Electronic Supplementary Information: Pyrazole analogues of porphyrins and oxophlorins

Alexandra M. Young, Amber L. Von Ruden and Timothy D. Lash,

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

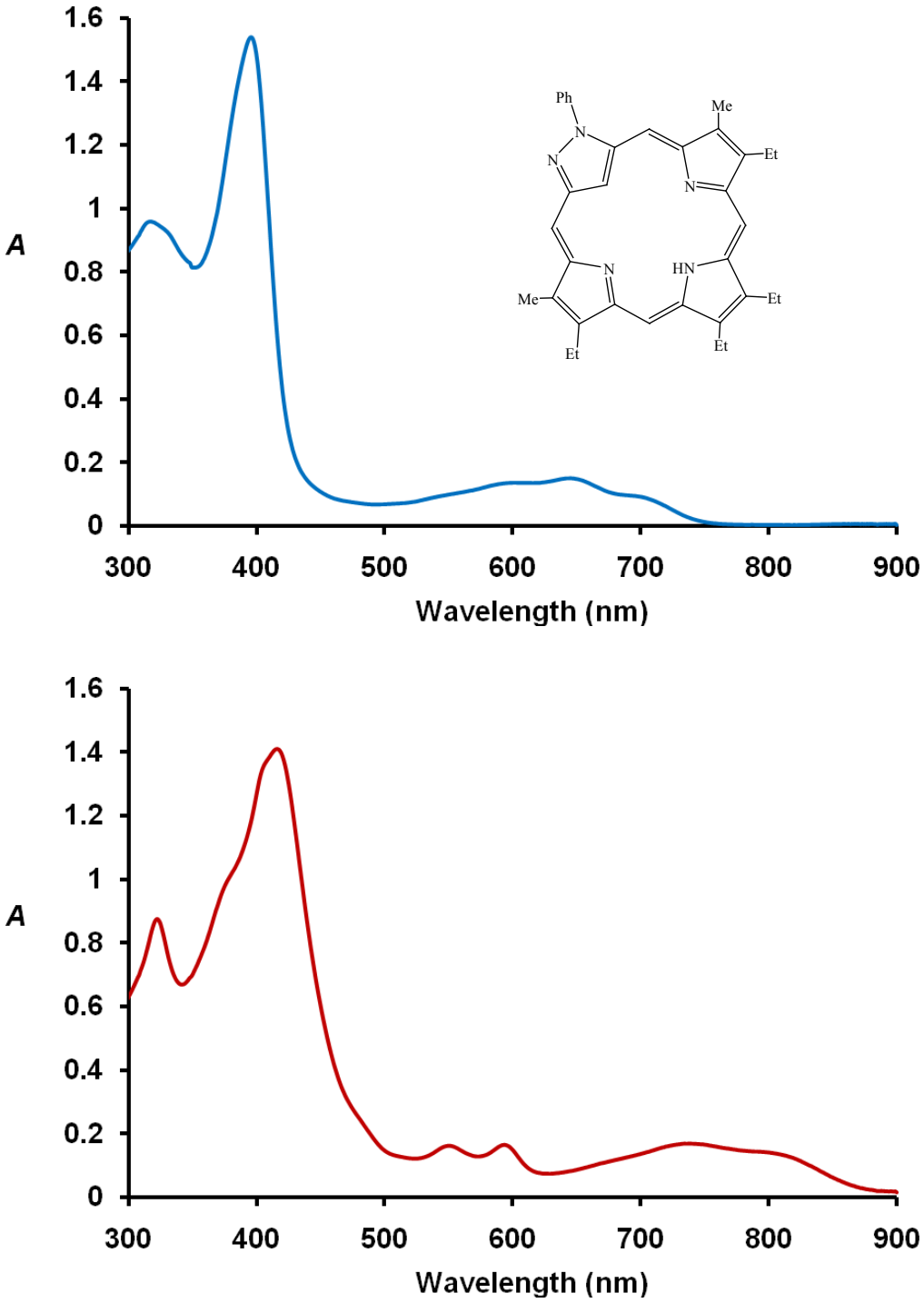


Figure 1. UV-vis spectra of pyrazoloporphyrin **25a** in 1% Et_3N-chloroform (top spectrum) and 1% TFA-chloroform (bottom spectrum).

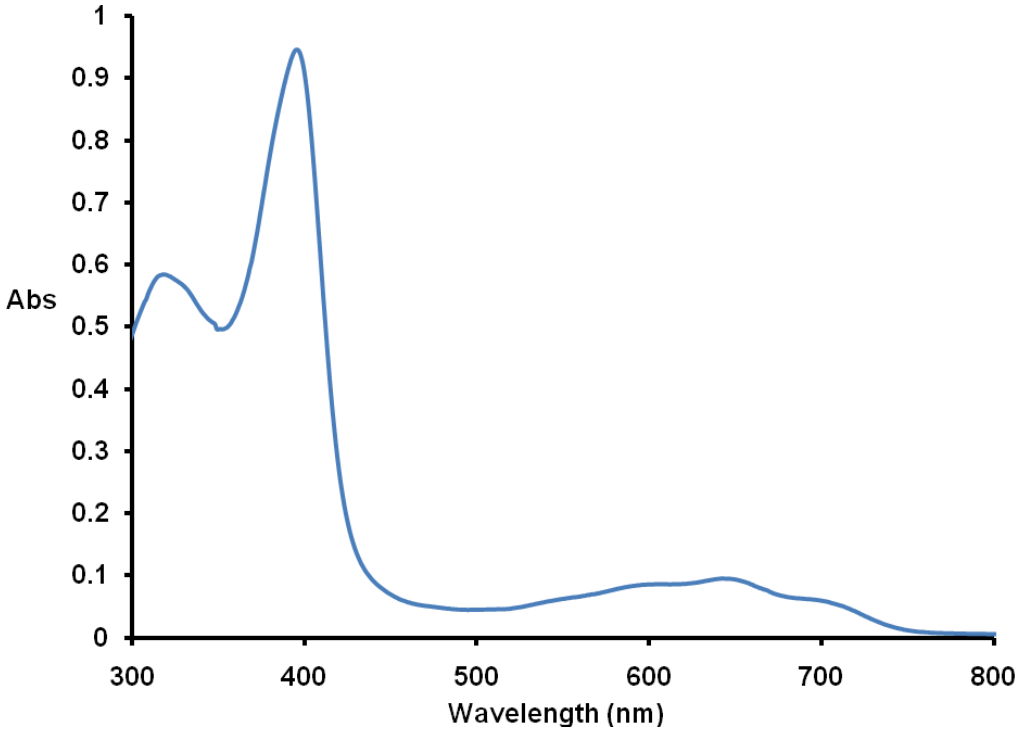


Figure 2. UV-vis spectrum of pyrazoloporphyrin **25a** in 0.5% Et_3N-chloroform.

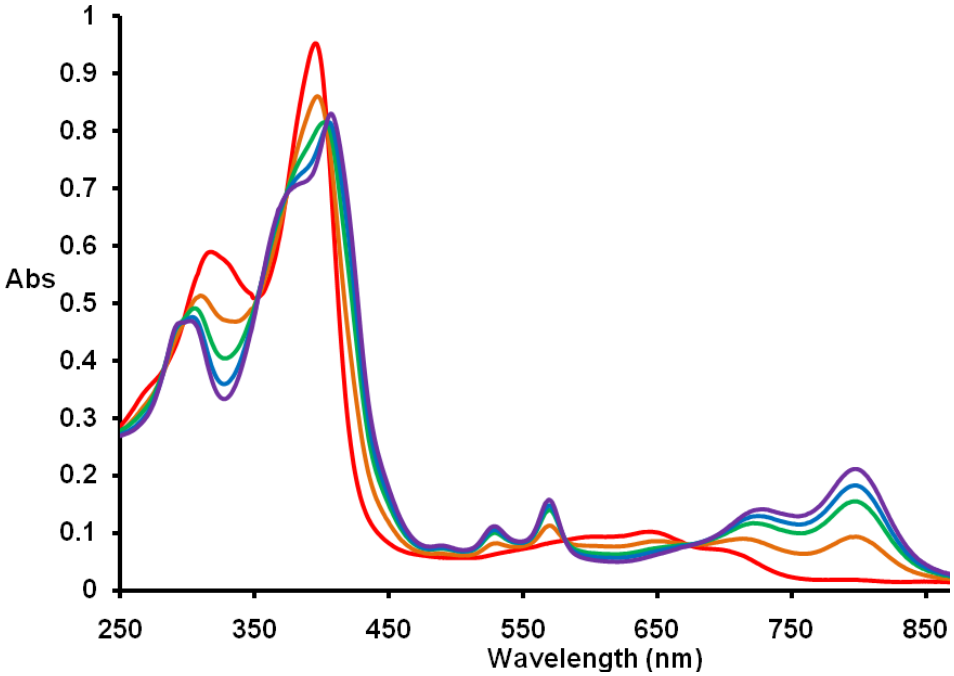


Figure 3. UV-vis spectra of pyrazoloporphyrin **25a** in chloroform with 0 equiv (red line), 1 equiv (orange line), 2 equiv (green line), 3 equiv (blue line) and 5 equiv (purple line) showing the formation of a monoprotonated species.

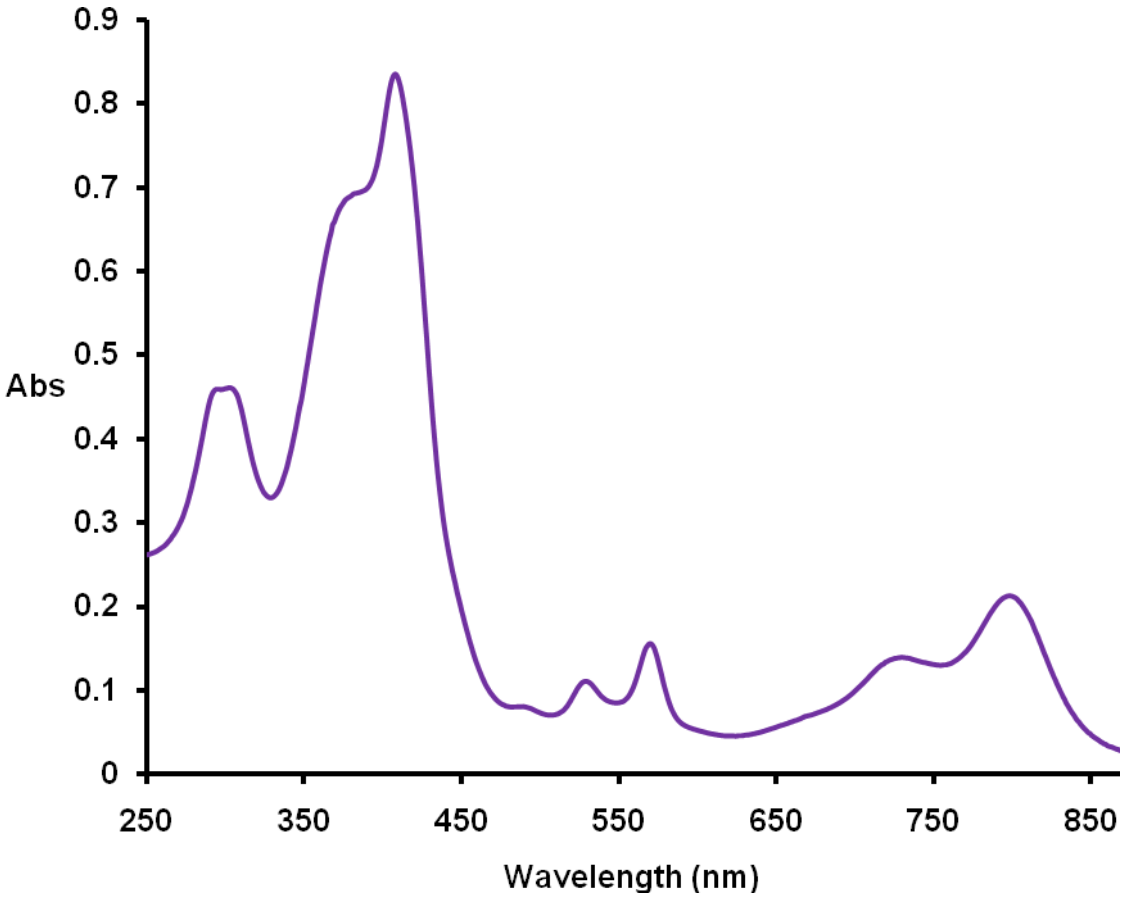


Figure 4. UV-vis spectrum of pyrazoloporphyrin monocation **25a**H^+ in 1% Et_3N-chloroform (top spectrum) and 1% TFA-chloroform (bottom spectrum).

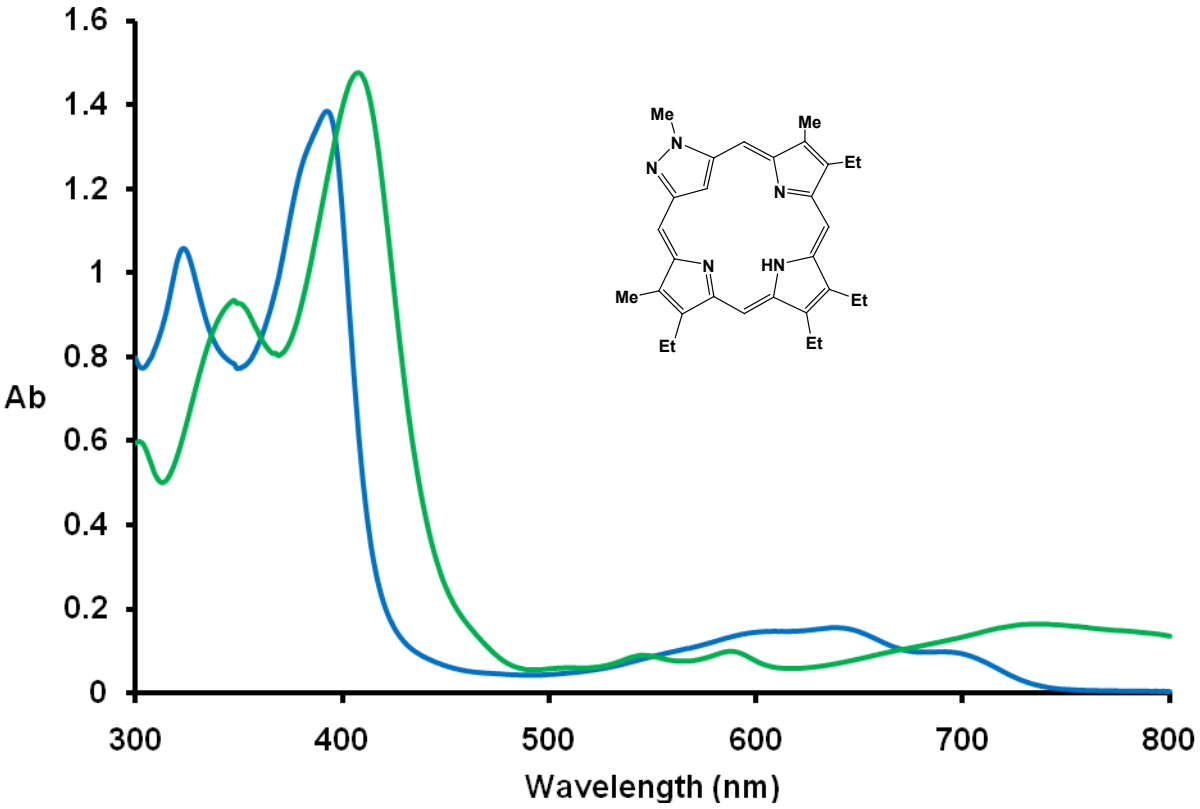


Figure S5. UV-visible spectra of methyl pyrazoloporphyrin **91b** in 1% triethylamine-chloroform (blue line) and 5% TFA-chloroform (green line).

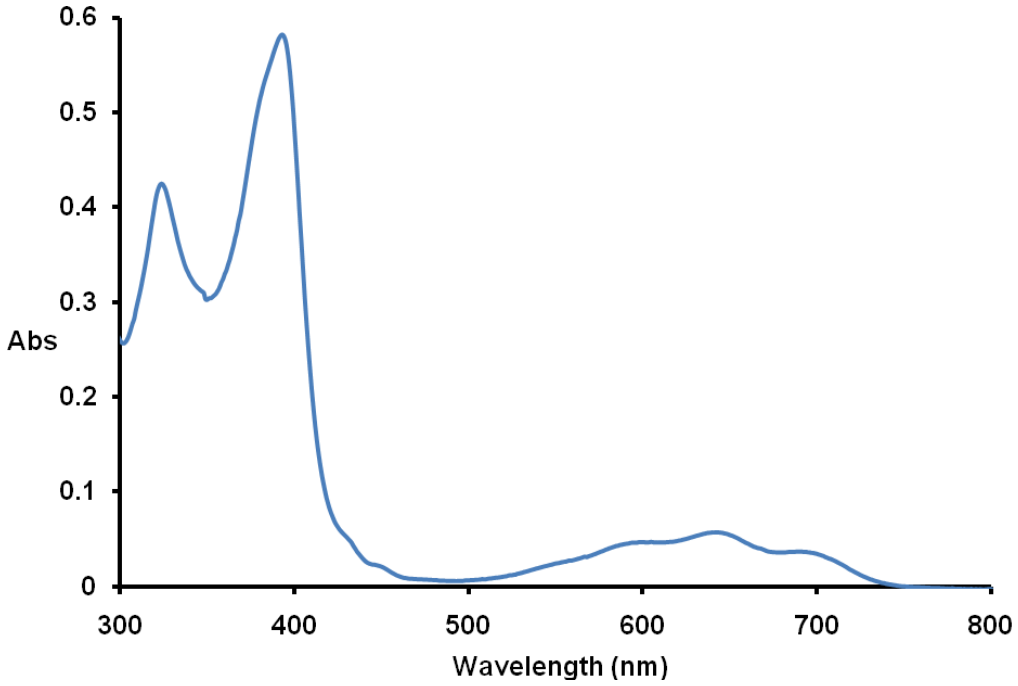


Figure 6. UV-vis spectrum of pyrazoloporphyrin **25c** in 1% Et_3N-chloroform.

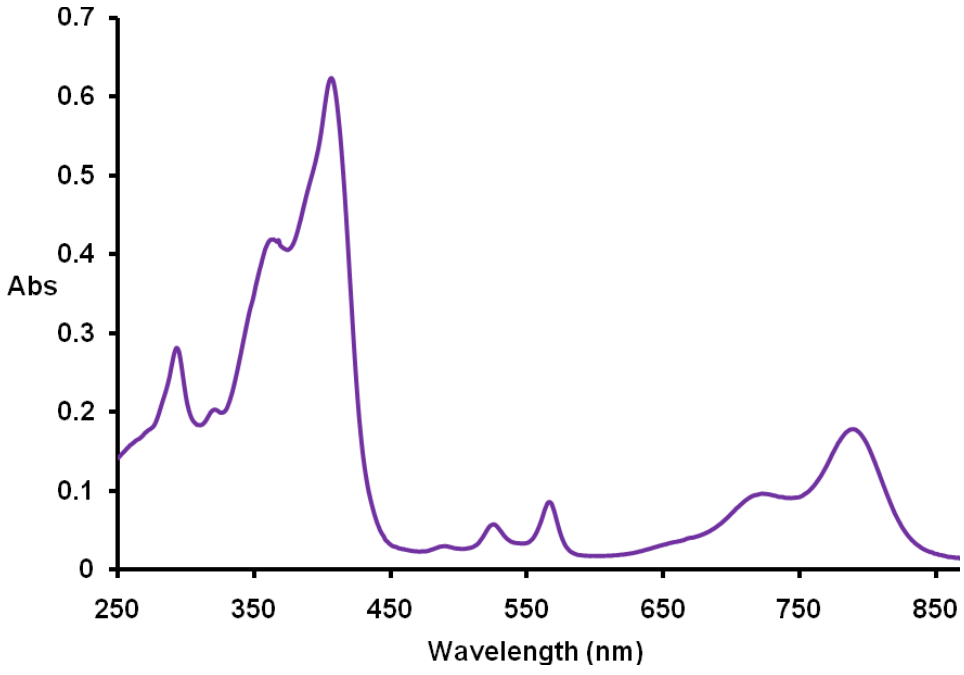


Figure 7. UV-vis spectra of pyrazoloporphyrin **25c** with 20 equiv TFA in chloroform.

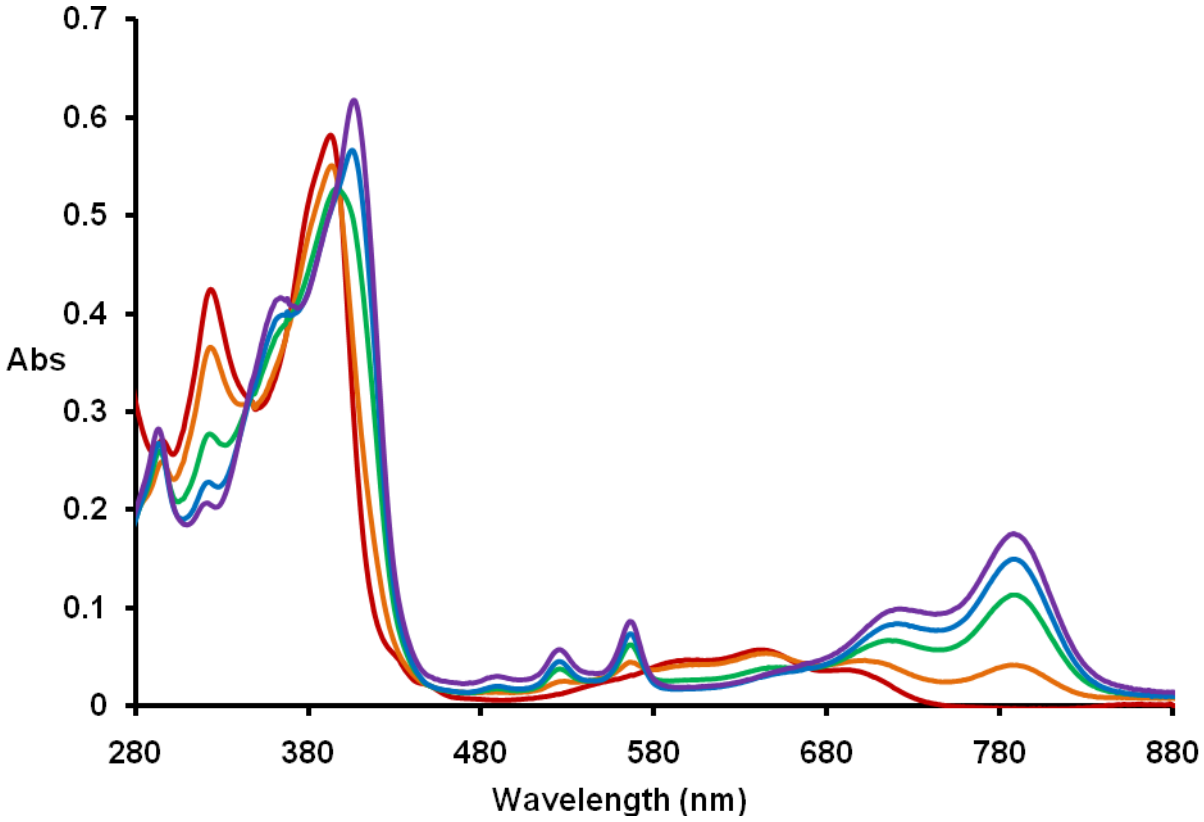


Figure 8. UV-vis spectra of pyrazoloporphyrin **25c** in 0.5% Et_3N-chloroform (red line), chloroform (orange line), 1 equiv TFA in chloroform (green line), 2 equiv TFA in chloroform (blue line) and 5 equiv TFA in chloroform. The chloroform was deacidified by running it through basic alumina, but the chloroform spectrum still shows a small degree of protonation..

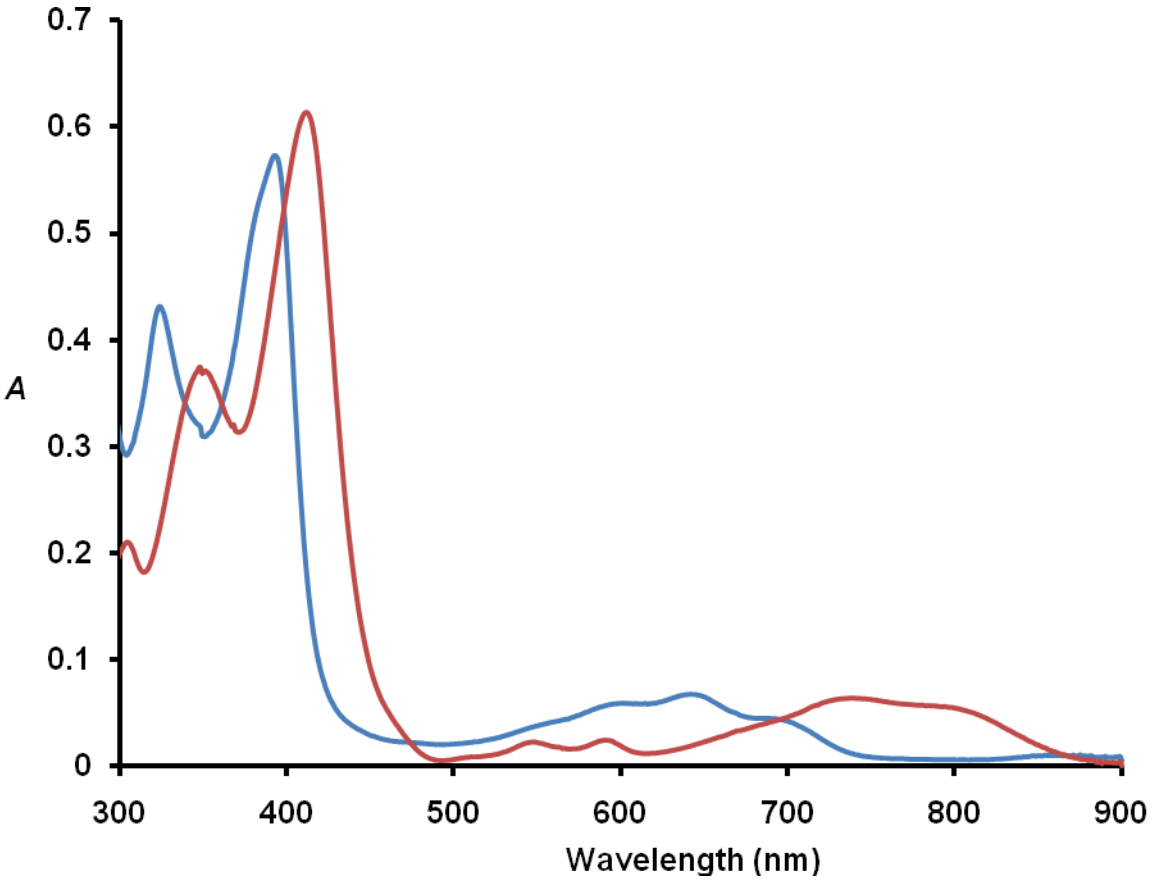


Figure 9. UV-visible spectra of ethyl pyrazoloporphyrin **25c** in 1% triethylamine-chloroform (blue line) and 5% TFA-chloroform (red line).

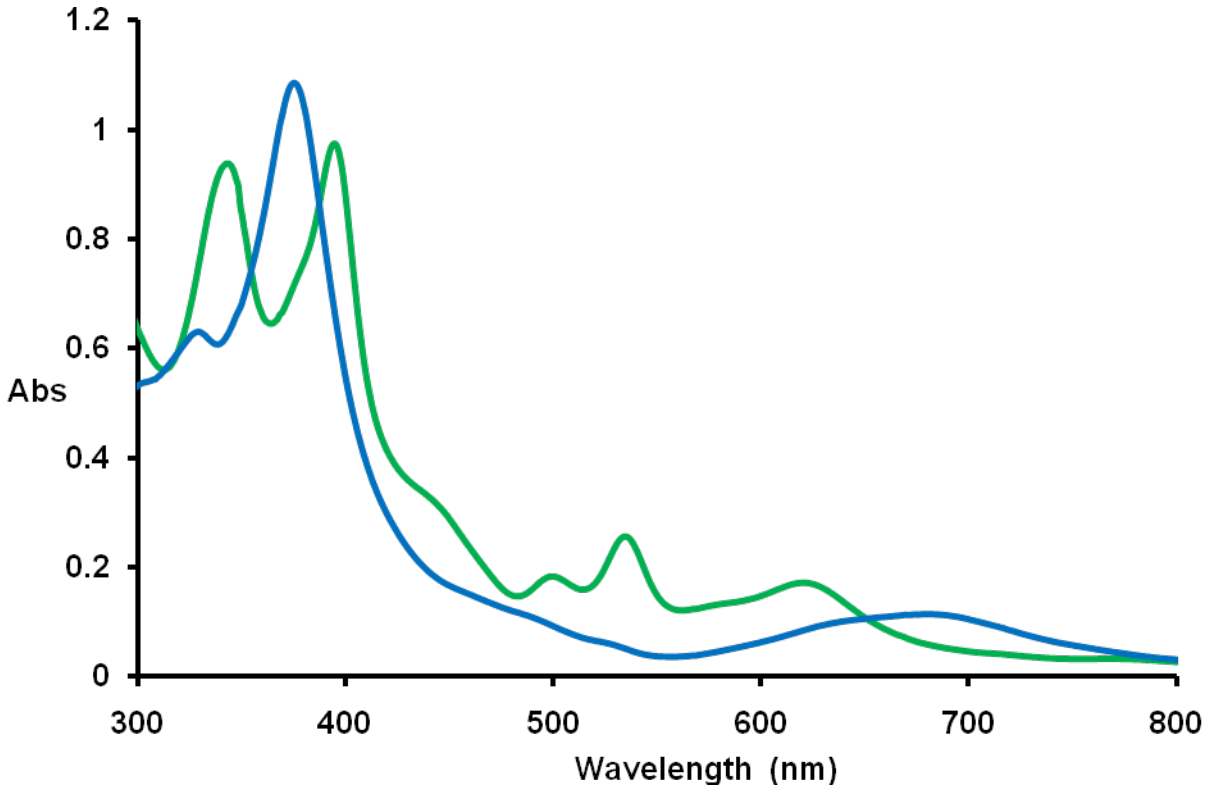


Figure 10. UV-vis spectra of nickel(II) pyrazoloporphyrin **31a** in chloroform (green line) and 1% TFA-chloroform (blue line).

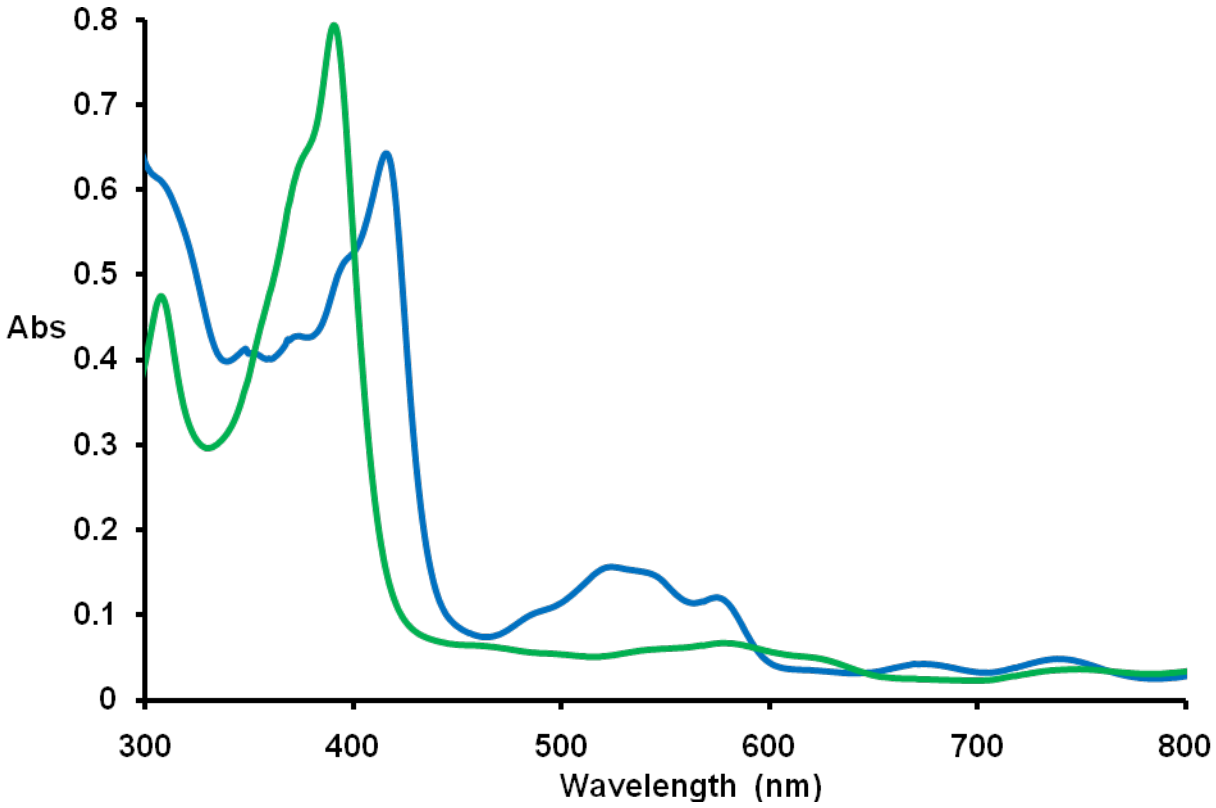


Figure 11. UV-vis spectra of palladium(II) pyrazoloporphyrin **32a** in chloroform (blue line) and 1% TFA-chloroform (green line).

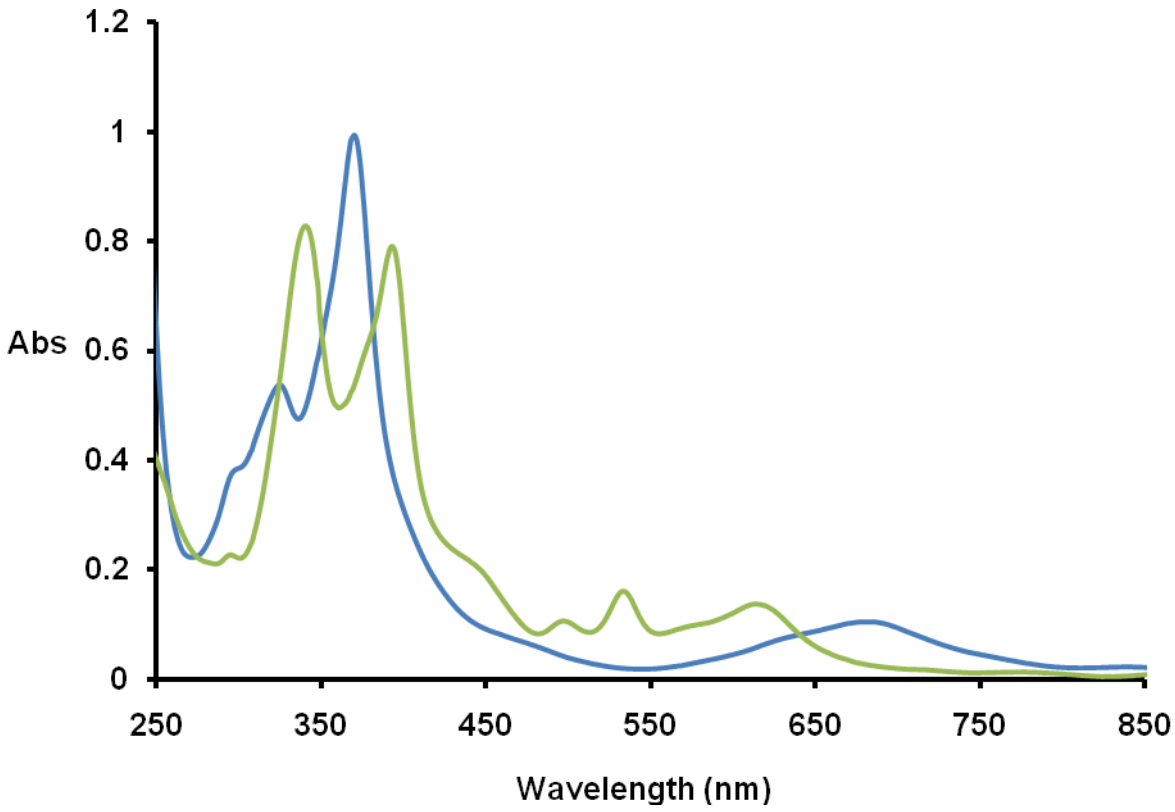


Figure 12. UV-vis spectra of nickel(II) pyrazoloporphyrin **31b** in chloroform (green line) and 1% TFA-chloroform (blue line).

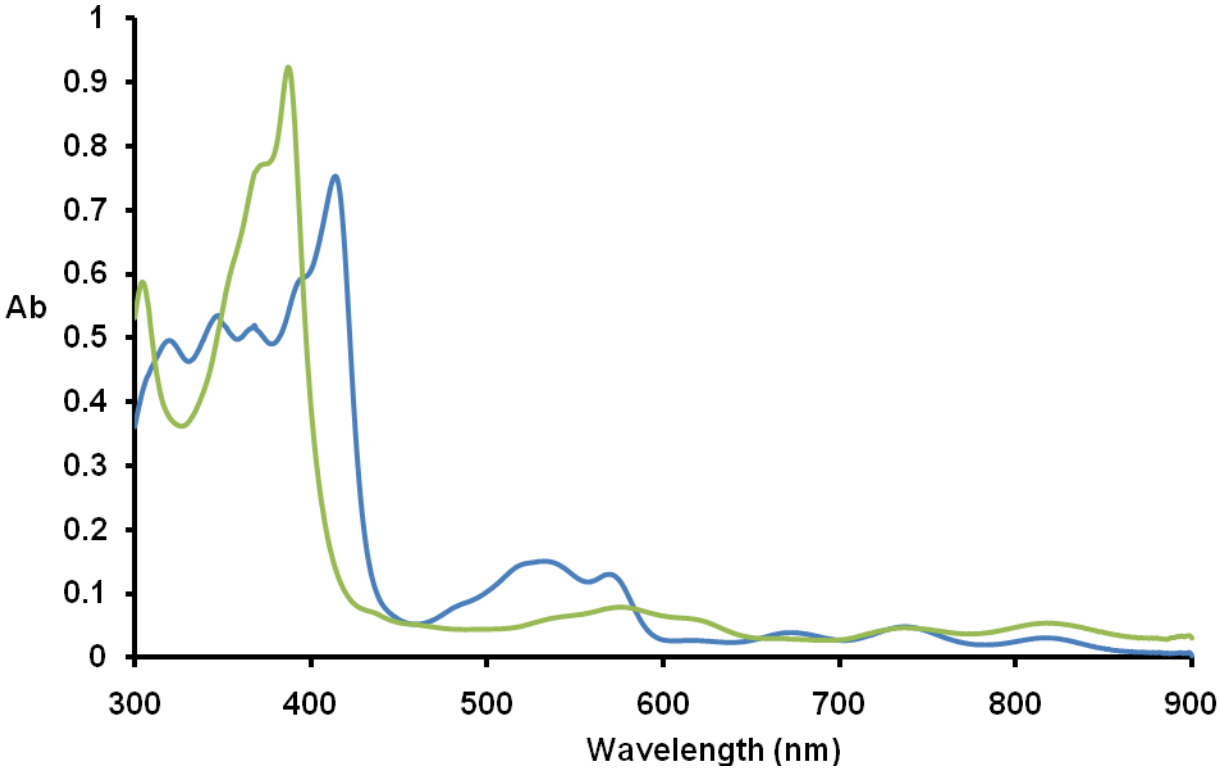


Figure 13. UV-vis spectra of palladium(II) pyrazoloporphyrin **32b** in chloroform (blue line) and 1% TFA-chloroform (green line).

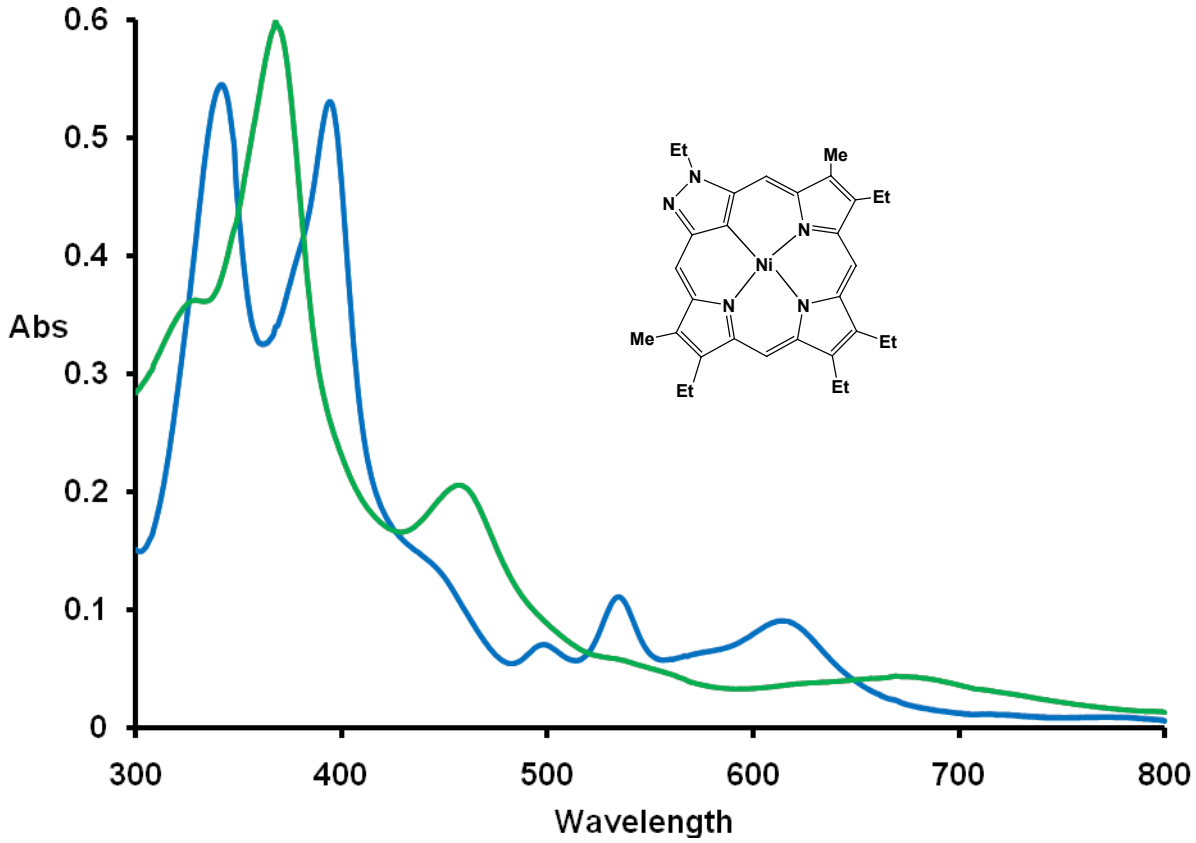


Figure 14. UV-vis spectra of nickel(II) pyrazoloporphyrin **31c** in chloroform (blue line) and with 500 equiv TFA in chloroform (green line).

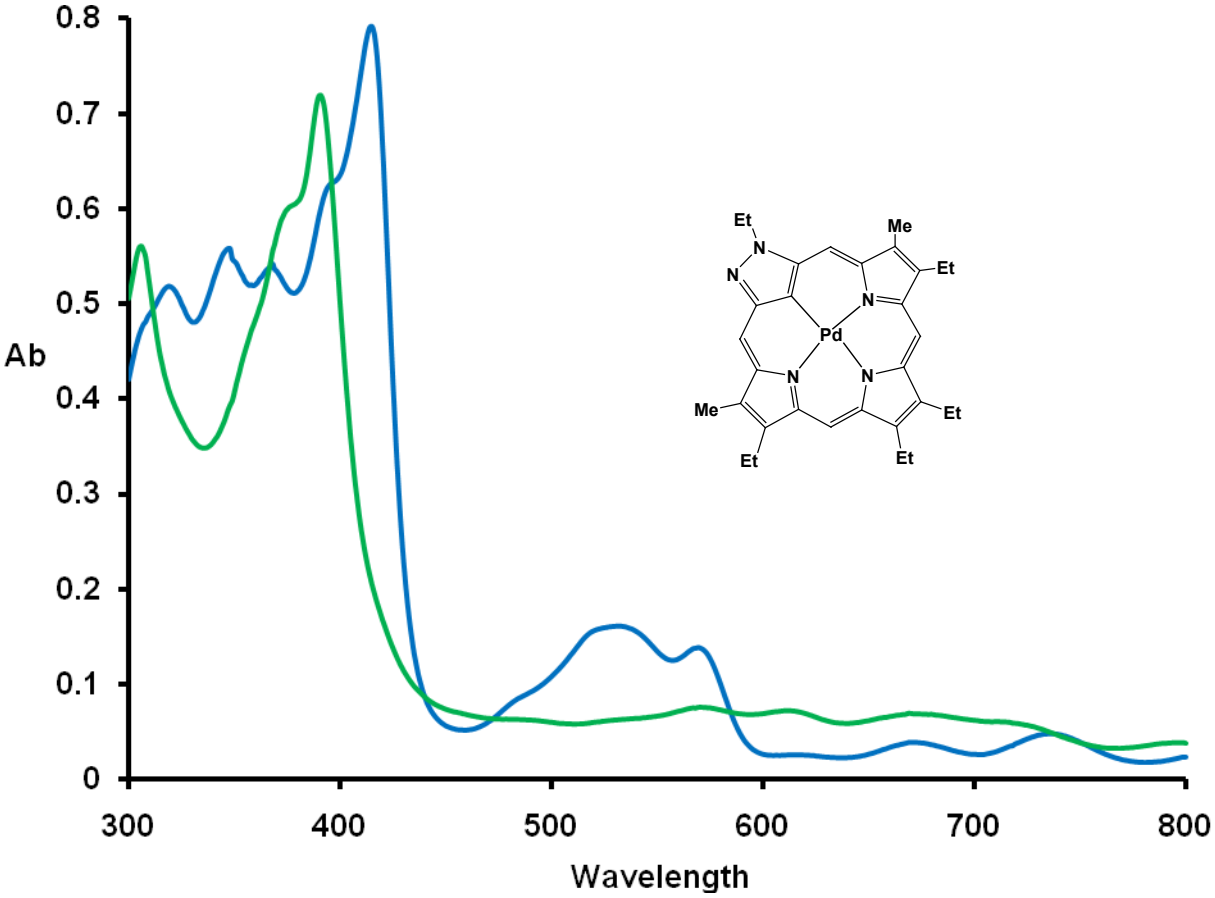


Figure 15. UV-vis spectra of palladium(II) pyrazoloporphyrin **32c** in chloroform (blue line) and with 500 equiv TFA in chloroform (blue line).

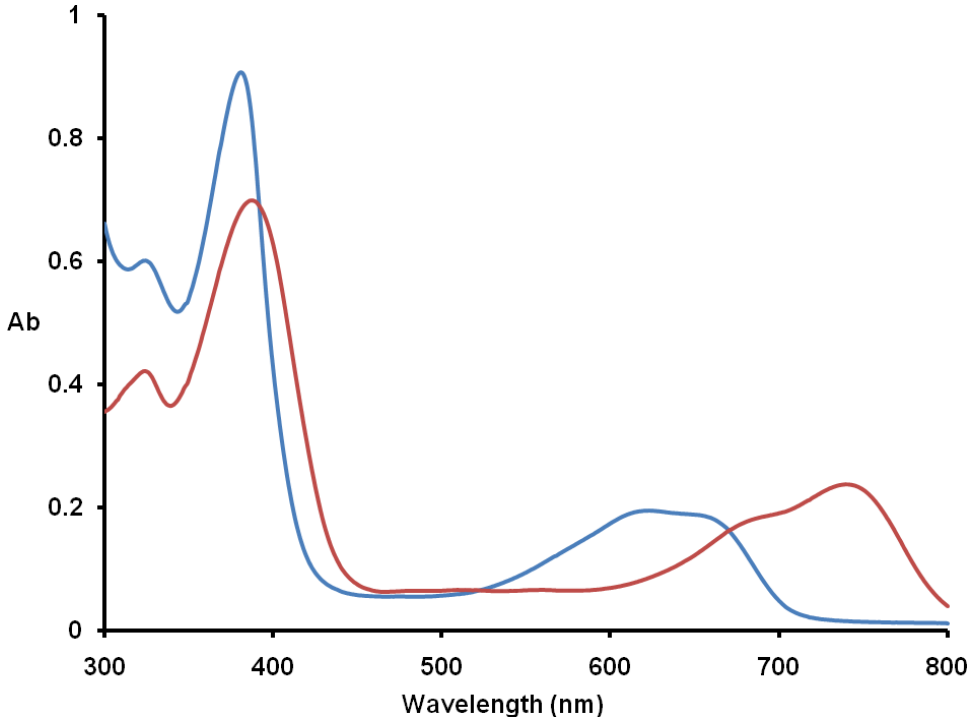


Figure 16. UV-vis spectra of oxophlorin analogue **28a** in 1% Et_3N-chloroform (blue line) and 1% TFA-chloroform (red line).

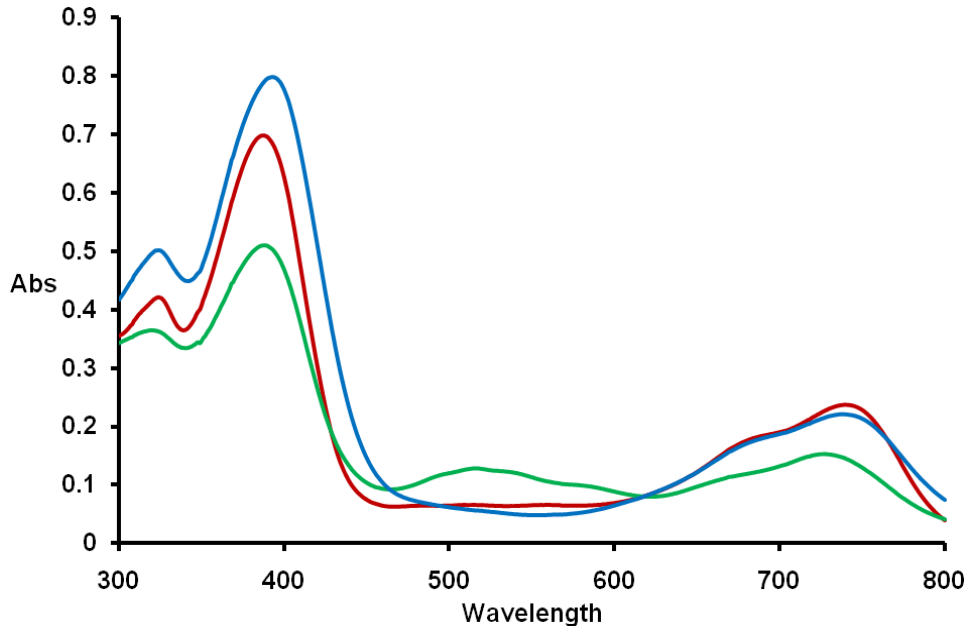


Figure 17. UV-vis spectra of oxophlorin analogue **28a** in 1% TFA-chloroform (red line), 5% TFA chloroform (green line) and 10% TFA-chloroform (blue line).

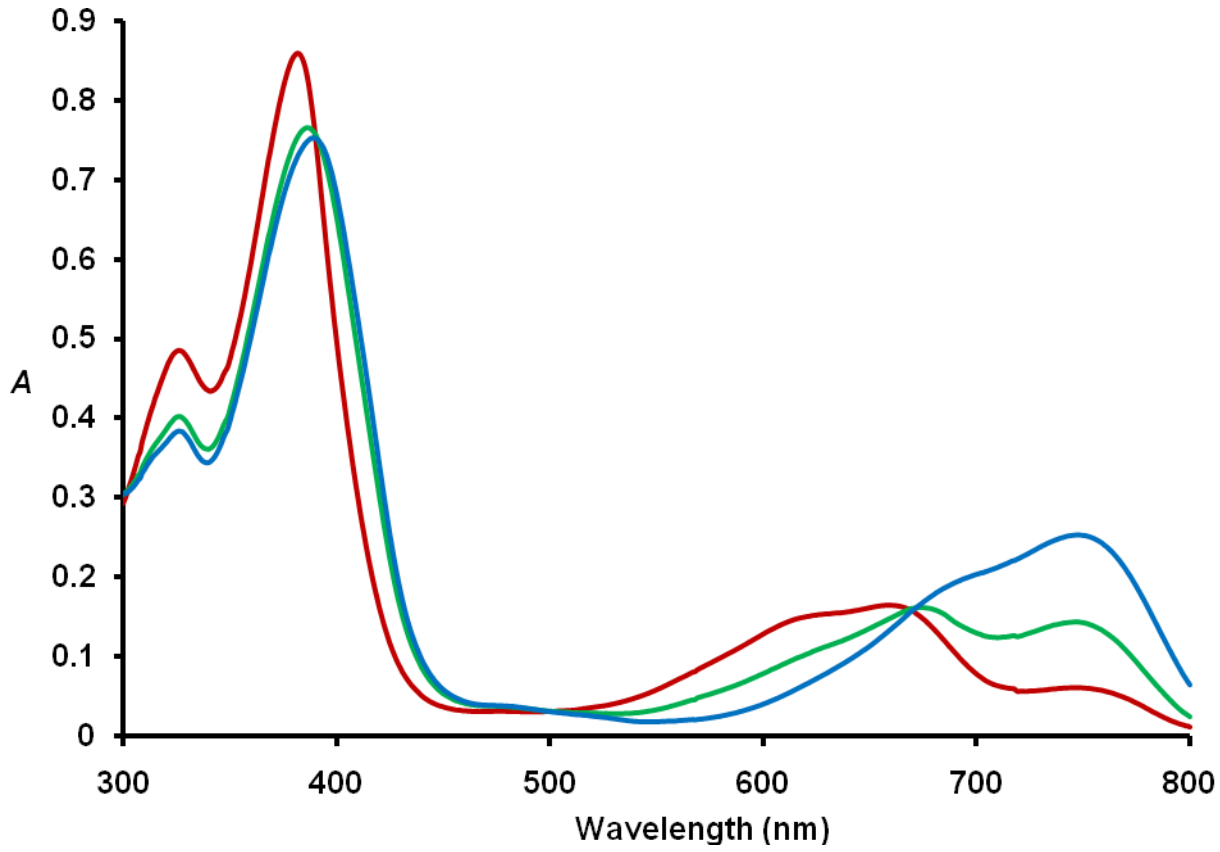


Figure 18. UV-vis spectra of oxophlorin analogue **28a** in chloroform with 2 equiv (red line), 5 equiv (green line) and 10 equiv of TFA in chloroform (blue line).

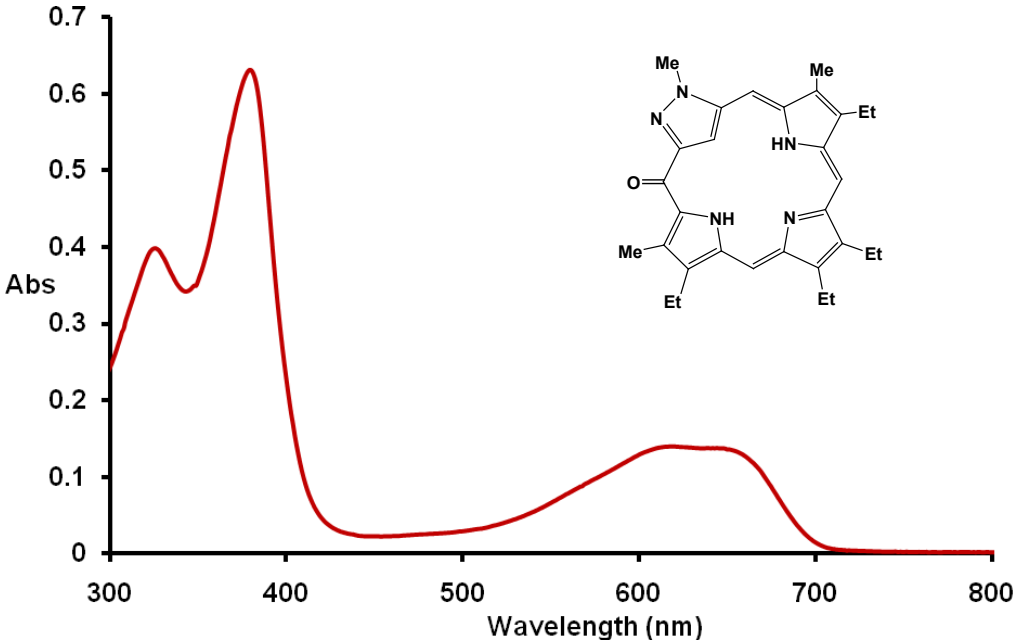


Figure 19. UV-vis spectrum of oxophlorin analogue **28b** in 0.5% Et_3N-chloroform.

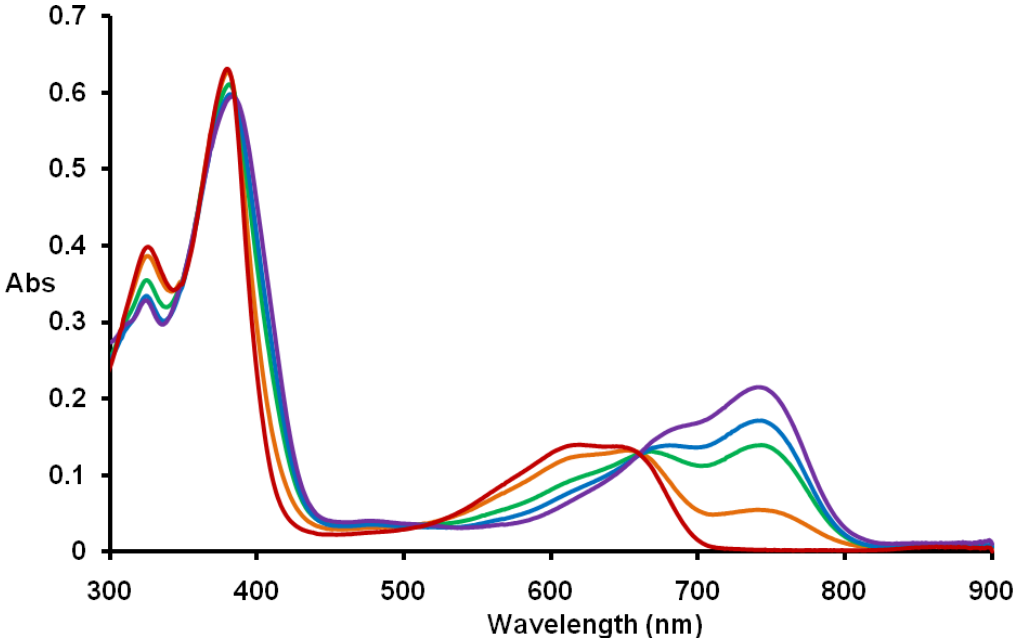


Figure 20. UV-vis spectra of oxophlorin analogue **28b** in 0.5% TEA-chloroform (red line), chloroform (orange line), 1 equiv TFA in chloroform (green line), 2 equiv TFA in chloroform (blue line) and 5 eqiv TFA in chloroform (purple line).

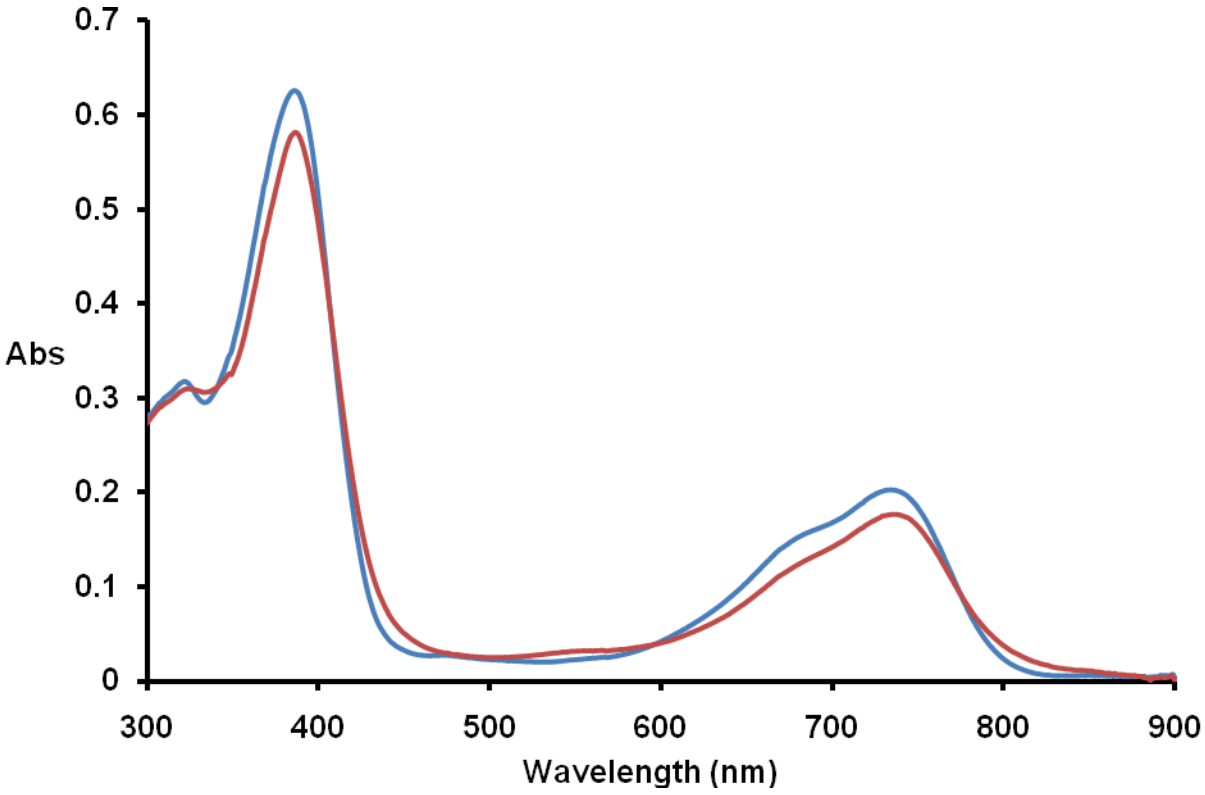


Figure 21. UV-vis spectra of pyrazoloporphyrin **28b** in 1% TFA-chloroform (blue line) and 5% TFA-chloroform (red line).

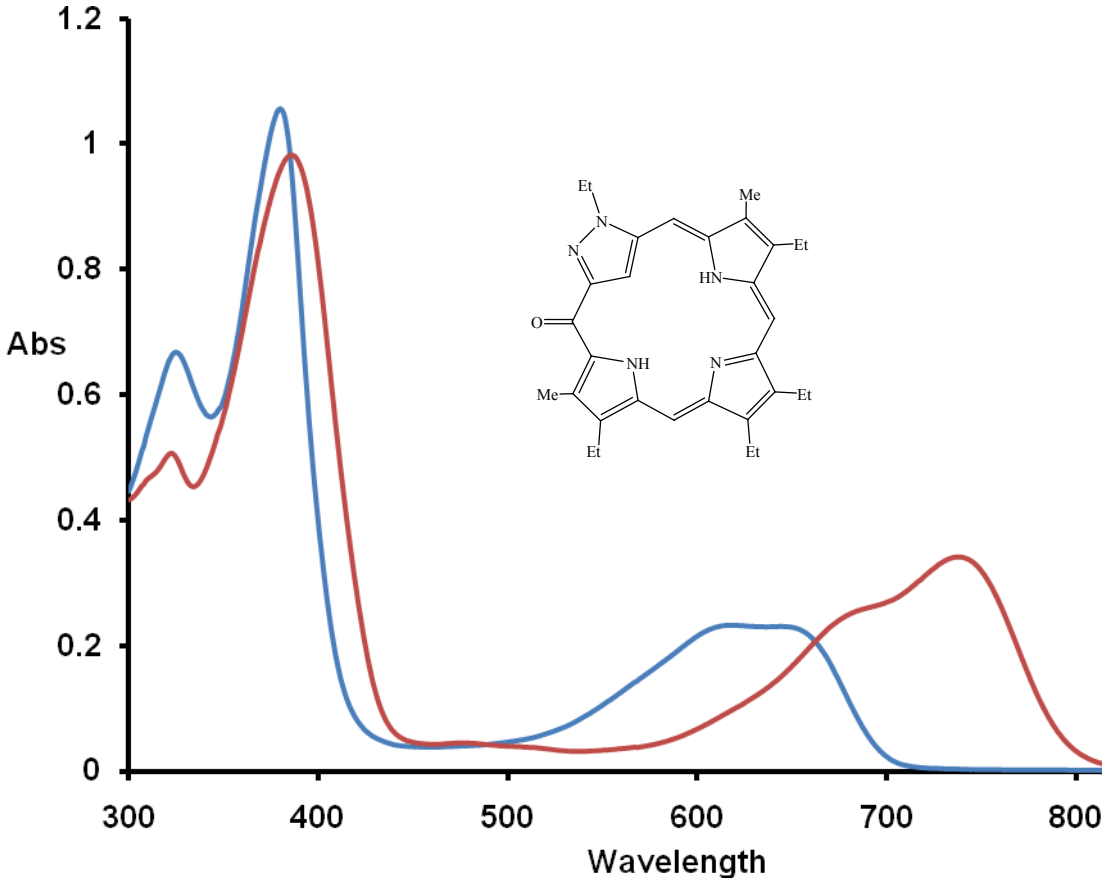


Figure 22. UV-vis spectra of oxophlorin analogue **28a** in 1% Et_3N-chloroform (blue line) and 1% TFA-chloroform (red line).

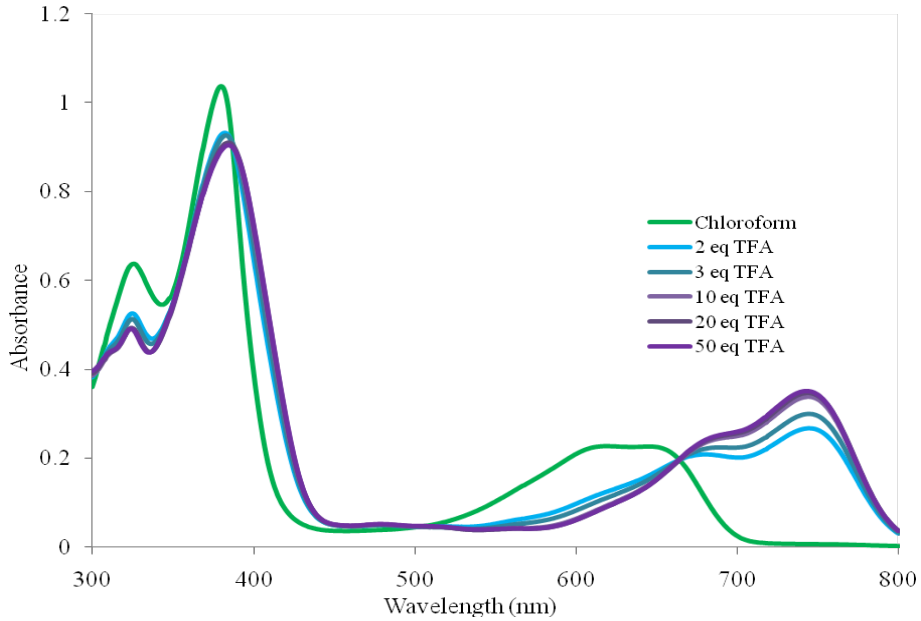


Figure 23. UV-vis spectra of oxophlorin analogue **28c** in chloroform and with 2-50 equiv TFA in chloroform.

.

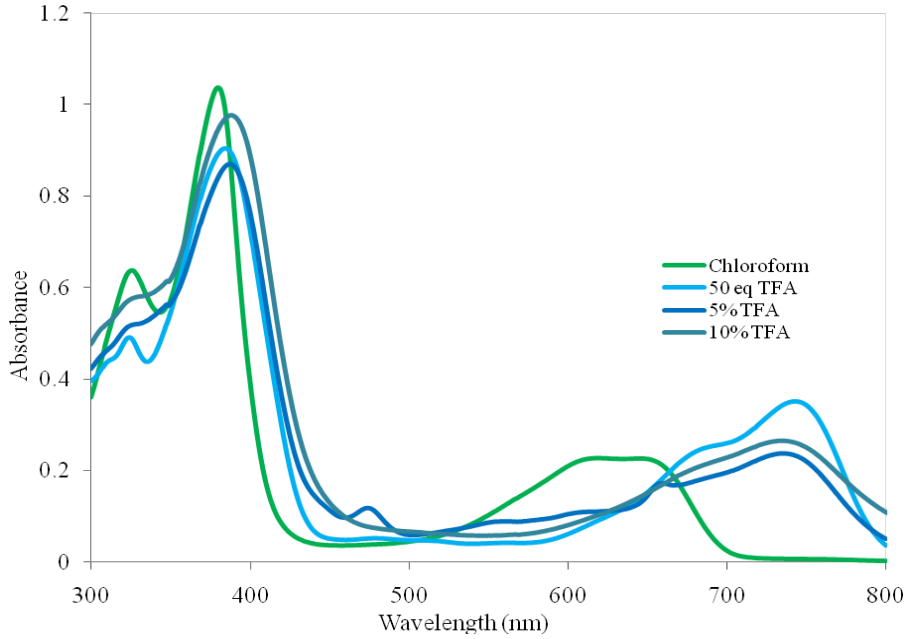


Figure 24. UV-vis spectra of pyrazoloporphyrin **25a** in chloroform, 50 equiv TFA in chloroform, 5% TFA-chloroform and 10% TFA-chloroform.

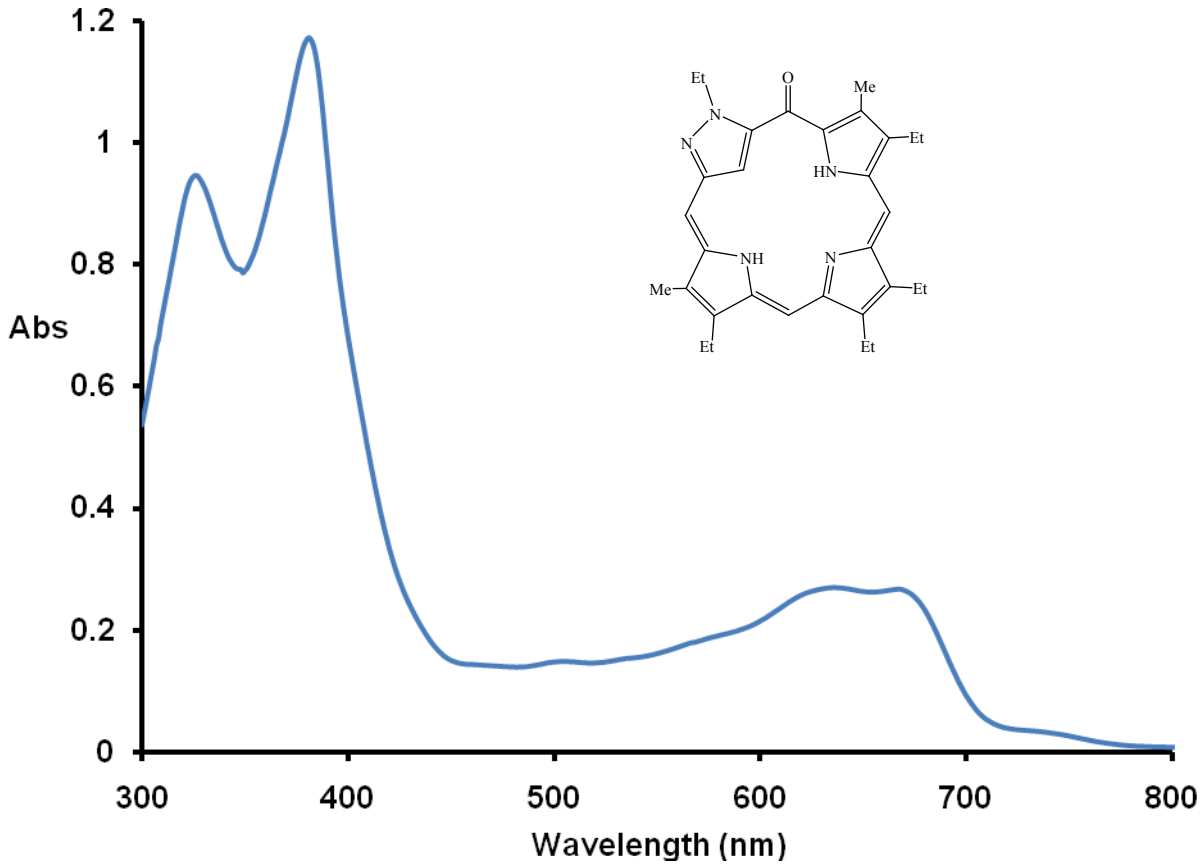


Figure 25. UV-vis spectrum of oxophlorin analogue **29** in chloroform.

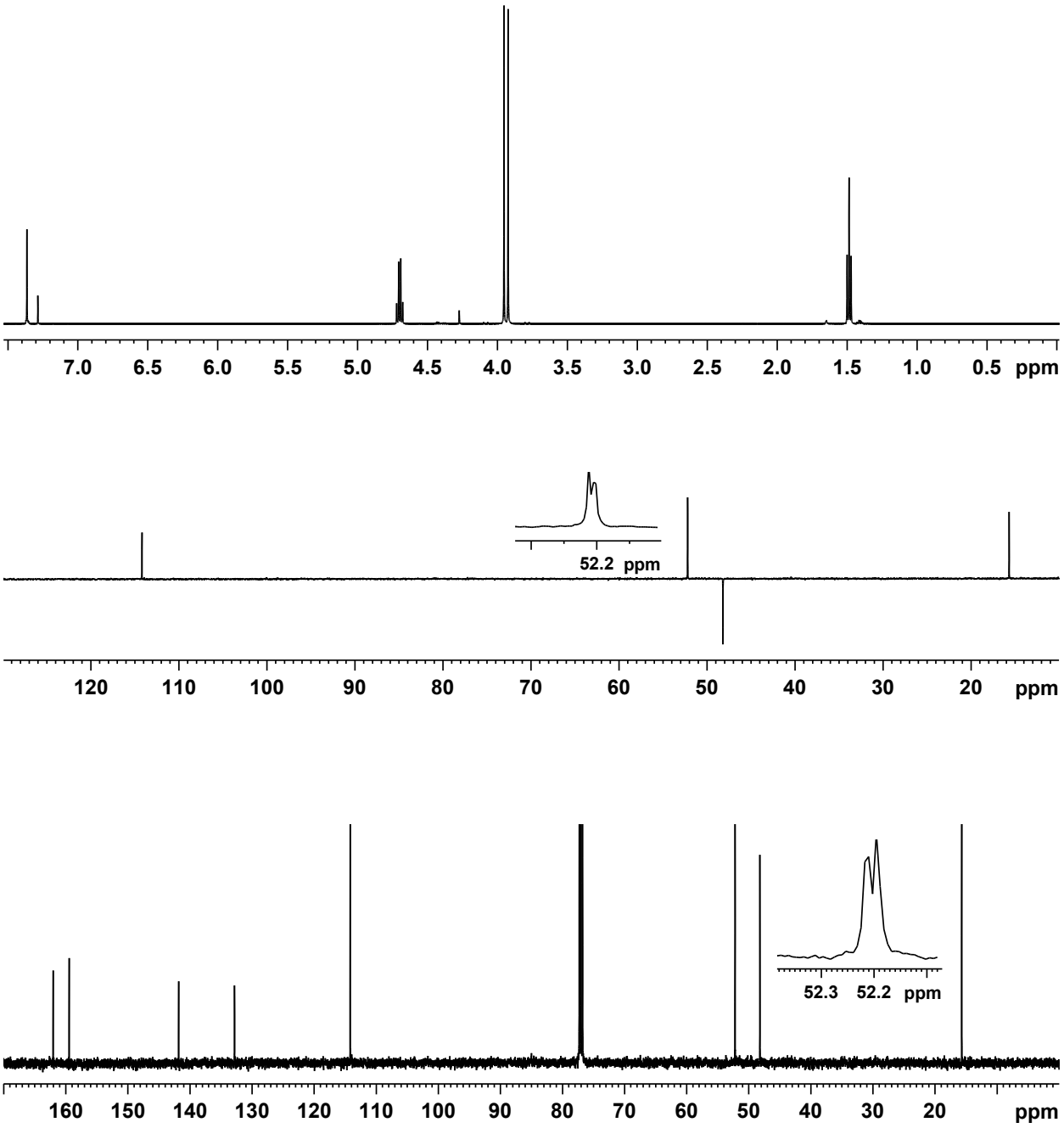


Figure 26. 500 MHz proton NMR, DEPT-135 and 125 MHz carbon-13 NMR spectra of *N*-ethylpyrazole dimethyl ester **22**.

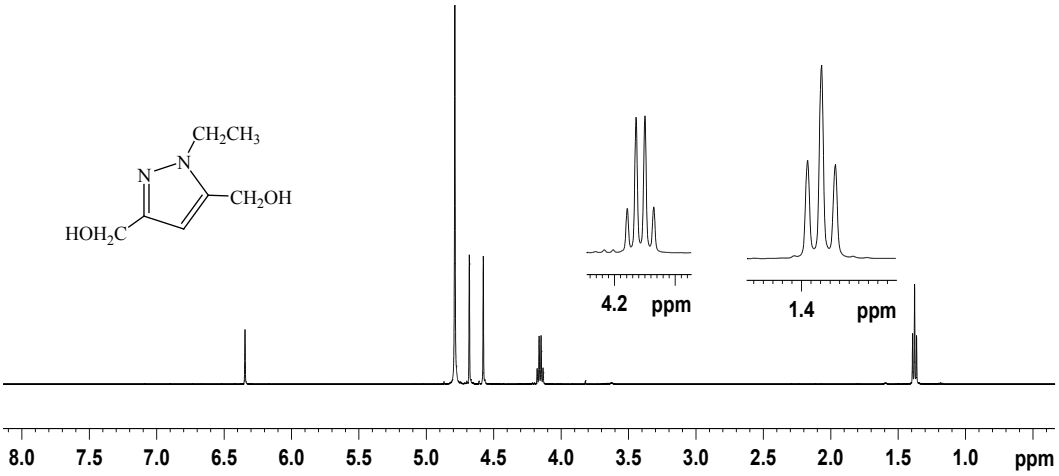


Figure 27. 500 MHz Proton NMR spectrum of 1-ethyl-3,5-bis(hydroxymethyl)pyrazole in $CDCl_3$.

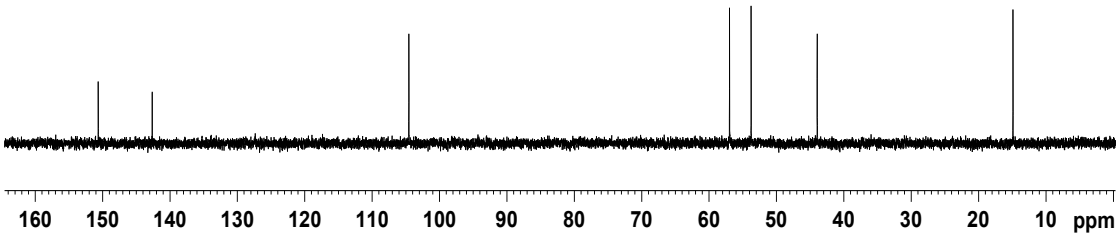
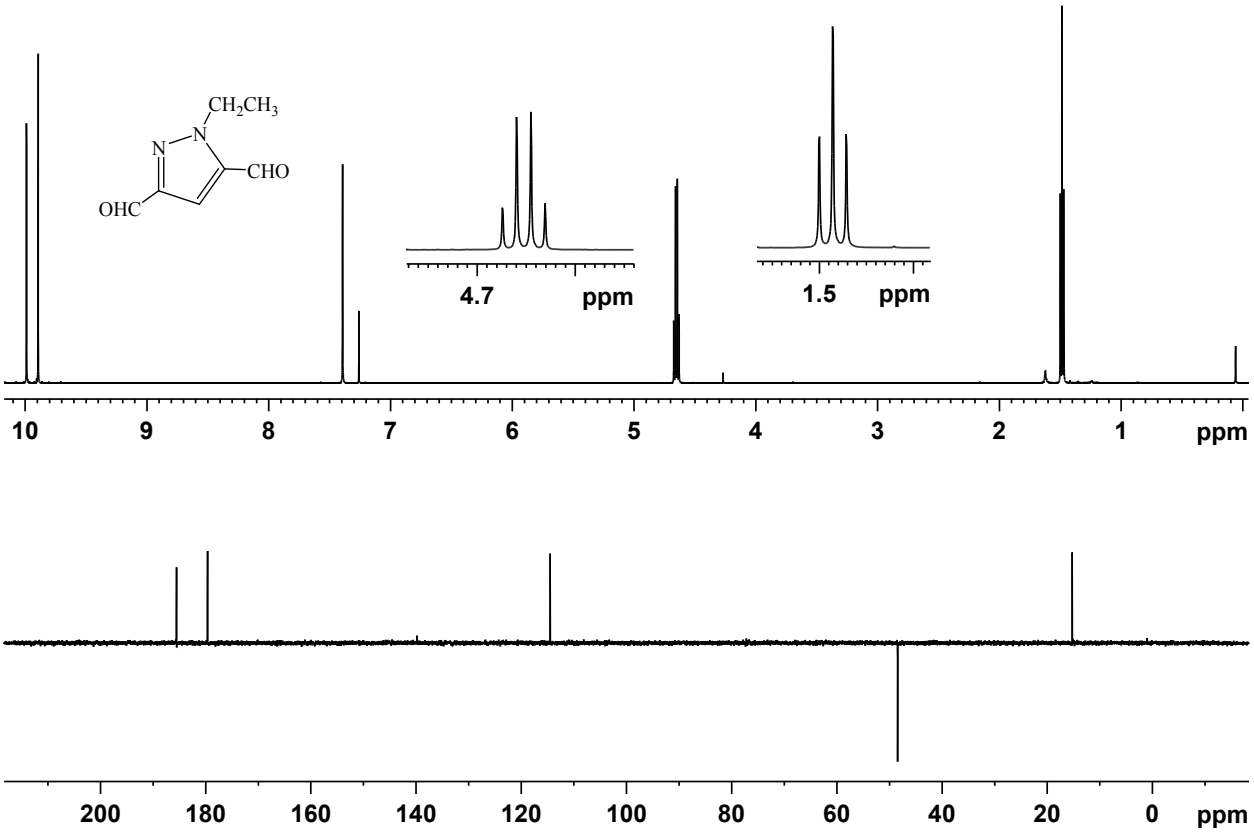


Figure 28. 125 MHz carbon-13 NMR spectrum of 1-ethyl-3,5-bis(hydroxymethyl)pyrazole in $CDCl_3$.



DEPT-135

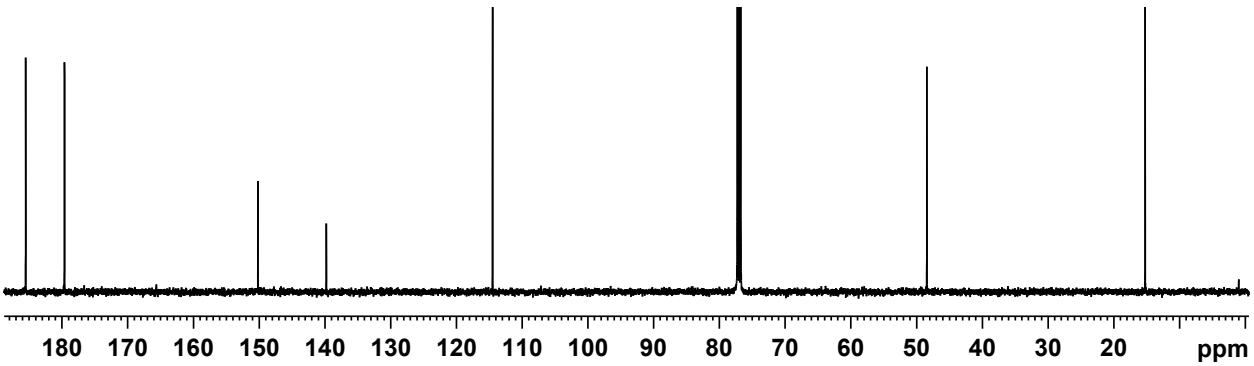


Figure 29. 500 MHz proton NMR, DEPT-135 and 125 MHz carbon-13 NMR spectra of *N*-ethylpyrazole dialdehyde **20c**.

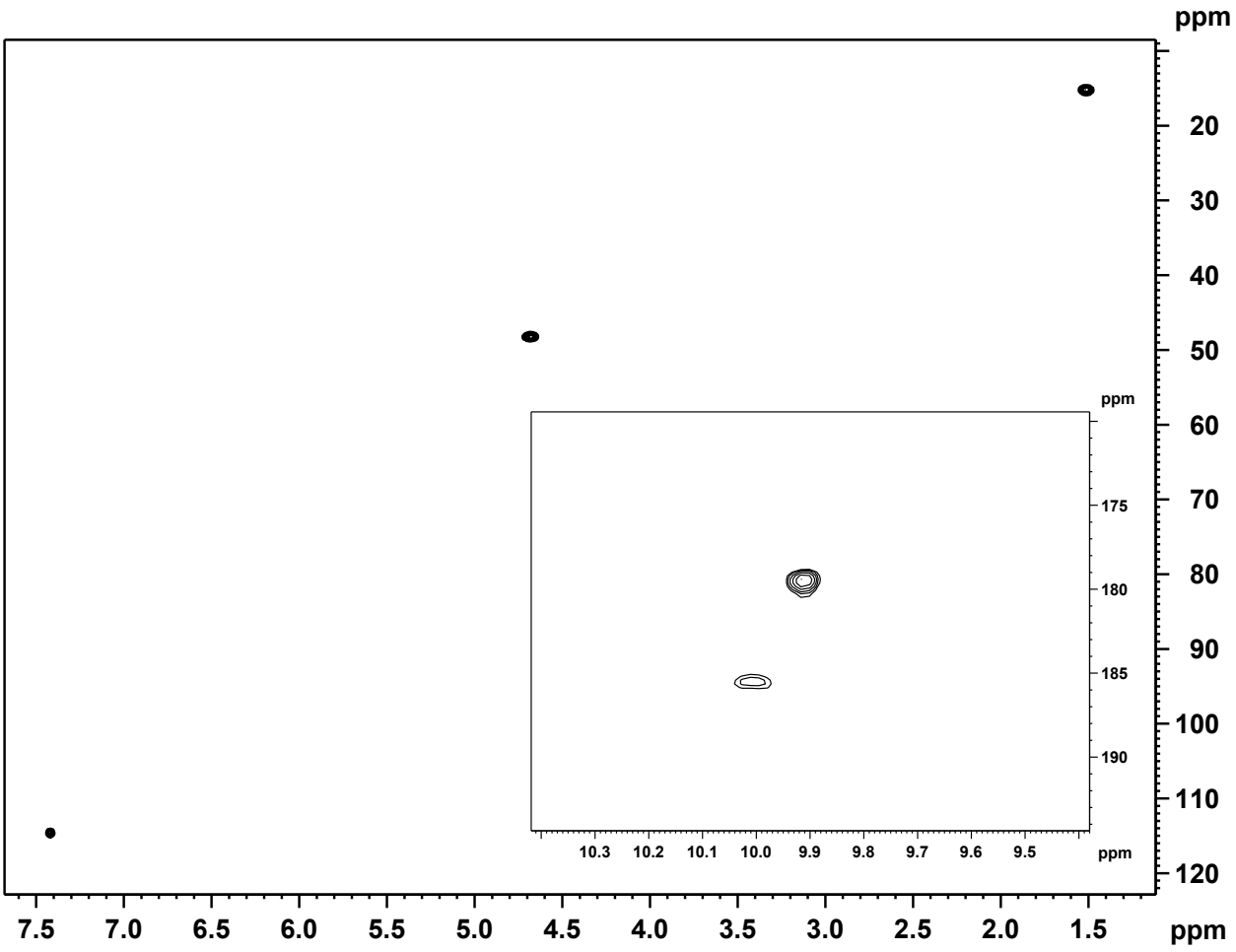


Figure 30. HSQC NMR spectrum of 1-ethylpyrazole-3,5-dicarbaldehyde in $CDCl_3$.

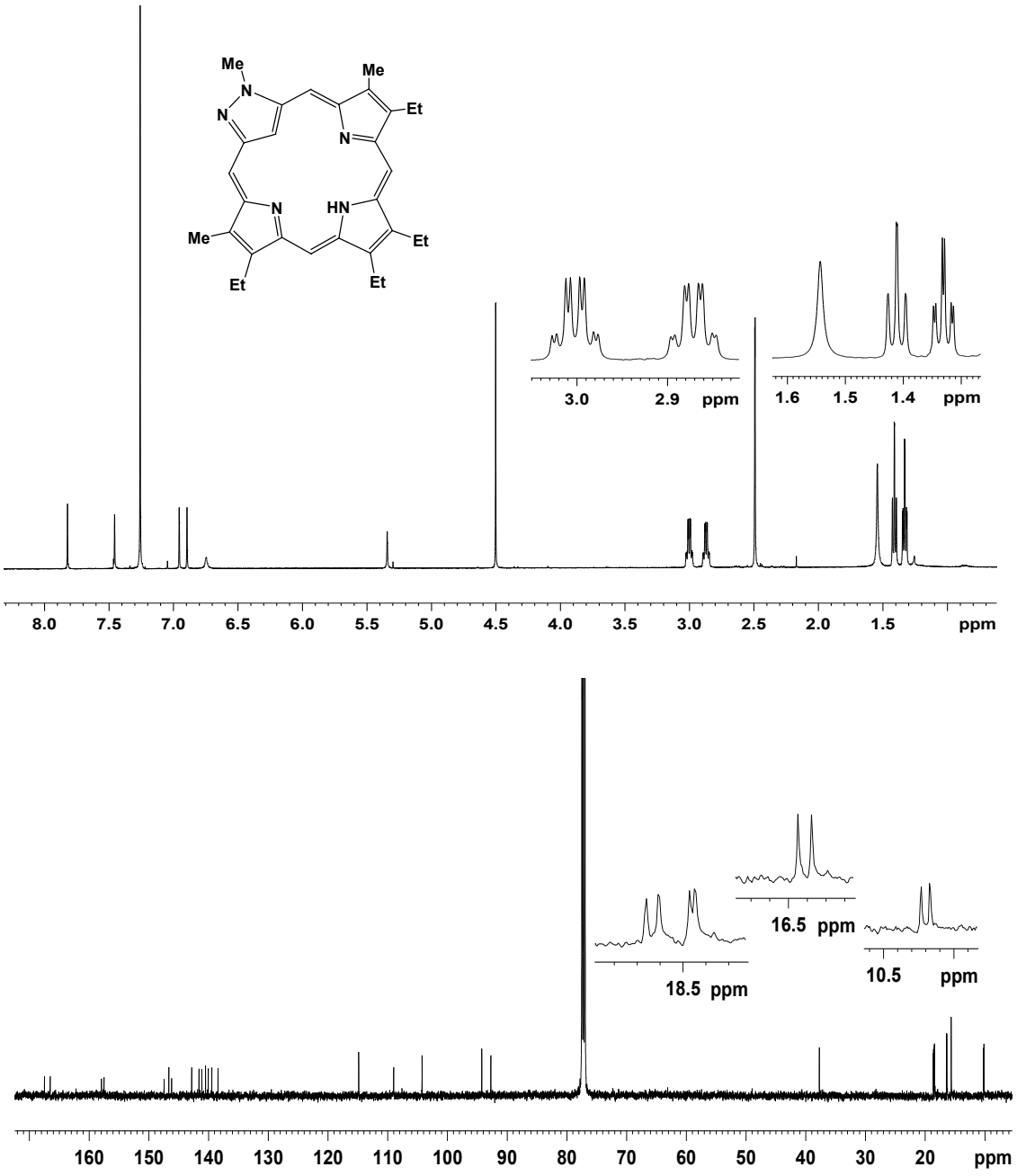


Figure 31. 500 MHz proton NMR and 125 MHz carbon-13 NMR spectra of pyrazoloporphyrin **25b** in $CDCl_3$.

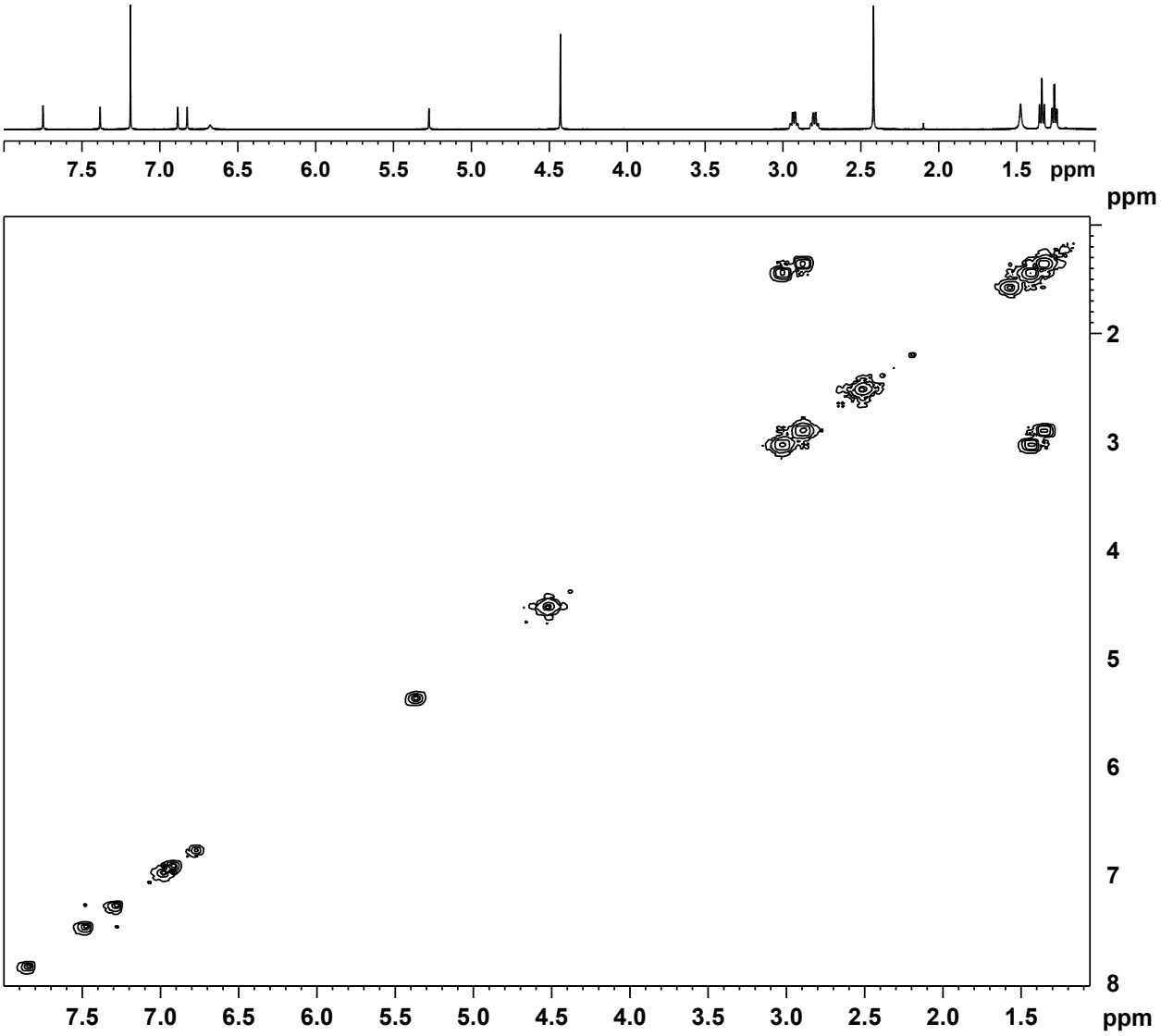


Figure 32. ^{1}H-^{1}H COSY NMR spectrum of pyrazoloporphyrin **25b** in $CDCl_3$.

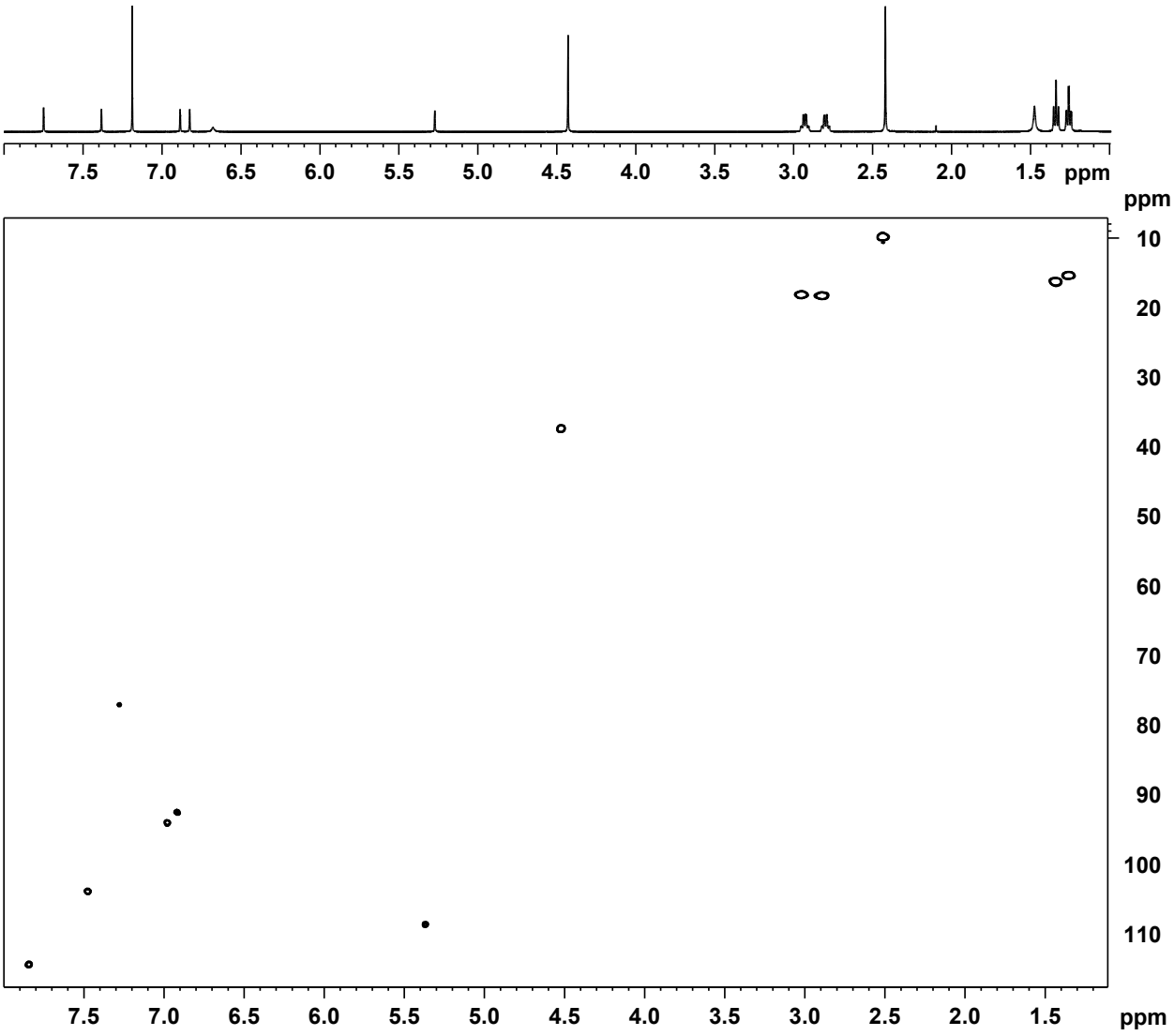


Figure 33. HSQC NMR spectrum of pyrazoloporphyrin **25b** in $CDCl_3$.

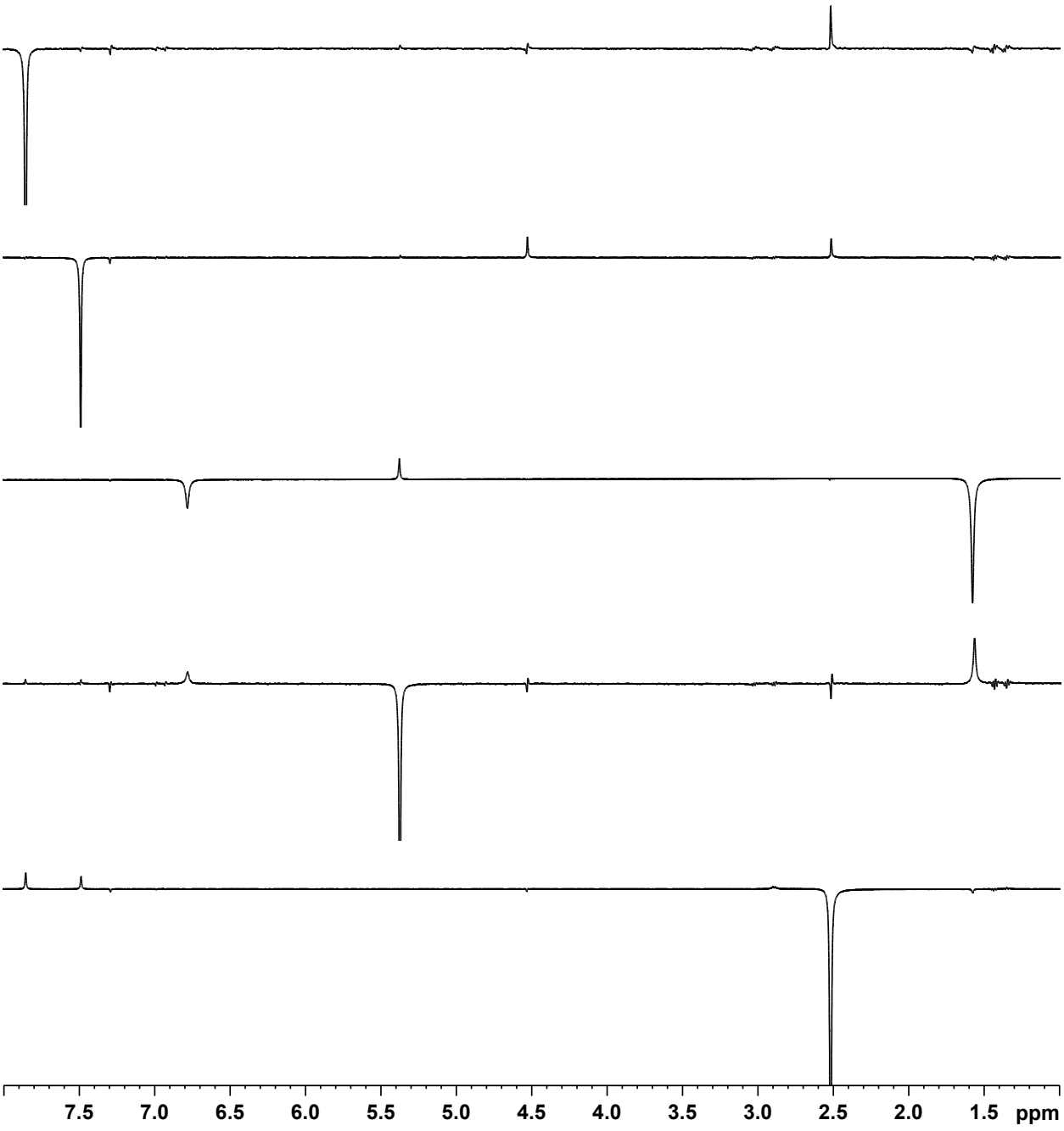


Figure 34. Selected nOe difference proton NMR spectra for pyrazoloporphyrin **25b** in $CDCl_3$.

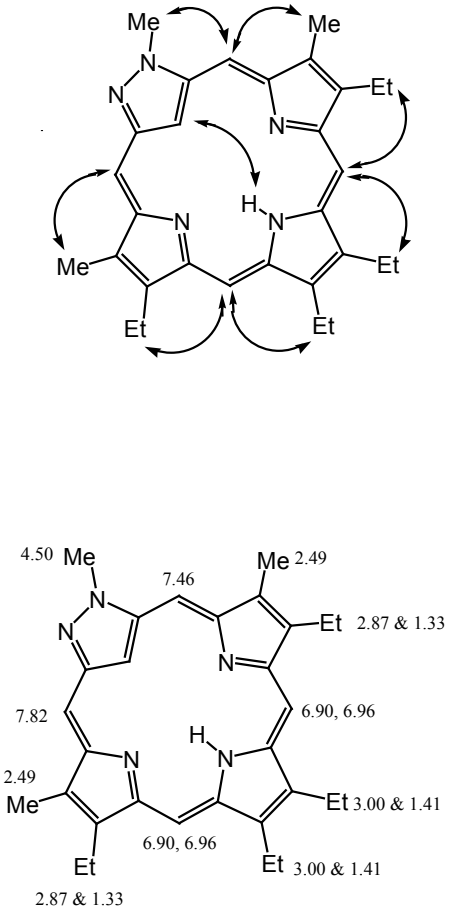


Figure 35. NOE correlations and partial proton NMR assignments for pyrazoloporphyrin **25b**.

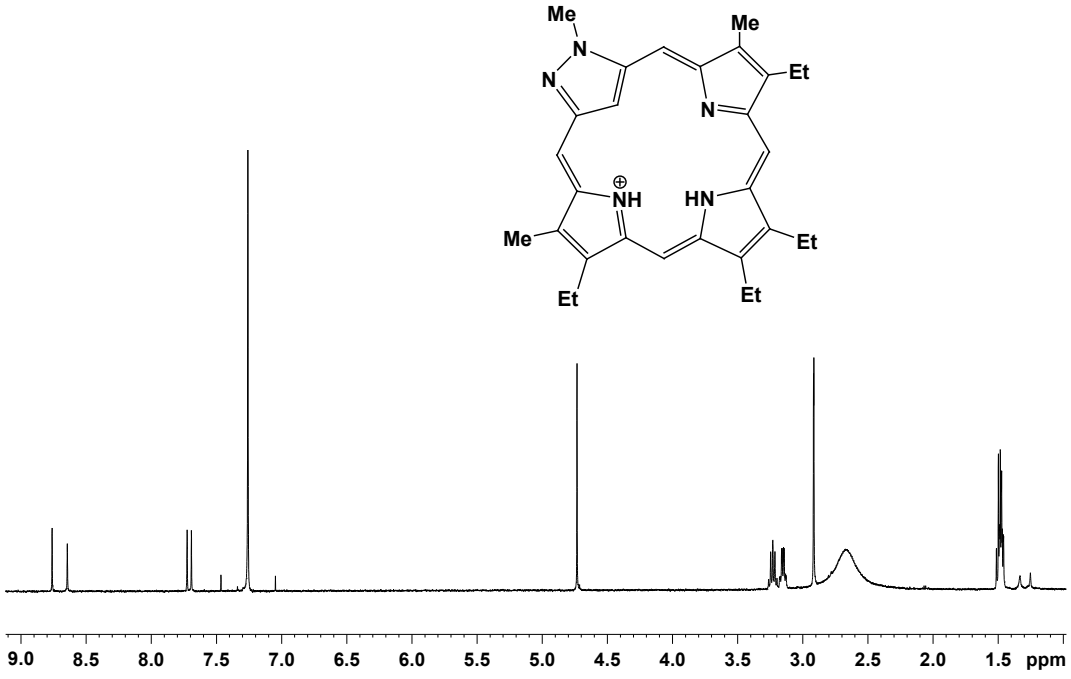


Figure 36. 500 MHz proton NMR spectrum of pyrazoloporphyrin **25b** in trace TFA-$CDCl_3$.

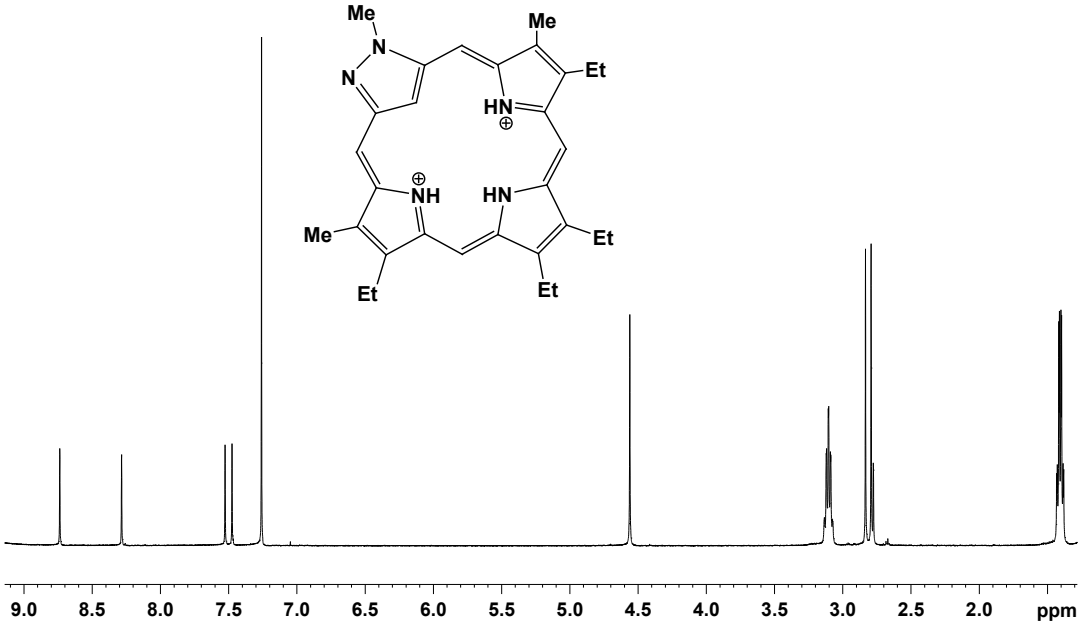


Figure 37. 500 MHz proton NMR spectrum of pyrazoloporphyrin **25b** in TFA-$CDCl_3$.

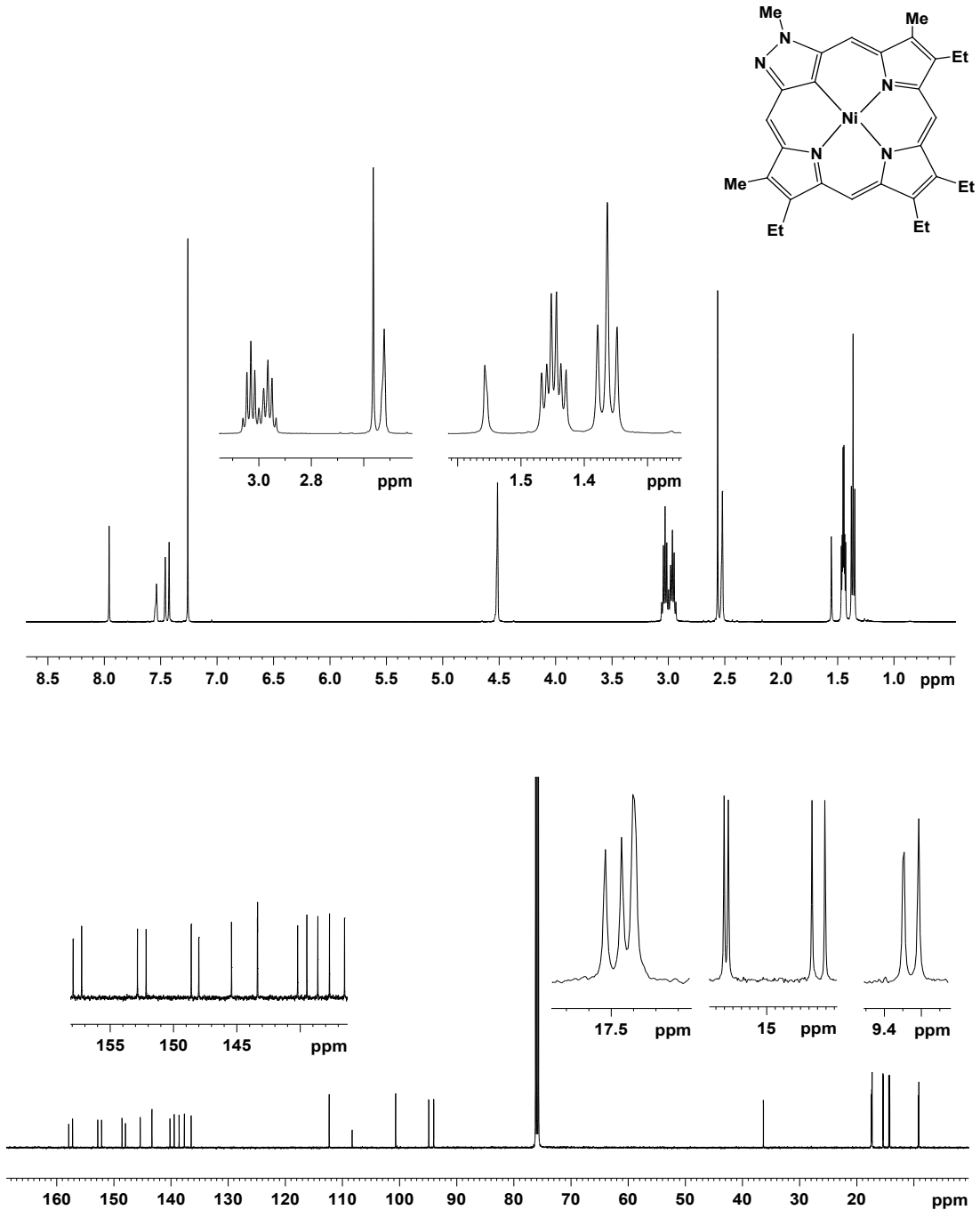


Figure 38. 500 MHz proton NMR and 125 MHz carbon-13 NMR spectra of nickel(II) pyrazoloporphyrin **31b** in $CDCl_3$.

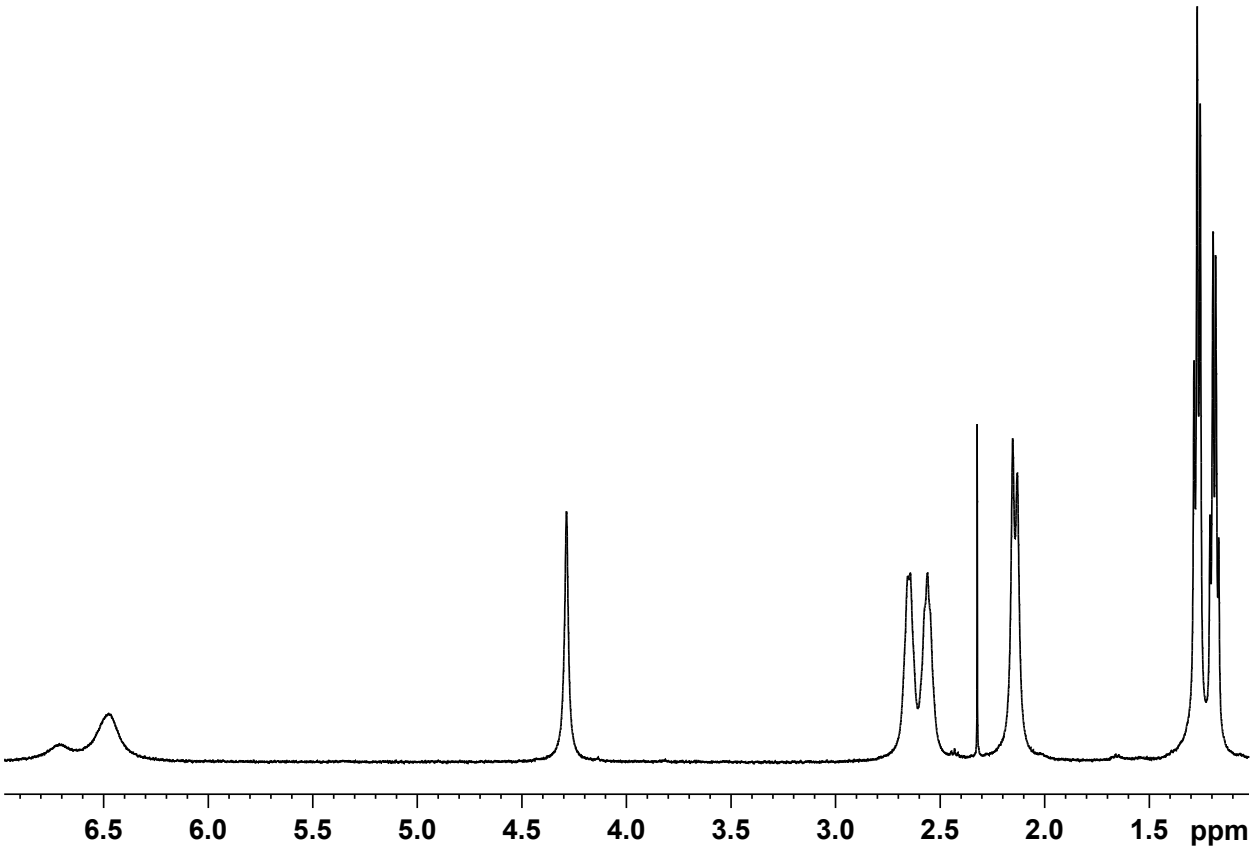


Figure 39. 500 MHz proton NMR spectrum of nickel(II) pyrazoloporphyrin **31b** in TFA-$CDCl_3$.

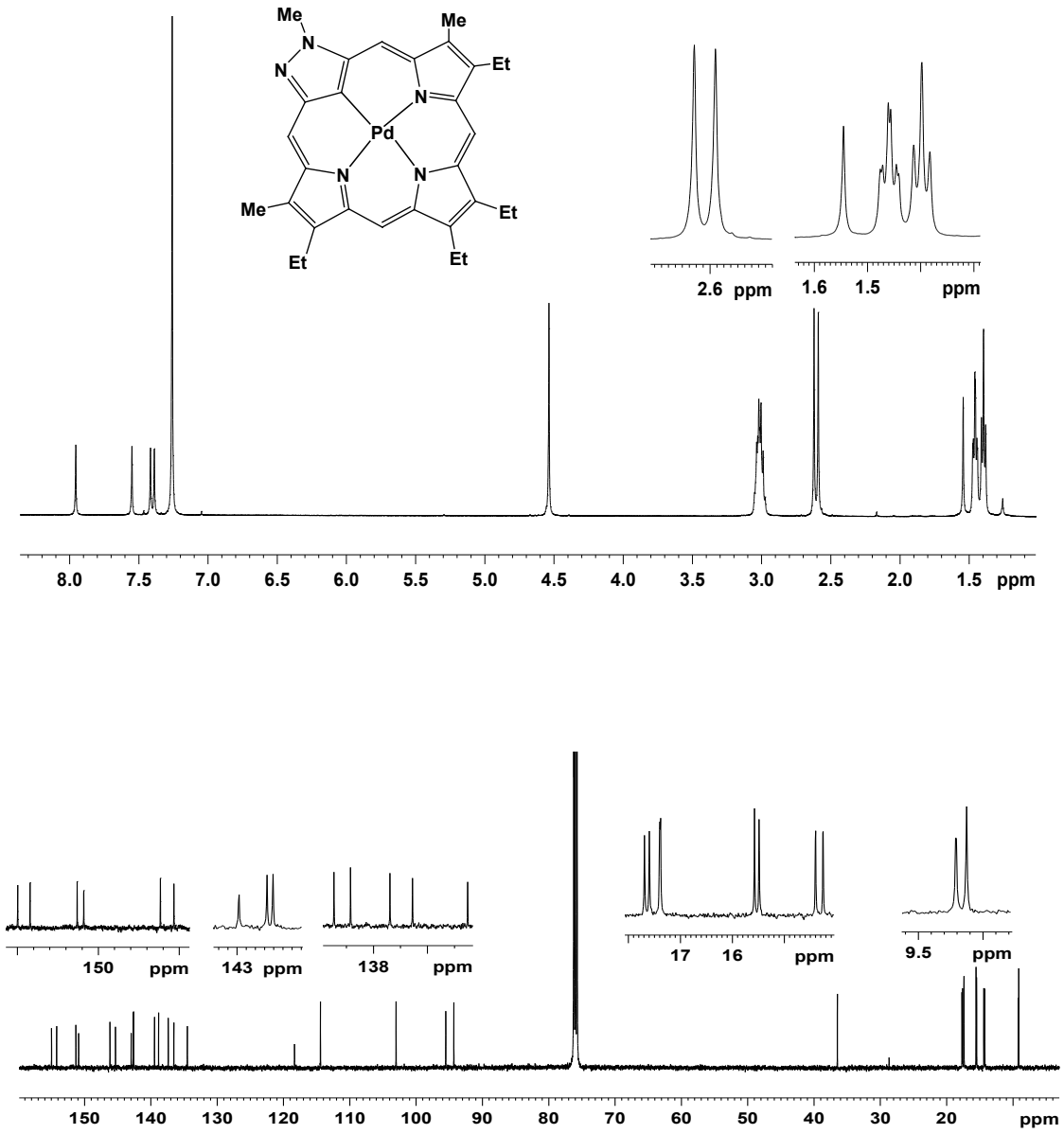


Figure 40. 500 MHz proton NMR and 125 MHz carbon-13 NMR spectra of palladium(II) pyrazoloporphyrin **31b** in $CDCl_3$.

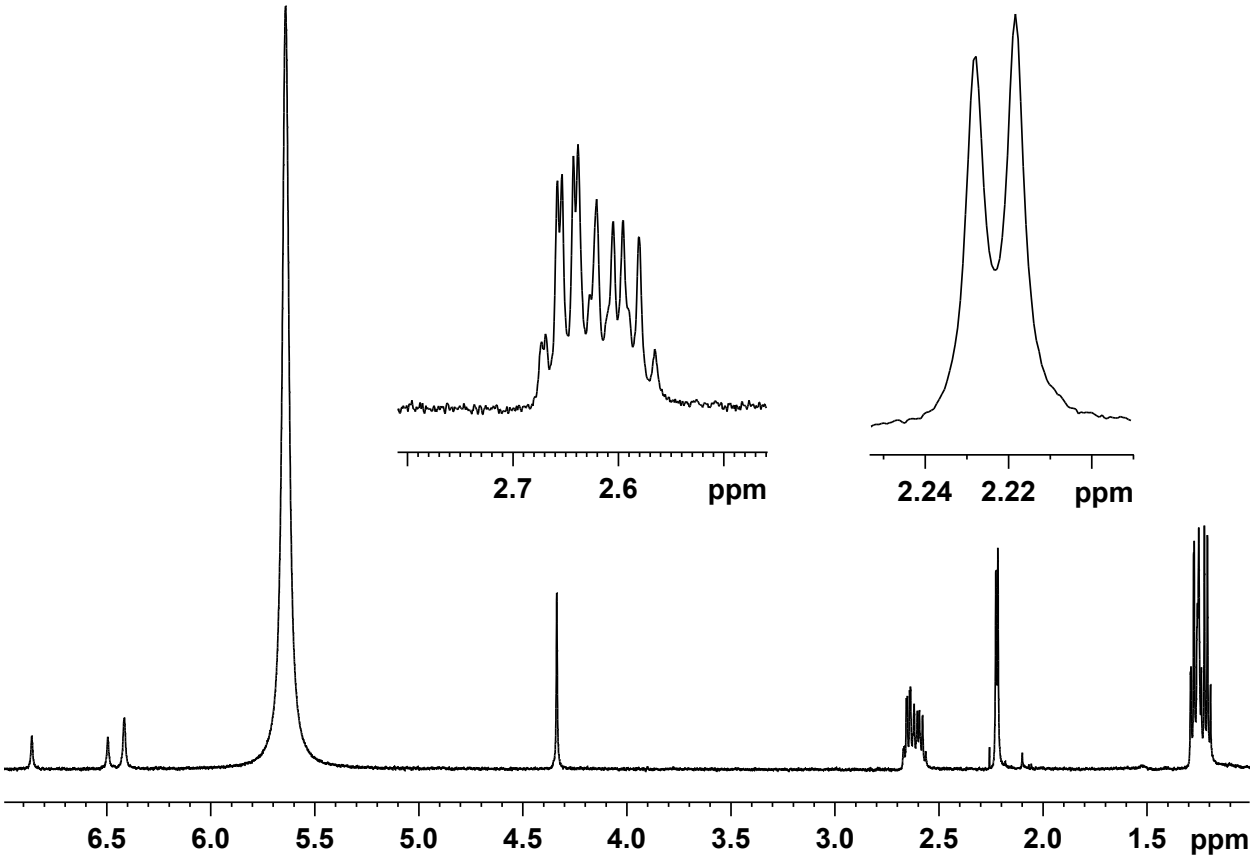


Figure 41. 500 MHz proton NMR spectrum of palladium(II) pyrazoloporphyrin **31b** in TFA-$CDCl_3$.

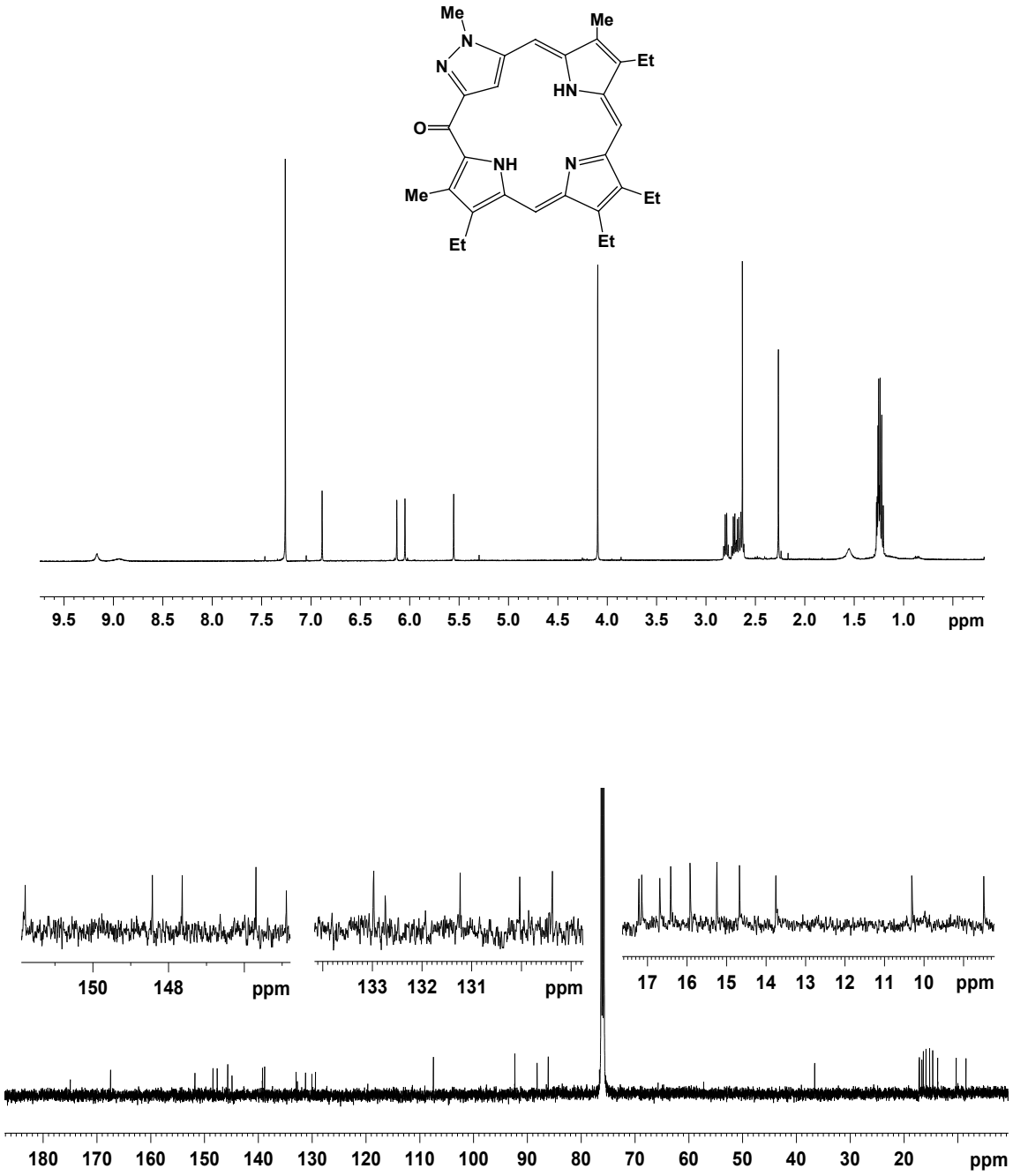


Figure 42. 500 MHz proton NMR and 125 MHz carbon-13 NMR spectra of oxophlorin analogue **28b** in $CDCl_3$.

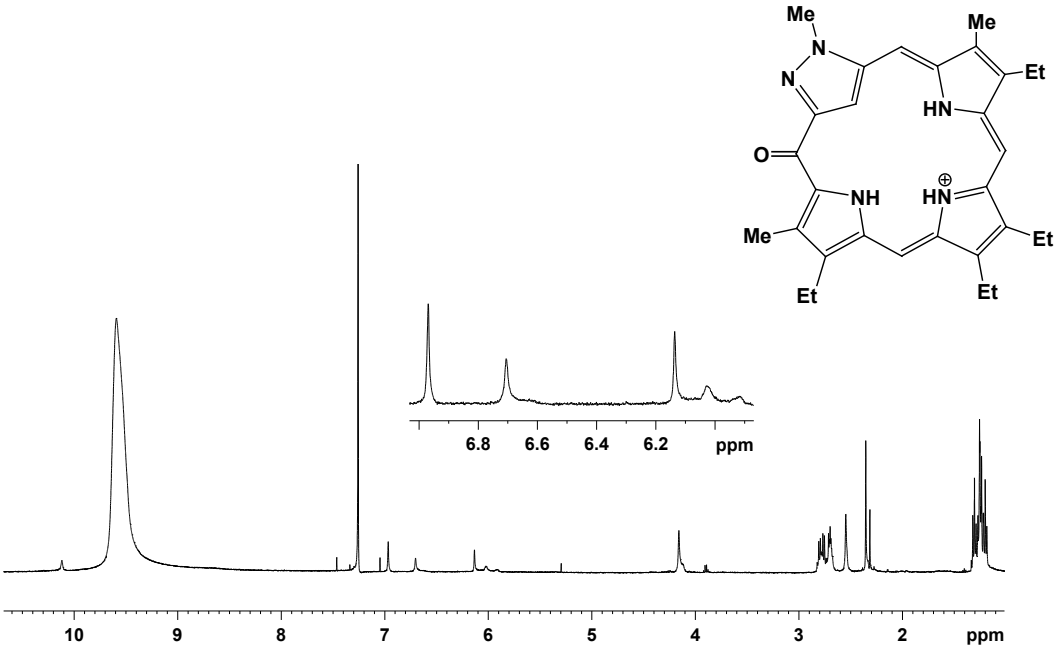


Figure 43. 500 MHz proton NMR spectrum of oxophlorin **28b** in trace TFA-$CDCl_3$.

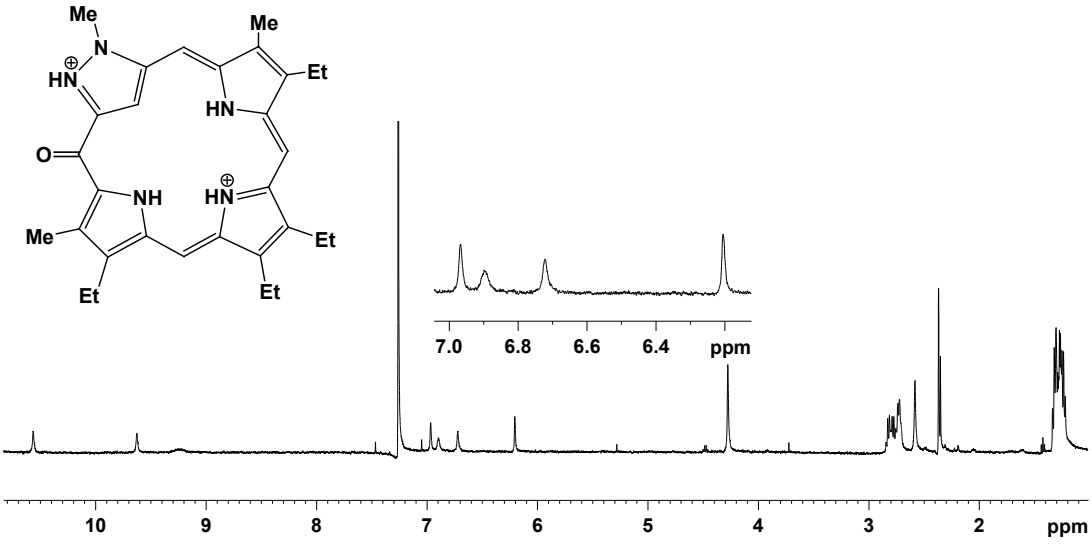


Figure 44. 500 MHz proton NMR spectrum of **28b** in TFA-$CDCl_3$.

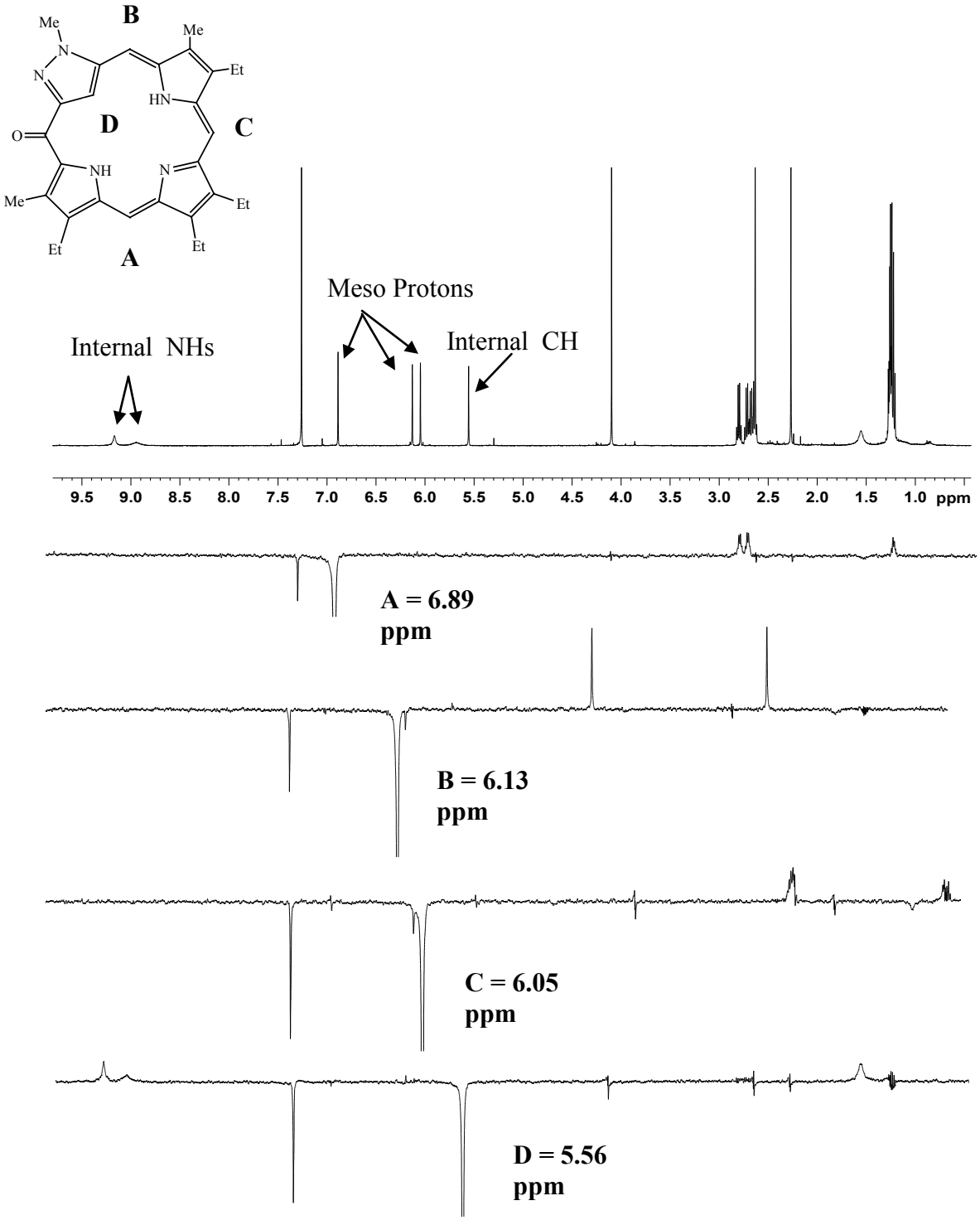


Figure 45. Selected nOe difference proton NMR spectra of *N*-methylpyrazole oxophlorin **28b** in $CDCl_3$.

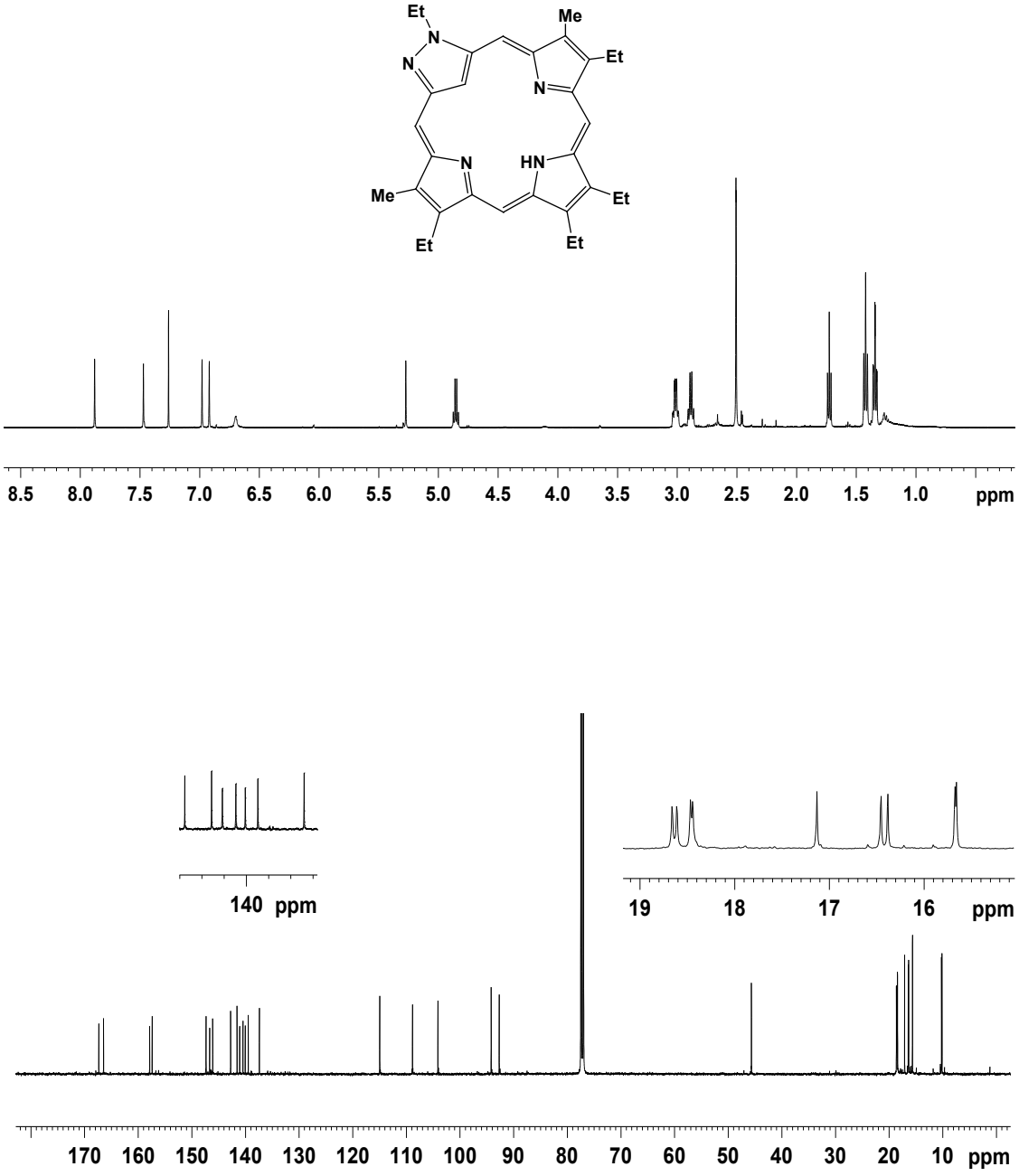


Figure 46. 500 MHz proton NMR and 125 MHz carbon-13 NMR spectra of pyrazoloporphyrin **25c** in trace $CDCl_3$.

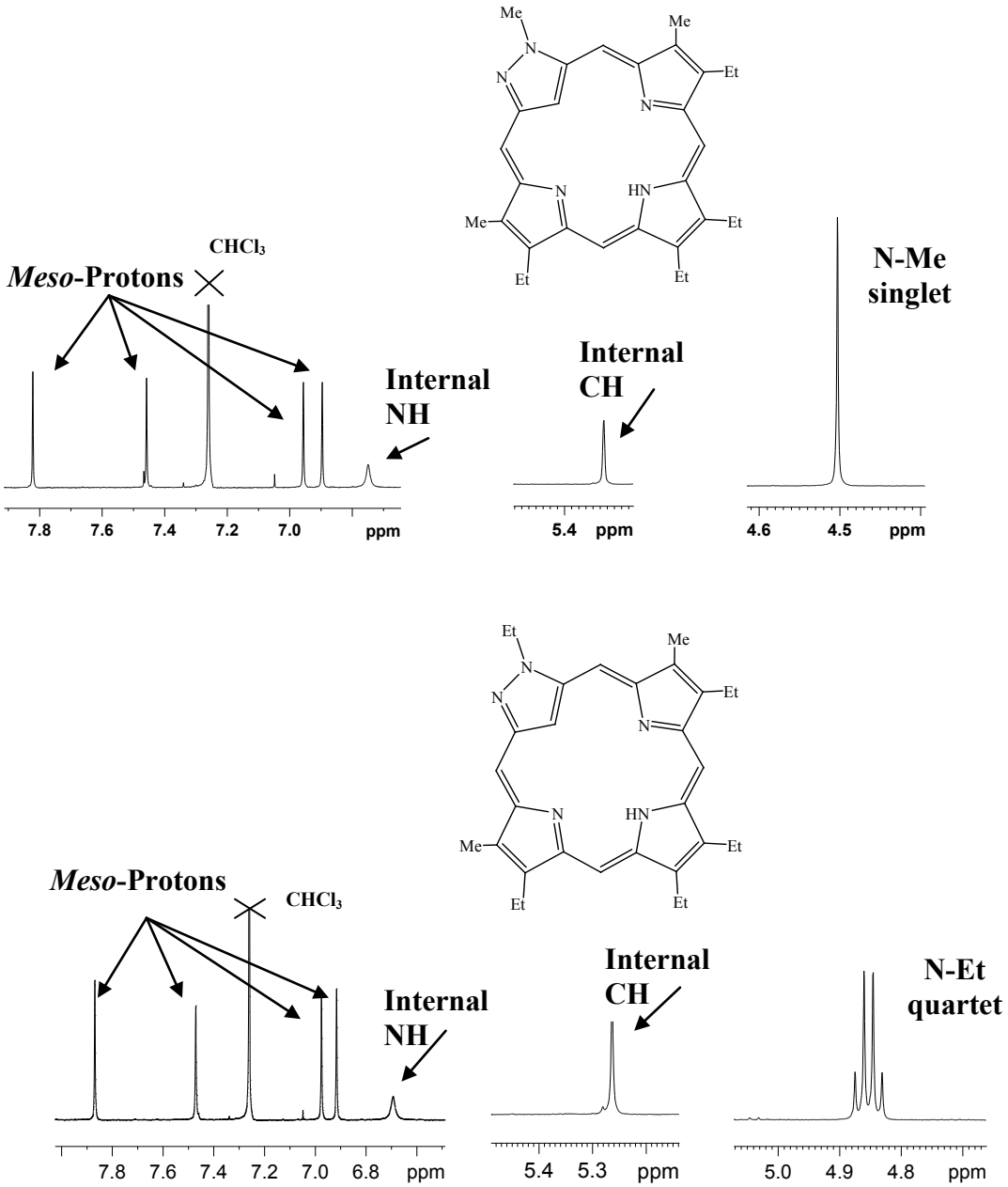


Figure 47. Partial 500 MHz proton NMR spectra of pyrazoloporphyrins **25b** and **25c** in $CDCl_3$.

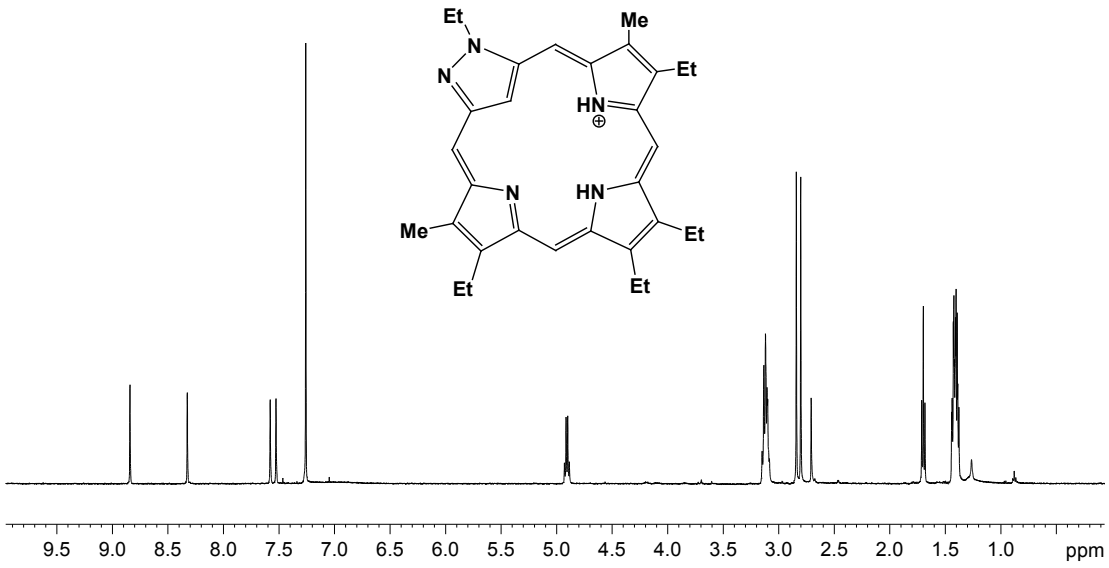


Figure 48. 500 MHz proton NMR spectrum of pyrazoloporphyrin **25c** in trace TFA-$CDCl_3$.

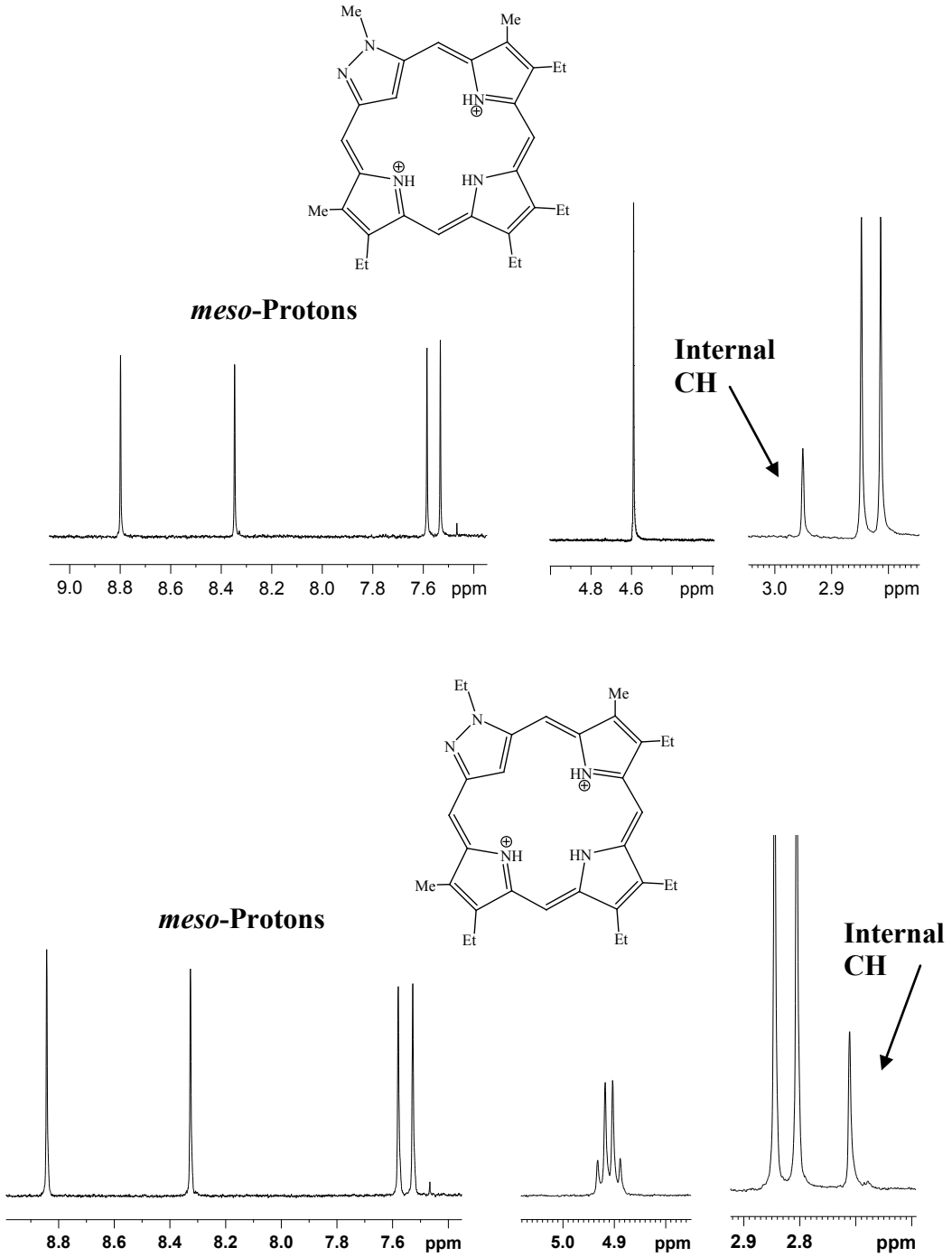


Figure 49. Partial 500 MHz proton NMR spectra of pyrazoloporphyrins **25b** and **25c** in TFA-$CDCl_3$.

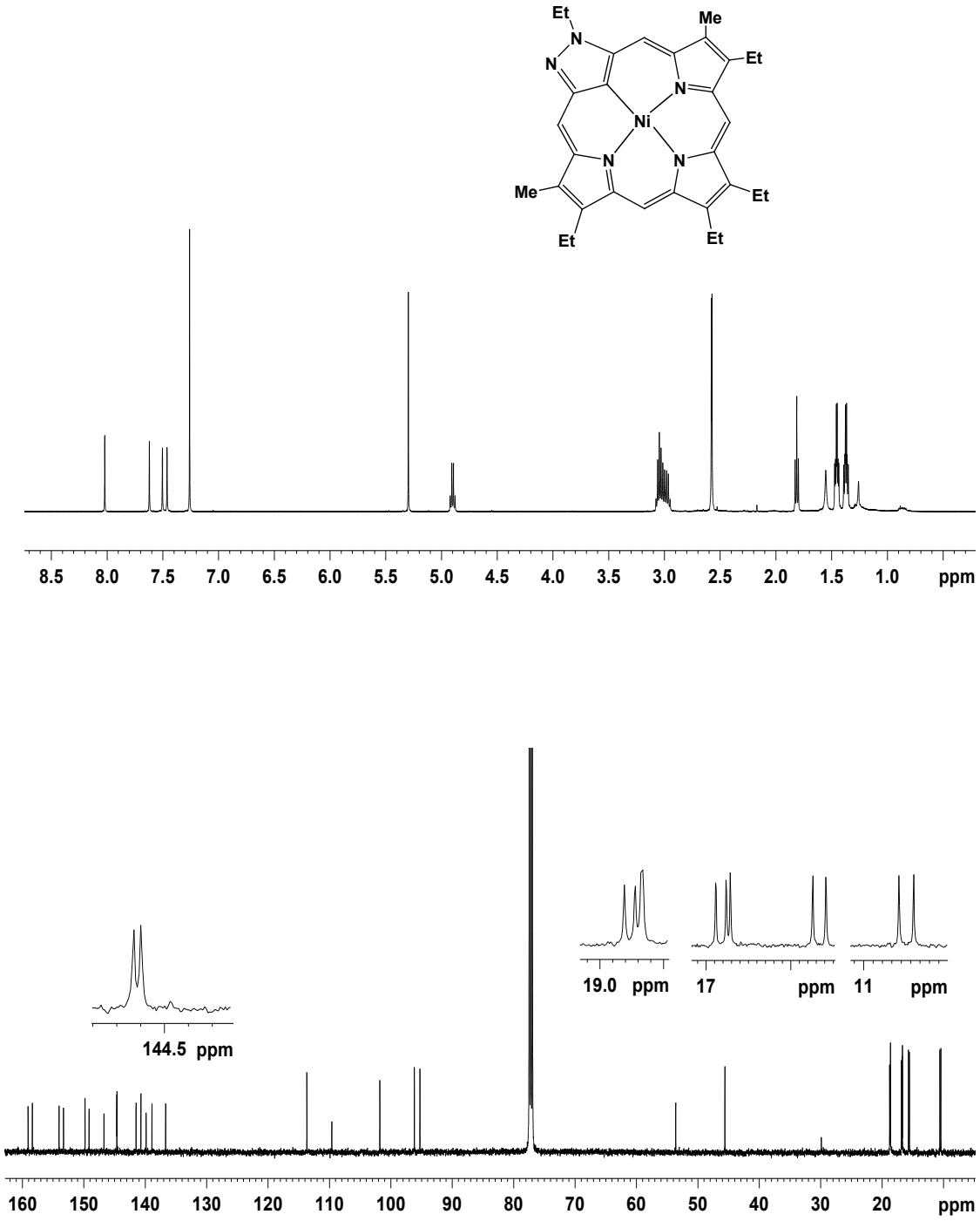


Figure 50. 500 MHz proton NMR and carbon-13 NMR spectra of nickel(II) pyrazoloporphyrin **31c** in $CDCl_3$.

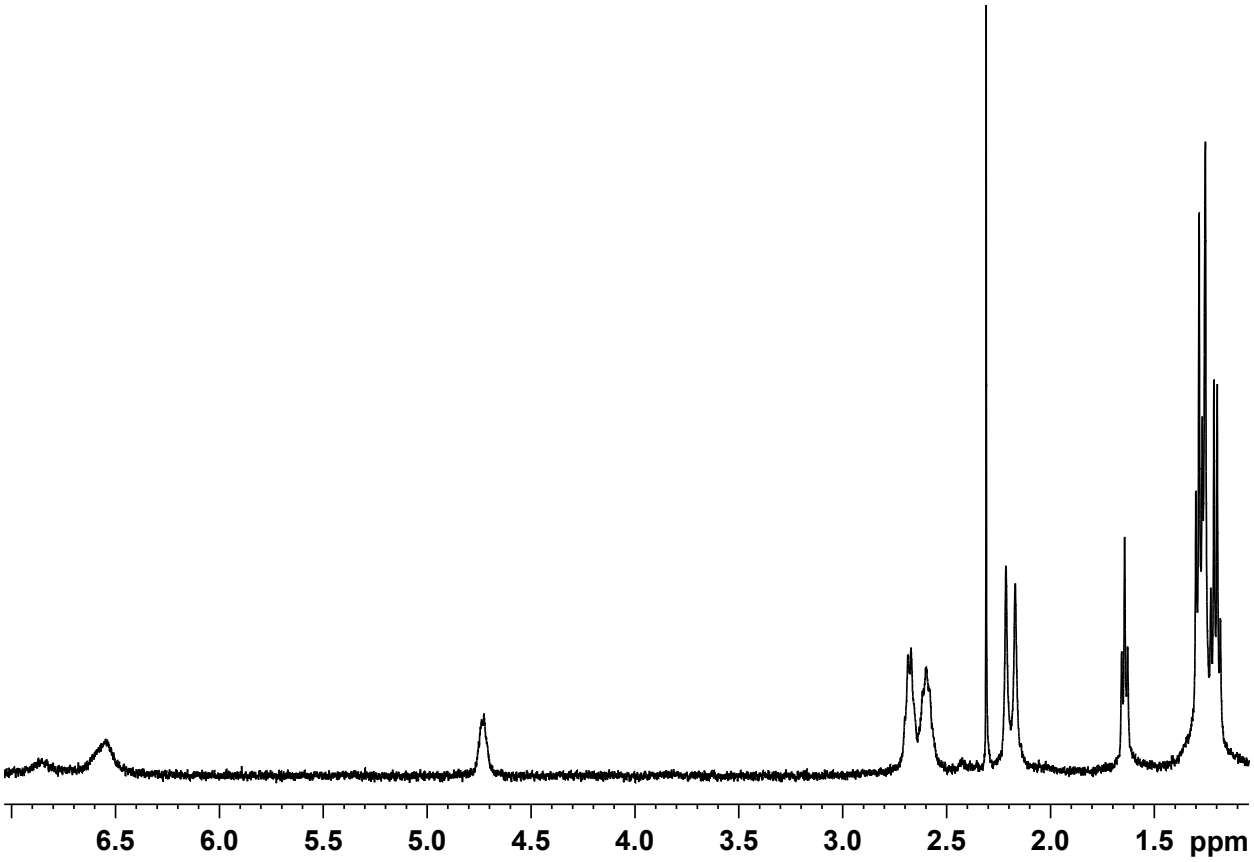


Figure 51. 500 MHz proton NMR spectrum of nickel(II) pyrazoloporphyrin **31c** in TFA-$CDCl_3$.

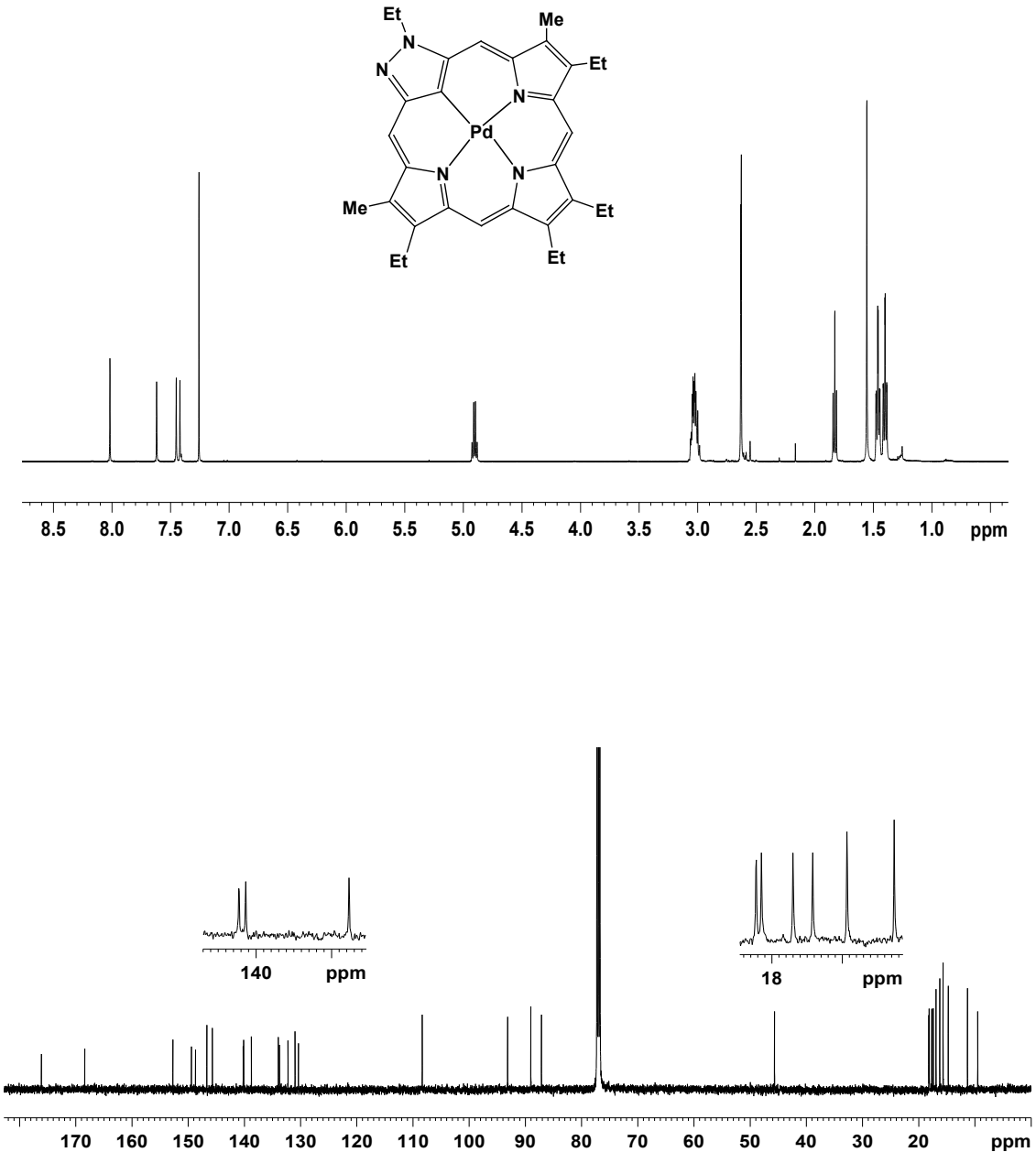


Figure 52. 500 MHz proton NMR and 125 MHz carbon-13 NMR spectra of palladium(II) pyrazoloporphyrin **32c** in $CDCl_3$.

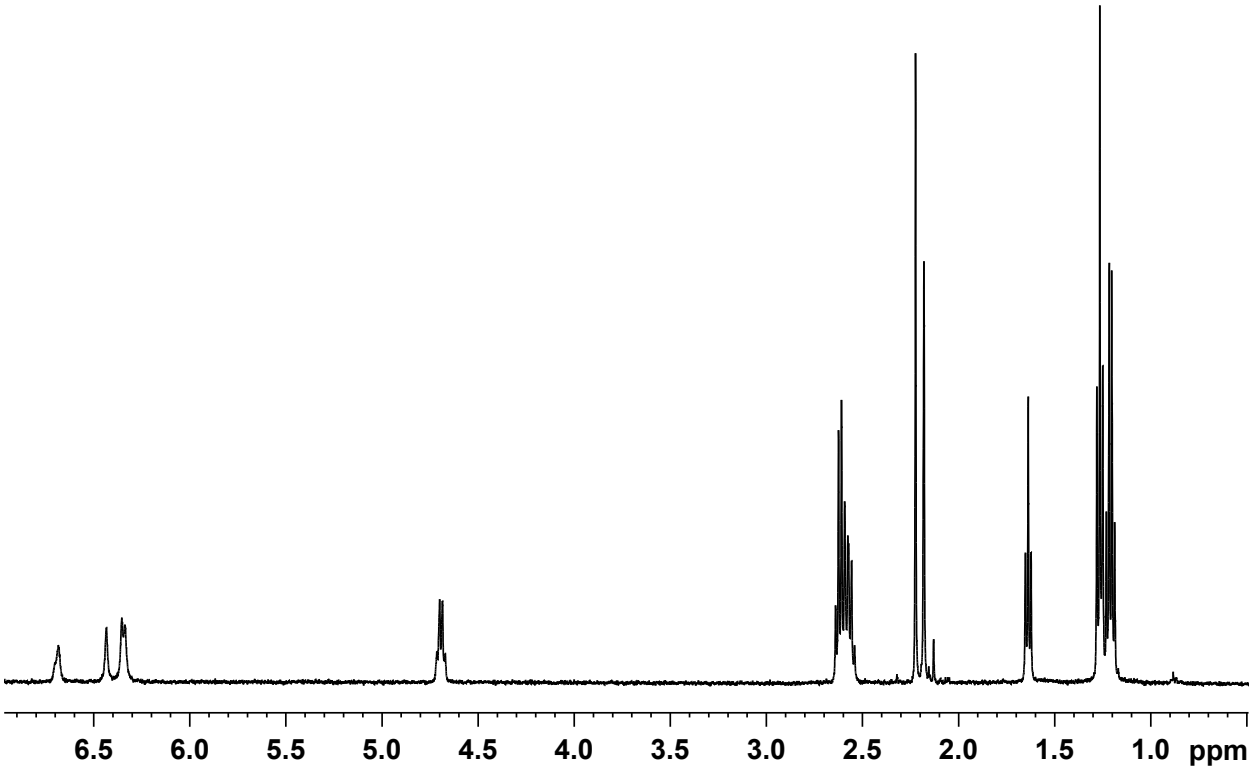


Figure 53. 500 MHz proton NMR spectrum of palladium(II) pyrazoloporphyrin **32c** in TFA-$CDCl_3$.

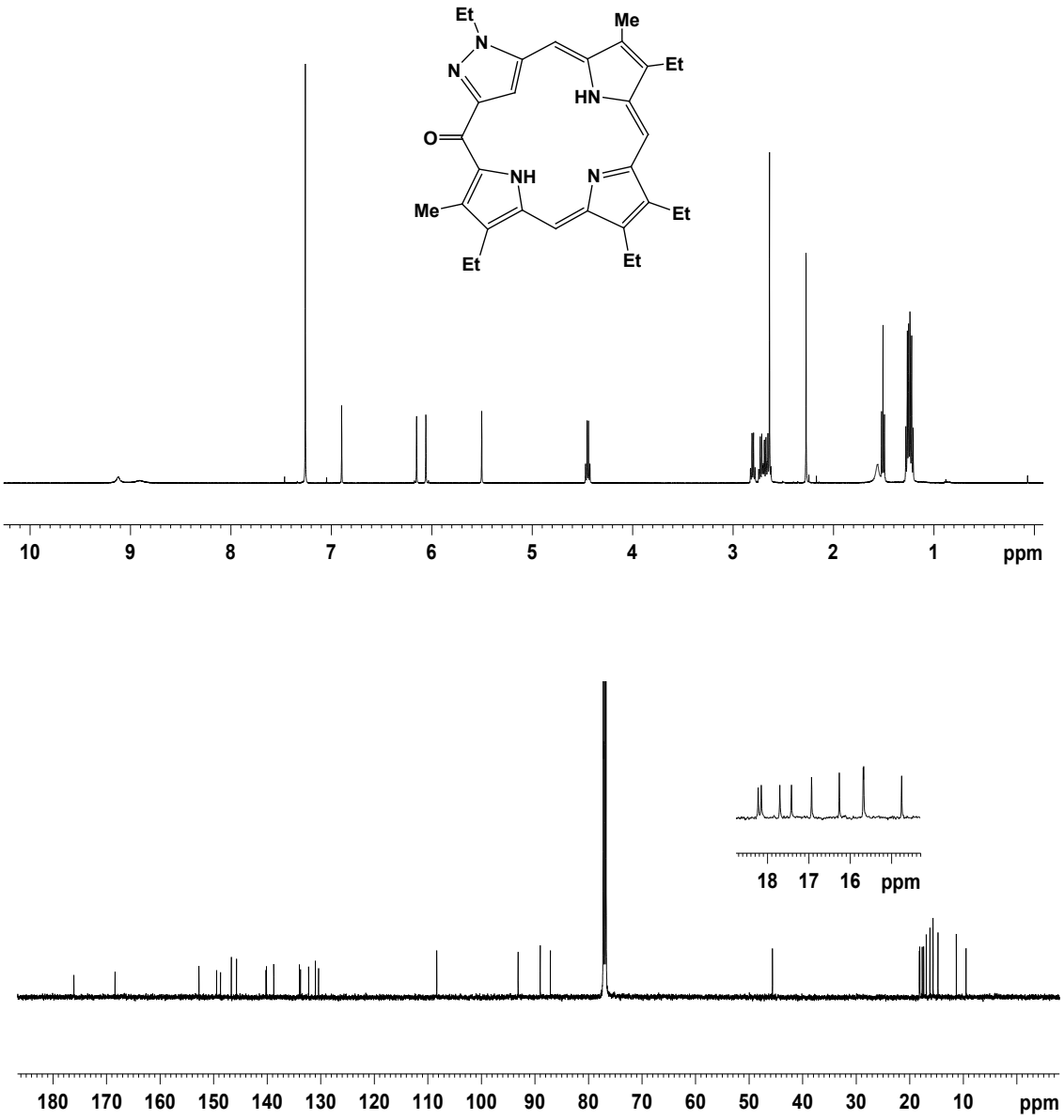


Figure 54. 500 MHz proton NMR and 125 MHz carbon-13 NMR spectra of pyrazolo-oxophlorin **28c** in $CDCl_3$.

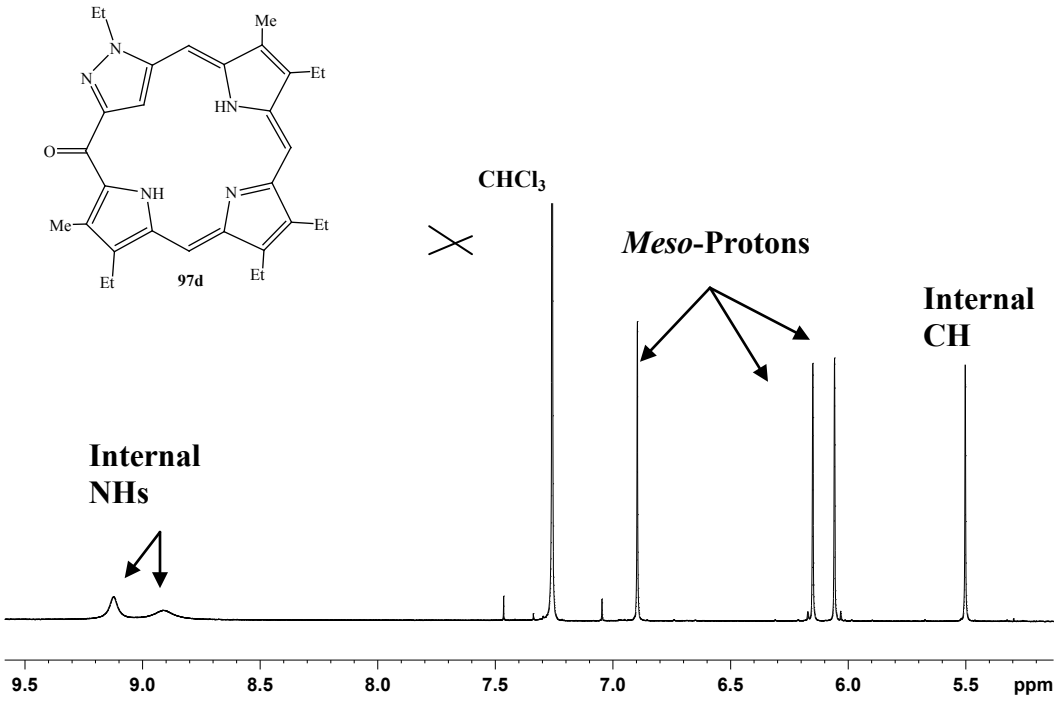


Figure 55. Partial 500 MHz proton NMR spectrum of oxophlorin analogue **28c** in $CDCl_3$ showing details of the downfield region.

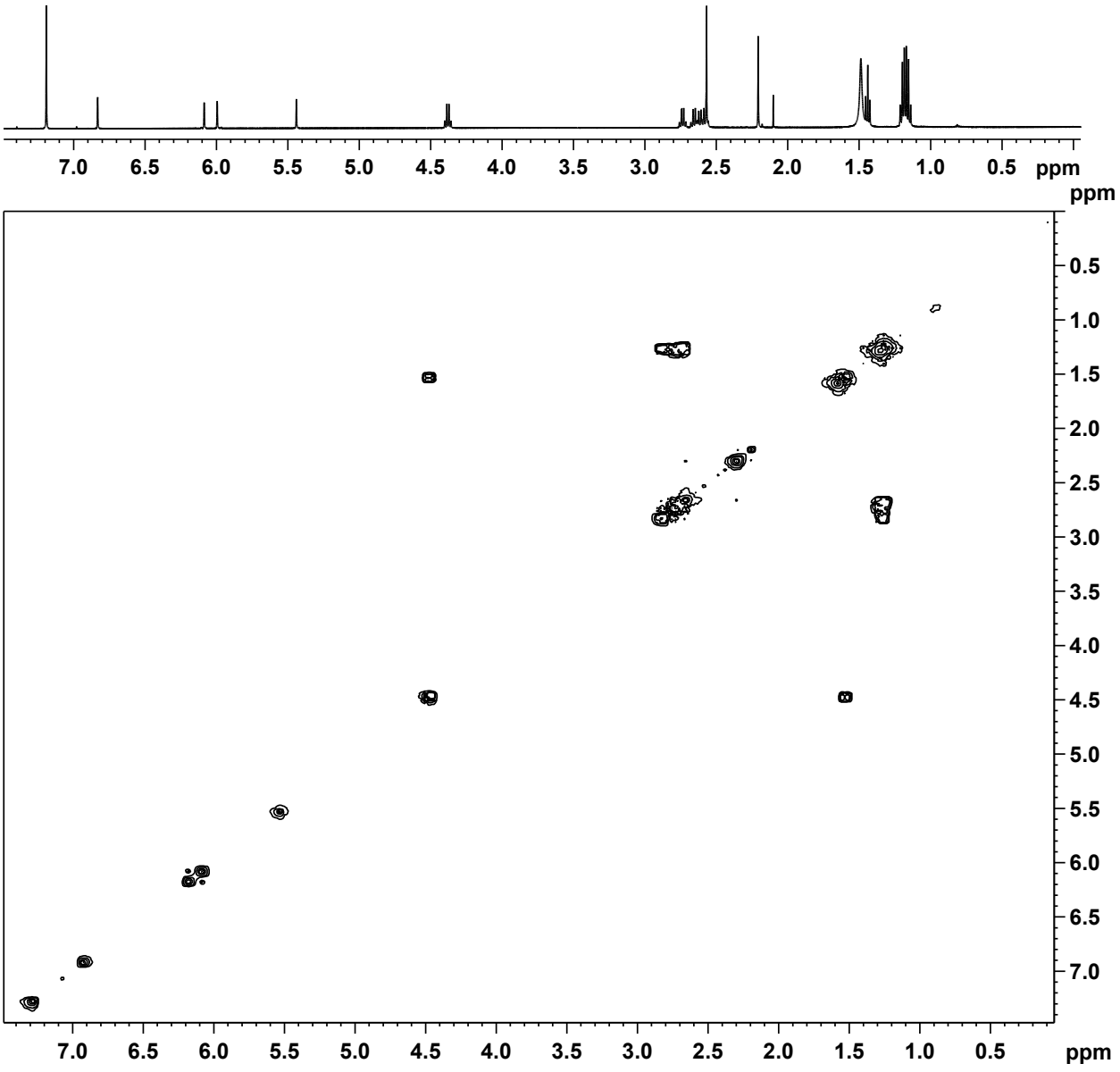


Figure 56. ^{1}H-^{1}H COSY NMR spectrum of **28c** in $CDCl_3$.

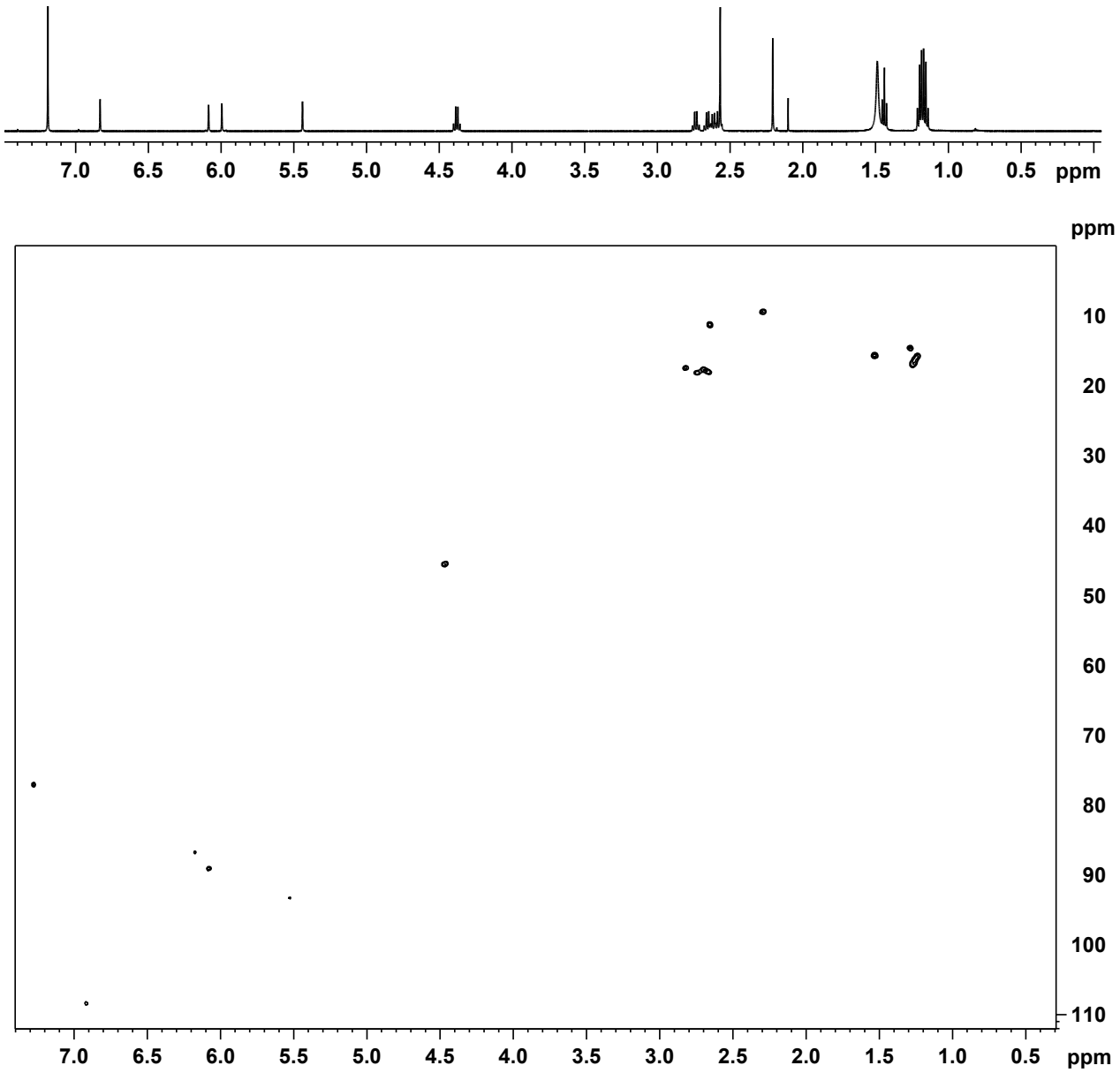


Figure 57. HSQC NMR spectrum of pyrazolo-oxophlorin **28c** in $CDCl_3$.

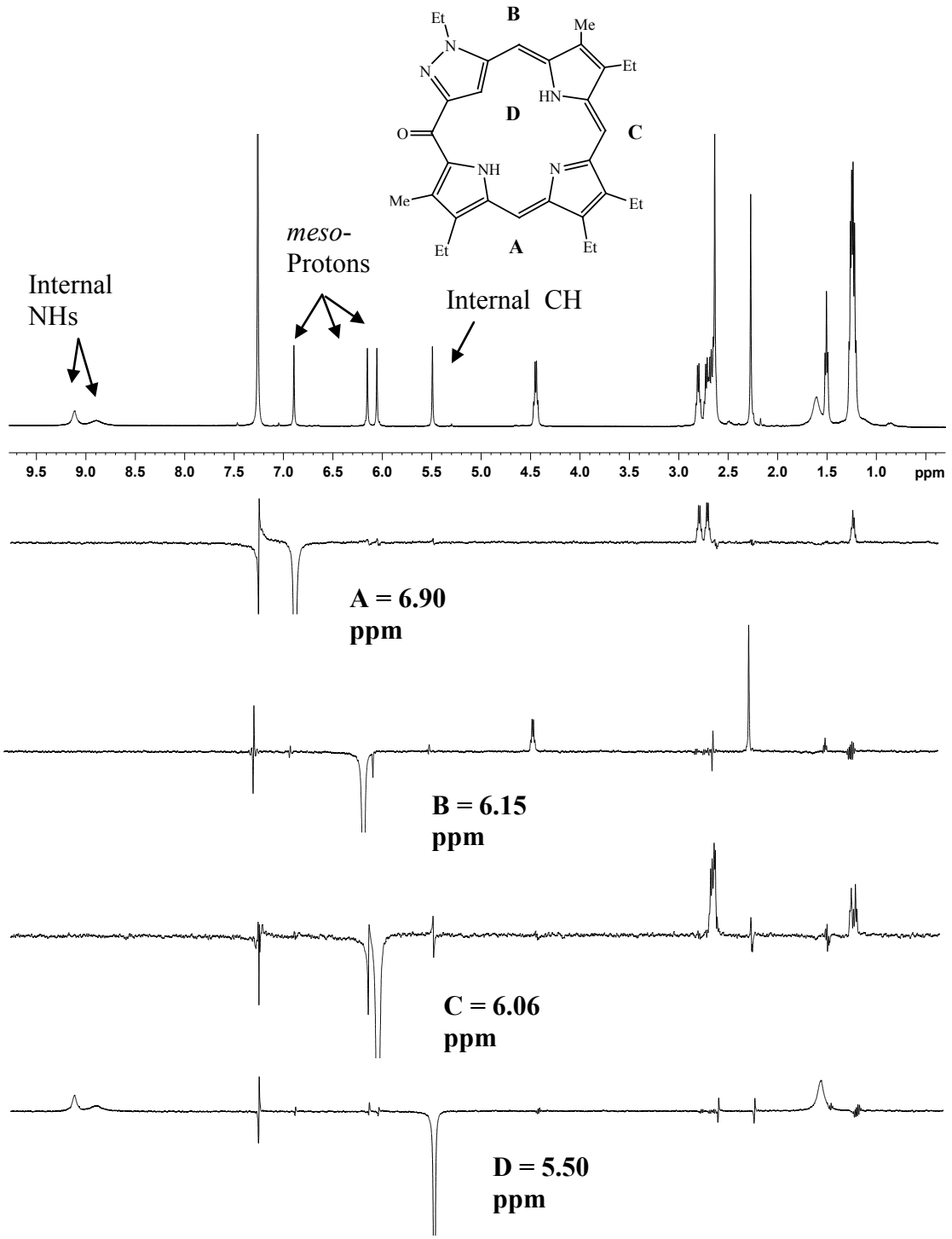


Figure 58. Selected nOe difference proton NMR spectra of oxophlorin analogue **28c** in $CDCl_3$.

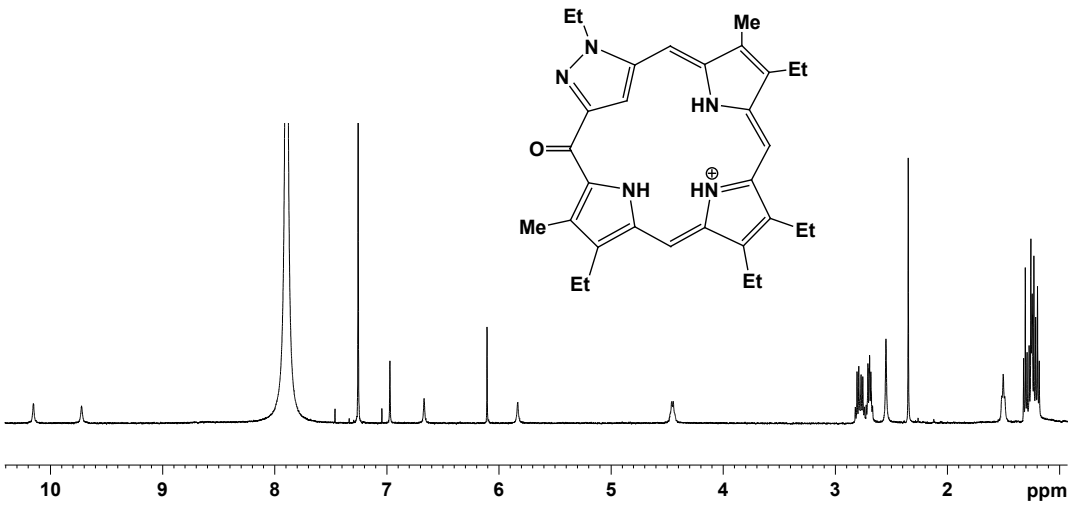


Figure 59. 500 MHz proton NMR spectrum of **28c** in trace TFA-$CDCl_3$.

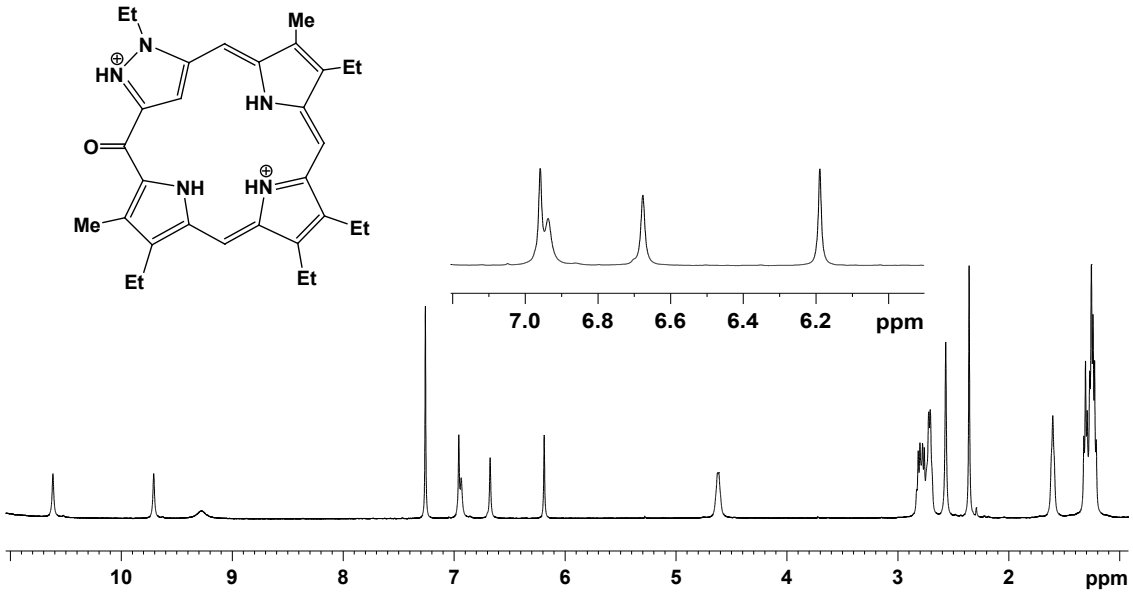


Figure 60. 500 MHz proton NMR spectrum of **28c** in TFA-$CDCl_3$.

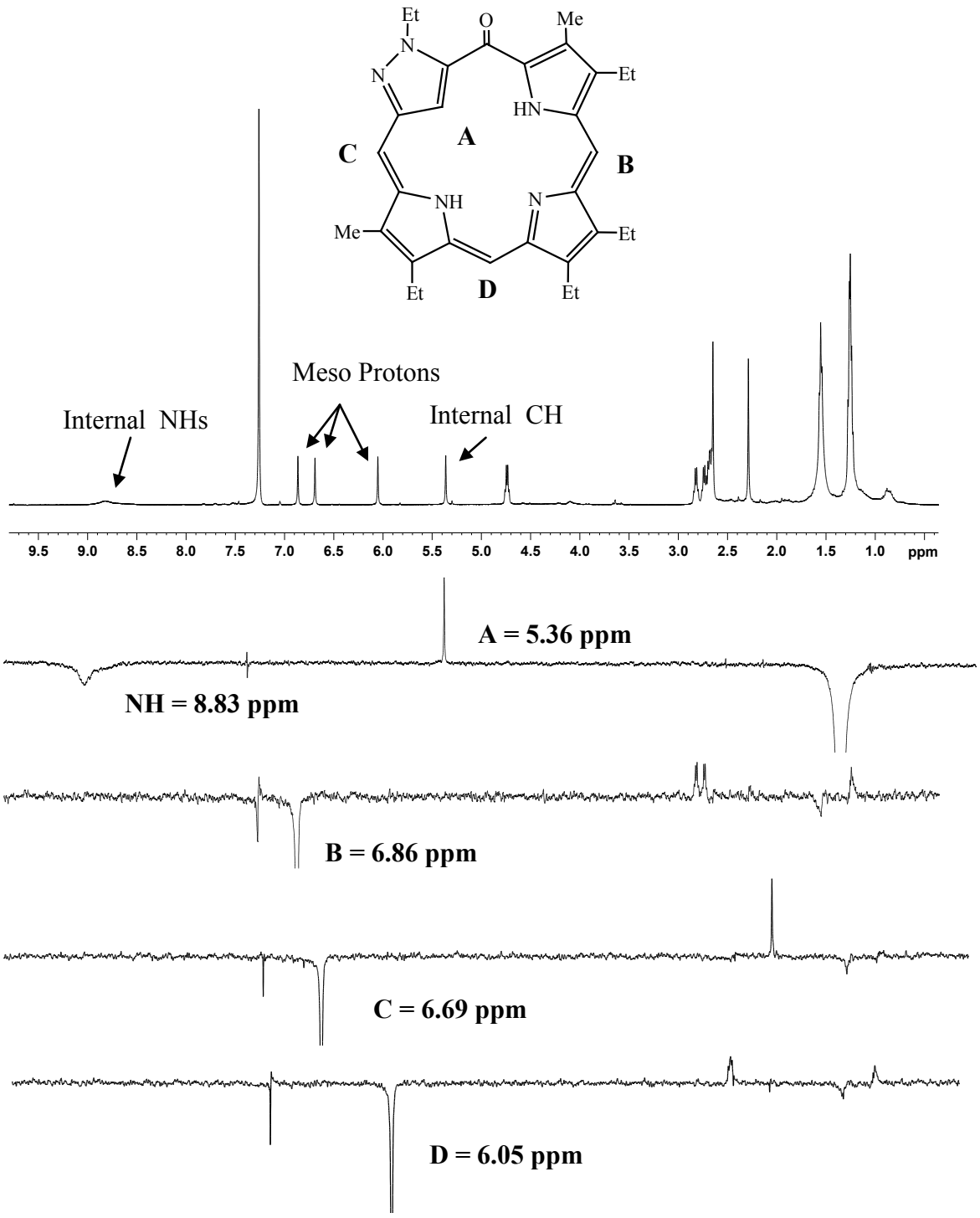
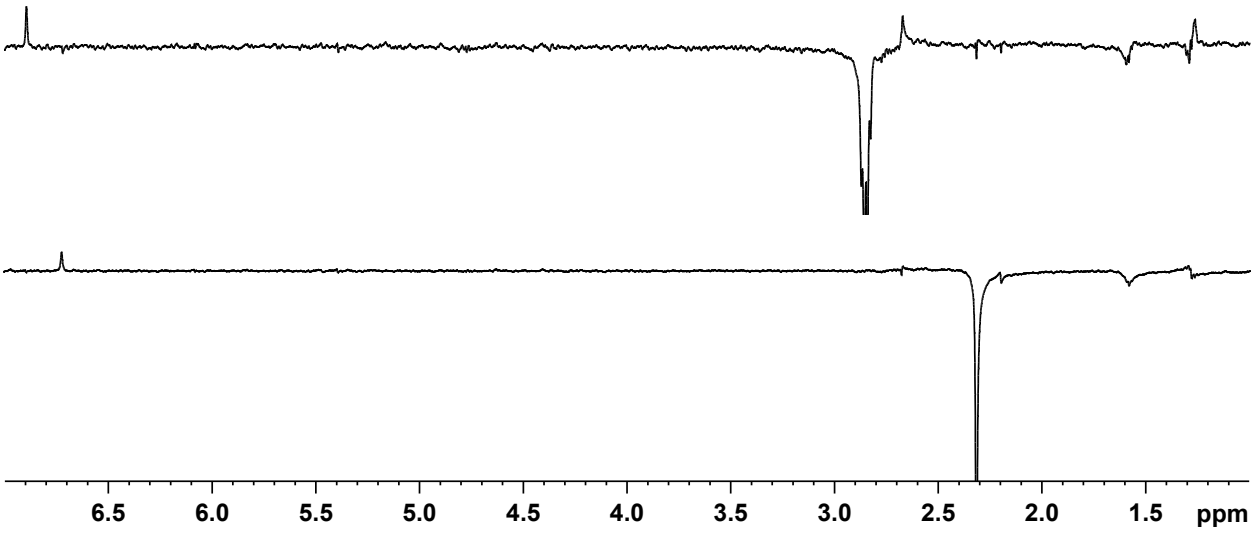


Figure 61. Selected nOe difference proton NMR spectra of **29** in $CDCl_3$.



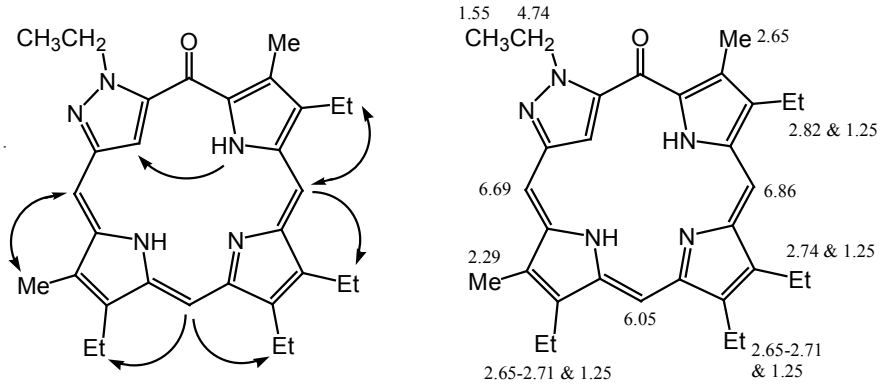


Figure 62. Further nOe difference proton NMR spectra, nOe correlations and partial proton NMR assignments for pyrazolo-oxophlorin **29** in $CDCl_3$.

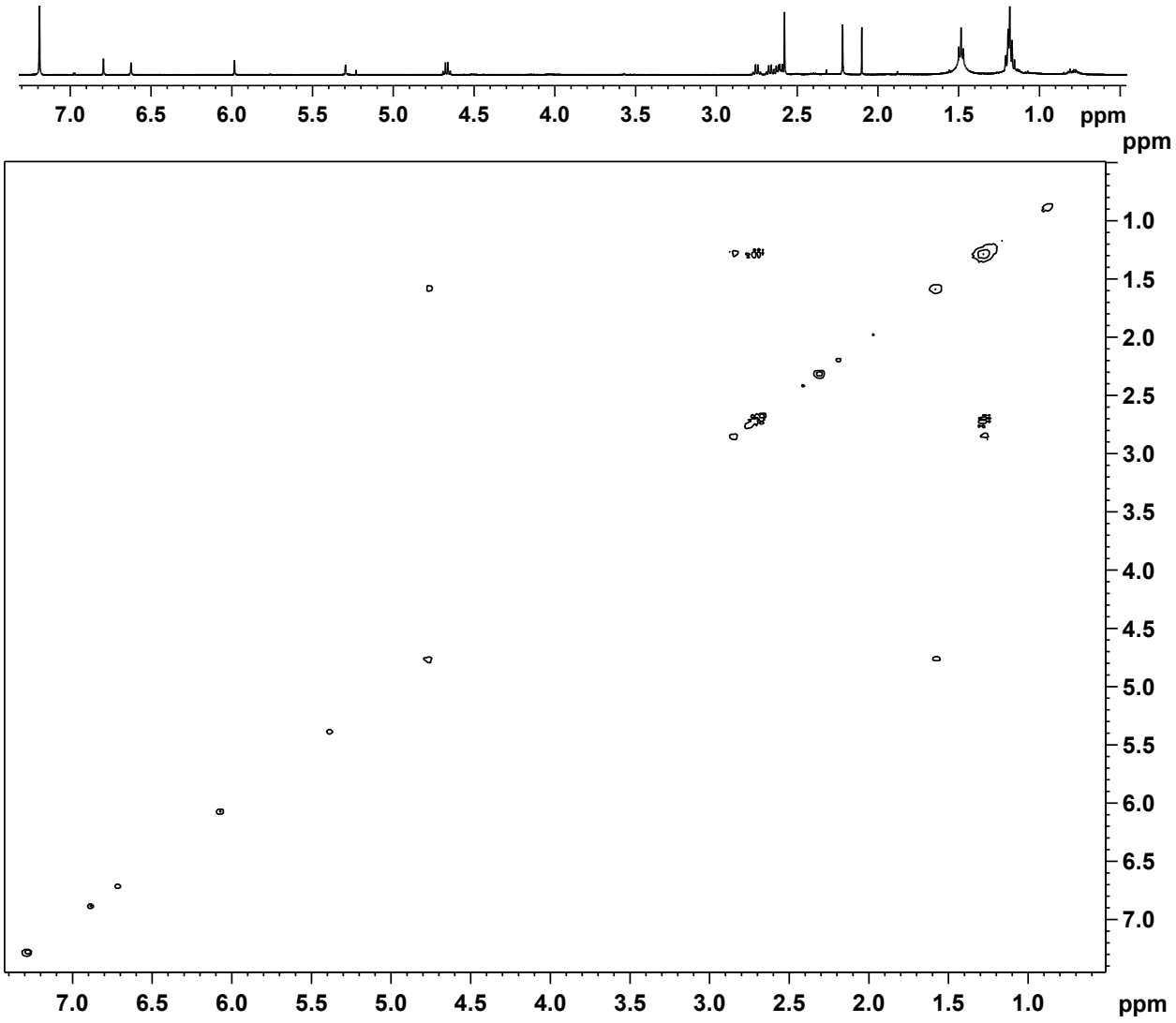


Figure 63. ^{1}H-^{1}H COSY NMR spectrum of pyrazolo-oxophlorin **29** in $CDCl_3$.

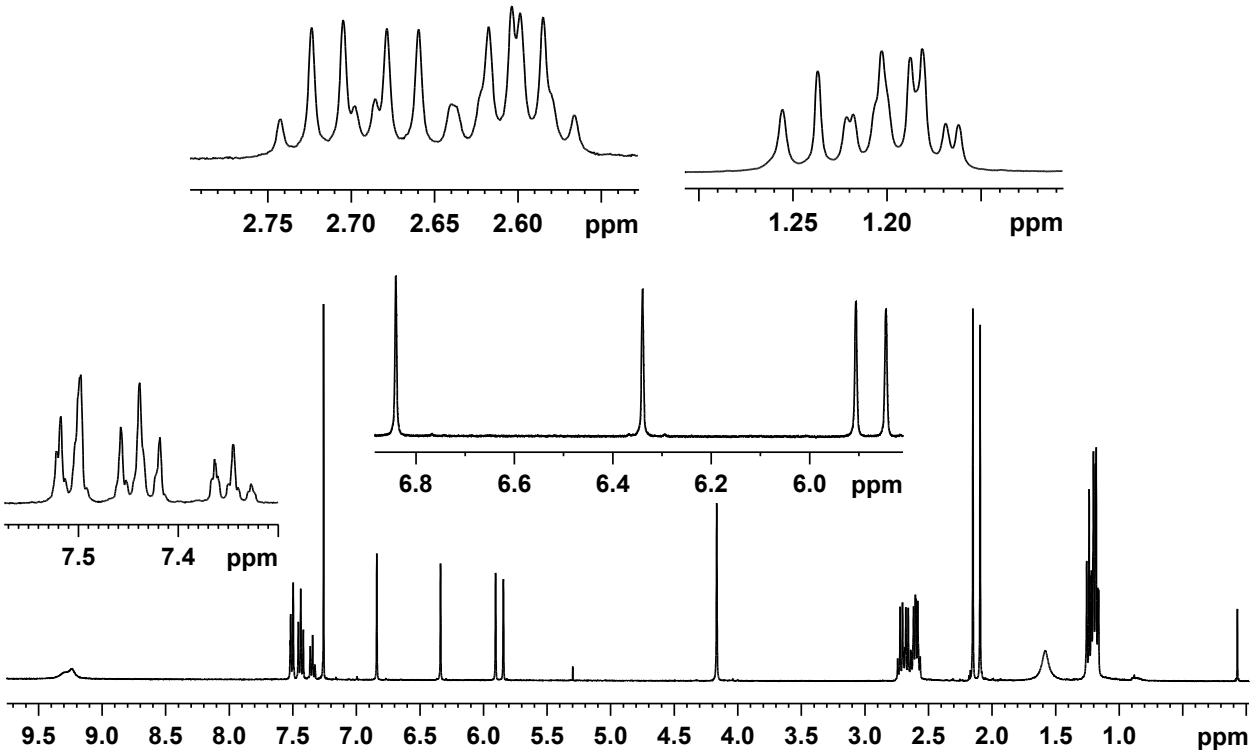


Figure 64. 400 MHz proton NMR spectrum of pyrazolophlorin **24a** in $CDCl_3$.

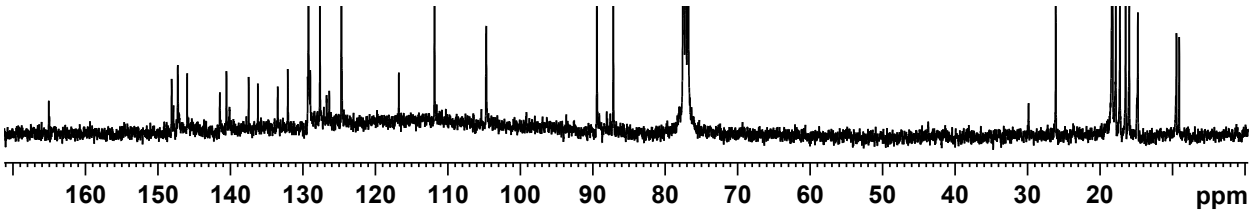


Figure 65. 100 MHz proton NMR spectrum of pyrazolophlorin **24a** in $CDCl_3$.

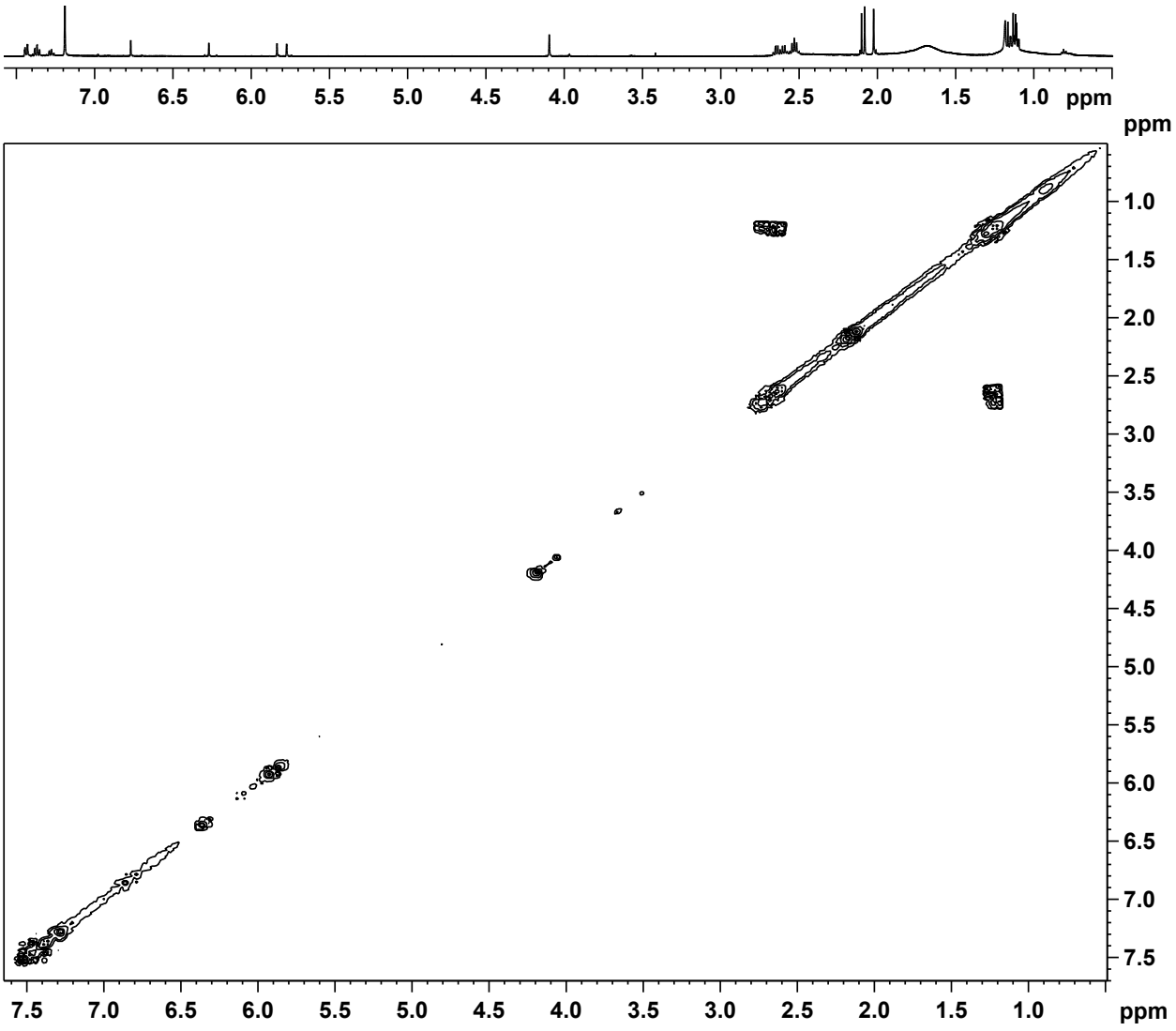


Figure 66. ^{1}H-^{1}H COSY NMR spectrum of pyrazolophlorin **24a** in $CDCl_3$.

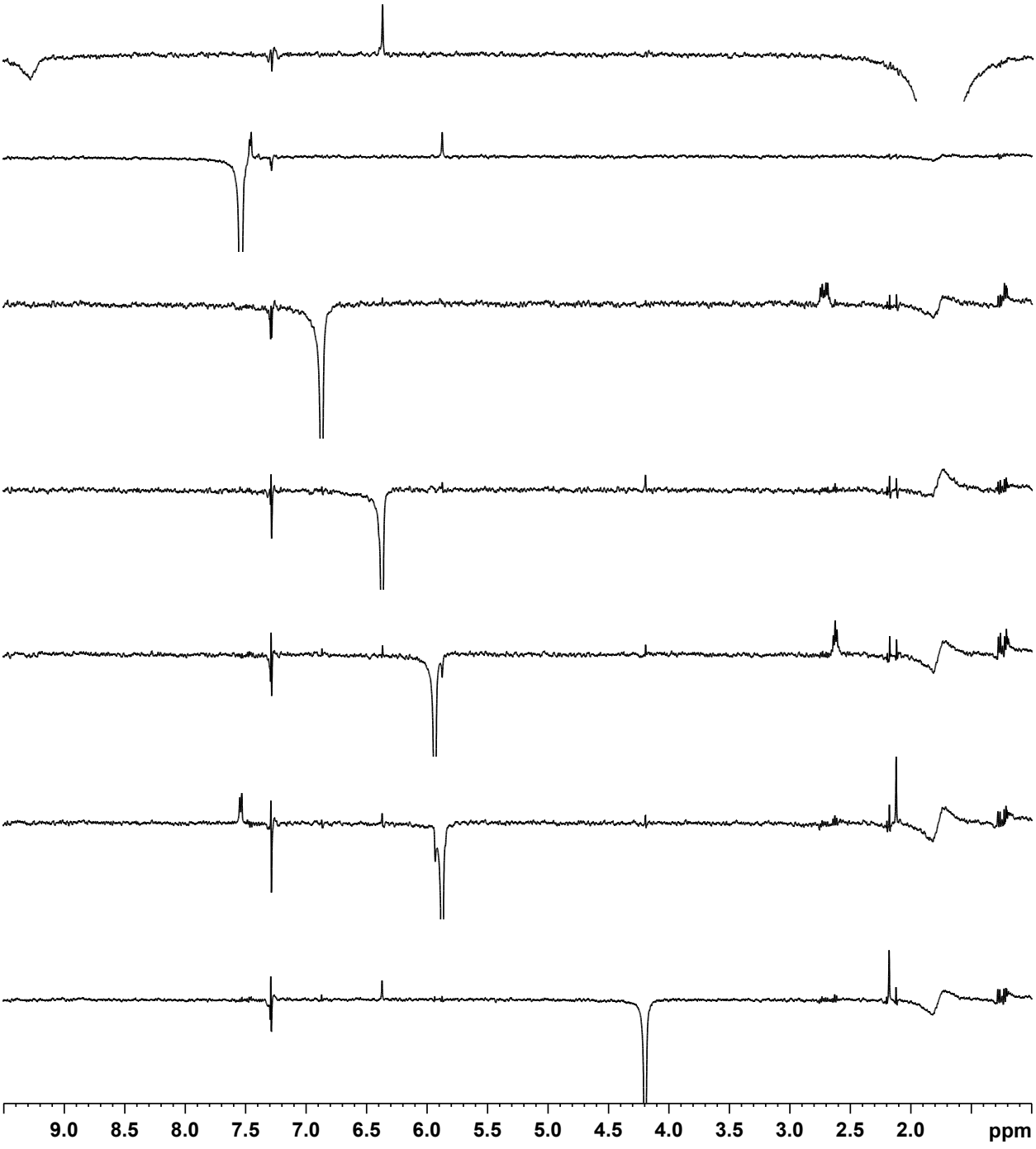


Figure 67. Selected nOe difference proton NMR spectra of pyrazolophlorin **24a** in $CDCl_3$.

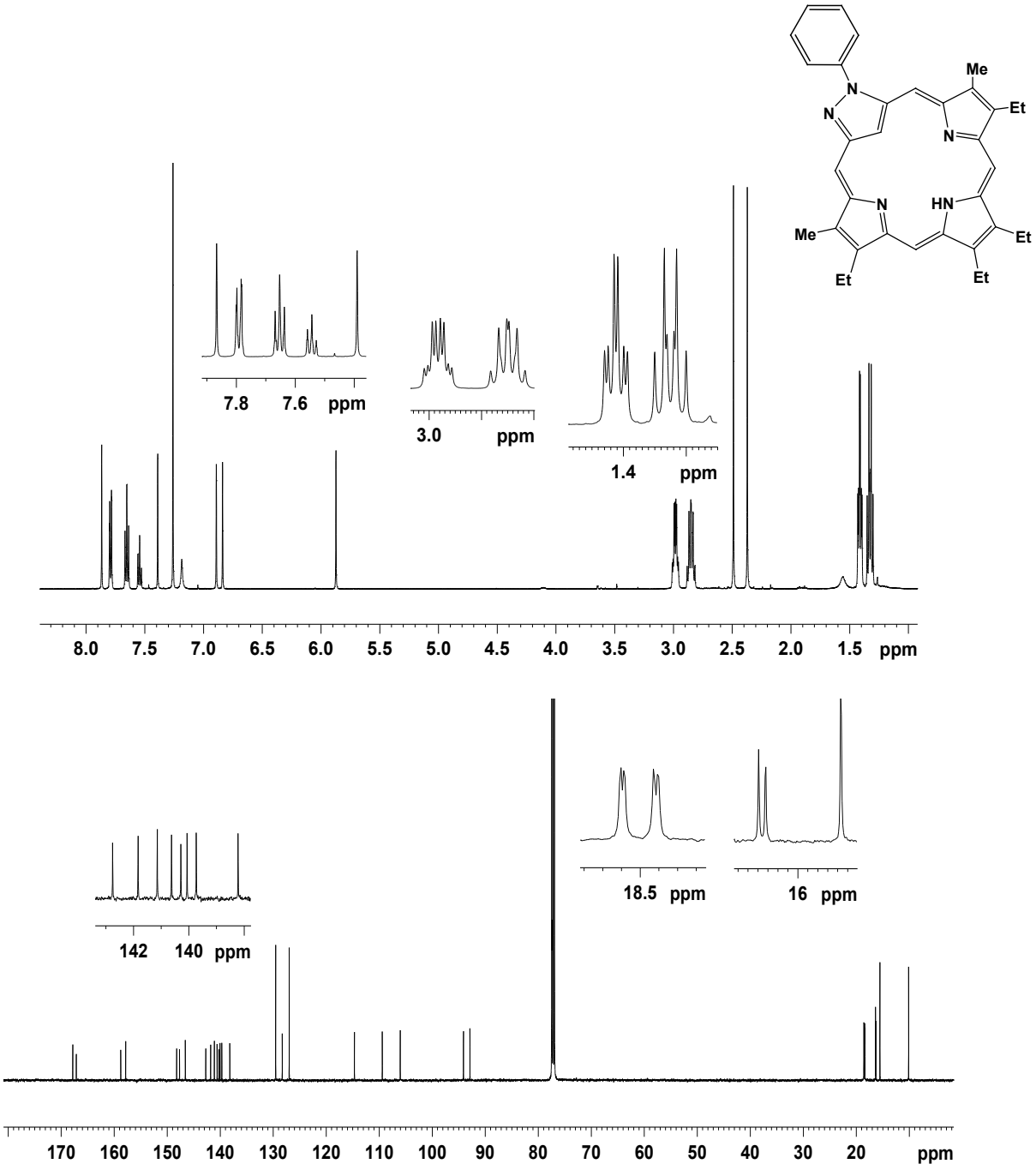


Figure 68. 500 MHz proton NMR and 125 MHz carbon-13 NMR spectra of pyrazoloporphyrin **25a** in $CDCl_3$.

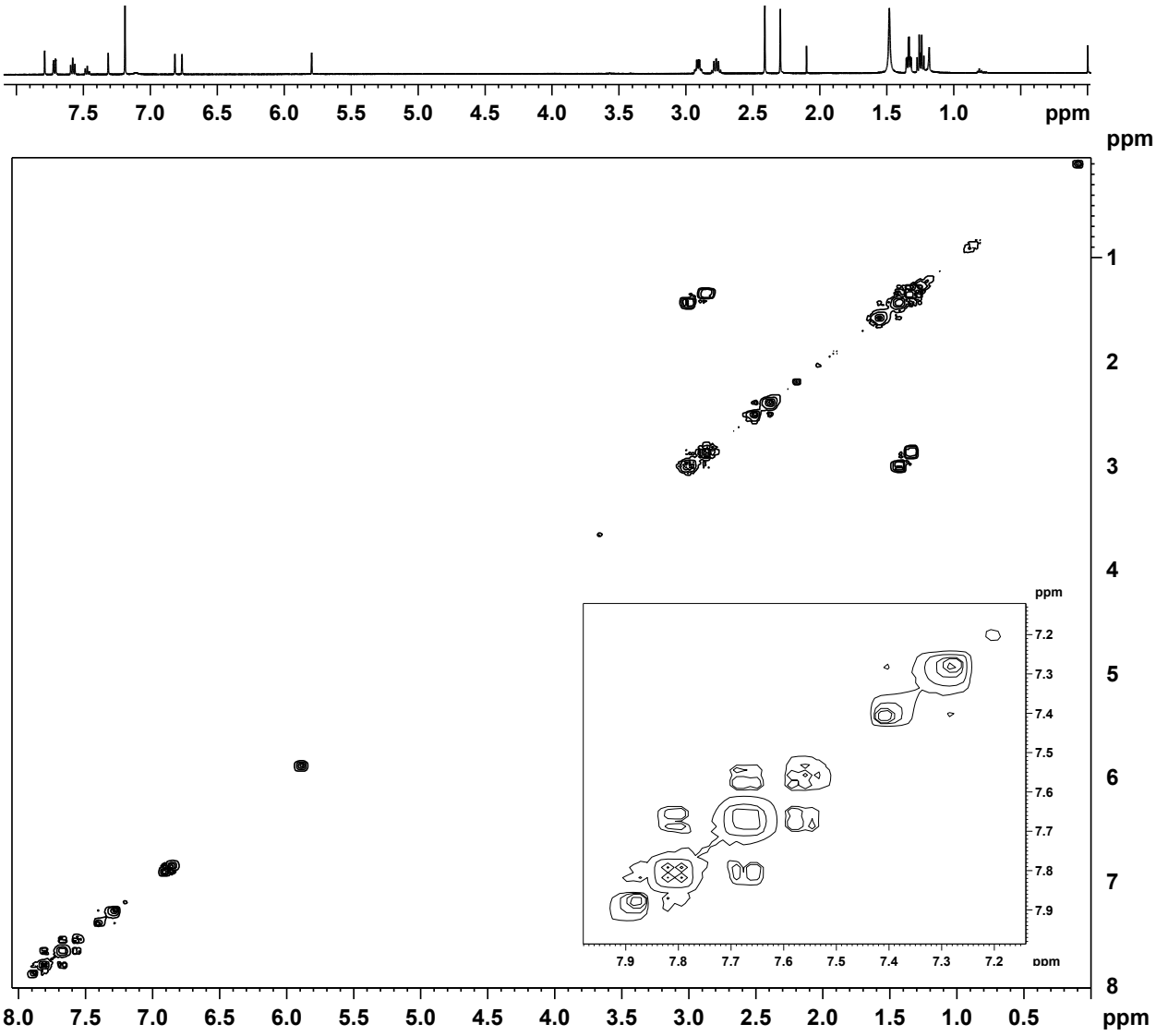


Figure 69. 500 MHz proton NMR spectrum of pyrazoloporphyrin **25b** in $CDCl_3$.

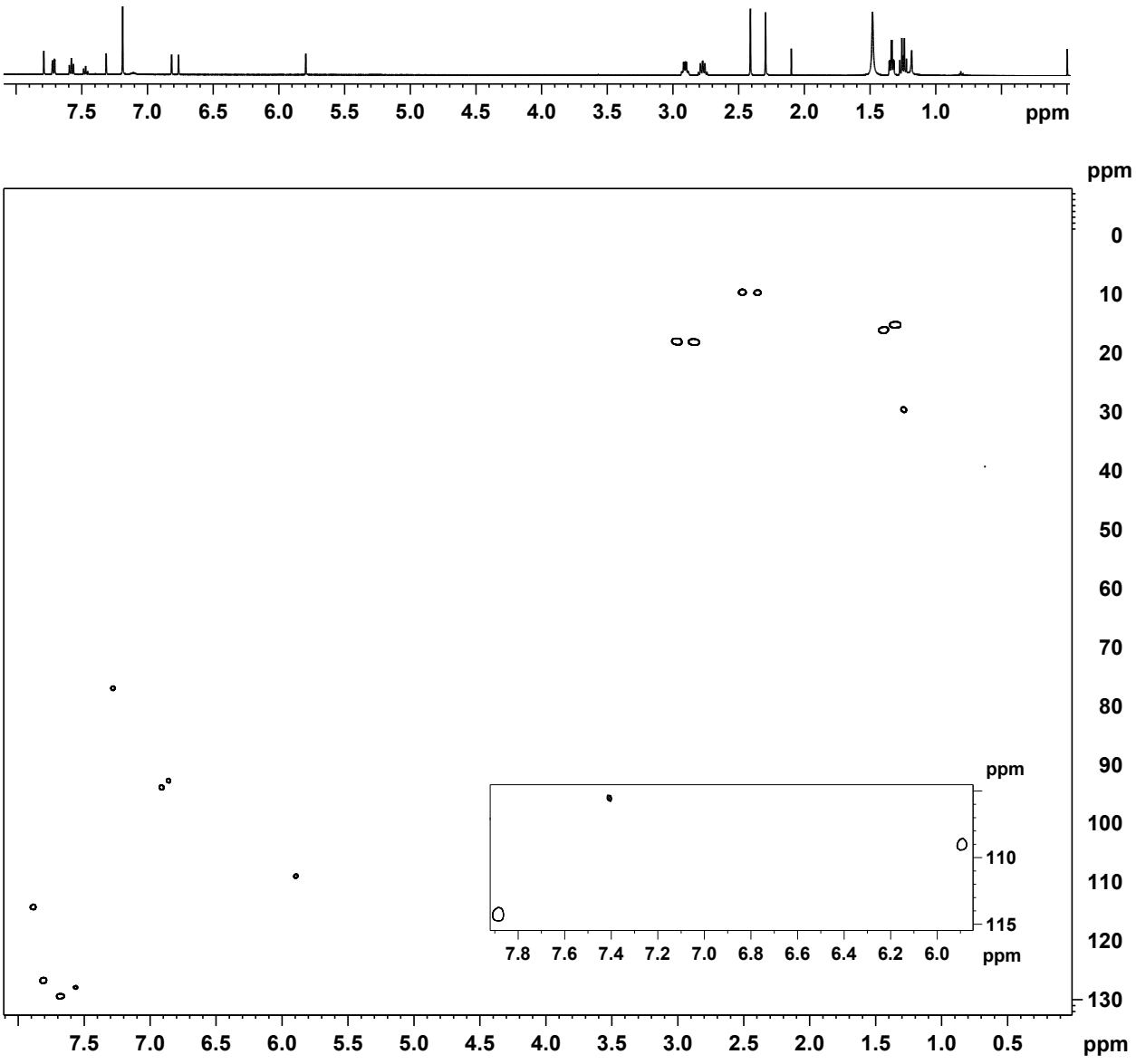


Figure 70. HSQC NMR spectrum of pyrazoloporphyrin **25a** in $CDCl_3$.

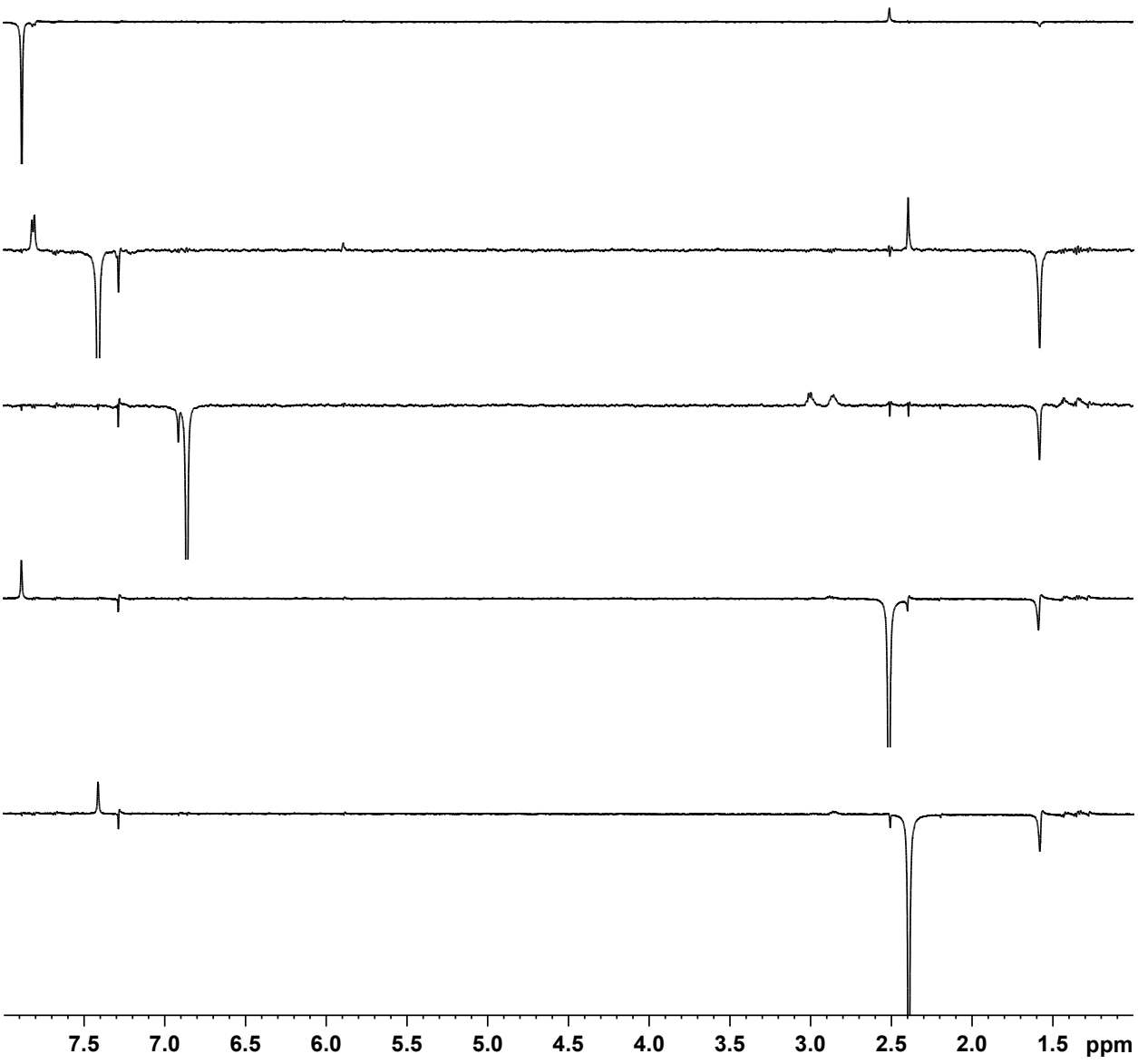


Figure 71. Selected nOe difference proton NMR spectra of pyrazoloporphyrin **25a** in $CDCl_3$.

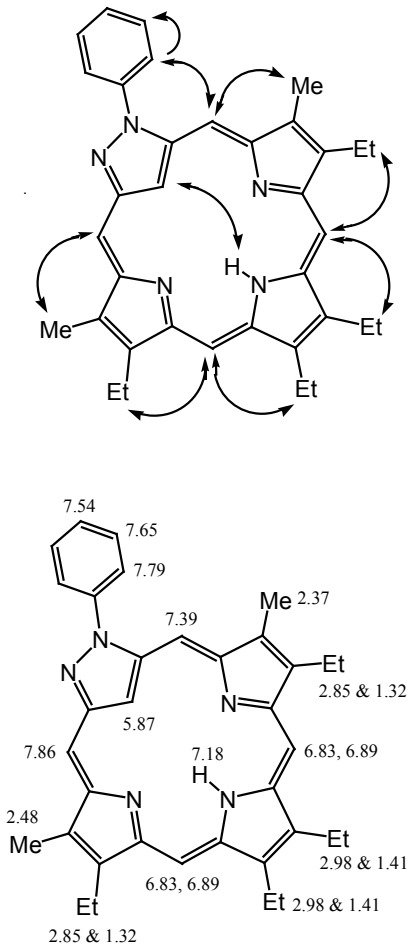


Figure 72. NOE correlations and partial proton NMR assignments for pyrazoloporphyrin **25a** in $CDCl_3$.

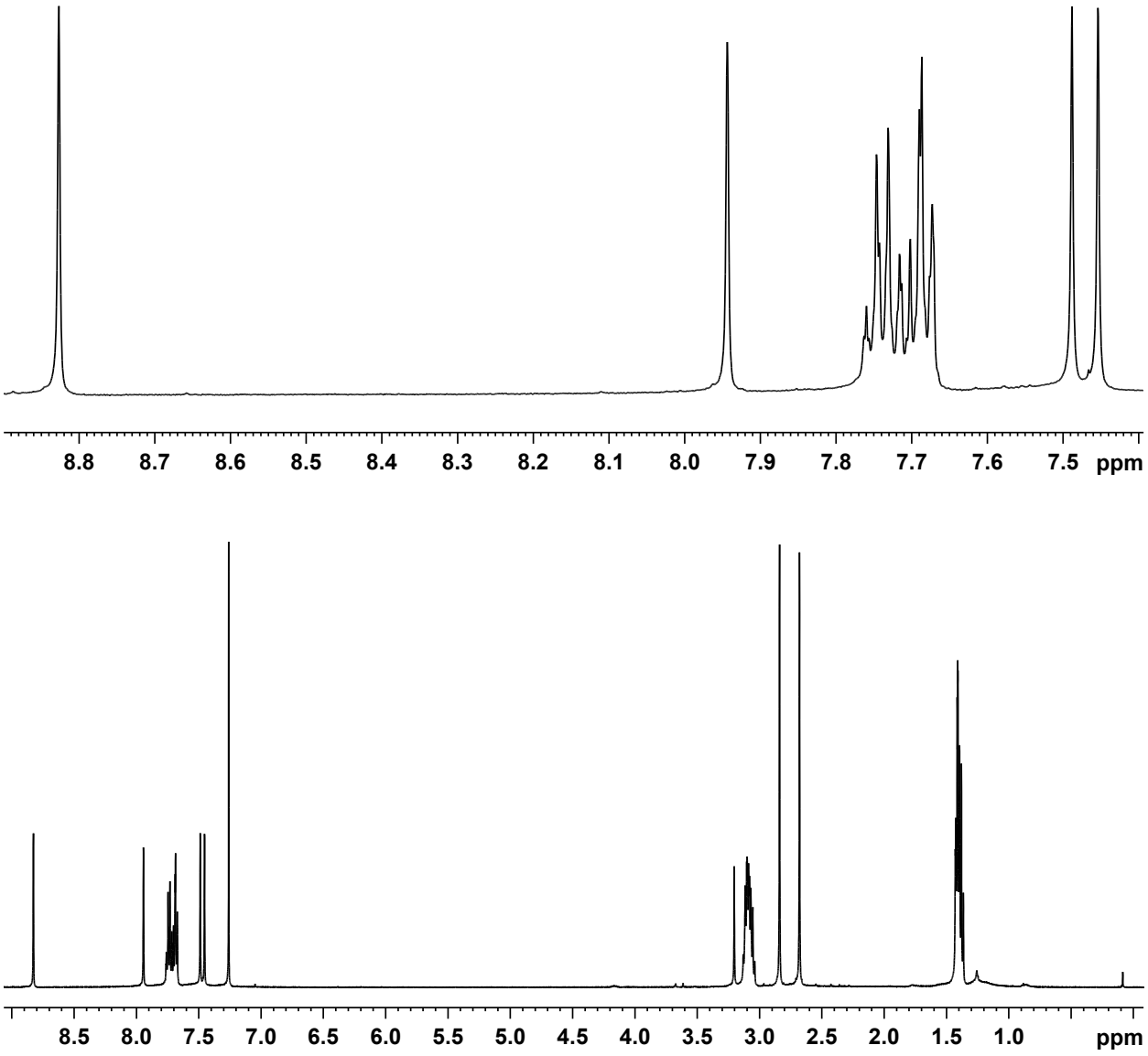


Figure 73. 500 MHz proton NMR spectrum of pyrazoloporphyrin **25a** in TFA-$CDCl_3$.

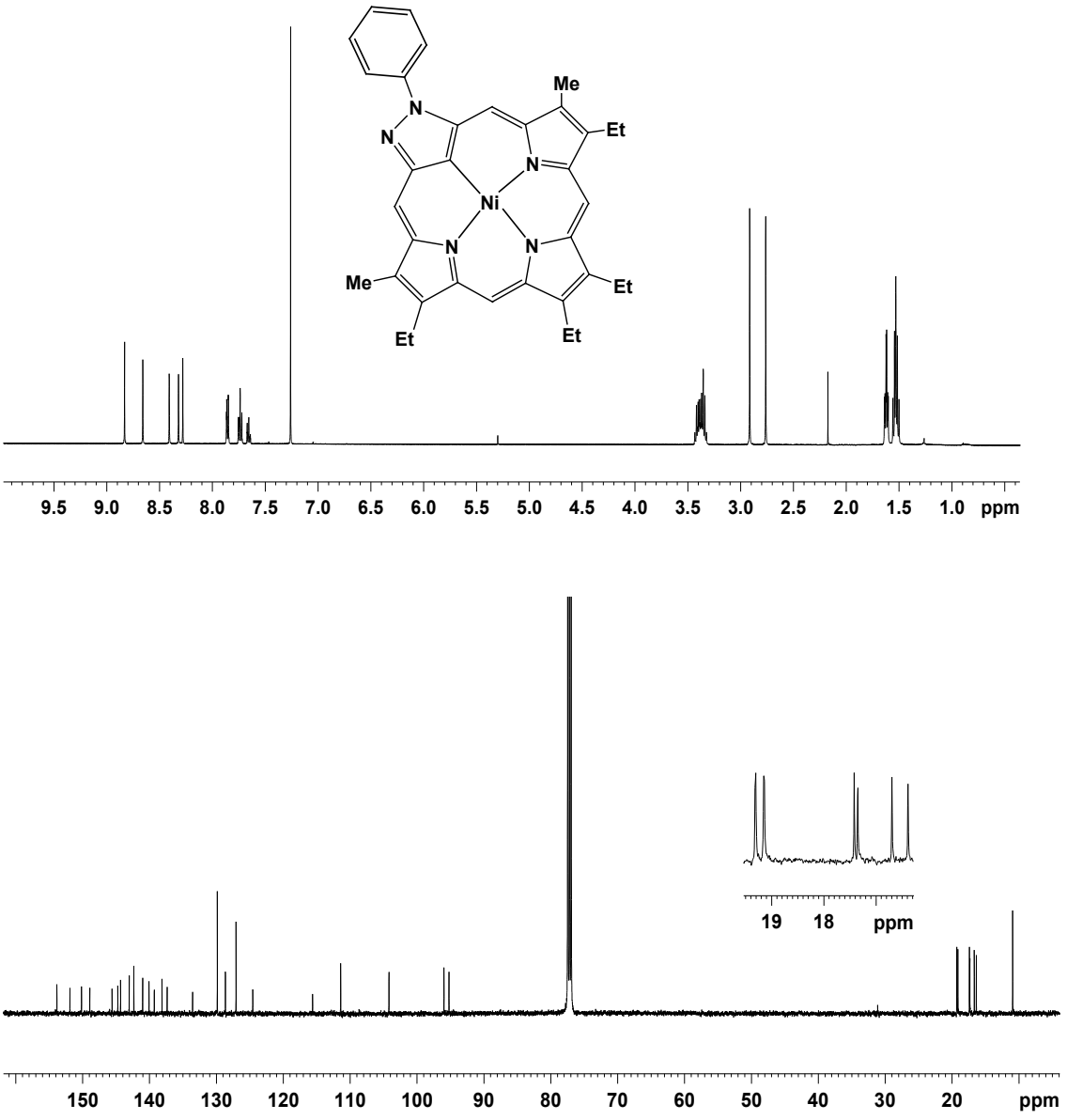


Figure 74. 500 MHz proton NMR and 125 MHz carbon-13 NMR spectra of nickel(II) pyrazoloporphyrin **31a** in $CDCl_3$.

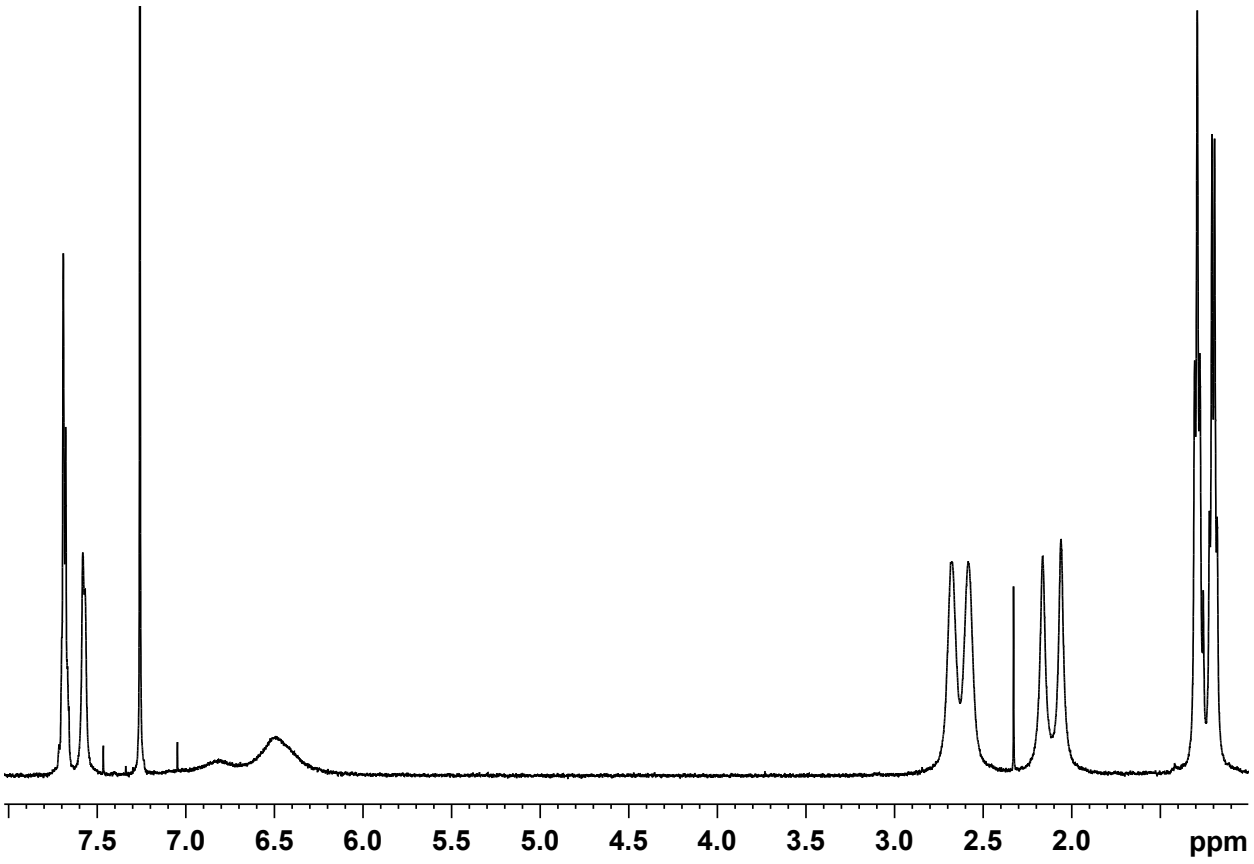


Figure 75. 500 MHz proton NMR and 125 MHz carbon-13 NMR spectra of nickel(II) pyrazoloporphyrin **31a** in TFA-$CDCl_3$.

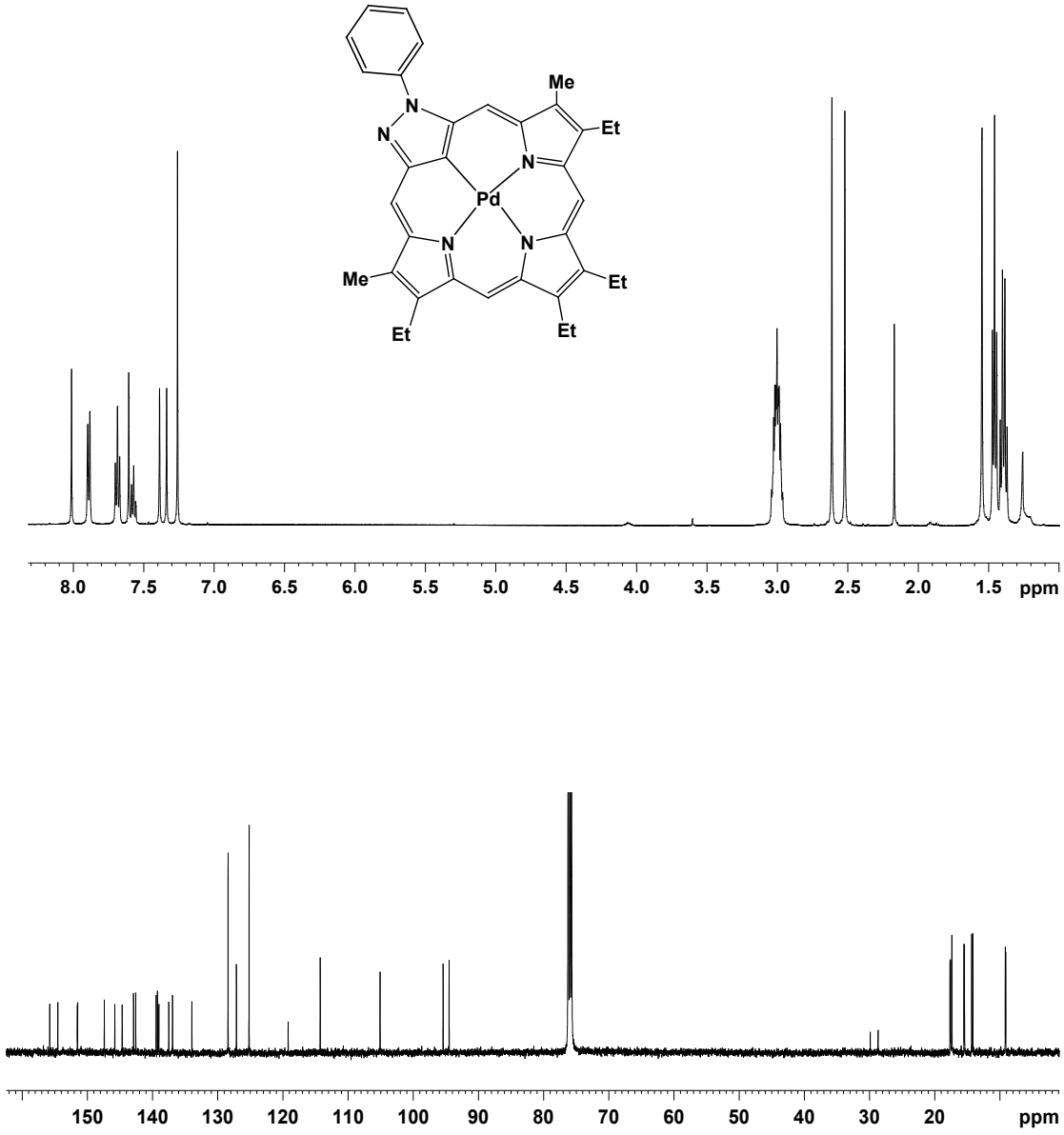


Figure 76. 500 MHz proton NMR and 125 MHz carbon-13 NMR spectra of palladium(II) pyrazoloporphyrin **32a** in $CDCl_3$.

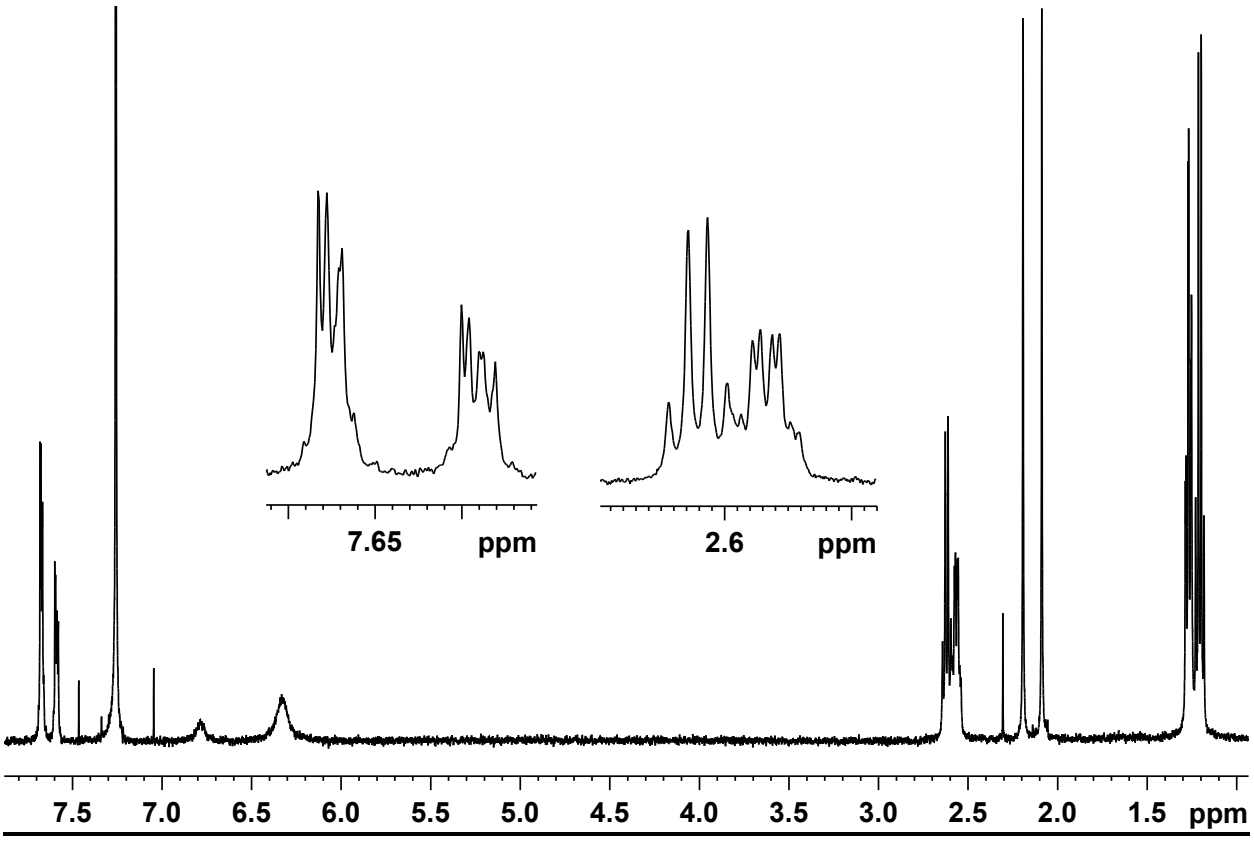


Figure 77. 500 MHz proton NMR spectrum of palladium(II) pyrazoloporphyrin **32a** in TFA-$CDCl_3$.

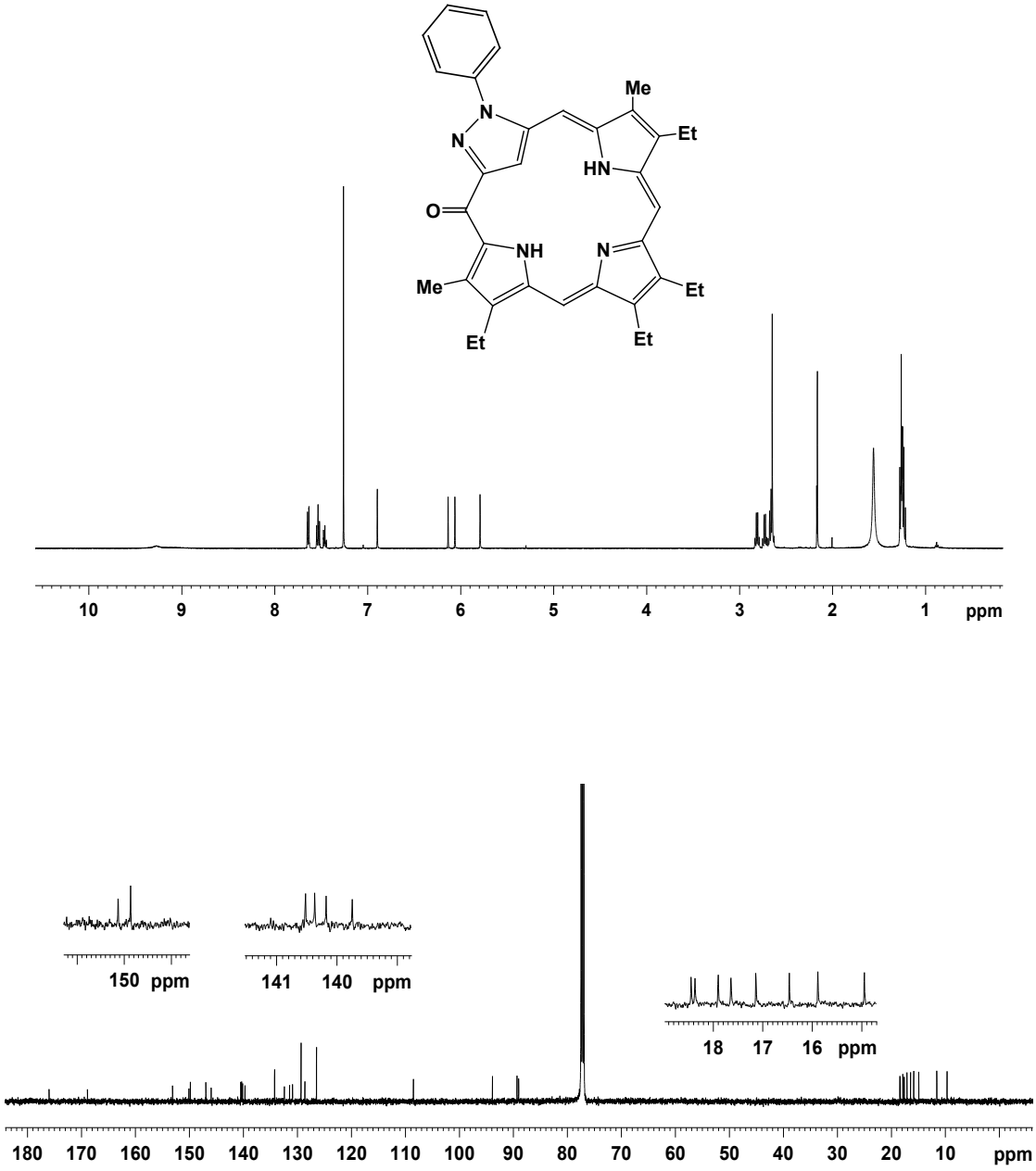


Figure 78. 500 MHz proton NMR and 125 MHz carbon-13 NMR spectra of oxophlorin analogue **28a** in $CDCl_3$.

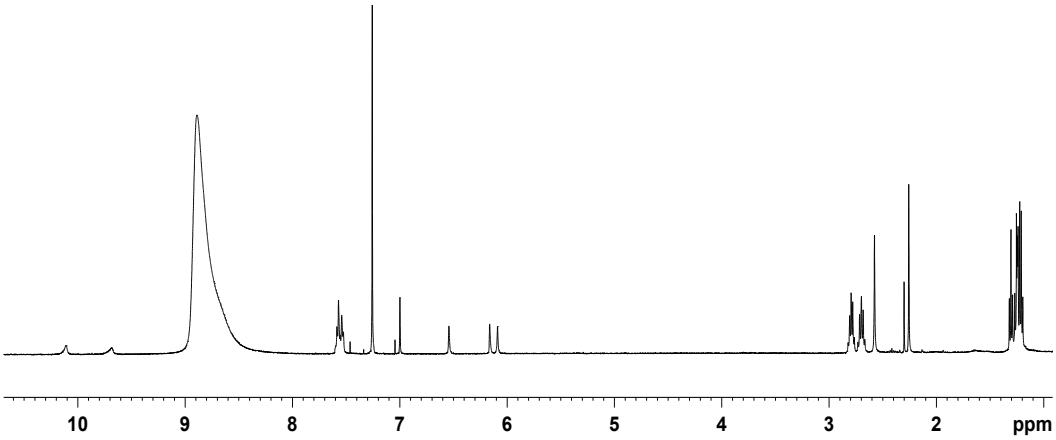


Figure 79. 500 MHz proton NMR spectrum **28a** in trace TFA-$CDCl_3$.

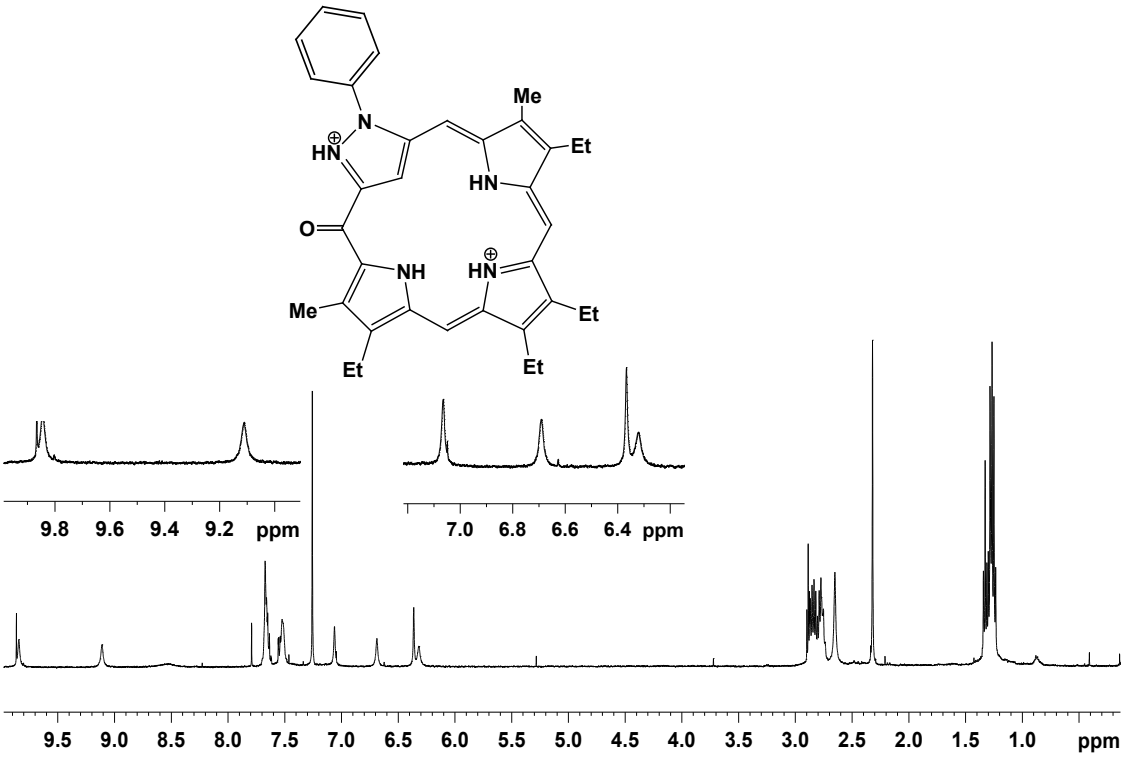


Figure 80. 500 MHz proton NMR spectrum of **28a** in TFA-$CDCl_3$.

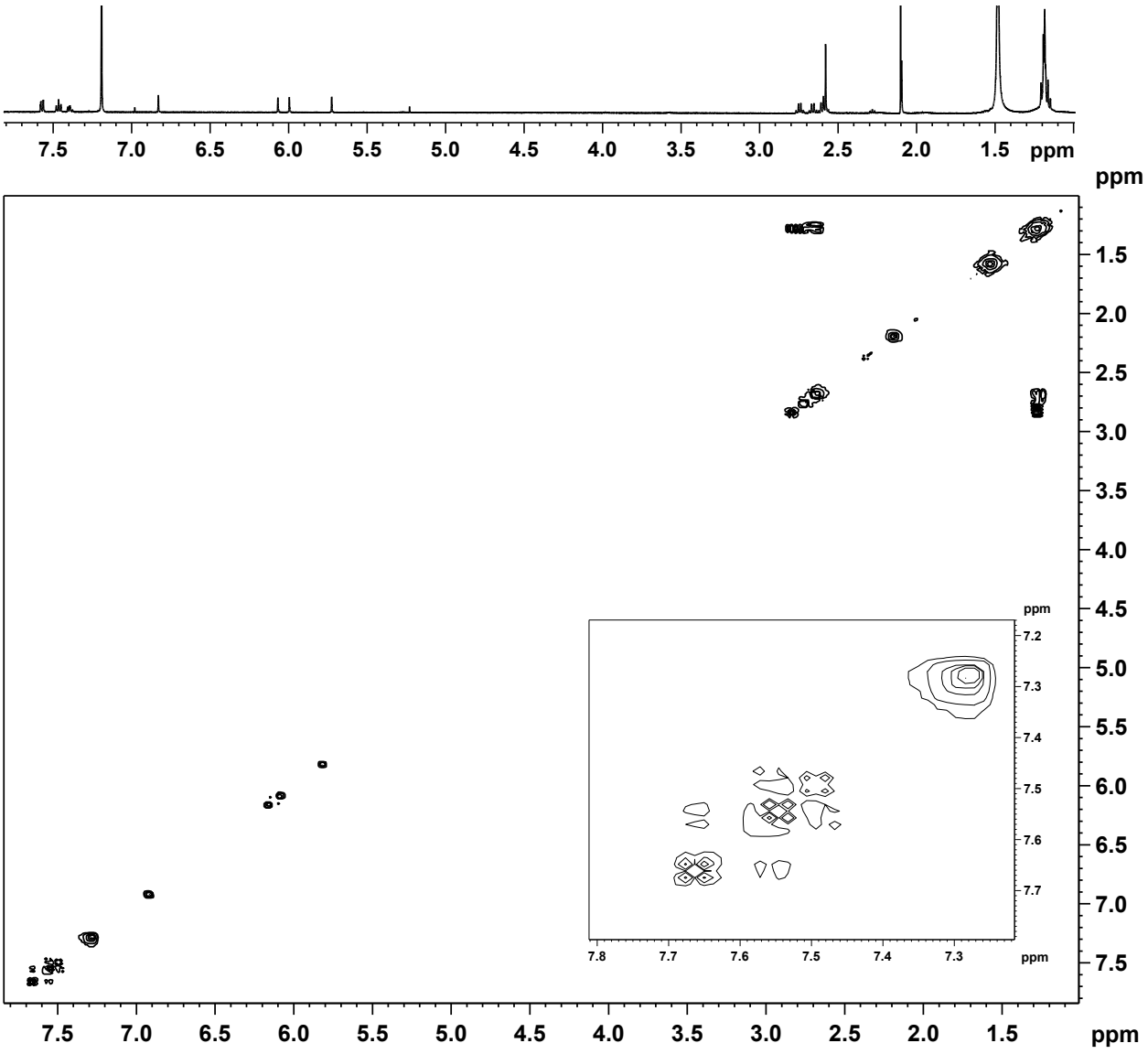


Figure 81. ^{1}H-^{1}H COSY NMR spectrum of pyrazolo-oxophlorin **28a** in $CDCl_3$.

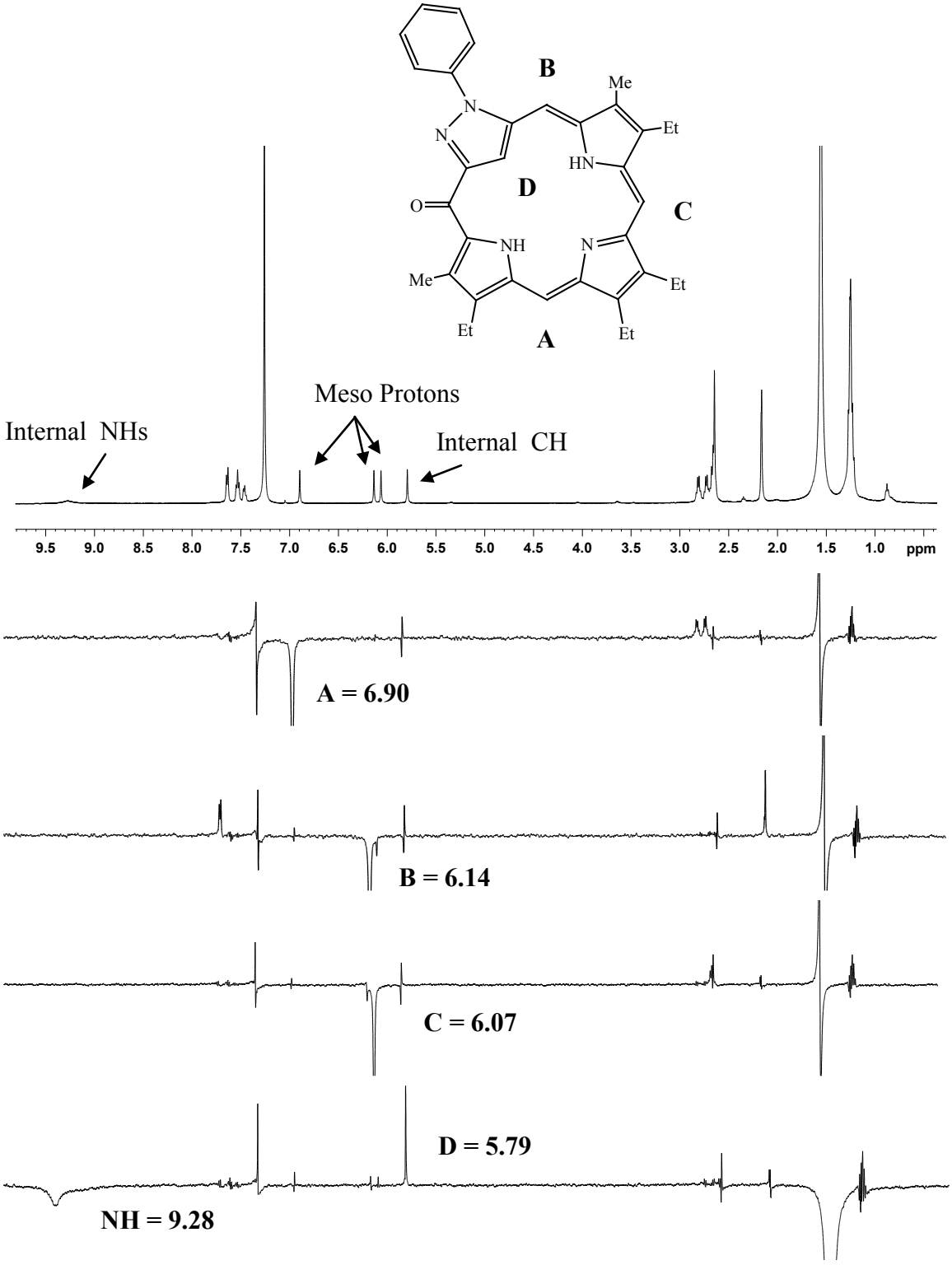
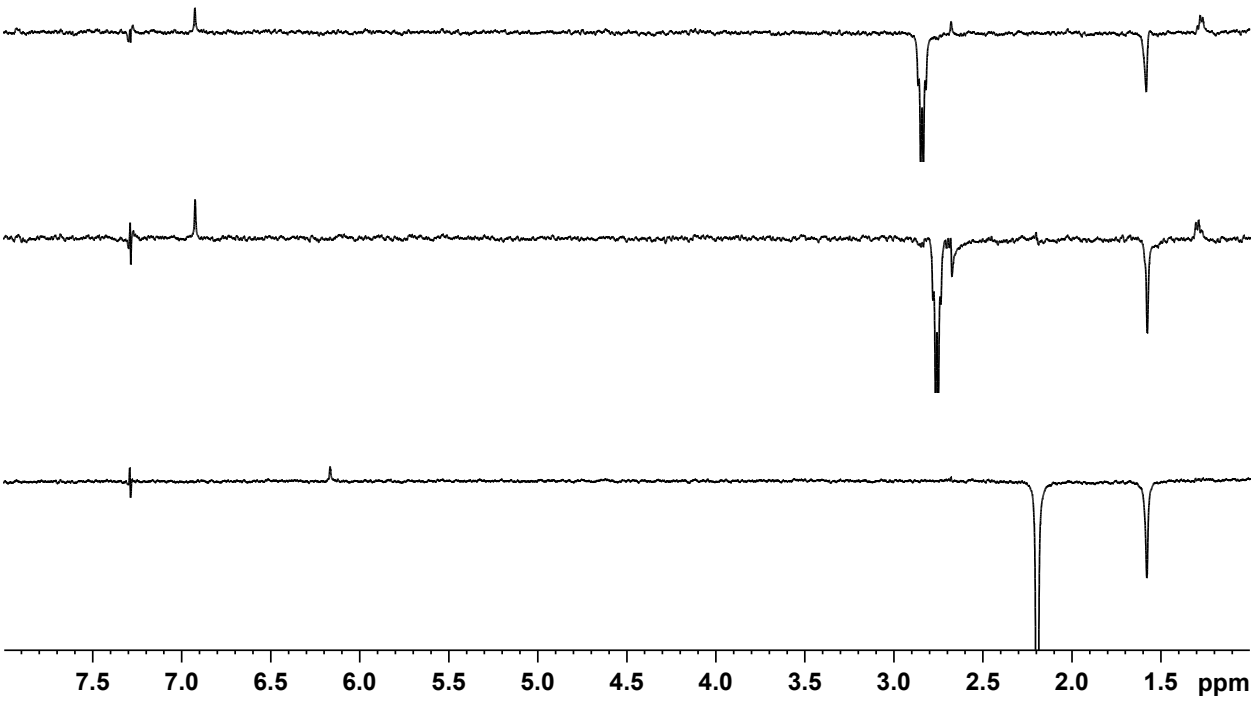


Figure 82. Selected nOe difference proton NMR spectra of **28a** in $CDCl_3$.



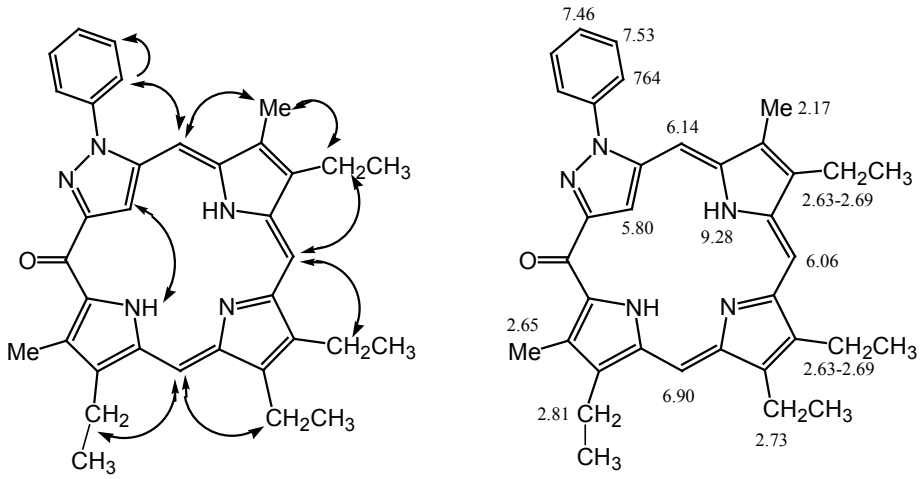


Figure 83. Further nOe difference proton NMR spectra, nOe correlations, and partial proton NMR assignments for pyrazolo-oxophlorin **28a** in $CDCl_3$.

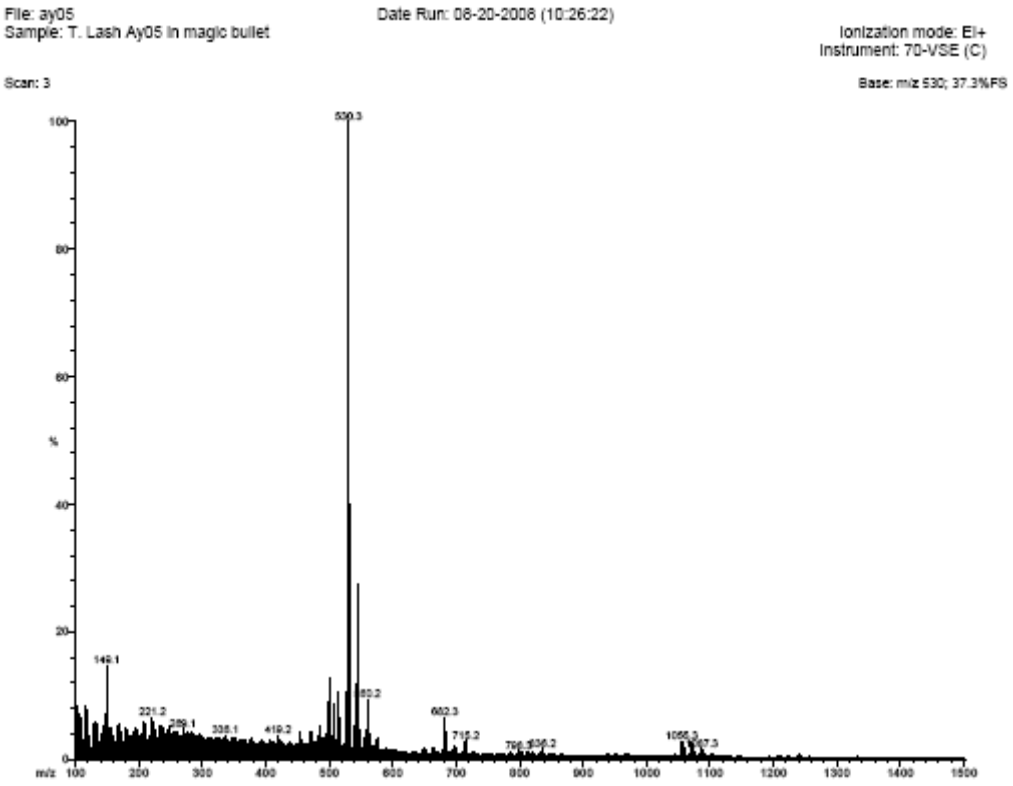
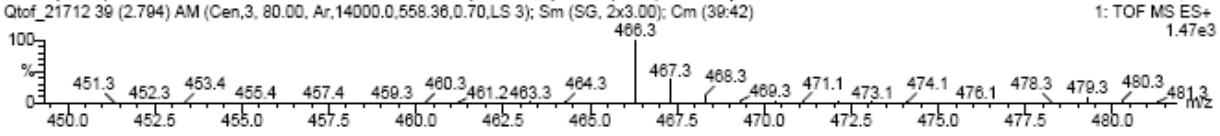


Figure 84. FAB MS of 2-phenyl phlorin analogue **24a**.

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -50.0, max = 200.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
50 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-70 H: 1-100 N: 3-5 O: 0-1

Timothy Lash, AY 02e Mass Spectrometry Center, SCS, University of Illinois QTOF
Qtof_21712 39 (2.794) AM (Cen,3, 80.00, Ar,14000.0,558.36,0.70,LS 3); Sm (SG, 2x3.00); Cm (39:42) 1: TOF MS ES+
1.47e3



Minimum:				-50.0		
Maximum:		5.0	10.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
466.2970	466.2971	-0.1	-0.2	15.5	21.0	C30 H36 N5

Figure 85. ESI MS of 2-methyl pyrazoloporphyrin **25b**.

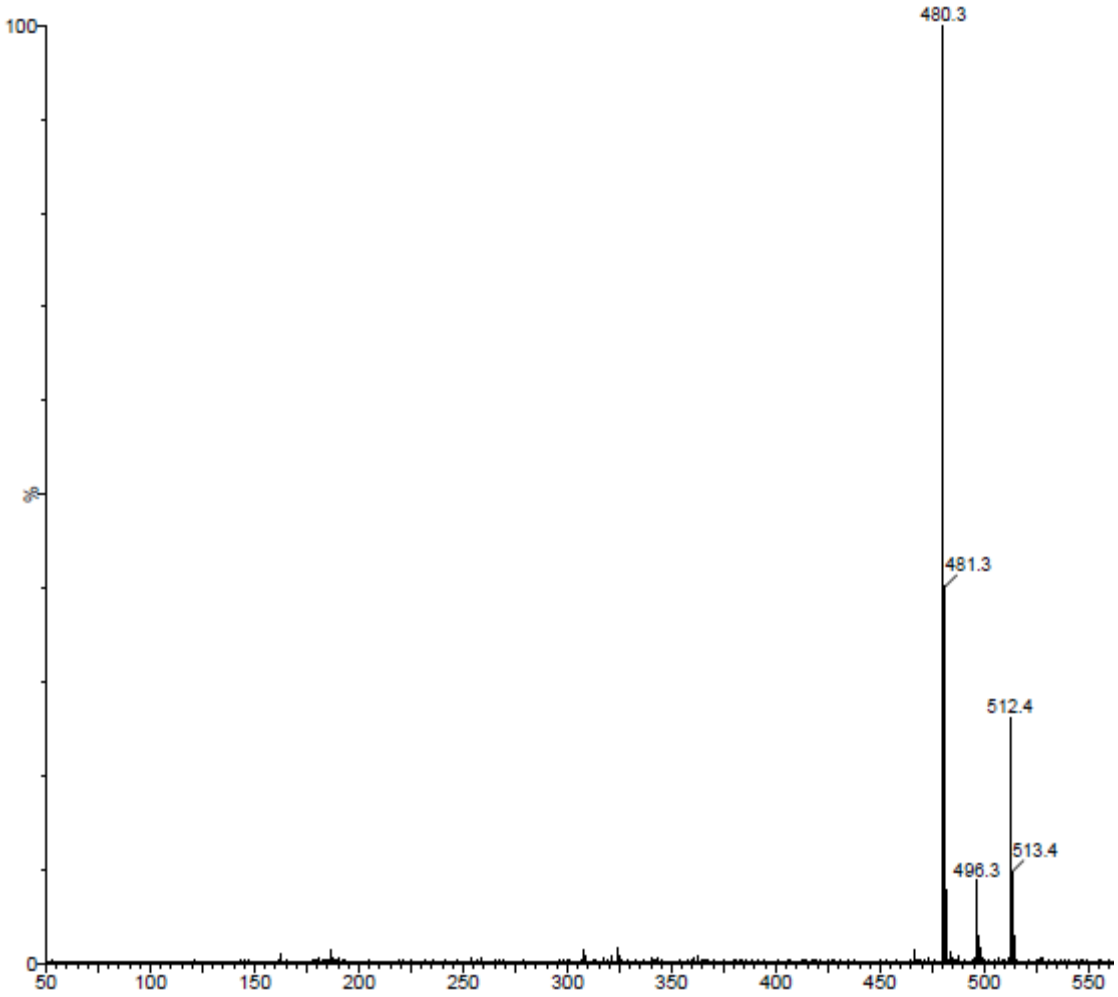


Figure 86. ESI MS of 2-ethyl pyrazoloporphyrin **25c**.

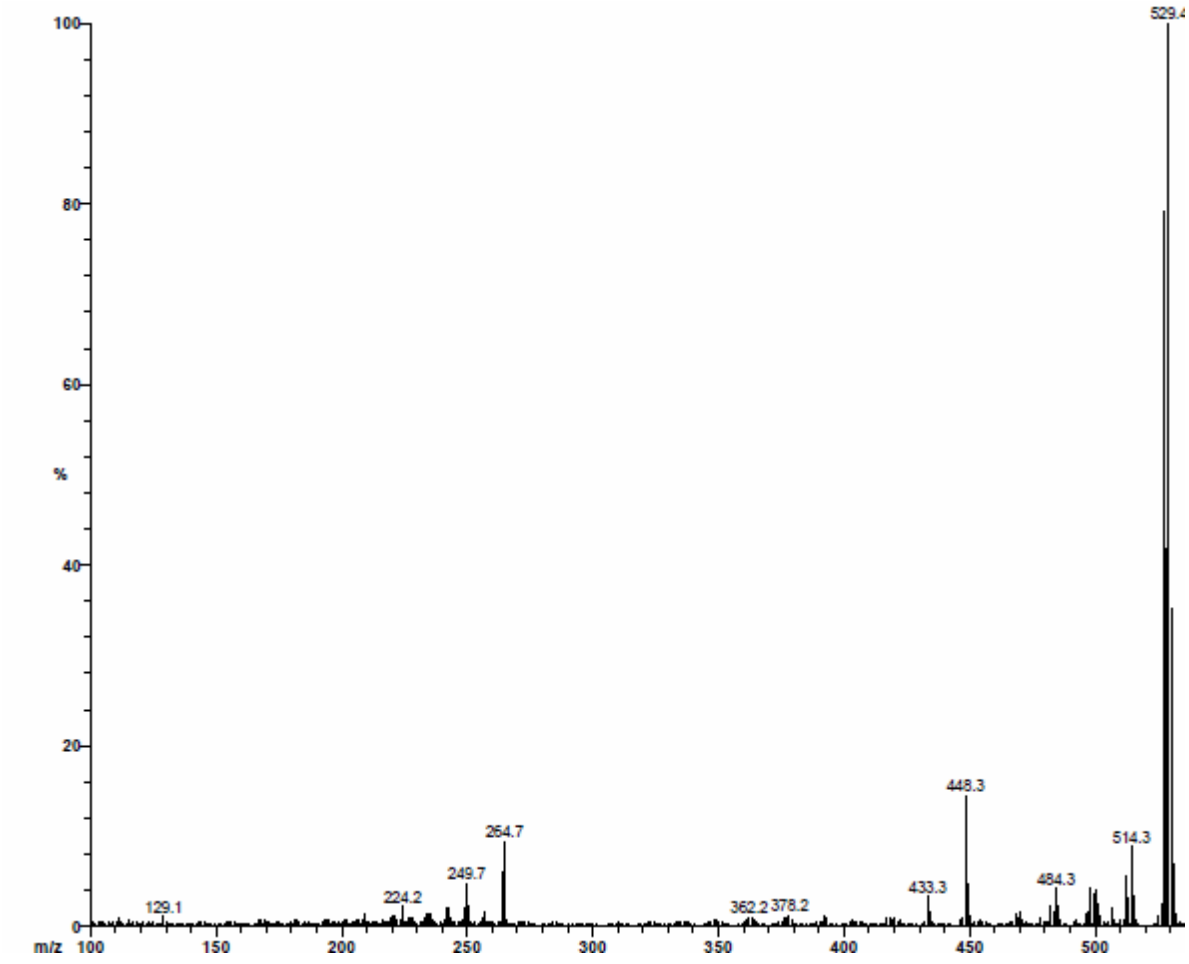


Figure 87. EI MS of 2-phenyl pyrazoloporphyrin **25a**.

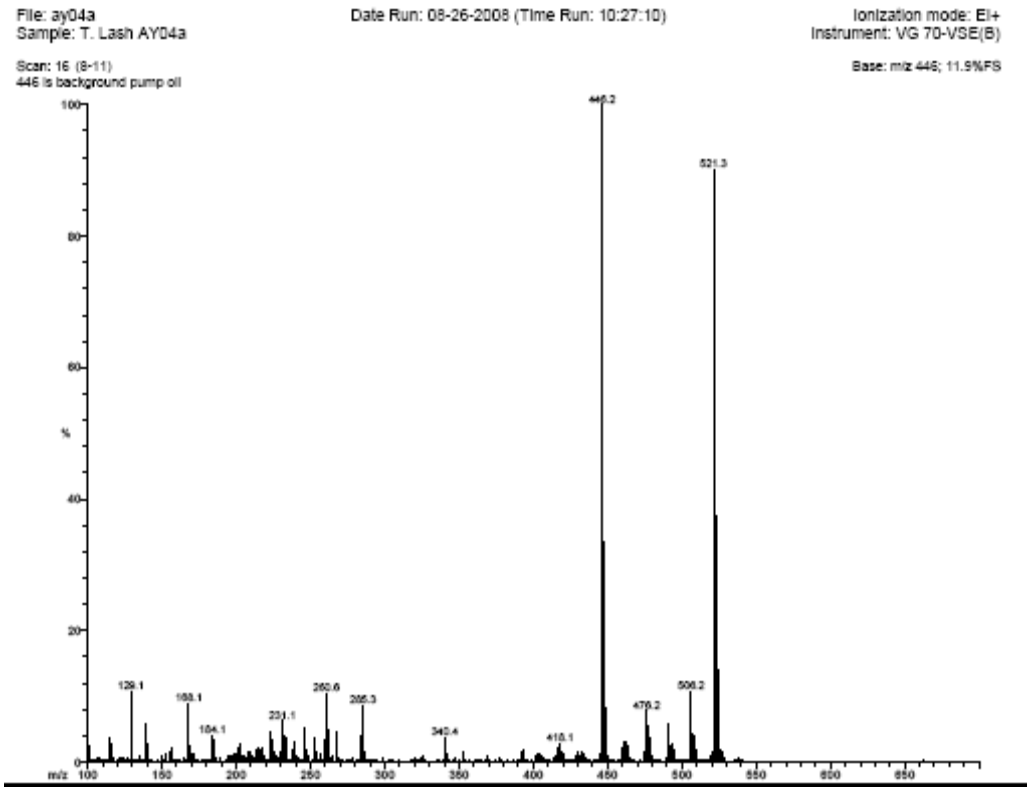


Figure 88. EI MS of nickel(II) pyrazoloporphyrin **31b**. The peak at 446 is due to pump oil.

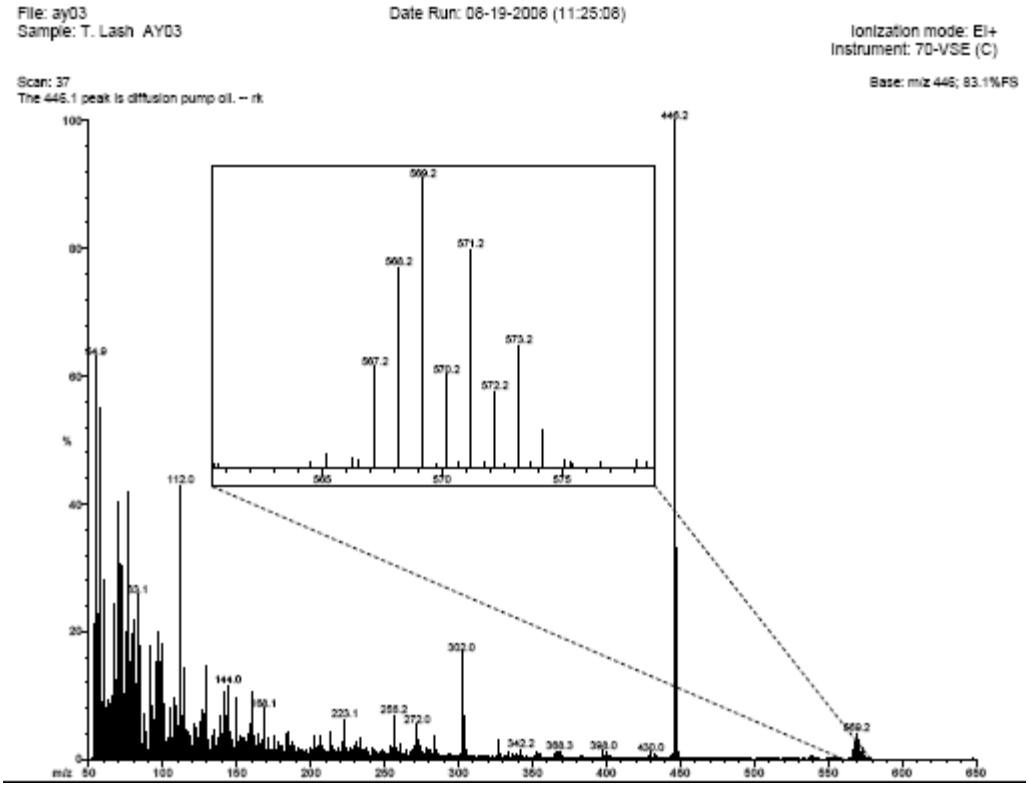


Figure 89. EI MS of palladium(II) pyrazoloporphyrin **32b**. The peak at 446 is due to pump oil.

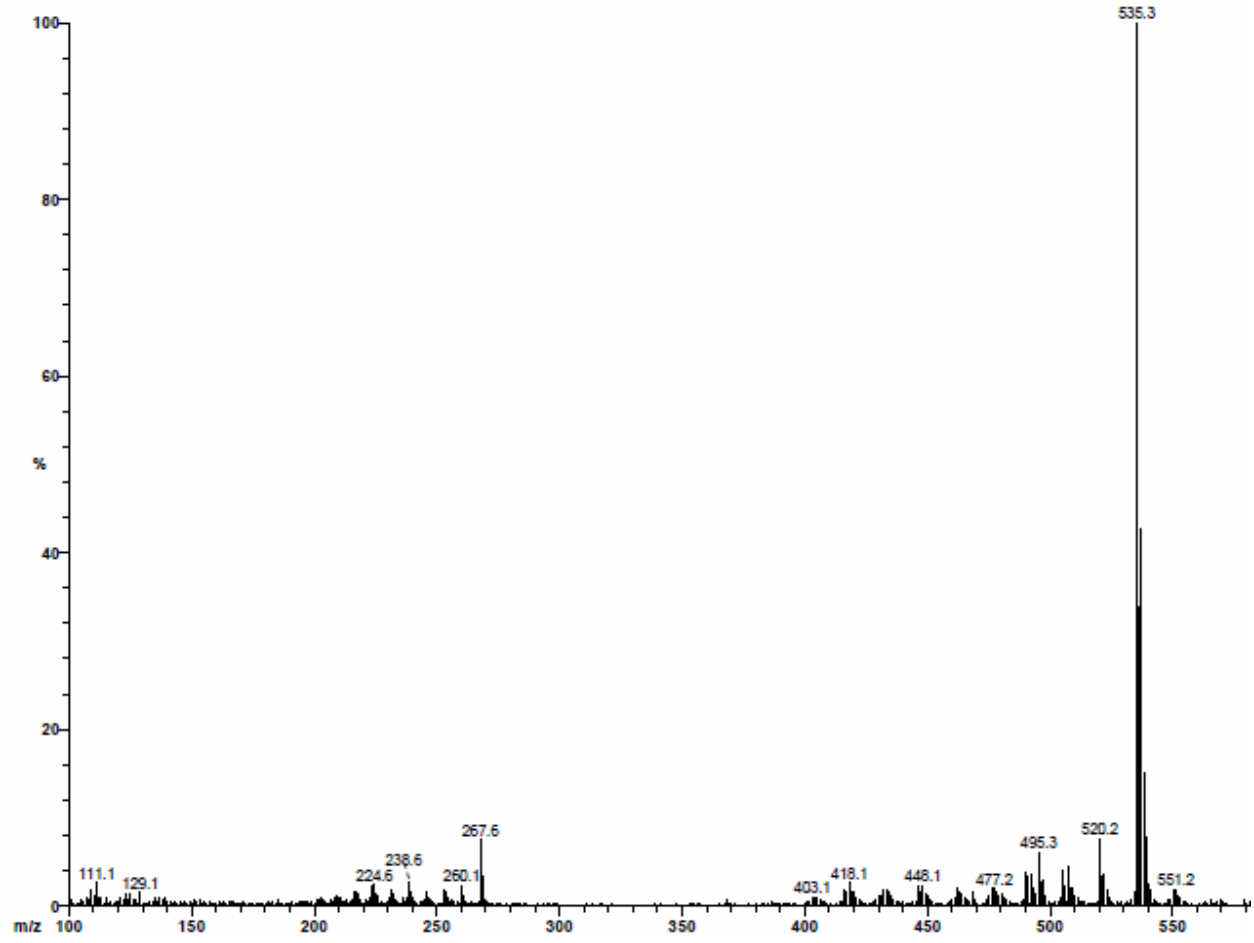


Figure 90. EI MS of nickel(II) pyrazoloporphyrin **31c**.

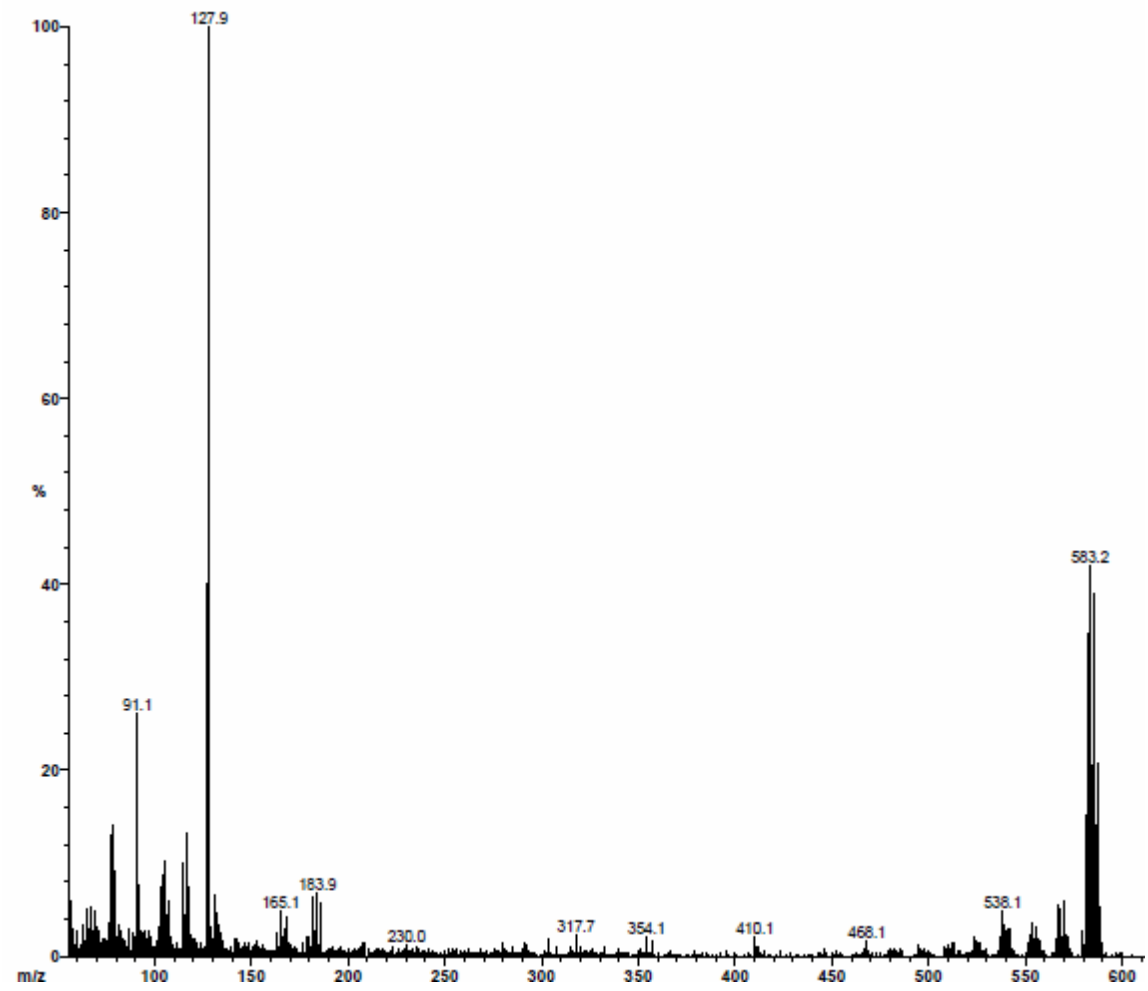


Figure 91. EI MS of palladium(II) pyrazoloporphyrin **32c**.

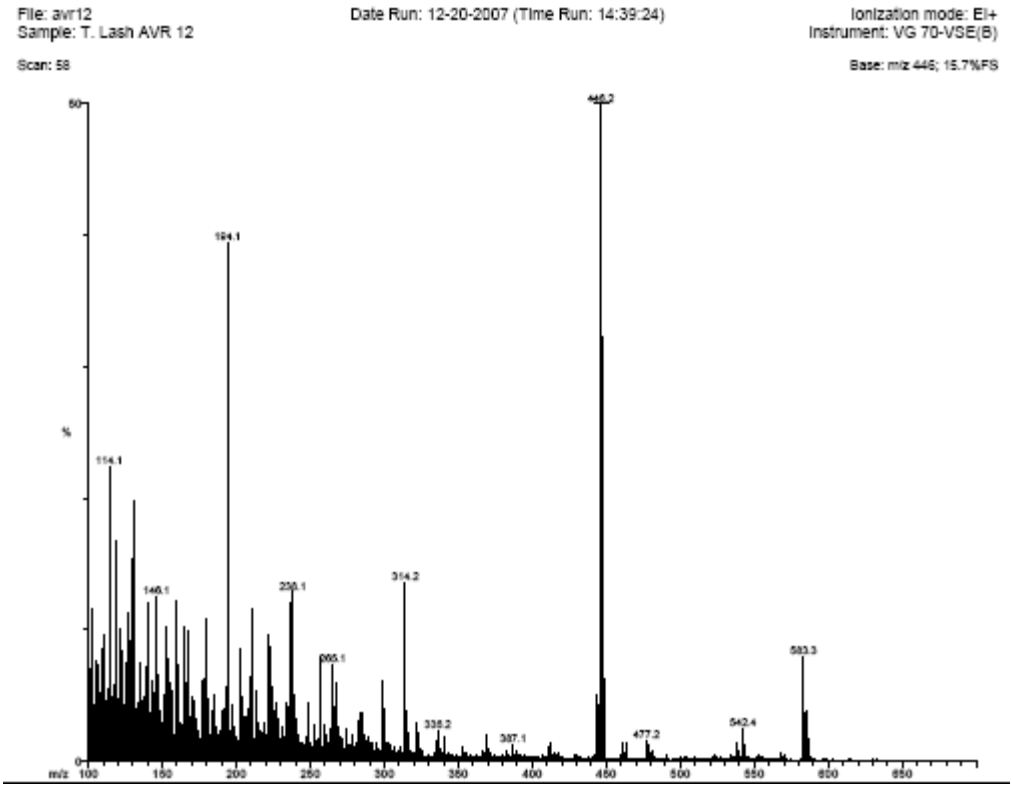


Figure 92. EI MS of nickel(II) 2-phenylpyrazoloporphyrin **31a**. The peak at 446 is due to pump oil.

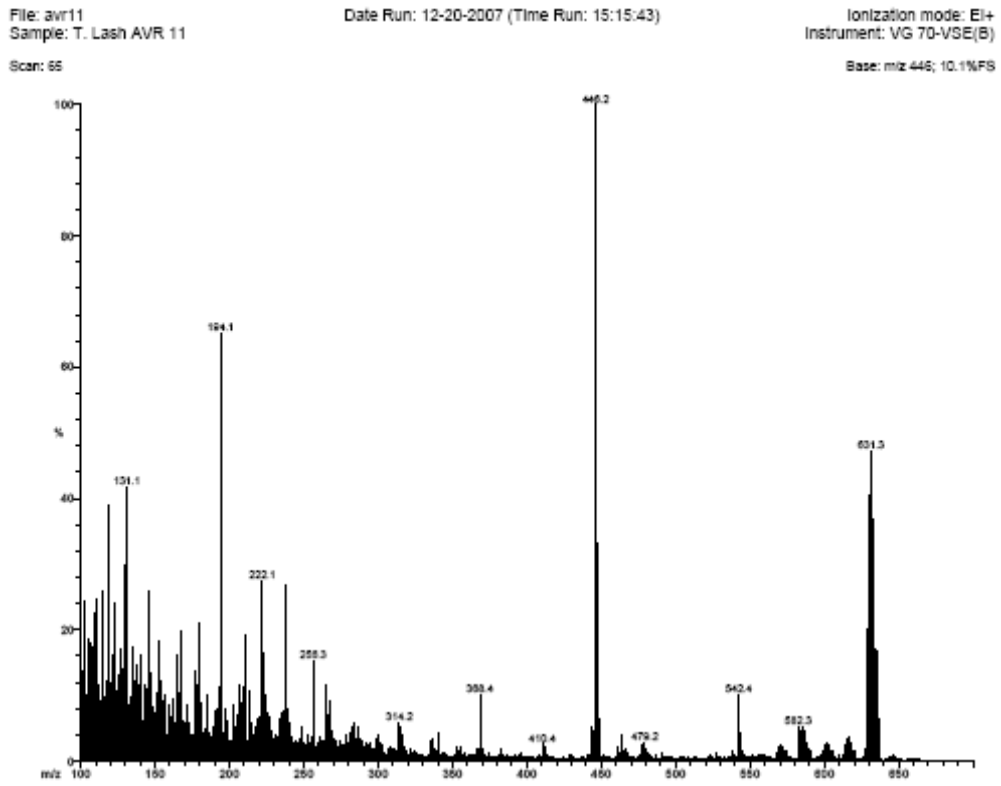


Figure 93. ESI MS of palladium(II) 2-phenylpyrazoloporphyrin **32a**. The peak at 446 is due to pump oil.

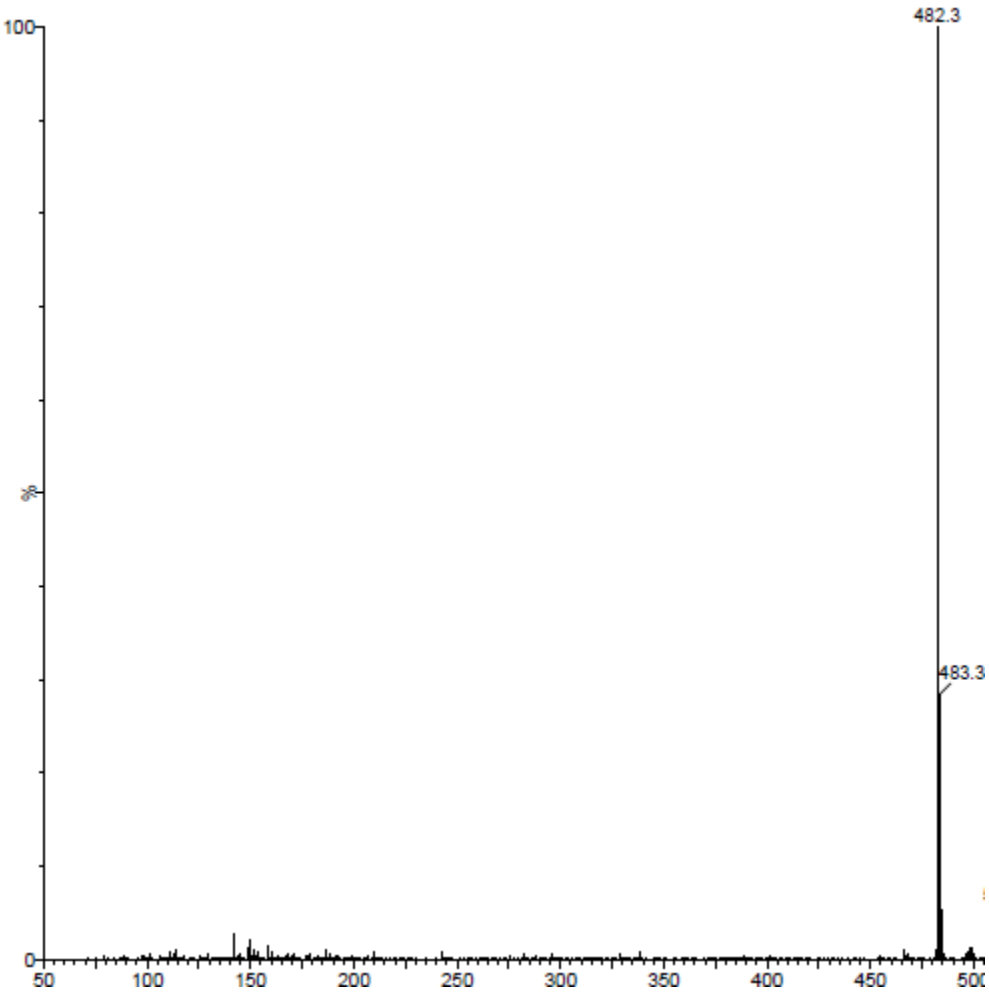


Figure 94. ESI MS of oxophlorin analogue **28b**.

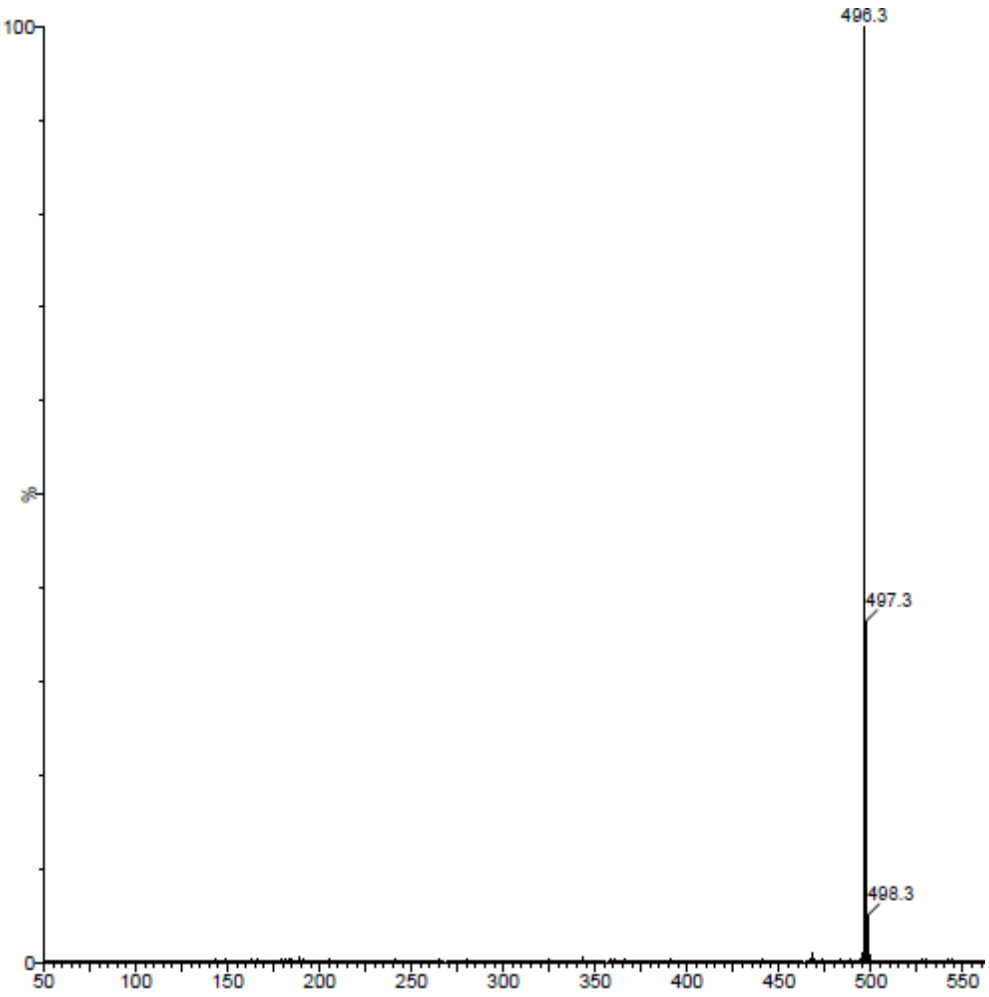


Figure 95. ESI MS of 2-ethyl pyrazolo-oxophlorin **28c**.

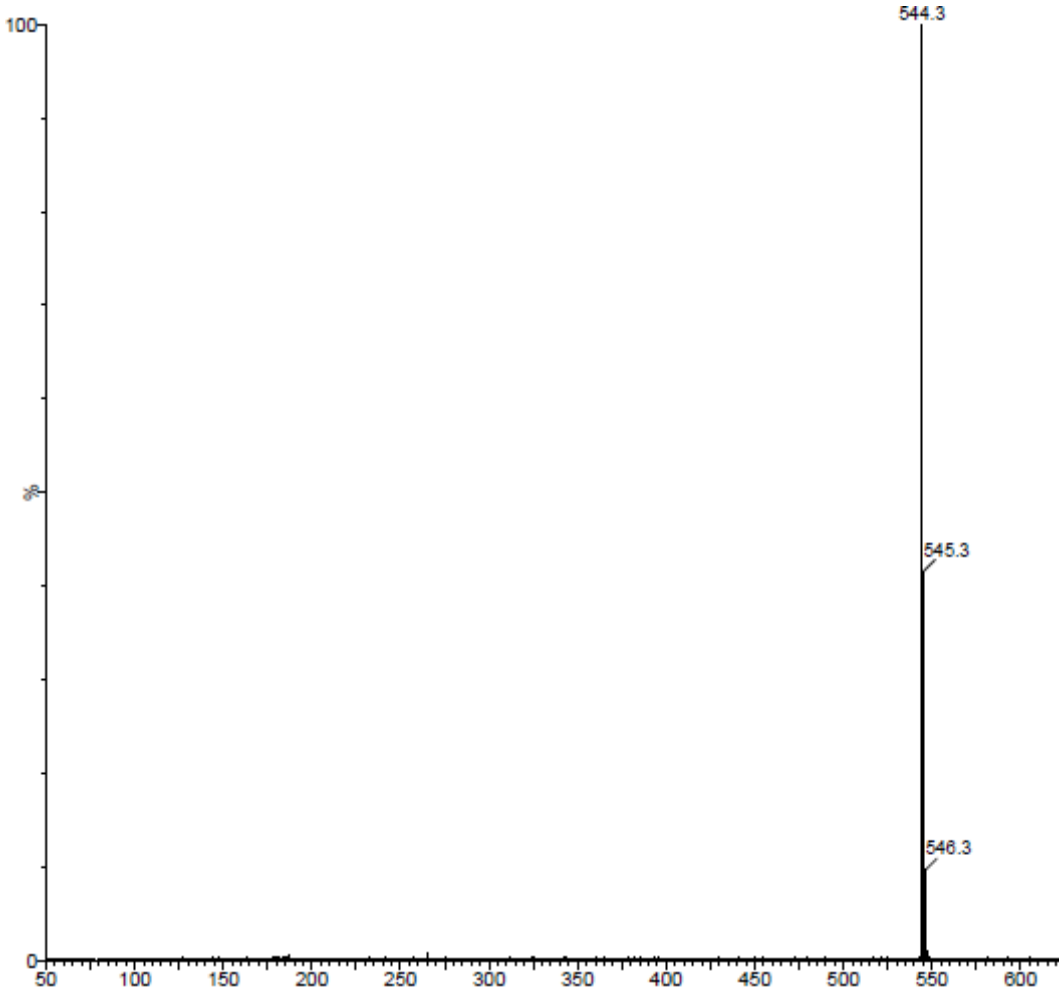


Figure 96. ESI MS of 2-phenyl pyrazolo-oxophlorin **28a**.

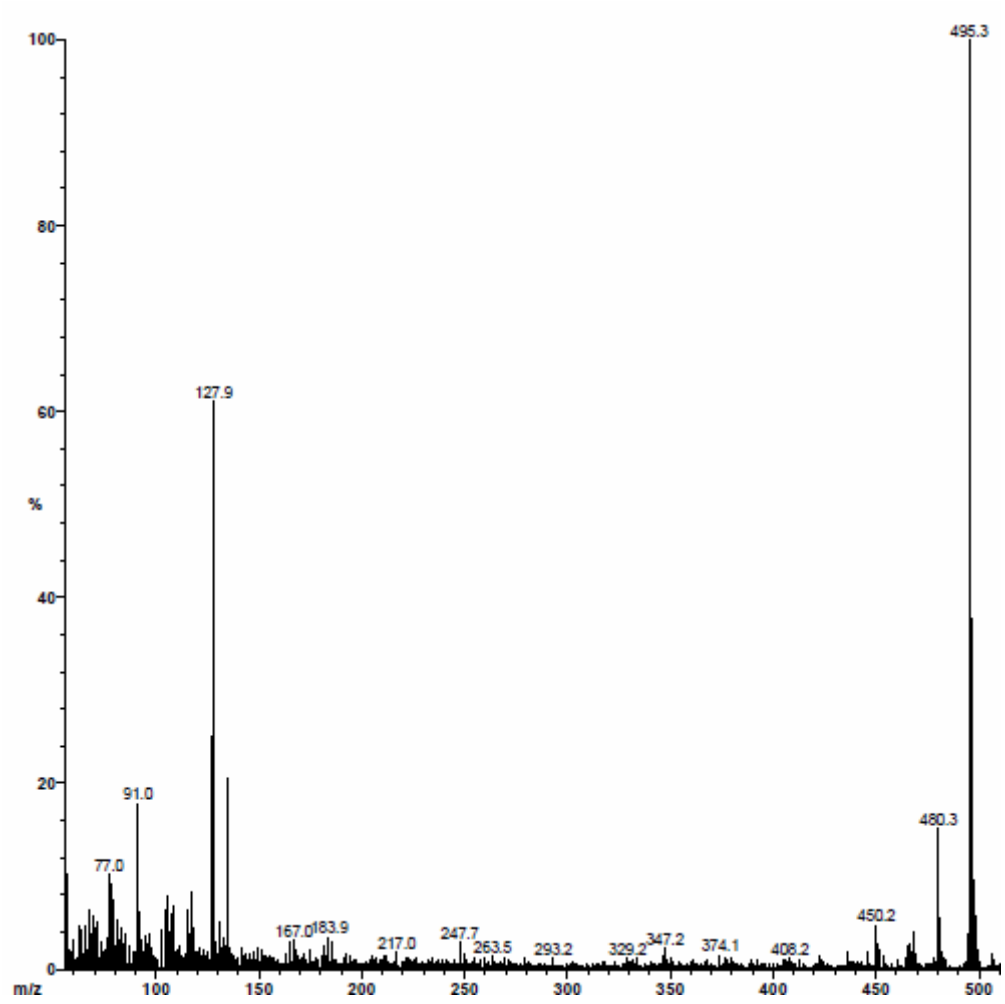


Figure 97. EI MS of the minor 2-ethyl pyrazolo-oxophlorin isomer **29**.