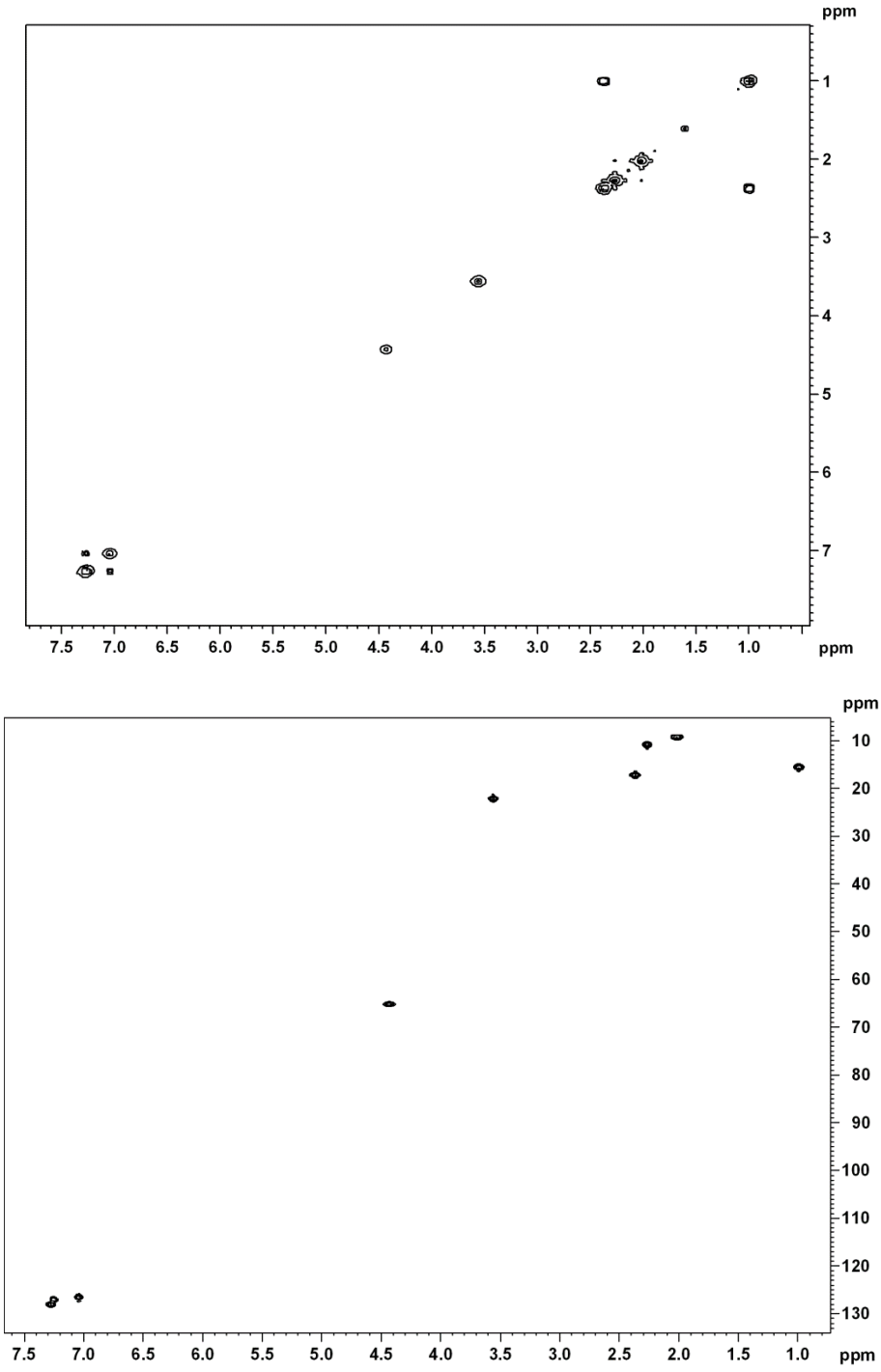


Figure S14. ^{1}H-^{1}H COSY and HSQC NMR spectra of tripyrrane **20b** in $CDCl_3$.

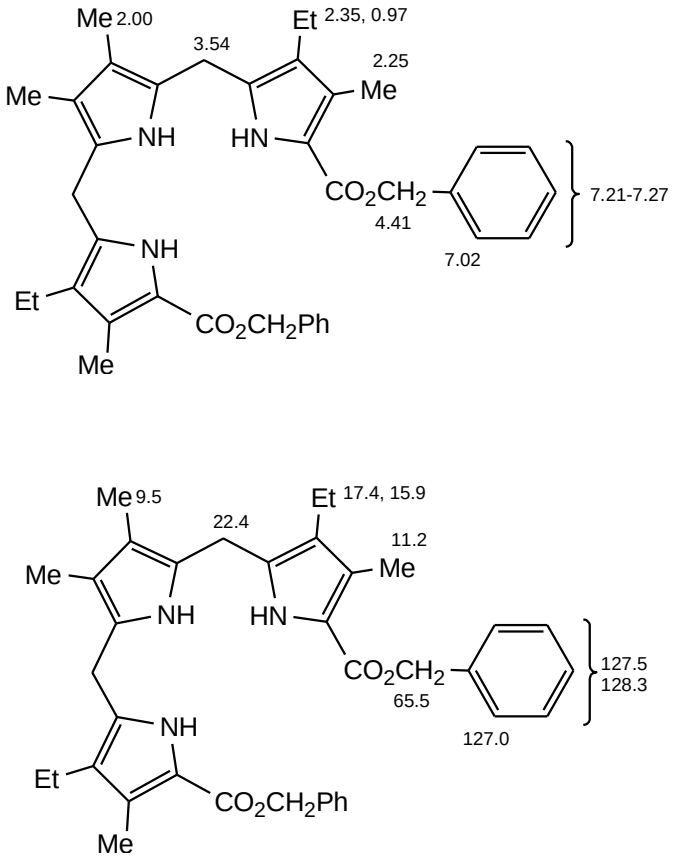


Figure S15. Partial assignments for the proton and carbon-13 NMR spectra of tripyrrane dibenzyl ester **20b** based on the foregoing data.

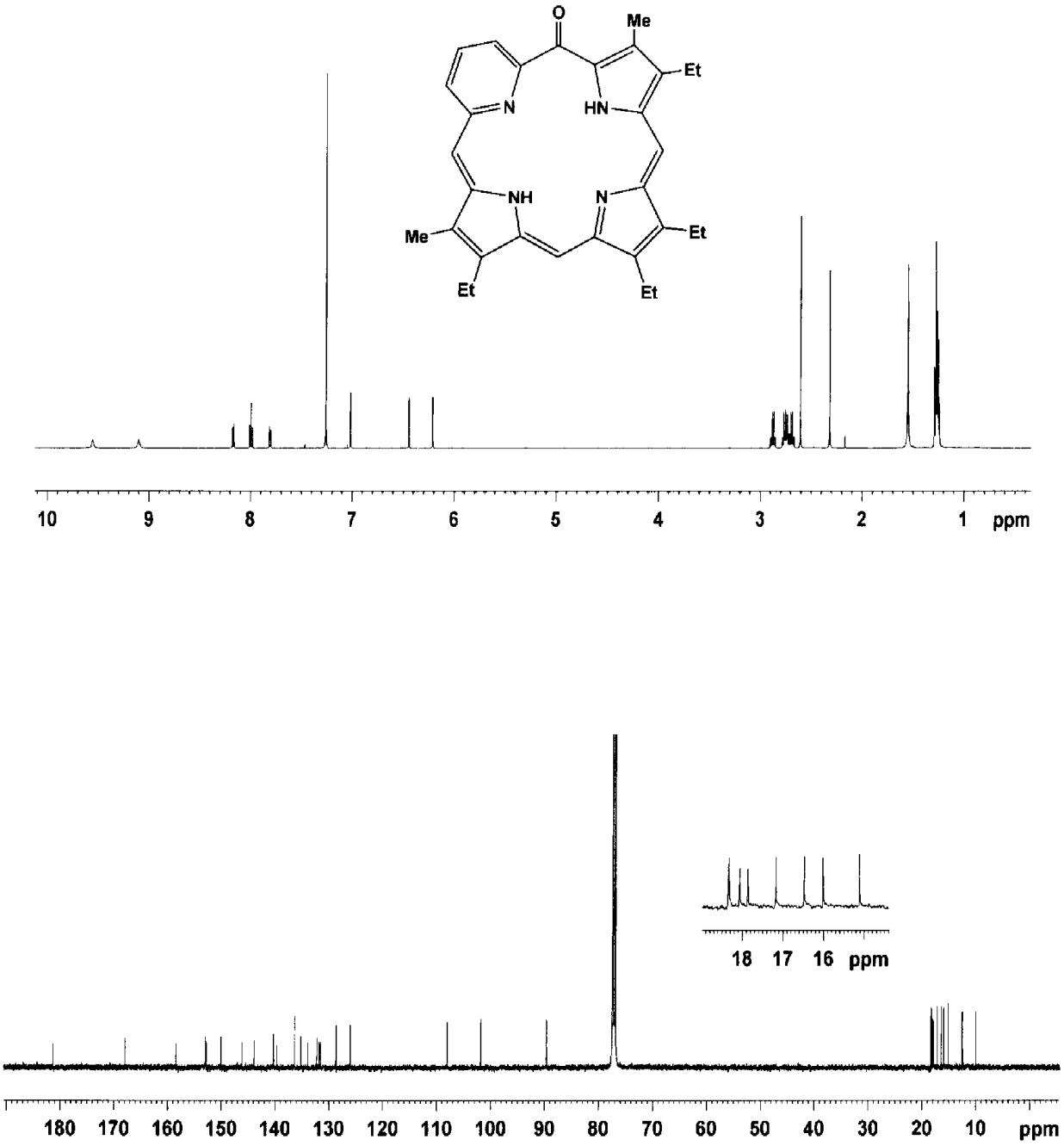


Figure S16. 500 MHz proton and 125 MHz carbon-13 NMR spectra of oxopyriphlorin **6a** in $CDCl_3$.

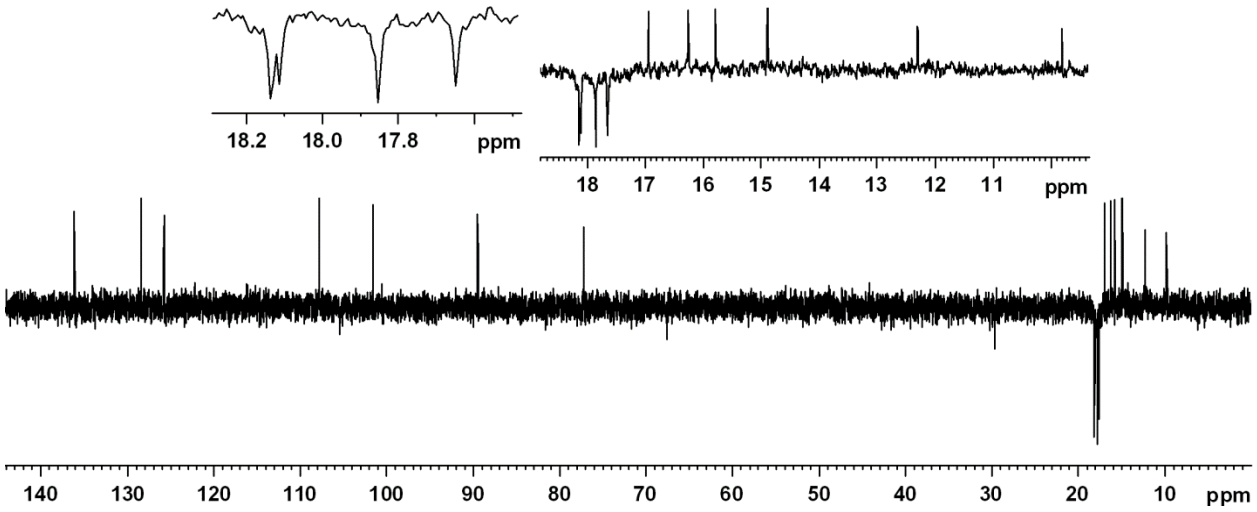


Figure S17. DEPT-135 NMR spectrum of oxopyriphlorin **6a** in $CDCl_3$.

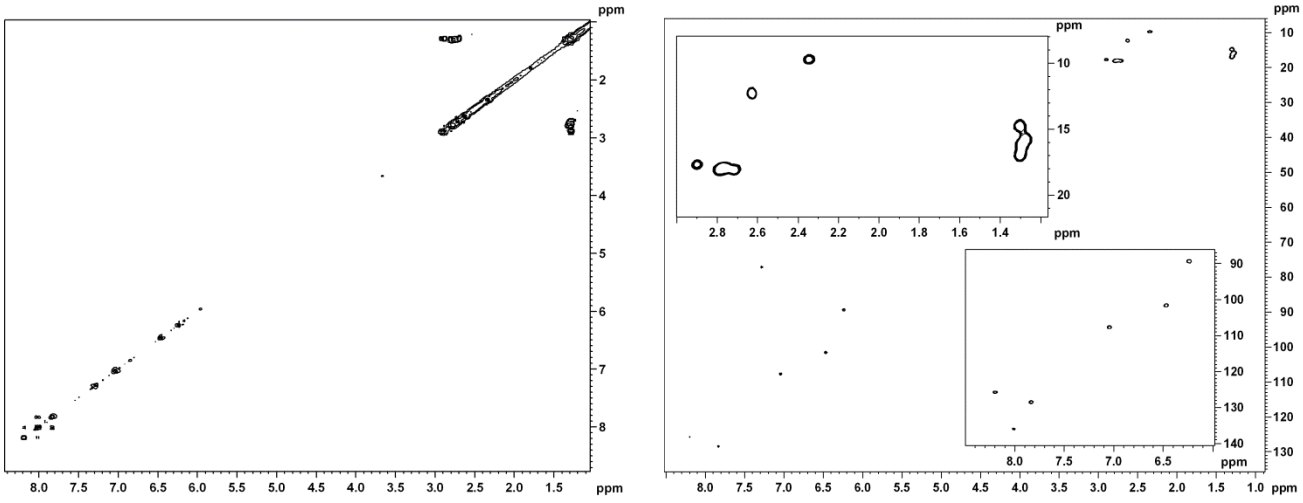


Figure S18. ^{1}H-^{1}H COSY and HSQC NMR spectra of oxopyriphlorin **6a** in $CDCl_3$.

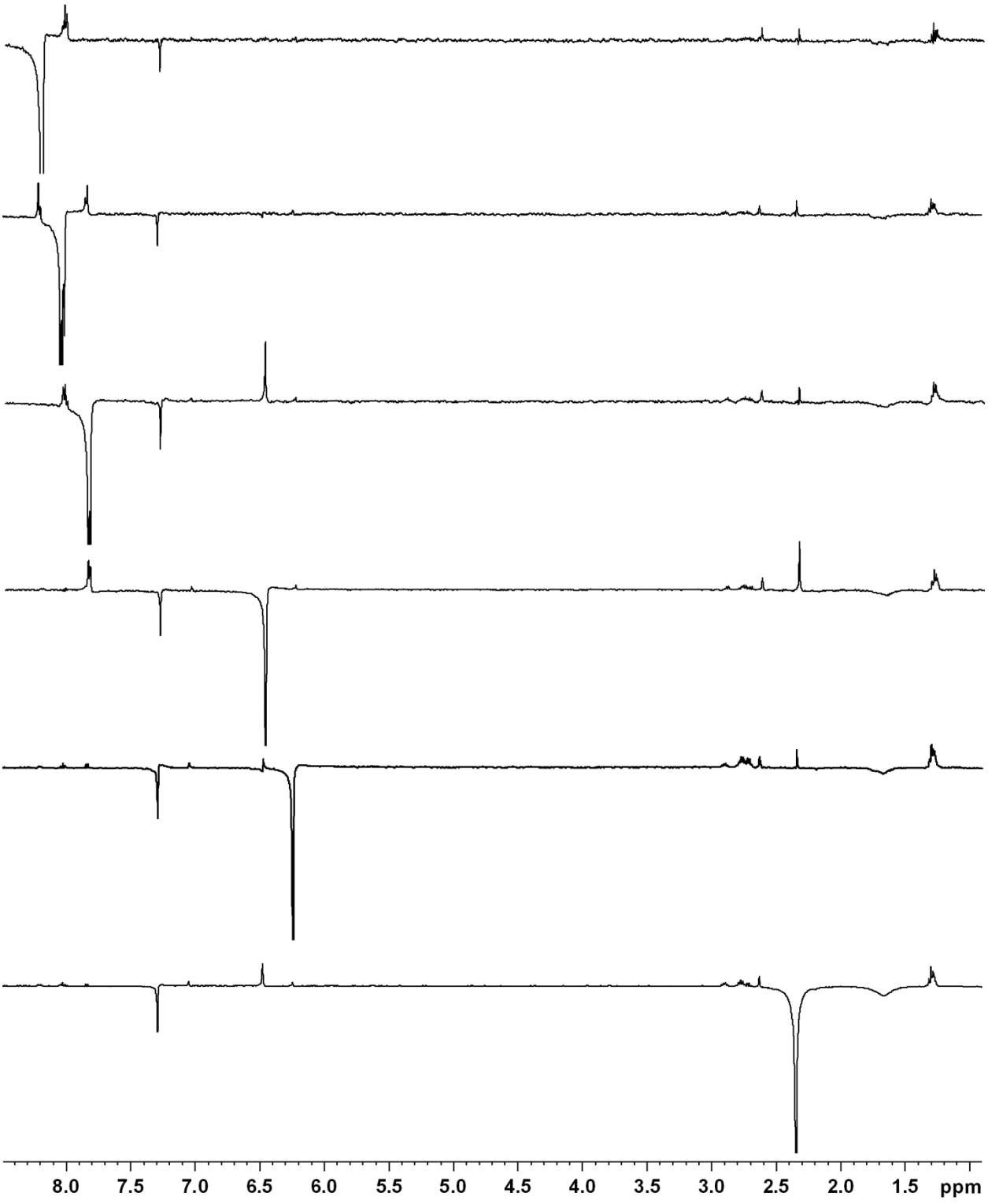


Figure S19. Selected nOe difference proton NMR spectra of oxopyriphlorin **6a** in $CDCl_3$.

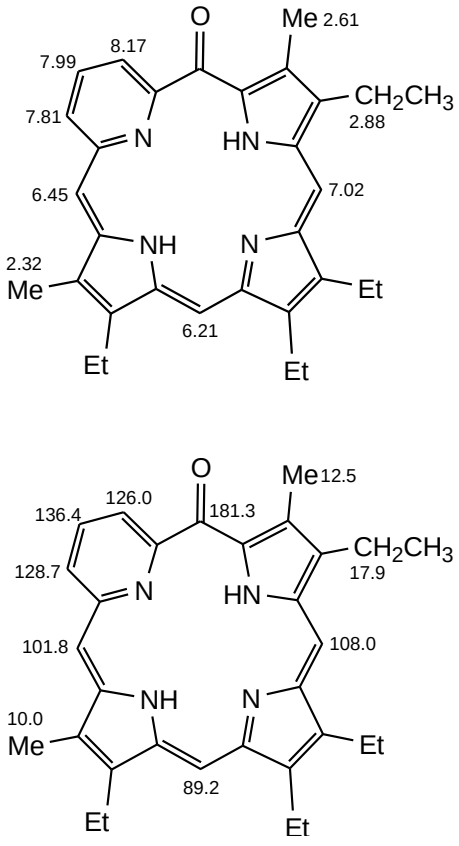


Figure S20. Partial assignments for the proton and carbon-13 NMR spectra of 6-oxopyriphlorin **6a** based on the foregoing data.

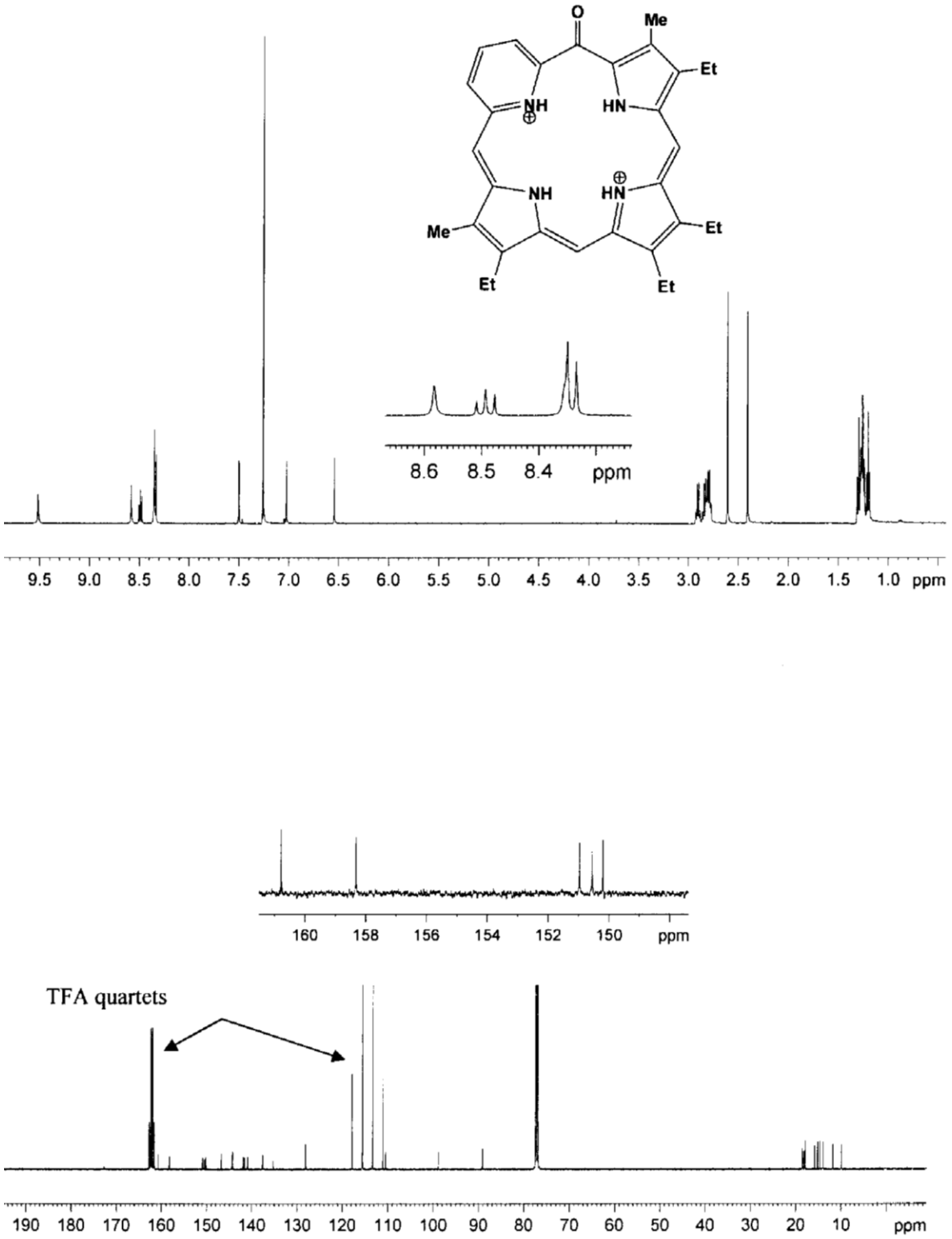


Figure S21. 500 MHz proton and 125 MHz carbon-13 NMR spectra of **6a** in TFA-$CDCl_3$.

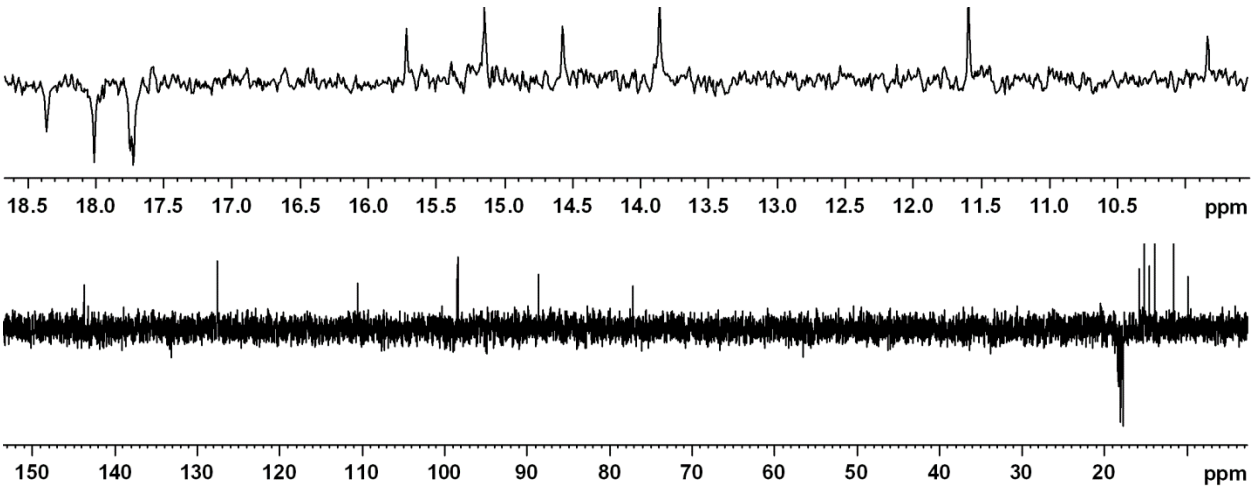


Figure S22. DEPT-135 NMR spectrum of oxopyriphlorin **6a** in TFA-$CDCl_3$.

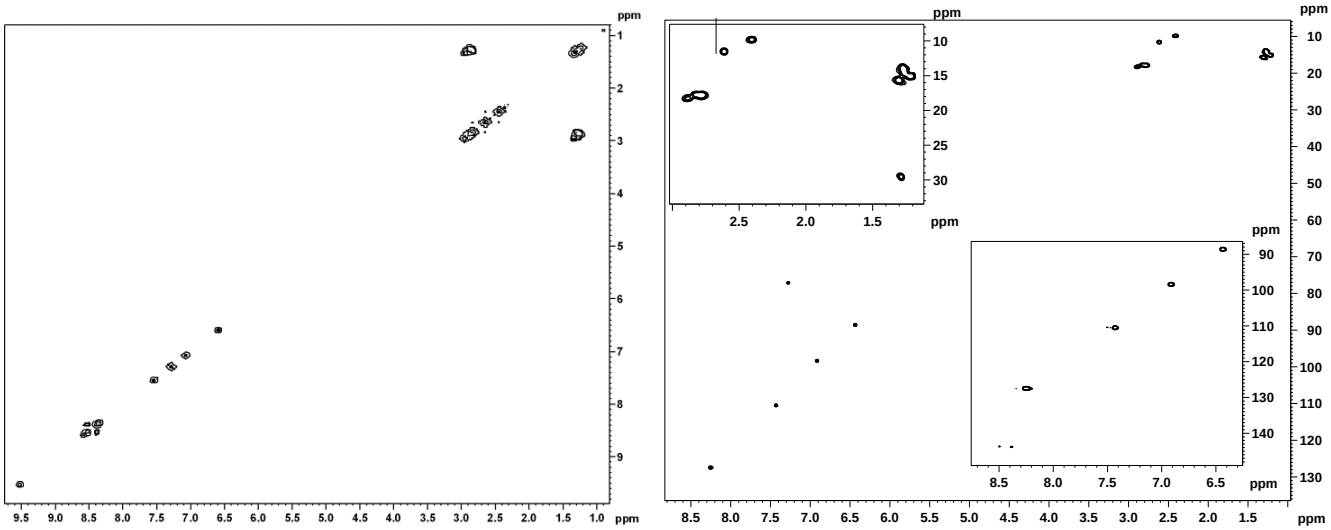


Figure S23. ^{1}H-^{1}H COSY and HSQC NMR spectra of oxopyriphlorin **6a** in TFA-$CDCl_3$.

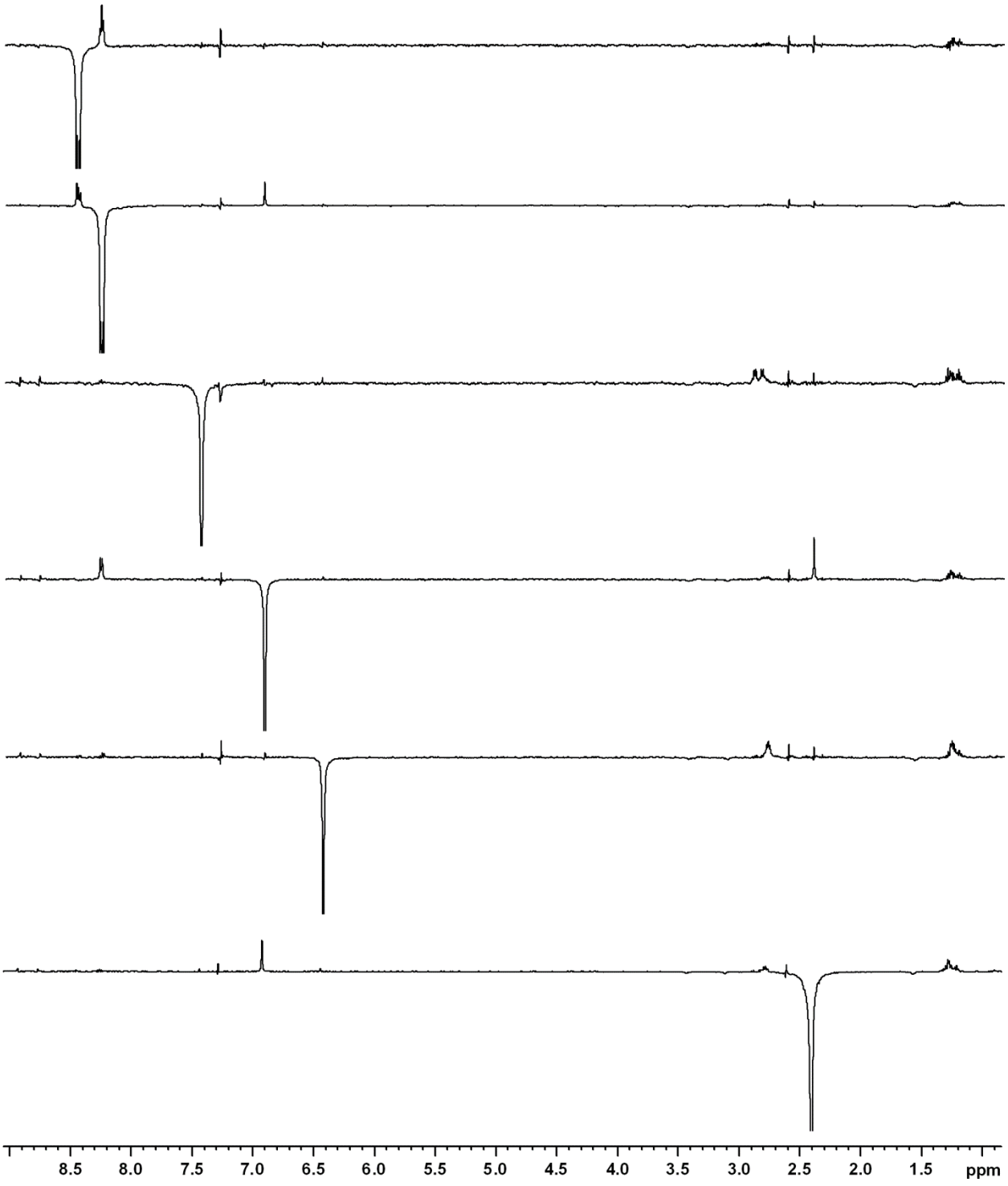


Figure S24. Selected nOe difference proton NMR spectra of **6a** in TFA-$CDCl_3$.

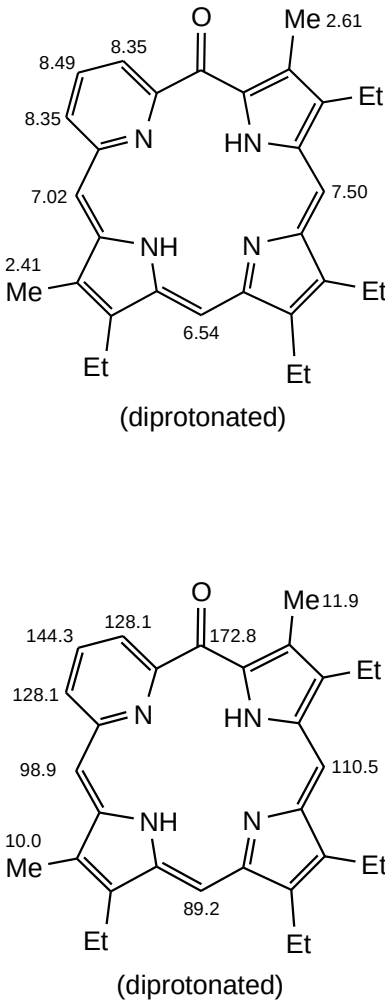


Figure S25. Partial assignments for the proton and carbon-13 NMR spectra of 6-oxopyriphlorin **6a** in TFA-$CDCl_3$ based on the foregoing data.

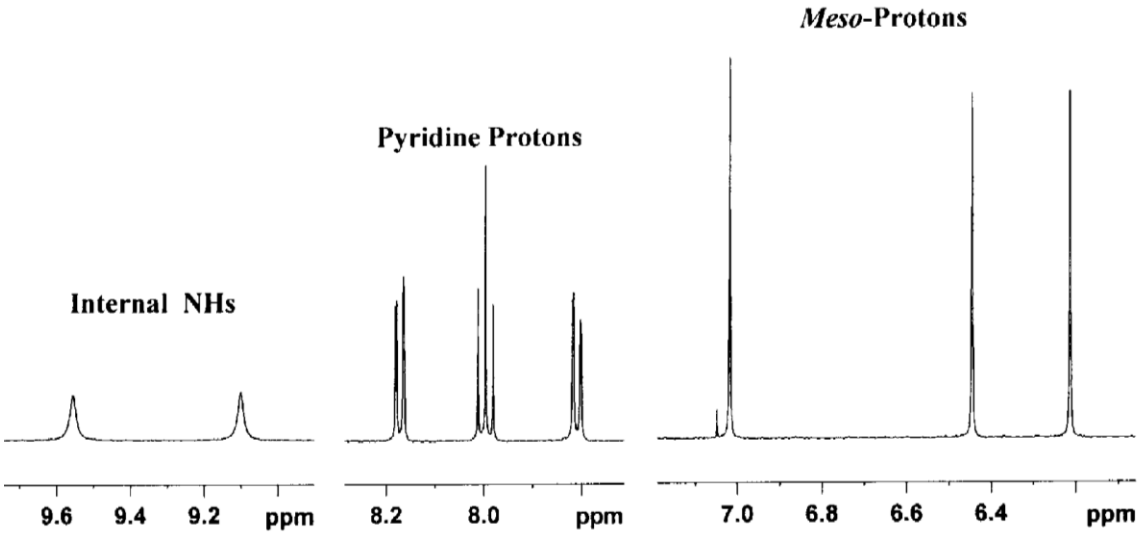


Figure S26. Partial 500 MHz proton NMR spectrum of free base **6a** in $CDCl_3$.

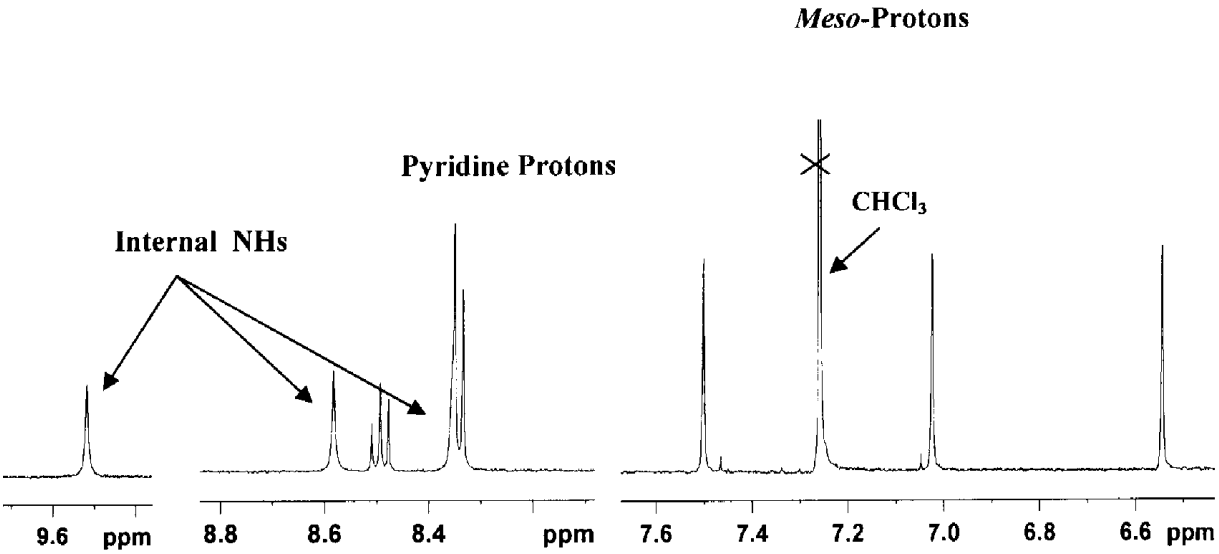


Figure S27. Partial 500 MHz proton NMR spectrum of protonated **6a** in TFA-$CDCl_3$.

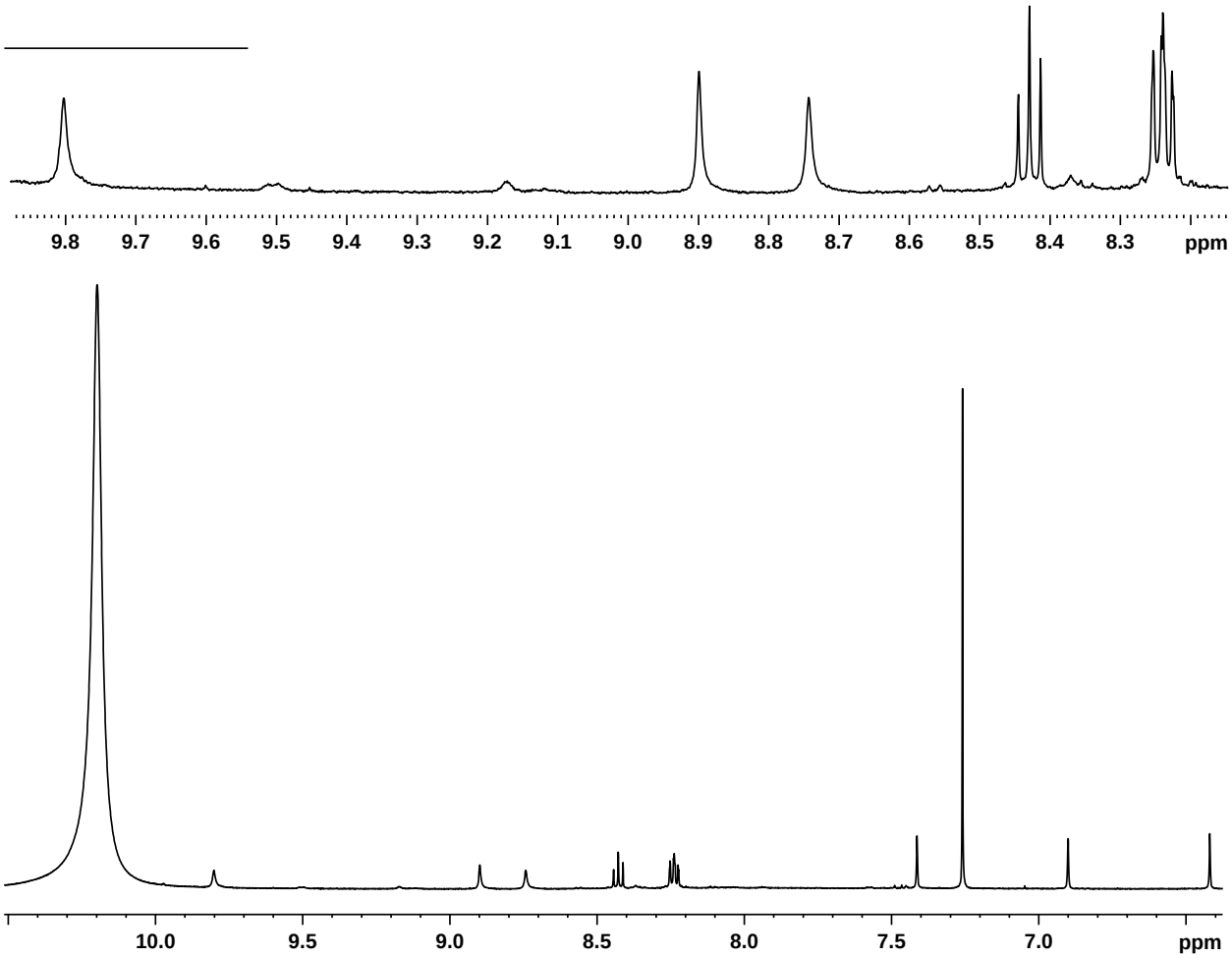


Figure S28. 500 MHz proton NMR spectrum of **6a** in $CDCl_3$ with a higher concentration of TFA showing a downfield shift to the NH resonances.

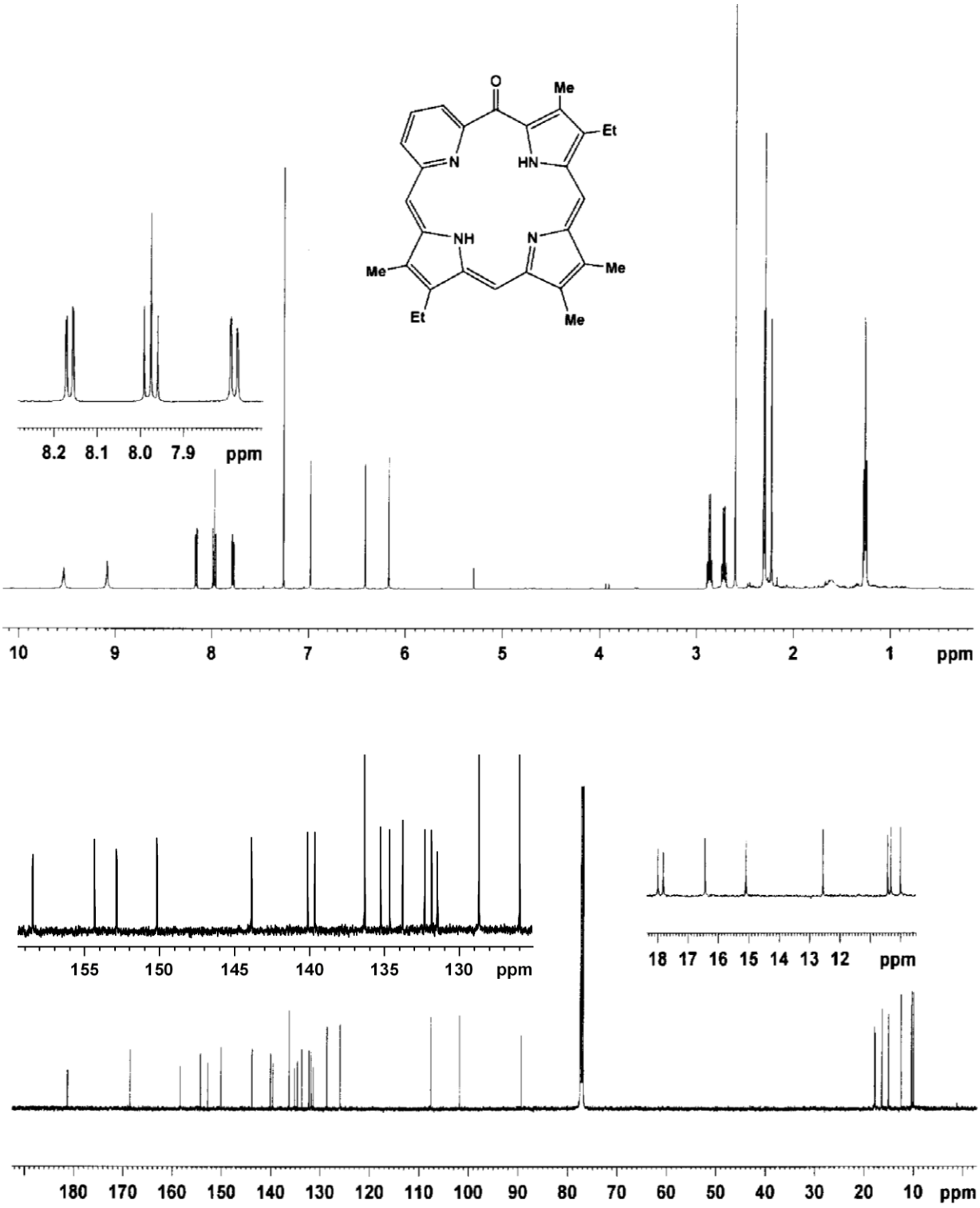


Figure S29. 500 MHz proton and 125 MHz carbon-13 NMR spectra of **6b** in $CDCl_3$.

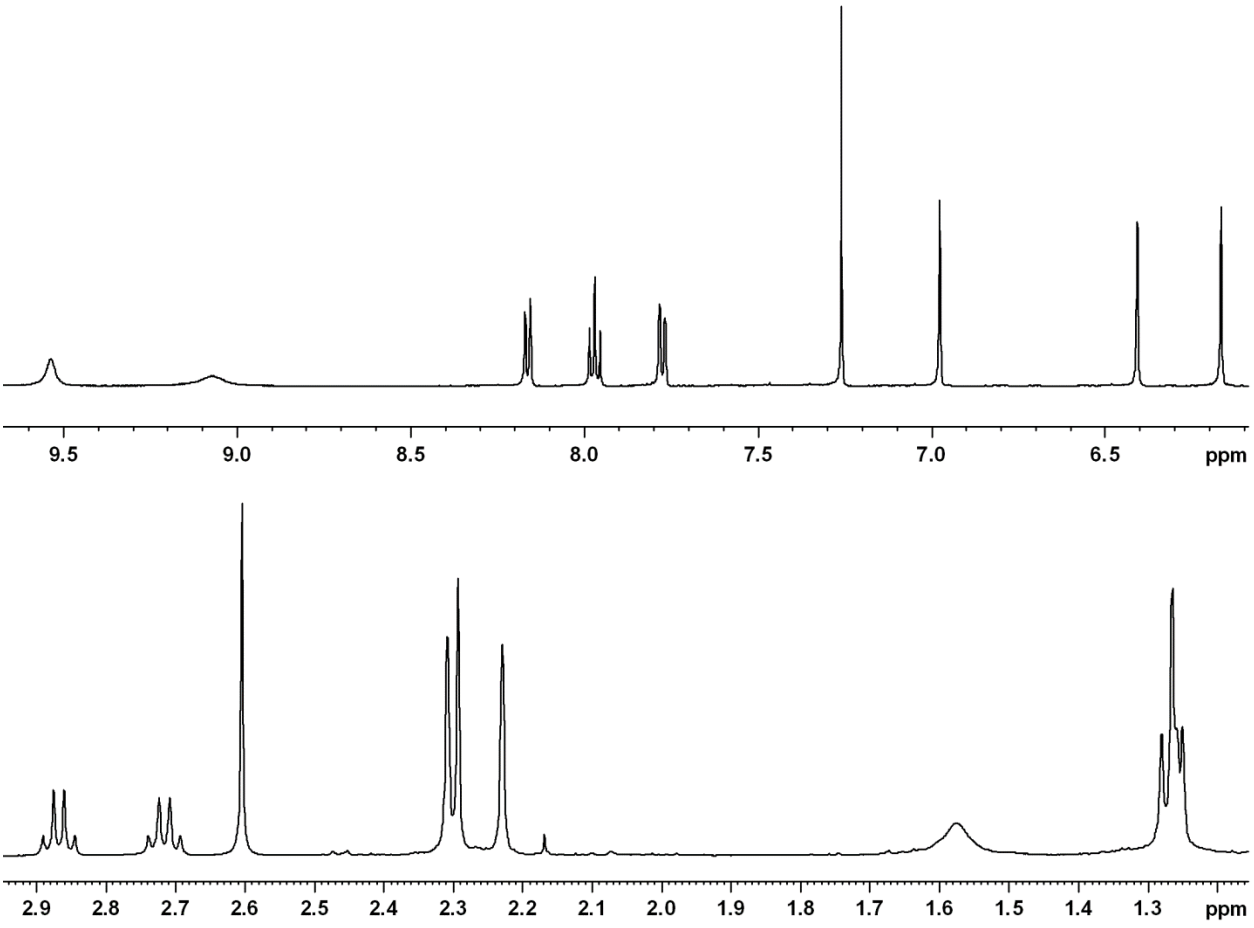


Figure S30. Details of the upfield and downfield regions for the 500 MHz proton NMR spectrum of **6b** in $CDCl_3$.

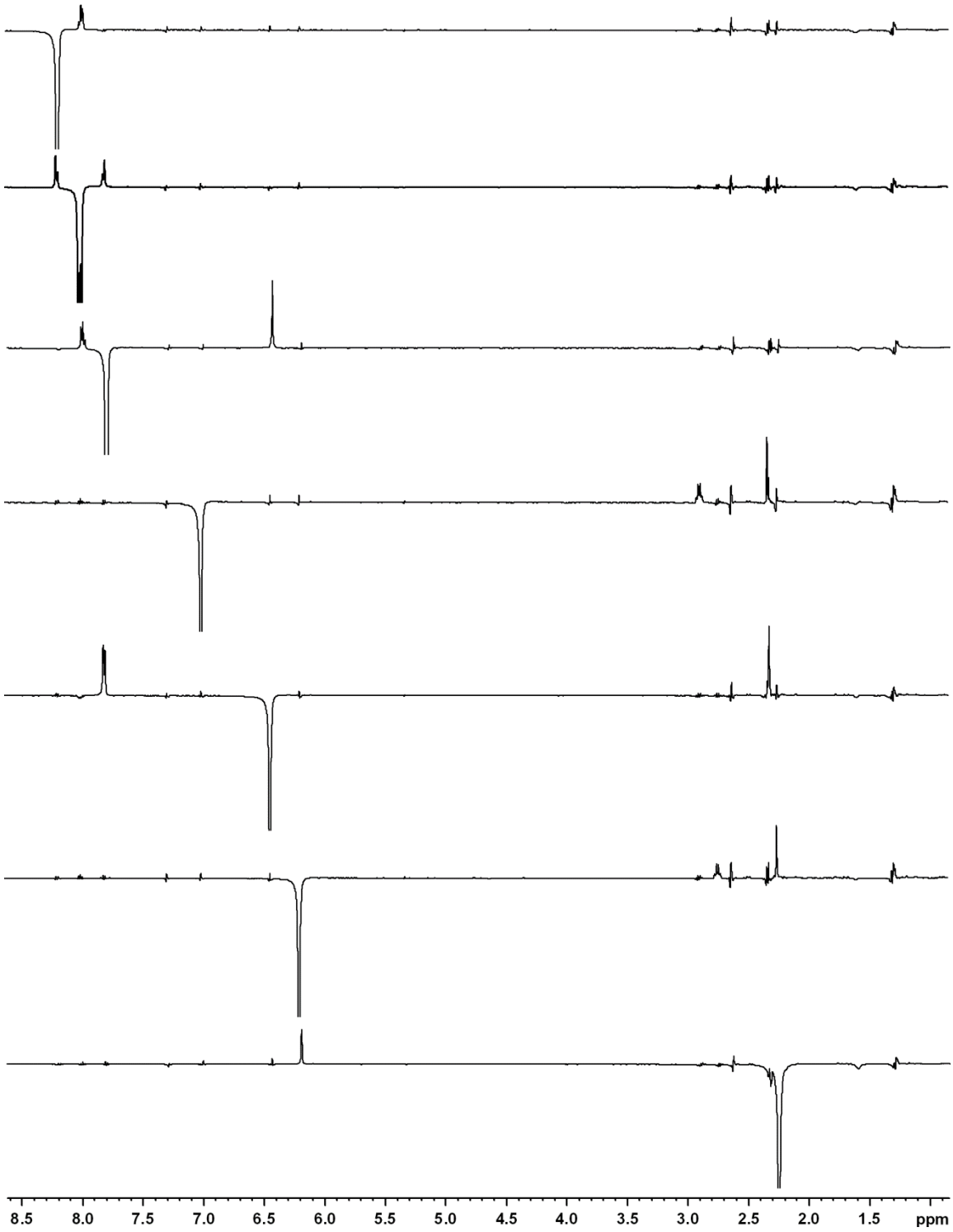


Figure S31. Selected nOe difference proton NMR spectra of **6b** in $CDCl_3$.

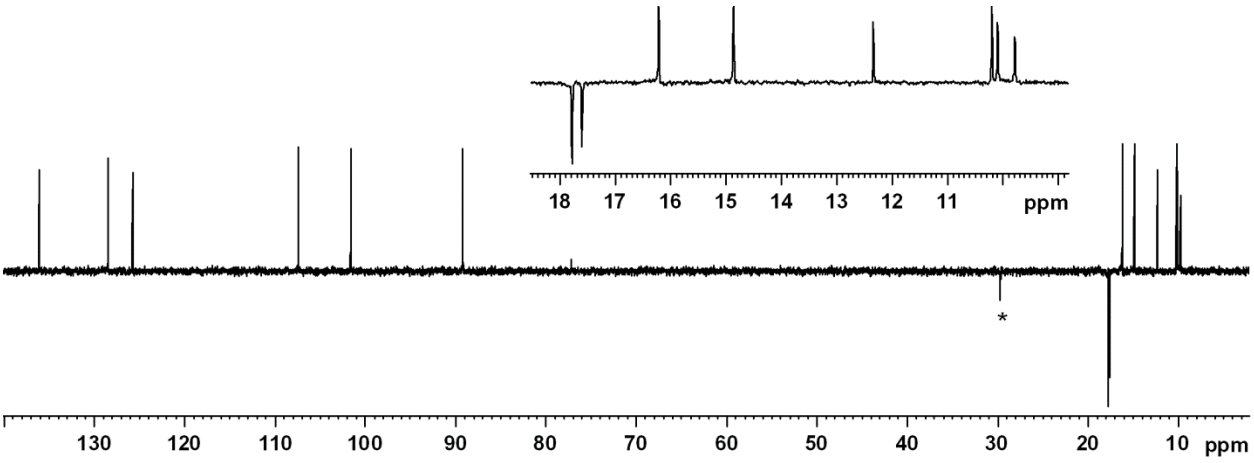


Figure S32. DEPT-135 NMR spectrum of **6b** in $CDCl_3$. * = trace acetone

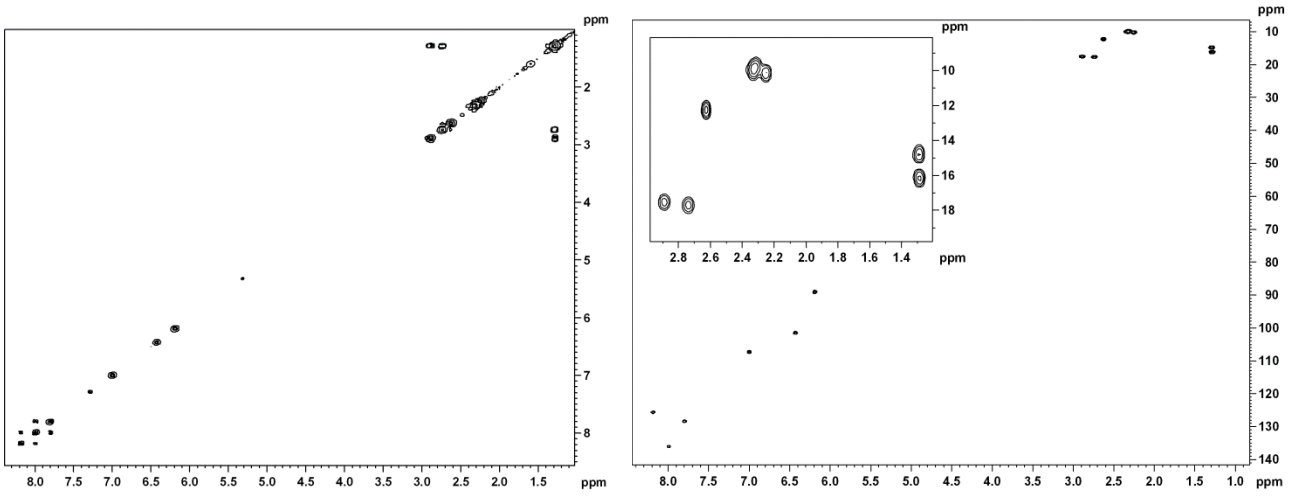


Figure S33. ^{1}H-^{1}H COSY and HSQC NMR spectra of **6b** in $CDCl_3$.

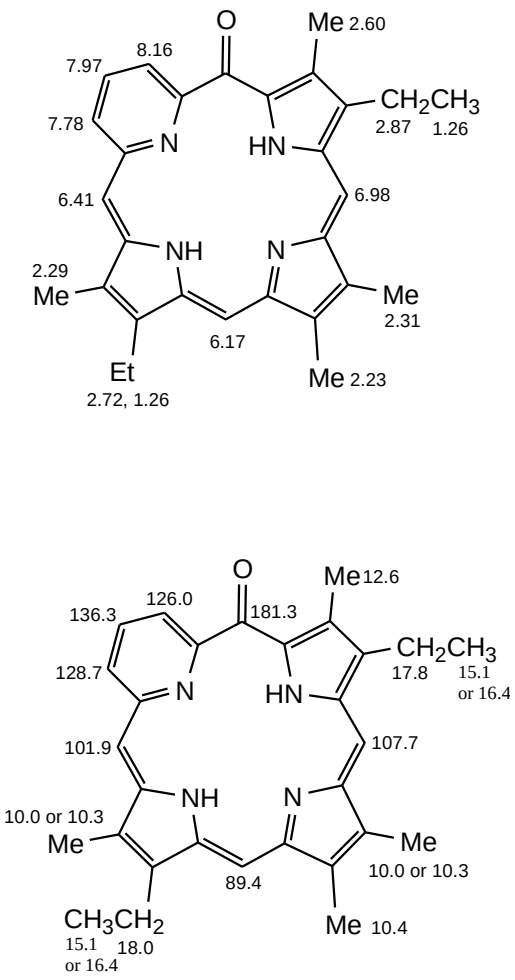


Figure S34. Partial assignments for the proton and carbon-13 NMR spectra of 6-oxopyriphlorin **6b** in $CDCl_3$ based on the foregoing data.

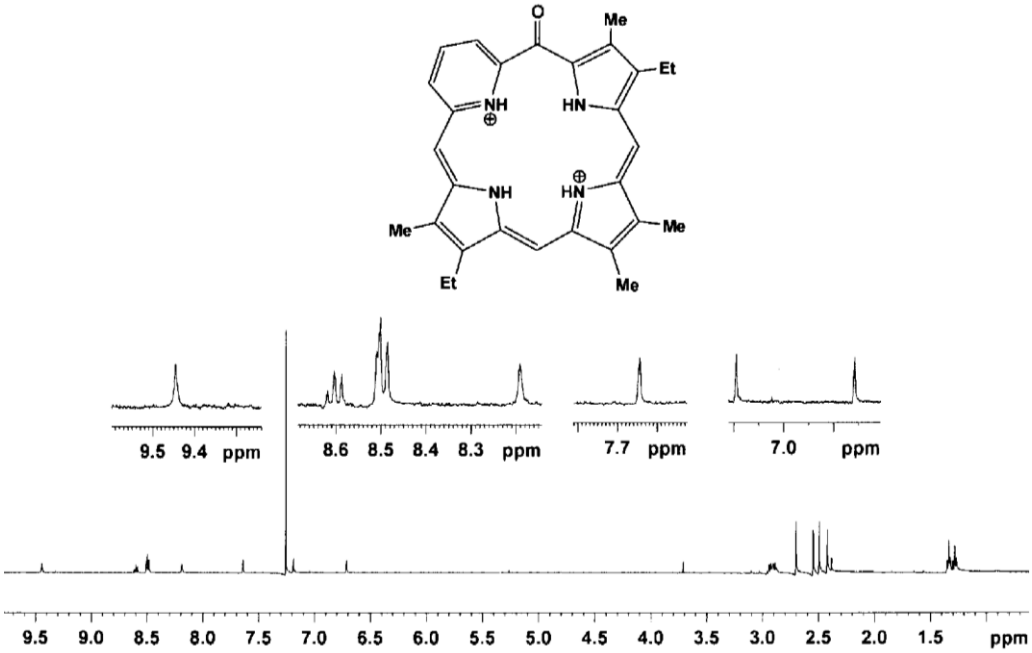


Figure S35. Proton NMR spectrum of oxopyriphlorin **6b** in TFA-$CDCl_3$.

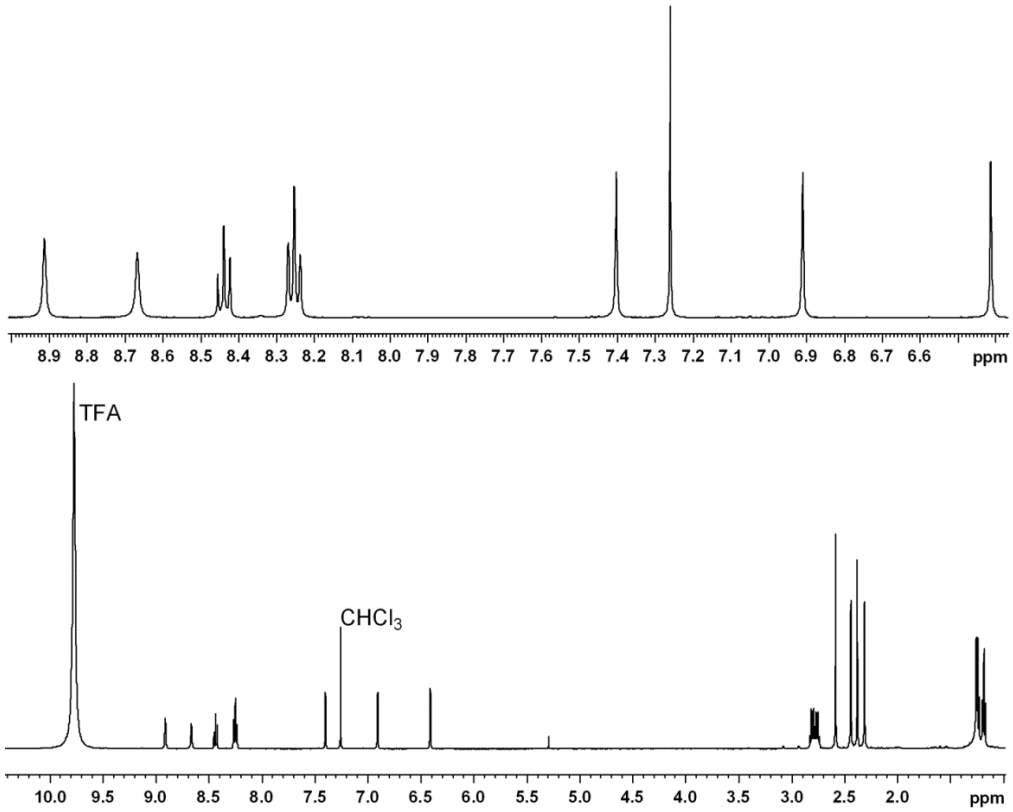


Figure S36. 500 MHz proton NMR spectrum of **6b** in $CDCl_3$ with a higher concentration of TFA showing a downfield shift to the NH resonances. One of the NH peaks is overlapped with the TFA signal.

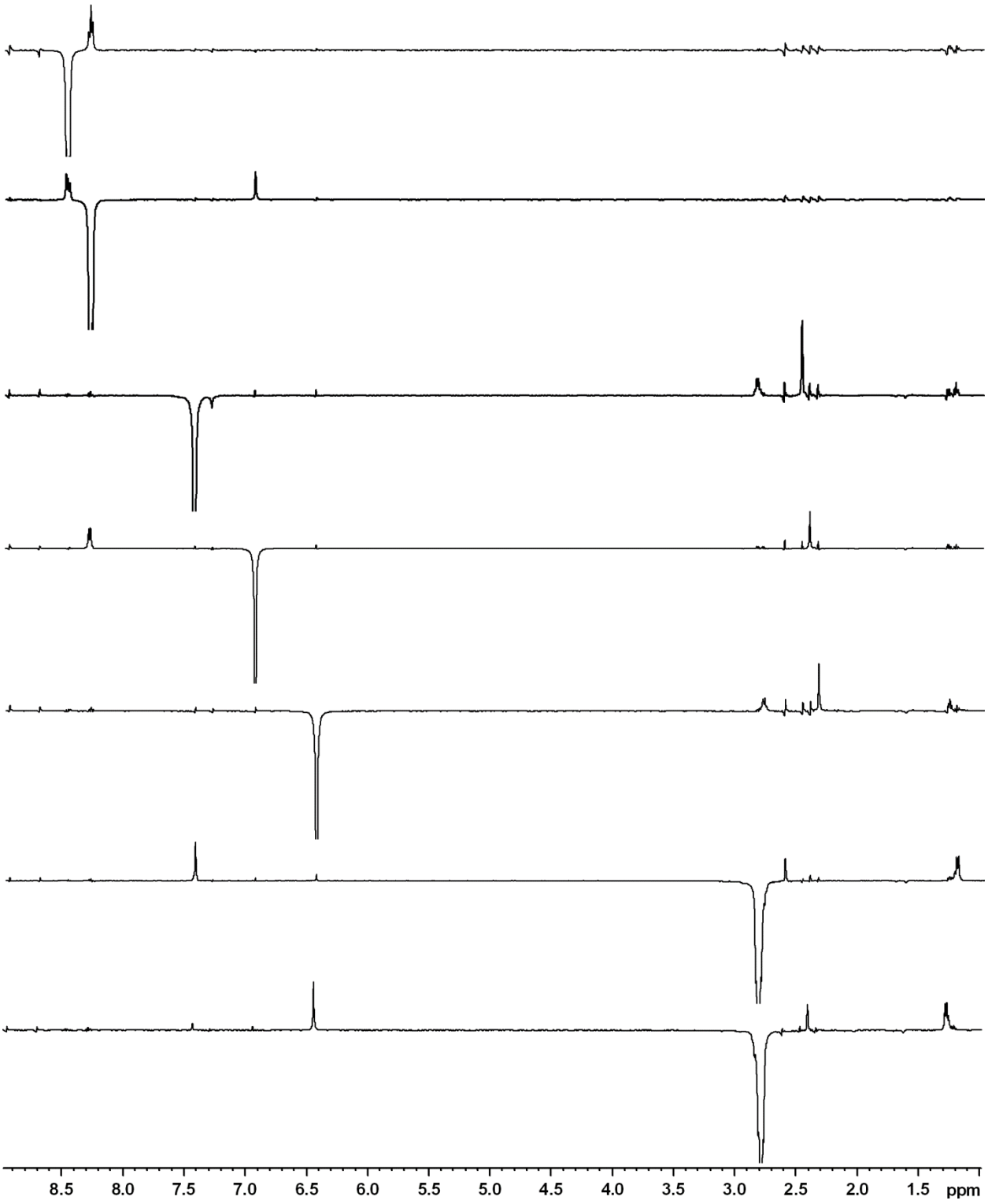


Figure S37. Selected nOe difference proton NMR spectra of **6b** in TFA-$CDCl_3$.

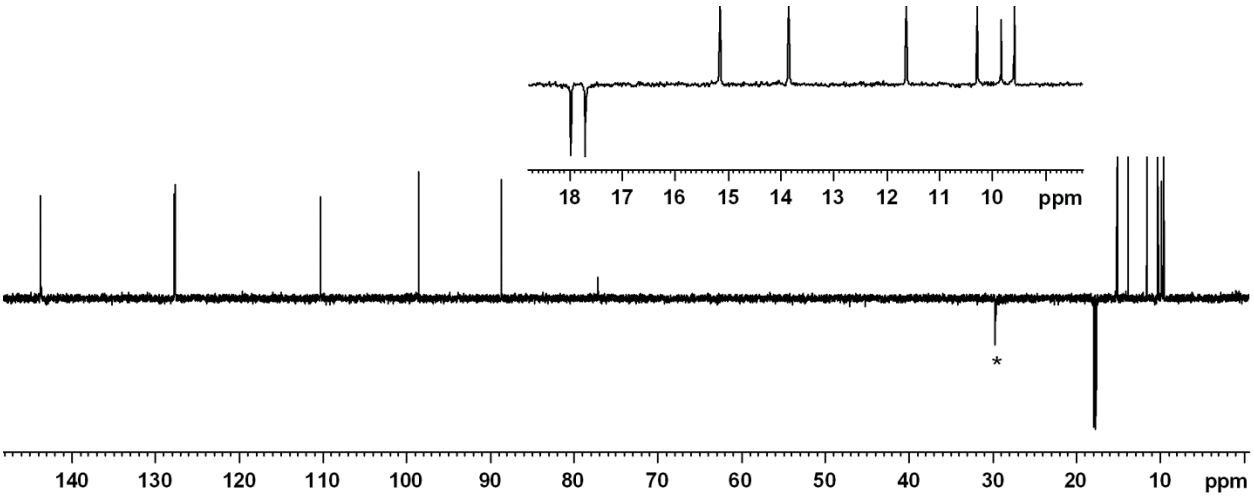


Figure S38. DEPT-135 NMR spectrum of **6b** in TFA-$CDCl_3$. * = trace acetone.

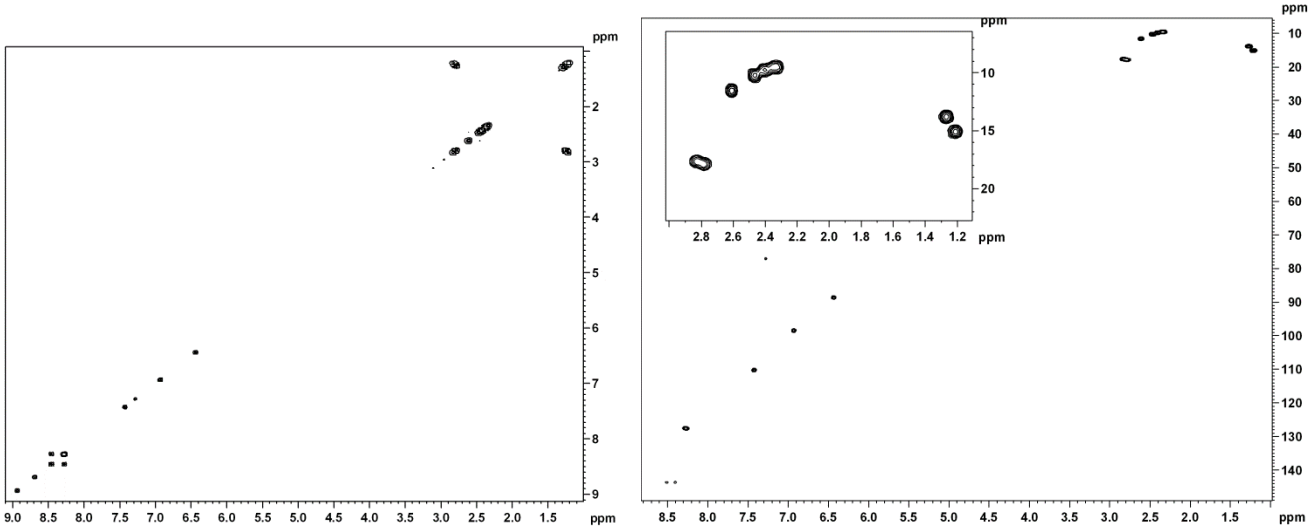


Figure S39. ^{1}H-^{1}H COSY and HSQC NMR spectra of **6b** in TFA-$CDCl_3$.

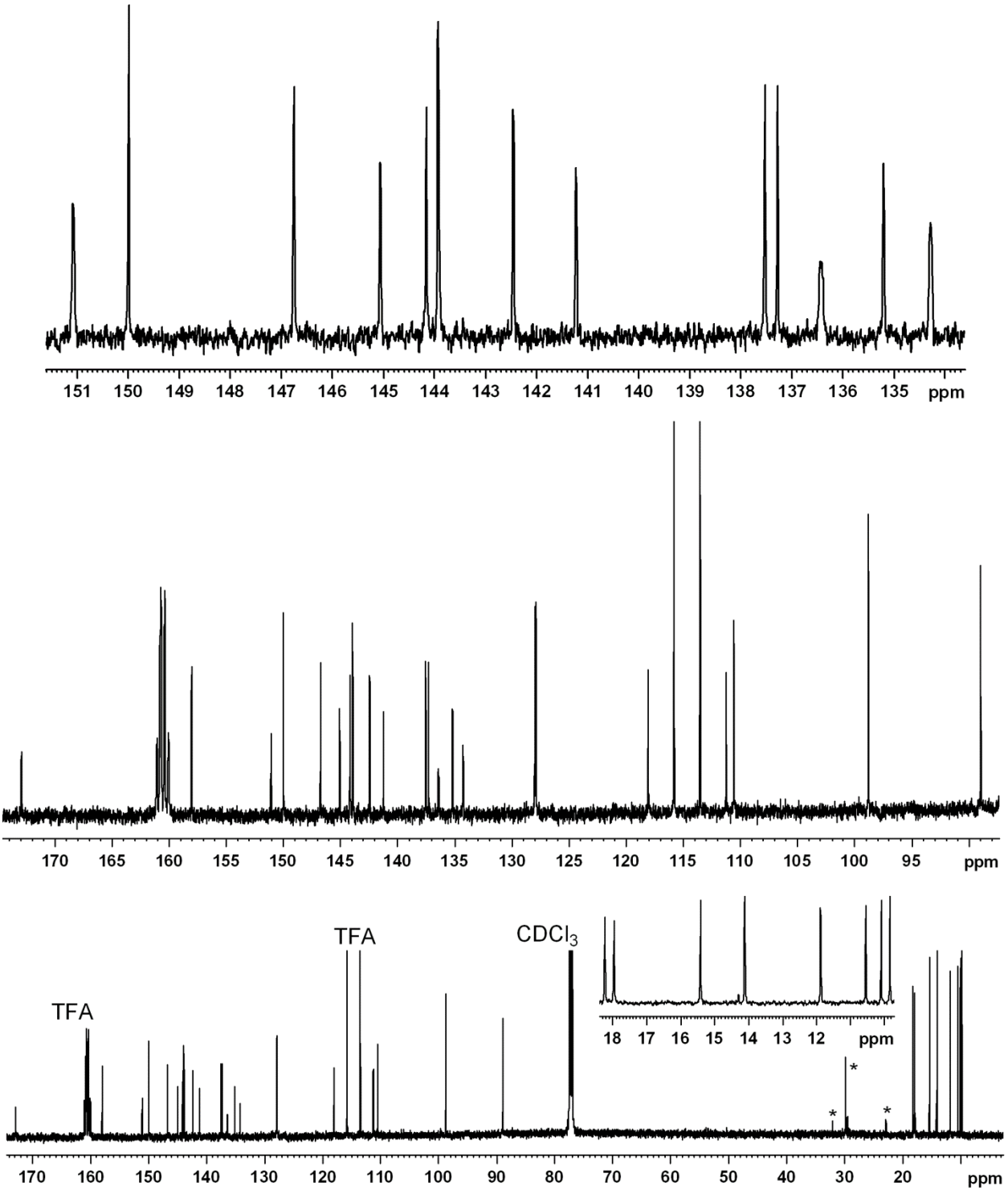


Figure S40. 125 MHz carbon-13 NMR spectrum of **6b** in TFA-$CDCl_3$. * = impurity peaks

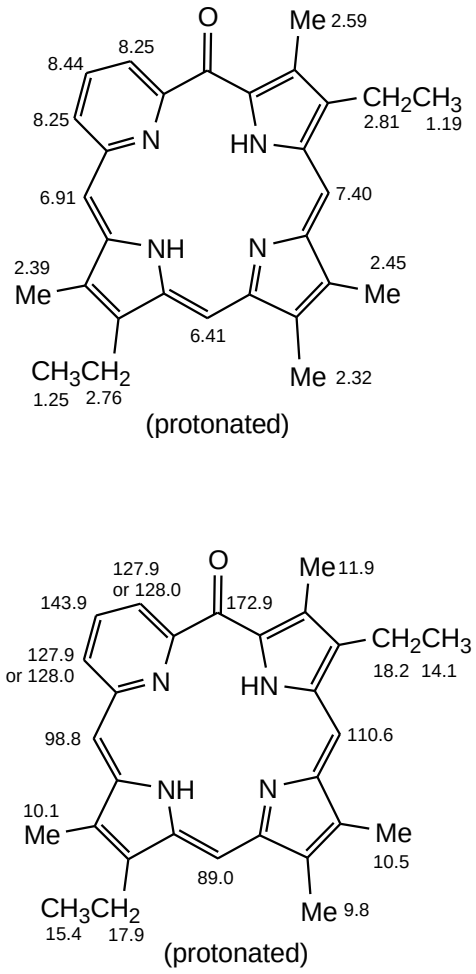


Figure S41. Partial assignments for the proton and carbon-13 NMR spectra of 6-oxopyriphlorin **6b** in TFA-$CDCl_3$ based on the foregoing data.

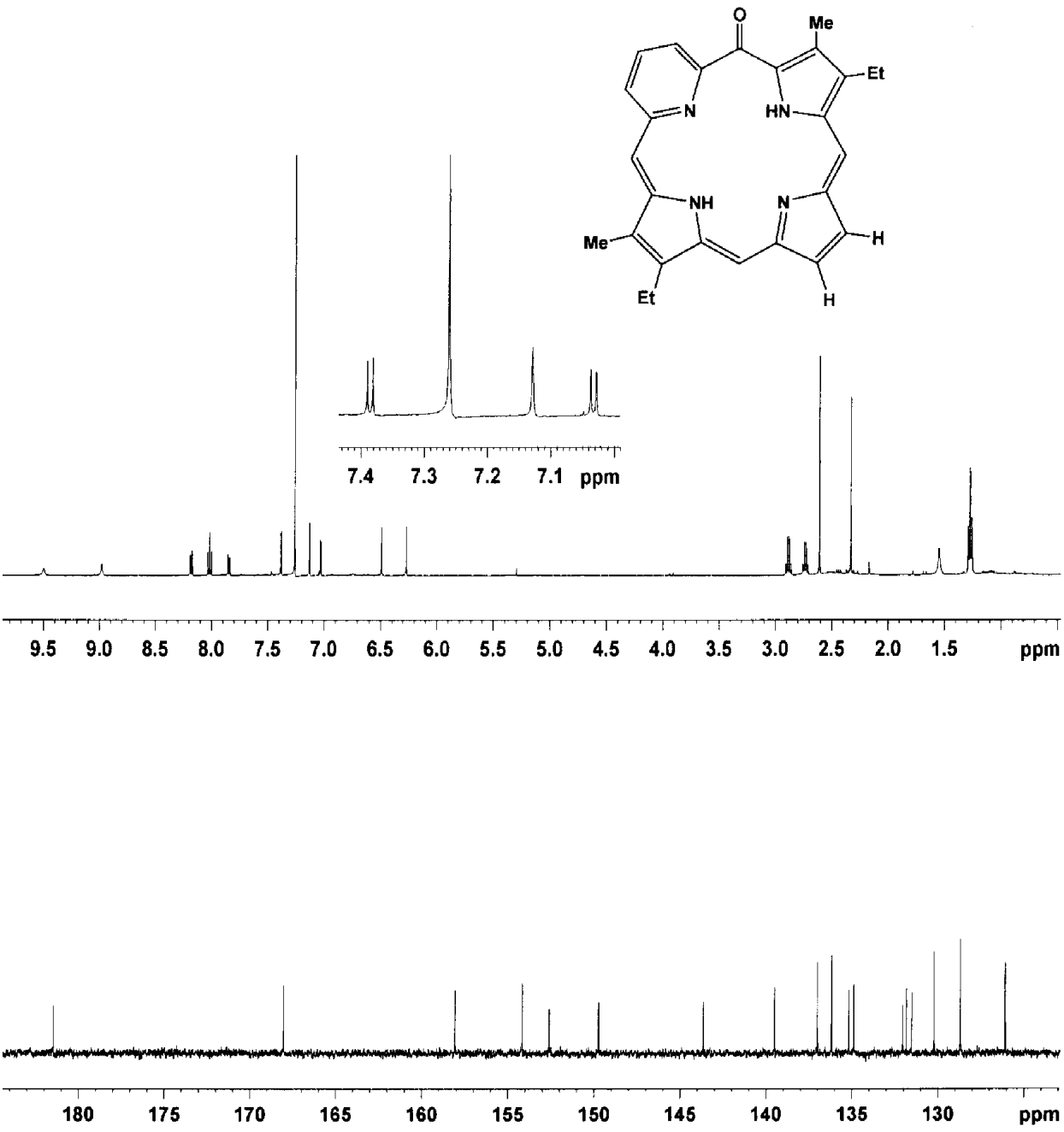


Figure S42. 500 MHz proton and 125 MHz carbon-13 NMR spectra of oxopyriphlorin **6c** in $CDCl_3$.

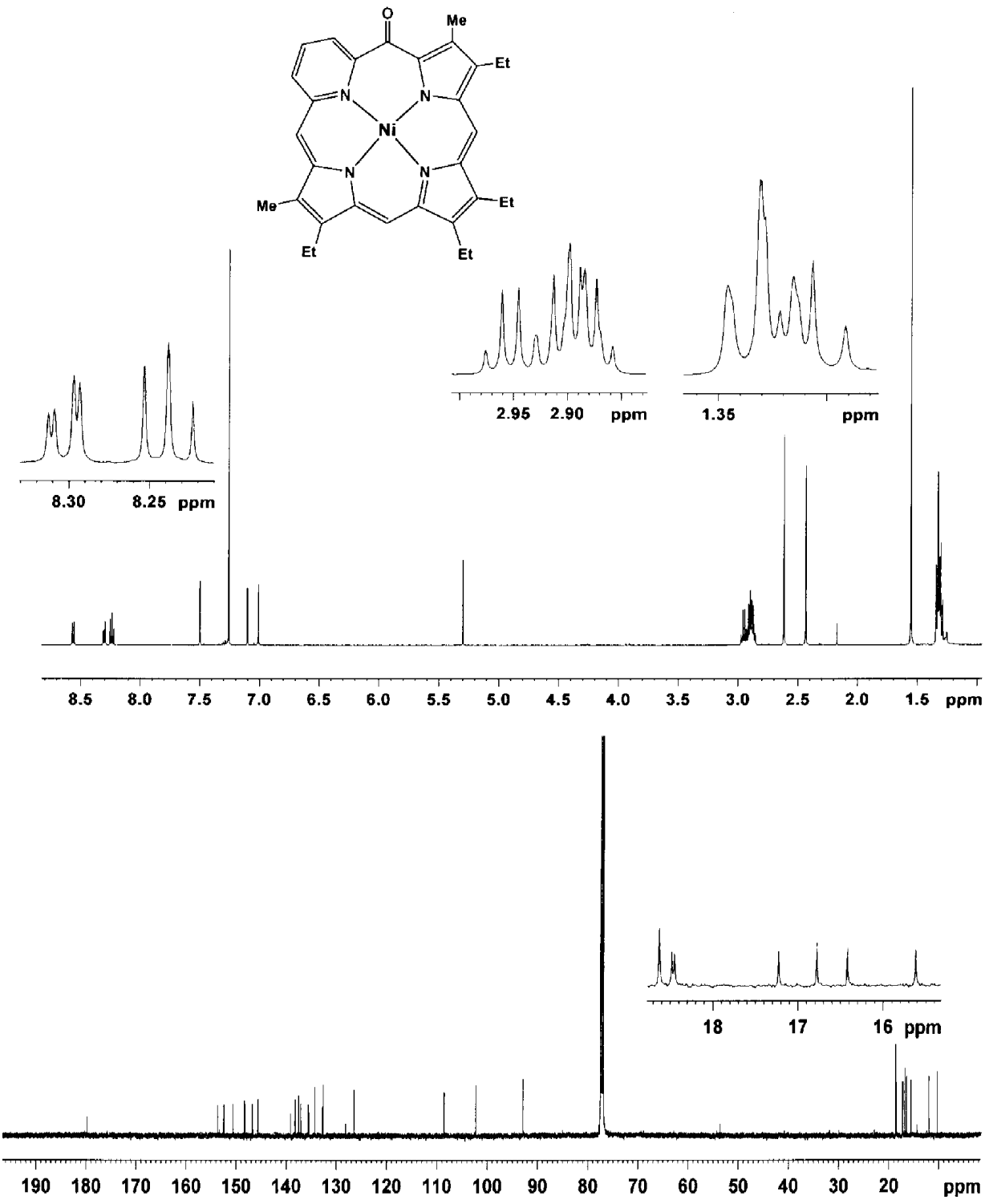


Figure S43. 500 MHz proton and 125 MHz carbon-13 NMR spectra of nickel(II) complex **28c** in $CDCl_3$.

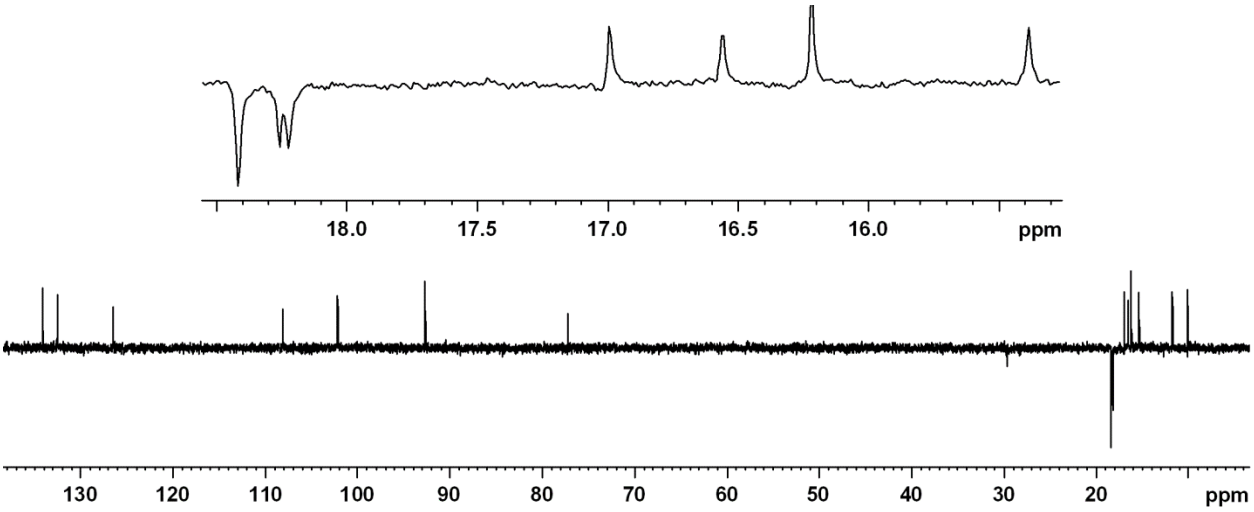


Figure S44. DEPT-135 NMR spectrum of nickel(II) complex **28a** in $CDCl_3$.

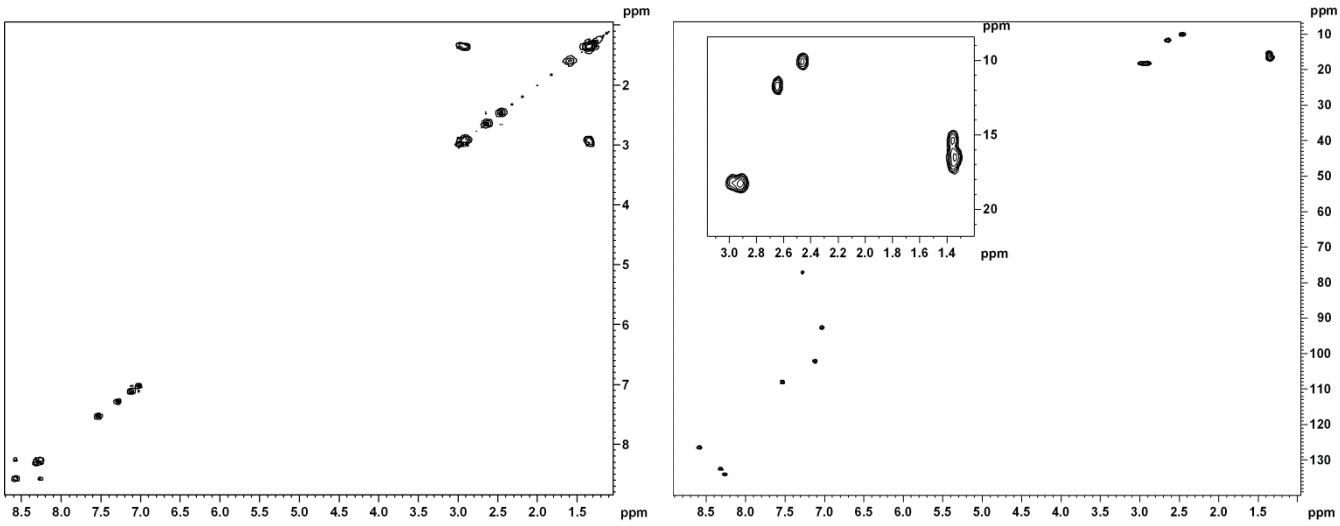


Figure S45. COSY and HSQC NMR spectra of nickel complex **28a** in $CDCl_3$.

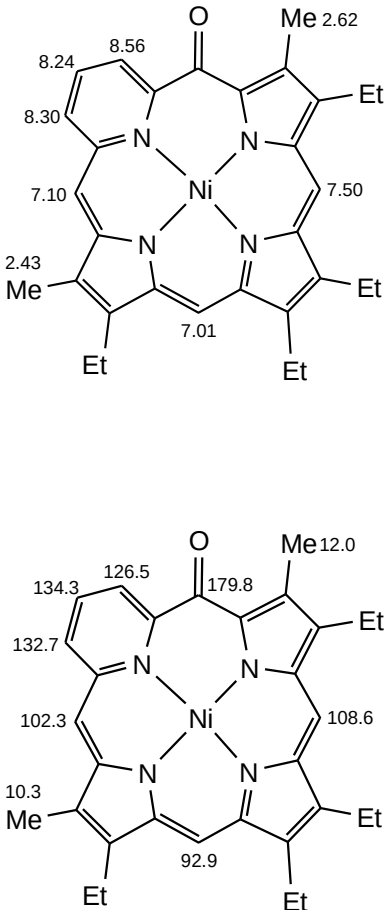


Figure S46. Partial assignments for the proton and carbon-13 NMR spectra of nickel(II) complex **28a** based on the foregoing data.

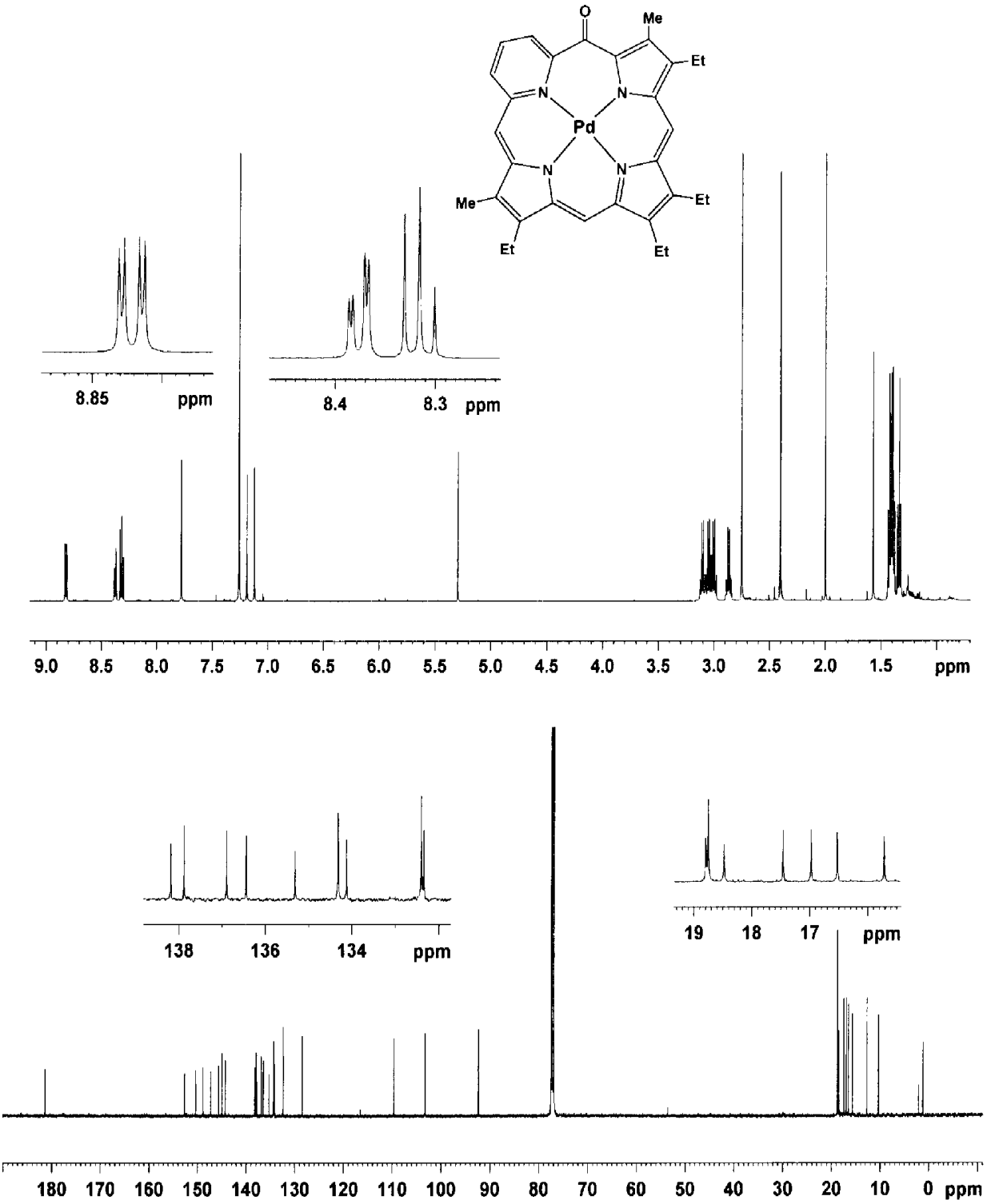


Figure S47. 500 MHz proton and 125 MHz carbon-13 NMR spectra of palladium(II) complex **28b** in $CDCl_3$.

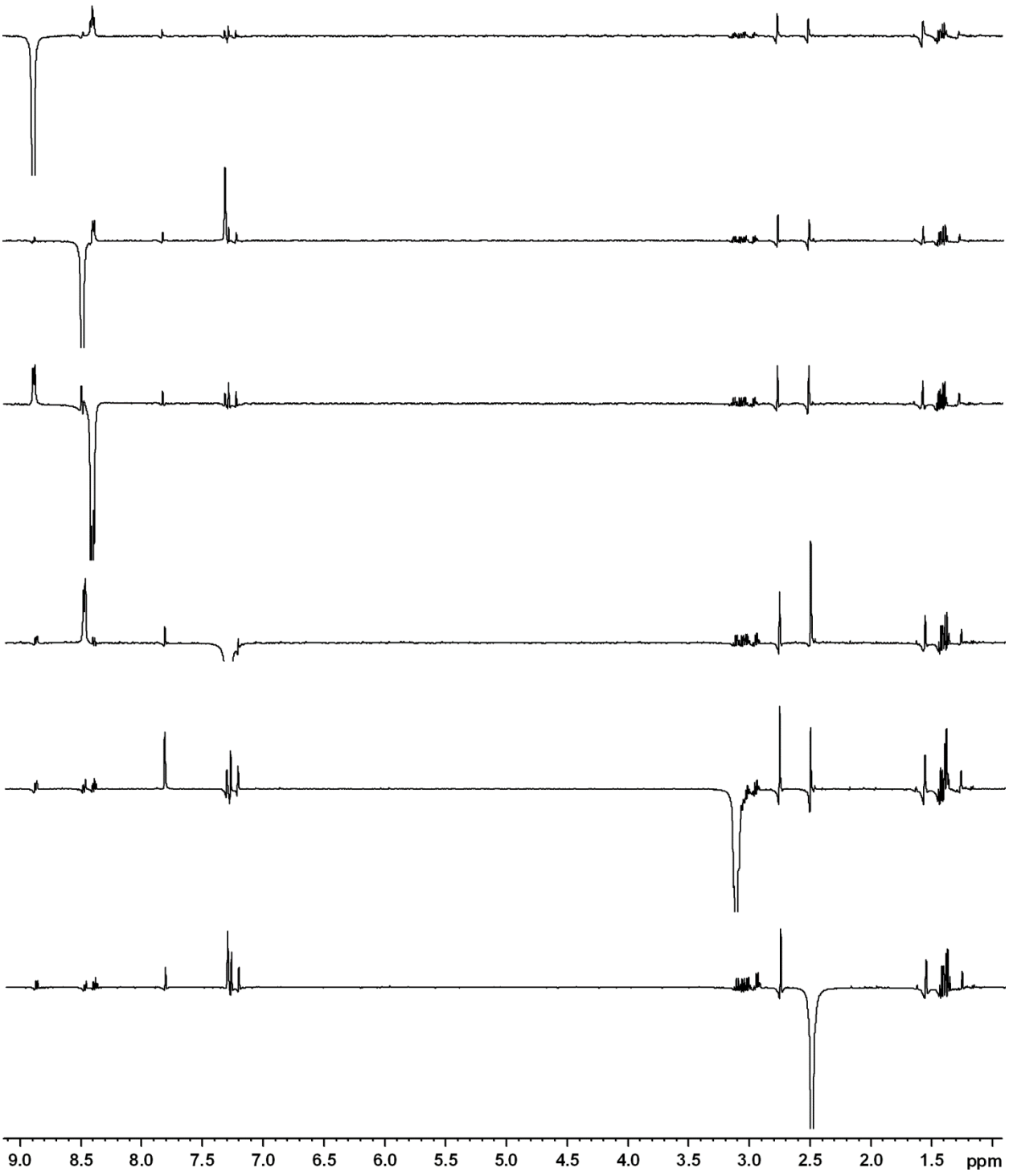


Figure S48. Selected nOe difference proton NMR spectra of palladium complex **28b** in $CDCl_3$.

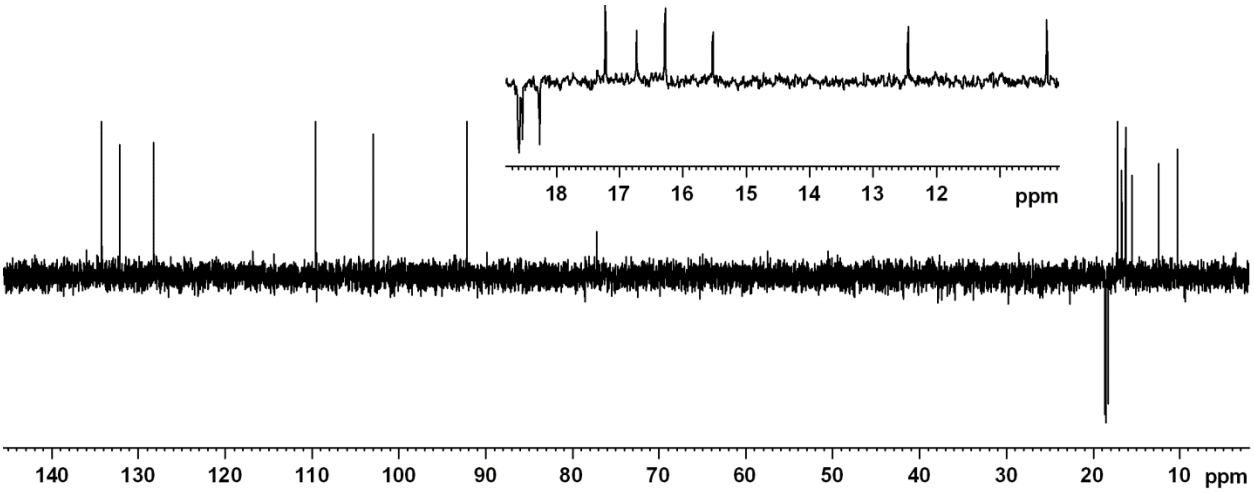


Figure S49. DEPT-135 NMR spectrum of palladium(II) complex **28b** in $CDCl_3$.

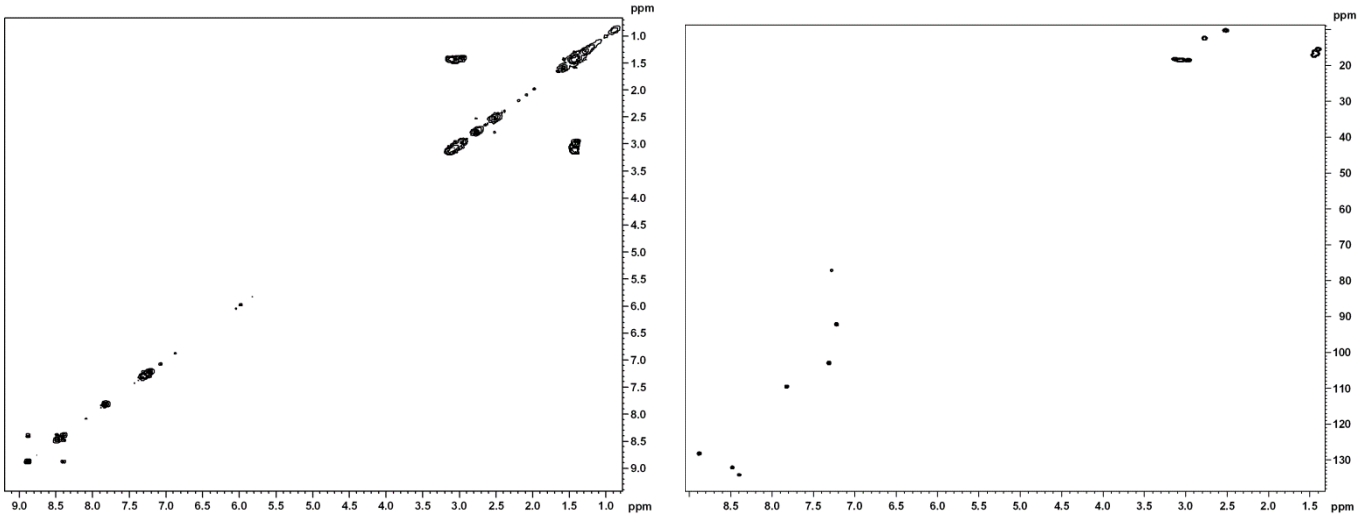


Figure S50. ^{1}H-^{1}H COSY and HSQC NMR spectra of palladium(II) complex **28b** in $CDCl_3$.

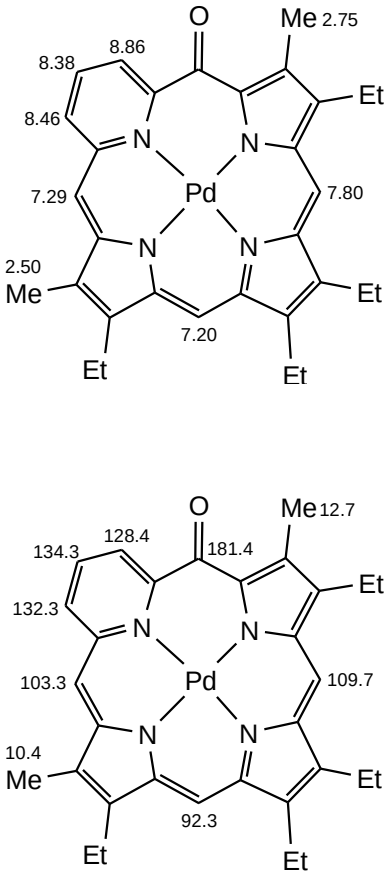


Figure S51. Partial assignments for the proton and carbon-13 NMR spectra of palladium(II) complex **28b** based on the foregoing data.

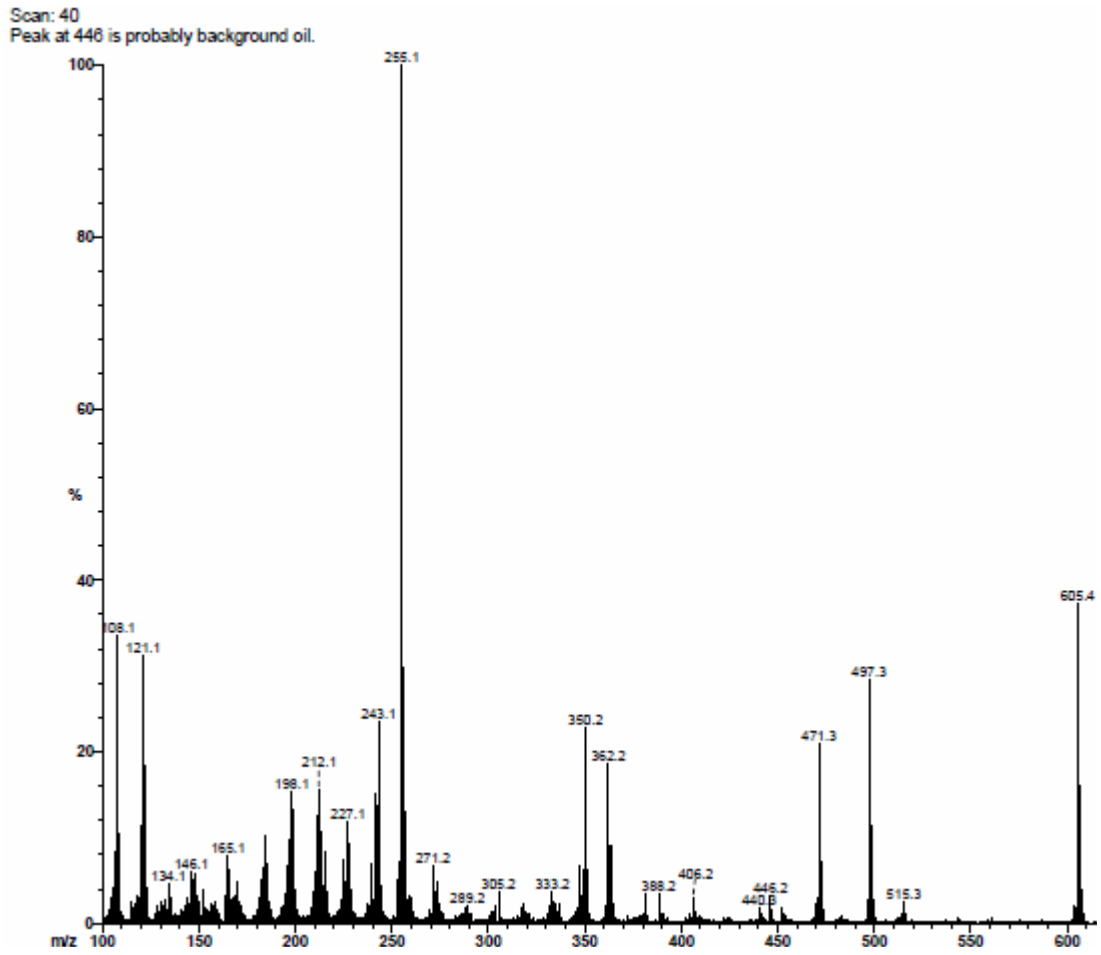
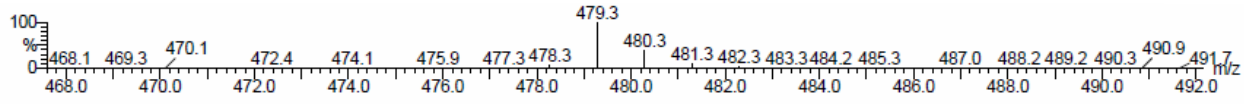
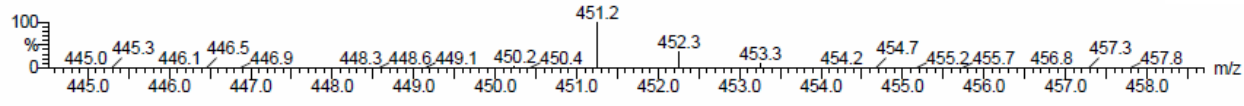


Figure S52. Electron impact mass spectrum of tripyrrane **20b**.



Minimum:				-1.5		
Maximum:		5.0	10.0	150.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
479.2813	479.2811	0.2	0.4	16.5	4.9	C31 H35 N4 O

Figure S53. ESI MS of 6-oxopyriphlorin **6a**.



Minimum:				-1.5		
Maximum:		5.0	10.0	150.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
451.2496	451.2498	-0.2	-0.4	16.5	3.8	C29 H31 N4 O

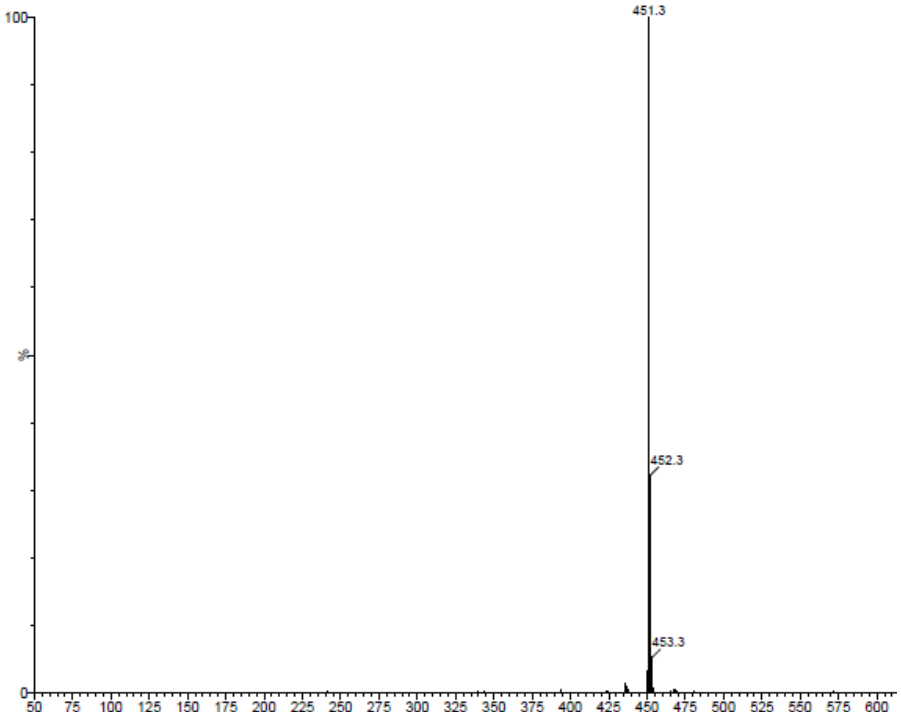
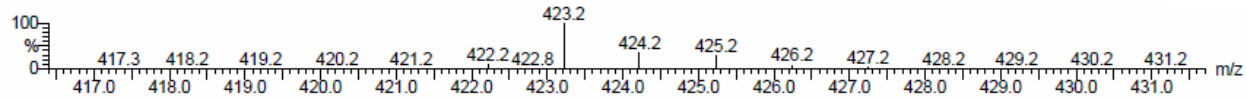


Figure S54. ESI MS of 6-oxopyriphlorin **6b**.



Minimum:				-1.5		
Maximum:		5.0	10.0	150.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
423.2180	423.2185	-0.5	-1.2	16.5	107.7	C27 H27 N4 O

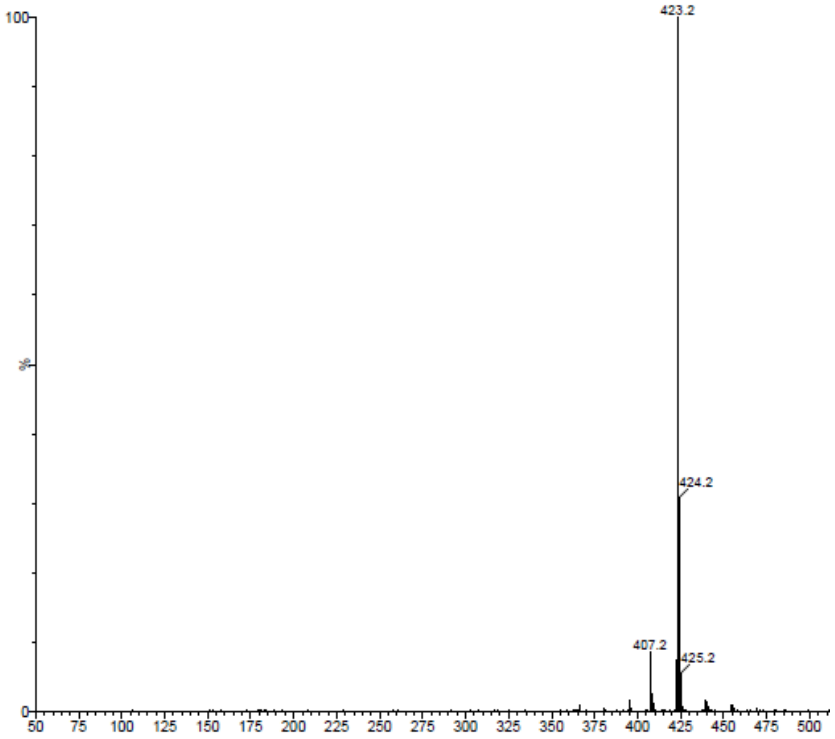
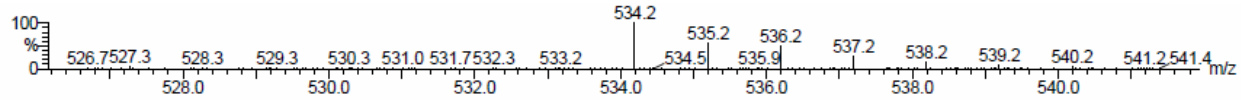


Figure S55. ESI MS of 6-oxopyriphlorin **6c**.



Minimum:				-1.5		
Maximum:		5.0	10.0	150.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
534.1919	534.1930	-1.1	-2.1	18.5	37.8	C31 H32 N4 O Ni
	534.1970	-5.1	-9.5	29.5	201.7	C39 H24 N3

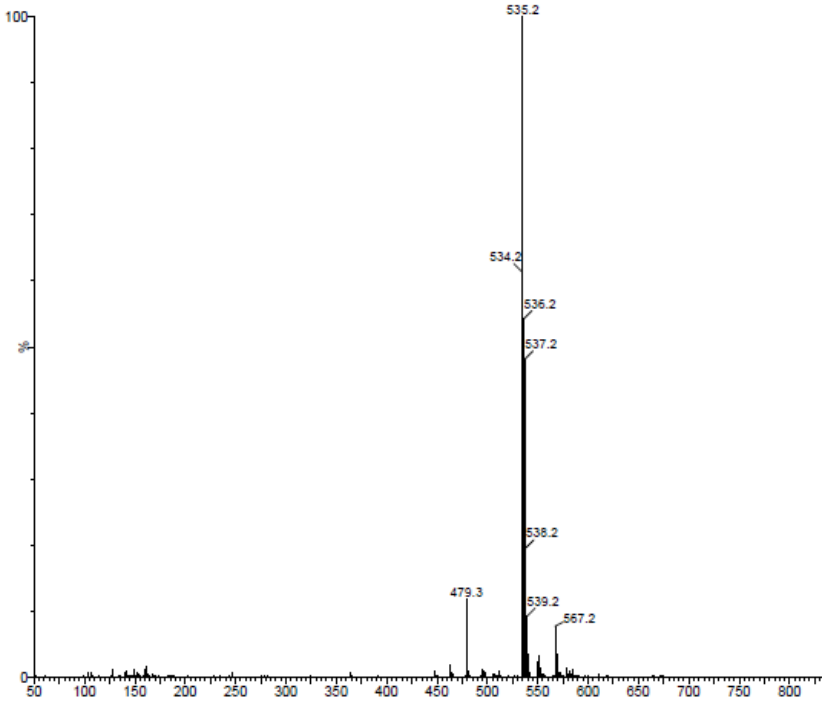


Figure S56. ESI MS of nickel(II) complex **28a**.

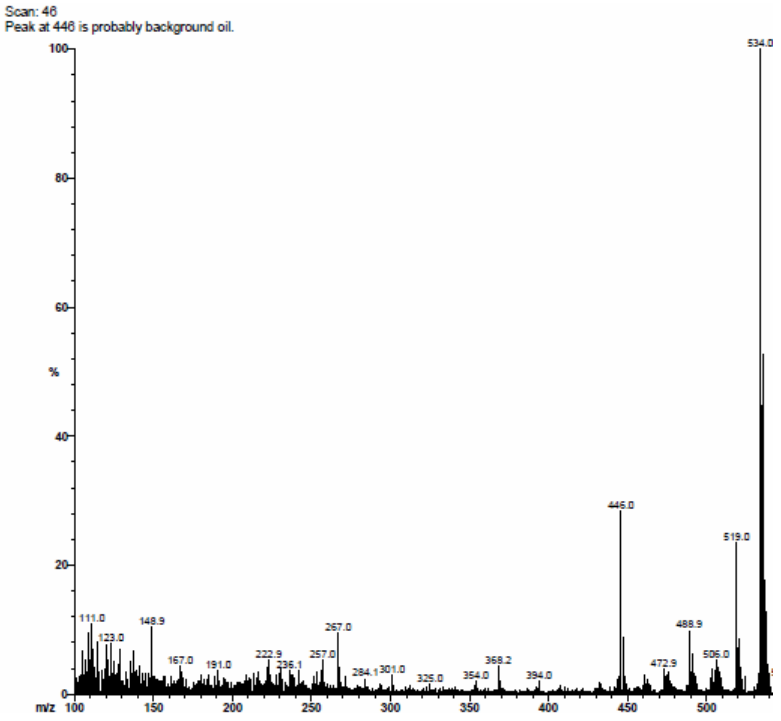


Figure S57. Electron impact mass spectrum of nickel(II) complex **28a**.

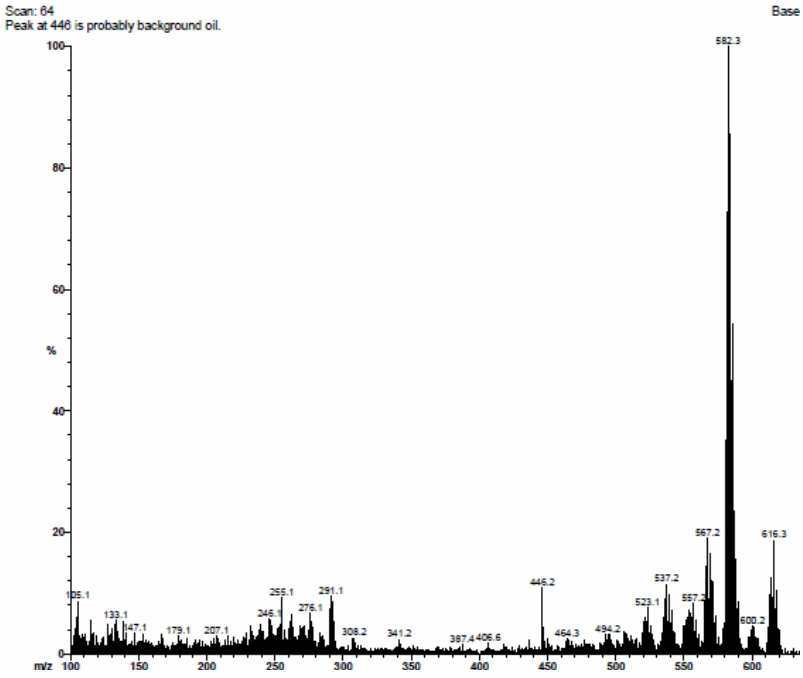


Figure S58. Electron impact mass spctrum of palladium(II) complex **28b**.