

Supporting information

Exploring Three Avenues: Chemo- and Regioselective Transformations of 1,2,4-Triketone Analogs into Pyrazoles and Pyridazinones

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Figure S1. ^1H NMR spectrum of compound **1**.

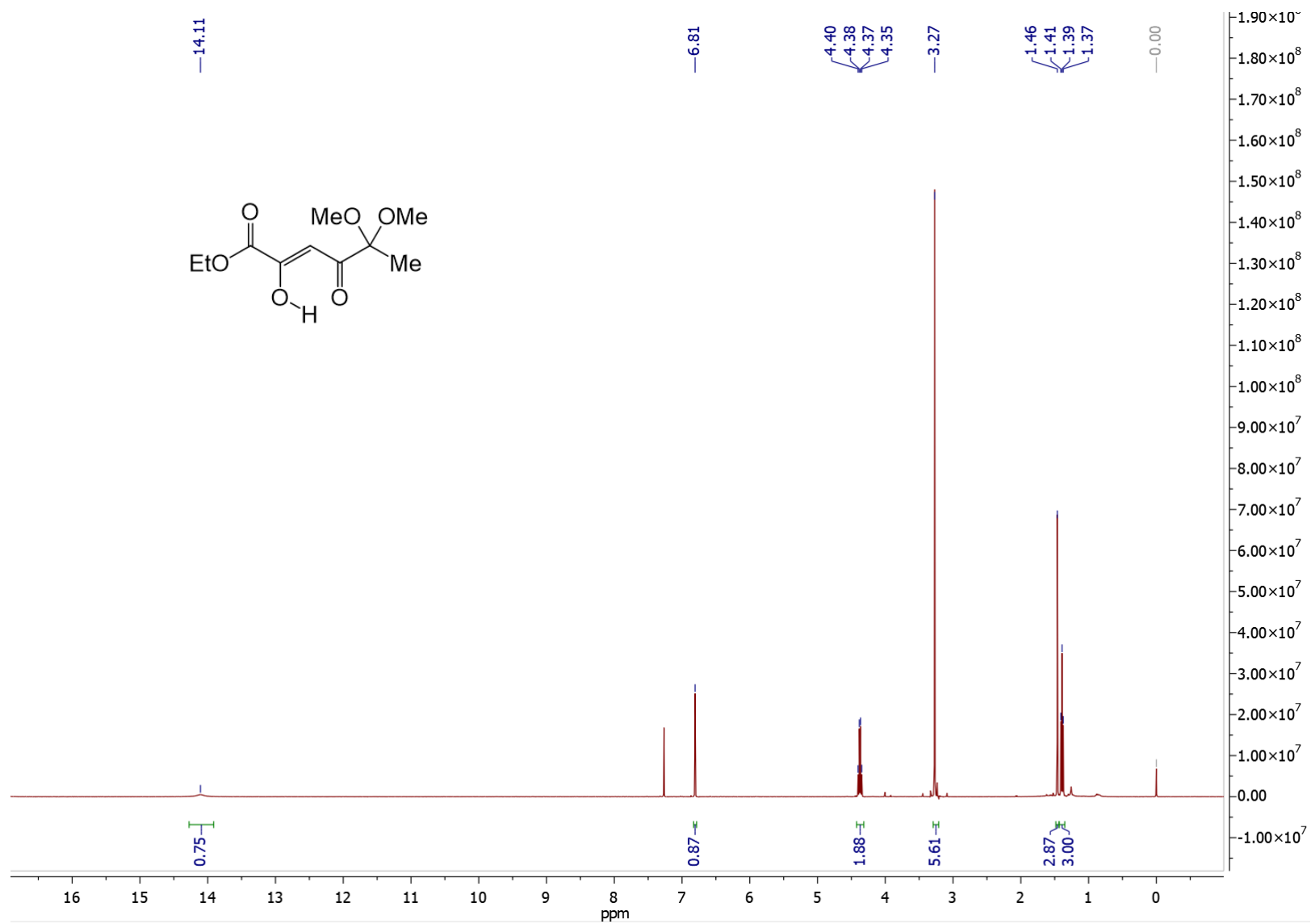


Figure S2. ^{13}C NMR spectrum of compound 1.

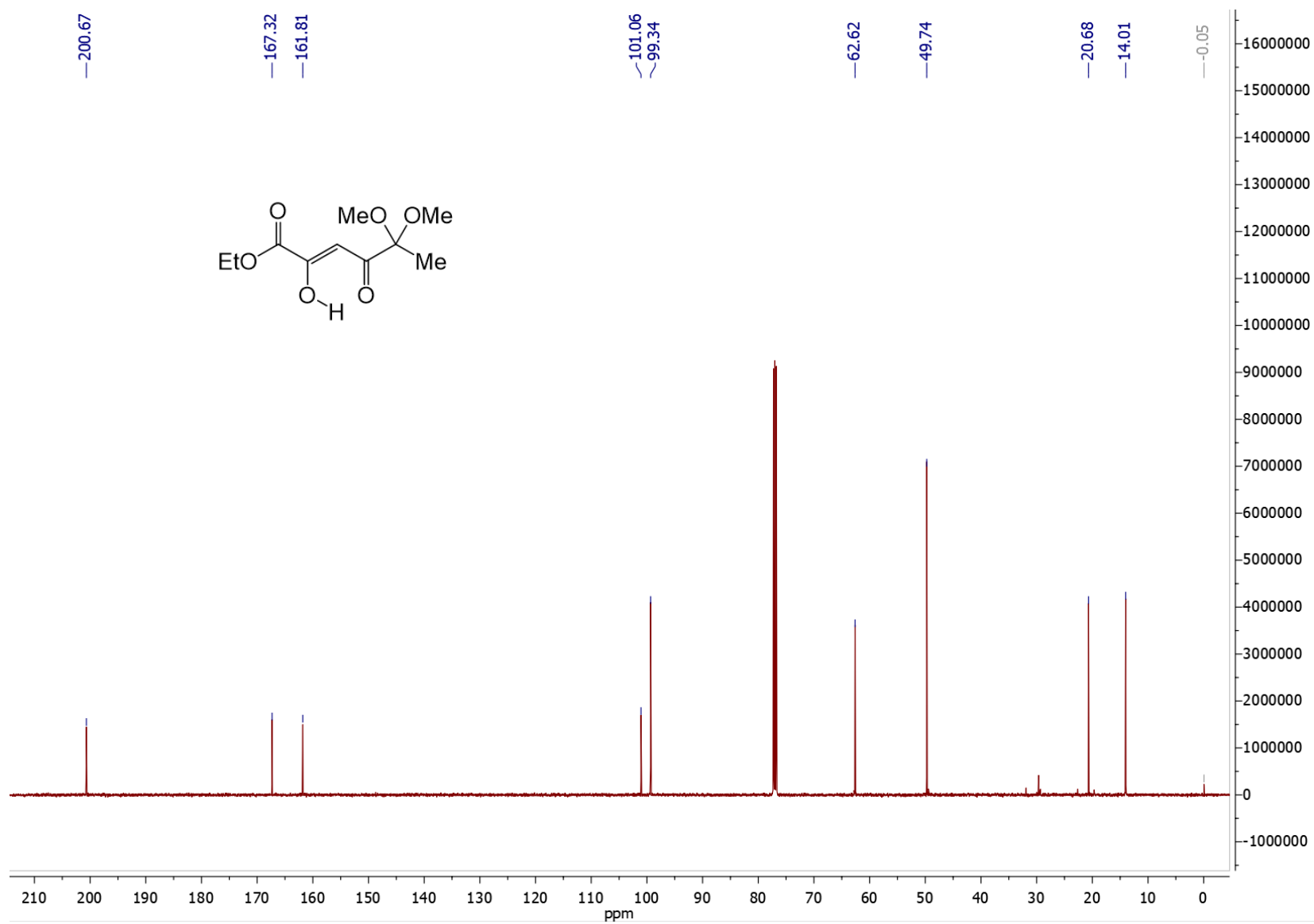


Figure S3. ^1H NMR spectrum of compound **2a**.

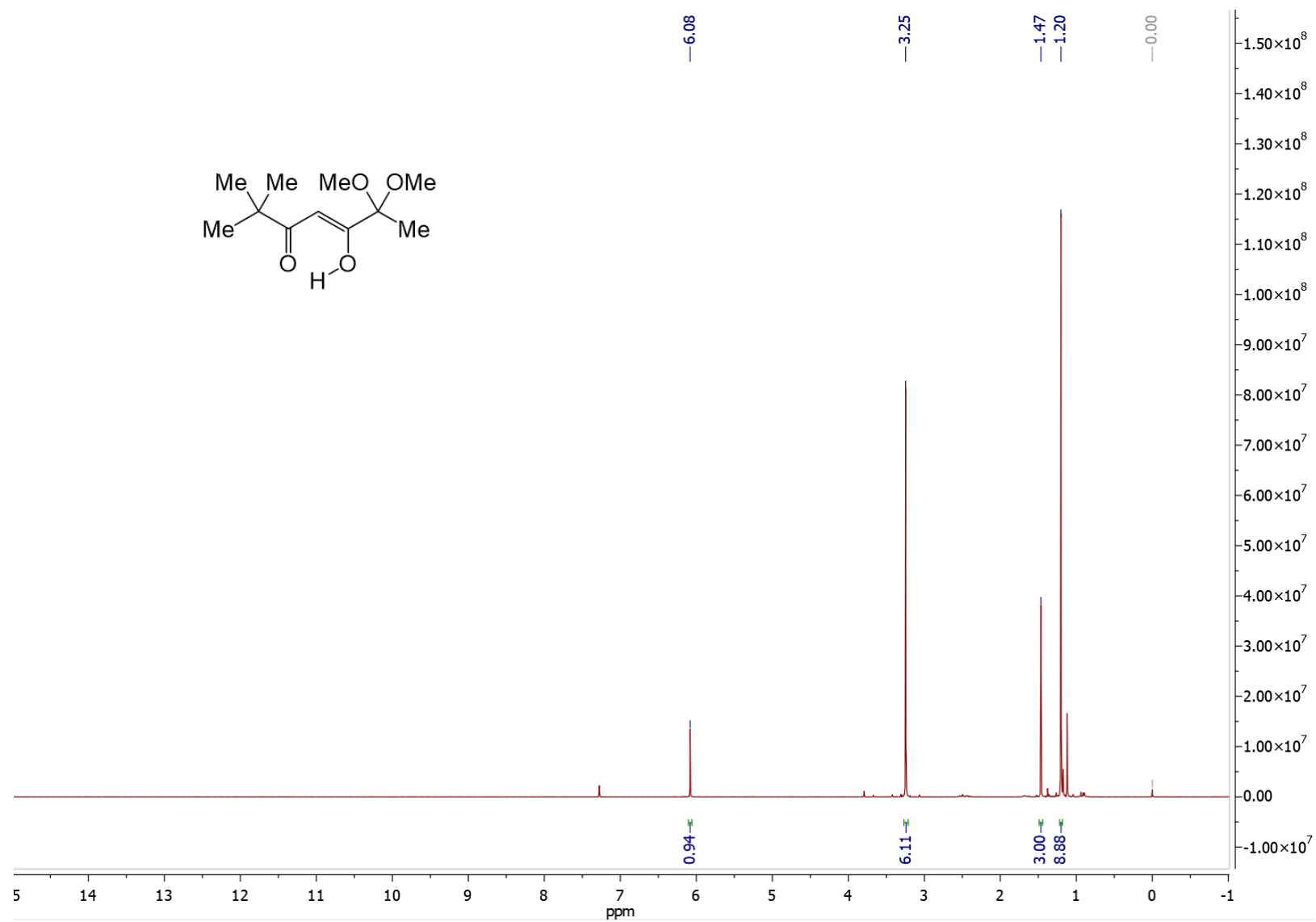


Figure S4. ^{13}C NMR spectrum of compound **2a**.

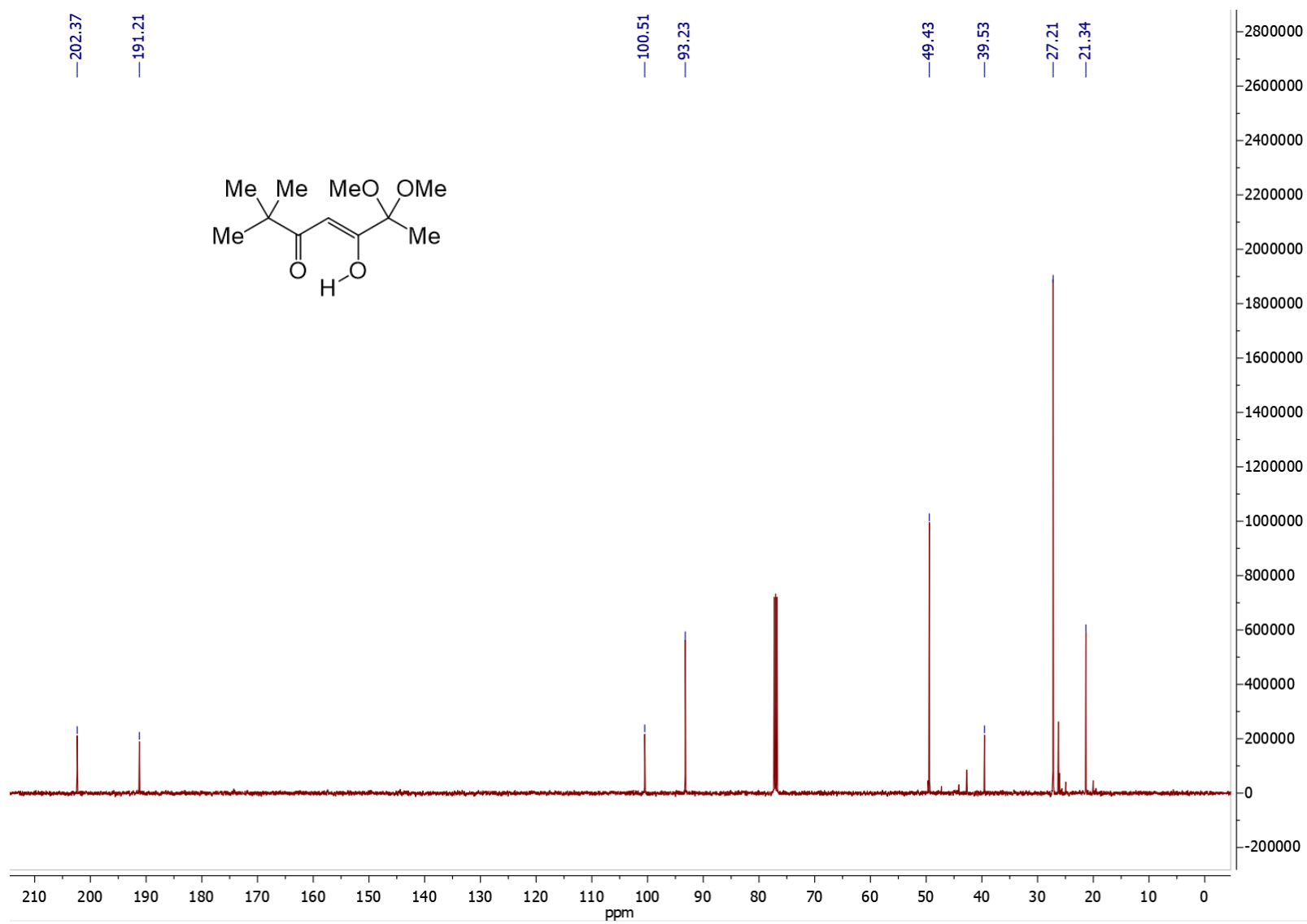


Figure S5. ^1H NMR spectrum of compound **2b**.

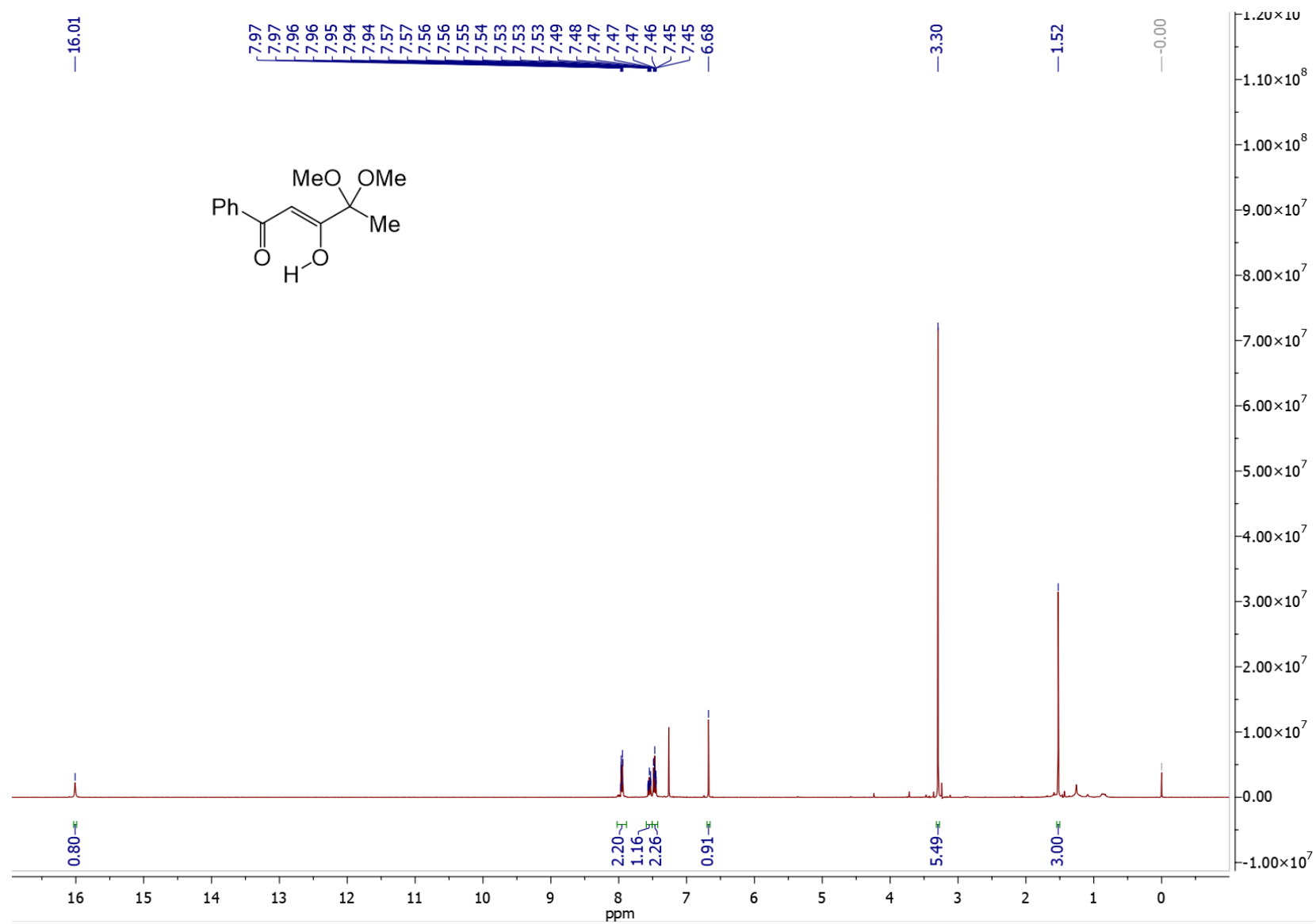


Figure S6. ^{13}C NMR spectrum of compound **2b**.

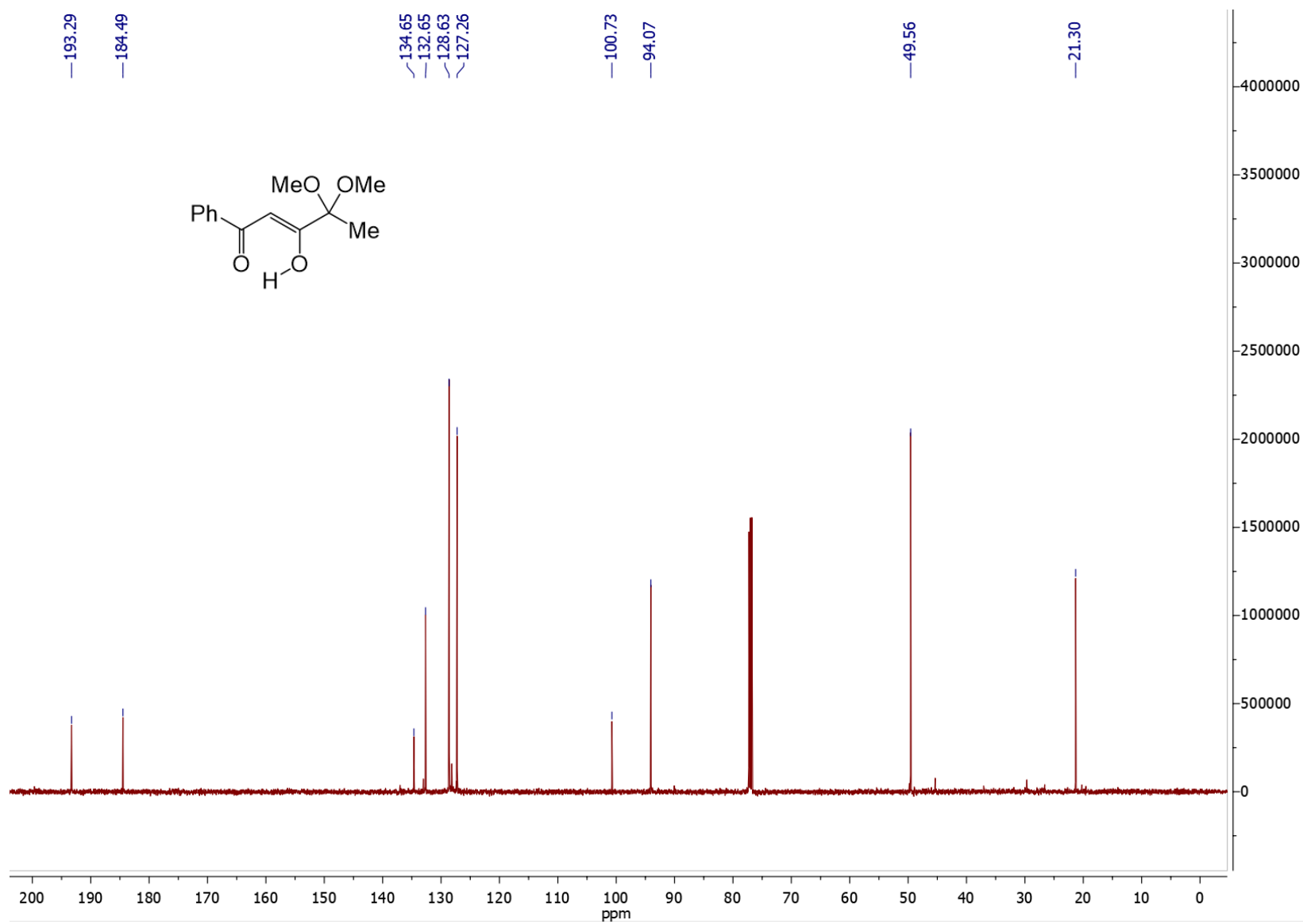


Figure S7. ^1H NMR spectrum of compound **2c**.

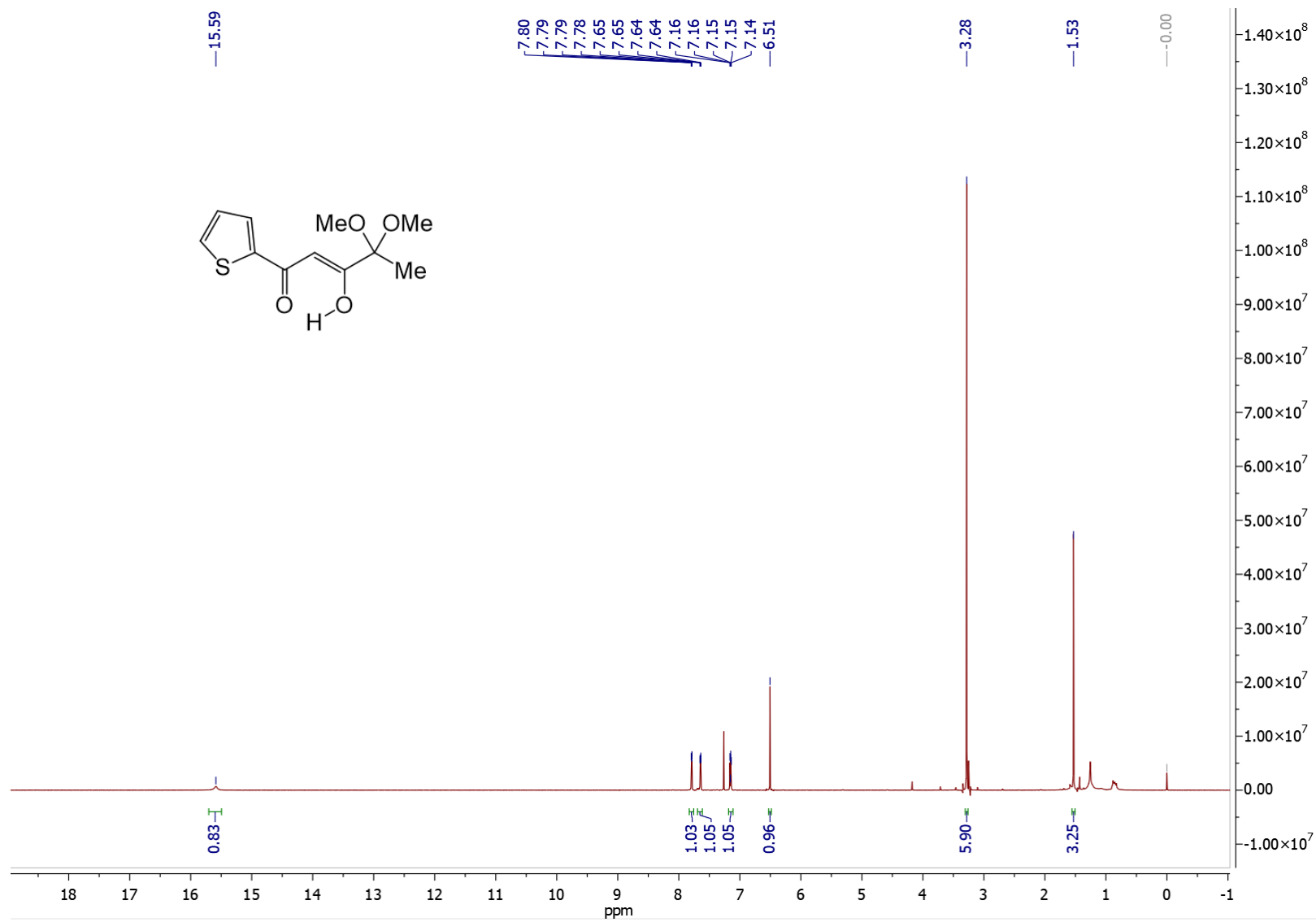


Figure S8. ^{13}C NMR spectrum of compound **2c**.

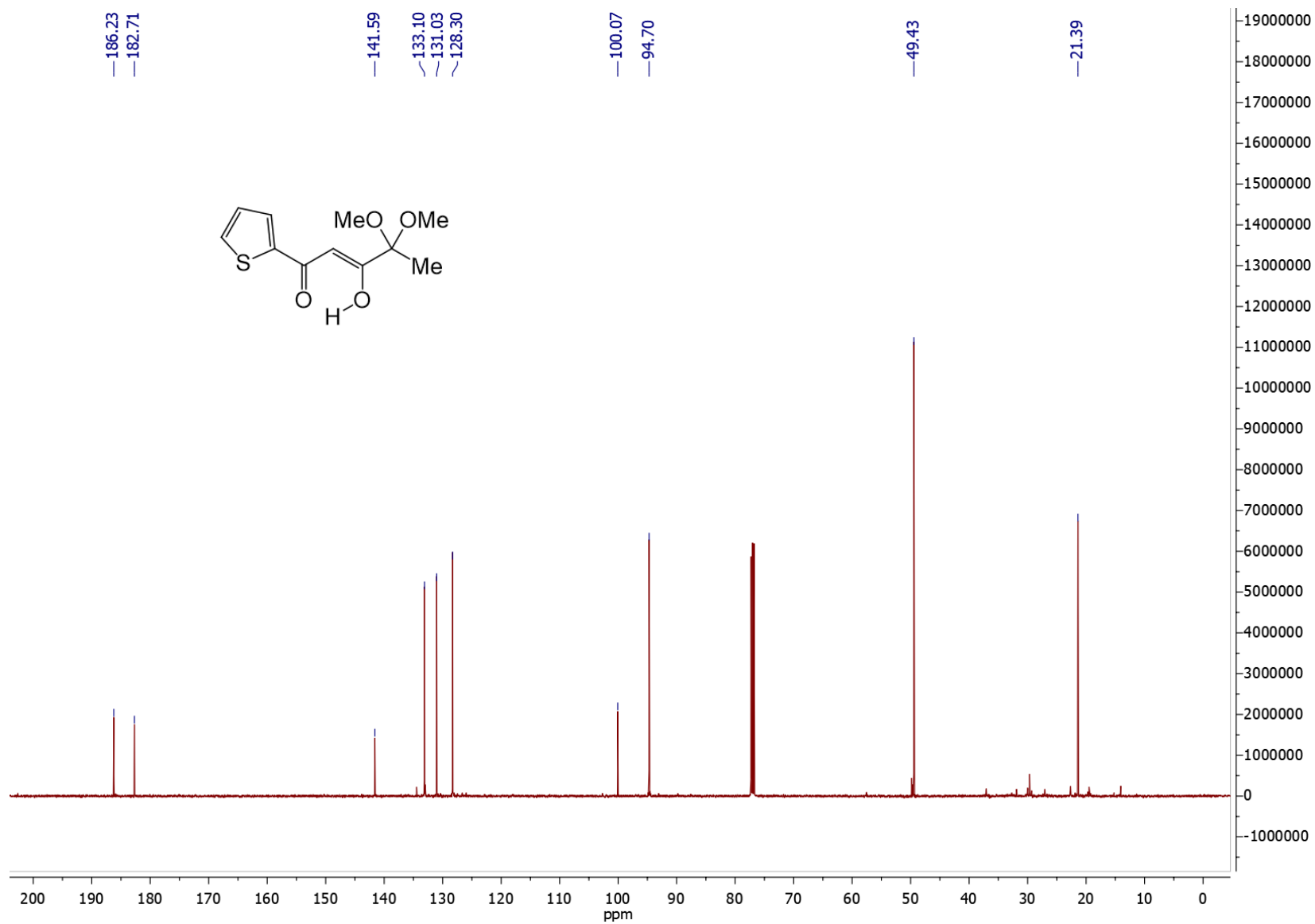


Figure S9. ^1H NMR spectrum of compound **3**.

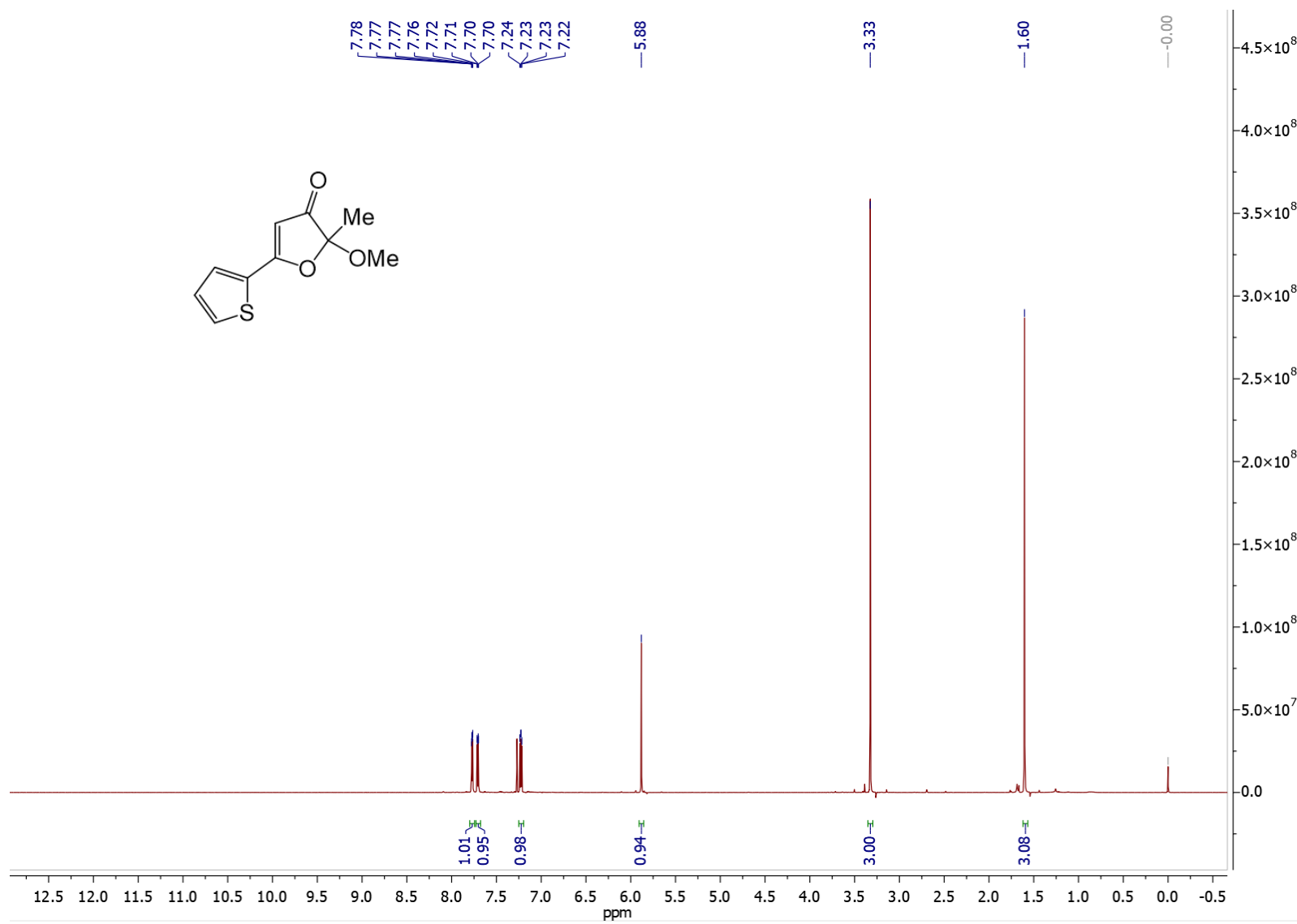


Figure S10. ^{13}C NMR spectrum of compound 3.

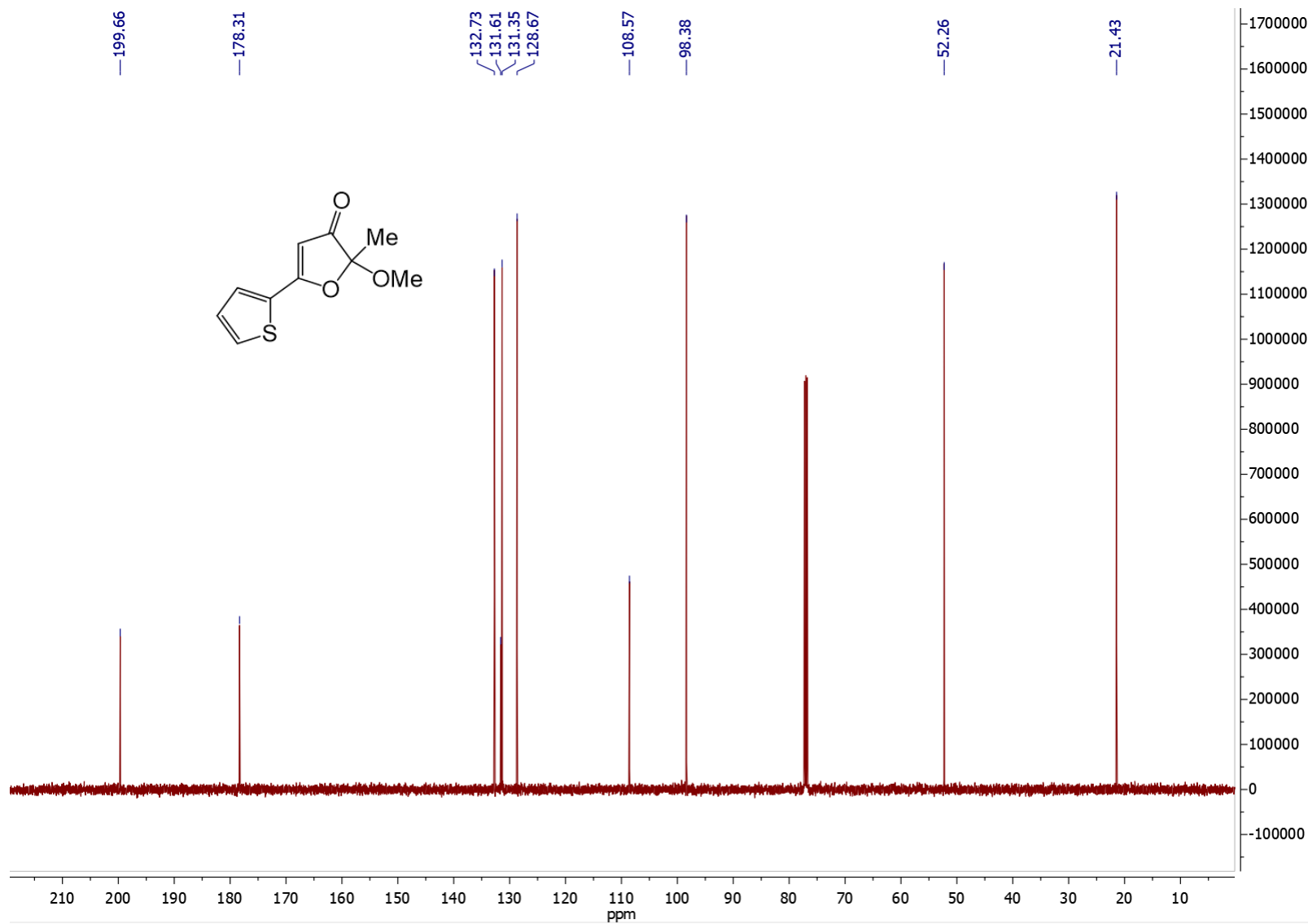


Figure S11. ^1H NMR spectrum of compound **4a**.

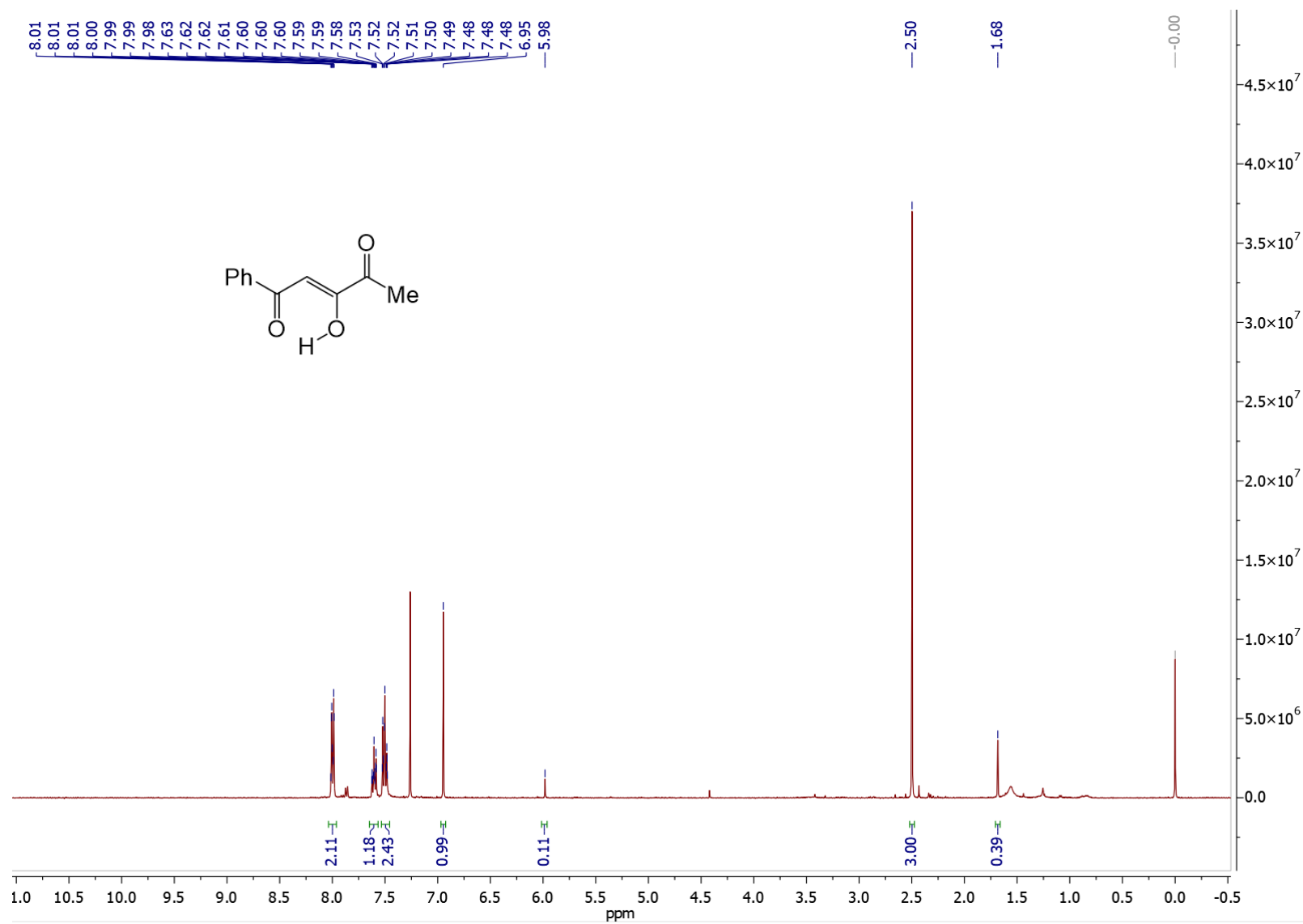


Figure S12. ^{13}C NMR spectrum of compound **4a**.

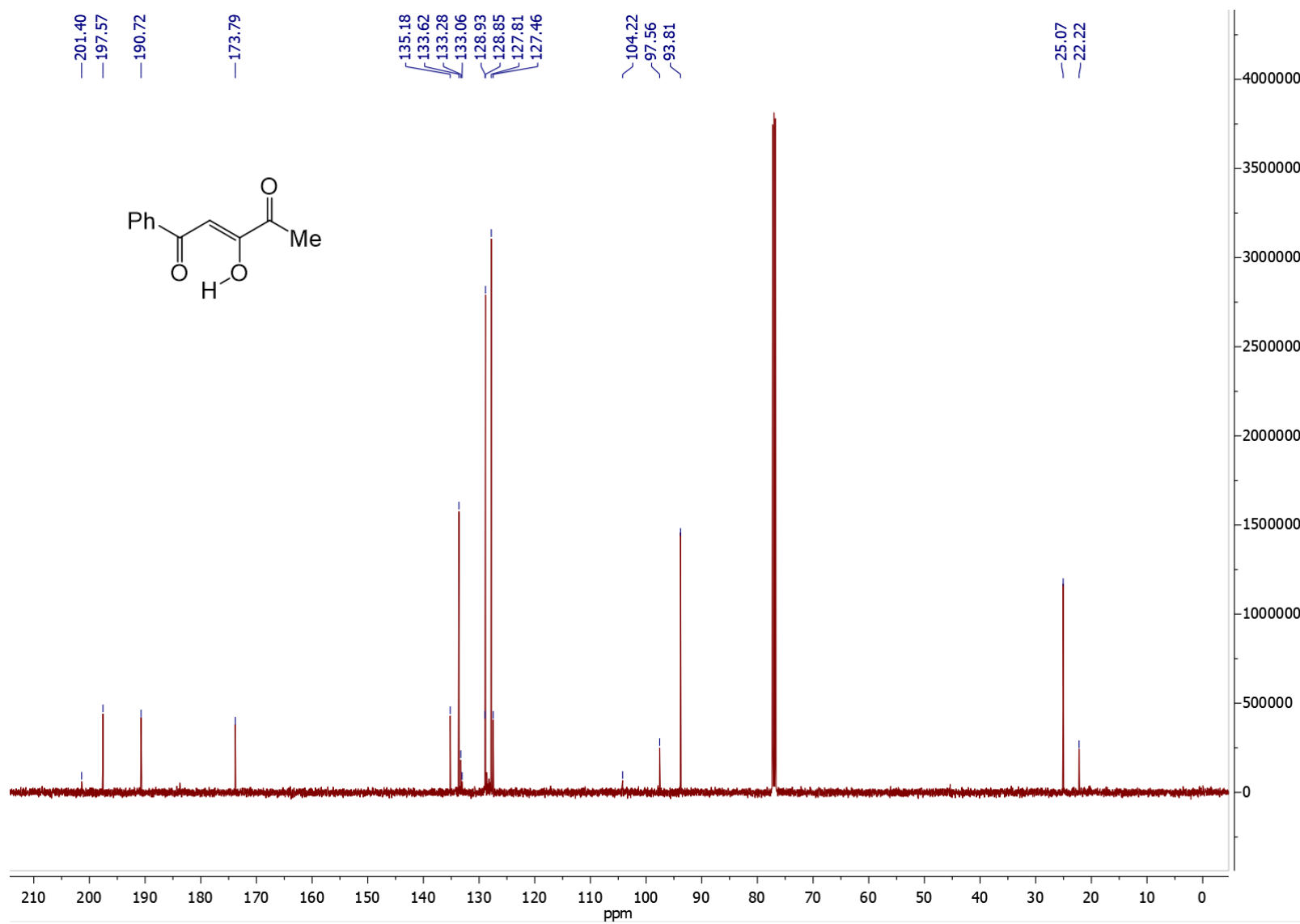


Figure S13. ^1H NMR spectrum of compound **4b**.

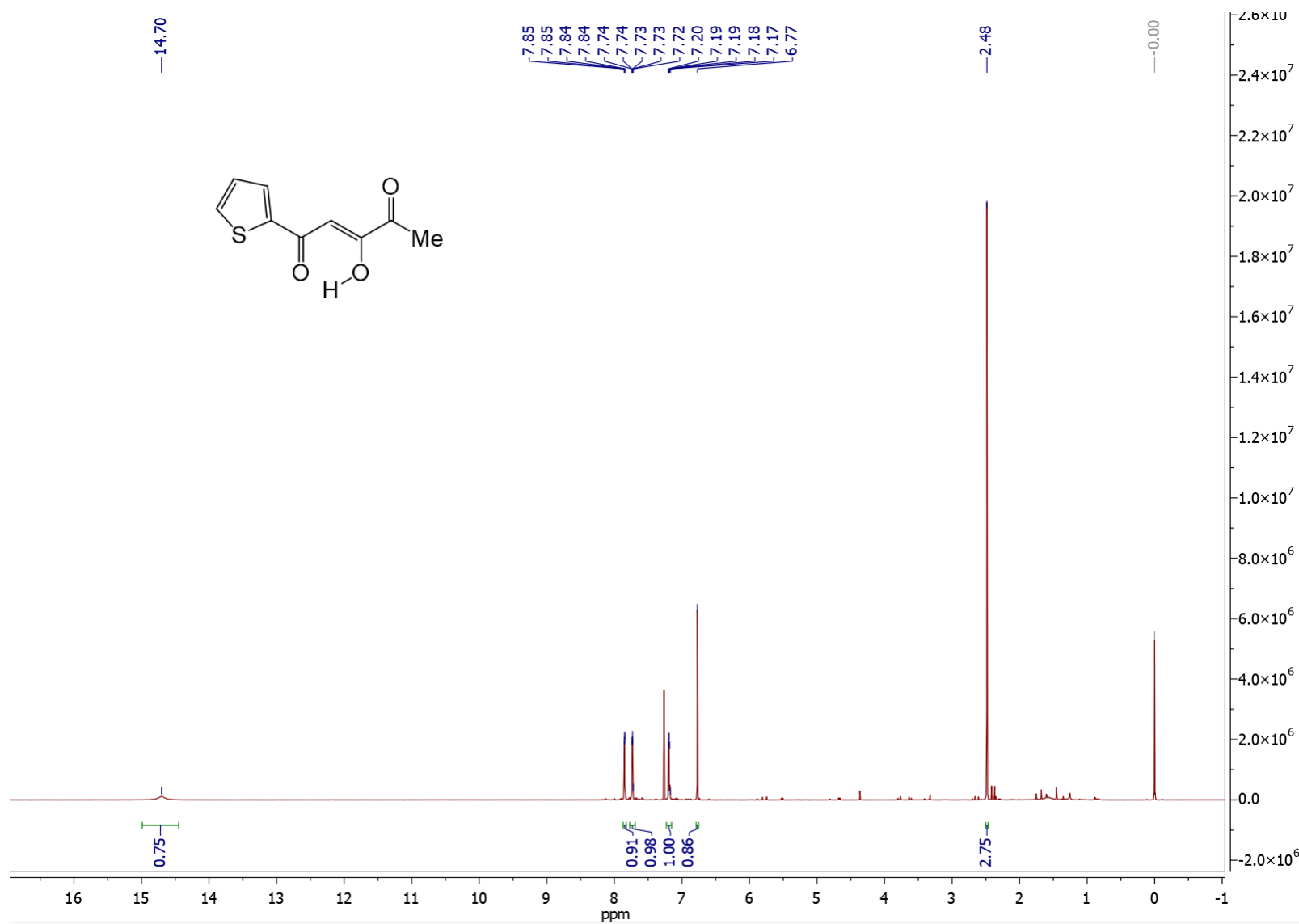


Figure S14. ^{13}C NMR spectrum of compound **4b**.

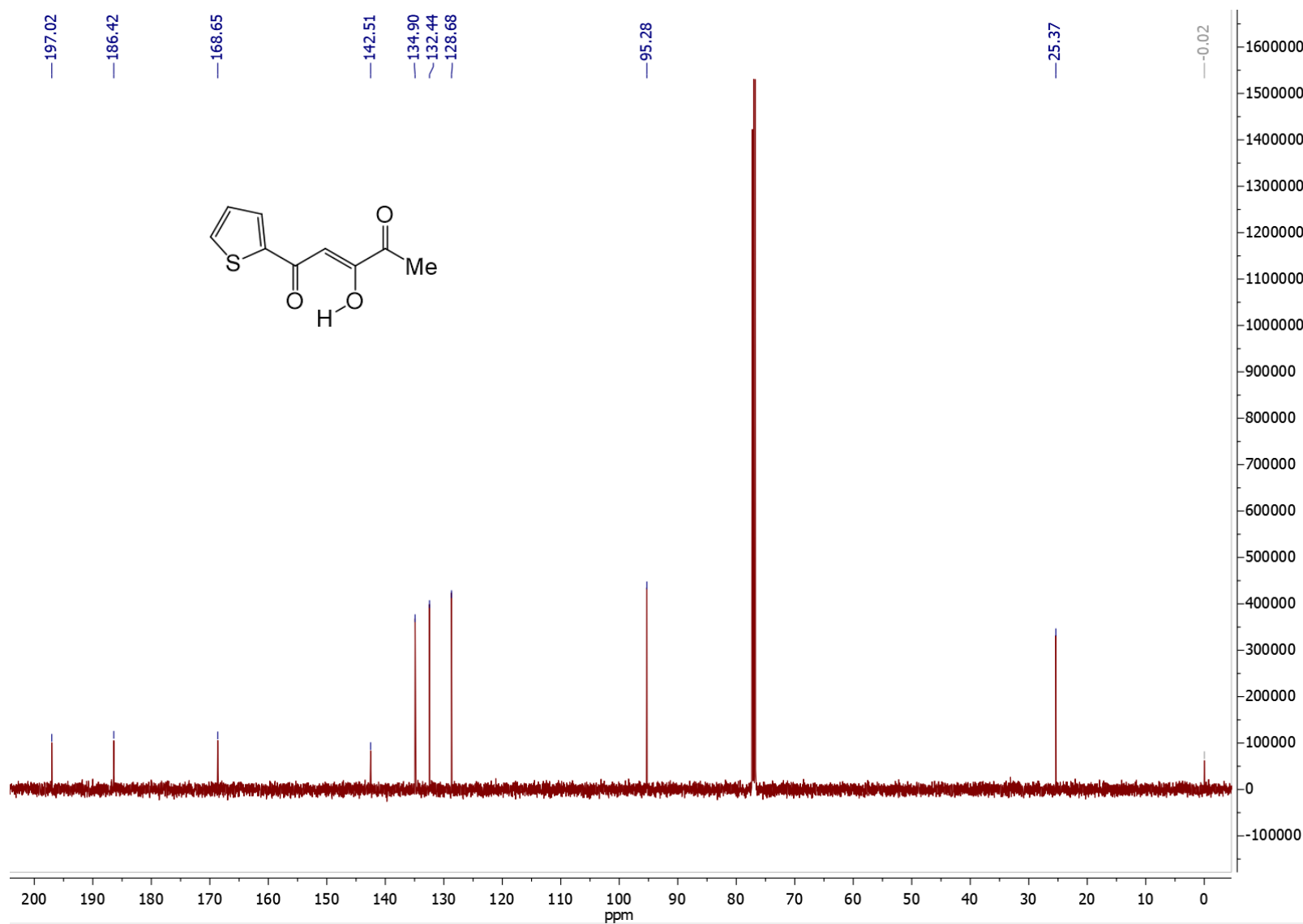


Figure S15. ^1H NMR spectrum of compound **6**.

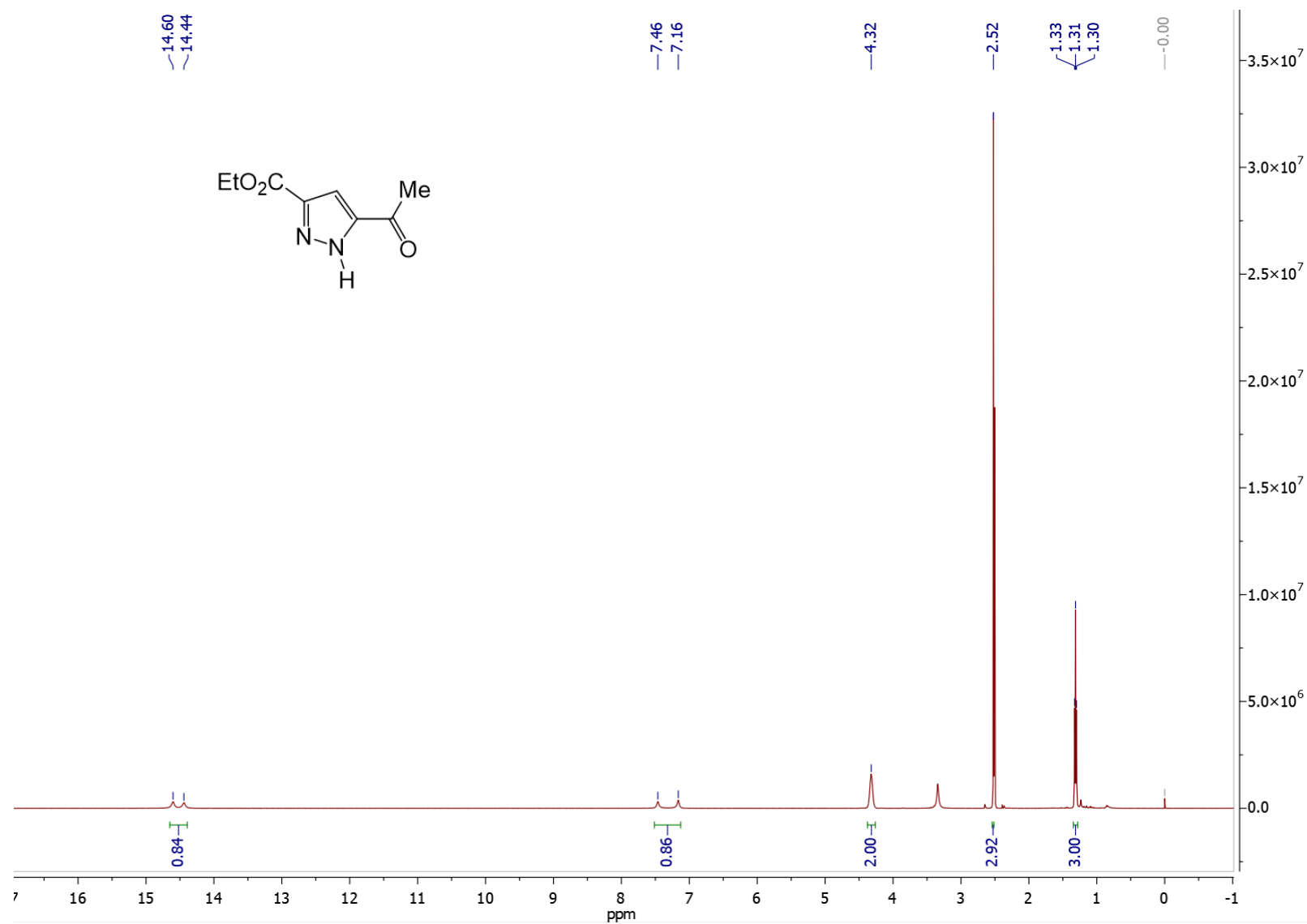


Figure S16. ^{13}C NMR spectrum of compound **6**.

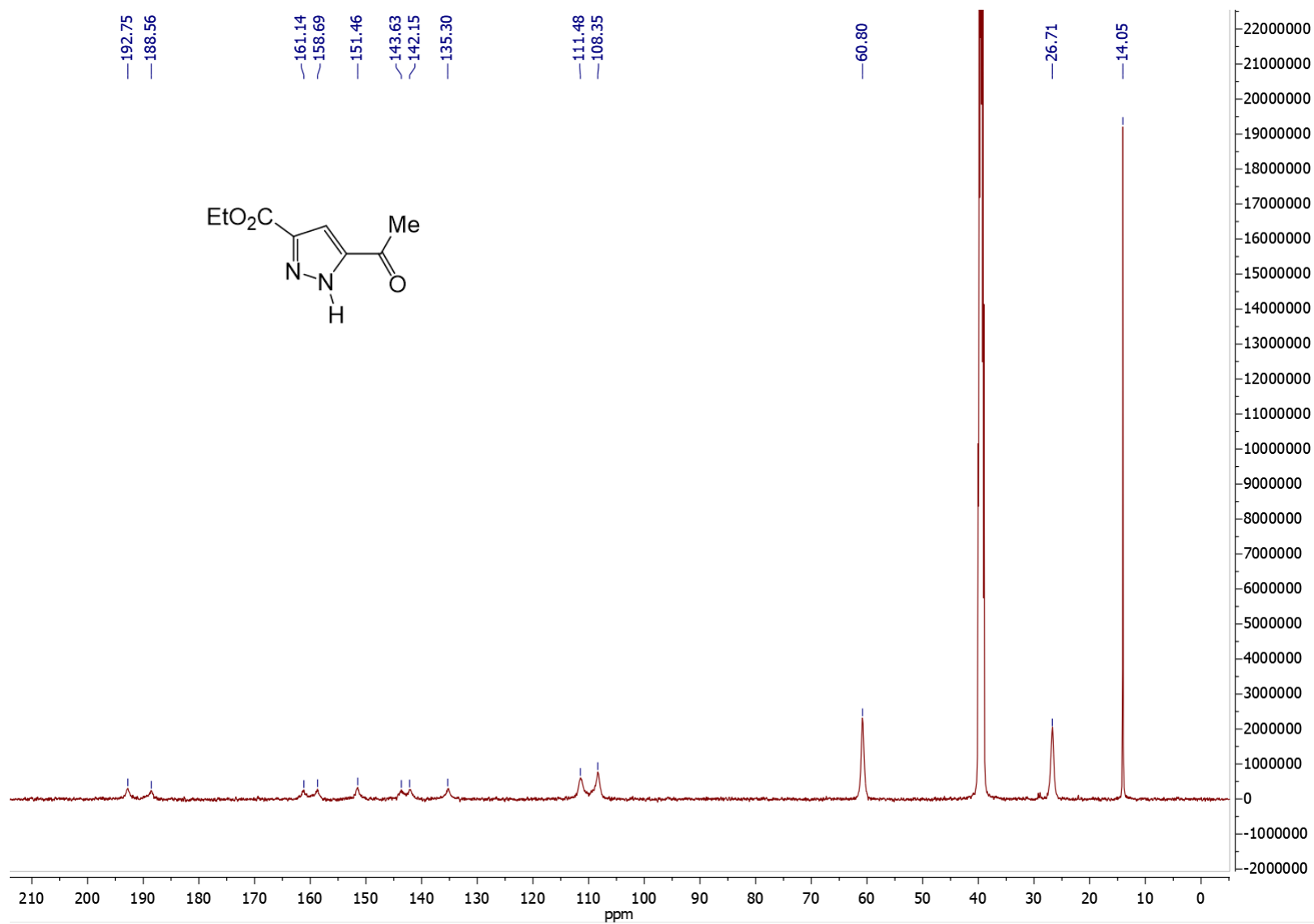


Figure S17. ^1H NMR spectrum of compound **7a**.

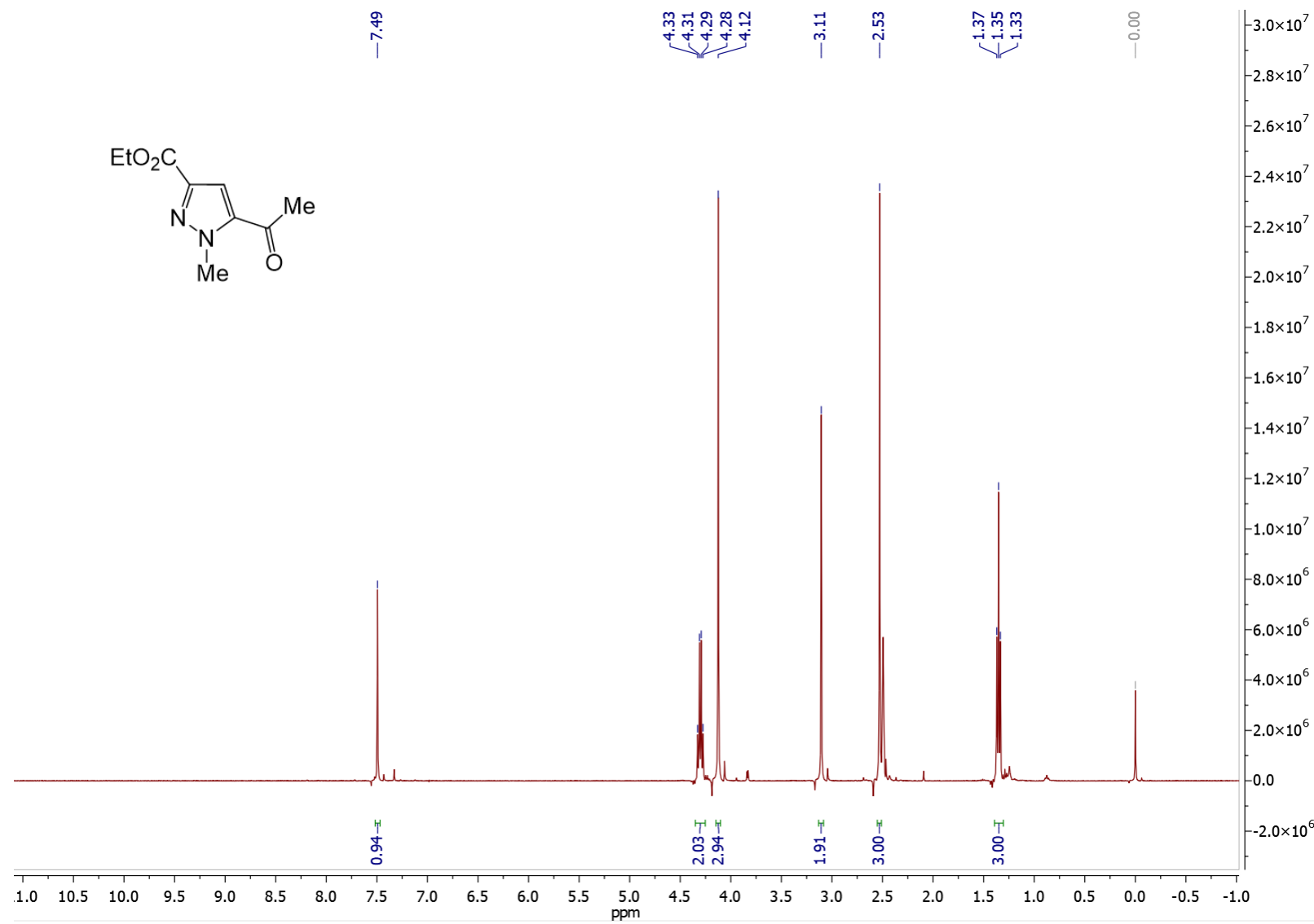


Figure S18. ^{13}C NMR spectrum of compound **7a**.

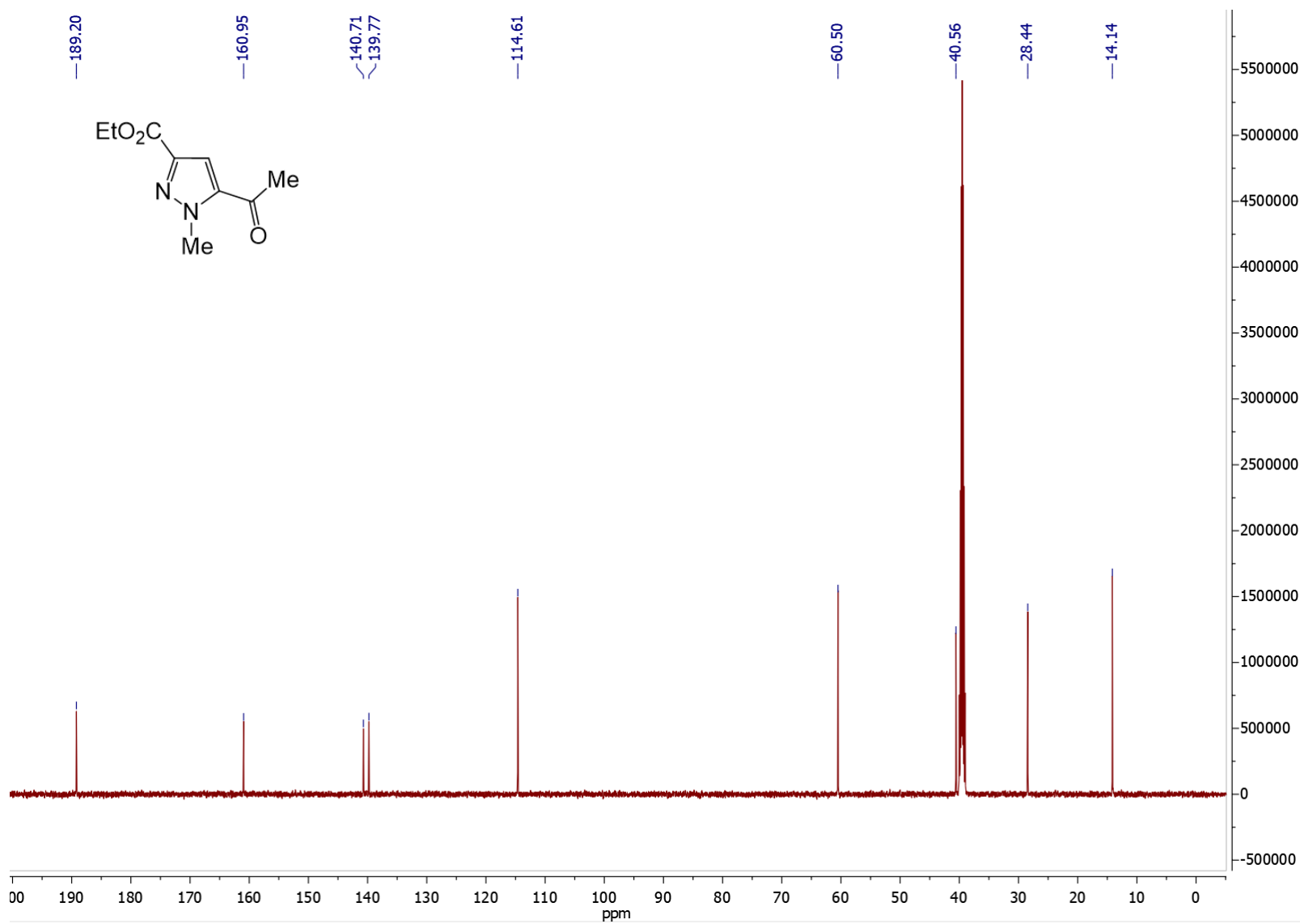


Figure S19. ^1H NMR spectrum of compound **7b**.

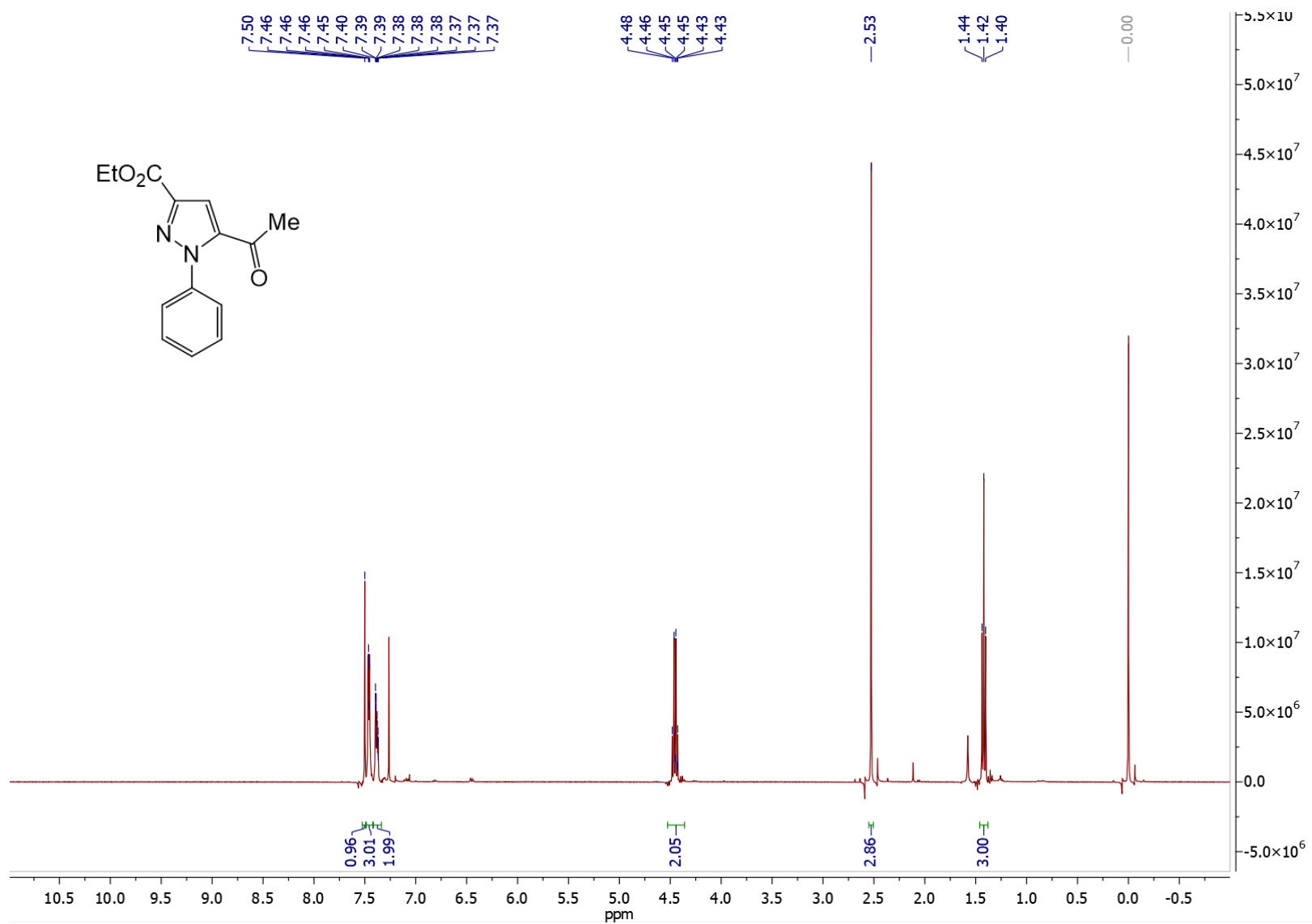


Figure S20. ^{13}C NMR spectrum of compound **7b**.

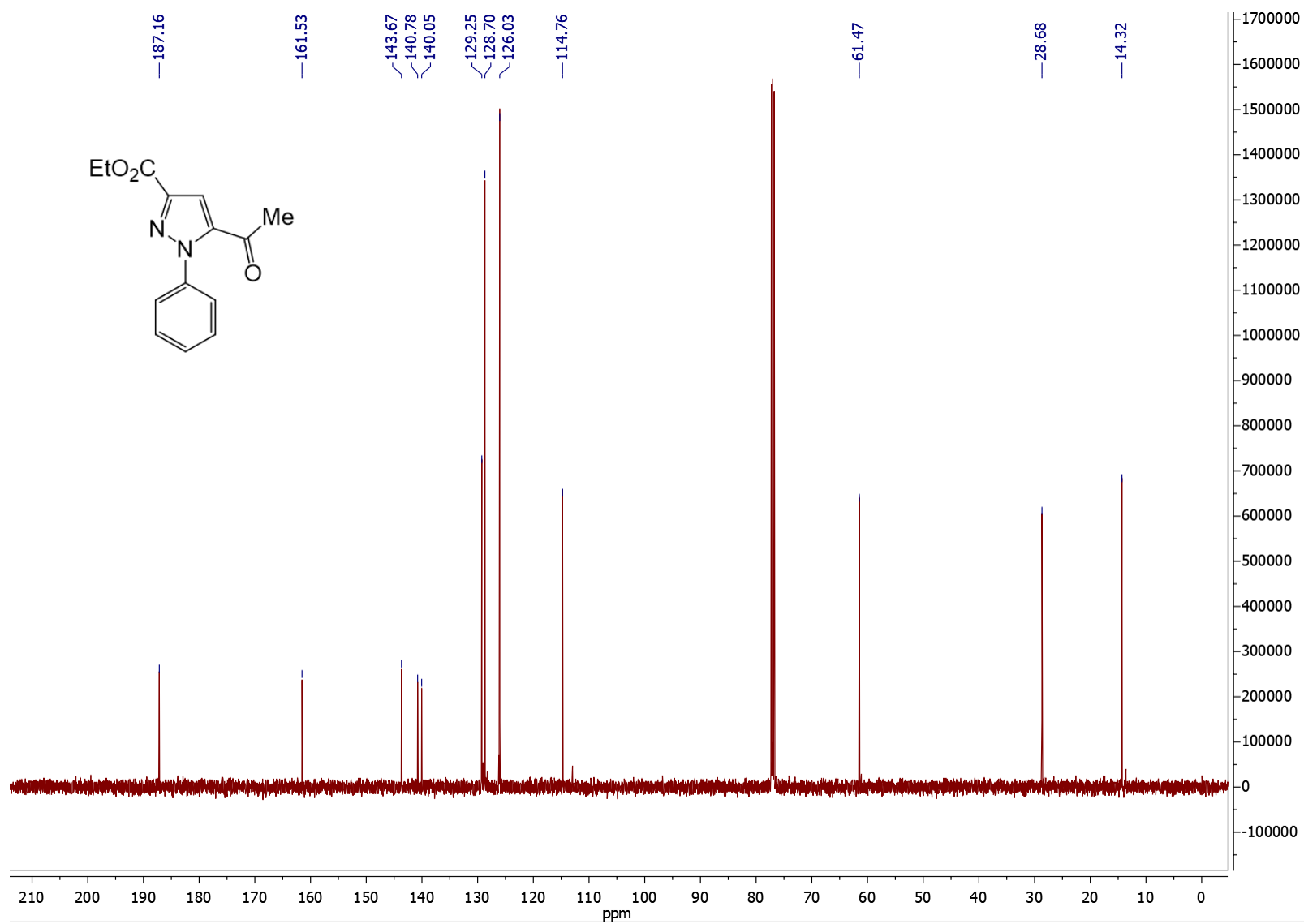


Figure S21. ^1H NMR spectrum of compound **7c**.

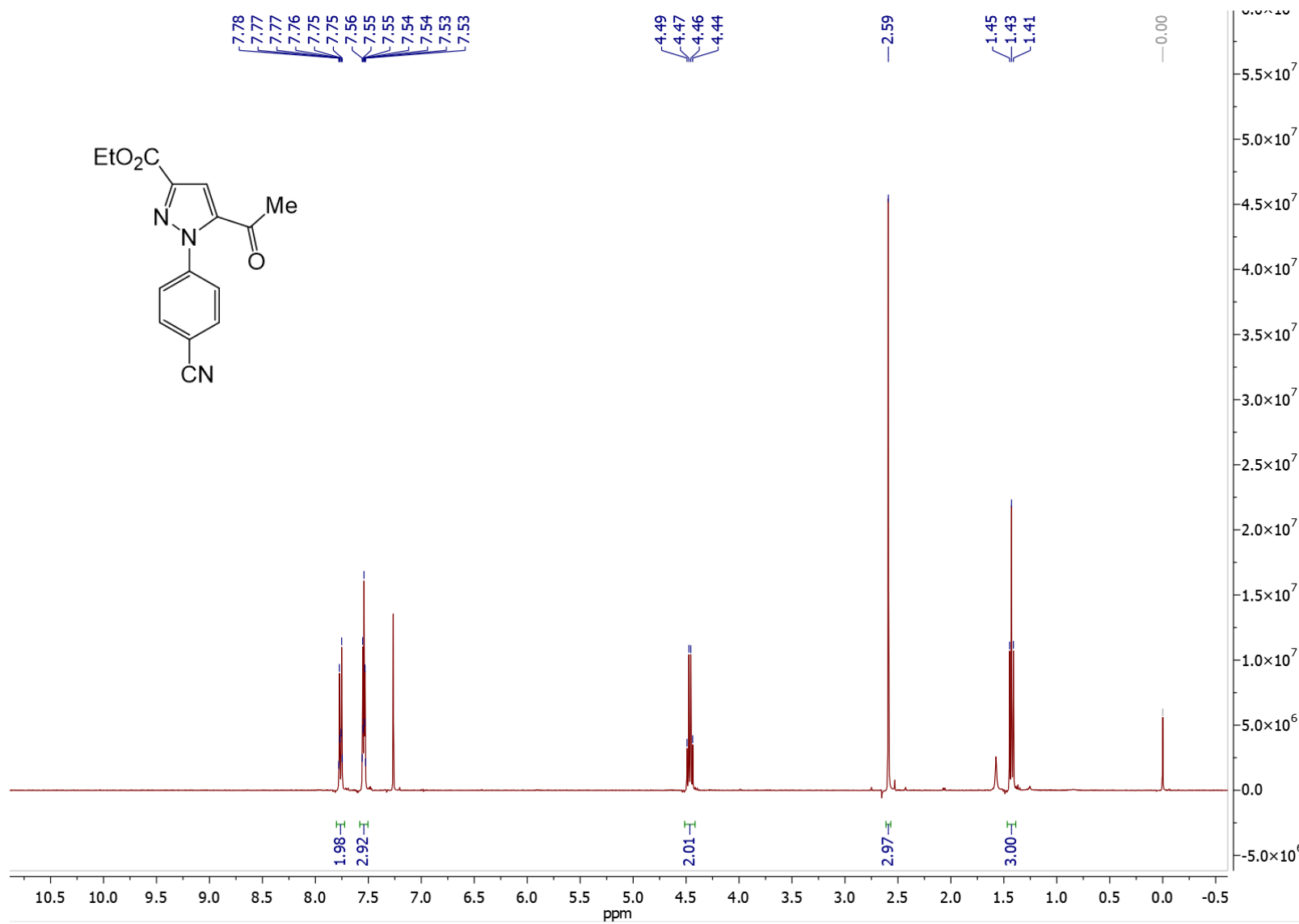


Figure S22. ^{13}C NMR spectrum of compound **7c**.

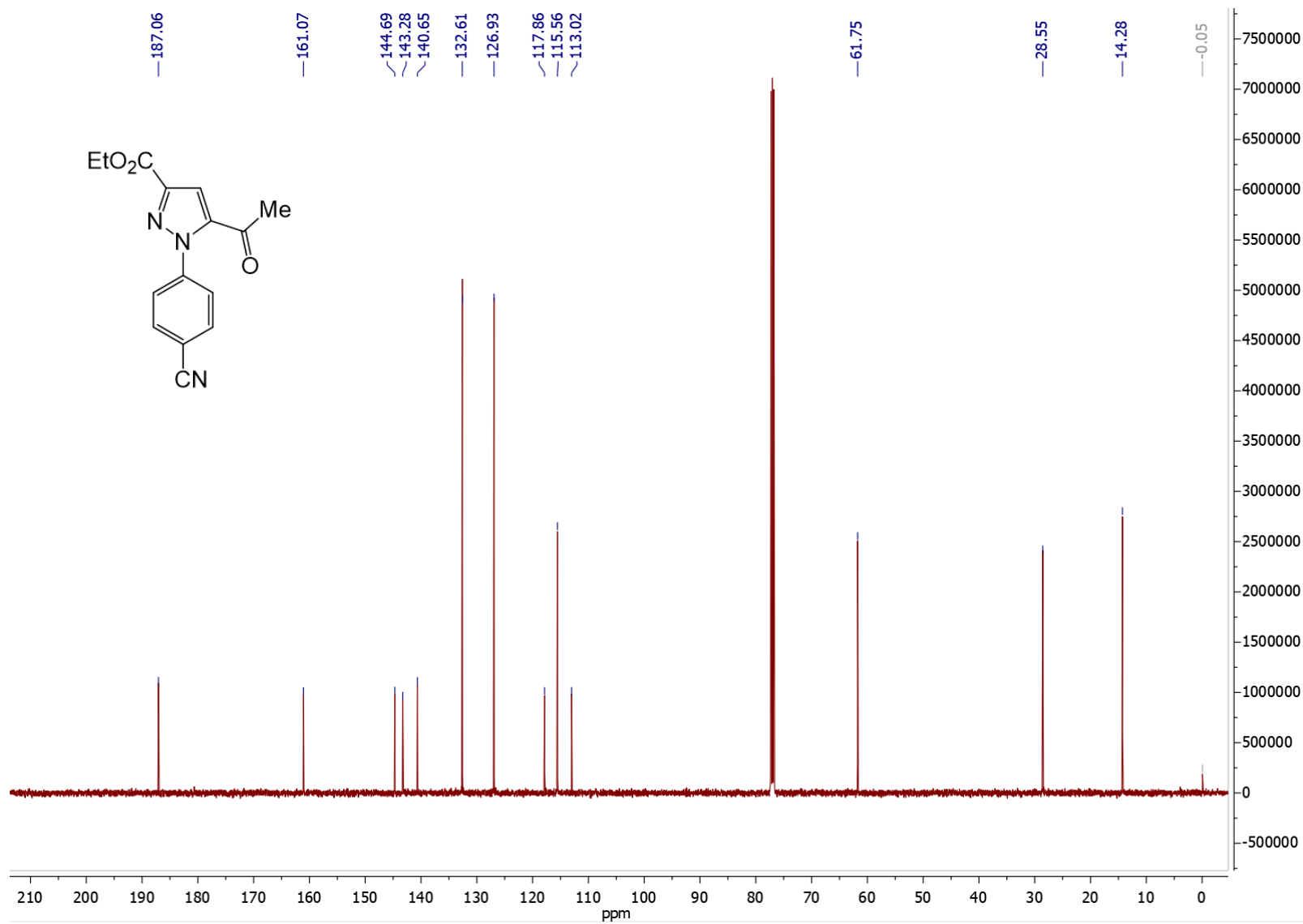


Figure S23. ^1H NMR spectrum of compound **7d**.

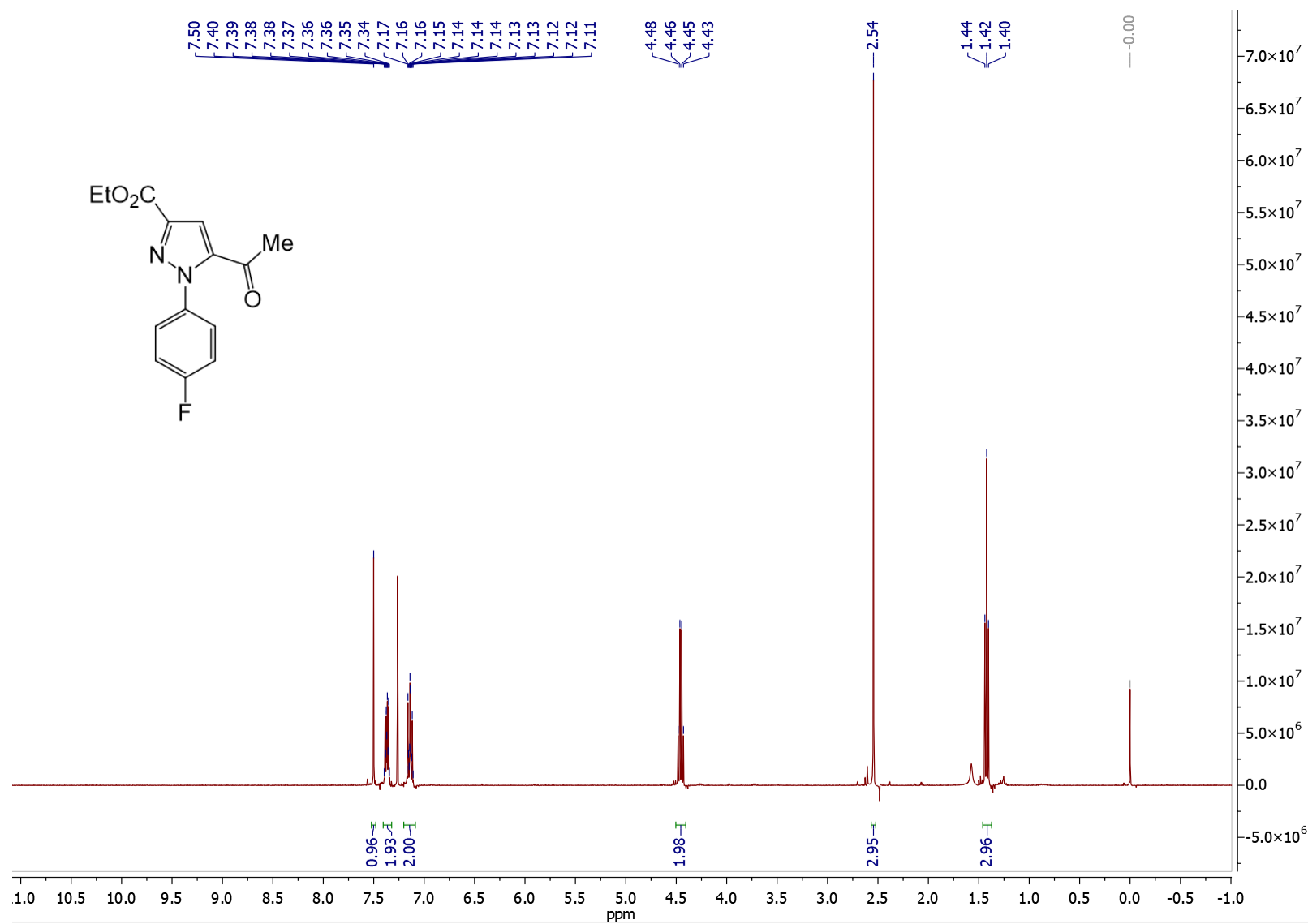


Figure S24. ^{13}C NMR spectrum of compound **7d**.

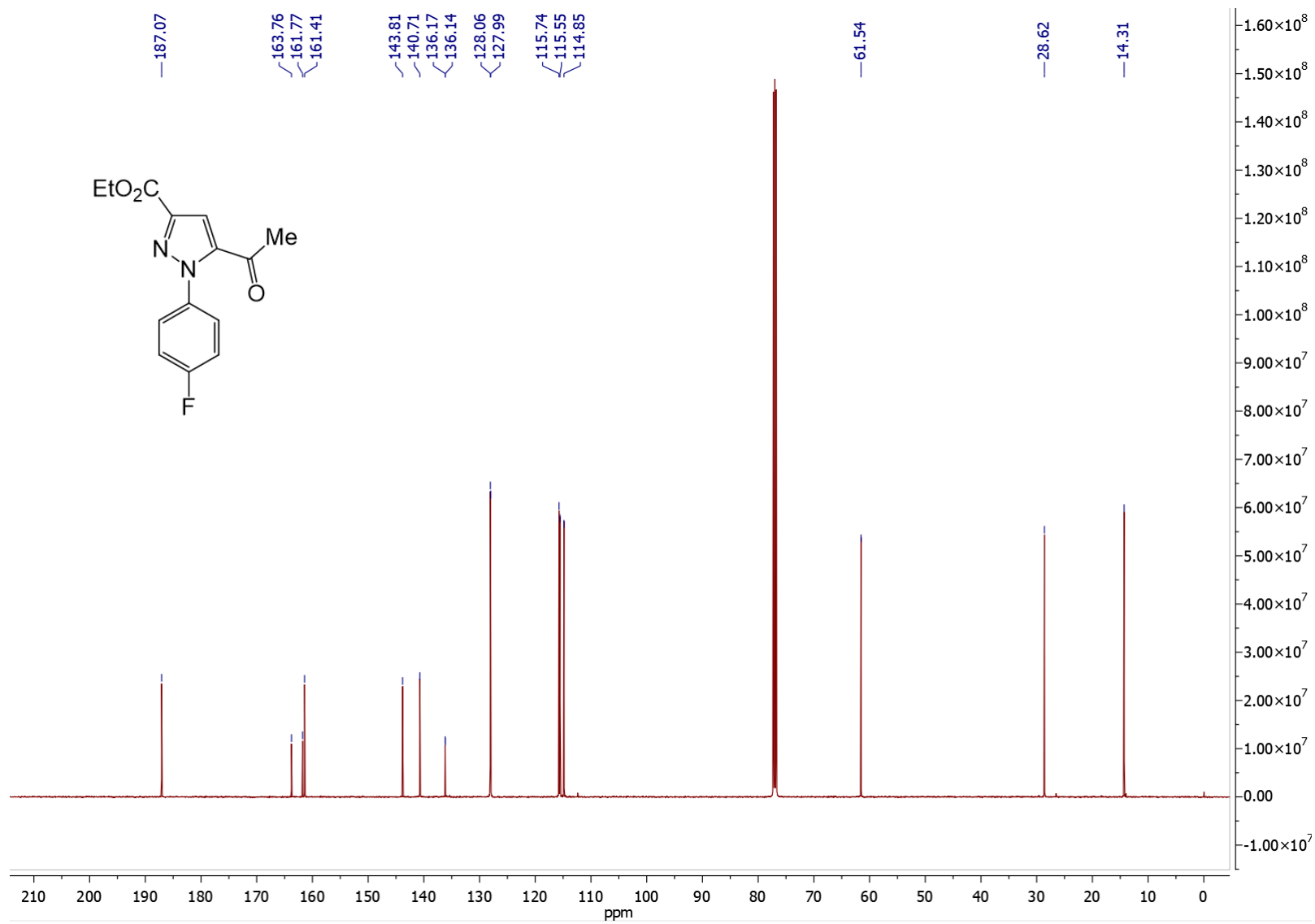


Figure S25. ^{19}F NMR spectrum of compound **7d**.

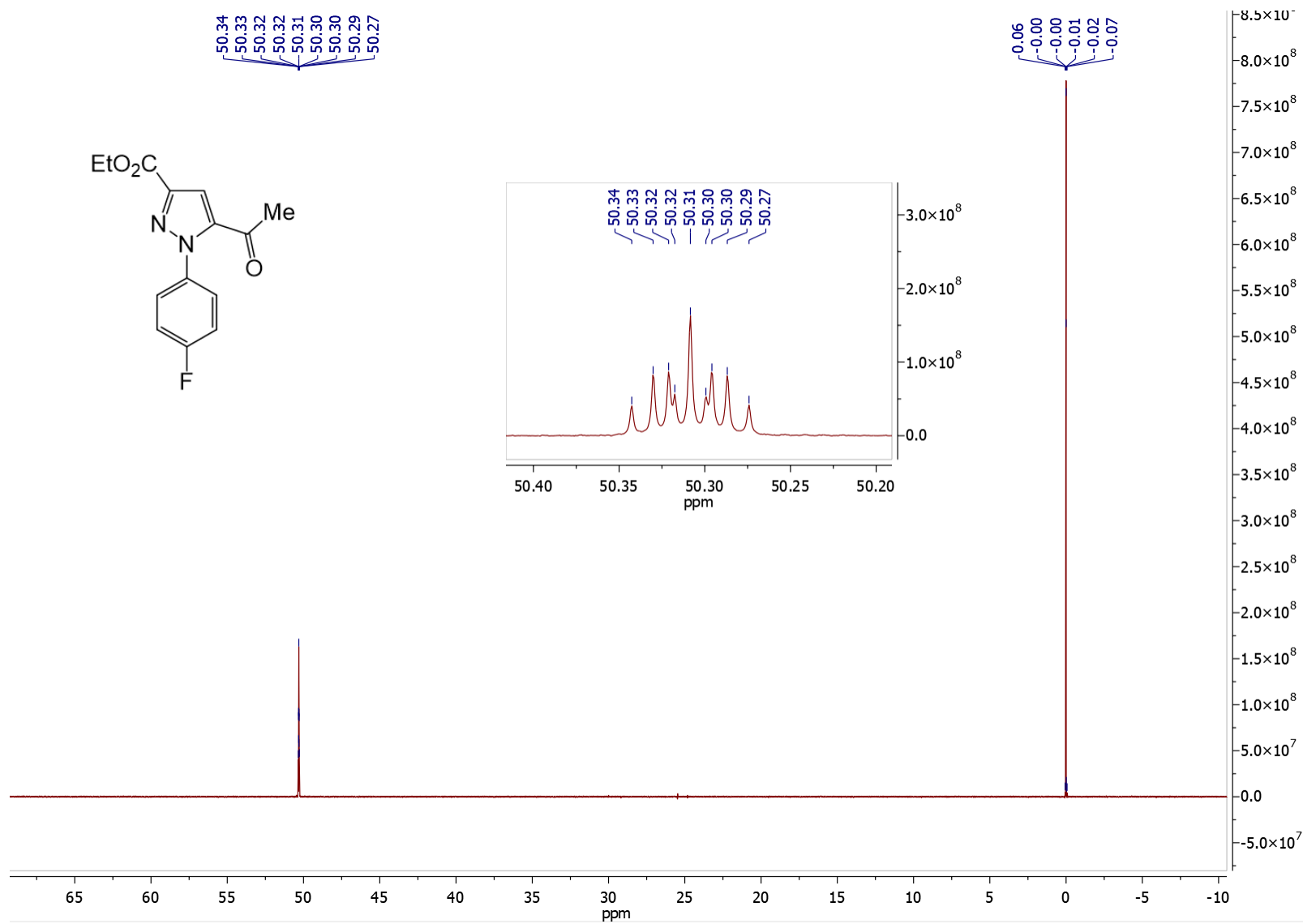


Figure S26. ^1H NMR spectrum of compound **7e**.

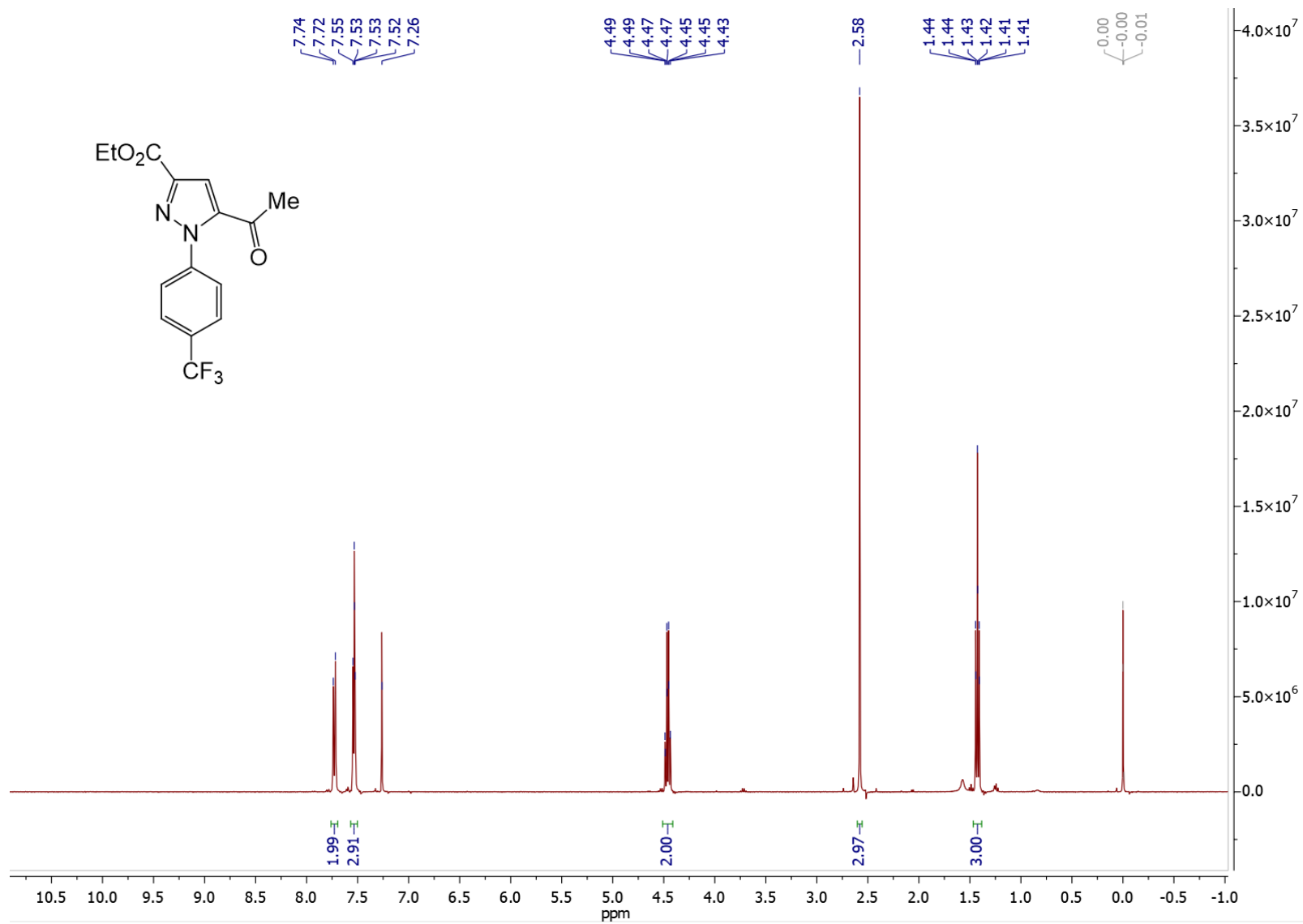


Figure S27. ^{13}C NMR spectrum of compound **7e**.

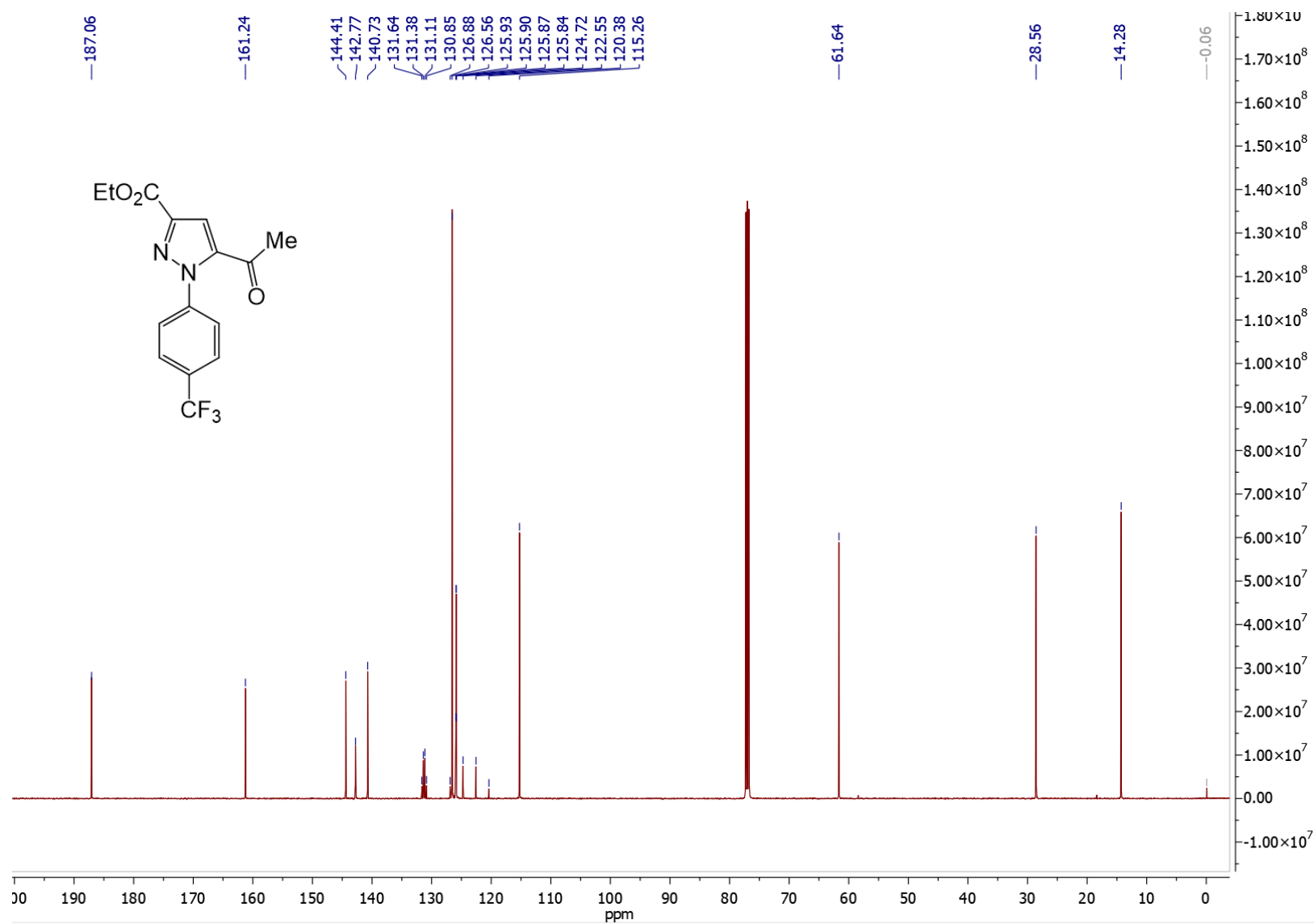


Figure S28. ^{19}F NMR spectrum of compound **7e**.



Figure S29. ^1H NMR spectrum of compound **7f**.

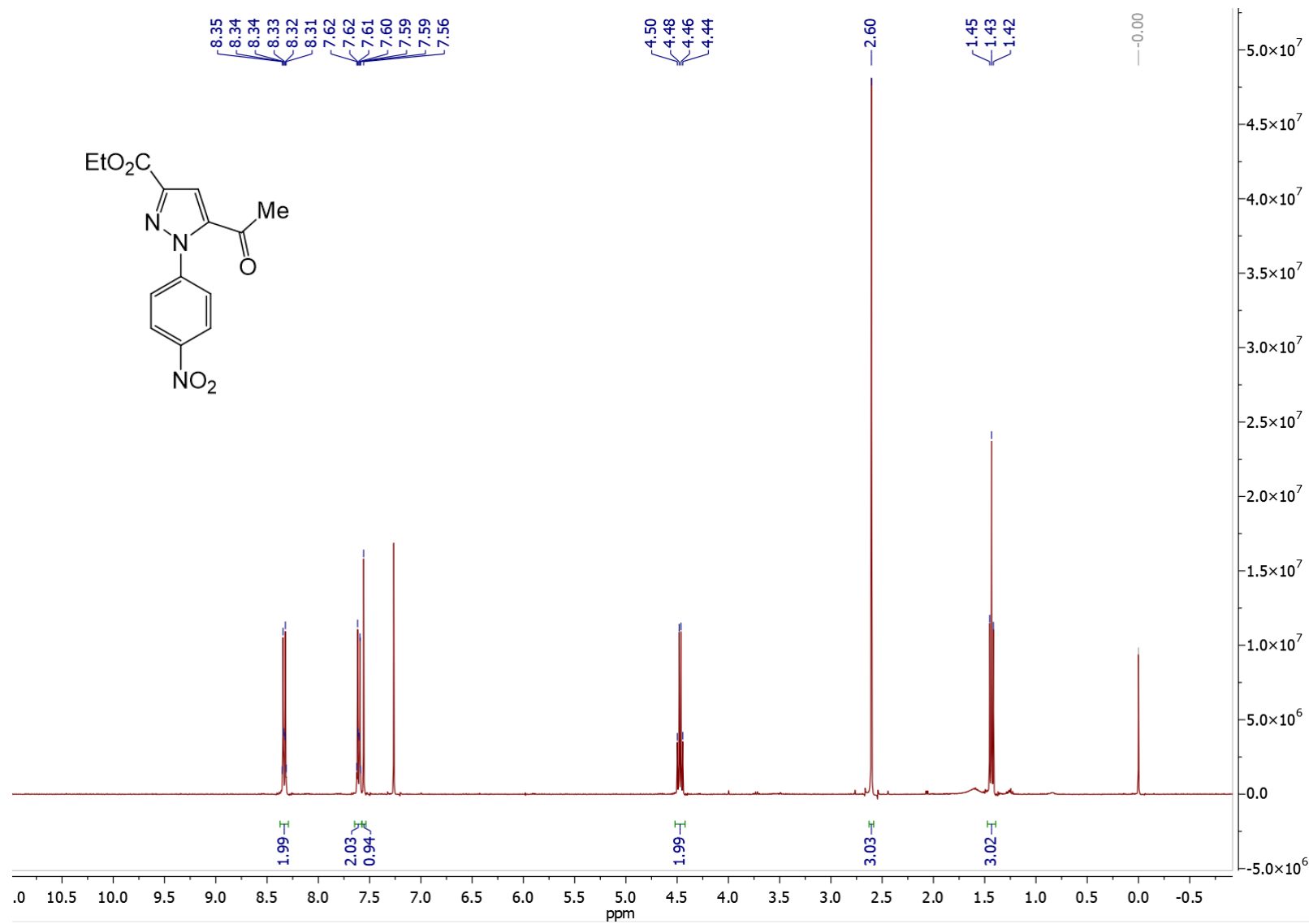


Figure S30. ^{13}C NMR spectrum of compound **7f**.

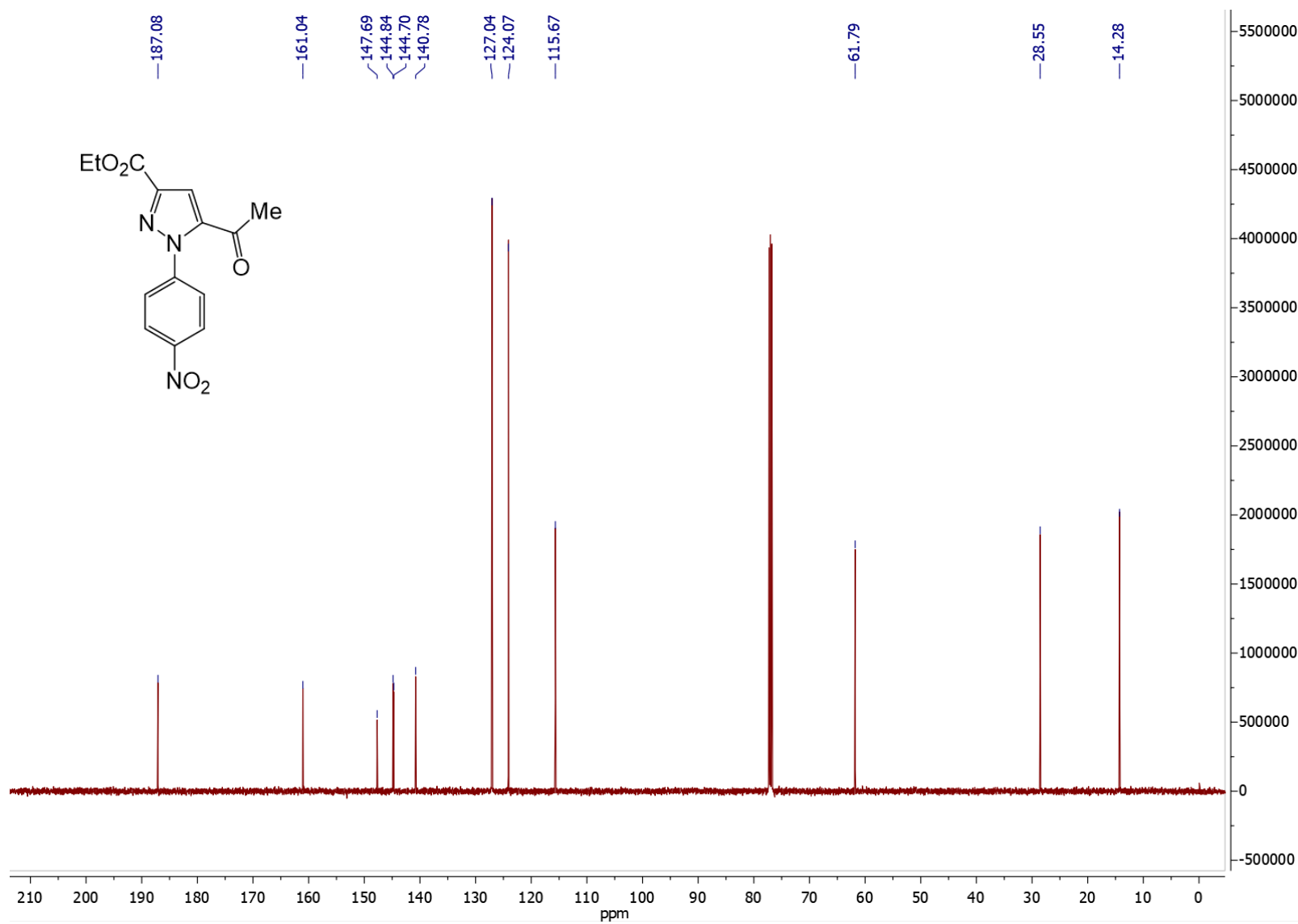


Figure S31. ^1H NMR spectrum of compound **7g**.

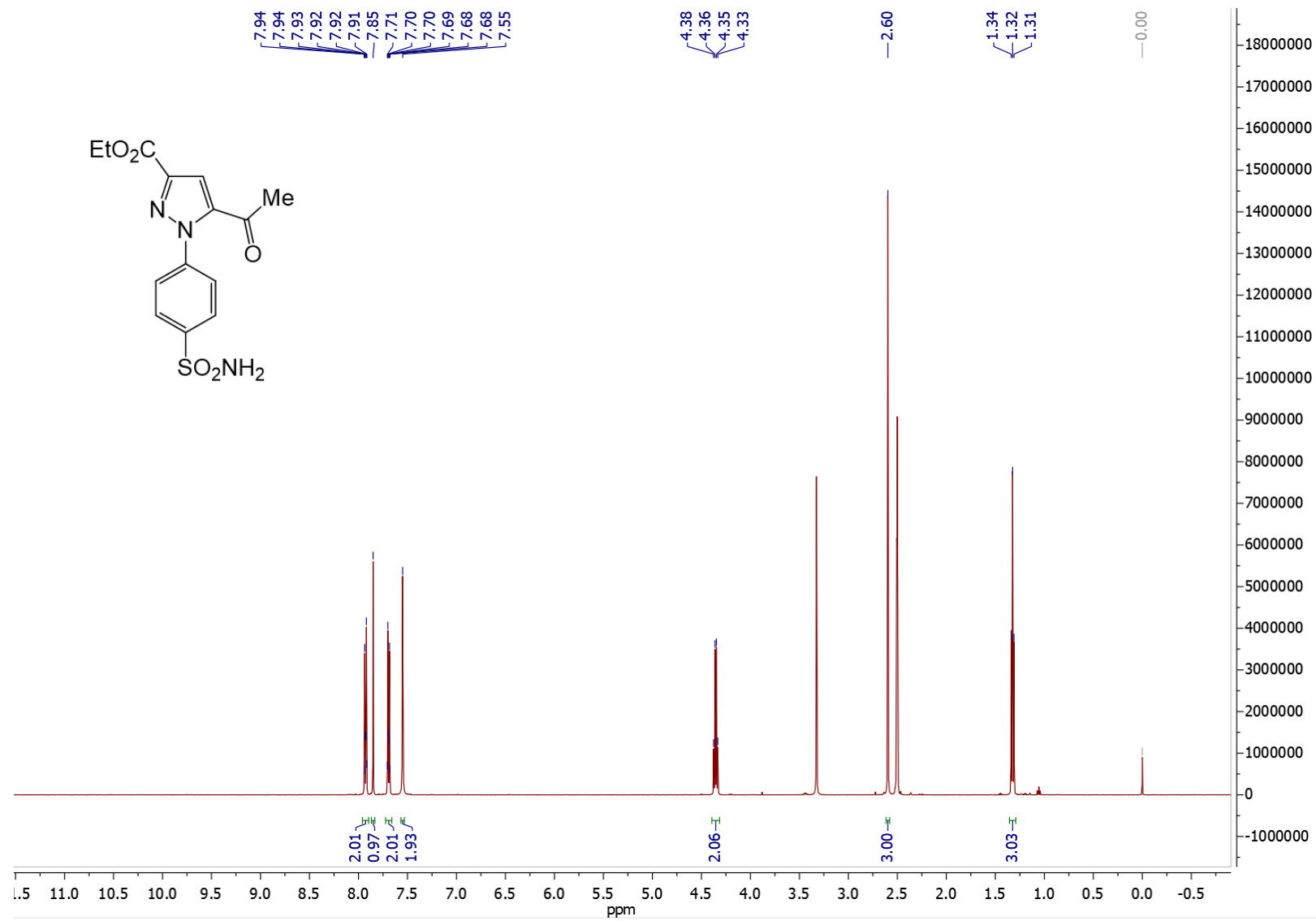


Figure S32. ^{13}C NMR spectrum of compound **7g**.

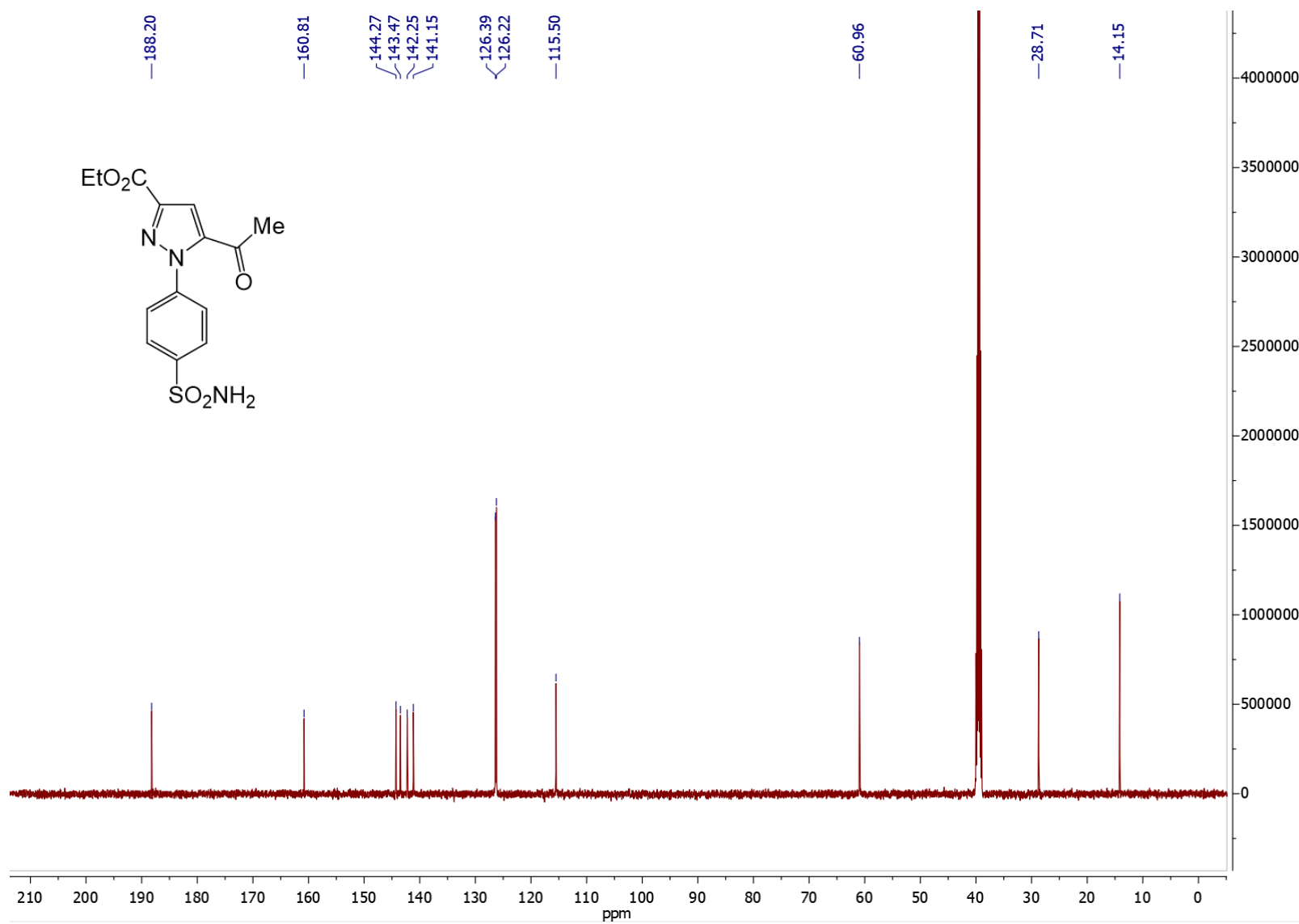


Figure S33. ^1H NMR spectrum of compound **7h**.

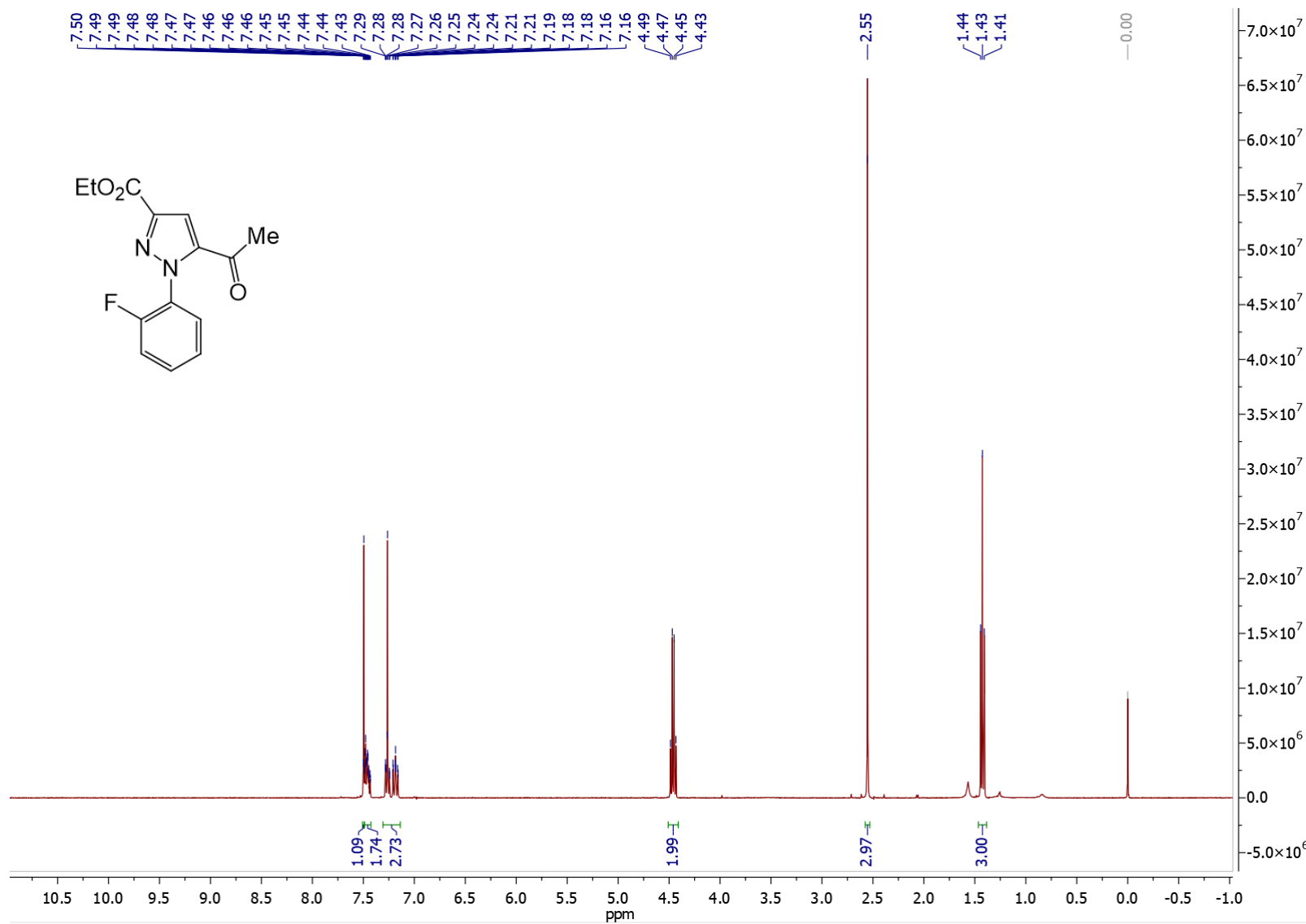


Figure S34. ^{13}C NMR spectrum of compound **7h**.

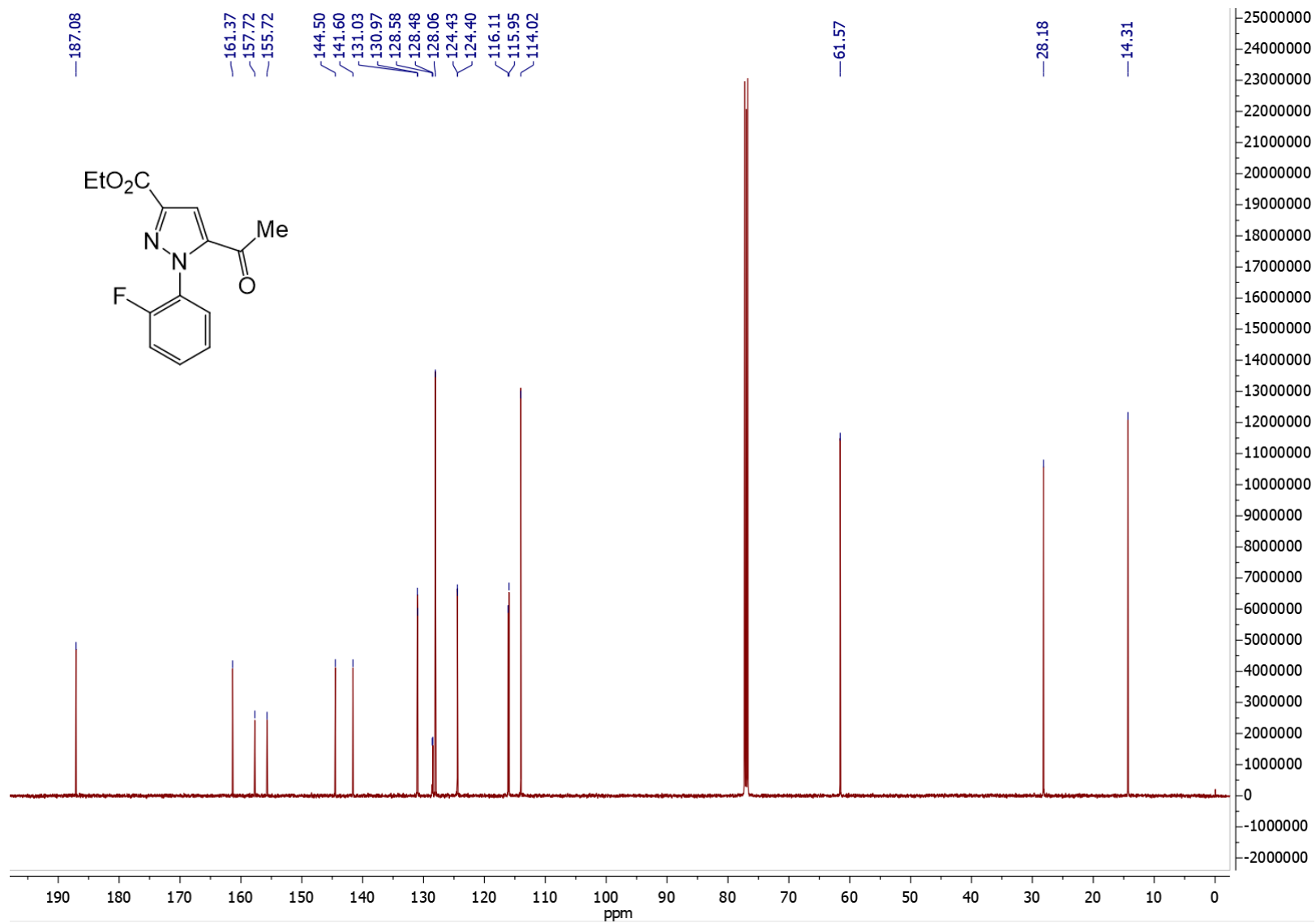


Figure S35. ^{19}F NMR spectrum of compound **7h**.

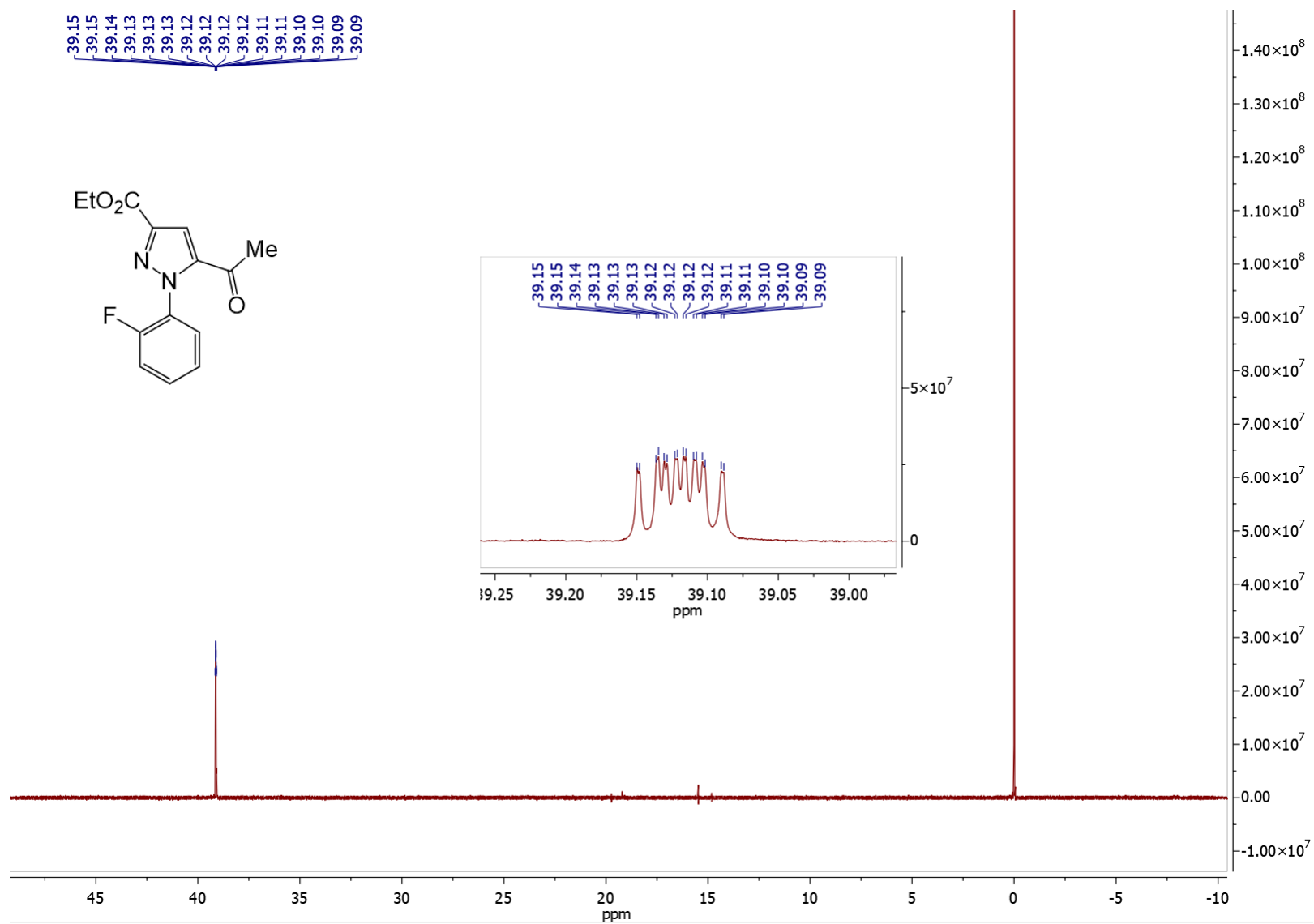


Figure S36. ^1H NMR spectrum of compound **7i**.

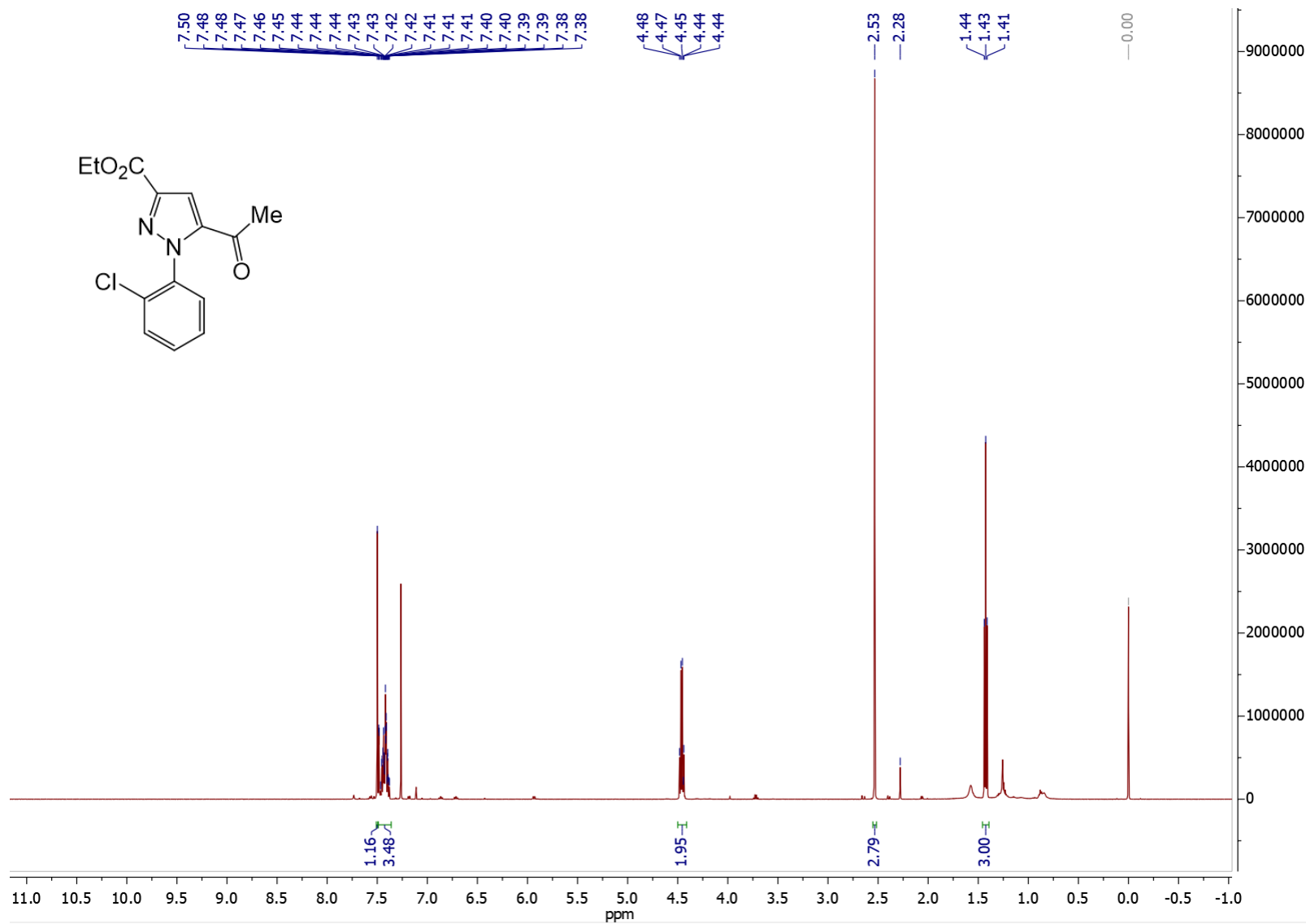


Figure S37. ^{13}C NMR spectrum of compound **7i**.

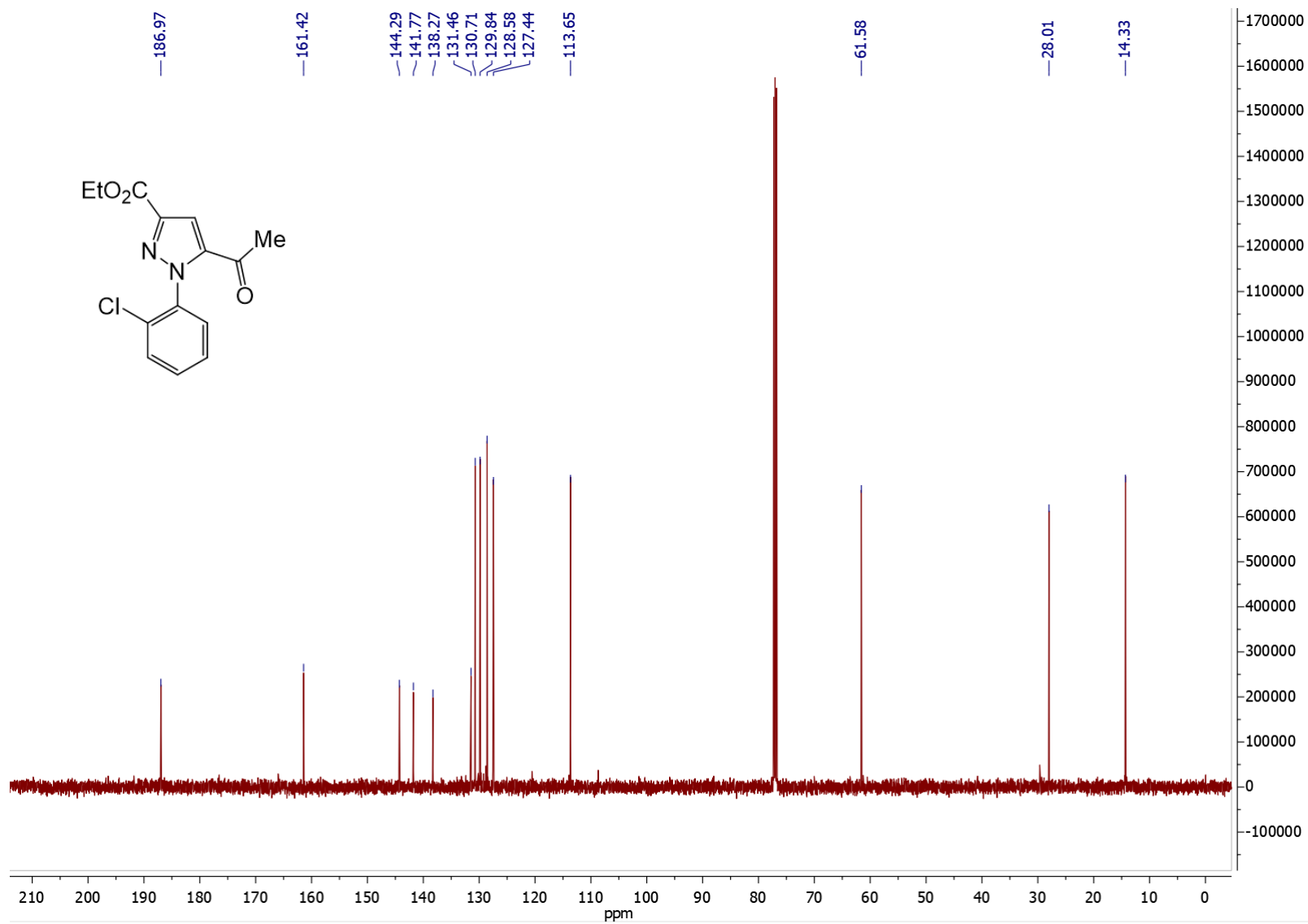


Figure S38. ^1H NMR spectrum of compound 7j.

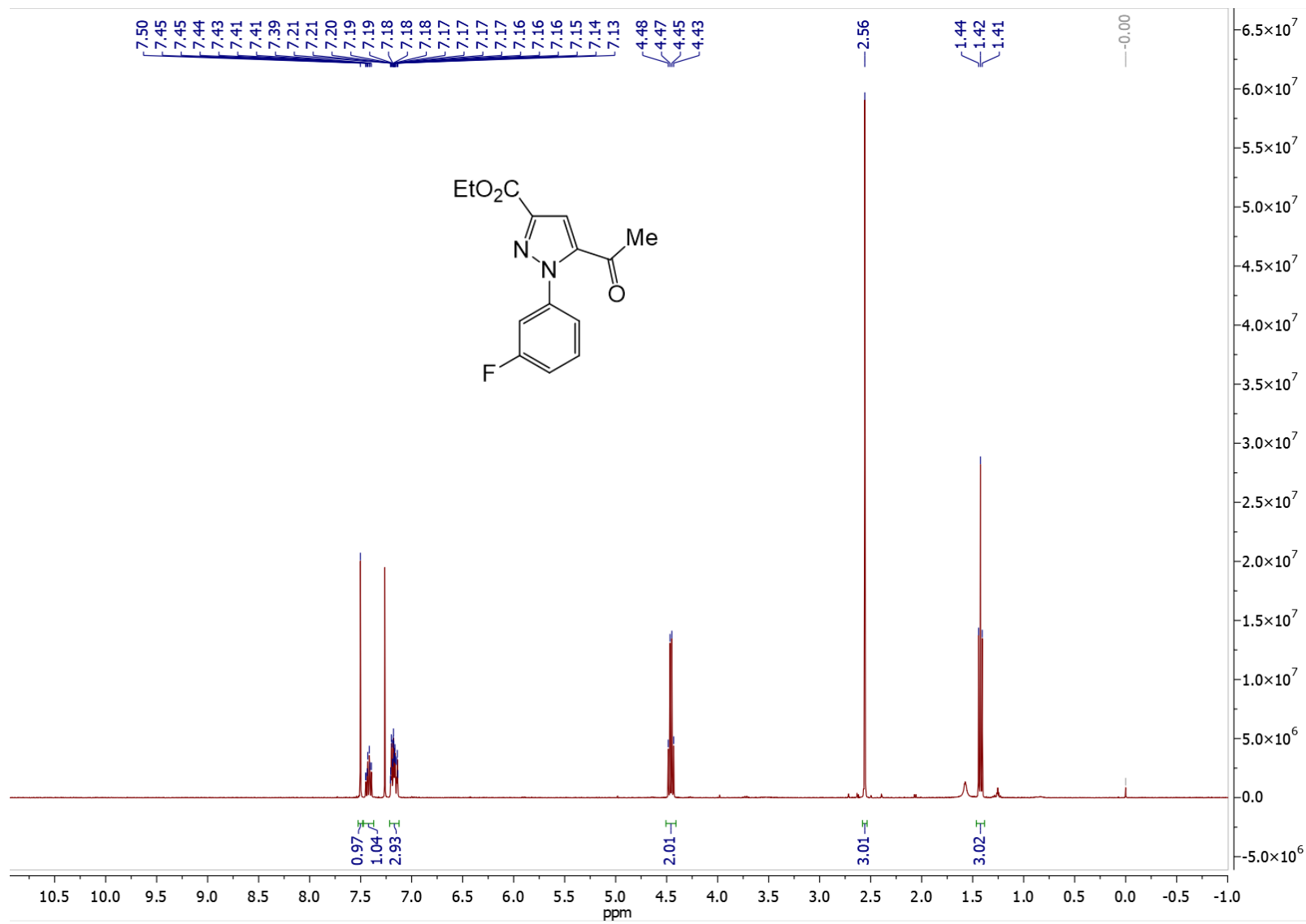


Figure S39. ^{13}C NMR spectrum of compound **7j**.

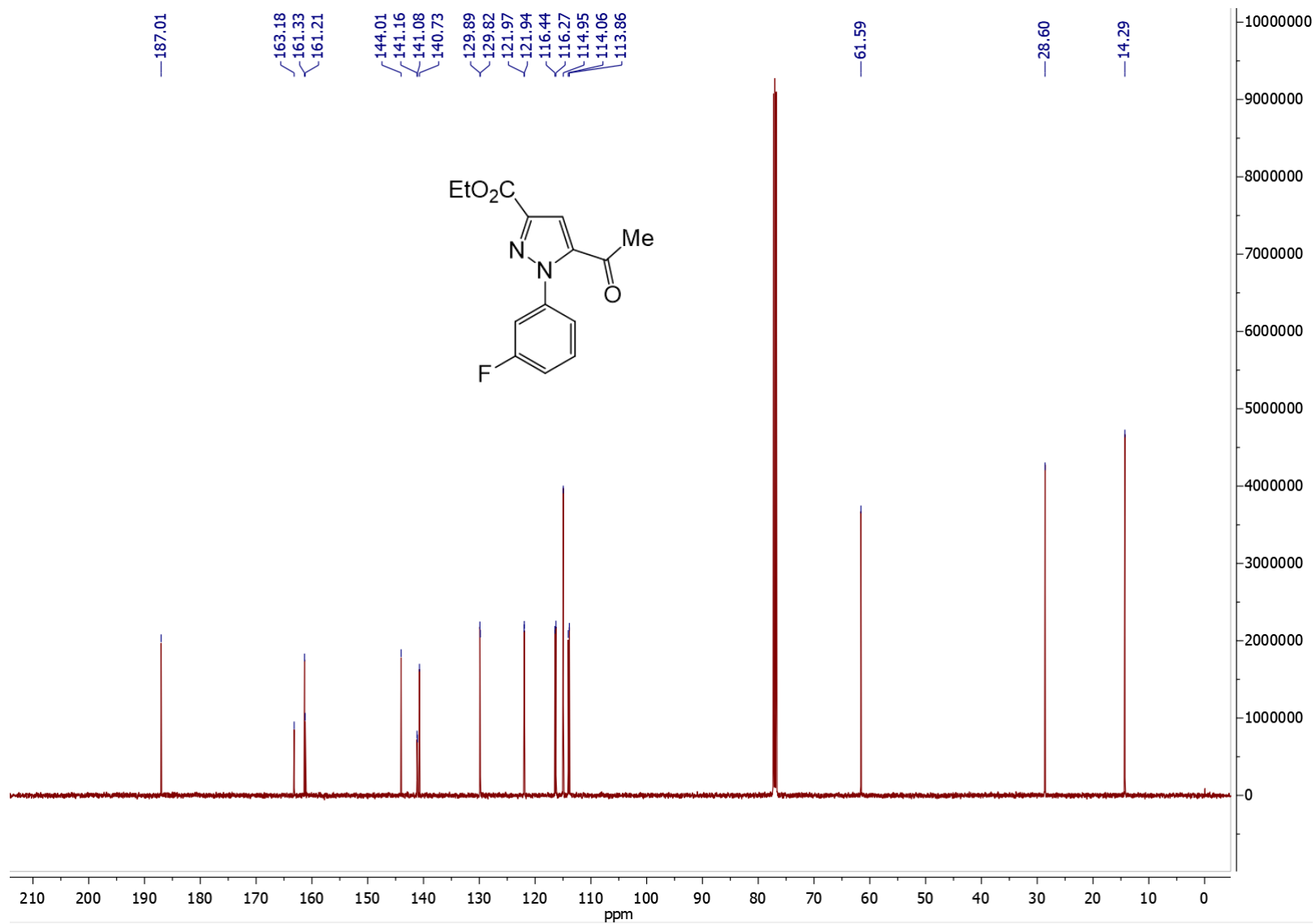


Figure S40. ^{19}F NMR spectrum of compound **7j**.

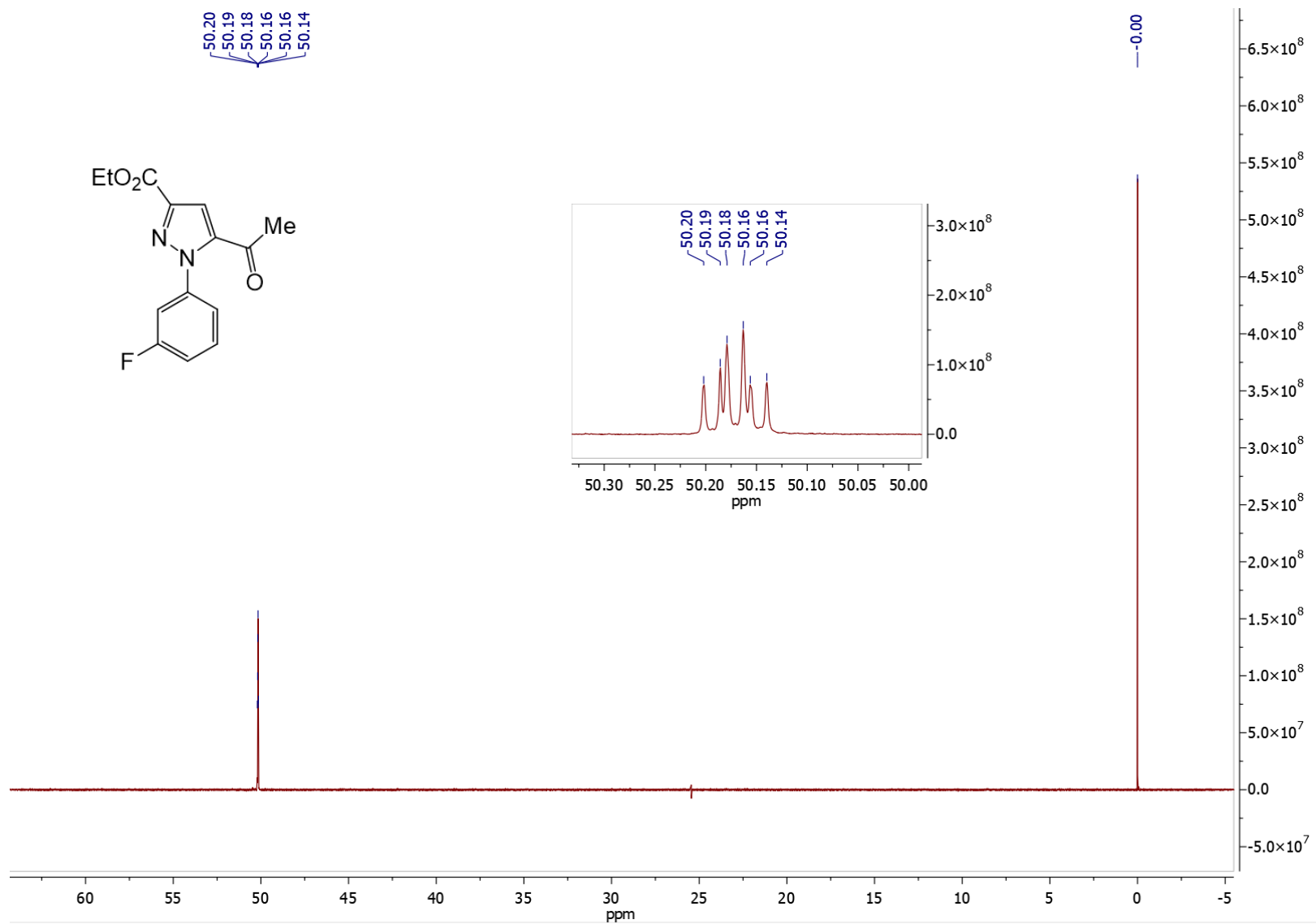


Figure S41. ^1H NMR spectrum of compound **7k**.

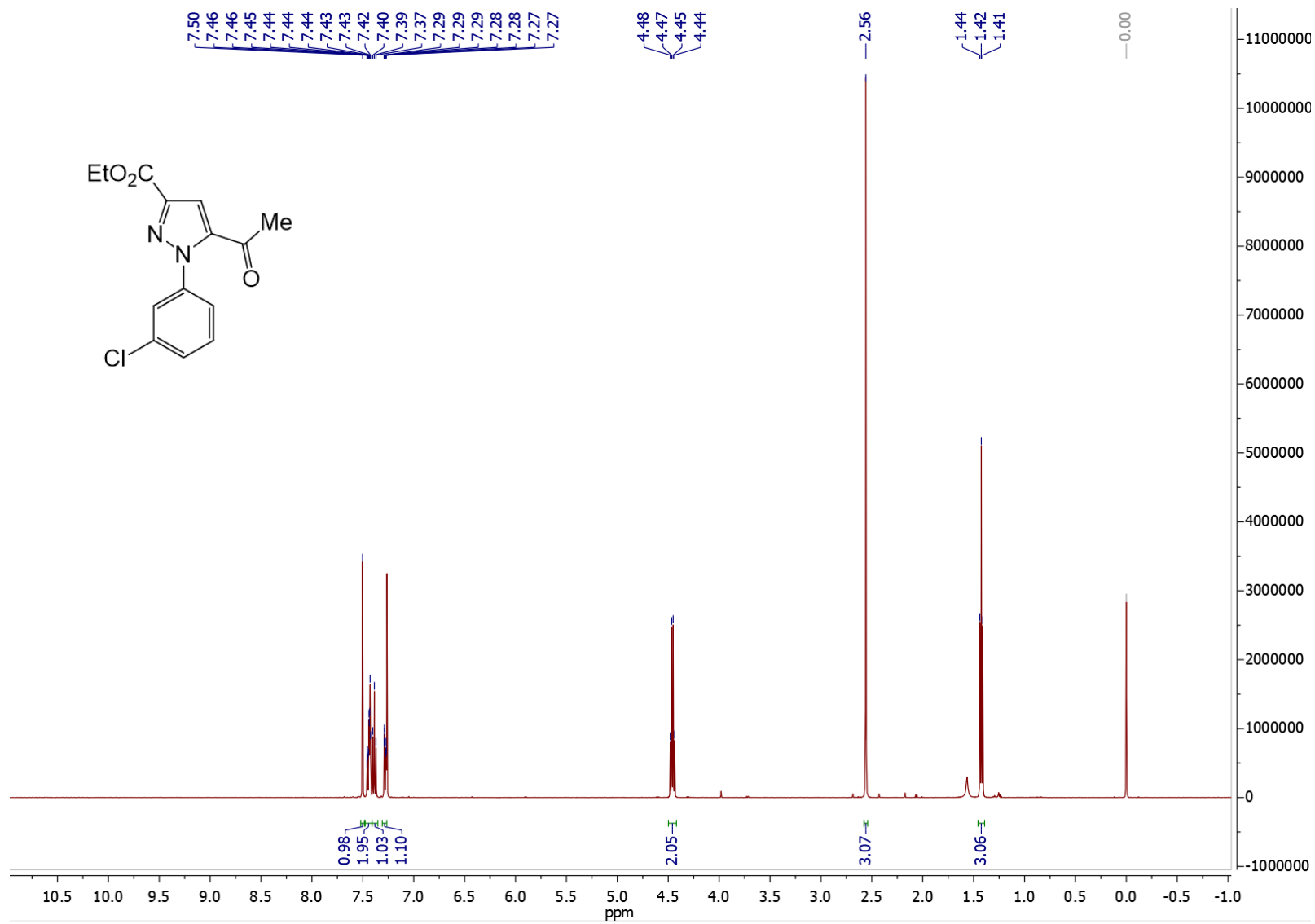


Figure S42. ^{13}C NMR spectrum of compound **7k**.

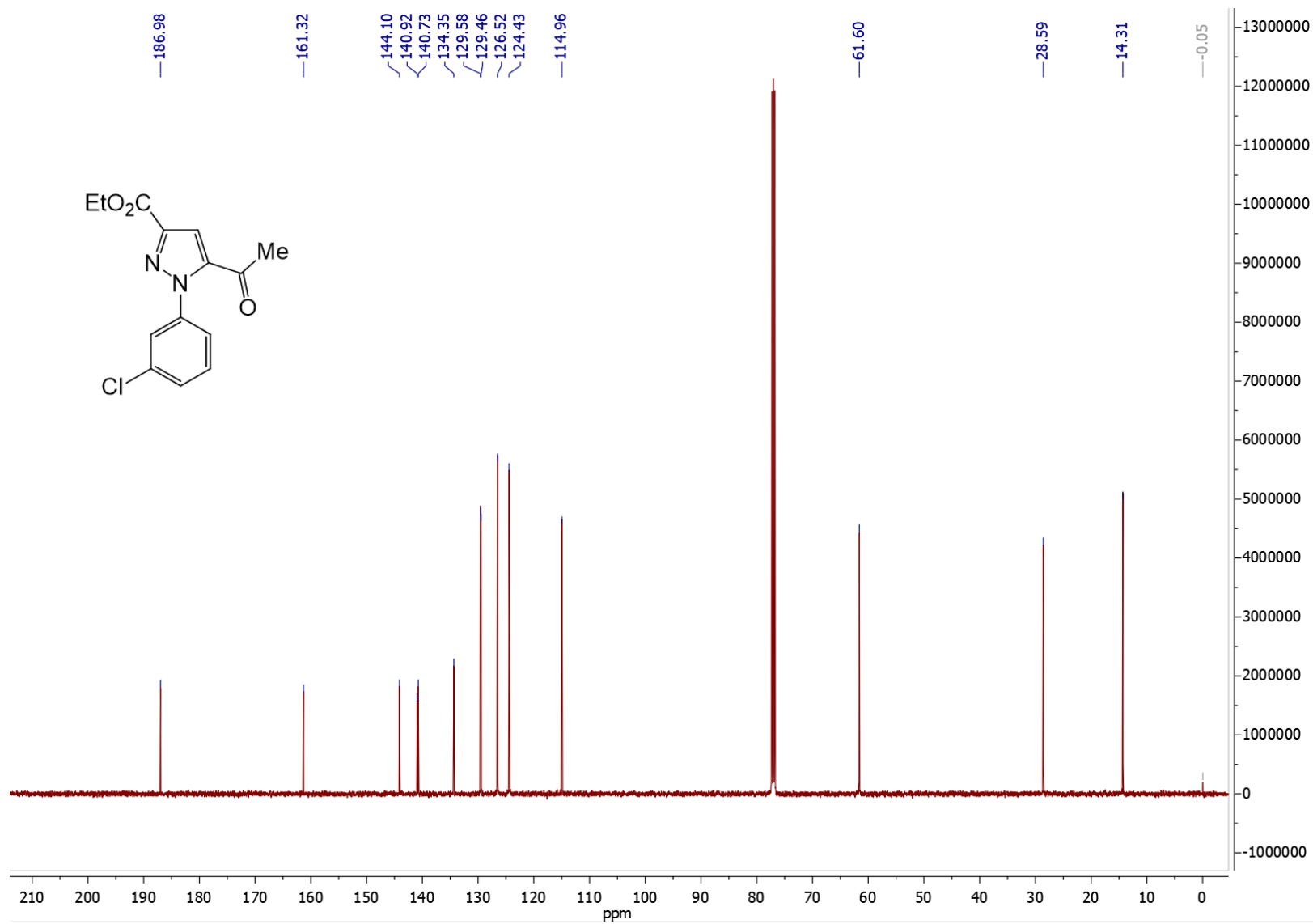


Figure S43. ^1H NMR spectrum of compound **71**.

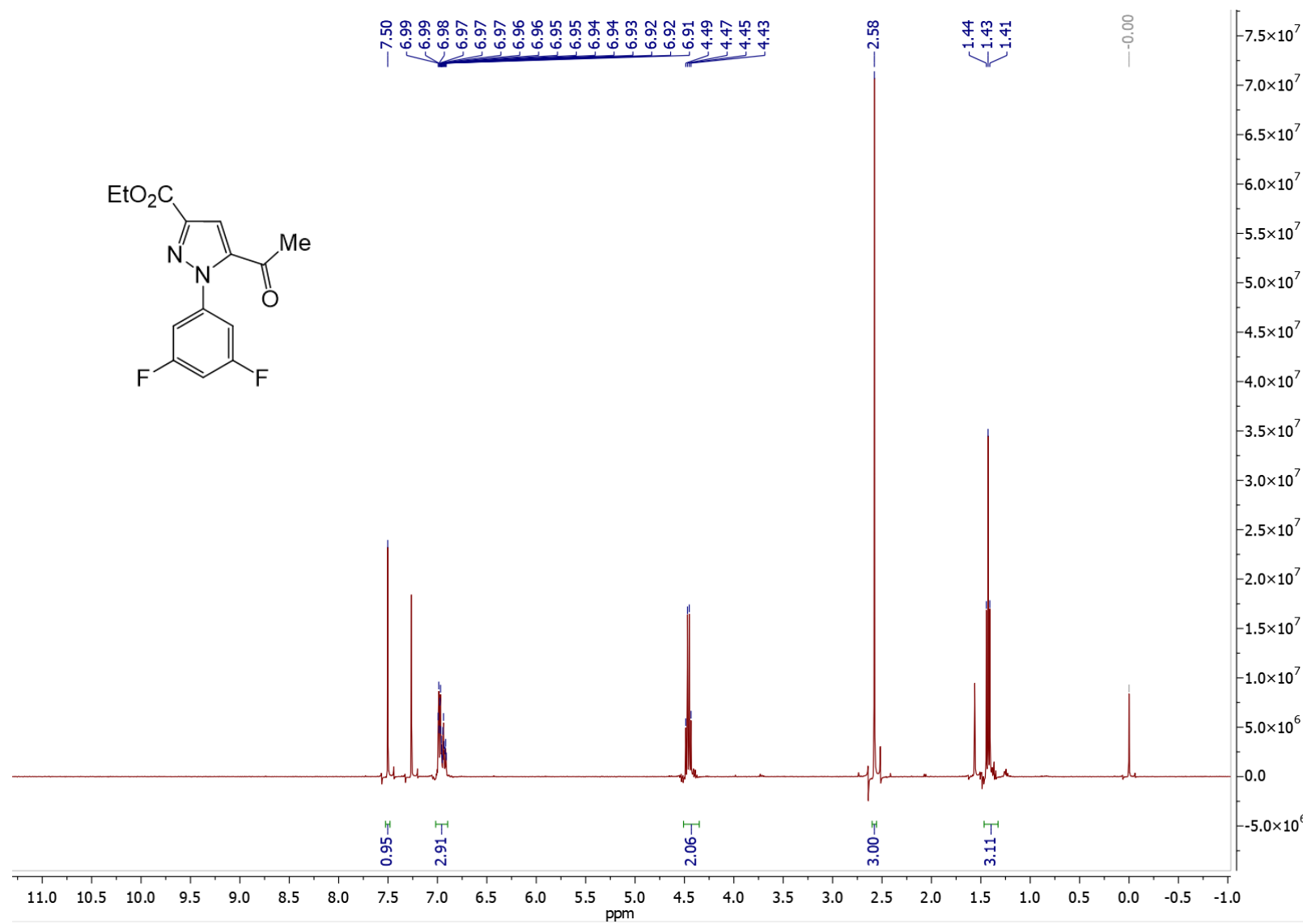


Figure S44. ^{13}C NMR spectrum of compound **7l**.

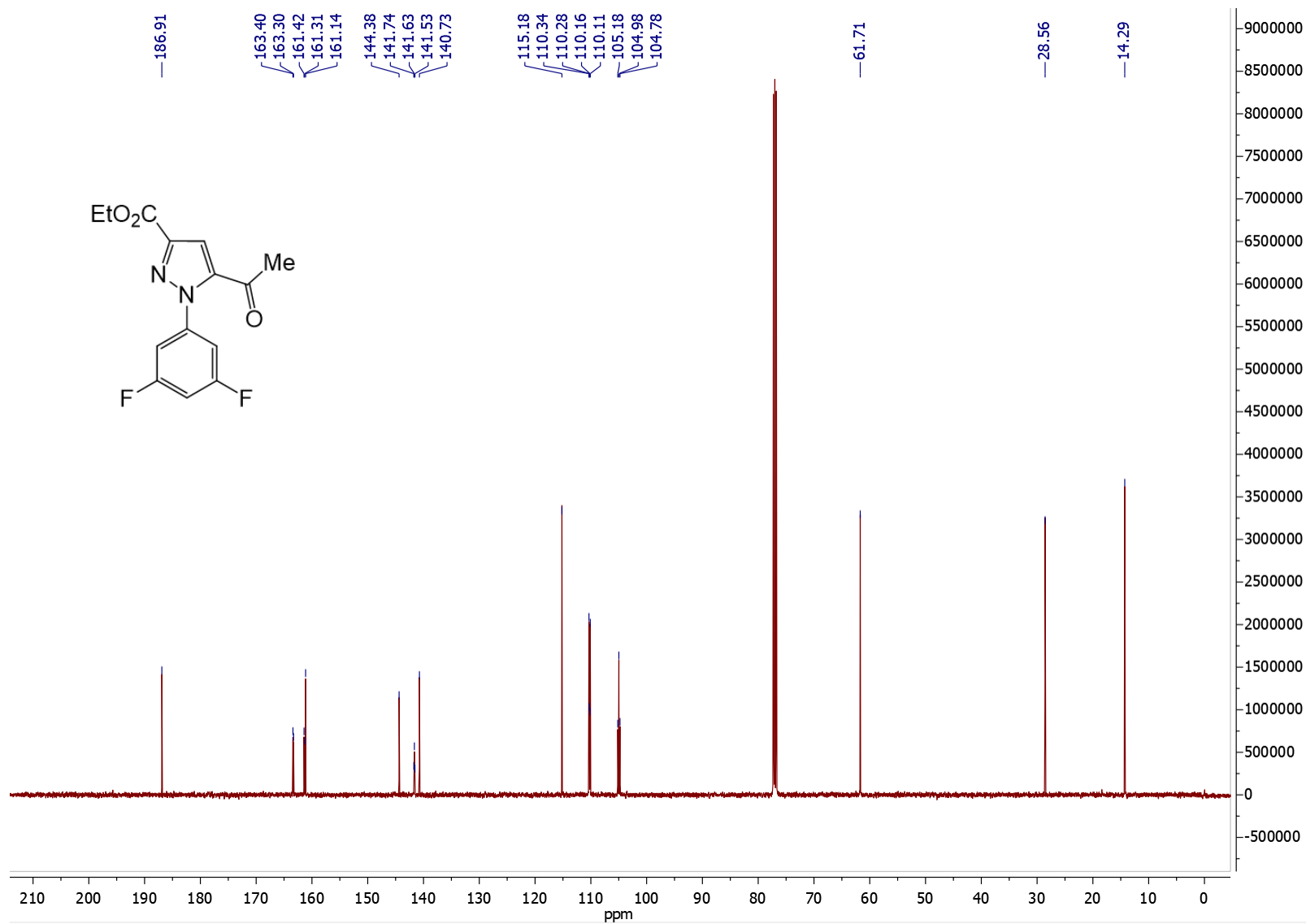


Figure S45. ^{19}F NMR spectrum of compound **71**.

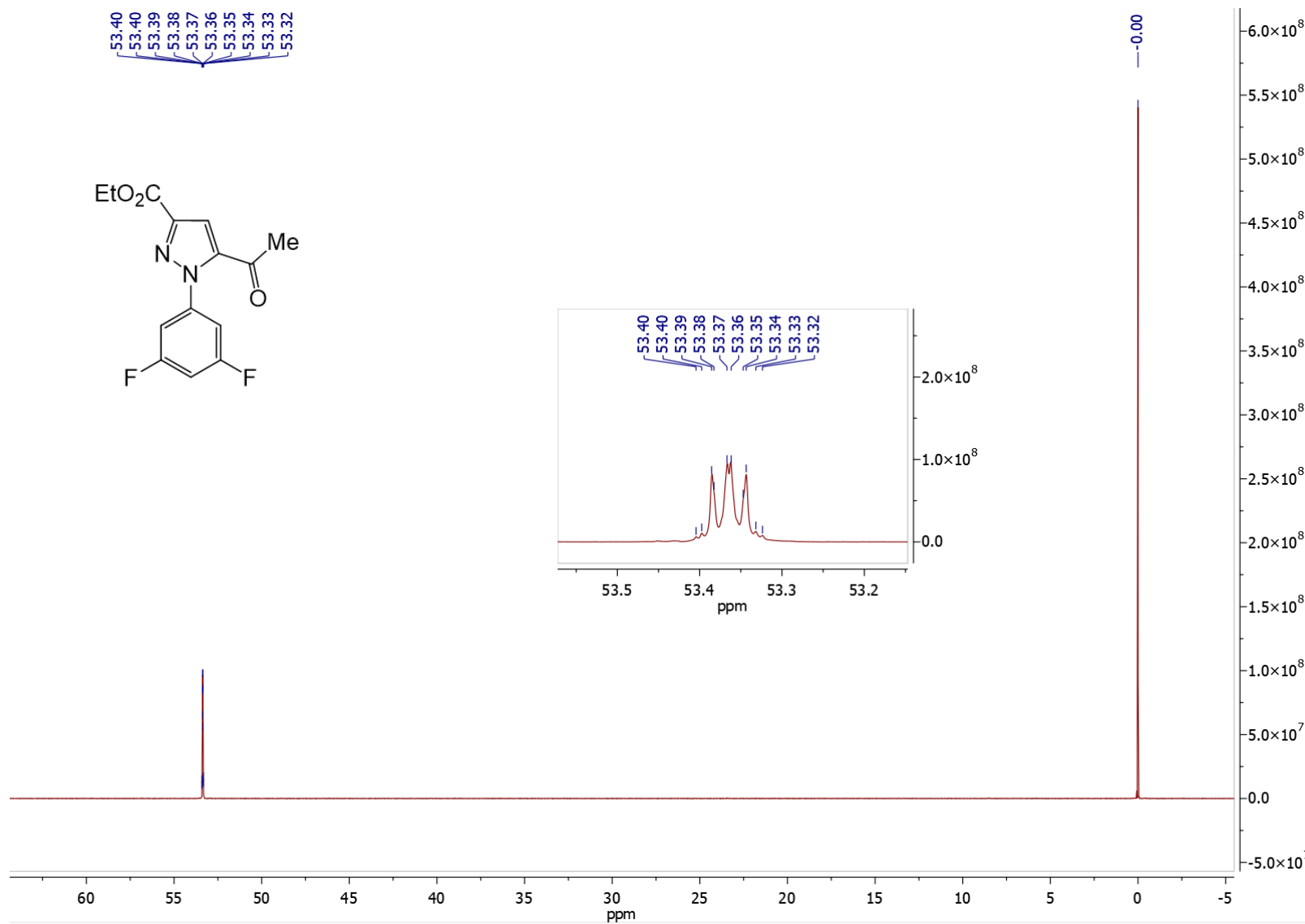


Figure S46. ^1H NMR spectrum of compound 8.

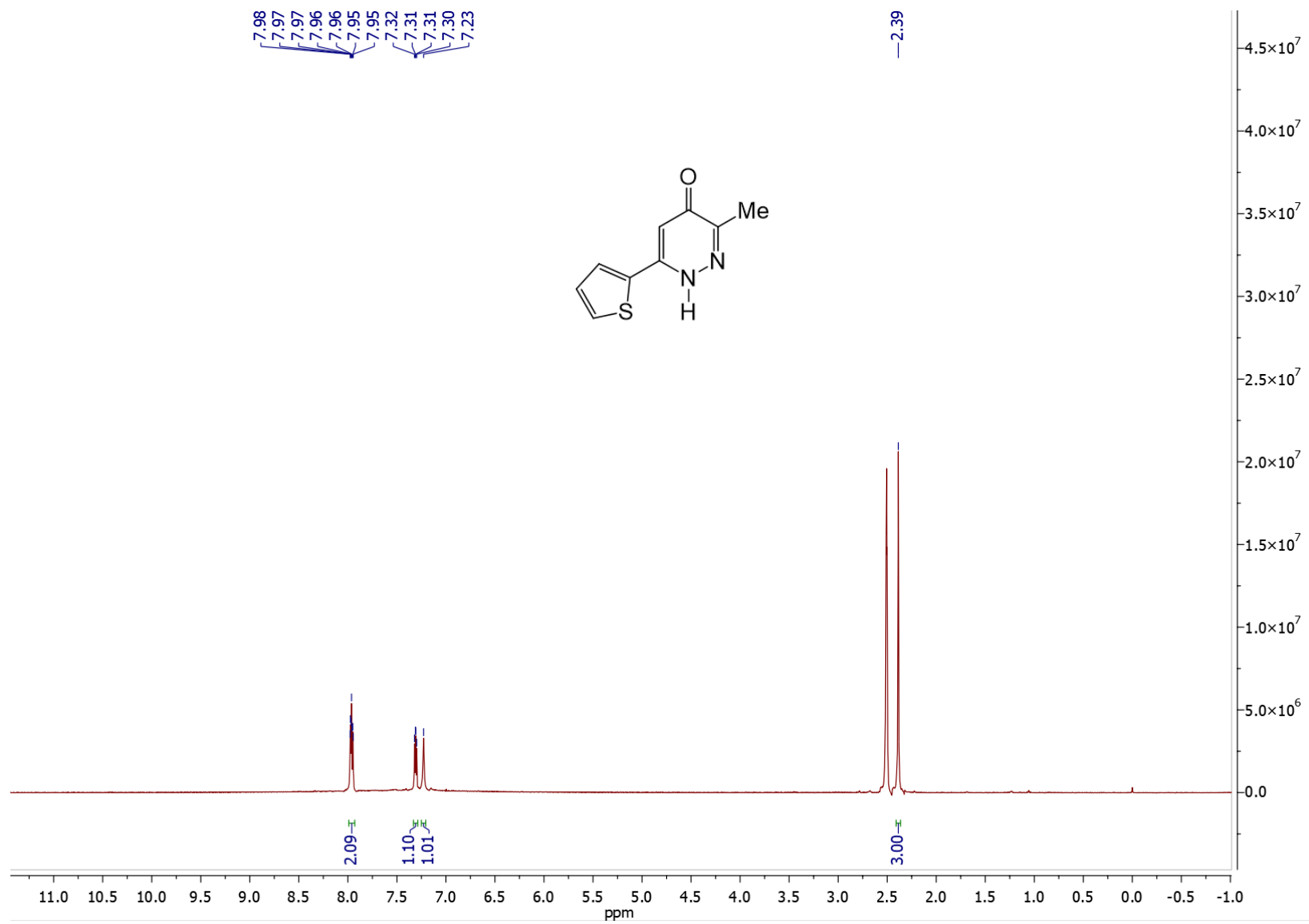


Figure S47. ^{13}C NMR spectrum of compound 8.

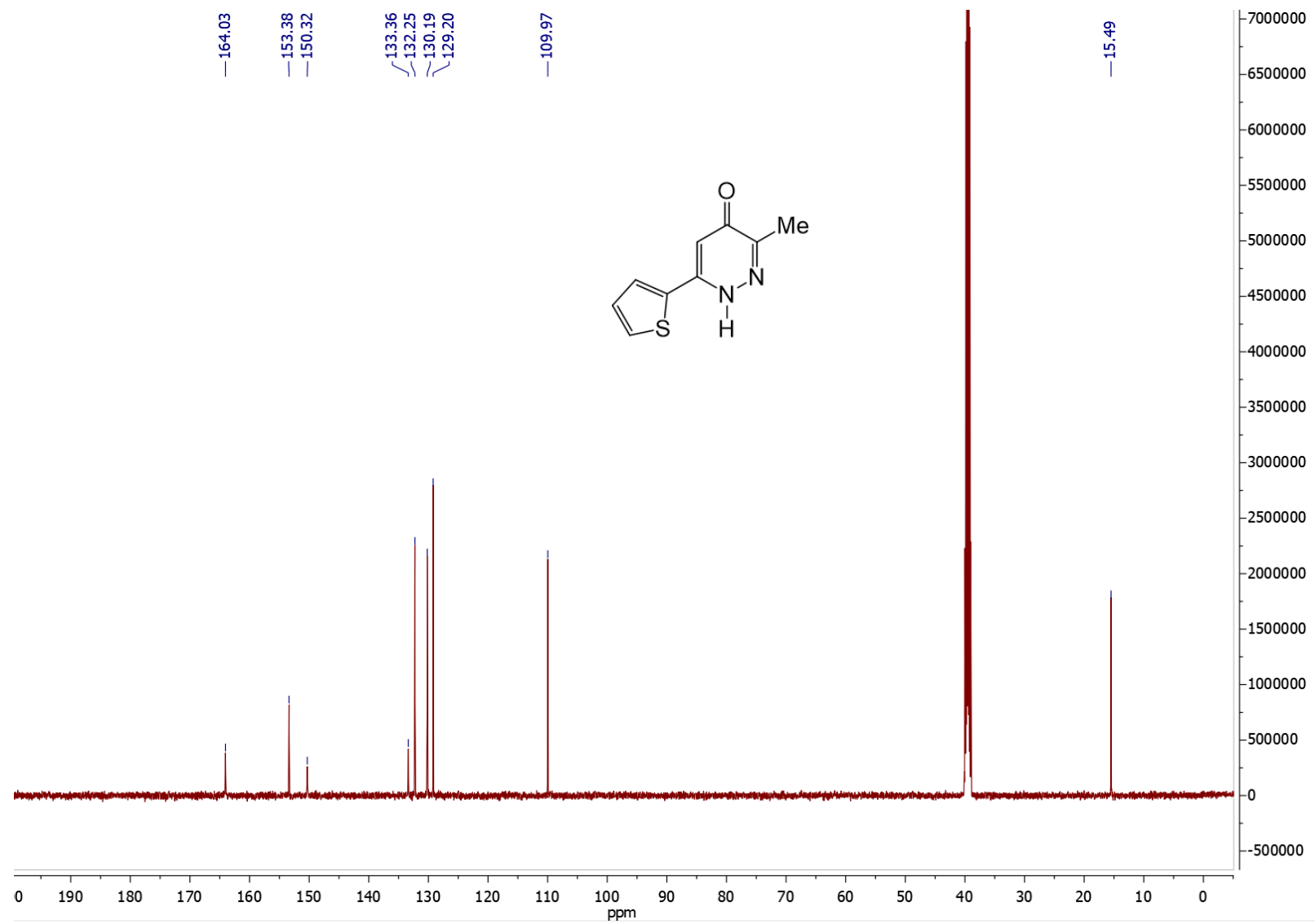


Figure S48. ^1H NMR spectrum of compound **9a**.

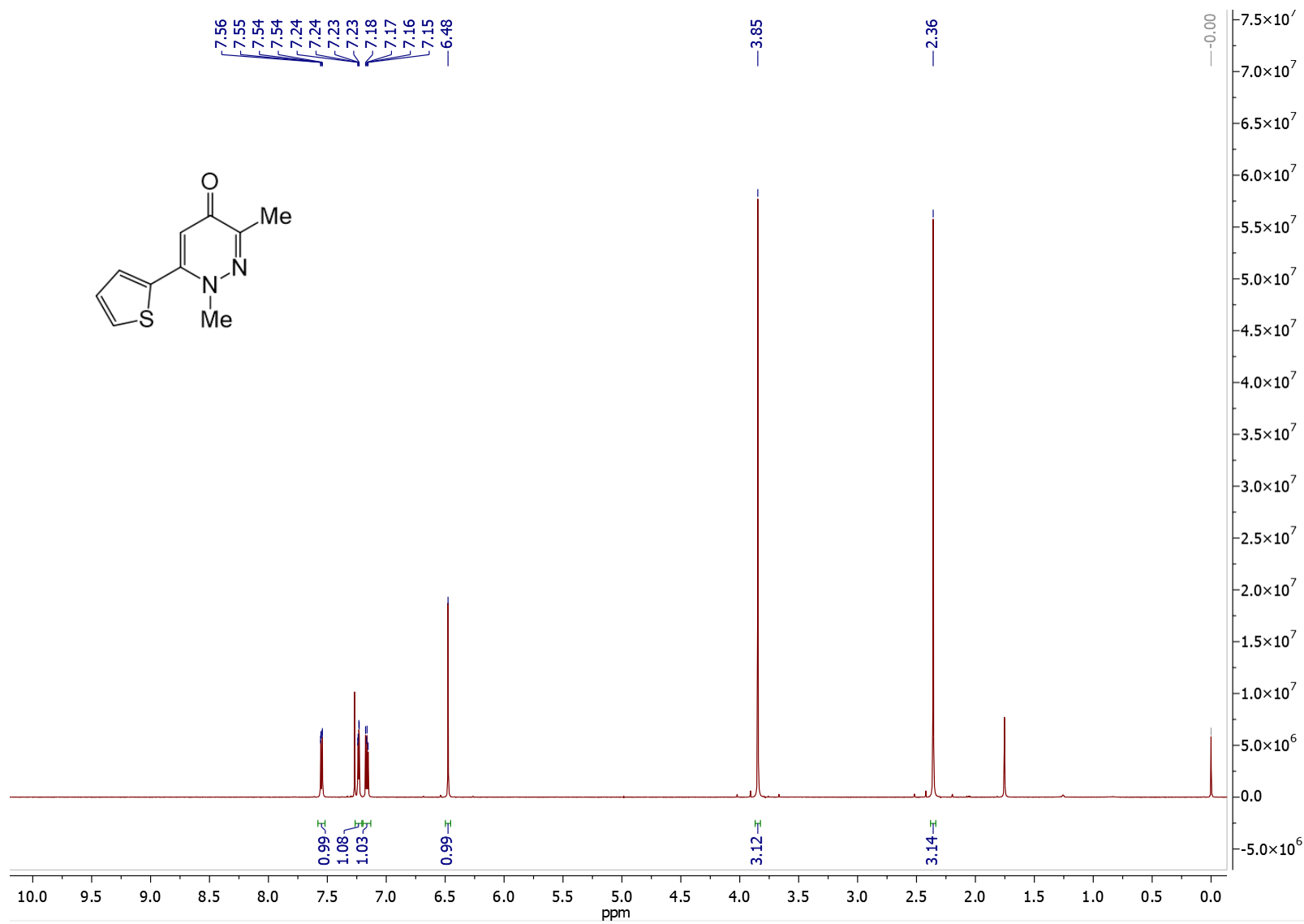


Figure S49. ^{13}C NMR spectrum of compound **9a**.

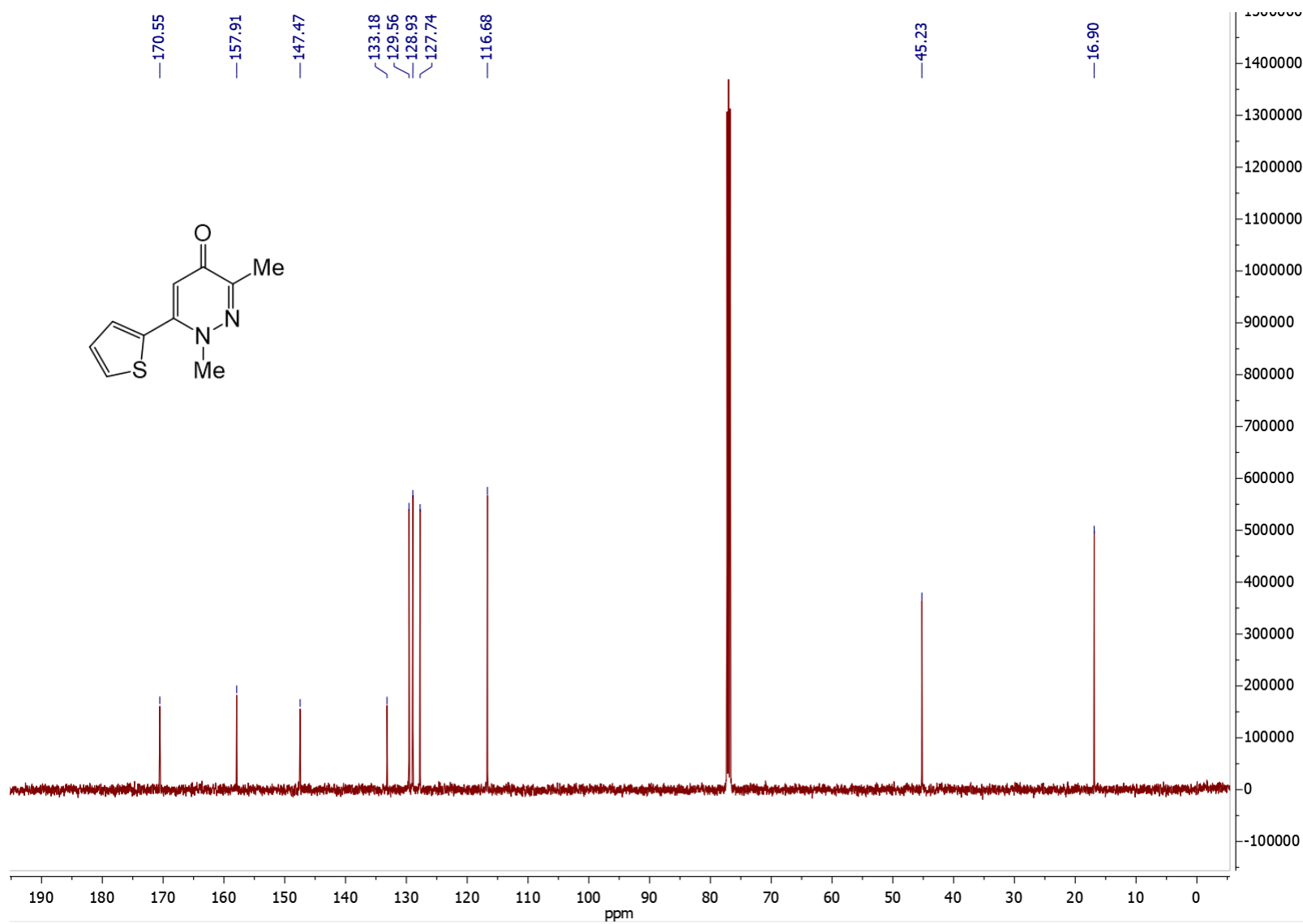


Figure S50. ^1H NMR spectrum of compound **9b**.

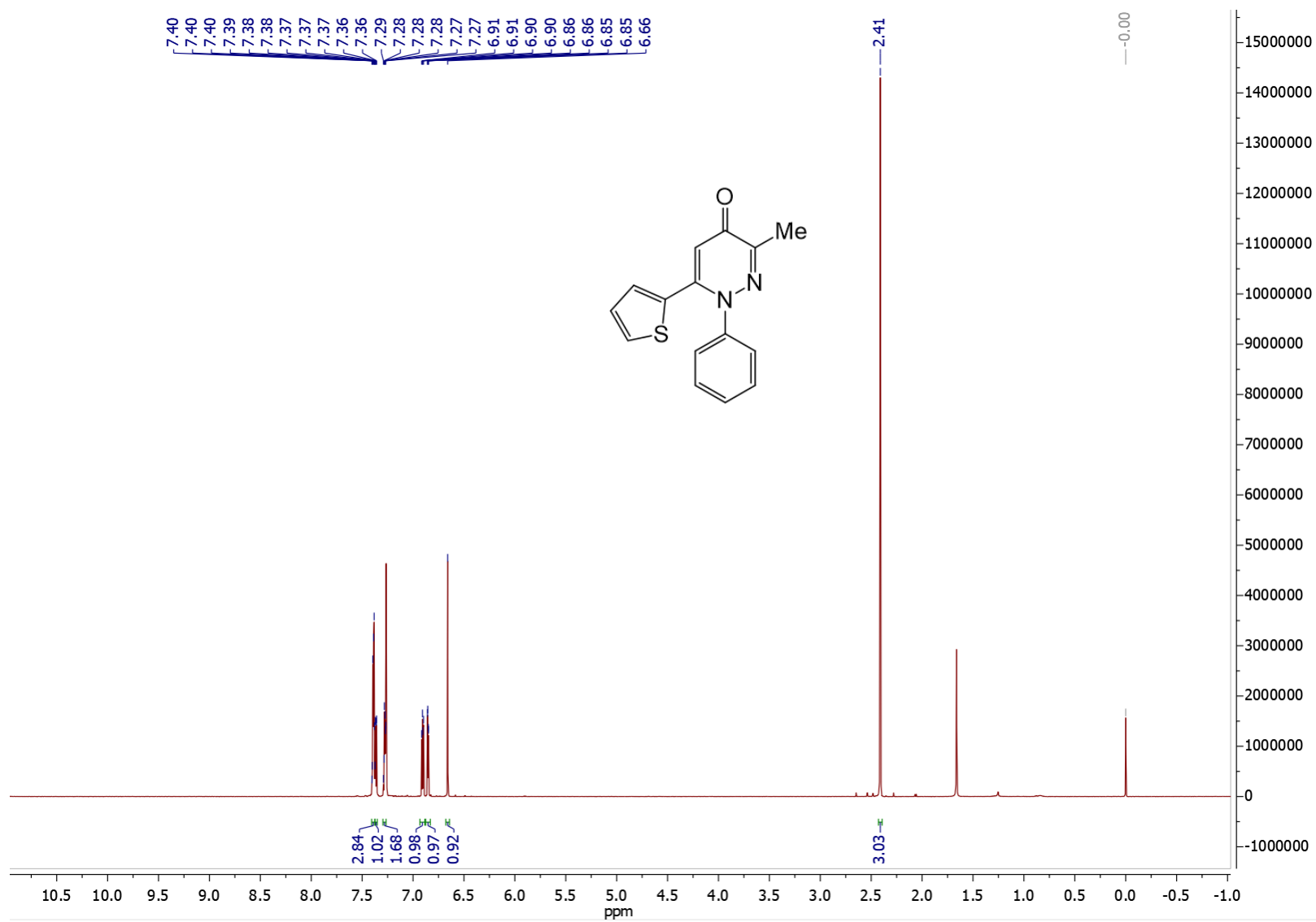


Figure S51. ^{13}C NMR spectrum of compound **9b**.

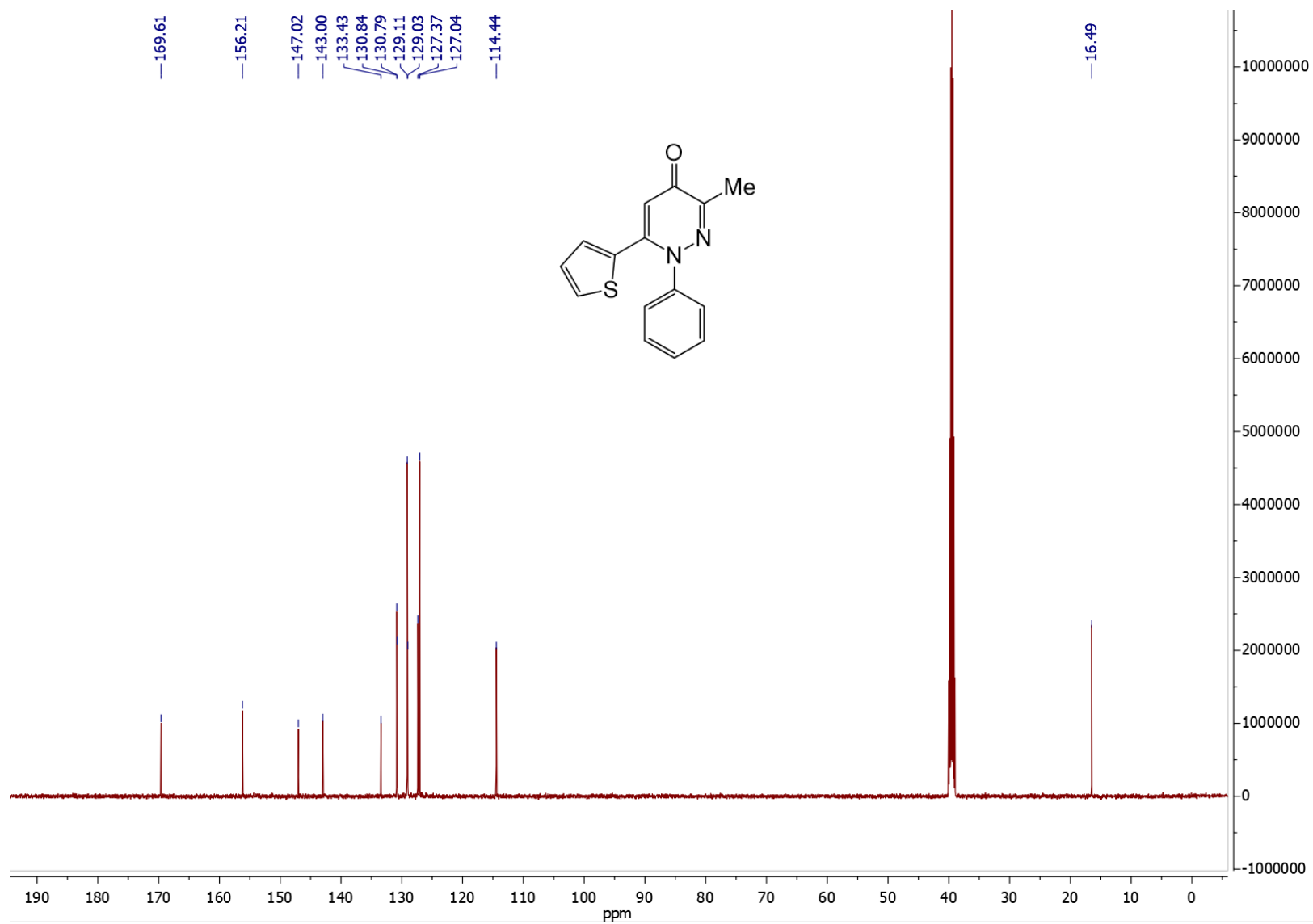


Figure S52. ^1H NMR spectrum of compound **10a**.

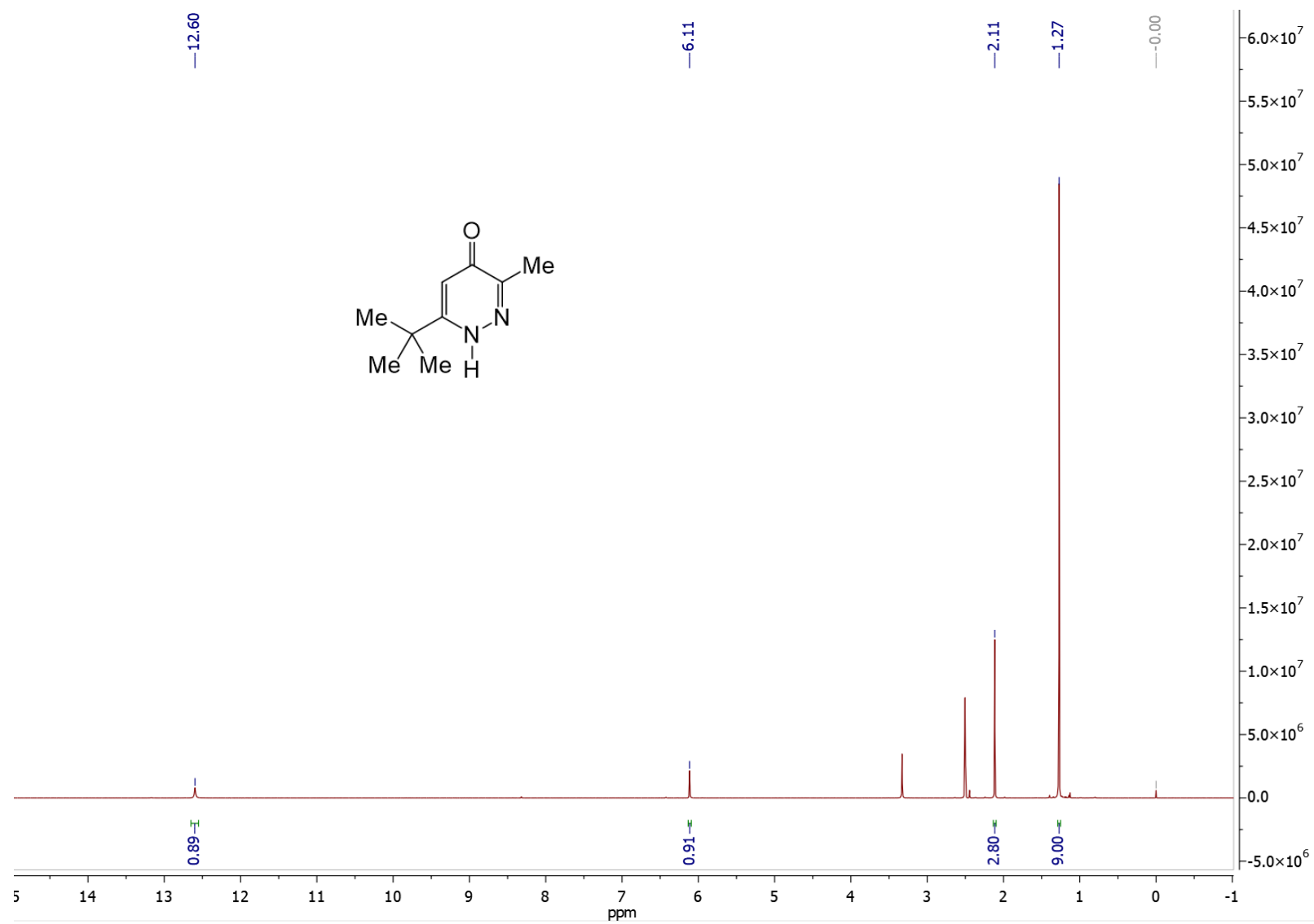


Figure S53. ^{13}C NMR spectrum of compound **10a**.

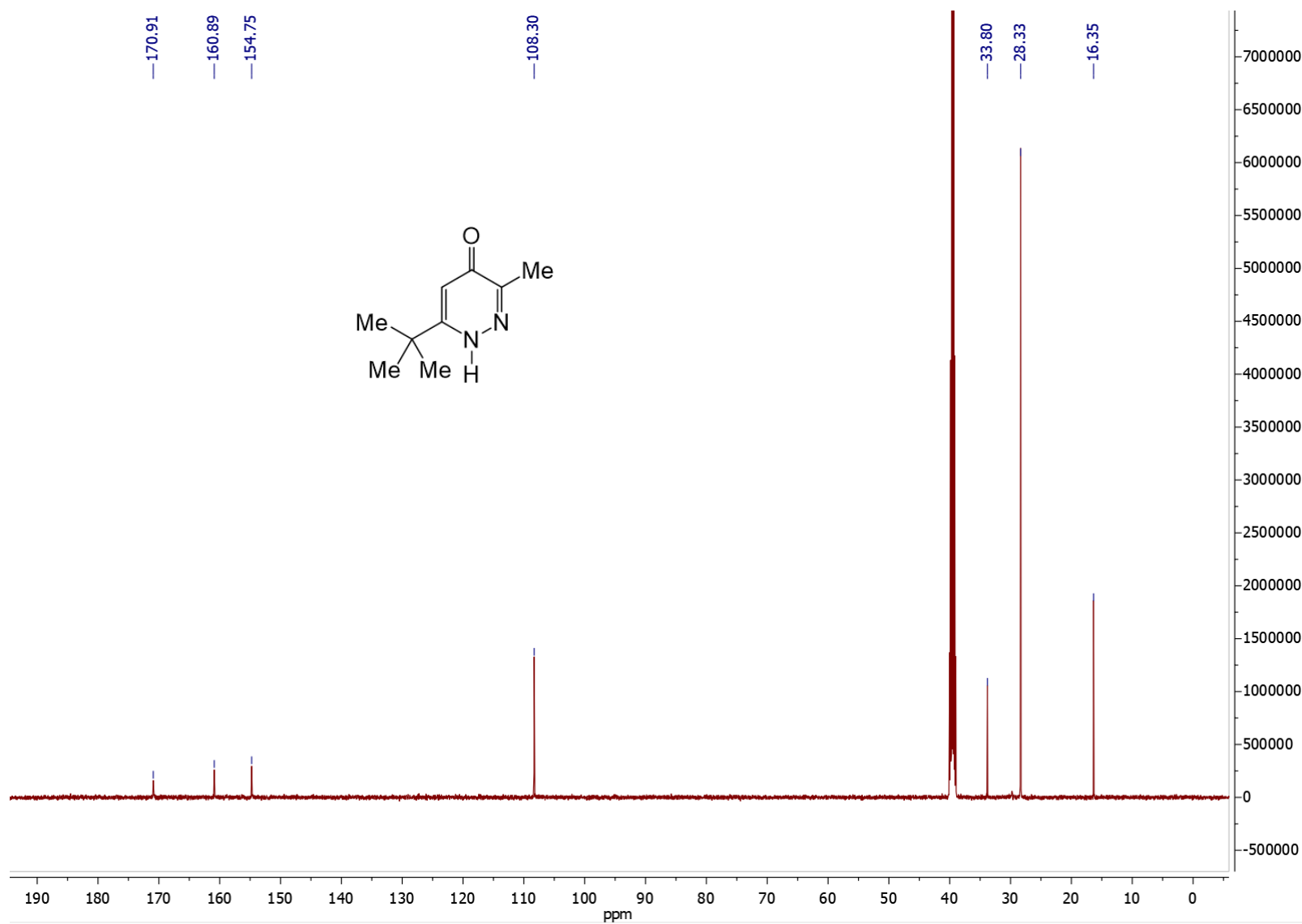


Figure S54. ^1H NMR spectrum of compound **10b**.

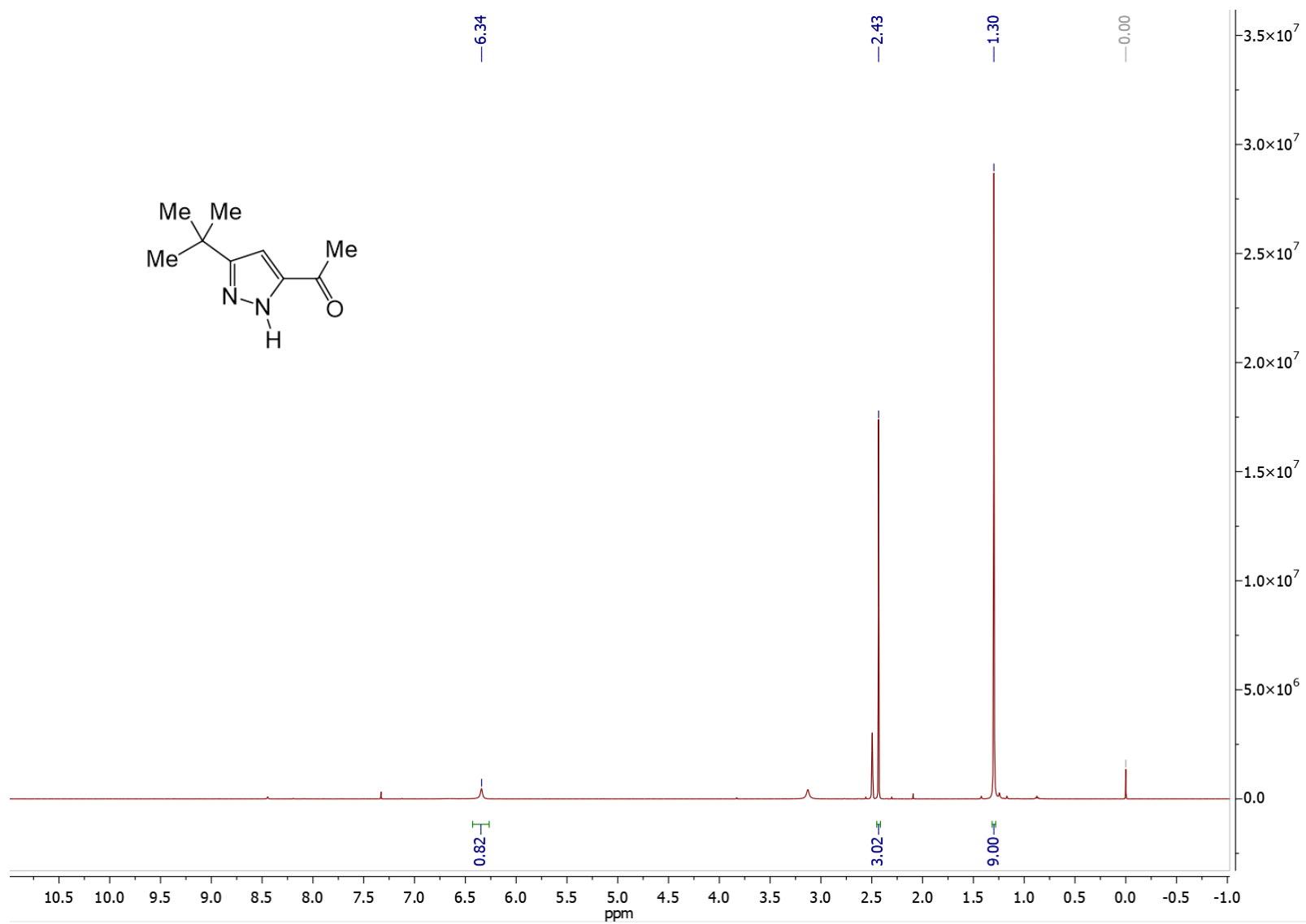


Figure S55. ^{13}C NMR spectrum of compound **10b**.

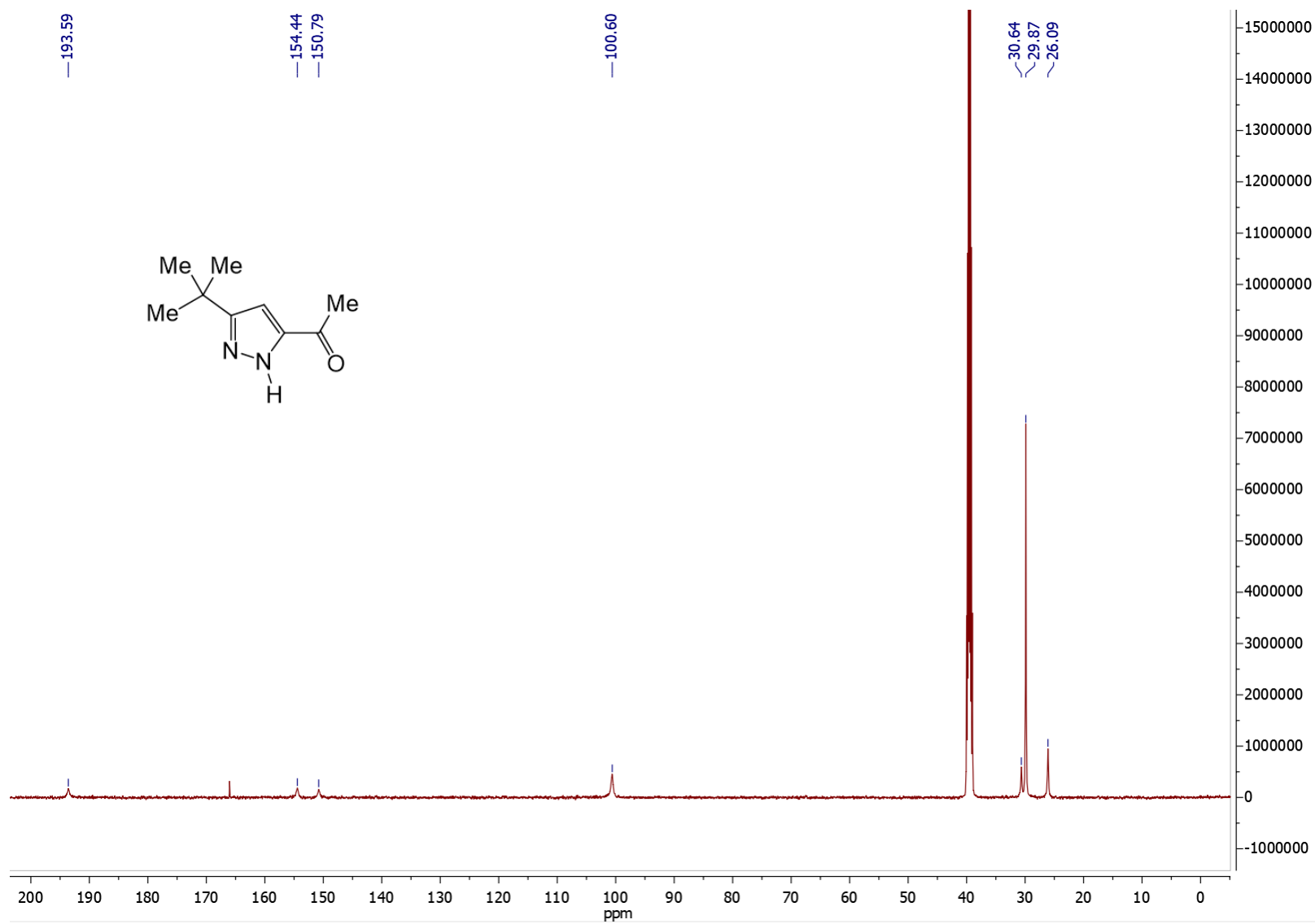


Figure S56. ^1H NMR spectrum of compound **11**.

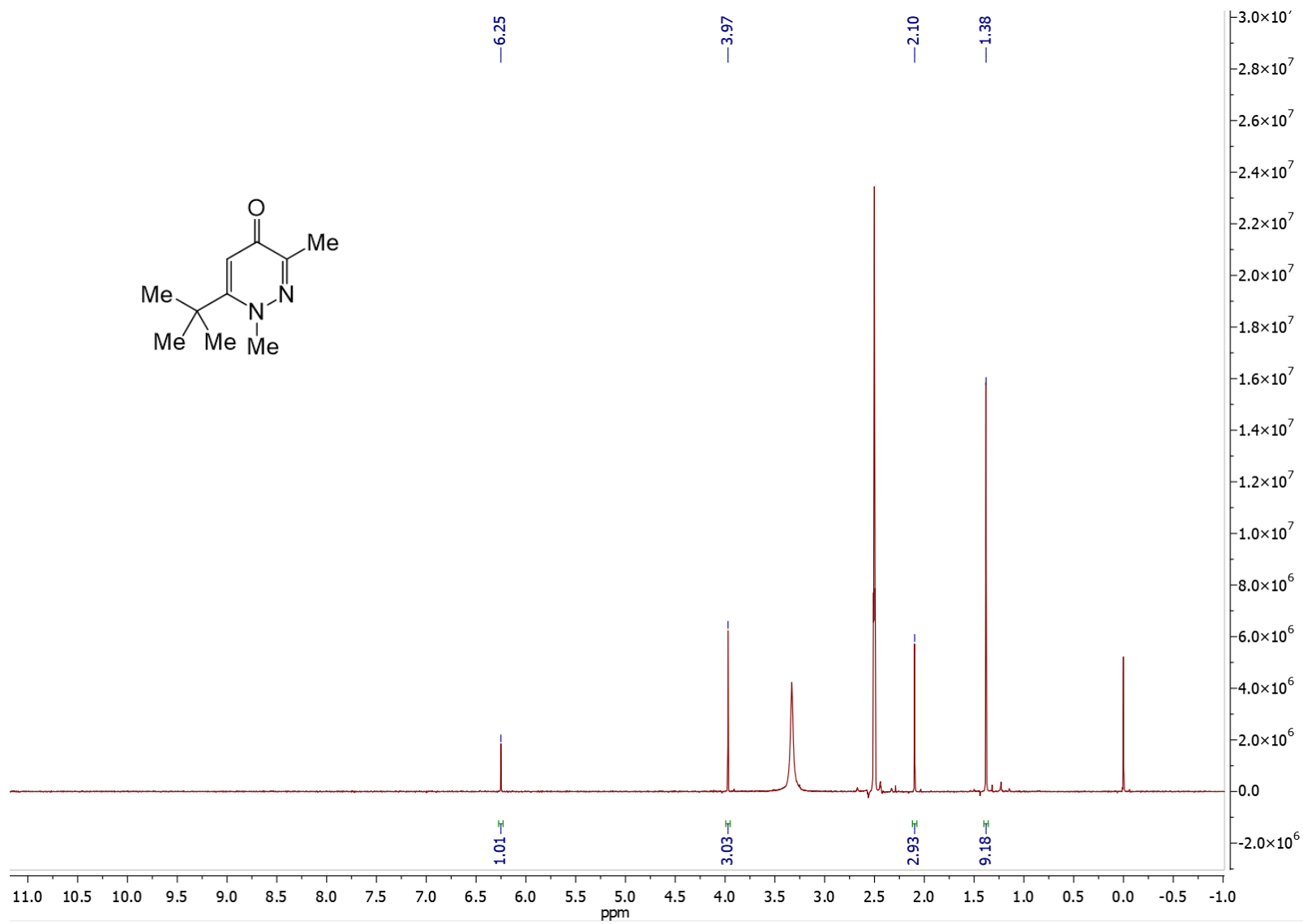


Figure S57. ^{13}C NMR spectrum of compound **11**.

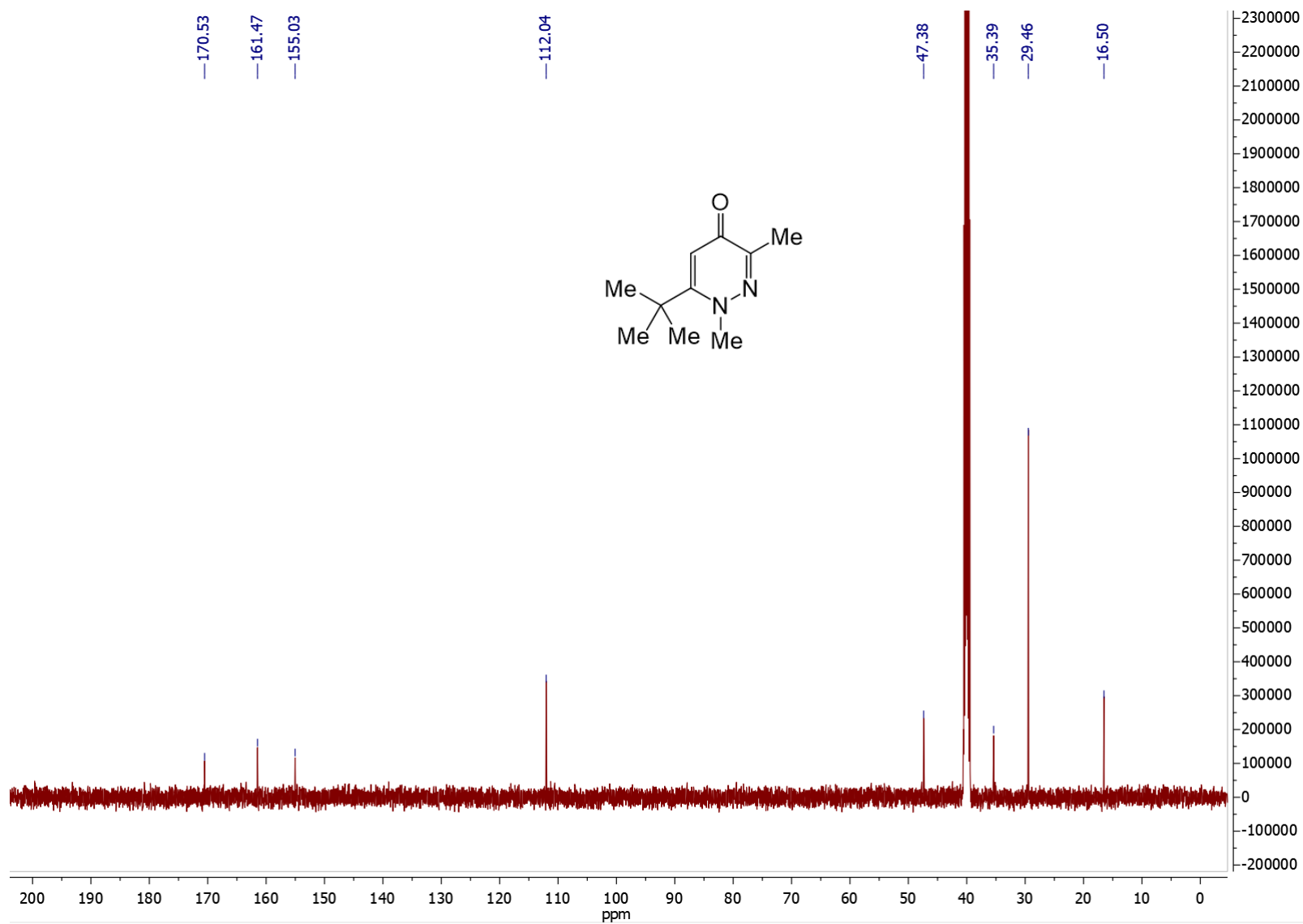


Figure S58. ^1H NMR spectrum of compound **12**.

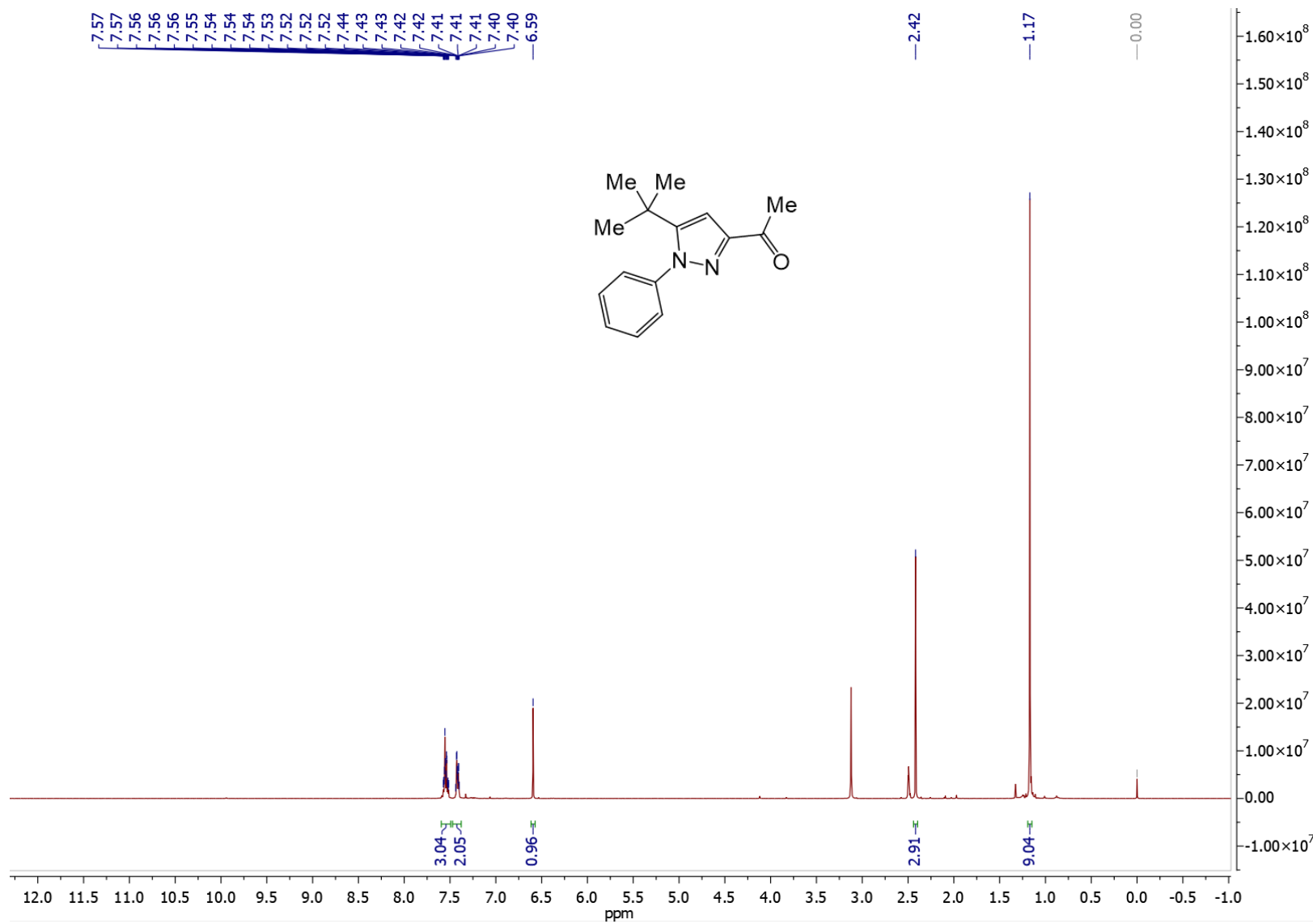


Figure S59. ^{13}C NMR spectrum of compound **12**.

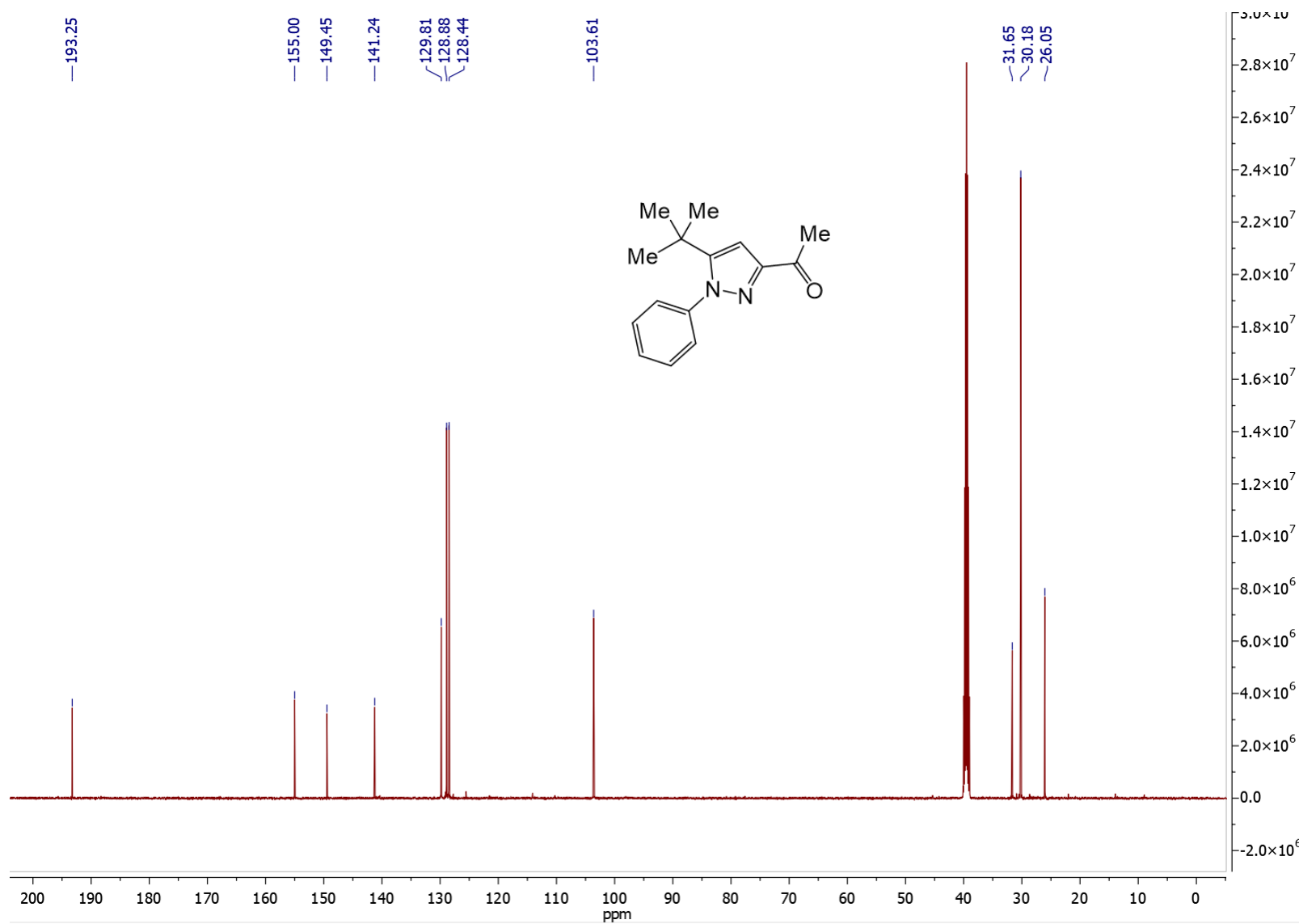


Figure S60. ^1H NMR spectrum of compound **13a**.

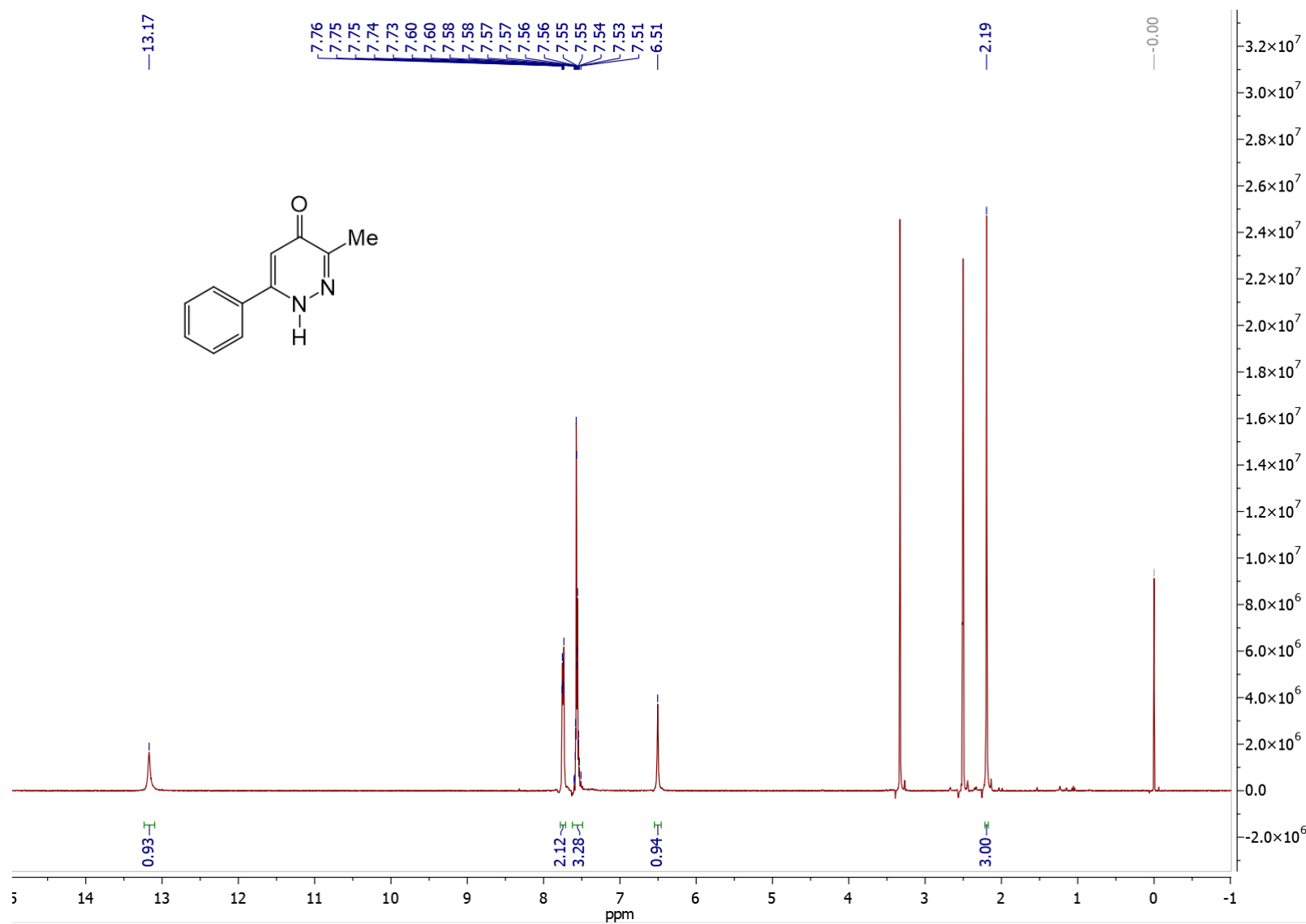


Figure S61. ^{13}C NMR spectrum of compound **13a**.

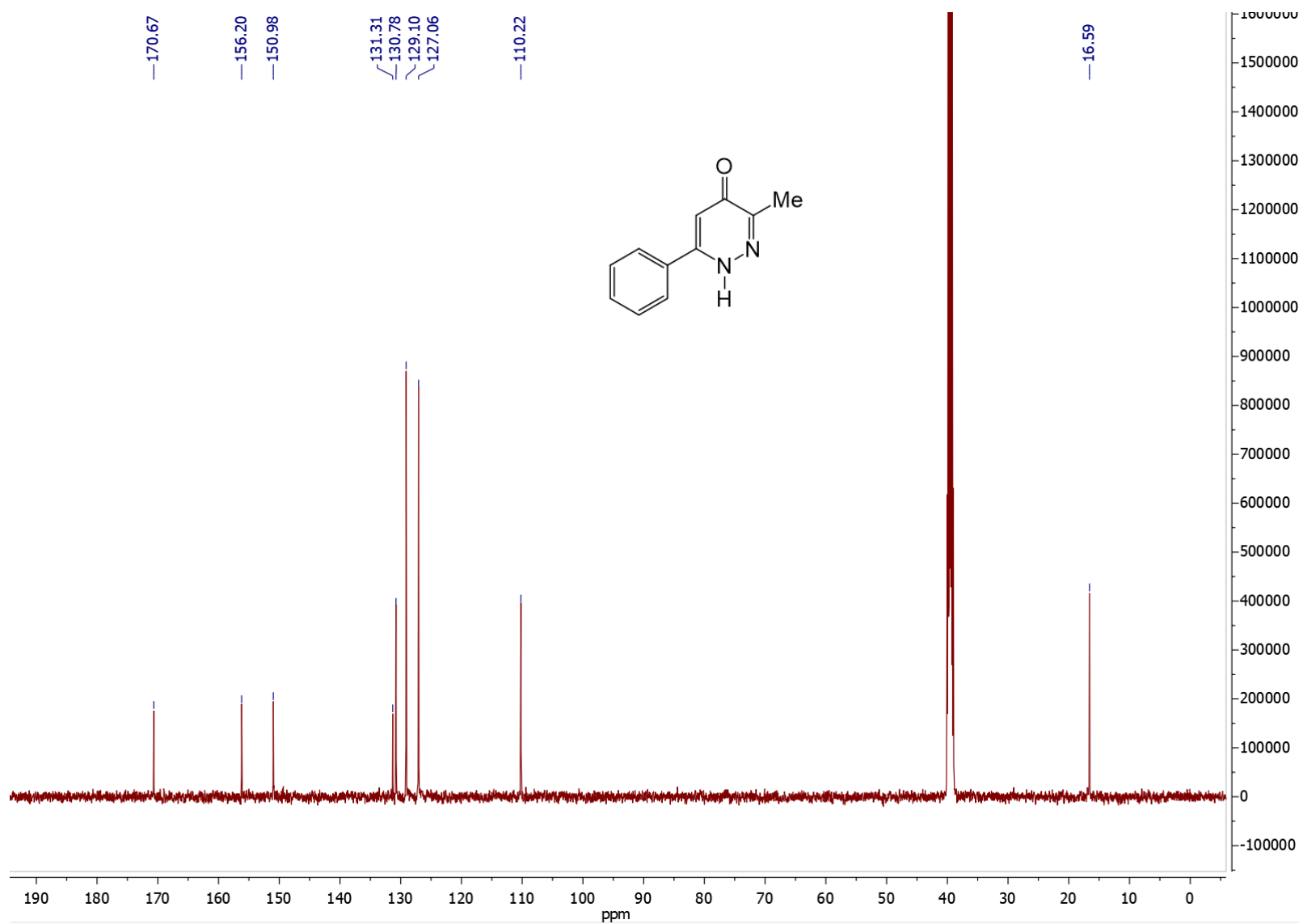


Figure S62. ^1H NMR spectrum of compound **13b**.

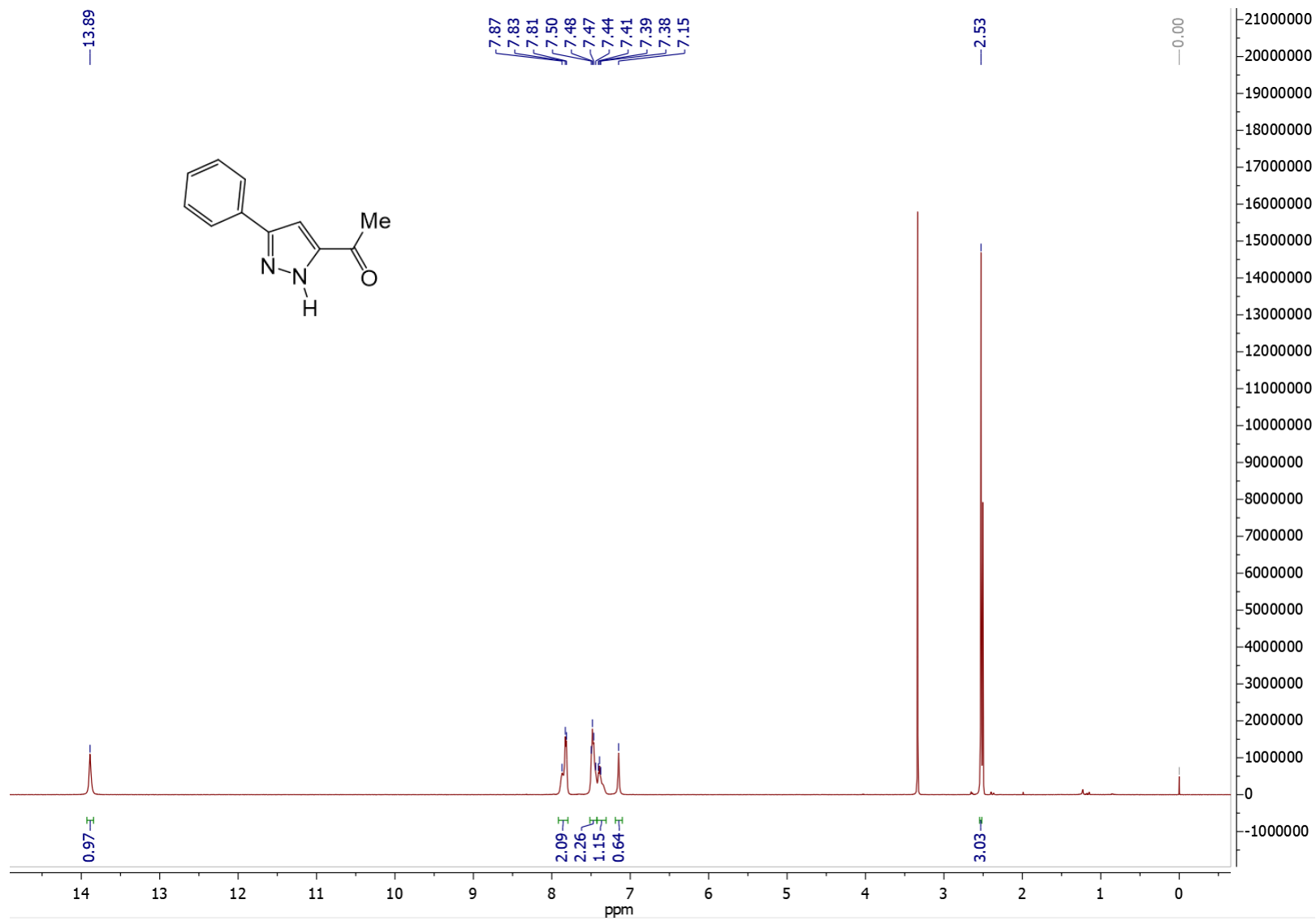


Figure S63. ^{13}C NMR spectrum of compound **13b**.

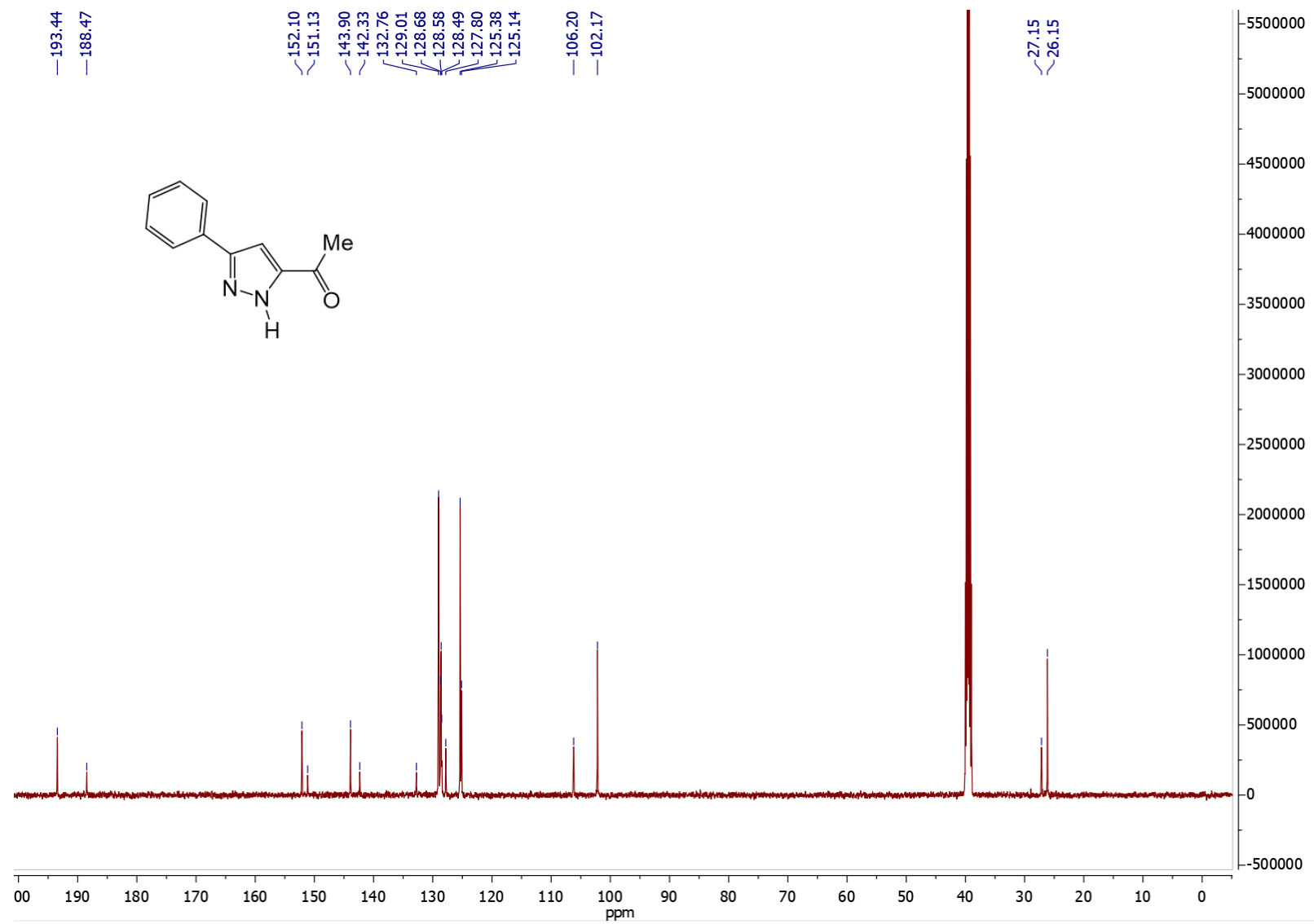


Figure S64. ^1H NMR spectrum of compound **14**.

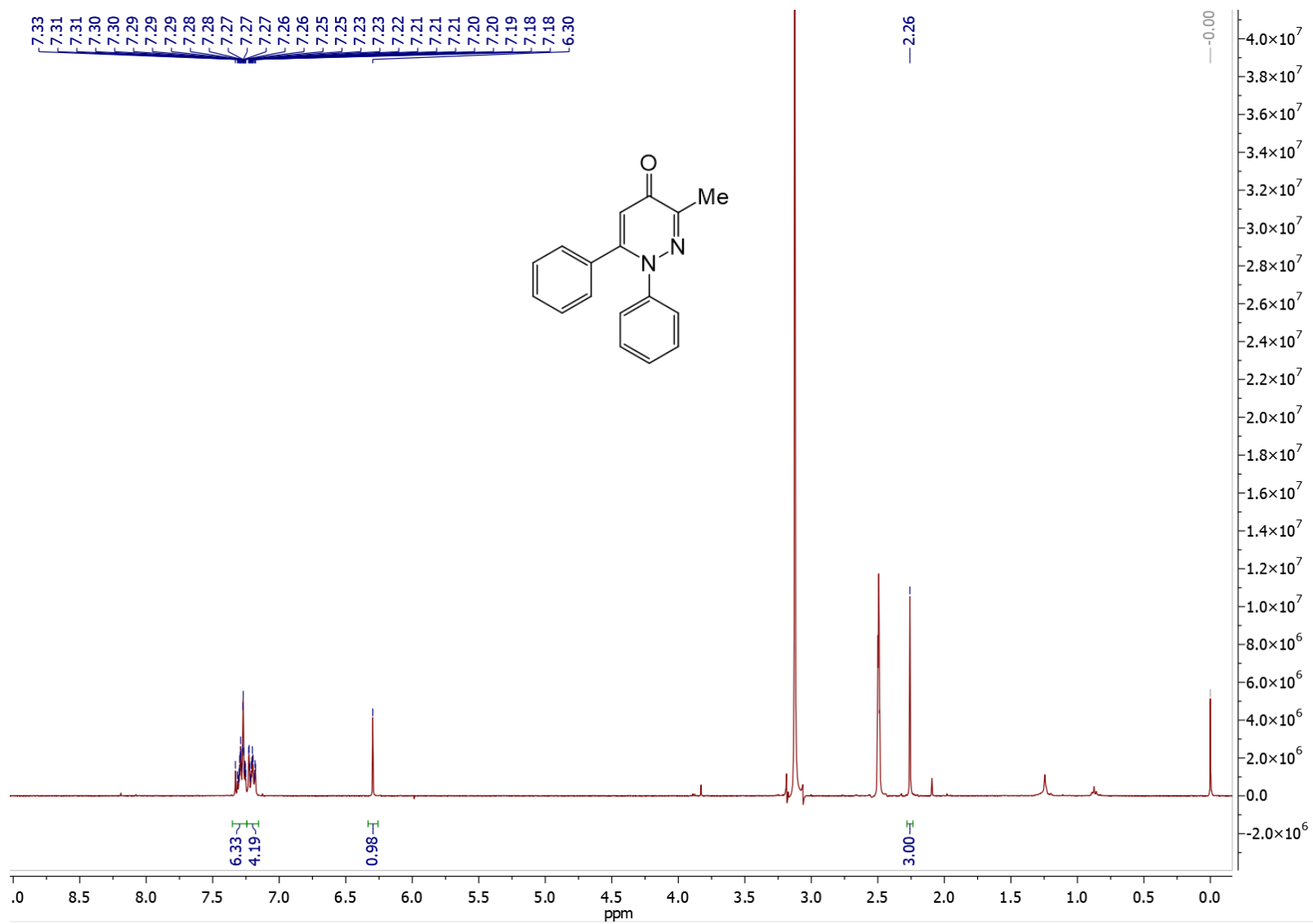


Figure S65. ^{13}C NMR spectrum of compound **14**.

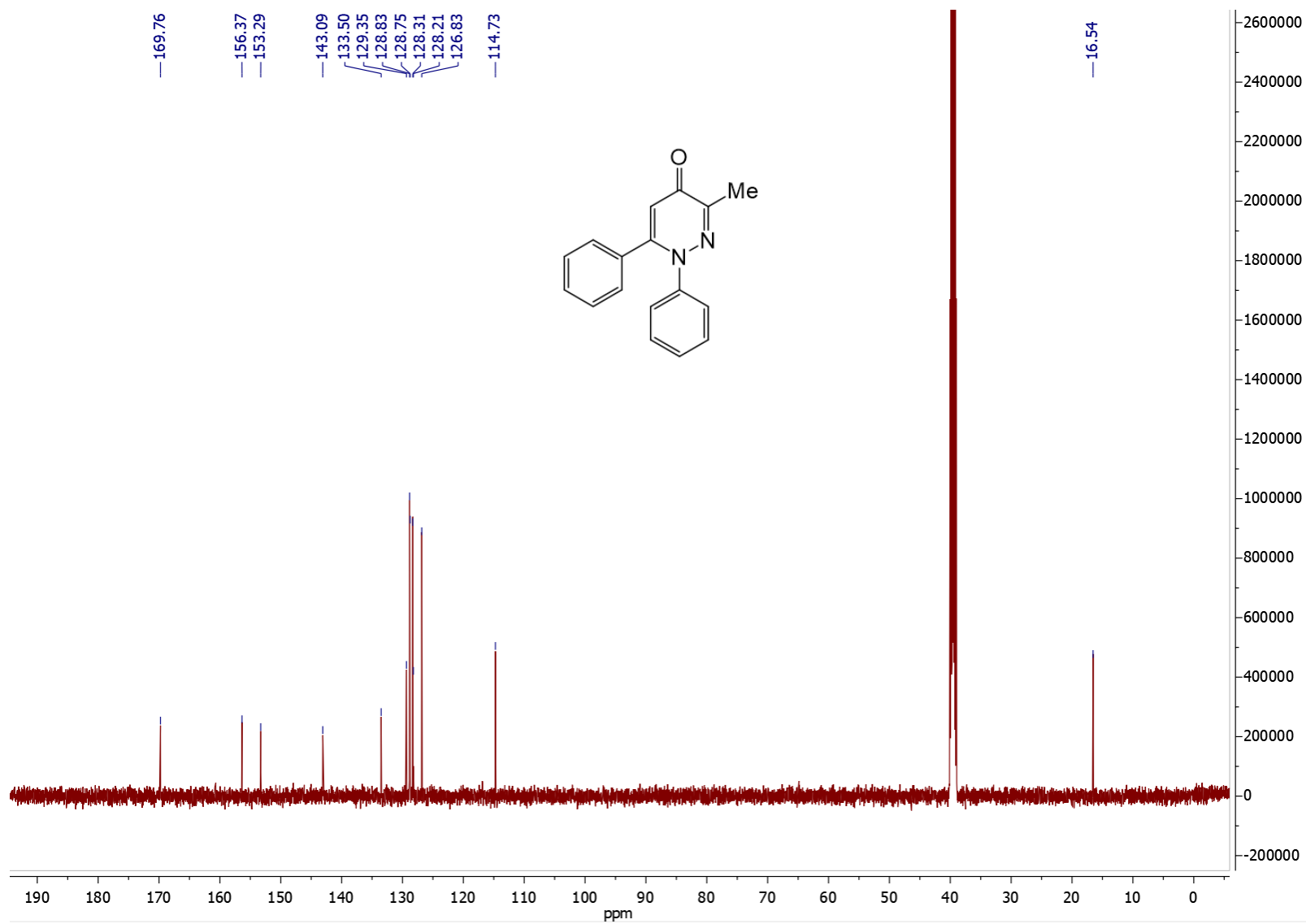


Figure S66. ^1H NMR spectrum of compound **15a**.

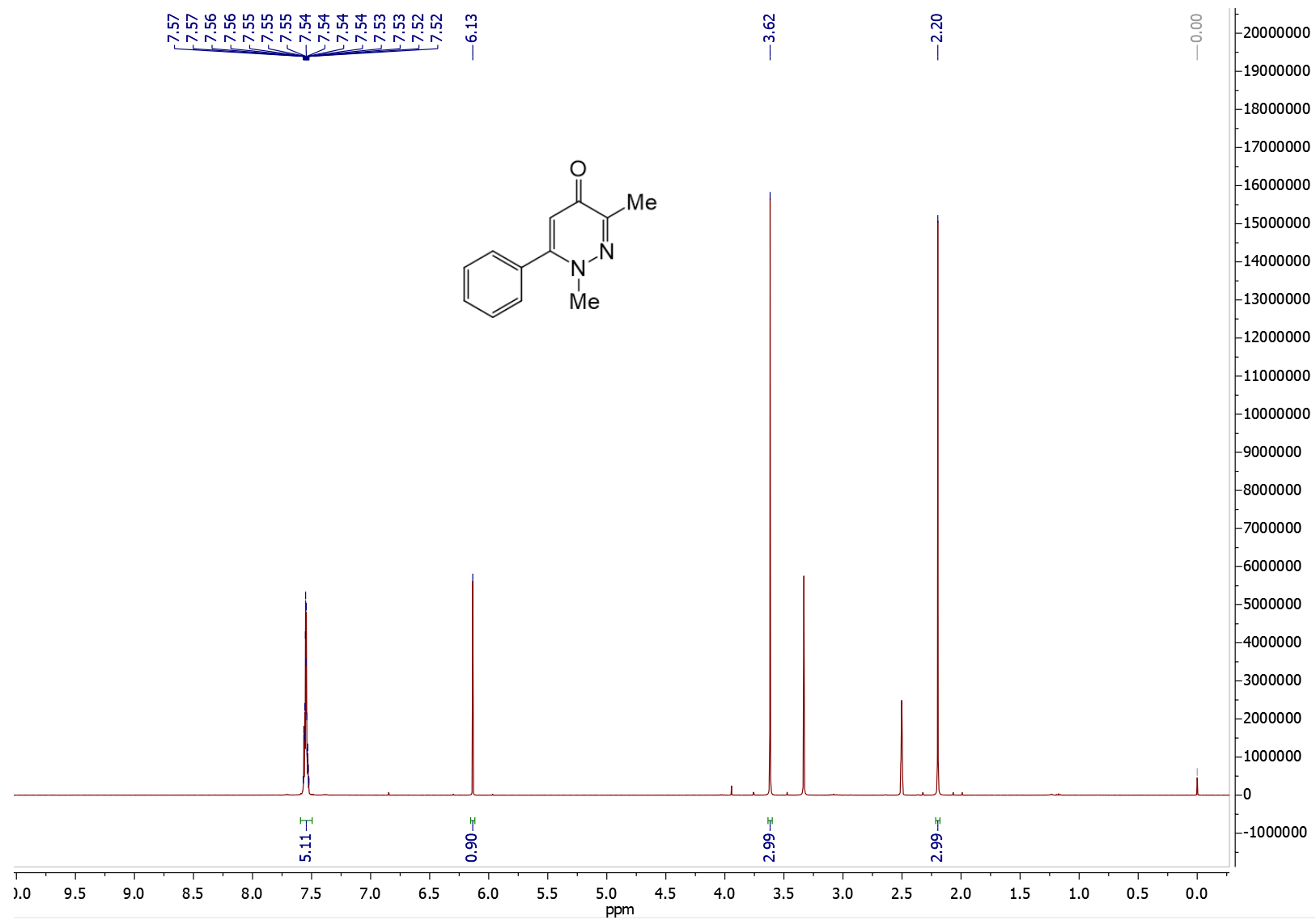


Figure S67. ^{13}C NMR spectrum of compound **15a**.

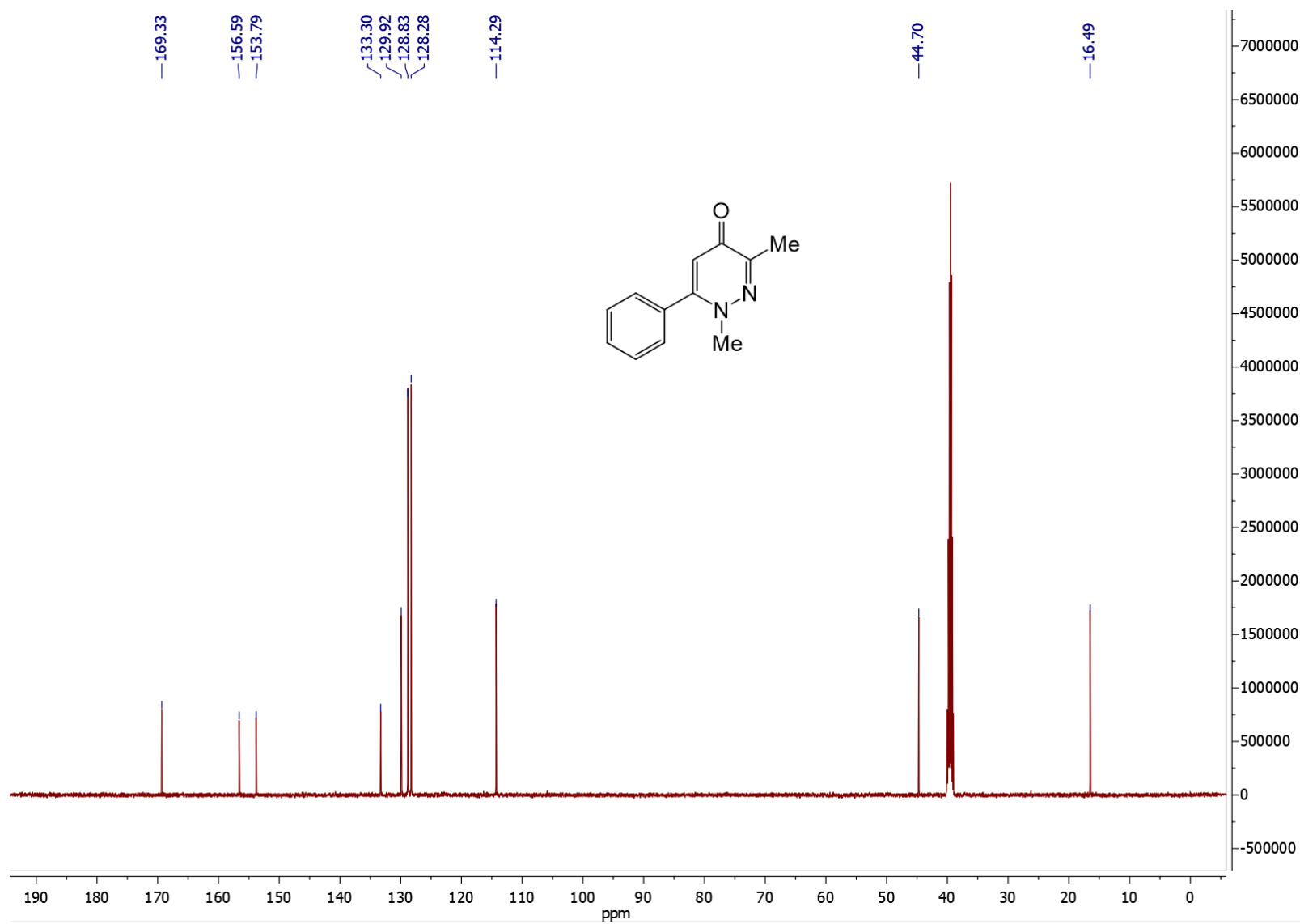


Figure S68. ^1H NMR spectrum of compound **15b**.

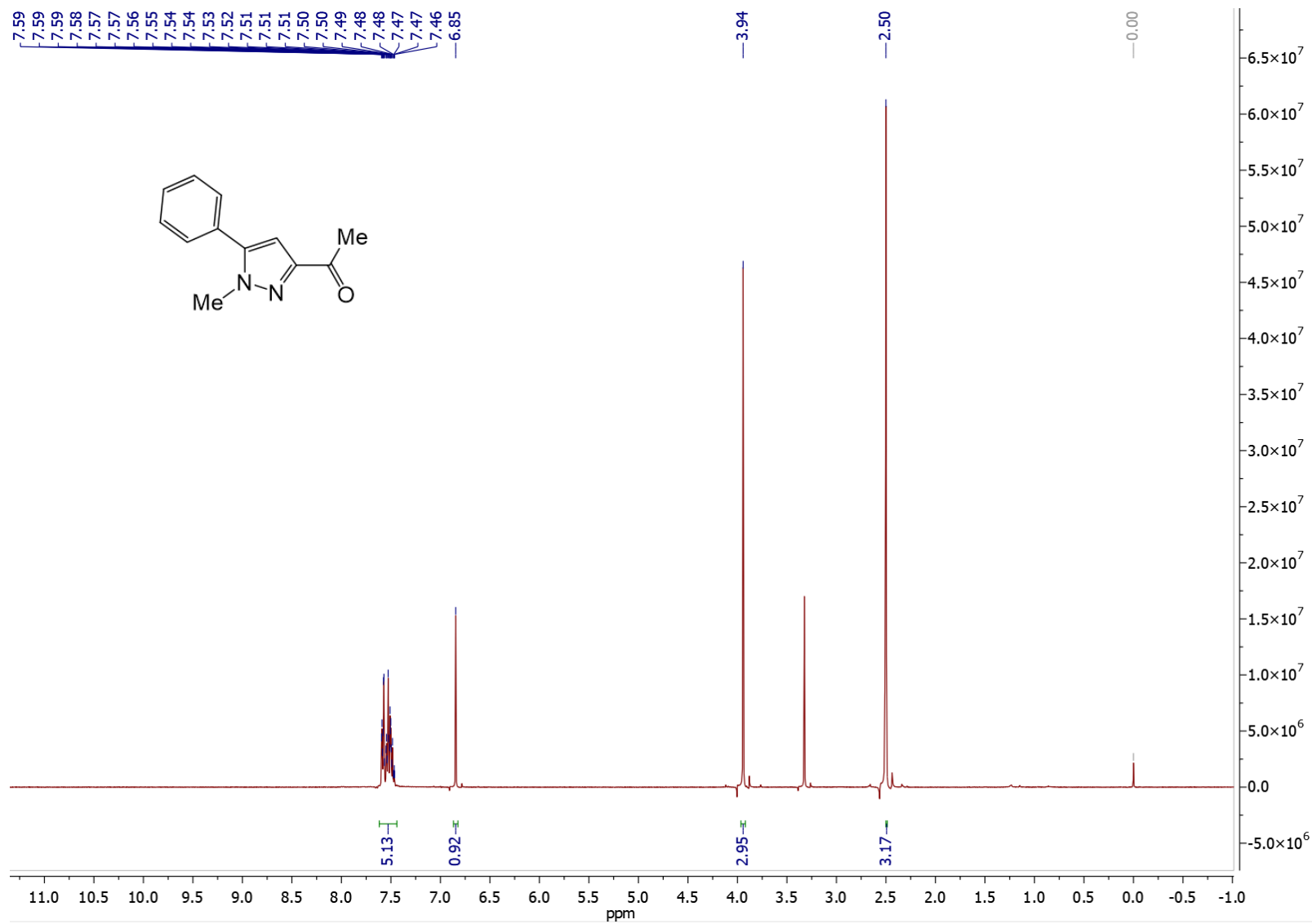


Figure S69. ^{13}C NMR spectrum of compound **15b**.

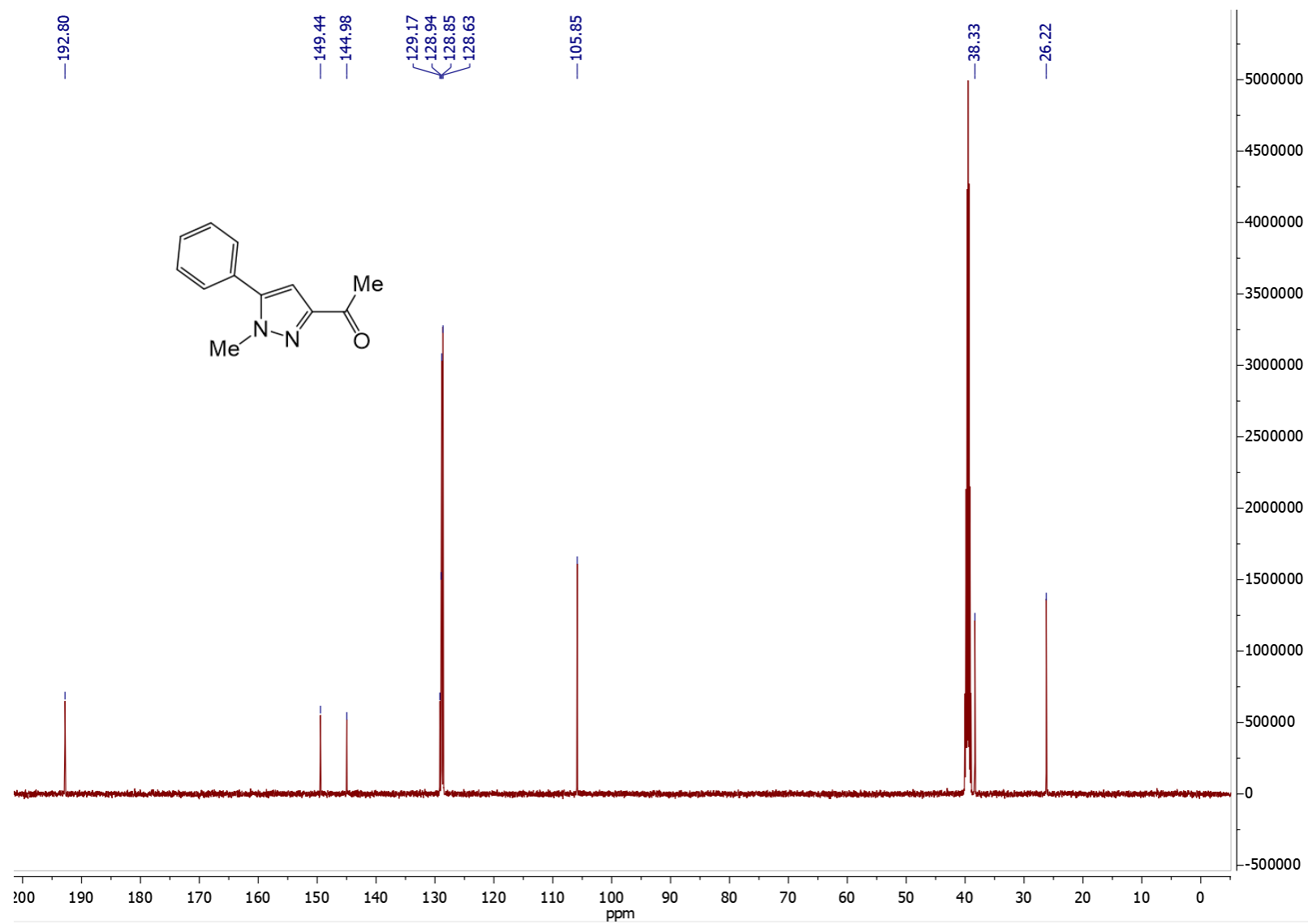


Figure S70. ^1H NMR spectrum of compound **16**.

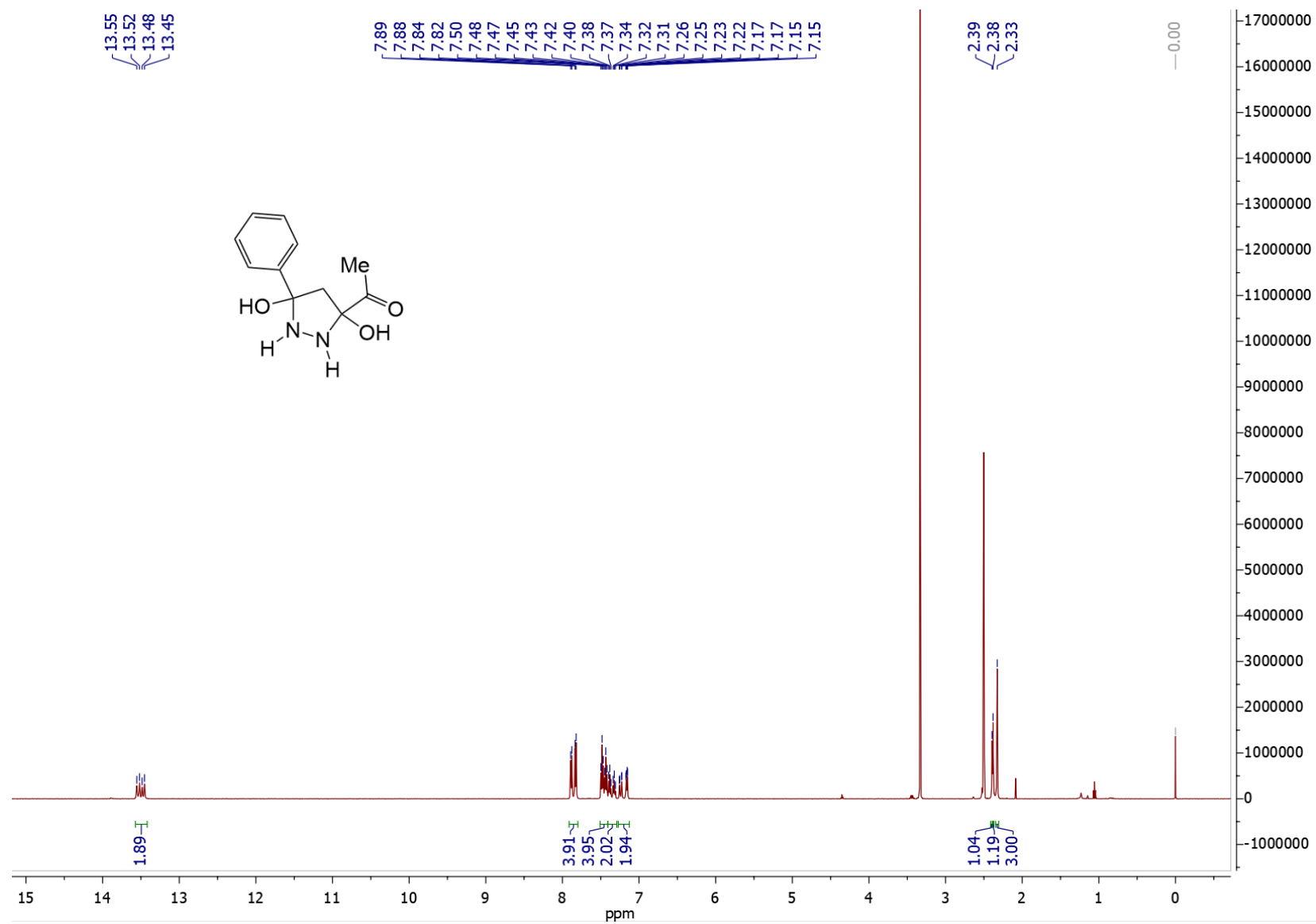


Figure S71. ^1H NMR spectrum of compound **17**.

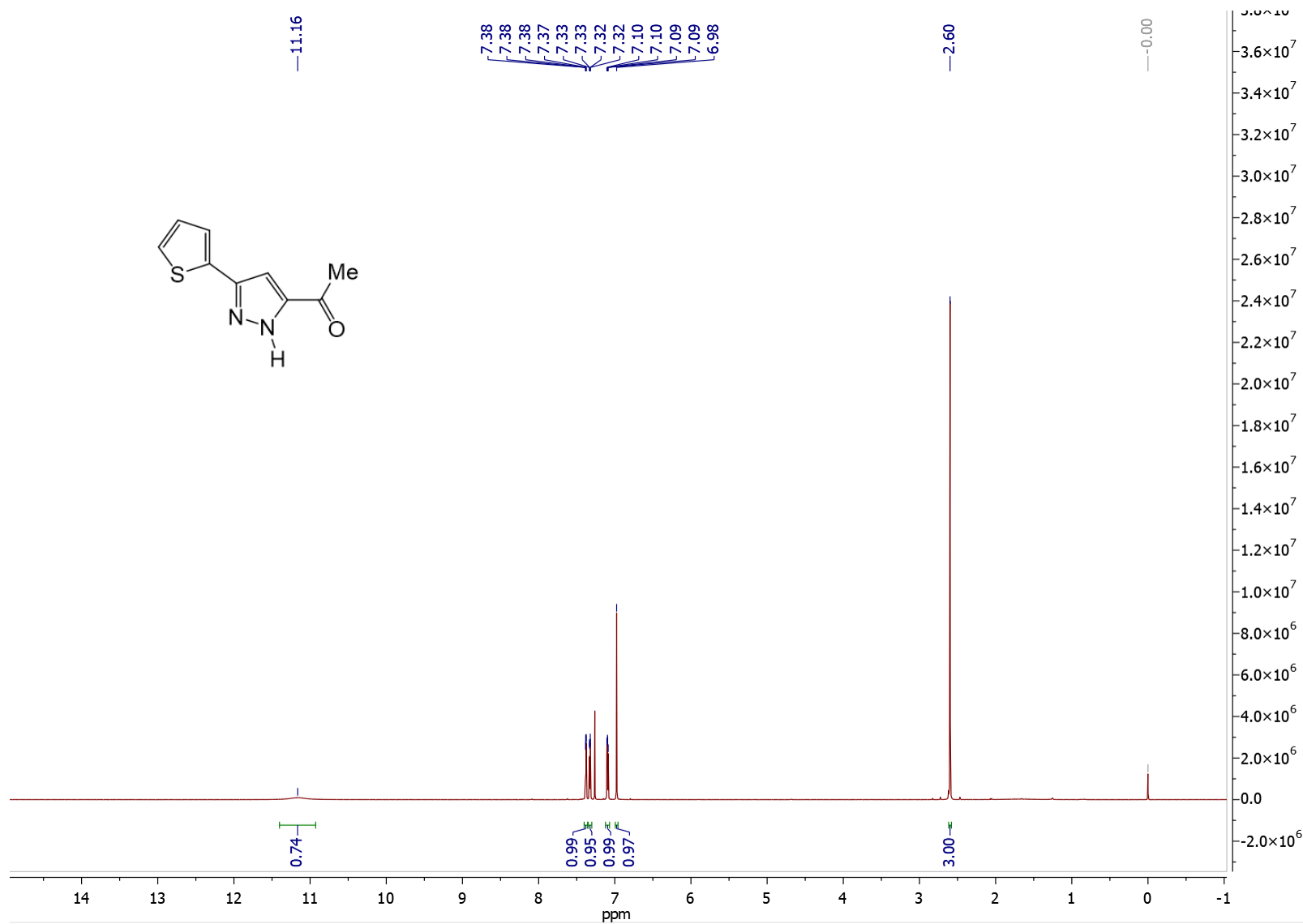


Figure S72. ^{13}C NMR spectrum of compound **17**.

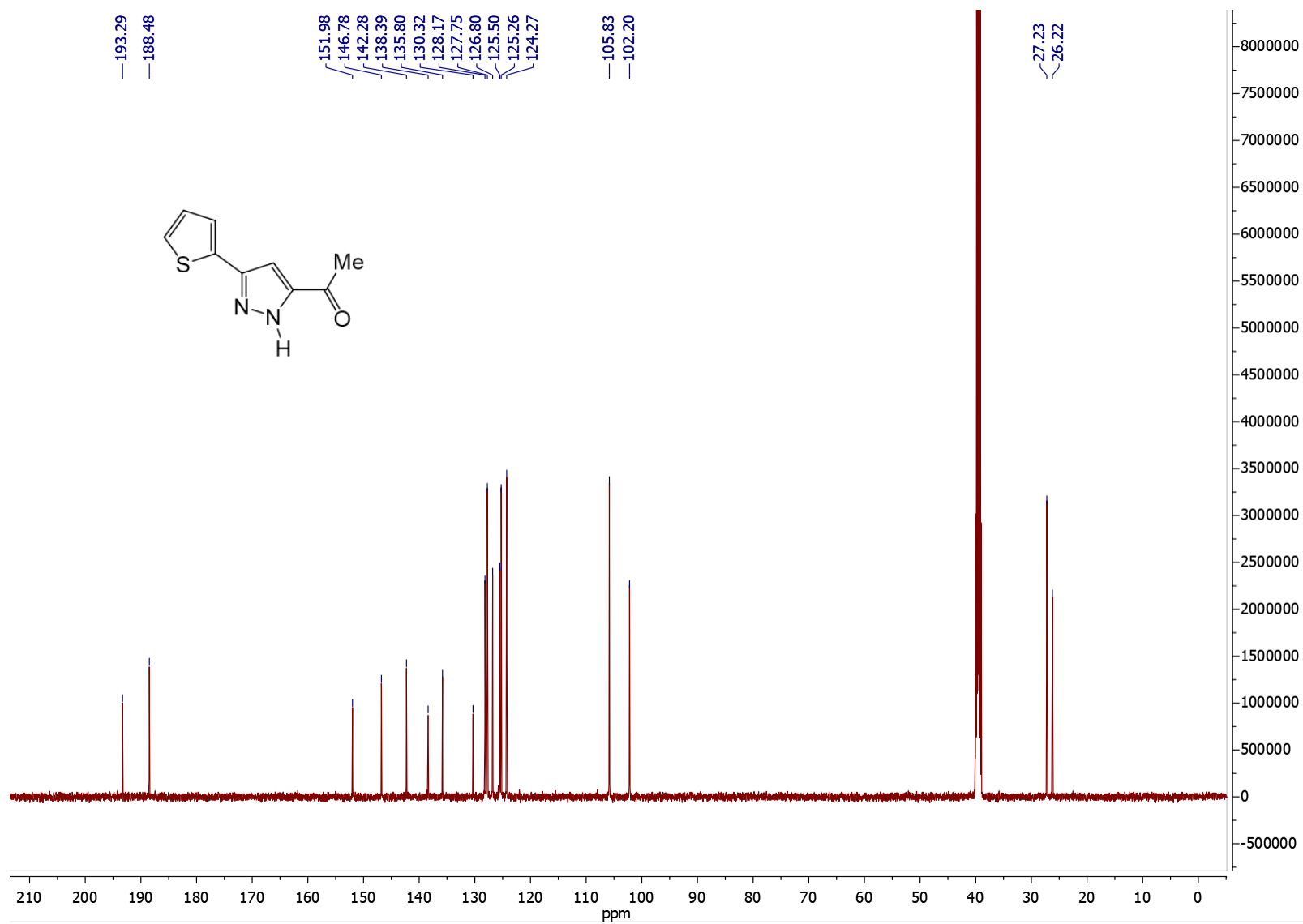


Figure S73. ^1H NMR spectrum of compound **18a**.

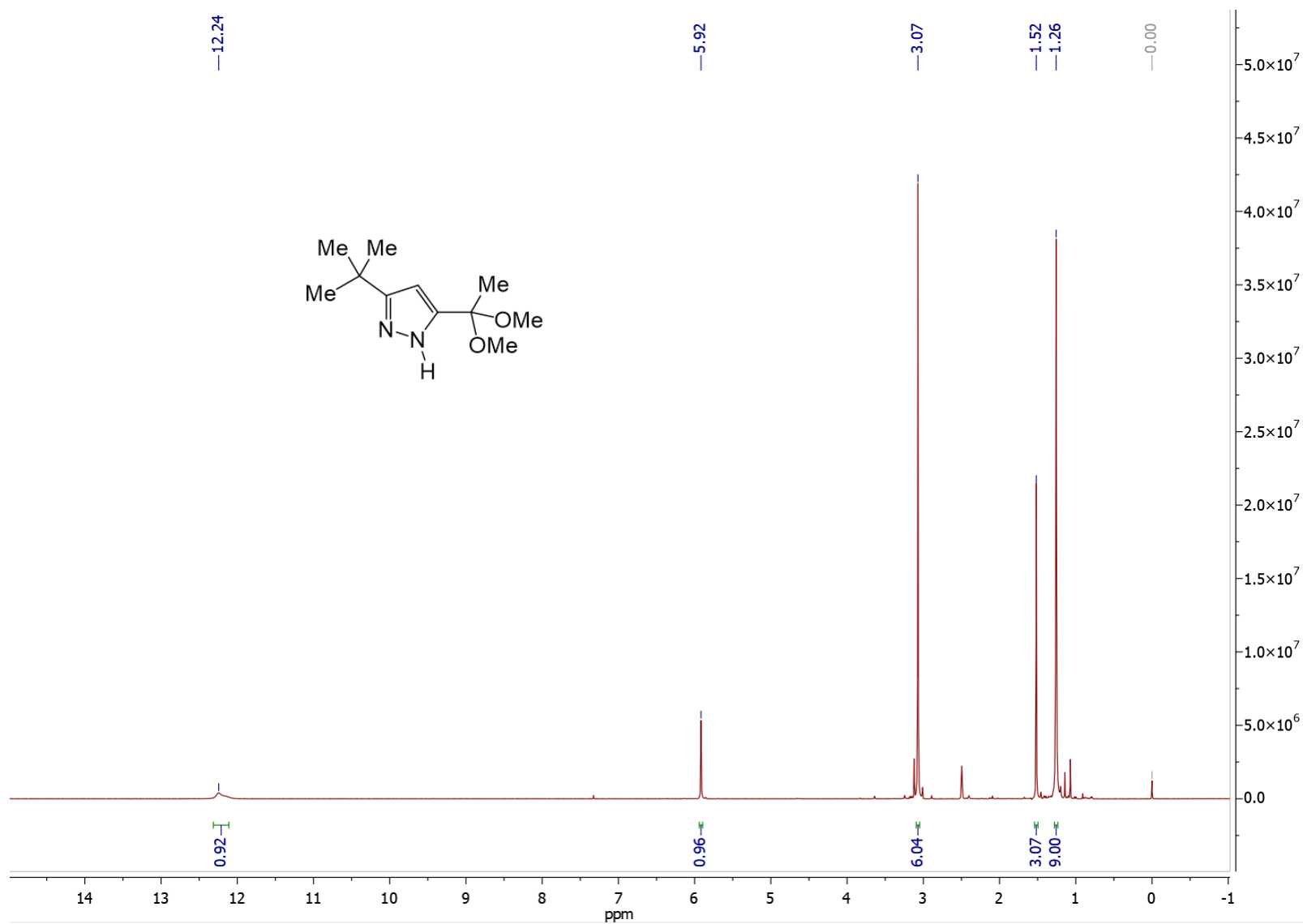


Figure S74. ^{13}C NMR spectrum of compound **18a**.

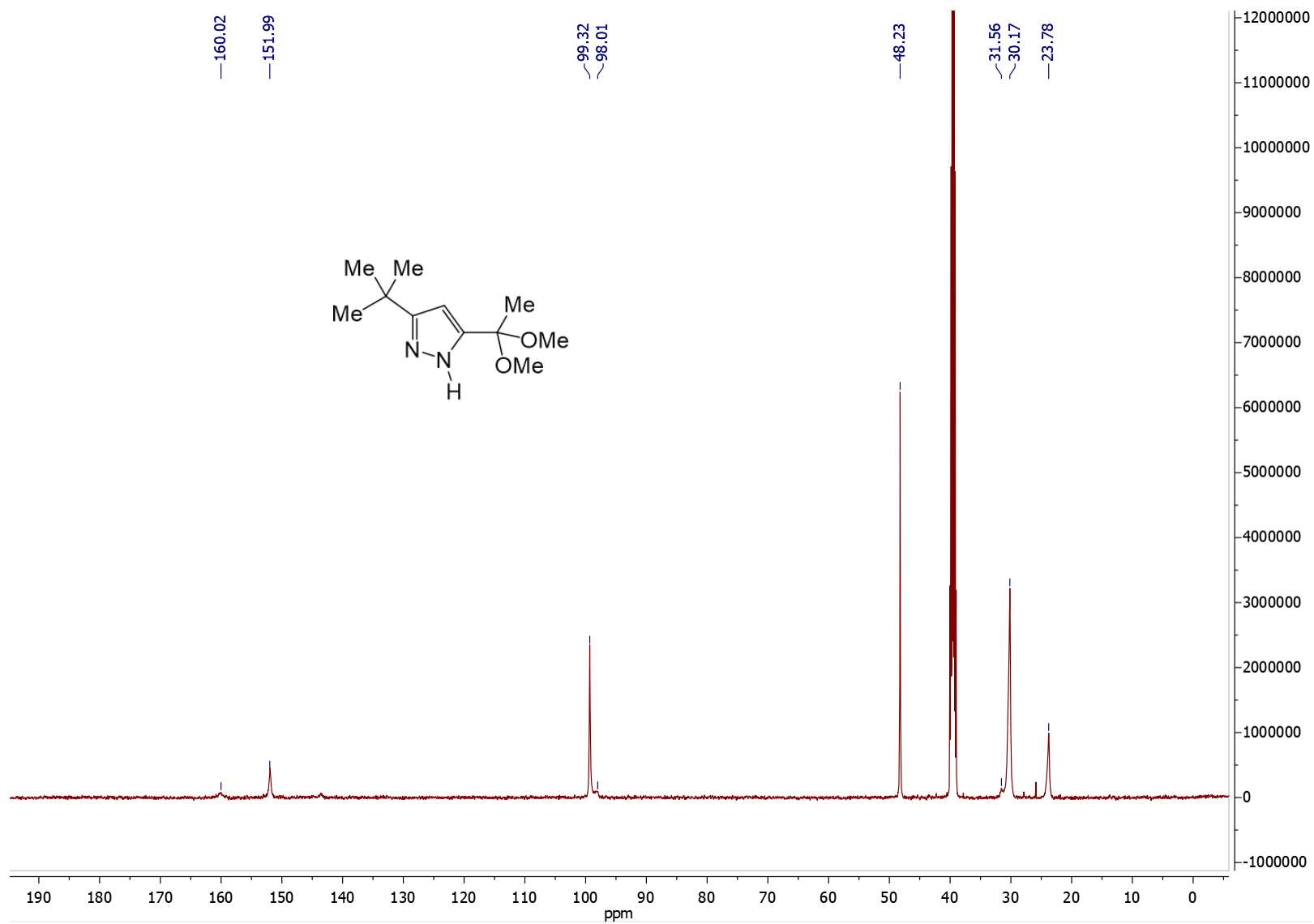


Figure S75. ^1H NMR spectrum of compound **18b**.

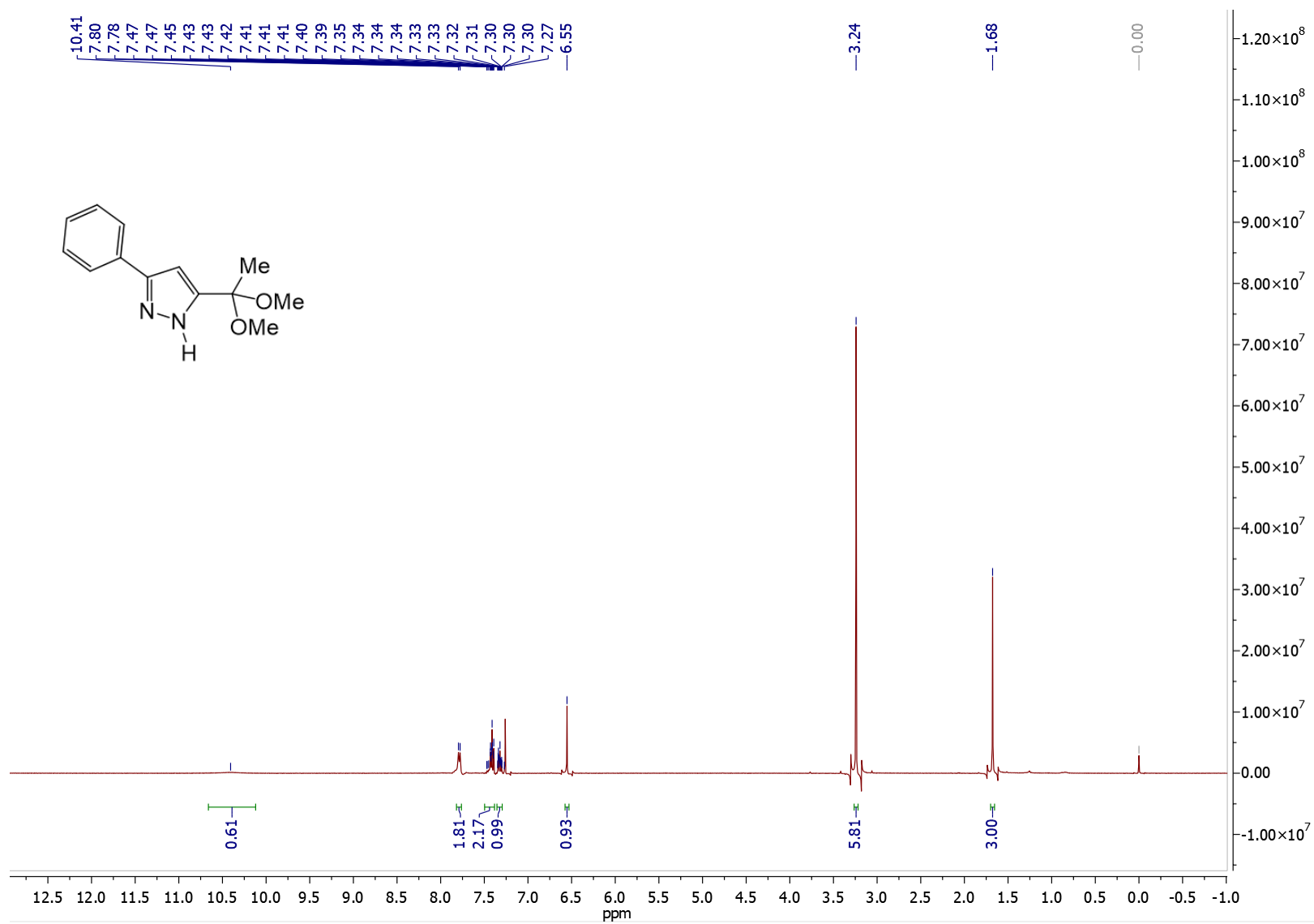


Figure S76. ^{13}C NMR spectrum of compound **18b**.

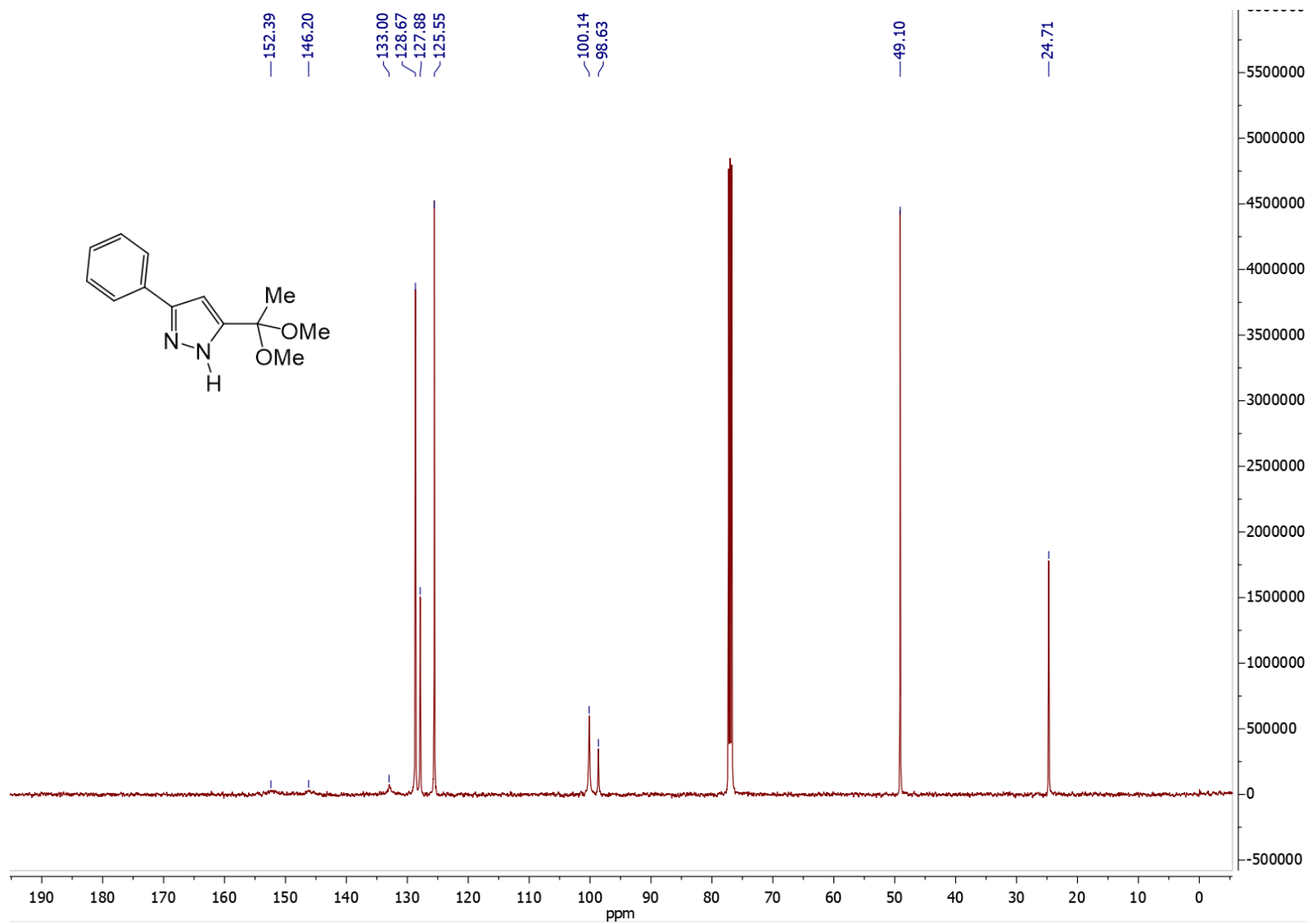


Figure S77. ^1H NMR spectrum of compound **18c**.

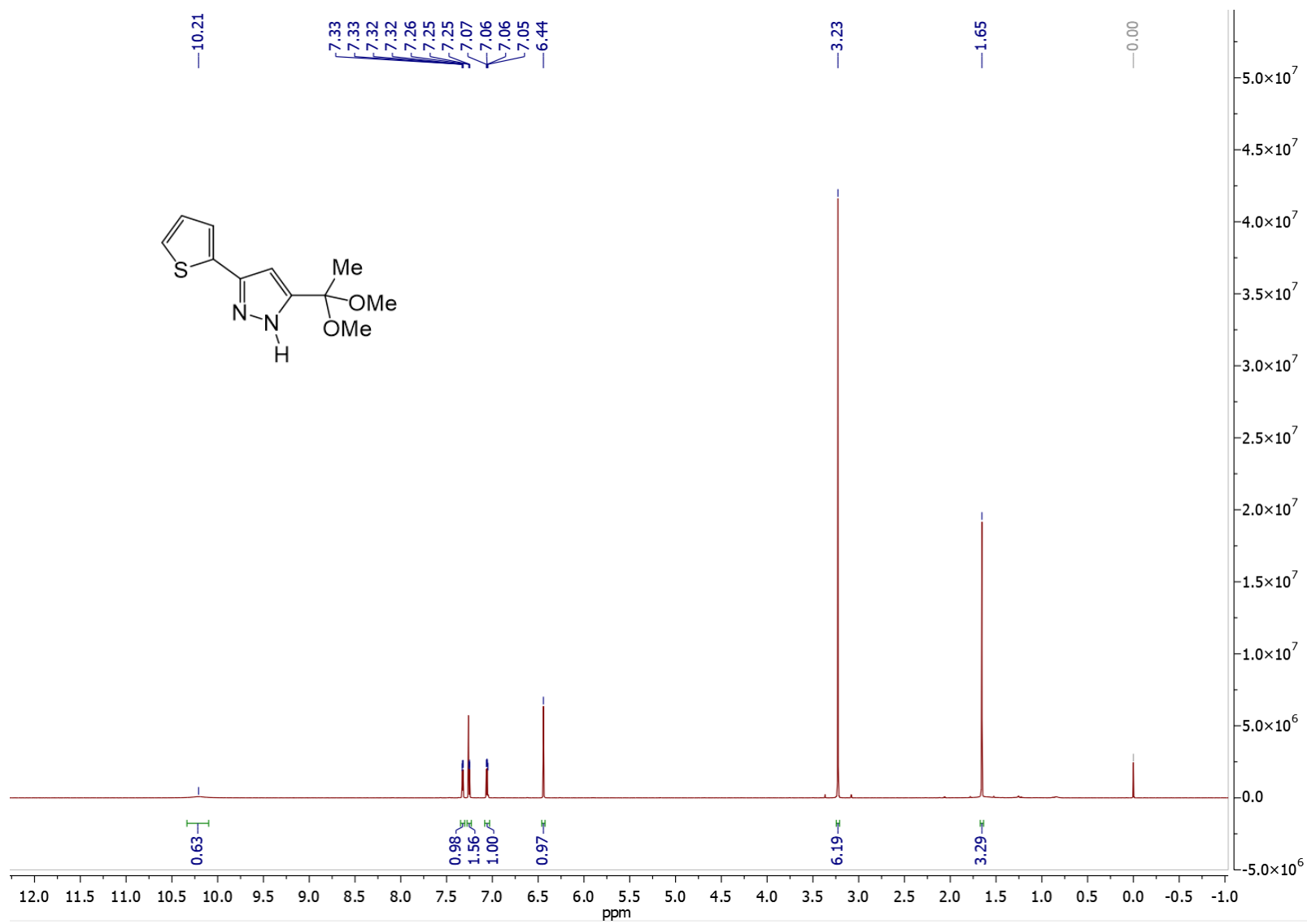


Figure S78. ^{13}C NMR spectrum of compound **18c**.

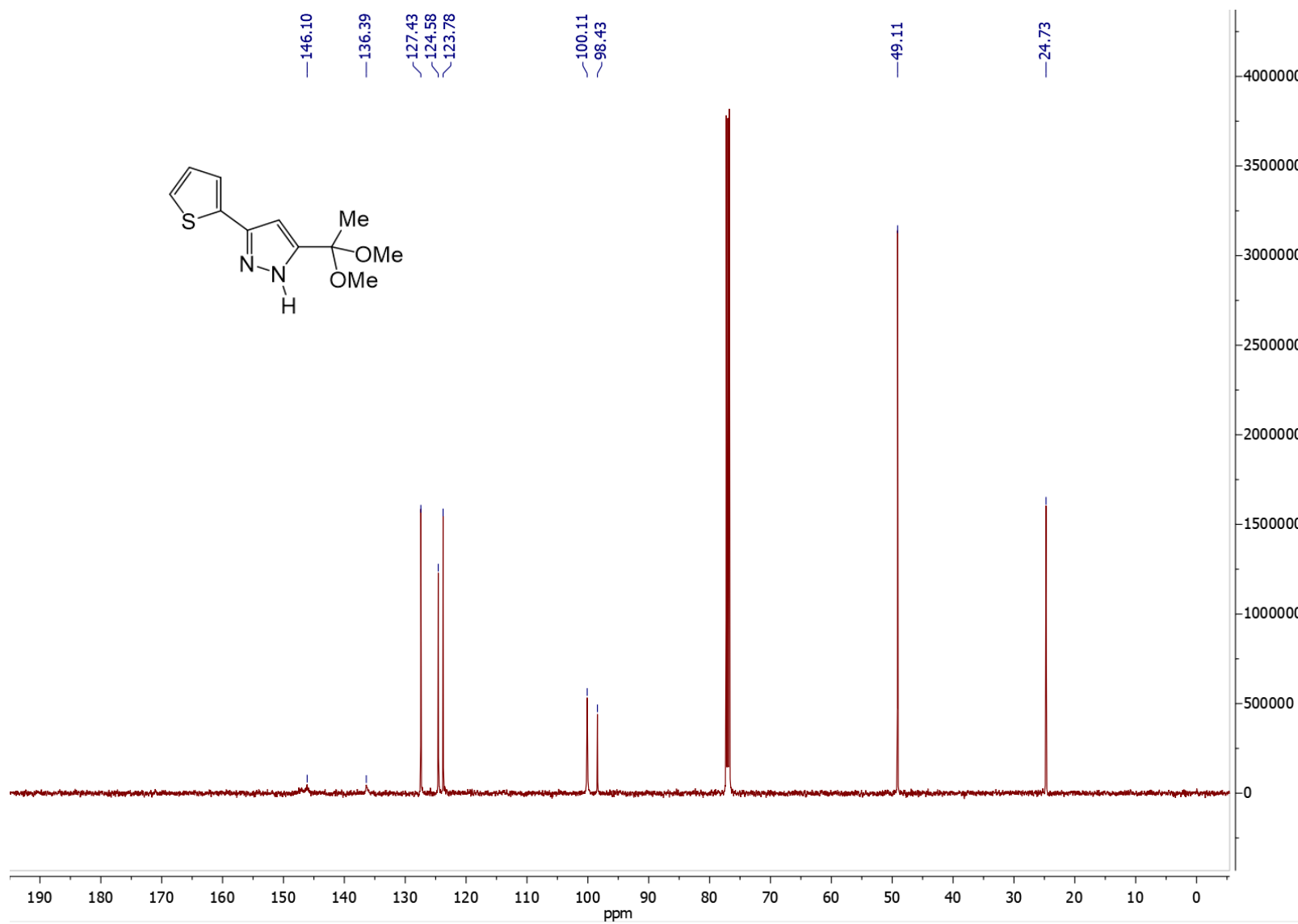


Figure S79. ^1H NMR spectrum of compound **19a**.

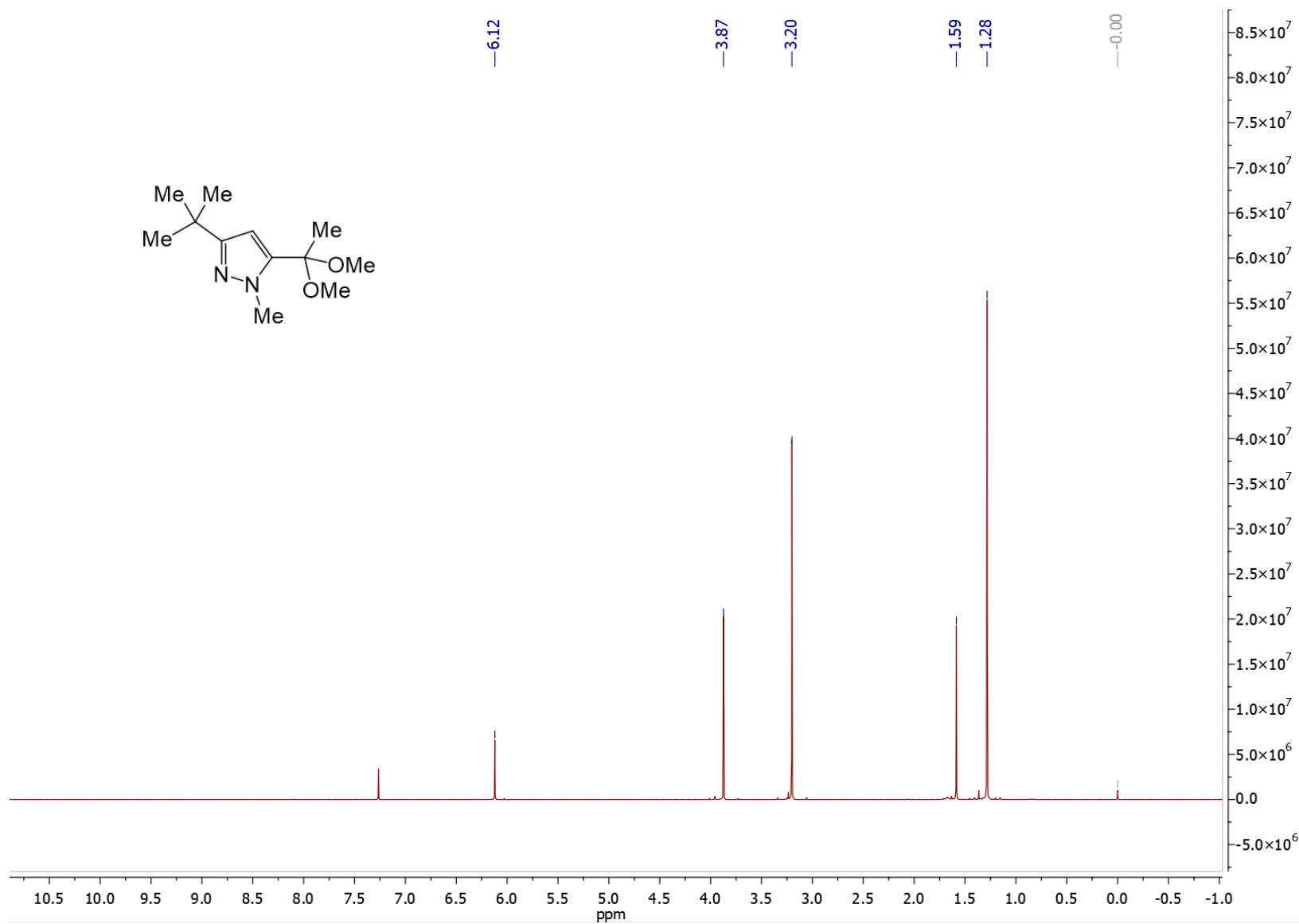


Figure S80. ^{13}C NMR spectrum of compound **19a**.

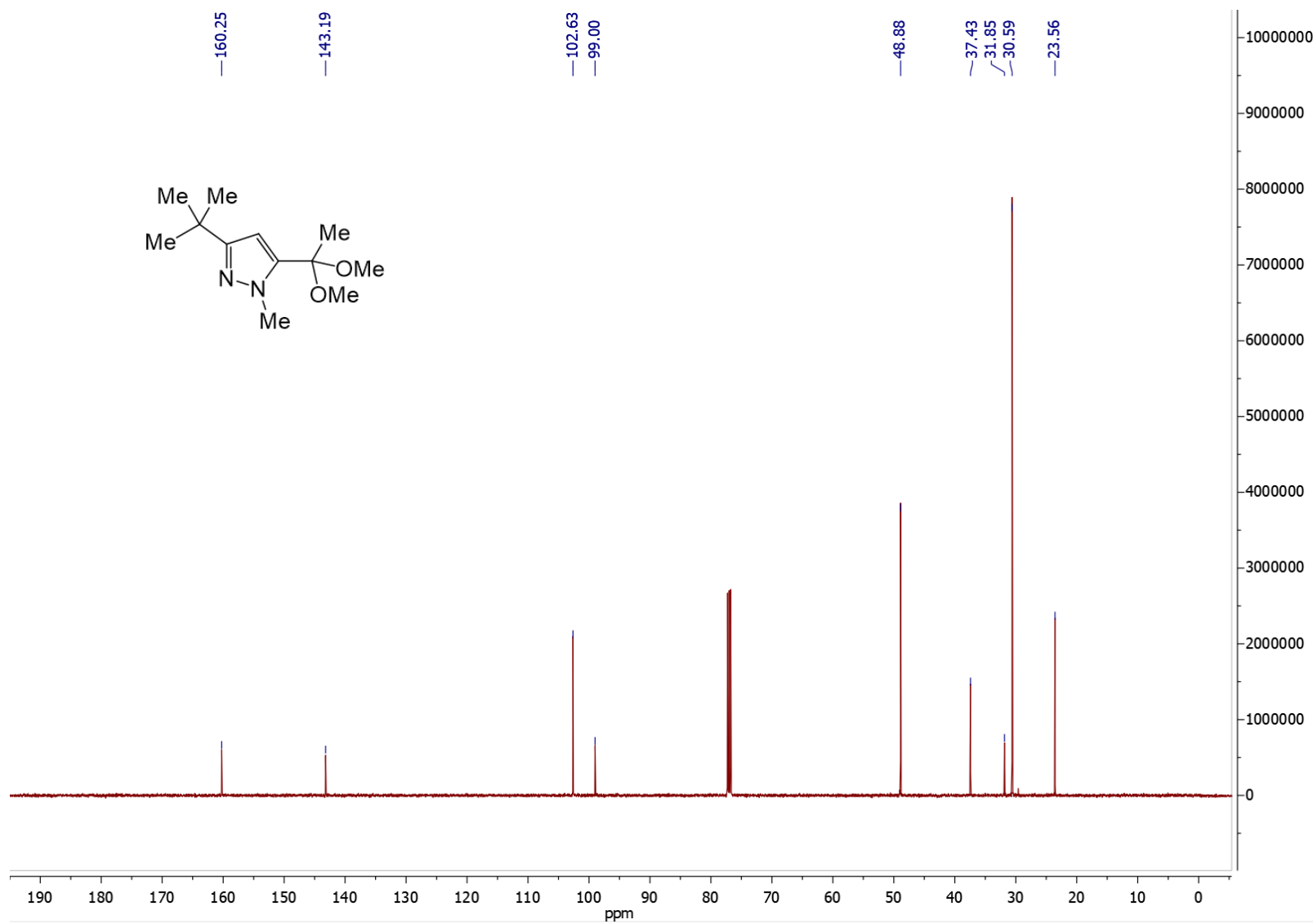


Figure S81. ^1H NMR spectrum of compound **19b**.

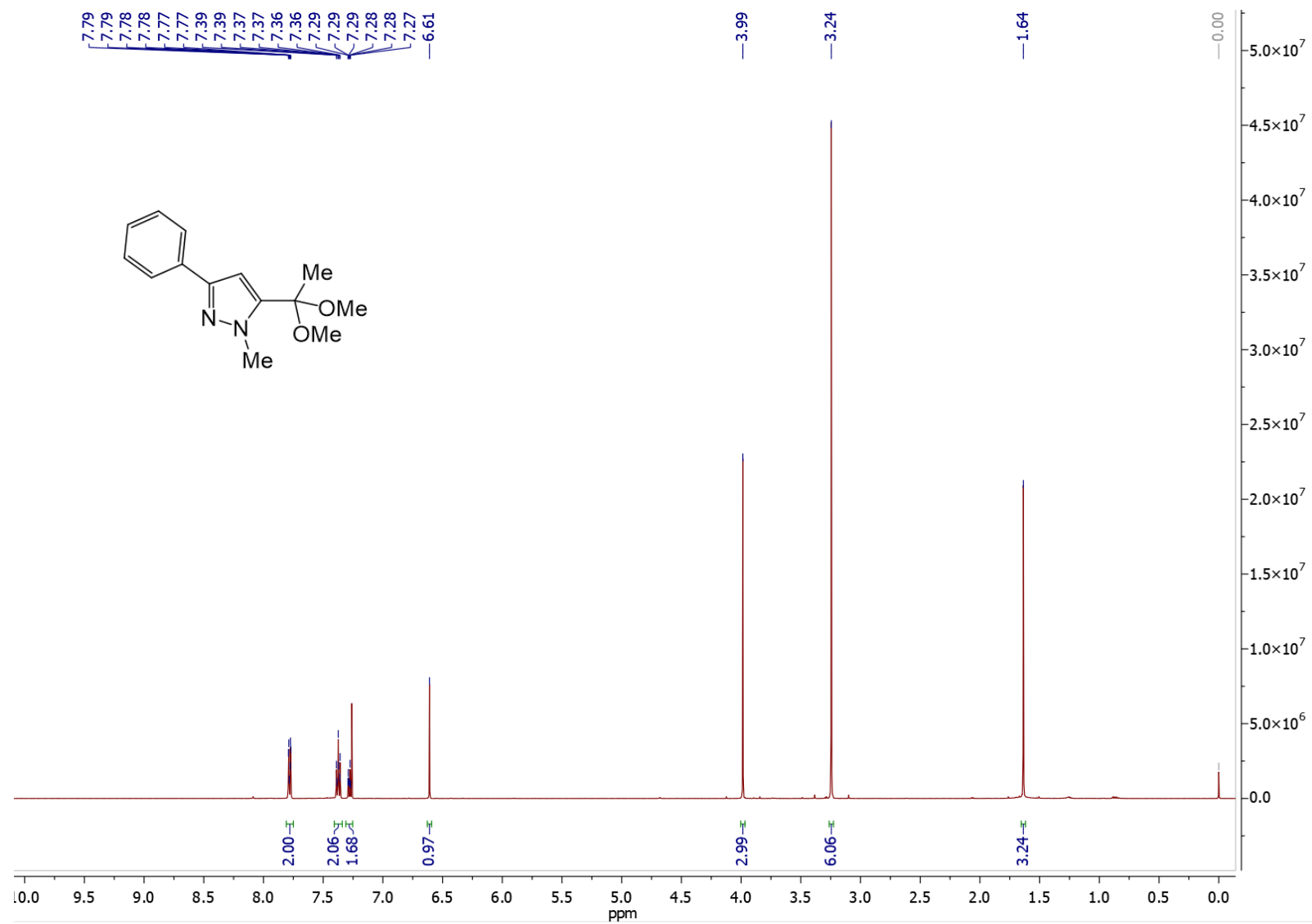


Figure S82. ^{13}C NMR spectrum of compound **19b**.

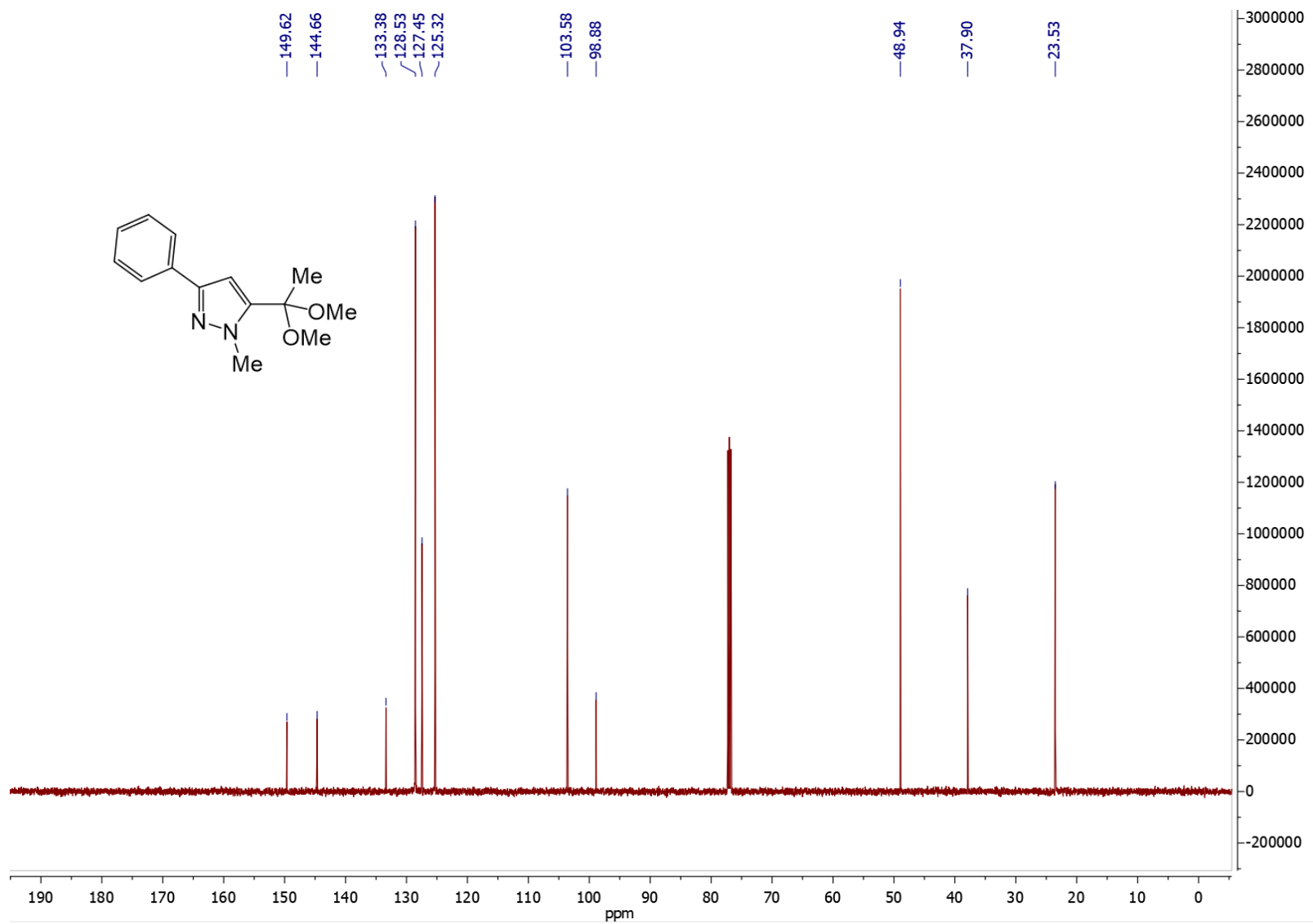


Figure S83. ^1H NMR spectrum of compound **19c**.

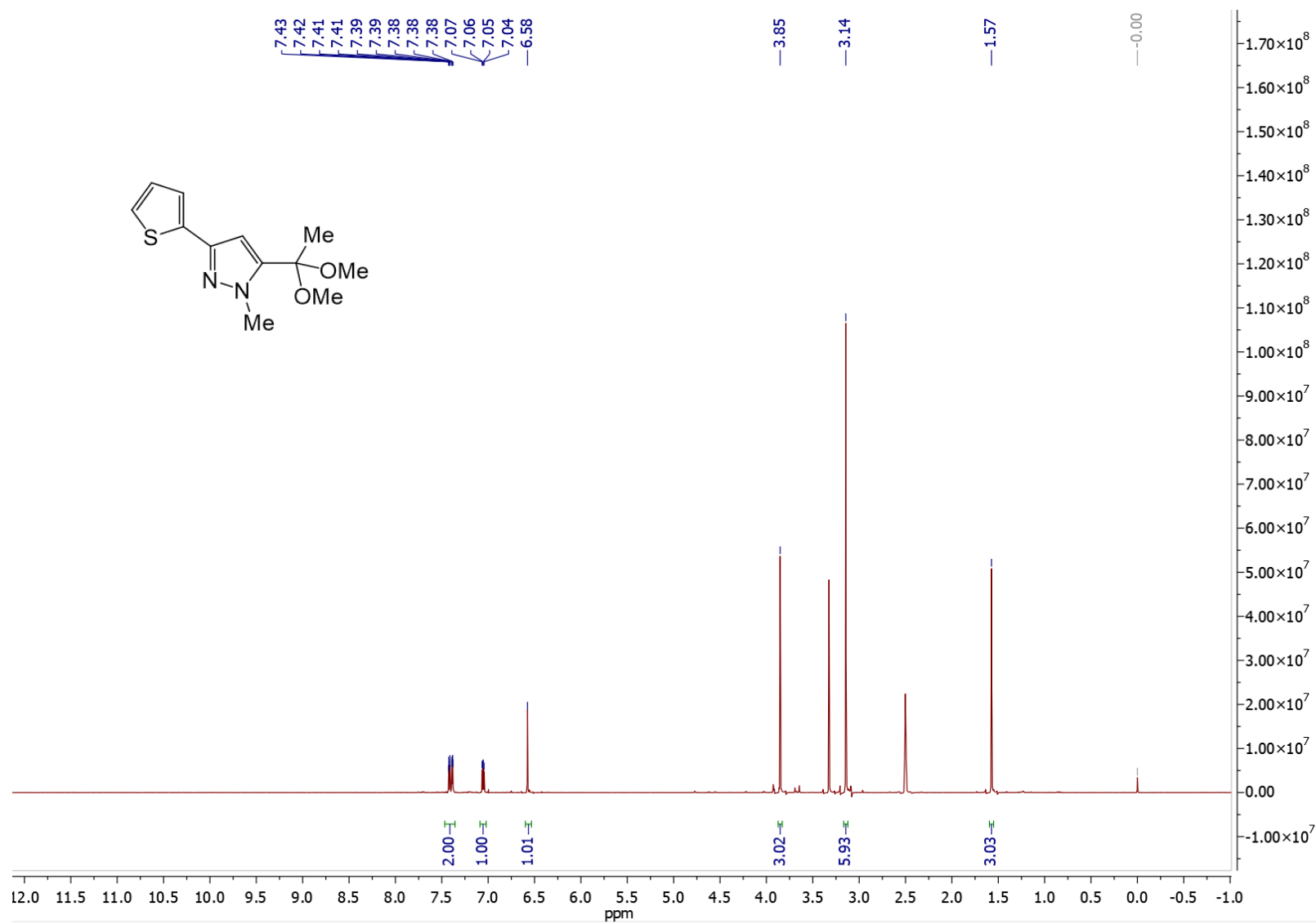


Figure S84. ^{13}C NMR spectrum of compound **19c**.

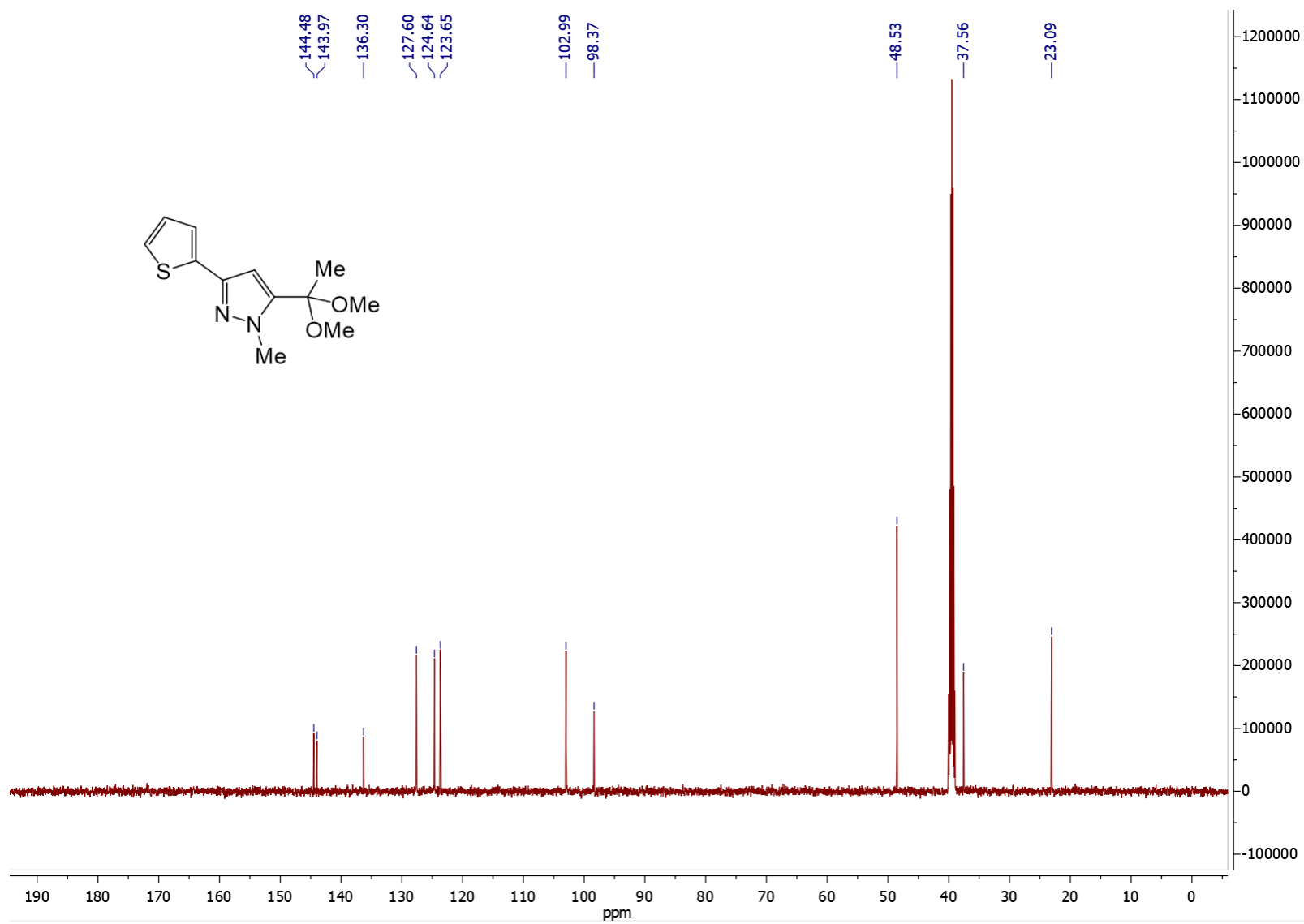


Figure S85. ^1H NMR spectrum of compound **20a**.

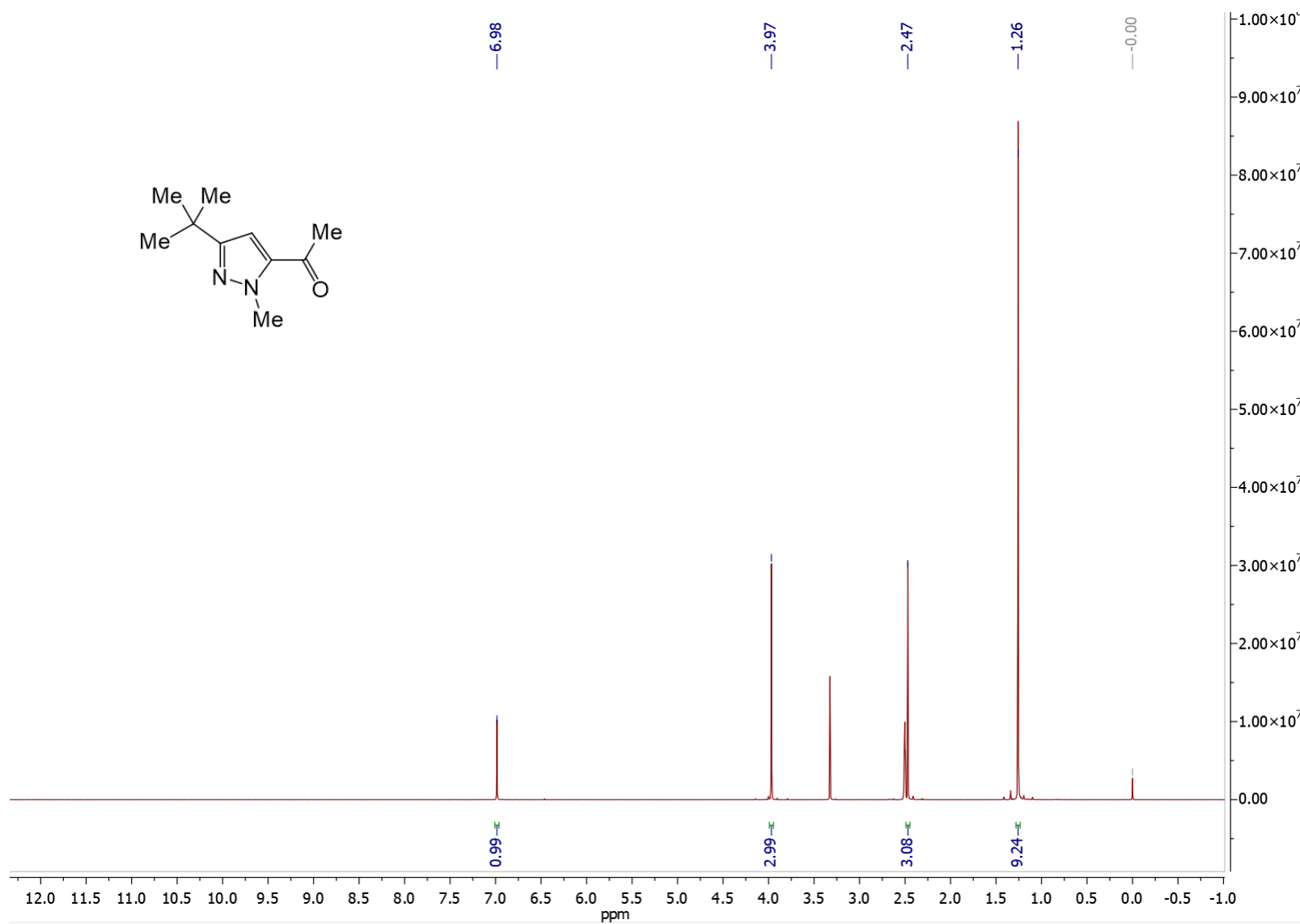


Figure S86 ^{13}C NMR spectrum of compound **20a**.

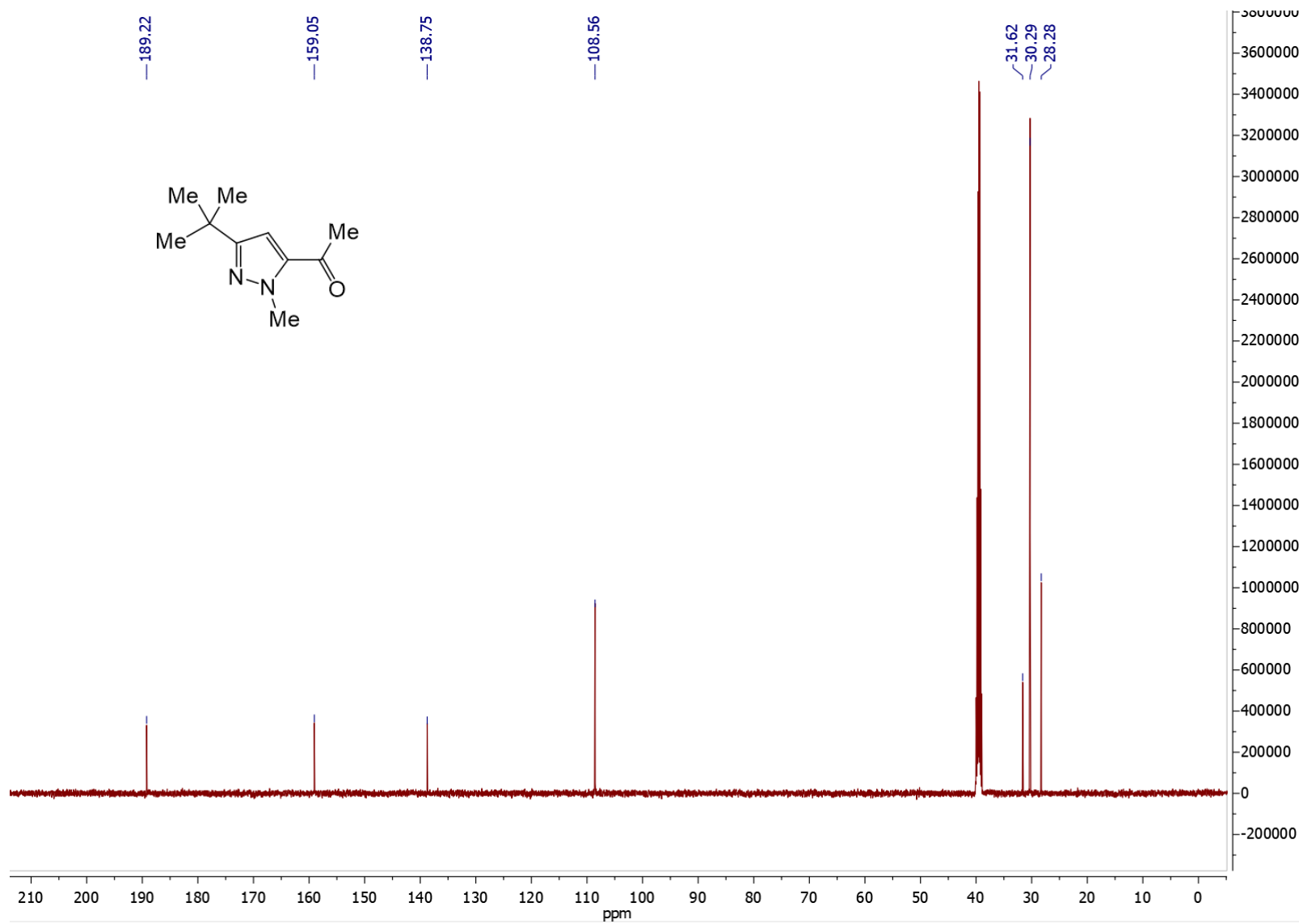


Figure S87. ^1H NMR spectrum of compound **20b**.

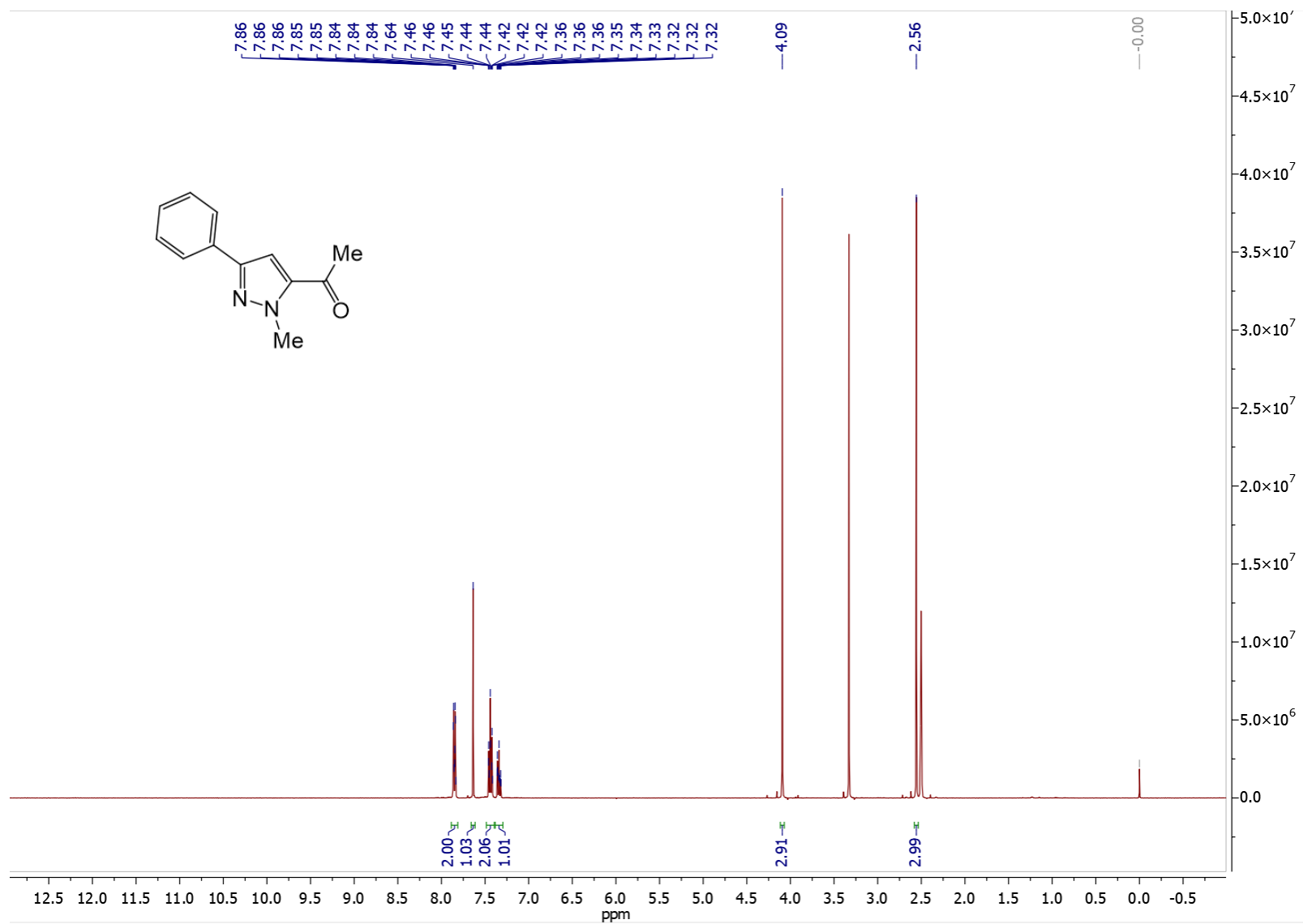


Figure S88. ^{13}C NMR spectrum of compound **20b**.

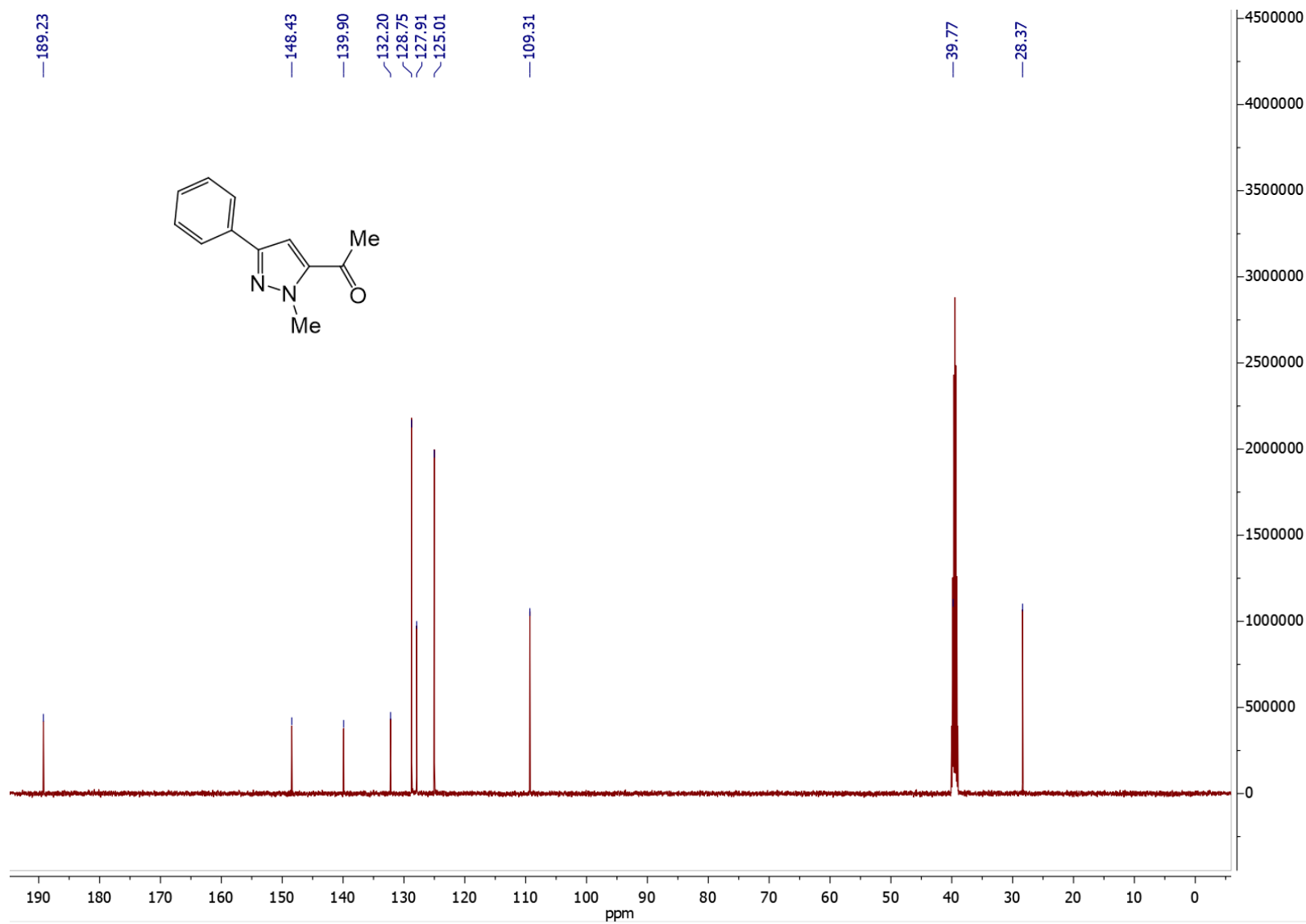


Figure S89. ^1H NMR spectrum of compound **20c**.

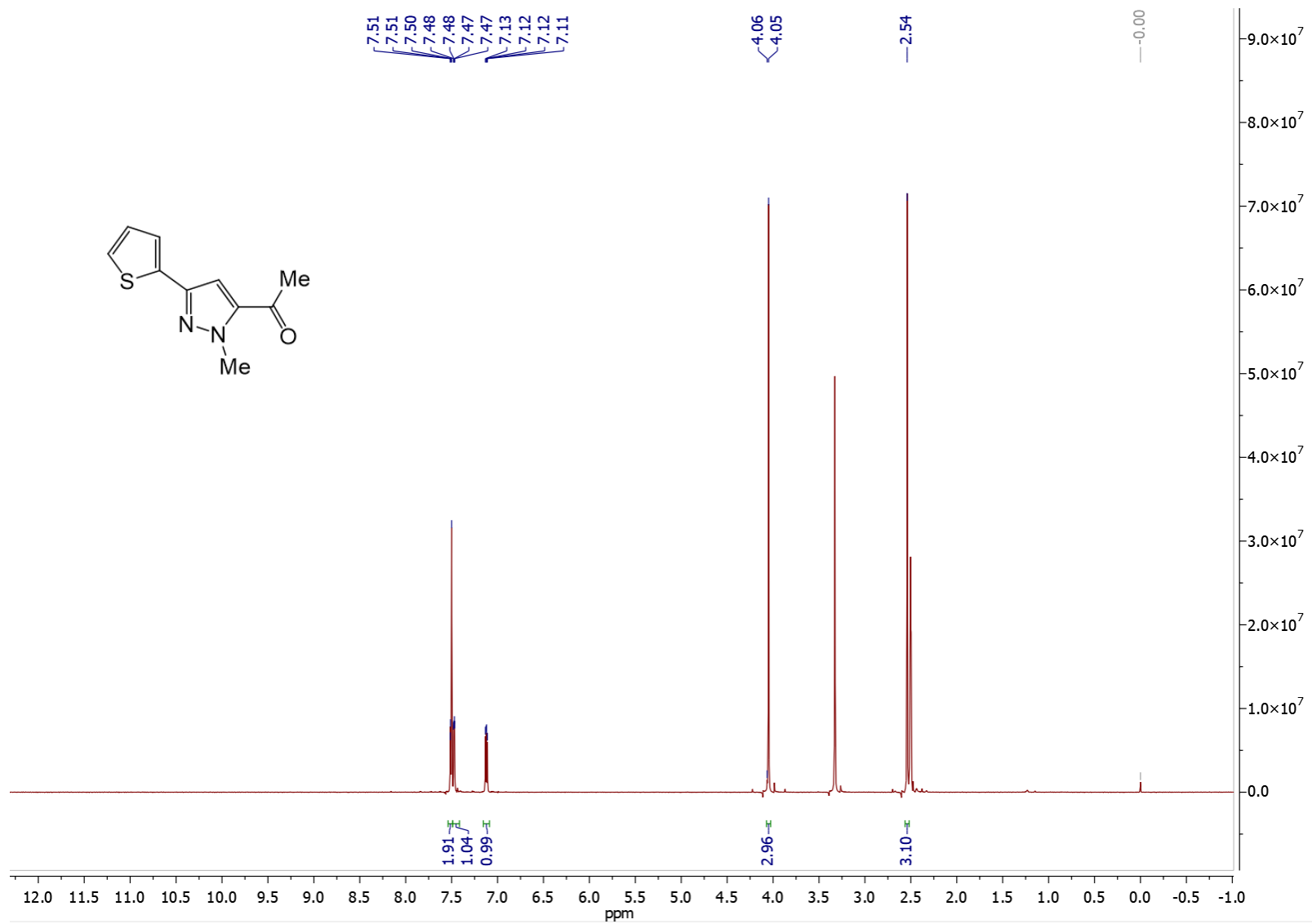


Figure S90. ^{13}C NMR spectrum of compound **20c**.

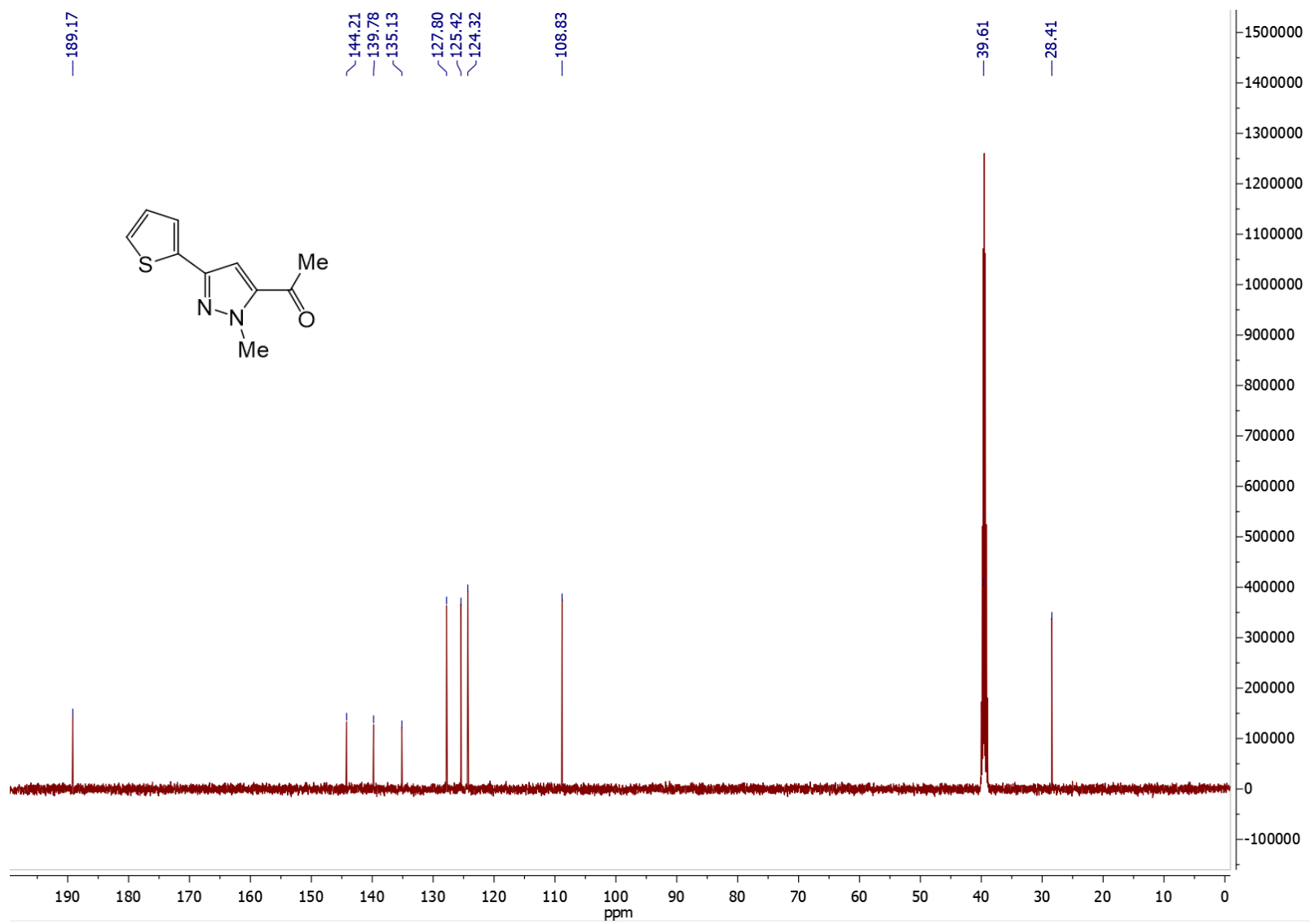


Figure S91. ^1H NMR spectrum of compound **21a**.

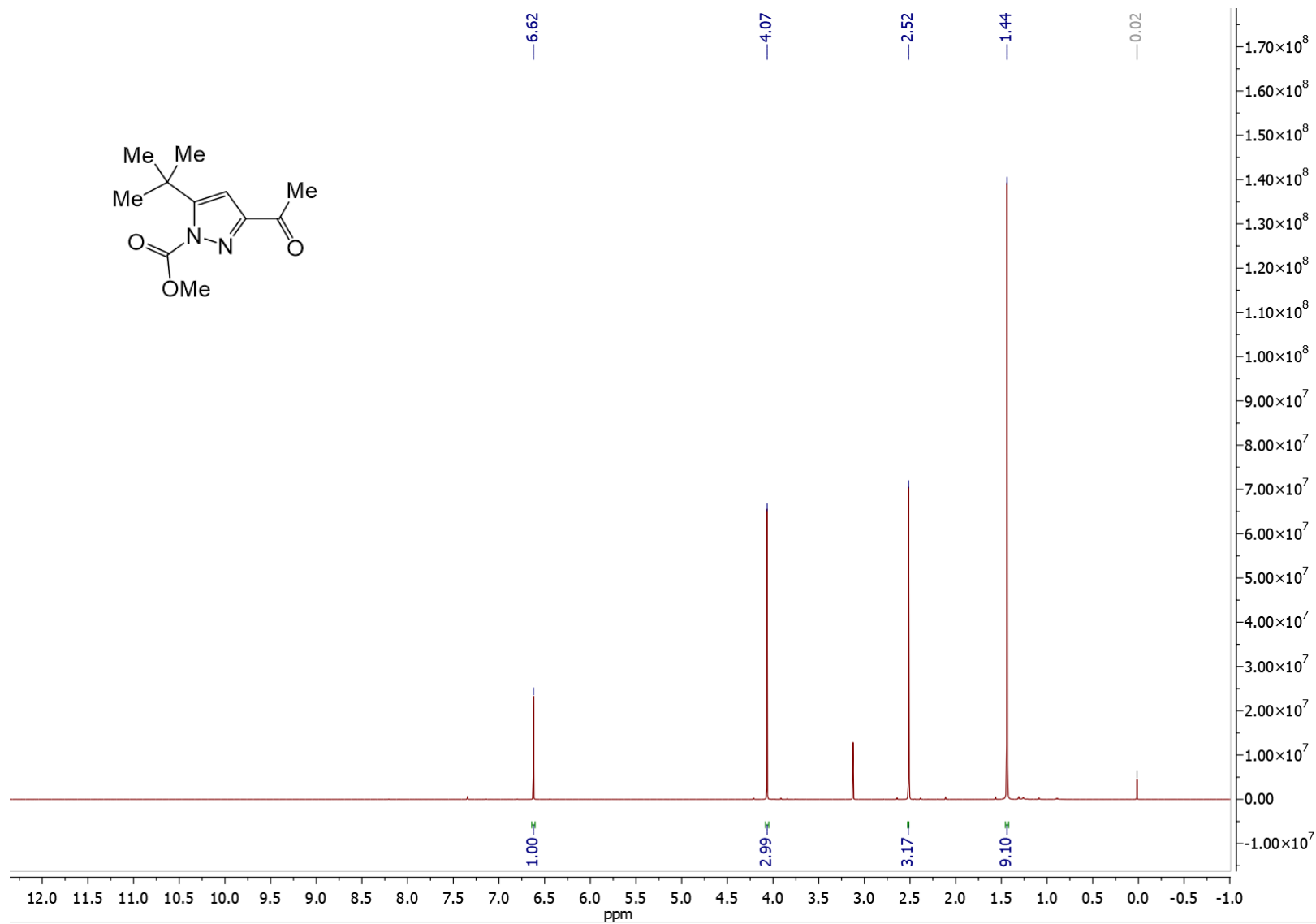


Figure S92. ^{13}C NMR spectrum of compound **21a**.

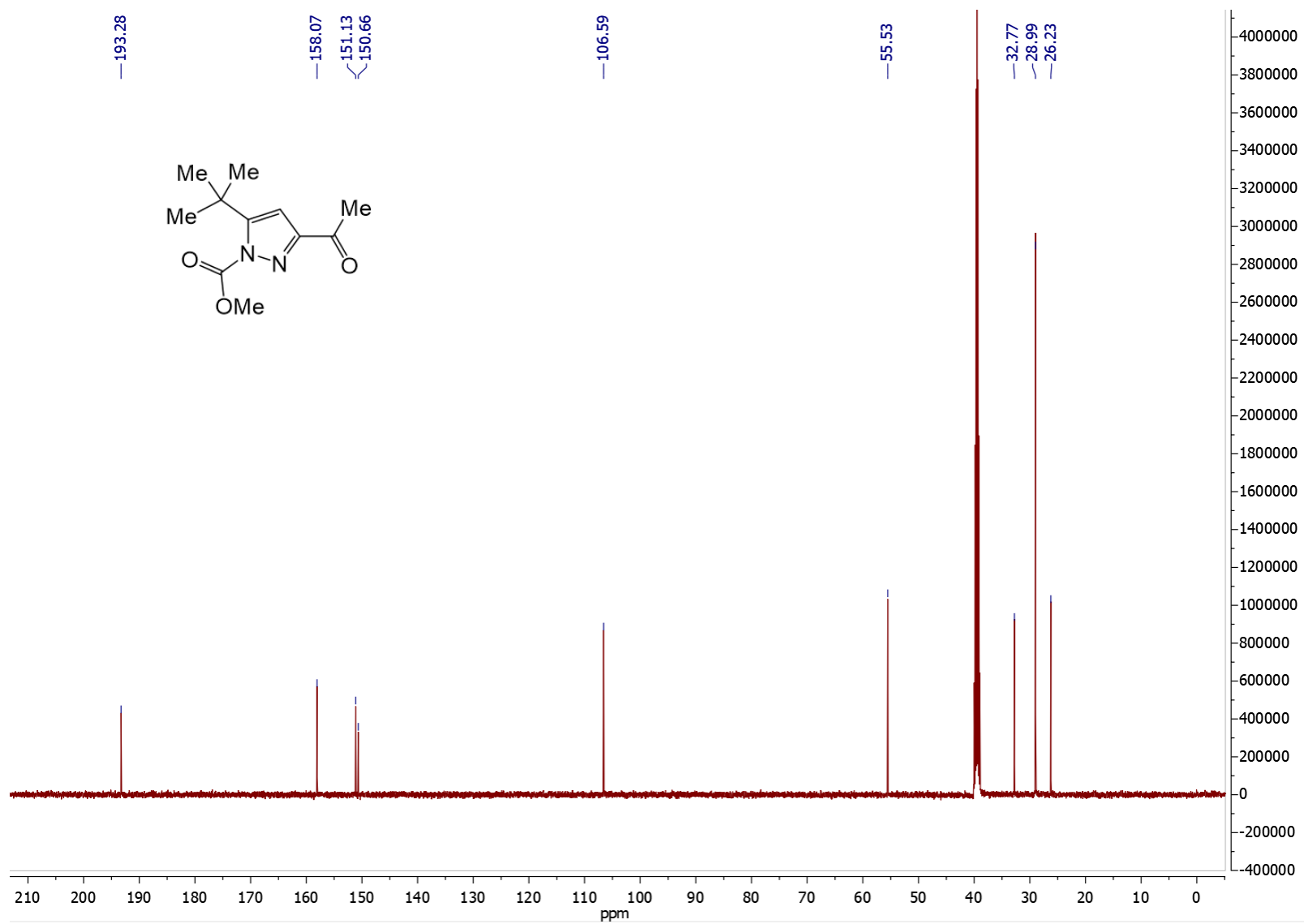


Figure S93. ^1H NMR spectrum of compound **21b**.

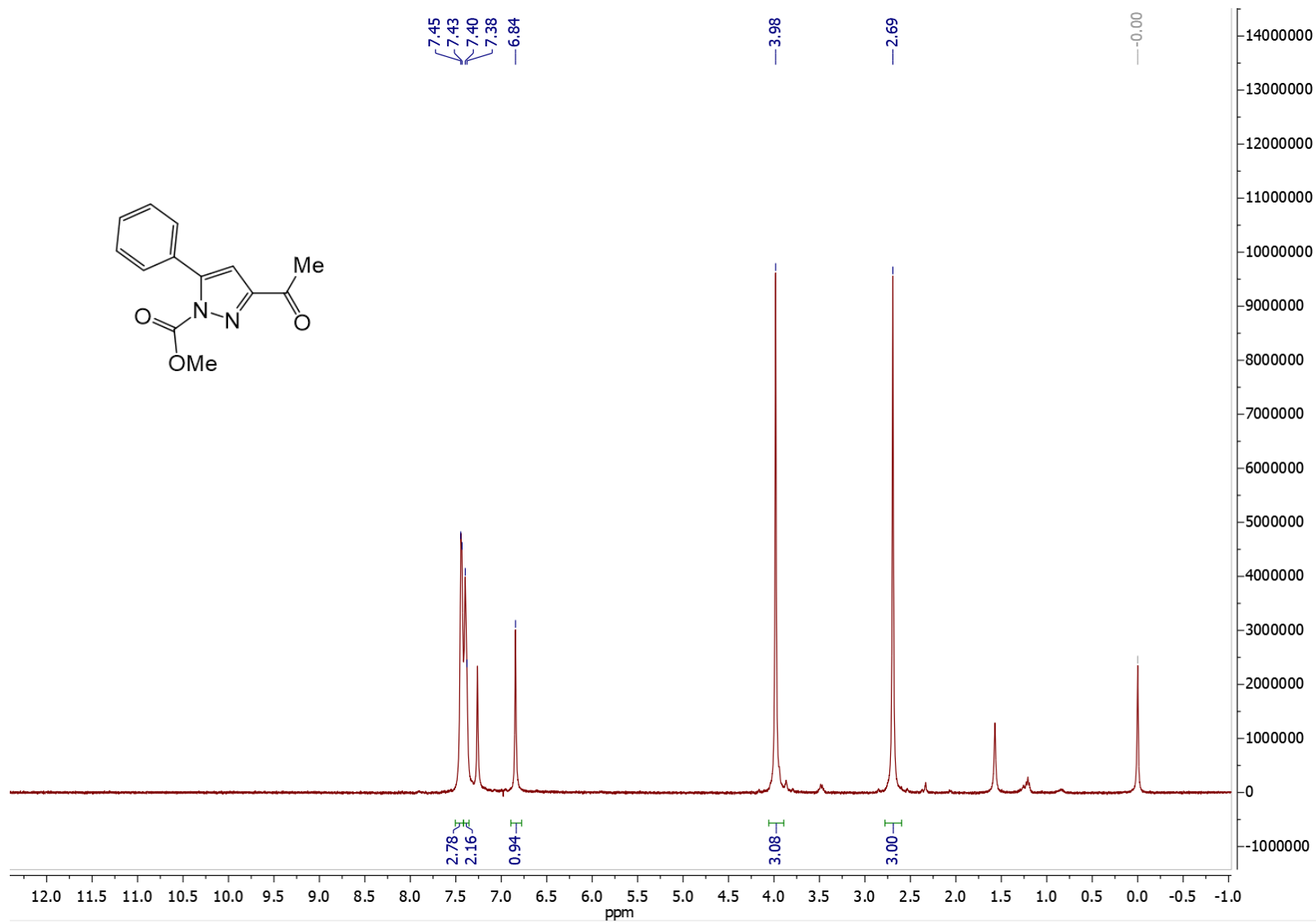


Figure S94. ^{13}C NMR spectrum of compound **21b**.

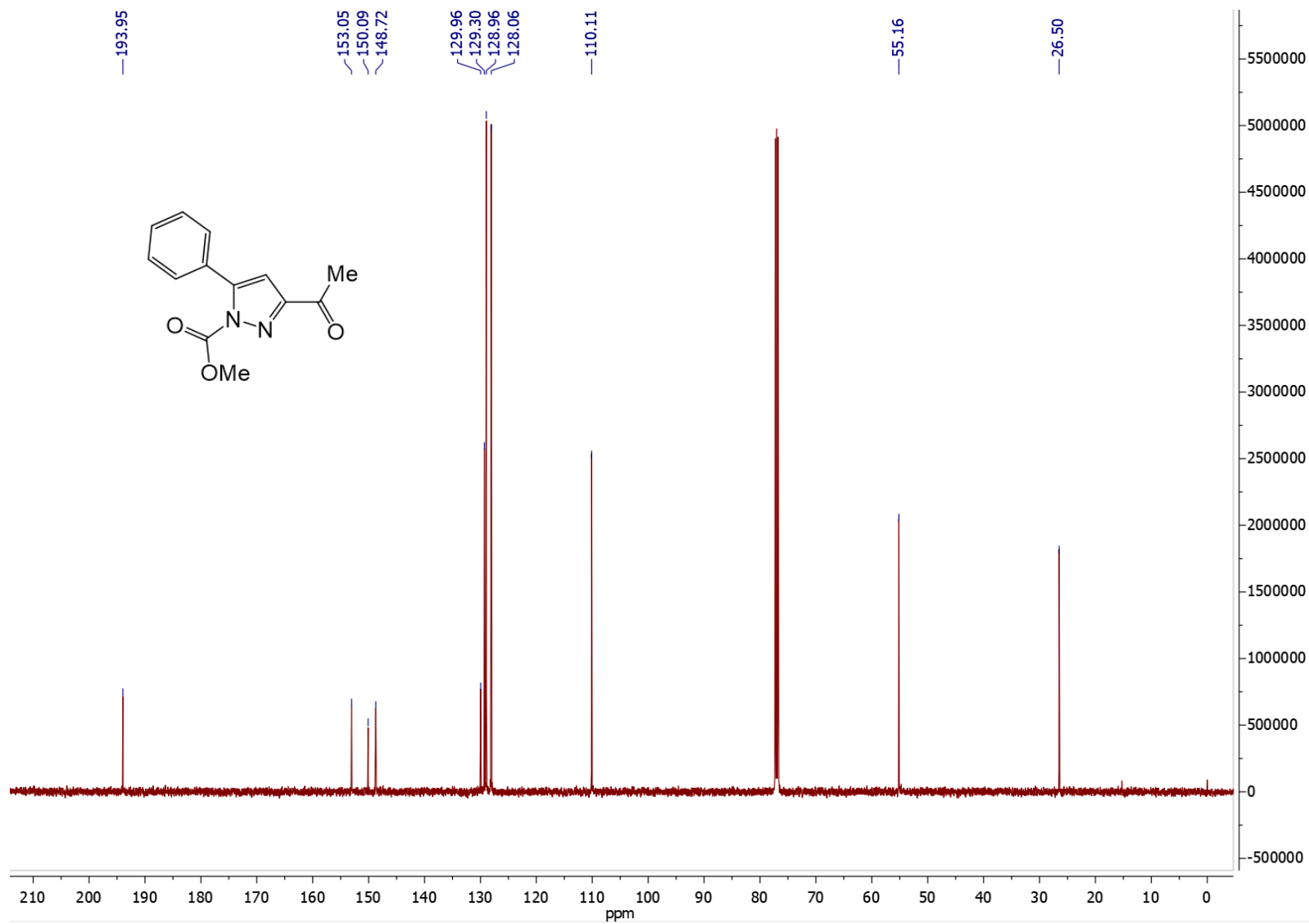


Figure S95. ^1H NMR spectrum of compound **21c**.

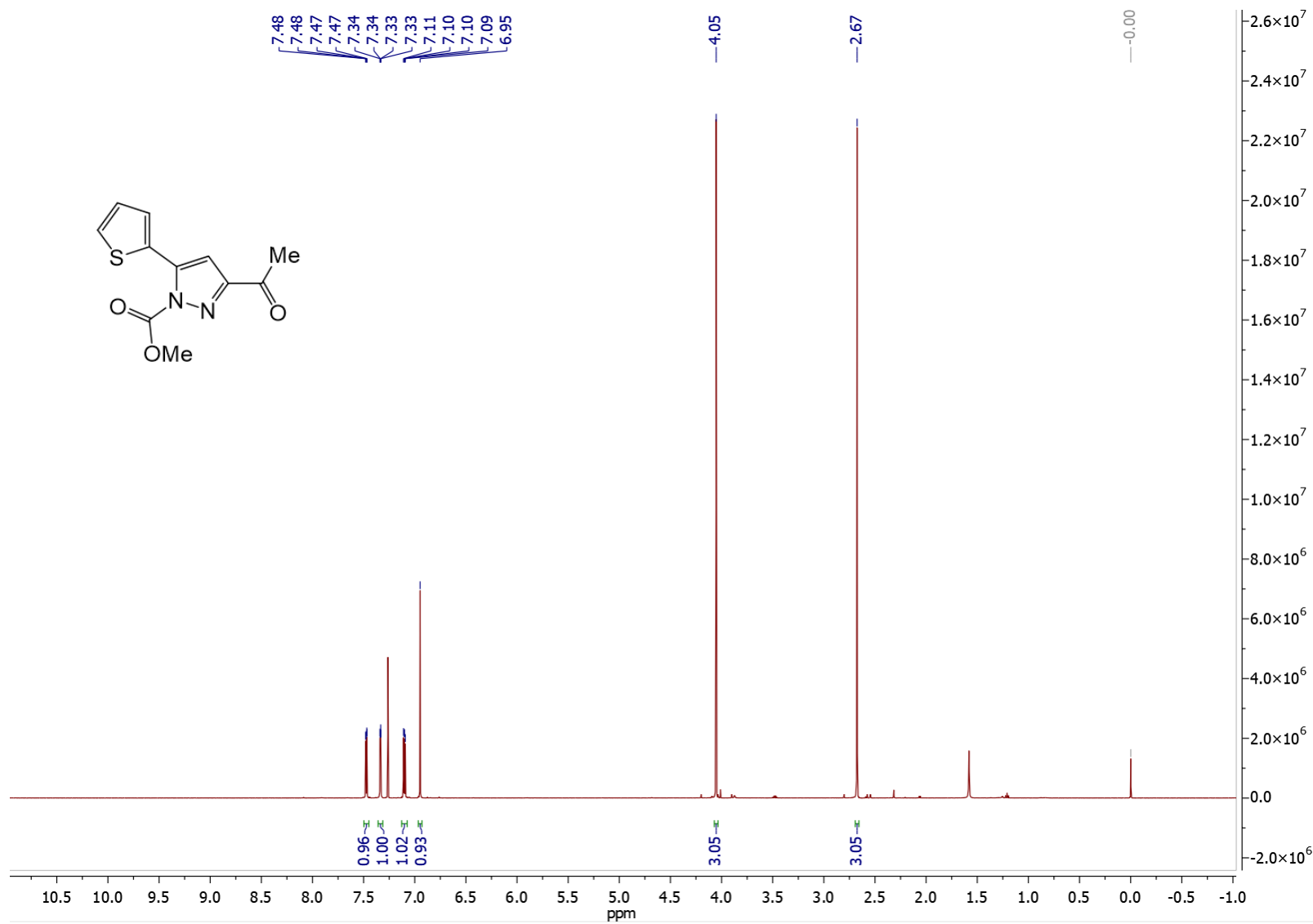


Figure S96. ^{13}C NMR spectrum of compound **21c**.

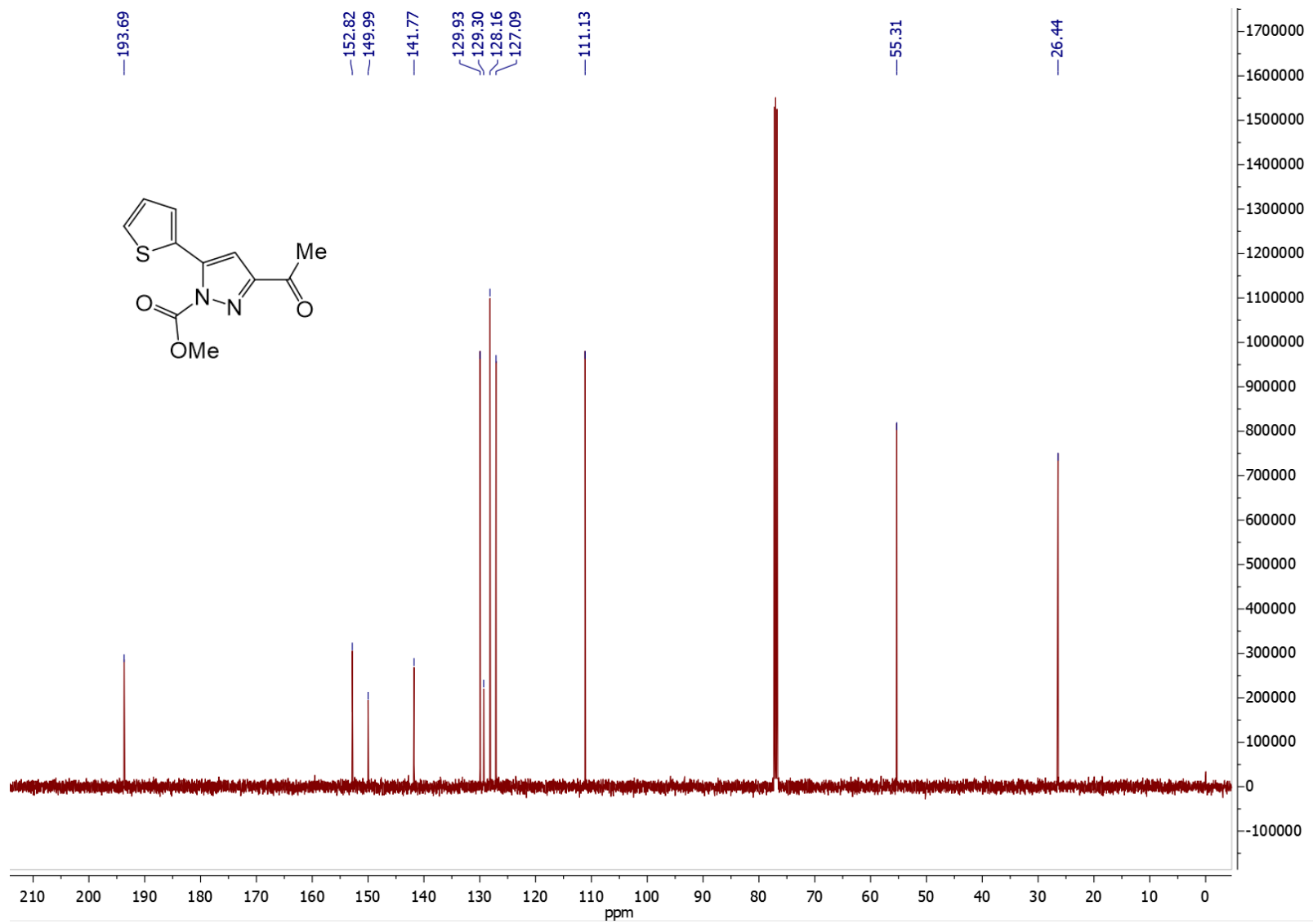


Figure S97. ^1H NMR spectrum of compound **22**.

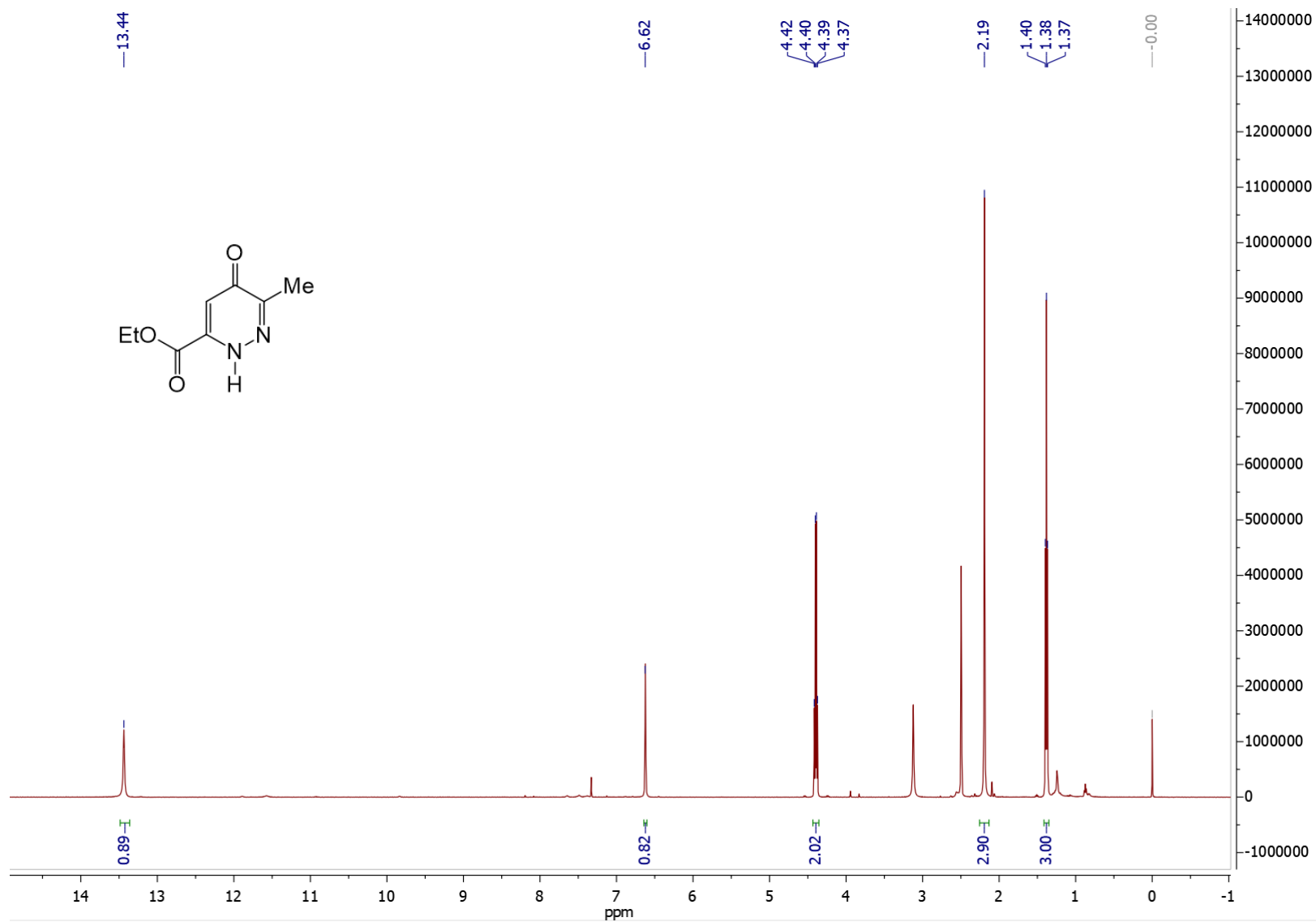
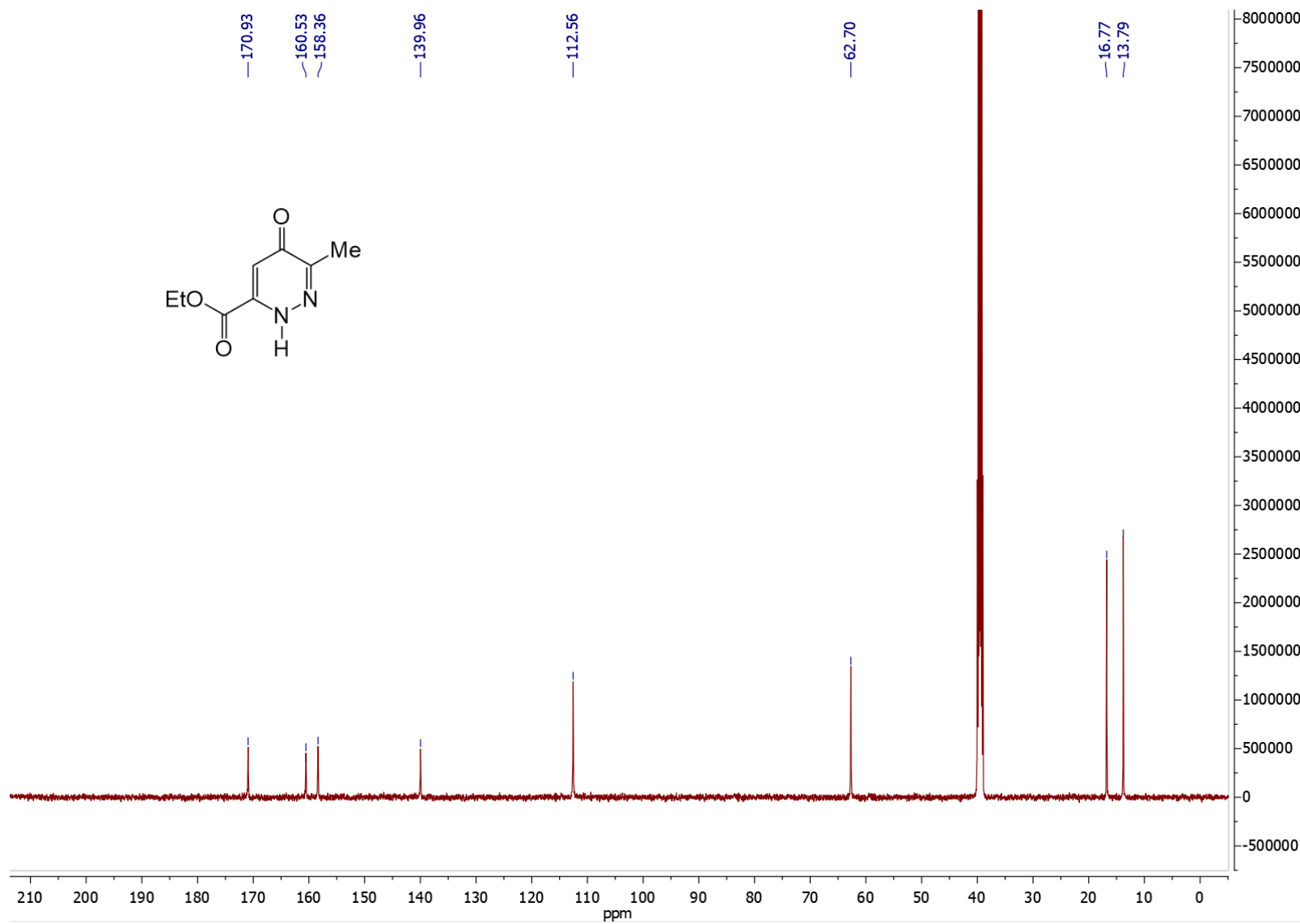


Figure S98. ^{13}C NMR spectrum of compound **22**.



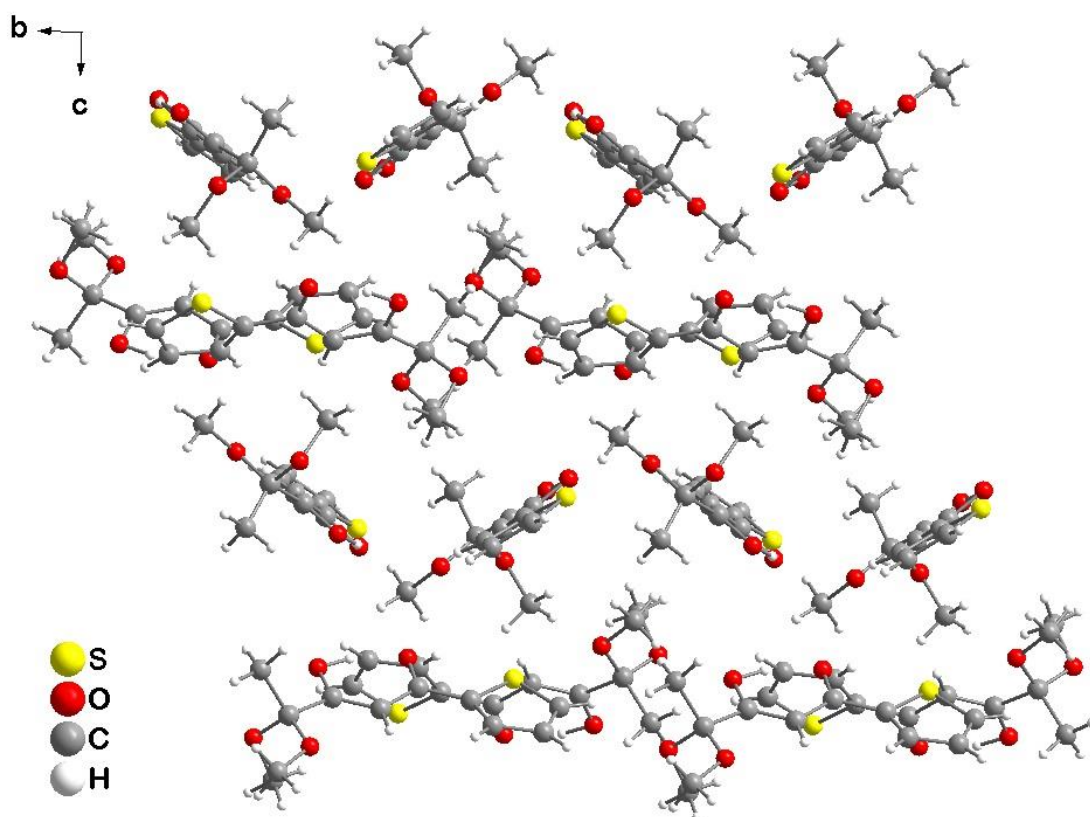


Figure S99. Crystal packing of diketone **2c** along *a* axis.

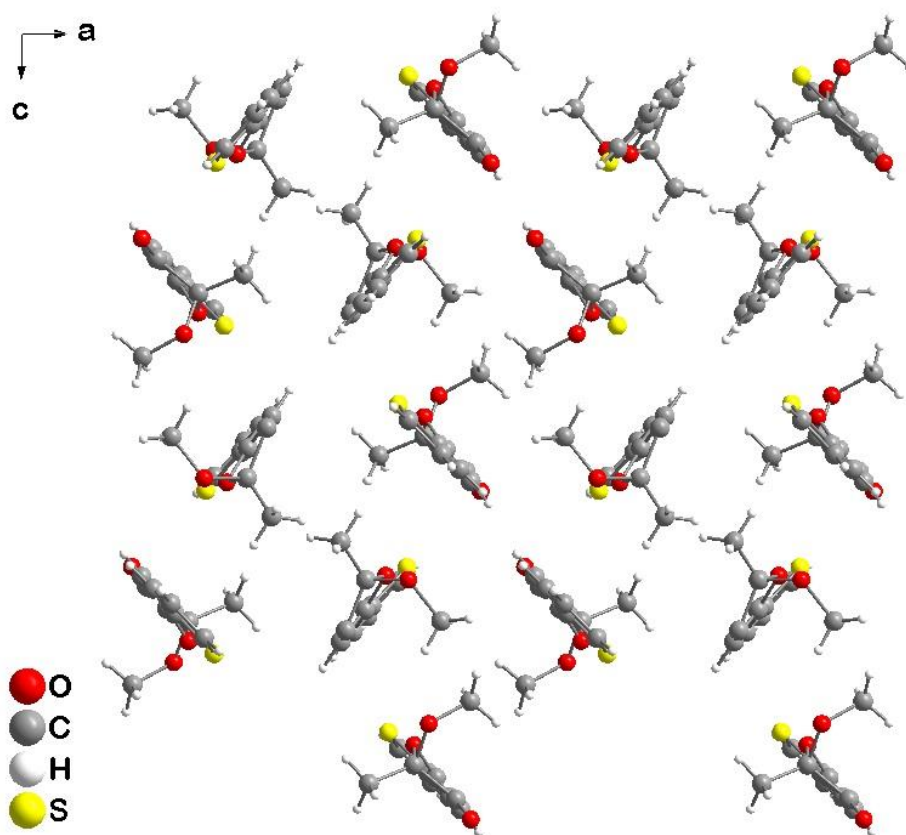


Figure S100. Crystal packing of furanone **3** along *b* axis.

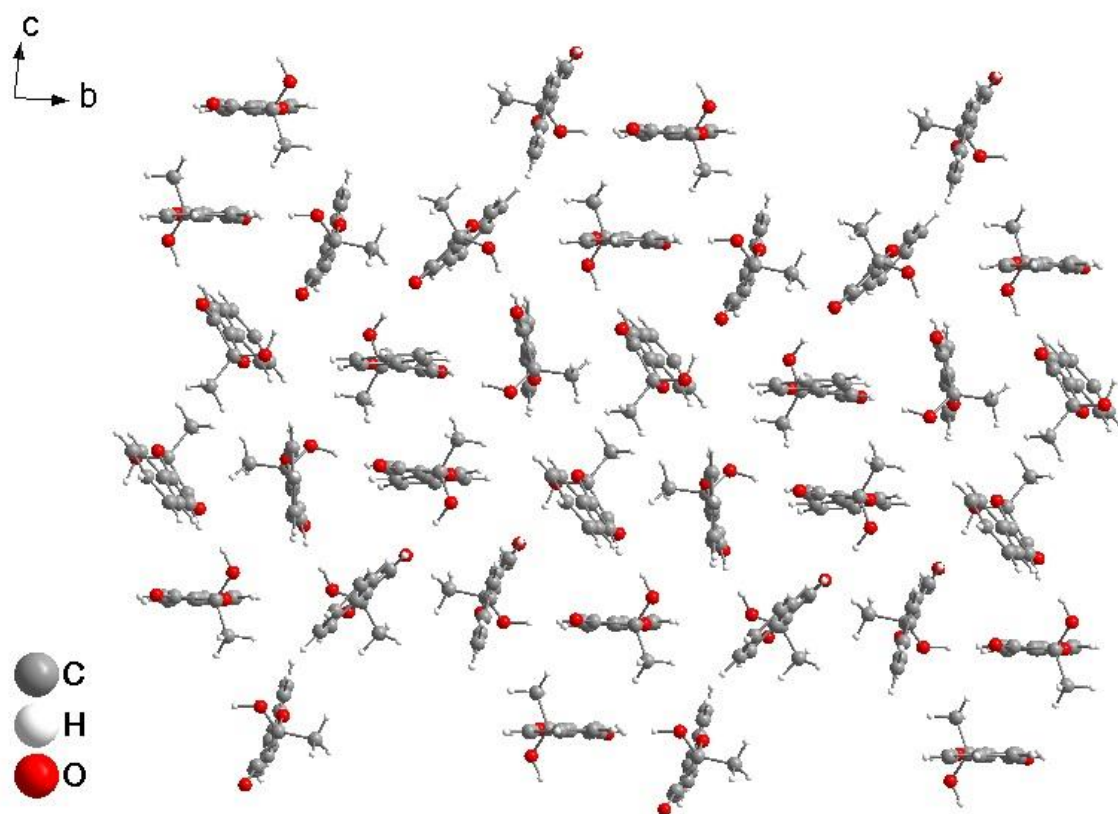
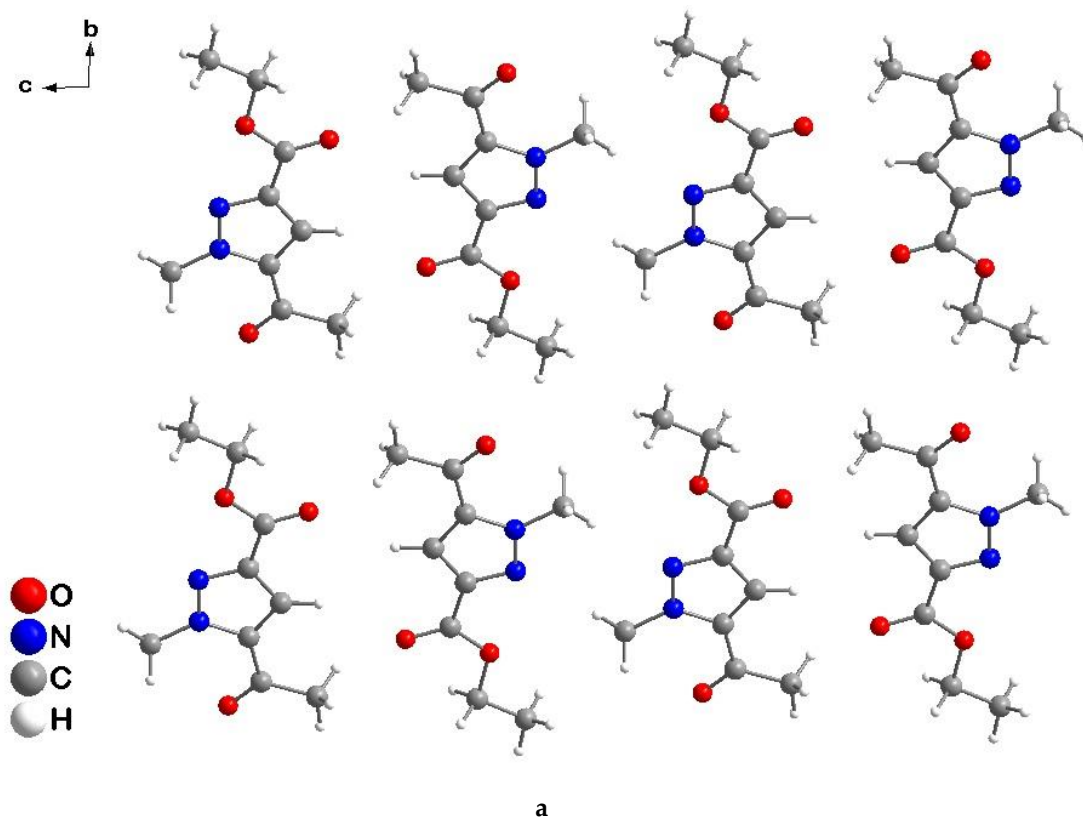


Figure S101. Crystal packing of furanone 5.



a

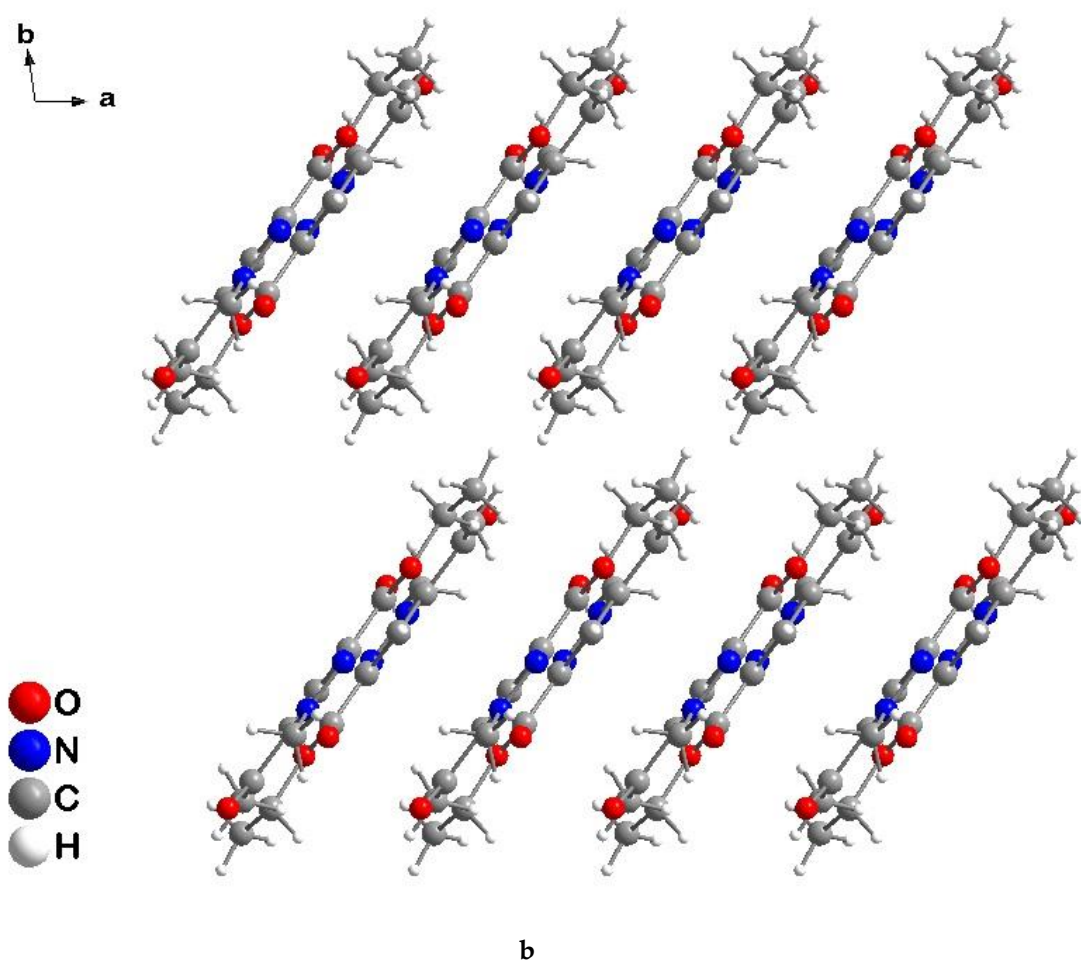
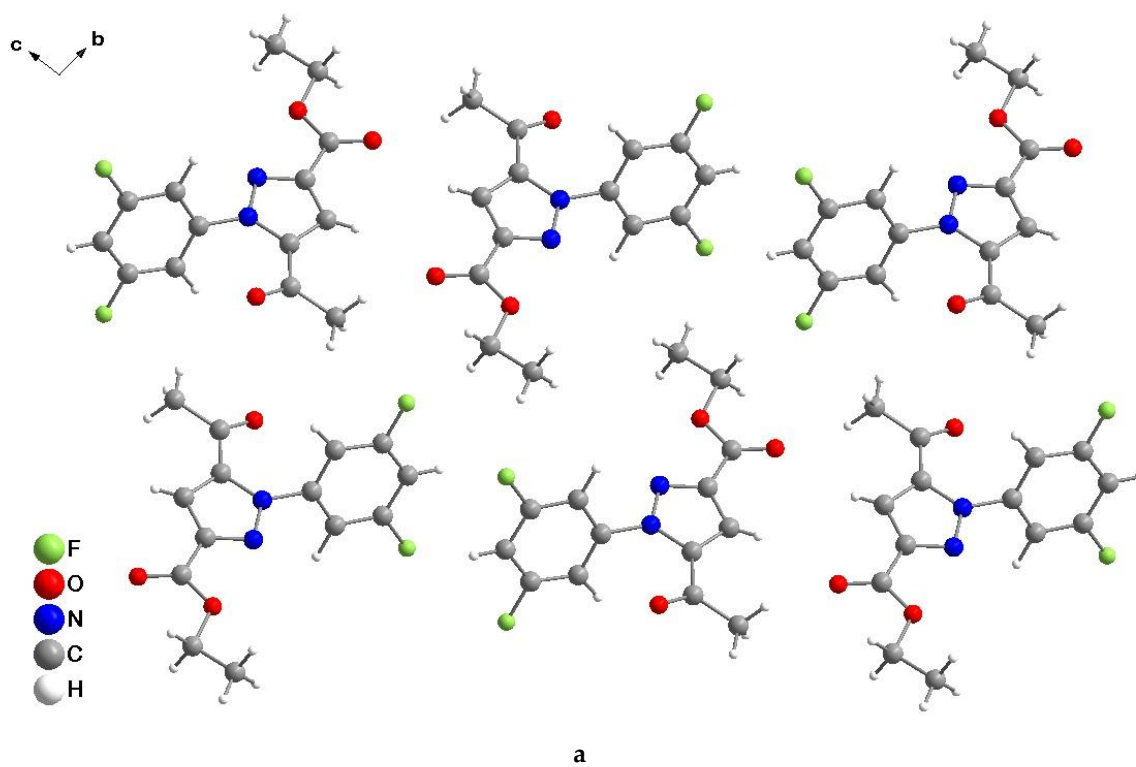


Figure S102. Crystal packing of pyrazole **7a** along *a* (a) and *c* (b) axis.



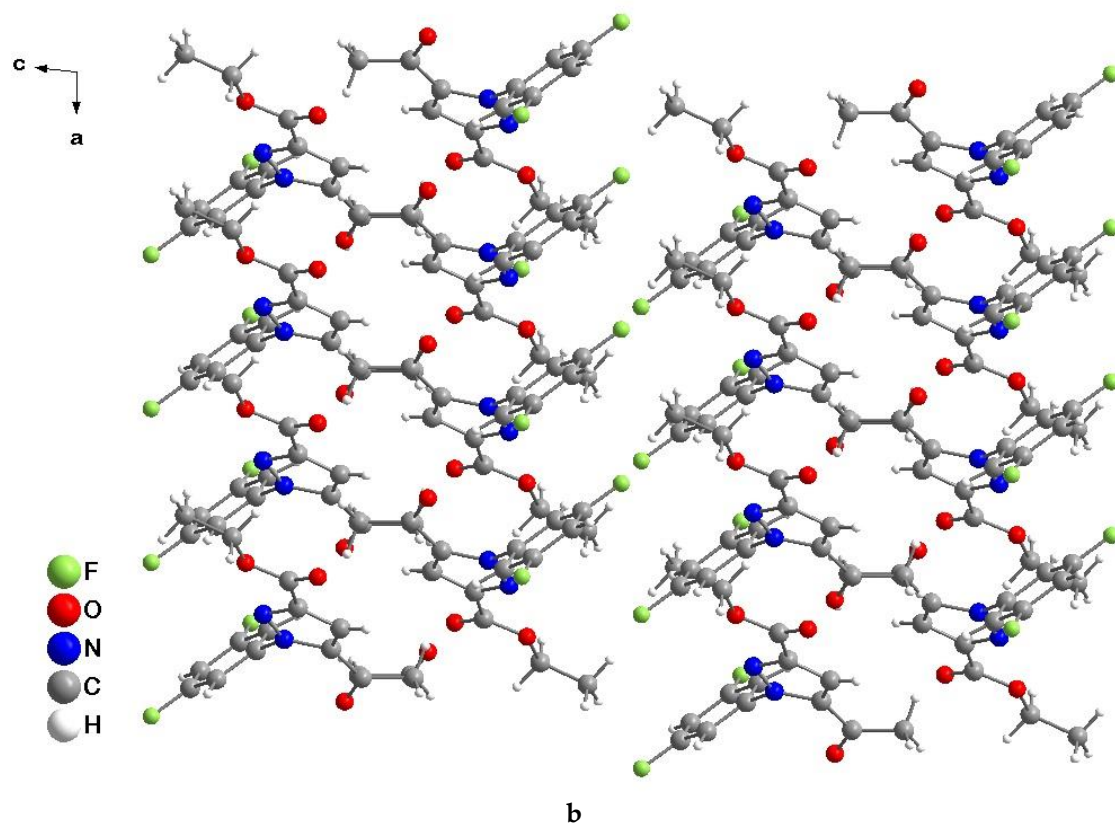
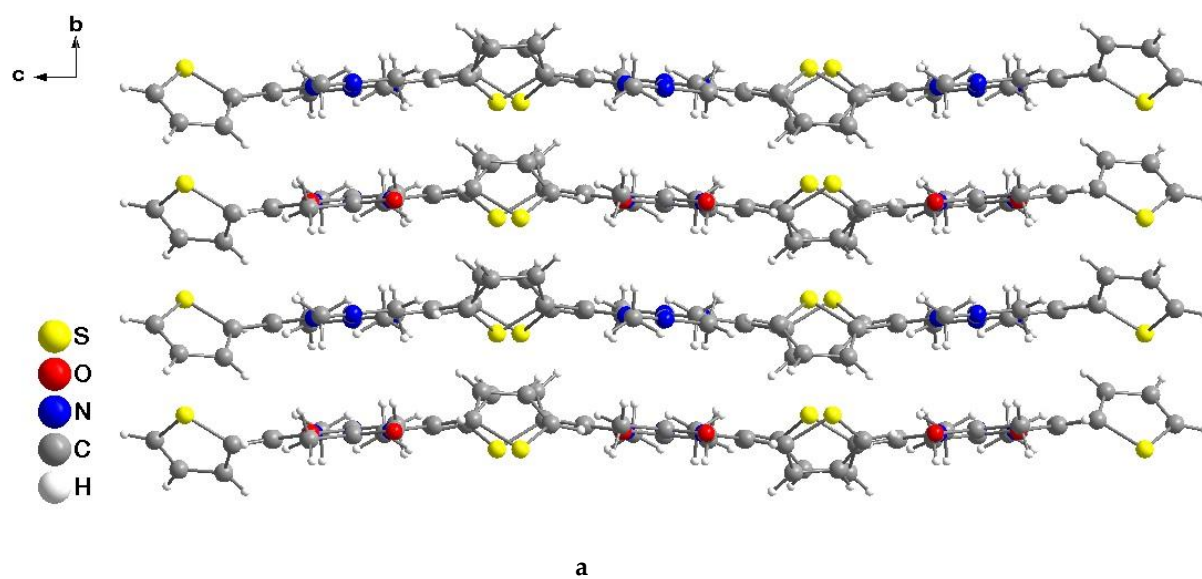
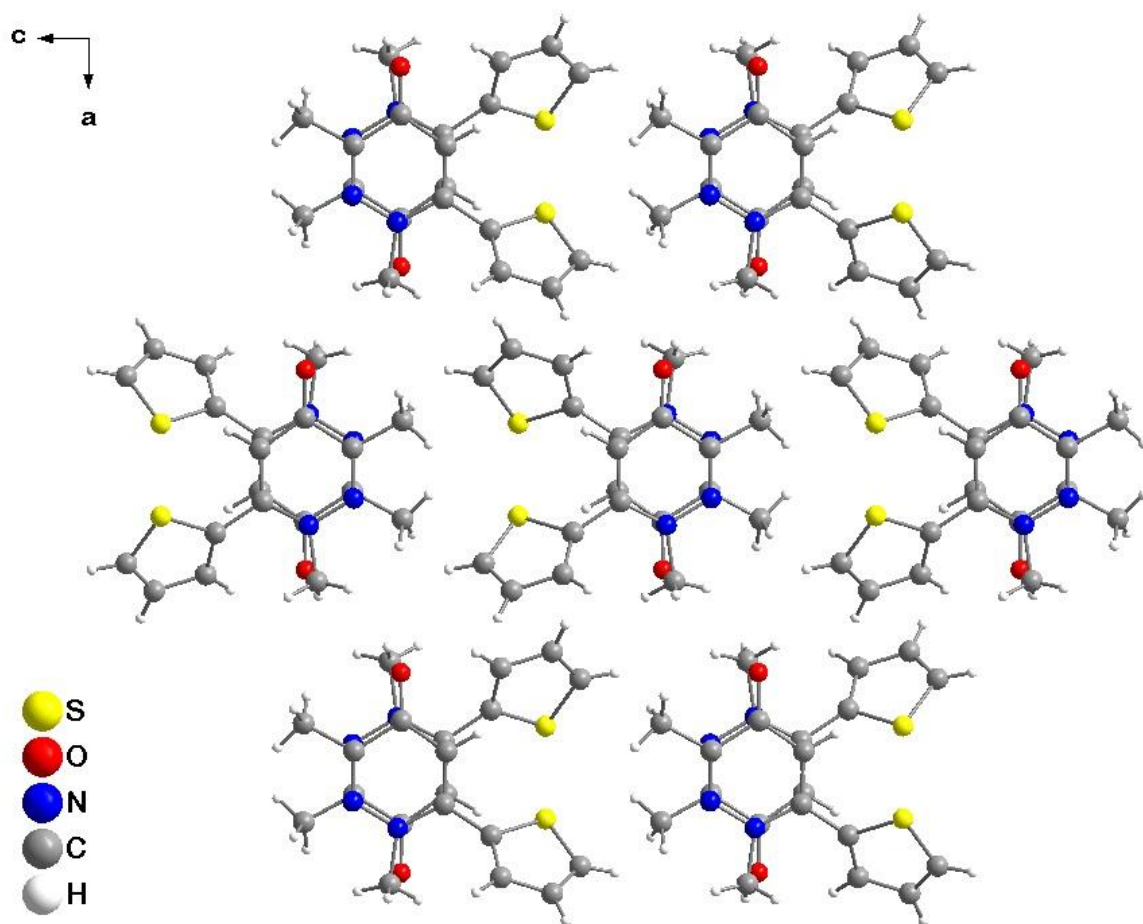
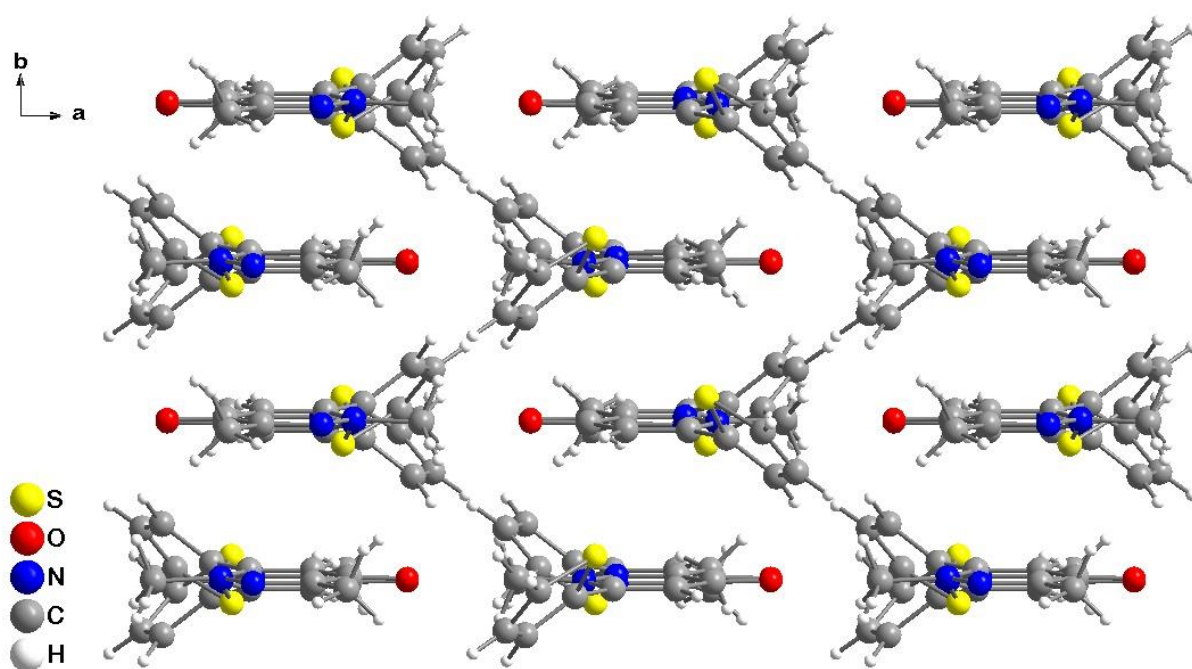


Figure S103. Crystal packing of pyrazole **71** along *a* (**a**) and *b* (**b**) axis.





b



c

Figure S104. Crystal packing of pyridazinone **9a** along *a* (a), *b* (b) and *c* (c) axis.

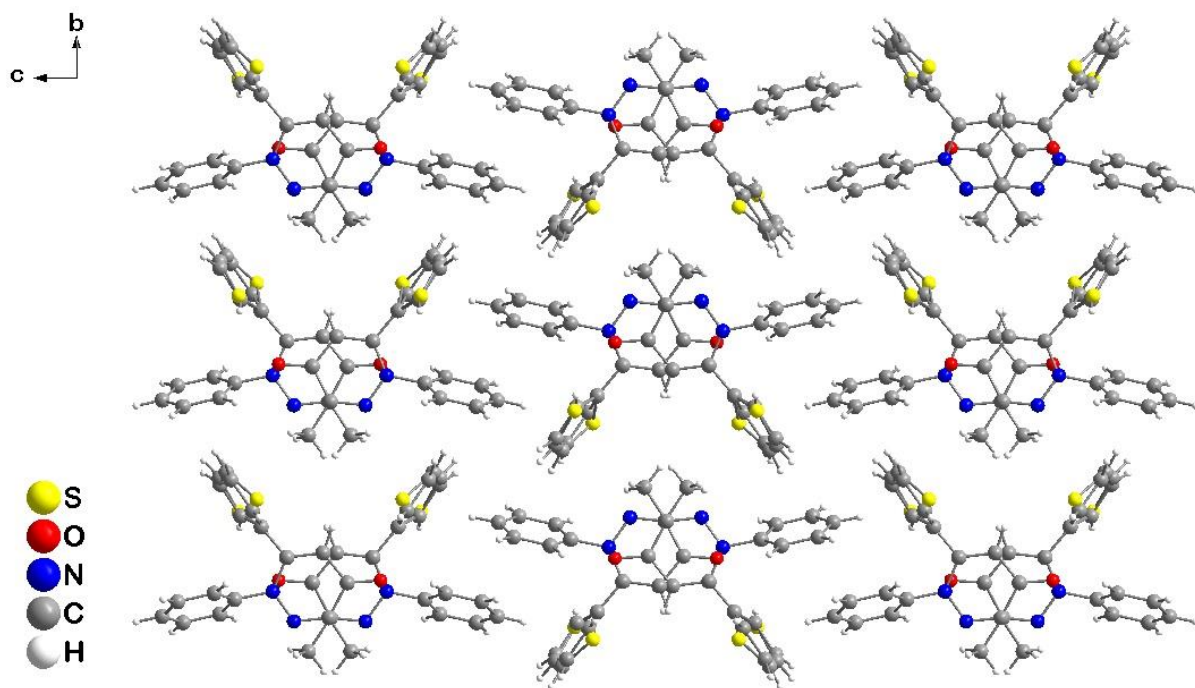
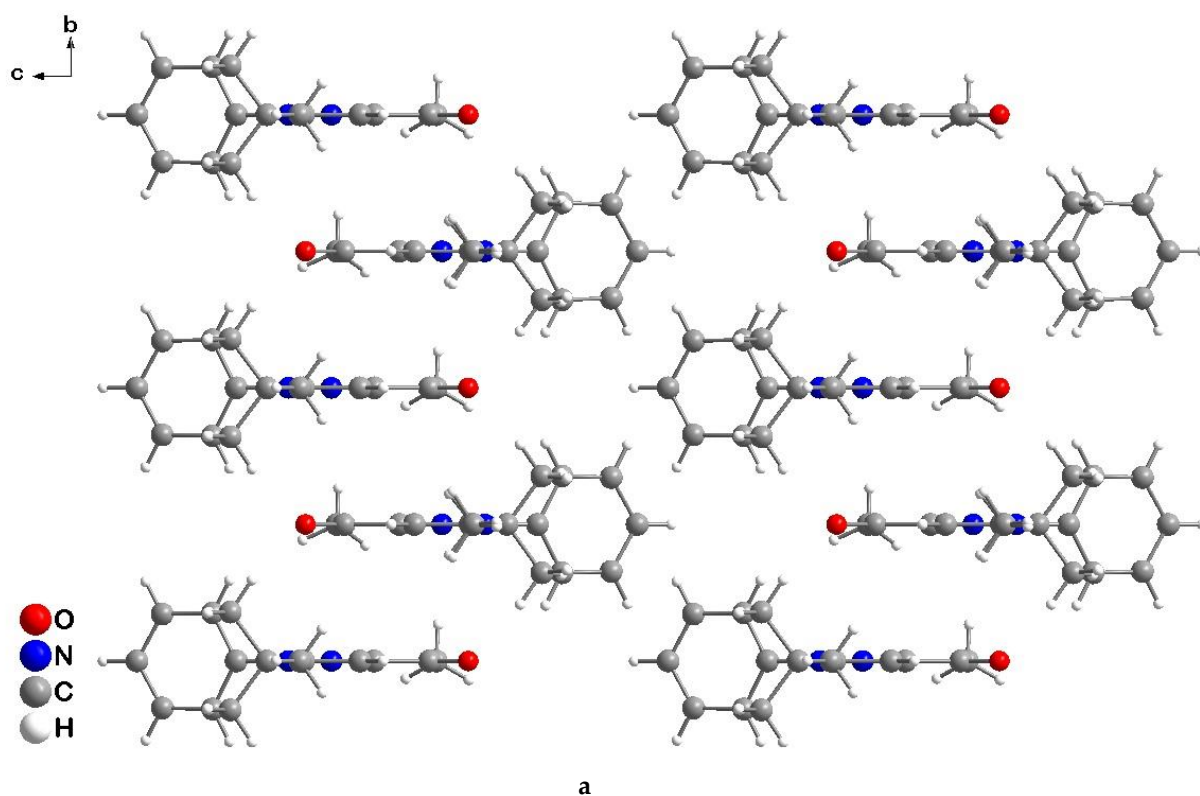


Figure S105. Crystal packing of pyridazinone **9b** along *a* axis.



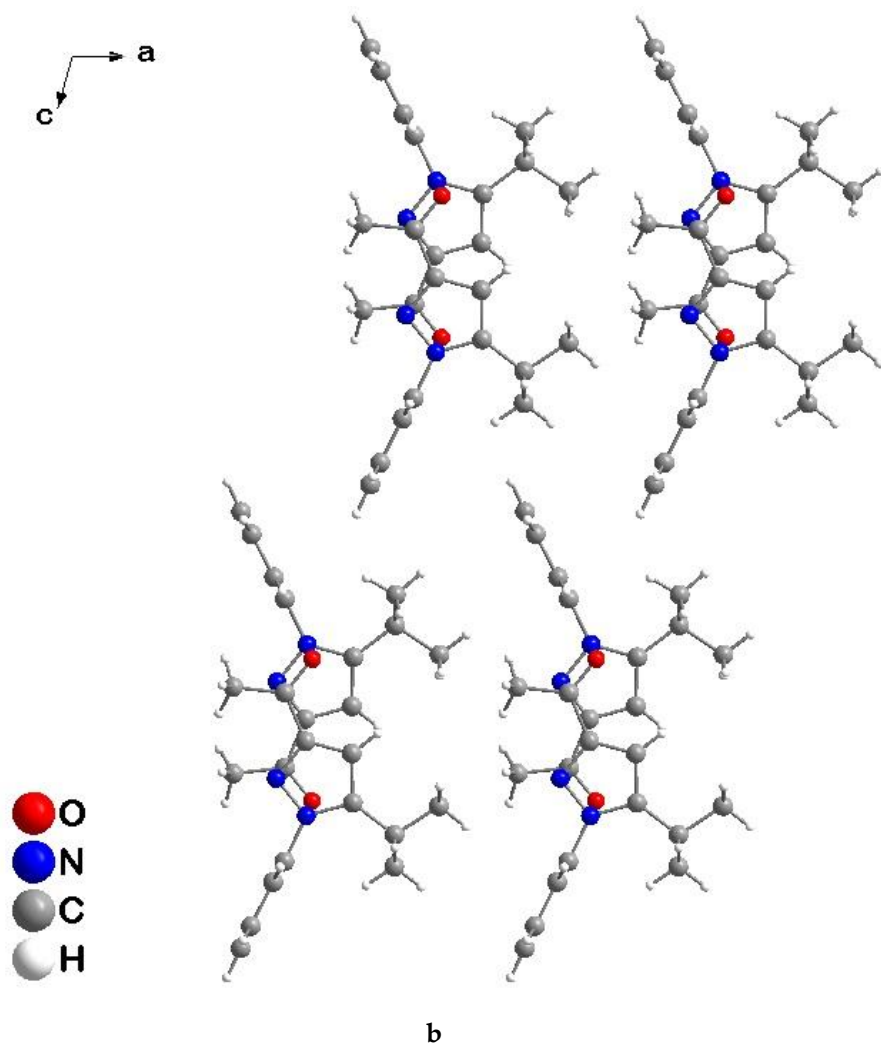


Figure S106. Crystal packing of pyrazole 12 along *a* (**a**) and *b* (**b**) axis.

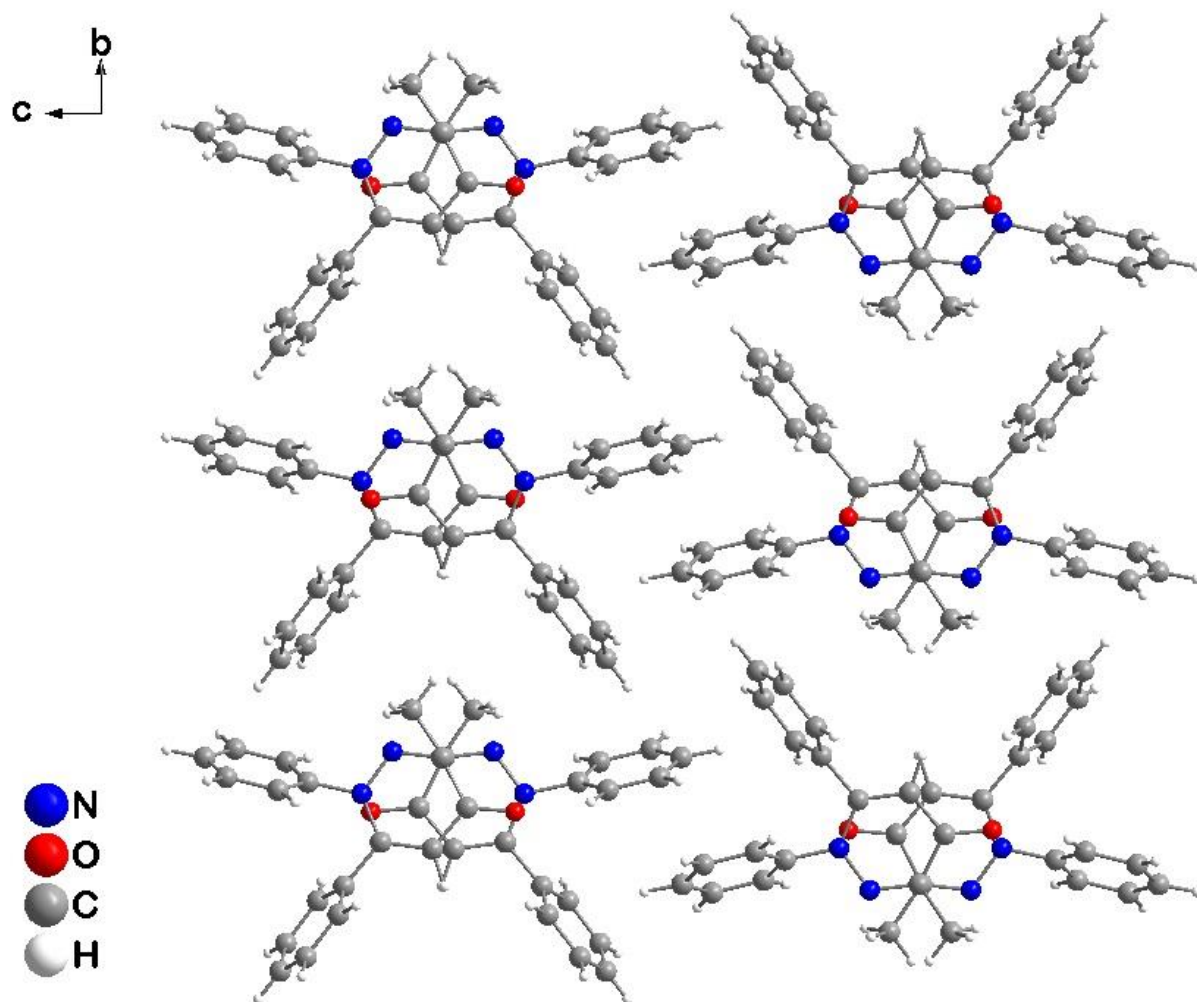
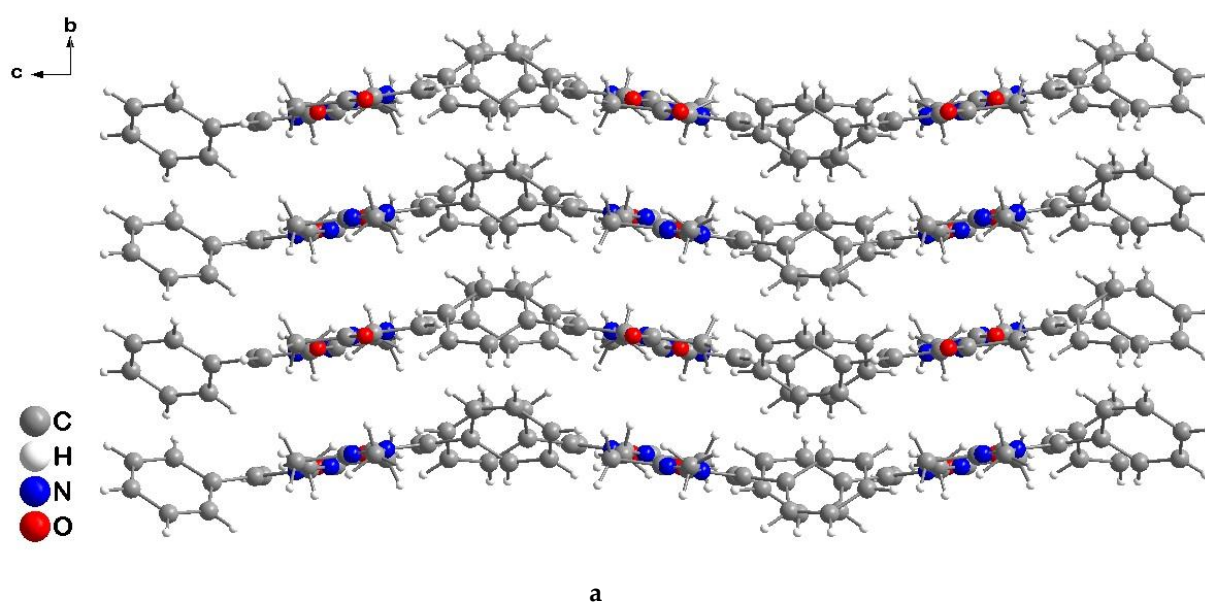


Figure S107. Crystal packing of pyridazinone **14** along *a* axis.



a

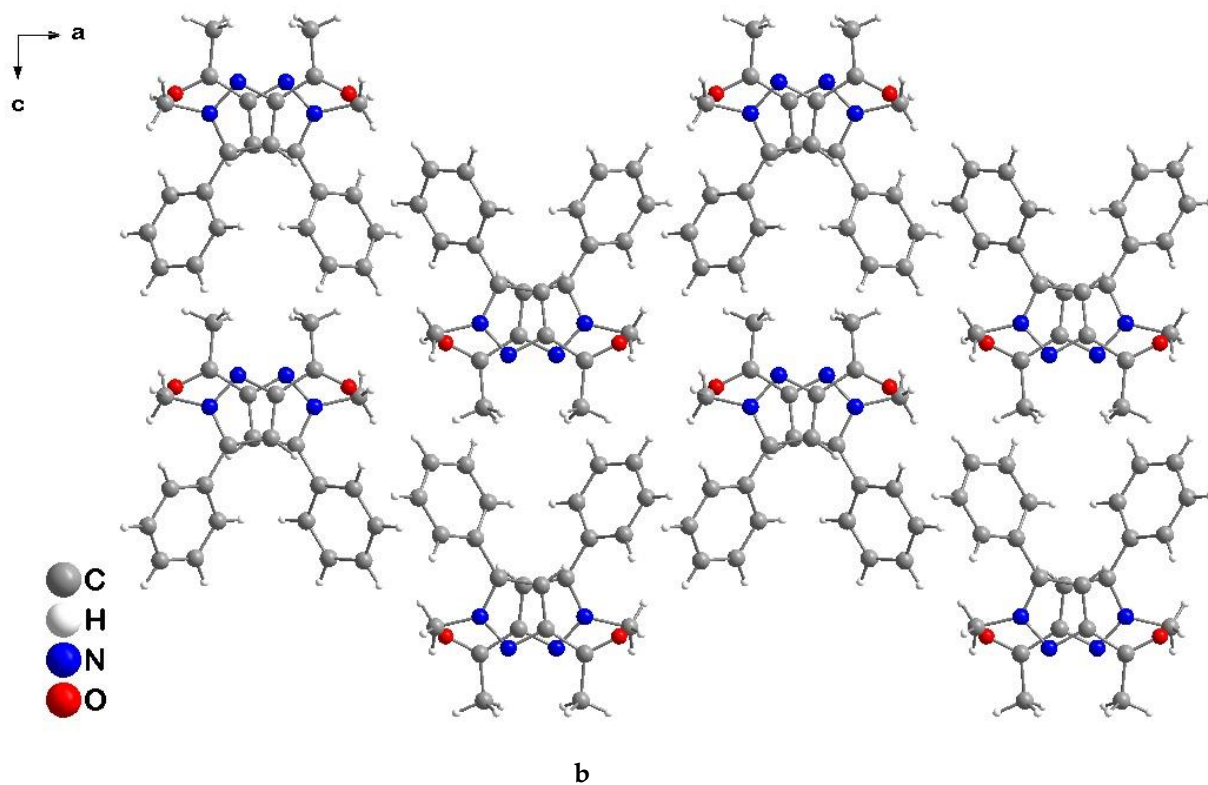


Figure S108. Crystal packing of pyrazole **15b** along *a* (a) and *b* (b) axis.

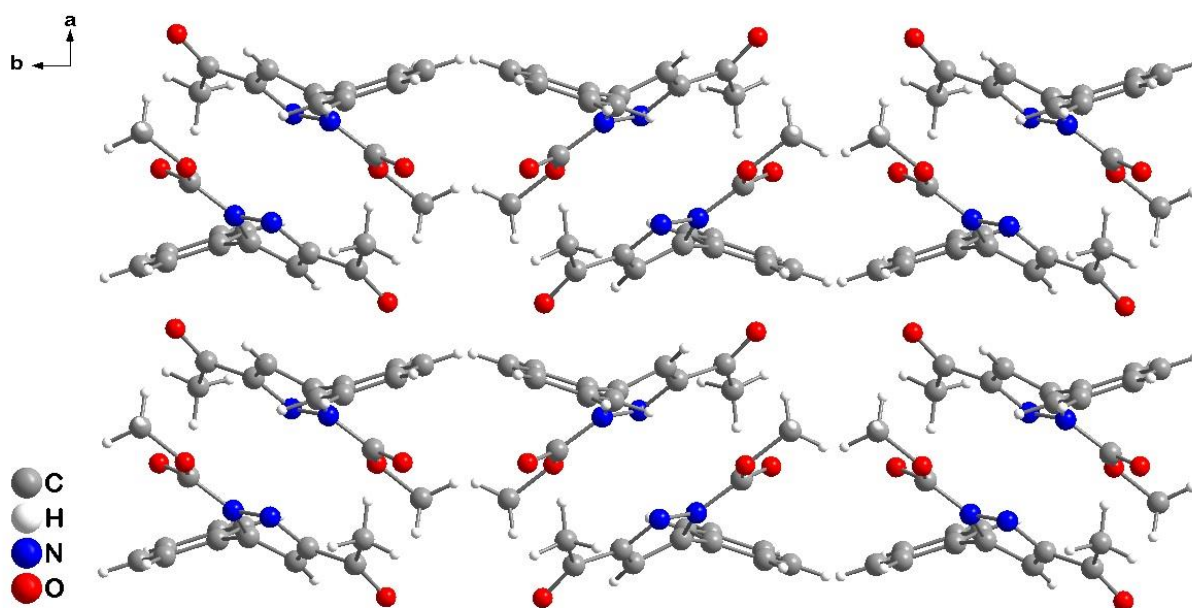


Figure S109. Crystal packing of pyrazole **21b** along *c* axis.

Table S1. Selected bond distances (Å) in diketone **2c**.

β-Diketone fragment			
C–C	C–O	O–H	O–H...O
1.358(9)-1.435(9)	1.257(9)-1.302(11)	1.027(93)	1.57(10)
Acetal fragment			
1.569(12)	1.371(10)-1.427(11)	–	–

Table S2. Selected bond distances (Å) in furanones **3** and **5**.

Compound	Furanone fragment			
	C=C	C–C	C–O	C–Me
3	1.344(4)	1.408(4)-1.541(8)	1.322(4)-1.522(9)	1.503(2)
5	1.354(4)	1.402(6)-1.531(4)	1.336(4)-1.470(4)	1.505(5)
Aromatic ring				
3	1.353(6)-1.409(5)	–	–	–
5	1.349(8)-1.386(6)	–	–	–

Table S3. Dihedral angles between the azaheterocyclic and aryl planes in the crystals of compounds **7l**, **9a**, **9b**, **12**, **14**, **15b**, **21b**.

Compound	Aromatic substituent at heterocyclic atom N	Aromatic substituent at heterocyclic atom C	Dihedral angle between planes (°)
7l	difluorophenyl	–	63.19(23)
9a	–	thienyl	46.06(23)
9b	phenyl	–	66.32(7)
–	–	thienyl	65.84(25)
12	phenyl	–	89.71(44)
14	phenyl	–	64.21(17)
–	–	phenyl	68.20(24)
15b	–	phenyl	44.71(16)
21b	–	phenyl	53.05(13)

Table S4. Selected bond distances in pyrazoles **7a**, **7l**, **12**, **15b**, **21b**.

Parameter, Å	7a	7l	12	15b	21b
C–C (Ph)	–	1.361(6)-1.391(5)	1.363(9)-1.382(9)	1.365(6)-1.398(4)	1.378(5)-1.388(5)
C–C (pyr)	1.374(3)-1.392(3)	1.377(5)-1.387(5)	1.374(1)-1.391(1)	1.370(4)-1.399(5)	1.356(4)-1.399(4)
N–N	1.335(3)	1.346(4)	1.366(9)	1.342(3)	1.363(4)
C–N (pyr)	1.345(3)-1.371(3)	1.336(5)-1.372(4)	1.322(8)-1.361(9)	1.322(8)-1.361(9)	1.327(3)-1.340(4)
C–N	1.451(3)	1.435(4)	1.446(8)	1.452(4)	1.412(3)
C–O (acetyl)	1.210(3)	1.218(5)	1.220(9)	1.218(4)	1.218(4)
C–O (ester)	1.207(3)	1.205(5)	–	–	1.193(4)
	1.333(3)	1.317(5)			1.310(4)

Table S5. Selected bond distances in pyridazinones **9a**, **9b**, **14**.

Parameter, Å	9a	9b	14
C–C (Ph)	-	1.378(3)–1.389(3)	1.361(5)–1.395(4)
C–C (thienyl)	1.329(6)–1.400(5)	1.352(9)–1.440(2)	-
C–C (pyridazinone)	1.370(4)–1.461(4)	1.360(3)–1.469(3)	1.358(3)–1.472(4)
N–N	1.354(4)	1.356(2)	1.359(3)
C–N (pyridazinone)	1.303(4)–1.353(4)	1.304(3)–1.370(3)	1.297(3)–1.363(3)
C–N	1.468(4)	1.444(2)	1.439(3)
C–O	1.249(4)	1.240(3)	1.254(3)

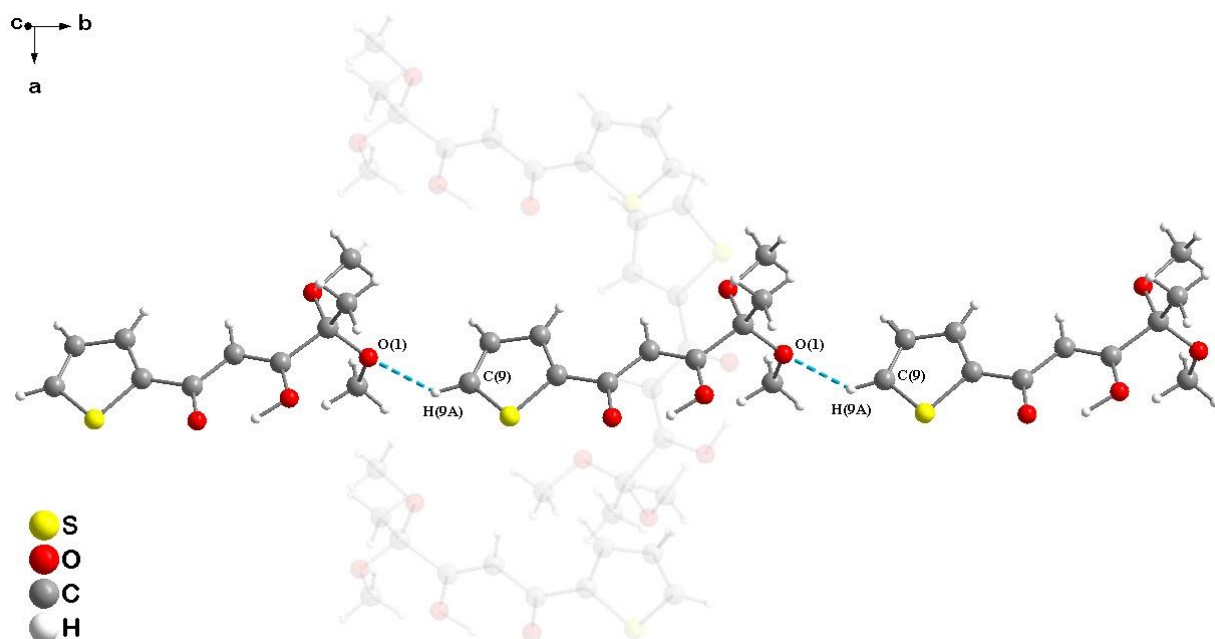


Figure S110. H-contacts in the crystal packing of 2c.

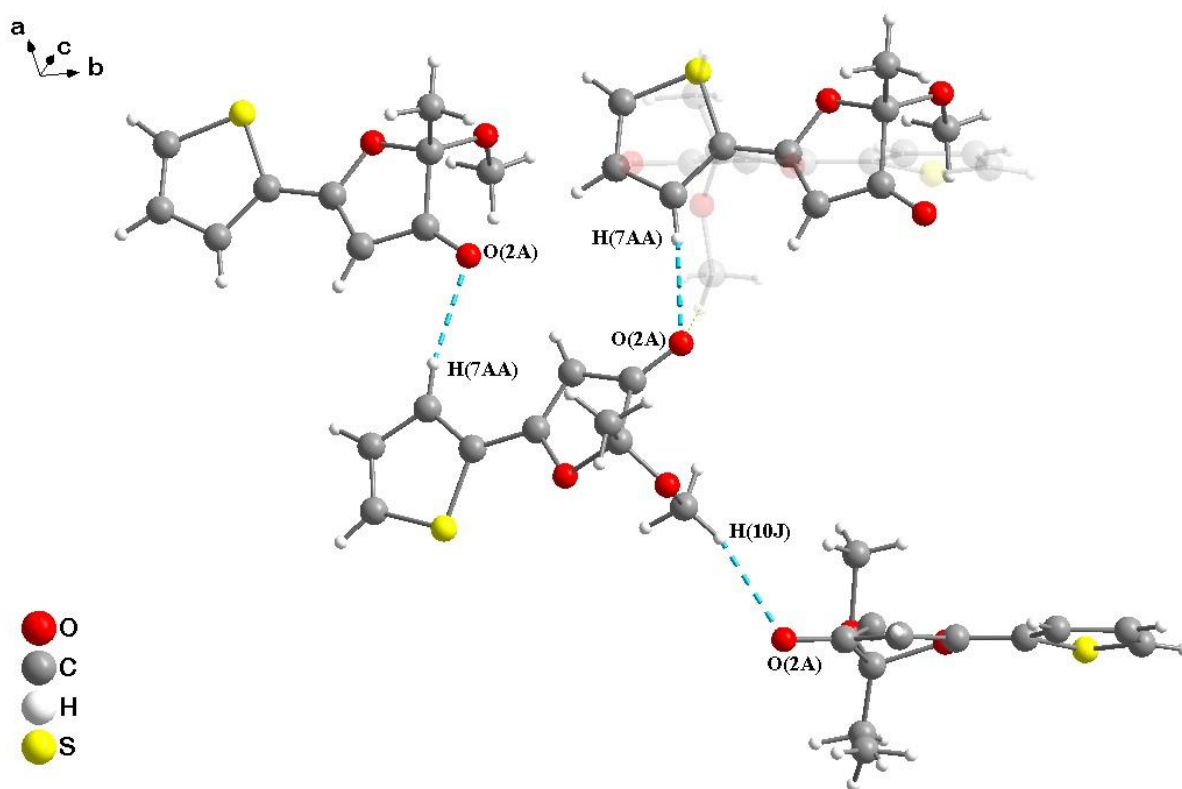


Figure S111. H-contacts in the crystal packing of 3.

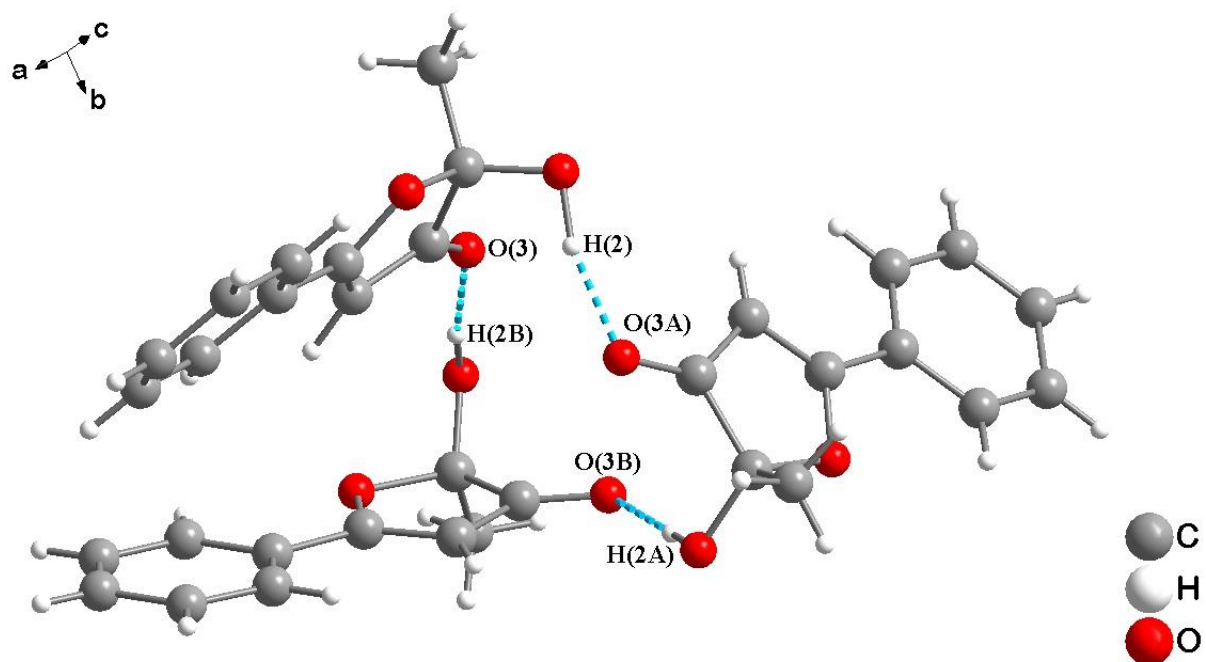


Figure S112. Intermolecular hydrogen bonds in the crystal packing of 5.

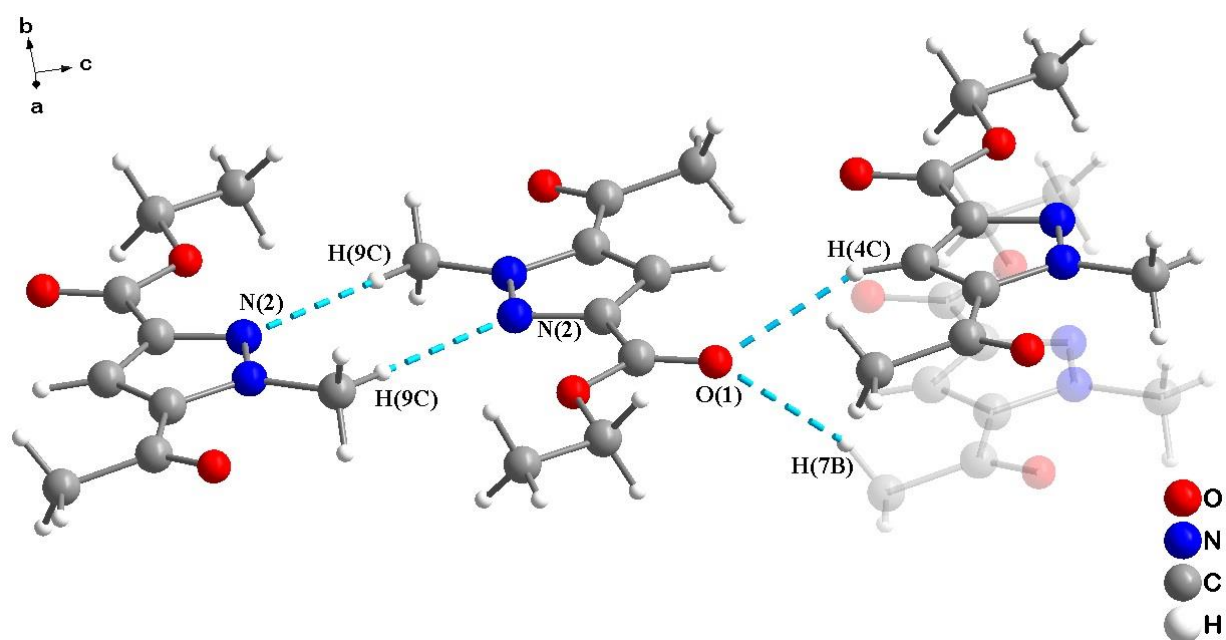


Figure S113. H-contacts in the crystal packing of 7a.

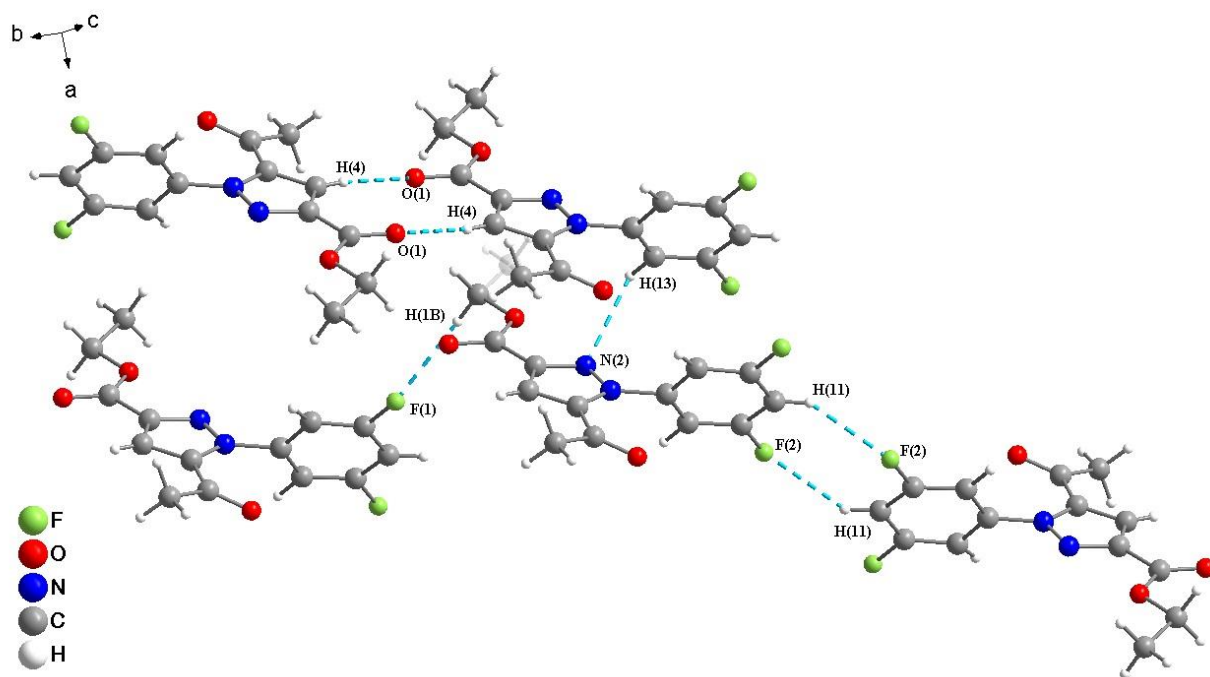


Figure S114. H-contacts in the crystal packing of 7l.

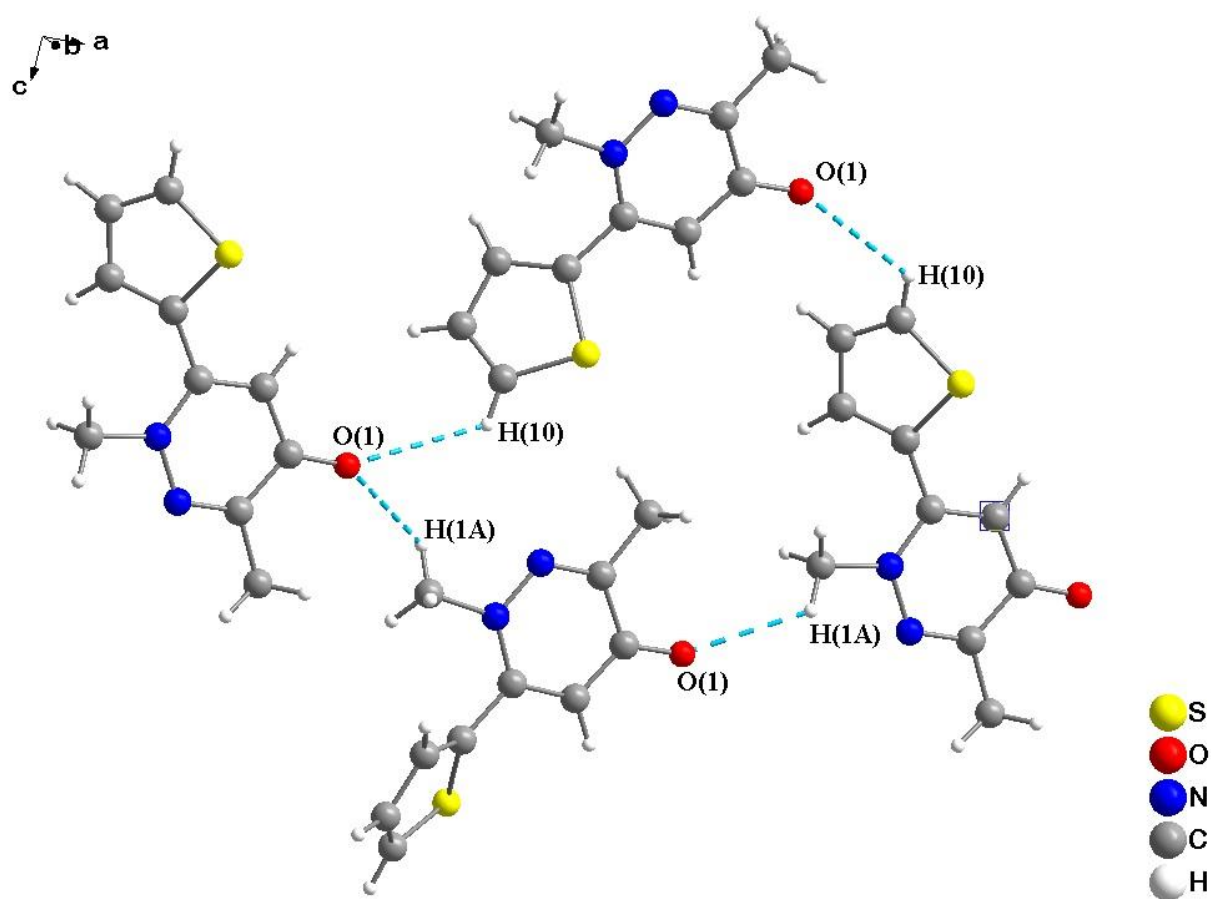


Figure S115. H-contacts in the crystal packing of 9a.

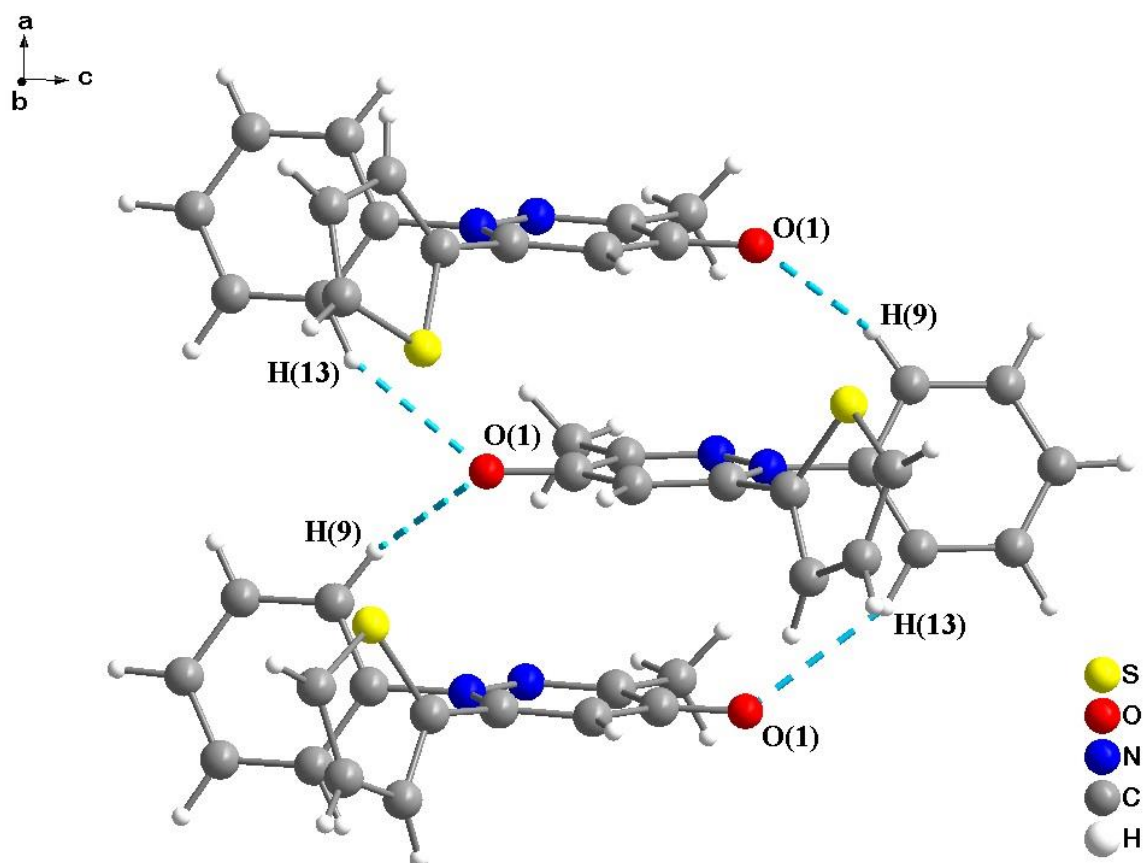


Figure S116. H-contacts in the crystal packing of **9b**.

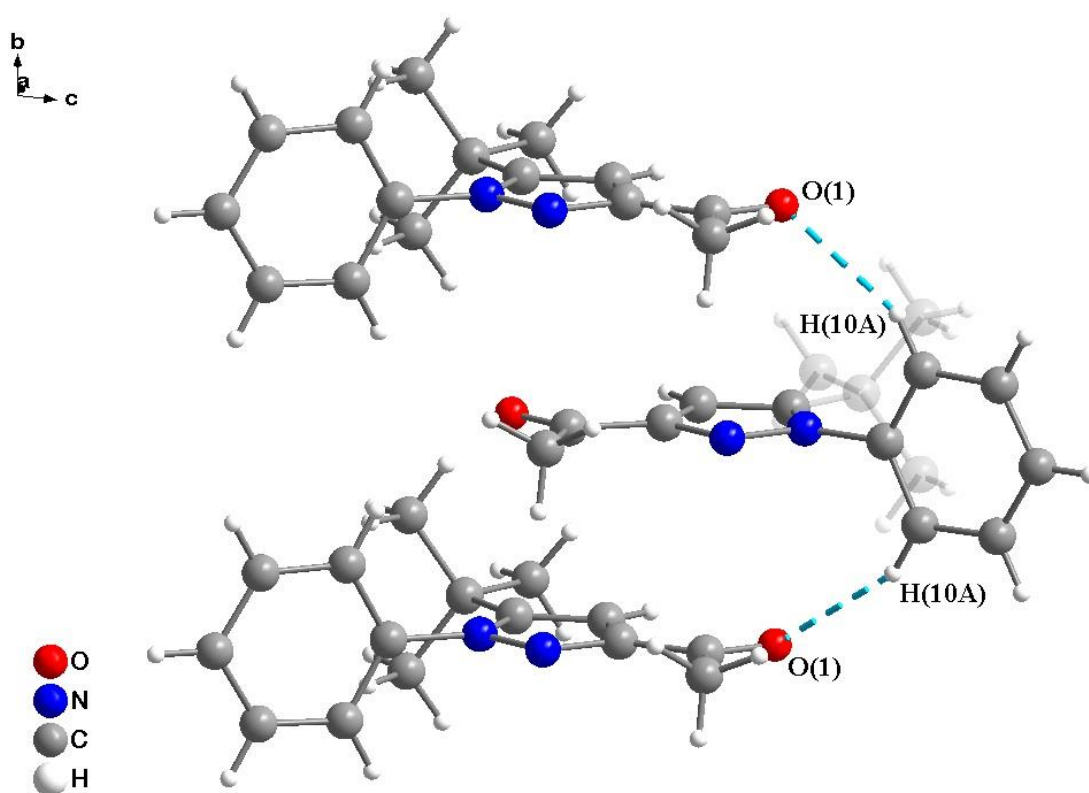


Figure S117. H-contacts in the crystal packing of **12**.

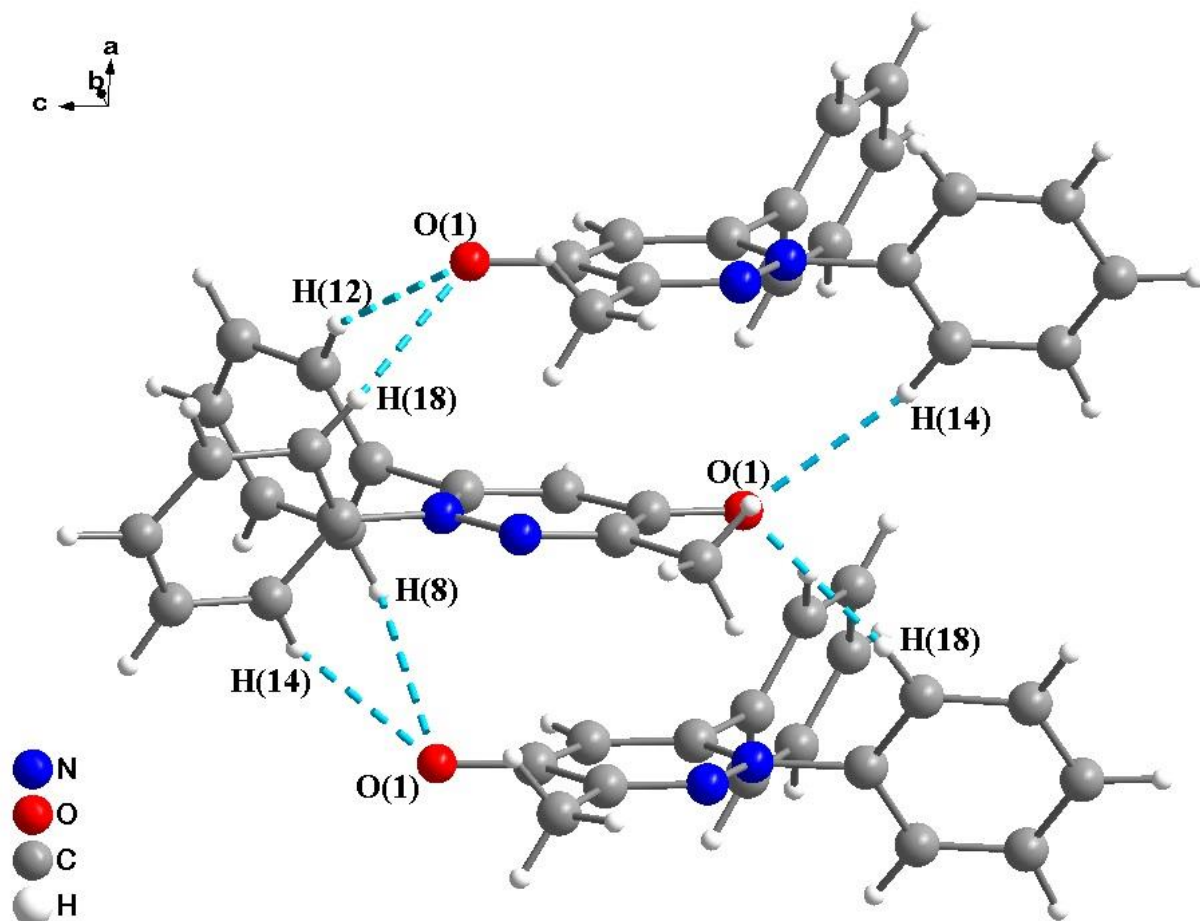


Figure S118. H-contacts in the crystal packing of **14**.

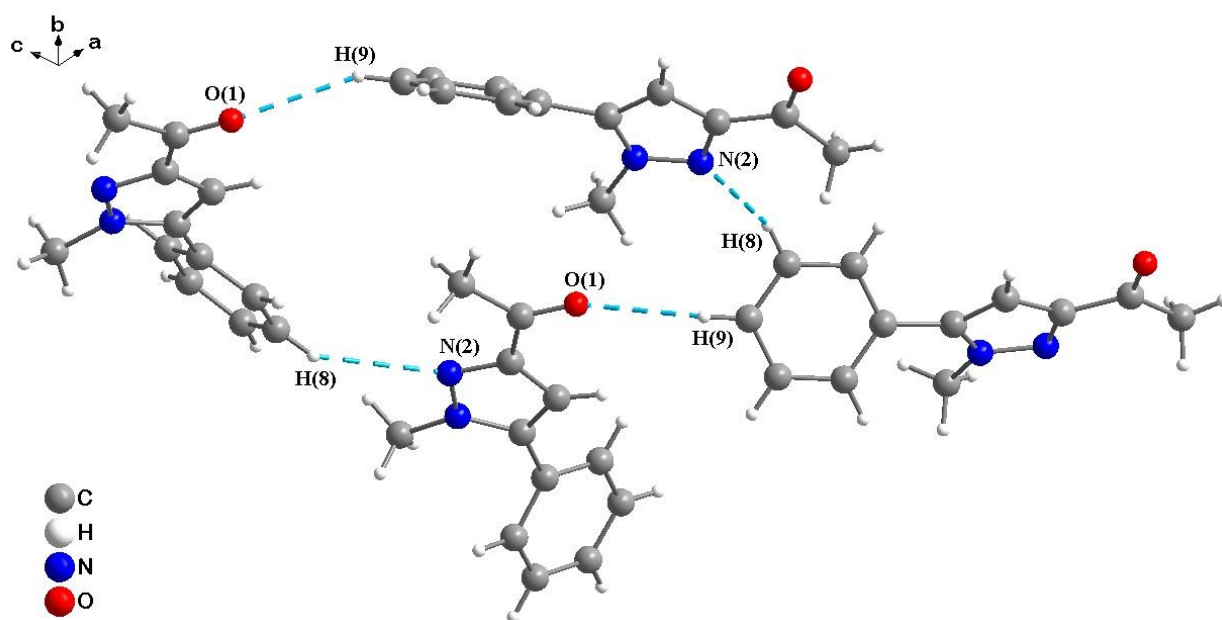


Figure S119. H-contacts in the crystal packing of **15b**.

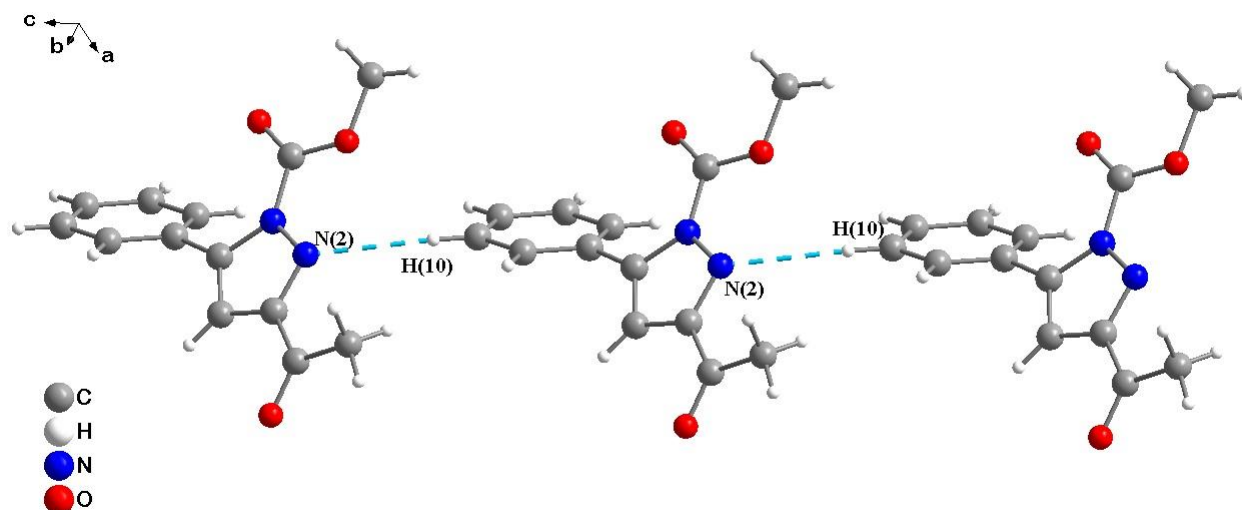


Figure S120. H-contacts in the crystal packing of **21b**.

Table S6. Intermolecular hydrogen bonds and hydrogen-contacts geometry (distances in Å, angles in degrees) in **2c**, **3**, **5**, **7l**, **9a**, **9b**, **12**, **14**, **15b**, **21b**.

Compound	<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	∠ <i>D</i> –H··· <i>A</i>	Symmetry
2c	C(9)–H(9A)···O(1)	0.930(8)	2.548(7)	3.232(9)	130	$x, -1+y, z$
3	C(7A)–H(7AA)···O(2A)	0.930(3)	2.475(2)	3.379(4)	164	$1-x, 1/2+y, 1/2-z$
	C(10B)–H(10J)···O(2A)	0.960(3)	2.411(2)	3.342(3)	163	$1+x, 3/2-y, 1/2+z$
5	O(2B)–H(2B)···O(3)	0.929(51)	1.778(52)	2.699(4)	171	$2-x, 1-y, 1-z$
	O(2)–H(2)···O(3A)	1.052(66)	1.680(62)	2.695(4)	160	$-1+x, y, z$
	O(2A)–H(2B)···O(3B)	1.008(56)	1.731(55)	2.729(4)	169	–
7a	C(9)–H(9C)···N(2)	0.960(3)	2.610(2)	3.567(3)	174	$1-x, 1-y, -z$
	C(4)–H(4C)···O(1)	0.987(2)	2.473(25)	3.401(3)	156	$-x, 1-y, 1-z$
	C(7)–H(7B)···O(1)	0.960(3)	2.680(2)	3.517(4)	146	$2-x, 1-y, 1-z$
7l	C(11)–H(11)···F(2)	0.907(37)	2.591(33)	3.381(5)	146	$2-x, -y, 1-z$
	C(13)–H(13)···N(2)	1.049(44)	2.719(43)	3.295(5)	114	$-1+x, y, z$
	C(1)–H(1B)···F(1)	0.971(4)	2.620(3)	3.570(5)	163	$x, 1+y, z$
	C(4)–H(4)···O(1)	0.825(45)	2.574(43)	3.376(5)	165	$1+x, y, 1+z$
9a	C(1)–H(1A)···O(1)	0.960(4)	2.604(2)	3.206(4)	121	$-1/2+x, 3/2-y, 1-z$
	C(10)–H(10)···O(1)	0.929(4)	2.945(2)	3.558(5)	125	$-x, -1/2+y, z$
9b	C(9)–H(9)···O(1)	0.943(32)	2.518(31)	3.244(3)	134	$1/2+x, y, 1/2-z$
	C(1)–H(1A)···O(1)	0.987(26)	2.488(24)	3.388(3)	152	$-1/2+x, y, 1/2-z$
12	C(10A)–H(10A)···O(1)	0.930(7)	2.510(5)	3.367(8)	153	$x, 1+y, 1+z$
14	C(14)–H(14)···O(1)	0.969(27)	2.598(26)	3.502(31)	156	$-1/2+x, y, 1/2-z$
	C(8)–H(8)···O(1)	0.930(3)	2.850(22)	3.564(4)	134	$-1/2+x, y, 1/2-z$
	C(18)–H(18)···O(1)	0.919(26)	2.535(25)	3.275(3)	138	$-1/2+x, y, 1/2-z$
	C(12)–H(12)···O(1)	0.930(3)	2.709(2)	3.559(3)	152	$1/2+x, y, 1/2-z$
15b	C(8)–H(8)···N(2)	0.930(4)	2.944(2)	3.744(5)	145	$-1/2+x, 1/2-y, 1-z$
	C(9)–H(9)···O(1)	0.930(3)	2.730(3)	3.585(4)	153	$-1/2+x, -1+y, 1/2-z$
	C(10)–H(10)···N(2)	0.930(4)	2.635(3)	3.540(5)	164	–