Supplementary Materials

Convenient Access to Ferrocene Fused *aza*-Heterocycles via the Intramolecular Ritter Reaction: Synthesis of Novel Racemic Planar-Chiral 3,4-Dihydroferroceno[*c*]pyridines and 1*H*-Ferroceno[*c*]pyrroles

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Table of contents

1. ^{1}H NMR monitoring of the conversion of thioimine **11g** to enaminone **3u** S3
2. The proposed mechanism for the transformation of thioimine **11g** to enaminone **3u** S3
3. The proposed mechanism for the thermolysis of ferroceno[*c*]pyrrole **12g** S4
4. Copies of NMR spectra S5

Copies of ^{1}H and ^{13}C NMR spectra for compounds **10g**, **j** S5

Copies of ^{1}H and ^{13}C NMR spectra for compounds **3a**–**m, o**–**s, u**–**x**; ^{19}F NMR spectra for compounds **3k**–**m** S7

Copies of ^{1}H and ^{13}C NMR spectra for compounds **8a**–**c** and **9a**–**c** S31

Copies of ^{1}H and ^{13}C NMR spectra for compounds **11a**–**g** S36

Copies of ^{1}H and ^{13}C NMR spectra for compounds **12a**–**g** S43

Copies of ^{1}H and ^{13}C NMR spectra for compound **4** S50

Copies of ^{1}H and ^{13}C NMR spectra for a mixture of compounds **5** and **6** S51

Copies of ^{1}H and ^{13}C NMR spectra for compound **13** S52

Copies of 2D spectra for compounds **3a**, **3u**–**x**, **11a** and **12a** S53

1. Aiming to provide spectroscopic evidence for the spontaneous formation of enaminone **3u** from thioimine **11g**, ^{1}H NMR monitoring of the reaction was performed (Figure S1, Table S1).

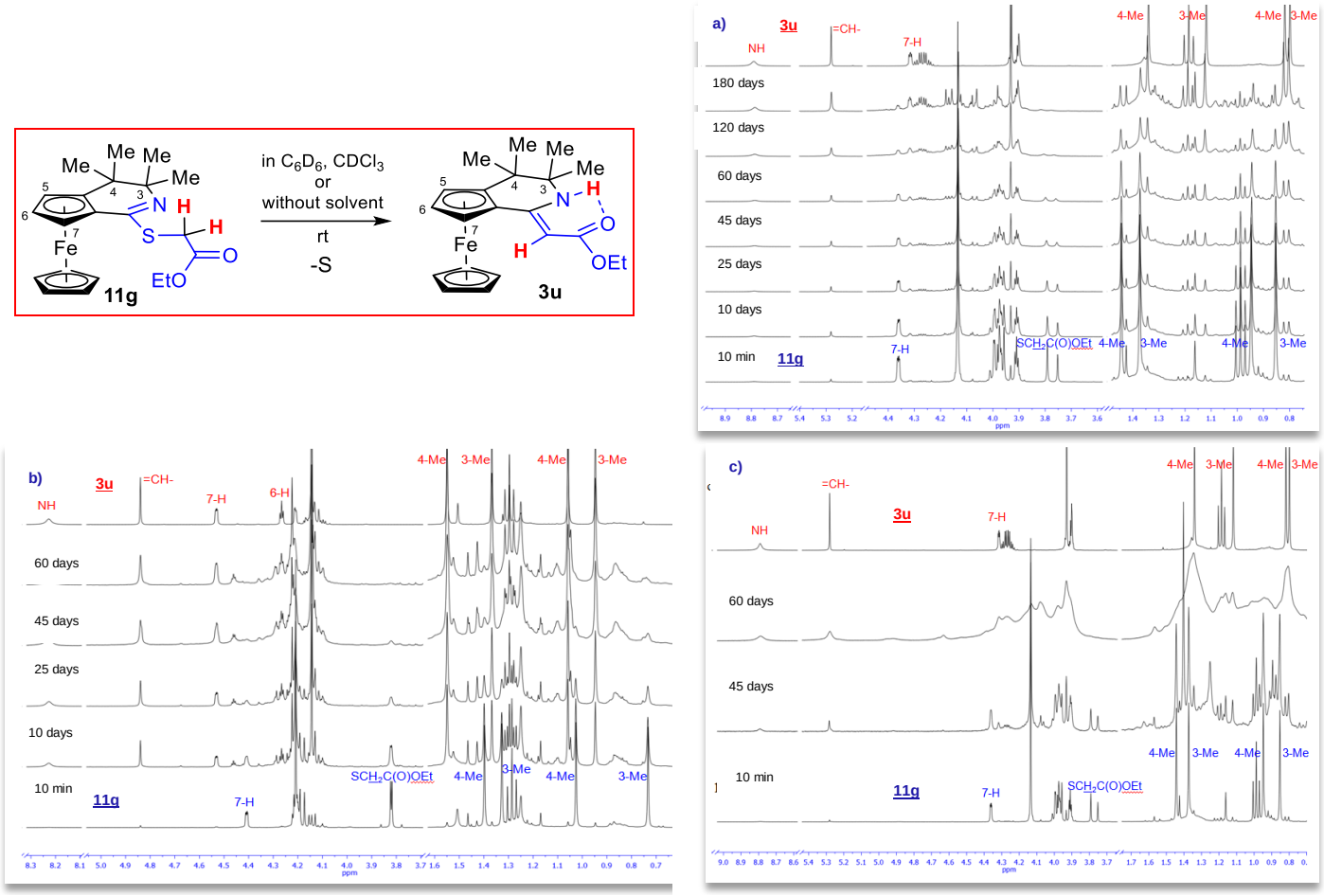


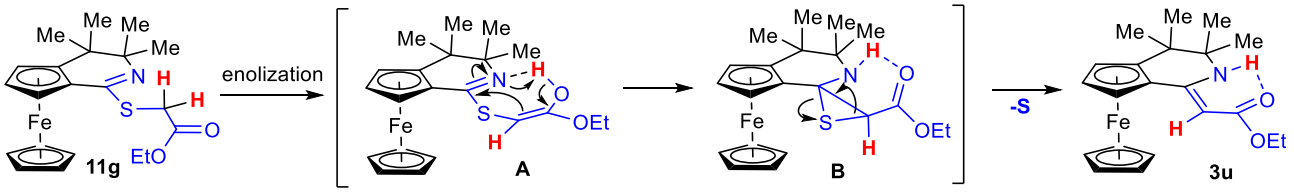
Figure S1. ^{1}H NMR (400 MHz) monitoring of the conversion of thioimine **11g** to enaminone **3u** at rt. a) in C_6D_6 b) in $CDCl_3$ c) without solvent, ^{1}H NMR spectra were recorded in C_6D_6.

Table S1. ^{1}H NMR (400 MHz) monitoring of the conversion of thioimine **11g** to enaminone **3u**.[1]

		Ratio of **11g**/**3u** [2]						
Entry	**Solvent**	**10 min**	**10 days**	**25 days**	**45 days**	**60 days**	**120 days**	**180 days**
1 [3]	C_6D_6	96:4	88:12	84:16	79:21	70:30	50:50	31:69
2 [3]	$CDCl_3$	96:4	53:47	30:70	11:89	0:100	-	-
3 [4]	-	96:4	[5]	[5]	80:20	[6]	-	-

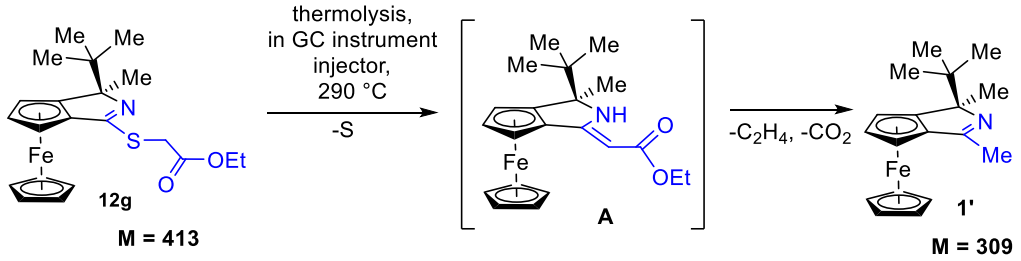
[1] Compound **11g** was obtained in the reaction of alcohol **1** with thiocyanate **10g** at 80 °C (Table 6, entry 2). [2] According to ^{1}H NMR analysis. [3] 5 mg of compound **11g** was dissolved in 0.5 mL of deuterated solvent in NMR ampoules. Ampoules with each solution were stored at room temperature. [4] Compound **11g** was stored without solvent at room temperature; ^{1}H NMR spectra were recorded in C_6D_6. [5] ^{1}H NMR spectrum was not recorded. [6] The ratio of **11g**/**3u** could not be determined because of a great broadening of the signals.

2.



Scheme S1. Proposed mechanism for the transformation of thioimine **11g** to enaminone **3u**.

3.



Scheme S2. Proposed mechanism for the thermolysis of ferroceno[*c*]pyrrole **12g**.

4. Copies of NMR spectra

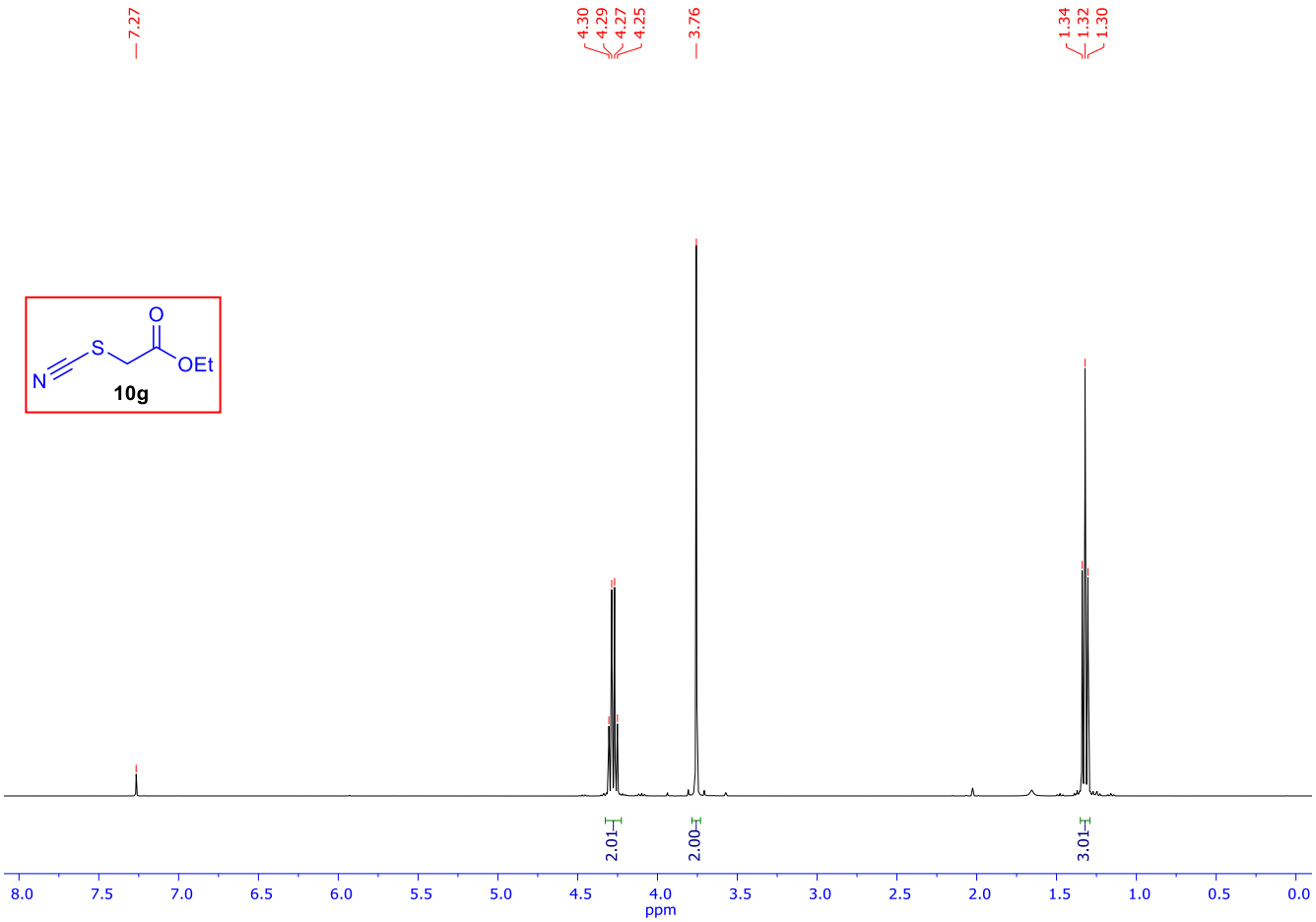


Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **10g**.

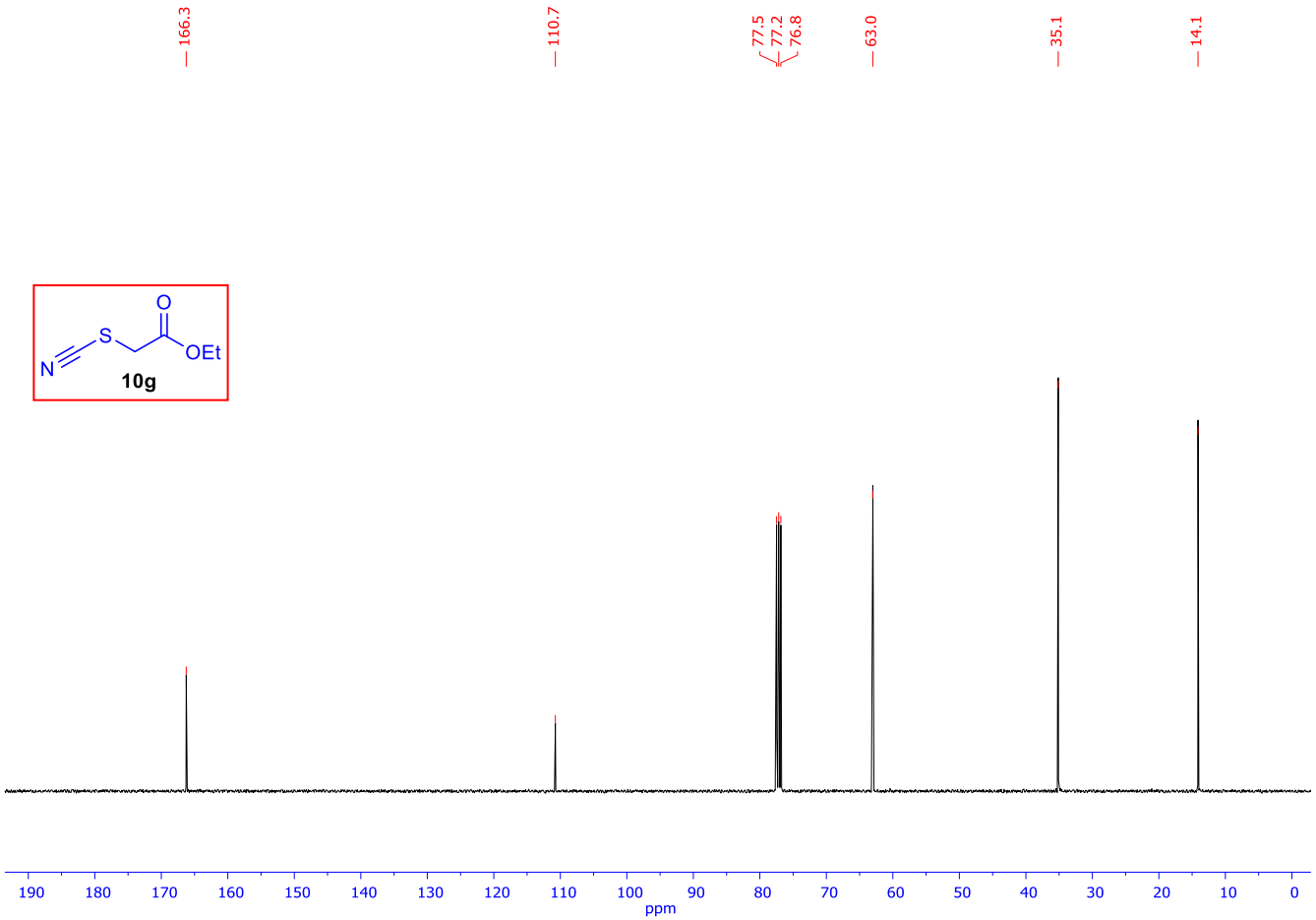


Figure S3. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **10g**.

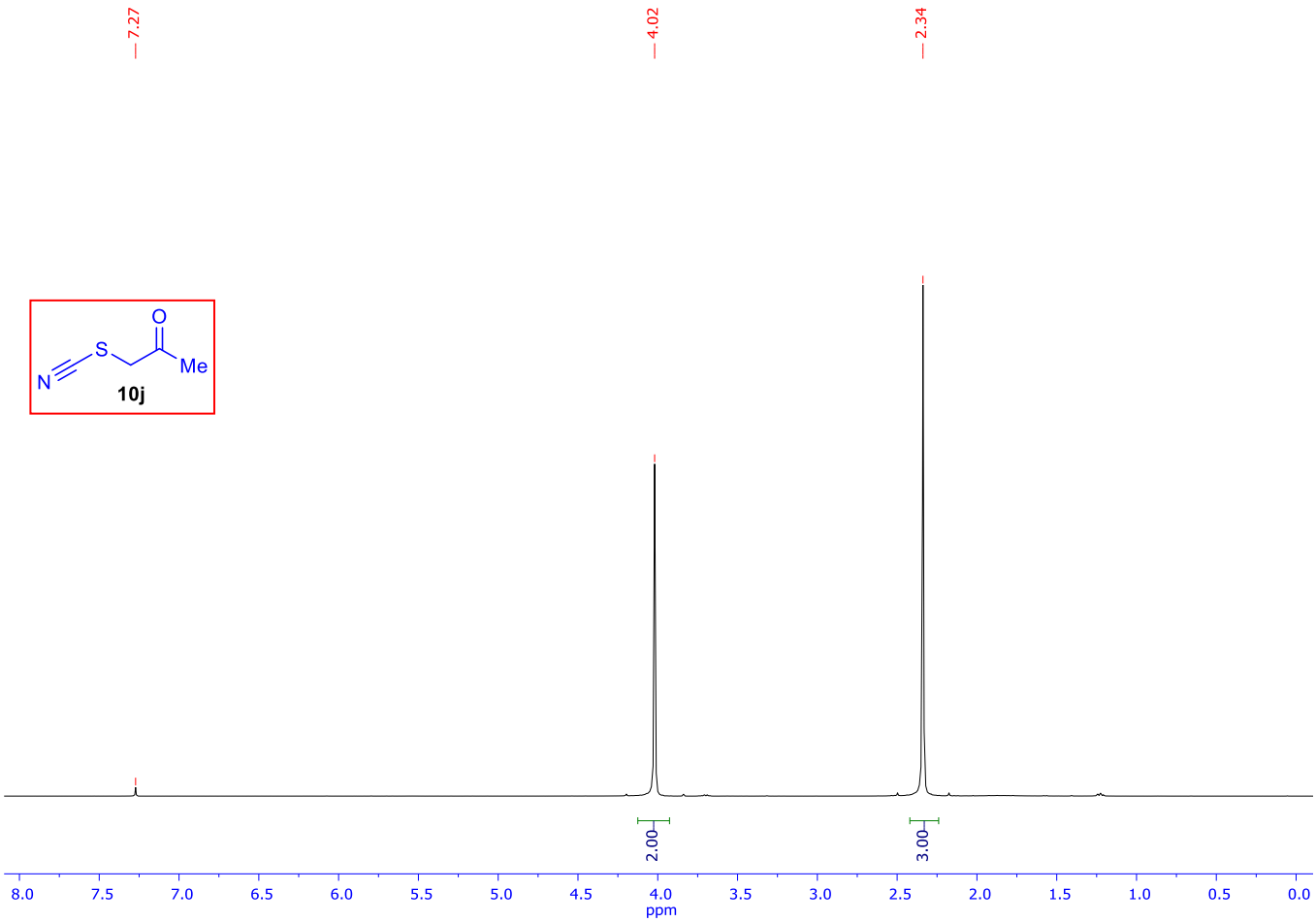


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **10j**.

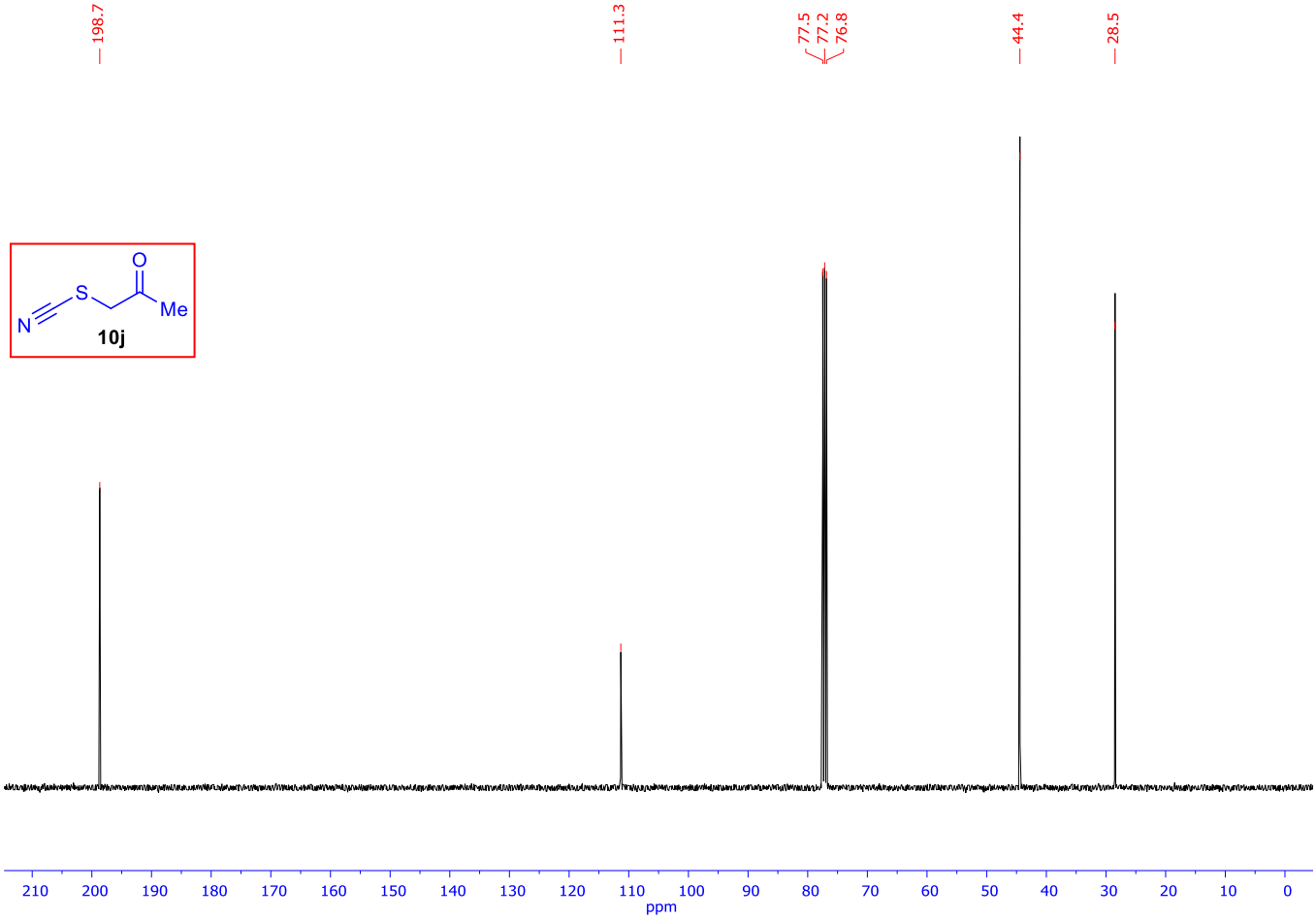


Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **10j**.

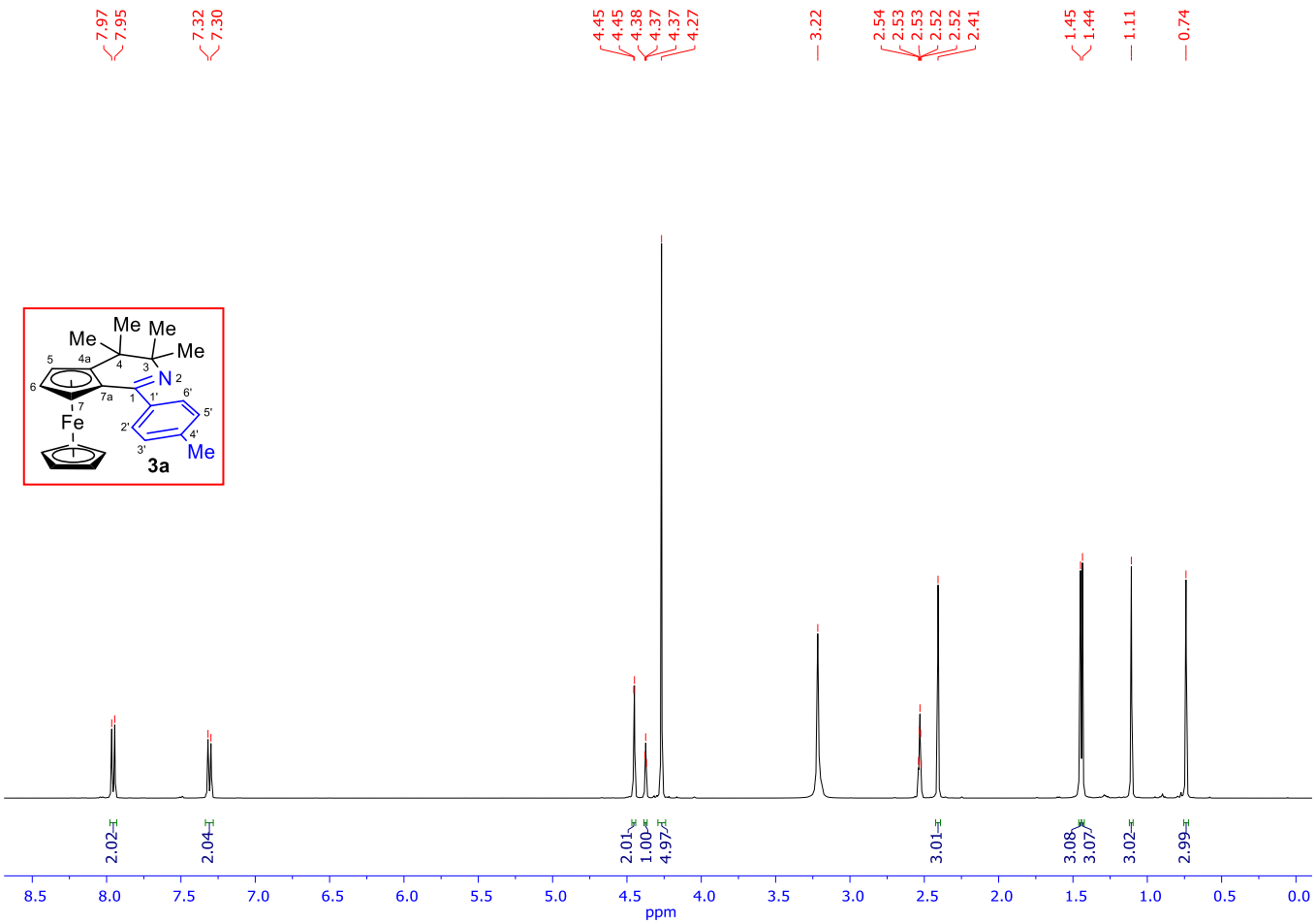


Figure S6. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3a**.

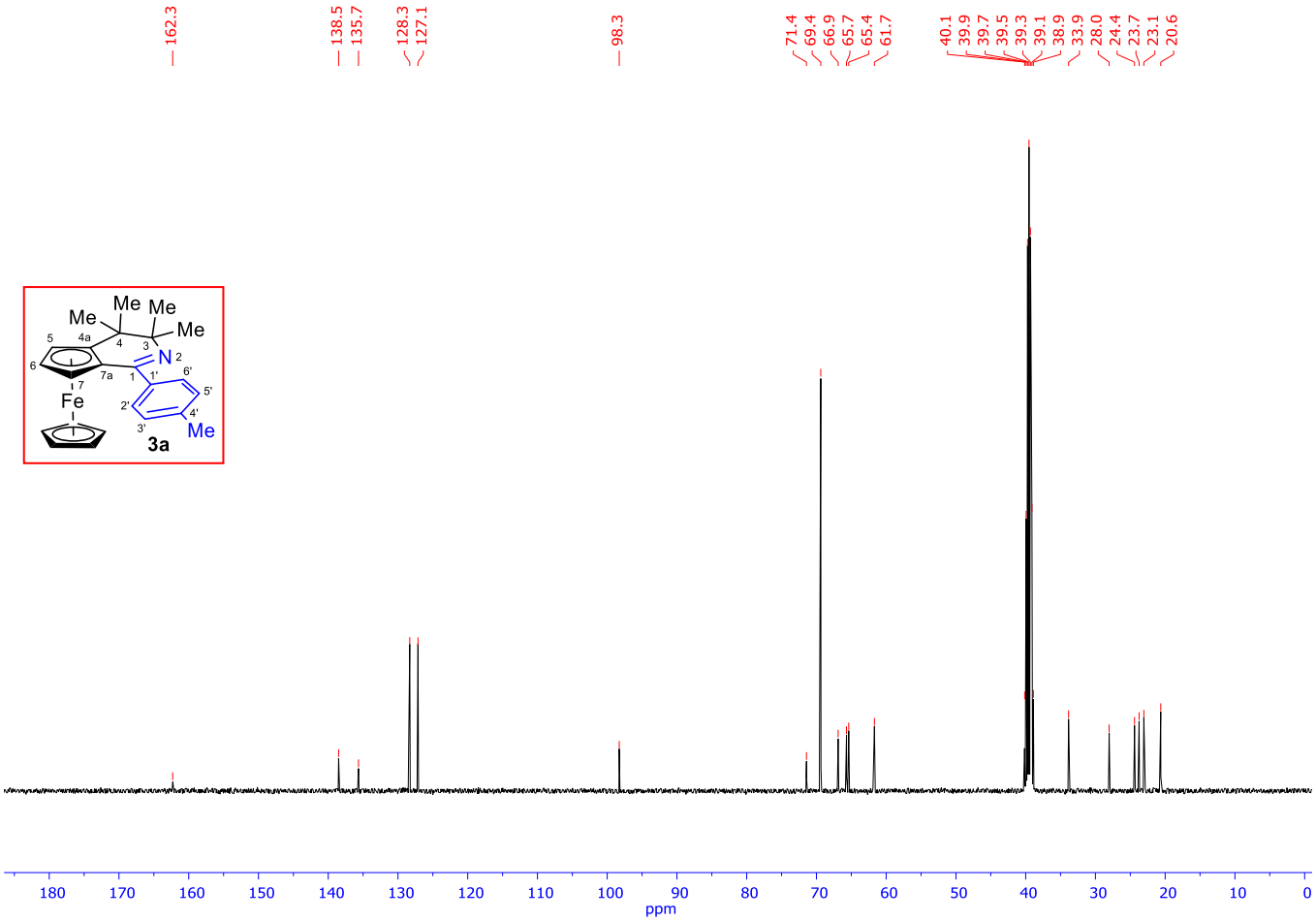


Figure S7. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3a**.

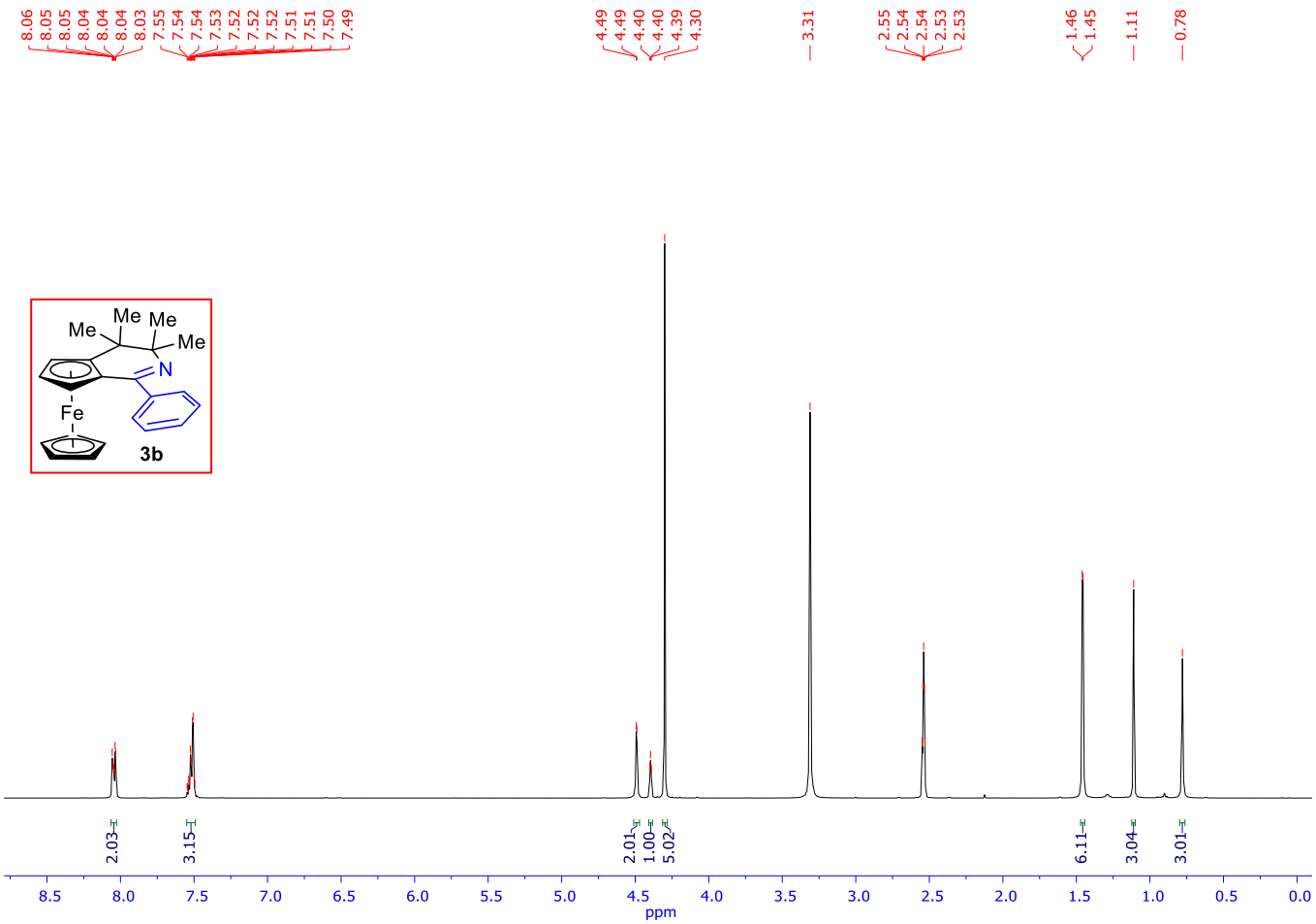


Figure S8. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3b**.

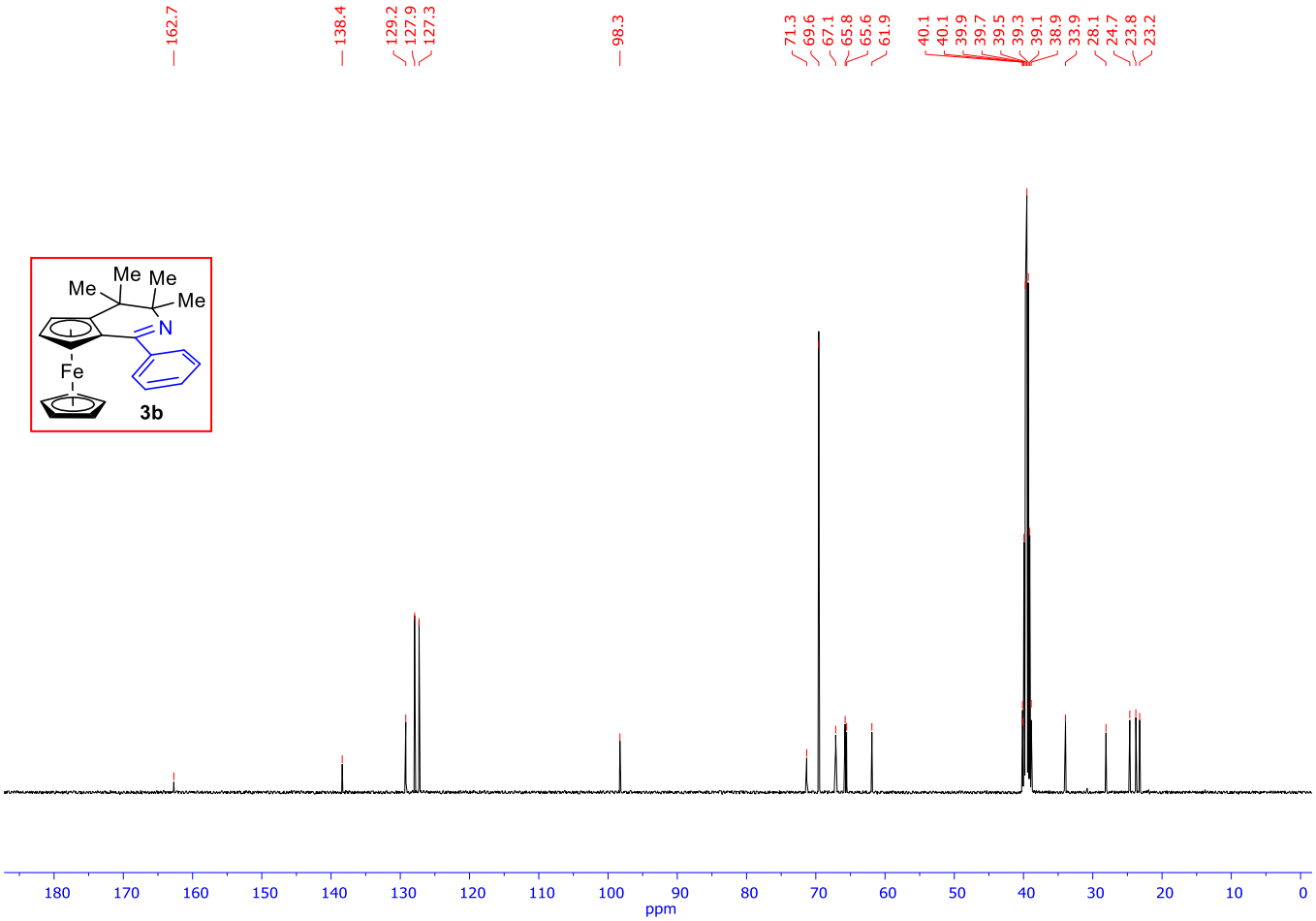


Figure S9. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3b**.

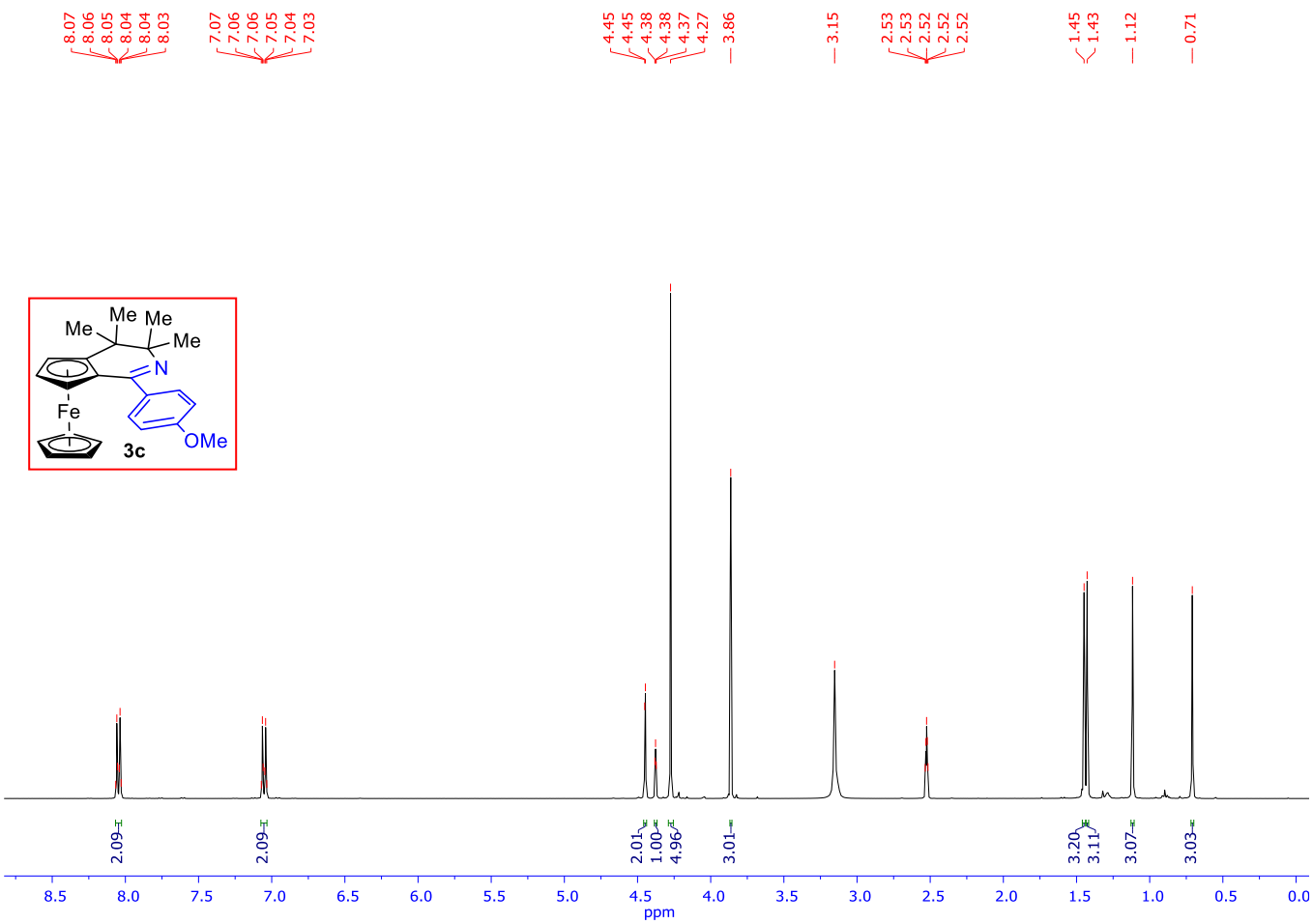


Figure S10. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3c**.

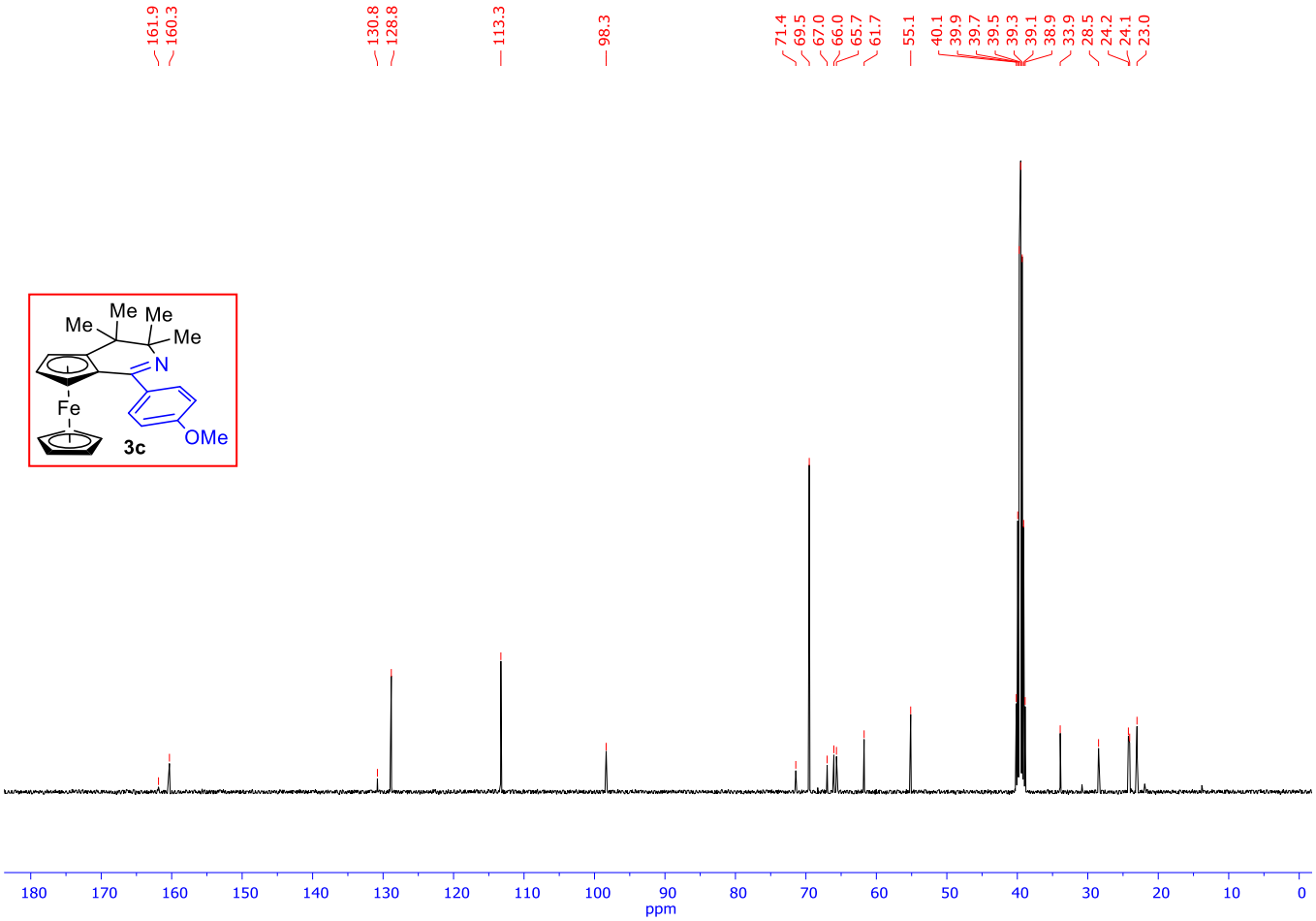


Figure S11. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3c**.

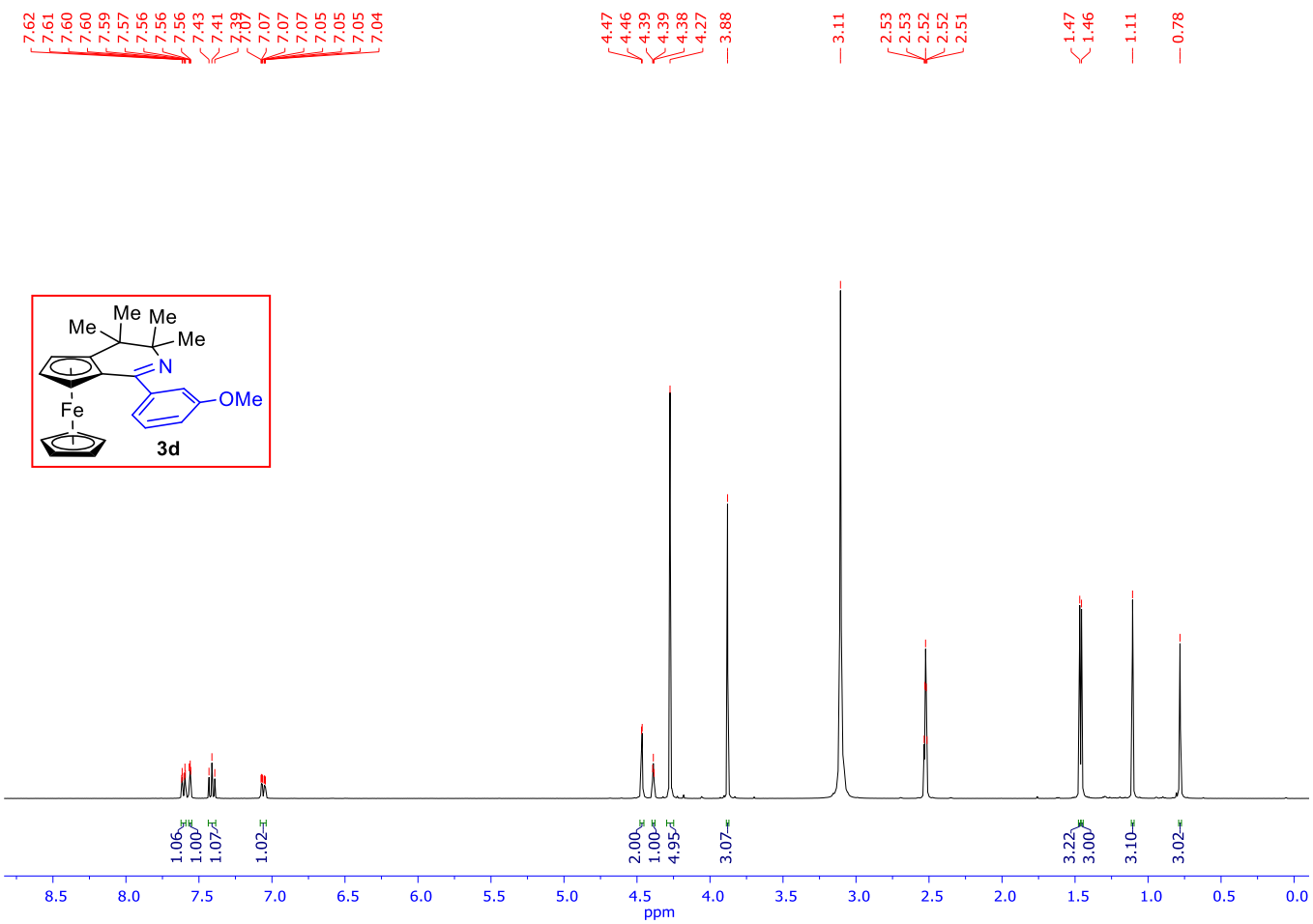


Figure S12. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3d**.

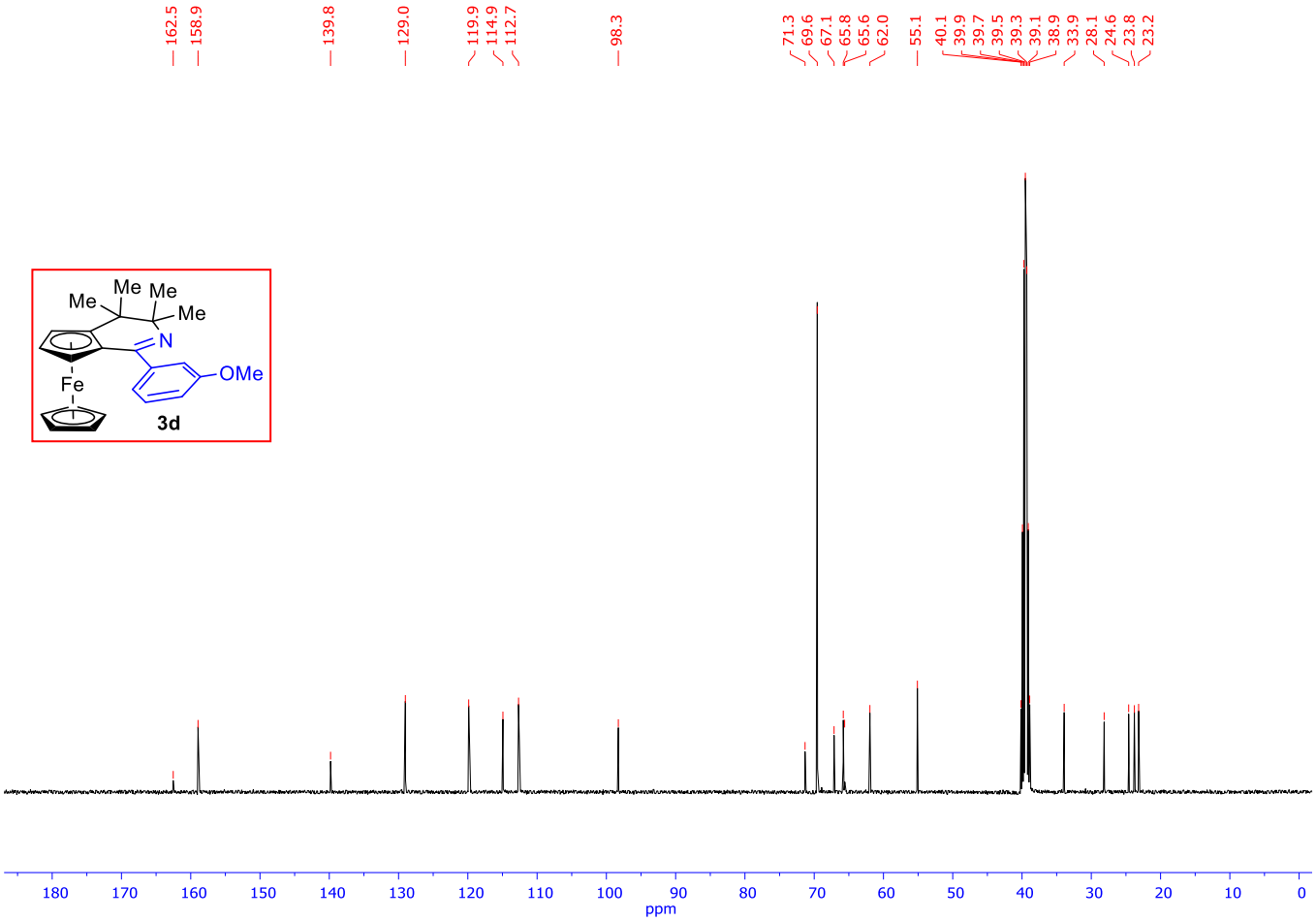


Figure S13. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3d**.

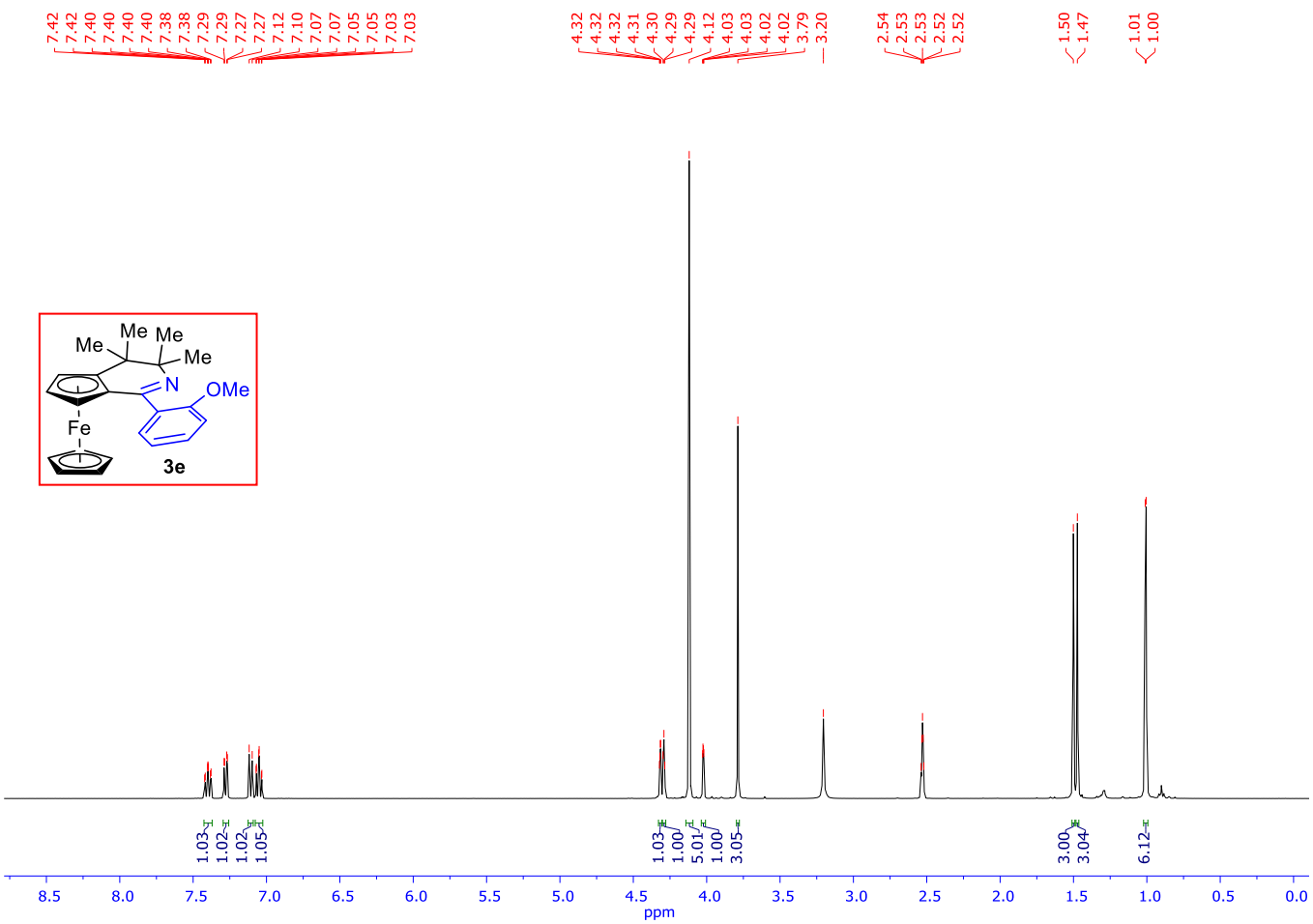


Figure S14. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3e**.

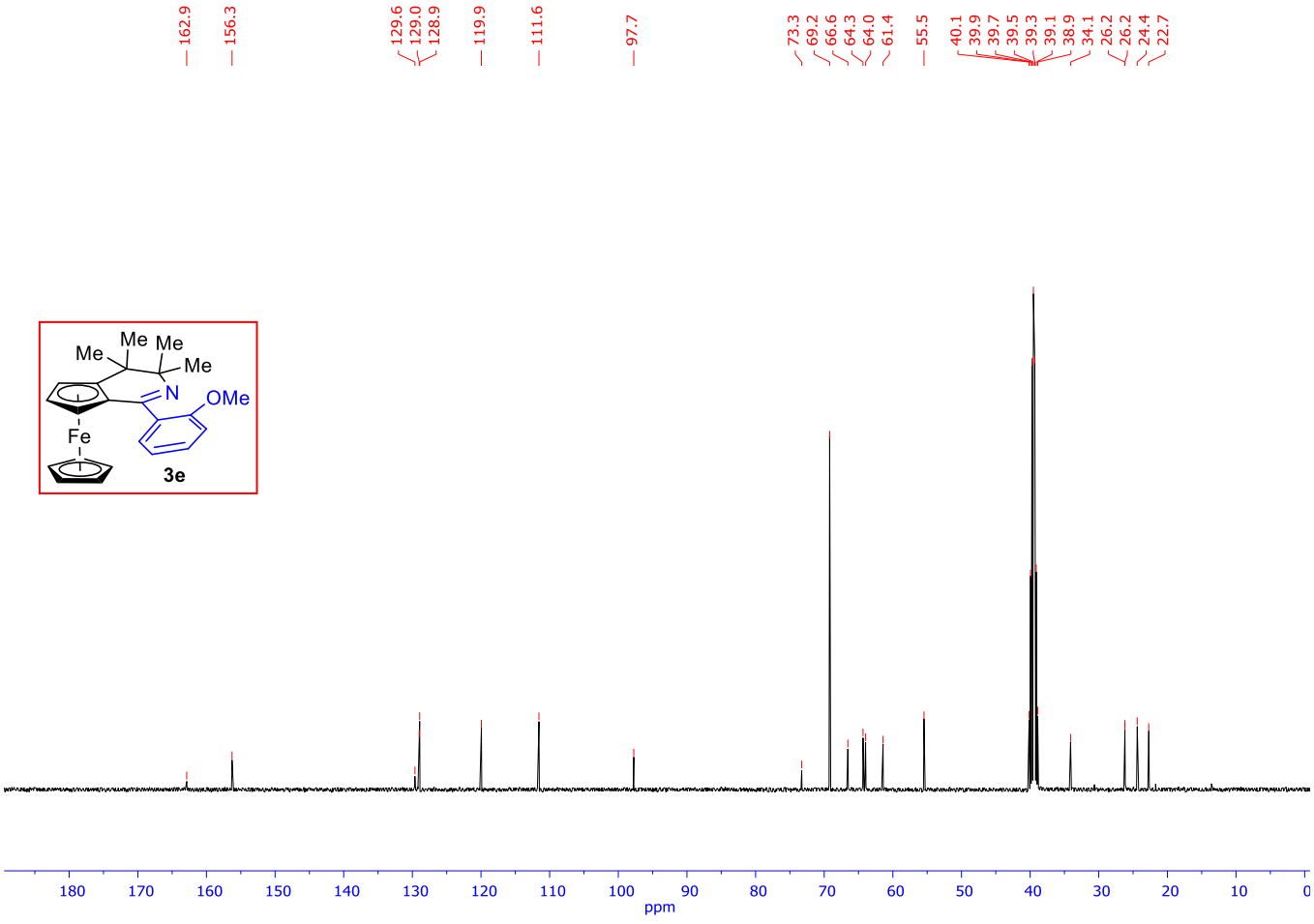


Figure S15. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3e**.

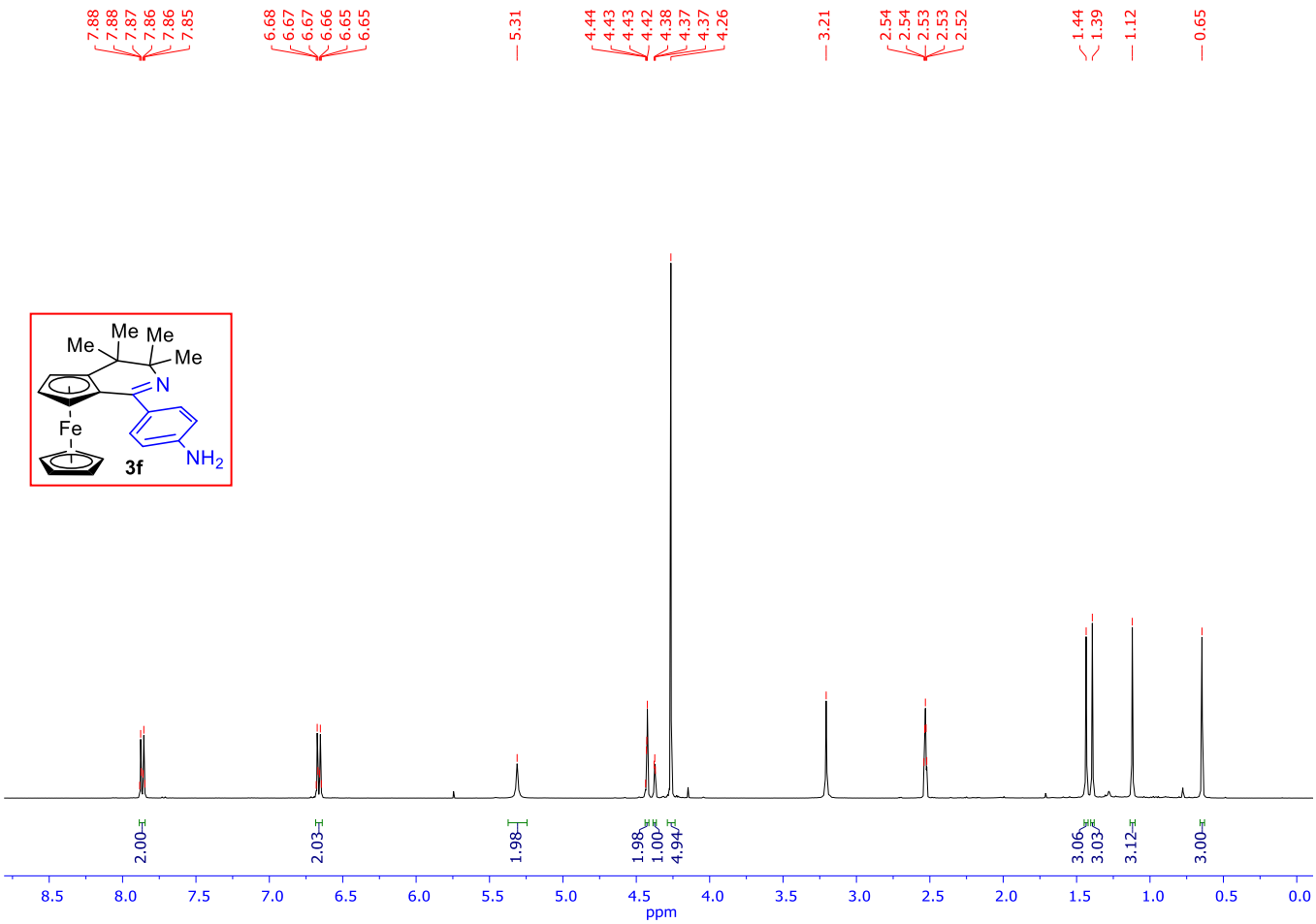


Figure S16. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3f**.

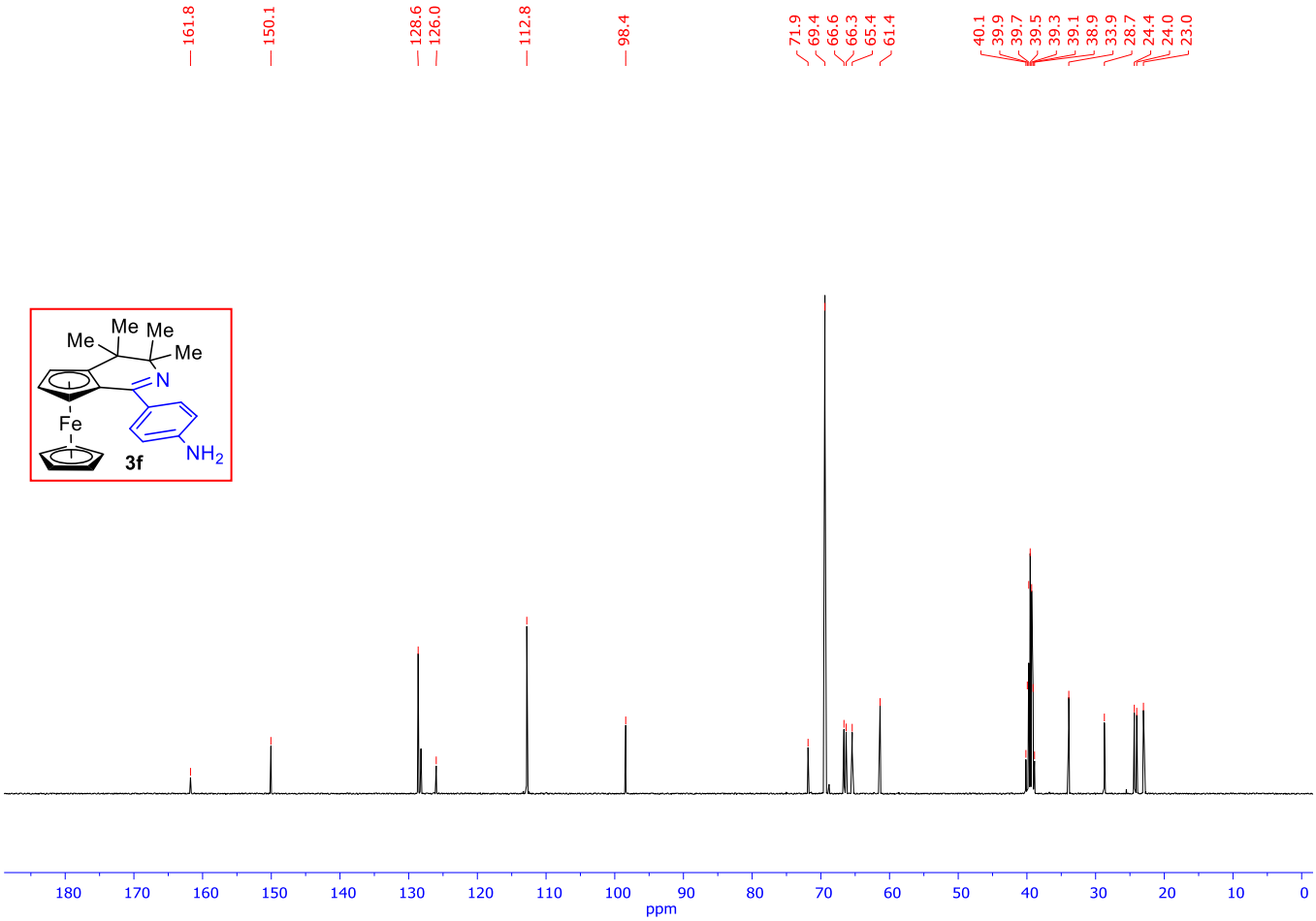


Figure S17. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3f**.

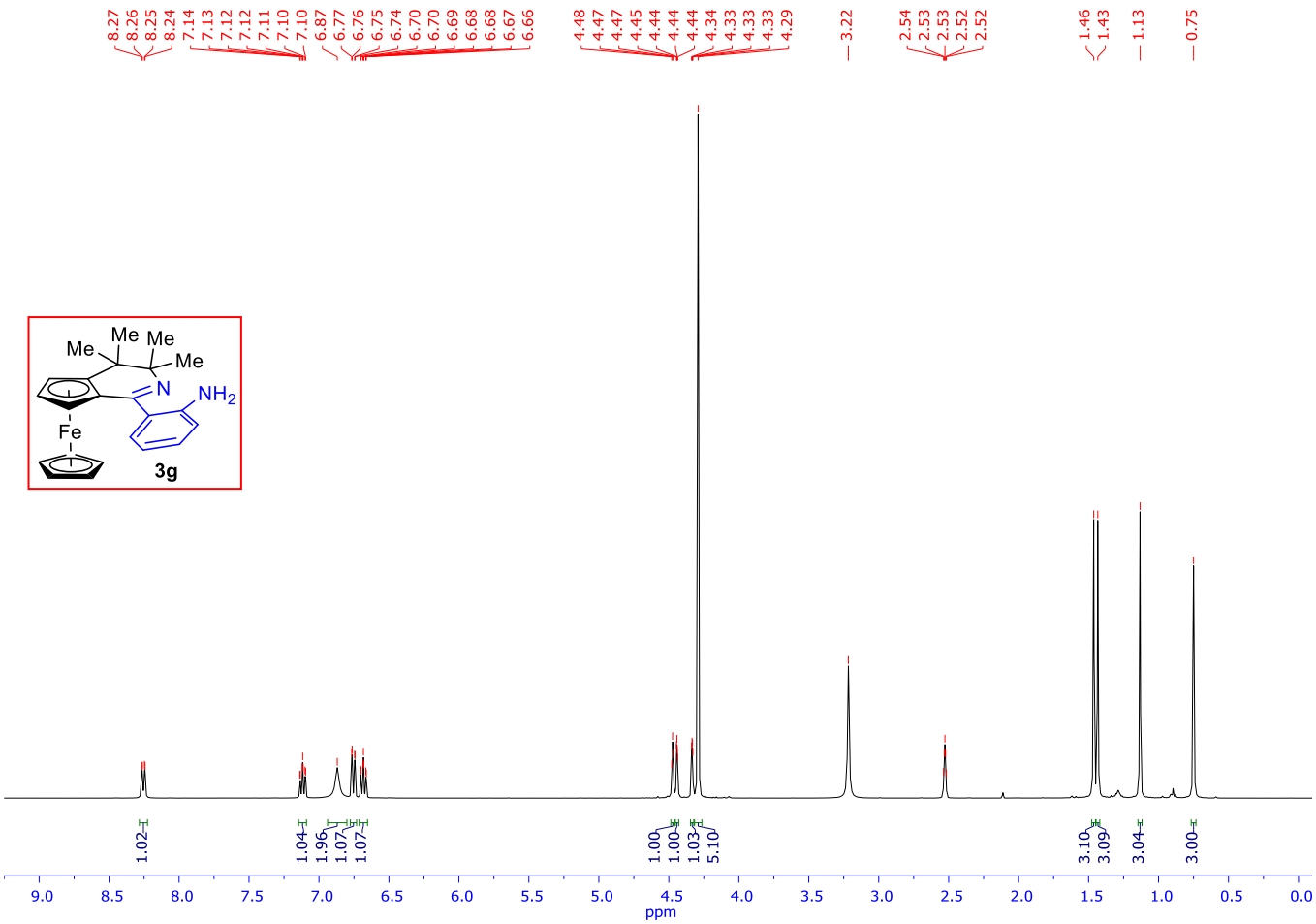


Figure S18. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3g**.

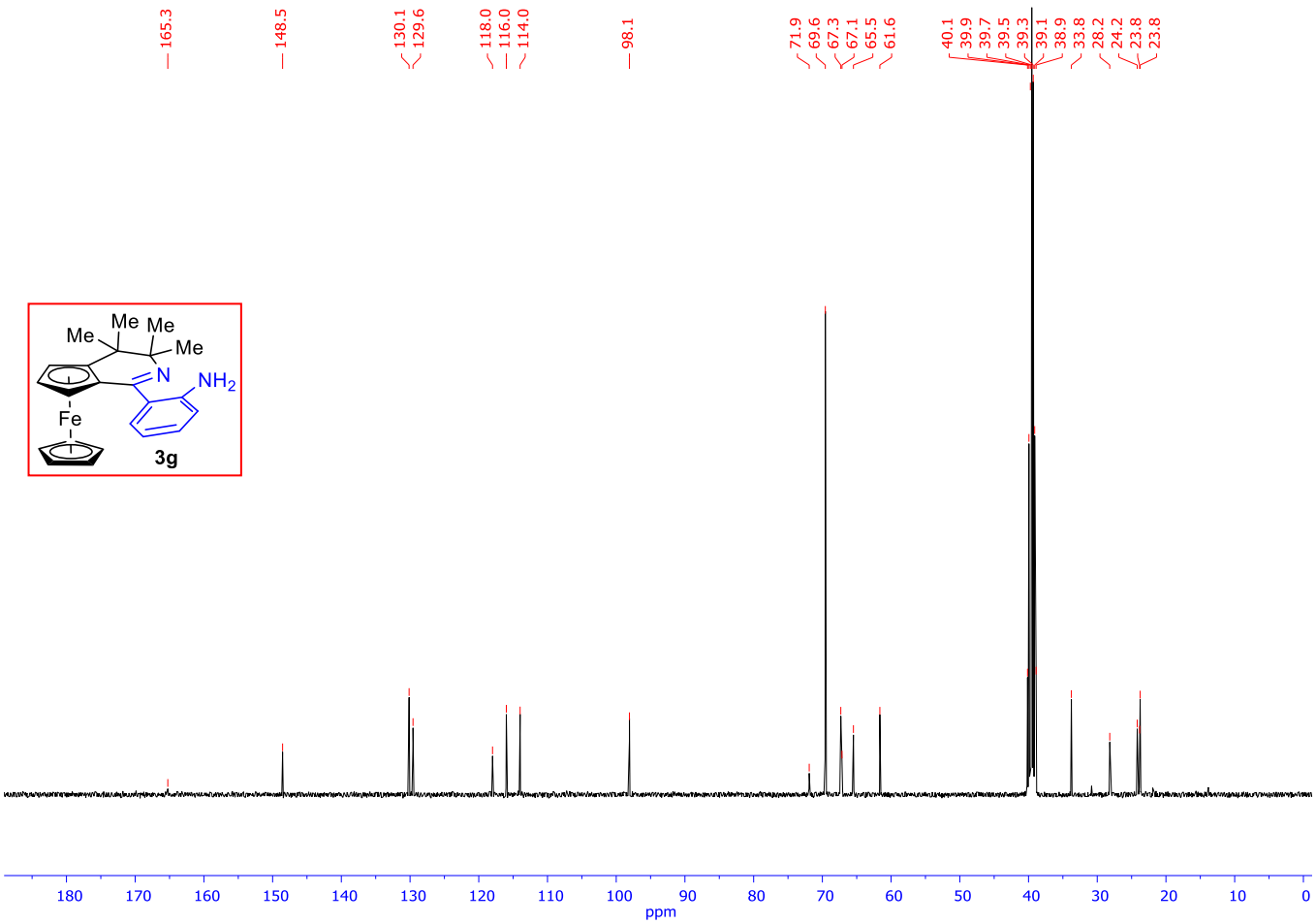


Figure S19. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3g**.

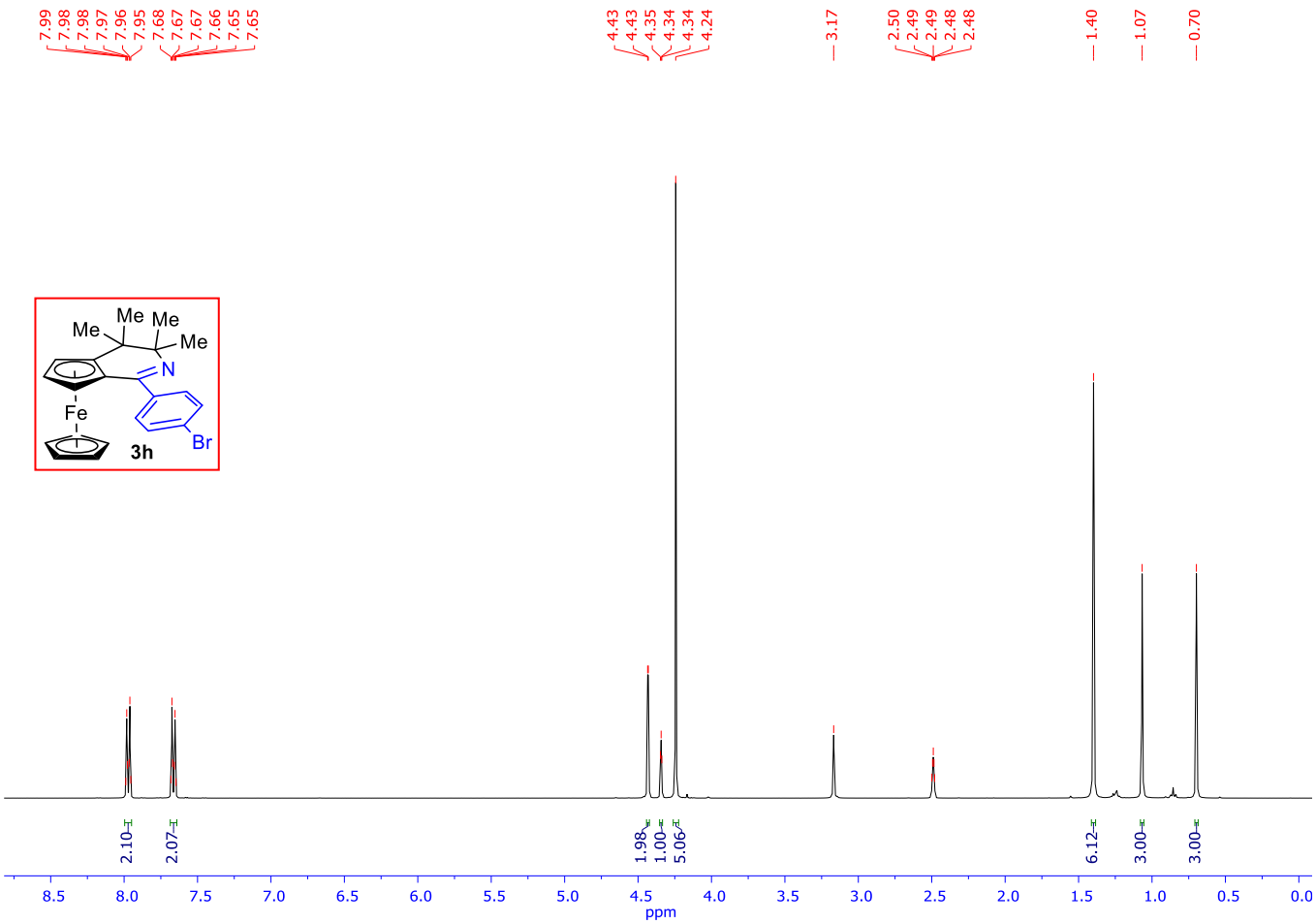


Figure S20. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3h**.

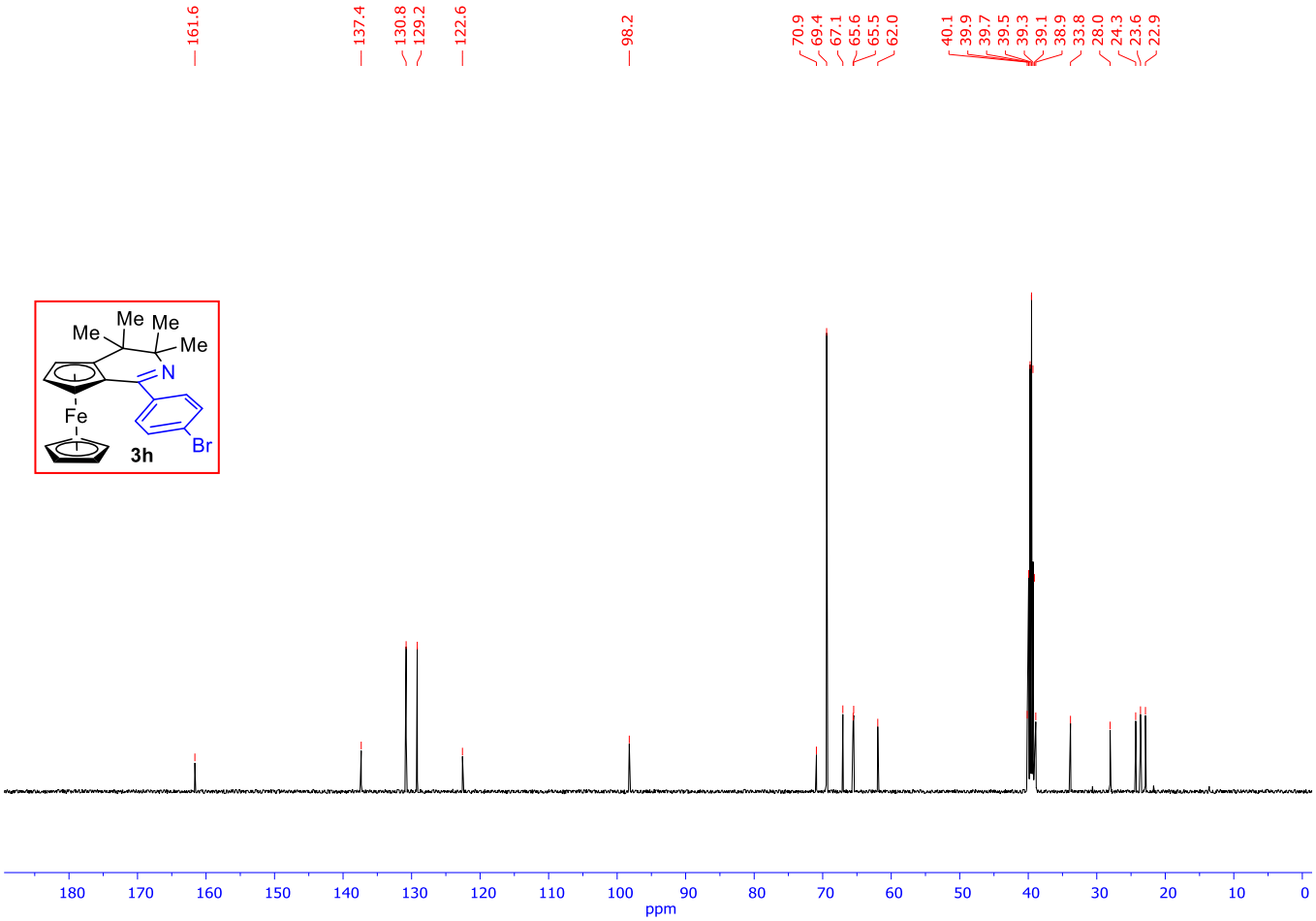


Figure S21. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3h**.

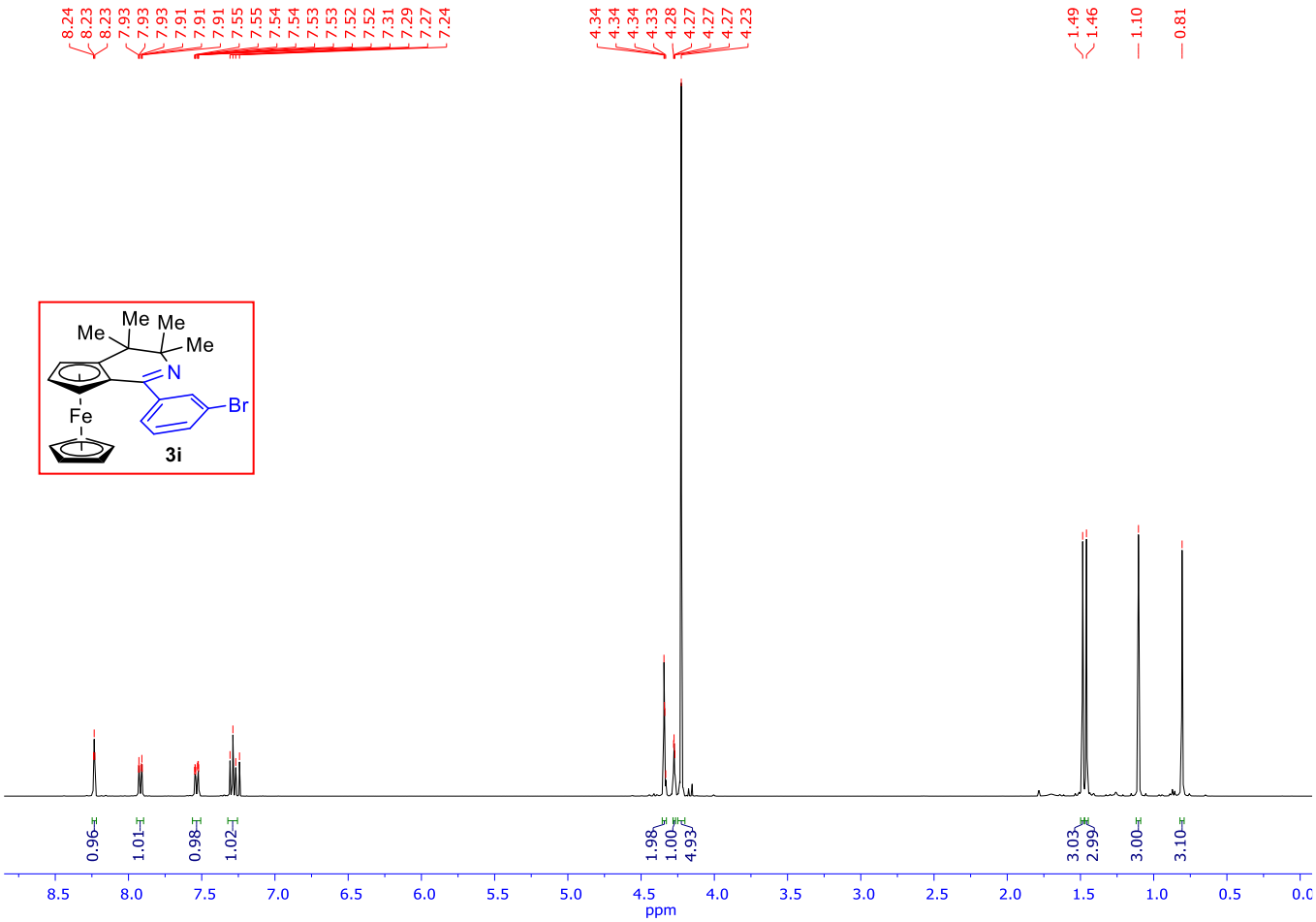


Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3i**.

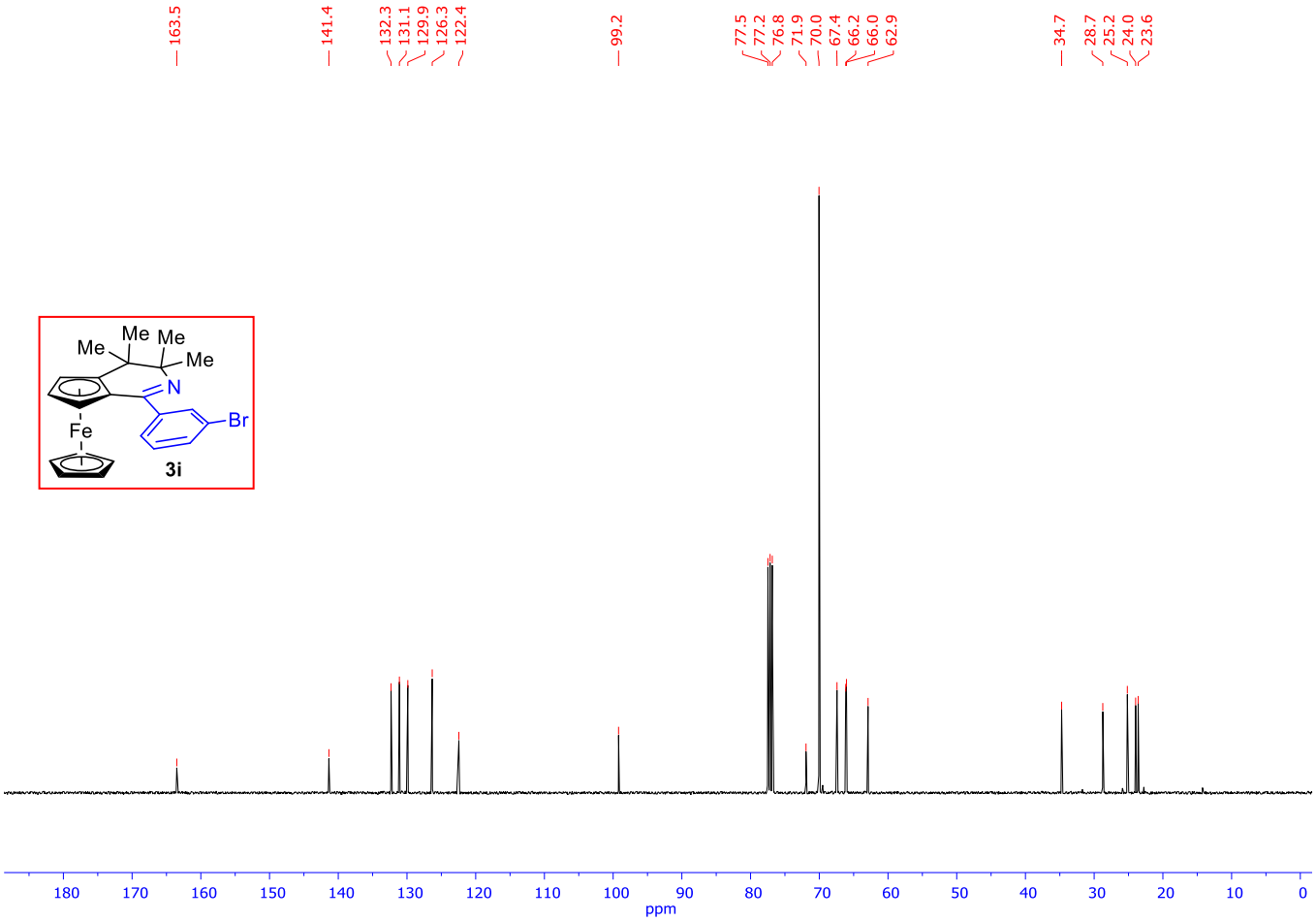


Figure S23. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3i**.

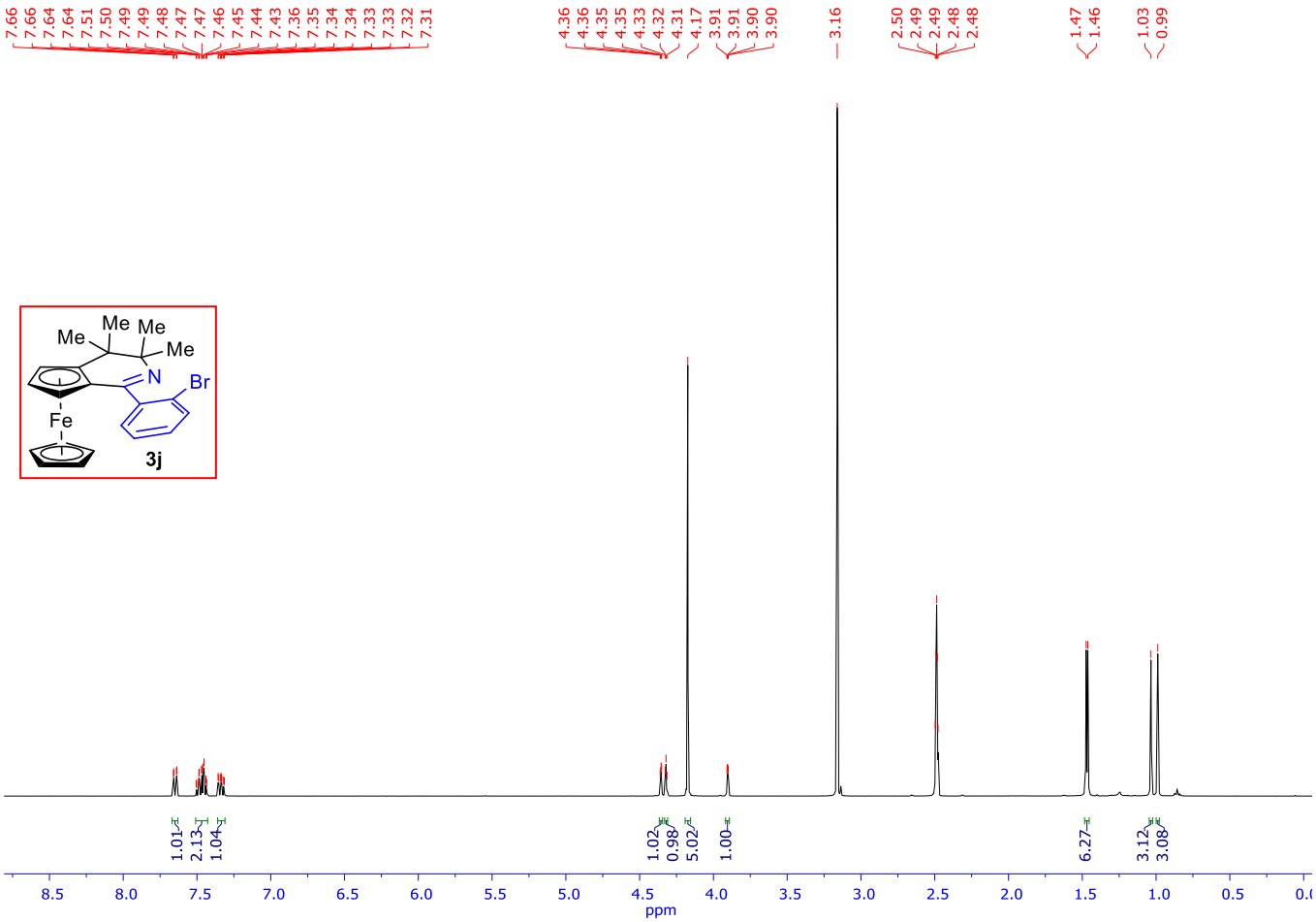


Figure S24. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3j**.

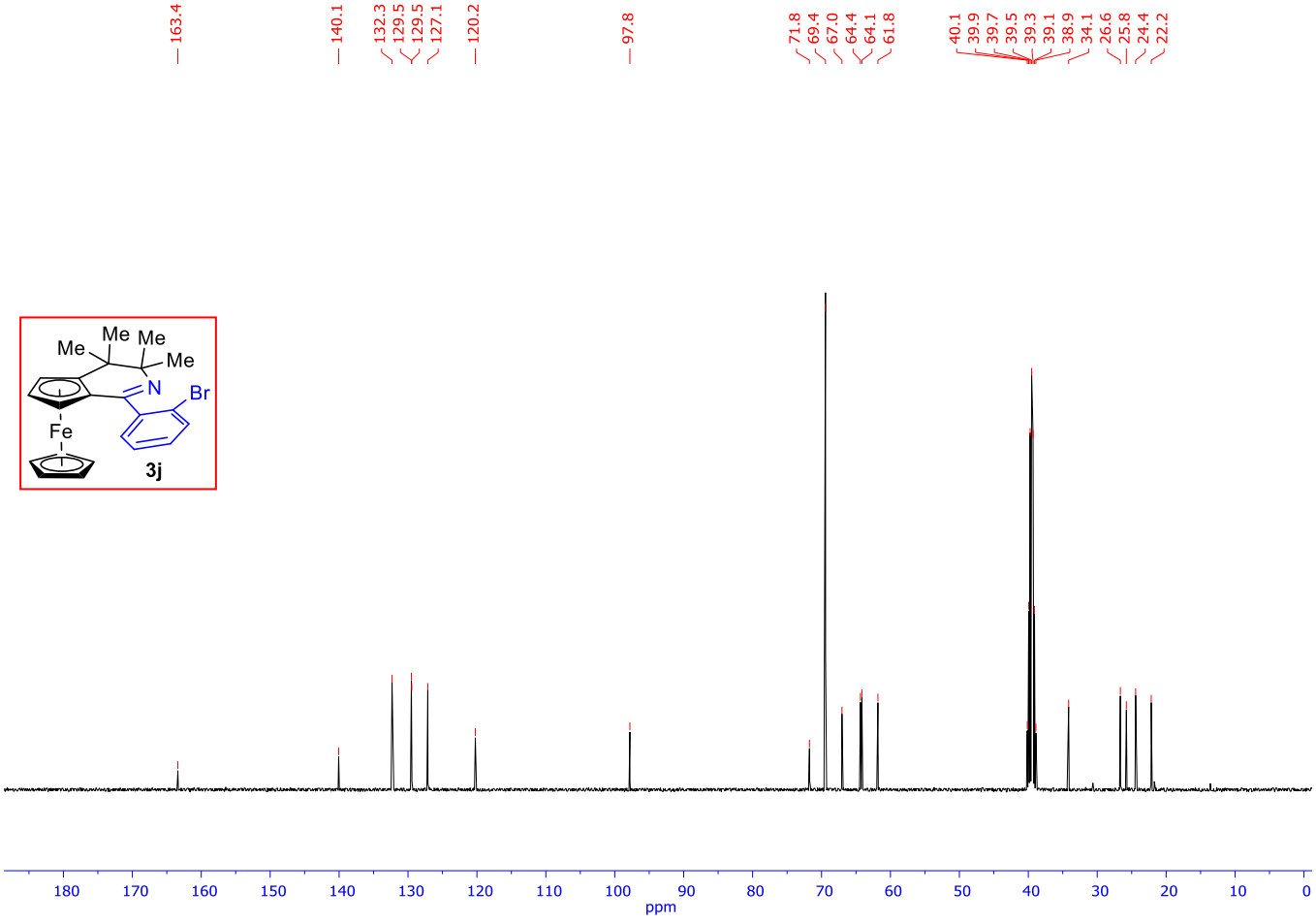


Figure S25. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3j**.

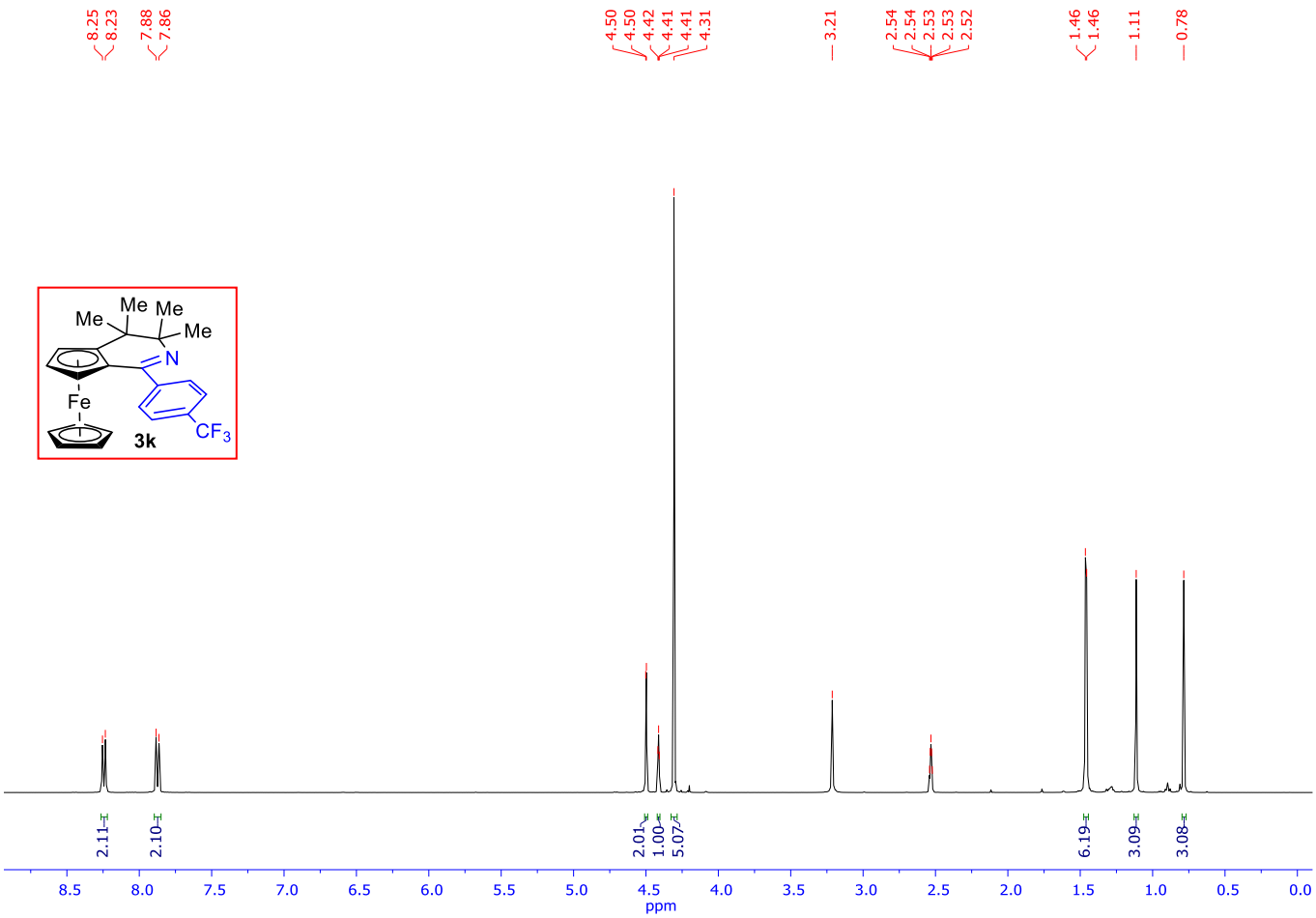


Figure S26. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3k**.

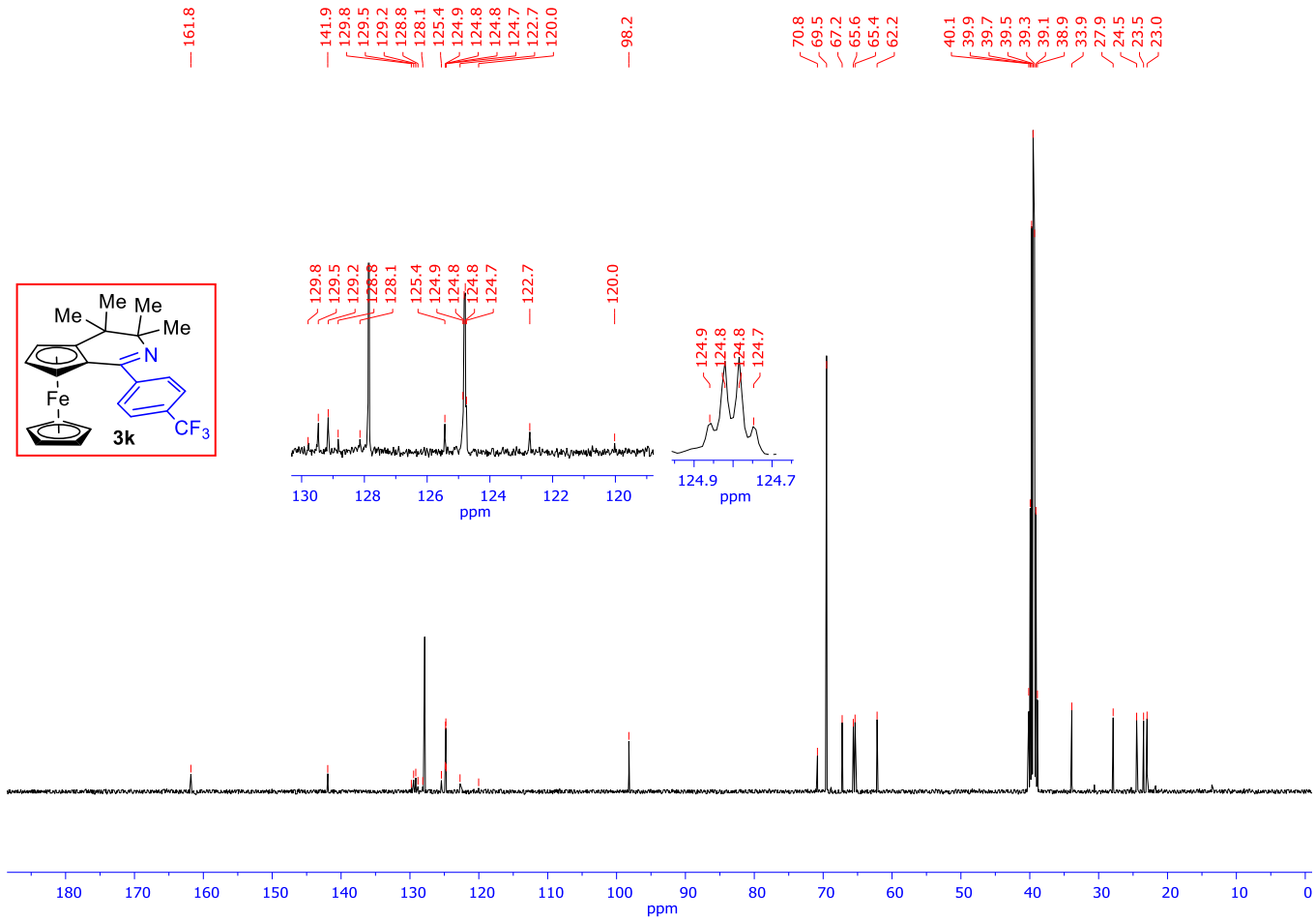


Figure S27. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3k**.

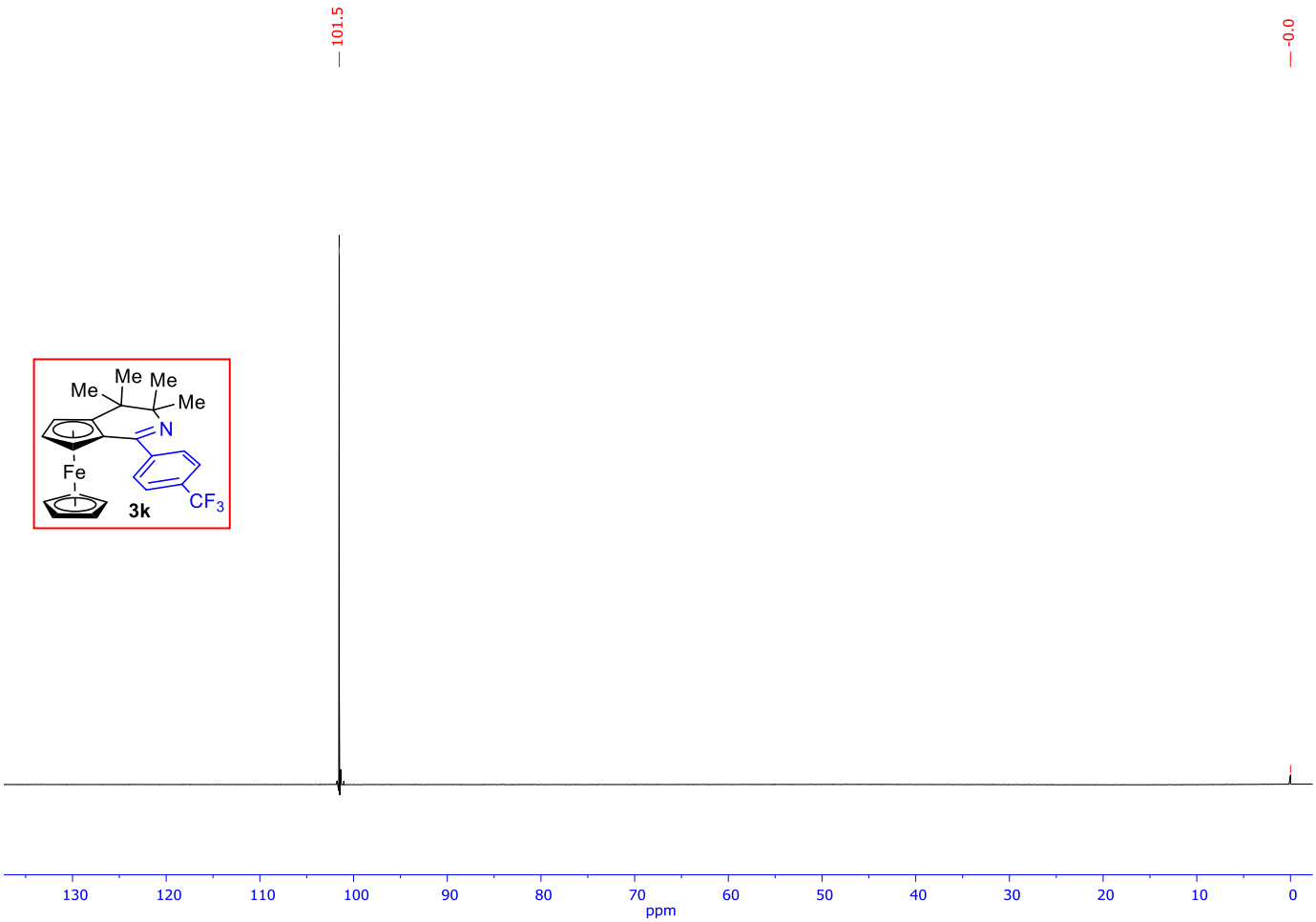


Figure S28. ^{19}F NMR spectrum (377 MHz, $CDCl_3$) of **3k**.

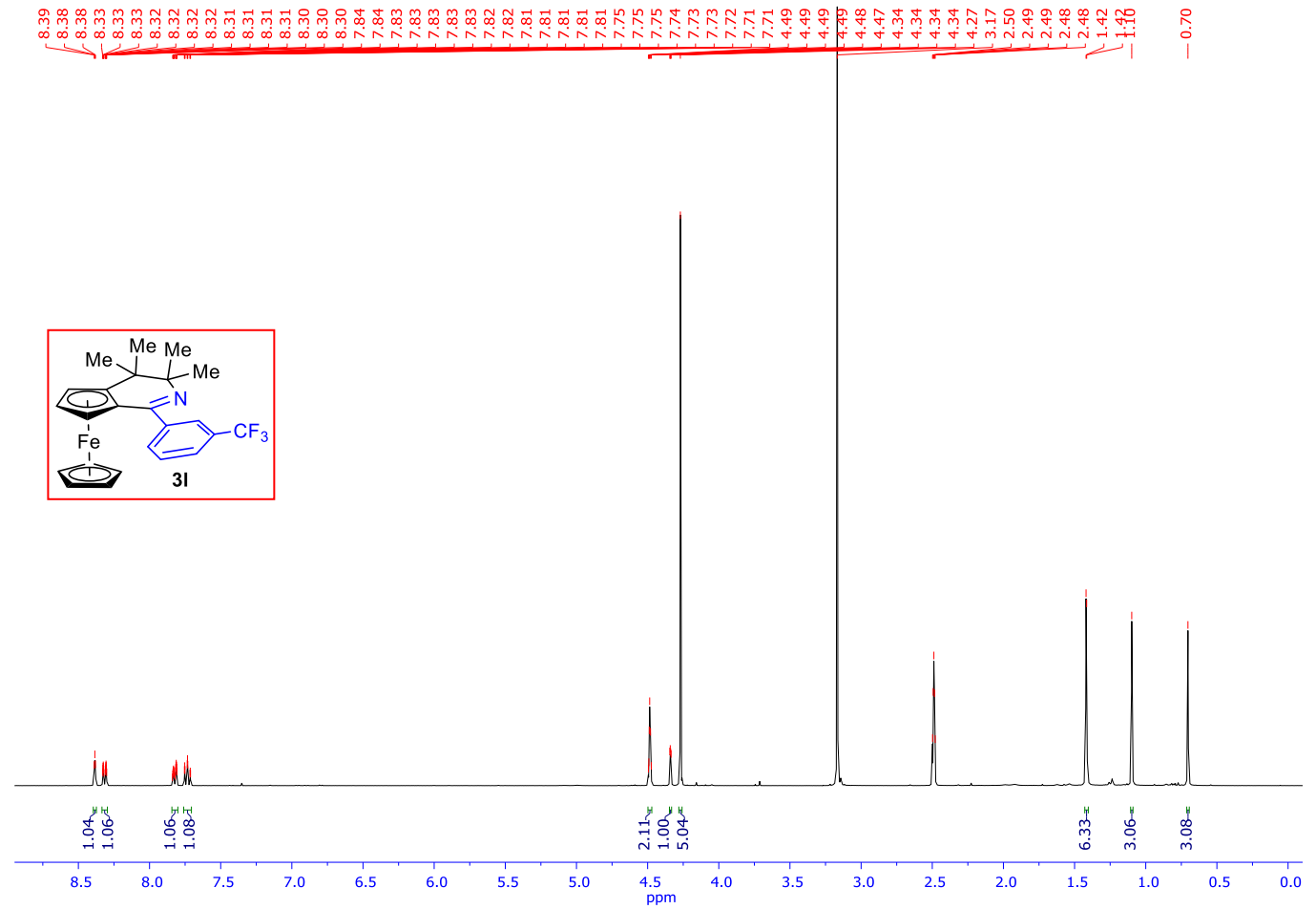


Figure S29. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3l**.

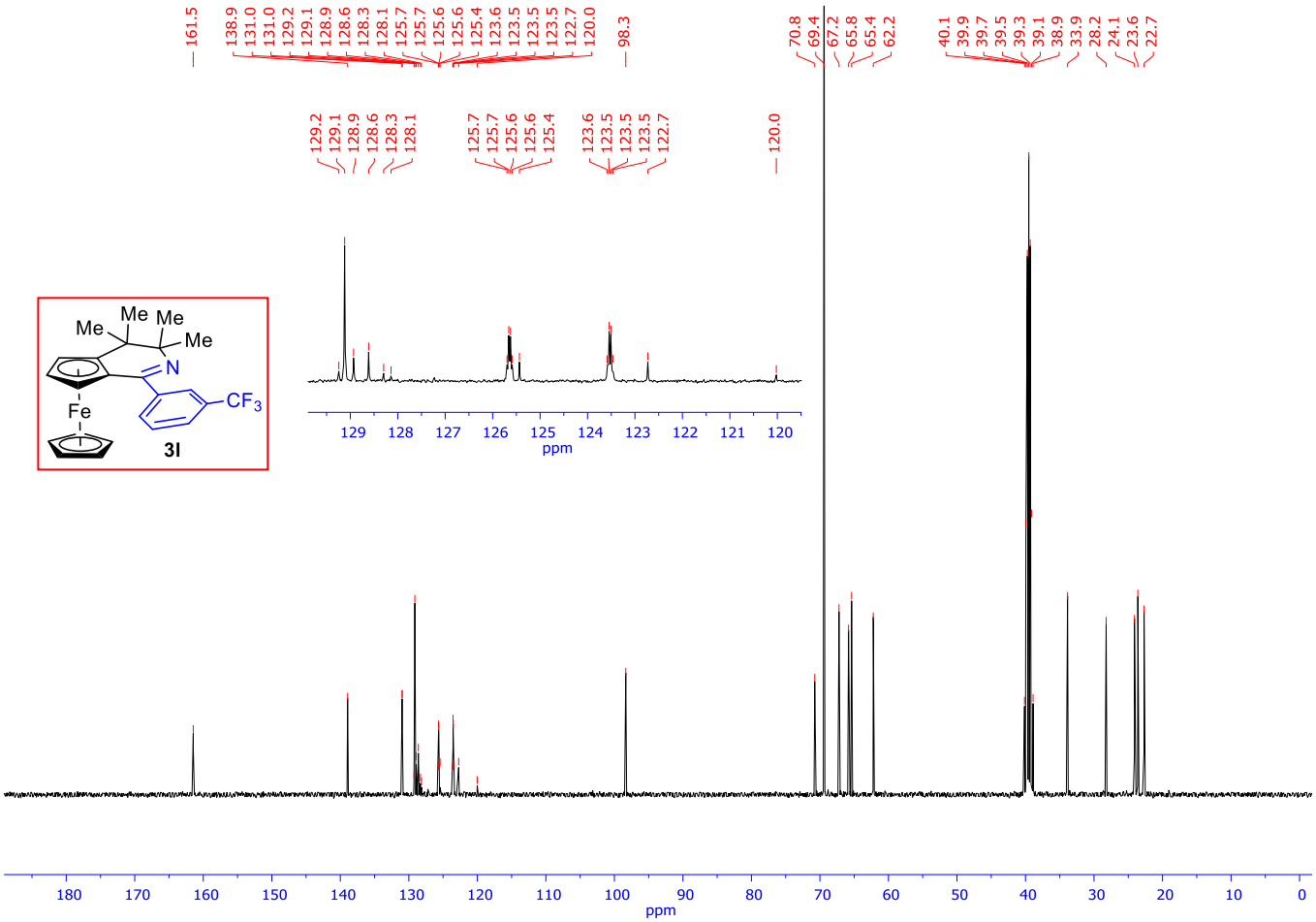


Figure S30. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3l**.

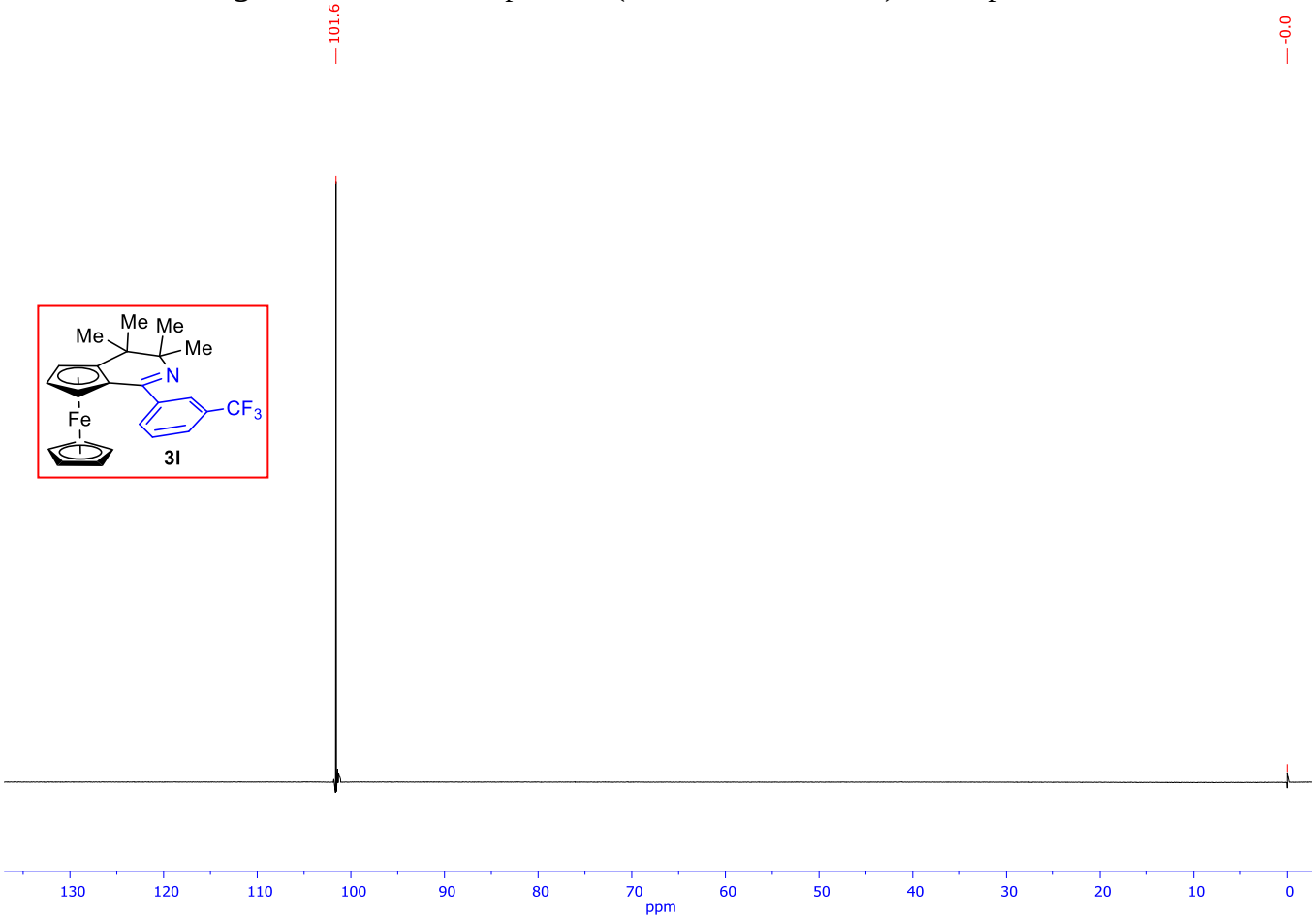


Figure S31. ^{19}F NMR spectrum (377 MHz, $CDCl_3$) of **3k**.

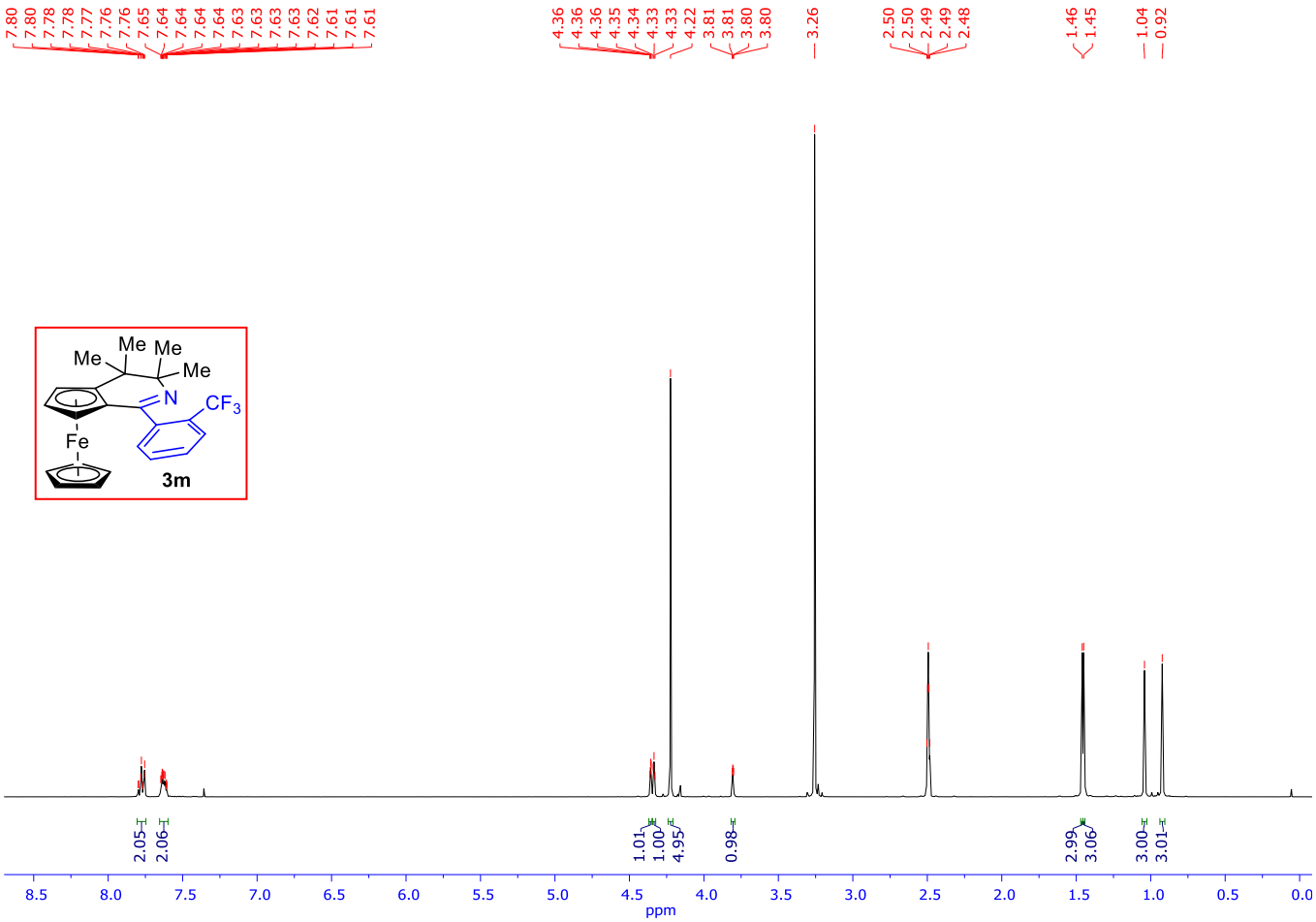


Figure S32. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3m**.

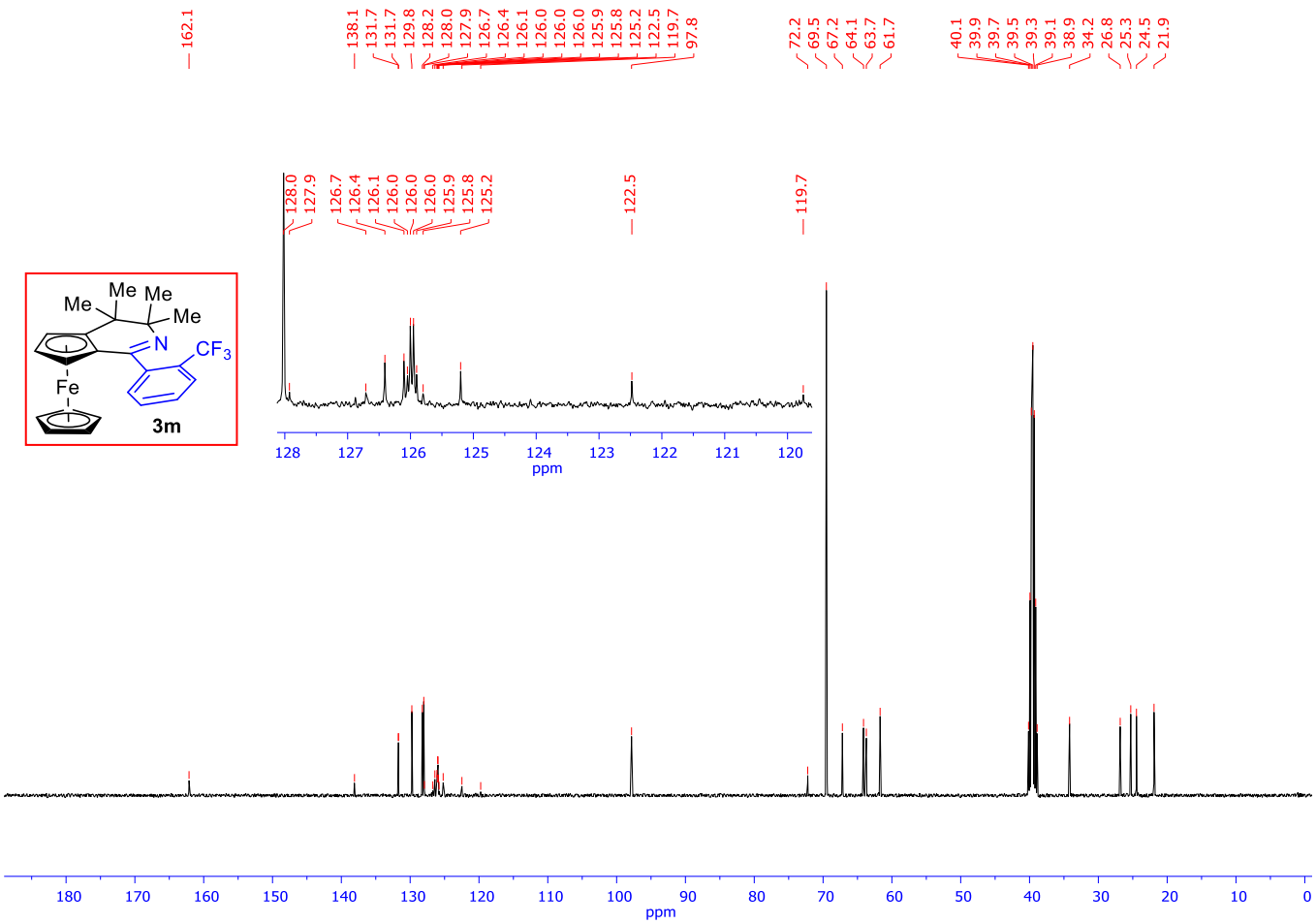


Figure S33. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3m**.

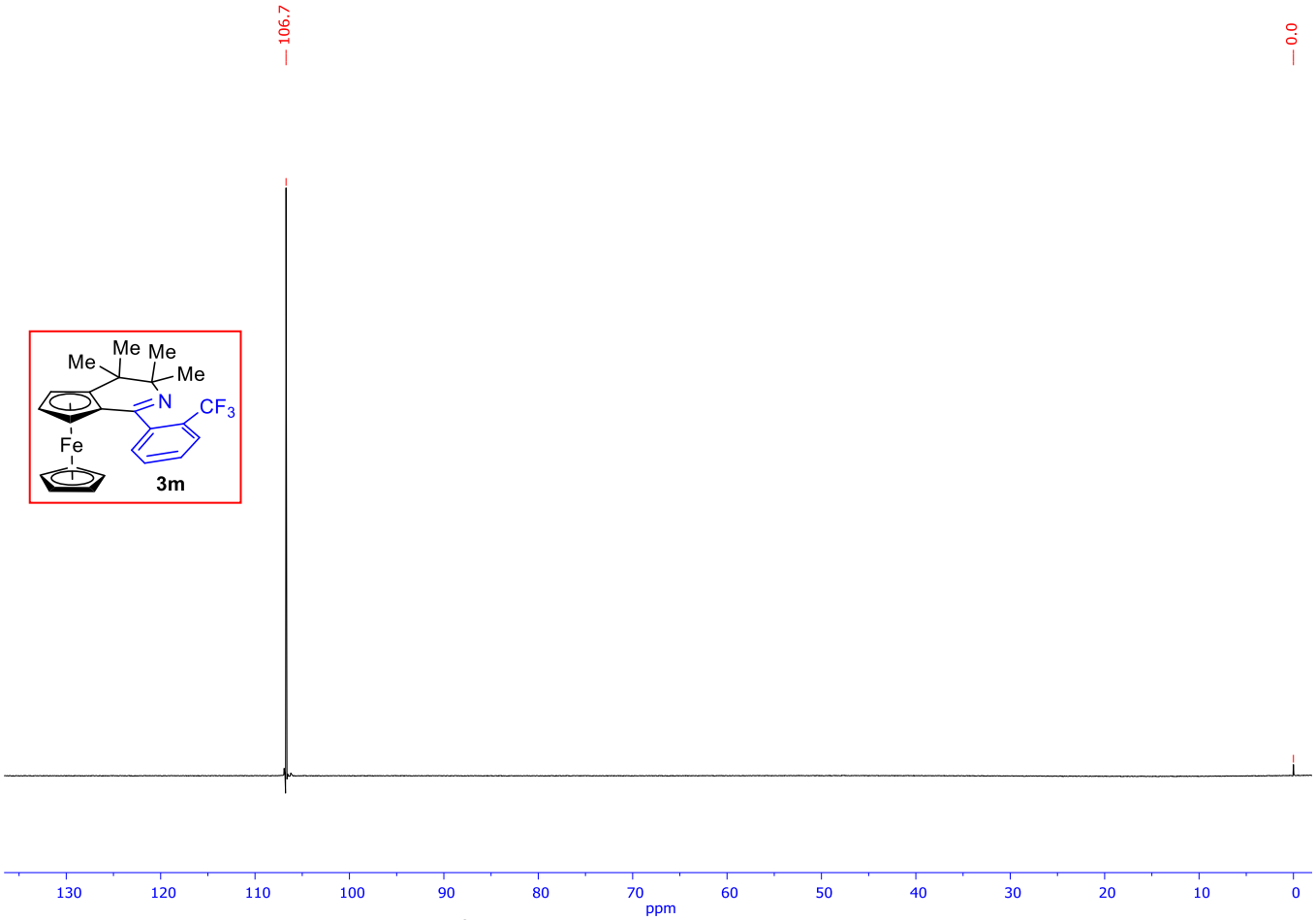


Figure S34. ^{19}F NMR spectrum (377 MHz, $CDCl_3$) of **3m**.

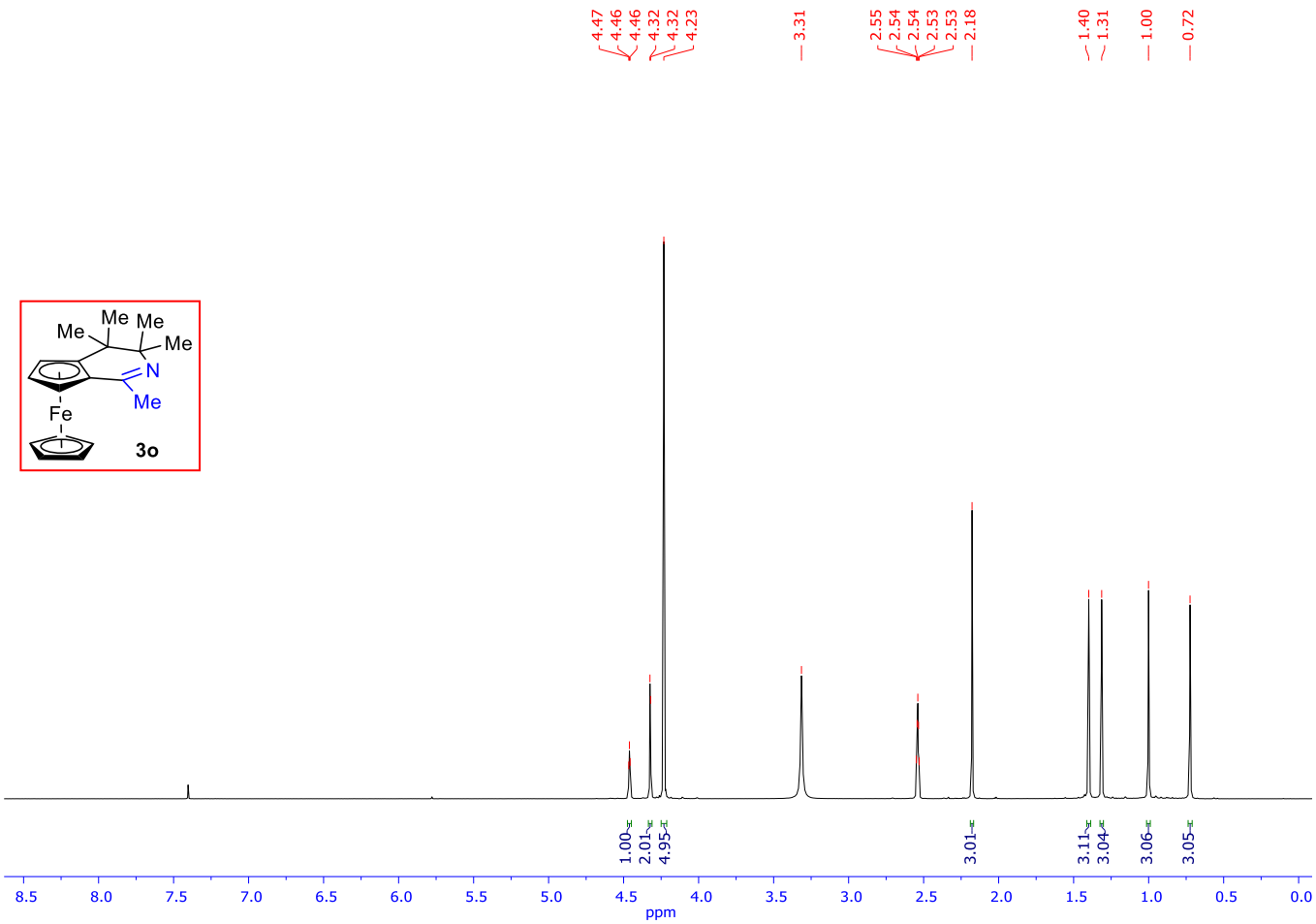


Figure S35. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3o**.

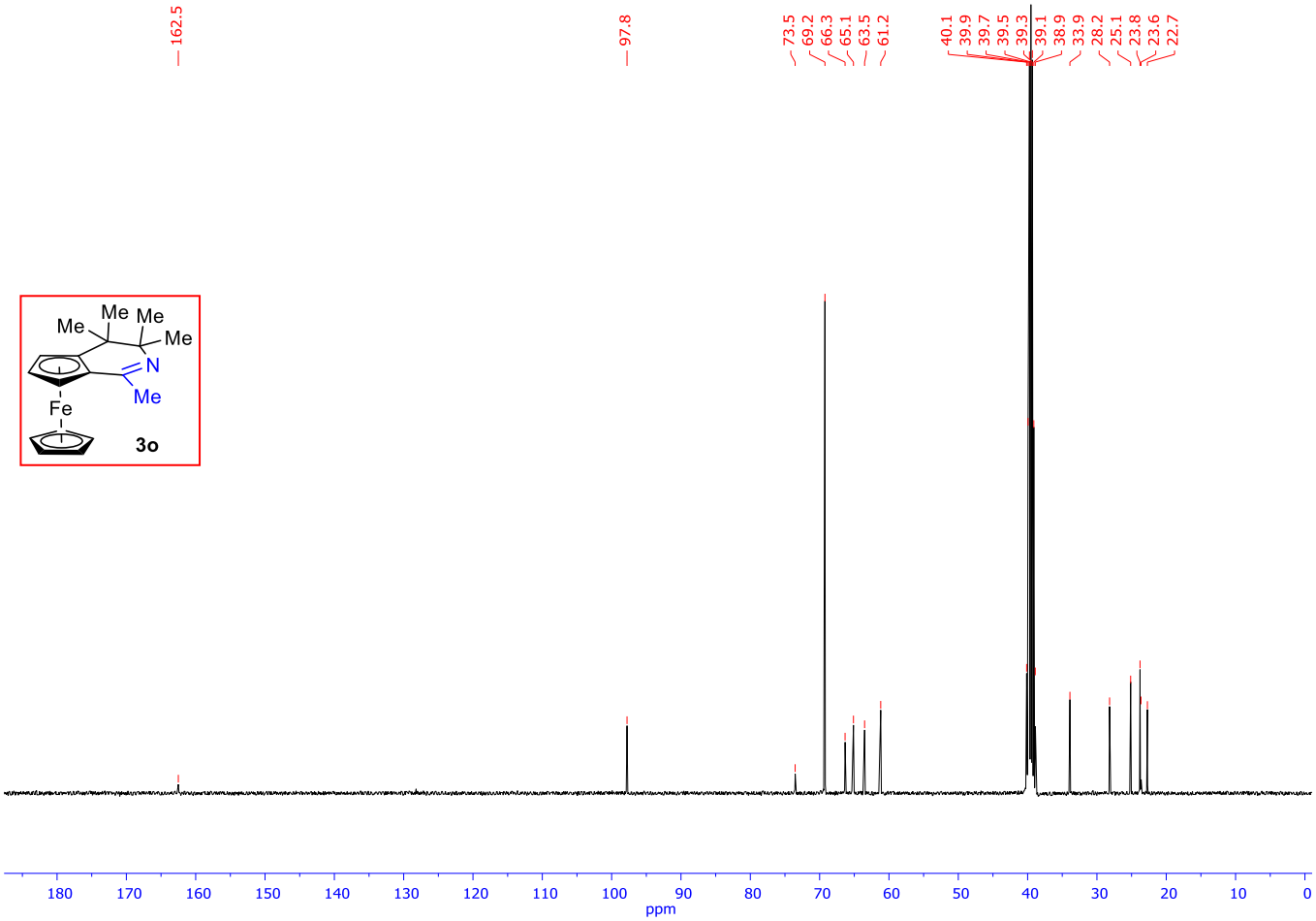


Figure S36. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **3o**.

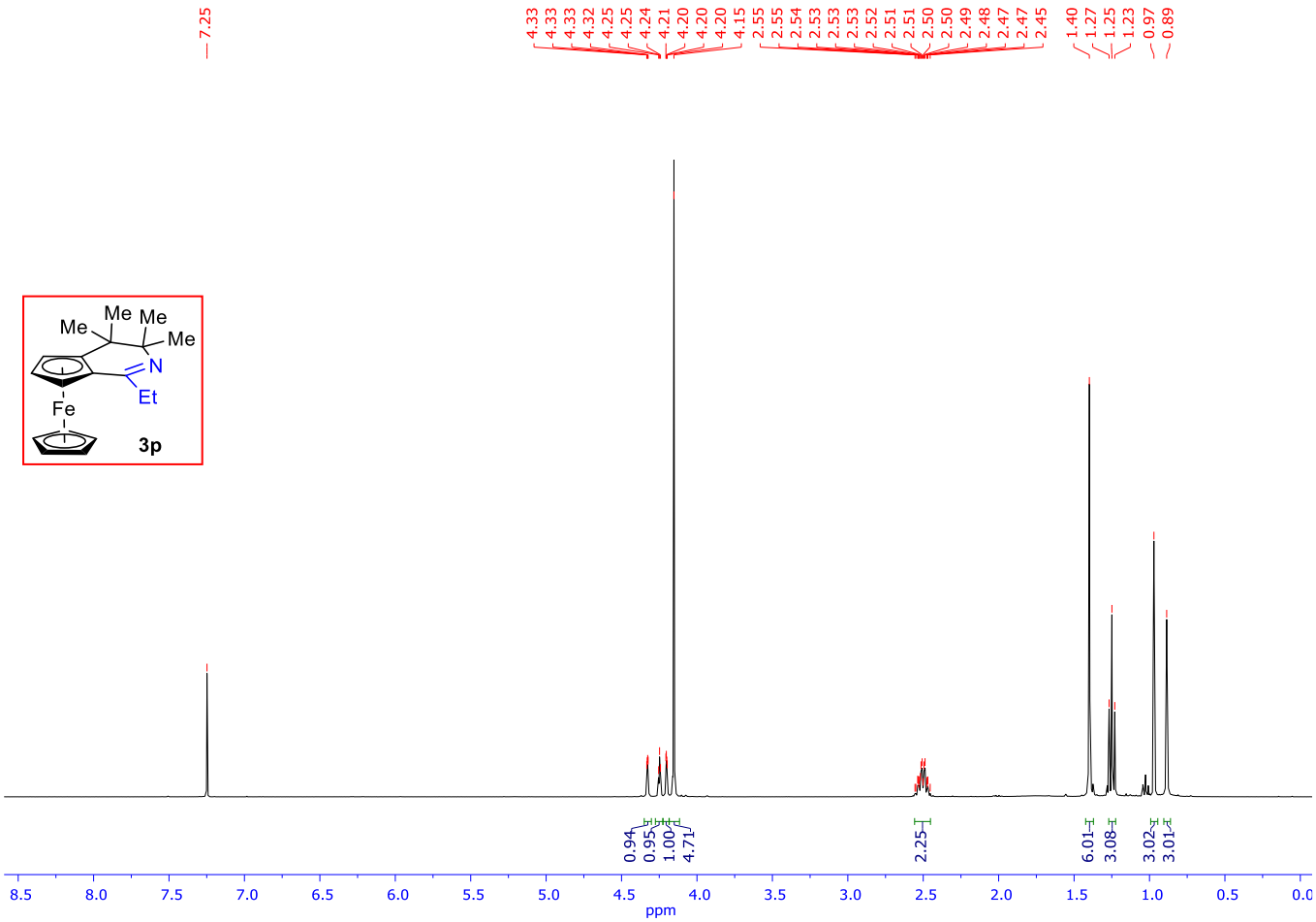


Figure S37. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3p**.

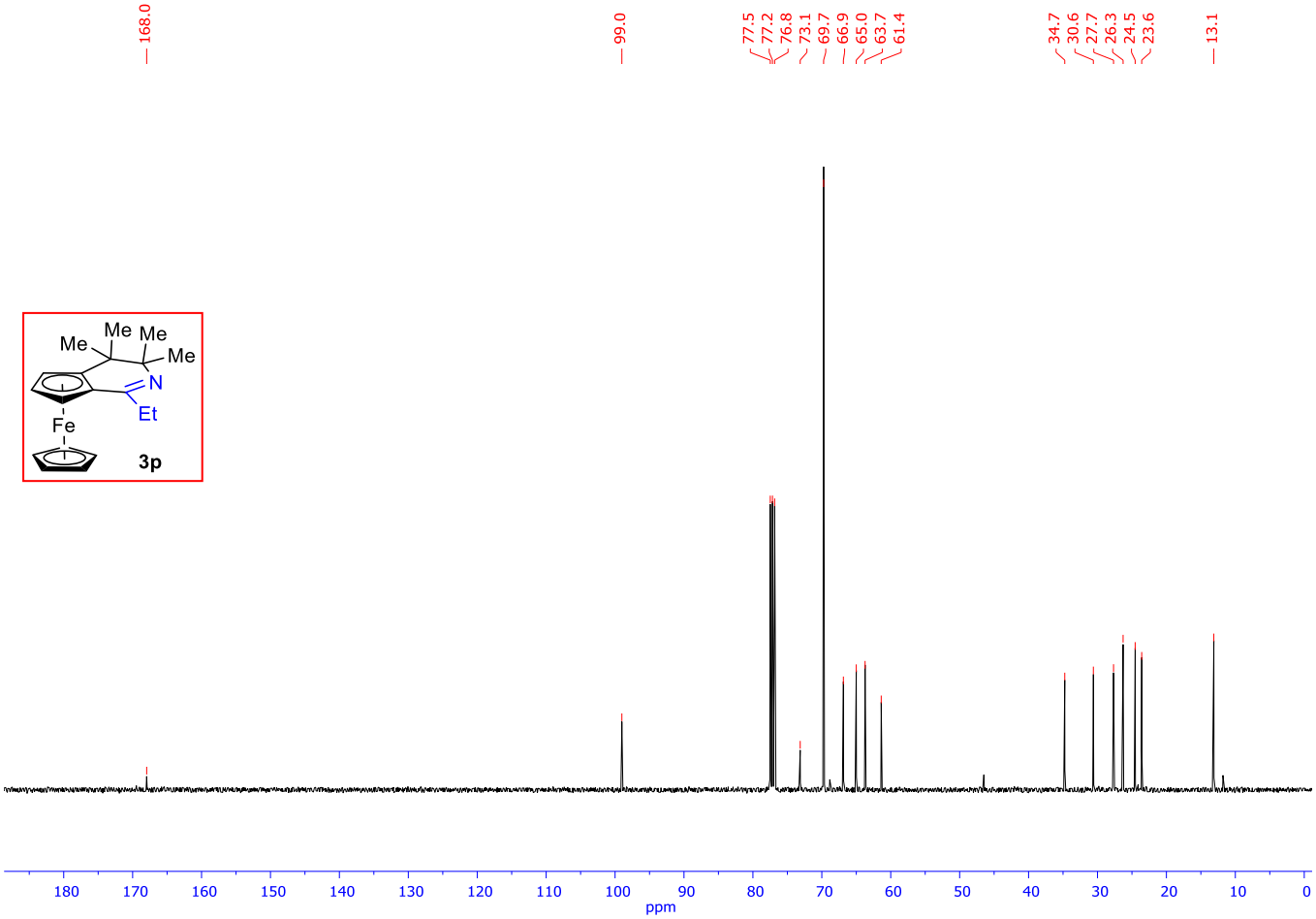


Figure S38. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3p**.

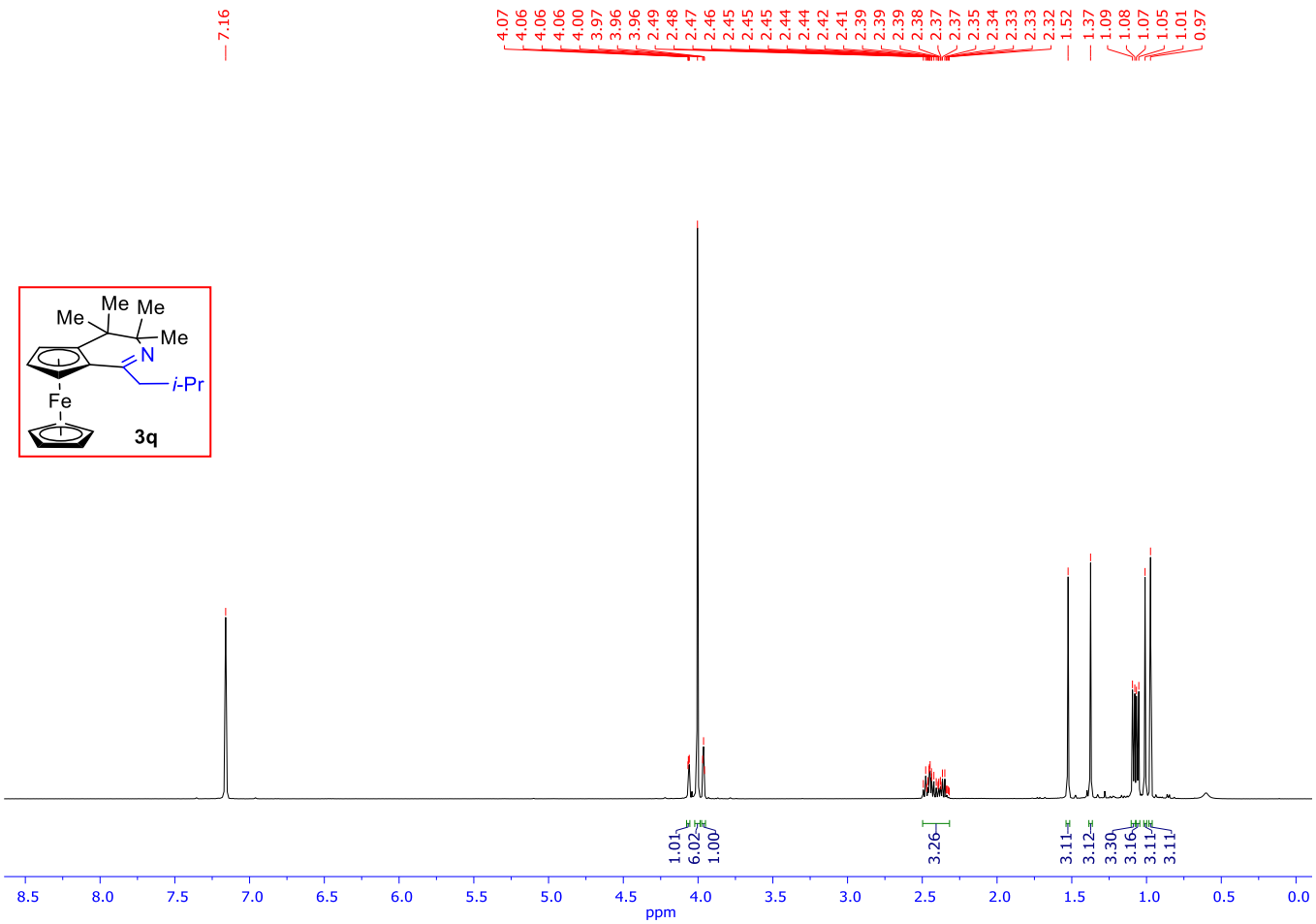


Figure S39. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **3q**.

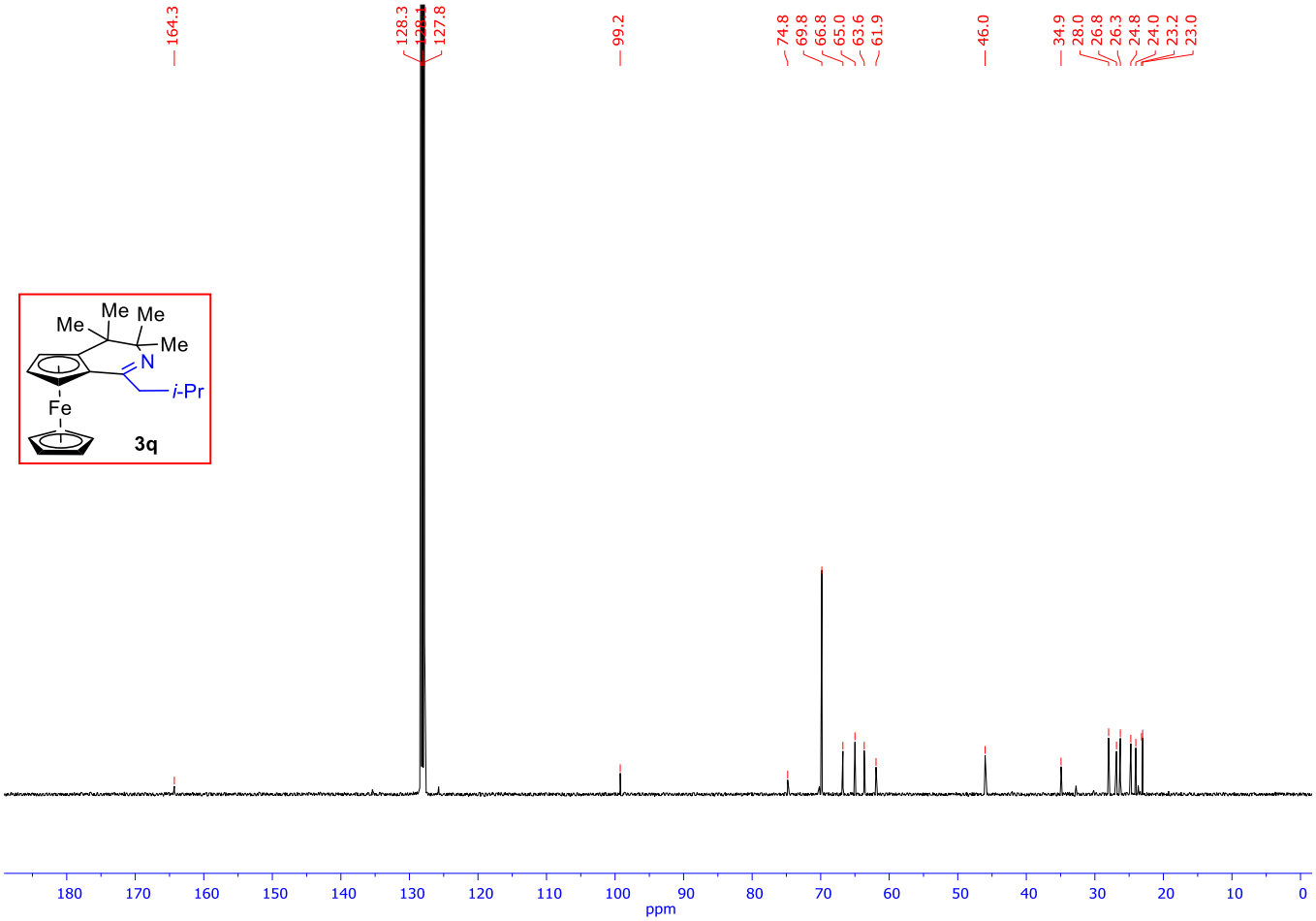


Figure S40. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **3q**.

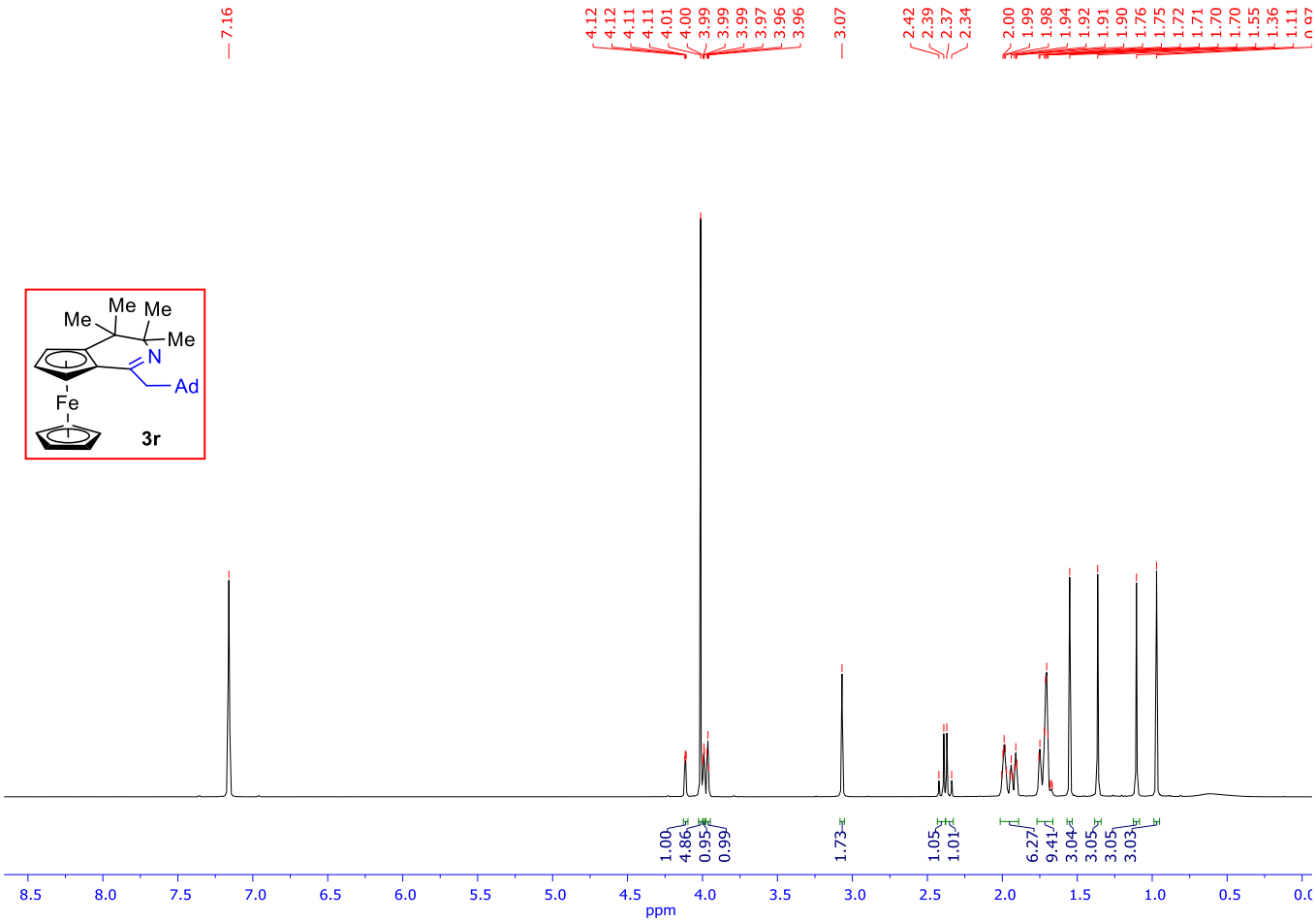


Figure S41 . ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **3r**.

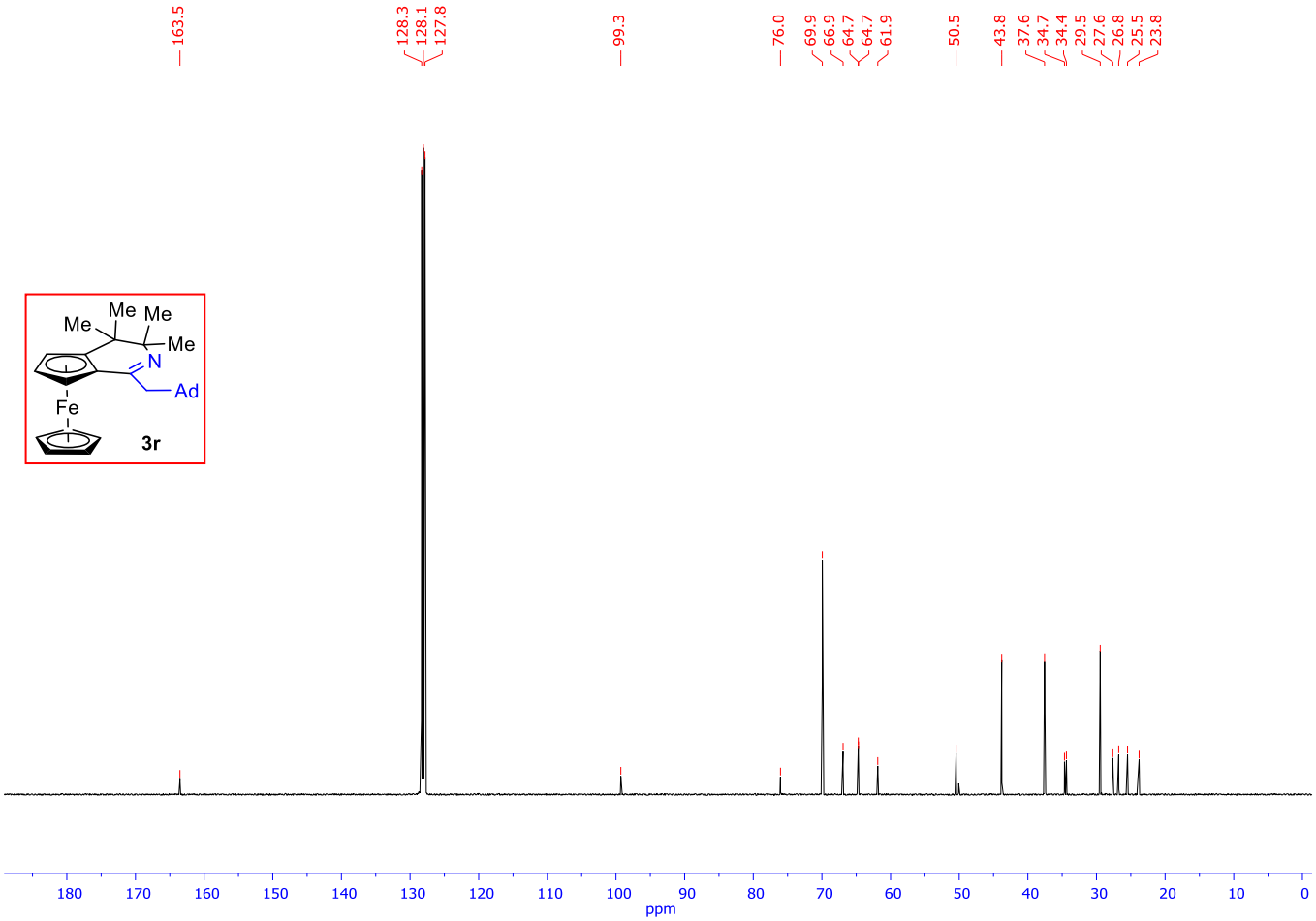


Figure S42. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **3r**.

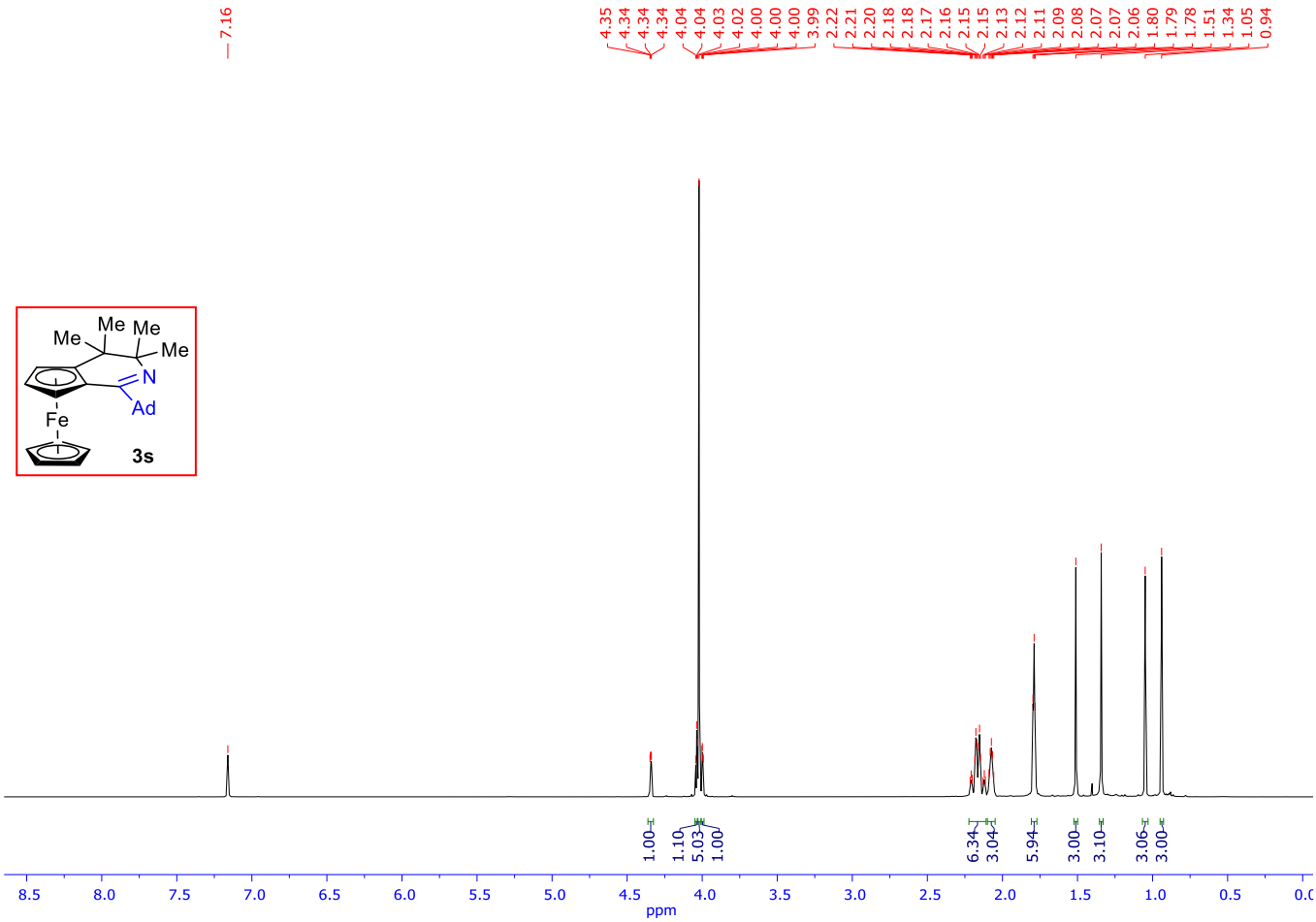


Figure S43. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **3s**.

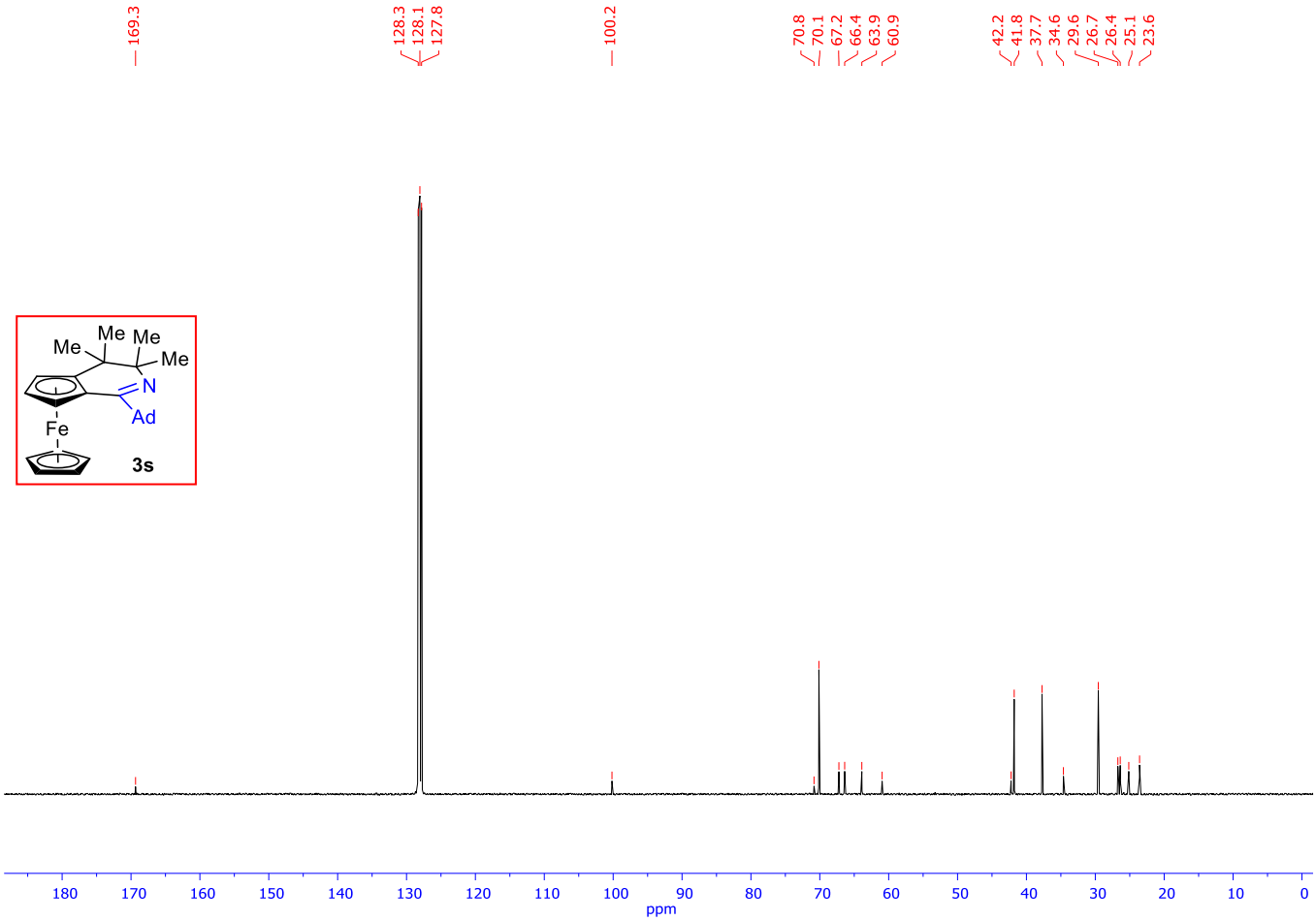


Figure S44. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **3s**.

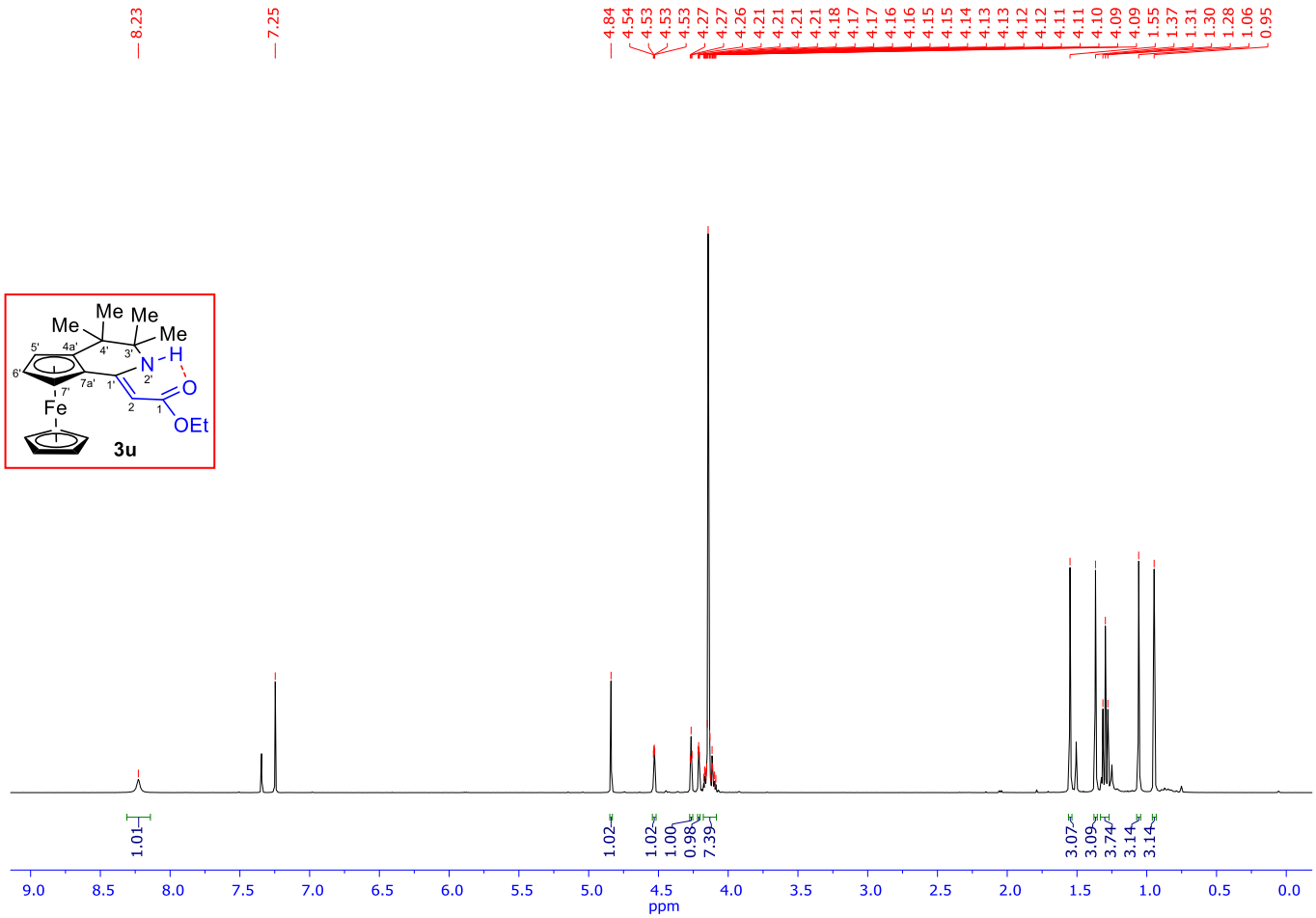


Figure S45. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3u**.

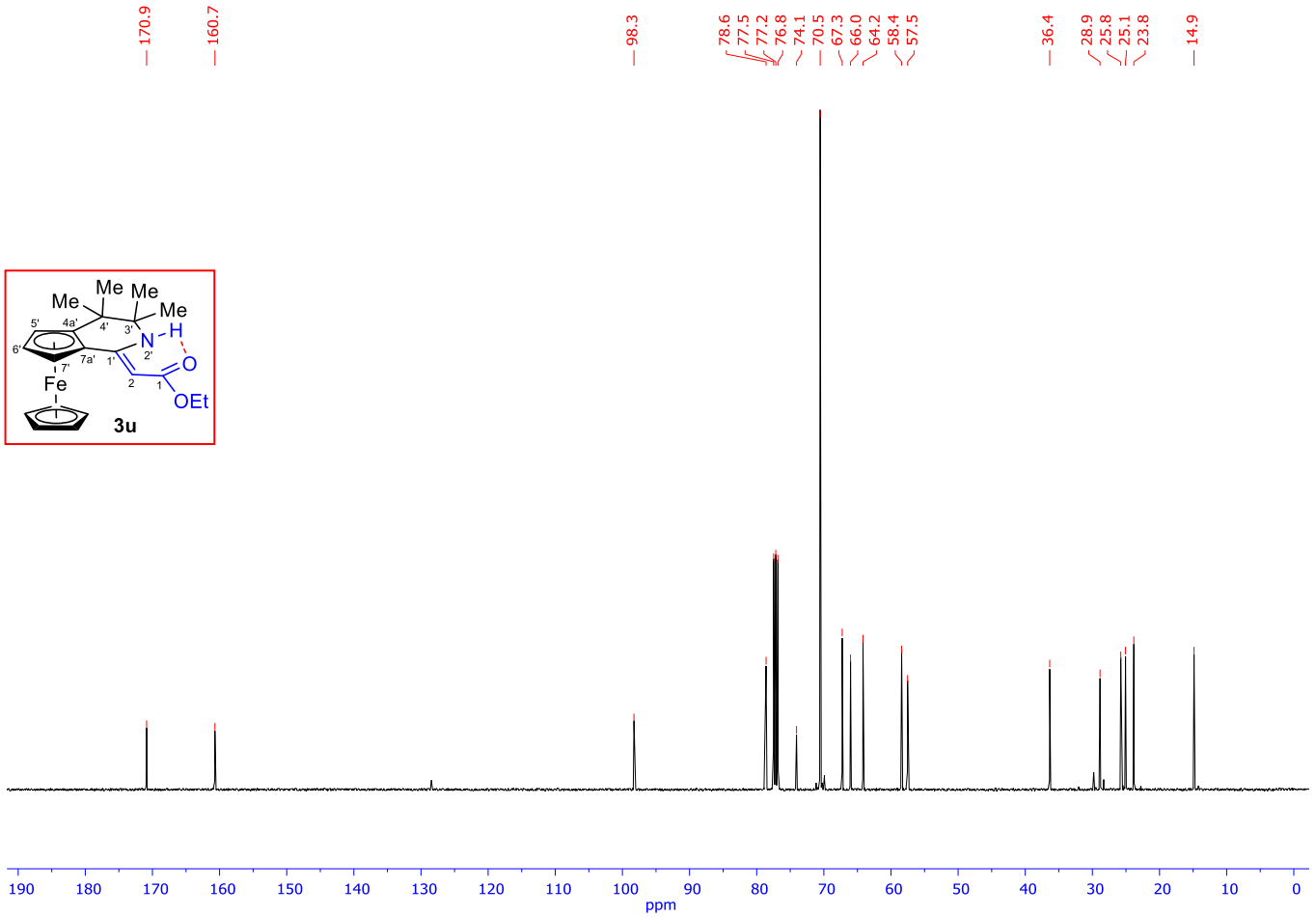


Figure S46. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3u**.

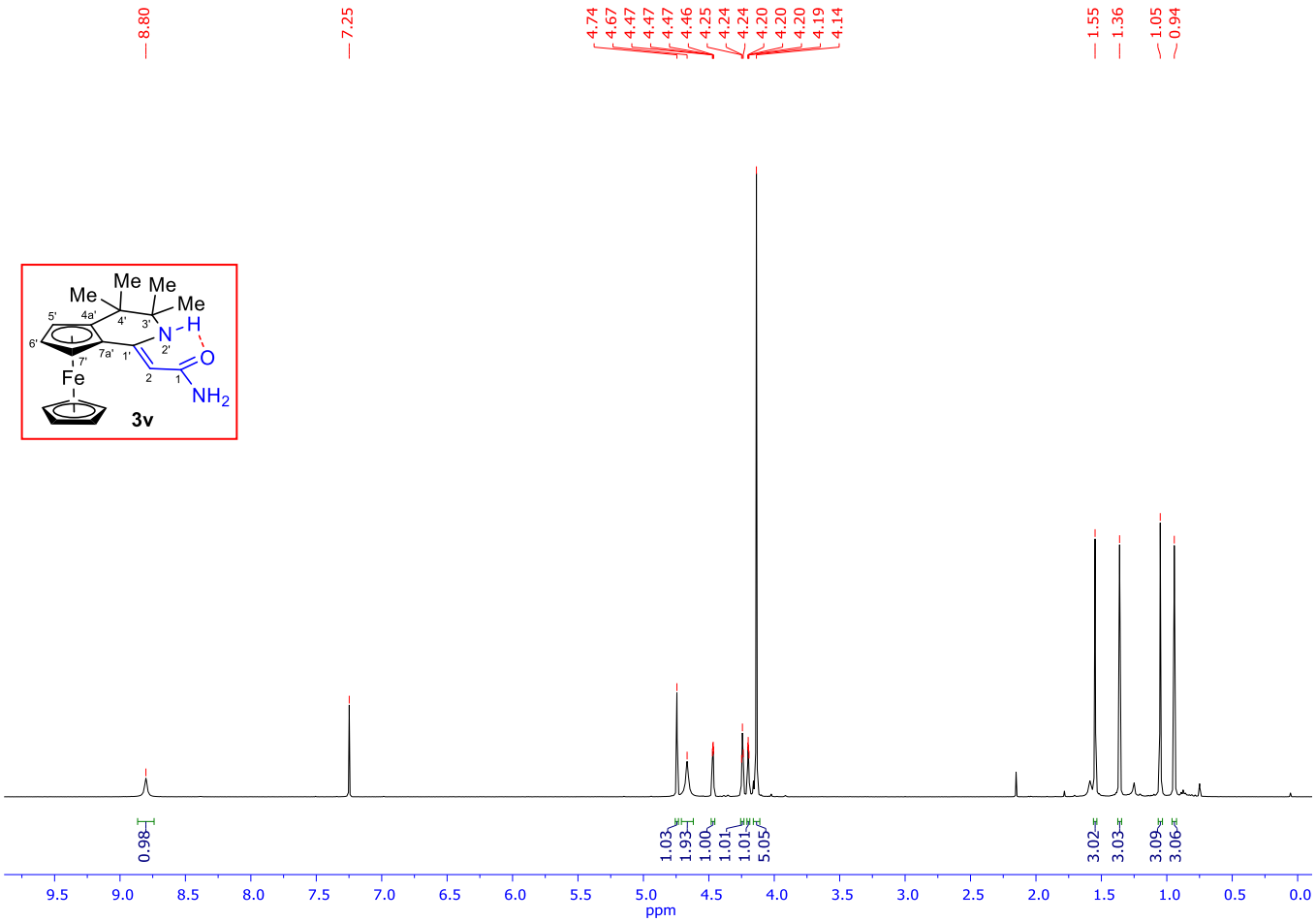


Figure S47. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3v**.

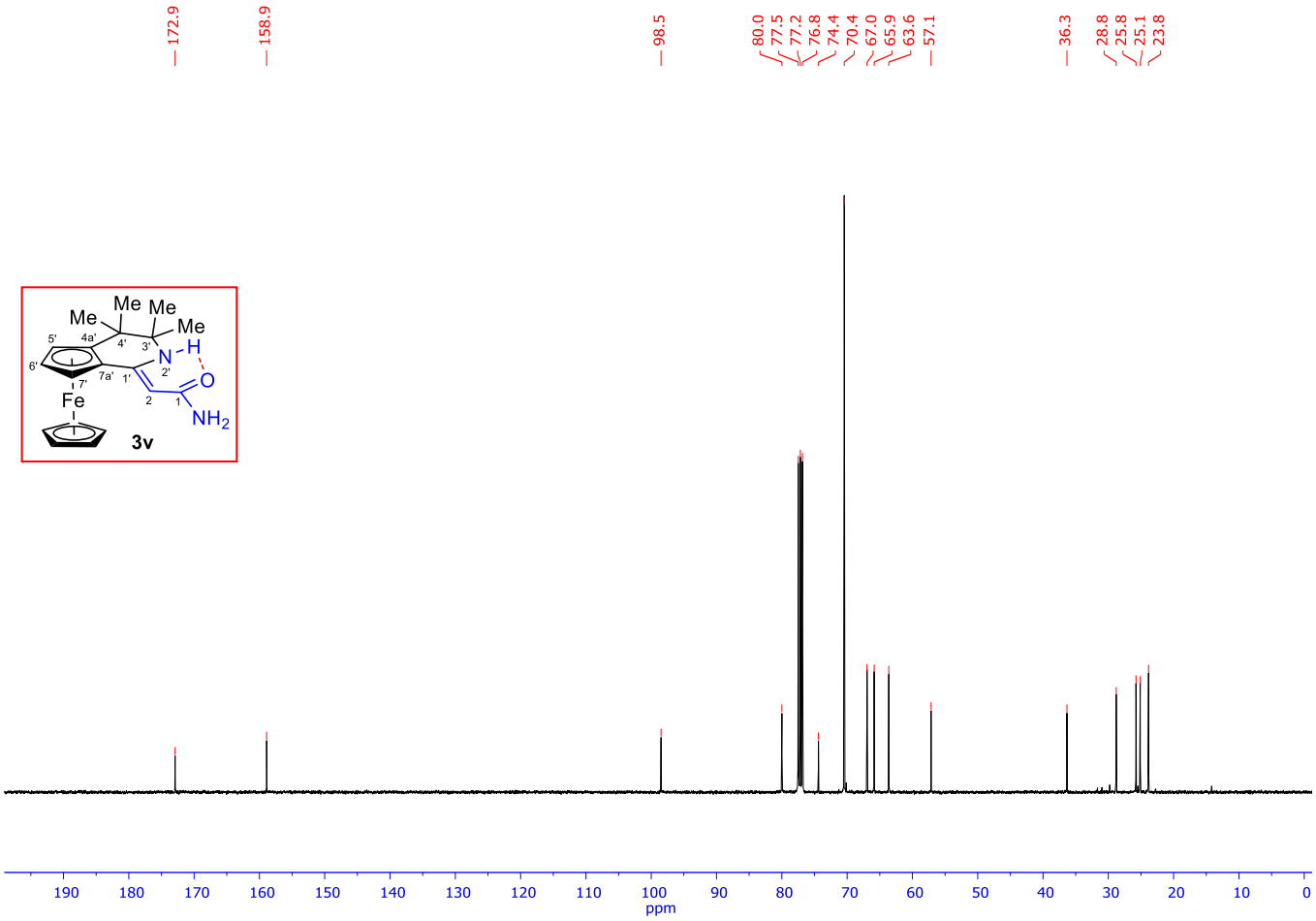


Figure S48. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3v**.

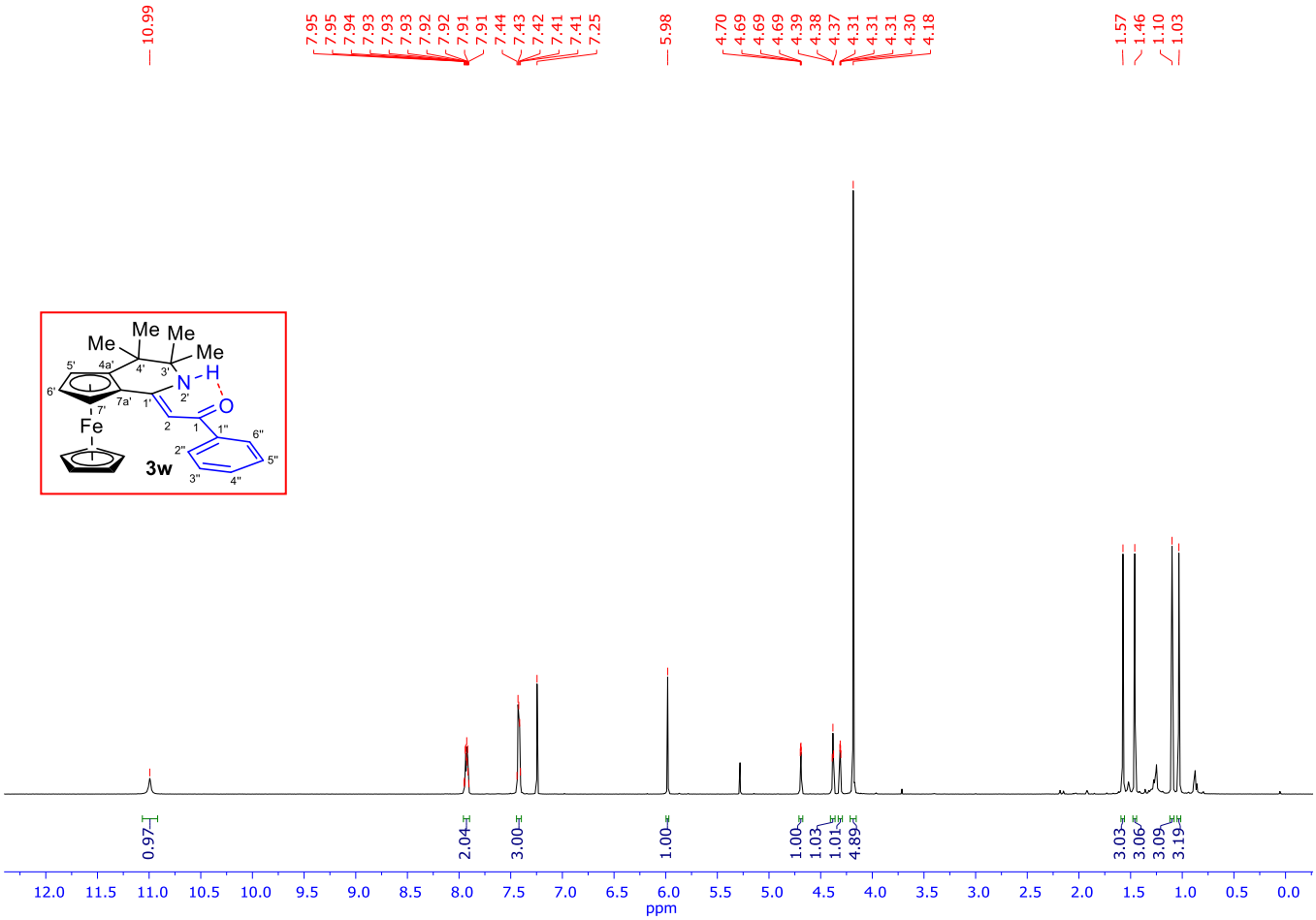


Figure S49. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3w**.

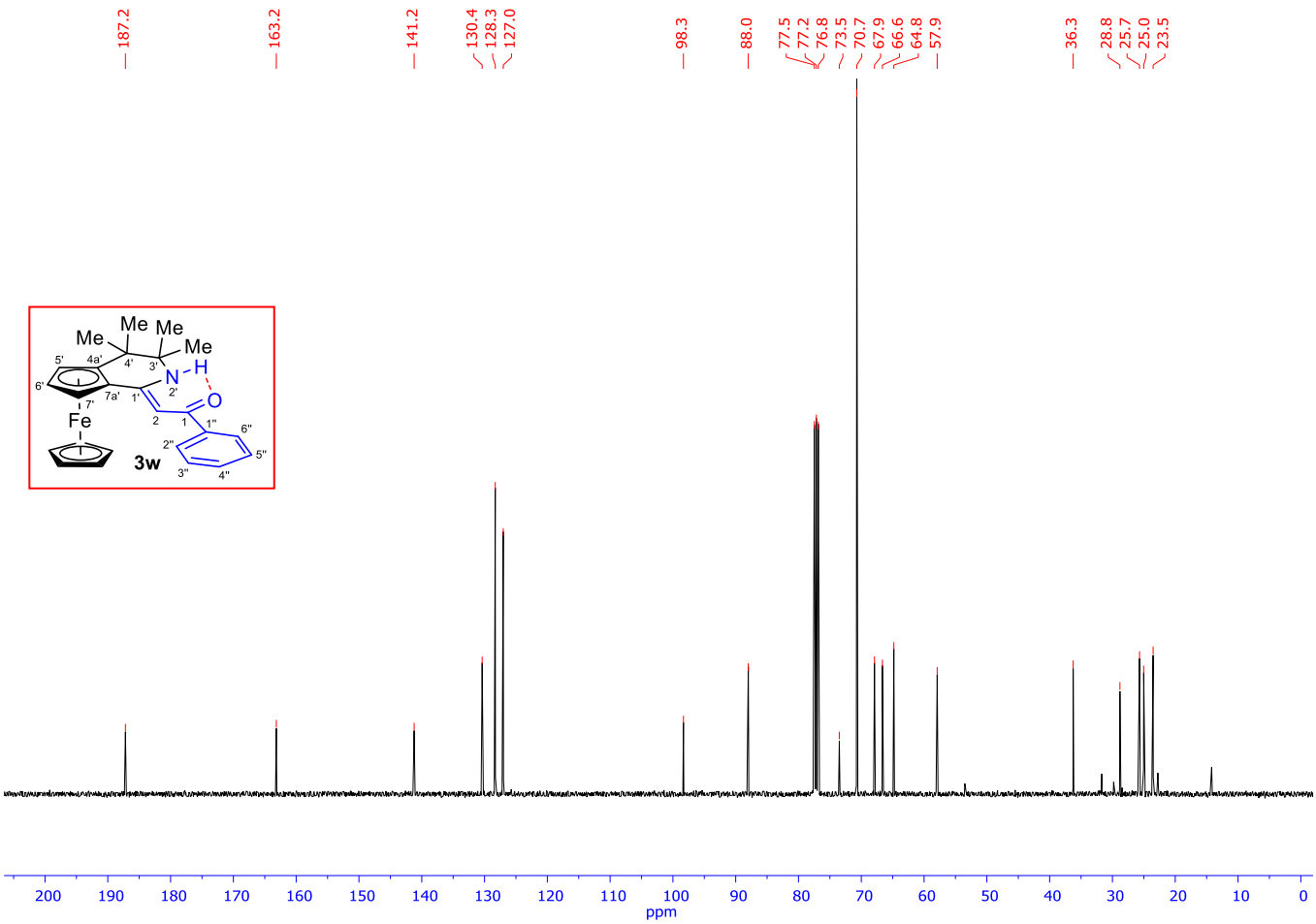


Figure S50. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3w**.

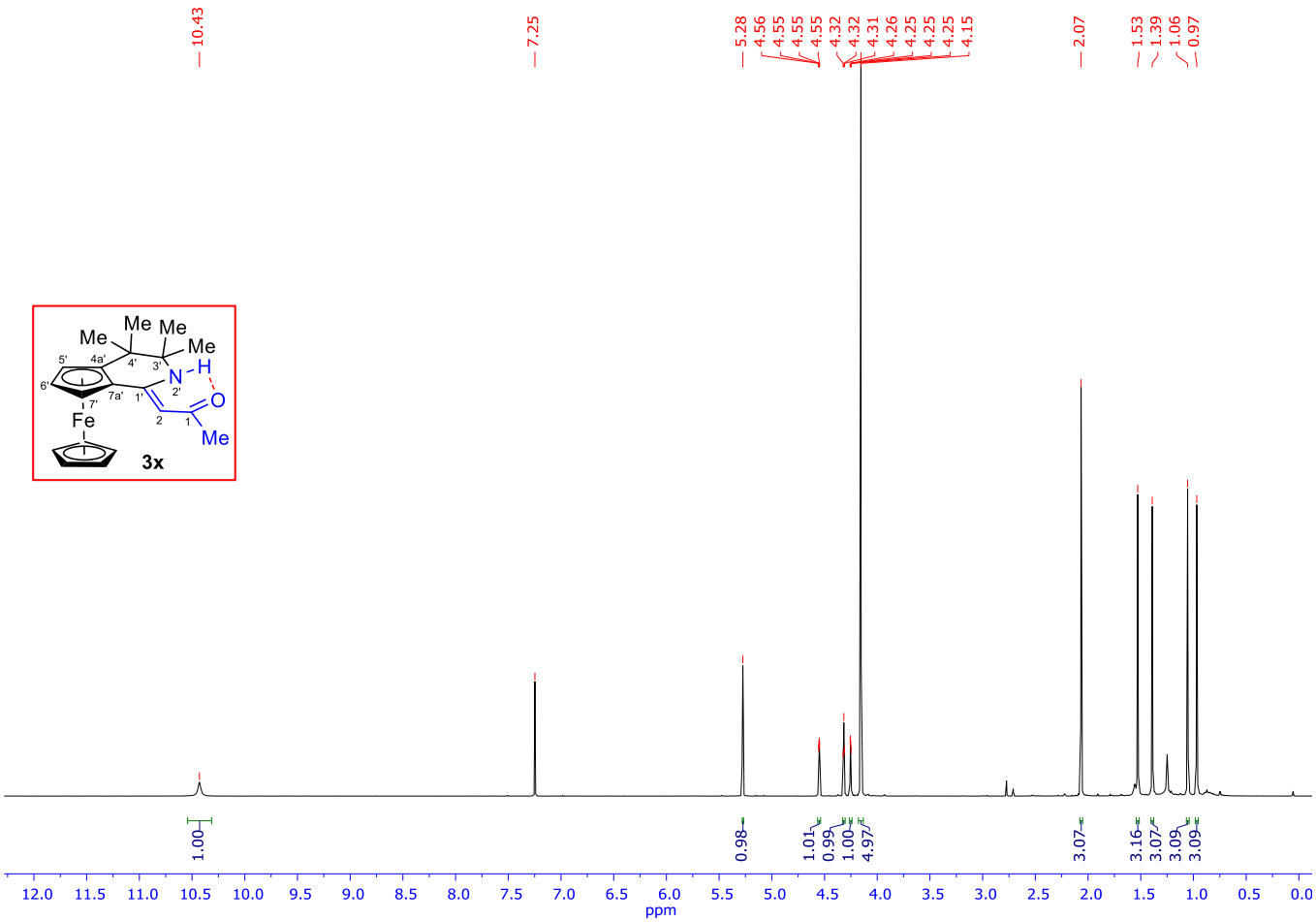


Figure S51. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3x**.

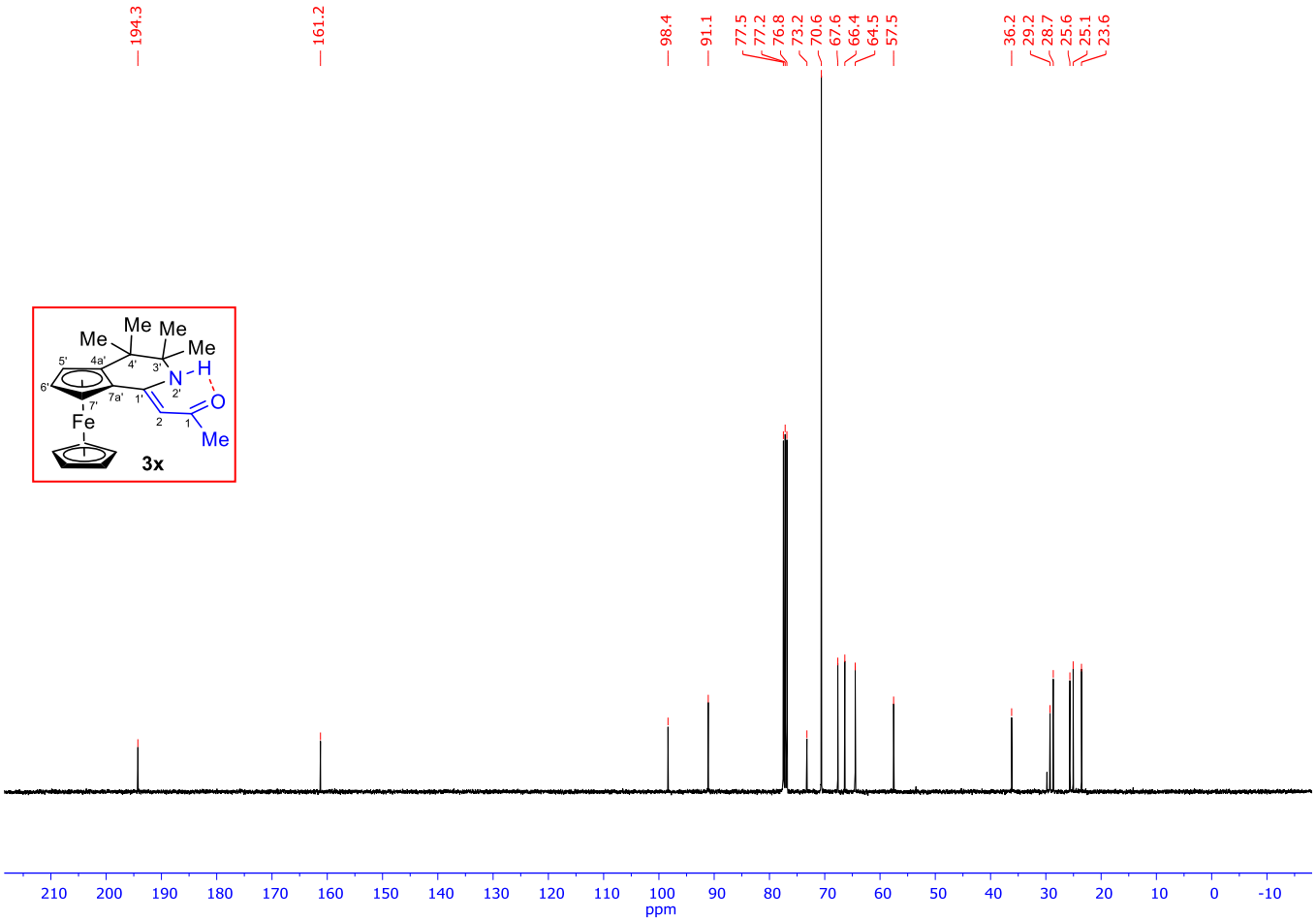


Figure S52. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3x**.

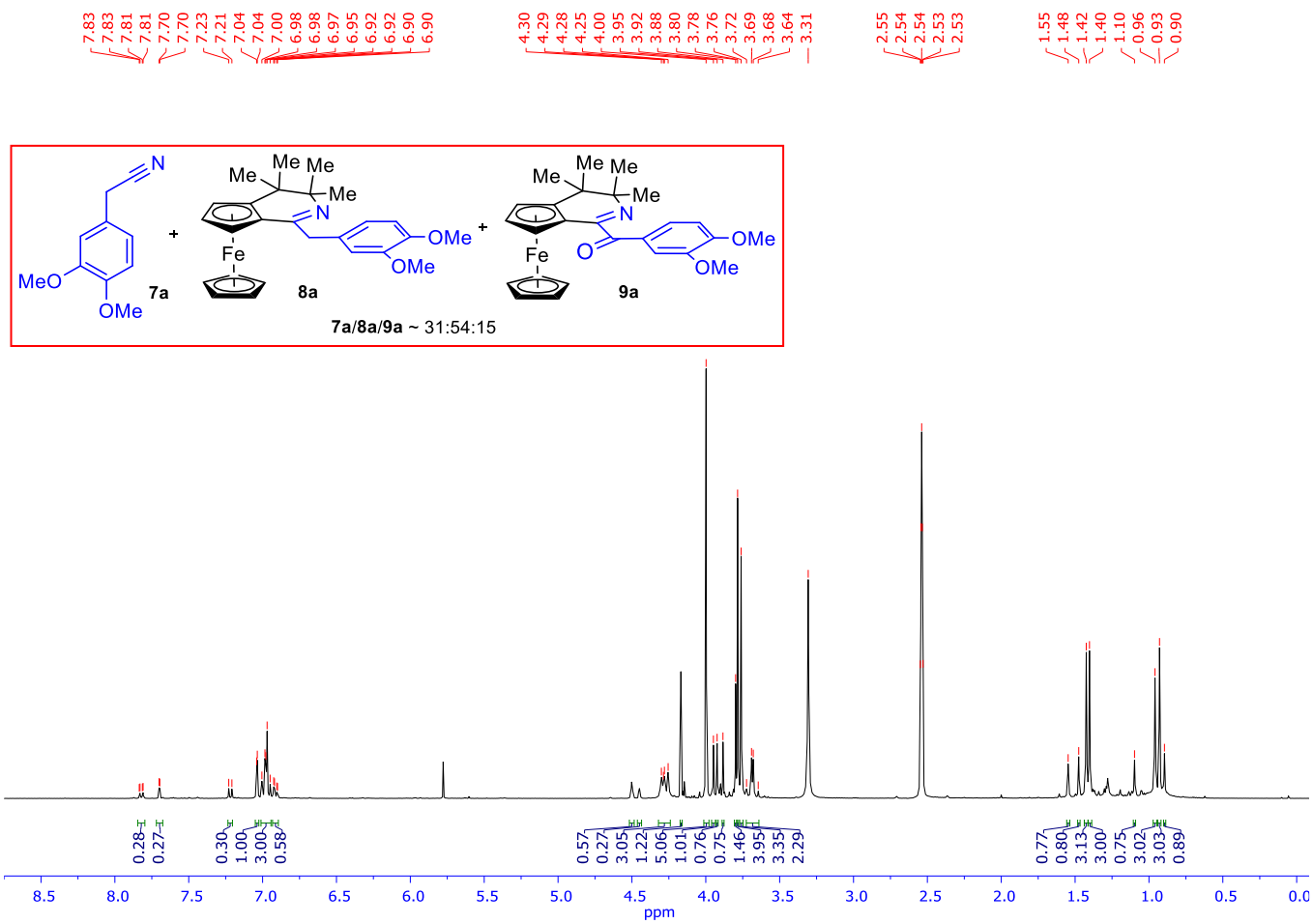


Figure S53. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of mixture of compounds **7a**, **8a** and **9a**.

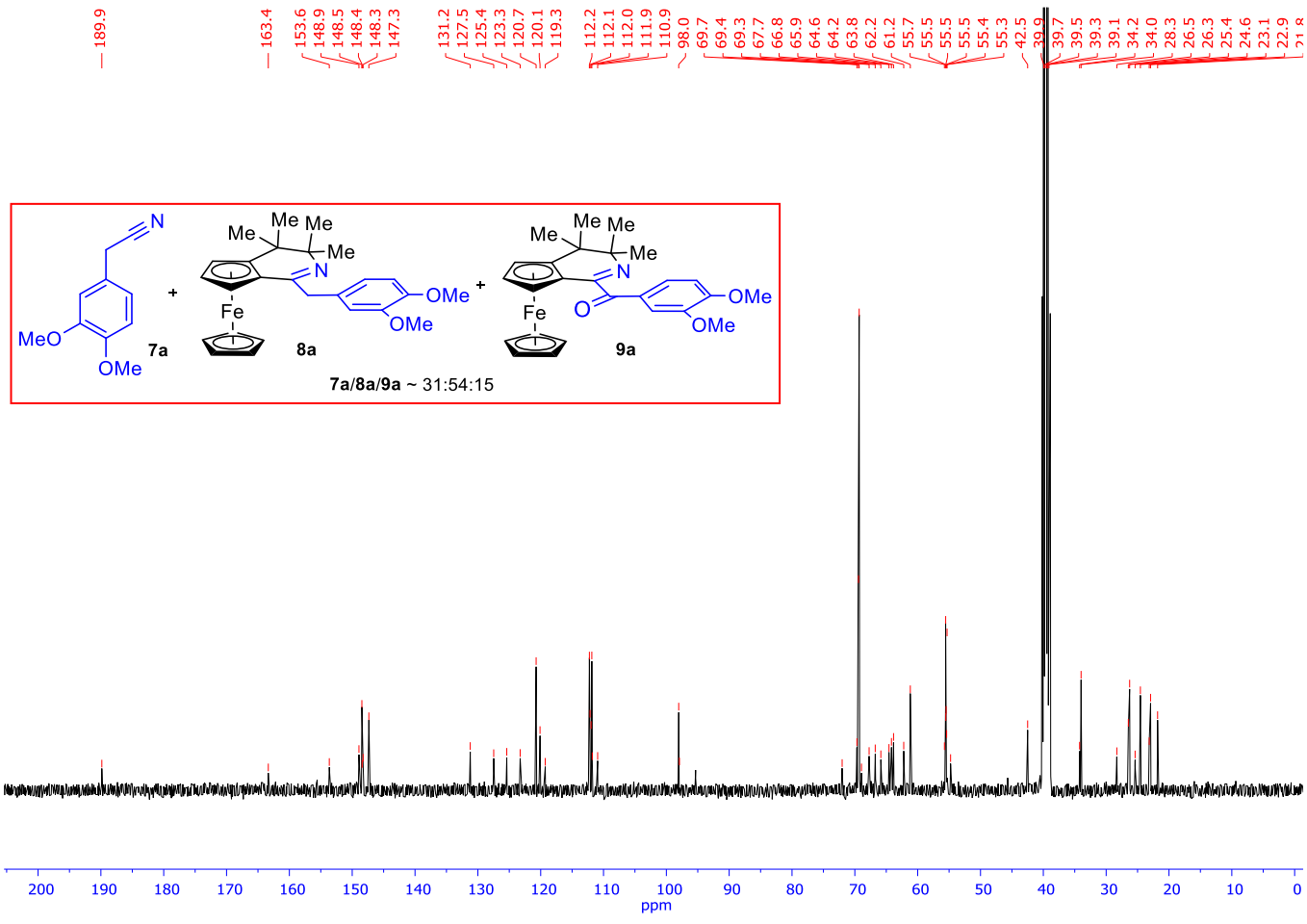


Figure S54. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of mixture of compounds **7a**, **8a** and **9a**.

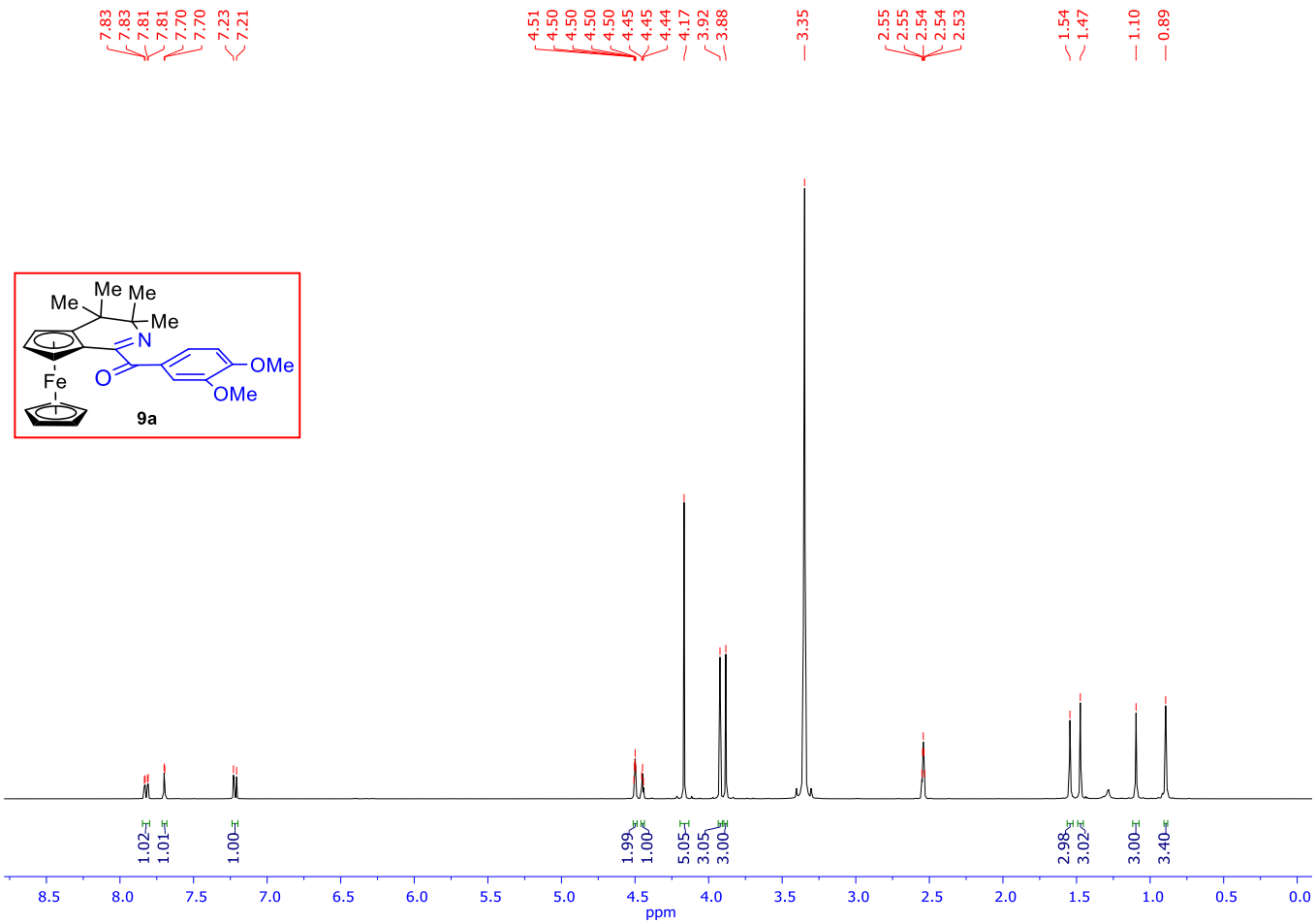


Figure S55. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **9a**.

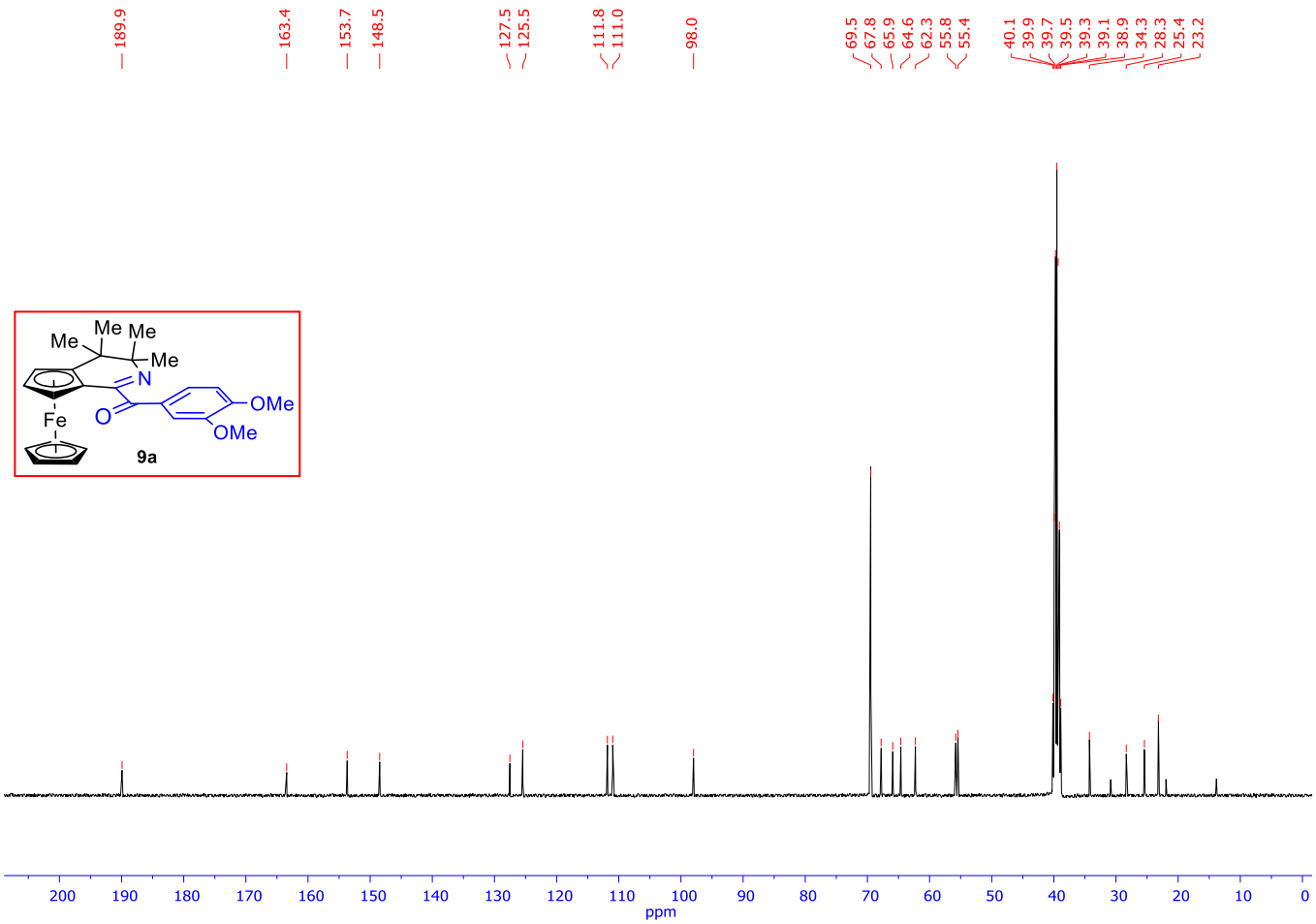


Figure S56. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **9a**.

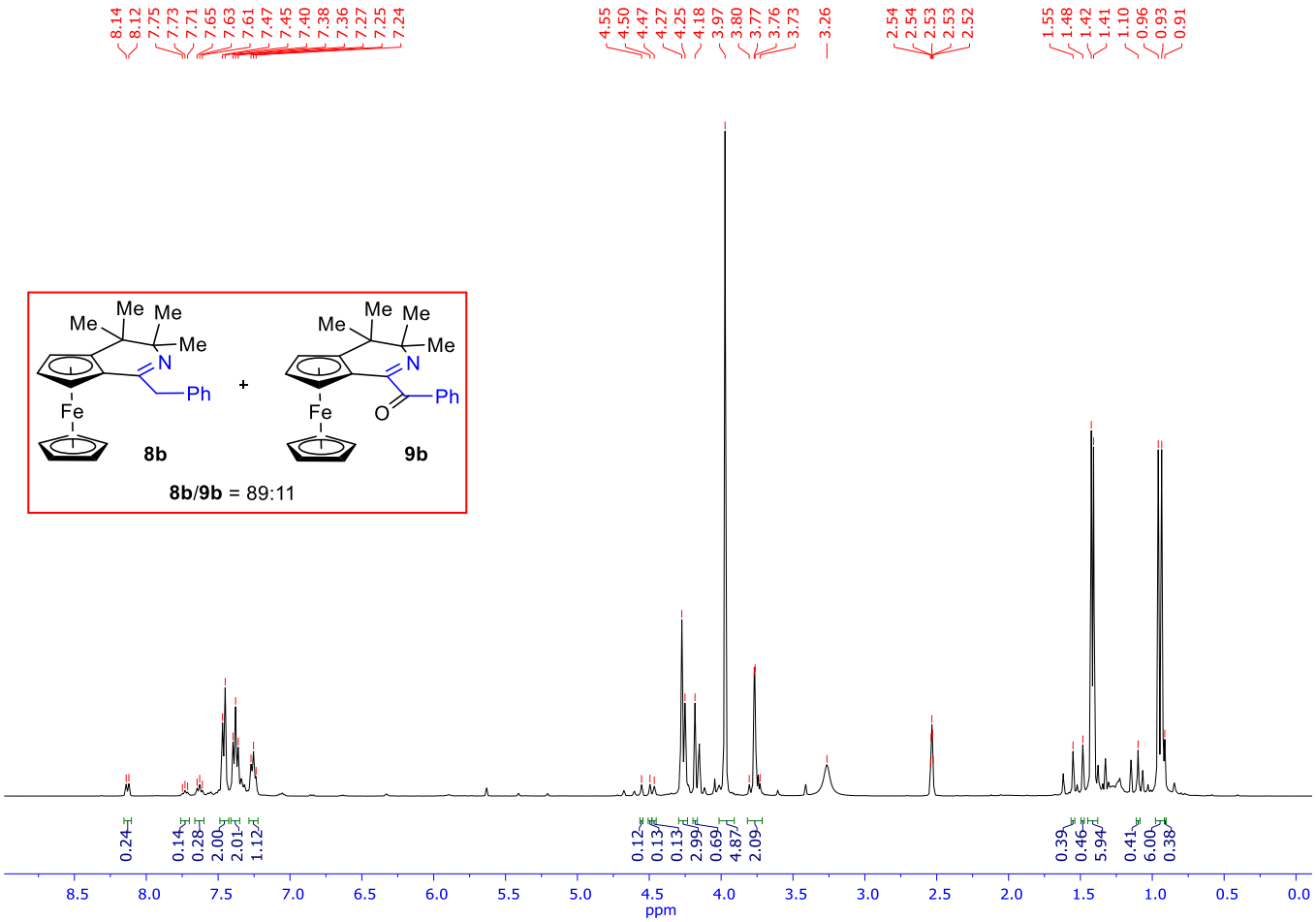


Figure S57. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of mixture of compounds **8b** and **9b**.

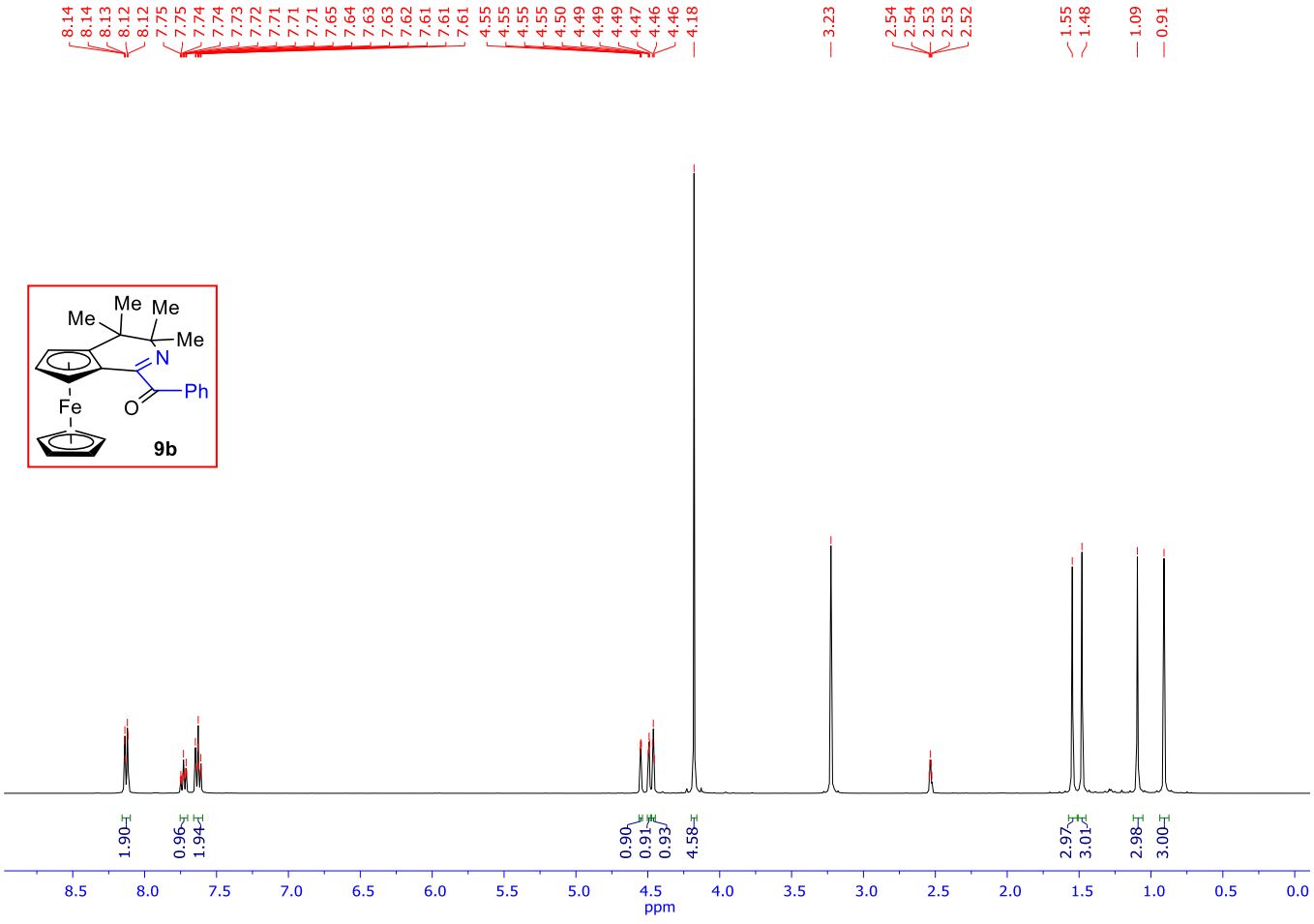


Figure S58. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **9b**.

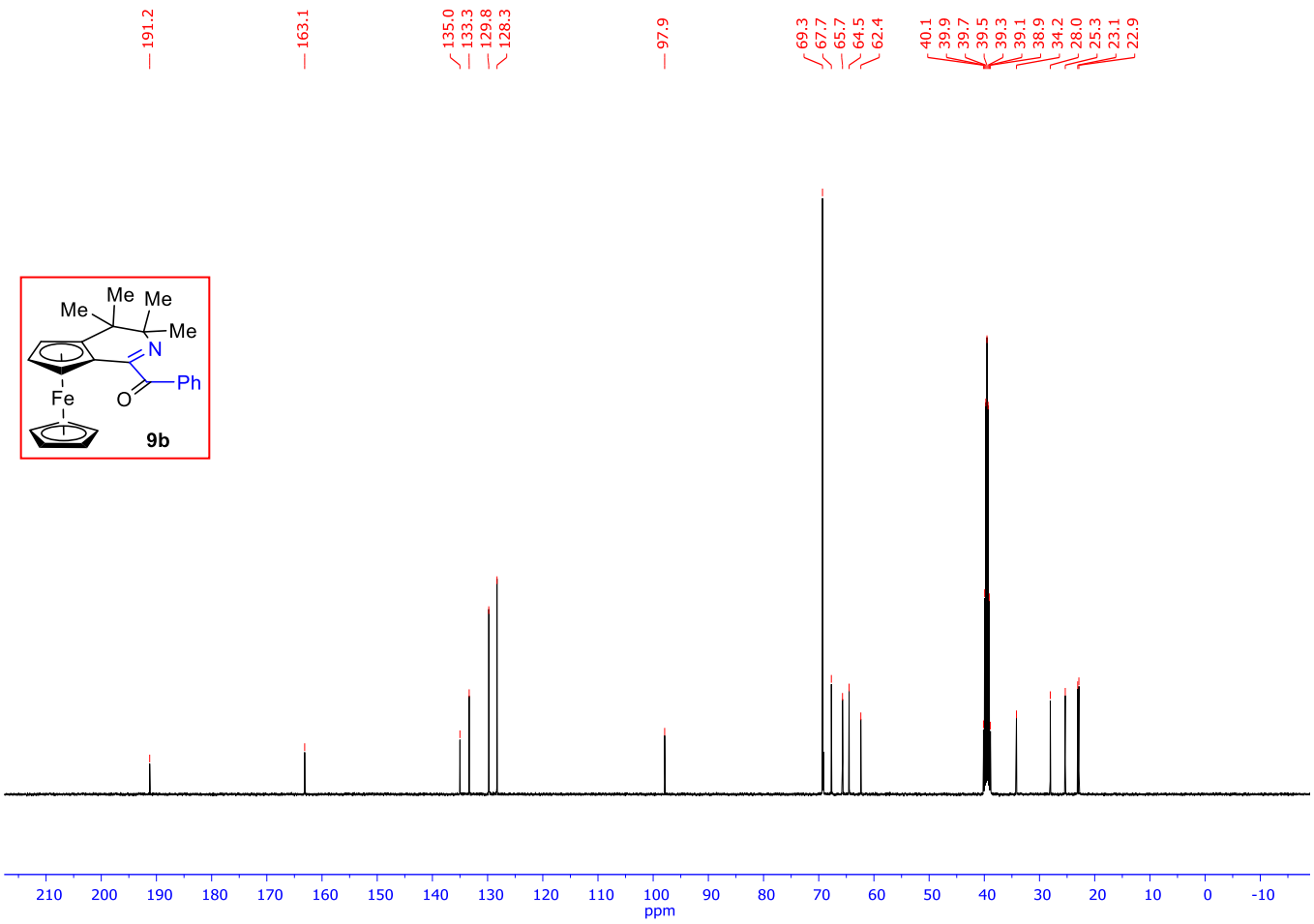


Figure S59. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **9b**.

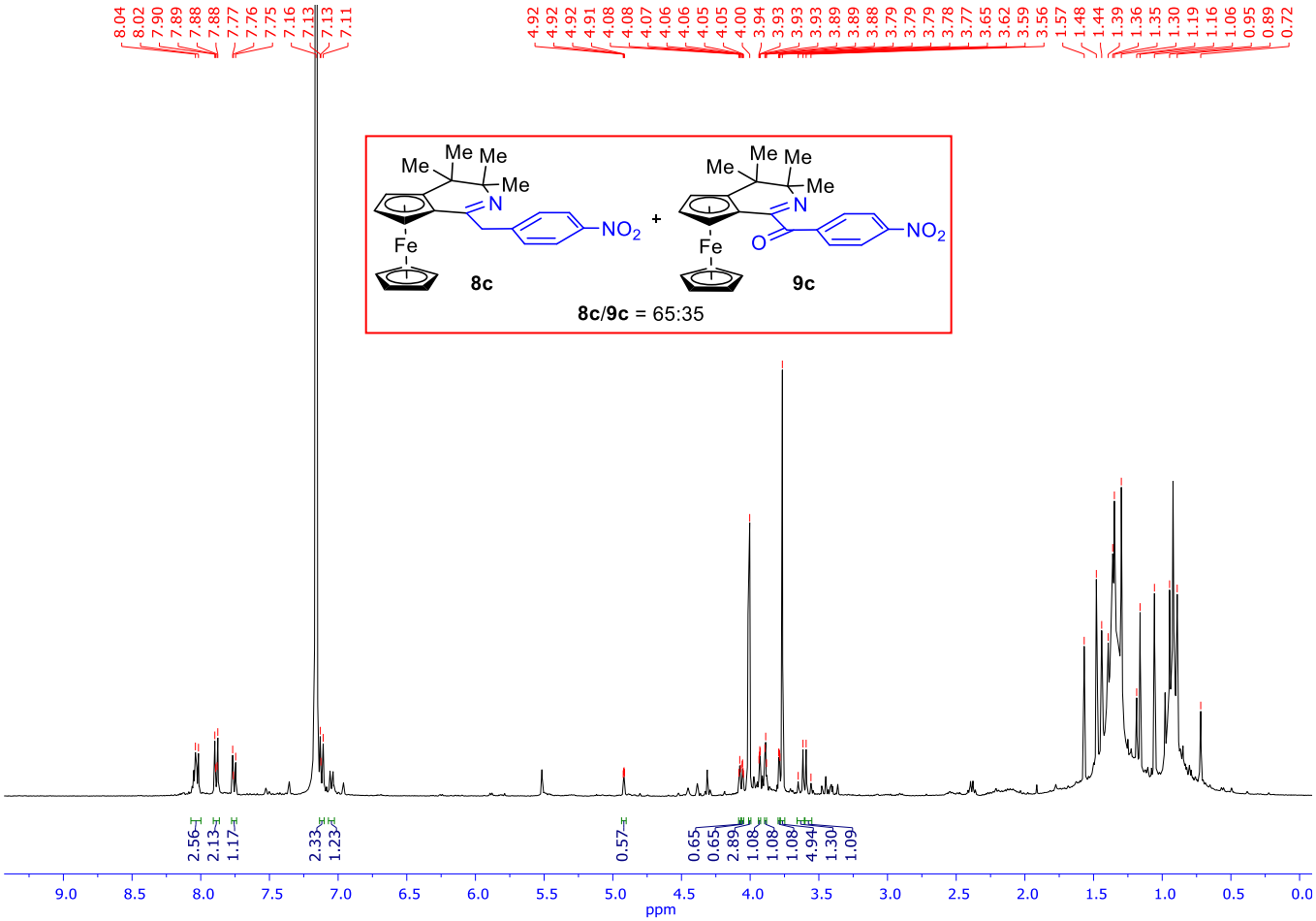


Figure S60. ^{1}H NMR spectrum (400 MHz, C_6D_6) of mixture of compounds **8c** and **9c**.

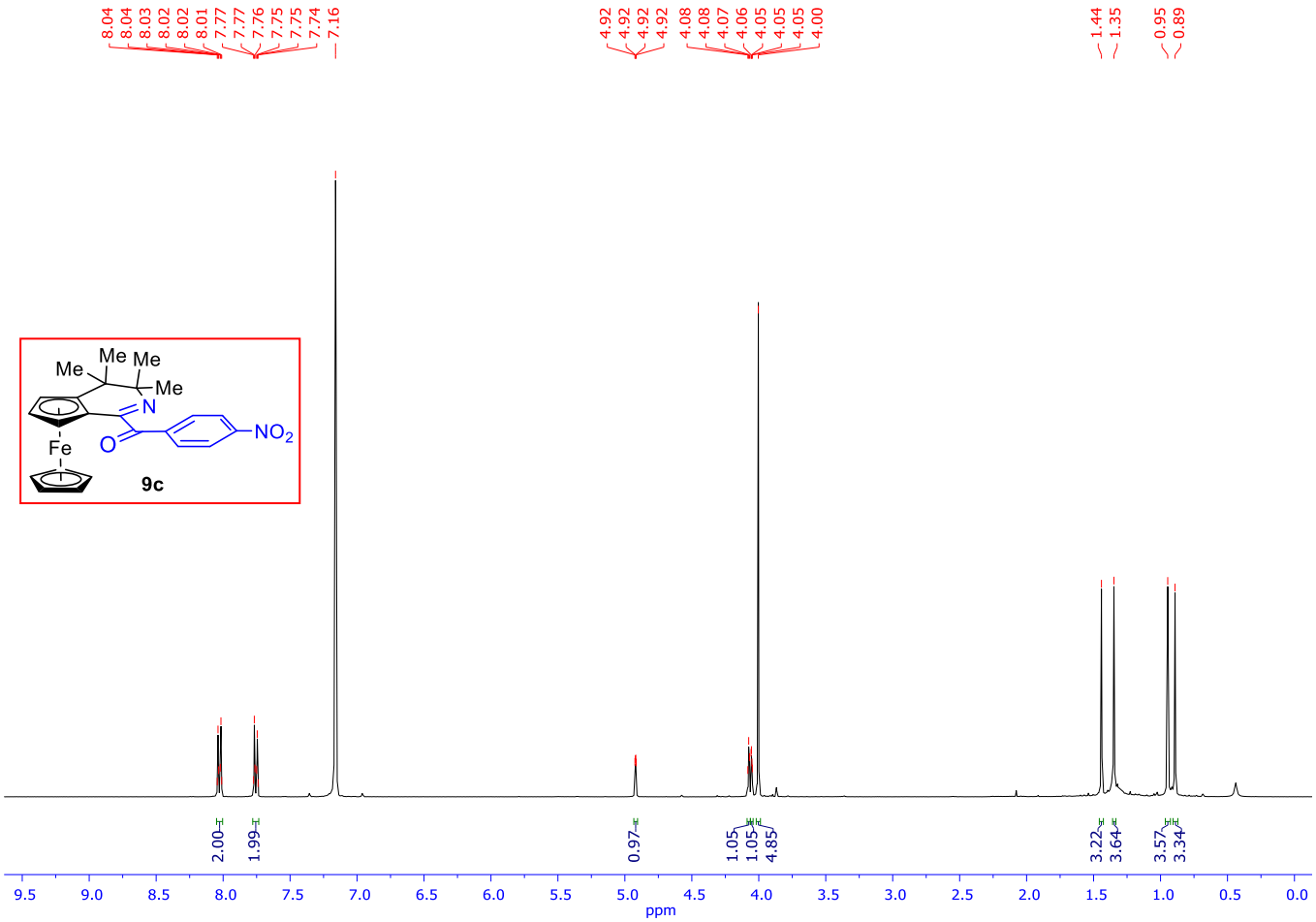


Figure S61. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **9c**.

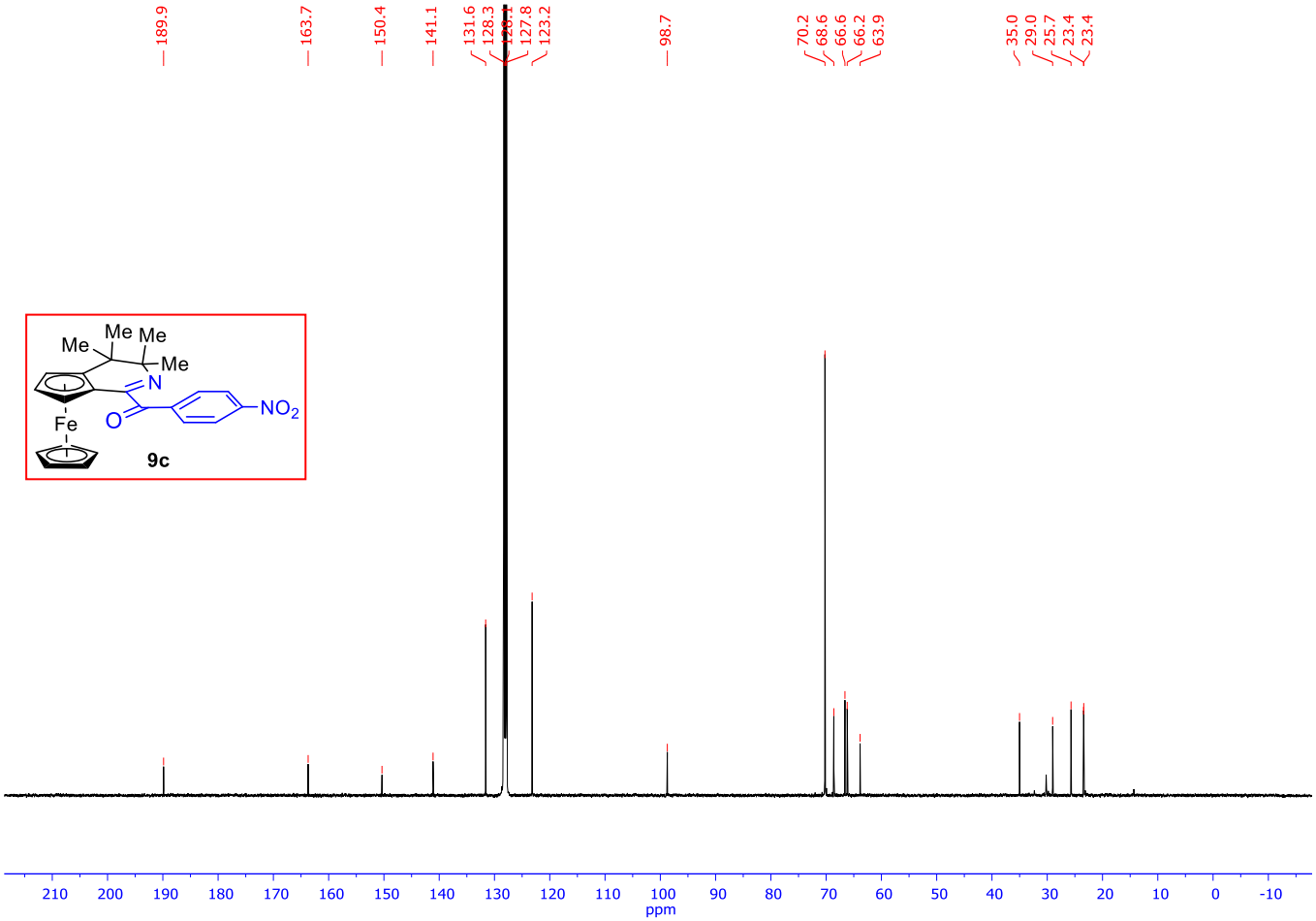


Figure S62. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **9c**.

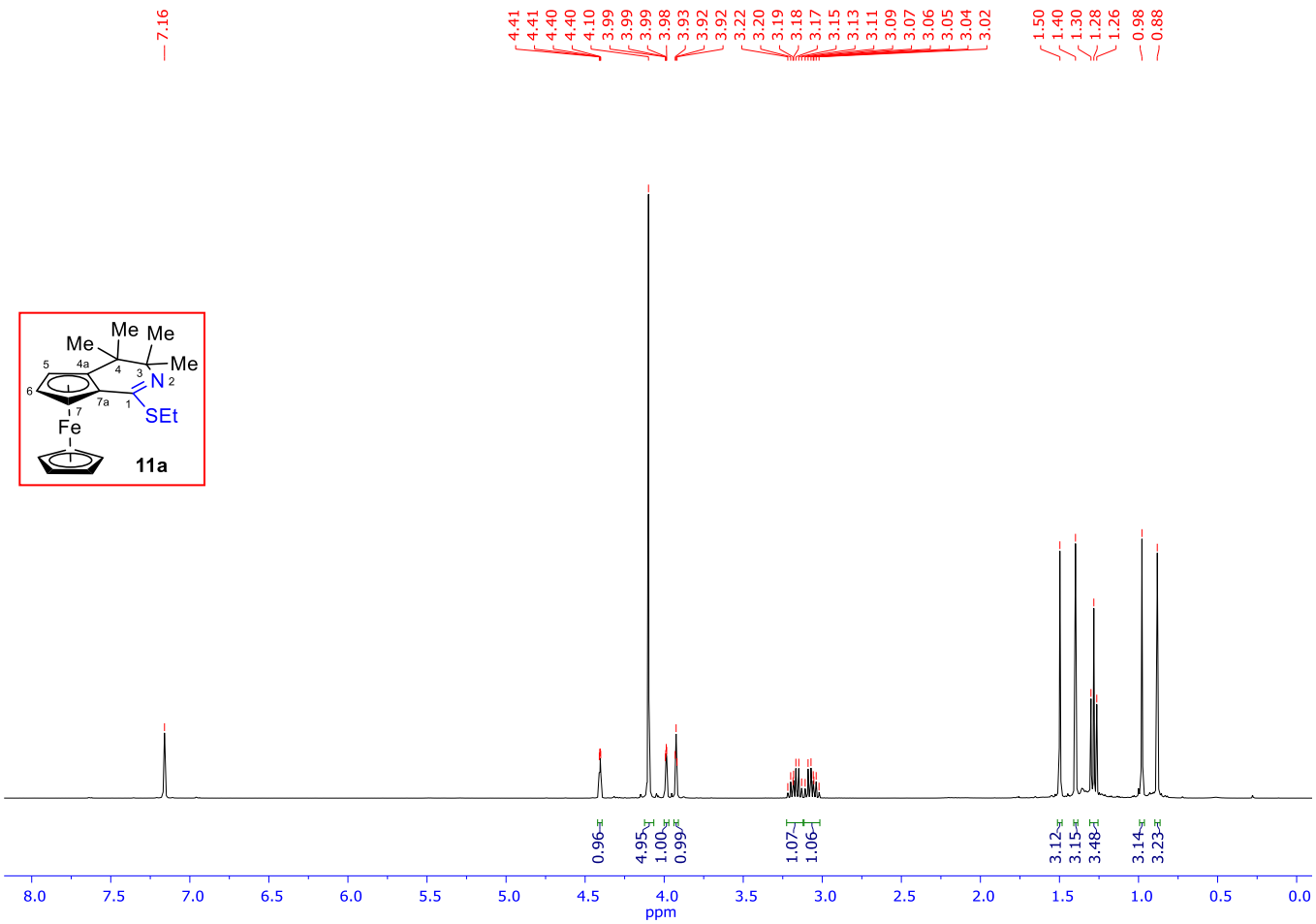


Figure S63. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **11a**.

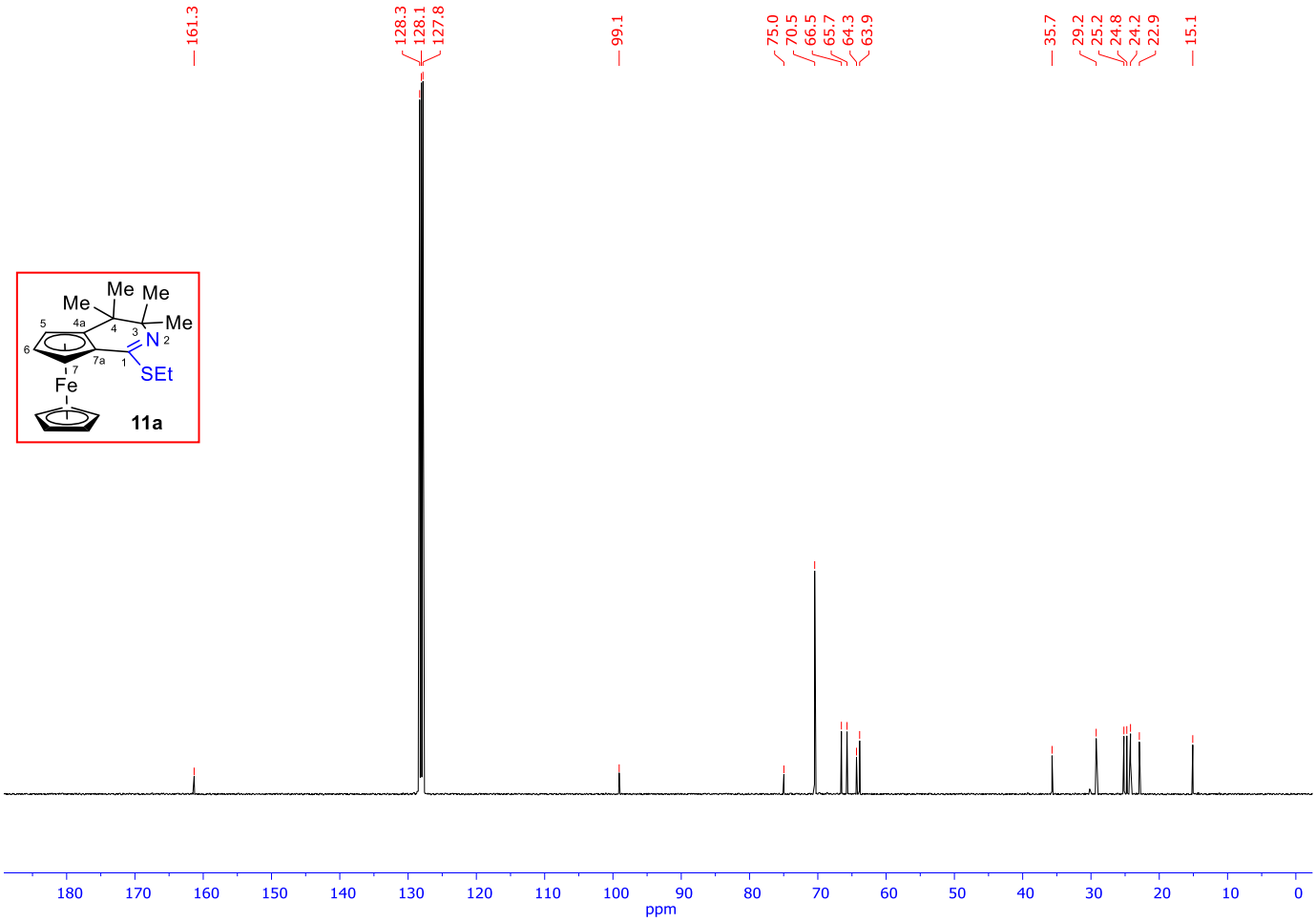


Figure S64. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **11a**.

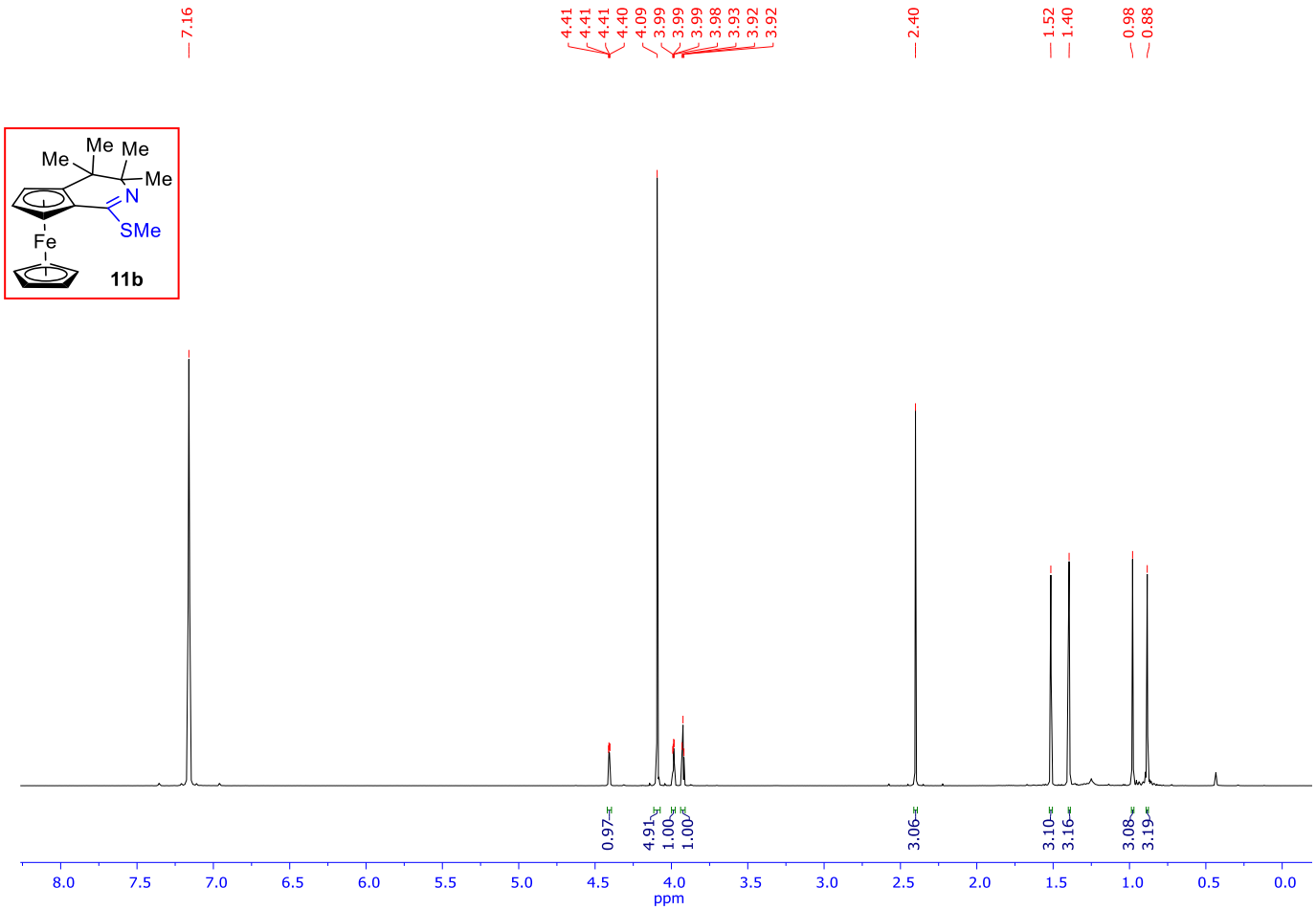


Figure S65. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **11b**.

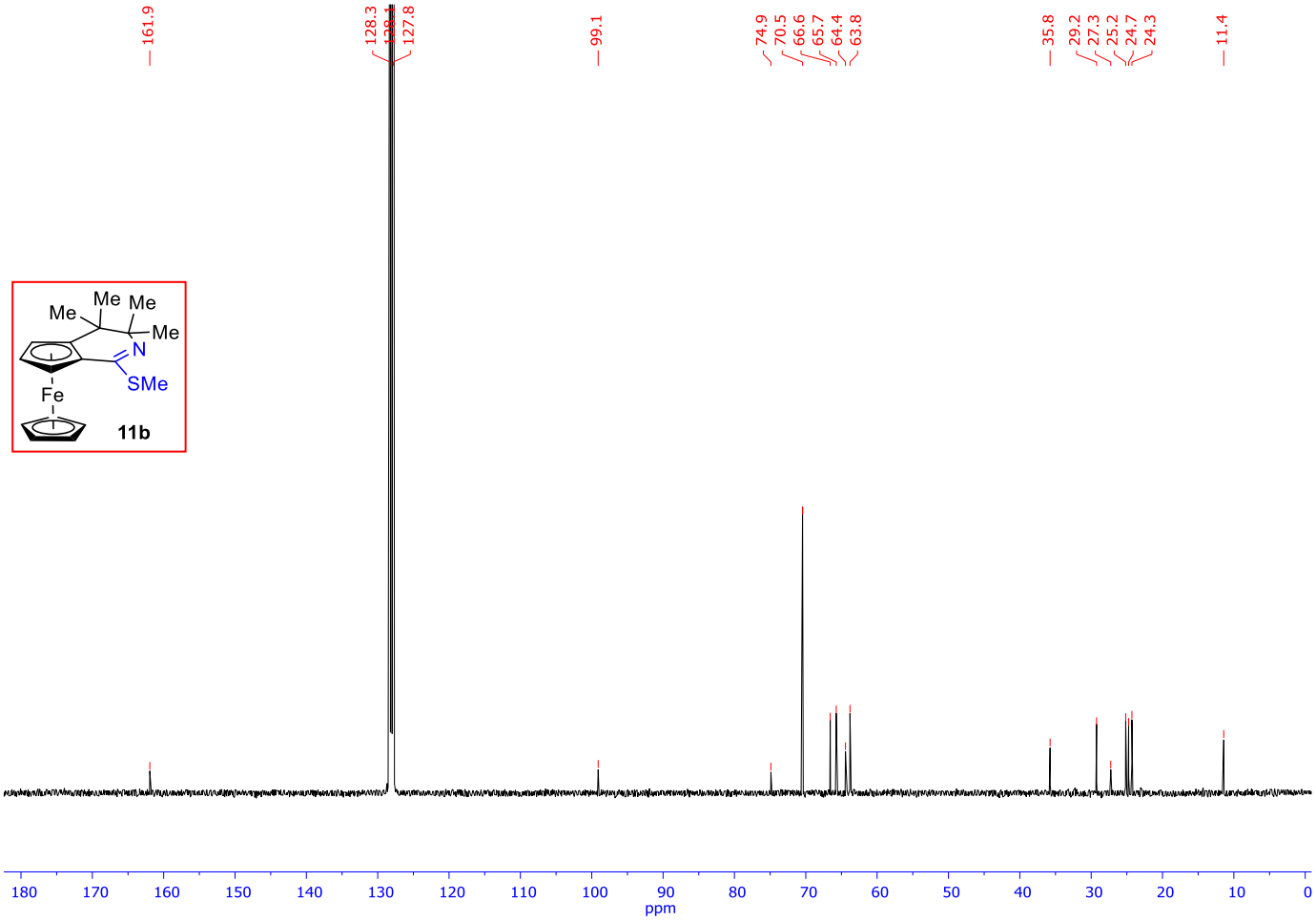


Figure S66. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **11b**.

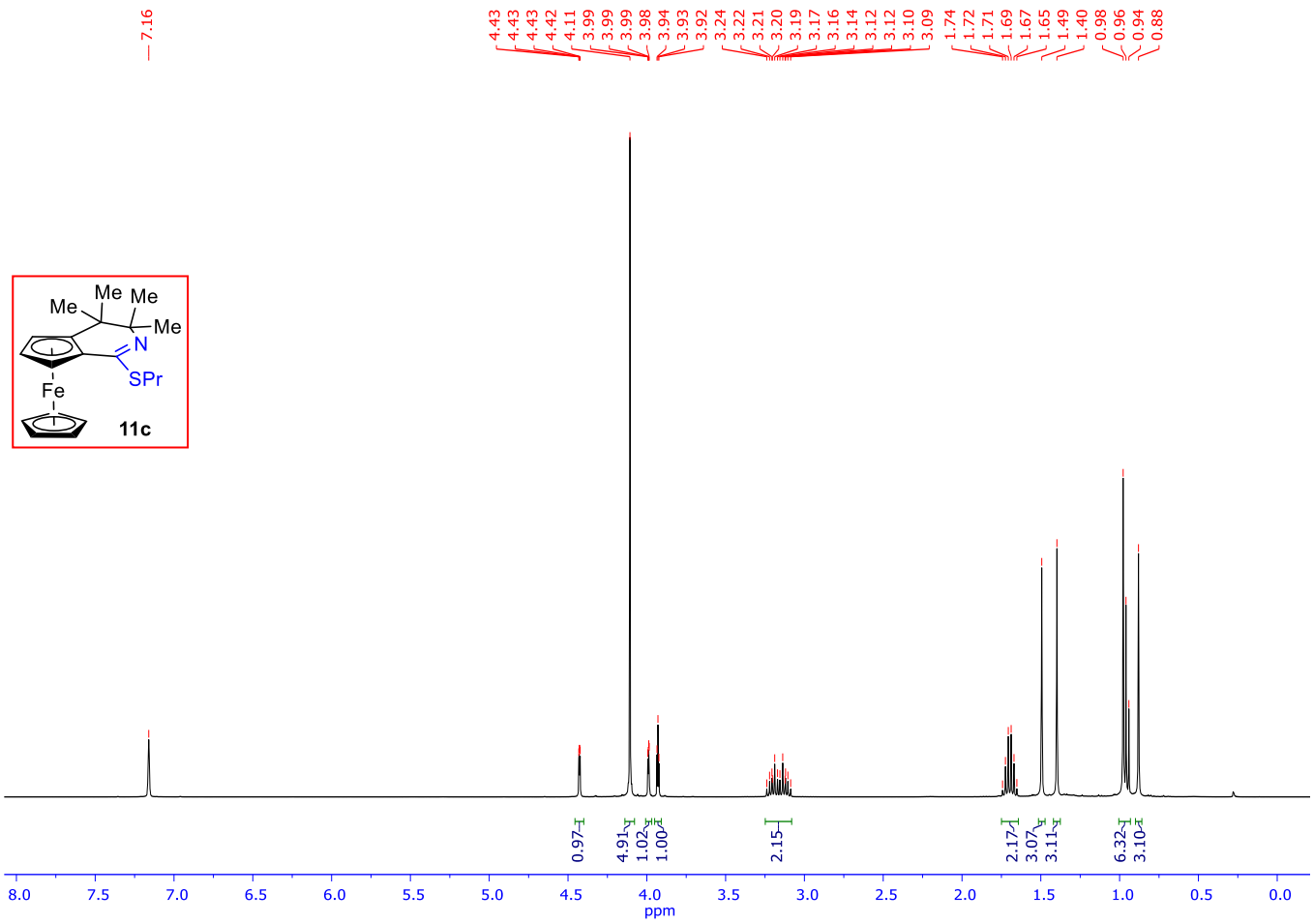


Figure S67. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **11c**.

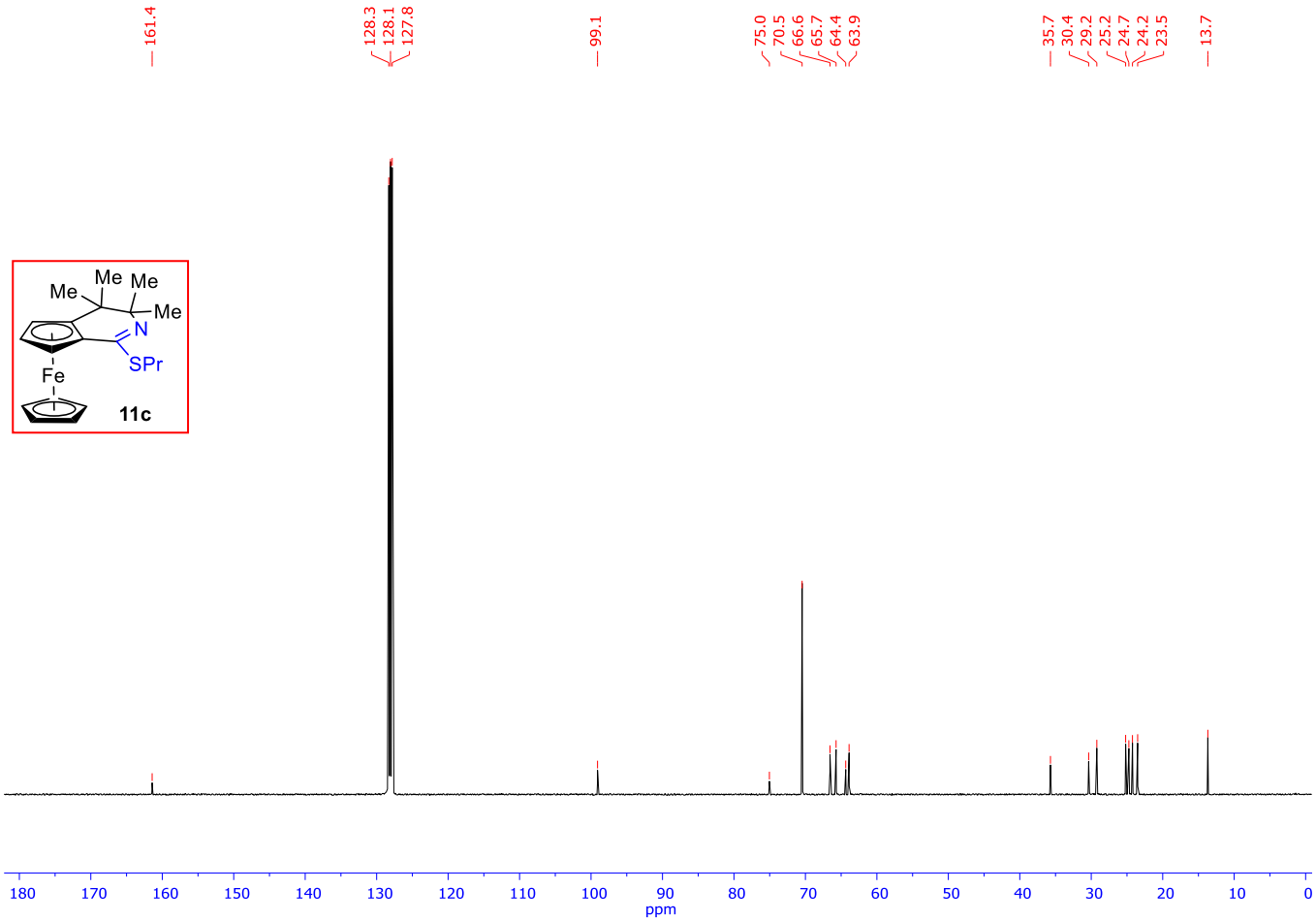


Figure S68. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **11c**.

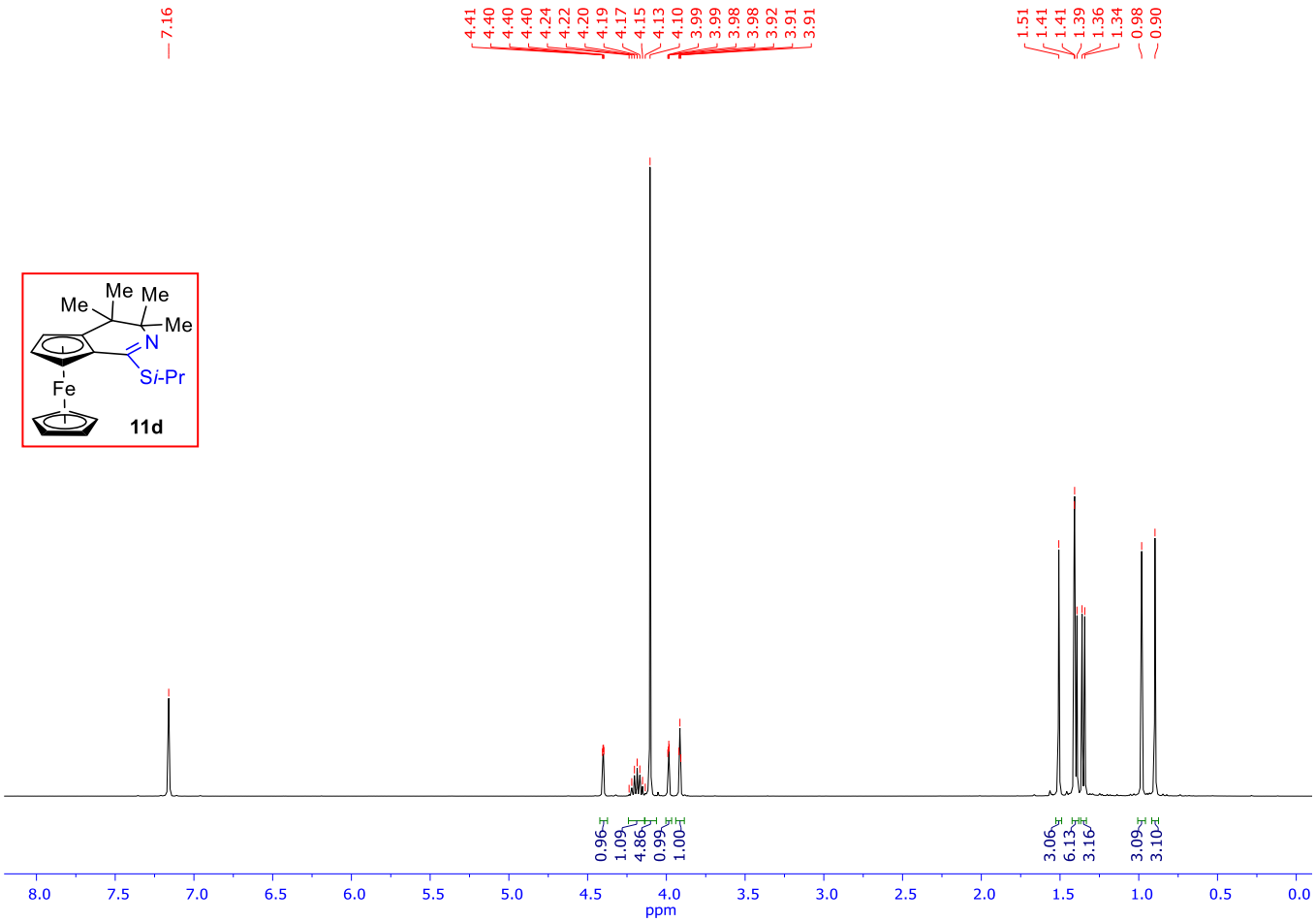


Figure S69. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **11d**.

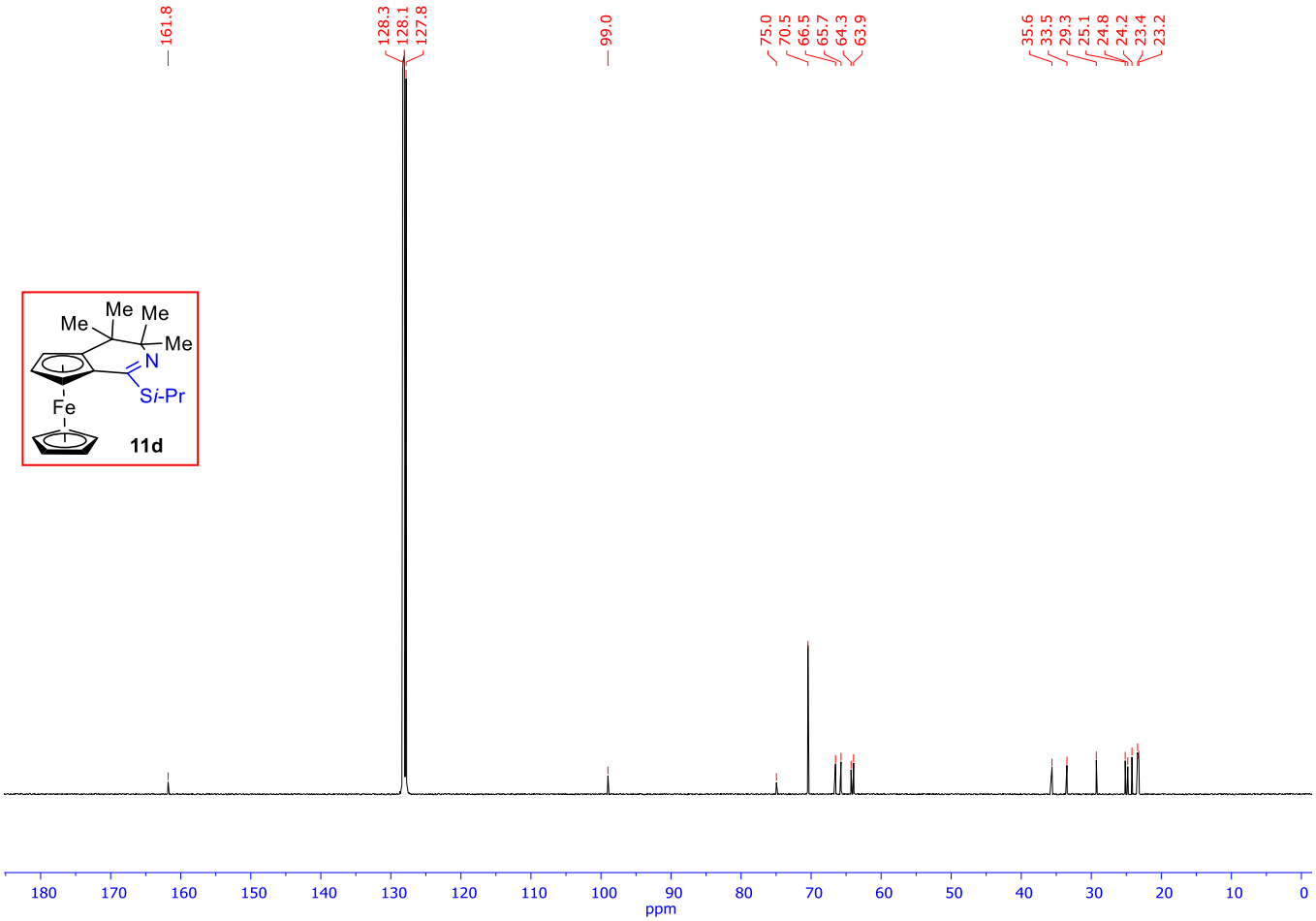


Figure S70. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **11d**.

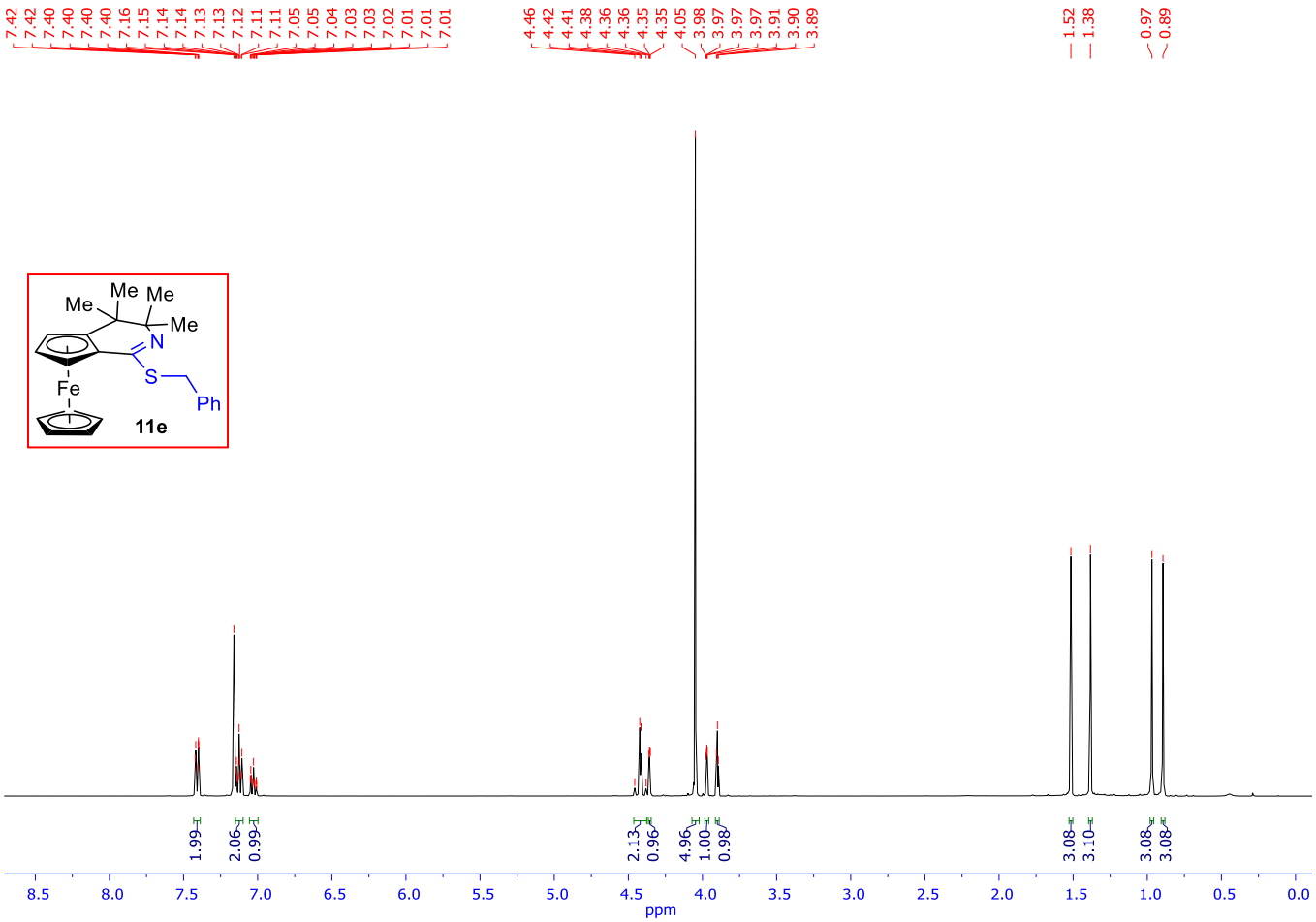


Figure S71. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **11e**.

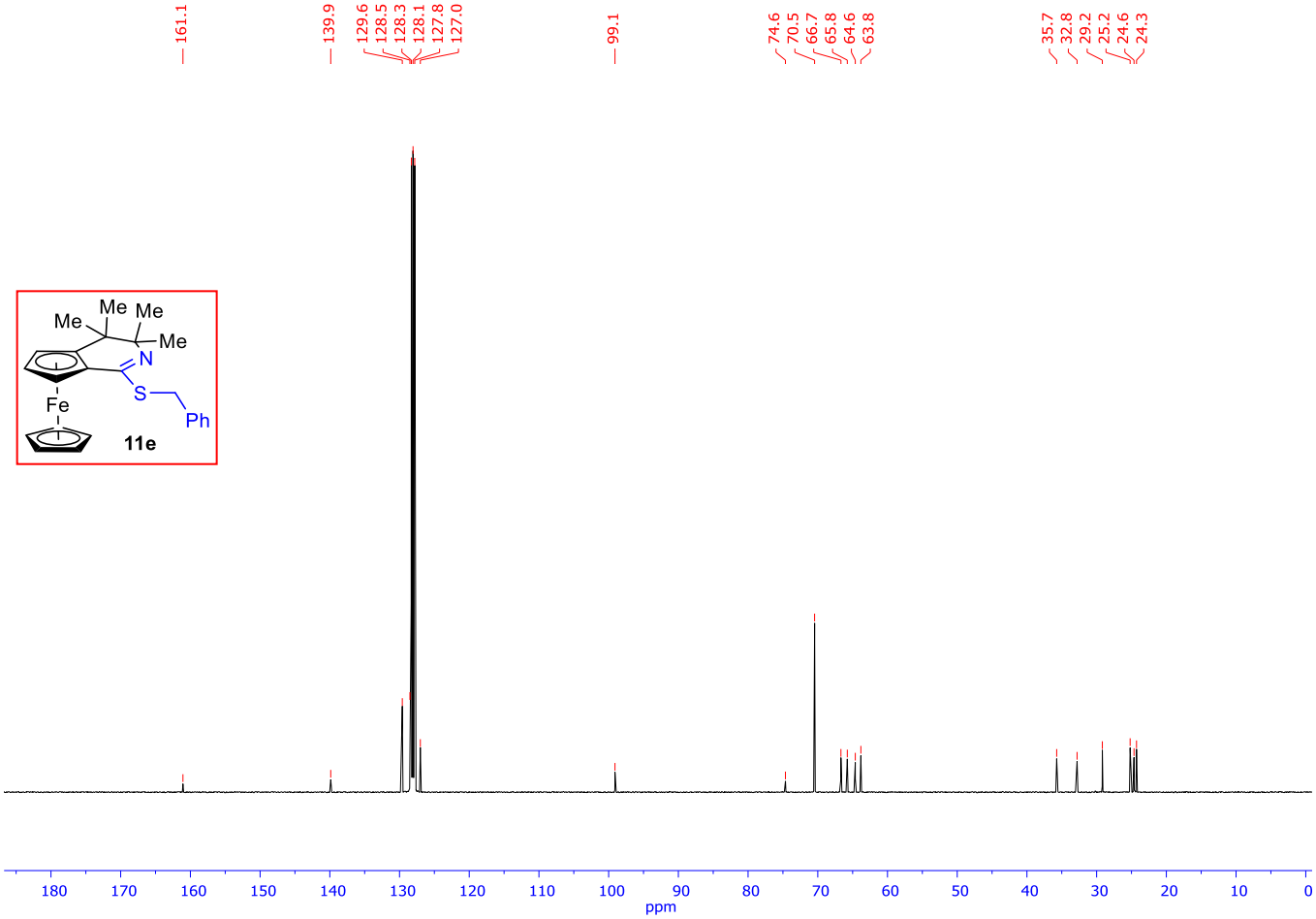


Figure S72. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **11e**.

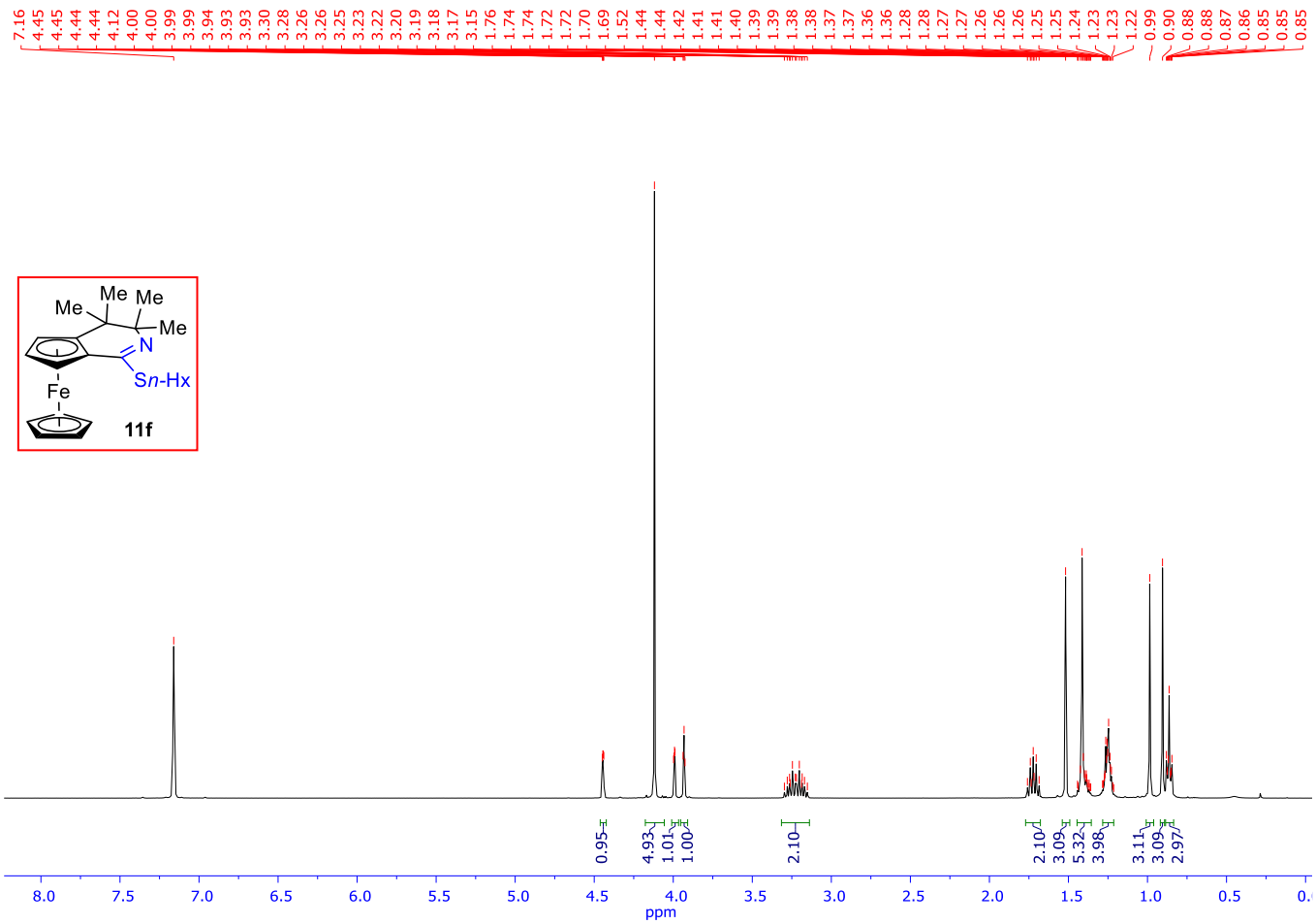


Figure S73. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **11f**.

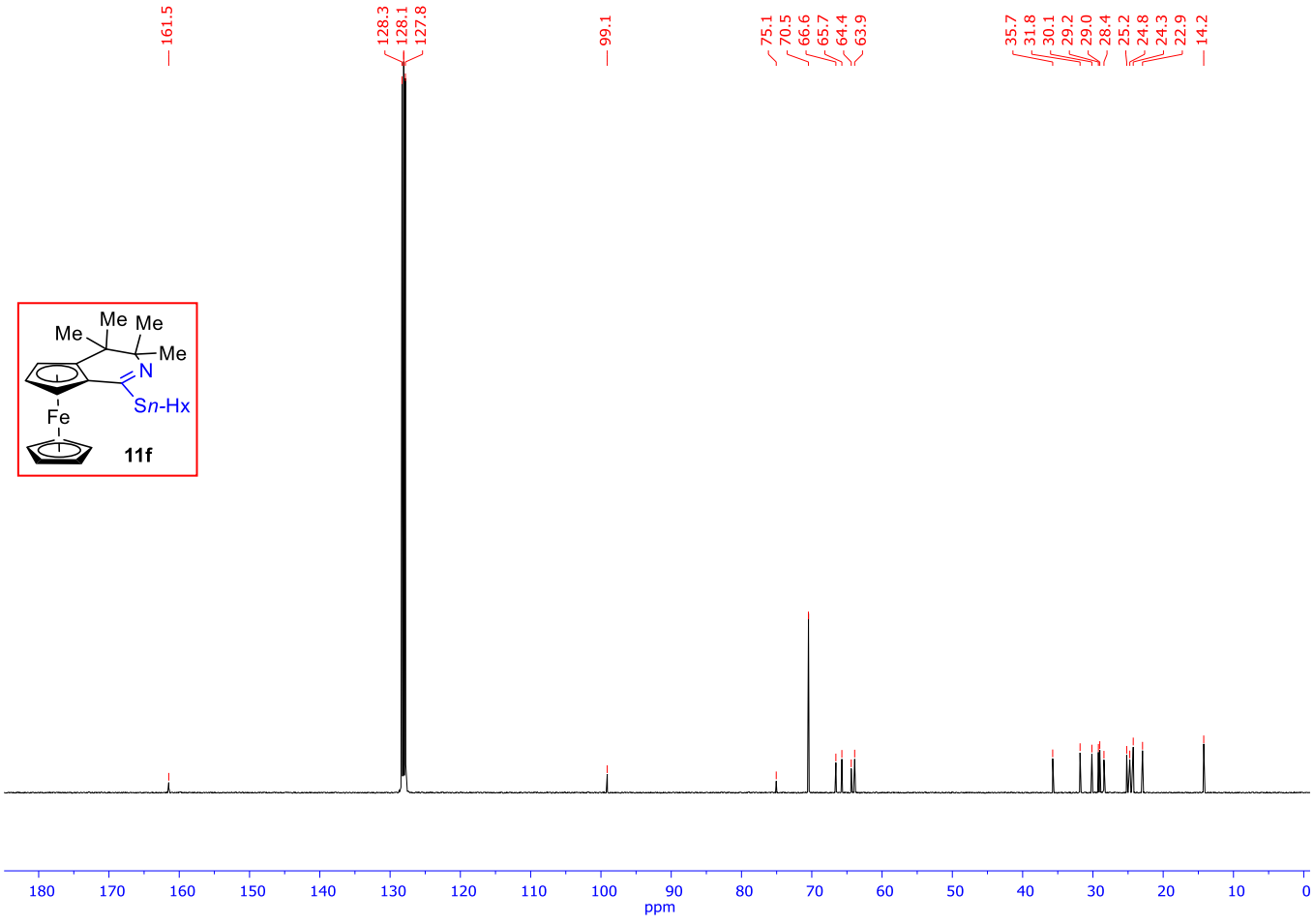


Figure S74. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **11f**.

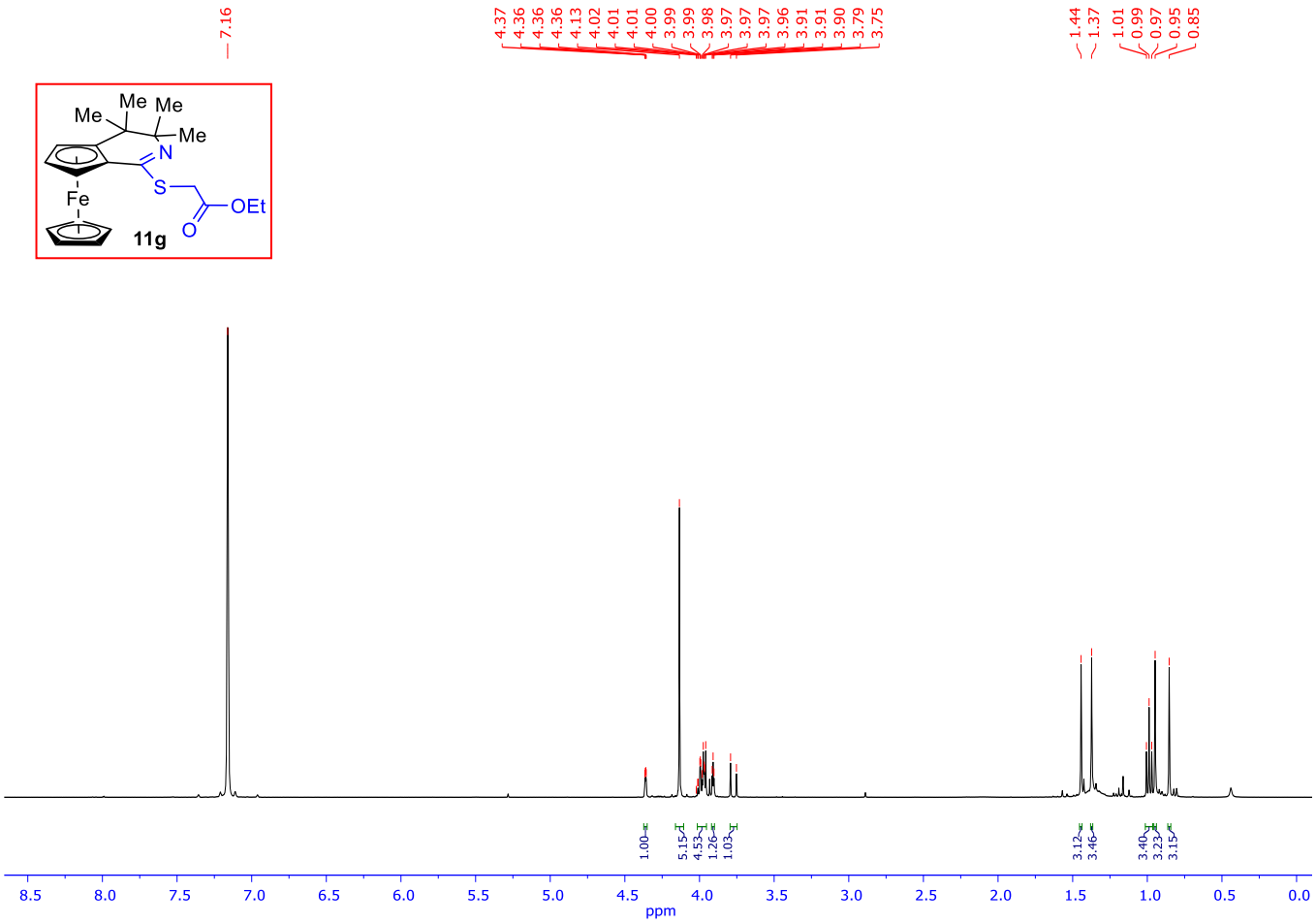


Figure S75. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **11g**.

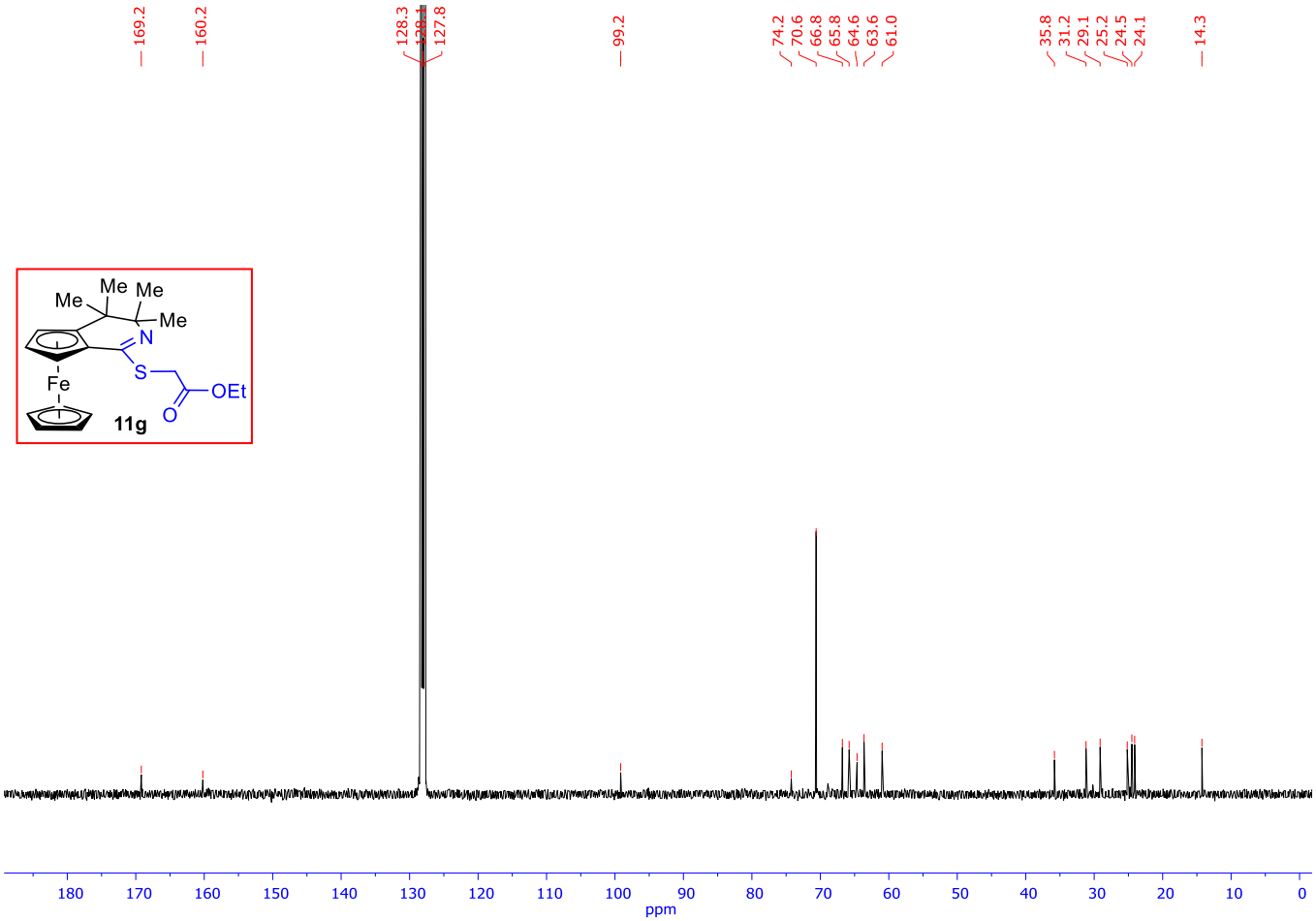


Figure S76. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **11g**.

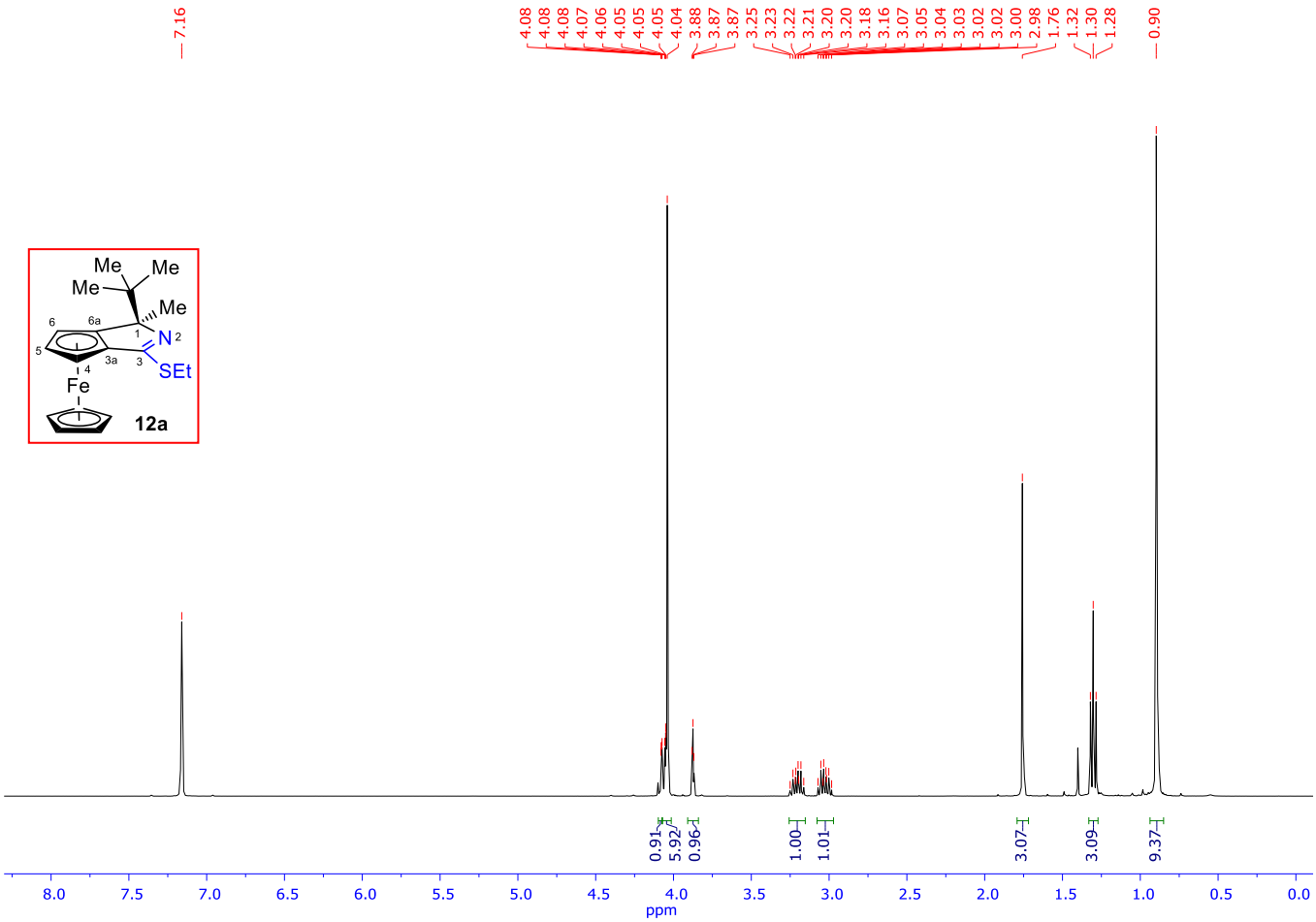


Figure S77. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **12a**.

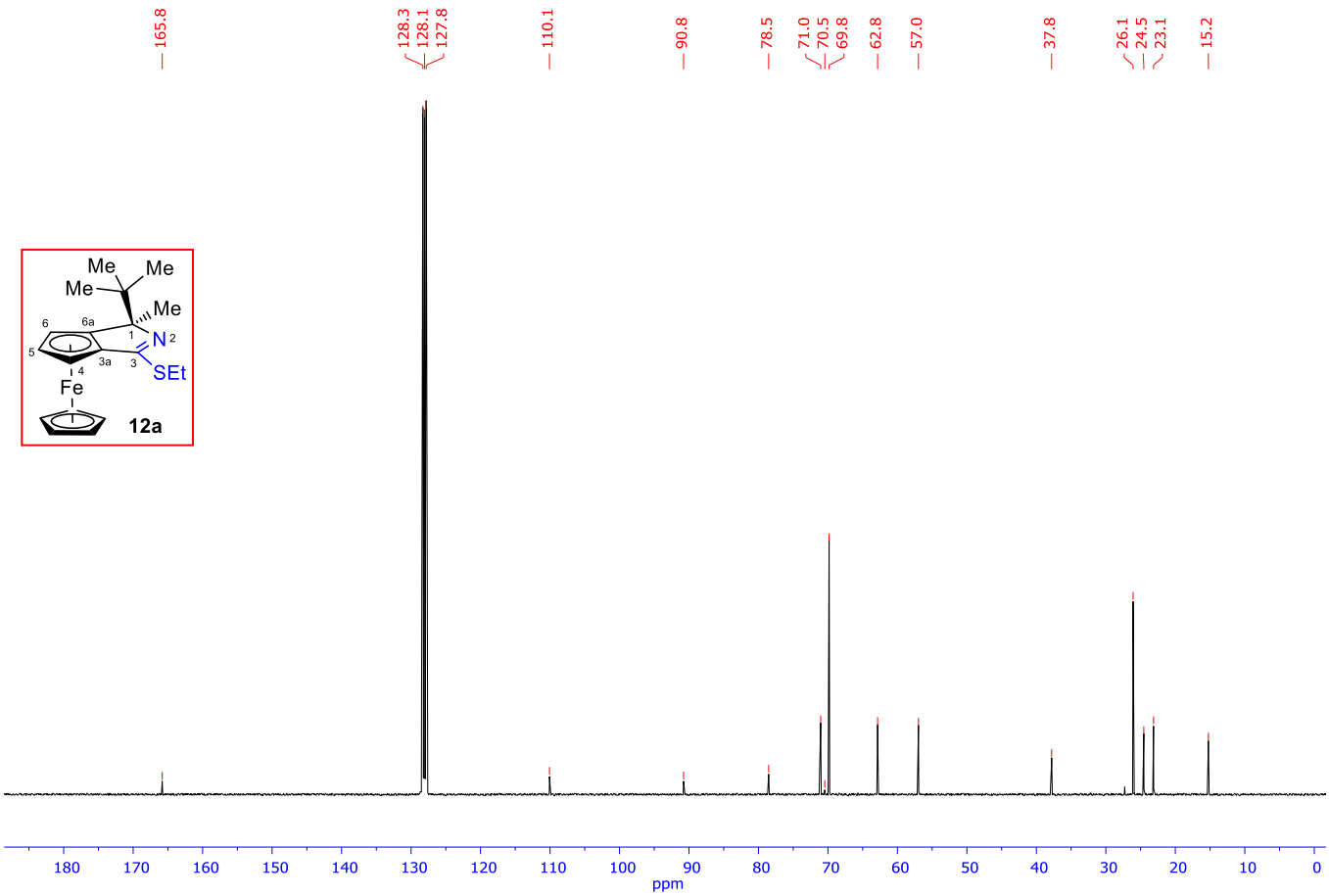


Figure S78. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **12a**.

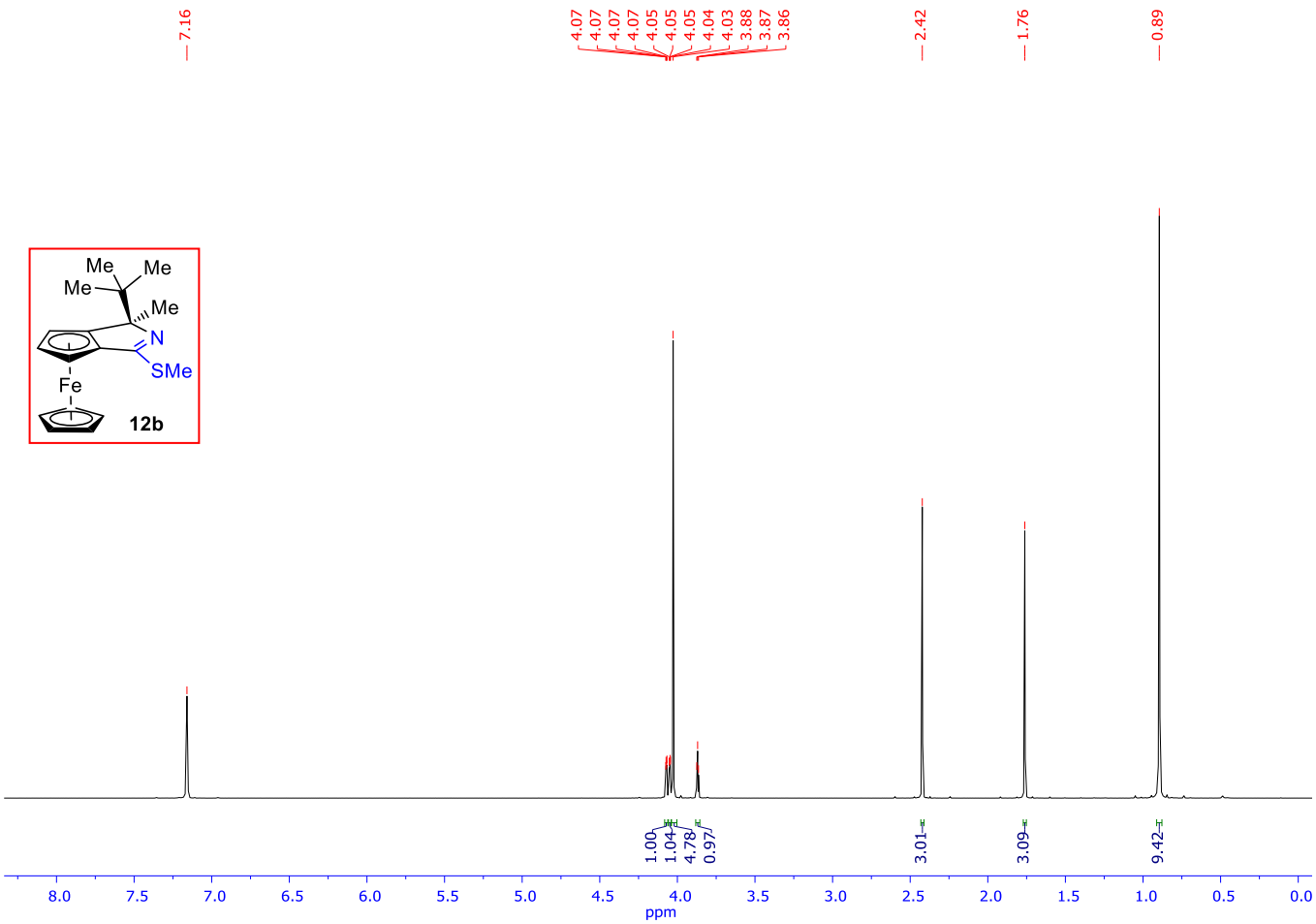


Figure S79. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **12b**.

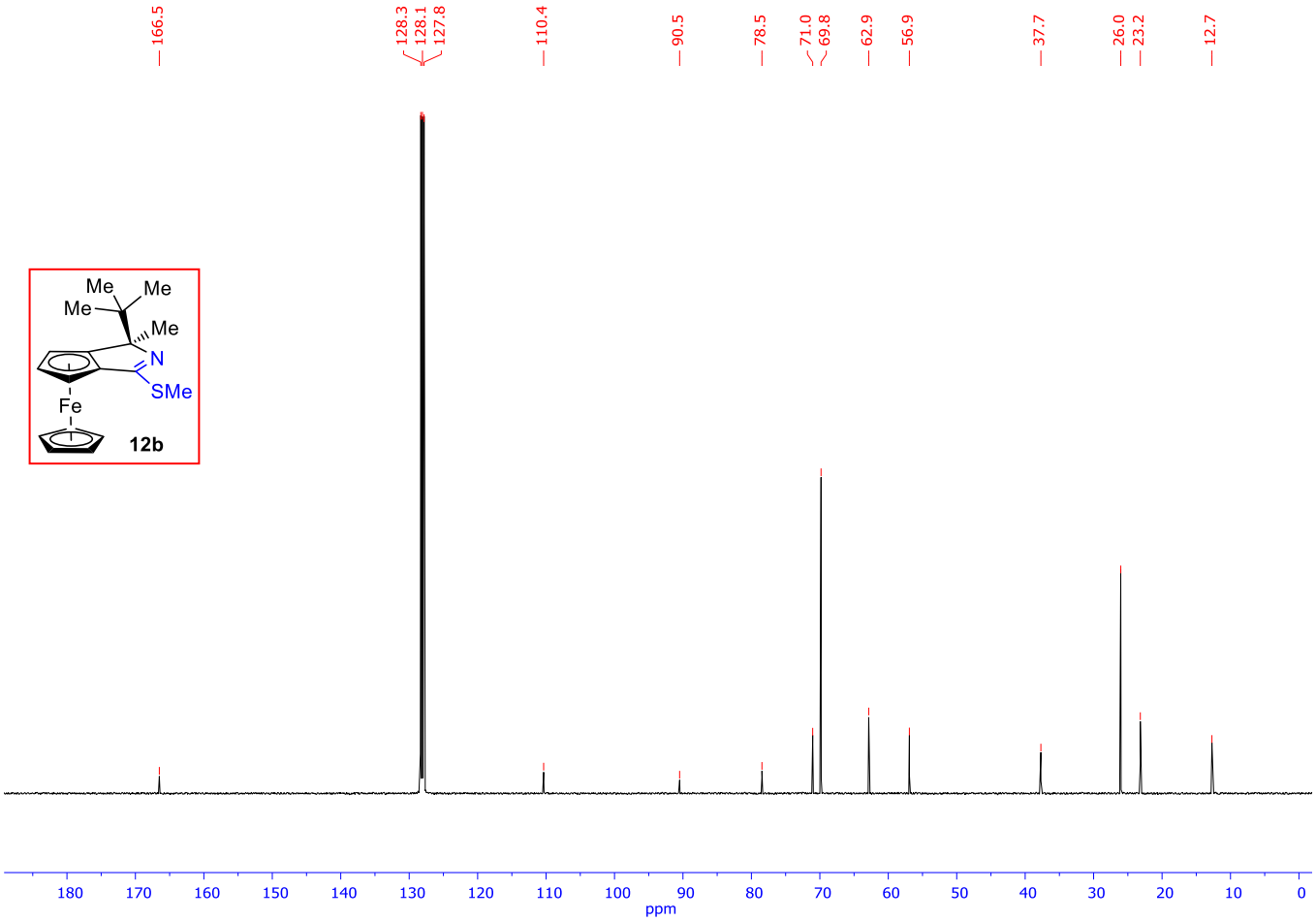


Figure S80. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **12b**.

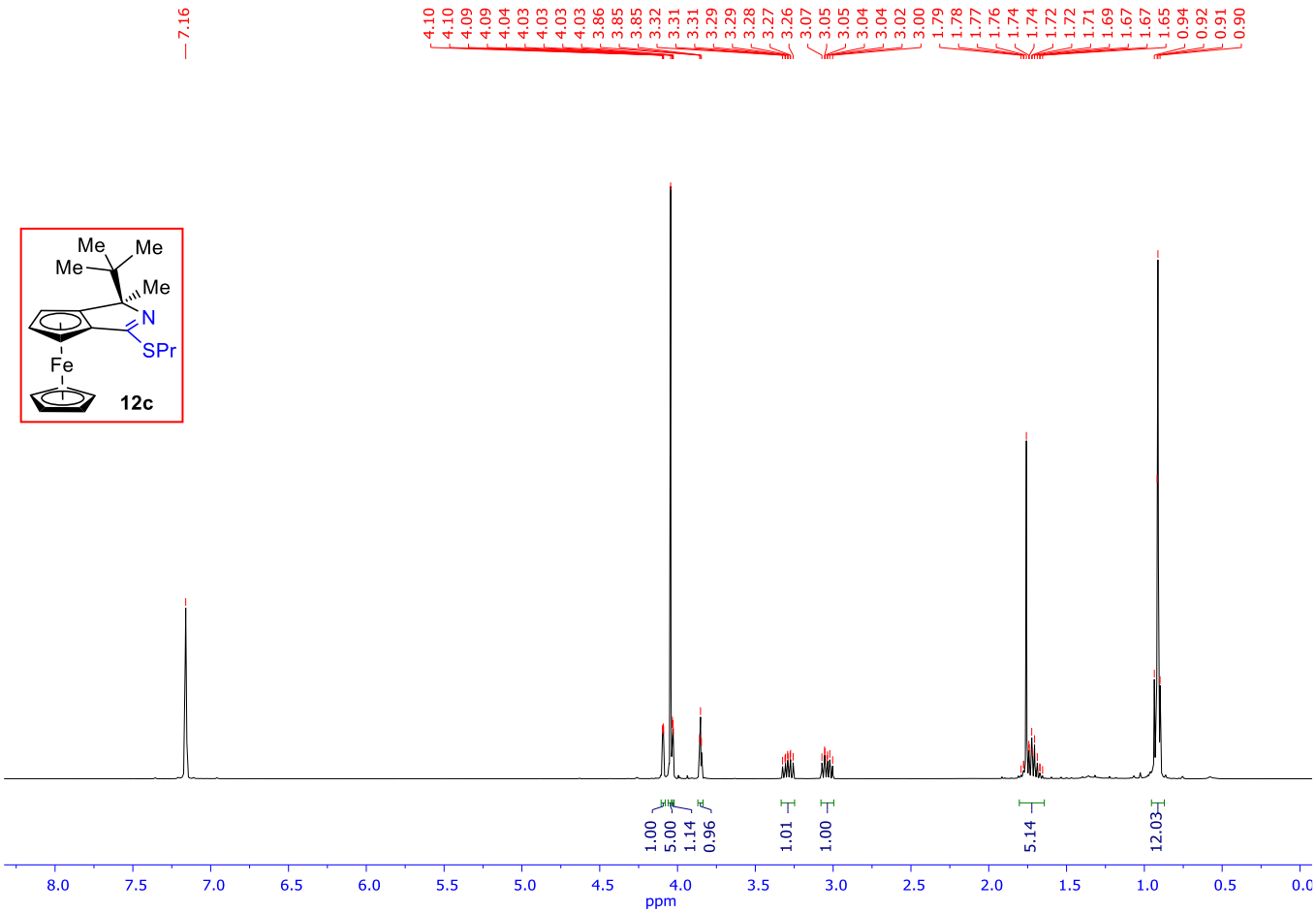


Figure S81. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **12c**.

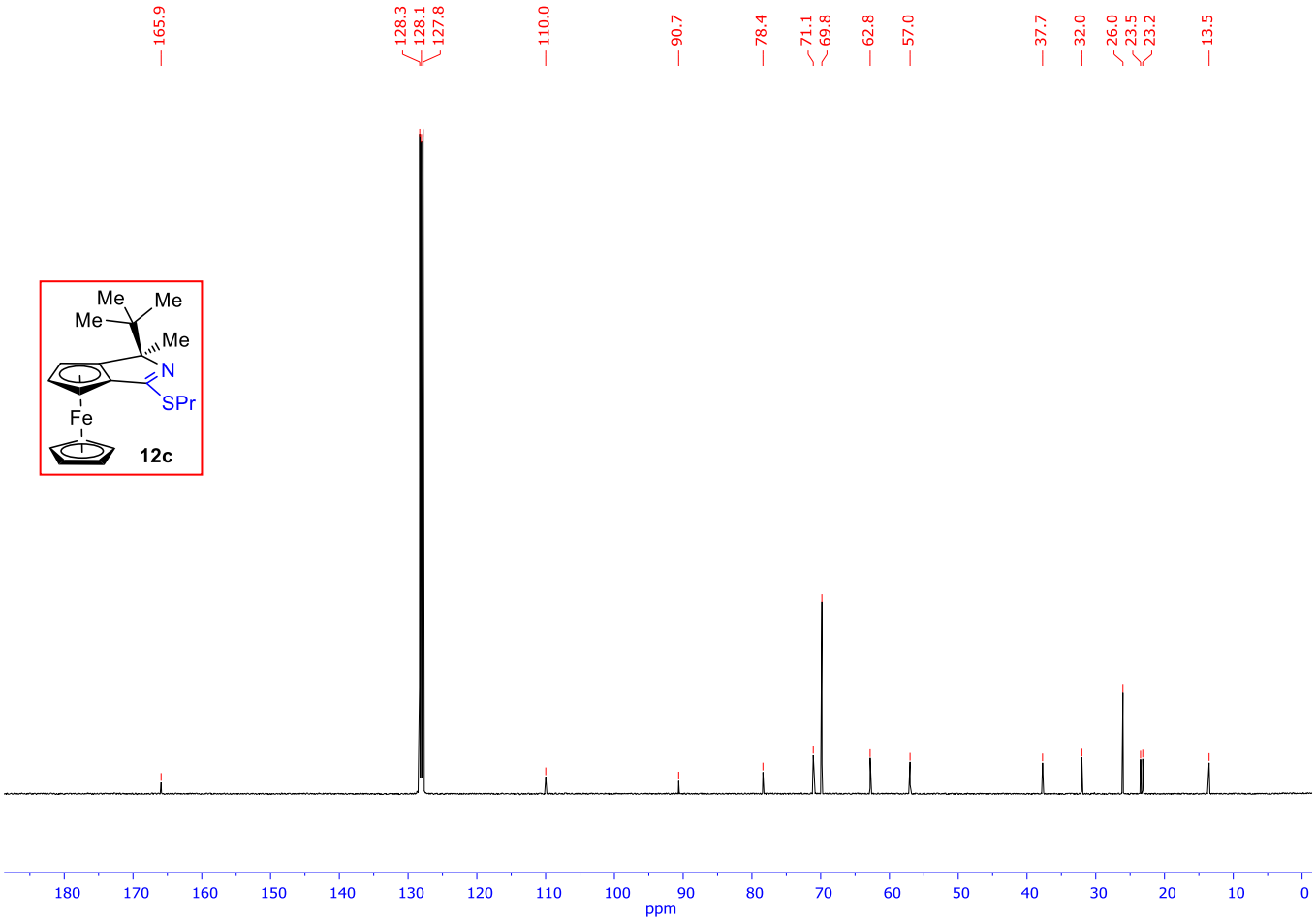


Figure S82. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **12c**.

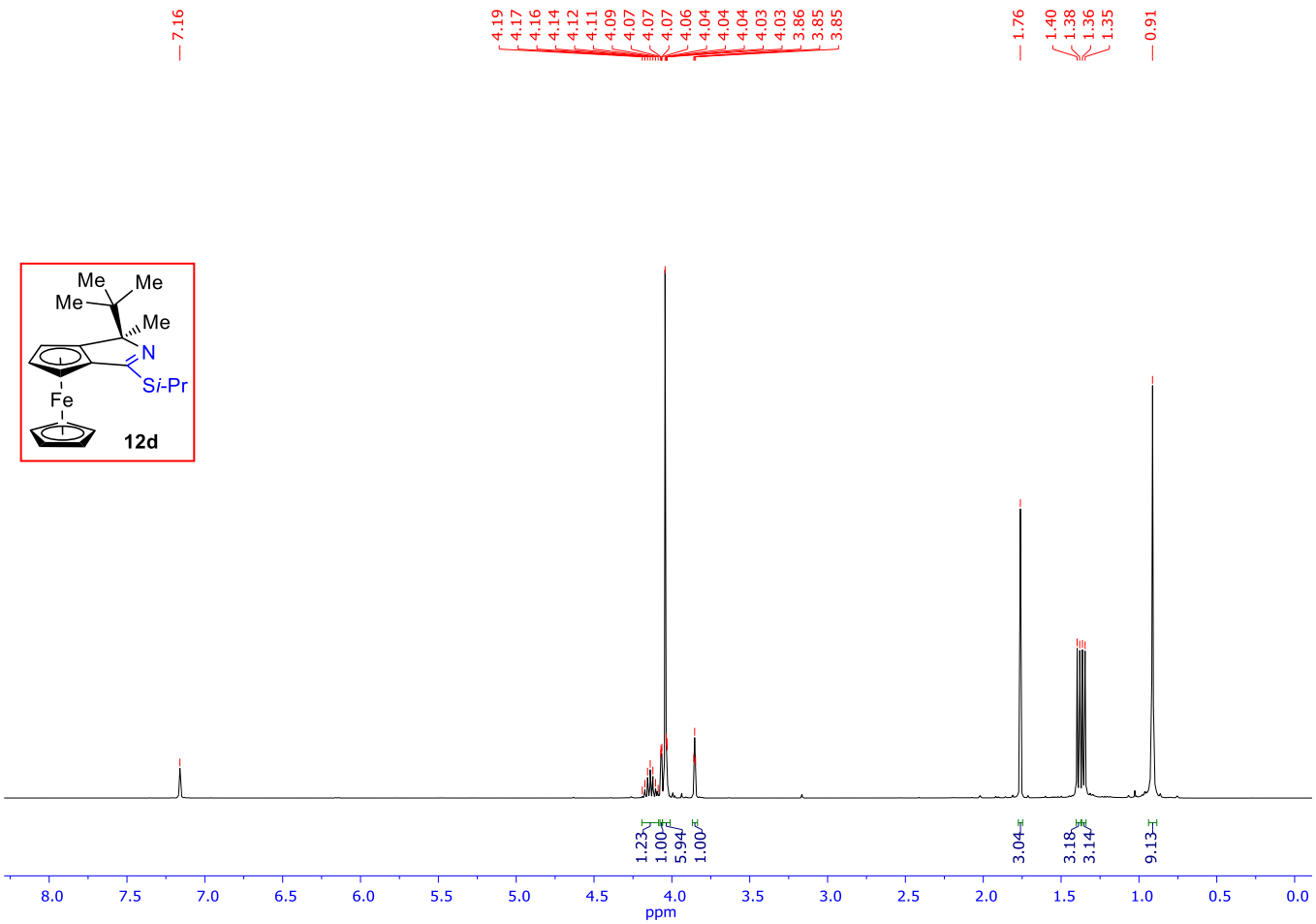


Figure S83. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **12d**.

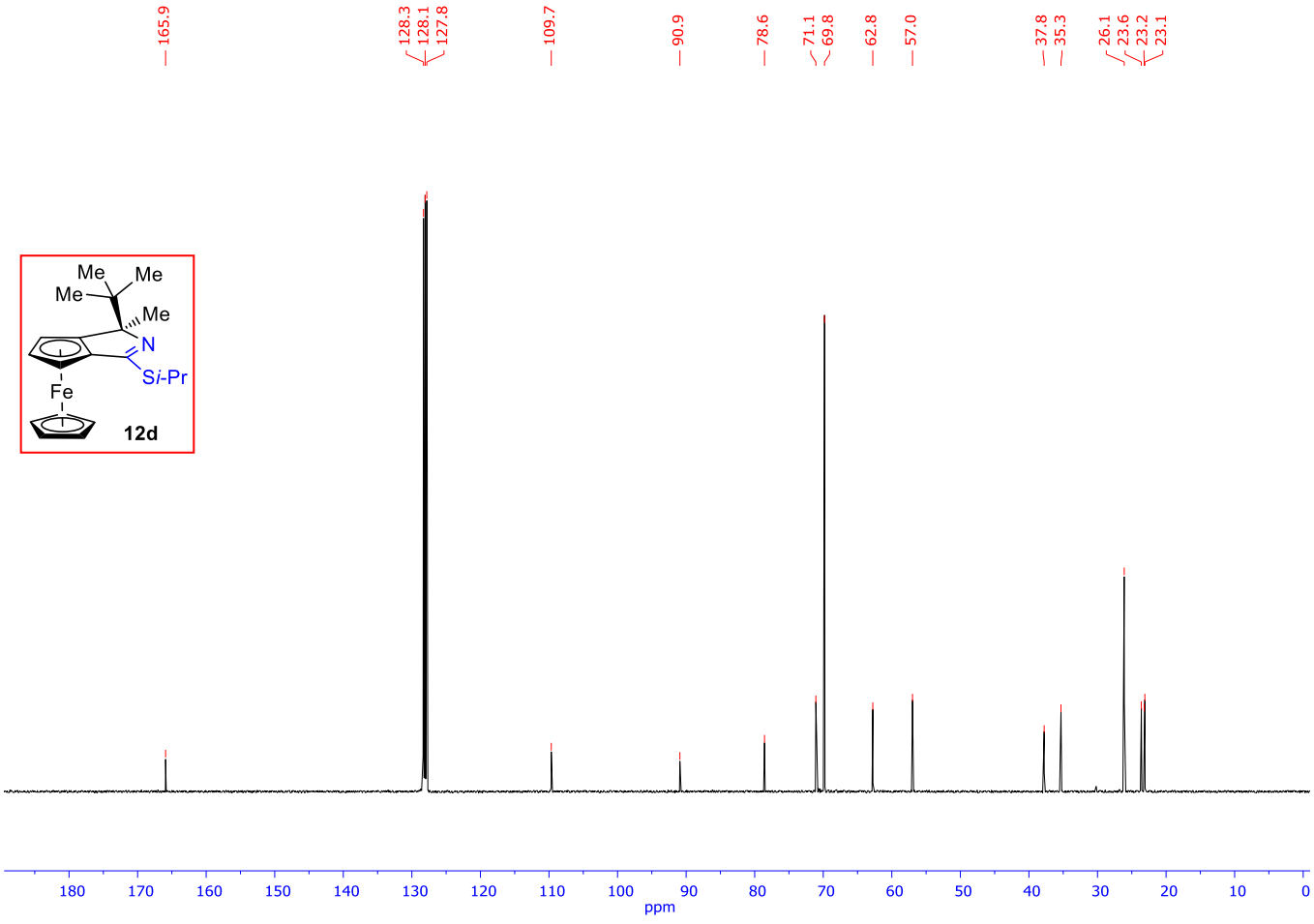


Figure S84. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **12d**.

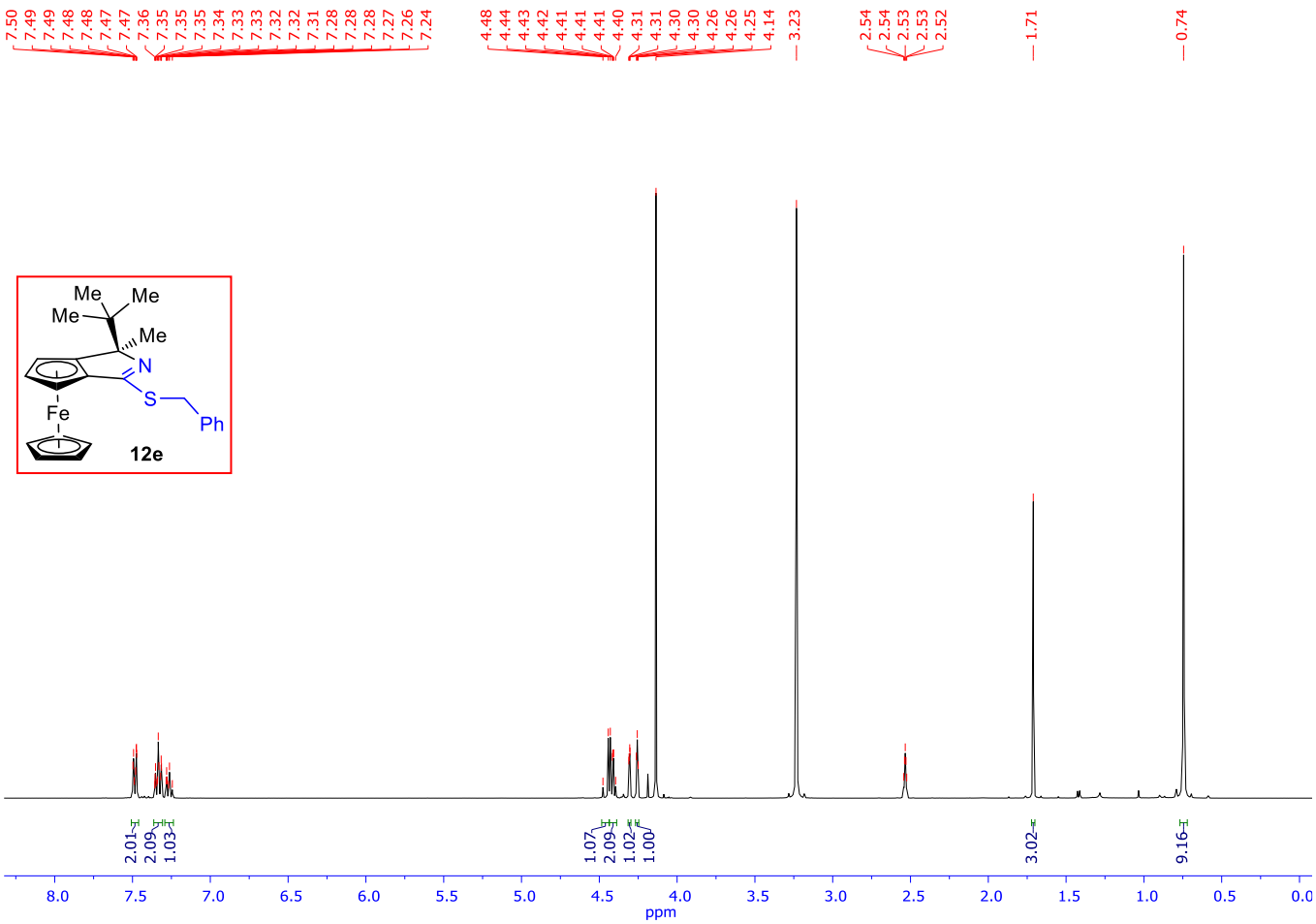


Figure S85. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **12e**.

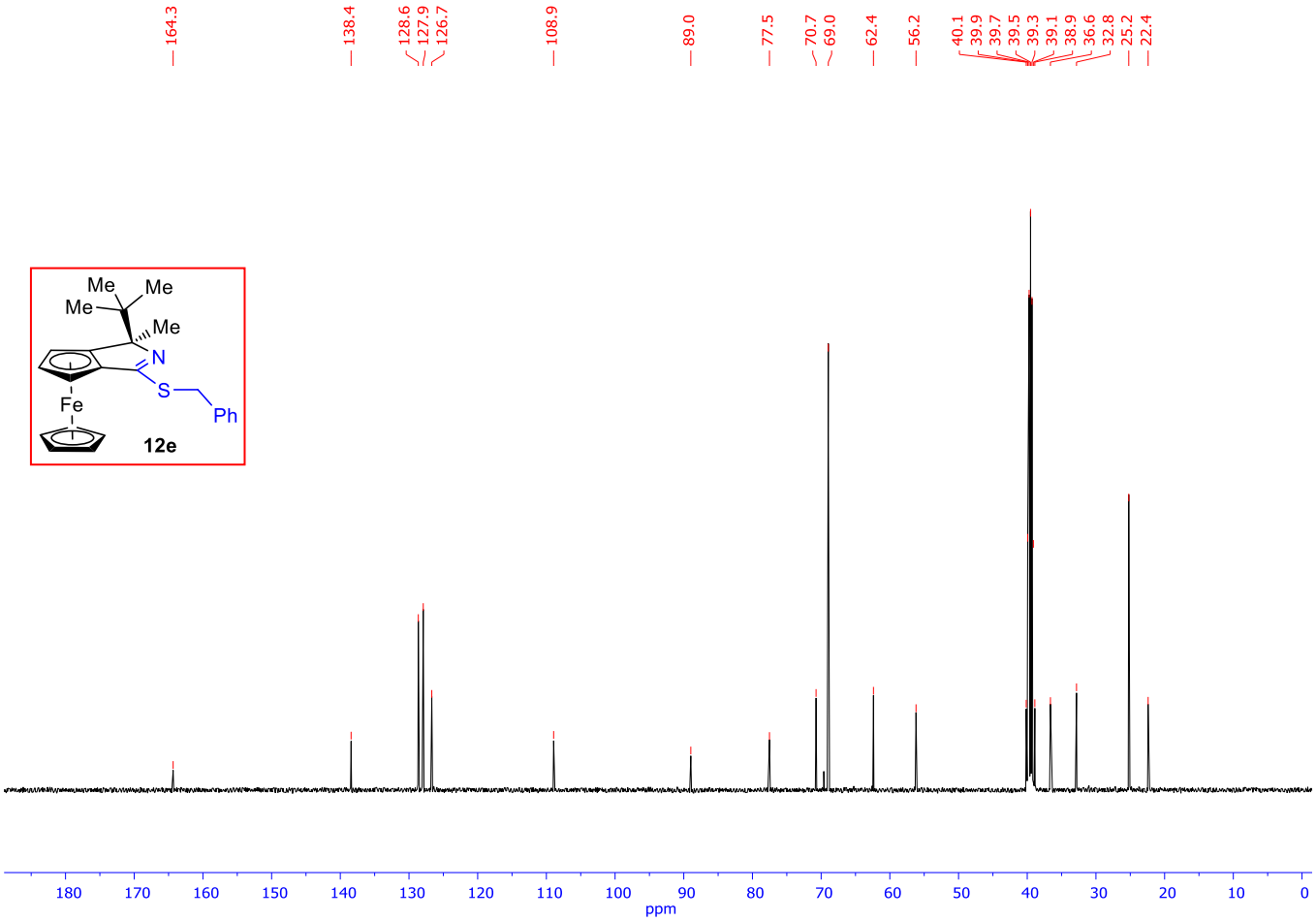


Figure S86. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **12e**.

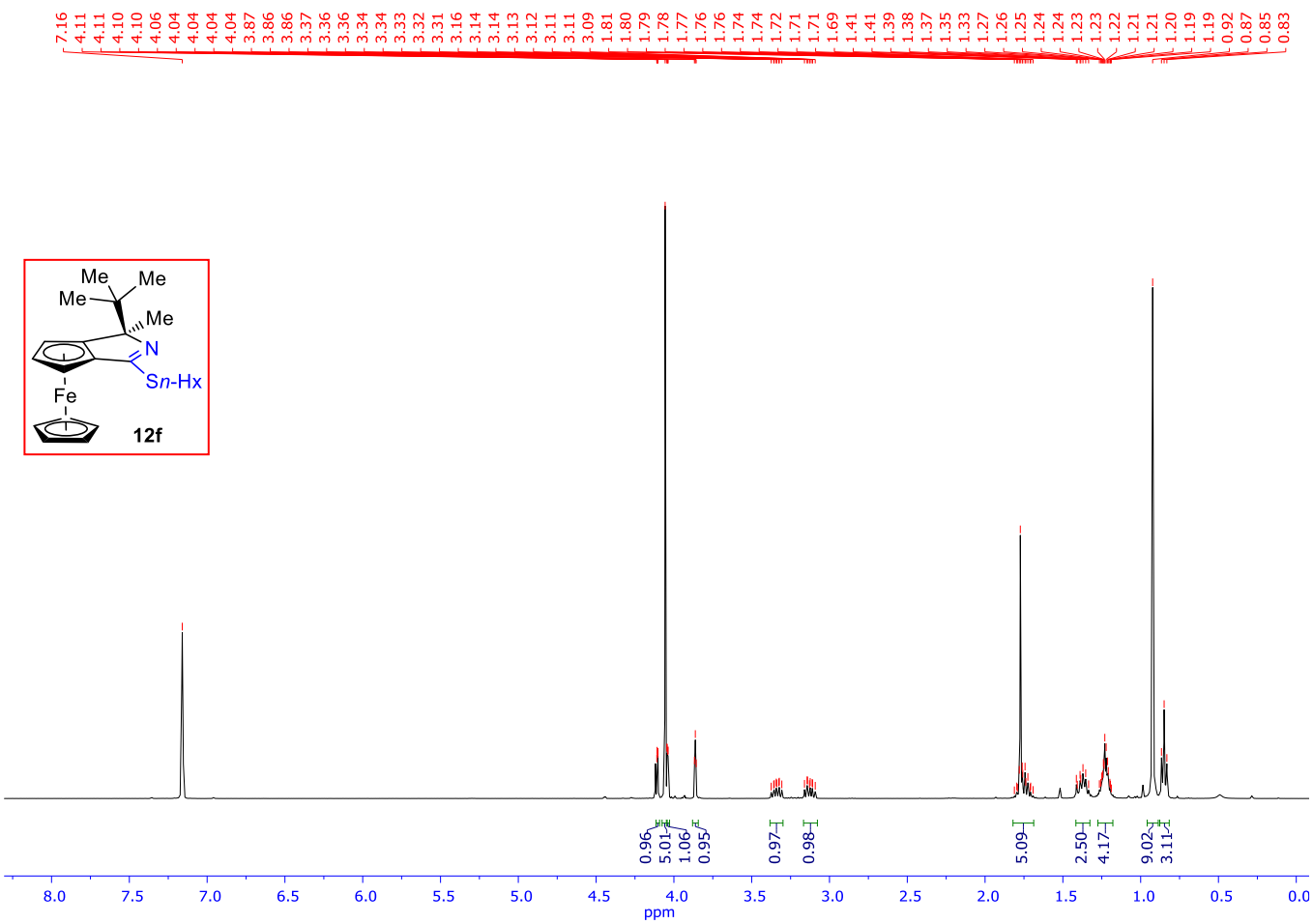


Figure S87. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **12f**.

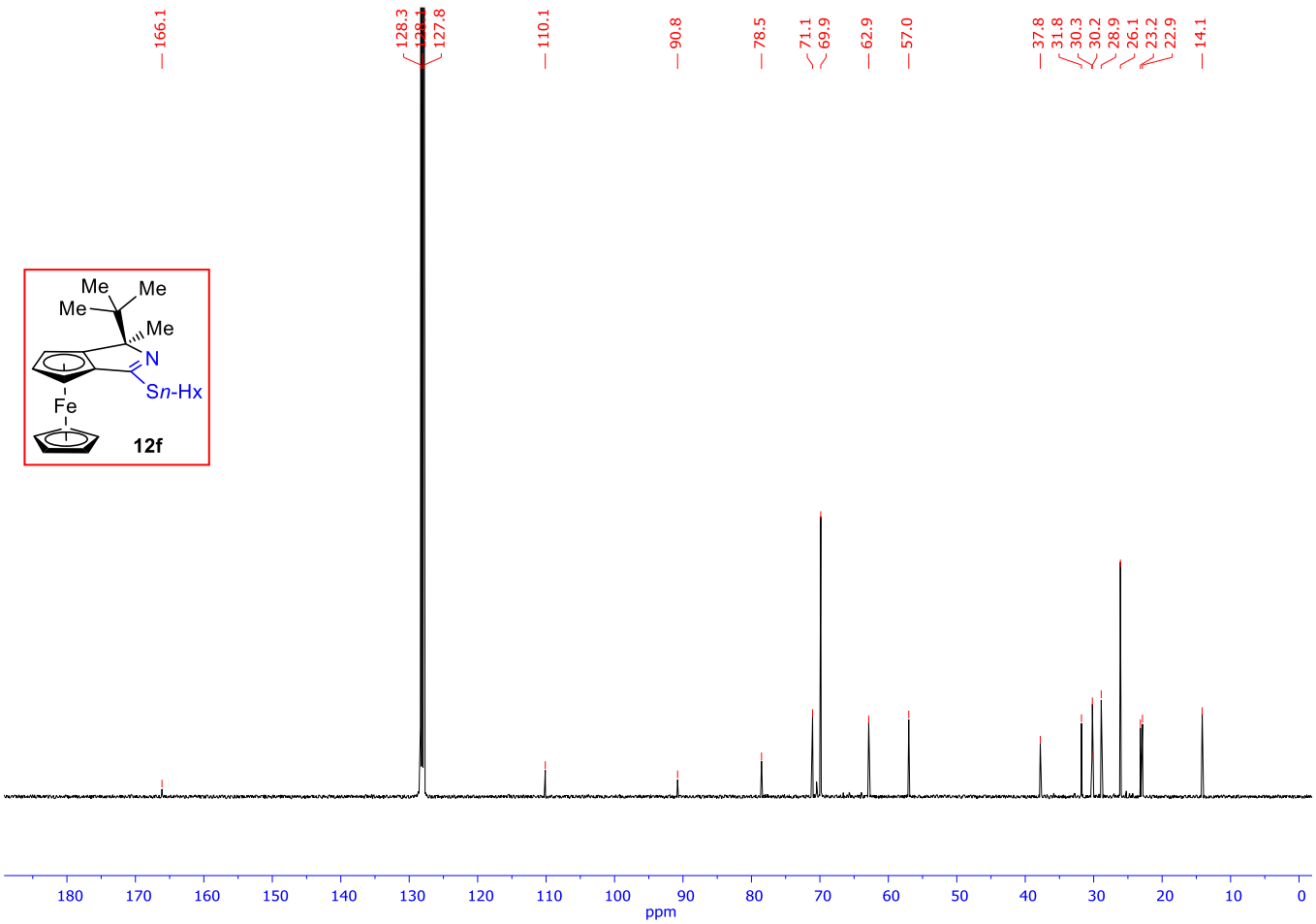


Figure S89. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **12f**.

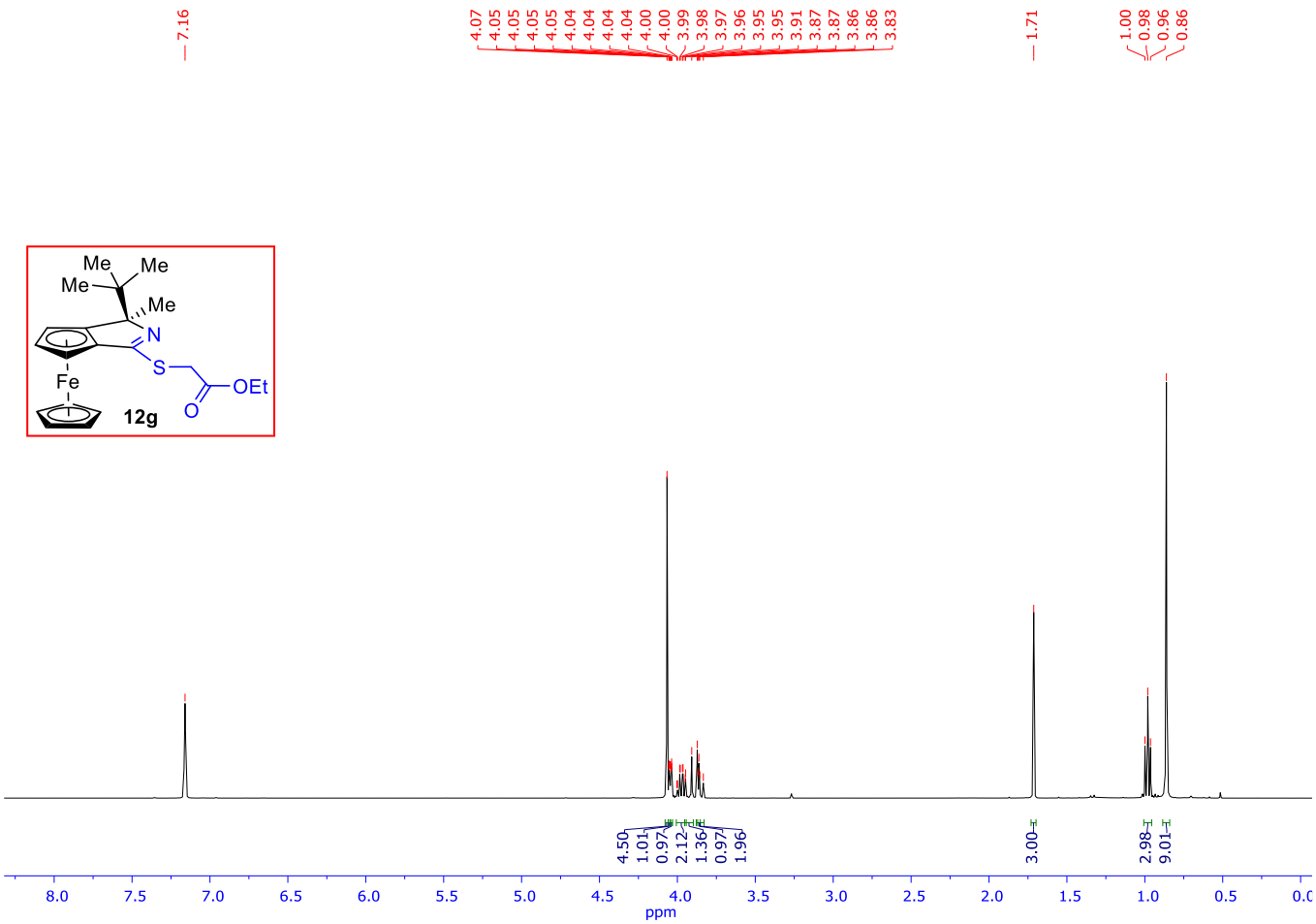


Figure S90. ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **12g**.

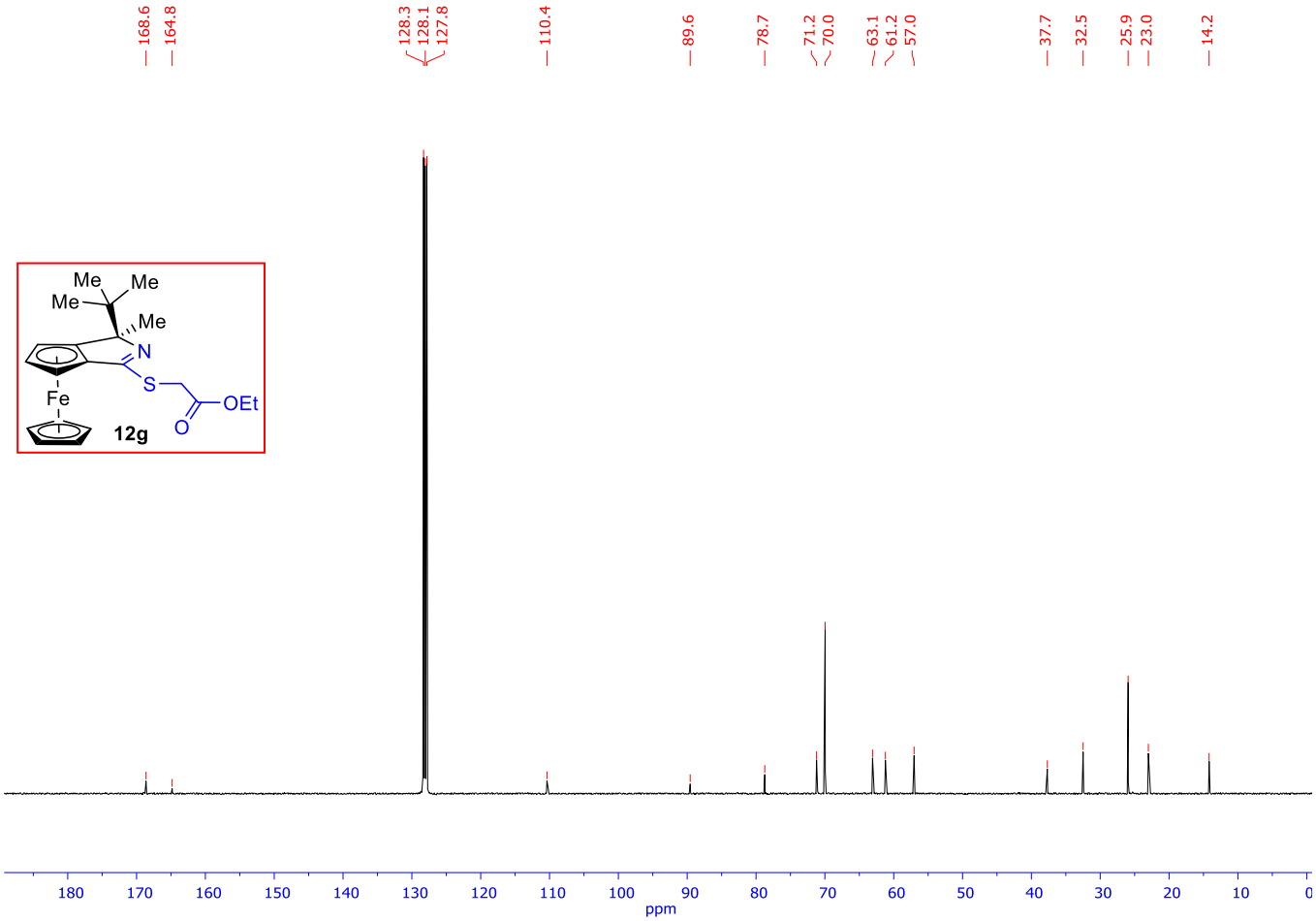


Figure S91. ^{13}C NMR spectrum (100 MHz, C_6D_6) of compound **12g**.

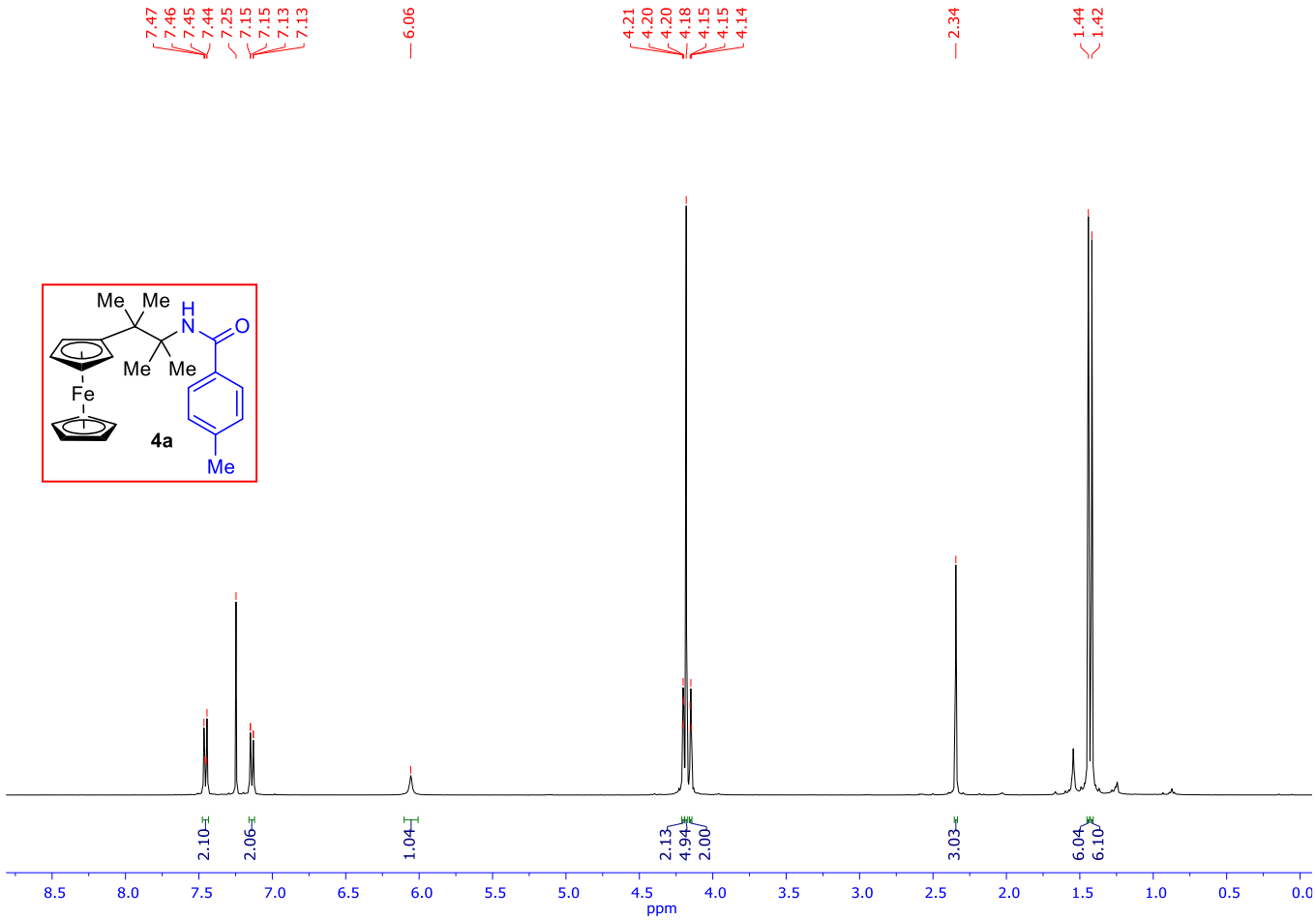


Figure S92. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4a**.

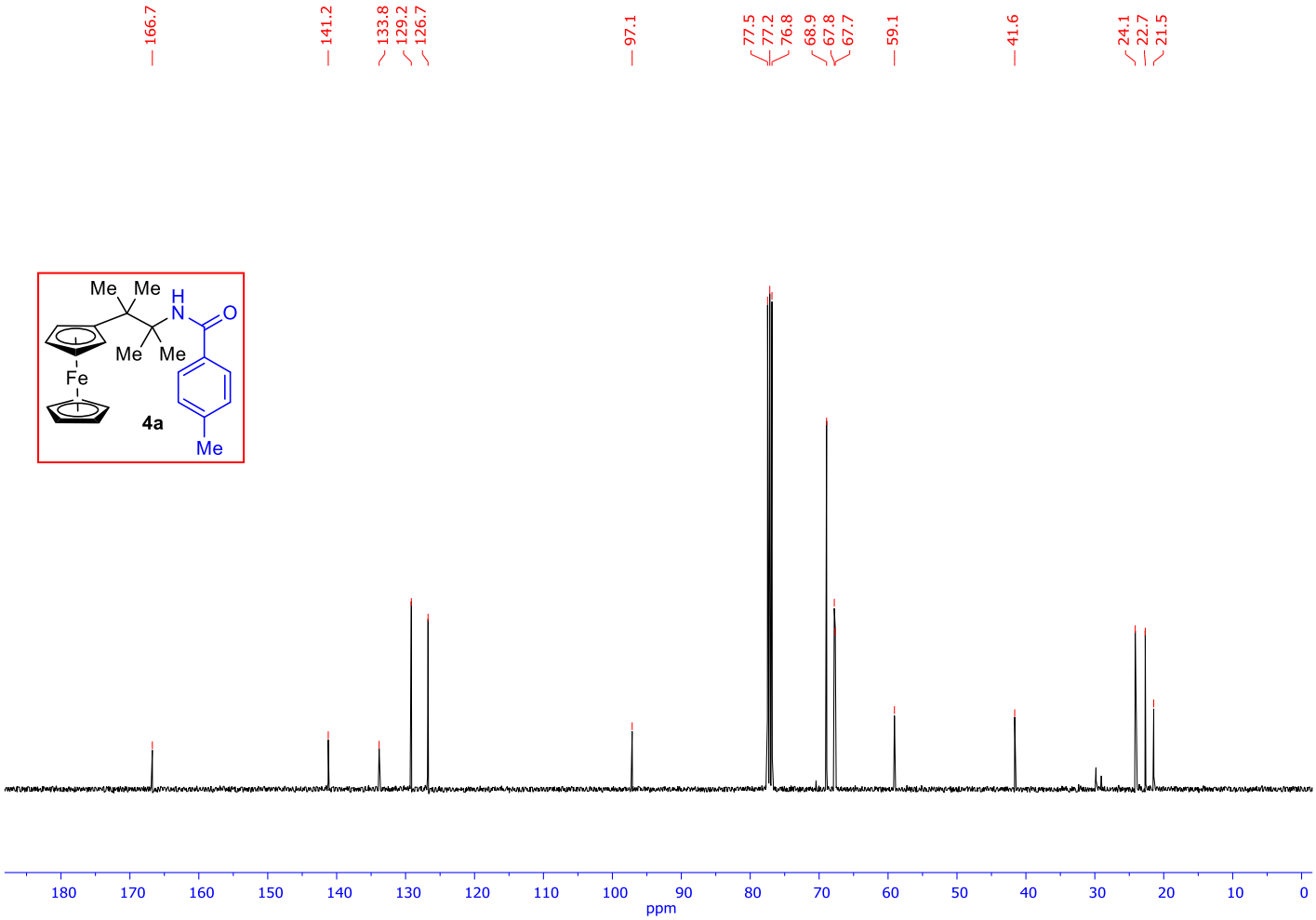


Figure S93. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **4a**.

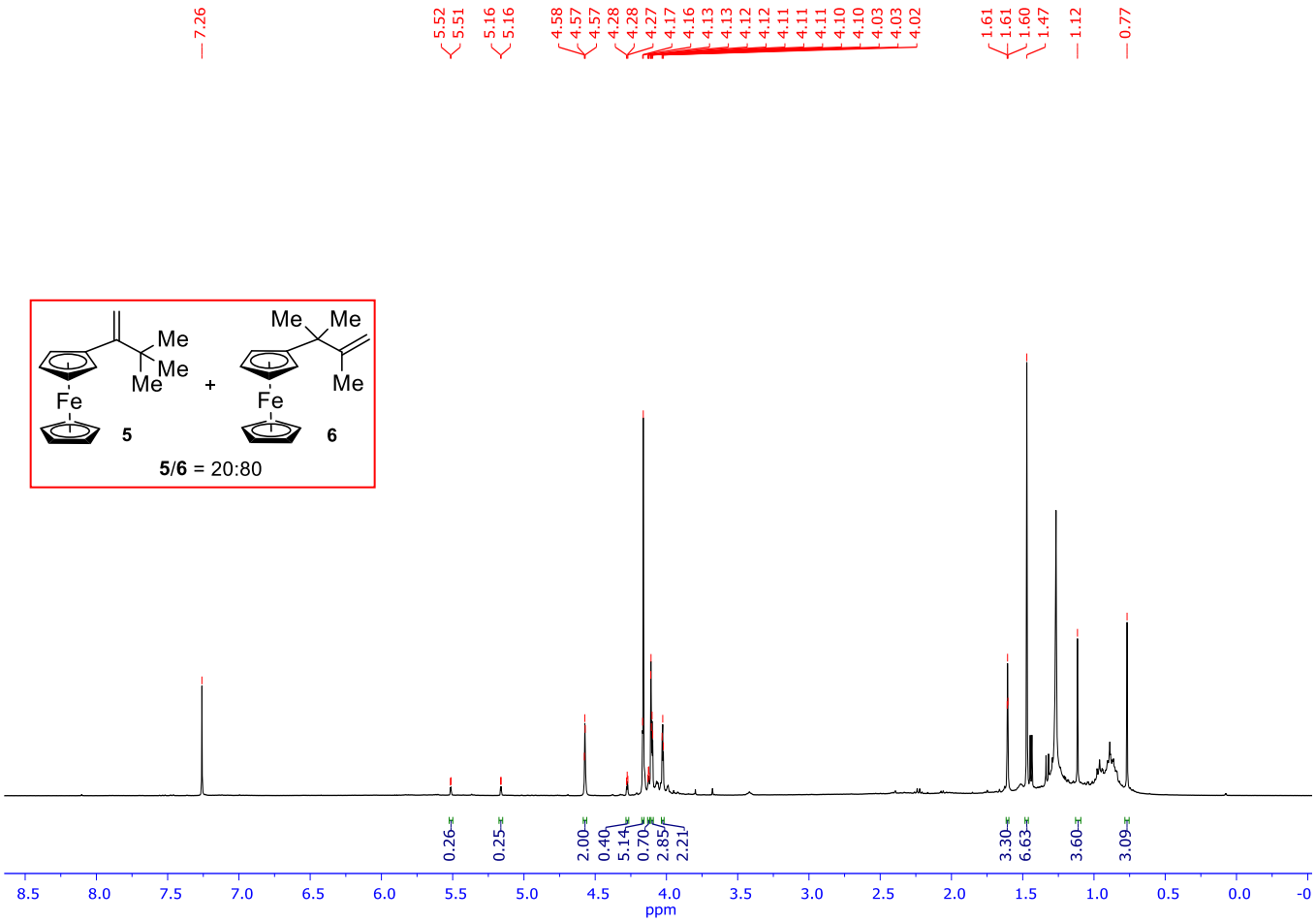


Figure S94. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of mixture of compounds **5** and **6**.

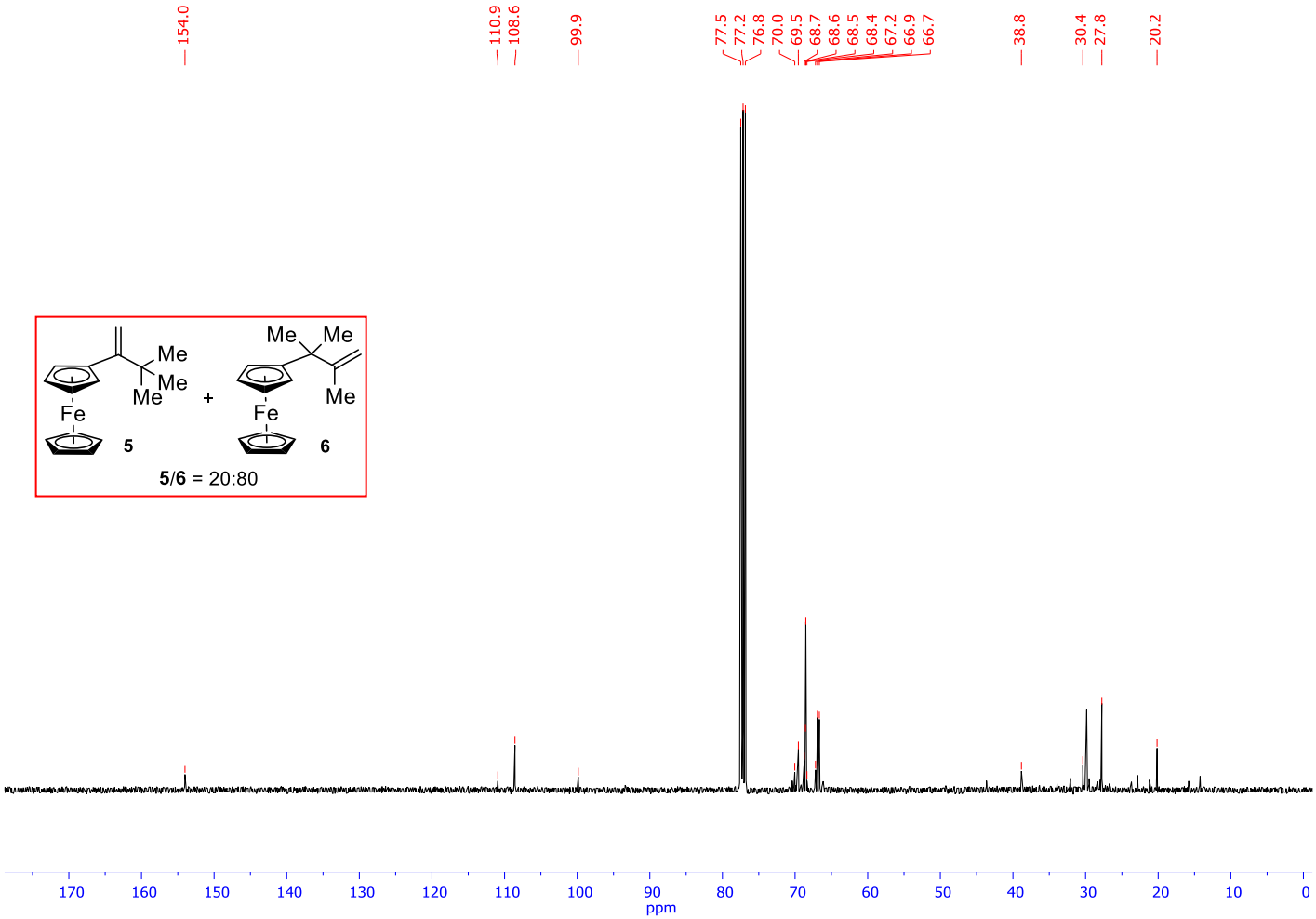


Figure S95. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of mixture of compounds **5** and **6**.

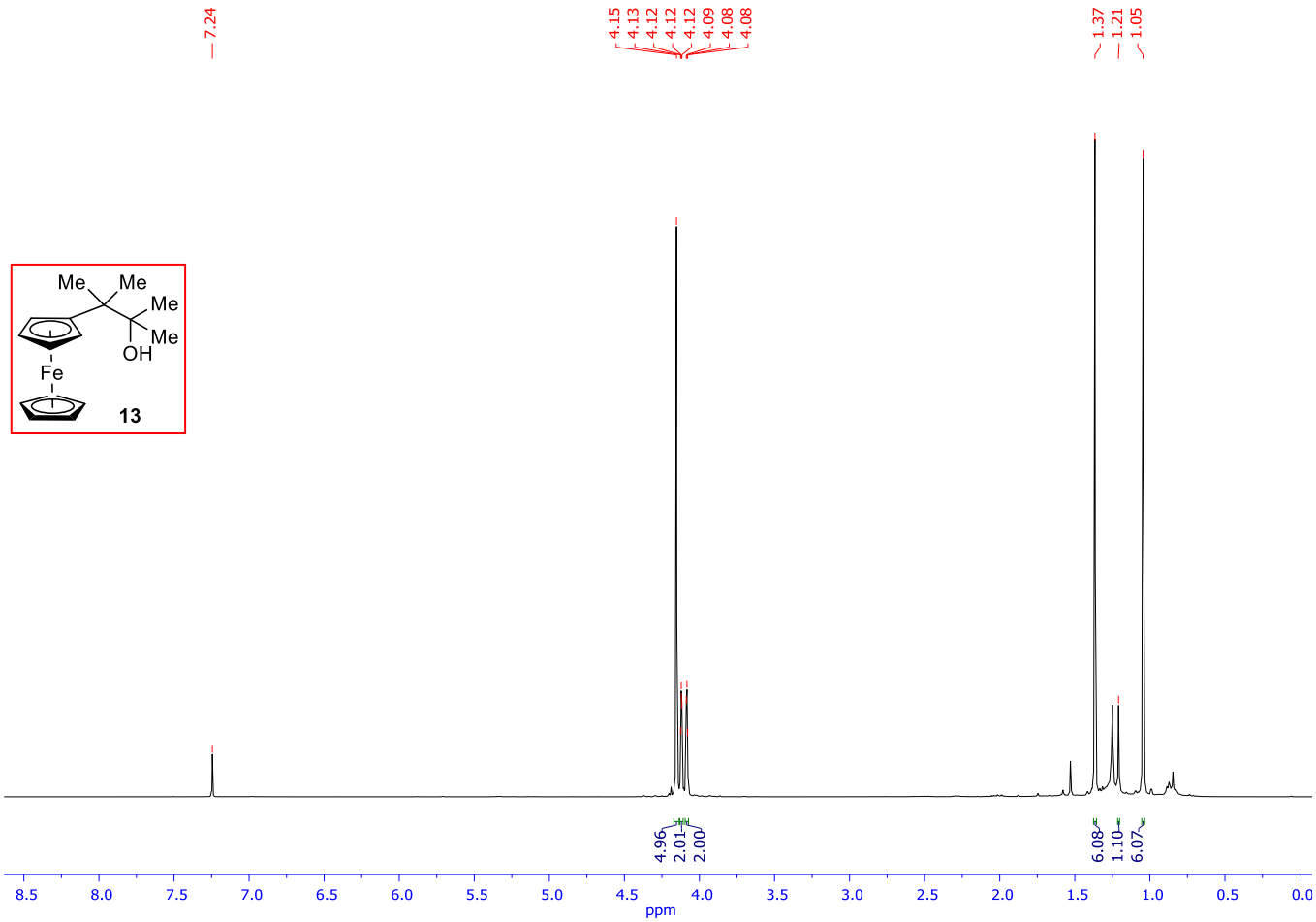


Figure S96. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **13**.

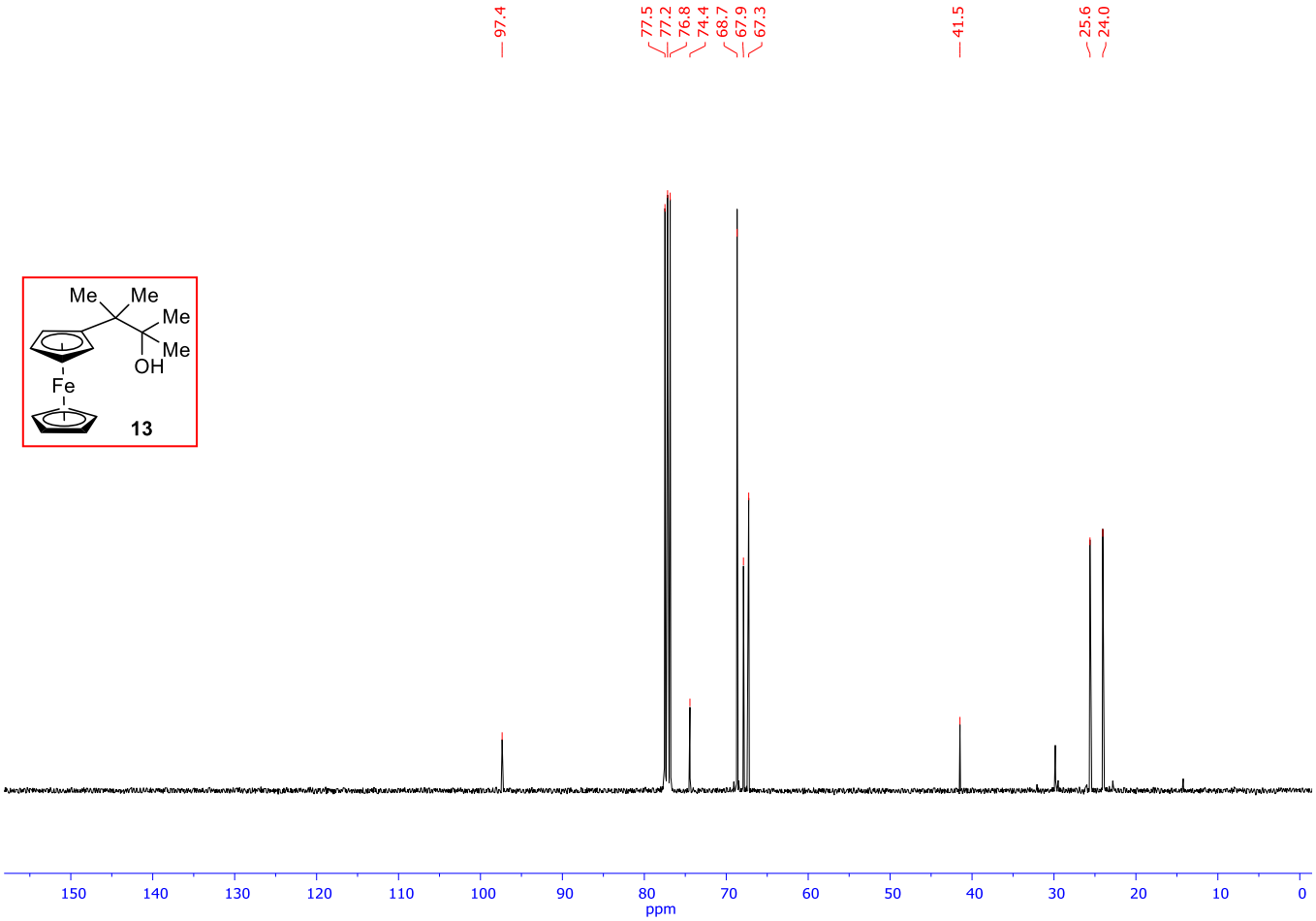


Figure S97. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **13**.

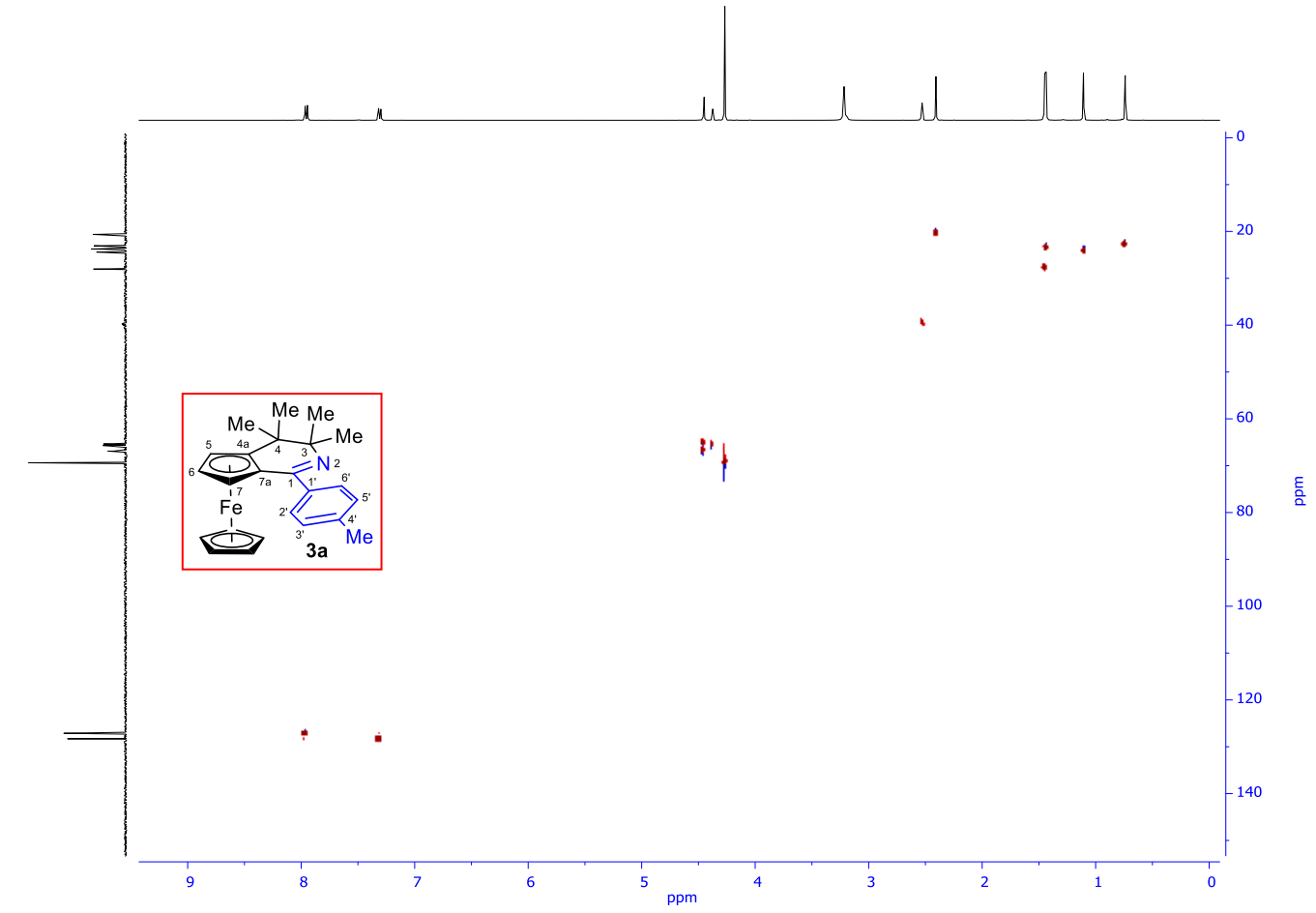


Figure S98. HSQC spectrum (400 MHz, DMSO-d_6) of compound **3a**.

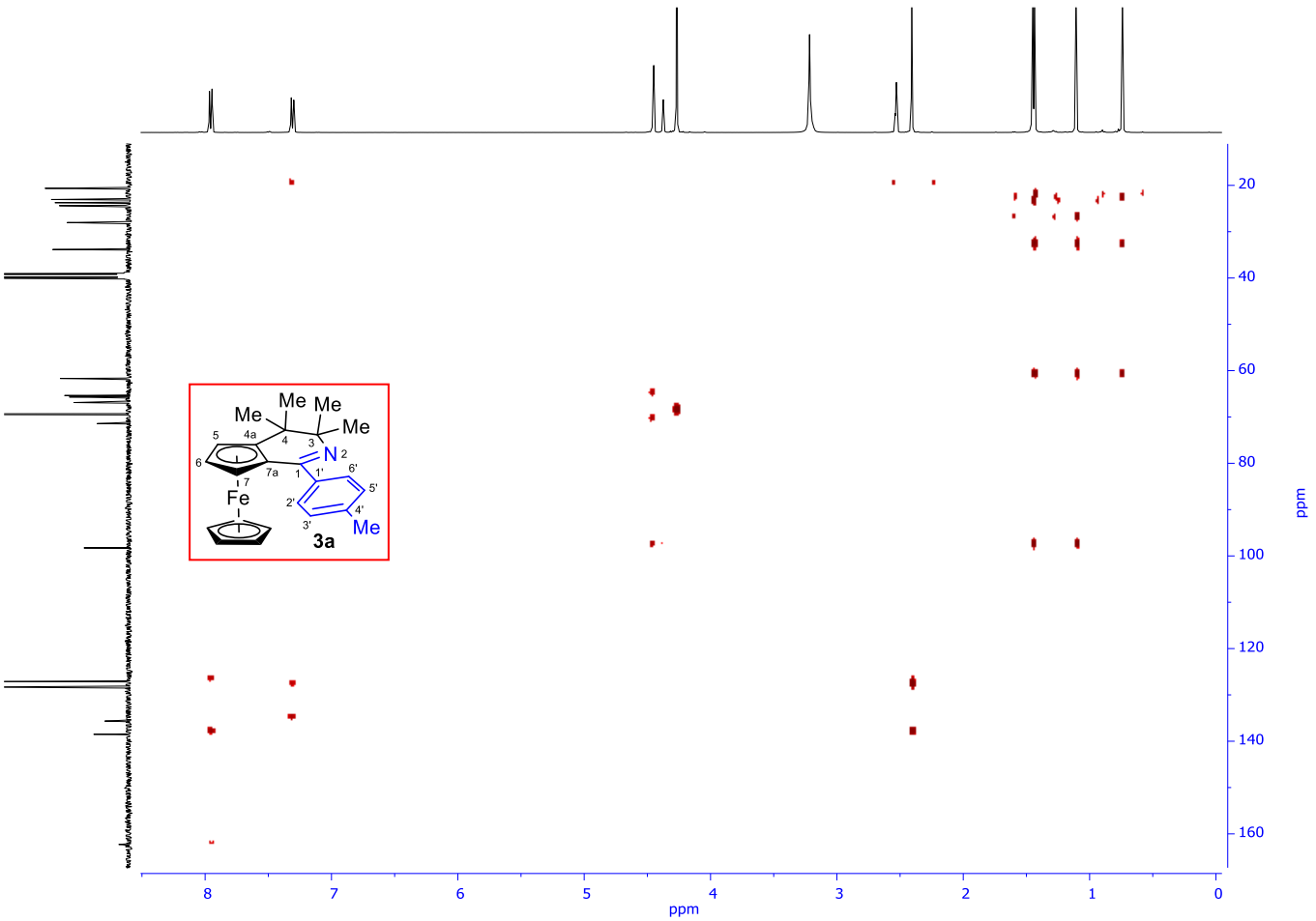


Figure S99. HMBC spectrum (400 MHz, DMSO-d_6) of compound **3a**.

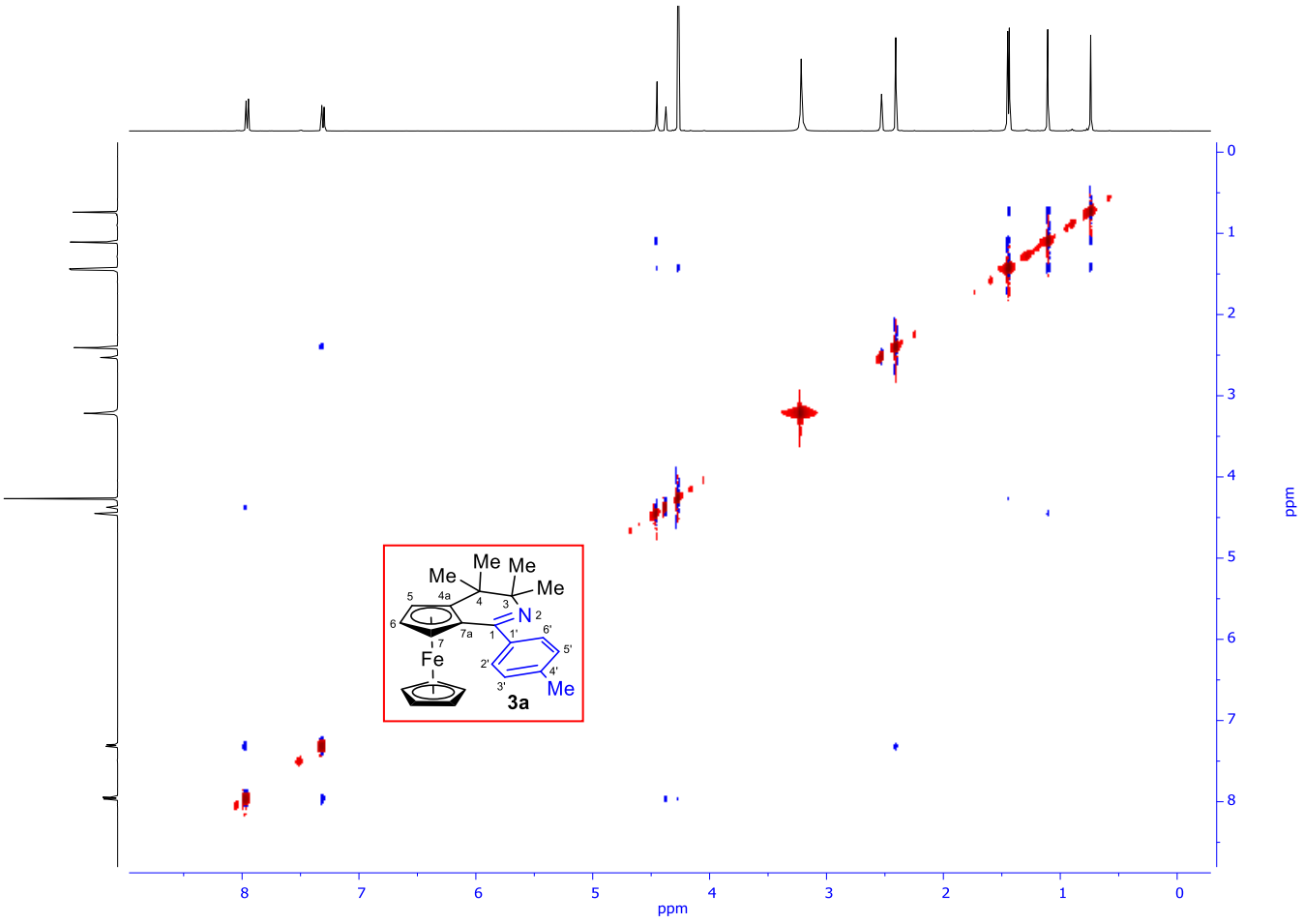


Figure S100. 2D NOESY spectrum (400 MHz, DMSO-d_6) of compound **3a**.

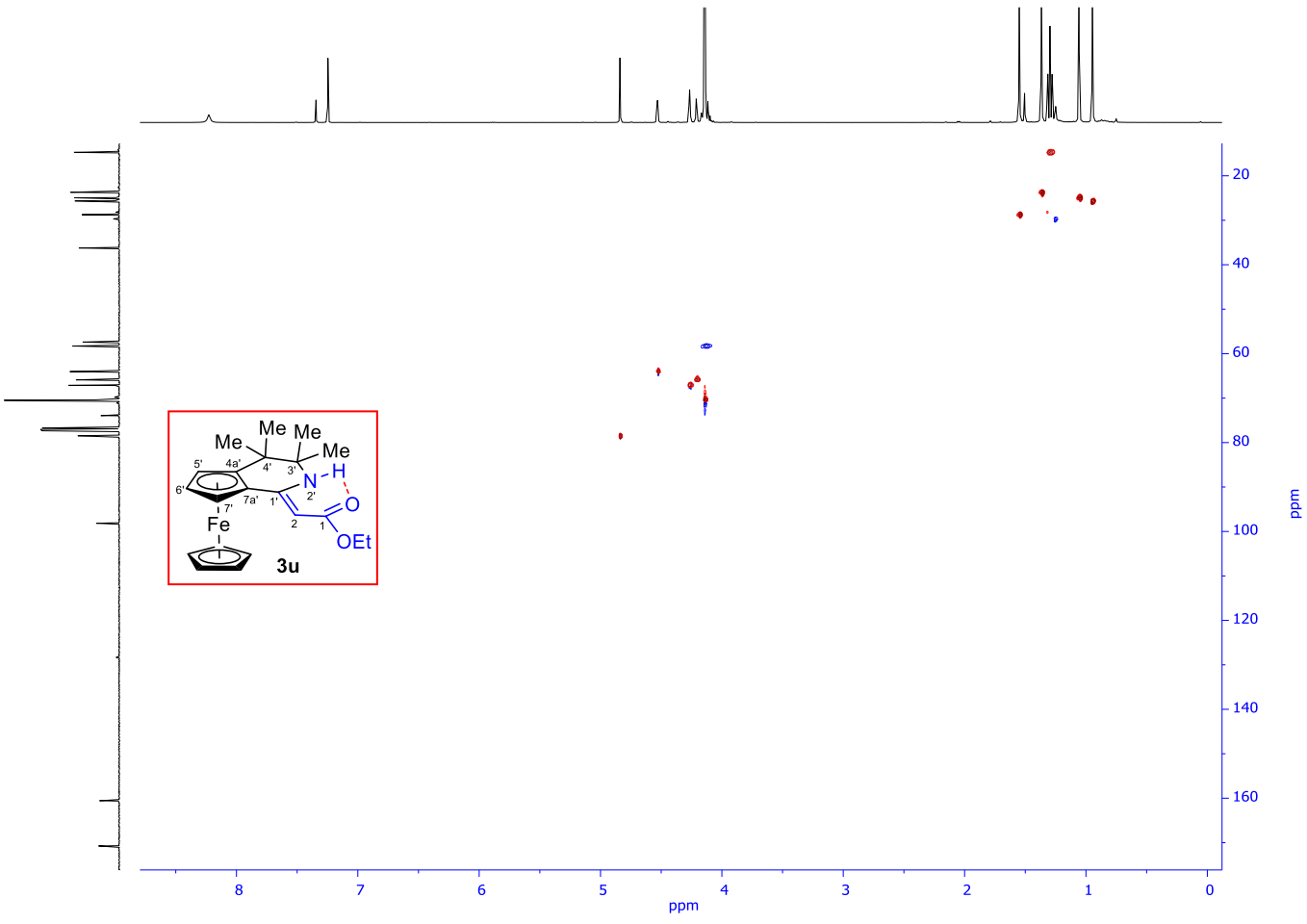


Figure S101. HSQC spectrum (400 MHz, $CDCl_3$) of compound **3u**.

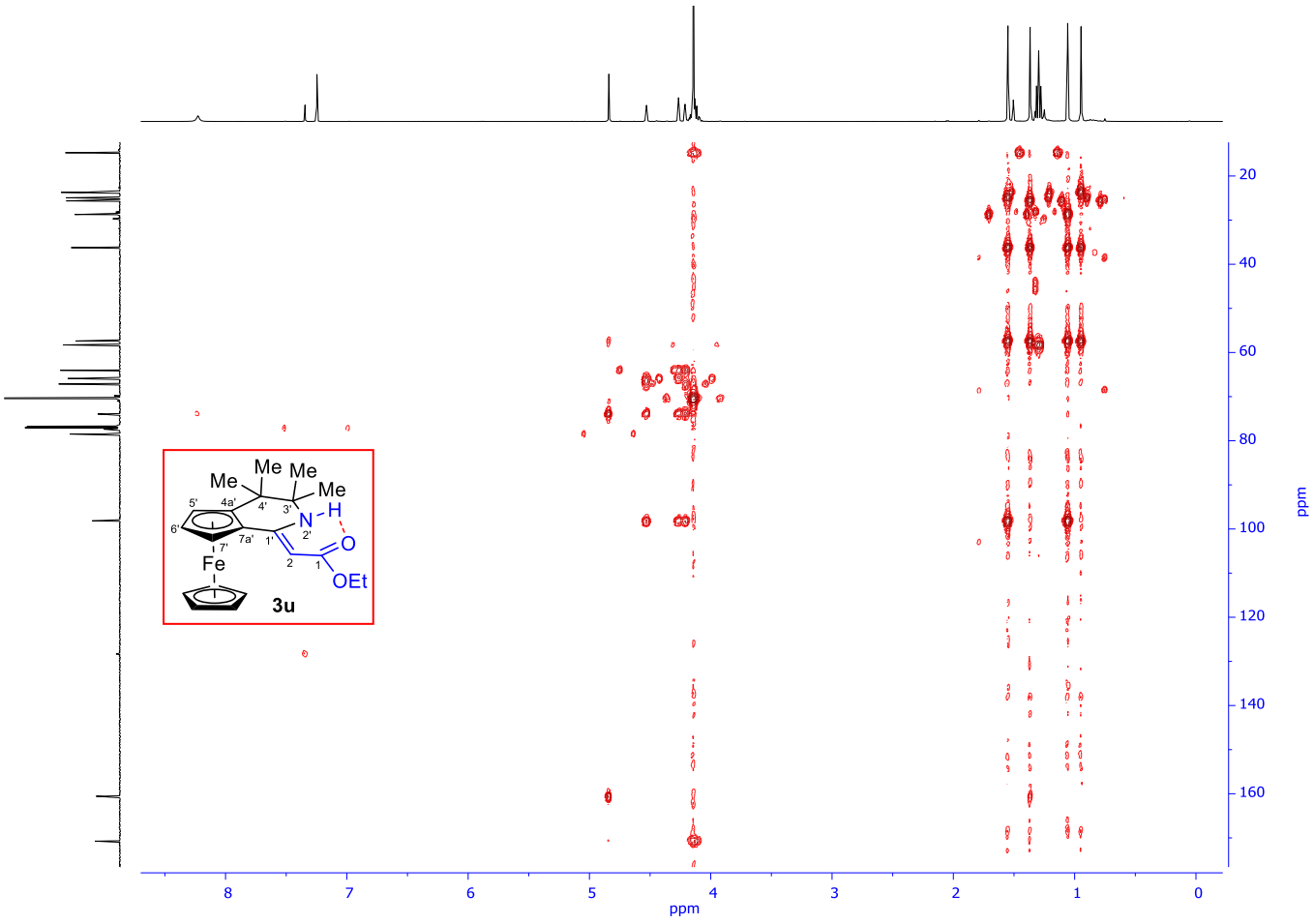


Figure S102. HMBC spectrum (400 MHz, $CDCl_3$) of compound **3u**.

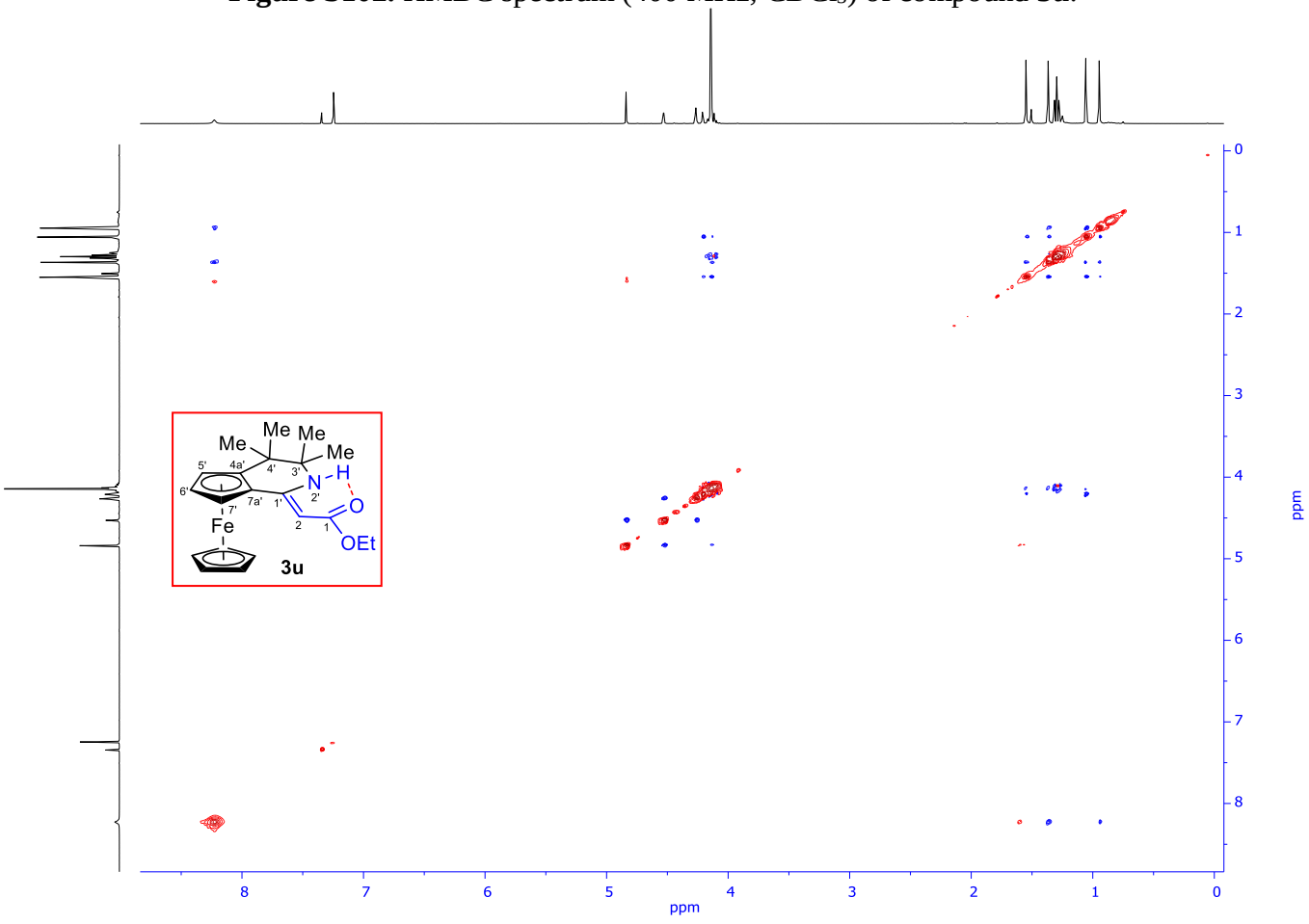


Figure S103. 2D NOESY spectrum (400 MHz, $CDCl_3$) of compound **3u**.

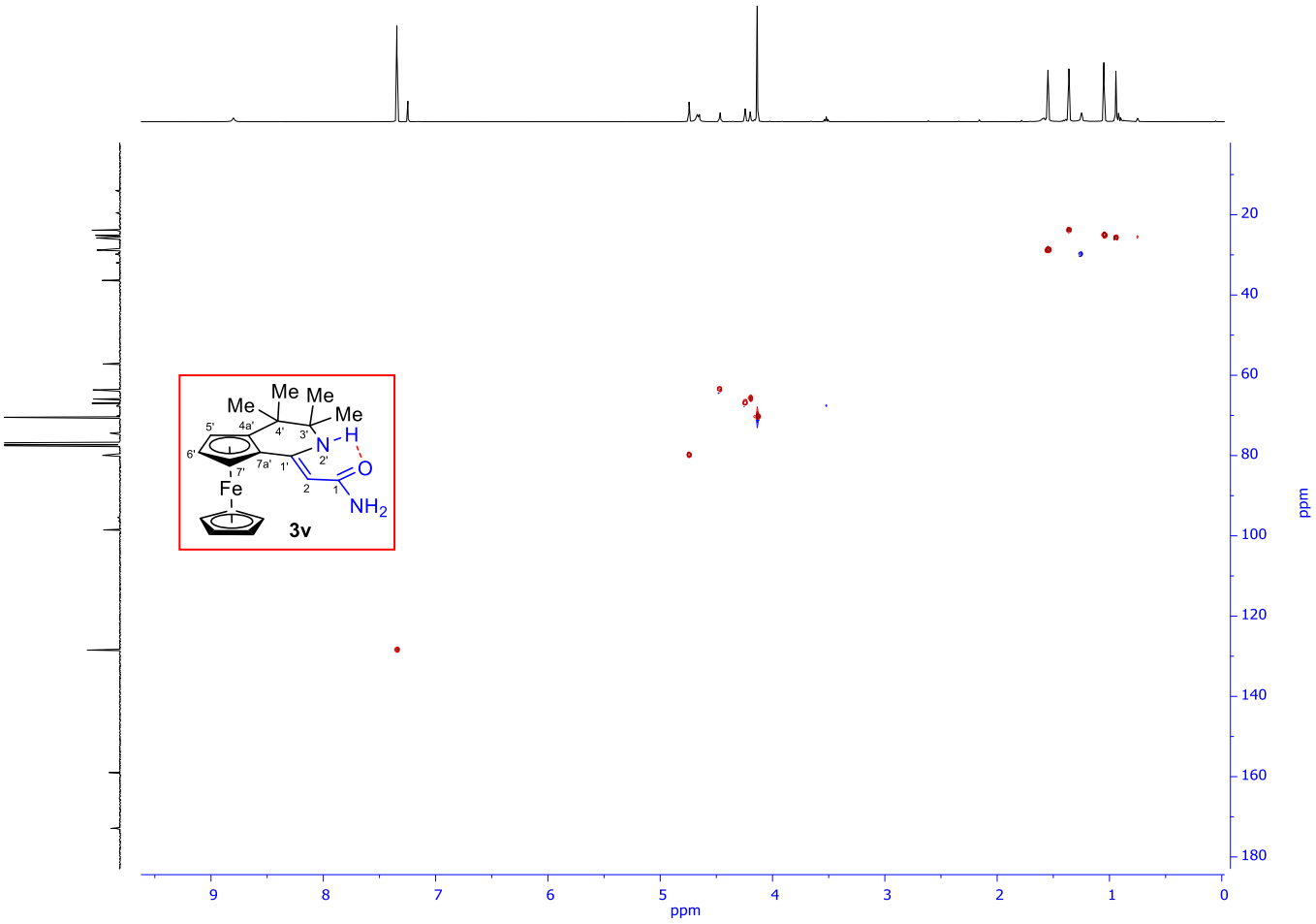


Figure S104. HSQC spectrum (400 MHz, $CDCl_3$) of compound **3v**.

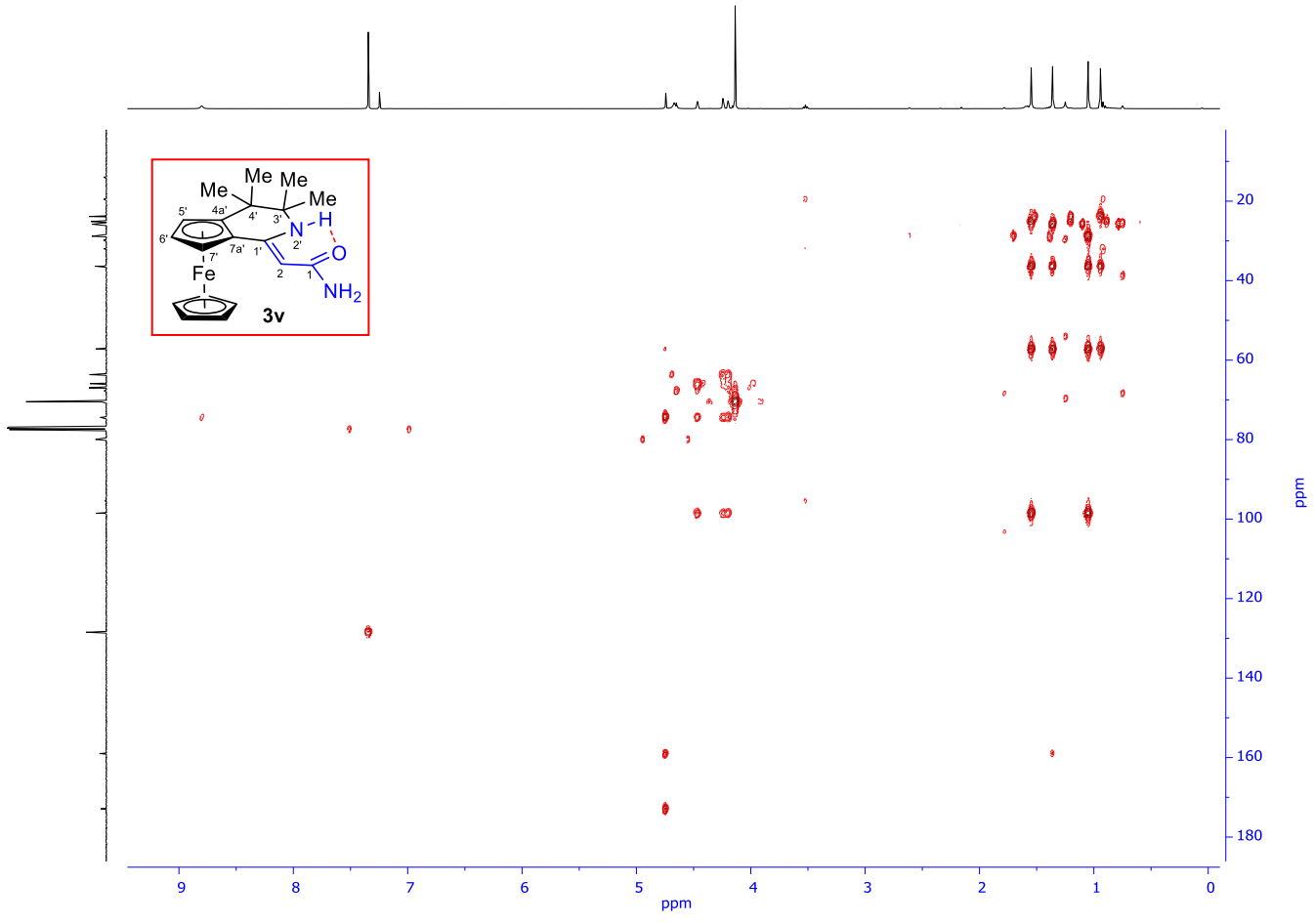


Figure S105. HMBC spectrum (100 MHz, $CDCl_3$) of compound **3v**.

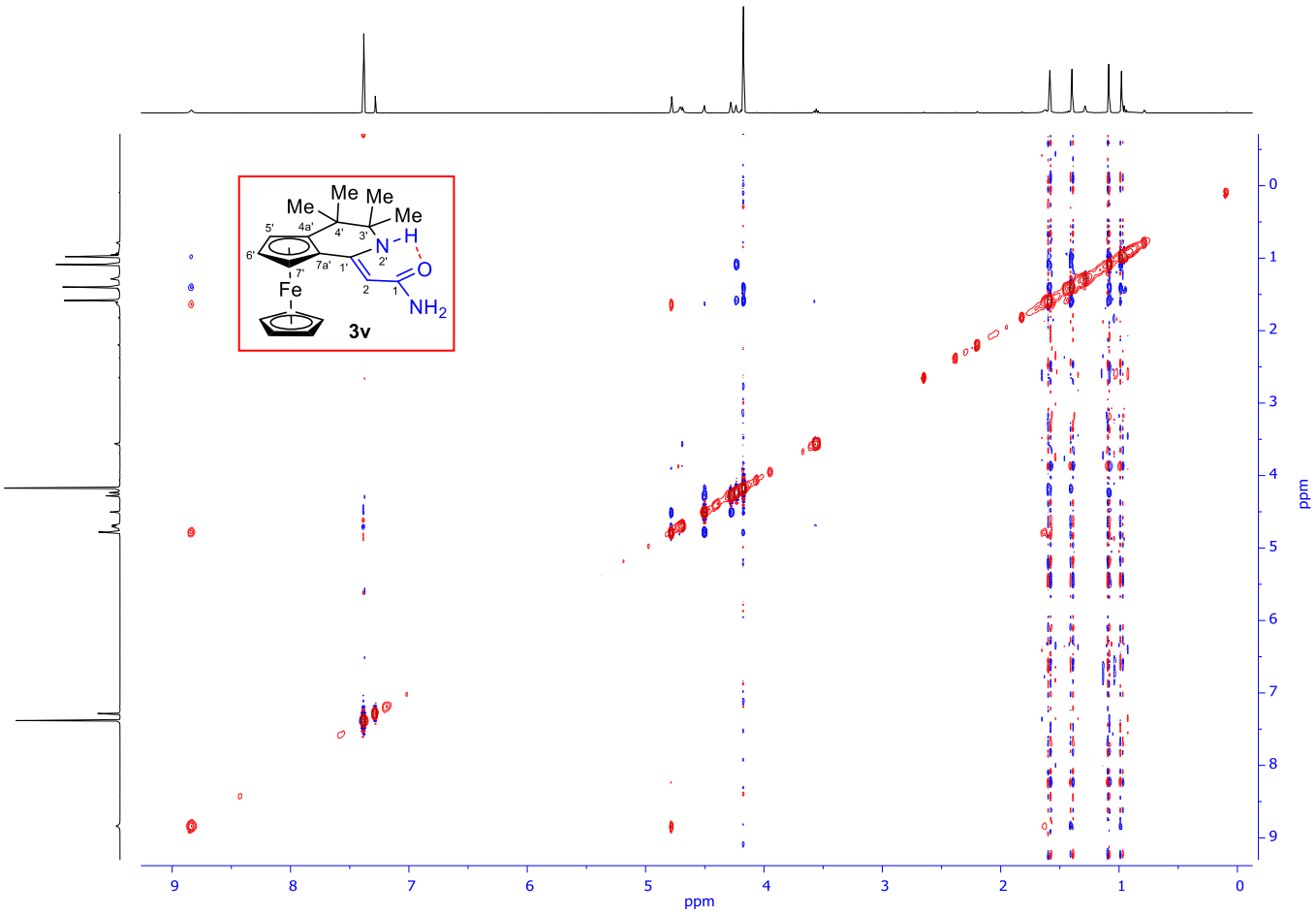


Figure S106. 2D NOESY spectrum (400 MHz, $CDCl_3$) of compound **3v**.

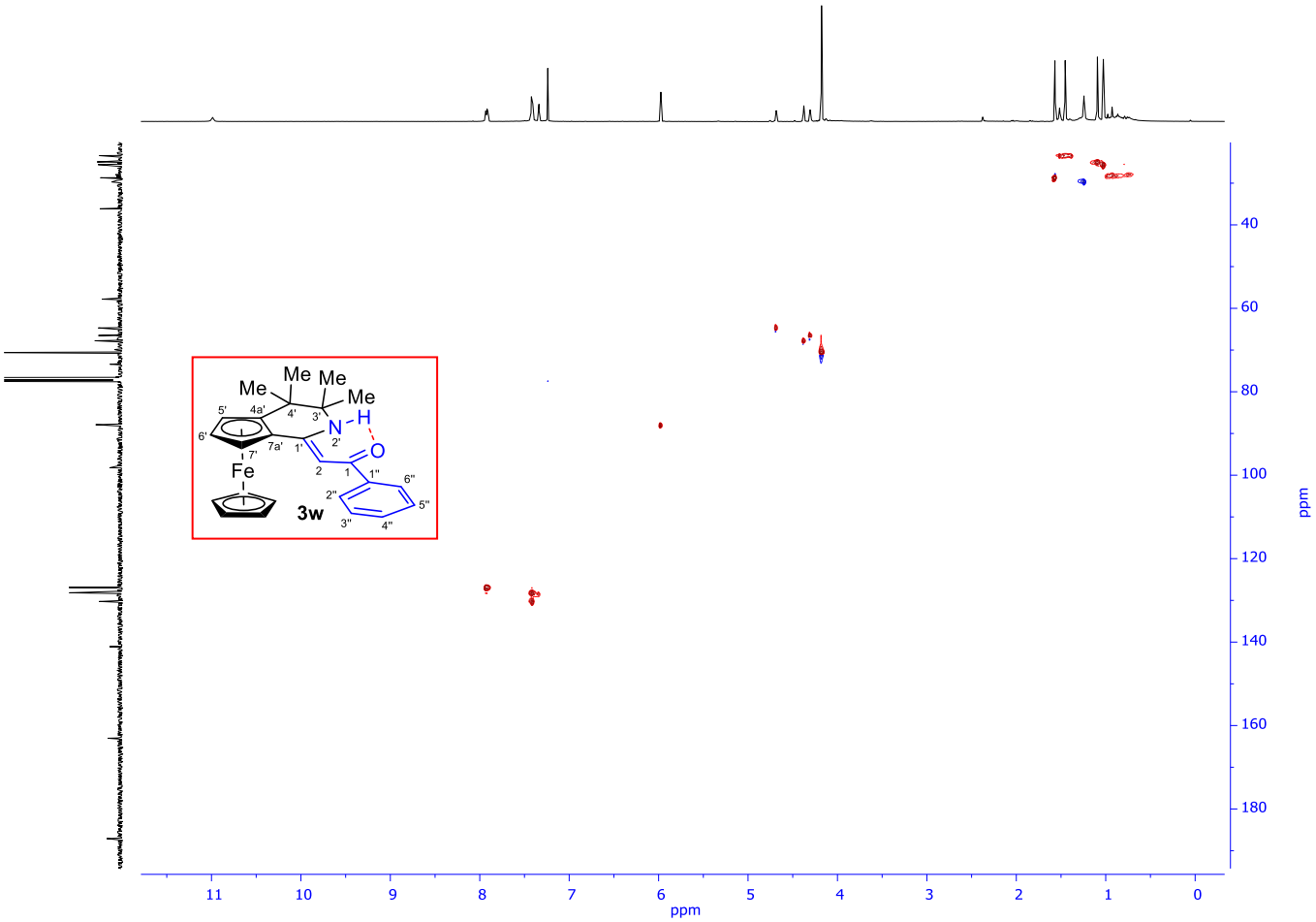


Figure S107. HSQC spectrum (400 MHz, $CDCl_3$) of compound **3w**.

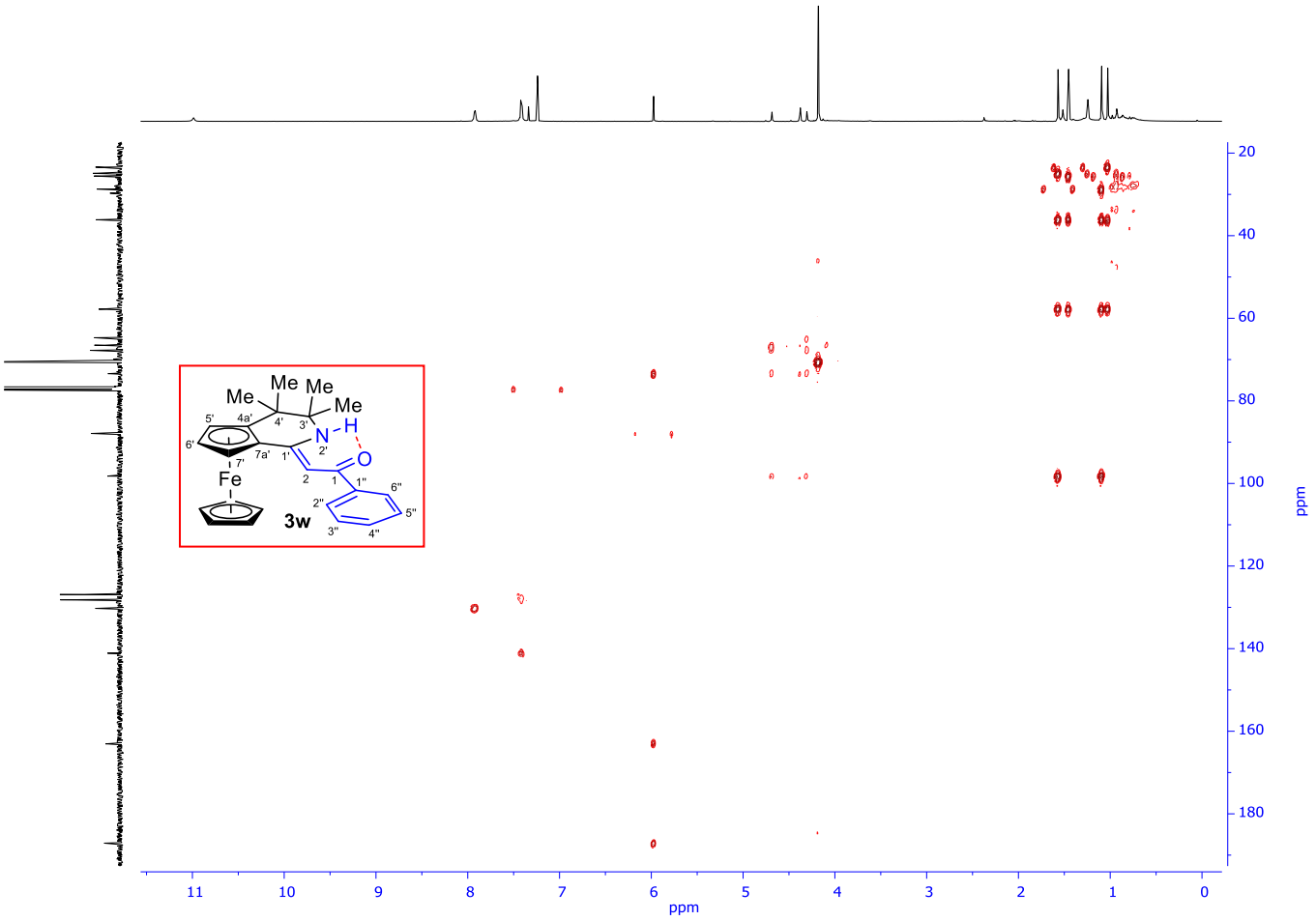


Figure S108. HMBC spectrum (100 MHz, $CDCl_3$) of compound **3w**.

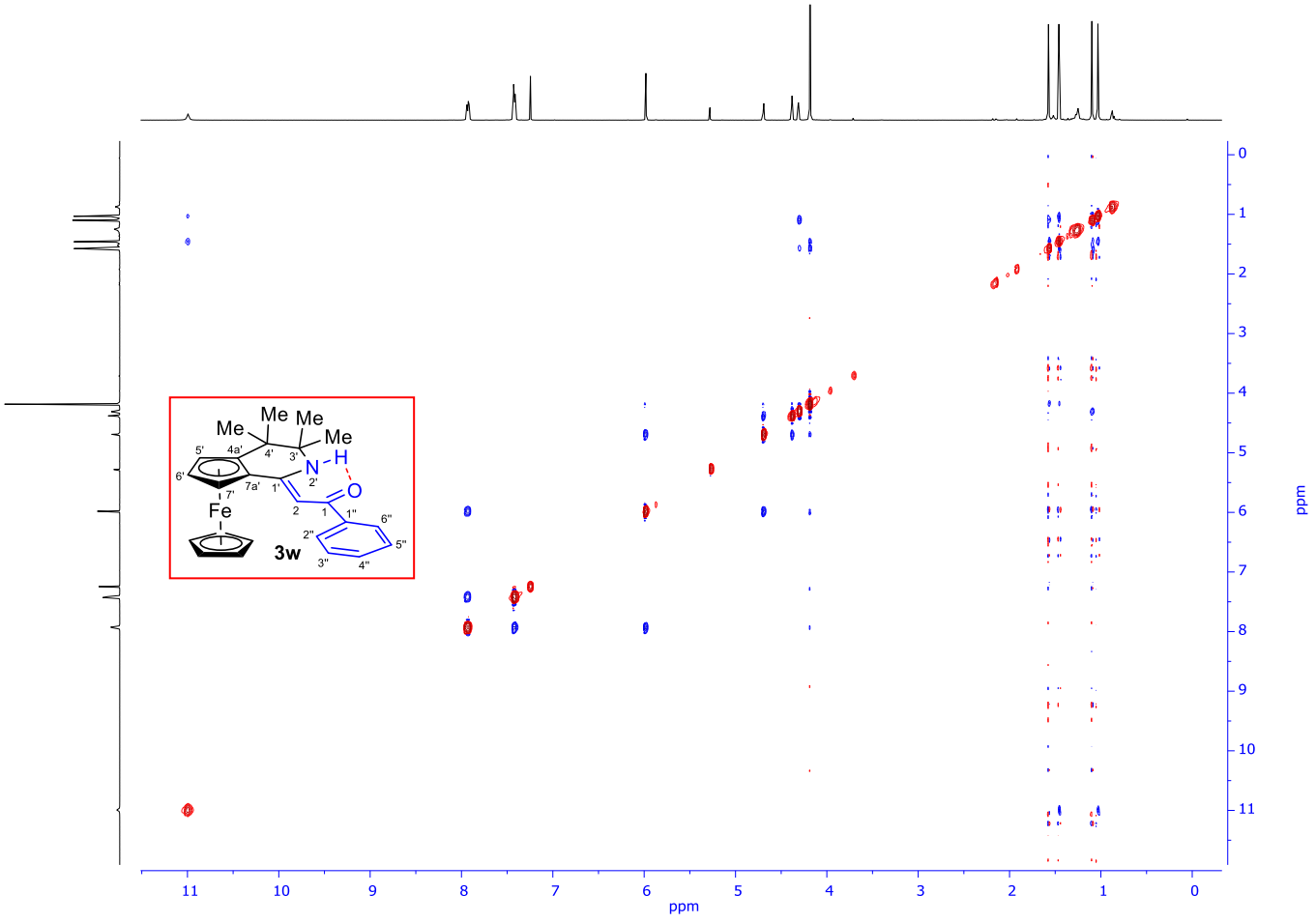


Figure S109. 2D NOESY spectrum (400 MHz, $CDCl_3$) of compound **3w**.

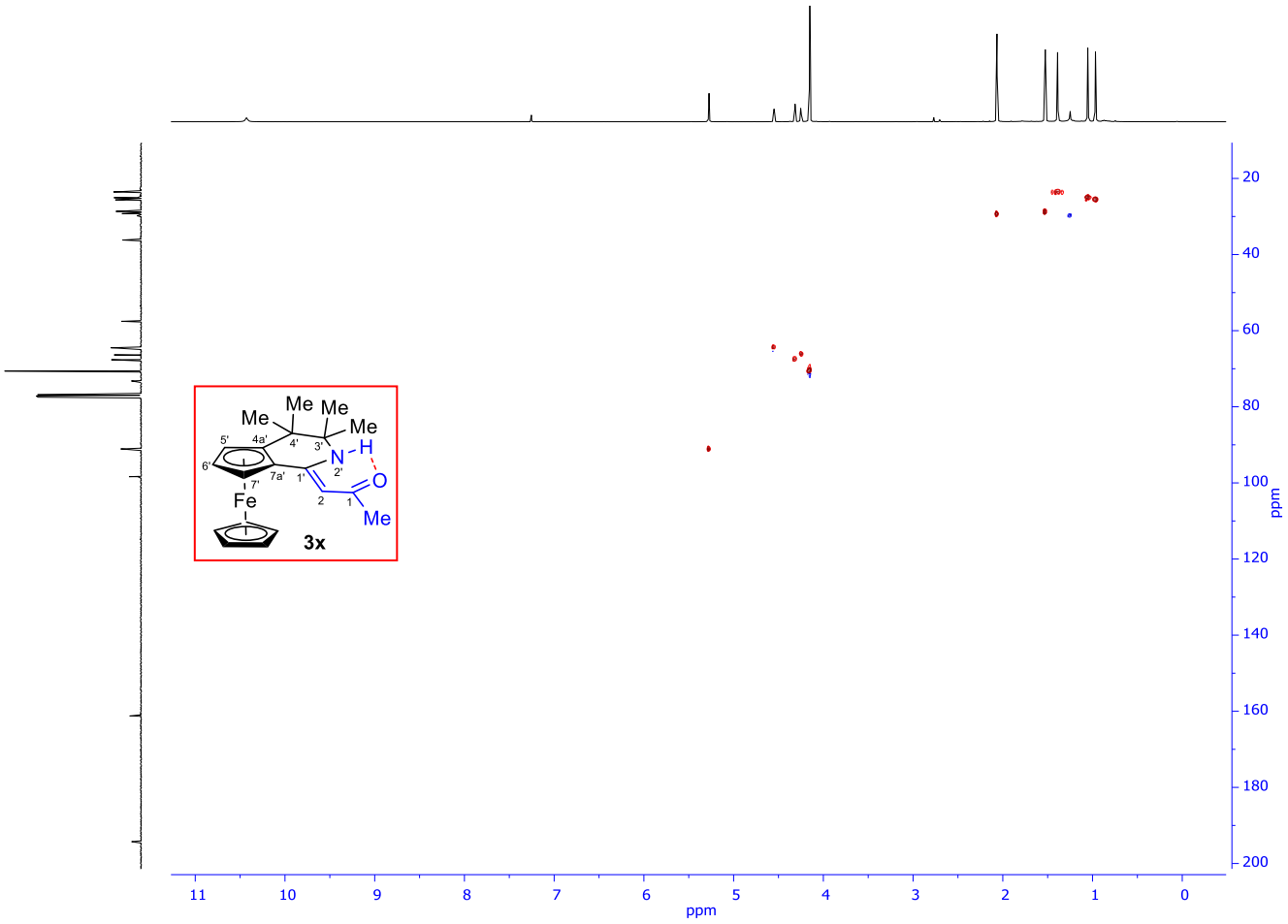


Figure S110. HSQC spectrum (400 MHz, $CDCl_3$) of compound **3x**.

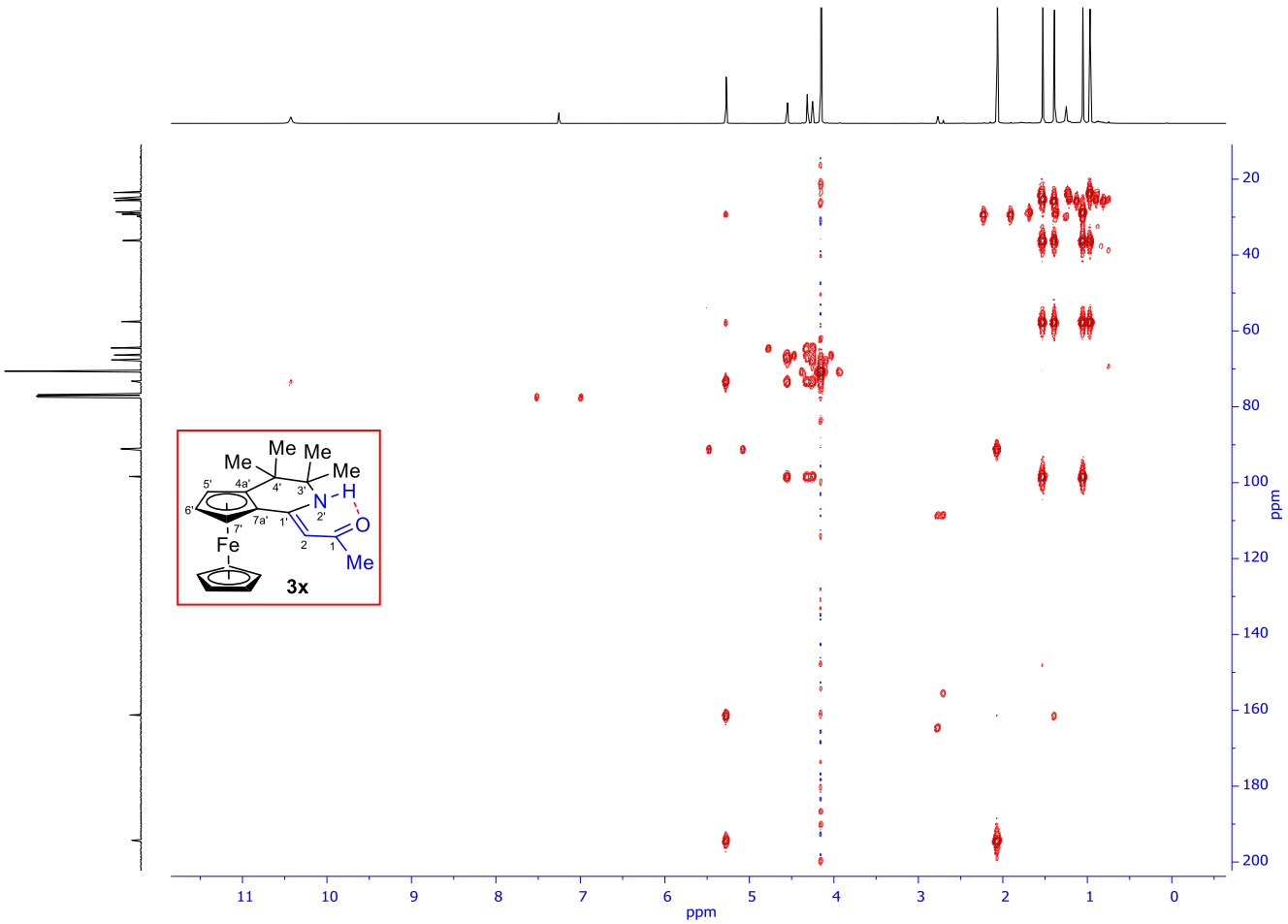


Figure S111. HMBC spectrum (400 MHz, $CDCl_3$) of compound **3x**.

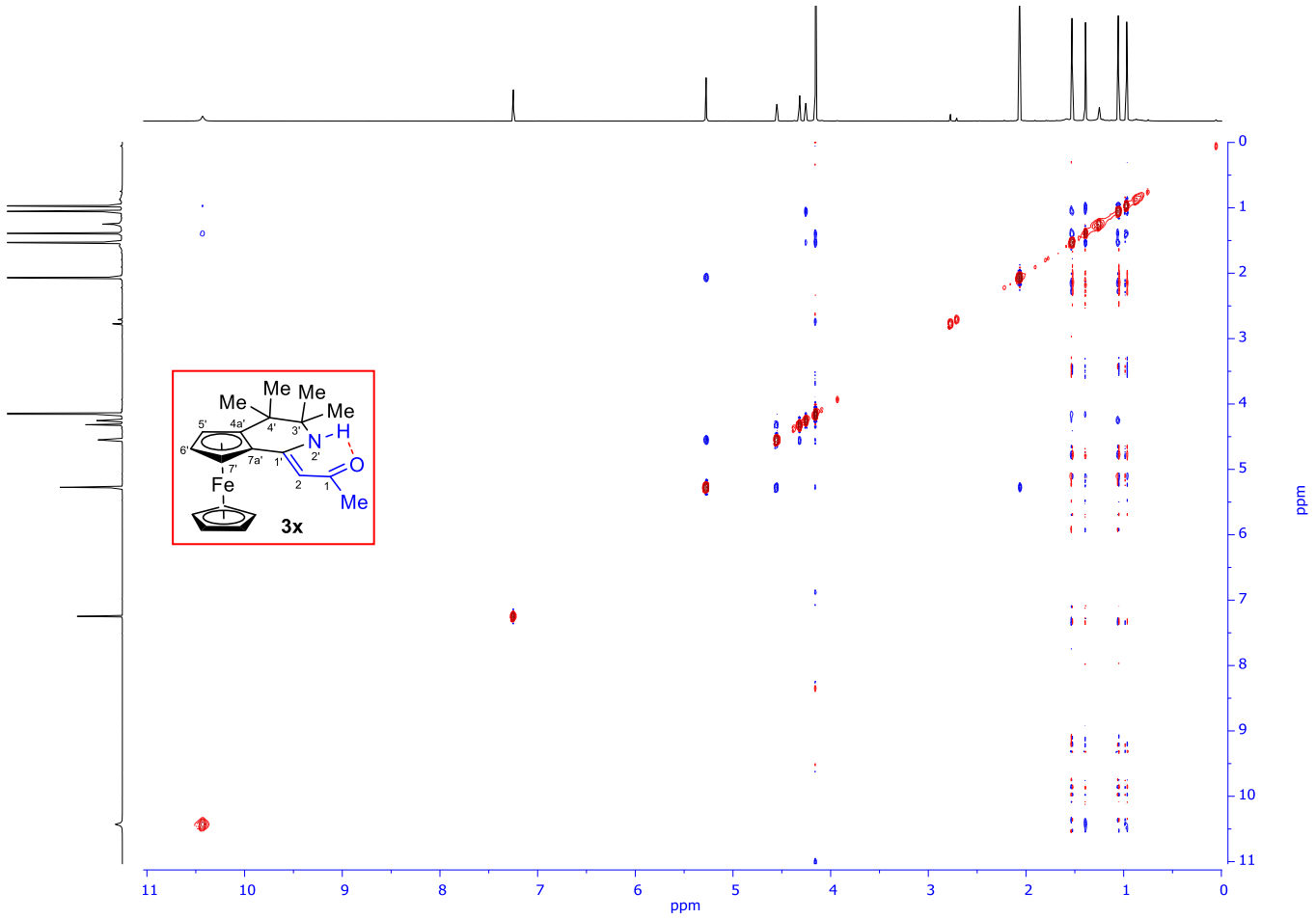


Figure S112. 2D NOESY spectrum (400 MHz, $CDCl_3$) of compound **3x**.

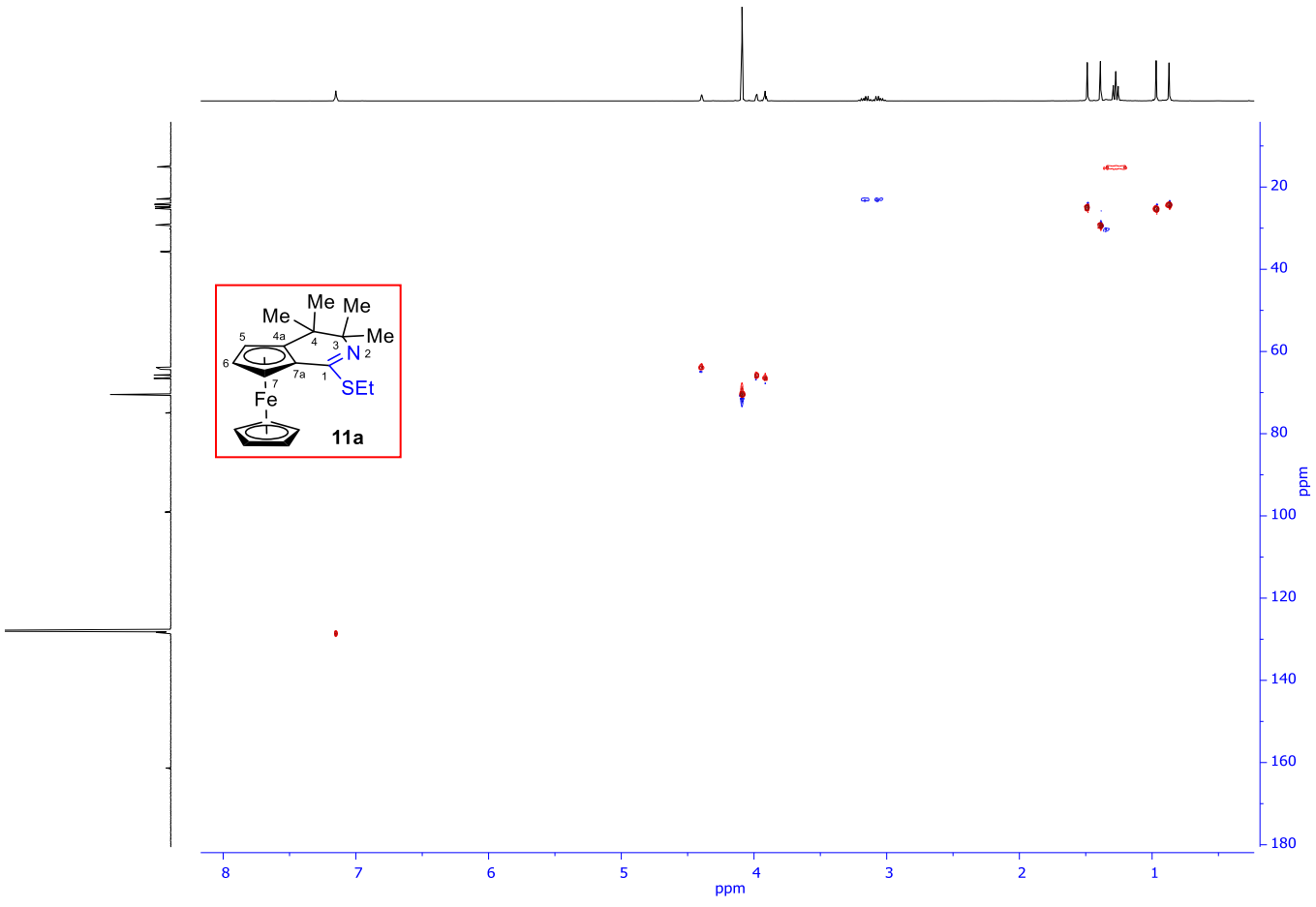


Figure S113. HSQC spectrum (400 MHz, C_6D_6) of compound **11a**.

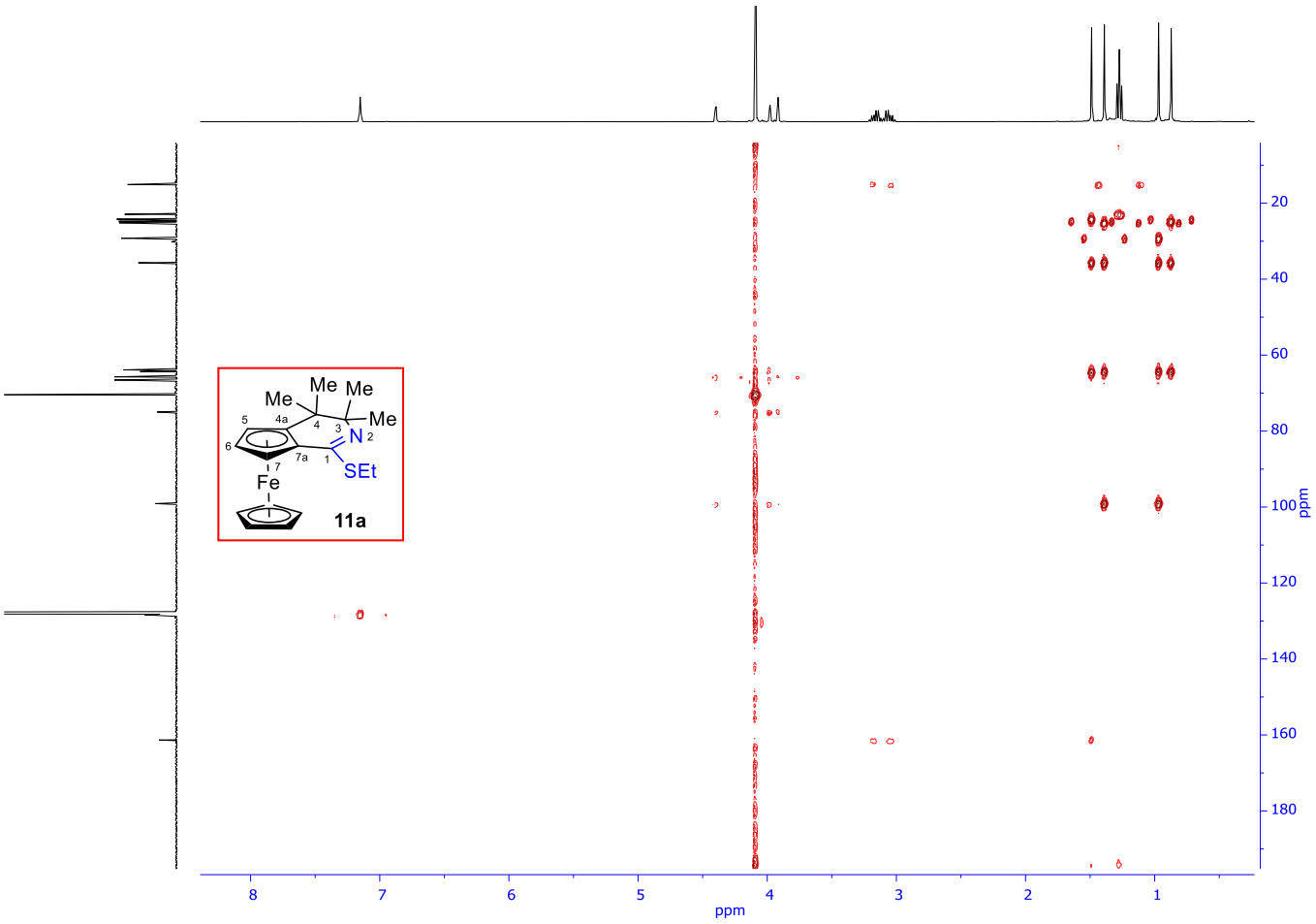


Figure S114. HMBC spectrum (400 MHz, C_6D_6) of compound **11a**.

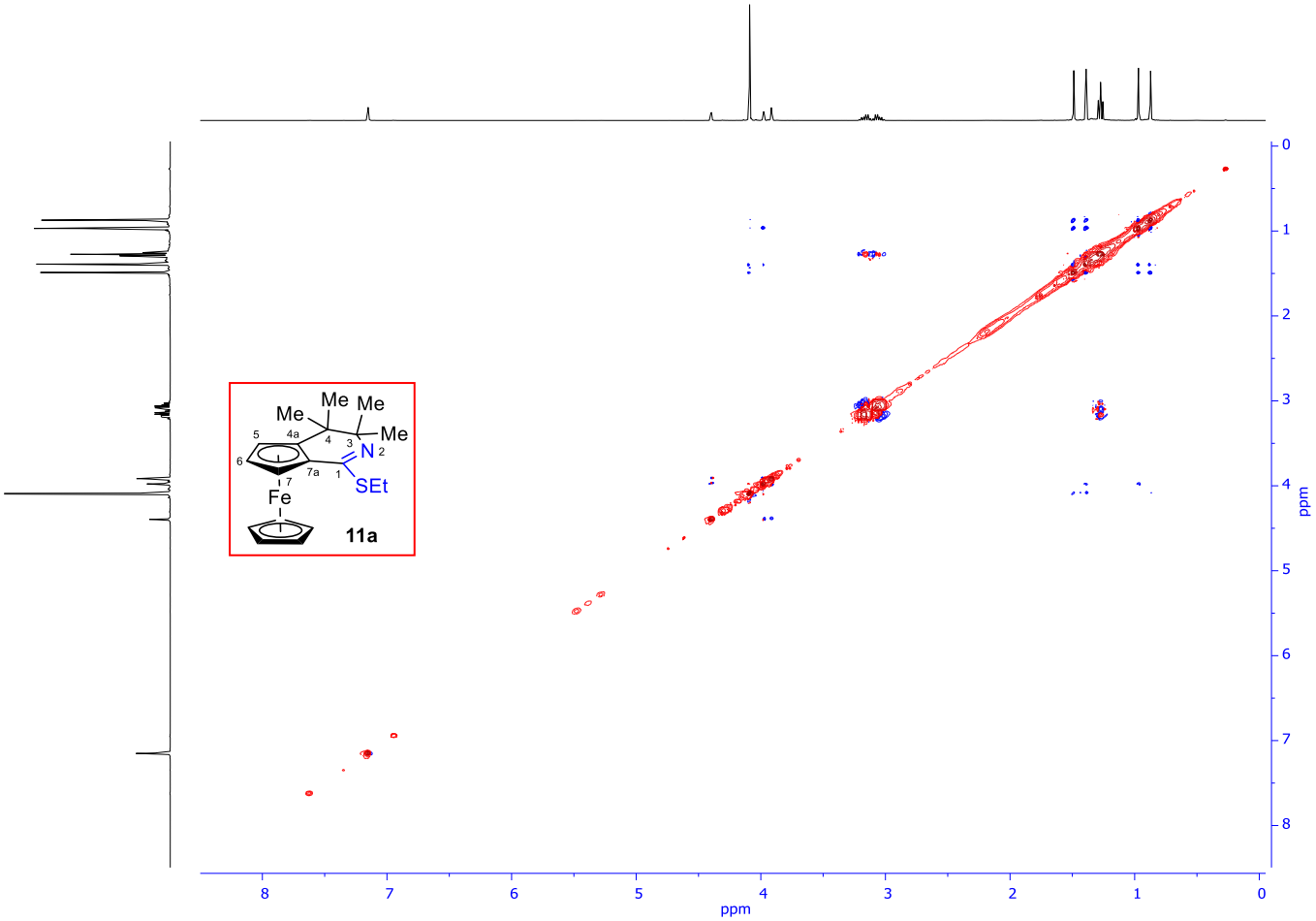


Figure S115. 2D NOESY spectrum (400 MHz, C_6D_6) of compound **11a**.

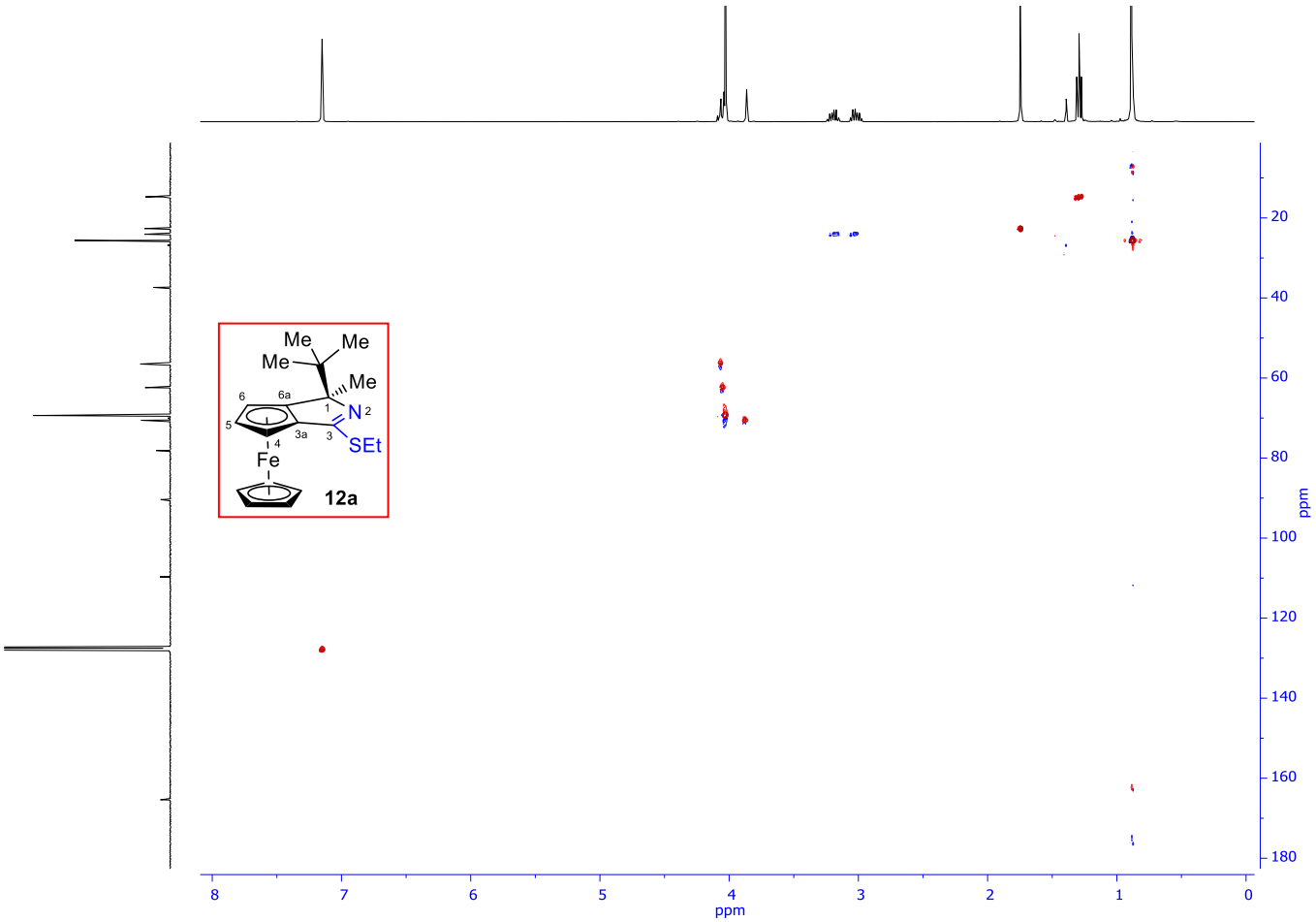


Figure S116. HSQC spectrum (400 MHz, C_6D_6) of compound **12a**.

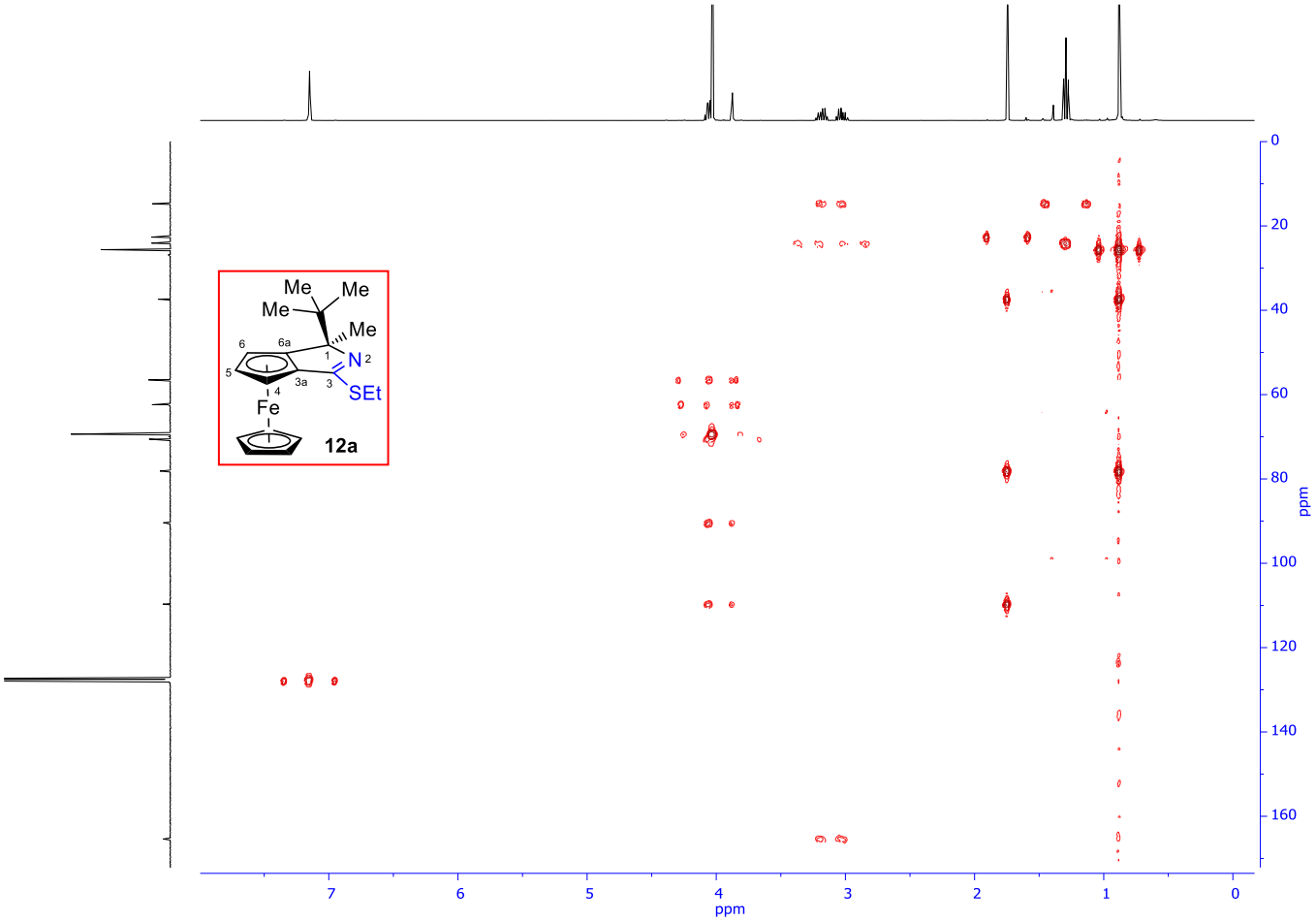


Figure S117. HMBC spectrum (400 MHz, C_6D_6) of compound **12a**.

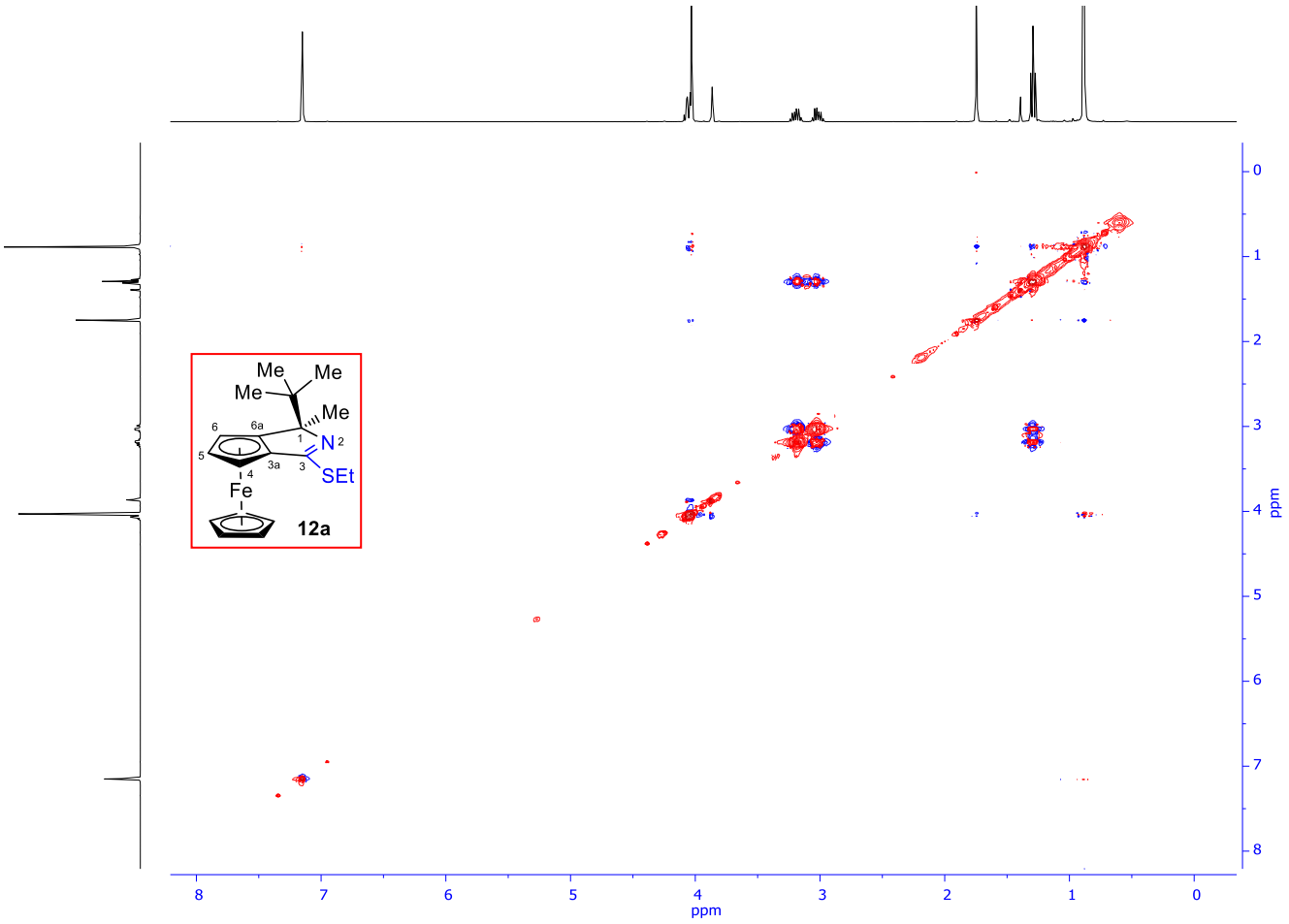


Figure S118 . 2D NOESY spectrum (400 MHz, C_6D_6) of compound **12a**.