

Supporting information

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

Yulia O. Edilova ^{1*}, Ekaterina A. Osipova ^{1,2}, Pavel A. Slepukhin ¹, Victor I. Saloutin ¹ and Denis N. Bazhin ^{1,2*}

¹Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 620108, Yekaterinburg, Russian Federation

²Department of Organic and Biomolecular Chemistry, Ural Federal University named after the First President of Russia B.N. Eltsin, 620002, Yekaterinburg, Russian Federation

*Correspondence: edilova_yuliya@mail.ru (Y.O.E.); dnbazhin@gmail.com (D.N.B.)

Table of contents

Figure S1. ¹ H NMR spectrum of compound 1	5
Figure S2. ¹³ C NMR spectrum of compound 1	6
Figure S3. ¹ H NMR spectrum of compound 2a	7
Figure S4. ¹³ C NMR spectrum of compound 2a	8
Figure S5. ¹ H NMR spectrum of compound 2b	9
Figure S6. ¹³ C NMR spectrum of compound 2b	10
Figure S7. ¹ H NMR spectrum of compound 2c	11
Figure S8. ¹³ C NMR spectrum of compound 2c	12
Figure S9. ¹ H NMR spectrum of compound 3	13
Figure S10. ¹³ C NMR spectrum of compound 3	14
Figure S11. ¹ H NMR spectrum of compound 4a	15
Figure S12. ¹³ C NMR spectrum of compound 4a	16
Figure S13. ¹ H NMR spectrum of compound 4b	17
Figure S14. ¹³ C NMR spectrum of compound 4b	18
Figure S15. ¹ H NMR spectrum of compound 6	19
Figure S16. ¹³ C NMR spectrum of compound 6	20
Figure S17. ¹ H NMR spectrum of compound 7a	21
Figure S18. ¹³ C NMR spectrum of compound 7a	22
Figure S19. ¹ H NMR spectrum of compound 7b	23
Figure S20. ¹³ C NMR spectrum of compound 7b	24

Figure S21. ¹ H NMR spectrum of compound 7c	25
Figure S22. ¹³ C NMR spectrum of compound 7c	26
Figure S23. ¹ H NMR spectrum of compound 7d	27
Figure S24. ¹³ C NMR spectrum of compound 7d	28
Figure S25. ¹⁹ F NMR spectrum of compound 7d	29
Figure S26. ¹ H NMR spectrum of compound 7e	30
Figure S27. ¹³ C NMR spectrum of compound 7e	31
Figure S28. ¹⁹ F NMR spectrum of compound 7e	32
Figure S29. ¹ H NMR spectrum of compound 7f	33
Figure S30. ¹³ C NMR spectrum of compound 7f	34
Figure S31. ¹ H NMR spectrum of compound 7g	35
Figure S32. ¹³ C NMR spectrum of compound 7g	36
Figure S33. ¹ H NMR spectrum of compound 7h	37
Figure S34. ¹³ C NMR spectrum of compound 7h	38
Figure S35. ¹⁹ F NMR spectrum of compound 7h	39
Figure S36. ¹ H NMR spectrum of compound 7i	40
Figure S37. ¹³ C NMR spectrum of compound 7i	41
Figure S38. ¹ H NMR spectrum of compound 7j	42
Figure S39. ¹³ C NMR spectrum of compound 7j	43
Figure S40. ¹⁹ F NMR spectrum of compound 7j	44
Figure S41. ¹ H NMR spectrum of compound 7k	45
Figure S42. ¹³ C NMR spectrum of compound 7k	46
Figure S43. ¹ H NMR spectrum of compound 7l	47
Figure S44. ¹³ C NMR spectrum of compound 7l	48
Figure S45. ¹⁹ F NMR spectrum of compound 7l	49
Figure S46. ¹ H NMR spectrum of compound 8	50
Figure S47. ¹³ C NMR spectrum of compound 8	51
Figure S48. ¹ H NMR spectrum of compound 9a	52
Figure S49. ¹³ C NMR spectrum of compound 9a	53
Figure S50. ¹ H NMR spectrum of compound 9b	54
Figure S51. ¹³ C NMR spectrum of compound 9b	55
Figure S52. ¹ H NMR spectrum of compound 10a	56
Figure S53. ¹³ C NMR spectrum of compound 10a	57
Figure S54. ¹ H NMR spectrum of compound 10b	58
Figure S55. ¹³ C NMR spectrum of compound 10b	59
Figure S56. ¹ H NMR spectrum of compound 11	60

Figure S57. ¹³ C NMR spectrum of compound 11	61
Figure S58. ¹ H NMR spectrum of compound 12	62
Figure S59. ¹³ C NMR spectrum of compound 12	63
Figure S60. ¹ H NMR spectrum of compound 13a	64
Figure S61. ¹³ C NMR spectrum of compound 13a	65
Figure S62. ¹ H NMR spectrum of compound 13b	66
Figure S63. ¹³ C NMR spectrum of compound 13b	67
Figure S64. ¹ H NMR spectrum of compound 14	68
Figure S65. ¹³ C NMR spectrum of compound 14	69
Figure S66. ¹ H NMR spectrum of compound 15a	70
Figure S67. ¹³ C NMR spectrum of compound 15a	71
Figure S68. ¹ H NMR spectrum of compound 15b	72
Figure S69. ¹³ C NMR spectrum of compound 15b	73
Figure S70. ¹ H NMR spectrum of compound 16	74
Figure S71. ¹ H NMR spectrum of compound 17	75
Figure S72. ¹³ C NMR spectrum of compound 17	76
Figure S73. ¹ H NMR spectrum of compound 18a	77
Figure S74. ¹³ C NMR spectrum of compound 18a	78
Figure S75. ¹ H NMR spectrum of compound 18b	79
Figure S76. ¹³ C NMR spectrum of compound 18b	80
Figure S77. ¹ H NMR spectrum of compound 18c	81
Figure S78. ¹³ C NMR spectrum of compound 18c	82
Figure S79. ¹ H NMR spectrum of compound 19a	83
Figure S80. ¹³ C NMR spectrum of compound 19a	84
Figure S81. ¹ H NMR spectrum of compound 19b	85
Figure S82. ¹³ C NMR spectrum of compound 19b	86
Figure S83. ¹ H NMR spectrum of compound 19c	87
Figure S84. ¹³ C NMR spectrum of compound 19c	88
Figure S85. ¹ H NMR spectrum of compound 20a	89
Figure S86. ¹³ C NMR spectrum of compound 20a	90
Figure S87. ¹ H NMR spectrum of compound 20b	91
Figure S88. ¹³ C NMR spectrum of compound 20b	92
Figure S89. ¹ H NMR spectrum of compound 20c	93
Figure S90. ¹³ C NMR spectrum of compound 20c	94
Figure S91. ¹ H NMR spectrum of compound 21a	95
Figure S92. ¹³ C NMR spectrum of compound 21a	96

Figure S93. ^1H NMR spectrum of compound 21b	97
Figure S94. ^{13}C NMR spectrum of compound 21b	98
Figure S95. ^1H NMR spectrum of compound 21c	99
Figure S96. ^{13}C NMR spectrum of compound 21c	100
Figure S97. ^1H NMR spectrum of compound 22	101
Figure S98. ^{13}C NMR spectrum of compound 22	102
Figure S99. Crystal packing of diketone 2c along <i>a</i> axis.....	103
Figure S100. Crystal packing of furanone 3 along <i>b</i> axis.....	103
Figure S101. Crystal packing of furanone 5	104
Figure S102. Crystal packing of pyrazole 7a along <i>a</i> (a) and <i>c</i> (b) axis.....	105
Figure S103. Crystal packing of pyrazole 7l along <i>a</i> (a) and <i>b</i> (b) axis.....	106
Figure S104. Crystal packing of pyridazinone 9a along <i>a</i> (a), <i>b</i> (b) and <i>c</i> (c) axis.....	107
Figure S105. Crystal packing of pyridazinone 9b along <i>a</i> axis.....	108
Figure S106. Crystal packing of pyrazole 12 along <i>a</i> (a) and <i>b</i> (b) axis.....	109
Figure S107. Crystal packing of pyridazinone 14 along <i>a</i> axis.....	110
Figure S108. Crystal packing of pyrazole 15b along <i>a</i> (a) and <i>b</i> (b) axis.....	111
Figure S109. Crystal packing of pyrazole 21b along <i>c</i> axis.....	111
Table S1. Selected bond distances (\AA) in diketone 2c	112
Table S2. Selected bond distances (\AA) in furanones 3 and 5	112
Table S3. Dihedral angles between the azaheterocyclic and aryl planes in the crystals of compounds 7l , 9a , 9b , 12 , 14 , 15b , 21b	112
Table S4. Selected bond distances in pyrazoles 7a , 7l , 12 , 15b , 21b	112
Table S5. Selected bond distances in pyridazinones 9a , 9b , 14	113
Figure S110. H-contacts in the crystal packing of 2c	114
Figure S111. H-contacts in the crystal packing of 3	114
Figure S112. Intermolecular hydrogen bonds in the crystal packing of 5	115
Figure S113. H-contacts in the crystal packing of 7a	115
Figure S114. H-contacts in the crystal packing of 7l	116
Figure S115. H-contacts in the crystal packing of 9a	116
Figure S116. H-contacts in the crystal packing of 9b	117
Figure S117. H-contacts in the crystal packing of 12	117
Figure S118. H-contacts in the crystal packing of 14	118
Figure S119. H-contacts in the crystal packing of 15b	118
Figure S120. H-contacts in the crystal packing of 21b	119
Table S6. Intermolecular hydrogen bonds and hydrogen-contacts geometry (distances in \AA , angles in degrees) in 2c , 3 , 5 , 7l , 9a , 9b , 12 , 14 , 15b , 21b	119

Figure S1. ¹H NMR spectrum of compound 1.

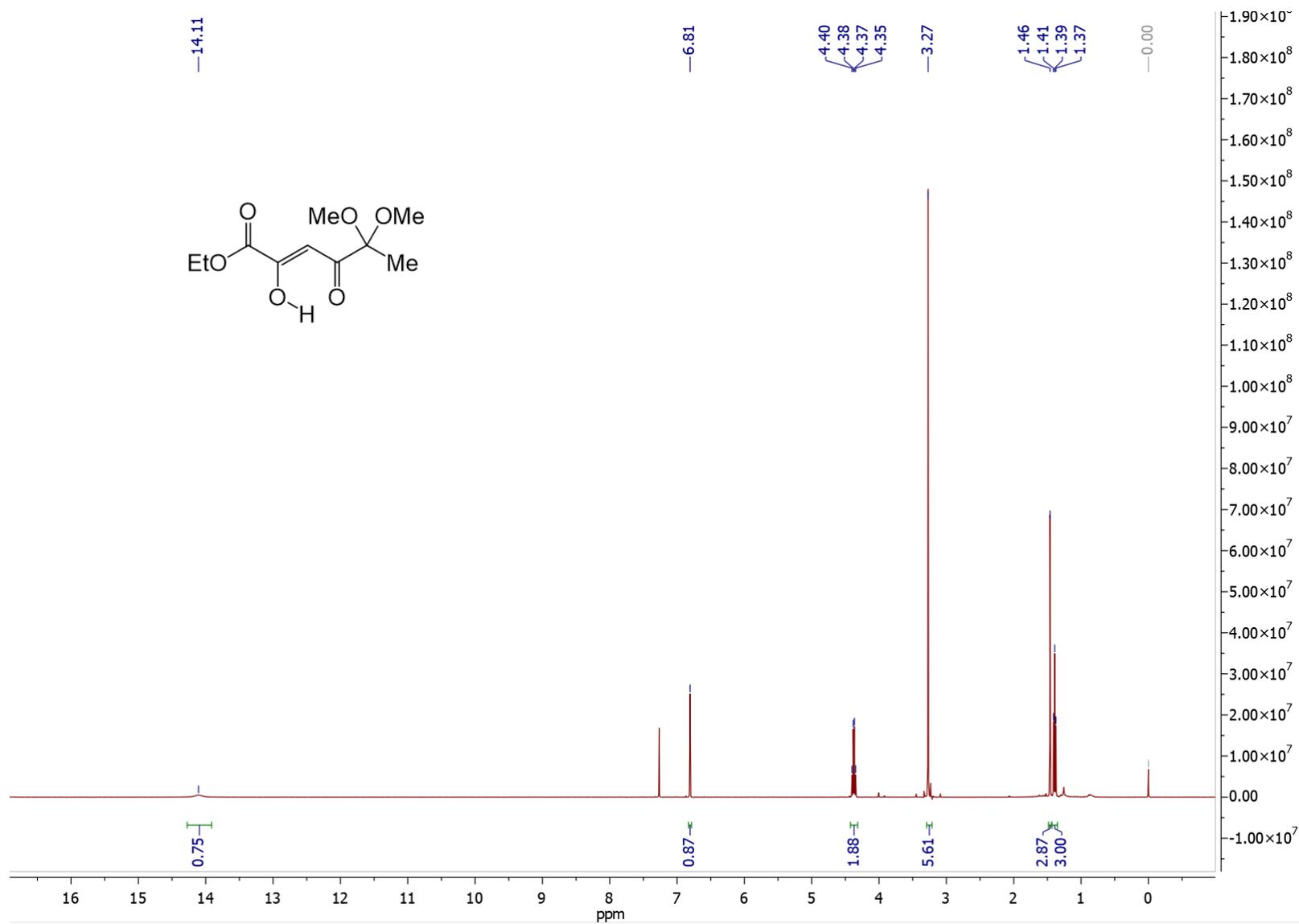


Figure S2. ^{13}C NMR spectrum of compound 1.

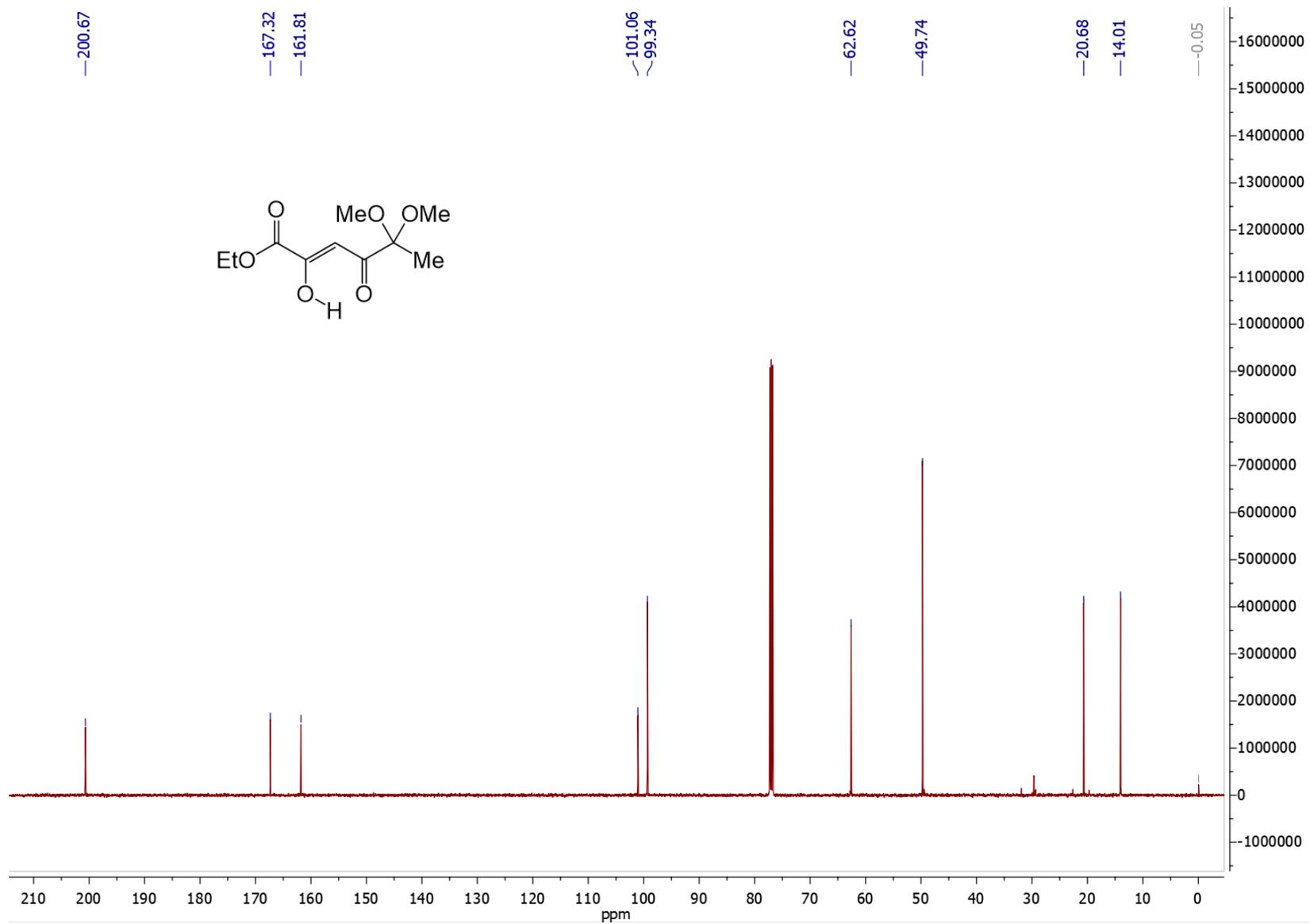


Figure S3. ¹H NMR spectrum of compound **2a**.

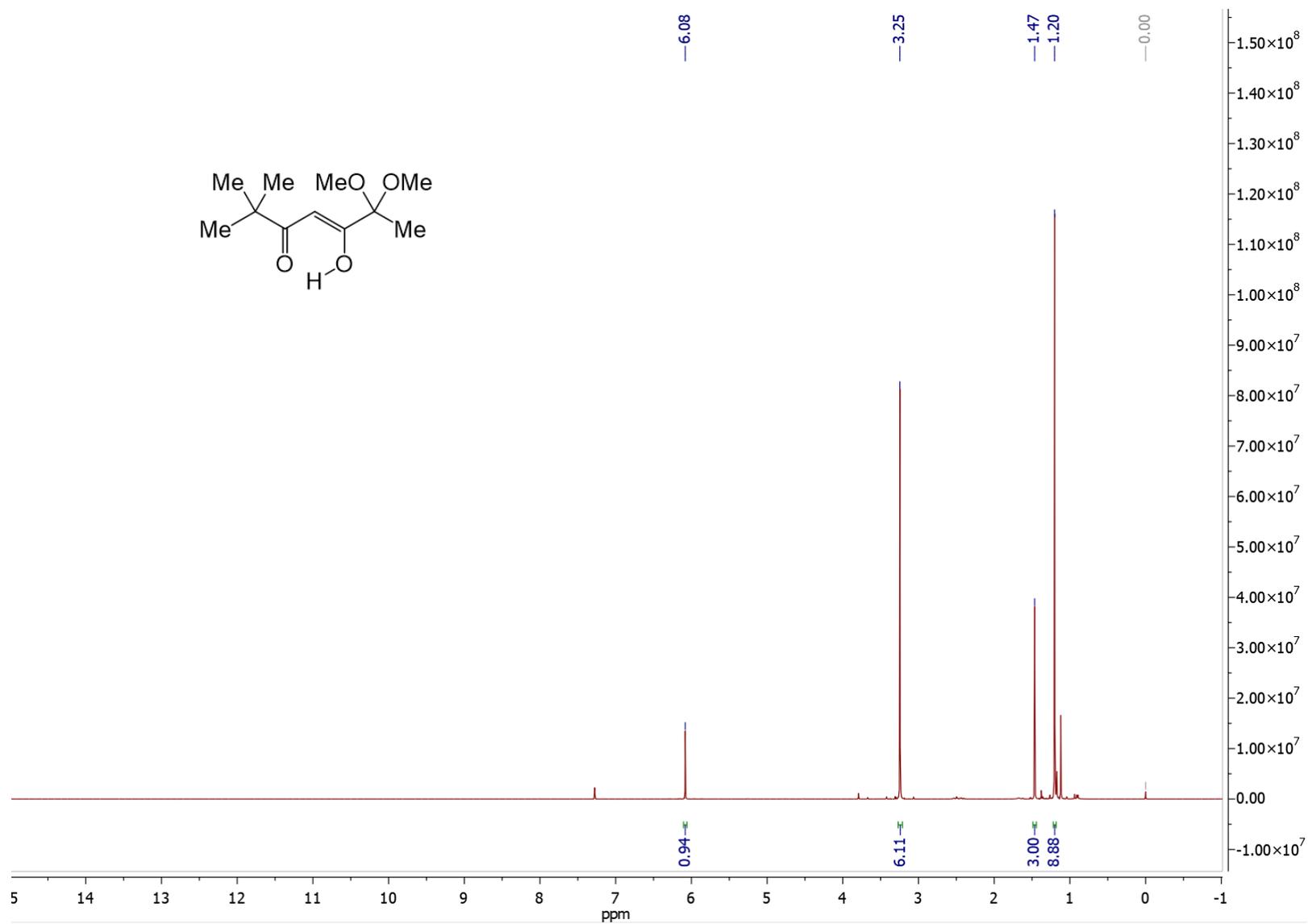


Figure S4. ^{13}C NMR spectrum of compound **2a**.

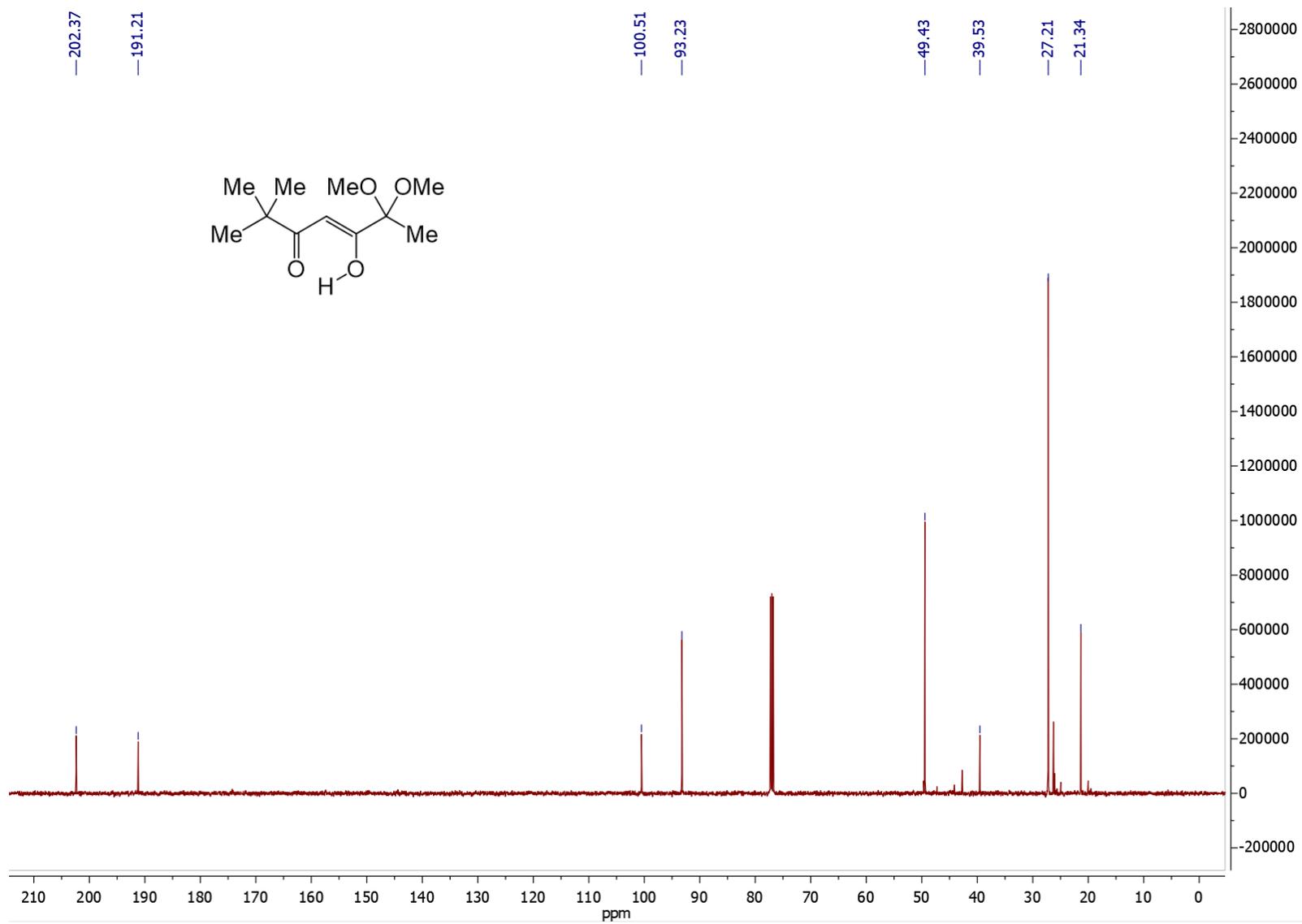


Figure S5. ^1H NMR spectrum of compound **2b**.

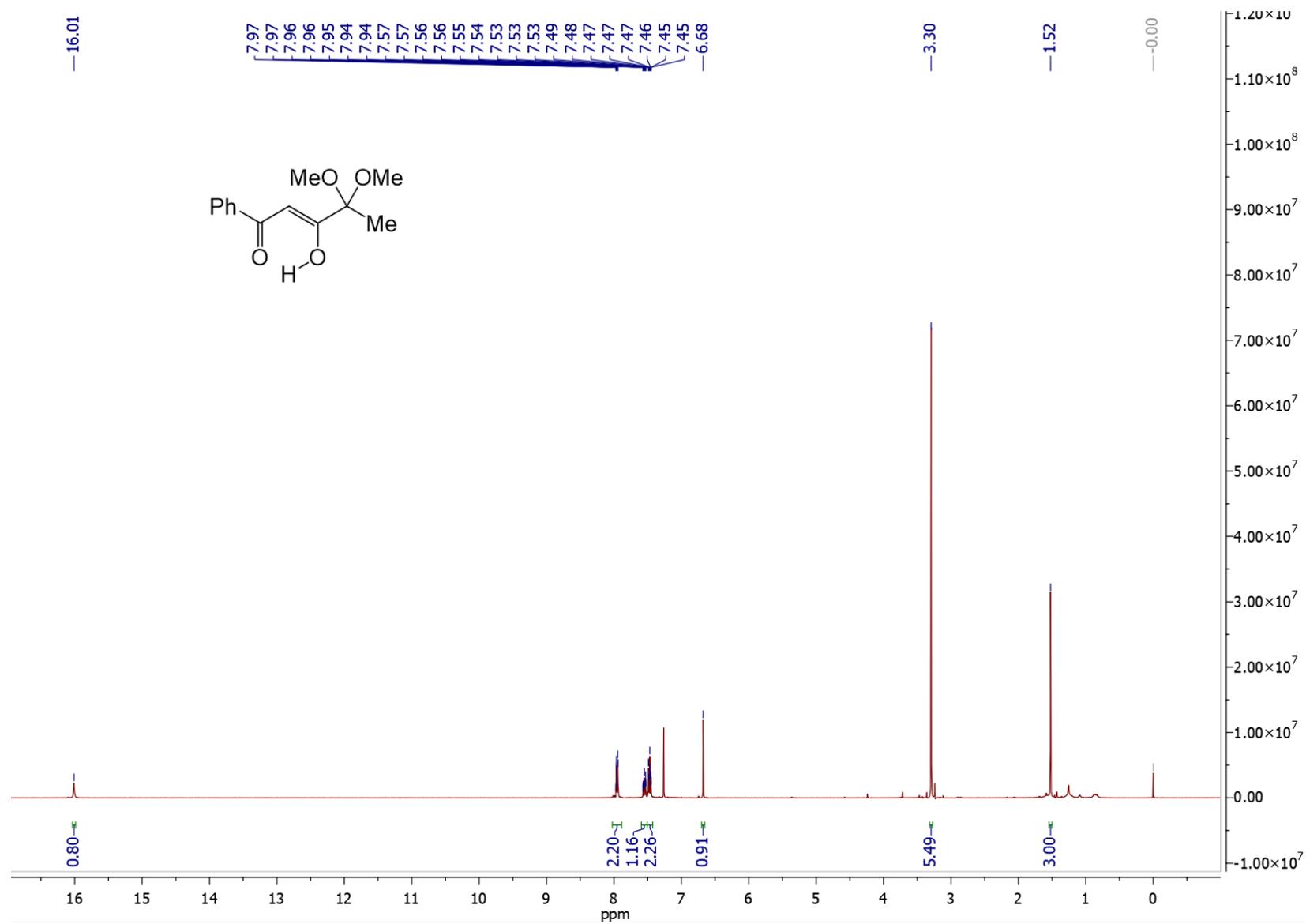


Figure S6. ^{13}C NMR spectrum of compound **2b**.

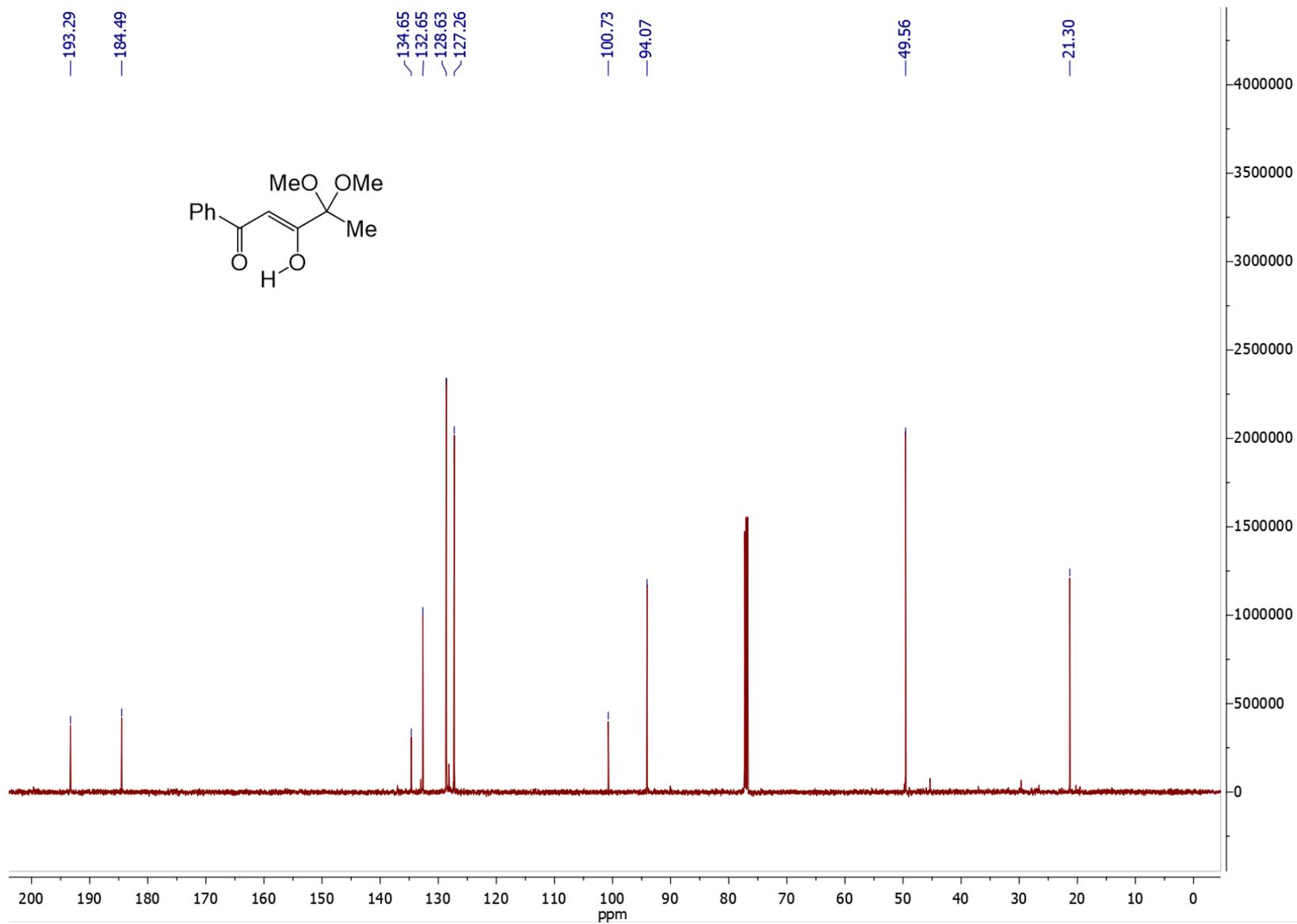


Figure S8. ^{13}C NMR spectrum of compound **2c**.

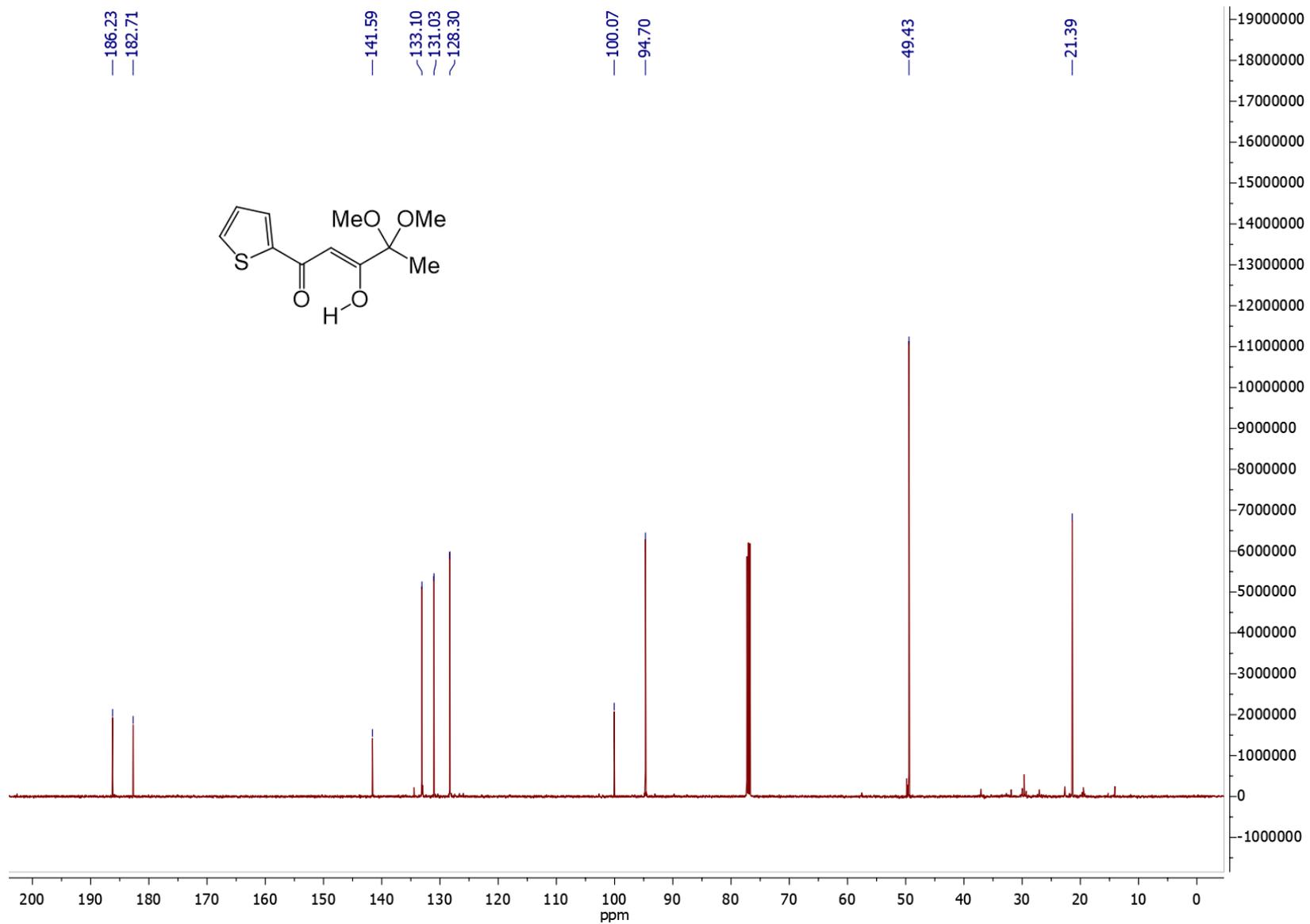


Figure S9. ¹H NMR spectrum of compound 3.

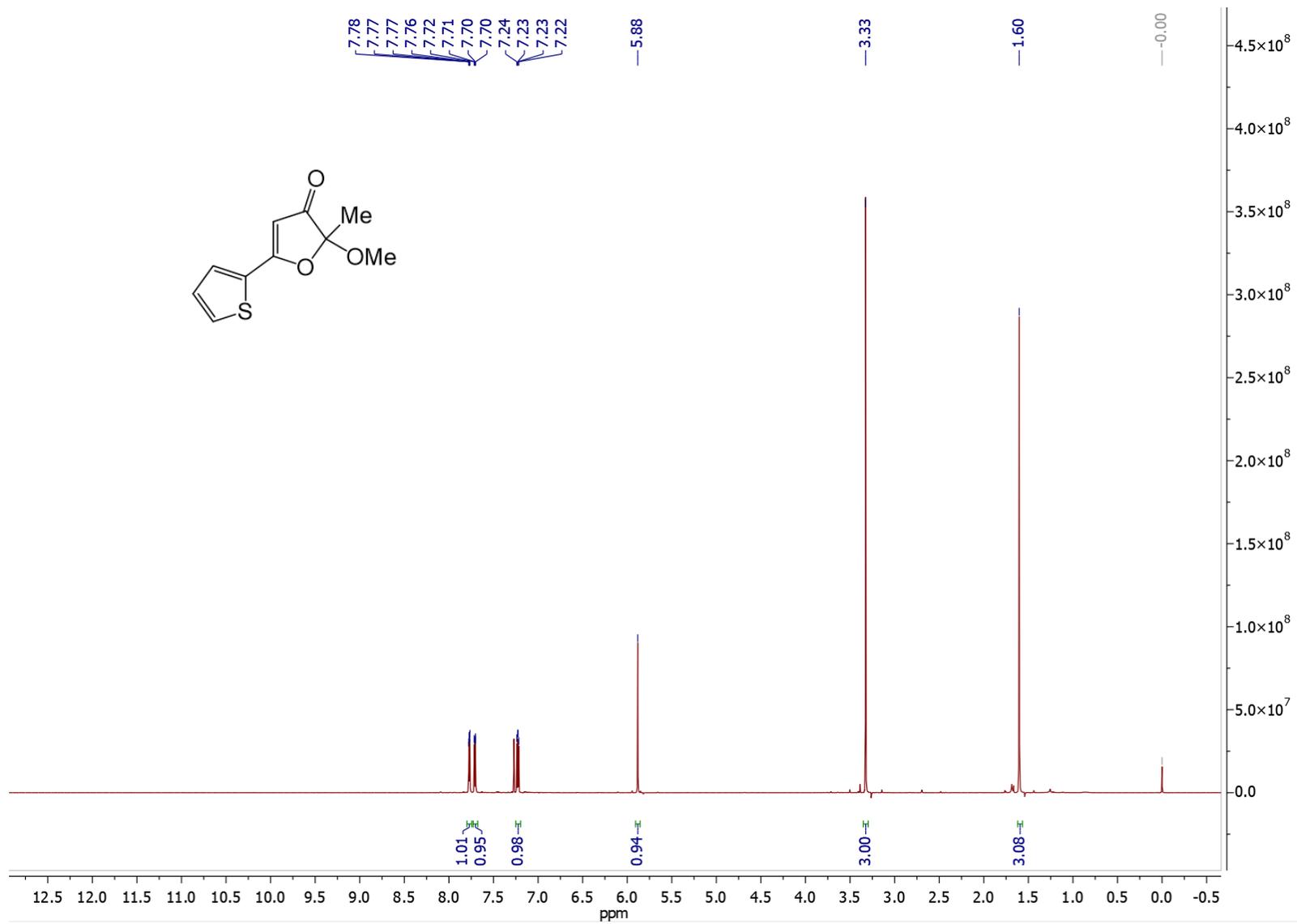


Figure S10. ^{13}C NMR spectrum of compound 3.

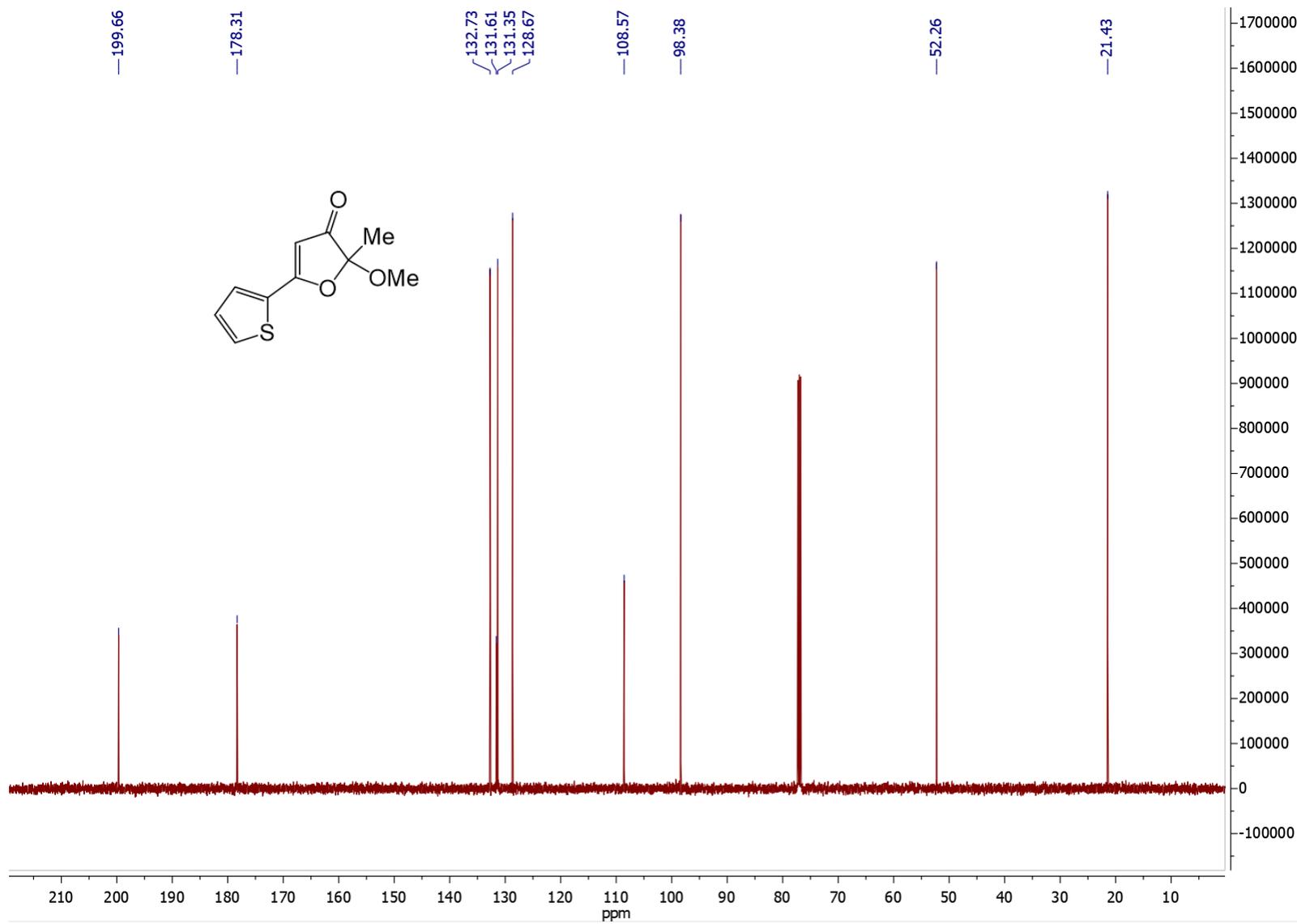


Figure S11. ¹H NMR spectrum of compound 4a.

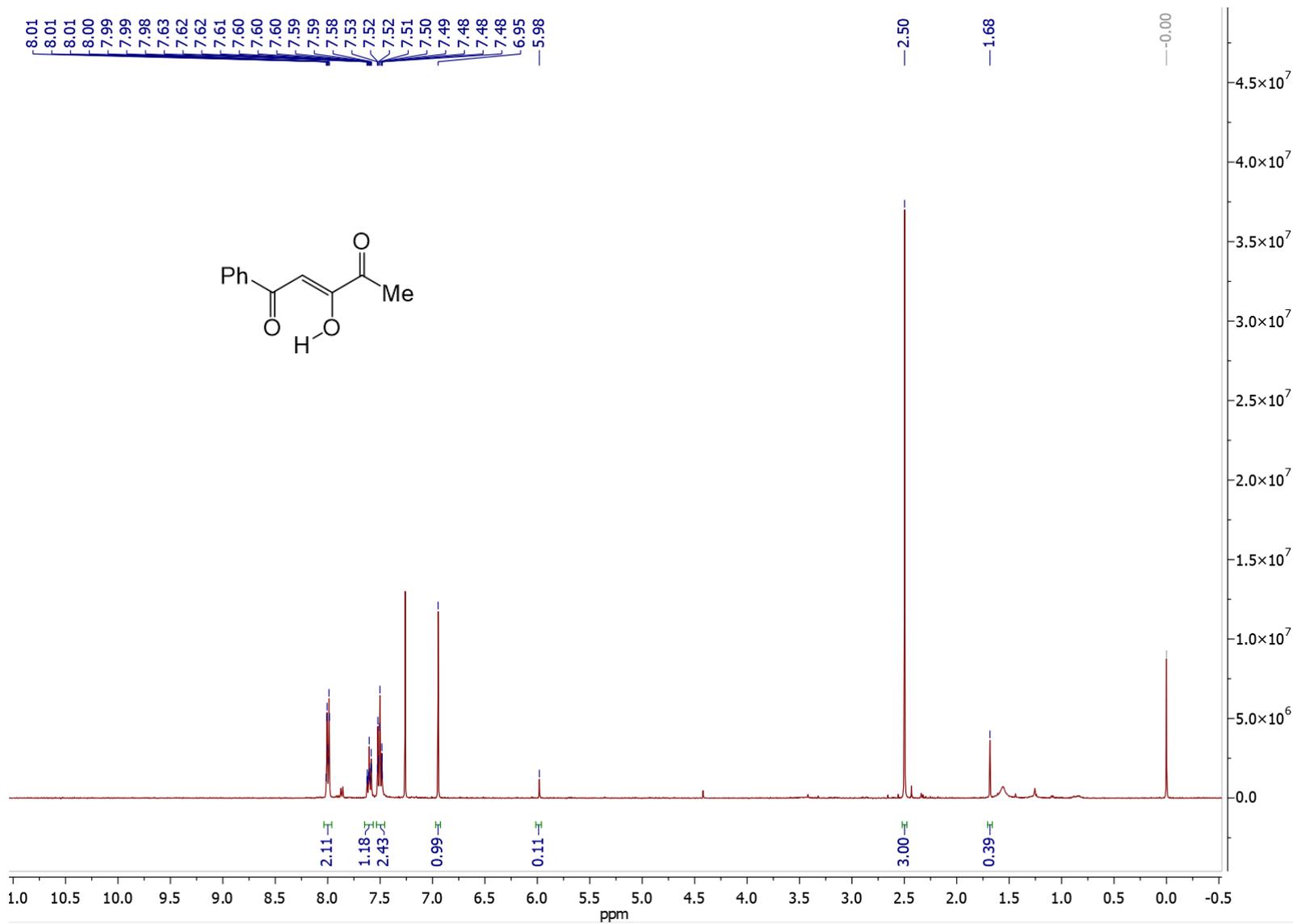


Figure S12. ^{13}C NMR spectrum of compound **4a**.

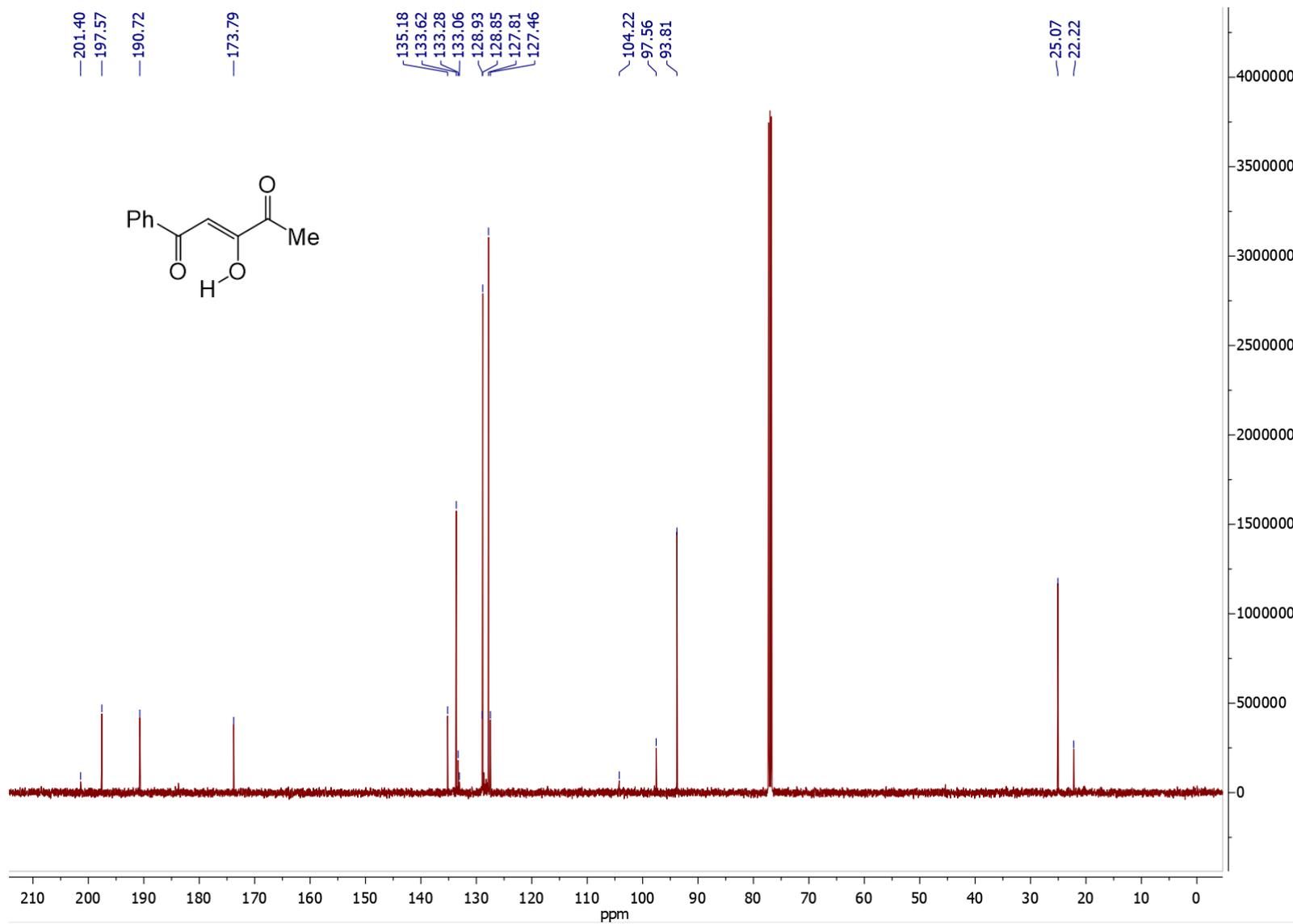


Figure S13. ¹H NMR spectrum of compound **4b**.

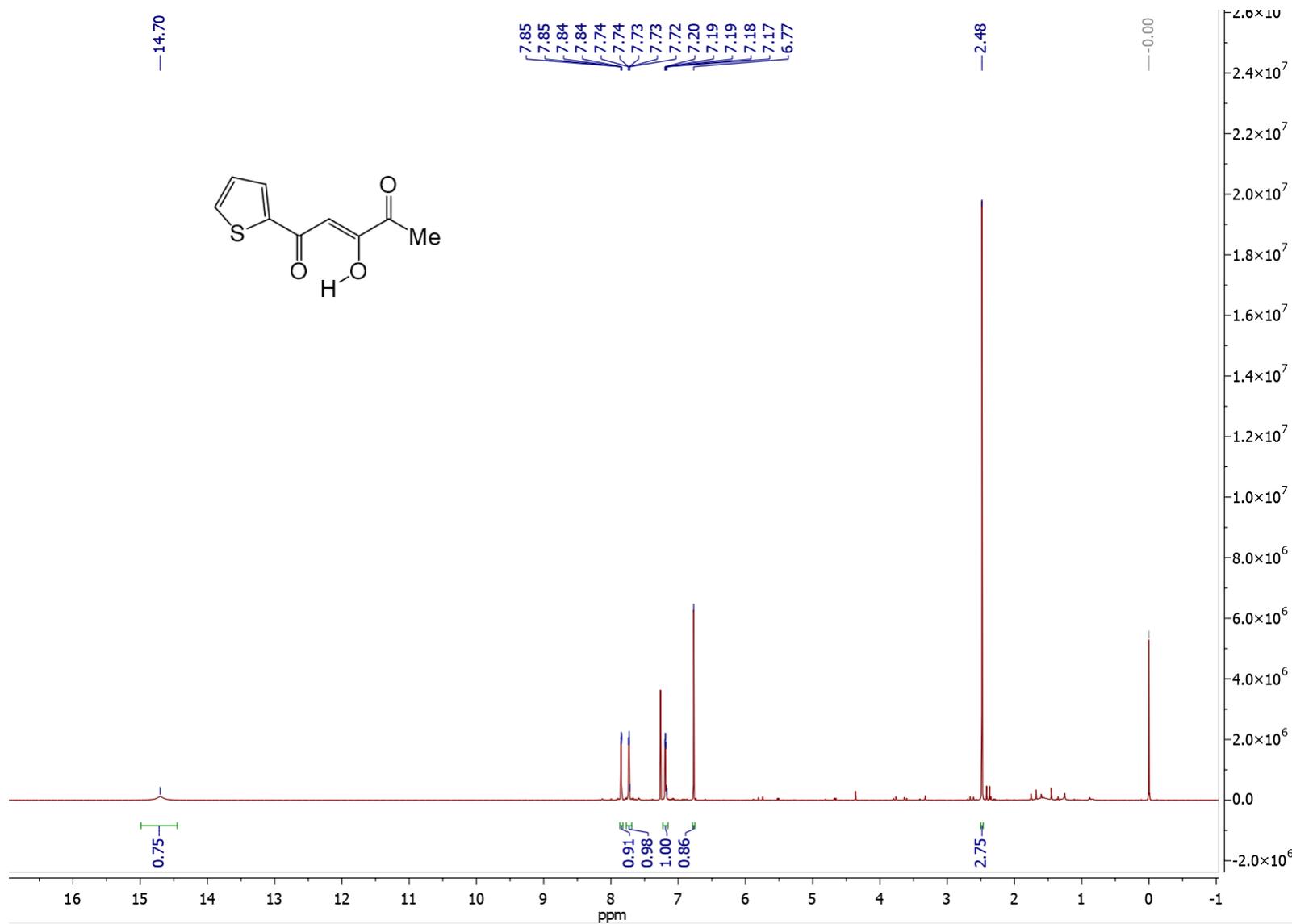


Figure S14. ¹³C NMR spectrum of compound **4b**.

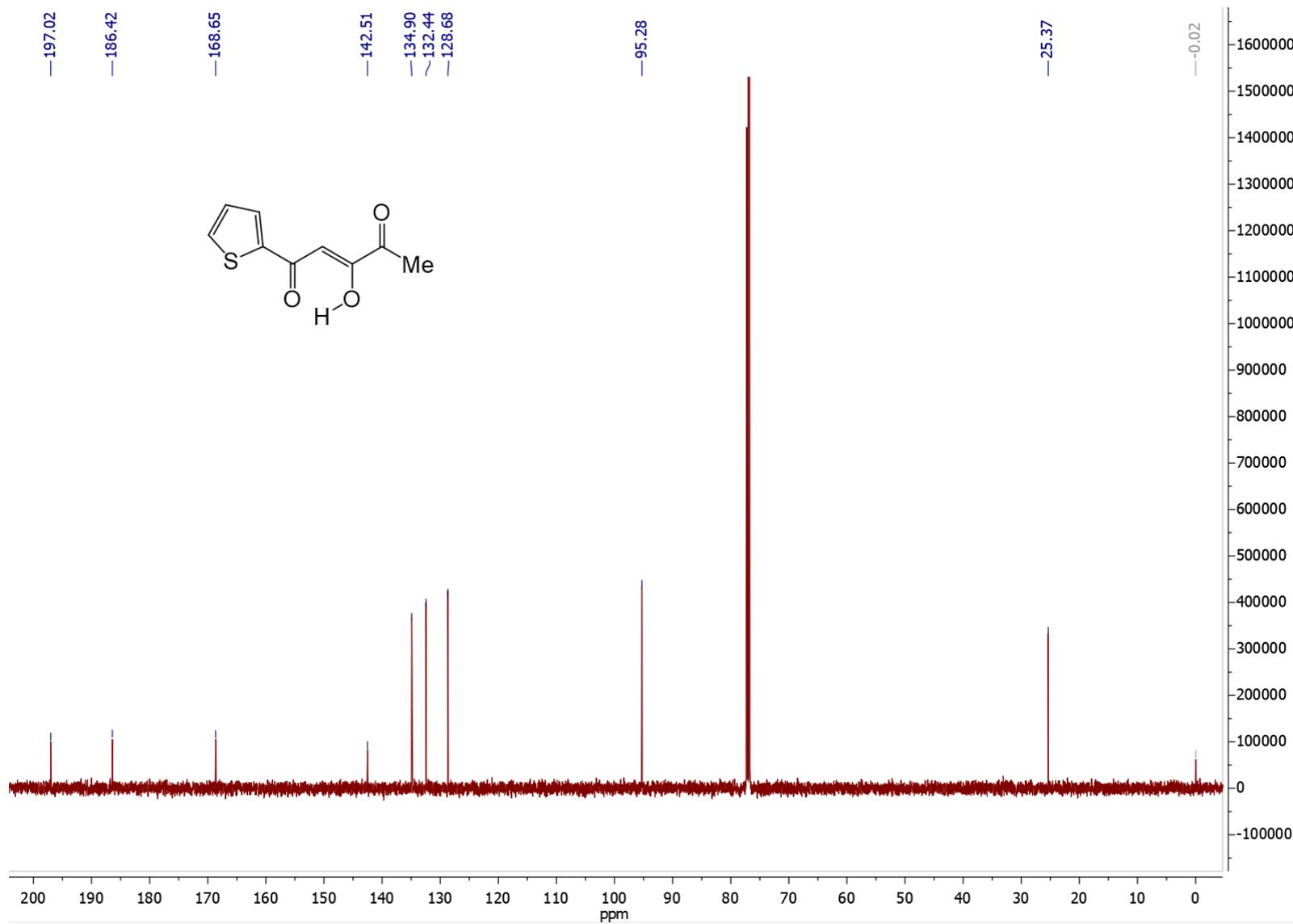


Figure S15. ¹H NMR spectrum of compound 6.

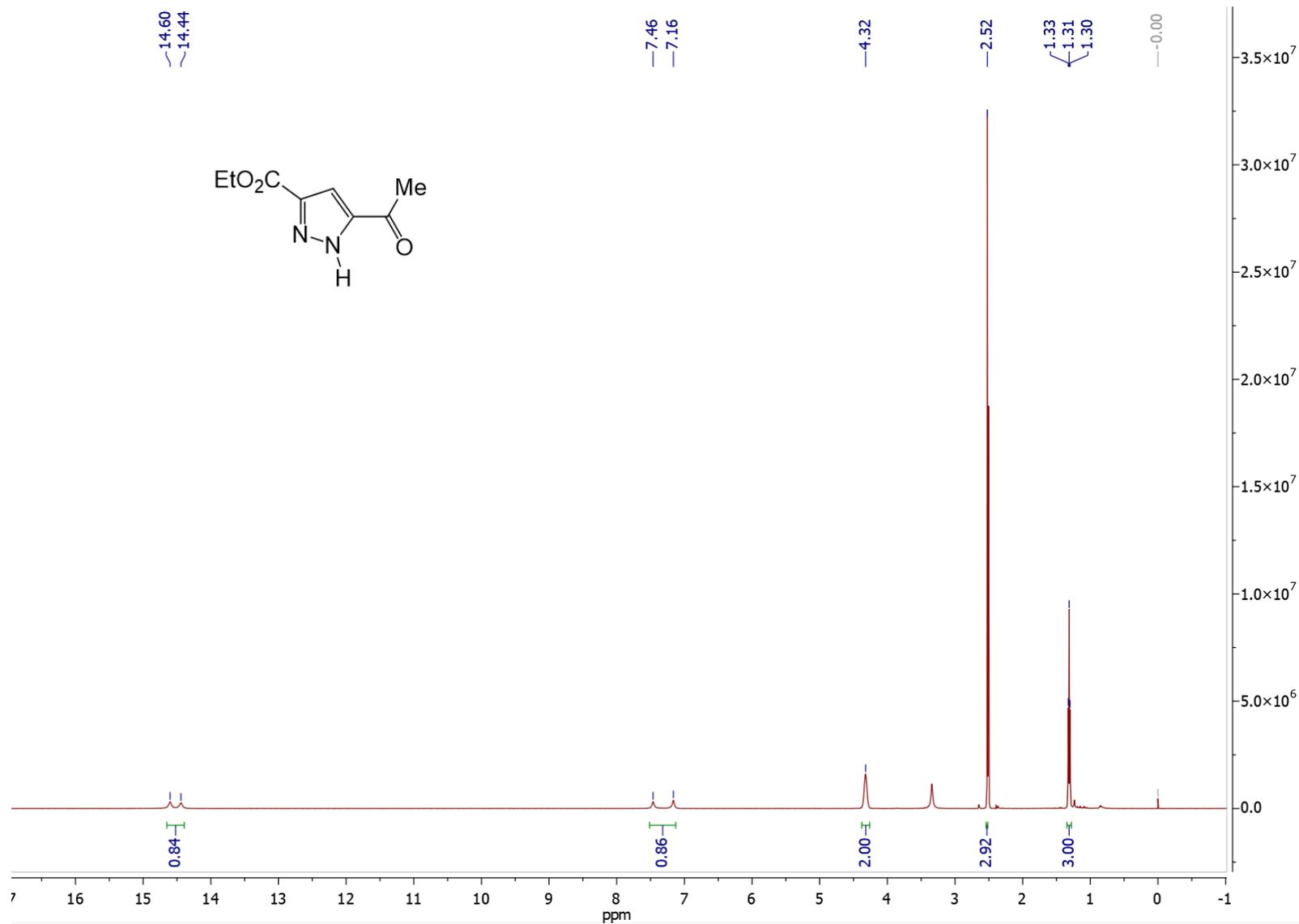


Figure S16. ^{13}C NMR spectrum of compound **6**.

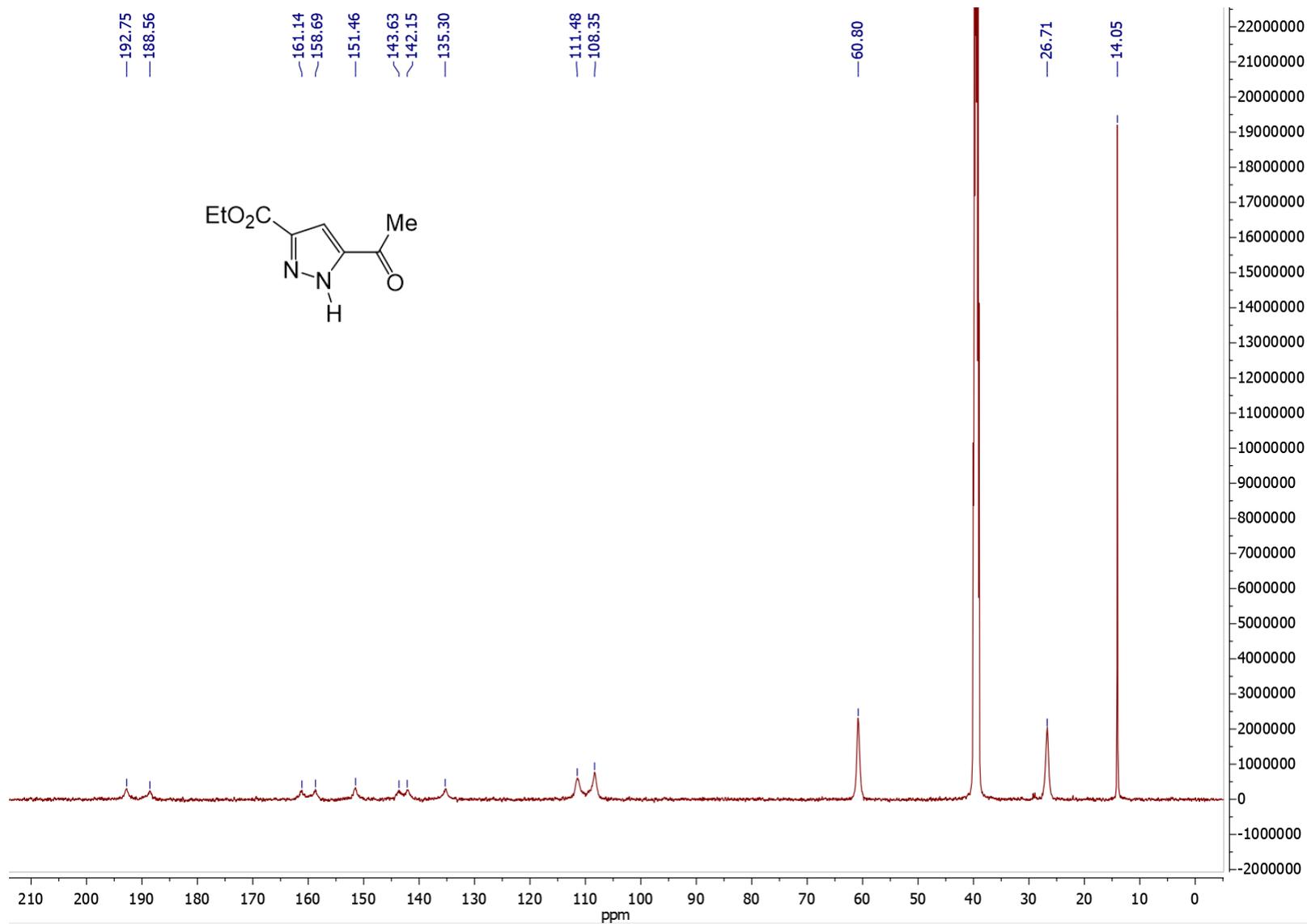


Figure S17. ¹H NMR spectrum of compound 7a.

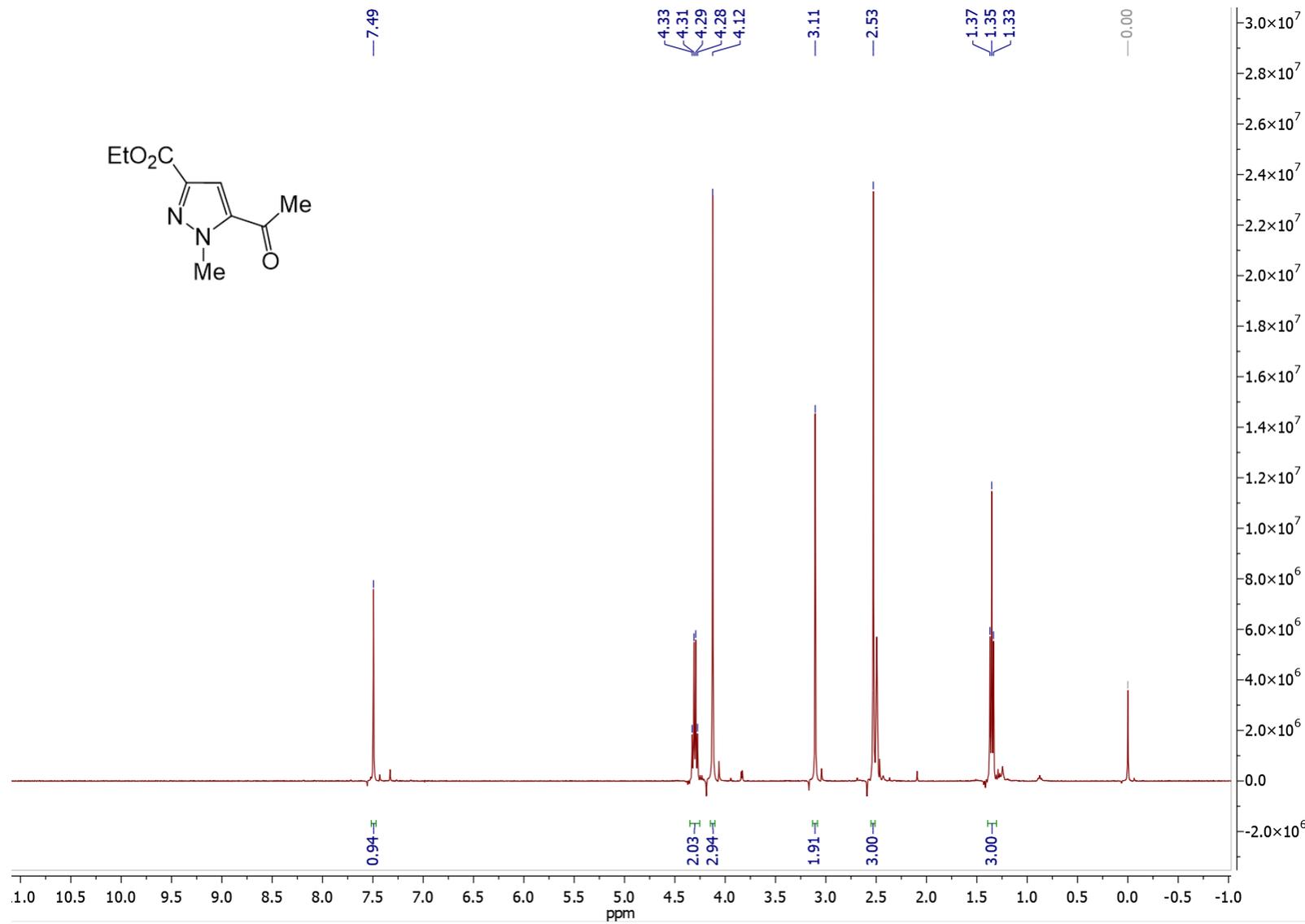


Figure S18. ^{13}C NMR spectrum of compound **7a**.

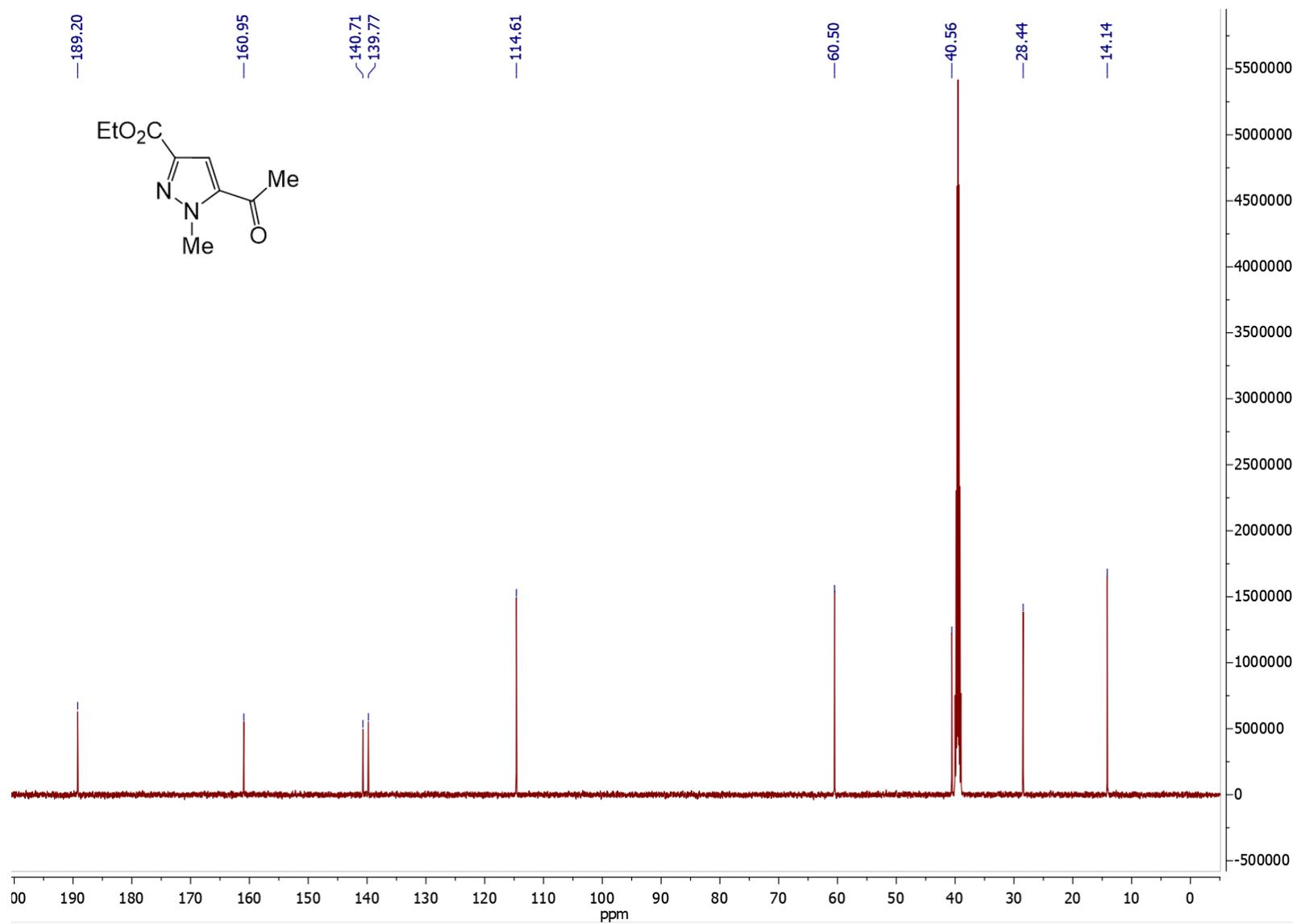


Figure S19. ¹H NMR spectrum of compound **7b**.

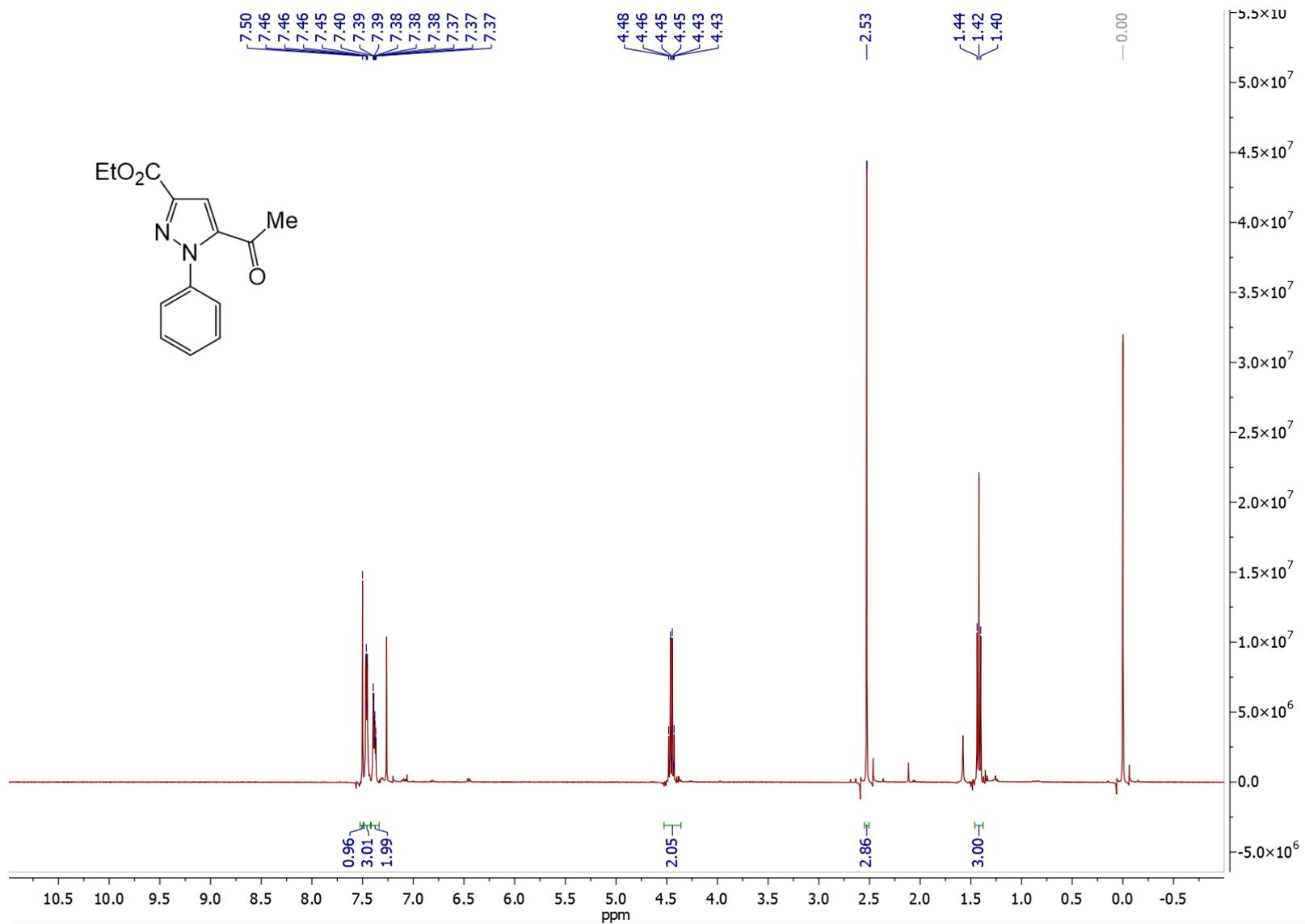


Figure S20. ¹³C NMR spectrum of compound **7b**.

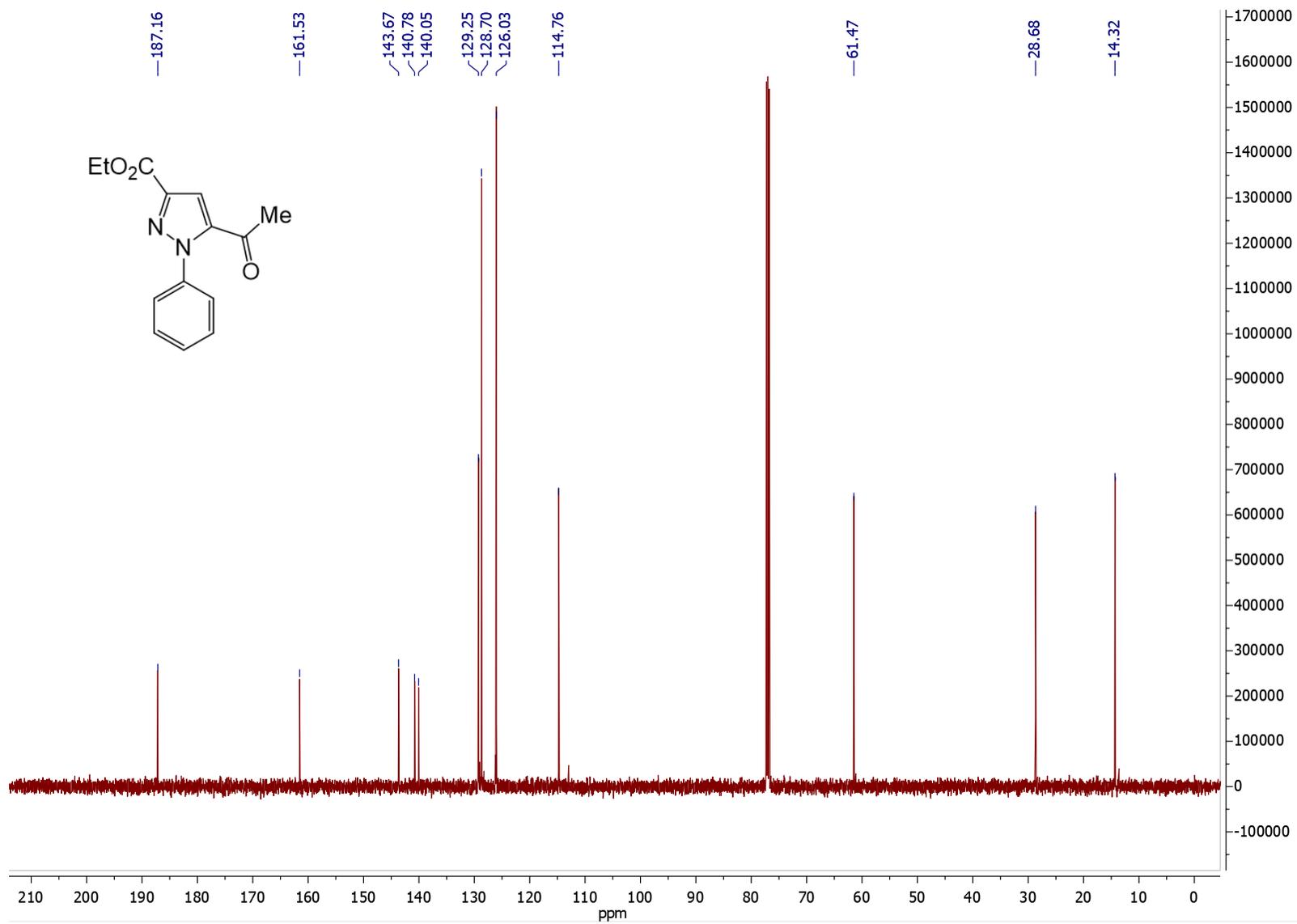


Figure S21. ¹H NMR spectrum of compound 7c.

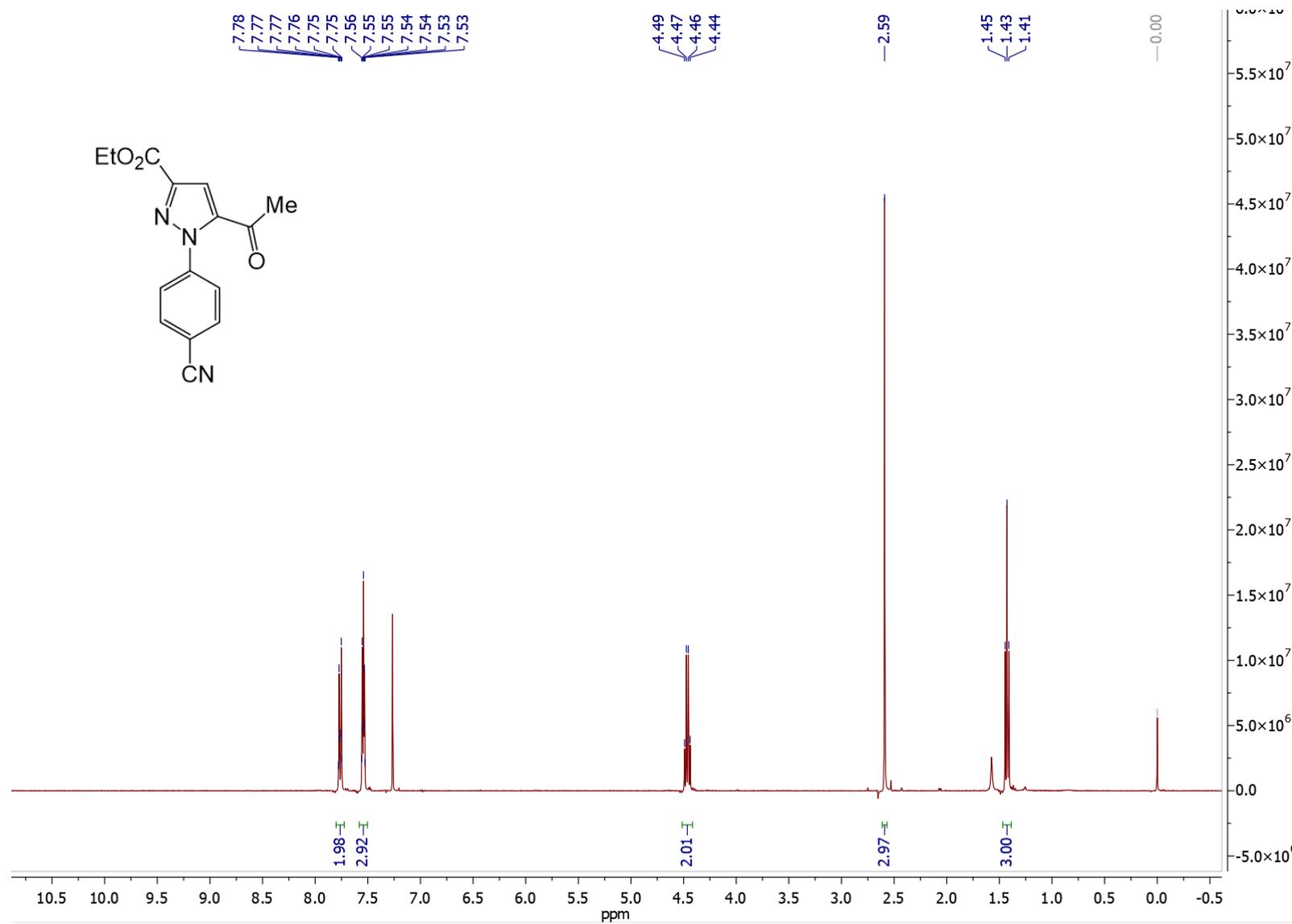


Figure S22. ¹³C NMR spectrum of compound 7c.

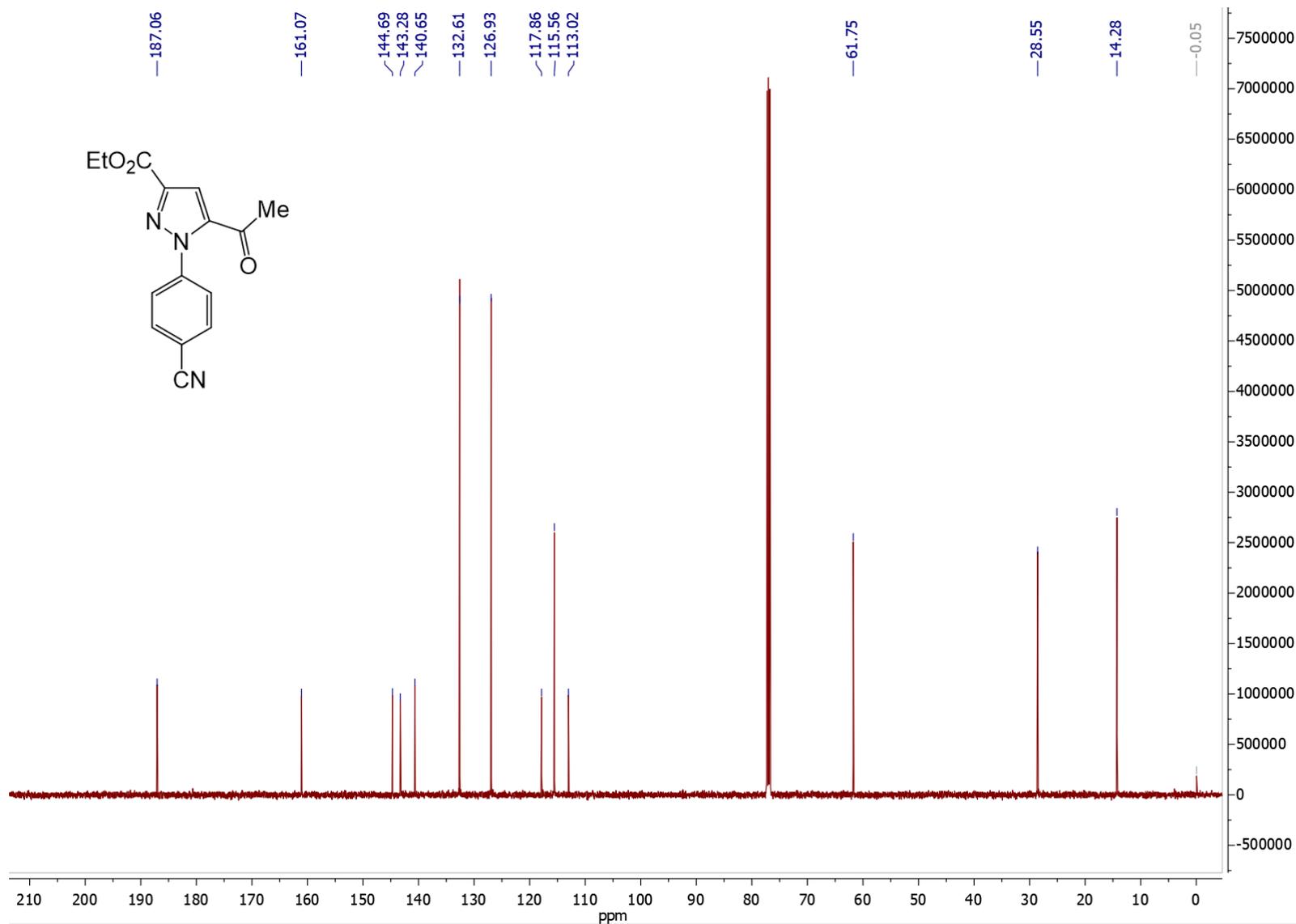


Figure S23. ¹H NMR spectrum of compound 7d.

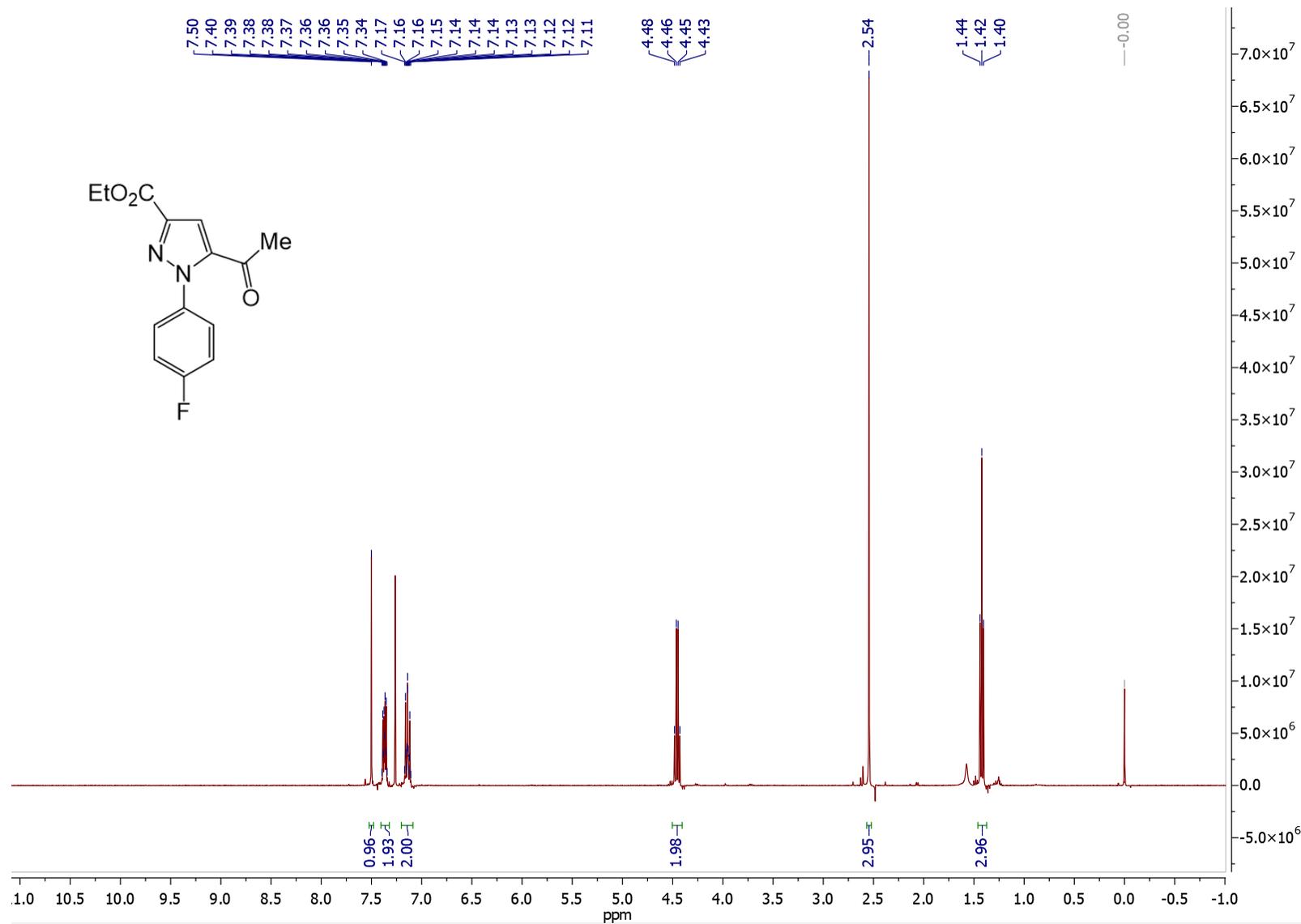


Figure S24. ¹³C NMR spectrum of compound 7d.

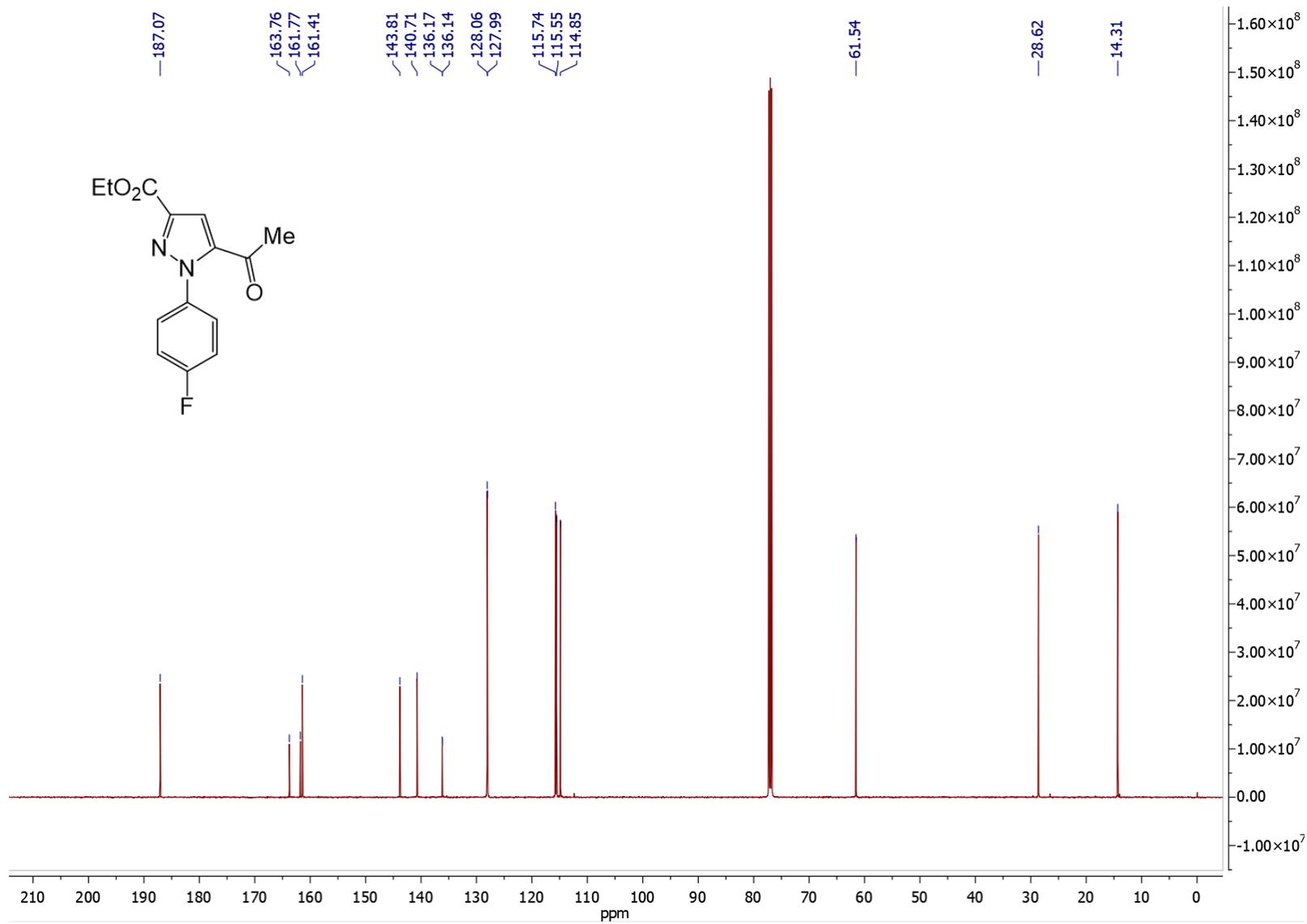


Figure S25. ^{19}F NMR spectrum of compound **7d**.

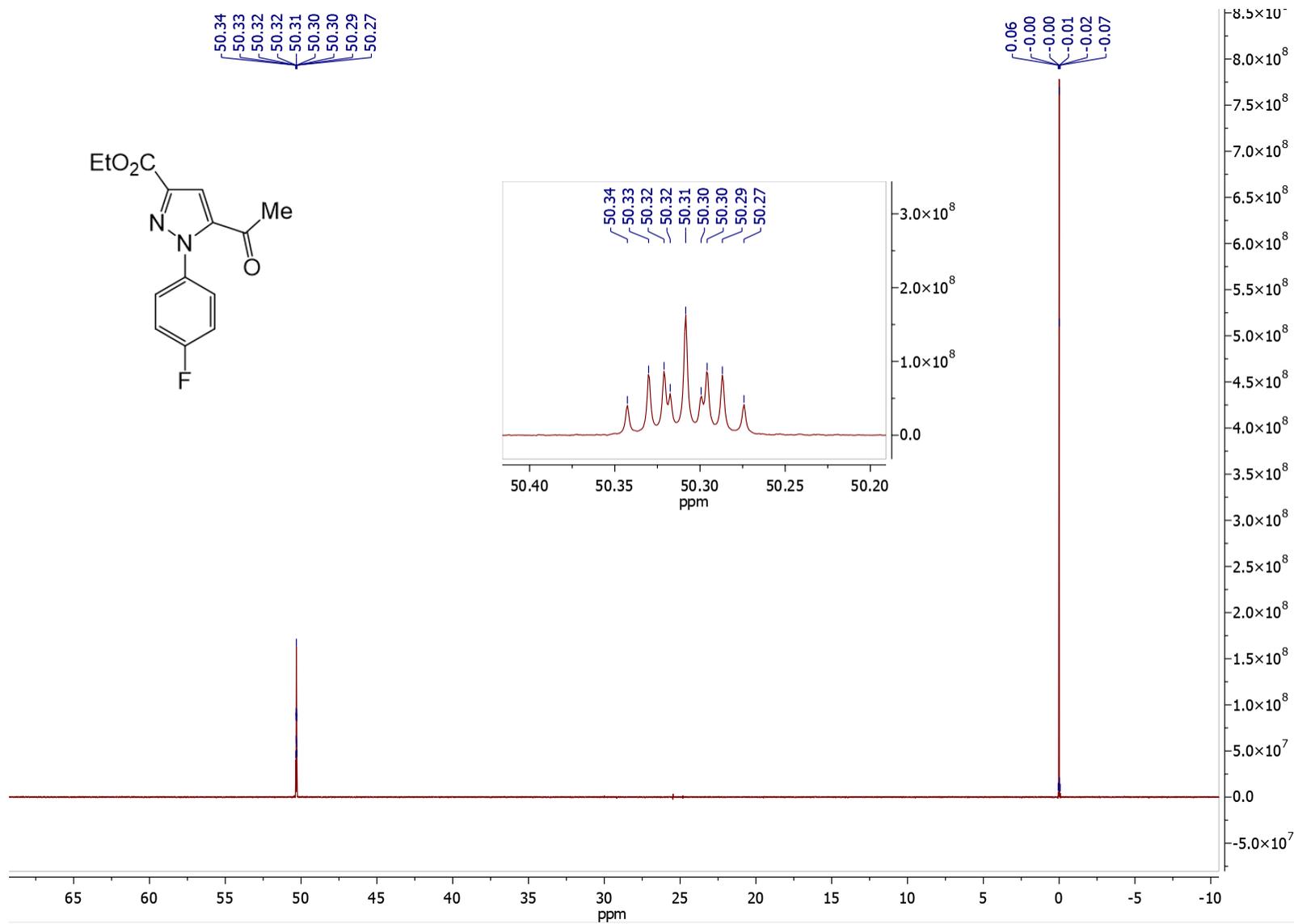


Figure S26. ¹H NMR spectrum of compound 7e.

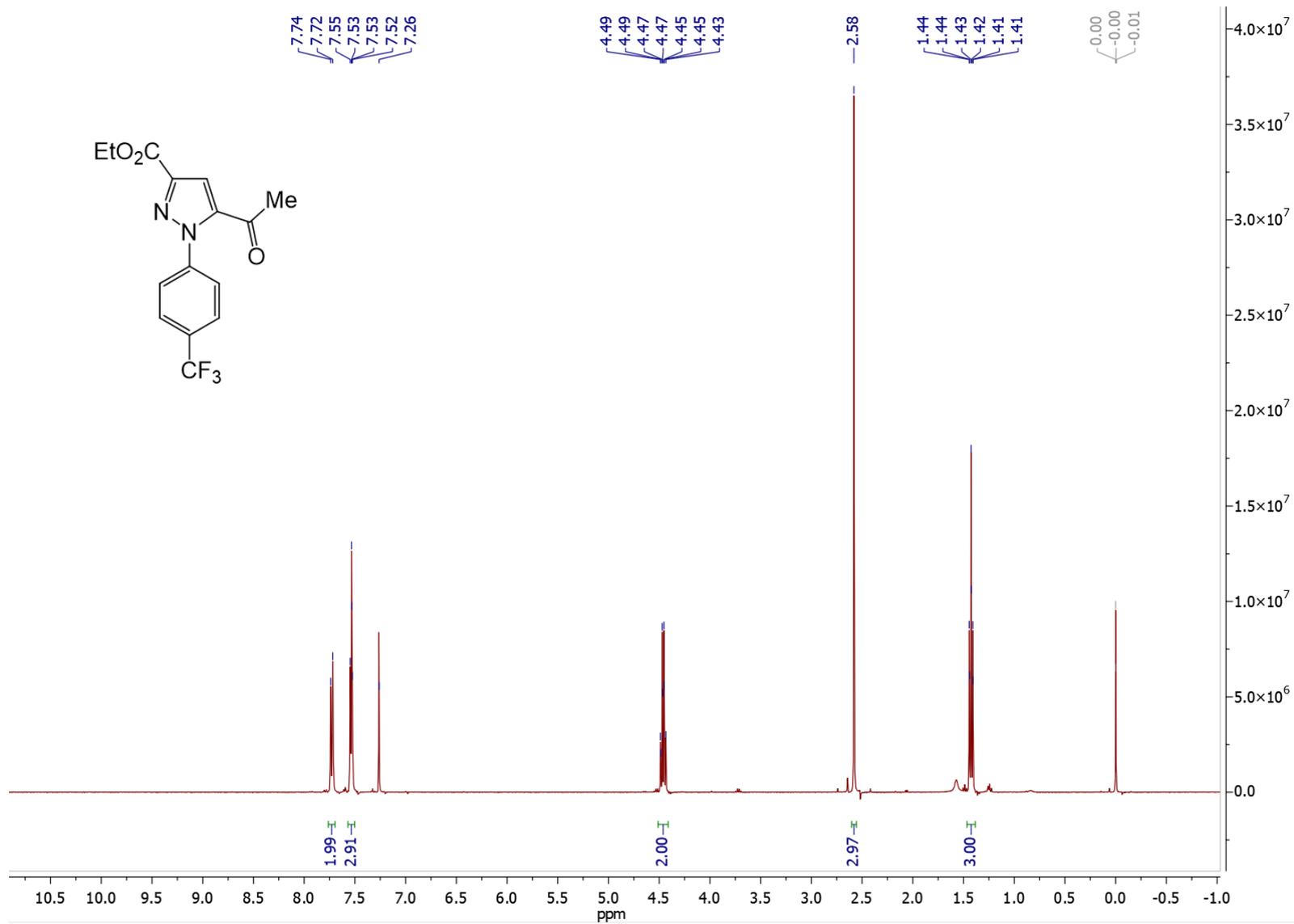


Figure S27. ¹³C NMR spectrum of compound 7e.

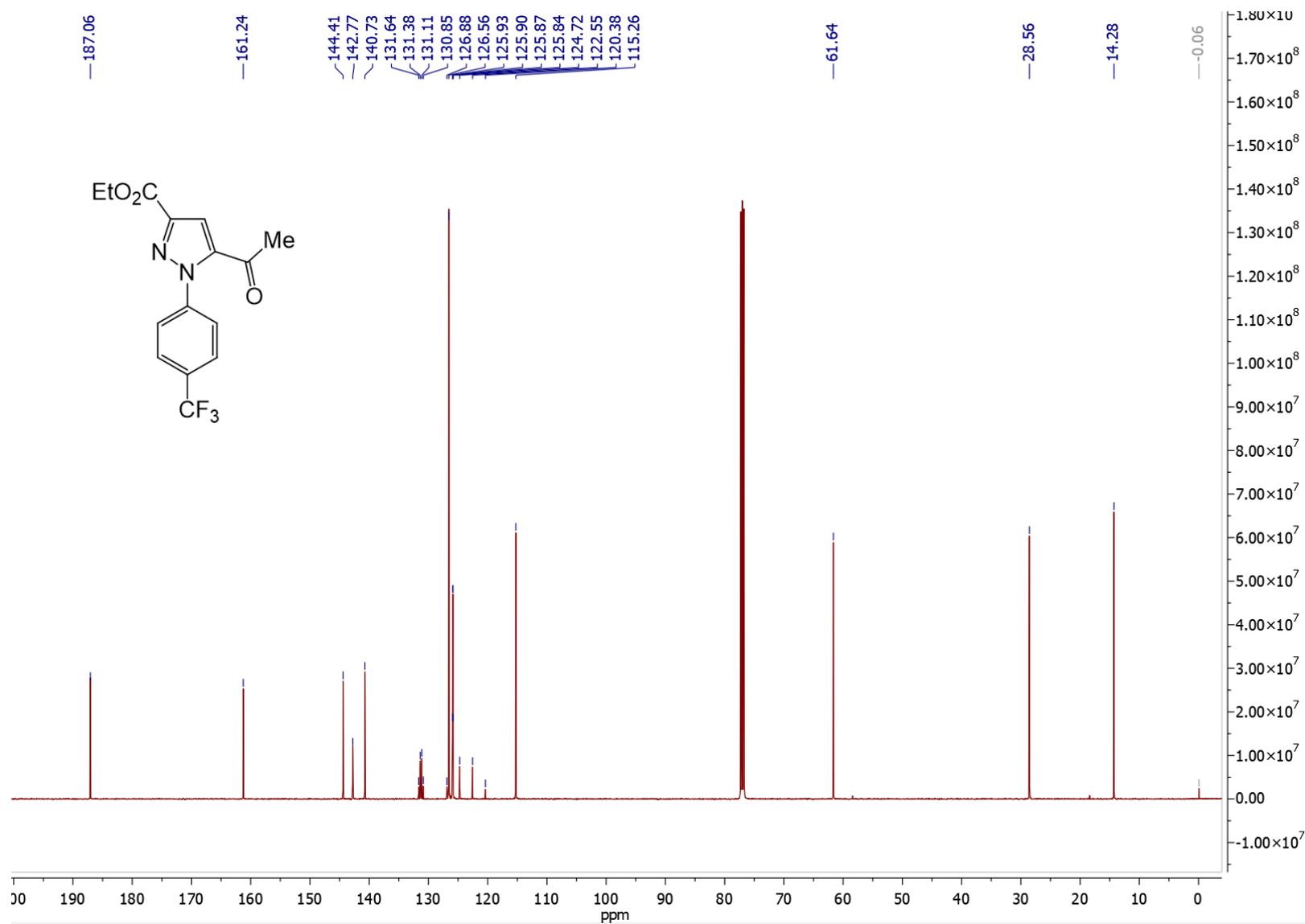


Figure S28. ^{19}F NMR spectrum of compound **7e**.

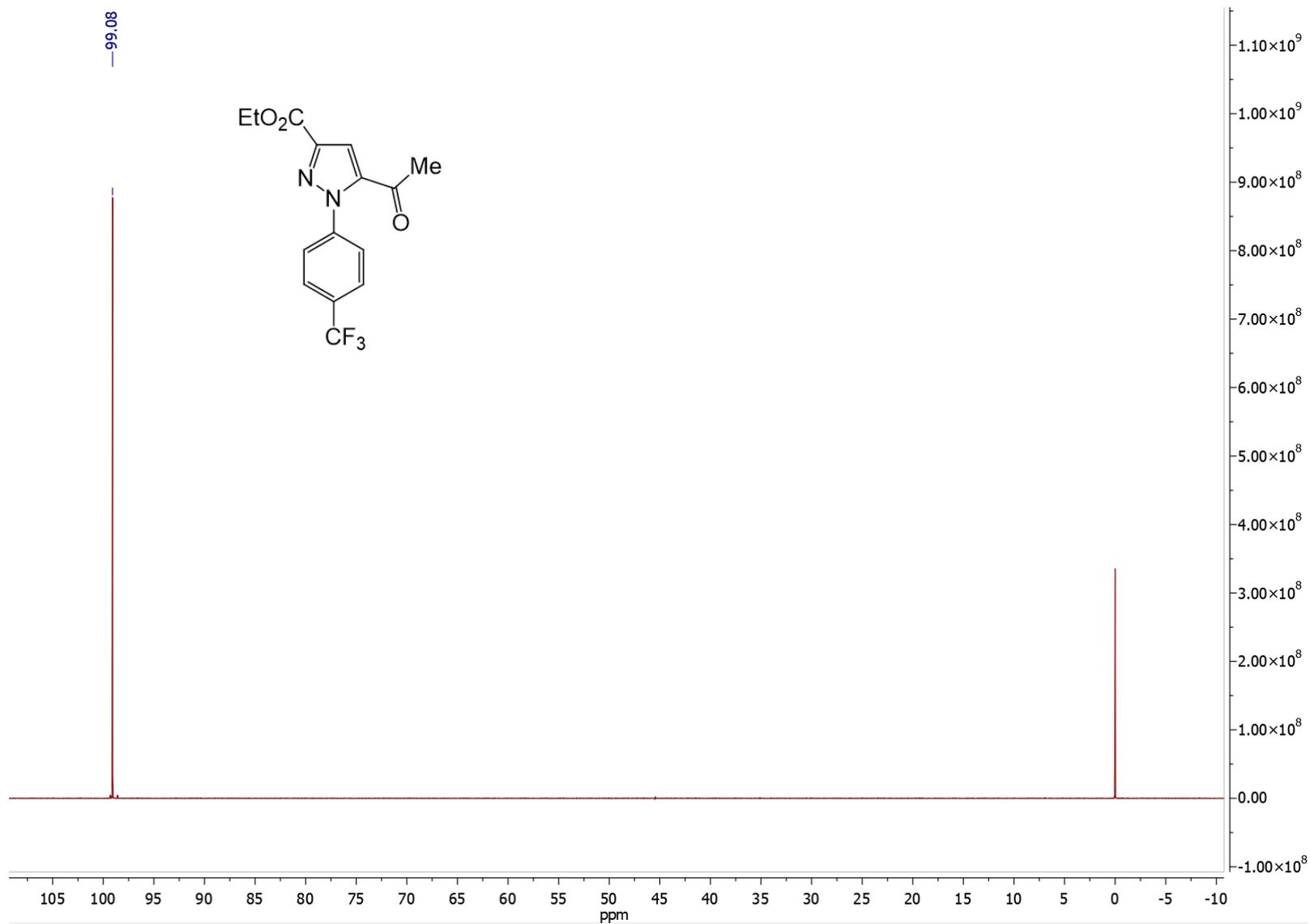


Figure S29. ¹H NMR spectrum of compound 7f.

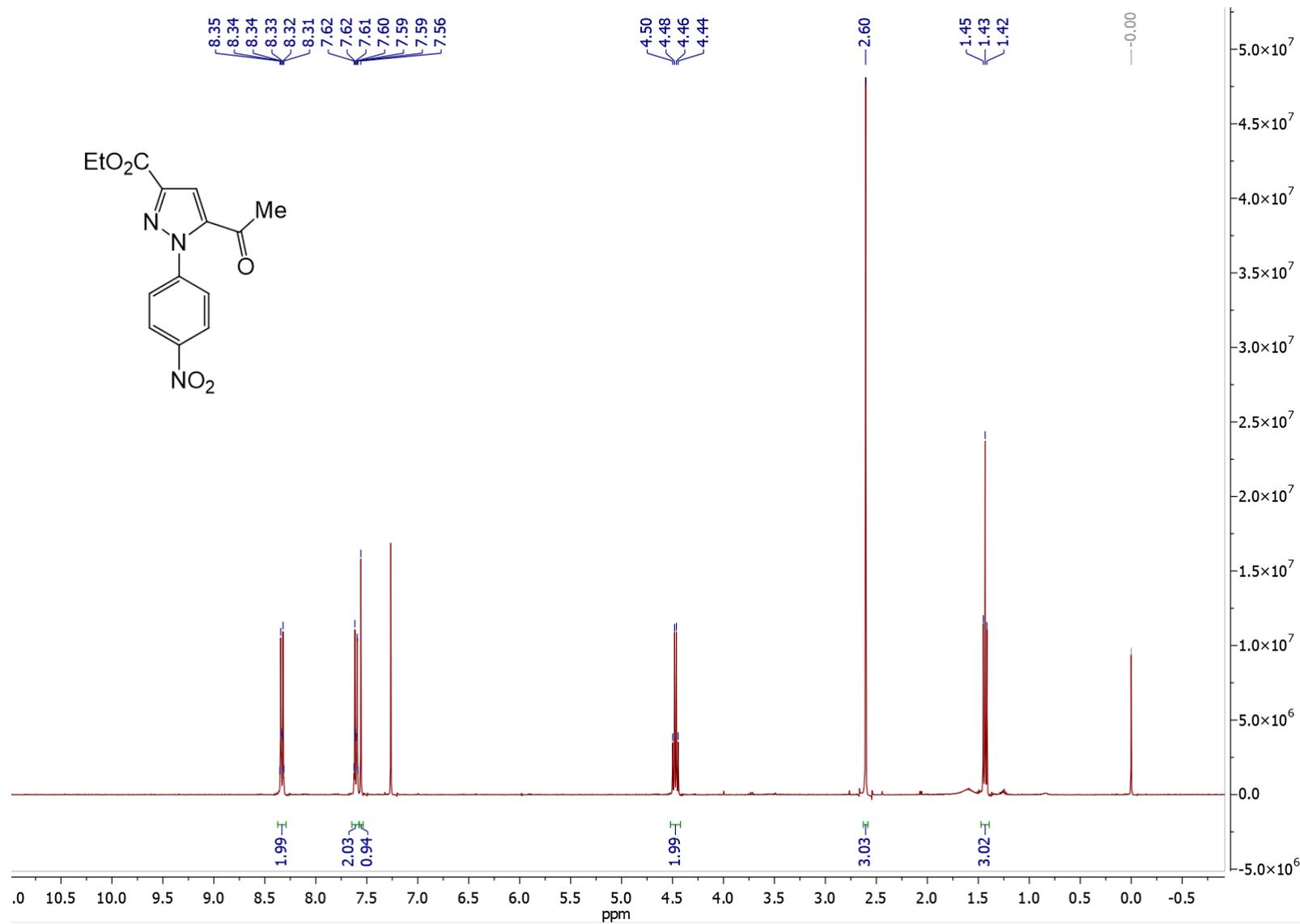


Figure S30. ^{13}C NMR spectrum of compound **7f**.

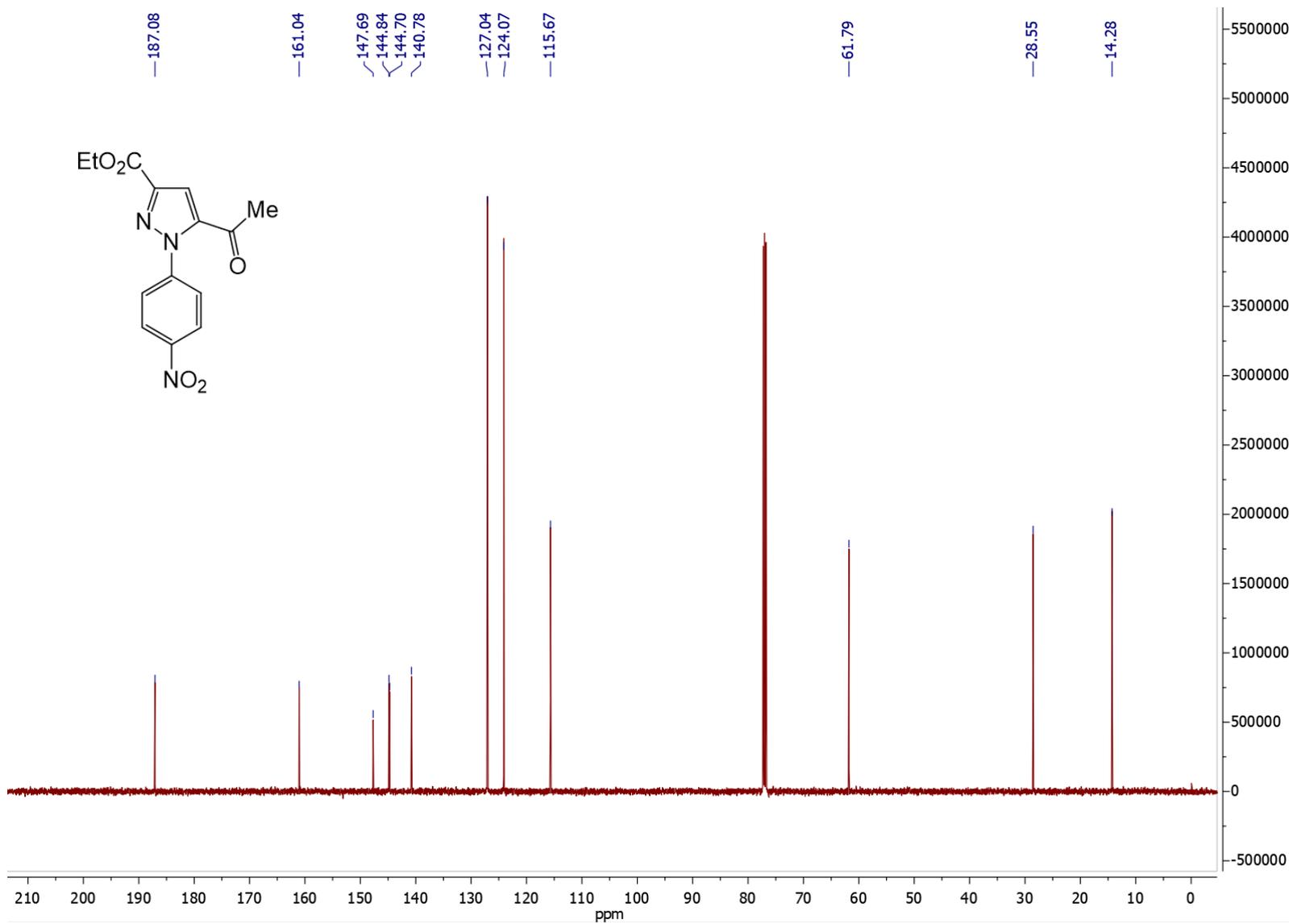


Figure S31. ¹H NMR spectrum of compound 7g.

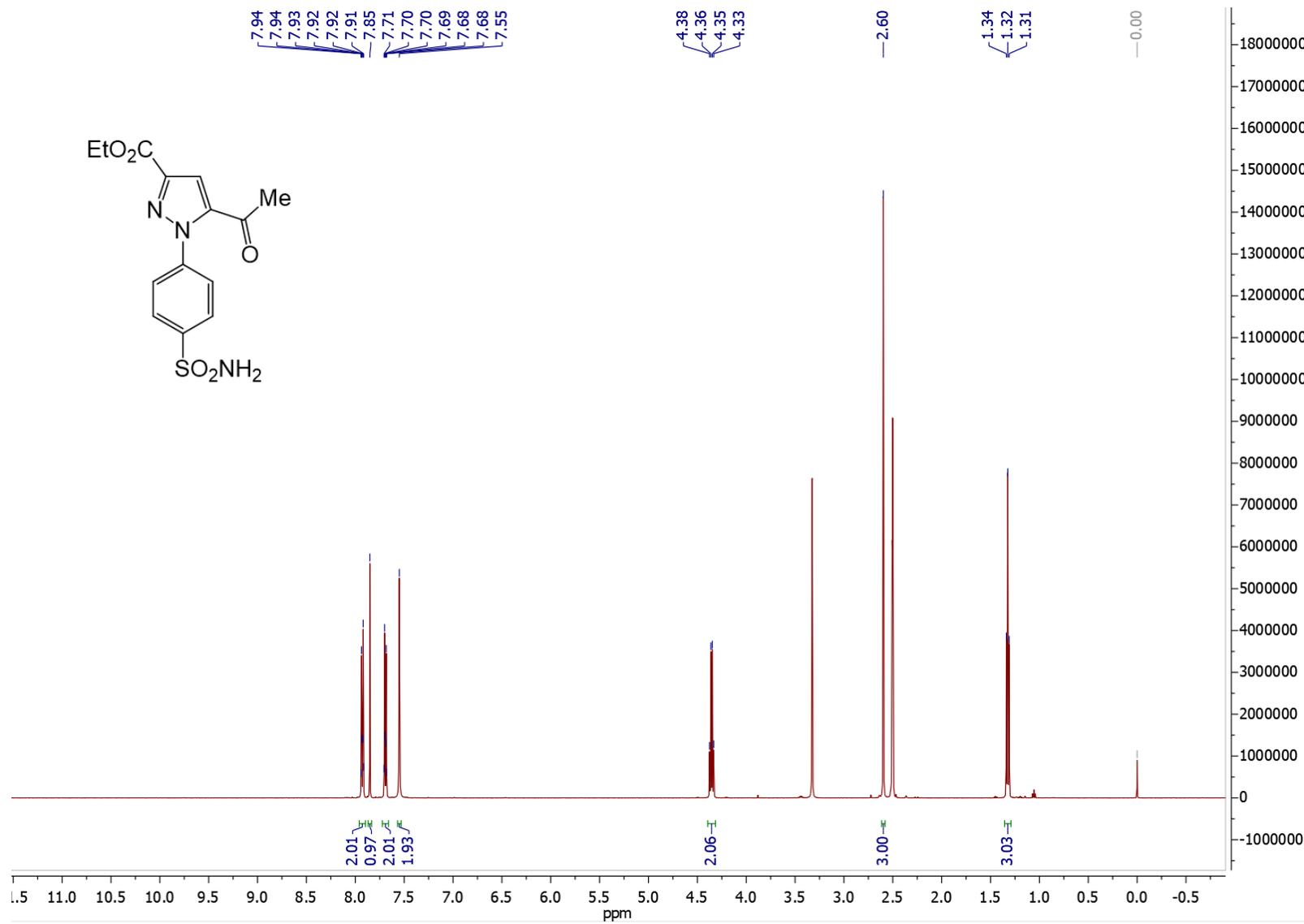


Figure S32. ^{13}C NMR spectrum of compound **7g**.

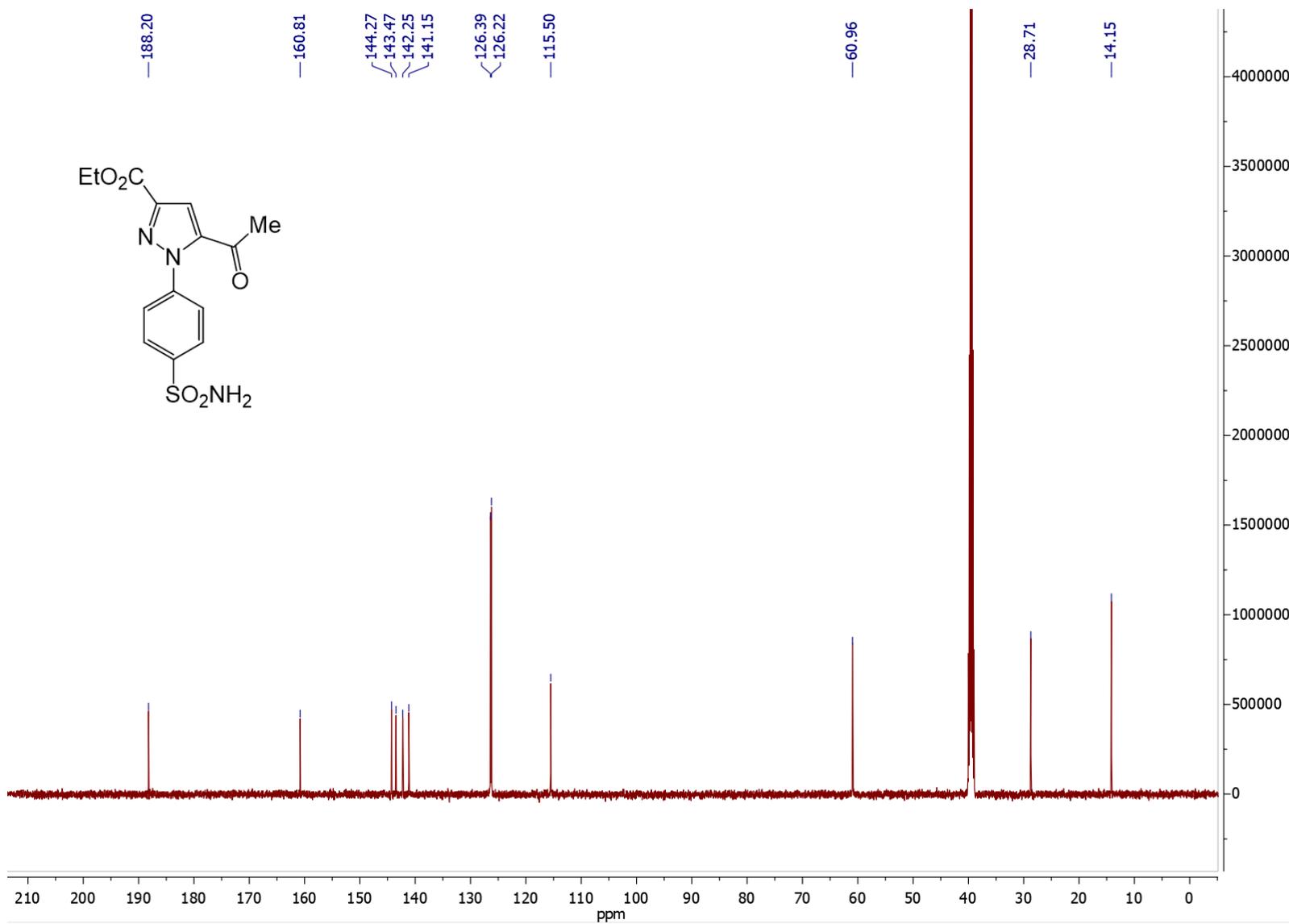


Figure S33. ¹H NMR spectrum of compound **7h**.

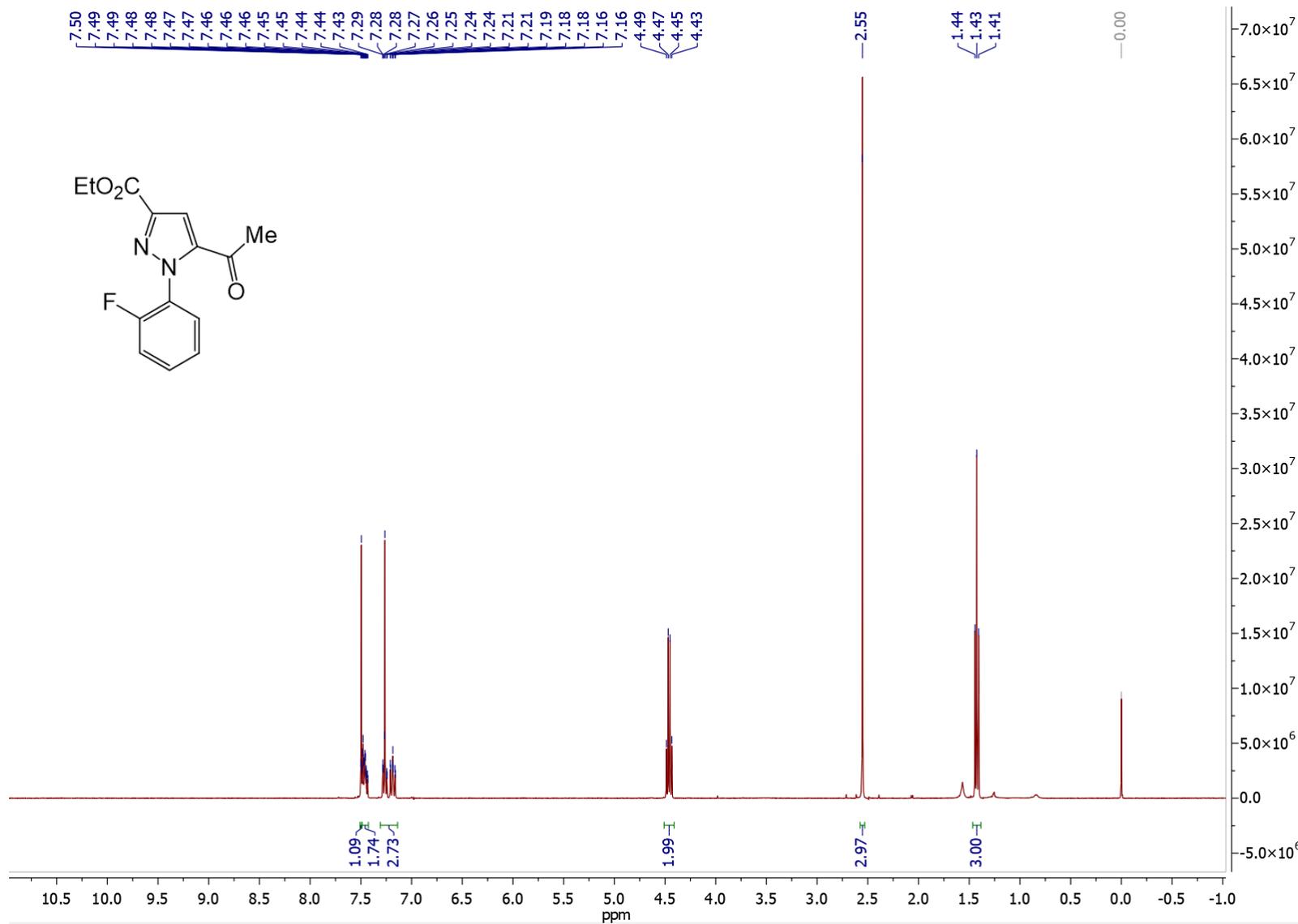


Figure S34. ^{13}C NMR spectrum of compound **7h**.

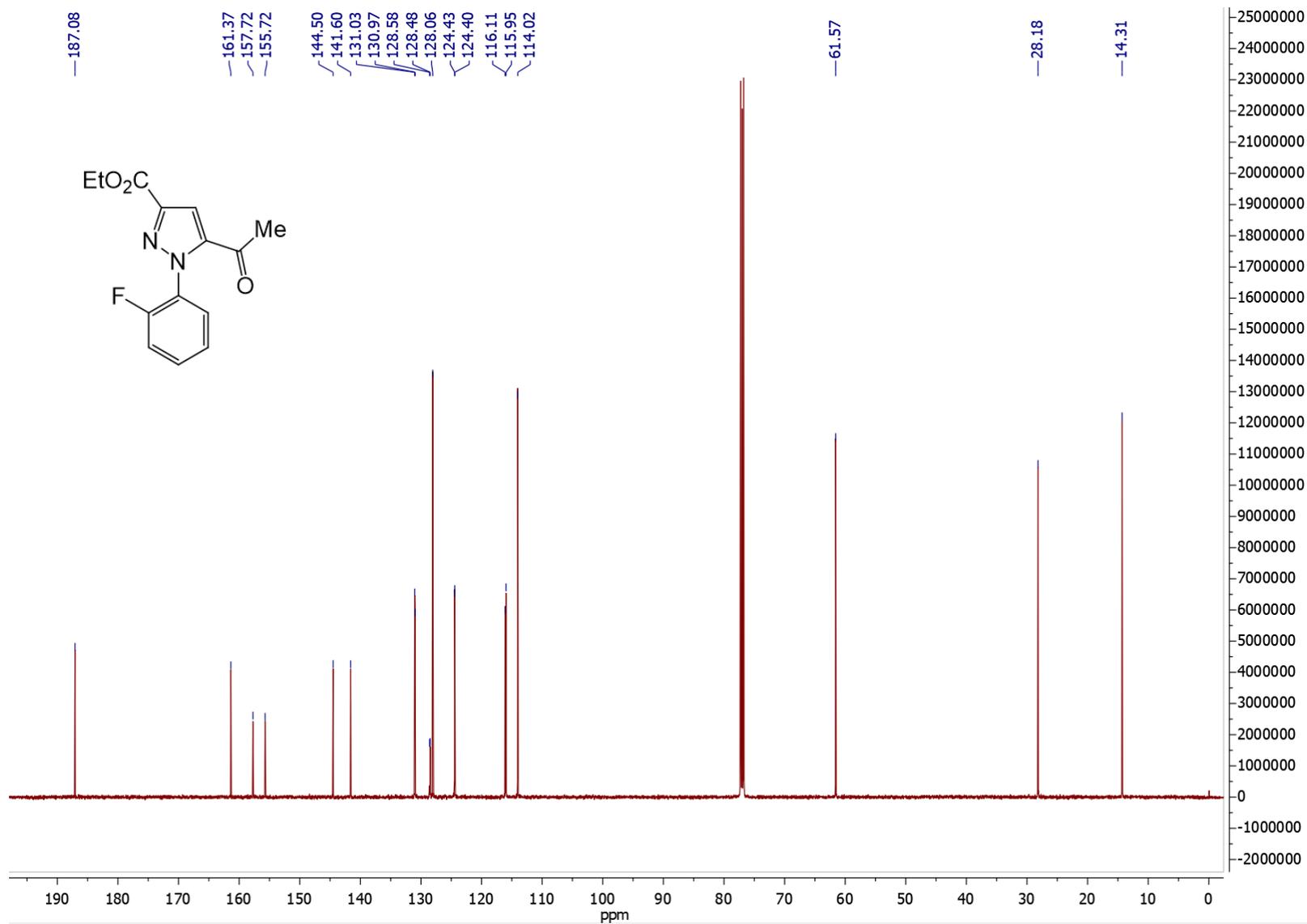


Figure S35. ^{19}F NMR spectrum of compound **7h**.

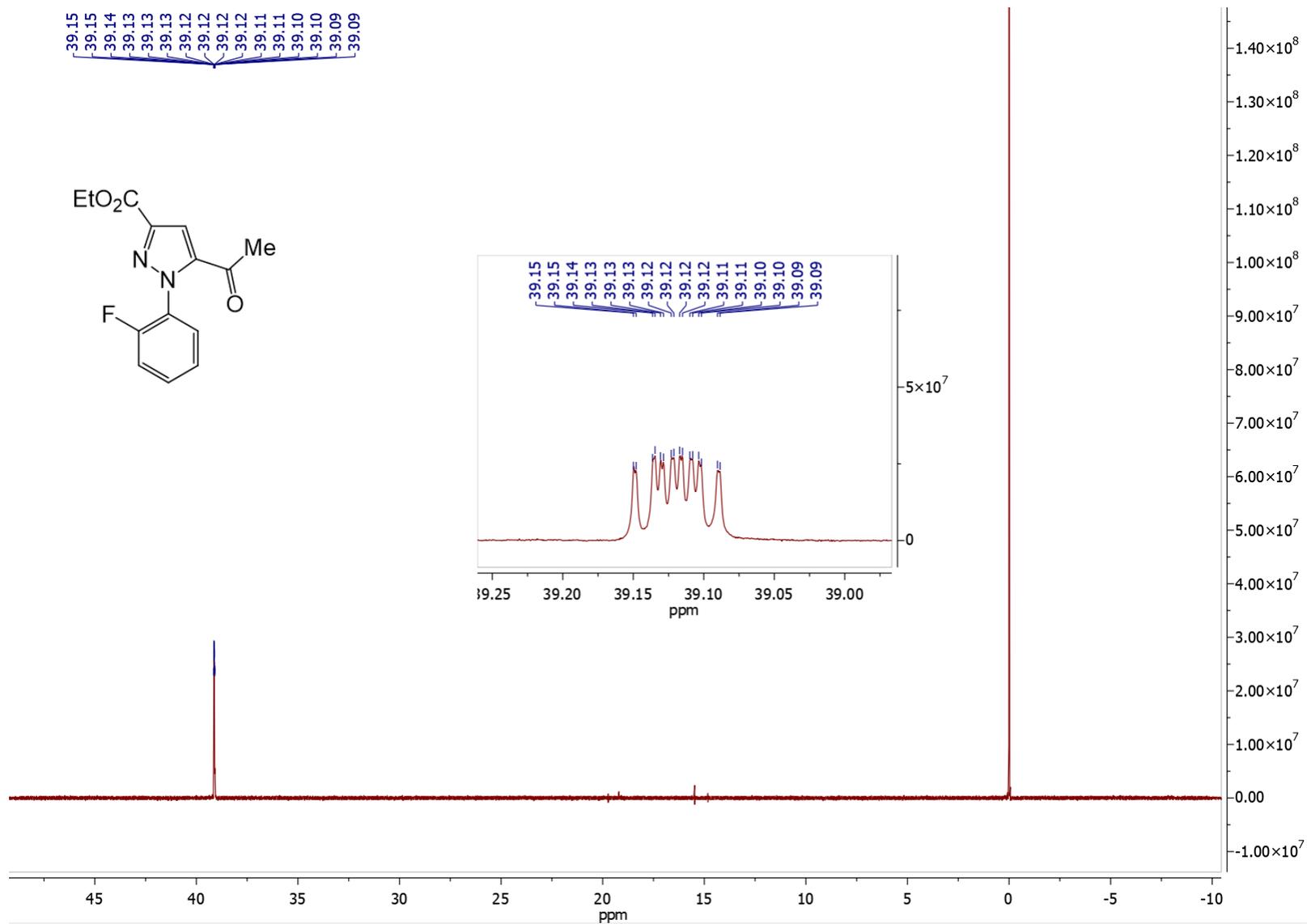


Figure S36. ¹H NMR spectrum of compound **7i**.

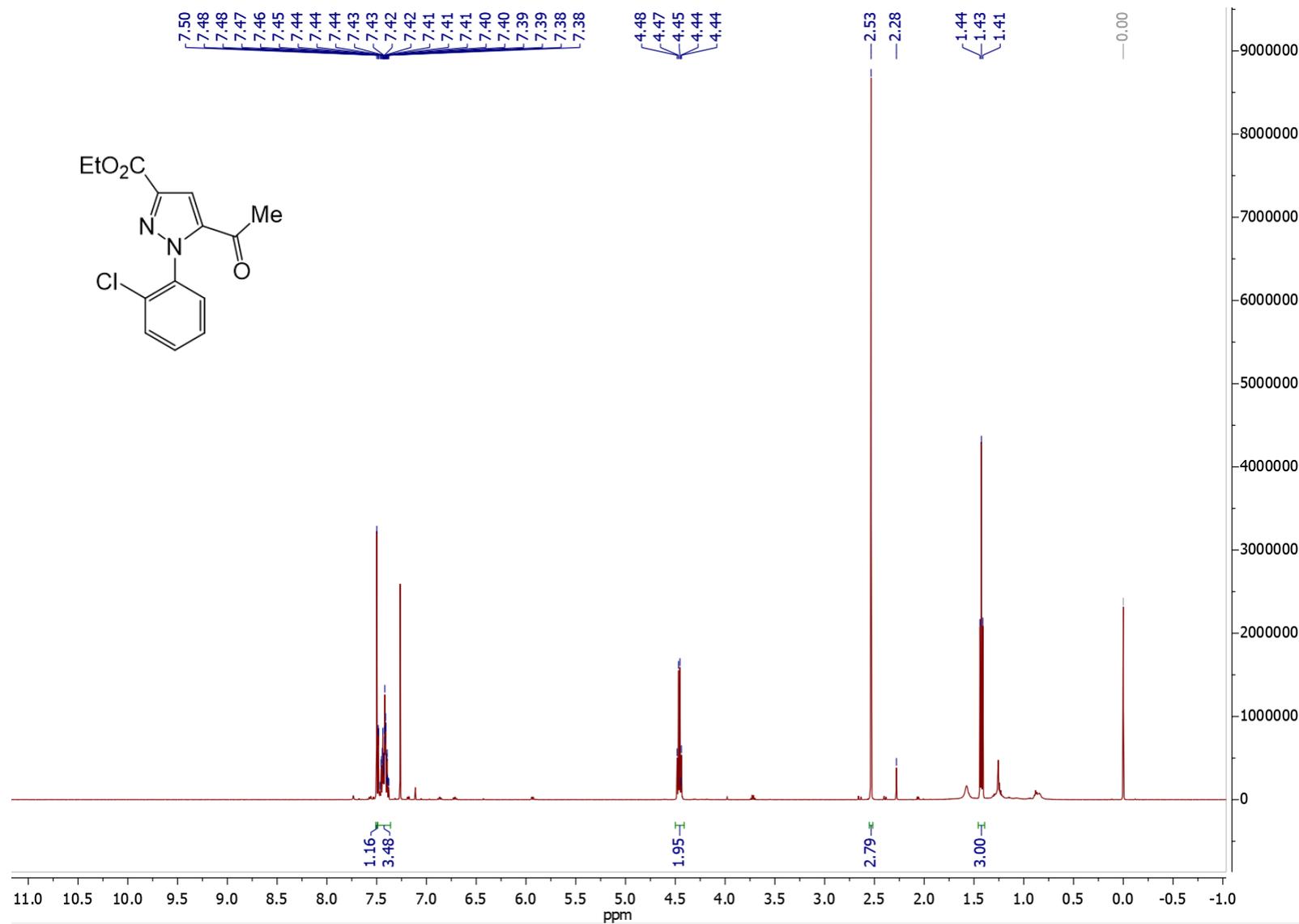


Figure S37. ¹³C NMR spectrum of compound **7i**.

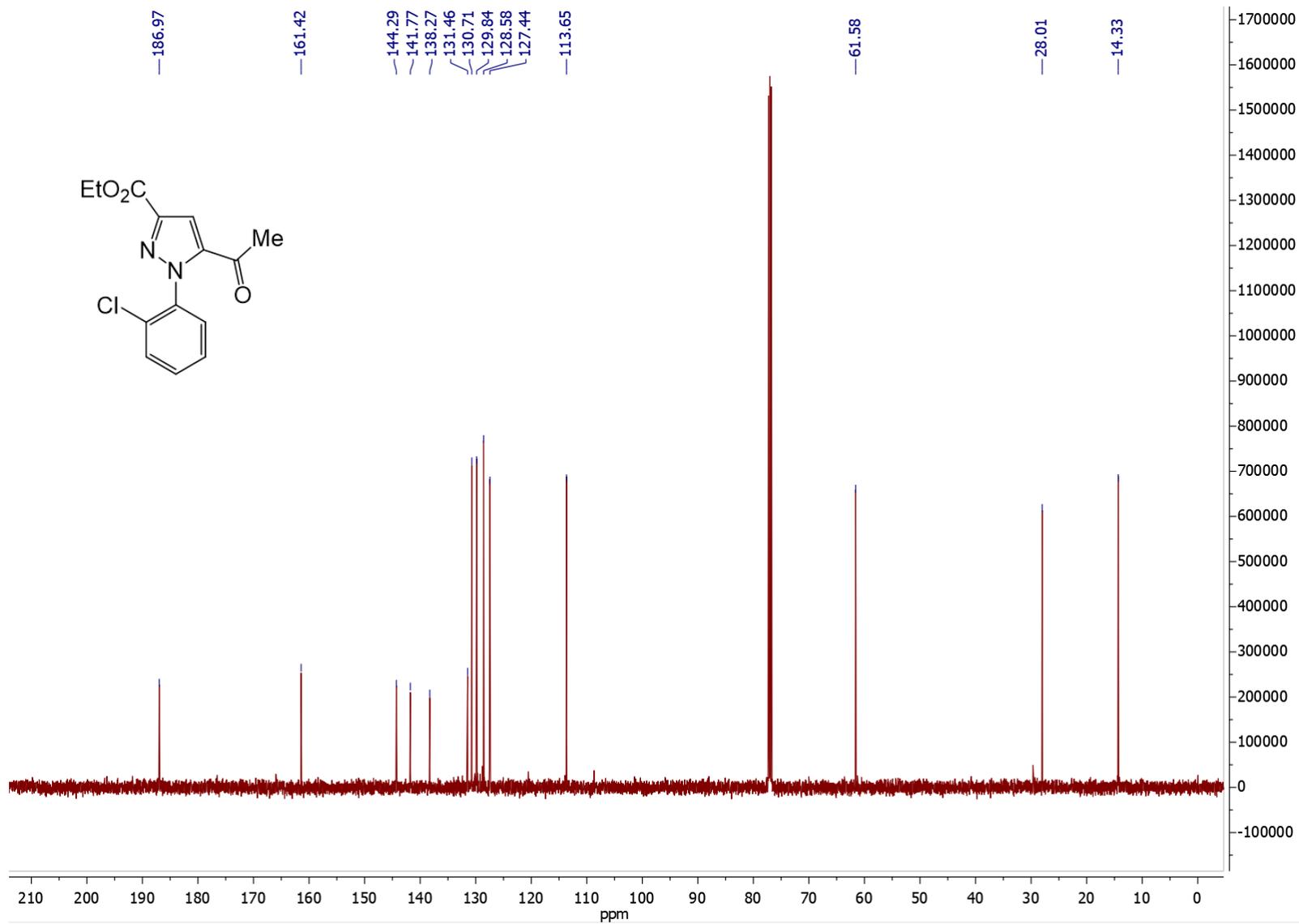


Figure S38. ¹H NMR spectrum of compound 7j.

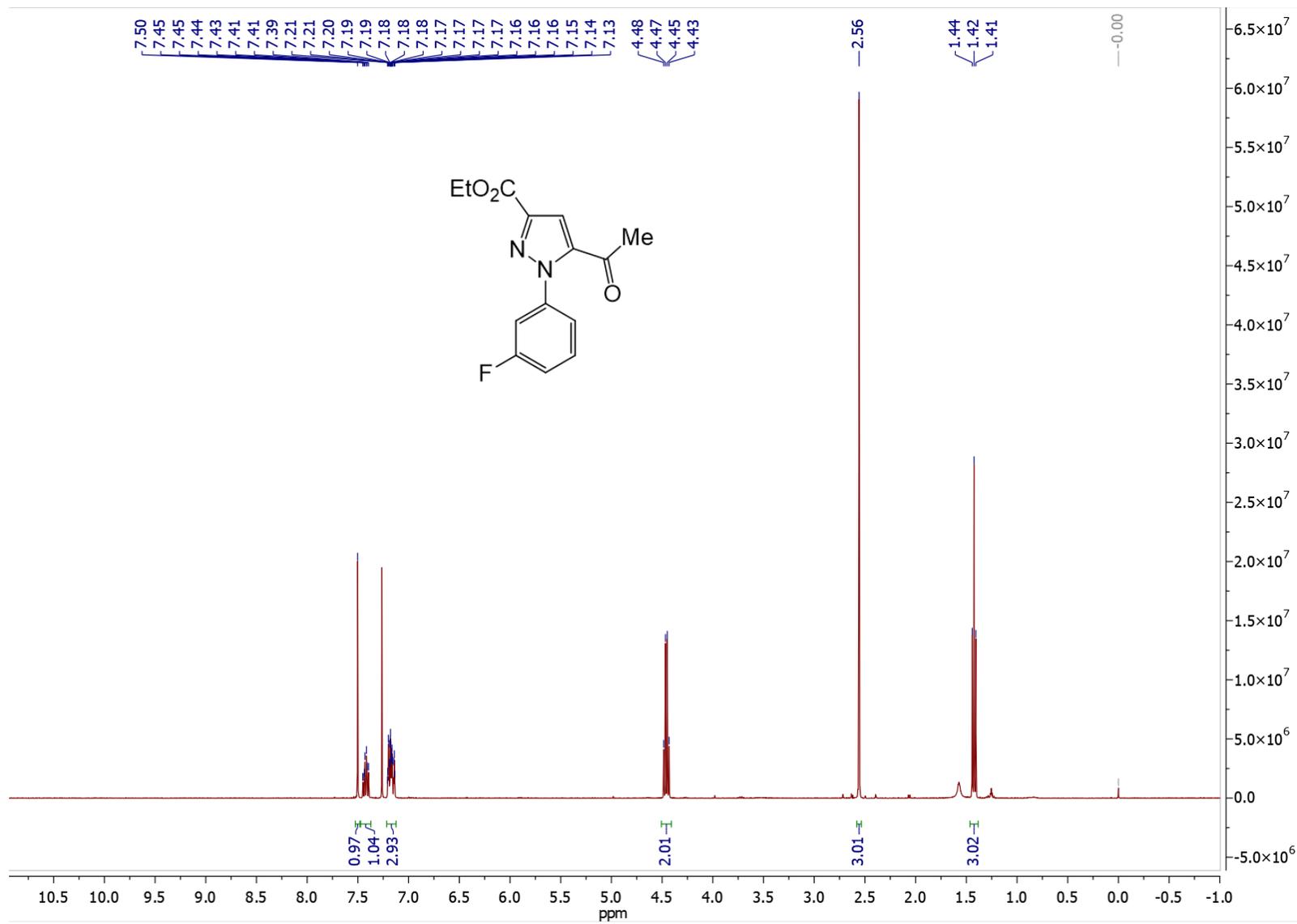


Figure S39. ^{13}C NMR spectrum of compound 7j.

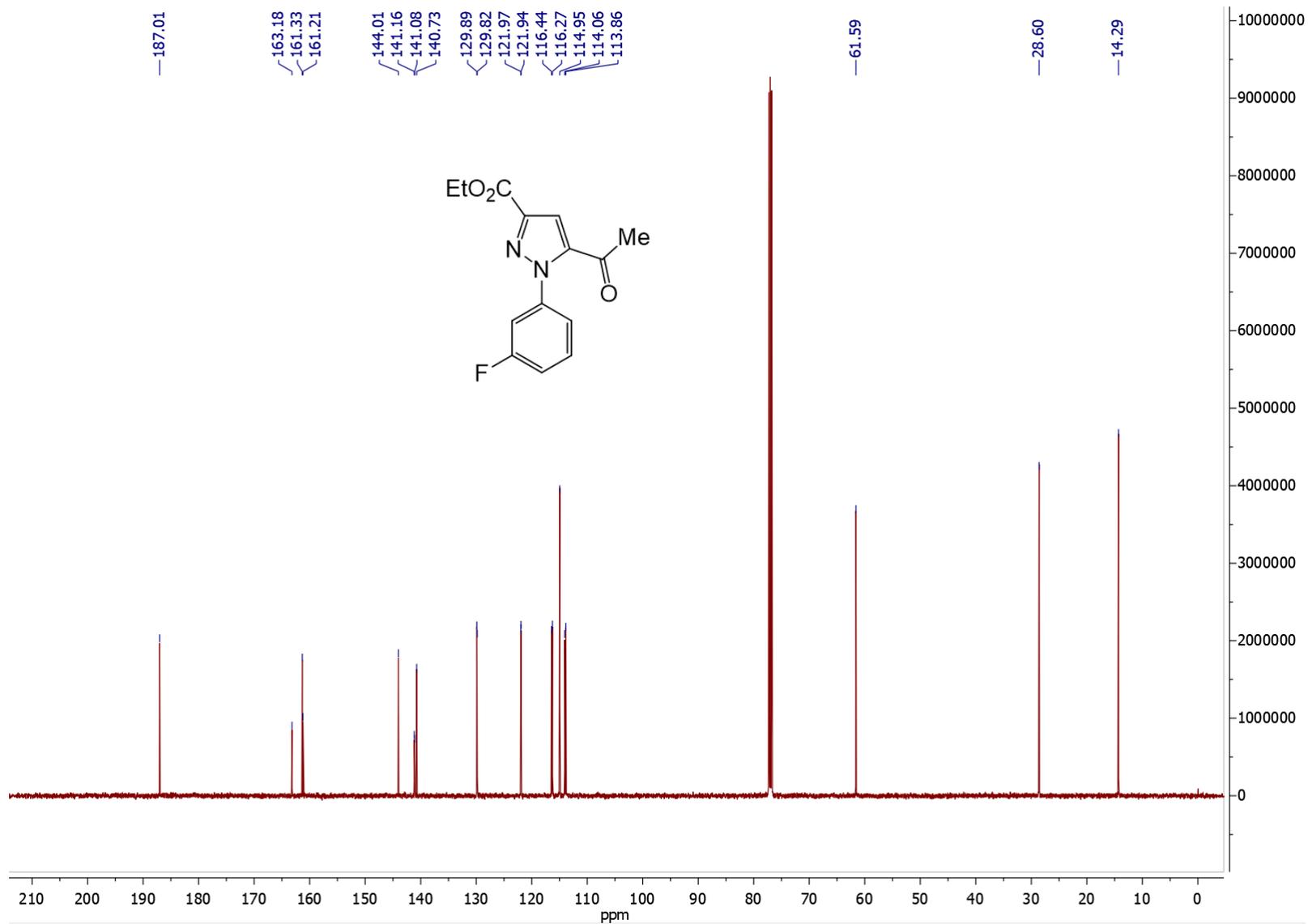


Figure S40. ^{19}F NMR spectrum of compound 7j.

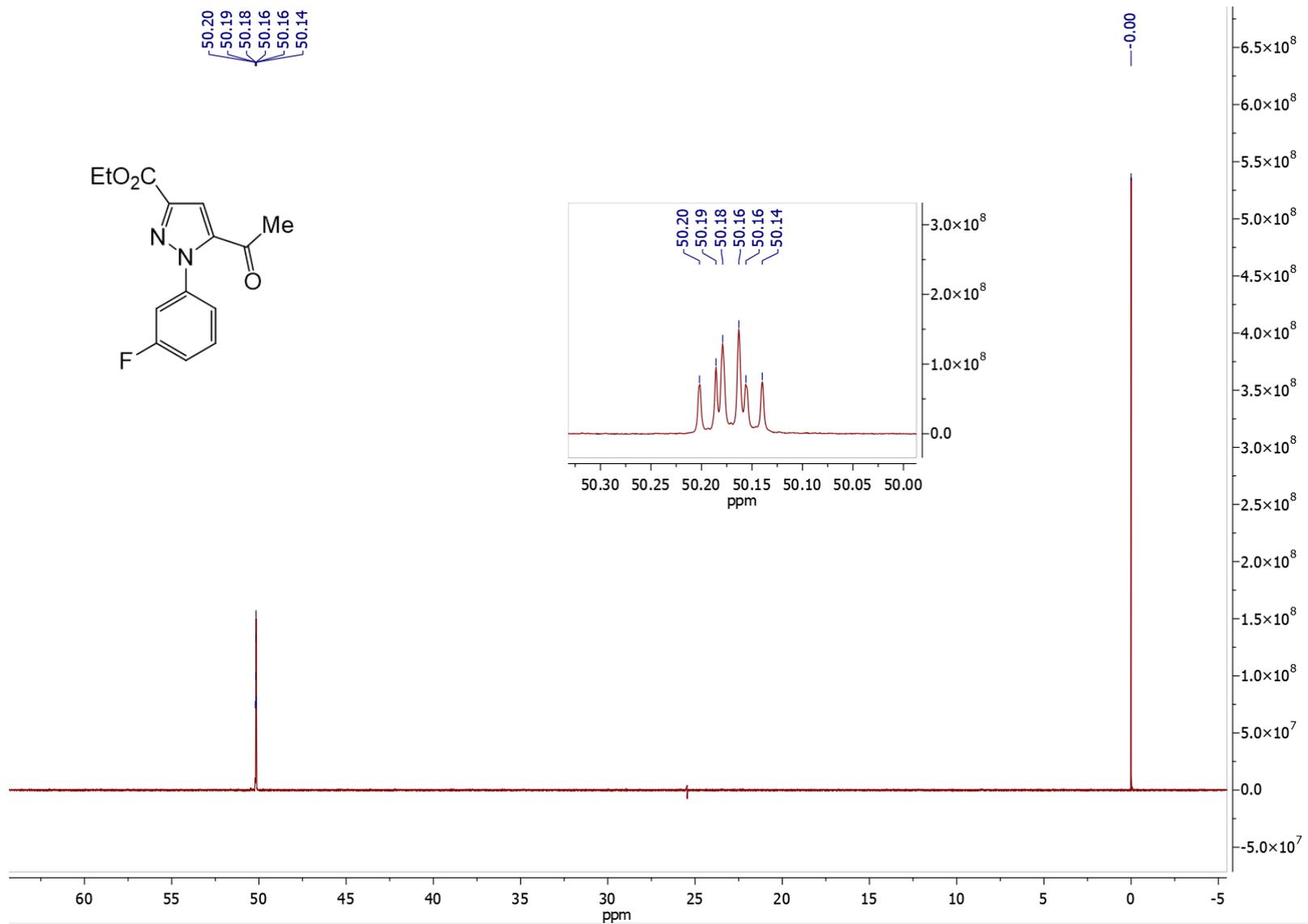


Figure S41. ¹H NMR spectrum of compound 7k.

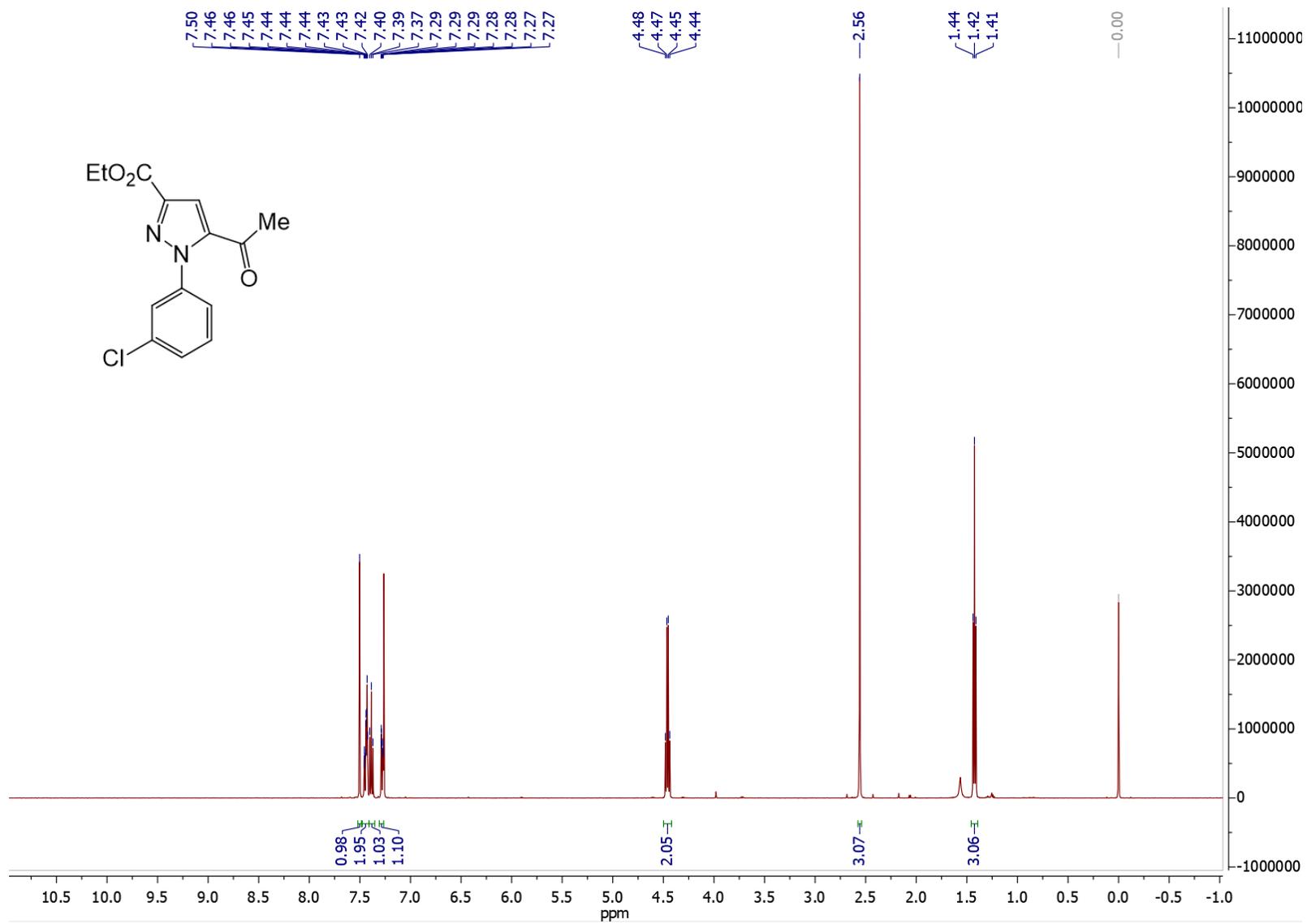


Figure S42. ^{13}C NMR spectrum of compound **7k**.

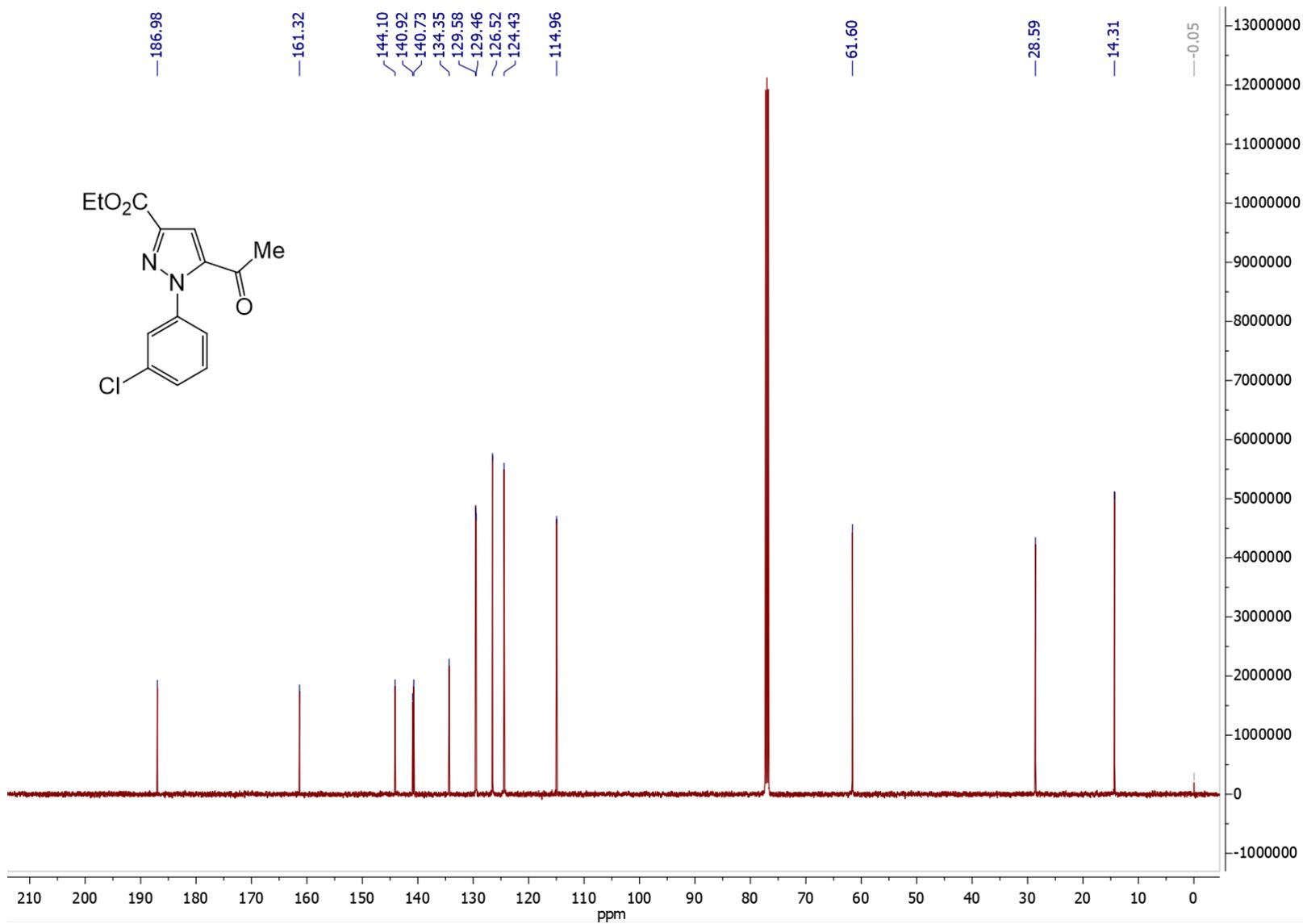


Figure S43. ¹H NMR spectrum of compound 71.

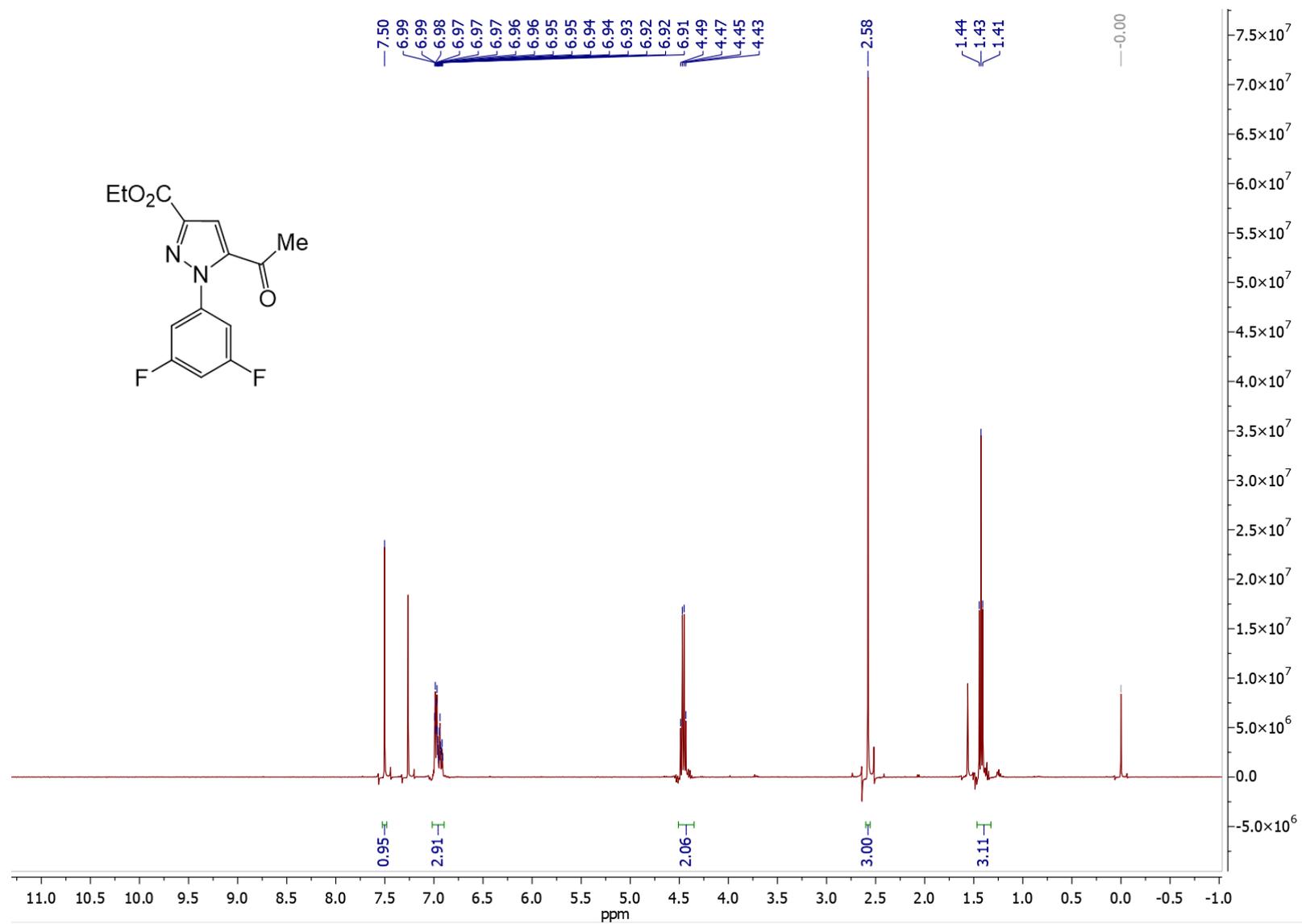


Figure S44. ^{13}C NMR spectrum of compound **7l**.

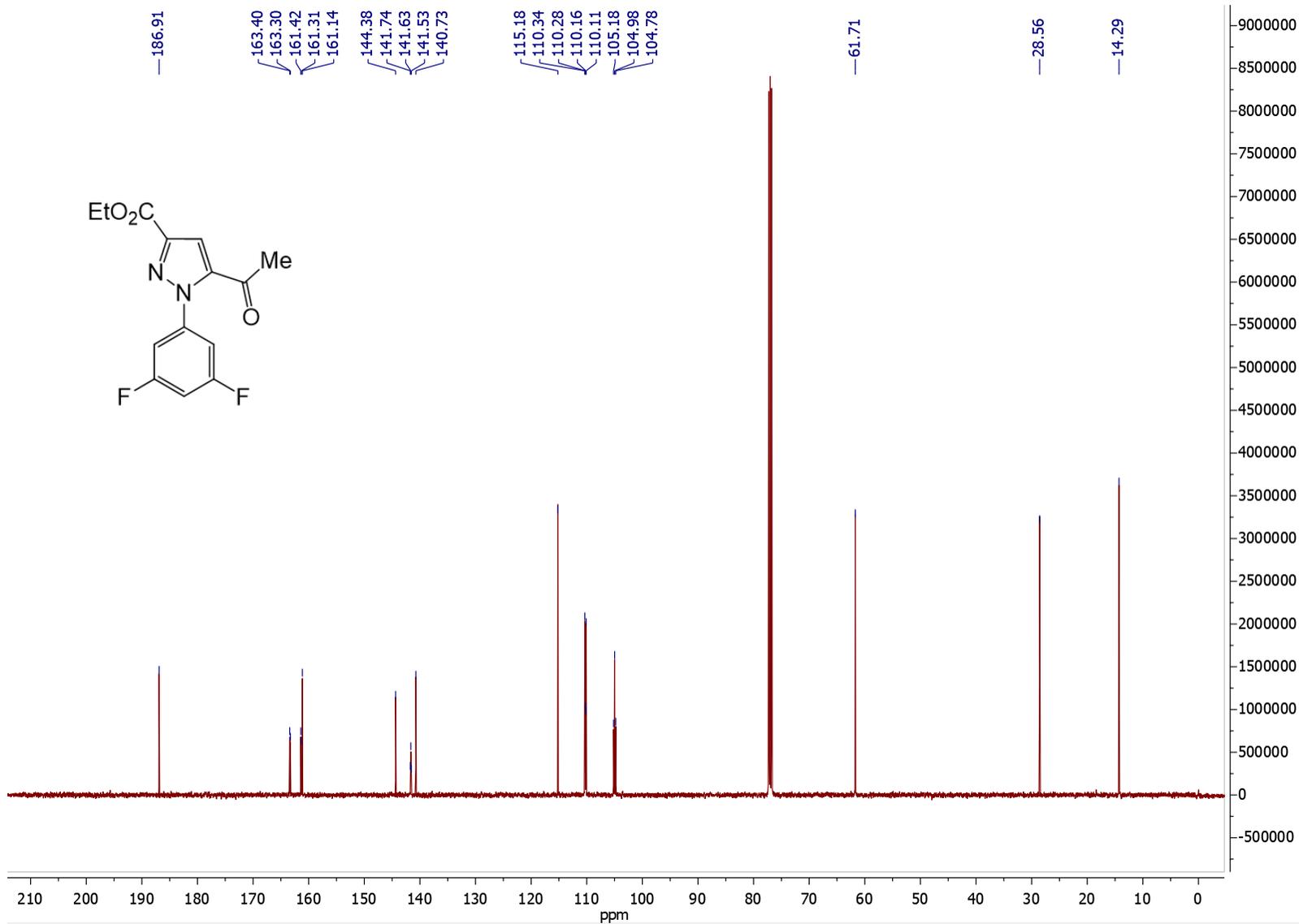


Figure S45. ^{19}F NMR spectrum of compound **71**.

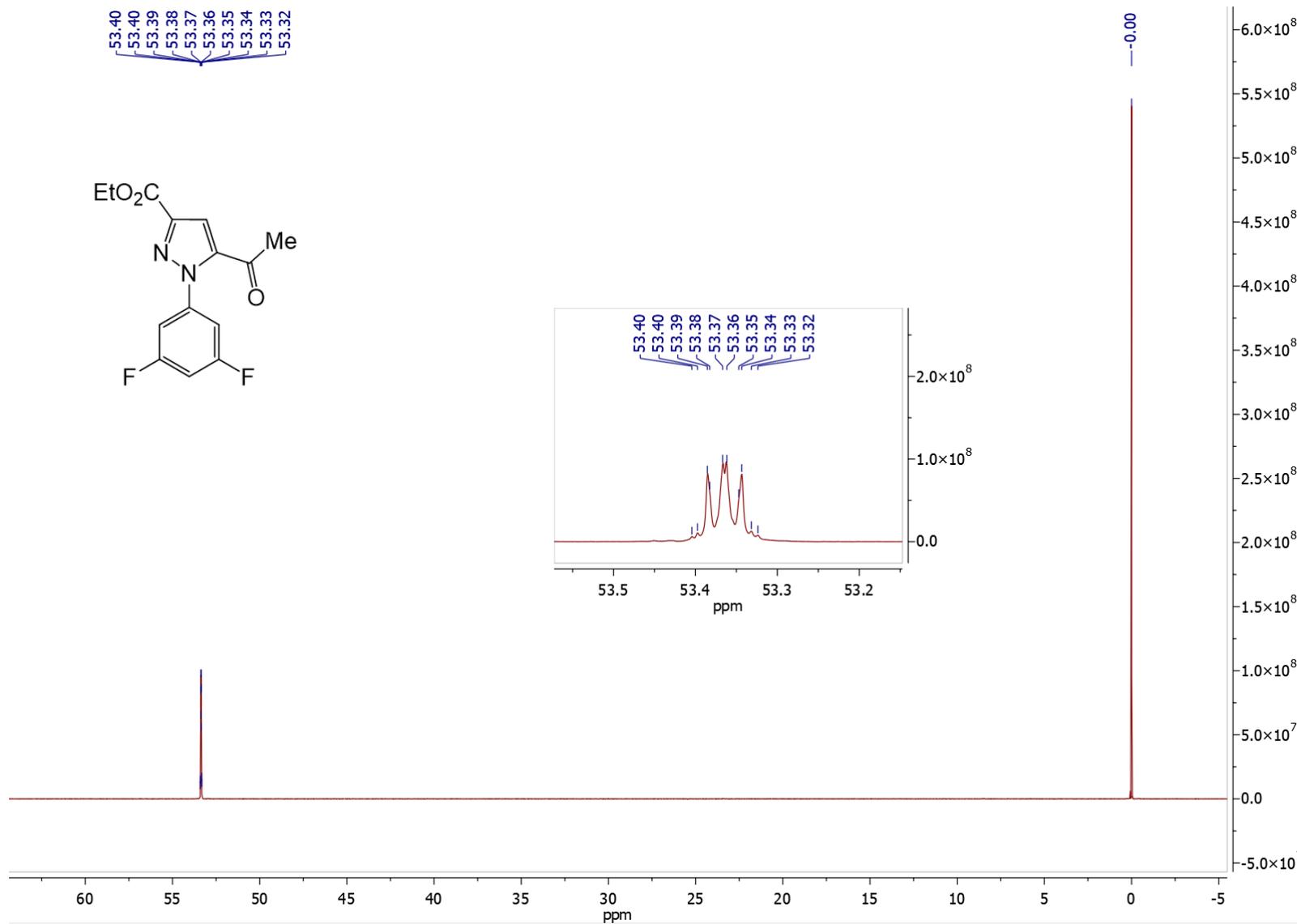


Figure S46. ¹H NMR spectrum of compound 8.

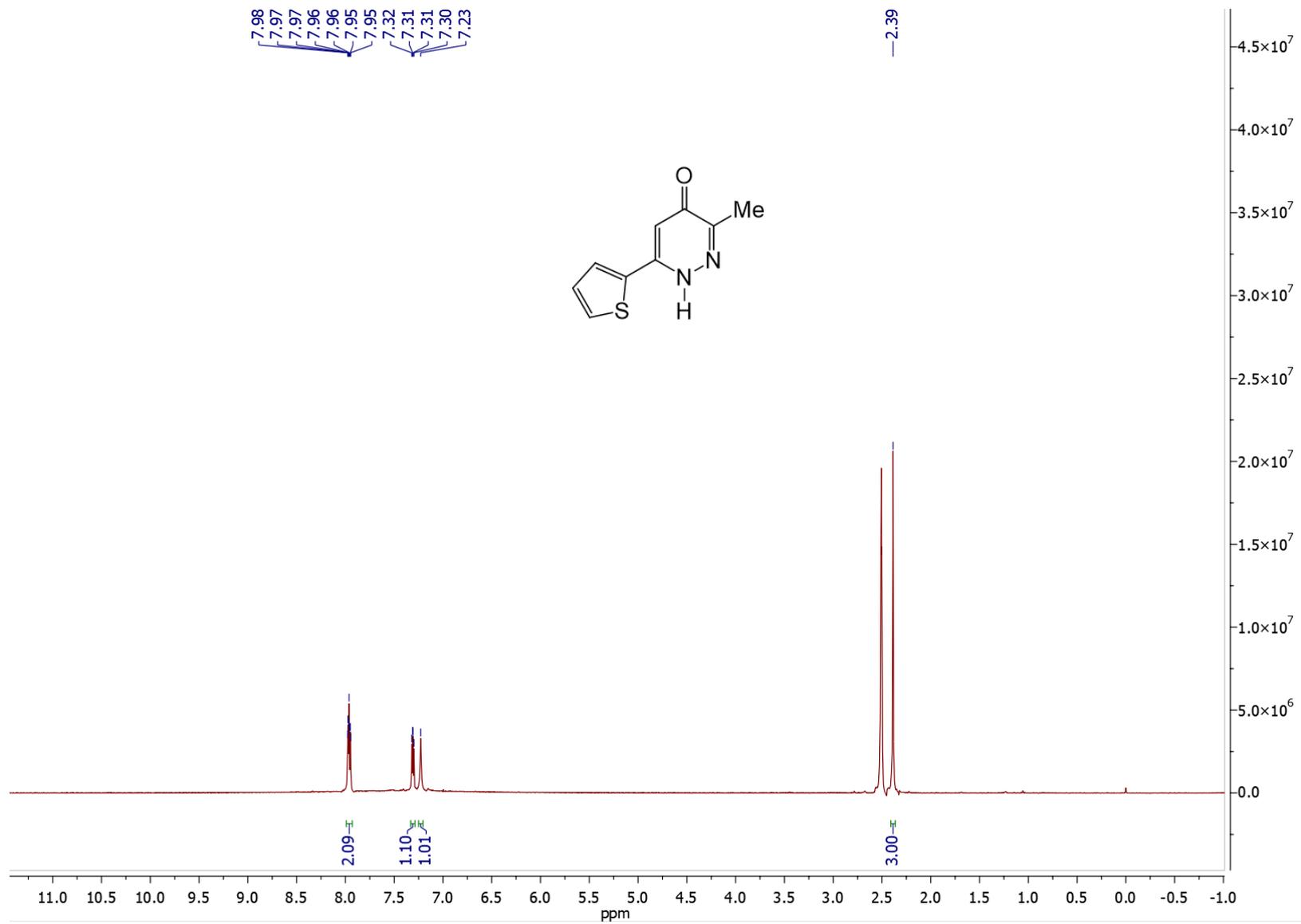


Figure S47. ^{13}C NMR spectrum of compound 8.

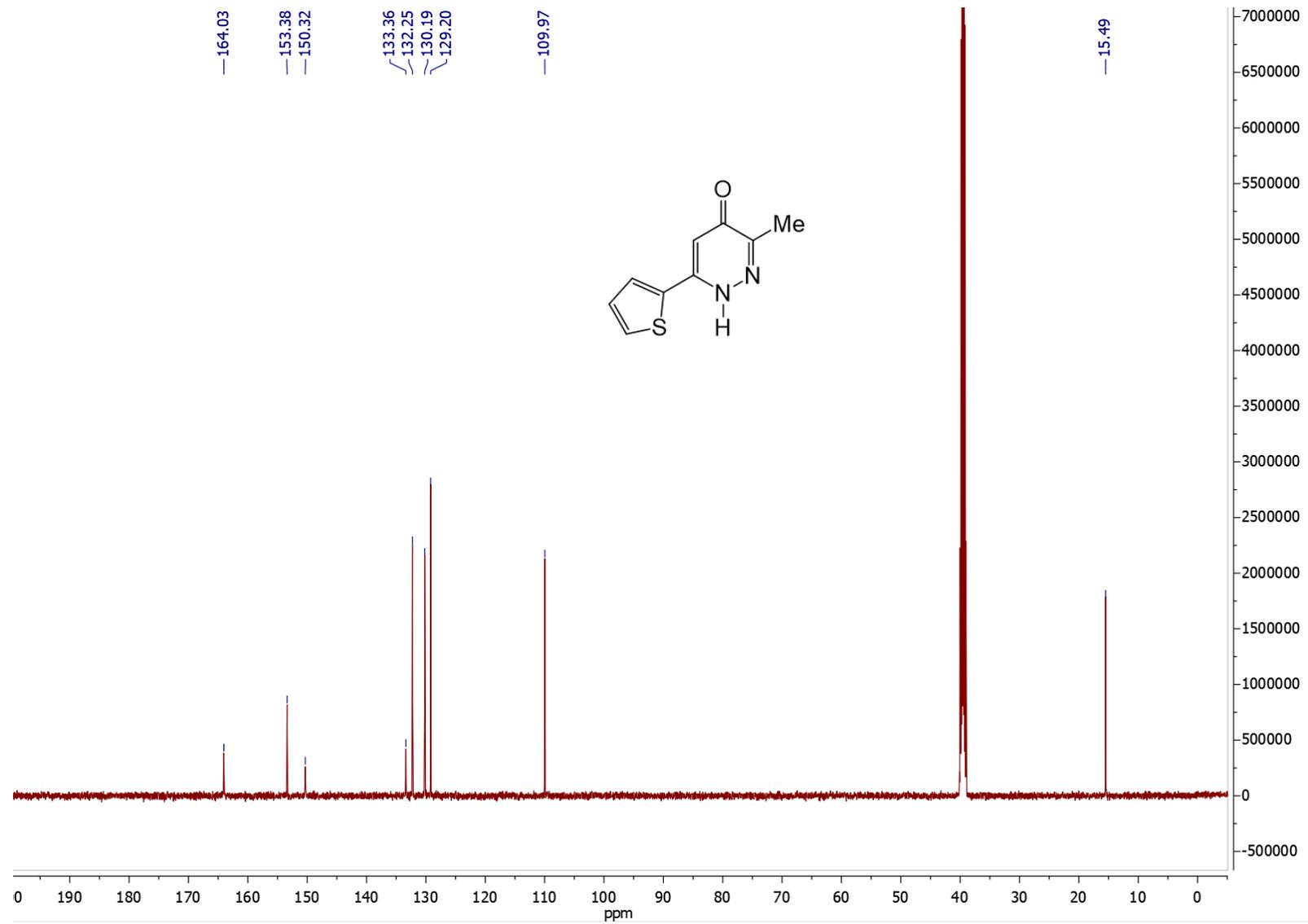


Figure S48. ¹H NMR spectrum of compound 9a.

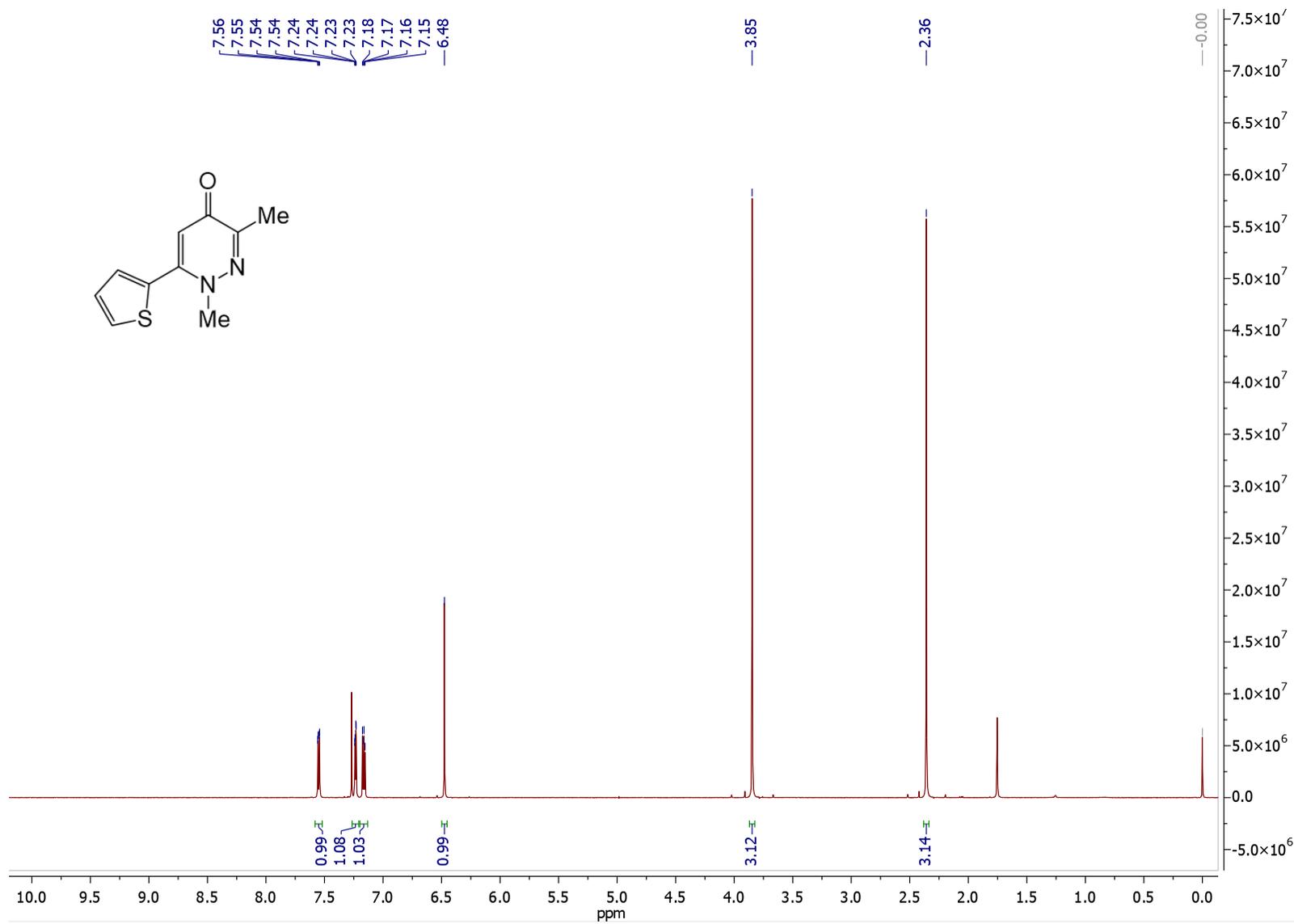


Figure S49. ^{13}C NMR spectrum of compound **9a**.

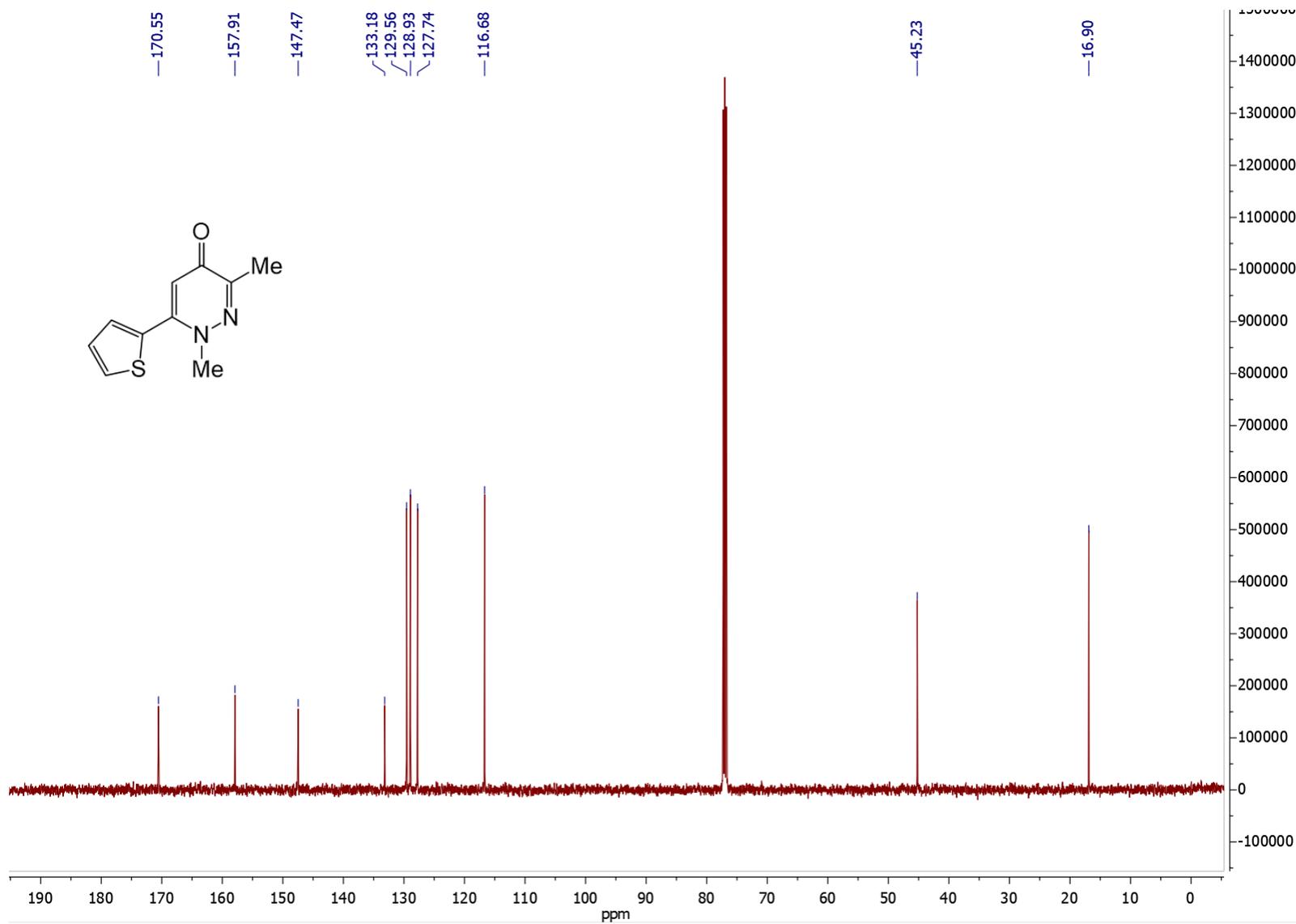


Figure S50. ¹H NMR spectrum of compound **9b**.

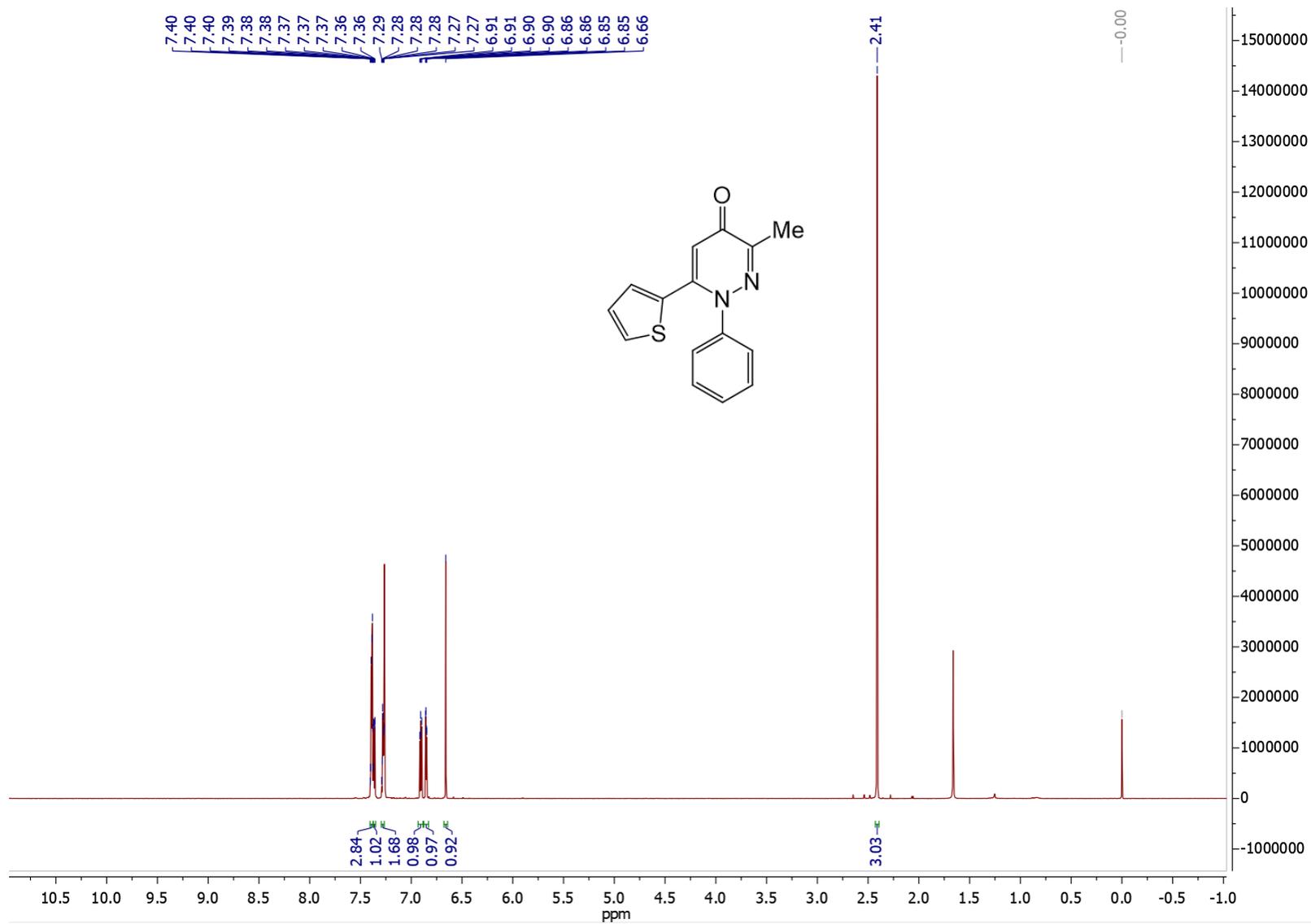


Figure S51. ^{13}C NMR spectrum of compound **9b**.

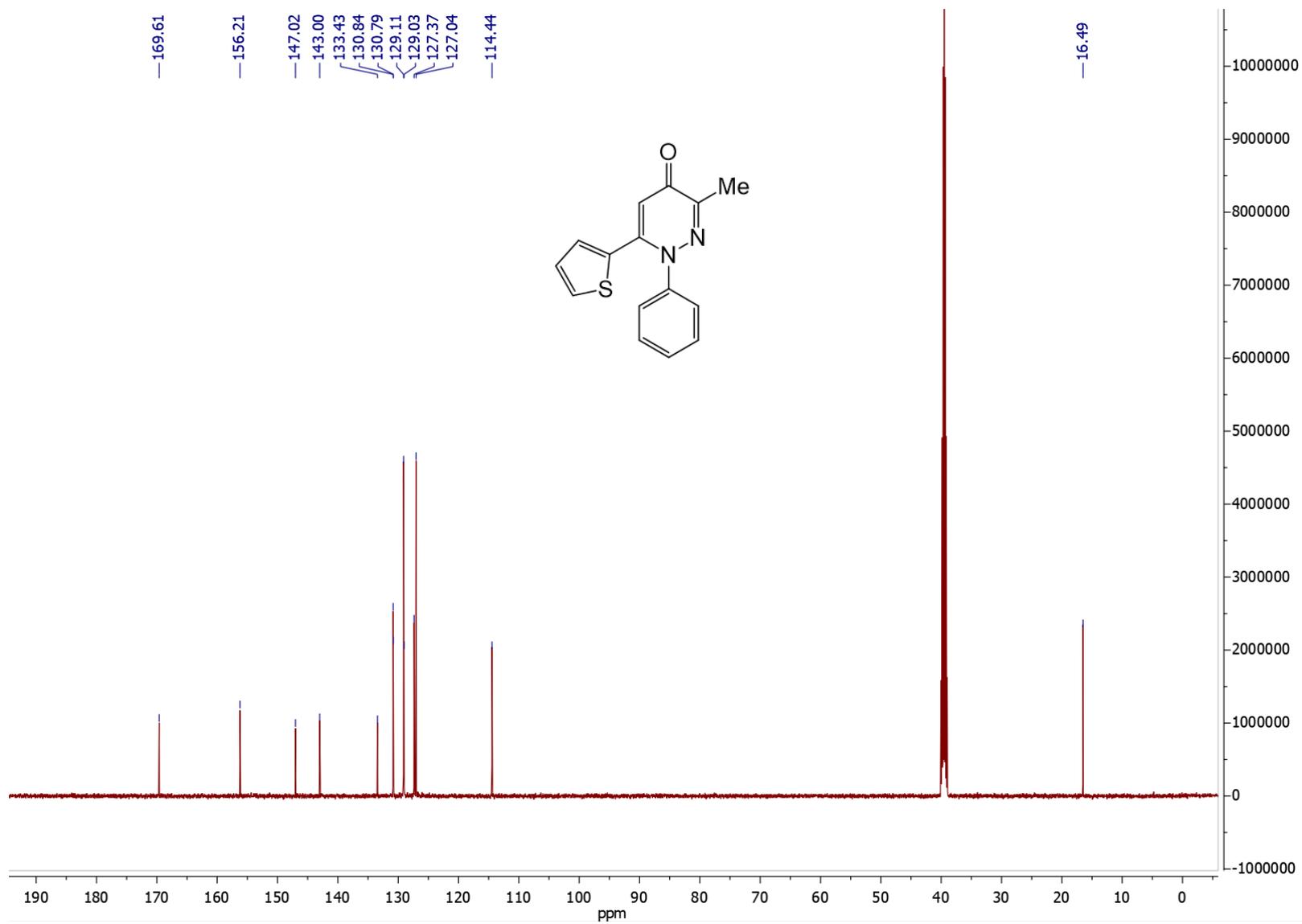


Figure S52. ¹H NMR spectrum of compound 10a.

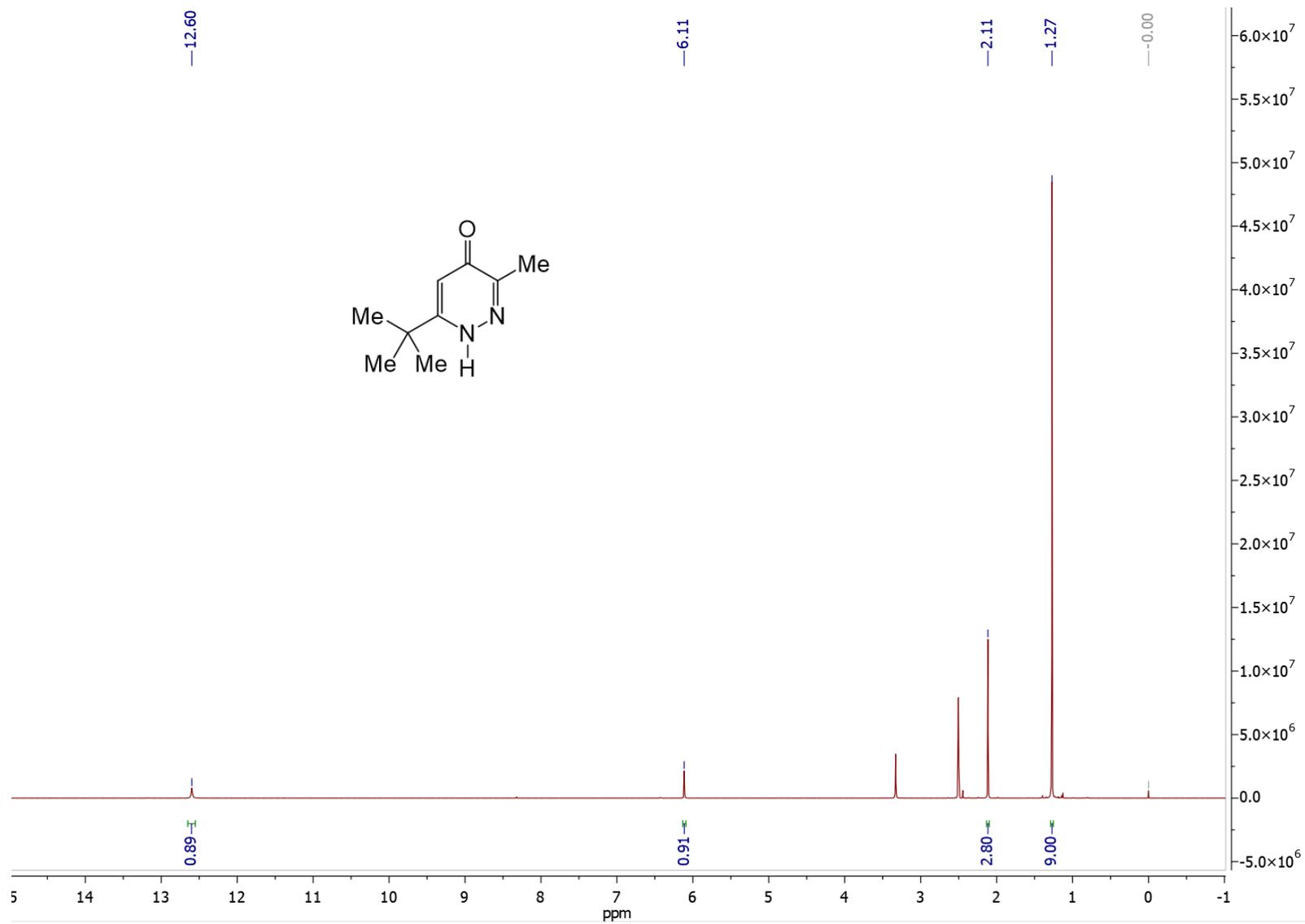


Figure S53. ^{13}C NMR spectrum of compound **10a**.

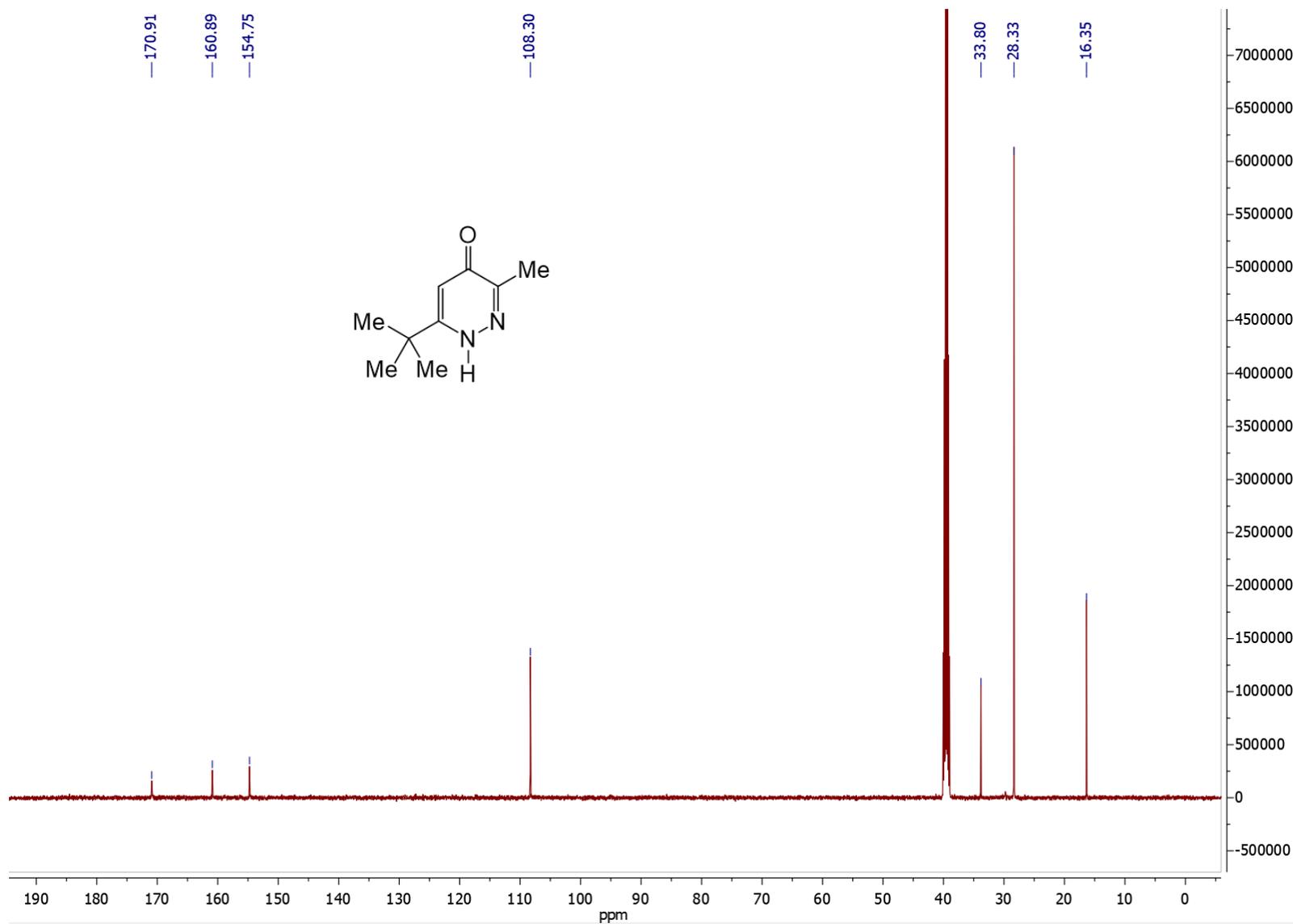


Figure S54. ¹H NMR spectrum of compound **10b**.

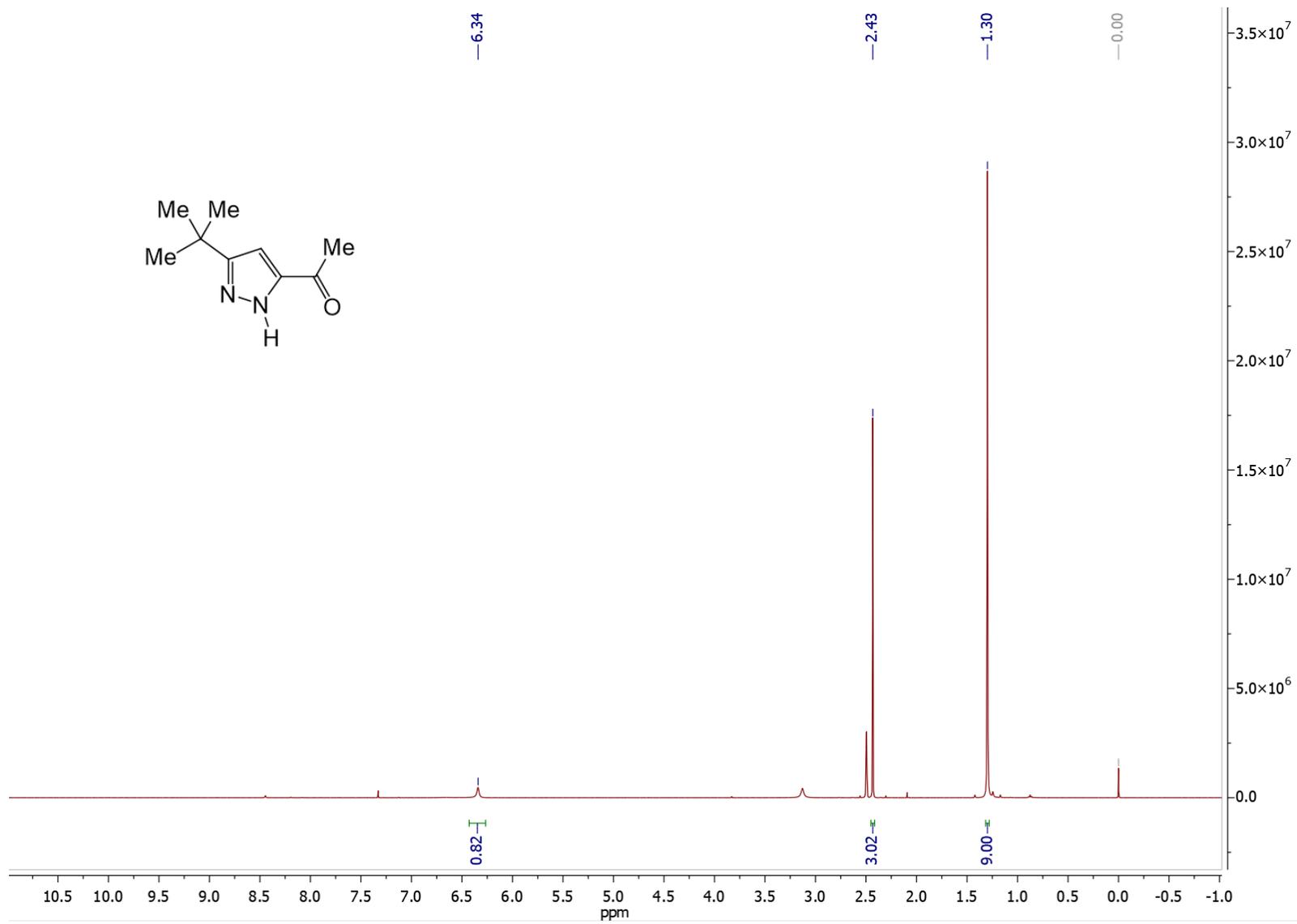


Figure S55. ^{13}C NMR spectrum of compound **10b**.

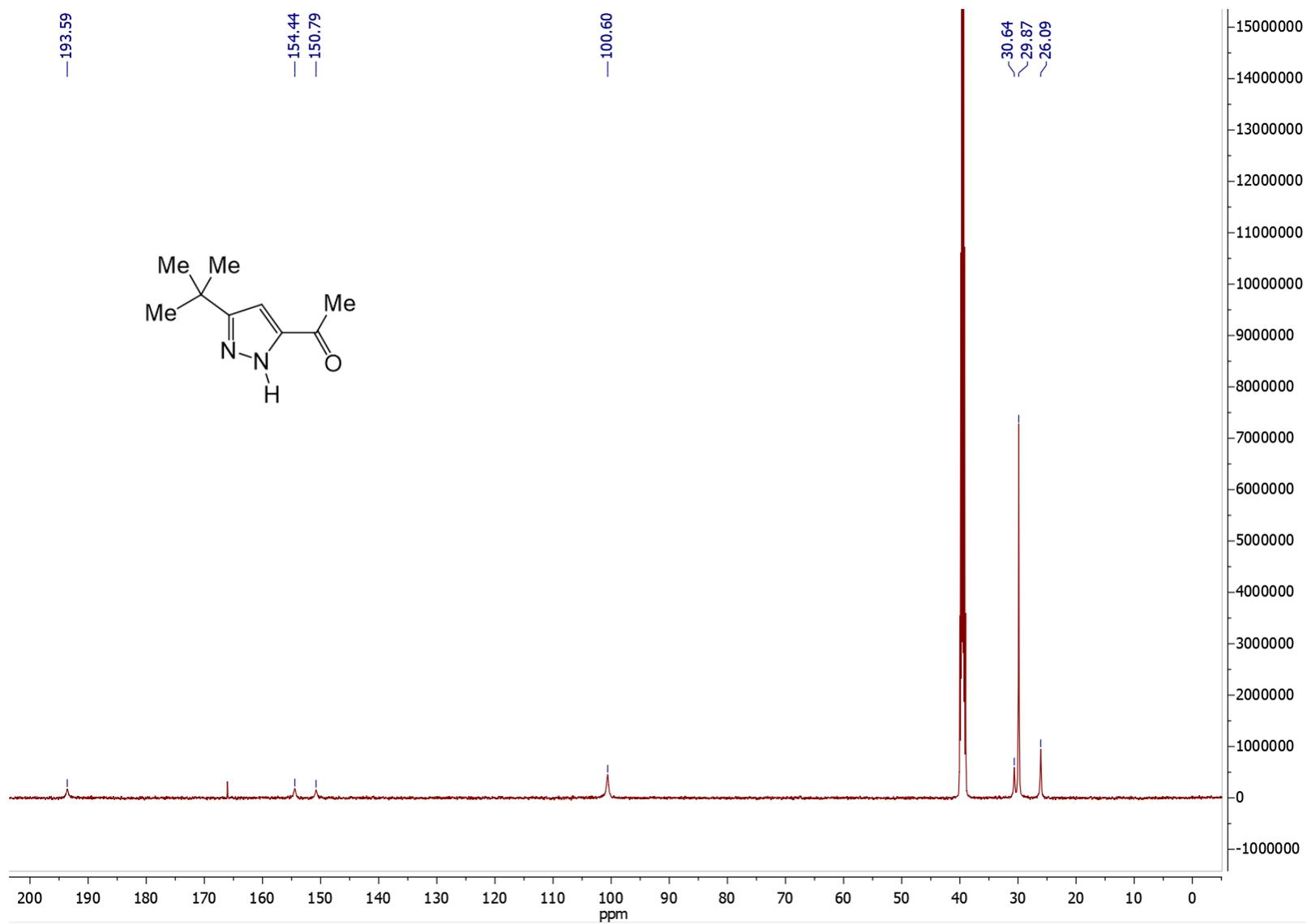


Figure S56. ¹H NMR spectrum of compound **11**.

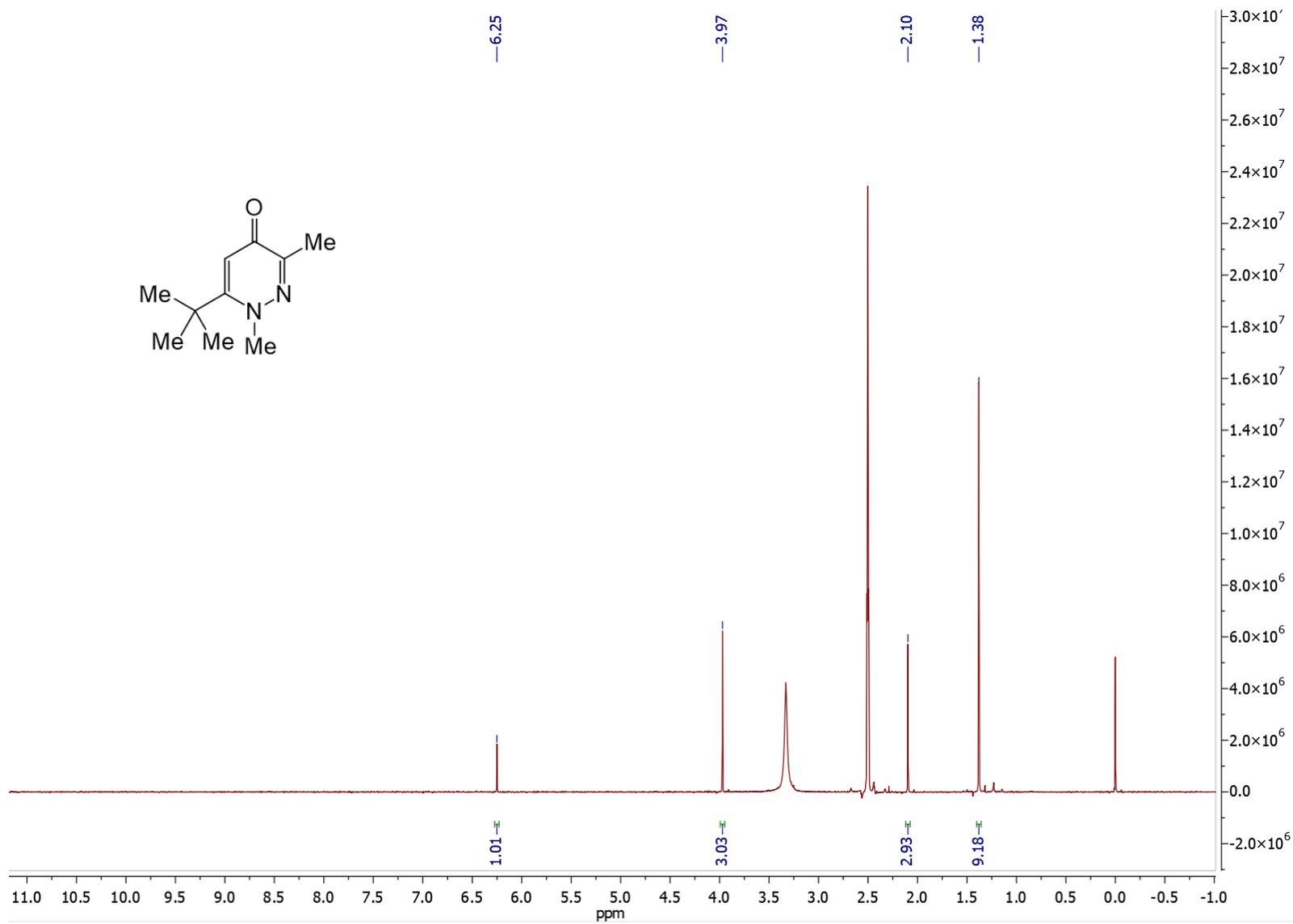


Figure S57. ¹³C NMR spectrum of compound **11**.

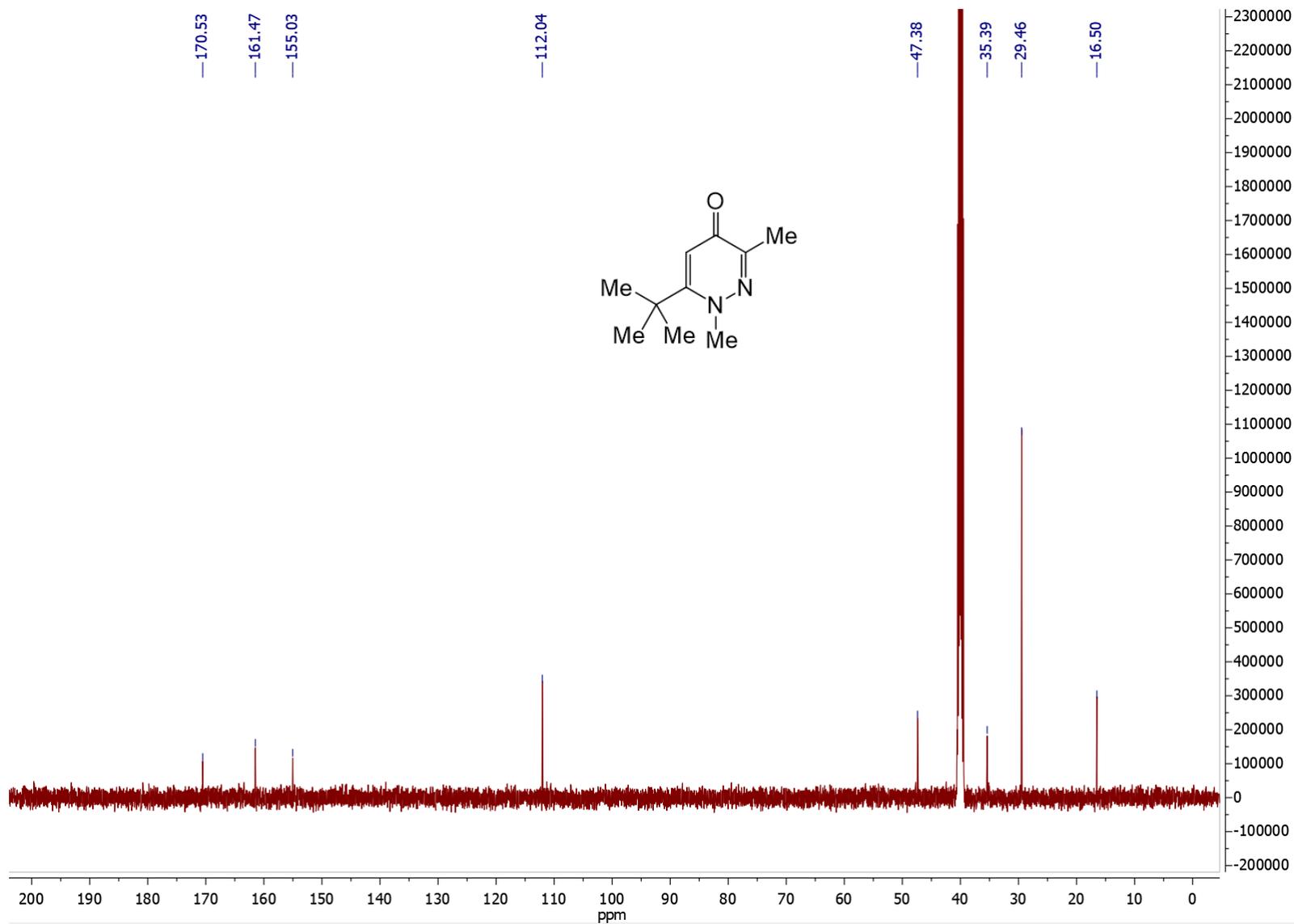


Figure S58. ¹H NMR spectrum of compound **12**.

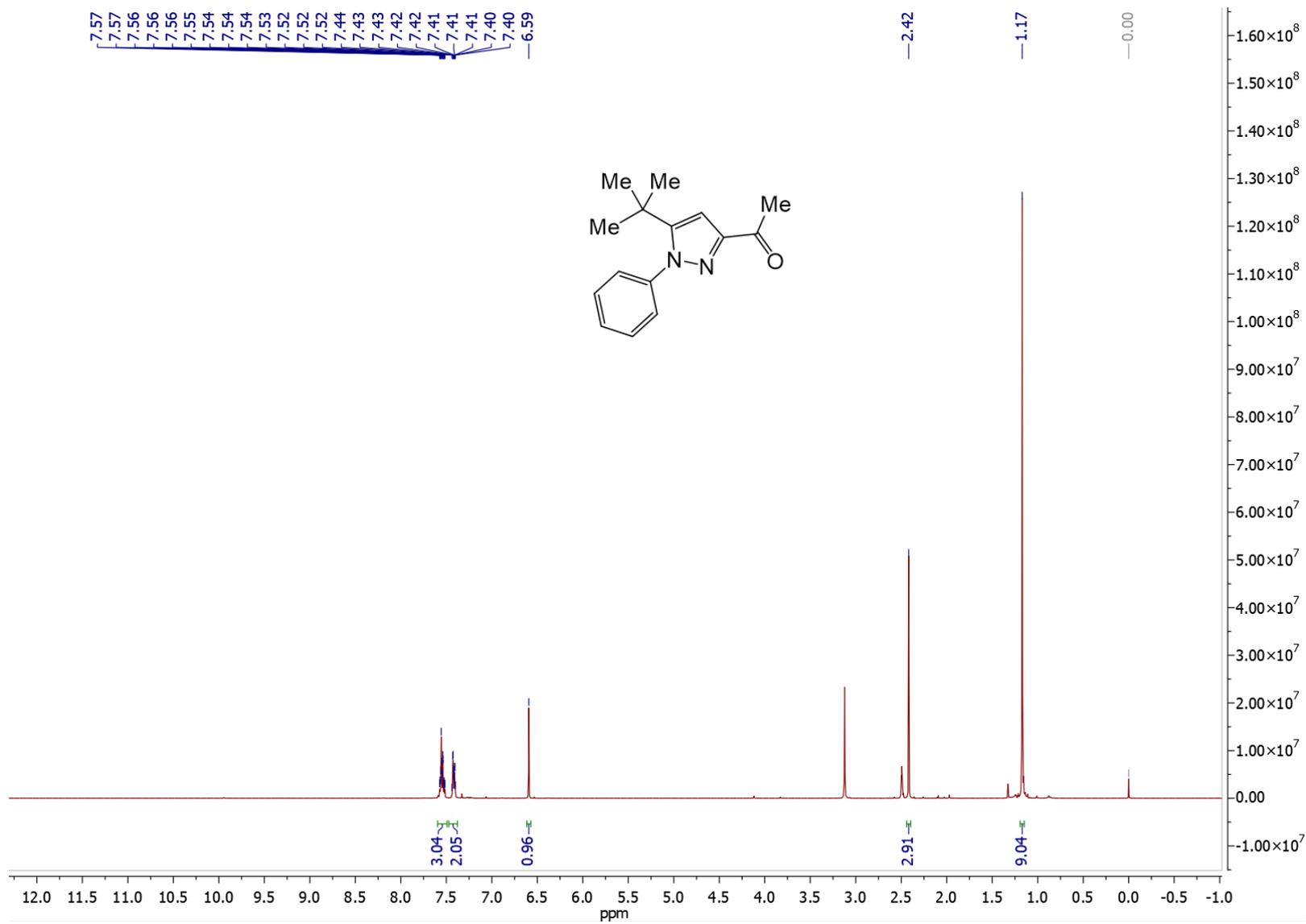


Figure S59. ¹³C NMR spectrum of compound **12**.

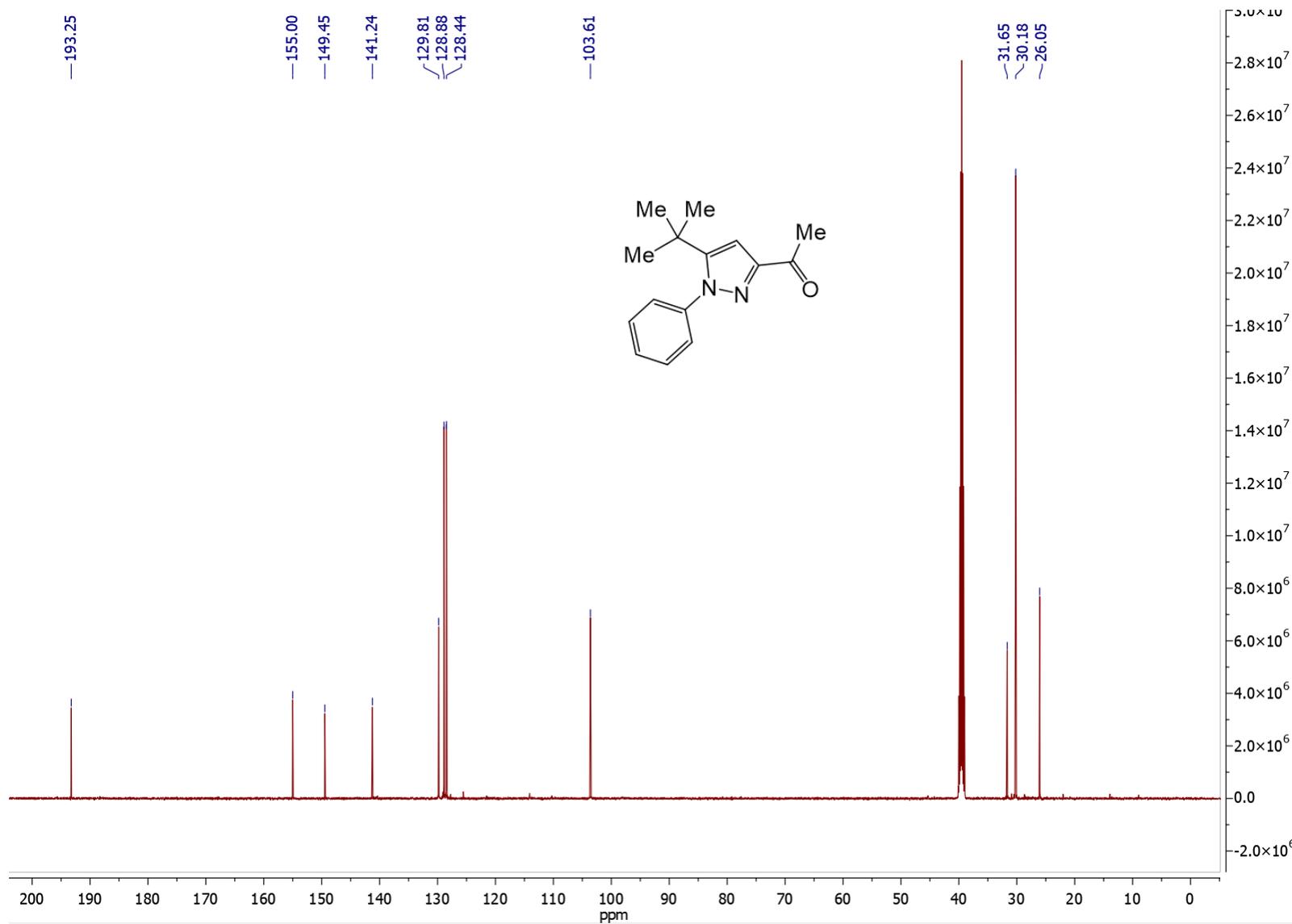


Figure S60. ¹H NMR spectrum of compound **13a**.

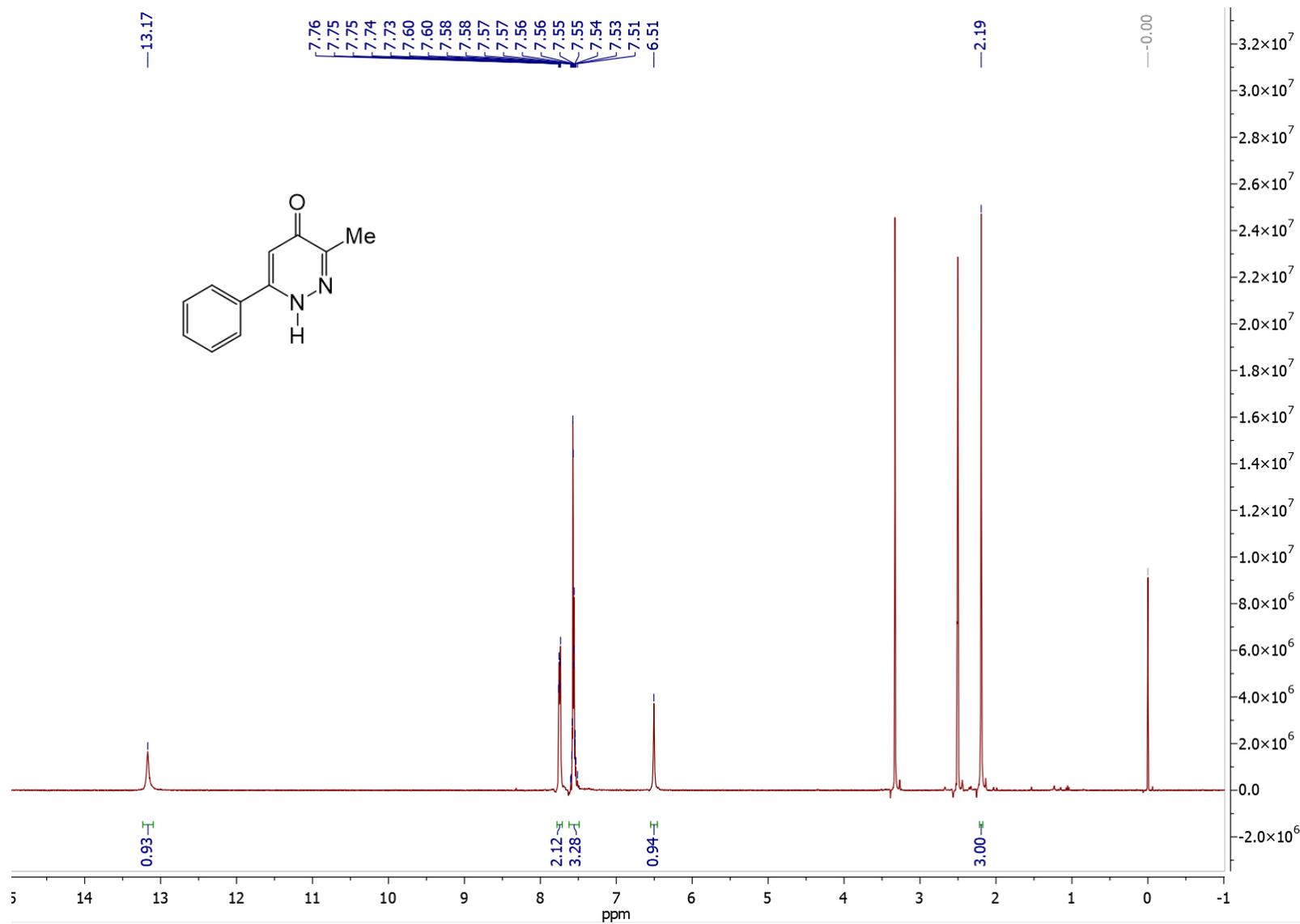


Figure S61. ^{13}C NMR spectrum of compound **13a**.

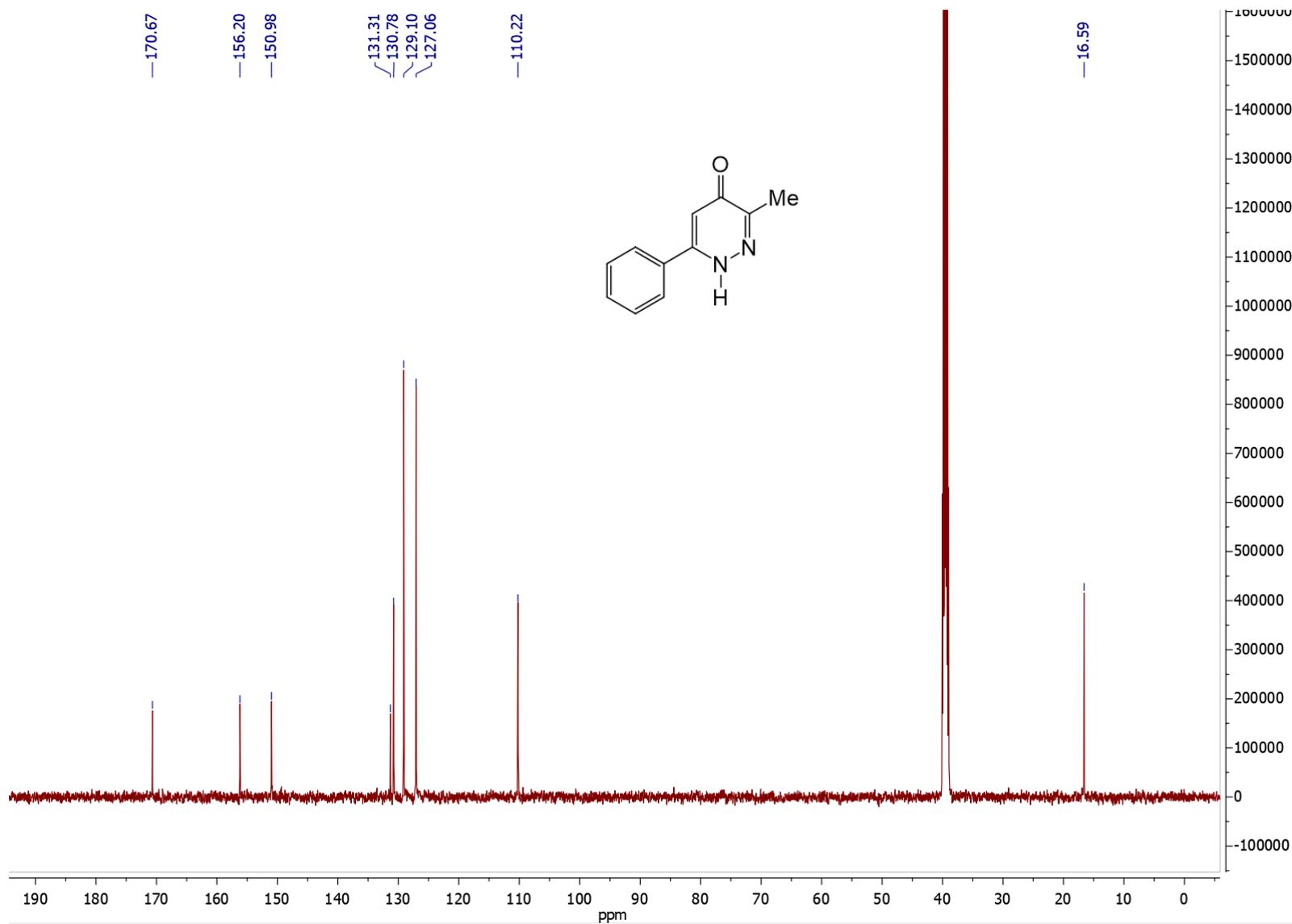


Figure S62. ¹H NMR spectrum of compound **13b**.

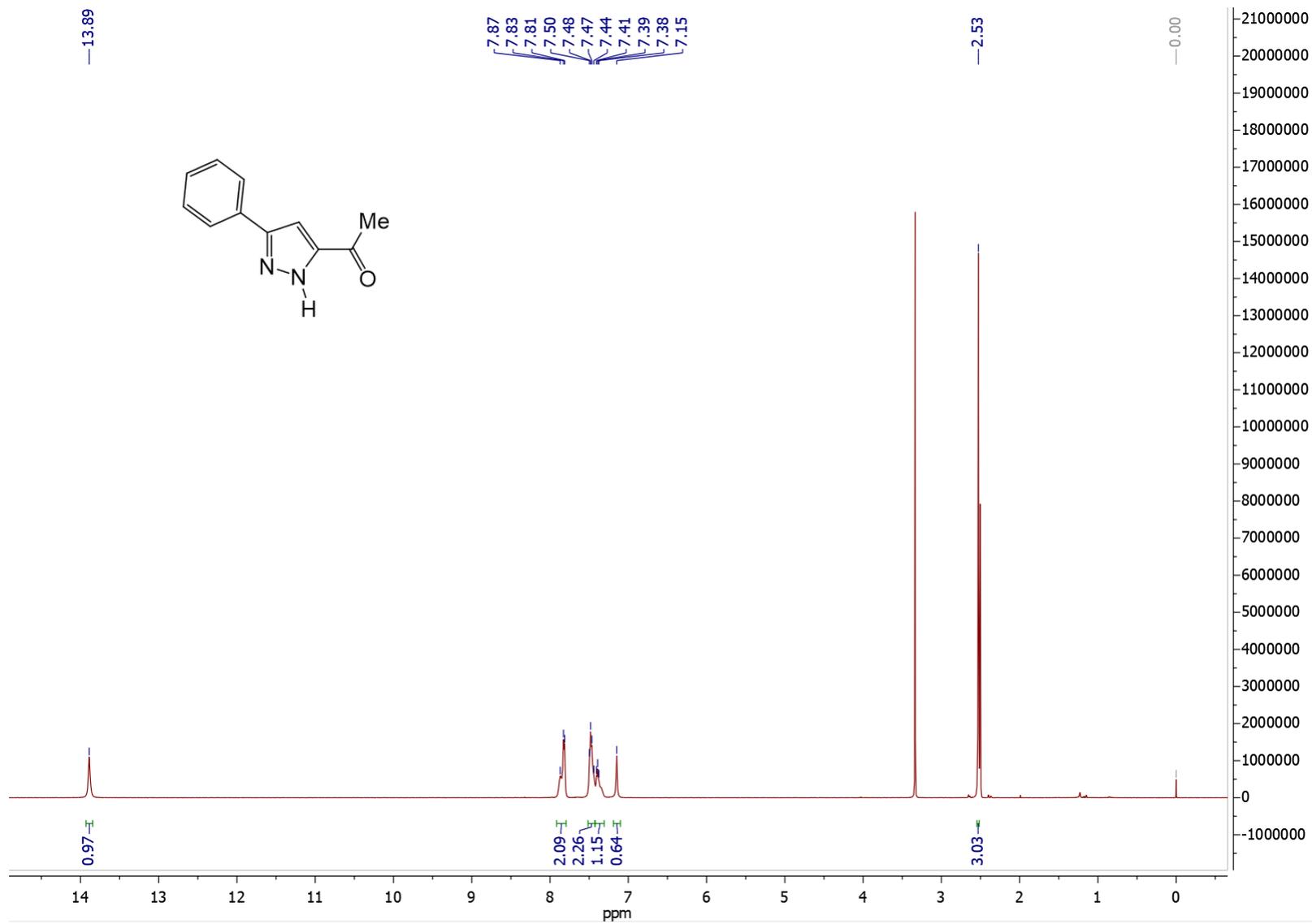


Figure S63. ^{13}C NMR spectrum of compound **13b**.

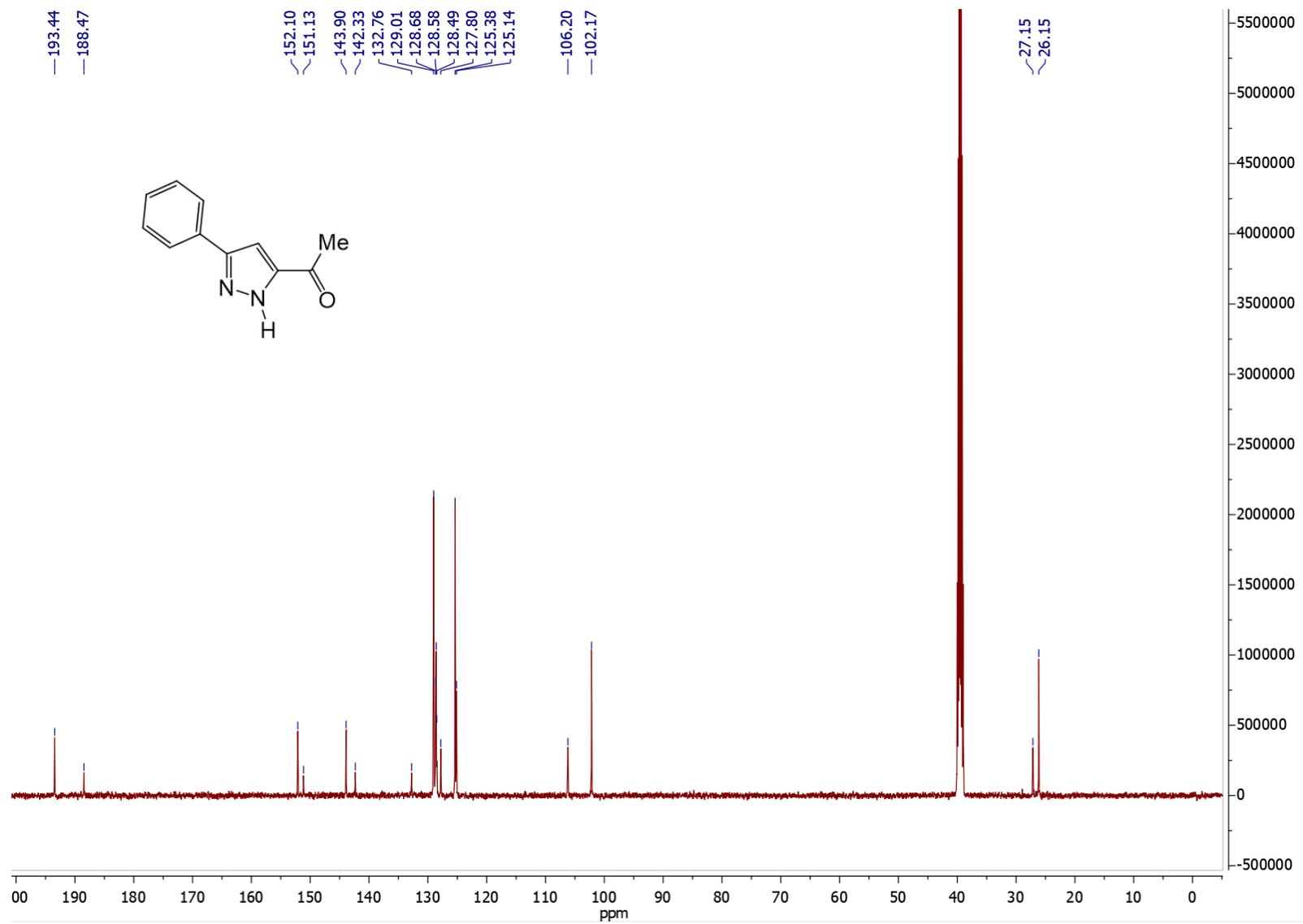


Figure S64. ¹H NMR spectrum of compound 14.

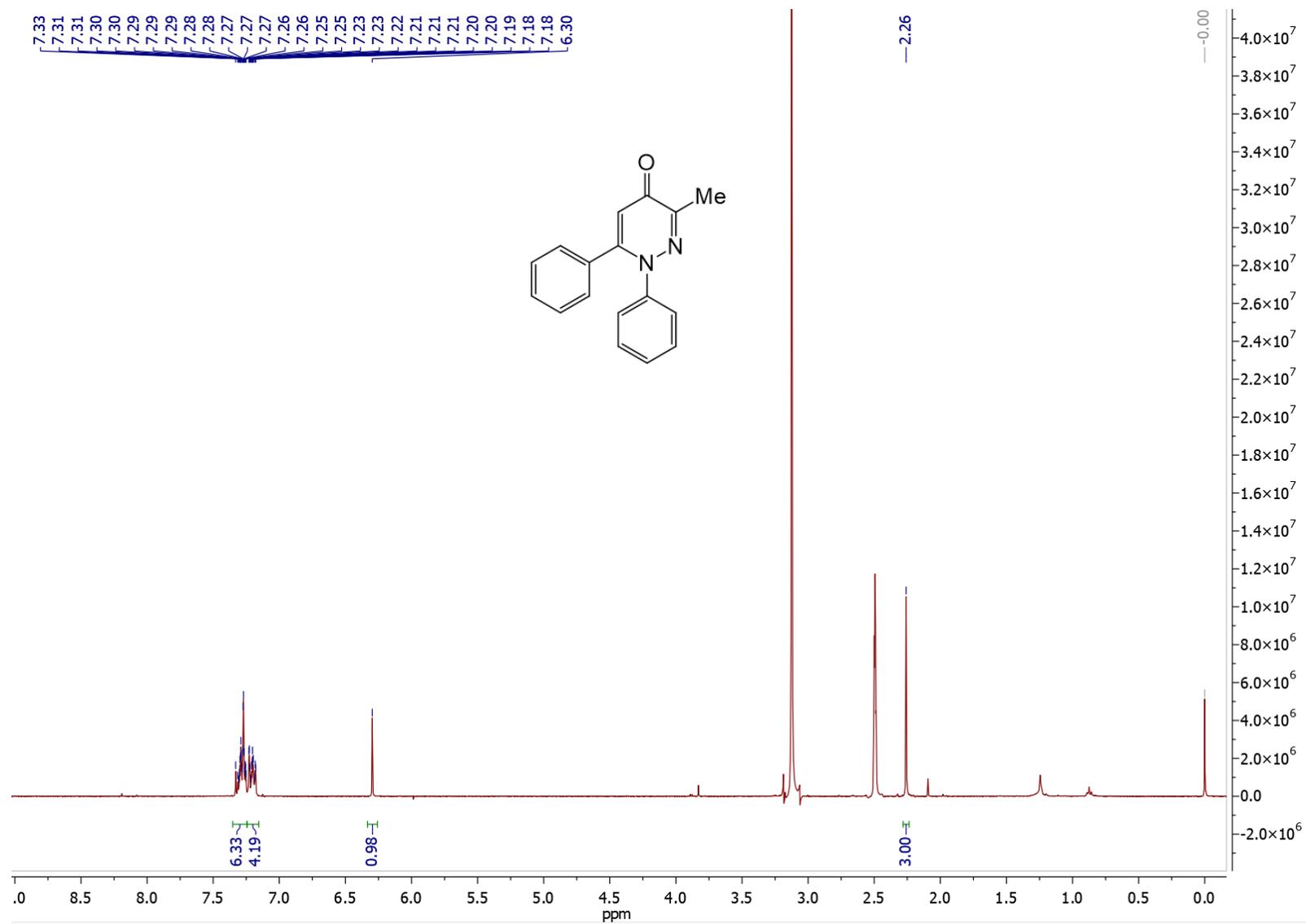


Figure S65. ^{13}C NMR spectrum of compound **14**.

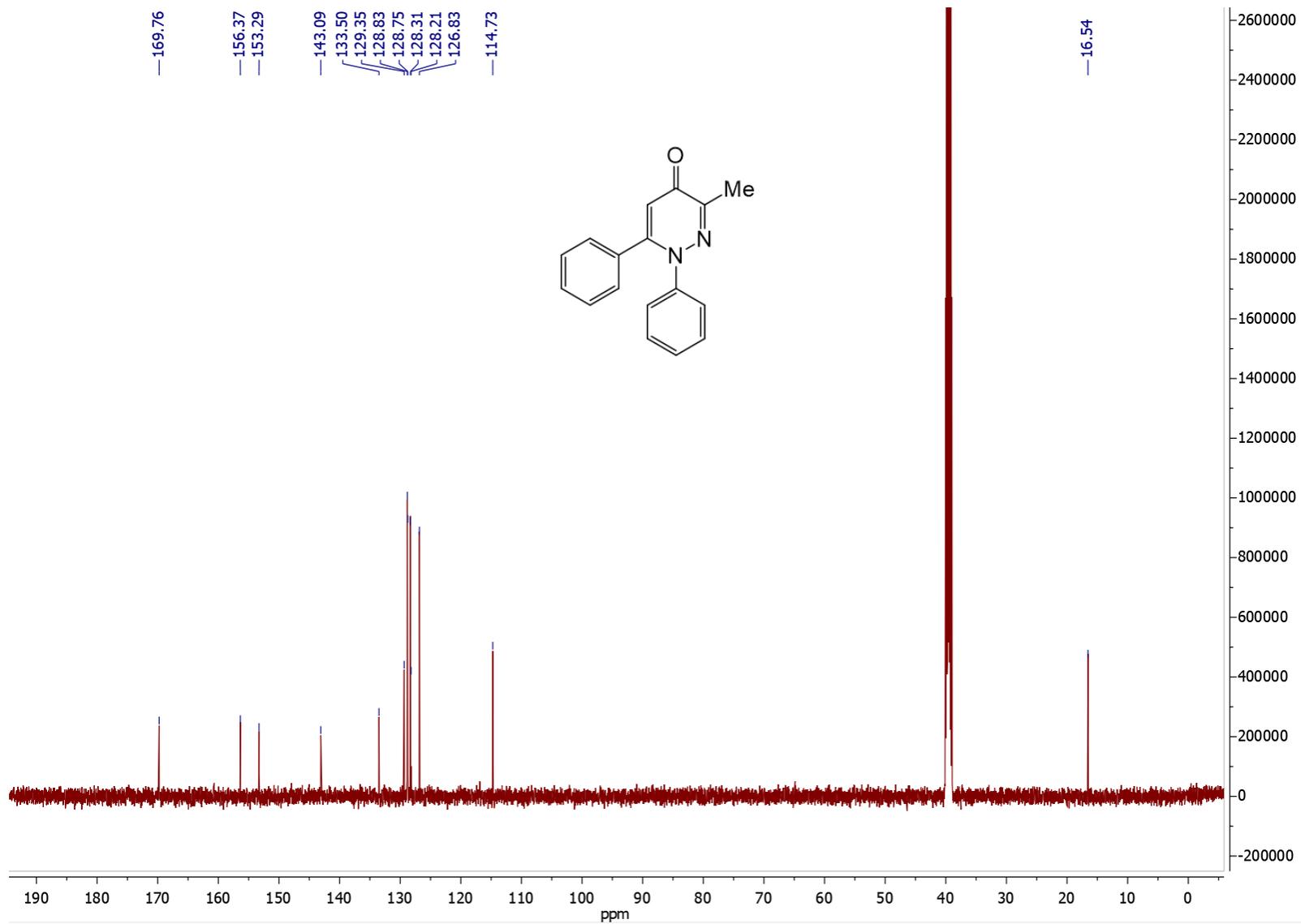


Figure S66. ¹H NMR spectrum of compound **15a**.

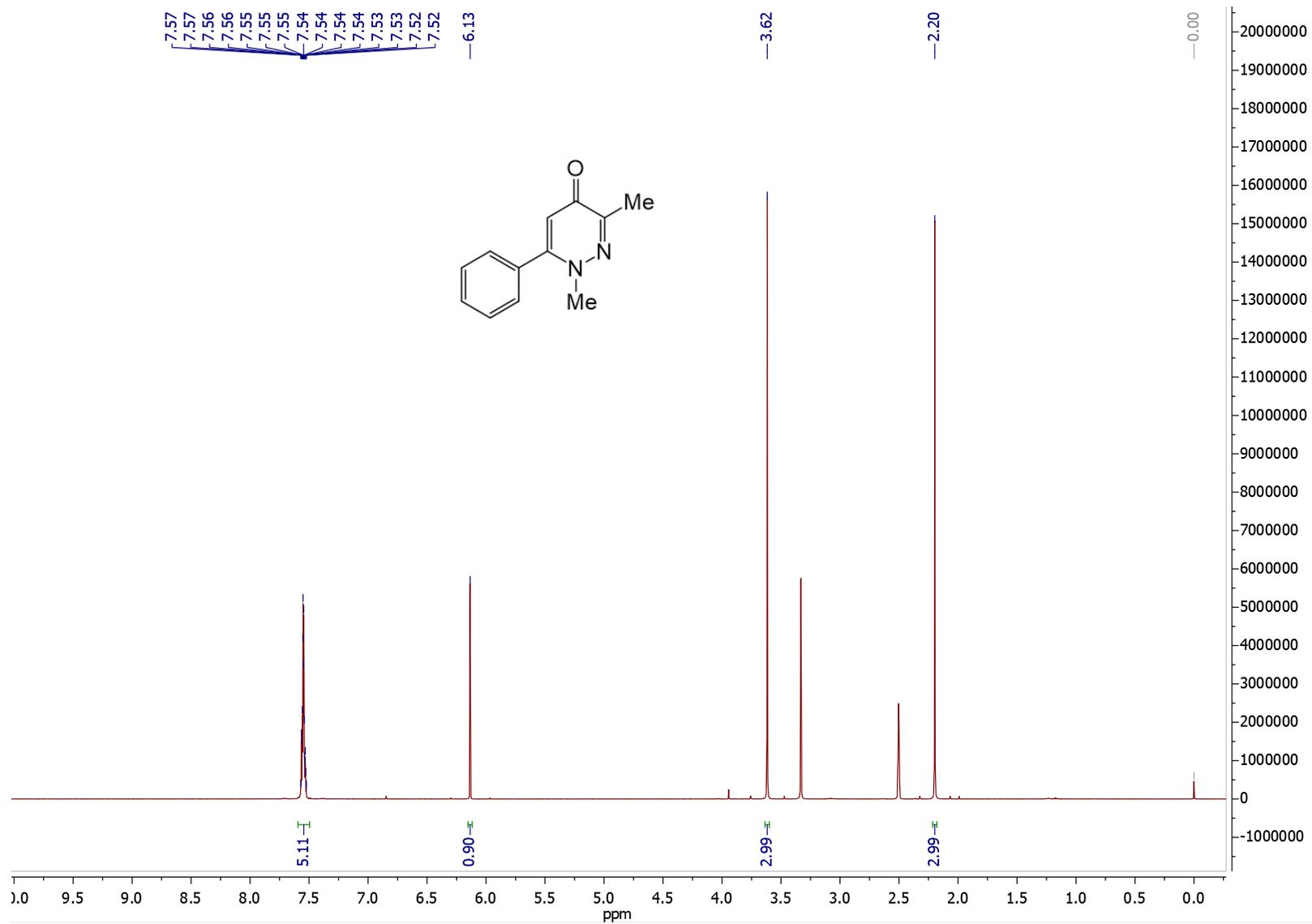


Figure S67. ¹³C NMR spectrum of compound **15a**.

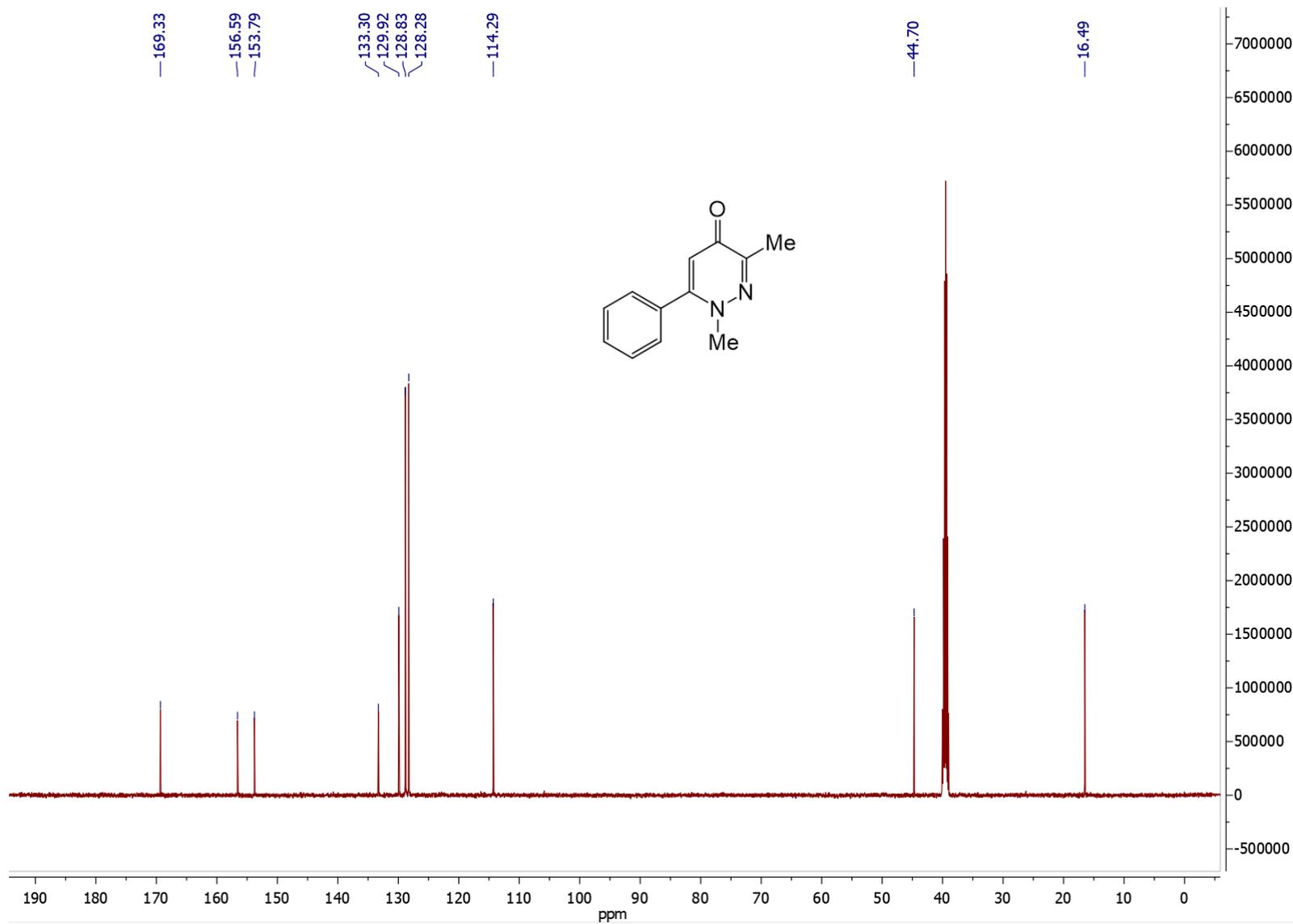


Figure S68. ¹H NMR spectrum of compound **15b**.

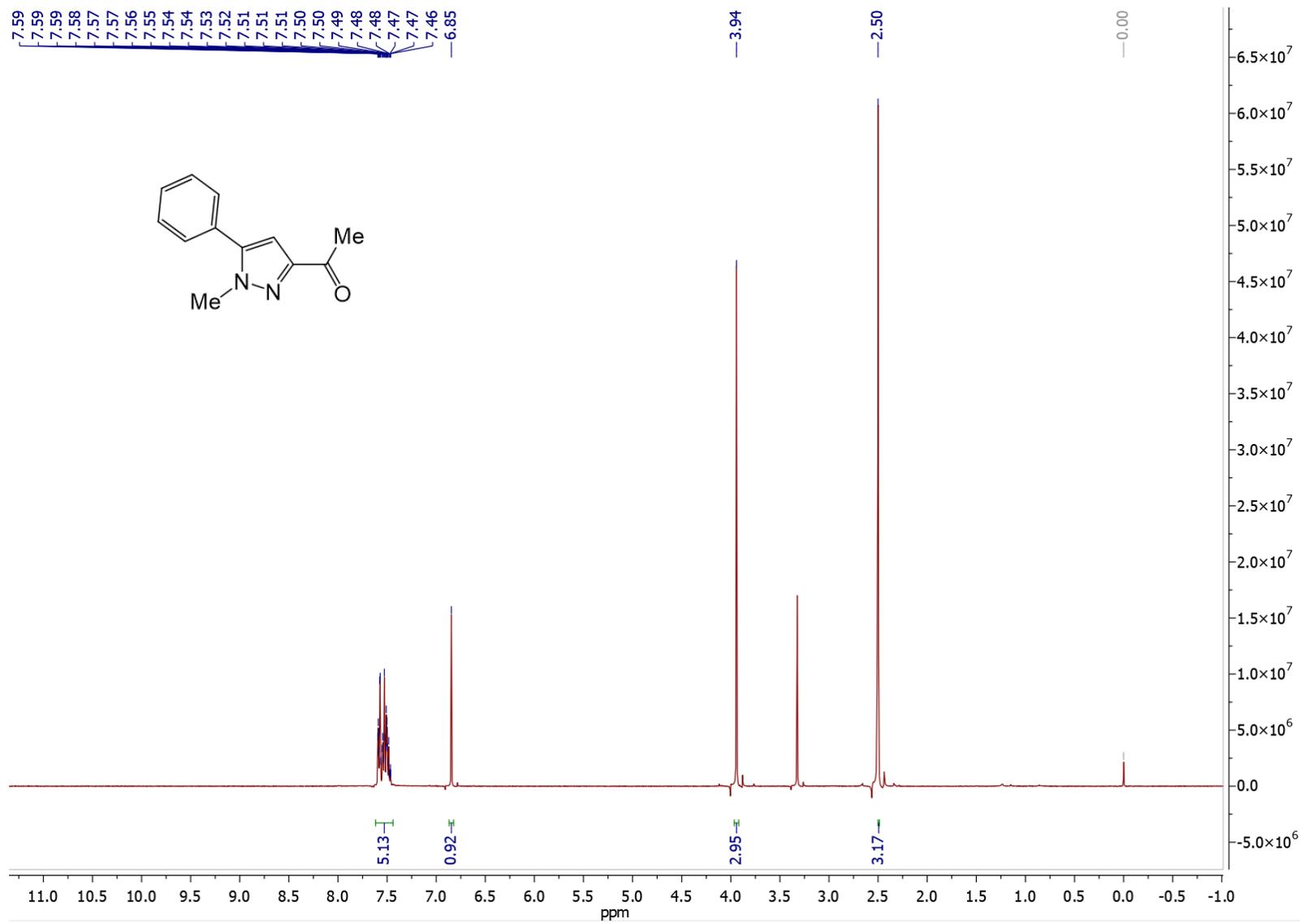


Figure S69. ^{13}C NMR spectrum of compound **15b**.

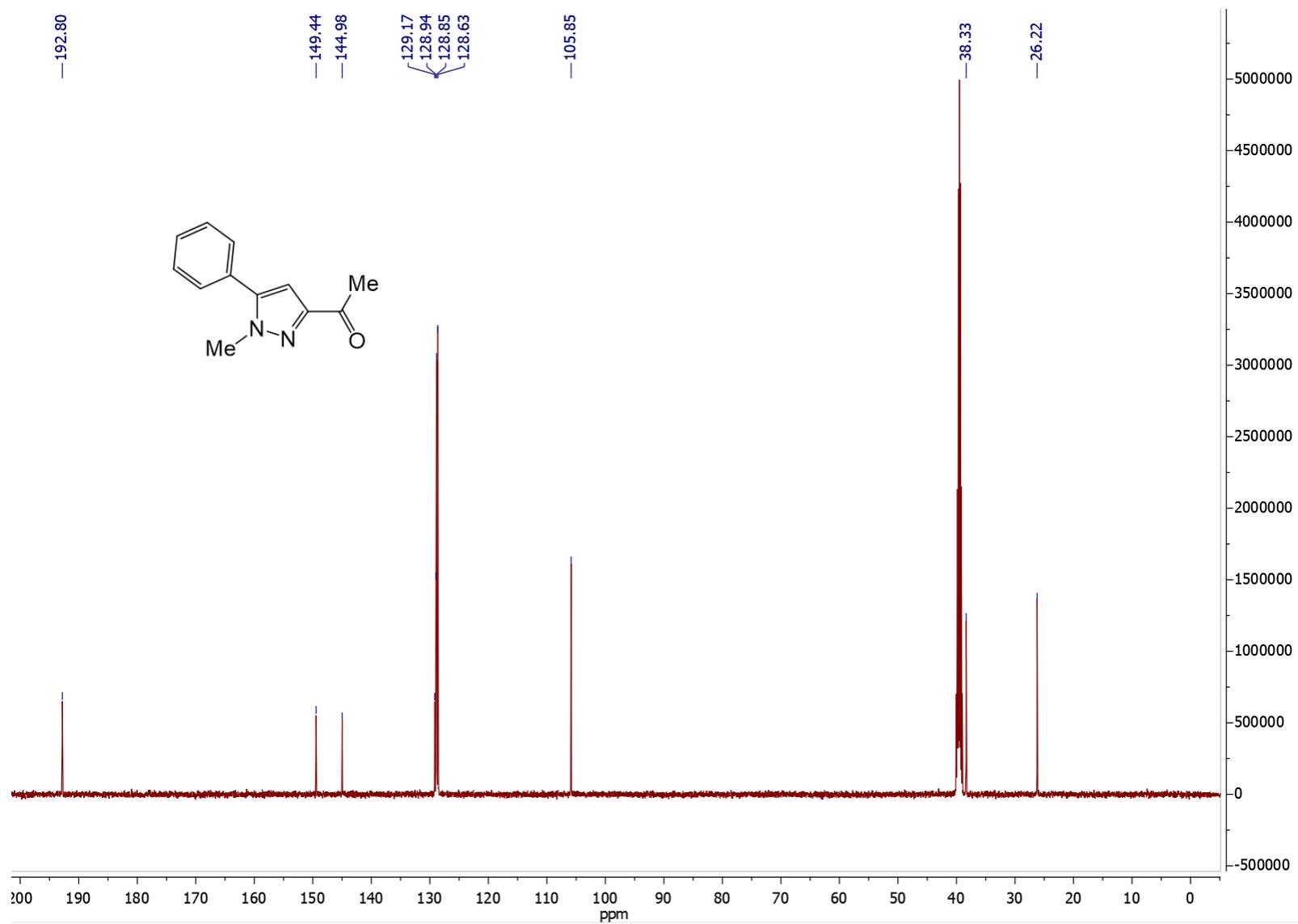


Figure S70. ¹H NMR spectrum of compound 16.

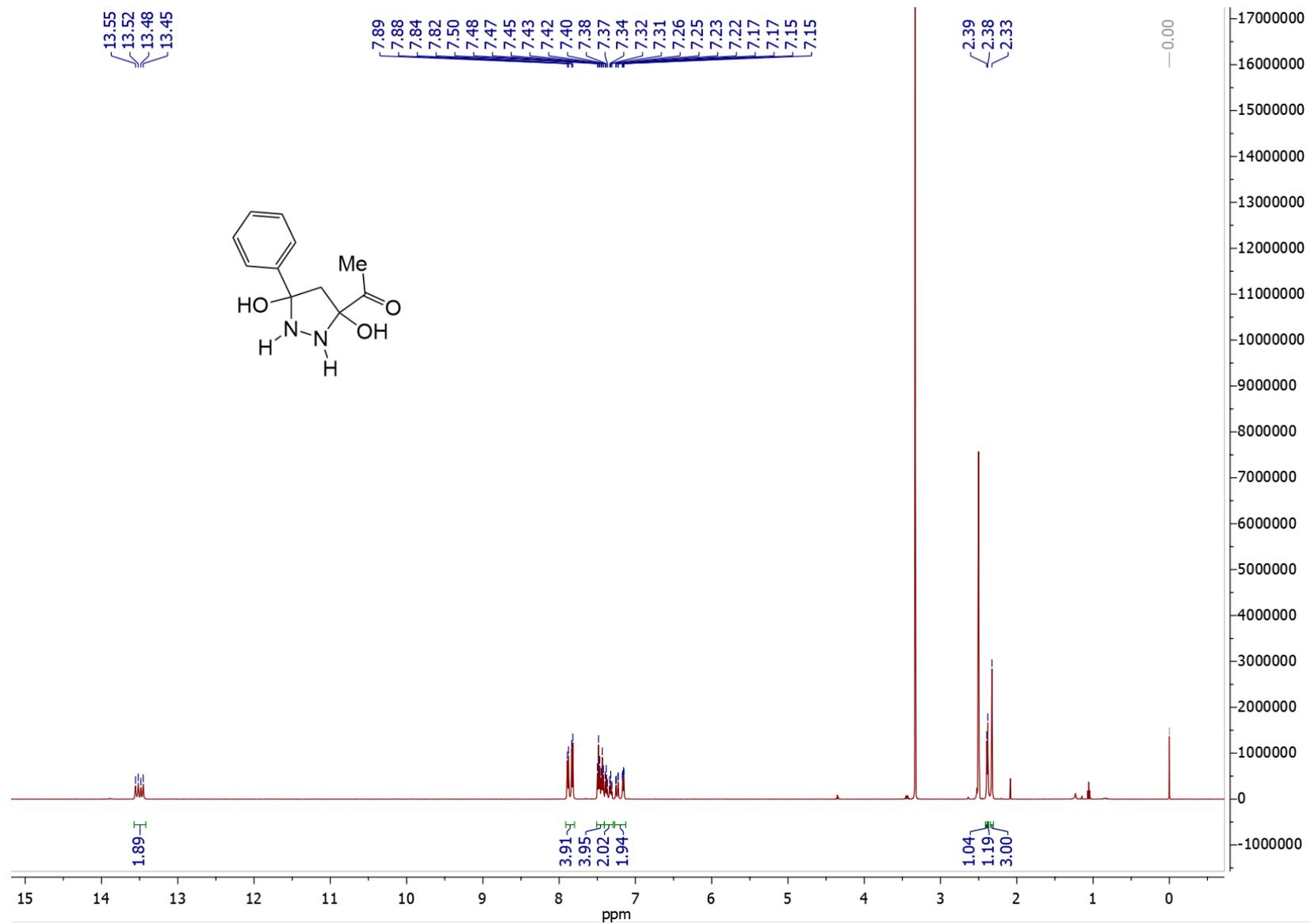


Figure S71. ¹H NMR spectrum of compound 17.

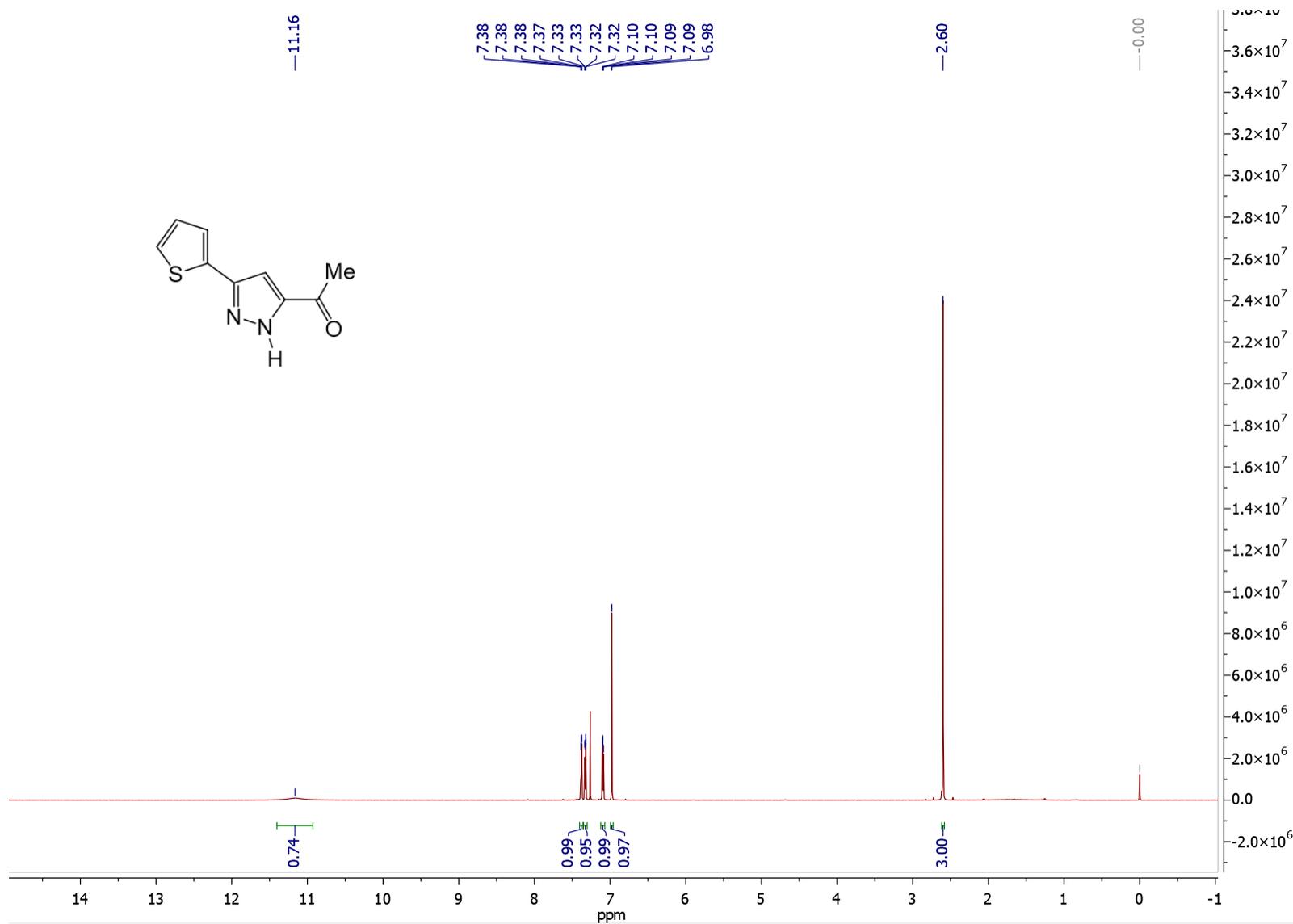


Figure S72. ¹³C NMR spectrum of compound **17**.

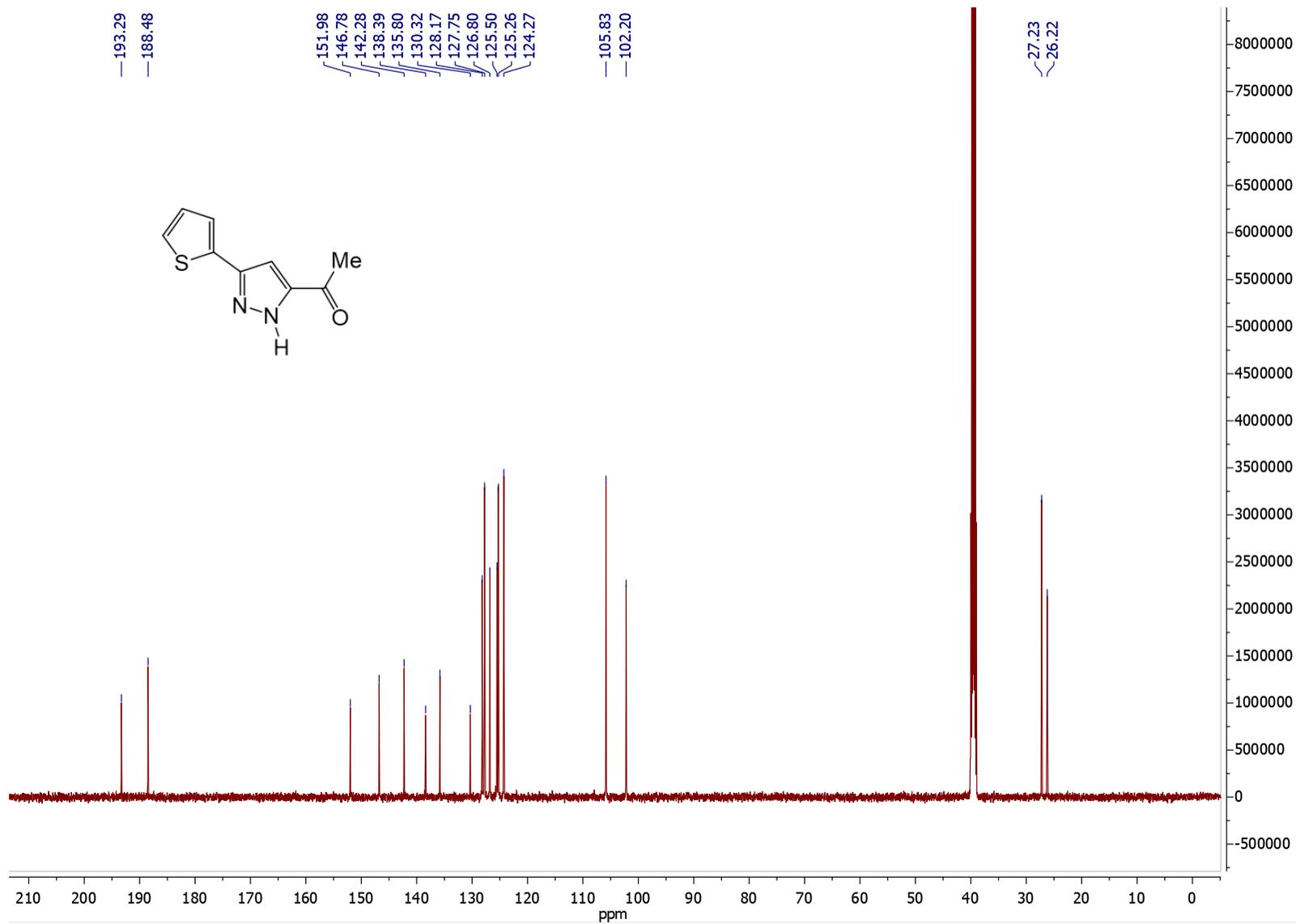


Figure S73. ¹H NMR spectrum of compound **18a**.

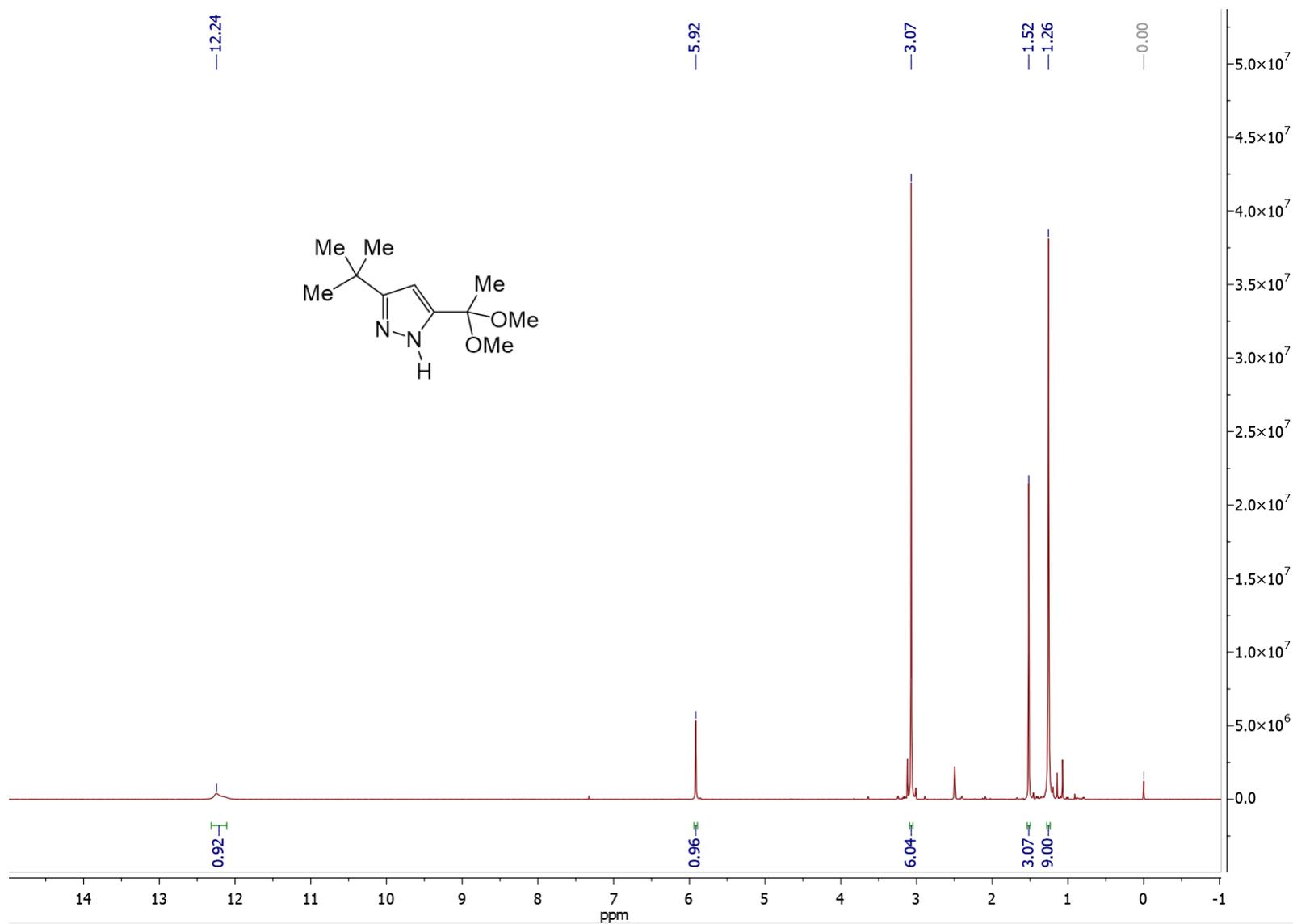


Figure S74. ^{13}C NMR spectrum of compound **18a**.

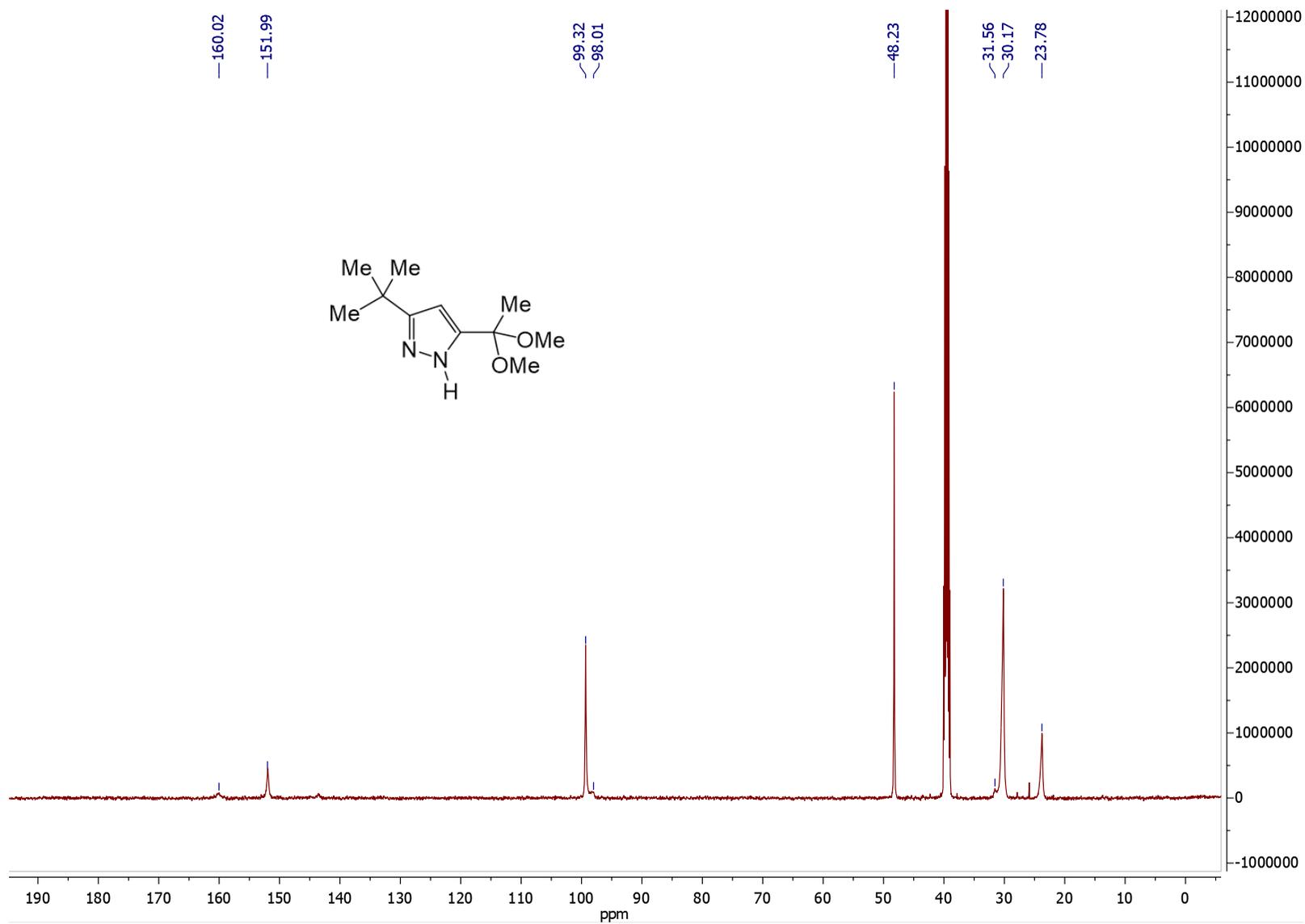


Figure S75. ¹H NMR spectrum of compound **18b**.

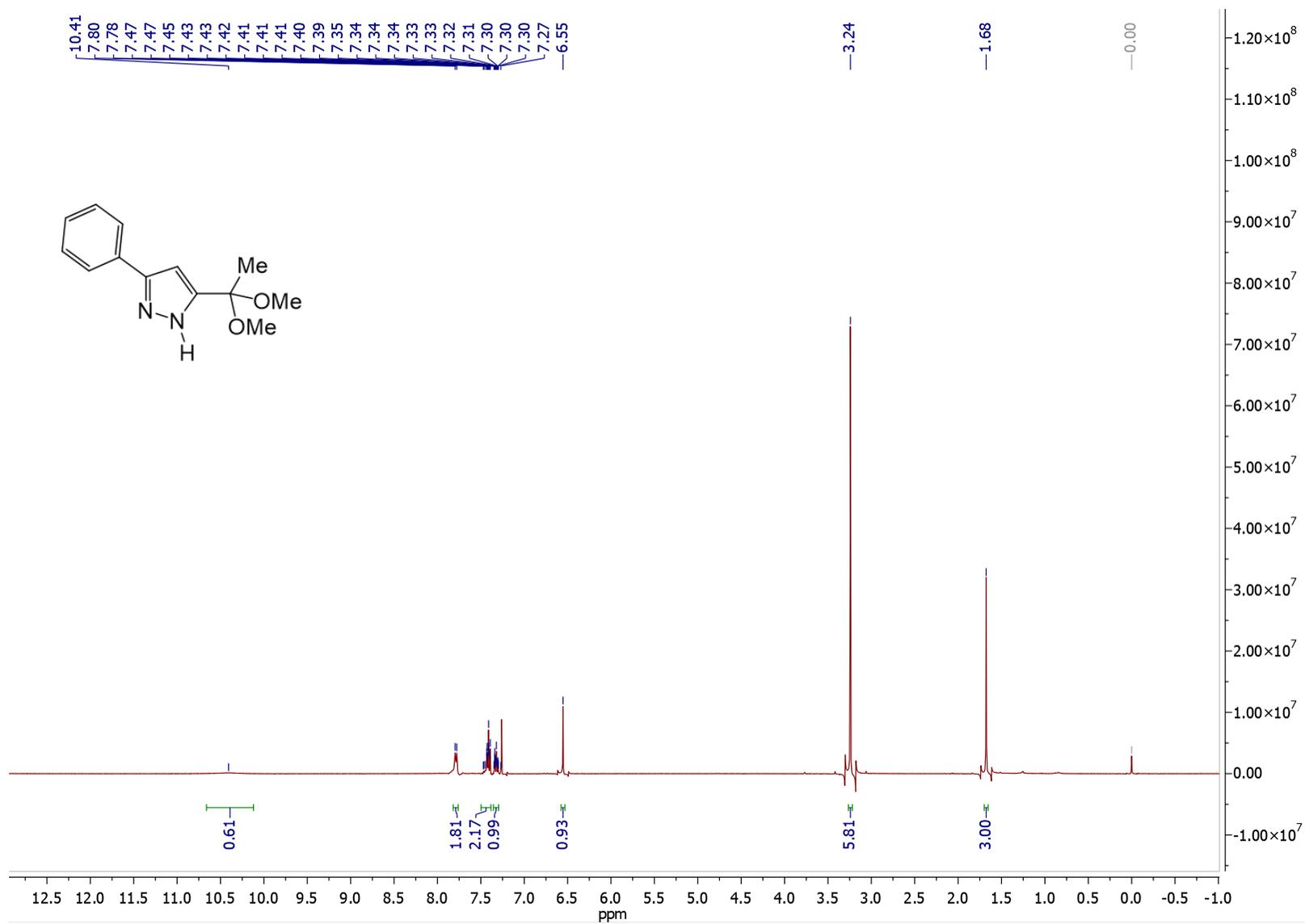


Figure S76. ^{13}C NMR spectrum of compound **18b**.

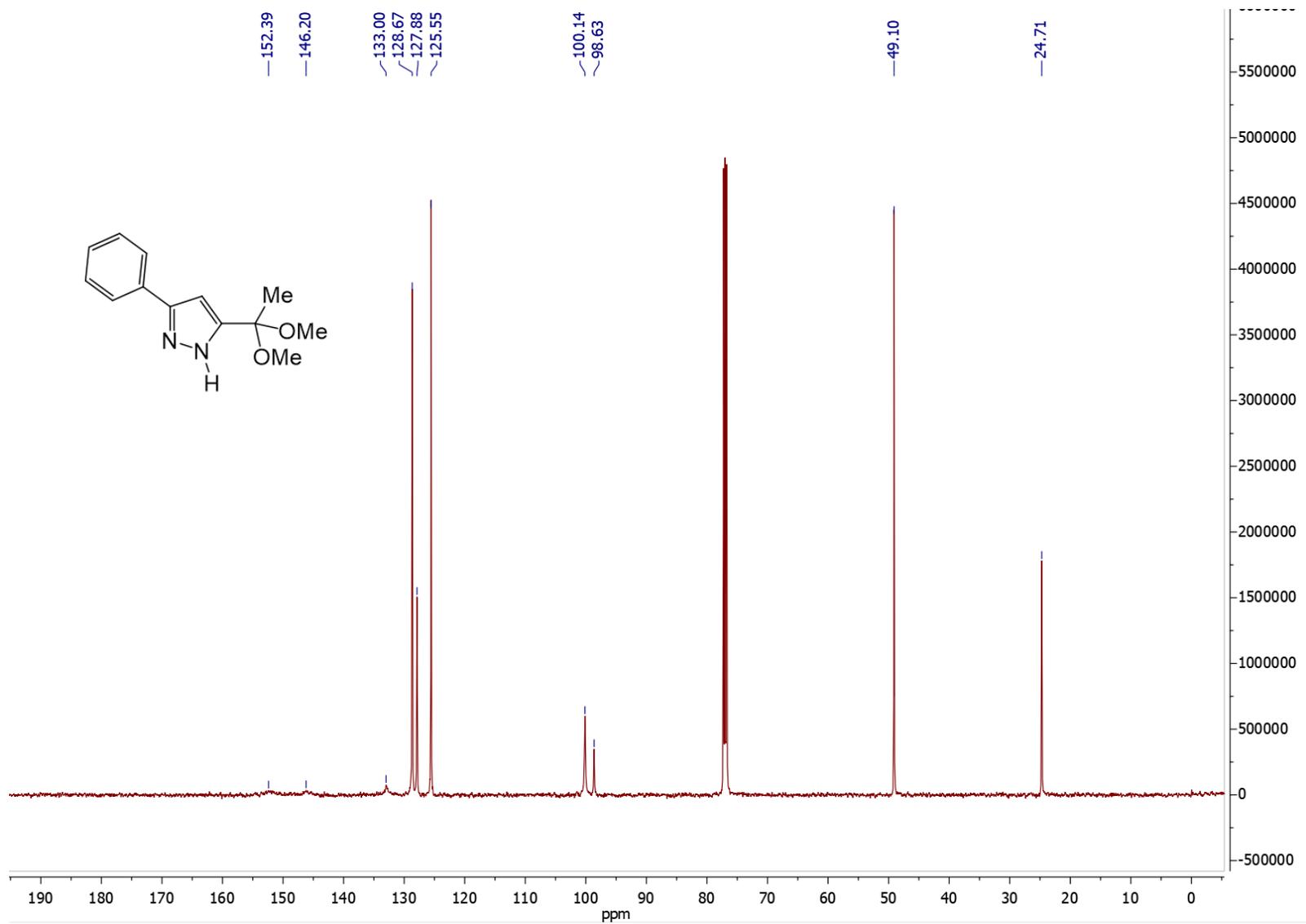


Figure S77. ¹H NMR spectrum of compound **18c**.

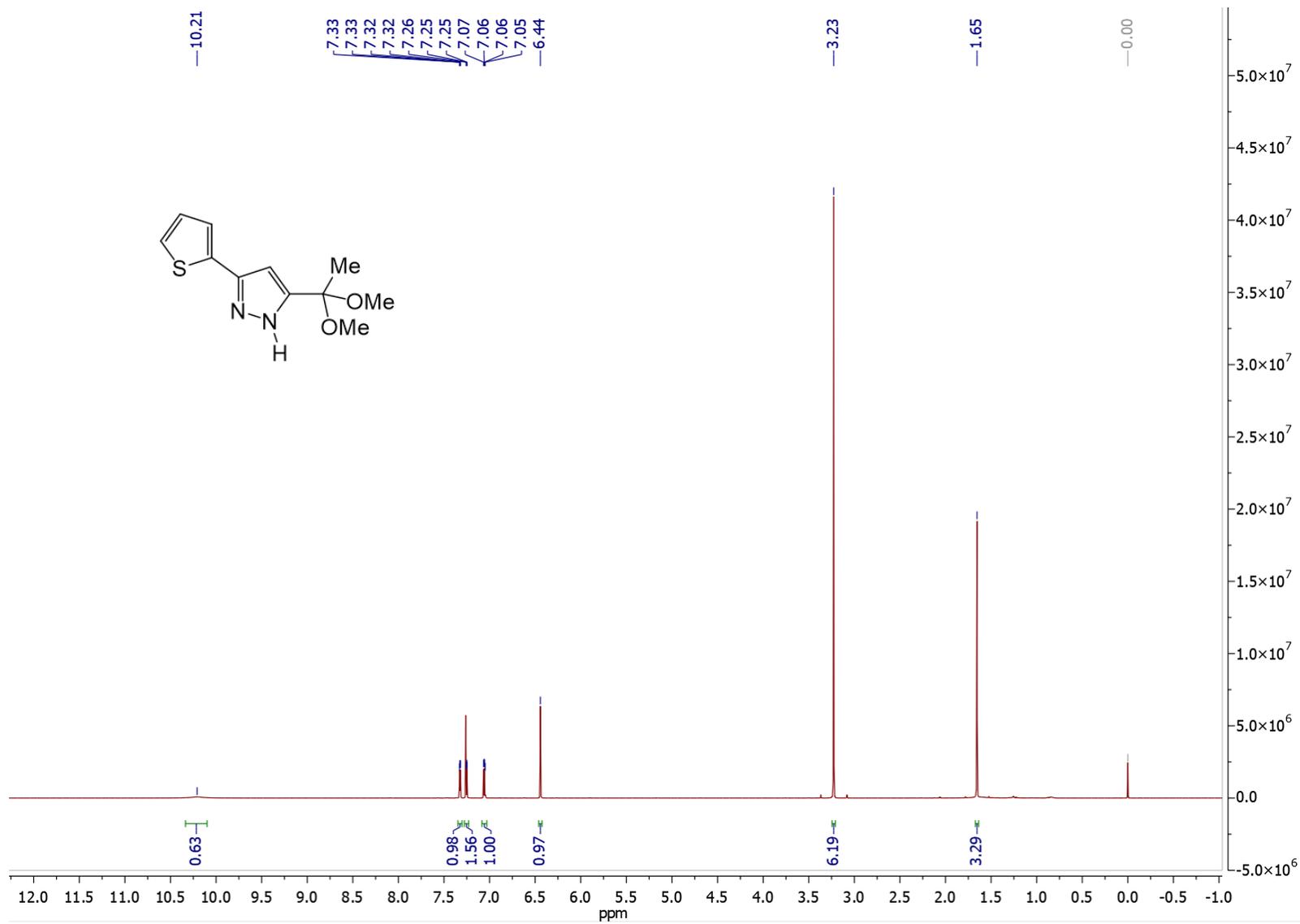


Figure S78. ^{13}C NMR spectrum of compound **18c**.

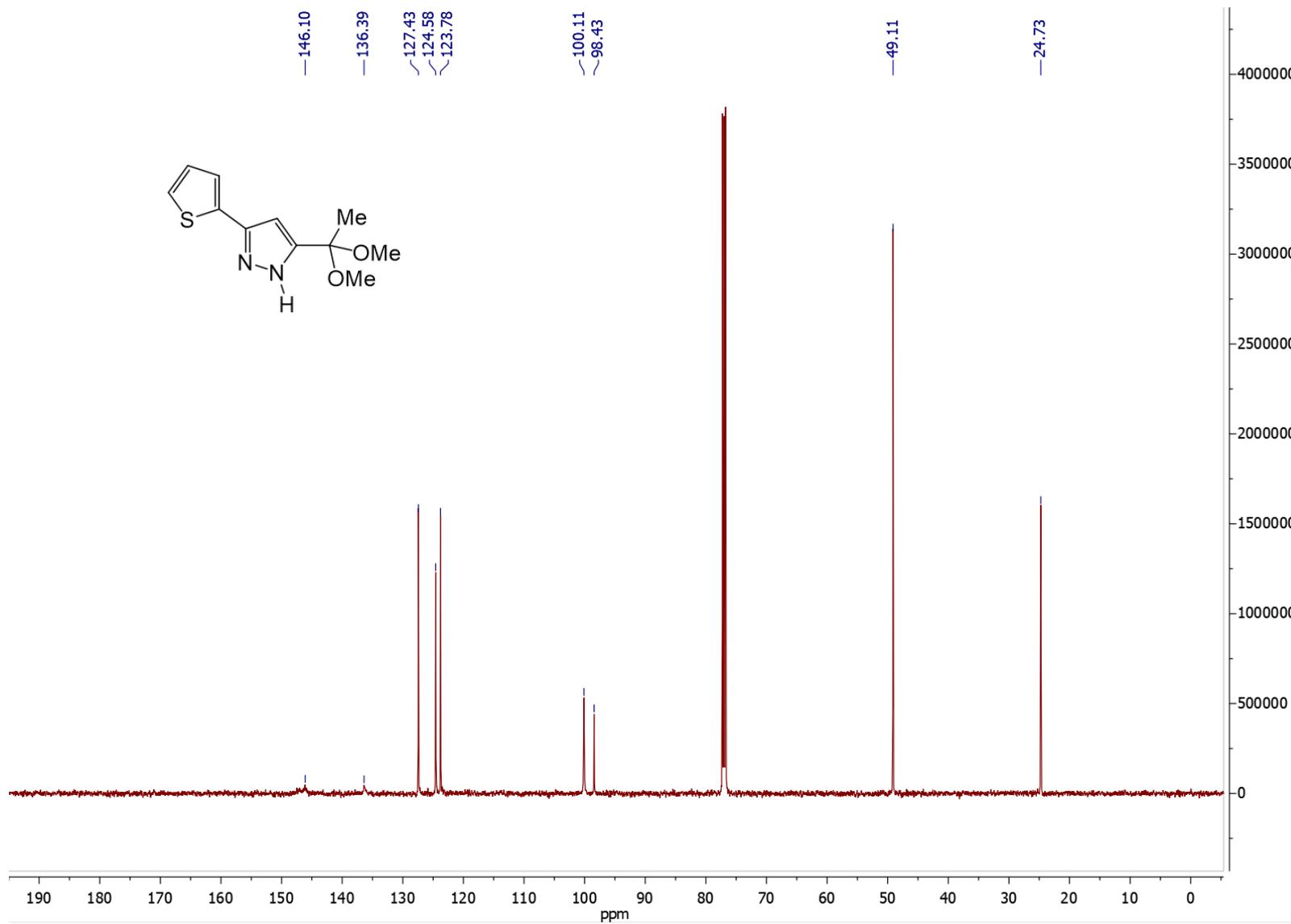


Figure S79. ¹H NMR spectrum of compound **19a**.

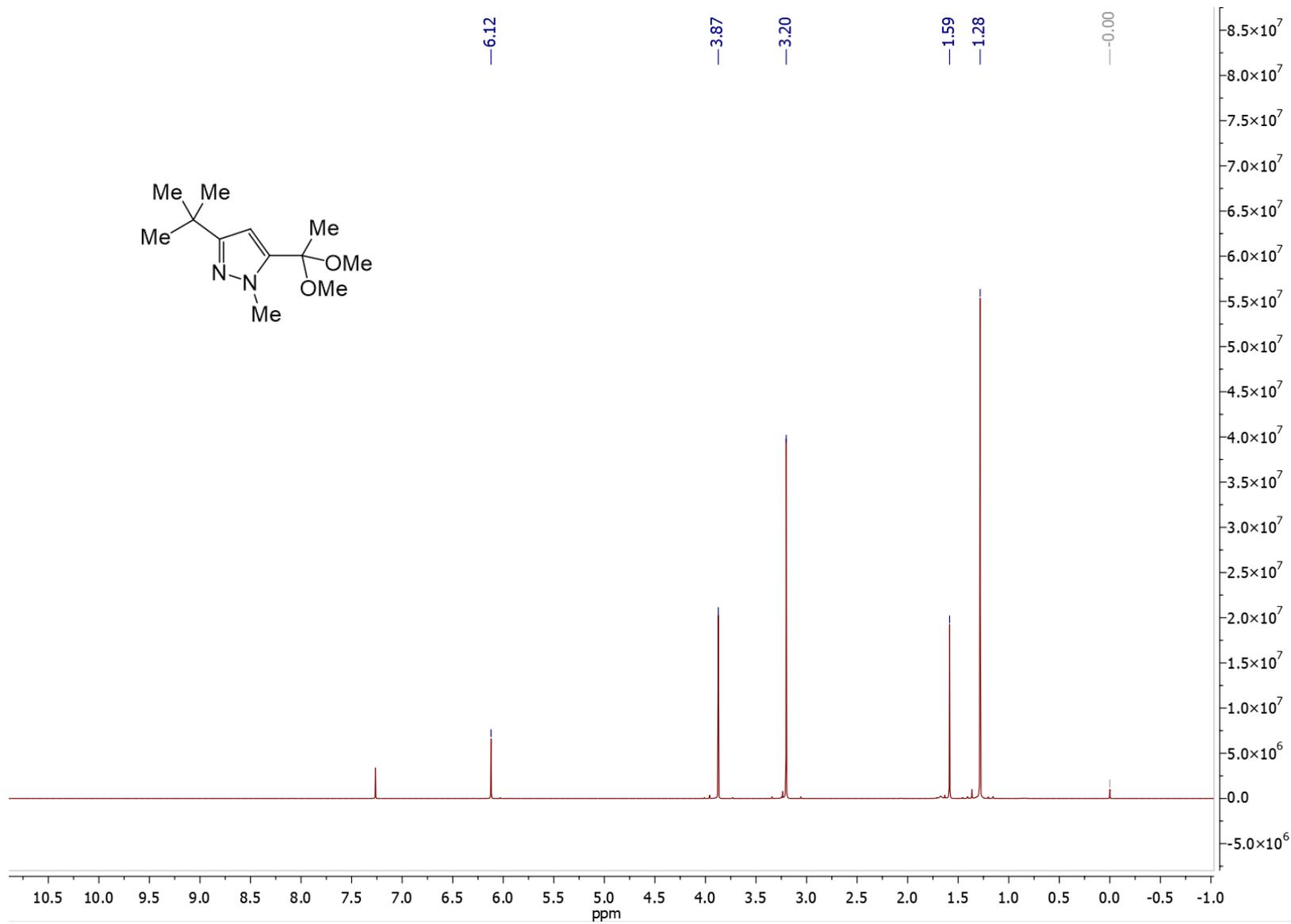


Figure S80. ^{13}C NMR spectrum of compound **19a**.

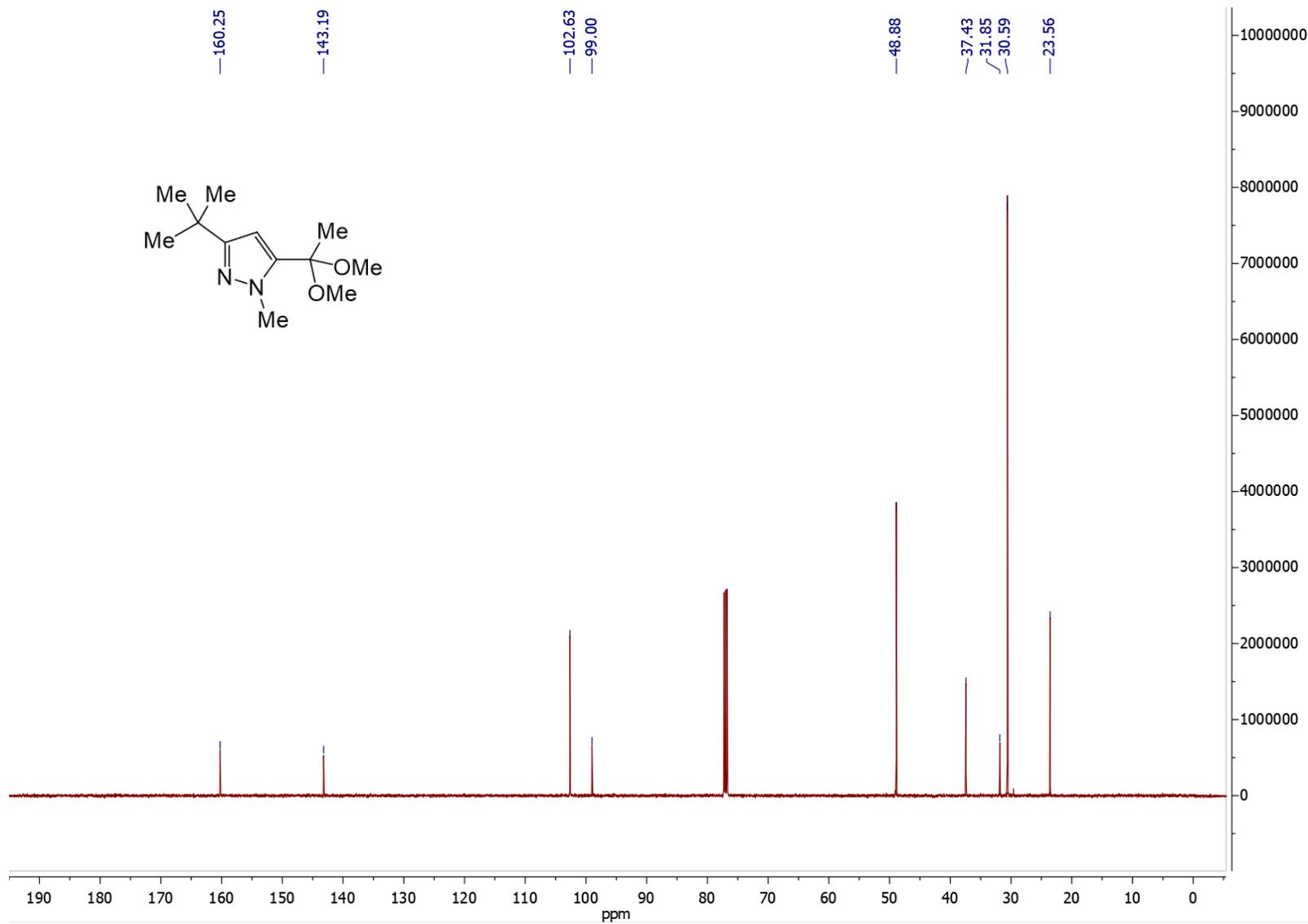


Figure S81. ¹H NMR spectrum of compound **19b**.

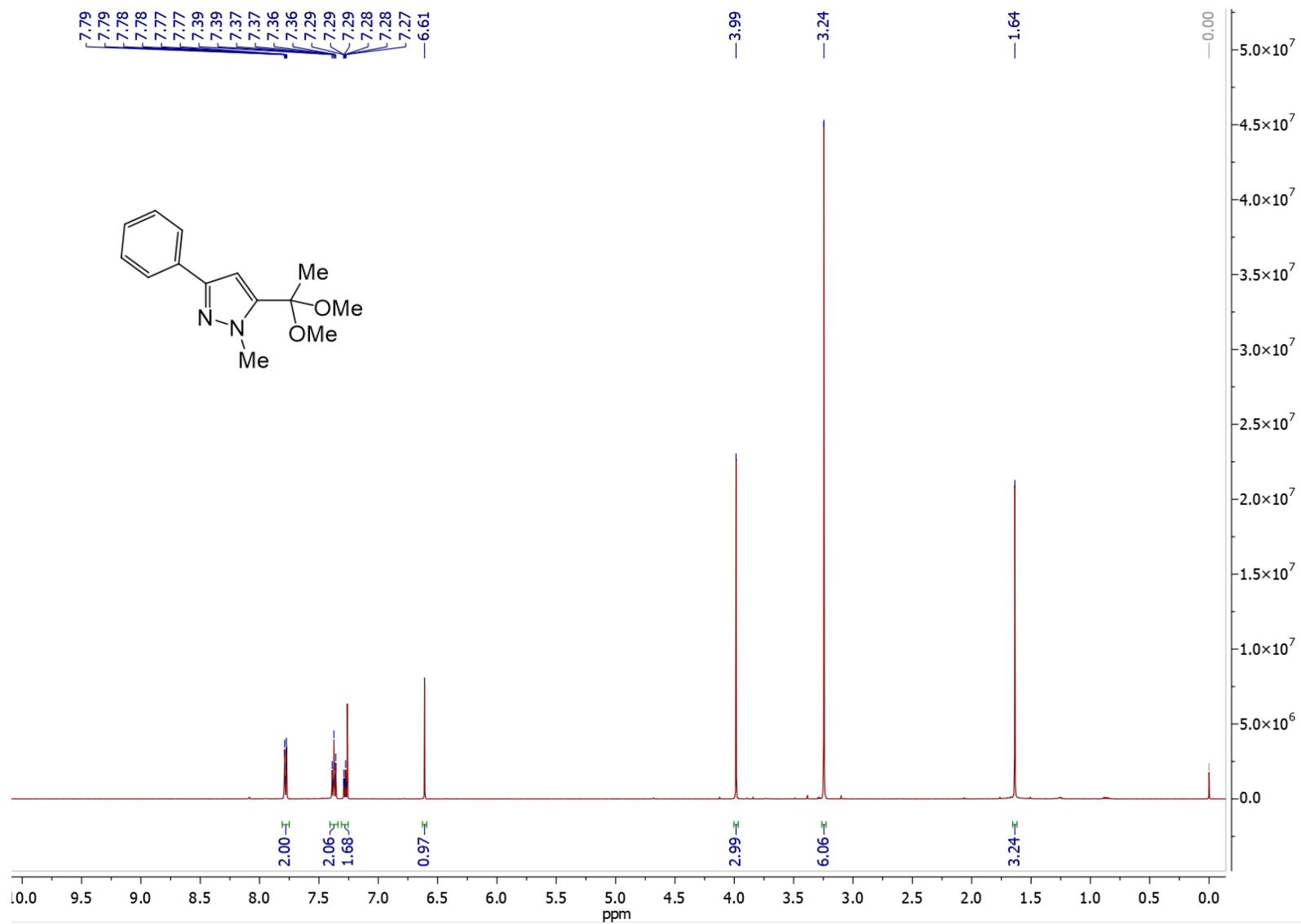


Figure S82. ^{13}C NMR spectrum of compound **19b**.

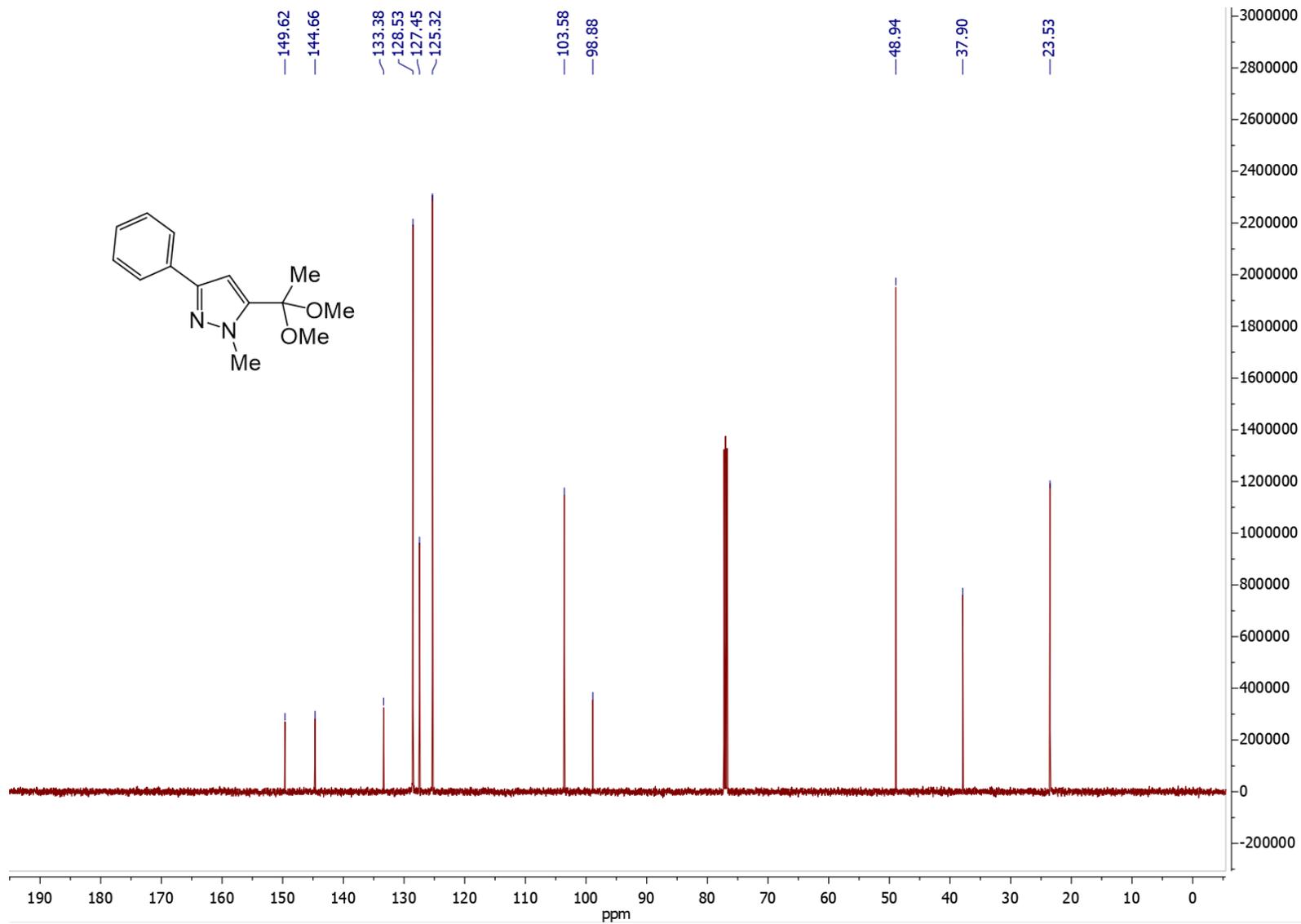


Figure S83. ¹H NMR spectrum of compound **19c**.

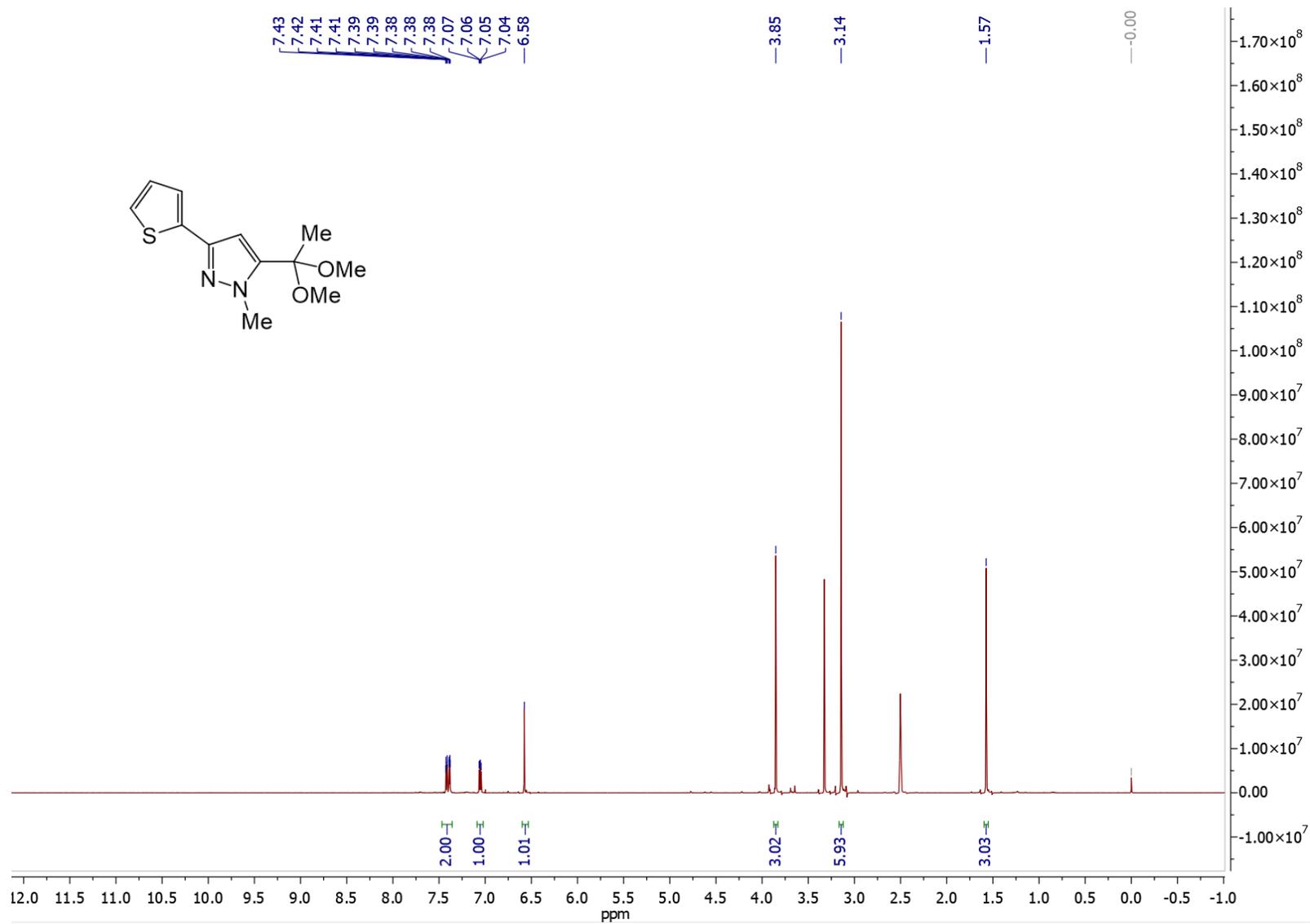


Figure S84. ^{13}C NMR spectrum of compound **19c**.

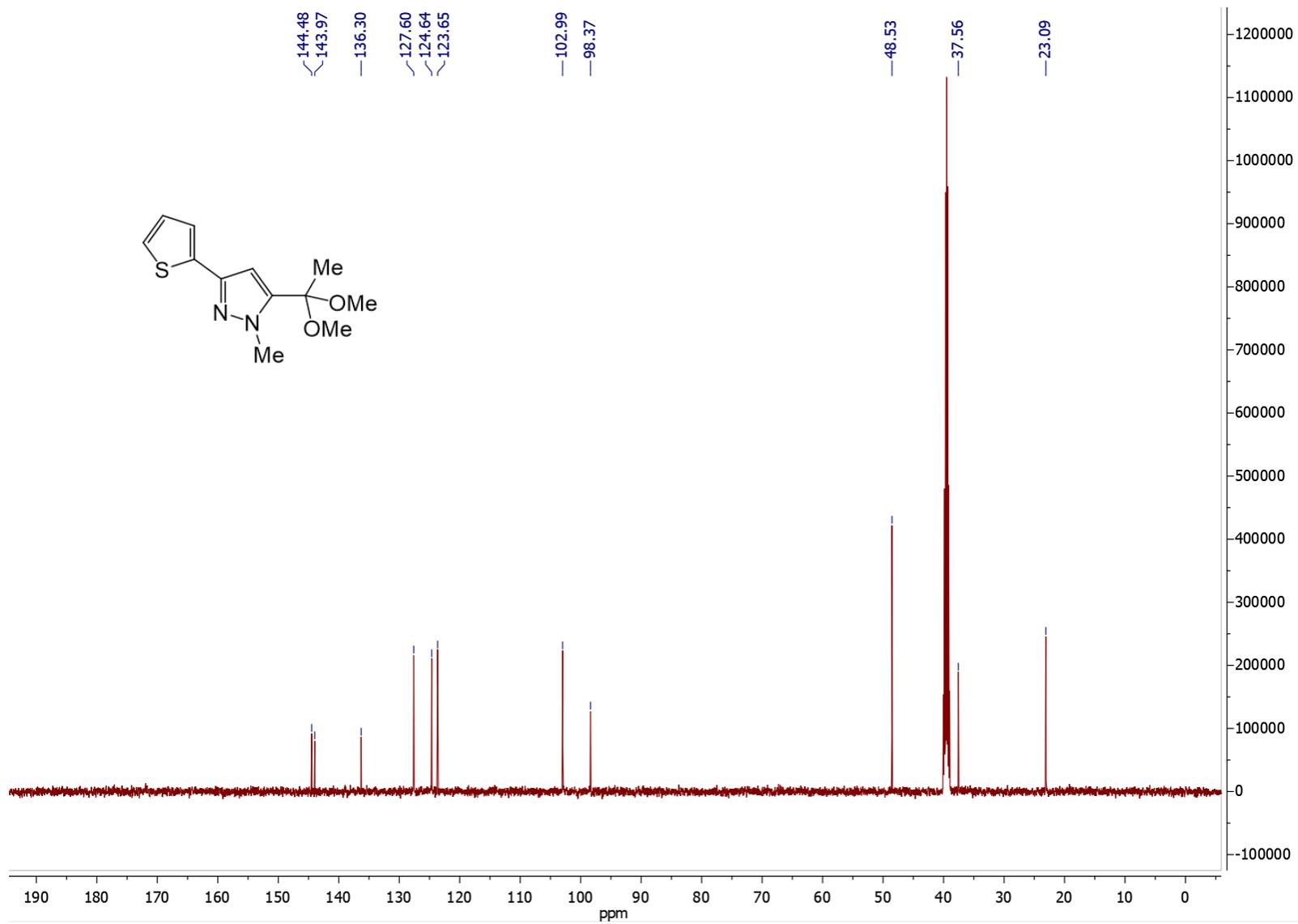


Figure S85. ¹H NMR spectrum of compound 20a.

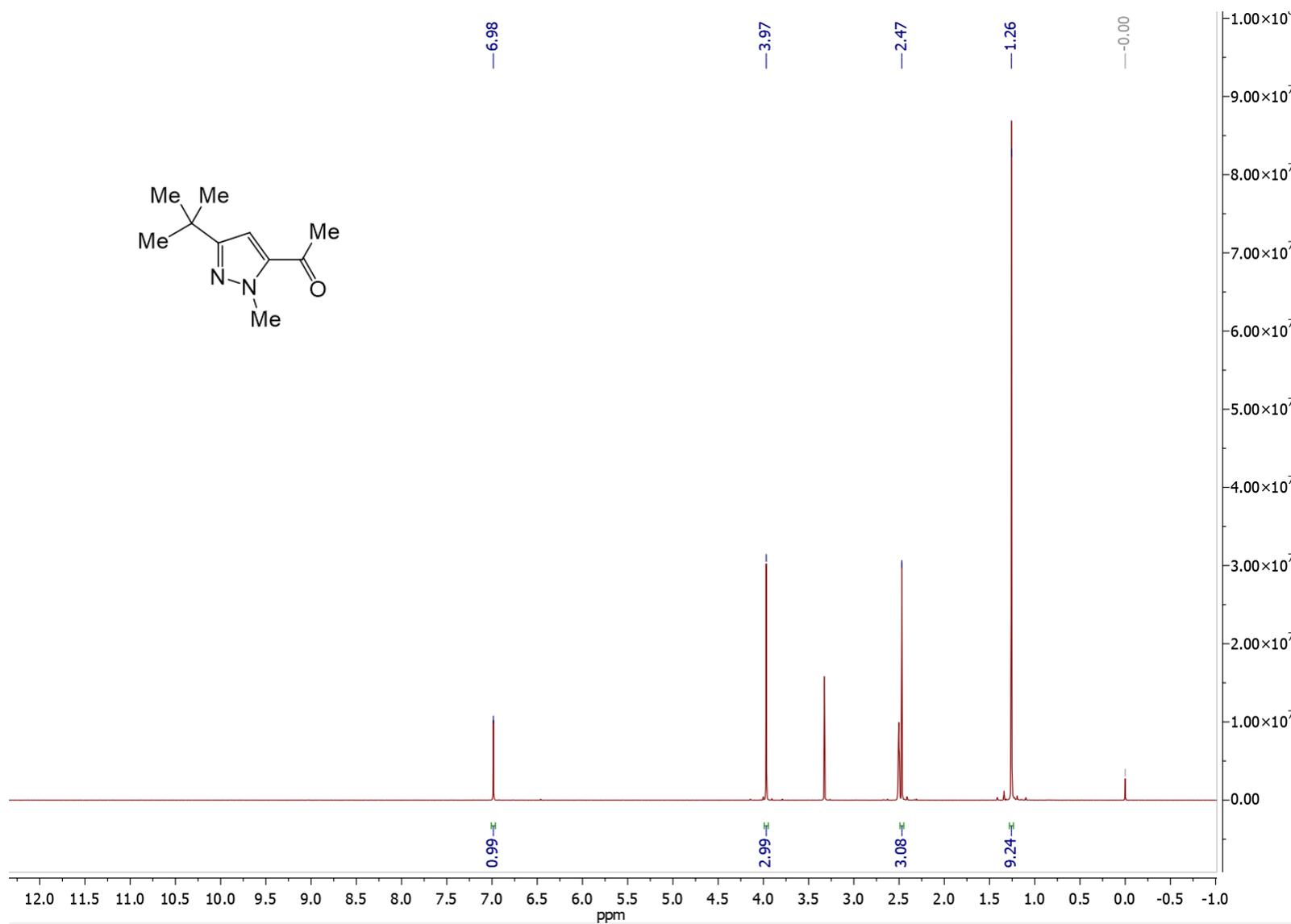


Figure S86 ^{13}C NMR spectrum of compound **20a**.

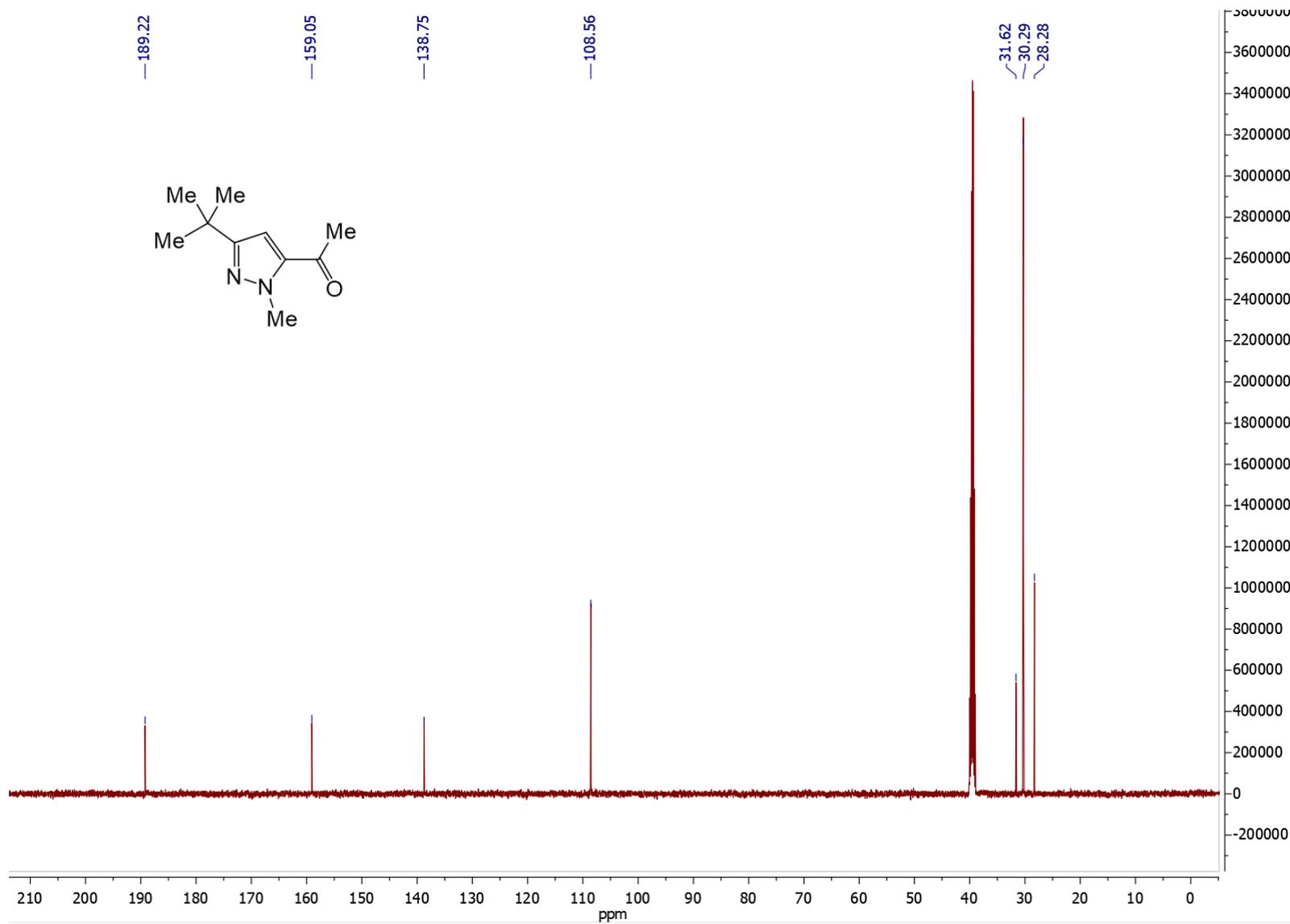


Figure S88. ^{13}C NMR spectrum of compound **20b**.

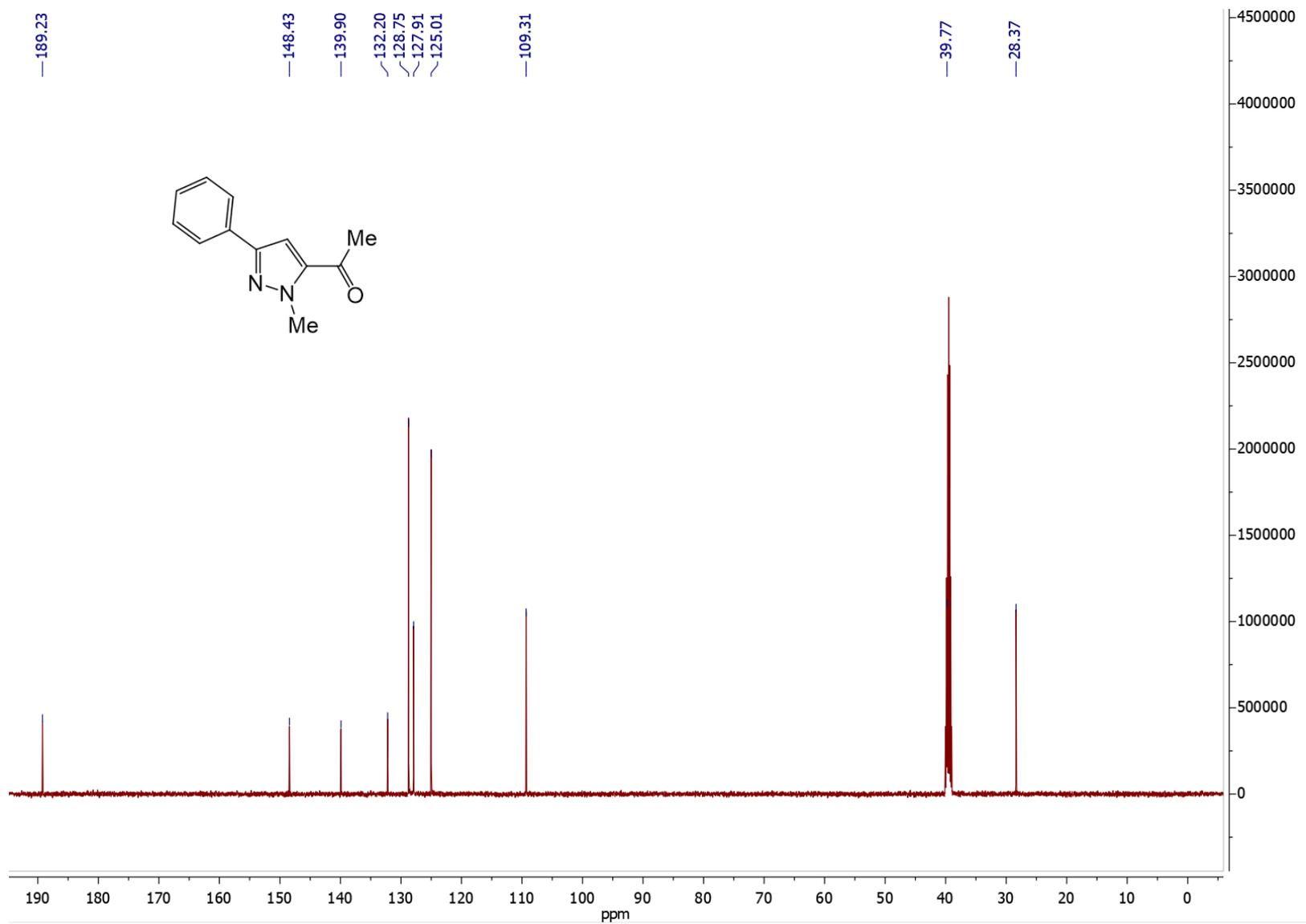


Figure S89. ¹H NMR spectrum of compound 20c.

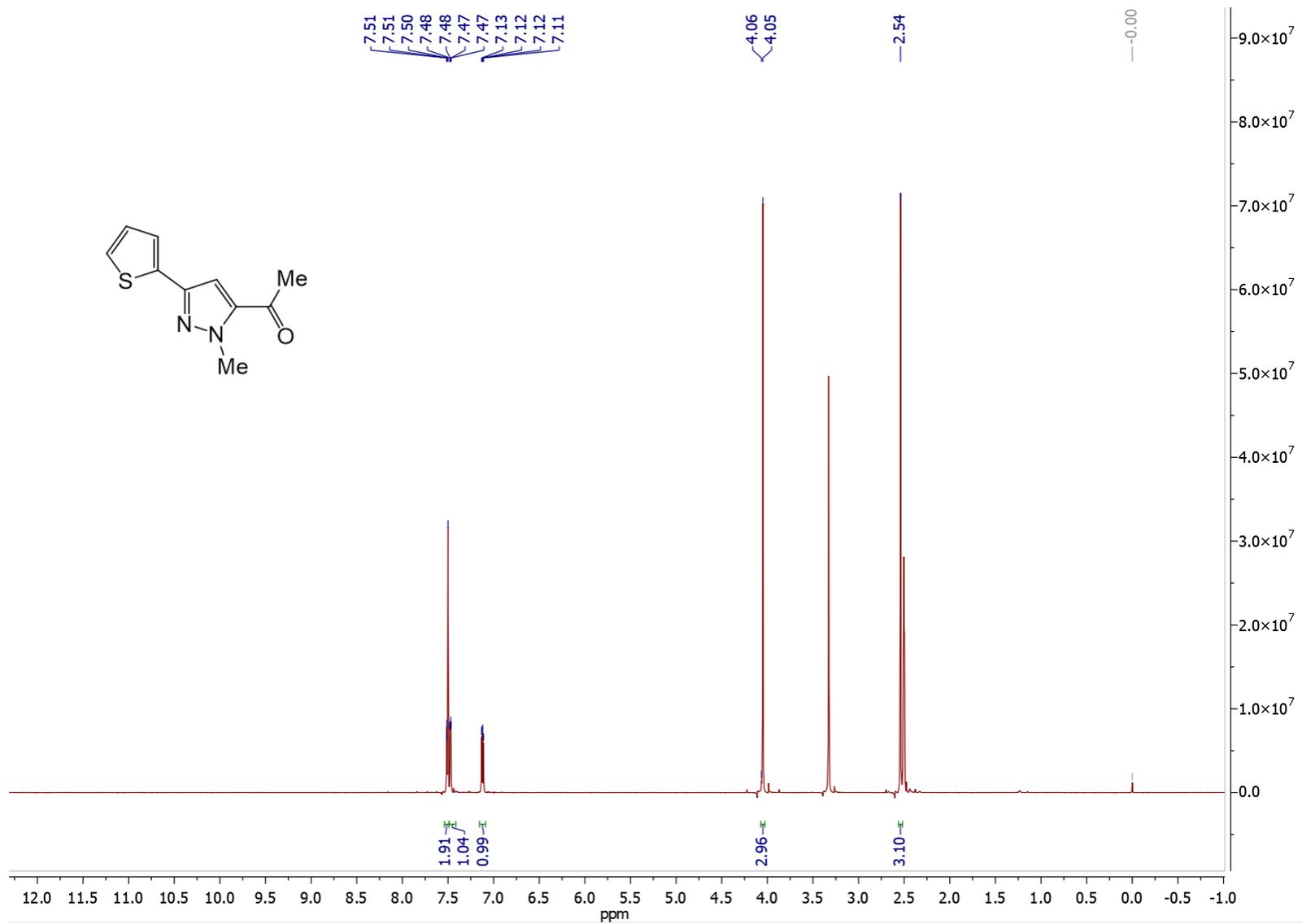


Figure S90. ^{13}C NMR spectrum of compound **20c**.

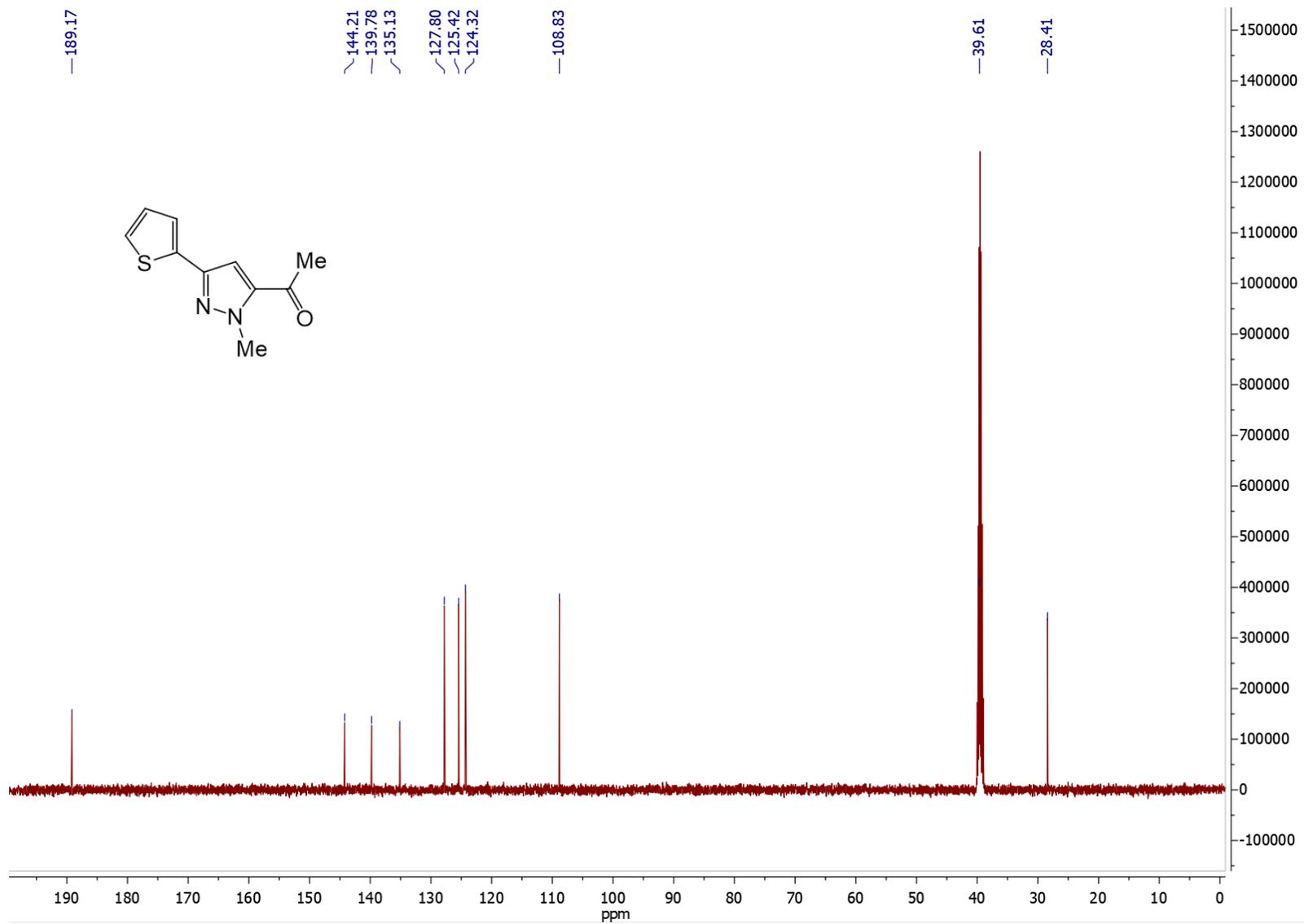


Figure S91. ¹H NMR spectrum of compound **21a**.

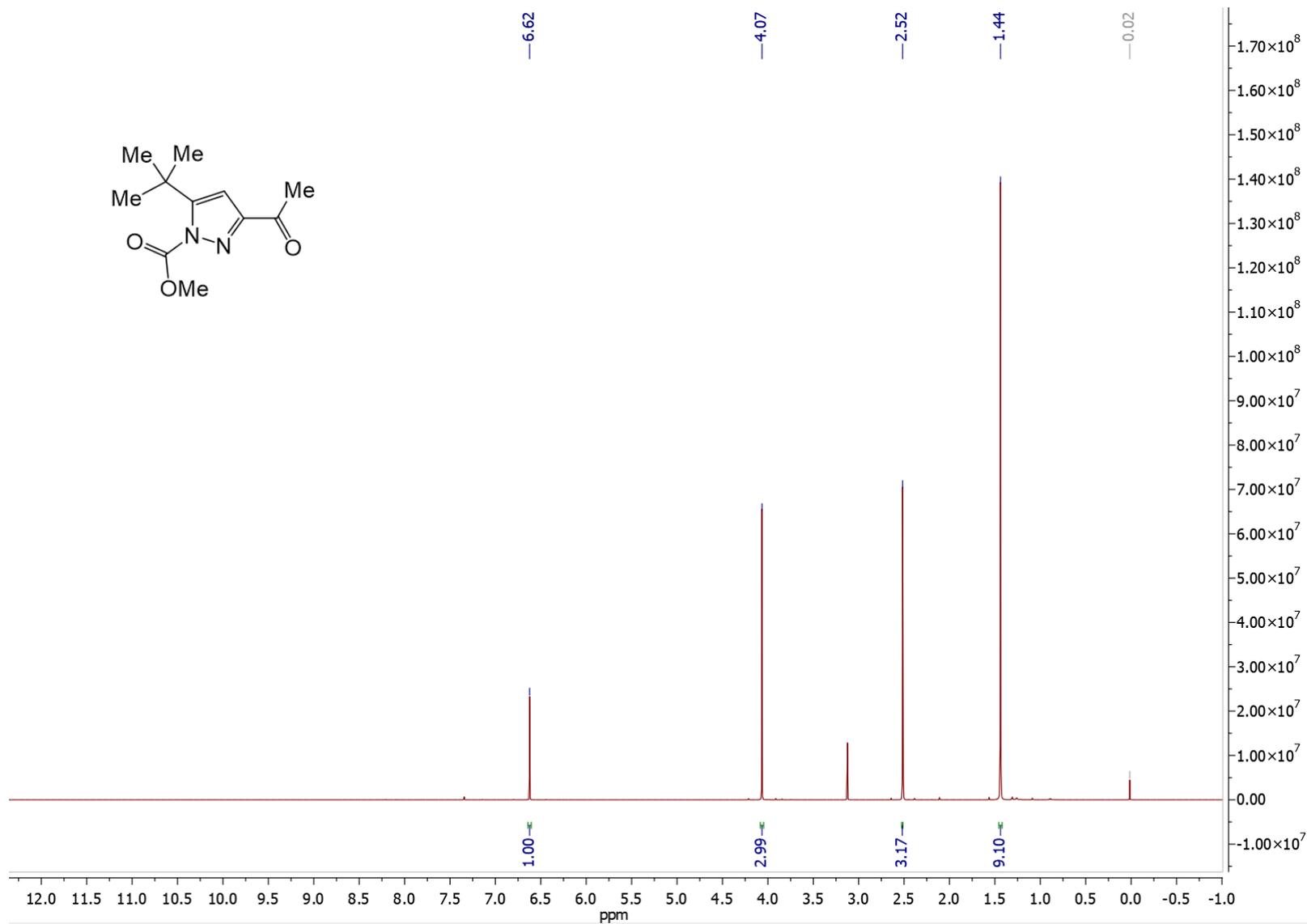


Figure S92. ¹³C NMR spectrum of compound **21a**.

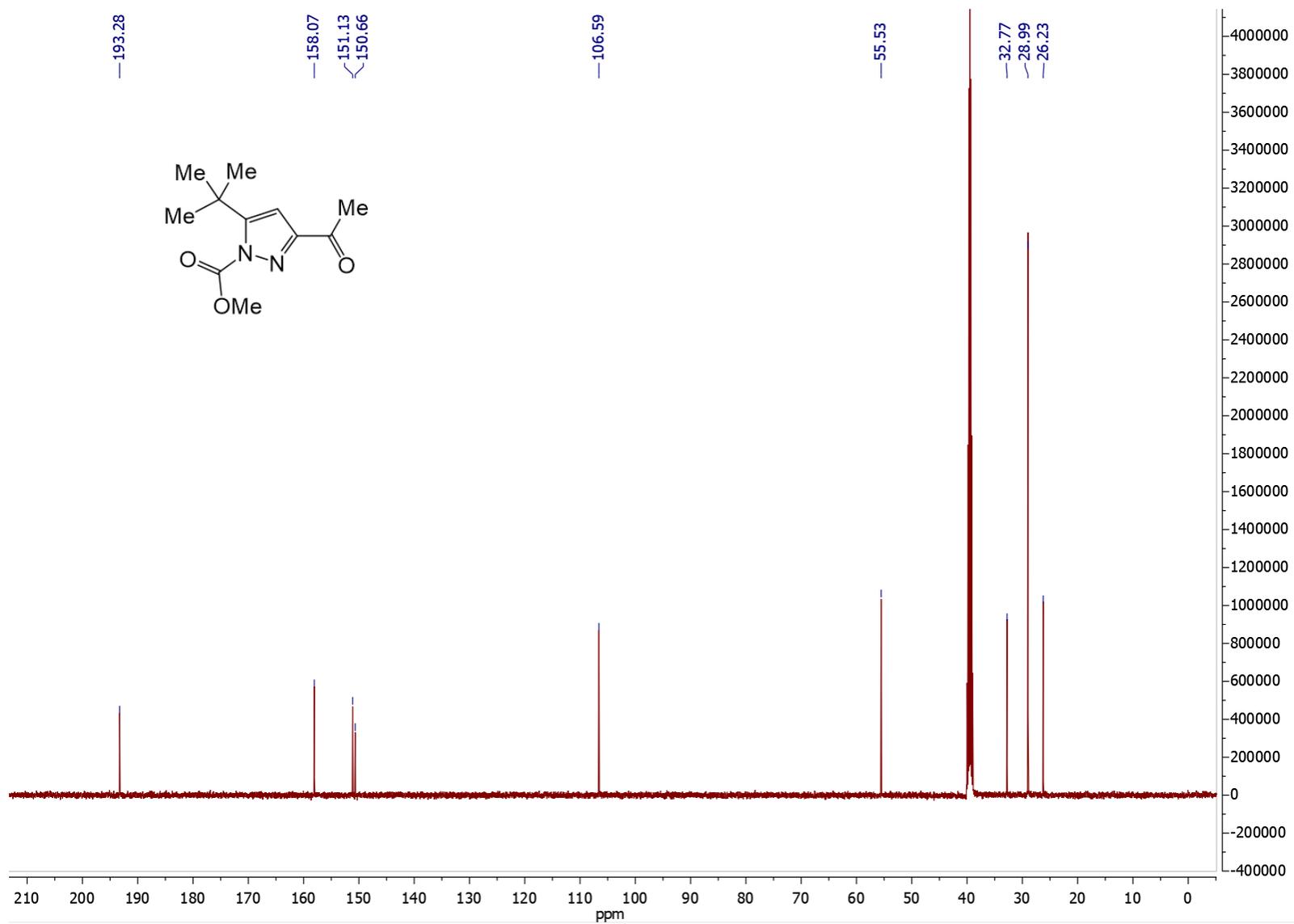


Figure S93. ¹H NMR spectrum of compound **21b**.

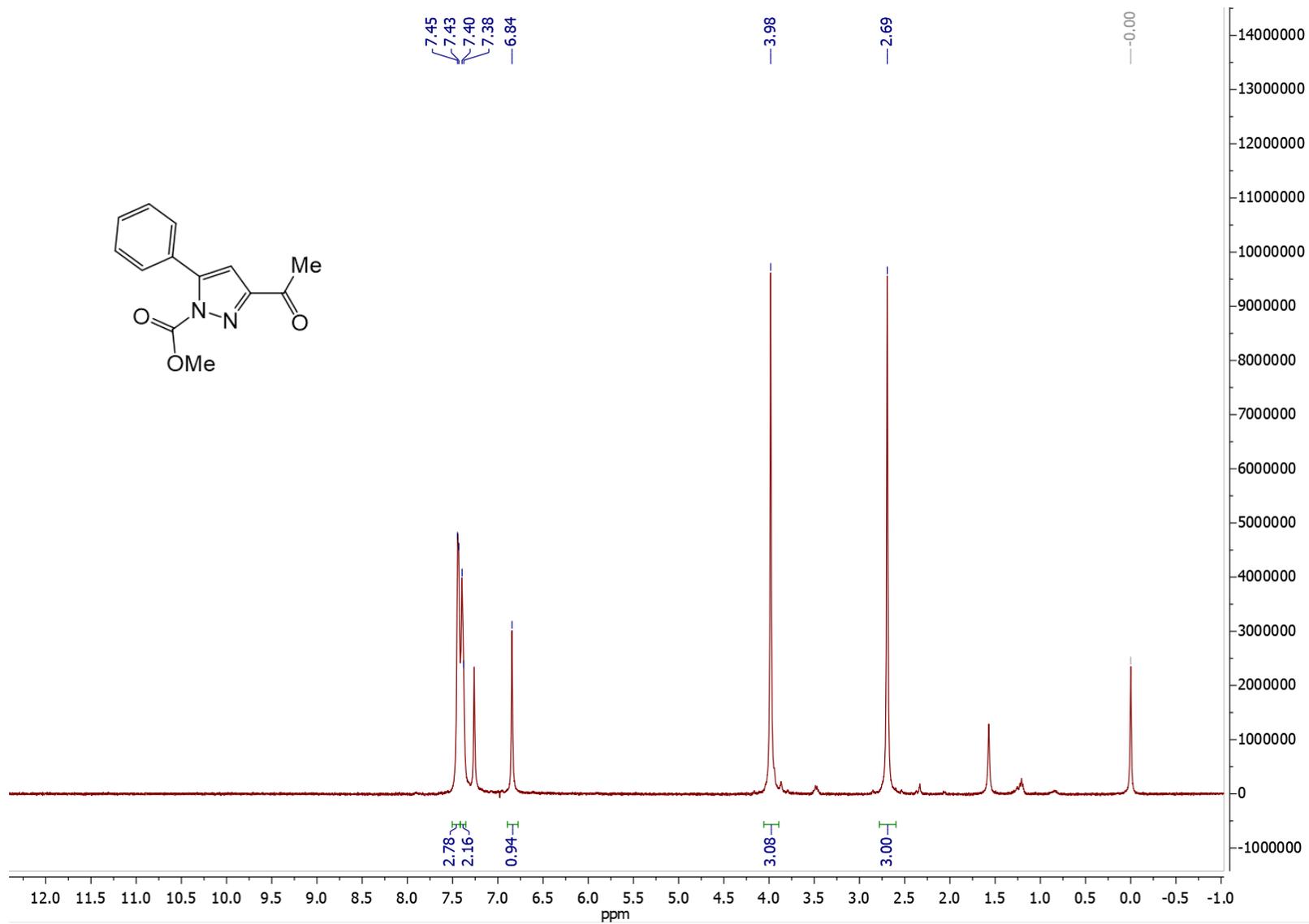


Figure S94. ^{13}C NMR spectrum of compound **21b**.

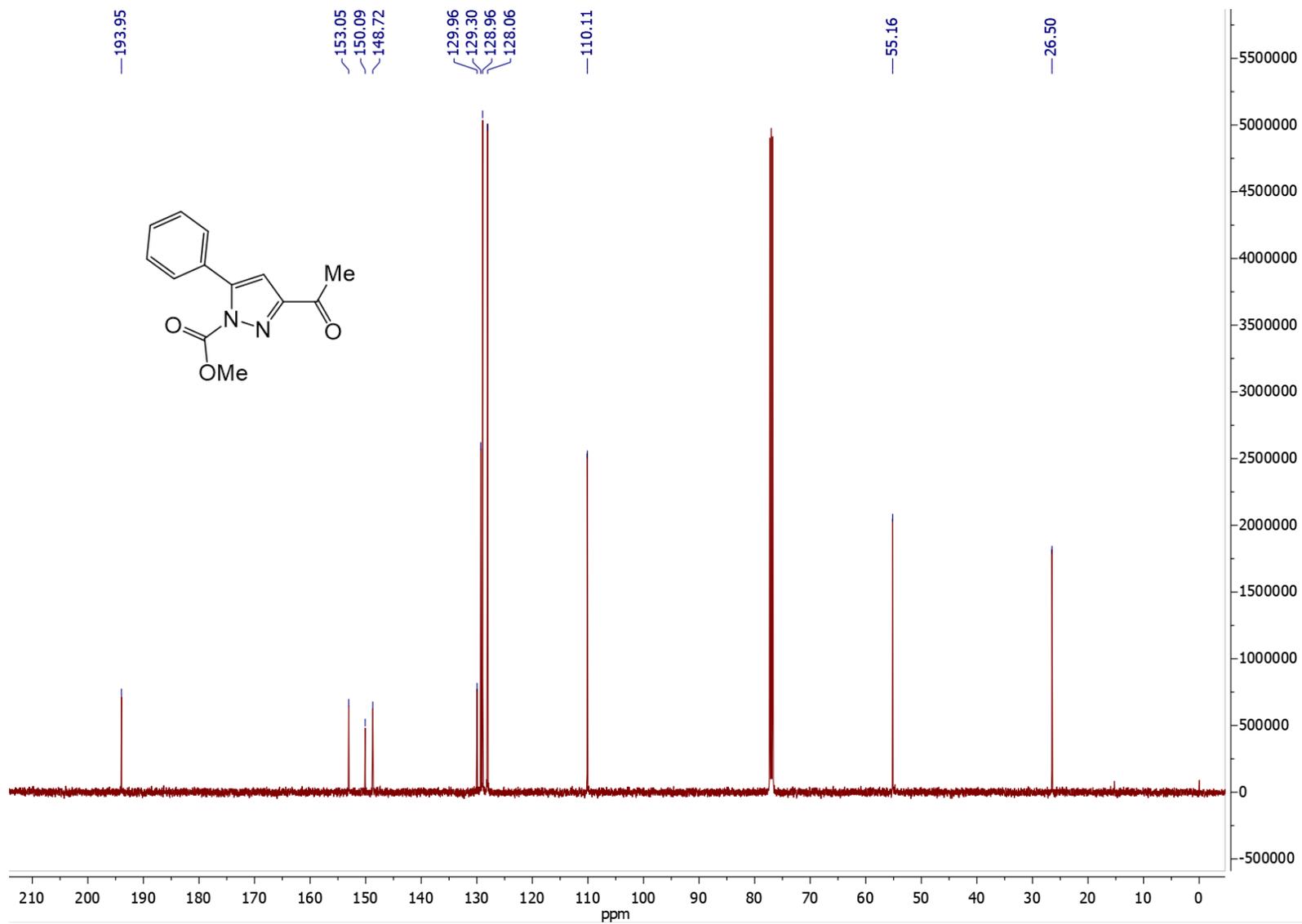


Figure S95. ¹H NMR spectrum of compound **21c**.

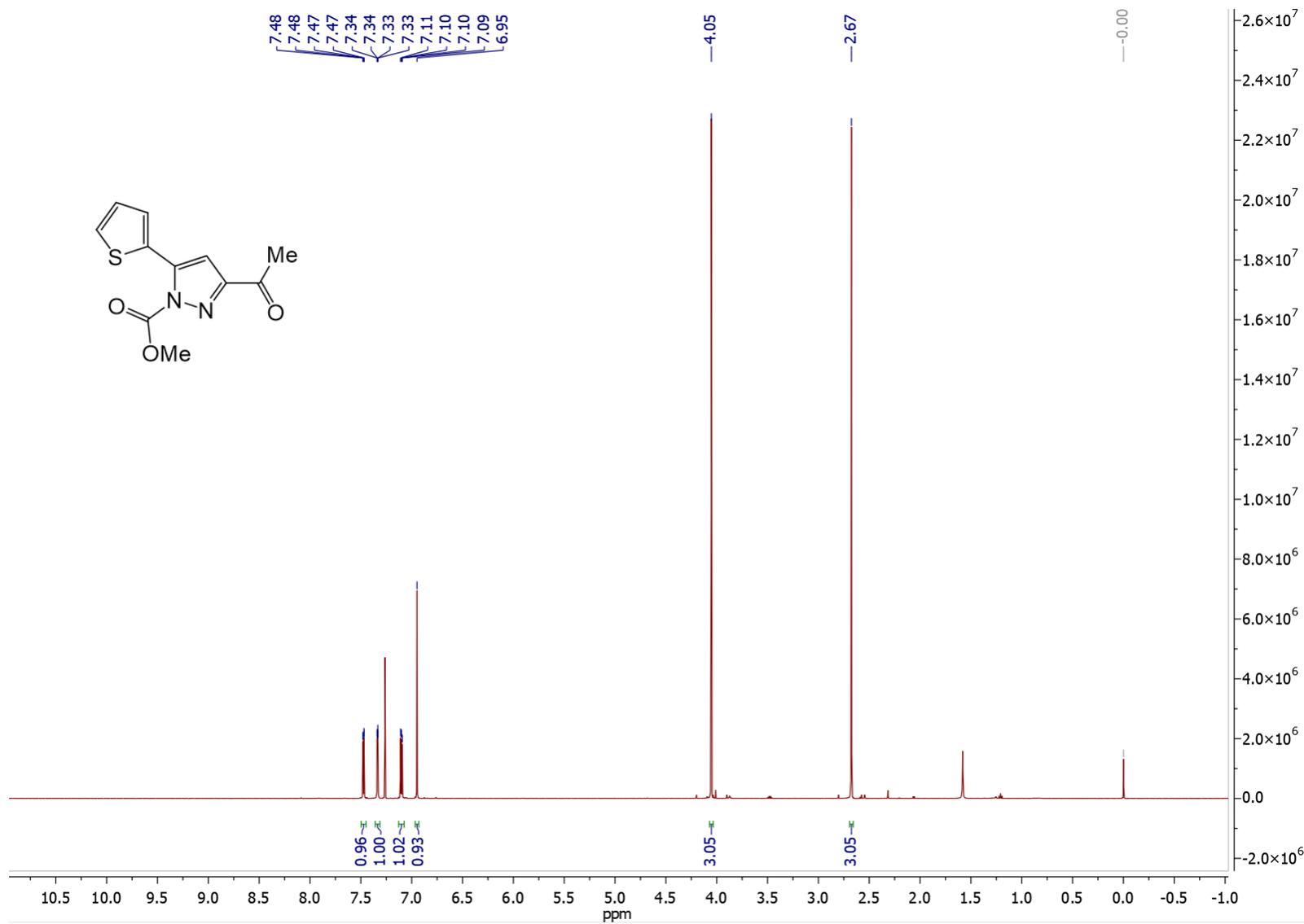


Figure S96. ^{13}C NMR spectrum of compound **21c**.

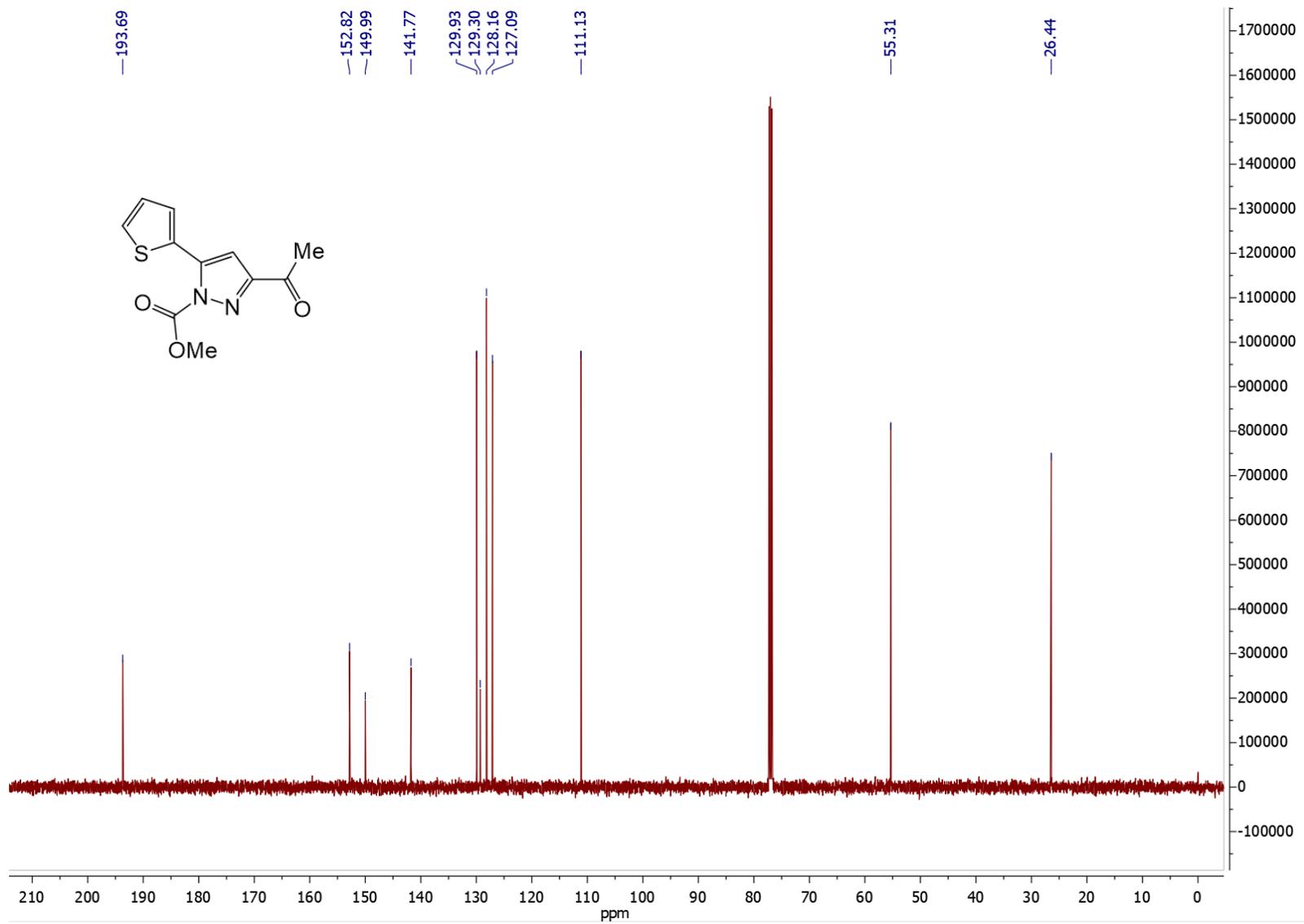


Figure S97. ¹H NMR spectrum of compound **22**.

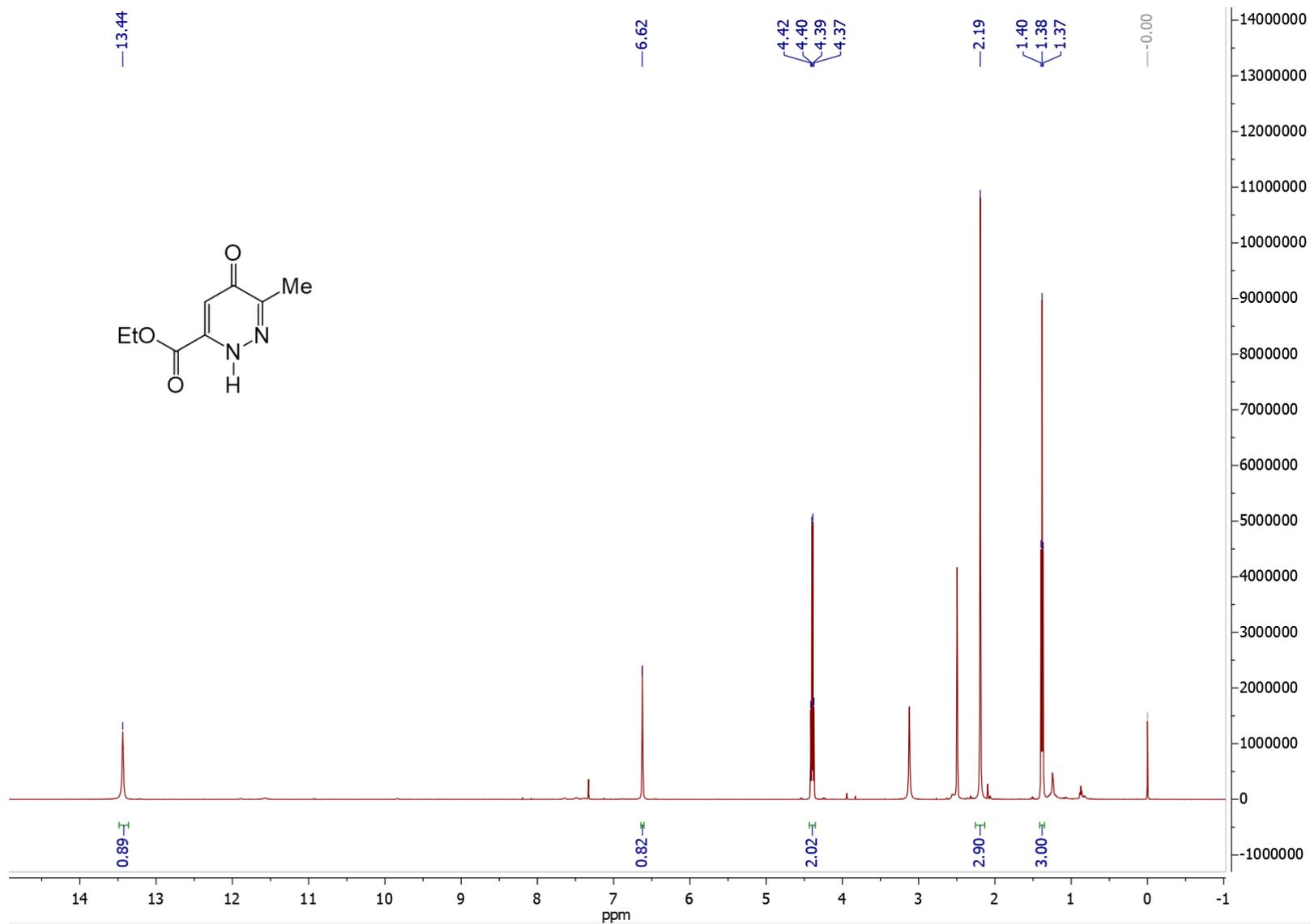
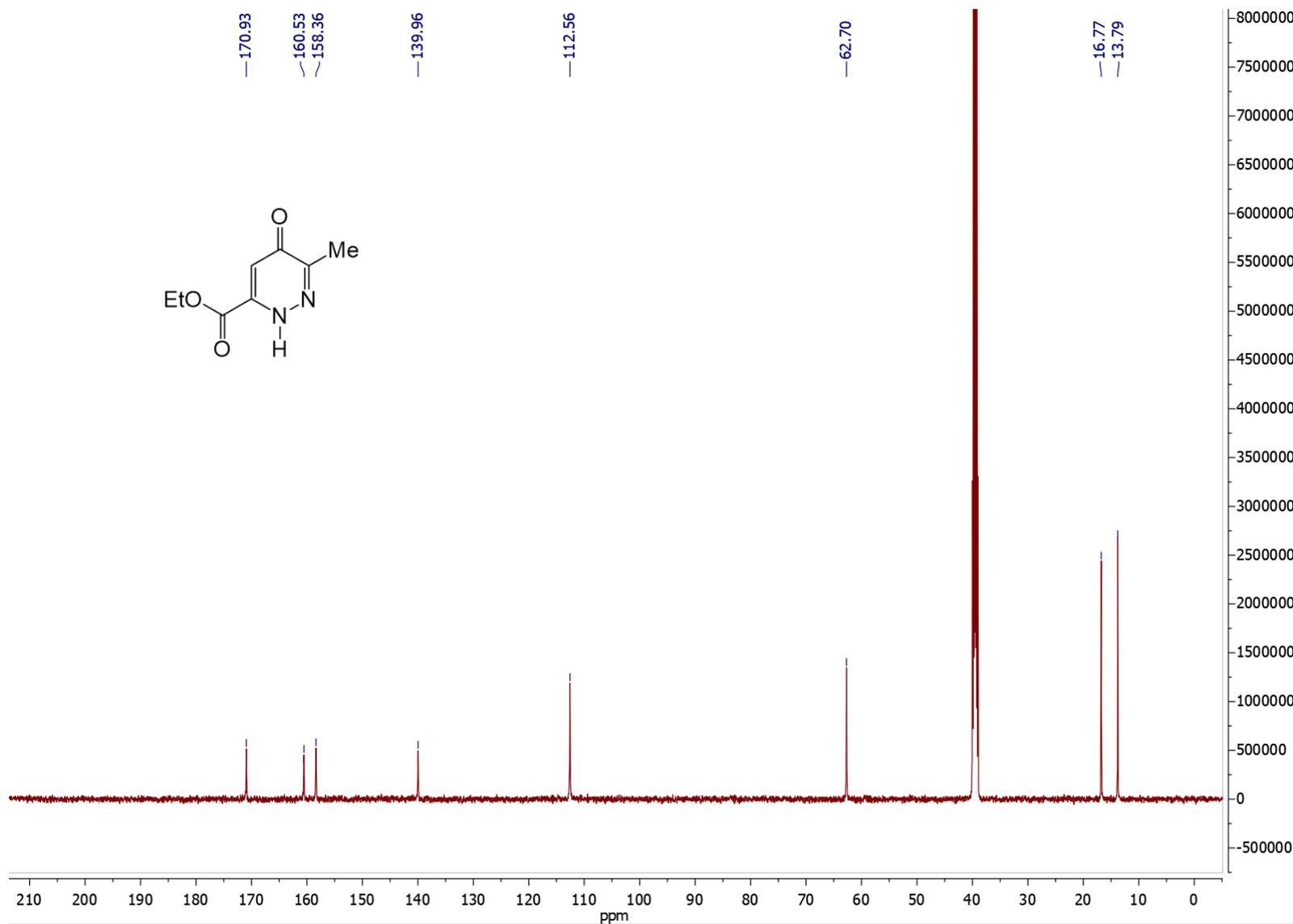


Figure S98. ^{13}C NMR spectrum of compound **22**.



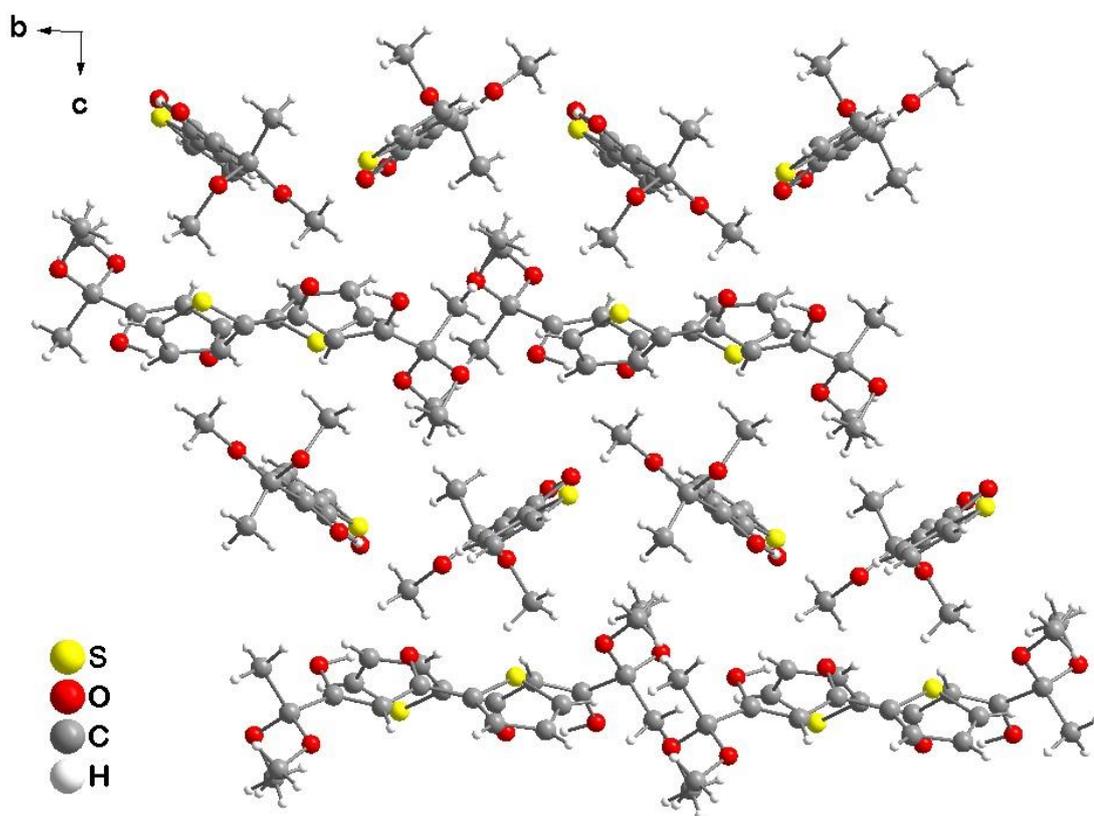


Figure S99. Crystal packing of diketone **2c** along *a* axis.

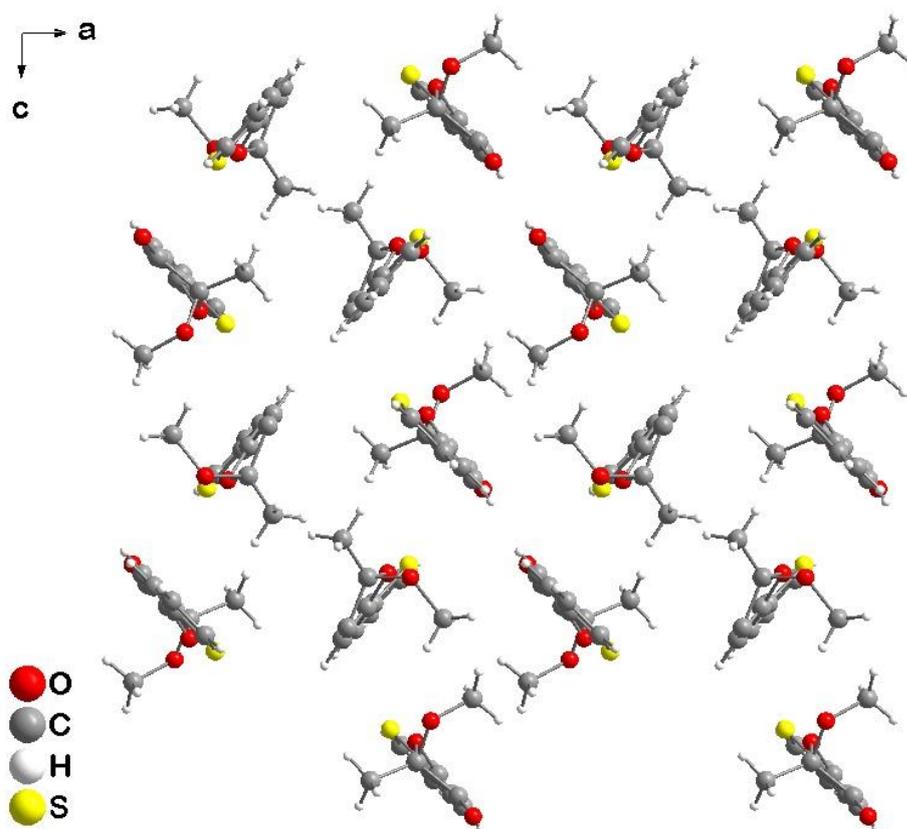


Figure S100. Crystal packing of furanone **3** along *b* axis.

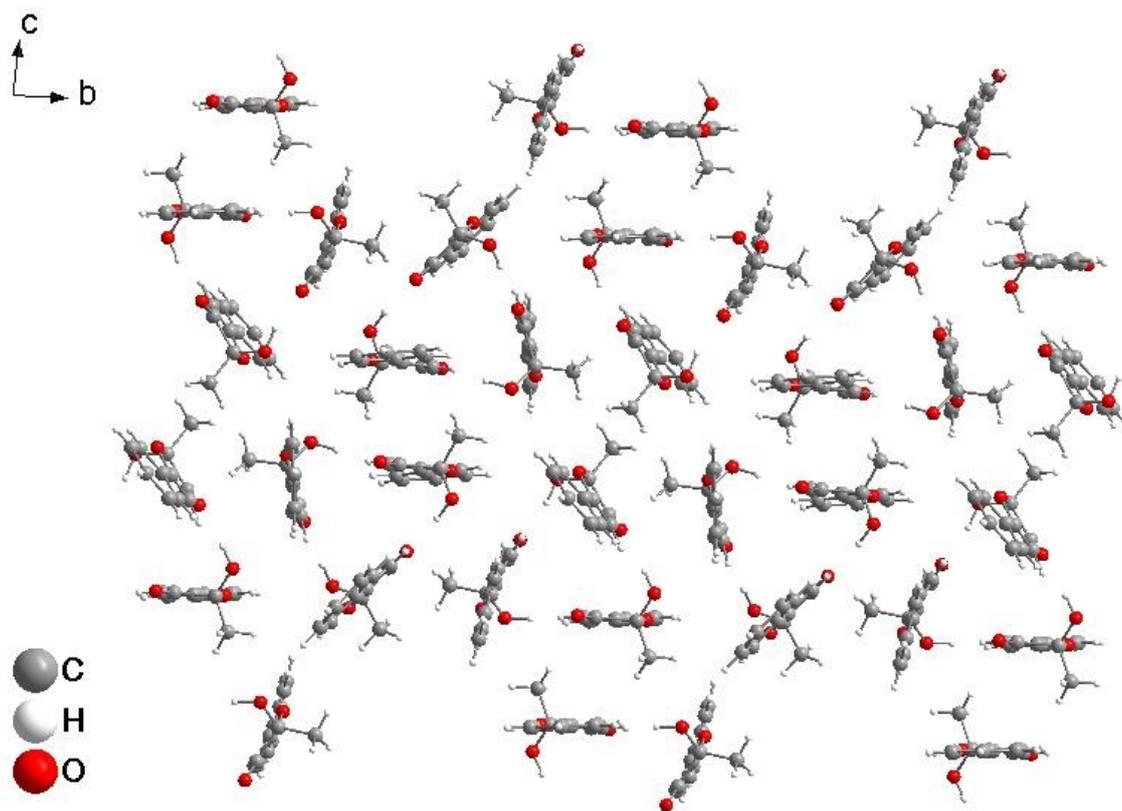
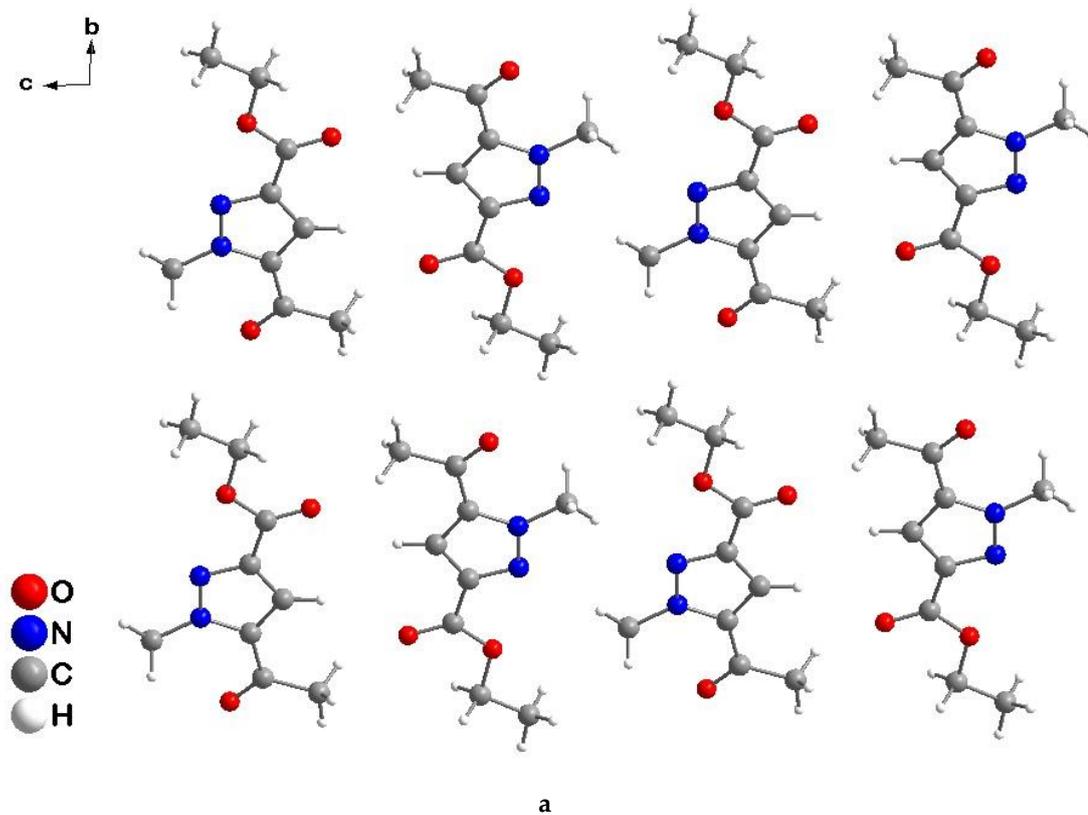


Figure S101. Crystal packing of furanone 5.



a

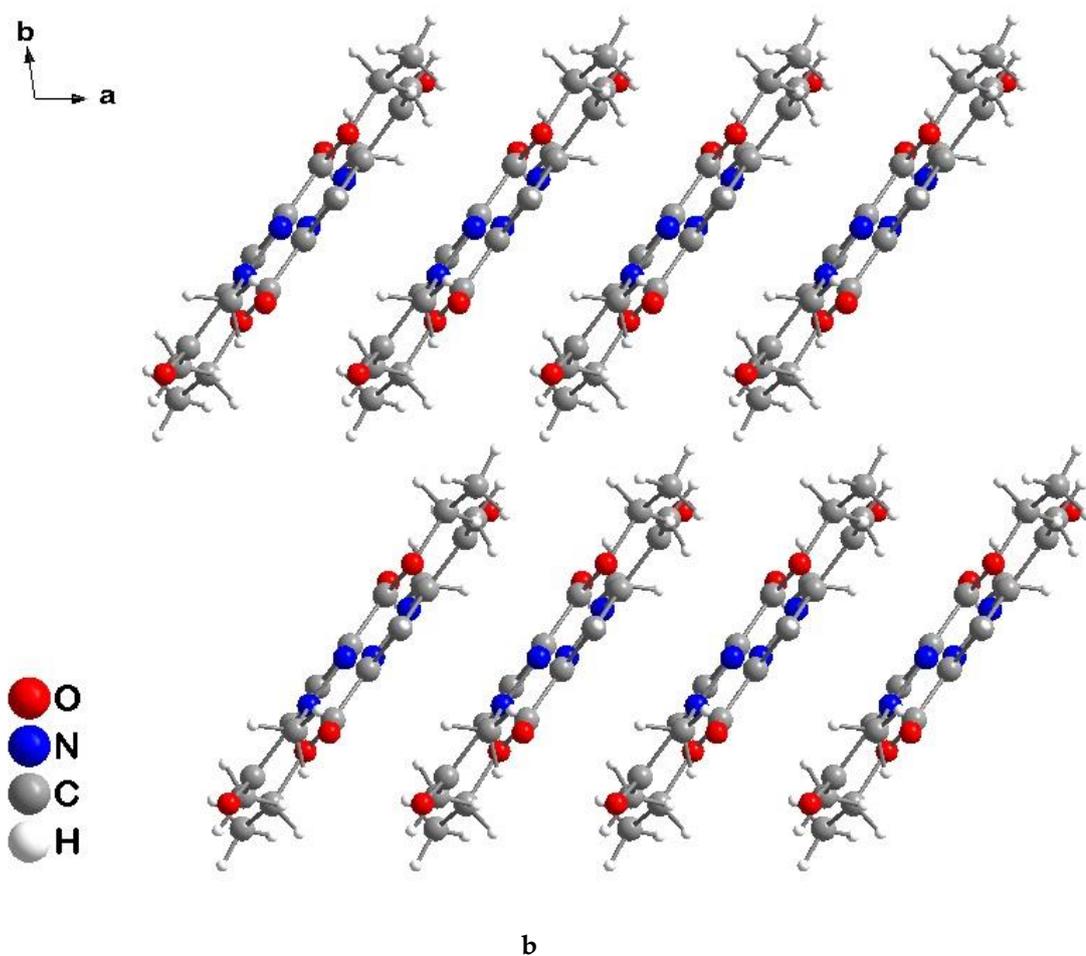
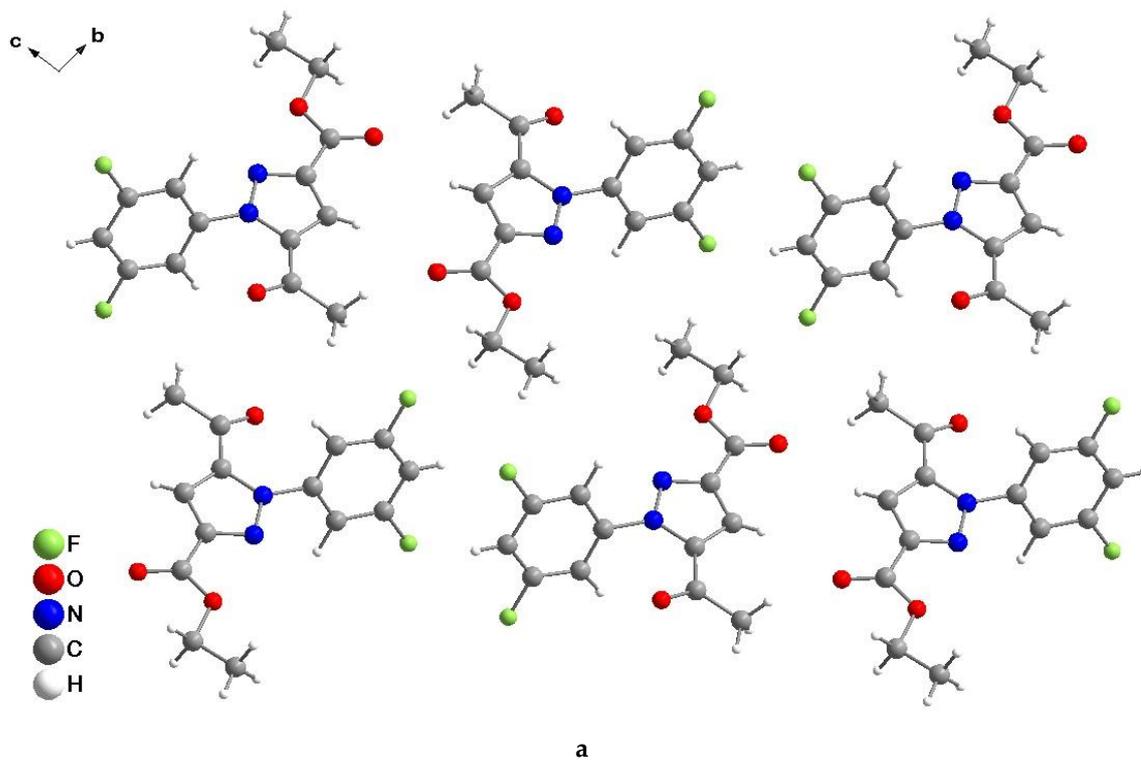


Figure S102. Crystal packing of pyrazole 7a along *a* (a) and *c* (b) axis.



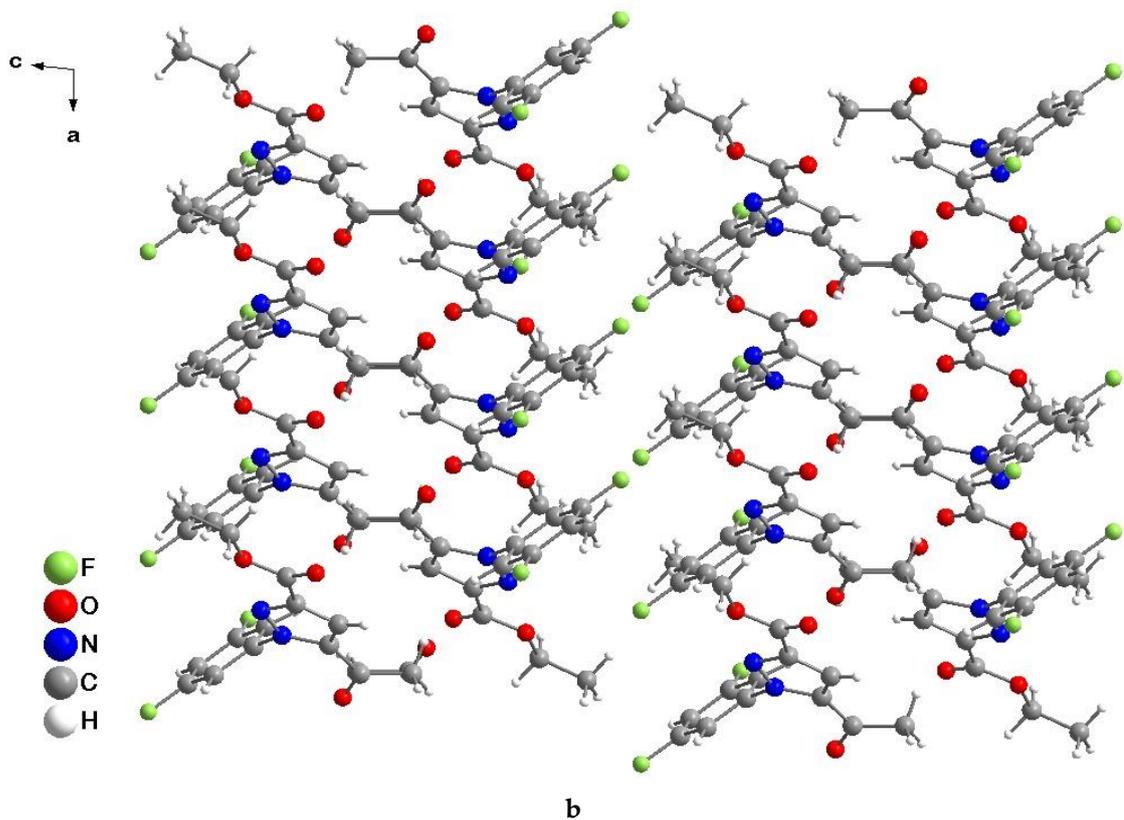
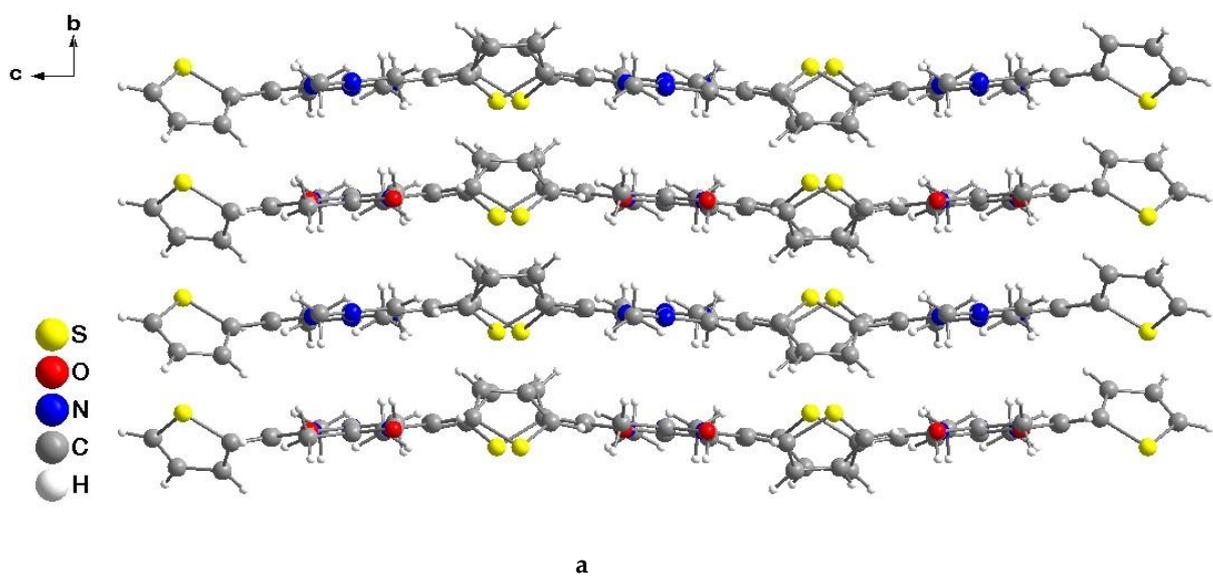


Figure S103. Crystal packing of pyrazole 71 along *a* (a) and *b* (b) axis.



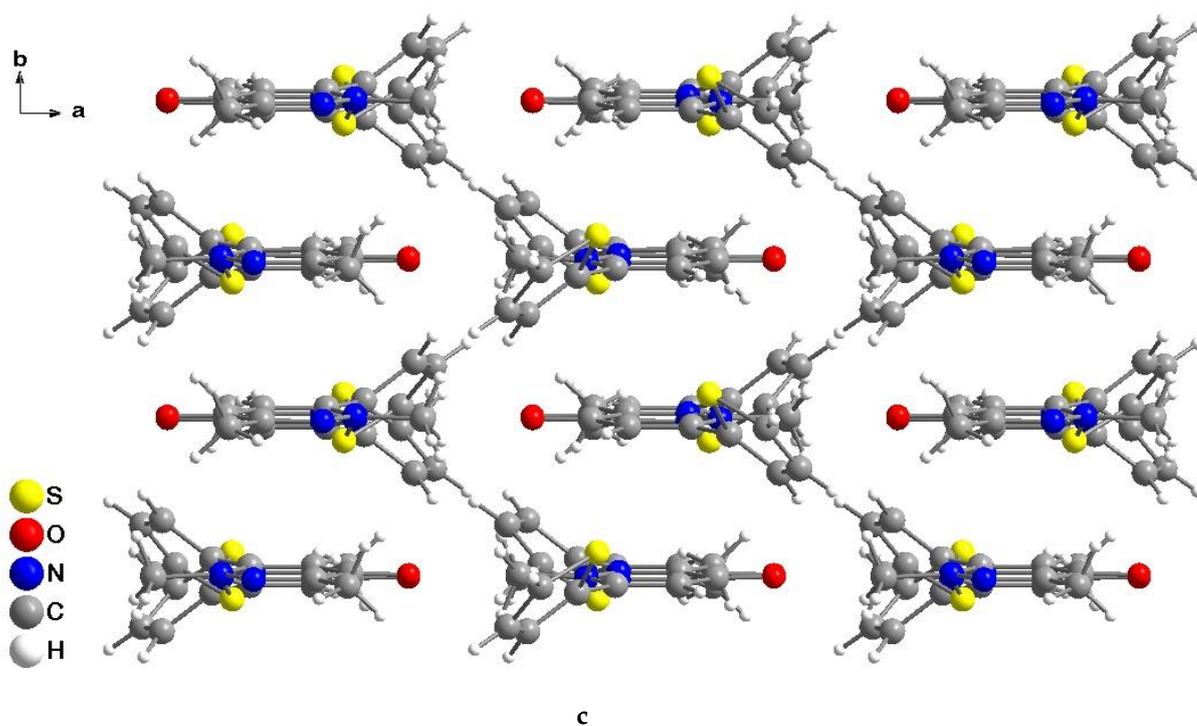
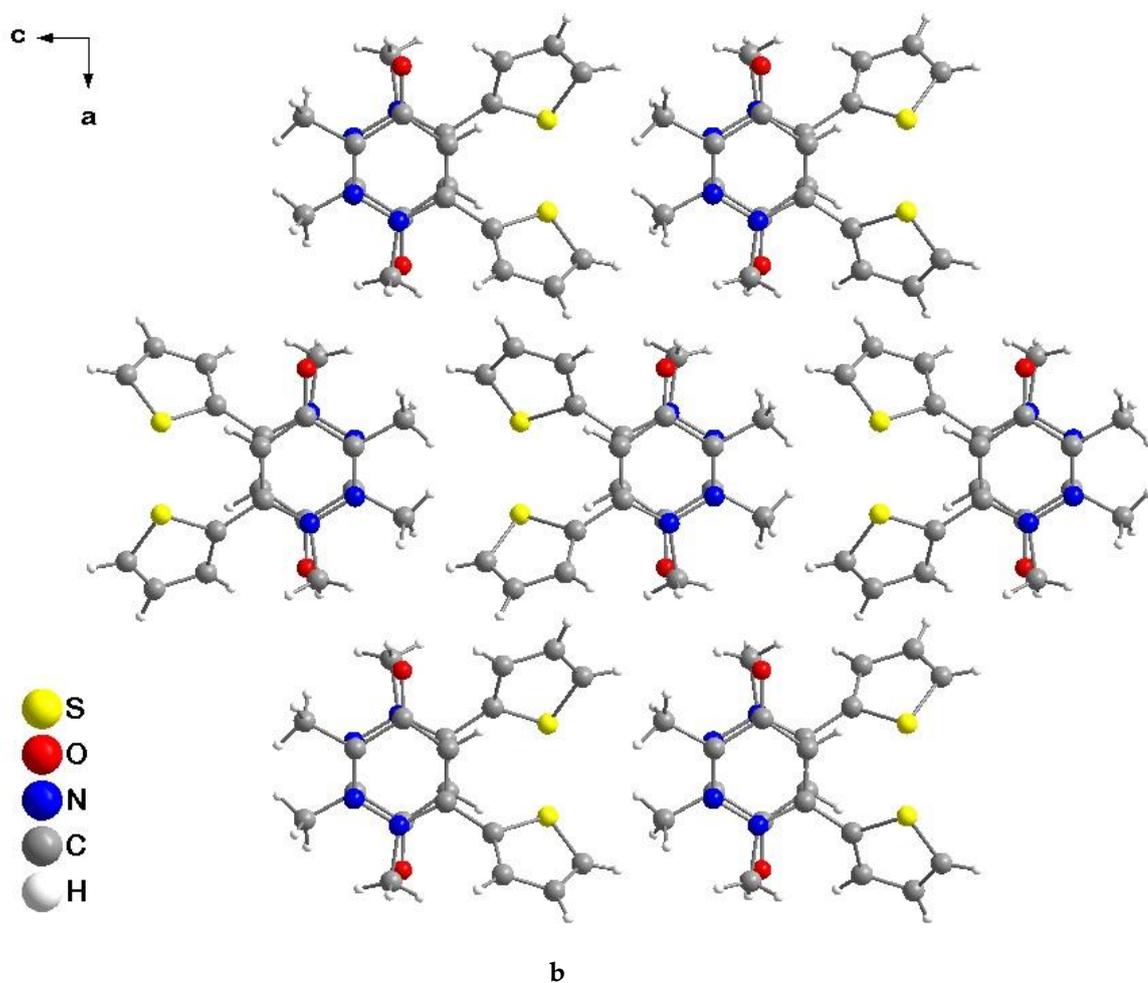


Figure S104. Crystal packing of pyridazinone 9a along *a* (a), *b* (b) and *c* (c) axis.

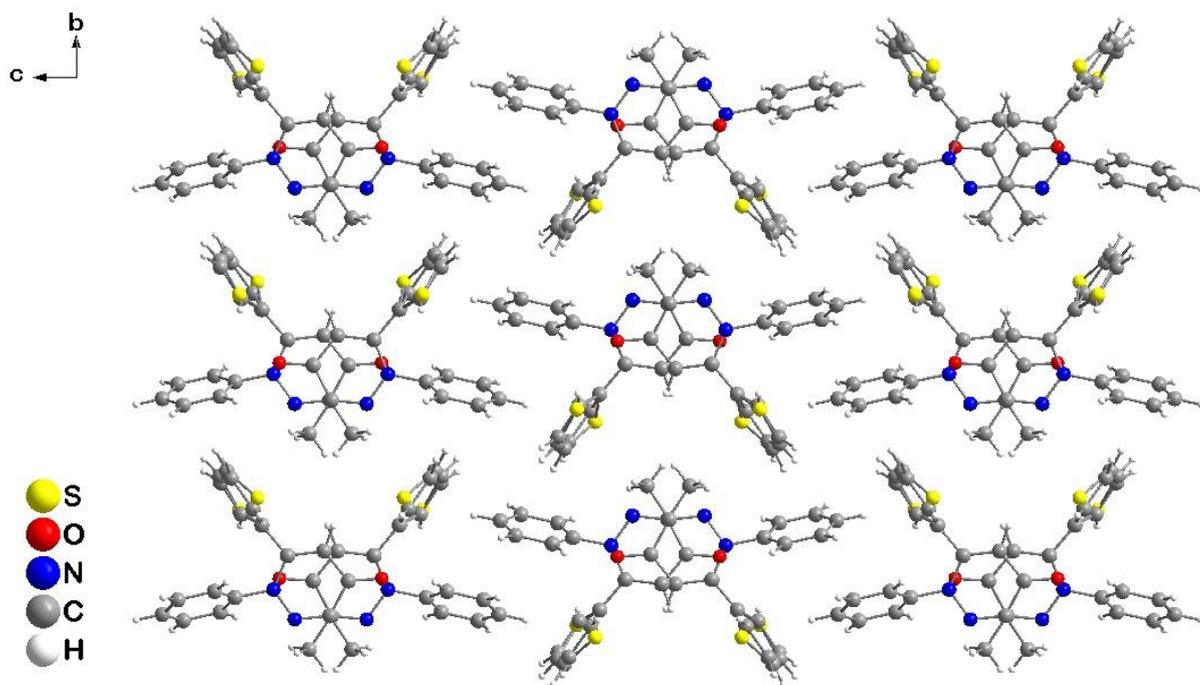
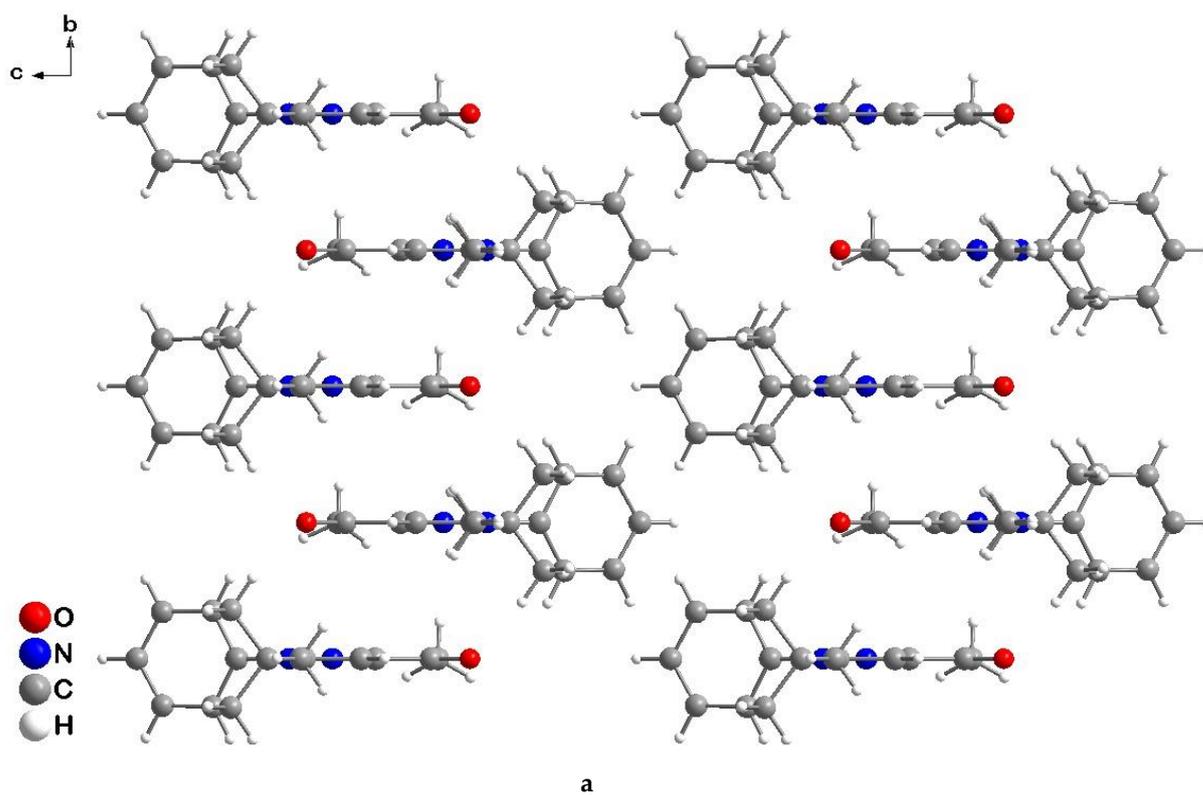


Figure S105. Crystal packing of pyridazinone **9b** along *a* axis.



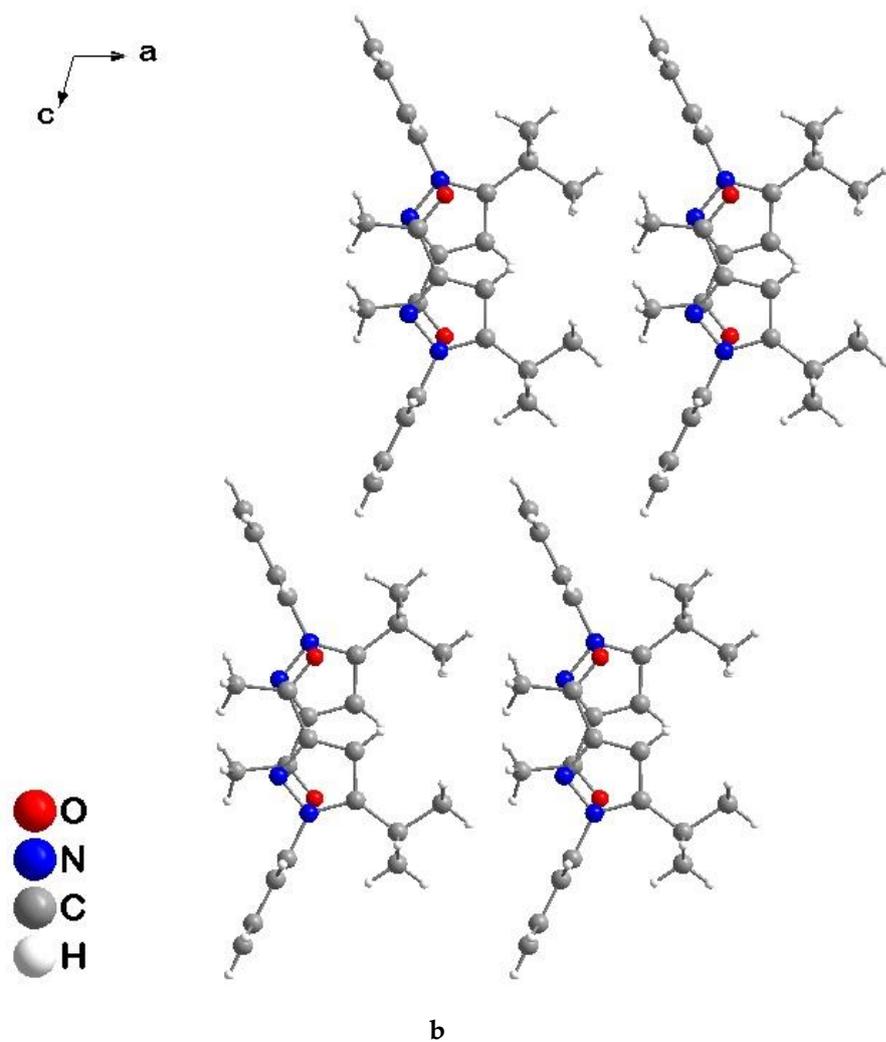


Figure S106. Crystal packing of pyrazole 12 along *a* (a) and *b* (b) axis.

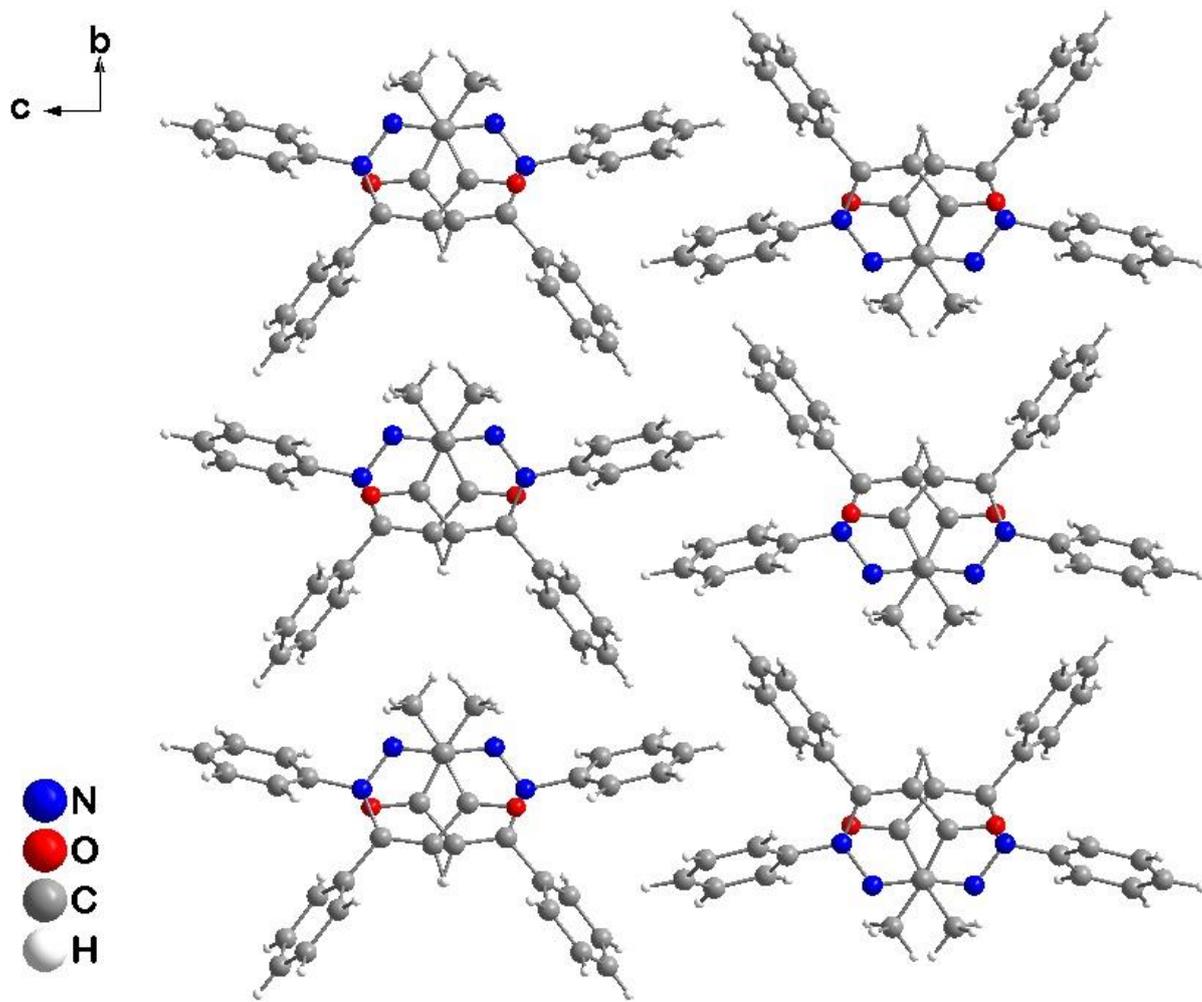
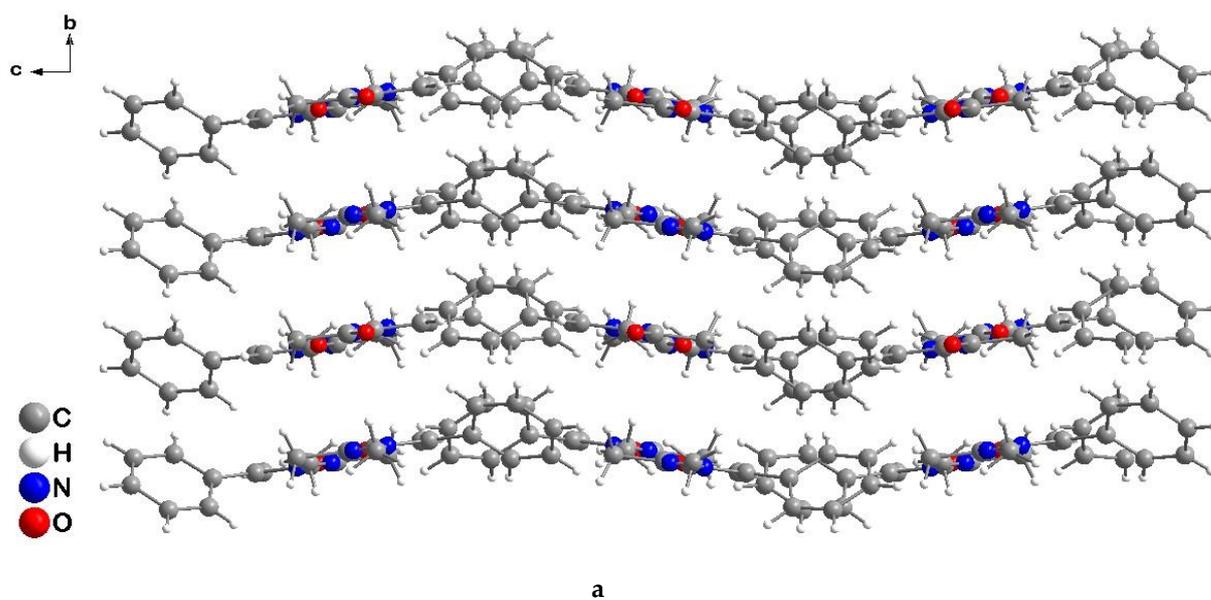


Figure S107. Crystal packing of pyridazinone **14** along *a* axis.



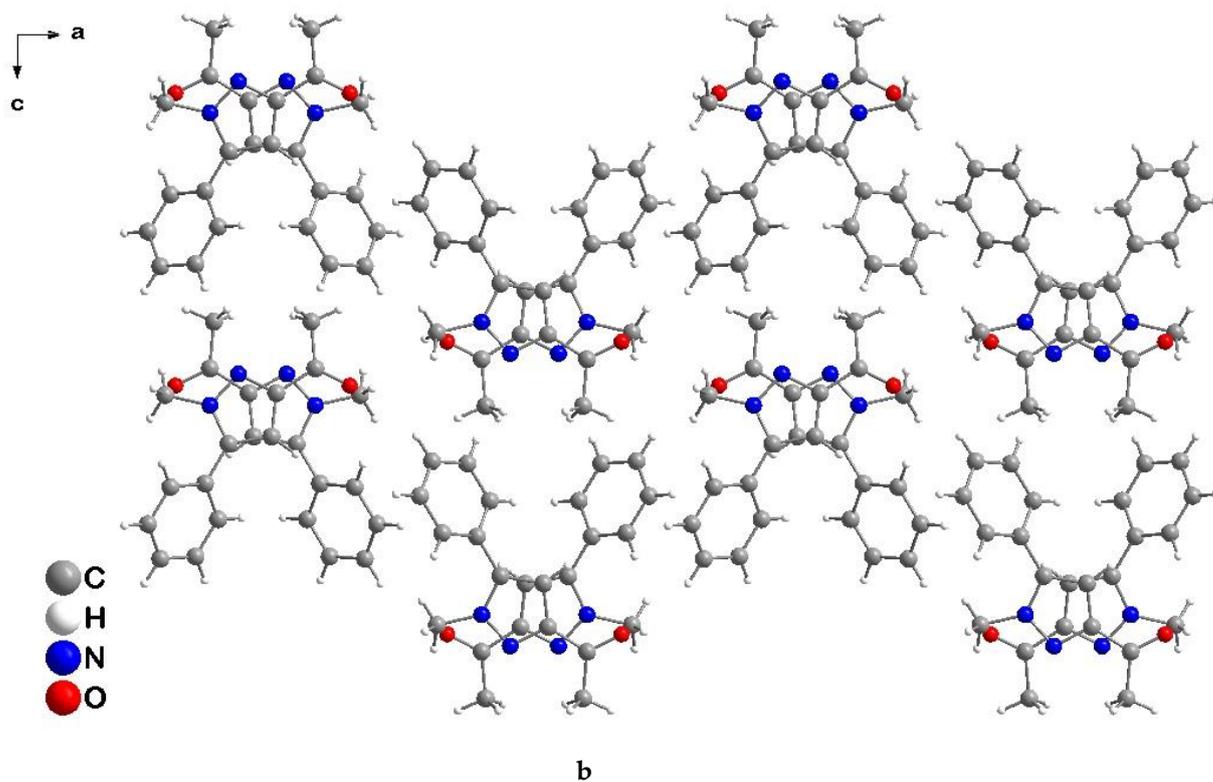


Figure S108. Crystal packing of pyrazole **15b** along *a* (a) and *b* (b) axis.

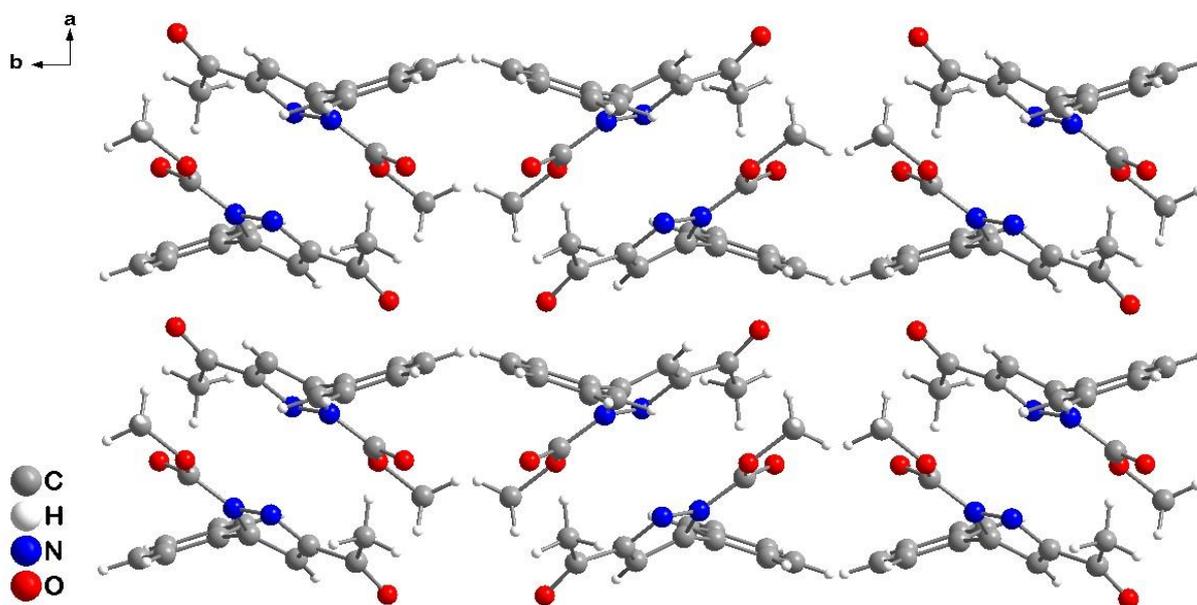


Figure S109. Crystal packing of pyrazole **21b** along *c* axis.

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)-1.42.7(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)

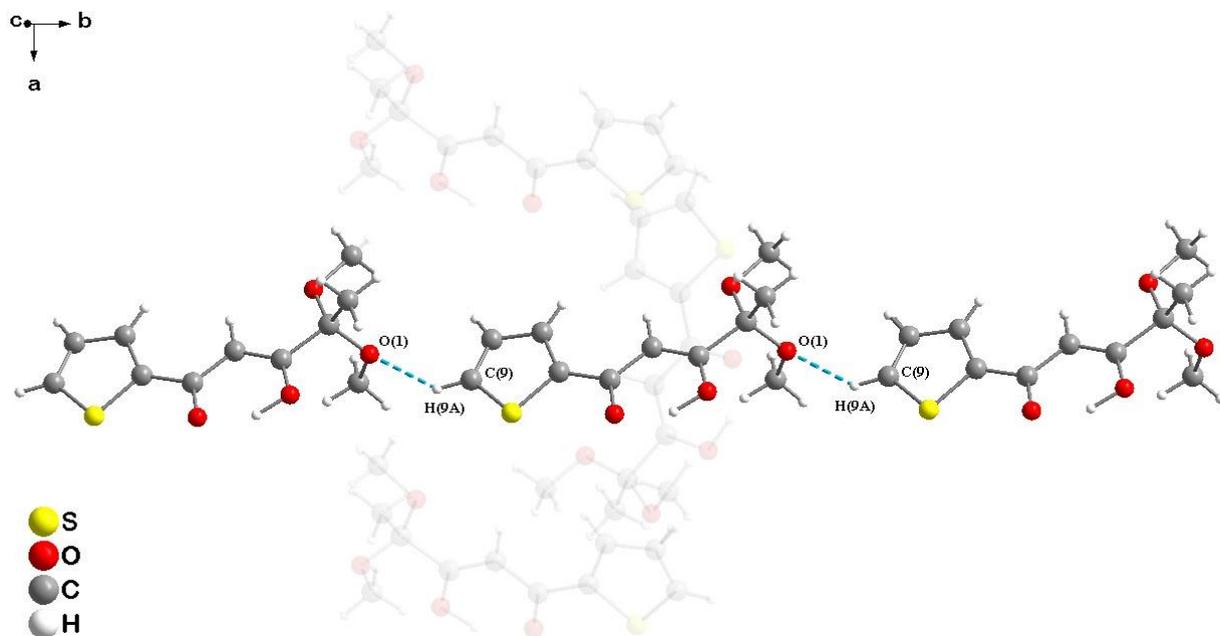


Figure S110. H-contacts in the crystal packing of 2c.

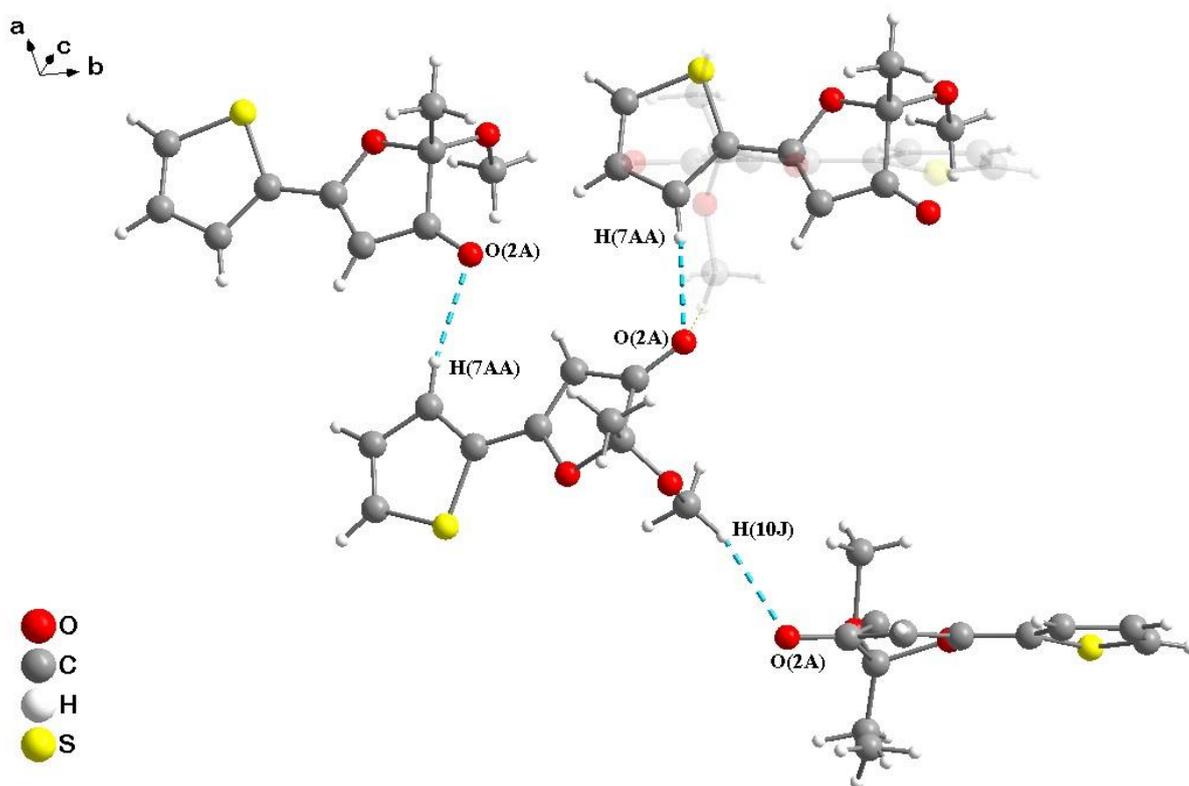


Figure S111. H-contacts in the crystal packing of 3.

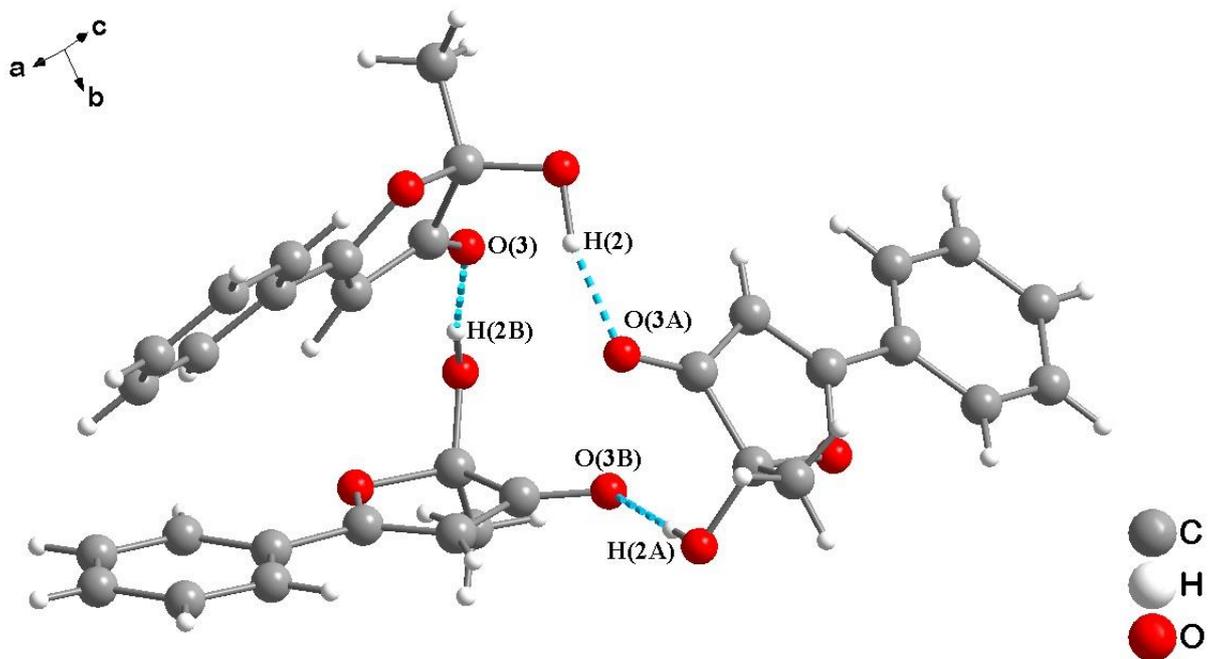


Figure S112. Intermolecular hydrogen bonds in the crystal packing of 5.

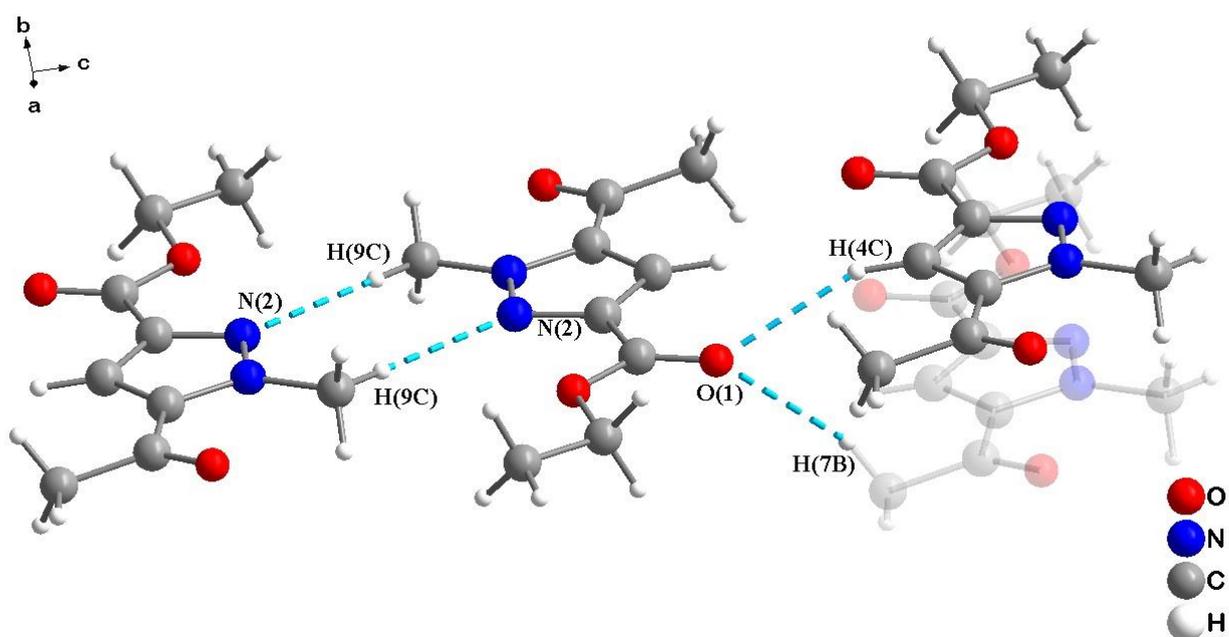


Figure S113. H-contacts in the crystal packing of 7a.

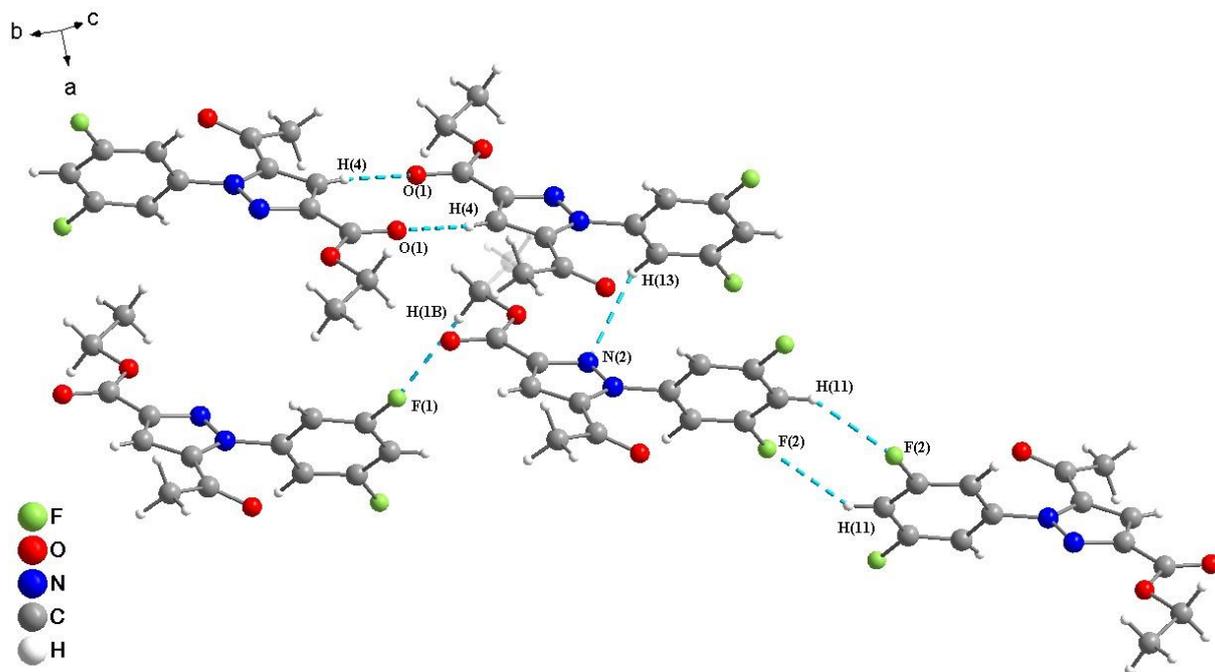


Figure S114. H-contacts in the crystal packing of 7l.

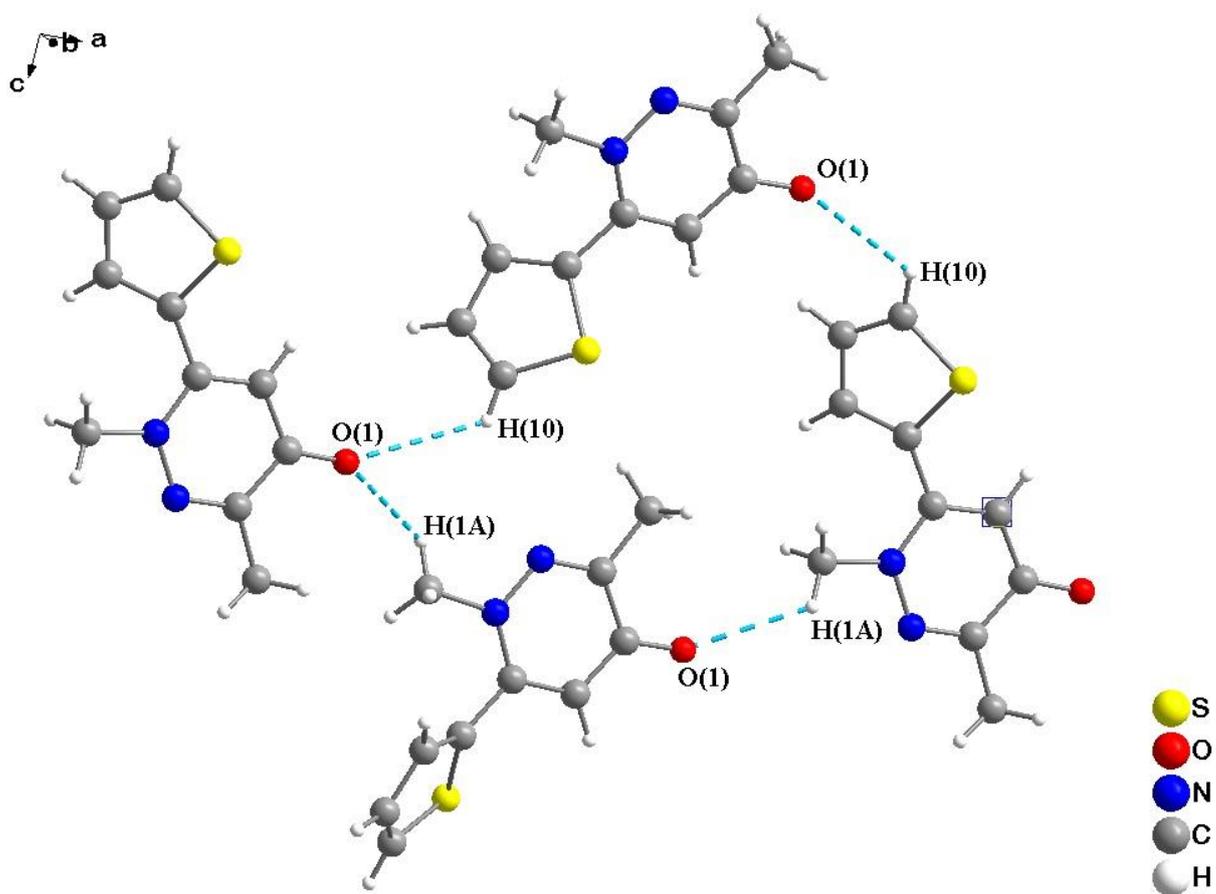


Figure S115. H-contacts in the crystal packing of 9a.

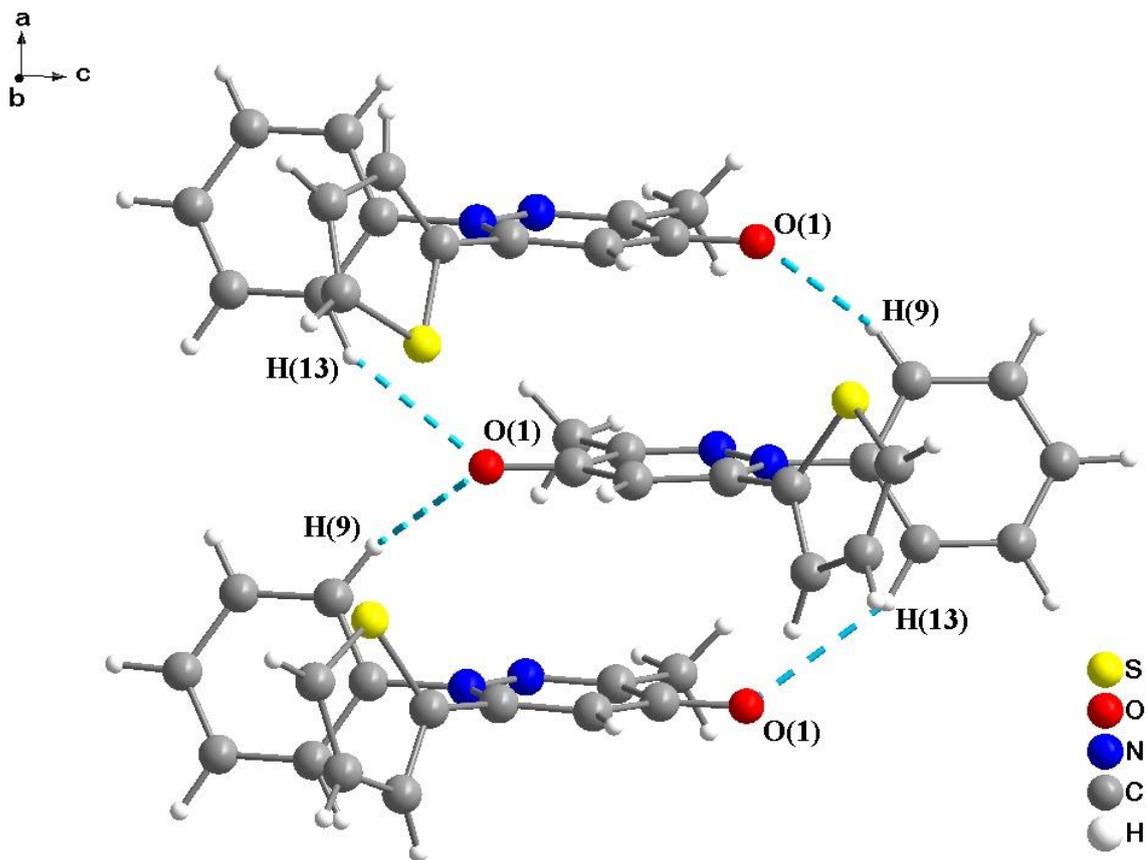


Figure S116. H-contacts in the crystal packing of 9b.

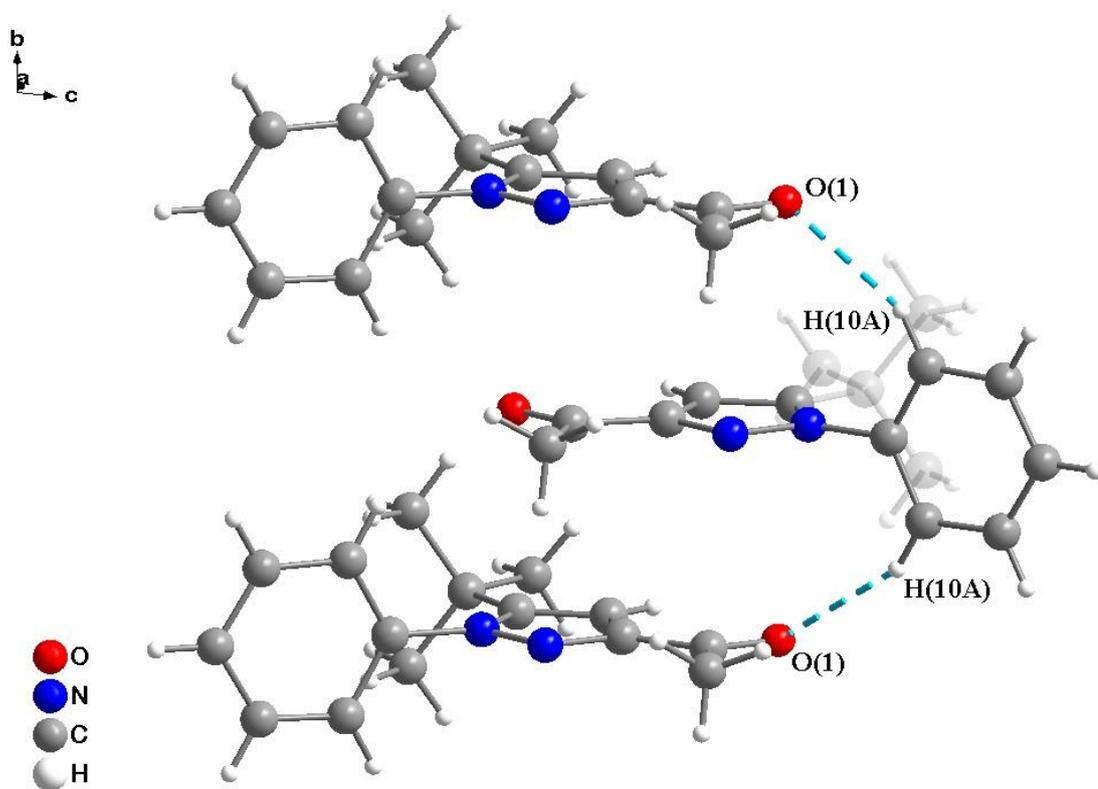


Figure S117. H-contacts in the crystal packing of 12.

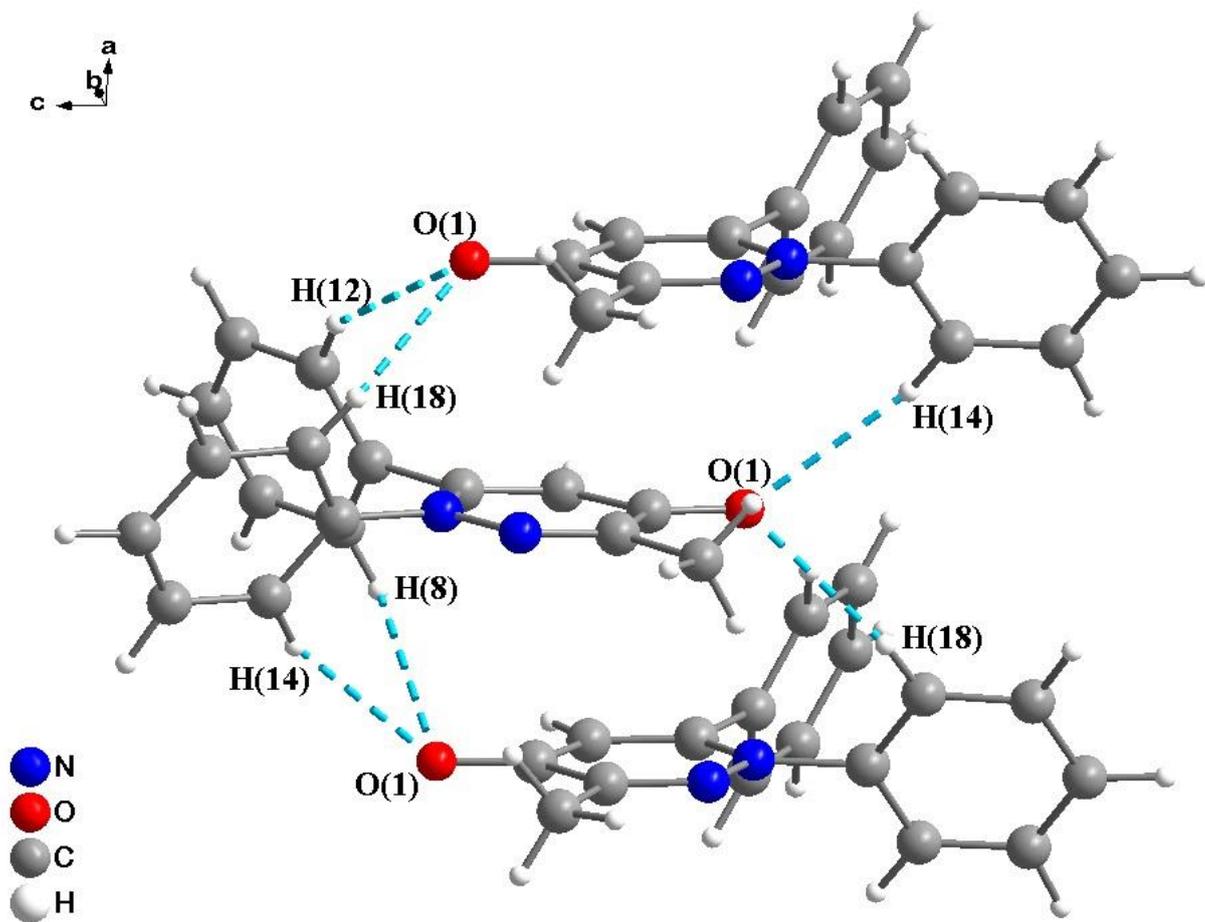


Figure S118. H-contacts in the crystal packing of 14.

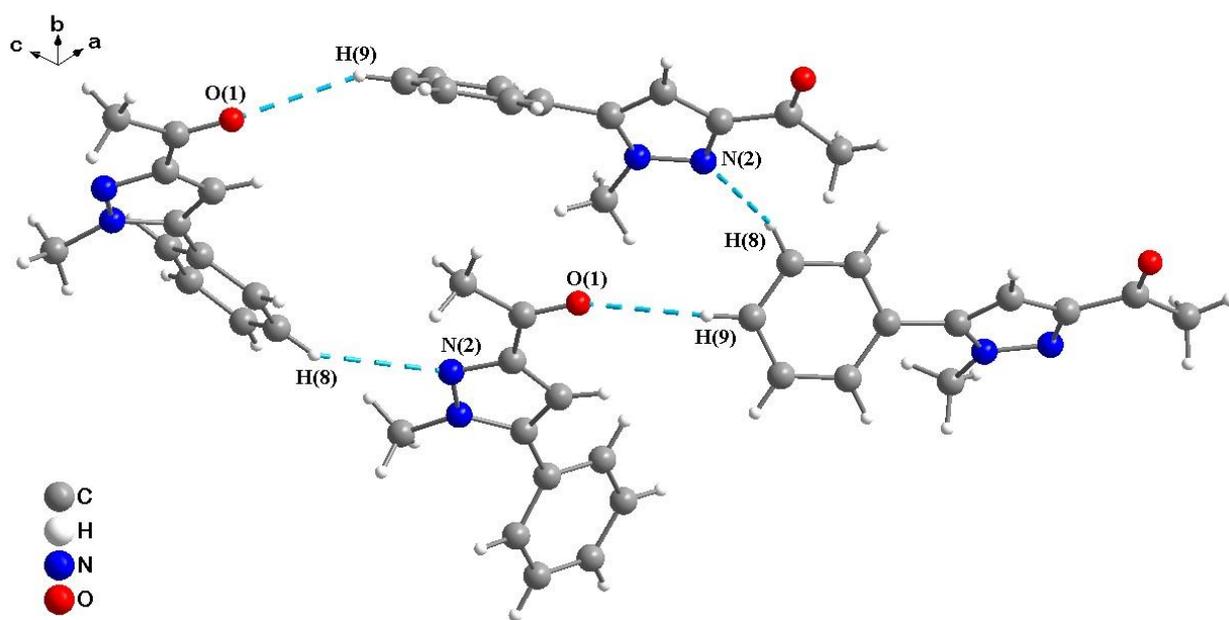


Figure S119. H-contacts in the crystal packing of 15b.

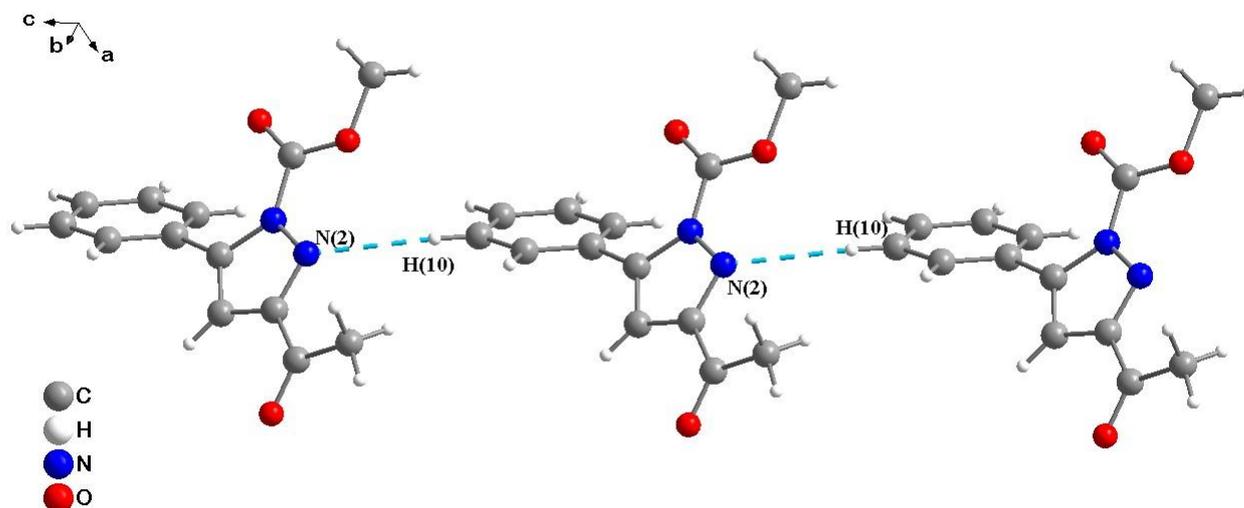


Figure S120. H-contacts in the crystal packing of **21b**.

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>	D-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	<i>x</i> , -1+ <i>y</i> , <i>z</i>
	C(7A)-H(7AA)...O(2A)	0.930(3)	2.475(2)	3.379(4)	164	1- <i>x</i> , 1/2+ <i>y</i> , 1/2- <i>z</i>
3	C(10B)-H(10J)...O(2A)	0.960(3)	2.411(2)	3.342(3)	163	1+ <i>x</i> , 3/2- <i>y</i> , 1/2+ <i>z</i> -
	O(2B)-H(2B)...O(3)	0.929(51)	1.778(52)	2.699(4)	171	2- <i>x</i> , 1- <i>y</i> , 1- <i>z</i>
5	O(2)-H(2)...O(3A)	1.052(66)	1.680(62)	2.695(4)	160	-1+ <i>x</i> , <i>y</i> , <i>z</i>
	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- <i>x</i> , 1- <i>y</i> , - <i>z</i>
	C(4)-H(4C)...O(1)	0.987(2)	2.473(25)	3.401(3)	156	- <i>x</i> , 1- <i>y</i> , 1- <i>z</i>
	C(7)-H(7B)...O(1)	0.960(3)	2.680(2)	3.517(4)	146	2- <i>x</i> , 1- <i>y</i> , 1- <i>z</i>
7l	C(11)-H(11)...F(2)	0.907(37)	2.591(33)	3.381(5)	146	2- <i>x</i> , - <i>y</i> , 1- <i>z</i>
	C(13)-H(13)...N(2)	1.049(44)	2.719(43)	3.295(5)	114	-1+ <i>x</i> , <i>y</i> , <i>z</i>
	C(1)-H(1B)...F(1)	0.971(4)	2.620(3)	3.570(5)	163	<i>x</i> , 1+ <i>y</i> , <i>z</i>
9a	C(4)-H(4)...O(1)	0.825(45)	2.574(43)	3.376(5)	165	1+ <i>x</i> , <i>y</i> , 1+ <i>z</i>
	C(1)-H(1A)...O(1)	0.960(4)	2.604(2)	3.206(4)	121	-1/2+ <i>x</i> , 3/2- <i>y</i> , 1- <i>z</i>
9b	C(10)-H(10)...O(1)	0.929(4)	2.945(2)	3.558(5)	125	- <i>x</i> , -1/2+ <i>y</i> , <i>z</i>
	C(9)-H(9)...O(1)	0.943(32)	2.518(31)	3.244(3)	134	1/2+ <i>x</i> , <i>y</i> , 1/2- <i>z</i>
12	C(1)-H(1A)...O(1)	0.987(26)	2.488(24)	3.388(3)	152	-1/2+ <i>x</i> , <i>y</i> , 1/2- <i>z</i>
	C(10A)-H(10A)...O(1)	0.930(7)	2.510(5)	3.367(8)	153	<i>x</i> , 1+ <i>y</i> , 1+ <i>z</i>
14	C(14)-H(14)...O(1)	0.969(27)	2.598(26)	3.502(31)	156	-1/2+ <i>x</i> , <i>y</i> , 1/2- <i>z</i>
	C(8)-H(8)...O(1)	0.930(3)	2.850(22)	3.564(4)	134	-1/2+ <i>x</i> , <i>y</i> , 1/2- <i>z</i>
15b	C(18)-H(18)...O(1)	0.919(26)	2.535(25)	3.275(3)	138	-1/2+ <i>x</i> , <i>y</i> , 1/2- <i>z</i>
	C(12)-H(12)...O(1)	0.930(3)	2.709(2)	3.559(3)	152	1/2+ <i>x</i> , <i>y</i> , 1/2- <i>z</i>
	C(8)-H(8)...N(2)	0.930(4)	2.944(2)	3.744(5)	145	-1/2+ <i>x</i> , 1/2- <i>y</i> , 1- <i>z</i>
21b	C(9)-H(9)...O(1)	0.930(3)	2.730(3)	3.585(4)	153	-1/2+ <i>x</i> , -1+ <i>y</i> , 1/2- <i>z</i>
	C(10)-H(10)...N(2)	0.930(4)	2.635(3)	3.540(5)	164	-