

Supporting information for**Synthesis, Metalation and Spectroscopic Characterization of 3-Alkoxybenzoporphyrins**

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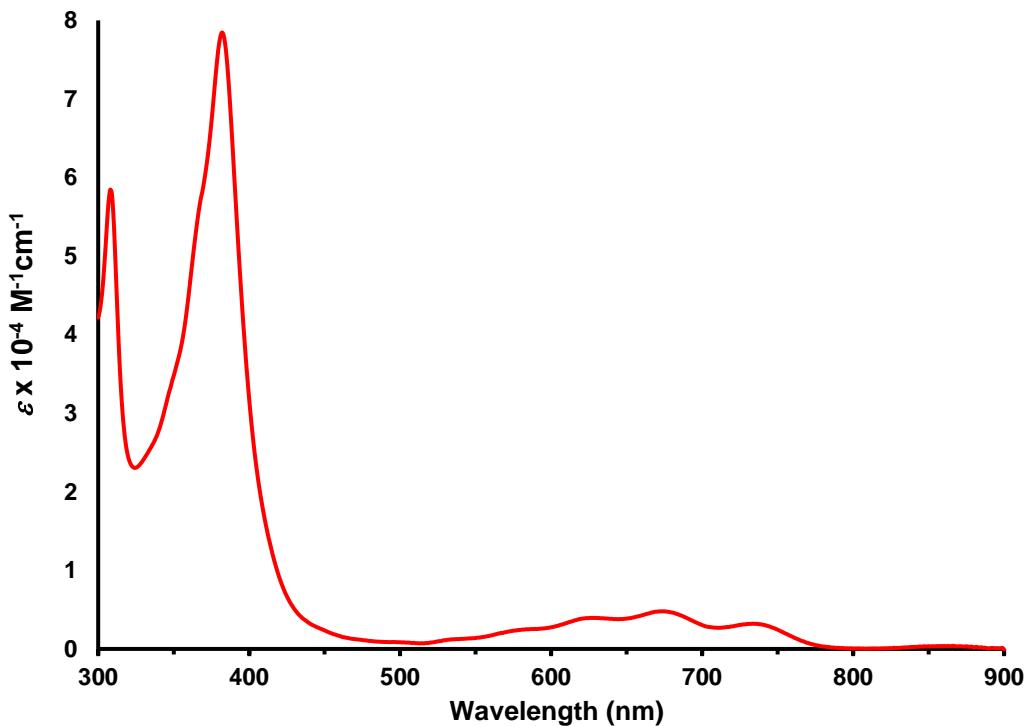


Figure S1. UV-vis spectrum of 3-ethoxybenzoporphyrin **7b** in CH_2Cl_2 .

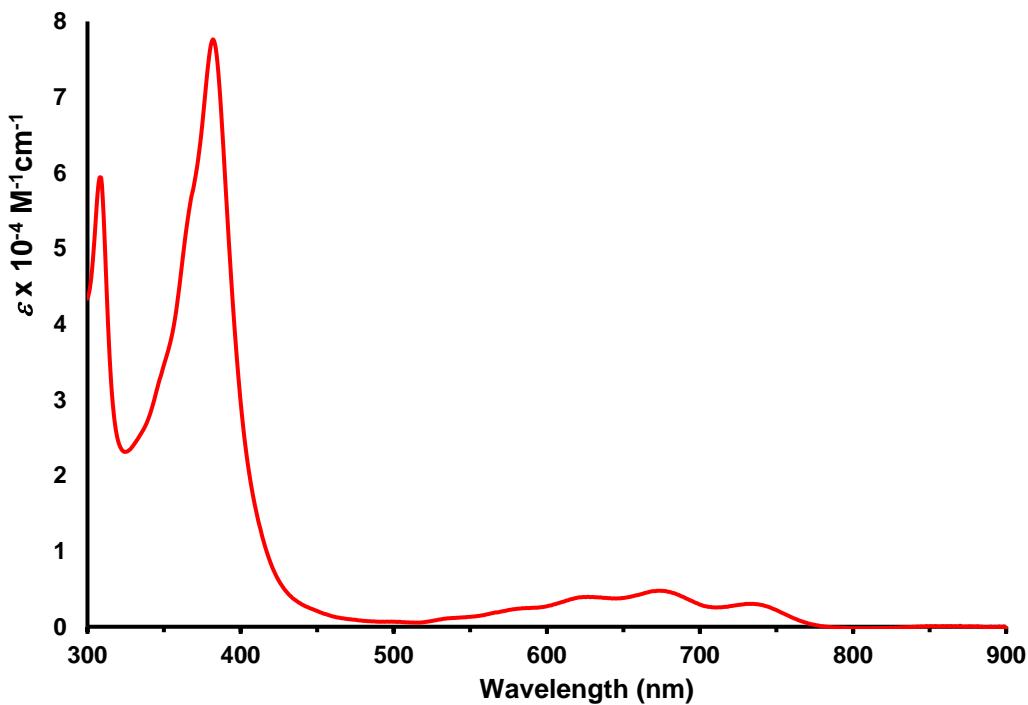


Figure S2. UV-vis spectrum of 3-ethoxybenzoporphyrin **7b** in 1% $Et_3N\text{-}CH_2Cl_2$.

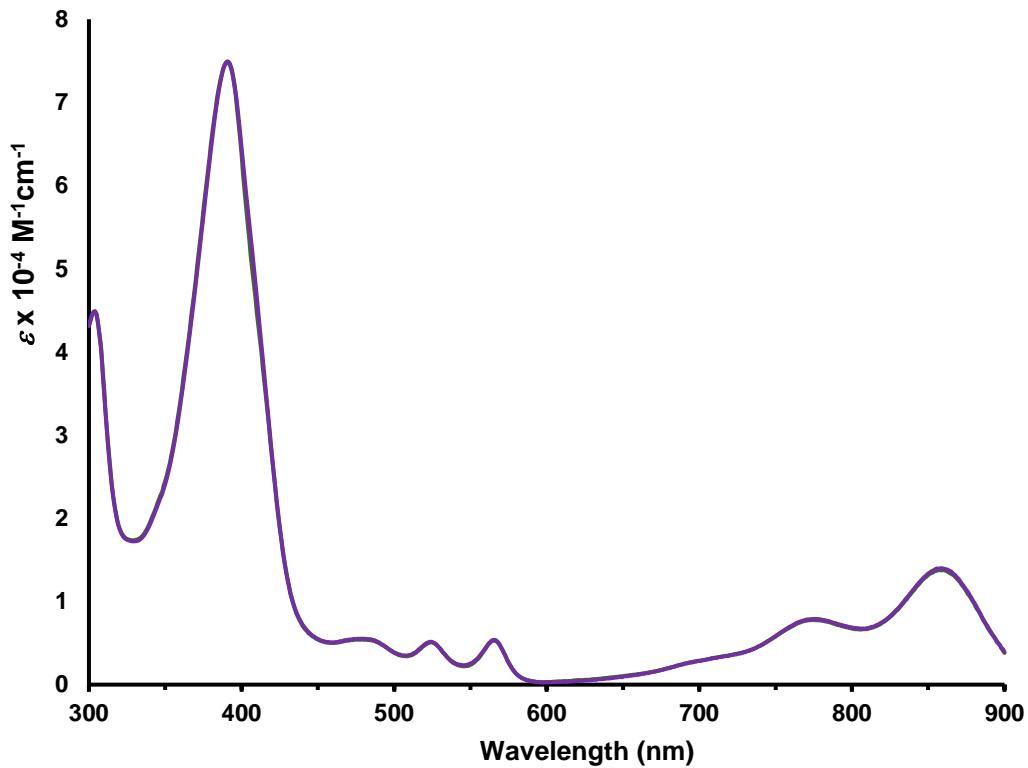


Figure S3. UV-vis spectrum of 3-ethoxybenzoporphyrin **7b** in CH_2Cl_2 with 5 equivalents of TFA.

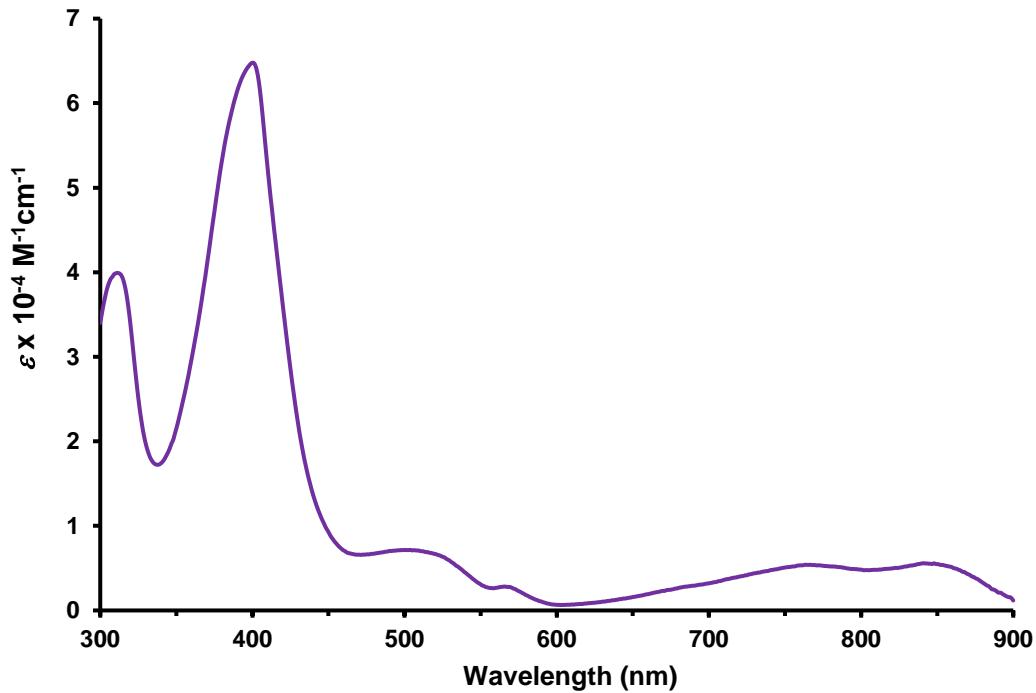


Figure S4. UV-vis spectrum of 3-ethoxybenzoporphyrin **7b** in CH_2Cl_2 with 500 equivalents of TFA.

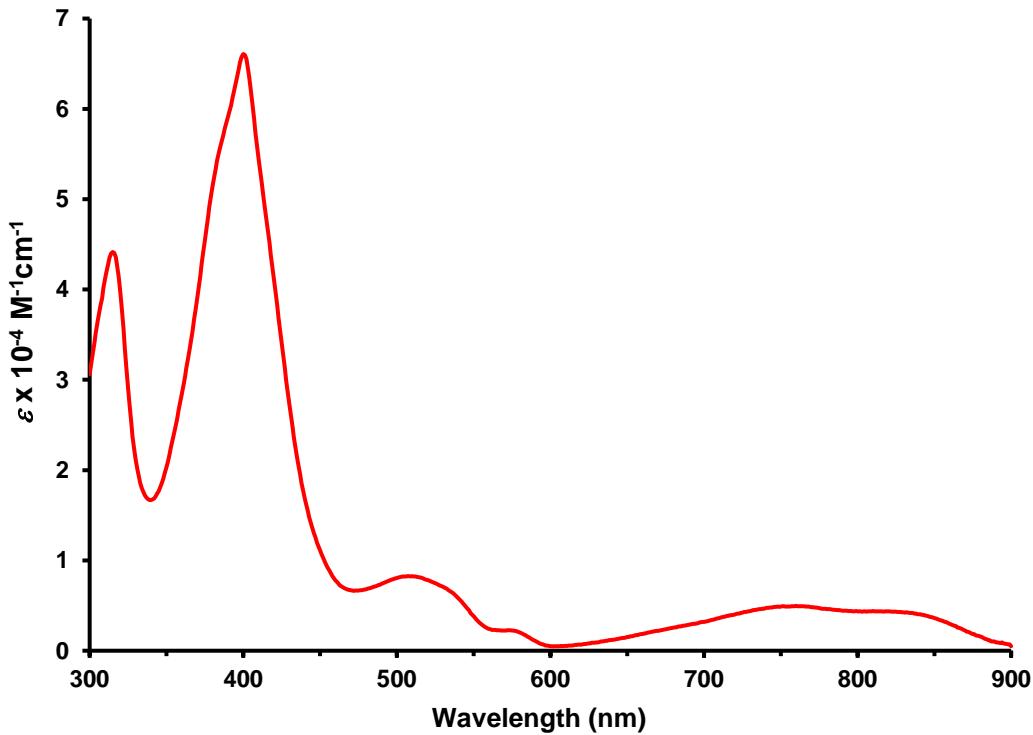


Figure S5. UV-vis spectrum of 3-ethoxybenzoporphyrin **7b** in 1% TFA-CH₂Cl₂.

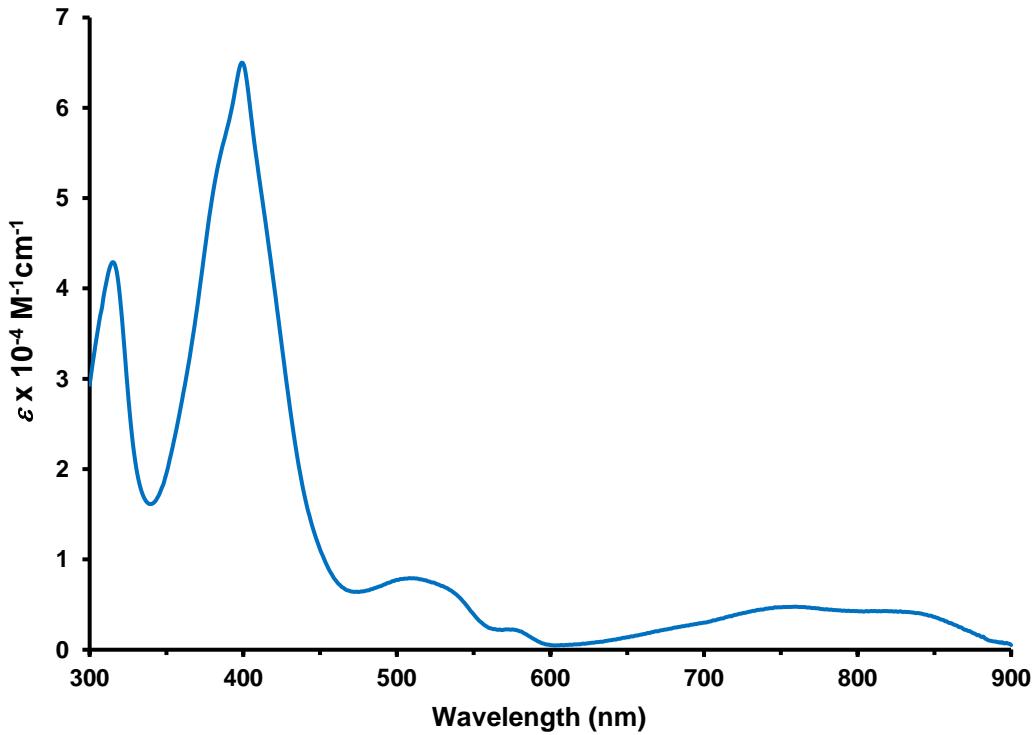


Figure S6. UV-vis spectrum of 3-ethoxybenzoporphyrin **7b** in 5% TFA- CH₂Cl₂.

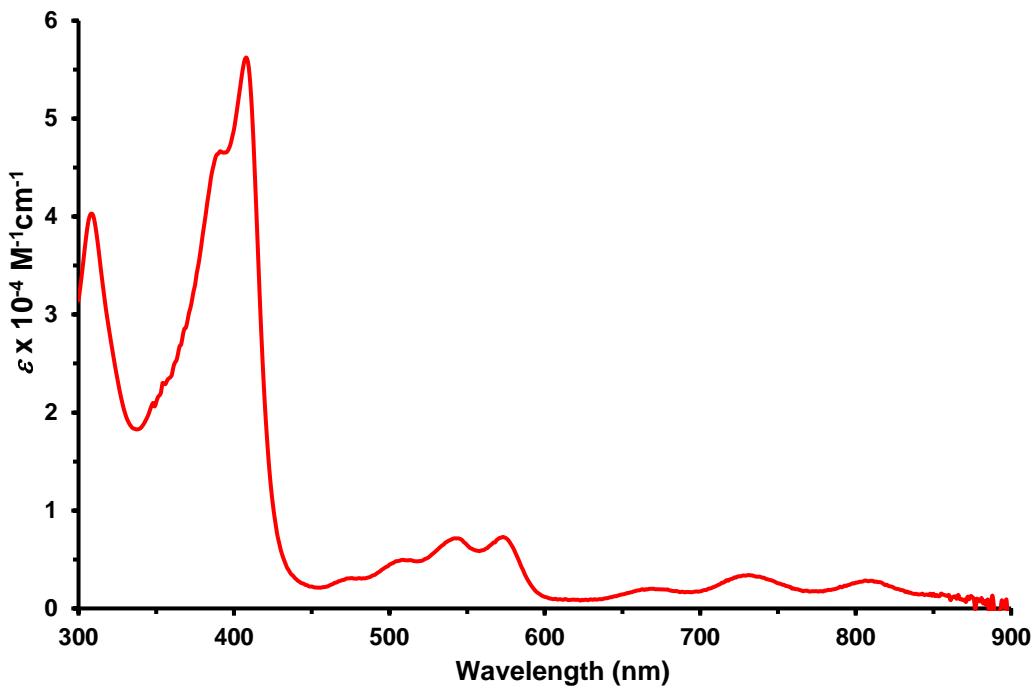


Figure S7. UV-vis spectrum of Pd(II) complex **7bPd** in CH_2Cl_2 .

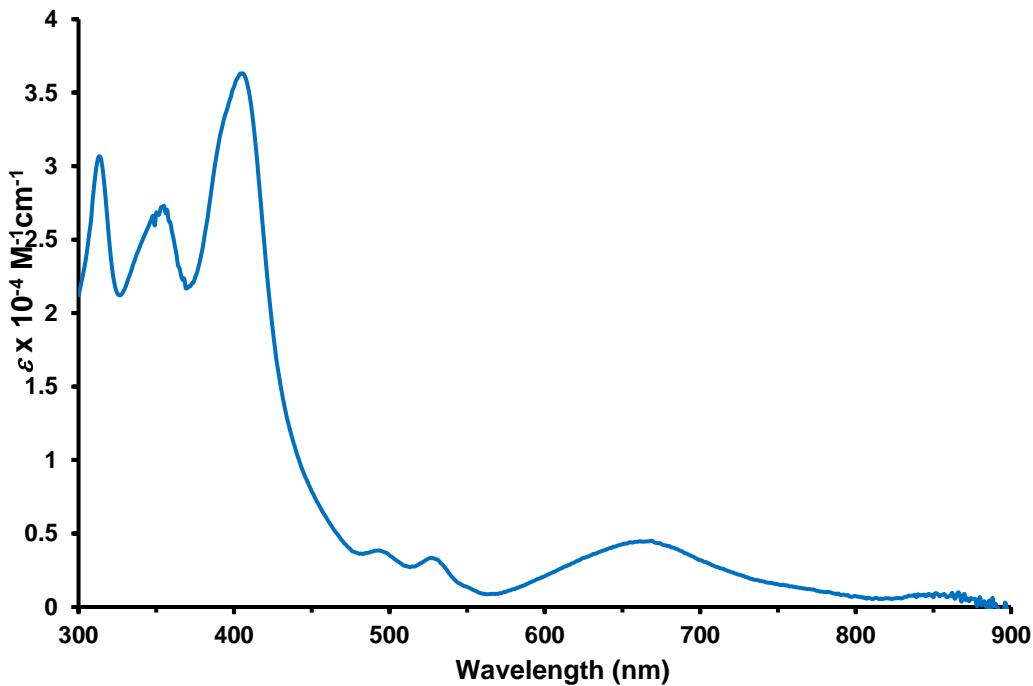


Figure S8. UV-vis spectrum of Ni(II) complex **7bNi** in CH_2Cl_2 .

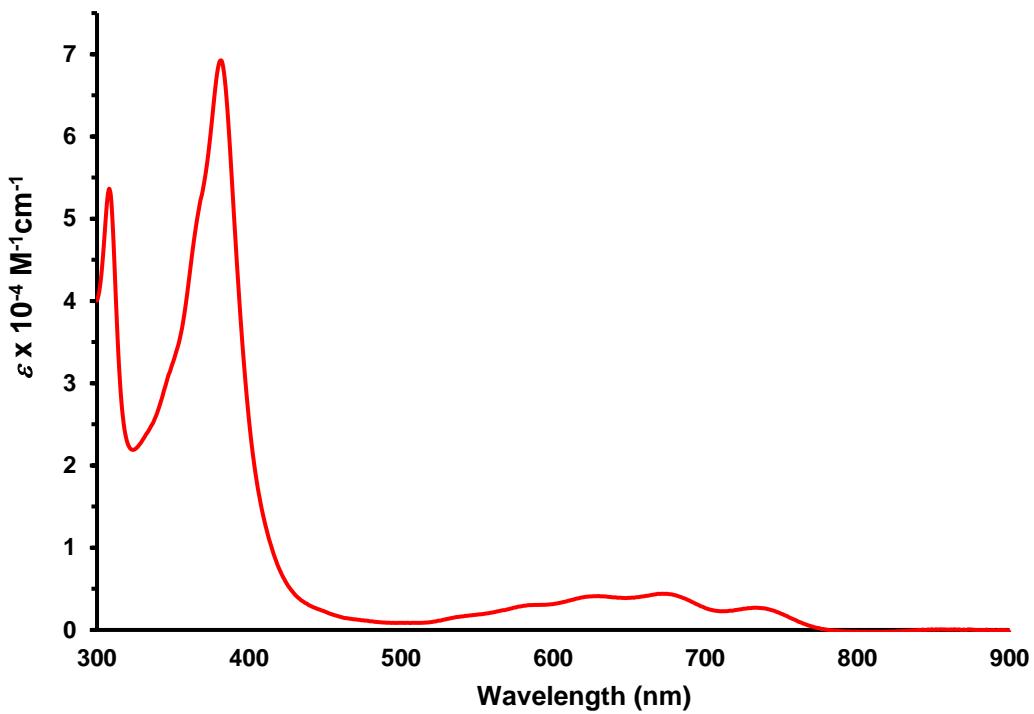


Figure S9. UV-vis spectrum of methoxybenzoporphyrin **7a** in 1% $Et_3N\text{-CH}_2\text{Cl}_2$.

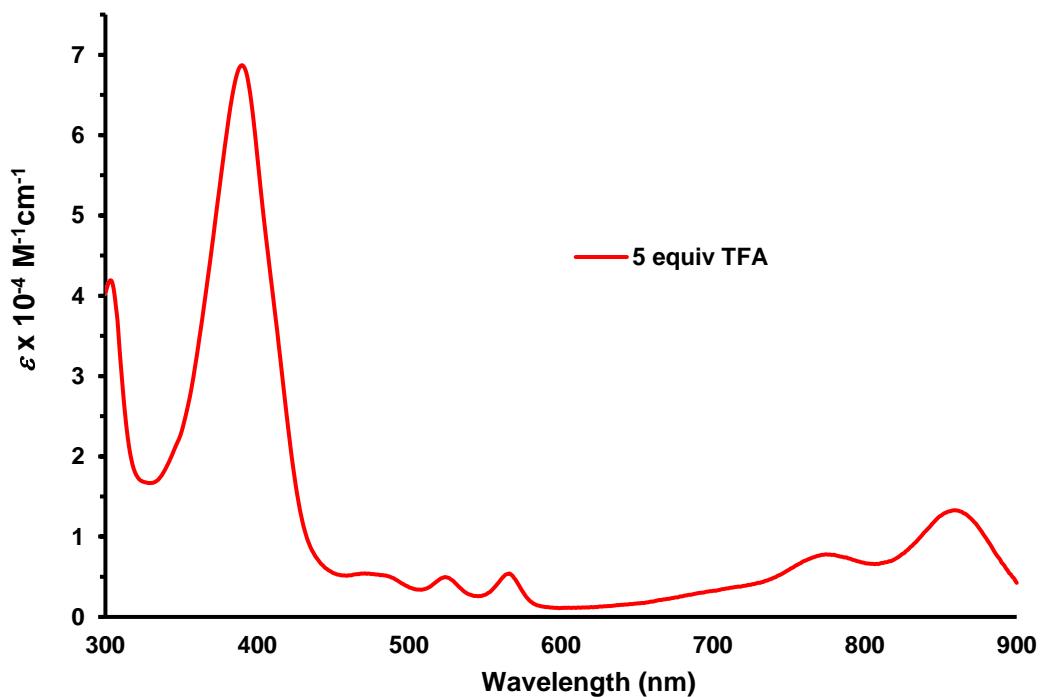


Figure S10. UV-vis spectrum of methoxybenzoporphyrin **7a** in $CH_2\text{Cl}_2$ with 5 equivalents of TFA.

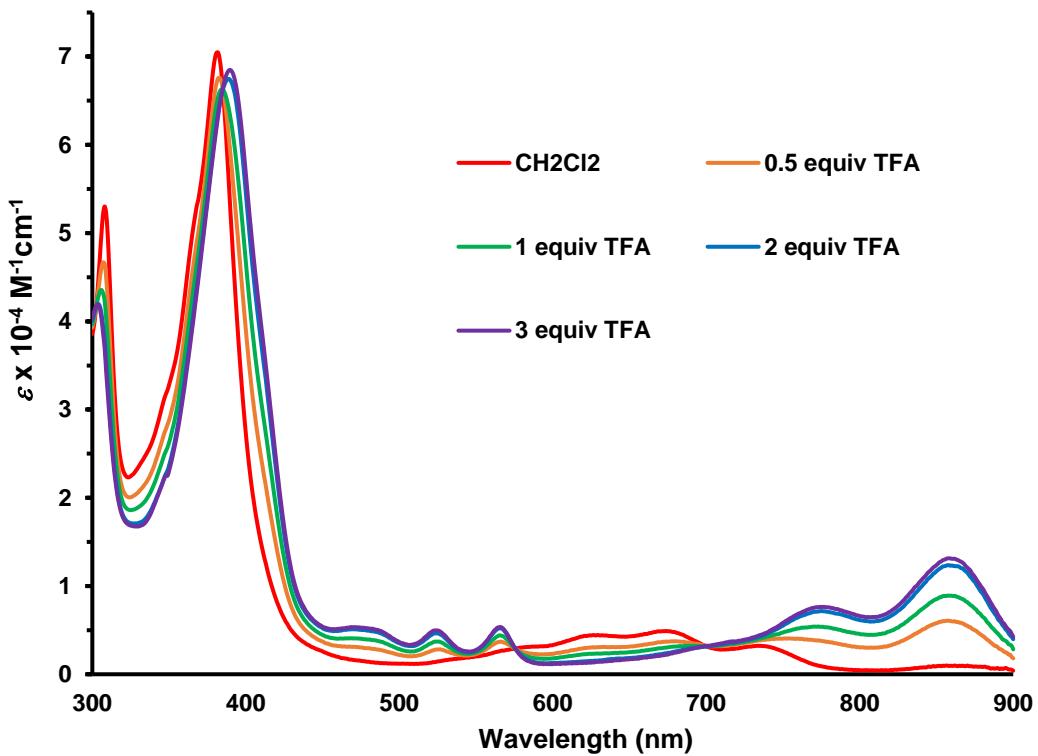


Figure S11. UV-vis spectra of methoxybenzoporphyrin **7a** in CH_2Cl_2 with 0-3 equivalents of TFA.

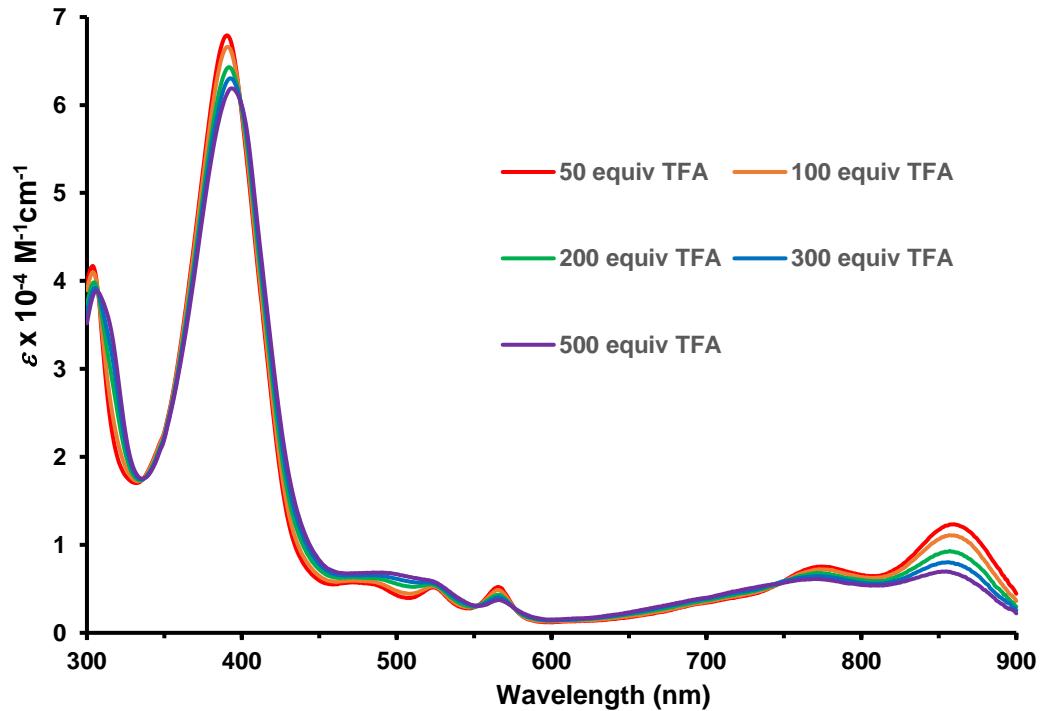


Figure S12. UV-vis spectra of methoxybenzoporphyrin **7a** in CH_2Cl_2 with 50-500 equivalents of TFA.

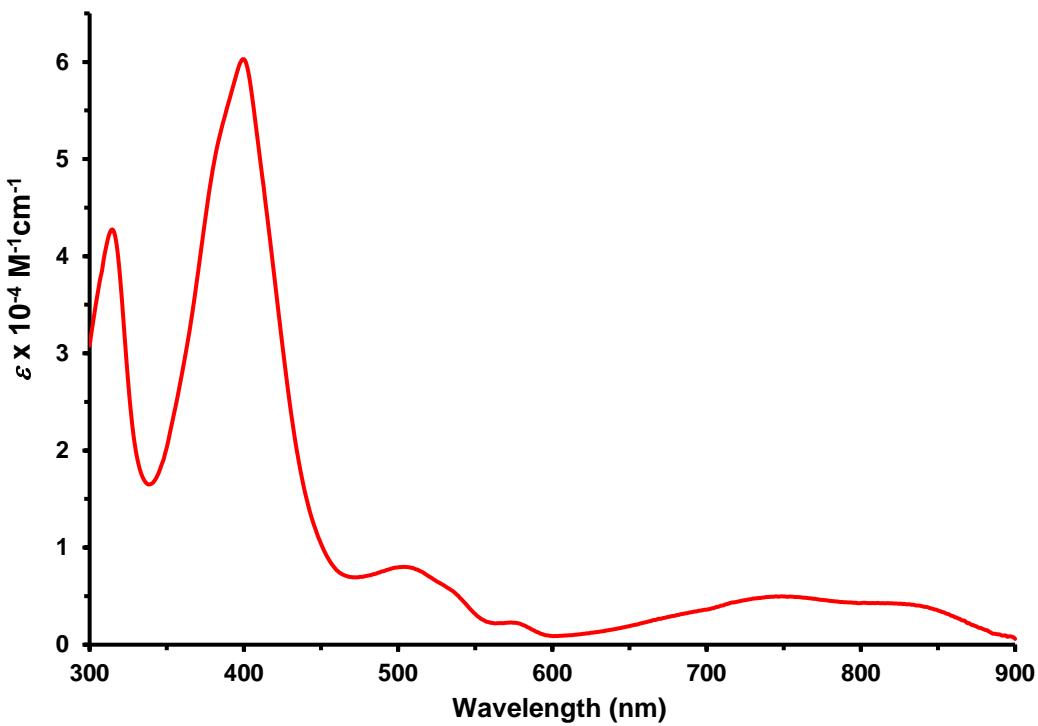


Figure S13. UV-vis spectrum of methoxybenzoporphyrin **7a** in 1% TFA-CH₂Cl₂.

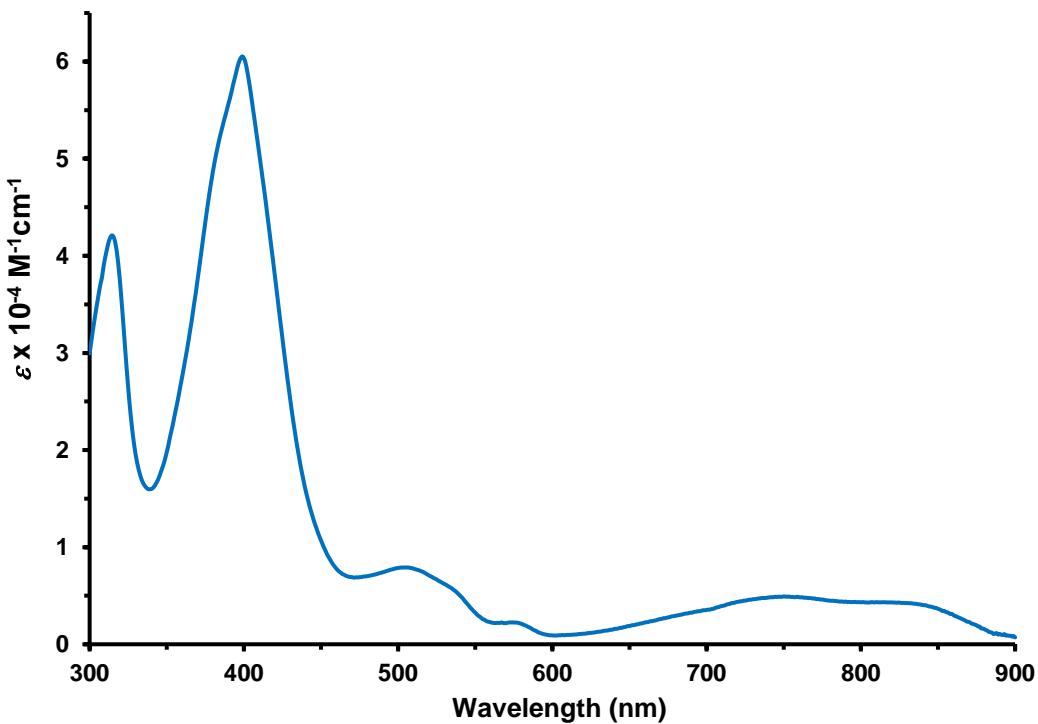


Figure S14. UV-vis spectrum of methoxybenzoporphyrin **7a** in 5% TFA-CH₂Cl₂.

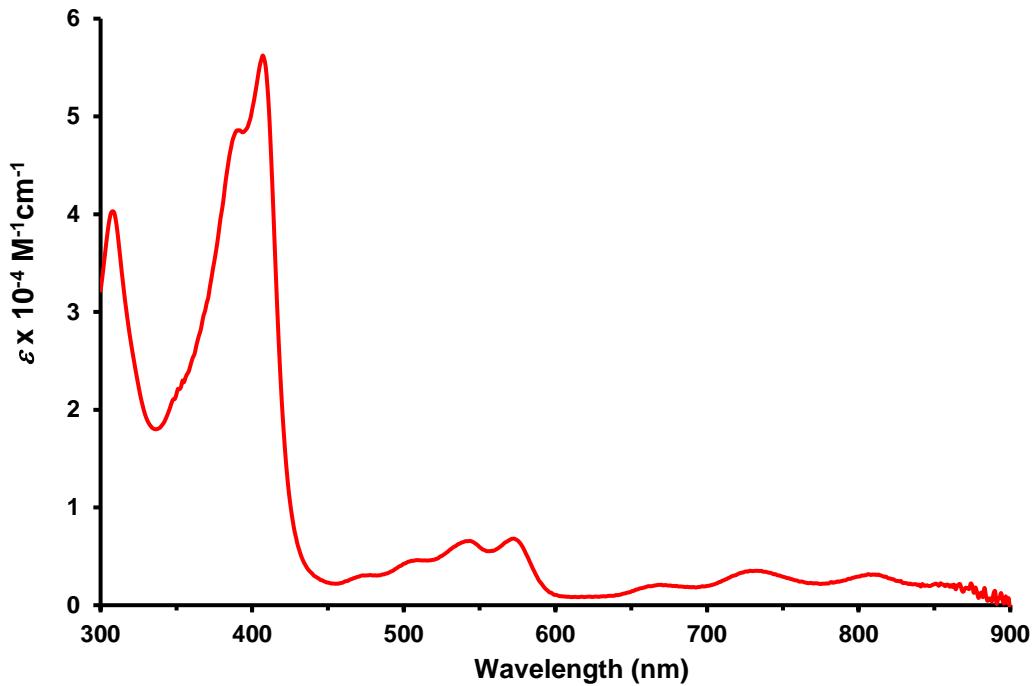


Figure S15. UV-vis spectrum of palladium(II) complex **7aPd** in CH_2Cl_2 .

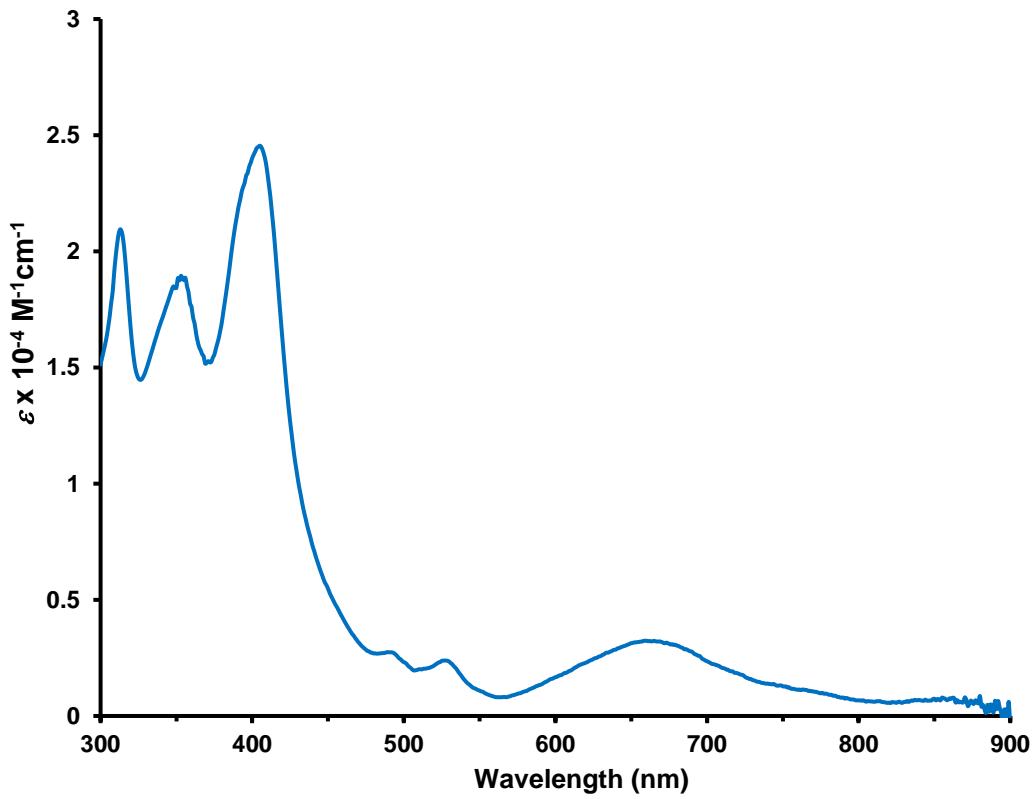


Figure S16. UV-vis spectrum of nickel(II) complex **7aNi** in CH_2Cl_2 .

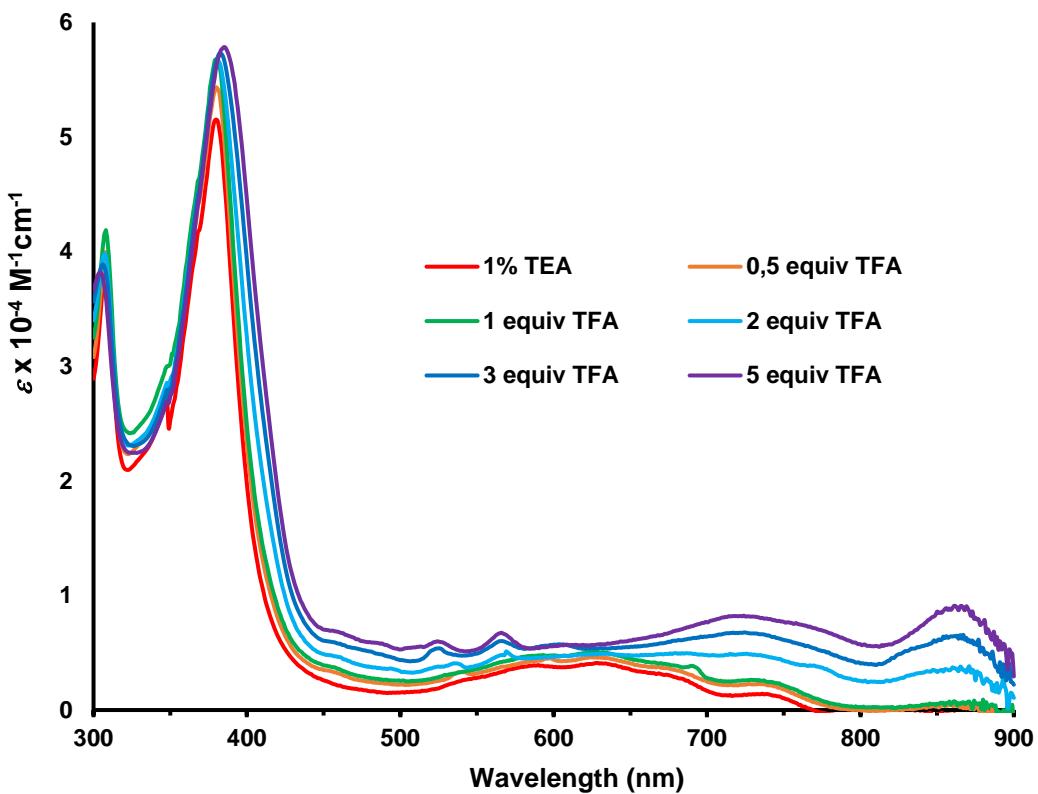


Figure S17. UV-vis spectra of methoxycarbonylmethoxybenzoporphyrin **7c** in 1% $Et_3N\text{-}CH_2Cl_2$ and with 0.5-5 equivalents of TFA in CH_2Cl_2 .

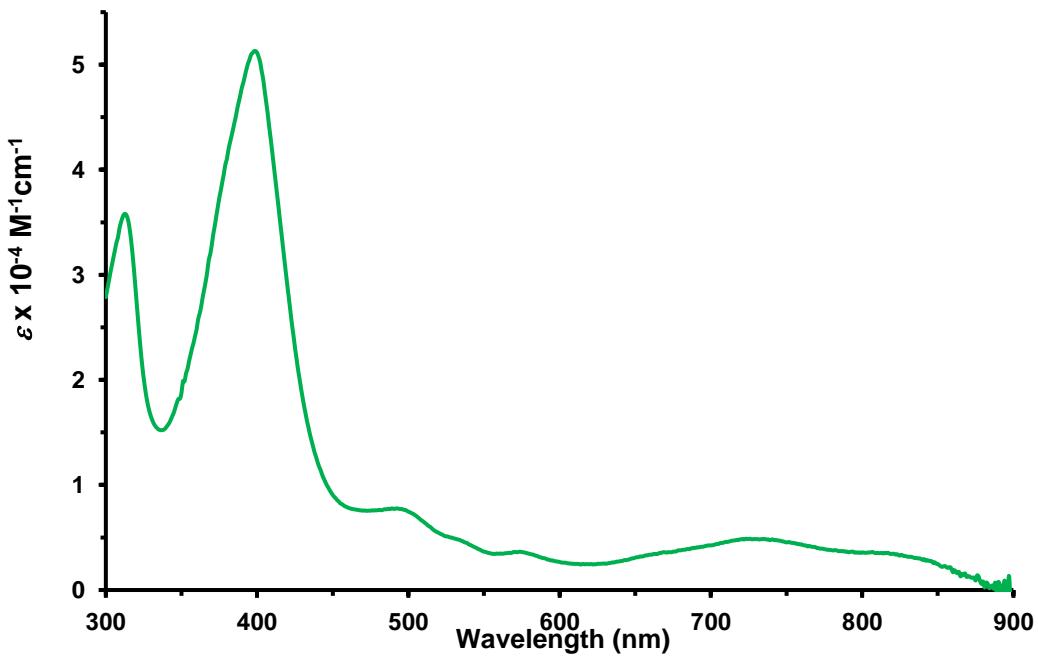


Figure S18. UV-vis spectrum of **7c** in 1% TFA- CH_2Cl_2 .

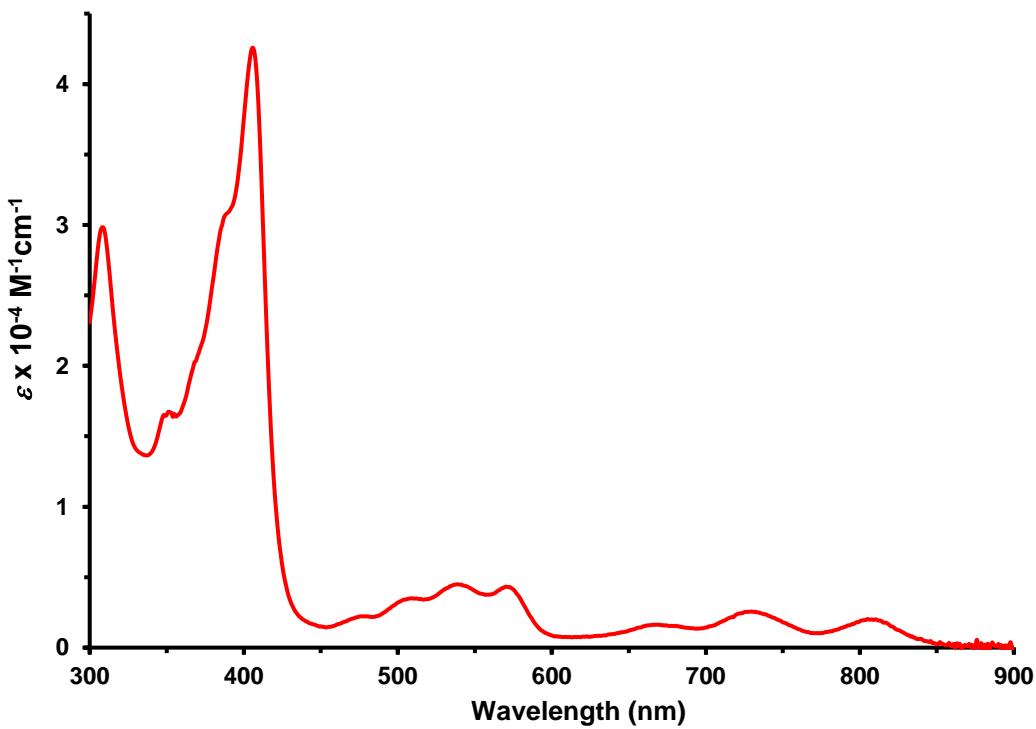


Figure S19. UV-vis spectrum of palladium(II) complex **7cPd** in CH_2Cl_2 .

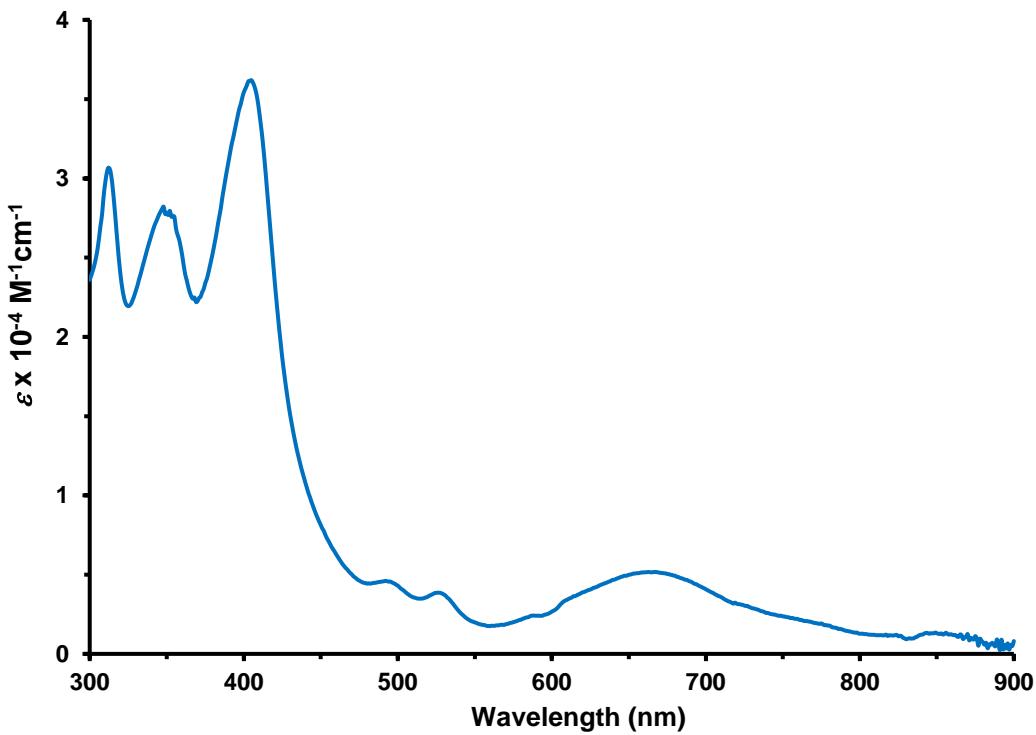


Figure S20. UV-vis spectrum of nickel(II) complex **7cNi** in CH_2Cl_2 .

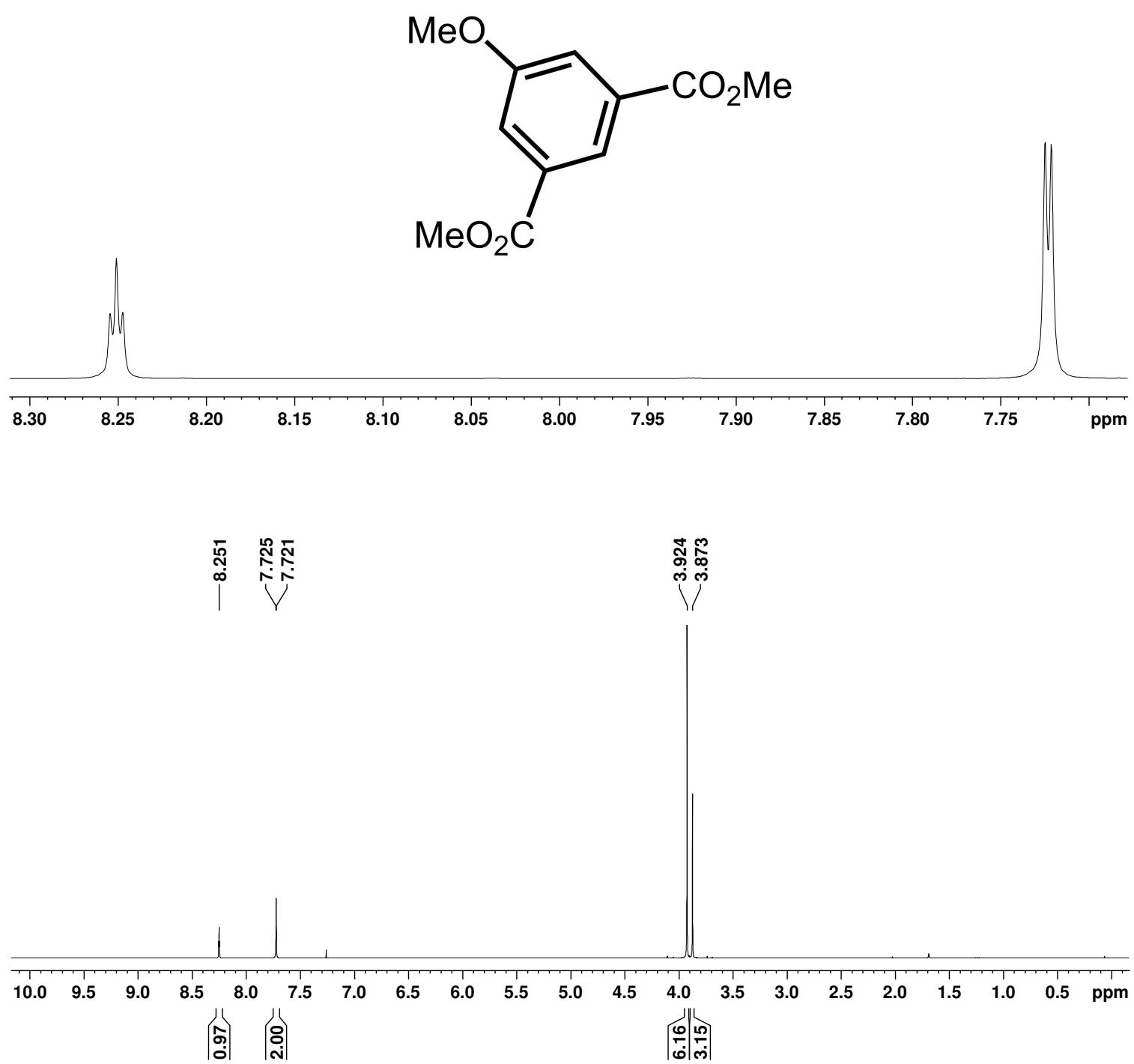


Figure S21. 400 MHz proton NMR spectrum of dimethyl 5-methoxy-1,3-benzenedicarboxylate **11a** in CDCl_3 .

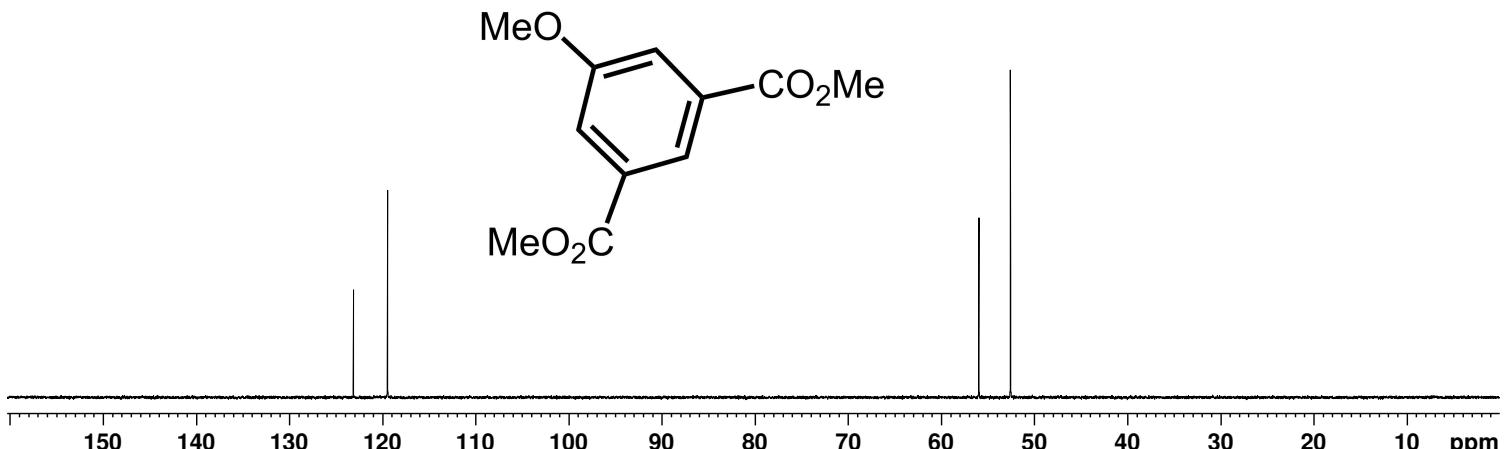


Figure S22. DEPT-135 NMR spectrum of dimethyl 5-methoxy-1,3-benzenedicarboxylate in CDCl_3 .

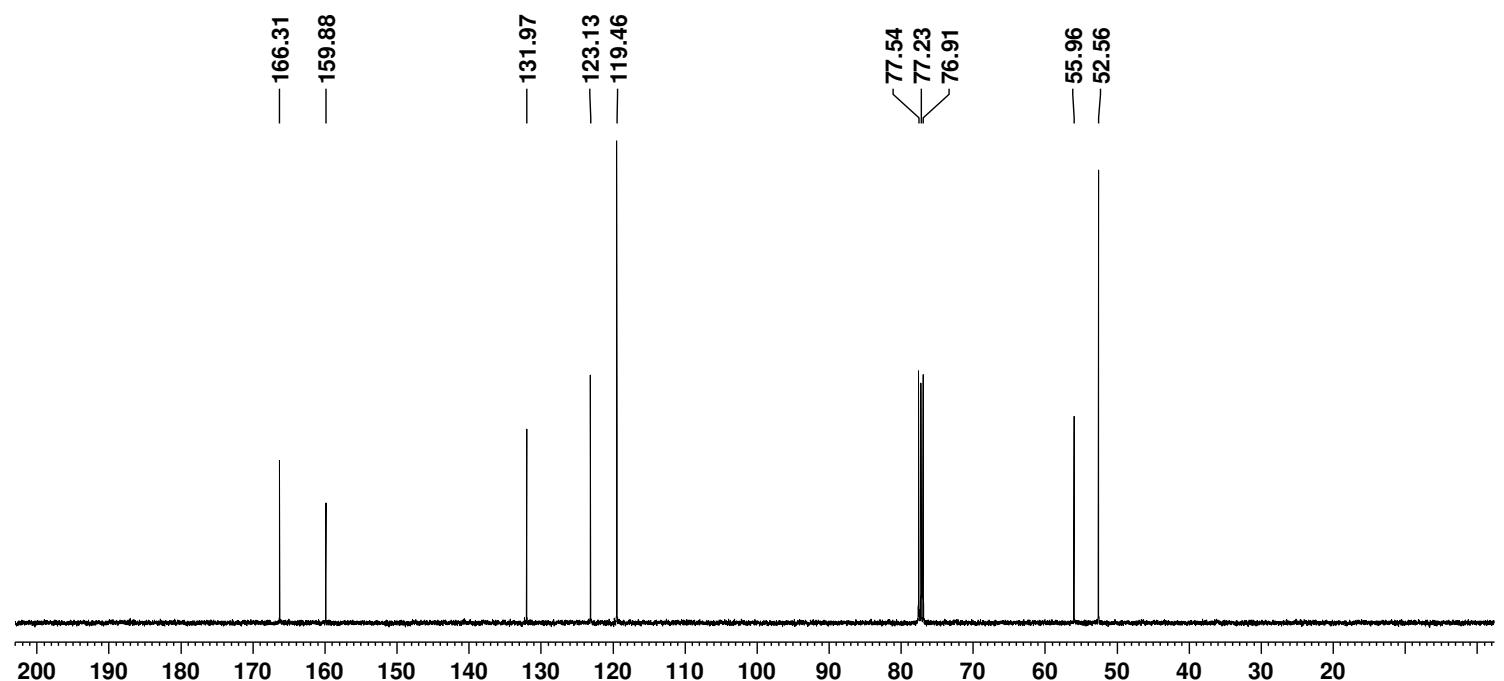


Figure S23. 100 MHz carbon-13 NMR spectrum of dimethyl 5-methoxy-1,3-benzenedicarboxylate in CDCl_3 .

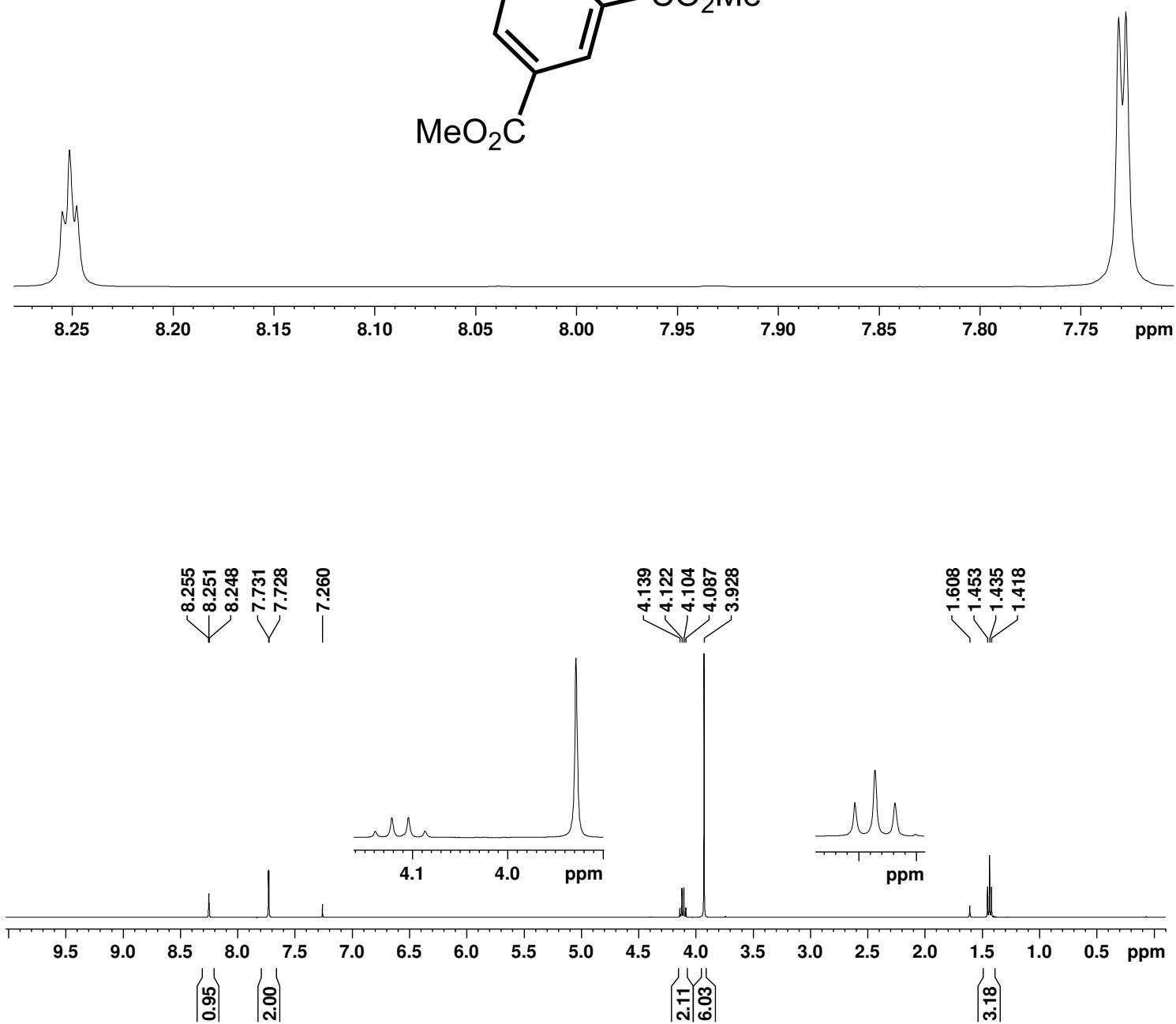
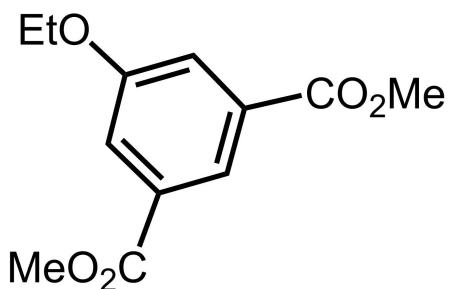


Figure S24. 400 MHz proton NMR spectrum of dimethyl 5-ethoxy-1,3-benzenedicarboxylate **11b** in CDCl_3 .

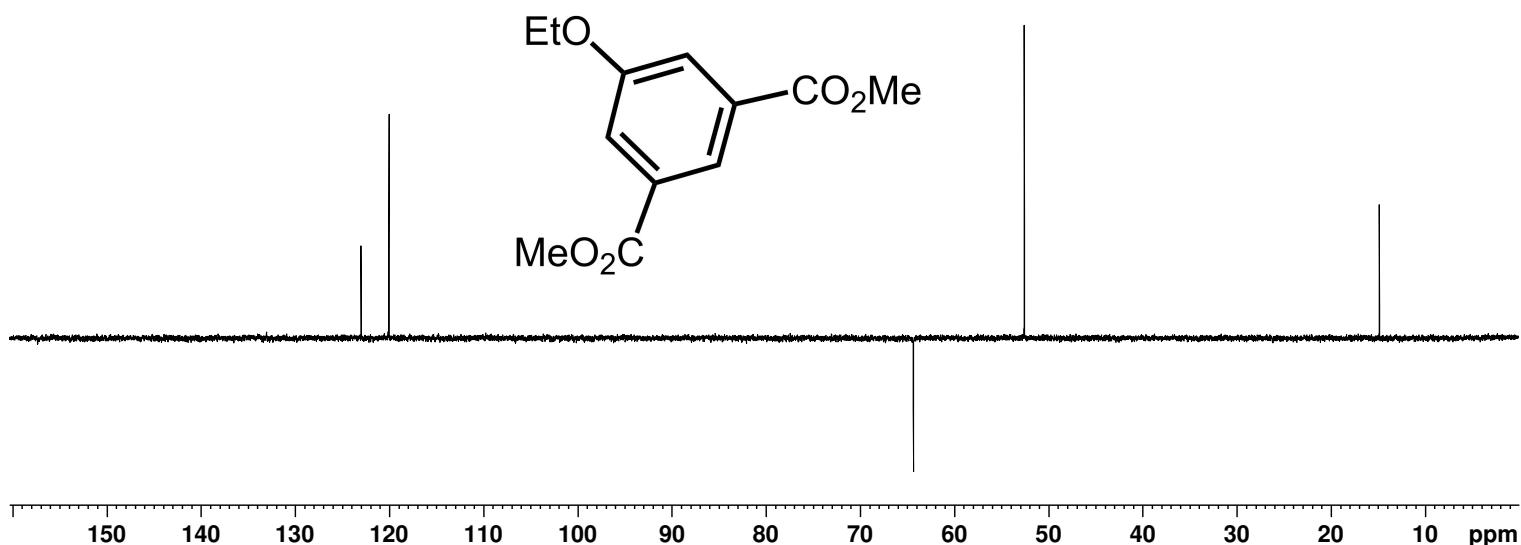


Figure S25. DEPT-135 NMR spectrum of dimethyl 5-ethoxy-1,3-benzenedicarboxylate in CDCl₃.

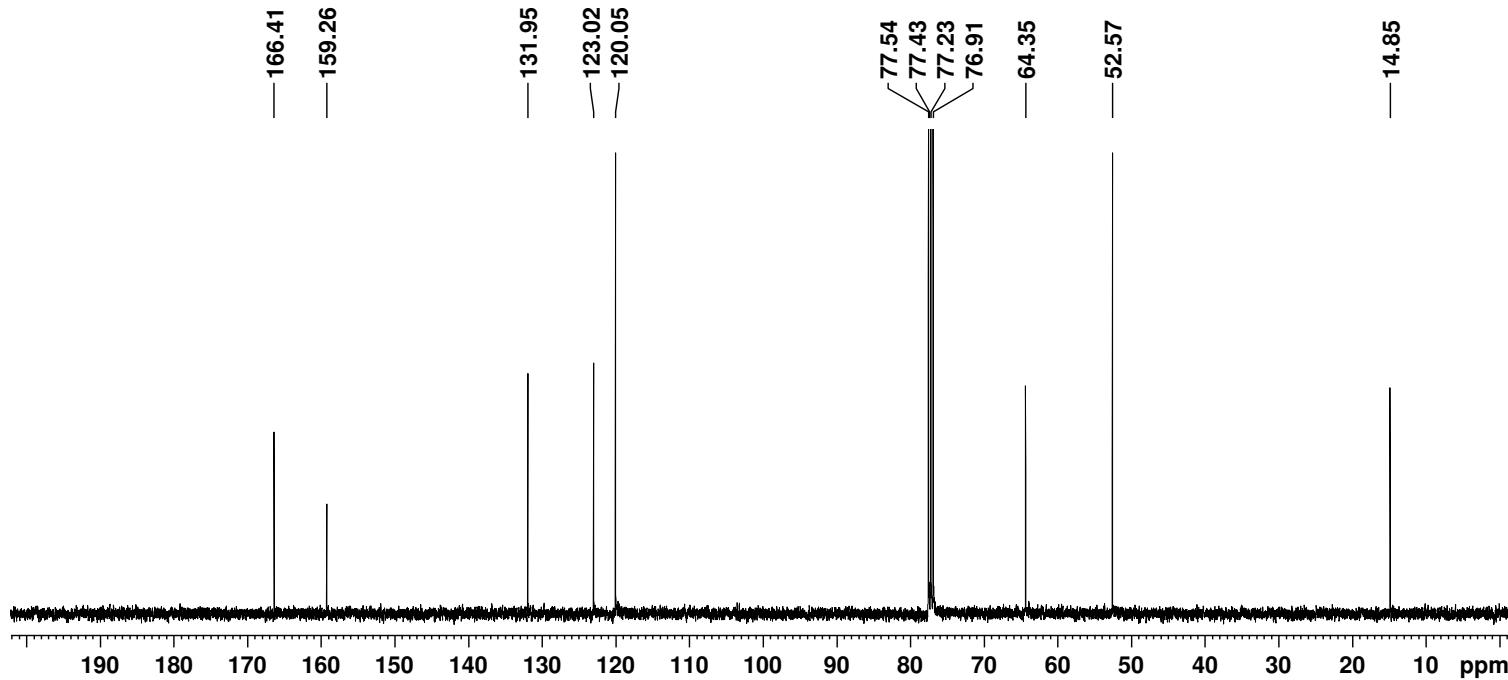
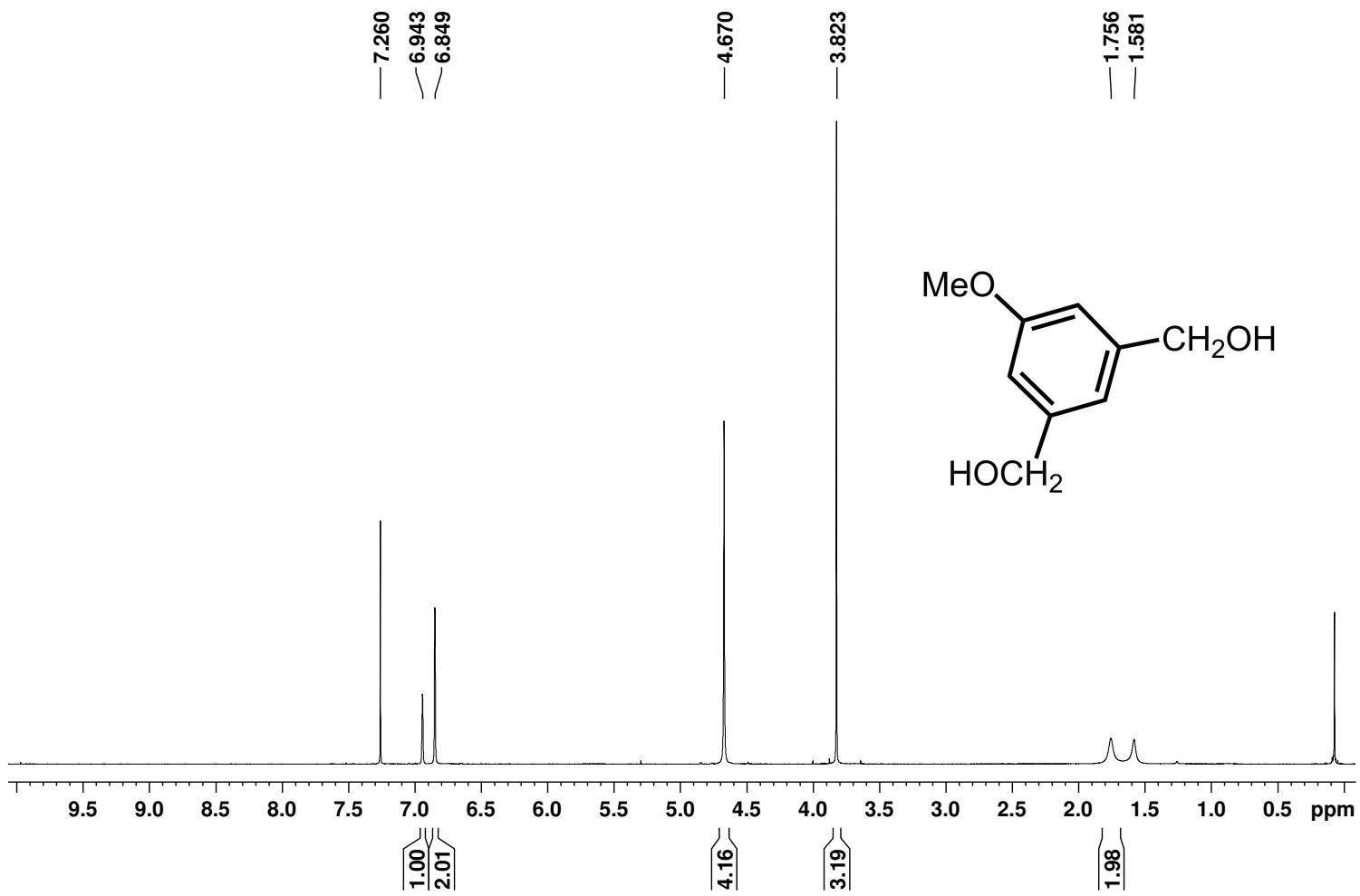
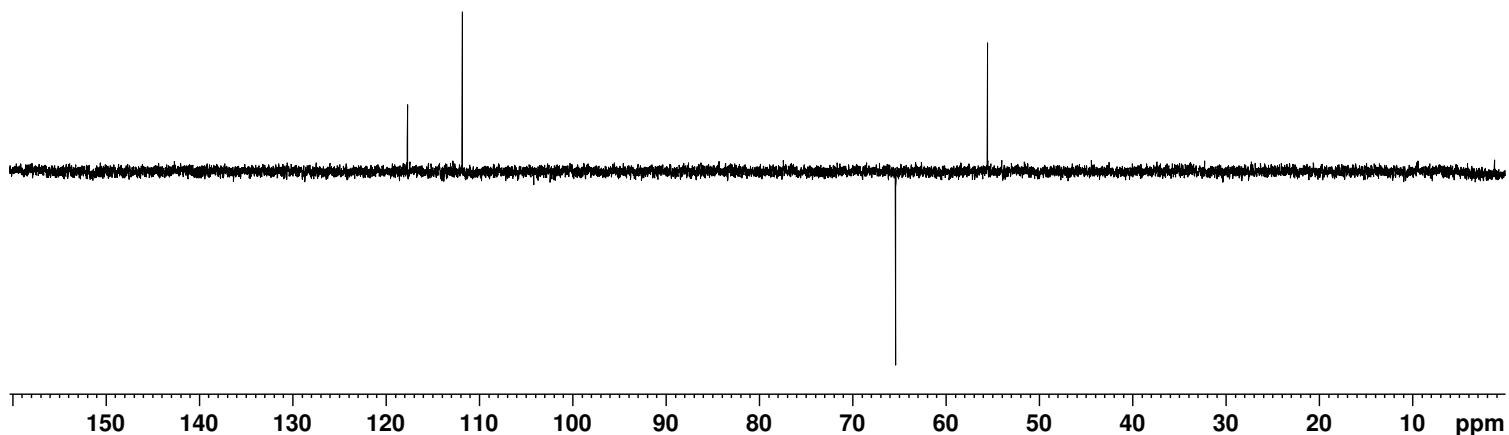


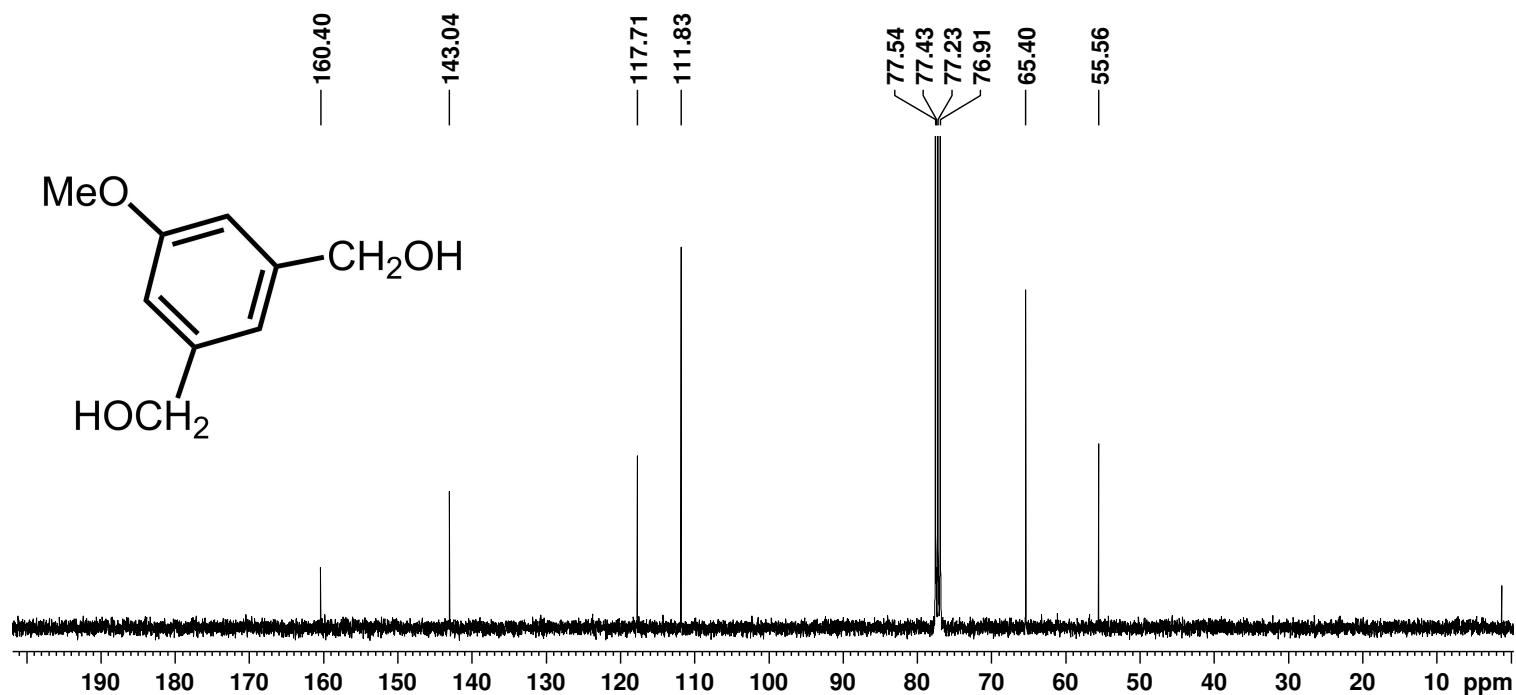
Figure S26. 100 MHz carbon-13 NMR spectrum of dimethyl 5-ethoxy-1,3-benzenedicarboxylate in CDCl₃.



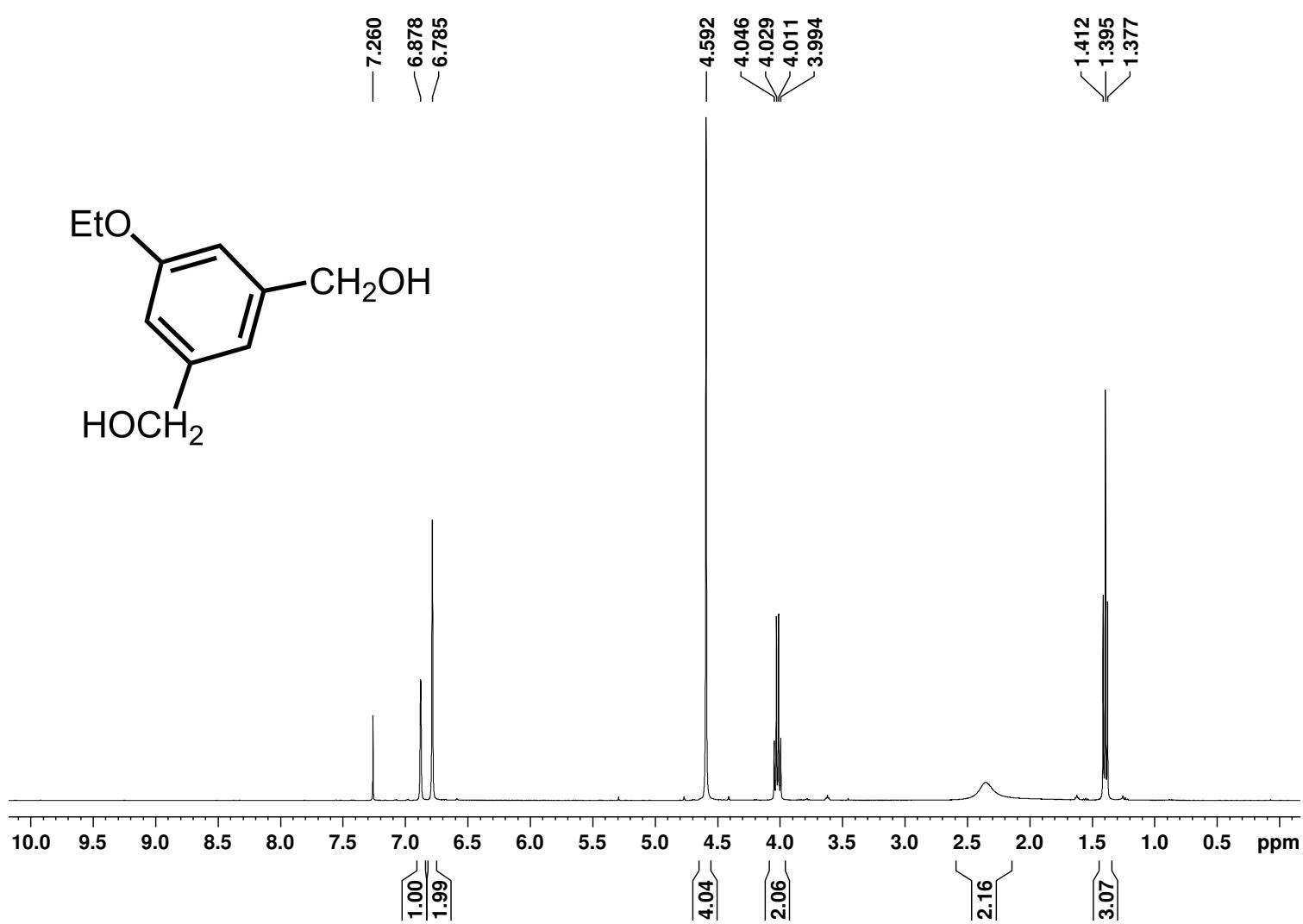
Scheme S27. 400 MHz proton NMR spectrum of methoxybenzenedicarbinol **12a** in CDCl_3 .



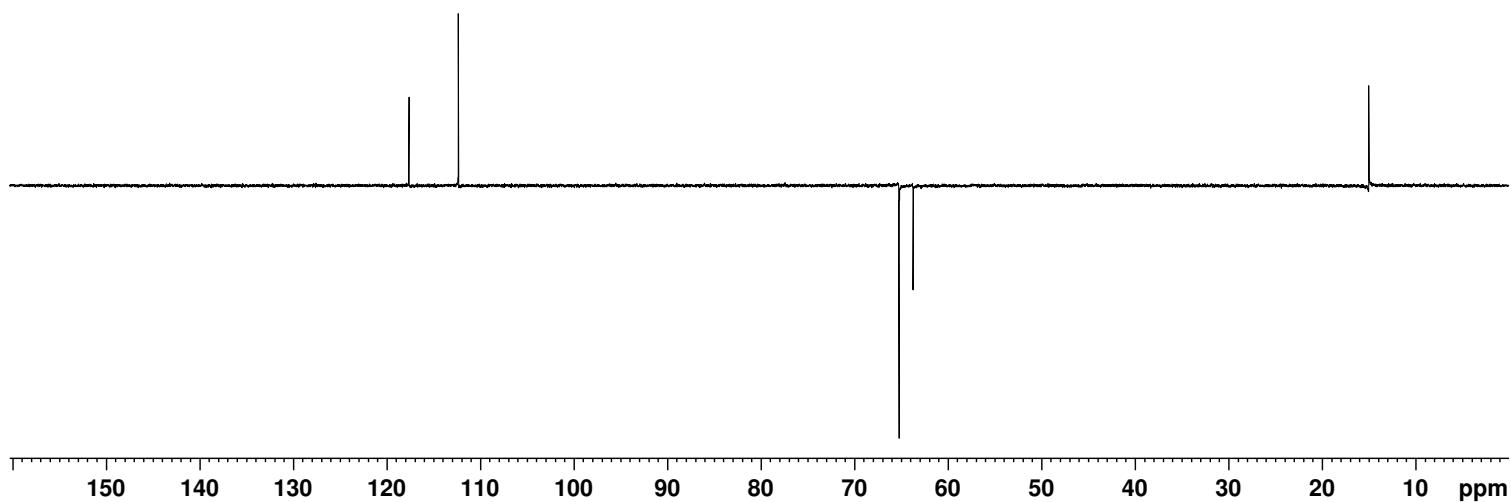
Scheme S28. DEPT-135 NMR spectrum of methoxybenzenedicarbinol **12a** in CDCl_3 .



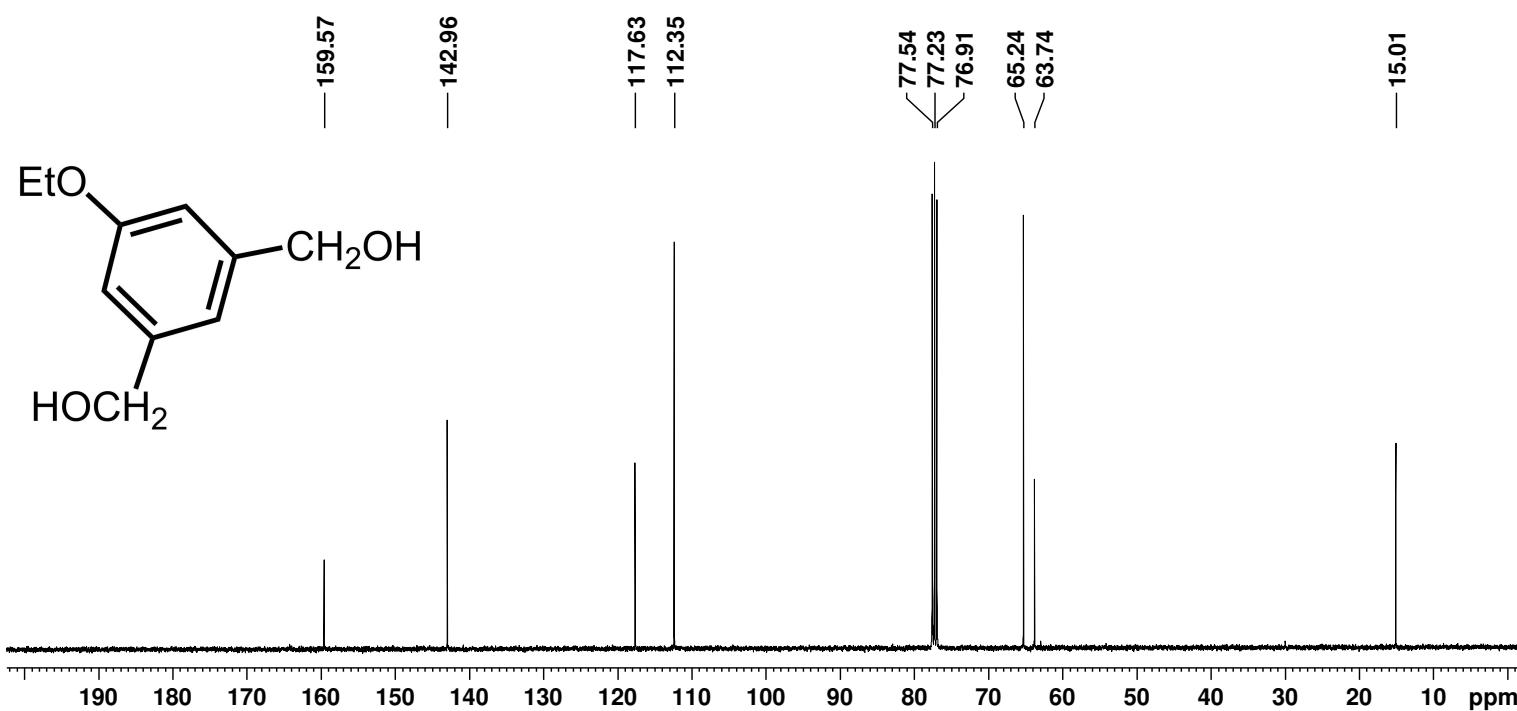
Scheme S29. 100 MHz carbon-13 NMR spectrum of methoxybenzenedicarbinol **12a** in CDCl_3 .



Scheme S30. 400 MHz proton NMR spectrum of ethoxybenzenedicarbinol **12b** in CDCl_3 .



Scheme S31. DEPT-135 NMR spectrum of ethoxybenzenedicarbinol **12b** in CDCl_3 .



Scheme S32. 100 MHz carbon-13 NMR spectrum of ethoxybenzenedicarbinol **12b** in CDCl_3 .

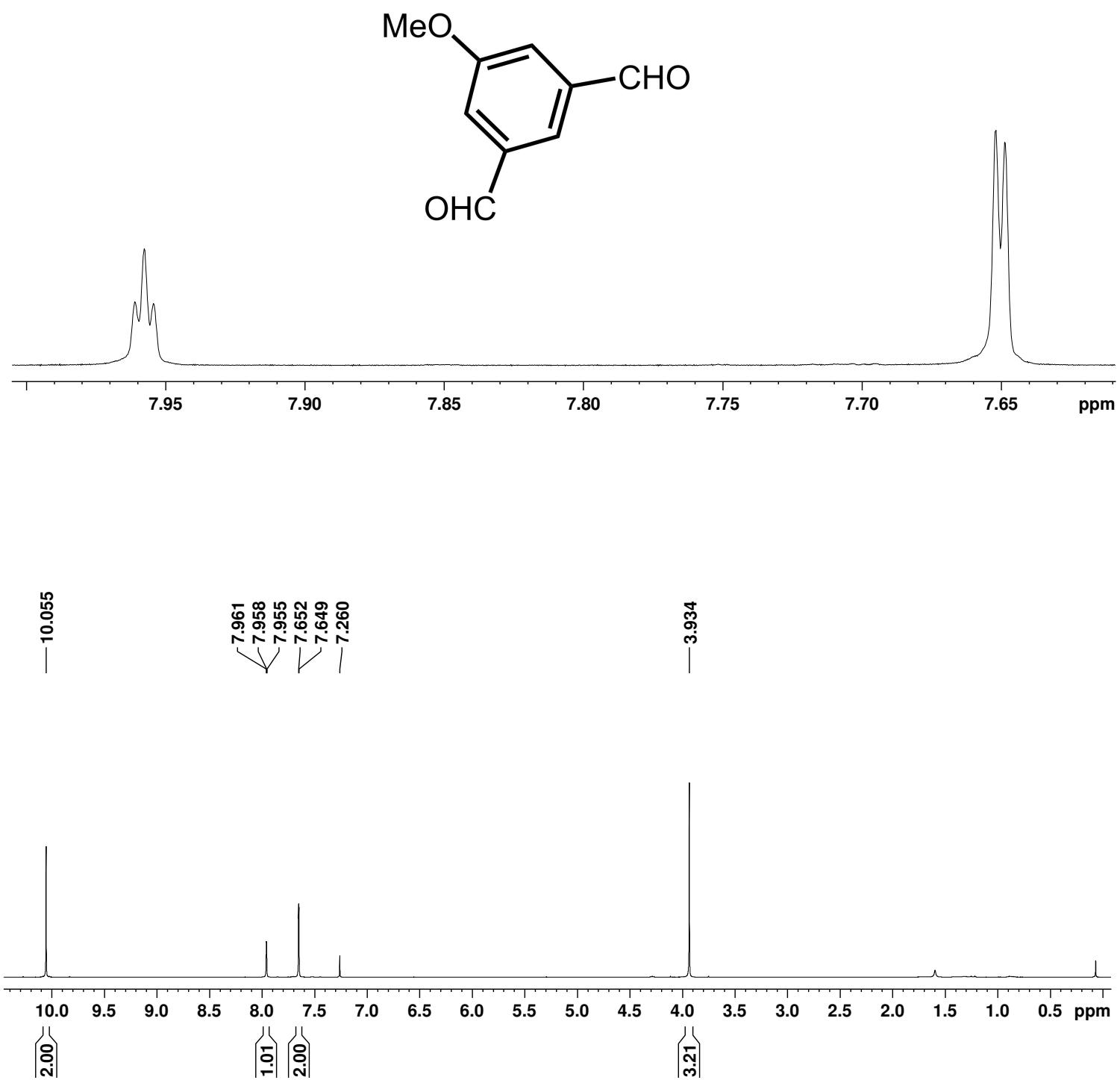


Figure S33. 400 MHz proton NMR spectrum of 5-methoxy-1,3-benzene dicarbaldehyde (**8a**) in CDCl_3 .

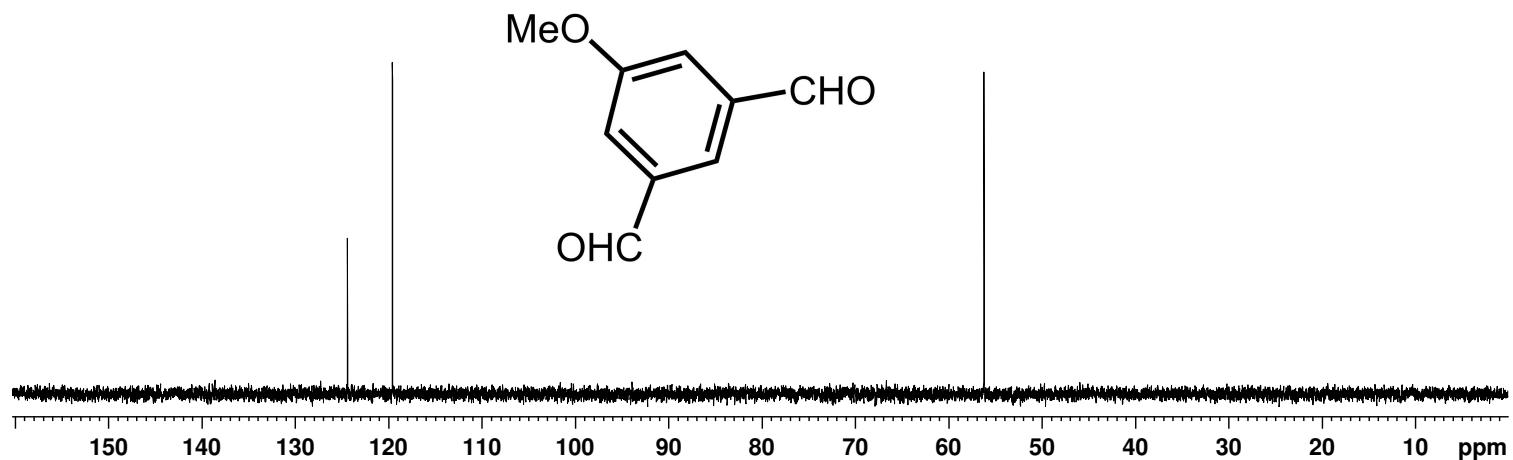


Figure S34. DEPT-135 NMR spectrum of 5-methoxy-1,3-benzene dicarbaldehyde (**8a**) in CDCl_3 .

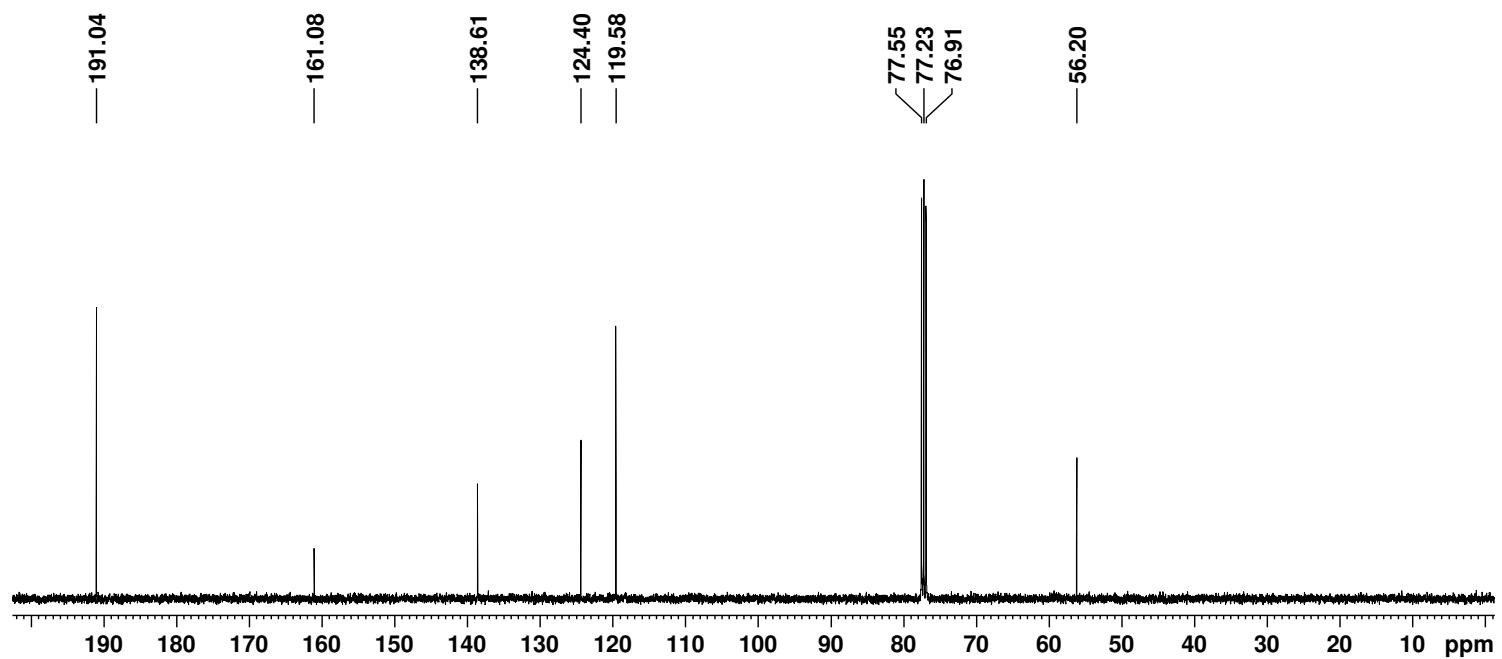


Figure S35. 100 MHz carbon-13 NMR spectrum of 5-methoxy-1,3-benzene dicarbaldehyde (**8a**) in CDCl_3 .

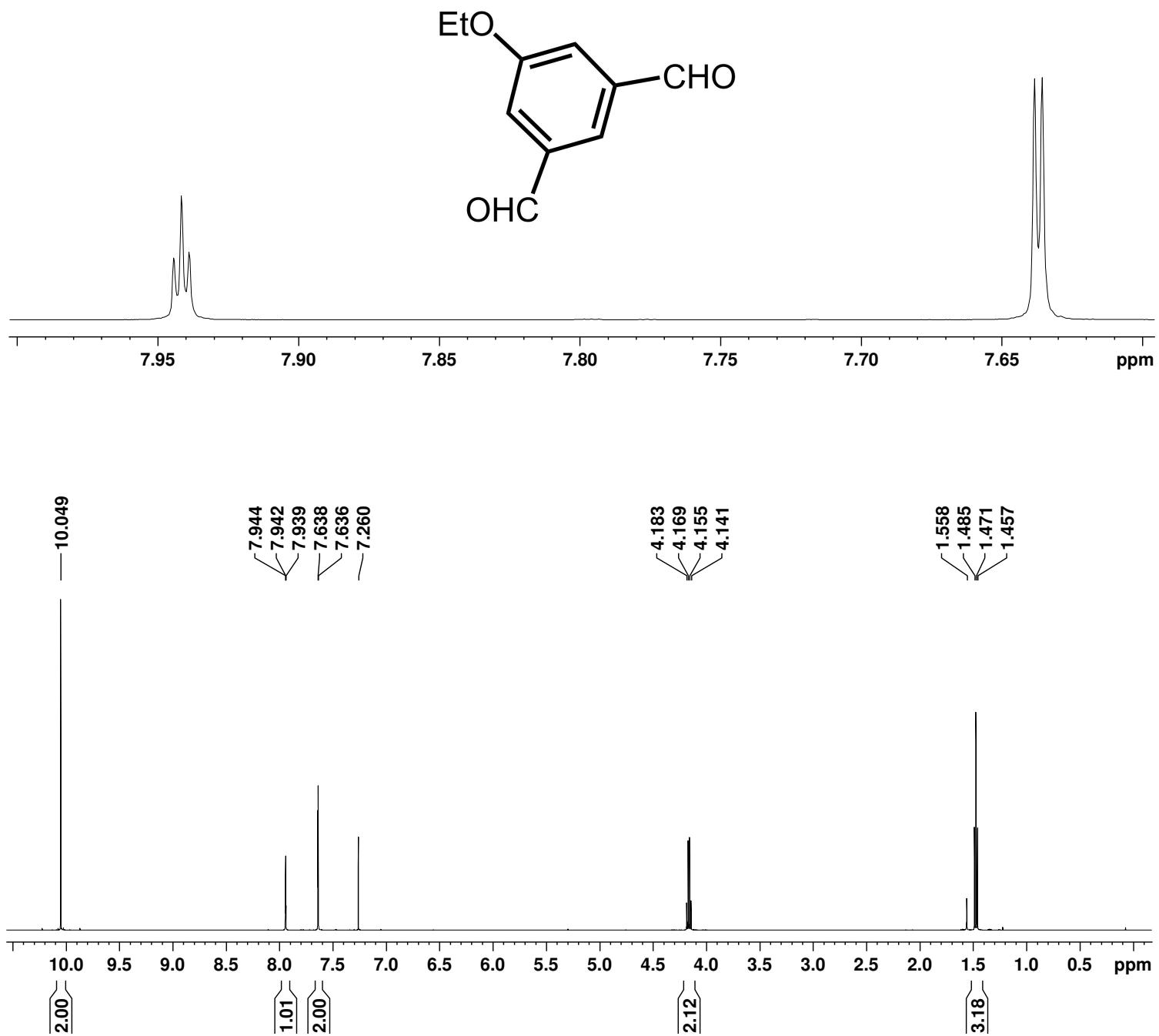


Figure S36. 500 MHz proton NMR spectrum of 5-ethoxy-1,3-benzene dicarbaldehyde (**8b**) in CDCl_3 .

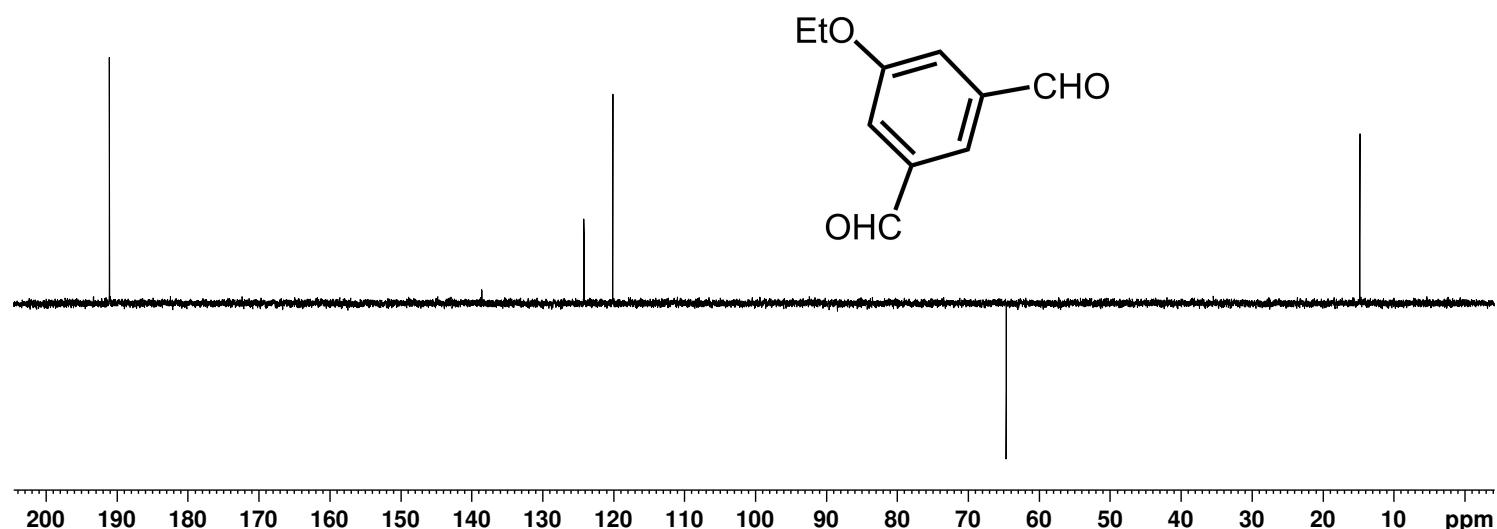


Figure S37. DEPT-135 NMR spectrum of 5-ethoxy-1,3-benzene dicarbaldehyde (**8b**) in CDCl_3 .

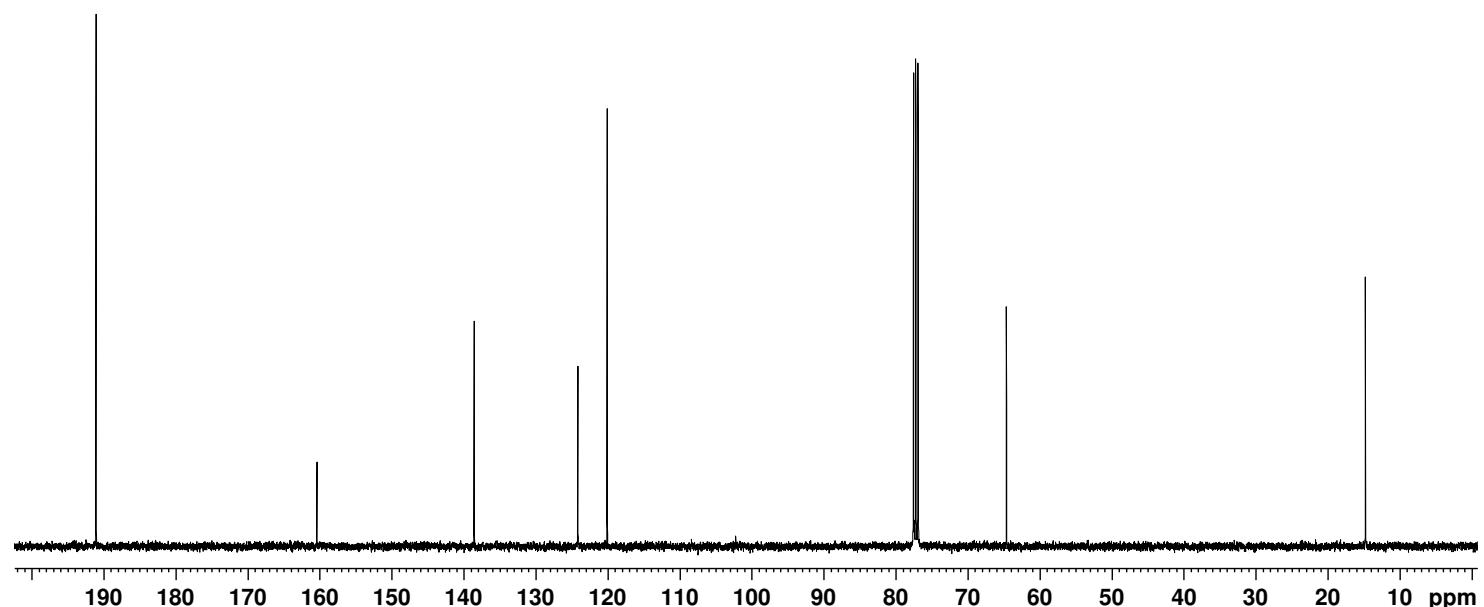


Figure S38. 125 MHz carbon-13 NMR spectrum of 5-ethoxy-1,3-benzene dicarbaldehyde (**8b**) in CDCl_3 .

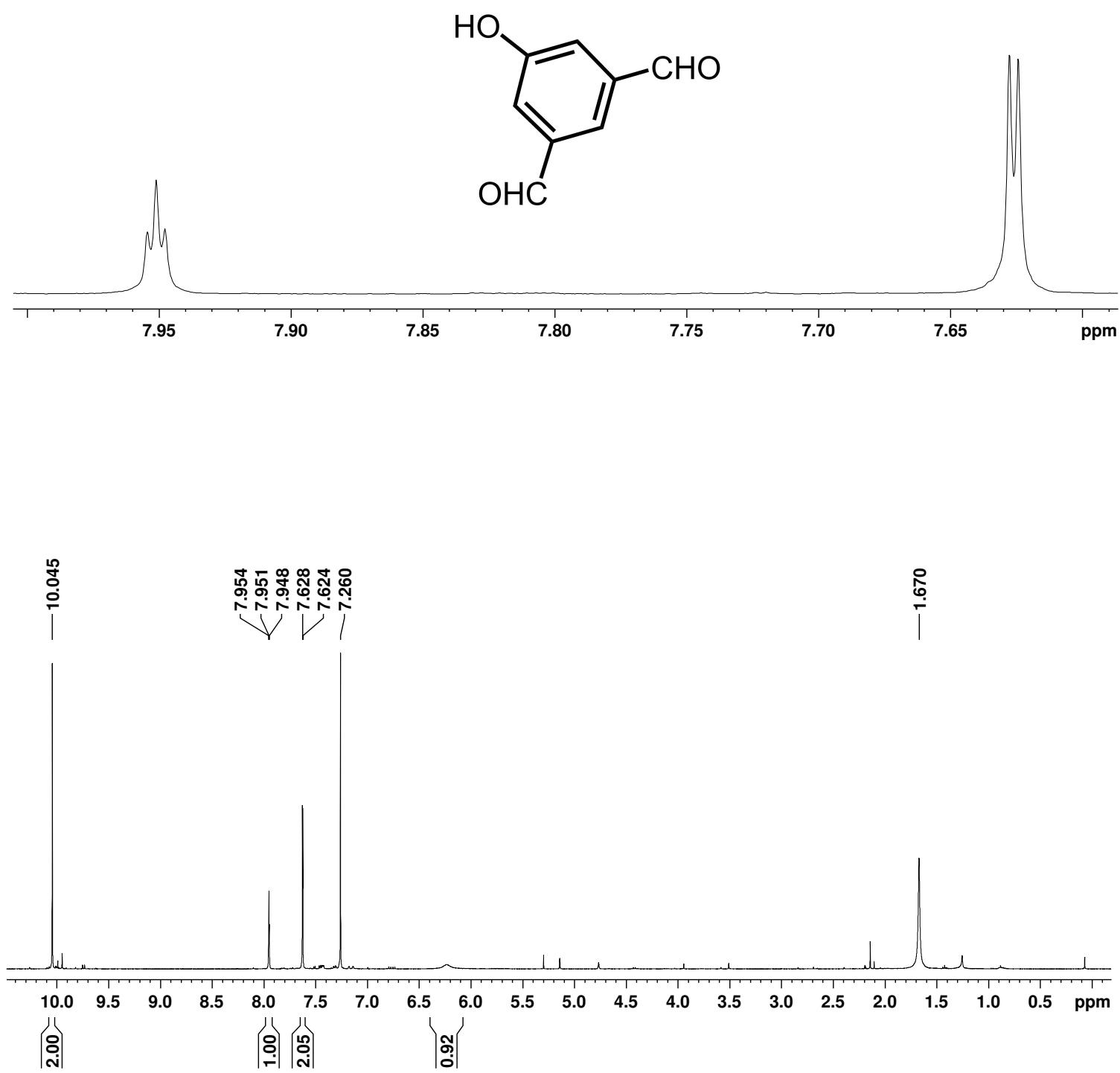


Figure S39. 400 MHz proton NMR spectrum of 5-hydroxy-1,3-benzene dicarbaldehyde (**14**) in CDCl_3 .

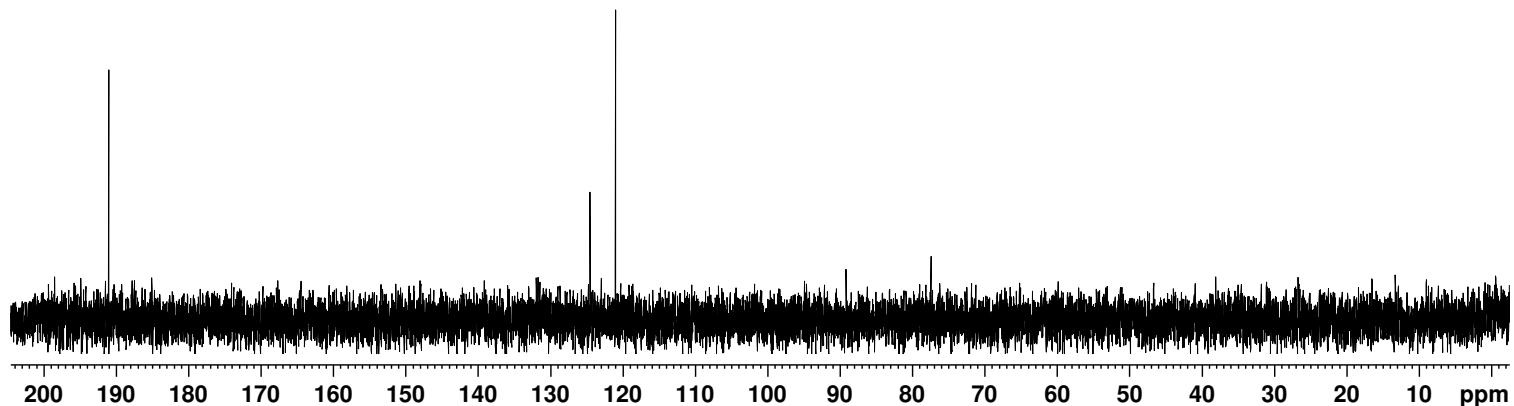


Figure S40. DEPT-135 NMR spectrum of 5-hydroxy-1,3-benzene dicarbaldehyde (**14**) in CDCl_3 .

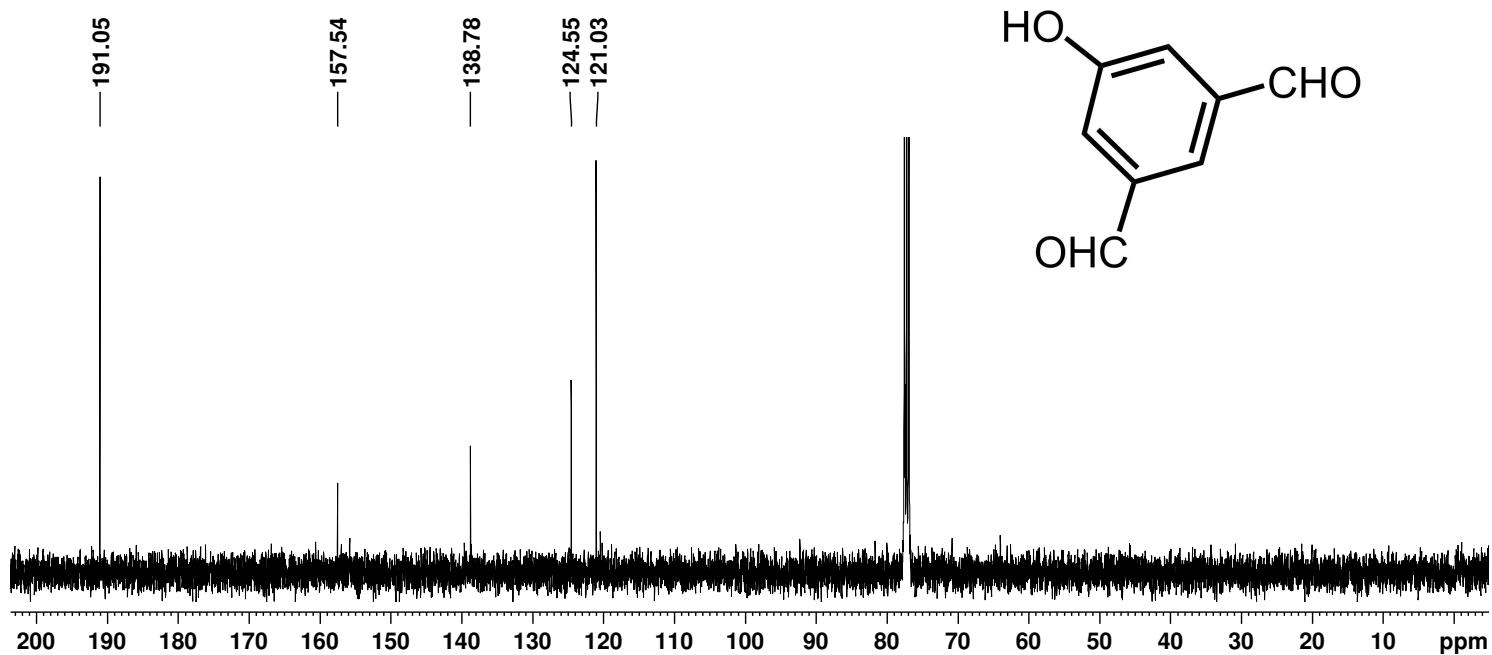


Figure S41. 100 MHz carbon-13 NMR spectrum of 5-hydroxy-1,3-benzene dicarbaldehyde (**14**) in CDCl_3 .

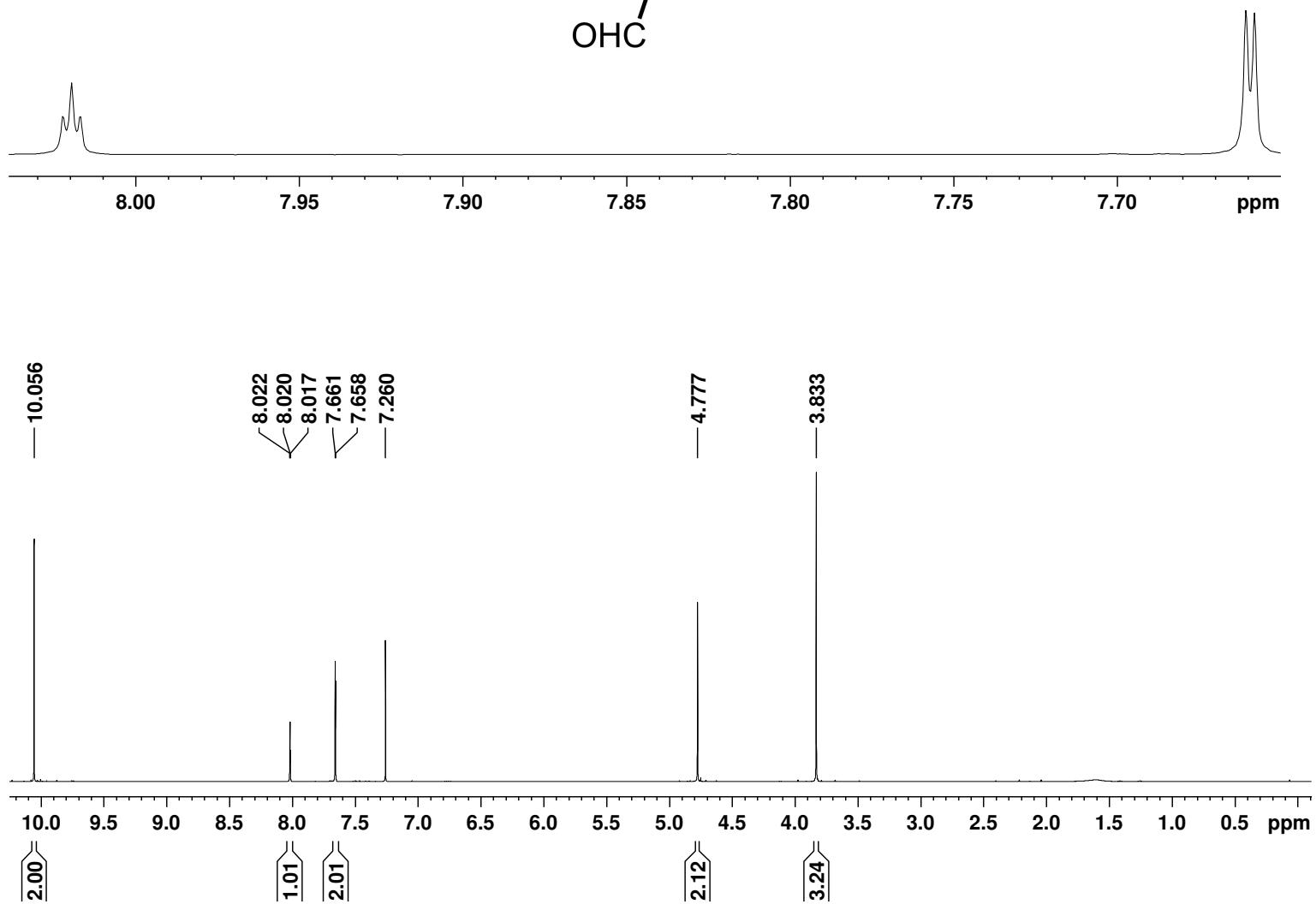
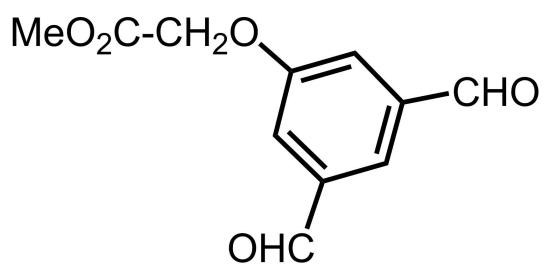


Figure S42. 500 MHz proton NMR spectrum of 5(methoxycarbonylmethyl)-1,3-benzene dicarbaldehyde (**8c**) in CDCl_3 .

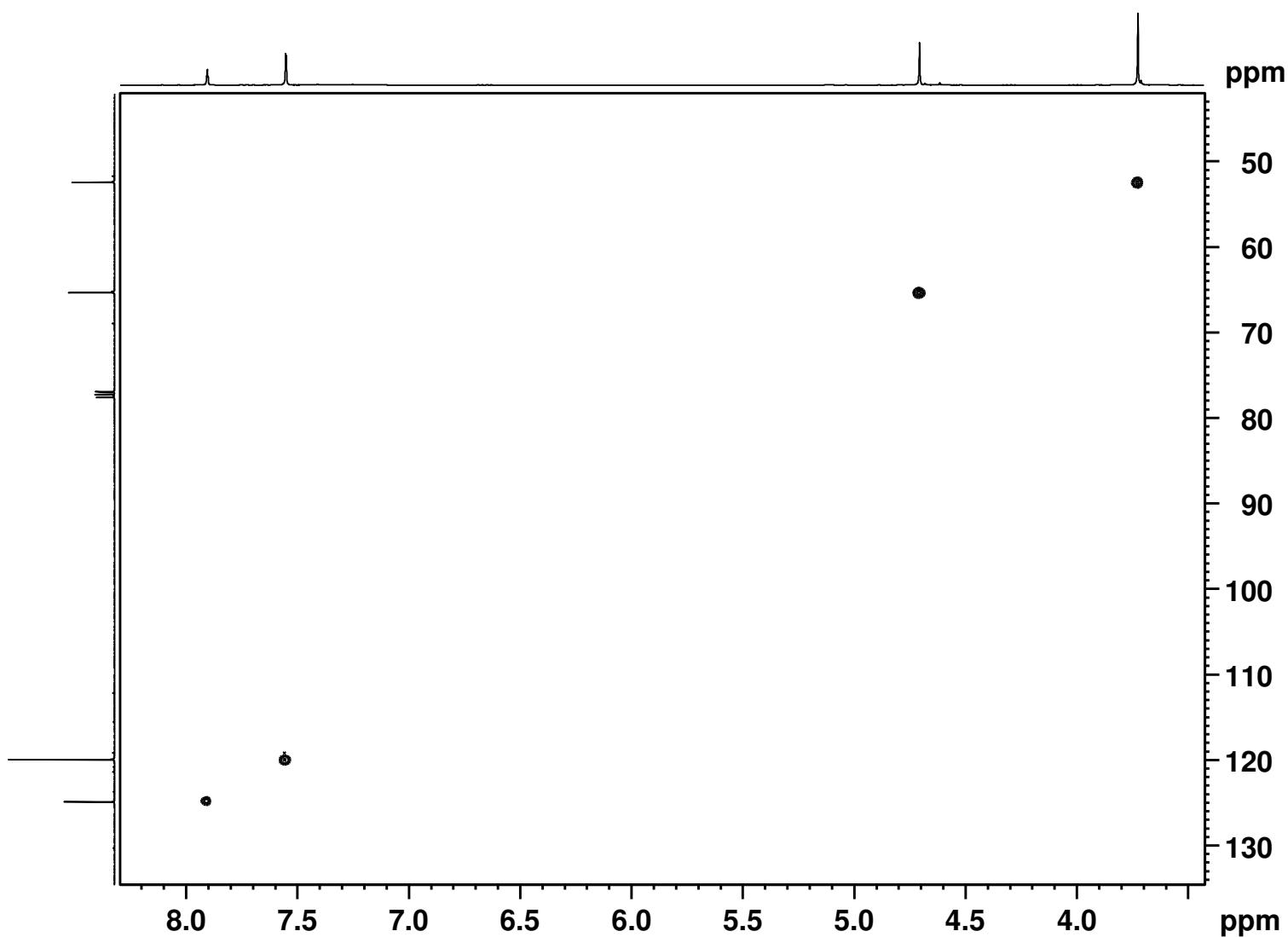


Figure S43. HSQC NMR spectrum of **8c** in CDCl_3 .

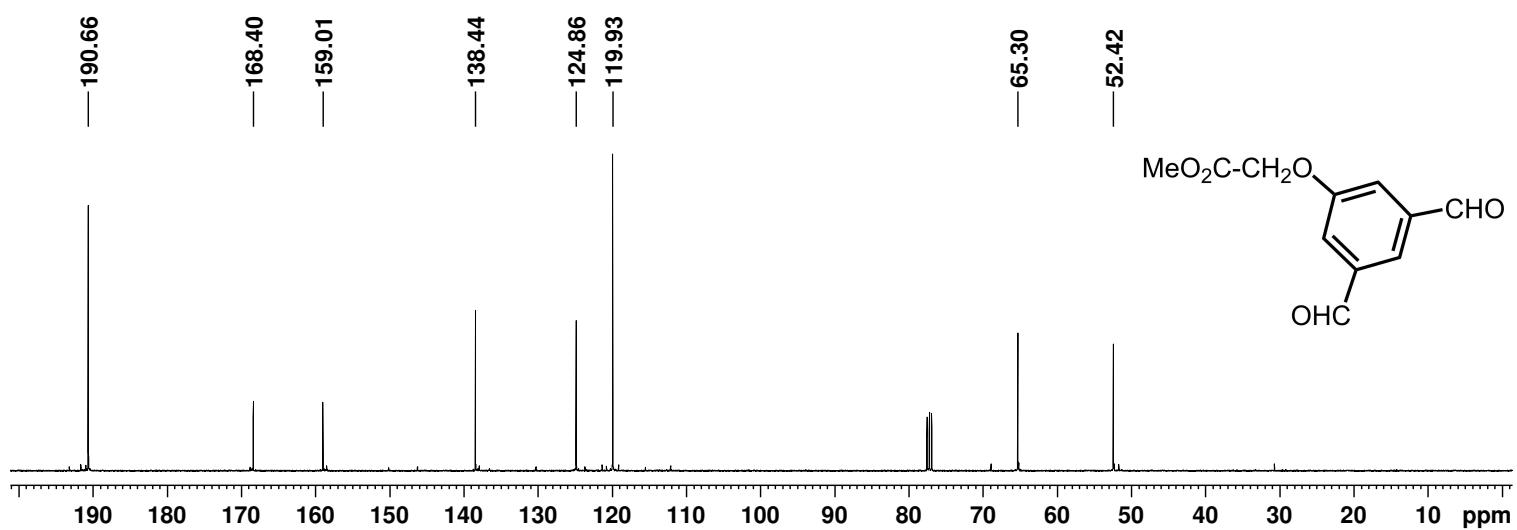


Figure S44. 100 MHz carbon-13 NMR spectrum of **8c** in CDCl_3 .

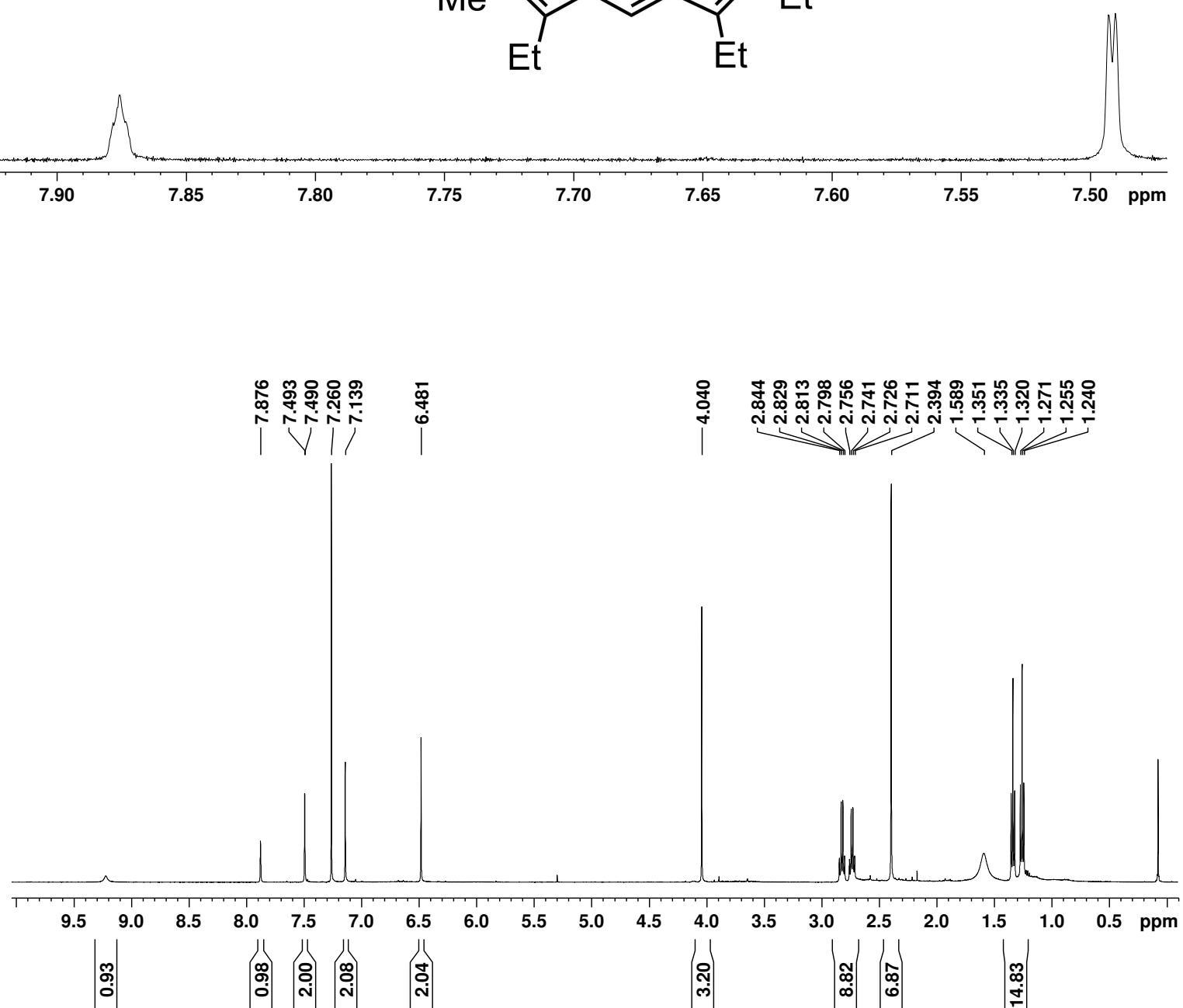
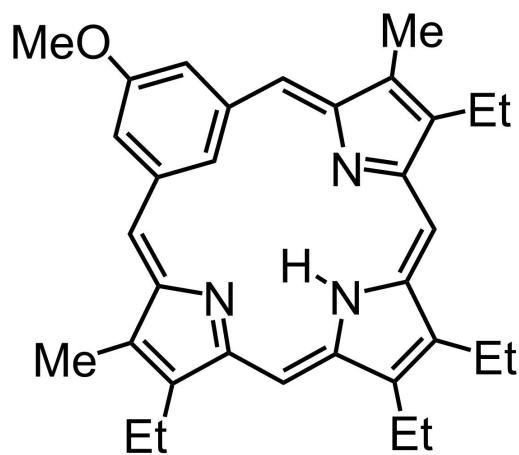


Figure S45. 500 MHz proton NMR spectrum of methoxybenzoporphyrin **7a** in CDCl_3 .

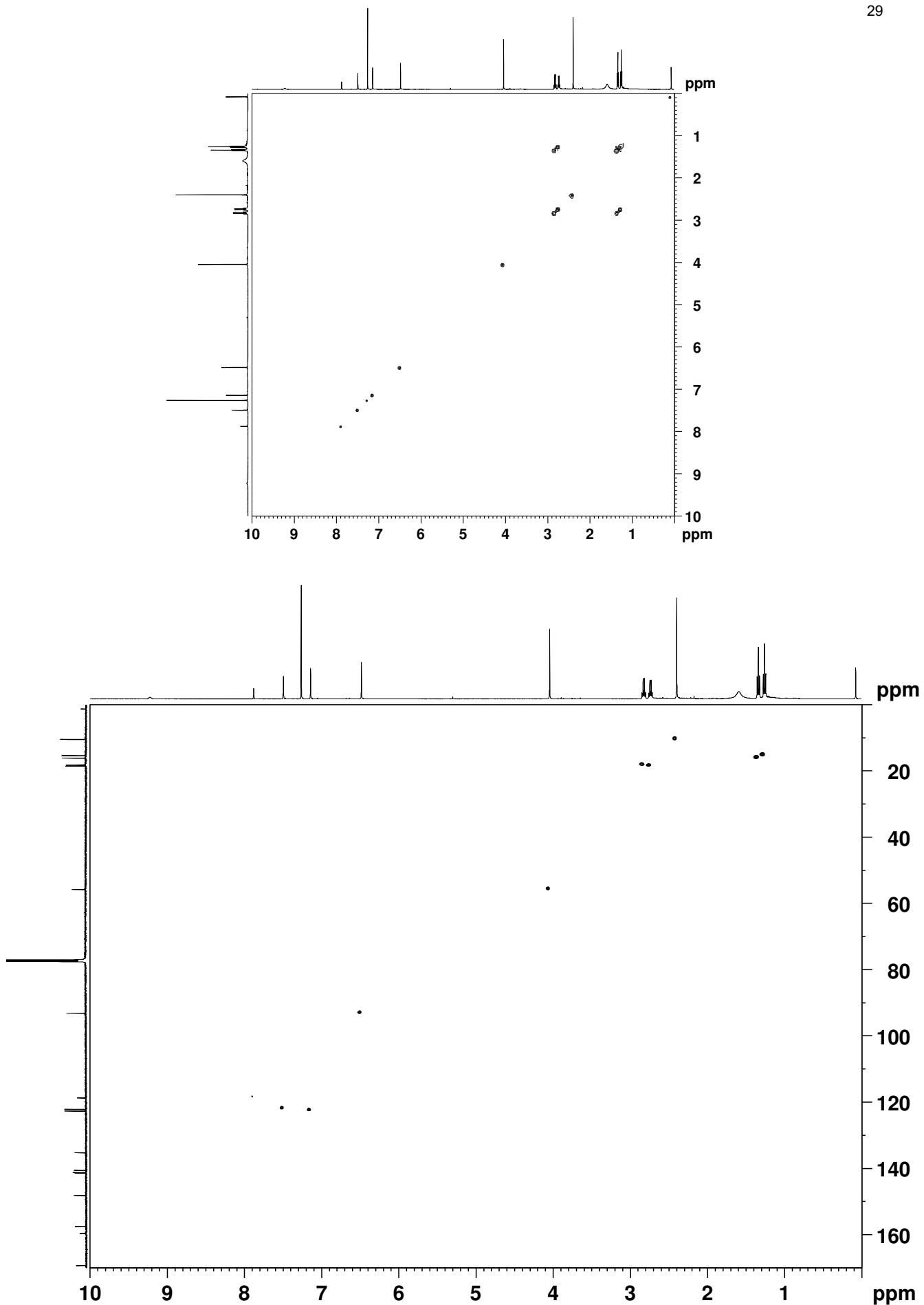


Figure S46. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of methoxybenzoporphyrin **7a** in CDCl_3 .

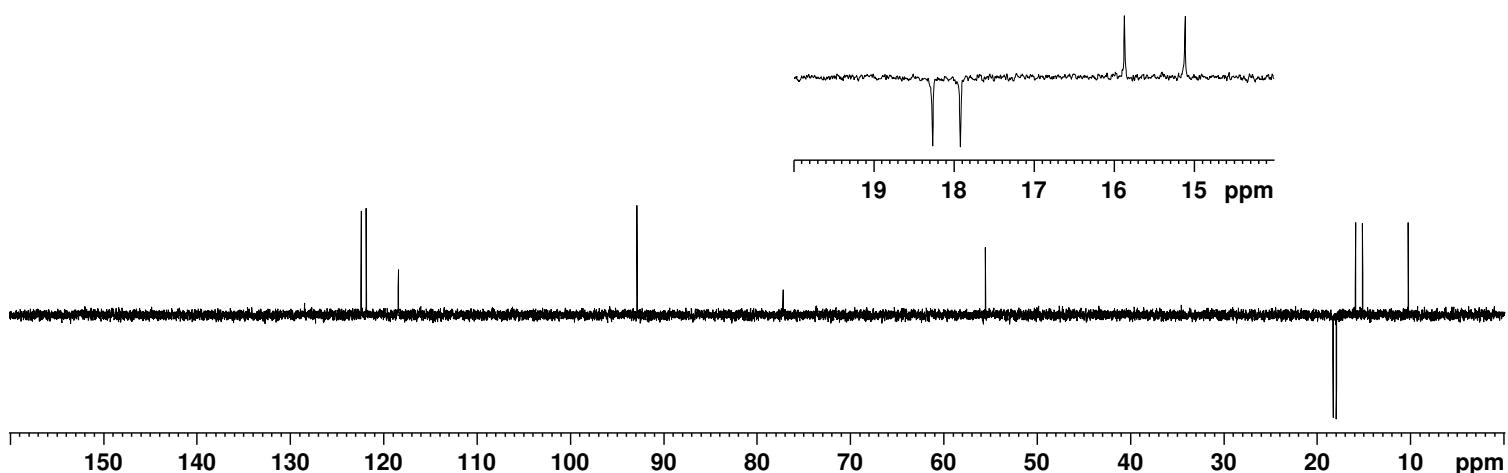


Figure S47. DEPT-135 NMR spectrum of **7a** in CDCl_3 .

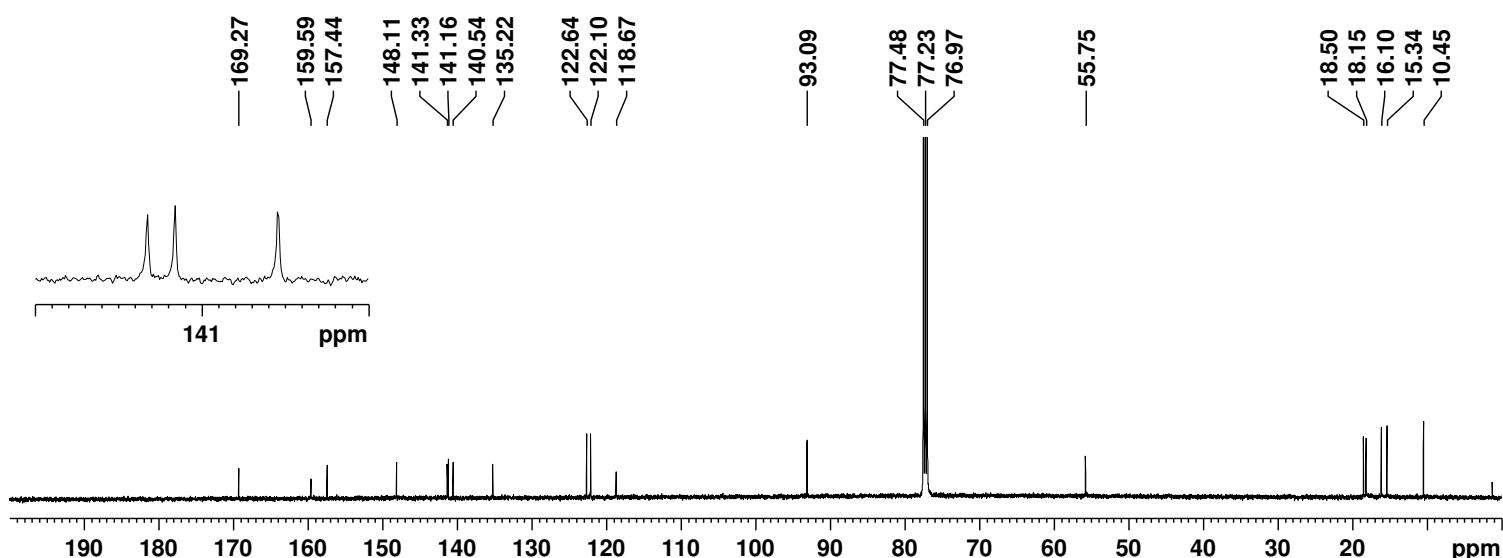
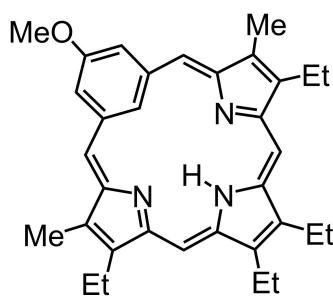


Figure S48. 125 MHz carbon-13 NMR spectrum of methoxybenzoporphyrin **7a** in CDCl_3 .

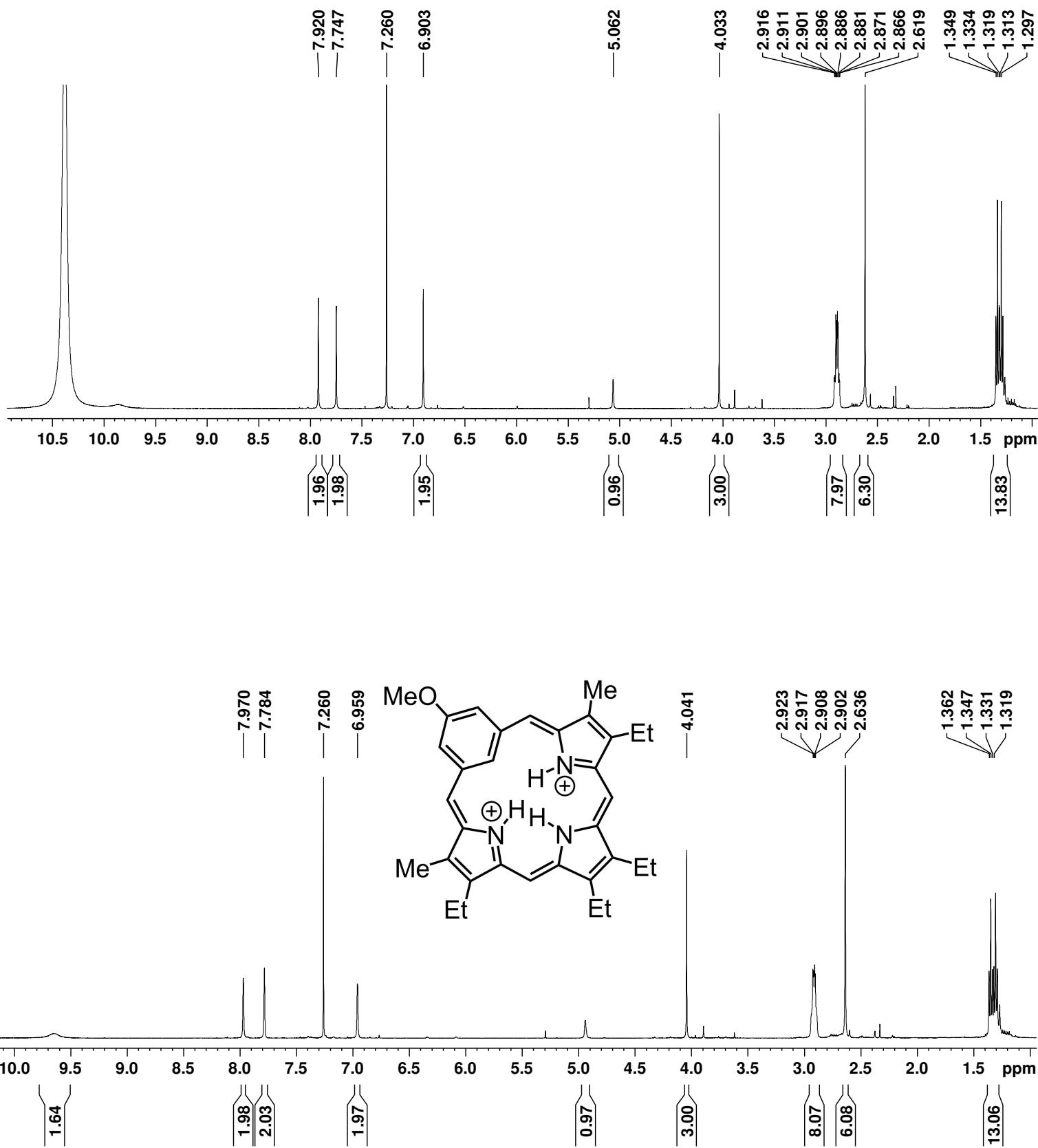


Figure S49. 500 MHz proton NMR spectra of **7a** in the presence of TFA and CDCl_3 . The second spectrum shows the results from adding several additional drops of TFA.

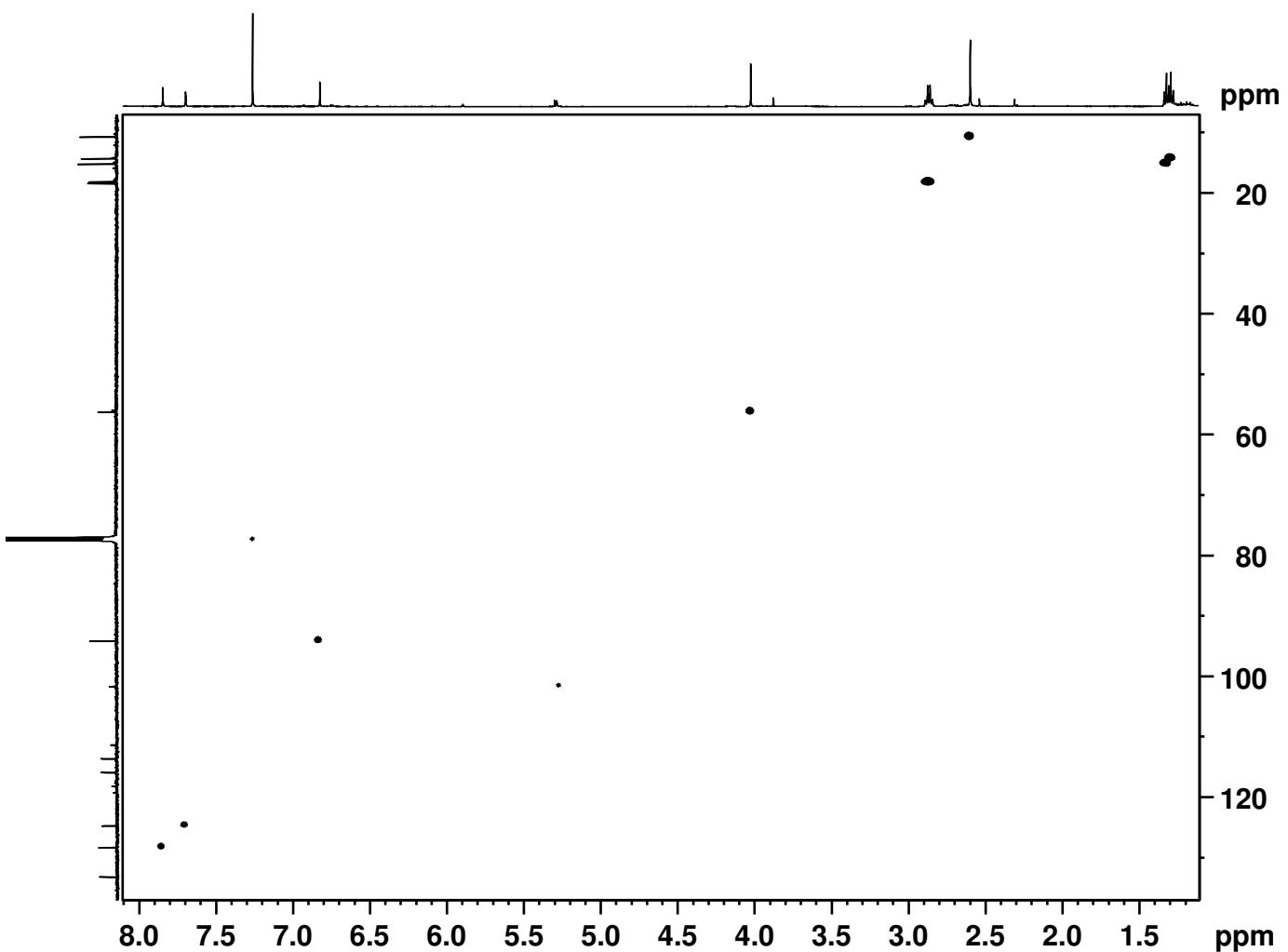
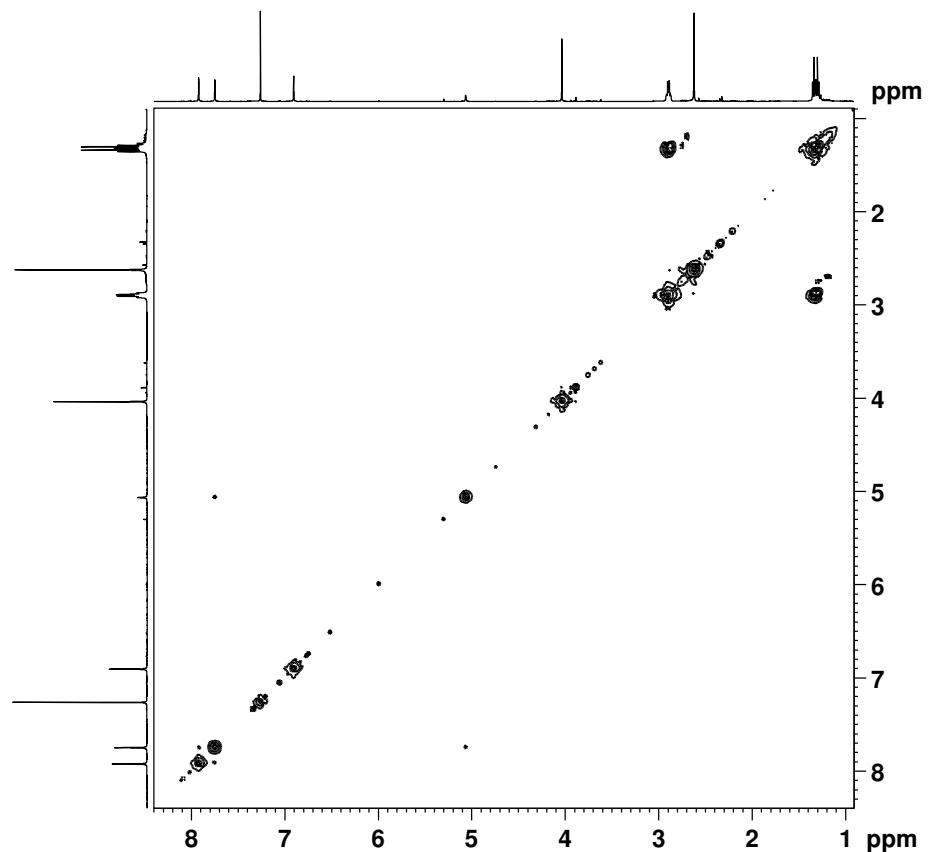


Figure S50. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of 7aH_2^{2+} in TFA- CDCl_3 .

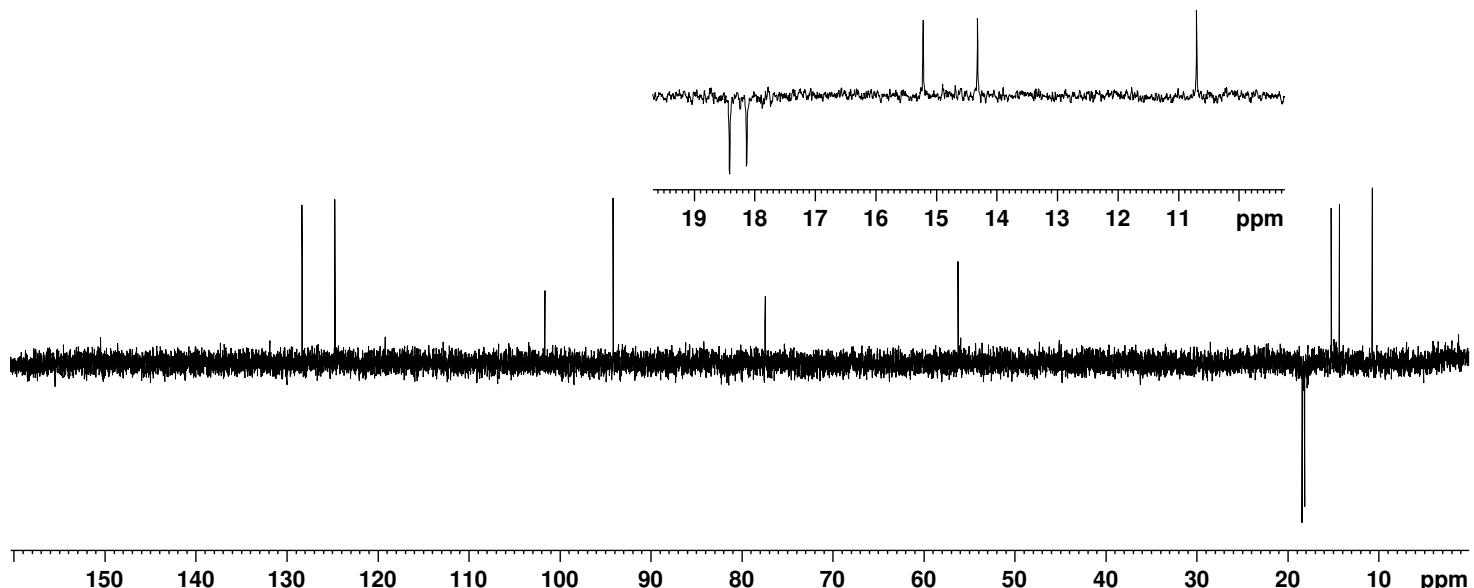


Figure S51. DEPT-135 NMR spectrum of 7aH_2^{2+} in TFA- CDCl_3 .

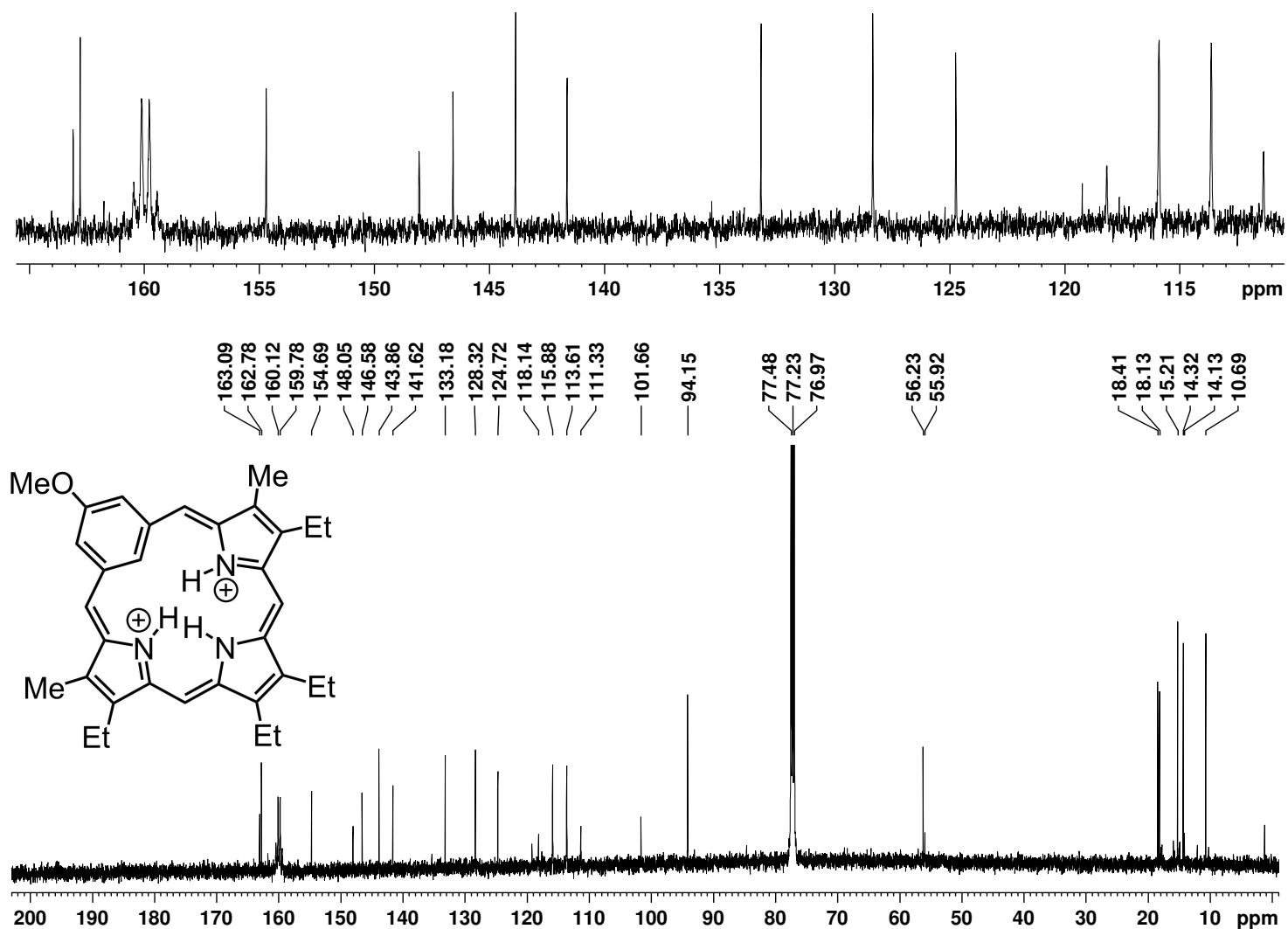


Figure S52. 125 MHz carbon-13 NMR spectrum of 7aH_2^{2+} in TFA- CDCl_3 .

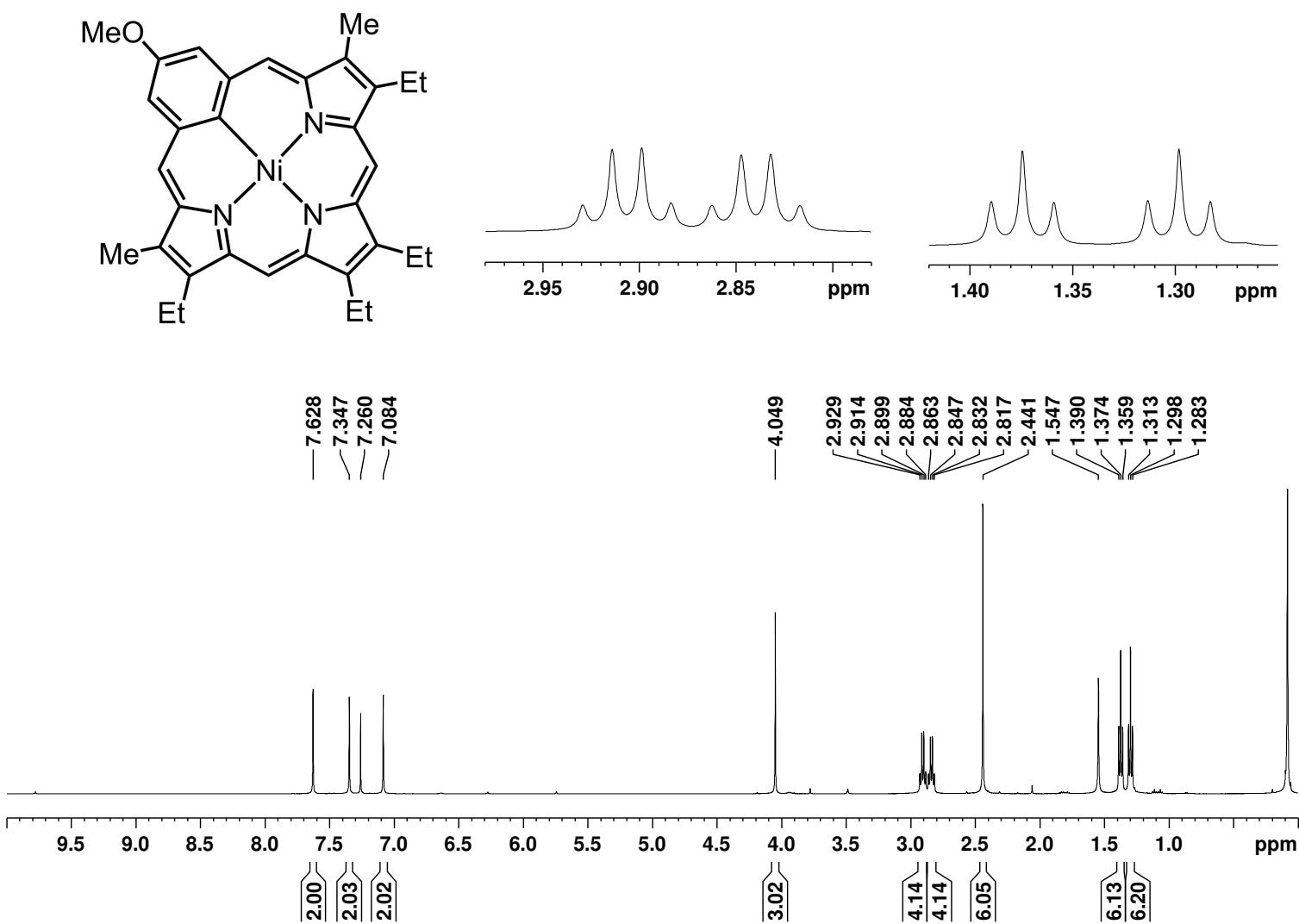


Figure S53, 500 MHz proton NMR spectrum of nickel(II) complex **7aNi** in CDCl_3 .

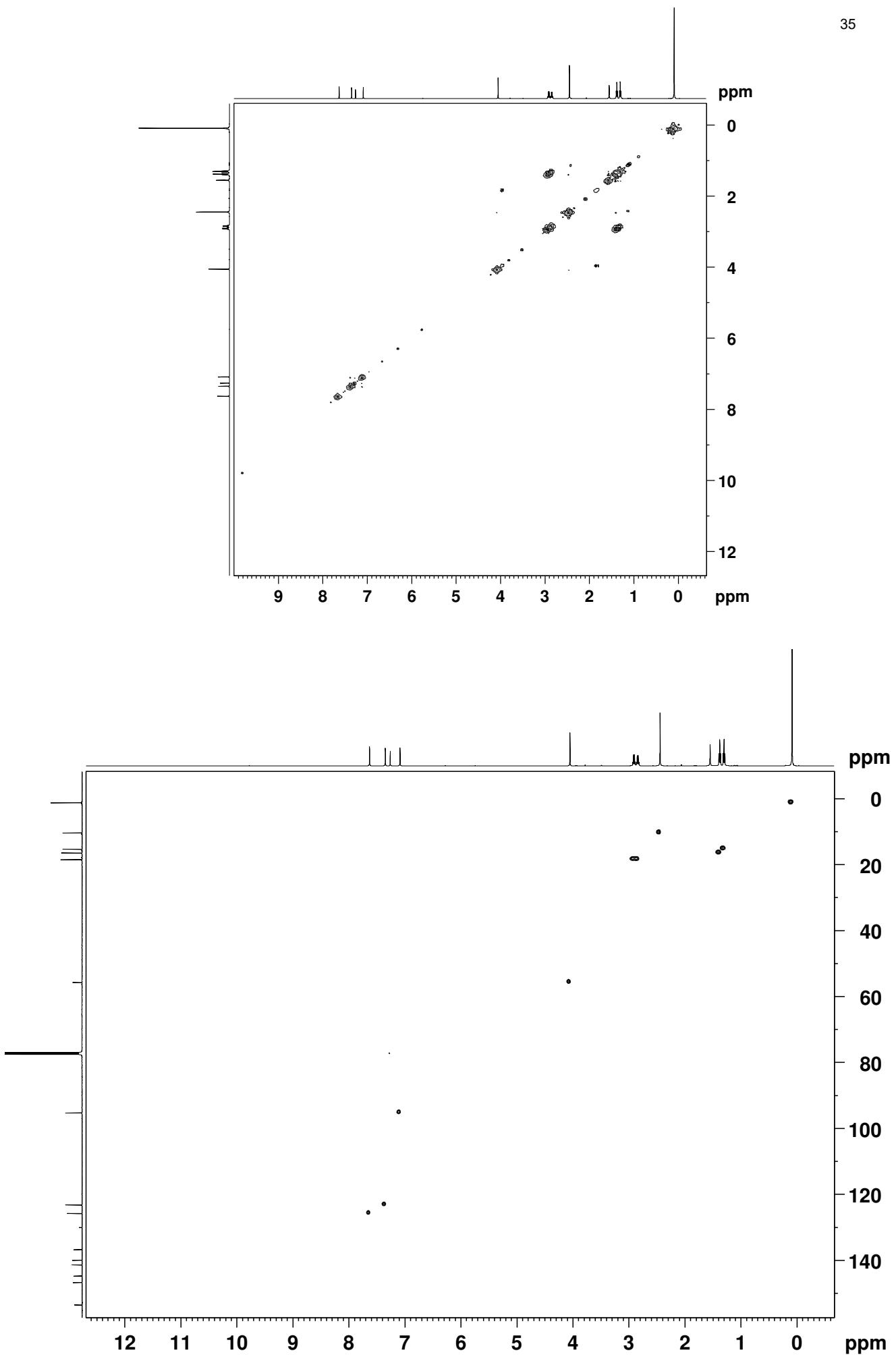


Figure S54. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of **7aNi** in CDCl_3 .

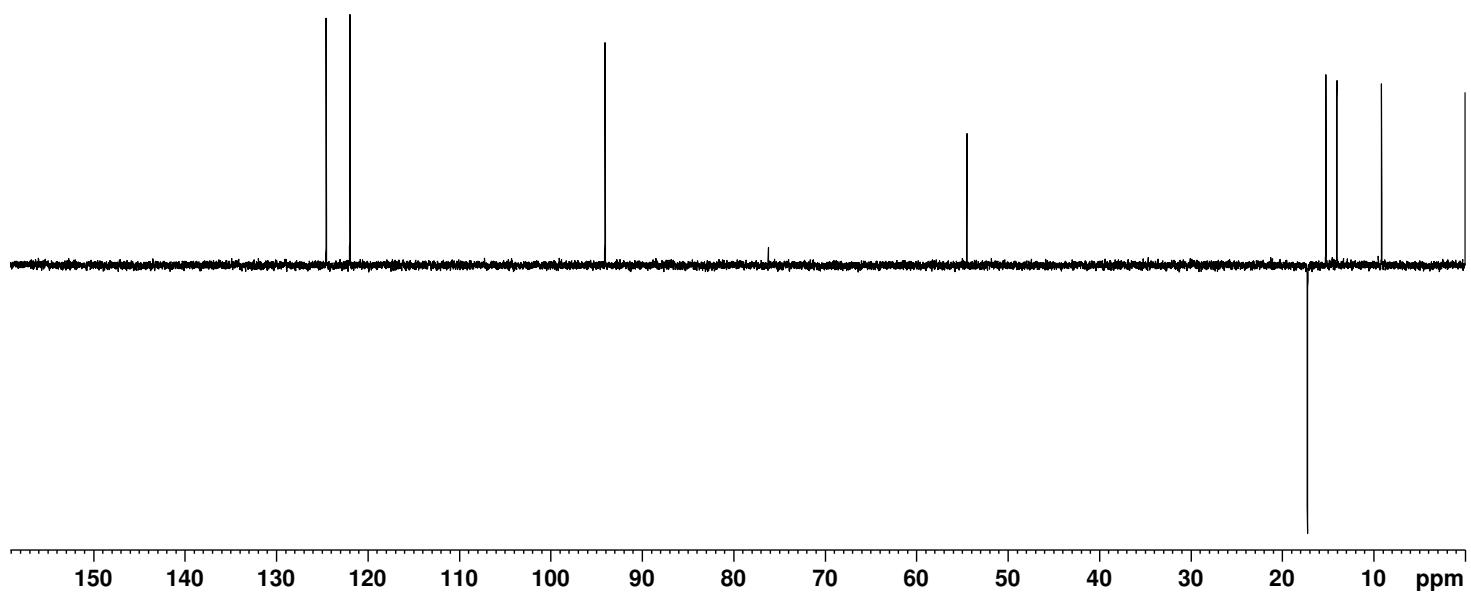


Figure S55. DEPT-135 NMR spectrum of **7aNi** in CDCl_3 .

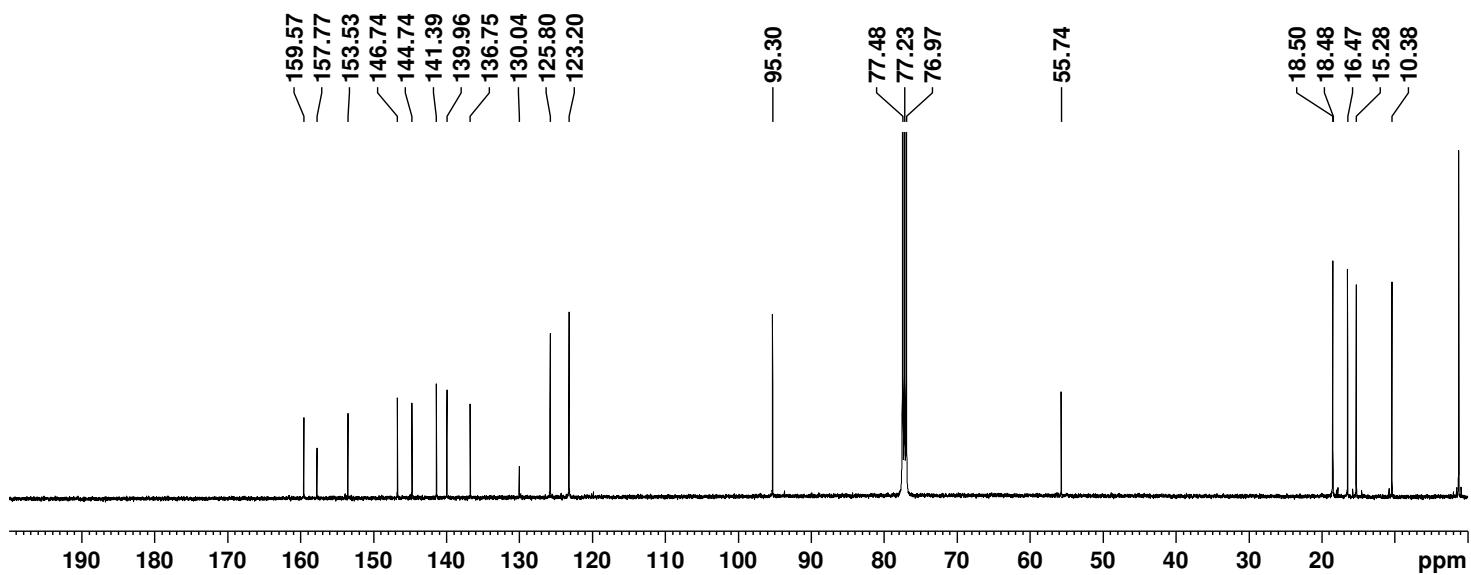
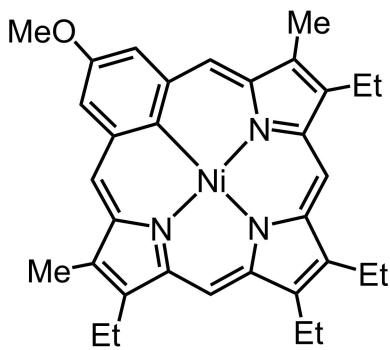


Figure S56. 125 MHz carbon-13 NMR spectrum of **7aNi** in CDCl_3 .

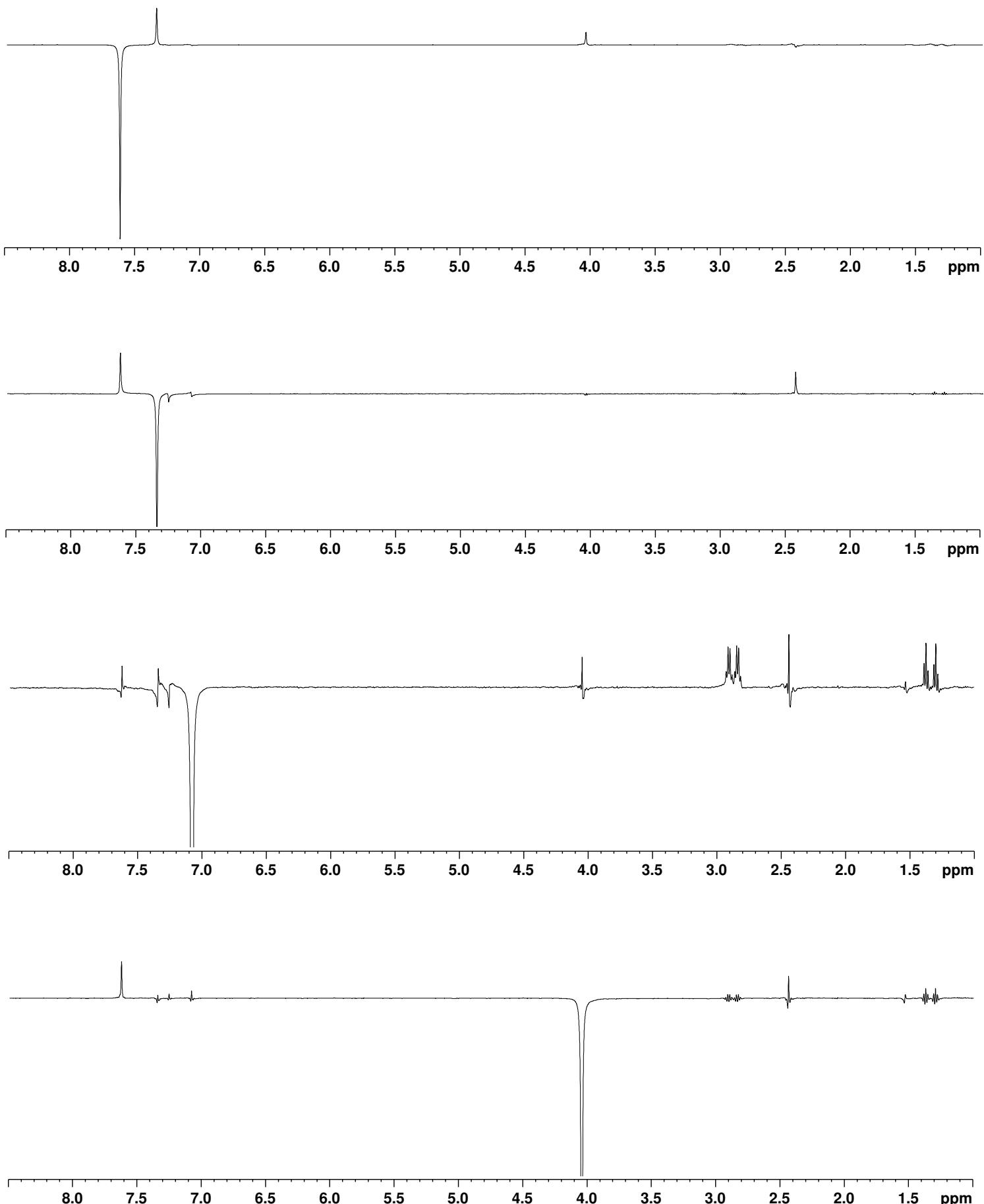


Figure S57. Selected nOe difference proton NMR spectra of **7aNi** in CDCl_3 .

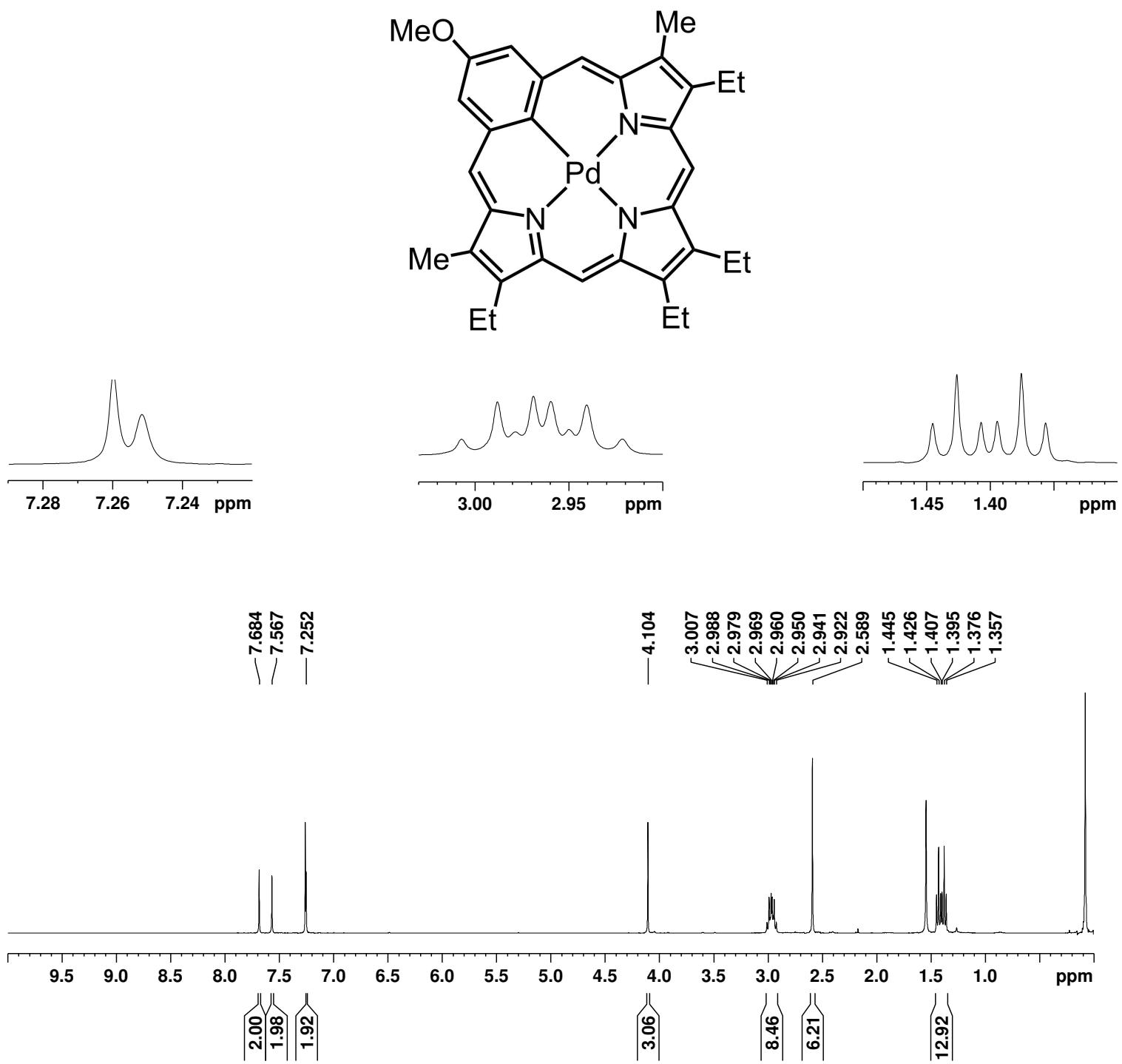


Figure S58. 500 MHz proton NMR spectrum of palladium(II) complex **7aPd** in CDCl_3 .

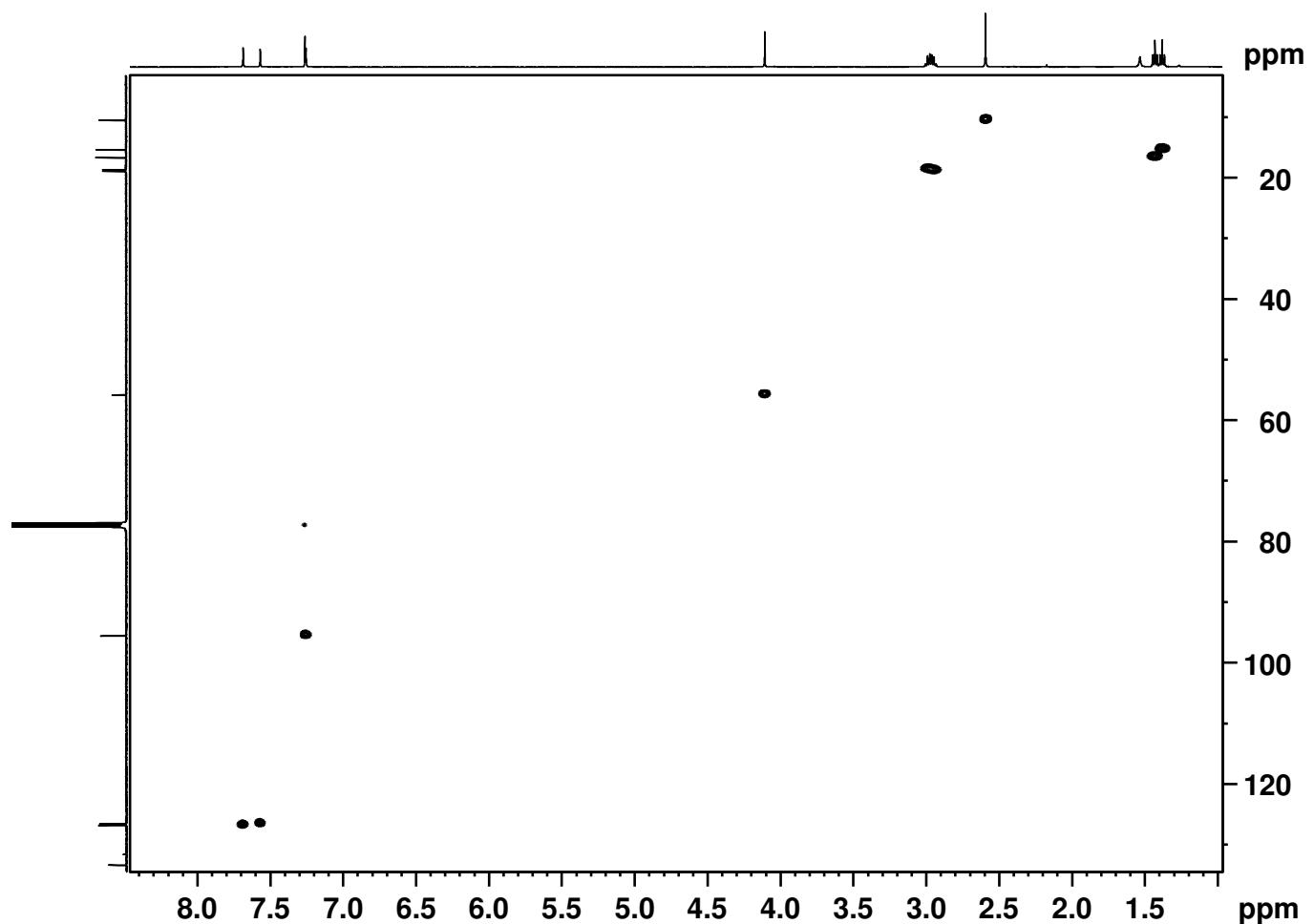
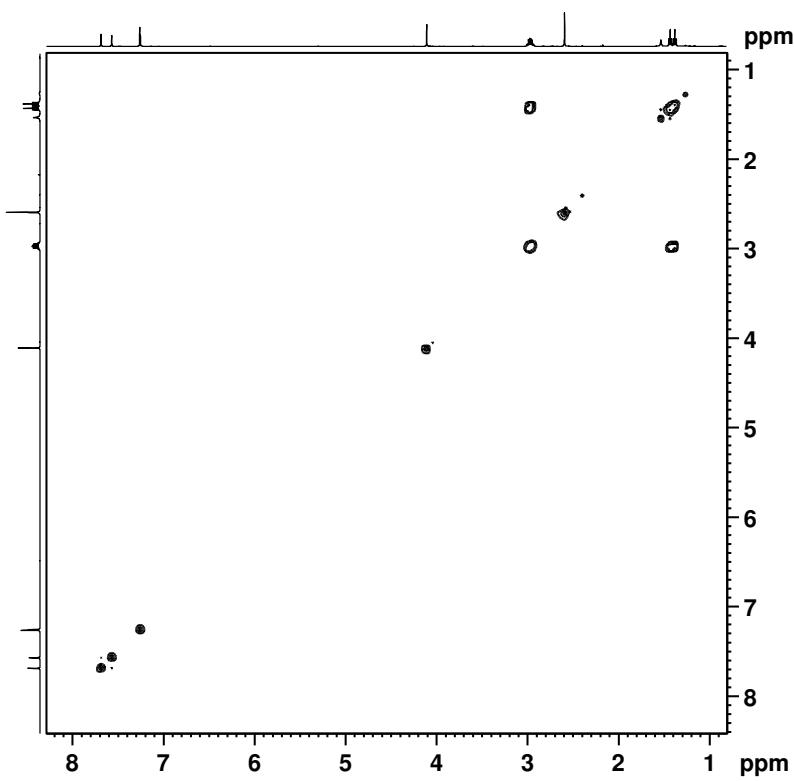


Figure S59. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of 7aPd in CDCl_3 .

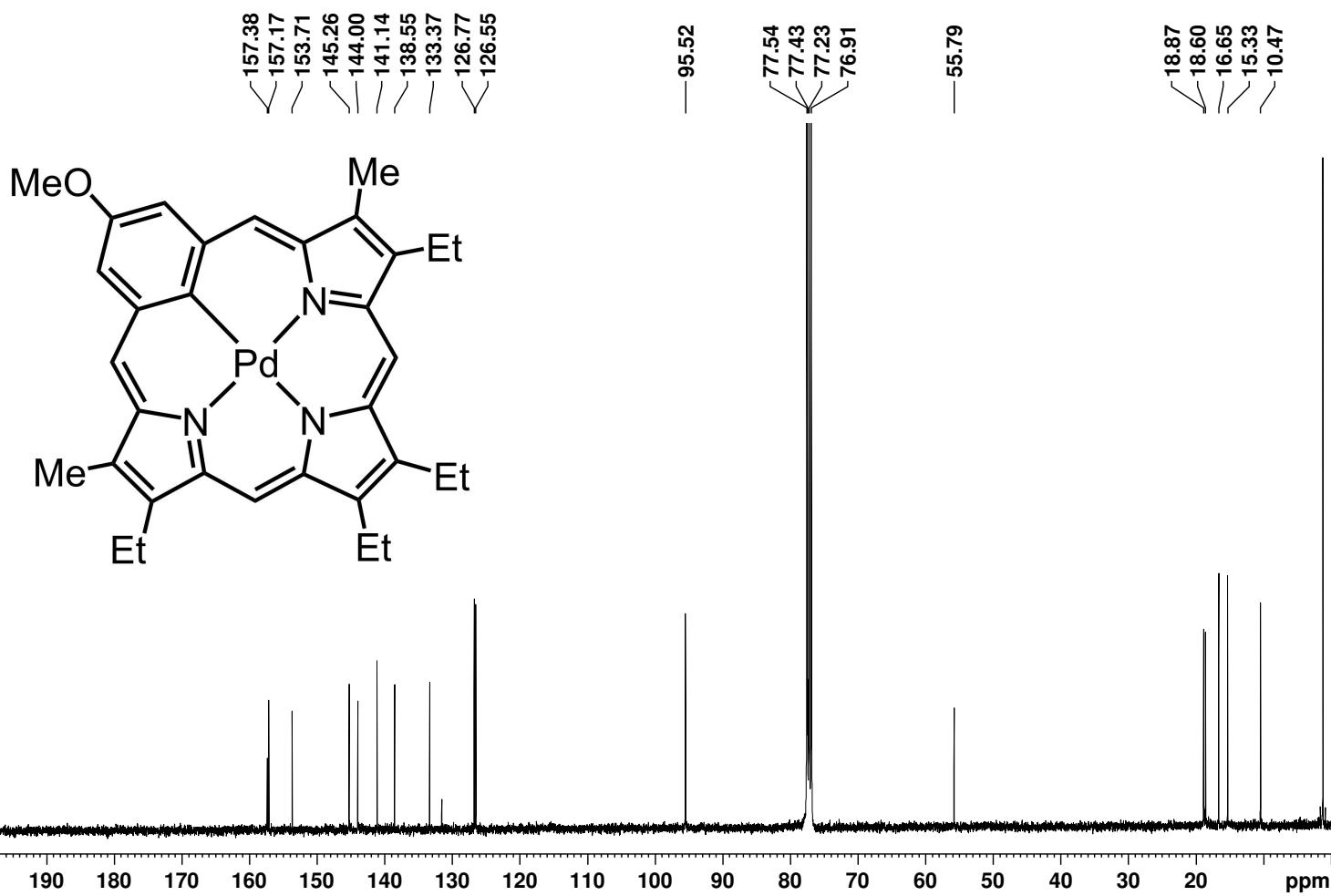
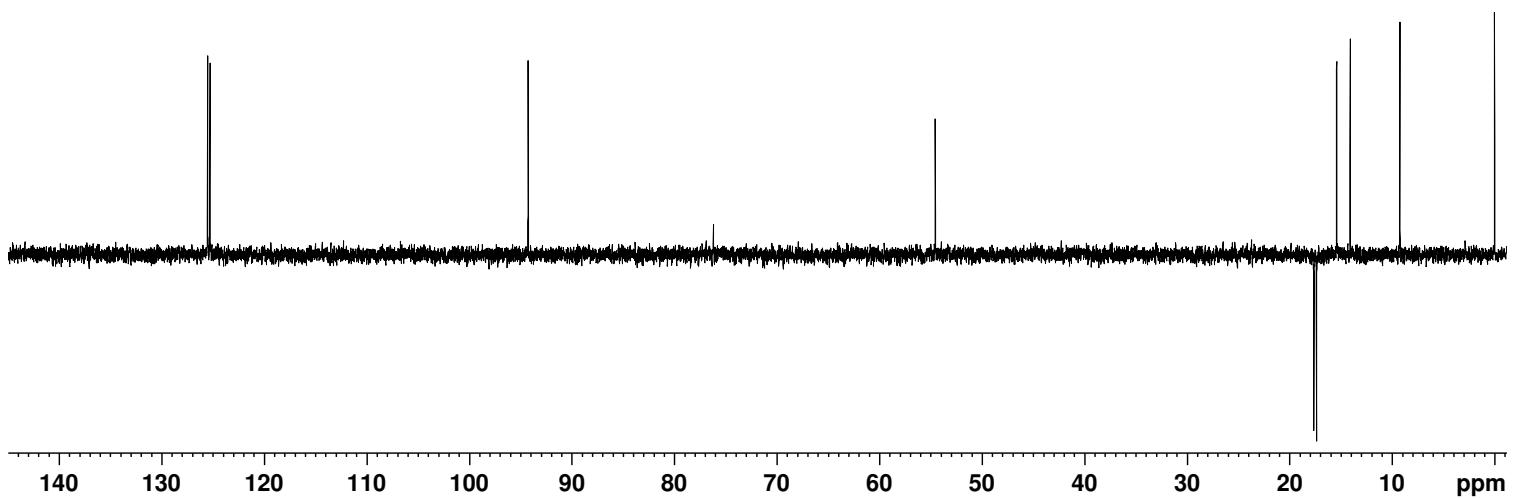


Figure S61. ^{13}C NMR spectrum of **7aPd** in CDCl_3 .

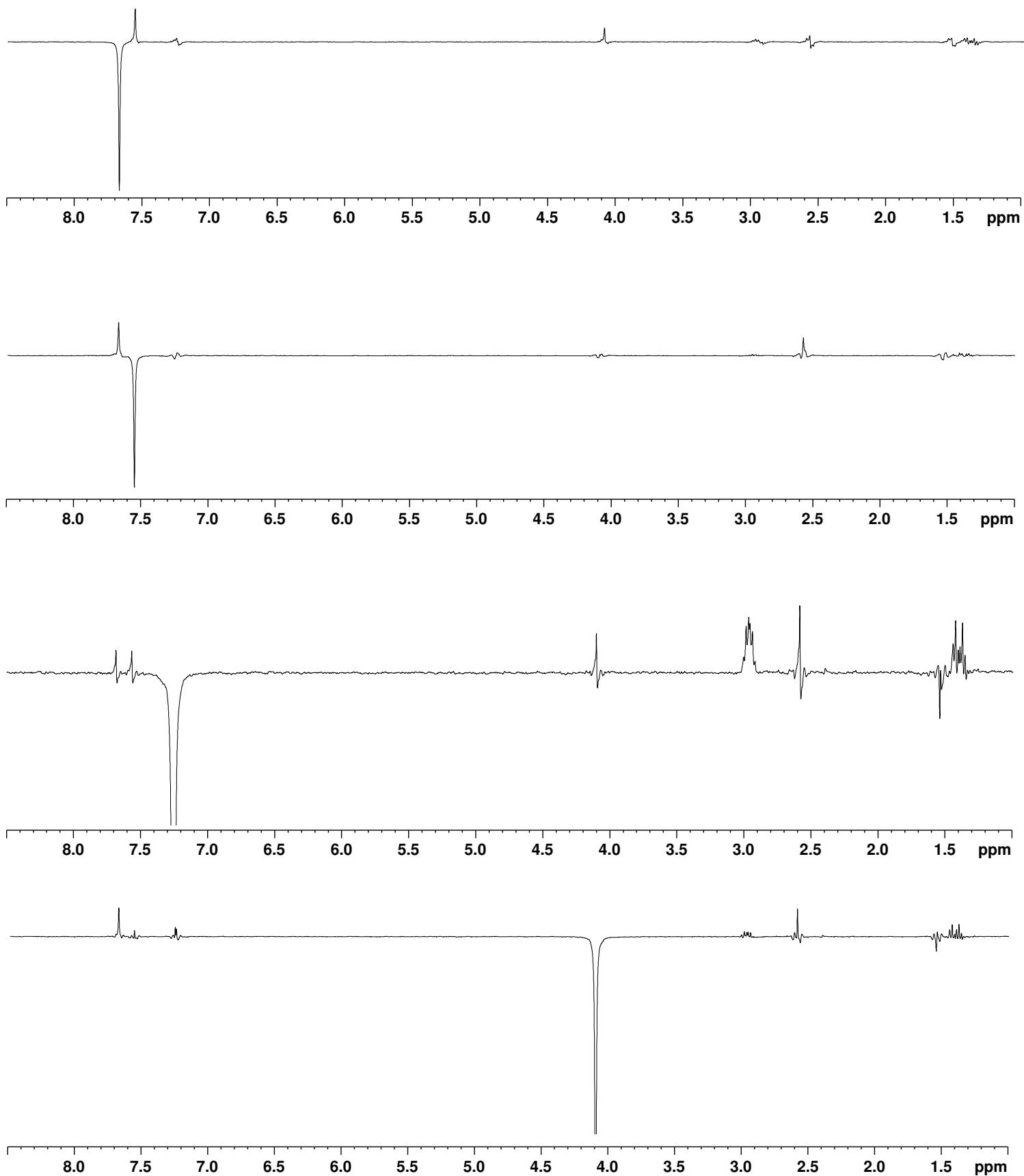


Figure S62. Selected nOe difference proton NMR spectra of **7aPd** in CDCl_3 .

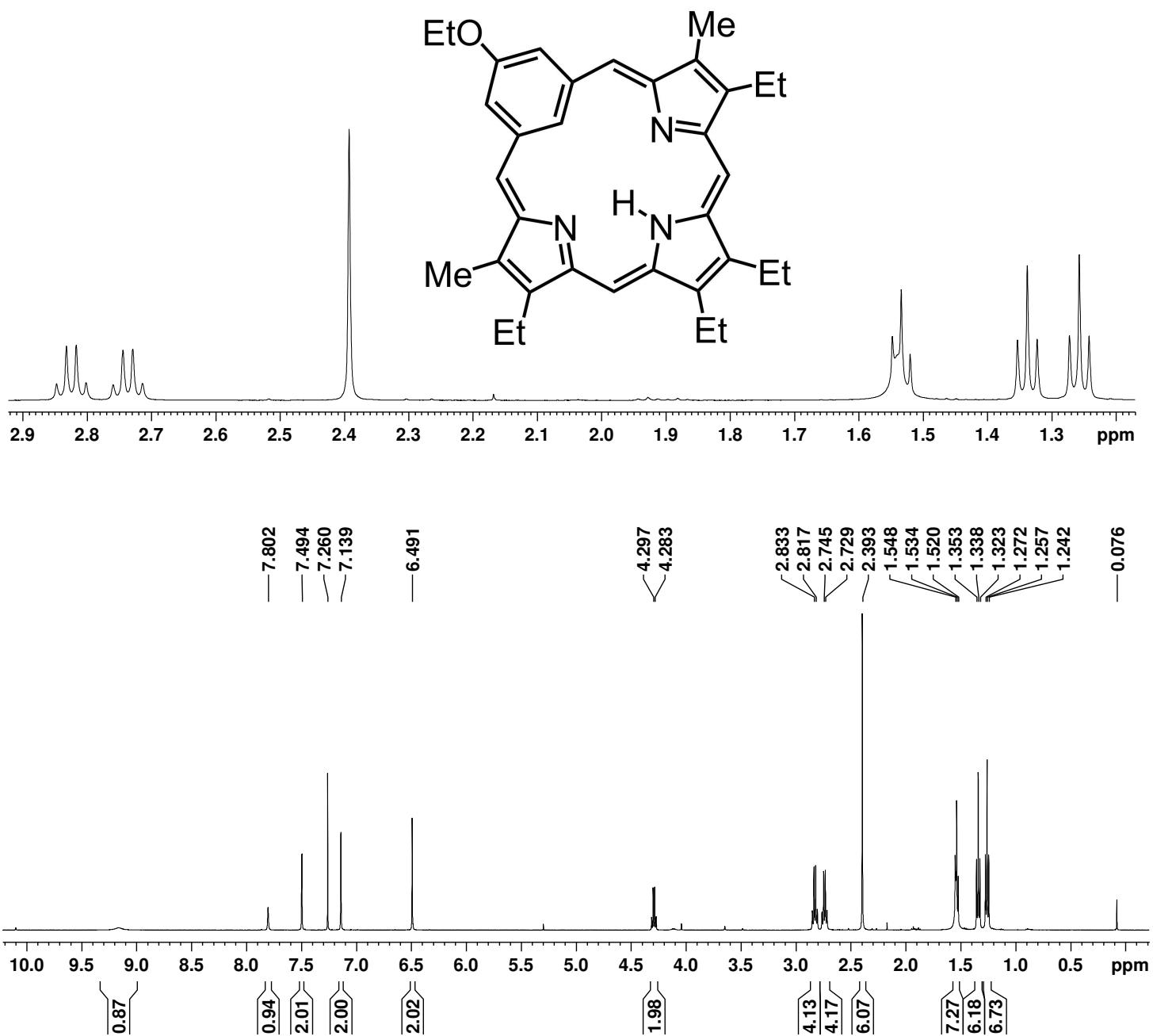


Figure 63. 500 MHz proton NMR spectrum of ethoxybenzoporphyrin **7b** in CDCl_3 .

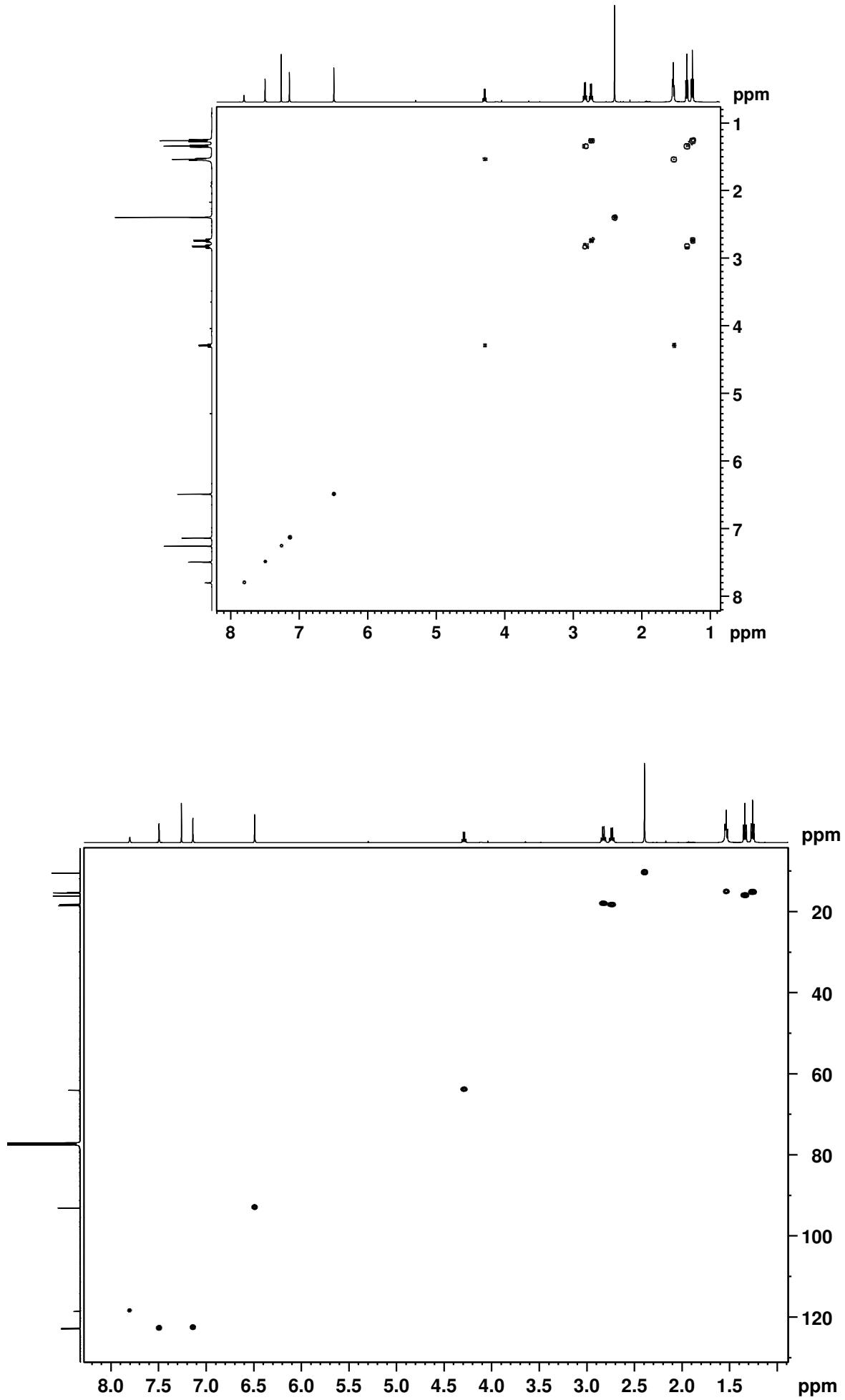


Figure S64. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of **7b** in CDCl_3 .

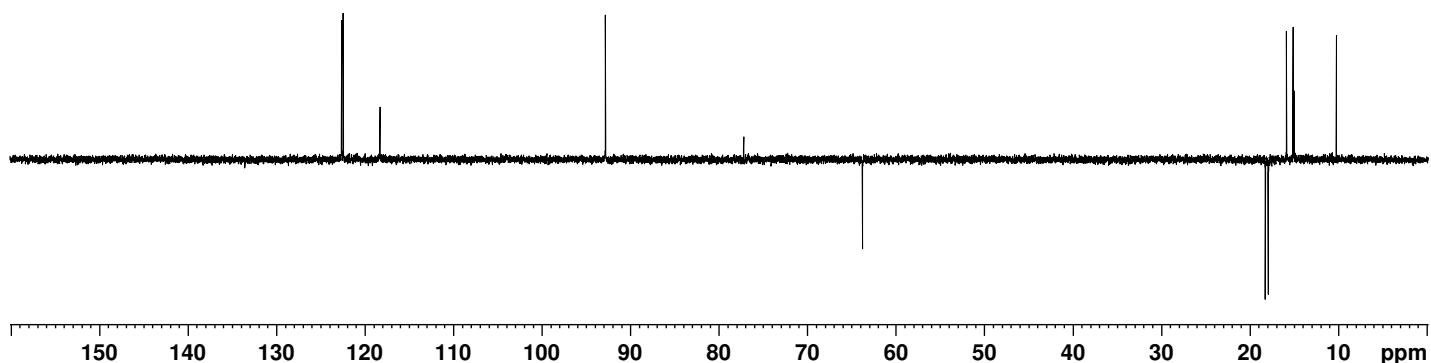


Figure S65. DEPT-135 NMR spectrum of **7b** in CDCl_3 .

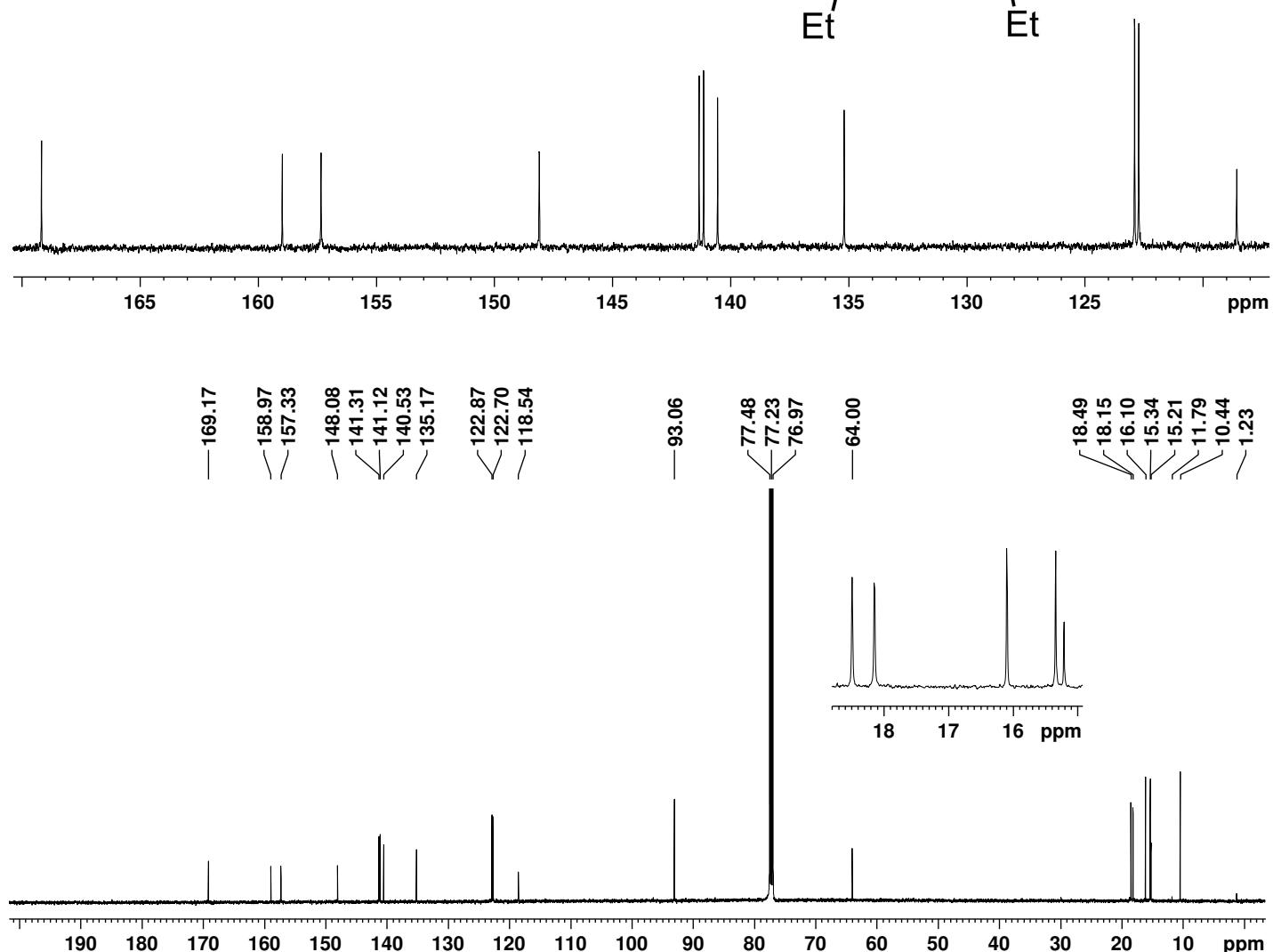
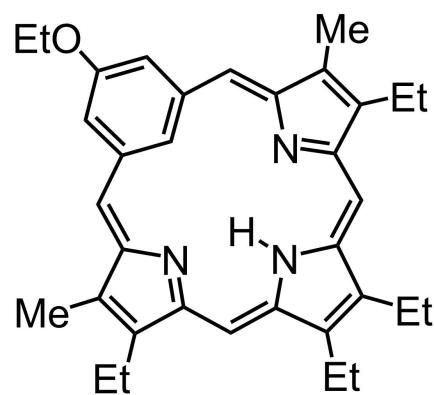


Figure S66. 125 MHz carbon-13 NMR spectrum of **7b** in CDCl_3 .

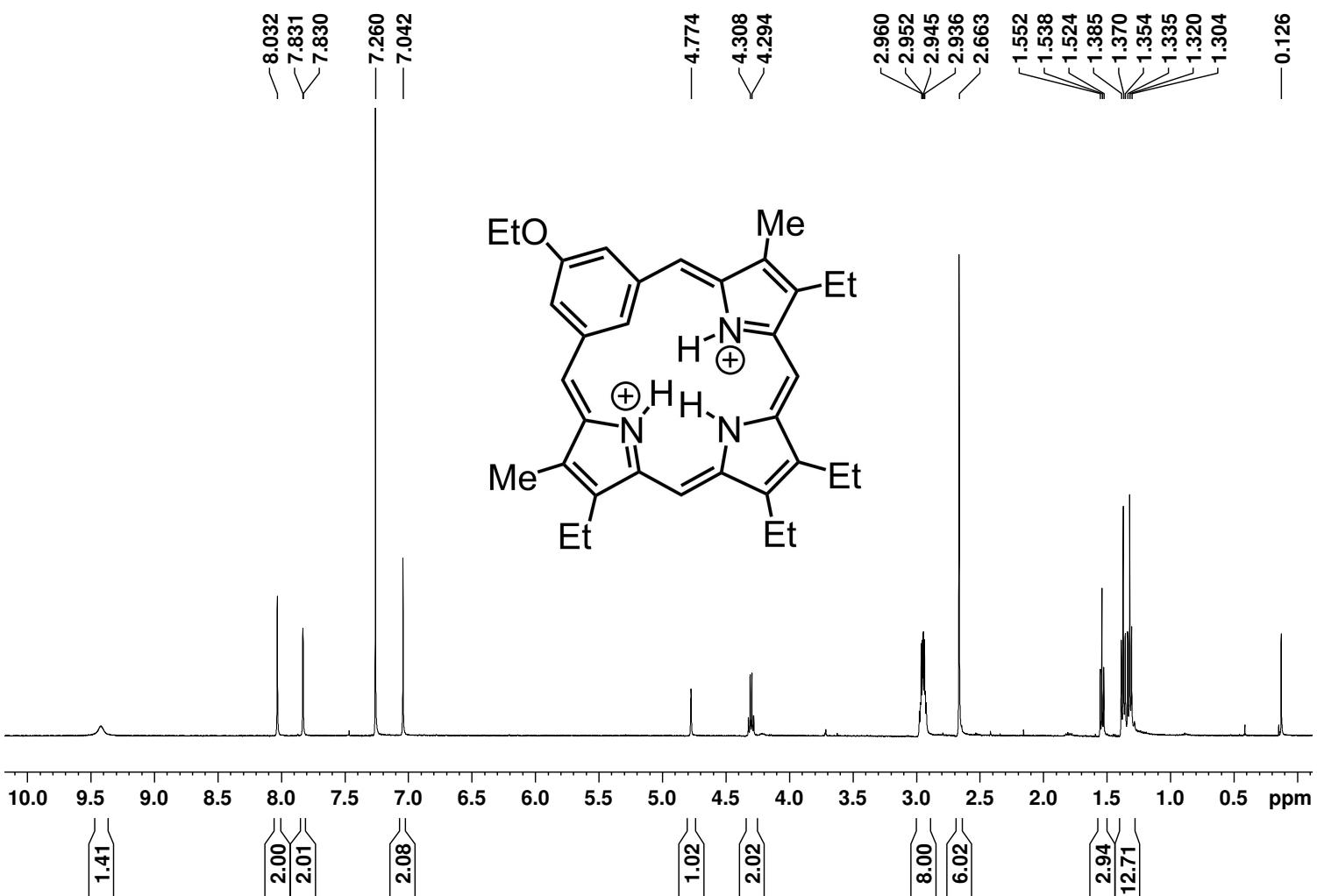


Figure S67. 500 MHz proton NMR spectrum of ethoxybenzoporphyrin dication $7\mathbf{b}\mathbf{H}_2^{2+}$ in TFA-CDCl₃.

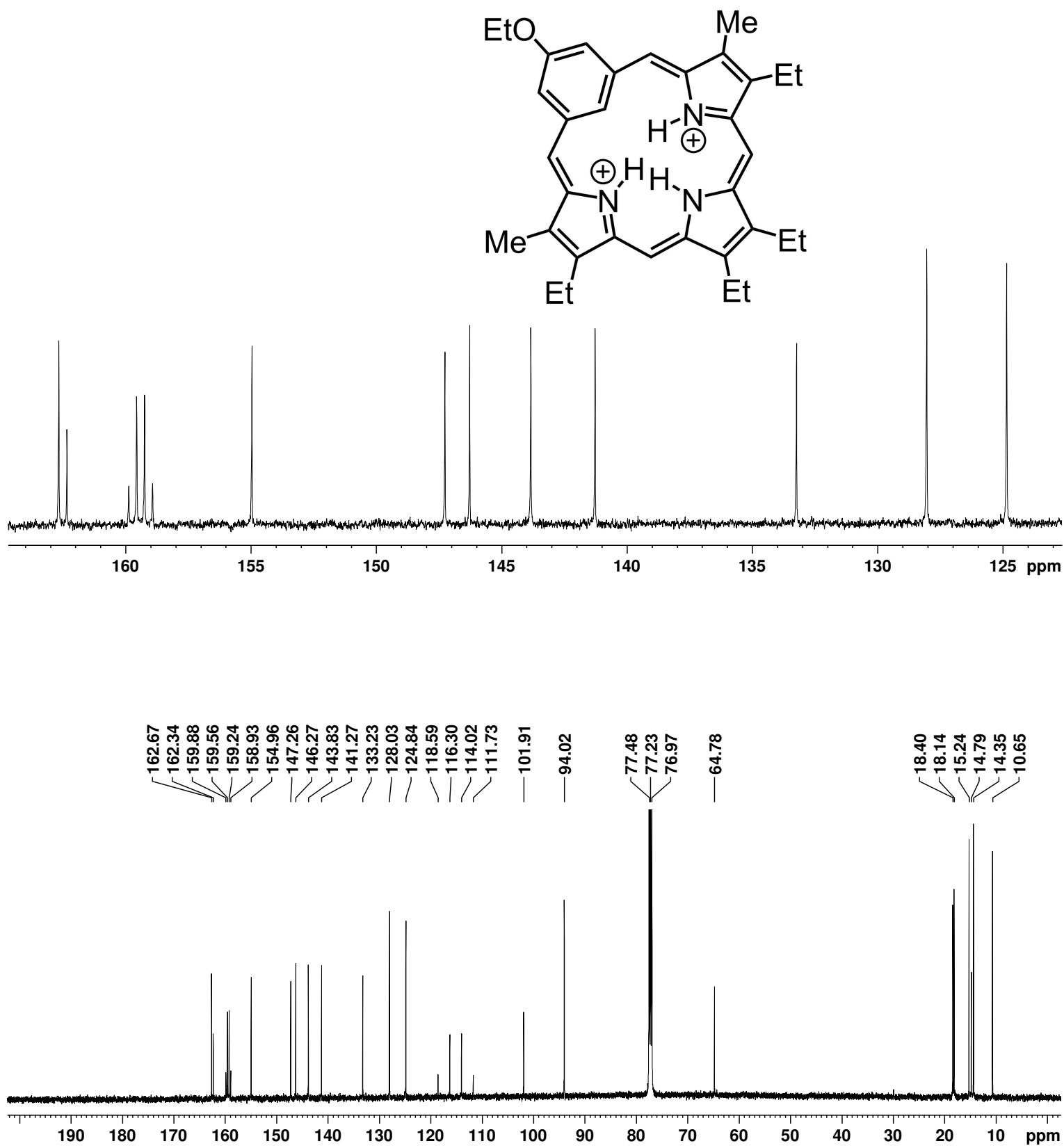


Figure S68. 125 MHz carbon-13 NMR spectrum of $7\mathbf{b}\mathbf{H}_2^{2+}$ in TFA- CDCl_3 .

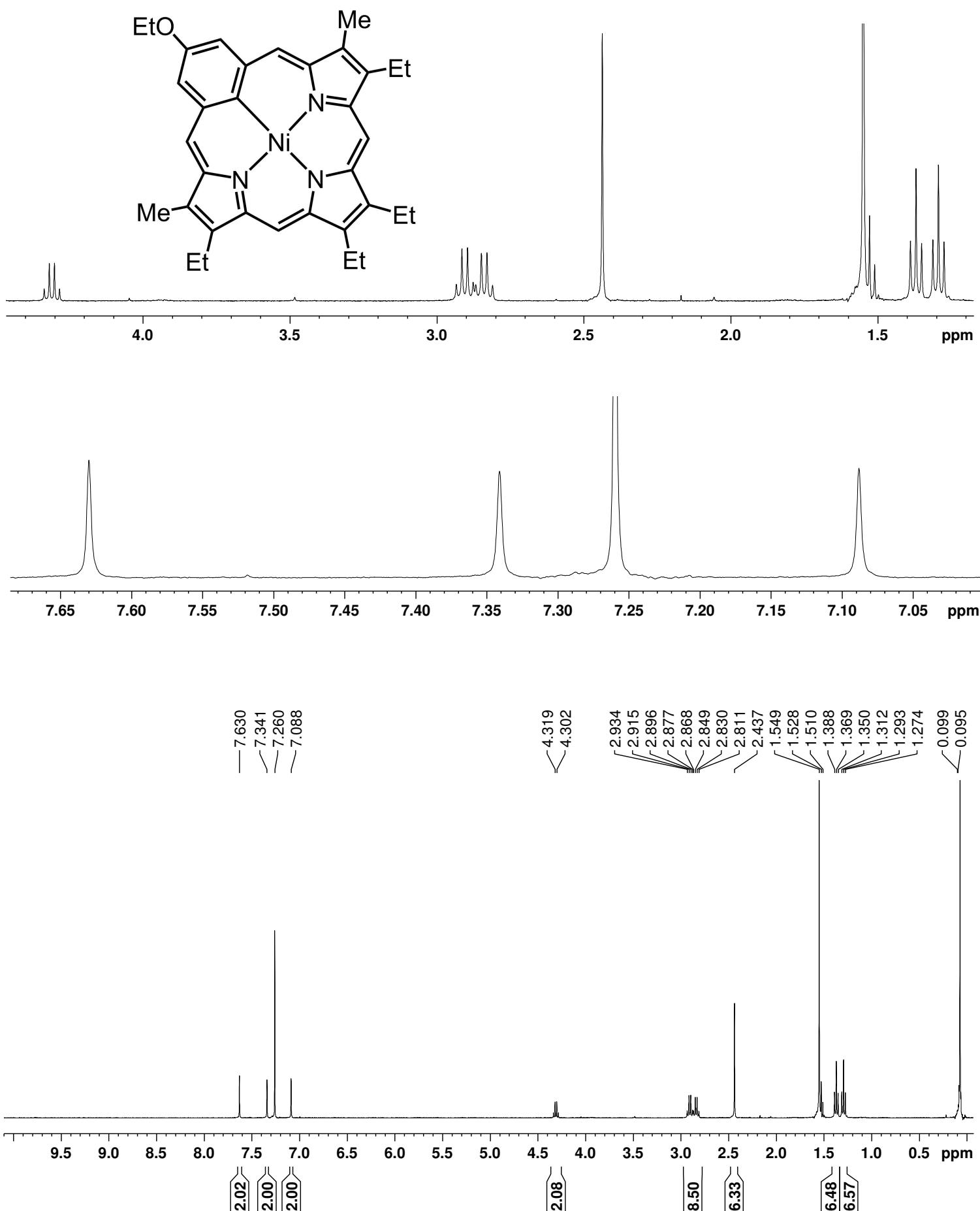


Figure S69. 500 MHz proton NMR spectrum of nickel(II) complex **7bNi** in CDCl_3 .

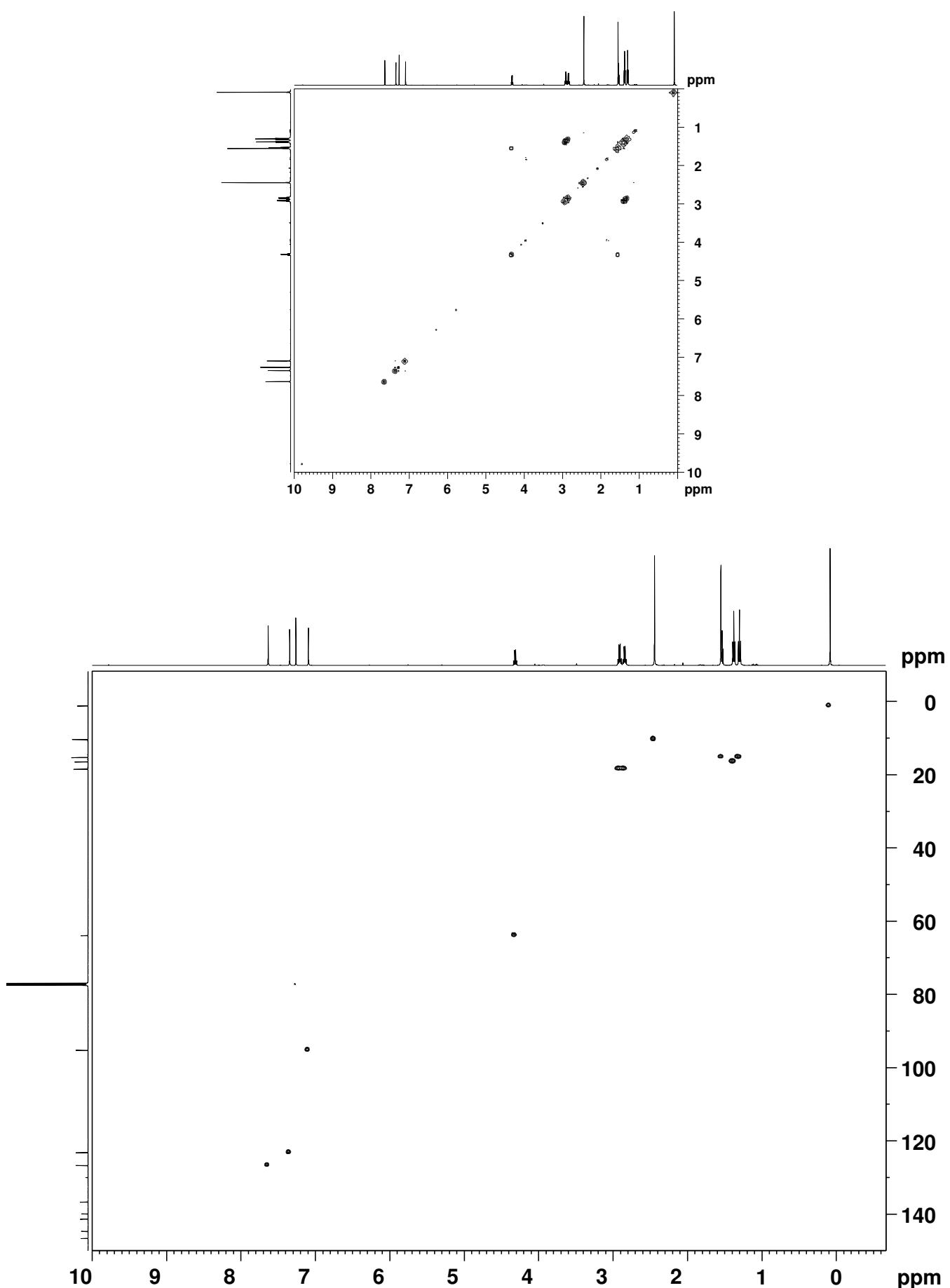


Figure S70. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of **7bNi** in CDCl_3 .

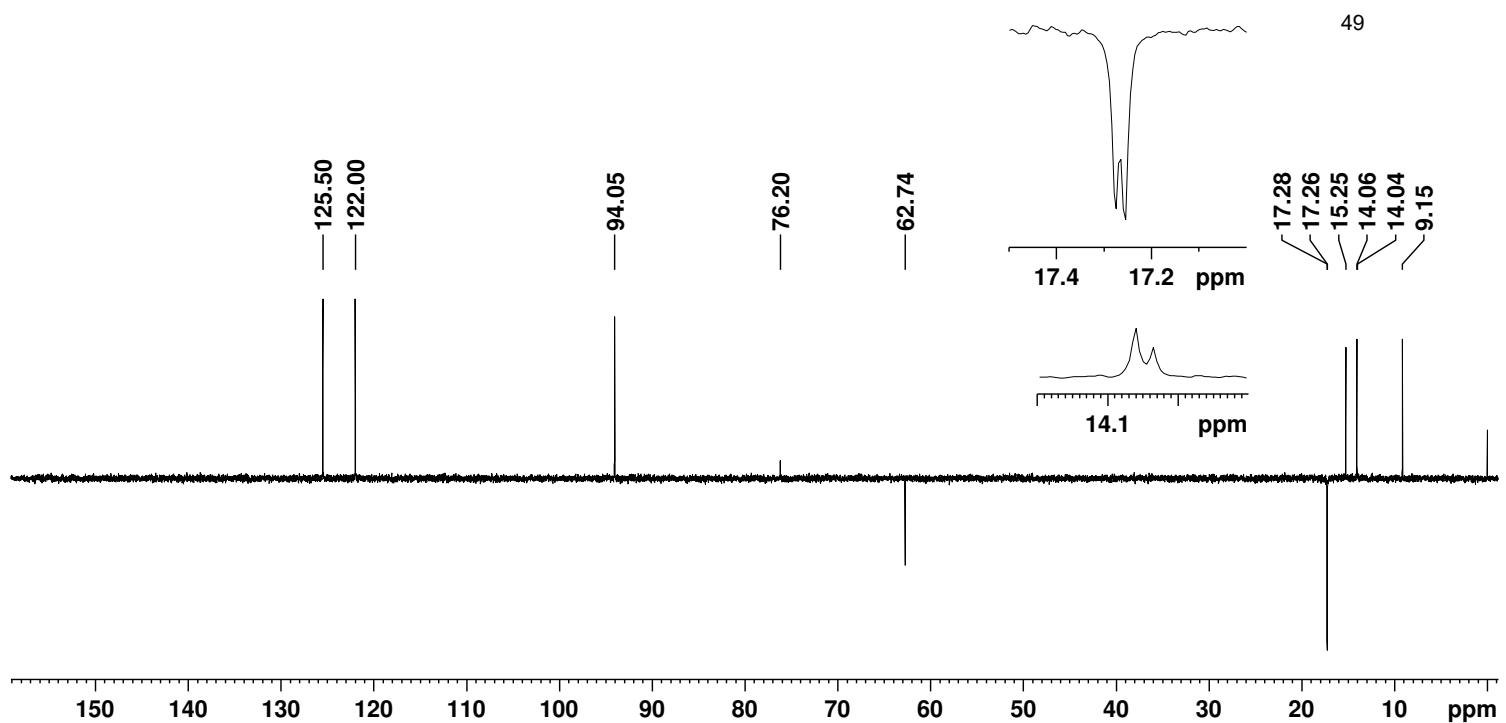


Figure S71. DEPT-135 NMR spectrum of **7bNi** in CDCl_3 .

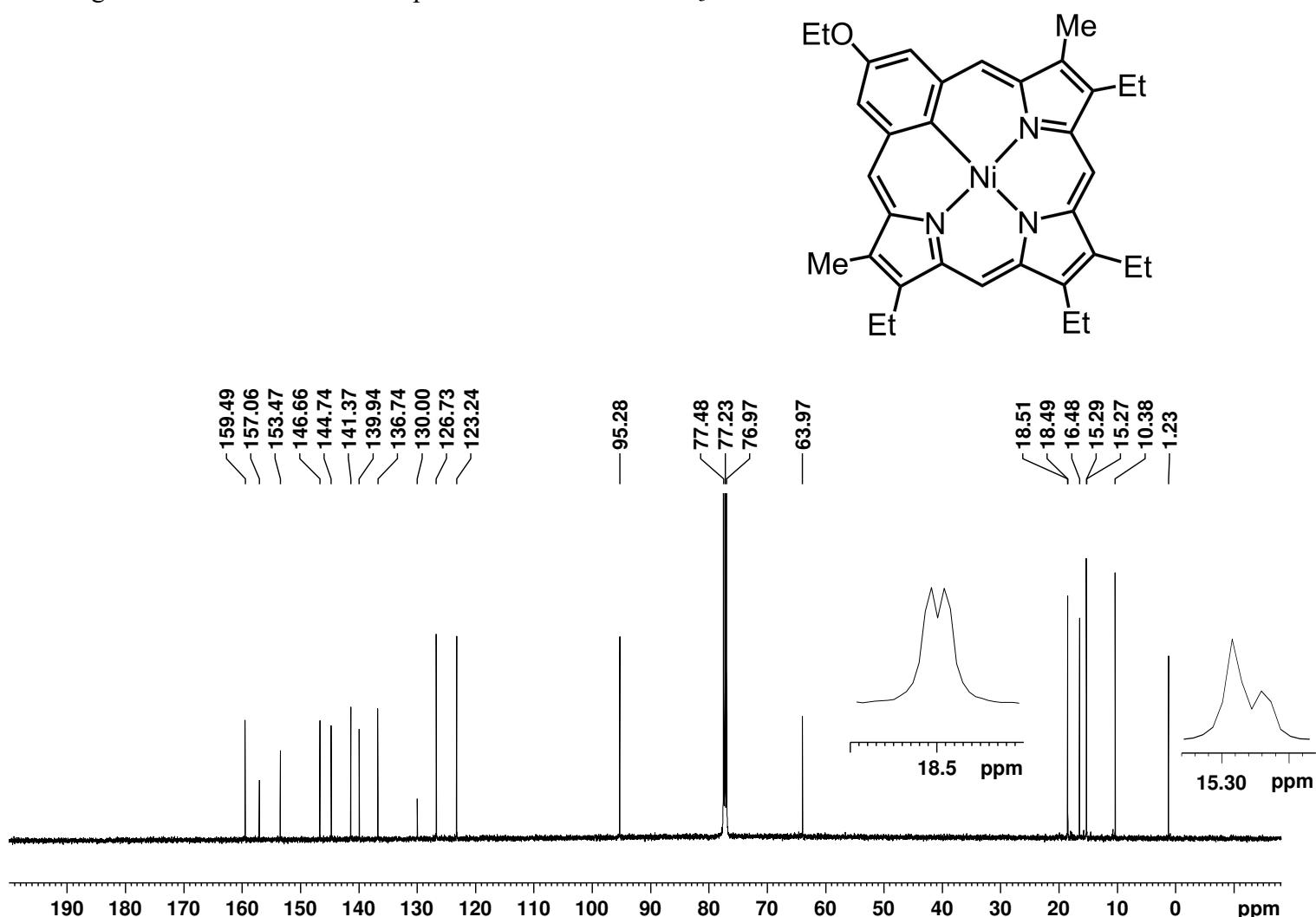


Figure S72. 125 MHz carbon-13 NMR spectrum of **7bNi** in CDCl_3 .

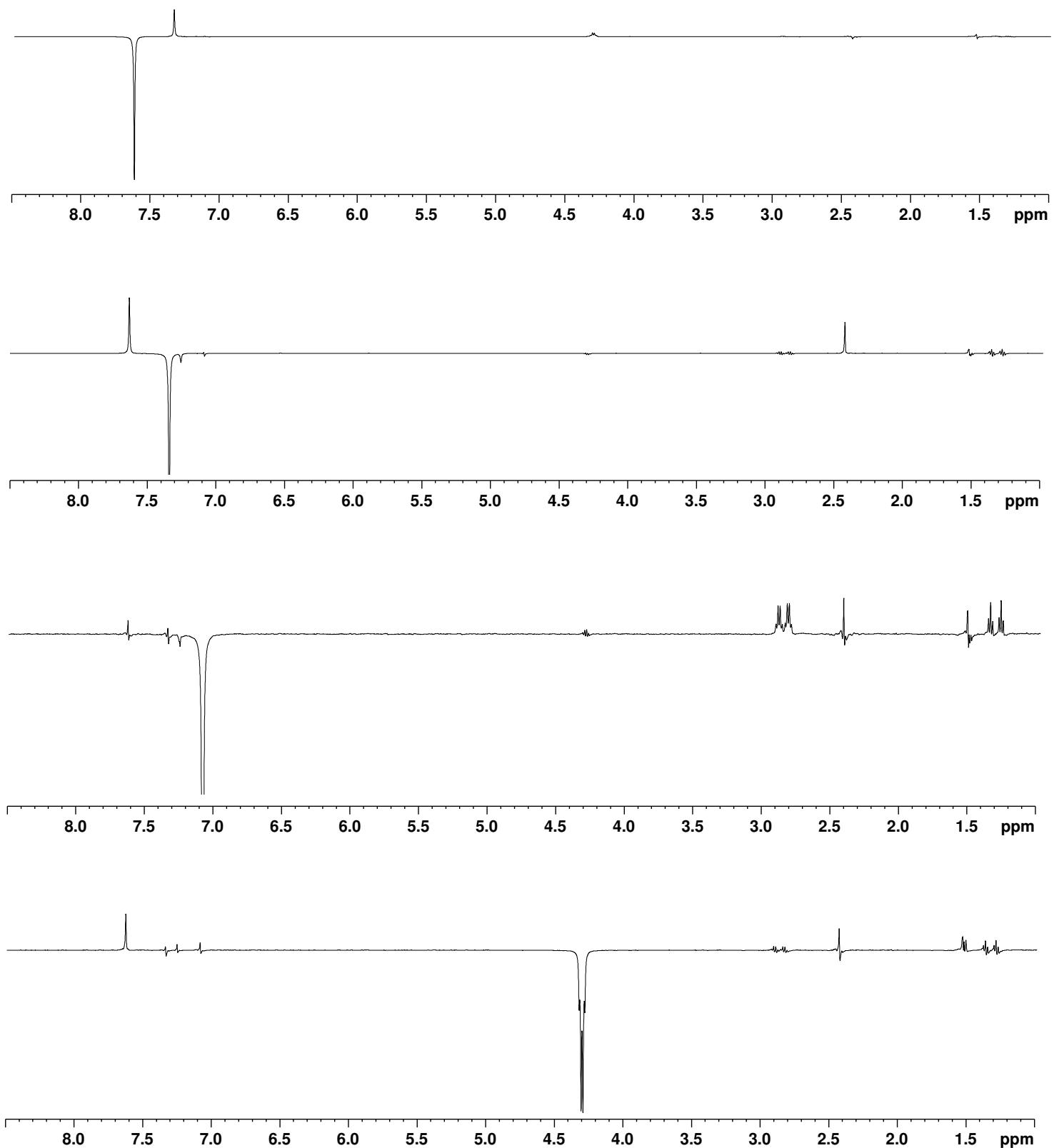


Figure S73. Selected nOe difference proton NMR spectra of **7bNi** in CDCl_3 .

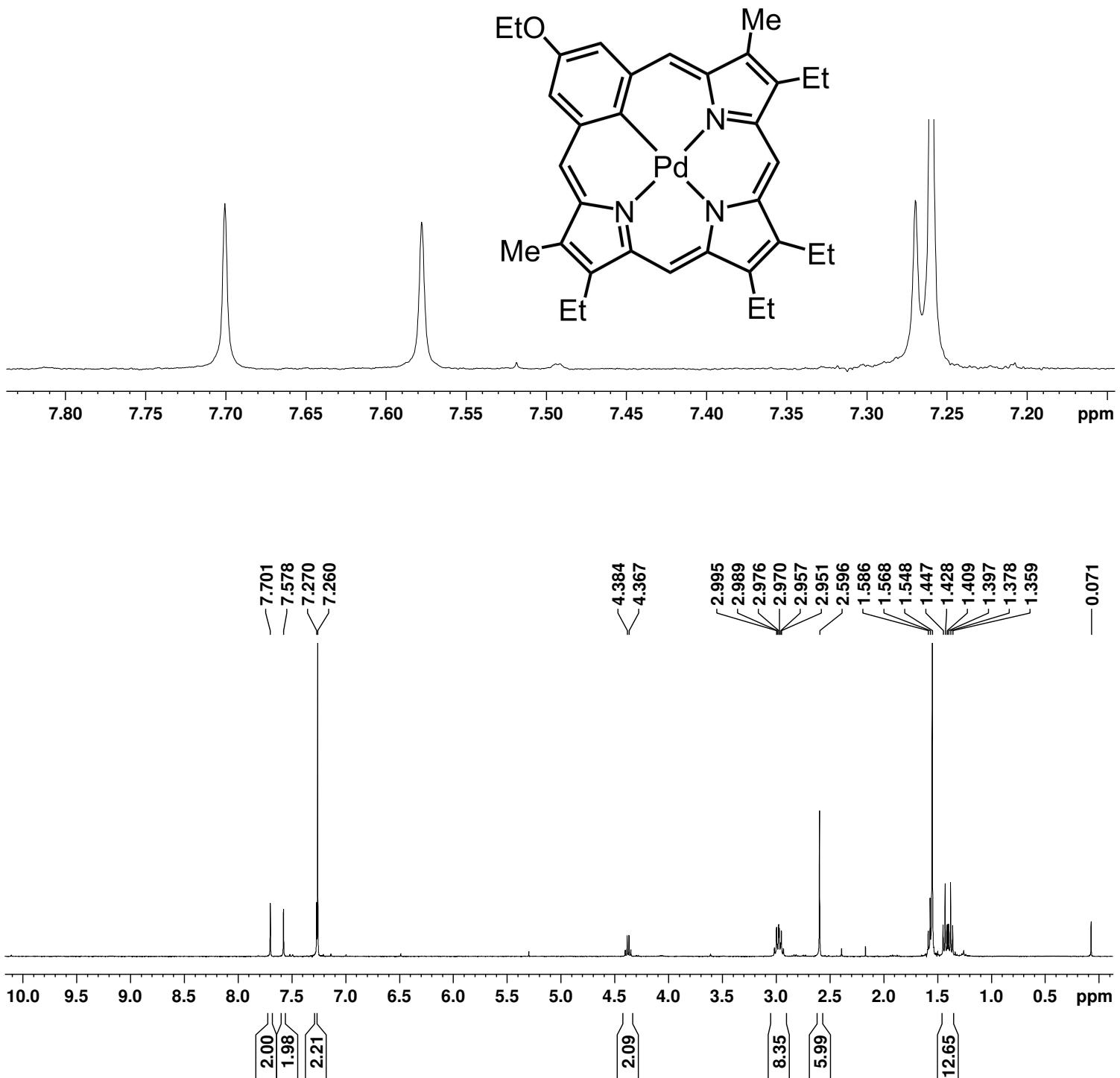


Figure S74. 500 MHz proton NMR spectrum of palladium complex **7bPd** in CDCl_3 .

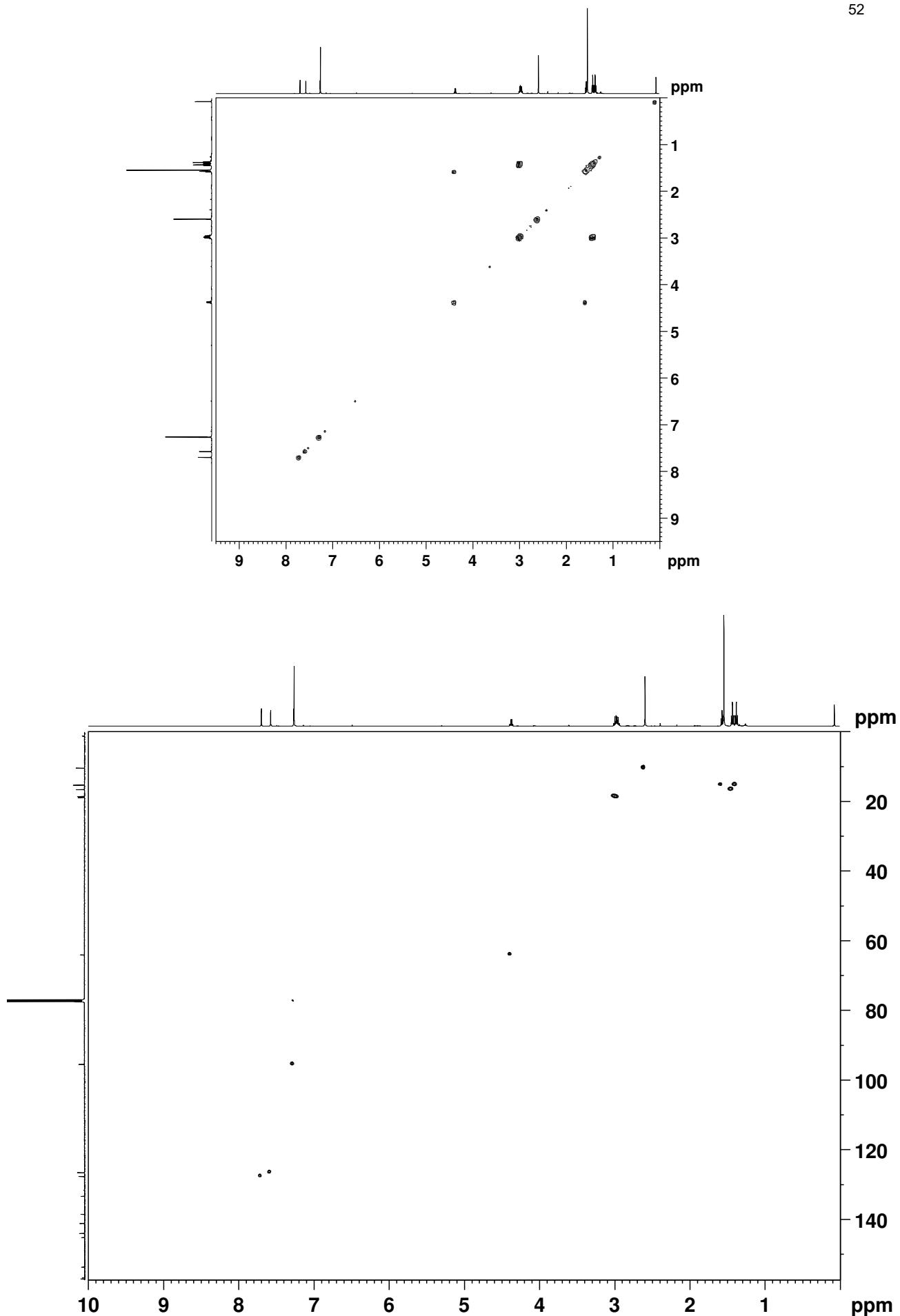


Figure S75. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of **7bPd** in CDCl_3 .

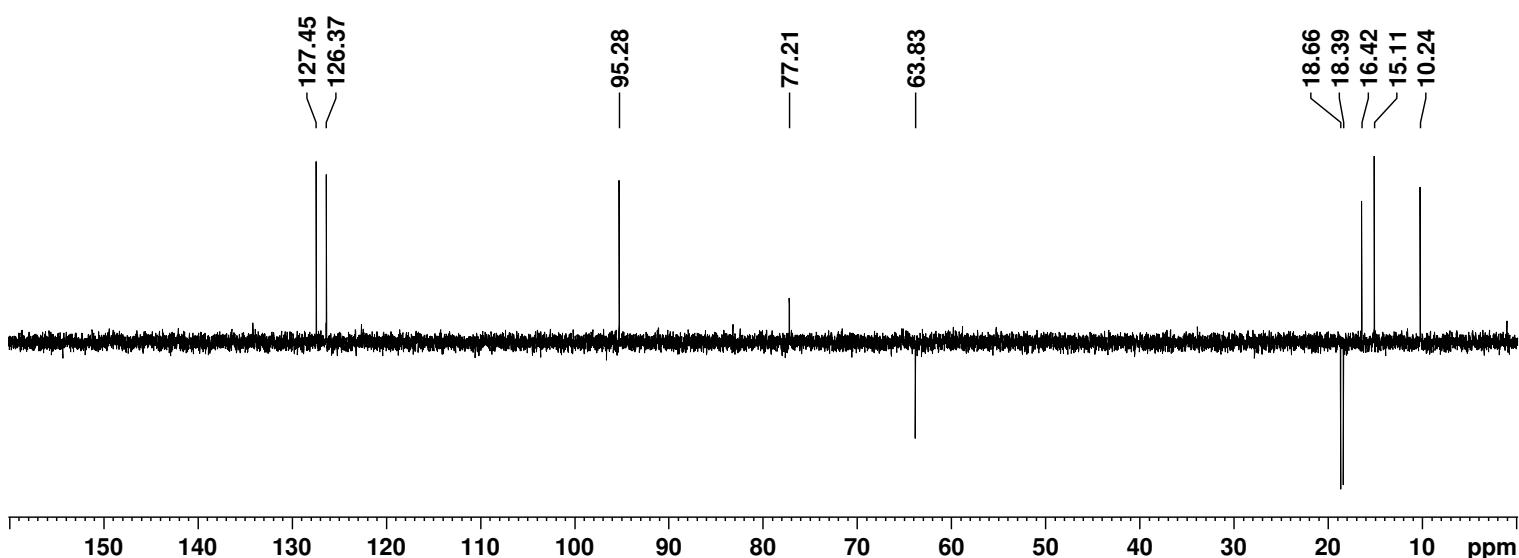


Figure S76. DEPT-135 NMR spectrum of **7bPd** in CDCl_3 .

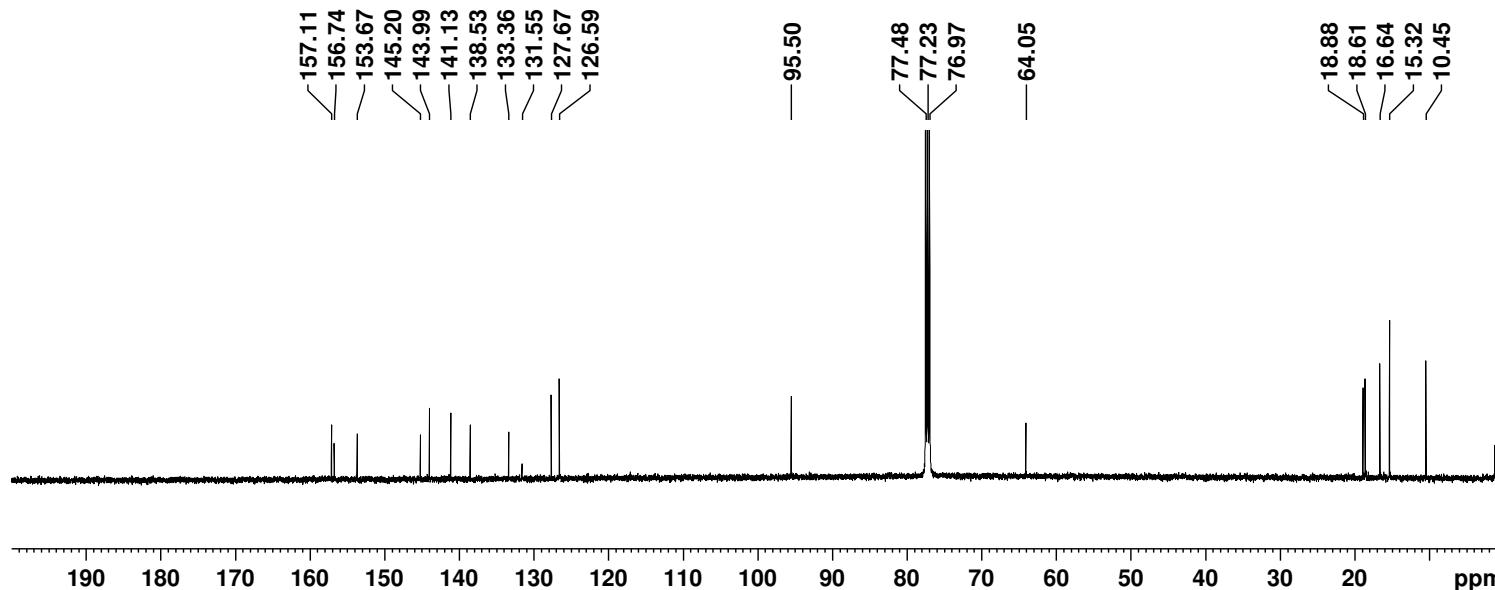
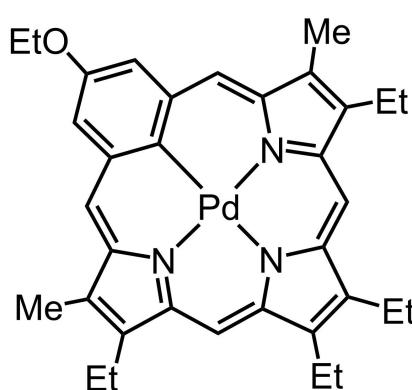


Figure S77. 125 MHz carbon-13 NMR spectrum of **7bPd** in CDCl_3 .

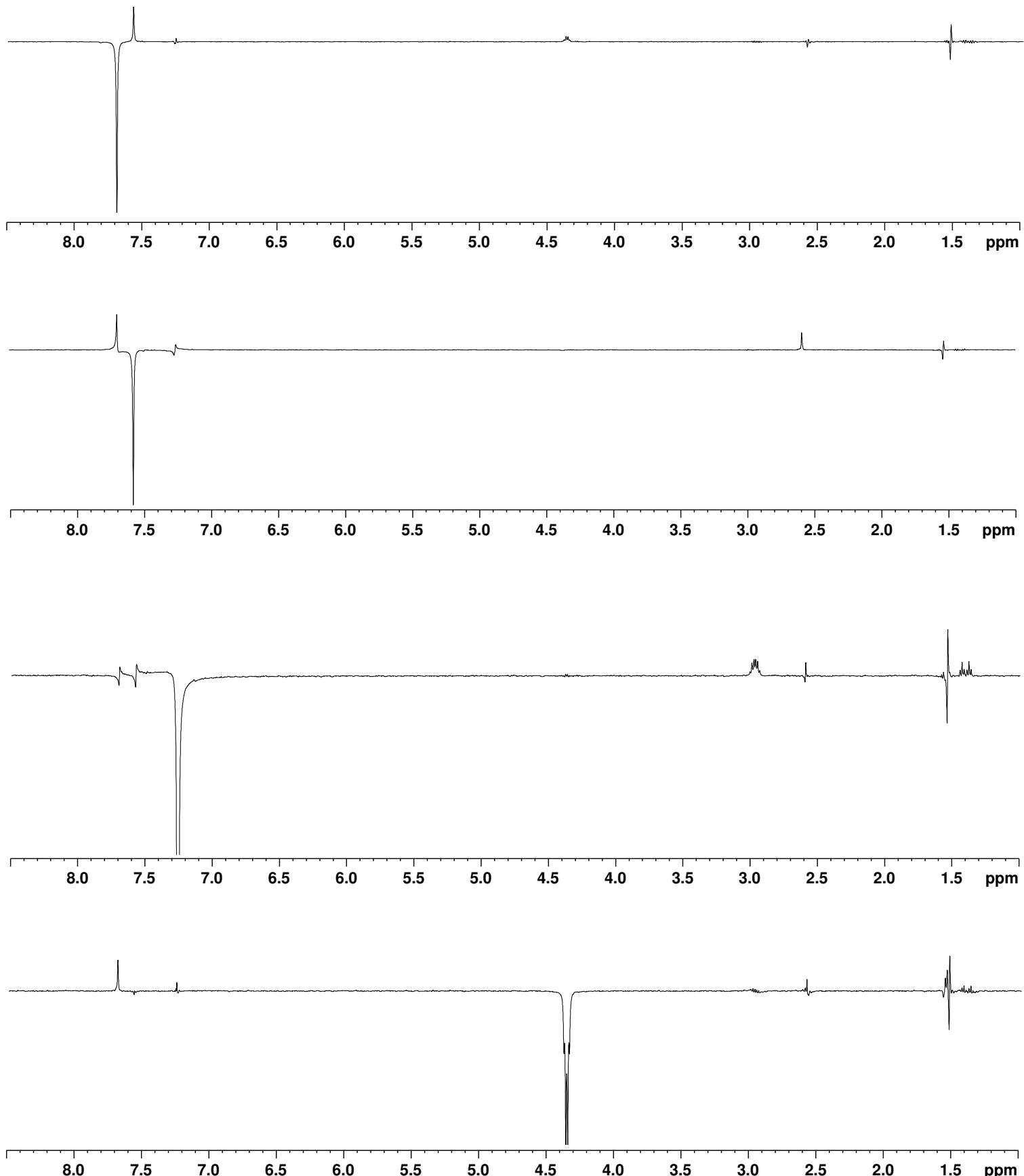


Figure S78. Selected nOe difference proton NMR spectra of **7bPd** in CDCl_3 .

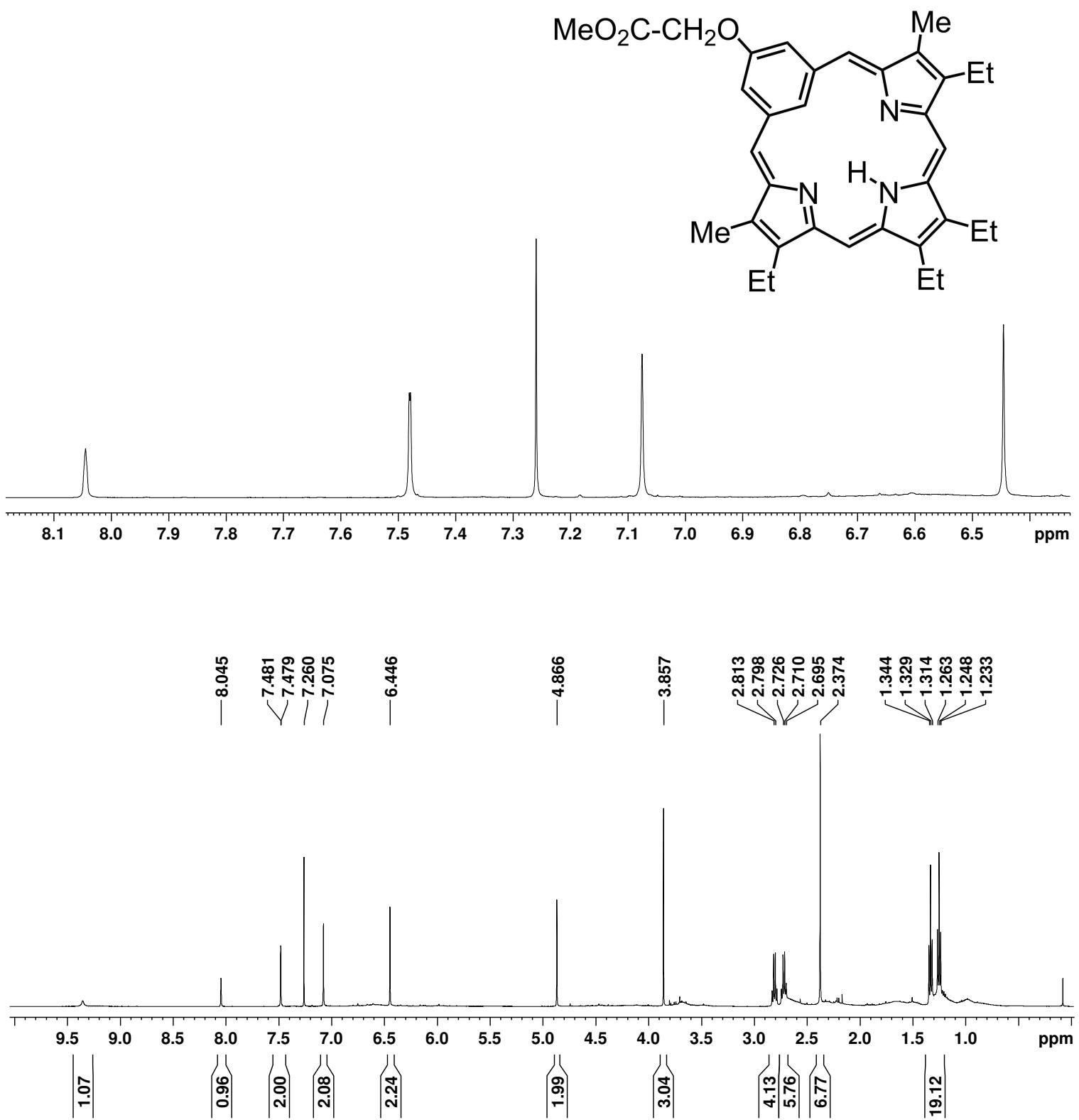


Figure S79. 500 MHz proton NMR spectrum of methoxycarbonylmethoxybenzoporphyrin **7c** in CDCl_3 .

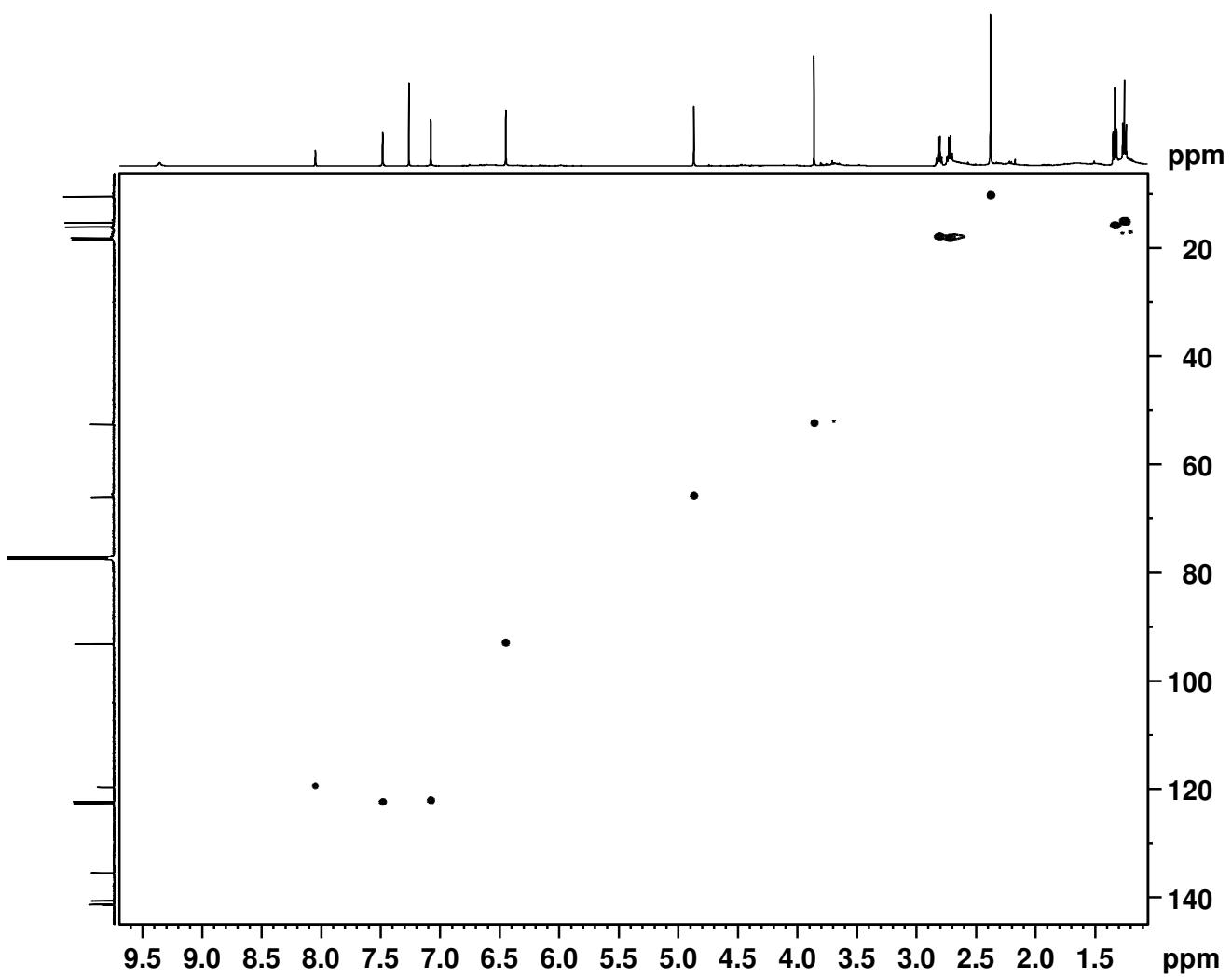
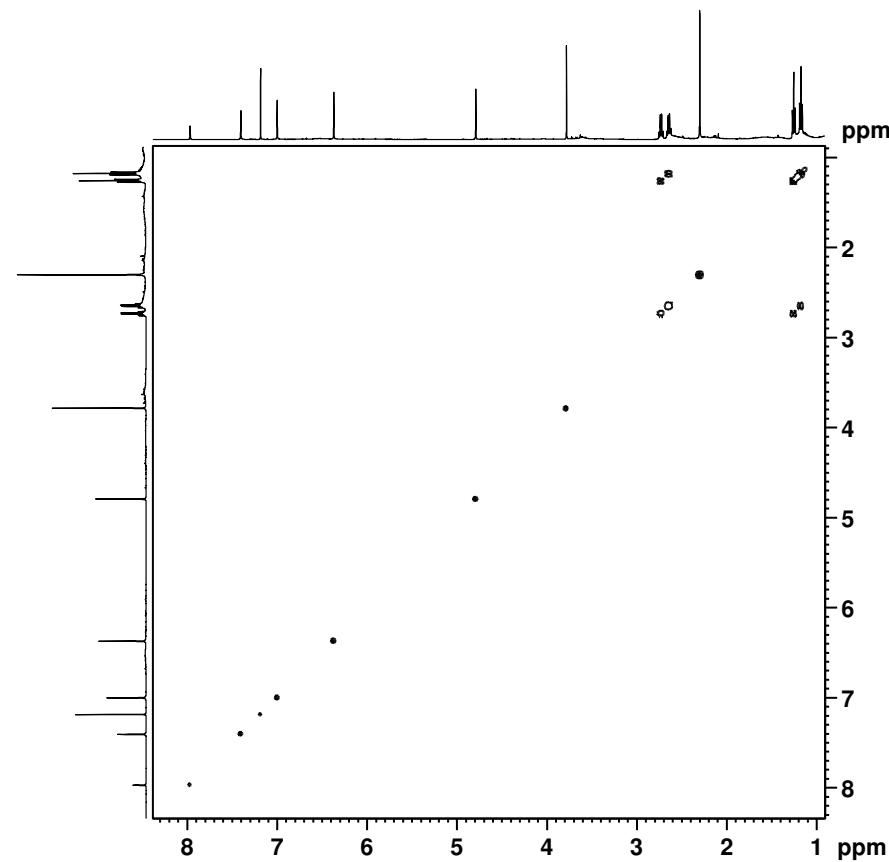


Figure S80. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of **7c** in CDCl_3 .

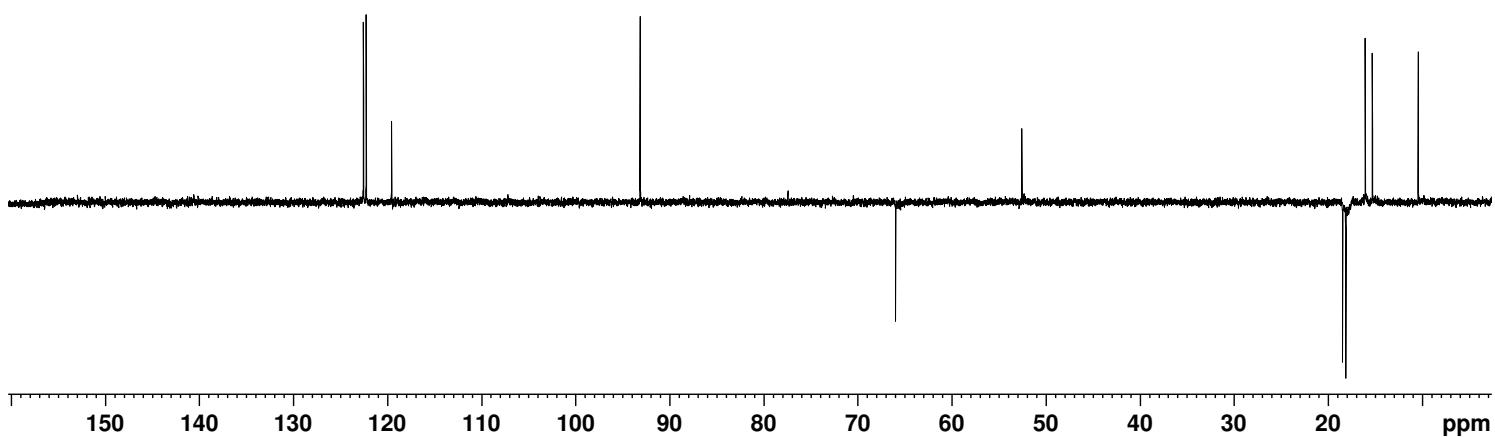


Figure S81. DEPT-135 NMR spectrum of **7c** in CDCl_3 .

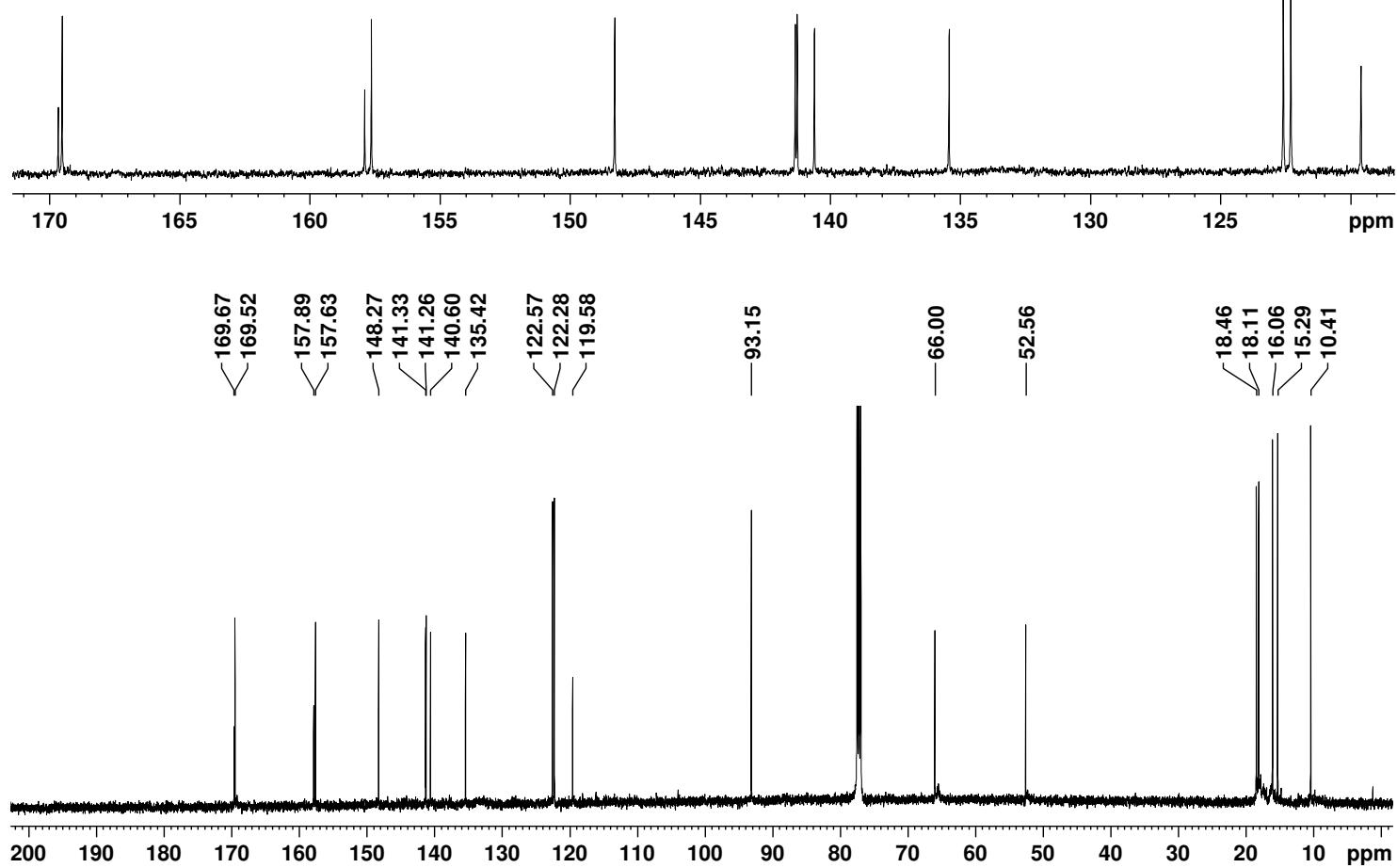
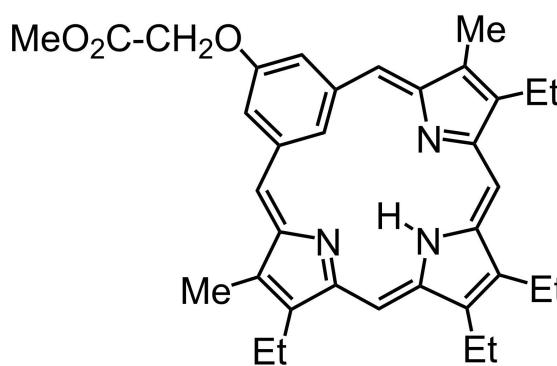


Figure S82. 125 MHz carbon-13 NMR spectrum of **7c** in CDCl_3 .

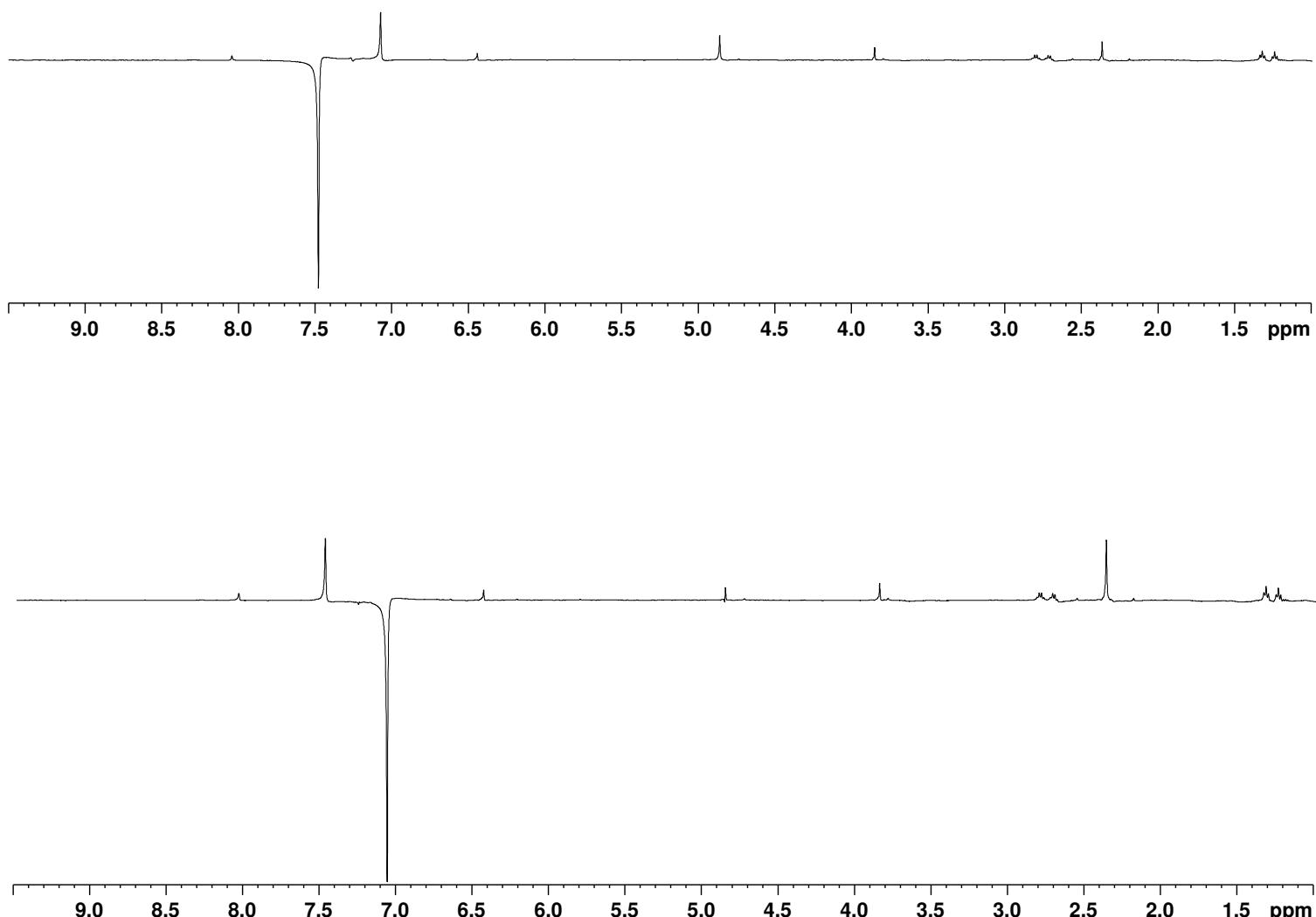


Figure S83. Selected nOe difference proton NMR spectra of **7c** in CDCl_3 .

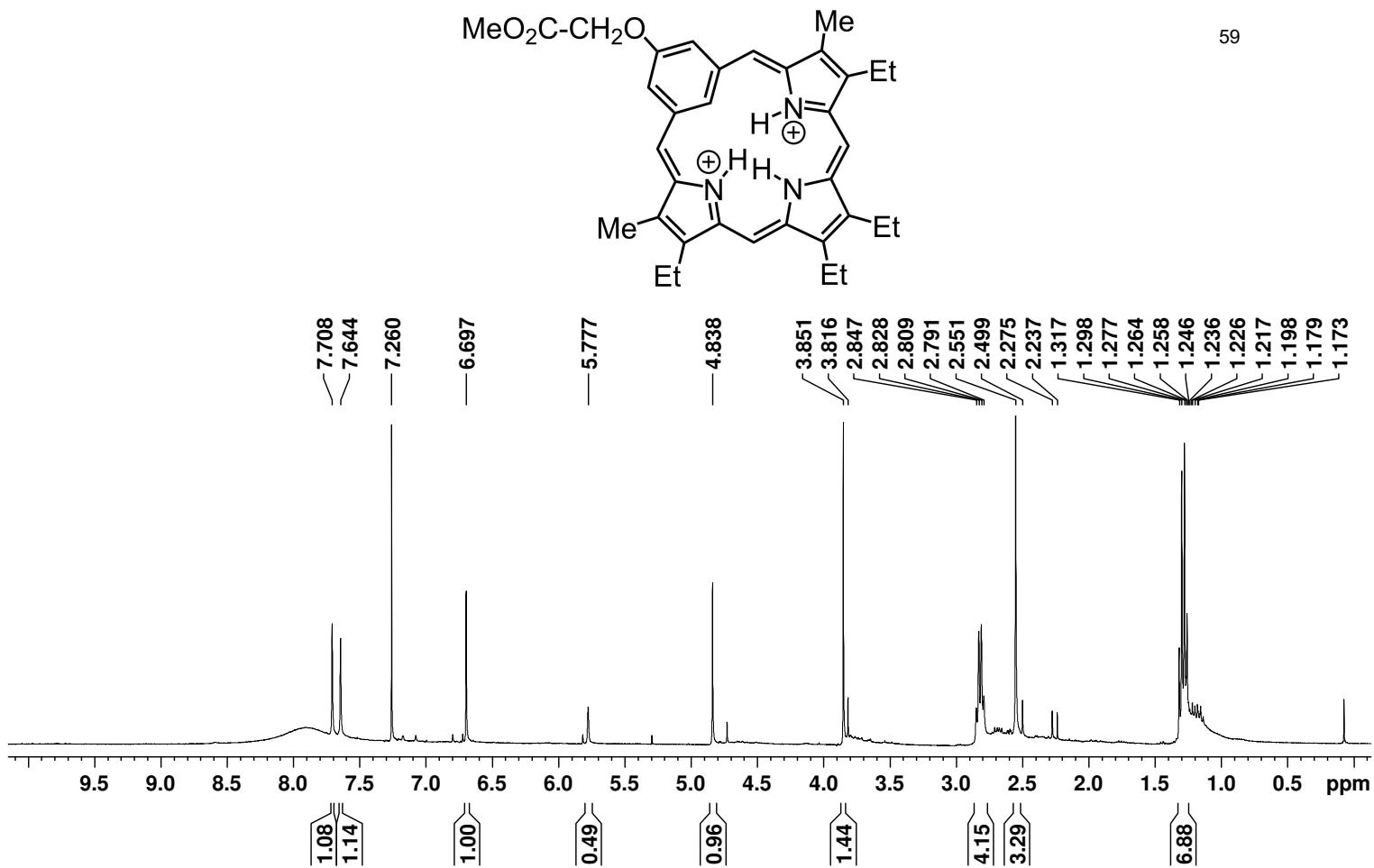


Figure S84. 500 MHz proton NMR spectrum of 7cH_2^{2+} in TFA- CDCl_3 .

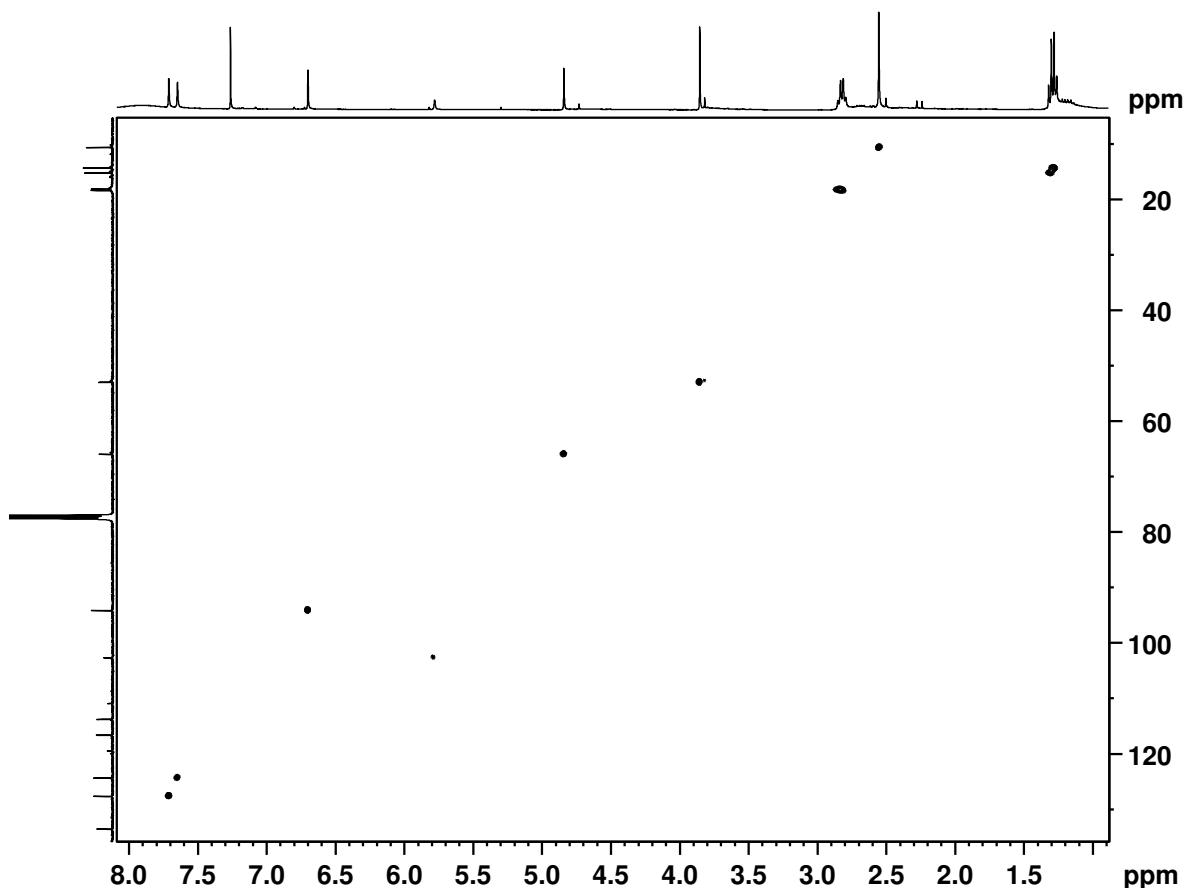


Figure S85. HSQC NMR spectrum of 7cH_2^{2+} in TFA- CDCl_3 .

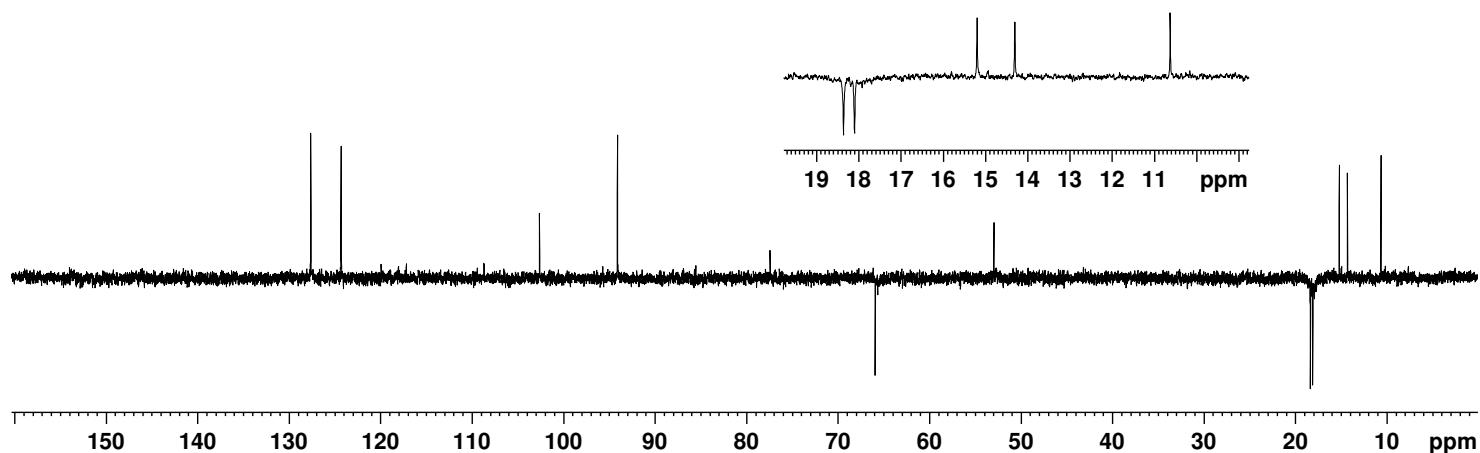


Figure S86. DEPT-135 NMR spectrum of 7cH_2^{2+} in TFA- CDCl_3 .

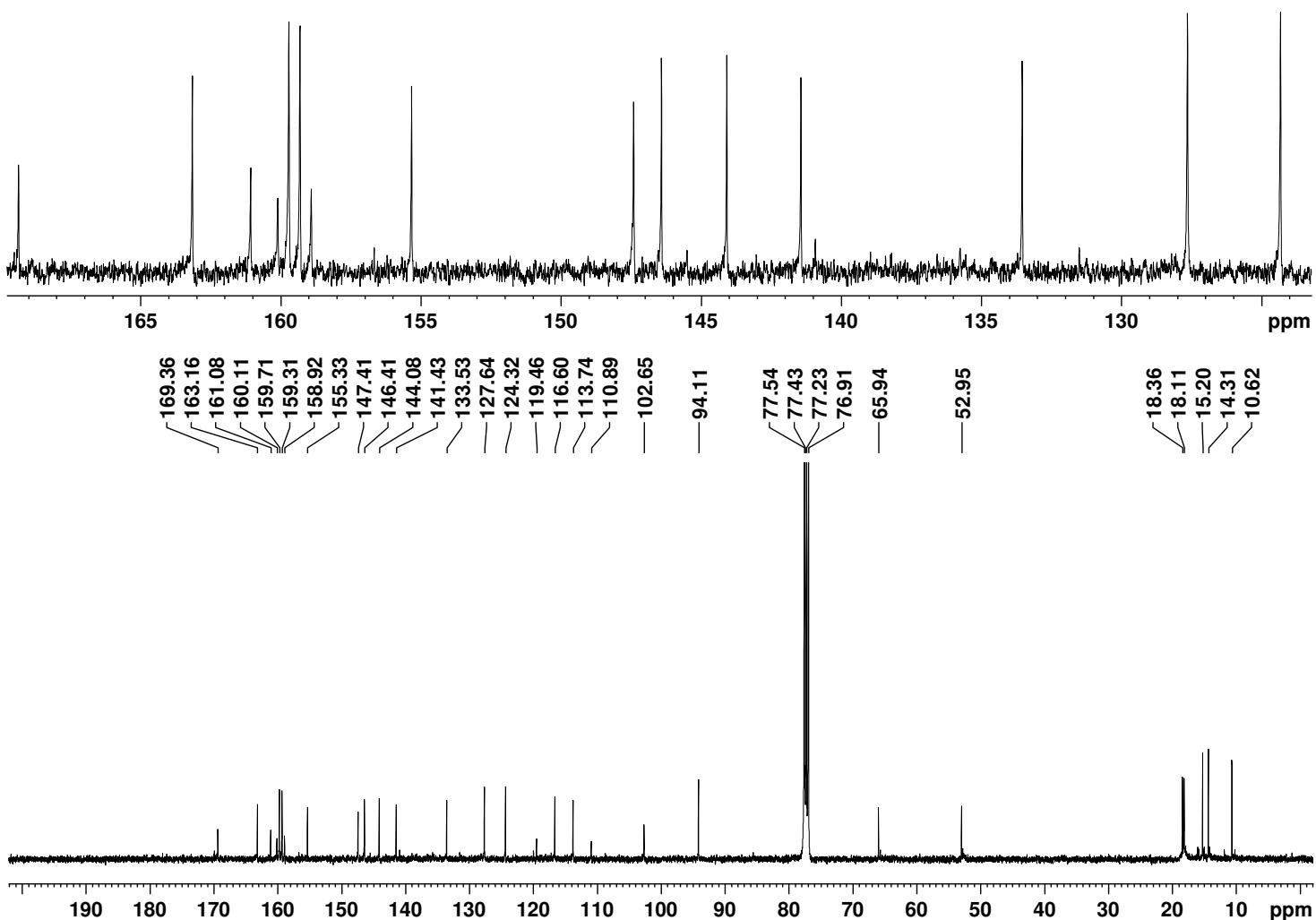
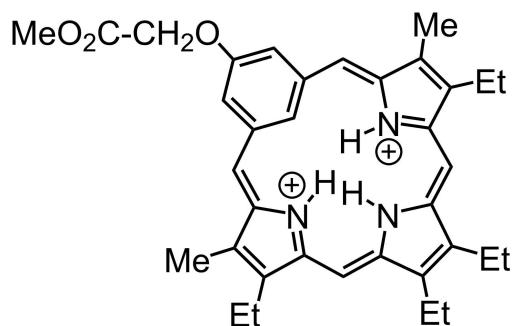


Figure S87. 125 MHz carbon-13 NMR spectrum of 7cH_2^{2+} in TFA- CDCl_3 .

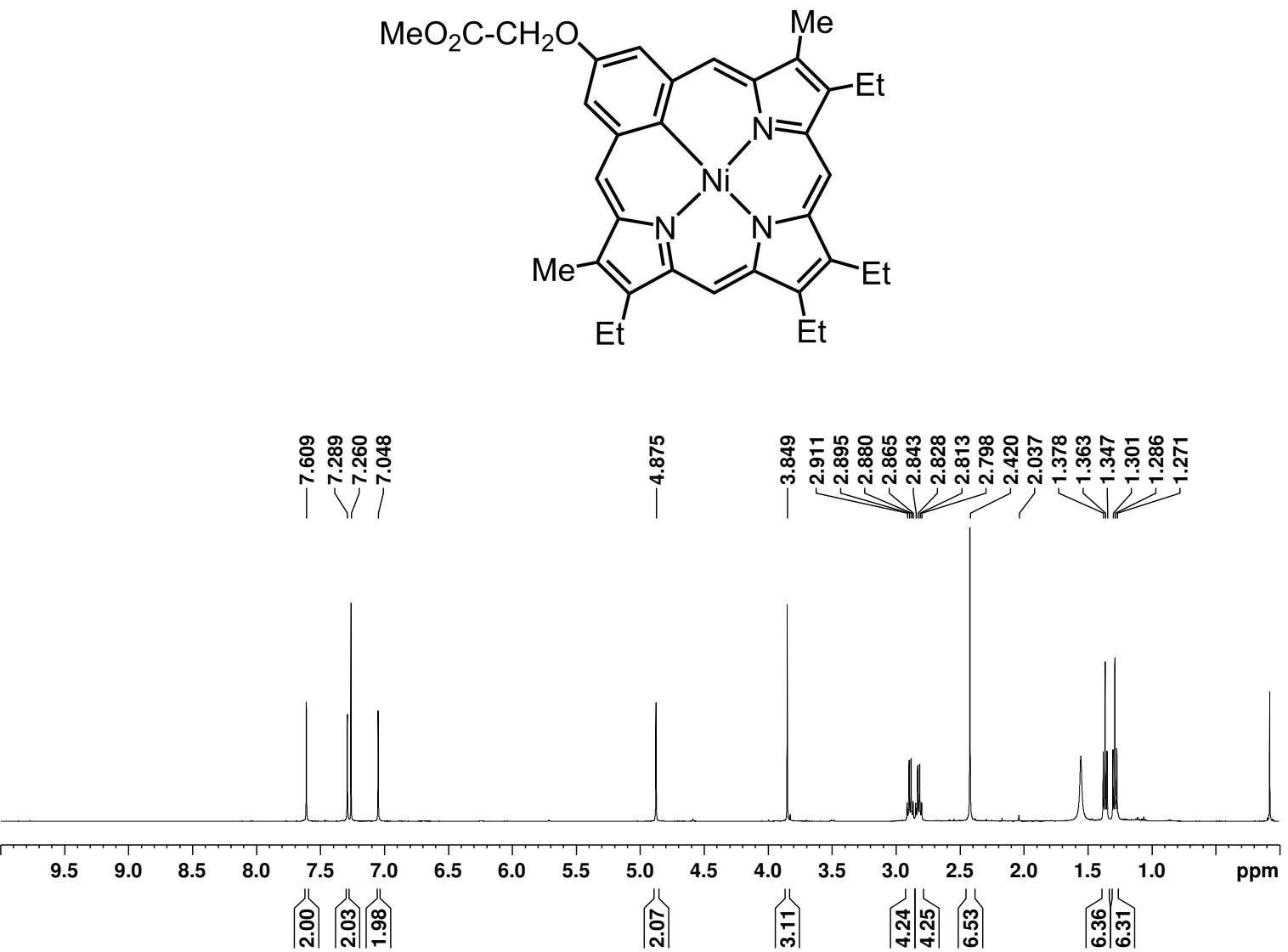


Figure S88. 500 MHz proton NMR spectrum of nickel(II) complex **7cNi** in CDCl_3 .

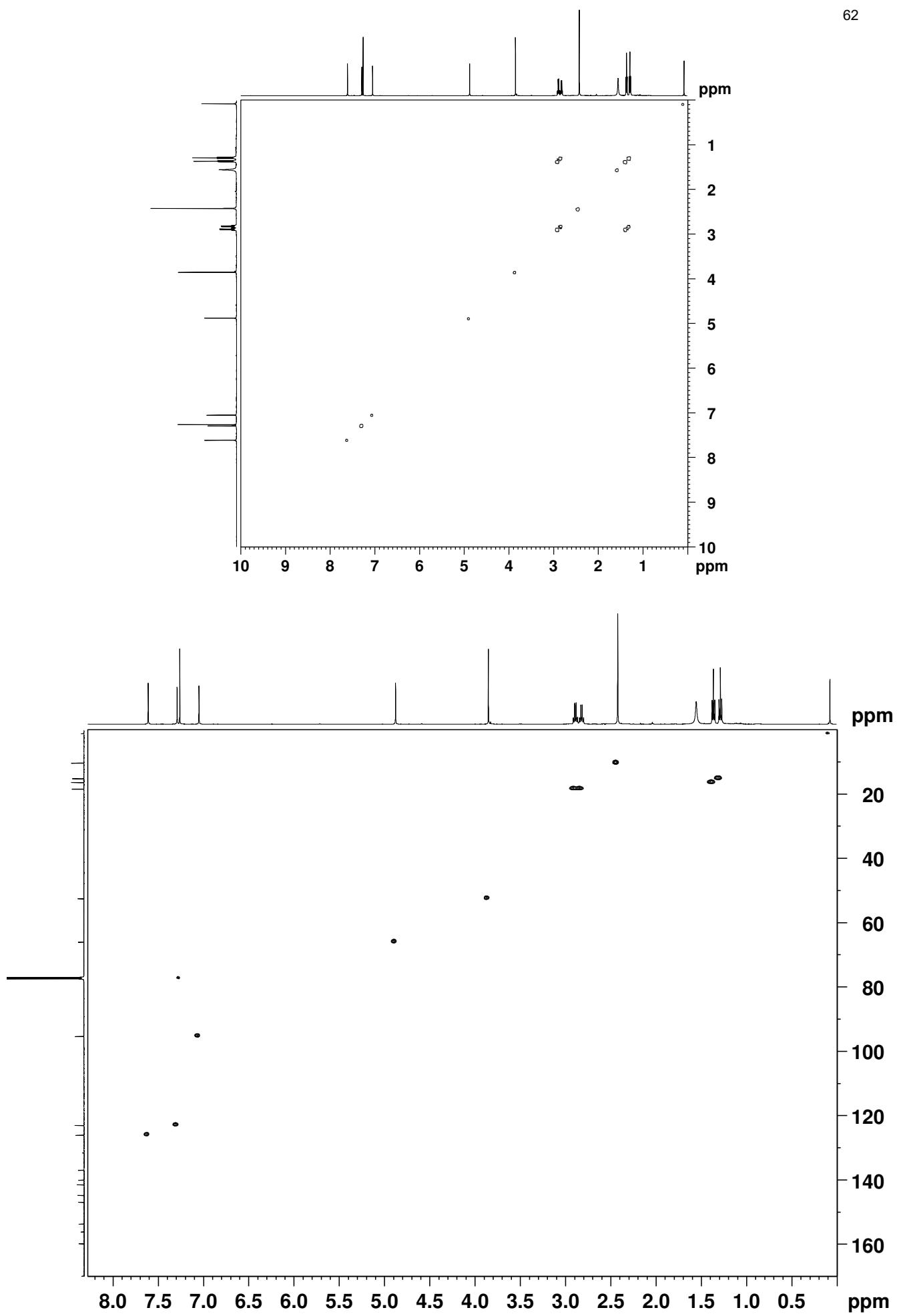


Figure S89. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of **7cNi** in CDCl_3 .

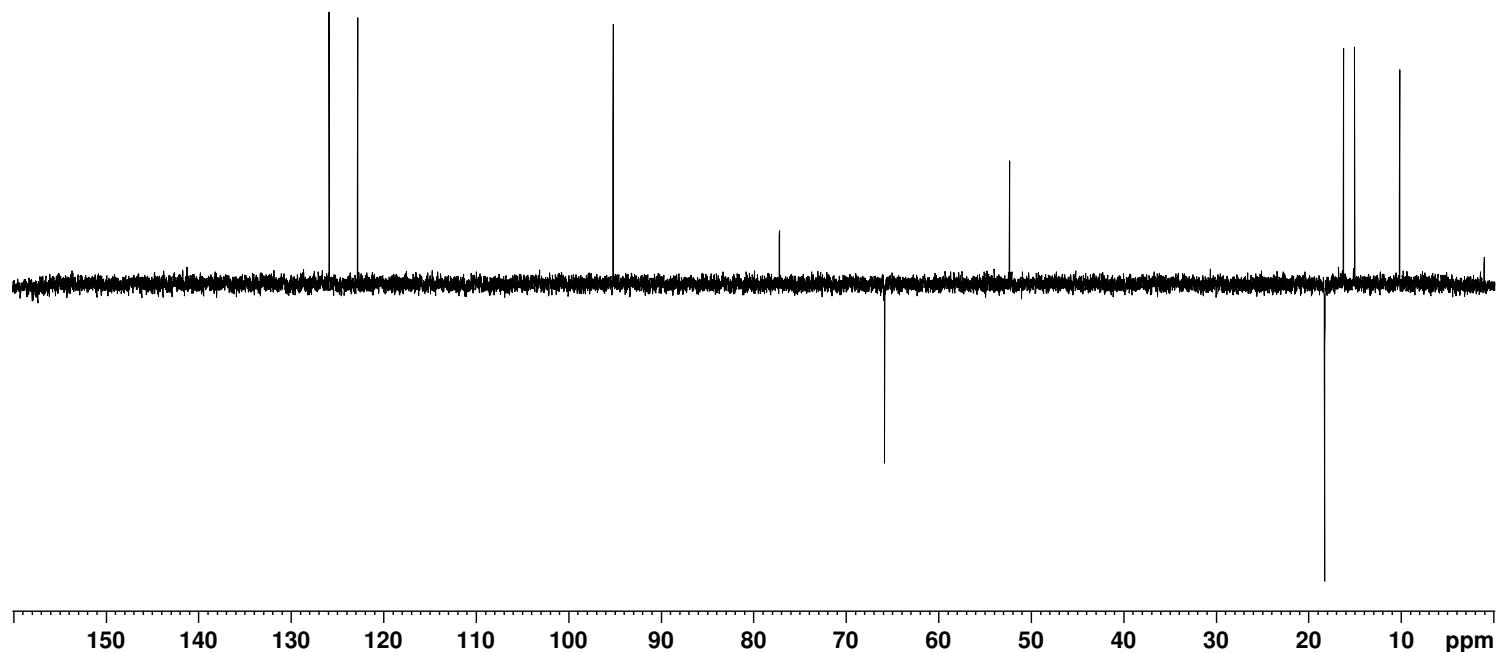


Figure S90. DEPT-135 NMR spectrum of **7cNi** in CDCl_3 .

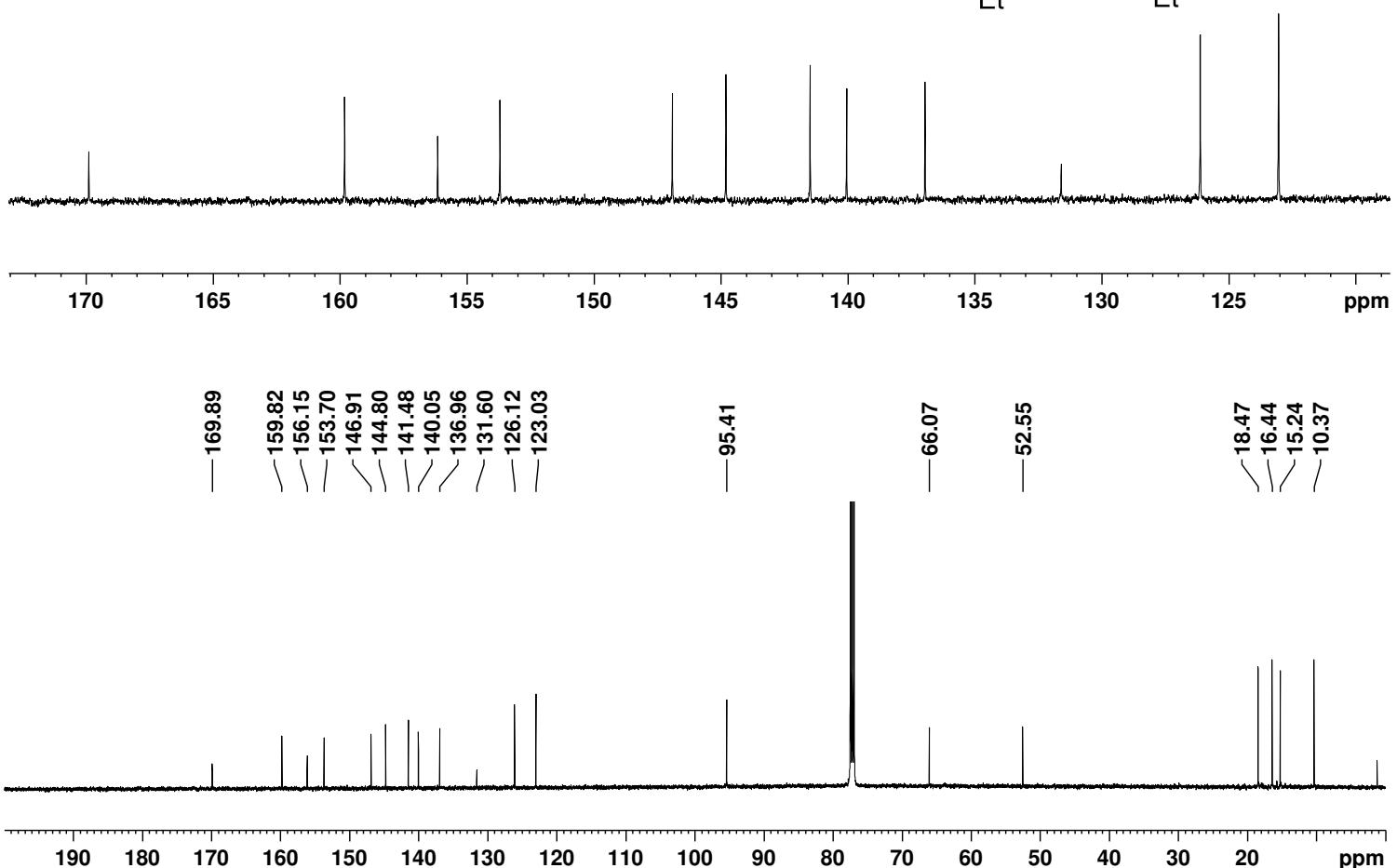
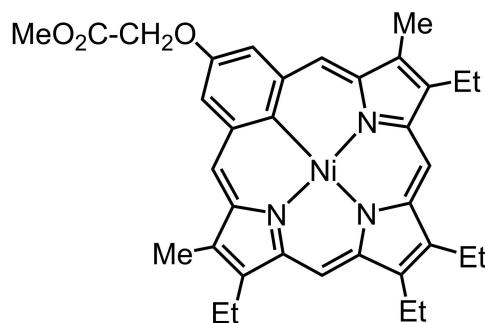


Figure S91. 125 MHz carbon-13 NMR spectrum of **7cNi** in CDCl_3 .

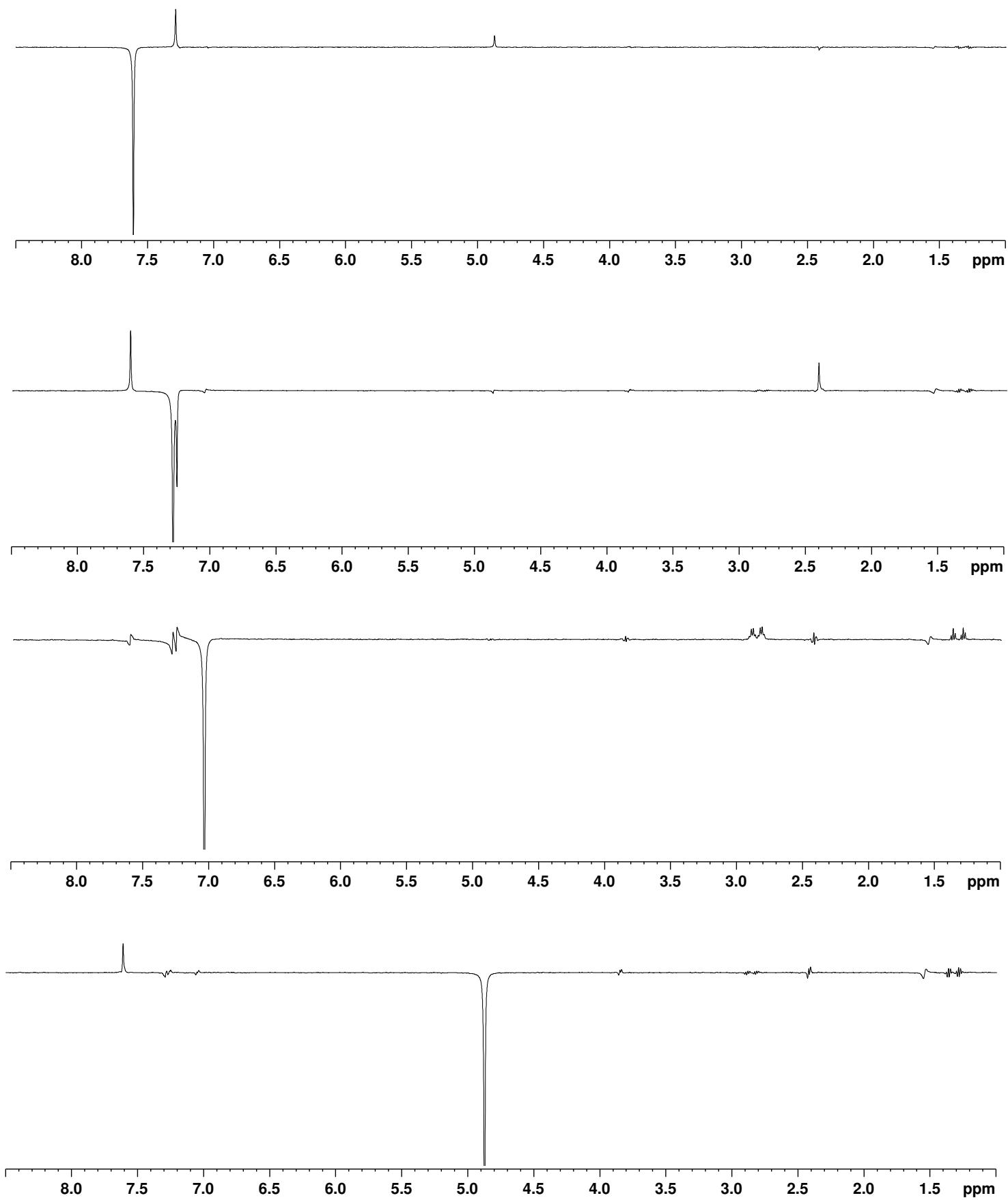


Figure S92. Selected nOe difference proton NMR spectra of **7cNi** in CDCl_3 .

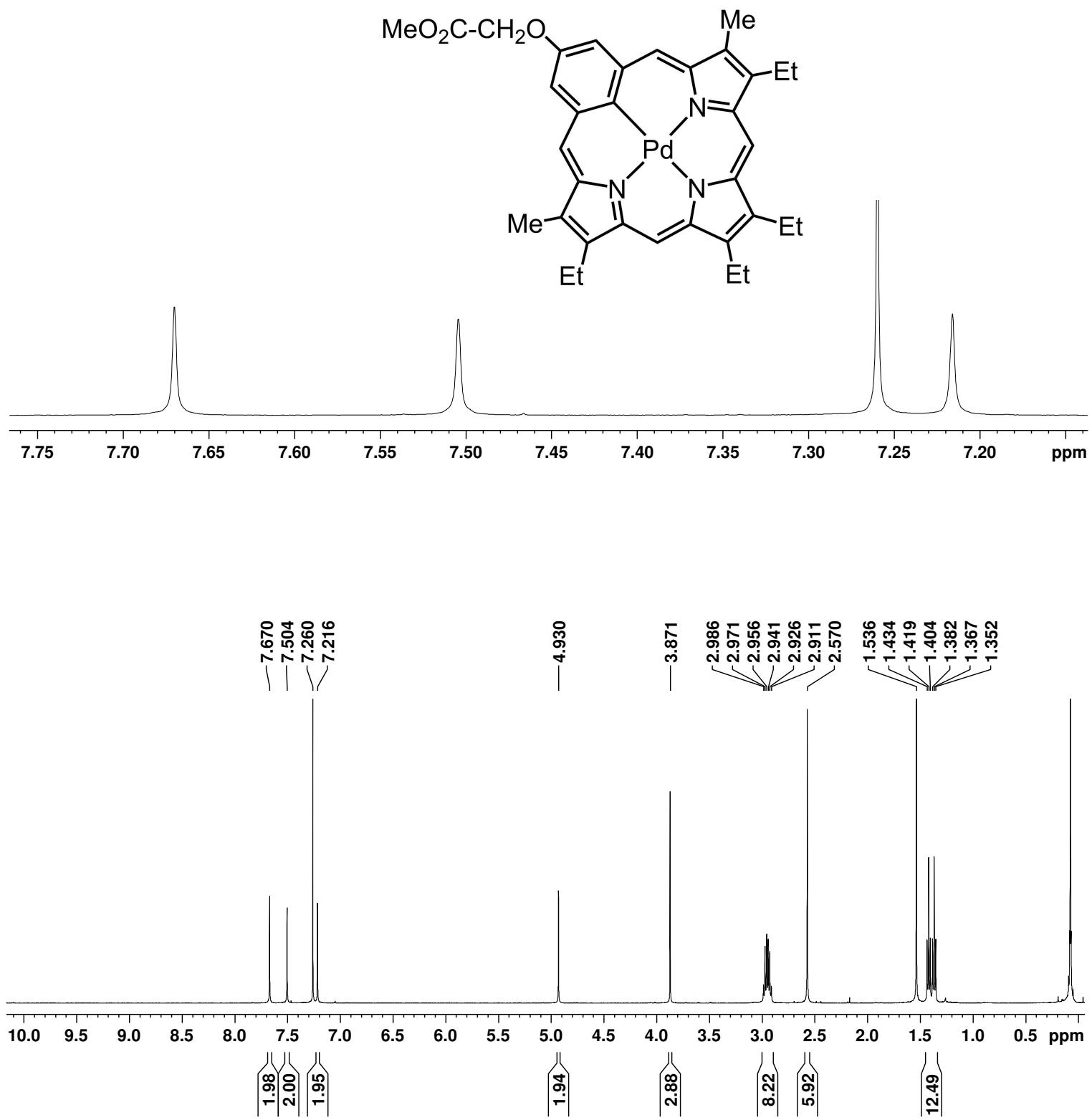


Figure S93. 500 MHz proton NMR spectrum of palladium(II) complex **7cPd** in CDCl_3 .

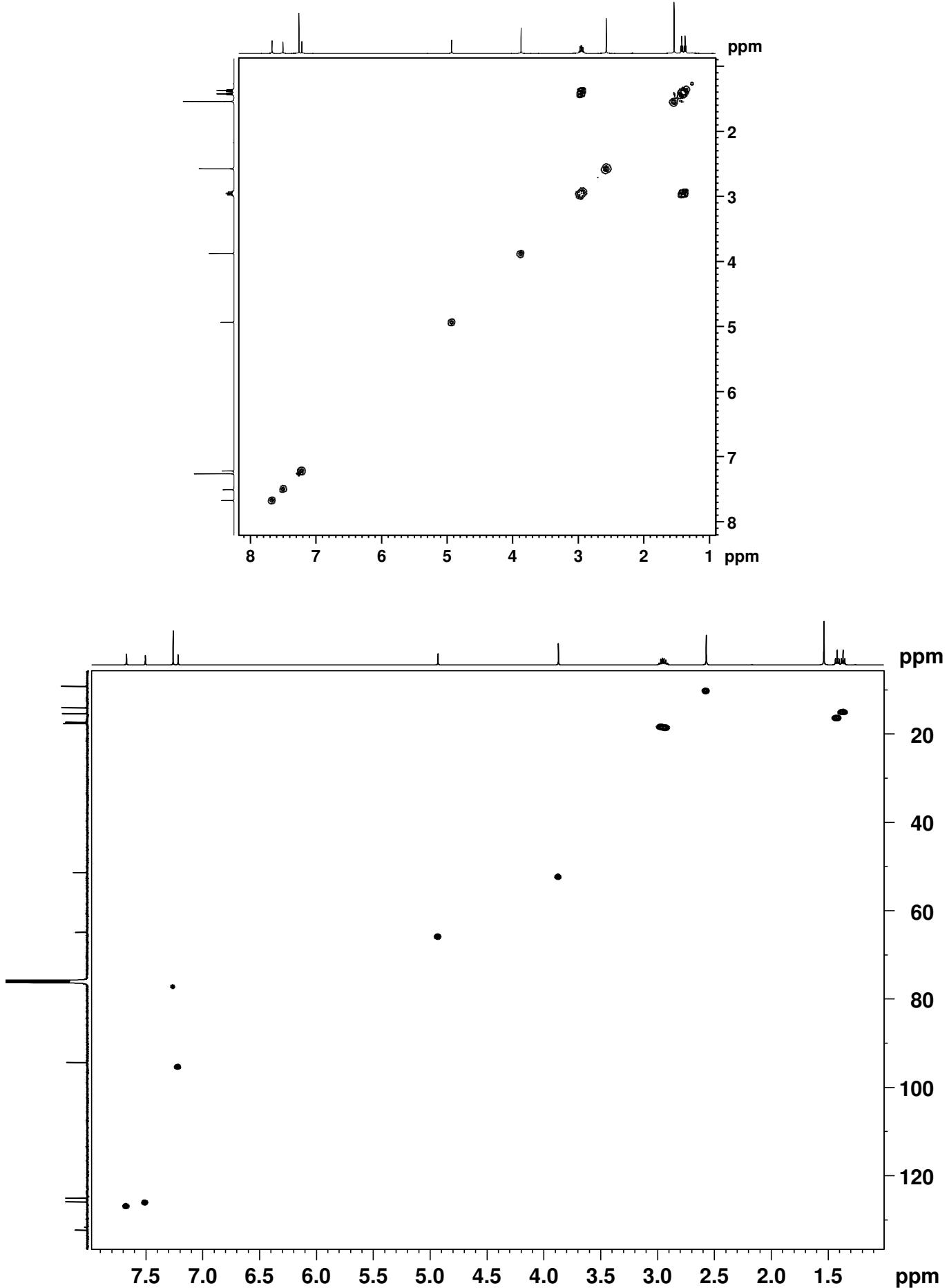


Figure S94. ^1H - ^1H COSY (top) and HSQC (bottom) spectra of **7cPd** in CDCl_3 .

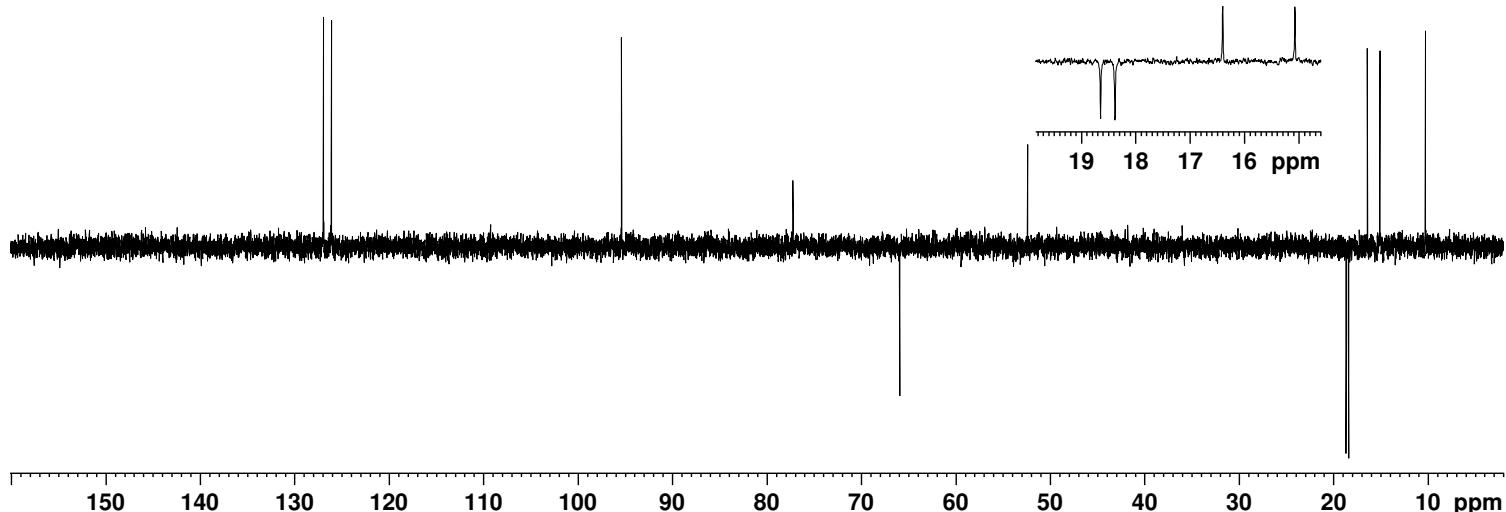


Figure S95. DEPT-135 NMR spectrum of **7cPd** in CDCl_3 .

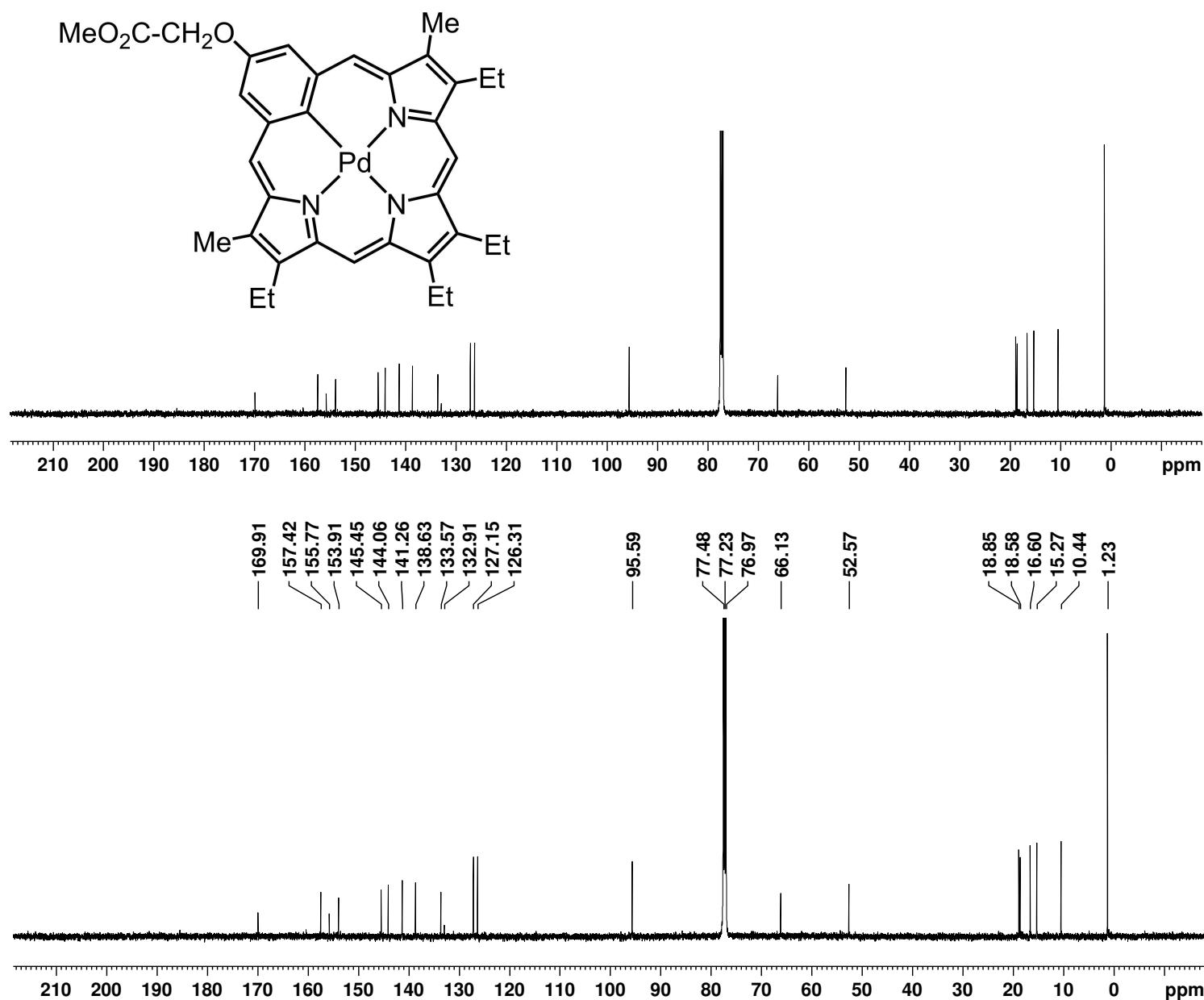


Figure S96. 125 MHz carbon-13 NMR spectrum of **7cPd** in CDCl_3 .

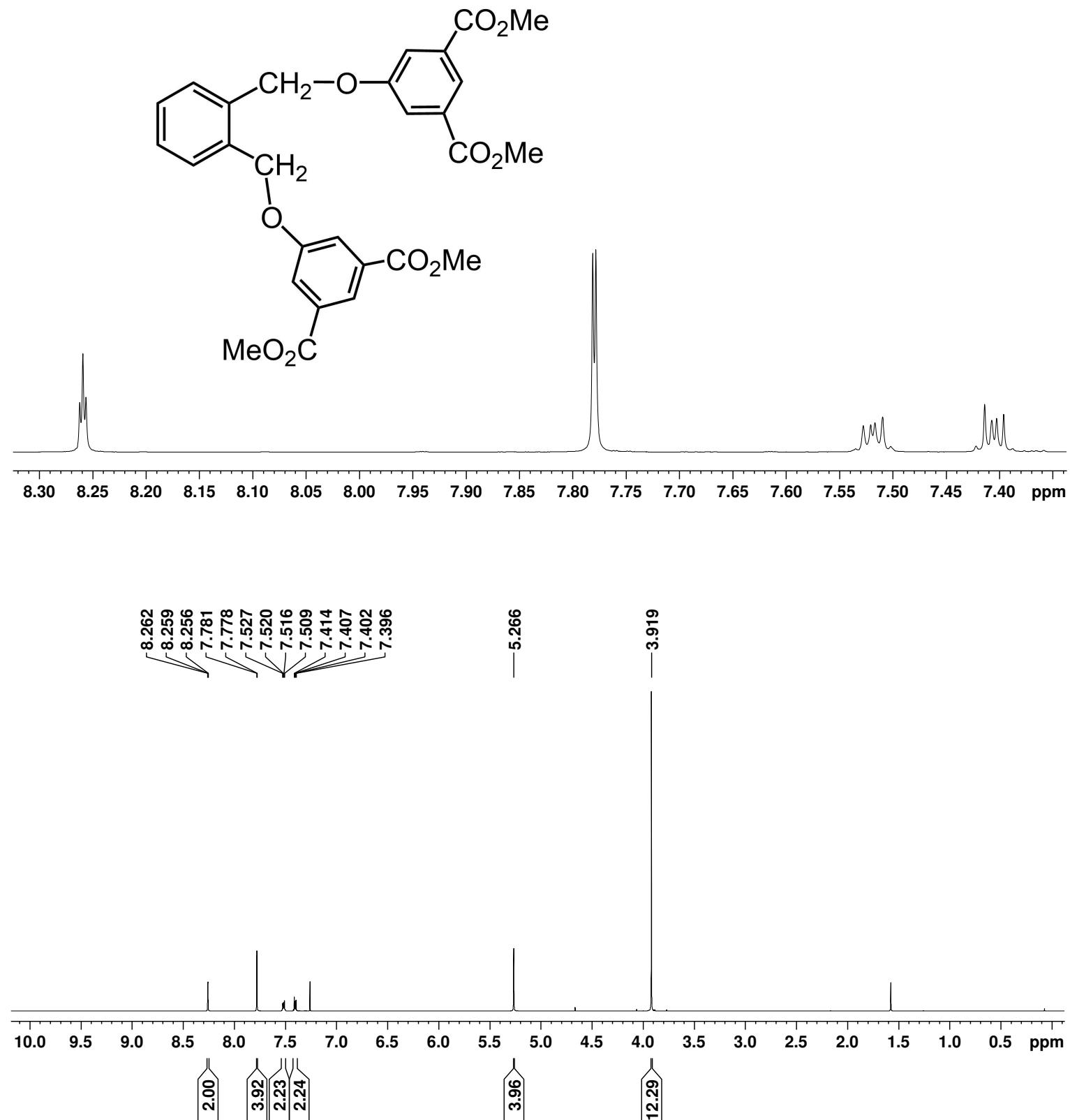


Figure S97. 500 MHz proton NMR spectrum of tetraester **16a** in CDCl_3 .

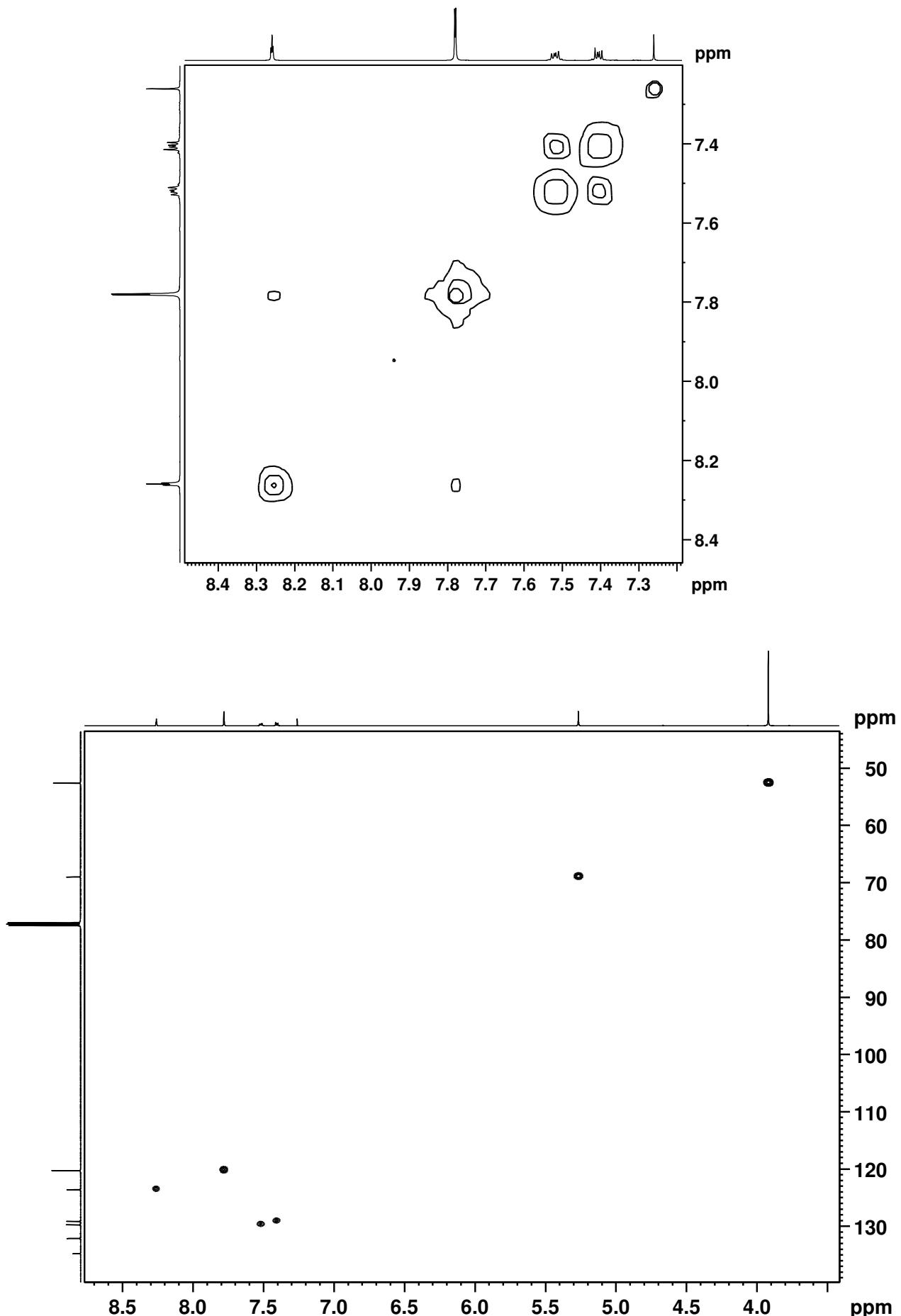


Figure S98. ^1H - ^1H COSY and HSQC NMR spectra of **16a** in CDCl_3 .

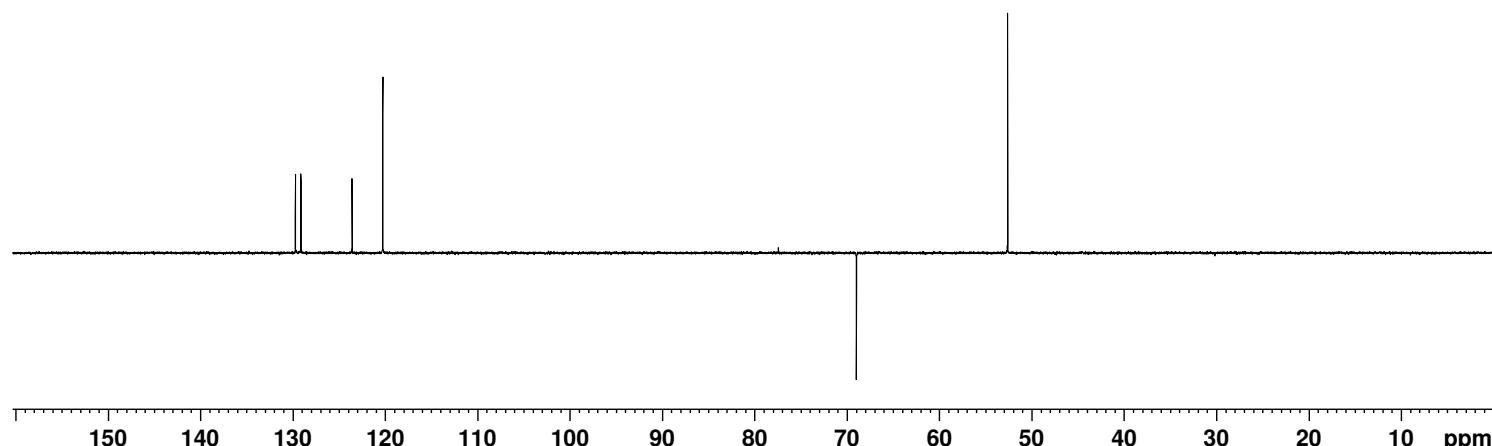


Figure S99. DEPT-135 NMR spectrum of **16a** in CDCl_3 .

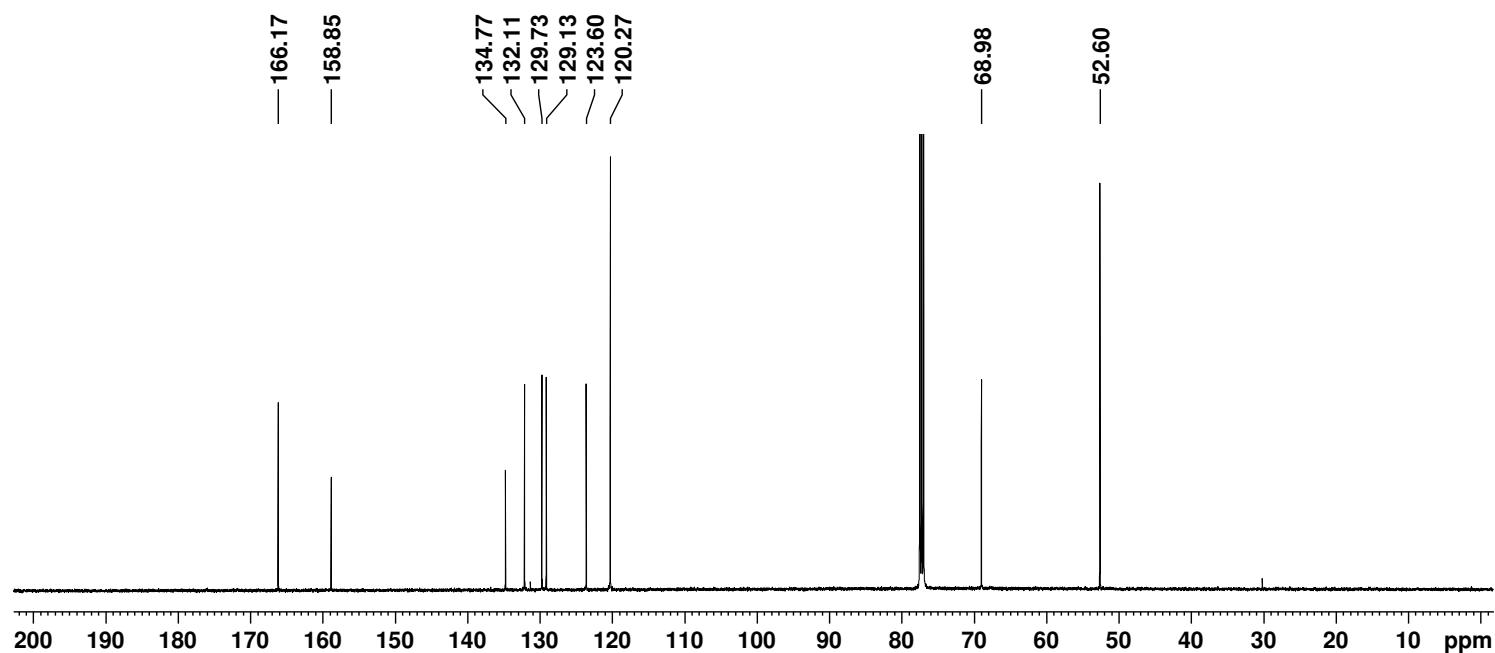
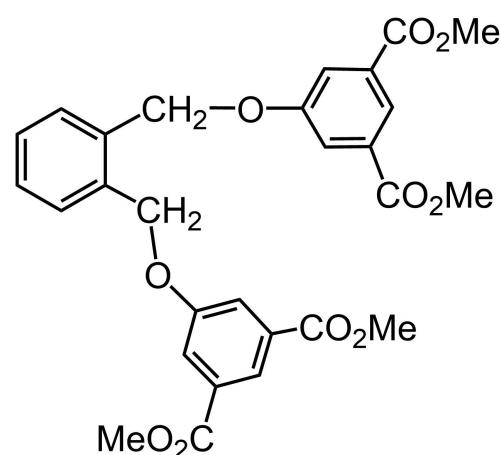


Figure S100. 125 MHz carbon-13 NMR spectrum of **16a** in CDCl_3 .

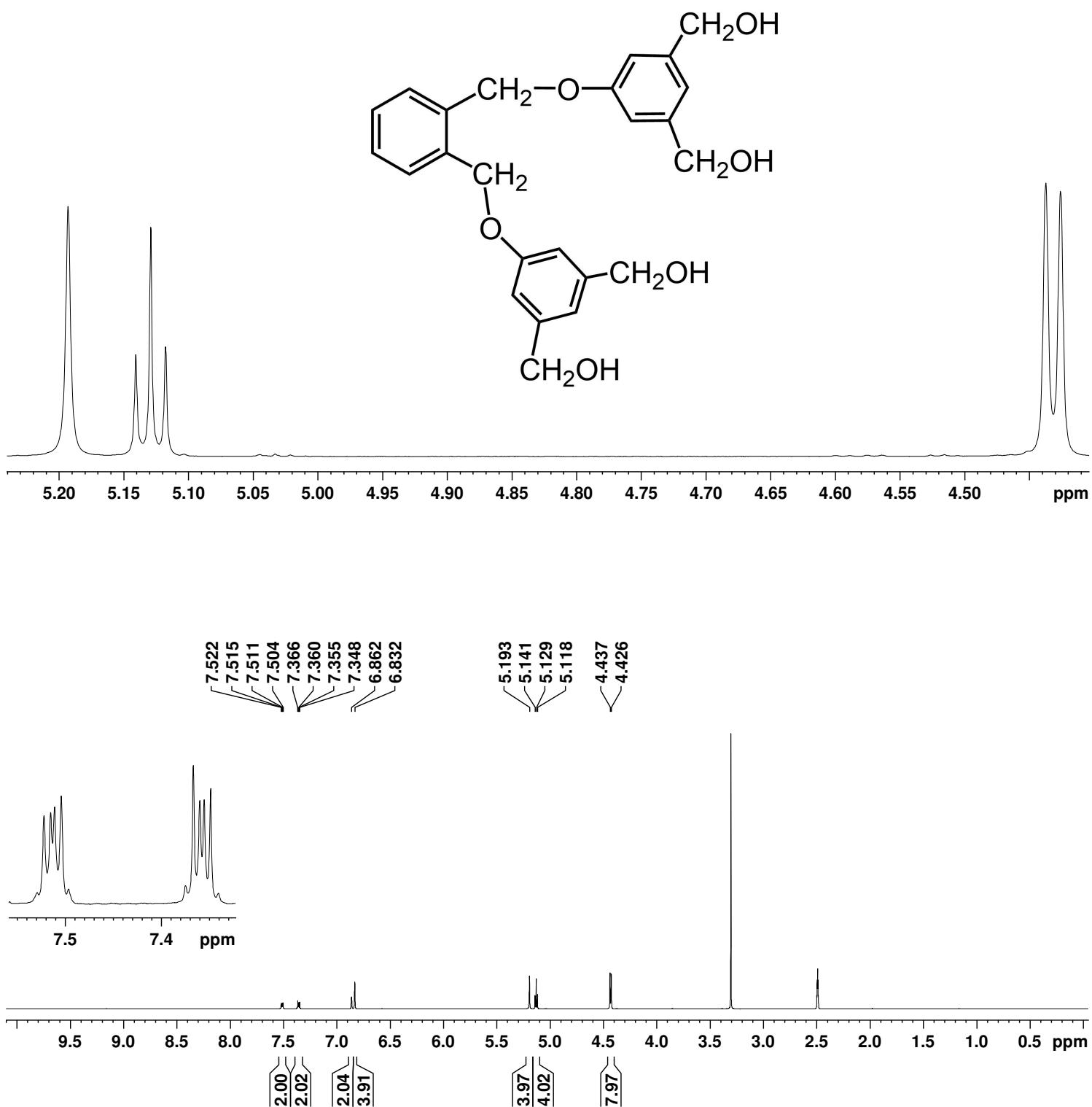


Figure S101. 500 MHz proton NMR spectrum of tetraalcohol **17a** in DMSO-*d*₆.

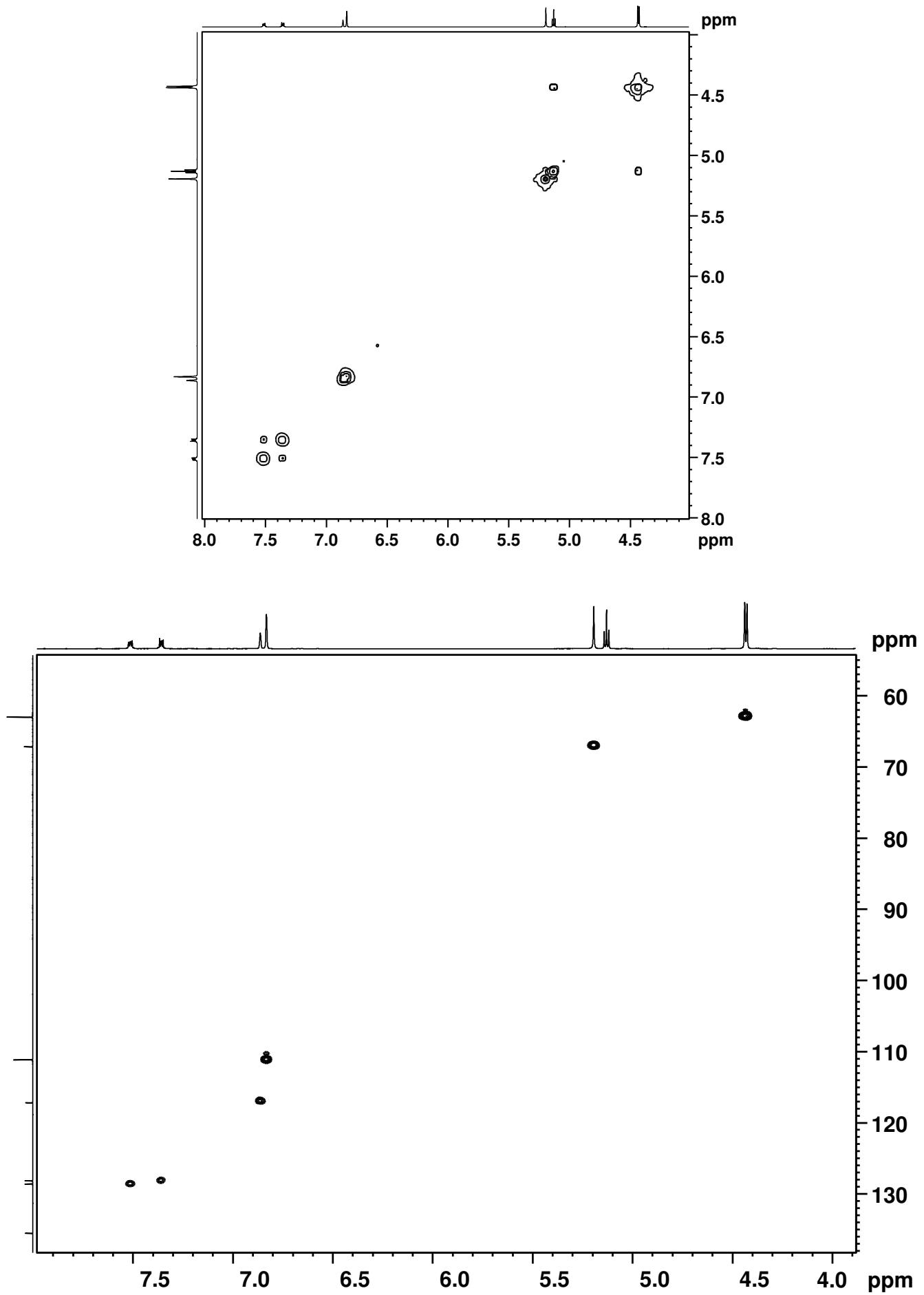


Figure S102. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of **17a** in $\text{DMSO}-d_6$.

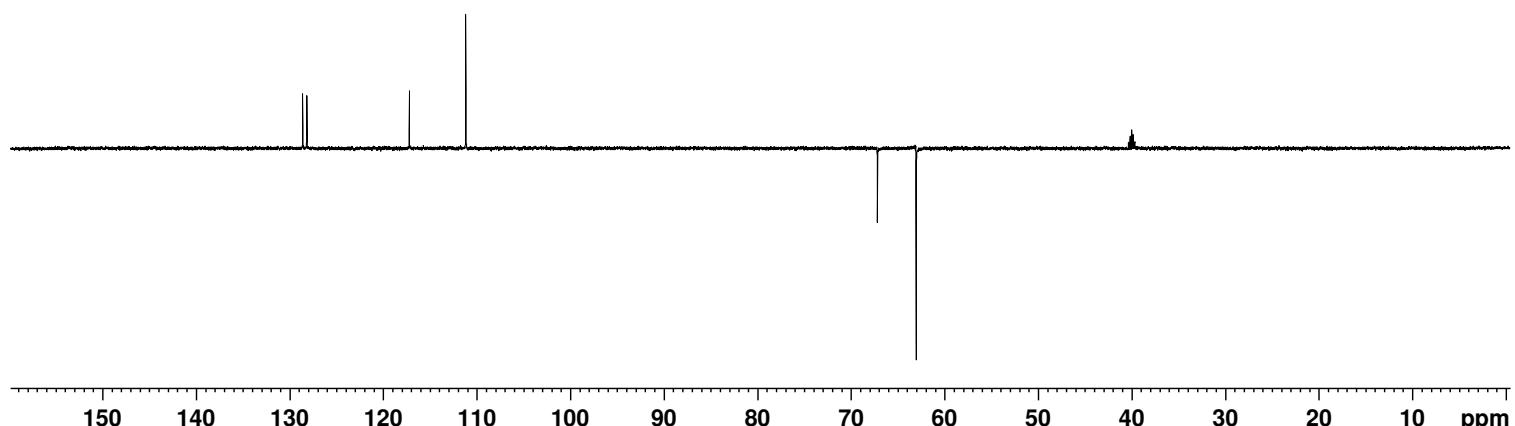


Figure 103. DEPT-135 NMR spectrum of **17a** in $\text{DMSO}-d_6$.

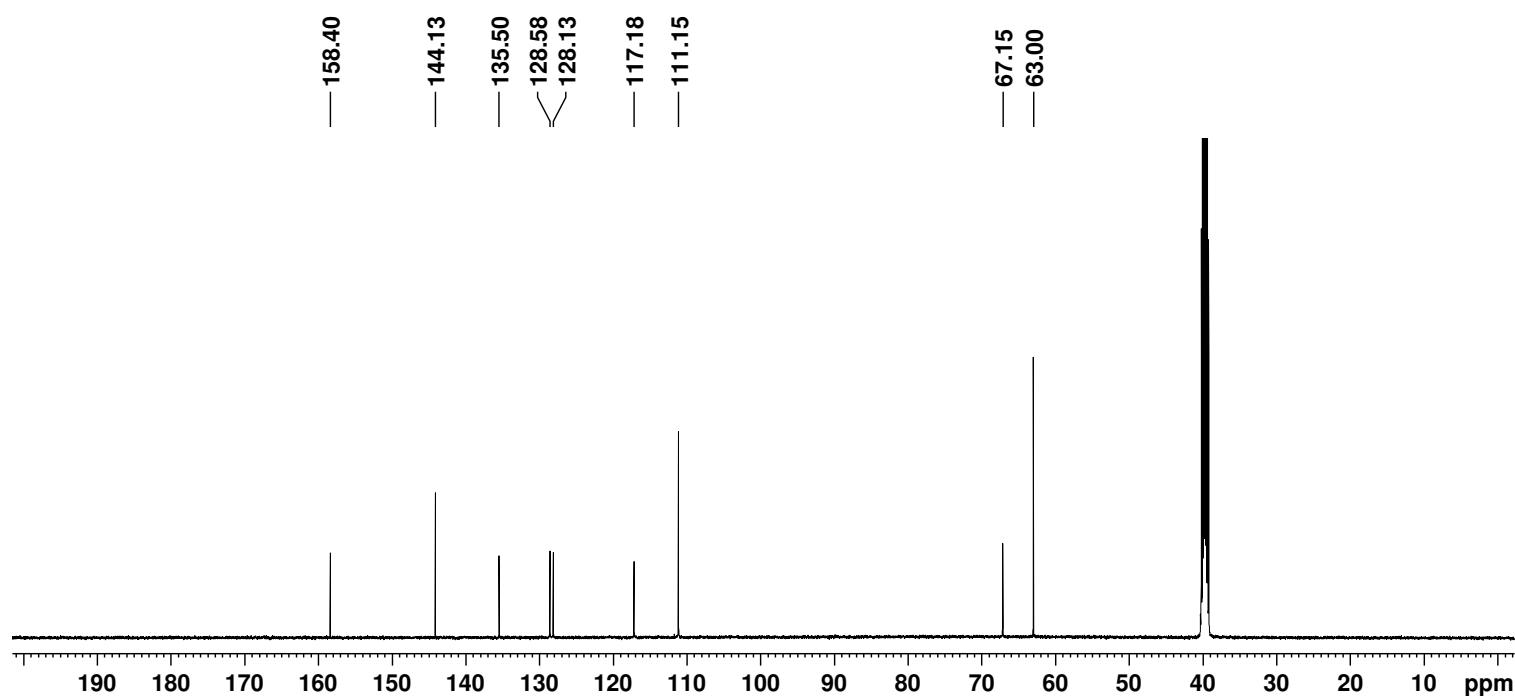
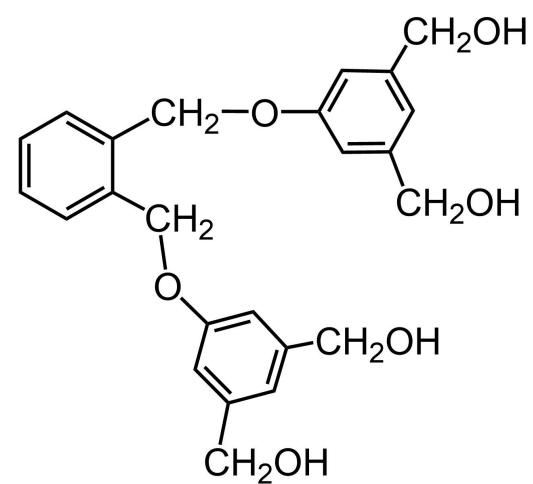


Figure S104. 125 MHz carbon-13 NMR spectrum of **17a** in $\text{DMSO}-d_6$.

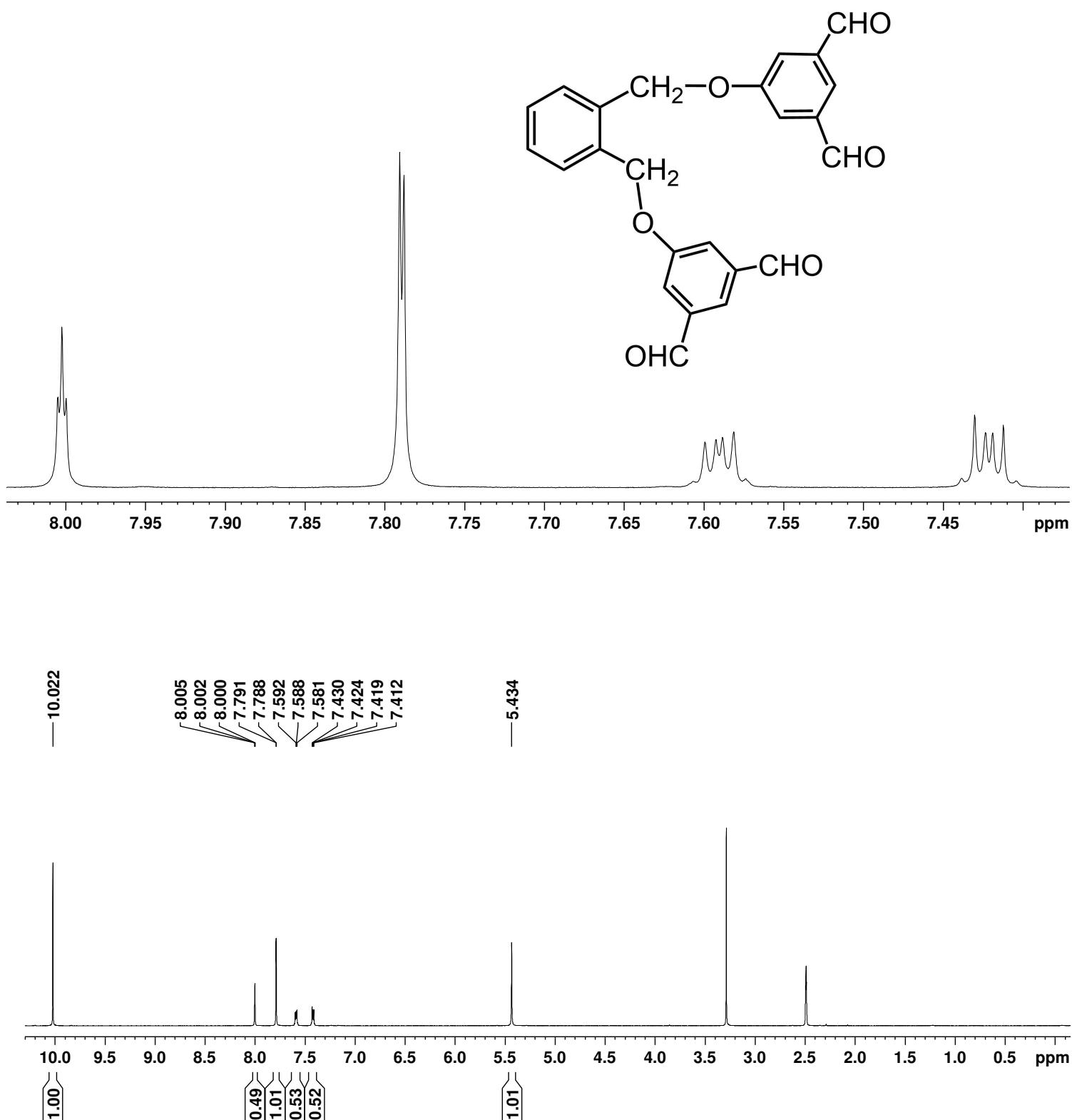


Figure S105. Proton NMR spectrum of tetraaldehyde **18a** in DMSO-*d*₆.

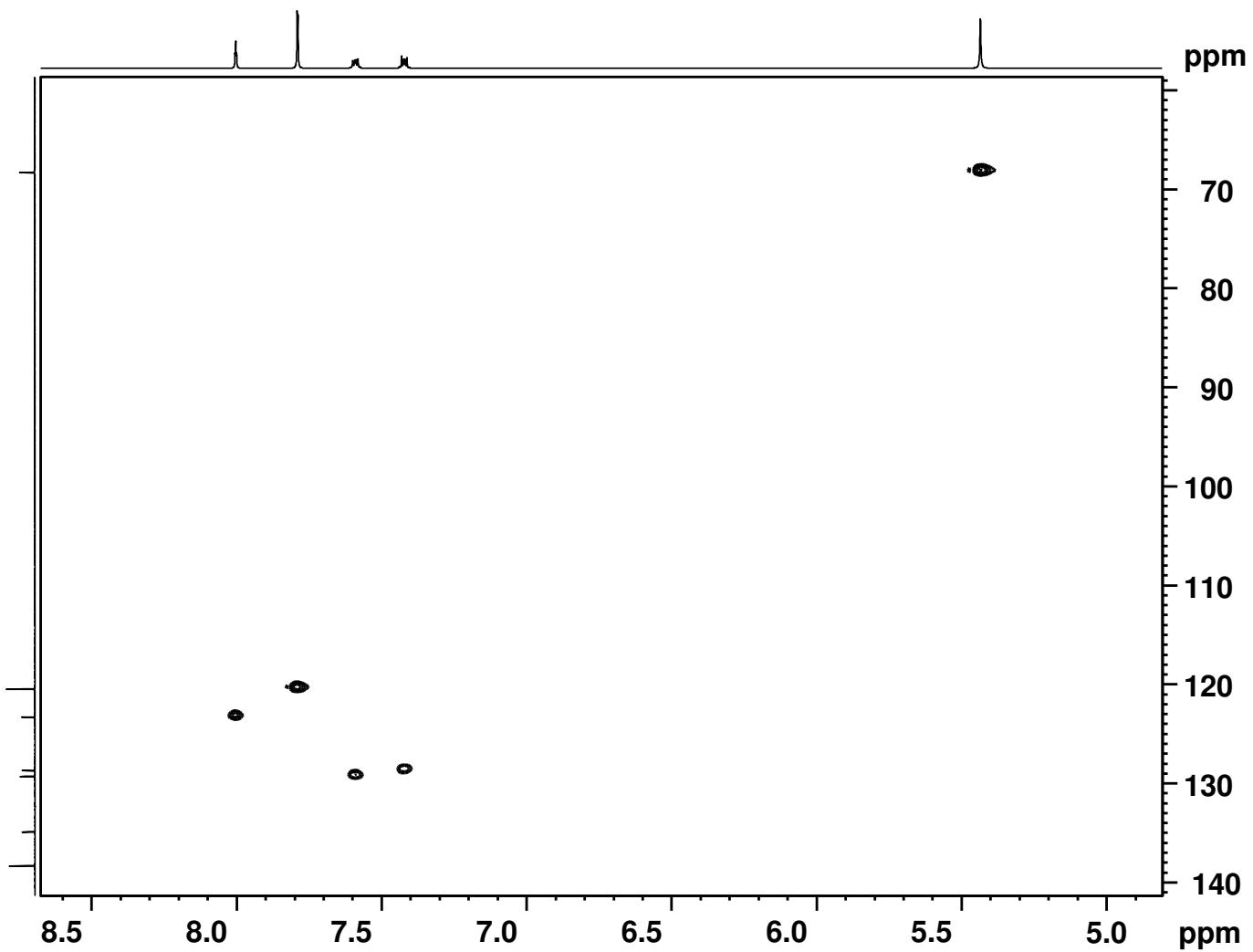
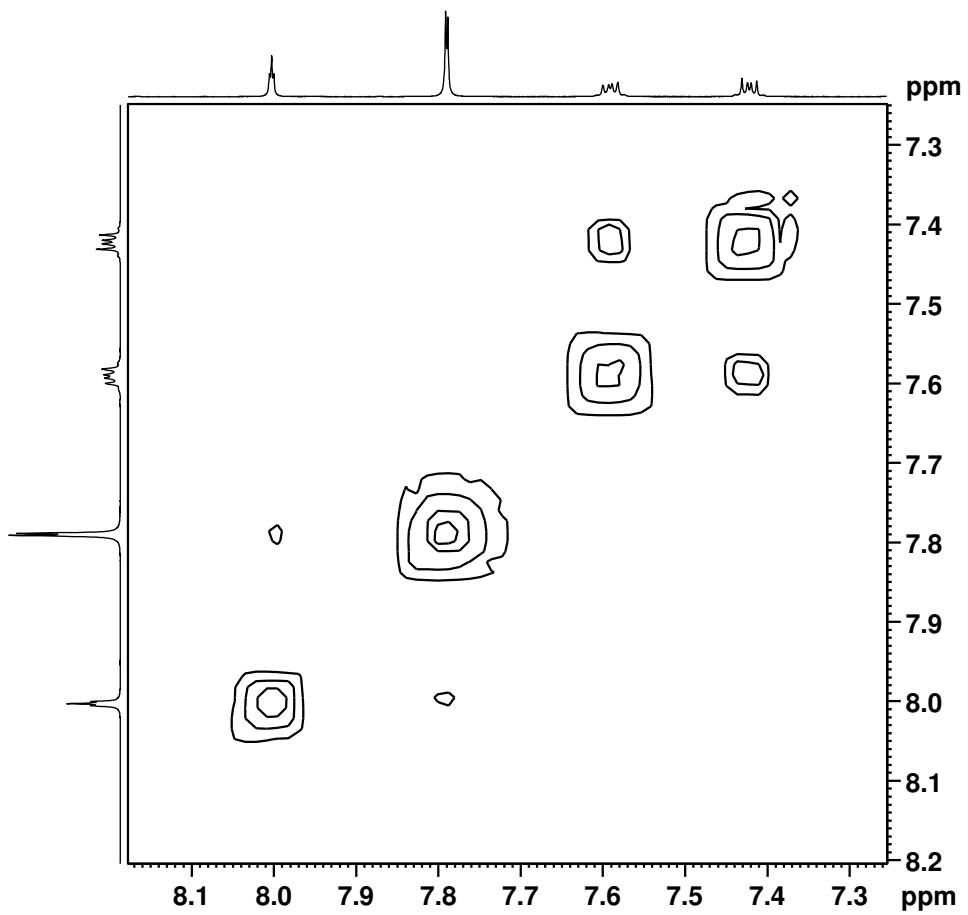


Figure S106. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of **18a** in $\text{DMSO}-d_6$.

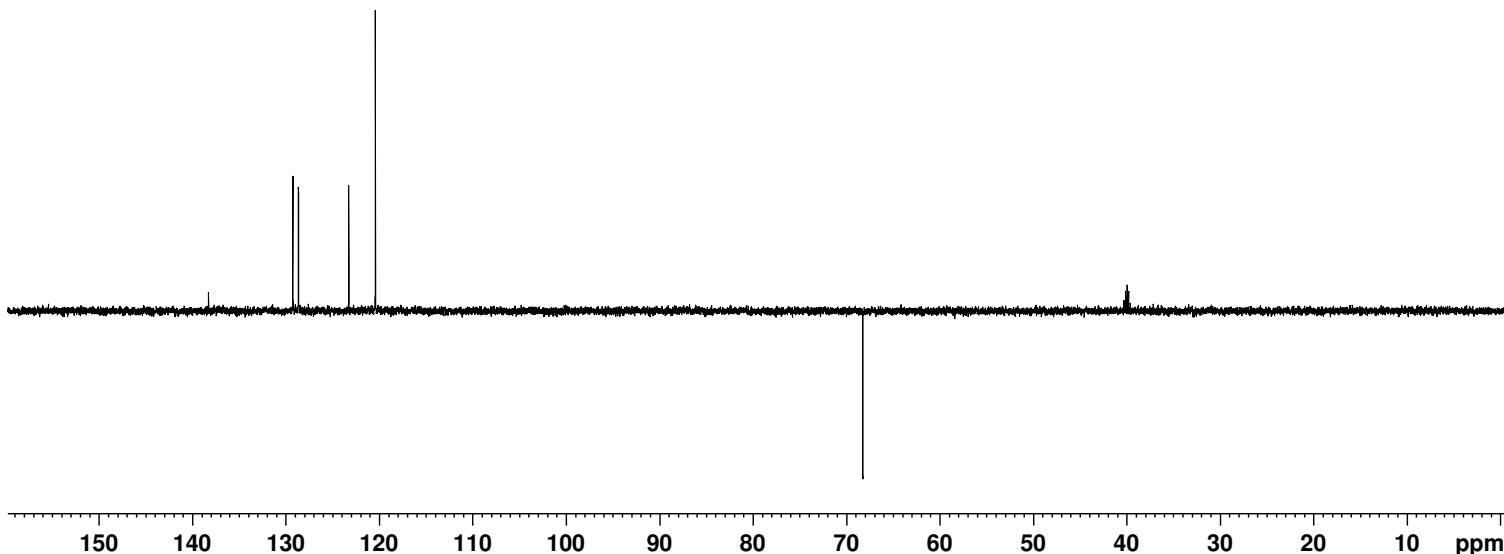


Figure S107. DEPT-135 NMR spectrum of **18a** in $\text{DMSO}-d_6$.

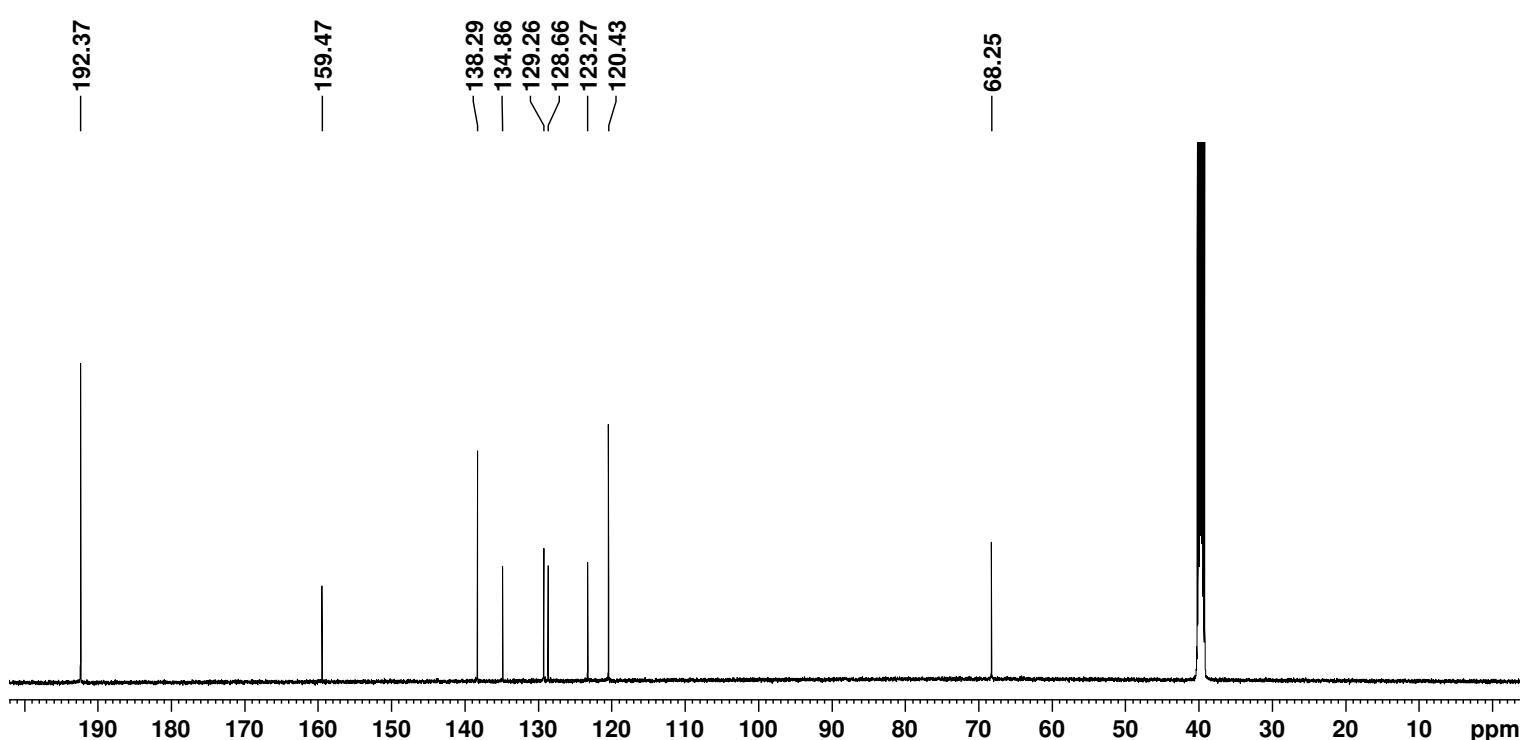
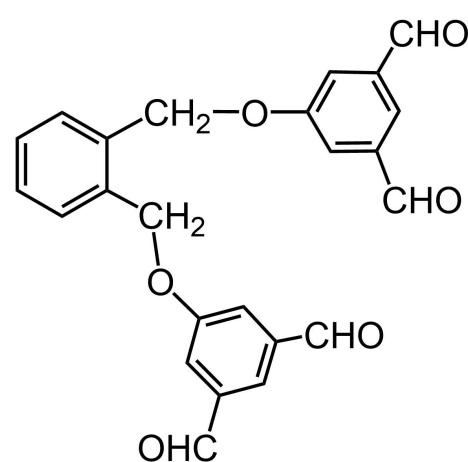


Figure S108. 125 MHz carbon-13 NMR spectrum of **18a** in $\text{DMSO}-d_6$.

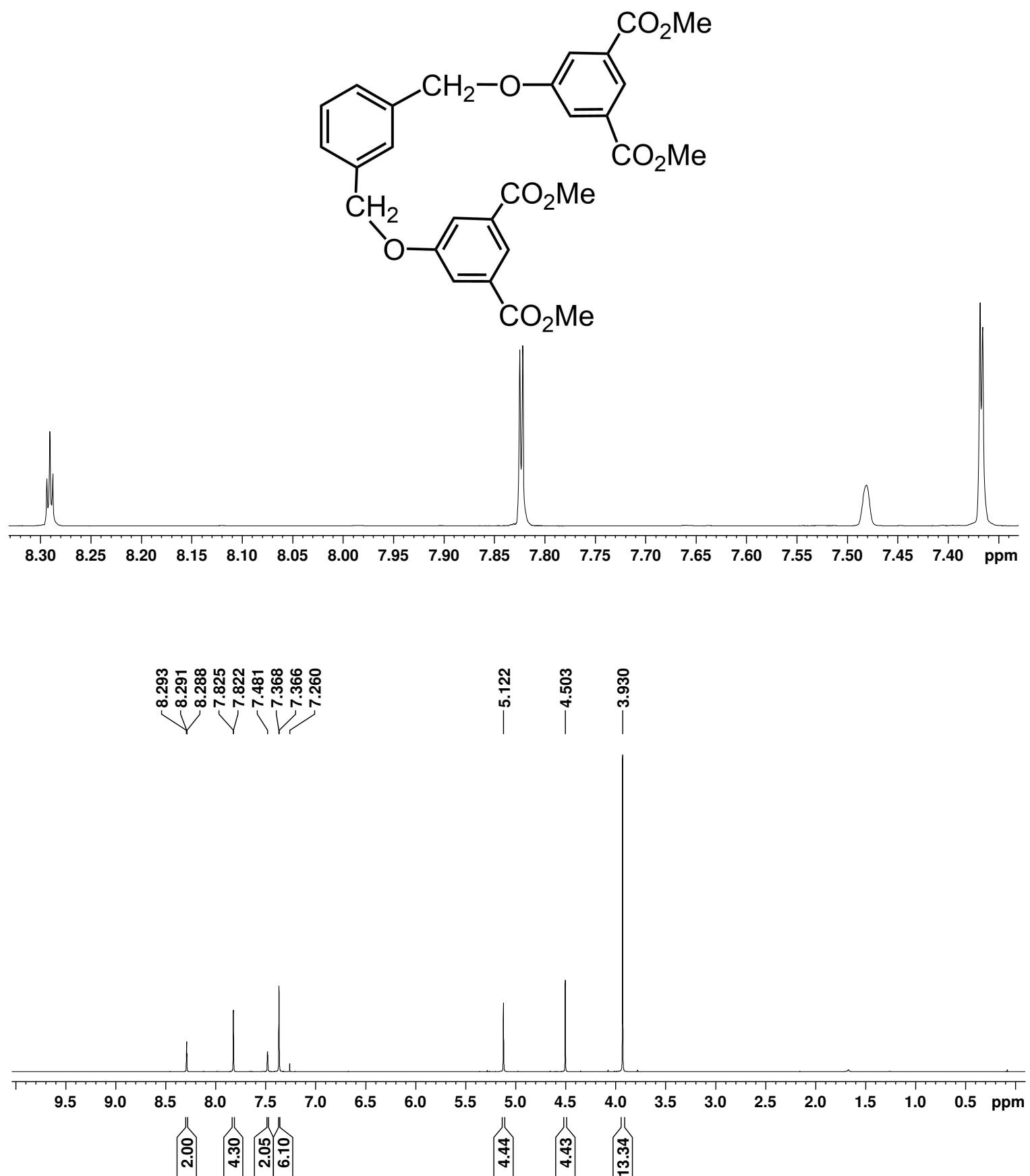


Figure S109. 500 MHz proton NMR spectrum of tetraester **16b** in CDCl_3 .

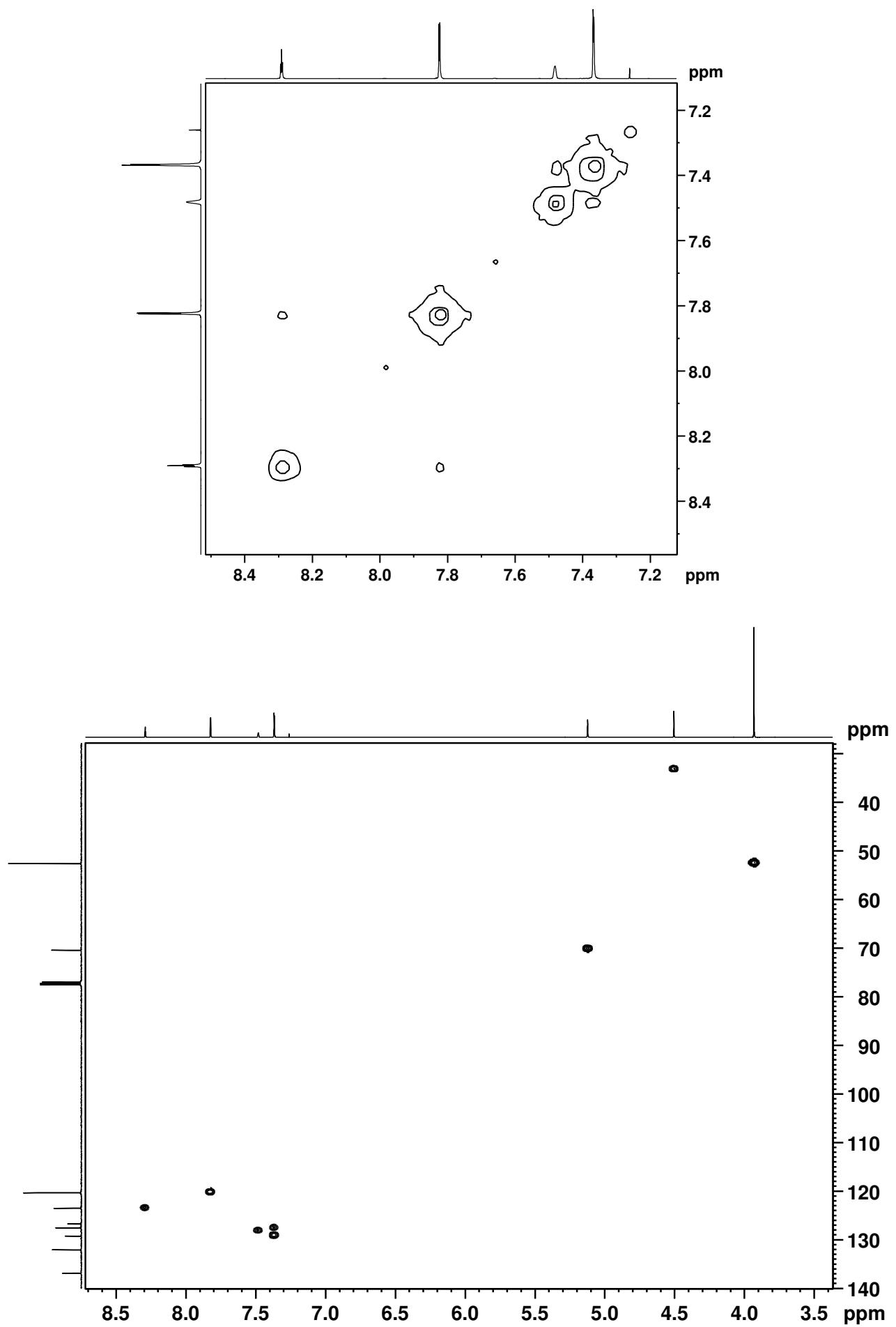


Figure S110. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of **16b** in CDCl_3 .

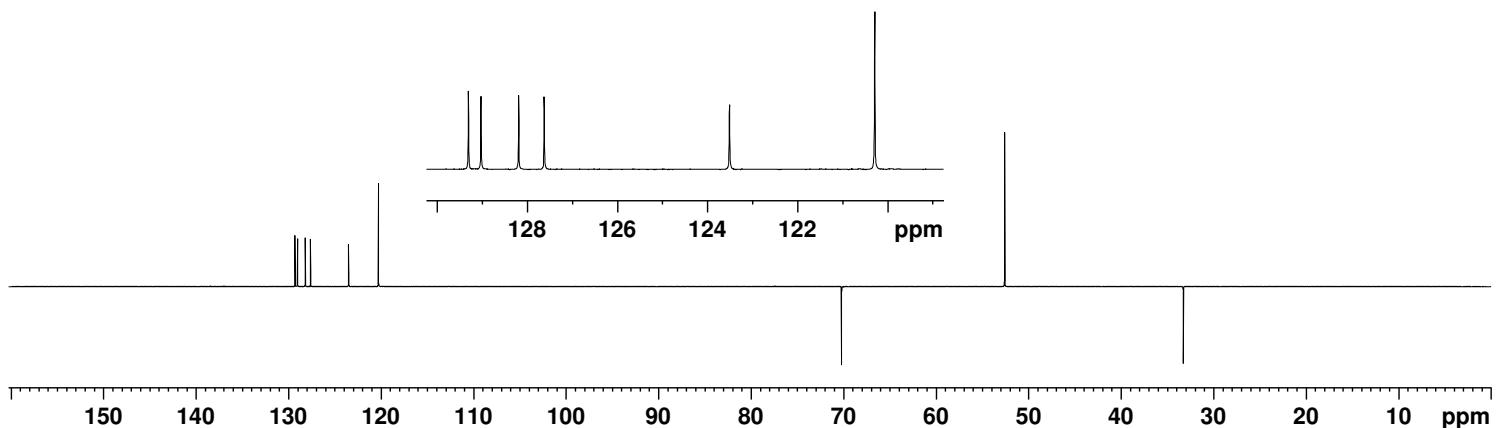


Figure S111. DEPT-135 NMR spectrum of **16b** in CDCl_3 .

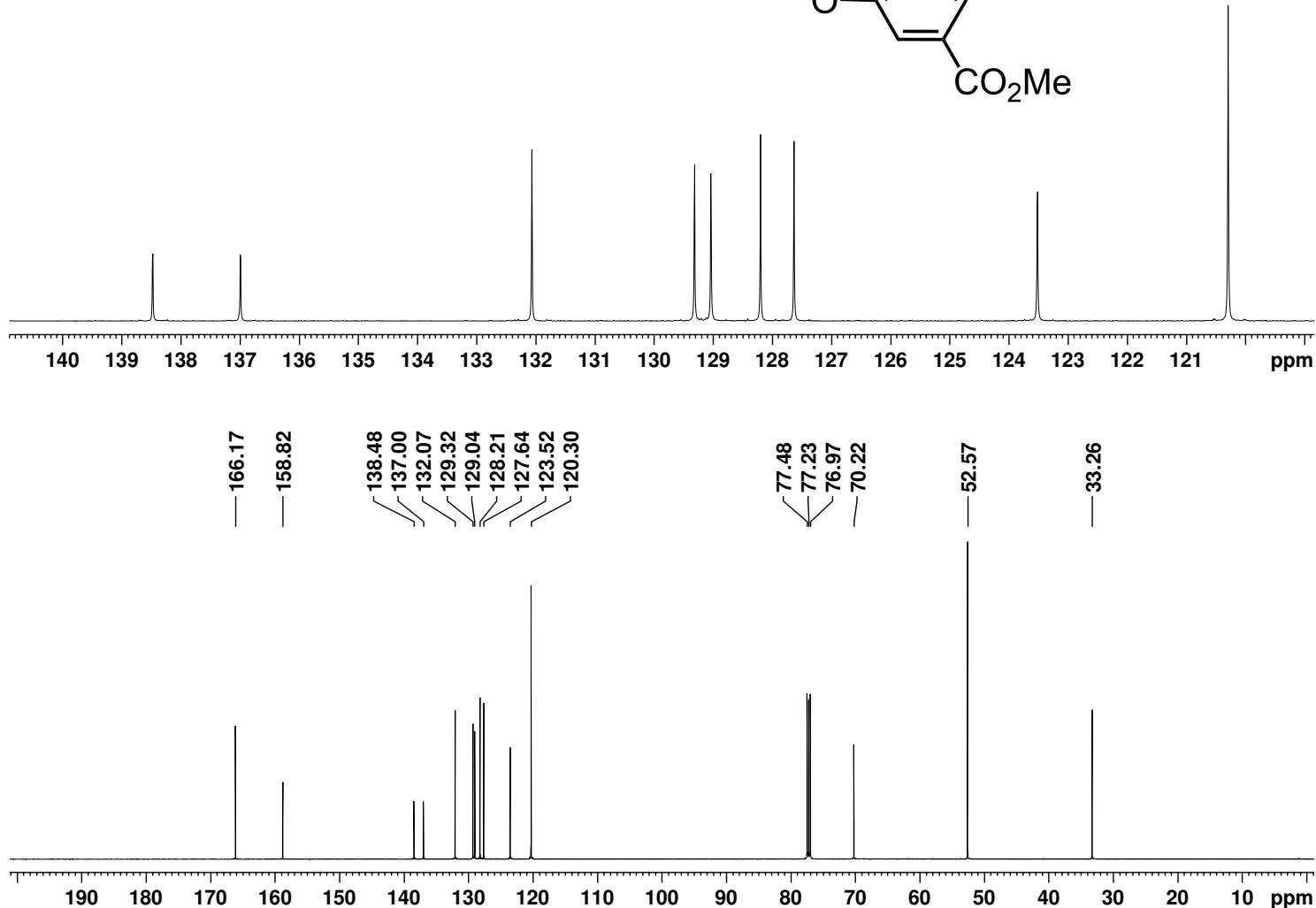
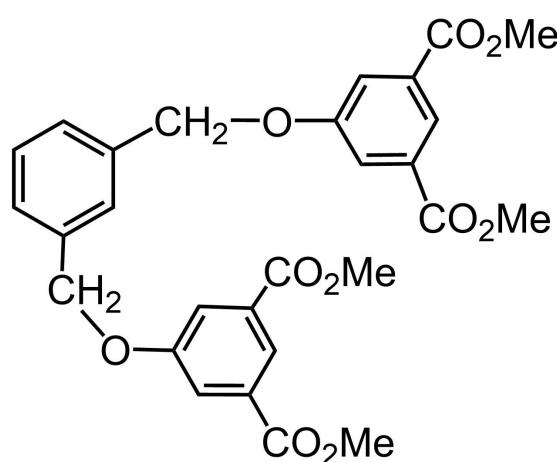


Figure S112. 125 MHz carbon-13 NMR spectrum of **16b** in CDCl_3 .

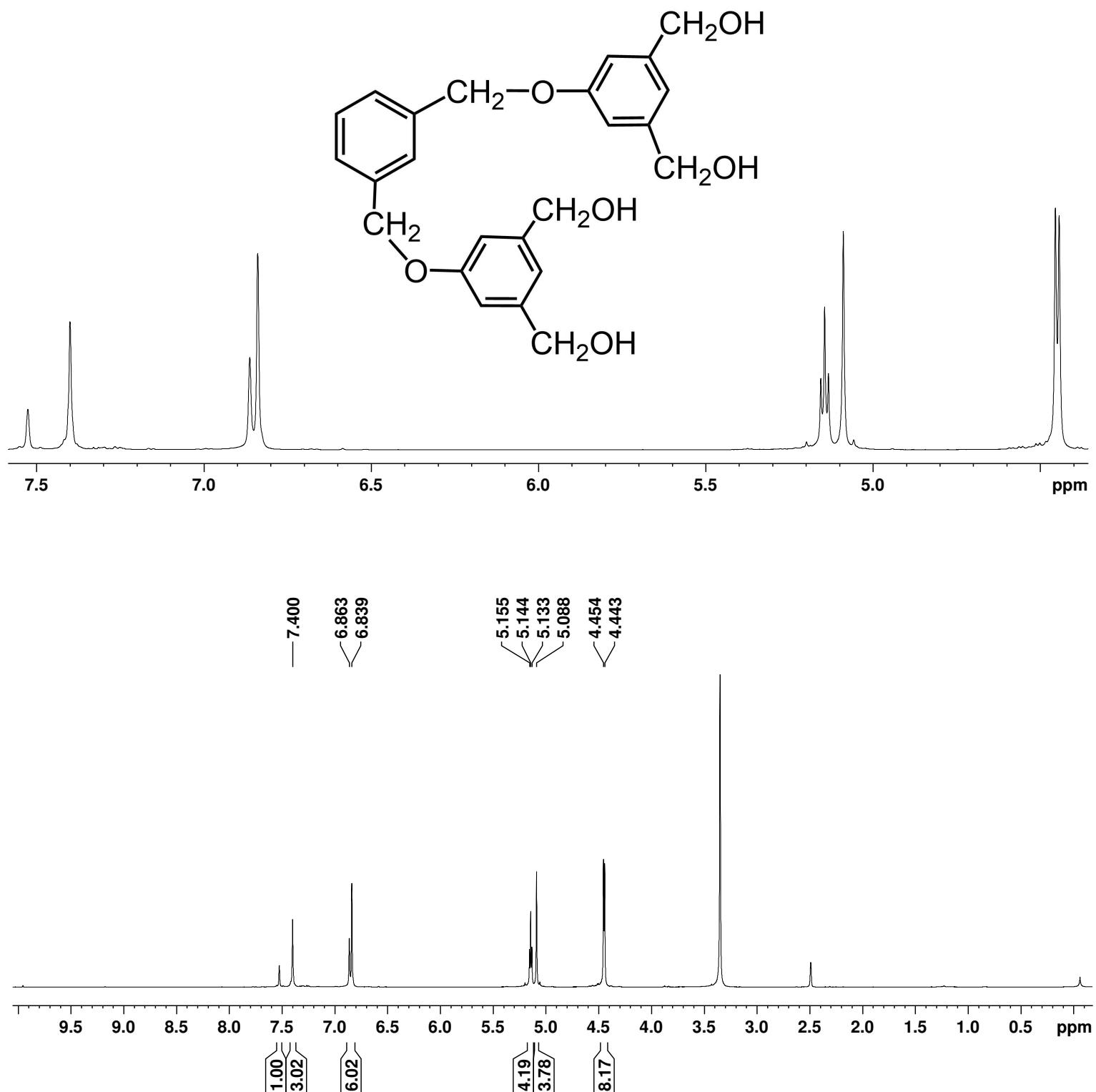


Figure S113. 500 MHz proton NMR spectrum of tetraalcohol **17b** in $\text{DMSO}-d_6$.

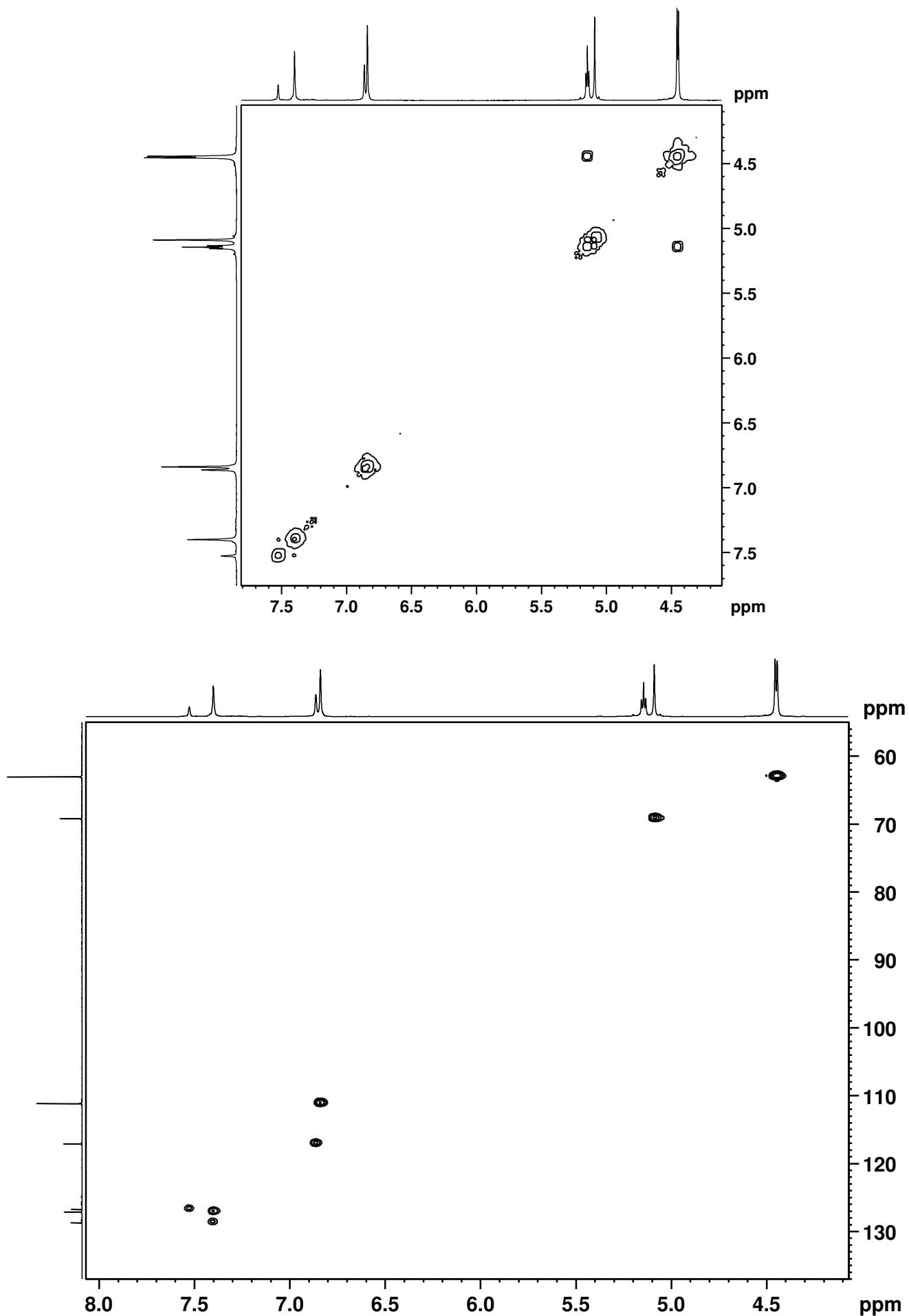


Figure S114. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of **17b** in $\text{DMSO}-d_6$.

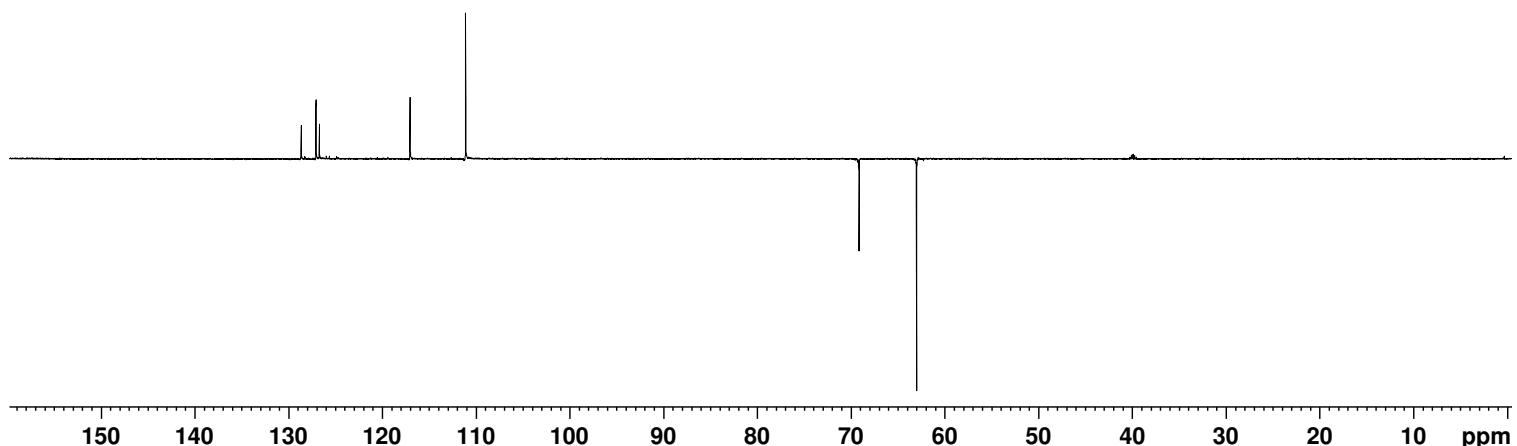


Figure S115. DEPT-135 NMR spectrum of **17b** in $\text{DMSO}-d_6$.

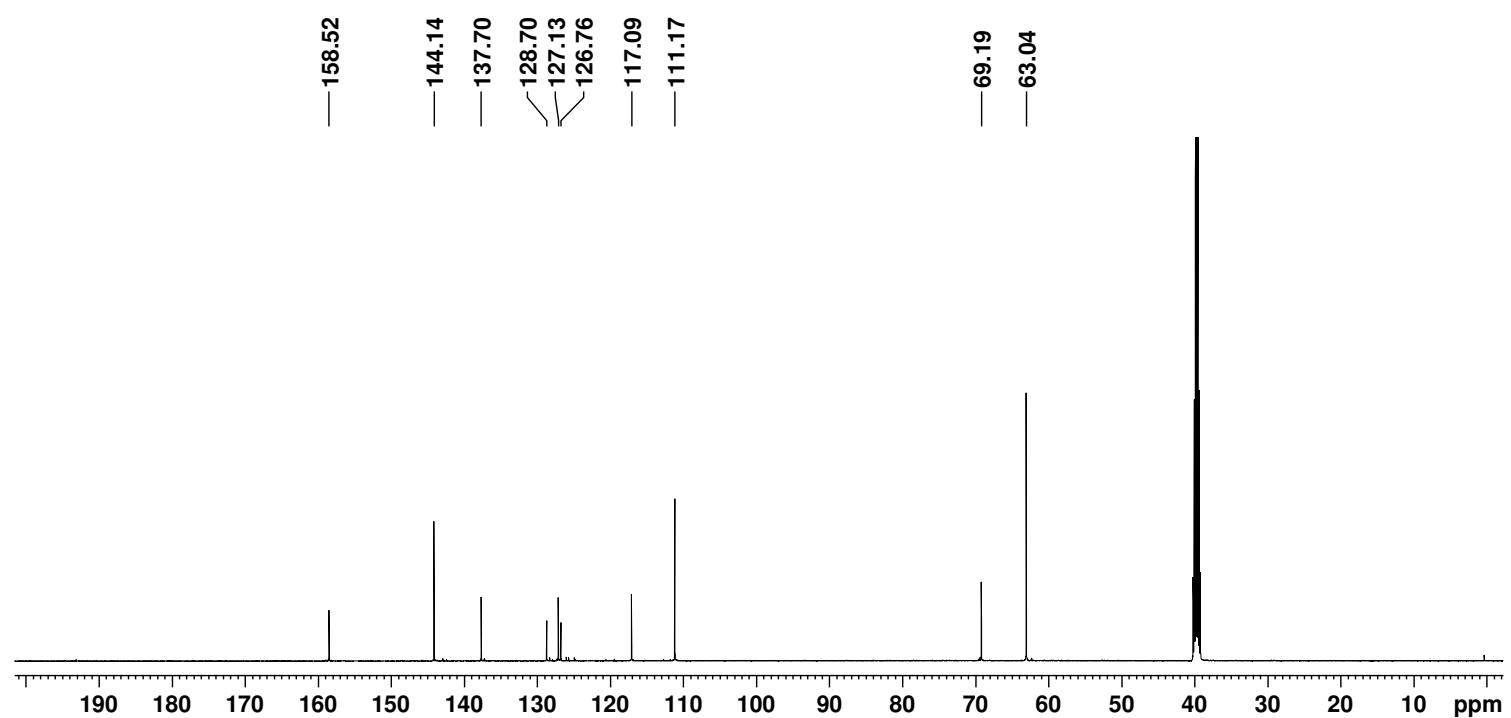
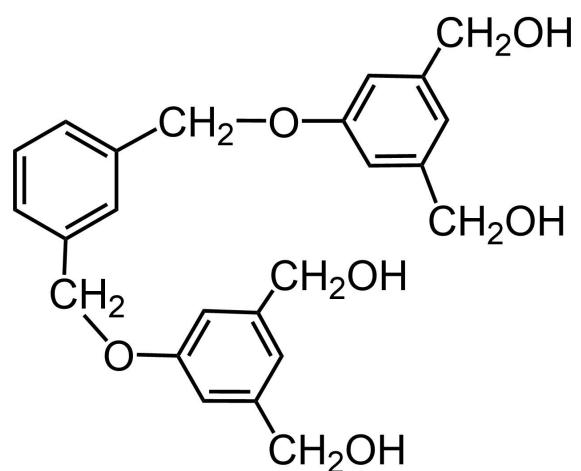


Figure S116. Carbon-13 NMR spectrum of **17b** in $\text{DMSO}-d_6$.

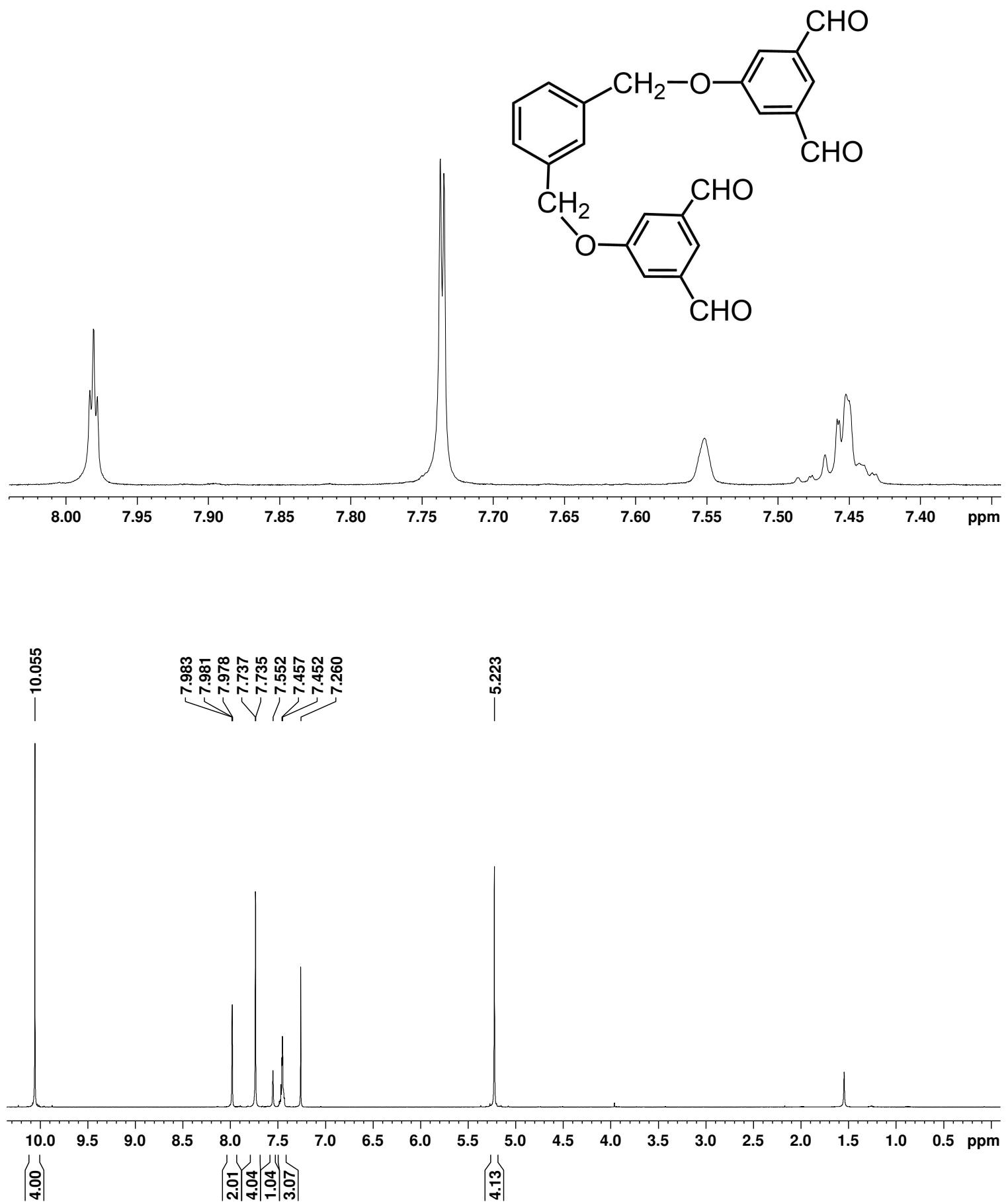


Figure S117. 500 MHz proton NMR spectrum of tetraaldehyde **18b** in CDCl₃.

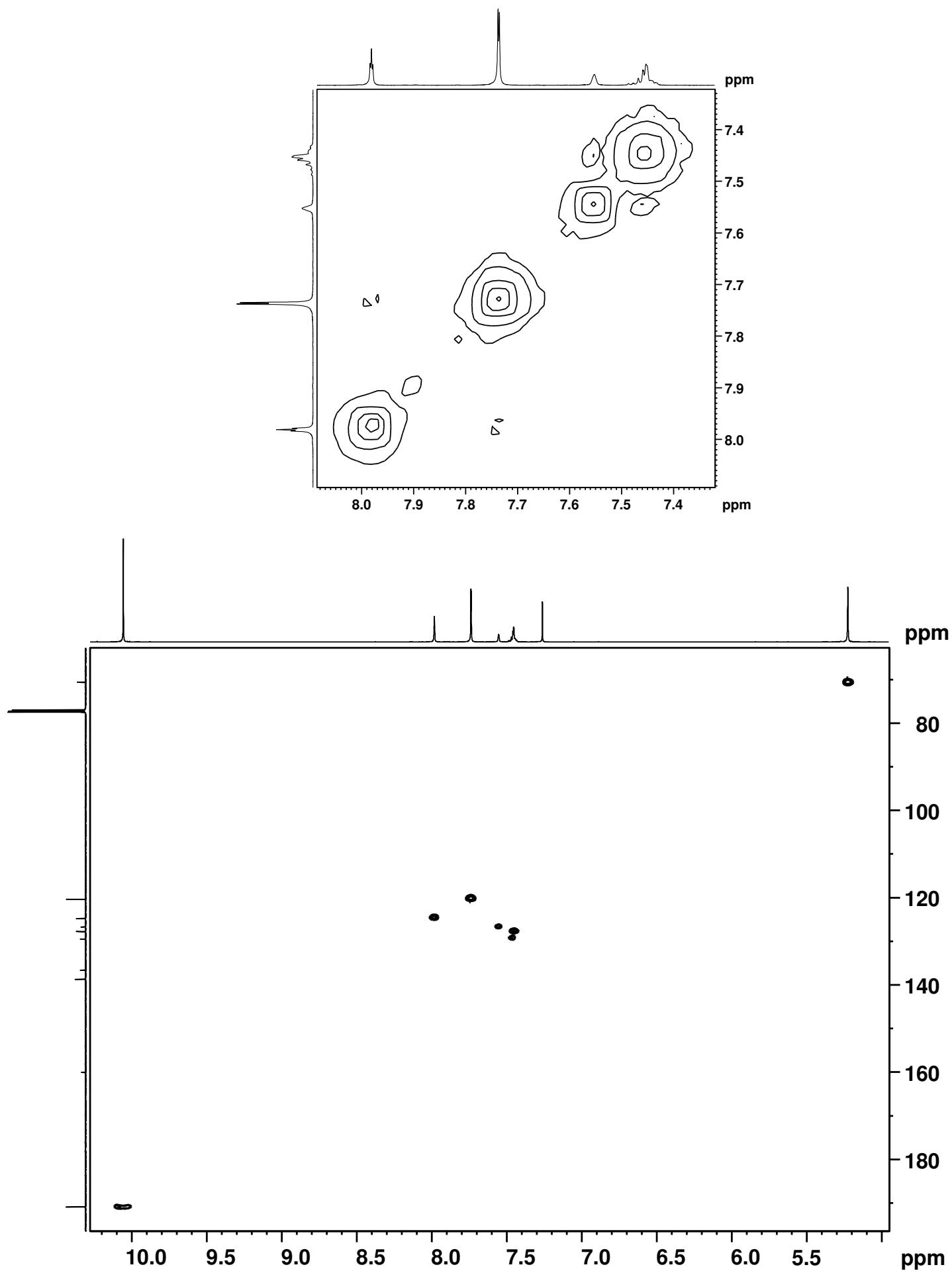


Figure S118. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of **18b** in CDCl_3 .

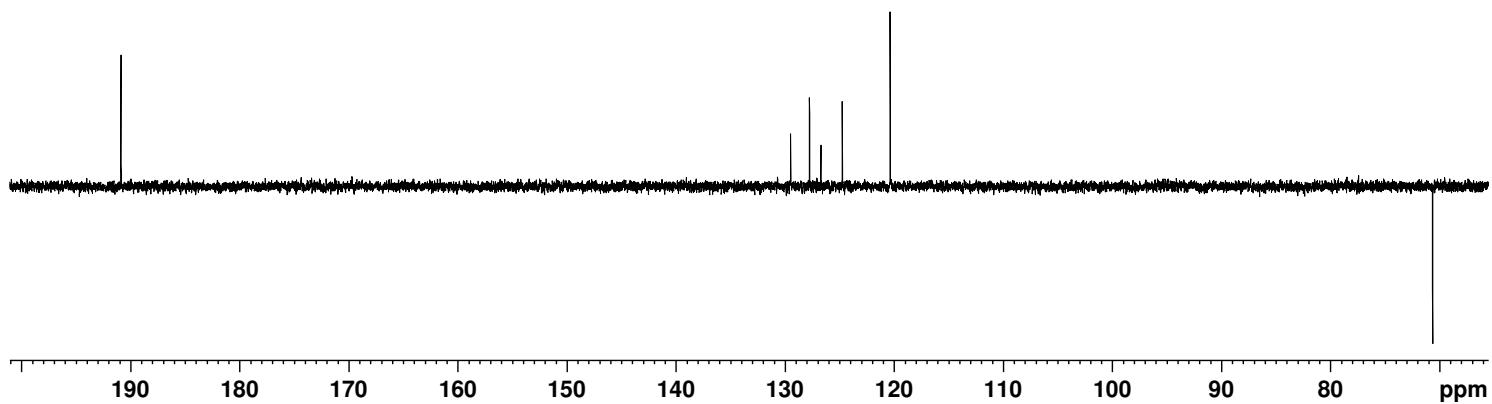


Figure S119. DEPT-135 NMR spectrum of **18b** in CDCl₃.

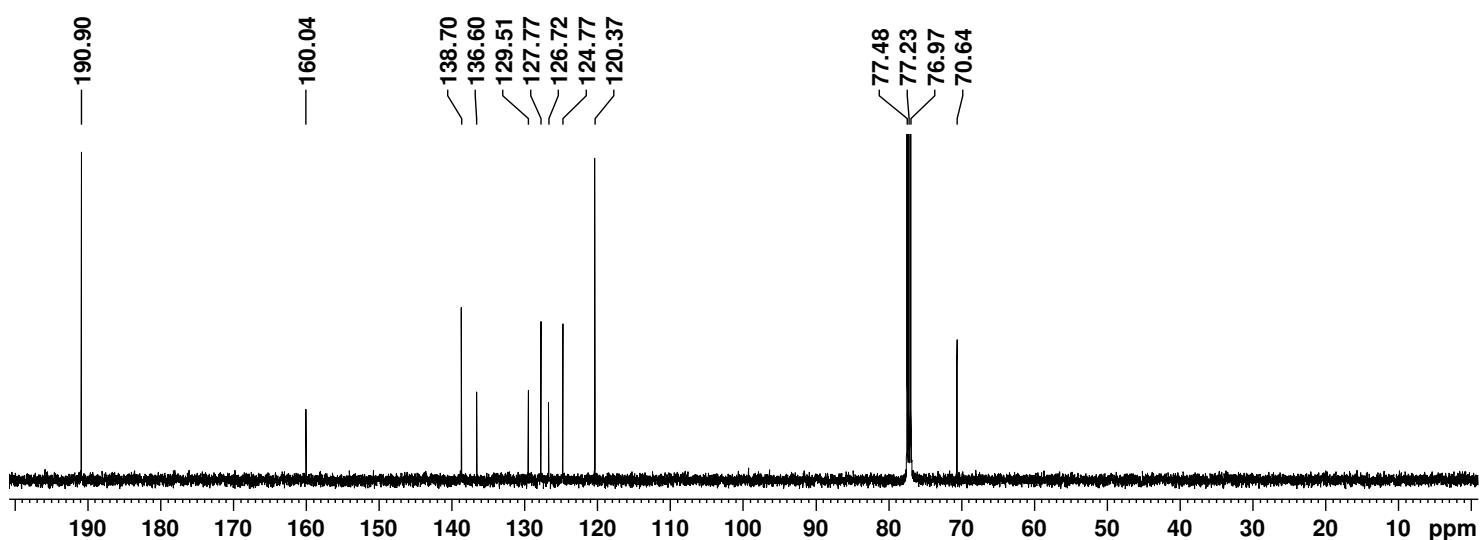
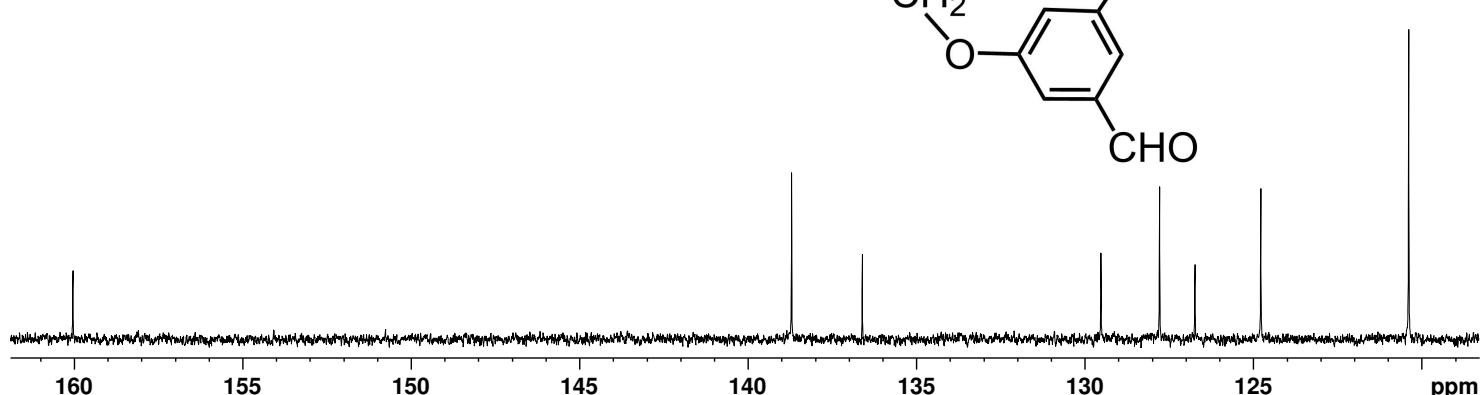
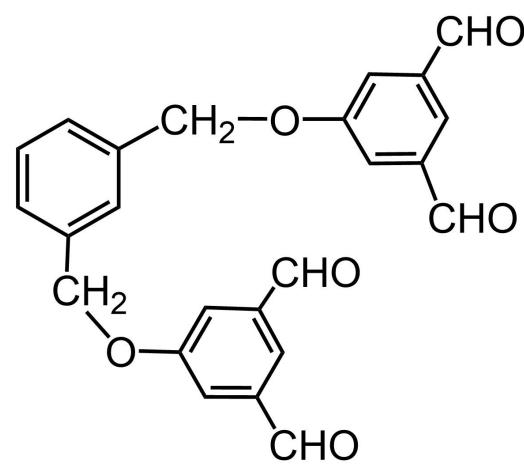


Figure S120. 125 MHz carbon-13 NMR spectrum of **18b** in CDCl₃.

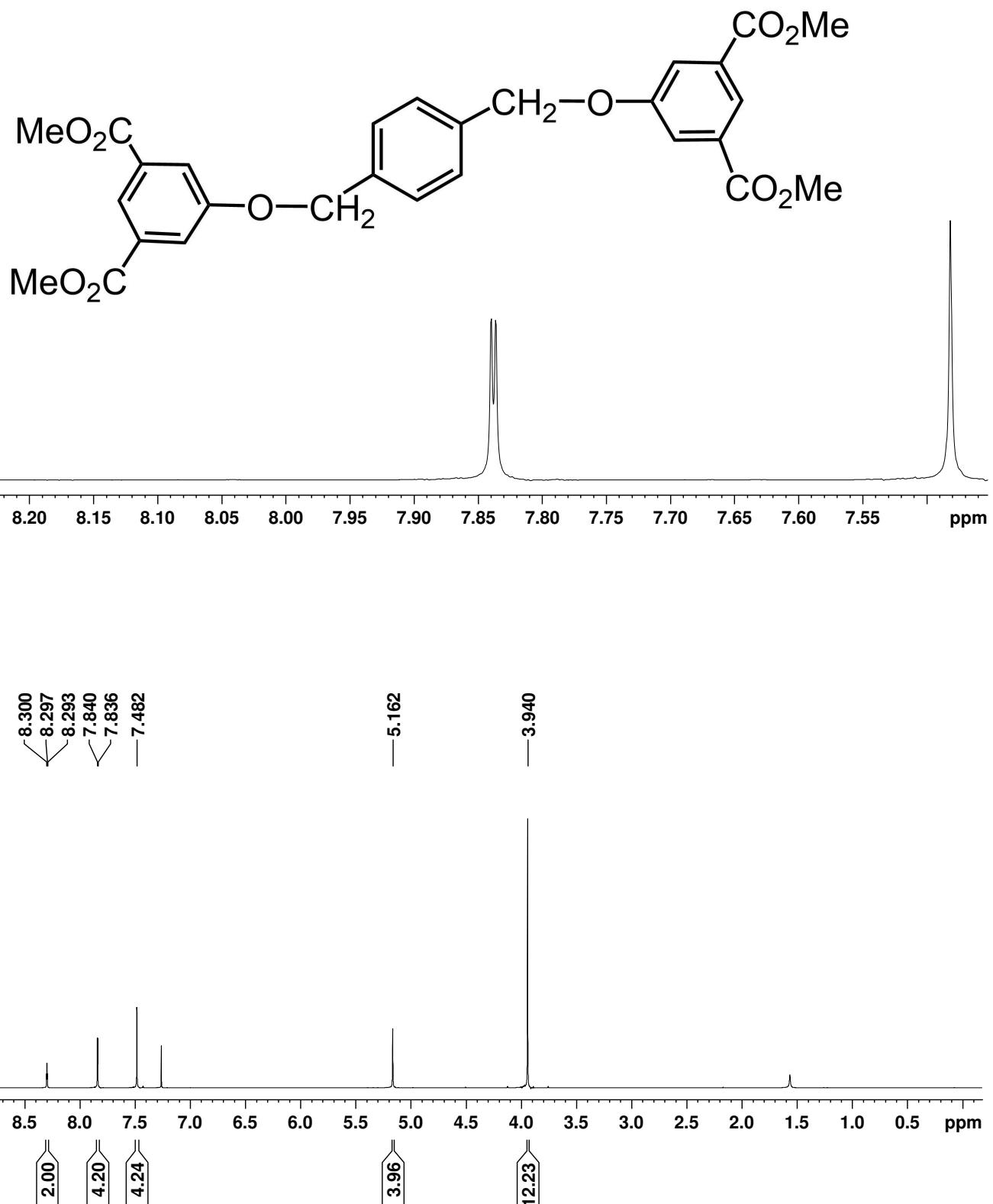


Figure S121. 500 MHz proton NMR spectrum of tetraester **16c** in CDCl₃.

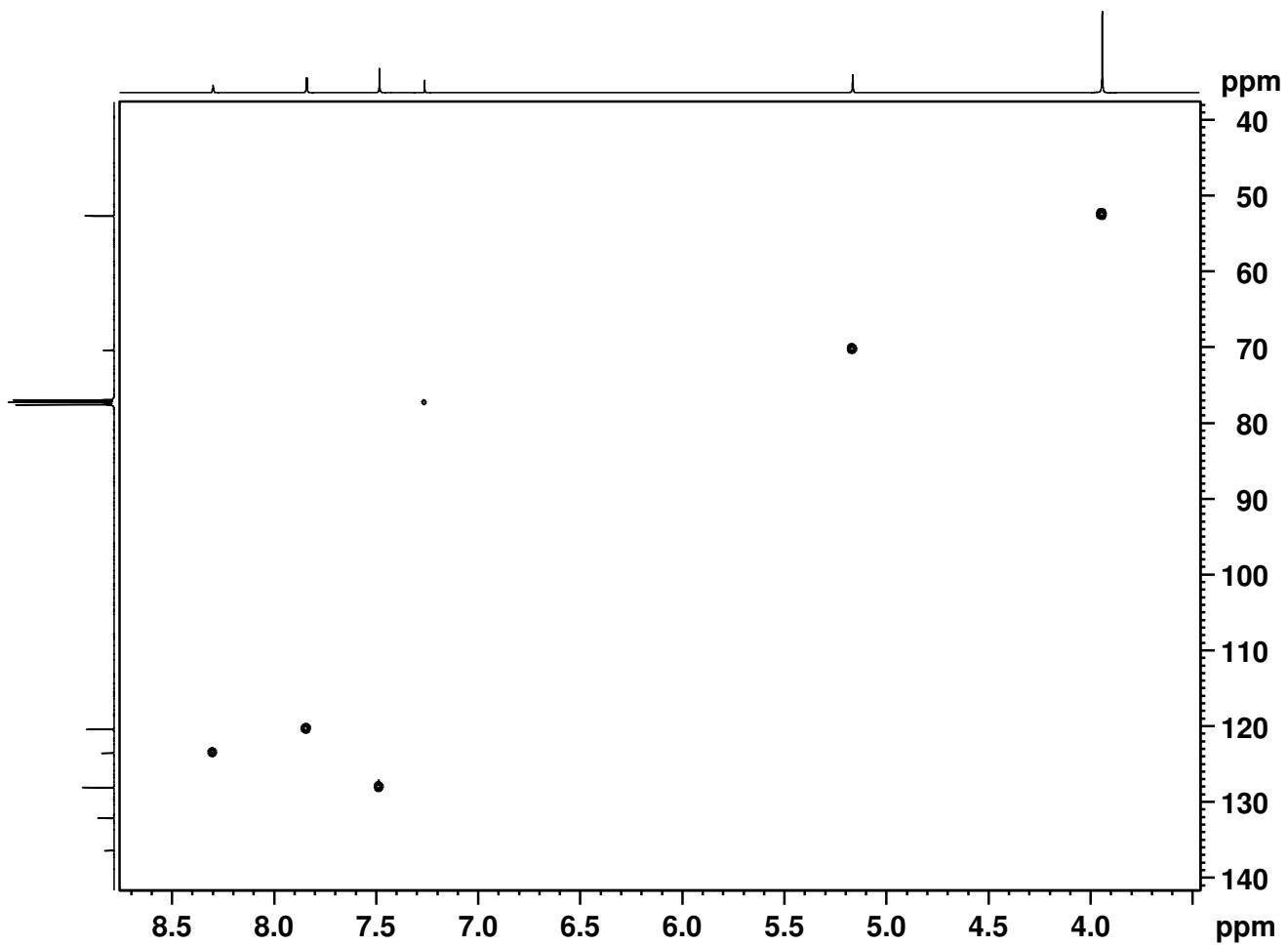
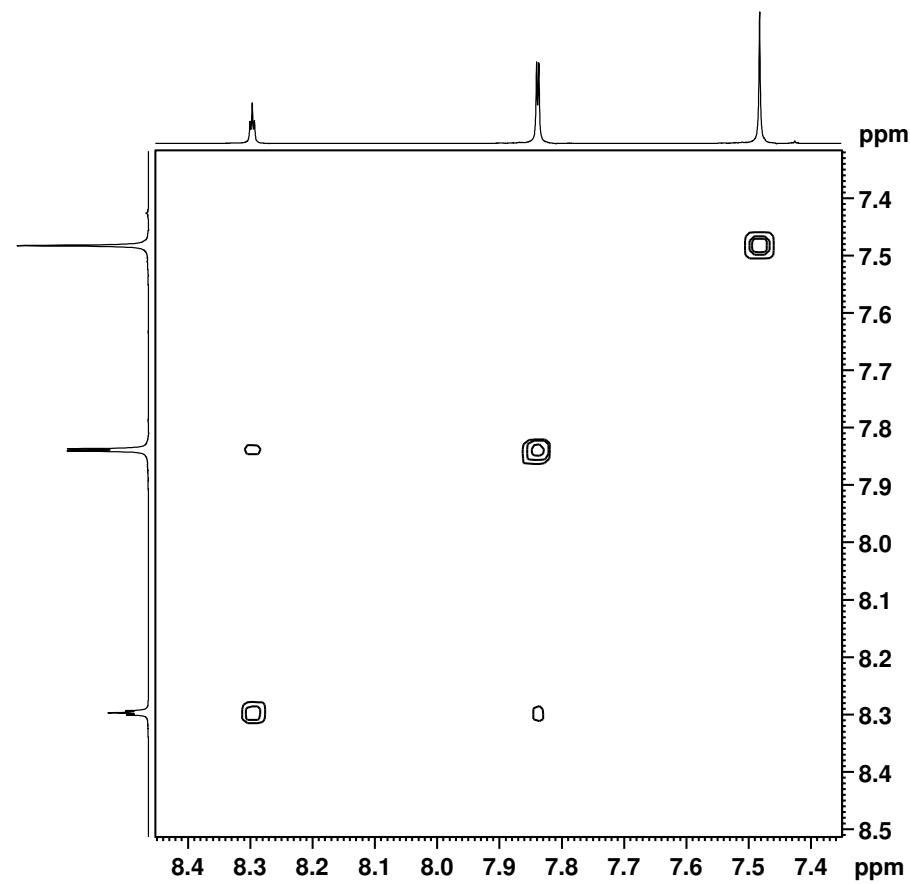


Figure S122. ¹H-¹H COSY (top) and HSQC (bottom) NMR spectra of **16c** in CDCl₃.

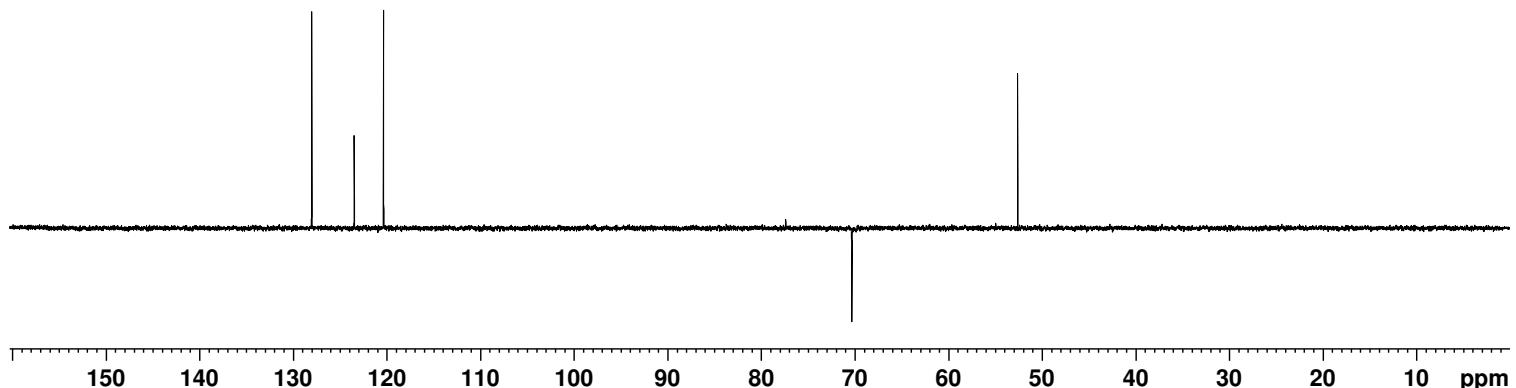


Figure S123. DEPT-135 NMR spectrum of **16c** in CDCl_3 .

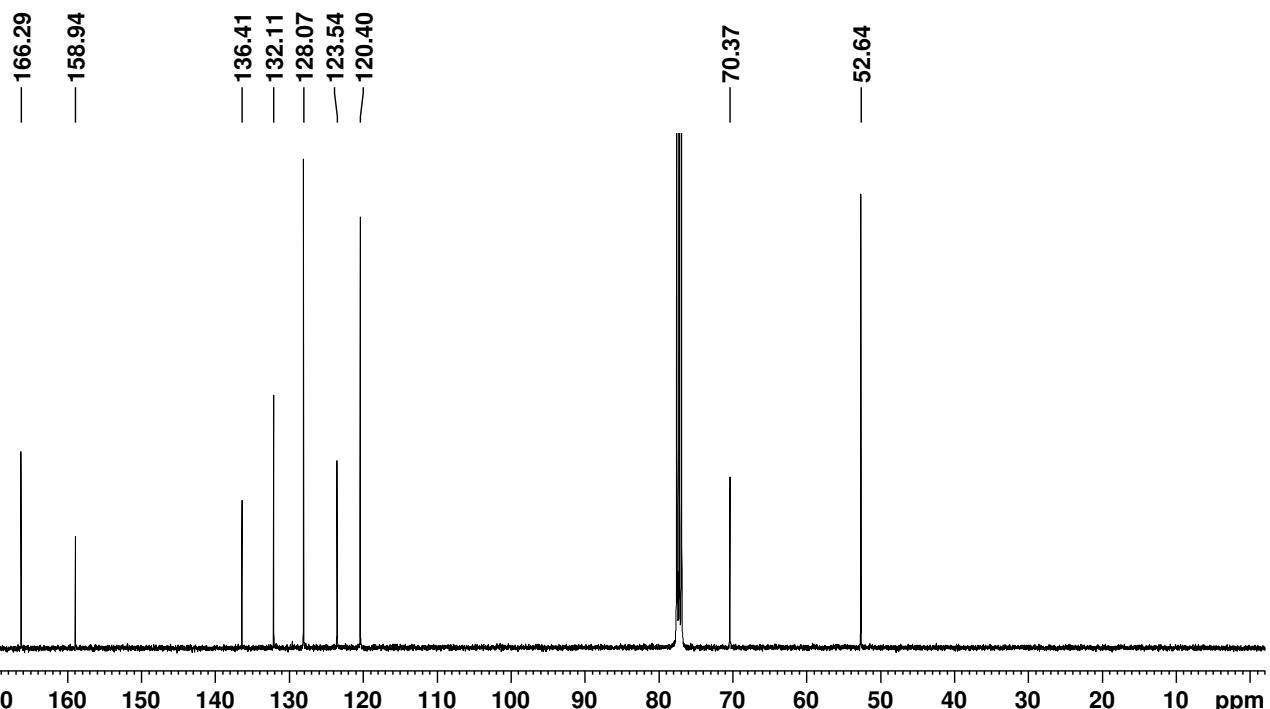
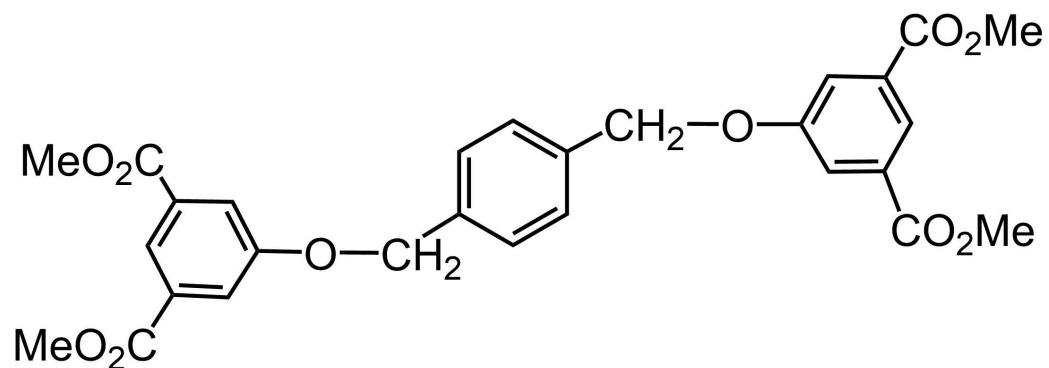


Figure S124. 125 MHz carbon-13 NMR spectrum of dimer **16c** in CDCl_3 .

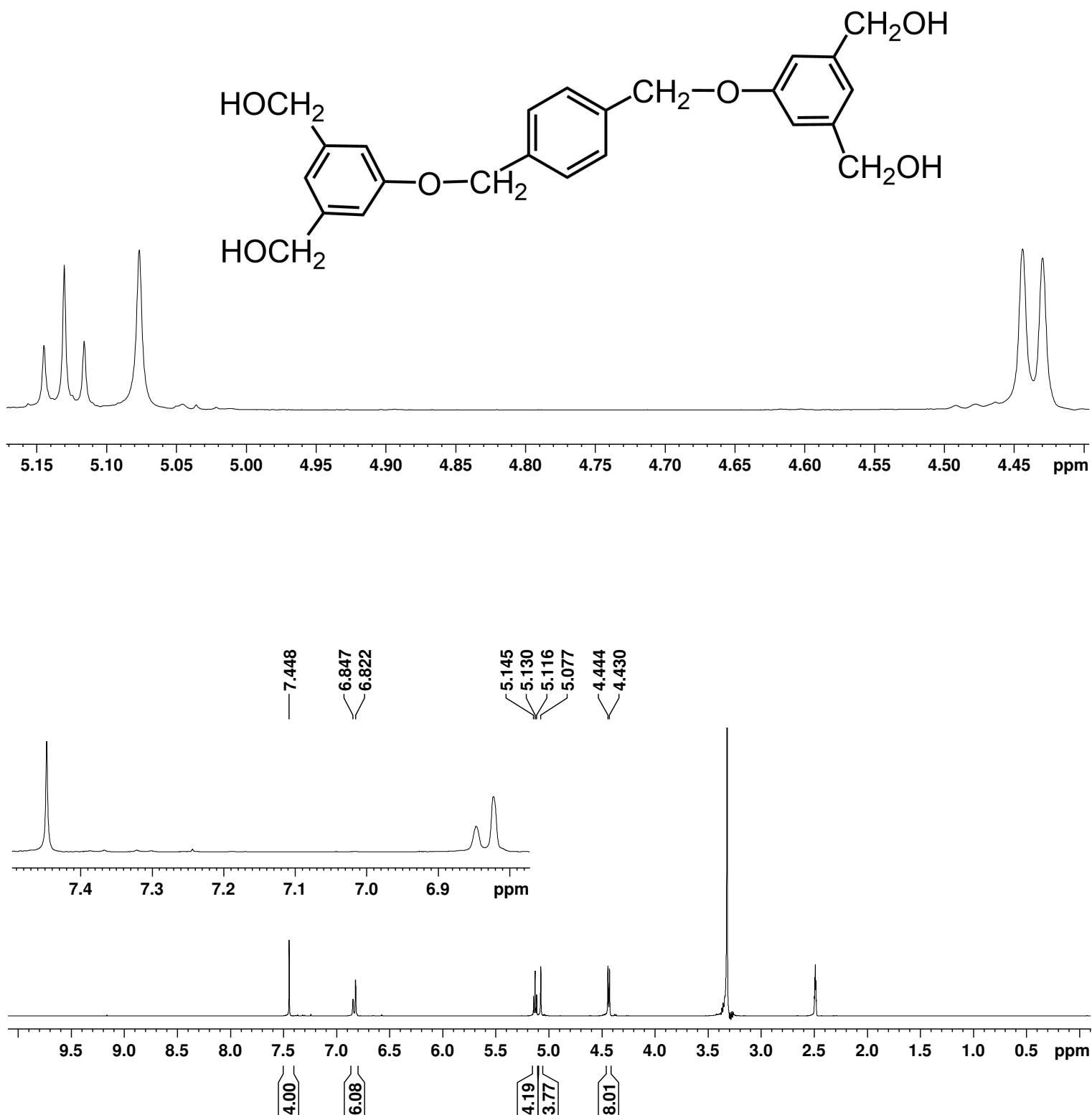


Figure S125. 400 MHz proton NMR spectrum of tetra-alcohol 17c in DMSO-*d*₆.

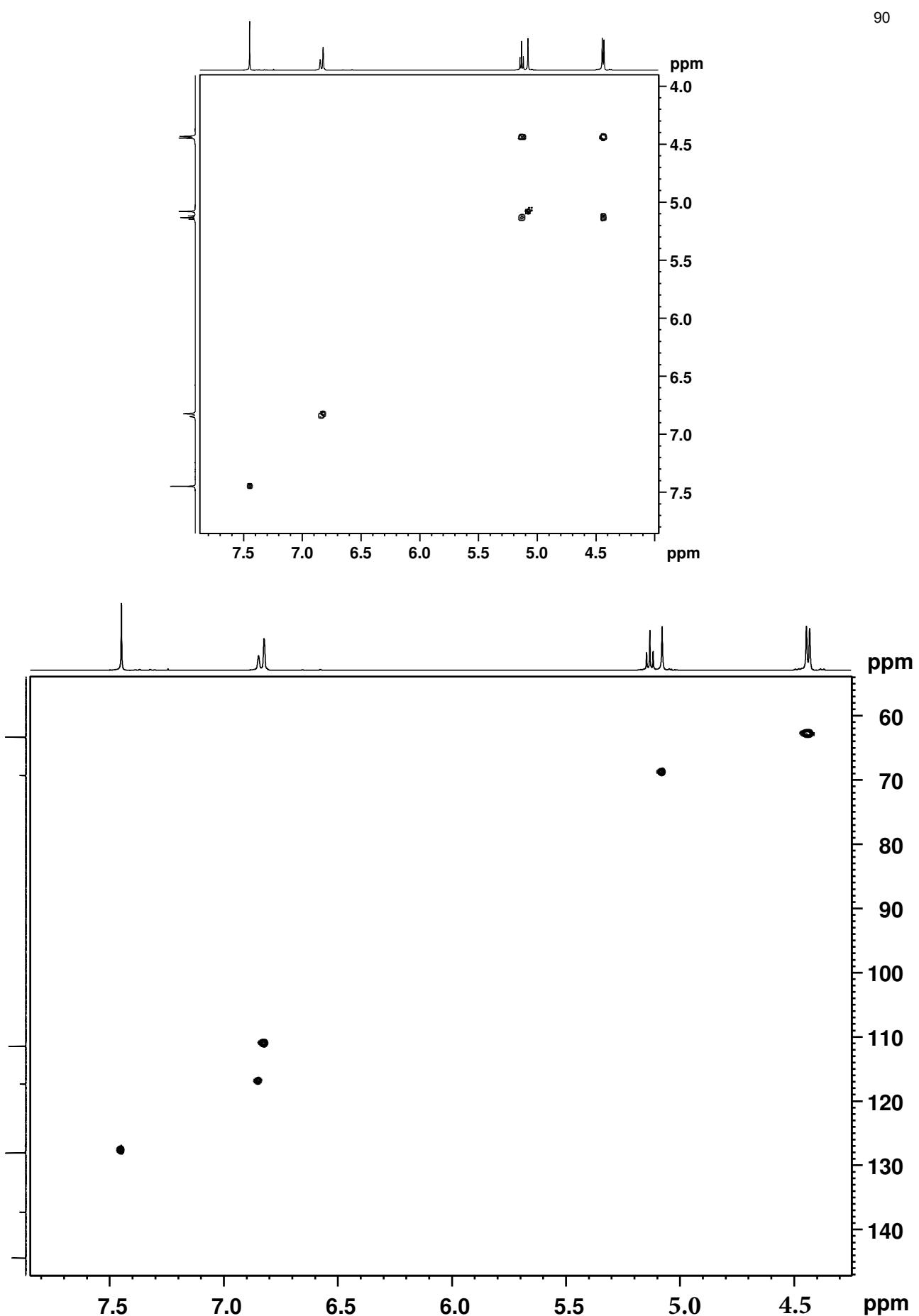


Figure S126. ^1H - ^1H COSY (top) and HSQC (bottom) NMR spectra of tetra-alcohol **17c** in $\text{DMSO}-d_6$.

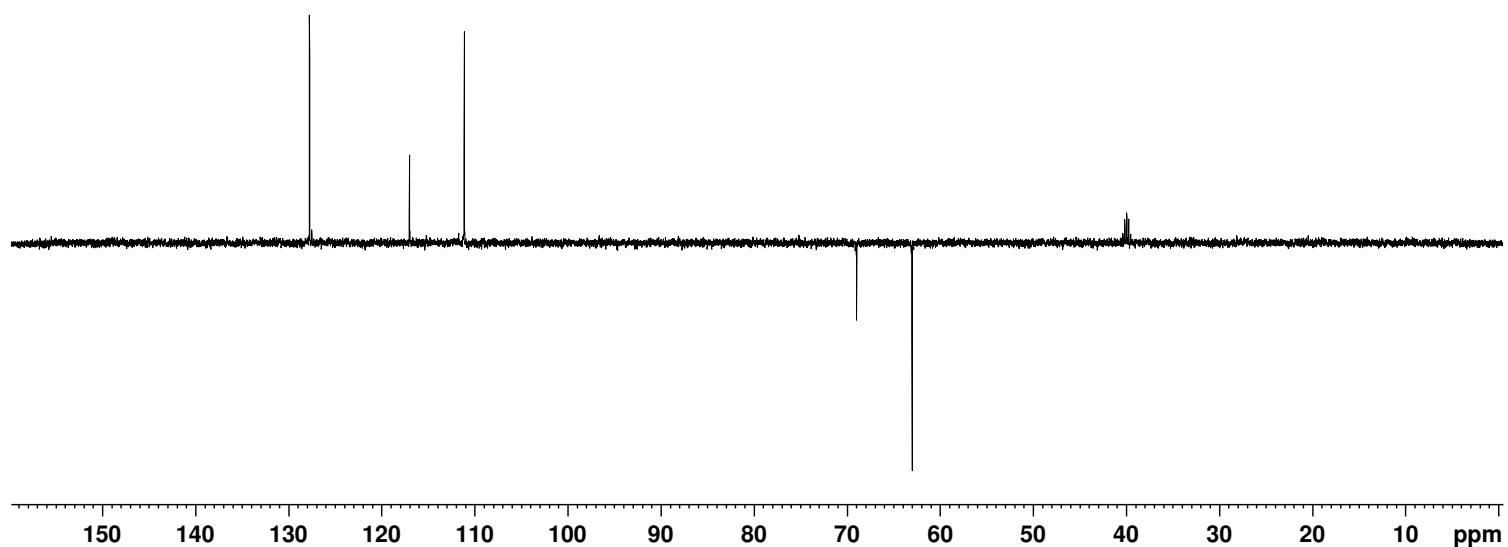


Figure S127. DEPT-135 NMR spectrum of tetra-alcohol **17c** in DMSO-*d*₆.

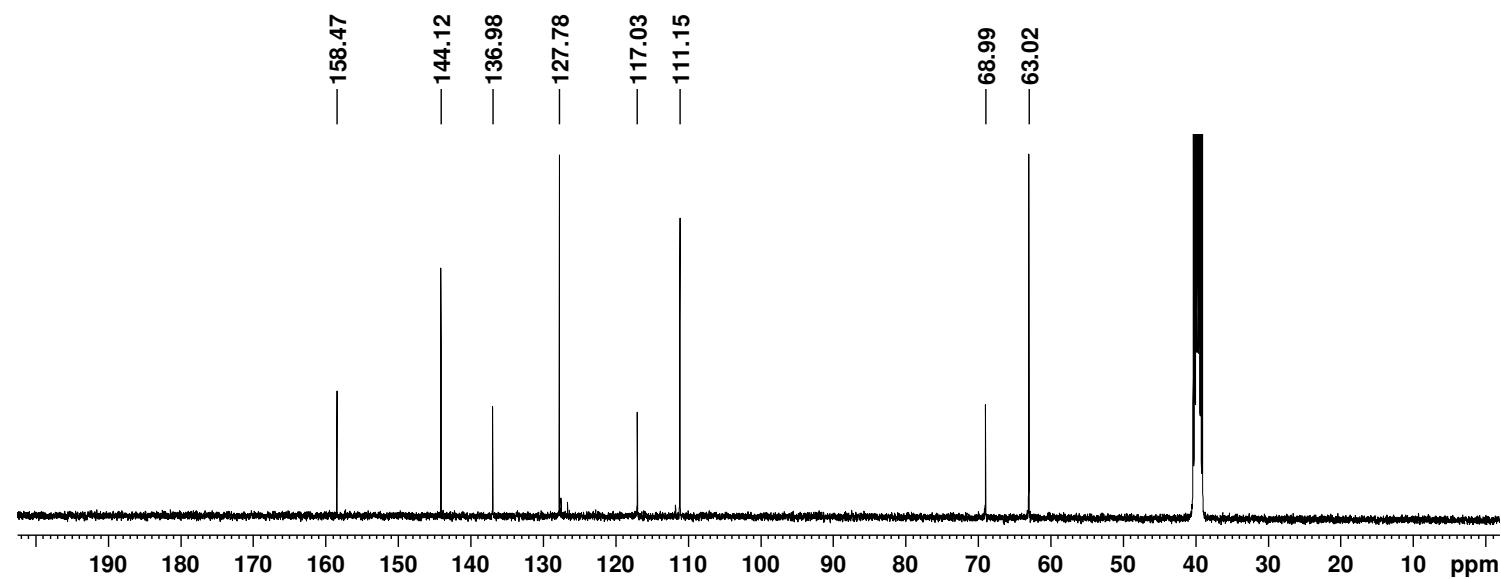
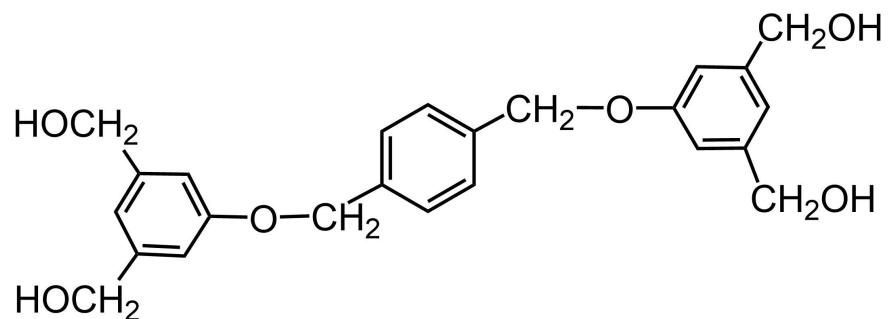


Figure S128. 100 MHz carbon-13 NMR spectrum of tetra-alcohol **17c** in DMSO-*d*₆.

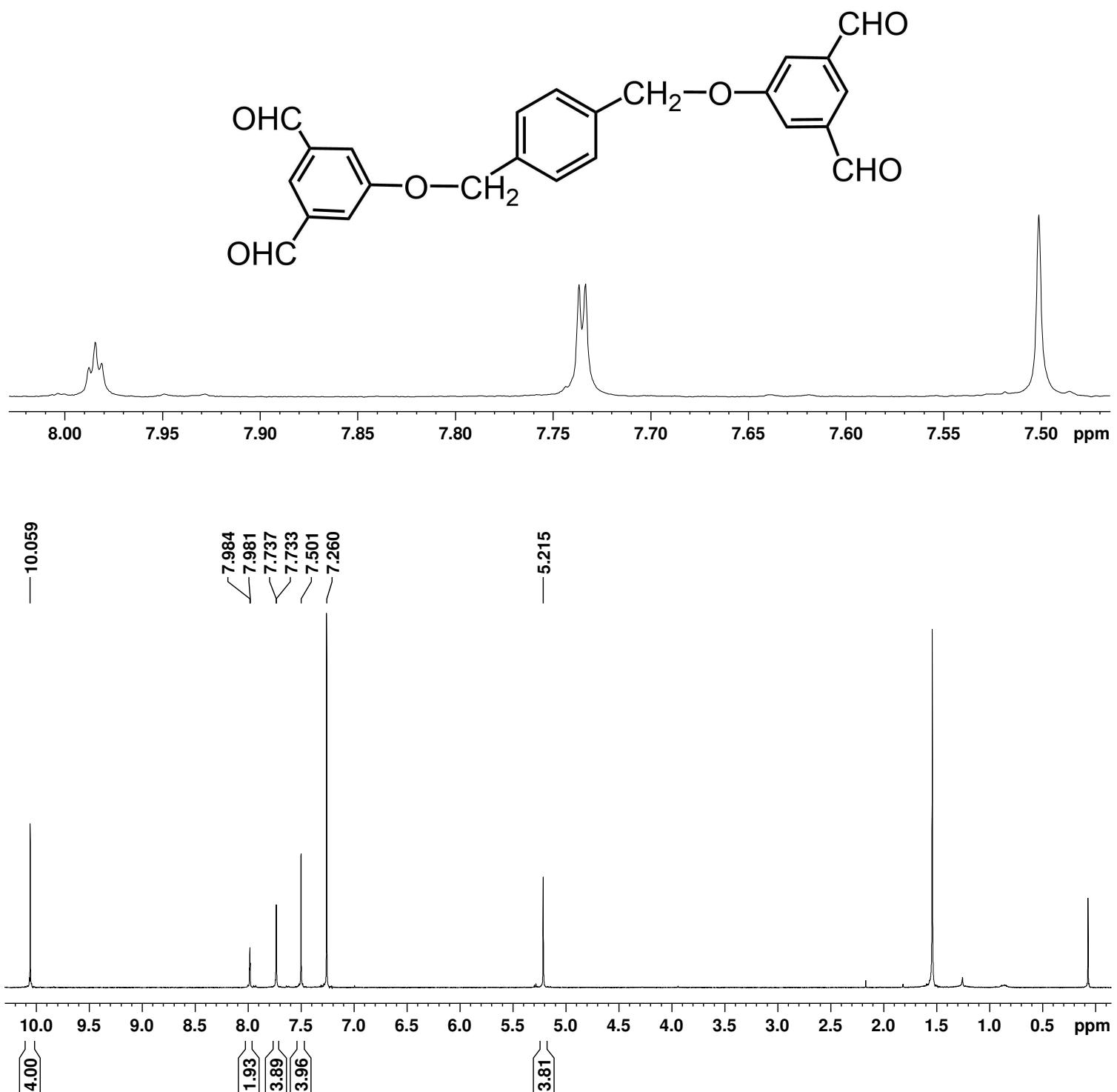


Figure S129. Proton NMR spectrum of *p*-phenylene-linked tetraaldehyde in CDCl₃.

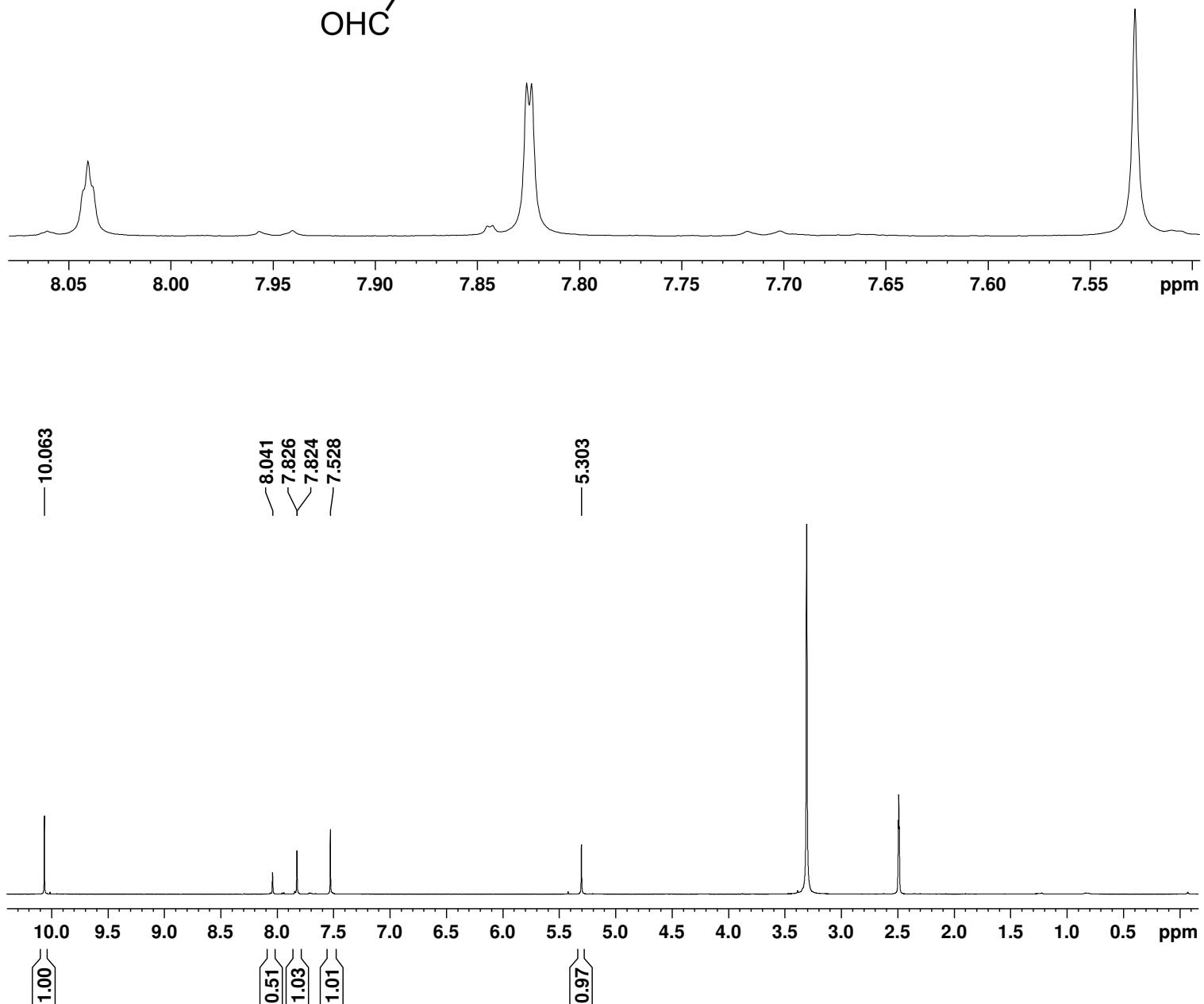
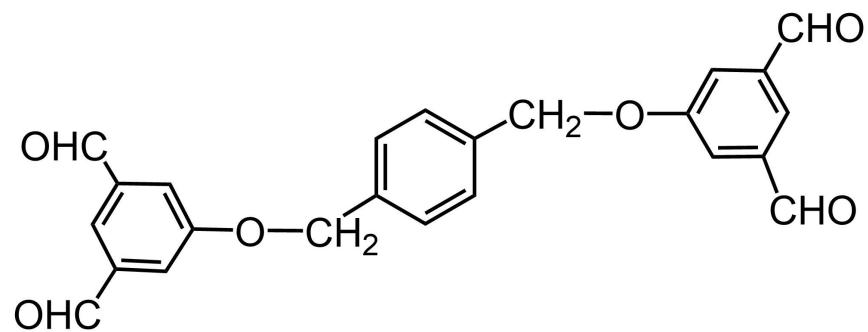


Figure S130. Proton NMR spectrum of *p*-phenylene-linked tetraaldehyde **18c** in DMSO-*d*₆.

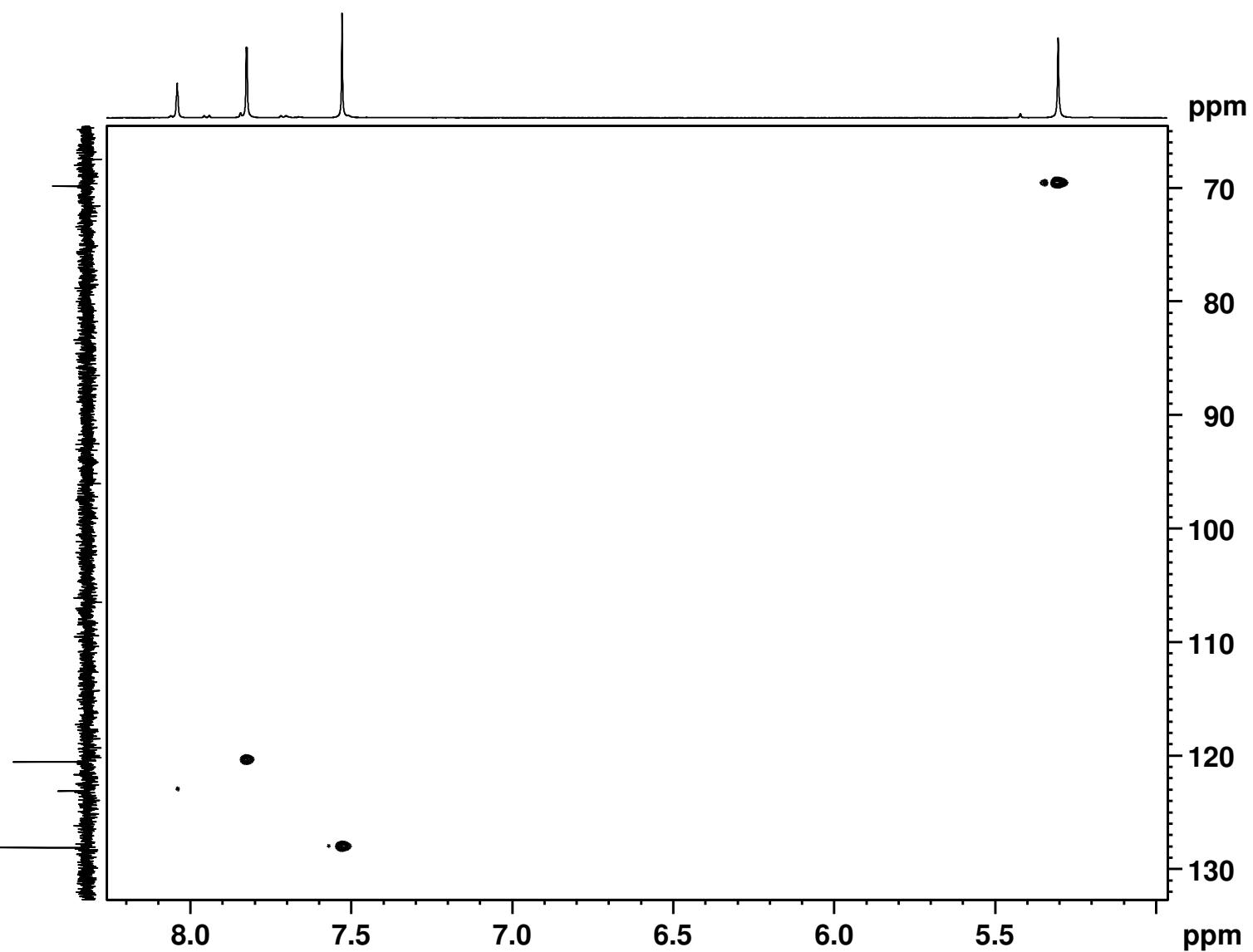


Figure S131. ^1H - ^1H COSY NMR spectrum of *p*-phenylene-linked tetraaldehyde **18c** in $\text{DMSO}-d_6$.

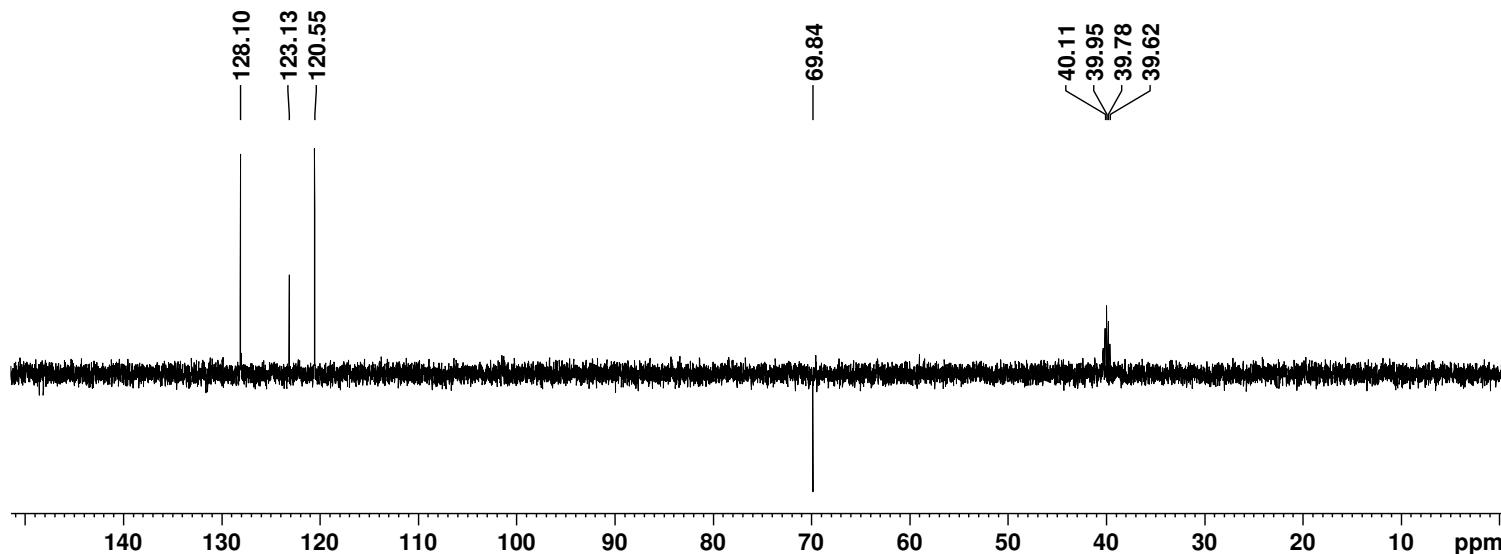


Figure S132. DEPT-135 NMR spectrum of *p*-phenylene-linked tetraaldehyde **18c** in $\text{DMSO}-d_6$.

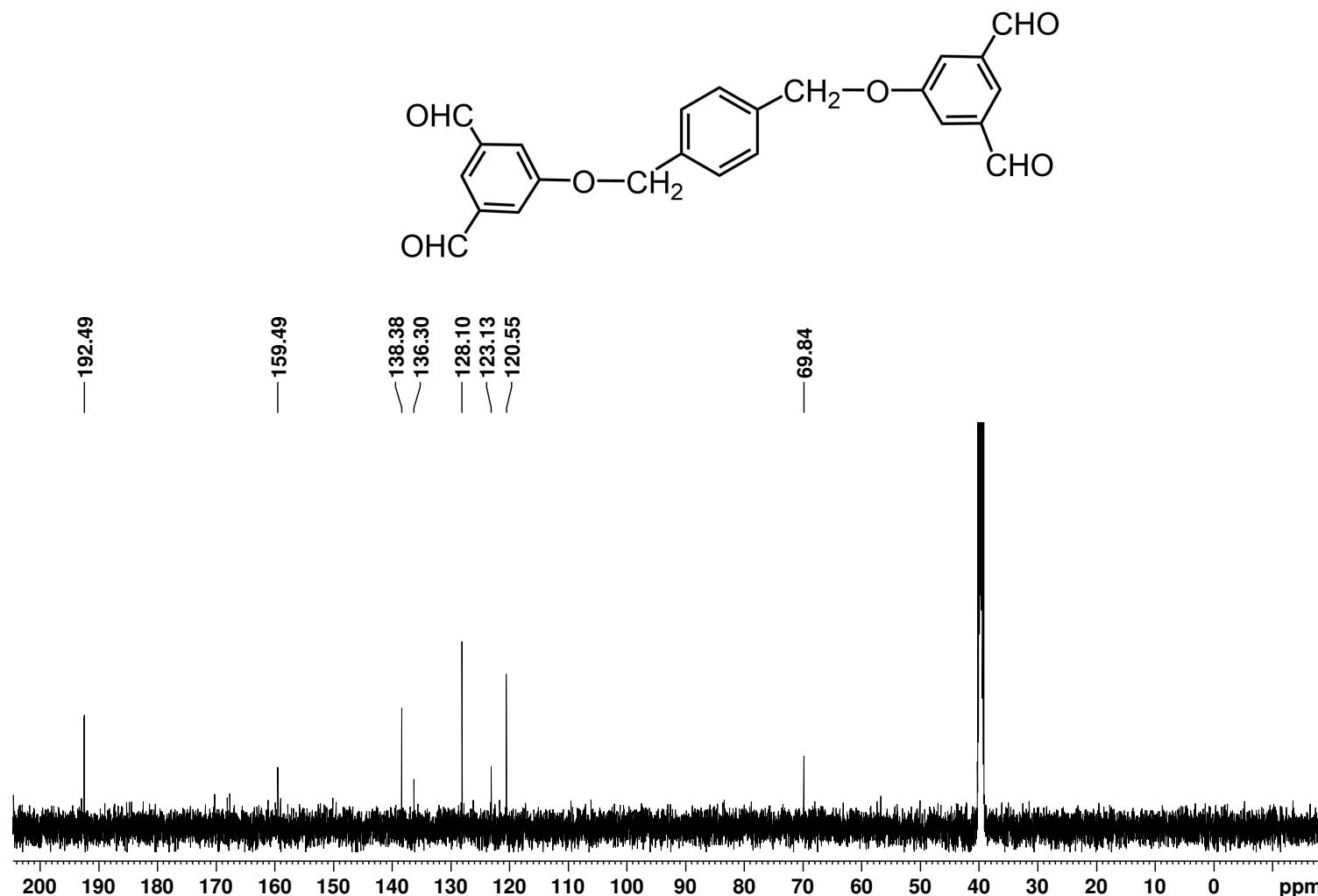


Figure S133. 100 MHz carbon-13 NMR spectrum of *p*-phenylene-linked tetraaldehyde **18c** in $\text{DMSO}-d_6$.

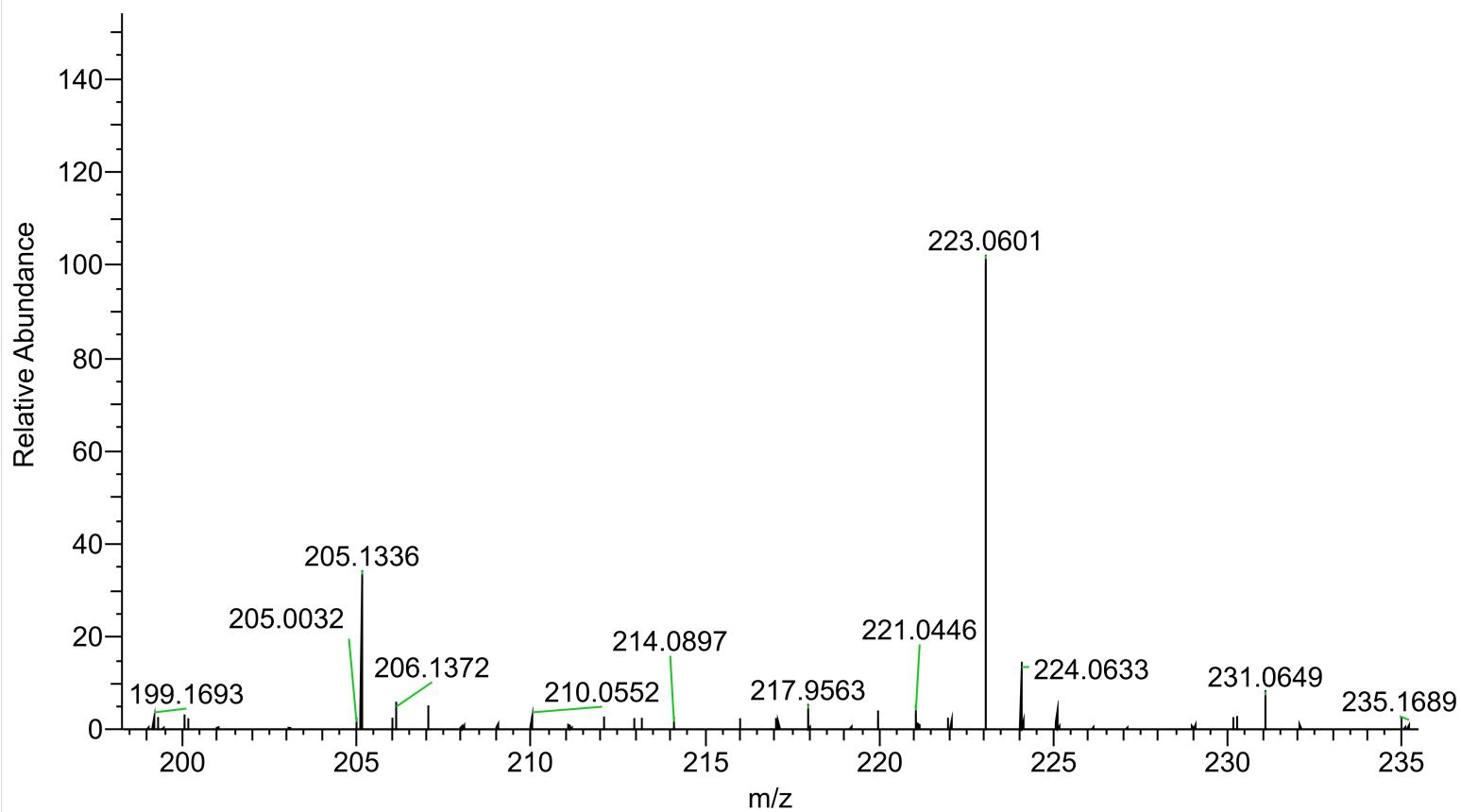


Figure S134. High resolution time-of-flight electrospray ionization mass spectrum of dialdehyde **8c**.

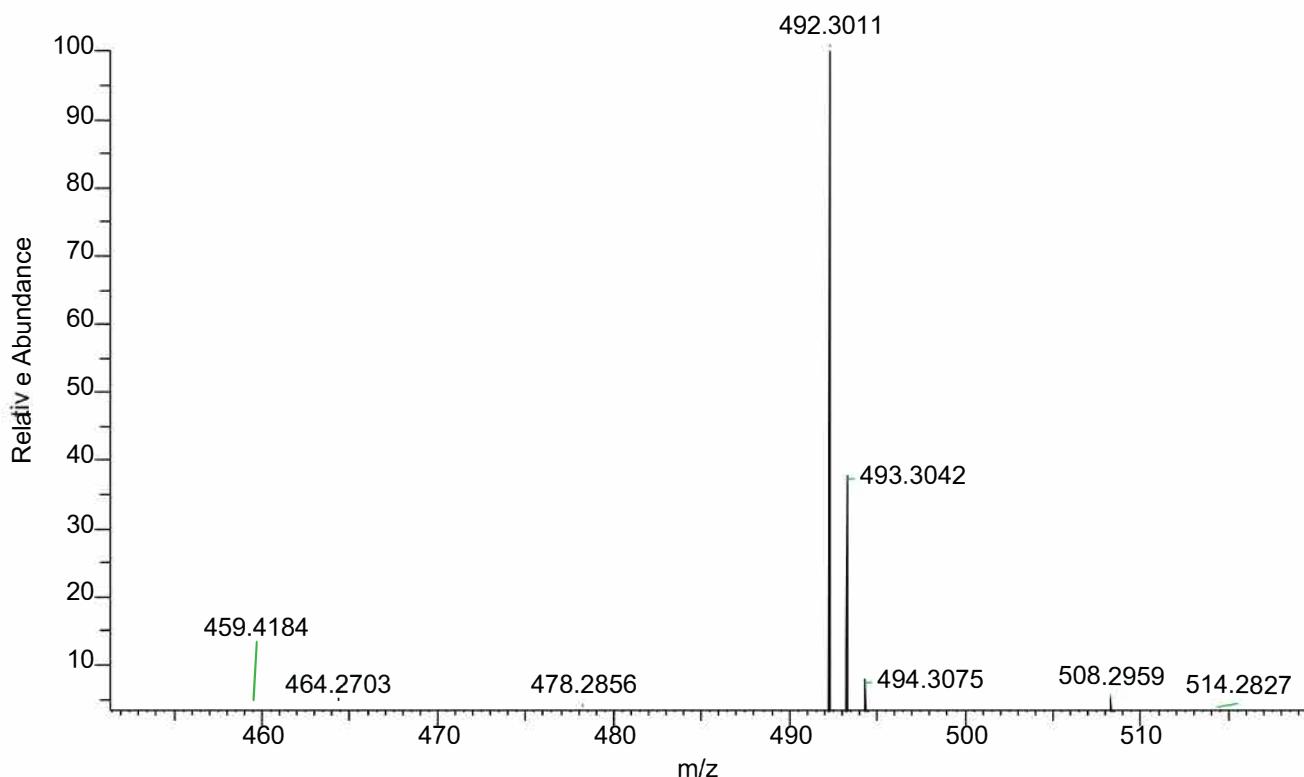


Figure S135. High resolution time-of-flight electrospray ionization mass spectrum of methoxybenzoporphyrin **7a**.

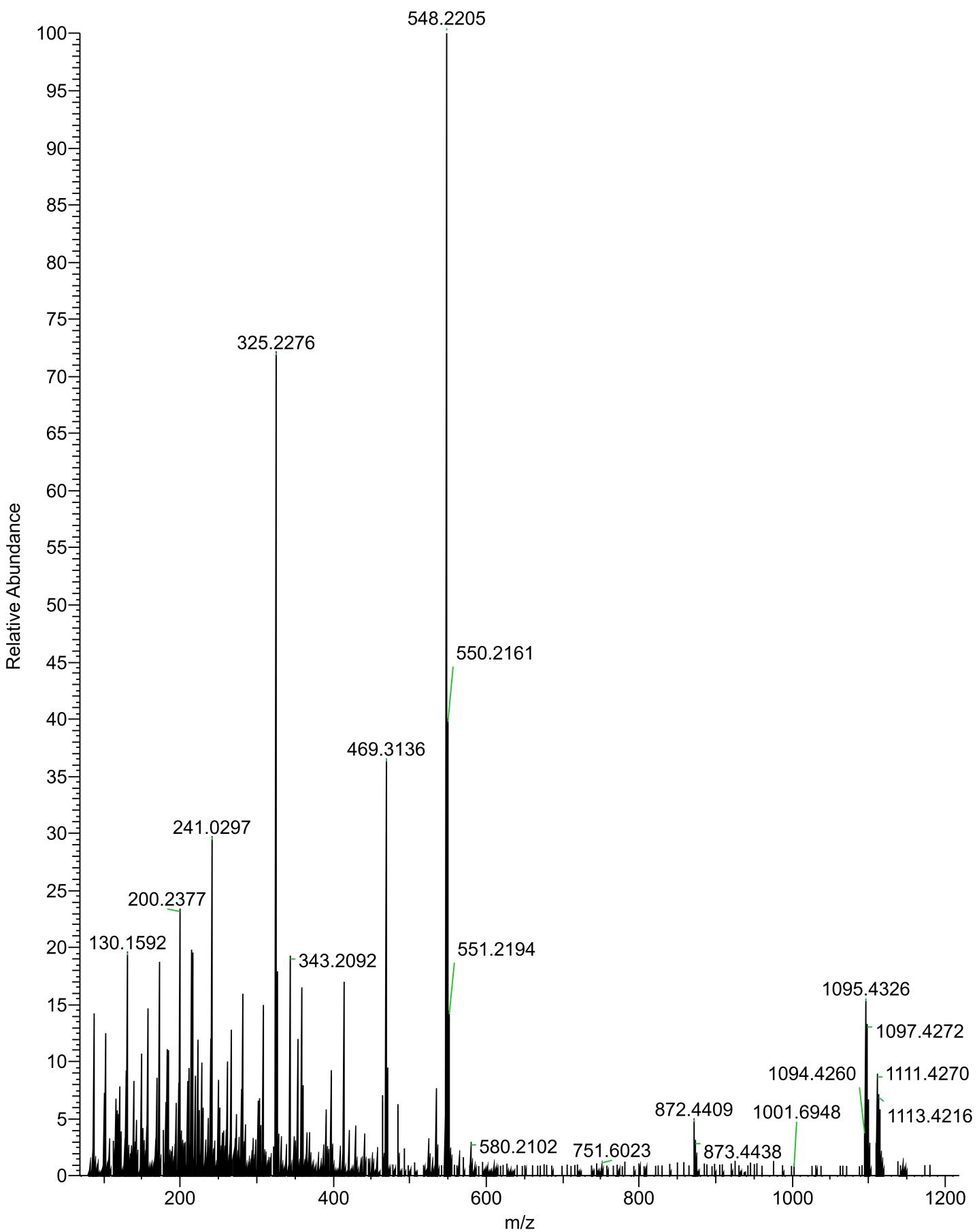


Figure S136. High resolution time-of-flight electrospray ionization mass spectrum of nickel complex 7aNi.

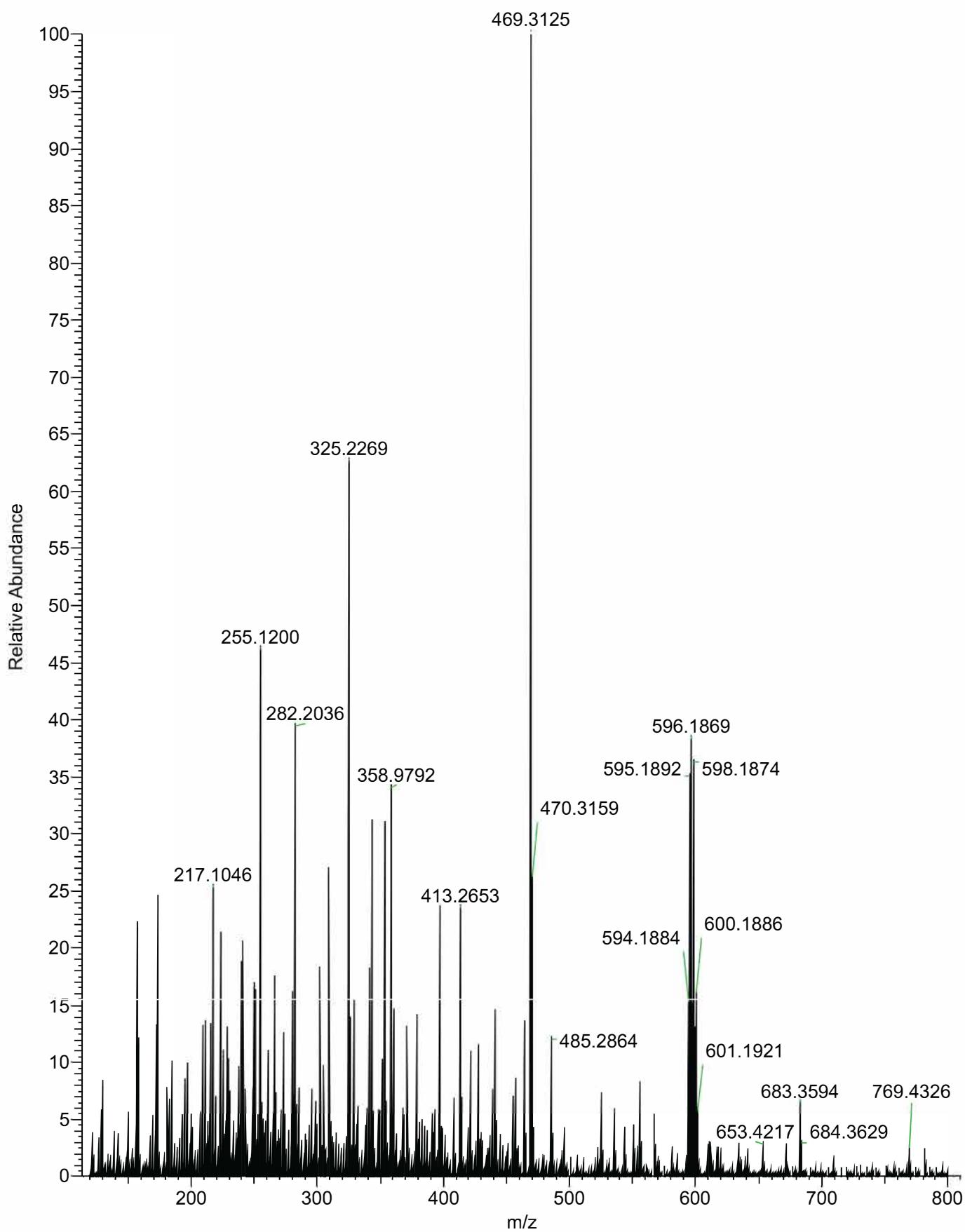


Figure S137. High resolution time-of-flight electrospray ionization mass spectrum of palladium complex **7aPd**.

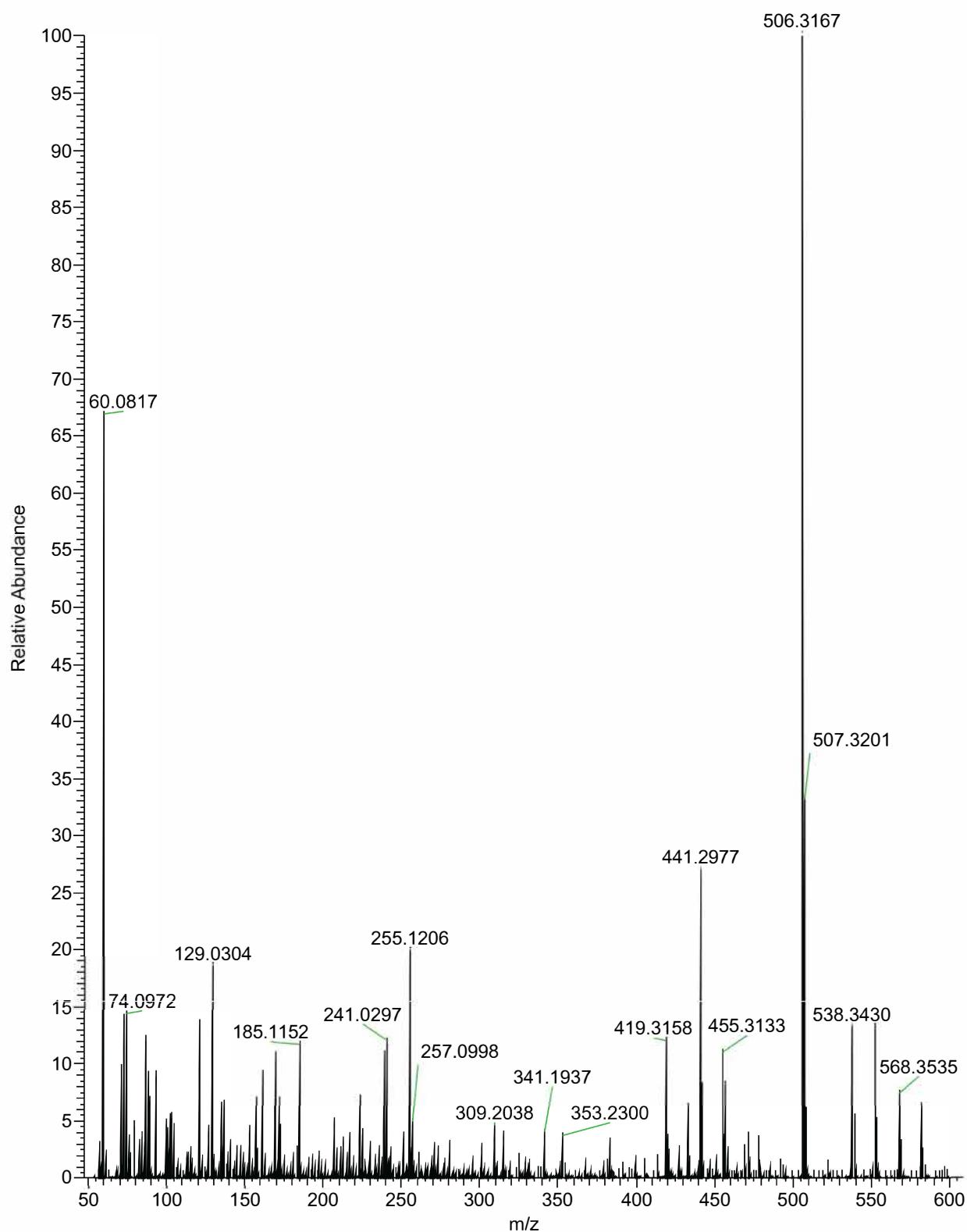


Figure S138. High resolution time-of-flight electrospray ionization mass spectrum of ethoxybenzoporphyrin **7b**.

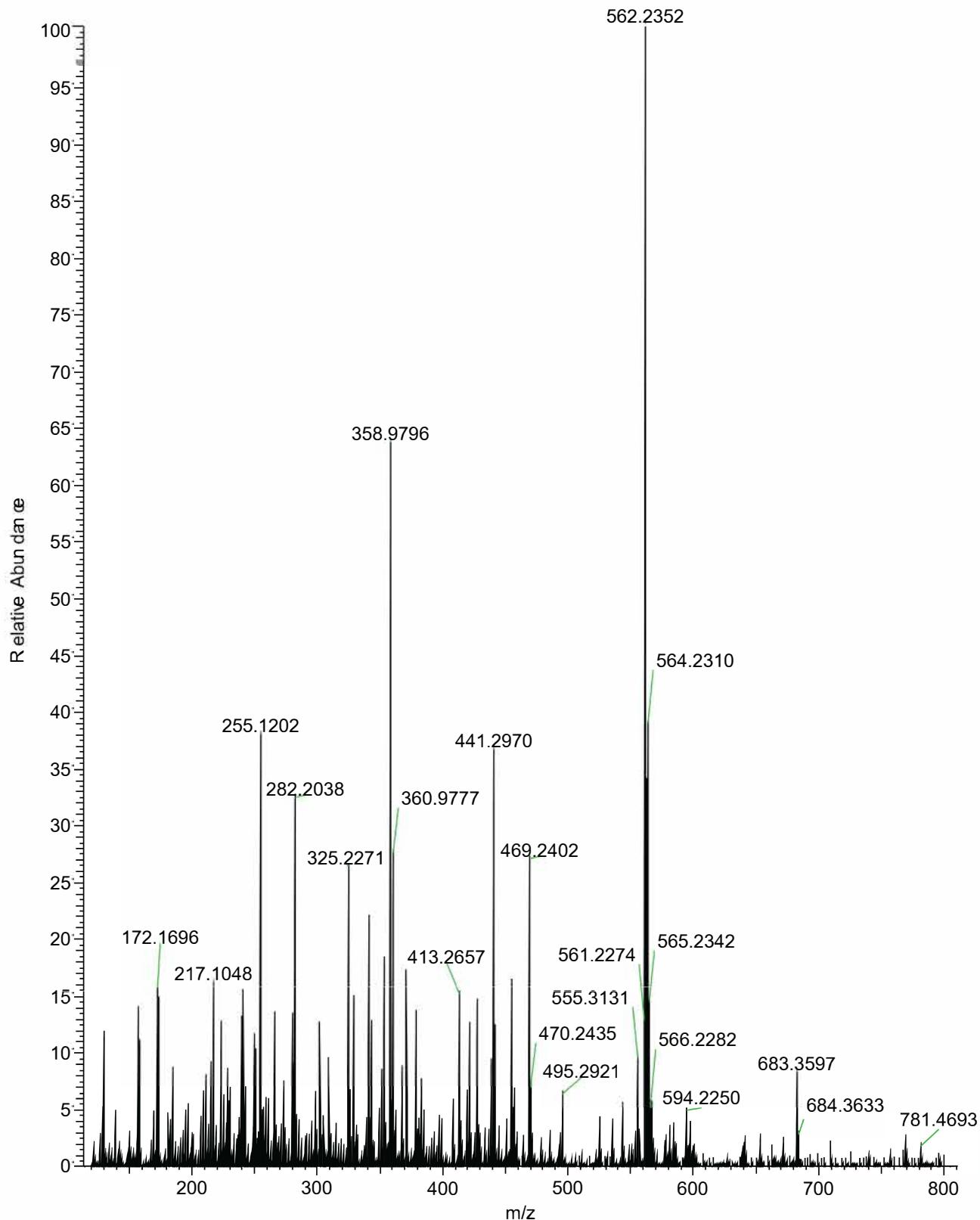


Figure S139. High resolution time-of-flight electrospray ionization mass spectrum of nickel complex **7bNi**.

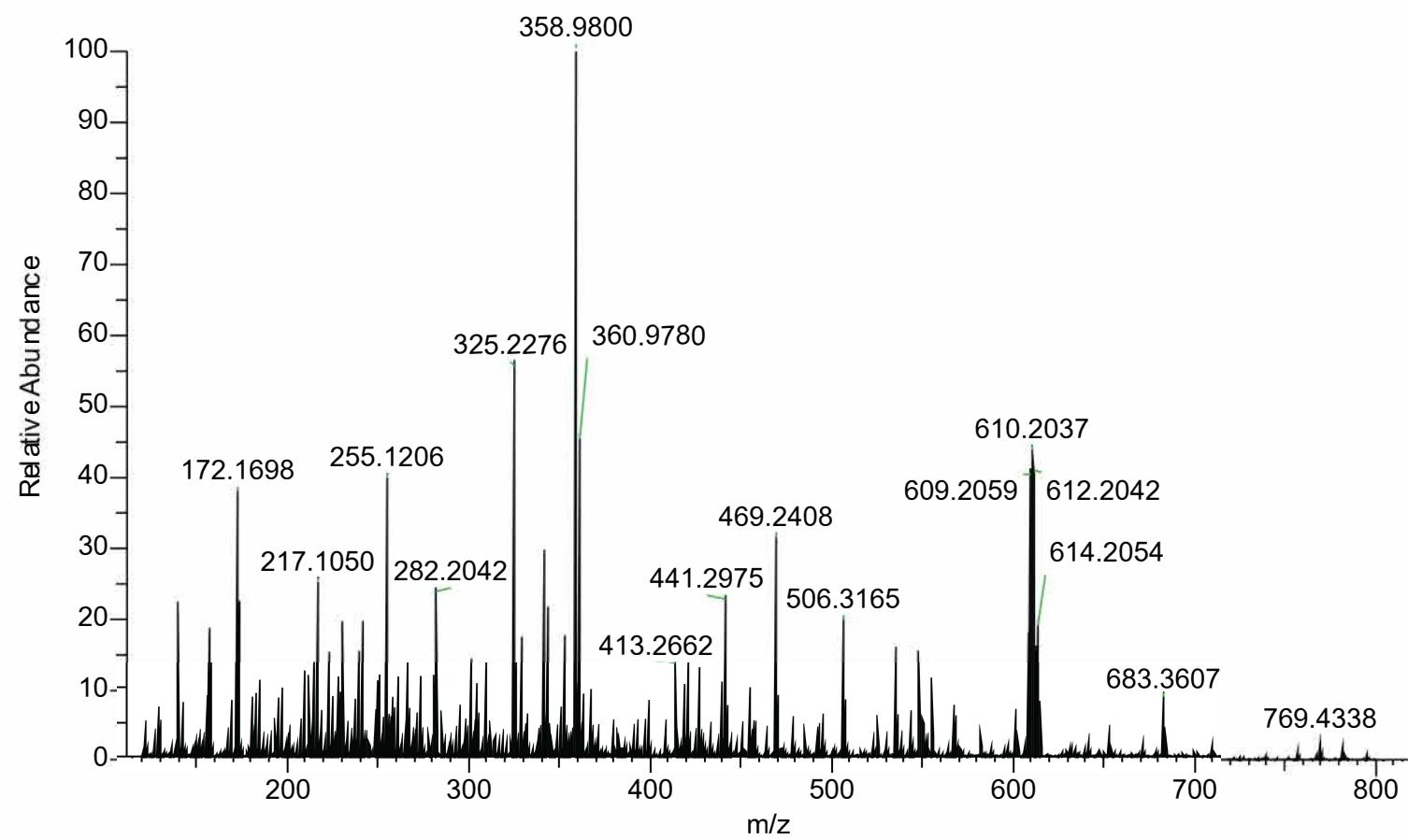


Figure S140. High resolution time-of-flight electrospray ionization mass spectrum of palladium complex **7bPd**.

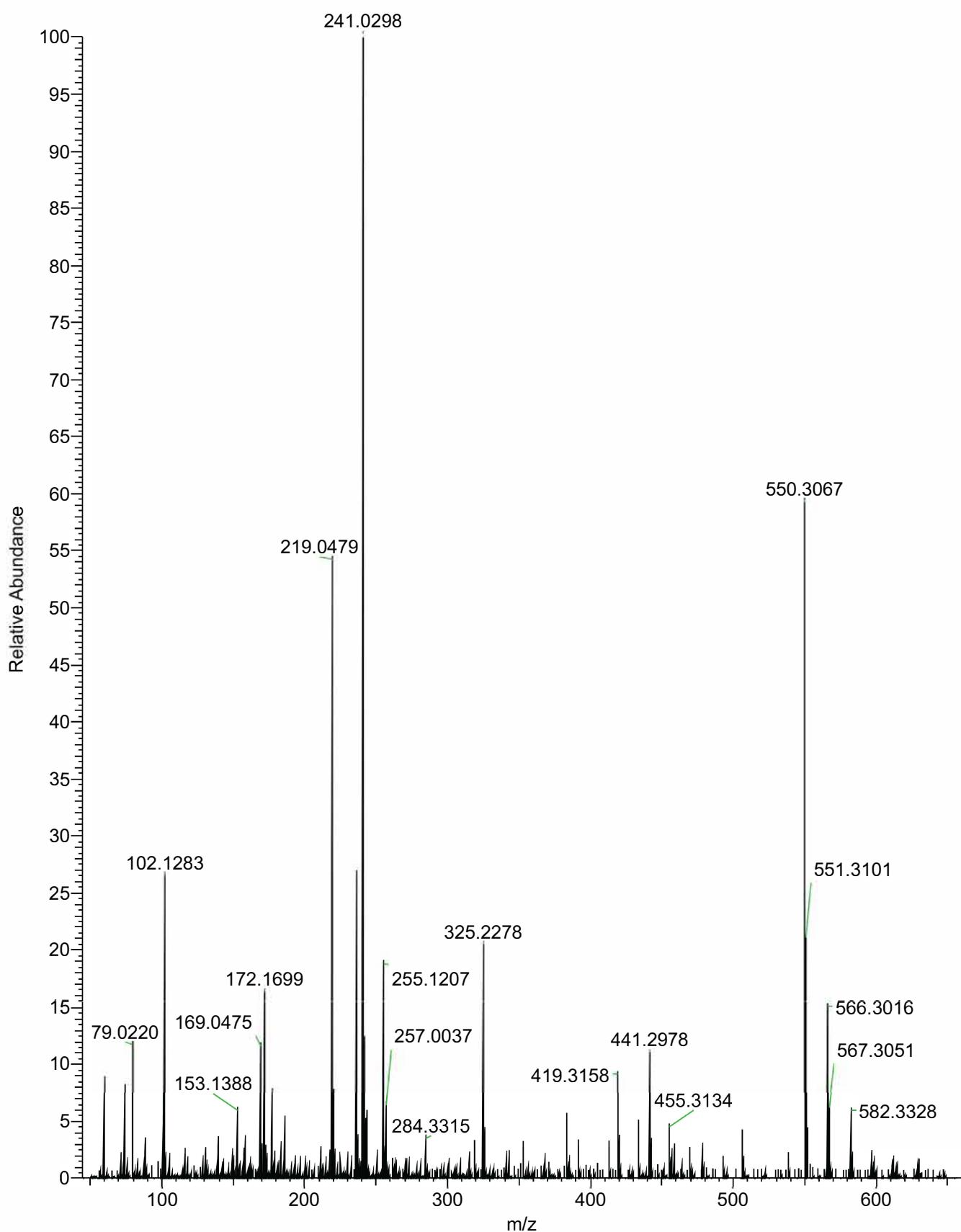


Figure S141. High resolution time-of-flight electrospray ionization mass spectrum of benziporphyrin 7c.

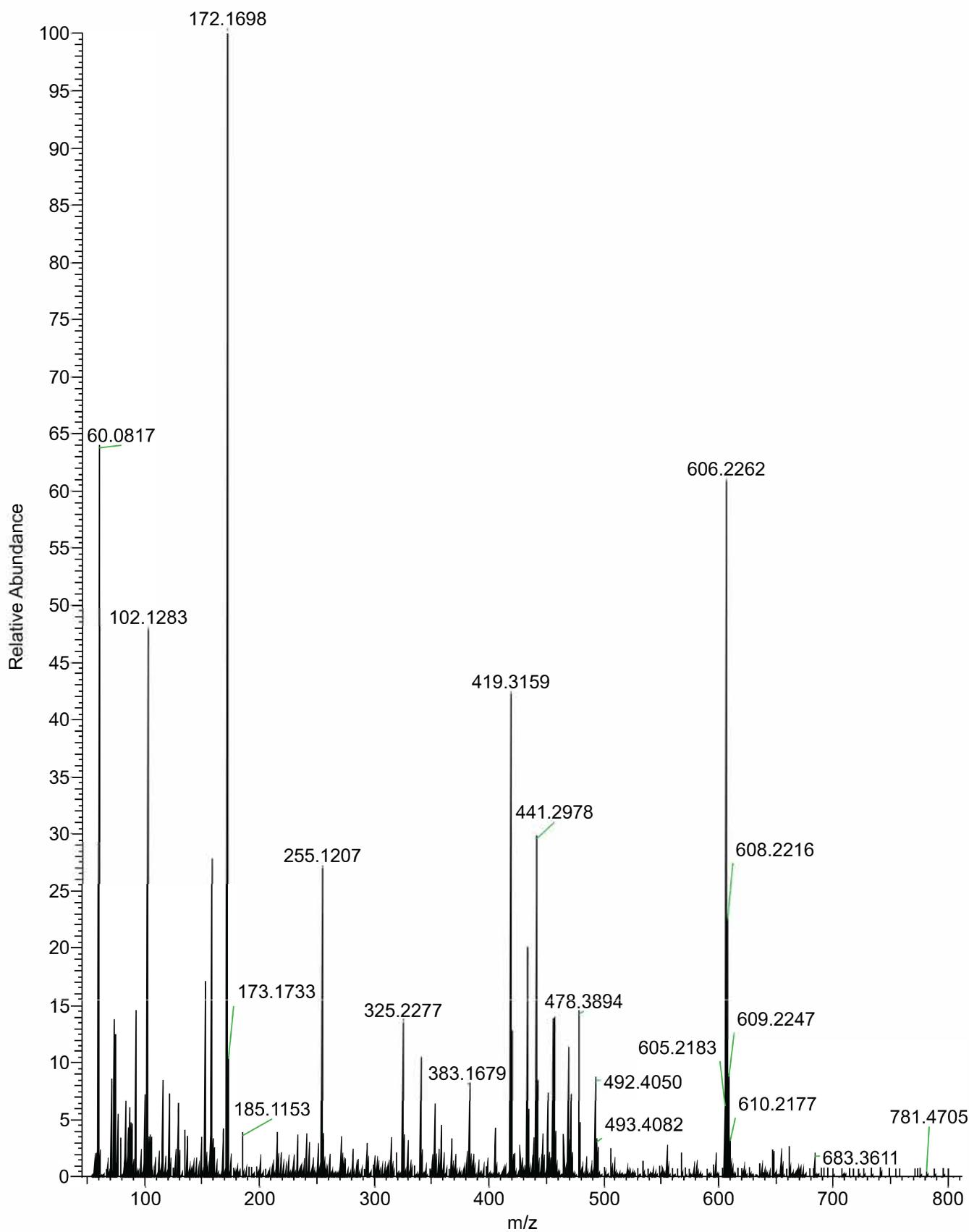


Figure S142. High resolution time-of-flight electrospray ionization mass spectrum of nickel complex 7cNi.

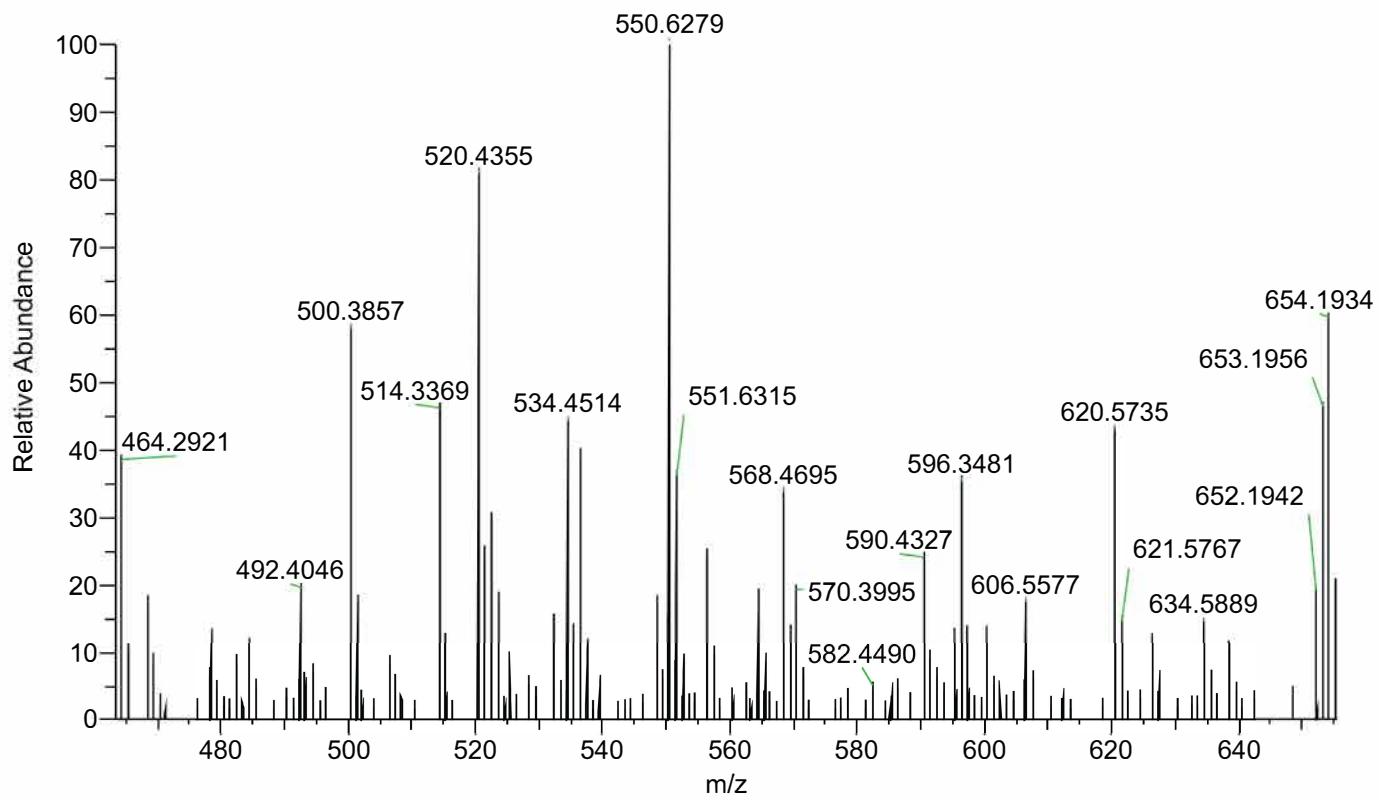


Figure S143. High resolution time-of-flight electrospray ionization mass spectrum of palladium complex **7cPd**.

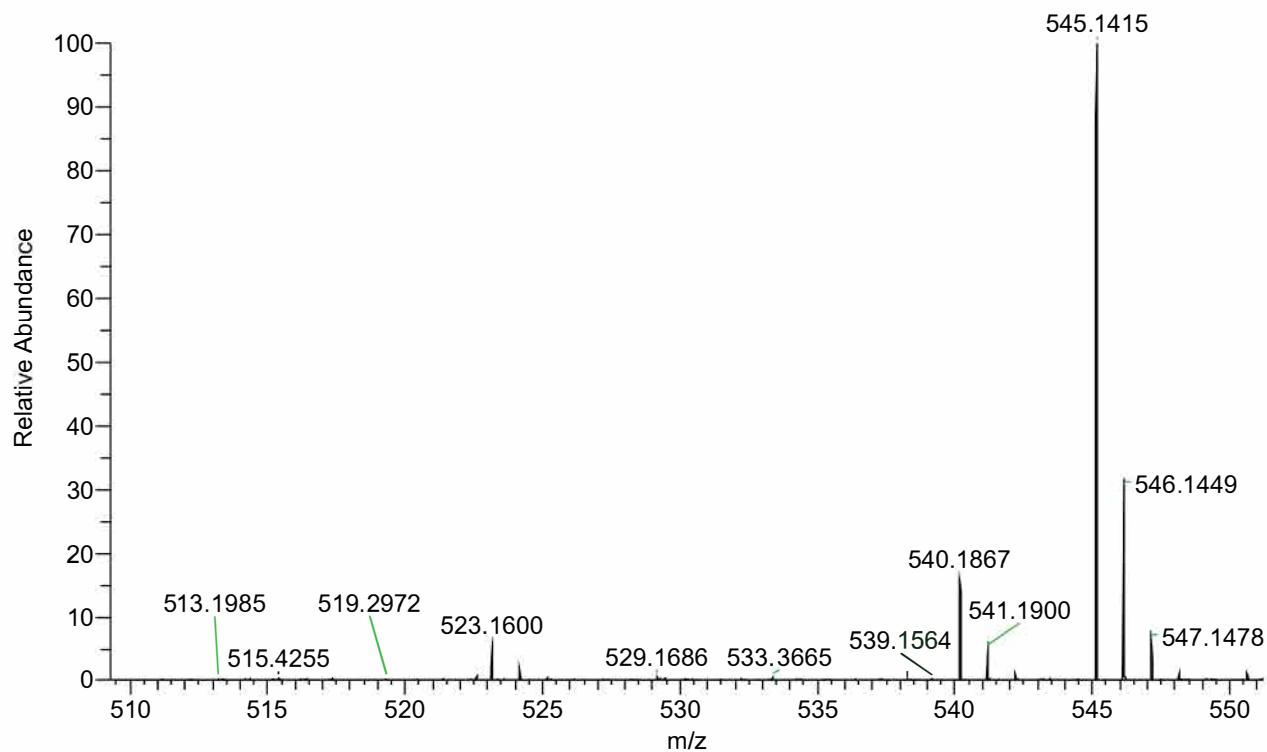


Figure S144. High resolution time-of-flight electrospray ionization mass spectrum of **16a**.

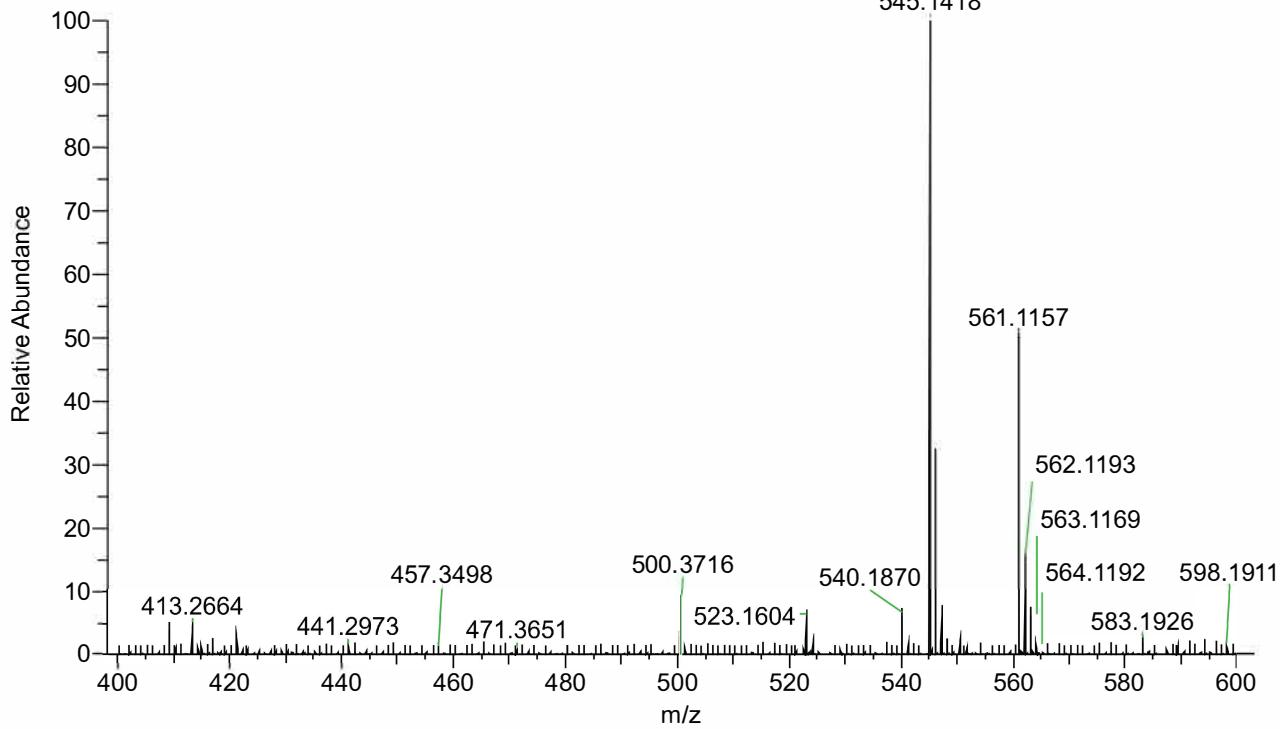


Figure S145. High resolution time-of-flight electrospray ionization mass spectrum of **16b**.

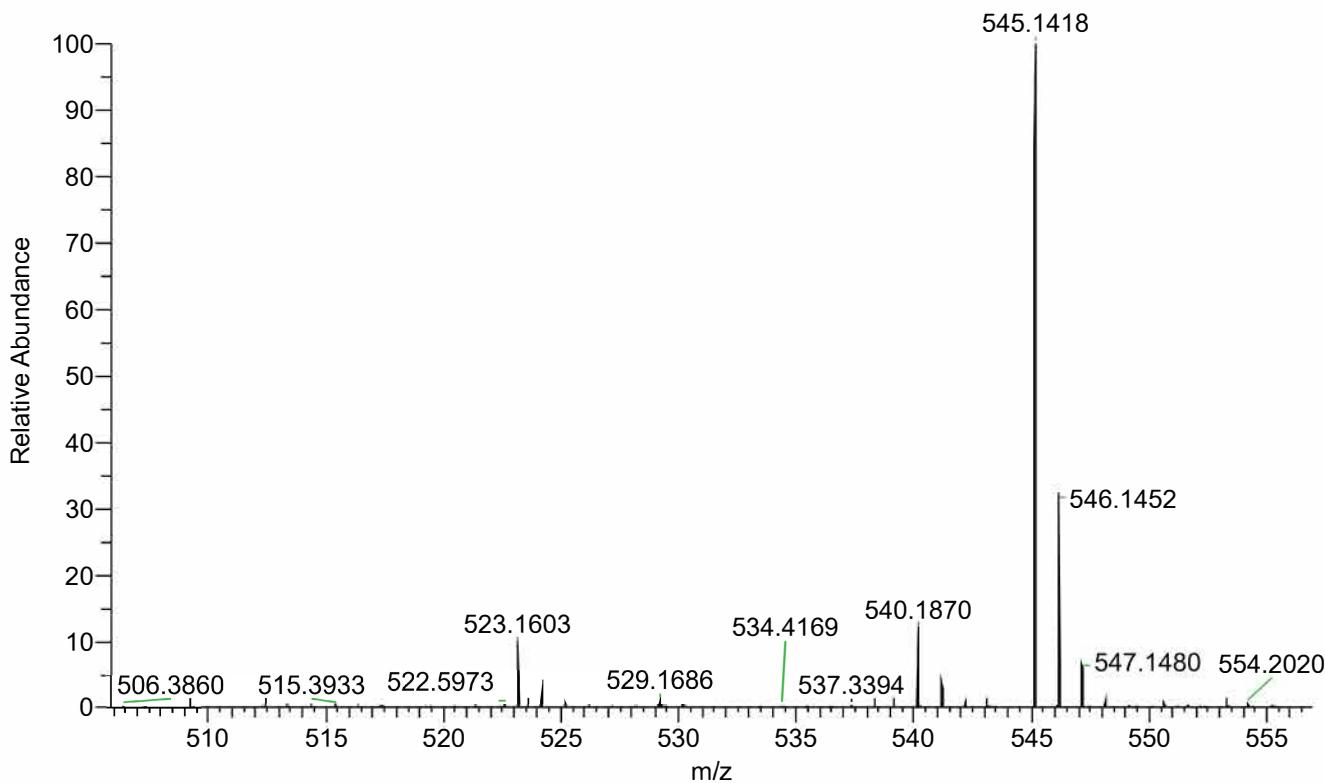


Figure S146. High resolution time-of-flight electrospray ionization mass spectrum of **16c**.

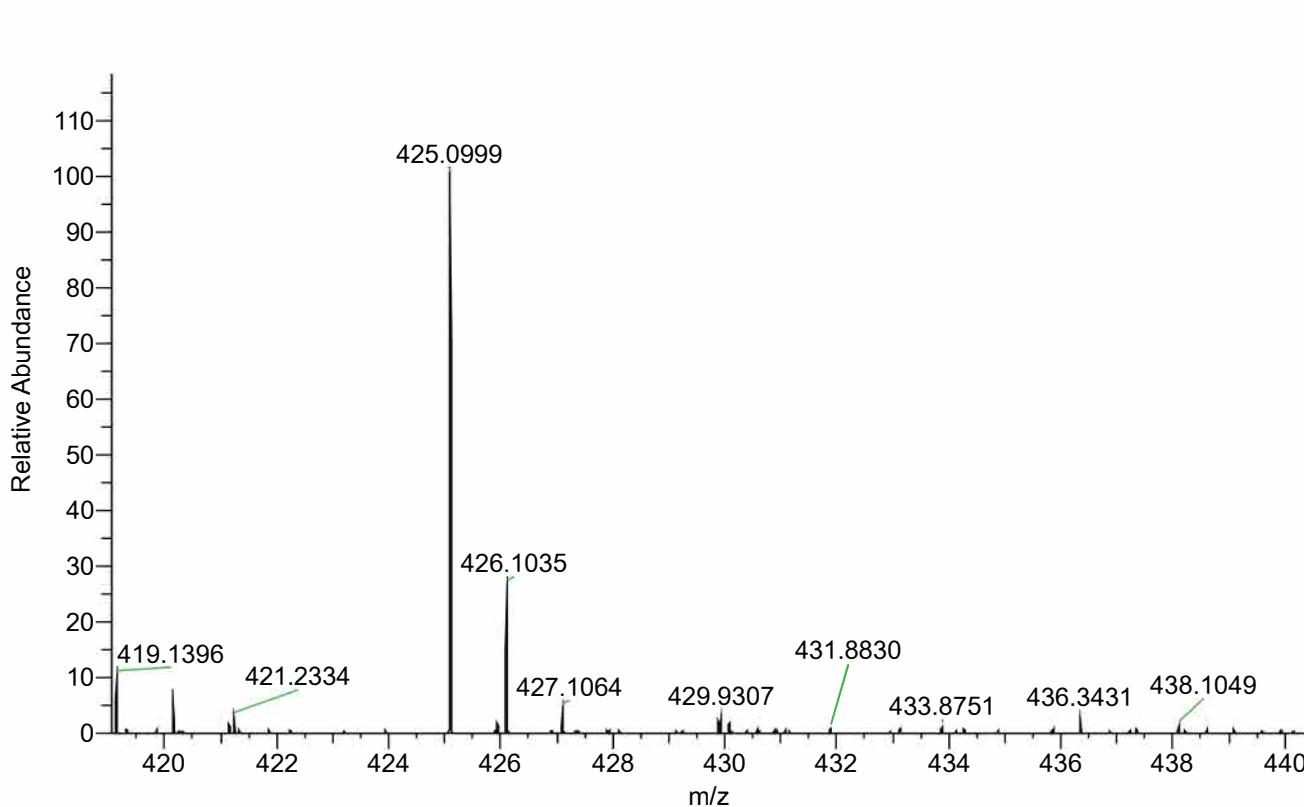


Figure S147. High resolution time-of-flight electrospray ionization mass spectrum of **18a**.

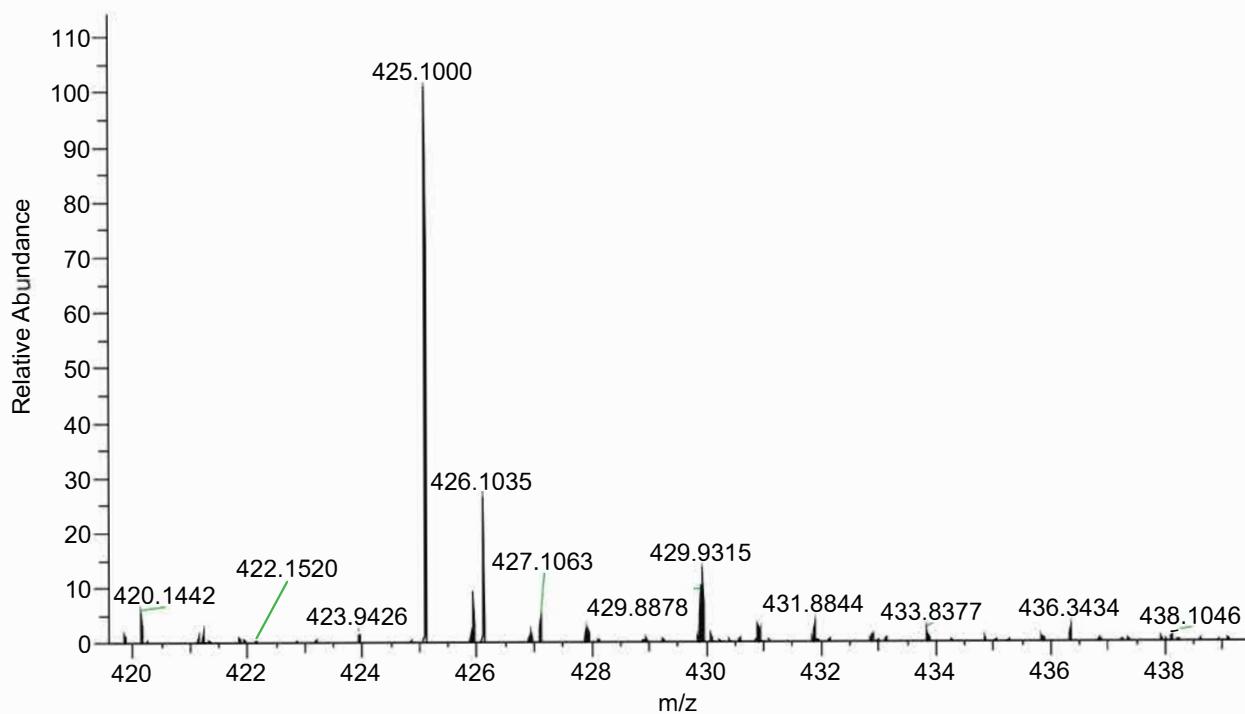


Figure S148. High resolution time-of-flight electrospray ionization mass spectrum of **18b**.

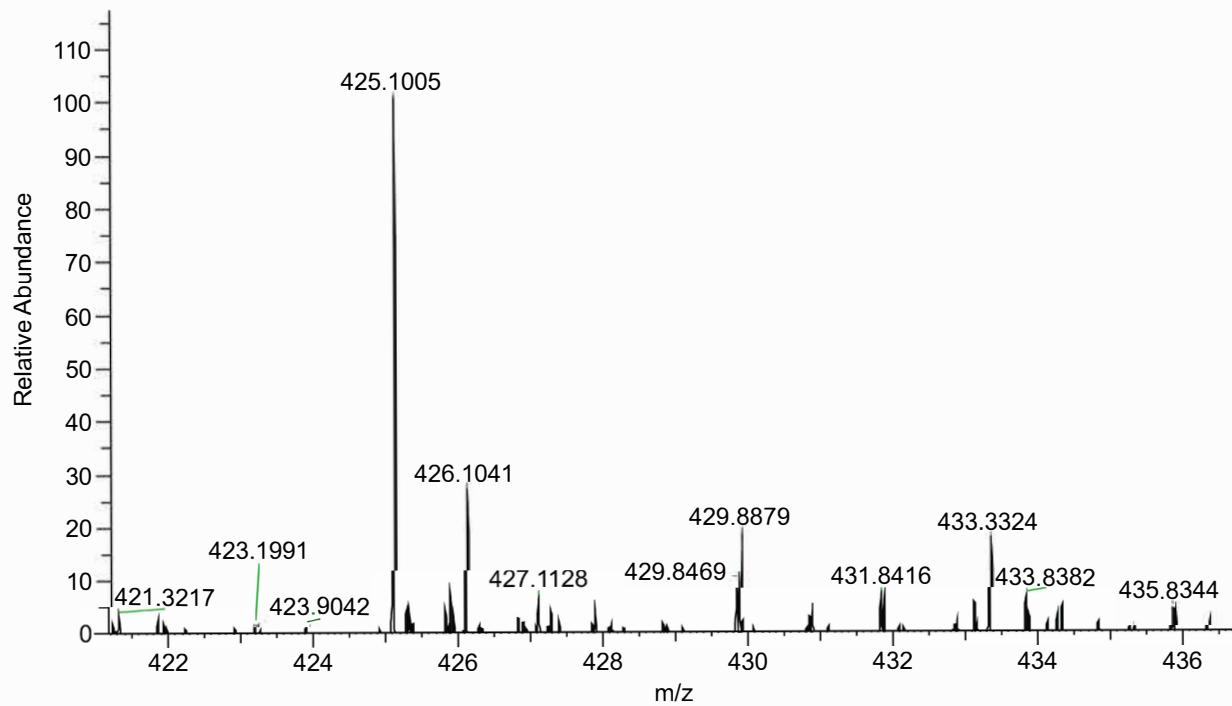


Figure S149. High resolution time-of-flight electrospray ionization mass spectrum of **18c**.