

Article

First example of fluorinated phenanthroline diamides for complexation with lanthanides. Synthesis and structural study

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Supplementary Materials

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1. NMR and IR spectra of synthesized compounds

N2,N9-bis(4-butylphenyl)-4,7-dichloro-N2,N9-diethyl-1,10-phenanthroline -2,9- dicarboxamide (4c)

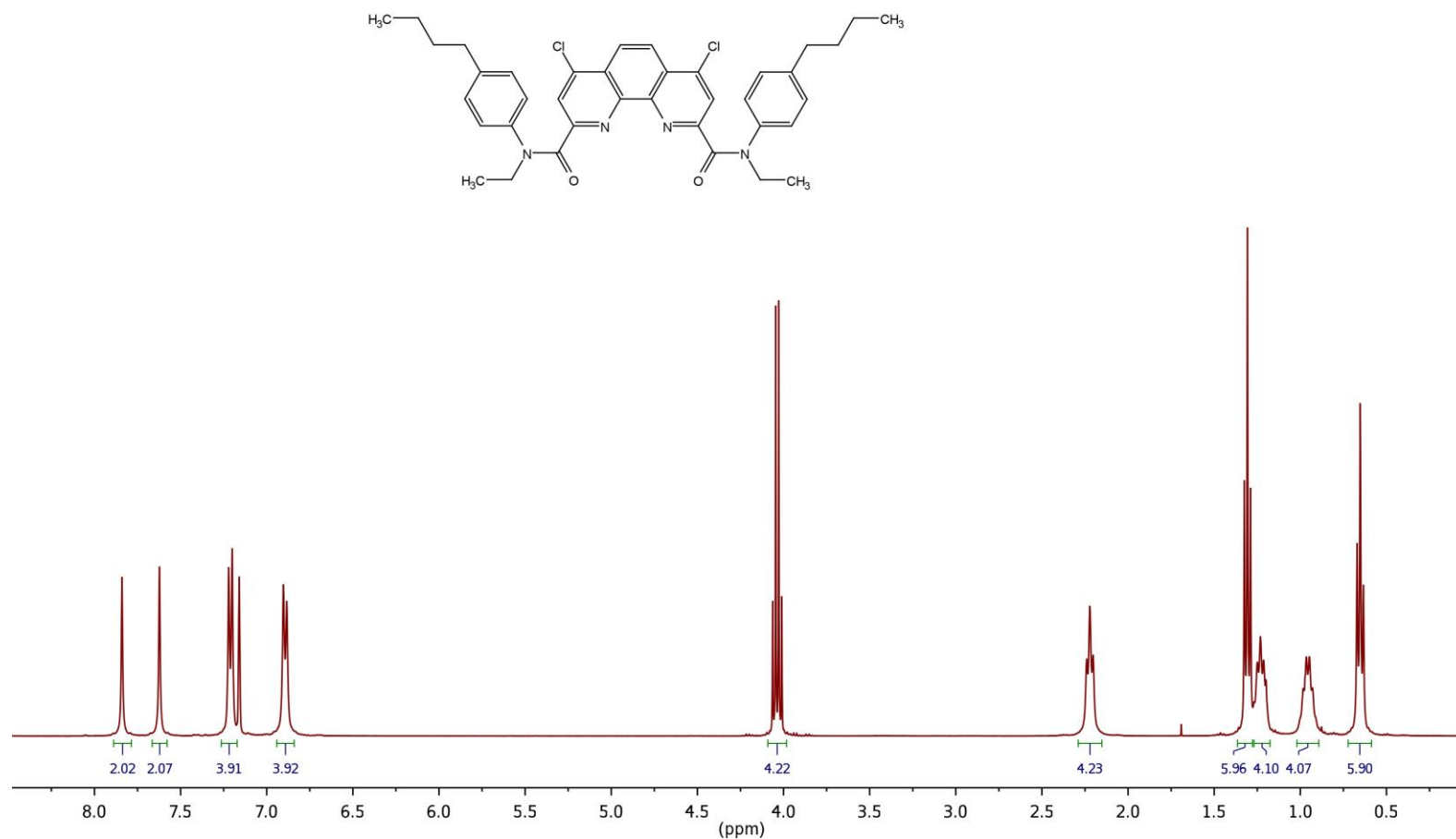


Figure S1. ¹H NMR spectrum in C₆D₆ at 60°C

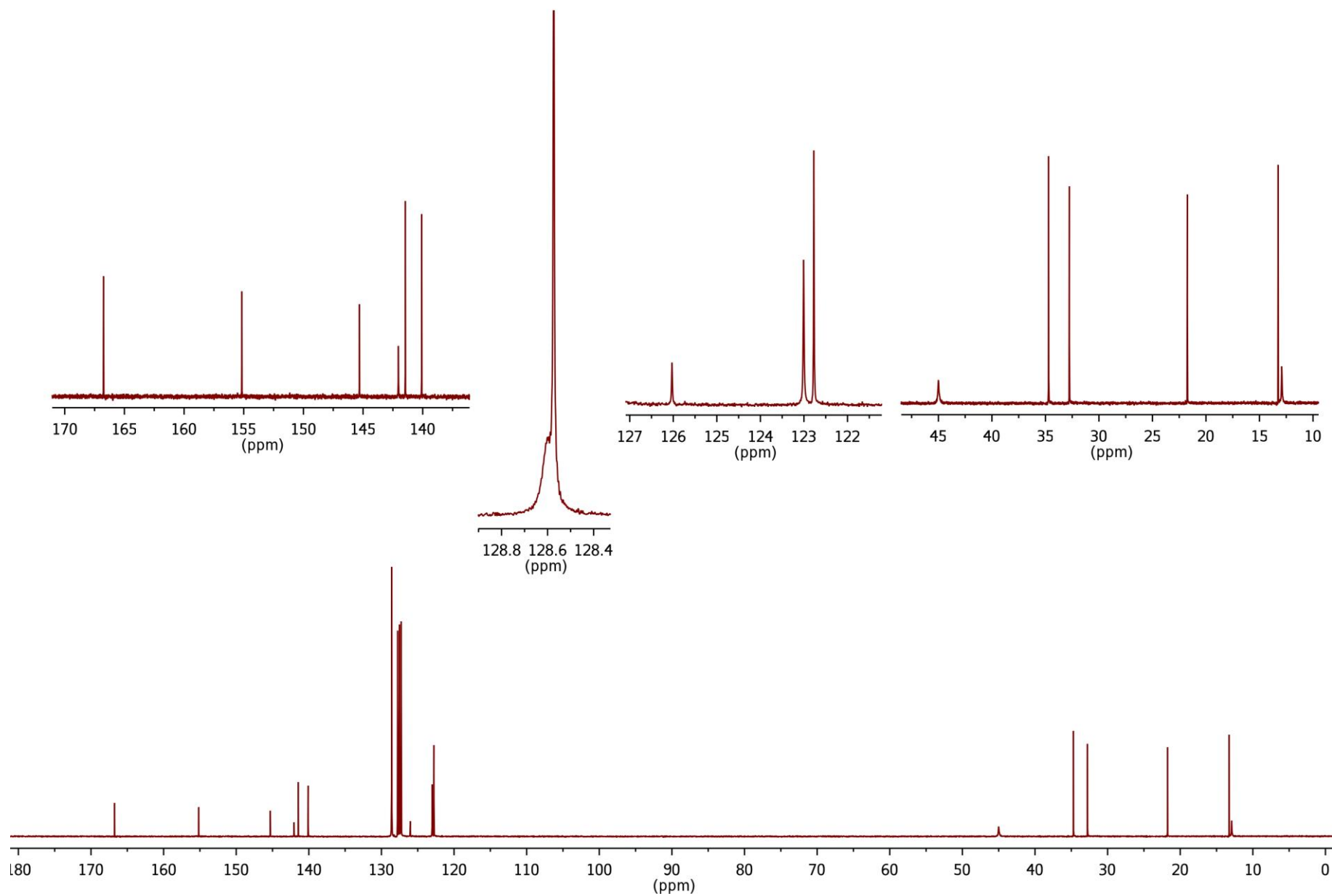


Figure S2. ^{13}C NMR spectrum in C_6D_6 at 60°C

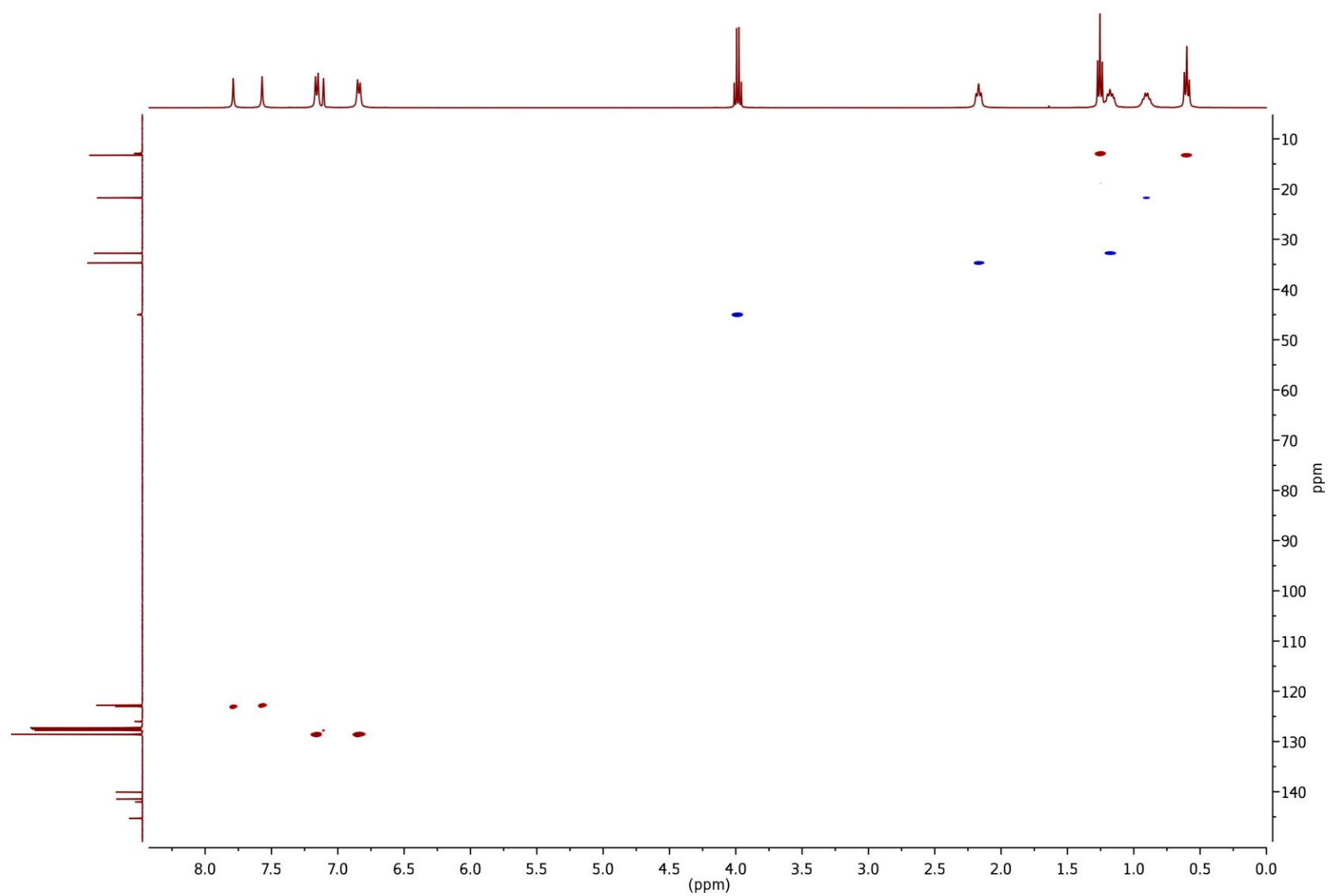


Figure S3. $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum in C_6D_6 at 60°C

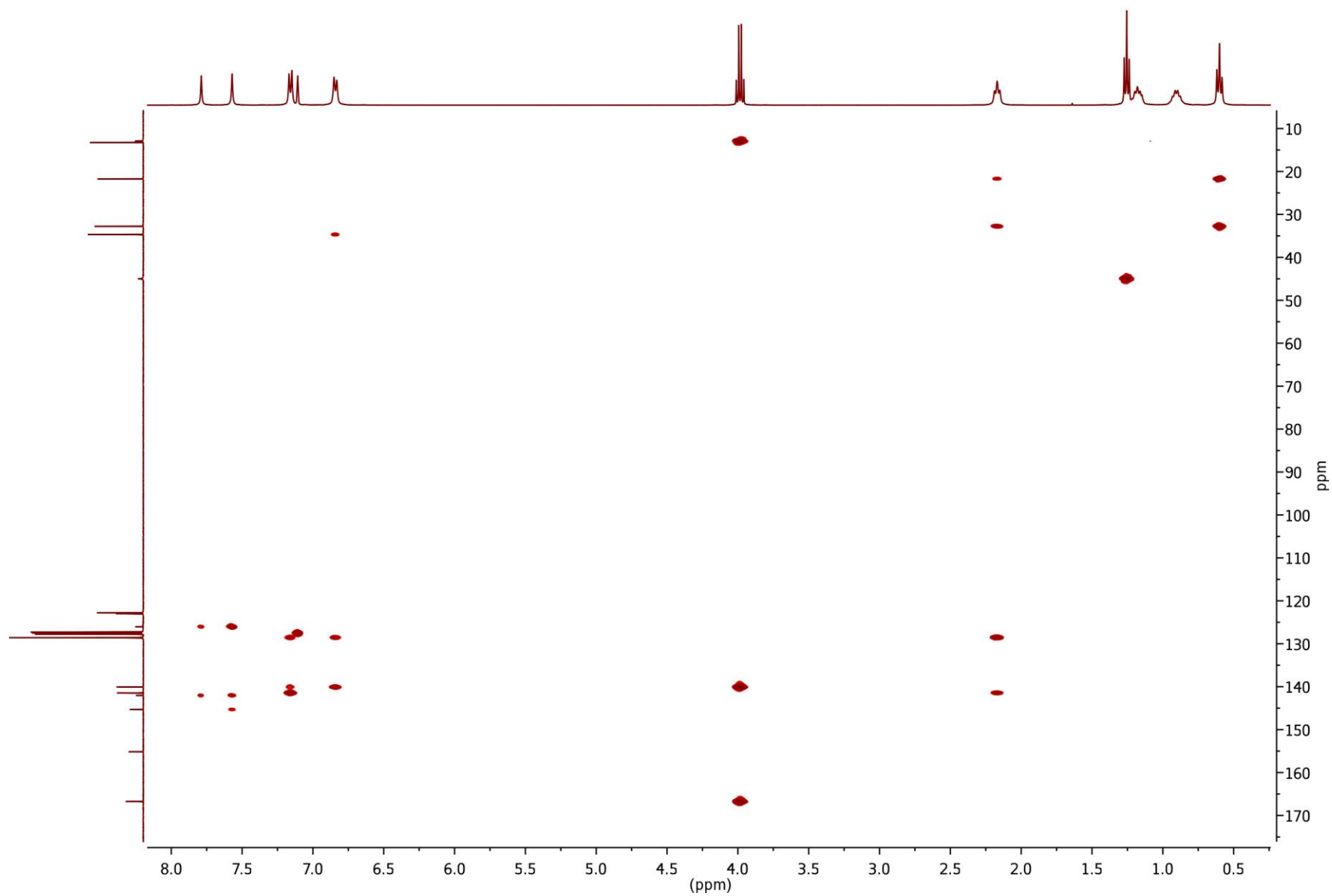


Figure S4. $^1\text{H}/^{13}\text{C}$ HMBC NMR spectrum in C_6D_6 at 60°C

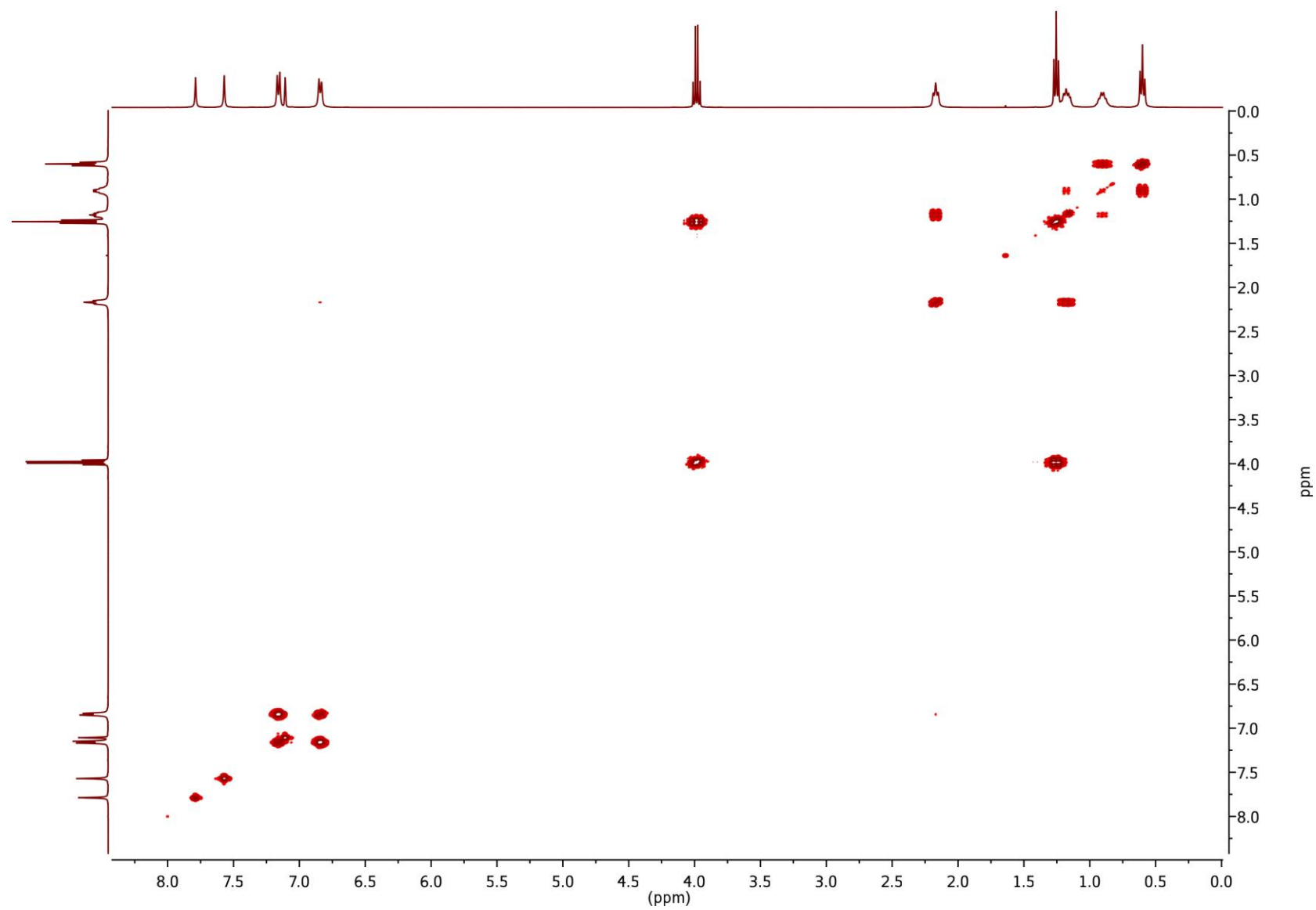


Figure S5. $^1\text{H}/^1\text{H}$ COSY NMR spectrum in C_6D_6 at 60°C

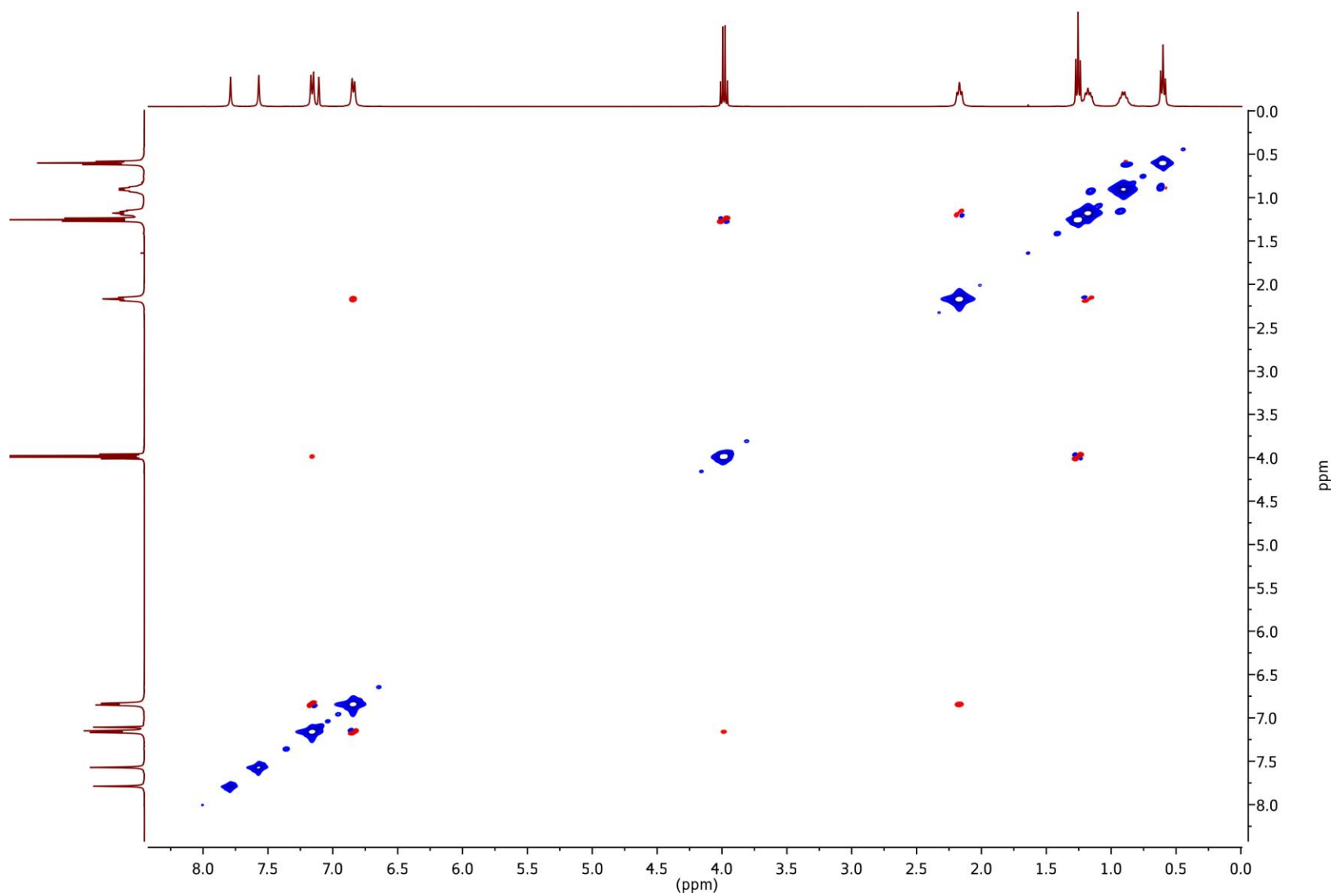


Figure S6. $^1\text{H}/^1\text{H}$ NOESY NMR spectrum in C_6D_6 at 60°C

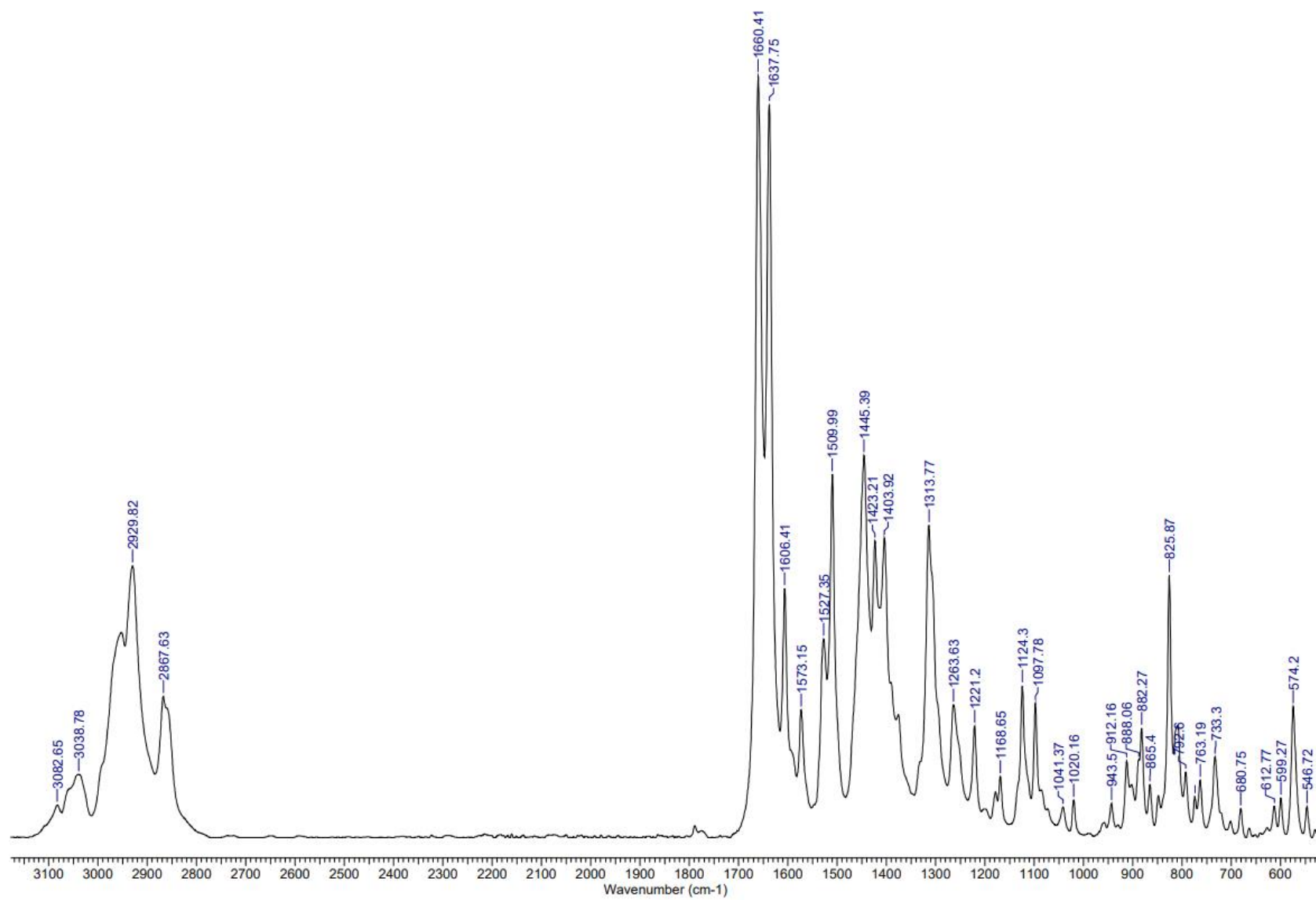


Figure S7. Solid-state IR spectrum at 25°C

4,7-difluoro-2,9-dimethyl-1,10-phenanthroline (6).

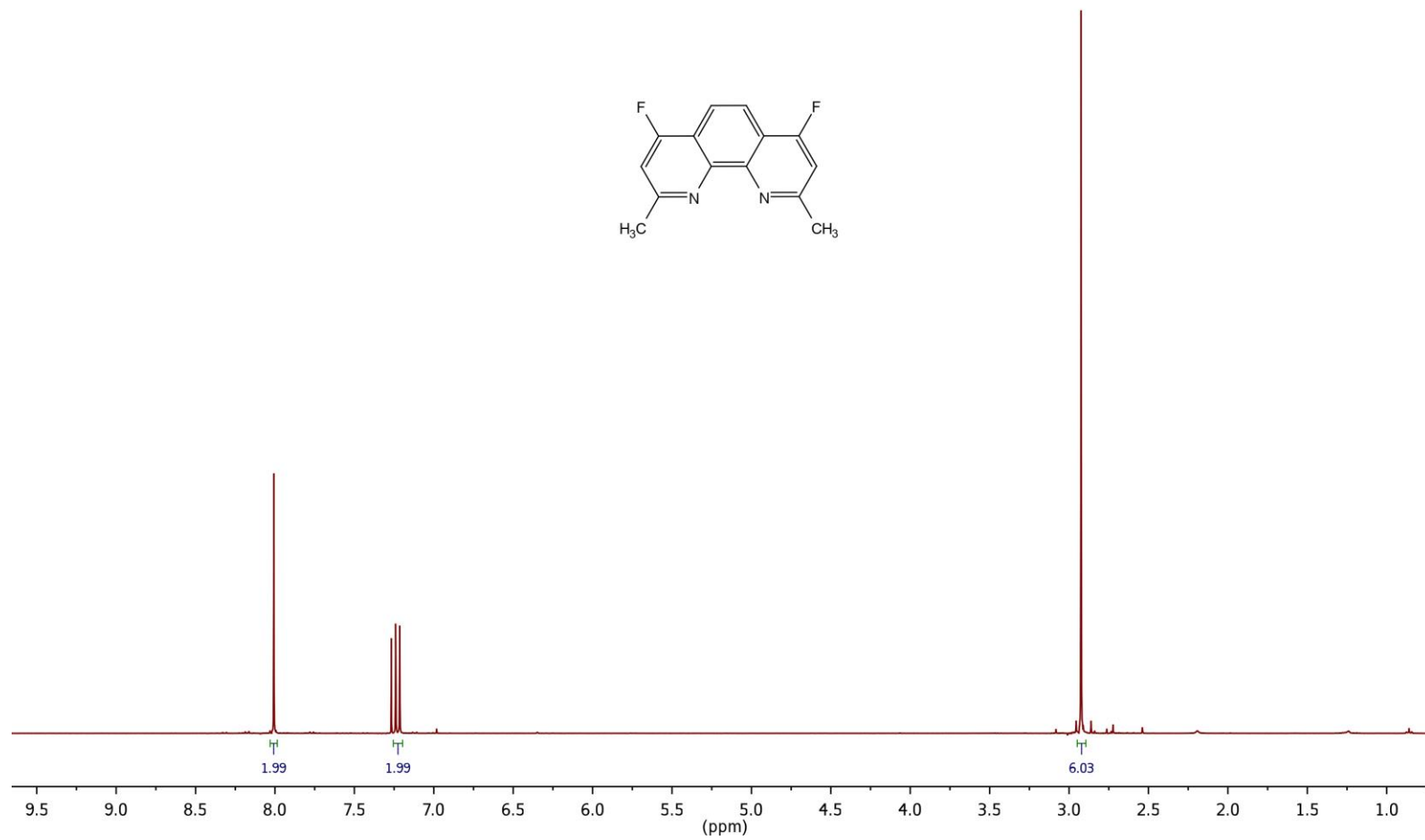


Figure S8. ¹H NMR spectrum in CDCl₃ at 25°C

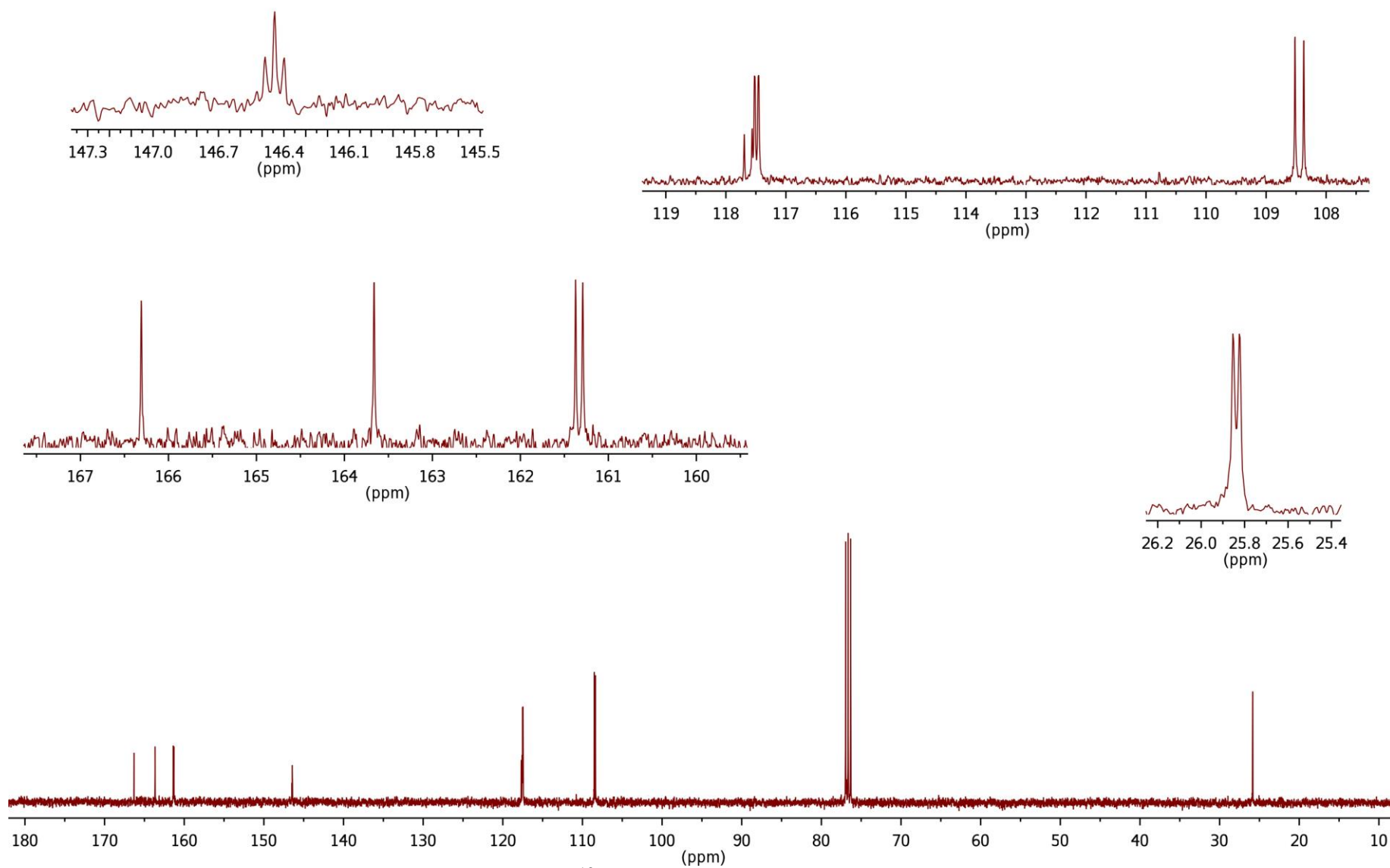


Figure S9. ^{13}C NMR spectrum in CDCl_3 at 25°C

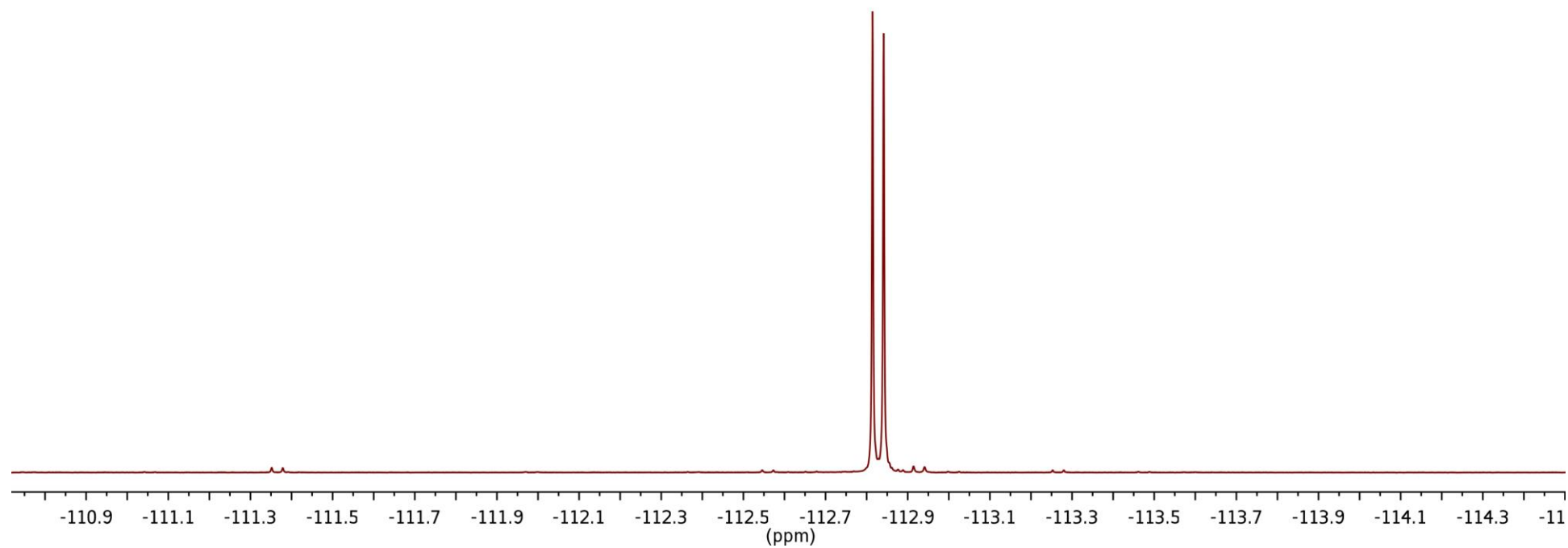


Figure S10. ^{19}F NMR spectrum in CDCl_3 at 25°C

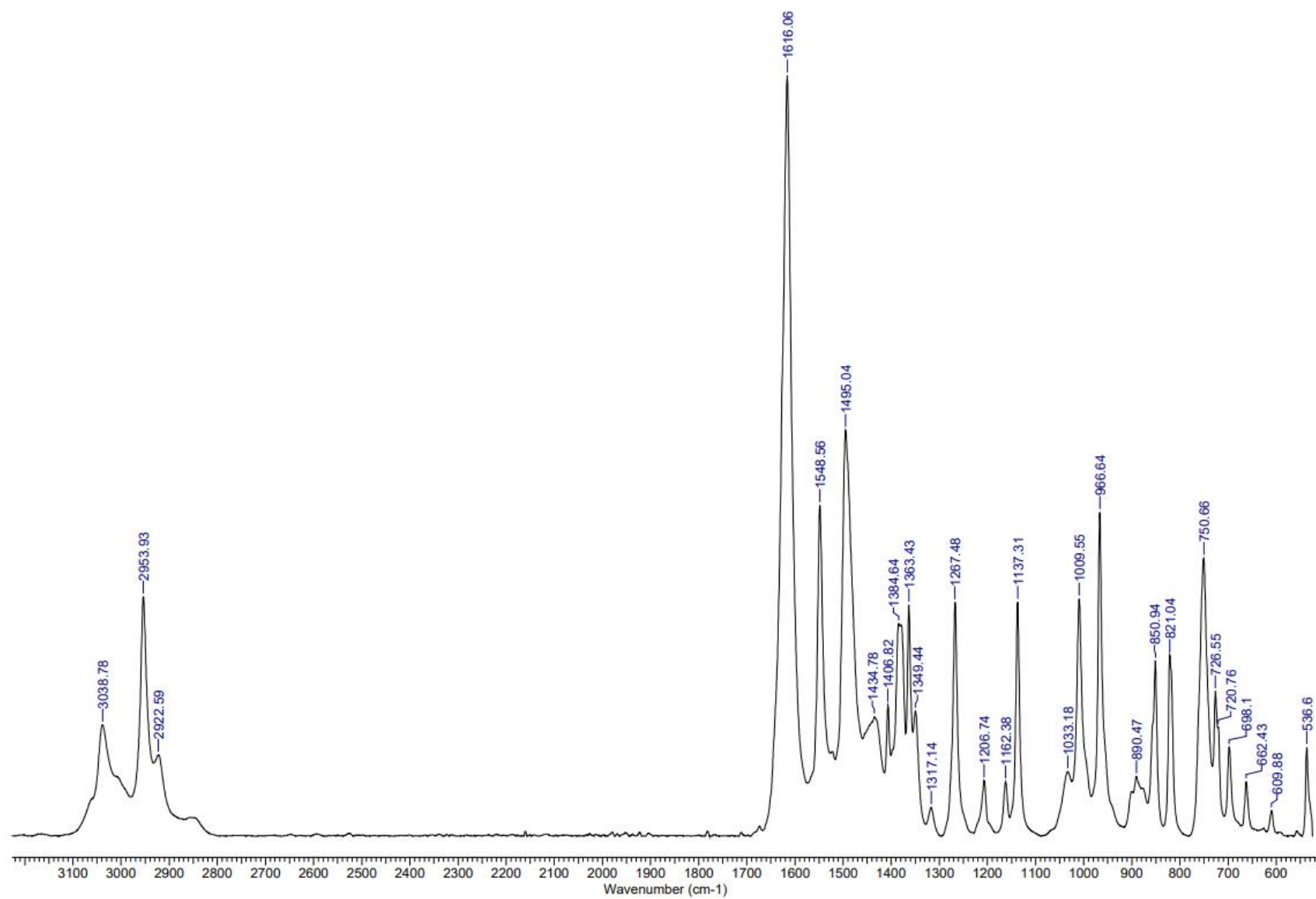


Figure S11. Solid-state IR spectrum at 25°C

*N*²,*N*²,*N*⁹,*N*⁹- tetrabutyl -4,7- difluoro -1,10- phenanthroline -2,9- dicarboxamide (**7a**)

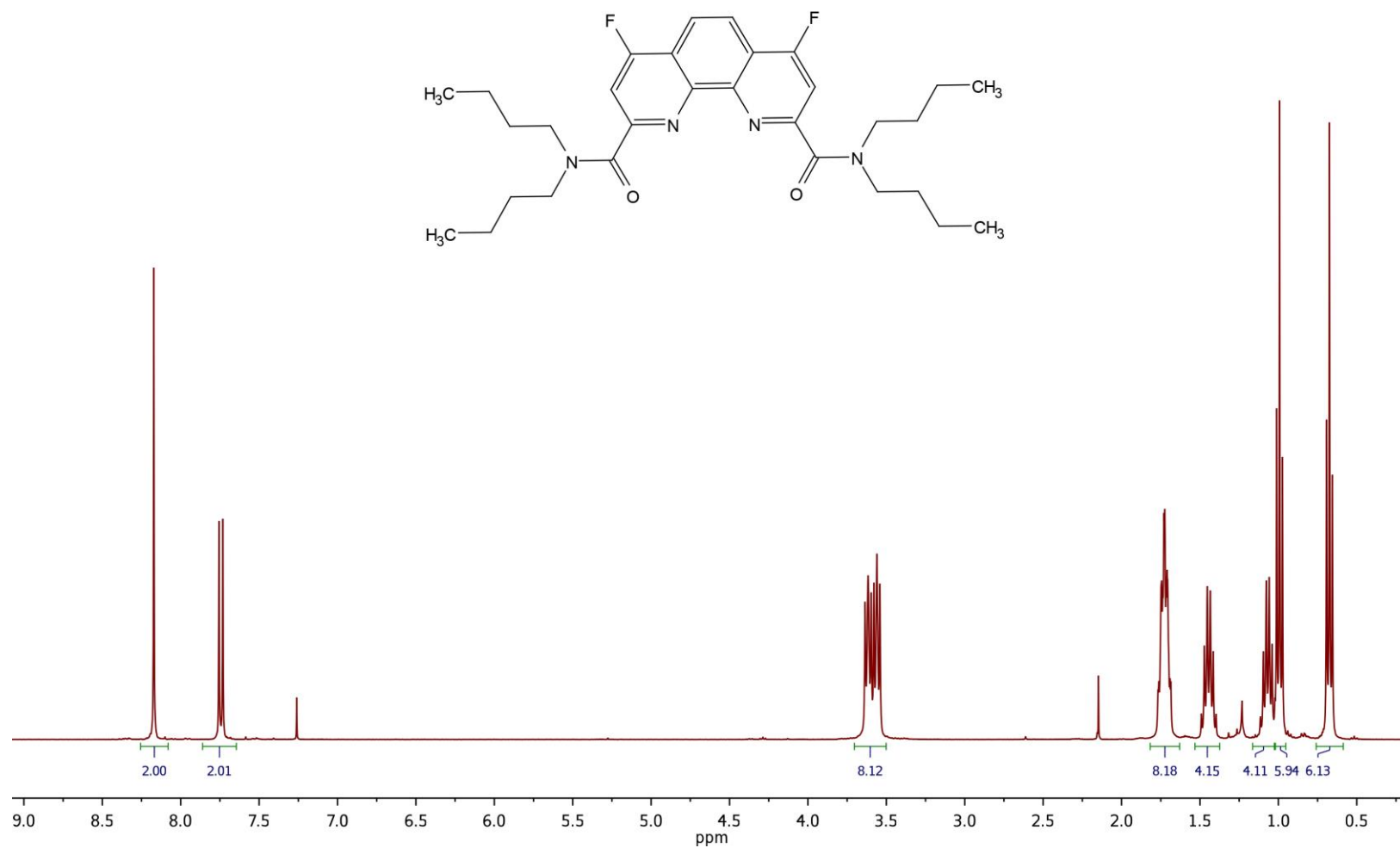


Figure S12. ¹H NMR spectrum in CDCl₃ at 25°C

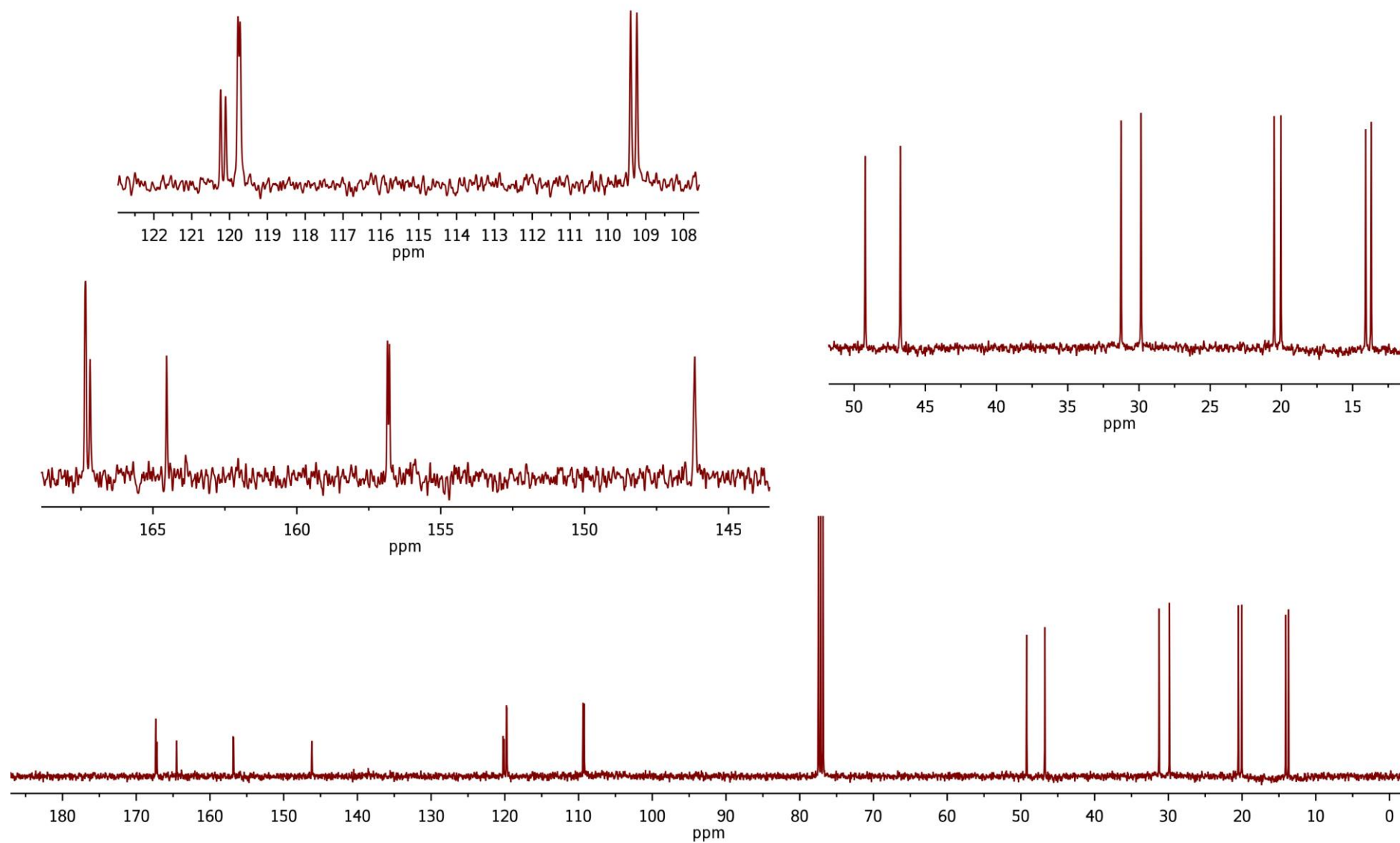


Figure S13. ^{13}C NMR spectrum in CDCl_3 at 25°C

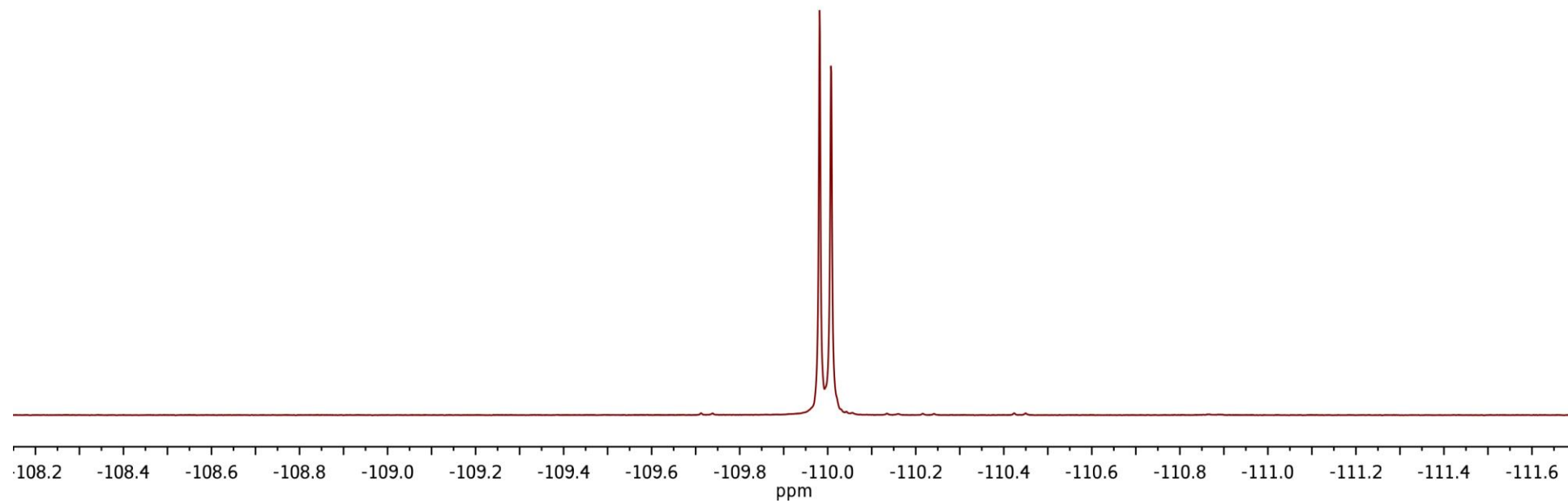


Figure S14. ^{19}F NMR spectrum in CDCl_3 at 25°C

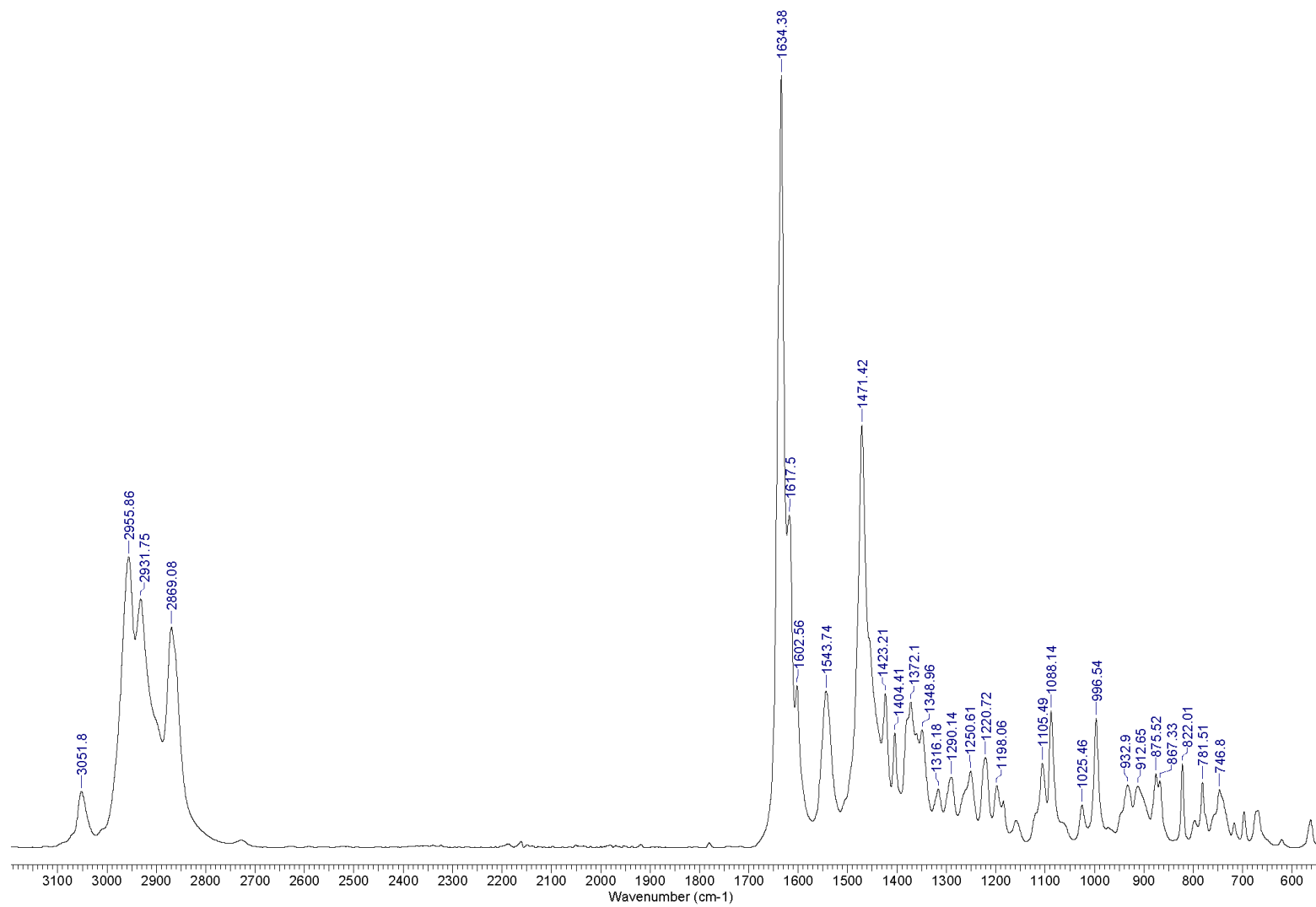


Figure S15. Solid-state IR spectrum at 25°C

N²,N⁹-bis(pyrrolidine) -4,7- difluoro -N²,N⁹- diethyl -1,10- phenanthroline-2,9- dicarboxamide (7b)

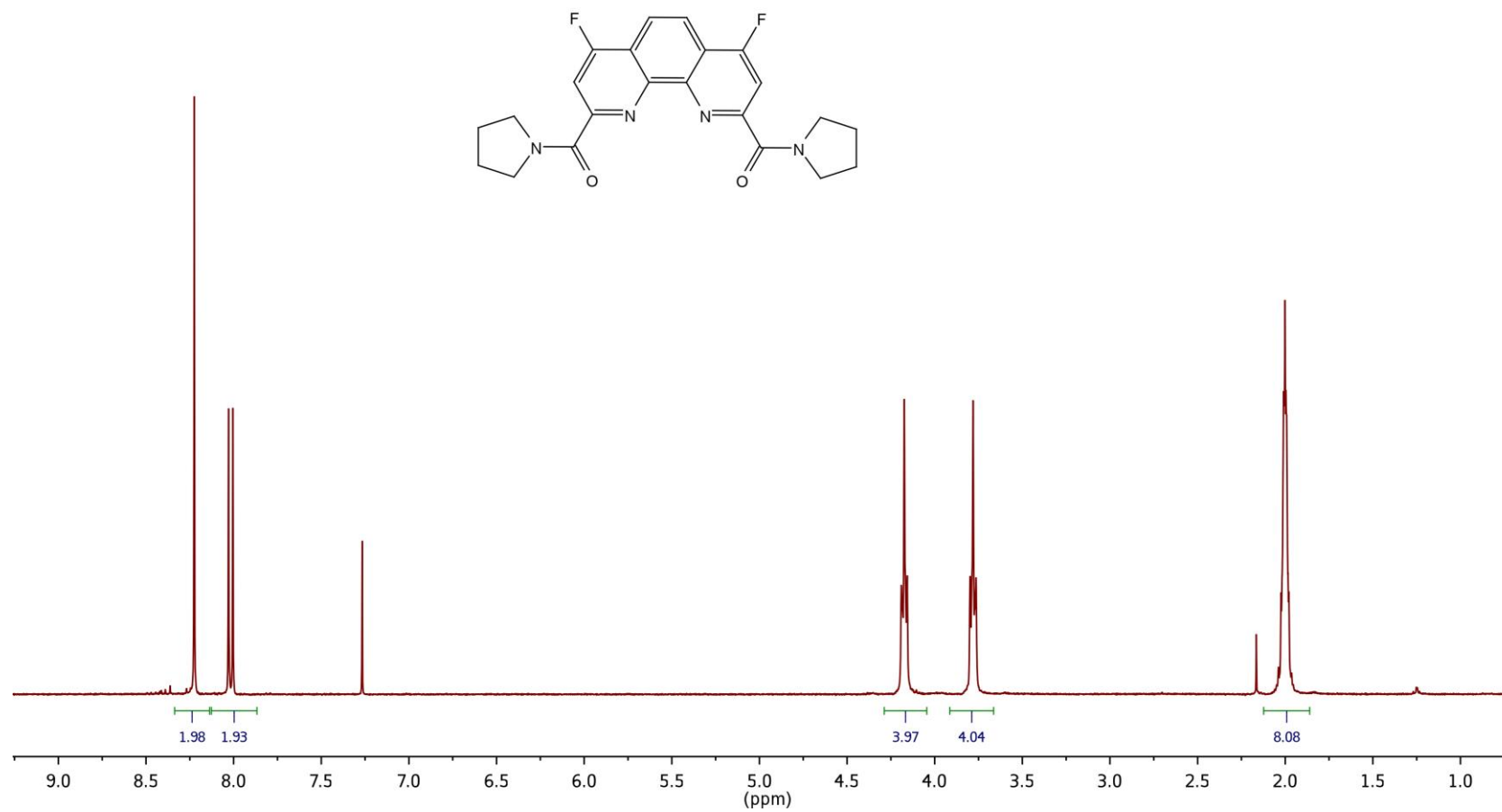


Figure S16. ¹H NMR spectrum in CDCl₃ at 25°C

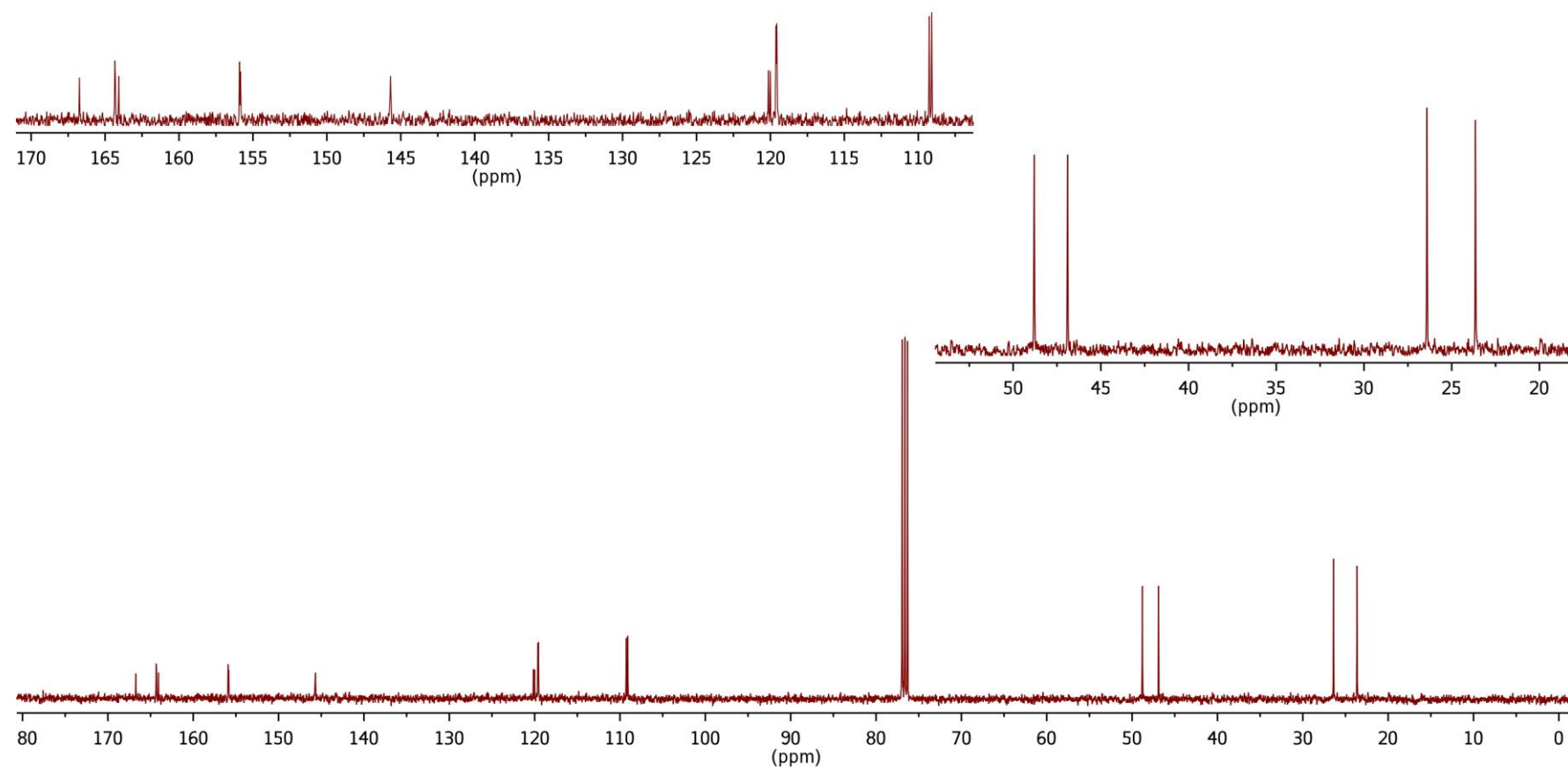


Figure S17. ^{13}C NMR spectrum in CDCl_3 at 25°C

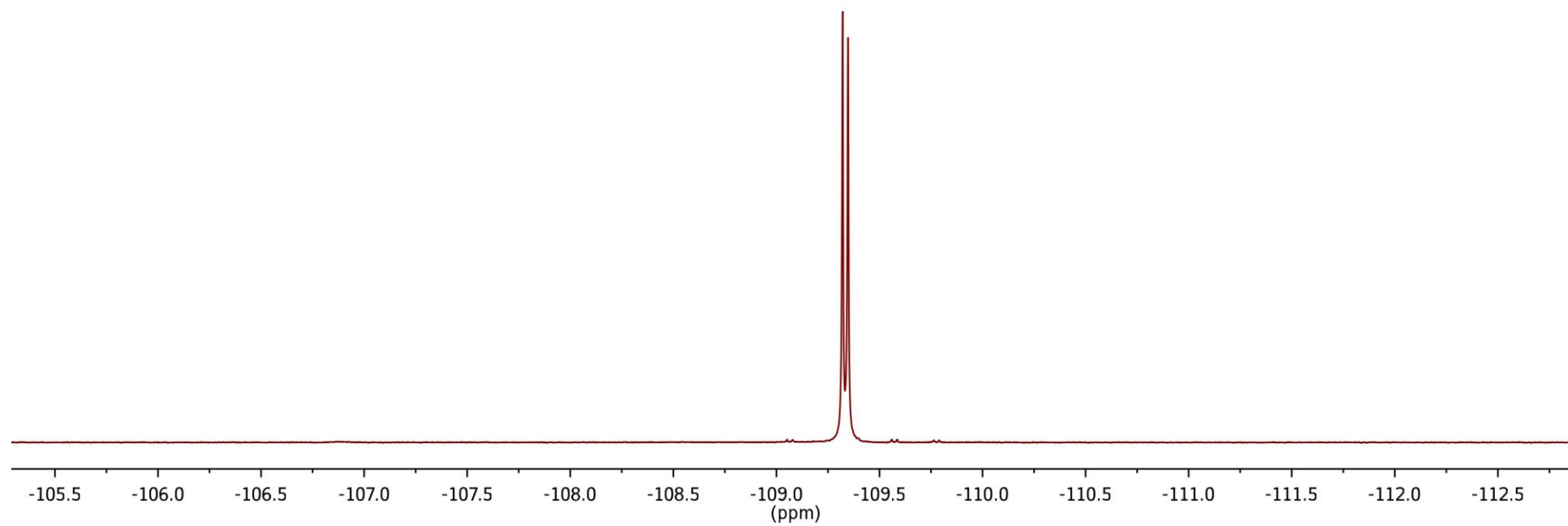


Figure S18. ^{19}F NMR spectrum in CDCl_3 at 25°C

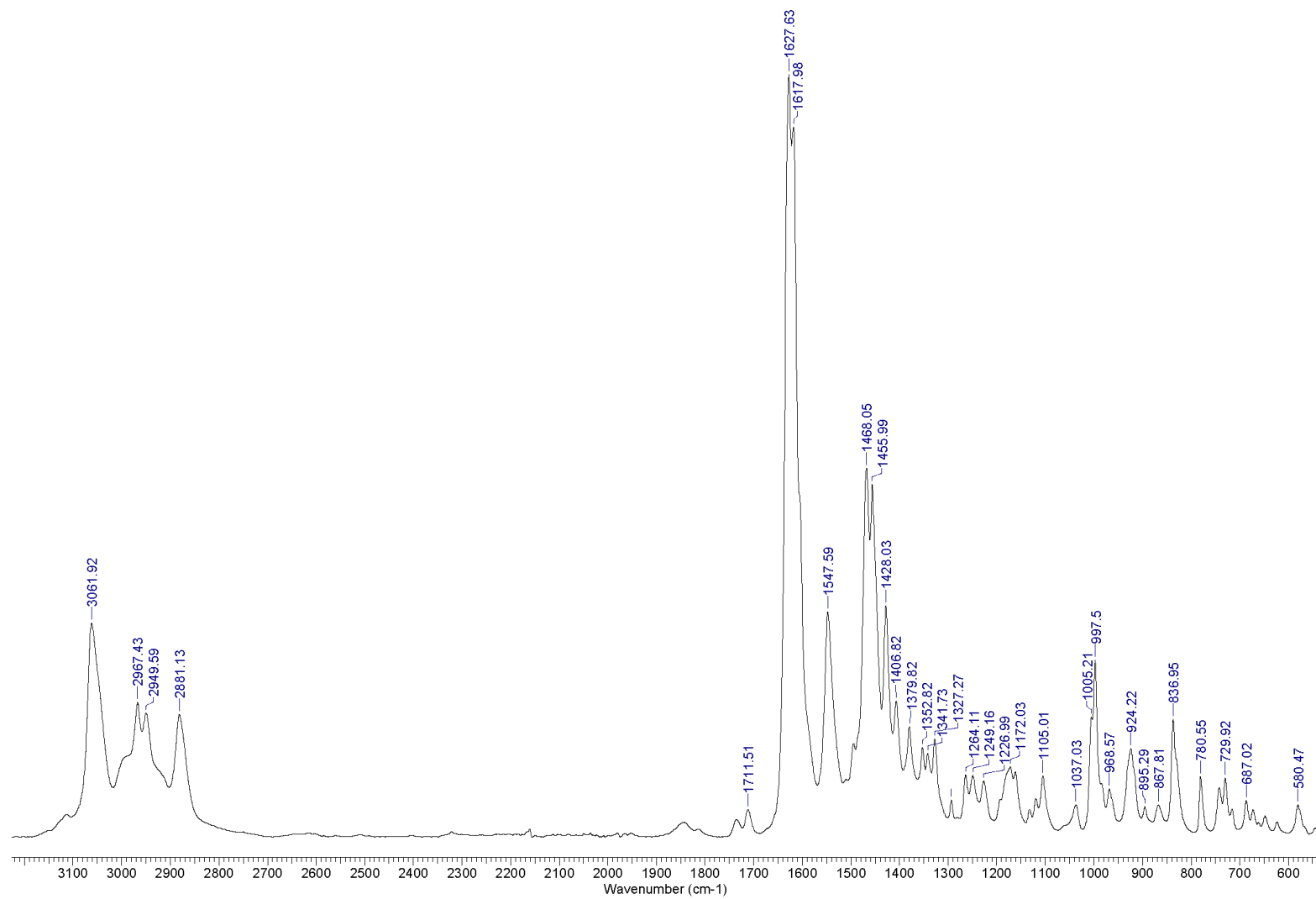


Figure S19. Solid-state IR spectrum at 25°C

N²,N⁹-bis(4-butylphenyl)-4,7-difluoro-N²,N⁹-diethyl-1,10-phenanthroline-2,9-dicarboxamide (7c)

T = 25 °C

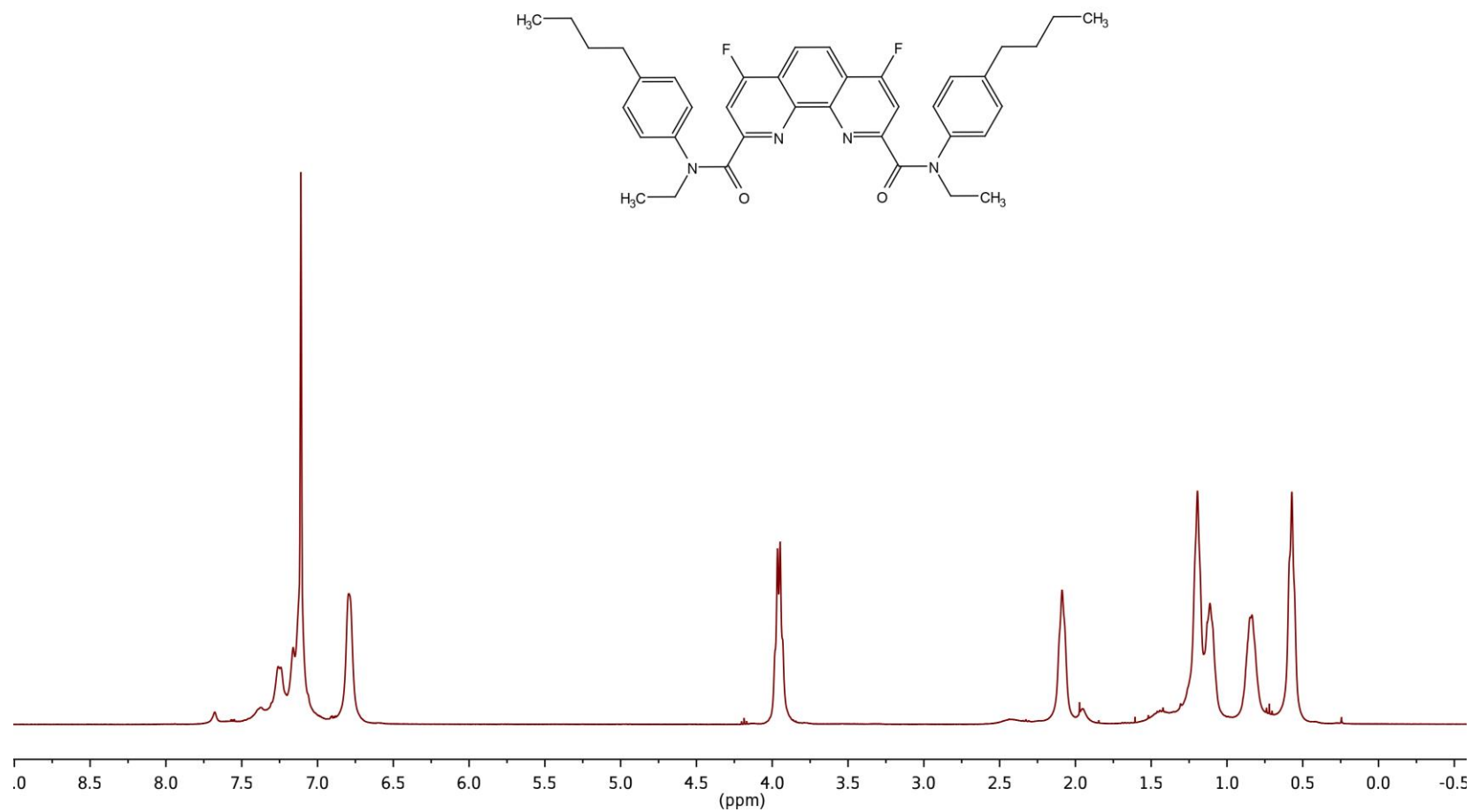


Figure S20. ¹H NMR spectrum in C₆D₆ at 25°C

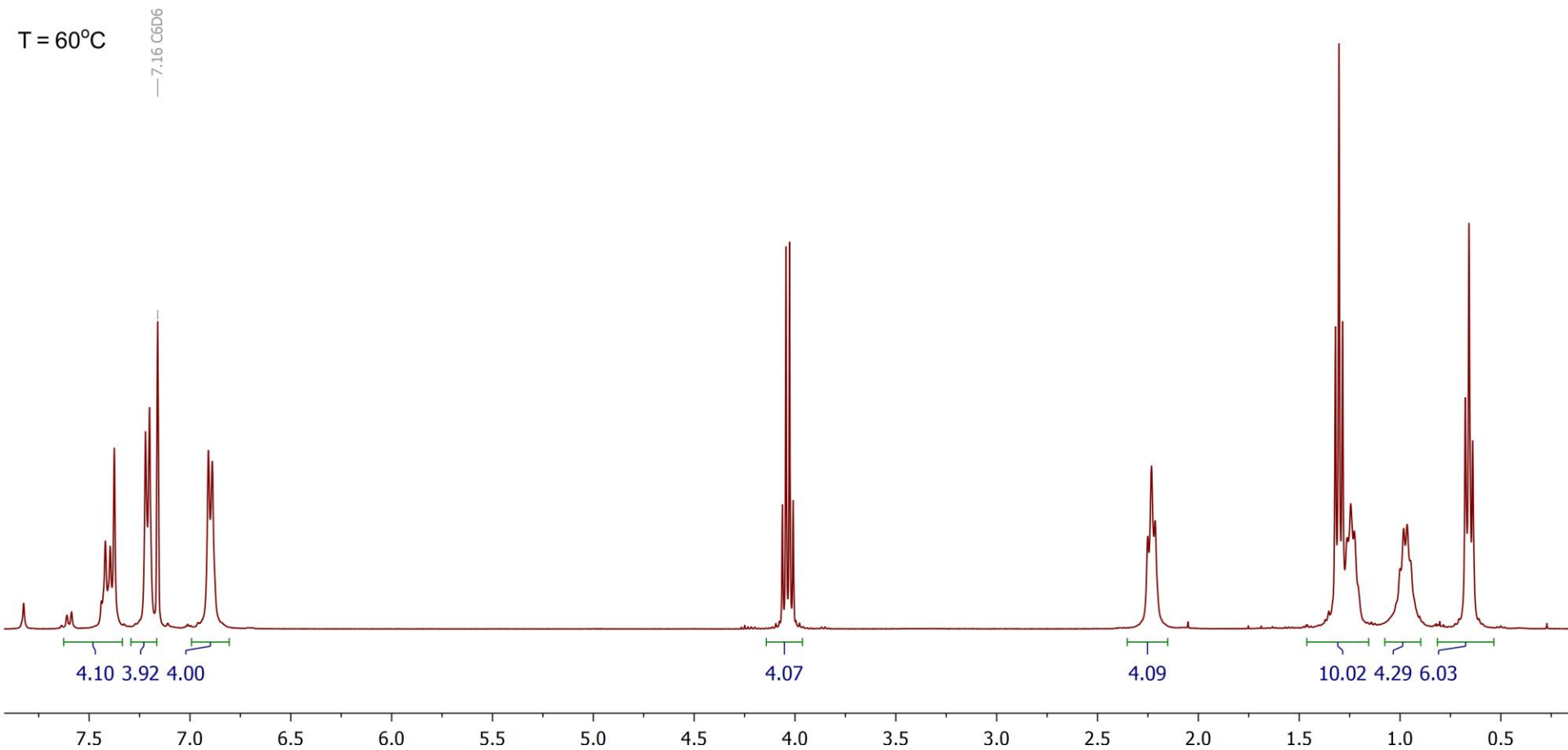


Figure S21. ^1H NMR spectrum in C_6D_6 at 60°C

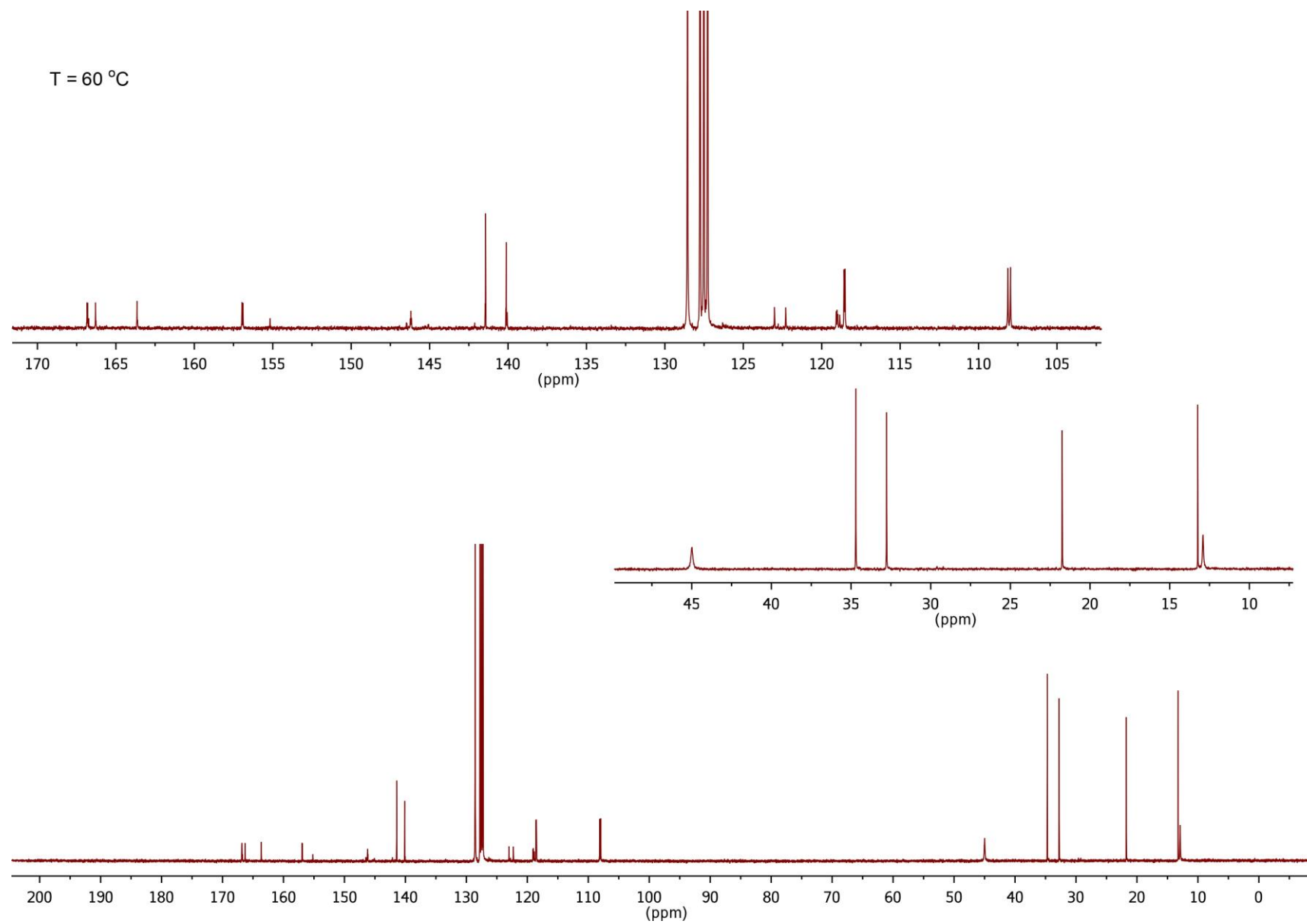


Figure S22. ^{13}C NMR spectrum in C_6D_6 at 60°C

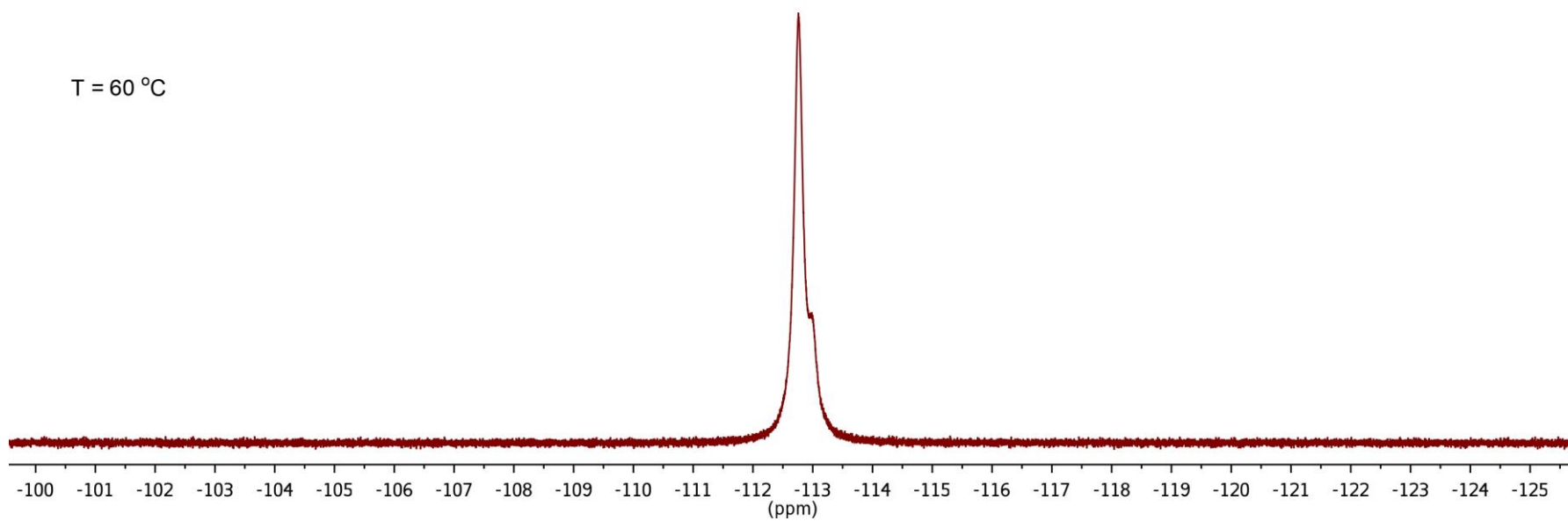
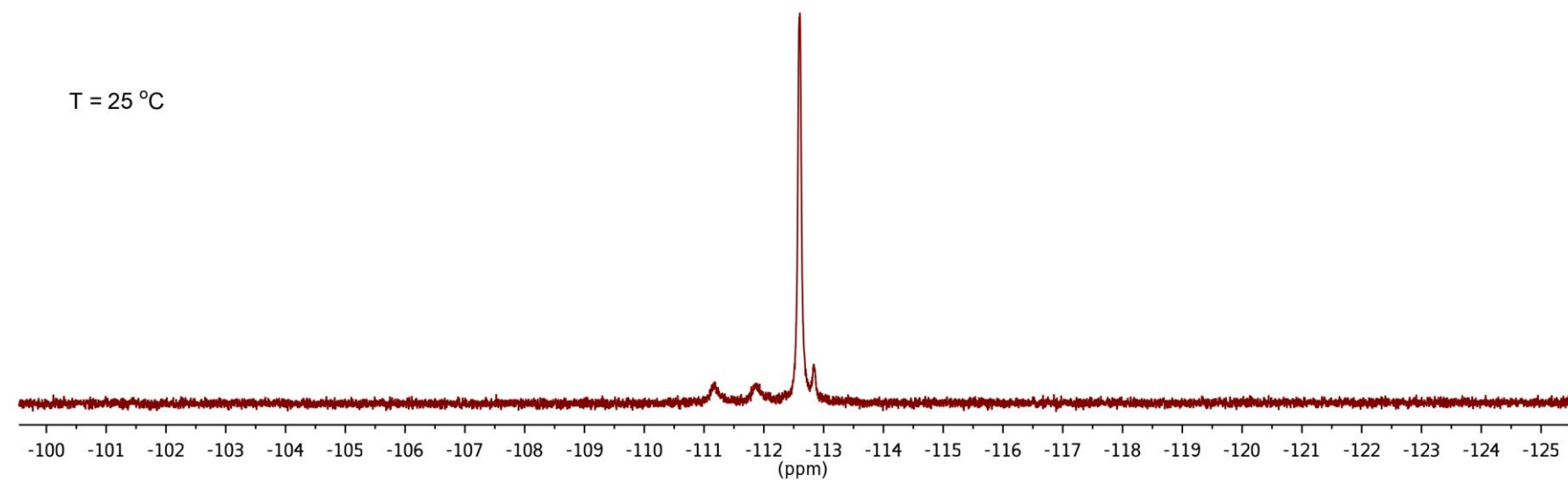


Figure S23. ^{19}F NMR spectra in C_6D_6 at 25 °C and 60°C

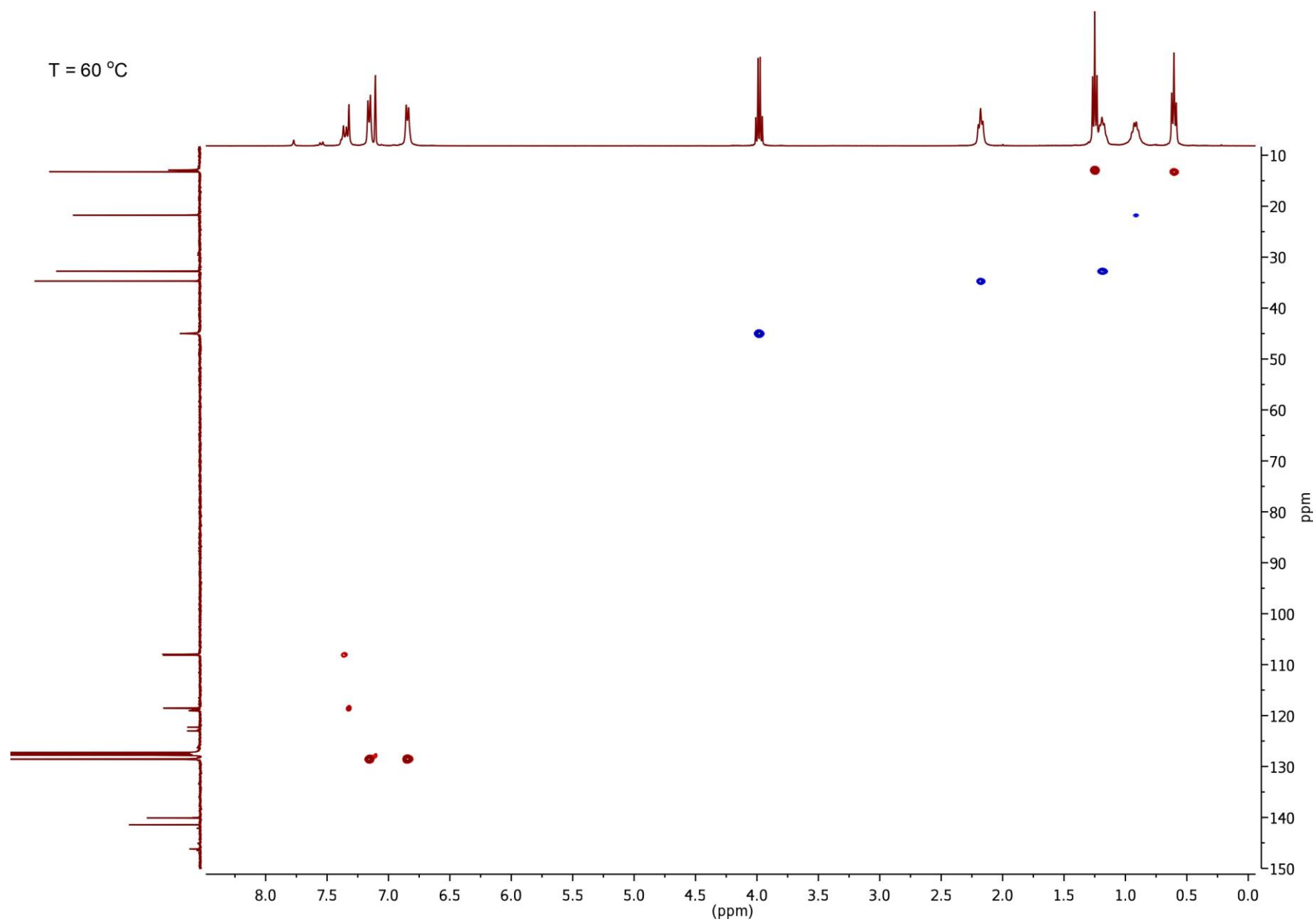


Figure S24. $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum in C_6D_6 at 60°C

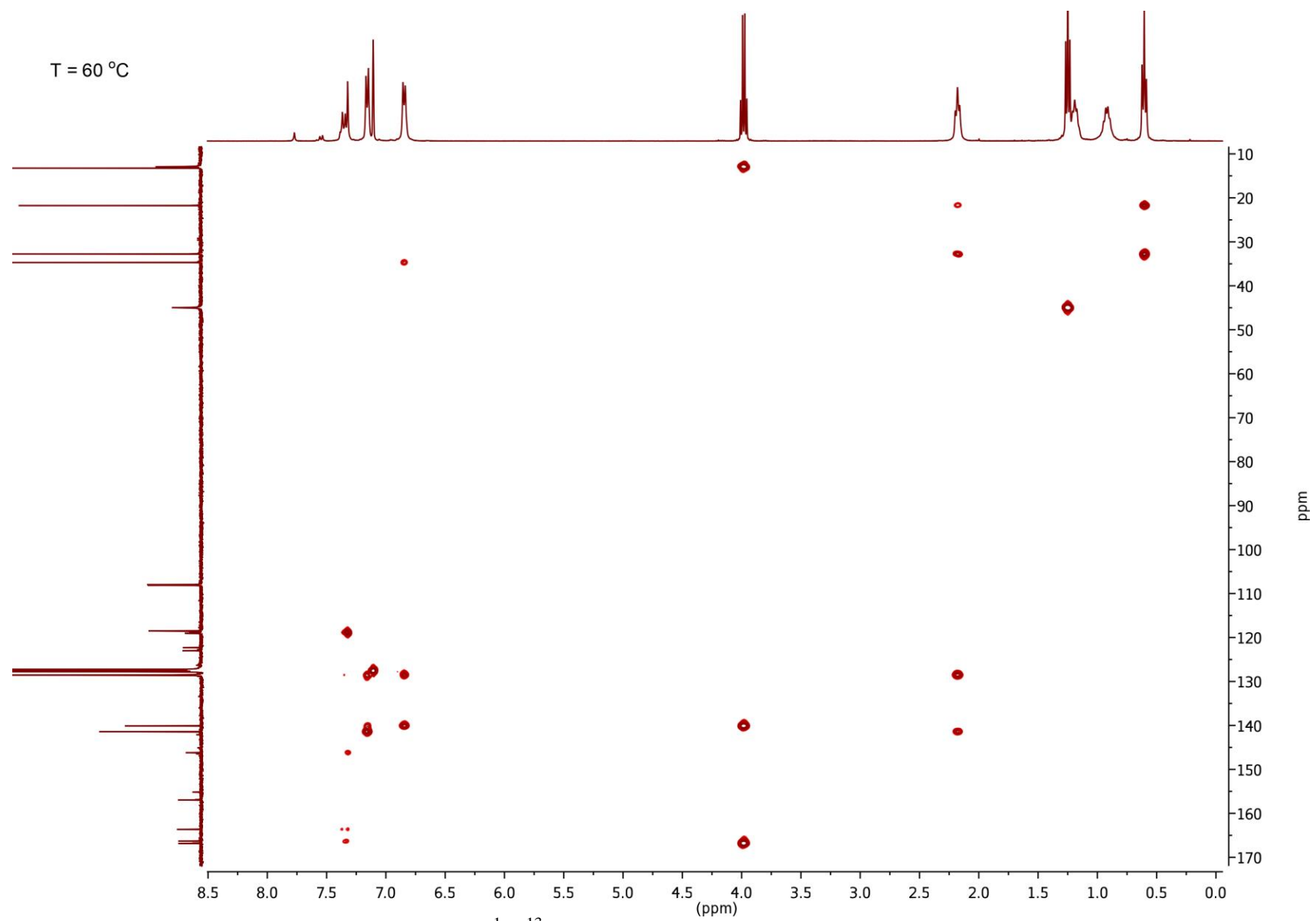


Figure S25. $^1\text{H}/^{13}\text{C}$ HMBC NMR spectrum in C_6D_6 at 60°C

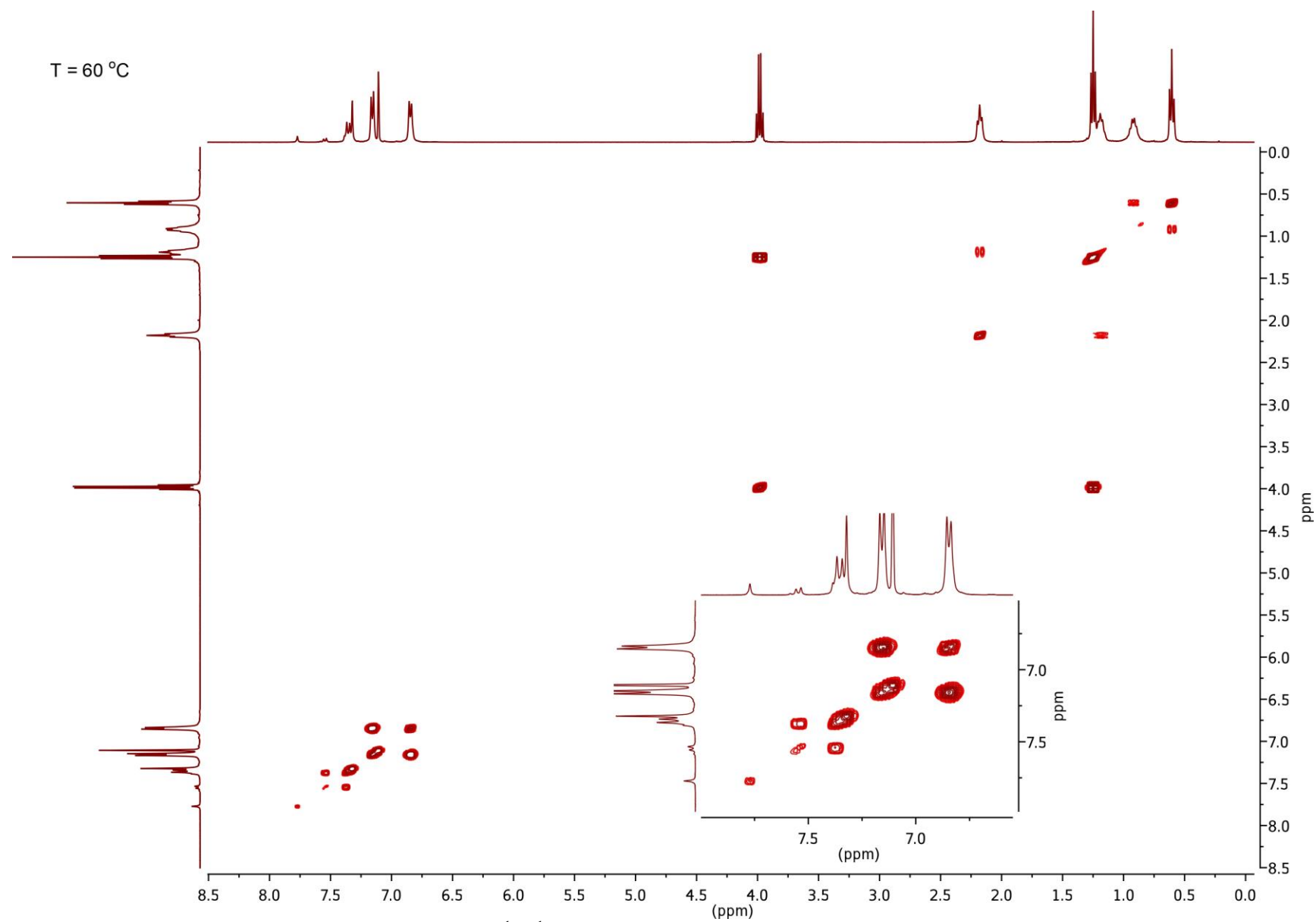


Figure S26. $^1\text{H}/^1\text{H}$ COSY NMR spectrum in C_6D_6 at 60°C

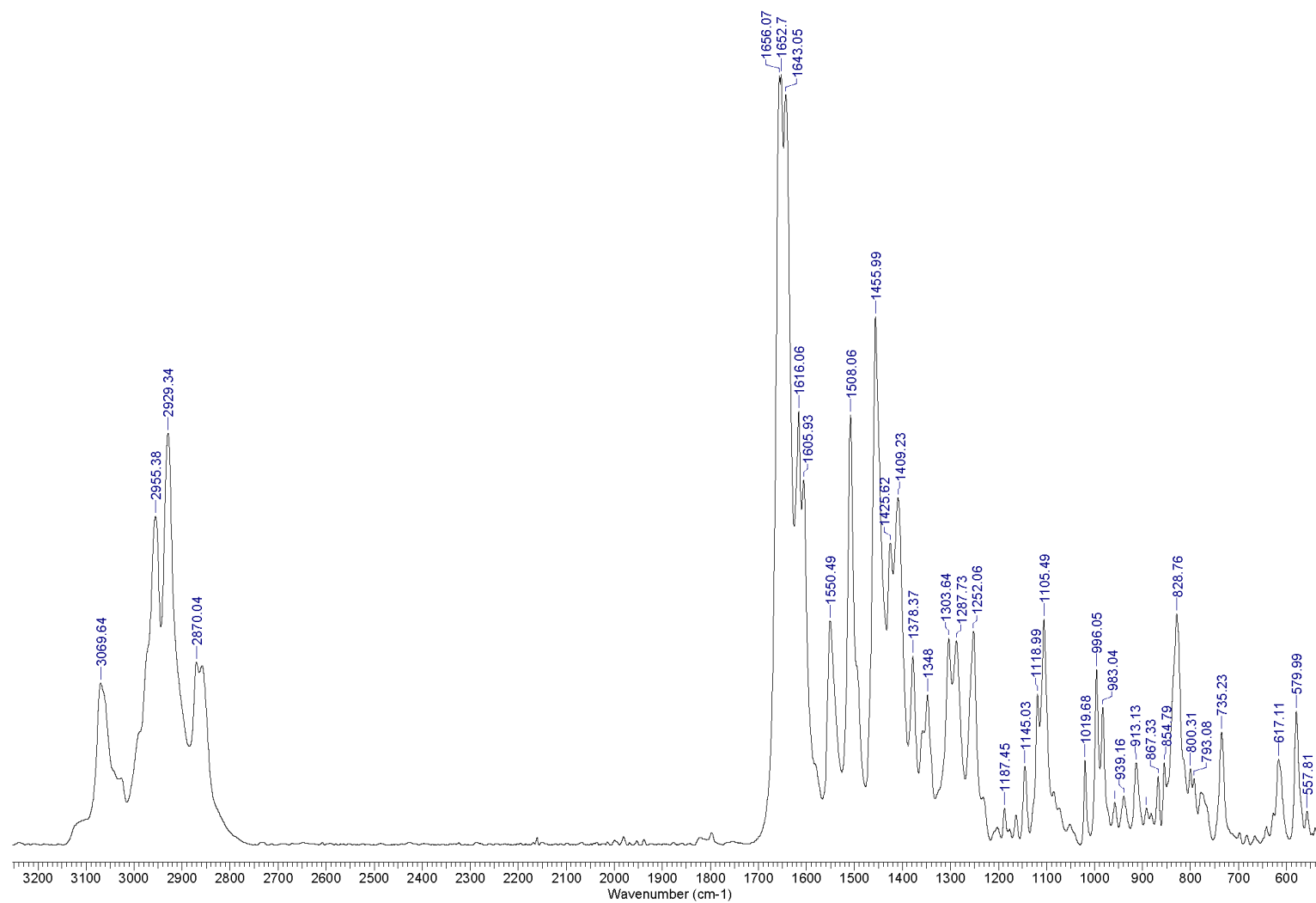


Figure S27. Solid-state IR spectrum at 25°C

N²,N⁹-bis(4-hexylphenyl)-4,7-difluoro-N²,N⁹-diethyl-1,10-phenanthroline-2,9-dicarboxamide (7d)

T= 60 °C

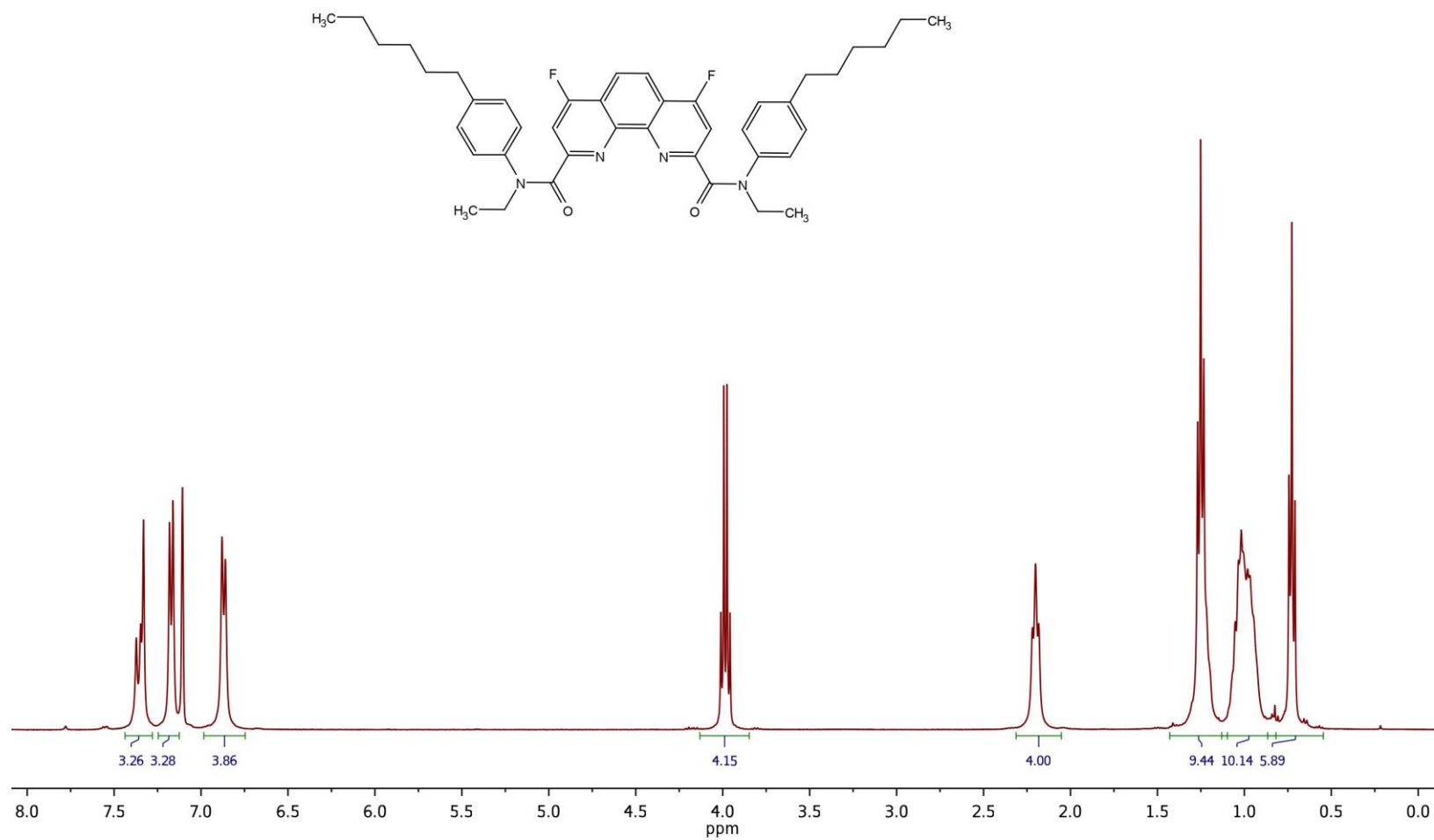


Figure S28. ¹H NMR spectrum in C₆D₆ at 60°C

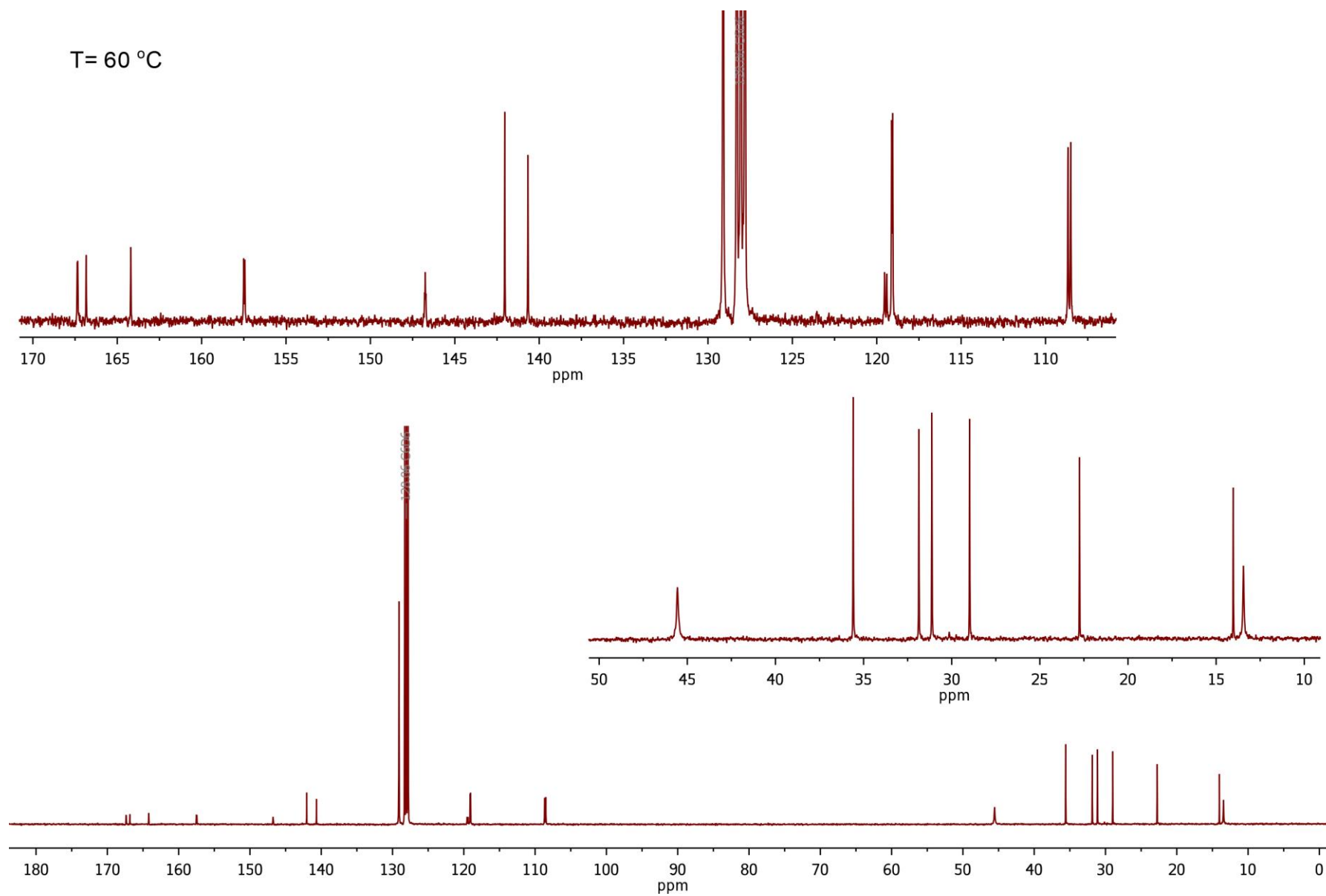


Figure S29. ^{13}C NMR spectrum in C_6D_6 at 60°C

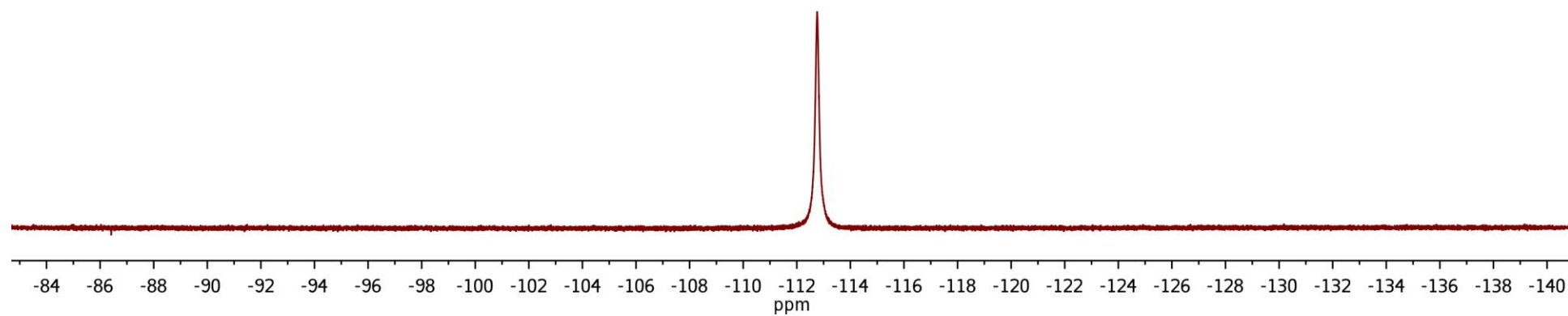


Figure S30. ^{19}F NMR spectrum in C_6D_6 at 60°C

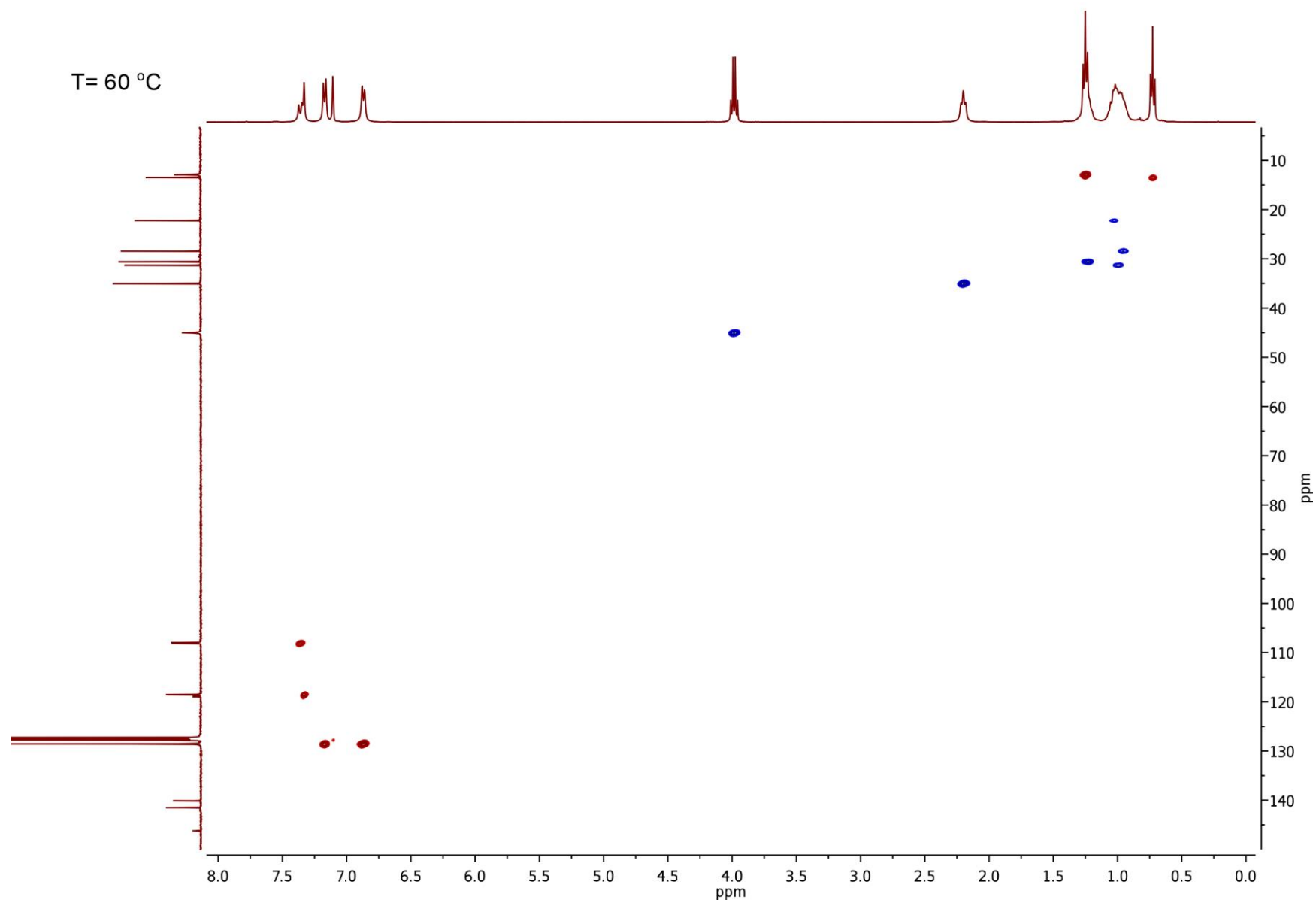


Figure S31. $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum in C_6D_6 at 60°C

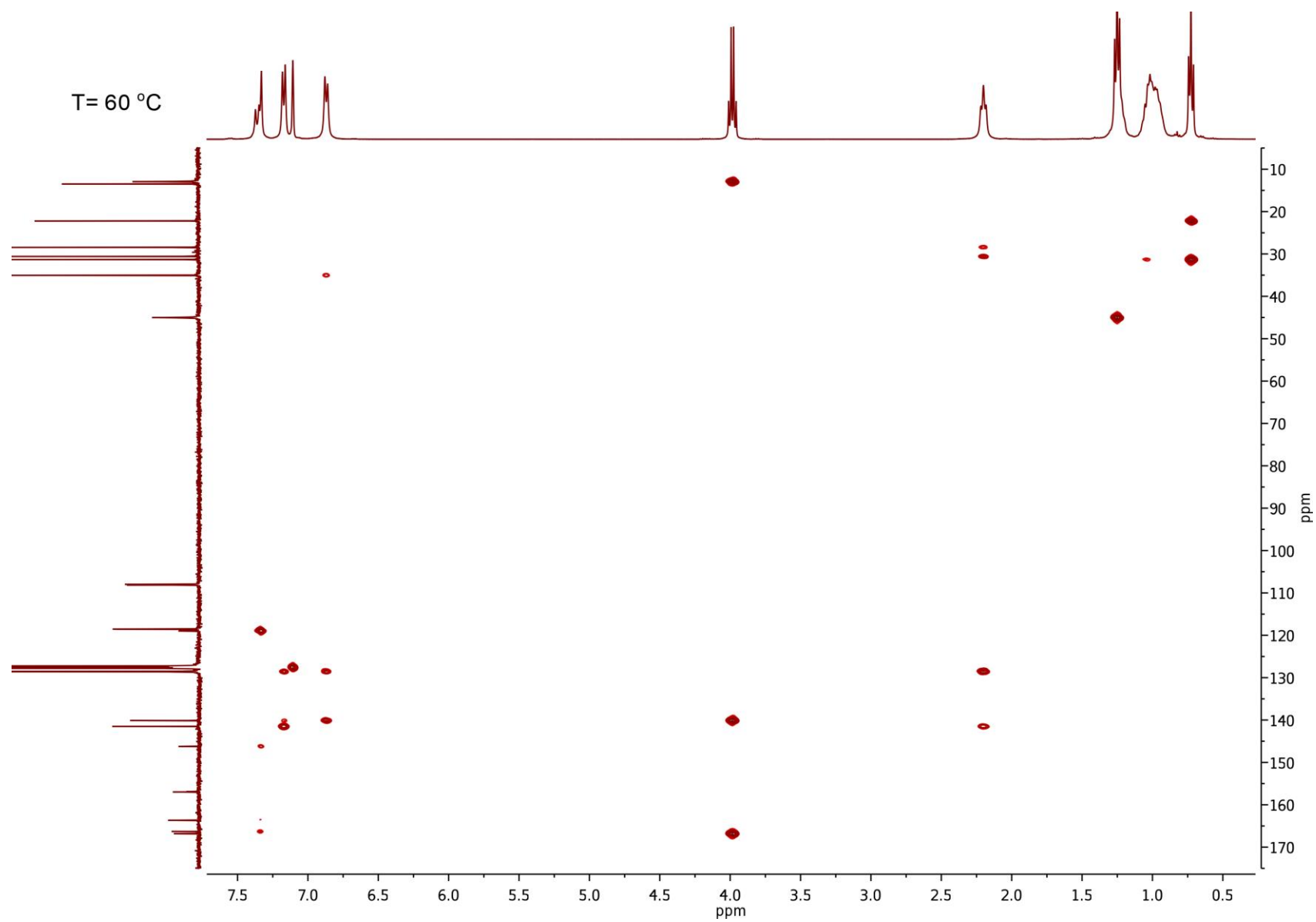


Figure S32. $^1\text{H}/^{13}\text{C}$ HMBC NMR spectrum in C_6D_6 at 60°C

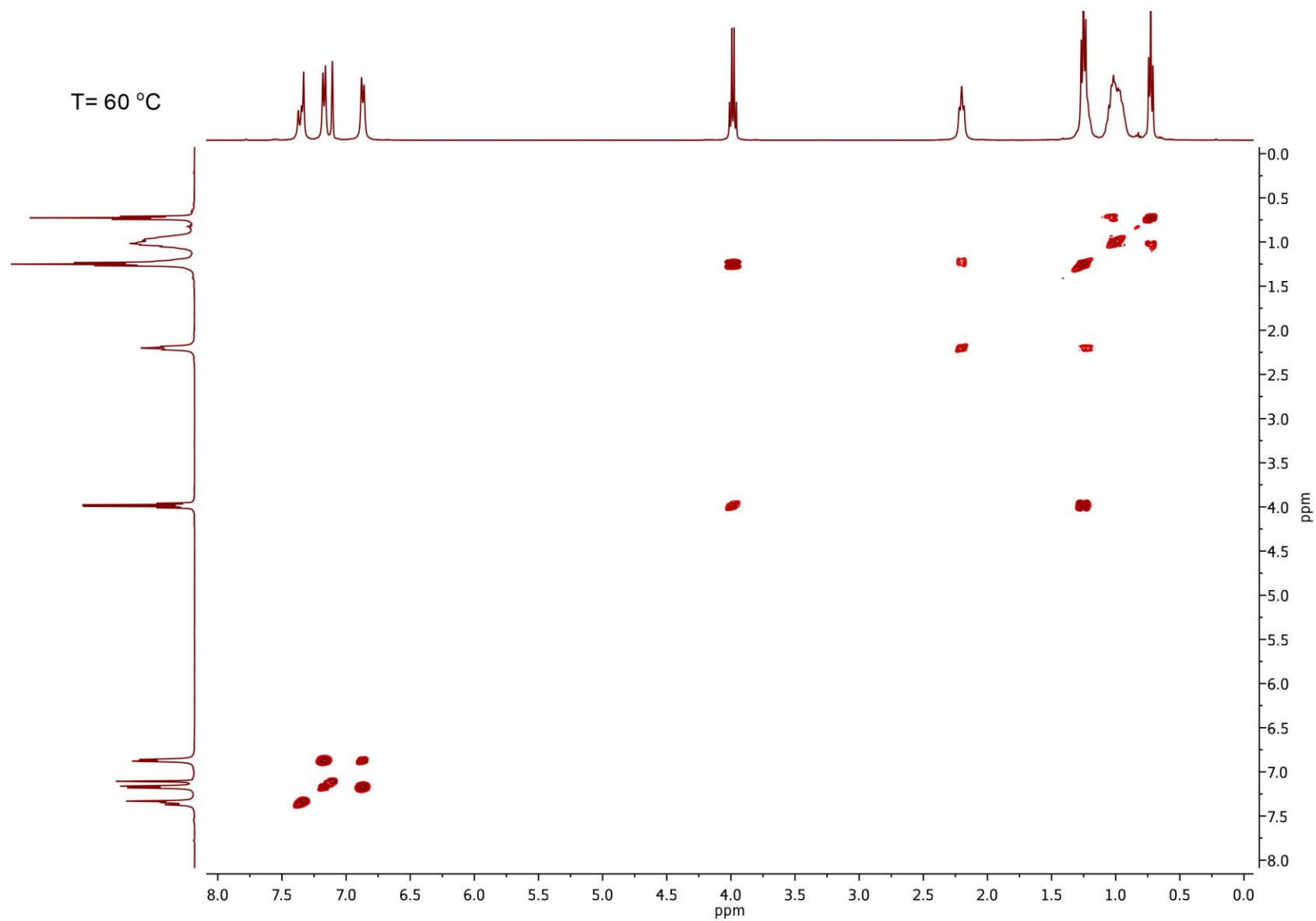


Figure S33. $^1\text{H}/^1\text{H}$ COSY NMR spectrum in C_6D_6 at 60°C

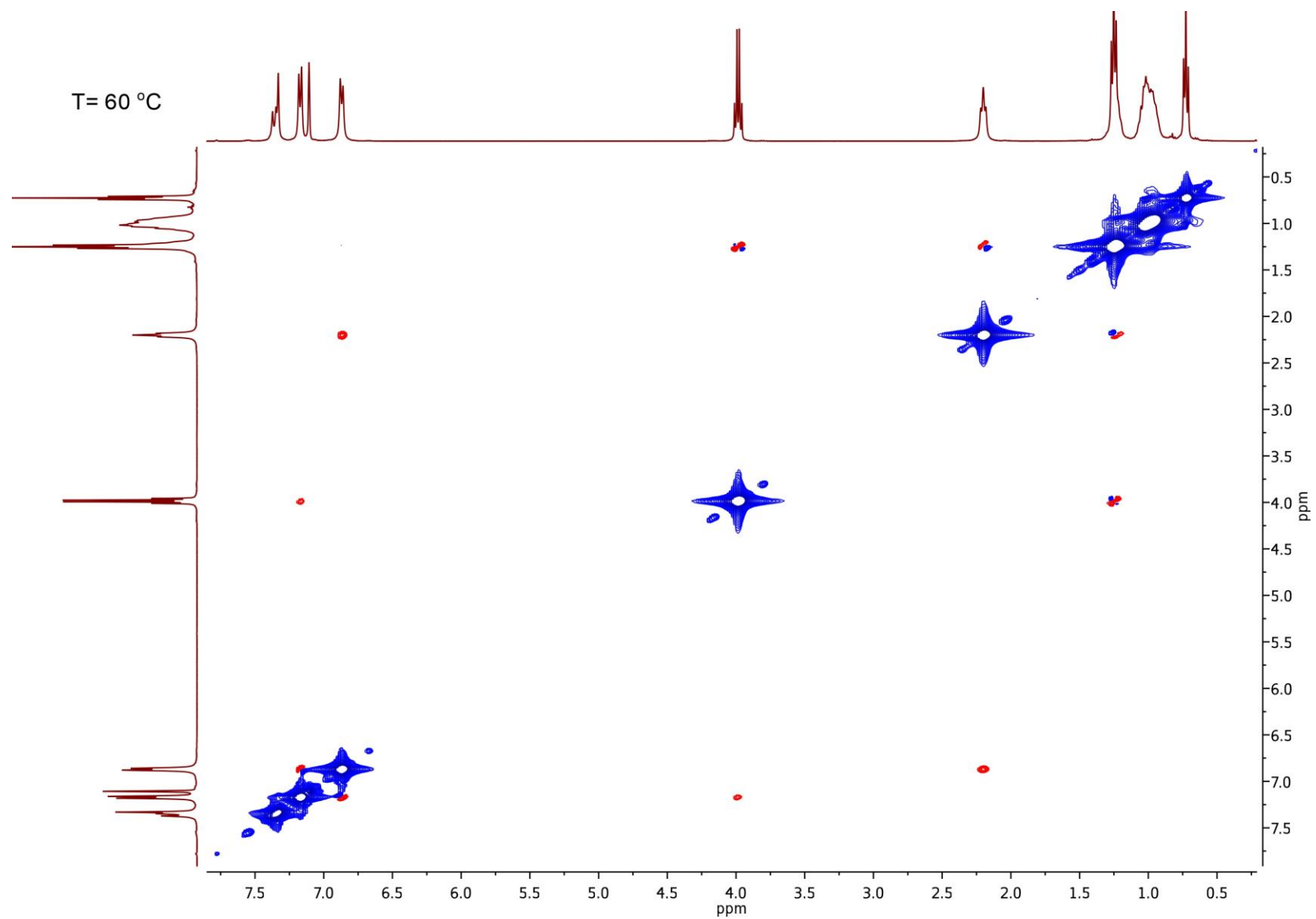


Figure S34. $^1\text{H}/^1\text{H}$ NOESY NMR spectrum in C_6D_6 at 60°C

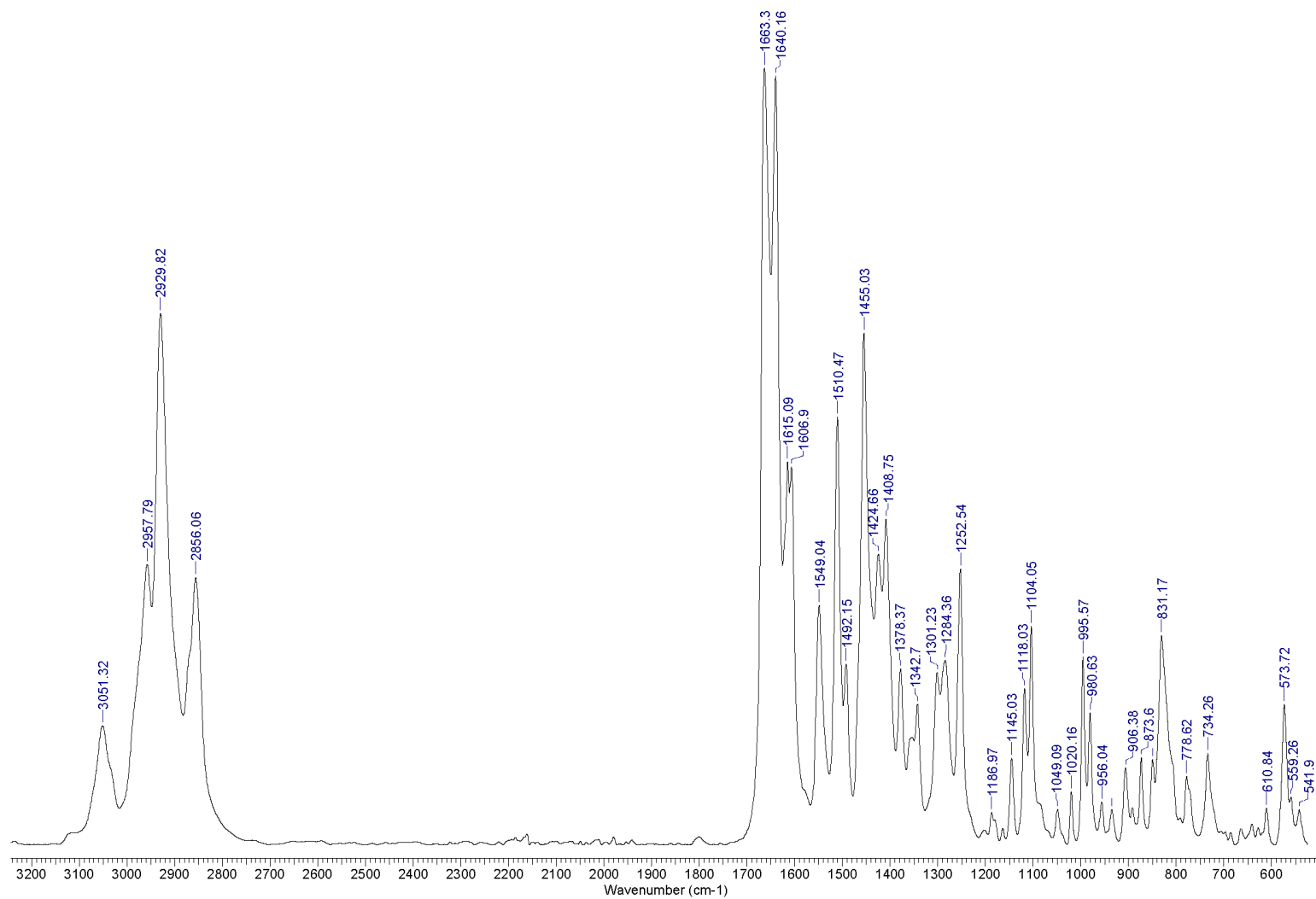


Figure S35. Solid-state IR spectrum at 25°C

NMR and IR spectra of complexes

Complex 7a*La(NO₃)₃

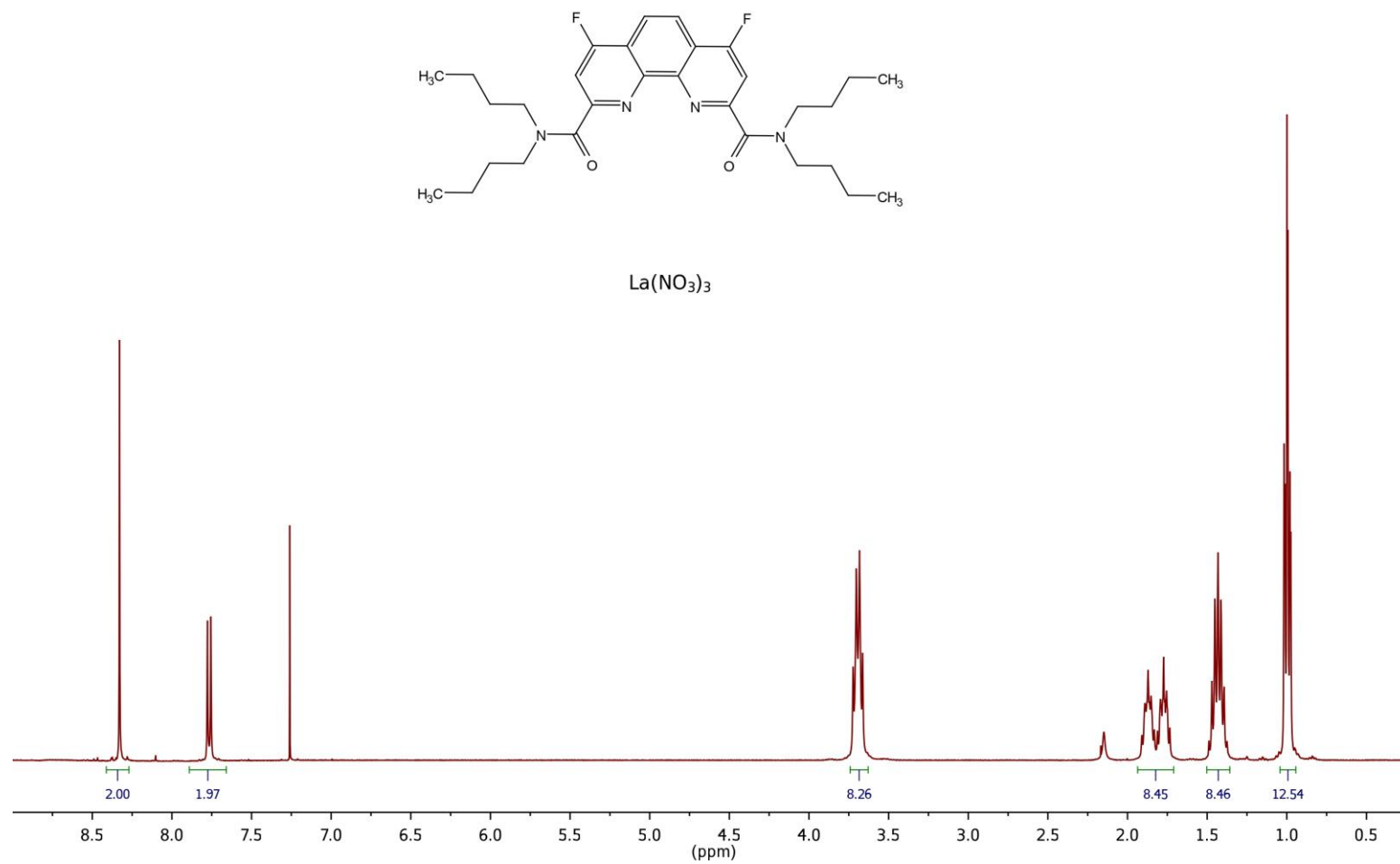


Figure S36. ¹H NMR spectrum in CDCl₃ at 25°C

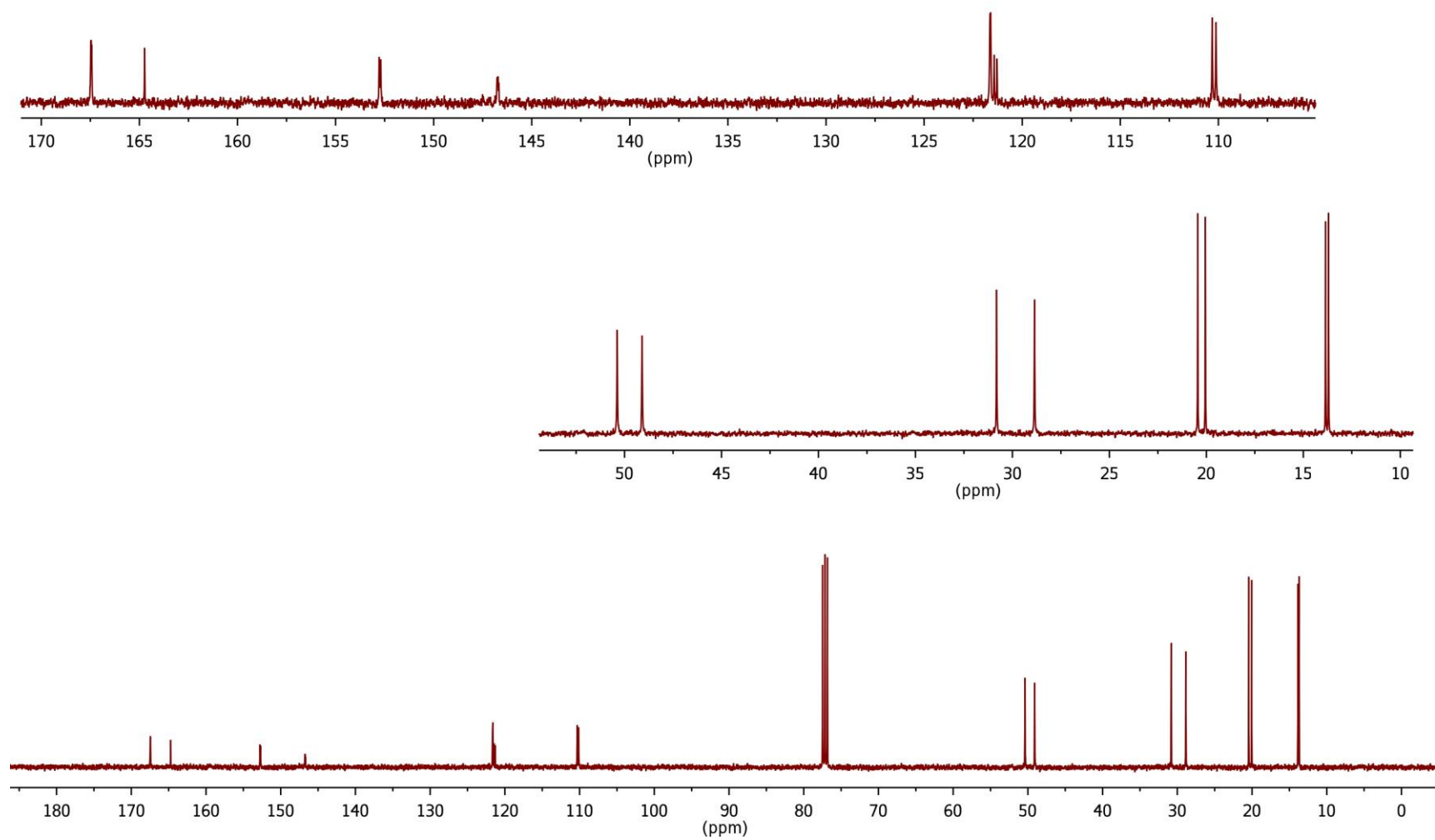


Figure S37. ^{13}C NMR spectrum in CDCl_3 at 25°C

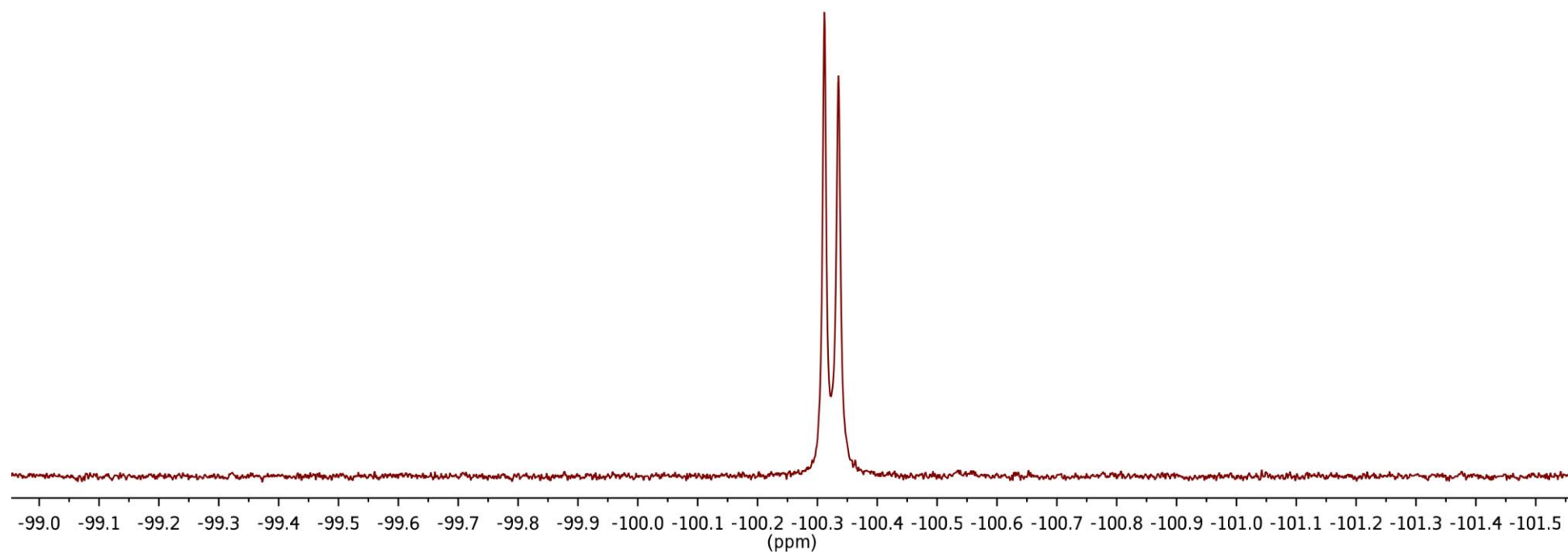


Figure S38. ^{19}F NMR spectrum in CDCl_3 at 25°C

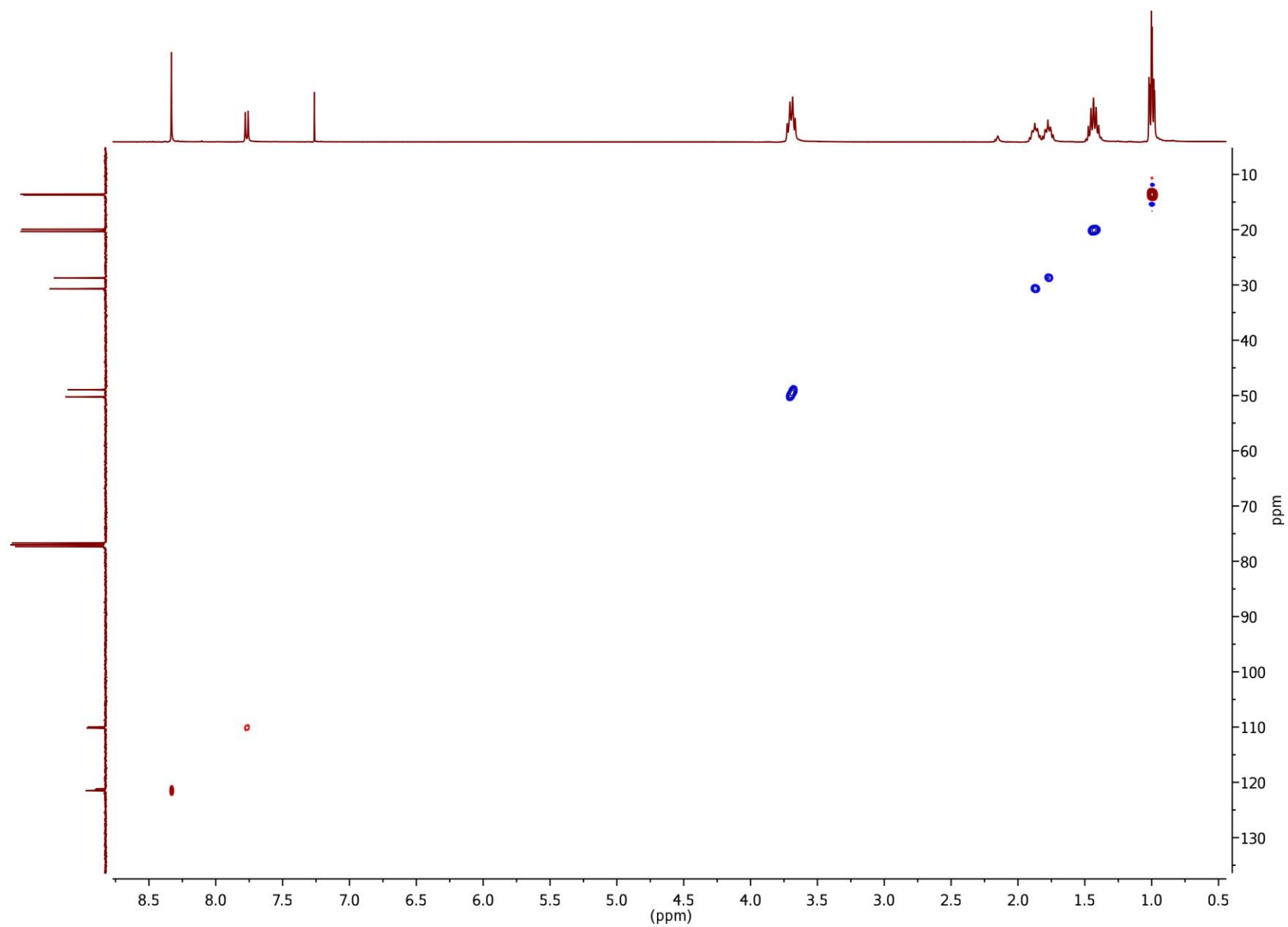


Figure S39. $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum in CDCl_3 at 25°C

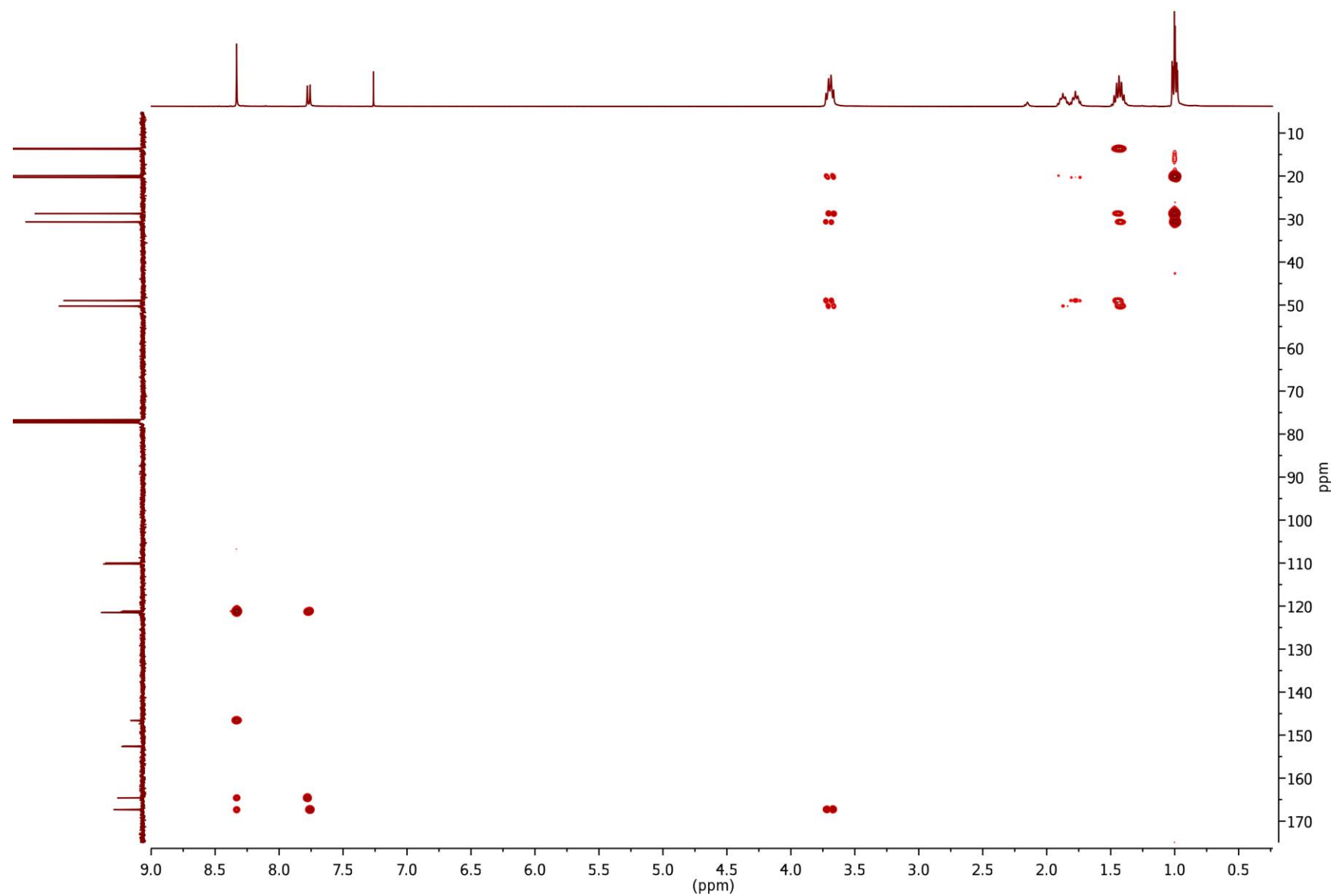


Figure S40. $^1\text{H}/^{13}\text{C}$ HMBC NMR spectrum in CDCl_3 at 25°C

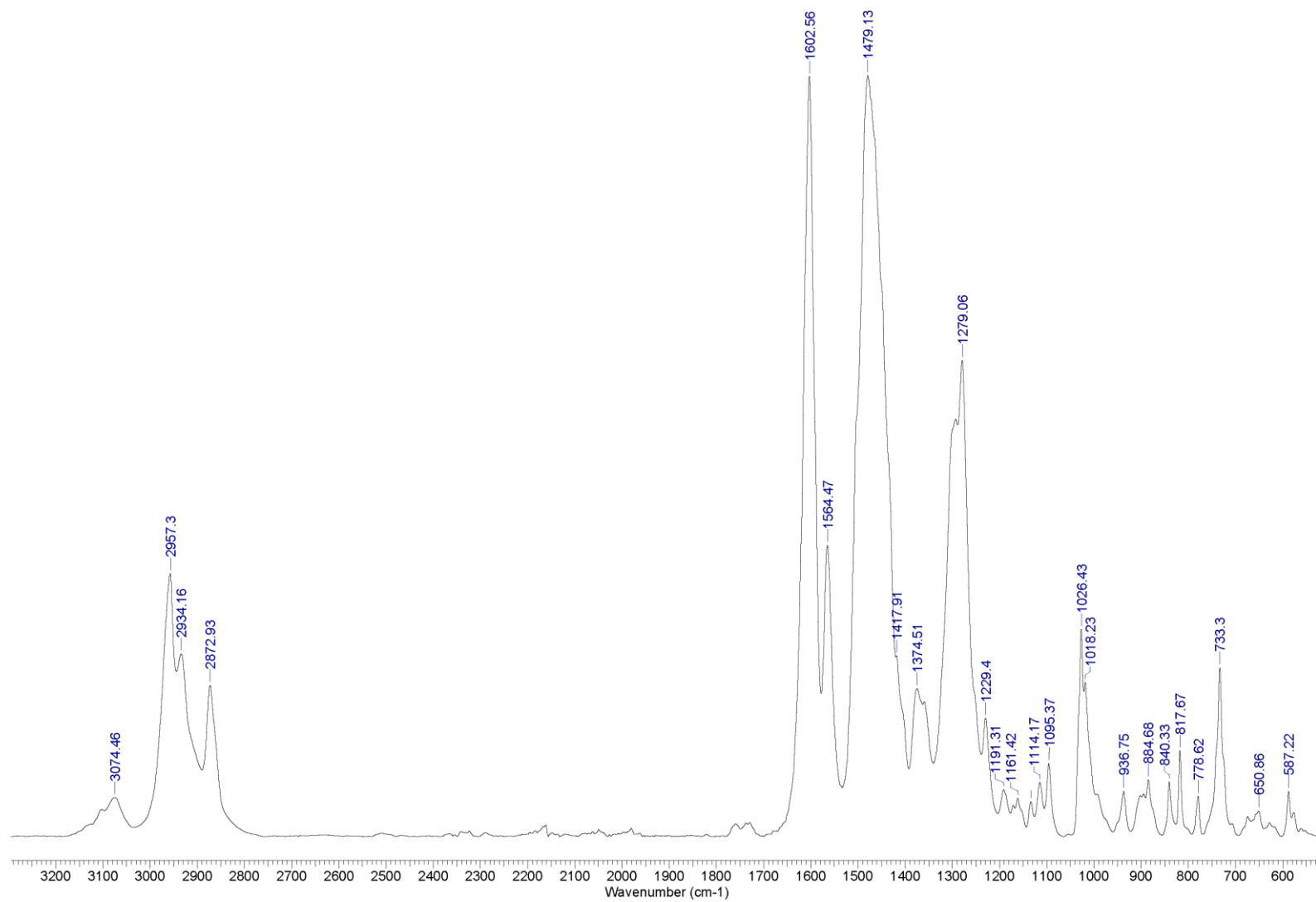
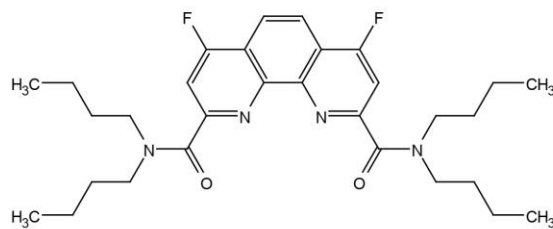


Figure S41. Solid-state IR spectrum at 25°C

Complex 7a* $\text{Nd}(\text{NO}_3)_3$



$\text{Nd}(\text{NO}_3)_3$

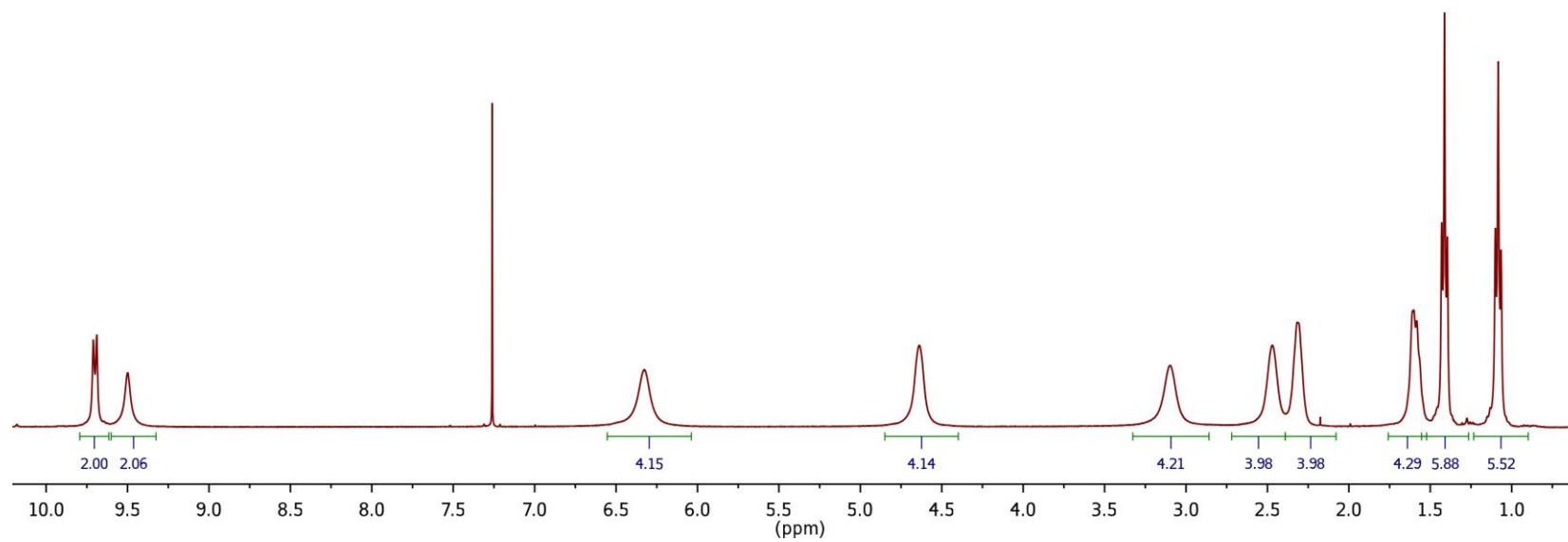


Figure S42. ^1H NMR spectrum in CDCl_3 at 25°C

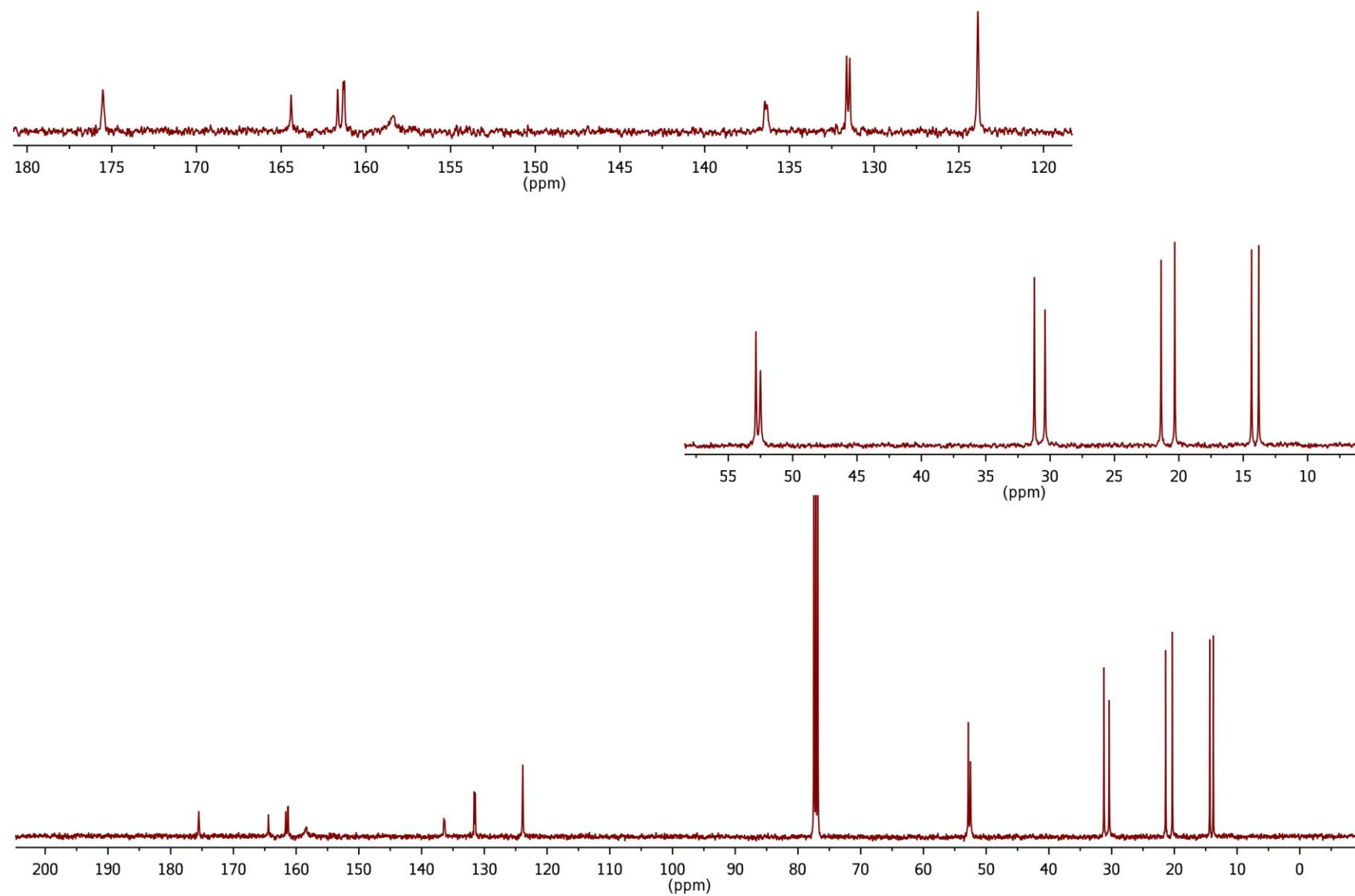


Figure S43. ^{13}C NMR spectrum in CDCl_3 at 25°C

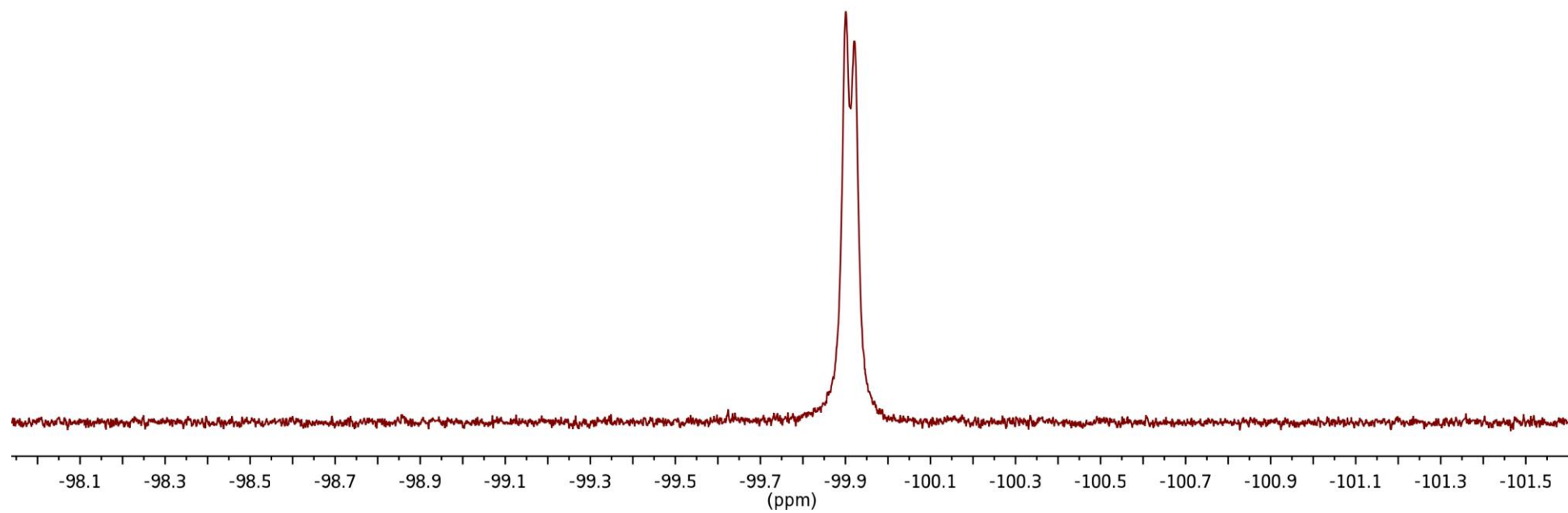


Figure S44. ^{19}F NMR spectrum in CDCl_3 at 25°C

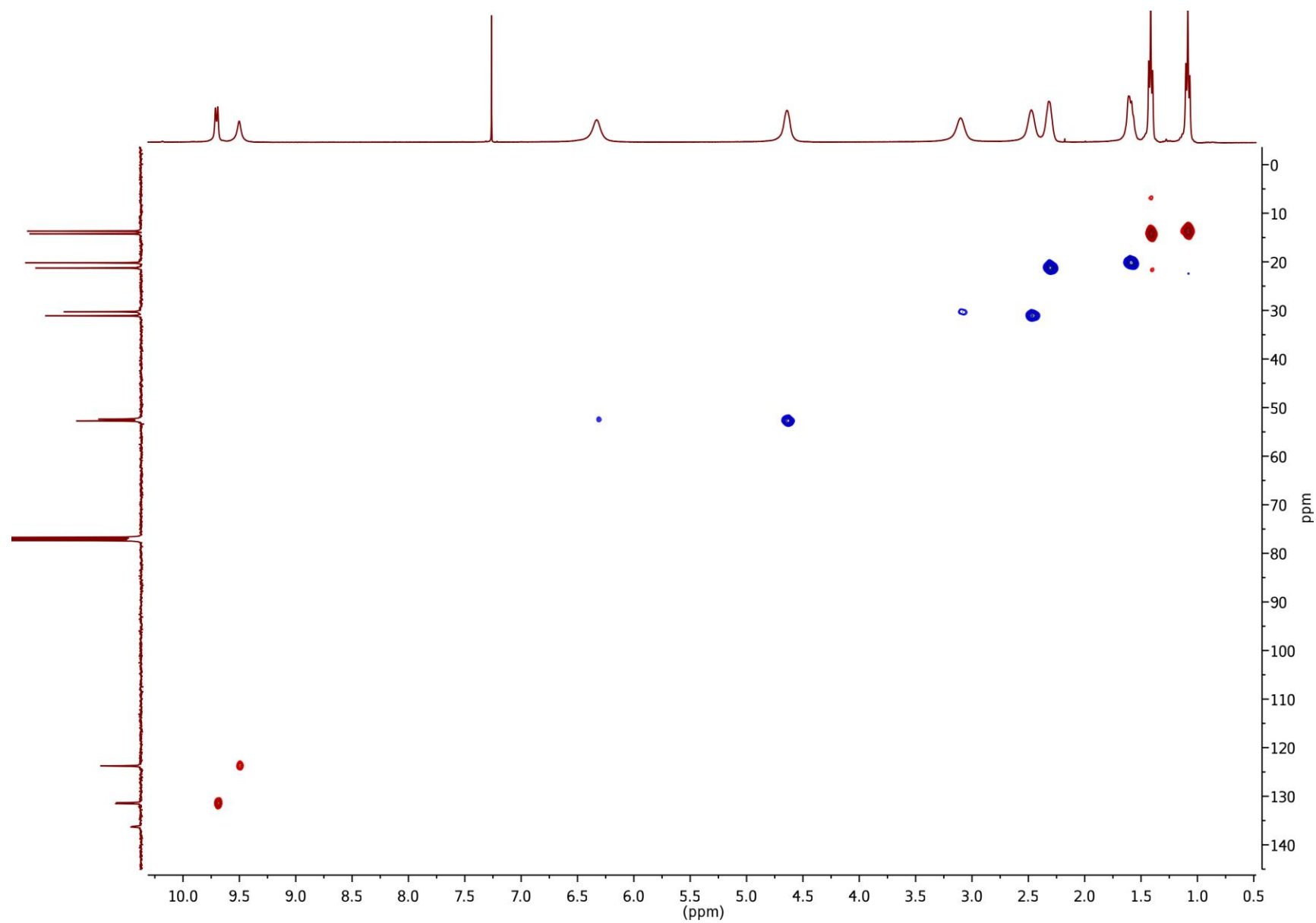


Figure S45. $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum in CDCl_3 at 25°C

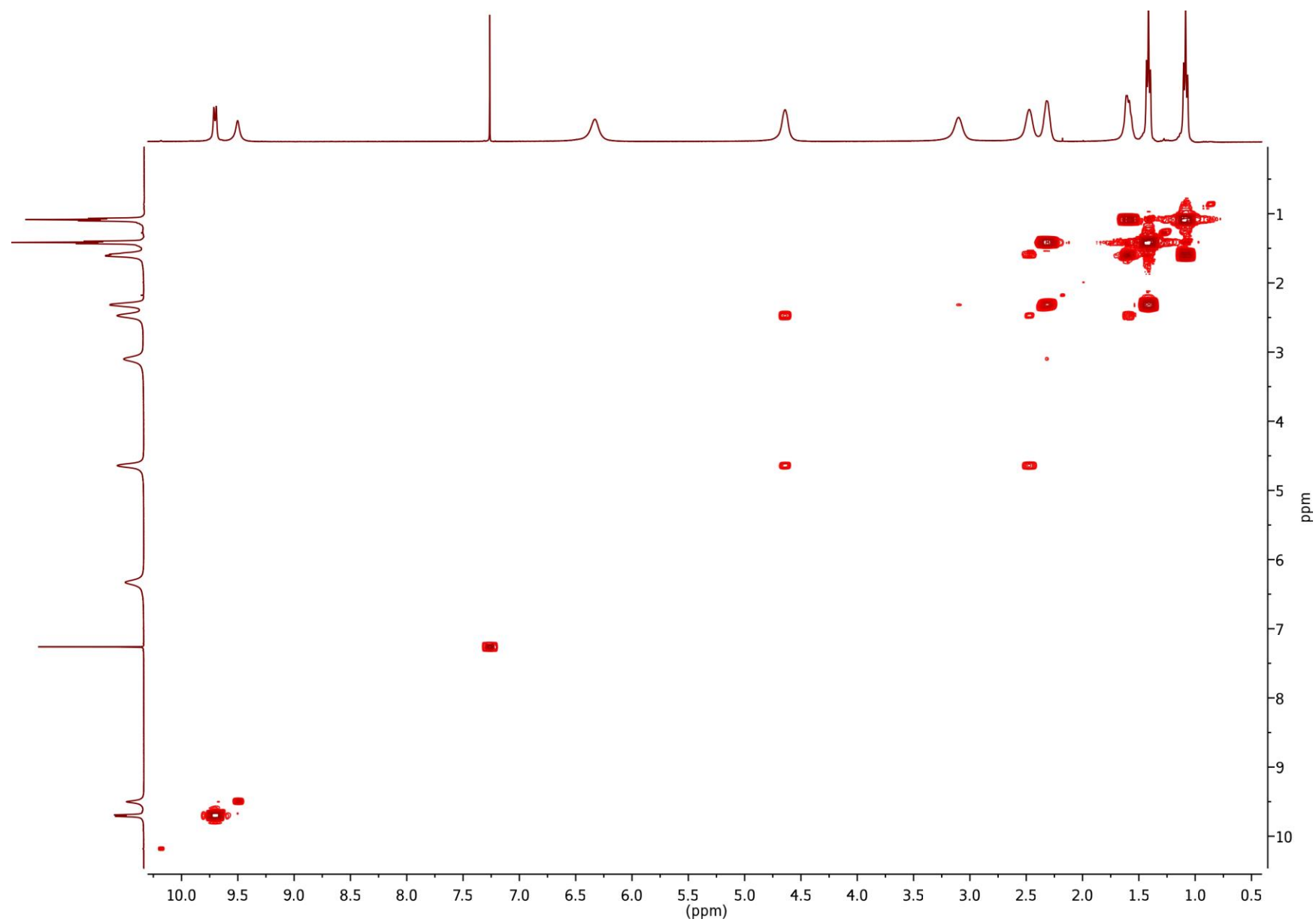


Figure S46. $^1\text{H}/^{13}\text{C}$ HMBC NMR spectrum in CDCl_3 at 25°C

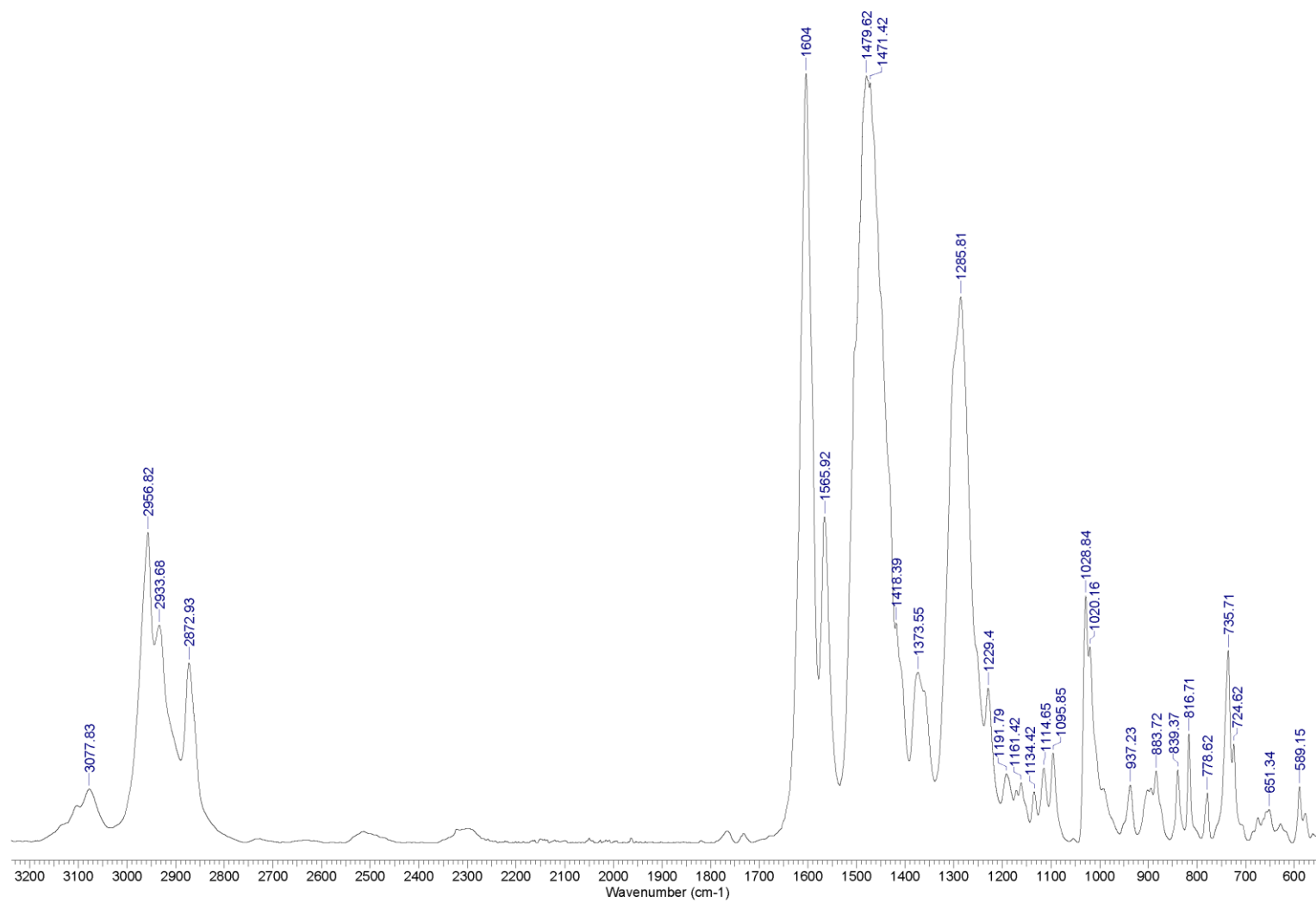


Figure S47. Solid-state IR spectrum at 25°C

Complex 7a*Eu(NO₃)₃

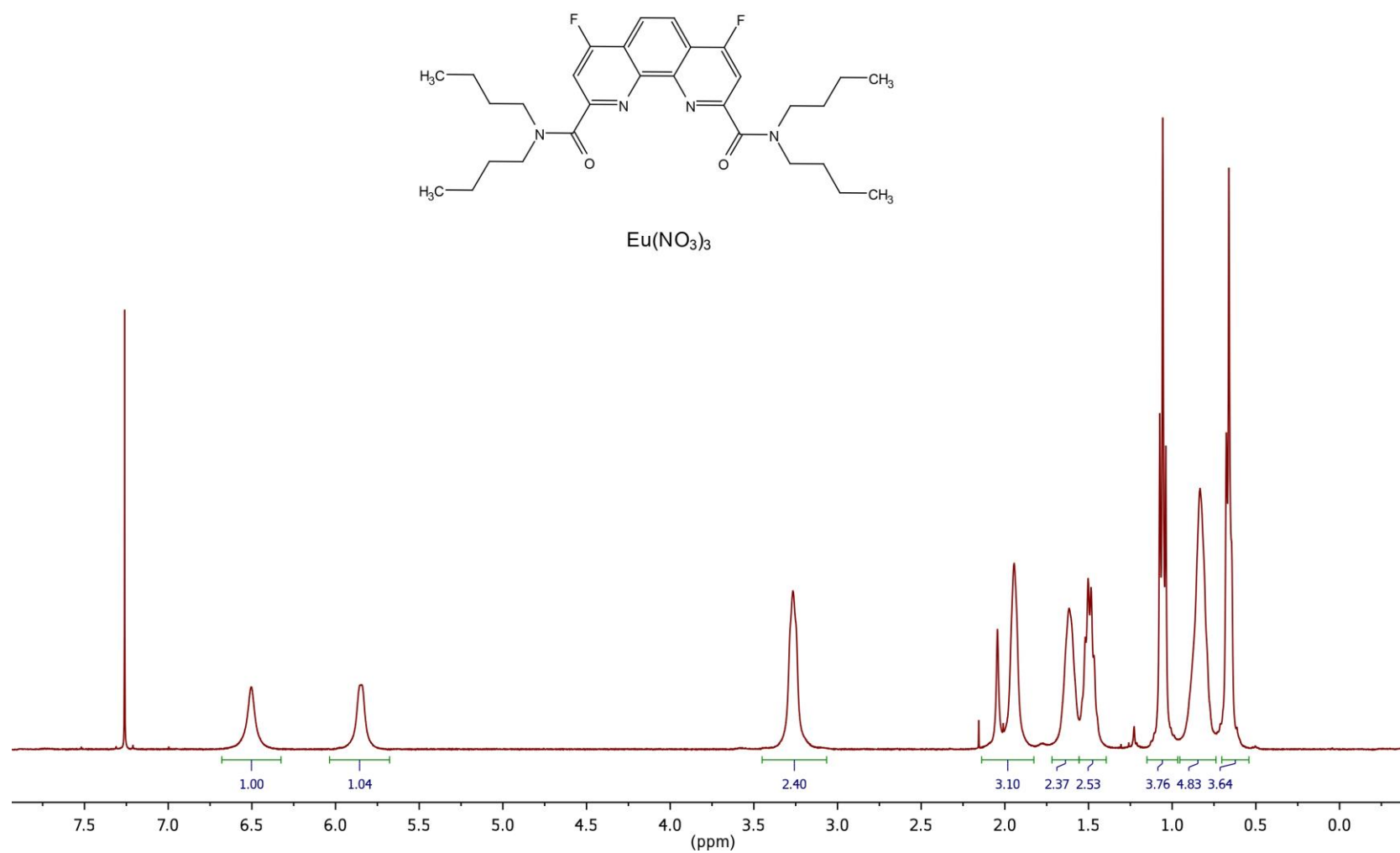


Figure S48. ^1H NMR spectrum in CDCl_3 at 25°C

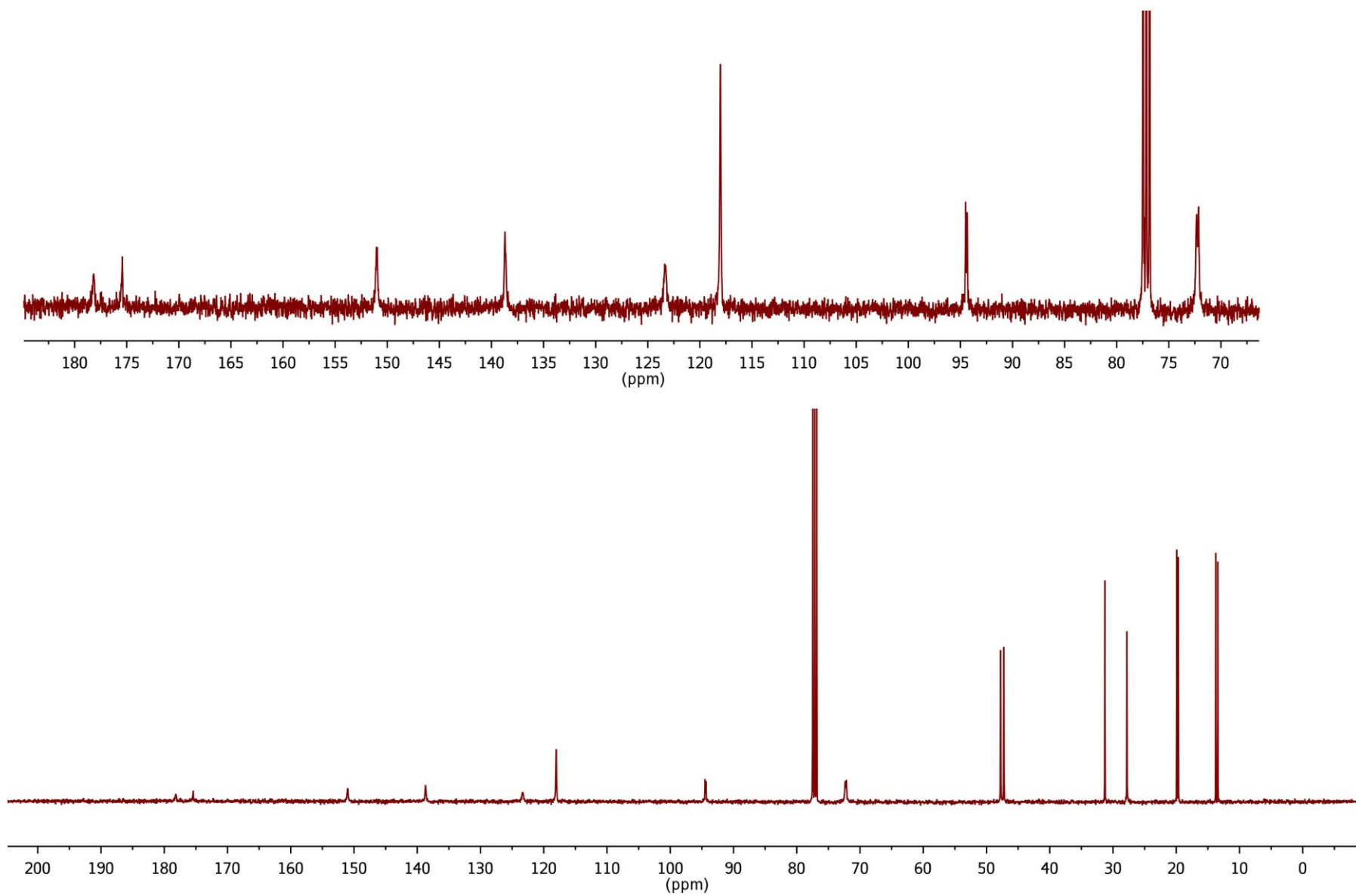


Figure S49. ^{13}C NMR spectrum in CDCl_3 at 25°C

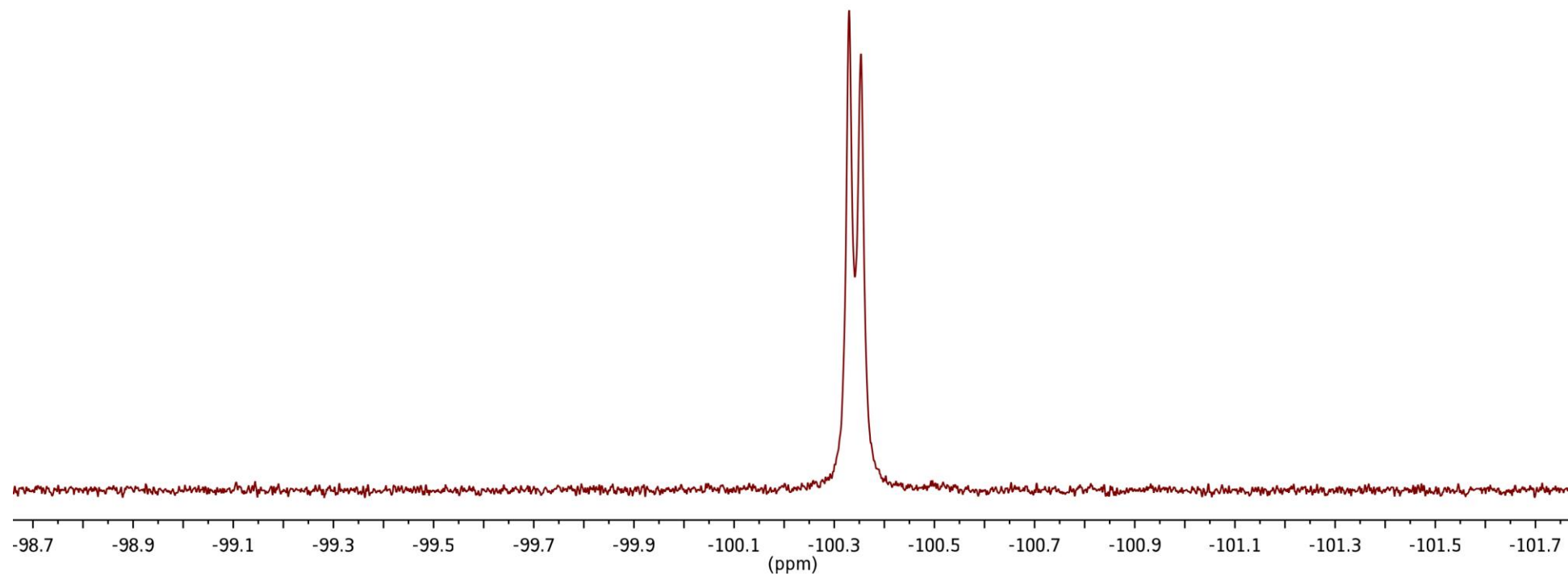


Figure S50. ^{19}F NMR spectrum in CDCl_3 at 25°C

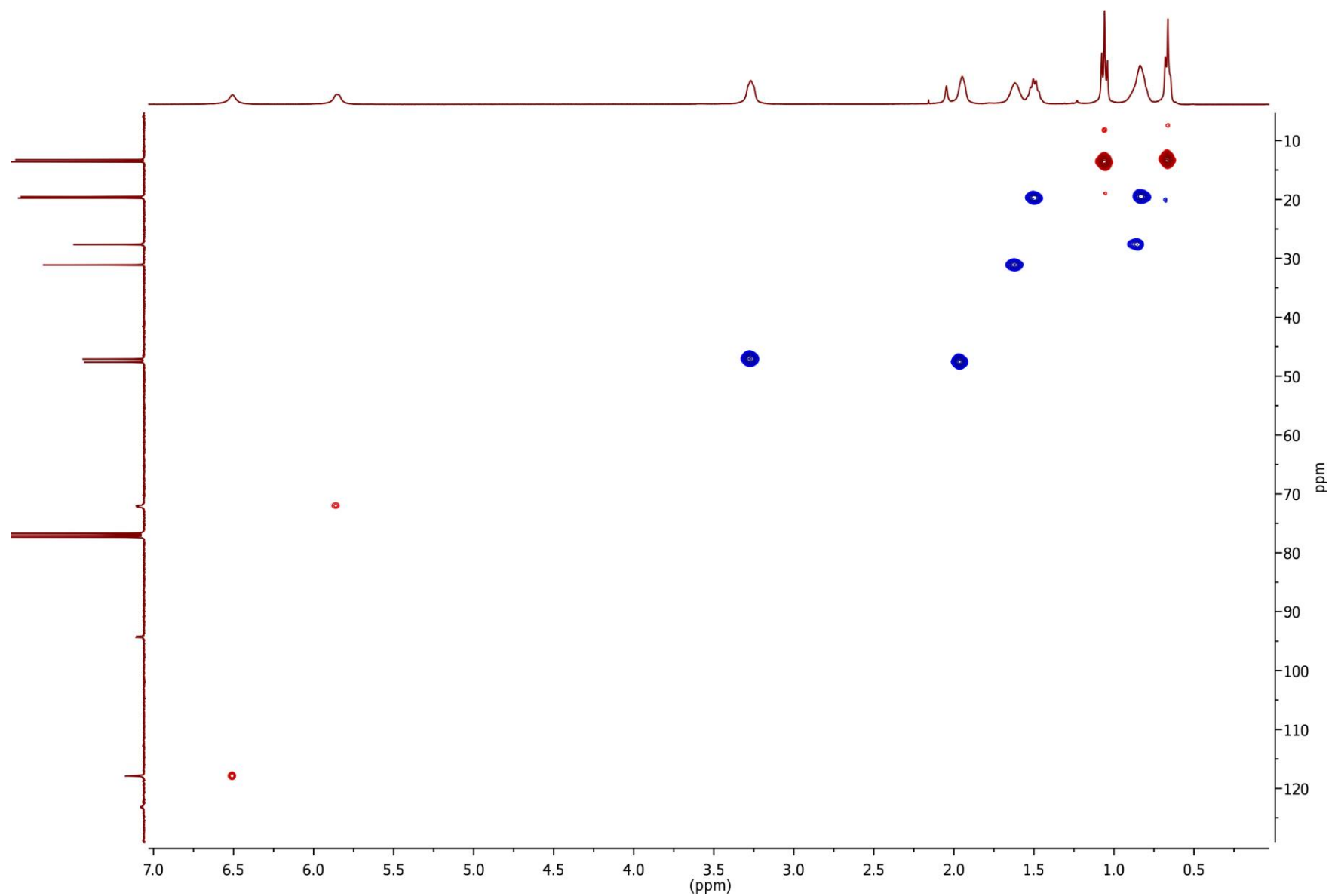


Figure S51. $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum in CDCl_3 at 25°C

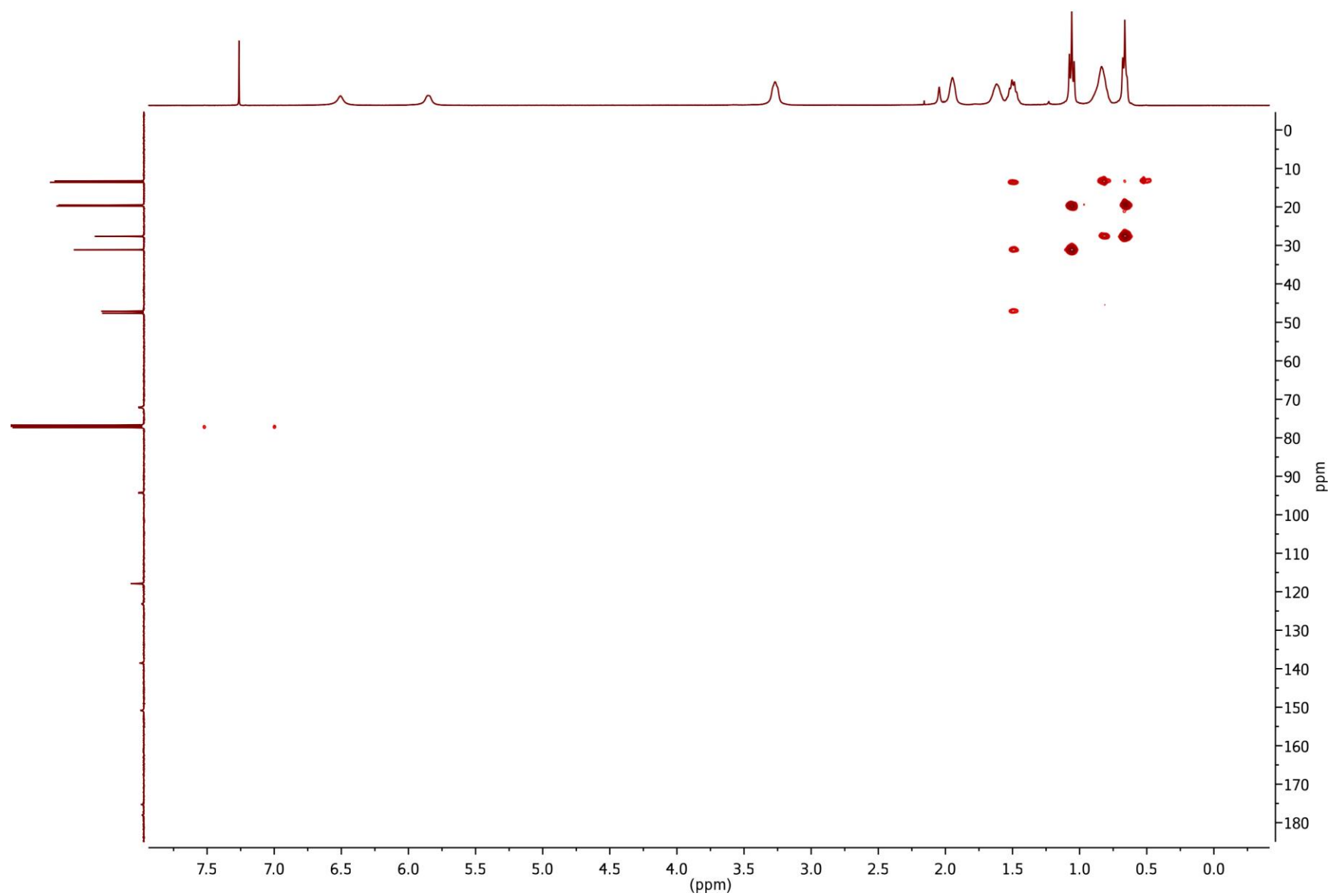


Figure S52. $^1\text{H}/^{13}\text{C}$ HMBC NMR spectrum in CDCl_3 at 25°C

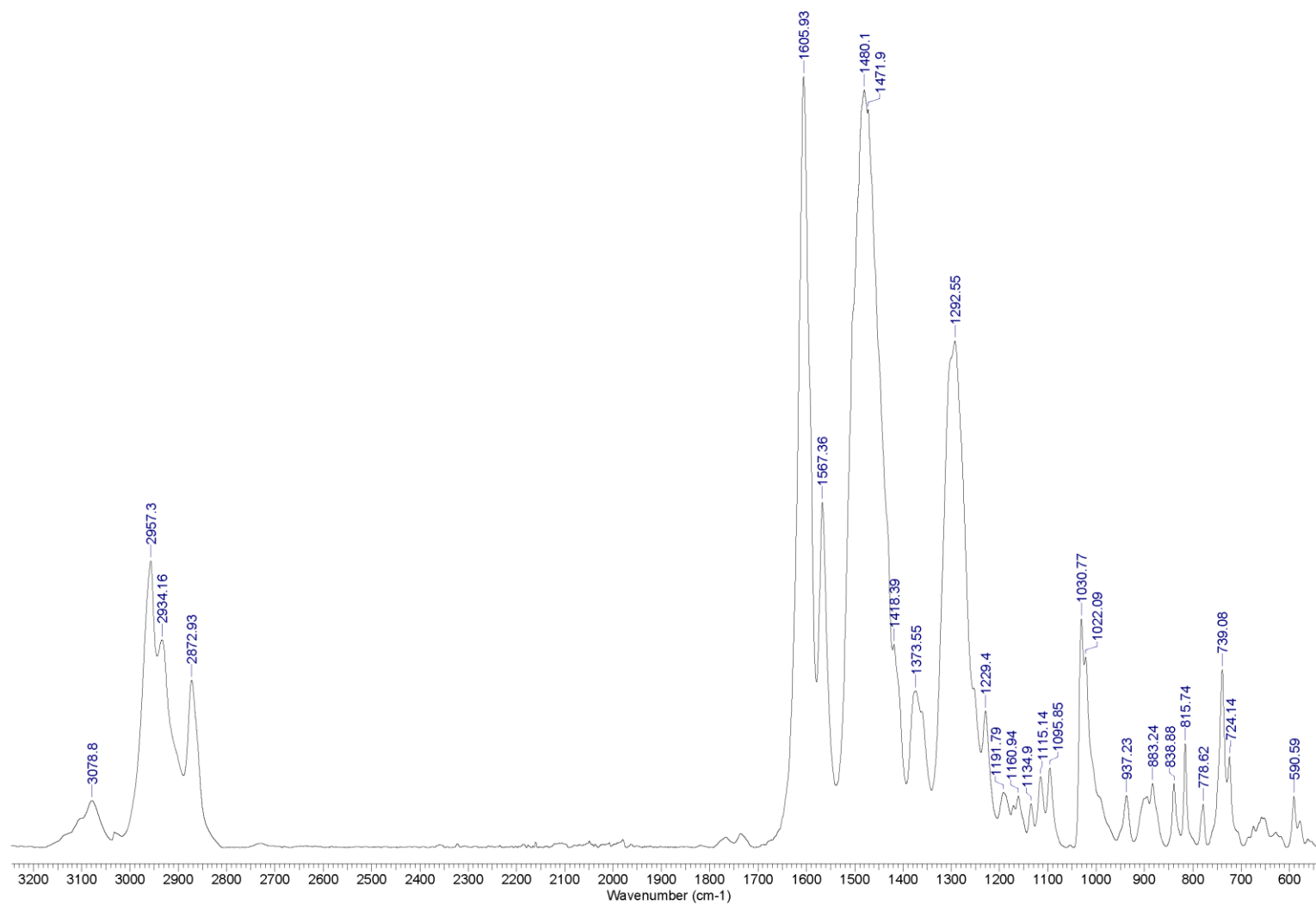


Figure S53. Solid-state IR spectrum at 25°C

Complex 7a*Lu(NO₃)₃

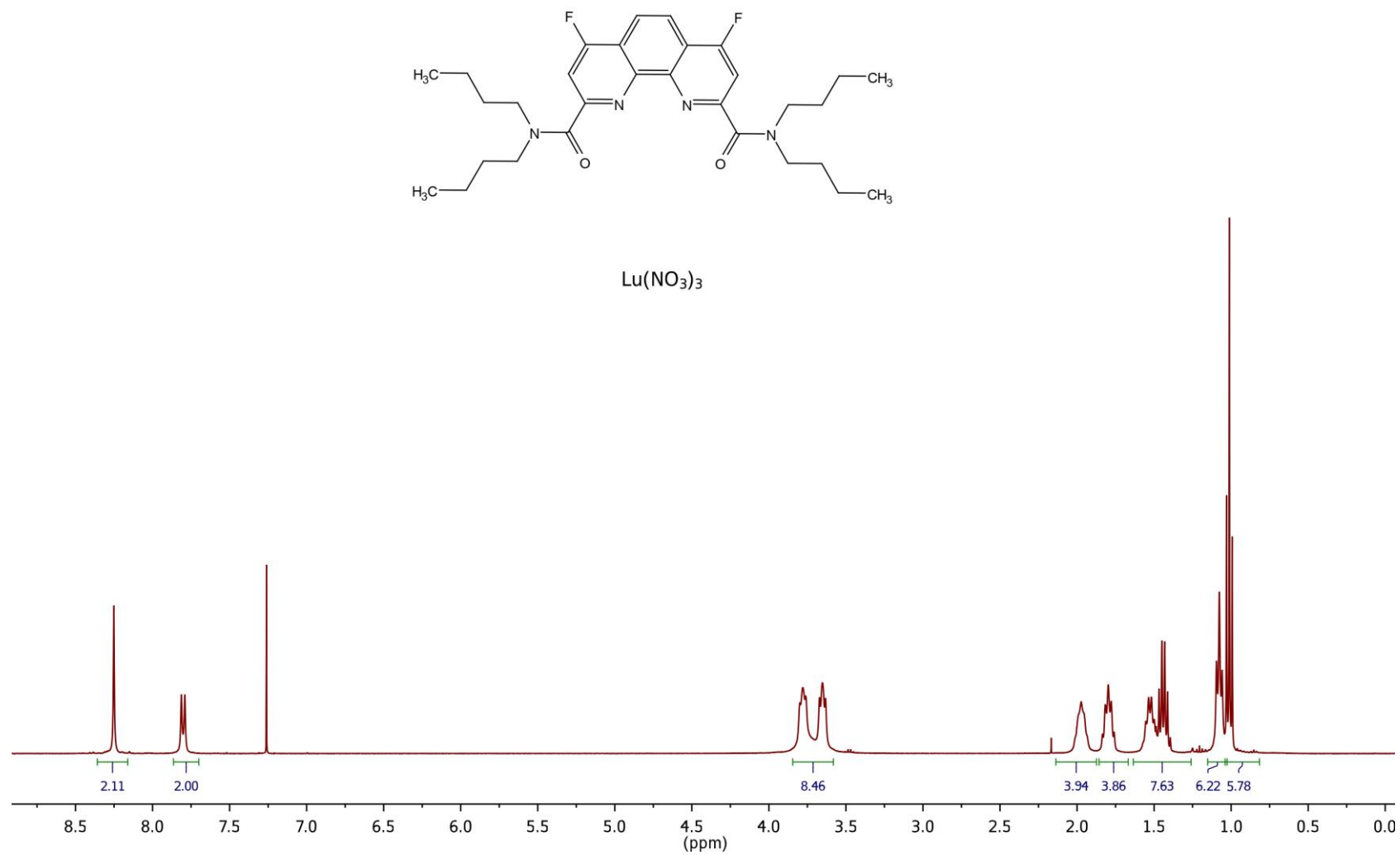


Figure S54. ¹H NMR spectrum in CDCl₃ at 25°C

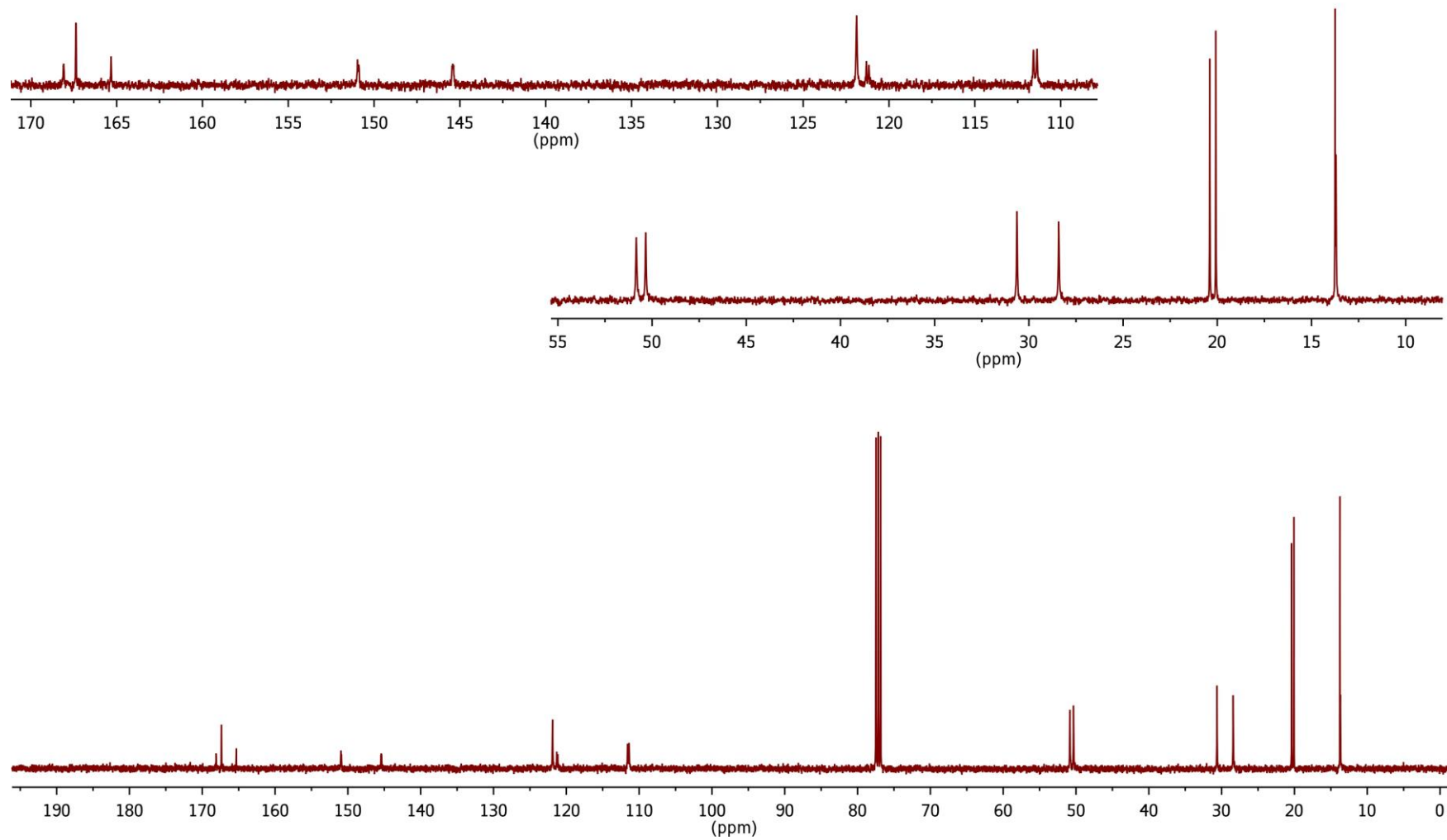


Figure S55. ^{13}C NMR spectrum in CDCl_3 at 25°C

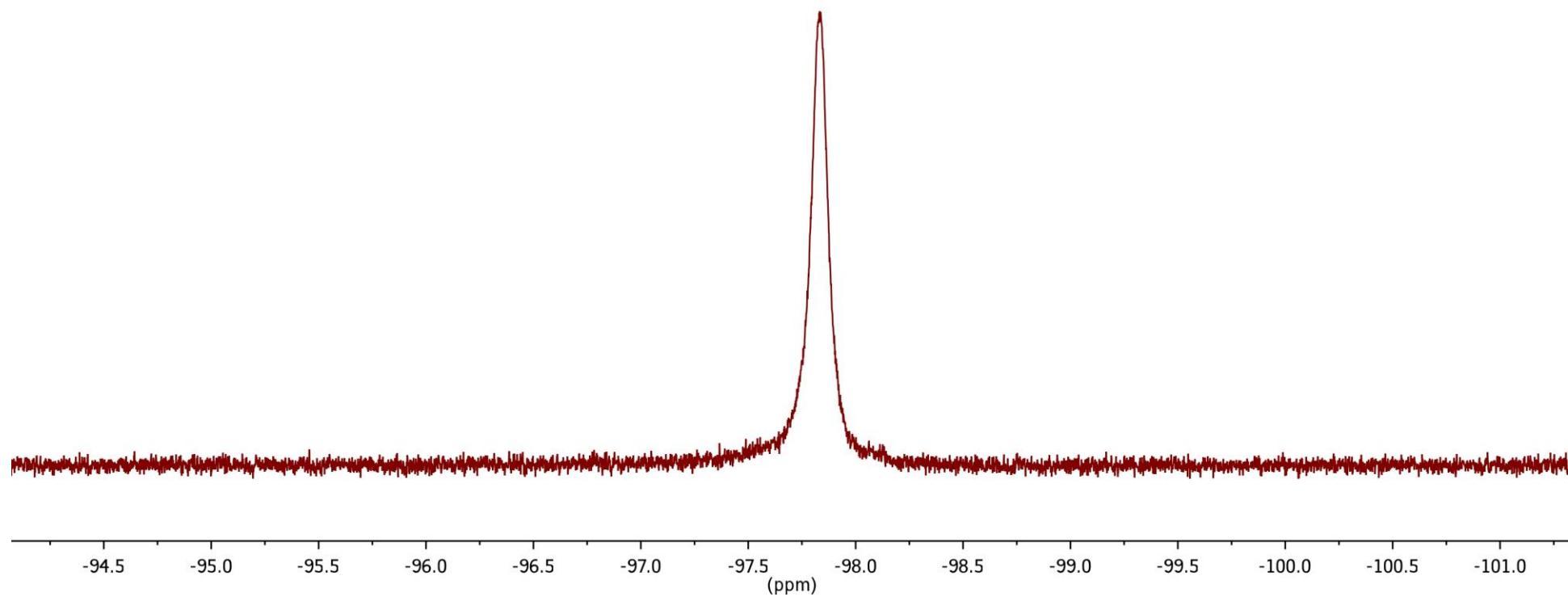


Figure S56. ^{19}F NMR spectrum in CDCl_3 at 25°C

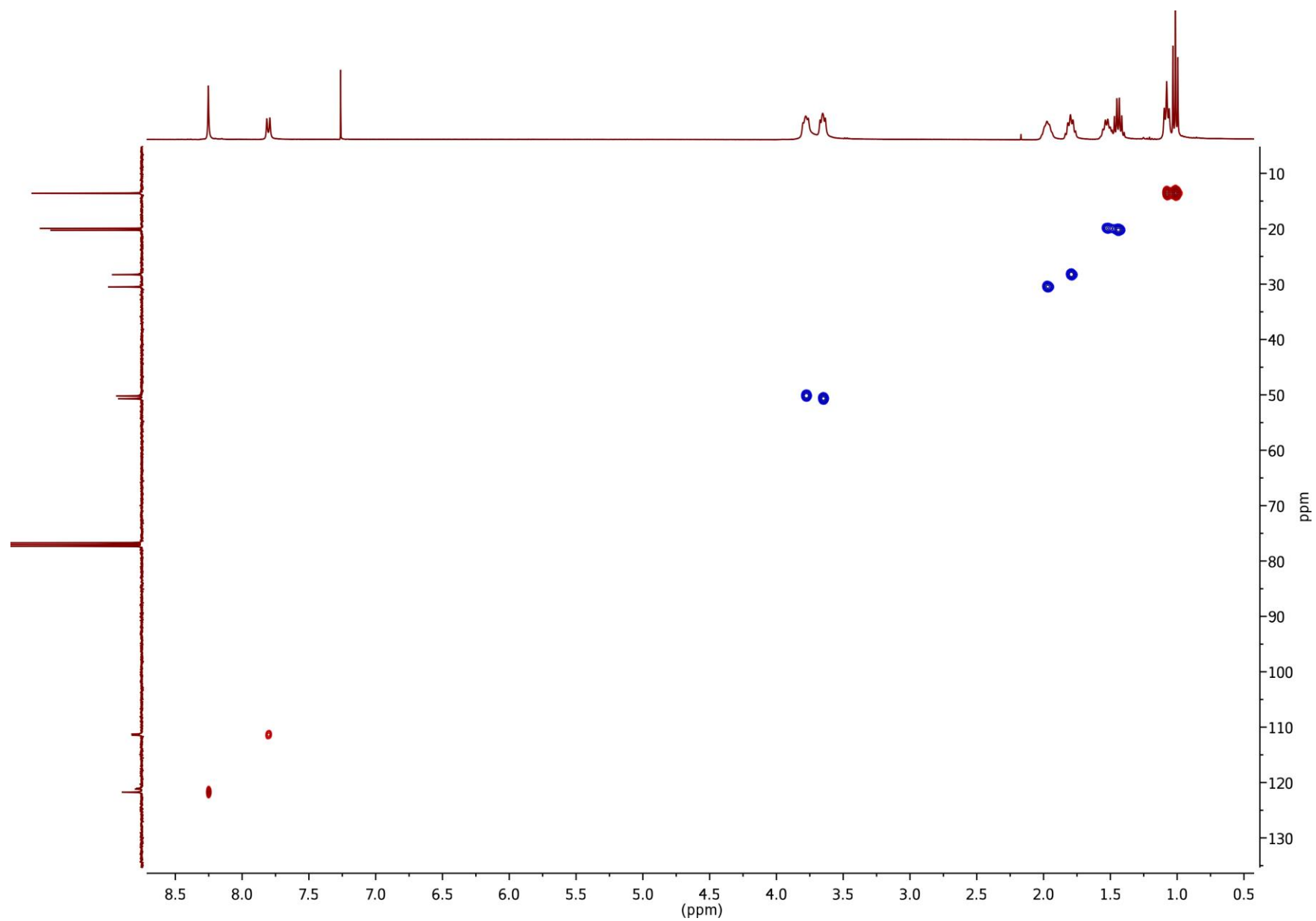


Figure S57. $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum in CDCl_3 at 25°C

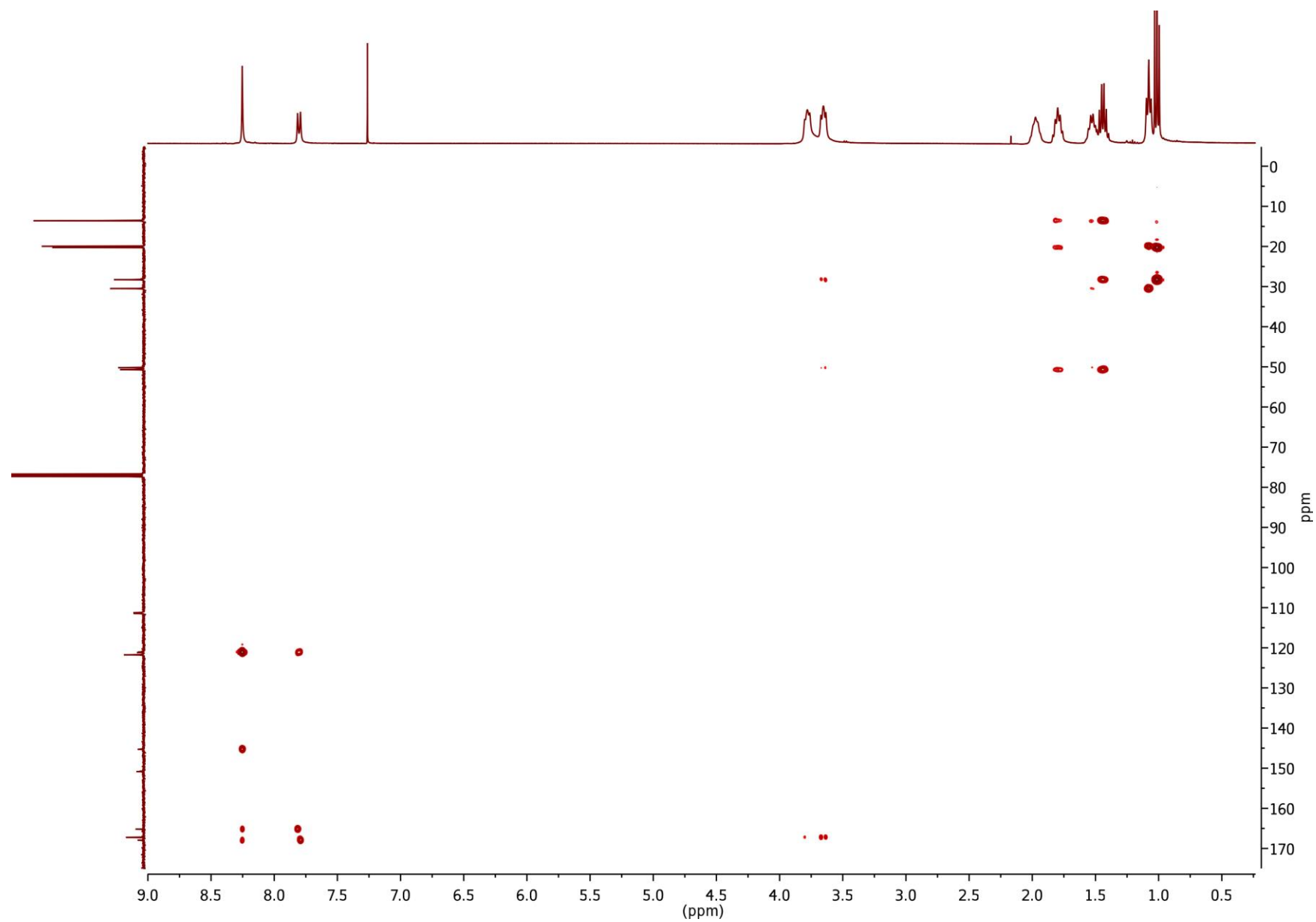


Figure S58. $^1\text{H}/^{13}\text{C}$ HMBC NMR spectrum in CDCl_3 at 25°C

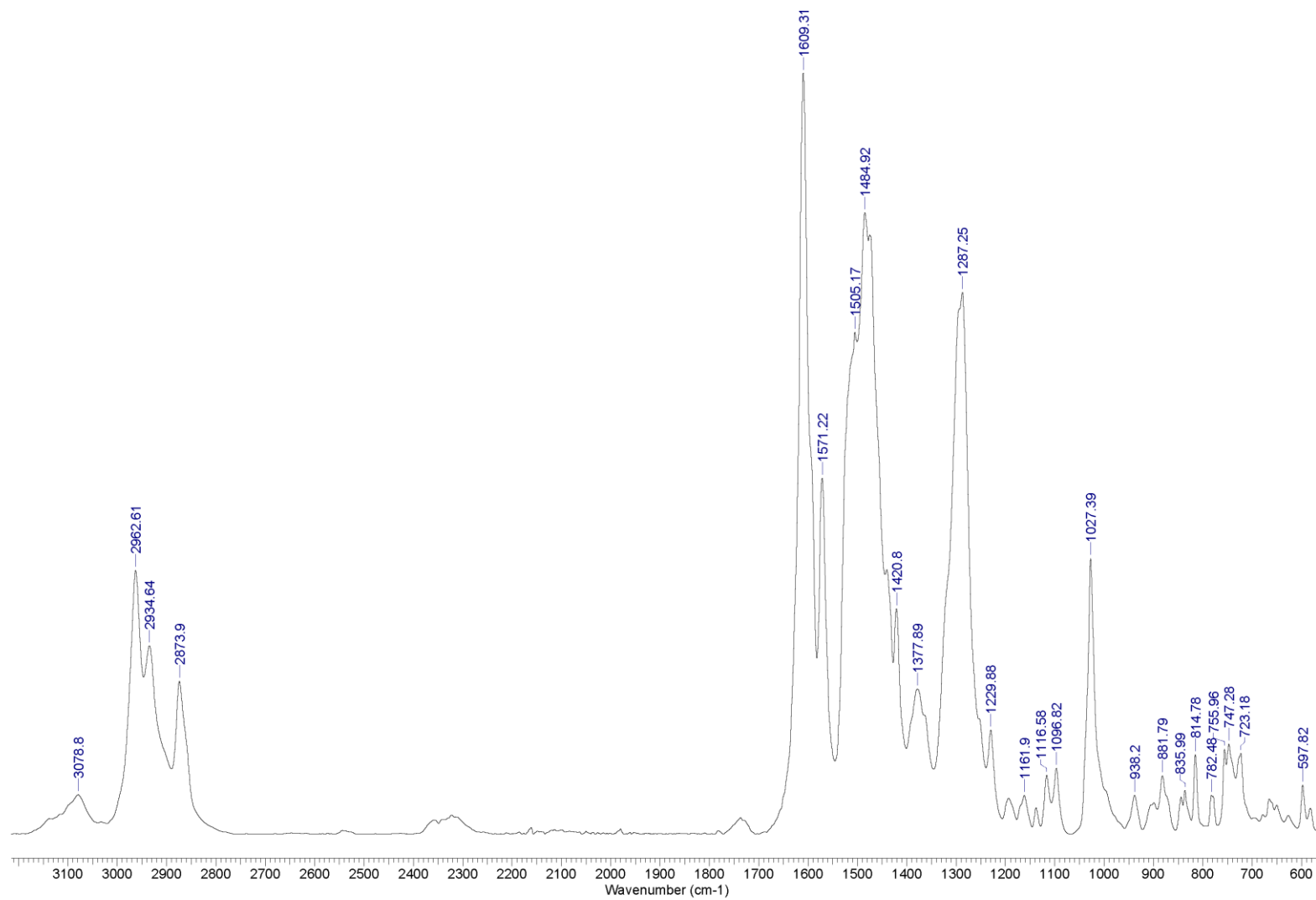


Figure S59. Solid-state IR spectrum at 25°C

2. X-ray analysis data

Table S1. Crystallographic data for **7a** and **7c**, **7a•La(NO₃)₃**, **7a•Nd(NO₃)₃** and **7a•Eu(NO₃)₃**,

	7a	7c	7a•La(NO₃)₃	7a•Nd(NO₃)₃	7a•Eu(NO₃)₃
Empirical formula	C ₃₀ H ₄₀ F ₂ N ₄ O	C ₃₈ H ₄₀ F ₂ N ₄ O ₂	C ₃₄ H ₄₆ F ₂ LaN ₉ O ₁₁	C ₃₄ H ₄₆ F ₂ NdN ₉ O ₁₁	C ₃₄ H ₄₆ F ₂ EuN ₉ O ₁₁
Formula weight	526.66	622.74	933.71	939.04	946.76
Temperature (K)	110	100	100	110	110
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a (Å)	8.6883(10)	11.261(6)	9.1881(8)	9.1881(8)	9.1770(9)
b (Å)	9.1327(11)	13.610(7)	25.461(2)	25.461(2)	25.434(3)
c (Å)	17.932(2)	21.358(10)	17.639(2)	17.639(2)	17.5925(16)
α (°)	88.166(4)	90	90	90	90
β (°)	77.855(4)	95.572(15)	92.330(3)	92.330(3)	92.357(3)
γ (°)	81.117(4)	90	90	90	90
Volume (Å ³)	1374.3(3)	3258(3)	4122.9(7)	4122.9(7)	4102.7(7)
Z(Z')	2(1)	4(1)	4(1)	4(1)	4(1)
d _{calc} , g·cm ⁻³	1.273	1.270	1.504	1.513	1.533
μ, cm ⁻¹	0.9	0.87	11.12	13.35	16.04
F(000)	564	1320	1904	1916	1928
2θ _{max} , °	58	52	58	58	58
Completeness to Θ _{max}	0.999	0.999	0.999	0.999	0.998
Refl. collected	20747	19620	37287	40657	39319
Refl. unique (R _{int})	7303	6390	10960	10900	10887
Refl. with I > 2σ(I)	5114	2325	7843	8071	8747
Parameters	347	430	530	520	520
R ₁ with I>2σ(I)	0.0501	0.0843	0.0630	0.0430	0.0351
wR ₂ (all data)	0.1235	0.2259	0.1672	0.0964	0.0855
Goodness-of-fit on F ²	1.053	0.941	1.028	1.021	1.050
Largest difference in peak / hole (e/Å ³)	0.365/-0.288	0.364/-0.286	1.639/-0.993	0.666/-0.575	0.743/-0.693
CCDC	2183813	2183814	2183815	2183816	2183817