Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Stereoselective Amination via Vinyl-Silver Intermediates derived from Silver-Catalyzed Carboxylative Cyclization of Propargylamines

Yuta Sadamitsu, Kodai Saito, and Tohru Yamada*

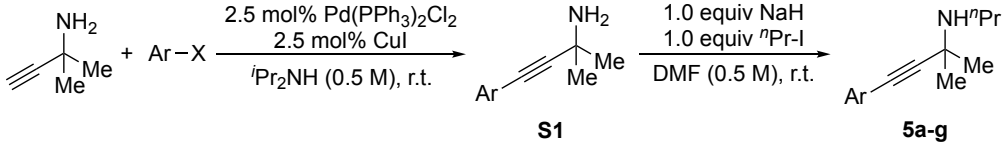
Contents

1. General

The ^{1}H and ^{13}C NMR spectra were recorded with a JEOL model AL-400, ECX-400, or ECS-400 spectrometer using CD_3CN or DMSO-d_6 as the solvent. The IR spectra were measured with a Thermo Electron Corporation model NICOLET 6700 FT-IR spectrometer. The melting points were measured with a Stanford Research Systems MPA100. The ESI high resolution mass spectra were obtained using a Waters LCT Premier XE mass spectrometer. Column chromatography was conducted on silica gel (CHROMATOREX PSQ 100B Fuji Silysia). The CH_3CN (anhydrous), DBU, DEAD, and AgOAc were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. DBAD was purchased from Aldrich. MS 3A was purchased from Junsei Chemical Co., Inc.

2. General Procedure & Characterization Data

2.1 Procedure for the Synthesis of Propargylamines



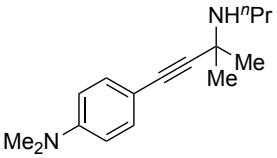
Propargylamines **1a**-**1g** were synthesized by the following literature. To the solution of Pd $(PPh_3)_2Cl_2$ (0.25 mmol, 2.5 mol%), CuI(I) (0.25 mmol, 2.5 mol%) and the corresponding aryl iodide or aryl bromide (10 mmol, 1.0 equiv) in $^{i}Pr_2NH$ (20 mL), 2-methyl-3-buthyn-2-amine (11 mmol, 1.1 equiv) was added dropwise and the mixture was stirred at room temperature for 12 h. Then, the reaction mixture was filtered through a celite® pad, and the filtrate was evaporated under reduced pressure. After the solvent was removed, the residue was purified by column chromatography (SiO_2, eluent: *n*-hexane:EtOAc=5:1, then *n*-hexane:EtOAc:Et_3N=75:25:1) to afford the desired compounds (**S1)**.

To the solution of NaH (1.0 equiv) in DMF (10 mL), **S1** (1.0 equiv) in DMF (10 mL) was added dropwise and the mixture was stirred for 30 min at room temperature. After that 1-iodopropane (1.0 equiv) was added dropwise and the mixture was stirred. The reaction mixture was quenched with ice water and the mixture was extracted three times with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (SiO_2, eluent: *n*-hexane:EtOAc=4:1, then *n*-hexane:EtOAc:Et_3N=67:33:1) and the bulb-to-bulb distillation or recrystallization to afford the desired starting materials (**5**).

The synthesis and characterization data for propargyl amines **1a** (Ar = Ph)[1], **1b** (Ar = PMP)[2], **1d** (Ar = *p*-chlorophenyl)[3], and **1e** (Ar = thienyl)[2] were previously reported. The

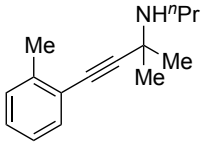
propargylamines **S1c** (Ar = *p*-dimethylaminophenyl)[4], **S1f** (Ar = *o*-Tolyl)[5], and **S1g** (Ar = 1-naphthyl)[5] were already known compounds.

_N_,_N_-Dimethyl-4-(3-methyl-3-(propylamino)but-1-yn-1-yl)aniline (1c)



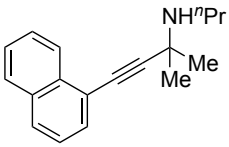
The reaction was carried out with the corresponding propargylamine **S1c** (1.55 g, 7.66 mmol), NaH (336 mg, 55%, 7.70 mmol), and iodopropane (0.75 mL, 7.7 mmol) in DMF (15 mL). The product was recrystallized by cold *n*-hexane; Pale yellow solid (1.08 g, 57%); mp 60-61 °C; ^{1}H NMR (400 MHz, CD_3CN): δ = 0.93 (t, *J* = 7.2 Hz, 3H), 1.34 (s, 6H), 1.45 (tq, *J* = 7.2, 7.2 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H), 2.91 (s, 6H), 6.61 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ = 12.3, 24.5, 30.2, 40.4, 46.9, 50.8, 82.9, 93.4, 111.1, 112.8, 133.1, 151.0; IR (KBr): 2962, 2213, 1613, 1524, 1363, 1161, 816; HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{25}N_2^+$, 245.2012; found, m/z 245.2005.

2-Methyl-_N_-propyl-4-(*o*-tolyl)but-3-yn-2-amine (1f)

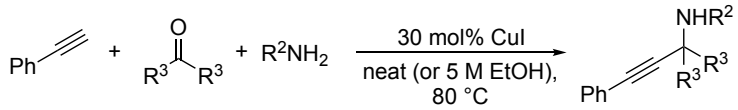


The reaction was carried out with the corresponding propargylamine **S1f** (1.88 g, 10.9 mmol), NaH (436 mg, 55%, 10.0 mmol), and iodopropane (0.98 mL, 10 mmol) in DMF (20 mL); Colorless liquid (1.62 g, 70%); ^{1}H NMR (400 MHz, CD_3CN): δ = 0.93 (t, *J* = 7.2 Hz, 3H), 1.38 (s, 6H), 1.46 (tq, *J* = 7.2, 7.6 Hz, 2H), 2.38 (s, 3H), 2.70 (t, *J* = 7.6 Hz, 2H), 7.06-7.15 (m, 1H), 7.16-7.24 (m, 2H), 7.27-7.34 (m, 1H); ^{13}C NMR (100 MHz, CD_3CN): δ = 12.3, 20.9, 24.5, 30.2, 47.1, 51.1, 81.0, 100.5, 124.2, 126.6, 128.8, 130.3, 132.4, 140.7; IR (KBr): 2996, 1485, 1458, 1378, 1262, 1173, 756; HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{22}N^+$, 216.1747; found, m/z 216.1744.

2-Methyl-4-(naphthalen-1-yl)-_N_-propylbut-3-yn-2-amine (1g)



The reaction was carried out with the corresponding propargylamine **S1g** (2.24 g, 10.7 mmol), NaH (436 mg, 55%, 10 mmol), and iodopropane (0.98 mL, 10 mmol) in DMF (20 mL); Pale yellow liquid (1.67 g, 62%);^{1}H NMR (400 MHz, CD_3CN): δ = 0.94 (t, *J* = 7.6 Hz, 3H), 1.31-1.54 (m, 8H), 2.77 (t, *J* = 7.2 Hz, 2H), 7.37-7.46 (m, 1H), 7.48-7.63 (m, 3H), 7.76-7.92 (m, 2H), 8.26-8.35 (m, 1H); ^{13}C NMR (100 MHz, CD_3CN): δ = 12.3, 24.5, 30.1, 47.2, 51.2, 80.1, 101.6, 121.9, 126.4, 126.7, 127.4, 127.7, 129.1, 129.2, 130.9, 134.0, 134.2; IR (KBr): 3058, 2966, 2213, 1587, 1460, 1279, 1245, 1016, 799, 562; HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{22}N^+$, 252.1747; found, m/z 252.1747.

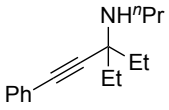


5h-j

Propargylic amines **1h**-**1j** were synthesized by the following literature.[6] The mixture of alkyne (20 mmol, 1.0 equiv), ketone (20 mmol, 1.0 equiv), and amine (20 mmol, 1.0 equiv) together with CuI (6.0 mmol, 30 mol%) was heated at 80 °C for 8 h. After cooled to room temperature, the reaction mixture was diluted by Et_2O and filtered through a short pad of silica gel. The filtrate was evaporated under reduced pressure, and the residue was purified by column chromatography (SiO_2, eluent: *n*-hexane:EtOAc=4:1, then *n*-hexane:EtOAc:Et_3N=67:33:1). The further purification was conducted by bulb-to-bulb distillation to afford the desired propargylamine (**5**).

The synthesis and characterization data for propargyl amines **5h** (R^2 = Bn, R^3 = Me)[2] and **5i** (R^2 = PMB, R^3 = Me)[2] was previously reported.

3-Ethyl-1-phenyl-*N*-propylpent-1-yn-3-amine (1j)

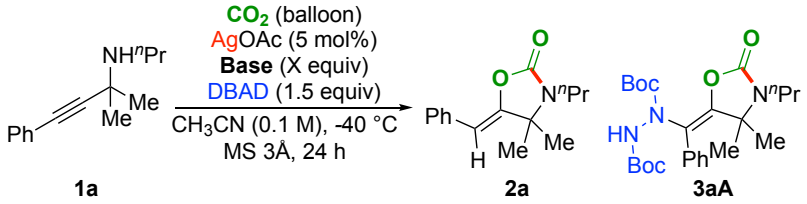


The reaction was carried out with ethynyl benzene (3.3 mL, 30 mmol), 3-pentanone (3.2 mL, 20 mmol), *n*-propylamine (2.5 mL, 30 mmol), and CuI (1.71 g, 9.00 mmol); Pale yellow liquid (792 mg, 12%); ^{1}H NMR (400 MHz, CD_3CN): δ =0.83-1.01 (m, 9H), 1.36-1.51 (m, 2H), 1.53-1.70 (m, 4H), 2.61 (t, *J* = 7.2 Hz, 2H), 7.25-7.33 (m, 3H), 7.34-7.40 (m, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ = 8.5, 12.4 24.6, 31.2, 46.0, 58.3, 84.1, 95.1, 124.6, 128.8, 129.4, 132.3; IR (KBr): 3057, 2965, 2218, 1599, 1489, 1379, 1147, 755, 691; HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{24}N^+$, 230.1903; found, m/z 230.1905.

2.2 Examination of the Effect of Bases

In a 30 mL Schlenk flask, molecular sieves 3A (200 mg) was added, and the equipment with MS 3A was heated under reduced pressure. After cooled to room temperature, the flask was purged with N_2, then AgOAc (1.7 mg, 0.010 mol), propargylamine **1a** (40.3 mg, 0.200 mmol), CH_3CN (2 mL), base, and DBAD (69.1 mg, 0.300 mmol) were added sequentially. After the mixture was cooled to -40 °C for 10 min, CO_2 (balloon) was charged. The temperature was kept at -40 °C until the reaction was completed. After 12 h, the reaction mixture was diluted by EtOAc and filtered through a short pad of silica gel (eluent: EtOAc). The filtrate was evaporated under reduced pressure, and the residue was dried *in vacuo*.

Yields of products were determined by ^{1}H NMR using trimethylphenylsilane as an internal standard. Results of the examination were summarized in Table S1.



1a **2a** **3aA**

Table S1. Examination of the effect of bases

Entry	**Base**	X / equiv	Yield[a]	**2a** /%	**3aA** /%	**2**:**3**
1	PPh_3	1.0		>99	nd	100:0
2	Et_3N	1.0		65[c]	nd	100:0
3	MTBD	1.0		51	29	64:36
4	BTMG	1.0		25	73	26:74
5	DBU[b]	1.0		9	87	9:91
6	DBU	0.50		53	42	56:44
7	DBU	0.25		62	37	63:37
8	DBU	0.10		67	32	68:32

a) Determined by ^{1}H NMR. b) 12 h. c) The starting material **1a** was recovered in 30% yield.

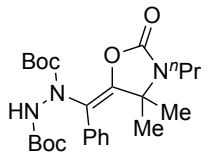
2.3 Procedure for the Synthesis of Aminovinyloxazolidiones

The procedure using DBAD was described below. In a 30 mL Schlenk flask, molecular sieves 3A (200 mg) was added, and the equipment with MS 3A was heated under reduced pressure. After cooled to room temperature, the flask was purged with N_2, then AgOAc (1.7 mg, 0.010 mol), propargylamine **1a** (40.3 mg, 0.200 mmol), CH_3CN (2 mL), DBU (30 μL, 0.20 mmol), and DBAD (69.1 mg, 0.300 mmol) were added sequentially. After the mixture was cooled to -40 °C for 10 min, CO_2 (balloon) was charged. The temperature was kept at -40 °C until the reaction was completed. After 12 h, the reaction mixture was diluted by EtOAc and filtered through a short pad of silica gel (eluent: EtOAc). The filtrate was evaporated under reduced pressure, and the residue was purified by preparative thin layer chromatography (SiO_2, eluent: *n*-hexane:EtOAc=3:1) to afford the desired product **3aA** (76.4 mg, 80% yield).

The procedure using DEAD was described below. In a 30 mL Schlenk flask, molecular sieves 3A (200 mg) was added, and the equipment with MS 3A was heated under reduced pressure. After cooled to room temperature, the flask was purged with N_2, then AgOAc (1.7 mg, 0.010 mol), propargylamine **1a** (40.3 mg, 0.200 mmol), CH_3CN (2 mL), and DBU (30 μL, 0.20 mmol) were added sequentially. After the mixture was cooled to -40 °C for 10 min,

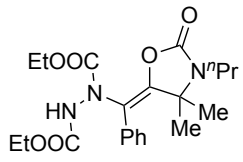
DEAD (14 mL, 0.3 mmol, 40% solution in toluene) was added dropwise, and then CO_2 (balloon) was charged. The temperature was kept at -40 °C until the reaction was completed. After 12 h, the reaction mixture was diluted by EtOAc and filtered through a short pad of silica gel (eluent: EtOAc). The filtrate was evaporated under reduced pressure, and the residue was purified by preparative thin layer chromatography (SiO_2, eluent: *n*-hexane:Et_2O = 1:2) to afford the desired product **3aB** (84.0 mg, quant).

Di-tert-butyl-(*Z*)-1-((4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene)(phenyl) methyl)hydrazine-1,2-dicarboxylate (3aA)



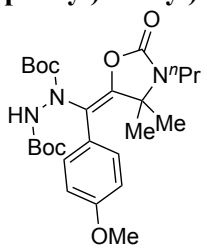
White solid (76.4 mg, 80%); mp 146-147 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 0.87 (t, *J* = 7.2 Hz, 3H), 1.14 (s, 6H), 1.20 (s, 9H), 1.47 (s, 9H), 1.58 (tq, *J* = 7.2 Hz, 7.2 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H), 7.30-7.45 (m, 5H), 8.43 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 10.4, 21.3, 25.0, 27.2, 27.4, 40.7, 60.6, 78.5, 79.7, 116.1, 126.9, 127.9, 130.9, 132.2, 147.9, 151.8, 152.0, 153.8 ; IR (KBr): 3290, 2979, 2936, 2879, 1776, 1717, 1365, 1163, 1022, 725;HRMS (ESI): $[M+Na]^+$ calcd for $C_{25}H_{37}N_3NaO_6^+$, 498.2575; found, m/z 498.2583.

Diethyl (*Z*)-1-((4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene)(phenyl)methyl) hydrazine-1,2-dicarboxylate (3aB)



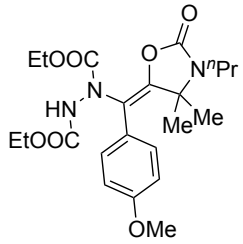
White amorphous (84.0 mg, quant); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 0.87 (t, *J* = 7.6 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H), 1.15 (s, 6H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.58 (tq, *J* = 7.2, 7.6 Hz, 2H), 3.05 (q, *J* = 7.2 Hz, 2H), 3.85 (q, *J* = 7.2 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 7.30-7.45 (m, 5H), 8.95 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 10.4, 13.5, 13.6, 21.3, 24.7, 40.7, 59.8, 60.7, 61.3, 115.7, 127.1, 128.1, 131.0, 132.0, 148.9, 152.0, 153.2, 154.8 ; IR (KBr): 3290, 2979, 2936, 2877, 1782, 1728, 1402, 1336, 1234, 1090, 1025, 758, 712; HRMS (ESI): $[M+Na]^+$ calcd for $C_{21}H_{29}N_3NaO_6^+$, 442.1949; found, m/z 442.1956.

Di-*tert*-butyl(*Z*)-1-((4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene)(4-methoxy phenyl)methyl)hydrazine-1,2-dicarboxylate (3bA)



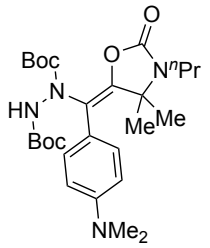
White solid (95.1 mg, 94%); mp 180-182 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 0.87 (t, *J* = 7.6 Hz, 3H), 1.15 (s, 6H), 1.22 (s, 9H), 1.44 (s, 9H), 1.58 (tq, *J* = 7.6, 7.6 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H), 3.78 (s, 3H), 6.92 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 8.36 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 10.4, 21.3, 25.0, 27.3, 27.4, 40.7, 54.7, 60.6, 78.5, 79.6, 112.8, 115.8, 124.5, 132.2, 147.7, 151.8, 152.1, 153.8, 159.2; IR (KBr): 3301, 2978, 2934, 1771, 1718, 1514, 1369, 1246, 1159, 1141, 835, 760; HRMS (ESI): $[M+Na]^+$ calcd for $C_{26}H_{39}N_3NaO_7^+$, 528.2680; found, m/z 528.2679.

Diethyl (*Z*)-1-((4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene)(4-methoxyphenyl) methyl)hydrazine-1,2-dicarboxylate (3bB)



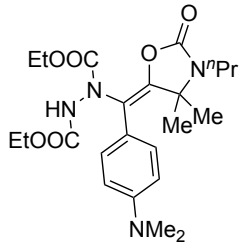
White amorphous (90.0 mg, quant); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 0.87 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H), 1.16 (s, 6H), 1.19 (t, *J* = 7.2 Hz, 3H) 1.58 (tq, *J* = 7.2, 7.6, 2H), 3.05 (q, *J* = 7.6 Hz, 2H), 3.78 (s, 3H), 3.88 (q, *J* = 7.2 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 8.88 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 10.3, 13.5, 13.6, 21.3, 24.7, 40.7, 54.7, 59.8, 60.7, 61.2, 112.8, 115.4, 124.2, 132.3, 148.7, 152.1, 153.2, 154.8, 159.3 ; IR (KBr): 2978, 2936, 1780, 1727, 1402, 1356, 1248, 1028, 759; HRMS (ESI): $[M+H]^+$ calcd for $C_{22}H_{32}N_3O_7^+$, 450.2235; found, m/z 450.2230.

Di-*tert*-butyl (*Z*)-1-((4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene)(4-(dimethyl amino)phenyl)methyl)hydrazine-1,2-dicarboxylate (3cA)



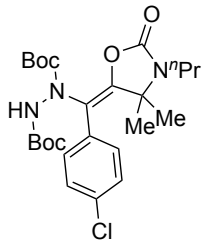
White solid (101.9 mg, 98%); mp 174-175 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 0.87 (t, *J* = 6.8 Hz, 3H), 1.17 (s, 6H), 1.24 (s, 9H), 1.44 (s, 9H), 1.51-1.54 (m, 2H), 2.91 (s, 6H) 3.05 (t, *J* = 6.8 Hz, 2H), 6.69 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 8.26 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 10.4, 21.4, 25.0, 27.3, 27.4, 39.4, 40.7, 60.7, 78.4, 79.5, 110.7, 116.4, 119.5, 131.6, 147.3, 150.2, 152.0, 152.3, 153.9 ; IR (KBr): 3315, 2976, 2933, 2876, 1776, 1716, 1366, 1162, 757; HRMS (ESI): $[M+H]^+$ calcd for $C_{27}H_{43}N_4O_6^+$, 519.3177; found, m/z 519.3180.

Diethyl (*Z*)-1-((4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene)(4-(dimethylamino) phenyl)methyl)hydrazine-1,2-dicarboxylate (3cB)



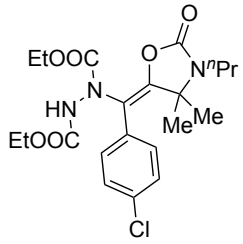
White amorphous (92.7 mg, quant); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 0.87 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 6.8 Hz, 3H), 1.17 (s, 6H), 1.19 (t, *J* = 6.8 Hz, 3H), 1.59 (tq, *J* = 7.2, 7.2 Hz, 2H), 2.92 (s, 6H), 3.04 (t, *J* = 7.2 Hz, 2H), 3.88 (q, *J* = 6.8 Hz, 2H), 4.11 (q, *J* = 6.8 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 8.81 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 10.4, 13.6, 13.7, 21.3, 25.0, 39.3 40.7, 59.8, 60.8, 61.1, 110.7, 116.1, 119.1, 131.6, 148.1, 150.1, 152.2, 153.3, 154.8; IR (KBr): 3301, 2980, 2935, 1778, 1724, 1371, 1336, 1239, 761; HRMS (ESI): $[M+H]^+$ calcd for $C_{23}H_{35}N_4O_6^+$, 463.2551; found, m/z 463.2556.

Di-*tert*-butyl (*Z*)-1-((4-chlorophenyl)(4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene) methyl)hydrazine-1,2-dicarboxylate (3dA)



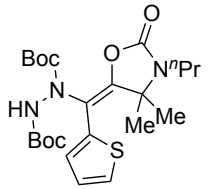
White solid (47.6 mg, 47%); mp 180-181 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 0.87 (t, *J* = 7.2 Hz, 3H), 1.16 (s, 6H), 1.22 (s, 9H), 1.44 (s, 9H), 1.58 (tq, *J* = 7.2, 7.6 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 8.49 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 10.3, 21.3, 25.0, 27.2, 27.3, 40.7, 60.6, 78.6, 79.9, 114.9, 127.2, 131.2, 132.7, 133.1, 148.4, 151.7, 151.9, 153.8; IR (KBr): 3301, 2978, 2935, 2882, 1771, 1755, 1718, 1370, 1156, 1017, 834, 757; HRMS (ESI): $[M+Na]^+$ calcd for $C_{25}H_{36}ClN_3NaO_6^+$, 532.2185; found, m/z 532.2194.

Diethyl (*Z*)-1-((4-chlorophenyl)(4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene) methyl)hydrazine-1,2-dicarboxylate (3dB)



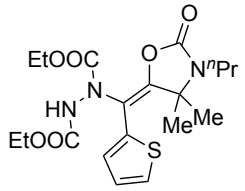
White amorphous (61.6 mg, 68%); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 0.87 (t, *J* = 7.6 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H), 1.17 (s, 6H) 1.19 (t, *J* = 7.2 Hz, 3H), 1.59 (tq, *J* = 7.6, 7.6 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H), 3.88 (q, *J* = 7.2 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 9.00 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 10.3, 13.5, 13.6, 21.3, 25.0, 40.8, 60.0, 60.7, 61.4, 114.5, 127.3, 130.9, 132.7, 133.3, 149.5, 151.9, 153.2, 154.8 ; IR (KBr): 2980, 2937, 2878, 1783, 1729, 1401, 1336, 1234, 1090, 947, 758; HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{29}ClN_3O_6^+$, 454.1739; found, m/z 454.1742.

Di-*tert*-butyl (*Z*)-1-((4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene)(thiophen-2-yl) methyl)hydrazine-1,2-dicarboxylate (3eA)



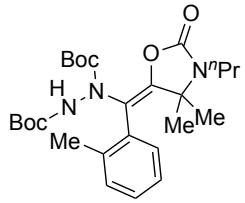
White solid (24.4 mg, 25%); mp 144-145 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 0.87 (t, *J* = 7.6 Hz, 3H), 1.19-1.31 (m, 15H), 1.45 (s, 9H), 1.59 (tq, *J* = 7.6, 7.6 Hz, 2H), 3.08 (t, *J* = 7.6 Hz, 2H), 7.00-7.07 (m, 2H), 7.59 (d, *J* = 5.2 Hz, 2H), 8.46 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 10.4, 21.3, 24.7, 27.3, 27.4, 40.8, 61.0, 78.6, 79.9, 109.2, 125.6, 127.7, 130.4, 133.0, 151.4, 151.7, 151.8, 153.9; IR (KBr): 3242, 3156, 2975, 2939, 2880, 1782, 1717, 1369, 1331, 1159, 1018, 758, 717; HRMS (ESI): $[M+Na]^+$ calcd for $C_{23}H_{35}N_3NaO_6S^+$, 504.2139; found, m/z 504.2136.

Diethyl (*Z*)-1-((4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene)(thiophen-2-yl) methyl)hydrazine-1,2-dicarboxylate (3eB)



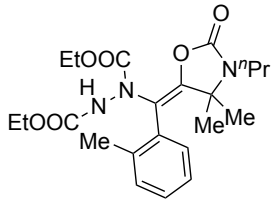
White amorphous (70.1 mg, 82%); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 0.87 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.27 (s, 6H), 1.59 (tq, J = 7.2, 7.6 Hz, 2H), 3.08 (t, *J* = 7.6 Hz, 2H), 3.91 (q, *J* = 7.2 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 7.02 (dd, *J* = 3.2, 4.8 Hz, 1H), 7.06 (d, *J* = 3.2 Hz, 1H), 7.60 (d, *J* = 4.8 Hz, 1H), 9.00 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 10.4, 13.6, 13.6, 21.2, 24.7, 40.8, 59.9, 61.1, 61.3, 108.8, 125.6, 128.0, 130.7, 132.6, 151.6, 152.1, 153.0, 154.8; IR (KBr): 3303, 2979, 2935, 2877, 1785, 1729, 1402, 1334, 1233, 1088, 1022, 758, 713; HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{28}N_3O_6S^+$, 426.1693; found, m/z 426.1697.

Di-*tert*-butyl (*Z*)-1-((4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene)(*o*-tolyl)methyl) hydrazine-1,2-dicarboxylate (3fA)



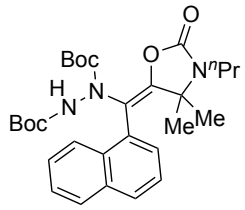
White solid (86.5 mg, 89%); mp 178-179 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 0.87 (t, *J* = 7.2 Hz, 3H), 1.02 (s, 3H), 1.11-1.25 (m, 12H), 1.46 (s, 9H), 1.52-1.64 (m, 2H), 2.35 (s, 3H), 3.01-3.13 (m, 2H), 7.11-7.24 (m, 3H), 7.25-7.32 (m, 1H), 8.37 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 10.4, 19.2, 21.4, 22.9, 25.6, 27.2, 27.3, 40.7, 60.7, 78.4, 79.8, 114.9, 123.9, 128.4, 129.3, 130.8, 133.1, 138.9, 146.6, 151.5, 152.2, 153.8 ; IR (KBr): 3316, 2979, 2935, 2877, 1786, 1729, 1402, 1334, 1233, 1088, 1022, 758, 713 ; HRMS (ESI): $[M+Na]^+$ calcd for $C_{26}H_{39}N_3NaO_6^+$, 512.2731; found, m/z 512.2729.

Diethyl (*Z*)-1-((4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene)(*o*-tolyl)methyl) hydrazine-1,2-dicarboxylate (3fB)



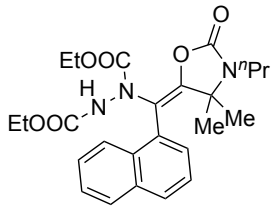
White amorphous (85.5 mg, 99%); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 0.87 (t, *J* = 7.6 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H), 1.03 (s, 3H), 1.19 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.51-1.66 (m, 2H), 3.01-3.09 (m, 2H), 3.68-3.90 (m, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 7.12-7.18 (m, 1H), 7.18-7.23 (m, 2H), 7.25-7.31 (m, 1H), 8.88 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 10.4, 13.5, 13.6, 19.0, 21.3, 22.9, 25.5, 40.7, 59.8, 60.8, 61.3, 114.4, 124.0, 128.5, 129.3, 130.4, 133.1, 138.9, 147.5, 152.1, 152.9, 154.7; IR (KBr): 3301, 2980, 2936, 2877, 1779, 1726, 1403, 1334, 1233, 1088, 1029, 757; HRMS (ESI): $[M+H]^+$ calcd for $C_{22}H_{32}N_3O_6^+$, 434.2286; found, m/z 434.2281.

Di-*tert*-butyl (*Z*)-1-((4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene)(naphthalen-1-yl)methyl)hydrazine-1,2-dicarboxylate (3gA)



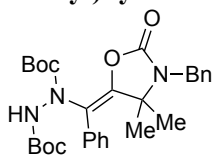
Pale yellow solid (69.1 mg, 66%); mp 182-184 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6, 150 °C): δ = 0.82 (s, 3H), 0.87 (t, J = 7.2 Hz, 3H), 0.97 (s, 9H), 1.19 (s, 3H), 1.45-1.64 (m, 11H), 2.97-3.10 (m, 2H), 7.43-7.55 (m, 4H), 7.83-7.99 (m, 2H), 8.09-8.25 (m, 1H), 8.35 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 150 °C): δ = 10.1, 21.1, 23.6, 25.1, 26.8, 27.3, 40.6, 60.7, 78.2, 80.0, 113.6, 123.8, 125.0, 126.1, 127.2, 128.6, 129.1, 130.7, 132.7, 132.9, 148.5, 151.6, 152.0, 153.6; IR (KBr): 3276, 2974, 2934, 2879, 1775, 1718, 1366, 1330, 1161, 1092, 1020, 785; HRMS (ESI): $[M+Na]^+$ calcd for $C_{29}H_{39}N_3NaO_6^+$, 548.2731; found, m/z 548.2737.

Diethyl (*Z*)-1-((4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene)(naphthalen-1-yl) methyl)hydrazine-1,2-dicarboxylate (3gB)



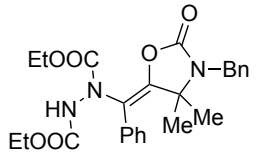
Pale yellow amorphous (89.7 mg, 96%); ^{1}H NMR (400 MHz, DMSO-d_6, 150 °C): δ = 0.69-0.92 (m, 9H), 1.19 (s, 3H), 1.25-1.36 (m, 3H), 1.52-1.65 (m, 2H), 2.96-3.11 (m, 2H), 3.53-3.74 (m, 2H), 4.12-4.29 (m, 2H), 7.41-7.56 (m, 4H), 7.85-7.99 (m, 2H), 8.24-8.33 (m, 1H), 8.71 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 150 °C): δ = 10.1, 12.9, 13.4, 21.0, 23.6, 25.1, 40.7, 59.4, 60.8, 61.2, 113.1, 123.8, 125.0, 125.2, 125.8, 127.2, 128.8, 130.7, 132.7, 132.9, 149.3, 151.9, 153.0, 154.5 ; IR (KBr): 2977, 2933, 2876, 1781, 1726, 1403, 1374, 1338, 1216, 1096, 786; HRMS (ESI): $[M+H]^+$ calcd for $C_{25}H_{32}N_3O_6^+$, 470.2286; found, m/z 470.2293.

Di-*tert*-butyl (*Z*)-1-((3-benzyl-4,4-dimethyl-2-oxooxazolidin-5-ylidene)(phenyl) methyl)hydrazine-1,2-dicarboxylate (3hA)



White solid (83.4 mg, 80%); mp 189-190 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 1.09 (s, 6H), 1.21 (s, 9H), 1.46 (s, 9H), 4.39 (s, 2H), 7.19-7.43 (m, 10H), 8.45 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 25.1, 27.3, 27.4, 42.4, 61.0, 78.6, 79.9, 116.4, 126.7, 126.8, 127.0, 127.1, 127.4, 127.7, 128.0, 130.9, 132.2, 137.5, 147.8, 151.8, 152.7, 153.8; IR (KBr): 3326, 2979, 2936, 1775, 1719, 1364, 1153, 1060, 710; HRMS (ESI): $[M+Na]^+$ calcd for $C_{29}H_{37}N_3NaO_6^+$, 546.2575; found, m/z 546.2584.

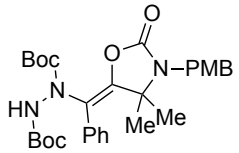
Diethyl (*Z*)-1-((3-benzyl-4,4-dimethyl-2-oxooxazolidin-5-ylidene)(phenyl)methyl) hydrazine-1,2-dicarboxylate (3hB)



White amorphous (93.6 mg, quant); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 1.02 (t, J = 6.8 Hz, 3H), 1.10 (s, 6H), 1.21 (t, J = 7.2 Hz, 3H), 3.86 (q, J = 6.8 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 4.39 (s, 2H), 7.19-7.49 (m, 10H), 8.98 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 13.5, 13.6, 25.1, 42.4, 59.9, 61.1, 61.3, 116.0, 126.7, 126.8, 127.1, 127.8, 128.2,

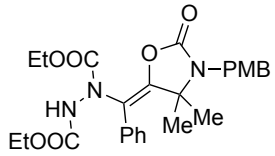
130.9, 131.9, 137.4, 148.7, 152.5, 153.2, 154.8; IR (KBr): 2982, 2926, 2854, 1781, 1727, 1401, 1336, 1234, 1057, 756, 711; HRMS (ESI): $[M+H]^+$ calcd for $C_{25}H_{30}N_3O_6^+$, 468.2129; found, m/z 468.2116.

Di-*tert*-butyl (*Z*)-1-((3-(4-methoxybenzyl)-4,4-dimethyl-2-oxooxazolidin-5-ylidene) (phenyl)methyl)hydrazine-1,2-dicarboxylate (3iA)



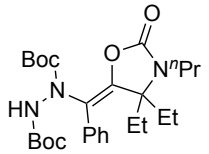
White amorphous (67.2 mg, 61%); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 1.08 (s, 6H), 1.20 (s, 9H), 1.45 (s, 9H), 3.74 (s, 3H), 4.32 (s, 2H), 6.86 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.29-7.40 (m, 5H), 8.43 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 25.2, 27.2, 27.4, 30.3, 41.9, 54.7, 61.0, 78.6, 79.8, 113.5, 116.3, 127.0, 128.0, 128.3, 129.5, 130.9, 132.2, 147.9, 151.8, 152.6, 153.8, 158.3; IR (KBr): 2978, 2933, 1779, 1725, 1368, 1248, 1156, 1060, 961, 779, 707; HRMS (ESI): $[M+Na]^+$ calcd for $C_{30}H_{39}N_3NaO_7^+$, 576.2680; found, m/z 576.2688.

Diethyl (*Z*)-1-((3-(4-methoxybenzyl)-4,4-dimethyl-2-oxooxazolidin-5-ylidene)(phenyl) methyl)hydrazine-1,2-dicarboxylate (3iB)



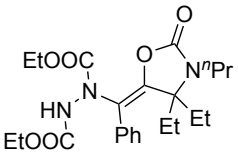
White amorphous (98.2 mg, 99%); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 1.01 (t, J = 7.2 Hz, 3H), 1.10 (s, 6H), 1.20 (t, J = 7.2 Hz, 3H), 3.74 (s, 3H), 3.86 (q, J = 7.2 Hz, 2H), 4.16 (q, J = 7.2 Hz, 2H), 4.32 (s, 2H), 6.87 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.30-7.41 (m, 5H), 8.97 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 13.5, 13.6, 25.1, 41.9, 54.7, 59.9, 61.1, 61.3, 113.6, 115.9, 127.1, 128.2, 128.3, 129.4, 130.9, 131.9, 148.7, 152.5, 153.2, 154.8, 158.4; IR (KBr): 2986, 2937, 1780, 1726, 1400, 1332, 1246, 1178, 1059, 962, 780, 710; HRMS (ESI): $[M+Na]^+$ calcd for $C_{26}H_{31}N_3NaO_7^+$, 520.2054; found, m/z 520.2061.

Di-*tert*-butyl (*Z*)-1-((4,4-diethyl-2-oxo-3-propyloxazolidin-5-ylidene)(phenyl)methyl) hydrazine-1,2-dicarboxylate (3jA)



White solid (72.9 mg, 72%); mp 170-171 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6, 110 °C): δ = 0.80-0.94 (m, 9H), 1.01-1.14 (m, 2H), 1.21 (s, 9H), 1.40-1.66 (m, 13H), 2.96 (t, J = 8.0 Hz, 2H). 7.27-7.43 (m, 5H), 8.50 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 6.9, 10.7, 20.9, 27.2, 27.5, 28.6, 40.7, 69.1, 78.4, 80.0, 115.9, 126.9, 128.0, 129.8, 132.3, 144.4, 152.0, 153.3, 153.8; IR (KBr): 3307, 2973, 2935, 2881, 1774, 1717, 1445, 1366, 1159, 1095, 1022, 960, 758, 726, 712 ; HRMS (ESI): $[M+Na]^+$ calcd for $C_{27}H_{41}N_3NaO_6^+$, 526.2888; found, m/z 526.2880.

Diethyl (*Z*)-1-((3-benzyl-4,4-dimethyl-2-oxooxazolidin-5-ylidene)(phenyl)methyl) hydrazine-1,2-dicarboxylate (3hB)

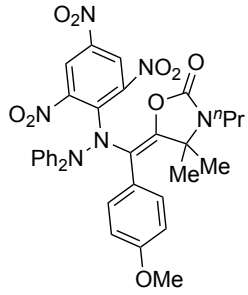


White amorphous (88.1 mg, 98%); ^{1}H NMR (400 MHz, CD_3CN, 75 °C): δ = 0.85-0.97 (m, 9H), 1.09 (t, *J* = 7.2 Hz, 3H), 1.12-1.21 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.46-1.57 (m, 2H), 1.59-1.71 (m, 2H), 2.98 (t, *J* = 7.6 Hz, 2H), 3.95 (q, *J* = 6.8 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 7.27-7.49 (m, 5H); ^{13}C NMR (100 MHz, DMSO-d_6, 110 °C): δ = 6.7, 10.7, 13.5, 13.7, 20.9, 28.6, 40.7, 59.8, 61.3, 69.3, 115.5, 127.1, 128.2, 129.8, 131.9, 145.4, 153.2, 153.3, 154.8; IR (KBr): 3267, 2973, 2936, 1778, 1726, 1406, 1343, 1184, 1095, 1059, 954, 758, 713; HRMS (ESI): $[M+H]^+$ calcd for $C_{23}H_{34}N_3O_6^+$, 448.2442; found, m/z 448.2441.

2.4 Procedure for the Control Experiment using DPPH

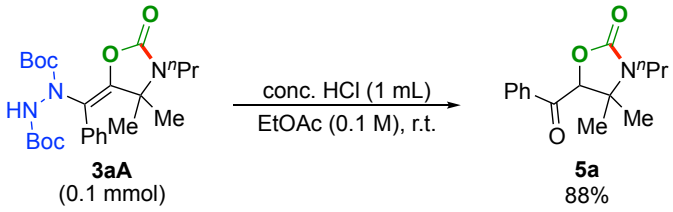
The procedure using DPPH was described below. In a 30 mL Schlenk flask, molecular sieves 3A (200 mg) was added, and the equipment with MS 3A was heated under reduced pressure. After cooled to room temperature, the flask was purged with N_2, then AgOAc (1.7 mg, 0.010 mol), propargylamine **1a** (40.3 mg, 0.200 mmol), CH_3CN (2 mL), and DBU (30 μL, 0.20 mmol) were added sequentially, and the mixture was degassed by three freeze-pump-thaw cycles. After the mixture was cooled to -40 °C for 10 min, the solution of DPPH (1.9 mL, 0.48 mmol, 0.25 M solution in CH_3CN) was added dropwise, and then CO_2 (balloon) was charged. The temperature was kept at -40 °C until the reaction was completed. After 24 h, the reaction mixture was diluted by EtOAc and filtered through a short pad of silica gel (eluent: EtOAc). AcOH (1 mL) was added to the filtrate and stirred for 12 h. The reaction mixture was then extracted by EtOAc and organic layer was washed by saturated $NaHCO_3$ aq.. After the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (SiO_2, eluent: *n*-hexane:Et_2O = 4:1 to 2:1) and preparative thin layer chromatography (SiO_2, eluent: *n*-hexane:EtOAc = 3:1) to afford the desired product **3aB** (10.4 mg, 8%).

(*Z*)-5-((2,2-Diphenyl-1-(2,4,6-trinitrophenyl)hydrazineyl)(4-methoxyphenyl) methylene)-4,4-dimethyl-3-propyloxazolidin-2-one (4b)



Dark purple amorphous (10.4 mg, 8%); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.79-0.91 (m, 3H), 0.98-1.09 (m, 3H), 1.48-1.70 (m, 5H), 3.02-3.20 (m, 2H), 3.82-3.86 (m, 3H), 7.01-7.14 (m, 6H), 7.16 (d, *J* = 1.6 Hz, 1H), 7.25-7.36 (m, 2H), 7.38-7.50 (m, 4H), 7.81 (d, *J* = 1.6 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 11.1, 19.6, 22.1, 22.9, 41.5, 55.7, 64.4, 108.0, 108.2, 108.3, 114.2, 114.3, 122.8, 123.5, 125.2, 127.4, 130.0, 130.1, 132.4, 132.5, 143.3, 143.7, 149.6, 153.5, 154.2, 163.6; IR (KBr): 2930, 2857, 1775, 1600, 1537, 1467, 1385, 1264, 1229, 1165, 1113, 1040, 969, 900, 757, 689; HRMS (ESI): $[M+H]^+$ calcd for $C_{34}H_{33}N_6O_9^+$, 669.2304; found, m/z 669.2296.

2.5 Transformation of Aminovinyloxazolidinone

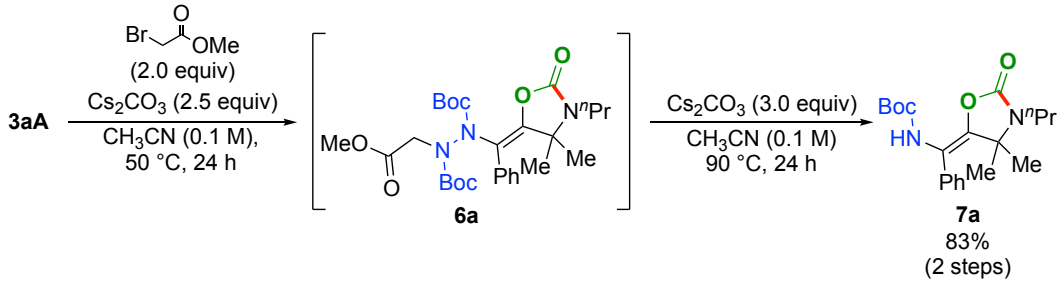


3aA
(0.1 mmol)

5a
88%

Hydrolysis of aminovinyloxazolidinone

3aA (47.6 mg, 0.100 mmol) was dissolved in EtOAc (1 mL) at room temperature. To the solution conc. HCl (1 mL) was added at 0 °C, the mixture was warmed to room temperature and was stirred for 5 min at the same temperature. After the reaction was completed, NaOH was added at 0 °C to neutralize the reaction. The reaction mixture was extracted three times with EtOAc and the combined organic layer was dried over Na_2SO_4. After the solvent was removed, the residue was purified by column chromatography (SiO_2, eluent: *n*-hexane:EtOAc=3:1) to afford **5a** (23.0 mg, 0.0880 mmol) in 88% yield.

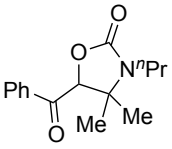


N-N bond cleavage[7]

Methyl bromoacetate (19.0 μL, 0.200 mmol) and Cs_2CO_3 (81.4 mg, 0.250 mmol) were added to acetonitrile (1 mL) solution of **3aA** (47.6 mg, 0.100 mmol) at room temperature. The mixture was warmed to 50 °C and stirred at the same temperature for 24 h. After the reaction was completed, saturated NH_4Cl (aq) was added to quench the reaction. The solution was then extracted with EtOAc. The extract was washed with brine, dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo. The crude was directly used for the next step without further purification.

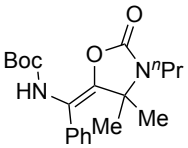
The crude was dissolved in CH_3CN (1 mL) and Cs_2CO_3 (97.7 mg, 0.300 mmol) was added to the solution at room temperature. Then, the solution was warmed to 90 °C and stirred at the same temperature for 24 h. After filtration through a short-plug of silica gel (ca. 10 g, EtOAc was used as eluent), volatile materials were removed under reduced pressure and the residue was purified by preparative thin layer chromatography (three times, *n*-hexane:EtOAc = 3:1) to afford **7a** (29.9 mg, 0.0830 mmol) in 83% yield.

5-benzoyl-4,4-dimethyl-3-propyloxazolidin-2-one (5a)



Colorless liquid (23.0 mg, 88%); ^{1}H NMR (400 MHz, CD_3CN): δ = 0.87 (t, *J* = 7.6 Hz, 3H), 0.96 (s, 3H), 1.43 (s, 3H), 1.54 (tq, *J* = 7.2, 7.6 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 5.64 (s, 1H), 7.52-7.58 (m, 2H), 7.66-7.71 (m, 1H), 7.92-7.96 (m, 1H); ^{13}C NMR (100 MHz, CD_3CN): δ =11.4, 22.3, 23.4, 26.6, 42.5, 61.9, 82.6, 129.4, 130.0, 135.1, 137.0, 157.4, 195.8; HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{20}NO_3^+$, 262.1438; found, m/z 262.1440.

***tert*-butyl (*Z*)-((4,4-dimethyl-2-oxo-3-propyloxazolidin-5-ylidene)(phenyl)methyl) carbamate (7a)**



White solid (29.9 mg, 83%); mp 155-156 °C; ^{1}H NMR (400 MHz, CD_3CN, 70 °C): δ = 0.95 (t, *J* = 7.6 Hz, 3H), 1.36 (s, 9H), 1.57 (s, 6H), 1.69 (tq, *J* = 7.6, 8.0 Hz, 2H), 3.15 (t, *J* = 8.0 Hz, 2H), 6.50 (bs, 1H), 7.23-7.28 (m, 1H), 7.33-7.39 (m, 2H), 7.52-7.56 (m, 1H); ^{13}C NMR (100 MHz, CD_3CN, 70 °C): δ = 11.8, 23.5, 25.2, 28.8, 43.0, 64.1, 80.8, 113.3, 128.5, 128.6, 129.2, 138.0, 154.4,

156.4; HRMS (ESI): $[M+Na]^+$ calcd for $C_{20}H_{29}N_2O_4^+$, 361.2122; found, m/z 361.2108.

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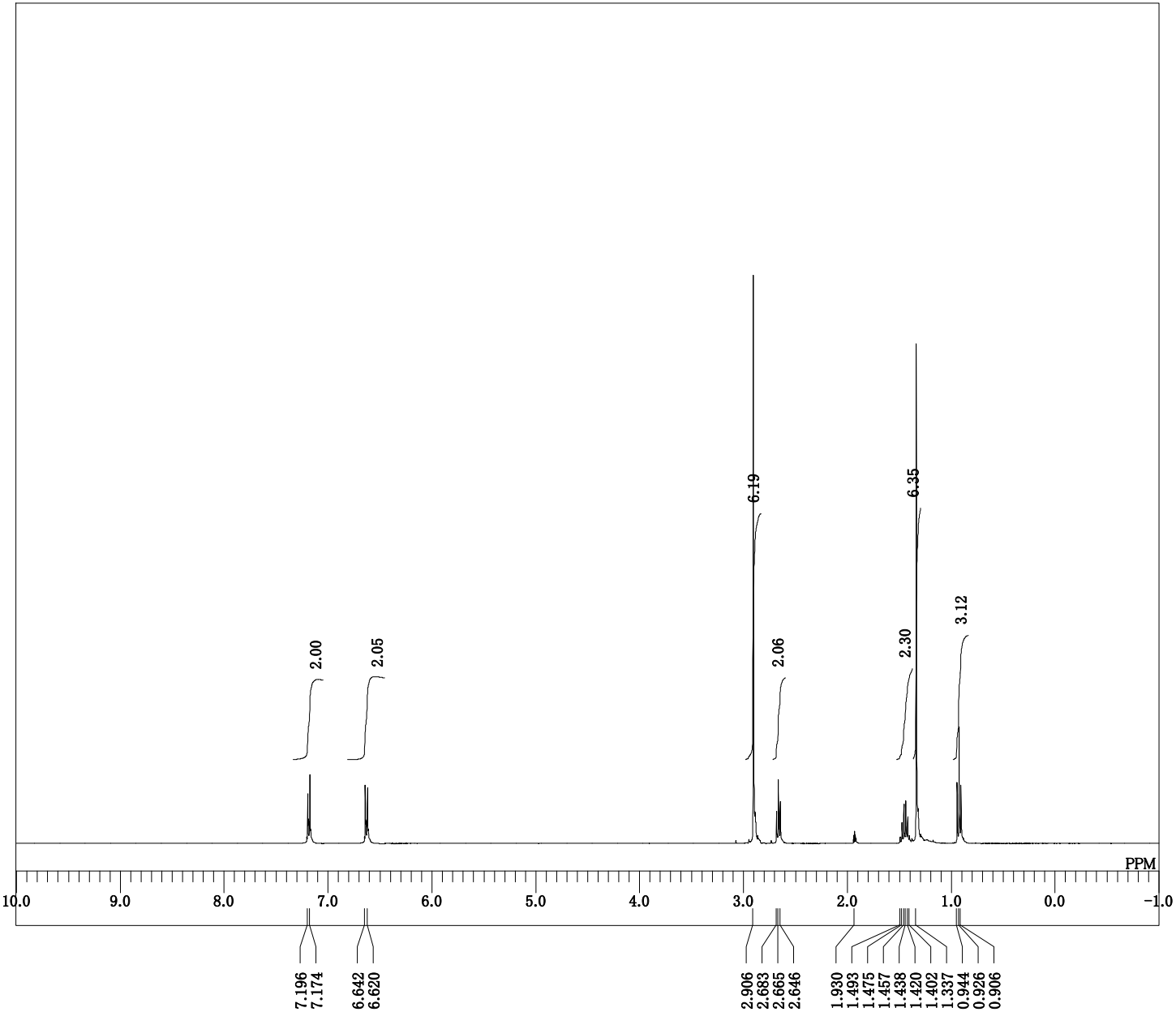
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PD 2.0000 sec
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CTEMP 6348.8 c
SLVNT CD3CN
EXREF 1.93 ppm
BF 0.12 Hz
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2.05
6.19
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6.35
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8.0
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6.0
5.0
4.0
3.0
2.0
1.0
0.0
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7.196
7.174
6.642
6.620
2.906
2.683
2.665
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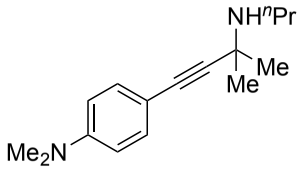
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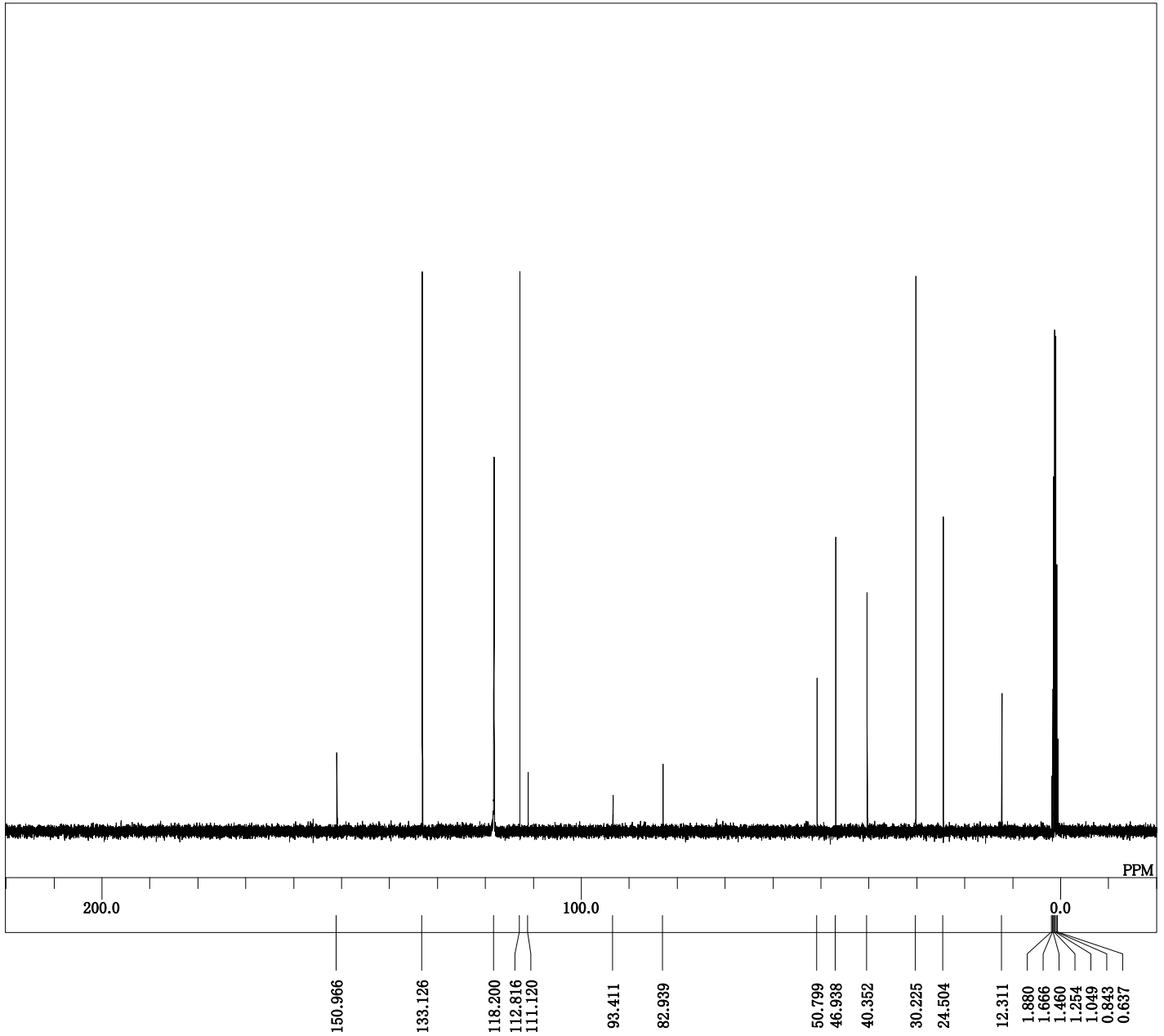
Me
Me
Me$_2$N

1c



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PD	3.0000 sec
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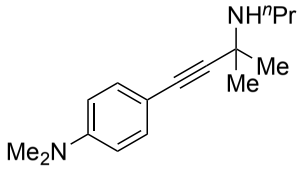

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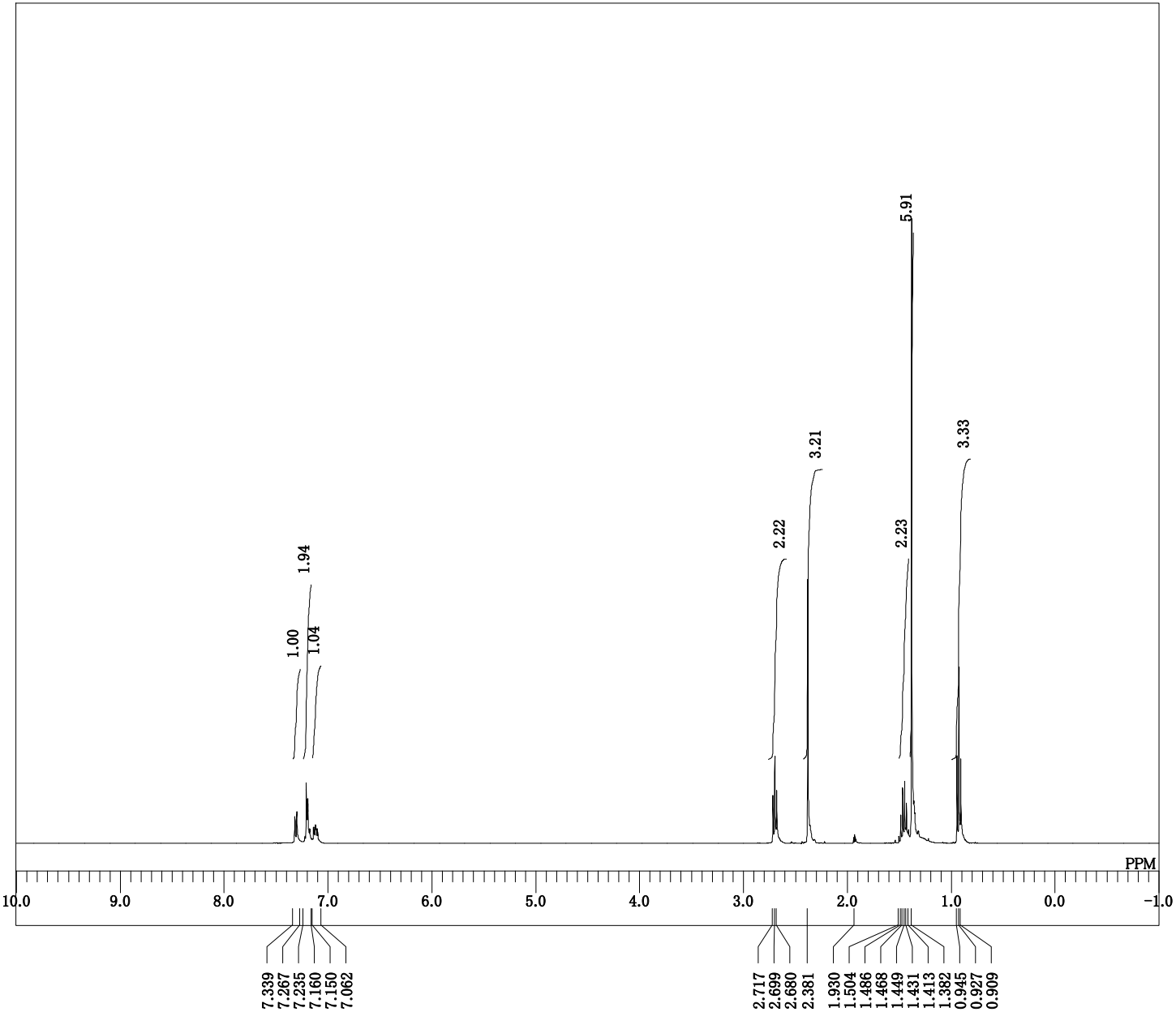
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CTEMP 6348.8 c
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7.160
7.150
7.062
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2.699
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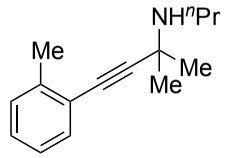
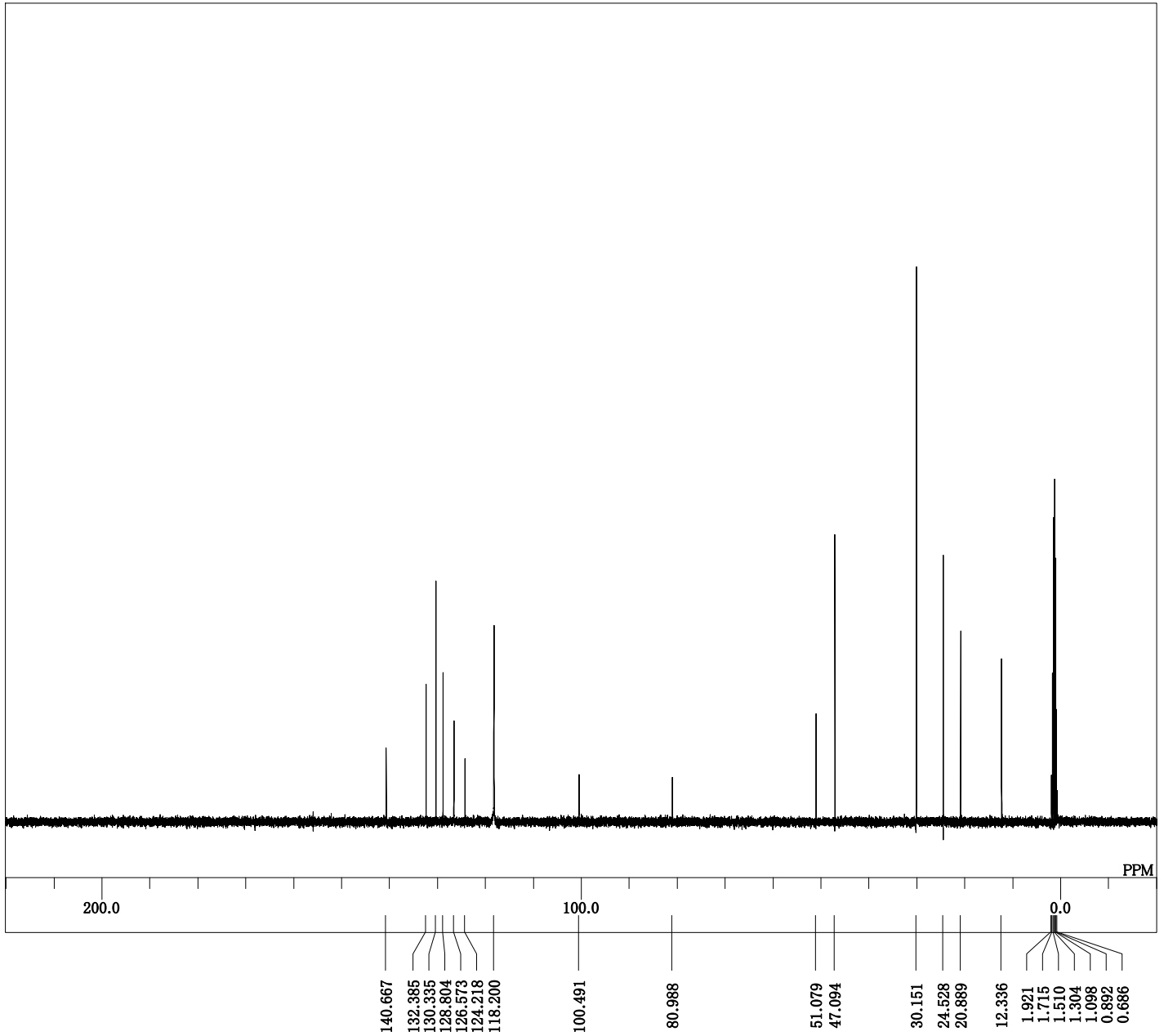

NH^{n}Pr
Me
Me
Me

1f



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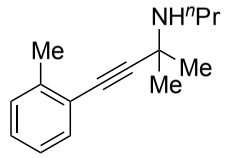
RGAIN	21



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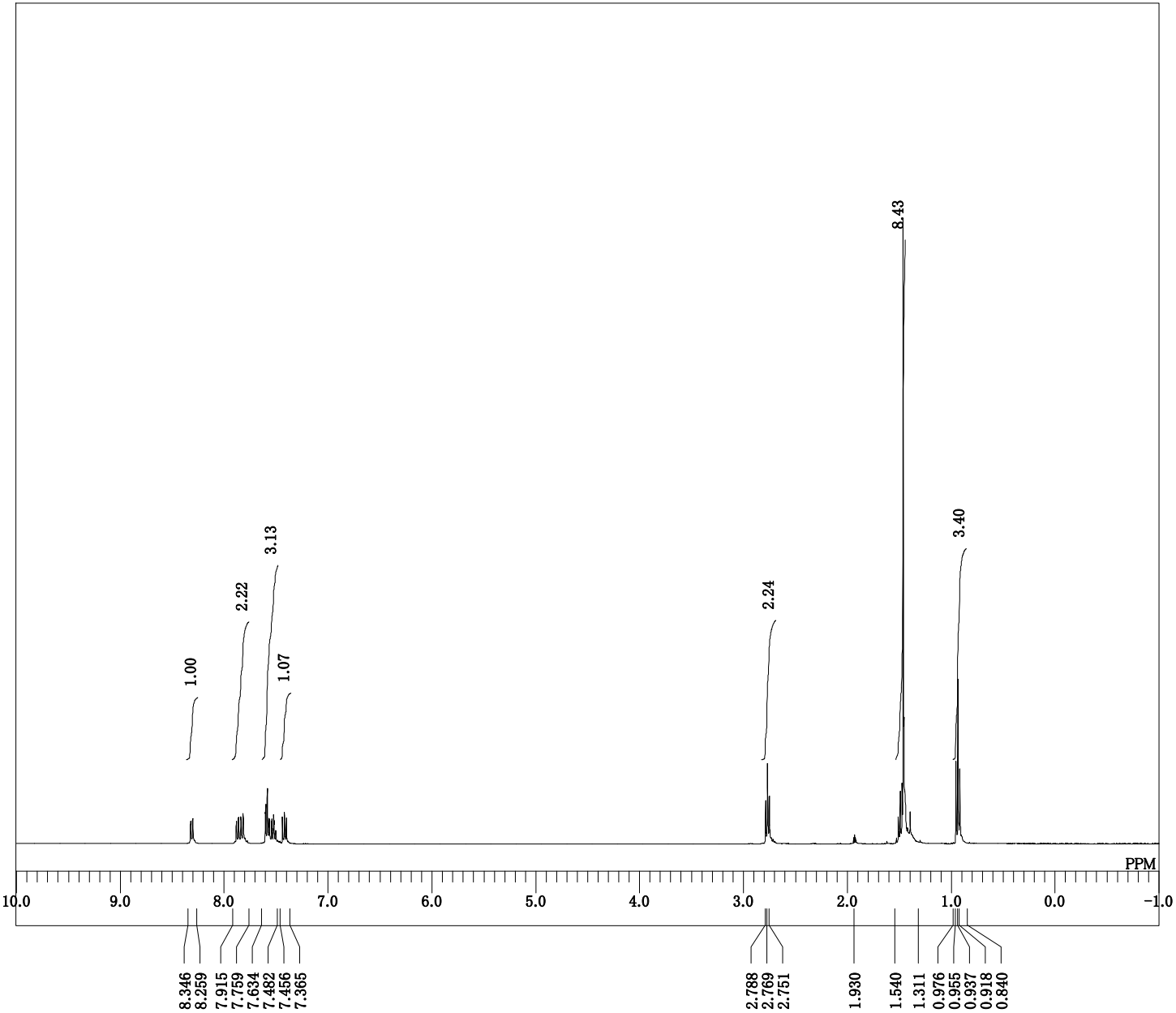

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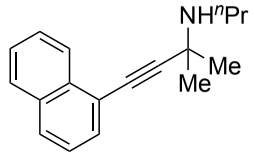

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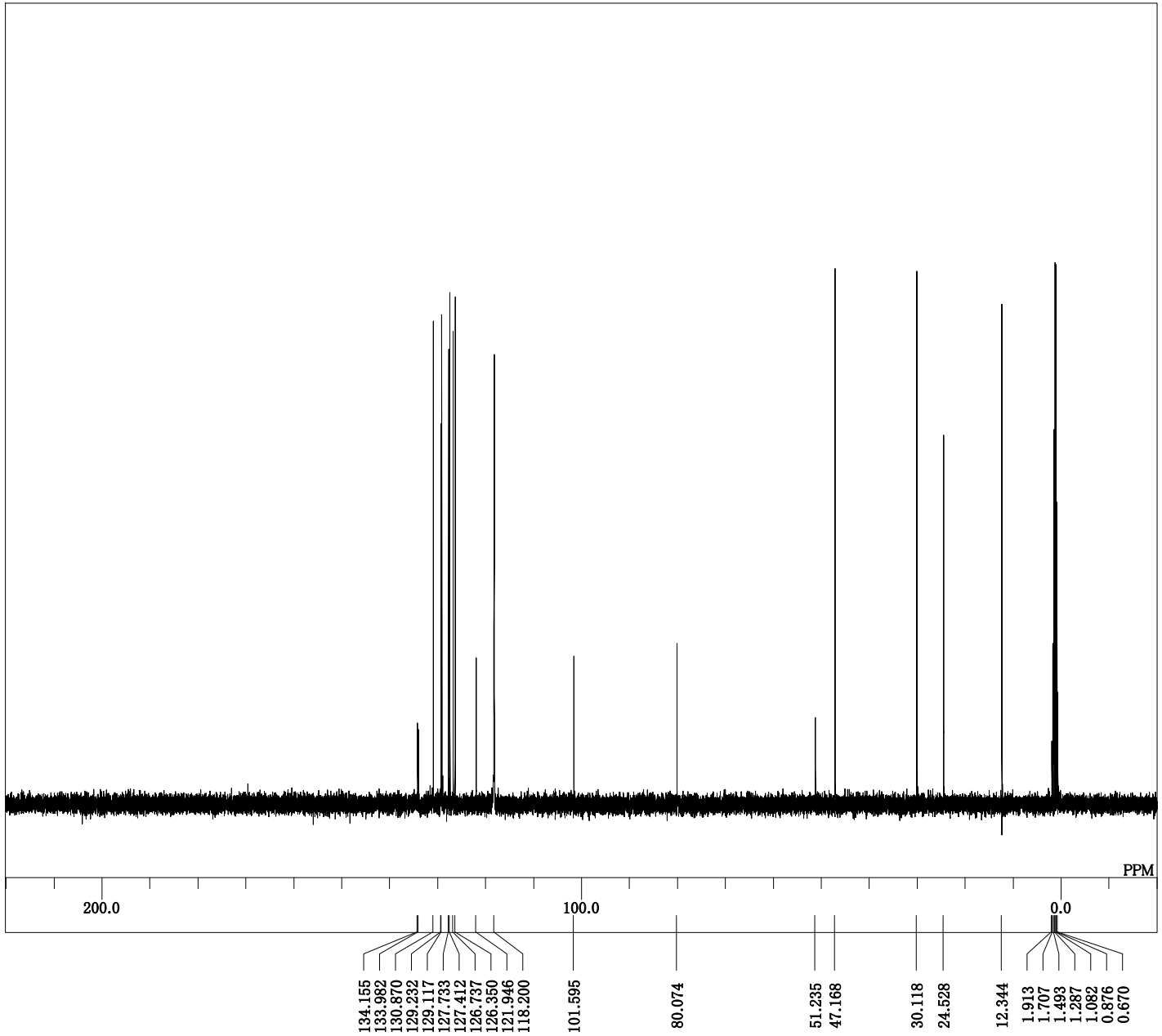

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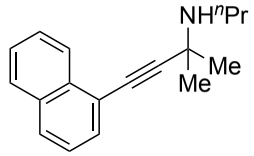
RGAIN	21



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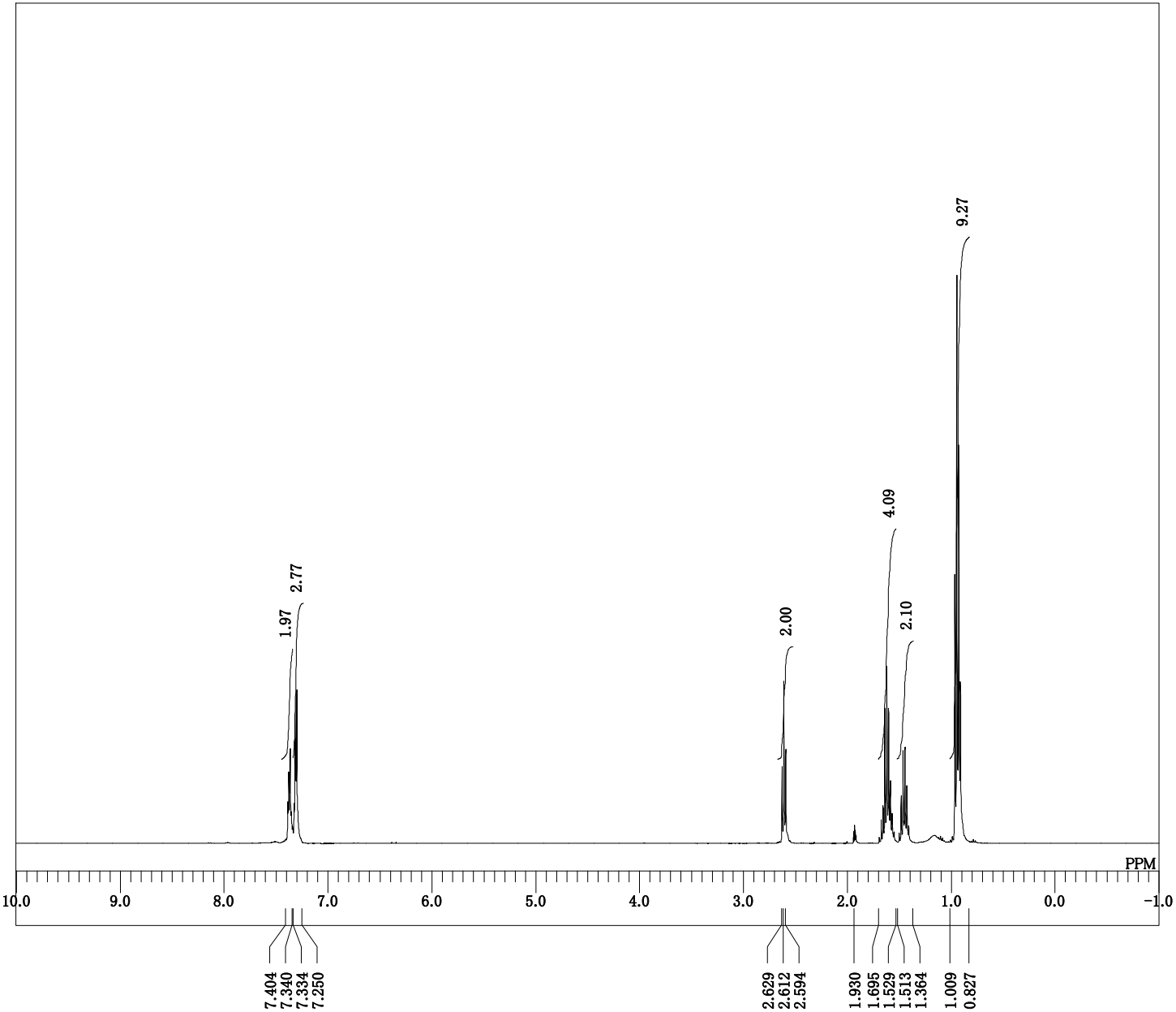

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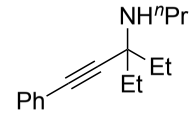
RGAIN 10



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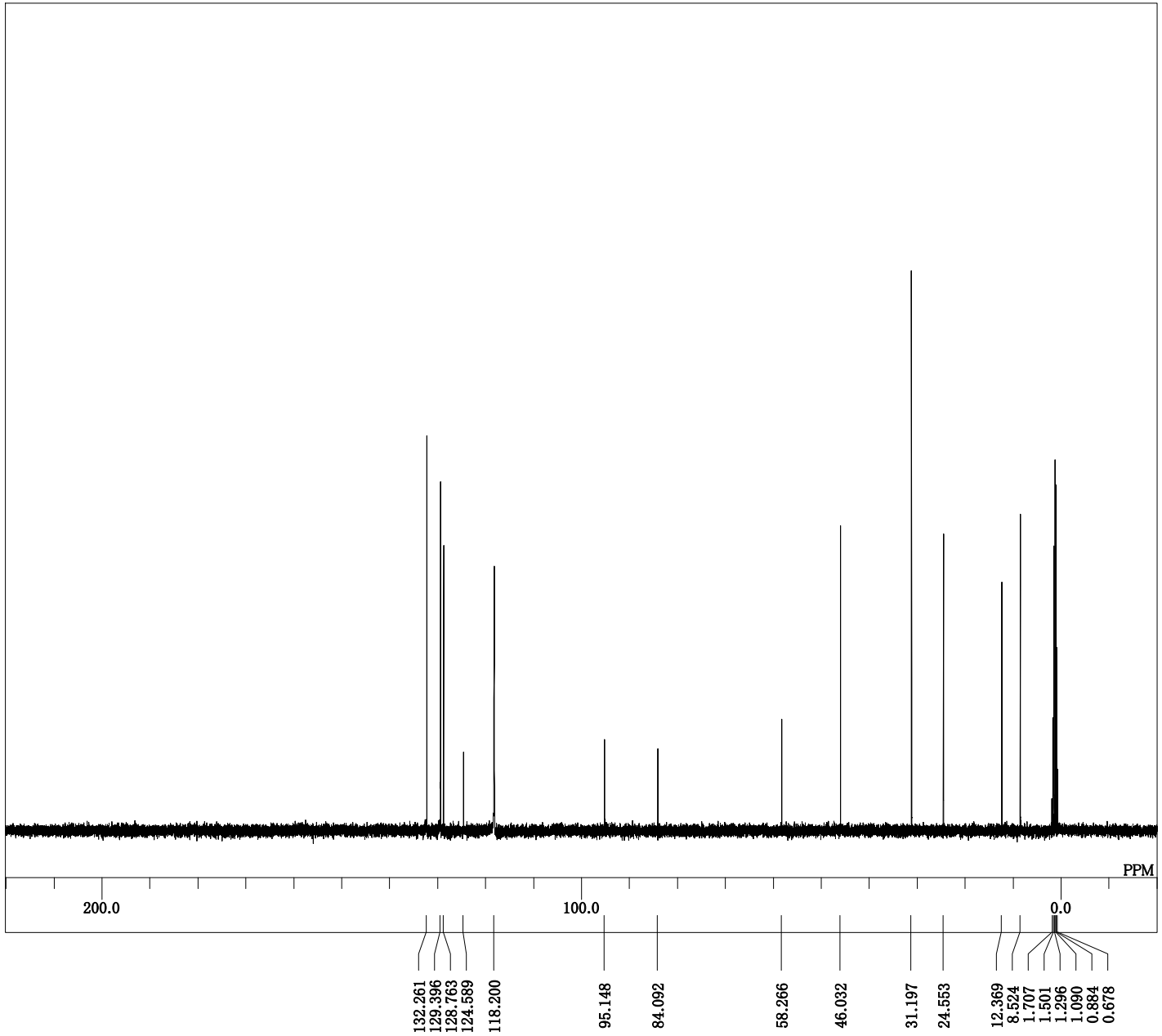

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CTEMP	6348.8 c
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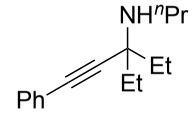
BF	0.12 Hz
RGAIN	21



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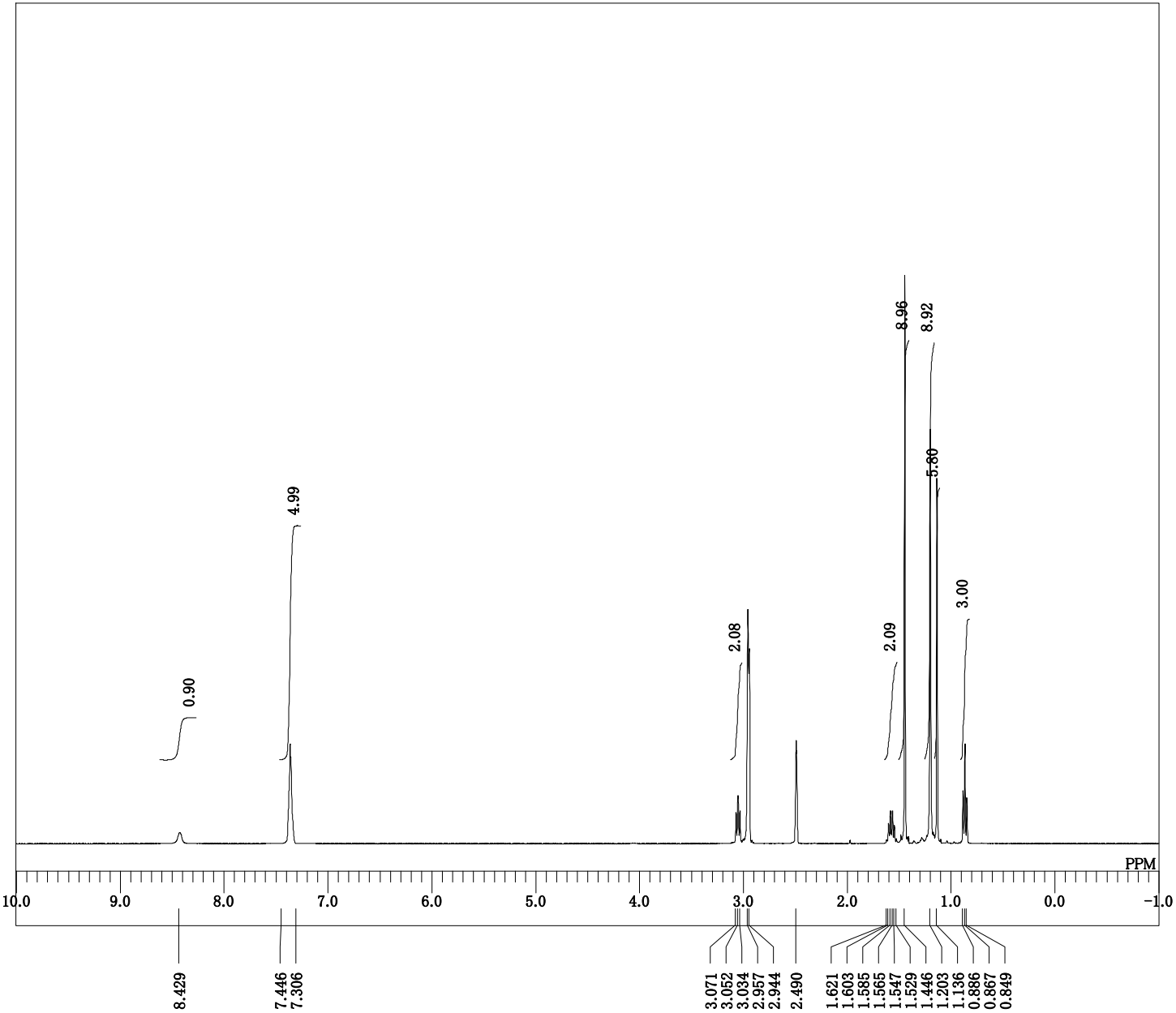
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CTEMP 110.0 c
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4.0
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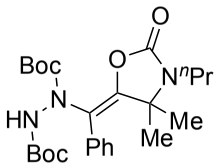
O
Boc
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nPr
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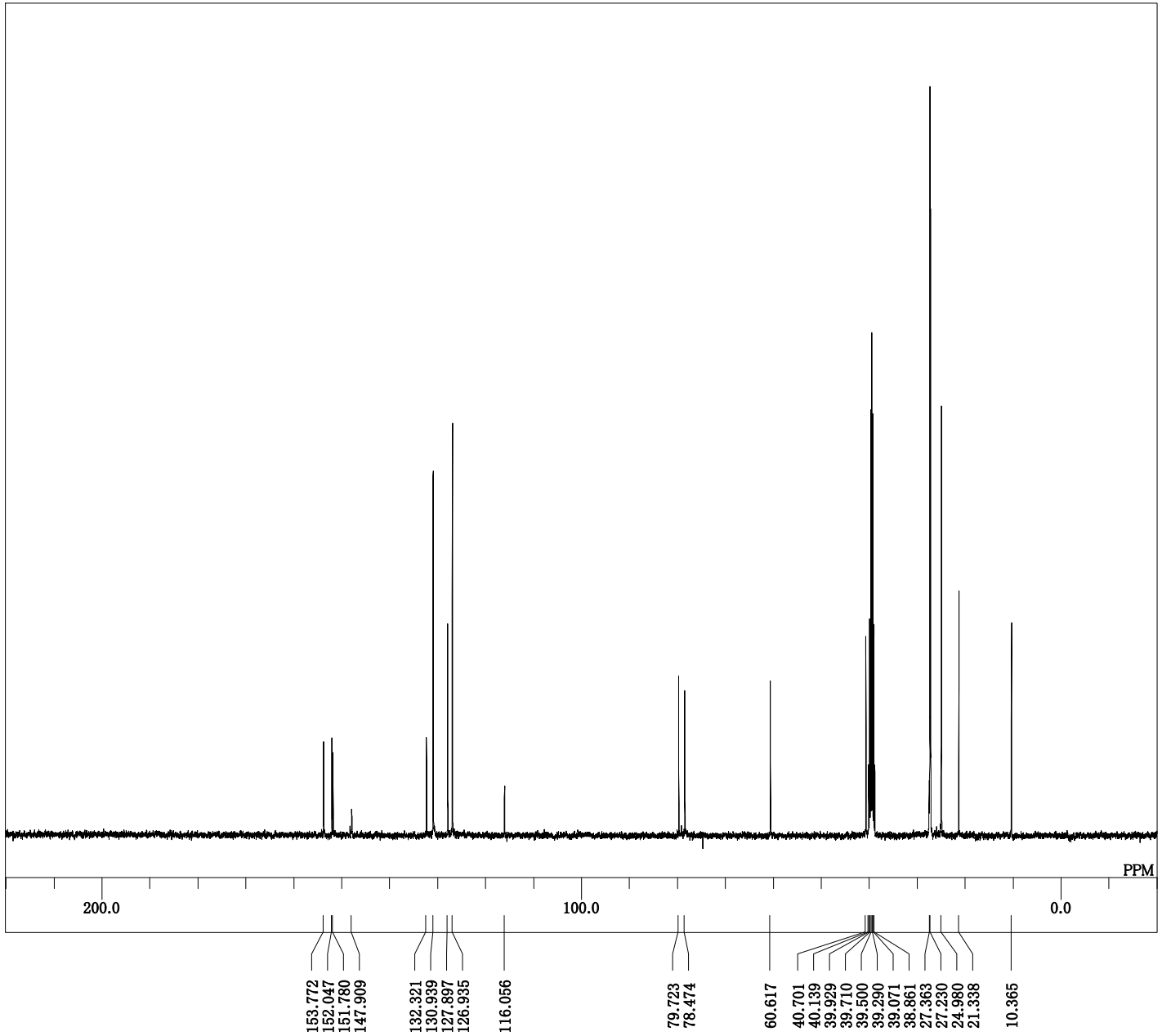
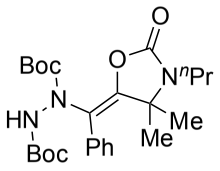
Me
Me
Ph
Boc

3aA



DFILE	20190418 amination_bcm_110deg-3
COMNT	single pulse decoupled gated NOE
DATIM	2019-04-18 18:48:08
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	98.52 MHz
OBSET	4.64 KHz
OBFIN	8.74 Hz
POINT	26224
FREQU	24630.17 Hz
SCANS	365
ACQTM	1.0643 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	107.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	36



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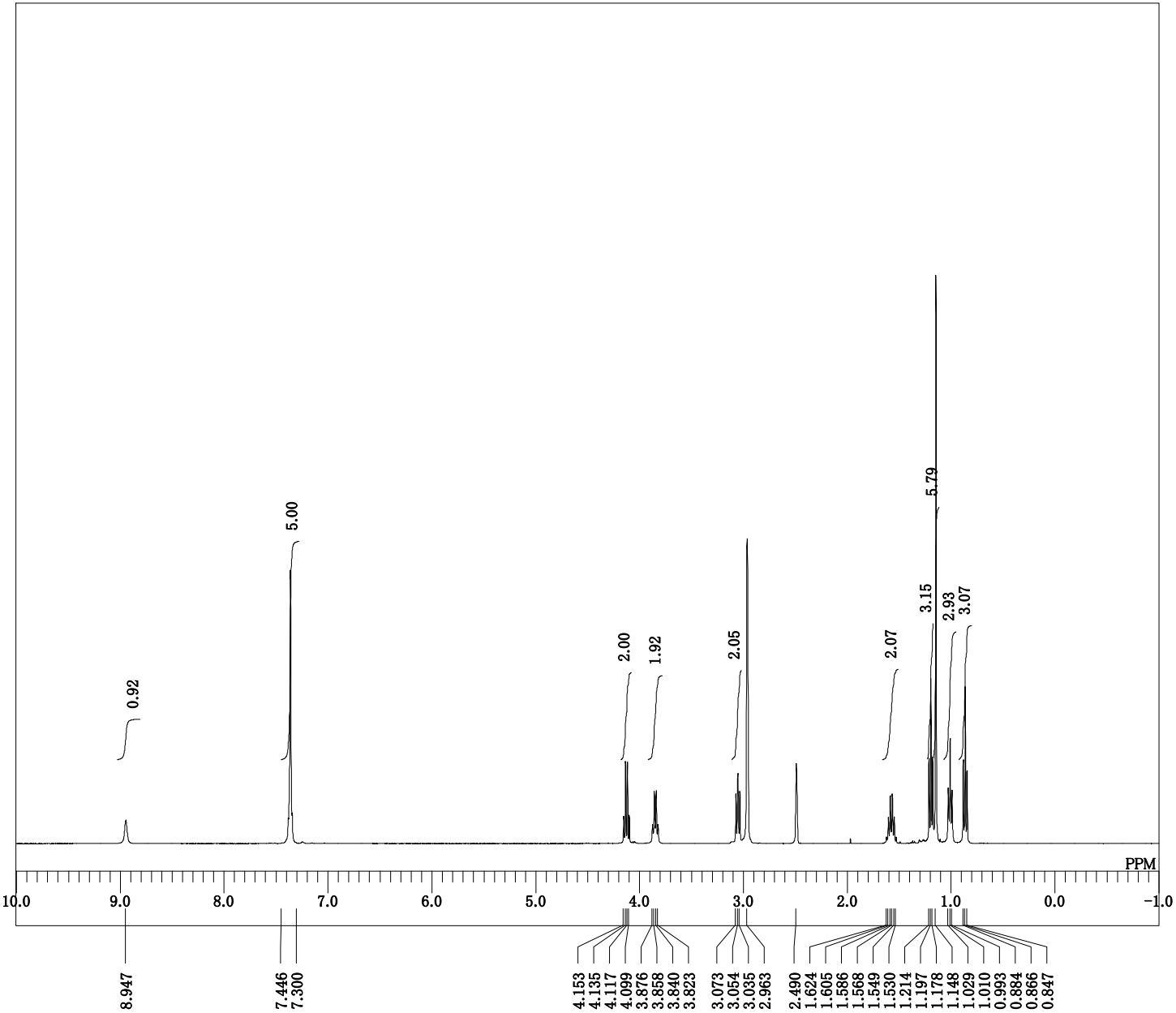
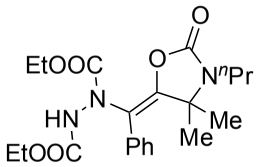
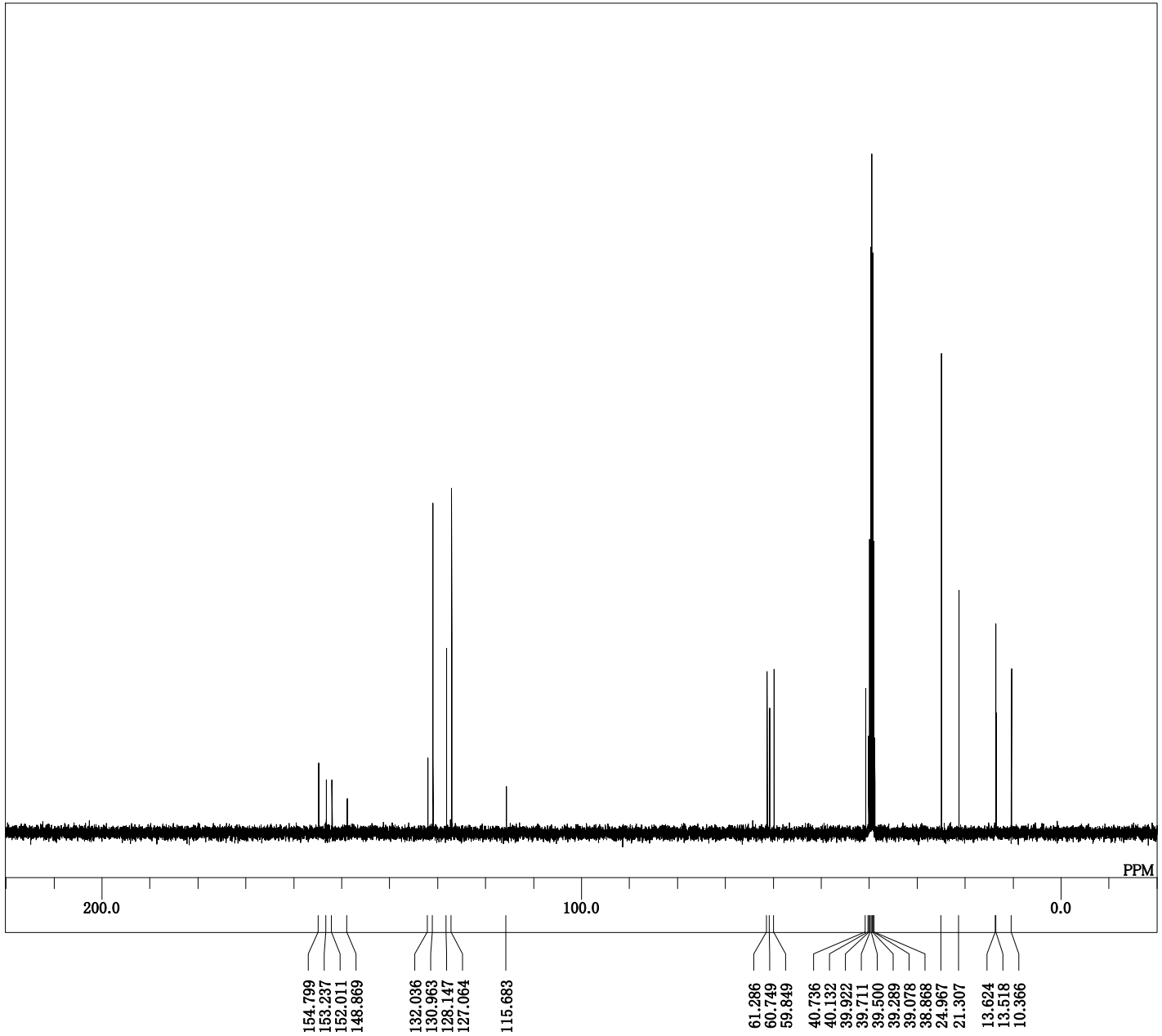


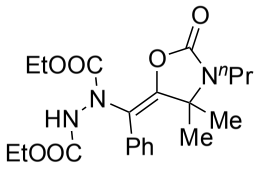
DFILE	20200225 Ph_DEAD_110deg_Proton
COMNT	single_pulse
DATIM	2020-02-25 13:36:24
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.24 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	3.14 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.42 Hz
RGAIN	24



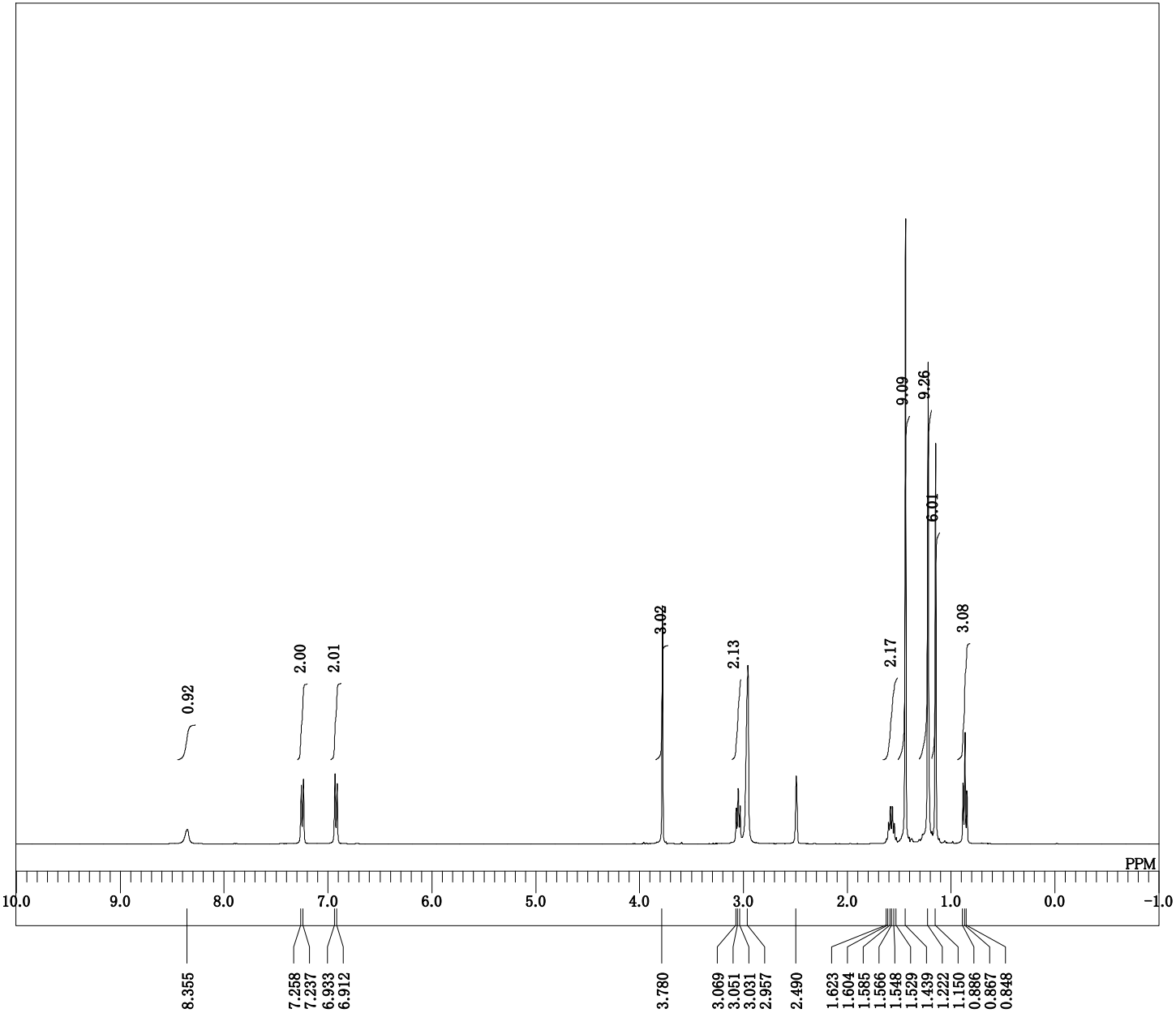
3aB



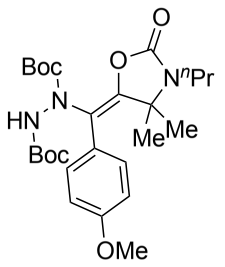
DFILE	20200225 Ph_DEAD_110deg_Carbo
COMNT	single pulse decoupled gated NOE
DATIM	2020-02-25 13:39:39
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	256
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60



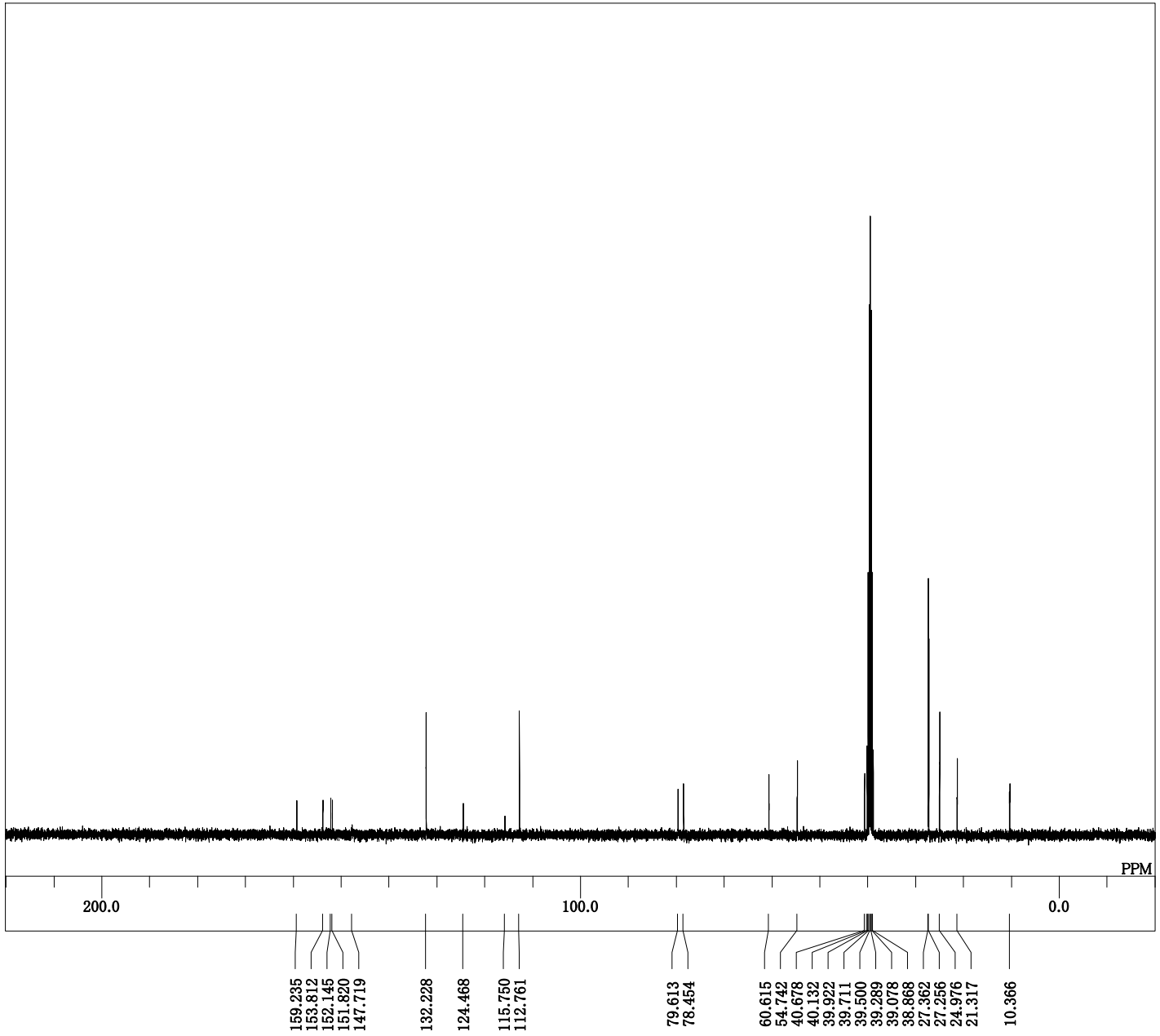
3aB



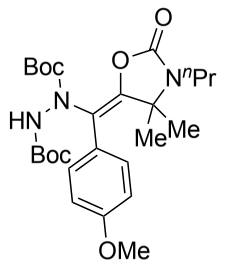
DFILE 20200222 OMe_DBAD_110deg_Prot
COMNT single_pulse
DATIM 2020-02-21 20:06:60
OBNUC 1H
EXMOD proton.jxp
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 16384
FREQU 7422.80 Hz
SCANS 8
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 3.14 usec
IRNUC 1H
CTEMP 110.0 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.42 Hz
RGAIN 22



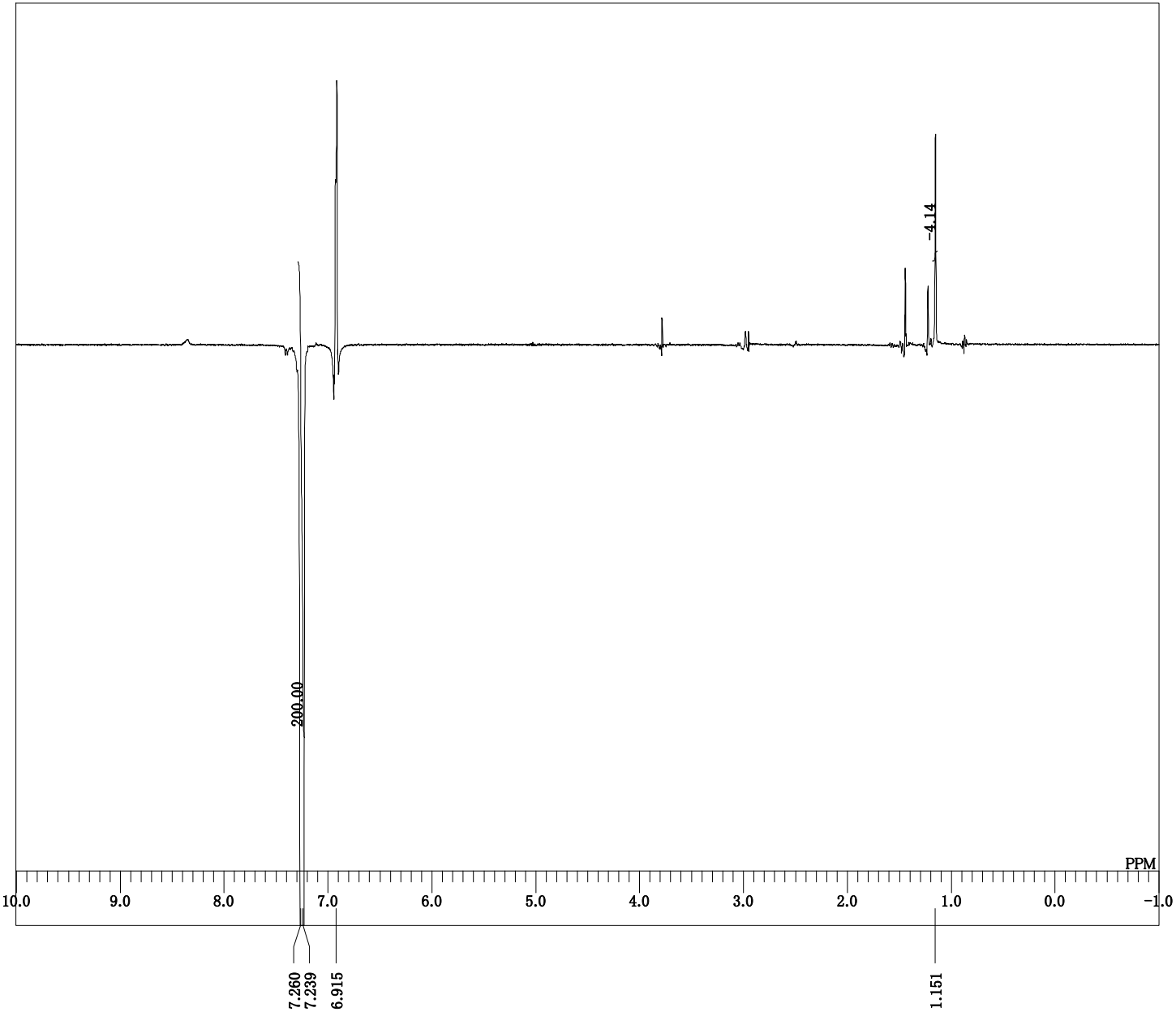
3bA



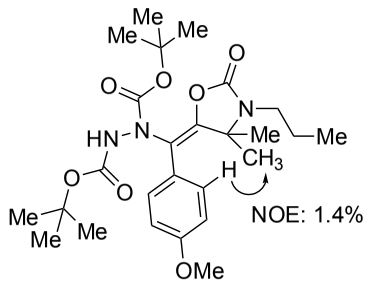
DFILE	20200327 OMe_DBAD_110deg_Carl
COMNT	single pulse decoupled gated NOE
DATIM	2020-03-27 17:47:02
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	512
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60



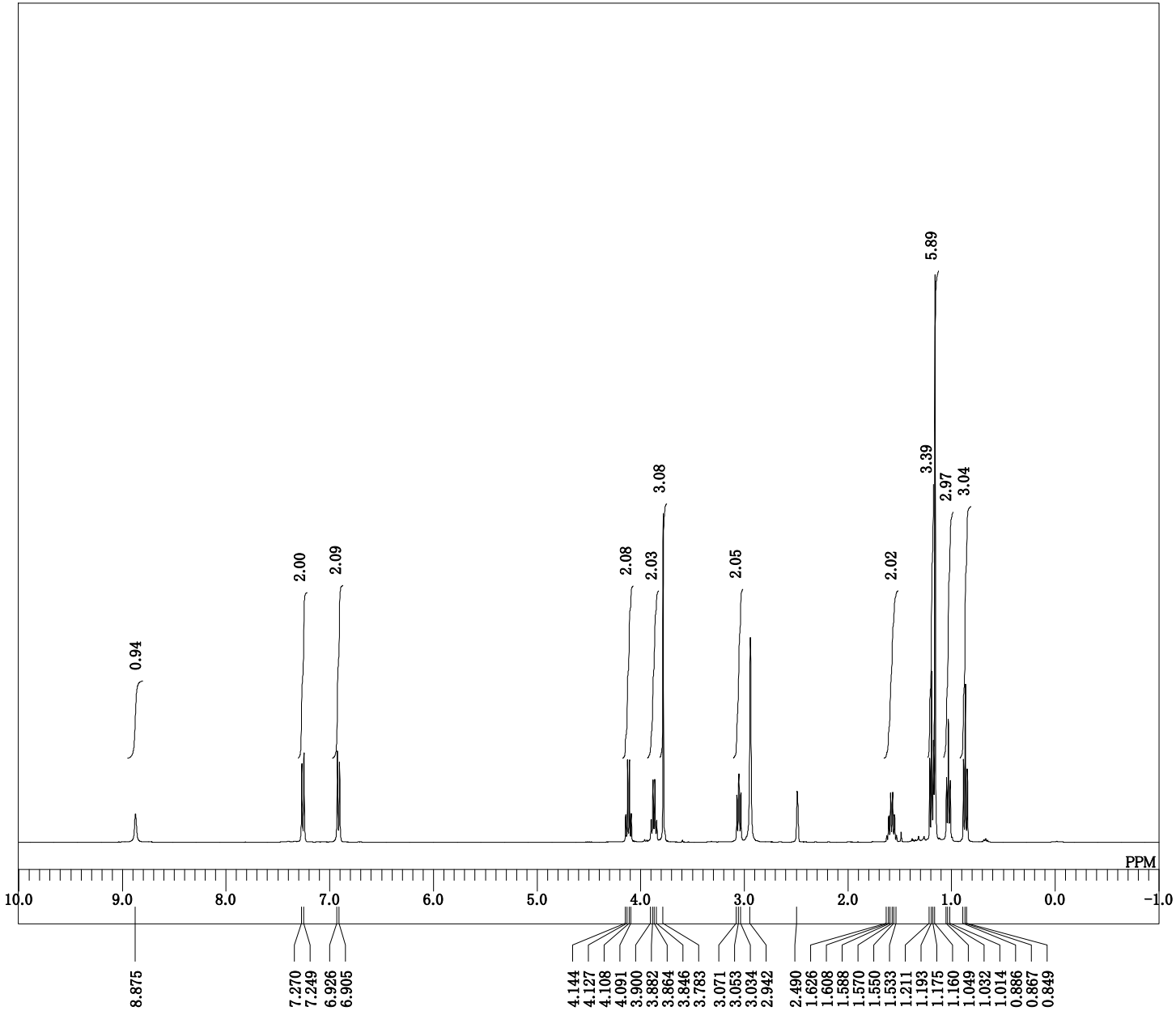
3bA



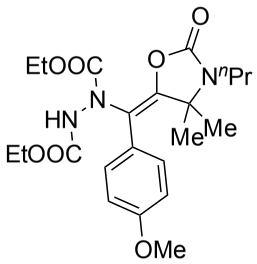
DFILE	20200222 OMe_DBAD_110deg_noe_
COMNT	DPFGSE NOE 1D
DATIM	2020-02-21 20:13:13
OBNUC	1H
EXMOD	noe_1d_dpfgse.jx
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	16384
FREQU	7422.80 Hz
SCANS	64
ACQTM	2.2073 sec
PD	7.0000 sec
PW1	6.28 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	7.25 ppm
BF	0.42 Hz
RGAIN	22



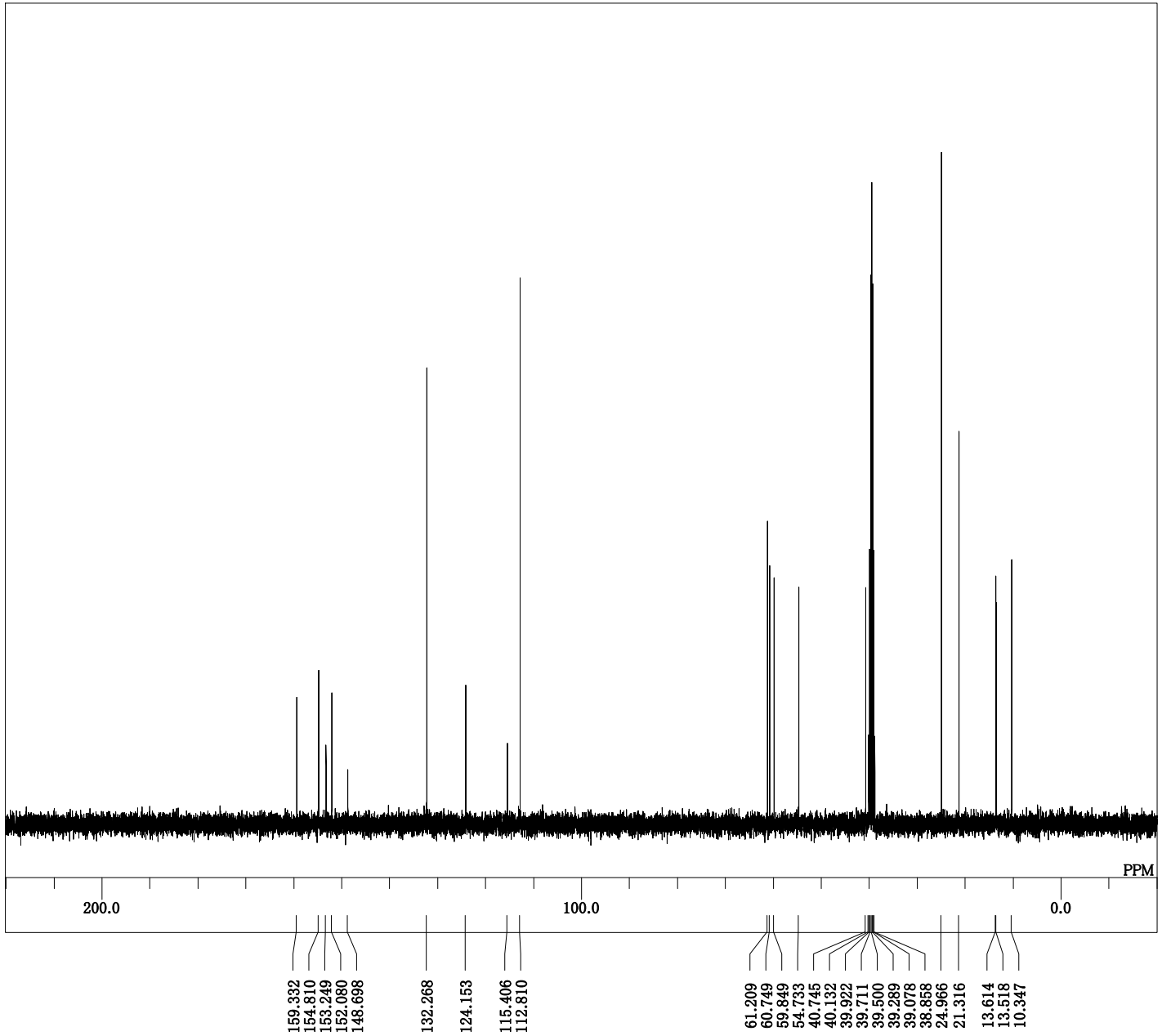
3bA



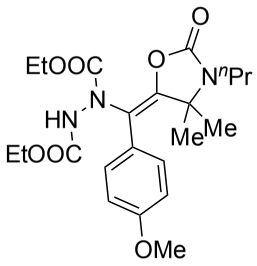
DFILE	OMe_DEAD_110deg_Proton-1-1.als
COMNT	single_pulse
DATIM	2019-11-28 13:44:08
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.24 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	3.14 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.42 Hz
RGAIN	22



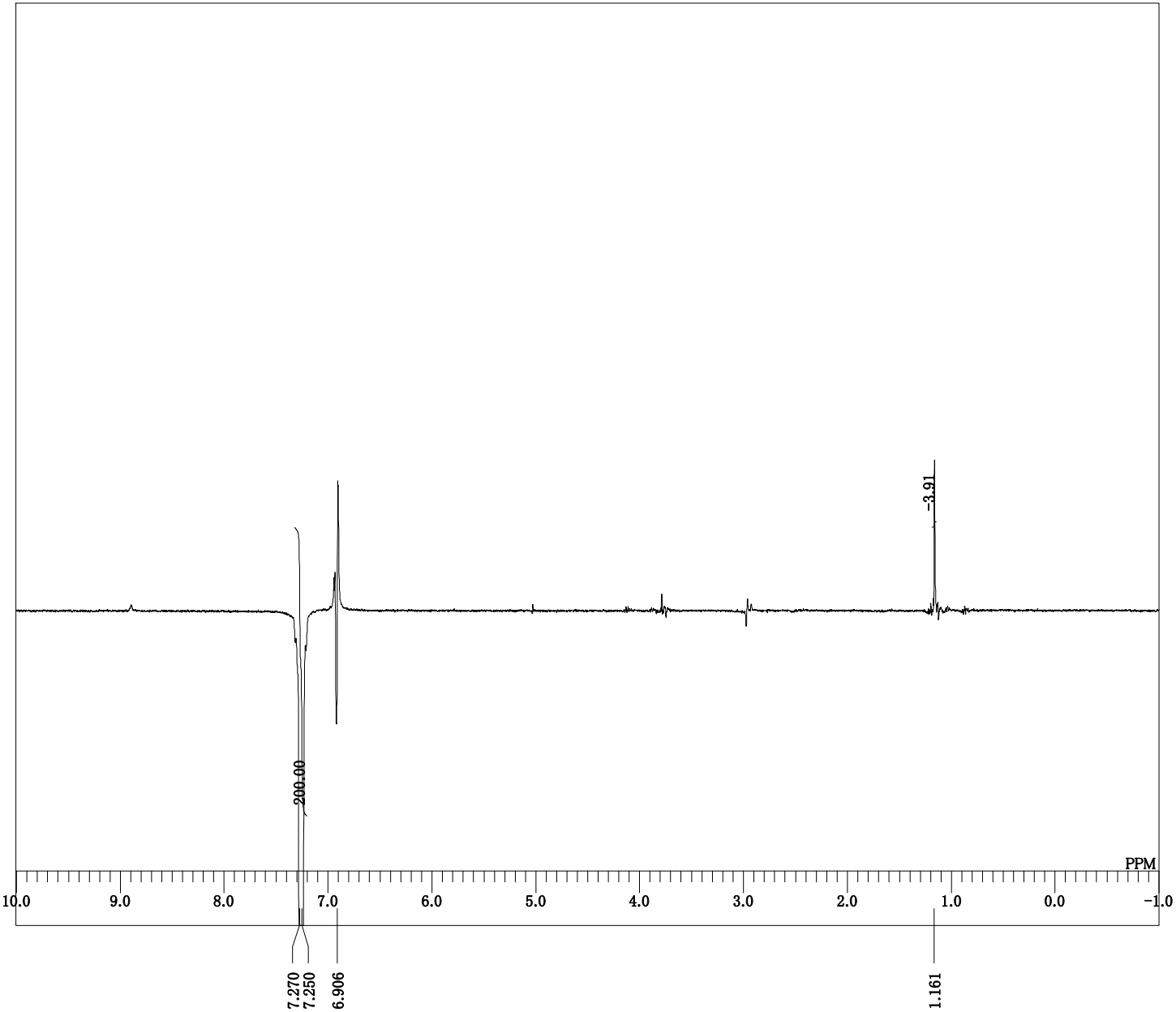
3bB



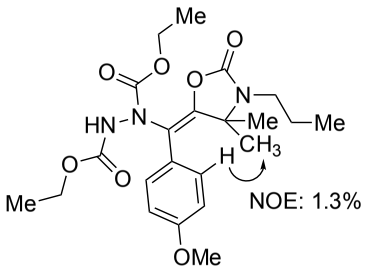
DFILE	OMe_DEAD_110deg_Carbon-1-1.al
COMNT	single pulse decoupled gated NOE
DATIM	2019-11-28 13:47:25
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	25000.00 Hz
SCANS	130
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60



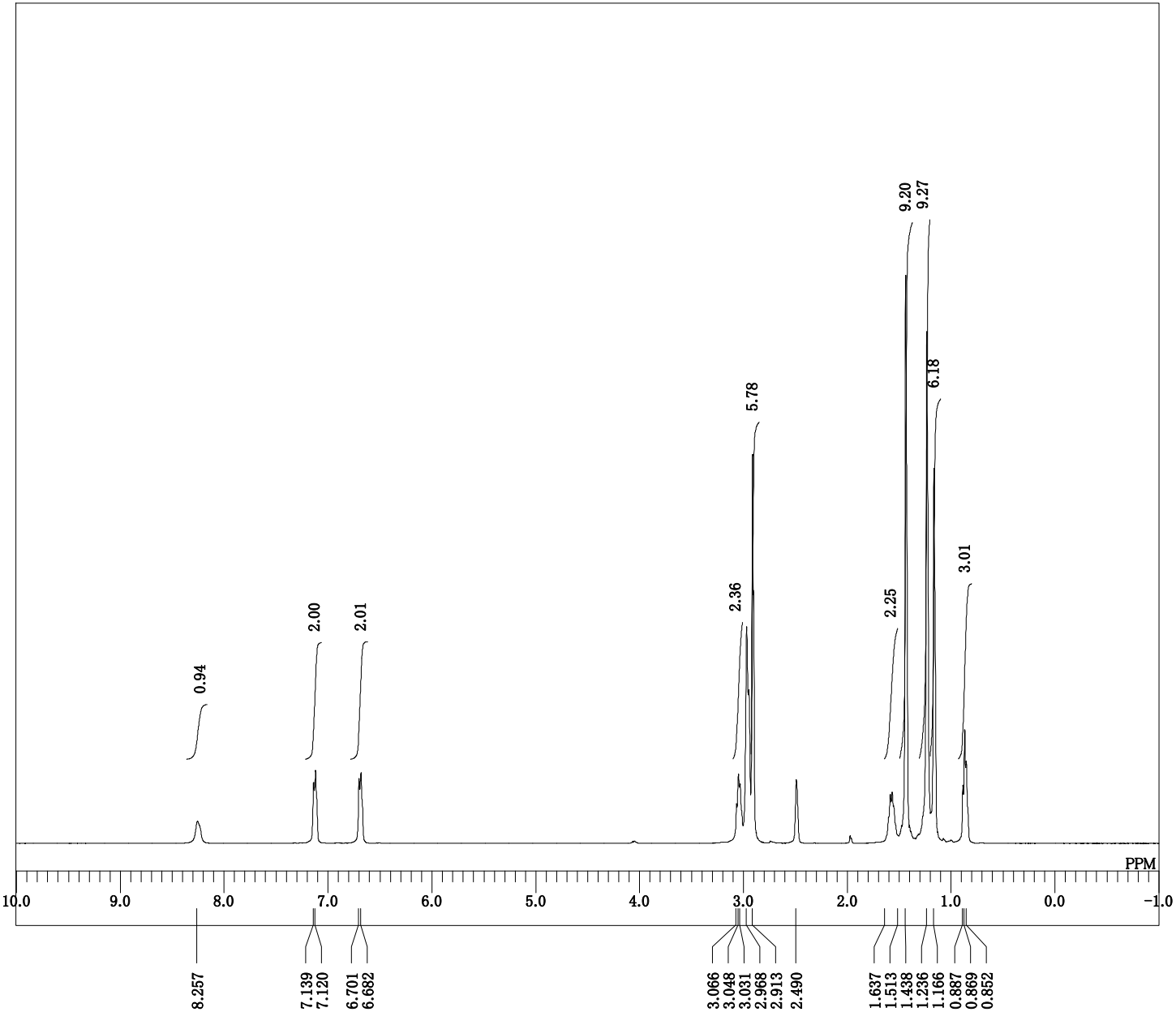
3bB



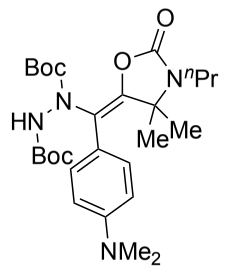
DFILE	20191205 OMeDEAD_noe-1.als
COMNT	DPFGSE NOE 1d
DATIM	2019-12-05 12:54:22
OBNUC	1H
EXMOD	noe_1d_dpfgse.ex
OBFRQ	391.78 MHz
OBSET	8.51 KHz
OBFIN	3.34 Hz
POINT	16384
FREQU	7352.94 Hz
SCANS	64
ACQTM	2.2282 sec
PD	7.0000 sec
PW1	11.80 usec
IRNUC	1H
CTEMP	109.9 c
SLVNT	DMSO
EXREF	7.26 ppm
BF	0.42 Hz
RGAIN	30



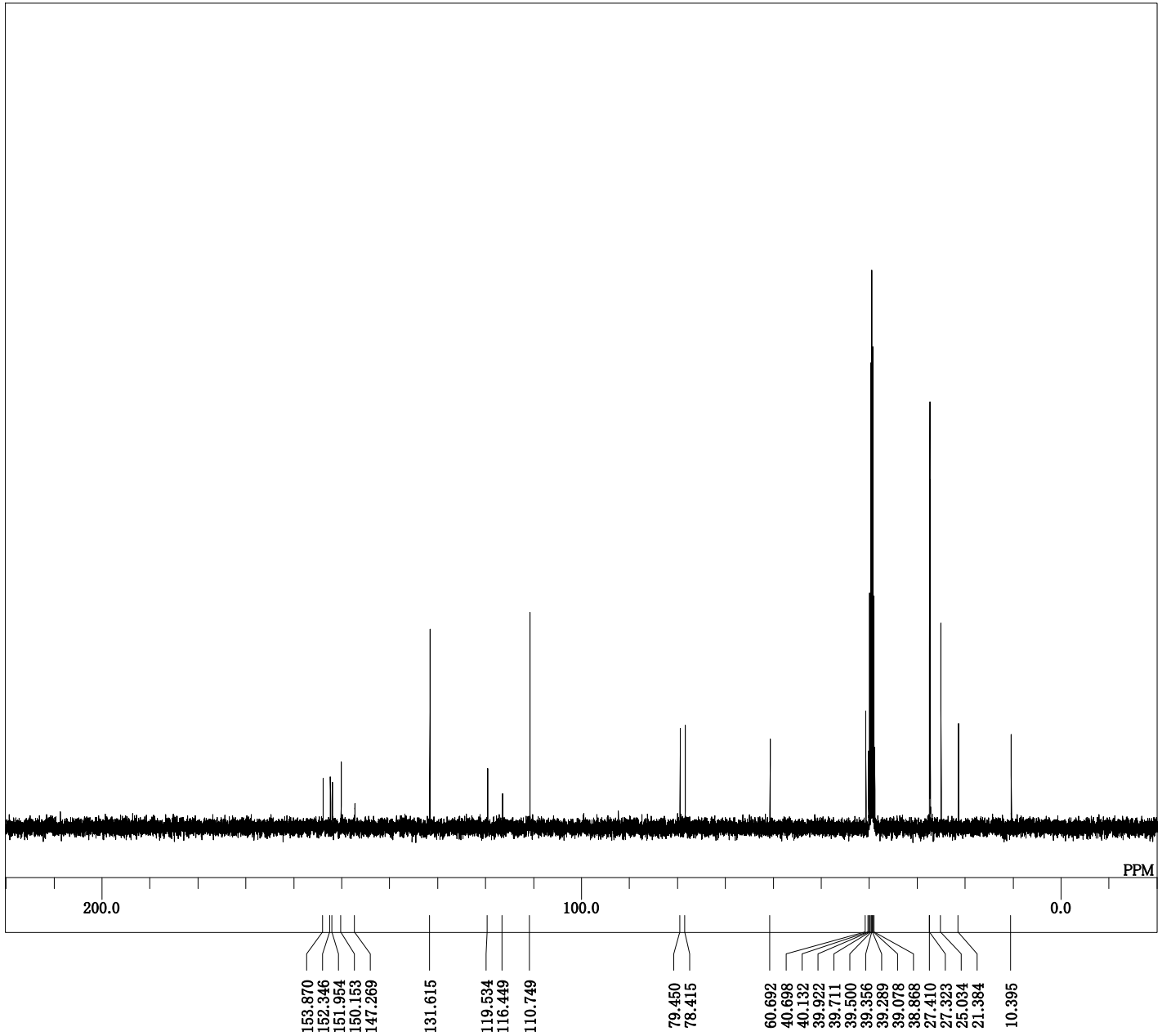
3bB



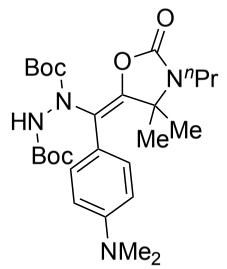
DFILE	20200220 DBAD_NMe2_110deg_Prc
COMNT	single_pulse
DATIM	2020-02-20 13:33:37
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.24 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	3.14 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.42 Hz
RGAIN	20



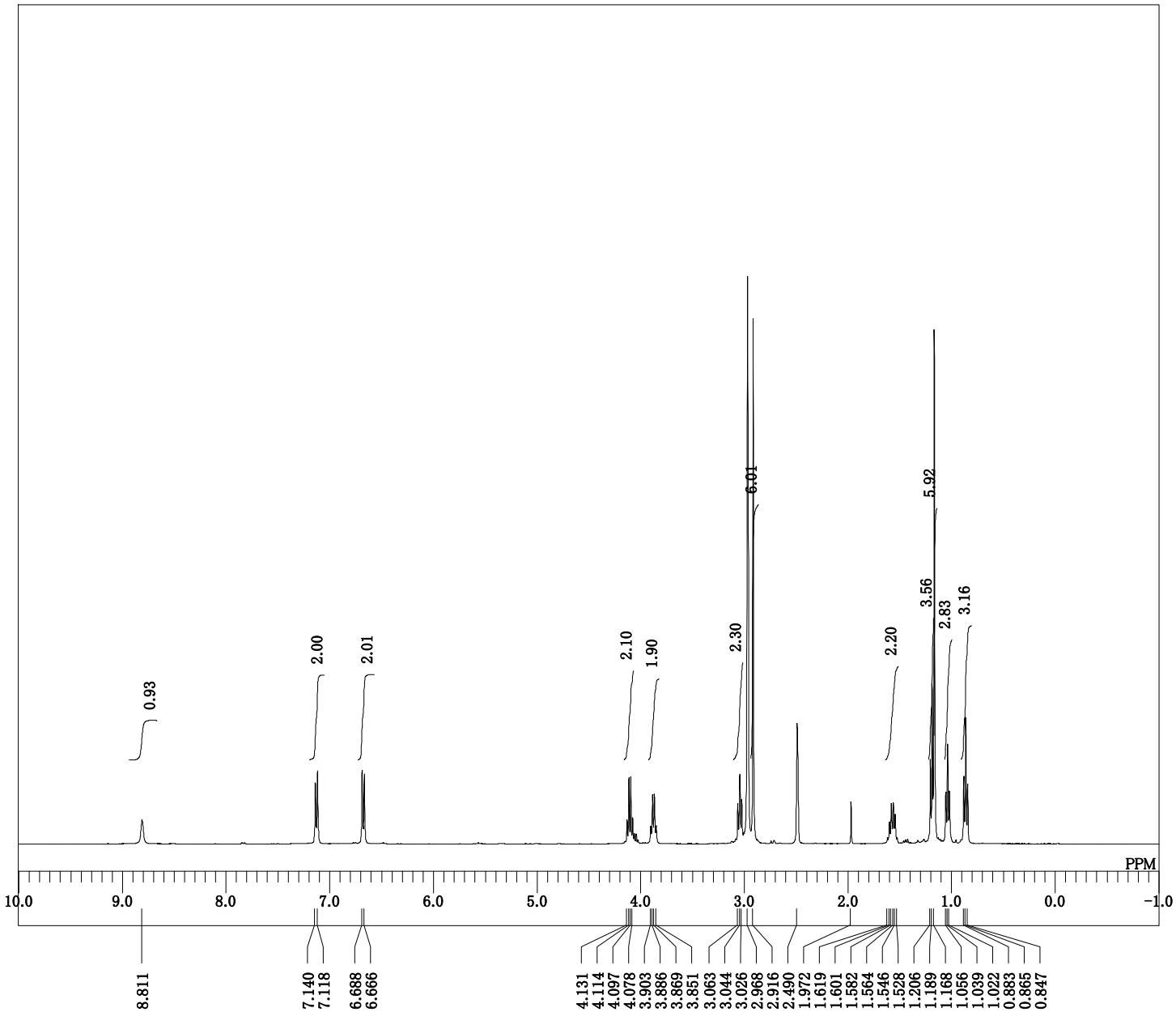
3cA



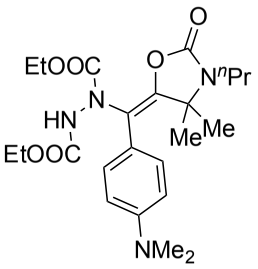
DFILE	20200220 DBAD_NMe2_110deg_Ca
COMNT	single pulse decoupled gated NOE
DATIM	2020-02-20 13:36:45
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	127
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60



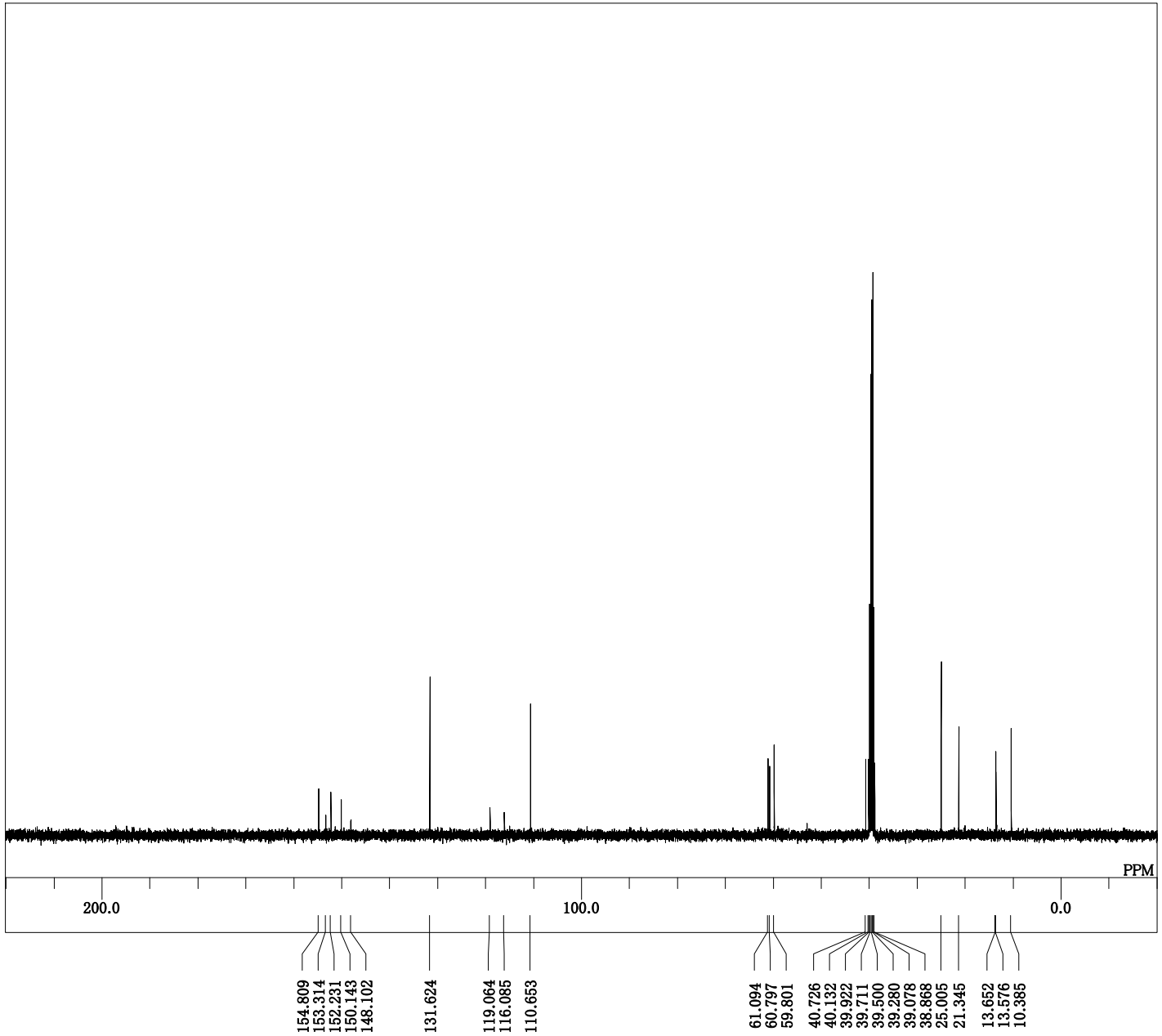
3cA



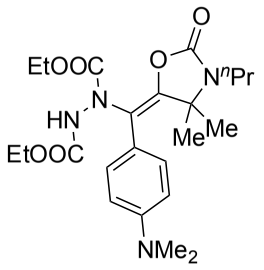
DFILE 20200217 DEAD_NMe2_110deg_Prc
COMNT single_pulse
DATIM 2020-02-17 16:54:08
OBNUC 1H
EXMOD proton.jxp
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.24 Hz
SCANS 8
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 3.14 usec
IRNUC 1H
CTEMP 110.0 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.42 Hz
RGAIN 24



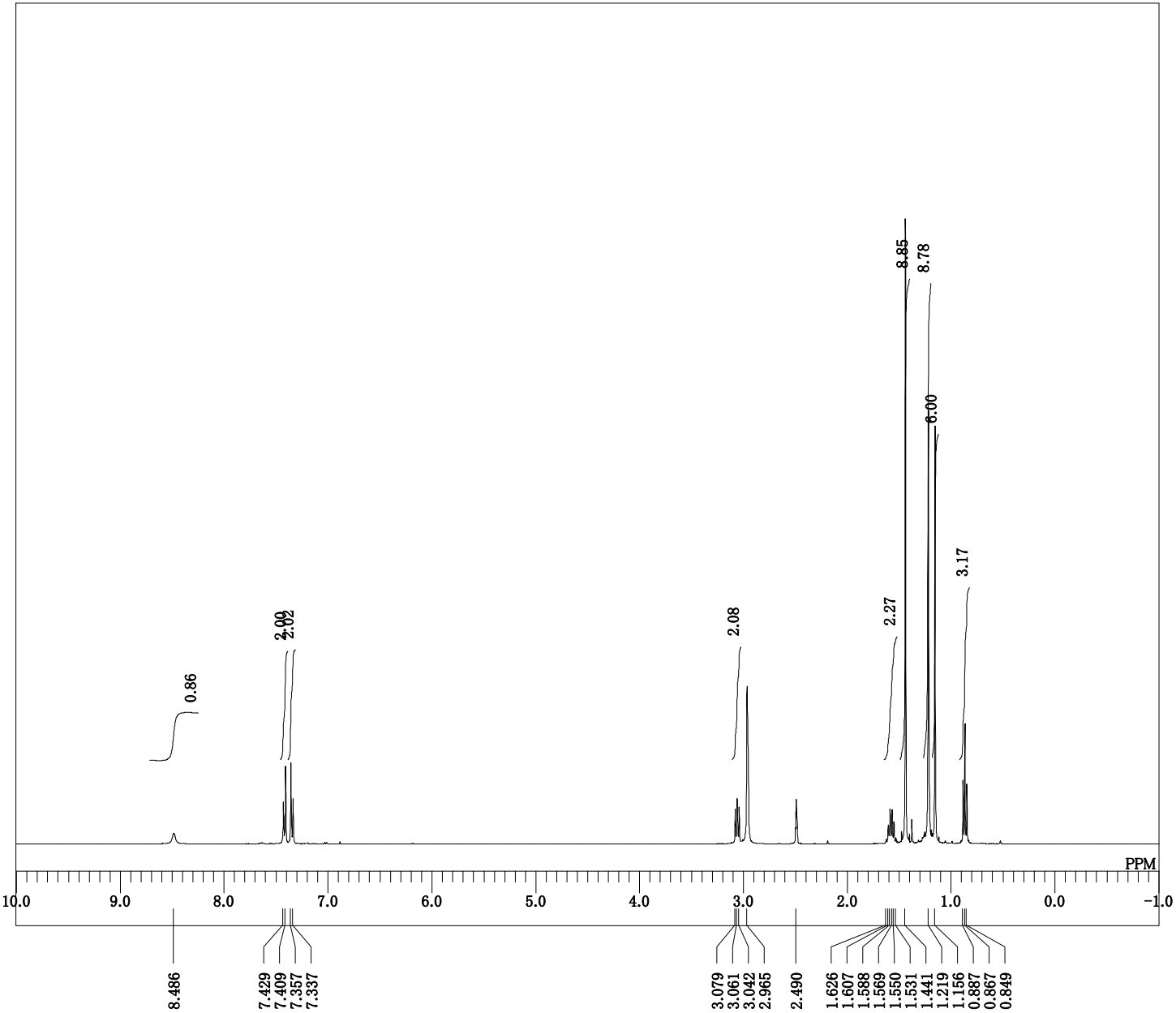
3cB



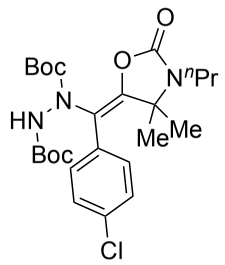
DFILE	20200217 DEAD_NMe2_110deg_Ca
COMNT	single pulse decoupled gated NOE
DATIM	2020-02-17 16:57:24
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	256
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60



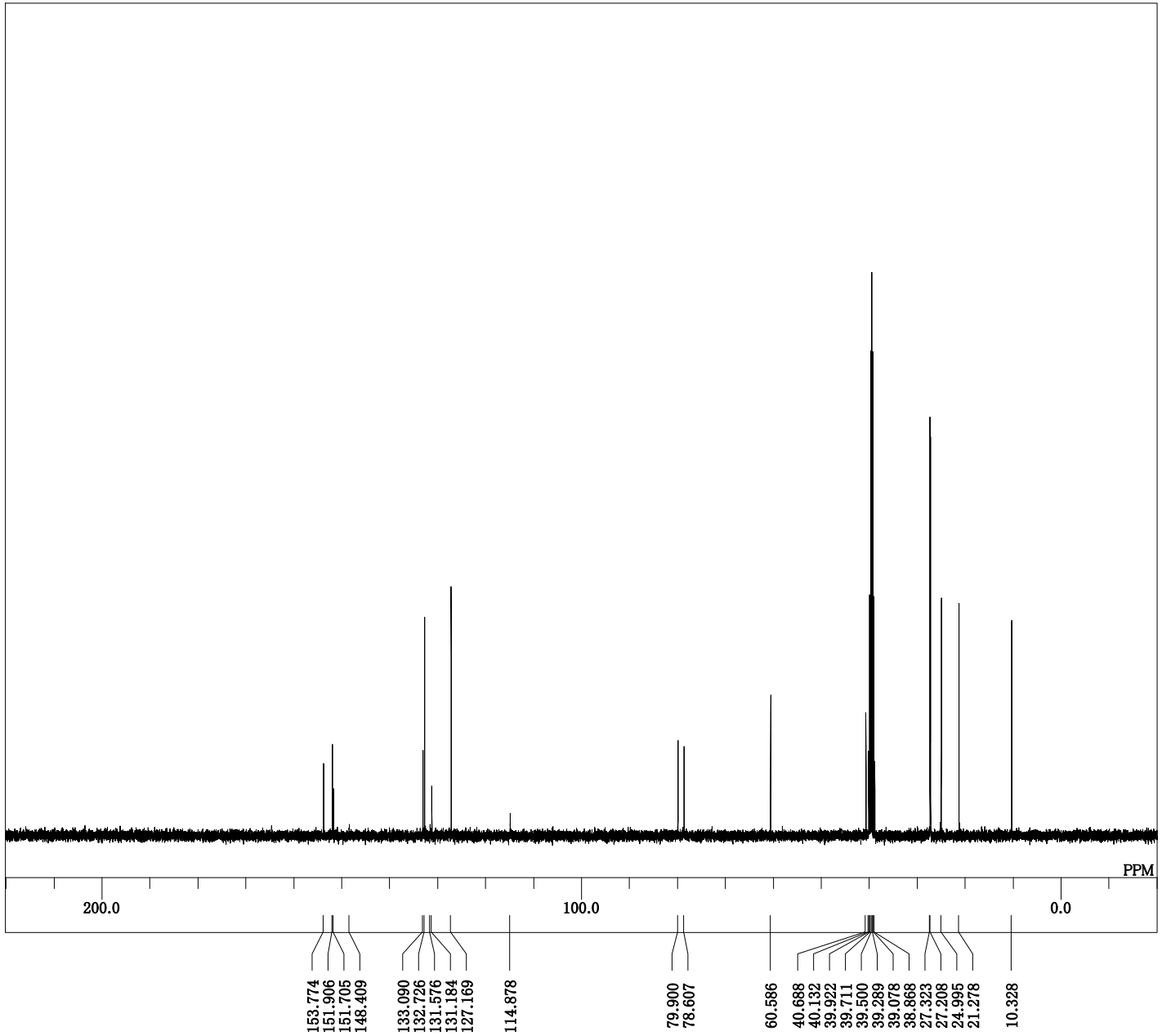
3cB



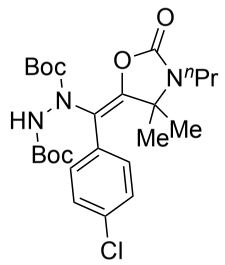
DFILE 20200307 Cl_DBAD_110deg_Proton
COMNT single_pulse
DATIM 2020-03-07 17:59:32
OBNUC 1H
EXMOD proton.jxp
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 16384
FREQU 7422.80 Hz
SCANS 8
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 3.14 usec
IRNUC 1H
CTEMP 110.0 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.42 Hz
RGAIN 20



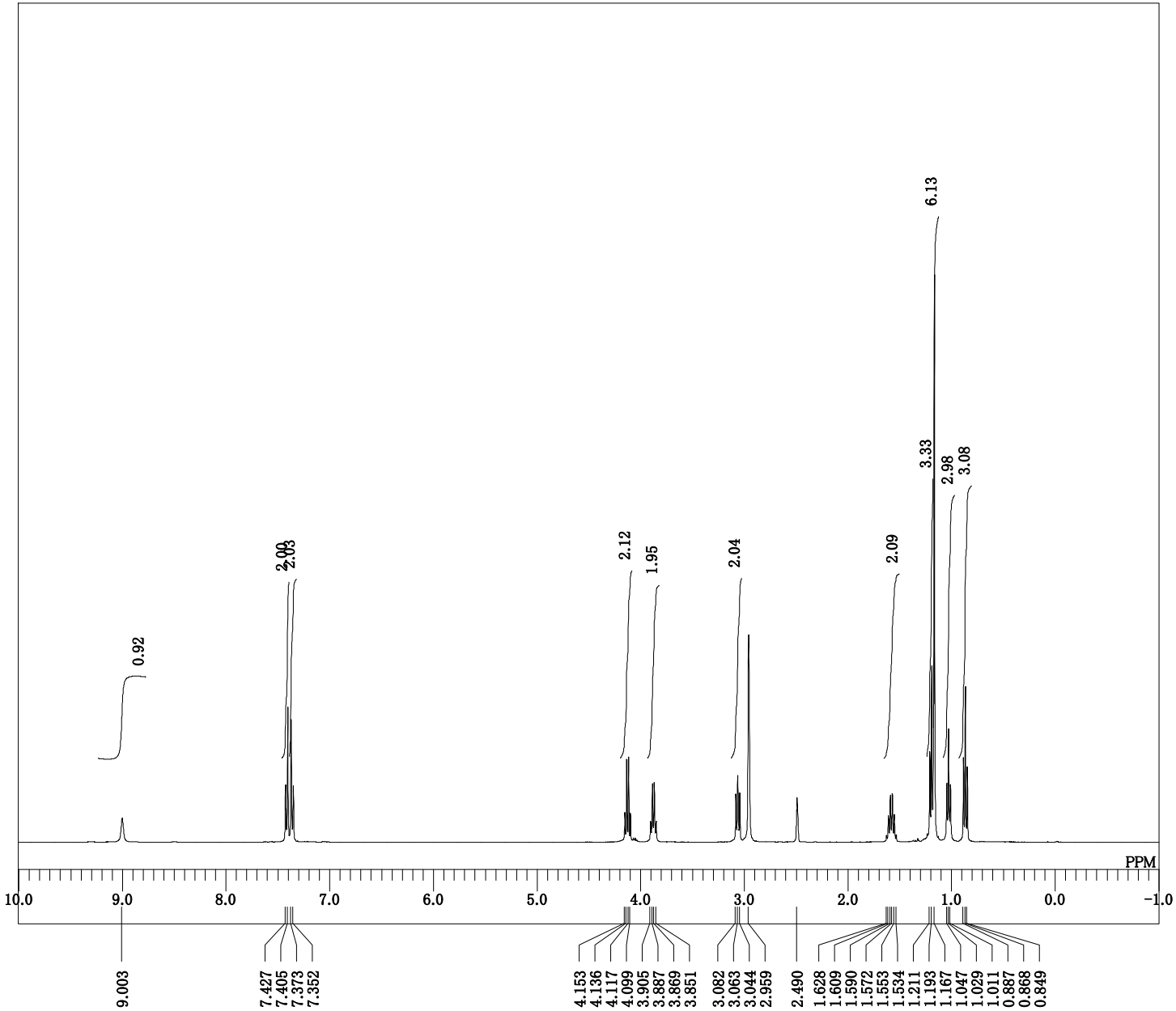
3dA



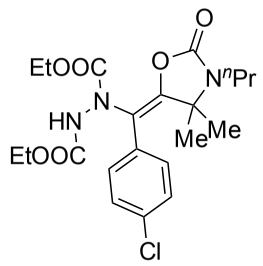
DFILE	20200317 Cl_DBAD_110deg_Carbor
COMNT	single pulse decoupled gated NOE
DATIM	2020-03-17 15:55:48
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	512
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.12 Hz
RGAIN	50



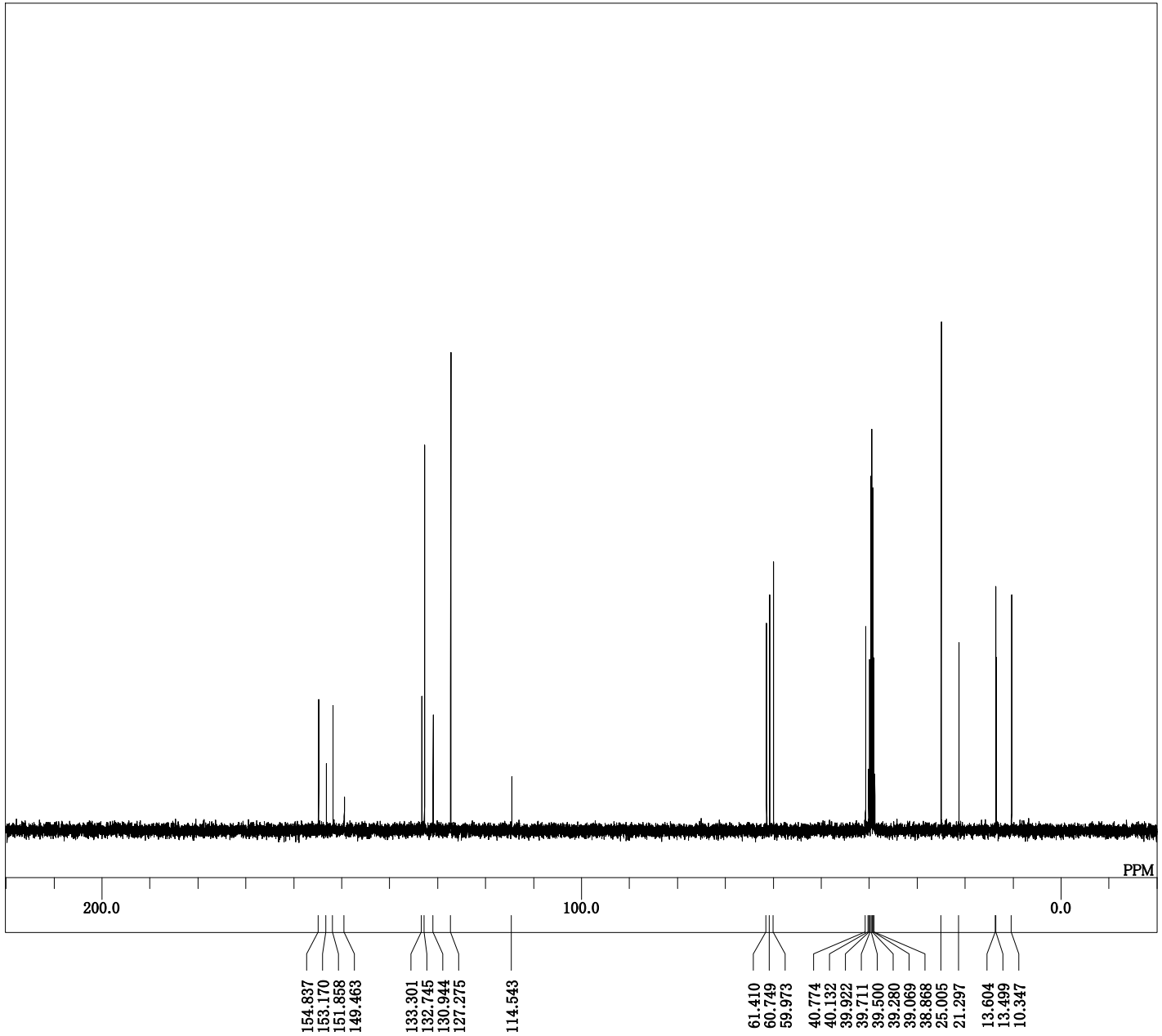
3dA



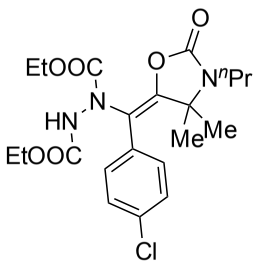
DFILE	20200218 DEAD_Cl_Proton-1-1.als
COMNT	single_pulse
DATIM	2020-02-18 19:05:43
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.24 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	3.14 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.42 Hz
RGAIN	20



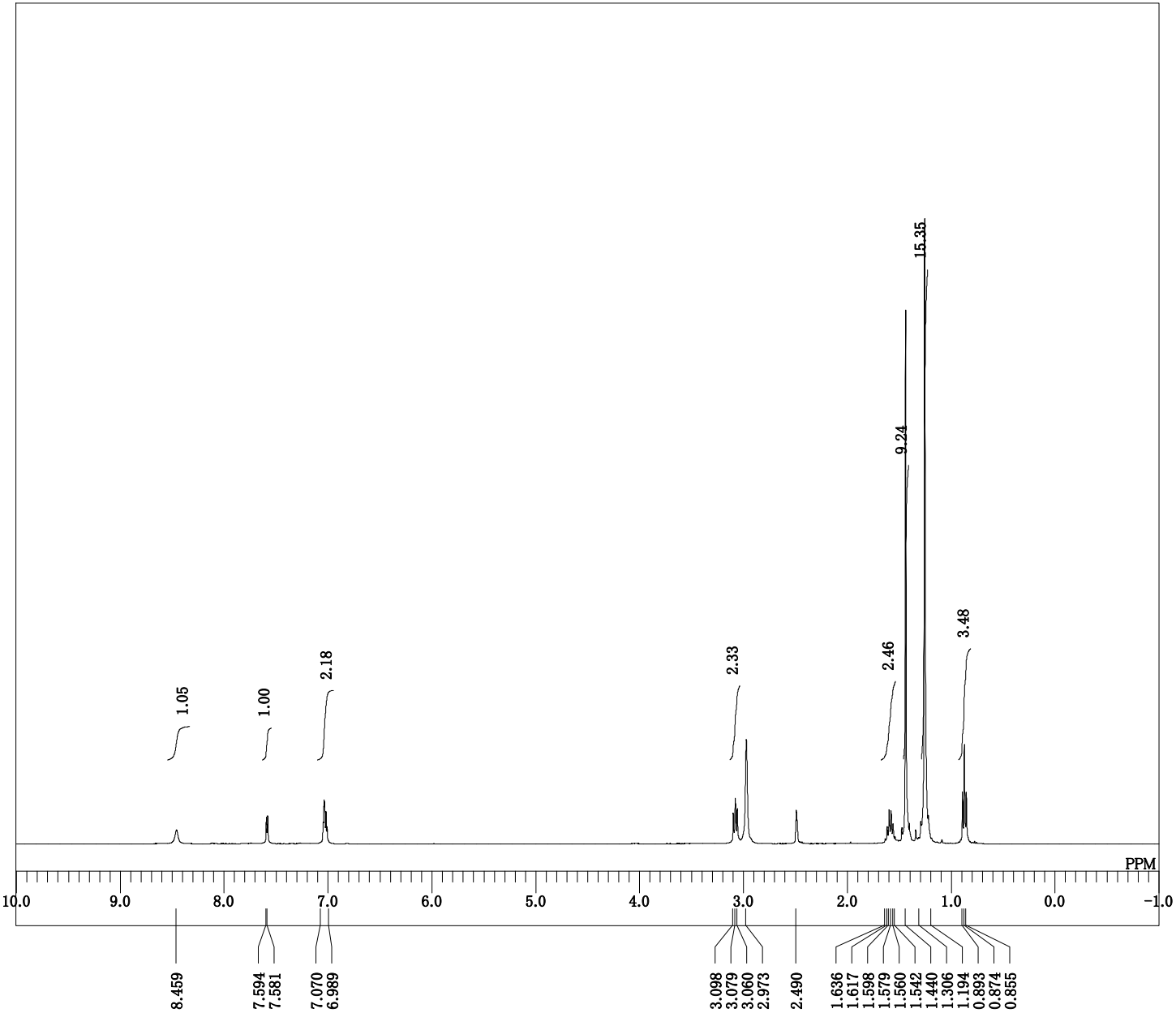
3dB



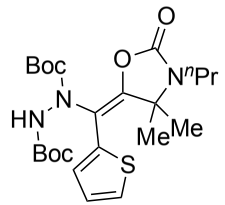
DFILE	20200218 DEAD_Cl_Carbon-1-1.al
COMNT	single pulse decoupled gated NOE
DATIM	2020-02-18 19:08:59
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	129
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60



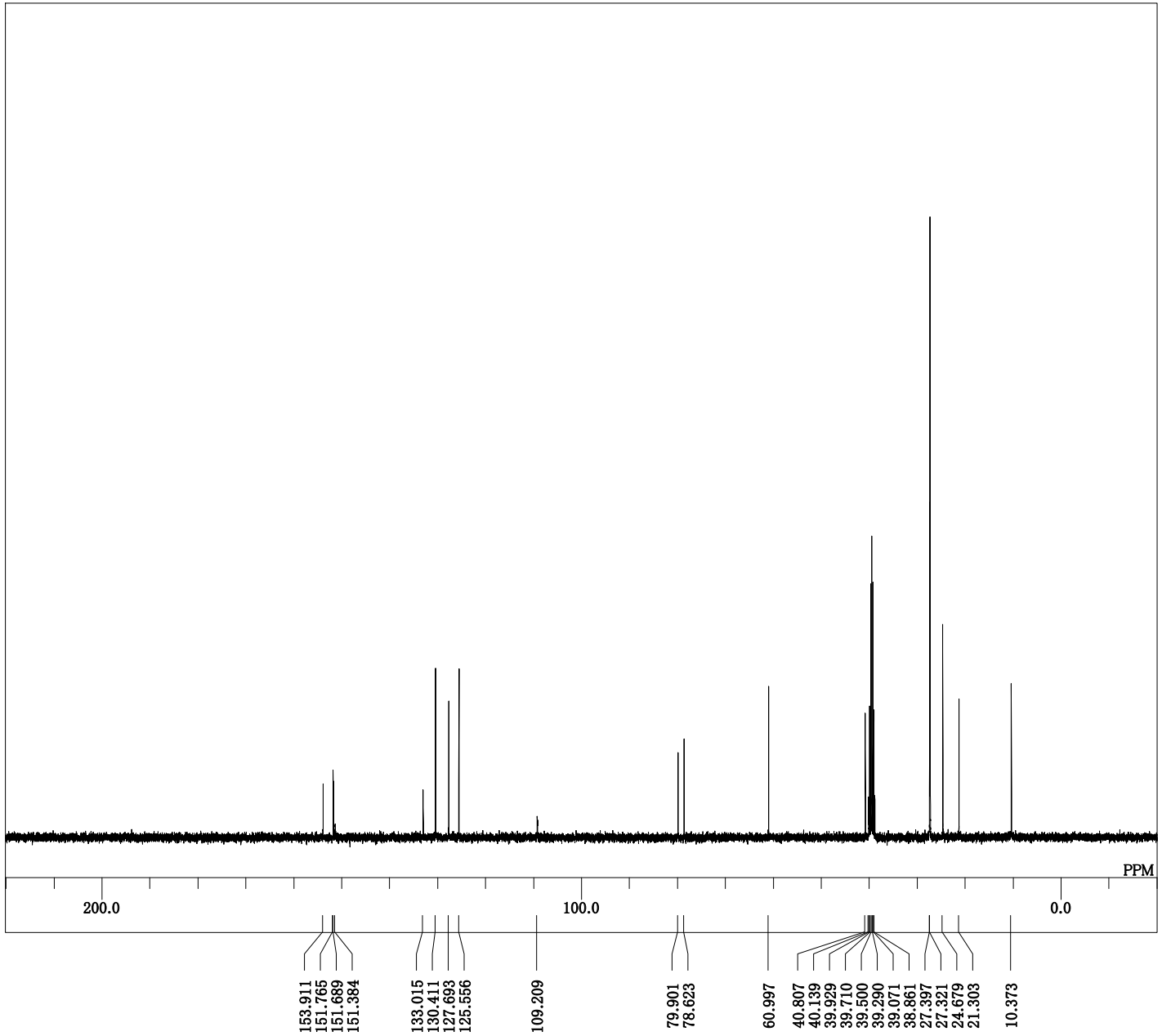
3dB



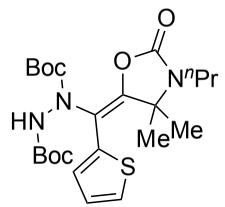
DFILE	20200220 DBAD_S_110deg-1.als
COMNT	single_pulse
DATIM	2020-02-20 14:02:45
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	391.78 MHz
OBSET	8.51 KHz
OBFIN	3.34 Hz
POINT	26214
FREQU	5882.26 Hz
SCANS	8
ACQTM	4.4564 sec
PD	3.0000 sec
PW1	5.90 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.42 Hz
RGAIN	30



3eA



DFILE	20200218 DBAD_S_110deg_bcm-1.a
COMNT	single pulse decoupled gated NOE
DATIM	2020-02-20 14:21:18
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	98.52 MHz
OBSET	4.64 KHz
OBFIN	8.74 Hz
POINT	32768
FREQU	30788.18 Hz
SCANS	256
ACQTM	1.0643 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	40



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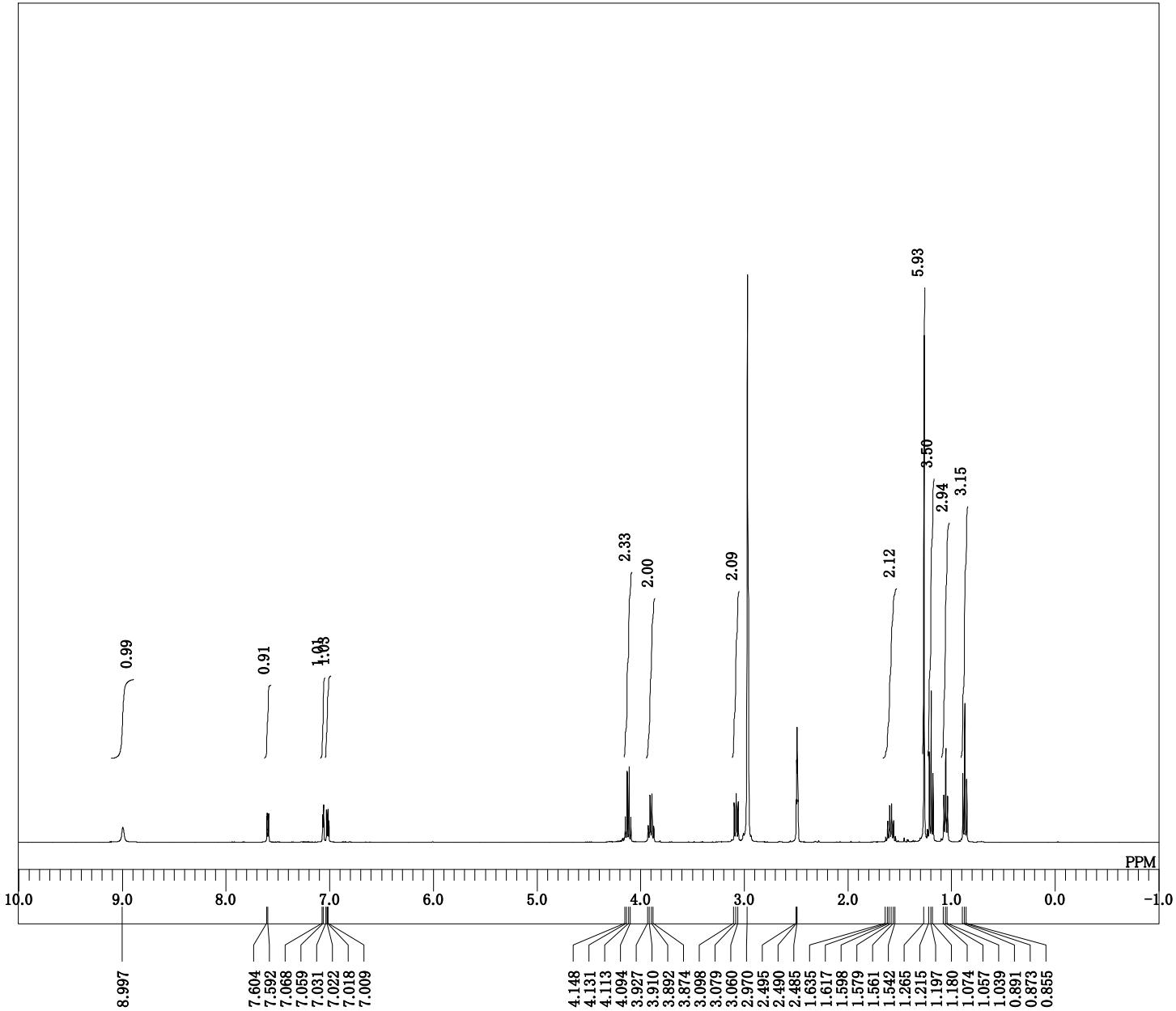
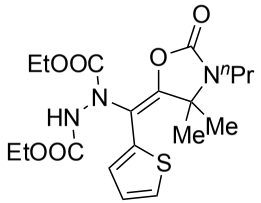
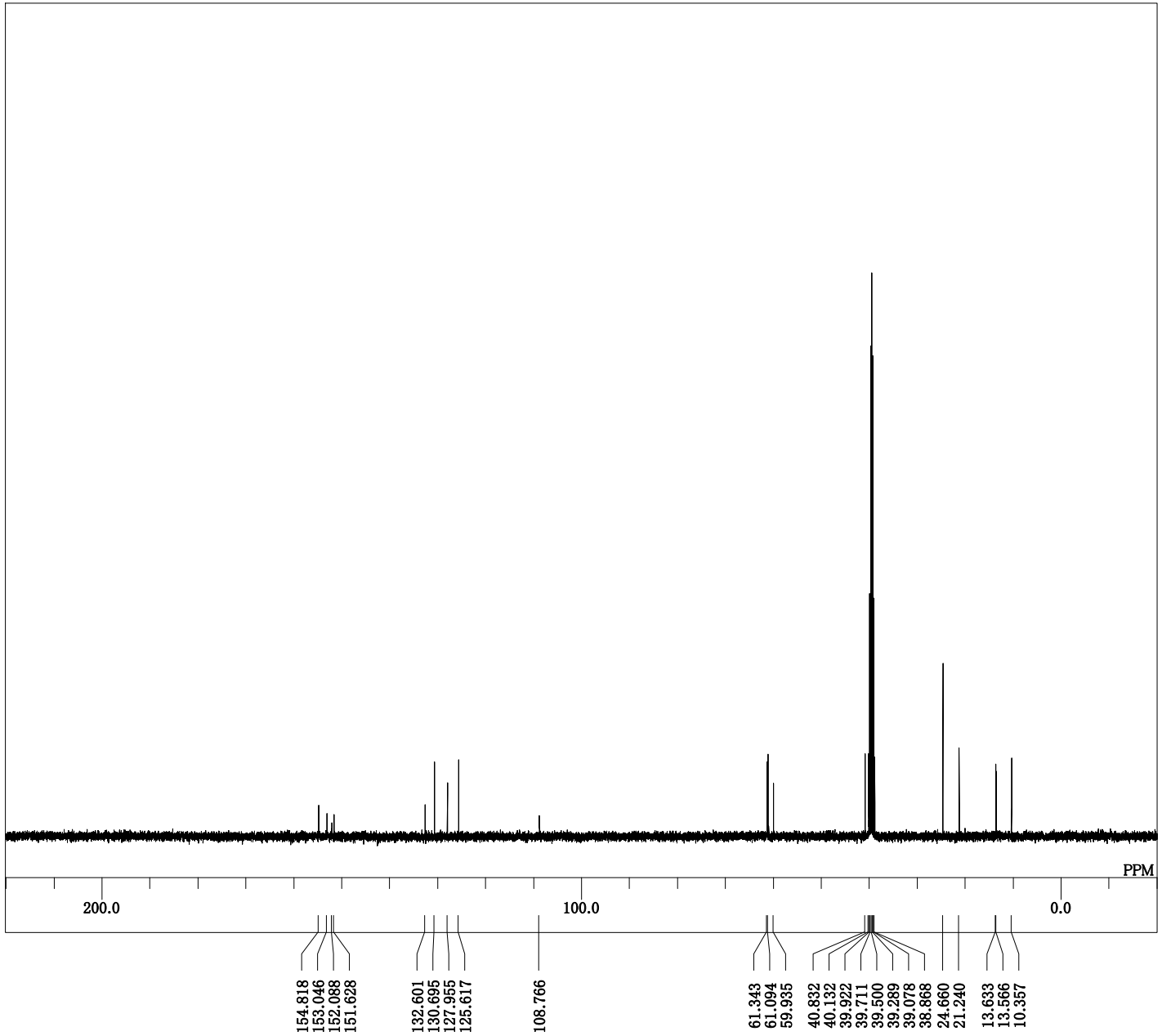
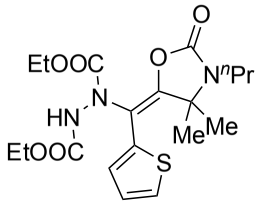

DFILE S_DEAD_110deg_rev_Proton-1-1.al
COMNT single_pulse
DATIM 2019-12-03 17:47:45
OBNUC 1H
EXMOD proton.jxp
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.24 Hz
SCANS 8
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 3.14 usec
IRNUC 1H
CTEMP 110.0 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.42 Hz
RGAIN 28
0.99
0.91
1.01
1.03
2.33
2.00
2.09
2.12
5.93
3.50
2.94
3.15
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
8.997
7.604
7.592
7.068
7.059
7.031
7.022
7.018
7.009
4.148
4.131
4.113
4.094
3.927
3.910
3.892
3.874
3.098
3.079
3.060
2.970
2.495
2.490
2.485
1.635
1.617
1.598
1.579
1.561
1.542
1.265
1.215
1.197
1.180
1.074
1.057
1.039
0.891
0.873
0.855


EtOOC
N
HN
EtOOC
O
O
N^{n}Pr
Me
Me
S

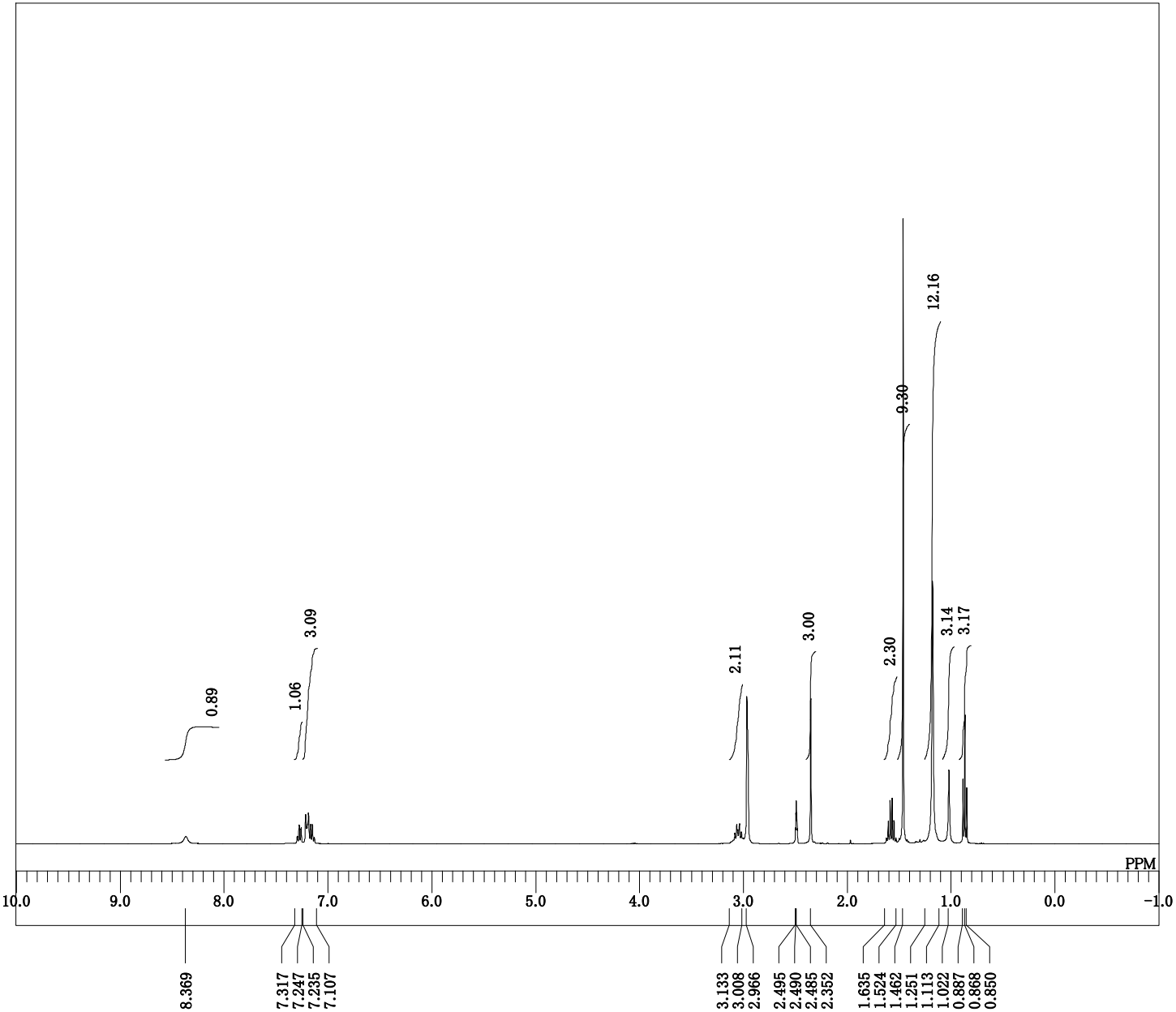
3eB



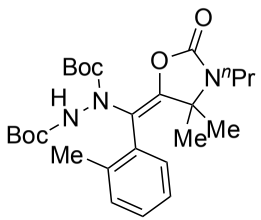
DFILE	S_DEAD_110deg_rev_Carbon-2-1.al
COMNT	single pulse decoupled gated NOE
DATIM	2019-12-03 18:07:08
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	512
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	50



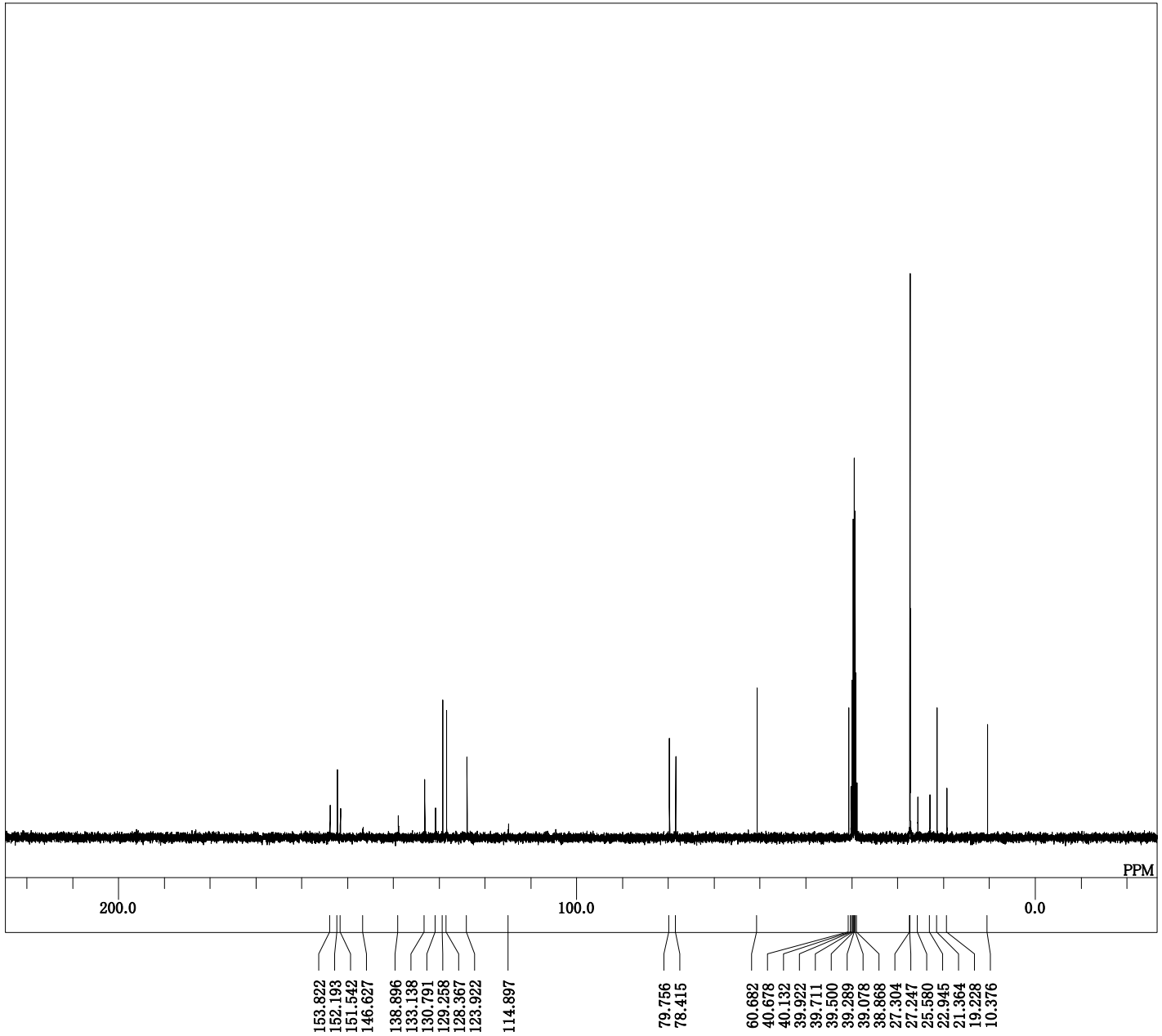
3eB



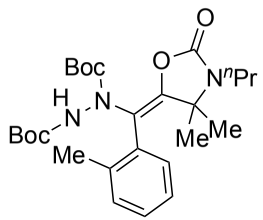
DFILE 20200222 oTol_DBAD_110deg_Prot
COMNT single_pulse
DATIM 2020-02-22 17:49:58
OBNUC 1H
EXMOD proton.jxp
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.24 Hz
SCANS 8
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 3.14 usec
IRNUC 1H
CTEMP 110.0 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.42 Hz
RGAIN 20



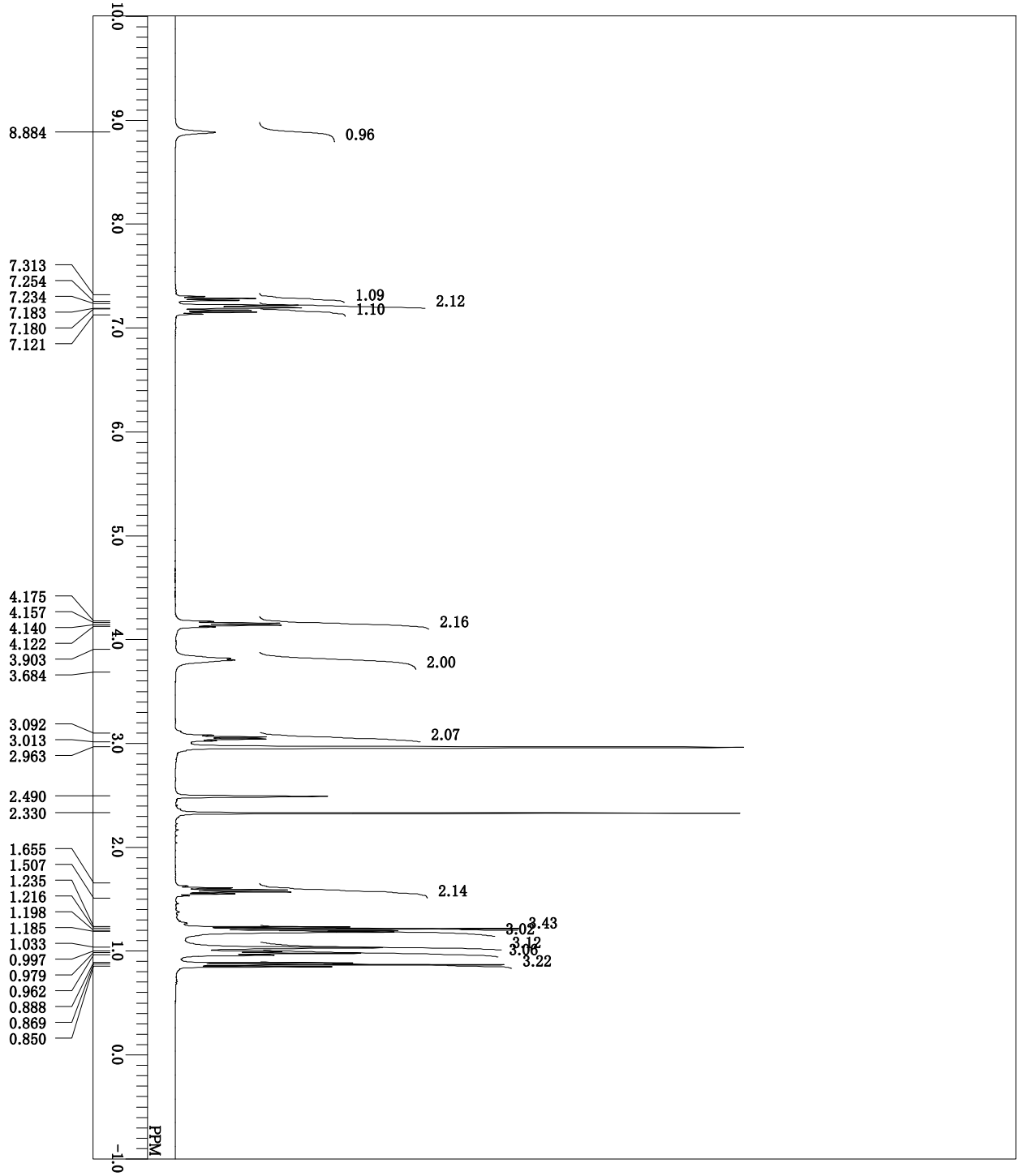
3fA

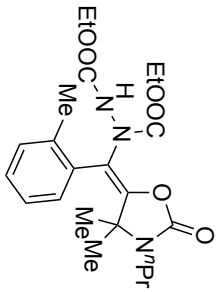


DFILE	20200222 oTol_DBAD_110deg_Cart
COMNT	single pulse decoupled gated NOE
DATIM	2020-02-22 17:53:12
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	256
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60

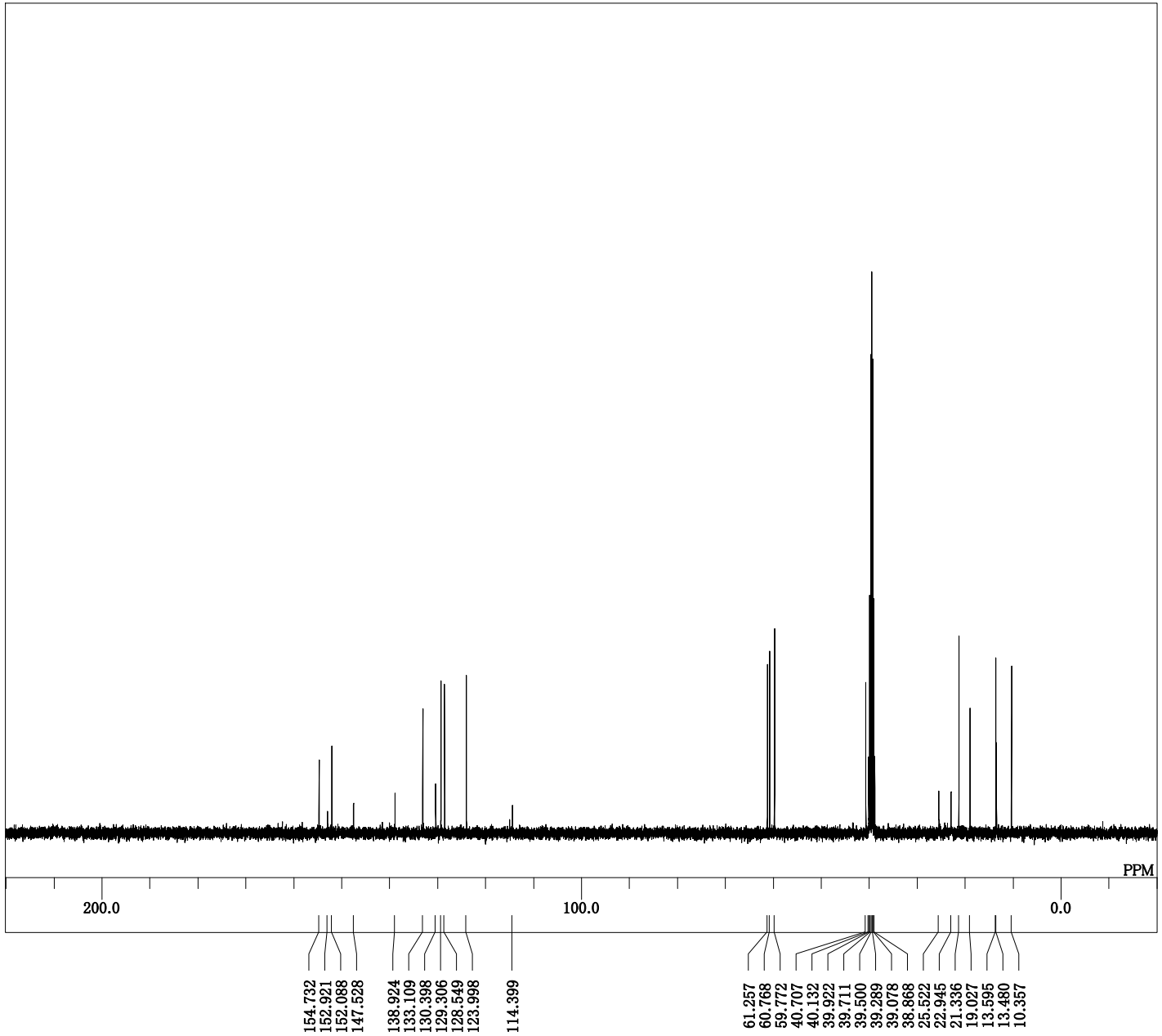


3fA

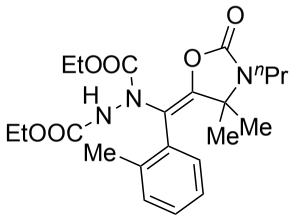

8.884
7.313
7.254
7.234
7.183
7.180
7.121
4.175
4.157
4.140
4.122
3.903
3.684
3.092
3.013
2.963
2.490
2.330
1.655
1.507
1.235
1.216
1.198
1.185
1.033
0.997
0.979
0.962
0.888
0.869
0.850
0.96
1.09
1.10
2.12
2.16
2.00
2.07
2.14
2.43
3.02
3.12
3.06
3.22
PPM
DFILE 20200225 oToLDEAD_110deg_Prot
COMNT single_pulse
DATIM 2020-02-25 15:09:53
OBNUC 1H
EXMOD proton.jxp
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.24 Hz
SCANS 8
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 3.14 usec
IRNUC 1H
CTEMP 110.0 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.42 Hz
RGAIN 22


EtOOC
H
N
N
EtOOC
Me
O
O
N
iPr
Me
Me

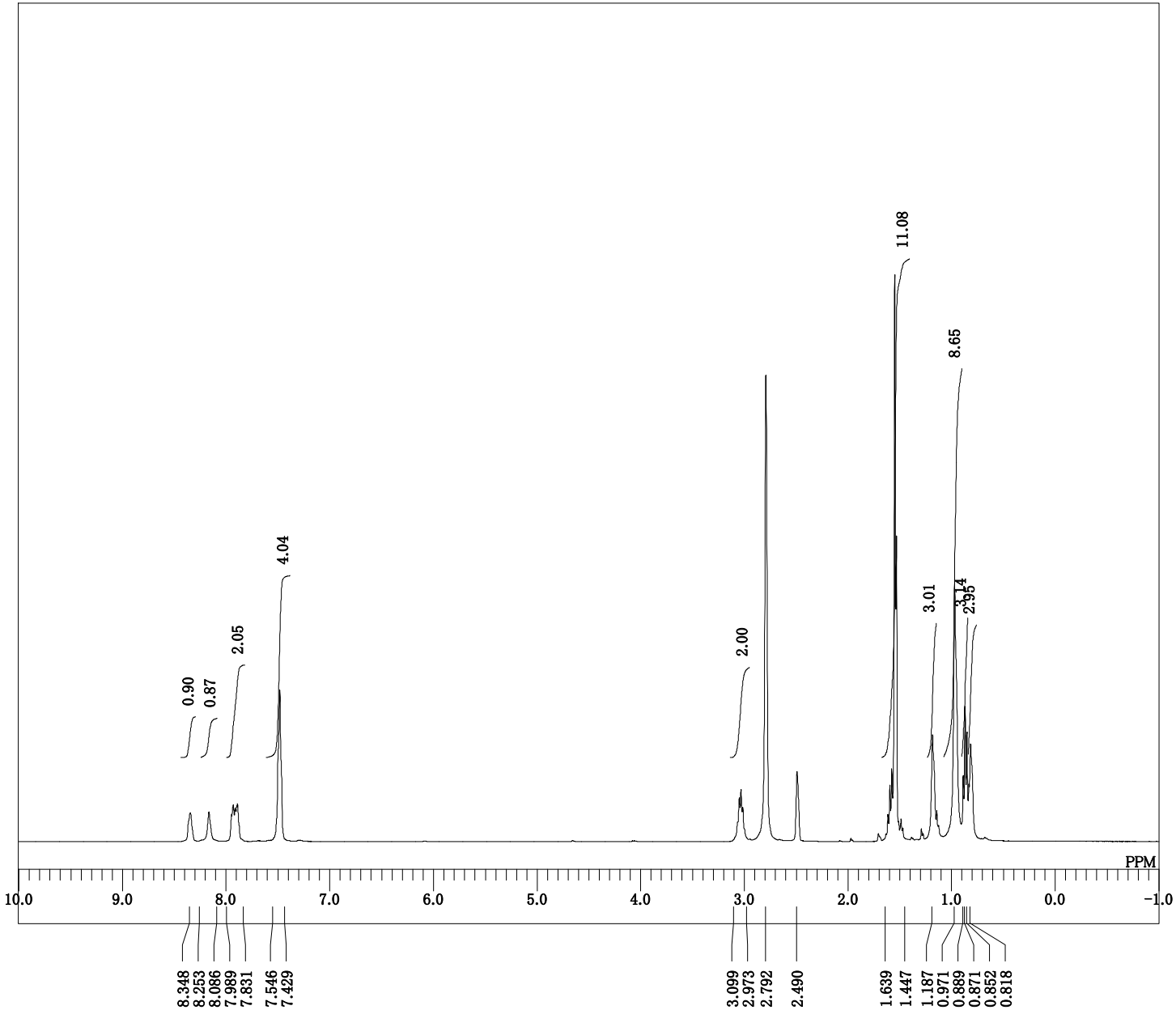
3fB

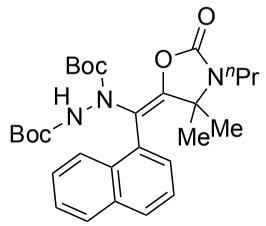


DFILE	20200225 oTol_DEAD_110deg_Cart
COMNT	single pulse decoupled gated NOE
DATIM	2020-02-25 15:13:03
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	256
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60

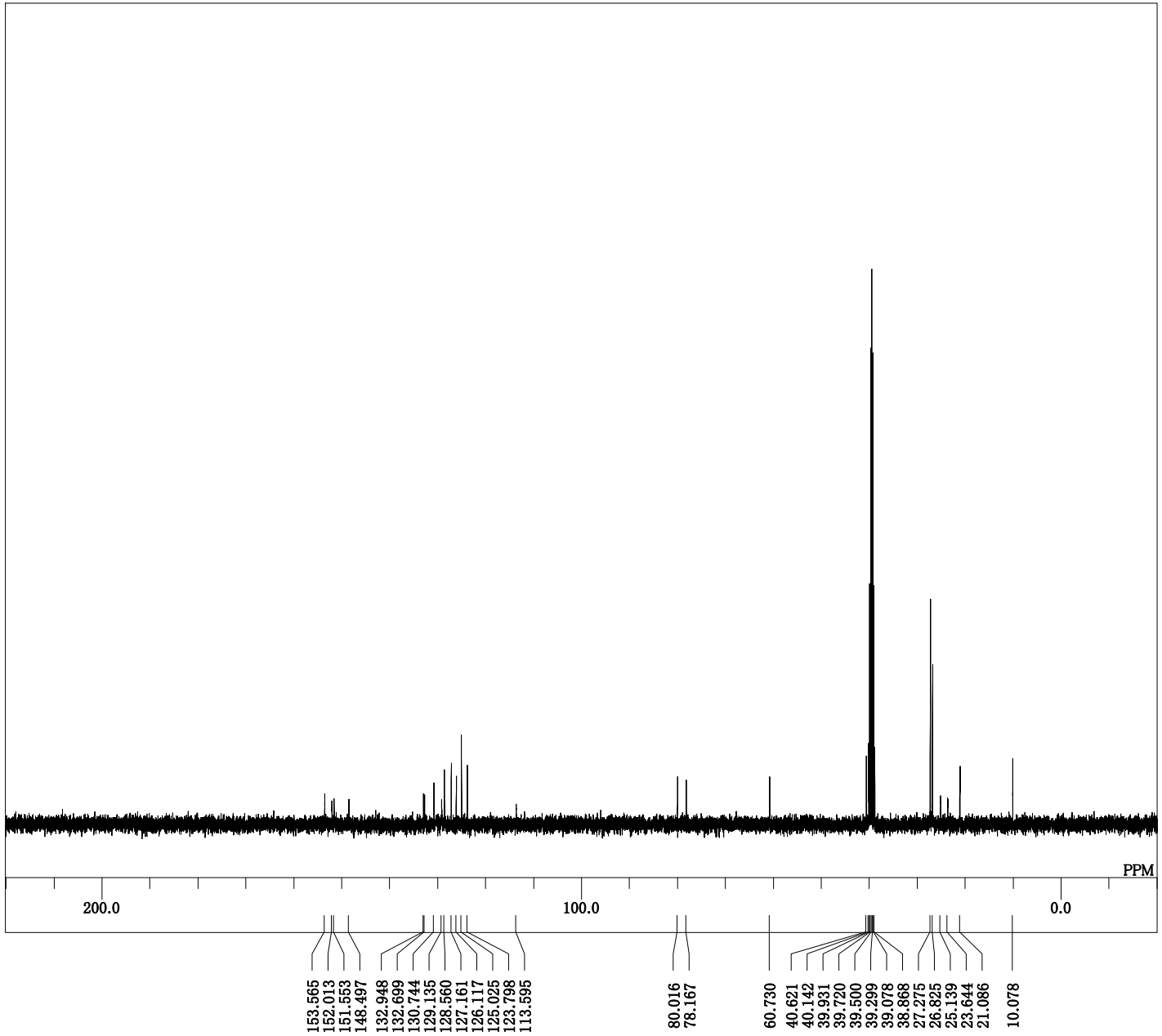


3fB

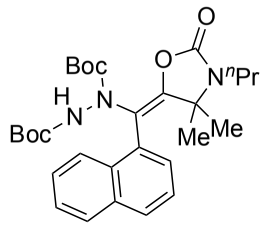

DFILE 20200306 1naph_DBAD_150deg_Prc
COMNT single_pulse
DATIM 2020-03-06 15:09:16
OBNUC 1H
EXMOD proton.jxp
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.24 Hz
SCANS 8
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 3.14 usec
IRNUC 1H
CTEMP 150.0 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.42 Hz
RGAIN 26
0.90
0.87
2.05
4.04
2.00
11.08
3.01
3.14
2.95
8.65
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
8.348
8.253
8.086
7.989
7.831
7.546
7.429
3.099
2.973
2.792
2.490
1.639
1.447
1.187
0.971
0.889
0.871
0.852
0.818


O
O
Boc
N
nPr
H
N
N
Boc
Me
Me

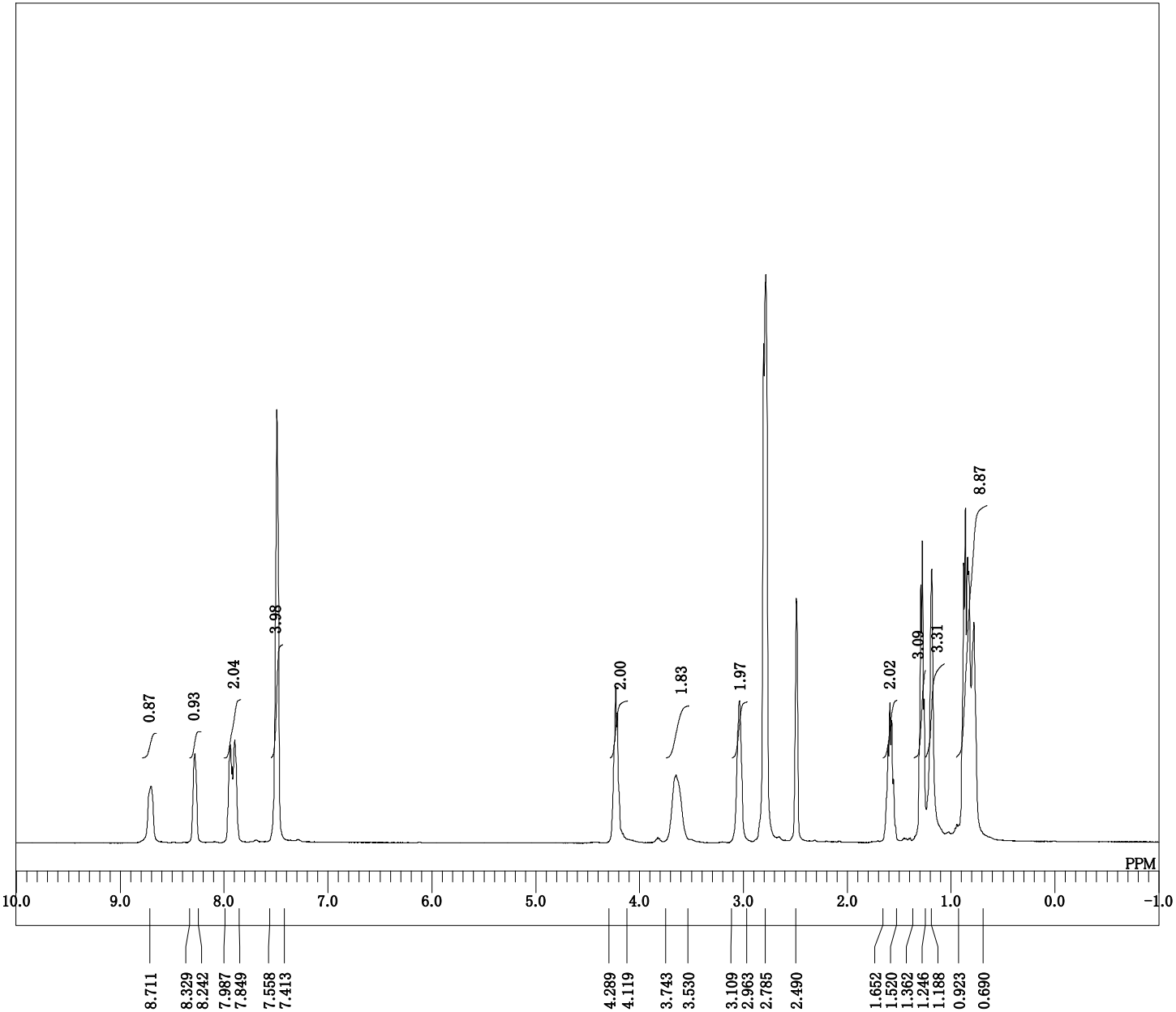
3gA



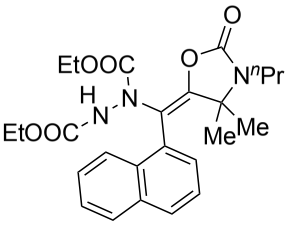
DFILE	20200306 1naph_DBAD_150deg_Ca
COMNT	single pulse decoupled gated NOE
DATIM	2020-03-06 14:20:16
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	25000.00 Hz
SCANS	262
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	150.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60



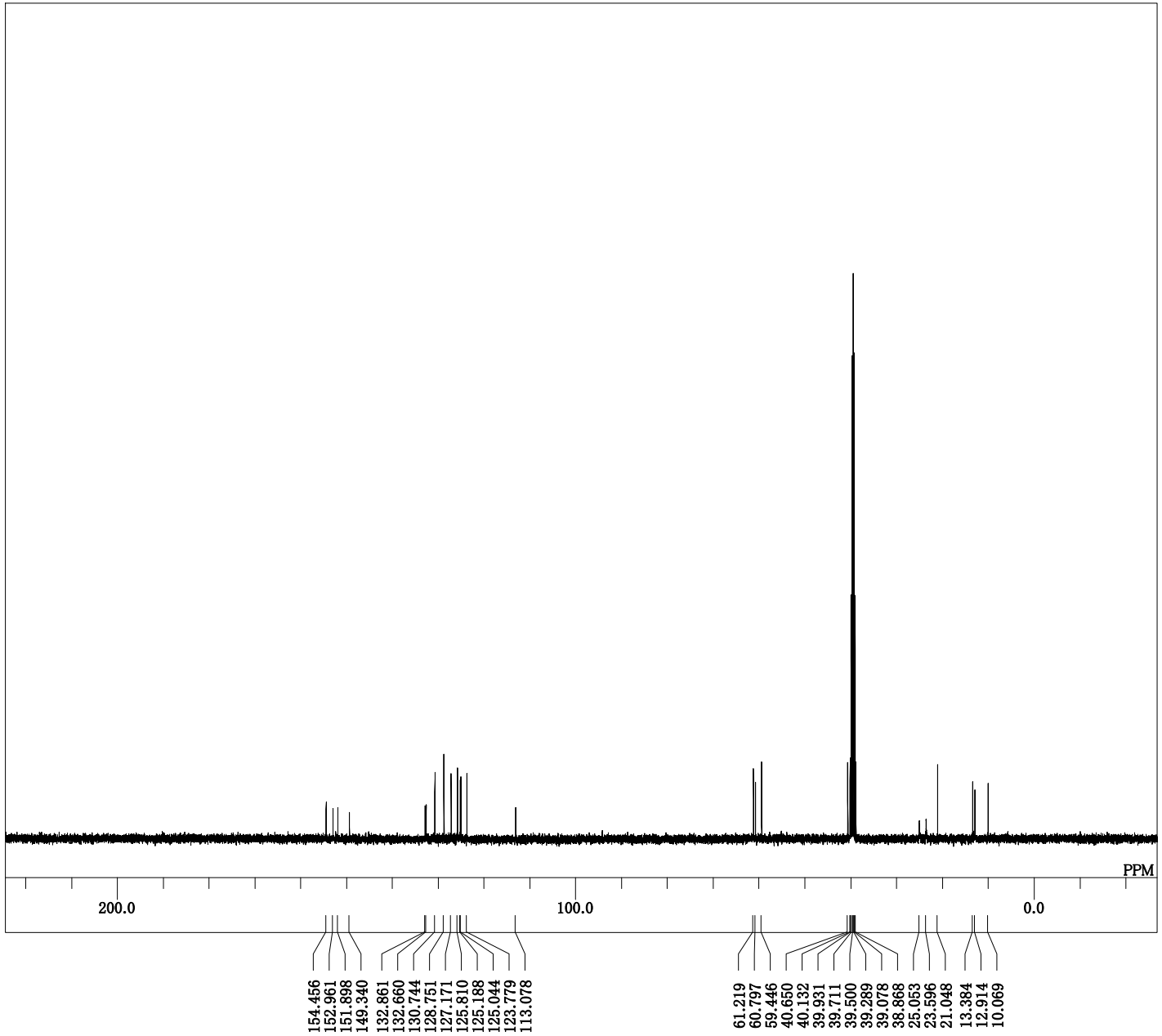
3gA



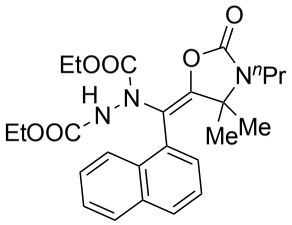
DFILE 1naph_DEAD_150deg_rev_Proton-1-
COMNT single_pulse
DATIM 2019-12-10 15:34:16
OBNUC 1H
EXMOD proton.jxp
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.24 Hz
SCANS 8
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 3.14 usec
IRNUC 1H
CTEMP 150.0 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.42 Hz
RGAIN 26



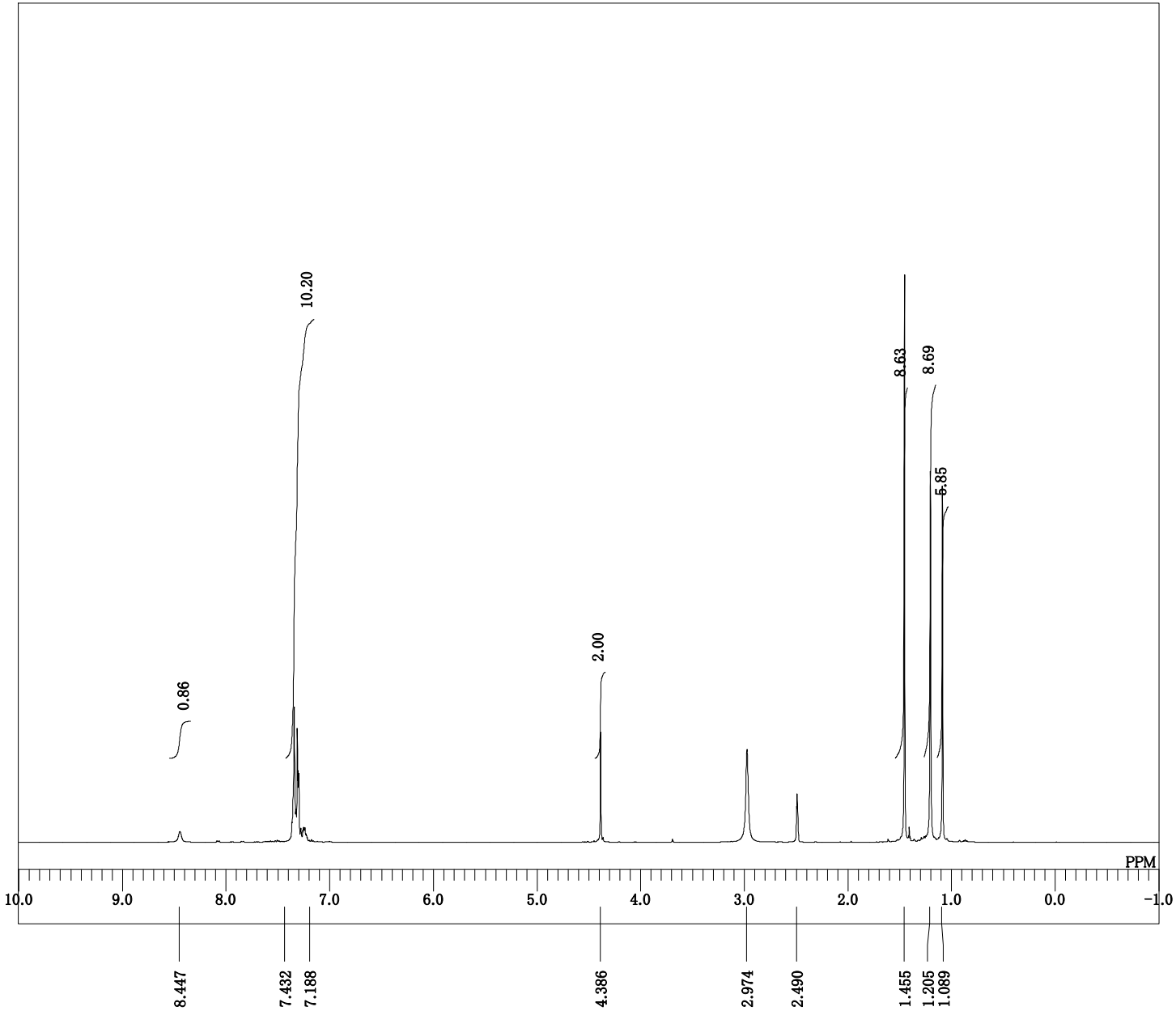
3gB



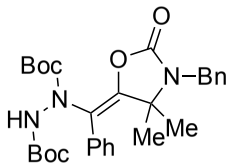
DFILE	1naph_DEAD_150deg_rev_Carbon-1
COMNT	single pulse decoupled gated NOE
DATIM	2019-12-10 15:37:26
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	25000.00 Hz
SCANS	1024
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	150.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60



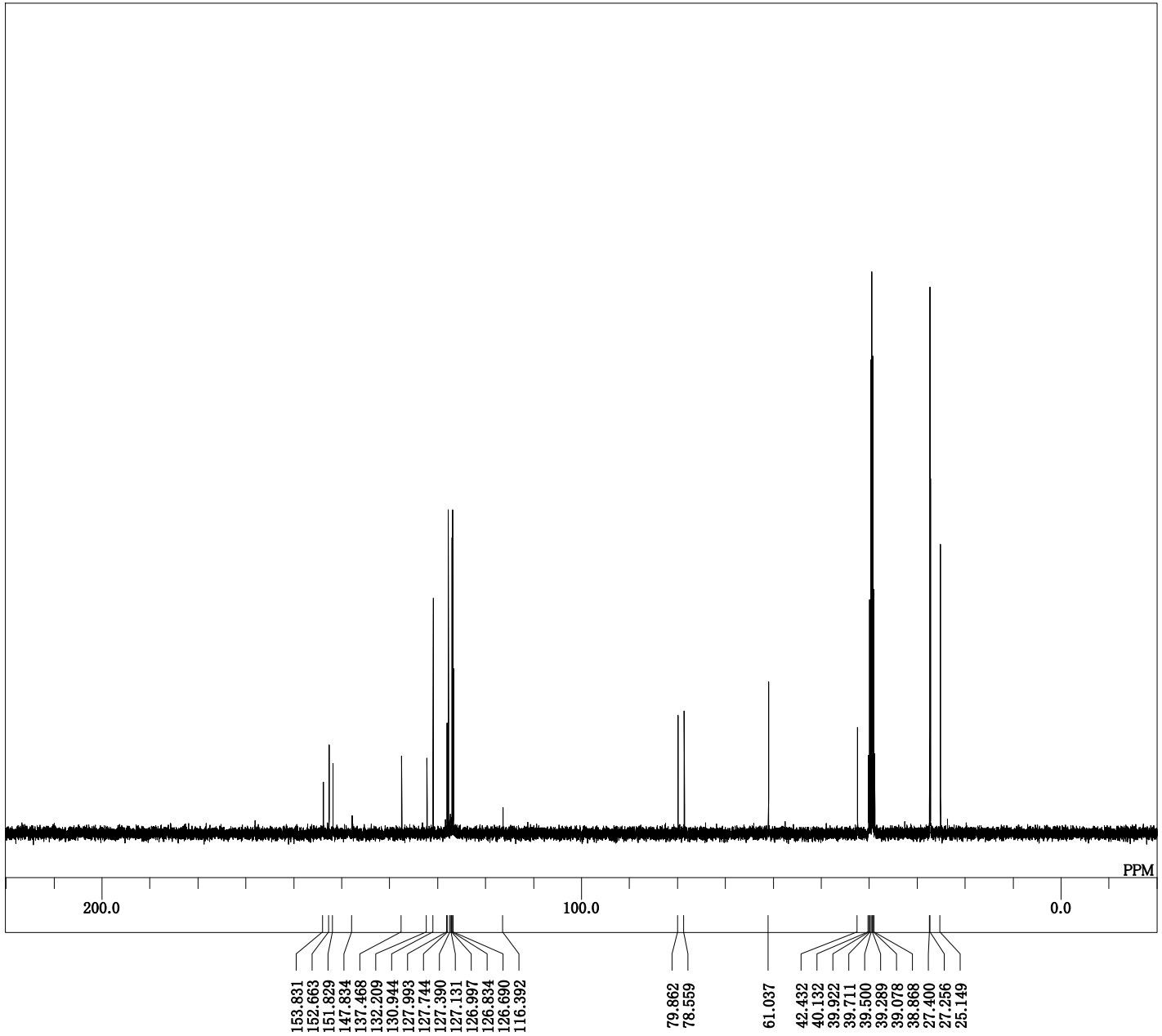
3gA



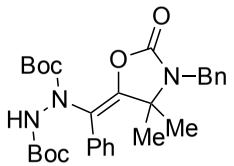
DFILE	20200229 NBn_DBAD_110deg_Prot
COMNT	single_pulse
DATIM	2020-02-29 16:59:21
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	16384
FREQU	7422.80 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	3.14 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.42 Hz
RGAIN	22



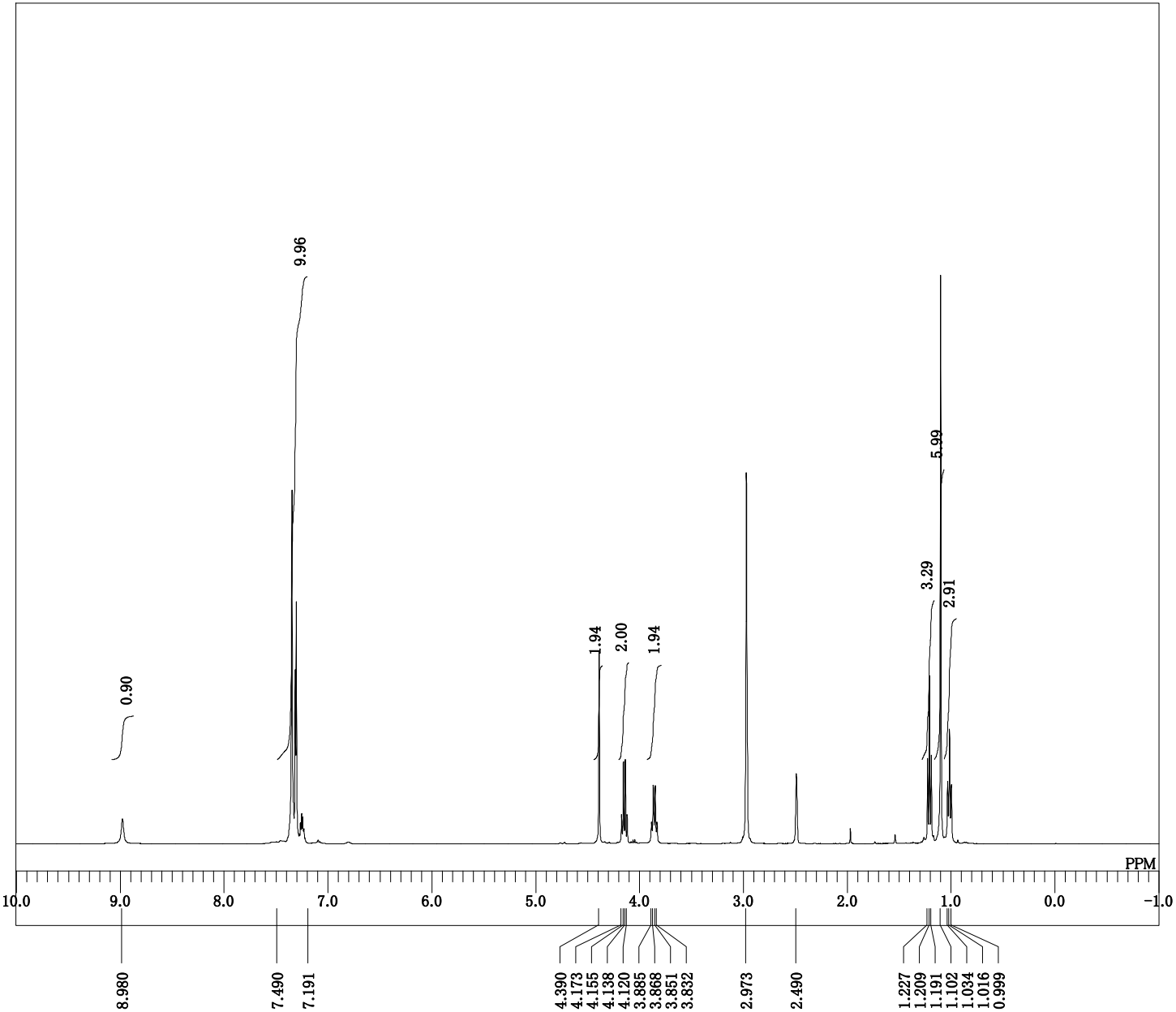
3hA



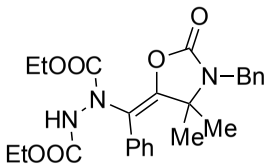
DFILE	20200229 NBn_DBAD_110deg_Carb
COMNT	single pulse decoupled gated NOE
DATIM	2020-02-29 17:02:36
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	256
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60



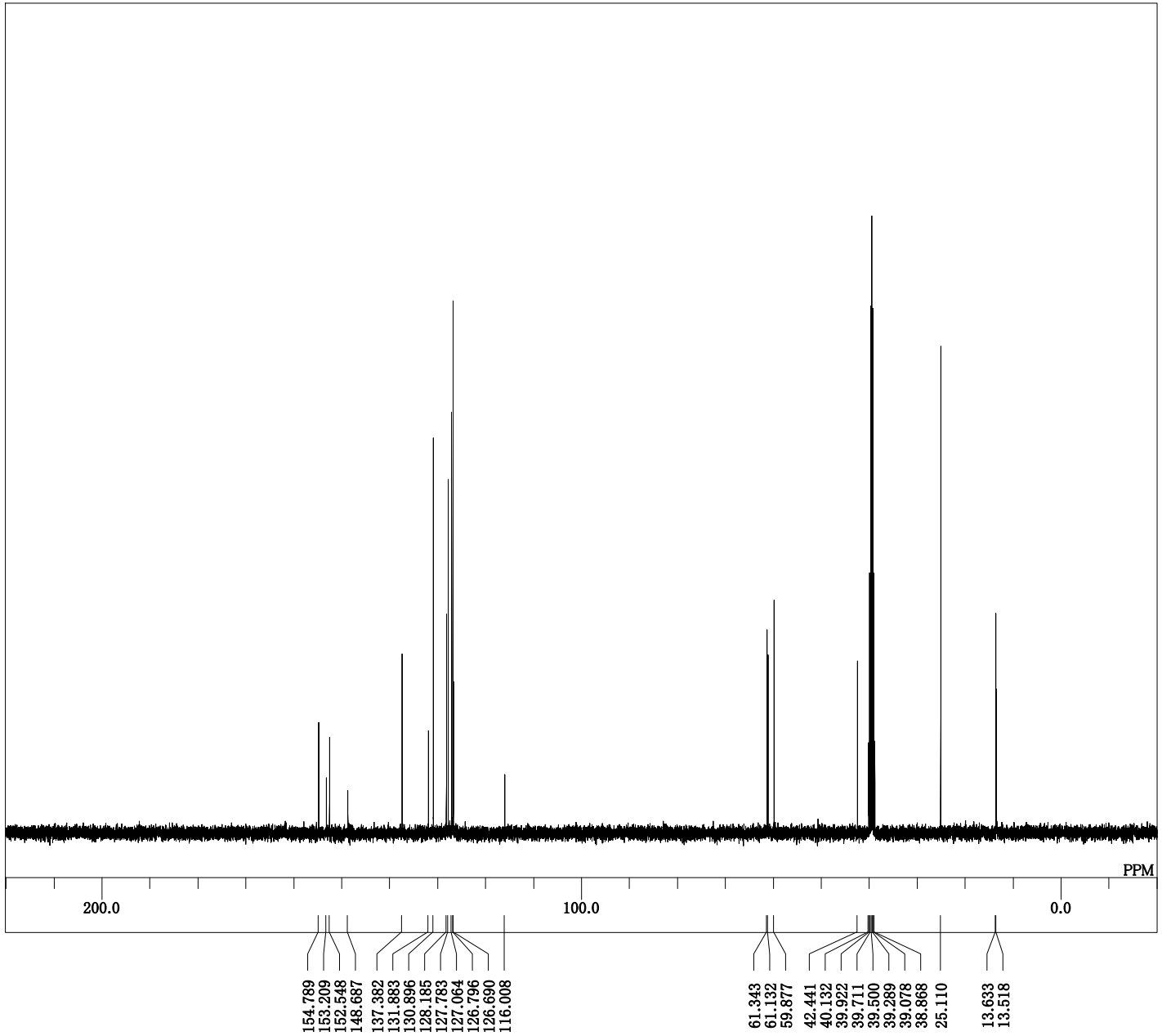
3hA



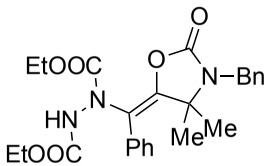
DFILE	NBn_DEAD_110deg_Proton-2-1.als
COMNT	single_pulse
DATIM	2019-12-05 16:42:35
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	16384
FREQU	7422.80 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	3.14 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.42 Hz
RGAIN	24



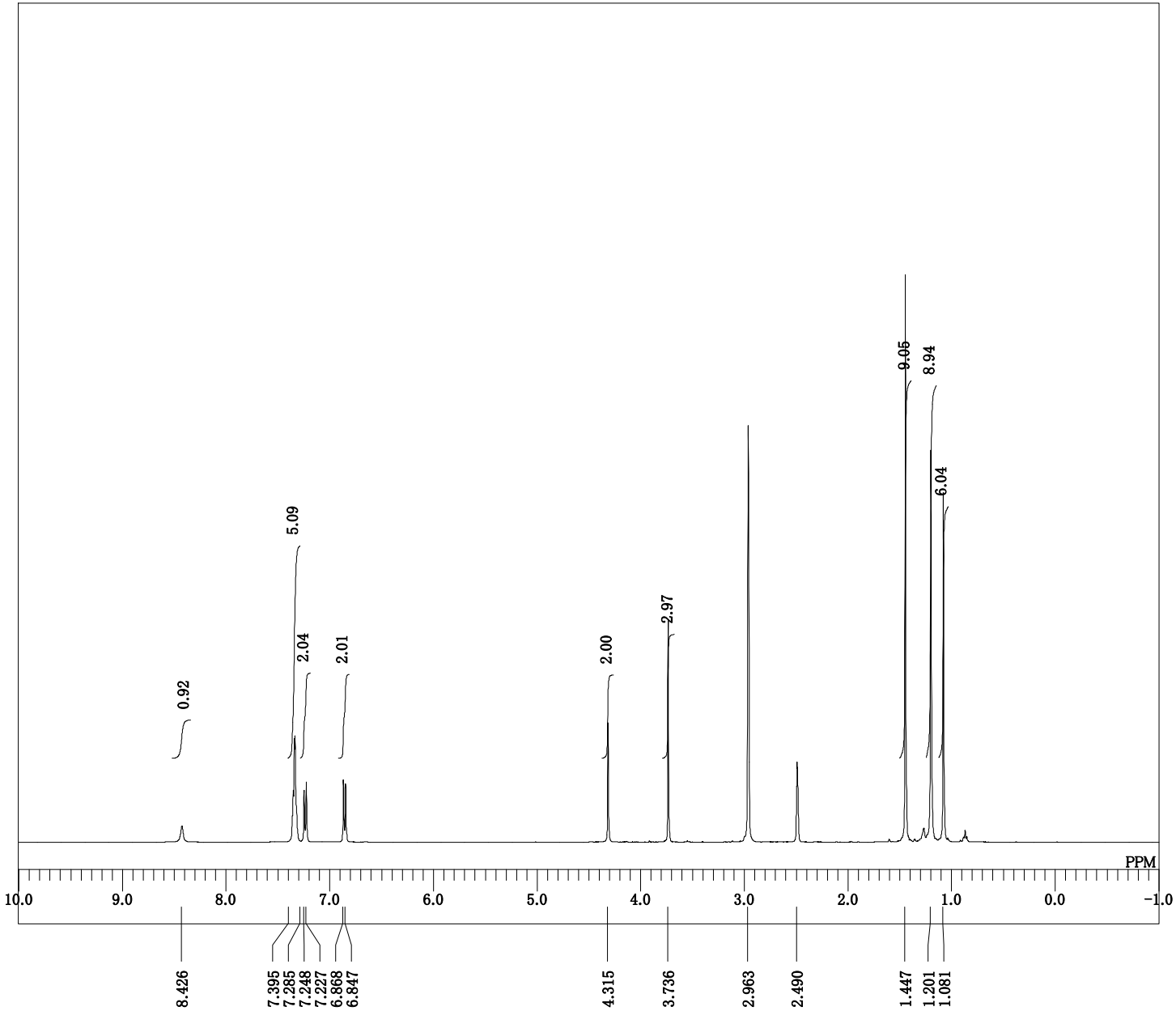
3hB



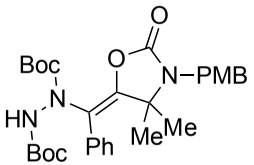
DFILE	NBn_DEAD_110deg_Carbon-2-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2019-12-05 16:45:50
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	256
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60



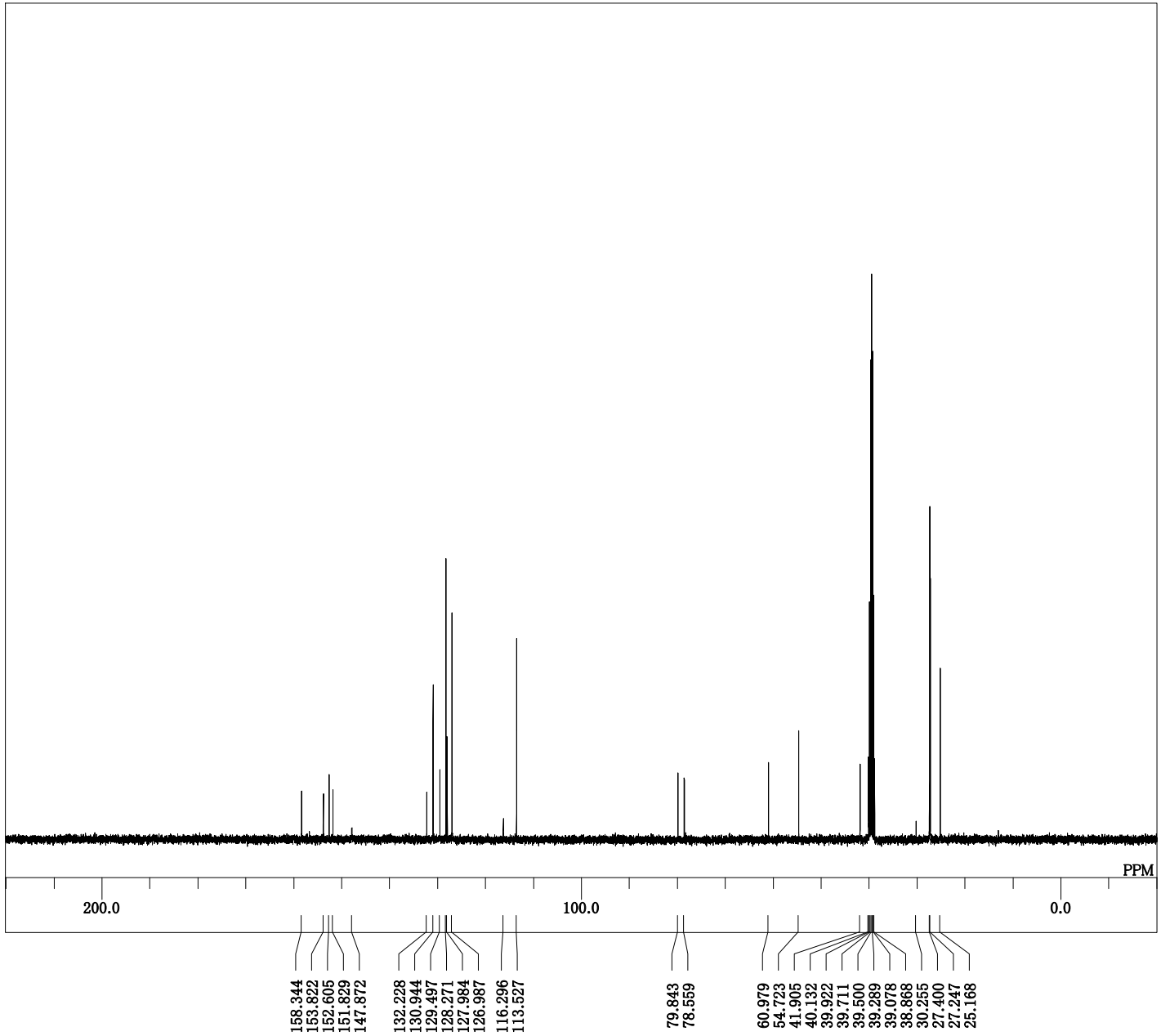
3hB



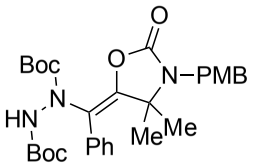
DFILE	20200225 NPMB_DBAD_110deg_Pr
COMNT	single_pulse
DATIM	2020-02-25 14:03:19
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	16384
FREQU	7422.80 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	3.14 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.42 Hz
RGAIN	24



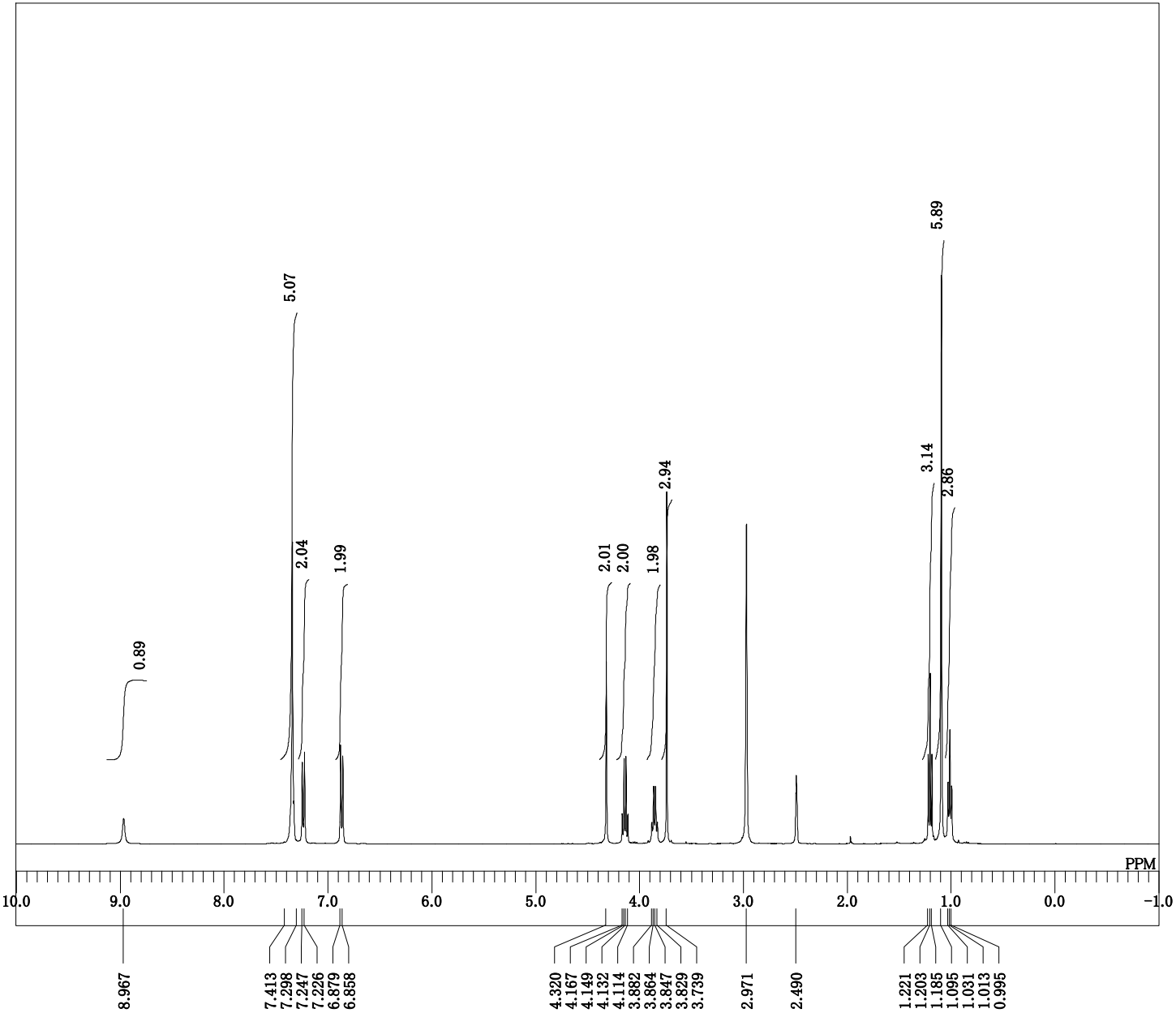
3iA



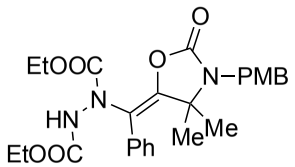
DFILE	20200225 NPMB_DBAD_110deg_Ca
COMNT	single pulse decoupled gated NOE
DATIM	2020-02-25 15:36:29
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	512
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60



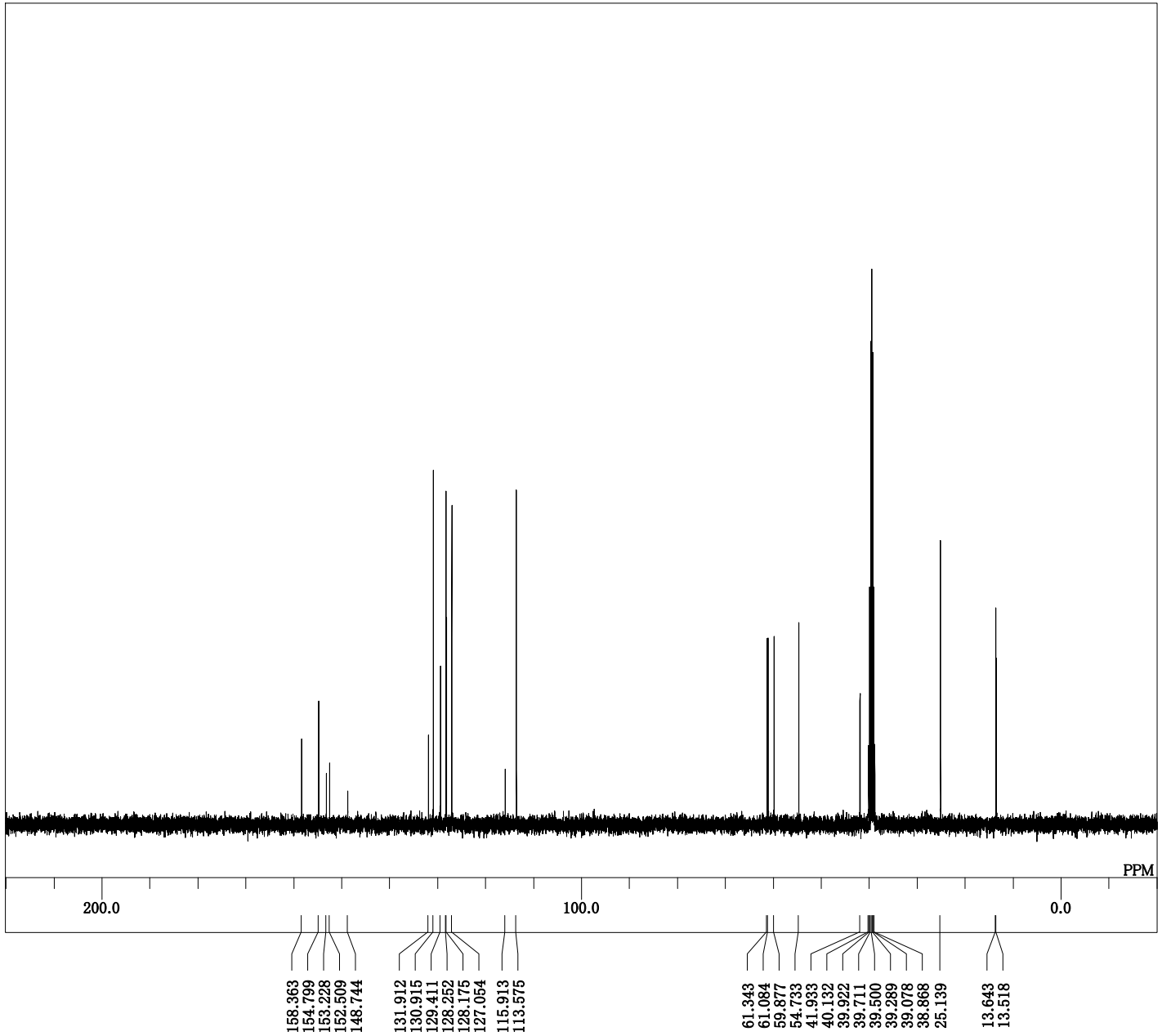
3iA



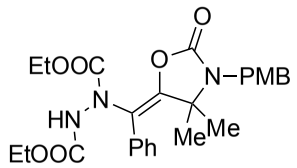
DFILE NPMB_DEAD_110deg_Proton-1-1.a
COMNT single_pulse
DATIM 2019-12-25 19:39:27
OBNUC 1H
EXMOD proton.jxp
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
POINT 13107
FREQU 5938.24 Hz
SCANS 8
ACQTM 2.2073 sec
PD 5.0000 sec
PW1 3.14 usec
IRNUC 1H
CTEMP 110.0 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.42 Hz
RGAIN 22



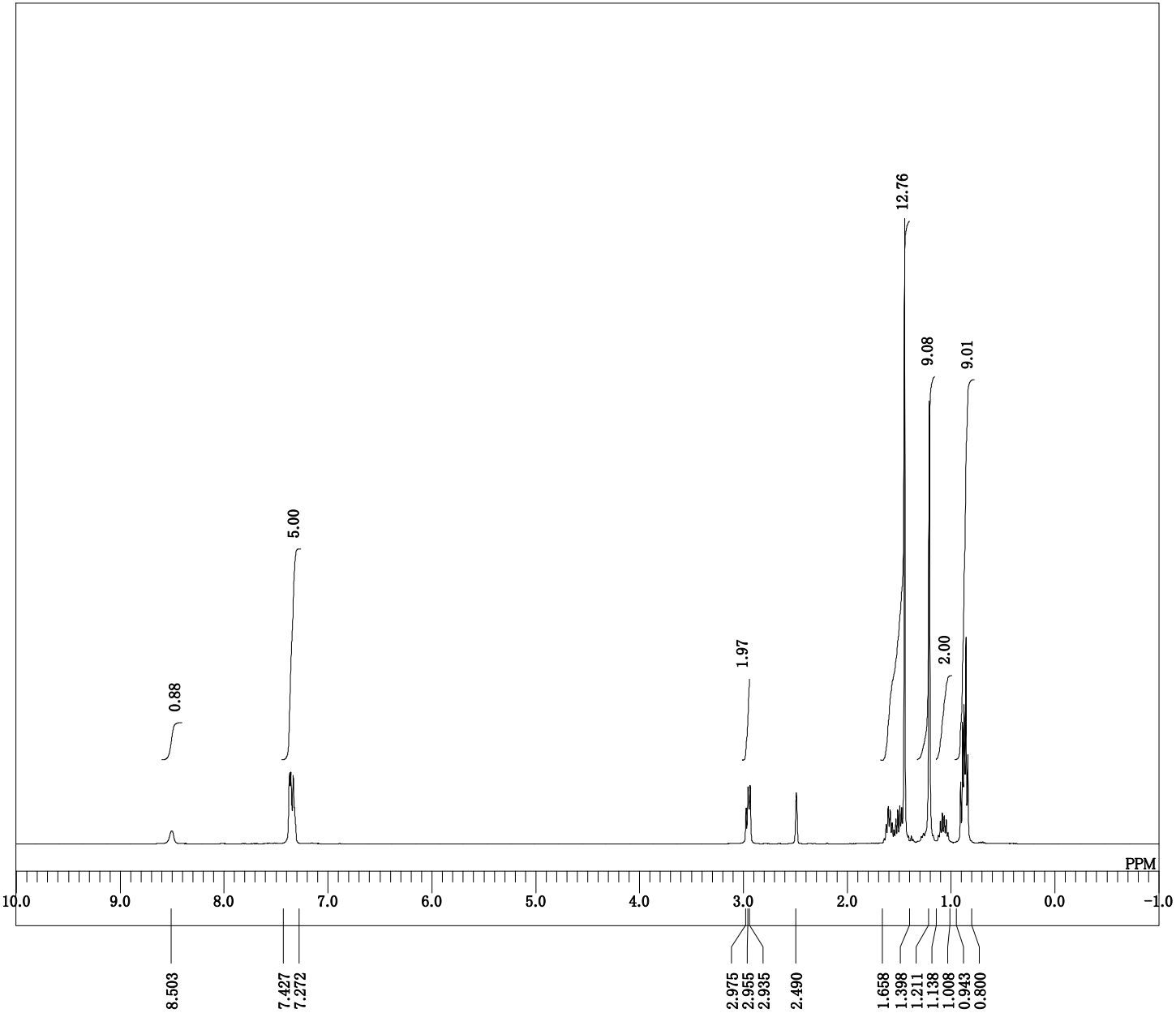
3iB



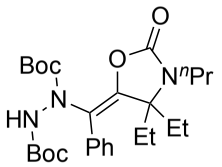
DFILE	NPMB_DEAD_110deg_Carbon-1-1.
COMNT	single pulse decoupled gated NOE
DATIM	2019-12-25 19:42:18
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	129
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	50



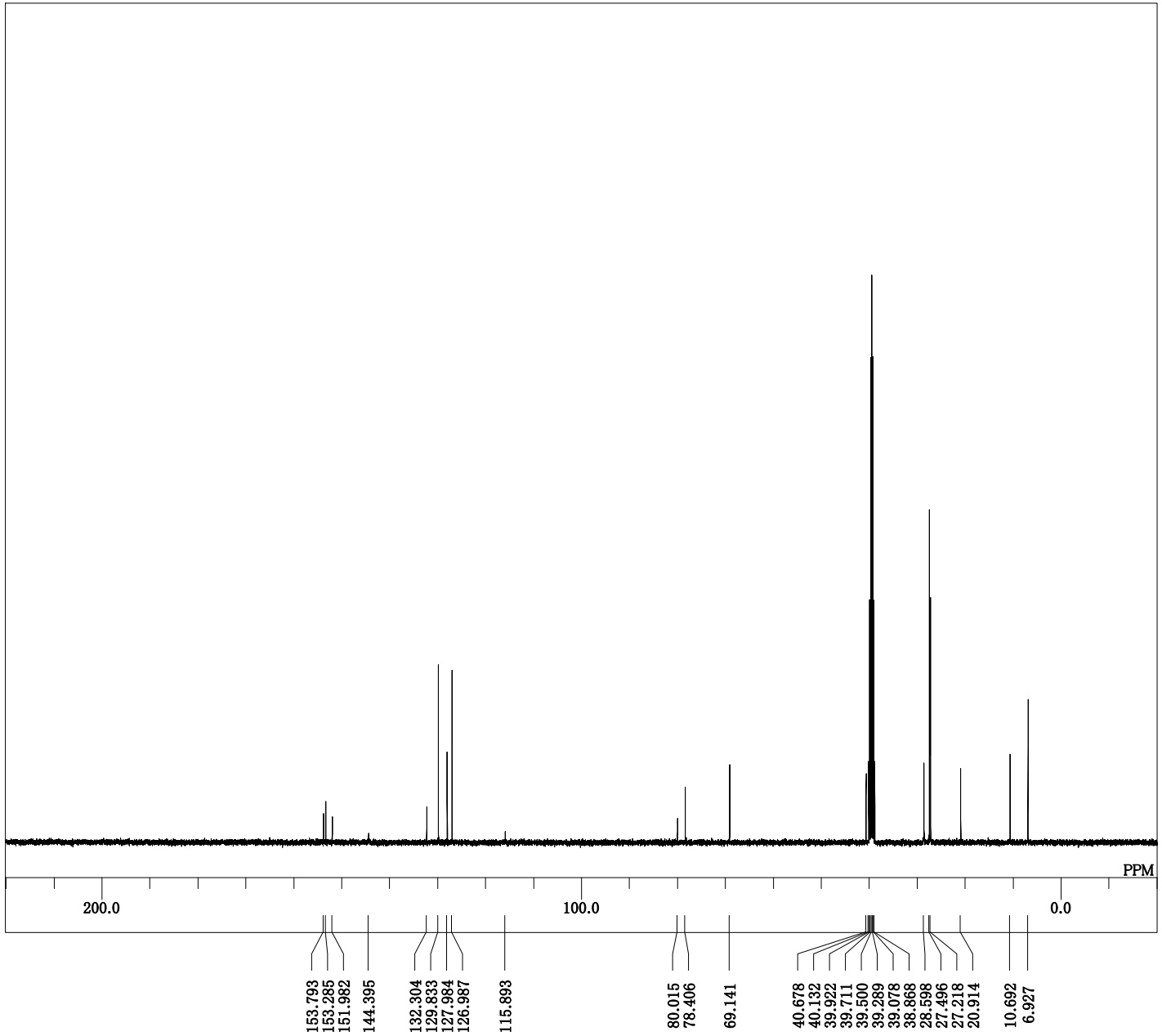
3iB



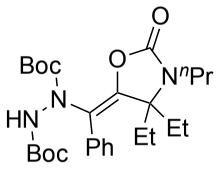
DFILE	20200317 diethyl_DBAD_110deg_Pr
COMNT	single_pulse
DATIM	2020-03-17 21:26:15
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	16384
FREQU	7422.80 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	3.14 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.42 Hz
RGAIN	24



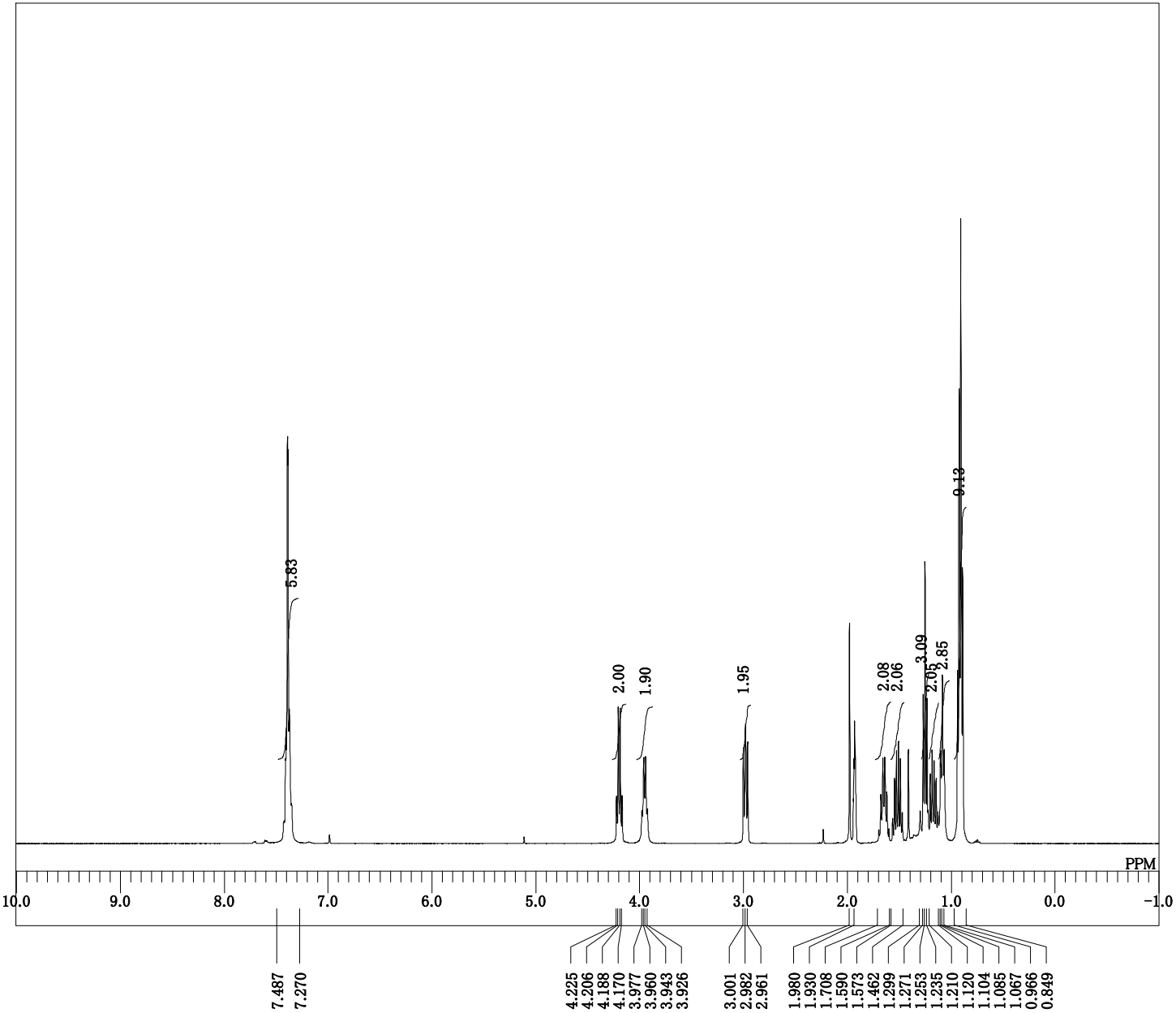
3jA



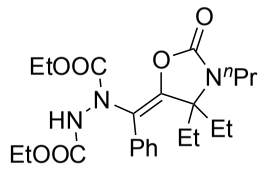
DFILE	20200318_diethyl_DBAD_110deg_C
COMNT	single pulse decoupled gated NOE
DATIM	2020-03-18 10:14:52
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	1024
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60



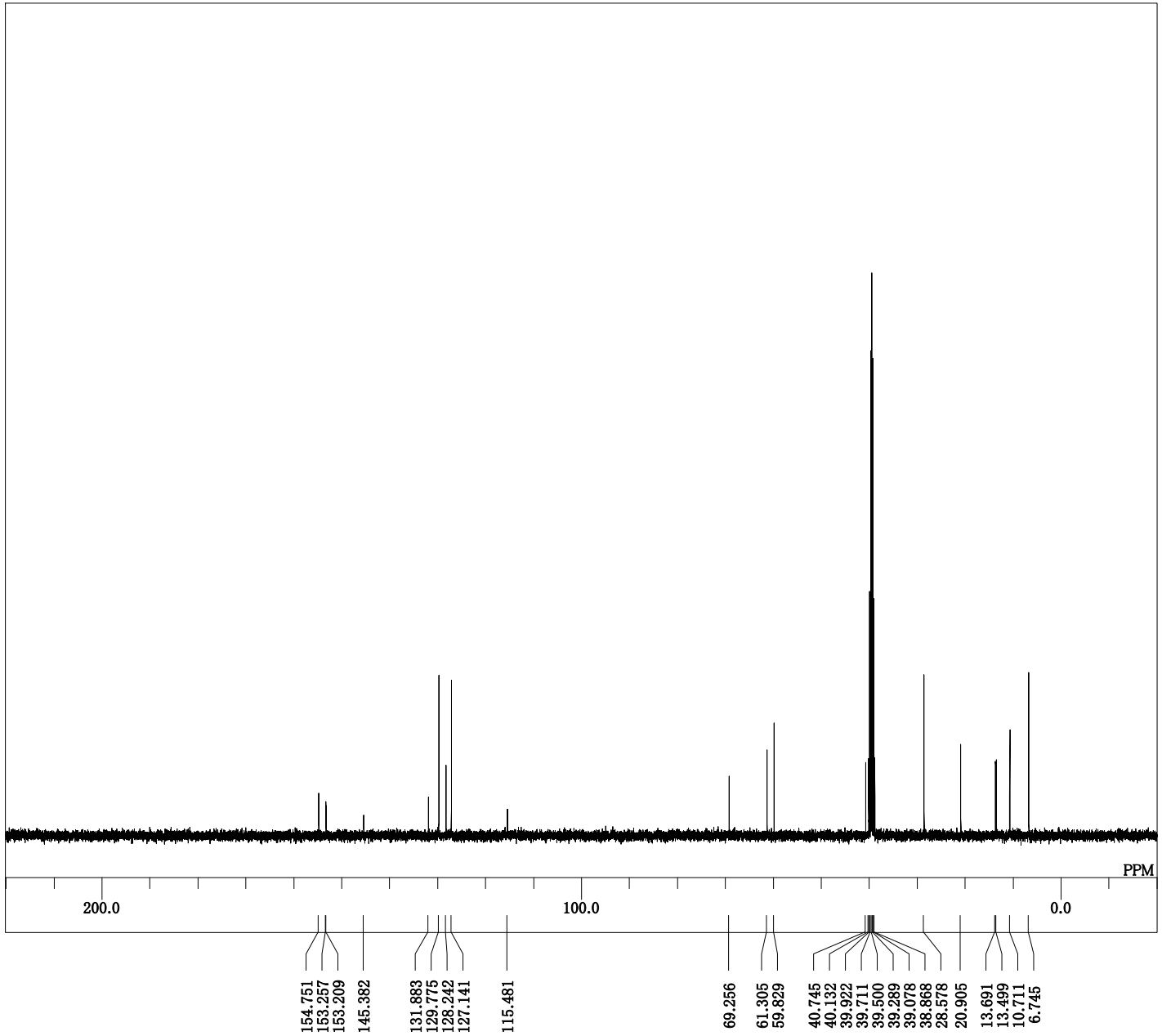
3jA



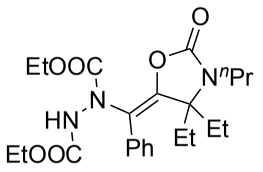
DFILE	20200323 Et_DEAD_75deg_Proton-single_pulse
COMNT	
DATIM	2020-03-23 14:26:08
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.24 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	3.14 usec
IRNUC	1H
CTEMP	75.0 c
SLVNT	CD3CN
EXREF	1.93 ppm
BF	0.42 Hz
RGAIN	30



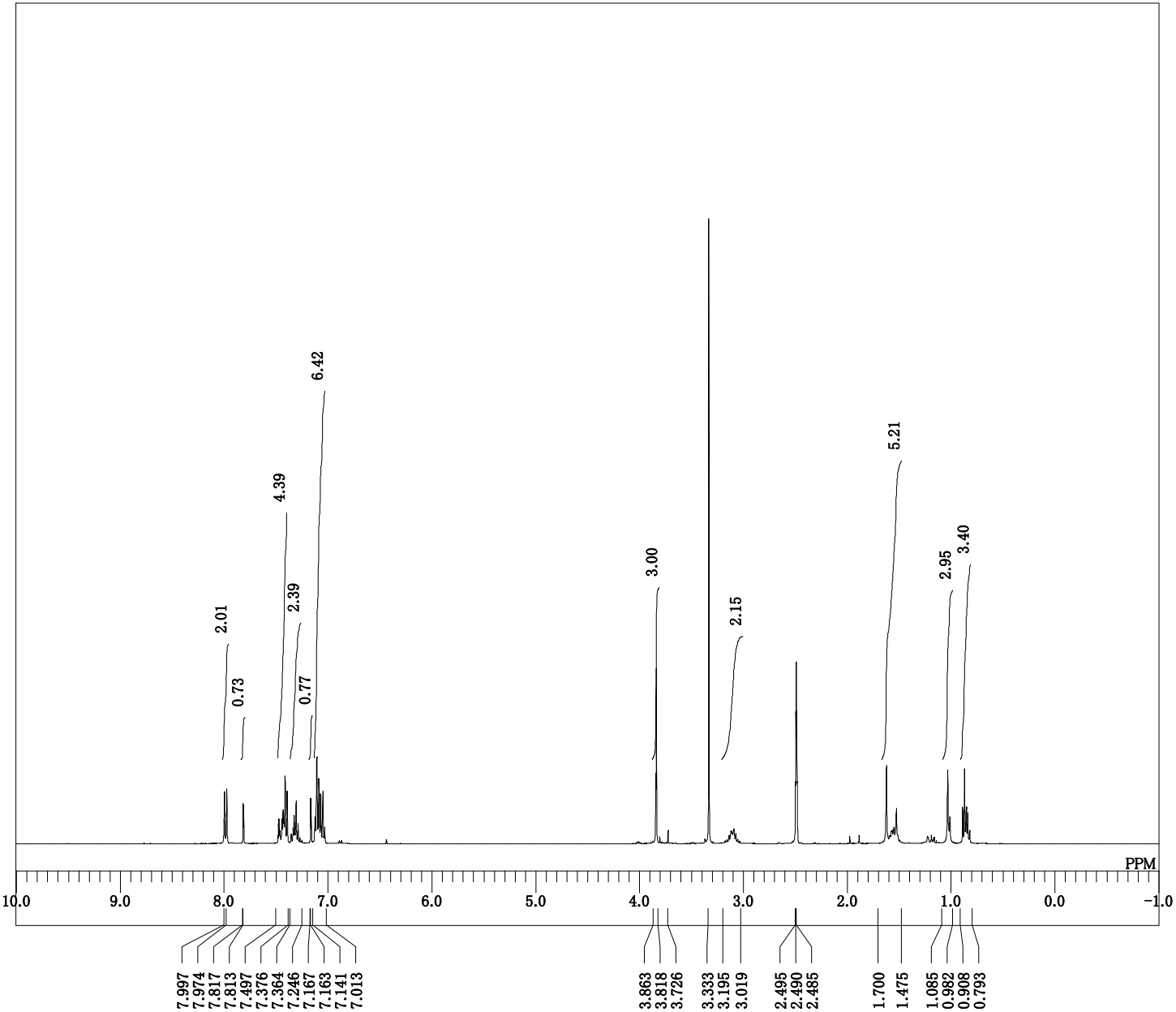
3jB



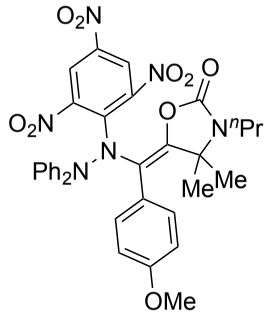
DFILE	diethyl_DEAD_110deg_Carbon-2-1.
COMNT	single pulse decoupled gated NOE
DATIM	2019-12-12 09:51:24
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	32767
FREQU	31250.00 Hz
SCANS	356
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	110.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	60



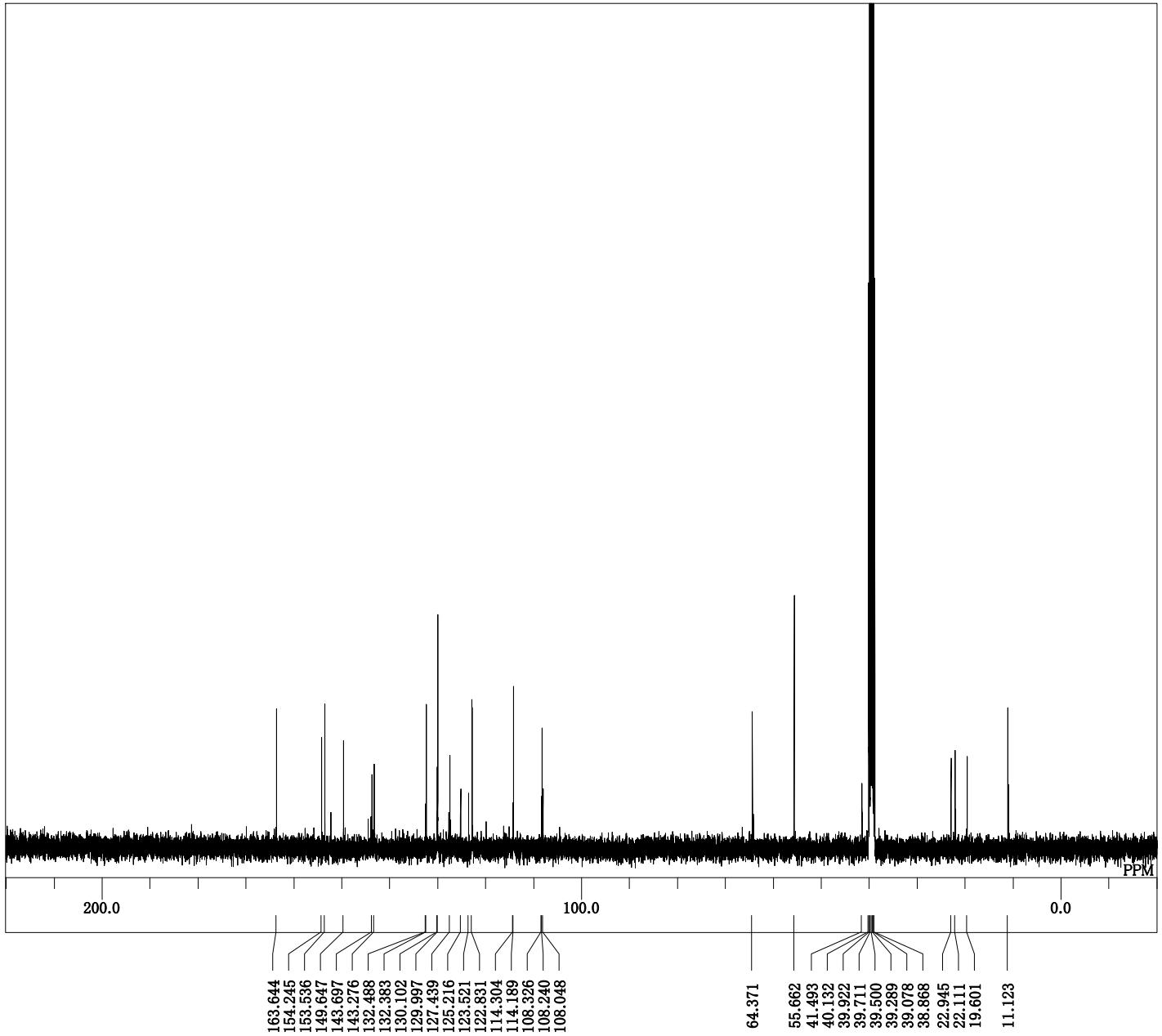
3jB



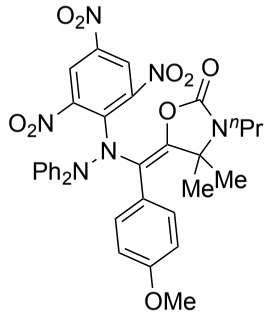
DFILE	20200326 DPPH_OMe_DMSO_Prot
COMNT	single_pulse
DATIM	2020-03-26 14:04:11
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	13107
FREQU	5938.24 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	3.14 usec
IRNUC	1H
CTEMP	19.7 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.12 Hz
RGAIN	32



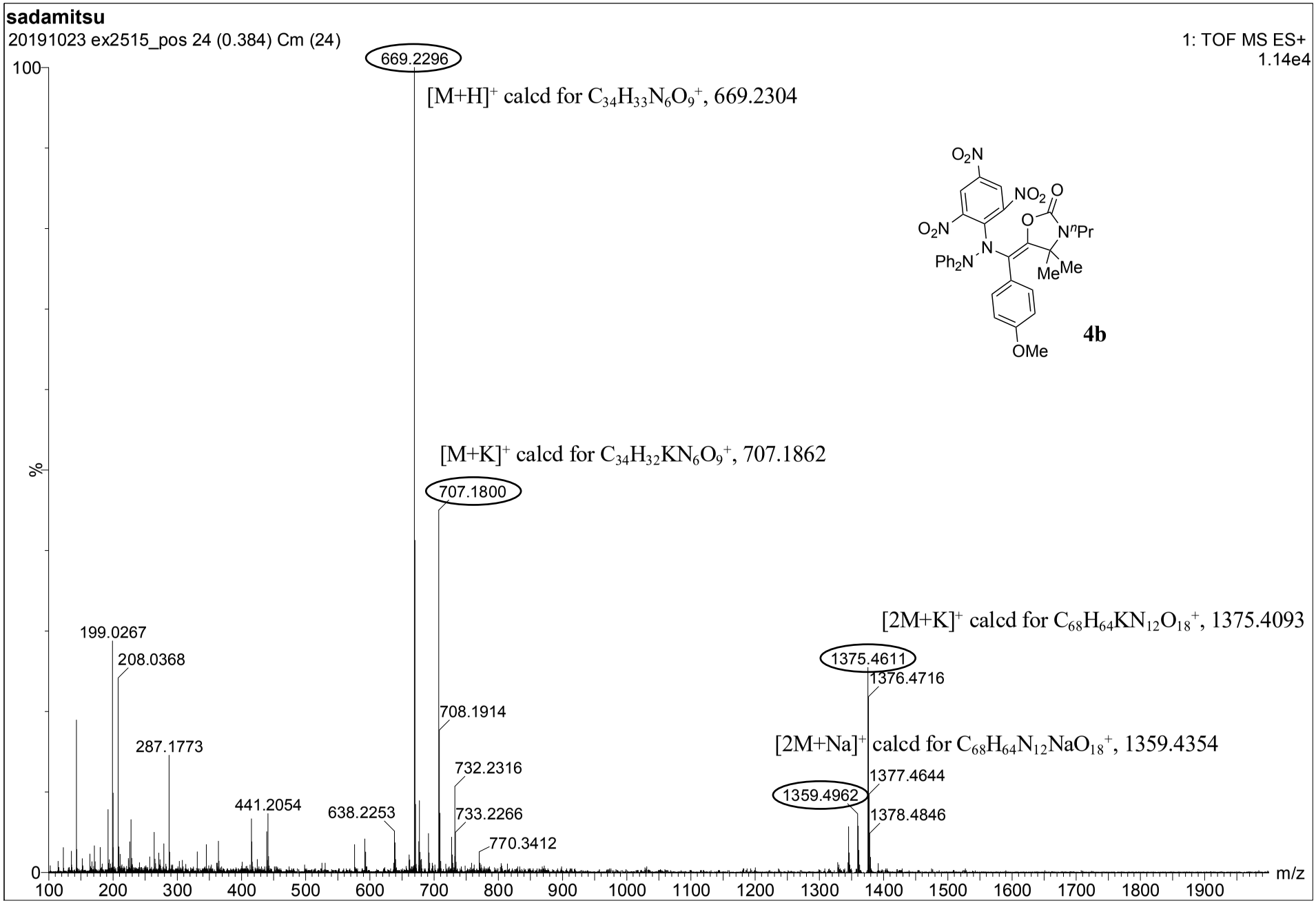
4b

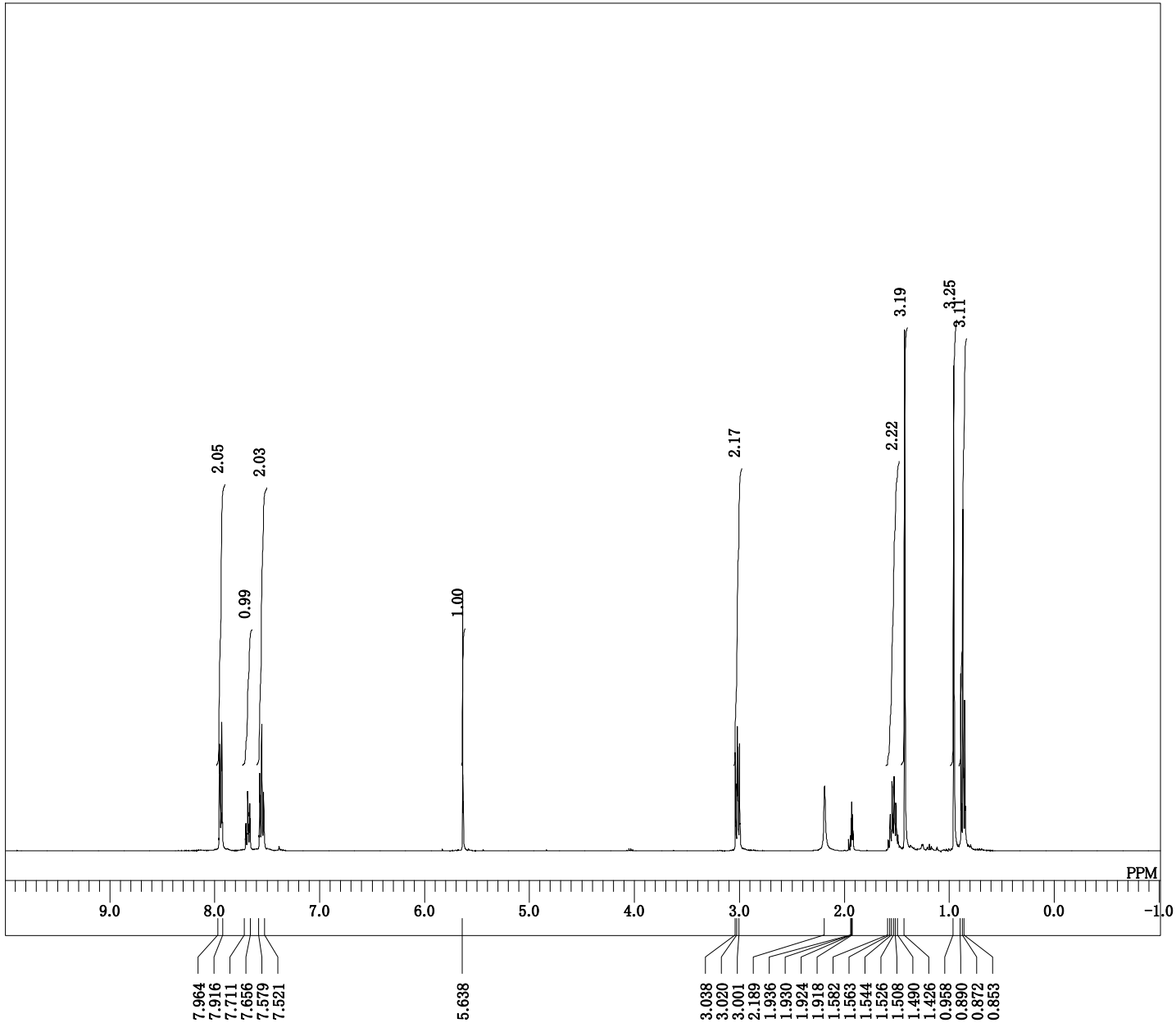


DFILE	20200326 DPPH_OMe_DMSO_Carb
COMNT	single pulse decoupled gated NOE
DATIM	2020-03-26 14:08:11
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26214
FREQU	25000.00 Hz
SCANS	2048
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	19.9 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.12 Hz
RGAIN	60

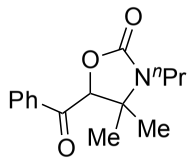


4b

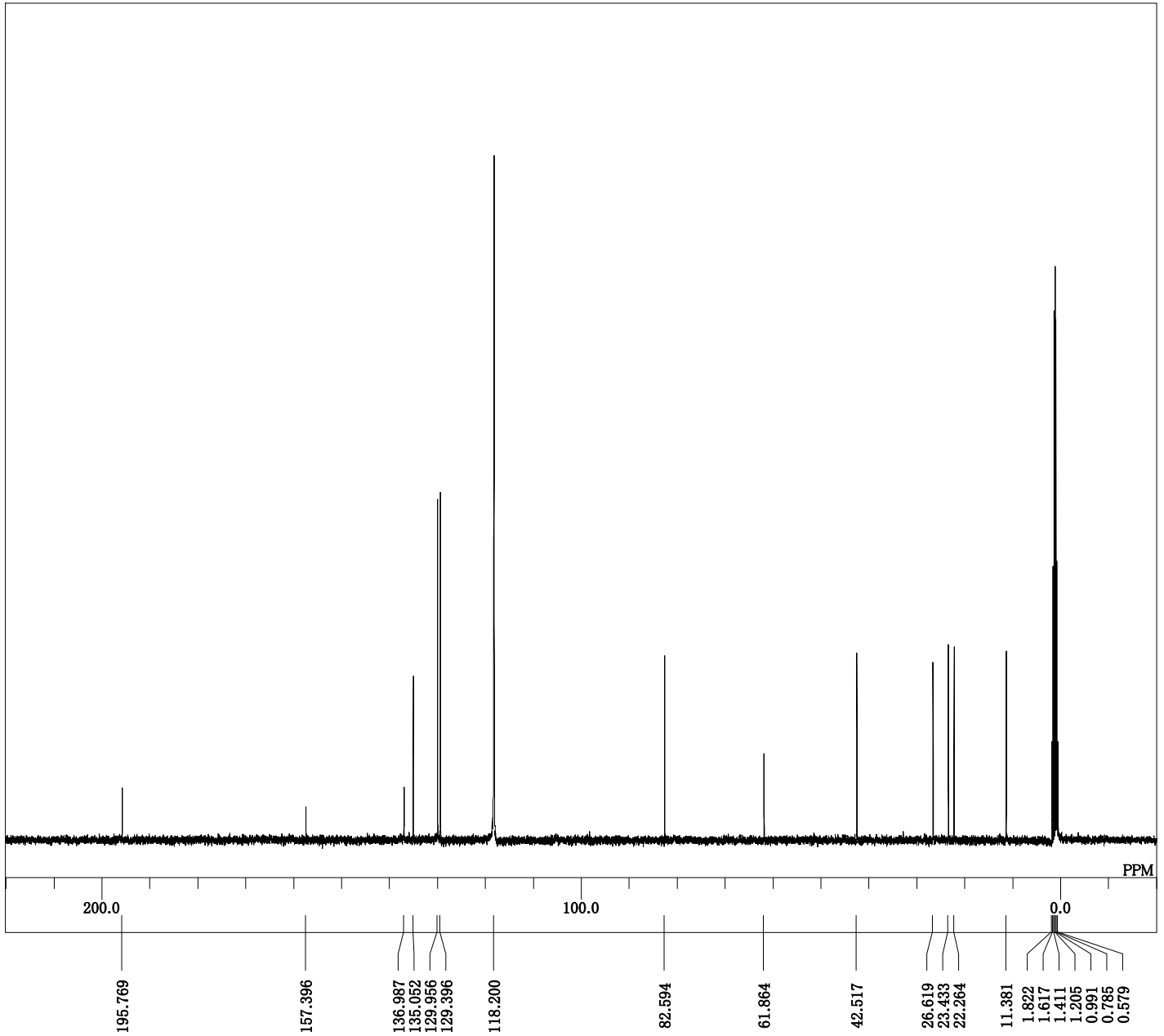

sadamitsu
20191023 ex2515_pos 24 (0.384) Cm (24)
1: TOF MS ES+
1.14e4
669.2296
[M+H]+ calcd for C34H33N6O9+, 669.2304
[M+K]+ calcd for C34H32KN6O9+, 707.1862
707.1800
[2M+K]+ calcd for C68H64KN12O18+, 1375.4093
1375.4611
1376.4716
[2M+Na]+ calcd for C68H64N12NaO18+, 1359.4354
1359.4962
1377.4644
1378.4846
199.0267
208.0368
287.1773
441.2054
638.2253
708.1914
732.2316
733.2266
770.3412
4b
%
m/z
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900



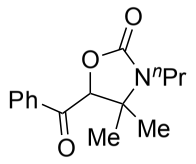
DFILE	20200702.als
COMNT	
DATIM	Thu Jul 02 22:04:32 2020
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	8
ACQTM	2.0500 sec
PD	2.0000 sec
PW1	6.60 usec
IRNUC	1H
CTEMP	6348.8 c
SLVNT	CD3CN
EXREF	1.93 ppm
BF	0.12 Hz
RGAIN	13



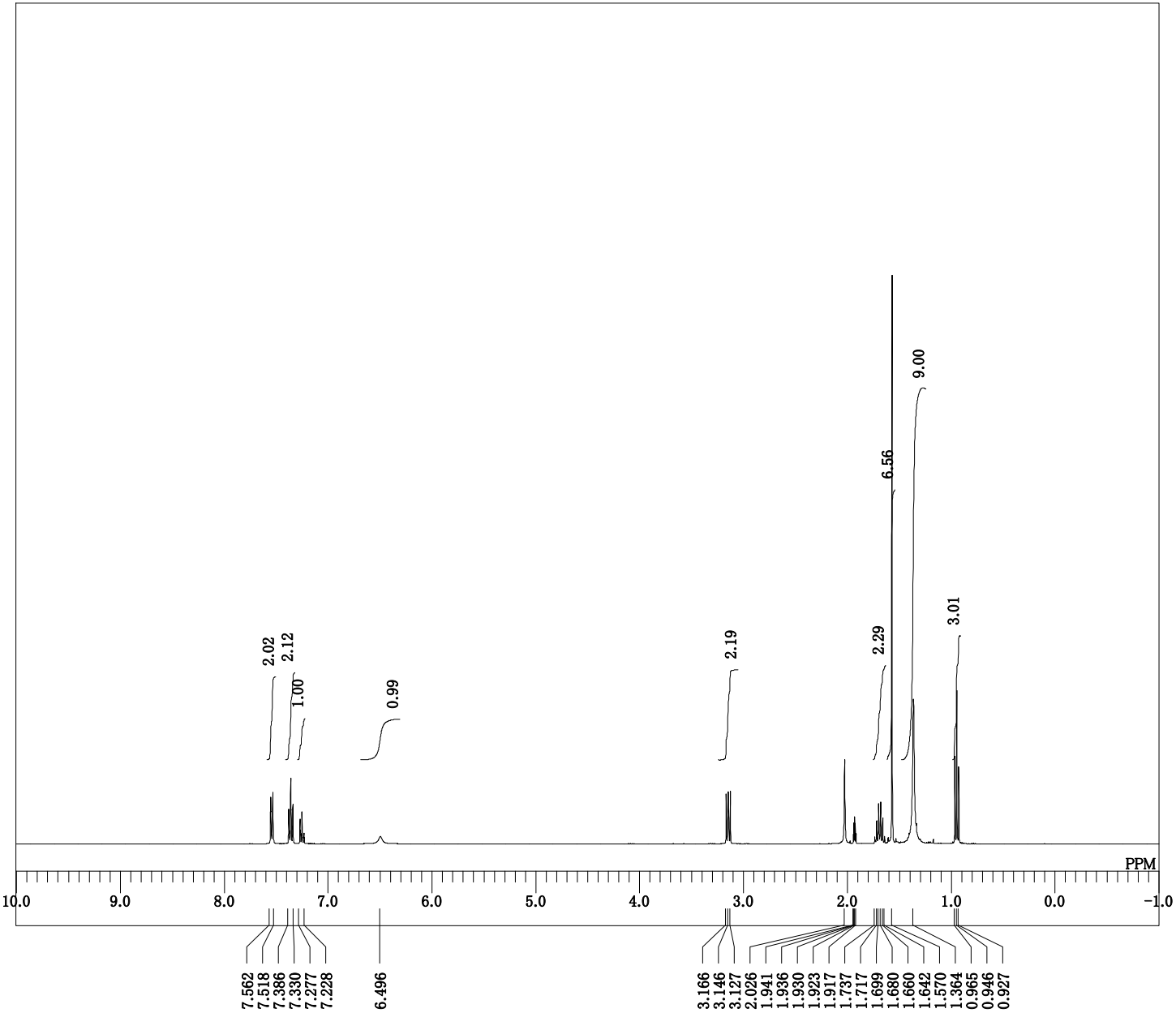
5a



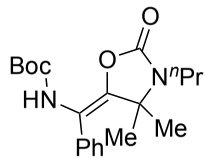
DFILE	20200702_bcm.als
COMNT	
DATIM	Thu Jul 02 22:17:28 2020
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	112
ACQTM	1.2083 sec
PD	3.0000 sec
PW1	4.70 usec
IRNUC	1H
CTEMP	6348.8 c
SLVNT	CD3CN
EXREF	118.20 ppm
BF	1.20 Hz
RGAIN	23



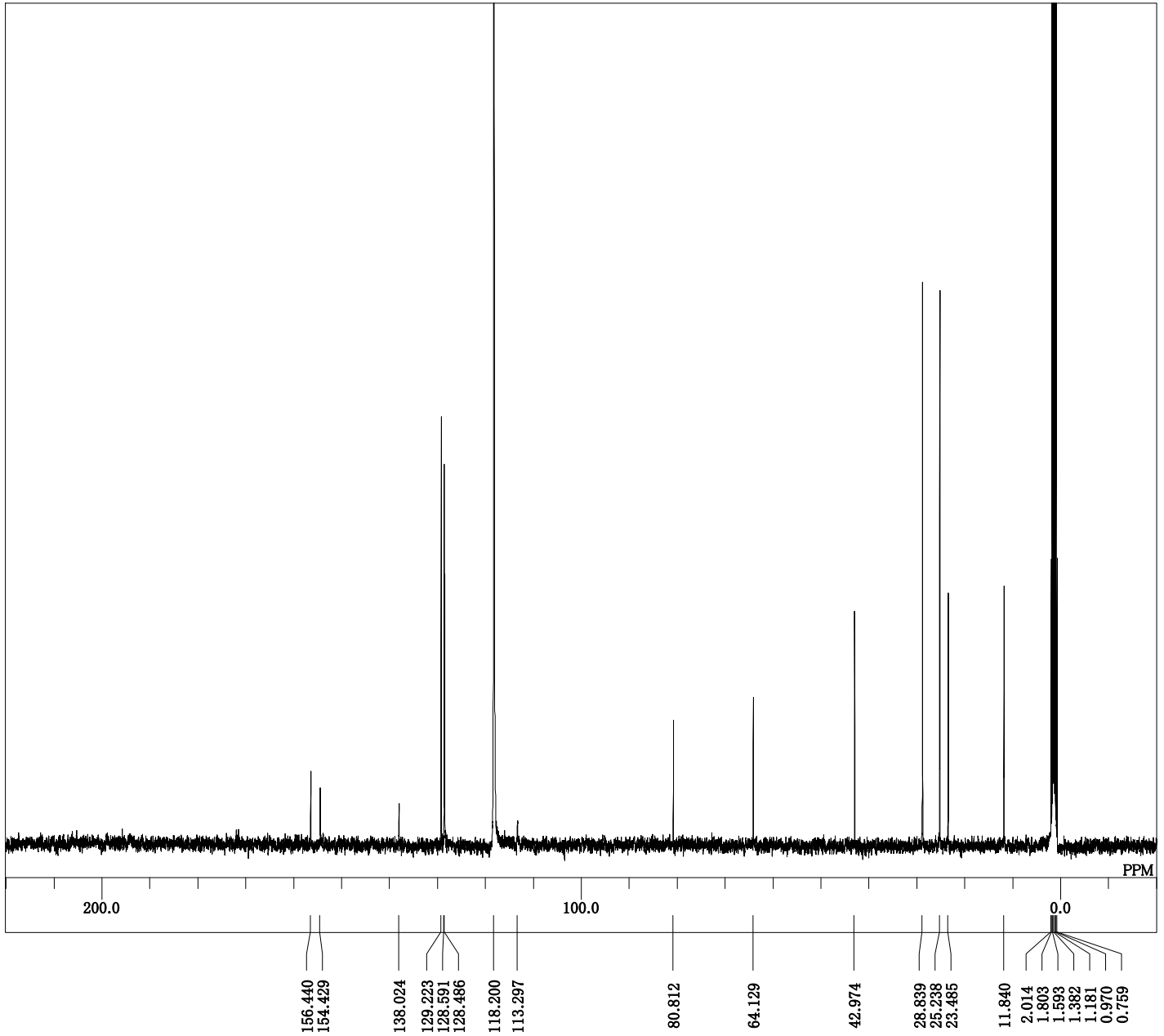
5a



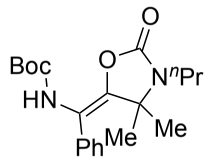
DFILE	20200702 NN_clev_Proton-1-2.als
COMNT	single_pulse
DATIM	2020-07-02 18:41:50
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
POINT	16400
FREQU	7422.80 Hz
SCANS	8
ACQTM	2.2073 sec
PD	5.0000 sec
PW1	3.14 usec
IRNUC	1H
CTEMP	70.0 c
SLVNT	CD3CN
EXREF	1.93 ppm
BF	0.12 Hz
RGAIN	26



7a



DFILE	20200702 NN_clev_Carbon-1-2.als
COMNT	single pulse decoupled gated NOE
DATIM	2020-07-02 18:43:02
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
POINT	26224
FREQU	25000.00 Hz
SCANS	512
ACQTM	1.0486 sec
PD	2.0000 sec
PW1	3.59 usec
IRNUC	1H
CTEMP	70.0 c
SLVNT	CD3CN
EXREF	118.20 ppm
BF	0.12 Hz
RGAIN	50



7a