

# Supporting Information

## AgNTf<sub>2</sub> Catalyzed Cycloaddition of *N*-Acyliminium ions with Alkynes for the Synthesis of 3,4-Dihydro-1,3-oxazin-2-one Skeleton

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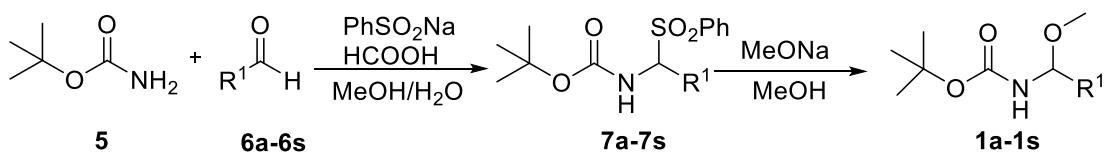
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## I. The synthetic details data for the substrates 1a-1s.



**General Procedure for the Synthesis of 1a-1s.** First, a mixture of an aldehyde **6a-6s** (20 mmol), *tert*-butyl carbamate **5** (10 mmol), sodium benzenesulfinate (25 mmol) and formic acid (20 mmol) in methanol/water 1/2 (30 mL) under nitrogen was stirred at room temperature for 24 h. After cooling at 0°C, the resulting solid was separated by filtration, solubilized in dichloromethane (30 mL) and the organic layer was dried ( $\text{MgSO}_4$ ). After concentration in vacuo, sulfones **7a-7s** was obtained without further purification.

Next, **7a-7s** (10 mmol), was added to a solution of sodium methoxide (30 mmol) in methanol (60 mL), and the mixture was stirred at room temperature for 2 hours. After dilution with water, the resulting mixture was extracted with dichloromethane and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the solvents were evaporated, The crude product was purified by flash chromatography on silica gel with PE/EtOAc to obtain **1a-1s**.

Among the following compounds, **1a**, **1b**, **1d**, **1e**, **1f**, **1g**, **1k**, **1o**, **1p** are known compounds, so this paper only tests their  $^1\text{H}$  NMR spectra, and their  $^1\text{H}$  NMR spectra data are consistent with the literature.<sup>23</sup>

**tert-Butyl (methoxy(phenyl)methyl)carbamate (1a).** White solid (2.73 g, 64%, PE:EA = 9:1,  $R_f$  = 0.25); mp 67–68 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44–7.40 (m, 2H), 7.38–7.29 (m, 3H), 5.82 (d,  $J$  = 10.0 Hz, 1H), 5.15 (d,  $J$  = 7.2 Hz, 1H), 3.44 (s, 3H), 1.48 (s, 9H) ppm.

**tert-Butyl (methoxy(p-tolyl)methyl)carbamate (1b).** White solid (3.29 g, 77%, PE:EA = 9:1,  $R_f$  = 0.25); mp 134–135 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33–7.26 (m, 2H), 7.20–7.12 (m, 2H), 5.78 (d,  $J$  = 9.2 Hz, 1H), 5.13 (d,  $J$  = 7.6 Hz, 1H), 3.43 (s, 3H), 2.34 (s, 3H), 1.47 (s, 9H) ppm.

**tert-Butyl ((4-(*tert*-butyl)phenyl)(methoxy)methyl)carbamate (1c).** White solid (4.03 g, 81%, PE:EA = 9:1, Rf = 0.25); IR (film):  $\nu_{\text{max}}$  2963, 2904, 1716, 1512, 1363, 1169, 1080, 892 cm<sup>-1</sup>; mp 83-84 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40-7.33 (m, 4H), 5.79 (d, J = 9.6 Hz, 1H), 5.10 (d, J = 7.6 Hz, 1H), 3.44 (s, 3H), 1.47 (s, 9H), 1.31 (s, 9H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 155.4, 151.6, 136.6, 125.7, 125.6, 83.5, 80.1, 55.6,

34.7, 31.4, 28.4 ppm; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>27</sub>NO<sub>3</sub>Na<sup>+</sup>, 316.1883, found 316.1885.

**tert-Butyl (methoxy(4-methoxyphenyl)methyl)carbamate (1d).** White solid (3.04 g, 67%, PE:EA = 9:1, Rf = 0.25); mp 135-136 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36-7.34 (m, 2H), 6.91-6.89 (m, 2H), 5.78 (d, J = 9.6 Hz, 1H), 5.16 (d, J = 8.0 Hz, 1H), 3.81 (s, 3H), 3.44 (s, 3H), 1.49 (s, 9H) ppm.

**tert-Butyl ((4-bromophenyl)(methoxy)methyl)carbamate (1e).** White solid (3.05 g, 57%, PE:EA = 9:1, Rf = 0.25); mp 89-90 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50-7.45 (m, 2H), 7.32-7.28 (m, 2H), 5.79 (d, J = 9.6 Hz, 1H), 5.10 (d, J = 8.4 Hz, 1H), 3.42 (s, 3H), 1.48 (s, 9H) ppm.

**tert-Butyl (methoxy(4-(trifluoromethyl)phenyl)methyl)carbamate (1f).** White solid (2.64 g, 51%, PE:EA = 9:1, Rf = 0.25); mp 161-162 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65-7.59 (m, 2H), 7.58-7.52 (m, 2H), 5.89 (d, J = 10.0 Hz, 1H), 5.09 (d, J = 7.6 Hz, 1H), 3.48 (s, 3H), 1.49 (s, 9H) ppm.

**tert-Butyl ((4-cyanophenyl)(methoxy)methyl)carbamate (1g).** White solid (2.41 g, 54%, PE:EA = 9:1, Rf = 0.25); mp 111-112 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68-7.62 (m, 2H), 7.58-7.53 (m, 2H), 5.87 (d, J = 9.6 Hz, 1H), 5.18-4.94 (d, J = 8.8 Hz, 1H), 3.48 (s, 3H), 1.49 (s, 9H) ppm.

**tert-Butyl (methoxy(m-tolyl)methyl)carbamate (1h).** Colorless oil (2.99 g, 70%, PE:EA = 9:1, Rf = 0.25); IR (film): v<sub>max</sub> 2978, 2930, 1713, 1514, 1367, 1248, 1165, 965 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28-7.16 (m, 3H), 7.16-7.09 (m, 1H), 5.77 (d, J = 9.6 Hz, 1H), 5.11 (s, 1H), 3.44 (s, 3H), 2.35 (s, 3H), 1.48 (s, 9H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 155.4, 139.5, 133.4, 129.3, 128.6, 126.6, 123.0, 83.7, 80.2, 55.6, 28.4, 21.5 ppm; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>21</sub>NO<sub>3</sub>Na<sup>+</sup>, 274.1414, found 274.1418.

**tert-Butyl ((3-chlorophenyl)(methoxy)methyl)carbamate (1i).** White solid (2.17 g, 47%, PE:EA = 9:1, Rf = 0.25); mp 87-88 °C; IR (film): v<sub>max</sub> 2980, 2933, 1712, 1518, 1363, 1242, 1171, 769 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43-7.38 (m, 1H), 7.31-7.25 (m, 3H), 5.79 (d, J = 9.6 Hz, 1H), 5.13 (d, J = 8.4 Hz, 1H), 3.45 (s, 3H), 1.48 (s, 9H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 155.4, 141.7, 134.6, 129.9, 128.6, 126.4, 124.3, 82.9, 80.4, 55.7, 28.4 ppm; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>18</sub>ClNO<sub>3</sub>Na<sup>+</sup>, 294.0867, found 294.0871.

**tert-Butyl ((3-bromophenyl)(methoxy)methyl)carbamate (1j).** White solid (2.51 g, 47%, PE:EA = 9:1, Rf = 0.25); mp 84-85 °C; IR (film): v<sub>max</sub> 2980, 2932, 1700, 1514, 1365,

1245, 1165, 782  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63-7.56 (m, 1H), 7.48-7.40 (m, 1H), 7.37-7.31 (m, 1H), 7.25-7.19 (m, 1H), 5.80 (d,  $J$  = 10.0 Hz, 1H), 5.11 (d,  $J$  = 5.6 Hz, 1H), 3.45 (s, 3H), 1.49 (s, 9H) ppm;  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.3, 141.9, 131.6, 130.2, 129.3, 124.8, 122.8, 82.8, 80.5, 55.8, 28.4 ppm; HRMS (ESI) m/z: [M + Na] $^+$  Calcd for  $\text{C}_{13}\text{H}_{18}\text{BrNO}_3\text{Na}^+$ , 338.0362, found 338.0365.

**tert-Butyl (methoxy(o-tolyl)methyl)carbamate (1k).** White solid (2.90 g, 72%, PE:EA = 9:1, Rf = 0.25); mp 131-132  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.44 (m, 1H), 7.23-7.14 (m, 3H), 5.91 (d,  $J$  = 10.0 Hz, 1H), 5.05 (d,  $J$  = 8.4 Hz, 1H), 3.44 (s, 3H), 2.33 (s, 3H), 1.46 (s, 9H) ppm.

**tert-Butyl (cyclopropyl(methoxy)methyl)carbamate (1l).** Colorless oil (2.39 g, 70%, PE:EA = 9:1, Rf = 0.25); IR (film):  $\nu_{\text{max}}$  2978, 2932, 1710, 1516, 1365, 1244, 1171, 782  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.06-4.91 (m, 1H), 4.58-4.43 (m, 1H), 3.34 (s, 3H), 1.46 (s, 9H), 1.08-0.99 (m, 1H), 0.55-0.36 (m, 4H) ppm;  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 84.8, 79.8, 55.6, 28.4, 15.6, 2.1, 1.3 ppm; HRMS (ESI) m/z: [M + Na] $^+$  Calcd for  $\text{C}_{15}\text{H}_{23}\text{NO}_3\text{Na}^+$ , 288.1570, found 288.1571.

**tert-Butyl (cyclohexyl(methoxy)methyl)carbamate (1m).** White solid (1.33 g, 79%, PE:EA = 9:1, Rf = 0.25); IR (film):  $\nu_{\text{max}}$  2929, 2853, 1700, 1516, 1365, 1173, 1078, 957  $\text{cm}^{-1}$ ; mp 74-75  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.82 (d,  $J$  = 10.0 Hz, 1H), 4.63-4.48 (m, 1H), 3.33 (s, 3H), 1.83-1.61 (m, 5H), 1.49-1.42 (m, 1H), 1.46 (s, 9H), 1.28-1.00 (m, 5H) ppm;  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.9, 86.7, 79.6, 55.6, 42.9, 28.4, 27.9, 26.4, 25.9, 25.8 ppm; HRMS (ESI) m/z: [M + Na] $^+$  Calcd for  $\text{C}_{13}\text{H}_{25}\text{NO}_3\text{Na}^+$ , 266.1727, found 266.1728.

**tert-Butyl (1-methoxybutyl)carbamate (1n).** Colorless oil (2.42 g, 70%, PE:EA = 9:1, Rf = 0.25); IR (film):  $\nu_{\text{max}}$  2963, 2871, 1710, 1514, 1365, 1175, 942, 767  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.96-4.72 (m, 2H), 3.34 (s, 3H), 1.69-1.57 (m, 1H), 1.54-1.49 (m, 1H), 1.46 (s, 9H), 1.43-1.34 (m, 2H), 0.93 (t, 3H) ppm;  $^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.7, 82.9, 79.7, 55.4, 37.8, 28.4, 18.3, 13.8 ppm; HRMS (ESI) m/z: [M + Na] $^+$  Calcd for  $\text{C}_{10}\text{H}_{21}\text{NO}_3\text{Na}^+$ , 226.1414, found 226.1411.

**tert-Butyl (1-methoxy-2-methylpropyl)carbamate (1o).** Colorless oil (1.98 g, 57%, PE:EA = 9:1, Rf = 0.25);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.79 (d,  $J$  = 9.6 Hz, 1H), 4.56 (dd,  $J$  = 10.0 Hz, 5.6 Hz, 1H), 3.34 (s, 3H), 1.84-1.72 (m, 1H), 1.46 (s, 9H), 0.96-0.89 (m, 6H) ppm.

**tert-Butyl (1-methoxy-3-methylbutyl)carbamate (1p).** Colorless oil (2.32 g, 63%, PE:EA = 9:1, Rf = 0.25);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.92-4.84 (m, 1H), 4.83-4.67 (m,

1H), 3.34 (s, 3H), 1.77-1.66 (m, 1H), 1.60-1.51 (m, 1H), 1.46 (s, 9H), 1.42-1.32 (m, 1H), 0.96-0.88 (m, 6H) ppm.

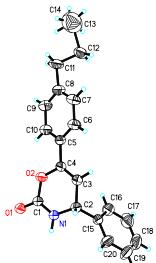
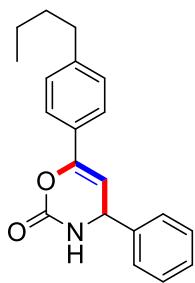
**tert-Butyl (1-methoxy-3-phenylpropyl)carbamate (1q).** White solid (3.56 g, 79%, PE:EA = 9:1, R<sub>f</sub> = 0.25); mp 78-79 °C; IR (film):  $\nu_{\text{max}}$  2976, 2933, 1712, 1514, 1363, 1167, 1045, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31-7.24 (m, 2H), 7.23-7.11 (m, 3H), 4.83 (s, 1H), 3.35 (s, 3H), 2.77-2.60 (m, 2H), 2.02-1.89 (m, 1H), 1.88-1.76 (m, 1H), 1.46 (s, 9H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 155.6, 141.4, 128.6, 128.5, 126.1, 82.6, 79.5, 55.4, 37.5, 31.4, 28.3 ppm; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>23</sub>NO<sub>3</sub>Na<sup>+</sup>, 288.1570, found 288.1571.

**tert-Butyl (2-(benzyloxy)-1-methoxyethyl)carbamate (1r).** Colorless oil (3.15 g, 66%, PE:EA = 9:1, R<sub>f</sub> = 0.25); IR (film):  $\nu_{\text{max}}$  2976, 2931, 1712, 1500, 1365, 1169, 739, 694 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37-7.27 (m, 5H), 5.28 (d, J = 9.2 Hz, 1H), 4.98 (d, J = 9.6 Hz, 1H), 4.61-4.53 (m, 2H), 3.60-3.48 (m, 2H), 3.38 (s, 3H), 1.46 (s, 9H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 155.5, 137.8, 128.5, 127.9, 81.3, 80.0, 73.7, 71.4, 55.7, 28.4 ppm; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>23</sub>NO<sub>4</sub>Na<sup>+</sup>, 304.1519, found 304.1512.

**tert-Butyl (methoxy(thiophen-2-yl)methyl)carbamate (1s).** White solid (1.74 g, 42%, PE:EA = 9:1, R<sub>f</sub> = 0.25); mp 78-79 °C; IR (film):  $\nu_{\text{max}}$  2980, 2929, 1710, 1504, 1242, 1165, 1076, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30-7.21 (m, 1H), 7.06-7.02 (m, 1H), 6.99-6.94 (m, 1H), 6.05 (d, J = 9.6 Hz, 1H), 5.26 (d, J = 4.8 Hz, 1H), 3.47 (s, 3H), 1.49 (s, 9H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 156.1, 143.2, 126.9, 125.6, 124.7, 80.8, 80.5, 55.8, 28.4 ppm; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>11</sub>H<sub>17</sub>NO<sub>3</sub>SNa<sup>+</sup>, 266.0821, found 266.0823.

## II.X-Ray Structure for compound 3ae

ORTEP drawing of the X-ray crystallographic structure of 3ae



CCDC 2168786. For detailed crystallographic data, please refer to the Cambridge Crystallographic Data Centre at <http://ccdc.cam.ac.uk>.

**Table 1.** Crystal data and structure refinement for **3ae**.

Identification code	<b>3ae</b>
Empirical formula	C <sub>20</sub> H <sub>21</sub> NO <sub>2</sub>
Formula weight	307.38
Temperature	293(2)K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 9.6668(6) Å      α = 91.153(2)°. b = 13.1481(7) Å      β = 94.071(2)°. c = 13.9023(9) Å      γ = 104.497(2)°.
Volume	1705.09(18) Å <sup>3</sup>
Z	4
Density (calculated)	1.197 Mg/m <sup>3</sup>
Absorption coefficient	0.077 mm <sup>-1</sup>
F(000)	656
Crystal size	0.190 x 0.150 x 0.110 mm <sup>3</sup>
Theta range for data collection	2.722 to 25.998°.
Index ranges	-11<=h<=11, -16<=k<=16, -17<=l<=17

Reflections collected	33470
Independent reflections	6677 [R(int) = 0.0549]
Completeness to theta = 25.242°	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.7006
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6677 / 112 / 492
Goodness-of-fit on F <sup>2</sup>	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0639, wR2 = 0.1495
R indices (all data)	R1 = 0.1155, wR2 = 0.1848
Extinction coefficient	0.028(5)
Largest diff. peak and hole	0.173 and -0.160 e.Å <sup>-3</sup>

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 3ae. U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
O(1)	3009(2)	3956(1)	3893(1)	85(1)
O(2)	3600(2)	5291(1)	2956(1)	73(1)
N(1)	5354(2)	4724(2)	3833(1)	66(1)
C(1)	3982(3)	4622(2)	3596(2)	65(1)
C(2)	6569(2)	5523(2)	3519(2)	62(1)
C(3)	6002(3)	6232(2)	2866(2)	66(1)
C(4)	4636(3)	6114(2)	2620(2)	60(1)
C(5)	3961(3)	6773(2)	1987(2)	65(1)
C(6)	4715(3)	7760(2)	1756(2)	88(1)
C(7)	4074(4)	8377(2)	1169(2)	102(1)
C(8)	2672(4)	8042(3)	801(2)	94(1)
C(9)	1934(3)	7060(3)	1034(2)	98(1)
C(10)	2559(3)	6434(2)	1618(2)	85(1)
C(11)	1838(11)	8631(8)	134(7)	101(3)
C(12)	2709(7)	9071(5)	-716(5)	98(2)
C(13)	1629(16)	9899(11)	-1198(11)	239(8)
C(14)	717(10)	9125(7)	-1947(7)	141(3)
C(11')	2221(19)	8976(11)	285(11)	110(6)

C(12')	1942(16)	8637(10)	-760(10)	149(5)
C(13')	2038(10)	9688(7)	-1426(6)	78(2)
C(14')	508(16)	9485(17)	-1442(17)	195(8)
C(15)	7617(2)	5013(2)	3062(2)	63(1)
C(16)	7448(3)	4709(2)	2108(2)	87(1)
C(17)	8414(5)	4232(3)	1708(3)	121(1)
C(18)	9553(5)	4073(3)	2277(5)	137(2)
C(19)	9723(4)	4375(3)	3214(4)	131(2)
C(20)	8769(3)	4848(2)	3616(2)	92(1)
O(3)	4202(2)	-3102(1)	4833(1)	69(1)
O(4)	4850(2)	-1532(1)	4225(1)	66(1)
N(2)	6506(2)	-2192(2)	5110(1)	67(1)
C(21)	5171(2)	-2322(2)	4748(2)	59(1)
C(22)	7727(2)	-1294(2)	5022(2)	67(1)
C(23)	7215(3)	-478(2)	4480(2)	71(1)
C(24)	5889(2)	-601(2)	4117(2)	60(1)
C(25)	5293(3)	151(2)	3561(2)	61(1)
C(26)	6120(3)	1151(2)	3414(2)	78(1)
C(27)	5580(3)	1857(2)	2886(2)	86(1)
C(28)	4197(4)	1603(2)	2487(2)	84(1)
C(29)	3369(3)	611(2)	2639(2)	89(1)
C(30)	3895(3)	-106(2)	3167(2)	81(1)
C(31)	3687(15)	2452(11)	1957(8)	88(3)
C(32)	3466(9)	2214(7)	878(7)	121(3)
C(33)	3693(11)	3422(10)	302(8)	159(3)
C(34)	2226(10)	3184(10)	-20(9)	206(5)
C(31')	3430(20)	2271(18)	1825(13)	121(9)
C(32')	4208(10)	2559(8)	892(8)	85(3)
C(33')	2740(15)	2903(8)	320(9)	129(4)
C(34')	3310(20)	4016(9)	406(12)	182(6)
C(35)	8917(2)	-1661(2)	4568(2)	66(1)
C(36)	9794(3)	-2136(2)	5128(2)	80(1)
C(37)	10837(3)	-2528(2)	4724(3)	96(1)
C(38)	11007(3)	-2447(2)	3761(3)	105(1)
C(39)	10149(4)	-1980(3)	3200(3)	111(1)
C(40)	9105(3)	-1583(2)	3595(2)	90(1)

---

### III. Copies of $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and $^{19}\text{F}$ NMR Spectrum

NMR spectra of compound 1a

7.428

7.407

7.377

7.373

7.368

7.356

7.352

7.337

7.329

7.325

7.321

7.315

7.308

7.299

7.293

7.290

7.286

5.834

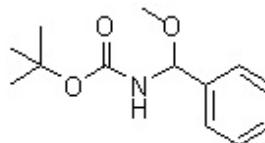
5.809

5.168

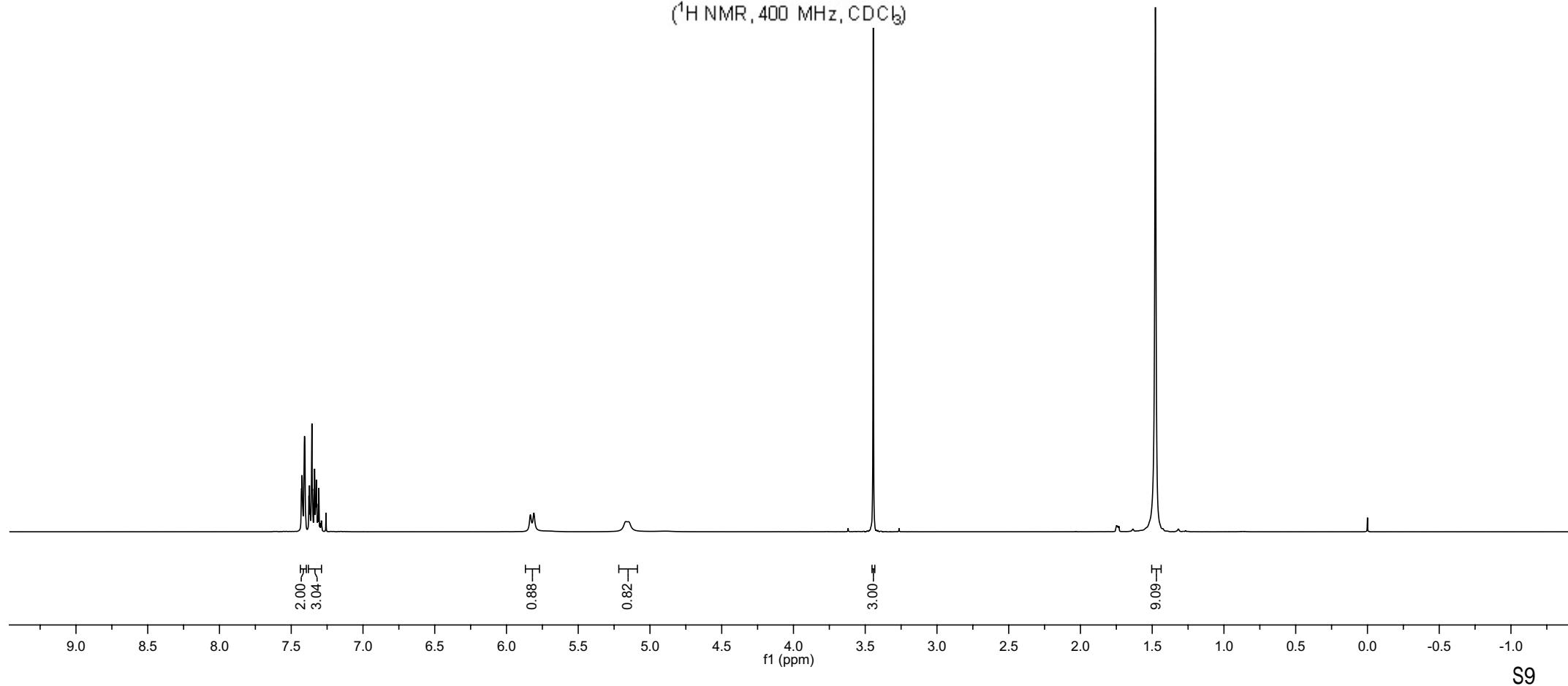
5.150

3.444

-1.478



( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )



NMR spectra of compound 1b

7.306  
7.286  
7.170  
7.150

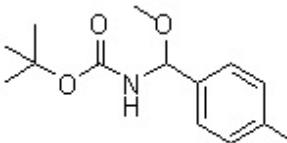
5.791  
5.768

5.136  
5.117

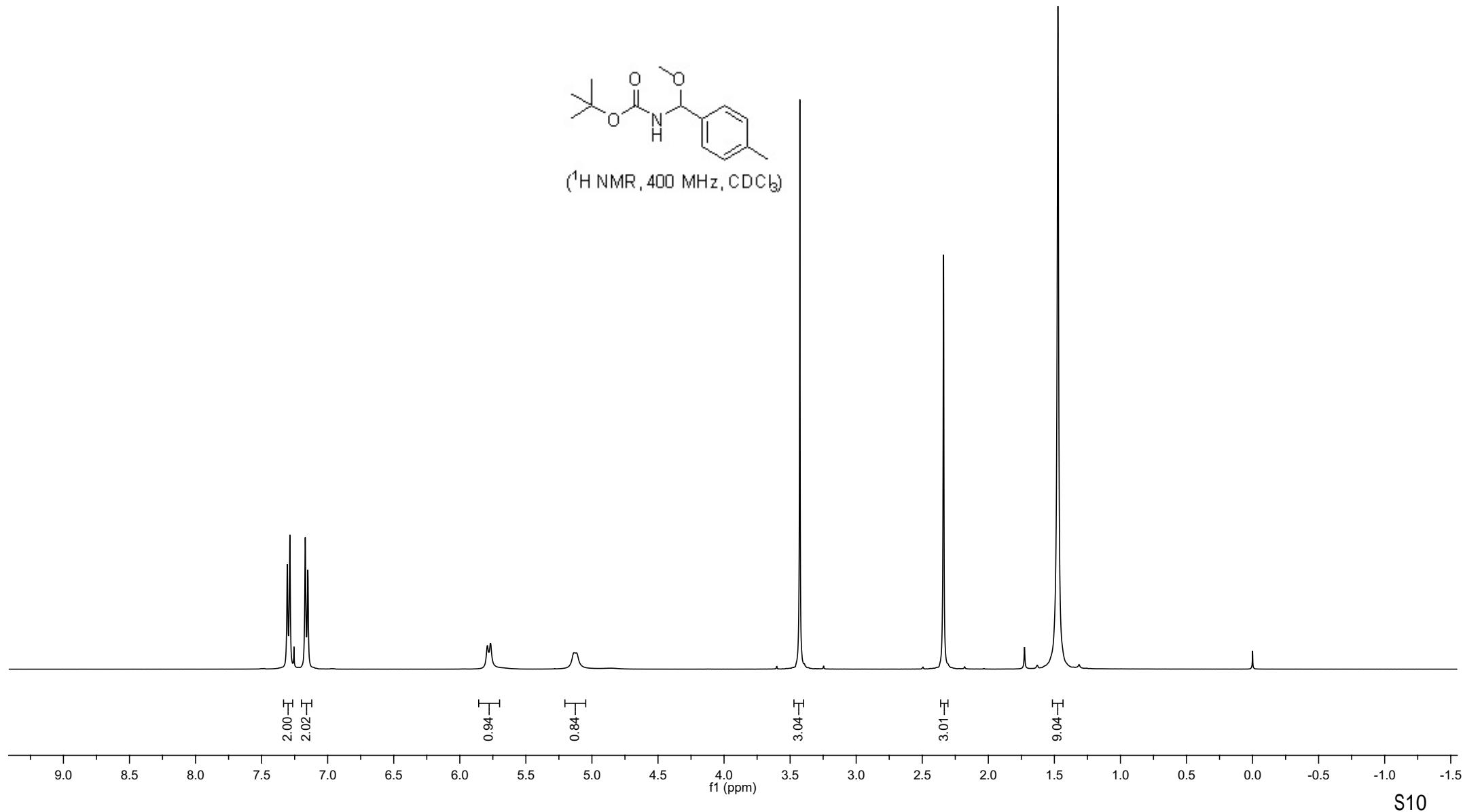
3.426

2.339

1.473



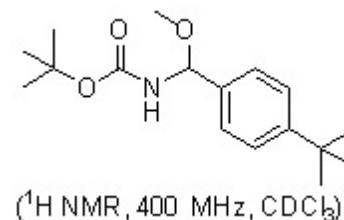
( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )



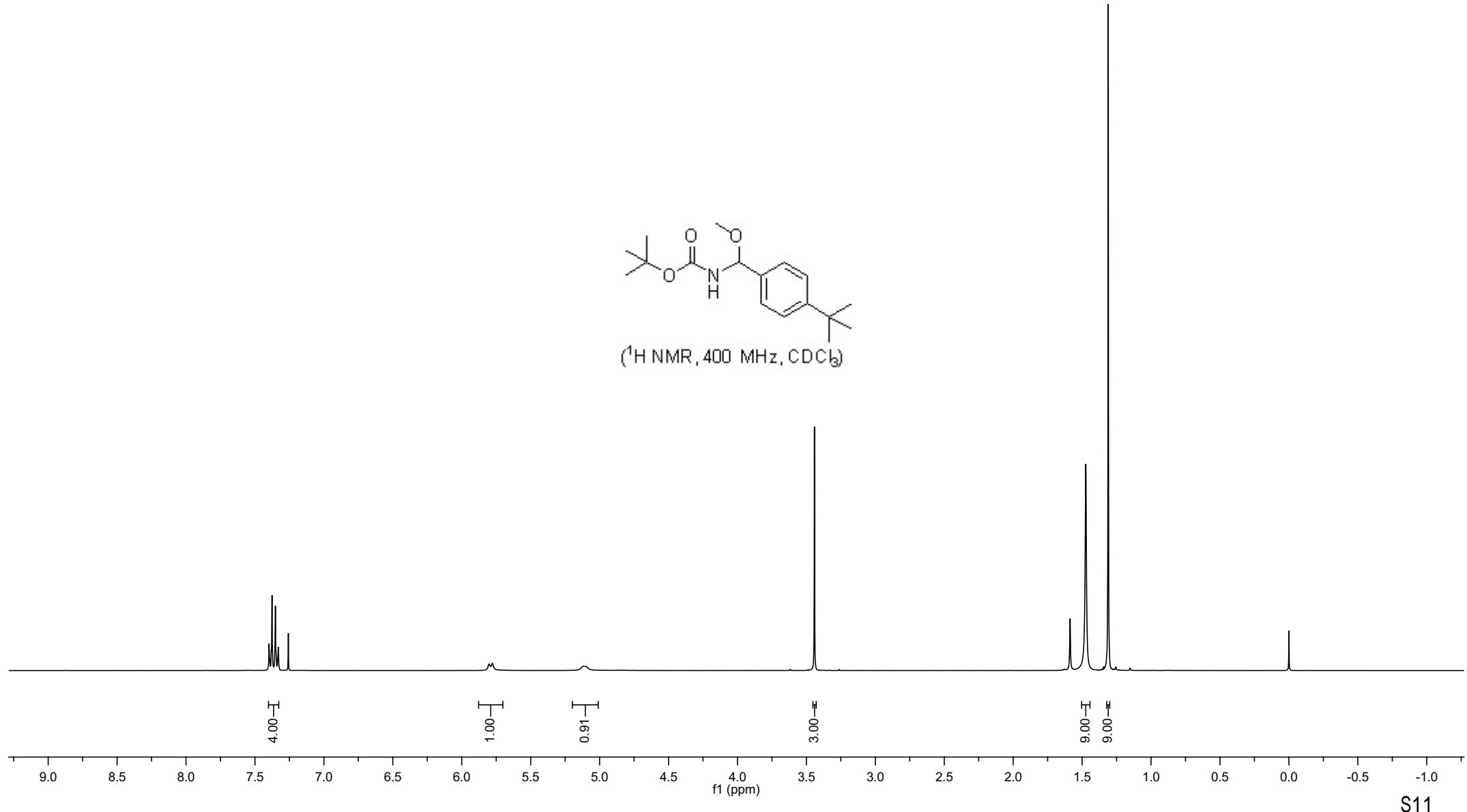
NMR spectra of compound 1c



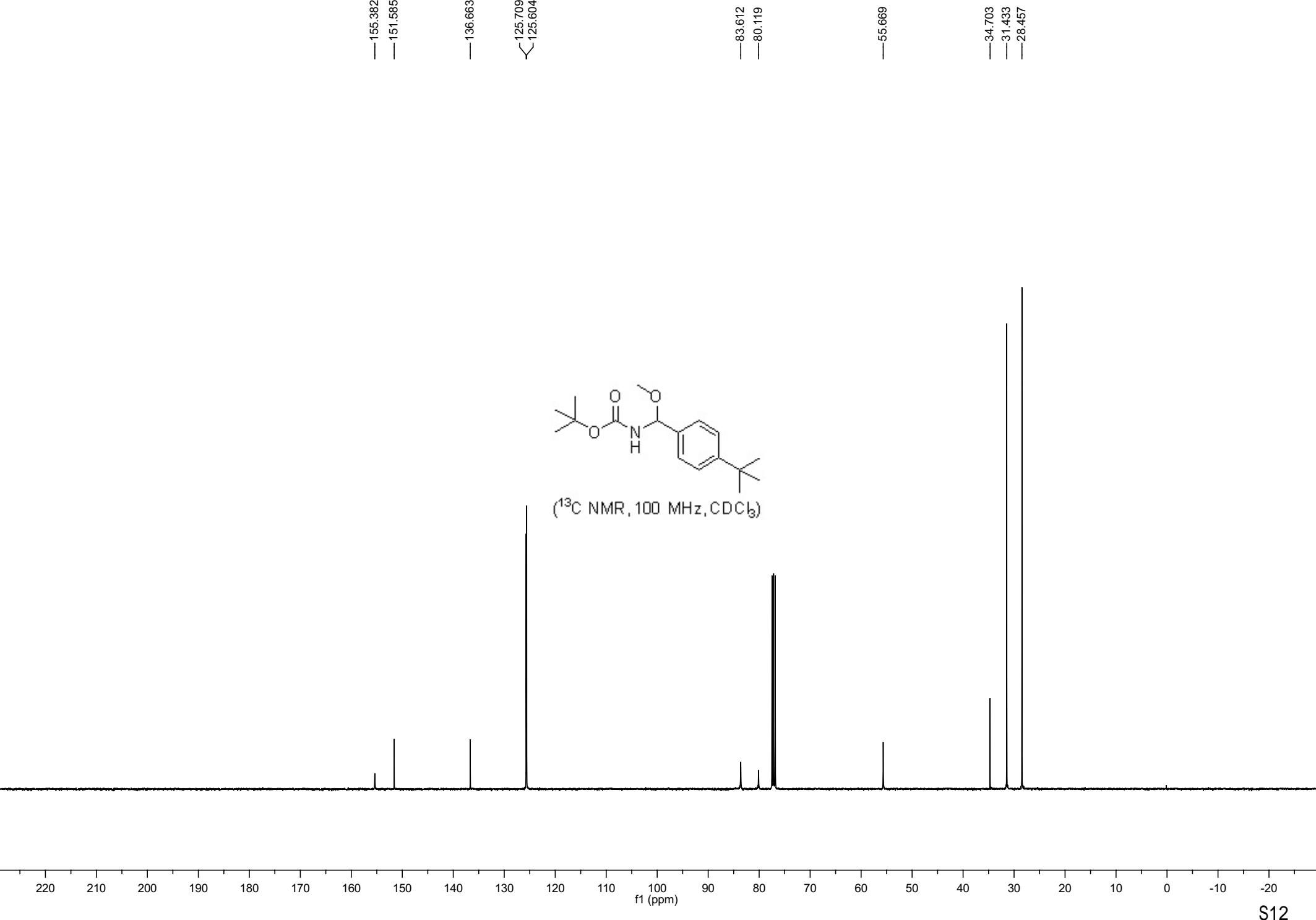
7.398  
7.393  
7.382  
7.376  
7.352  
7.331  
5.802  
5.778  
5.119  
5.100  
3.441  
-1.587  
-1.473  
-1.311



( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )

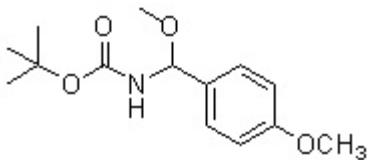


NMR spectra of compound 1c

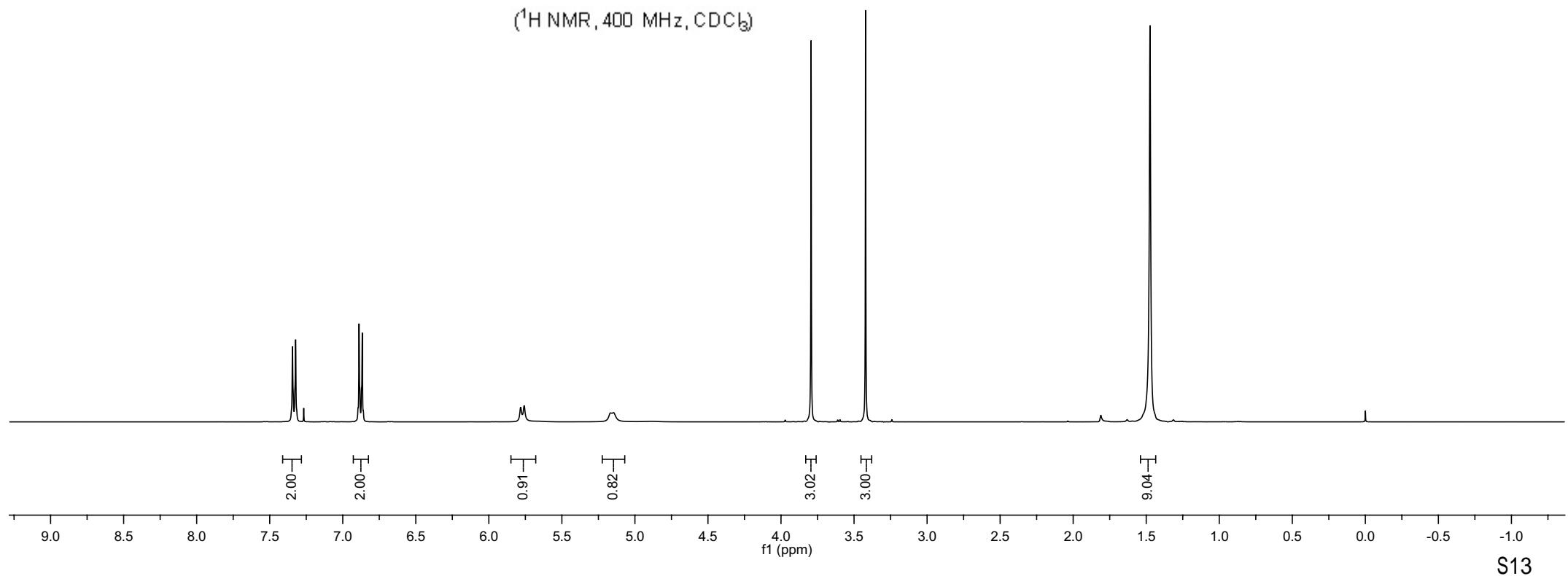


NMR spectra of compound 1d

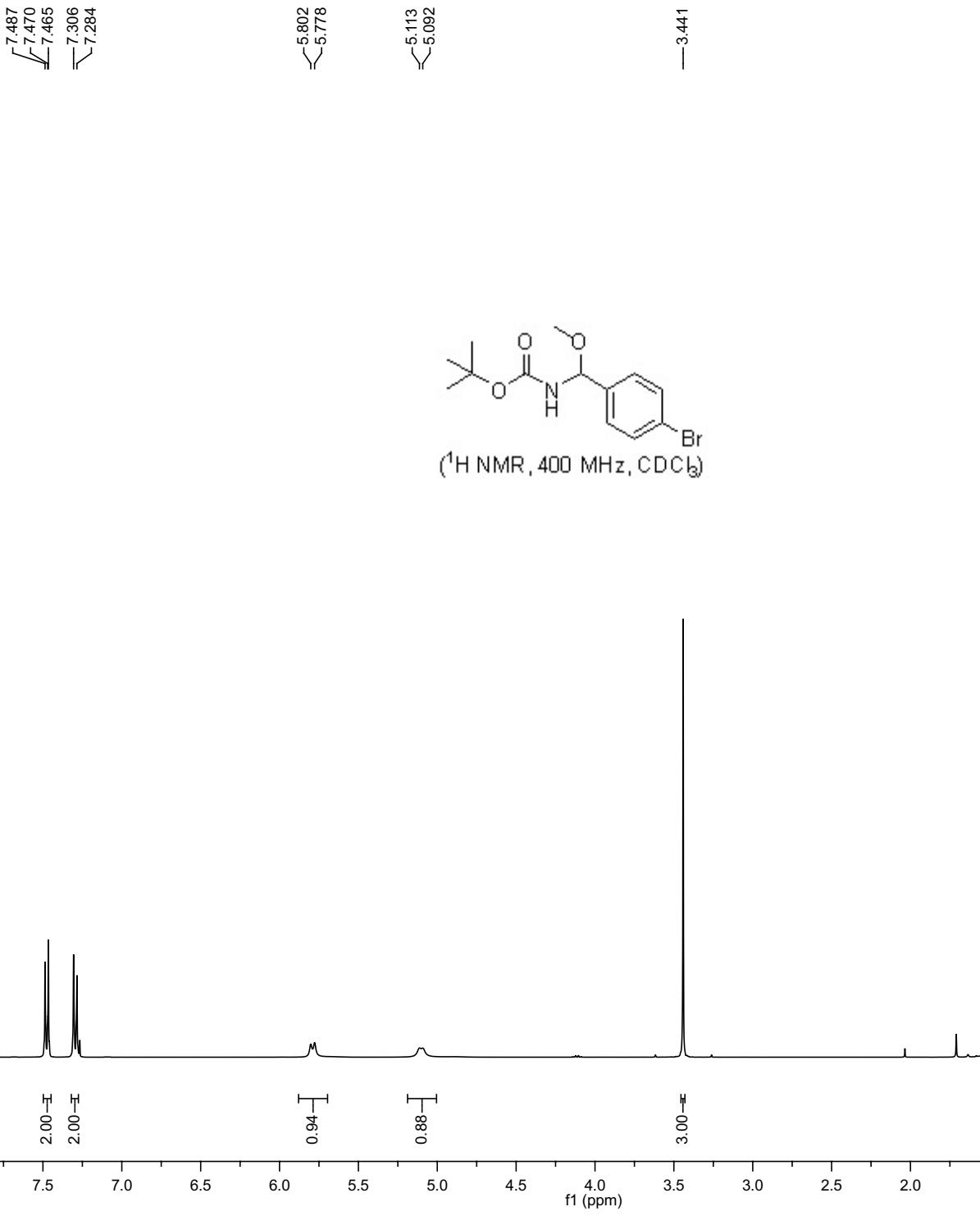
7.344  
7.323  
6.888  
6.866  
5.782  
5.758  
5.167  
5.147  
-3.794  
-3.421  
-1.474



( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )



NMR spectra of compound 1e



NMR spectra of compound 1f

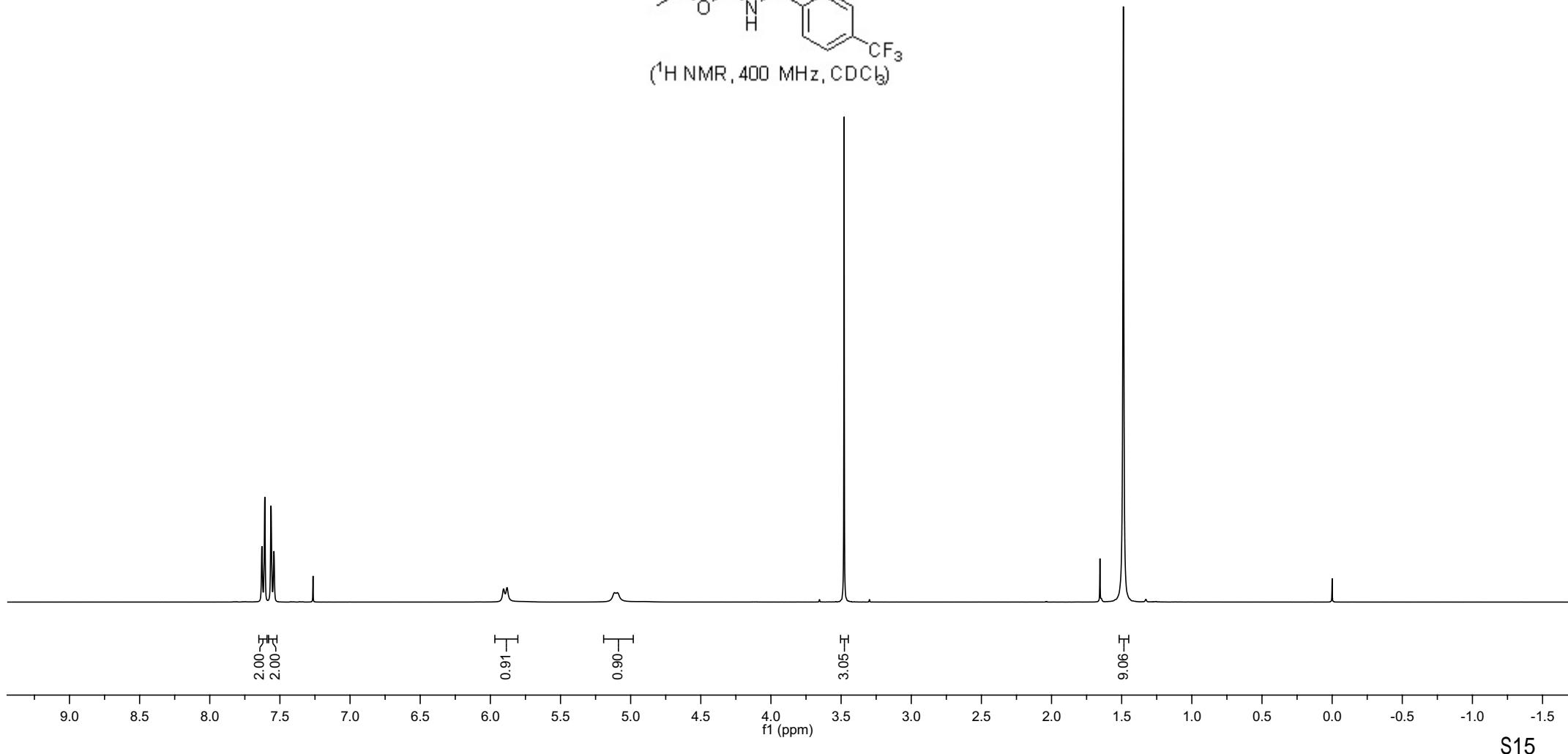
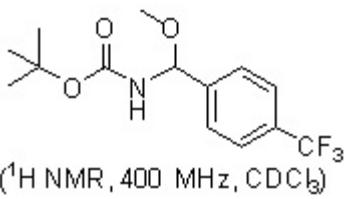
7.629  
7.608  
7.563  
7.543

5.906  
5.881

5.115  
5.094

3.478

1.488



NMR spectra of compound 1g

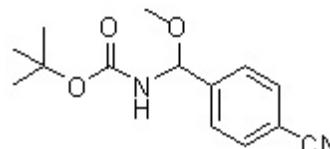
7.664  
7.643  
7.567  
7.546

5.904  
5.880

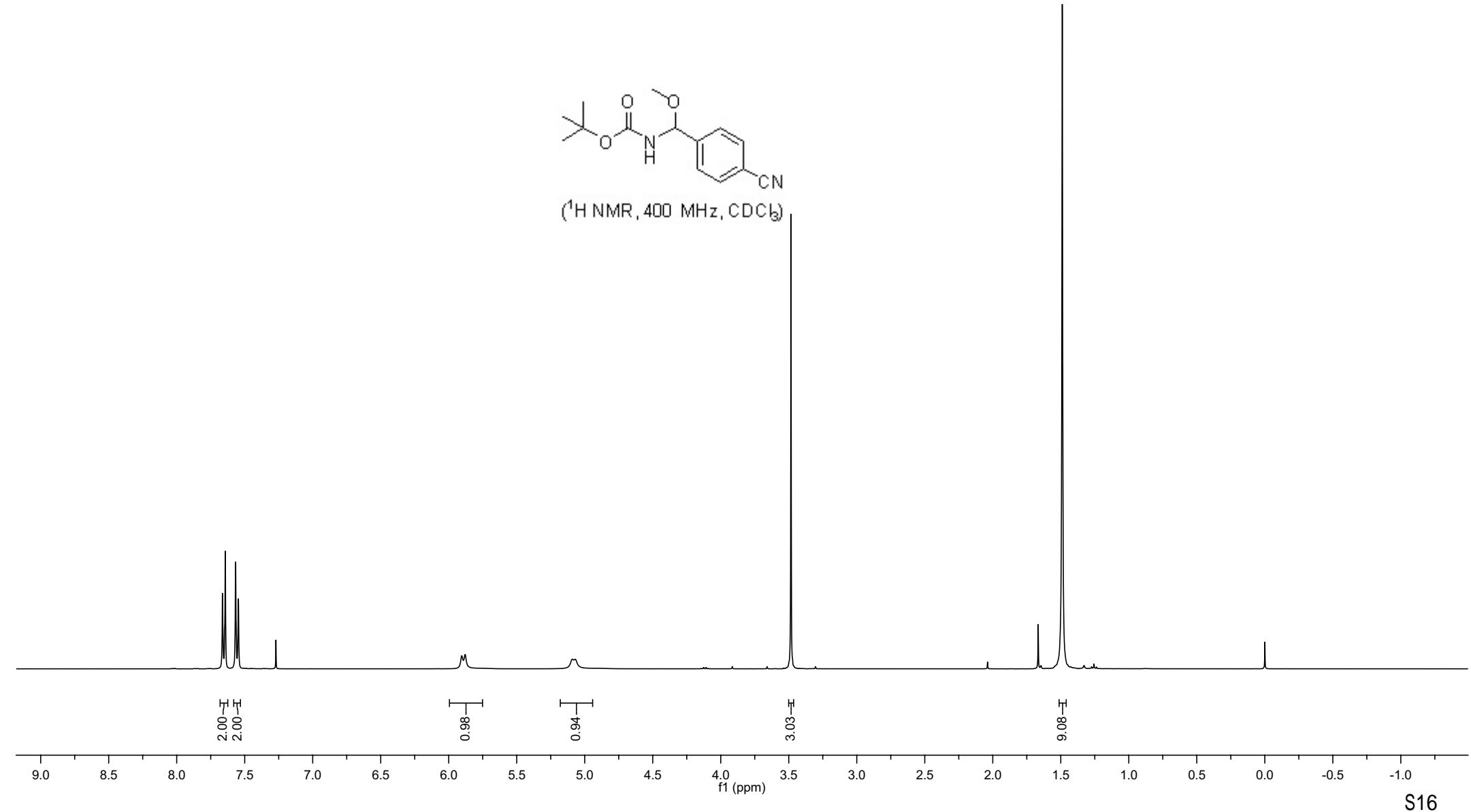
5.091  
5.069

3.484

1.489



( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )



NMR spectra of compound 1h

7.263  
7.255  
7.244  
7.226  
7.210  
7.191  
7.131  
7.114

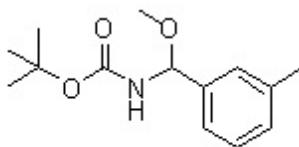
5.788  
5.764

-5.135

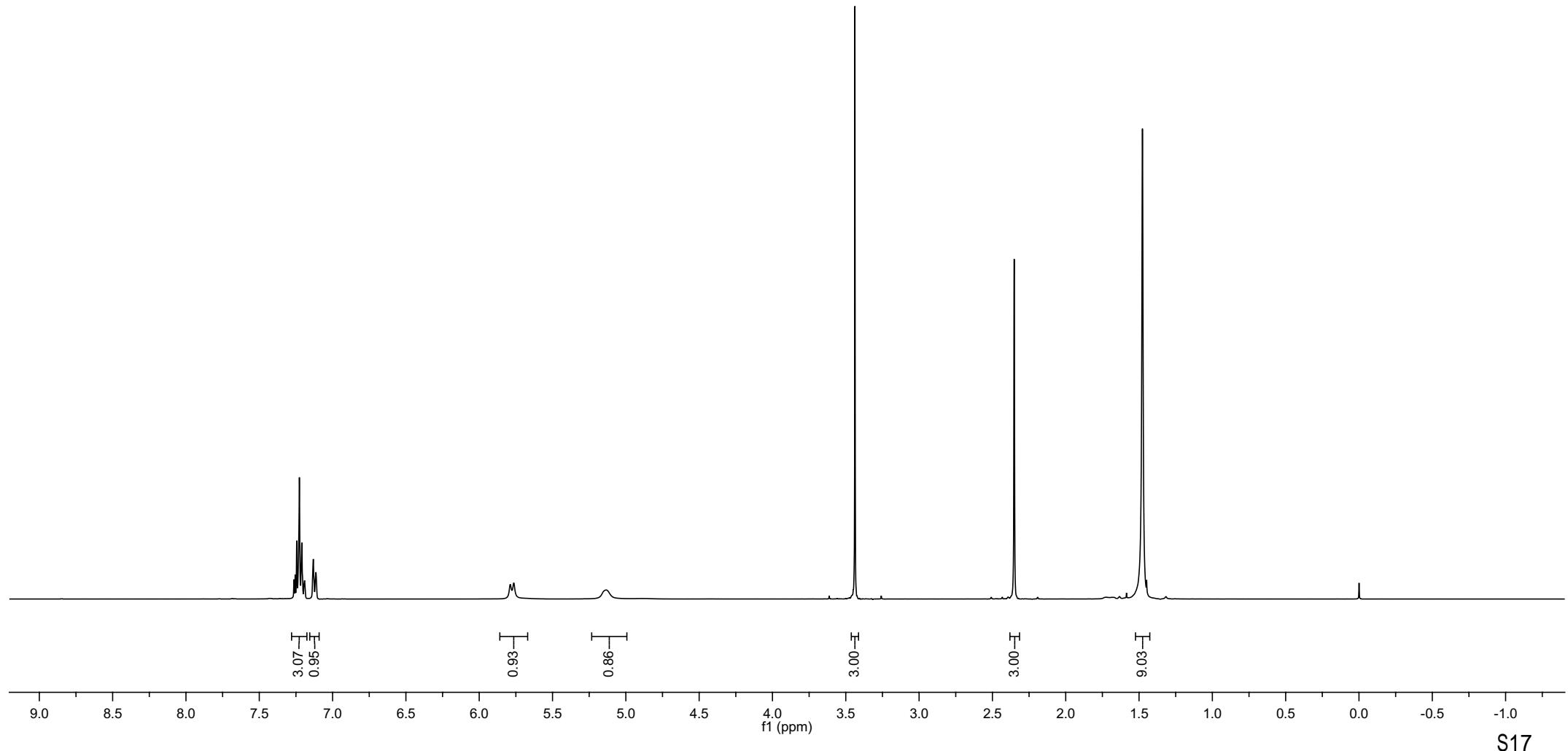
-3.438

-2.351

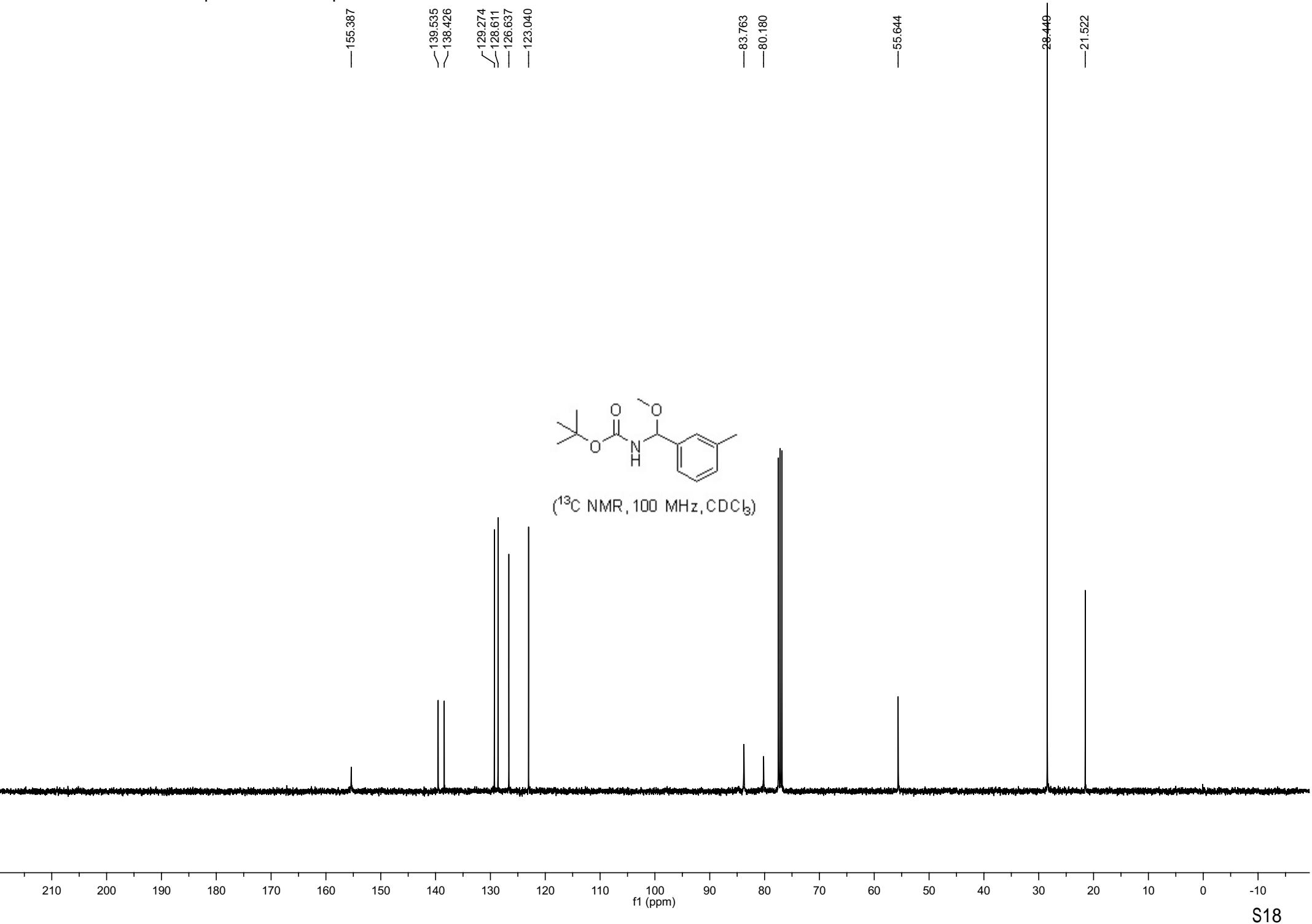
-1.477



( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )



NMR spectra of compound 1h



NMR spectra of compound 1i

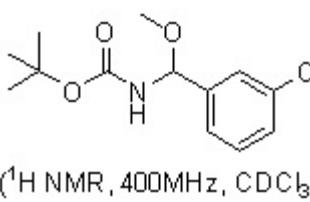
7.432  
7.299  
7.285  
7.283  
7.271  
7.267

5.818  
5.794

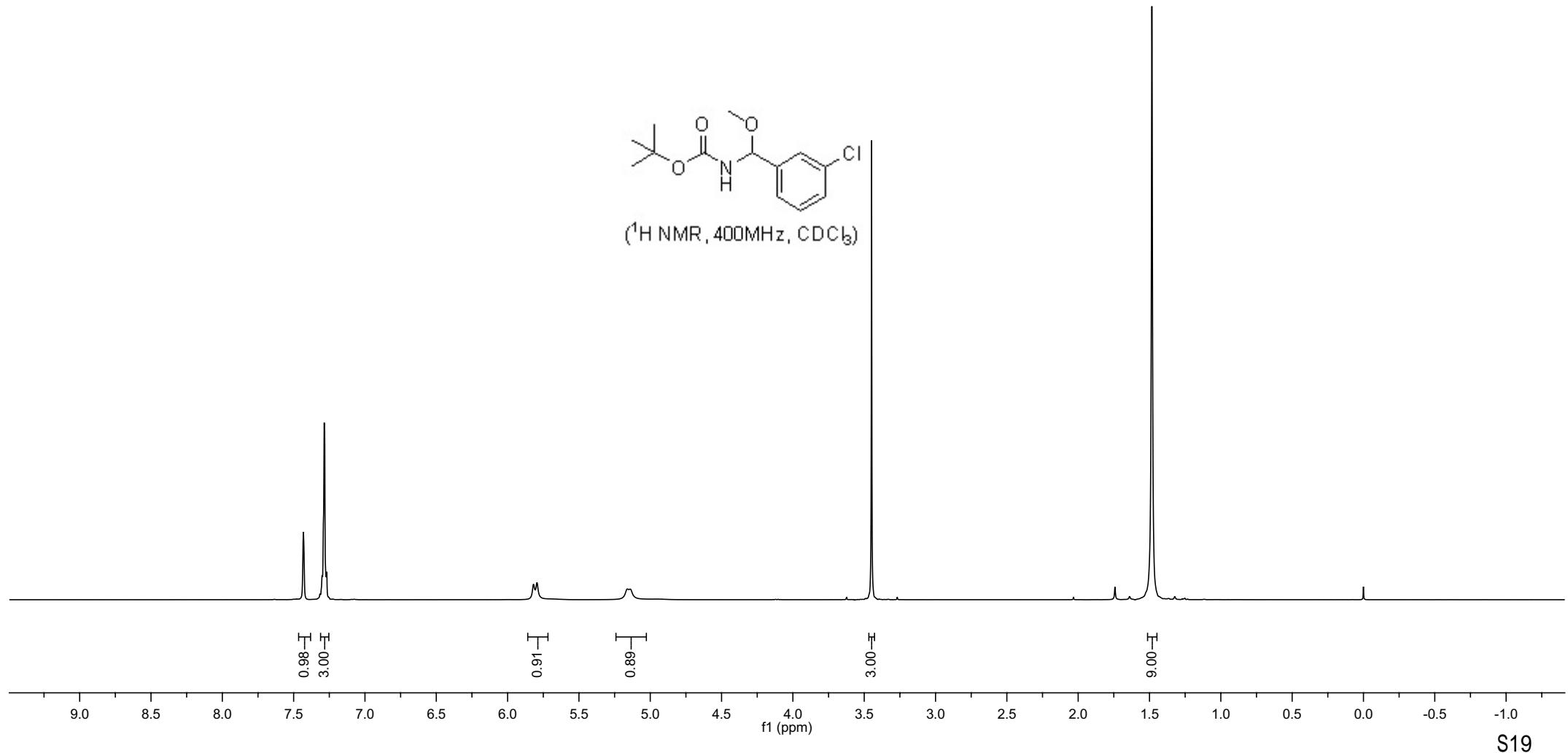
5.161  
5.140

3.448

1.483

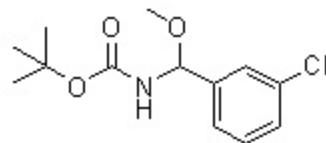


( $^1\text{H}$  NMR, 400MHz,  $\text{CDCl}_3$ )

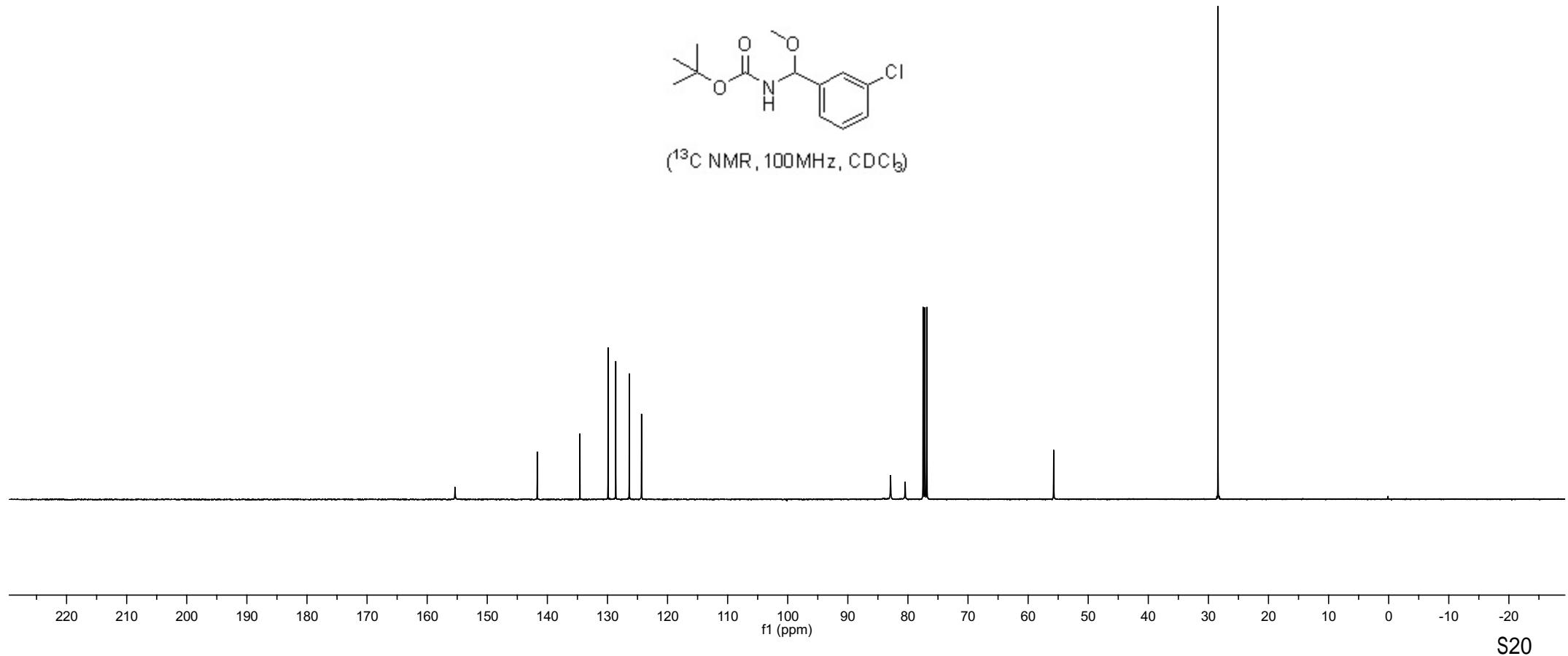


NMR spectra of compound 1i

—155.365  
—141.681  
—134.582  
—129.904  
—128.617  
—126.367  
—124.327  
—82.888  
—80.458  
—55.745  
—28.409



( $^{13}\text{C}$  NMR, 100MHz,  $\text{CDCl}_3$ )



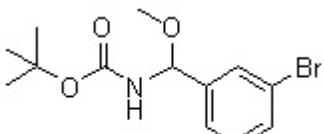
NMR spectra of compound 1j

-7.591  
-7.452  
-7.432  
-7.356  
-7.337  
-7.241  
-7.222  
-7.202

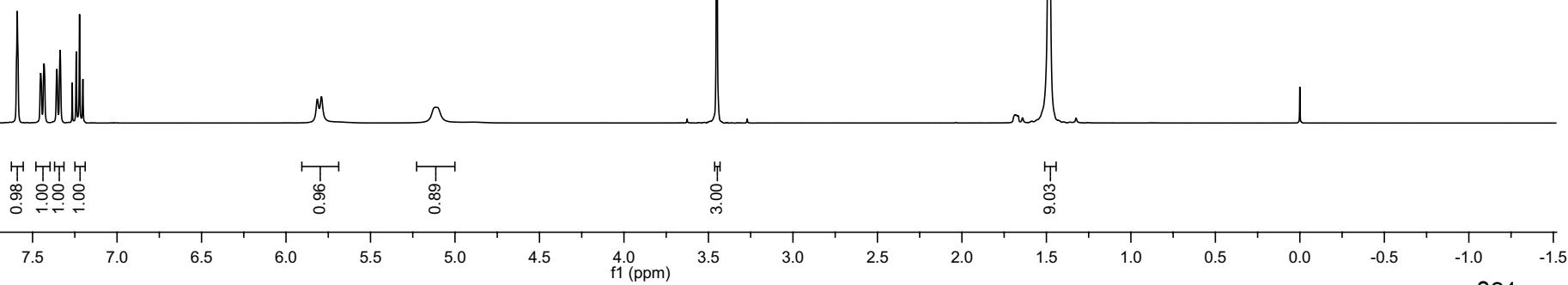
5.815  
5.790  
5.120  
5.106

-3.451

-1.485

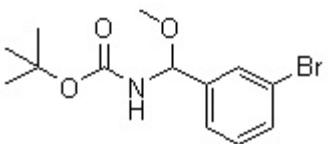


(<sup>1</sup>H NMR, 400MHz, CDCl<sub>3</sub>)

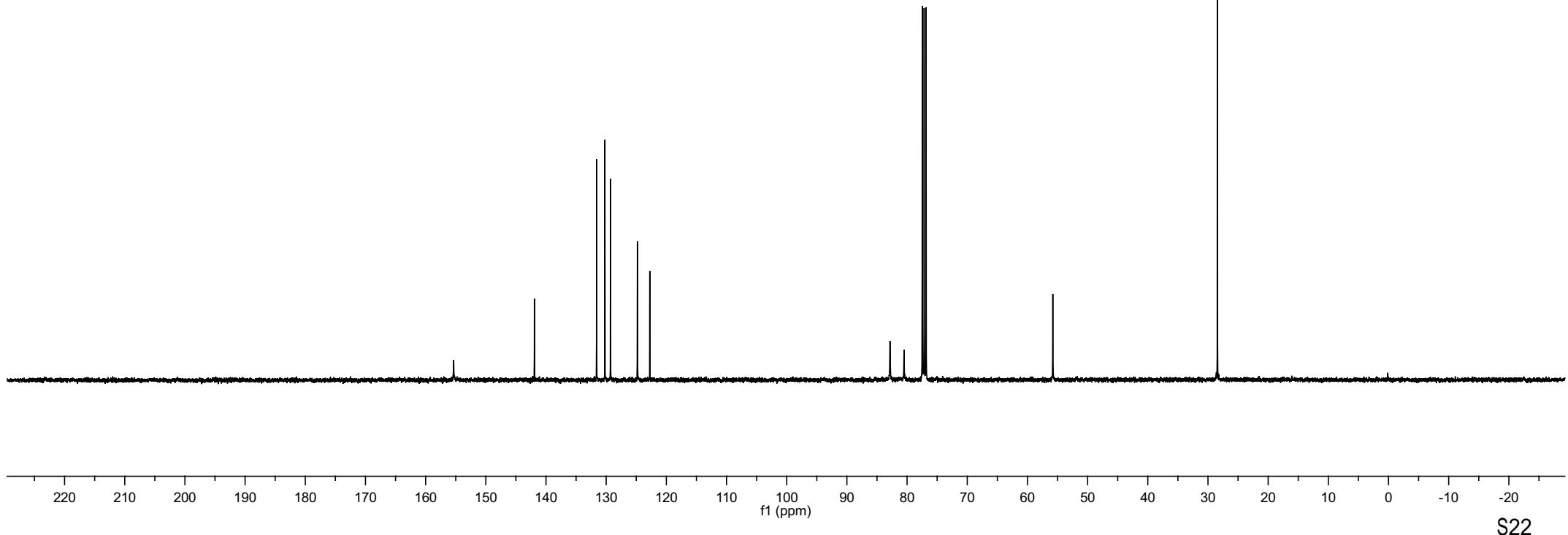


NMR spectra of compound 1j

—155.348  
—141.926  
—  
—131.591  
—  
—130.211  
—  
—129.282  
—  
—124.813  
—  
—122.754  
—  
—82.838  
—  
—80.496  
—  
—55.781  
—  
—28.429



(<sup>13</sup>C NMR, 100MHz, CDCl<sub>3</sub>)



NMR spectra of compound 1k

7.492  
7.478  
7.206  
7.197  
7.194  
7.181  
7.168  
7.158  
7.145

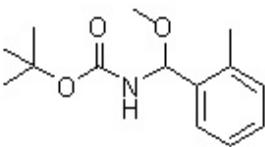
5.930  
5.906

5.073  
5.052

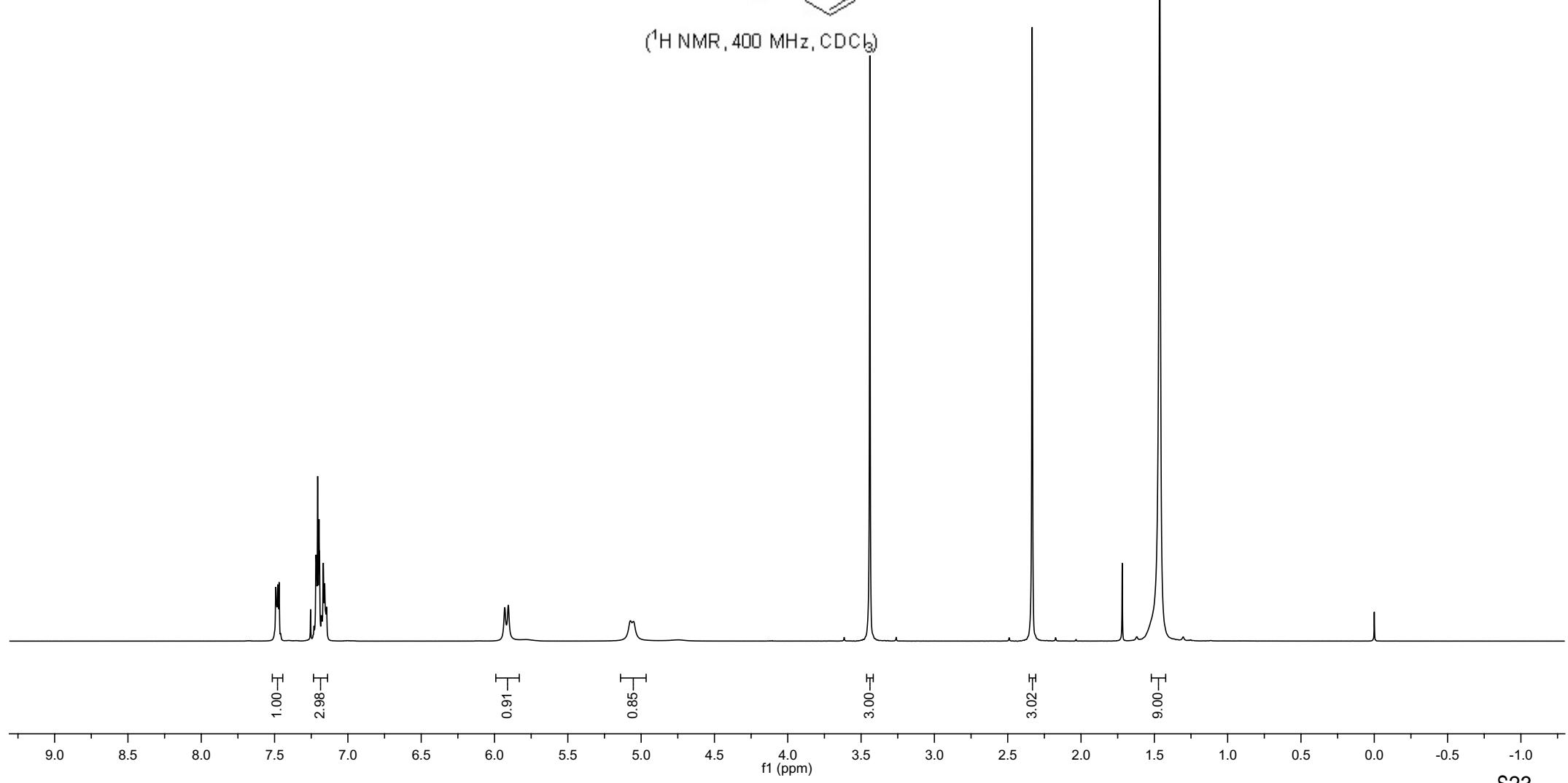
3.440

-2.333

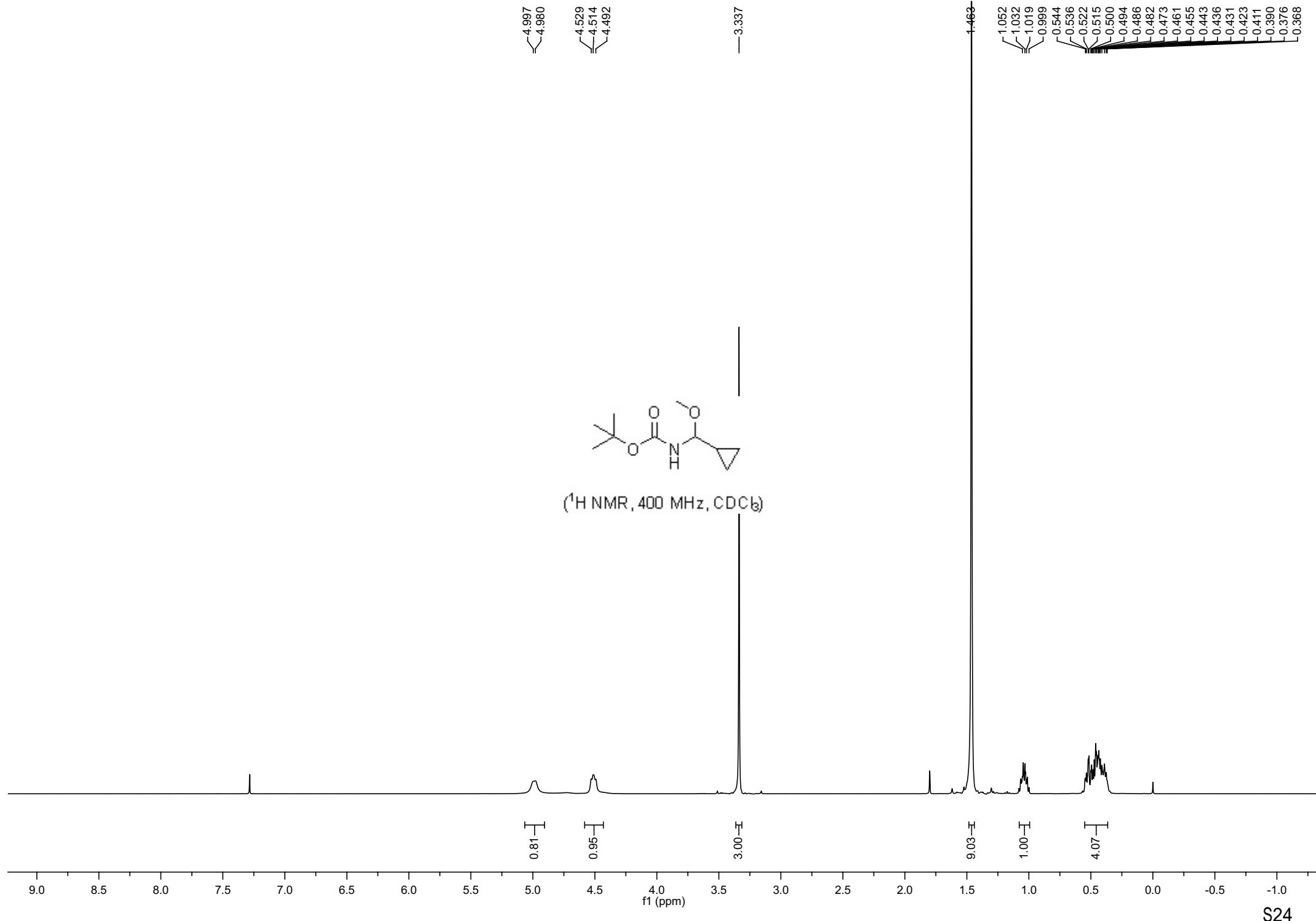
-1.464



( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )

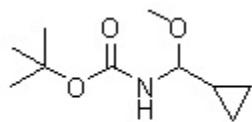


NMR spectra of compound 1I

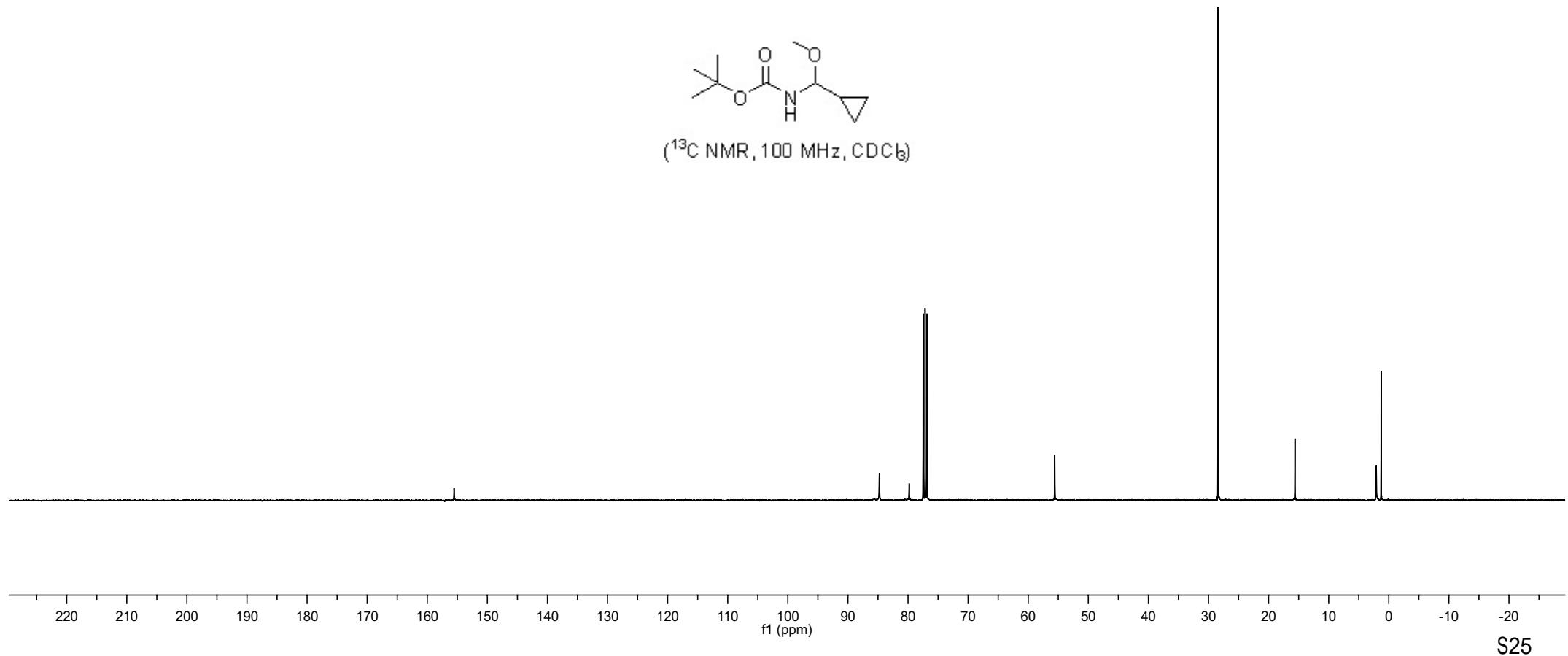


NMR spectra of compound 1I

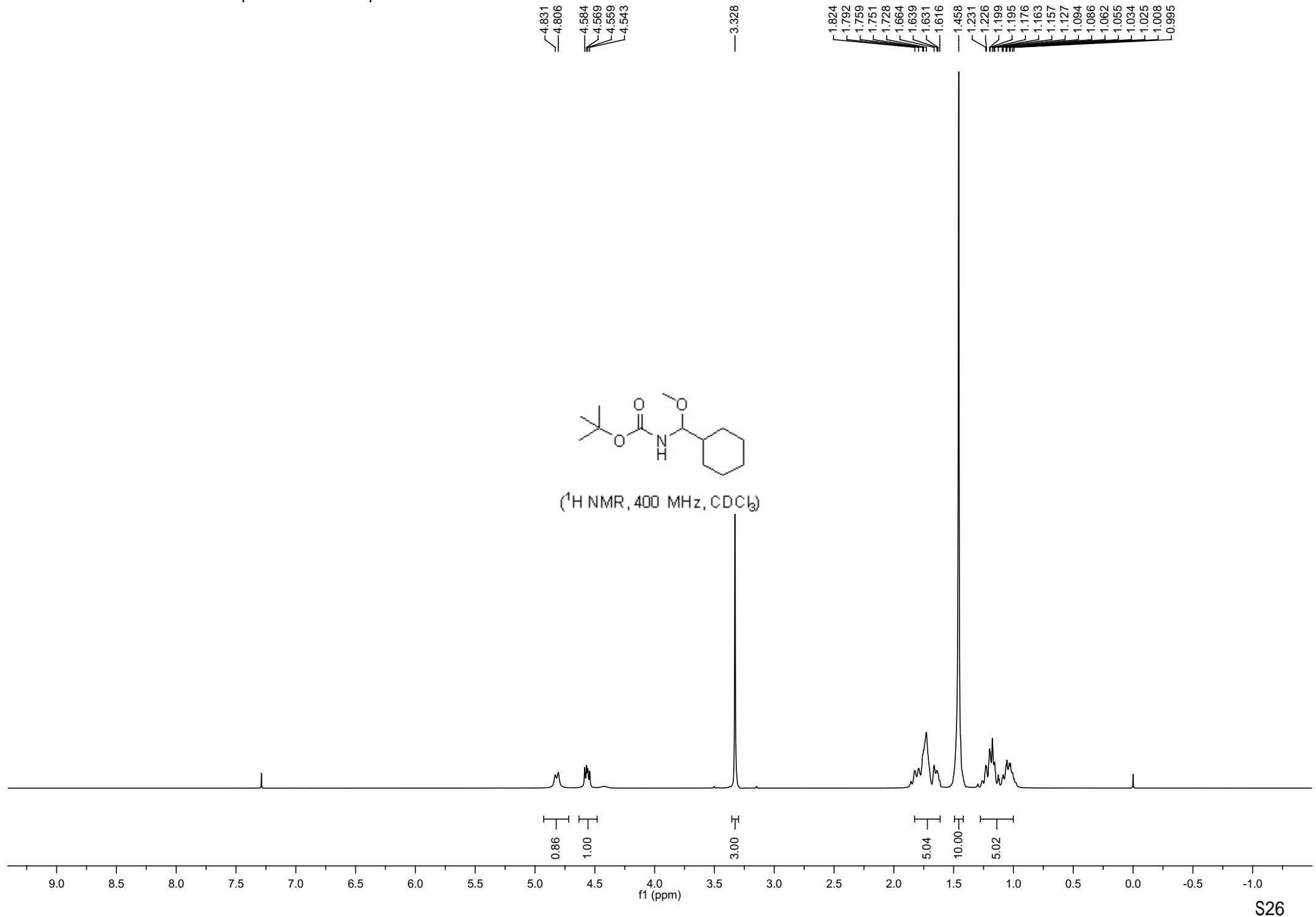
—155.537  
—84.772  
—79.805  
—55.585  
—28.421  
—15.610  
—2.077  
—1.271



( $^{13}\text{C}$  NMR, 100 MHz,  $\text{CDCl}_3$ )



NMR spectra of compound 1m



NMR spectra of compound 1m

—155.940

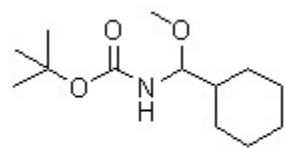
—86.743

—79.601

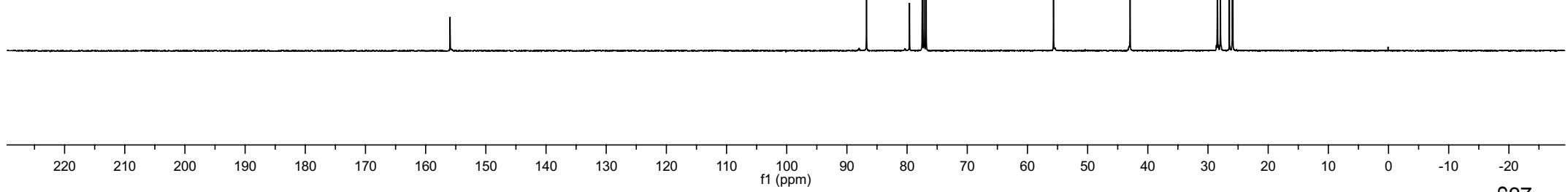
—55.673

—42.940

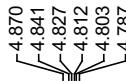
28.431  
27.936  
26.451  
25.950  
25.875



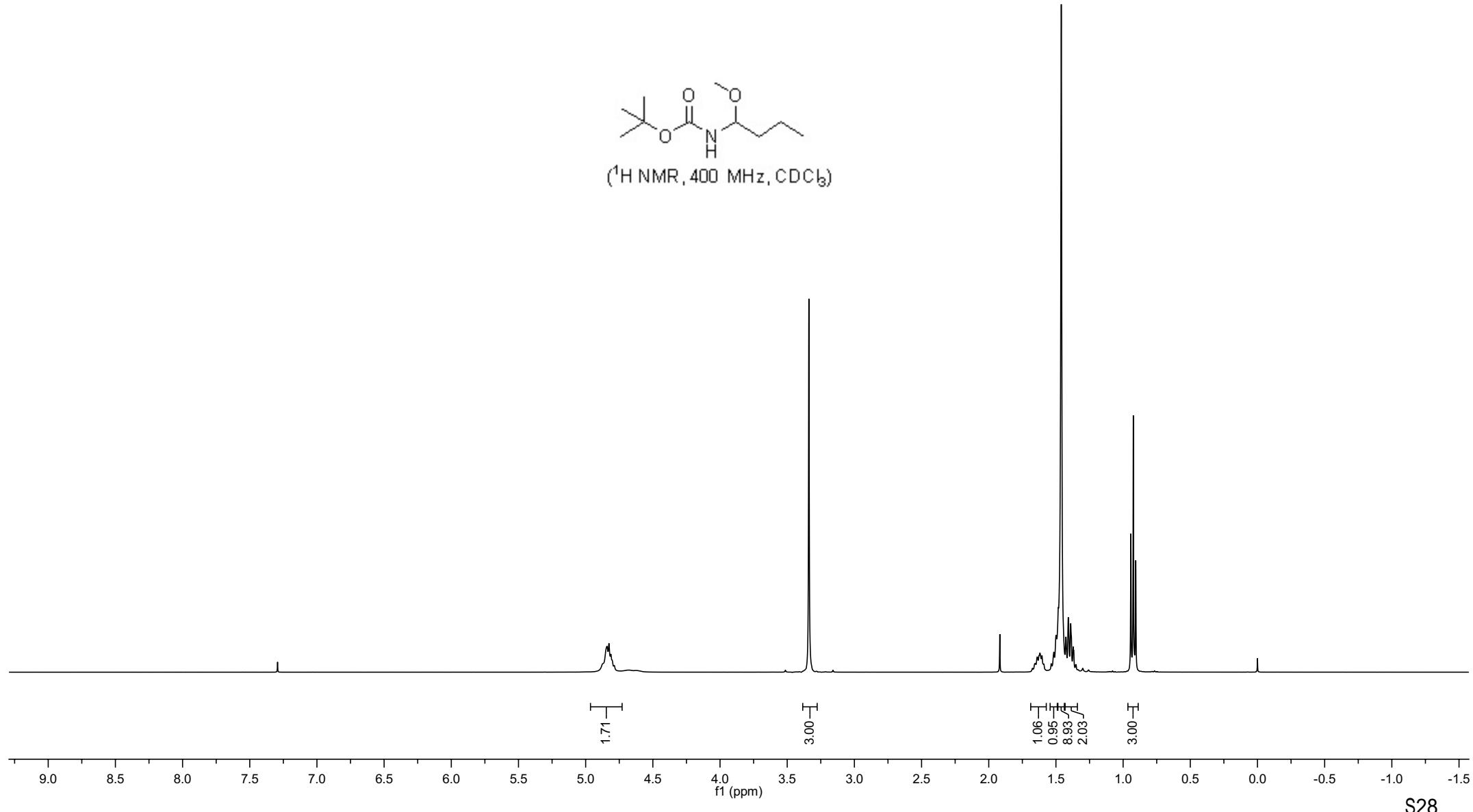
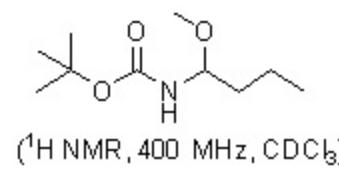
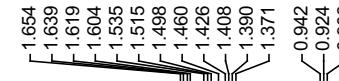
( $^{13}\text{C}$  NMR, 100 MHz,  $\text{CDCl}_3$ )



NMR spectra of compound 1n

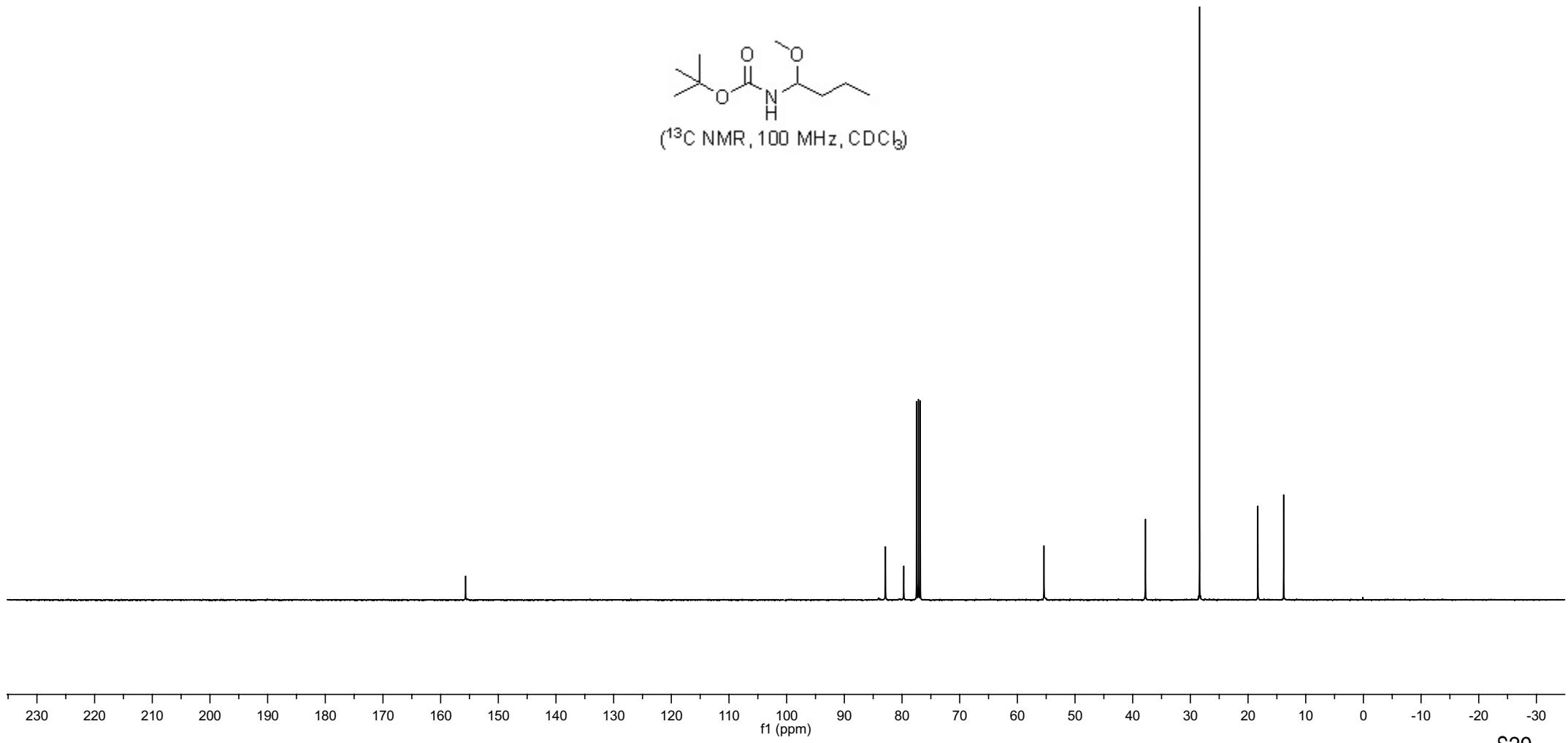
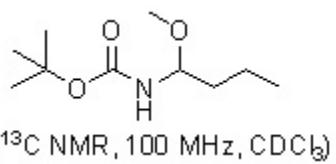


— 3.339 —

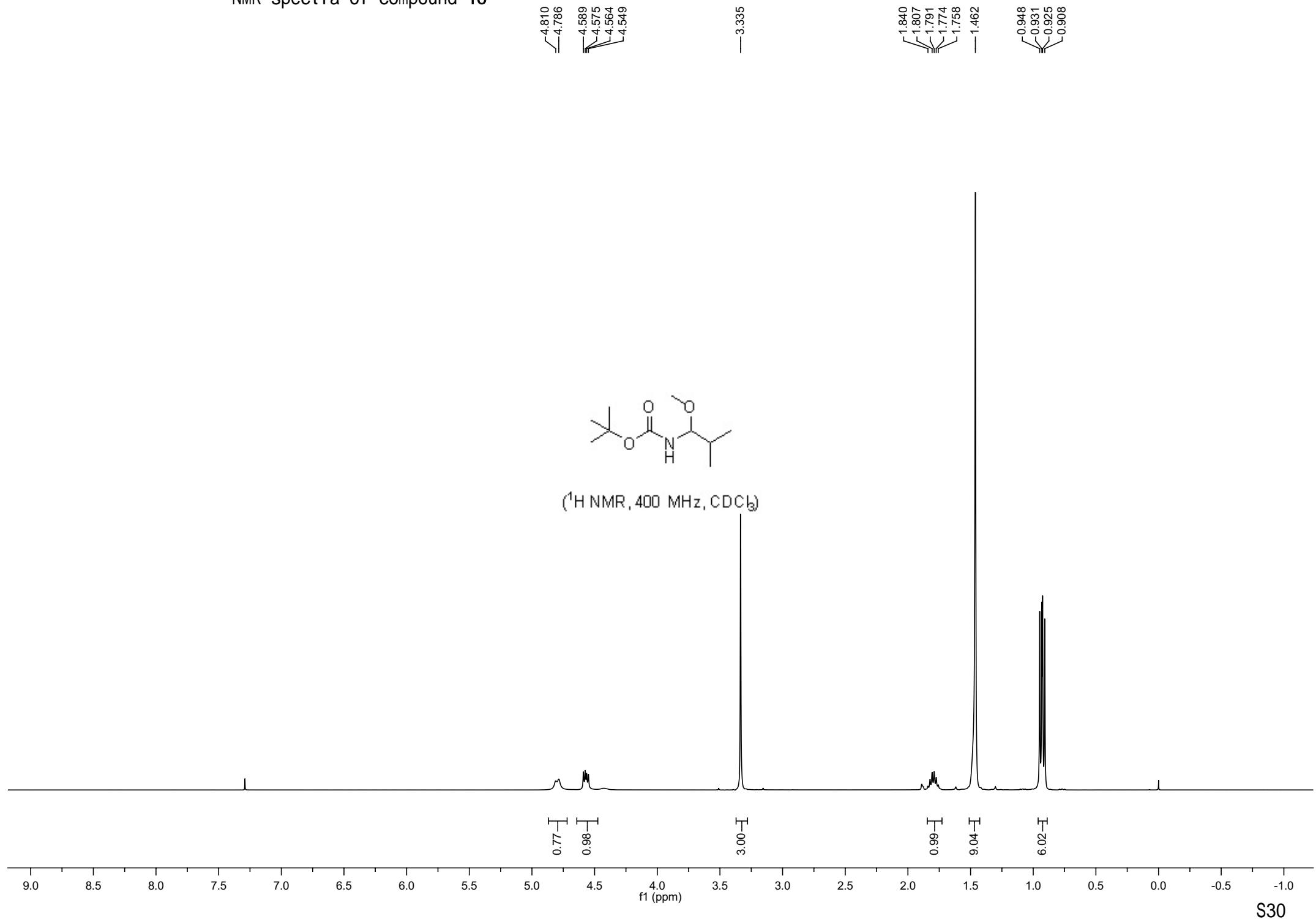


NMR spectra of compound 1n

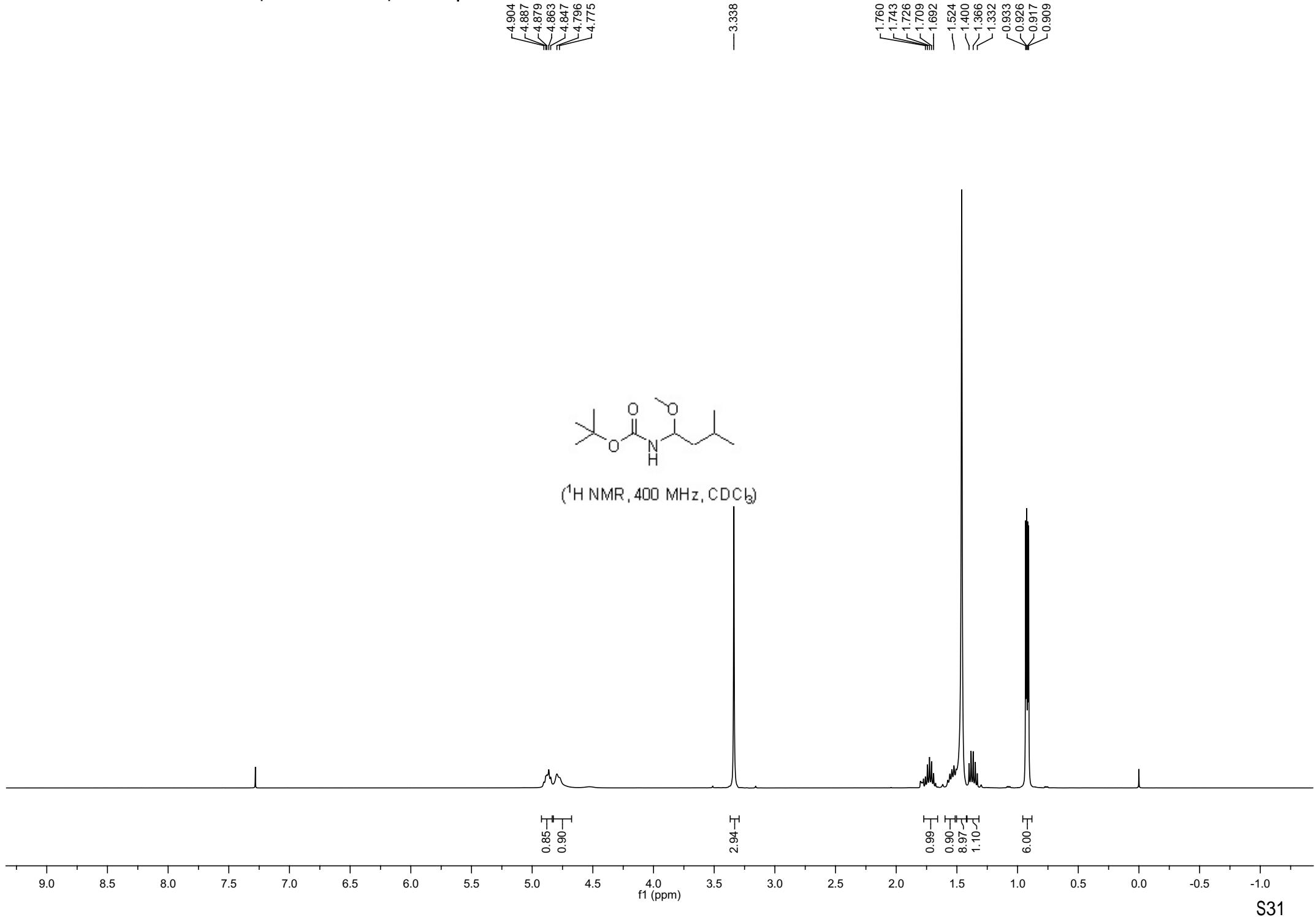
—155.680  
—82.878  
—79.701  
—55.387  
—37.786  
—28.408  
—18.303  
—13.826



NMR spectra of compound 1o



NMR spectra of compound 1p



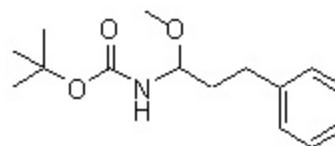
NMR spectra of compound 1q

7.292  
7.272  
7.254  
7.195  
7.181  
7.162

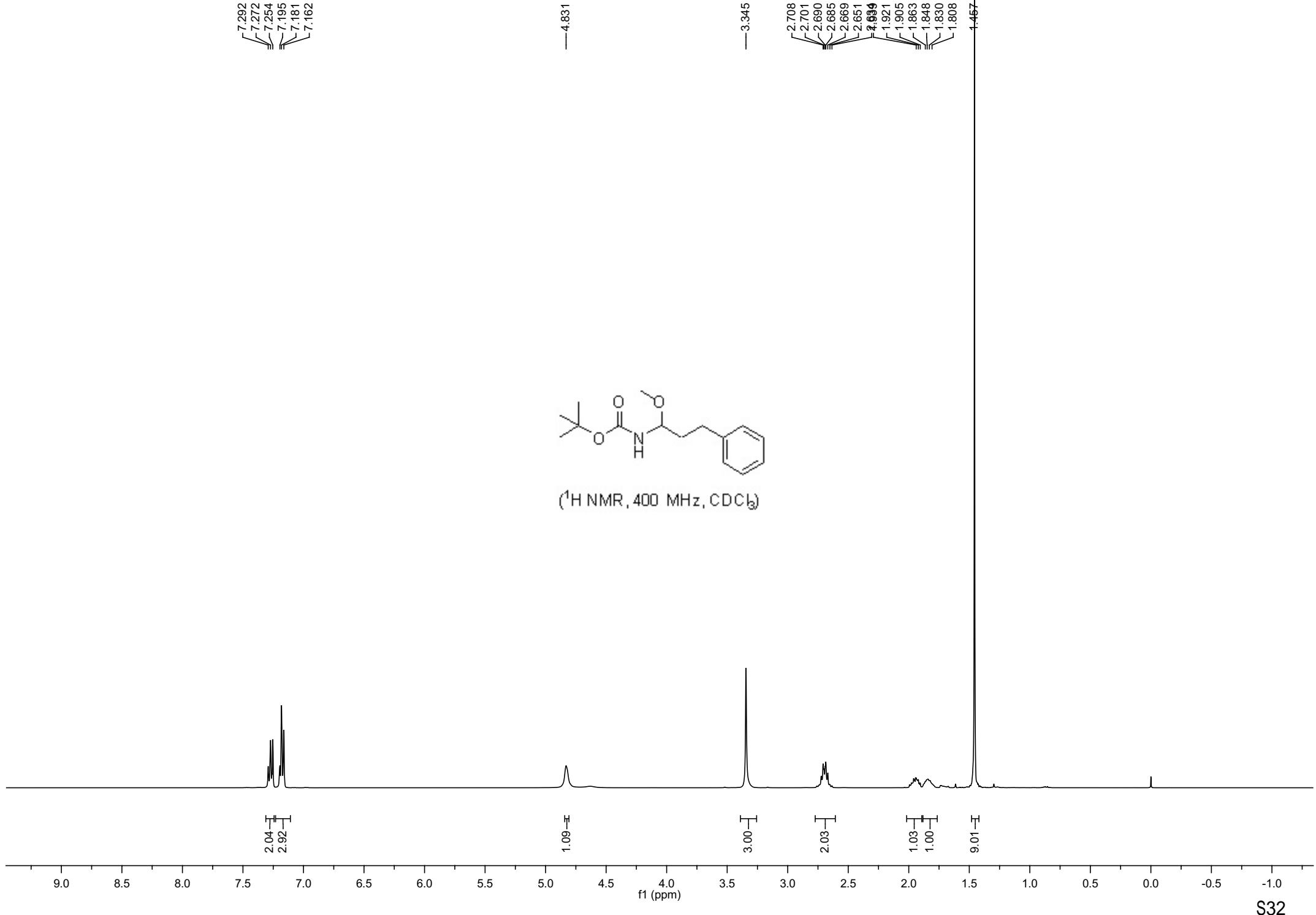
—4.831

—3.345

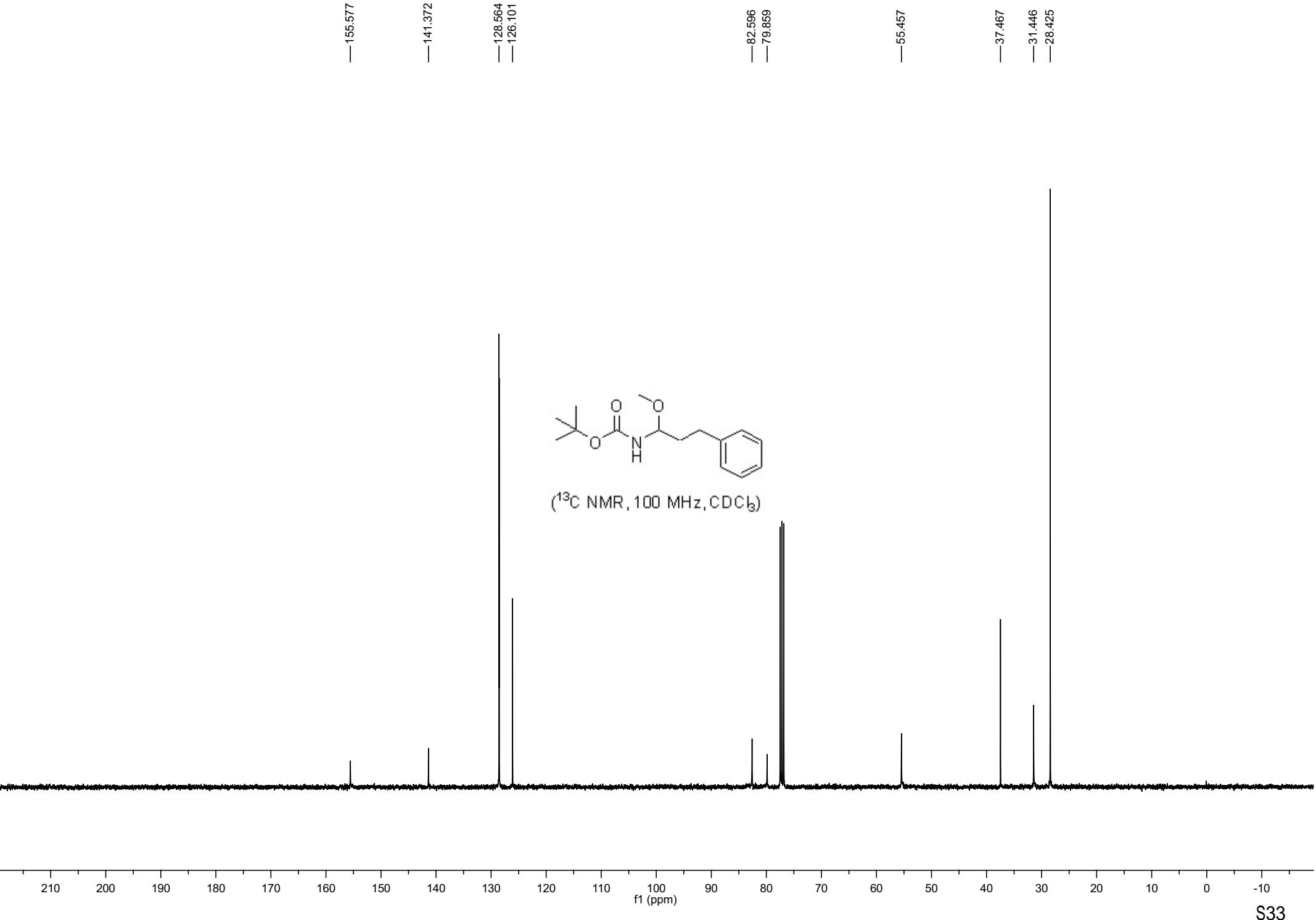
—4.457



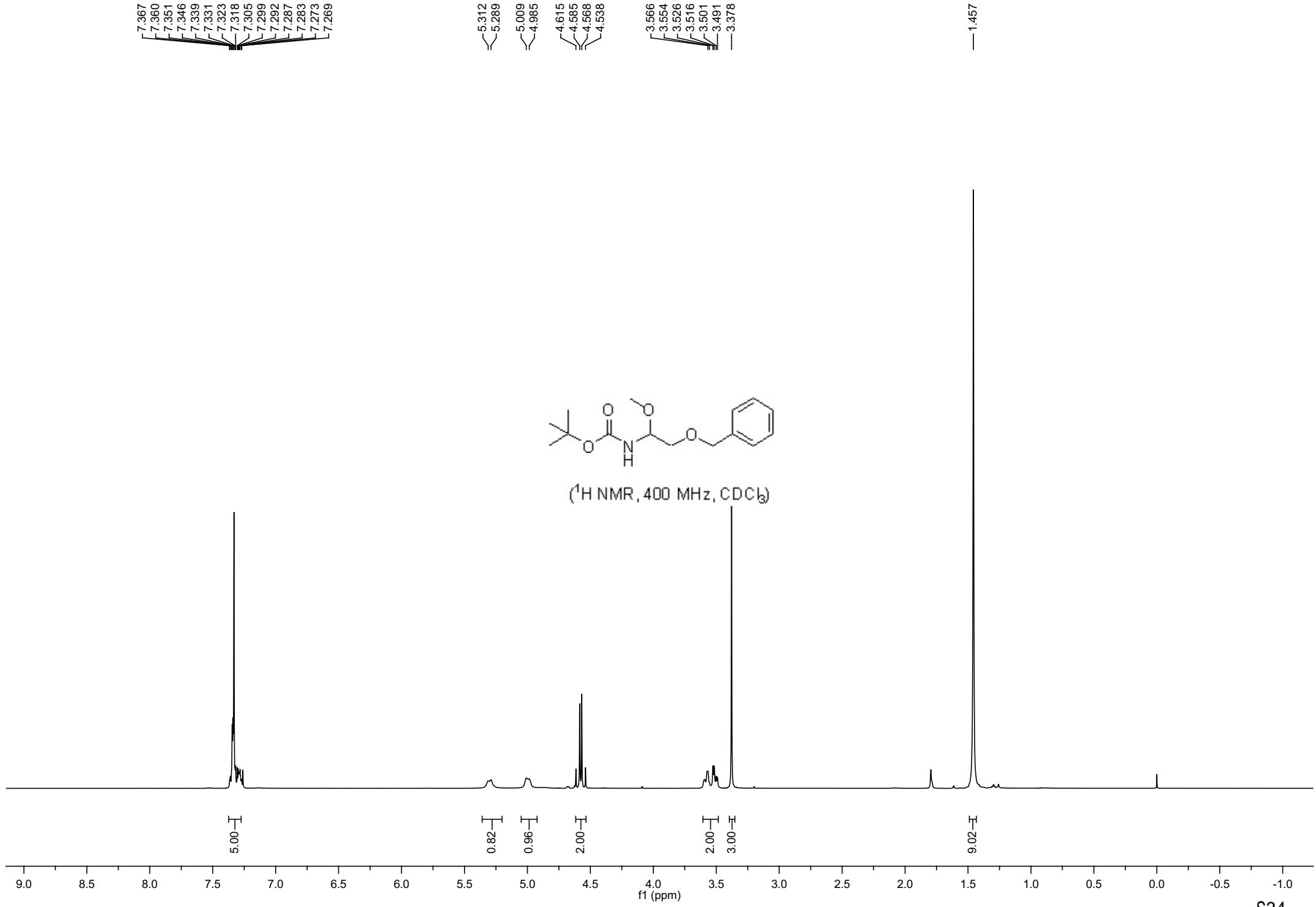
( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )



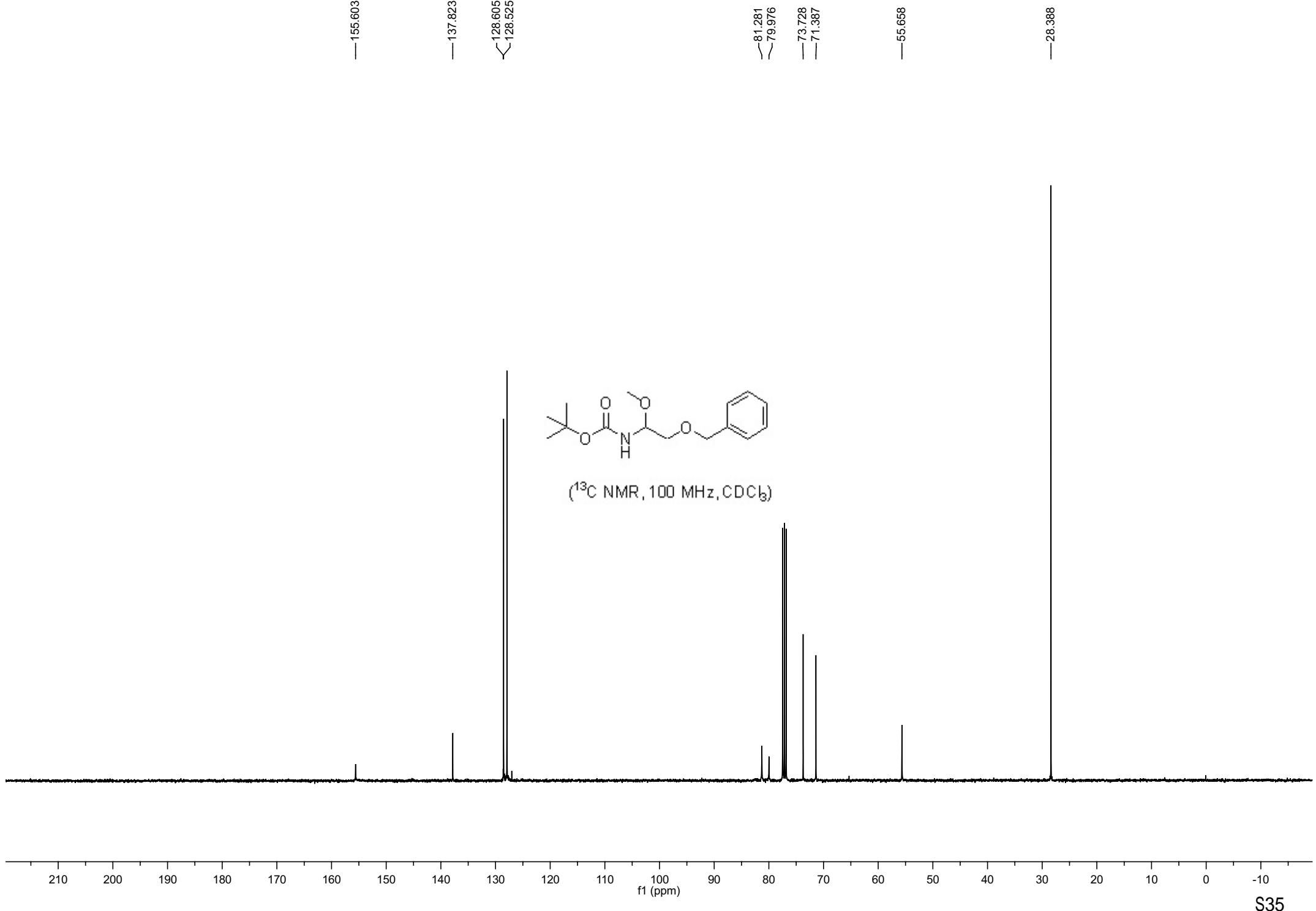
NMR spectra of compound 1q



NMR spectra of compound 1r



NMR spectra of compound 1r



NMR spectra of compound 1s

7.270  
7.268  
7.255  
7.258  
7.263

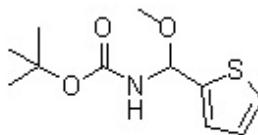
7.039  
6.982  
6.973

6.074  
6.050  
6.970  
6.961

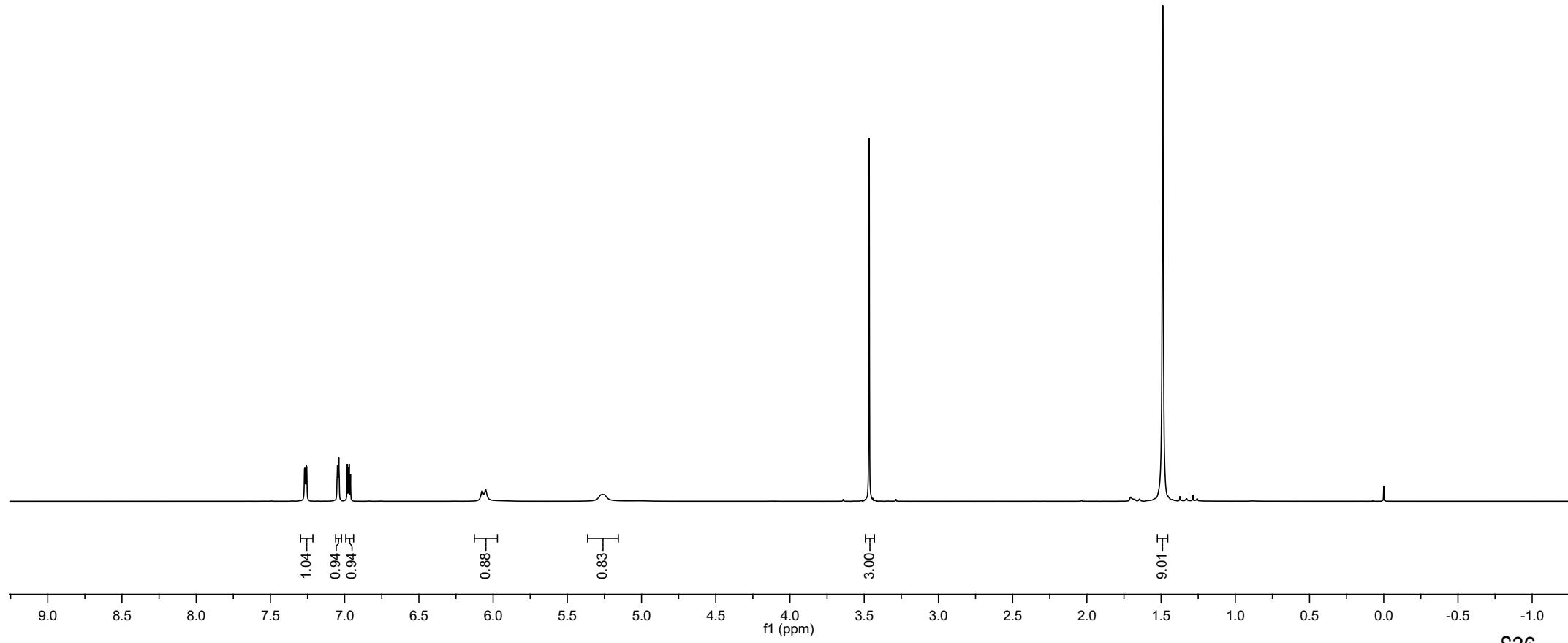
5.268  
5.256

-3.466

-1.489



(<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)



NMR spectra of compound 1s

—155.113

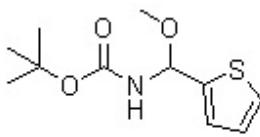
—143.199

—  
126.893  
125.627  
124.741

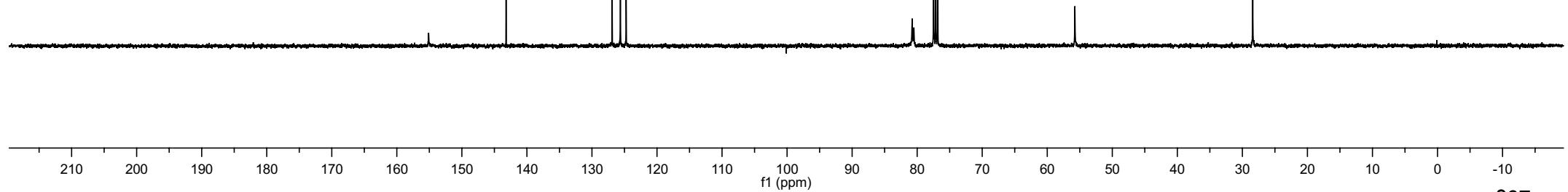
—  
80.767  
80.497

—55.754

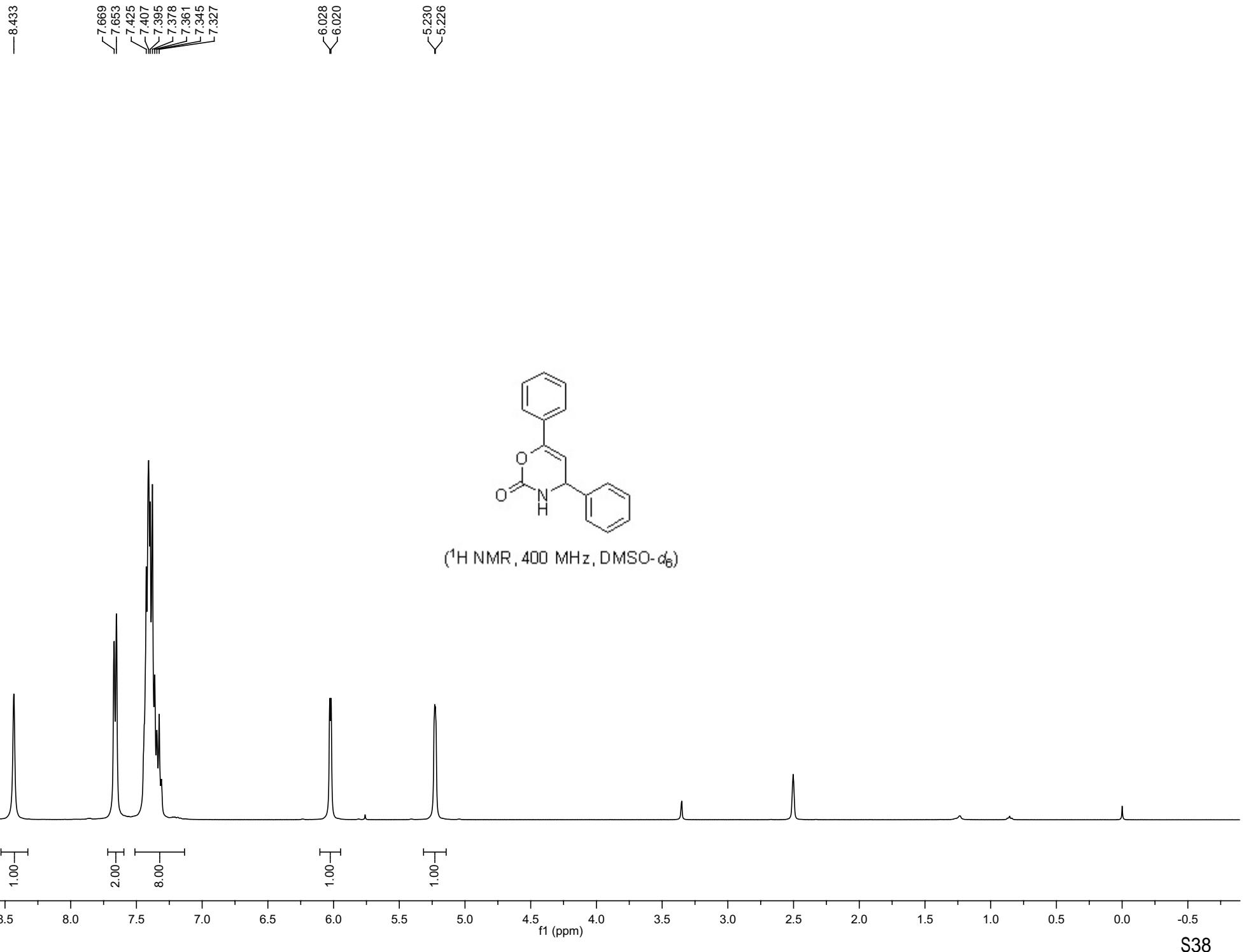
—28.414



( $^{13}\text{C}$  NMR, 100 MHz,  $\text{CDCl}_3$ )



NMR spectra of compound 3aa



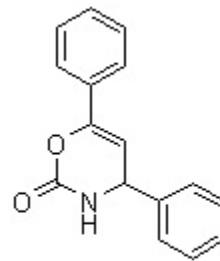
NMR spectra of compound 3aa

—149.137  
—146.106  
—142.679

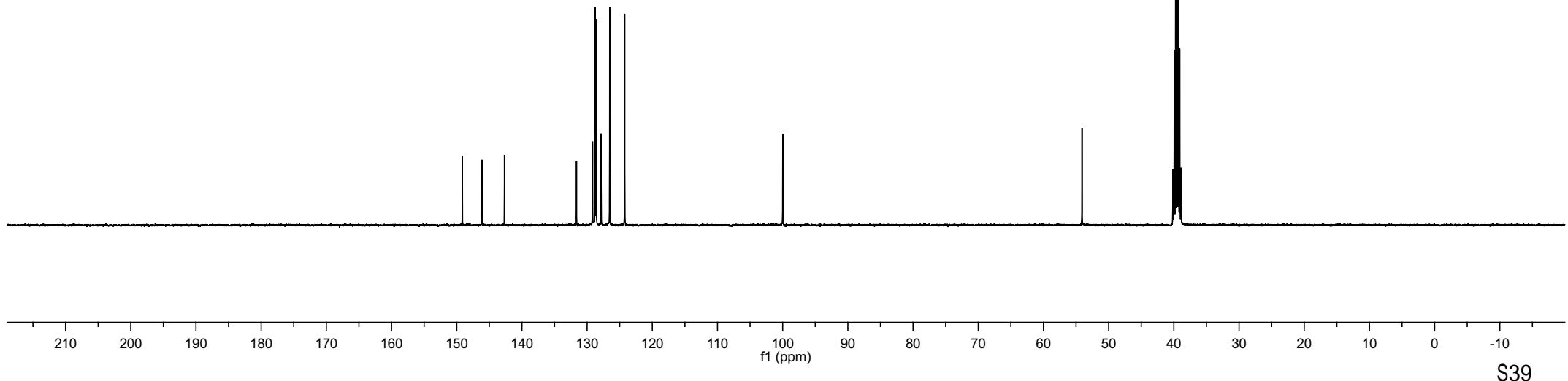
—131.627  
—129.162  
—128.768  
—128.611  
—127.852  
—126.537  
—124.236

—99.985

—54.084



( $^{13}\text{C}$  NMR, 100 MHz,  $\text{DMSO}-d_6$ )



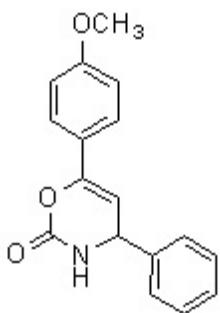
NMR spectra of compound 3ab

-8.354

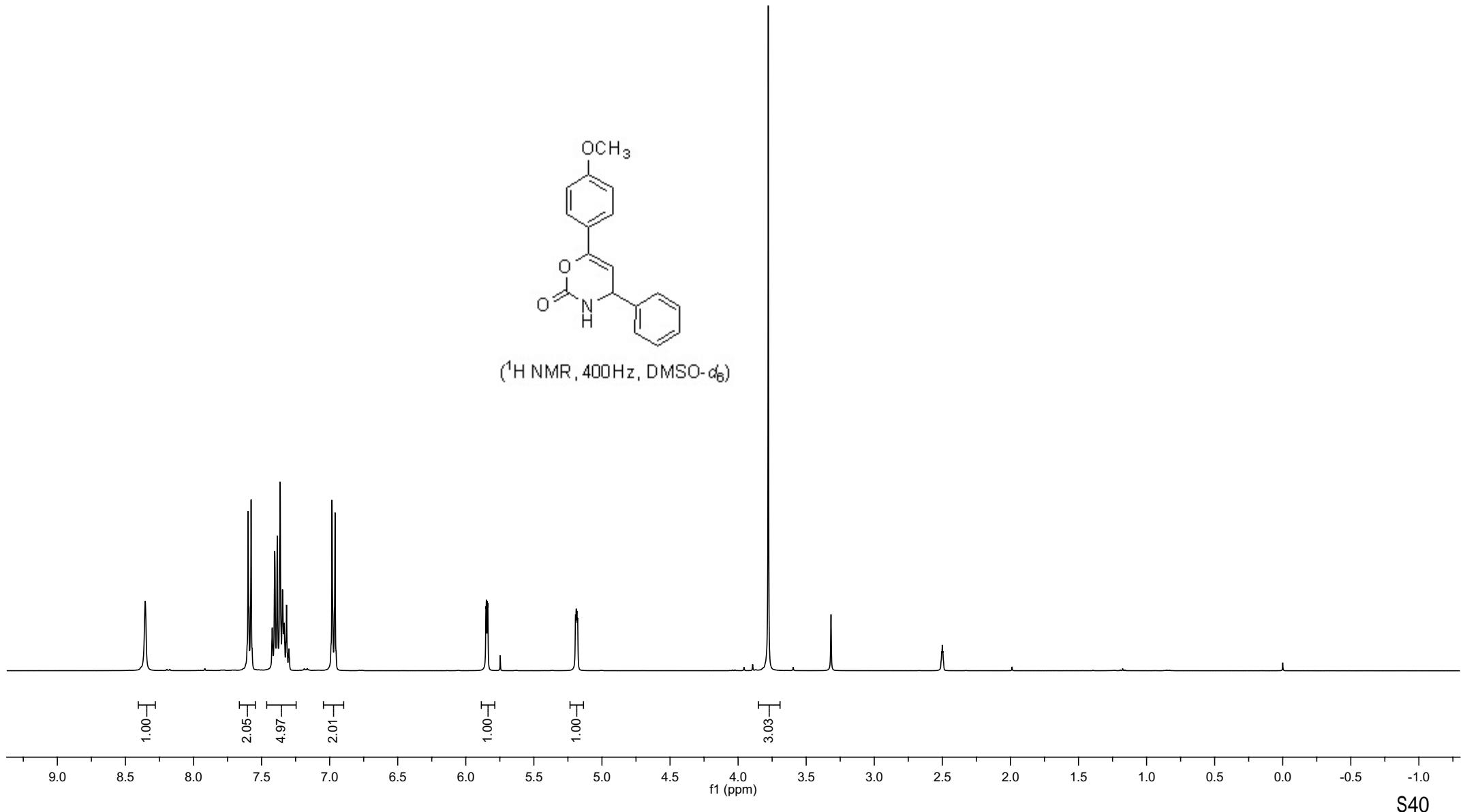
7.599  
7.577  
7.570  
7.367  
7.334  
7.299  
6.982  
6.960

5.852  
5.849  
5.842  
5.838  
5.194  
5.189  
5.184  
5.179

-3.778



( $^1\text{H}$  NMR, 400Hz,  $\text{DMSO}-d_6$ )



NMR spectra of compound 3ab

—159.962

—149.248

—146.080

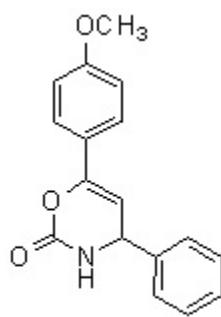
—142.916

128.725  
127.769  
126.486  
125.785  
124.105

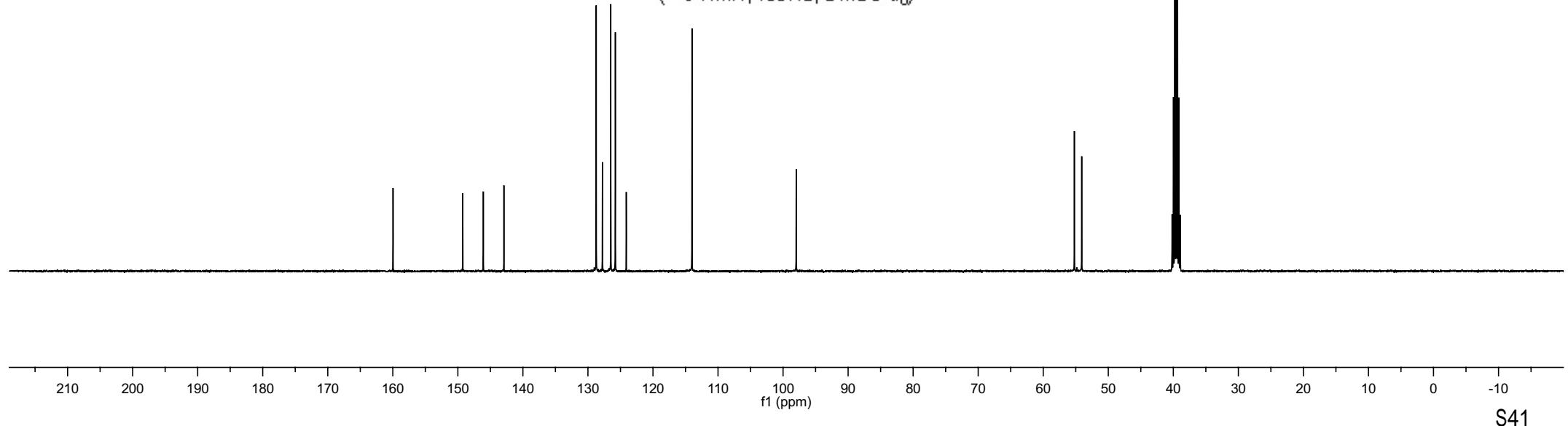
—114.000

—97.975

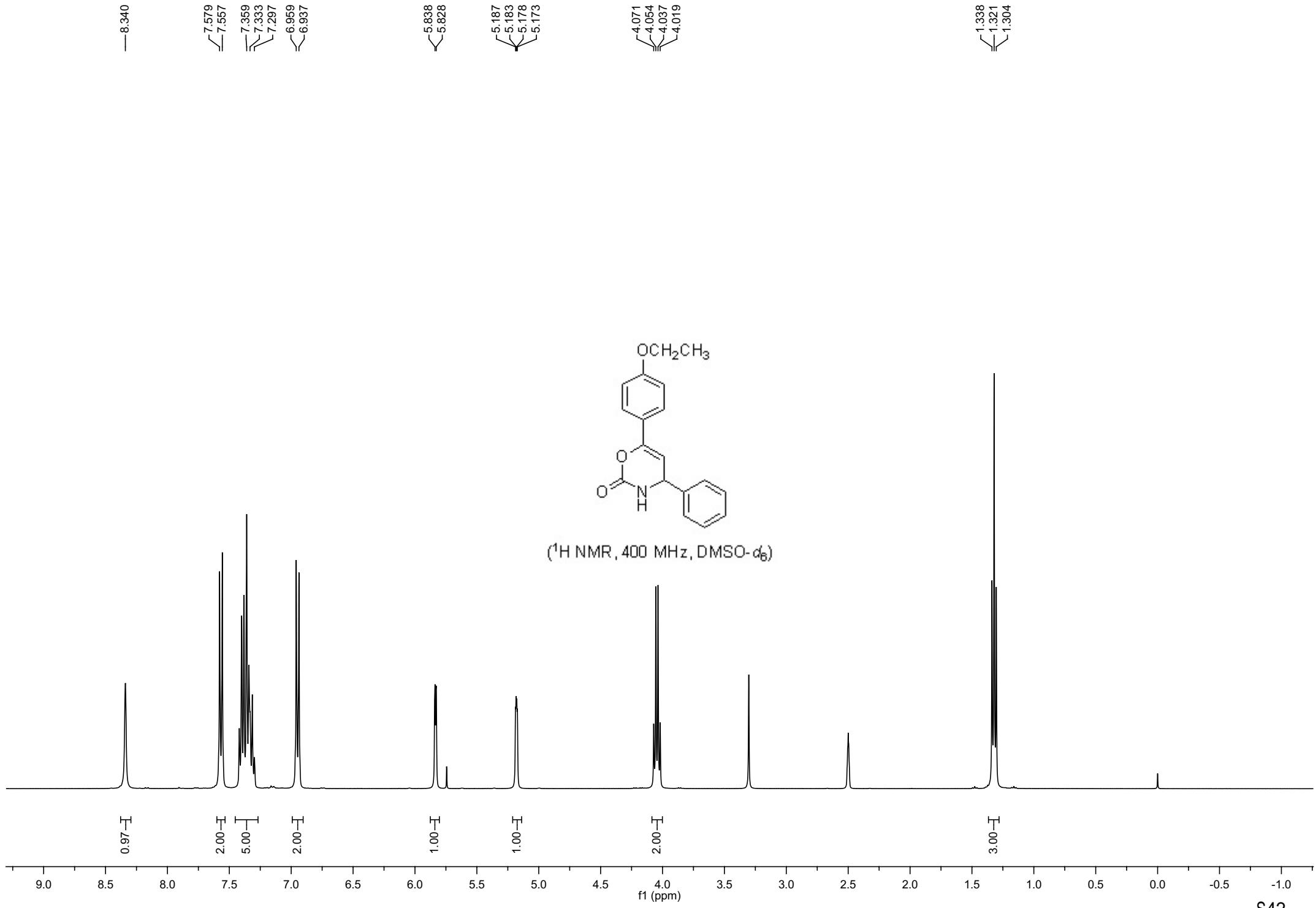
55.212  
54.083



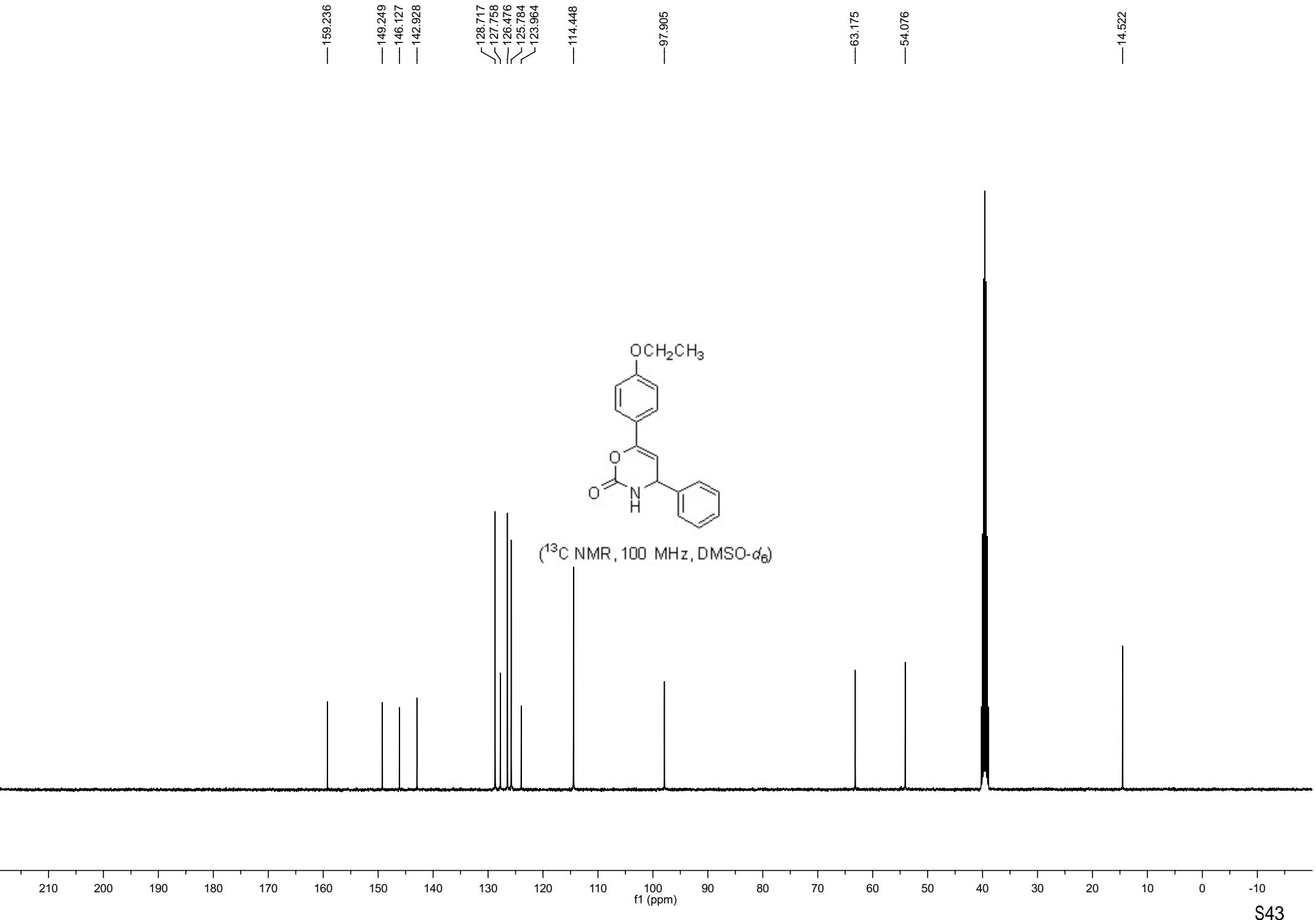
( $^{13}\text{C}$  NMR, 100Hz,  $\text{DMSO}-d_6$ )



NMR spectra of compound 3ac



NMR spectra of compound 3ac



NMR spectra of compound 3ad

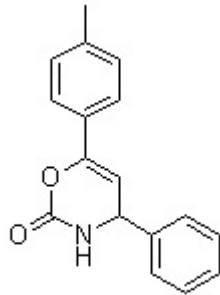
-8.395

7.546  
7.440  
7.421  
7.403  
7.377  
7.358  
7.336  
7.252  
7.232

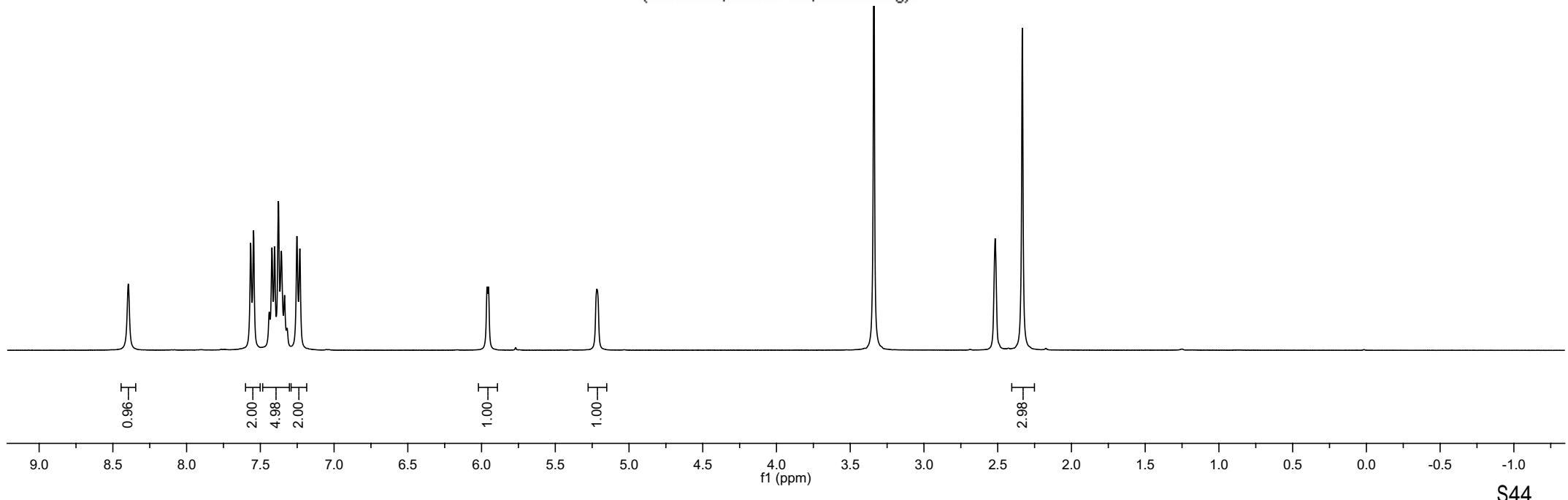
5.962  
5.954

-5.218

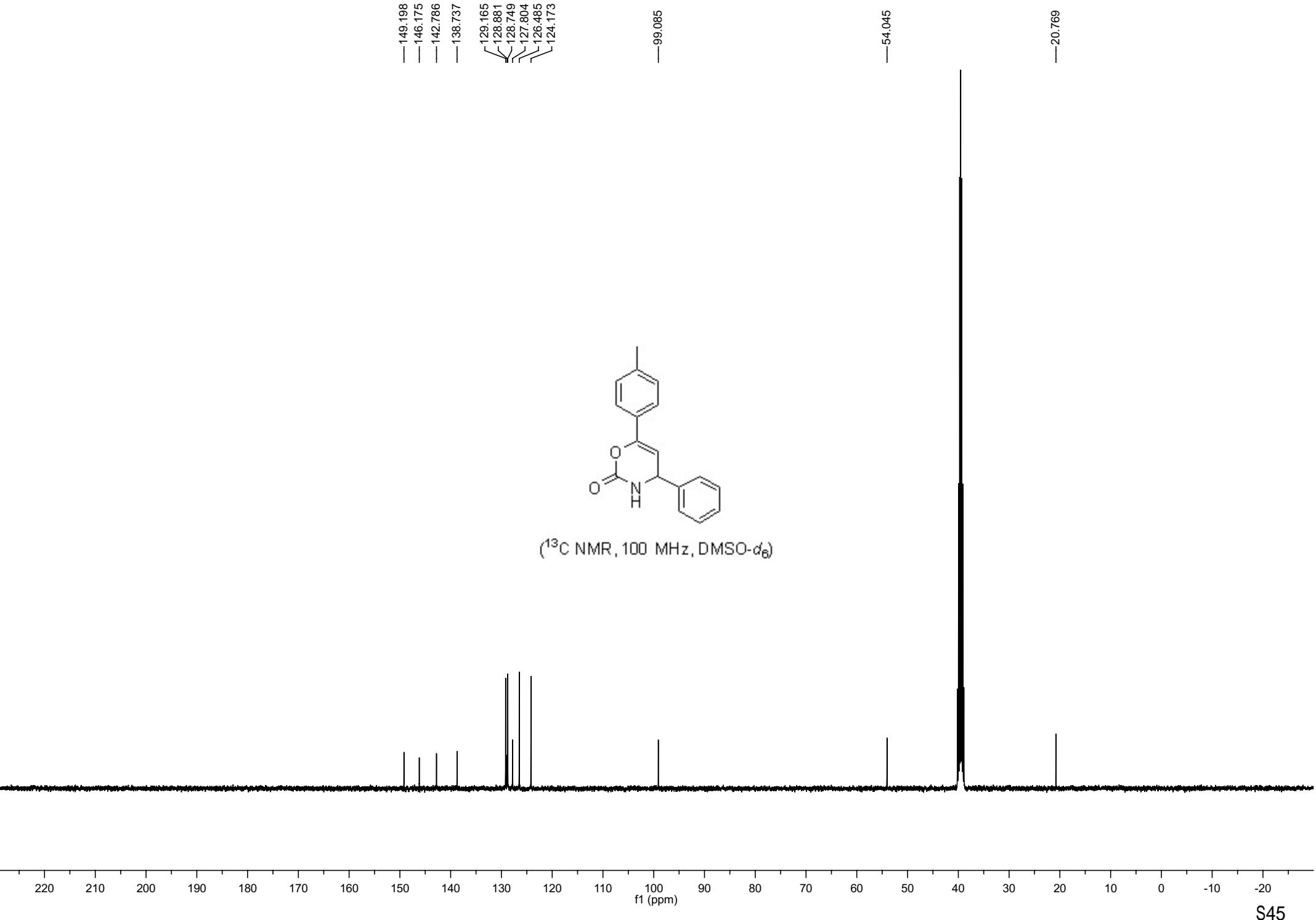
-2.333



( $^1\text{H}$  NMR, 400 MHz, DMSO- $d_6$ )



NMR spectra of compound 3ad



NMR spectra of compound 3ae

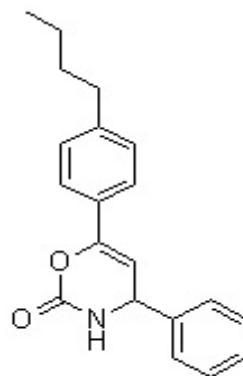
7.547  
7.526  
7.317  
7.183  
7.162

—6.252

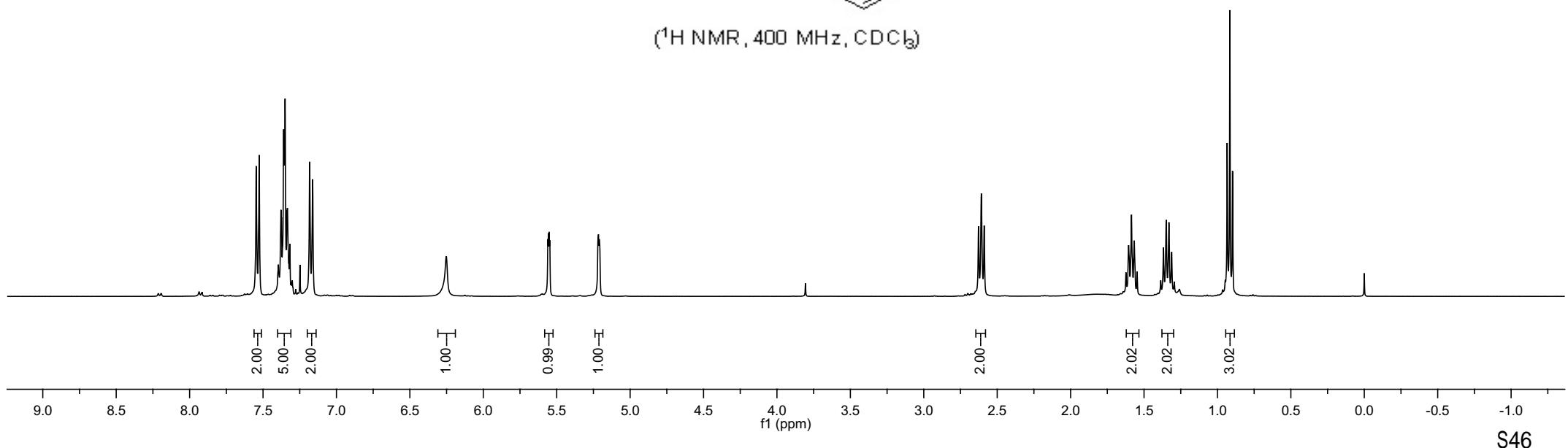
5.560  
5.556  
5.551  
5.547  
5.216  
5.210

2.627  
2.608  
2.589

1.623  
1.605  
1.585  
1.567  
1.547  
1.349  
1.312  
0.934  
0.915  
0.897



(<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)



NMR spectra of compound 3ae

—150.489  
—147.744  
—144.619  
—141.682

—129.159  
—128.956  
—128.617  
—128.567  
—126.717  
—124.723

—97.959

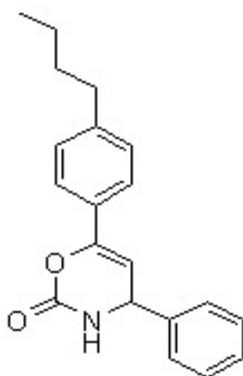
—55.776

—35.393

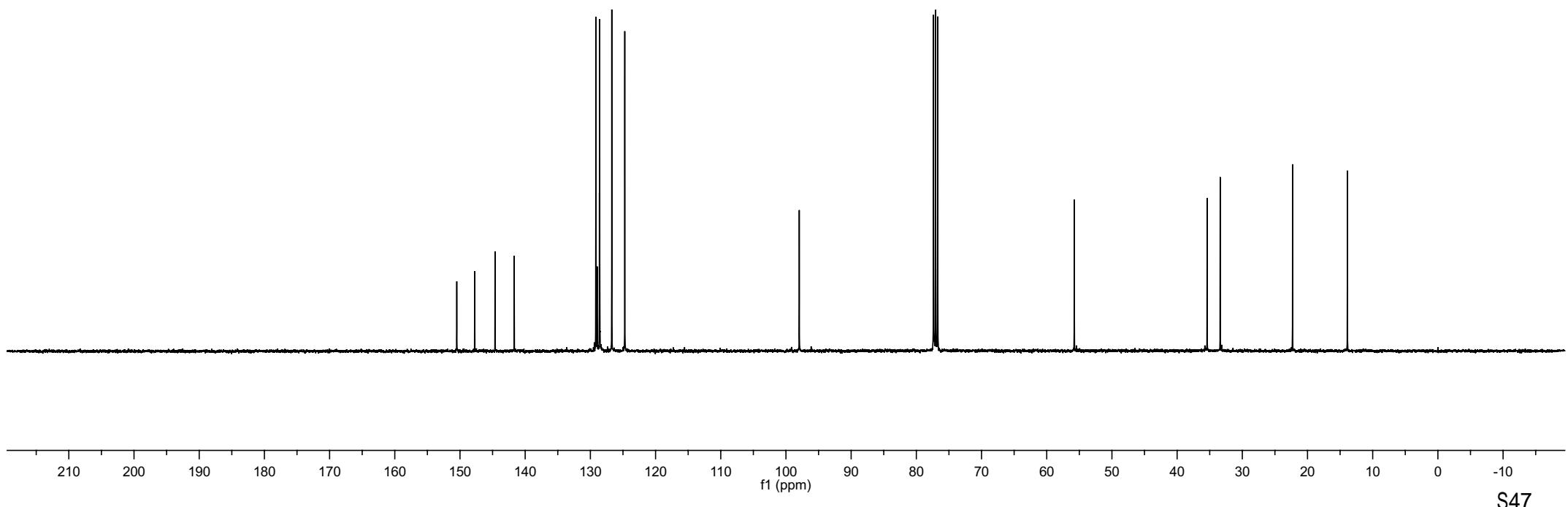
—33.389

—22.290

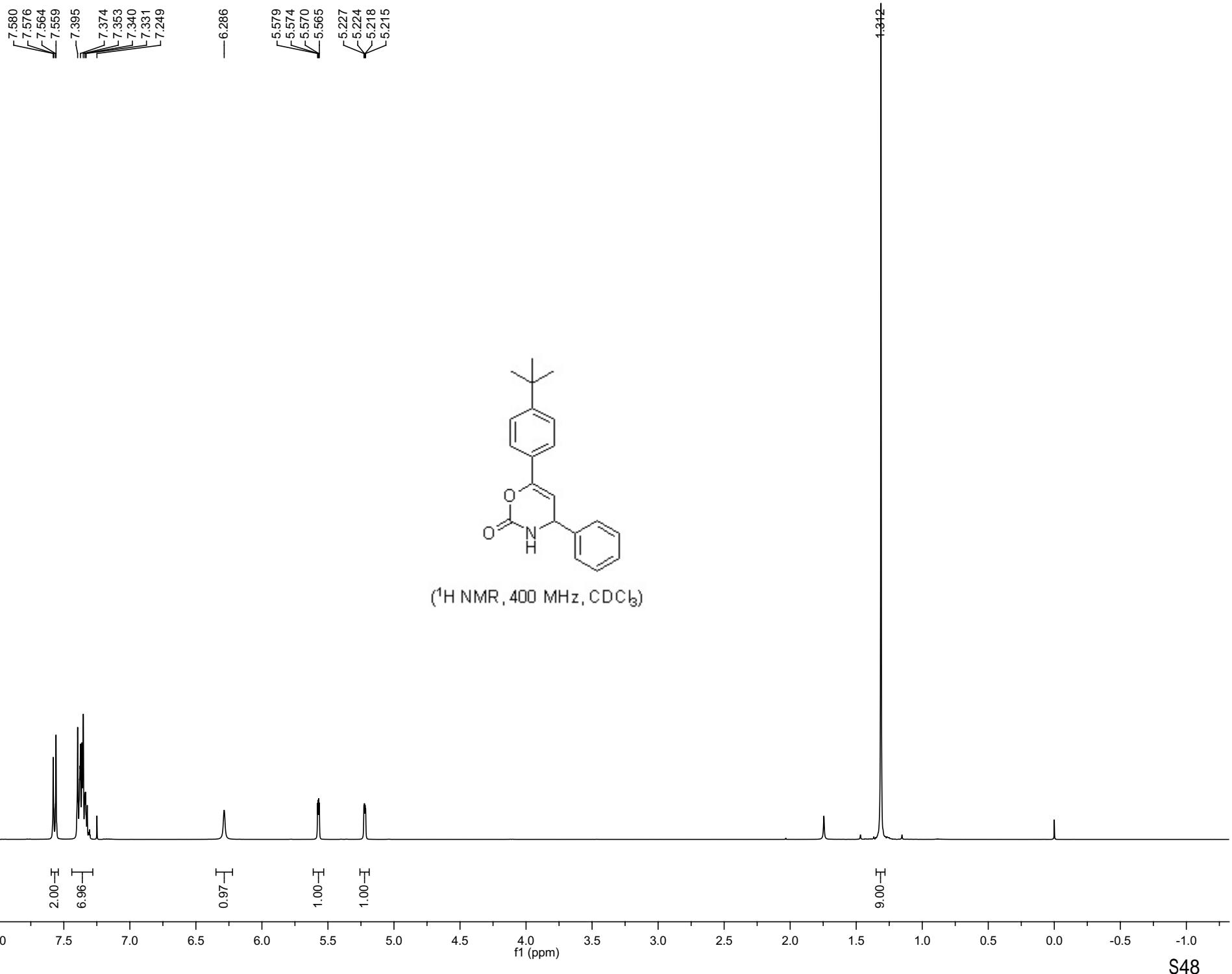
—13.879



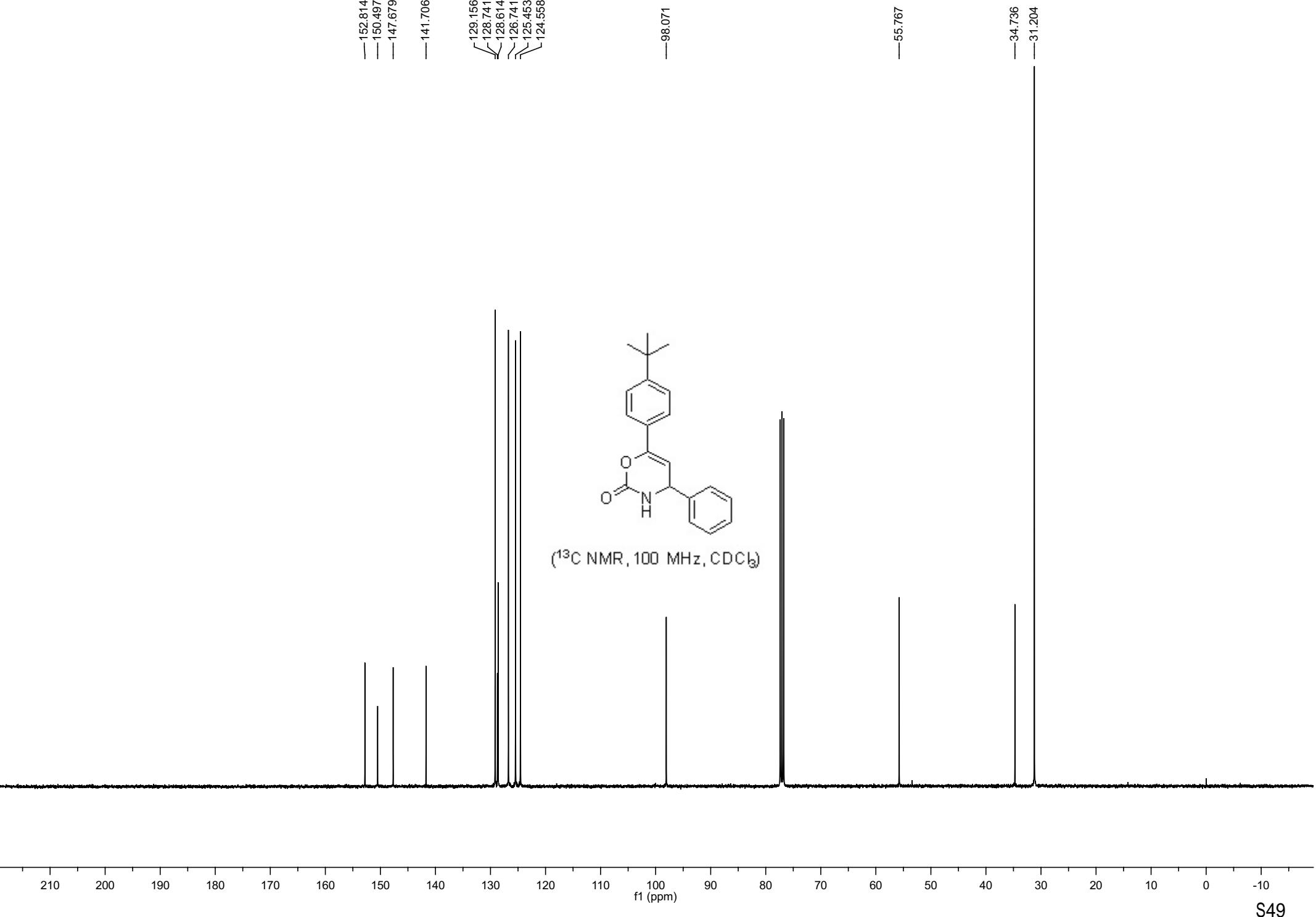
( $^{13}\text{C}$  NMR, 100 MHz,  $\text{CDCl}_3$ )



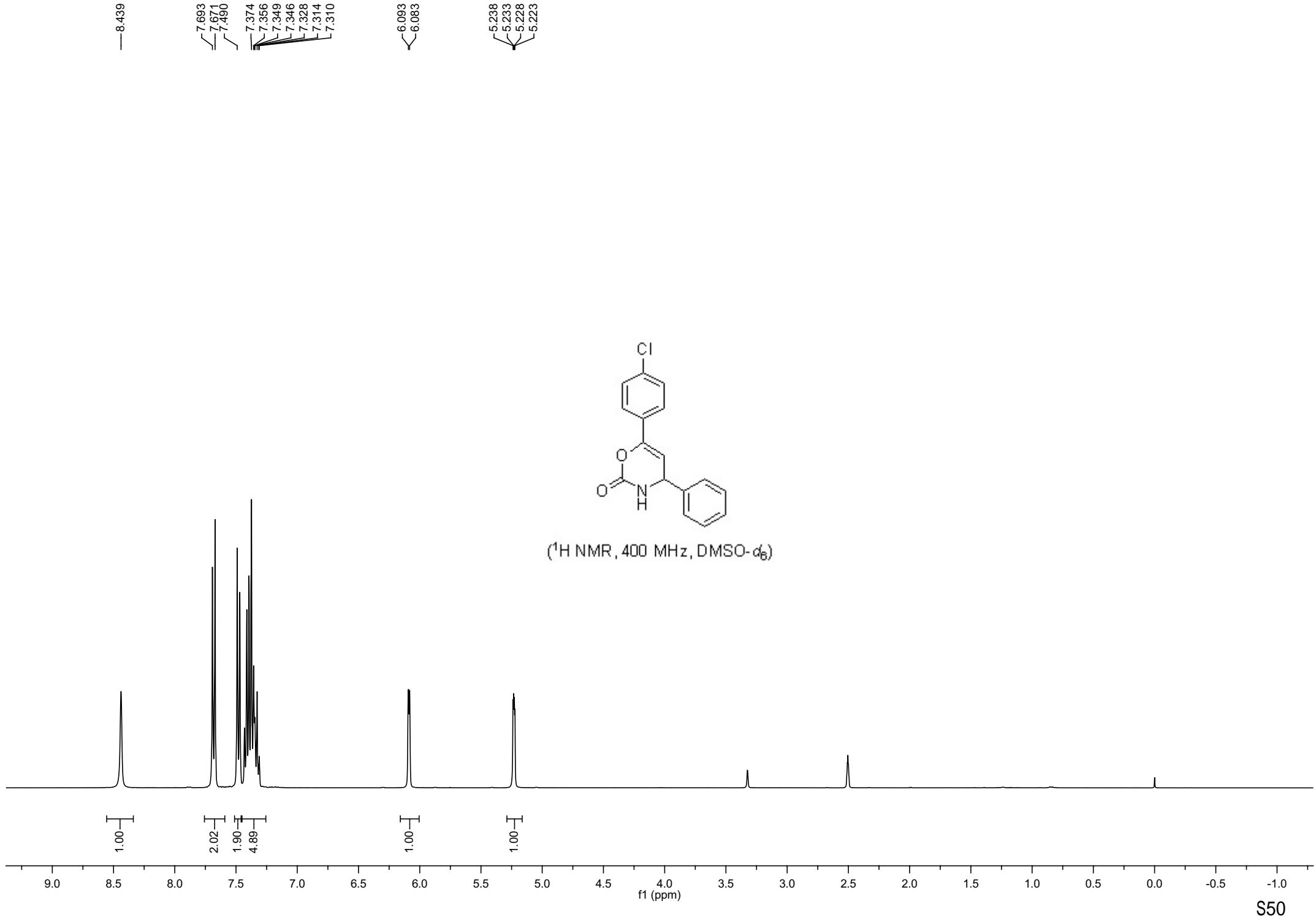
NMR spectra of compound 3af



NMR spectra of compound 3af

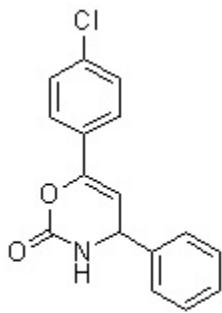


NMR spectra of compound 3ag

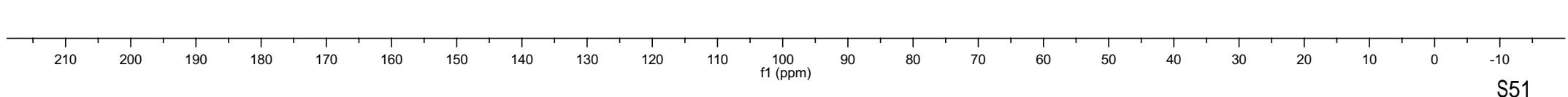


NMR spectra of compound 3ag

—148.907  
—145.140  
—142.473  
—133.711  
—130.514  
—128.769  
—128.654  
—127.882  
—126.545  
—126.063  
—10.701  
—54.095



( $^{13}\text{C}$  NMR, 100 MHz,  $\text{DMSO-d}_6$ )



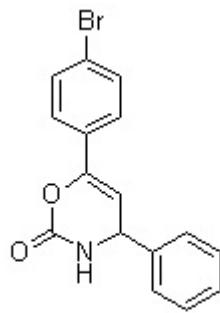
NMR spectra of compound 3ah

-8.443

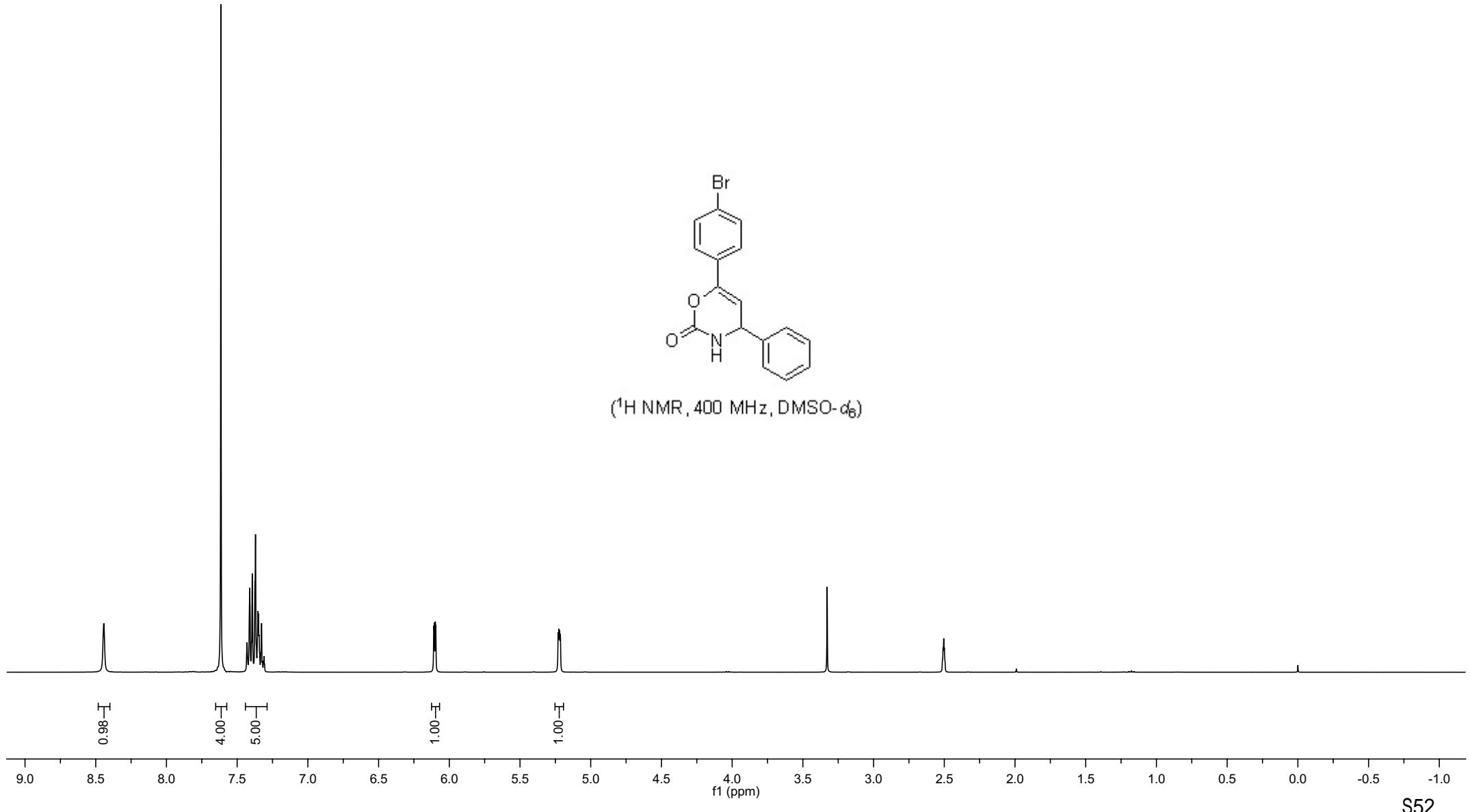
-7.615  
7.398  
7.374  
7.353  
7.345  
7.328  
7.314  
7.307

6.110  
6.106  
6.099  
6.096

5.230  
5.225  
5.220  
5.215

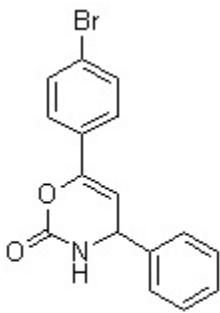


( $^1\text{H}$  NMR, 400 MHz, DMSO- $d_6$ )

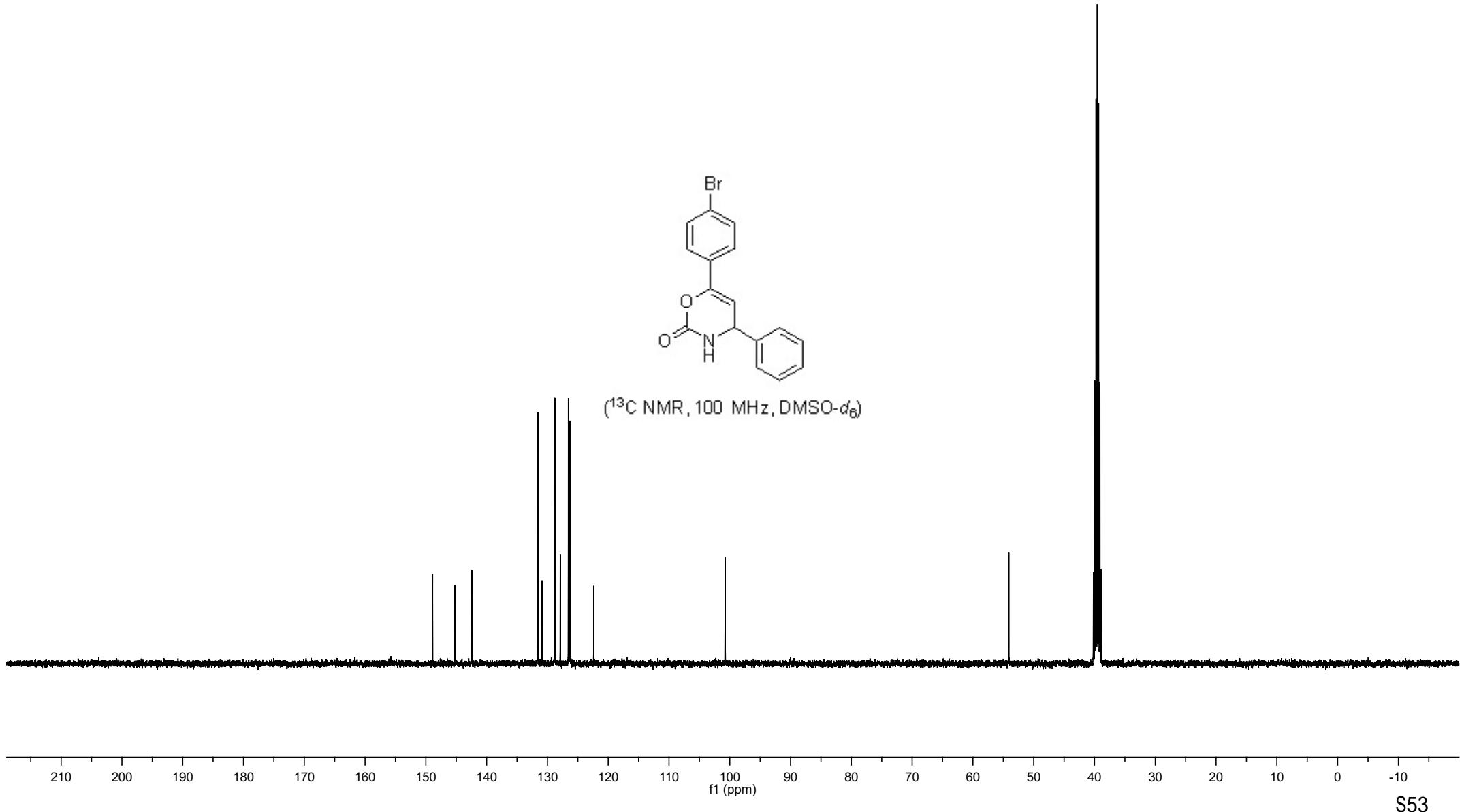


NMR spectra of compound 3ah

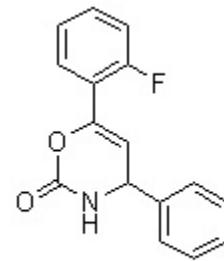
—148.893  
—145.196  
—142.439  
—131.576  
—128.773  
—127.887  
—126.543  
—126.305  
—122.375  
—100.756  
—54.097



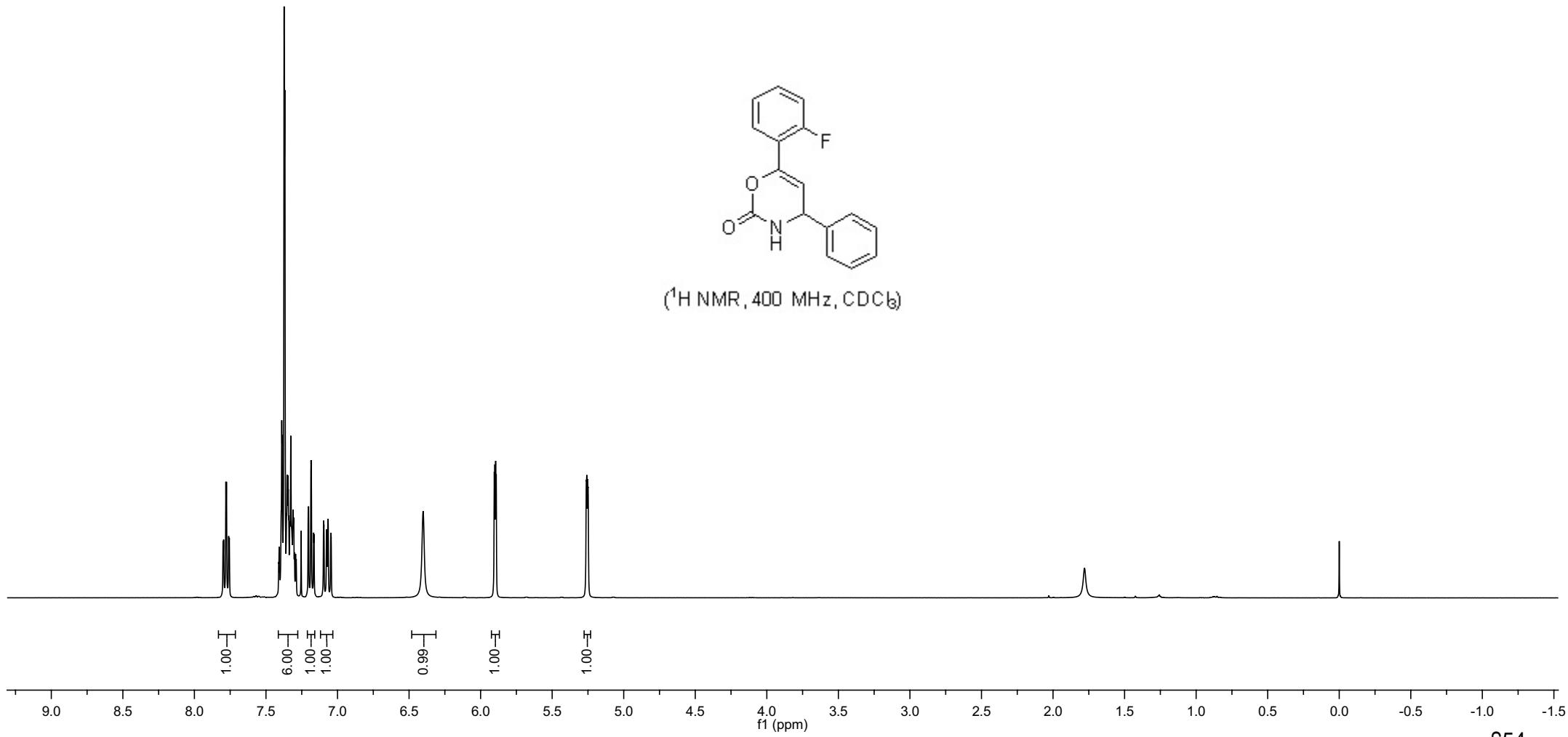
( $^{13}\text{C}$  NMR, 100 MHz,  $\text{DMSO}-d_6$ )



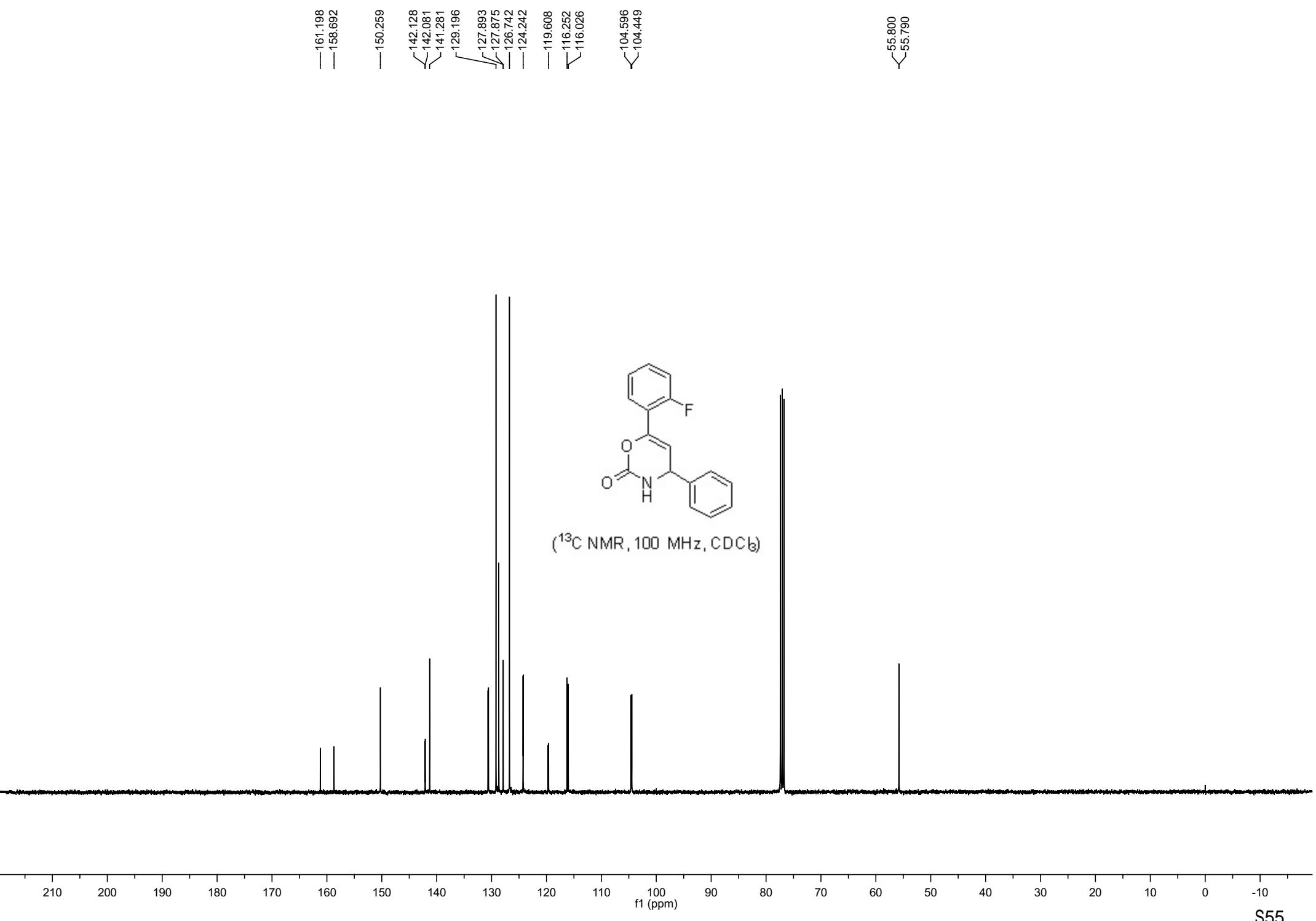
NMR spectra of compound 3ai



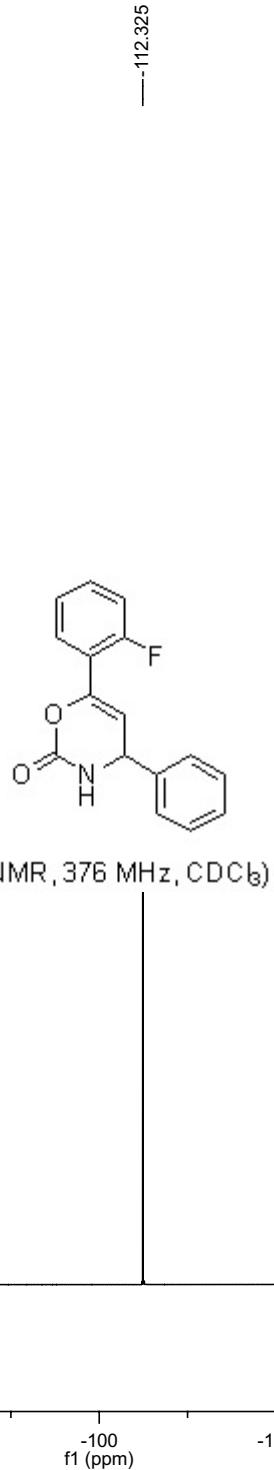
( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )



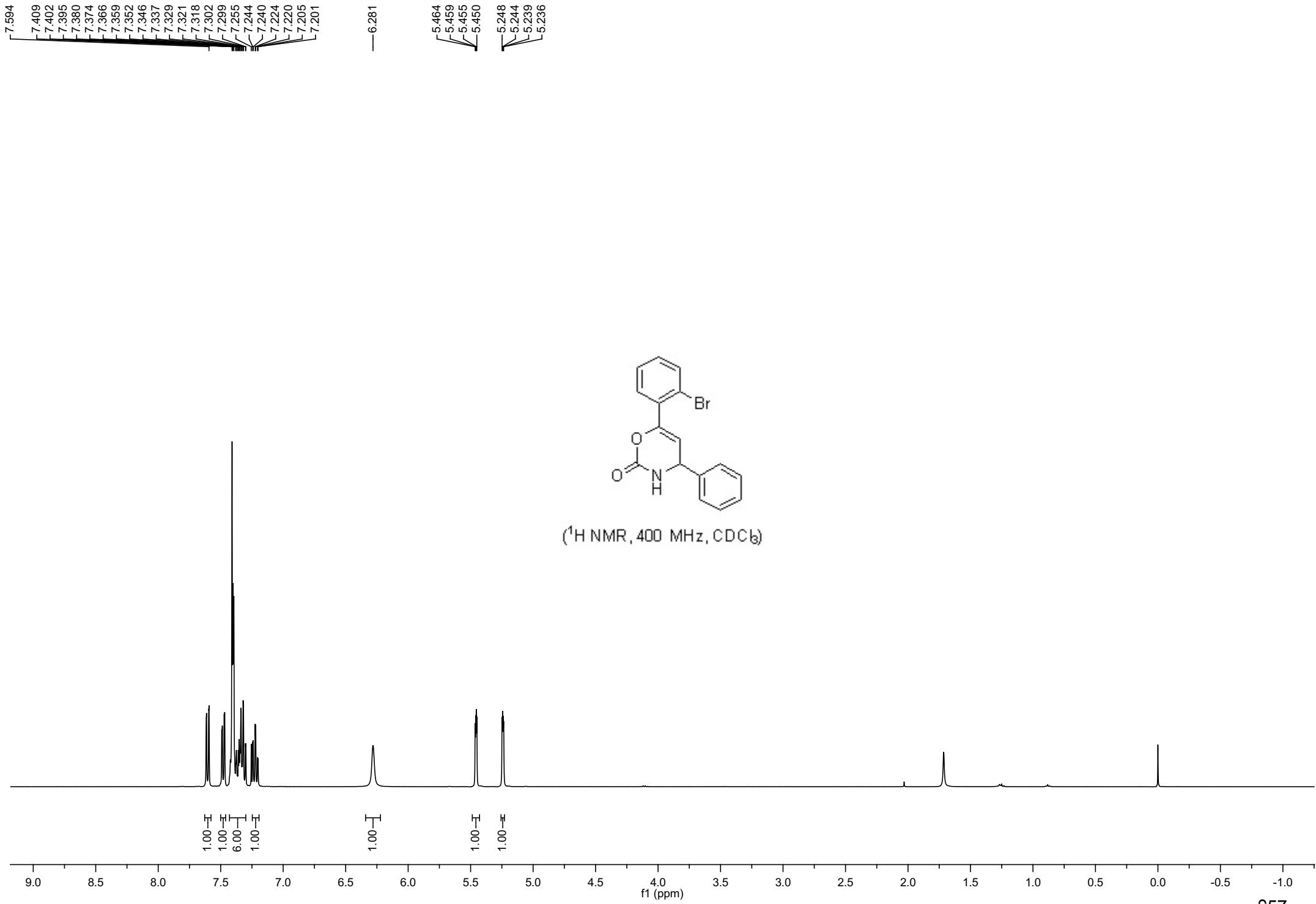
NMR spectra of compound 3ai



NMR spectra of compound 3ai

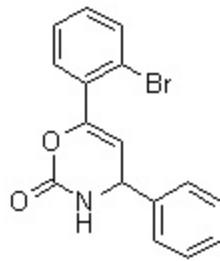


## NMR spectra of compound 3aj

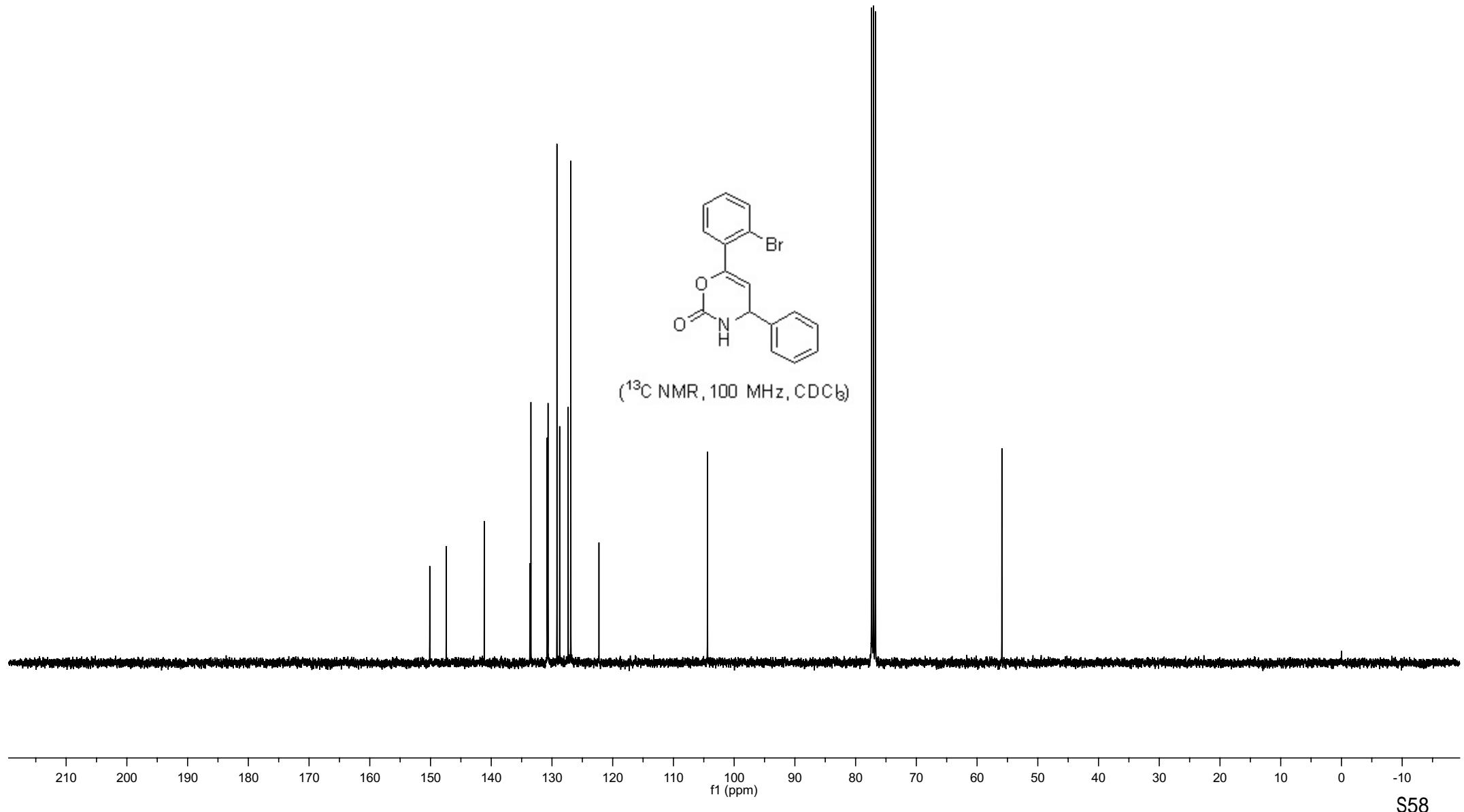


NMR spectra of compound 3aj

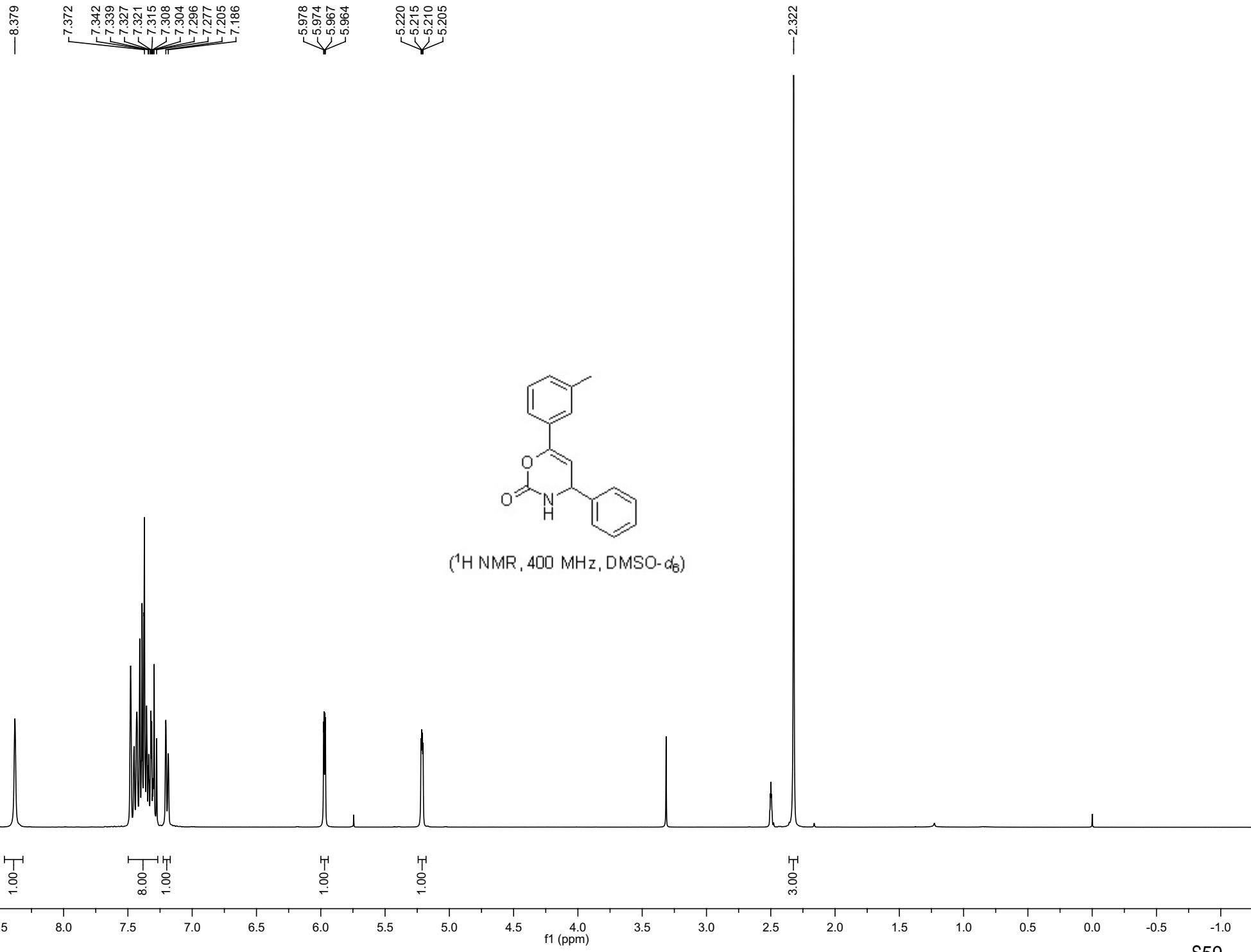
—150.127  
—147.410  
—141.153  
—133.641  
—133.465  
—129.185  
—126.903  
—122.263  
—104.396  
—55.915



( $^{13}\text{C}$  NMR, 100 MHz,  $\text{CDCl}_3$ )

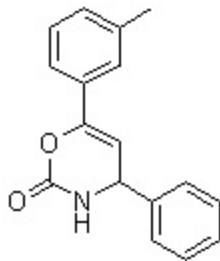


NMR spectra of compound 3ak

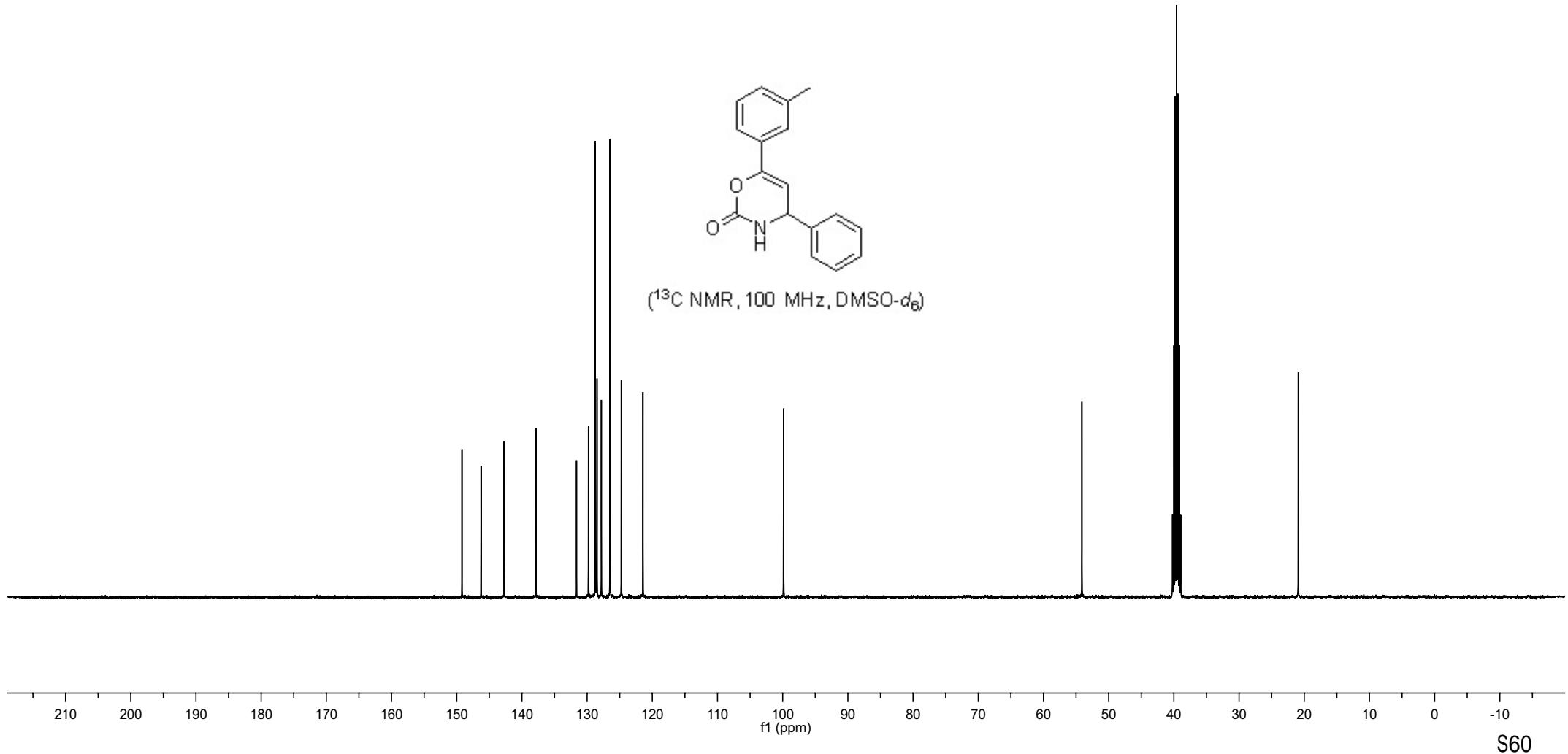


NMR spectra of compound 3ak

—149.195  
—146.268  
—142.731  
—137.851  
—128.745  
—128.480  
—127.814  
—126.491  
—124.758  
—121.439  
—99.864  
—54.103  
—20.915



( $^{13}\text{C}$  NMR, 100 MHz,  $\text{DMSO}-d_6$ )



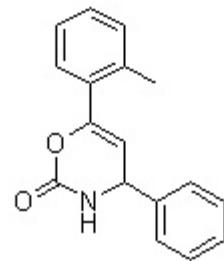
NMR spectra of compound 3al

—8.392

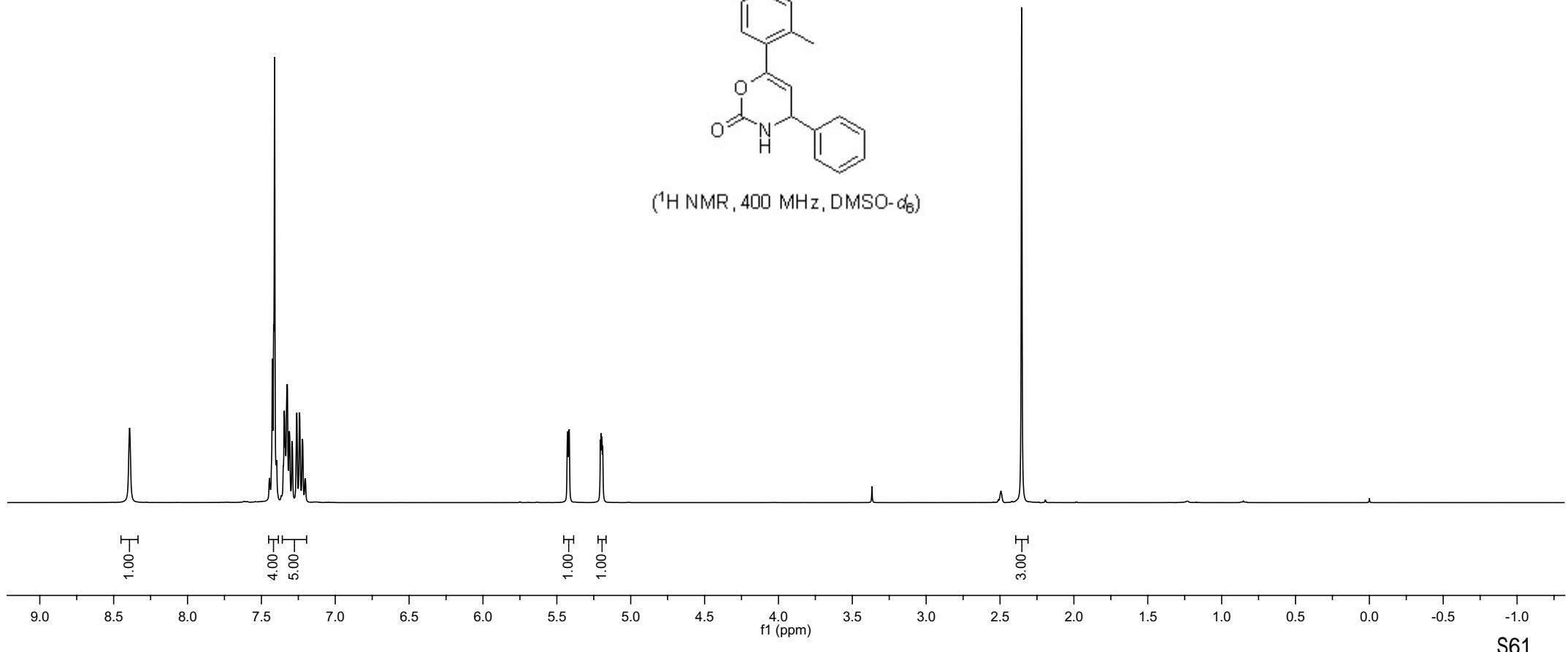
7.417  
7.400  
7.396  
7.351  
7.345  
7.338  
7.325  
7.311  
7.293  
7.260  
7.241  
7.222  
7.204

5.426  
5.419  
5.416  
5.205  
5.199  
5.195  
5.190

—2.354

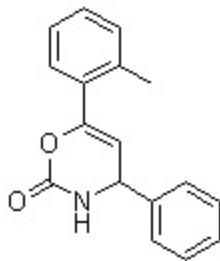


( $^1\text{H}$  NMR, 400 MHz, DMSO- $d_6$ )

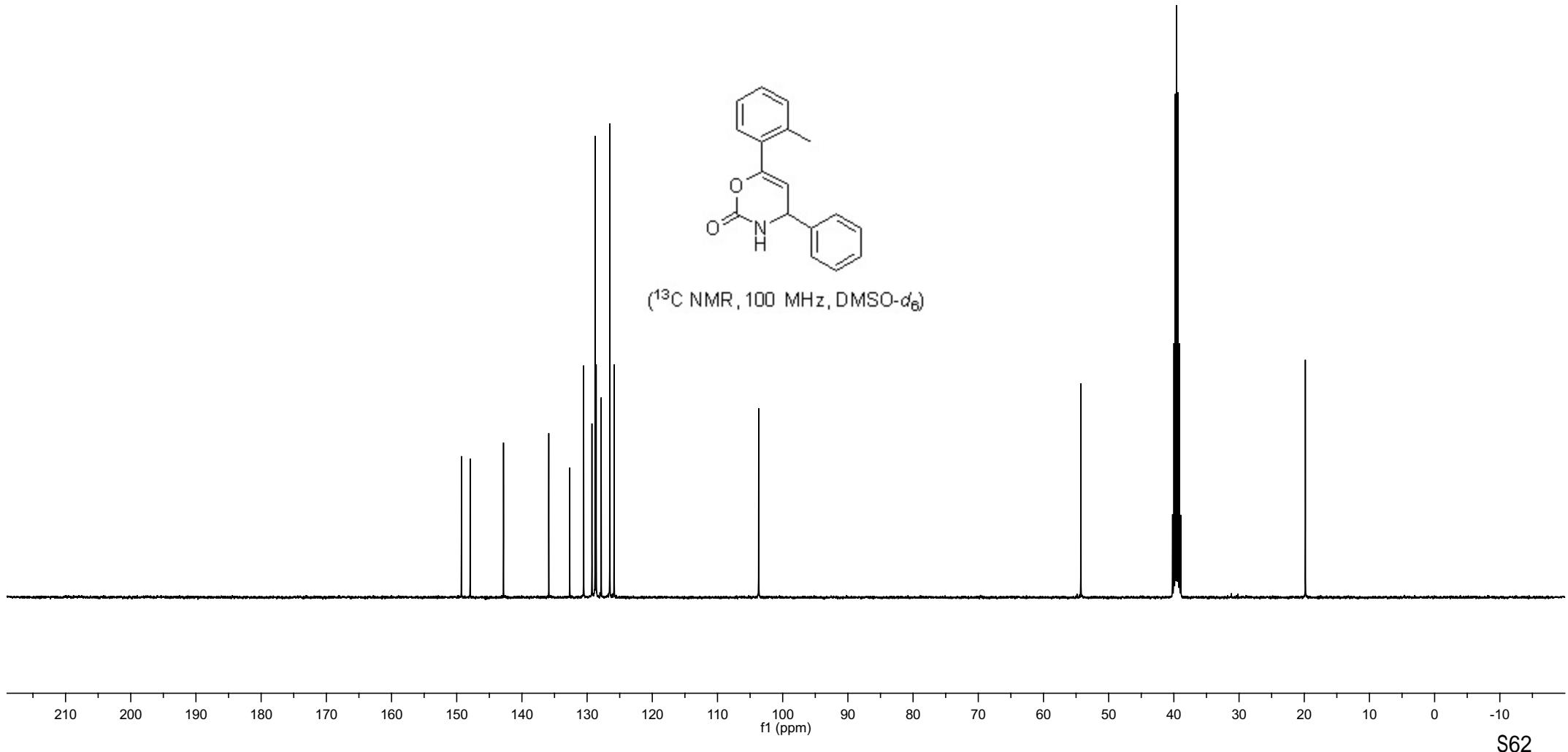


NMR spectra of compound 3al

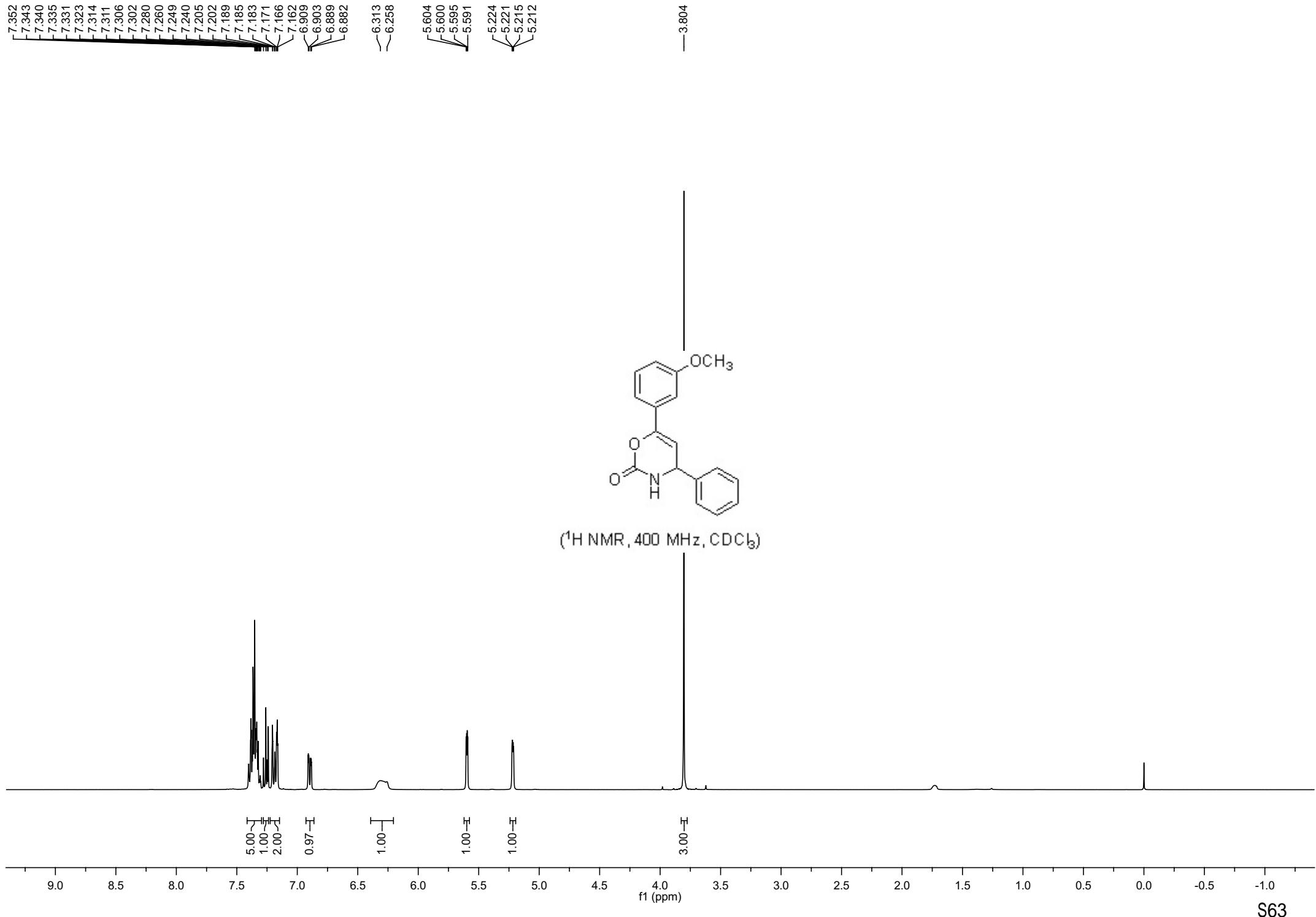
—149.278  
—147.936  
—142.822  
—135.877  
—132.665  
—130.534  
—129.255  
—128.774  
—128.607  
—127.844  
—126.516  
—125.859  
—103.680  
—54.265  
—19.828



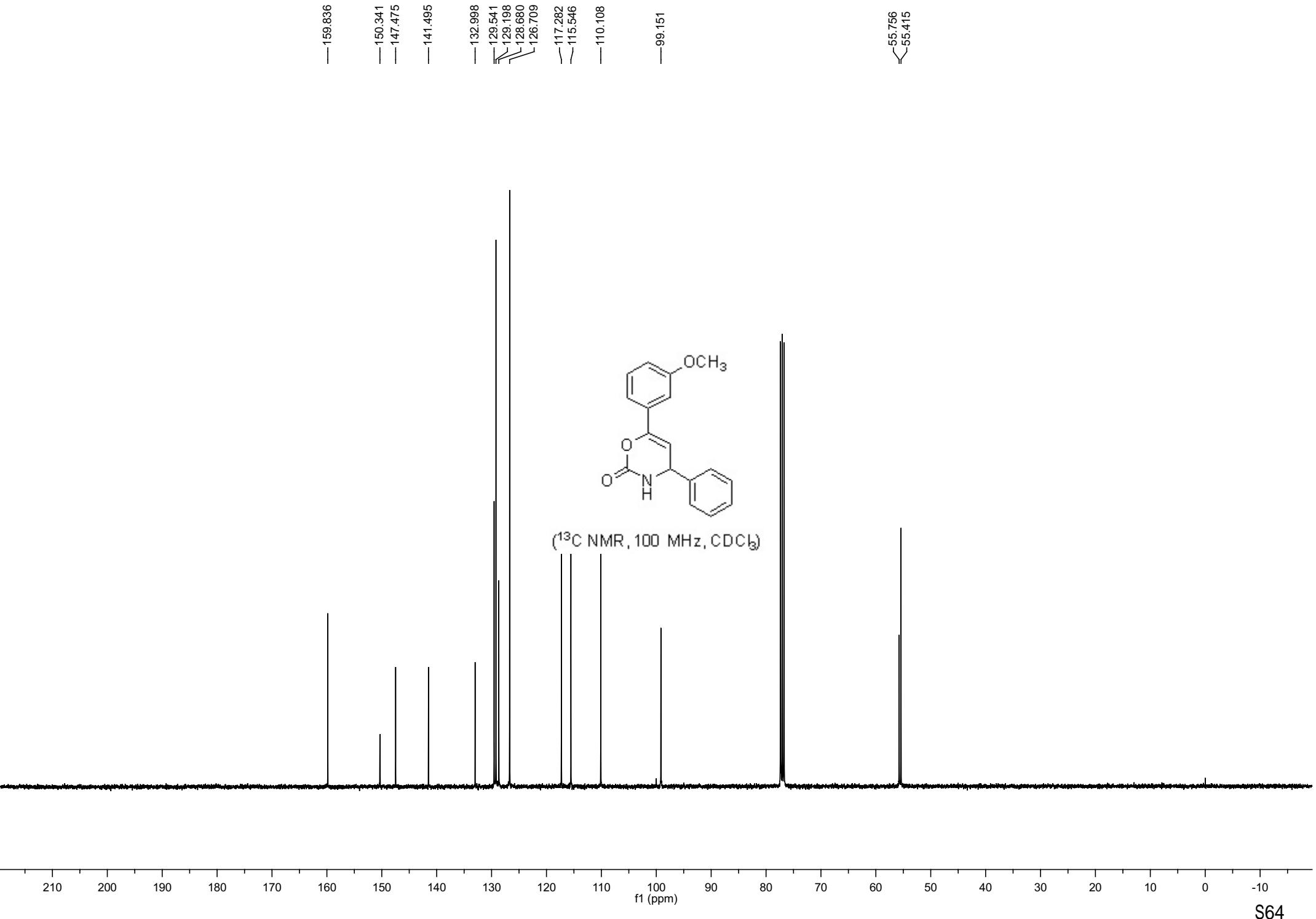
( $^{13}\text{C}$  NMR, 100 MHz,  $\text{DMSO-d}_6$ )



NMR spectra of compound 3am



NMR spectra of compound 3am



NMR spectra of compound 3an

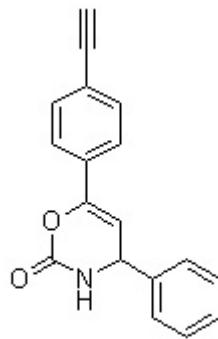
-8.450

7.688  
7.666  
7.512  
7.414  
7.396  
7.374  
7.351  
7.335  
7.312

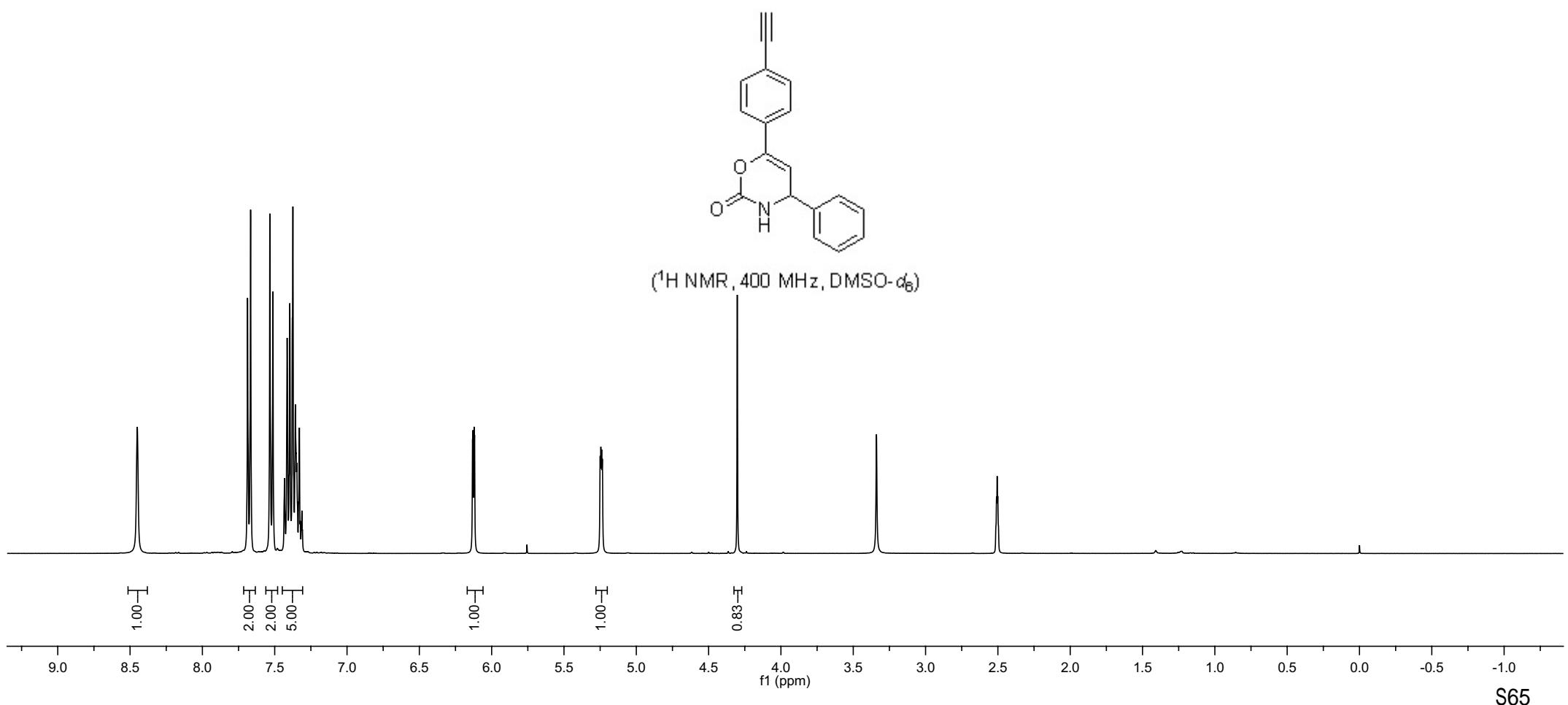
6.132  
6.129  
6.122  
6.118

5.250  
5.245  
5.240  
5.235

-4.302

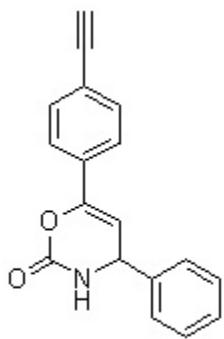


( $^1\text{H}$  NMR, 400 MHz, DMSO- $d_6$ )

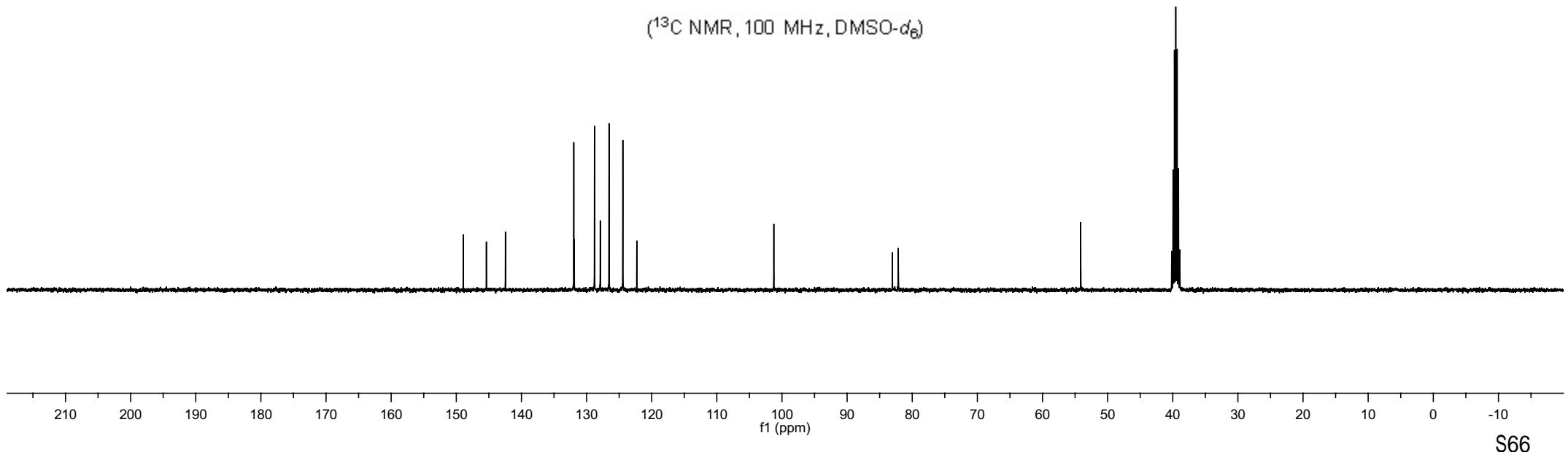


NMR spectra of compound 3an

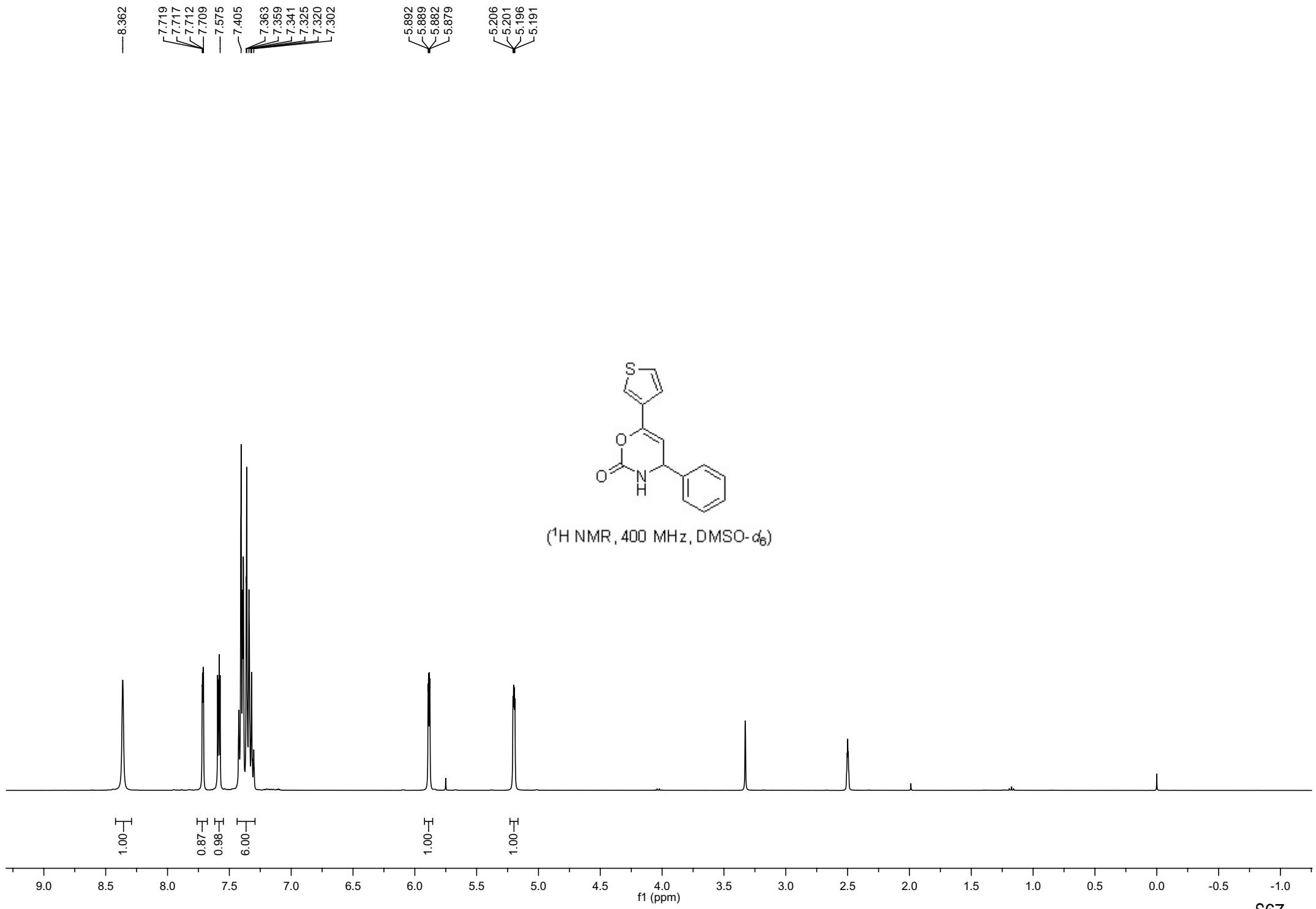
—148.937  
—145.383  
—142.455  
—131.958  
—131.895  
—128.780  
—127.894  
—126.548  
—124.429  
—122.286  
—101.247  
—83.047  
—82.137  
—54.130



( $^{13}\text{C}$  NMR, 100 MHz,  $\text{DMSO-d}_6$ )

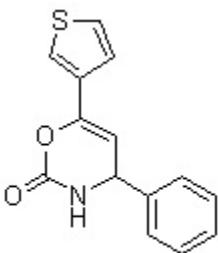


### NMR spectra of compound 3ao

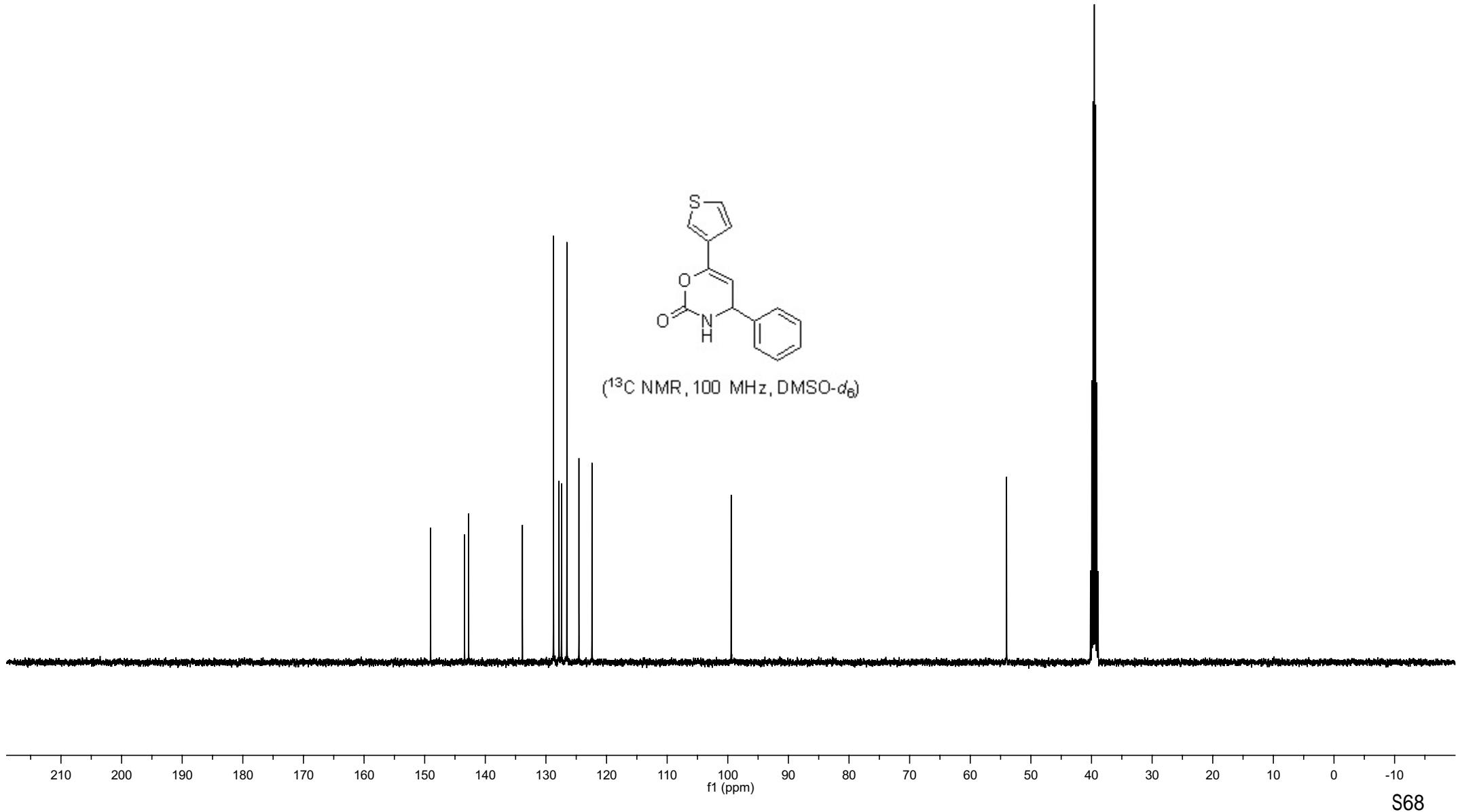


NMR spectra of compound 3ao

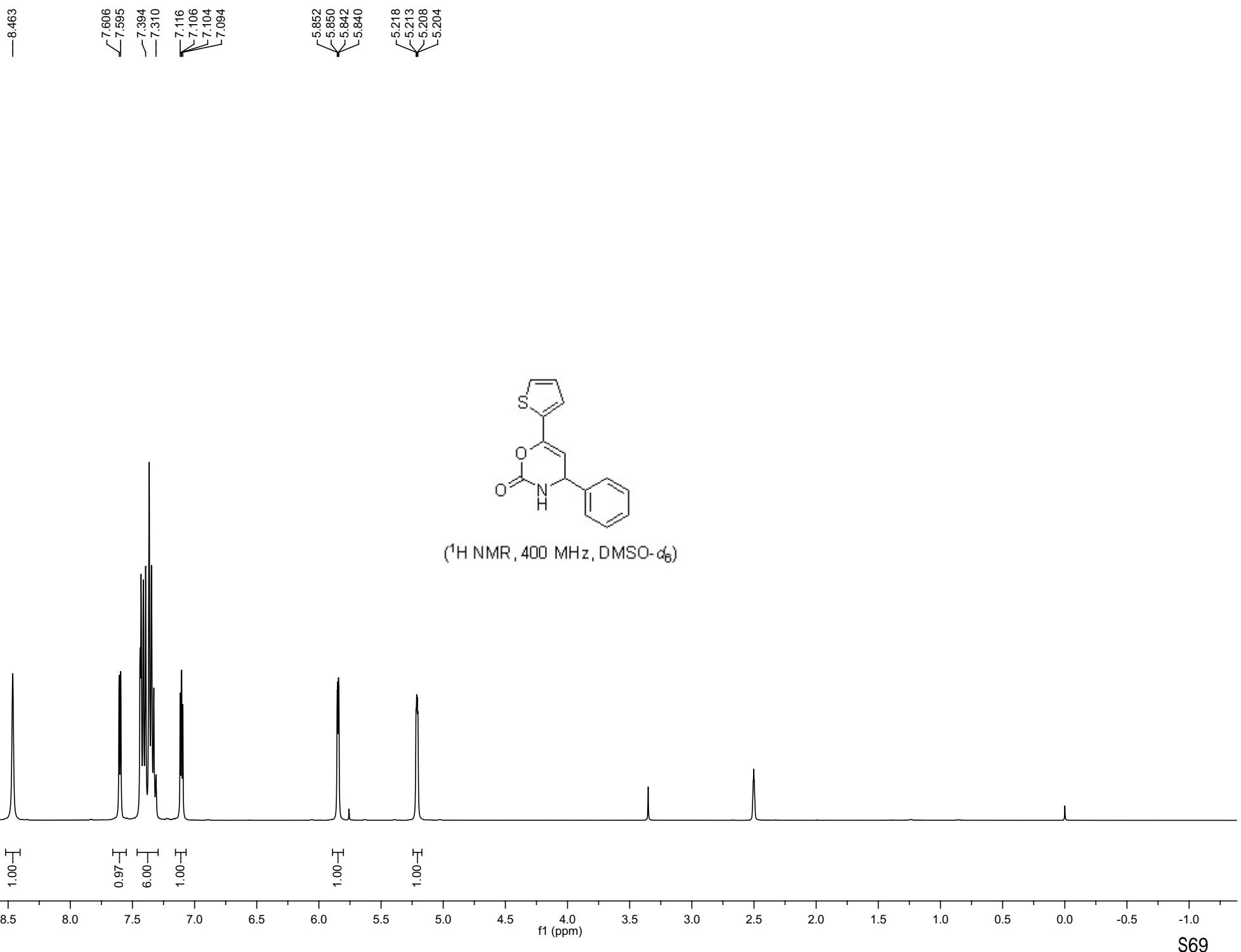
—149.025  
—143.426  
—142.749  
—133.875  
—128.751  
—127.843  
—127.424  
—126.539  
—124.553  
—122.399  
—99.440  
—54.013



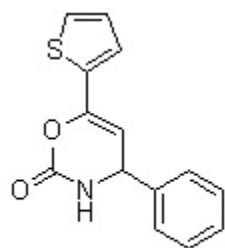
( $^{13}\text{C}$  NMR, 100 MHz,  $\text{DMSO}-d_6$ )



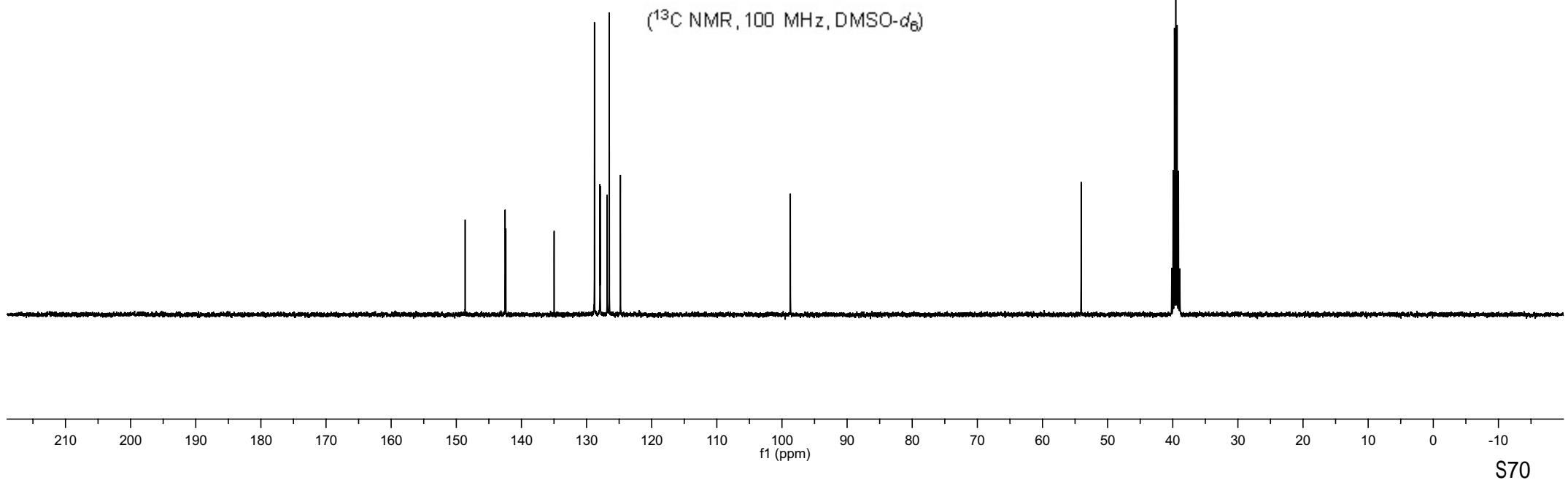
NMR spectra of compound 3ap



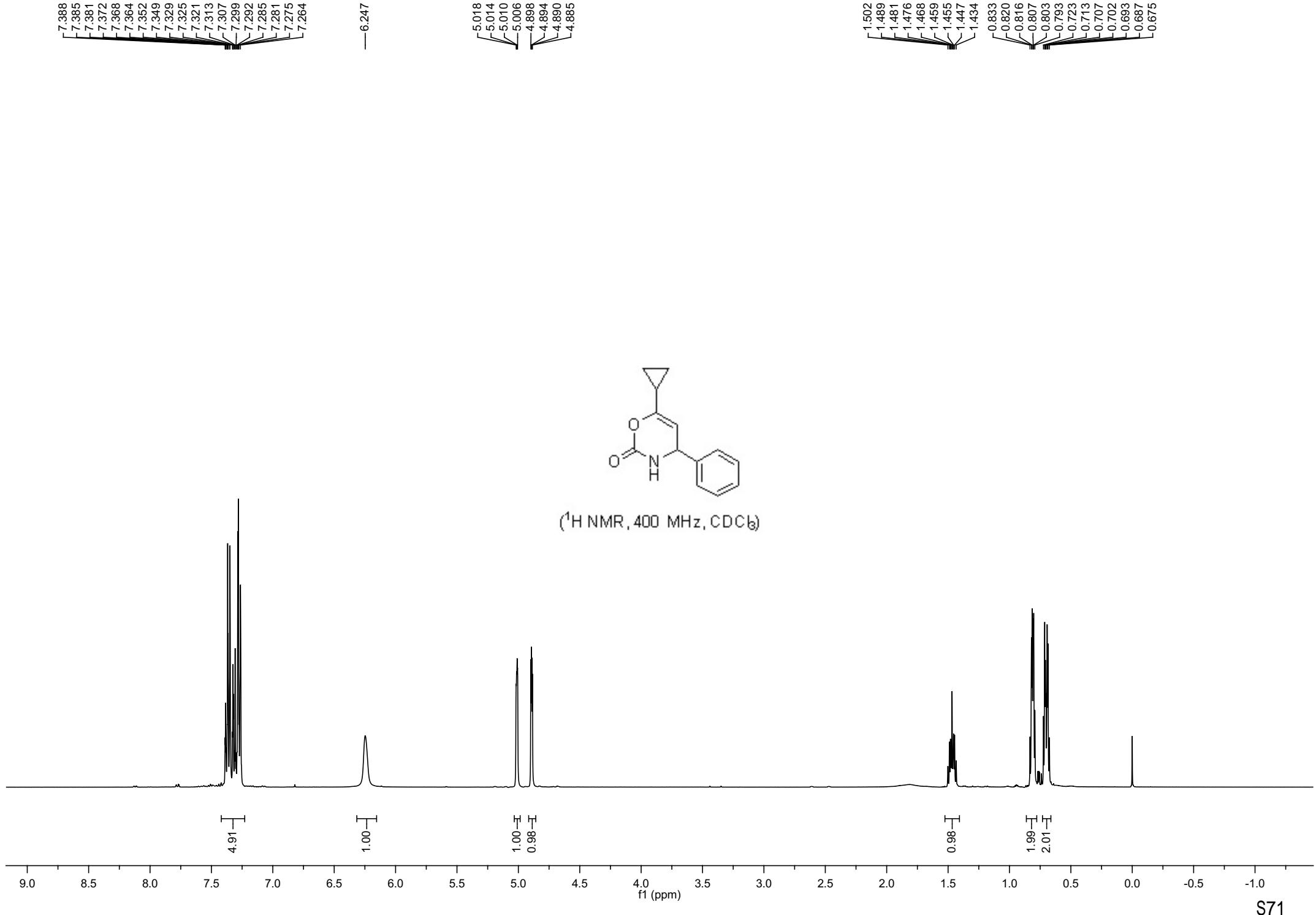
NMR spectra of compound 3ap



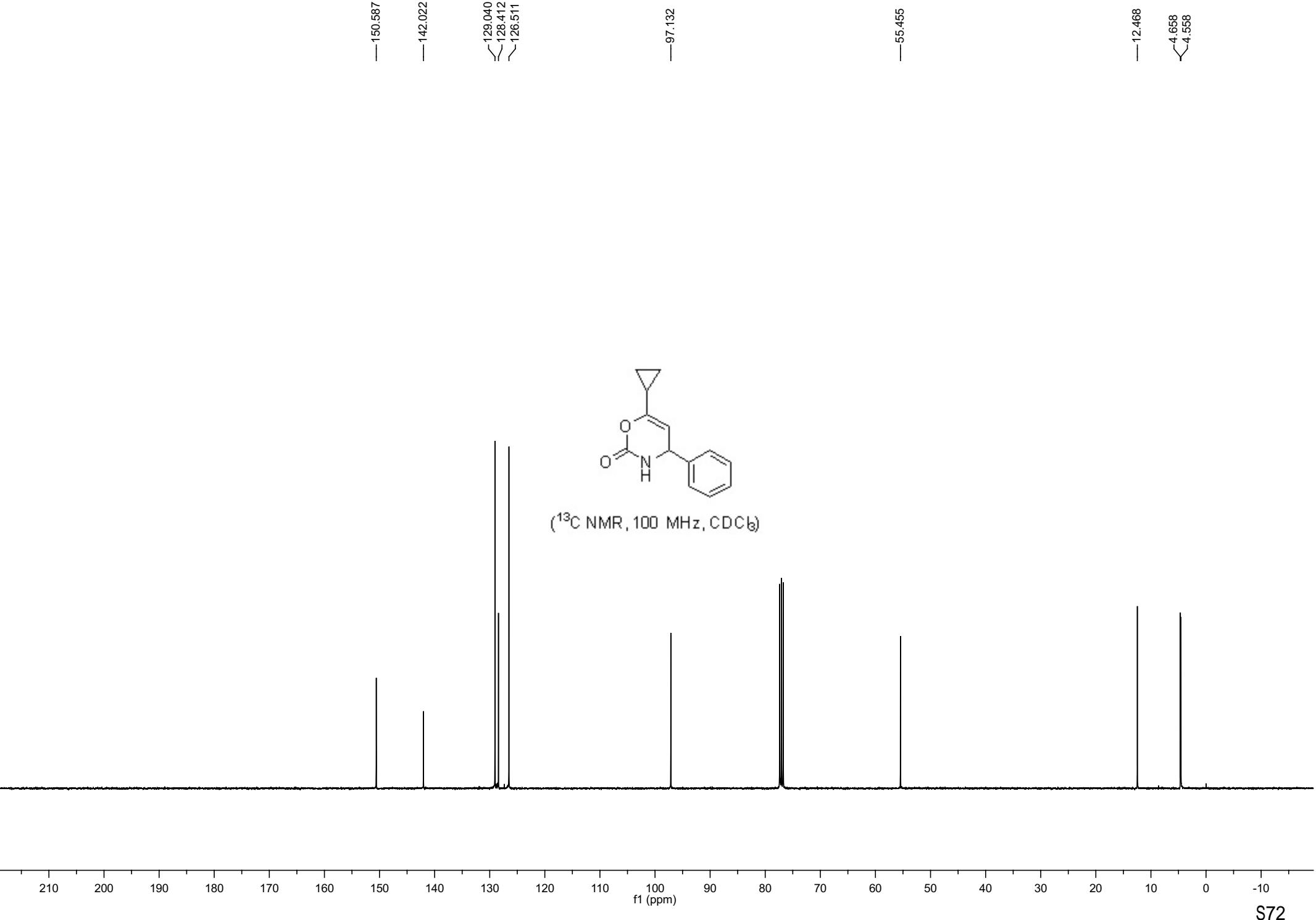
( $^{13}\text{C}$  NMR, 100 MHz,  $\text{DMSO}-d_6$ )



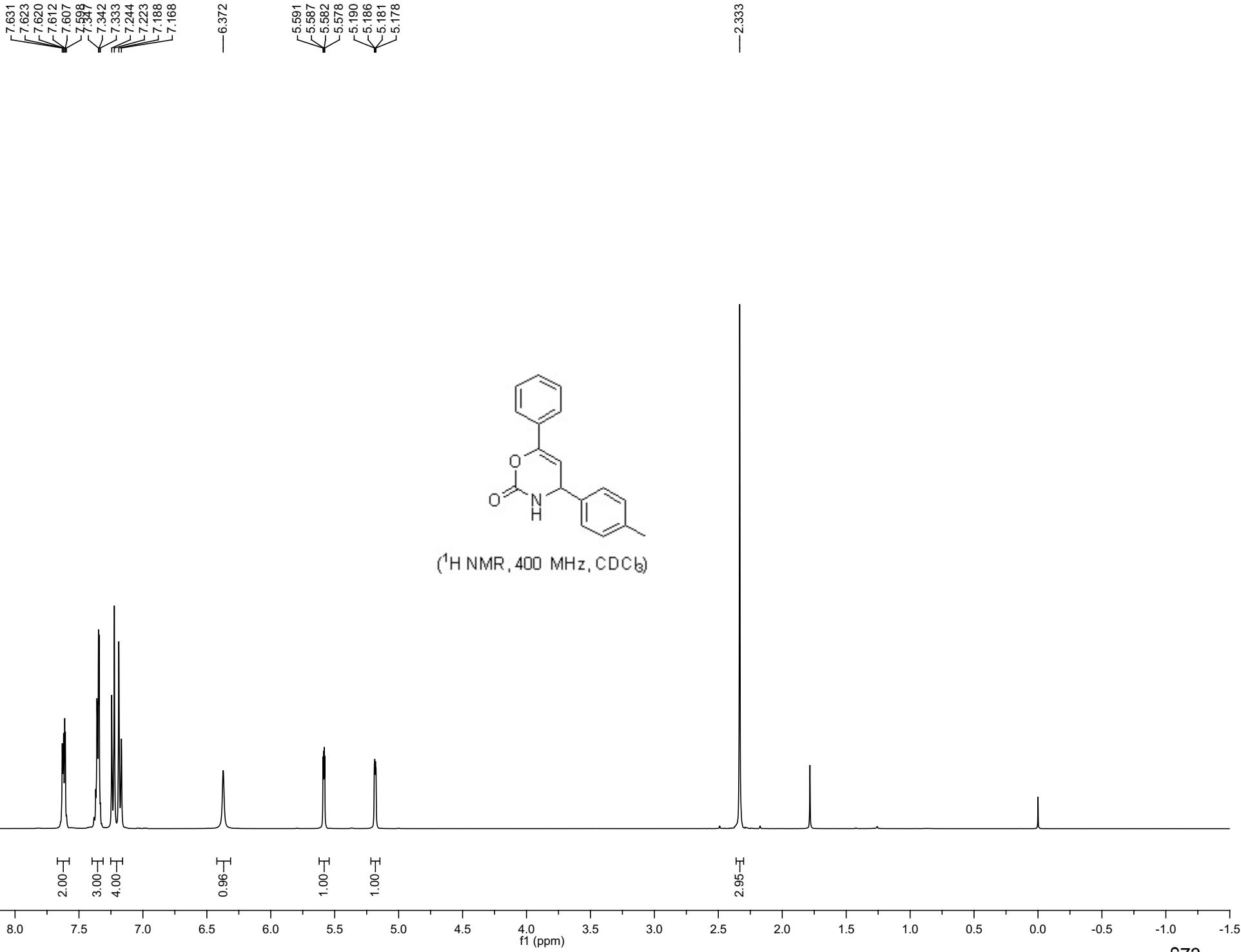
NMR spectra of compound 3aq



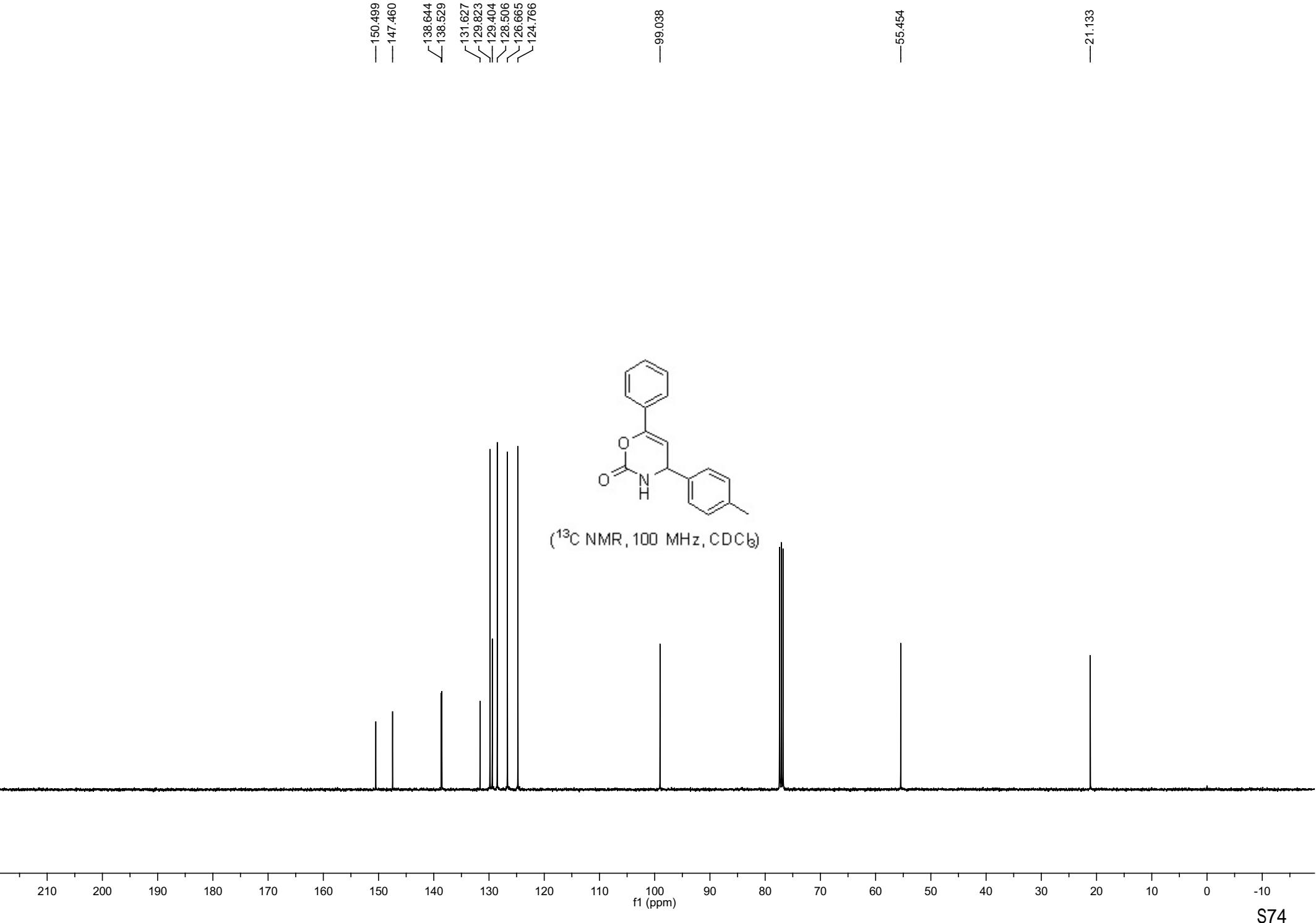
NMR spectra of compound 3aq



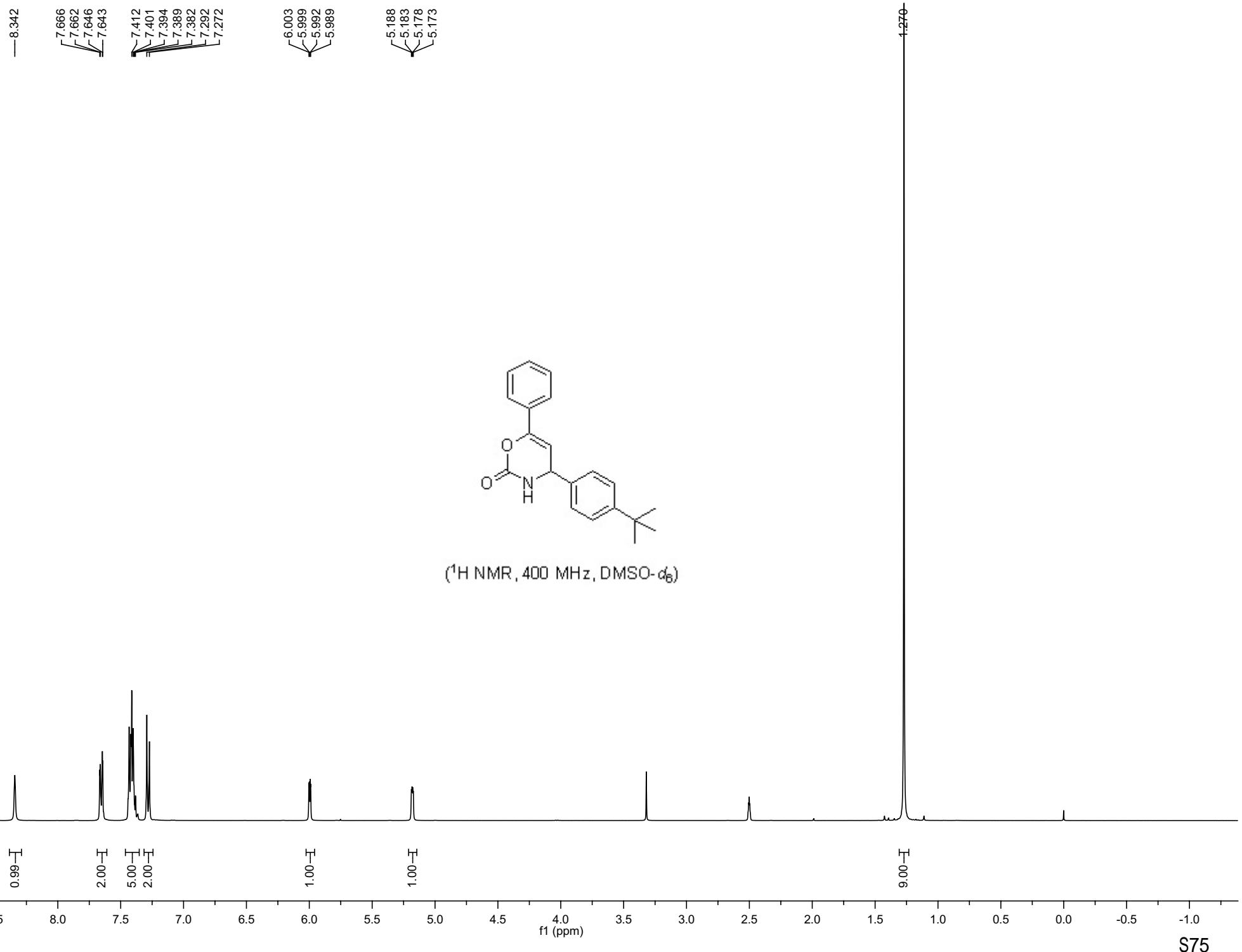
NMR spectra of compound 3ba



NMR spectra of compound 3ba

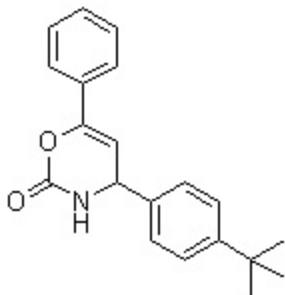


NMR spectra of compound 3ca

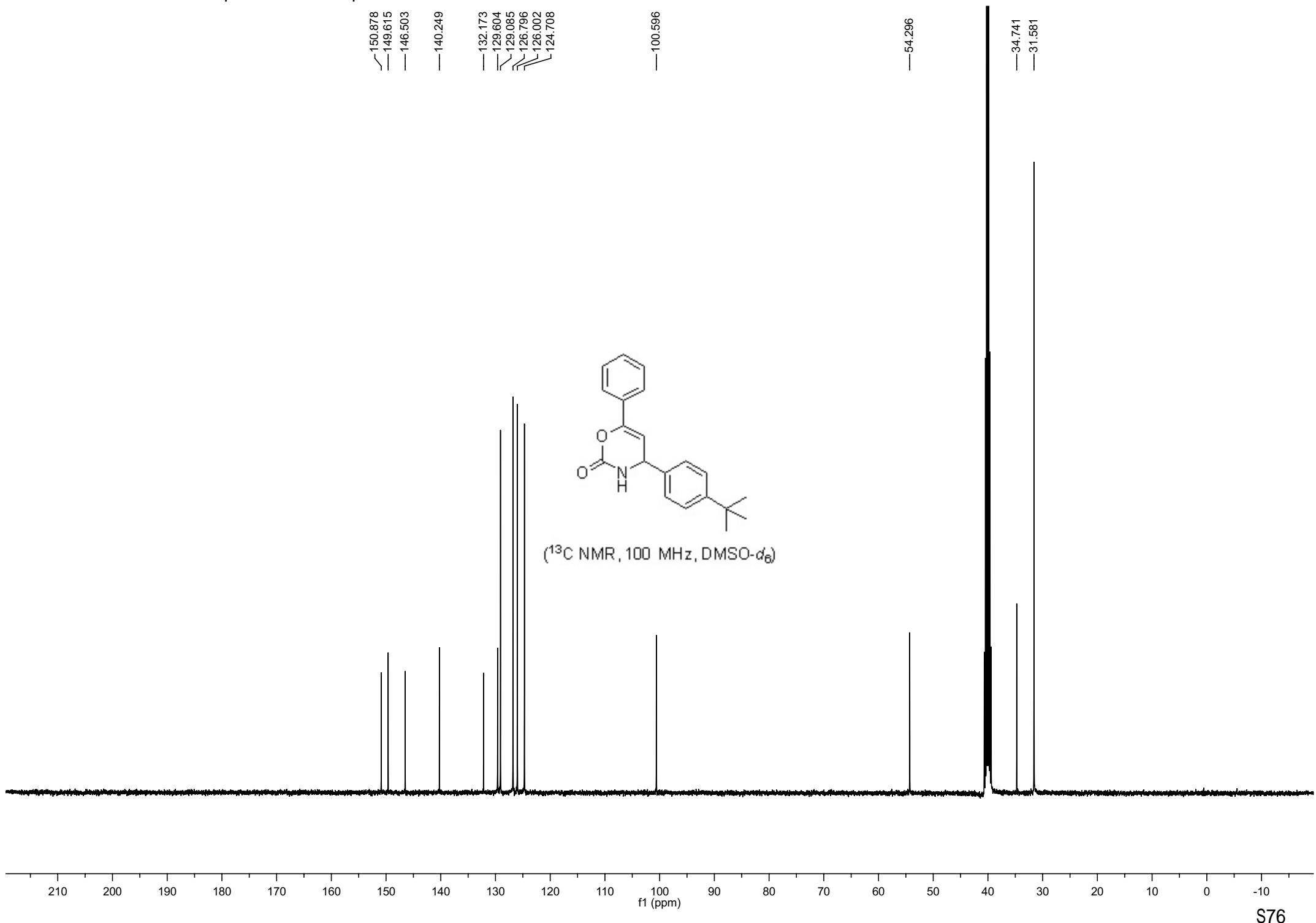


NMR spectra of compound 3ca

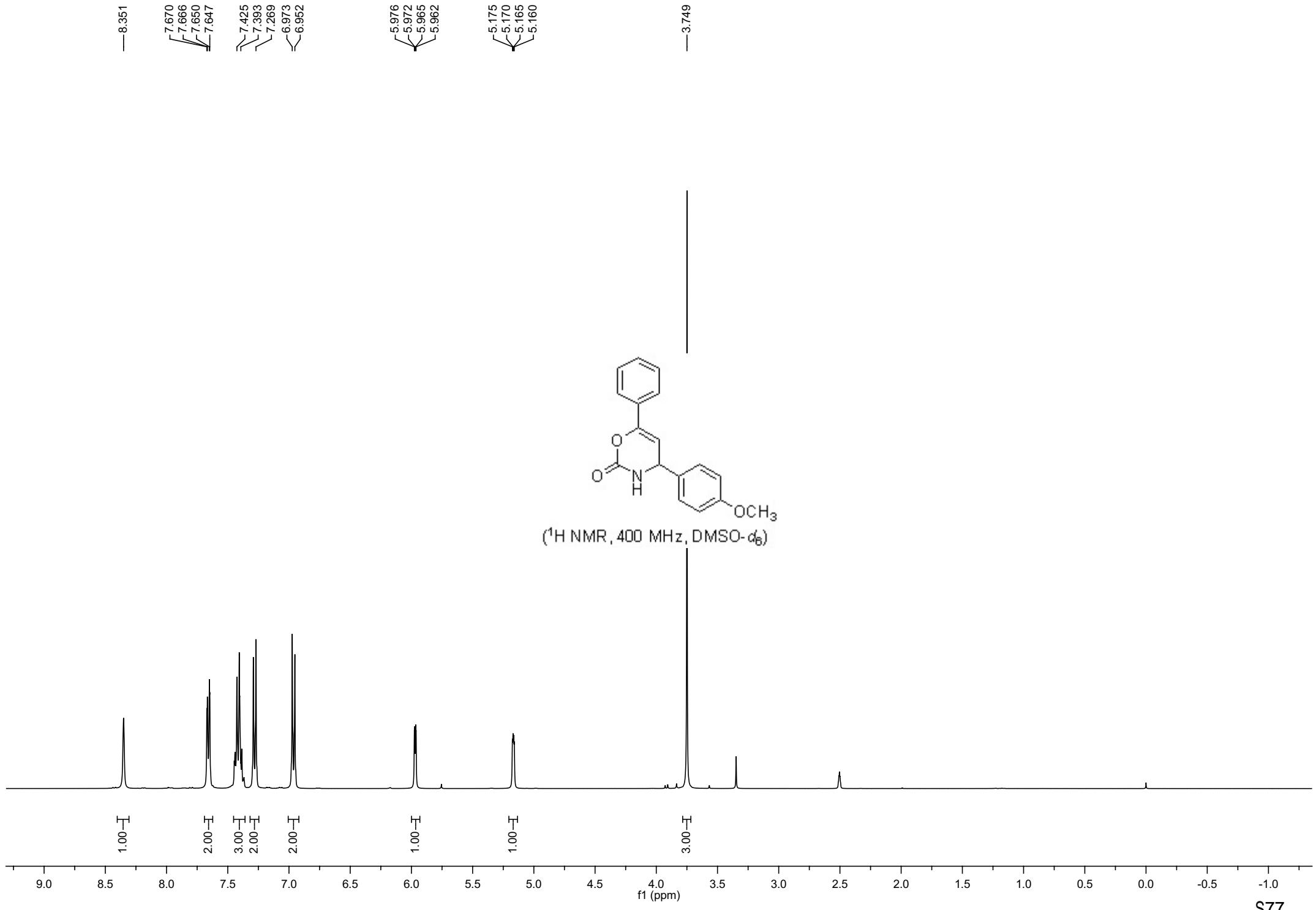
—150.878  
—149.615  
—146.503  
—140.249  
—132.173  
—129.604  
—129.085  
—126.796  
—126.002  
—124.708  
—100.596  
—54.296  
—34.741  
—31.581



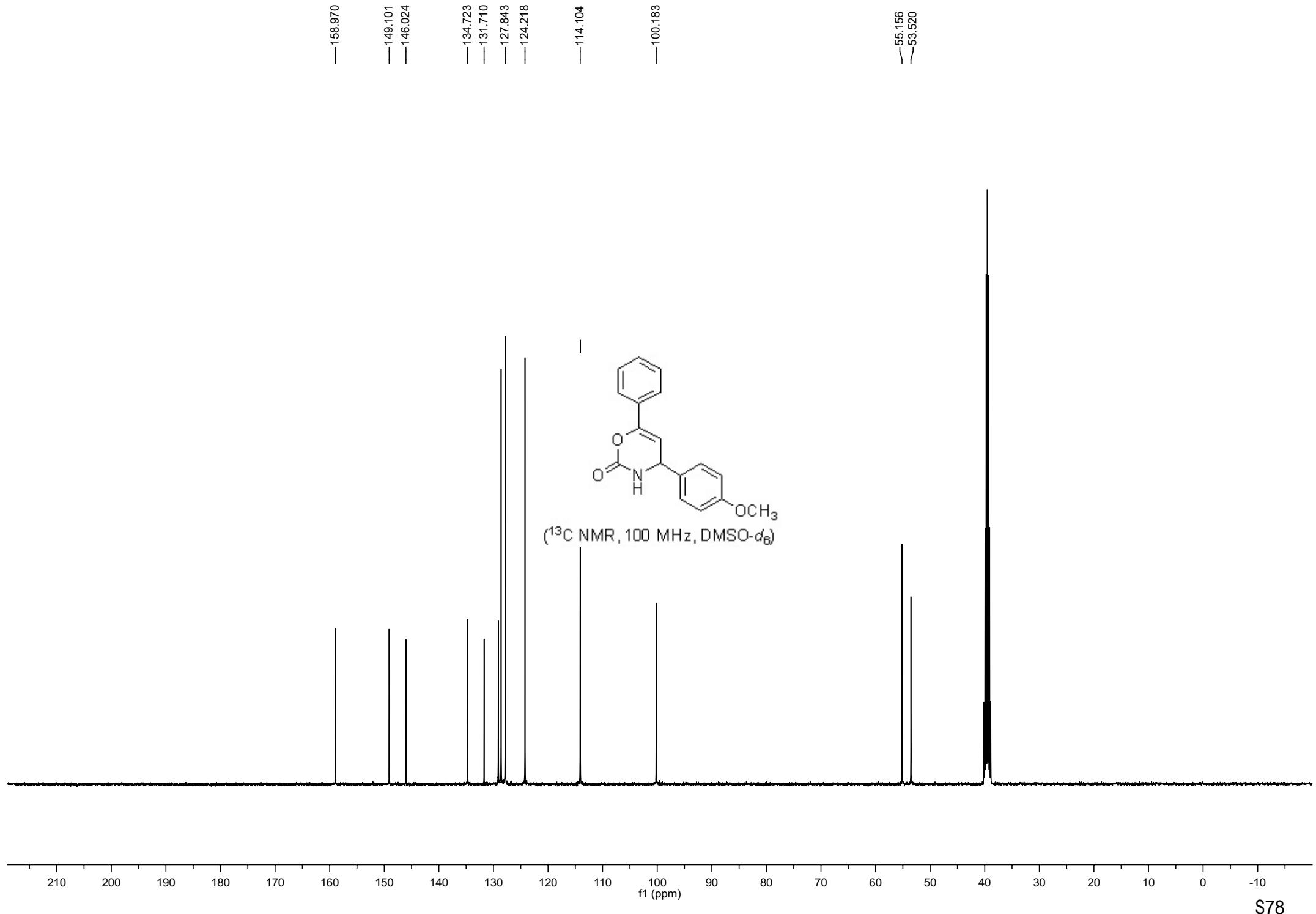
( $^{13}\text{C}$  NMR, 100 MHz,  $\text{DMSO}-d_6$ )



NMR spectra of compound 3da

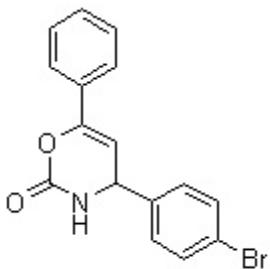


NMR spectra of compound 3da

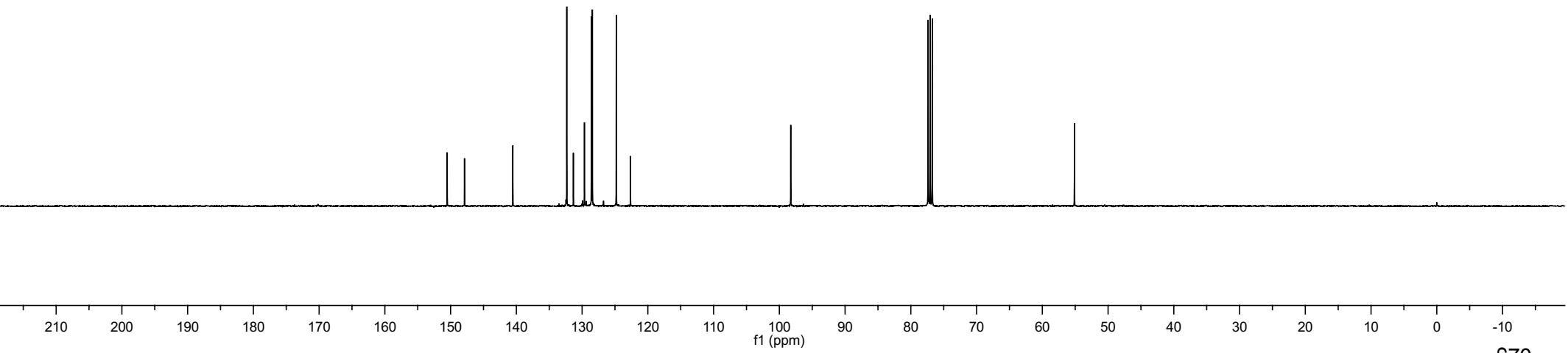


NMR spectra of compound 3ea

—150.518  
—147.889  
—140.538  
—132.331  
—129.647  
—128.580  
—128.437  
—124.798  
—122.648  
—98.265  
—55.110

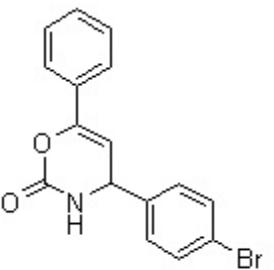


( $^{13}\text{C}$  NMR, 100 MHz,  $\text{CDCl}_3$ )

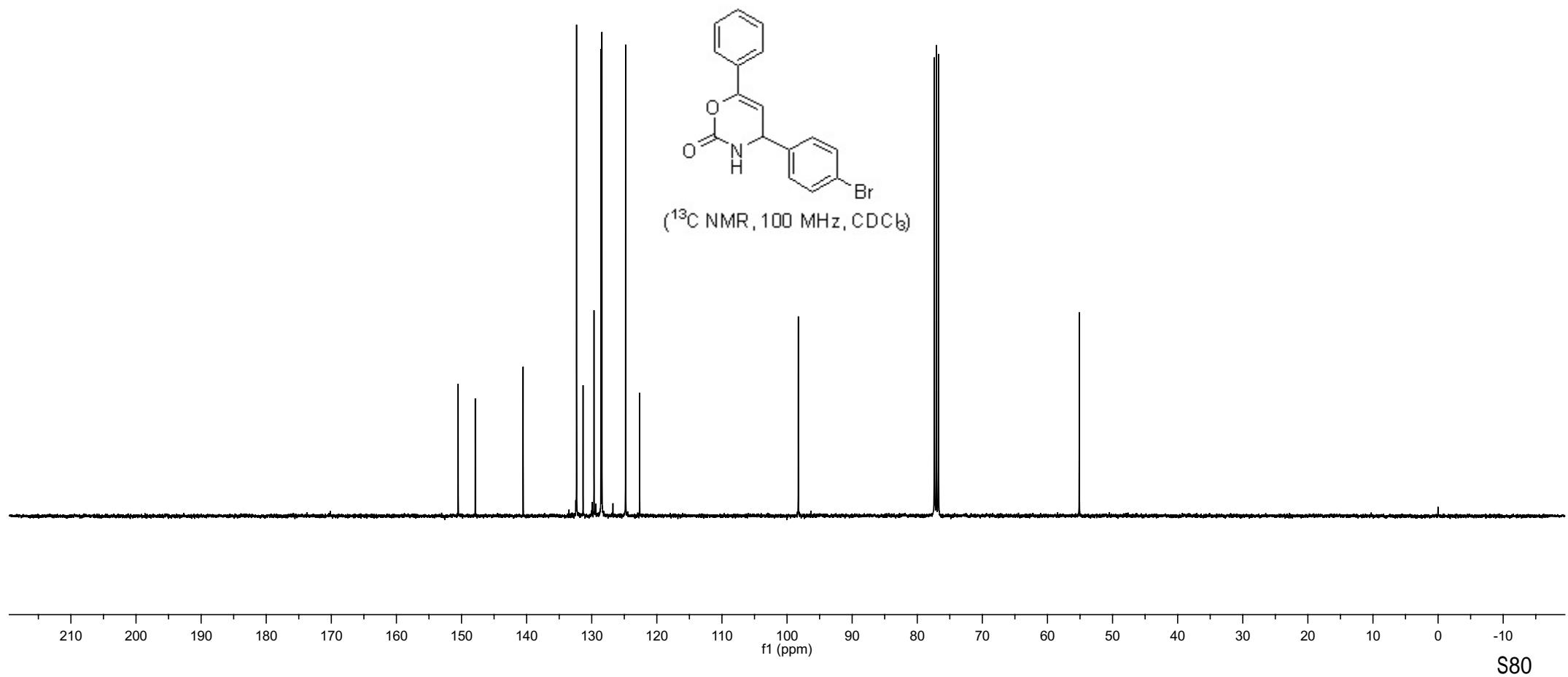


NMR spectra of compound 3ea

—150.518  
—147.889  
—140.538  
—132.331  
—129.647  
—128.580  
—128.437  
—124.798  
—122.648  
—98.265  
—55.110



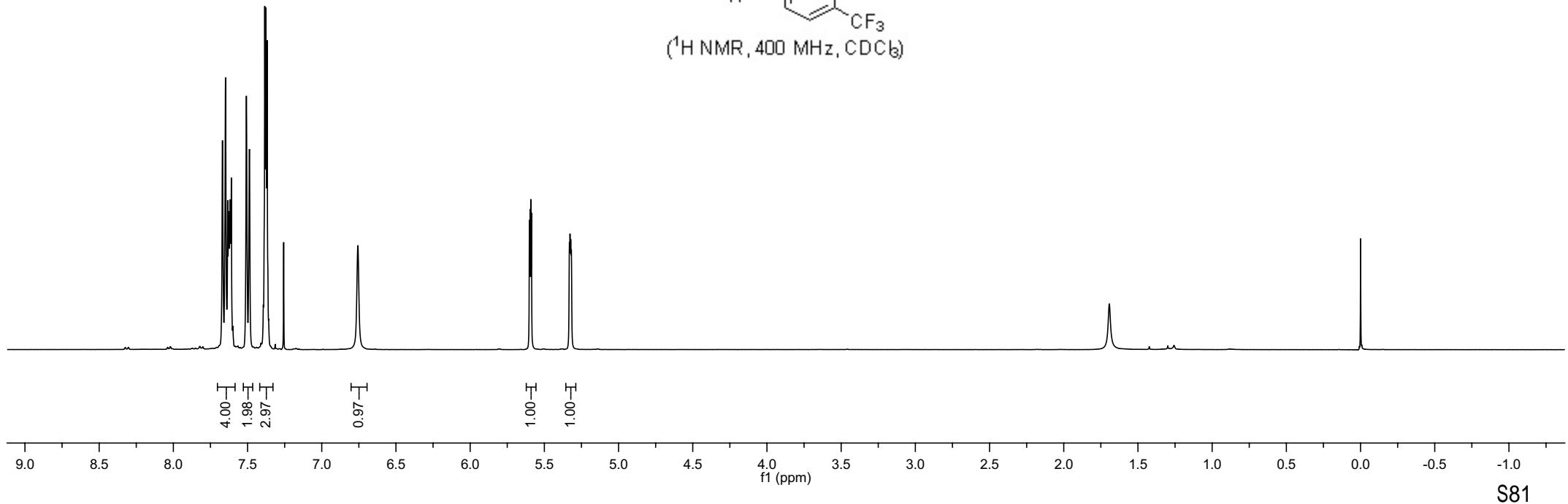
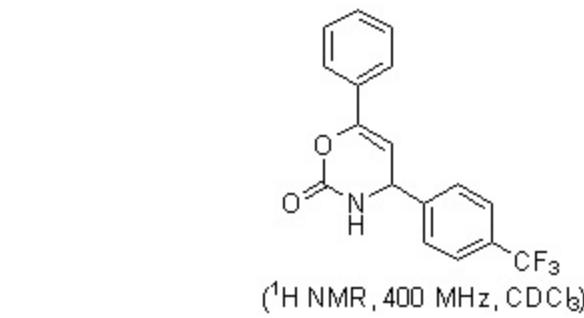
(<sup>13</sup>C NMR, 100 MHz, CDCl<sub>3</sub>)



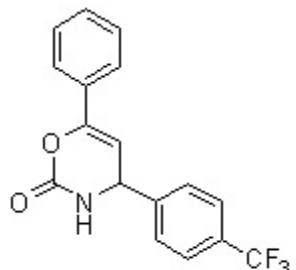
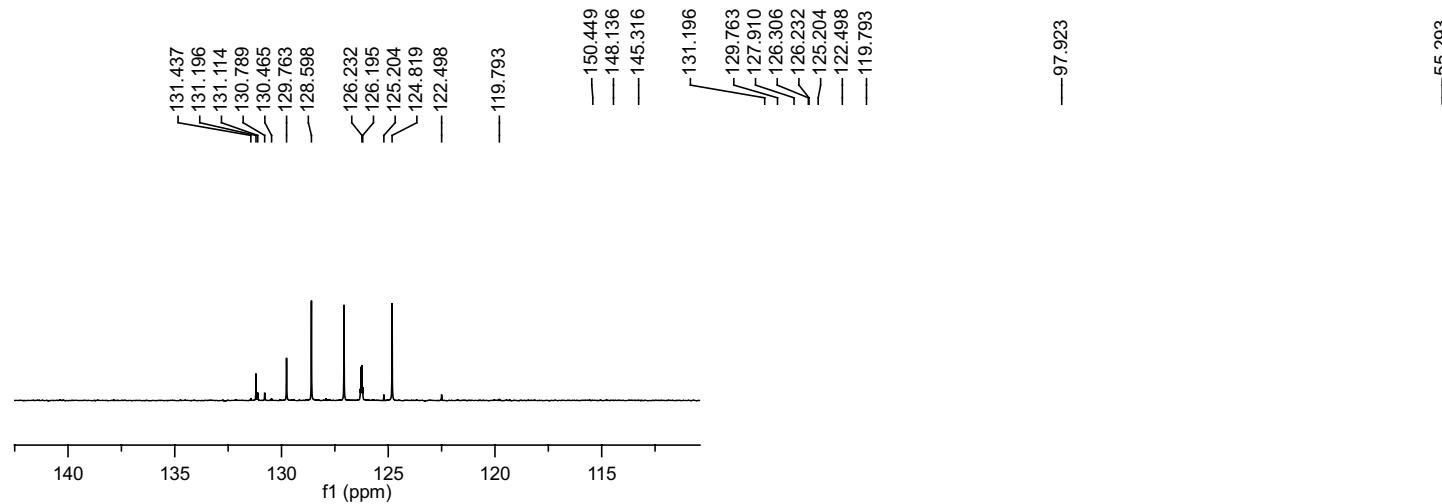
NMR spectra of compound 3fa

7.669  
7.649  
7.634  
7.626  
7.624  
7.620  
7.617  
7.613  
7.609  
7.508  
7.487  
7.394  
7.384  
7.376  
7.368  
7.257

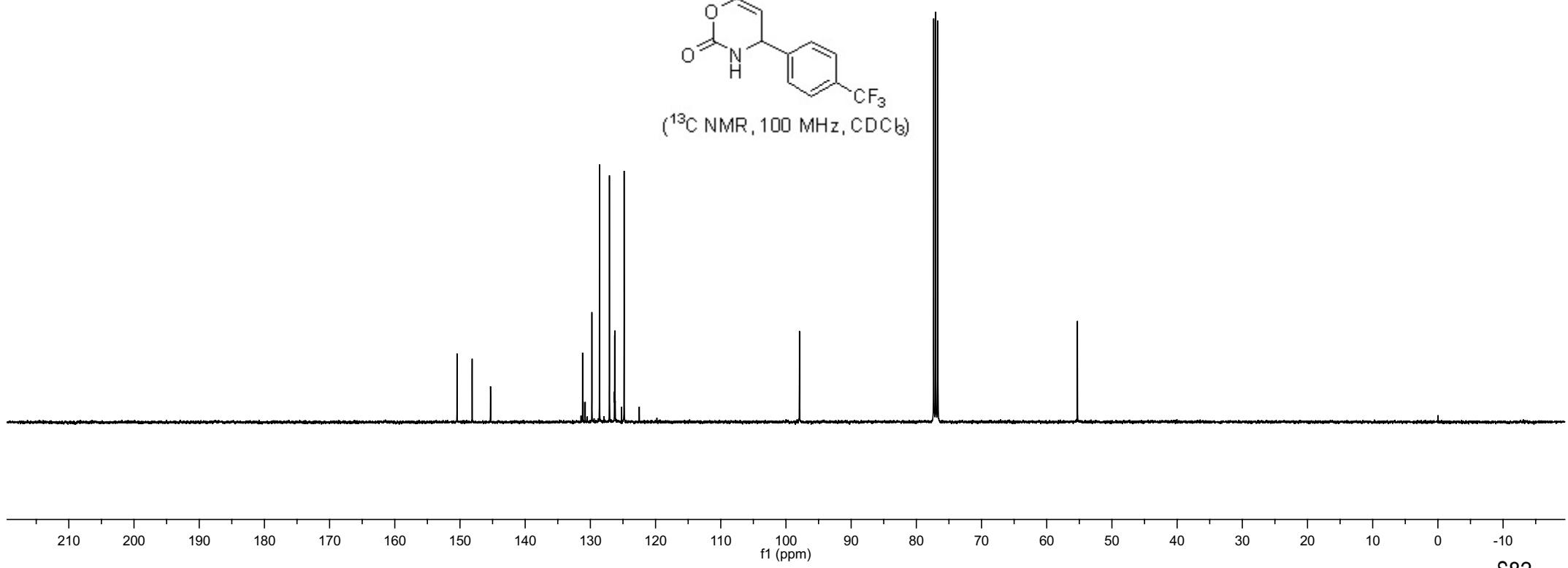
5.601  
5.596  
5.591  
5.587  
5.331  
5.327  
5.322  
5.318



NMR spectra of compound 3fa

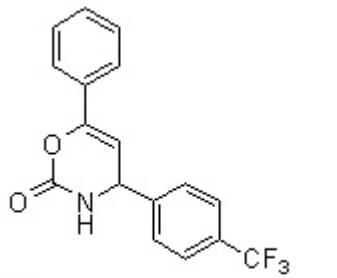


(<sup>13</sup>C NMR, 100 MHz, CDCl<sub>3</sub>)

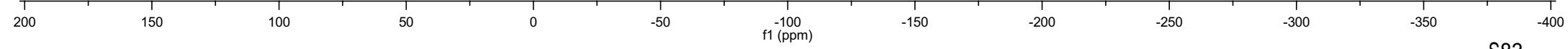


NMR spectra of compound 3fa

--62.650



( $^{19}\text{F}$  NMR, 376 MHz,  $\text{CDCl}_3$ )



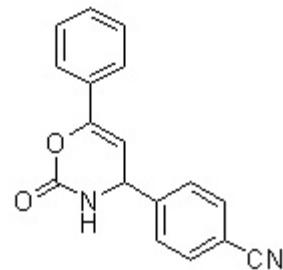
NMR spectra of compound 3ga

— 8.538

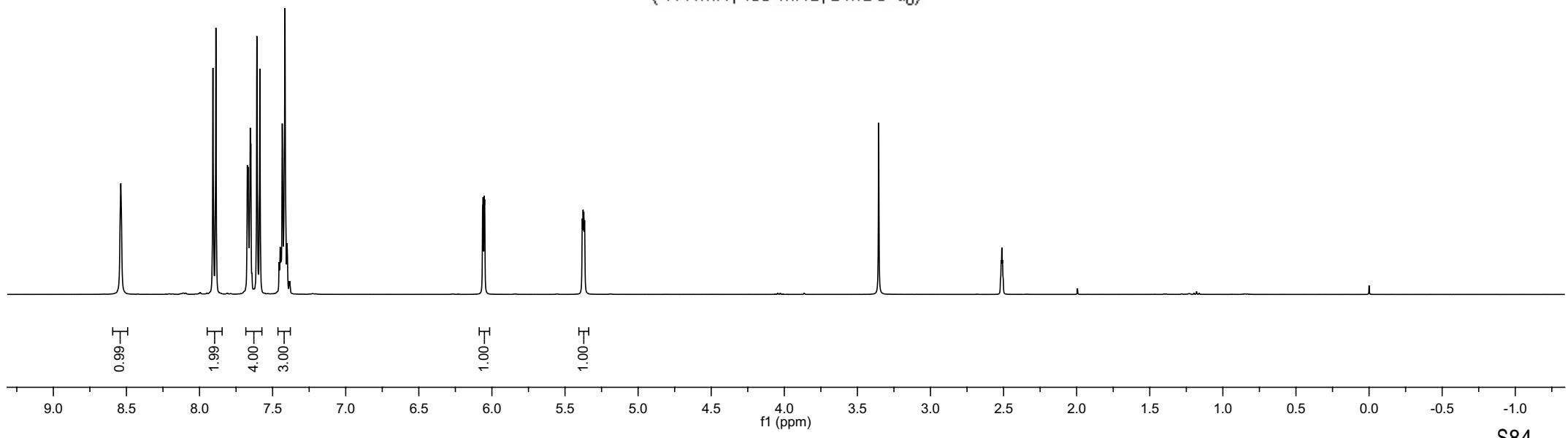
7.908  
7.888  
7.587  
7.456  
7.448  
7.443  
7.434  
7.416  
7.402

6.063  
6.060  
6.053  
6.050

5.381  
5.376  
5.371  
5.366

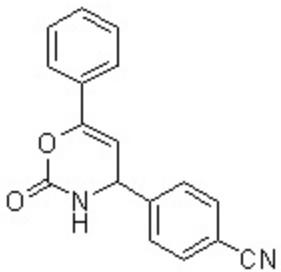


( $^1\text{H}$  NMR, 400 MHz, DMSO- $d_6$ )

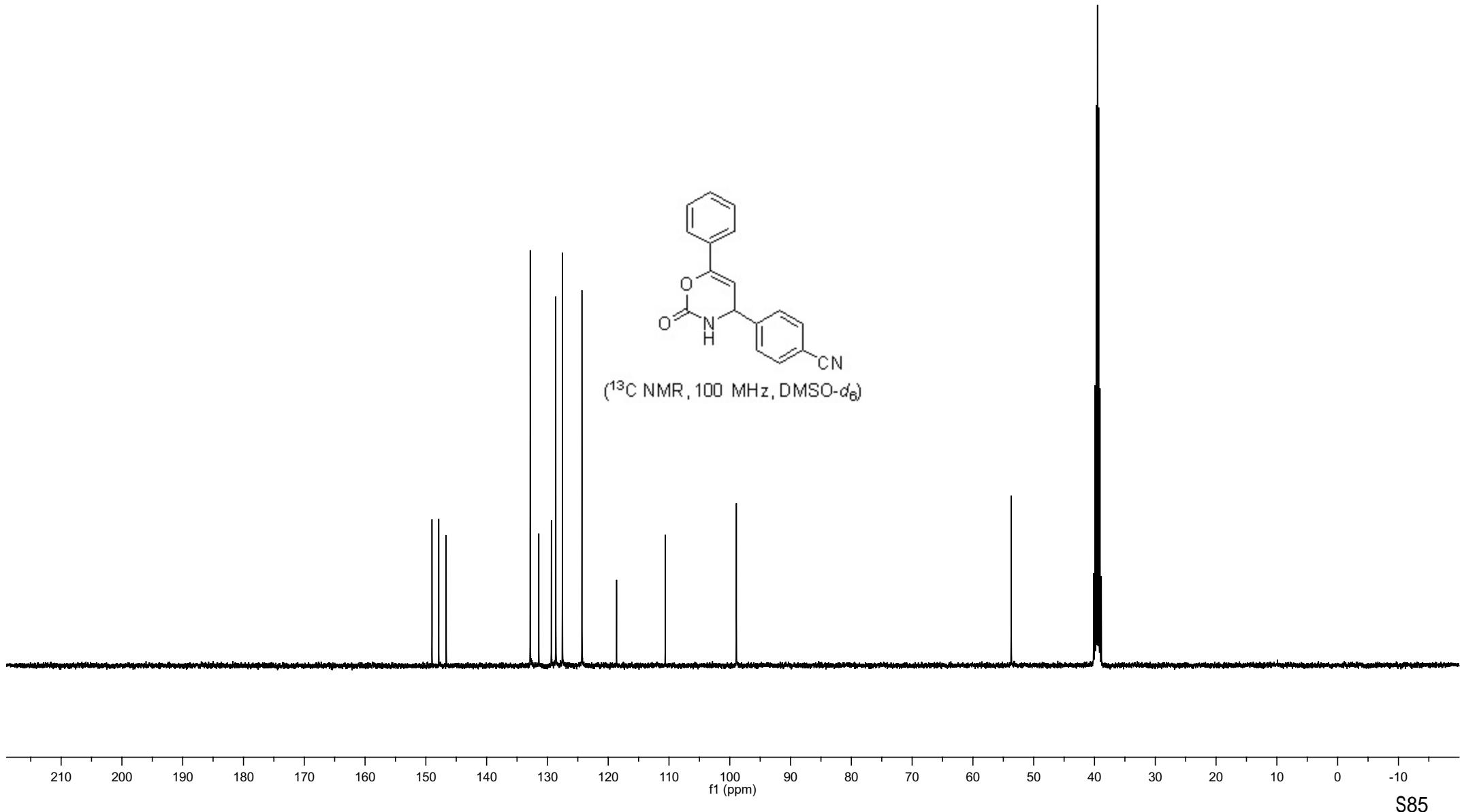


NMR spectra of compound 3ga

— 148.987  
— 147.876  
— 146.652  
— 132.827  
— 131.411  
— 129.345  
— 128.624  
— 127.535  
— 124.319  
— 118.621  
— 110.613  
— 98.919  
— 53.703



( $^{13}\text{C}$  NMR, 100 MHz,  $\text{DMSO}-d_6$ )



NMR spectra of compound 3ha

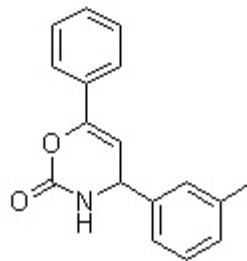
-8.392

7.677  
7.661  
7.658  
7.651  
7.436  
7.417  
7.405  
7.397  
7.379  
7.303  
7.182  
7.141

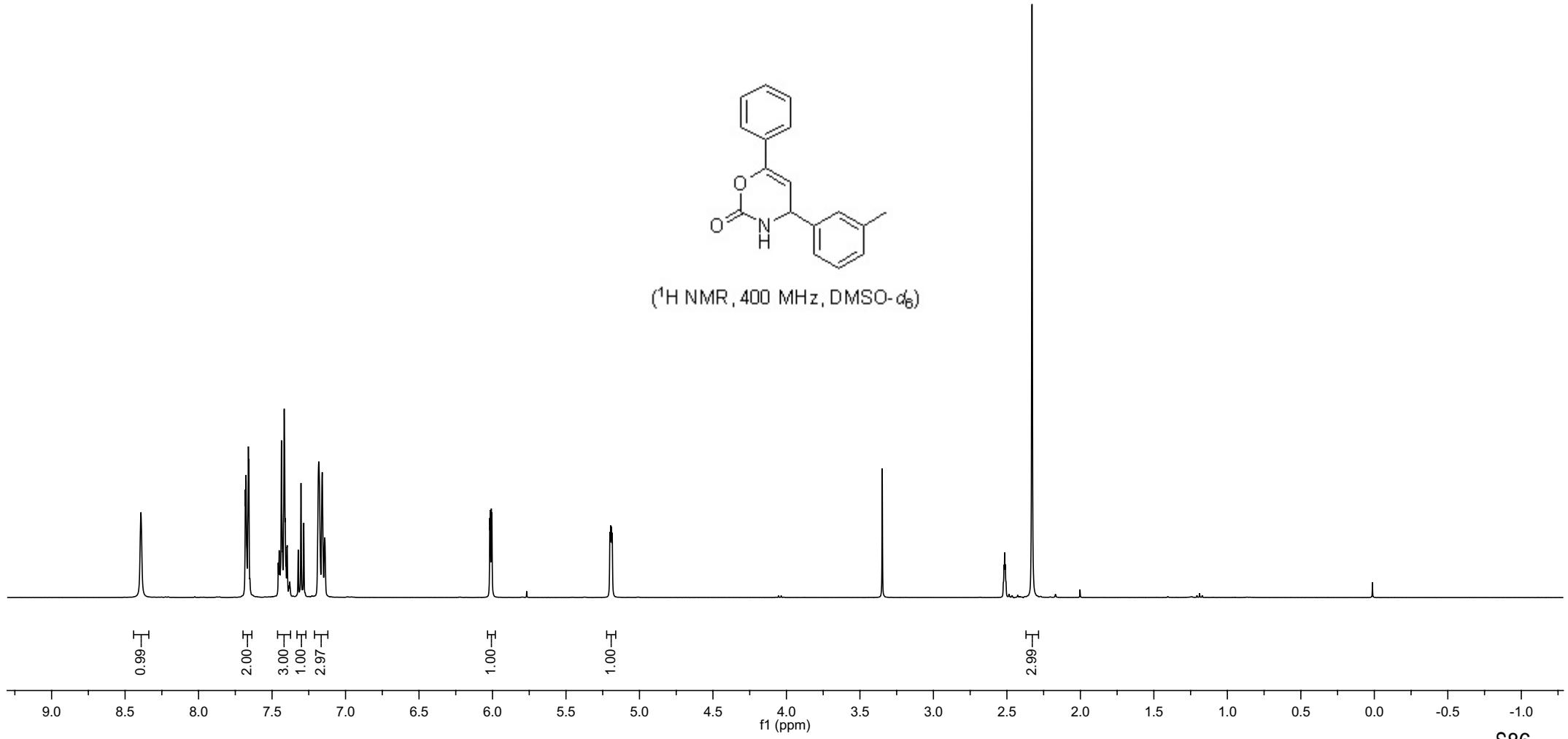
6.018  
6.015  
6.008  
6.004

5.201  
5.196  
5.191  
5.186

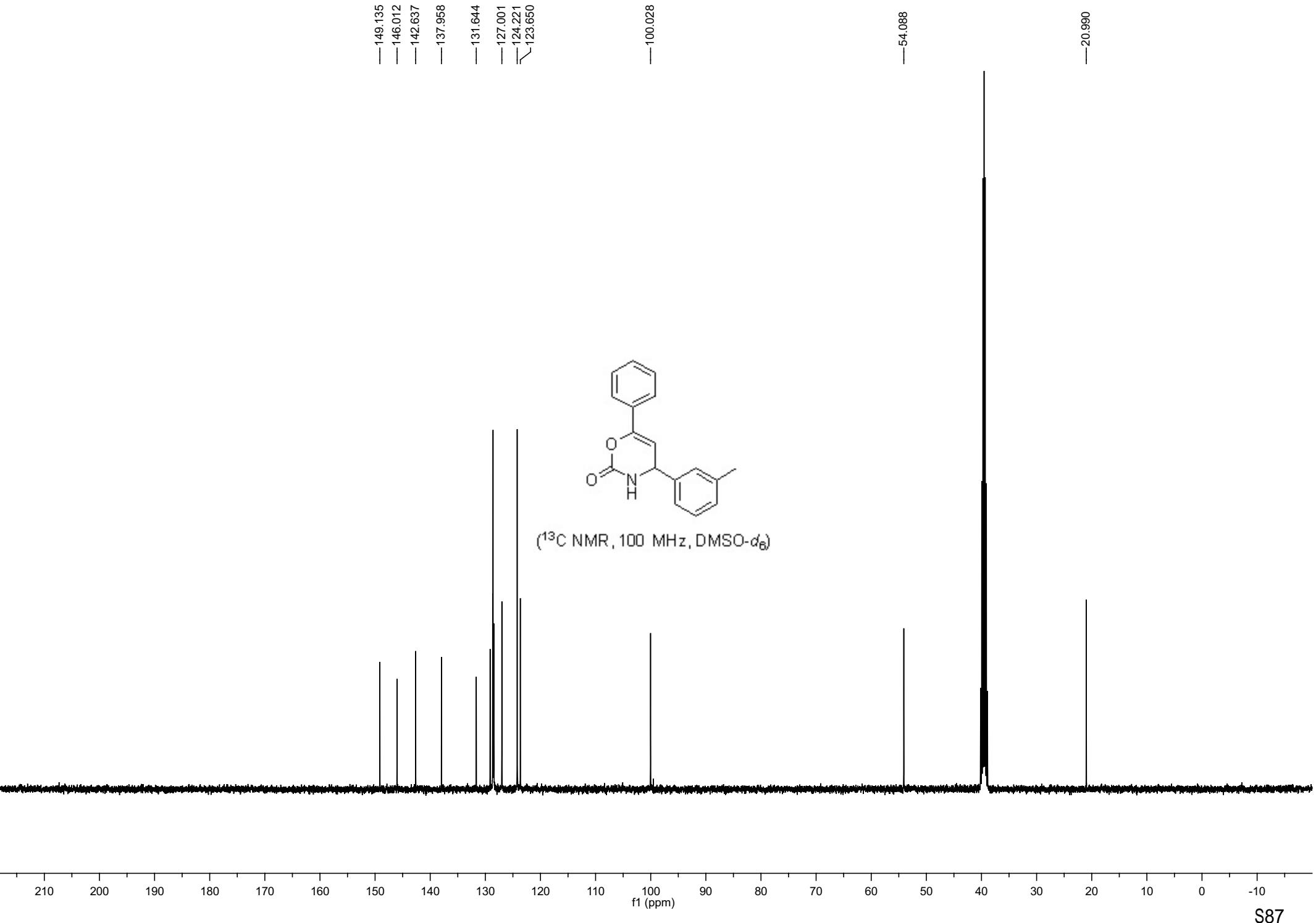
-2.329



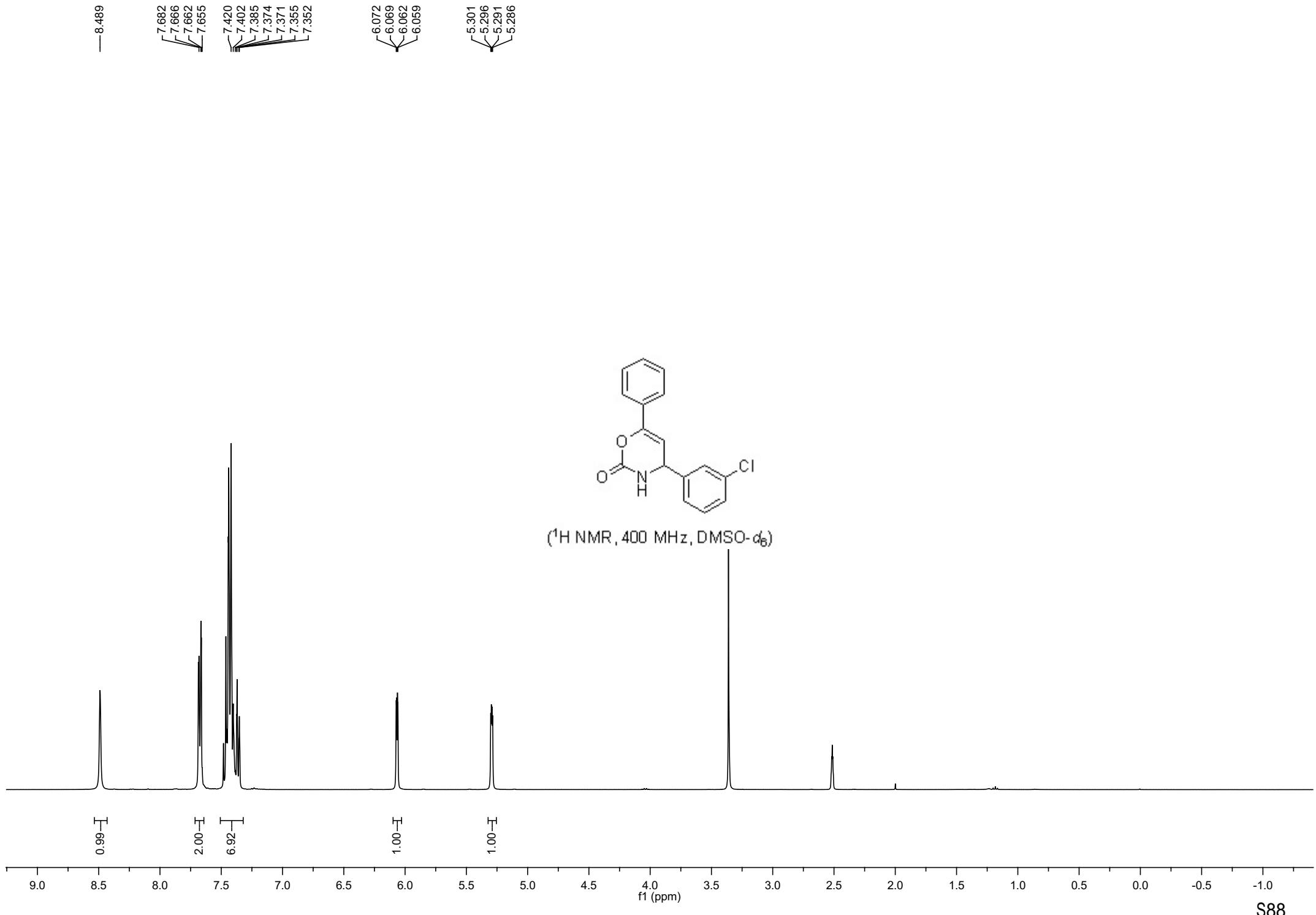
( $^1\text{H}$  NMR, 400 MHz, DMSO- $d_6$ )



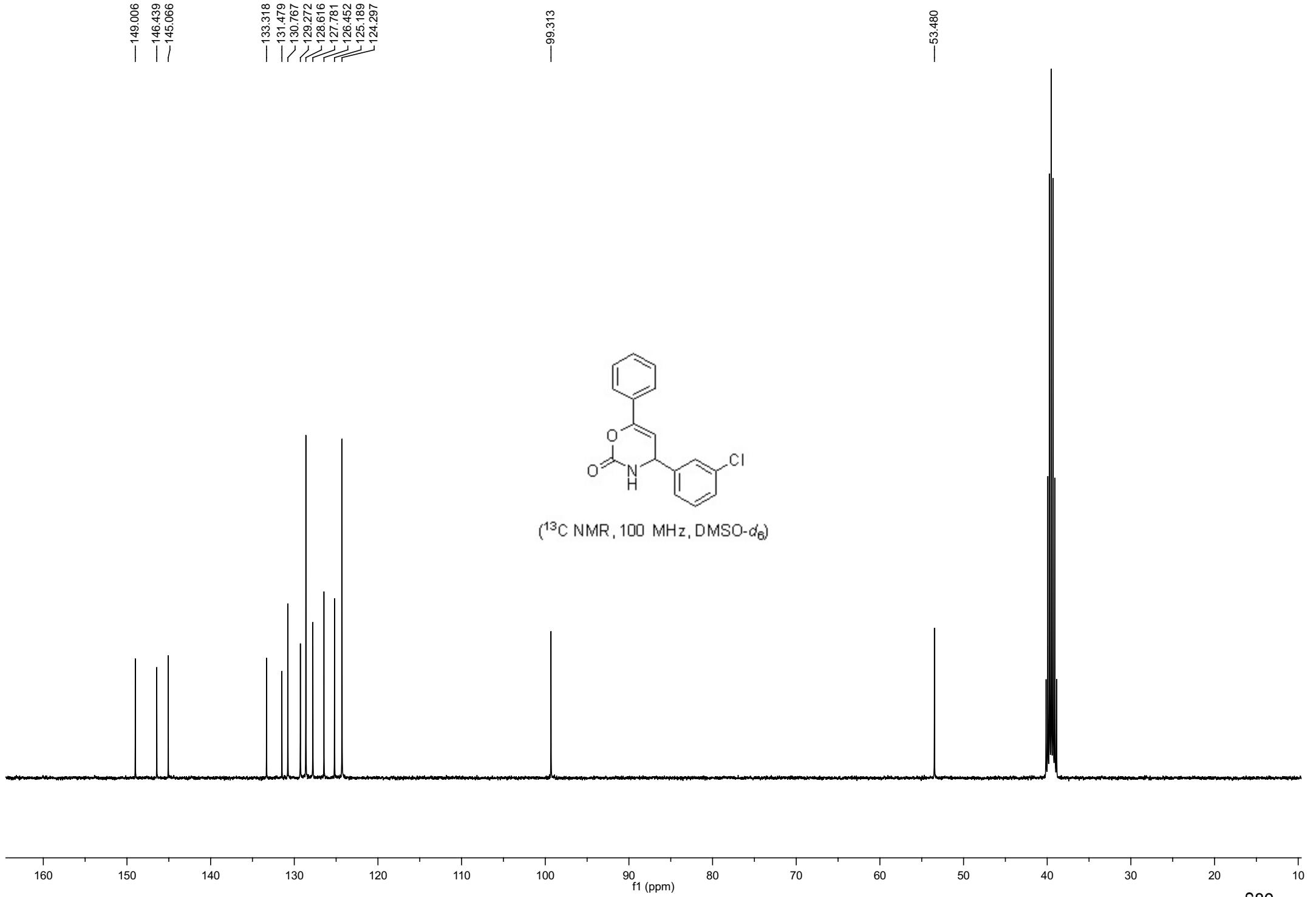
NMR spectra of compound 3ha



NMR spectra of compound 3ia



NMR spectra of compound 3ia



NMR spectra of compound 3ja

—8.474

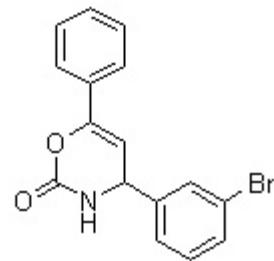
7.659  
7.537  
7.529  
7.524  
7.455  
7.447  
7.433  
7.414  
7.398  
7.397  
7.391  
7.384

6.065  
6.062  
6.055  
6.052

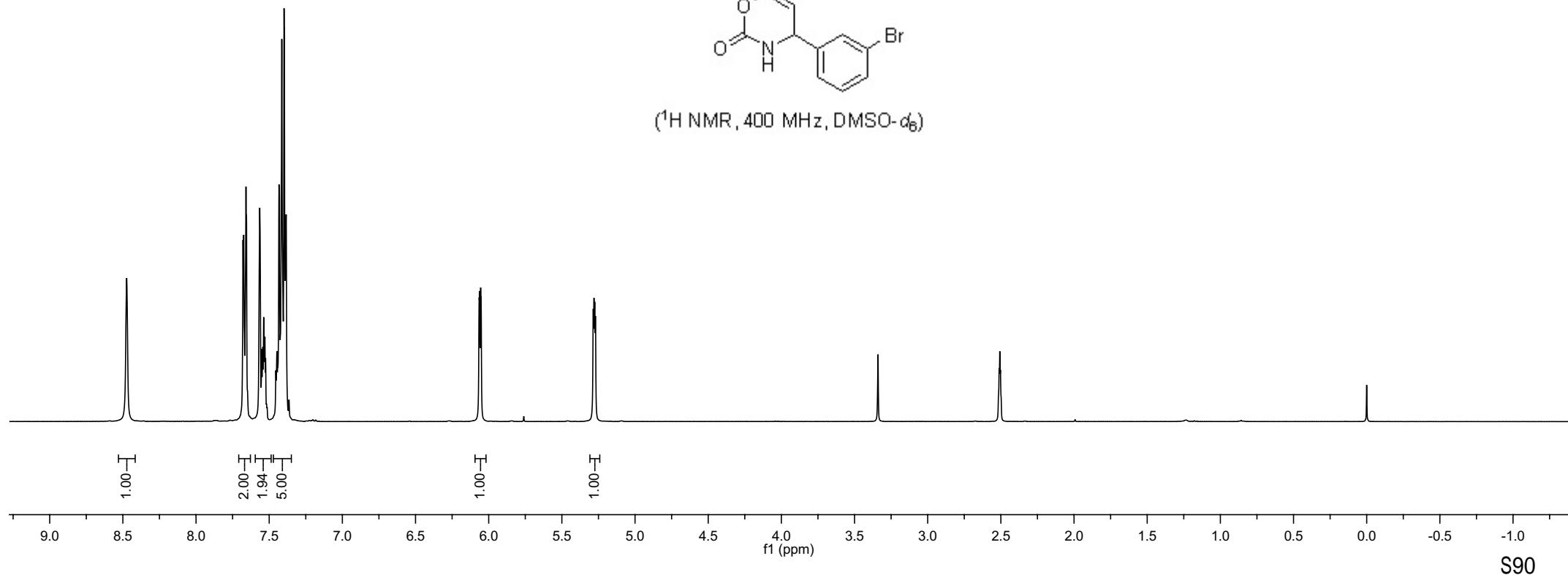
5.286  
5.280  
5.275  
5.270

—3.340

2.512  
2.507  
2.503

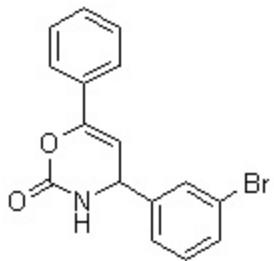


( $^1\text{H}$  NMR, 400 MHz,  $\text{DMSO}-d_6$ )

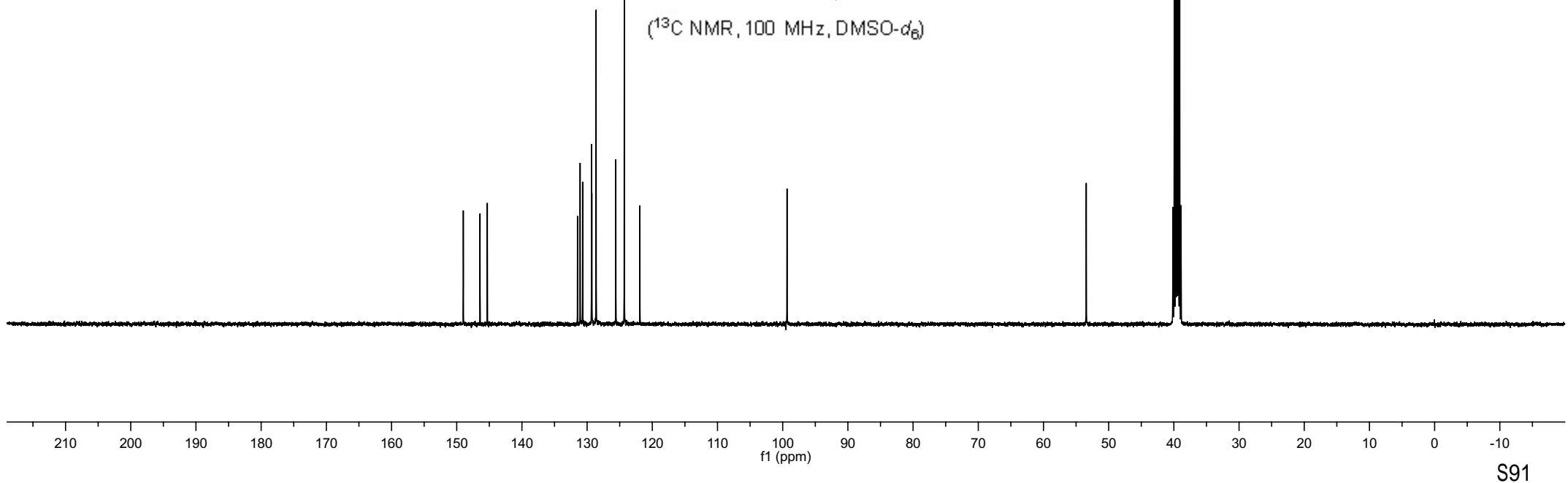


NMR spectra of compound 3ja

— 148.988  
— 146.425  
— 145.305  
— 131.069  
— 130.691  
— 129.326  
— 129.275  
— 128.620  
— 125.597  
— 124.298  
— 121.904  
— 99.334  
— 53.439



( $^{13}\text{C}$  NMR, 100 MHz,  $\text{DMSO}-d_6$ )



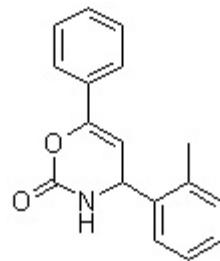
NMR spectra of compound 3ka

-8.286

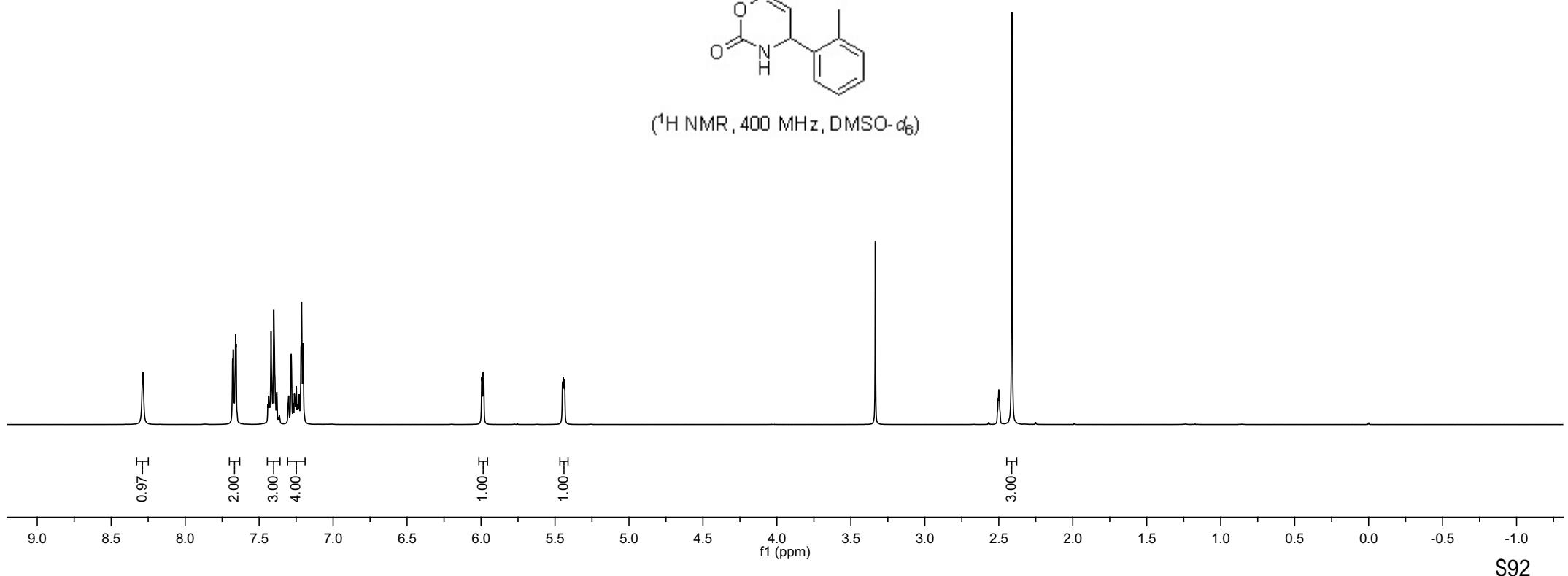
7.675  
7.659  
**7.466**  
7.380  
7.366  
7.300  
7.270  
7.249  
7.236  
7.217  
7.204

5.995  
5.992  
5.985  
5.982  
5.449  
5.444  
5.439  
5.435

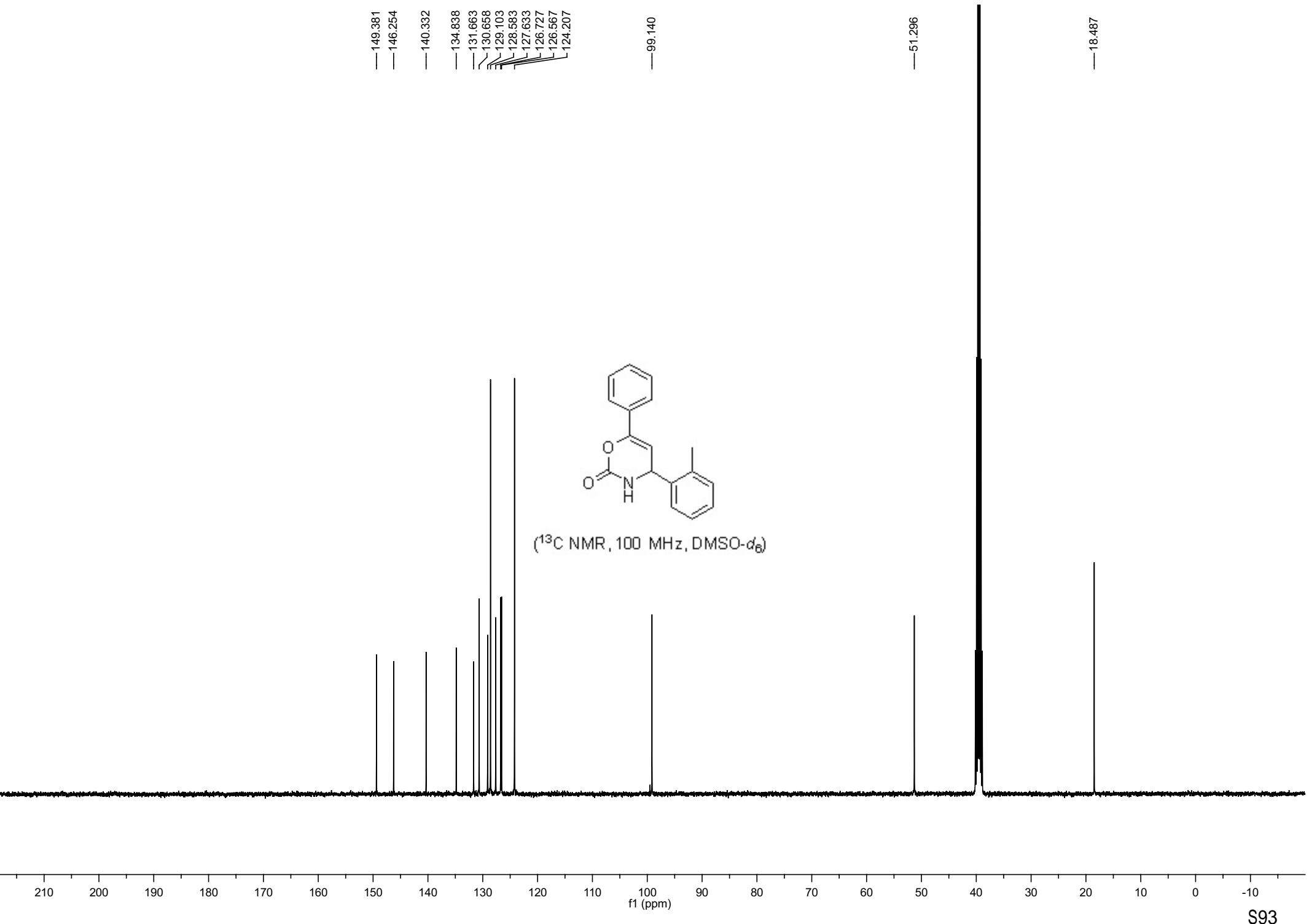
-2.411



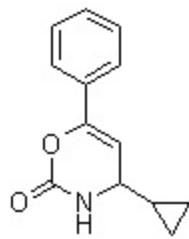
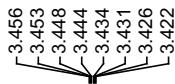
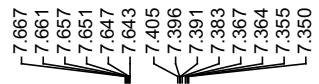
( $^1\text{H}$  NMR, 400 MHz, DMSO- $d_6$ )



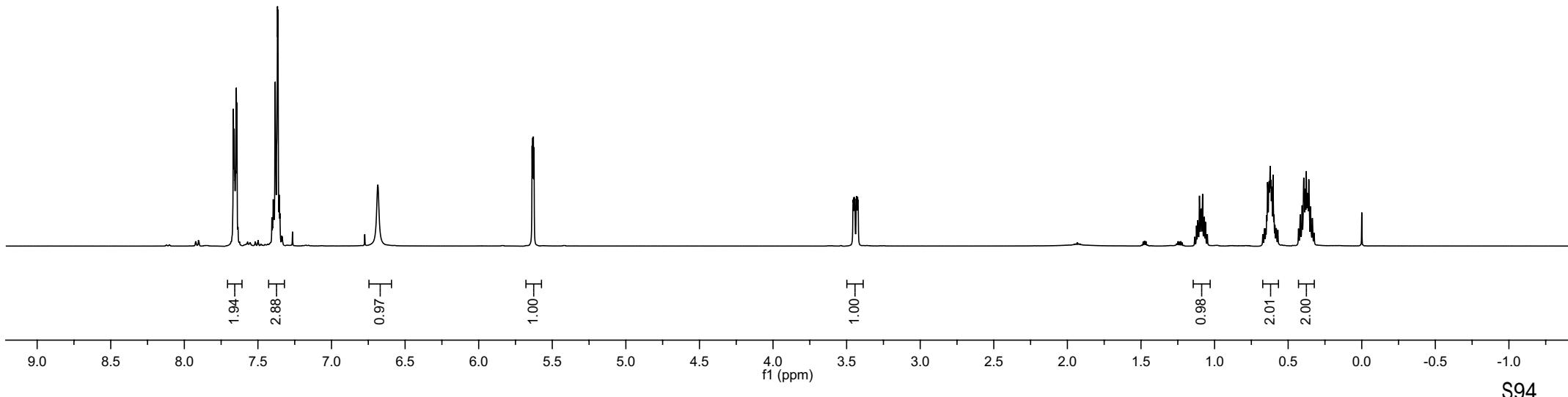
NMR spectra of compound 3ka



NMR spectra of compound 3Ia

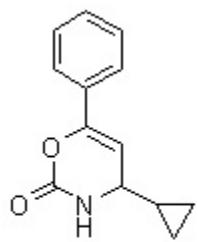


( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )

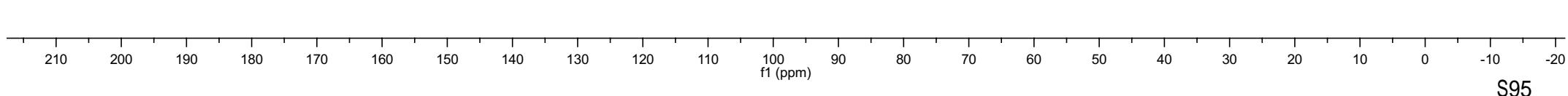


NMR spectra of compound 3la

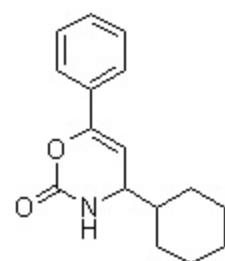
—149.186  
—145.992  
—129.845  
—126.515  
—122.783  
—96.328  
—54.469  
—16.312  
—0.984  
—0.003



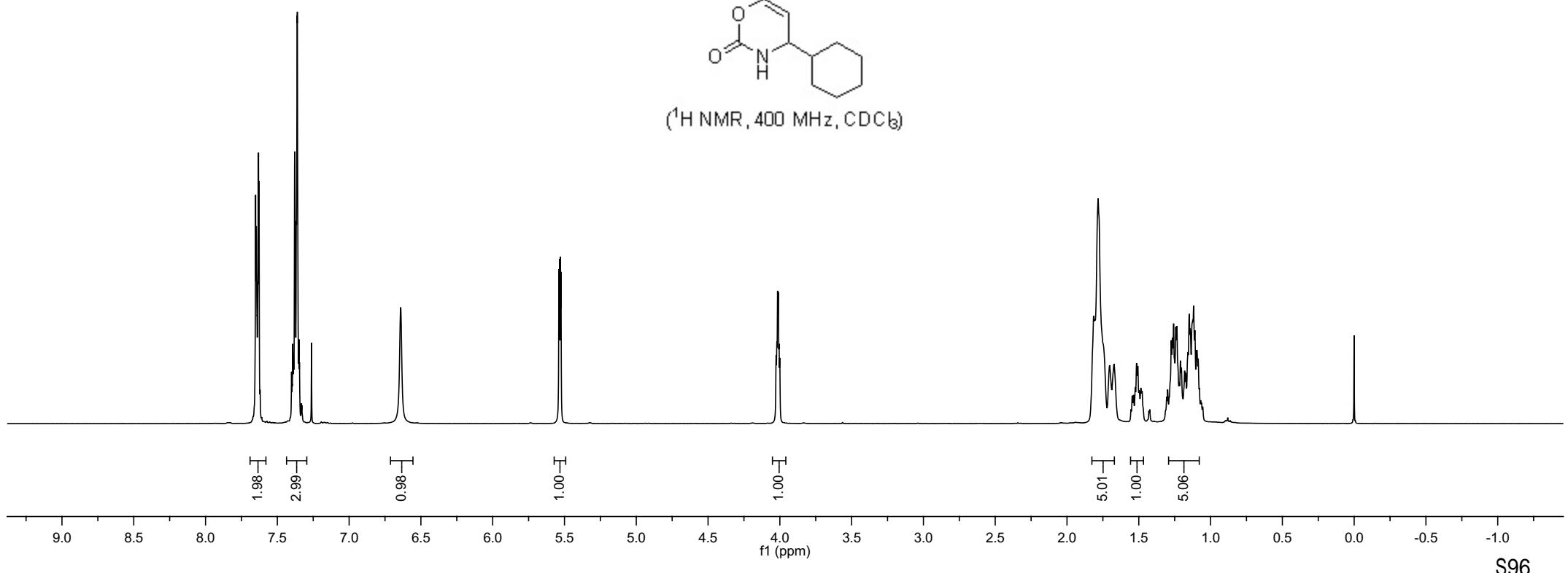
( $^{13}\text{C}$  NMR, 100 MHz,  $\text{CDCl}_3$ )



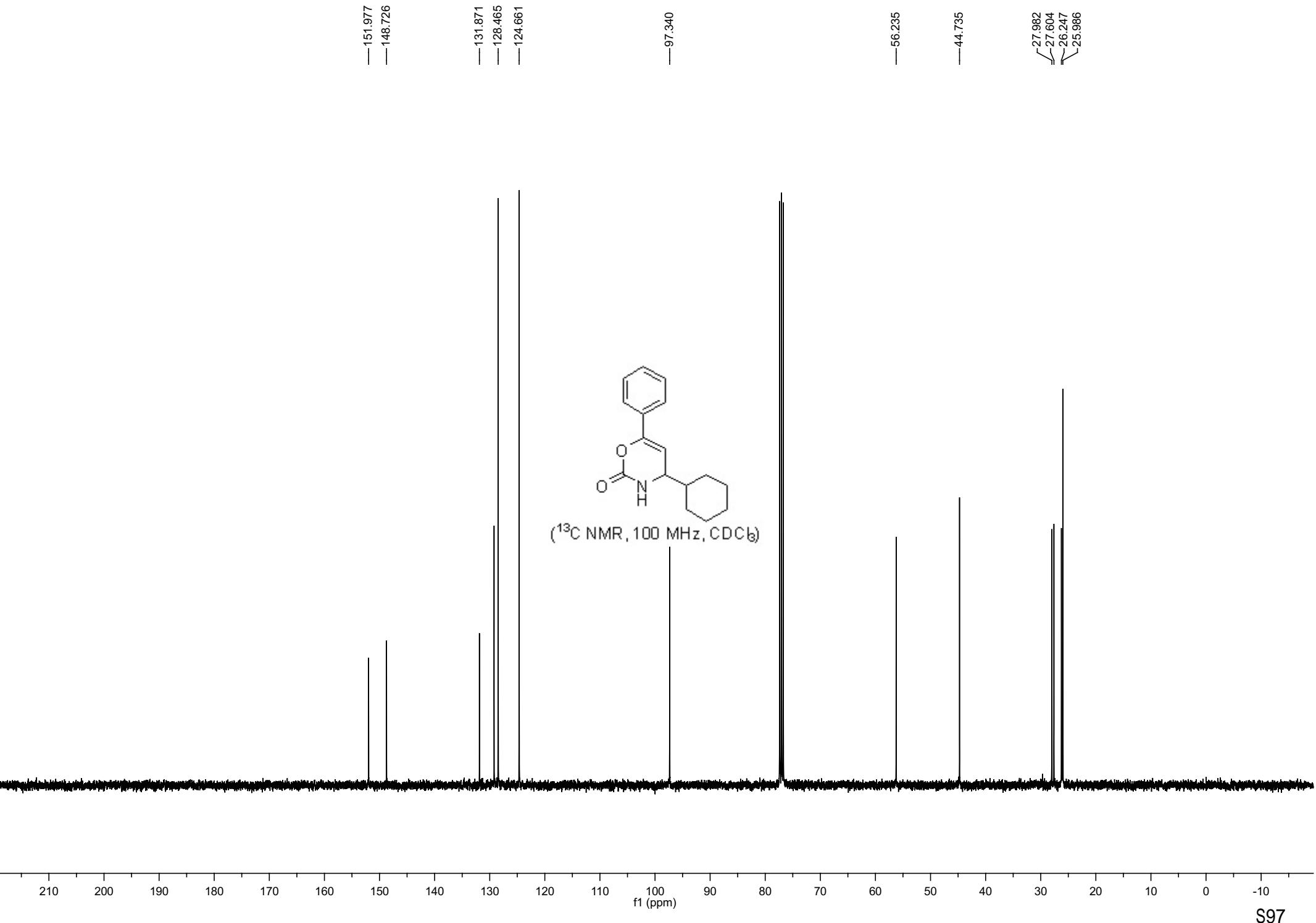
NMR spectra of compound 3ma



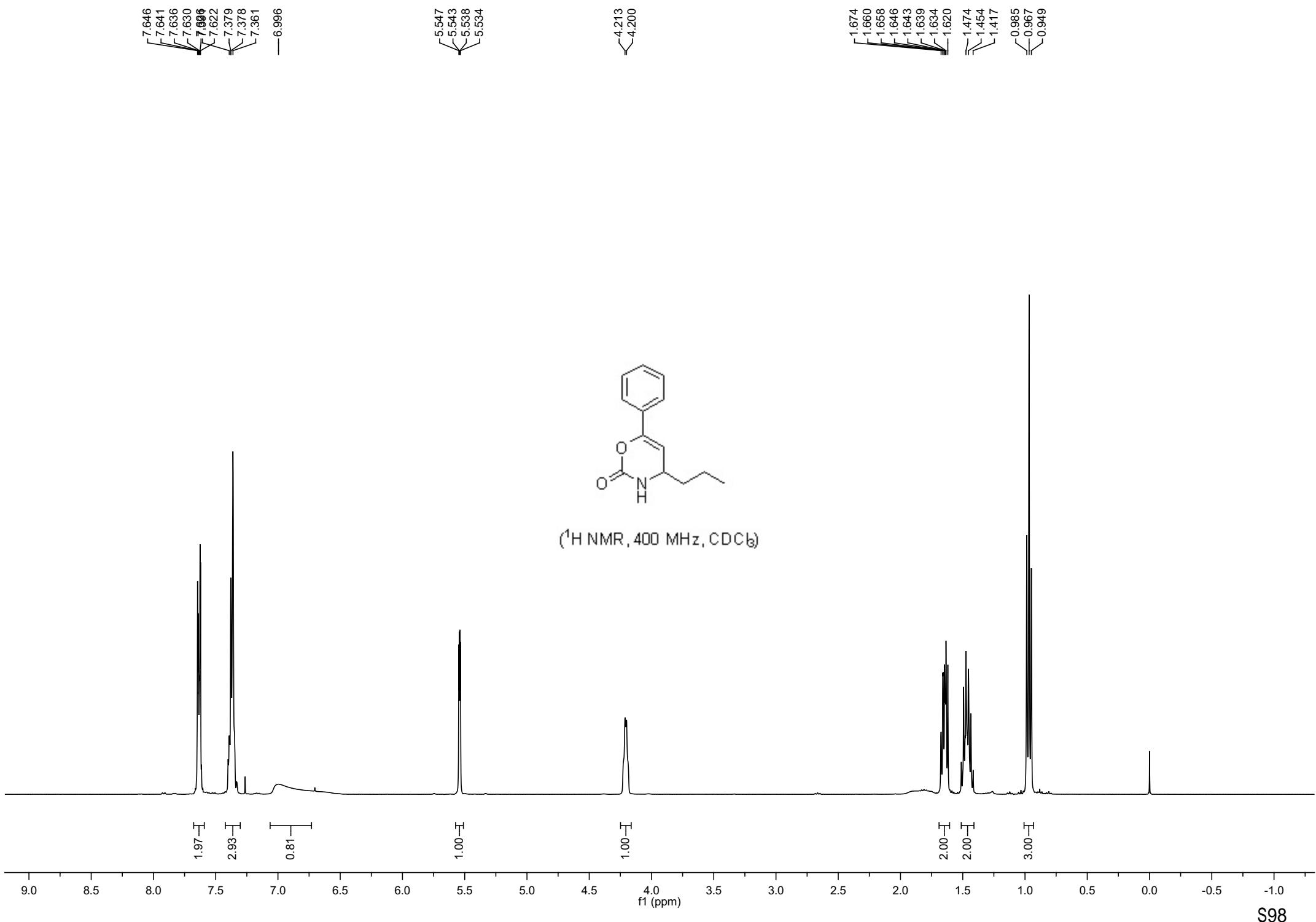
( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )



NMR spectra of compound 3ma

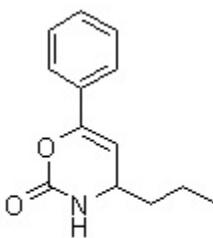


NMR spectra of compound 3na

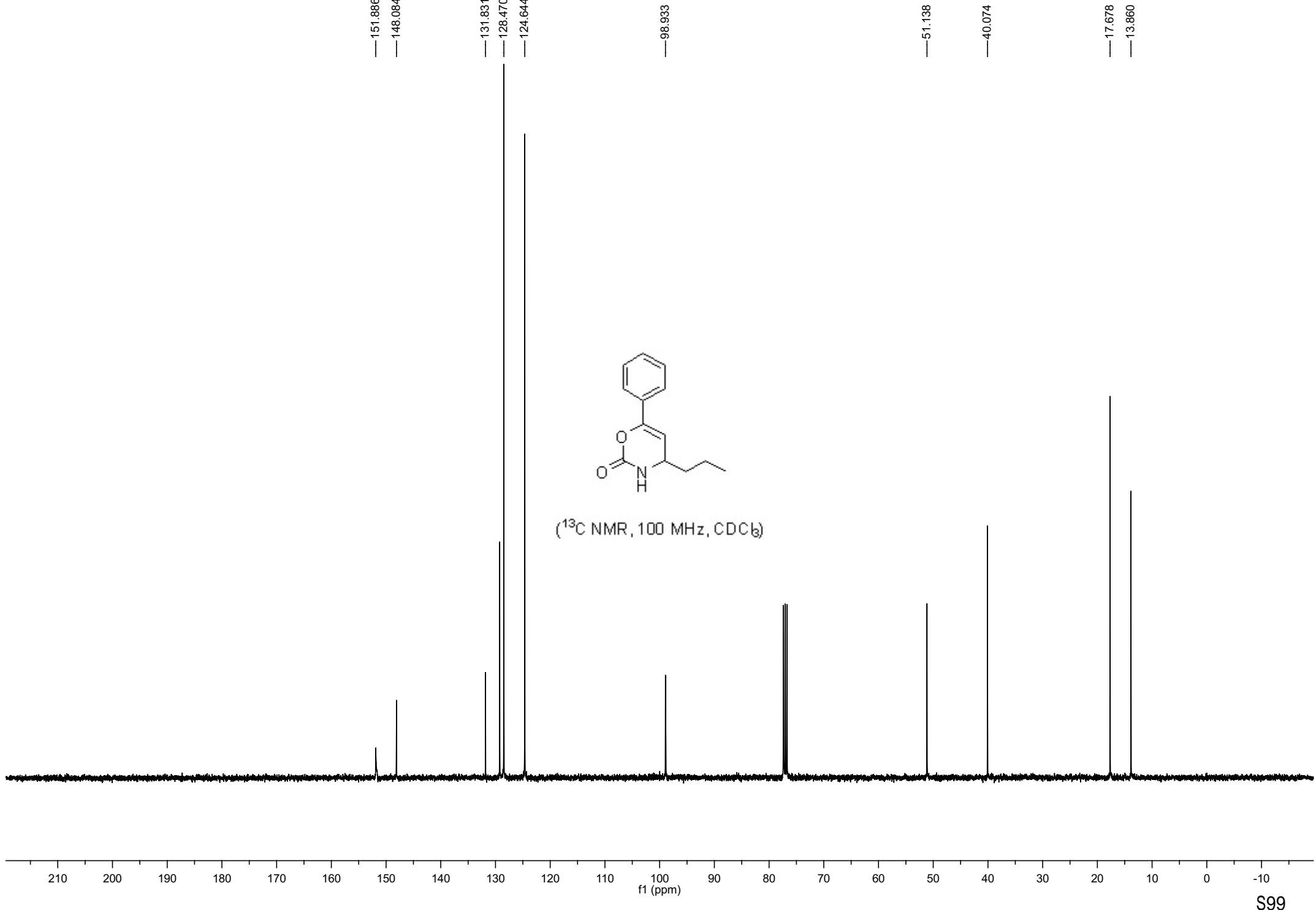


NMR spectra of compound 3na

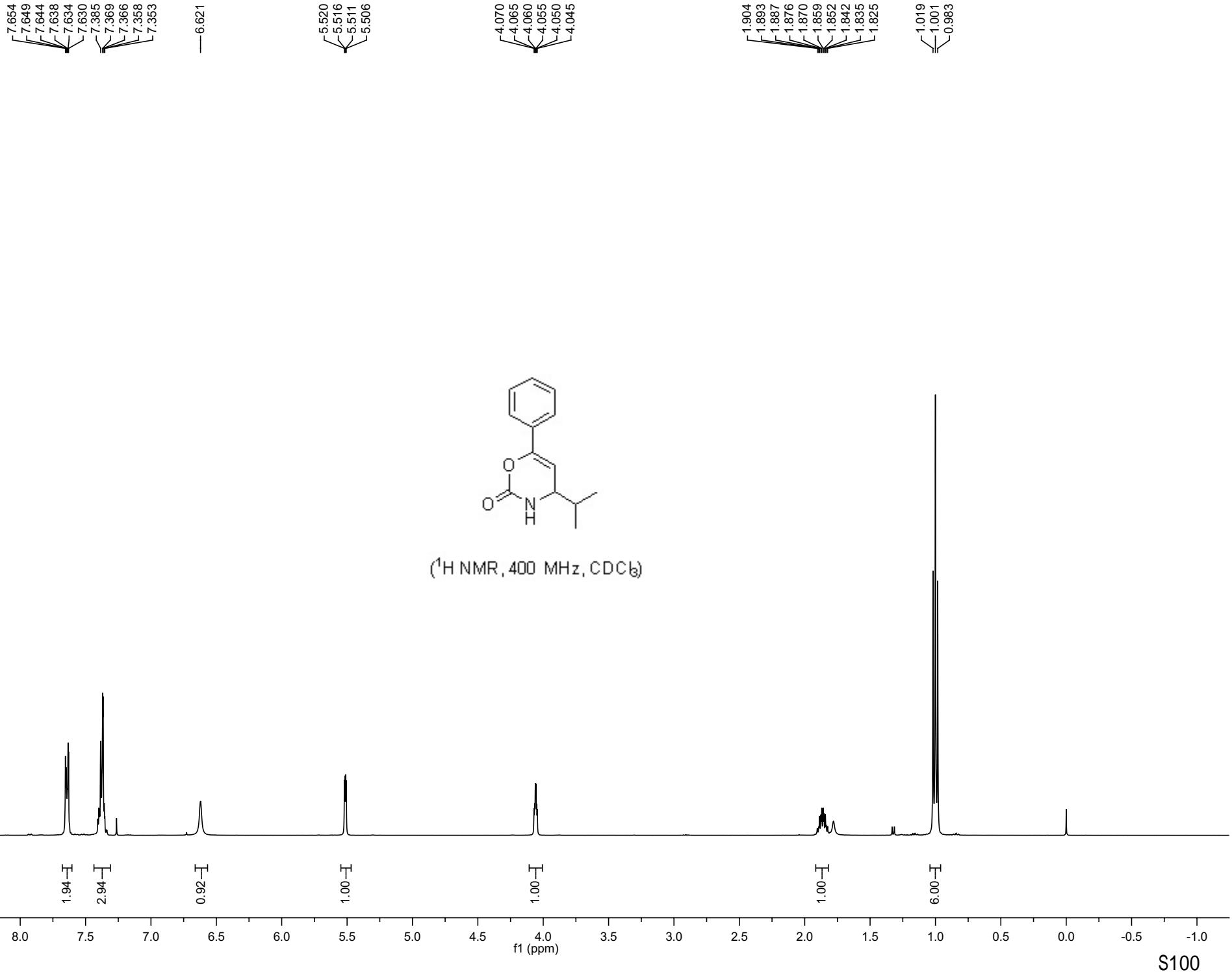
—151.886  
—148.084  
—131.831  
—128.470  
—124.644  
—98.933  
—51.138  
—40.074  
—17.678  
—13.860



( $^{13}\text{C}$  NMR, 100 MHz,  $\text{CDCl}_3$ )

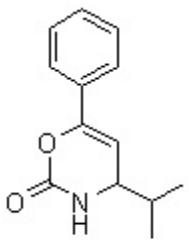


NMR spectra of compound 3oa

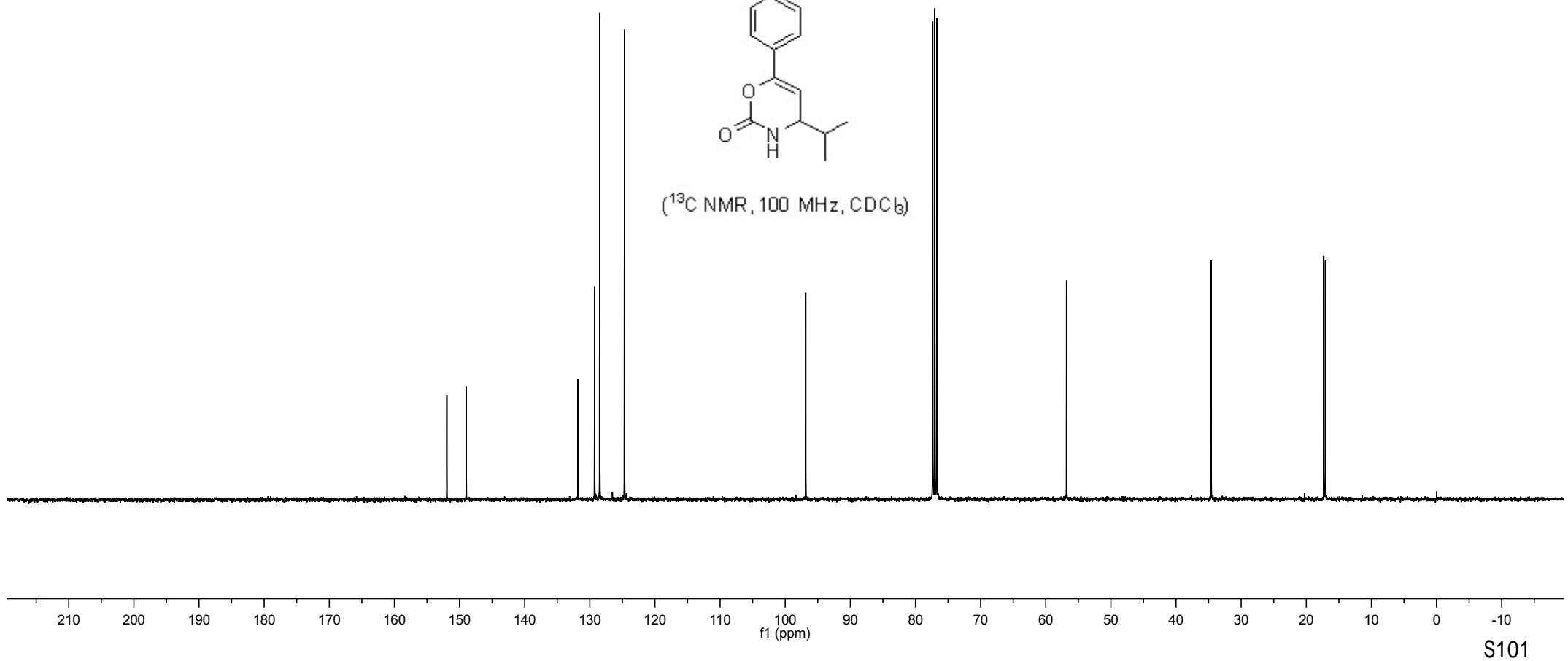


NMR spectra of compound 3oa

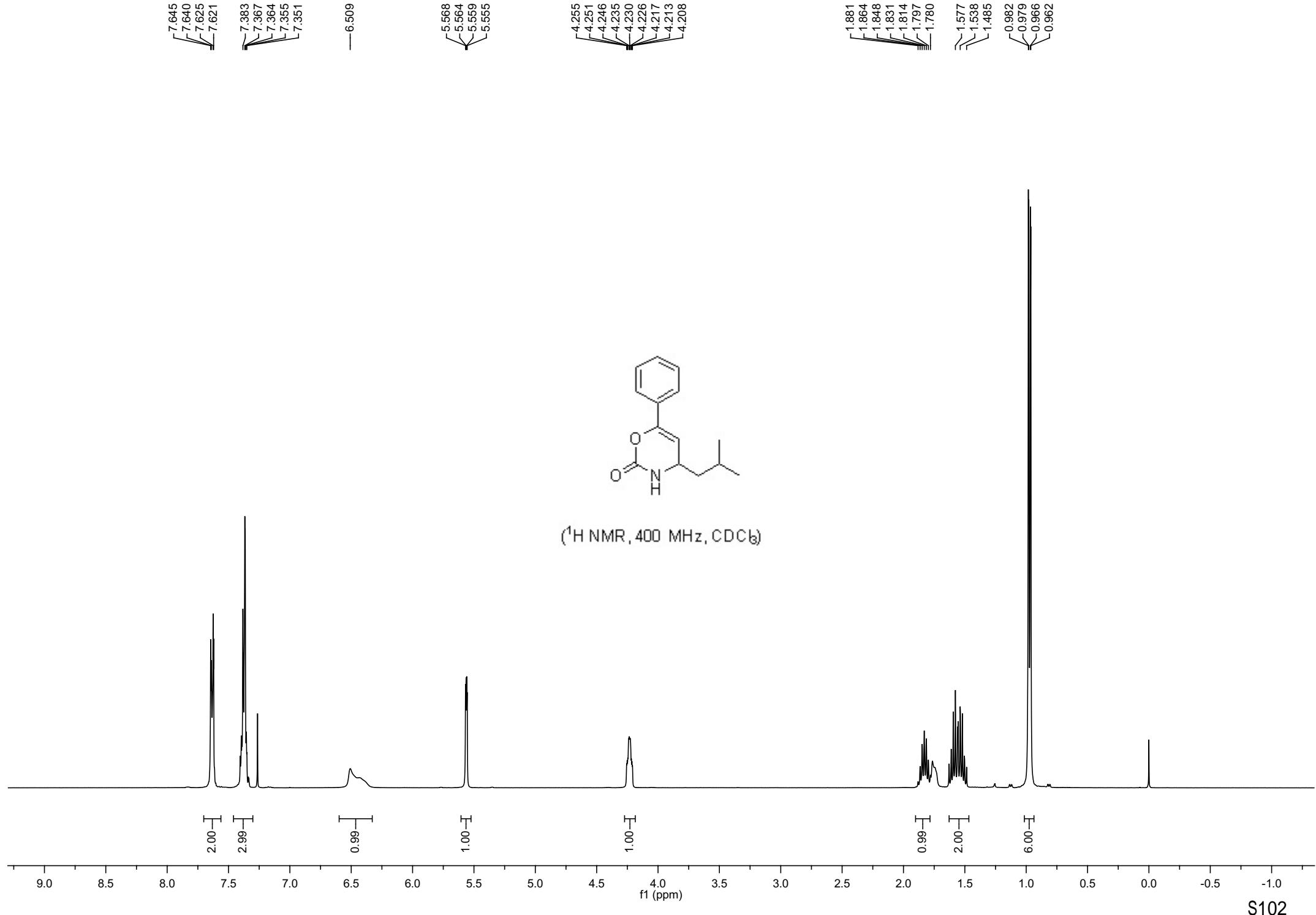
—151.945  
—148.971  
—131.827  
—128.478  
—124.680  
—96.849  
—56.808  
—34.604  
—17.313  
—17.055



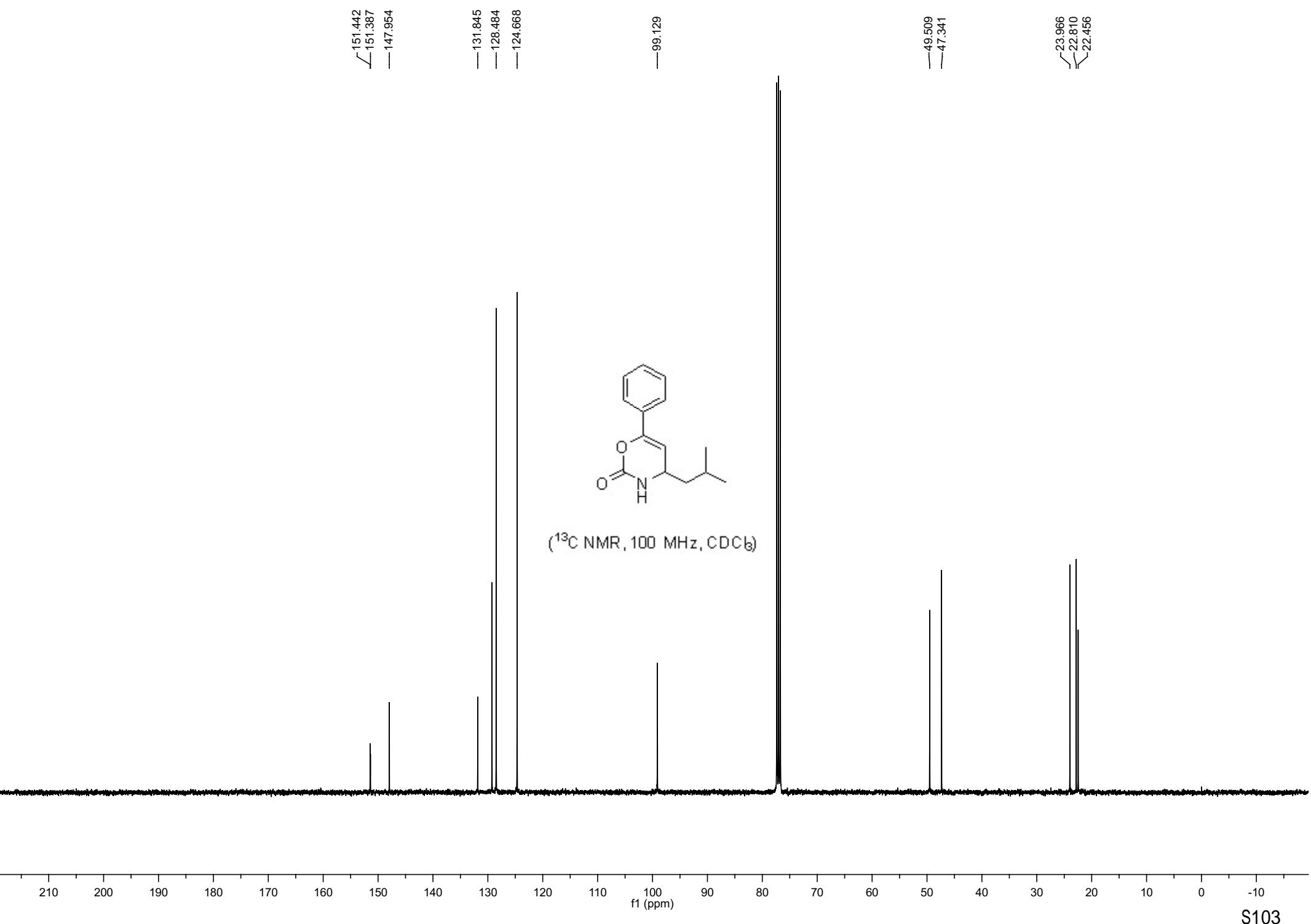
( $^{13}\text{C}$  NMR, 100 MHz,  $\text{CDCl}_3$ )



## NMR spectra of compound 3pa



NMR spectra of compound 3pa



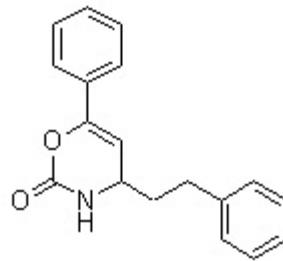
NMR spectra of compound 3qa

7.624  
7.618  
7.615  
7.613  
7.604  
7.600  
7.592  
7.370  
7.293  
7.208  
7.165  
6.897

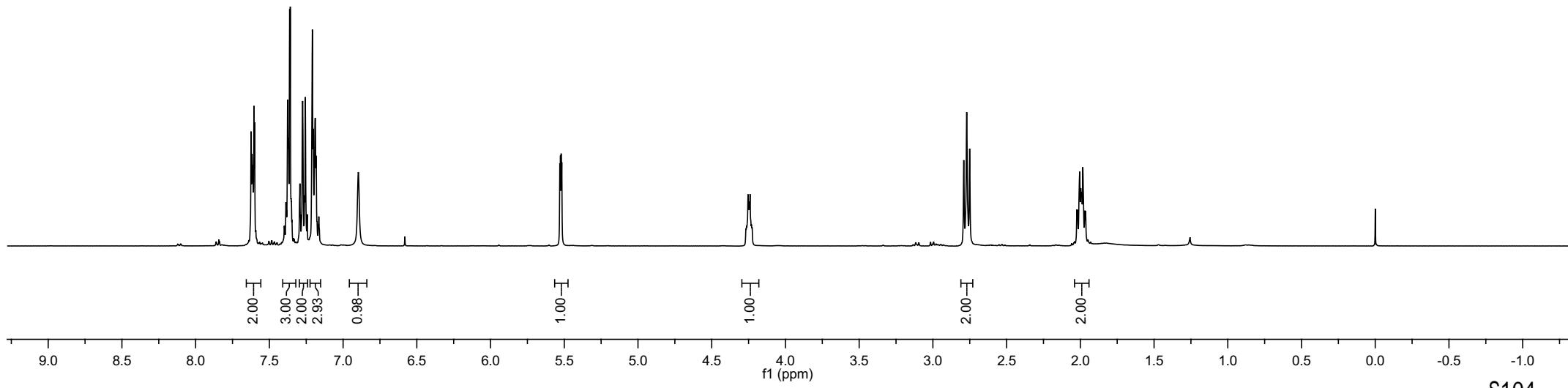
5.530  
5.526  
5.521  
5.517

4.268  
4.263  
4.254  
4.249  
4.244  
4.240  
4.230  
4.226

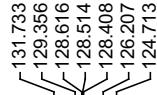
2.023  
2.019  
2.004  
2.004  
1.997  
1.992  
1.983  
1.969  
1.964

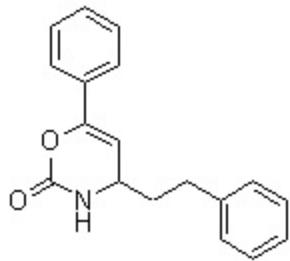


( $^1\text{H}$  NMR, 400 MHz, DMSO- $d_6$ )

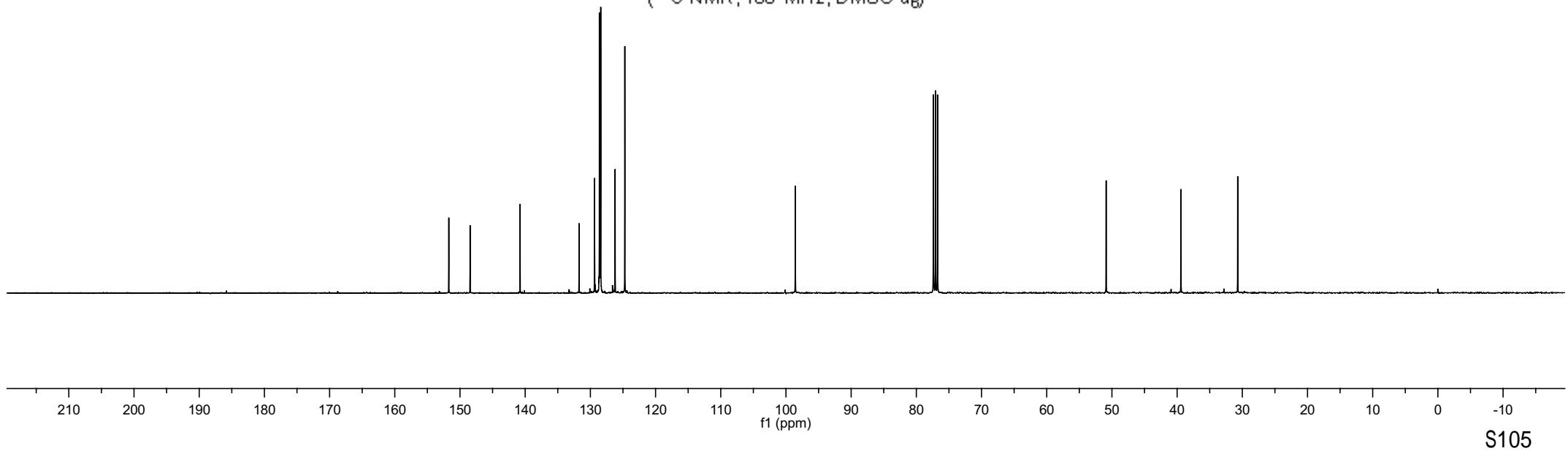


NMR spectra of compound 3qa

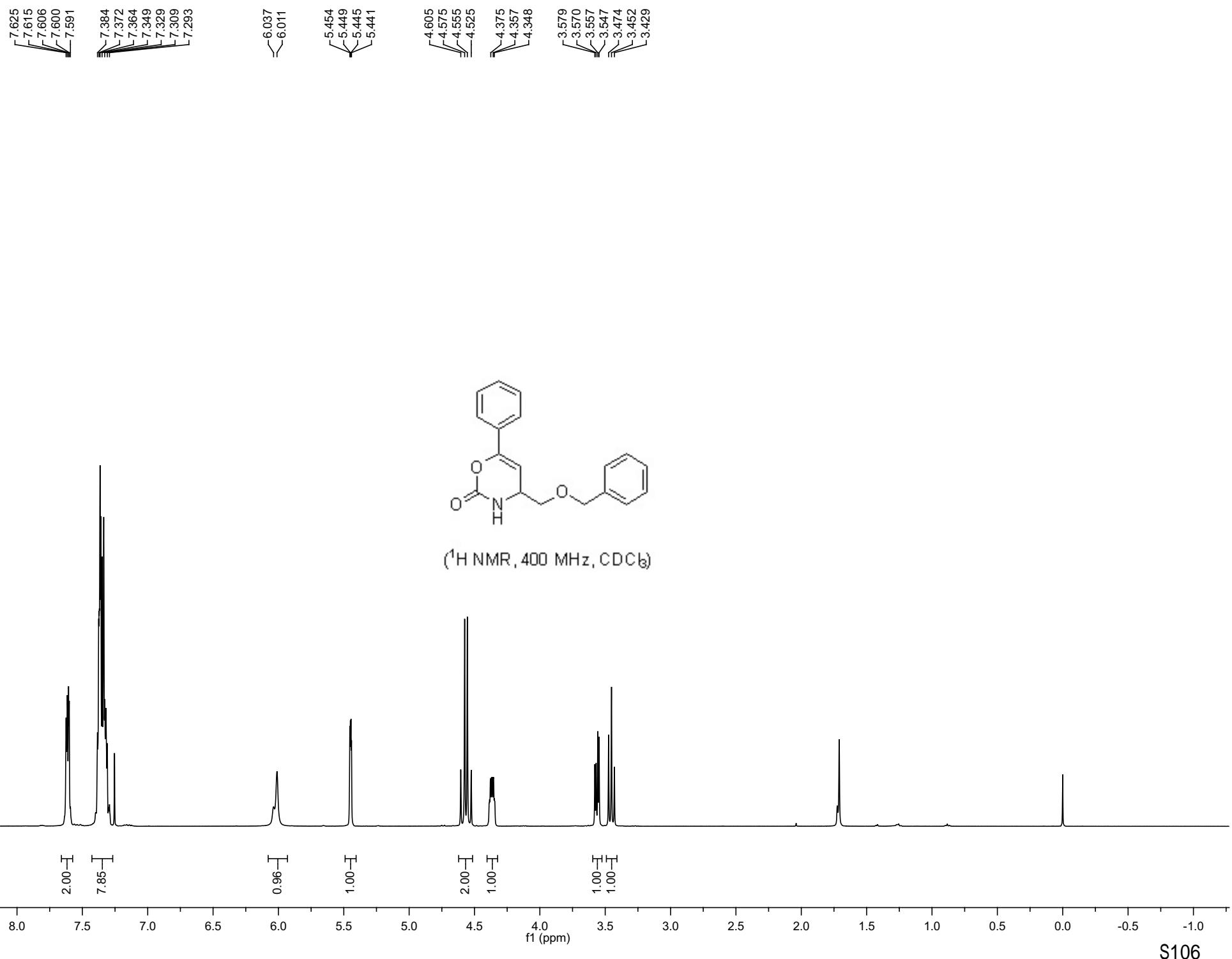
—151.712  
—148.449  
—140.789  
  
—131.733  
—129.356  
—128.616  
—128.514  
—128.408  
—126.207  
—124.713  
—98.563  
—50.887  
—39.415  
—30.707



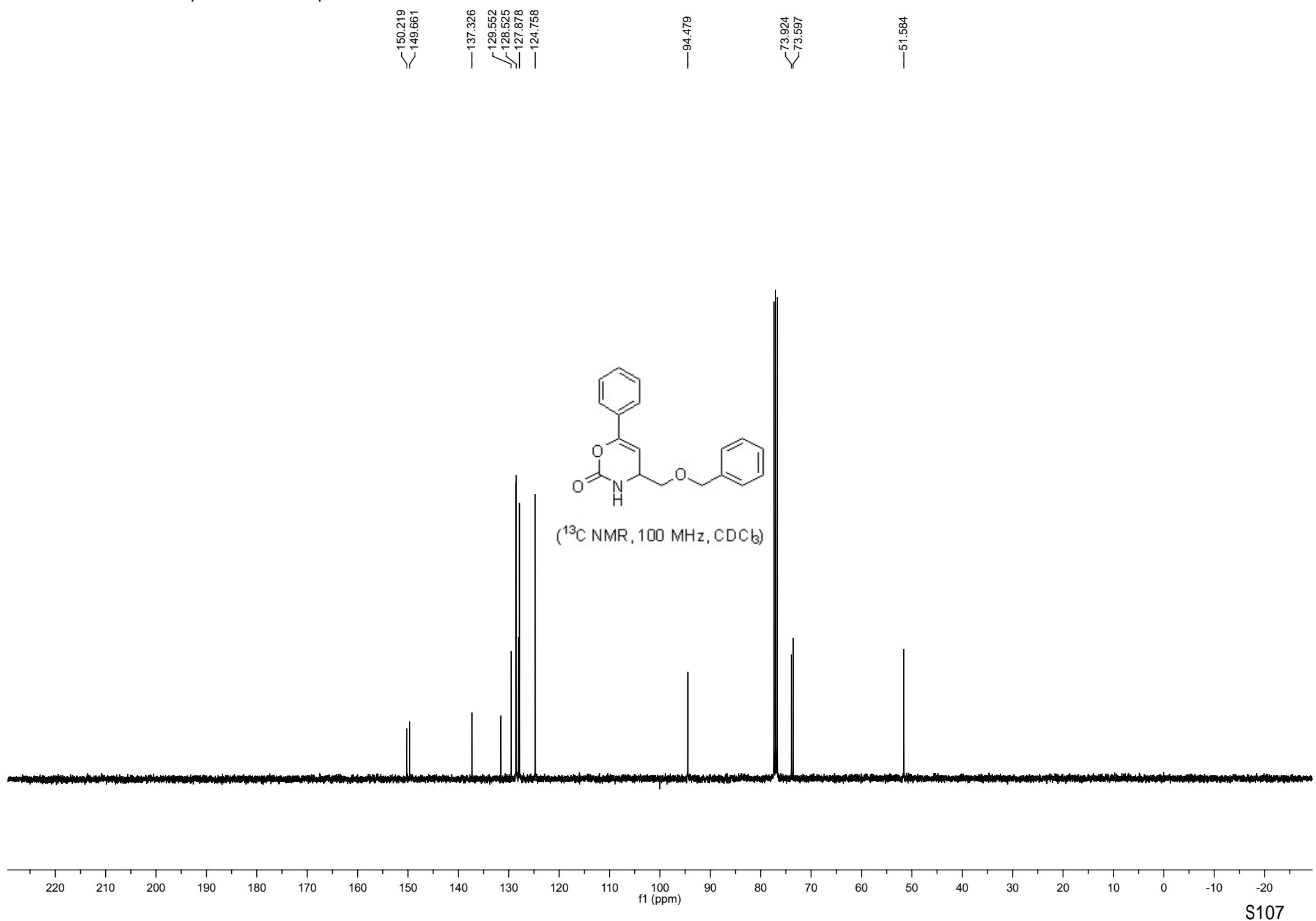
(<sup>13</sup>C NMR, 100 MHz, DMSO-d<sub>6</sub>)



NMR spectra of compound 3ra

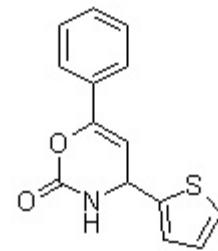
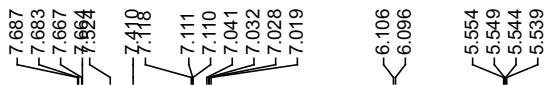


NMR spectra of compound 3ra

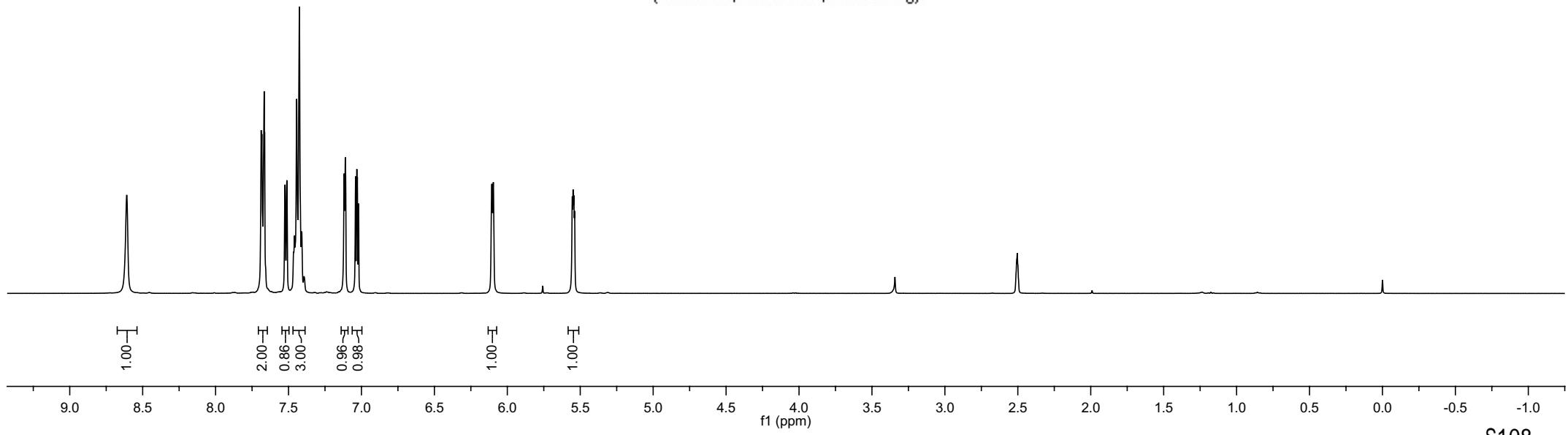


NMR spectra of compound 3sa

-8.609



( $^1\text{H}$  NMR, 400 MHz,  $\text{DMSO-d}_6$ )



NMR spectra of compound 3sa

