Electronic Supplementary Information

Iodine-Catalyzed Sulfenylation of Pyrazolones Using Dimethyl Sulfoxide as an Oxidant

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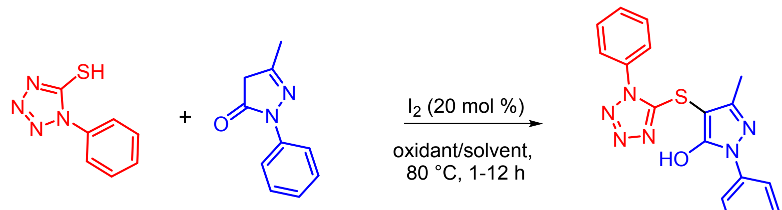
Contents

General experimental

NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ or DMSO-d6. Tetramethylsilane (TMS; δ = 0.00 ppm) for 1H NMR in $CDCl_3$, and residual non-deuterated solvent peak (δ = 2.50 ppm) in DMSO-d6, served as an internal standard. The solvent signal ($CDCl_3$, δ = 77.00 ppm; and DMSO-d6, δ = 39.5 ppm) was used as internal standard for ^{13}C NMR. IR spectra were measured using an FT-IR spectrometer. Mass spectra were obtained with a Q-TOF Mass Spectrometer (HRMS). Flash column chromatography was carried out by packing glass columns with commercial silica gel 230-400 mesh (commercial suppliers) and thin-layer chromatography was carried out using silica gel GF-254. All catalysts, reagents and reactants were procured from commercial suppliers. Dichloroethane was distilled over calcium hydride and stored over molecular sieves and used for all procedures. Other solvents, used for work up and chromatographic procedures were purchased from commercial suppliers.

Optimization for thiols

Optimization of solvent (Table 1)



1a (0.6 mmol) **2a** (0.66 mmol) **3a**

entry	oxidant/solvent	time	isolated yield (%)
1	**DMSO**	**1.5 h**	**90**
2	DMSO (3 equiv), DCE	2 h	26
3	DMSO (3 equiv), EtoAc	1.5 h	82
4	DMSO (3 equiv), ACN	1.5 h	48
5	DMSO (3 equiv), Toluene	1. 5h	81
6	DMSO (3 equiv), Trifluoroethanol	1.5 h	trace
7	DMSO (3 equiv), Water	12 h	ND
8	DMSO (3 equiv), Ethanol	12 h	trace
9	DMSO (3 equiv), DMF	12 h	21
10	DMSO (3 equiv), DMA	12 h	18
11	DMSO (3 equiv), NMP	12 h	11
12	**DMSO (3 equiv)**	**1.5 h**	**83**
13	none	12 h	ND
14	EtoAc	12 h	ND
15	Toluene	12 h	ND

ND= Not determined

Reaction with solvents DCE decomposition of the starting materials were observed (entry 2).

Optimization of catalyst or additive (Table 2)

entry	oxidant/solvent	Catalyst/additive	time	**3a** Isolated yield (%)
1	**DMSO**	**20 mol % aq. HI (55%)**	**2 h**	**77**
2	DMSO	20 mol % aq. HBr	12 h	trace
3	DMSO	20 mol % NBS	12 h	trace
4	DMSO	20 mol % NCS	12 h	trace
5	DMSO	20 mol % KI	12 h	trace
6	DMSO	-	12 h	NR

NCS = *N*-Chlorosuccinimide

NBS = *N*-Bromosuccinimide

KI = Potassium iodide

Optimization of equiv of 1a and 2a and mol % of iodine (Table 3)

entry	**1a** (equiv)	**2a** (equiv)	iodine (mol %)	time	**3a** isolated yield (%)
1	**1**	**1.5**	**20**	**1 h**	**90**
2	1.5	1.1	20	2 h	82
3	1	1.1	30	1 h	90
4	1	1.1	10	2 h	82
5	1	1.1	5	4 h	81

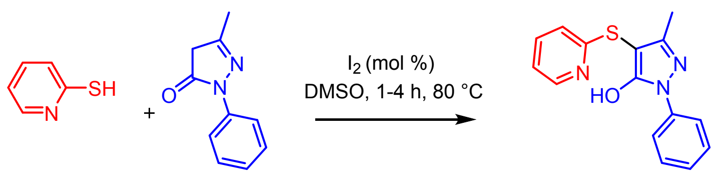
Optimization under Argon and Oxygen atmosphere (Table 4)

entry	**1a** (equiv)	**2a** (equiv)	iodine (mol %)		**3a** isolated yield (%)
1	1	1.1	20	reaction under O_2 atmosphere, 1.5h	88
2	1	1.1	20	reaction under Argon atmosphere, 1.5h	89

Effect of basic additives (Table 5)

entry	**1a** (equiv)	**2a** (equiv)	iodine (mol %)	basic additive (100 mol %)	**3a** isolated yield (%)
1	1	1.1	20	triethyl amine	33
2	1	1.1	20	pyridine	36
3	1	1.1	20	Sodium hydroxide	trace

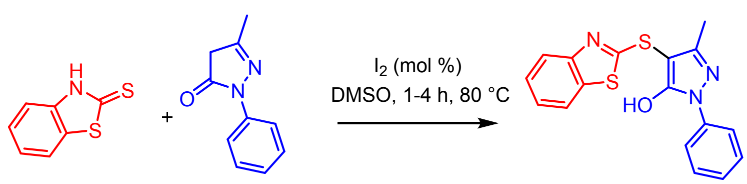
Optimization for pyridine-2-thiol (Table 6)



1, (0.6 mmol) **2a**, (0.66 mmol) **4b,** 81%

entry	**1a** (equiv)	**2** (equiv)	iodine (mol %)	time	**4b** isolated yield (%)
1	1	1.1	20	4 h	31
2	1	1.1	50	1 h	72
3	**1**	**1.1**	**100**	**1 h**	**80**

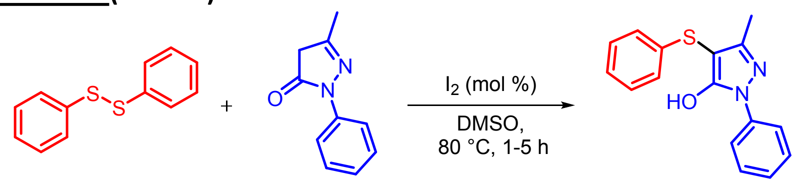
Optimization for thiones (Table 7)



1, (0.6 mmol) **2a**, (0.66 mmol) **4c**

entry	**1a** (equiv)	**2** (equiv)	iodine (mol %)	time	**4b** isolated yield (%)
1	1	1.1	20	4 h	28
2	1	1.1	50	1 h	64
3	**1**	**1.1**	**100**	**1 h**	**82**

<u>Optimization for disulfides</u> (Table 8)

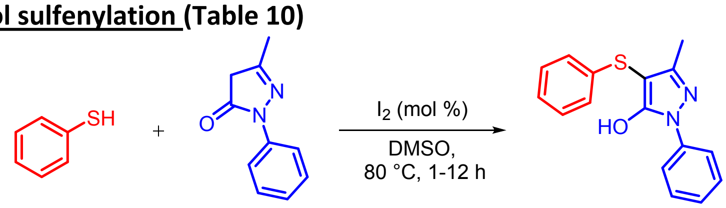


entry	**1a** (equiv)	**2** (equiv)	iodine (mol %)	time	**5** isolated yield (%)
1	1	2.2	5	5 h	76
2	1	2.2	10	4 h	86
3	**1**	**2.2**	**20**	**3 h**	**92**

Reactions in various solvents (Table 9)

entry	iodine (mol %)	**Time h**	solvent reaction under Argon atmosphere	**5** isolated yield (%)
1	5	3	DMSO	77
2	none	24	DMSO	78
3	5	3	Toluene	trace
4	5	3	DCE	trace
5	5	3	ACN	trace
6	5	3	DMF	trace
7	5	3	EtOH	trace

<u>Results for thiophenol sulfenylation</u> (Table 10)

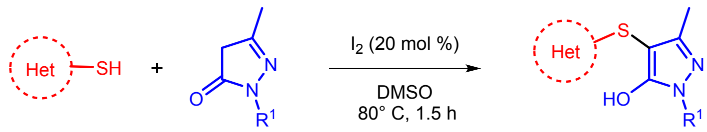


entry	**1a** (equiv)	**2** (equiv)	iodine (mol %)	Time **5**	isolated yield (%)
1	1	1.1	5	5 h	trace
2	1	1.1	10	6 h	11
3	1	1.1	20	2 h	26

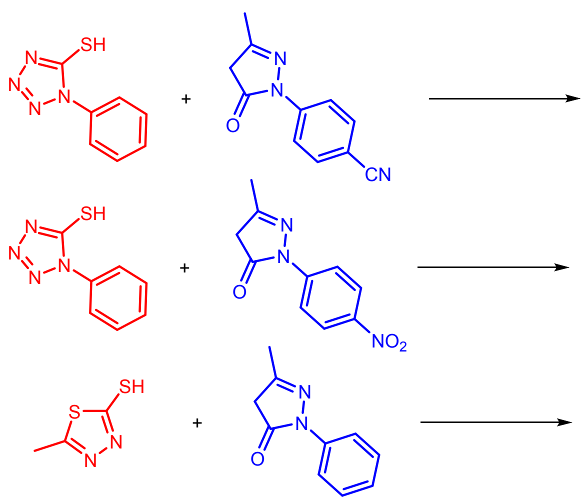
Decomposition of both the starting materials were observed in all the above reactions

<u>Results for insoluble compounds</u> (Table 11)

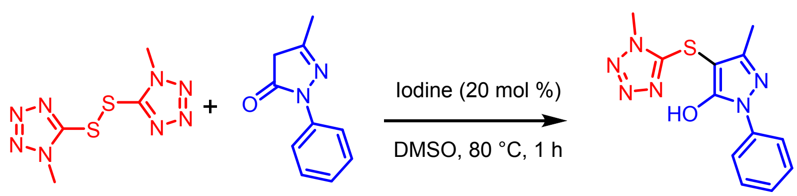
Pyrazolone derivatives 4-(3-Methyl-5-oxo-4, 5-dihydro-1*H*-pyrazol-1-yl)benzonitrile and 5-Methyl-2-(4-nitrophenyl)-2,4-dihydro-3*H*-pyrazol-3-one afforded insoluble compounds in DMSO. These compounds are insoluble in other solvents such as DCM, acetone, methanol, acetonitrile etc..,



1a (0.6 mmol) **2** (0.66 mmol)

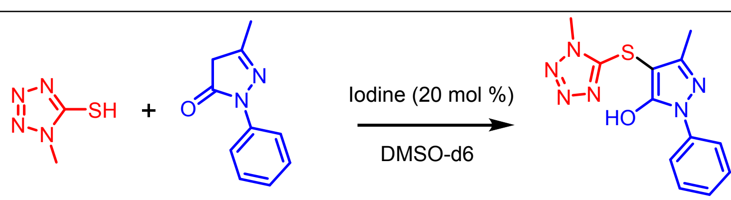


Control experiment with1,2-bis(1-methyl-1*H*-tetrazol-5-yl)disulfane (Table 12)

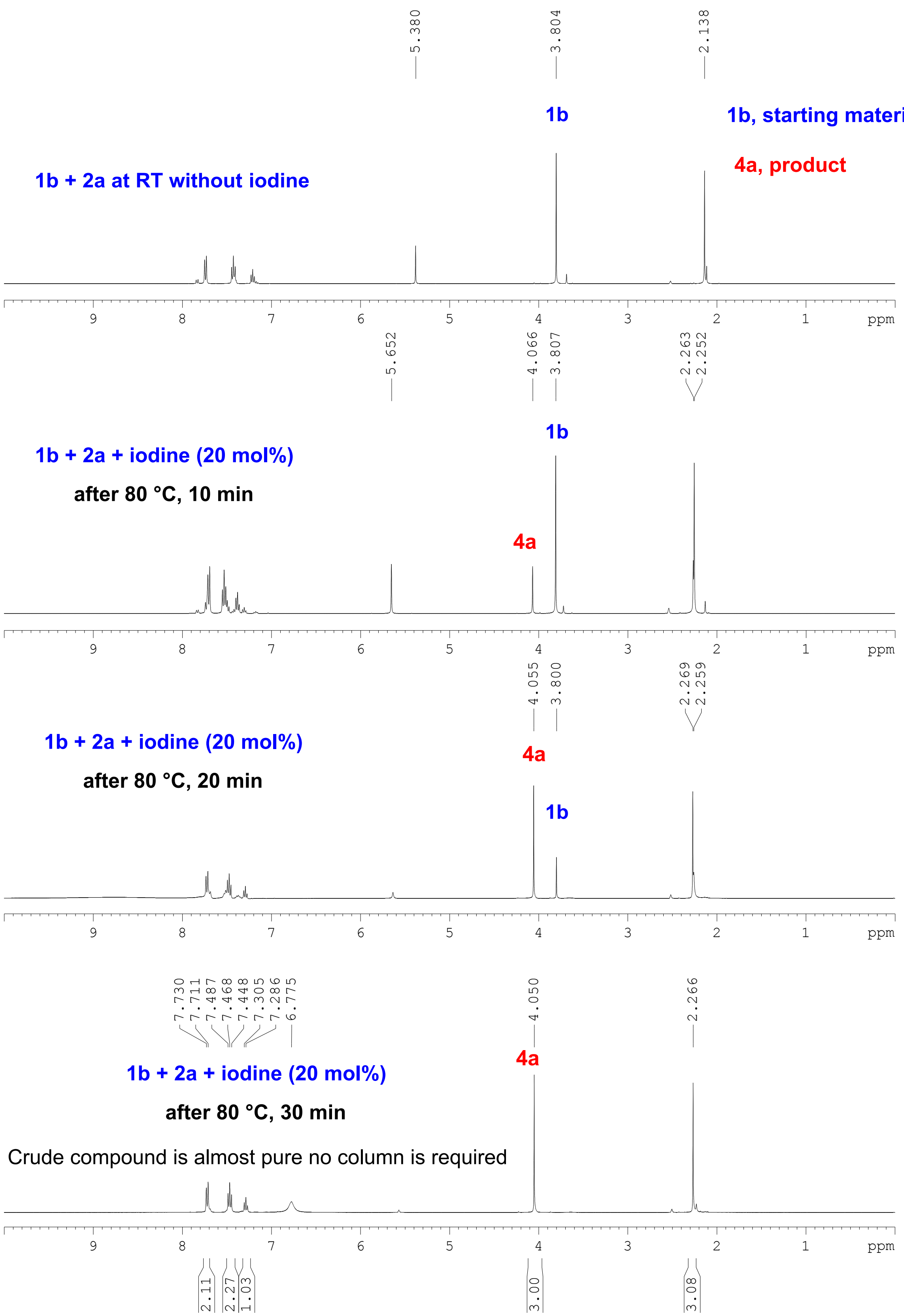


(0.3 mmol) **2a**, (0.66 equiv) **4a,** 78%

NMR STUDIES (Table 13)



1b, (1 equiv) **2a**, (1.1 equiv) **4a**


5.380
3.804
2.138
1b
1b, starting material
4a, product
1b + 2a at RT without iodine
9 8 7 6 5 4 3 2 1 ppm
5.652
4.066
3.807
2.263
2.252
1b
1b + 2a + iodine (20 mol%)
after 80 °C, 10 min
4a
9 8 7 6 5 4 3 2 1 ppm
4.055
3.800
2.269
2.259
1b + 2a + iodine (20 mol%)
4a
after 80 °C, 20 min
1b
9 8 7 6 5 4 3 2 1 ppm
7.730
7.711
7.487
7.468
7.448
7.305
7.286
6.775
4.050
2.266
4a
1b + 2a + iodine (20 mol%)
after 80 °C, 30 min
Crude compound is almost pure no column is required
9 8 7 6 5 4 3 2 1 ppm
2.11
2.27
1.03
3.00
3.08

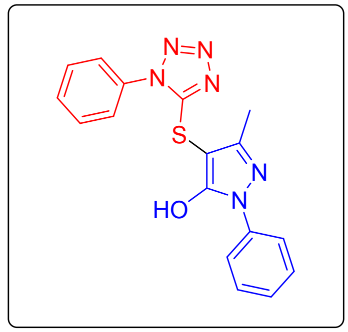
Experimental Section

Typical Experimental Procedure for sulfenylation of pyrazolones

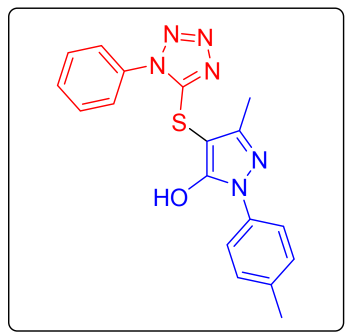
Heterocyclic thiol (0.6 mmol), and pyrazolone (0.66 mmol) were dissolved in DMSO (1 mL) and added iodine (0.12 mmol) (direct addition of iodine for thiols without solvent is highly exothermic and decomposition of thiol was observed). The reaction mixture was stirred at 80 °C for 1-2 h. After the completion of the reaction (monitored by TLC), added water (25 mL) and dilute sodium thiosulphate solution (5 mL) and extracted with EtOAc (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified on a silica gel column using 30-80% EtOAc/hexane to get the pure products.

Characterization data for products

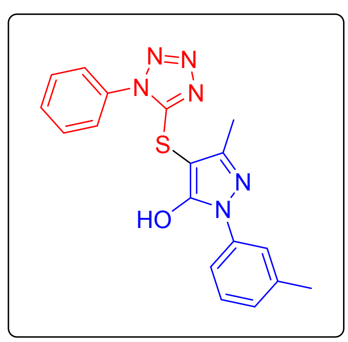
3-Methyl-1-phenyl-4-((1-phenyl-1H-tetrazol-5-yl)thio)-1H-pyrazol-5-ol (3a). Pale brown solid (mp. 82-86 °C); Yield 90% (189 mg); R_f (70% EtOAc/hexane) 0.2; **IR** (Neat, cm^{-1}) 3424, 2256, 2129, 1652, 1554, 1496, 1401; **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ 7.73 – 7.70 (m, 4H), 7.68 – 7.62 (m, 3H), 7.46 (t, J = 8.0 Hz, 2H), 7.27 (t, J = 7.2 Hz, 1H), 2.19 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d$_6$) δ 157.0, 154.7, 152.0, 137.9, 133.2, 130.7, 130.1, 129.1, 126.0, 124.6, 120.9, 81.8, 12.4; **HRESI-MS** (m/z) Calculated for $C_{17}H_{14}N_6OS$ (M^+ + Na) 373.0848, found (M^+ + Na) 373.0848.



3-Methyl-4-((1-phenyl-1H-tetrazol-5-yl)thio)-1-(p-tolyl)-1H-pyrazol-5-ol (3b). White solid (mp. 144-146 °C); Yield 93% (203 mg); R_f (70% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3052, 1977, 1623, 1550, 1505, 1395, 1361; **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ 7.73 – 7.63 (m, 5H), 7.57 (d, J = 7.6 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H), 2.17 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d$_6$) δ 156.6, 154.7, 151.5, 135.5, 135.3, 133.2, 130.6, 130.0, 129.5, 124.6, 120.9, 81.5, 20.6, 12.4; **HRESI-MS** (m/z) Calculated for $C_{18}H_{16}N_6OS$ (M^+ + Na) 387.1004, found (M^+ + Na) 387.1005.

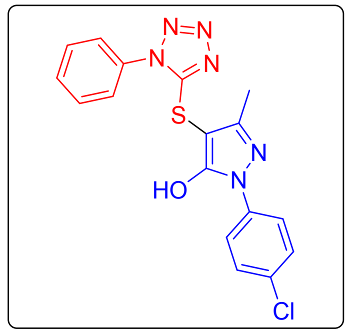


3-Methyl-4-((1-phenyl-1H-tetrazol-5-yl)thio)-1-(m-tolyl)-1H-pyrazol-5-ol (3c). White solid (mp. 161-163 °C); Yield 97% (212 mg); R_f (70% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3044, 2916, 2796, 2684, 2626, 2548, 1739, 1592, 1492; **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ 7.74

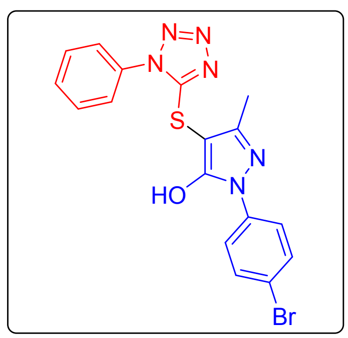


– 7.72 (m, 2H), 7.69 – 7.62 (m, 3H), 7.51 – 7.48 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 2.35 (s, 3H), 2.18 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d$_6$) δ 156.7, 154.5, 151.7, 138.4, 137.7, 133.2, 130.6, 130.0, 128.8, 126.6, 124.5, 121.3, 118.0, 82.0, 21.0, 12.2; **HRESI-MS** (m/z) Calculated for $C_{18}H_{16}N_6OS$ (M$^+$ + Na) 387.1004, found (M$^+$ + Na) 387.1001.

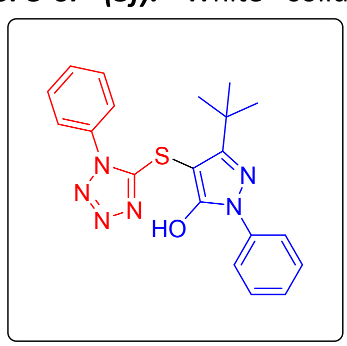
1-(4-Chlorophenyl)-3-methyl-4-((1-phenyl-1H-tetrazol-5-yl)thio)-1H-pyrazol-5-ol (3d). White solid (mp. 164-166 °C); Yield 81% (187 mg); R_f (70% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3064, 2920, 2461, 1882, 1640, 1592, 1490, 1451; **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ 7.75 – 7.71 (m, 4H), 7.68 – 7.61 (m, 3H), 7.50 (d, *J* = 8.8 Hz, 2H), 2.17 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d$_6$) δ 156.9, 154.6, 152.4, 136.8, 133.2, 130.7, 130.1, 130.0, 129.1, 124.6, 122.1, 82.0, 12.4; **HRESI-MS** (m/z) Calculated for $C_{17}H_{13}ClN_6OS$ (M$^+$ + Na) 407.0458, found (M$^+$ + Na) 407.0459.



1-(4-Bromophenyl)-3-methyl-4-((1-phenyl-1H-tetrazol-5-yl)thio)-1H-pyrazol-5-ol (3e). White solid (mp. 166-168 °C); Yield 85% (219 mg); R_f (70% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3417, 3059, 2920, 2533, 2462, 1884, 1588, 1527, 1489; **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ 7.73 – 7.64 (m, 9H), 2.17 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d$_6$) δ 157.0, 154.5, 152.4, 137.2, 133.2, 132.0, 130.7, 130.1, 124.6, 122.4, 118.2, 82.0, 12.4; **HRESI-MS** (m/z) Calculated for $C_{17}H_{13}BrN_6OS$ (M$^+$ + Na) 450.9953, found (M$^+$ + Na) 450.9955.

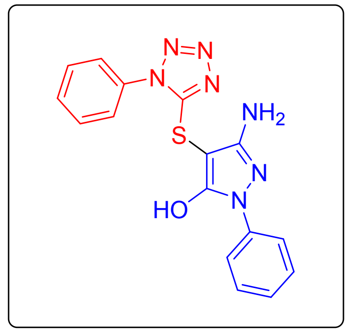


3-(Tert-butyl)-1-phenyl-4-((1-phenyl-1H-tetrazol-5-yl)thio)-1H-pyrazol-5-ol (3f). White solid (mp. 160-163 °C); Yield 94% (221 mg); R_f (70% EtOAc/hexane) 0.2;

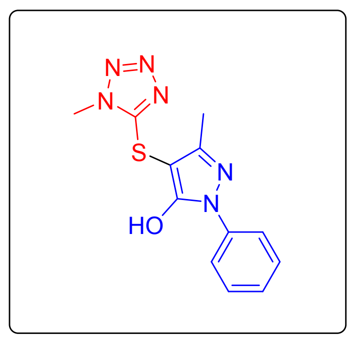


IR (KBr, cm^{-1}) 3061, 2965, 1597, 1551, 1512, 1387; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 7H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 1.29 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.7, 158.2, 155.1, 137.1, 133.0, 130.4, 129.8, 128.5, 126.2, 124.0, 121.6, 81.2, 33.7, 28.8; **HRESI-MS** (m/z) Calculated for $C_{20}H_{20}N_6OS$ (M^+ + Na) 415.1317, found (M^+ + Na) 415.1315.

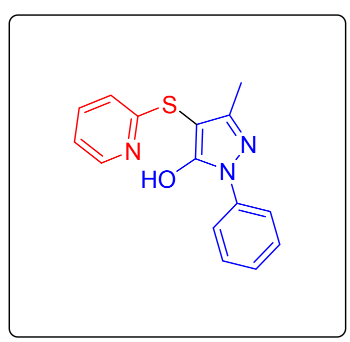
3-Amino-1-phenyl-4-((1-phenyl-1H-tetrazol-5-yl)thio)-1H-pyrazol-5-ol (3g). White solid (mp. 178-181 °C); Yield 78% (165 mg); R_f (70% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3424, 3322, 3095, 1945, 1623, 1553, 1491; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.67 – 7.59 (m, 5H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.19 (br, 2H), 7.09 (t, *J* = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 164.9, 161.4, 155.0, 139.1, 133.4, 130.5, 130.1, 128.8, 124.4, 123.2, 117.8, 65.6; **HRESI-MS** (m/z) Calculated for $C_{16}H_{13}N_7OS$ (M^+ + Na) 374.0800, found (M^+ + Na) 374.0802.



3-Methyl-4-((1-methyl-1H-tetrazol-5-yl)thio)-1-phenyl-1H-pyrazol-5-ol (4a). Pale yellow viscus liquid; Yield 88% (153 mg); R_f (80% EtOAc/hexane) 0.2 **(Column is not required crude compound is almost pure);** **IR** (Neat, cm^{-1}) 3580, 3411, 3062, 2919, 2376, 2311, 1711, 1633, 1598, 1497; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 4.01 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 157.7, 153.9, 152.0, 138.0, 129.0, 125.7, 120.6, 82.5, 33.8, 12.4; **HRESI-MS** (m/z) Calculated for $C_{12}H_{12}N_6OS$ (M^+ + Na) 311.0691, found (M^+ + Na) 311.0693.

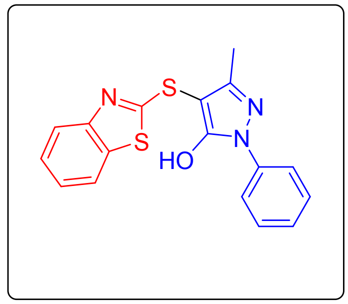


3-Methyl-1-phenyl-4-(pyridin-2-ylthio)-1H-pyrazol-5-ol (4b). Pale brown oily liquid; Yield 80% (137 mg); R_f (30% EtOAc/hexane) 0.2;

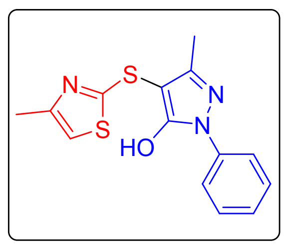


IR (Neat, cm^{-1}) 3424, 2920, 2256, 2128, 1644, 1553, 1496, 1451; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.38 (dd, *J* = 4.8, 0.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.60 (m, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.11 – 7.09 (m, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 2.14 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 161.0, 157.4, 152.4, 149.5, 138.2, 137.5, 129.3, 126.1, 121.1, 120.2, 119.1, 87.0, 12.5; **HRESI-MS** (m/z) Calculated for $C_{15}H_{13}N_3OS$ (M^+ + Na) 306.0677, found (M^+ + Na) 306.0677.

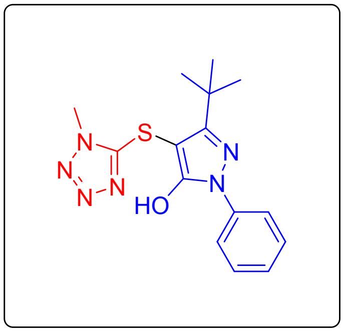
4-(Benzo[d]thiazol-2-ylthio)-3-methyl-1-phenyl-1H-pyrazol-5-ol (4c). White solid (mp. 173-175 °C); Yield 82% (166 mg); R_f (30% EtOAc/hexane) 0.2. **IR** (KBr, cm^{-1}) 3060, 2922, 2561, 2525, 2093, 1614, 1522, 1494; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.33 – 7.28 (m, 2H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 173.1, 156.8, 154.6, 151.6, 137.9, 134.8, 129.1, 126.3, 126.2, 124.1, 121.7, 121.2, 121.1, 86.2, 12.3; **HRESI-MS** (m/z) Calculated for $C_{17}H_{13}N_3OS_2$ (M^+ + Na) 362.0398, found (M^+ + Na) 362.0397;



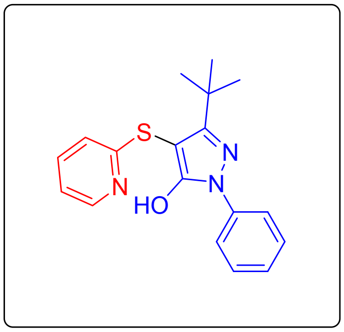
3-Methyl-4-((4-methylthiazol-2-yl)thio)-1-phenyl-1H-pyrazol-5-ol (4d). White solid (mp. 157-159 °C); Yield 78% (142 mg); R_f (30% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 2917, 2192, 2134, 1590, 1520, 1450, 1401; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.03 (s, 1H), 2.28 (s, 3H), 2.19 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 168.8, 156.5, 153.3, 151.5, 137.9, 129.0, 126.1, 121.0, 114.1, 87.0, 17.0, 12.2; **HRESI-MS** (m/z) Calculated for $C_{14}H_{13}N_3OS_2$ (M^+ + Na) 326.0398, found (M^+ + Na) 326.0398.



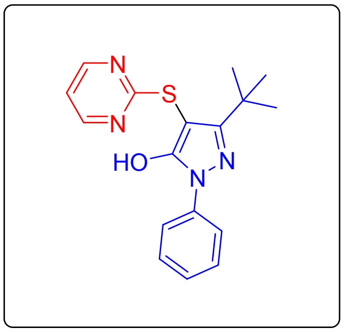
3-(Tert-butyl)-4-((1-methyl-1H-tetrazol-5-yl)thio)-1-phenyl-1H-pyrazol-5-ol (4e). White solid (mp. 194-196 °C); Yield 88% (175 mg); R_f (80% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3032, 2959, 2921, 2189, 2055, 1597, 1548, 1513; **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 4.01 (s, 3H), 1.34 (s, 9H); **^{13}C NMR** (100 MHz, DMSO-d$_6$) δ 160.4, 156.8, 154.4, 138.2, 129.0, 126.2, 121.3, 79.4, 33.7, 33.6, 29.0; **HRESI-MS** (m/z) Calculated for $C_{15}H_{18}N_6OS$ (M$^+$ + Na) 353.1161, found (M$^+$ + Na) 353.1163.



3-(Tert-butyl)-1-phenyl-4-(pyridin-2-ylthio)-1H-pyrazol-5-ol (4f). Pale yellow solid (mp. 212-214 °C); Yield 82% (161 mg); R_f (30% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 2963, 2319, 2319, 1731, 1588, 1514, 1450; **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ 8.38 (d, *J* = 4.8 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.10 – 7.06 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 1.30 (s, 9H); **^{13}C NMR** (100 MHz, DMSO-d$_6$) δ 161.7, 160.5, 156.9, 149.2, 138.6, 137.1, 129.0, 125.9, 121.2, 119.7, 119.0, 83.6, 33.7, 28.9; **HRESI-MS** (m/z) Calculated for $C_{18}H_{19}N_3OS$ (M$^+$ + Na) 348.1147, found (M$^+$ + Na) 348.1147;

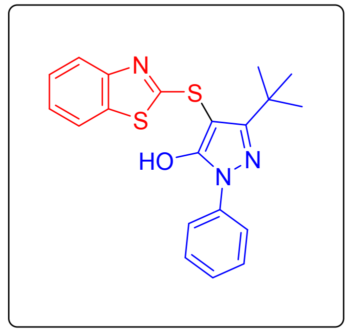


3-(Tert-butyl)-1-phenyl-4-(pyrimidin-2-ylthio)-1H-pyrazol-5-ol (4g). White solid (mp. 198-200 °C); Yield 60% (117 mg); R_f (50% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 2970, 2454, 1610, 1542, 1496, 1451; **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ 8.60 (d, *J* = 4.8 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 4.8 Hz, 1H), 1.30 (s, 9H); **^{13}C NMR** (100 MHz, DMSO-

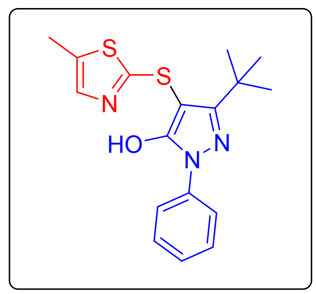


d$_6$) δ 171.7, 160.2, 157.9, 156.4, 138.7, 129.0, 125.8, 121.0, 117.7, 83.3, 33.6, 29.0; **HRESI-MS** (m/z) Calculated for $C_{17}H_{18}N_4OS$ (M^+ + Na) 349.1099, found (M^+ + Na) 349.1098.

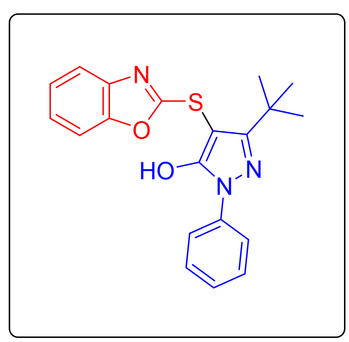
4-(Benzo[d]thiazol-2-ylthio)-3-(tert-butyl)-1-phenyl-1H-pyrazol-5-ol (4h). White solid (mp. 194-196 °C); Yield 81% (185 mg); R_f (30% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 2966, 2863, 2198, 1591, 1515, 1453, 1417; **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ 7.91 (d, J = 8.0 Hz, 1H), 7.83 – 7.78 (m, 3H), 7.50 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.34 – 7.27 (m, 2H), 1.36 (s, 9H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 173.6, 160.0, 156.6, 154.5, 138.3, 134.9, 129.0, 126.3, 126.2, 124.0, 121.8, 121.5, 121.1, 83.4, 33.8, 29.0; **HRESI-MS** (m/z) Calculated for $C_{20}H_{19}N_3OS_2$ (M^+ + Na) 404.0867, found (M^+ + Na) 404.0866.



3-(Tert-butyl)-4-((5-methylthiazol-2-yl)thio)-1-phenyl-1H-pyrazol-5-ol (4i). White solid (mp. 210-213 °C); Yield 80% (164 mg); R_f (30% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 2966, 2915, 2861, 2232, 2056, 1734, 1593, 1513; **^{1}H NMR** (400 MHz, DMSO-d$_6$) δ 7.73 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.02 (s, 1H), 2.28 (s, 3H), 1.32 (s, 9H); **^{13}C NMR** (100 MHz, DMSO-d$_6$) δ 169.4, 159.8, 156.4, 153.0, 138.3, 129.0, 126.2, 121.4, 114.0, 84.2, 33.7, 29.0, 17.0; **HRESI-MS** (m/z) Calculated for $C_{17}H_{19}N_3OS_2$ (M^+ + Na) 368.0867, found (M^+ + Na) 368.0865.

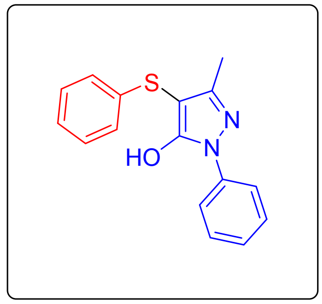


4-(Benzo[d]oxazol-2-ylthio)-3-(tert-butyl)-1-phenyl-1H-pyrazol-5-ol (4j). White solid (mp. 172-174 °C); Yield 54% (118 mg); R_f (30% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3039, 2967, 2038, 1992, 1595, 1550, 1506, 1444; **^{1}H NMR**

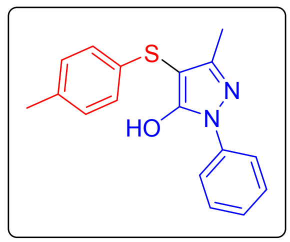


(400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.33 – 7.23 (m, 2H), 7.10 – 7.06 (m, 1H), 7.06– 6.89 (m, 2H), 1.42 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 160.5, 156.3, 150.4, 139.4, 138.8, 128.8, 126.0, 124.6, 124.3, 121.5, 117.2, 109.8, 78.7, 33.9, 29.2; **HRESI-MS** (m/z) Calculated for $C_{20}H_{19}N_3O_2S$ (M^+ + Na) 388.1096, found (M^+ + Na) 388.1098.

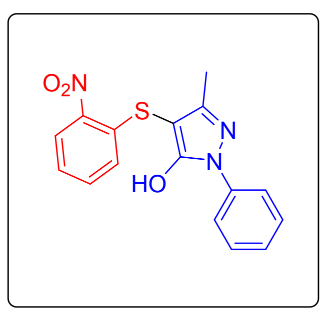
3-Methyl-1-phenyl-4-(phenylthio)-1H-pyrazol-5-ol (5a).[1,2] White solid (mp. 194-197 °C); Yield 92% (312 mg); R_f (20% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3057, 2924, 2057, 1617, 1586, 1542, 1497; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.77 (dd, *J* = 8.0, 0.8 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.29 – 7.25 (m, 3H), 7.13 – 7.09 (m, 3H), 2.15 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 157.0, 152.1, 138.4, 138.2, 129.0, 128.9, 125.7, 125.0, 124.9, 120.8, 87.6, 12.3; **HRESI-MS** (m/z) Calculated for $C_{16}H_{14}N_2OS$ (M^+ + Na) 305.0725, found (M^+ + Na) 305.0724.



3-Methyl-1-phenyl-4-(p-tolylthio)-1H-pyrazol-5-ol (5b).[1,2] White solid (mp. 202-204 °C); Yield 94% (335 mg); R_f (20% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3015, 2916, 1738, 1606, 1488, 1398, 1308; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 2.22 (s, 3H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 156.8, 152.0, 138.2, 134.8, 134.3, 129.7, 128.9, 125.7, 125.4, 120.7, 88.3, 20.4, 12.3. **HRESI-MS** (m/z) Calculated for $C_{17}H_{16}N_2OS$ (M^+ + Na) 319.0881, found (M^+ + Na) 319.0880;

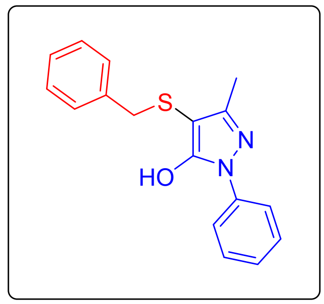


3-Methyl-4-((2-nitrophenyl)thio)-1-phenyl-1H-pyrazol-5-ol (5c).[3] Pale yellow solid (mp. 200-202 °C); Yield 79% (310 mg); R_f (50% EtOAc/hexane) 0.3; **IR** (KBr cm^{-1}) 3064, 2856, 2576, 1624, 1595, 1560, 1512, 1450, 1402, 1334; **^{1}H NMR**

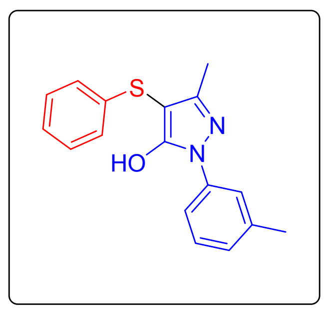


(400 MHz, DMSO-d_6) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 6.8 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 156.7, 152.1, 144.8, 138.5, 138.0, 134.5, 129.0, 126.9, 126.0, 126.0, 125.6, 120.9, 86.2, 12.3; **HRESI-MS** (m/z) Calculated for $C_{16}H_{13}N_3O_3S$ (M^+ + H) 328.0756, found (M^+ + Na) 328.0756.

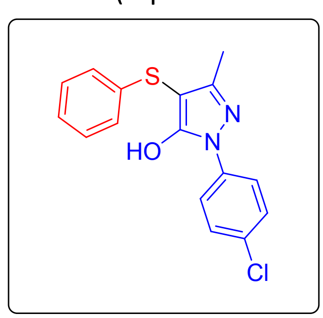
4-(Benzylthio)-3-methyl-1-phenyl-1H-pyrazol-5-ol (5d). White solid (mp. 180-182 °C); Yield 73% (260 mg); R_f (20% EtOAc/hexane) 0.2; **IR** (KBr cm^{-1}) 3034, 2916, 2603, 1724, 1614, 1539, 1494, 1456; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.26 – 7.21 (m, 4H), 7.16 (d, *J* = 7.6 Hz, 2H), 3.75 (s, 2H), 1.75 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 155.5, 152.3, 138.4, 138.1, 129.0, 128.9, 128.1, 126.7, 125.3, 120.3, 89.8, 39.1, 11.8; **HRESI-MS** (m/z) Calculated for $C_{17}H_{16}N_2OS$ (M^+ + Na) 319.0881, found (M^+ + Na) 319.0883.



3-Methyl-4-(phenylthio)-1-(m-tolyl)-1H-pyrazol-5-ol (5e). White solid (mp. 170-174 °C); Yield 86% (303 mg); R_f (20% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3053, 2916, 2502, 1605, 1578, 1480; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.57 – 7.53 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.13 – 7.07 (m, 4H), 2.35 (s, 3H), 2.13 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 156.6, 152.0, 138.5, 138.4, 138.1, 129.1, 128.8, 126.5, 125.0, 125.0, 121.4, 118.0, 87.2, 21.1, 12.3; **HRESI-MS** (m/z) Calculated for $C_{17}H_{16}N_2OS$ (M^+ + Na) 319.0881, found (M^+ + Na) 319.0882.

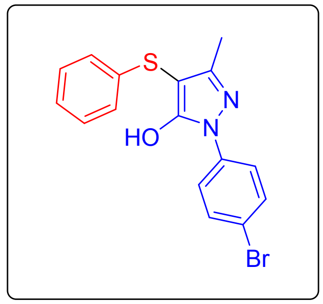


1-(4-Chlorophenyl)-3-methyl-4-(phenylthio)-1H-pyrazol-5-ol (5f). White solid (mp. 215-218 °C); Yield 82% (311 mg); R_f (20% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3066,

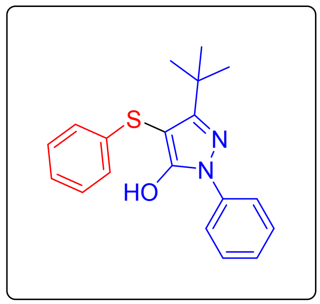


2674, 1623, 1542, 1487, 1392; ^{1}**H NMR** (400 MHz, DMSO-d_6) δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.53 – 7.51 (m, 2H), 7.27 (t, *J* = 8.0 Hz, 2H), 7.13 – 7.07 (m, 3H), 2.12 (s, 3H); ^{13}**C NMR** (100 MHz, DMSO-d_6) δ 157.0, 152.6, 138.2, 137.0, 129.8, 129.1, 129.0, 125.1, 125.0, 122.1, 87.6, 12.4; **HRESI-MS** (m/z) Calculated for $C_{16}H_{13}ClN_2OS$ (M^+ + Na) 339.0335, found (M^+ + Na) 339.0337;

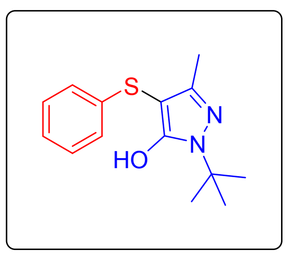
1-(4-Bromophenyl)-3-methyl-4-(phenylthio)-1H-pyrazol-5-ol (5g). White solid (mp. 212-214 °C); Yield 82% (355 mg); R_f (20% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3063, 2670, 1619, 1583, 1484, 1392; **1H NMR** (400 MHz, DMSO-d_6) δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 9.2 Hz, 2H), 7.27 (t, *J* = 7.7 Hz, 2H), 7.13 – 7.07 (m, 3H), 2.12 (s, 3H); ^{13}**C NMR** (100 MHz, DMSO-d_6) δ 157.1, 152.6, 138.2, 137.4, 131.9, 129.1, 125.0, 125.0, 122.3, 118.0, 87.7, 12.3; **HRESI-MS** (m/z) Calculated for $C_{16}H_{13}BrN_2OS$ (M^+ + Na) 382.9830, found (M^+ + Na) 382.9830.



3-(Tert-butyl)-1-phenyl-4-(phenylthio)-1H-pyrazol-5-ol (5h). White solid (mp. 180-182 °C); Yield 95% (370 mg); R_f (10% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 2960, 2665, 2188, 1618, 1580, 1454; ^{1}**H NMR** (400 MHz, DMSO-d_6) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.30 – 7.24 (m, 3H), 7.10 – 7.03 (m, 3H), 1.30 (s, 9H). ^{13}**C NMR** (100 MHz, DMSO-d_6) δ 160.5, 156.6, 139.1, 138.6, 128.9, 128.9, 125.9, 124.7, 124.5, 121.3, 83.8, 33.7, 29.0; **HRESI-MS** (m/z) Calculated for $C_{19}H_{20}N_2OS$ (M^+ + Na) 347.1194, found (M^+ + Na) 347.1195.

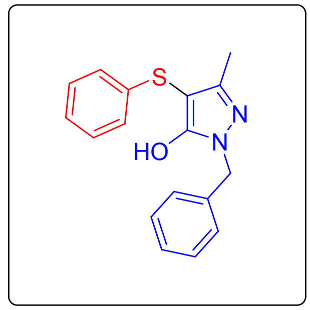


1-(Tert-butyl)-3-methyl-4-(phenylthio)-1H-pyrazol-5-ol (5i). White solid (mp. 220-222 °C); Yield 83% (260 mg); R_f (20% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3068, 2975, 2596, 1598, 1517, 1478; ^{1}**H NMR** (400 MHz, DMSO-d_6) δ 7.23 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz,



1H), 6.96 (d, J = 8.0 Hz, 1H), 1.97 (s, 3H), 1.51 (s, 9H); **^{13}C NMR** (100 MHz, DMSO-d$_6$) δ 170.2, 155.0, 147.3, 139.1, 128.8, 124.5, 84.9, 58.01, 28.4, 12.4; **HRESI-MS** (m/z) Calculated for $C_{14}H_{18}N_2OS$ (M^+ + Na) 285.1038, found (M^+ + Na) 285.1040.

1-Benzyl-3-methyl-4-(phenylthio)-1H-pyrazol-5-ol (5m) : White solid (mp. 182-184 °C); Yield 81% (288 mg); R_f (30% EtOAc/hexane) 0.2; **IR** (KBr, cm^{-1}) 3058, 2918, 2413, 2026, 1941, 1578, 1536, 1445; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (t, J = 8.0 Hz, 2H), 7.29 - 7.20 (m, 5H), 7.09 (t, J = 8.0 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 5.08 (s, 2H), 2.02 (s, 3H); **^{13}C NMR** (100 MHz, DMSO) δ 156.9, 150.2, 139.0, 137.5, 128.94, 128.5, 127.4, 127.2, 124.71, 124.6, 84.8, 49.2, 12.2; **HRESI-MS** (m/z) Calculated for $C_{17}H_{16}N_2OS$ (M^+ + H) 297.1062, found (M^+ + Na) 297.1064.



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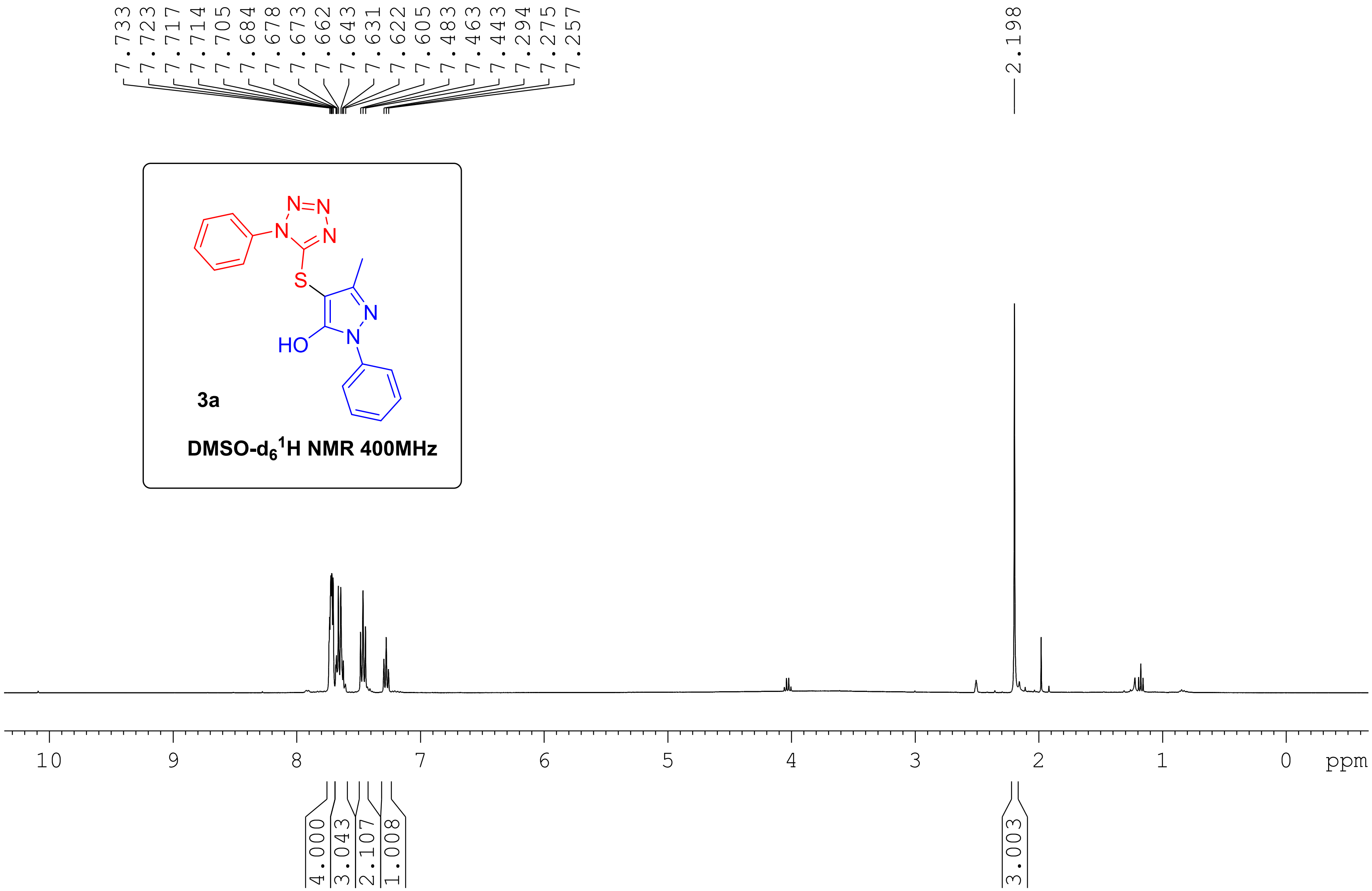
7.733
7.723
7.717
7.714
7.705
7.684
7.678
7.673
7.662
7.643
7.631
7.622
7.605
7.483
7.463
7.443
7.294
7.275
7.257
2.198
3a
DMSO-d$_6$ ^{1}H NMR 400MHz
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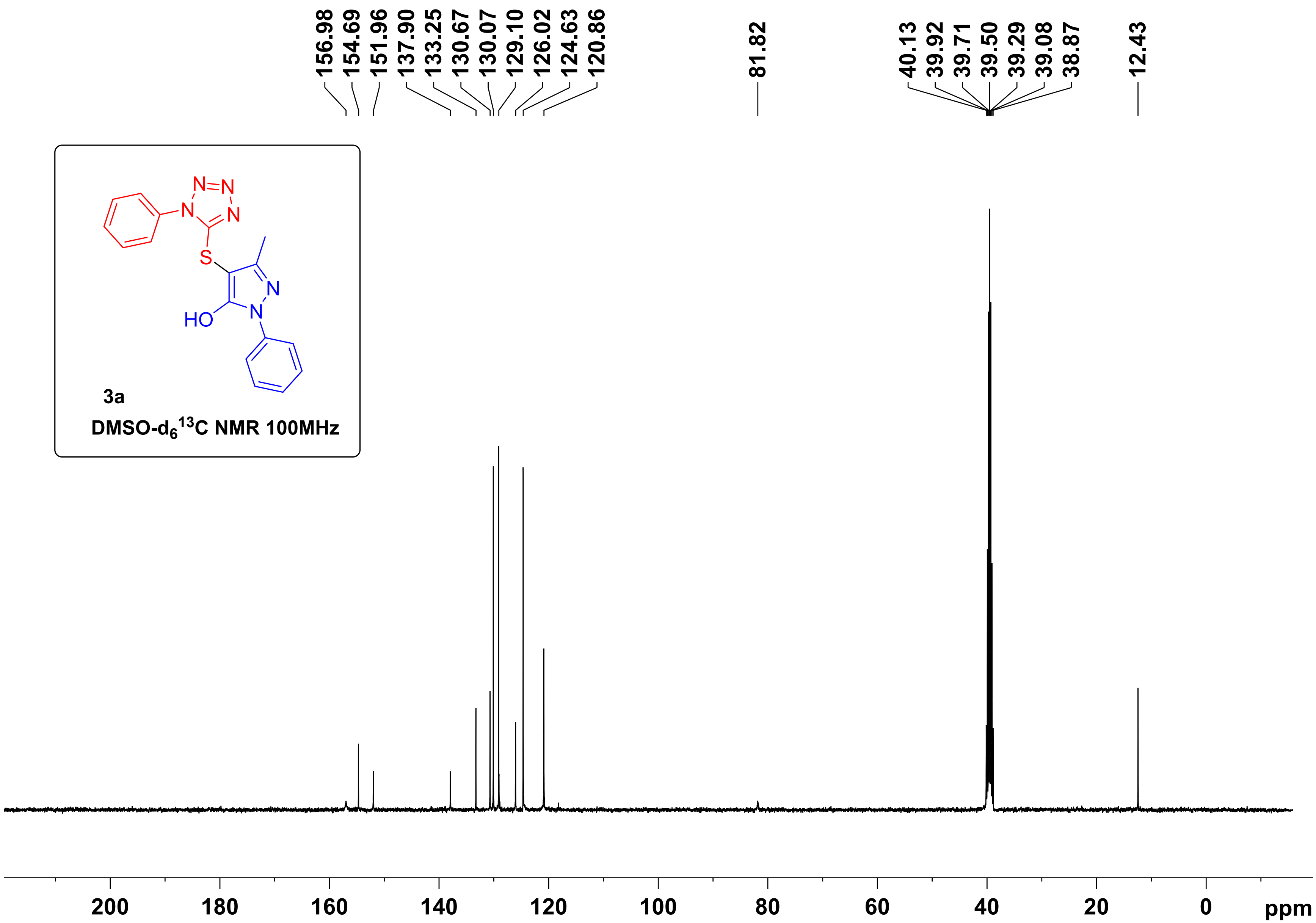
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124.63
120.86
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40.13
39.92
39.71
39.50
39.29
39.08
38.87
12.43
N=N
N
N
S
N
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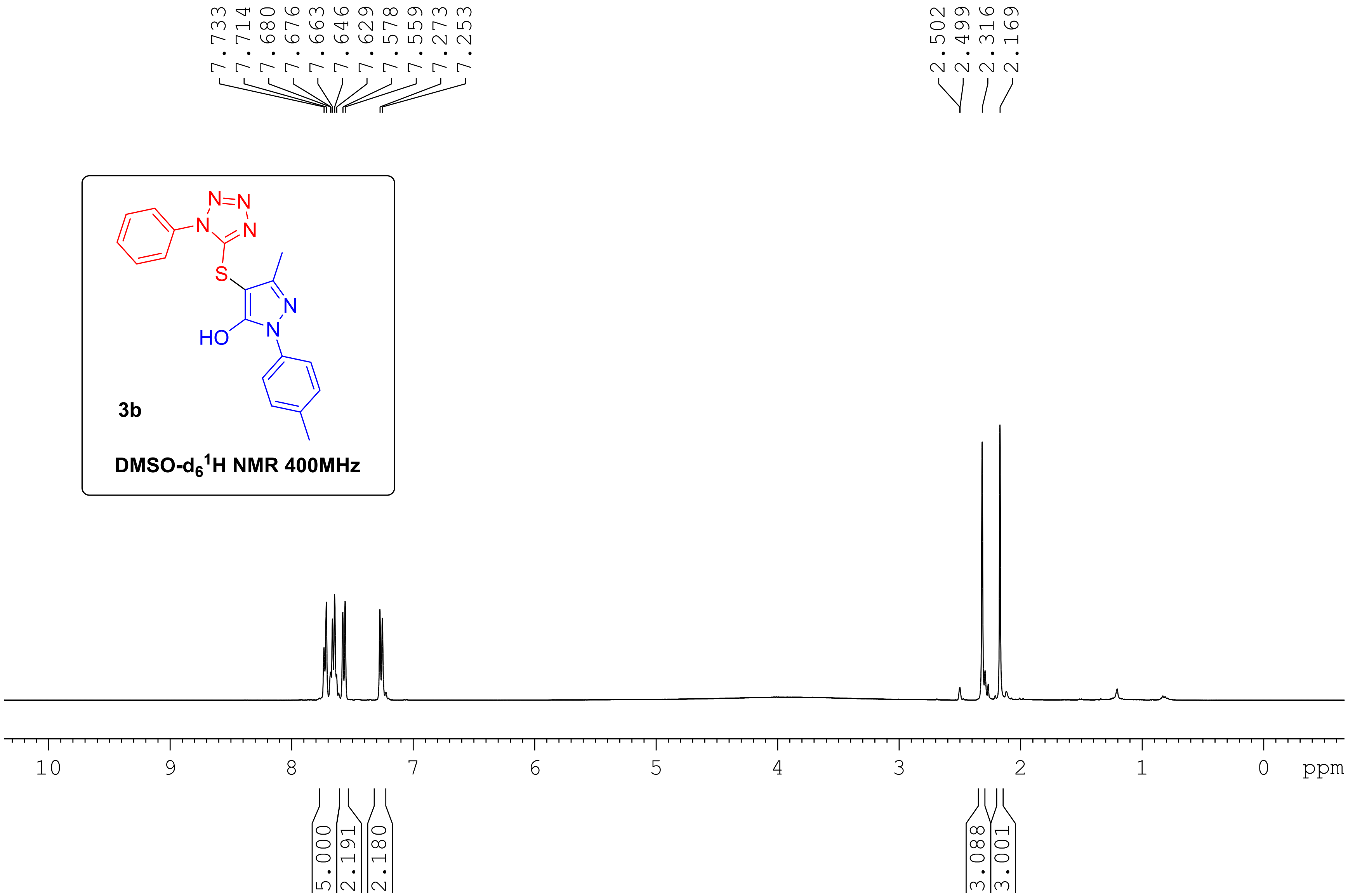
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7.273
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2.499
2.316
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N
S
N
N
HO
3b
DMSO-d6 1H NMR 400MHz
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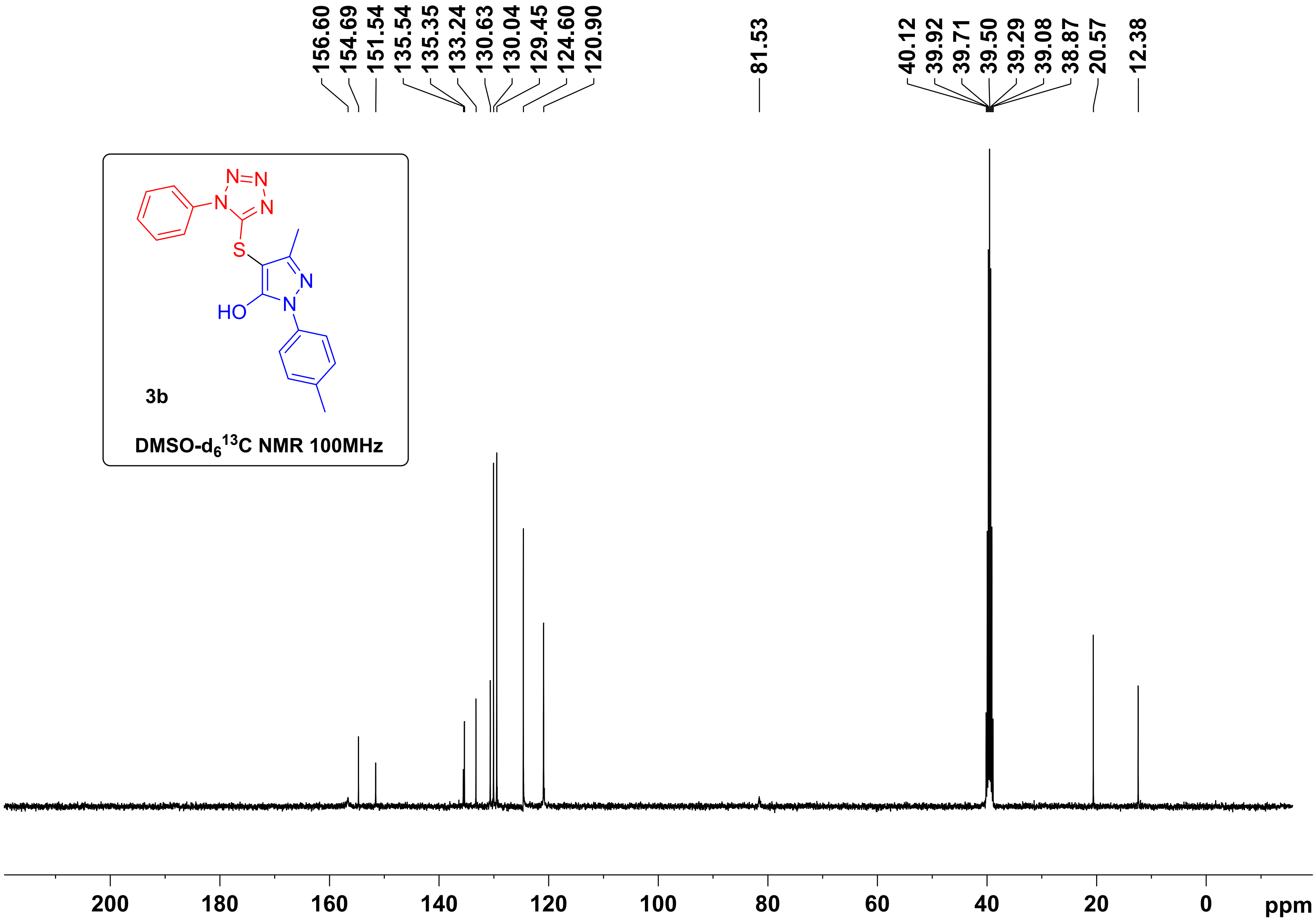
3.001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120.90
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40.12
39.92
39.71
39.50
39.29
39.08
38.87
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DMSO-d6 13C NMR 100MHz
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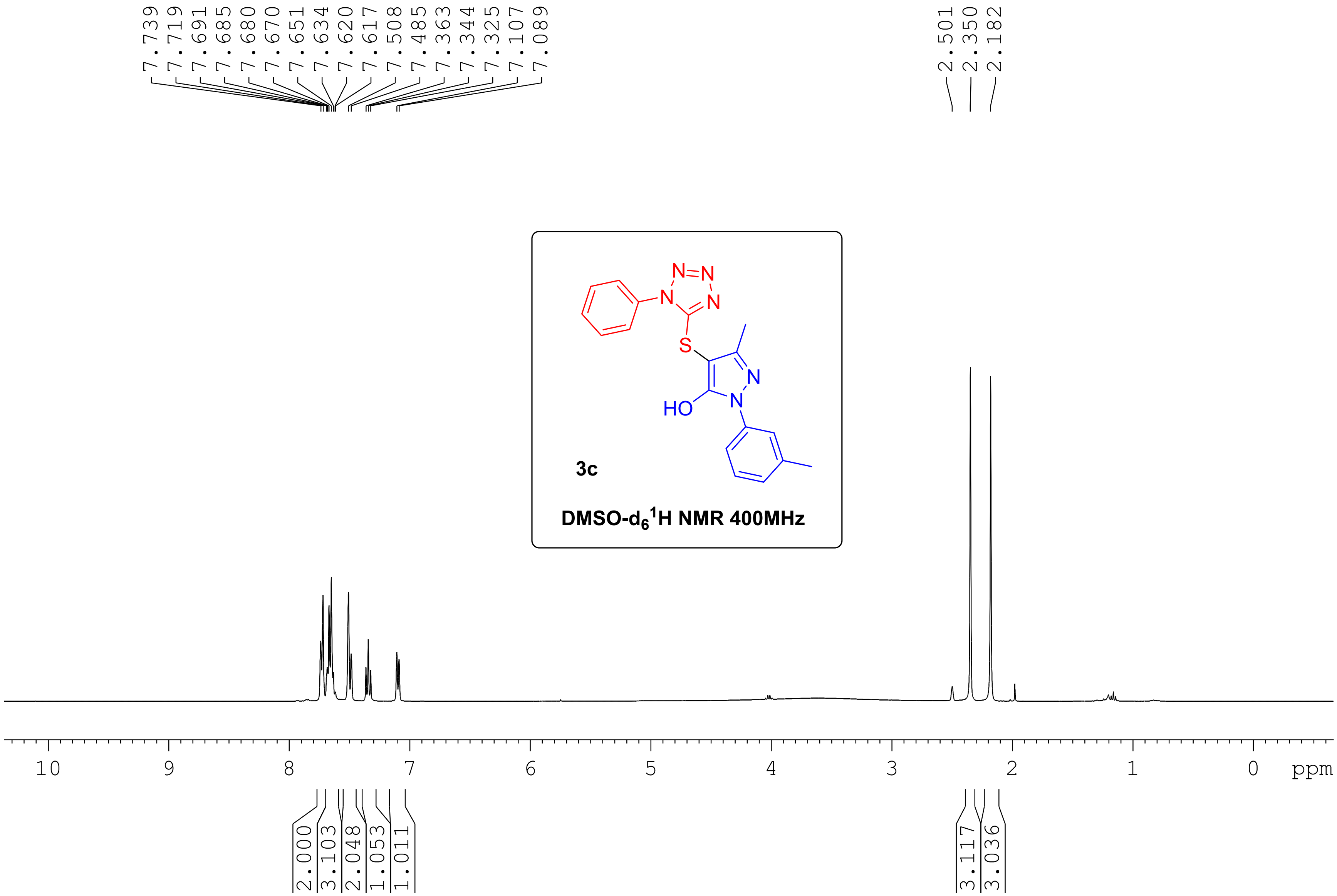

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7.363
7.344
7.325
7.107
7.089
2.501
2.350
2.182
N
N
N
N
S
N
N
HO
3c
DMSO-d6 1H NMR 400MHz
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9
8
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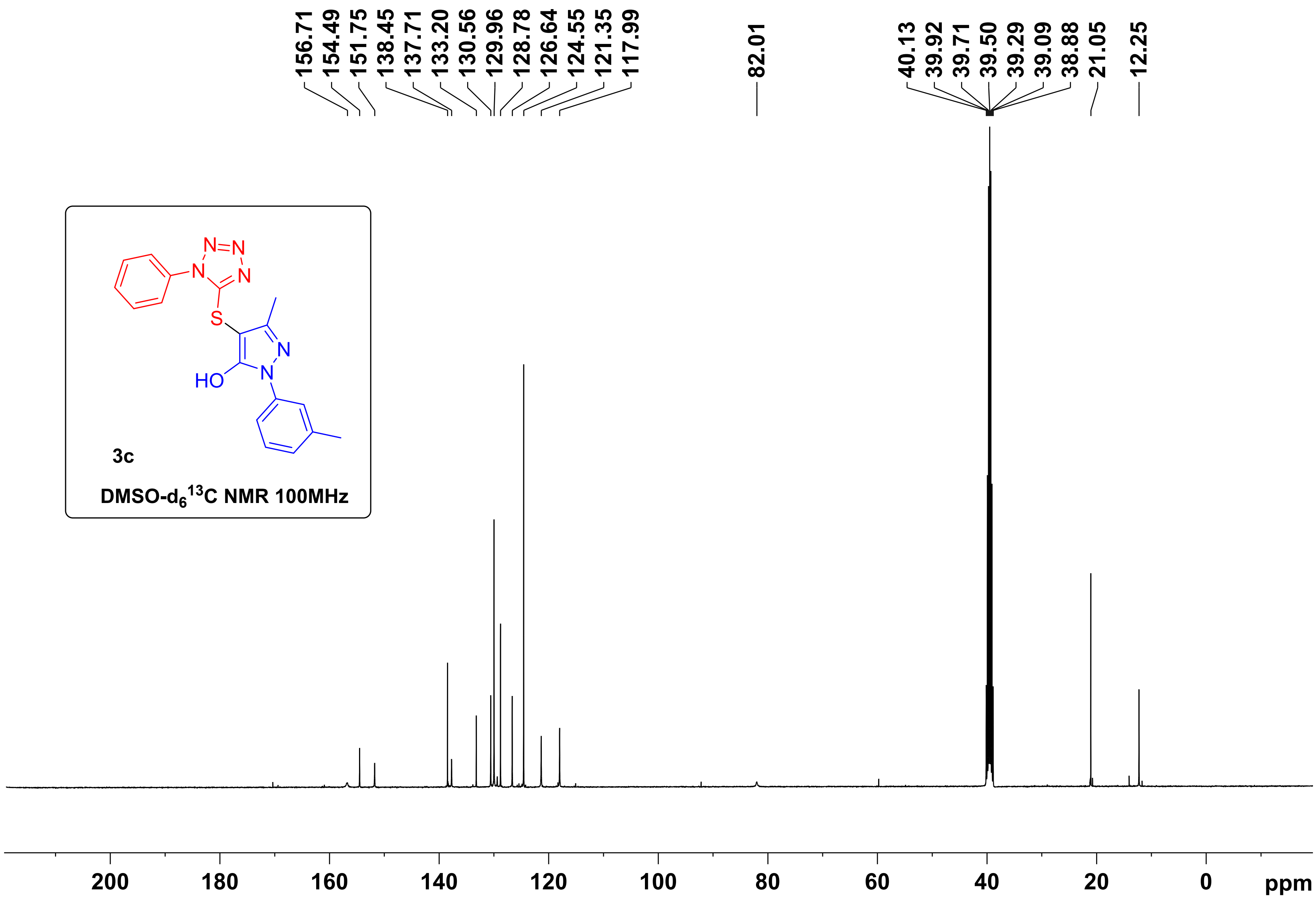
3.036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82.01
40.13
39.92
39.71
39.50
39.29
39.09
38.88
21.05
12.25
N
N
N
N
S
N
N
HO
3c
DMSO-d_6 ^{13}C NMR 100MHz
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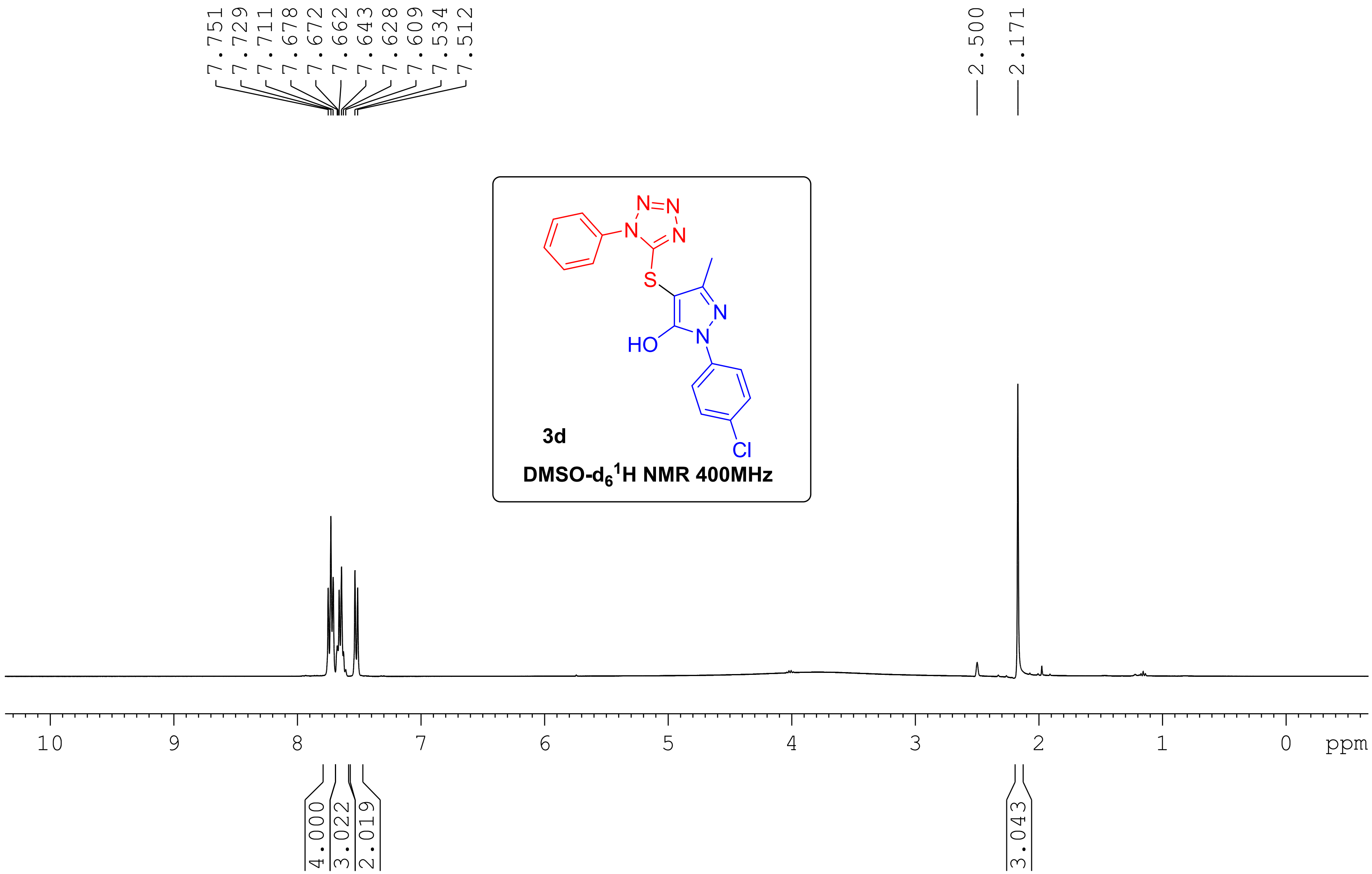
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N
N
N
S
N
N
HO
Cl
3d
DMSO-d6 1H NMR 400MHz
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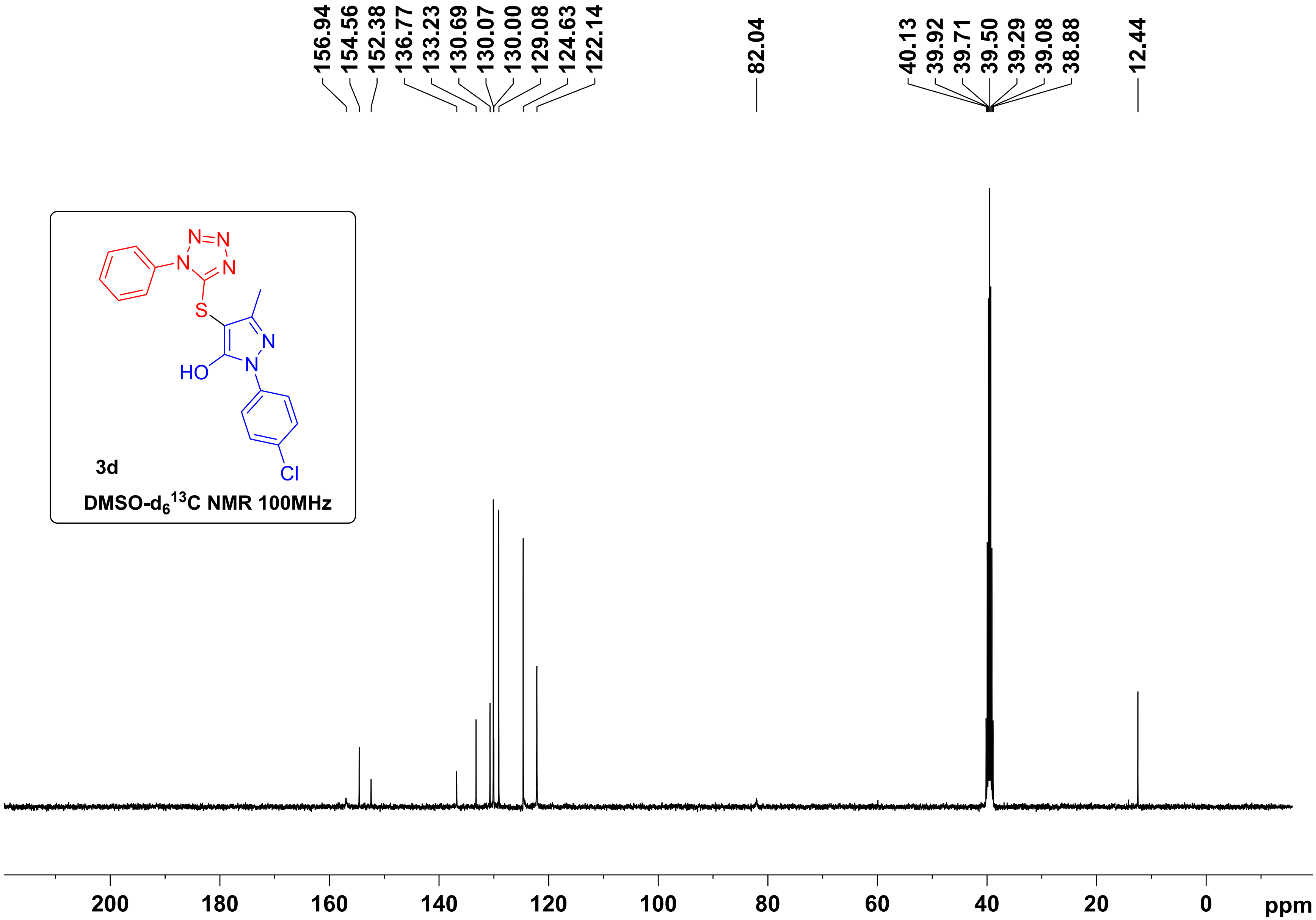
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122.14
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39.92
39.71
39.50
39.29
39.08
38.88
12.44
N
N
N
N
S
N
N
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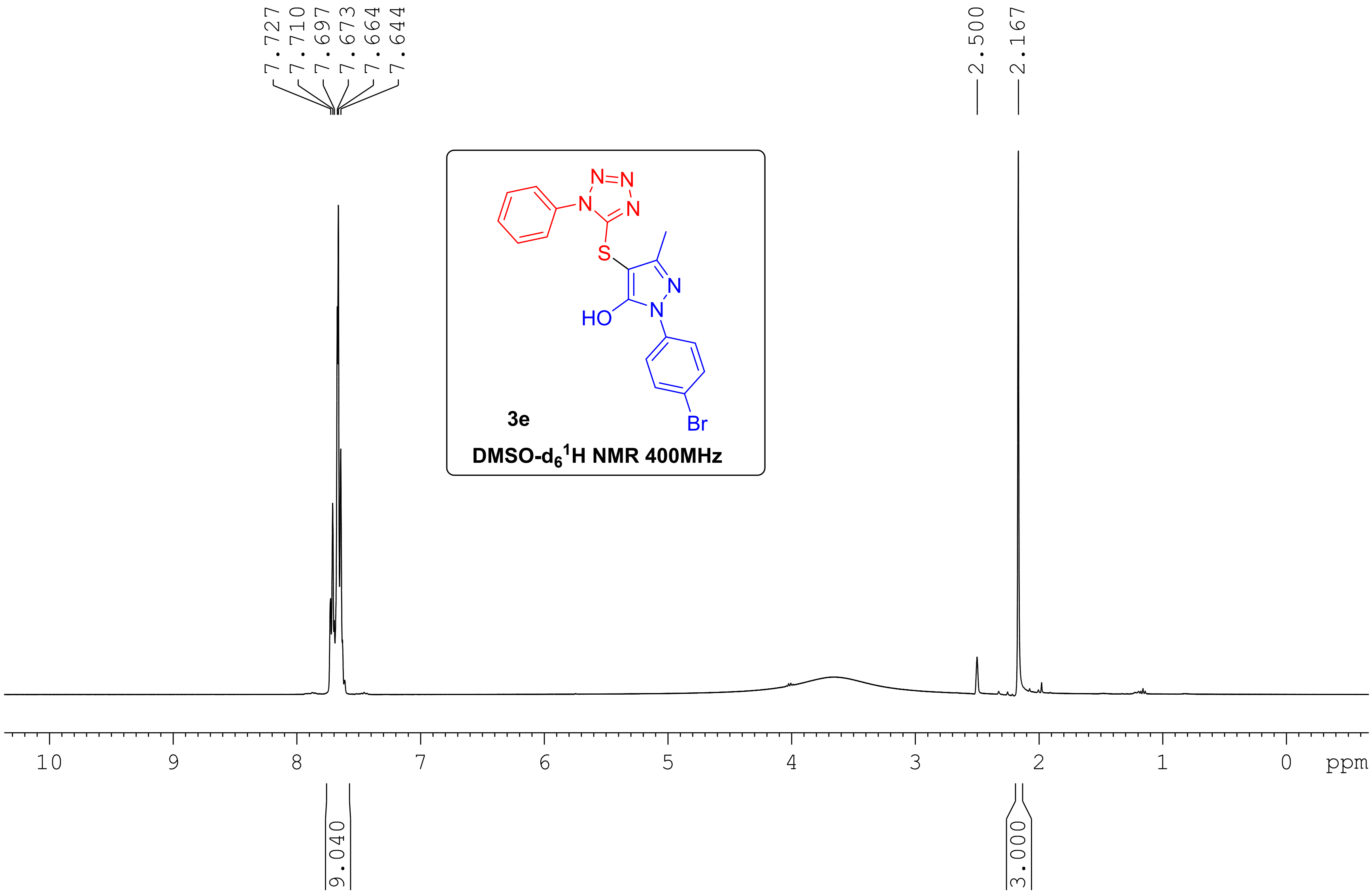
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2.167
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N
N
N
S
N
N
HO
Br
3e
DMSO-d_6 ^{1}H NMR 400MHz
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9
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2
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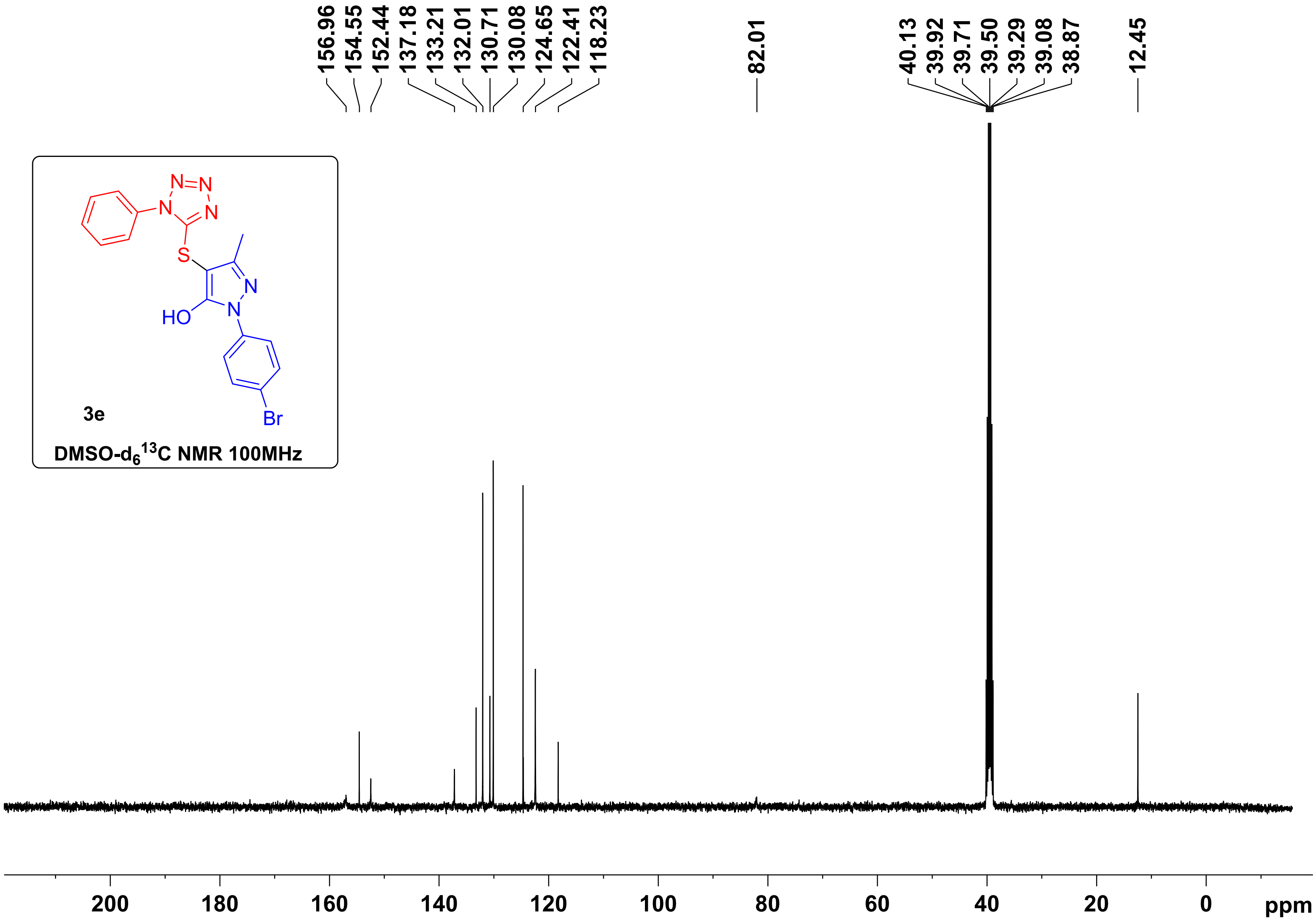
9.040
3.000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118.23
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40.13
39.92
39.71
39.50
39.29
39.08
38.87
12.45
N
N
N
N
S
N
N
HO
Br
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DMSO-d6 13C NMR 100MHz
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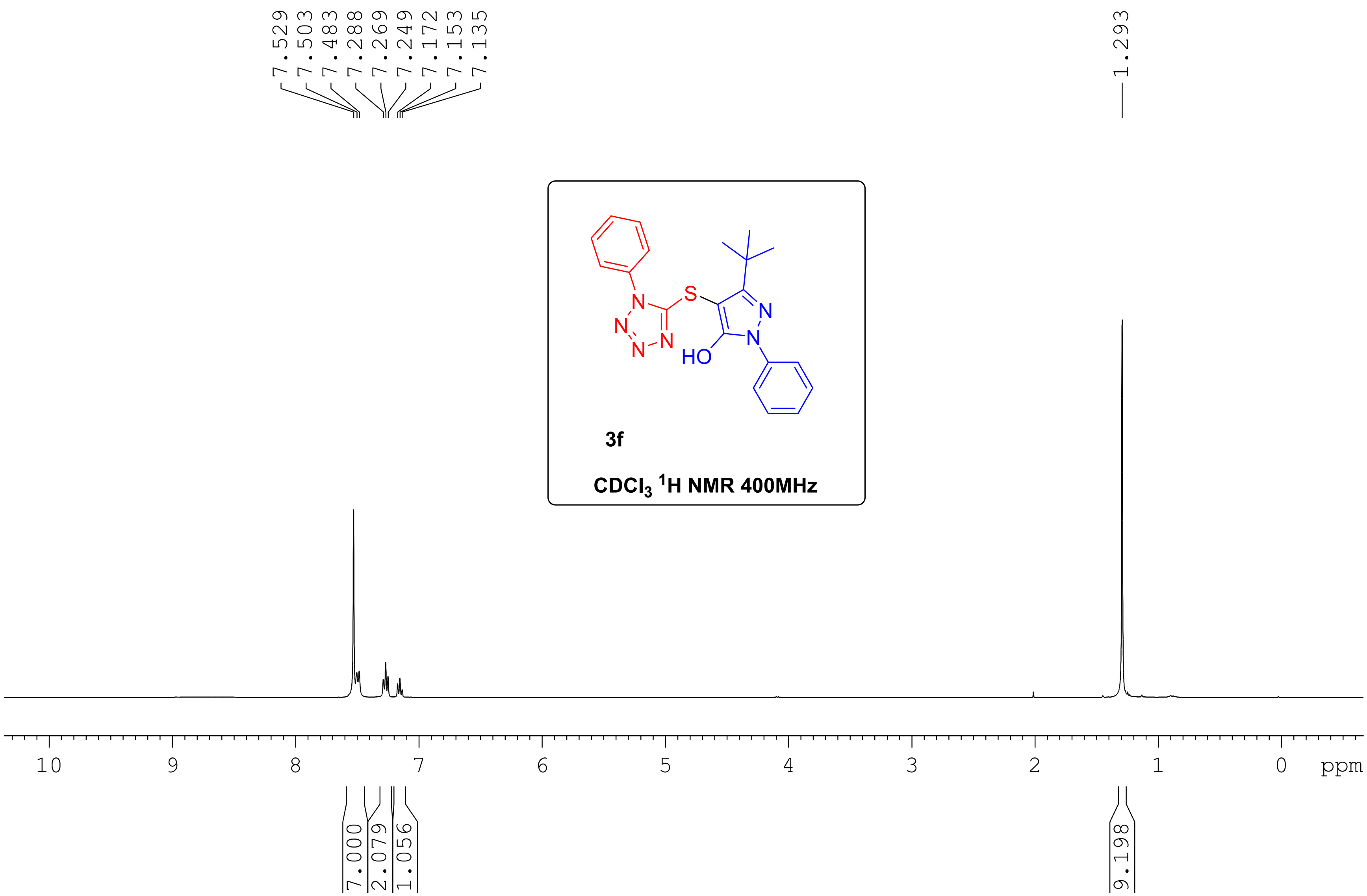
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7.249
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7.153
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3f
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7
6
5
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0
ppm
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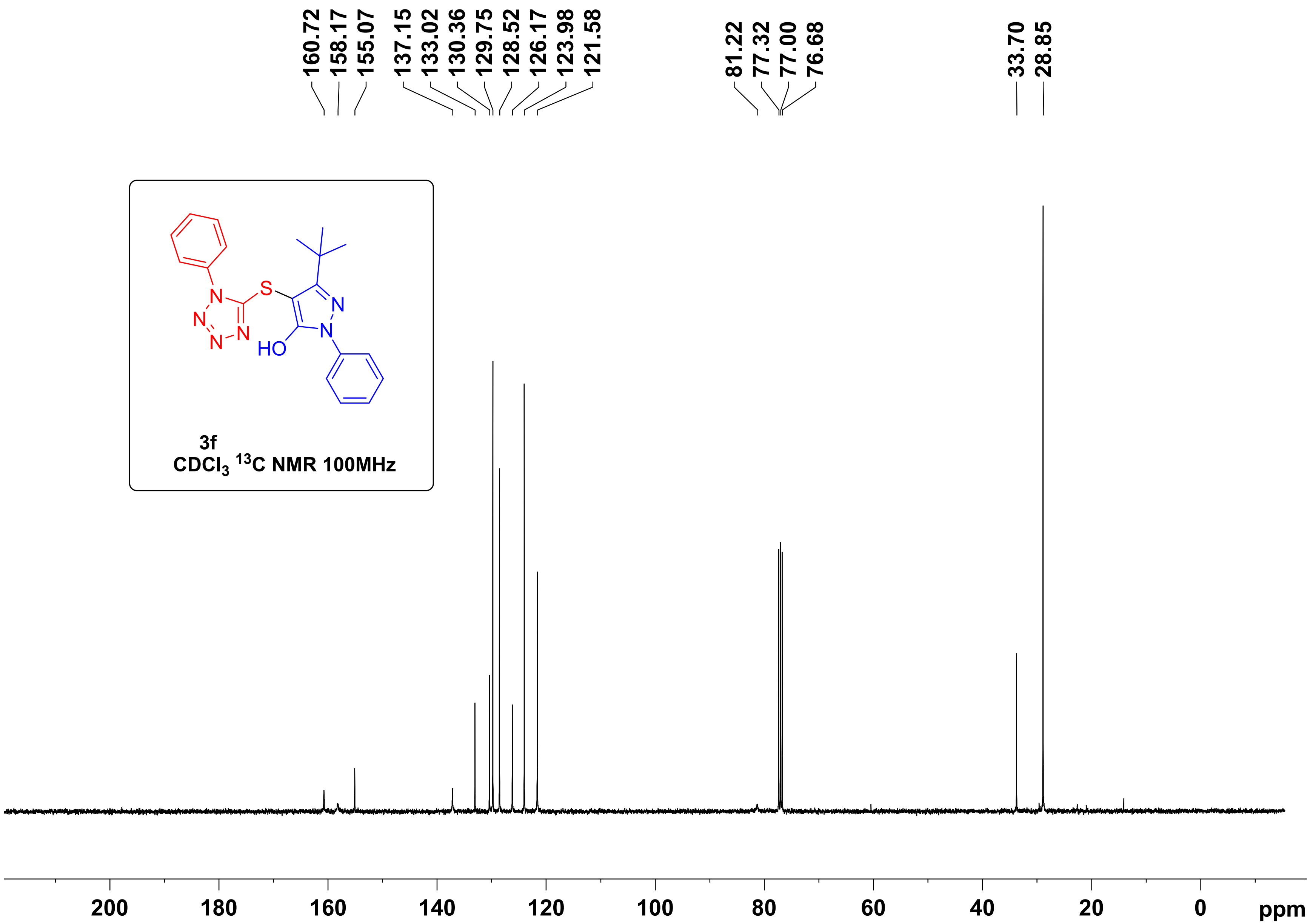
2.079
1.056
9.198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129.75
128.52
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123.98
121.58
81.22
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77.00
76.68
33.70
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S
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CDCl3 13C NMR 100MHz
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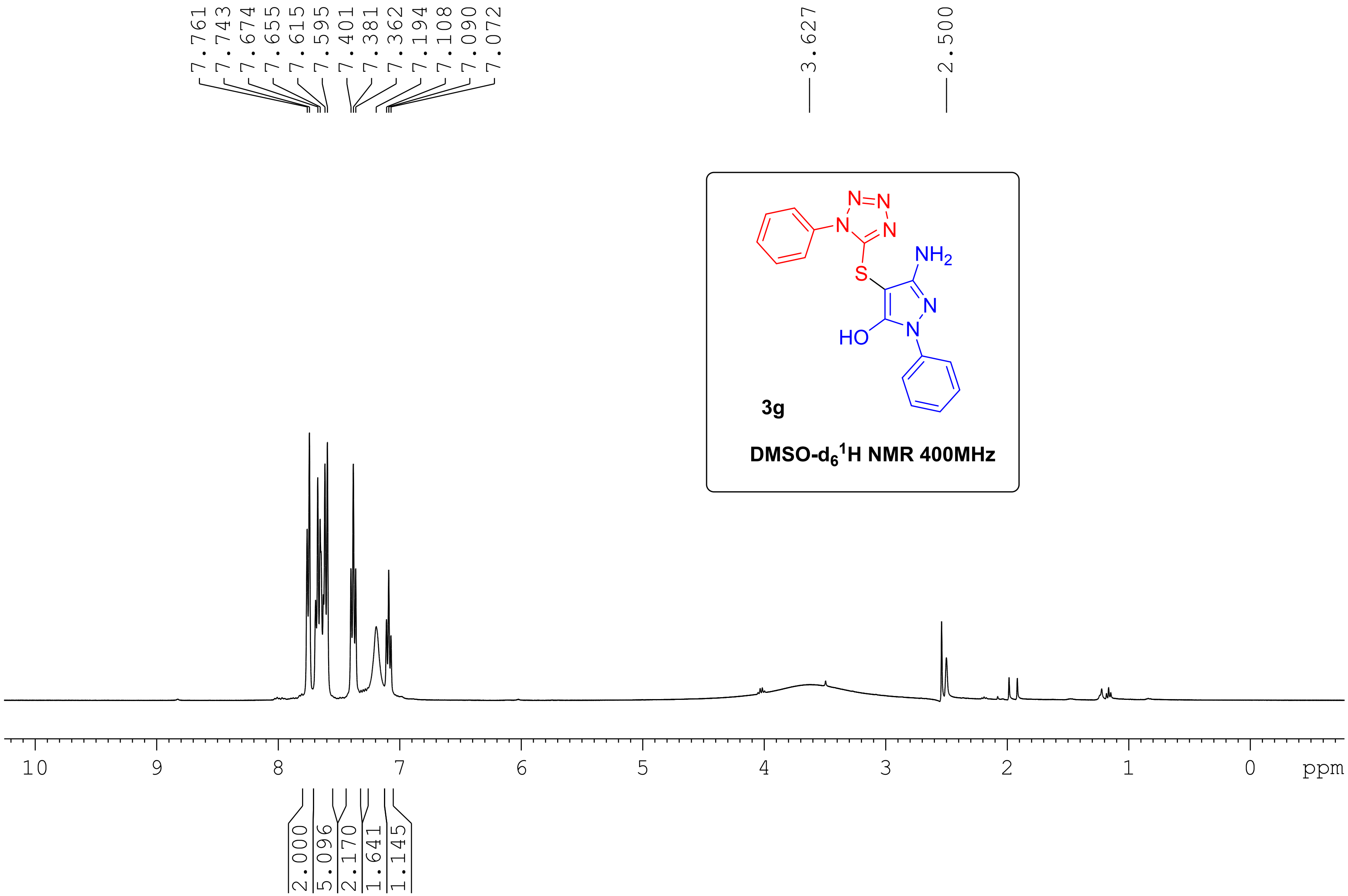
60
40
20
0
ppm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7.595
7.401
7.381
7.362
7.194
7.108
7.090
7.072
3.627
2.500
3g
DMSO-d6 1H NMR 400MHz
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5
4
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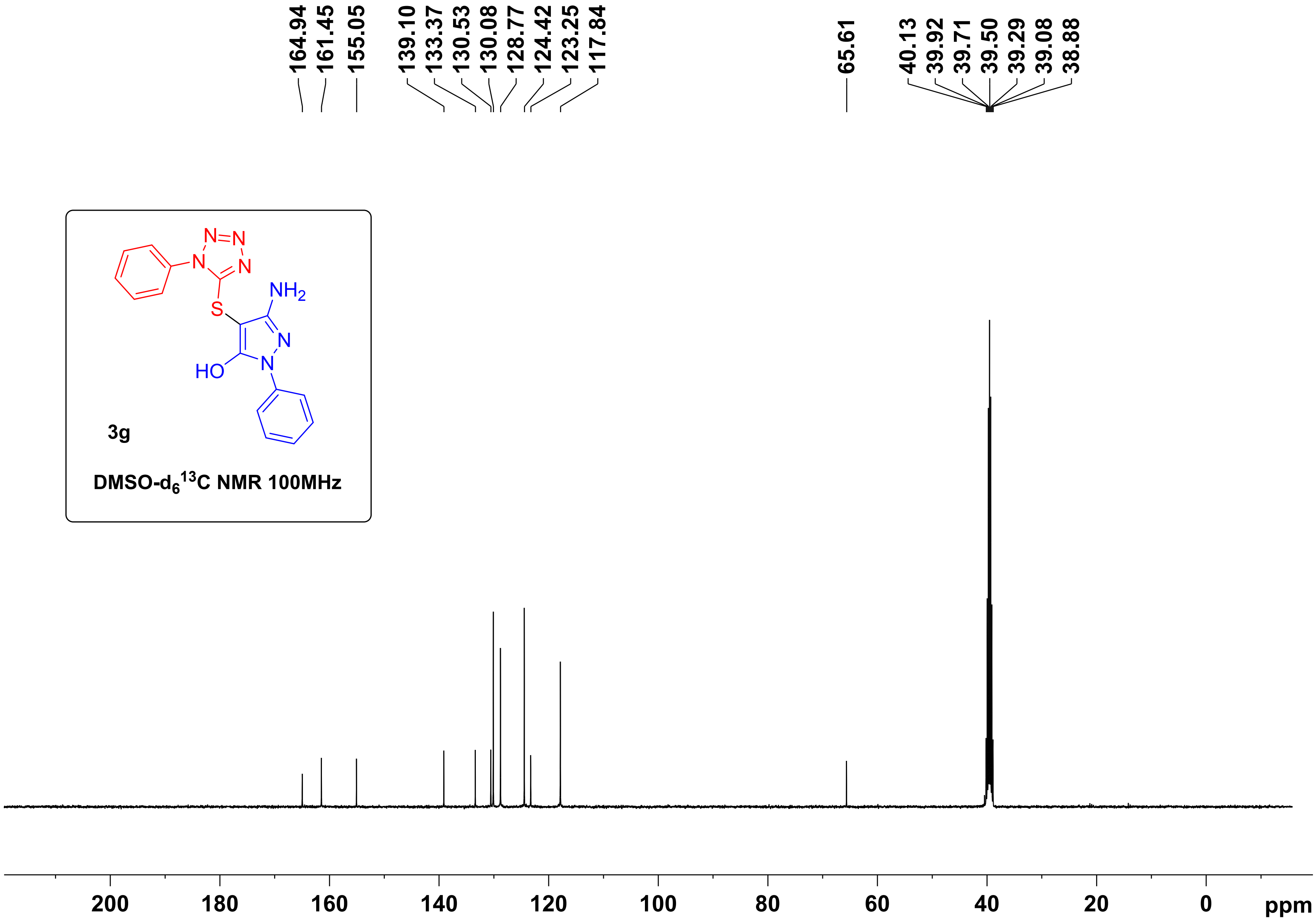
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40.13
39.92
39.71
39.50
39.29
39.08
38.88
NH2
N
N
N
N
S
N
N
HO
3g
DMSO-d6 13C NMR 100MHz
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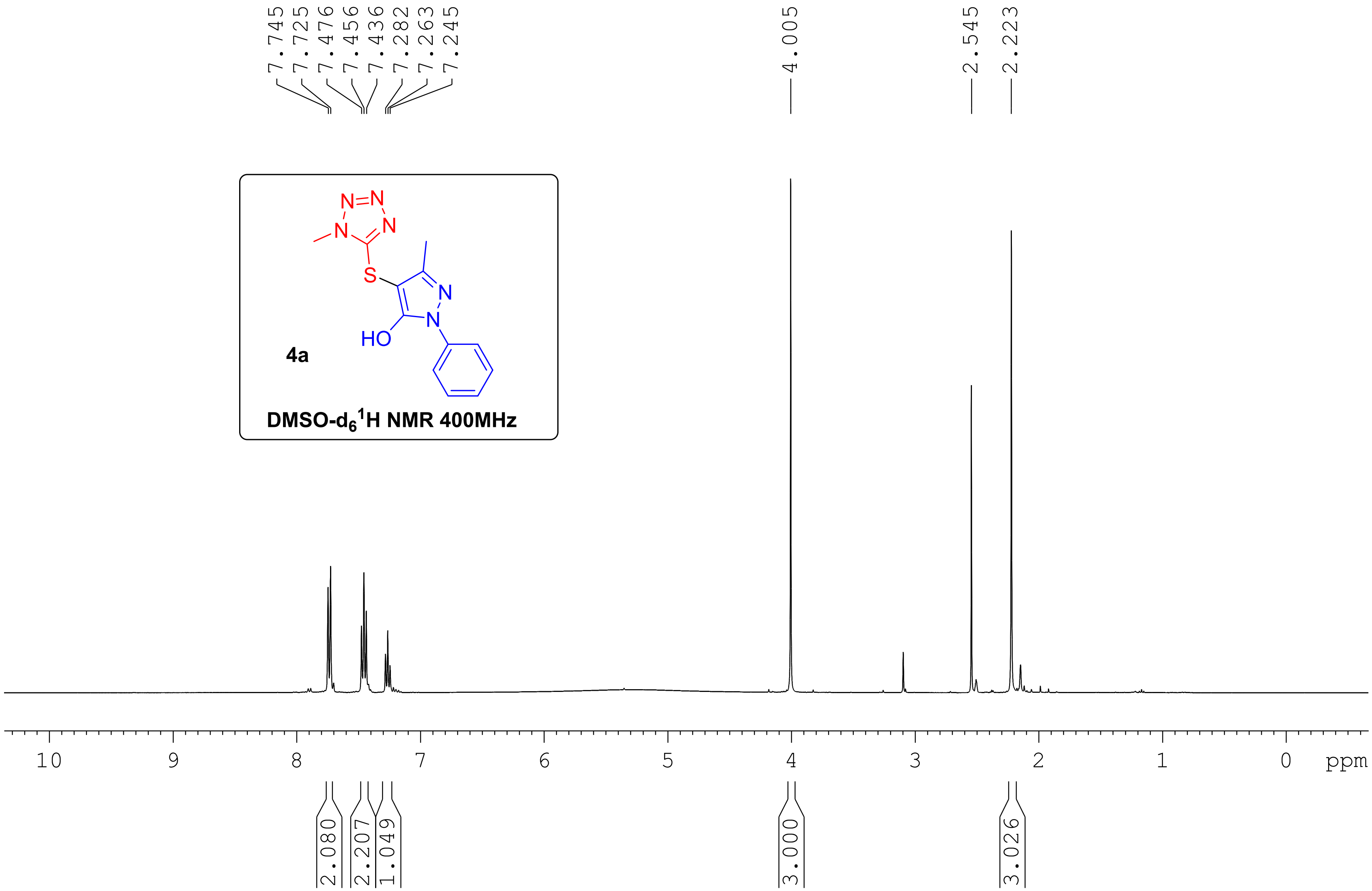
20
0
ppm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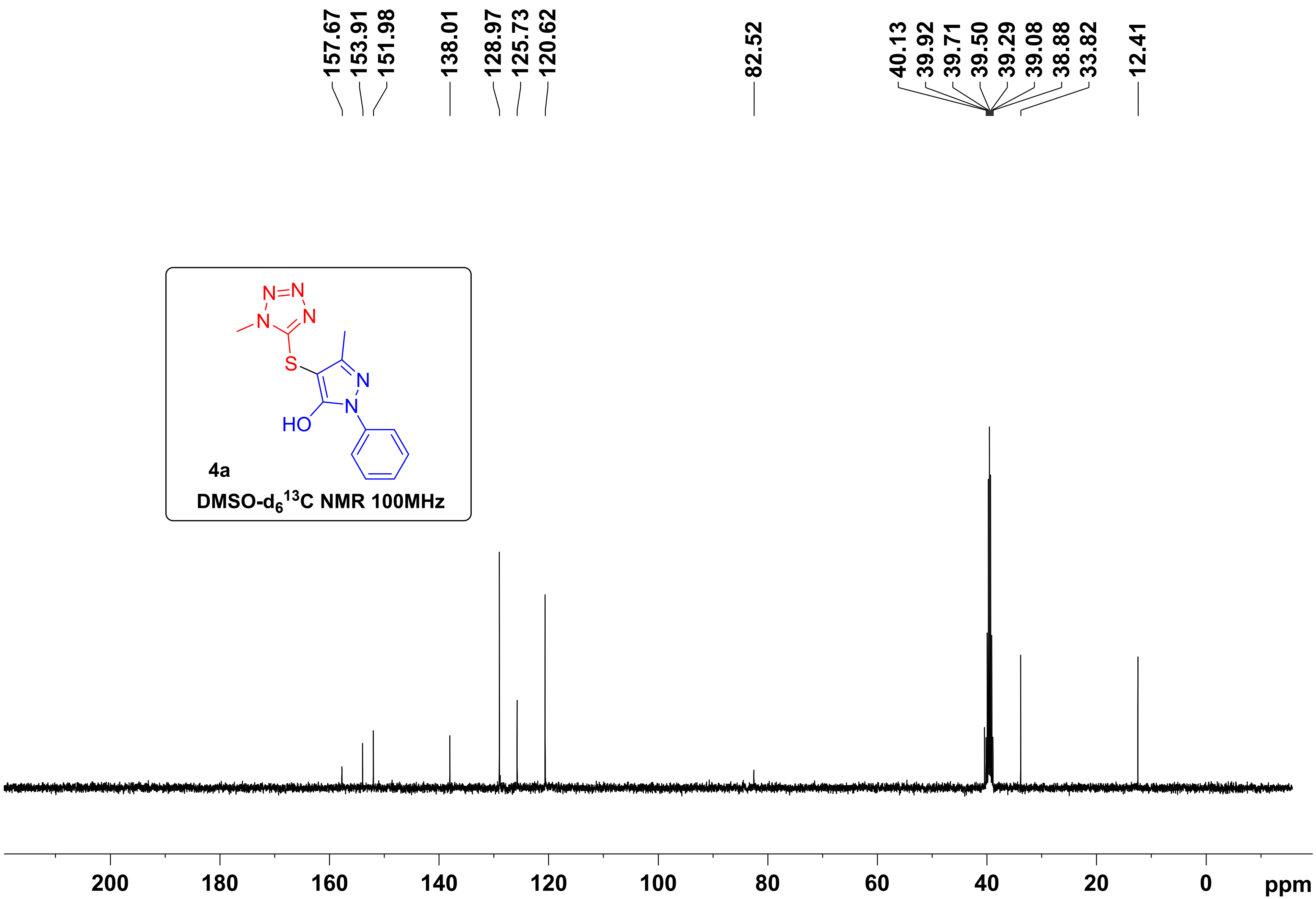
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39.92
39.71
39.50
39.29
39.08
38.88
33.82
12.41
N=N
N
N
S
N
N
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4a
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120
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60
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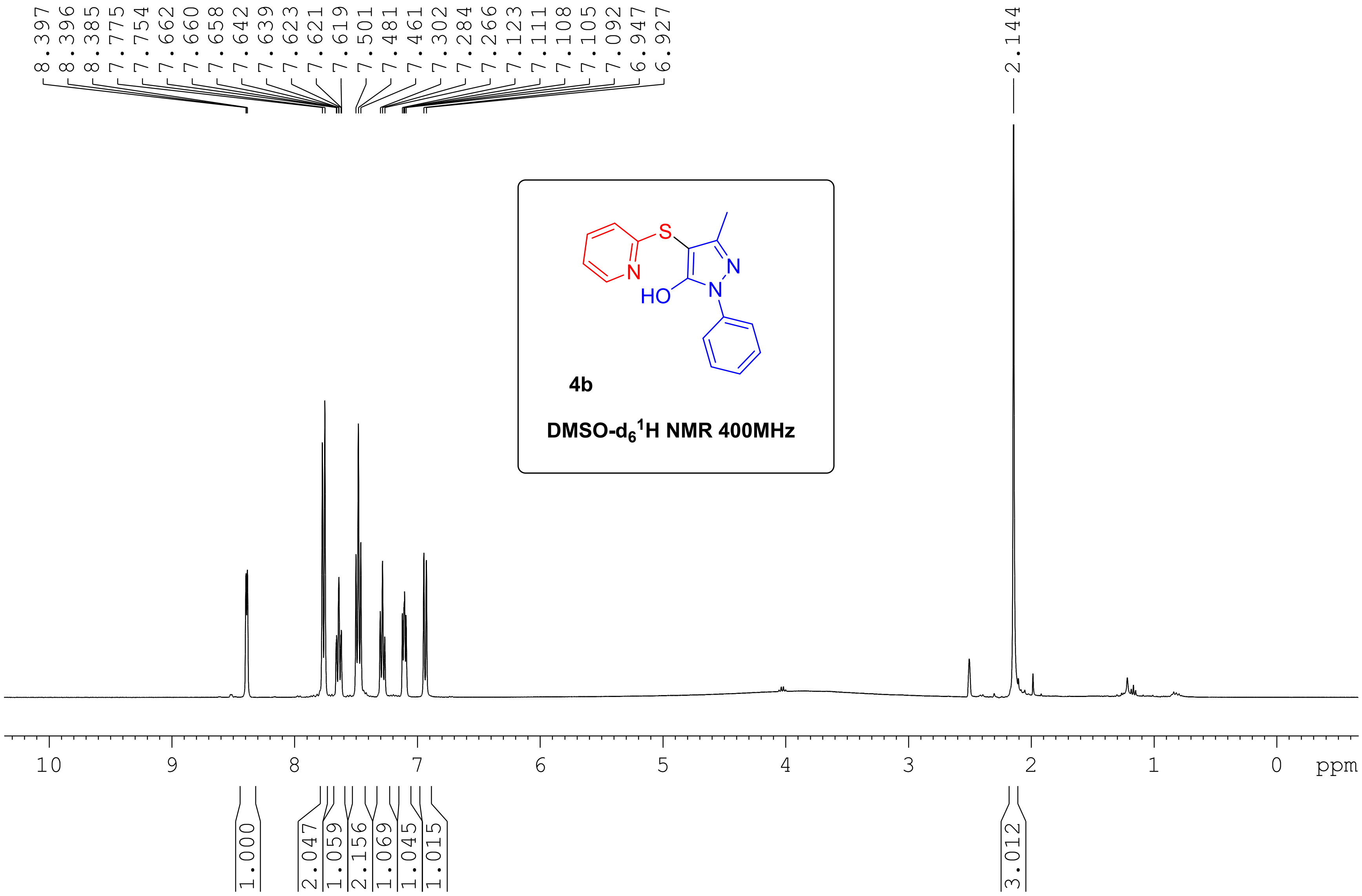
20
0
ppm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7.658
7.642
7.639
7.623
7.621
7.619
7.501
7.481
7.461
7.302
7.284
7.266
7.123
7.111
7.108
7.105
7.092
6.947
6.927
2.144
S
N
N
N
HO
4b
DMSO-d6 1H NMR 400MHz
10
9
8
7
6
5
4
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1
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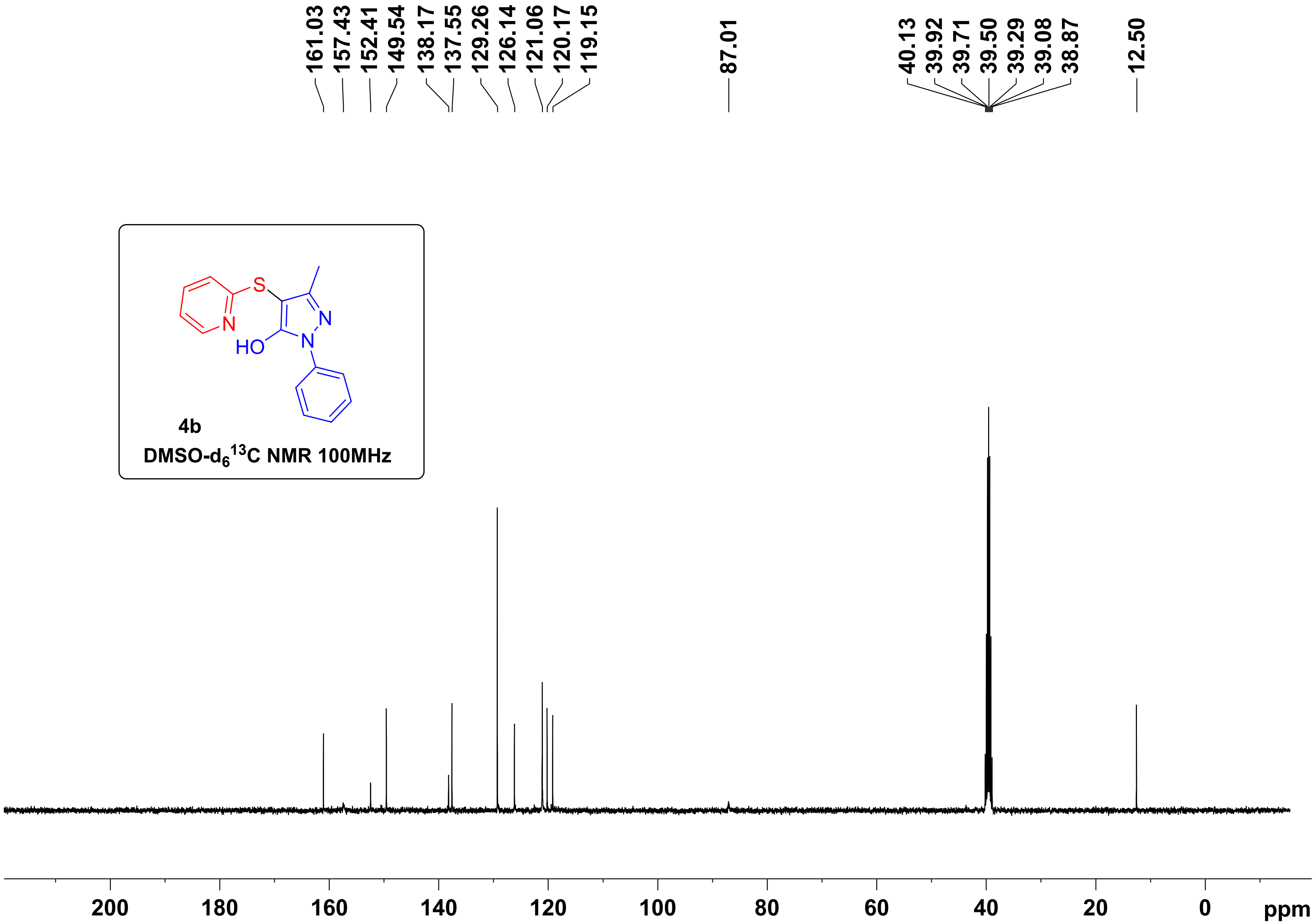
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126.14
121.06
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119.15
87.01
40.13
39.92
39.71
39.50
39.29
39.08
38.87
12.50
S
N
N
N
HO
4b
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180
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120
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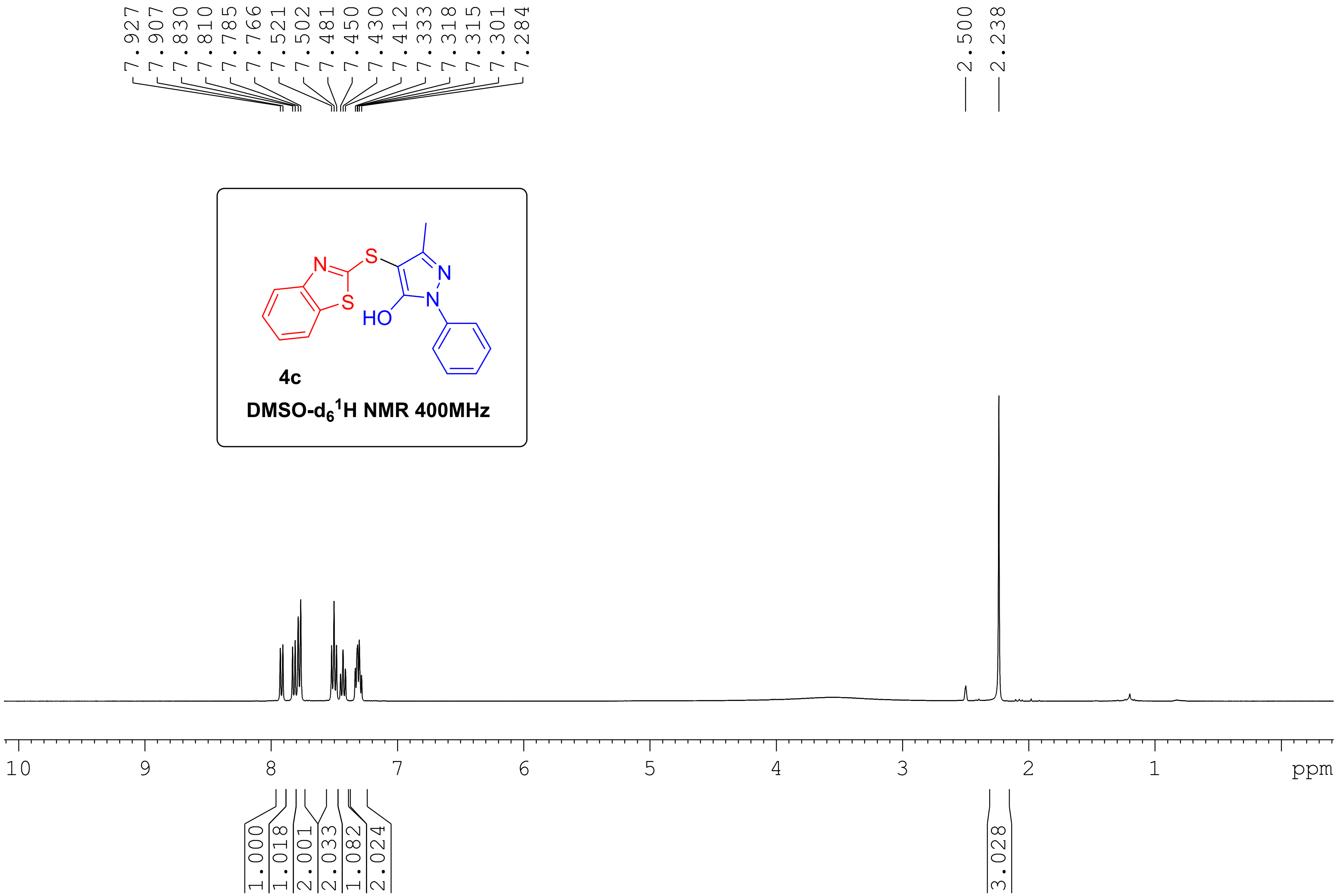
0
ppm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7.412
7.333
7.318
7.315
7.301
7.284
2.500
2.238
4c
DMSO-d6 1H NMR 400MHz
10
9
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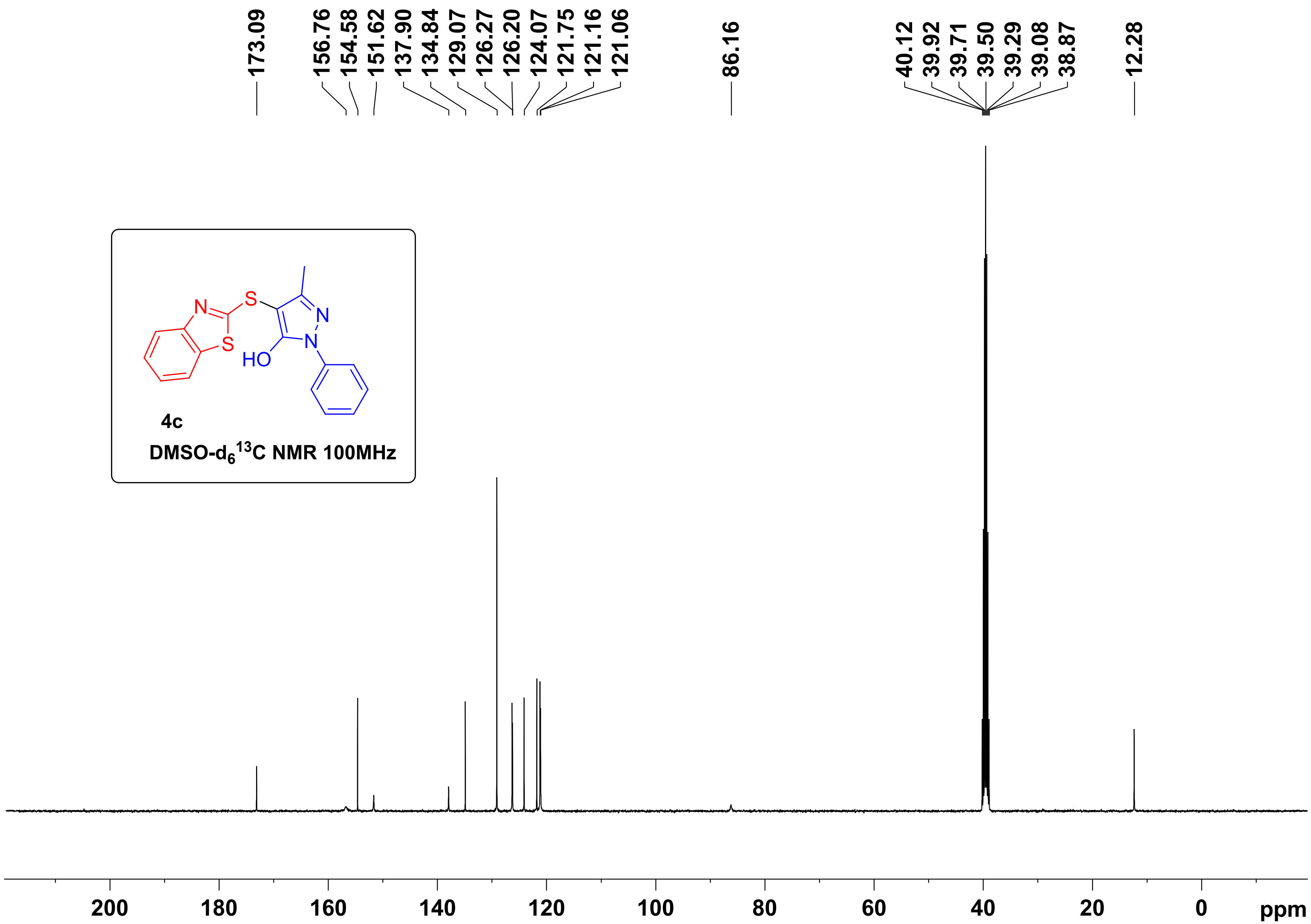
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86.16
40.12
39.92
39.71
39.50
39.29
39.08
38.87
12.28
N
S
S
N
N
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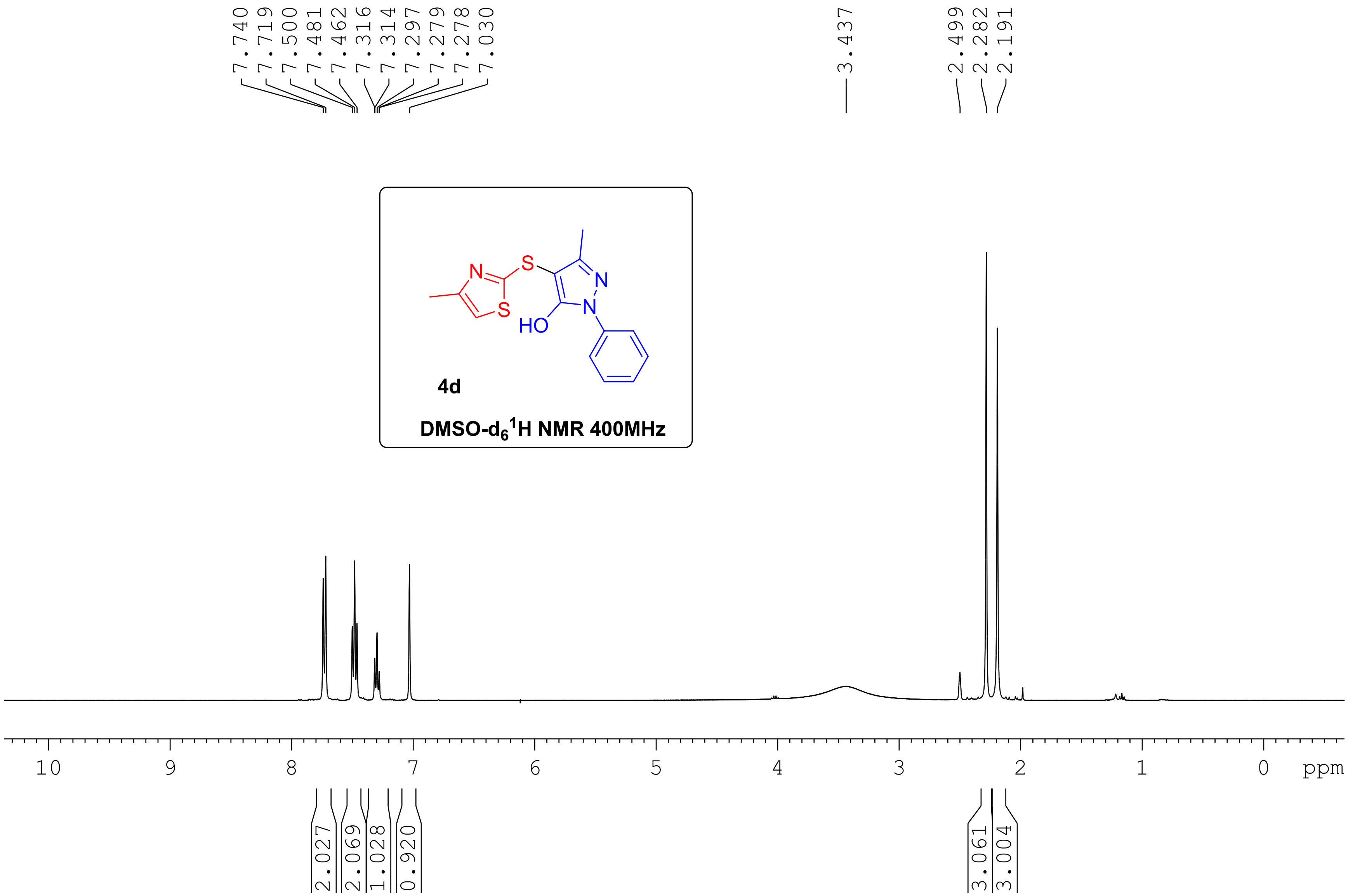
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S
S
N
N
HO
4d
DMSO-d6 1H NMR 400MHz
10
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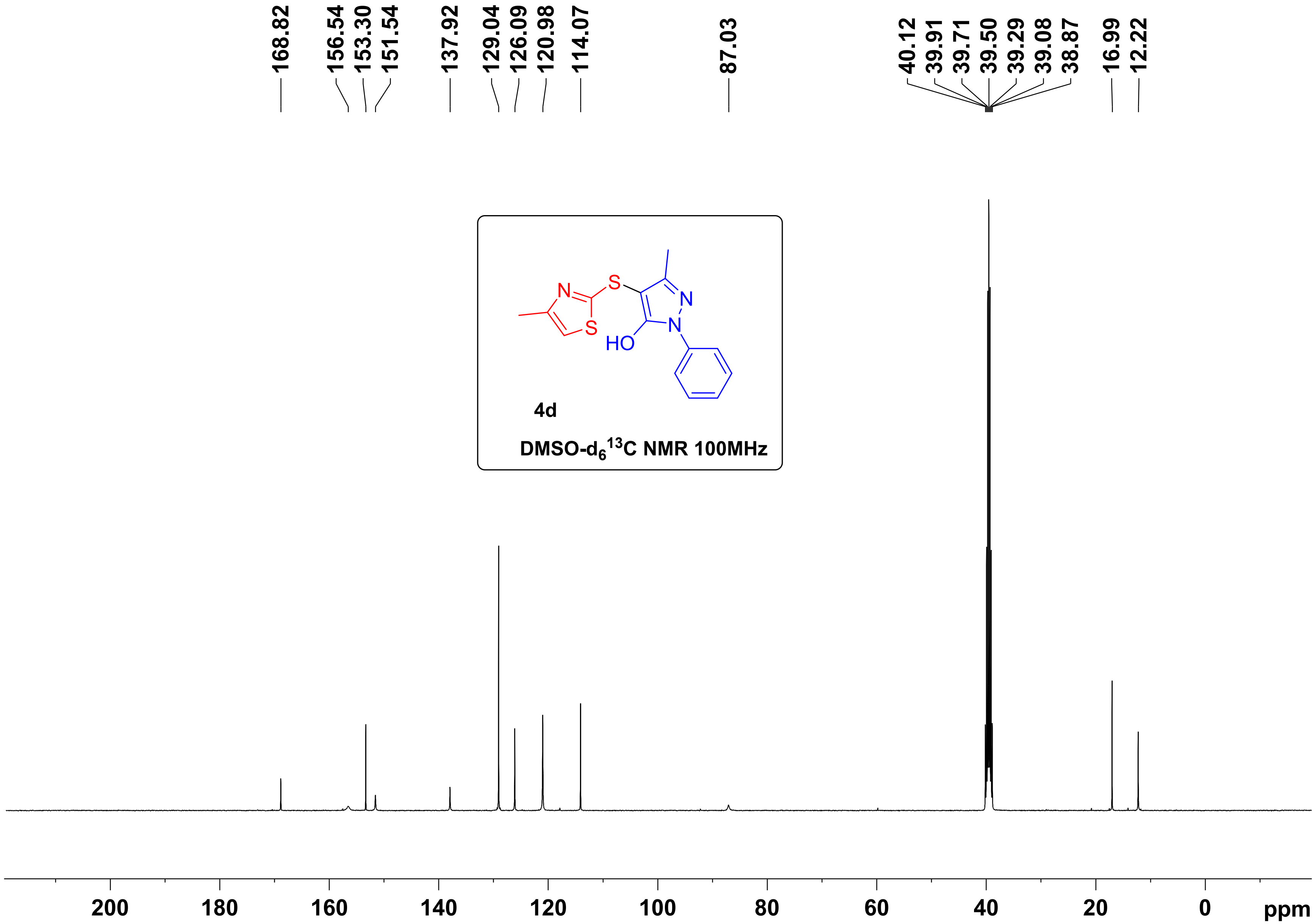
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38.87
16.99
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S
S
N
N
HO
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DMSO-d6 13C NMR 100MHz
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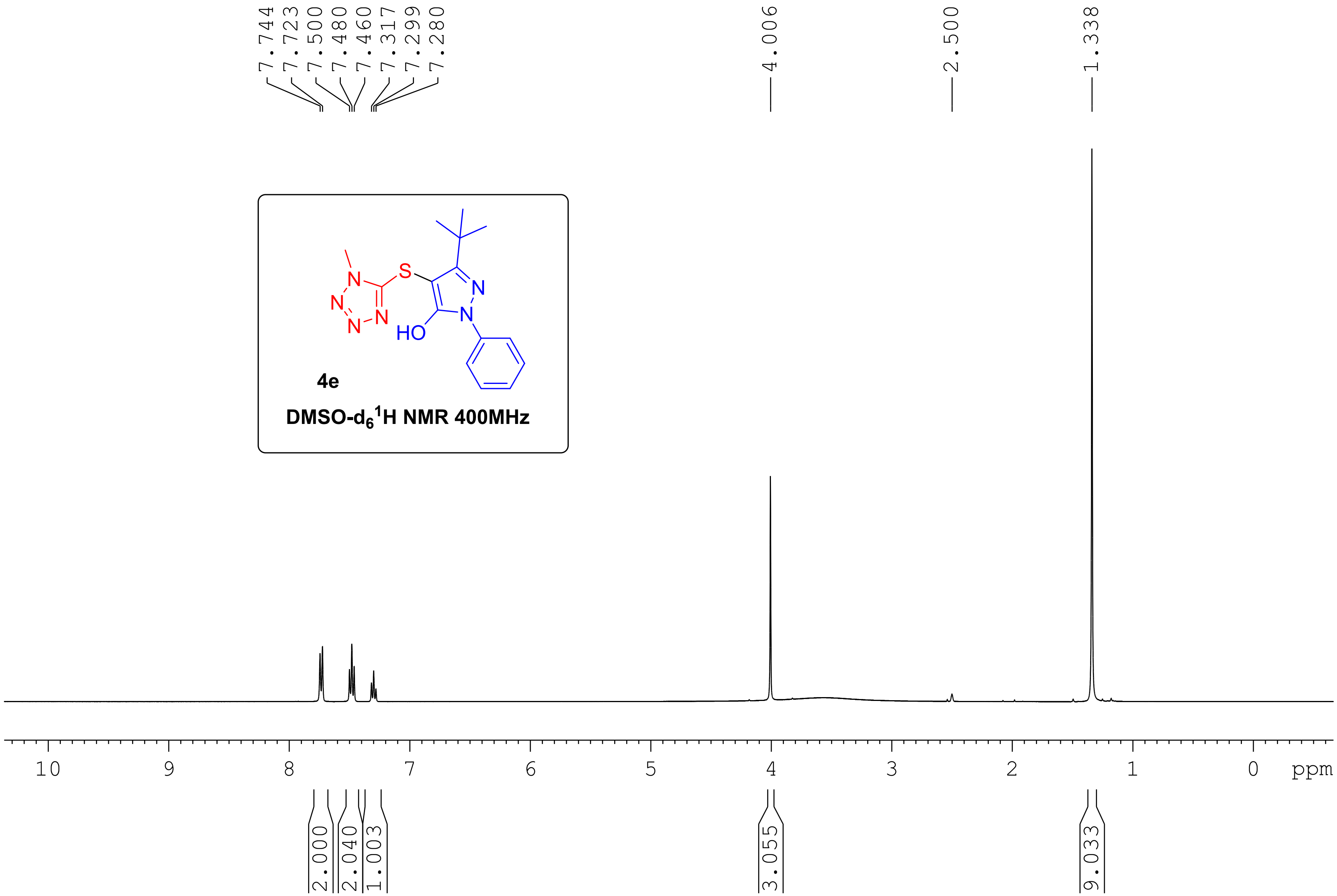
ppm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N
S
N
N
HO
4e
DMSO-d6 1H NMR 400MHz
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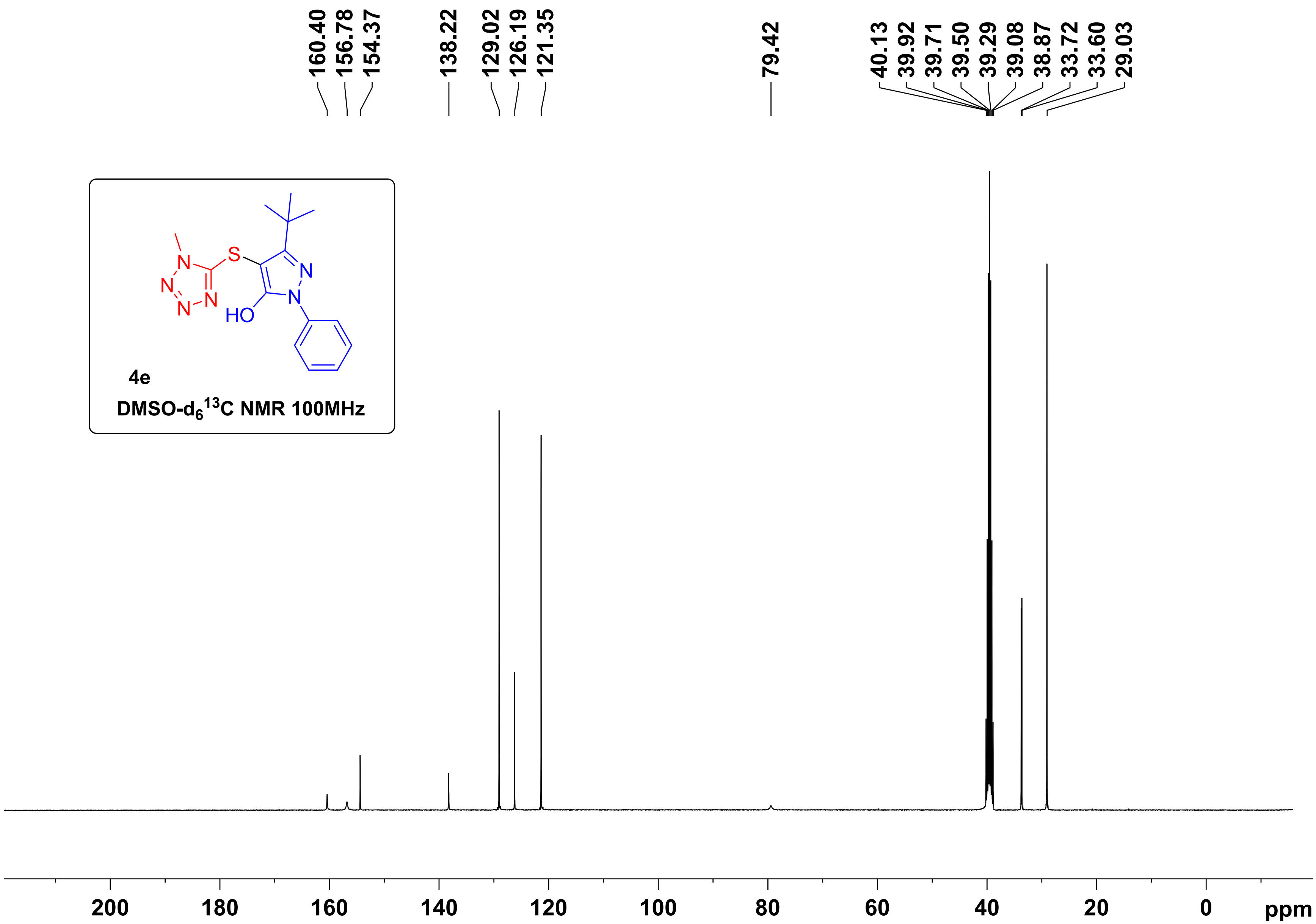

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39.29
39.08
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33.72
33.60
29.03
S
N
N
N
N
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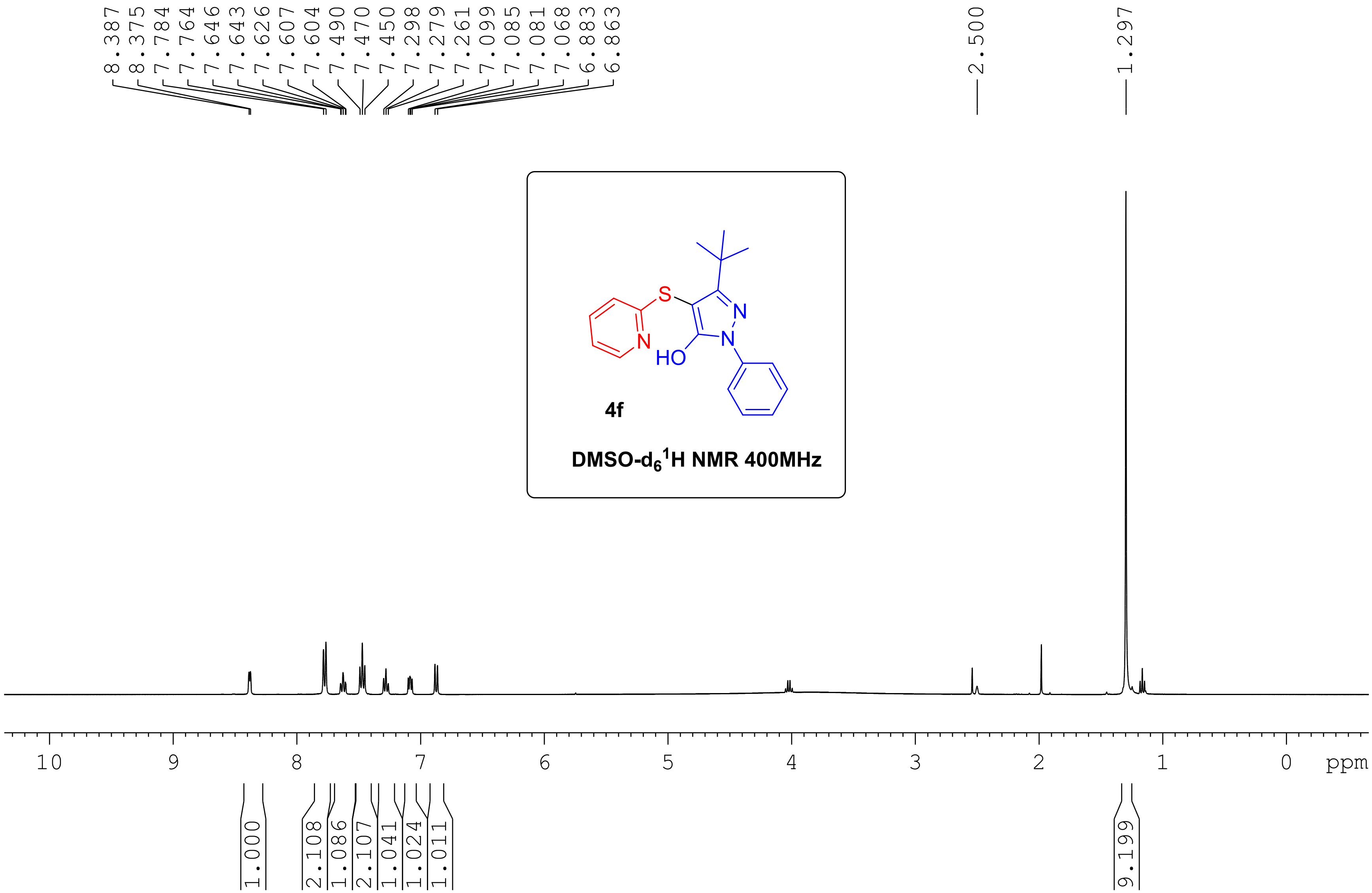
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7.298
7.279
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7.085
7.081
7.068
6.883
6.863
2.500
1.297
S
N
N
N
HO
4f
DMSO-d6 1H NMR 400MHz
10
9
8
7
6
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ppm
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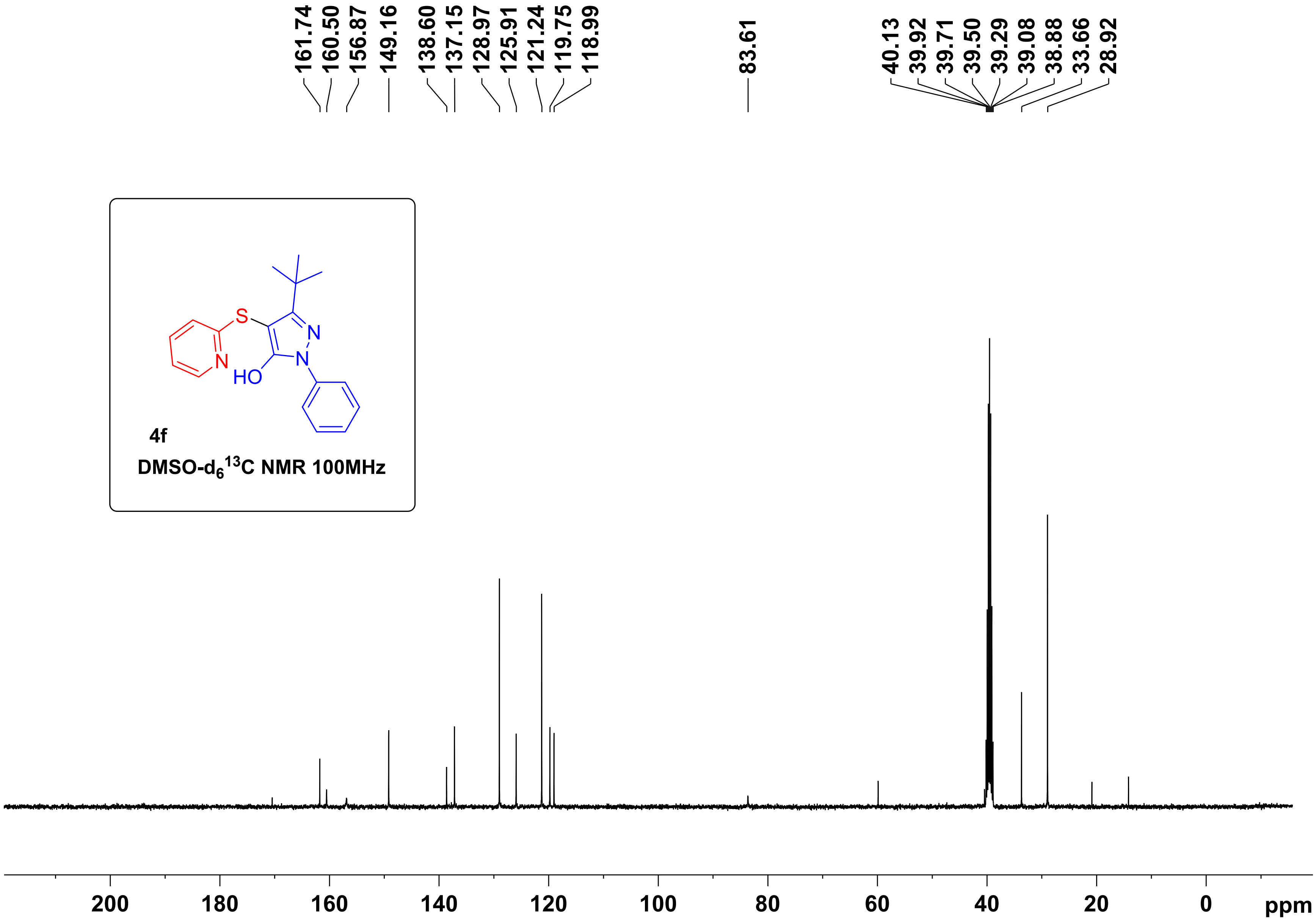
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39.71
39.50
39.29
39.08
38.88
33.66
28.92
S
N
N
N
HO
4f
DMSO-d6 13C NMR 100MHz
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180
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120
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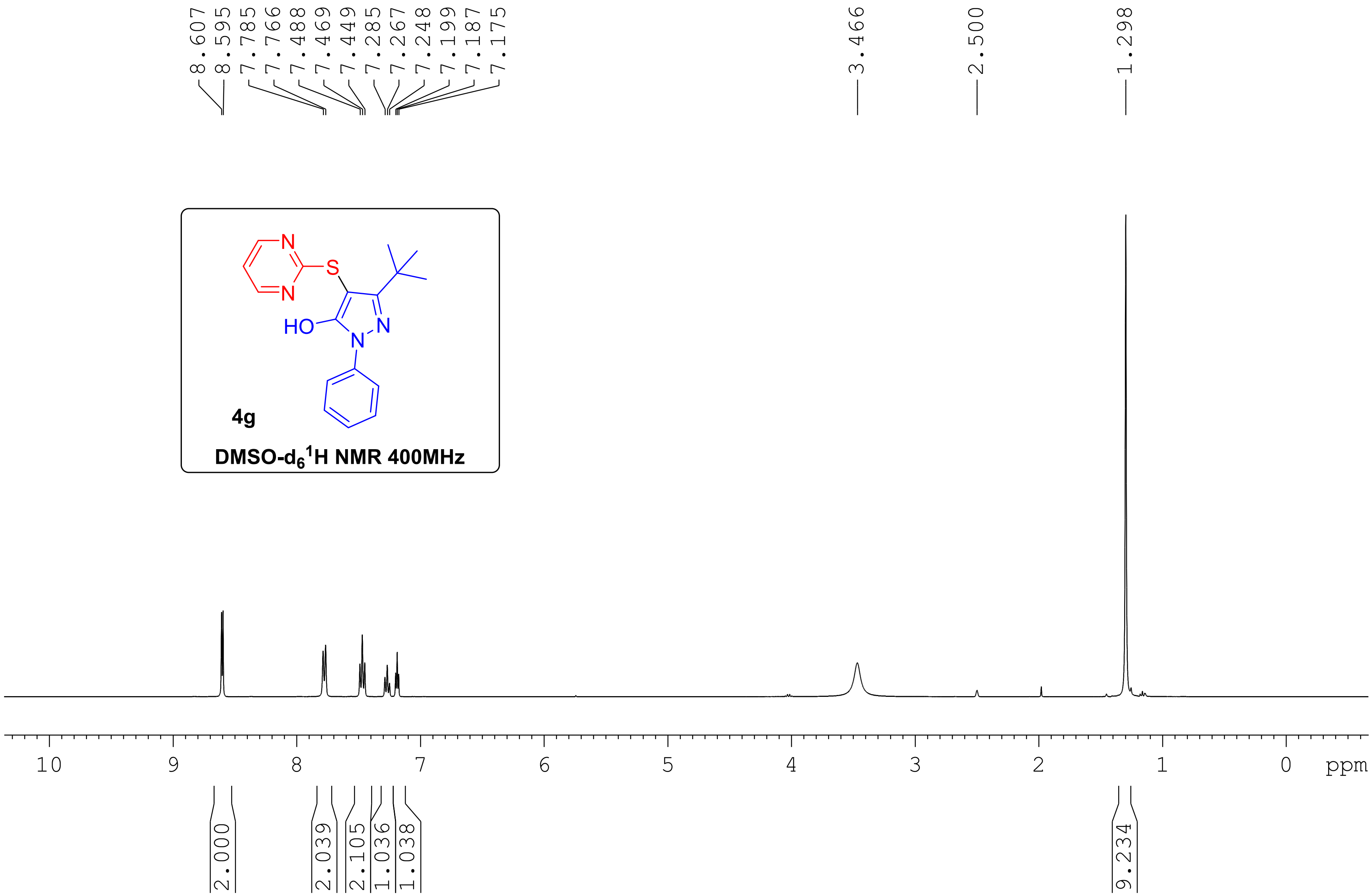
ppm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3.466
2.500
1.298
N
S
N
HO
N
N
4g
DMSO-d6 1H NMR 400MHz
10
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0
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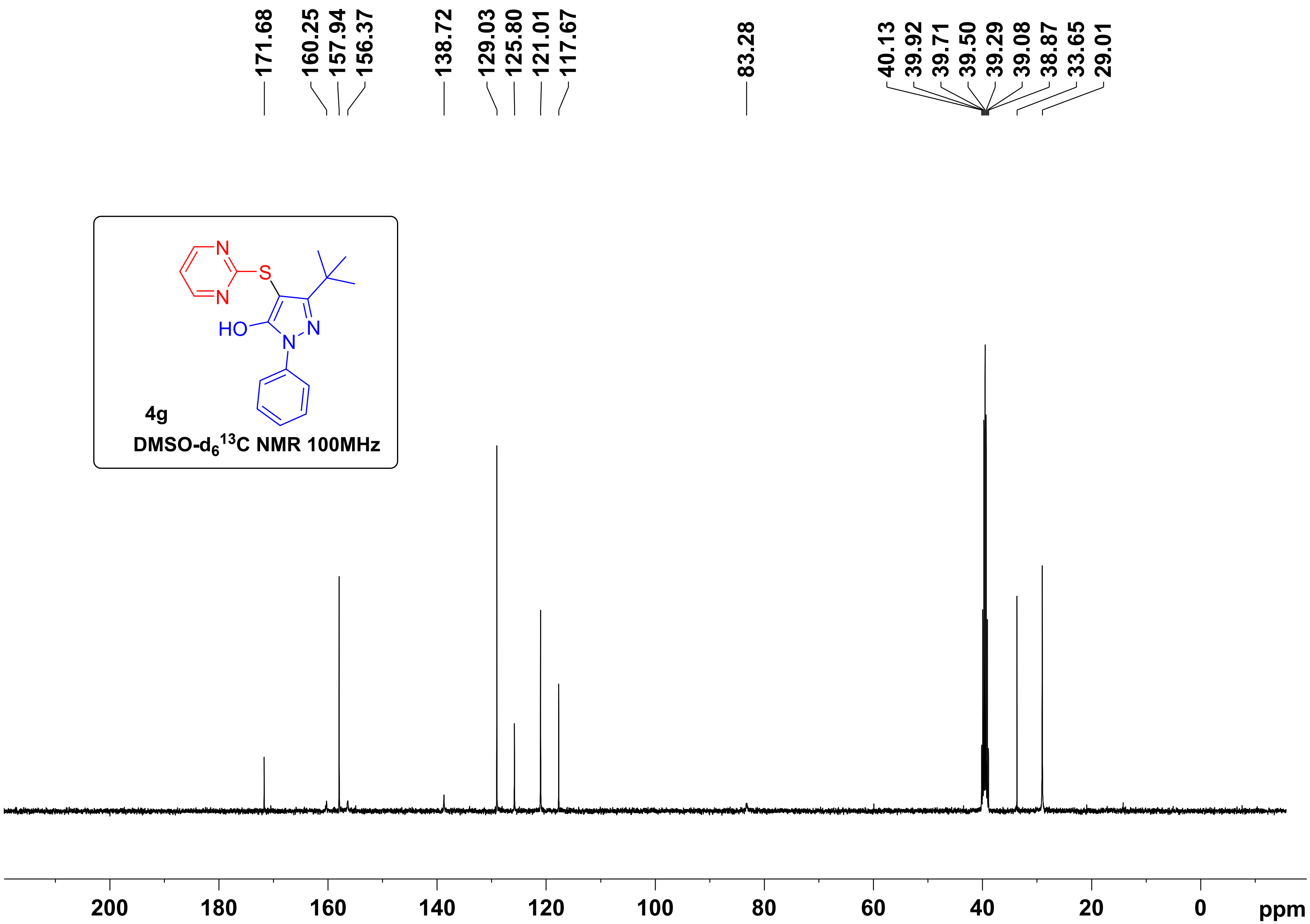
1.038
9.234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39.71
39.50
39.29
39.08
38.87
33.65
29.01
N
N
S
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DMSO-d6 13C NMR 100MHz
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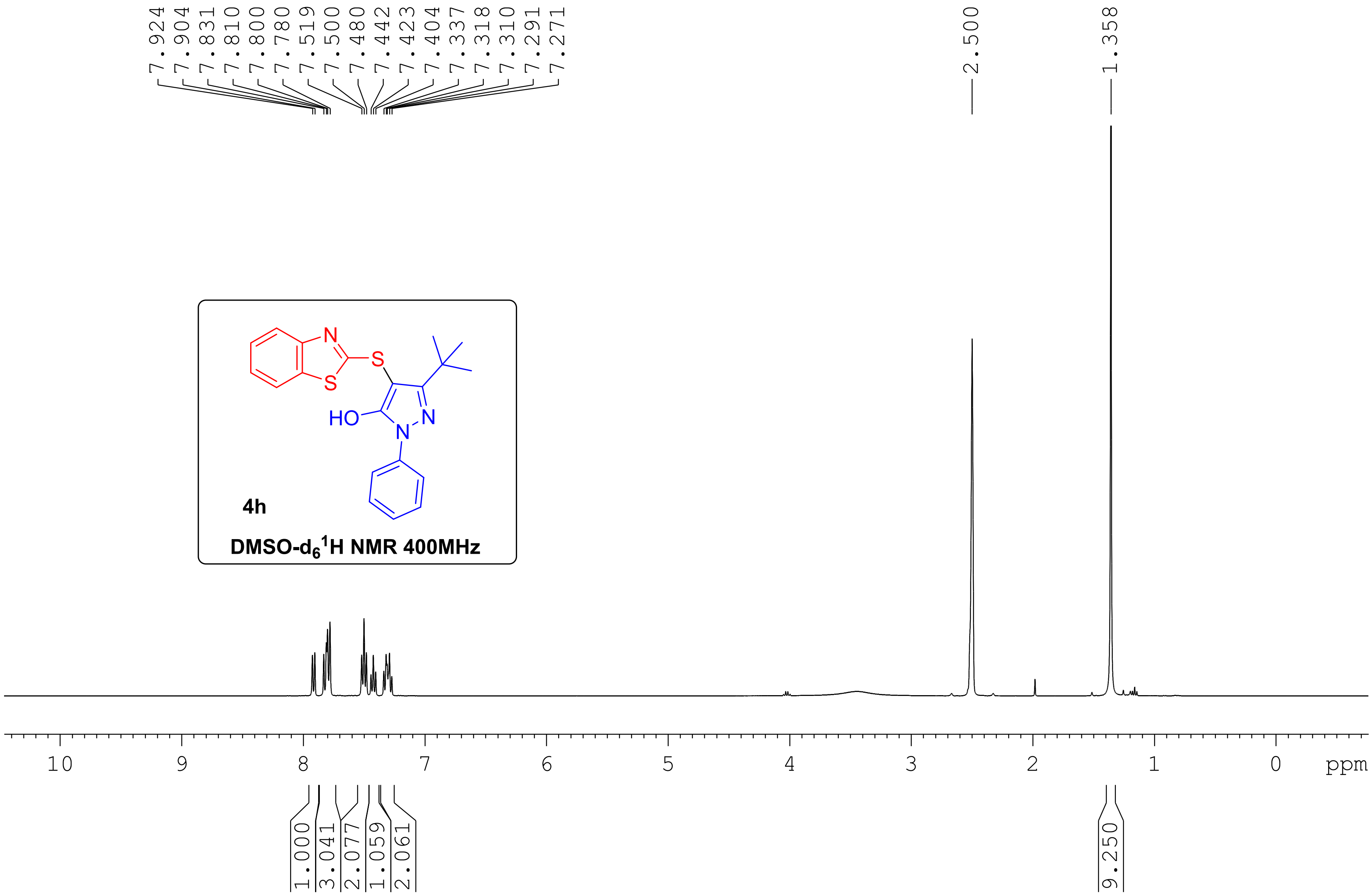
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7.404
7.337
7.318
7.310
7.291
7.271
2.500
1.358
4h
DMSO-d6 1H NMR 400MHz
HO
N
S
10
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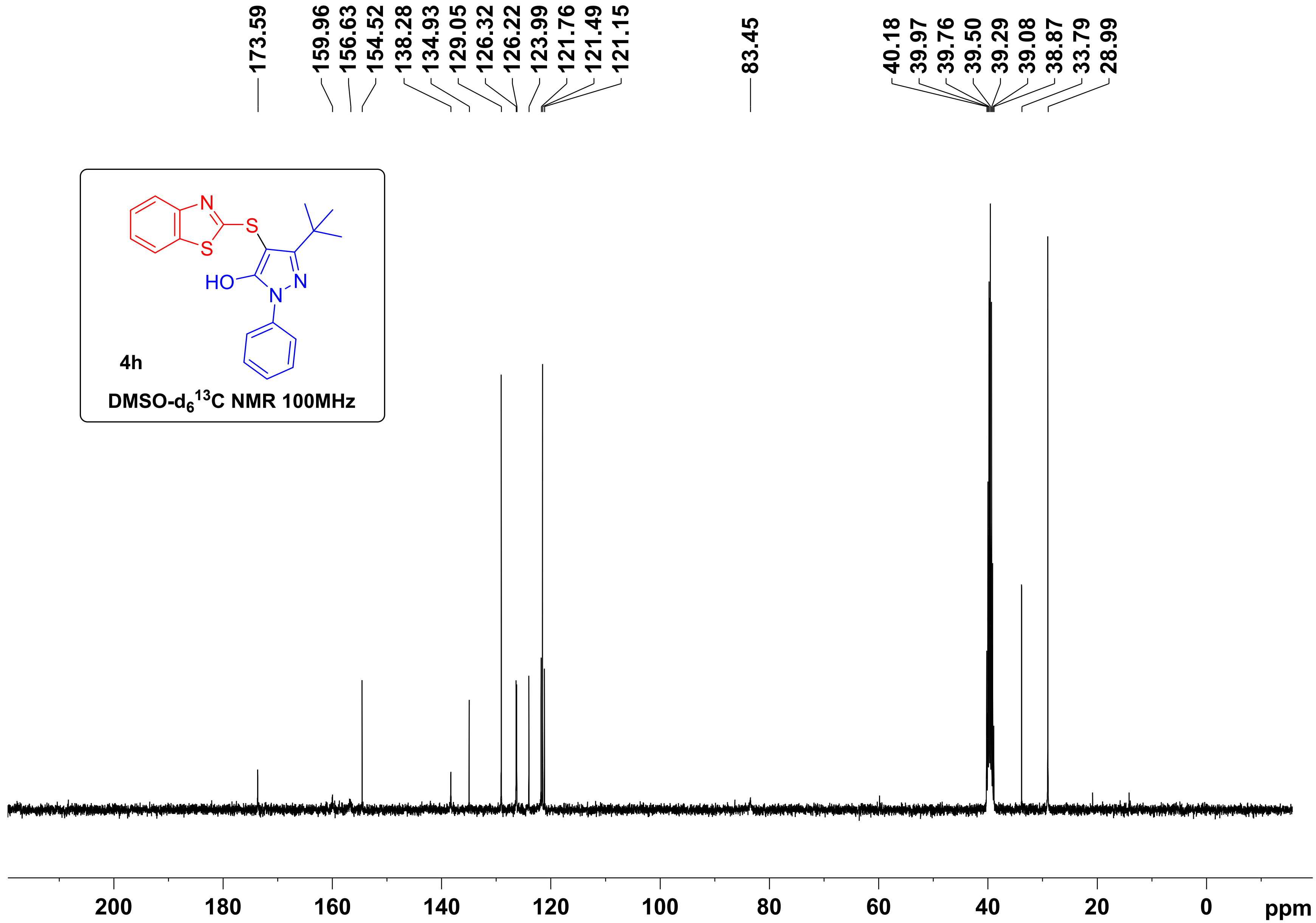
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39.76
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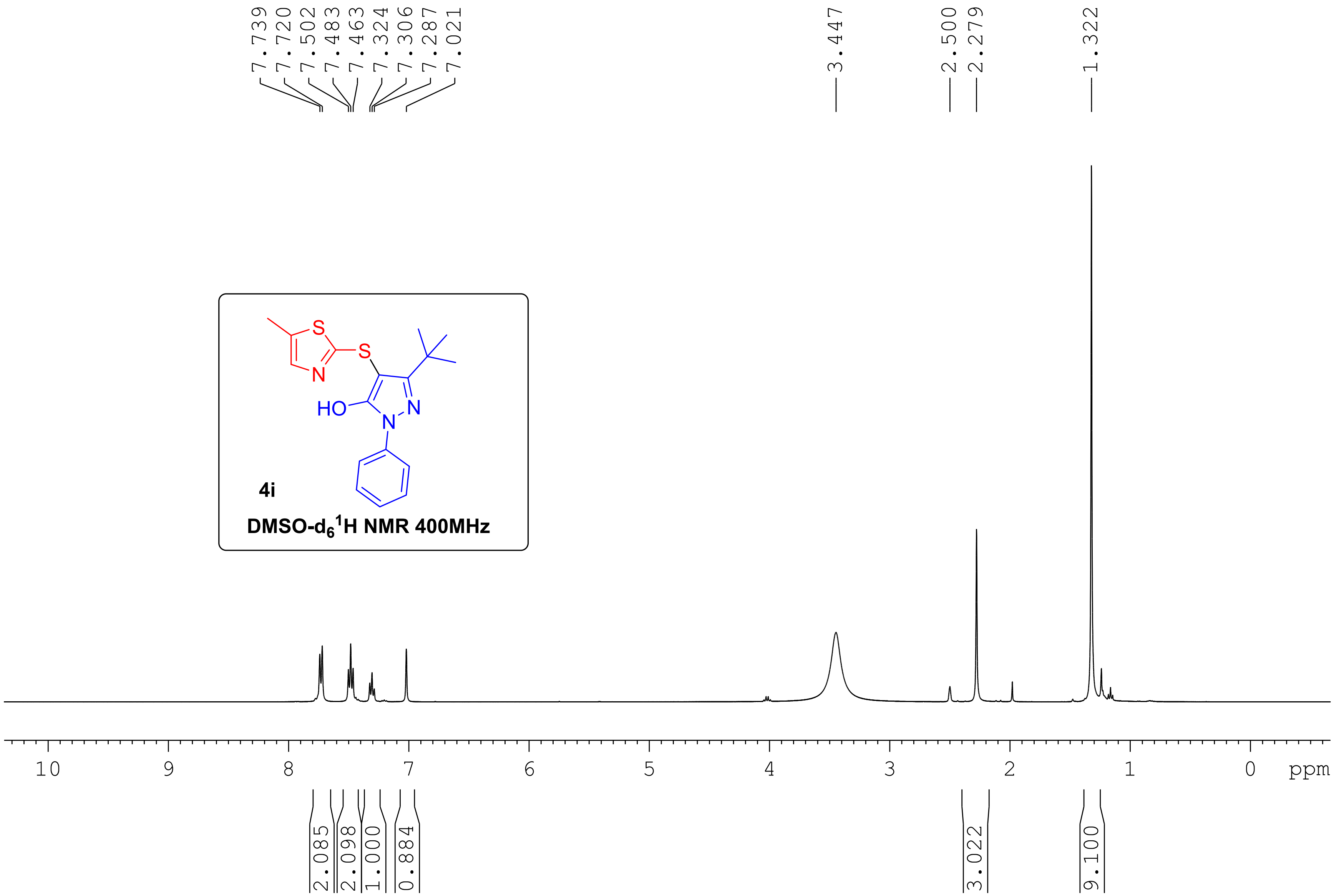
39.08
38.87
33.79
28.99
N
S
S
HO
N
N
4h
DMSO-d6 13C NMR 100MHz
200
180
160
140
120
100
80
60
40
20
0
ppm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1.322
S
S
N
HO
N
N
4i
DMSO-d6 1H NMR 400MHz
10
9
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4
3
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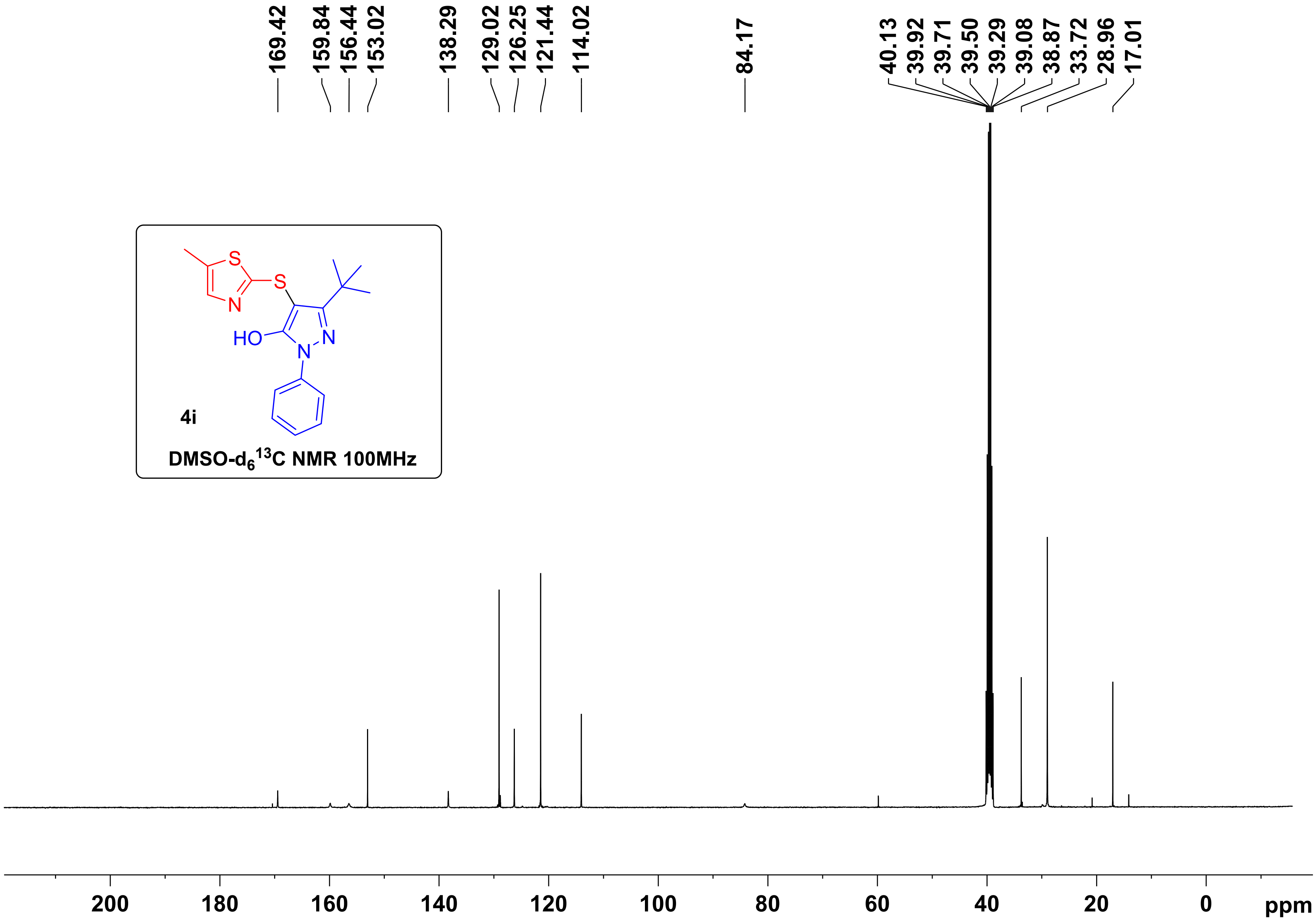
9.100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121.44
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39.71
39.50
39.29
39.08
38.87
33.72
28.96
17.01
S
S
N
HO
N
N
4i
DMSO-d6 13C NMR 100MHz
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180
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140
120
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60
40
20
0
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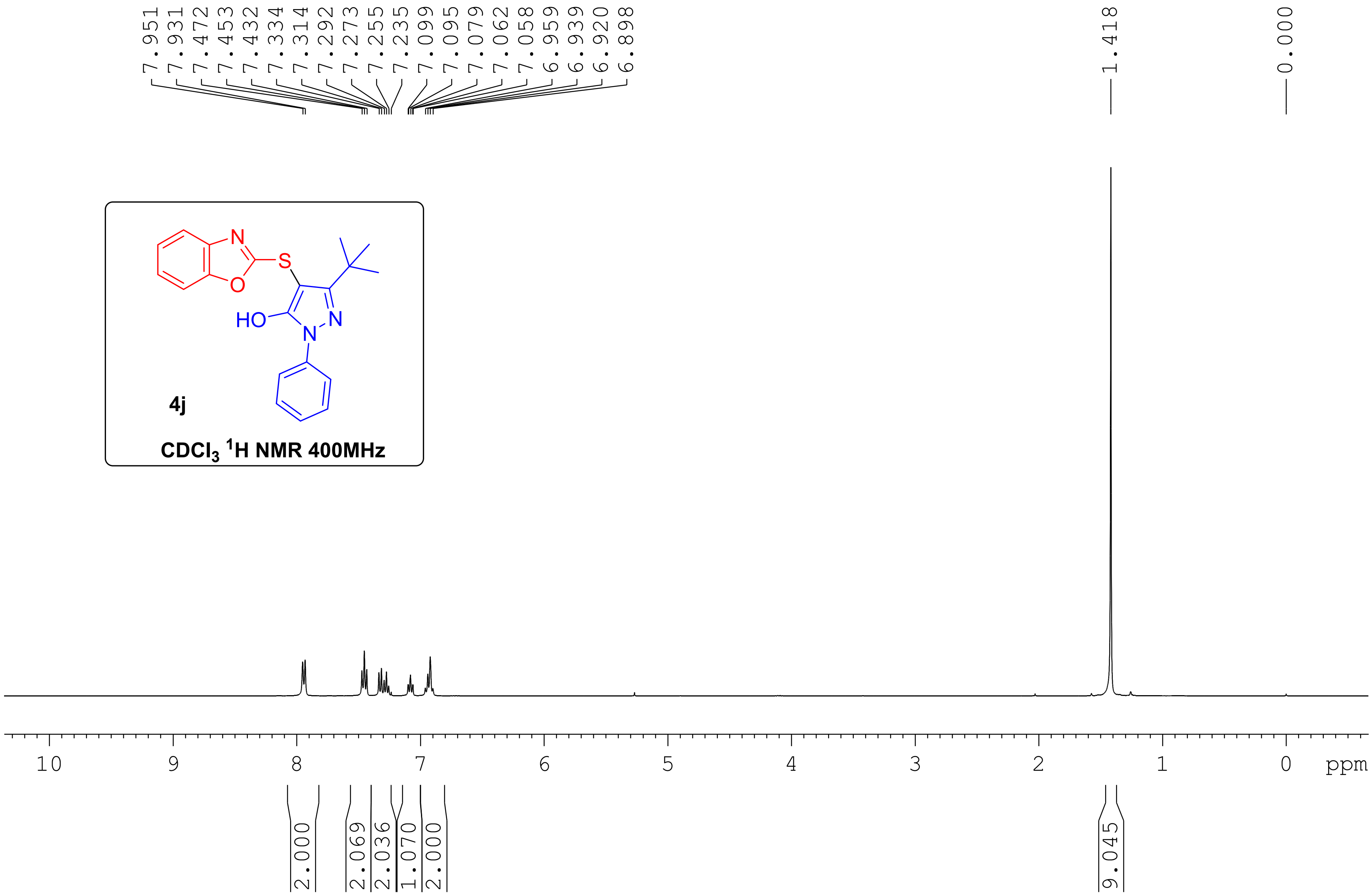
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7.292
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7.095
7.079
7.062
7.058
6.959
6.939
6.920
6.898
1.418
0.000
4j
CDCl3 1H NMR 400MHz
10
9
8
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6
5
4
3
2
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0
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2.069
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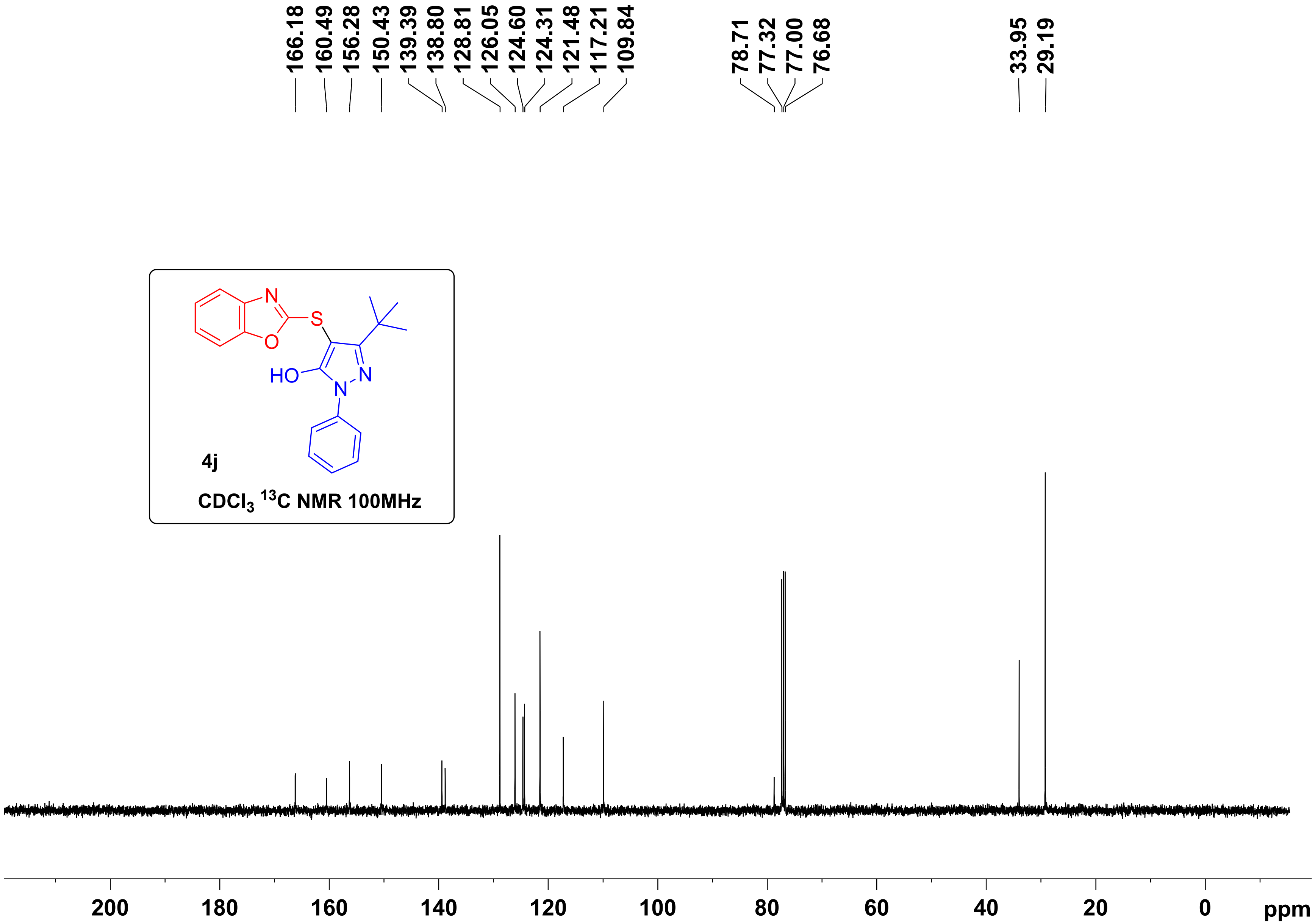
1.070
2.000
9.045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126.05
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109.84
78.71
77.32
77.00
76.68
33.95
29.19
N
S
O
HO
N
N
4j
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160
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120
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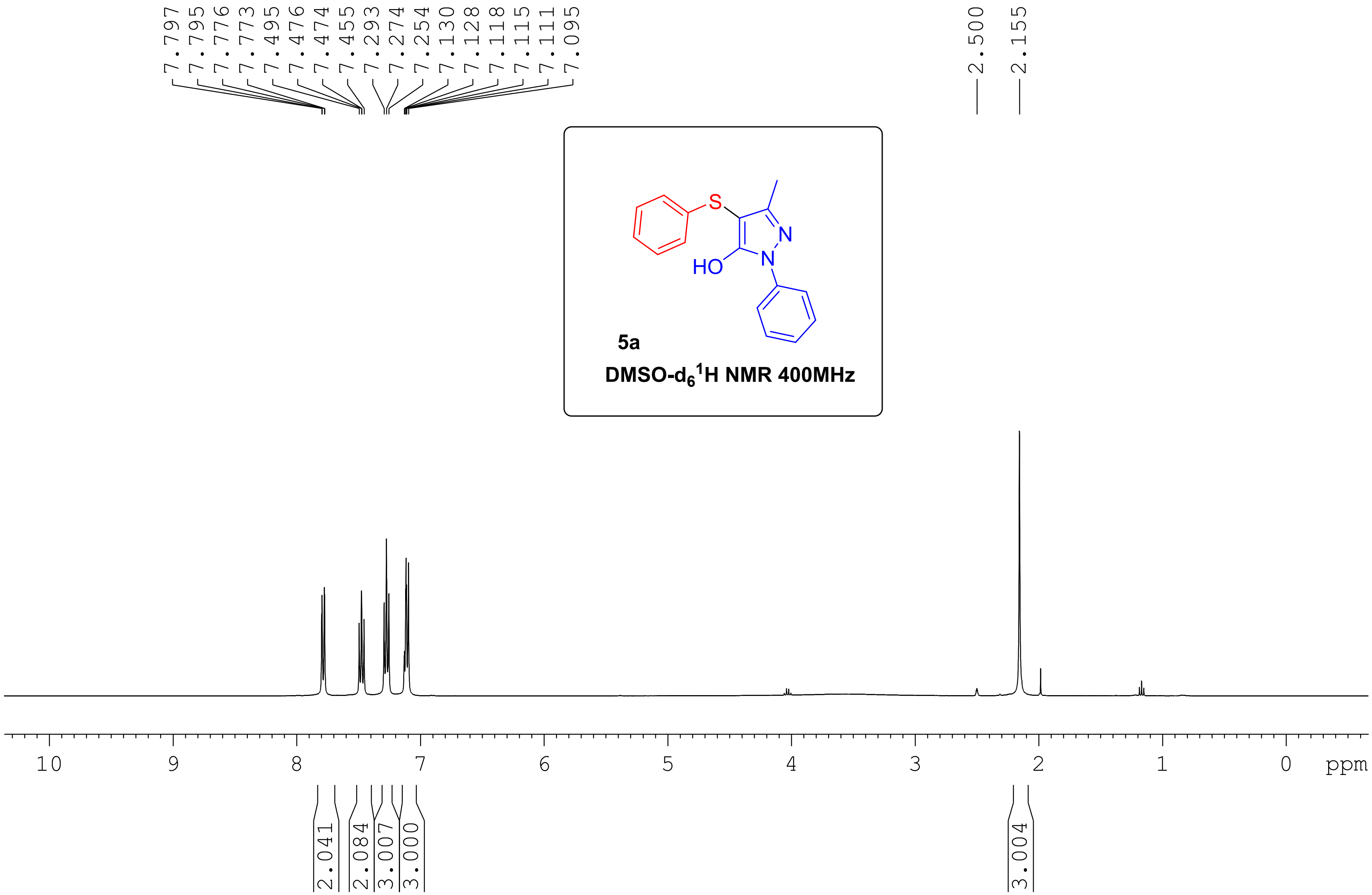
80
60
40
20
0
ppm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7.455
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7.274
7.254
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7.128
7.118
7.115
7.111
7.095
2.500
2.155
S
N
N
HO
5a
DMSO-d6 1H NMR 400MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
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2.084
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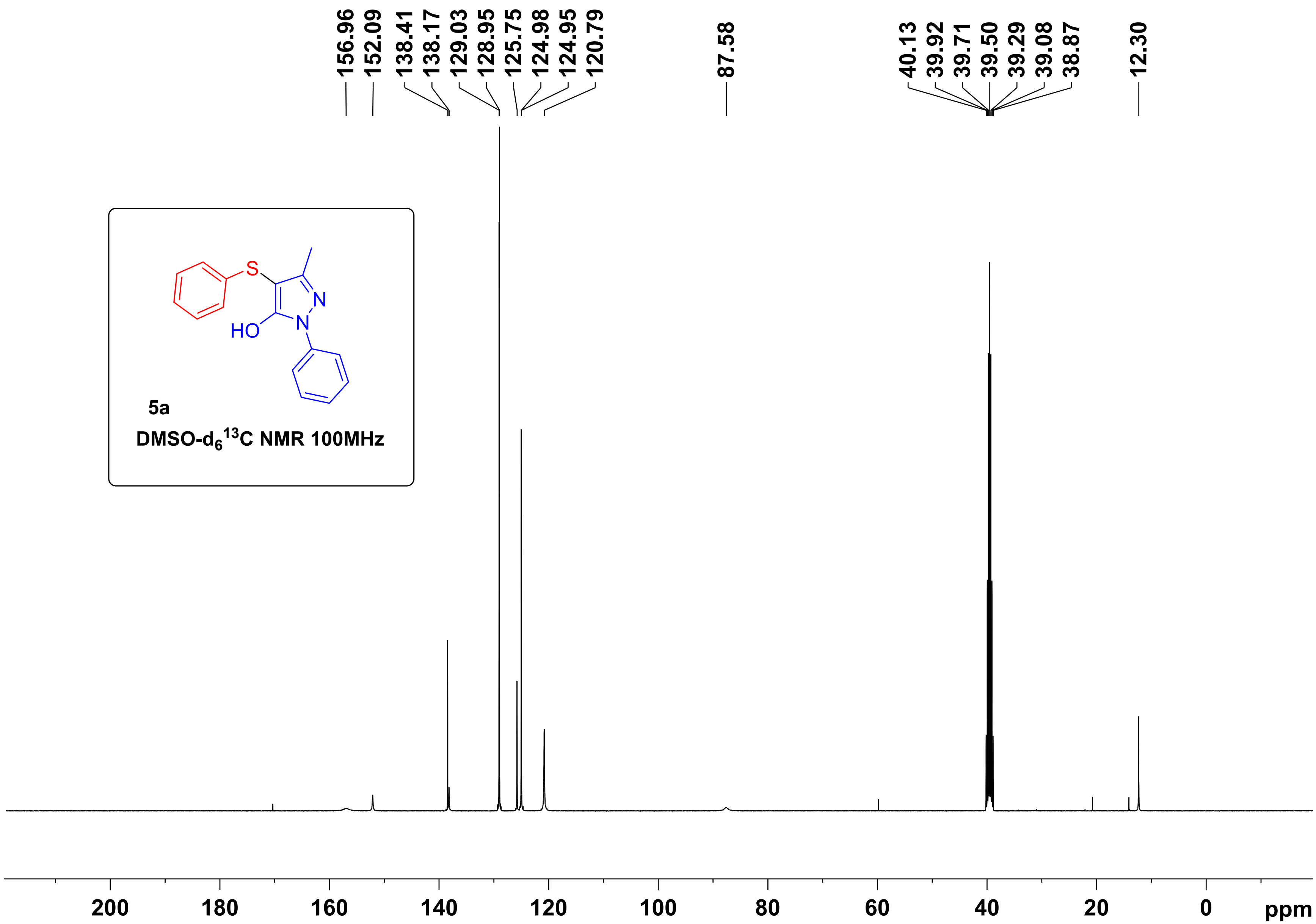
3.000
3.004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138.17
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124.98
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120.79
87.58
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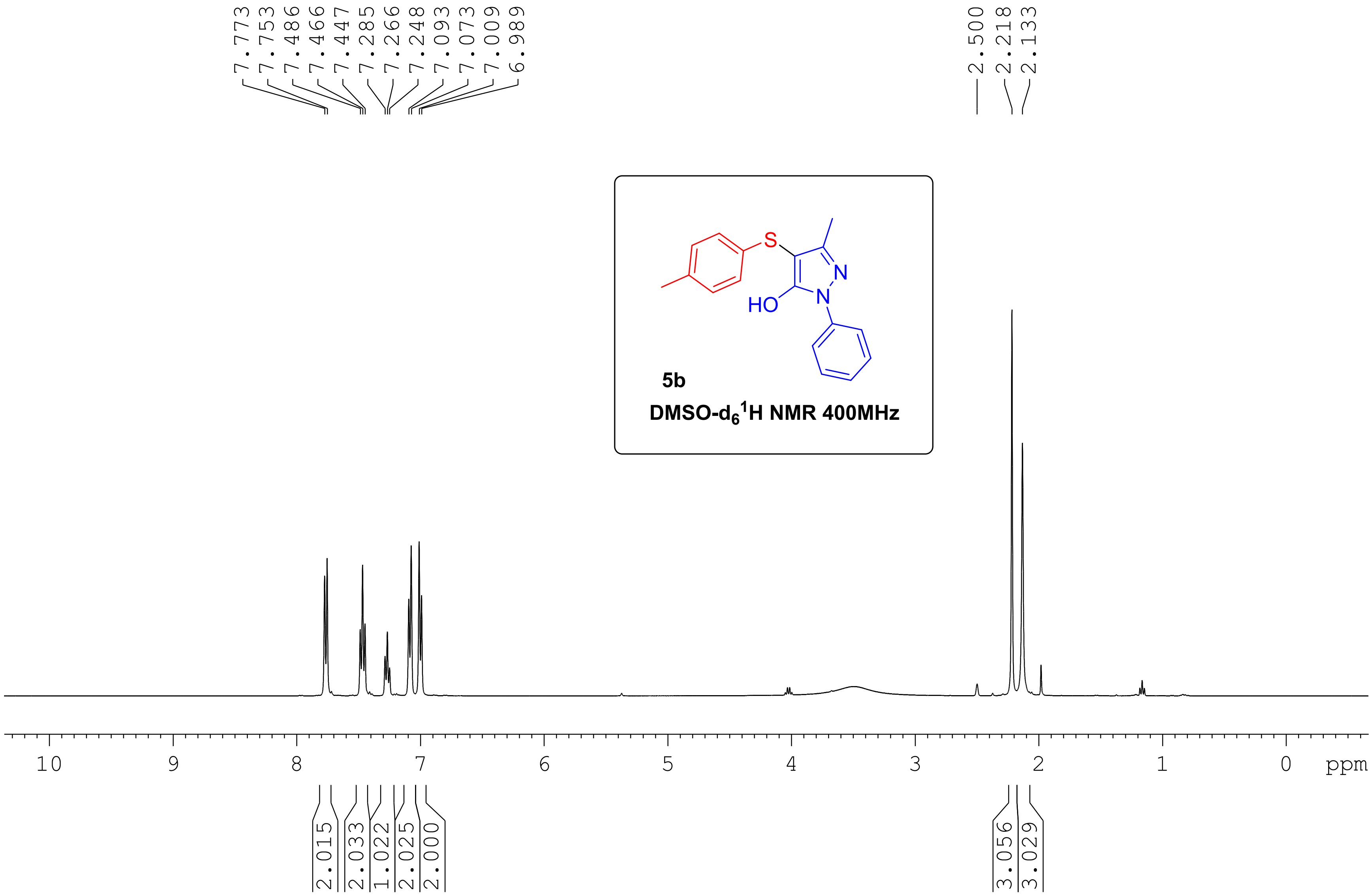
39.92
39.71
39.50
39.29
39.08
38.87
12.30
S
N
N
HO
5a
DMSO-d6 13C NMR 100MHz
200
180
160
140
120
100
80
60
40
20
0
ppm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7.248
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7.073
7.009
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2.500
2.218
2.133
S
N
N
HO
5b
DMSO-d6 1H NMR 400MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
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1.022
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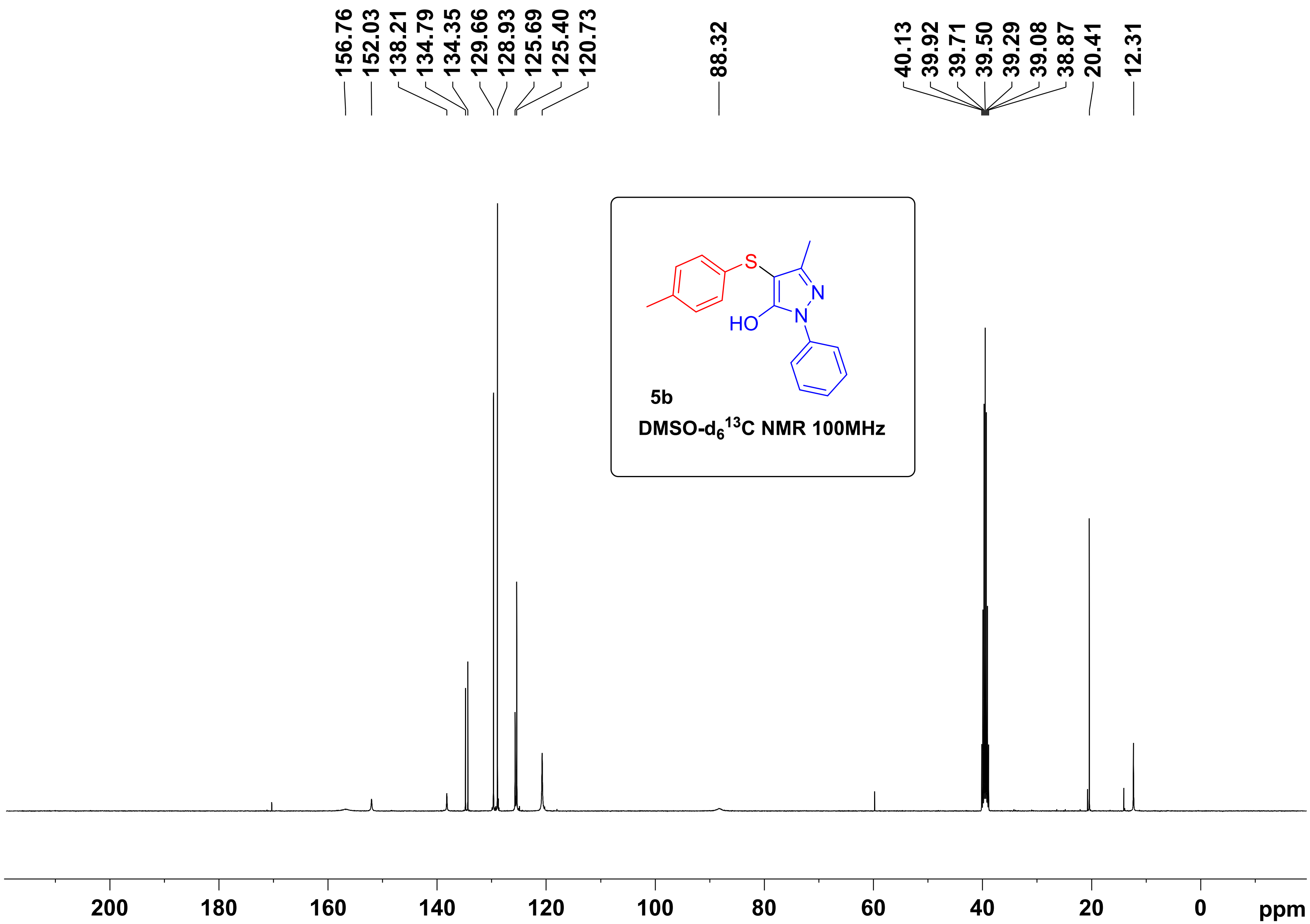
2.000
3.056
3.029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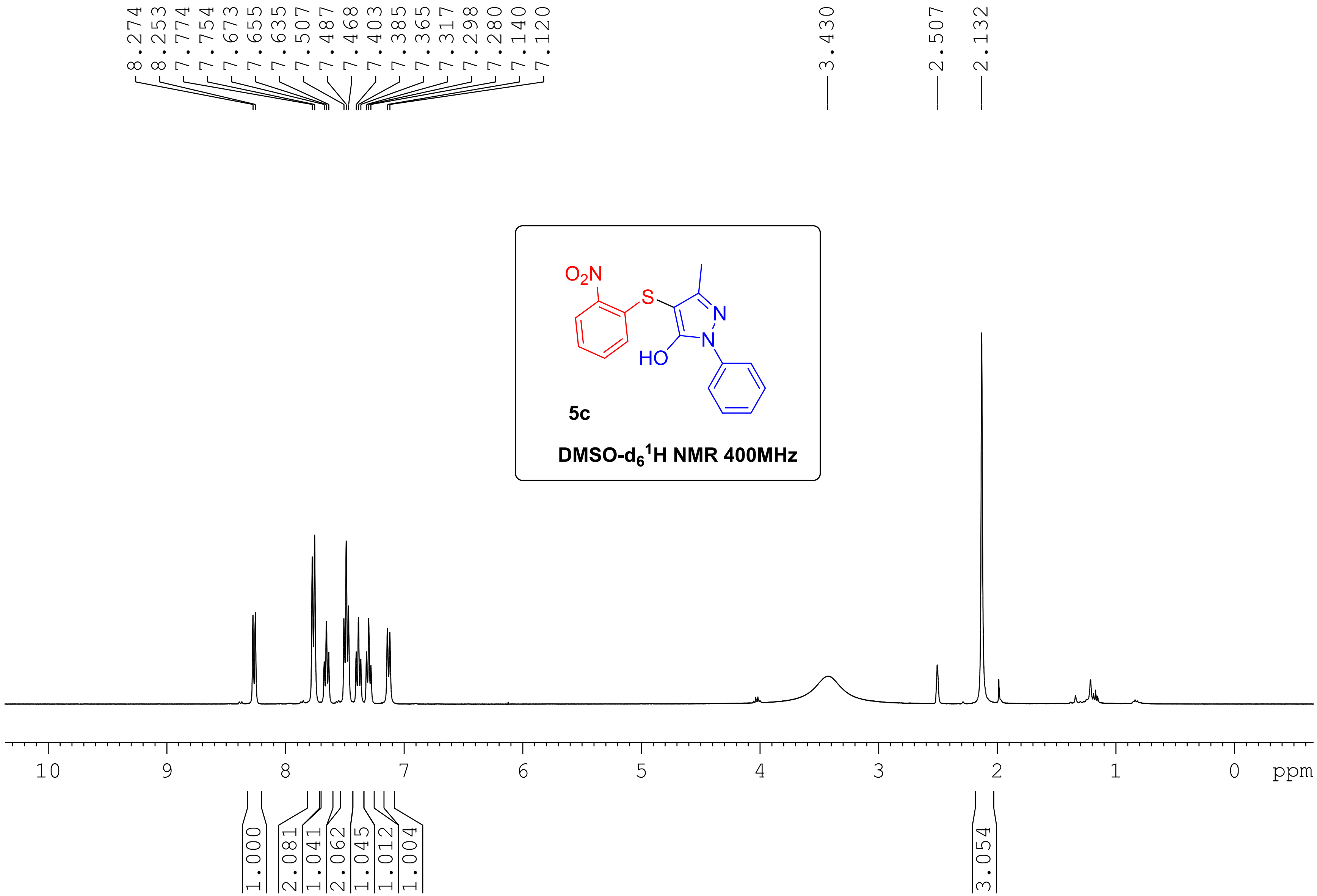
125.69
125.40
120.73
88.32
40.13
39.92
39.71
39.50
39.29
39.08
38.87
20.41
12.31
S
N
N
HO
5b
DMSO-d6 13C NMR 100MHz
200
180
160
140
120
100
80
60
40
20
0
ppm



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7.754
7.673
7.655
7.635
7.507
7.487
7.468
7.403
7.385
7.365
7.317
7.298
7.280
7.140
7.120
3.430
2.507
2.132
O2N
S
N
N
HO
5c
DMSO-d6 1H NMR 400MHz
10
9
8
7
6
5
4
3
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1
0
ppm
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2.081
1.041
2.062
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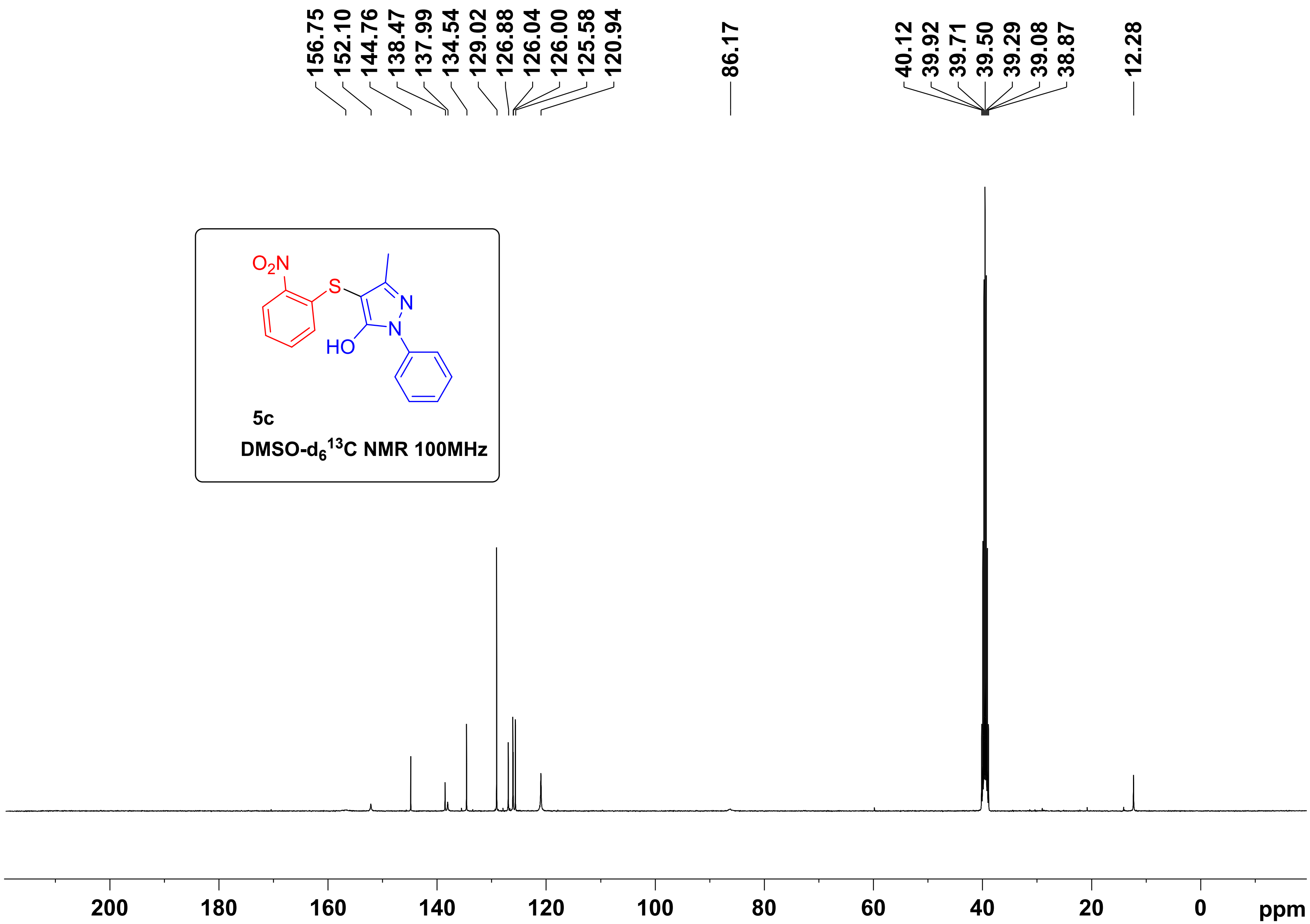
1.012
1.004
3.054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126.88
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126.00
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120.94
86.17
40.12
39.92
39.71
39.50
39.29
39.08
38.87
12.28
O2N
S
N
N
HO
5c
DMSO-d6 13C NMR 100MHz
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180
160
140
120
100
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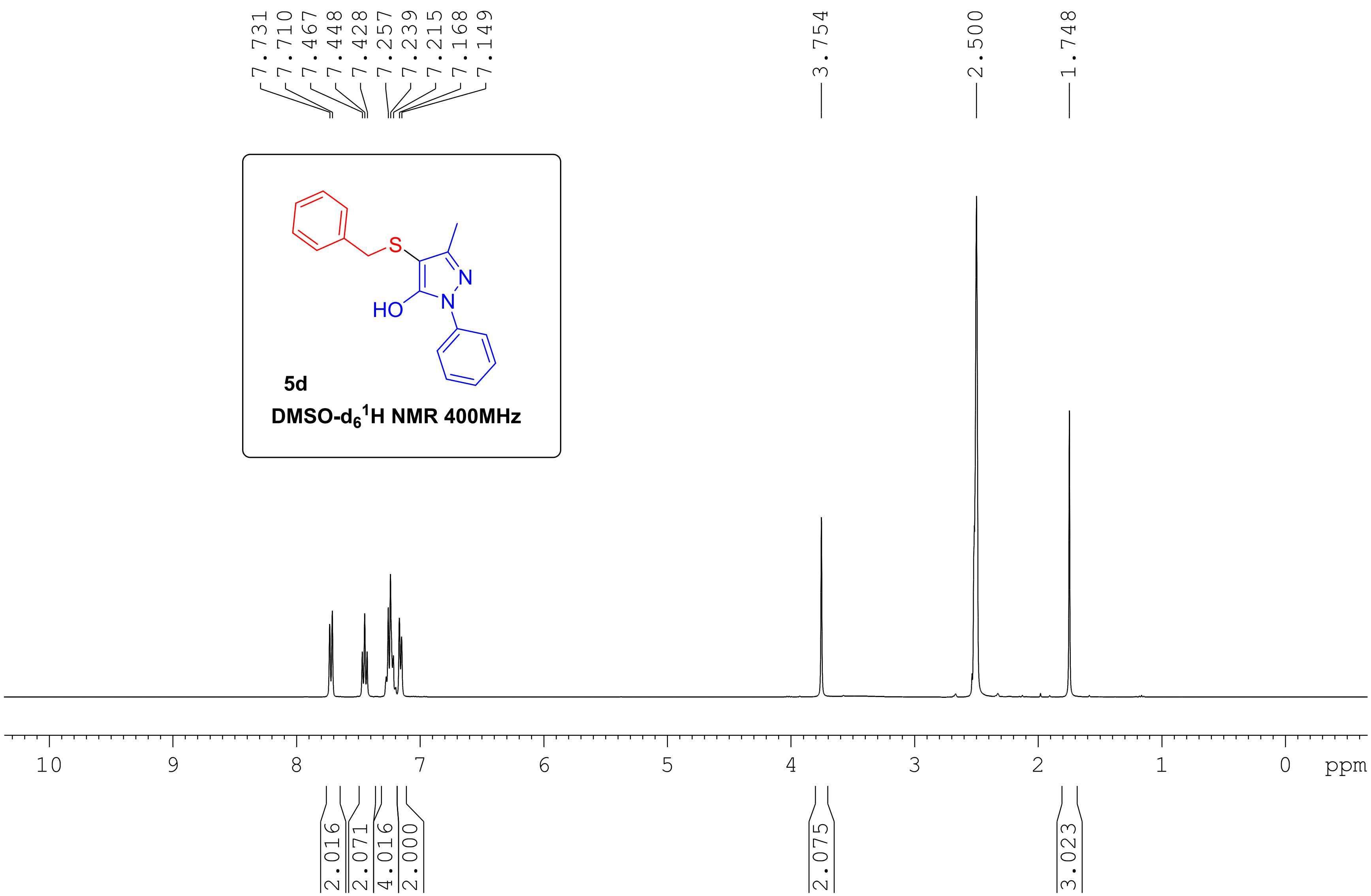
60
40
20
0
ppm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HO
S
N
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5d
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10 9 8 7 6 5 4 3 2 1 0 ppm
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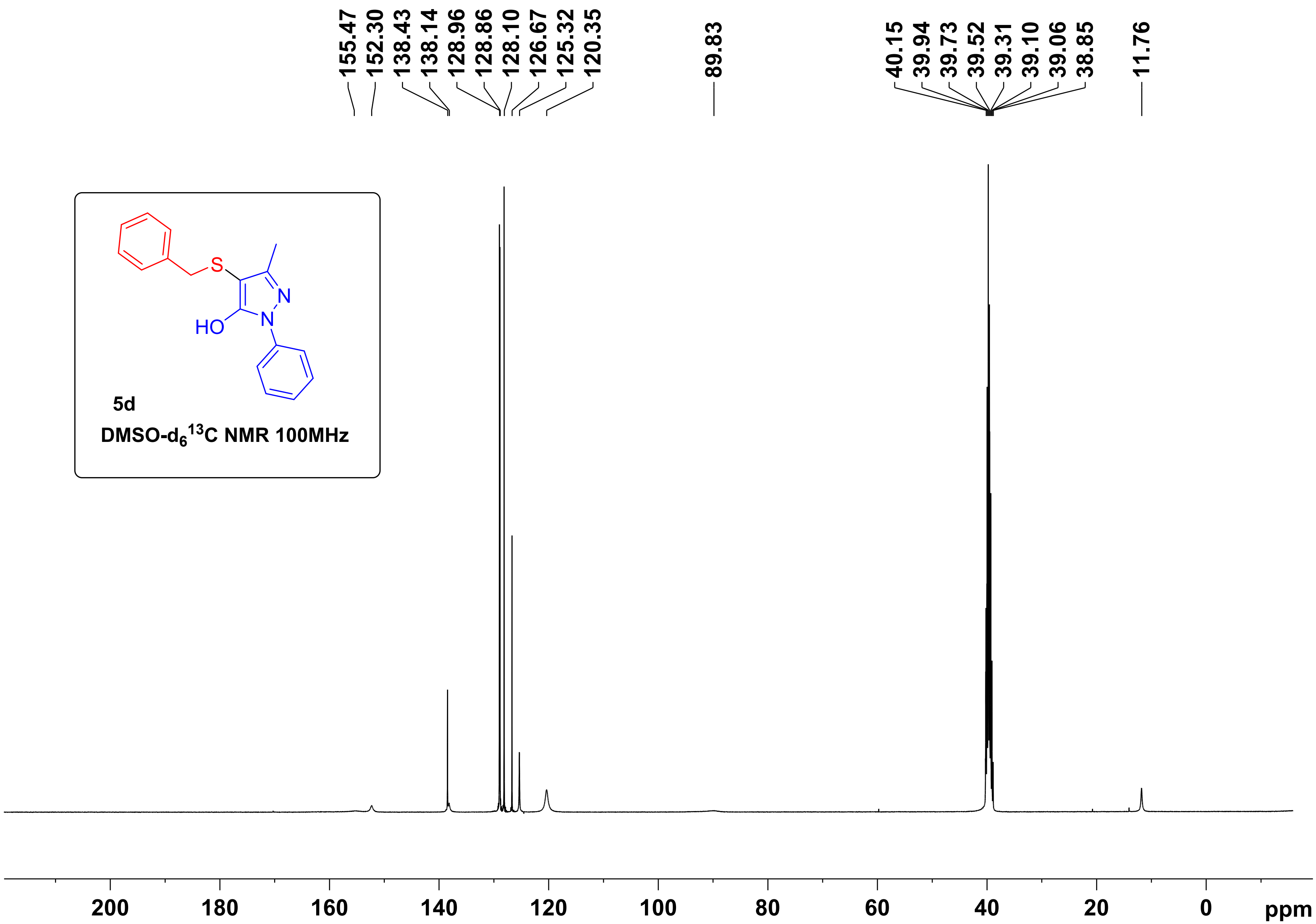
2.071
4.016
2.000
2.075
3.023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39.94
39.73
39.52
39.31
39.10
39.06
38.85
11.76
S
N
N
HO
5d
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40
20
0
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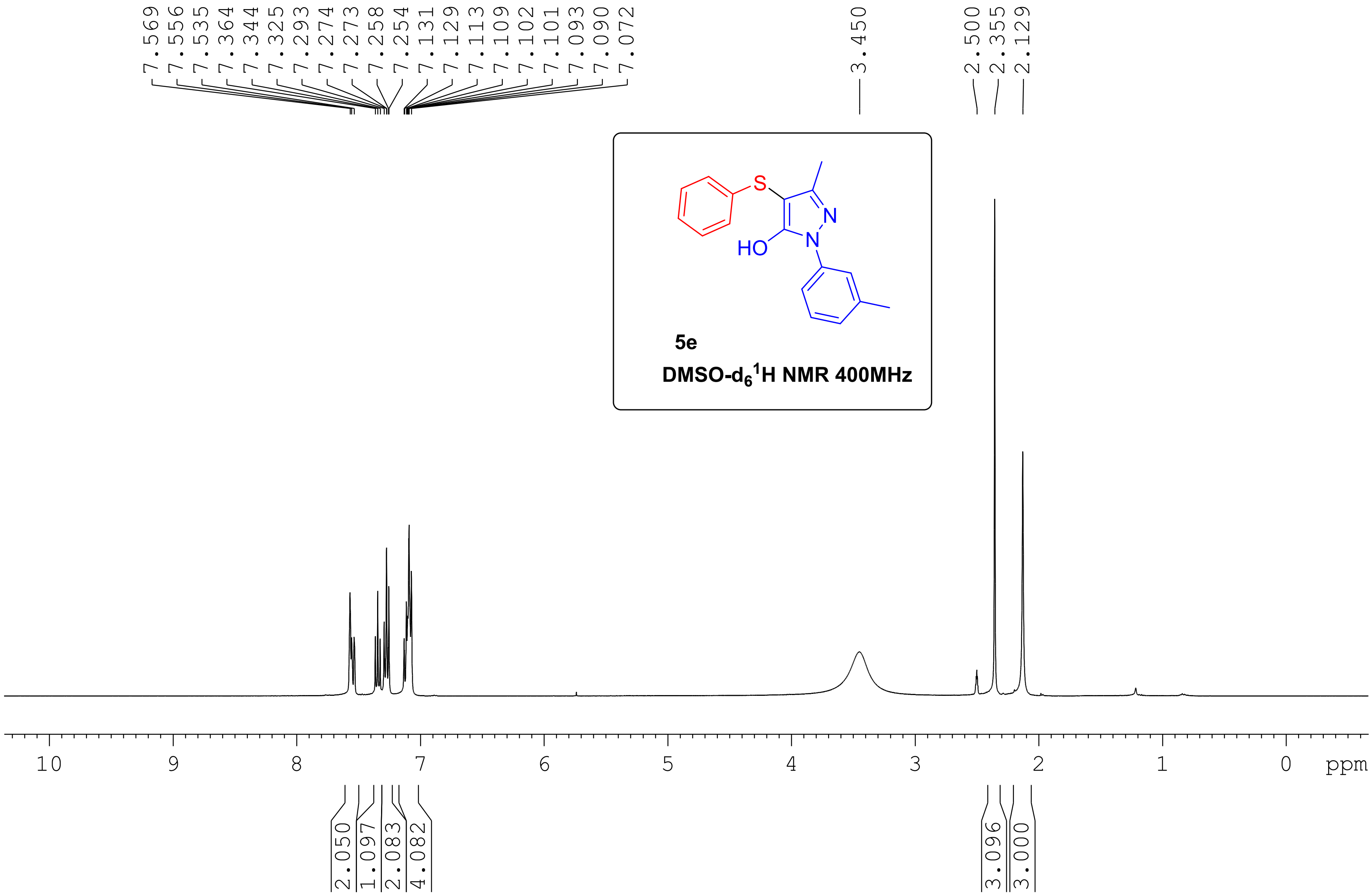
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7.129
7.113
7.109
7.102
7.101
7.093
7.090
7.072
3.450
2.500
2.355
2.129
S
N
N
HO
5e
DMSO-d6 1H NMR 400MHz
10
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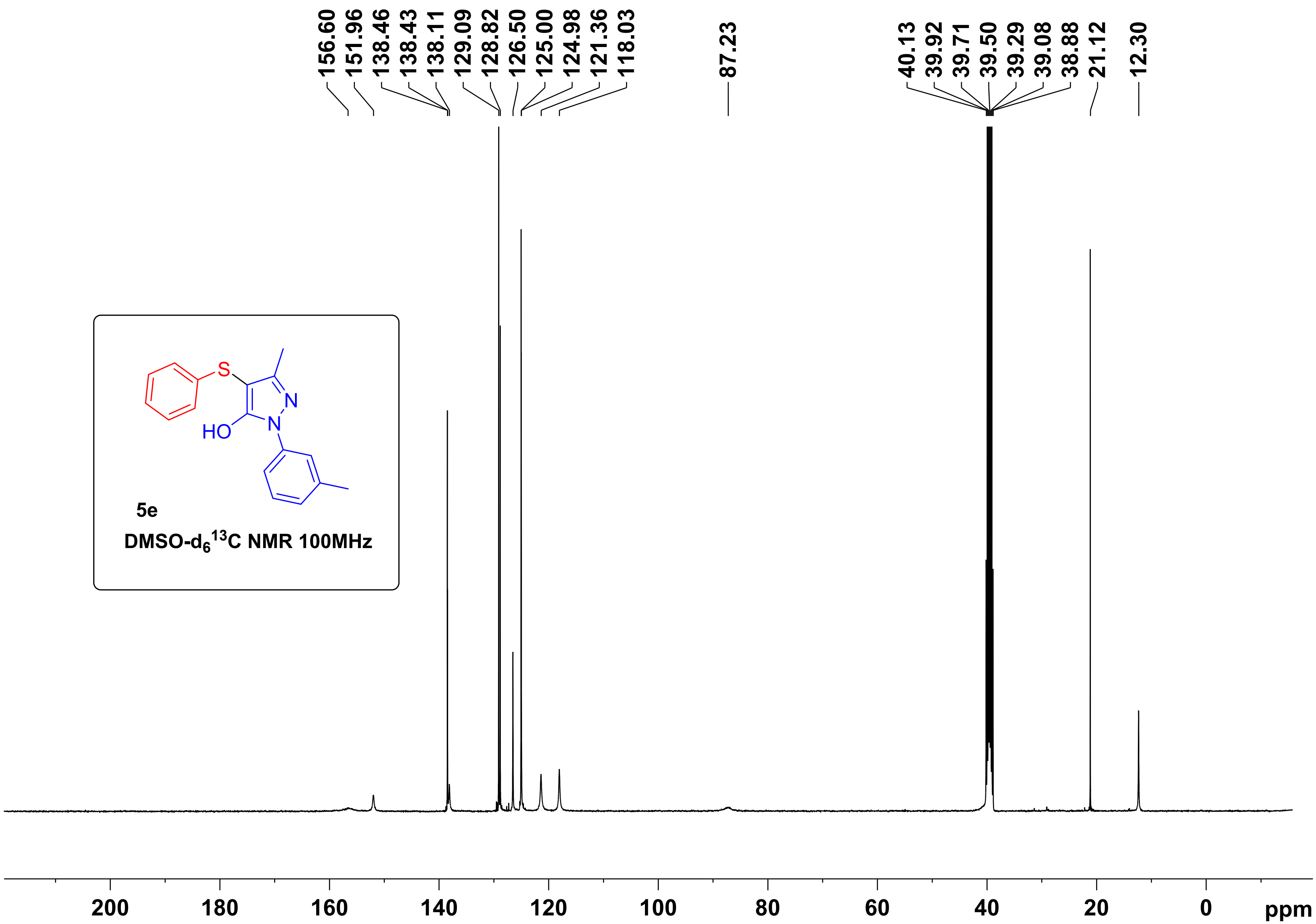
3.000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40.13
39.92
39.71
39.50
39.29
39.08
38.88
21.12
12.30
S
N
N
HO
5e
DMSO-d6 13C NMR 100MHz
200
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120
100
80
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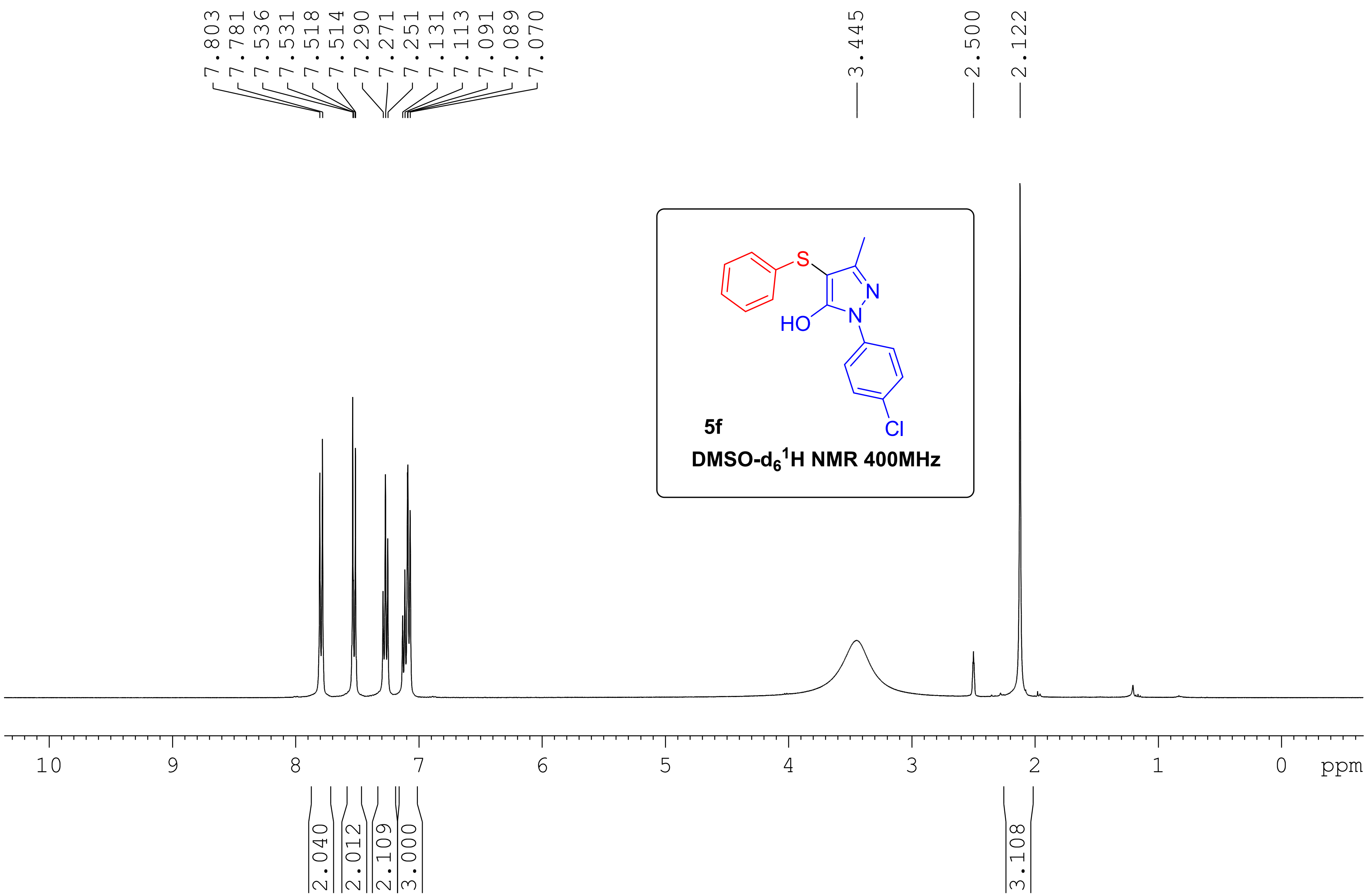
40
20
0
ppm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7.113
7.091
7.089
7.070
3.445
2.500
2.122
5f
HO
S
N
N
Cl
DMSO-d6 1H NMR 400MHz
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5
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ppm
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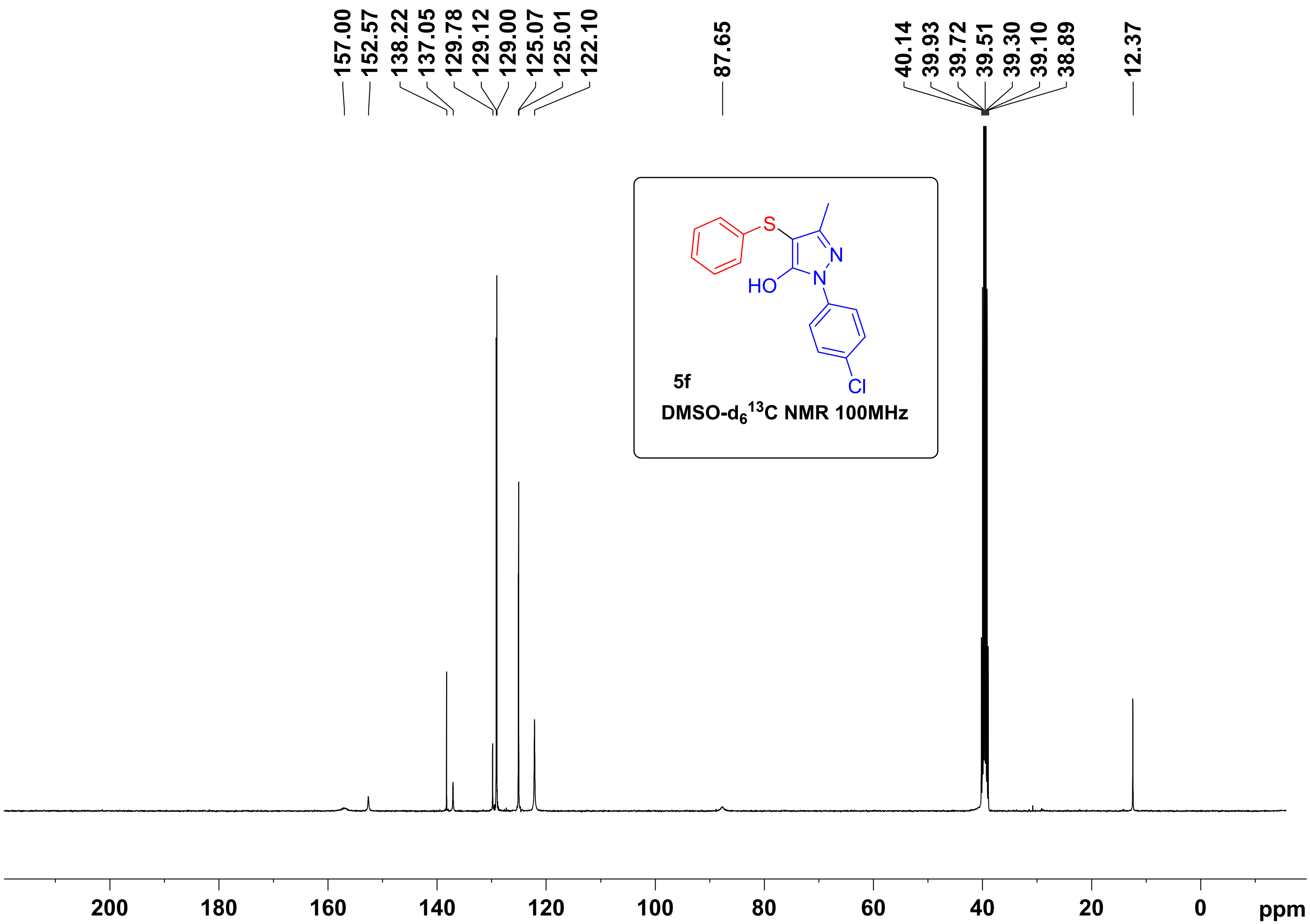
2.109
3.000
3.108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125.07
125.01
122.10
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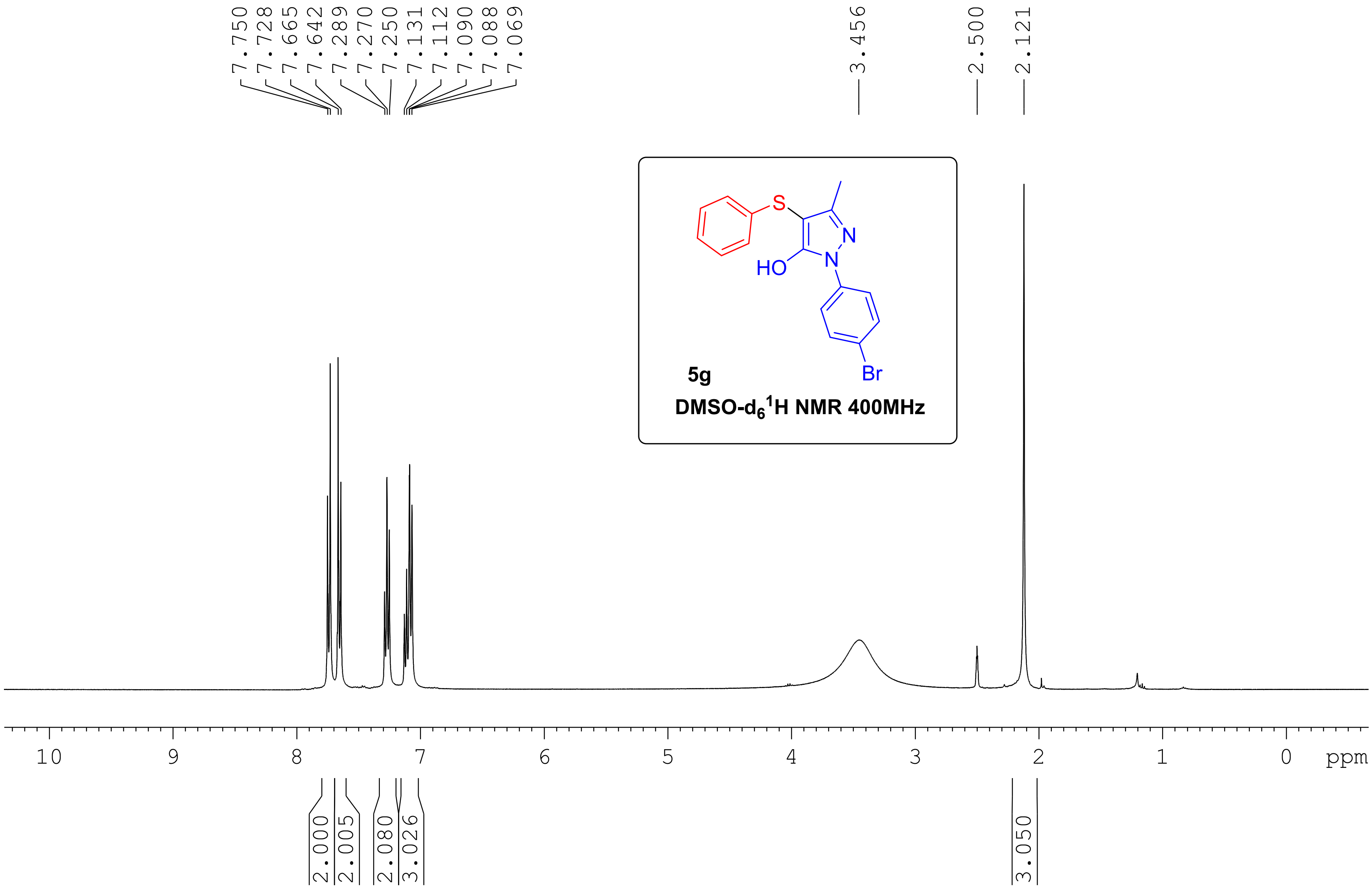
40.14
39.93
39.72
39.51
39.30
39.10
38.89
12.37
S
N
N
HO
Cl
5f
DMSO-d6 13C NMR 100MHz
200
180
160
140
120
100
80
60
40
20
0
ppm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7.090
7.088
7.069
3.456
2.500
2.121
S
N
N
HO
Br
5g
DMSO-d6 1H NMR 400MHz
10
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7
6
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4
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2
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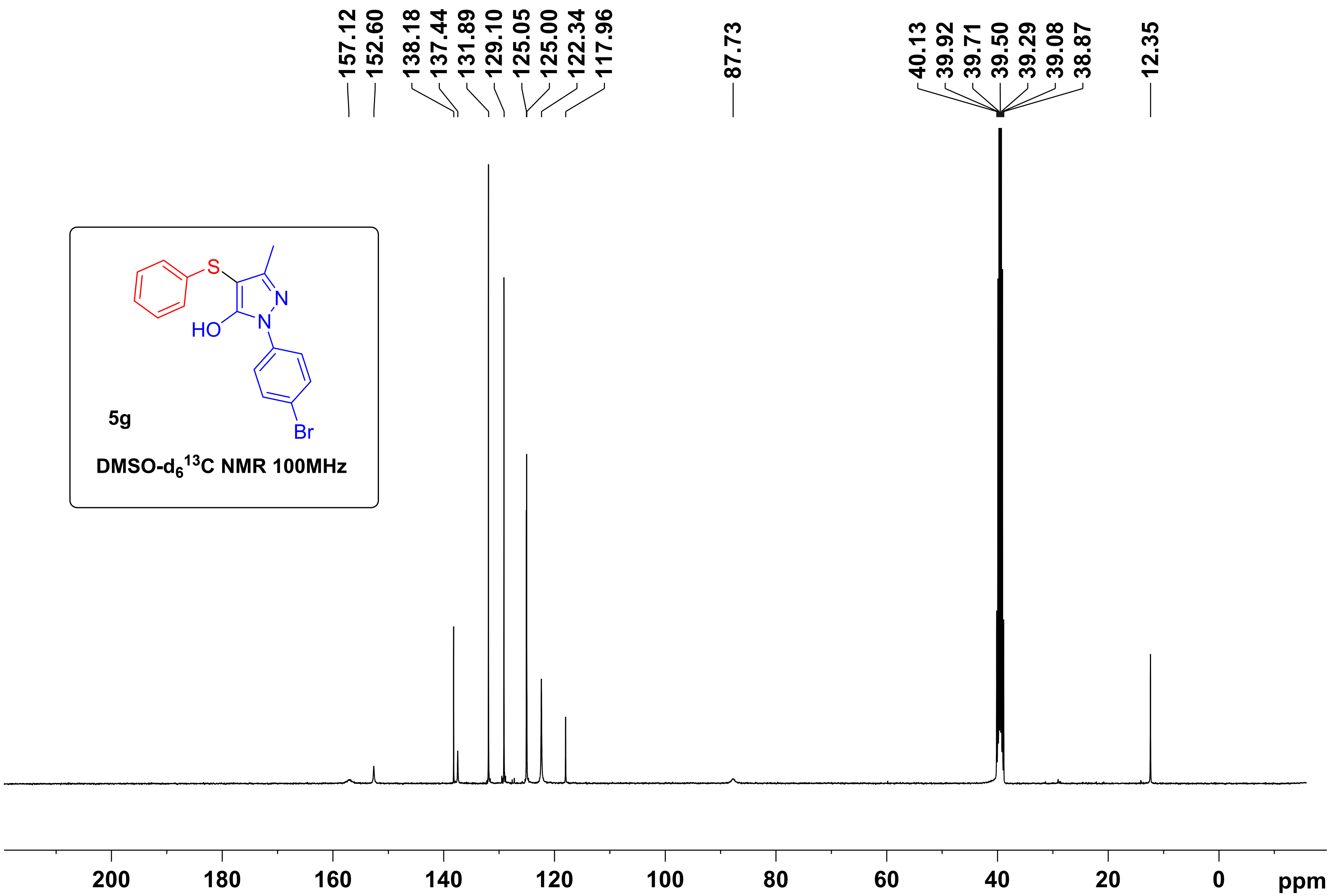
0
ppm
2.000
2.005
2.080
3.026
3.050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125.00
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117.96
87.73
40.13
39.92
39.71
39.50
39.29
39.08
38.87
12.35
S
N
N
HO
Br
5g
DMSO-d6 13C NMR 100MHz
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180
160
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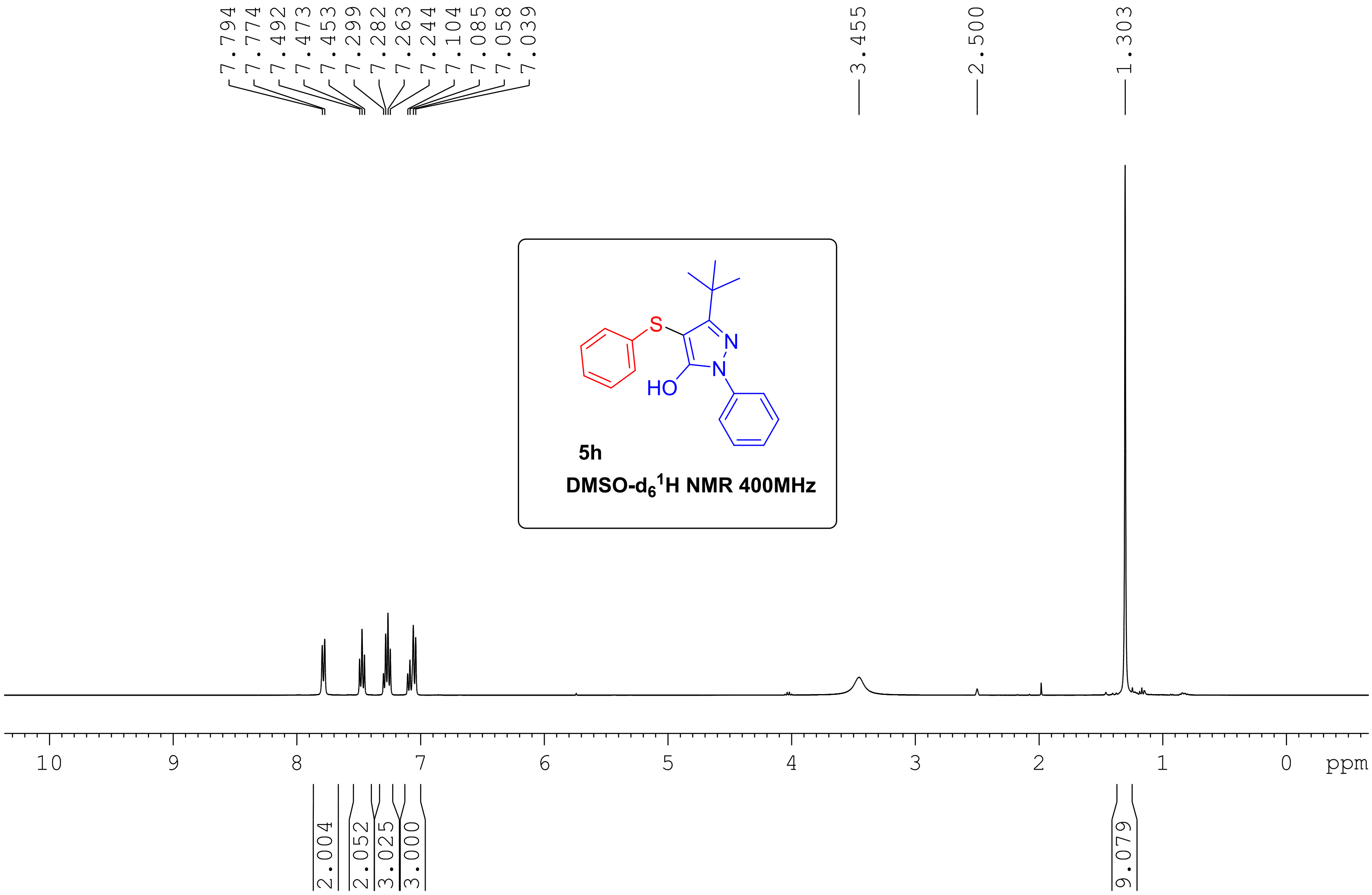
120
100
80
60
40
20
0
ppm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3.455
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S
N
N
HO
5h
DMSO-d6 1H NMR 400MHz
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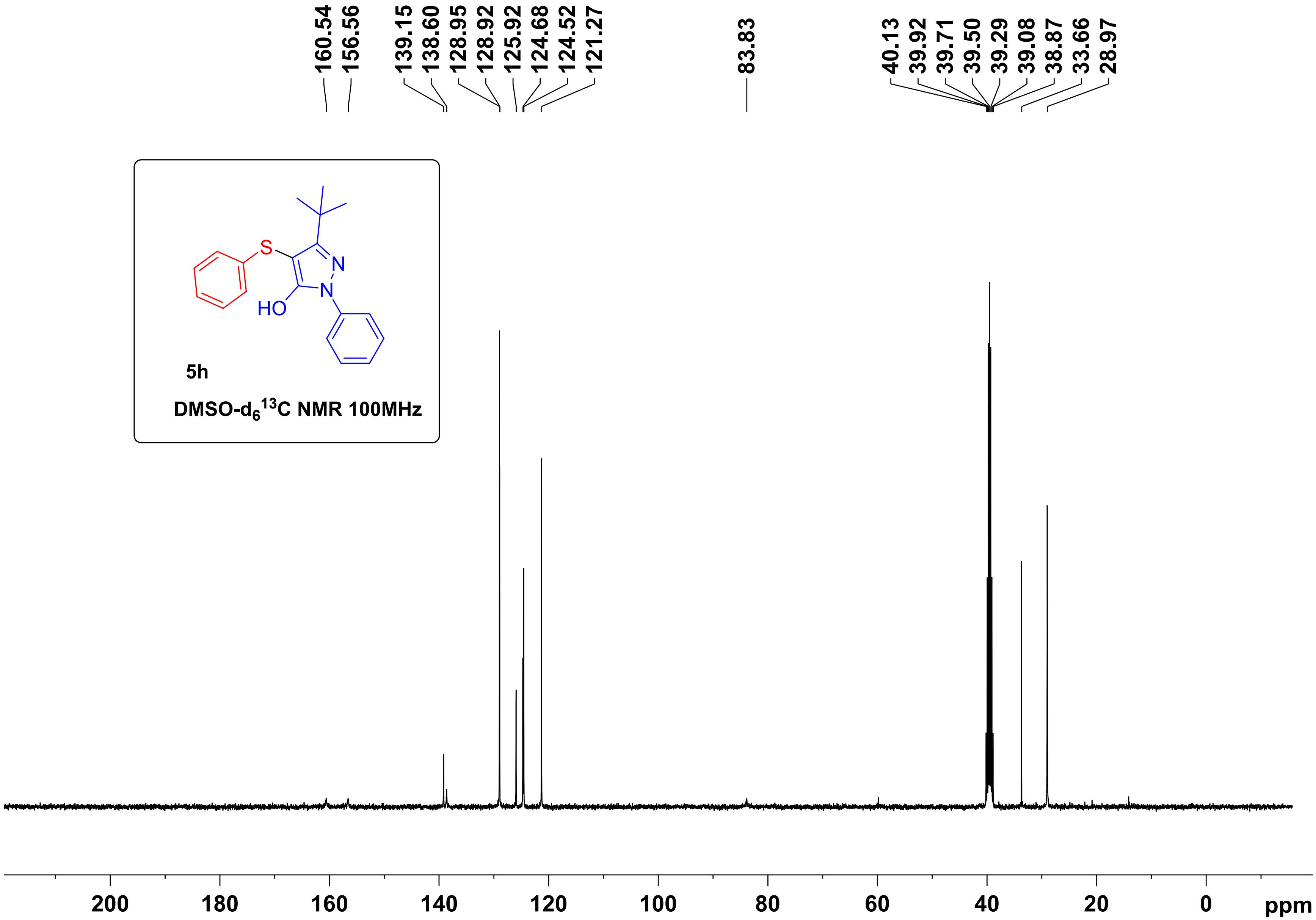
3.000
9.079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39.71
39.50
39.29
39.08
38.87
33.66
28.97
S
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5h
DMSO-d6 13C NMR 100MHz
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100
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60
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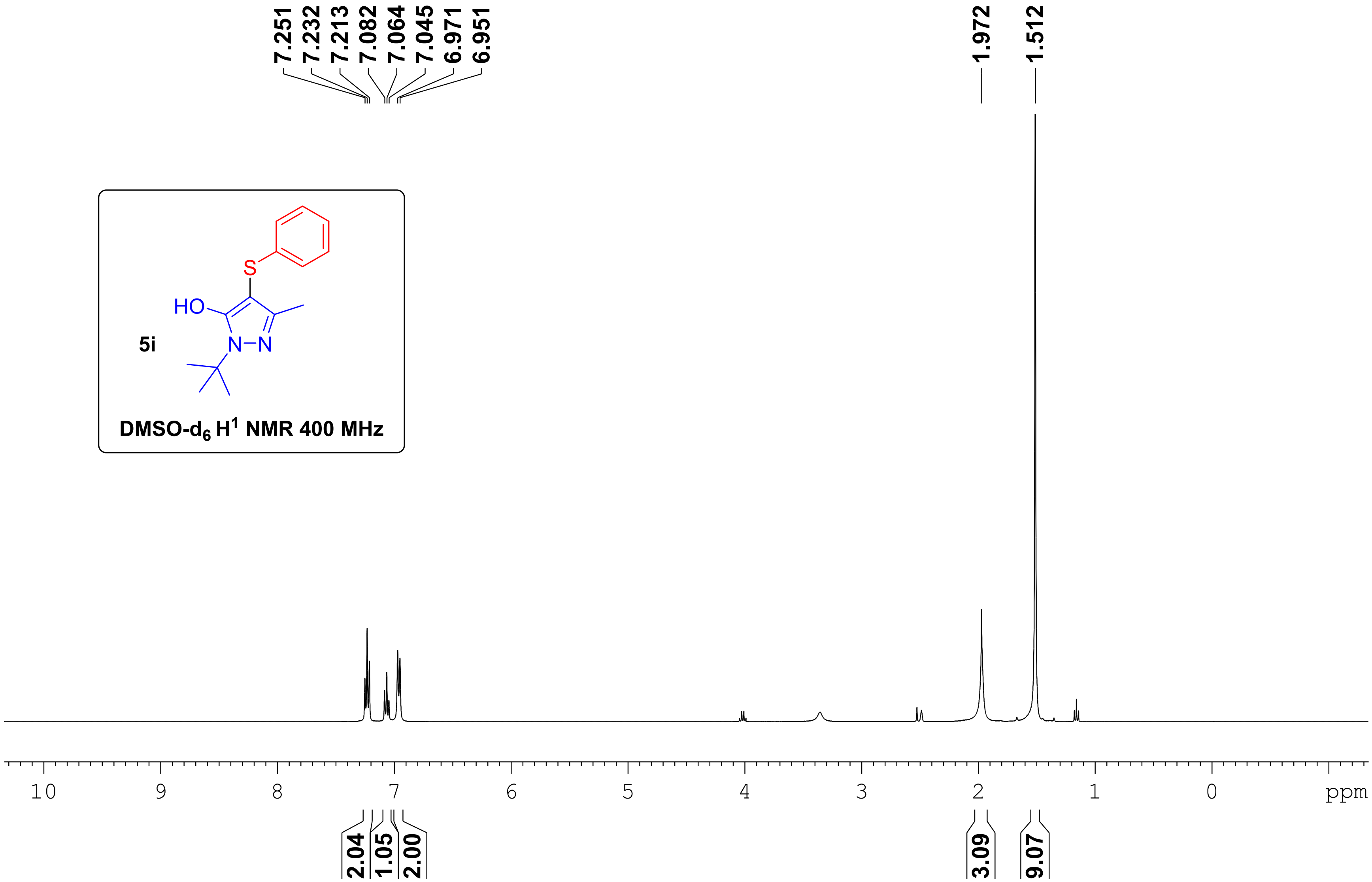
20
0
ppm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N
5i
DMSO-d6 H1 NMR 400 MHz
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2.00
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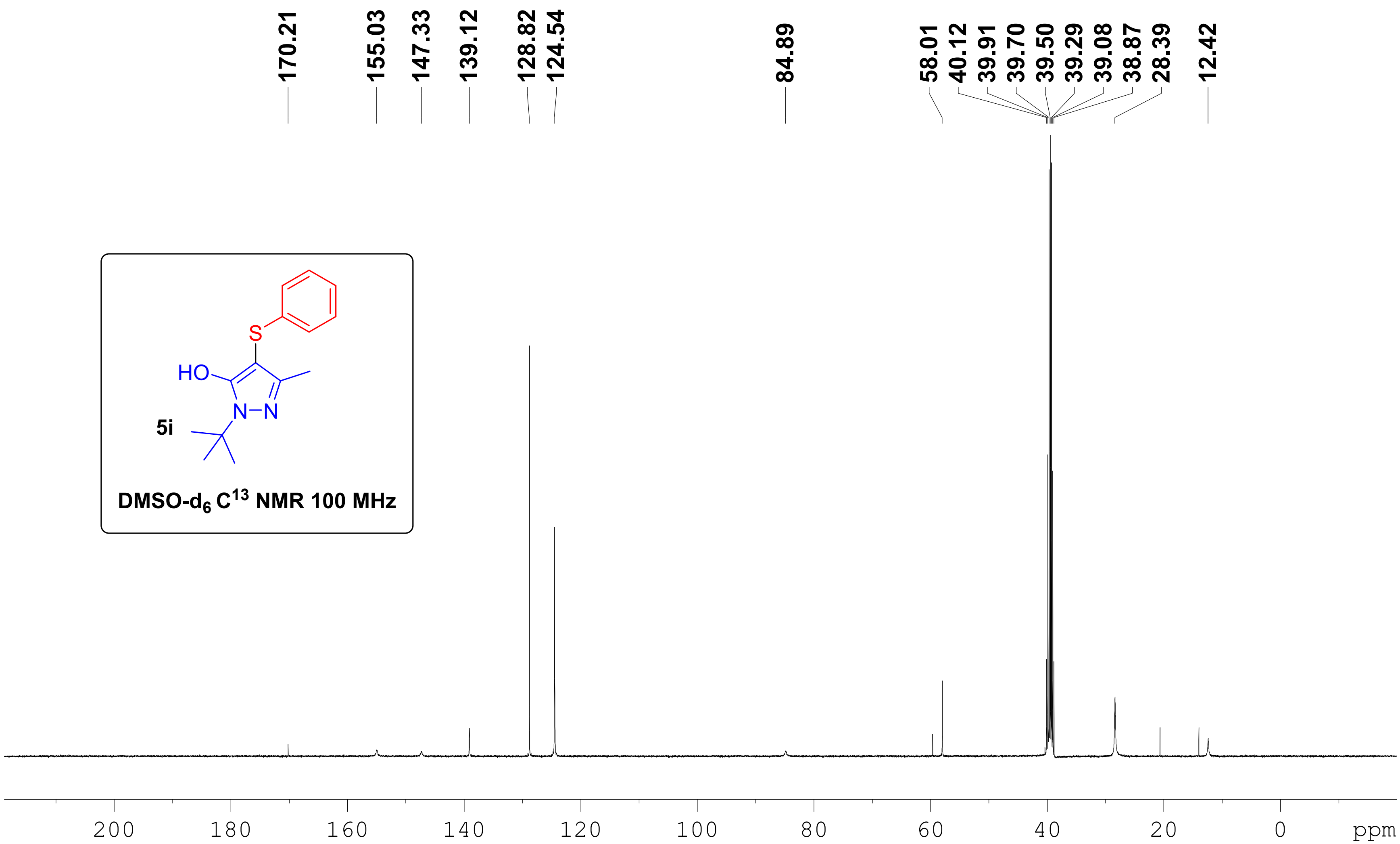
9.07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39.50
39.29
39.08
38.87
28.39
12.42
S
HO
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5i
DMSO-d6 C13 NMR 100 MHz
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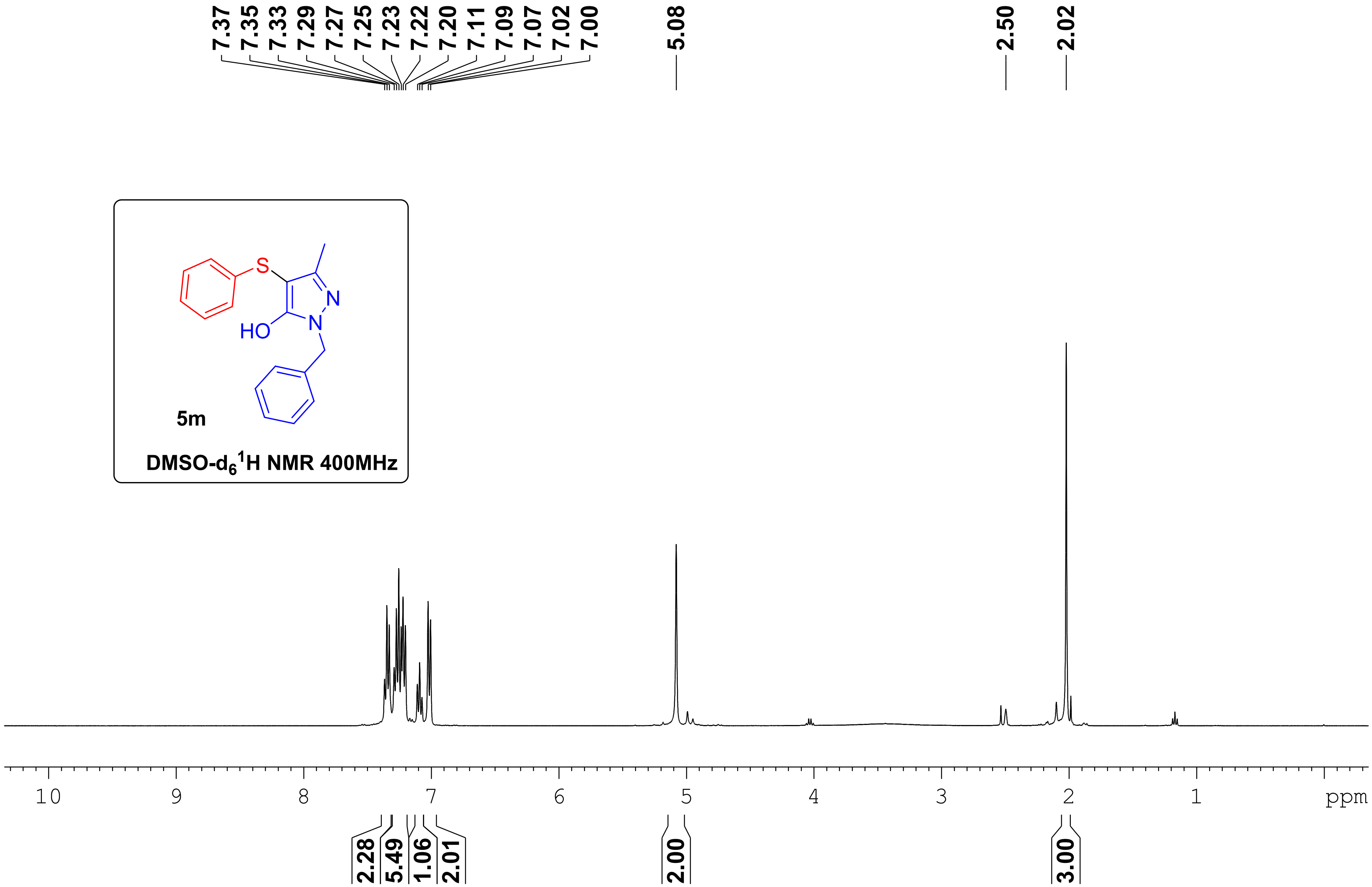
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7.07
7.02
7.00
5.08
2.50
2.02
S
N
HO
N
5m
DMSO-d6 1H NMR 400MHz
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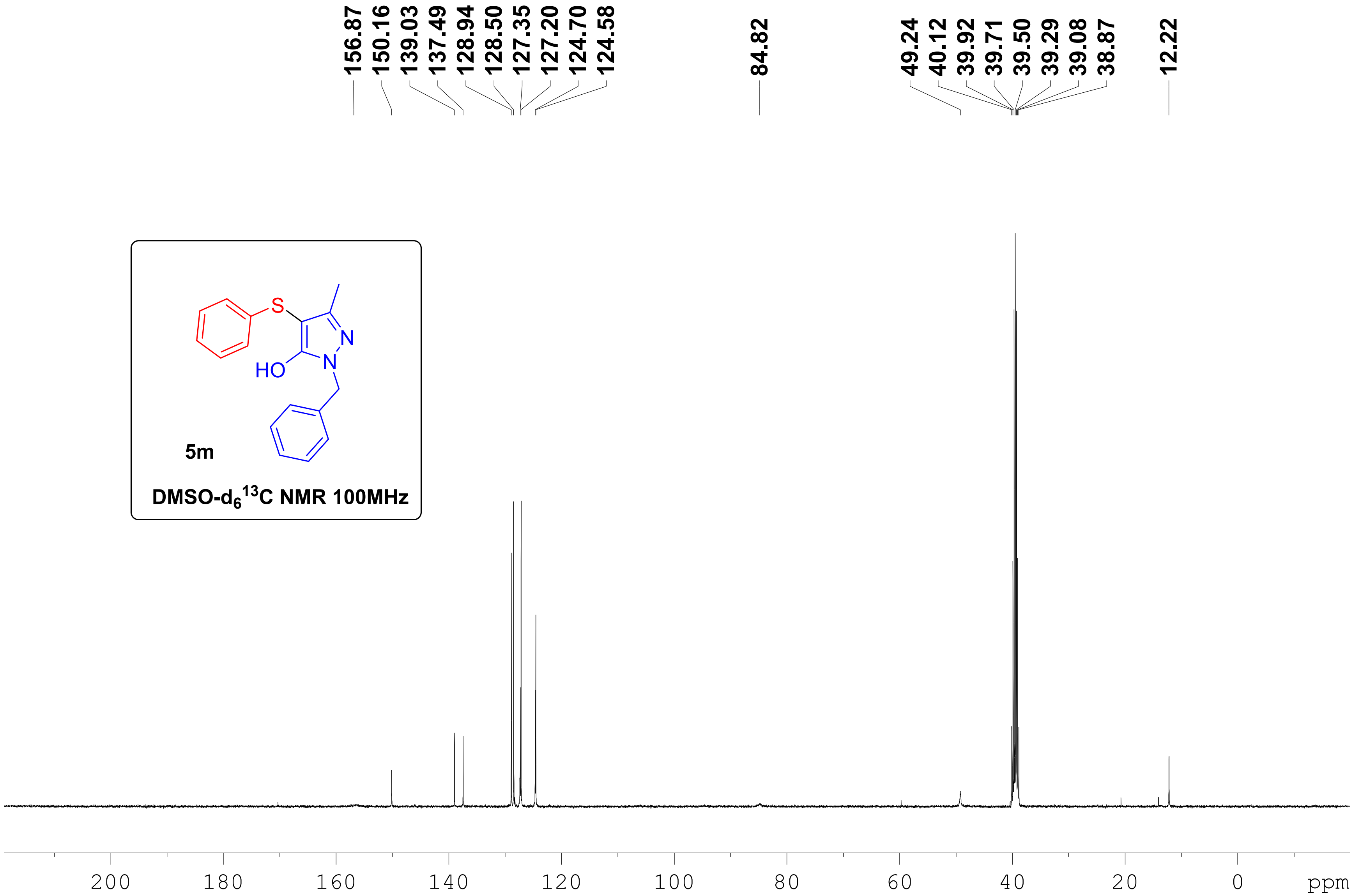
3.00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40.12
39.92
39.71
39.50
39.29
39.08
38.87
12.22
S
N
N
HO
5m
DMSO-d6 13C NMR 100MHz
200
180
160
140
120
100
80
60
40
20
0
ppm