Electronic Supplementary Information

Catalytic intermolecular aldol reactions of transient amide enolates in domino Michael/aldol reactions of nitroalkanes, acrylamides, and aldehydes

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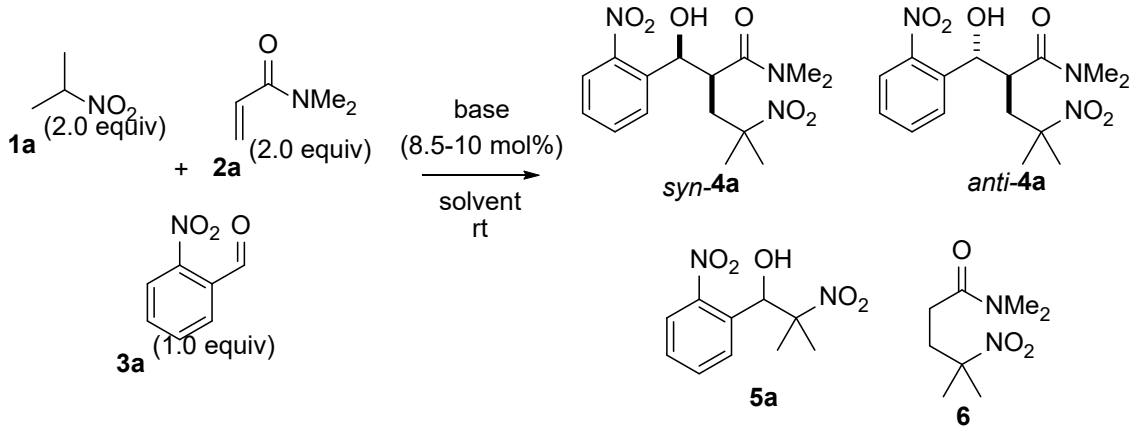
1. General

All melting points were determined on Yanagimoto micro melting point apparatus. Infrared spectra (IR) were recorded on Horiba IR-710. ^{1}H NMR spectra were recorded on a JEOL JNM ECA600 (600 MHz) or a JEOL JNM ECS400 (400 MHz) spectrometer at room temperature; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. Splitting pattern are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on a JEOL JNM ECS400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard $CDCl_3$. HRMS data were recorded on JEOL JMS-T100TD. Analytical TLC was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Silica gel column chromatography was carried out on silica gel 60 N (Kanto Kagaku Co., Ltd., spherical, neutral, 63-210 μm). All reactions were carried out under nitrogen atmosphere in a dried glassware with magnetic stirring. DMSO was distilled from CaH_2. DMSO-d_6 was dried with MS4A. KOH (85%) was purchased from Kanto Chemical Co., Ltd., and freshly powdered KOH was used. Compounds **1q**[1], **1r**[1], **2t**[2], **2u**[3], and **2v**[4] were prepared by the reported procedures.

Determination of the relative configuration (*syn* or *anti*) of three-component adducts **4** was based on X-ray crystallography of **4k** and the stereochemistry of compound **13**. The relative configuration of the minor isomer of **13** was found to be *anti* since its spectral data agreed with reported values.[5] This result suggested that the minor isomer of **4k** whose coupling constant between the benzylic proton and the carbonyl α-proton was 3.7 Hz was the *anti*-configuration, and the major isomer of **4k** whose coupling constant between the benzylic proton and the carbonyl α-proton was 4.7 Hz was the *syn*-configuration. For other products **4** except **4t**, the relative stereochemistry of the isomer that had the larger coupling constant between the benzylic proton and the carbonyl α-proton was assigned to the *syn*-configuration. In the case of **4t**, the coupling constant of one isomer of **4t** could not be measured.

2. Detailed experimental results

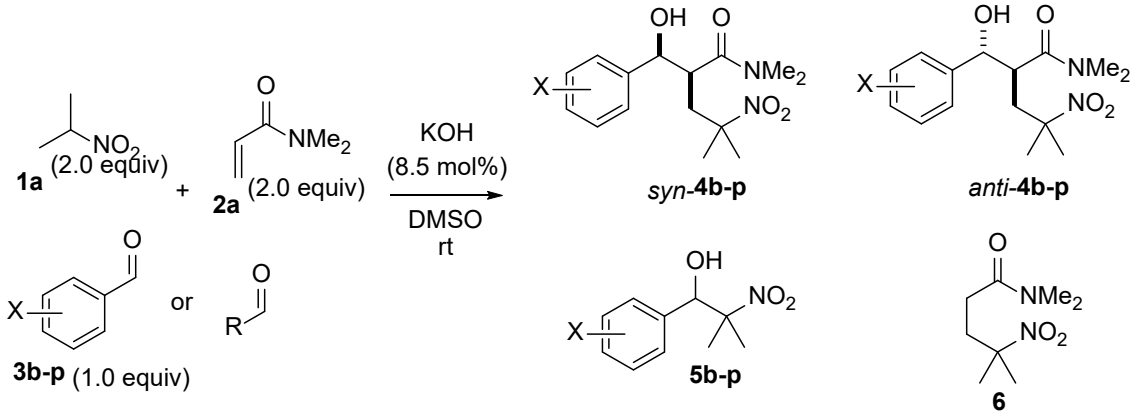
Table S1. Detailed experimental results for Table 1.



entry	solvent	Base (mol%)	time (h)[a]	**4a** (%)[b] (*syn*/*anti*)[c]	**5a** (%)[d]	**6** (%)[b]
1	THF	LHMDS (10)	24	34 (64:36)	24	29
2	THF	*t*-BuOK (10)	26	5 (56:44)	33	5
3	THF	*t*-BuOK/18-c-6 (10)	26	3 (56:44)	39	3
4	DMSO	LHMDS (10)	2.0	84 (62:38)	4	72
5	DMSO	*t*-BuOK (10)	1.0	87 (57:43)	0	72
6	DMSO	KOH (10)	2.0			
7	DMSO	KHMDS (10)	1.0	86 (62:38)	4	78
8	DMSO	CsOH (10)	24	63 (58:42)	17	71
9	DMSO	Cs_2CO_3 (10)	2.0	84 (57:43)	7	85
10	DMSO	Barton's base (10)	1.0	73 (54:46)	11	84
11	DMSO	KOH (8)	2.0	91 (56:44)	6	82
12	1% H_2O-DMSO	KOH (8)	24	17 (61:39)	54	22
13	DMF	KOH (8)	24	66 (56:44)	11	63
14	DMPU	KOH (8)	4	74 (52:48)	2	98
15	HMPA	KOH (8)	6.5	87 (55:45)	0	81

[a] Reactions were performed until either arylamide or aldehyde was not detected by TLC analysis. In the case of long reaction times (>23 h), acrylamide **2a** was still detected. [b] Isolated yield based on **3a**. [c] *Syn*/*anti* ratios were determined by isolation of each diastereomer or ^{1}H NMR analysis of a mixture of diastereomers. [d] Yields were determined by ^{1}H NMR analysis.

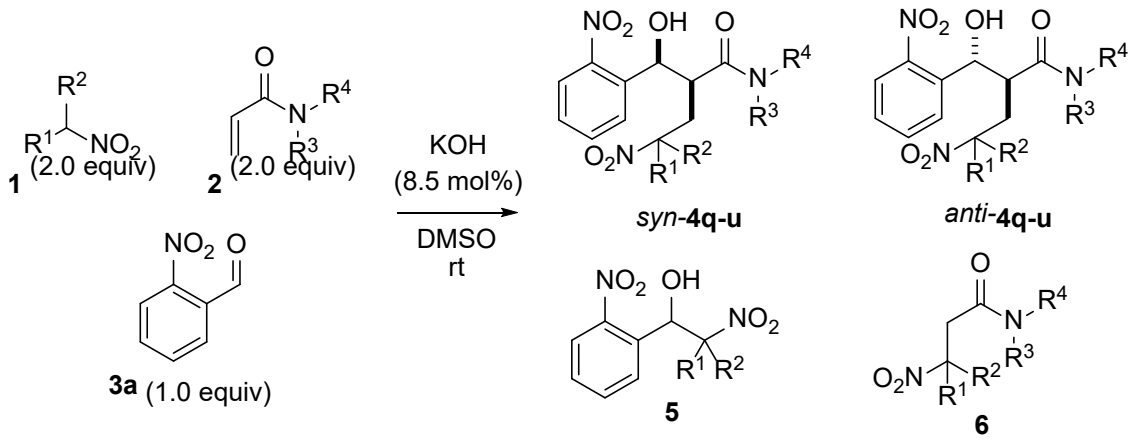
Table S2. Detailed experimental results for Table 2.

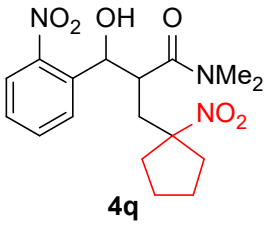
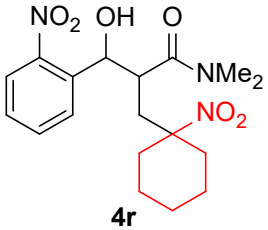
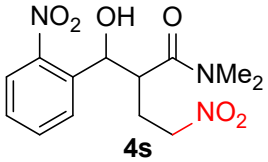
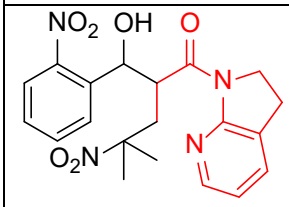


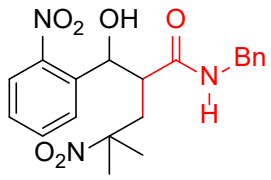
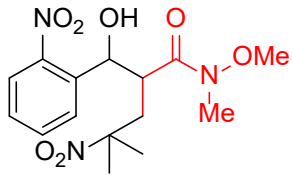
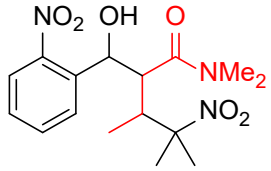
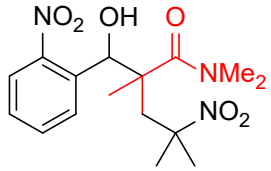
entry	aldehyde X (**3**)	time (h)[a]	yield (%)[b] of **4** (*syn*/*anti*)[c]	yield (%)[d] of **5**	yield (%)[b] of **6**
1	4-CN (**3b**)	1.5	74 (51:49)	9	93
2	2-CF_3 (**3c**)	24	76 (61:39)	6	76
3	4-CF_3 (**3d**)	24	69 (60:40)	9	113
4	2-Cl (**3e**)	1.5	61 (59:41)	<2	109
5	2-Br (**3f**)	24	54 (58:42)	15	90
6	2-pyridiyl (**3g**)	24	46 (46:54)	2	142
7	4-Br (**3h**)	24	64 (67:33)	16	86
8	4-Cl (**3i**)	24	64 (64:36)	15	88
9	4-F (**3j**)	3	42 (60:40)	0	138
10	H (**3k**)	2	71 (75:25)	0	115
11	1-Naphthyl (**3l**)	3	65 (79:21)	0	98
12	2-Me (**3m**)	15	63 (78:22)	0	107
13	4-Me (**3n**)	24	60 (73:27)	2	101
14	2-MeO (**3o**)	1	38 (65:35)	0	132
15[e]	4-MeO (**3p**)	3	43 (70:30)	0	133
16	*t*BuCHO	24	0	0	51
17	$Ph(CH_2)_2CHO$	23	0	0	<122

[a] Reactions were performed until either arylamide or aldehyde was not detected by TLC analysis. In the case of long reaction times (>23 h), acrylamide **2a** was still detected. [b] Isolated yield based on **3**. [c] *Syn*/*anti* ratios were determined by isolation of each diastereomer or ^{1}H NMR analysis of a mixture of diastereomers. [d] Yields were determined by ^{1}H NMR analysis. [e] Barton's base (10 mol%) was used instead of KOH.

Table S3. Detailed experimental results for Figure 1.

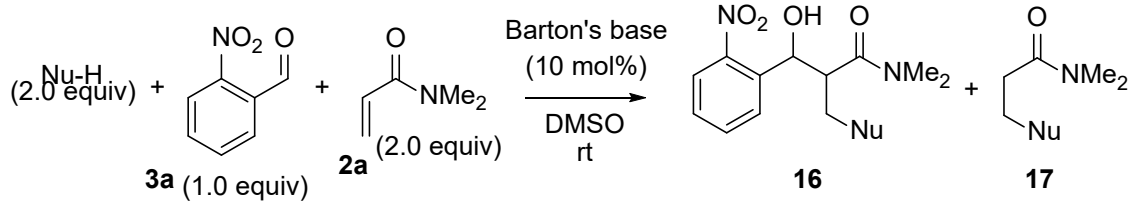


Product	Time (h)	**4** (%)[a]	*syn*/*anti*[b]	**5** (%)[c]	**6** (%)[a]
 **4q**	2 h	87	56:44	0	82
 **4r**	1.5 h	97	56:44	0	103
 **4s**	2 h	65	72:28	24	63
 **4t**	24 h	68	66:34[d]	0	125

 **4u**	28 h 13 h[e]	0 18[e]	— 56:44[e]	77 52[e]	0 58[e]
 **4v**	20 min	62	52:48	0	111
	24 h	0	—	77	0
	24 h	0	—	68	0

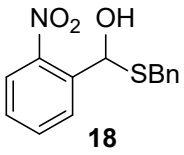
[a] Isolated yield based on **3a**. [b] The ratios were determined by isolation of each diastereomer or ^{1}H NMR analysis of a mixture of diastereomers. [c] Yields based on **3a** were determined by ^{1}H NMR analysis of a mixture of **3a** and **5**. [d] The relative configuration was not assigned. [e]10 mol% of Barton's base was used instead of KOH.

Table S4. Attempted three-component reactions with various nucleophiles

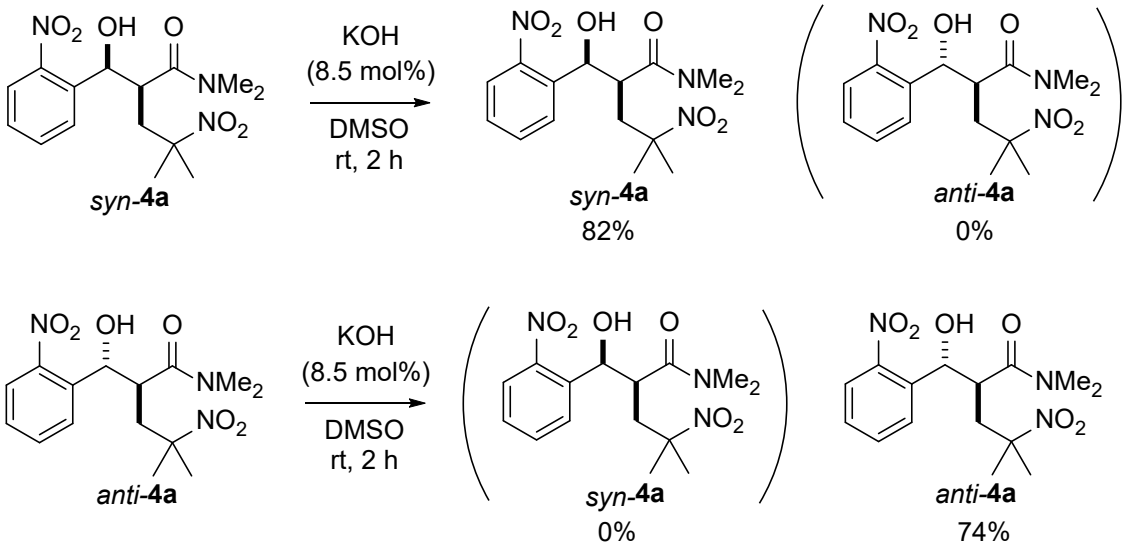


entry	Nu-H	time (h)	**16** (% yield)[a]	**17** (% yield)[a]
1[b]	BnSH	2	0	22
2	PhSH	19	0	79
3	TsNHMe	2	0	0
4	Phthalimide	19	0	0
5	Diethyl methylmalonate	2	0	0

[a] Isolated yield based on **3a**. [b] A mixture of **18** (55% yield based on **3a**, which was determined by ^{1}H NMR spectrum of the mixture), **3a**, and benzyl mercaptan was obtained.



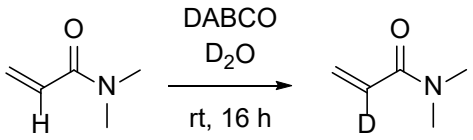
18



Scheme S1. Attempted epimerization of **4a**.

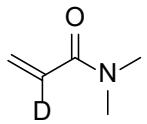
3. Experimental procedures and characterization data

3.1 Synthesis of *N*,*N*-dimethyl α-D-acrylamide (2a-D)



2a-D

A mixture of *N*,*N*-dimethylacrylamide (0.10 mL, 1.0 mmol) and DABCO (57 mg, 0.50 mmol) in D_2O (0.40 ml) was stirred at room temperature for 16 h. The reaction mixture was extracted with Et_2O, and the combined organic extracts were dried over anhydrous Na_2SO_4, filtrated, and concentrated. The residue was purified by column chromatography on silica gel (only Et_2O) to afford *N*,*N*-dimethyl α-D-acrylamide (**2a-D**) (81 mg, 81%). Its D-content (96%D) was determined by ^1H NMR analysis.

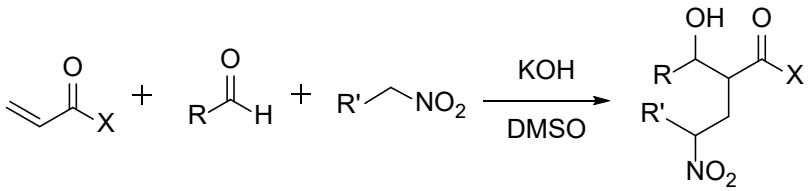


2a-D

***N*,*N*-Dimethyl α-D-acrylamide (2a-D)**

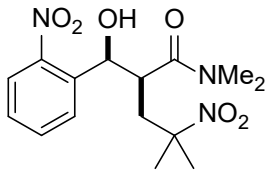
^1H NMR ($CDCl_3$, 400 MHz): δ 6.32-6.30 (1H, m), 5.68-5.67 (1H, m), 3.09 (3H, s), 3.02 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.4, 127.3, 37.1, 35.4; IR ($CHCl_3$, cm^{-1}): 3005, 1633, 1604, 1402.

3.2 General procedure for domino Michael/aldol reaction of nitroalkanes, acrylamides, and aldehydes.



To a mixture of freshly powdered KOH (85%, 1.7 mg, 26 μmol) in DMSO (0.25 mL) was added a solution of acrylamide (0.60 mmol) in DMSO (0.25 mL), a solution of aldehyde (0.30 mmol) in DMSO (0.25 mL), and a solution of nitroalkane (0.60 mmol) in DMSO (0.25 mL) in turn. The reaction mixture was stirred at room temperature until either arylamide or aldehyde was not detected by TLC analysis. The reaction mixture was quenched by adding saturated aqueous solution of NH_4Cl, and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with brine and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate) to afford β'-hydroxy-γ-

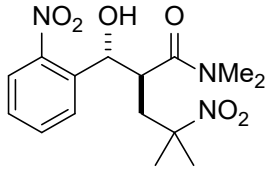
nitro carbonyl compounds **4**.



***syn*-4a**

(*R)-2-[(*R**)-Hydroxy(2-nitrophenyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4a)**

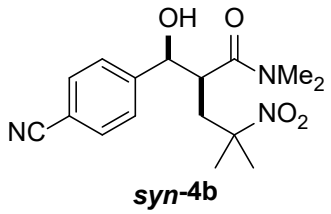
Yellow crystal, mp: 152.5-153.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.07 (1H, d, *J* = 8.4 Hz), 8.03 (1H, d, *J* = 8.0 Hz), 7.74 (1H, dd, *J* = 7.4, 8.0 Hz), 7.51 (1H, dd, *J* = 7.4, 8.4 Hz), 5.47 (1H, s), 5.02 (1H, s), 3.20-3.18 (1H, m), 3.18 (3H, s), 3.06 (3H, s), 2.54 (1H, dd, *J* = 10.2, 15.1 Hz), 2.04 (1H, d, *J* = 15.1 Hz), 1.41 (3H, s), 1.32 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.3, 147.2, 135.8, 133.6, 129.7, 128.7, 125.2, 99.9, 87.4, 69.8, 40.0, 37.8, 37.0, 36.2, 27.2, 24.9; IR ($CHCl_3$, cm^{-1}): 3384, 3008, 1618, 1537, 1350; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_3O_6$ [$(M+H)^+$]: 340.15086, found 340.15071.



***anti*-4a**

(*R)-2-[(*S**)-Hydroxy(2-nitrophenyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*anti*-4a)**

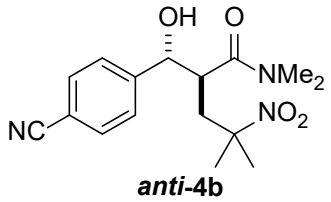
Yellow crystal, mp: 141.5-142.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.97 (1H, d, *J* = 8.0 Hz), 7.63 (1H, dd, *J* = 7.4, 7.8 Hz), 7.54 (1H, d, *J* = 7.8 Hz), 7.46 (1H, dd, *J* = 7.4, 8.0 Hz), 5.41 (1H, d, *J* = 9.0 Hz), 5.28 (1H, dd, *J* = 2.8, 9.0 Hz), 3.54 (1H, ddd, *J* = 2.6, 2.8, 9.4 Hz), 2.88 (1H, dd, *J* = 9.4, 15.2 Hz), 2.76 (3H, s), 2.46 (1H, dd, *J* = 2.6, 15.2 Hz), 2.36 (3H, s), 1.71 (3H, s), 1.57 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.5, 147.5, 138.0, 133.2, 128.7, 128.1, 124.5, 87.6, 72.2, 42.7, 40.7, 37.0, 35.4, 26.7, 25.8; IR ($CHCl_3$, cm^{-1}): 3367, 3024, 1618, 1529, 1348; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_3O_6$ [$(M+H)^+$]: 340.15086, found 340.15031.



***syn*-4b**

(*R)-2-[(*R**)-(4-Cyanophenyl)hydroxymethyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4b)**

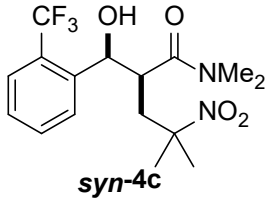
Colorless crystal, mp: 118.5-119.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.66 (2H, d, *J* = 8.6 Hz), 7.46 (2H, d, *J* = 8.6 Hz), 4.82 (1H, d, *J* = 4.0 Hz), 3.97 (1H, d, *J* = 7.6 Hz), 2.95-2.91 (1H, m), 2.91 (6H, s), 2.53 (1H, dd, *J* = 10.0, 15.0 Hz), 2.14 (1H, d, *J* = 15.0Hz), 1.44 (3H, s), 1.43 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.6, 146.1, 132.1, 126.6, 118.6, 111.5, 87.5, 73.3, 43.4, 37.8, 37.5, 36.0, 27.4, 24.6; IR ($CHCl_3$, cm^{-1}): 3406, 3026, 2231, 1628, 1537; HRMS (DART+) (*m/z*) calcd for $C_{16}H_{22}N_3O_4$ [$(M+H)^+$]: 320.16103, found 320.16093.



***anti*-4b**

(*R)-2-[(*S**)-(4-Cyanophenyl)hydroxymethyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*anti*-4b)**

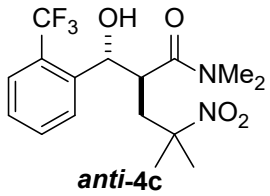
Colorless crystal, mp: 196.0-197.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.64 (2H, d, *J* = 8.4 Hz), 7.37 (2H, d, *J* = 8.4 Hz), 4.98 (1H, d, *J* = 9.2 Hz), 4.82 (1H, dd, *J* = 3.2, 9.2 Hz), 3.00-2.96 (1H, m), 2.76 (3H, s), 2.68 (1H, dd, *J* = 9.6, 15.0 Hz), 2.49 (1H, dd, *J* = 2.4, 15.0 Hz), 2.42 (3H, s), 1.67 (3H, s), 1.49 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.1, 147.9, 132.1, 126.2, 111.7, 99.9, 87.9, 75.9, 42.7, 37.1, 35.8, 35.5, 28.1, 26.0, 24.4; IR ($CHCl_3$, cm^{-1}): 3384, 3005, 2231, 1622, 1537; HRMS (DART+) (*m/z*) calcd for $C_{16}H_{22}N_3O_4$ [$(M+H)^+$]: 320.16103, found 320.16103.



***syn*-4c**

(*R)-2-{(*R**)-Hydroxy[2-(trifluoromethyl)phenyl]methyl}-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4c)**

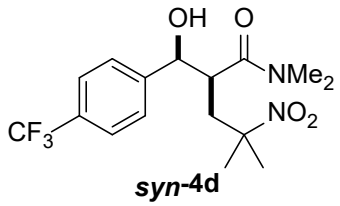
Colorless crystal, mp: 82.5-83.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.97 (1H, d, *J* = 7.8 Hz), 7.68 (1H, d, *J* = 7.8 Hz), 7.64 (1H, dd, *J* = 7.2, 7.8 Hz), 7.44 (1H, dd, *J* = 7.2, 7.8 Hz), 5.30 (1H, s), 4.99 (1H, s), 3.07-3.00 (1H, m), 3.07 (3H, s), 3.05 (3H, s), 2.56 (1H, dd, *J* = 10.2, 15.0 Hz), 2.12 (1H, d, *J* = 15.0 Hz), 1.41 (3H, s), 1.27 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.5, 138.5, 131.8, 129.0, 128.0, 126.5 (q, *J* = 5.7 Hz), 126.2, 126.0, 87.3, 69.4 (q, *J* = 2.9 Hz), 40.4, 37.5 (q, *J* = 1.9 Hz), 36.3, 36.1, 26.6, 25.4; IR ($CHCl_3$, cm^{-1}): 3398, 3008, 1618, 1539, 1311, 1167, 1124; HRMS (DART+) (*m/z*) calcd for $C_{16}H_{22}N_2O_4F_3$ [$(M+H)^+$]: 363.15317, found 363.15212.



***anti*-4c**

(*R)-2-{(*S**)-Hydroxy[2-(trifluoromethyl)phenyl]methyl}-*N*,*N*-4-trimethyl-4-nitropentamide (*anti*-4c)**

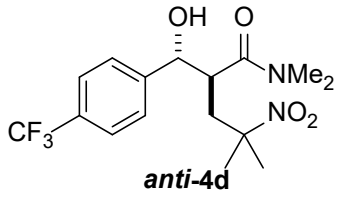
Colorless crystal, mp: 167.0-167.5 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.64 (1H, d, *J* = 7.8 Hz), 7.54 (1H, dd, *J* = 7.5, 7.8 Hz), 7.45 (1H, d, *J* = 7.8 Hz), 7.40 (1H, dd, *J* = 7.5, 7.8 Hz), 5.19 (1H, d, *J* = 8.7 Hz), 5.08 (1H, d, *J* = 8.7 Hz), 3.12 (1H, d, *J* = 9.6 Hz), 2.84-2.80 (1H, m), 2.80 (3H, s), 2.40 (1H, d, *J* = 15.0 Hz), 2.27 (3H, s), 1.64 (3H, s), 1.50 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.3, 141.1, 131.7, 127.9, 127.1, 125.8 (q, *J* = 5.7 Hz), 122.9, 87.7, 72.4-72.3 (m), 43.0, 41.9, 36.8, 35.5, 27.4, 24.9; IR ($CHCl_3$, cm^{-1}): 3386, 3010, 1620, 1539, 1311, 1167, 1126; HRMS (DART+) (*m/z*) calcd for $C_{16}H_{22}N_2O_4F_3$ [$(M+H)^+$]: 363.15317, found 363.15238.



***syn*-4d**

(*R)-2-{(*R**)-Hydroxy[4-(trifluoromethyl)phenyl]methyl}-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4d)**

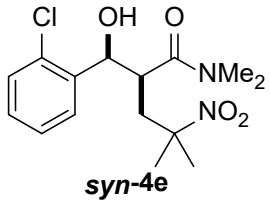
Colorless crystal, mp: 107.0-108.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.63 (2H, d, *J* = 8,4 Hz), 7.47 (2H, d, *J* = 8.4 Hz), 4.85 (1H, d, *J* = 3.6 Hz), 3.73 (1H, s), 2.98-2.93 (1H, m), 2.93 (6H, s), 2.56 (1H, dd, *J* = 10.0, 15.0 Hz), 2.14 (1H, d, *J* = 15.0 Hz), 1.43 (3H, s), 1.42 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.9, 144.6, 130.2, 129.9, 126.2, 125.3 (q, *J* = 3.8 Hz), 87.6, 73.4, 43.5, 37.7, 37.5, 36.0, 27.3, 24.8; IR ($CHCl_3$, cm^{-1}): 3402, 3005, 1624, 1537, 1327, 1169, 1130, 1068; HRMS (DART+) (*m/z*) calcd for $C_{16}H_{22}N_2O_4F_3$ [$(M+H)^+$]: 363.15317, found 363.15416.



***anti*-4d**

(*R)-2-{(*S**)-Hydroxy[4-(trifluoromethyl)phenyl]methyl}-*N*,*N*-4-trimethyl-4-nitropentamide (anti-4d)**

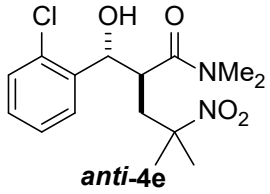
Colorless crystal, mp: 159.0-160.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.60 (2H, d, *J* = 7.8 Hz), 7.37 (2H, d, *J* = 7.8 Hz), 4.89-4.83 (2H, m), 3.00-2.94 (1H, m), 2.76 (3H, s), 2.70 (1H, dd, *J* = 10.0, 15.0 Hz), 2.48 (1H, d, *J* = 15.0 Hz), 2.39 (3H, s), 1.66 (3H, s), 1.49 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.2, 146.5, 125.8, 125.3 (q, *J* = 3.8 Hz), 88.0, 76.1, 43.0, 42.4, 37.1, 35.5, 28.1, 24.3; IR ($CHCl_3$, cm^{-1}): 3386, 3008, 1620, 1537, 1400, 1327, 1169, 1132, 1068; HRMS (DART+) (*m/z*) calcd for $C_{16}H_{22}N_2O_4F_3$ $[(M+H)^+]$: 363.15317, found 363.15238.



***syn*-4e**

(*R)-2-[(*R**)-(2-Chlorophenyl)hydroxymethyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4e)**

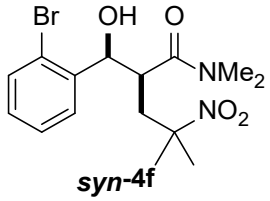
Colorless crystal, mp: 106.0-107.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.72 (1H, d, *J* = 7.2 Hz), 7.37-7.35 (2H, m), 7.28-7.26 (1H, m), 5.13 (1H, s), 4.67 (1H, s), 3,27 (1H, d, *J* = 9.6 Hz), 3.19 (3H, s), 3.05 (3H, s), 2.55 (1H, dd, *J* = 9.6, 15.0 Hz), 1.95 (1H, d, *J* = 15.0 Hz), 1.40 (3H, s), 1.22 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.5, 137.2, 131.1, 129.5, 128.9, 128.7, 126.9, 87.4, 70.7, 38.7, 37.8, 36.7, 36.2, 26.1, 25.6; IR ($CHCl_3$, cm^{-1}): 3410, 3010, 1620, 1537; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_2O_4Cl$ $[(M+H)^+]$: 329.12681, found 329.12685.



***anti*-4e**

(*R)-2-[(*S**)-(2-Chlorophenyl)hydroxymethyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*anti*-4e)**

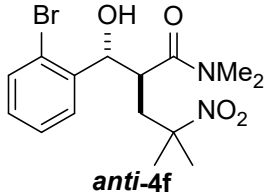
Colorless crystal, mp: 105.5-106.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.33-7.30 (2H, m), 7.28-7.20 (2H, m), 5.13-5.07 (2H, m), 3.35 (1H, ddd, *J* = 2.0, 2.7, 9.2 Hz), 2.78 (1H, dd, *J* = 9.2, 15.1 Hz), 2.70 (3H, s), 2.52 (1H, dd, *J* = 2.7, 15.1 Hz), 2.34 (3H, s), 1.70 (3H, s), 1.53 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.5, 139.5, 131.1, 129.2, 128.9, 126.84, 126.82, 87.9, 73.2, 42.4, 39.5, 36.8, 35.3, 27.4, 25.2; IR ($CHCl_3$, cm^{-1}): 3384, 3010, 1618, 1539; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_2O_4Cl$ $[(M+H)^+]$: 329.12681, found 329.12688.



***syn*-4f**

(*R)-2-[(*R**)-(2-Bromophenyl)hydroxymethyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4f)**

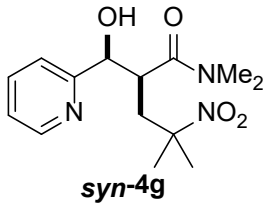
Colorless crystal, mp: 97.0-98.0 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (1H, d, *J* = 8.0 Hz), 7.55 (1H, d, *J* = 7.4 Hz), 7.40 (1H, dd, *J* = 7.2, 7.4 Hz), 7.20 (1H, dd, *J* = 7.2, 8.0 Hz), 5.08 (1H, s), 4.87 (1H, s), 3.29 (1H, d, *J* = 9.3 Hz), 3.22 (3H, s), 3.05 (3H, s), 2.55 (1H, dd, *J* = 9.3, 15.3 Hz), 1.96 (1H, d, *J* = 15.3 Hz), 1.40 (3H, s), 1.20 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.5, 138.6, 132.9, 129.3, 129.2, 127.5, 121.3, 87.4, 72.8, 38.5, 38.1, 36.7, 36.1, 26.0, 25.8; IR ($CHCl_3$, cm^{-1}): 3400, 3010, 1620, 1537; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_2O_4{}^{79}Br$ [$(M+H)^+$]: 373.07629, found 373.07659.



***anti*-4f**

(*R)-2-[(*S**)-(2-Bromophenyl)hydroxymethyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*anti*-4f)**

Colorless crystal, mp: 93.0-93.5 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (1H, d, *J* = 7.6 Hz), 7.31-7.29 (2H, m), 7.16-7.12 (1H, m), 5.13 (1H, d, *J* = 9.6 Hz), 5.04 (1H, dd, *J* = 2.7, 9.6 Hz), 3.38 (1H, ddd, *J* = 2.4, 2.7, 9.4 Hz), 2.79 (1H, dd, *J* = 9.4, 15.0 Hz), 2.70 (3H, s), 2.53 (1H, dd, *J* = 2.4, 15.0 Hz), 2.32 (3H, s), 1.70 (3H, s), 1.52 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.4, 140.9, 132.5, 129.2, 127.4, 127.1, 121.2, 87.9, 75.4, 42.6, 39.4, 36.8, 35.3, 27.5, 25.0; IR ($CHCl_3$, cm^{-1}): 3388, 3010, 1616, 1539; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_2O_4{}^{81}Br$ [$(M+H)^+$]: 375.07425, found 375.07429.

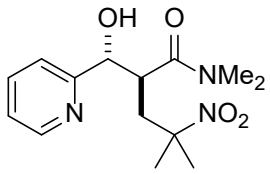


***syn*-4g**

(*R)-2-[(*R**)-Hydroxy-(2-pyridyl)methyl]-N,N-4-trimethyl-4-nitropentamide (*syn*-4g)**

Colorless crystal, mp: 107.0-108.0 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.55 (1H, d, *J* = 8.0 Hz), 7.68 (1H, dd, *J* = 7.6, 7.8 Hz), 7.33 (1H, d, *J* = 7.8 Hz), 7.22 (1H, dd, *J* = 7.6, 8.0 Hz),

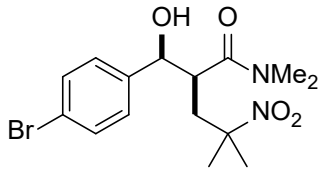
4.71 (1H, dd, *J* = 4.8, 5.3 Hz), 4.21 (1H, d, *J* = 4.8 Hz), 3.15 (1H, ddd, *J* = 1.3, 5.3, 9.9 Hz), 2.87 (3H, s), 2.76 (3H, s), 2.63 (1H, dd, *J* = 9.9, 14.9 Hz), 2.30 (1H, d, *J* = 14.9 Hz), 1.47 (3H, s), 1.44 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.6, 159.1, 148.8, 136.4, 122.9, 121.3, 87.8, 74.4, 43.9, 38.8, 37.3, 35.7, 27.1, 25.0; IR ($CHCl_3$, cm^{-1}): 3423, 3008, 1631, 1537; HRMS (DART+) (*m/z*) calcd for $C_{14}H_{22}N_3O_4$ [$(M+H)^+$]: 296.16103, found 296.16202.



***anti*-4g**

(*R)-2-[(*S**)-hydroxy-(2-pyridyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*anti-4g*)**

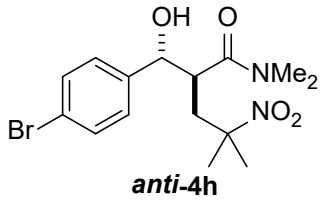
Colorless crystal, mp: 120.0-121.0 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.52 (1H, d, *J* = 4.8 Hz), 7.68 (1H, dd, *J* = 7.2, 7.8), 7.42 (1H, d, *J* = 7.8 Hz), 7.18 (1H, dd, *J* = 4.8, 7.2 Hz), 4.98 (1H, d, *J* = 9.6 Hz), 4,81 (1H, dd, *J* = 3.6, 9.6 Hz), 3.50-3.49 (1H, m), 2.76-2.71 (1H, m), 2.71 (3H, s), 2.63 (3H, s), 2.46 (1H, d, *J* = 15.0 Hz), 1.67 (3H, s), 1.53 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.8, 161.5, 148.6, 136.6, 122.5, 120.2, 87.8, 77.0, 41.8, 40.8, 37.3, 35.4, 27.3, 25.3; IR ($CHCl_3$, cm^{-1}): 3383, 3006, 1616, 1539; HRMS (DART+) (*m/z*) calcd for $C_{14}H_{22}N_3O_4$ [$(M+H)^+$]: 296.16103, found 296.16233.



***syn*-4h**

(*R)-2-[(*R**)-(4-Bromophenyl)hydroxymethyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4h)**

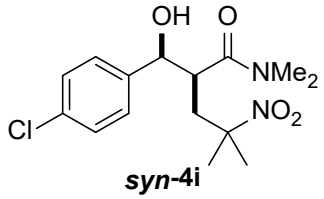
Colorless crystal, mp: 126.5-127.0 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.49 (2H, d, *J* = 8.6 Hz), 7.22 (2H, d, *J* = 8.6 Hz), 4.75 (1H, d, *J* = 3.8 Hz), 3.56 (1H, s), 2.92-2.91 (7H, m), 2.54 (1H, dd, *J* = 3.8, 14.9 Hz), 2.17 (1H, d, *J* = 14.9 Hz), 1.43 (3H, s), 1.43 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.7, 139.9, 131.4, 127.6, 121.6, 87.6, 73.5, 44.0, 38.1, 37.5, 35.9, 27.3, 24.9; IR ($CHCl_3$, cm^{-1}): 3406, 3008, 1628, 1537; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_2O_4{}^{81}Br$ [$(M+H)^+$]: 375.07425, found 375.07374.



***anti*-4h**

(*R)-2-[(*S**)-(4-bromophenyl)hydroxymethyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*anti*-4h)**

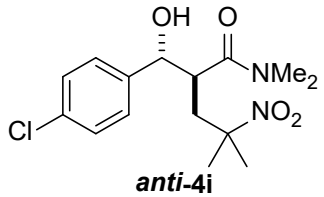
Colorless crystal, mp: 159.5-160.0 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.46 (2H, d, *J* = 8.4 Hz), 7.11 (2H, d, *J* = 8.4 Hz), 4.73-4.72 (2H, m), 2.95-2.91 (2H, m), 2.79 (3H, s), 2.67 (1H, dd, *J* = 9.6, 15.0 Hz), 2.44-2.43 (4H, m), 1.64 (3H, s), 1.48 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.4, 141.5, 131.4, 127.1, 121.6, 88.0, 76.0, 43.1, 42.3, 37.2, 35.6, 28.1, 24.3; IR ($CHCl_3$, cm^{-1}): 3392, 3008, 1618, 1537; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_2O_4{}^{79}Br$ [$(M+H)^+$]: 373.07629, found 373.07679.



***syn*-4i**

(*R)-2-[(*R**)-(4-chlorophenyl)hydroxymethyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4i)**

Colorless crystal, mp: 104.0-105.0 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.33 (2H, d, *J* = 8.1 Hz), 7.27 (2H, d, *J* = 8.1 Hz), 4.77 (1H, d, *J* = 4.2 Hz), 3.55 (1H, s), 2.92-2.91 (7H, m), 2.54 (1H, dd, *J* = 9.9, 14.9 Hz), 2.18 (1H, d, *J* = 14.9 Hz), 1.43 (3H, s), 1.43 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.7, 139.3, 133.4, 128.4, 127.2, 87.6, 73.4, 44.0, 38.0, 37.4, 35.9, 27.2, 24.8; IR ($CHCl_3$, cm^{-1}): 3410, 3006, 1628, 1537; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_2O_4Cl$ [$(M+H)^+$]: 329.12681, found 329.12712.

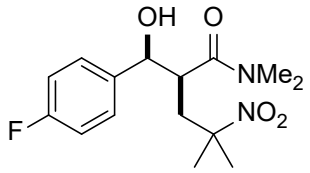


***anti*-4i**

(*R)-2-[(*S**)-(4-Chlorophenyl)hydroxymethyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*anti*-4i)**

Colorless crystal, mp: 155.0-156.0 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32-7.29 (2H, m), 7.19-7.15 (2H, m), 4.75 (1H, dd, *J* = 3.6, 8.8 Hz), 4.70 (1H, d, *J* = 8.8 Hz), 2.94 (1H, ddd, *J* = 2.2, 3.6, 9.6 Hz), 2.79 (3H, s), 2.68 (1H, dd, *J* = 9.6, 15.0 Hz), 2.44 (1H, dd, *J* = 2.2, 15.0 Hz), 2.44 (3H, s), 1.64 (3H, s), 1.48 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.4, 141.0, 133.5, 128.5,

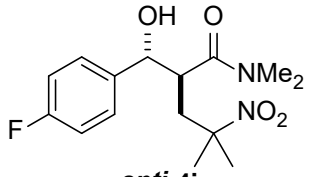
126.8, 88.0, 76.0, 43.2, 42.4, 37.2, 35.6, 28.1, 24.3; IR ($CHCl_3$, cm^{-1}): 3388, 3008, 1618, 1537; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_2O_4Cl$ [$(M+H)^+$]: 329.12681, found 329.12626.



***syn*-4j**

(*R)-2-[(*R**)-(4-Fluorophenyl)hydroxymethyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4j)**

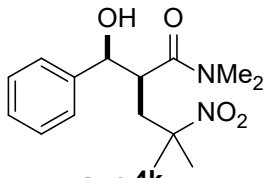
Colorless crystal, mp: 109.0-110.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.32 (2H, m), 7.04 (2H, dd, *J* = 8.4, 8.8 Hz), 4.75 (1H, d, *J* = 4.8 Hz), 3.59 (1H, s), 2.91-2.85 (1H, m), 2.88 (3H, s), 2.85 (3H, s), 2.54 (1H, dd, *J* = 9.8, 14.9 Hz), 2.26 (1H, d, *J* = 14.9 Hz), 1.44 (6H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.8, 162.2 (d, *J* = 245.0 Hz), 136.5 (d, *J* = 1.9 Hz), 127.4 (d, *J* = 8.6 Hz), 115.1 (d, *J* = 20.0 Hz), 87.7, 73.5, 44.2, 38.1, 37.4, 35.9, 27.3, 24.8; IR ($CHCl_3$, cm^{-1}): 3406, 3006, 1630, 1537, 1230; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_2O_4F$ [$(M+H)^+$]: 313.15636, found 313.15688.



***anti*-4j**

(*R)-2-[(*S**)-(4-Fluorophenyl)hydroxymethyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*anti*-4j)**

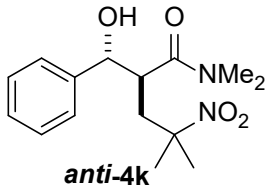
Colorless crystal, mp: 132.5-133.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.22-7.18 (2H, m), 7.02 (2H, dd, *J* = 8.4, 8.8 Hz), 4.75 (1H, dd, *J* = 3.6, 8.8 Hz), 4.64 (1H, d, *J* = 8.8 Hz), 2.93 (1H, ddd, *J* = 2.4, 3.6, 9.7 Hz), 2.79 (3H, s), 2.67 (1H, dd, *J* = 9.9, 14.9 Hz), 2.45 (3H, s), 2.41 (1H, d, *J* = 14.9 Hz), 1.63 (3H, s), 1.47 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.5, 162.3 (d, *J* = 245.0 Hz), 138.2 (d. *J* = 2.9 Hz), 127.0 (d, *J* = 8.5 Hz), 115.2 (d, *J* = 21.9 Hz), 88.0, 76.0, 43.4, 42.3, 37.1, 35.6, 28.1, 24.3; IR ($CHCl_3$, cm^{-1}): 3394, 3008, 1618, 1537, 1230; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_2O_4F$ [$(M+H)^+$]: 313.15636, found 313.15626.



***syn*-4k**

(*R)-2-[(*R**)-Hydroxy(phenyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4k)**

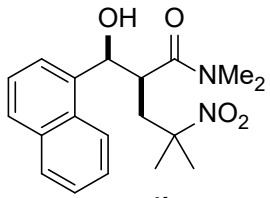
Colorless crystal, mp: 94.0-95.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.37-7.32 (4H, m), 7.30-7.29 (1H, m), 4.79 (1H, d, *J* = 4.7 Hz), 3.41 (1H, s), 2.94 (1H, ddd, *J* = 1.5, 4.7, 9.9 Hz), 2.90 (3H, s), 2.86 (3H, s), 2.58 (1H, dd, *J* = 9.9, 14.8 Hz), 2.26 (1H, d, *J* = 14.8 Hz), 1.43 (3H, s), 1.40 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.8, 140.9, 128.2, 127.8, 125.7, 87.7, 74.0, 44.4, 38.2, 37.3, 35.8, 27.0, 25.0; IR ($CHCl_3$, cm^{-1}): 3421, 3016, 1628, 1537; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{23}N_2O_4$ [$(M+H)^+$]: 295.16578, found 296.16483.



***anti*-4k**

(*R)-2-[(*S**)-Hydroxy(phenyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*anti*-4k)**

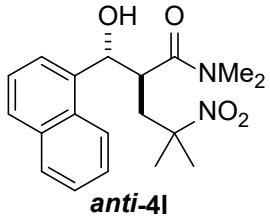
Colorless crystal, mp: 138.0-138.5 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.28 (2H, m), 7.23-7.21 (2H, m), 4.77 (1H, dd, *J* = 3.7, 8.6 Hz), 4.58 (1H, d, *J* = 8.6 Hz), 2.96 (1H, ddd, *J* = 2.3, 3.7, 10.1 Hz), 2.77 (3H, s), 2.70 (1H, dd, *J* = 10.1, 15.1 Hz), 2.44 (1H, dd, *J* = 2.3, 15.1 Hz), 2.37 (3H, s), 1.64 (3H, s), 1.47 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.5, 142.4, 128.3, 127.8, 125.3, 88.1, 43.4, 42.4, 37.0, 35.5, 28.1, 24.3; IR ($CHCl_3$, cm^{-1}): 3400, 3008, 1618, 1537; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{23}N_2O_4$ [$(M+H)^+$]: 295.16578, found 296.16622.



***syn*-4l**

(*R)-2-[(*R**)-Hydroxy-(1-naphthalenyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4l)**

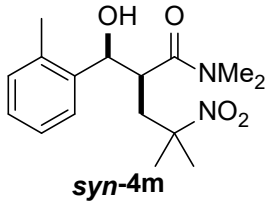
Colorless crystal, mp: 112.5-113.5 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.94-7.88 (2H, m), 7.82-7.76 (2H, m), 7.54-7.47 (3H, m), 5.57 (1H, d, *J* = 4.0 Hz), 4.18 (1H, s), 3.19 (1H, ddd, *J* = 1.8, 4.0, 9.3 Hz), 2.87 (3H, s), 2.86 (3H, s), 2.65 (1H, dd, *J* = 9.3, 15.1 Hz), 2.28 (1H, dd, *J* = 1.8, 15.1 Hz), 1.38 (3H, s), 1.06 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.9, 135.8, 133.7, 129.9, 129.3, 128.4, 126.2, 125.5, 125.2, 124.6, 122.1, 87.5, 71.5, 41.8, 38.2, 37.5, 35.8, 26.0, 25.9; IR ($CHCl_3$, cm^{-1}): 3410, 3010, 1620, 1537; HRMS (DART+) (*m/z*) calcd for $C_{19}H_{25}N_2O_4$ [$(M+H)^+$]: 345.18143, found 345.18156.



***anti*-4l**

(*R)-2-[(*S**)-hydroxy-(1-naphthalenyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*anti*-4l)**

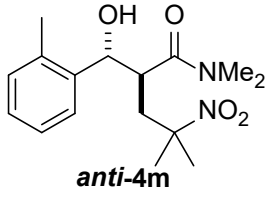
Colorless crystal, mp: 108.0-108.5 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.88-7.86 (2H, m), 7.77 (1H, dd, *J* = 2.6, 6.6 Hz), 7.61 (1H, m), 7.52-7.44 (3H, m), 5.62 (1H, dd, *J* = 2.9, 8.9 Hz), 4.98 (1H, d, *J* = 8.9 Hz), 3.32 (1H, ddd, *J* = 2.4, 2.9, 10.1 Hz), 2.85 (1H, dd, *J* = 10.1, 15.3 Hz), 2.73 (1H, dd, *J* = 2.4, 15.3 Hz), 2.64 (3H, s), 1.79 (3H, s), 1.69 (3H, s), 1.46 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.7, 137.4, 133.4, 129.6, 129.2, 128.1, 126.9, 125.7, 125.2, 122.6, 121.3, 88.3, 73.1, 42.9, 41.5, 36.6, 35.4, 28.6, 24.1; IR ($CHCl_3$, cm^{-1}): 3388, 3008, 1618, 1537; HRMS (DART+) (*m/z*) calcd for $C_{19}H_{25}N_2O_4$ [$(M+H)^+$]: 345.18143, found 345.18155.



***syn*-4m**

(*R)-2-[(*R**)-Hydroxy(2-methylphenyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4m)**

Colorless crystal, mp: 128.0-128.5 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.59 (1H, d, *J* = 7.8 Hz), 7.26-7.24 (1H, m), 7.20 (1H, ddd, *J* = 1.2, 7.2, 7.8 Hz), 7.13 (1H, d, *J* = 7.2 Hz), 5.01 (1H, d, *J* = 3.9 Hz), 3.85 (1H, d, *J* = 0.6 Hz), 2.97 (1H, ddd, *J* = 1.8, 3.9, 9.6 Hz), 2.93 (6H, s), 2.57 (1H, dd, *J* = 9.6, 15.0 Hz), 2.30 (1H, dd, *J* = 1.8, 15.0 Hz), 2.30 (3H, s), 1.44 (3H, s), 1.32 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.5, 138.6, 134.0, 130.5, 127.6, 126.6, 126.0, 87.7, 70.8, 41.2, 37.9, 37.4, 36.0, 26.6, 25.4, 19.1; IR ($CHCl_3$, cm^{-1}): 3417, 3010, 1622, 1537; HRMS (DART+) (*m/z*) calcd for $C_{16}H_{25}N_2O_4$ [$(M+H)^+$]: 309.18143, found 309.18169.

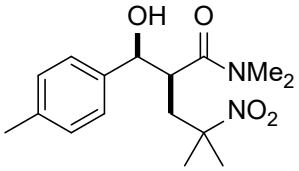


***anti*-4m**

(*R)-2-[(*S**)-Hydroxy(2-methylphenyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*anti*-4m)**

Colorless crystal, mp: 133.5-134.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.19-7.15 (3H, m), 7.10-7.09 (1H, m), 4.99 (1H, dd, *J* = 3.2, 8.8 Hz), 4.66 (1H, d, *J* = 8.8 Hz), 2.98-2.93

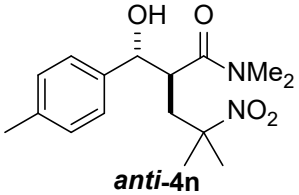
(1H, m), 2.79-2.73 (1H, m), 2.76 (3H, s), 2.49 (1H, d, J = 14.8 Hz), 2.31 (3H, s), 2.22 (3H, s), 1.65 (3H, s), 1.47 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.5, 140.1, 133.5, 130.4, 127.6, 126.0, 124.6, 88.3, 73.3, 42.7, 41.0, 36.6, 35.5, 28.3, 24.0, 18.7; IR ($CHCl_3$, cm^{-1}): 3403, 3010, 1618, 1537; HRMS (DART+) (*m/z*) calcd for $C_{16}H_{25}N_2O_4$ [$(M+H)^+$]: 309.18143, found 309.18334.



***syn*-4n**

(*R)-2-[(*R**)-Hydroxy(4-methylphenyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4n)**

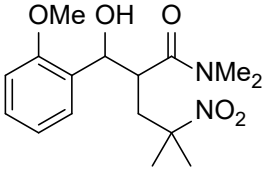
Colorless crystal, mp: 93.0-94.0 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.21 (2H, d, J = 8.1 Hz), 7.15 (2H, d, J = 8.1 Hz), 4.76 (1H, d, J = 4.7 Hz), 3.35 (1H, d, J = 1.5 Hz), 2.92 (1H, ddd, J = 1.5, 4.7, 9.8 Hz), 2.90 (3H, s), 2.87 (3H, s), 2.56 (1H, dd, J = 9.8, 14,4 Hz), 2.27 (3H, s), 2.26 (1H, dd, J = 1.5,14.4 Hz), 1.43 (3H, s), 1.41 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.1, 137.7, 137.4, 129.0, 125.6, 87.8, 73.9, 44.2, 37.9, 37.4, 35.9, 27.1, 25.0, 21.1; IR ($CHCl_3$, cm^{-1}): 3419, 3008, 1626, 1537; HRMS (DART+) (*m/z*) calcd for $C_{16}H_{25}N_2O_4$ [$(M+H)^+$]: 309.18143, found 309.18224.



***anti*-4n**

(*R)-2-[(*S**)-hydroxy(4-methylphenyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*anti*-4n)**

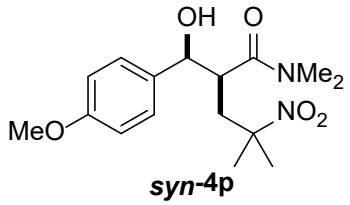
Colorless crystal, mp: 149.0-150.0 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.13-7.08 (4H, m), 4.72 (1H, dd, J = 4.3, 8.3 Hz), 4.42 (1H, d, J = 8.3 Hz), 2.94 (1H, ddd, J = 2.4, 4.3, 9.8 Hz), 2.79 (3H, s), 2.67 (1H, dd, J = 9.8, 14.8 Hz), 2.42 (3H, s), 2.38 (1H, d, J = 14.8 Hz), 2.33 (3H, s), 1.61 (3H, s), 1.47 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.6, 139.3, 137.5, 129.0, 125.3, 88.1, 76.6, 43.5, 42.3, 37.1, 35.6, 28.0, 24.3, 21.1; IR ($CHCl_3$, cm^{-1}): 3403, 3008, 1618, 1537; HRMS (DART+) (*m/z*) calcd for $C_{16}H_{25}N_2O_4$ [$(M+H)^+$]: 309.18143, found 309.18224.



4o

2-[Hydroxy(2-methoxyphenyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (4o)

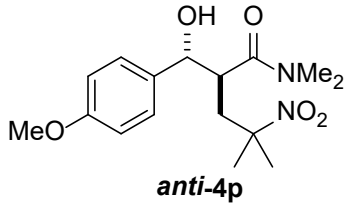
Colorless crystal, mp: 97.0-97.5 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.48 (1H, d, J = 7.6 Hz, *anti*), 7.30-7.22 (1H, m, *anti*), 7.30-7.22 (2H, m, *syn*), 7.01 (1H, dd, *J* = 7.2, 7.6 Hz, *anti*), 6.9 (1H, dd, *J* = 7.2, 7.6 Hz, *syn*), 6.88 (1H, d, *J* = 8.4 Hz, *anti*), 6.83 (1H, d, *J* = 8.0 Hz, *syn*), 5.04 (1H, dd, *J* = 3.4, 9.7 Hz, *syn*), 4.95-4.94 (1H, m, *anti*), 4.76 (1H, d, *J* = 9.7 Hz, *syn*), 3.97 (1H, d, *J* = 2.8 Hz, *anti*), 3.86 (3H, s, *syn*), 3.85 (3H, s, *anti*), 3.33-3.27 (1H, m, *anti*), 3.33-3.27 (1H, m, *syn*), 3.07 (3H, s, *anti*), 2.97 (3H, s, *anti*), 2.71-2.65 (1H, m, *syn*), 2.70 (3H, s, *syn*), 2.52 (1H, dd, *J* = 9.6, 15.0 Hz, *anti*), 2.49-2.45 (1H, m, *syn*), 2.37 (3H, s, *syn*), 2.07 (1H, d, *J* = 15.0 Hz, *anti*), 1.68 (3H, s, *syn*), 1.51 (3H, s, *syn*), 1.40 (3H, s, *anti*), 1.29 (3H, s, *anti*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.3, 174.2, 155.6, 155.4, 130.3, 128.6, 128.5, 128.0, 127.5, 125.9, 120.7, 120.6, 110.0, 109.7, 88.3, 87.9, 71.5, 70.3, 55.2, 55.1, 42.0, 40.1, 39.7, 37.2, 37.1, 36.7, 36.0, 35.3, 27.1, 26.6, 25.2, 25.1; IR ($CHCl_3$, cm^{-1}): 3427, 3008, 1620, 1537, 1238; HRMS (DART+) (*m/z*) calcd for $C_{16}H_{25}N_2O_5$ [$(M+H)^+$]: 325.17635, found 325.17557.



***syn*-4p**

(*R)-2-[(*R**)-Hydroxy(4-methoxyphenyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*syn*-4p)**

Colorless crystal, mp: 136.5-137.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.24 (2H, d, *J* = 8.8 Hz), 6.88 (2H, d, *J* = 8.8 Hz), 4.73 (1H, d, *J* = 4.8 Hz), 3.81 (3H, s), 3.27 (1H, s), 2.93-2.88 (1H, m), 2.88 (3H, s), 2.88 (3H, s), 2.56 (1H, dd, *J* = 9.8, 14.8 Hz), 2.29 (1H, dd, *J* = 1.4, 14.8 Hz), 1.44 (3H, s), 1.43 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.9, 159.1, 132.9, 126.9, 113.6, 87.8, 73.7, 55.2, 44.4, 38.2, 37.4, 35.9, 27.2, 25.0; IR ($CHCl_3$, cm^{-1}): 3421, 3006, 1626, 1537, 1248; HRMS (DART+) (*m/z*) calcd for $C_{16}H_{23}N_2O_4$ [$(M-OH)^+$]: 307.16578, found 307.16596.

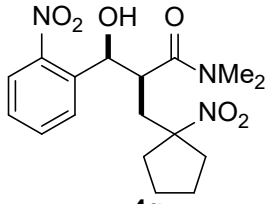


***anti*-4p**

(*R)-2-[(*S**)-Hydroxy(4-methoxyphenyl)methyl]-*N*,*N*-4-trimethyl-4-nitropentamide (*anti*-4p)**

Colorless crystal, mp: 141.0-141.5 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.14 (2H, d, *J* = 8.8 Hz), 6.85 (2H, d, *J* = 8.8 Hz), 4.72 (1H, dd, *J* = 3.8, 8.7 Hz), 4.38 (1H, d, *J* = 8.7 Hz), 3.80 (3H, s), 2.98-2.91 (1H, m), 2.70 (3H, s), 2.67 (1H, dd, *J* = 10.0, 15.0 Hz), 1.62 (3H, s), 1.47 (3H, s);

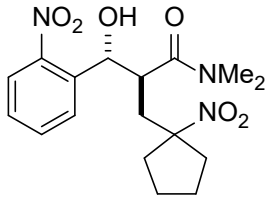
^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.0, 159.5, 134.8, 126.9, 114.0, 88.4, 55.6, 43.9, 42.6, 37.5, 35.9, 28.4, 26.3, 24.6; IR ($CHCl_3$, cm^{-1}): 3411, 3005, 1637, 1537, 1250; HRMS (DART+) (*m/z*) calcd for $C_{16}H_{23}N_2O_4$ [$(M\text{-}OH)^+$]: 307.16578, found 307.16596.



***syn*-4q**

(*R)-2-[(*R**)-Hydroxy-(2-nirophenyl)methyl]-3-cyclopentylnitromethyl-*N*,*N*-dimethylpropanamide (*syn*-4q)**

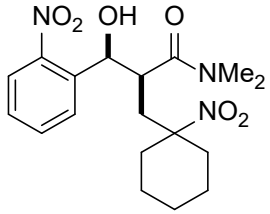
Colorless crystal, mp: 141.0-141.5 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.08 (1H, dd, *J* = 1.7, 8.3 Hz), 8.02 (1H, d, *J* = 7.5 Hz), 7.73 (1H, ddd, *J* = 1.2, 7.6, 7,6 Hz), 7.51 (1H, ddd, *J* = 1.7, 7.6, 8.3 Hz), 5.46 (1H, s), 5.12 (1H, s), 3.17 (3H, s), 3.15 (1H, ddd, *J* = 1.8, 1.8, 10.7 Hz), 3.06 (3H, s), 2.52 (1H, dd, *J* = 10.7, 15.2 Hz), 2.40-2.36 (1H, m), 2.32-2.29 (1H, m), 2.21 (1H, dd, *J* = 1.8, 15.2 Hz), 1.72-1.67 (2H, m), 1.63-1.54 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.3, 147.0, 135.8, 133.6, 129.6, 128.6, 125.2, 99.2, 69.8, 40.5, 39.5, 37.8, 36.2, 35.6, 34.7, 24.3, 23.1; IR ($CHCl_3$, cm^{-1}): 3384, 2966, 1616, 1533, 1350; HRMS (DART+) (*m/z*) calcd for $C_{17}H_{24}N_3O_6$ [$(M+H)^+$]: 366.16651, found 366.16660.



***anti*-4q**

(*R)-2-[(*S**)-hydroxy-(2-nirophenyl)methyl]- 3-cyclopentylnitromethyl-*N*,*N*-dimethylpropanamide (*anti*-4q)**

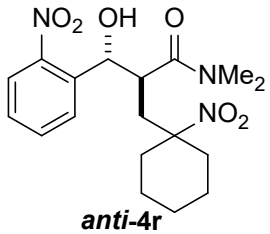
Colorless crystal, mp: 142.0-143.0 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.97 (1H, d, *J* = 8.1 Hz), 7.63 (1H, dd, *J* = 6.9, 7.8 Hz), 7.55 (1H, d, *J* = 6.9 Hz), 7.45 (1H, dd, *J* = 7.8, 8.1 Hz), 5.52 (1H, d, *J* = 9.3 Hz), 5.30 (1H, dd, *J* = 3.0, 9.3 Hz), 3.47 (1H, ddd, *J* = 2.9, 3.0, 9.7 Hz), 2.91 (1H, dd, *J* = 9.7, 15.0 Hz), 2.76 (3H, s), 2.73-2.69 (1H, m), 2.60 (1H, dd, *J* = 2.9, 15.0 Hz), 2.46-2.44 (1H, m), 2.37 (3H, s), 2.00-1.95 (1H, m), 1.76 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.4, 147.4, 138.2, 133.2, 128.6, 128.1, 124.5, 99.5, 71.9, 41.4, 41.3, 38.2, 37.1, 36.5, 35.4, 24.1, 23.6; IR ($CHCl_3$, cm^{-1}): 3361, 2962, 1616, 1531, 1350; HRMS (DART+) (*m/z*) calcd for $C_{17}H_{24}N_3O_6$ [$(M+H)^+$]: 366.16651, found 366.16660.



***syn*-4r**

(*R)-2-[(*R**)-Hydroxy-(2-nirophenyl)methyl]- 3-cyclohexylnitromethyl *N*,*N*-dimethylpropanamide (*syn*-4r)**

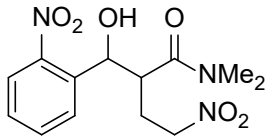
Yellow sticky oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (1H, d, *J* = 8.6 Hz), 8.00 (1H, d, *J* = 8.2 Hz), 7.72 (1H, dd, *J* = 7.4, 8.2 Hz), 7.50 (1H, dd, *J* = 7.4, 8.6 Hz), 5.45 (1H, s), 4.94 (1H, s), 3.23 (3H, s), 3.14 (1H, d, *J* = 10.7 Hz), 3.05 (3H, s), 2.55 (1H, dd, *J* = 10.7, 15.0 Hz), 2.17-2.10 (2H, m), 1.90 (1H, d, *J* = 15.0 Hz), 1.49-1.21 (8H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.2, 147.1, 135.7, 133.5, 129.7, 128.7, 125.2, 90.6, 69.9, 39.3, 37.8, 36.8, 36.3, 35.4, 33.0, 24.4, 22.11, 22.09; IR ($CHCl_3$, cm^{-1}): 3392, 2943, 1618, 1533, 1350; HRMS (DART+) (*m/z*) calcd for $C_{18}H_{26}N_3O_6$ [$(M+H)^+$]: 380.18216, found 380.18365.



***anti*-4r**

(*R)-2-[(*S**)-hydroxy-(2-nirophenyl)methyl]- 3-cyclohexylnitromethyl-*N*,*N*-dimethylpropanamide (*anti*-4r)**

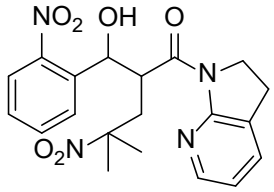
Slight yellow crystal, mp: 151.0-151.5 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (1H. d. *J* = 8.4 Hz), 7.63 (1H, dd, *J* = 7.0, 7.8 Hz), 7.51 (1H, d, *J* = 7.8 Hz), 7.46 (1H, dd, *J* = 7.0, 8.4 Hz), 5.33 (1H, d, *J* = 8.8 Hz), 5.23 (1H, dd, *J* = 2.4, 8.8 Hz), 3.52 (1H, ddd, *J* = 2.1, 2.4, 10.1 Hz), 2.86 (1H, dd, *J* = 10.1, 15.0 Hz), 2.75 (3H, s), 2.53-2.49 (1H, m), 2.35 (1H, dd, *J* = 2.1, 15.0 Hz), 2.35 (3H, s), 2.29-2.25 (1H, m), 1.78-1.25 (8H, m), 1.55 (6H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.2, 147.4, 138.1, 133.2, 128.7, 128.0, 124.4, 90.8, 72.3, 42.6, 39.9, 37.0, 35.4, 34.9, 33.8, 24.6, 22.3, 22.2 IR ($CHCl_3$, cm^{-1}): 3367, 2943, 1618, 1531, 1348; HRMS (DART+) (*m/z*) calcd for $C_{18}H_{26}N_3O_6$ [$(M+H)^+$]: 380.18216, found 380.18301.



4s

2-[Hydroxy-(2-nitrophenyl)methyl]-*N*,*N*-dimethyl-4-nitropentamide (4s)

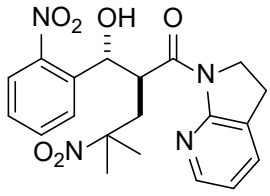
Colorless crystal, mp: 141.5-142.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.07 (1H, dd, *J* = 1.0, 8.2 Hz, *anti*), 8.04 (1H, dd, *J* = 1.2, 8.4 Hz, *syn*), 7.91 (1H, d, *J* = 7.6 Hz, *syn*), 7.79 (1H, d, *J* = 7.2 Hz, *anti*), 7.72-7.68 (2H, m, *syn* and *anti*), 7.54-7.49 (2H, m, *syn* and *anti*), 5.90-5.87 (1H, m, *syn*), 5.64-5.61 (1H, m, *anti*), 5.10-5.03 (2H, m, *syn* and *anti*), 4.56-4.55 (1H, m, *anti*), 4.01-4.00 (1H, m, *syn*), 3.03 (3H, s, *anti*), 2.974 (3H, s, *anti*), 2.968 (3H, s, *syn*), 2.93 (3H, s, *syn*), 2.60-2.21 (8H, m, *syn* and *anti*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.3, 171.1, 134.2, 134.0, 129.4, 129.32, 129.26, 129.1, 125.1, 124.9, 91.5, 89.9, 69.2, 68.6, 37.1, 35.8, 35.6, 28.7, 28.5, 24.6, 22.9; IR ($CHCl_3$, cm^{-1}): 3323, 2929, 1639, 1552, 1348; HRMS (DART+) (*m/z*) calcd for $C_{13}H_{18}N_3O_6$ [$(M+H)^+$]: 312.11956, found 312.11927.



the minor isomer of **4t**

***N*-{2-[Hydroxy(2-nitrophenyl)methyl]-4-methyl-4-nitropentanoyl}2,3-dihydro-1*H*-pyrrolo[2,3-b]pyridine (the minor isomer of 4t)**

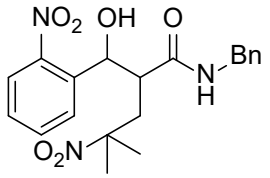
Colorless crystal, mp: 173.5-174.5 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.07 (1H, dd, *J* = 1.2, 5.1 Hz), 7.97-7.94 (2H, m), 7.65 (1H, ddd, *J* = 1.2, 7.0, 7.6 Hz), 7.50 (1H, dd, *J* = 1.2, 7.6 Hz), 7.45 (1H, ddd, *J* = 1.2, 7.0, 8.4 Hz), 6.95 (1H, dd, *J* = 5.1, 5.6 Hz), 5.79 (1H, d, *J* = 6.8 Hz), 5.12 (1H, d, *J* = 10.0 Hz), 4.52 (1H, s), 4.21-4.04 (2H, m), 3.07 (2H, t, *J* = 8.4 Hz), 2.67 (1H, dd, *J* = 9.6, 15.2 Hz), 2.07 (1H, dd, *J* = 1.2, 15.2 Hz), 1.39 (3H, s), 1.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.0, 154.8, 147.7, 145.9, 135.6, 134.0, 133.0, 129.3, 128.4, 126.2, 125.1, 119.1, 87.3, 70.2, 46.2, 43.1, 37.0, 26.8, 25.4, 24.1; IR ($CHCl_3$, cm^{-1}): 3450, 3028, 1628, 1593, 1539, 1427, 1348; HRMS (DART+) (*m/z*) calcd for $C_{20}H_{23}N_4O_6$ [$(M+H)^+$]: 415.16176, found 415.16177.



the major isomer of **4t**

***N*-{2-[Hydroxy(2-nitrophenyl)methyl]-4-methyl-4-nitropentanoyl}2,3-dihydro-1*H*-pyrrolo[2,3-b]pyridine (the major isomer of 4t)**

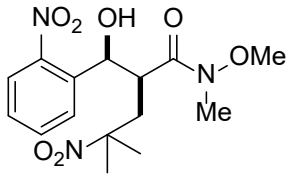
Colorless crystal, mp: 117.5-118.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.89 (1H, d, *J* = 4.9 Hz), 7.85 (1H, d, *J* = 8.2 Hz), 7.69 (1H, d, *J* = 7.6 Hz), 7.53 (1H, dd, *J* = 7.2 Hz, 7.6 Hz), 7.32 (1H, d, *J* = 7.3 Hz), 7.21 (1H, dd, *J* = 7.2, 8.2 Hz), 6.83 (4.9, 7.3 Hz), 5.86 (1H, s), 5.54 (1H, d, *J* = 9.6 Hz), 4.97 (1H, d, *J* = 9.6 Hz), 3.96 (1H, dt, *J* = 6.0. 11.5 Hz), 3.77 (1H, dt, *J* = 6.8, 11.5 Hz), 3.07 (1H, dd, *J* = 10.0, 14.6 Hz), 2.95-2.86 (1H, m), 2.72-2.64 (1H, m), 2.42 (1H, d, *J* = 14.6 Hz), 1.64 (3H, s), 1.63 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.5, 154.2, 146.9, 145.5, 138.8, 133.8, 133.2, 128.0, 127.6, 125.9, 124.7, 119.1, 87.7, 73.0, 45.6, 42.3, 42.1, 27.1, 25.3, 23.8; IR ($CHCl_3$, cm^{-1}): 3417, 3028, 1624, 1593, 1531, 1419, 1346; HRMS (DART+) (*m/z*) calcd for $C_{20}H_{23}N_4O_6$ [$(M+H)^+$]: 415.16176, found 415.16243.



4u

***N*-Benzyl-2-[Hydroxy(2-nitrophenyl)methyl]-*N*-4-dimethyl-4-nitropentamide (4u)**

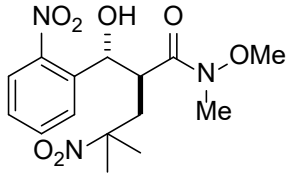
Colorless sticky oil; ^1H NMR ($CDCl_3$, 600 MHz): δ 8.10 (1H, d, *J* = 8.4 Hz), 7.98-7.95 (2H, m), 7.73 (1H, dd, *J* = 7.2, 7.8 Hz), 7.60 (1H, d, *J* = 7.8 Hz), 7.41 (1H, dd, *J* = 7.3, 7.6 Hz), 7.36-7.22 (8H, m), 6.934-6,926 (2H, m), 6.42 (1H, s), 5.89 (1H, s), 5.63 (1H, s), 5.35-5.30 (2H, m), 4.49-4.48 (2H, m), 4.32 (1H, dd, *J* = 6.3, 14.7 Hz), 4.09 (1H, dd, *J* = 4.8, 15.0 Hz), 3.97 (1H, s), 2.79 (1H, dd, *J* = 9.0, 15.0 Hz), 2.74 (1H, d, *J* = 9.0 Hz), 2.61 (1H, d, *J* = 9.0 Hz), 2.49 (1H, dd, *J* = 9.6, 15.0 Hz), 2.42 (1H, d, *J* = 8.4 Hz), 2.06 (1H, d, *J* = 15.0 Hz), 1.69 (3H, s), 1.60 (3H, s), 1.39 (3H, s), 1.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.5, 173.3, 146.7, 137.9, 137.2, 136.0, 134.0, 133.7, 129.1, 128.8, 128.6, 128.51, 128.49, 127.81, 127.75, 127.71, 127.6, 125.5, 124.8, 87.6, 87.5, 72.6, 70.8, 46.8, 46.6, 44.0, 43.5, 41.8, 35.2, 27.1, 26.4, 26.2, 24.7; IR ($CHCl_3$, cm^{-1}): 3432, 3028, 1653, 1527, 1346; HRMS (DART+) (*m/z*) calcd for $C_{20}H_{24}N_3O_6$ [$(M+H)^+$]: 402.16651, found 402.16730.



***syn*-4v**

(*R)-2-[(*R**)-Hydroxy(2-nitrophenyl)methyl]-*N*-methoxy-*N*-4-dimethyl-4-nitropentamide (*syn*-4v)**

Colorless crystal, mp: 120.0-121.0 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01 (1H, d, *J* = 8.2 Hz), 7.97 (1H, d, *J* = 7.8 Hz), 7.71 (1H, dd, *J* = 7.4, 7.8 Hz), 7.50 (1H, dd, *J* = 7.4, 8.2 Hz), 5.60 (1H, s), 4.74 (1H, s), 3.81 (3H, s), 3.40 (1H, d, *J* = 10.1 Hz), 3.19 (3H, s), 2.56 (1H, dd, *J* = 10.1, 15.3 Hz), 2.00 (1H, d, *J* = 15.3 Hz), 1.40 (3H, s), 1.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.3, 147.5, 135.3, 133.3, 129.8, 128.7, 125.0, 87.0, 70.4, 61.6, 39.5, 36.3, 32.4, 29.7, 26.1; IR ($CHCl_3$, cm^{-1}): 3419, 2941, 1631, 1539, 1350; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_3O_7$ [$(M+H)^+$]: 356.14577, found 356.14533.

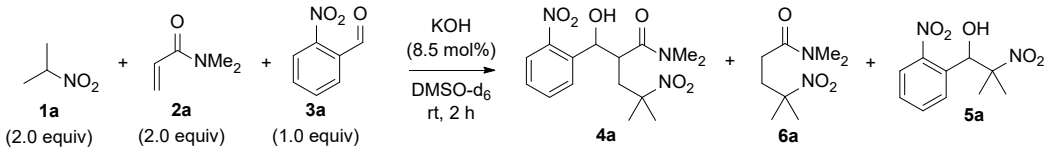


***anti*-4v**

(*R)-2-[(*S**)-Hydroxy(2-nitrophenyl)methyl]-*N*-methoxy-*N*-4-dimethyl-4-nitropentamide (*anti*-4v)**

Colorless crystal, mp: 131.0-131.5 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.99 (1H. dd. *J* = 1.8, 8.3 Hz), 7.66-7.61 (2H, m), 7.45 (1H, ddd, *J* = 1.8, 7.2, 8.3 Hz), 5.41 (1H, dd, *J* = 3.3, 9.3 Hz), 5.04 (1H, d, *J* = 9.3 Hz), 3.67 (1H, ddd, *J* = 2.3, 3.3, 9.6 Hz), 3.09 (3H, s), 2.95 (3H, s), 2.87 (1H, dd, *J* = 9.6, 15.2 Hz), 2.41 (1H, dd, *J* = 2.3, 15.2 Hz), 1.68 (3H, s), 1.61 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.9, 138.1, 133.4, 128.6, 128.3, 124.6, 87.3, 72.7, 60.8, 41.9, 40.1, 31.9, 29.7, 25.8; IR ($CHCl_3$, cm^{-1}): 3392, 2929, 1628, 1539, 1348; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{22}N_3O_7$ [$(M+H)^+$]: 356.14577, found 356.14659.

3.3 The real-time monitoring of the DNMA reaction of 1a, 2a, and 3a (Figure 2).

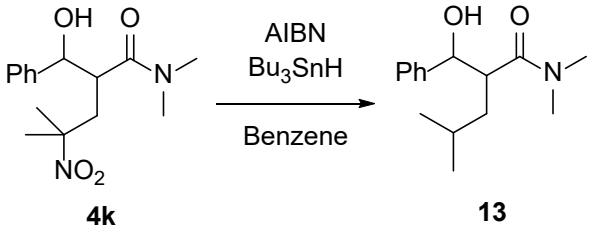


To a mixture of freshly powdered KOH (85%, 1.7 mg, 26 μmol) in DMSO-d_6 (0.4 mL) were added in turn 1,3,5-trimethoxybenzene (internal standard, 16.8 mg, 0.10 mmol), a solution of acrylamide **2a** (59.5 mg, 0.60 mmol) in DMSO-d_6 (0.3 mL), aldehyde **3a** (45.3 mg, 0.30 mmol), and a solution of nitroalkane **1a** (53.5 mg, 0.60 mmol) in DMSO-d_6 (0.3 mL). The reaction mixture was stirred at room temperature, and ^{1}H NMR of the aliquots (0.1 mL) of the reaction mixture after several reaction times were measured.

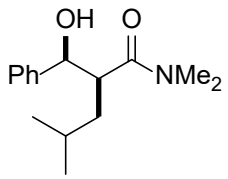
	7 min	20 min	40 min	60 min	80 min	100 min	120 min
4a (%)[a]	11	53	73	71	76	81	82
6a (%)[a]	3	26	48	59	61	64	64
5a (%)[a]	47	12	3	0	0	0	0

[a] Yield based on **3a**.

3.4 Synthesis of 2-[hydroxy(phenyl)methyl]-*N*,*N*-4-trimethylpentamide (13)



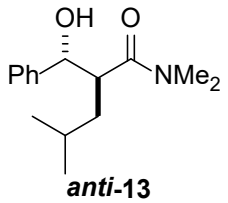
To a solution of **4k** (86 mg, 0.30 mmol, *syn*/*anti* = 72:28) in benzene (2.0 mL), AIBN (25 mg, 0.15 mmol) and Bu_3SnH (0.40 mL, 1.5 mmol) were added. The reaction mixture was refluxed for 10 h, then AIBN (25 mg, 0.15 mmol) and Bu_3SnH (0.40 mL, 1.5 mmol) were added at room temperature. The reaction mixture was refluxed for 2 days. After cooling to room temperature, benzene was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate = 1:2) to afford **13** (58 mg, 0.23 mmol, 77% yield, *syn*/*anti* = 72:28).



***syn*-13**

(*R)-2-[(*R**)-Hydroxy(phenyl)methyl]-*N*,*N*-4-trimethylpentamide (*syn*-13)**

Colorless crystal, mp: 87.0-88.0 ºC (recryst. from $CHCl_3$); ^1H NMR ($CDCl_3$, 600 MHz): δ 7.37-7.32 (4H, m), 7.27-7.24 (1H, m), 4.88 (1H, d, *J* = 3.6 Hz), 4.11 (1H, s), 3.03 (1H, ddd, *J* = 3.6, 4.2, 10.4 Hz), 2.94 (3H, s), 2.92 (3H, s), 1.83 (1H, dd, *J* = 9.6, 10.4 Hz), 1.33-1.32 (2H, m), 0.81 (3H, d, *J* = 6.0 Hz), 0.72 (3H, d, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.9, 142.0, 128.1, 127.2, 125.8, 74.1, 45.8, 37.5, 35.6, 35.5, 26.0, 23.5, 22.0; IR ($CHCl_3$, cm^{-1}): 3406, 2960, 1620; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{23}N_2O_4$ [$(M+H)^+$]: 250.18070, found 250.18037.

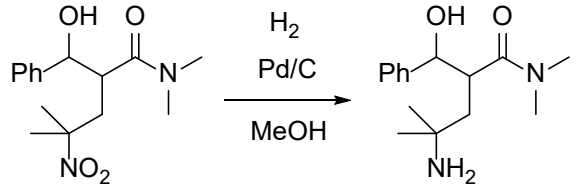


***anti*-13**

(*R)-2-[(*S**)-Hydroxy(phenyl)methyl]-*N*,*N*-4-trimethylpentamide (*anti*-13)[5]**

Colorless crystal, mp: 84.0-85.0 ºC (recryst. From $CHCl_3$) (lit[5] 85-86 °C); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.22 (5H, m), 5.03 (1H, d, *J* = 8.3 Hz), 4.80 (1H, dd, *J* = 3.4, 8.3 Hz), 3.11-3.06 (1H, m), 2.80 (3H, s), 2.57 (3H, s), 1.83 (1H, dd, *J* = 7.4, 8.6 Hz), 1.66-1.58 (2H, m), 0.930 (3H, d, *J* = 6.4 Hz), 0.926 (3H, d, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.3, 144.0, 128.2, 127.2, 125.4, 75.1, 45.4, 39.8, 37.2, 35.3, 25.9, 22.8, 22.7; IR ($CHCl_3$, cm^{-1}): 3388, 2960, 1614; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{23}N_2O_4$ [$(M+H)^+$]: 250.18070, found 250.18010.

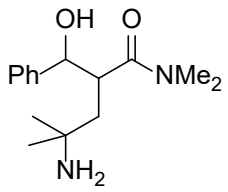
3.5 Synthesis of 4-amino-2-[hydroxy(phenyl)methyl]-*N*,*N*-4-trimethylpentamide (14)



4k **14**

To a solution of **4k** (86 mg, 0.30 mmol, *syn*/*anti* = 72:28) in MeOH (1.0 ml), Pd/C (10%, 20 mg) was added. The reaction vessel was purged three times with hydrogen gas and stirred at room temperature under H_2 atmosphere (1 atm) for 18 h. The reaction mixture was filtered through a pad

of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/Et_3N = 5:1:0.03) to afford **14** (53 mg, 0.20 mmol, 67% yield, *syn*/*anti* = 88:12).

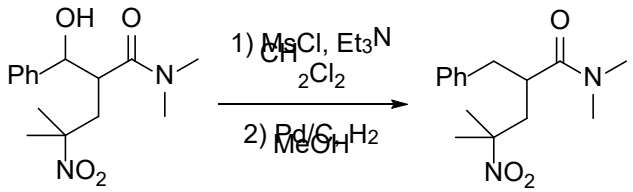


14

4-Amino-2-[hydroxy(phenyl)methyl]-*N*,*N*-4-trimethylpentamide (14)

Slight yellow sticky oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42-7.20 (10H, m, *syn* and *anti*), 5.34 (1H, d, *J* = 3.2 Hz, *syn*), 4.81 (1H, d, *J* = 6.8 Hz, *anti*), 3.30-3.25 (1H, m, *syn*), 3.20-2.15 (1H, m, *anti*), 3.11 (4H, brs, *syn* and *anti*), 2.76 (3H, s, *syn*), 2.69 (3H, s, *anti*), 2.65 (3H, s, *anti*), 2.55 (3H, s, *syn*), 2.27 (1H, dd, *J* = 5.4, 14.4 Hz, *syn*), 1.97 (1H, dd, *J* = 6.8, 15.1 Hz, *anti*), 1.88 (1H, dd, *J* = 5.0, 15.1 Hz, *anti*), 1.74 (1H, dd, *J* = 2.6, 14.2 Hz, *syn*), 1.18 (3H, s, *anti*), 1.17 (3H, s, *anti*), 1.12 (3H, s, *syn*), 1.07 (3H, s, *syn*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.7, 142.8, 127.8, 127.2, 126.4, 75.8, 49.5, 46.2, 43.6, 37.2, 35.3, 33.5, 28.1; IR ($CHCl_3$, cm^{-1}): 3369, 2999, 1623; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{25}N_2O_2$ [$(M+H)^+$]: 265.19160, found 265.19130.

3.6 Synthesis of 4-nitro-2-(phenylmethyl)-*N*,*N*-4-trimethylpentamide (15)

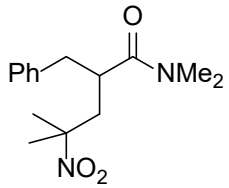


4k **15**

To a solution of **4k** (177 mg, 0.60 mmol, *syn*/*anti* = 72:28) in CH_2Cl_2 (4.0 mL), Et_3N (0.24 mL, 1.8 mmol) and MsCl (0.12 mL, 1.44 mmol) were added at 0 °C. After the mixture was stirred at room temperature for 24 h, it was quenched with 1N aq. HCl. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were washed with saturated aq. $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 1:2) to afford the corresponding mesylate.

To a solution of *anti*-mesylate (38 mg, 0.10 mmol) in MeOH (1.0 mL), Pd/C (10%, 10 mg) was added. The reaction vessel was purged three times with hydrogen gas, and the mixture was stirred

at room temperature under H_2 atmosphere for 18 h. The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate = 1:2) to afford **15** (21 mg, 75 μmol, 75% yield).

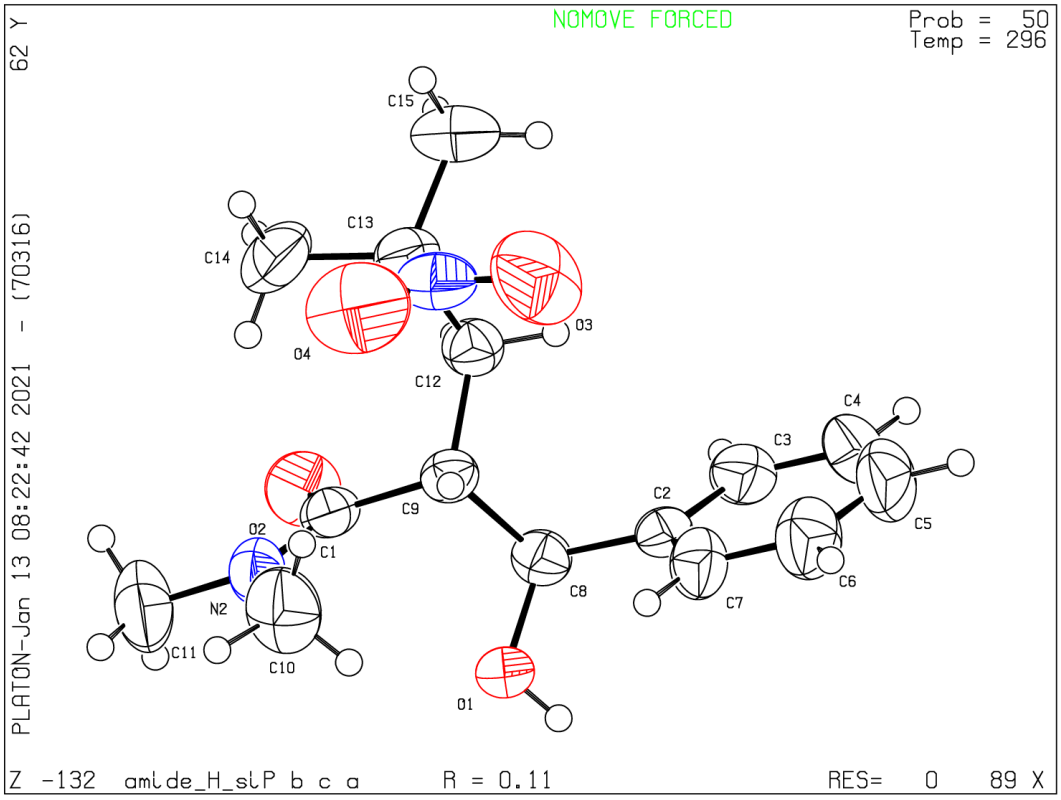


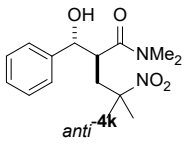
15

4-Nitro-2-(phenylmethyl)-*N*,*N*-4-trimethylpentamide (15)

Colorless crystal, mp: 66.5-67.0 ºC (recryst. from $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28-7.19 (3H, m), 7.12-7.10 (2H, m), 2.87-2.83 (2H, m), 2.81 (3H, s), 2.69-2.58 (2H, m), 2.46 (3H, s), 2.14 (1H, d, J = 14.8 Hz), 1.56 (3H, s), 1.44 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.1, 138.3, 128.9, 128.3, 126.7, 88.3, 43.3, 41.1, 39.5, 36.7, 35.7, 28.2, 23.9; IR ($CHCl_3$, cm^{-1}): 3001, 1637, 1537; HRMS (DART+) (*m/z*) calcd for $C_{15}H_{23}N_2O_3$ [$(M+H)^+$]: 279.17087, found 279.17144.

4. X-ray crystallography of *anti*-4k





CCDC 2055717 (compound *anti*-**4k**) contains the supplementary crystallographic data. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/getstructures.

5. References

1 K. E. Gilbert and W. T. Borden, *J. Org. Chem.,* 1979, **44**, 659-661.

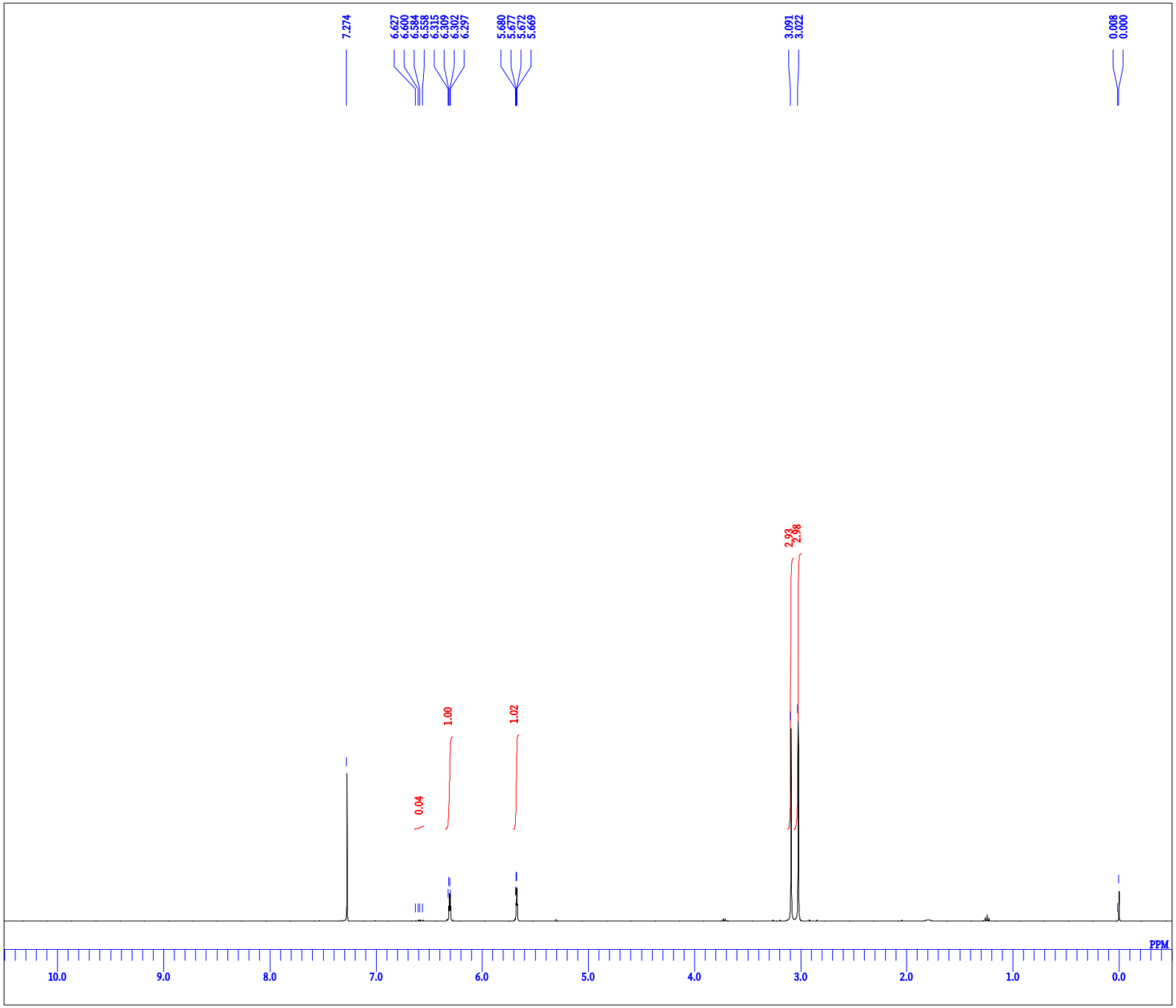
2 M. Zhang, N. Kumagai and M. Shibasaki, *Chem. Eur. J.*, 2017, **23**, 12450-12455.

3 H Miyabe, M Ueda, A Nishimura and T Naito, *Tetrahedron*, 2004, **60**, 4227-4235.

4 Y Nishimura, T Kubo, Y Okamoto and H Cho, *Tetrahedron Lett.*, 2016, **57**, 4492-4495.

5 L Zhang, Z Wang, Z Han and K Ding, *Angew. Chem., Int. Ed.,* 2020, **59**, 15565-15569.

6. ^{1}H and ^{13}C NMR spectra



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FREQU	6002.31 Hz
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PD	2.0000 sec
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SLVNT	CDCL3
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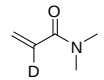
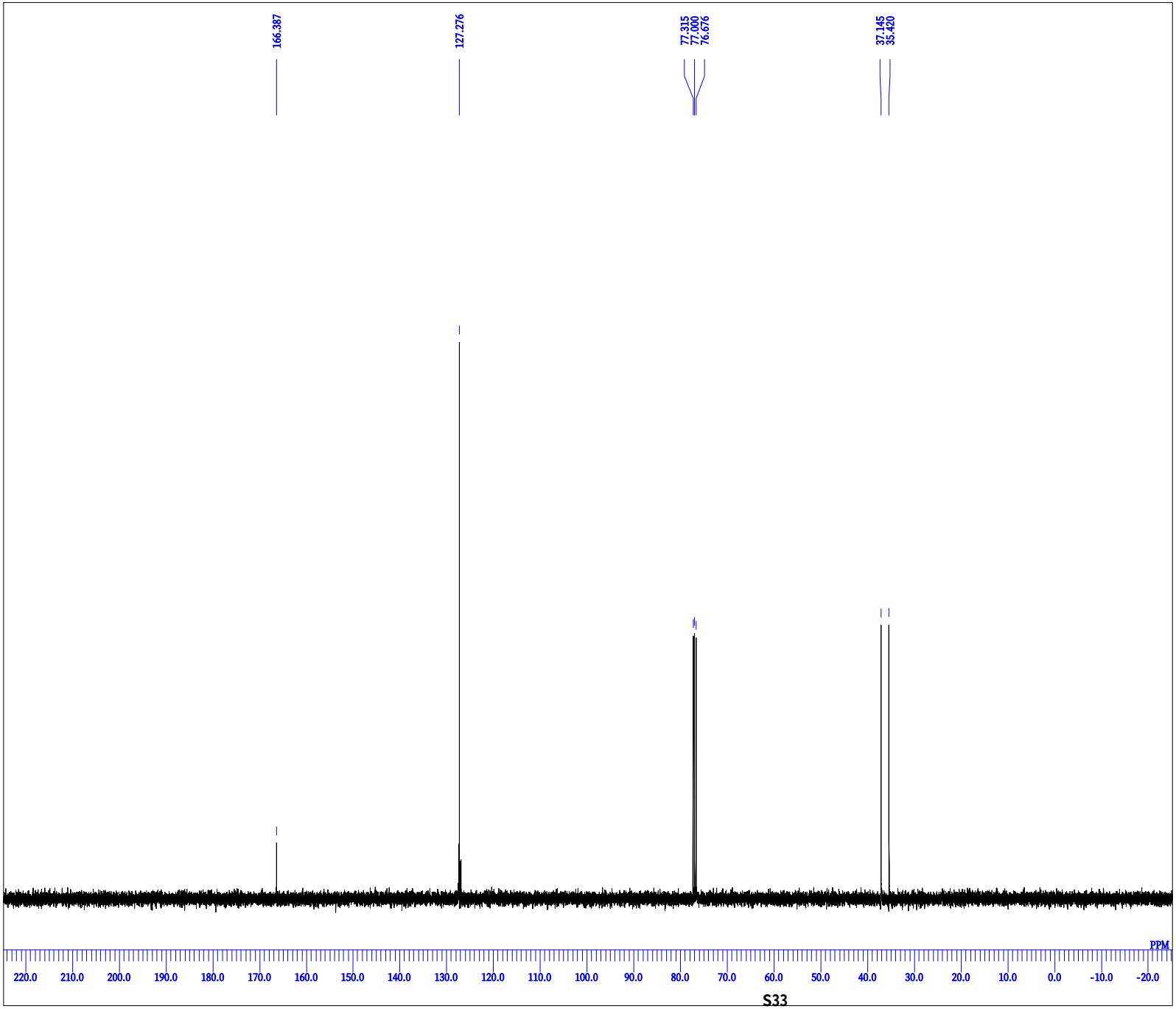


2a-D
(96%D)



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POINT	26214
FREQU	25125.24 Hz
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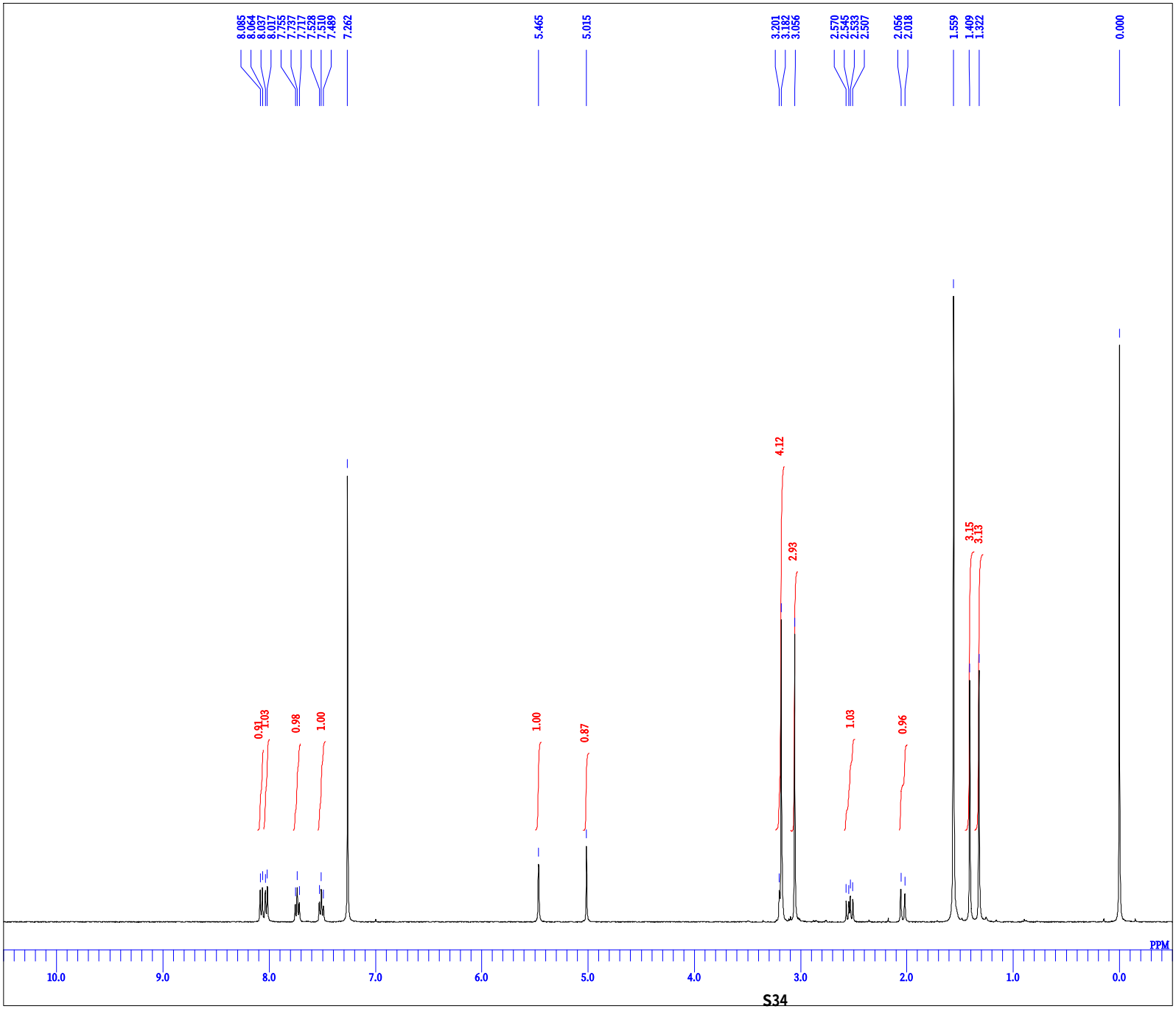
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.1 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60

2a-D



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POINT 13107
FREQU 6002.31 Hz
SCANS 8
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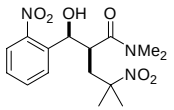
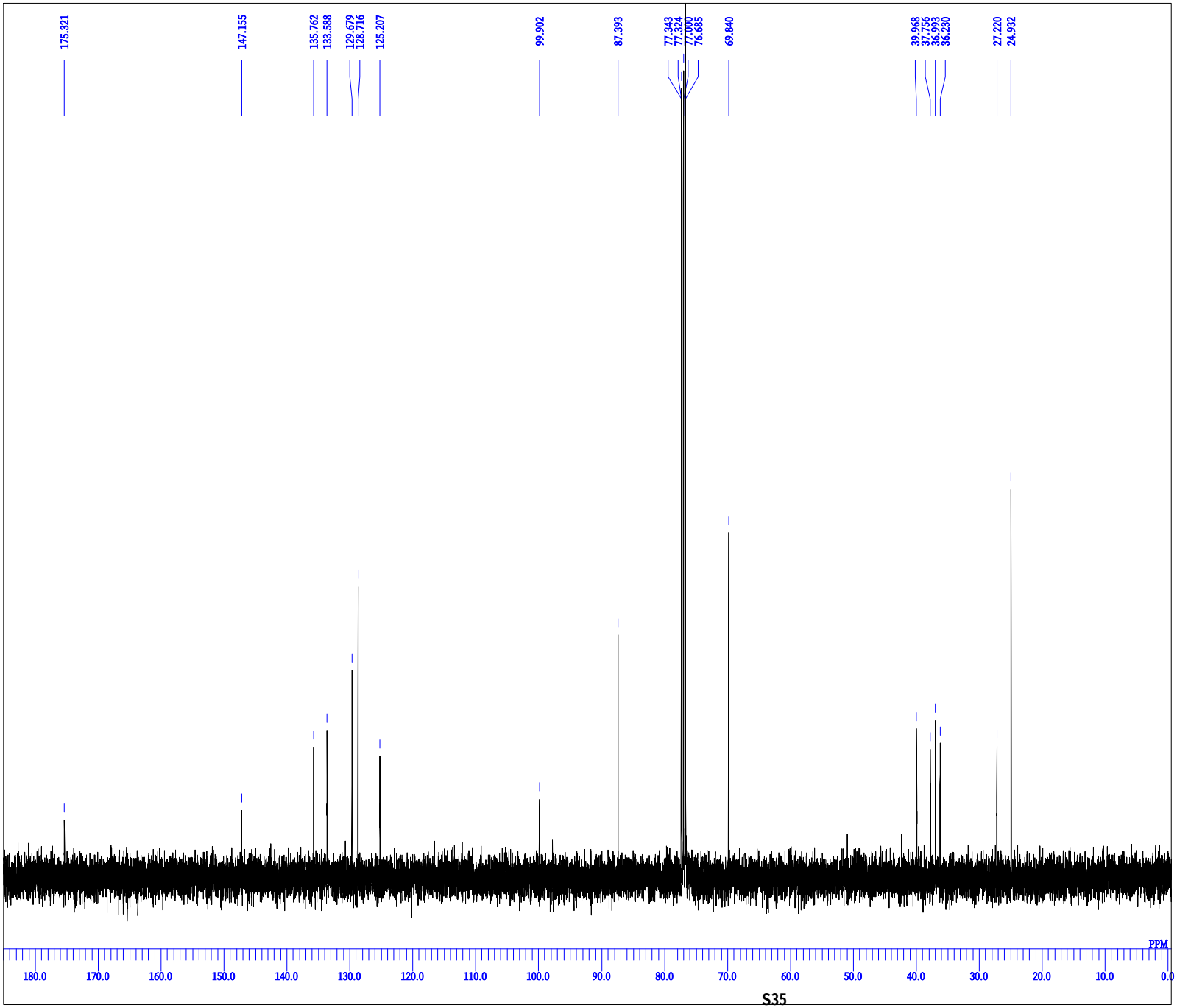


***syn*-4a**



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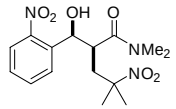
RGAIN	60



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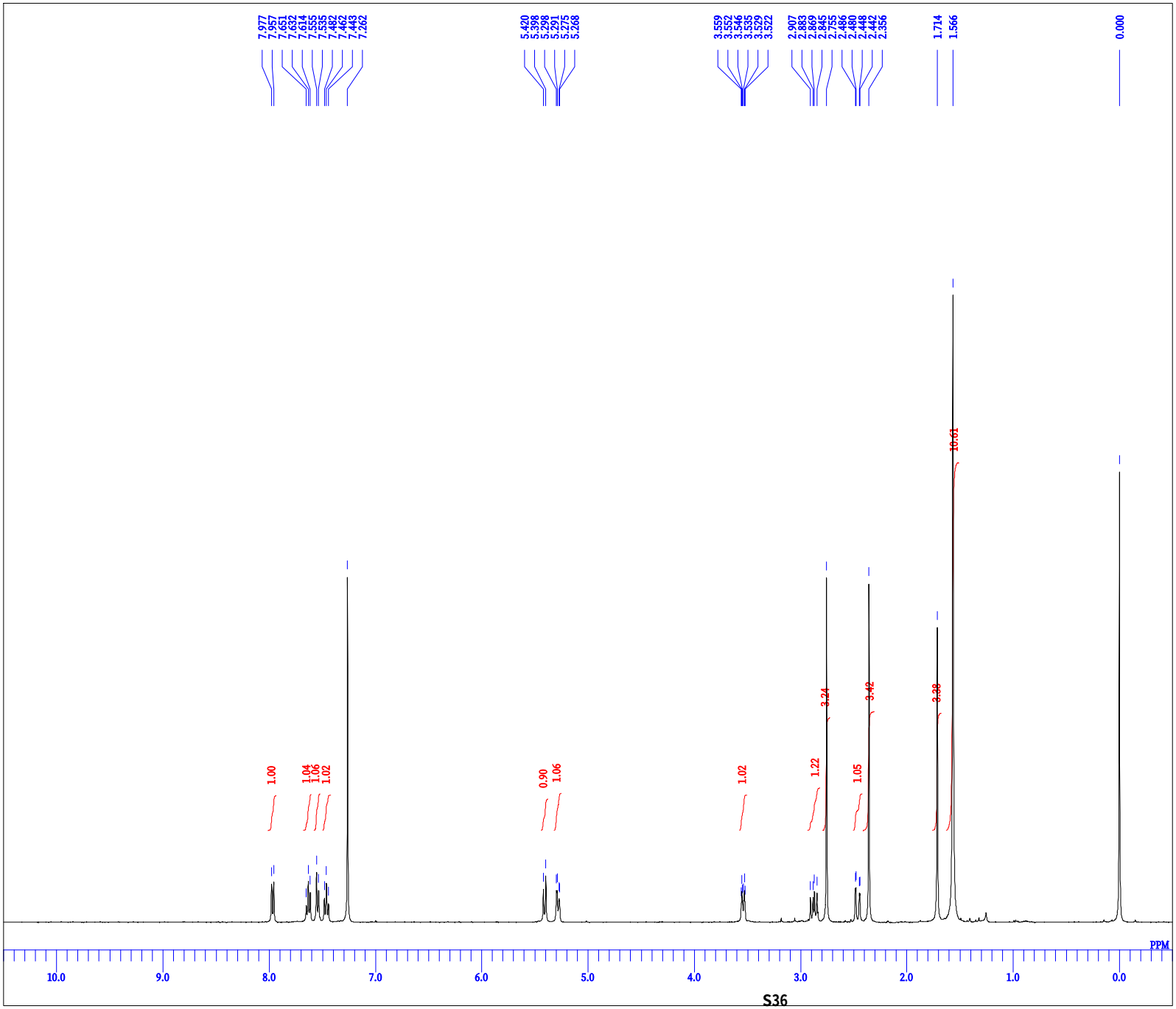

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SCANS	8
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PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	21.3 c
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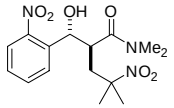

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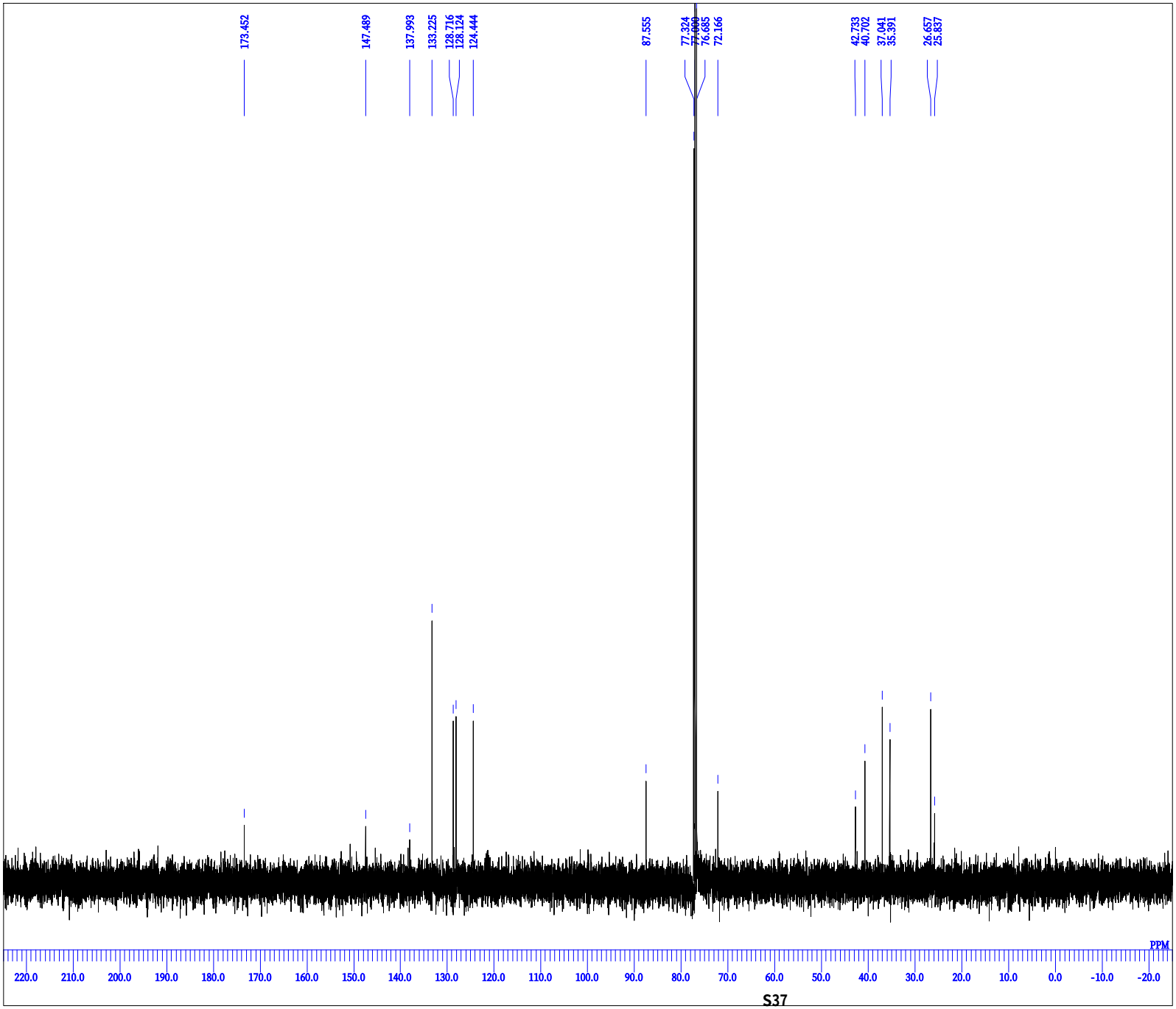

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FREQU	31407.03 Hz
SCANS	158
ACQTM	1.0433 sec
PD	1.2000 sec
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IRNUC	1H
CTEMP	21.6 c
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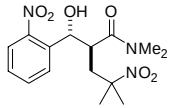
RGAIN	60



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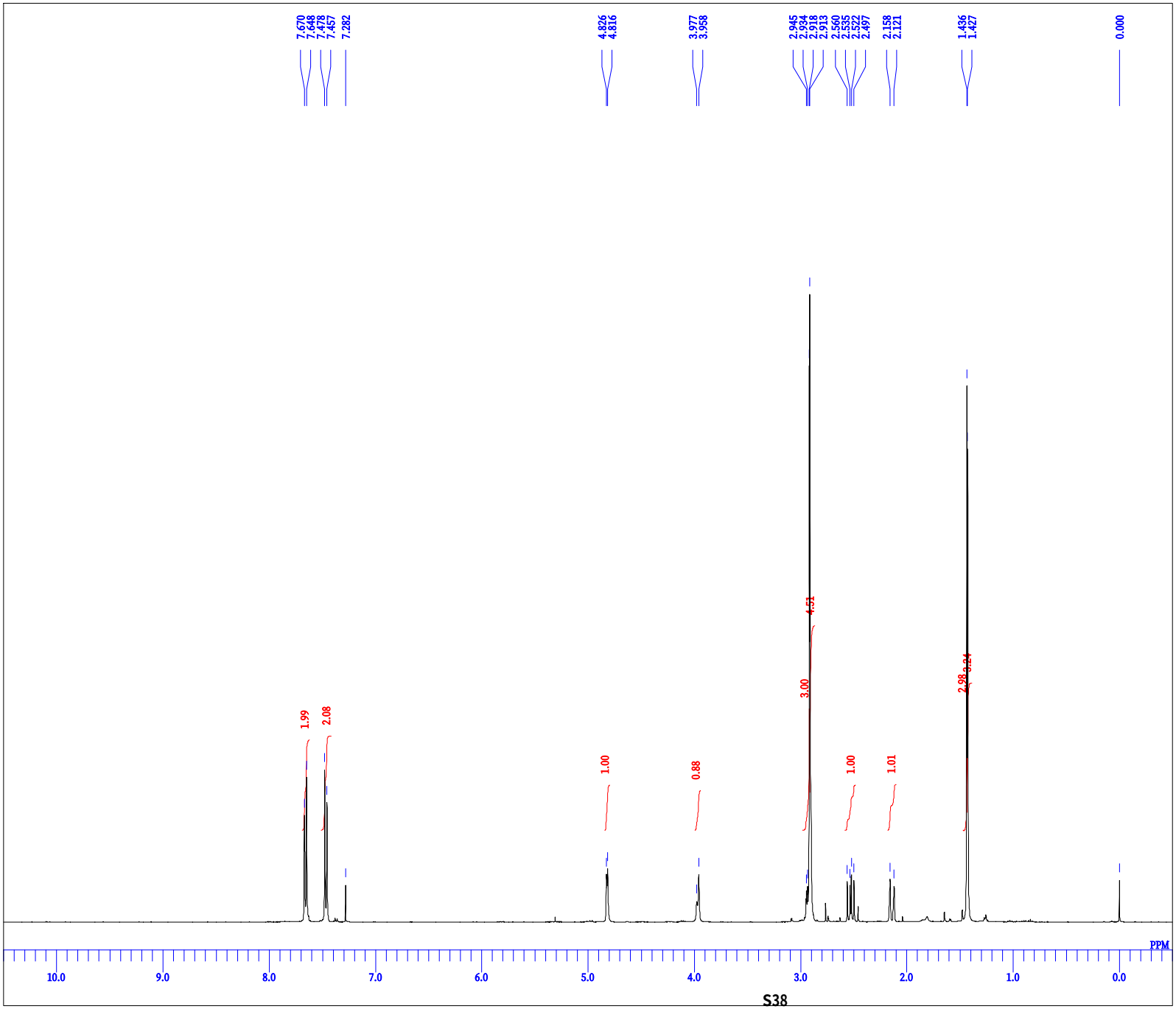

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POINT 13107
FREQU 6002.31 Hz
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PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 21.2 c
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BF 0.20 Hz
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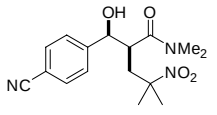

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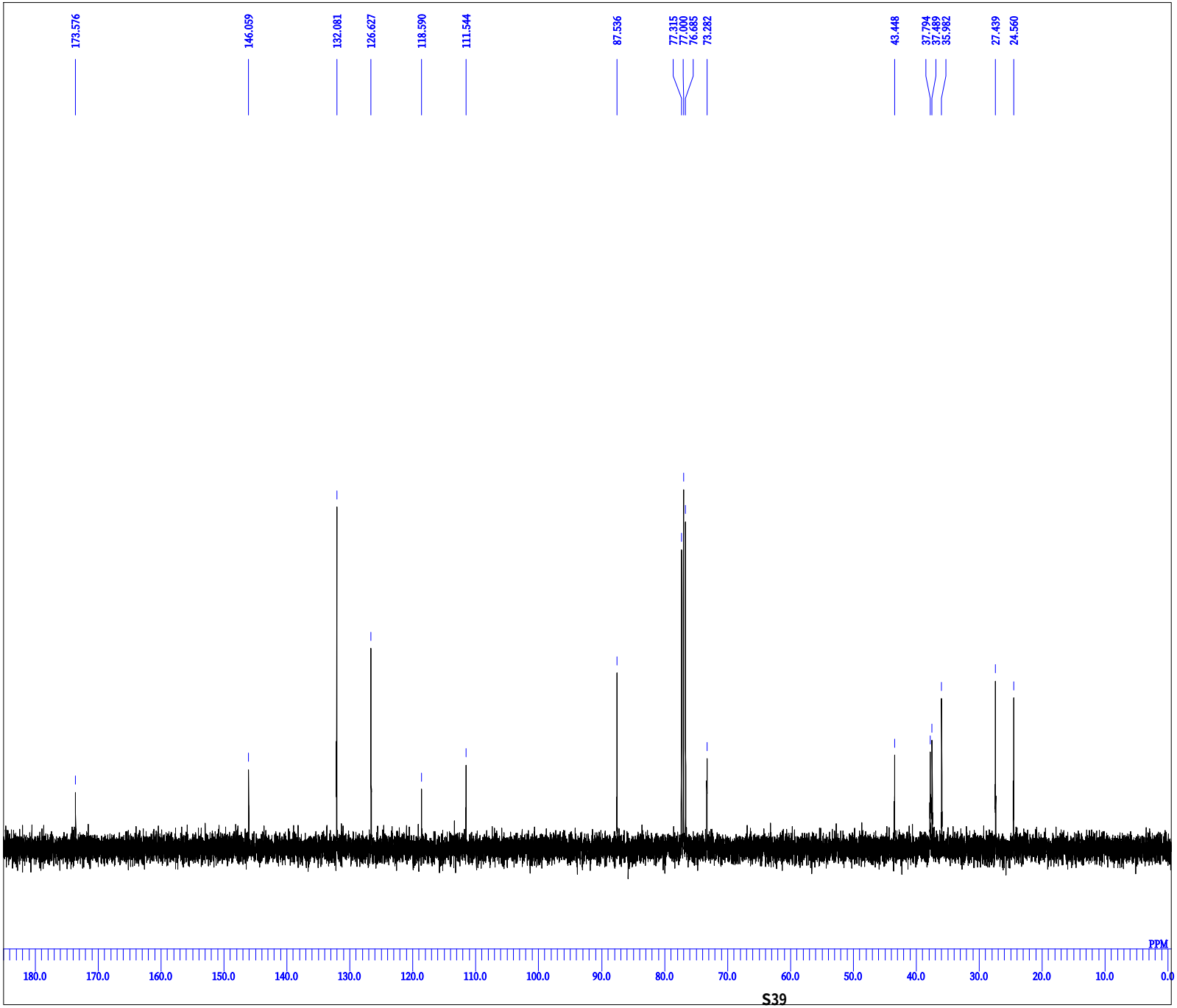

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OBFIN	5.86 Hz
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PD	1.2000 sec
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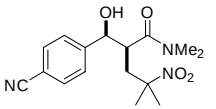

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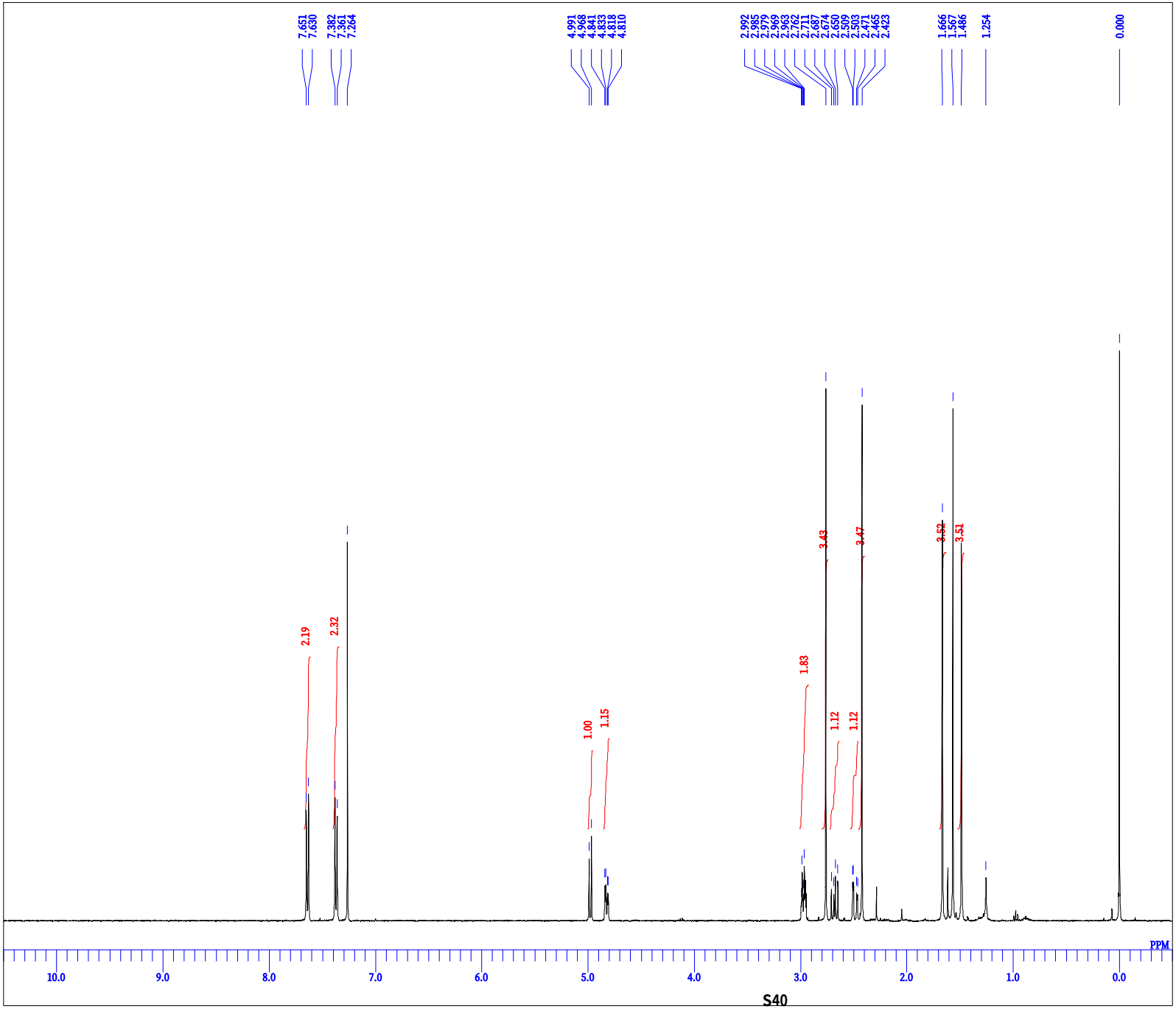

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POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
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IRNUC 1H
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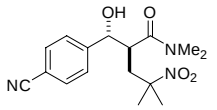
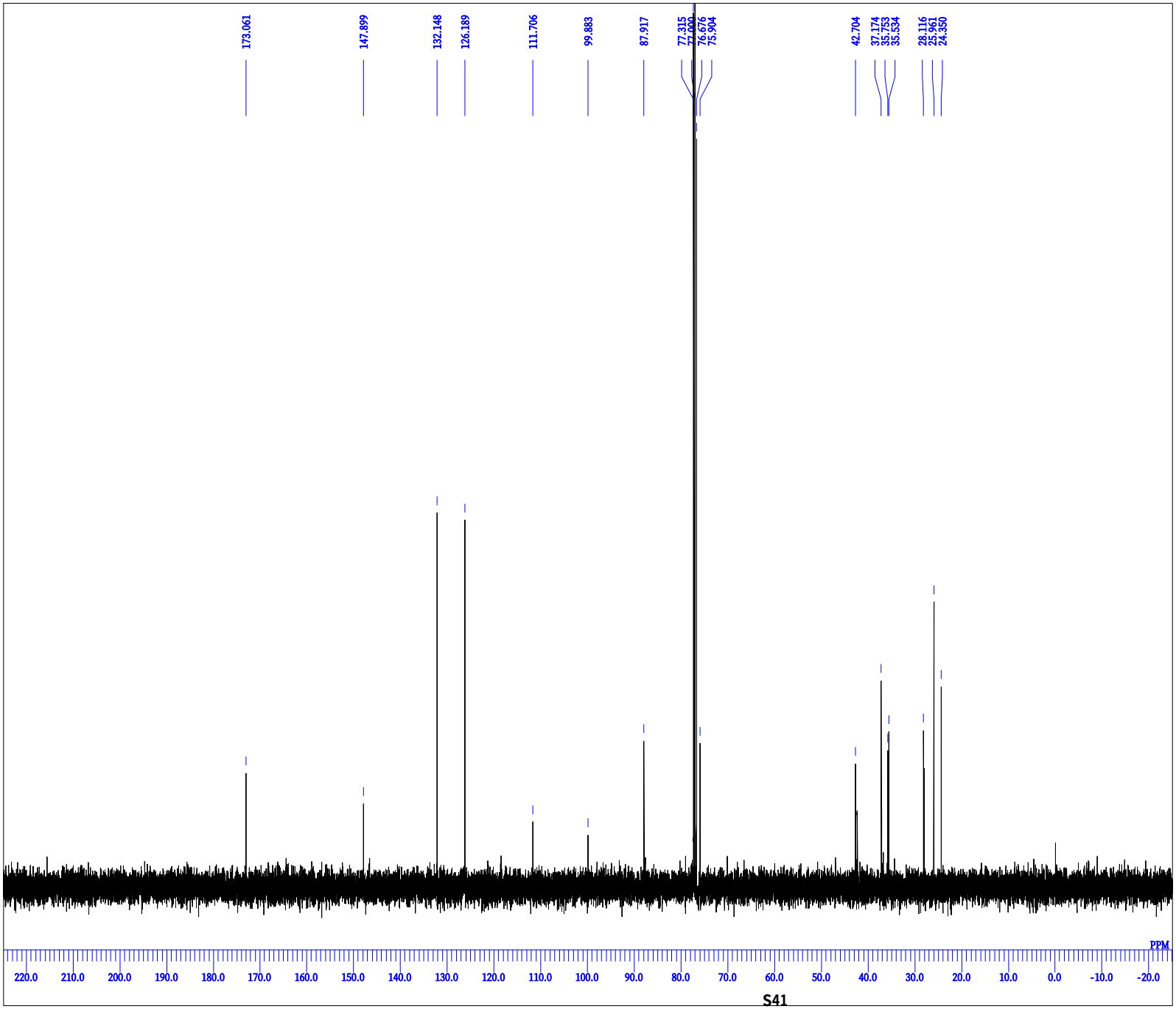


anti-4b



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PD	1.2000 sec
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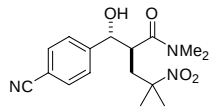

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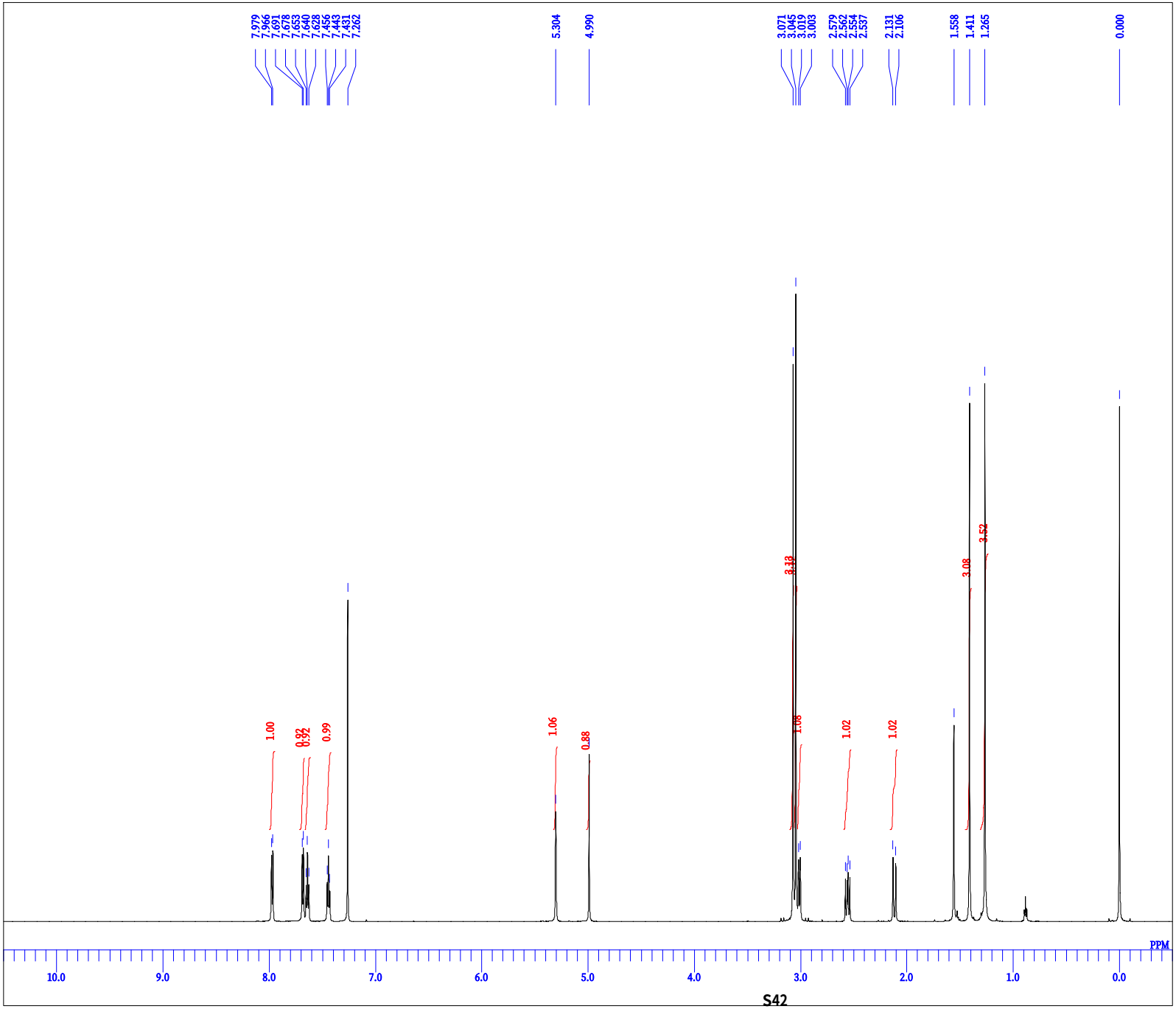

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PD	2.0000 sec
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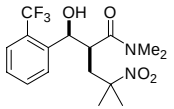
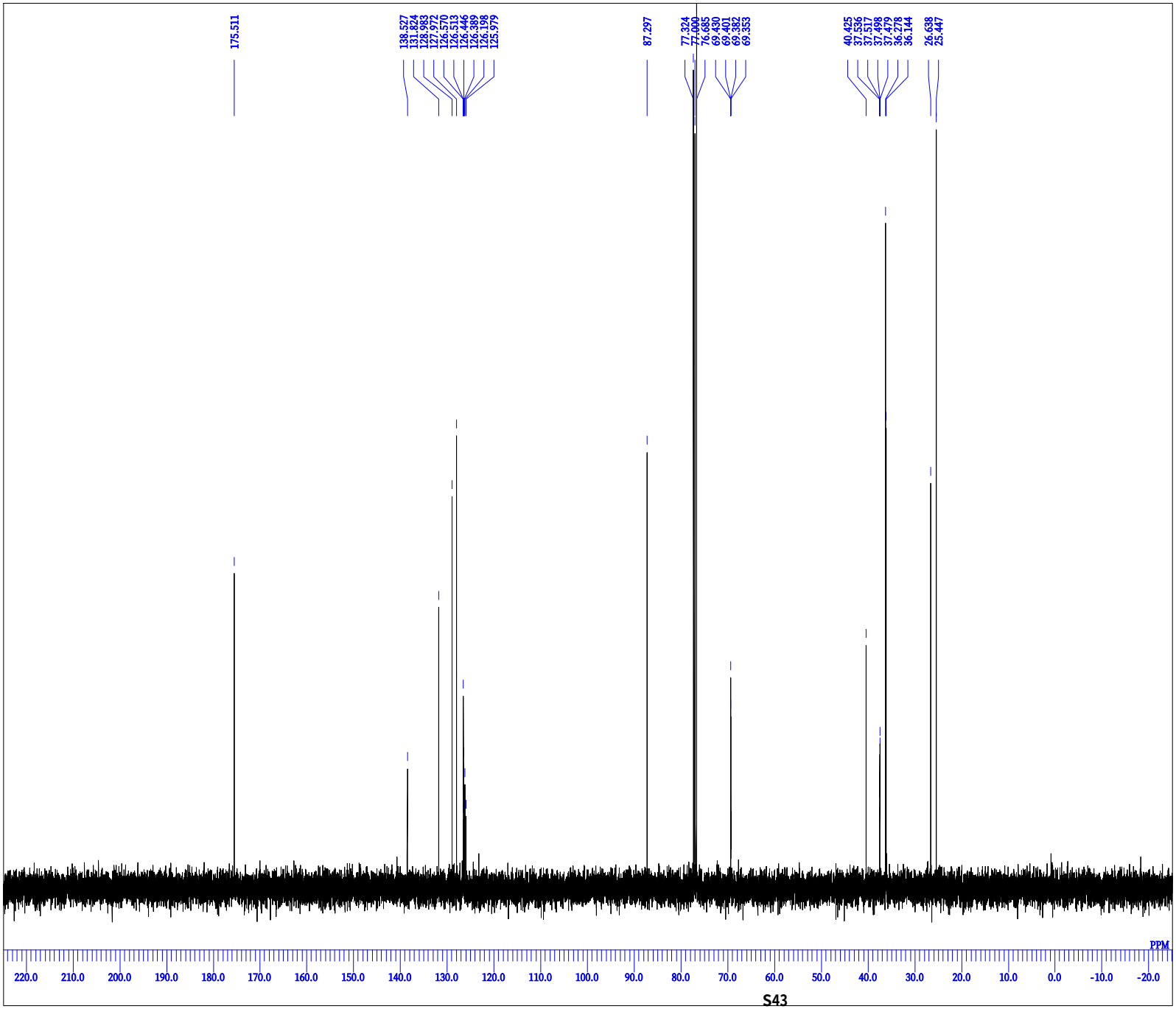


syn-4c



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POINT	26214
FREQU	25125.24 Hz
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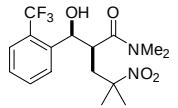

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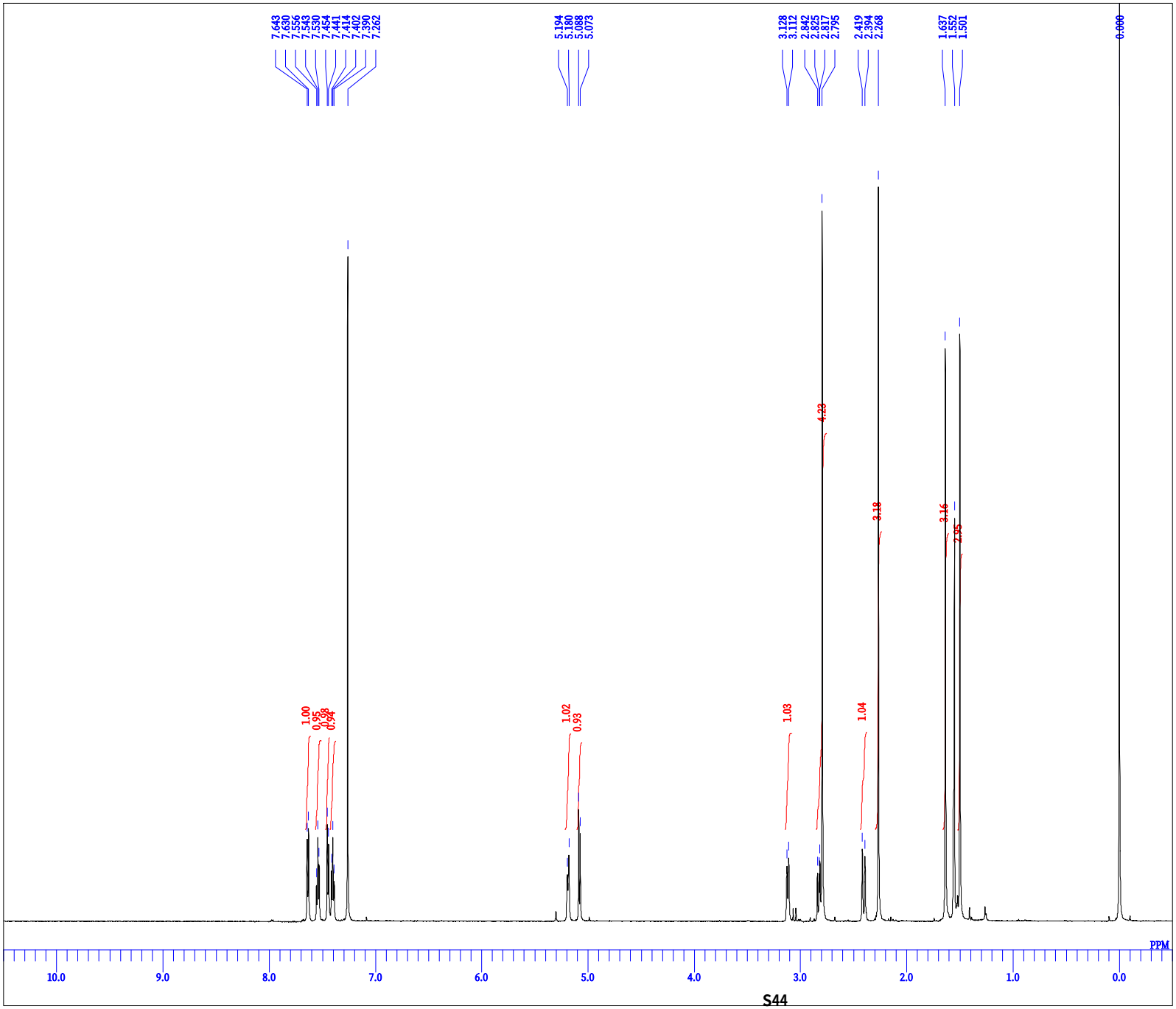

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POINT 32768
FREQU 11261.26 Hz
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ACQTM 2.9098 sec
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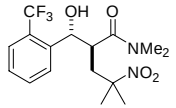
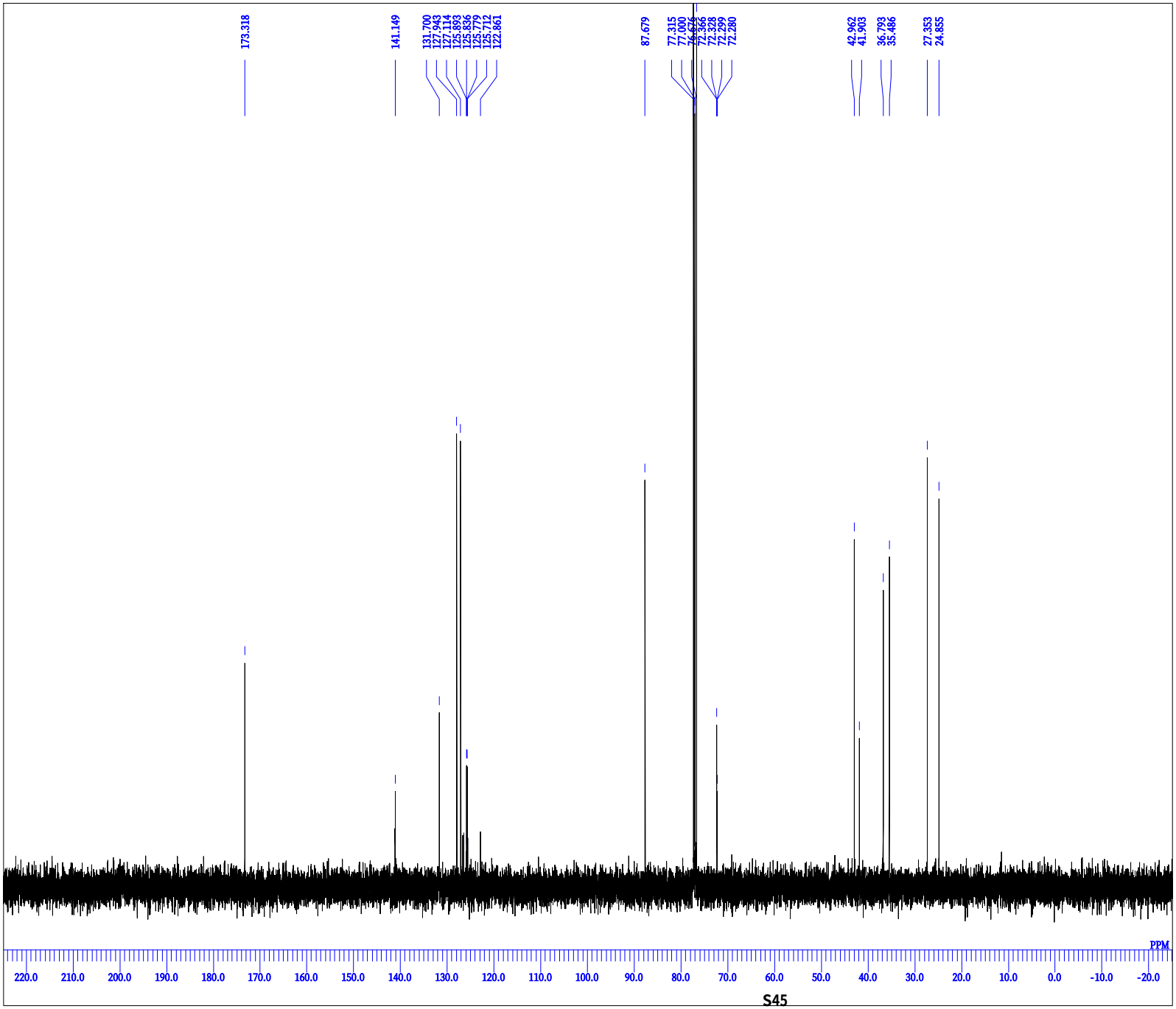


anti-**4c**



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POINT	26214
FREQU	25125.24 Hz
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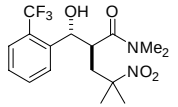
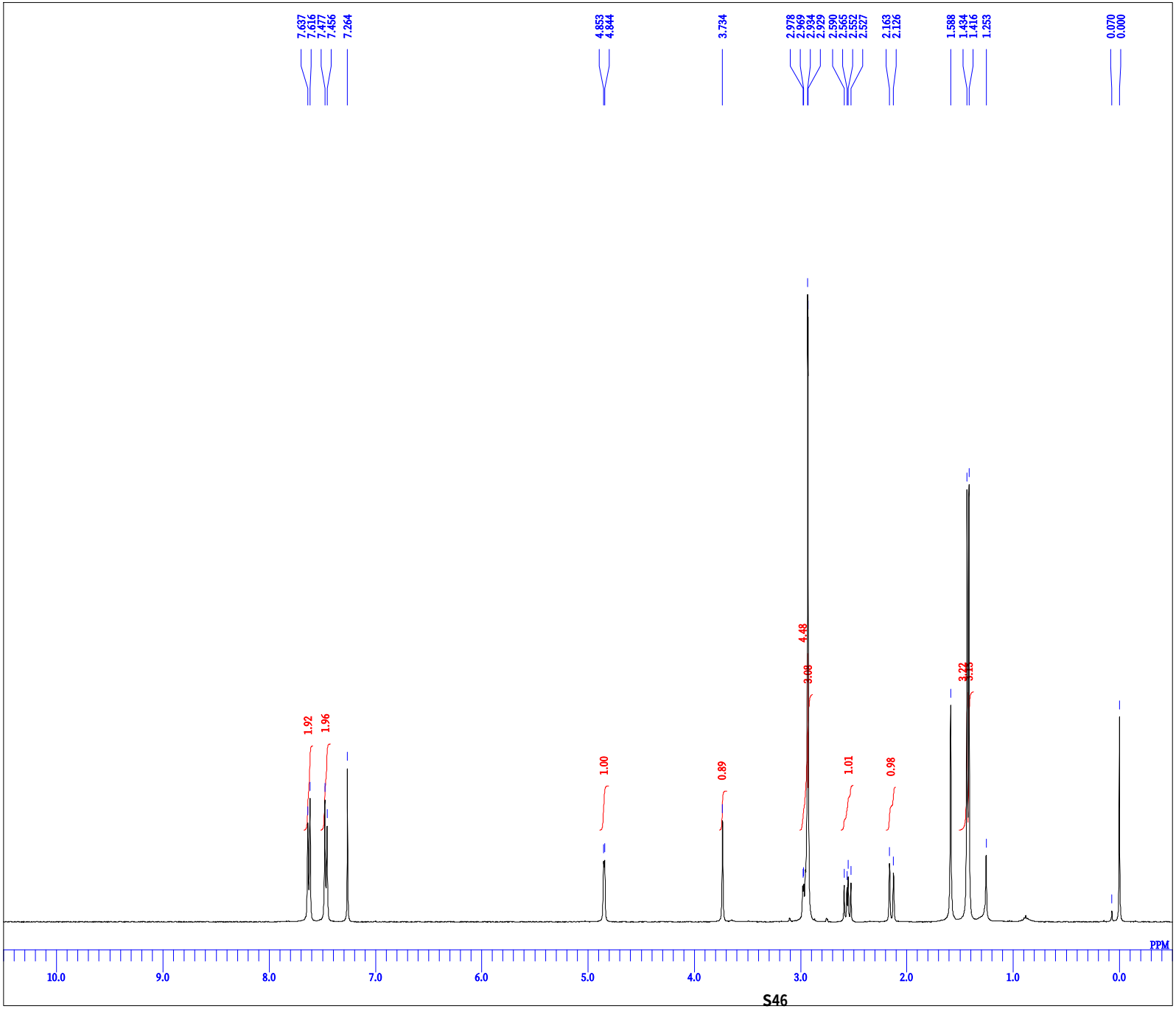
RGAIN	60



anti-4c



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OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 21.2 c
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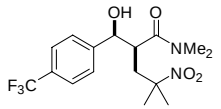
RGAIN 48



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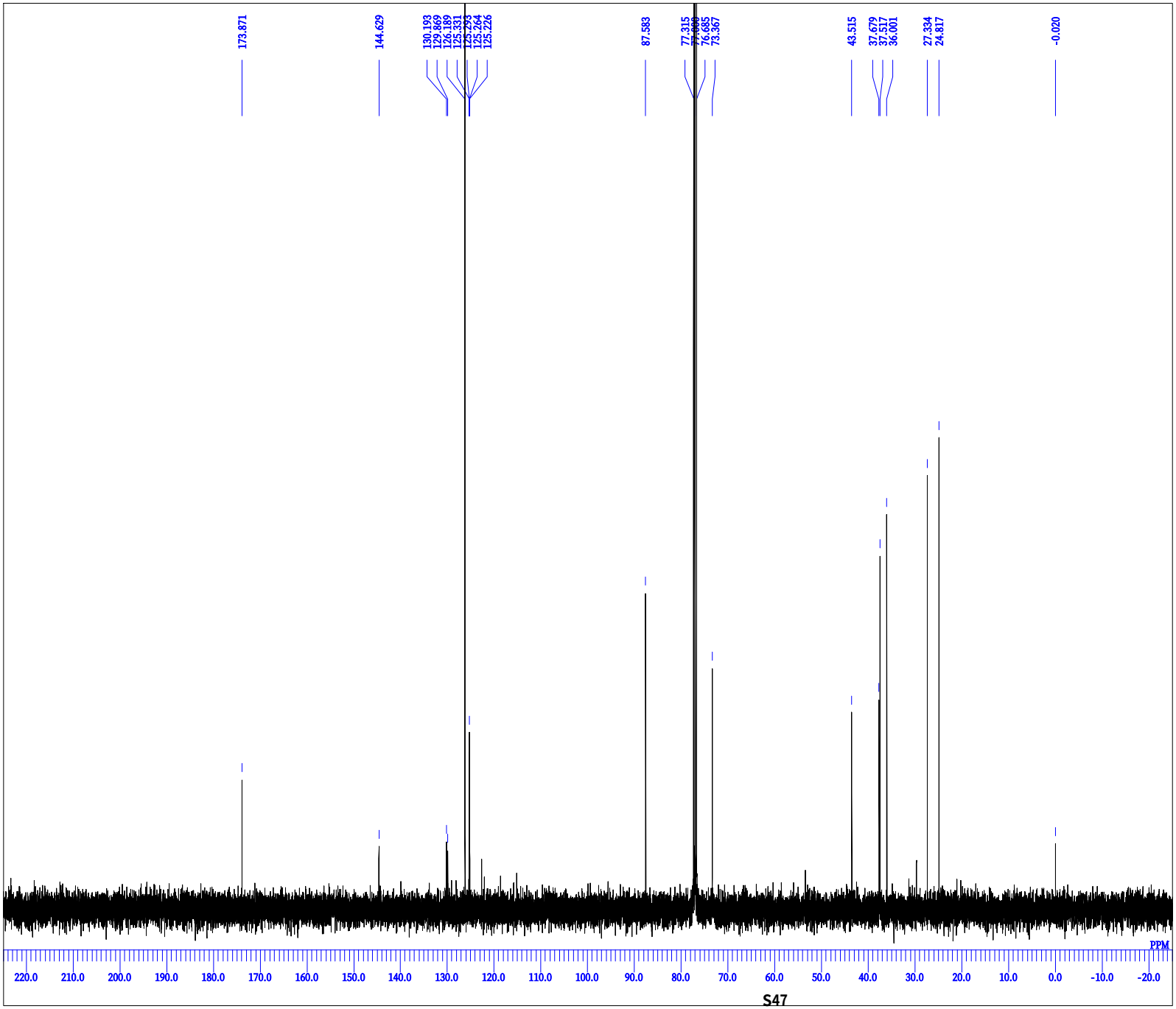

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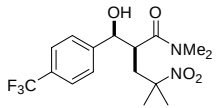
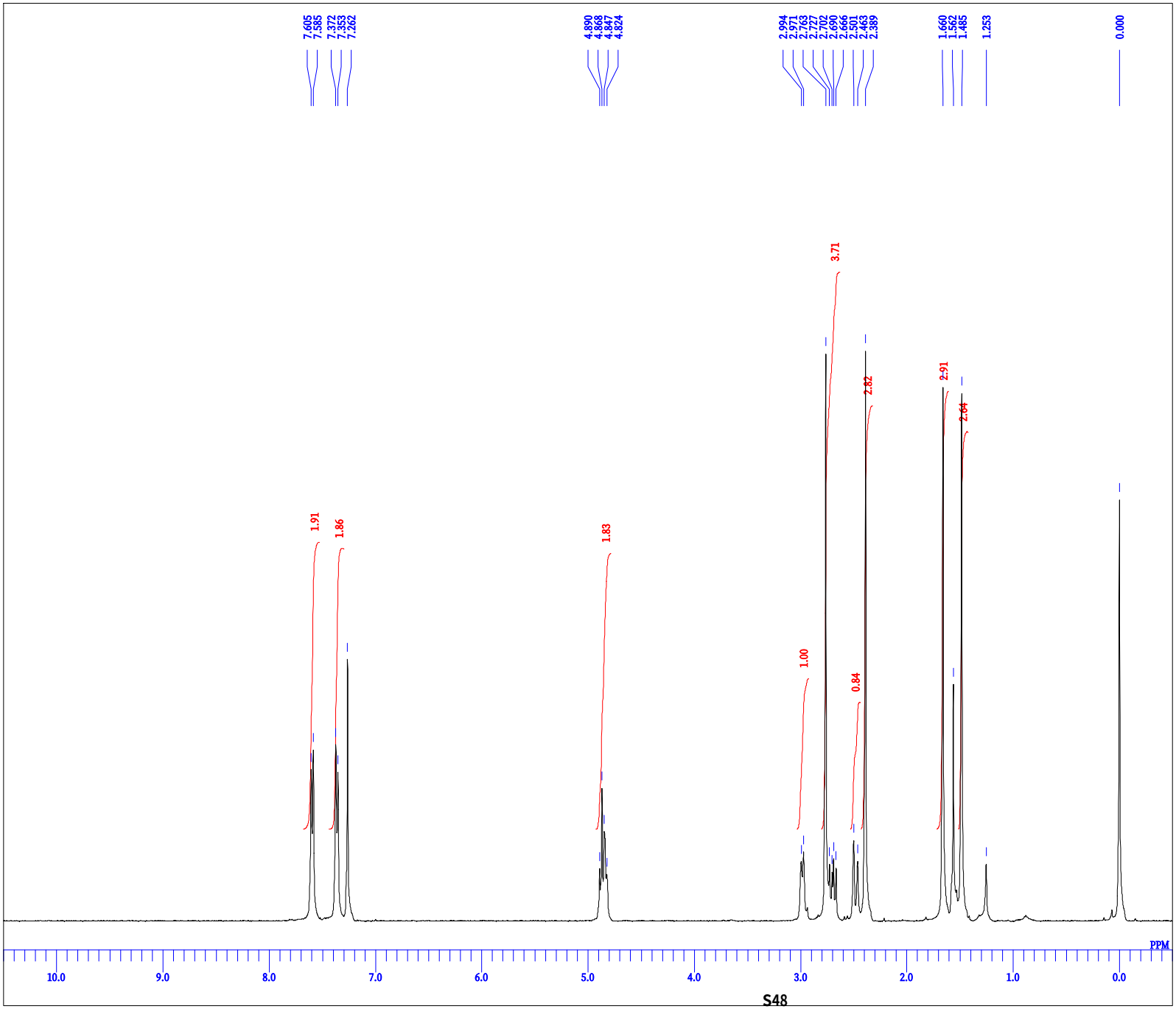
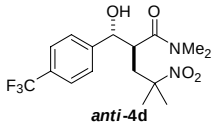
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



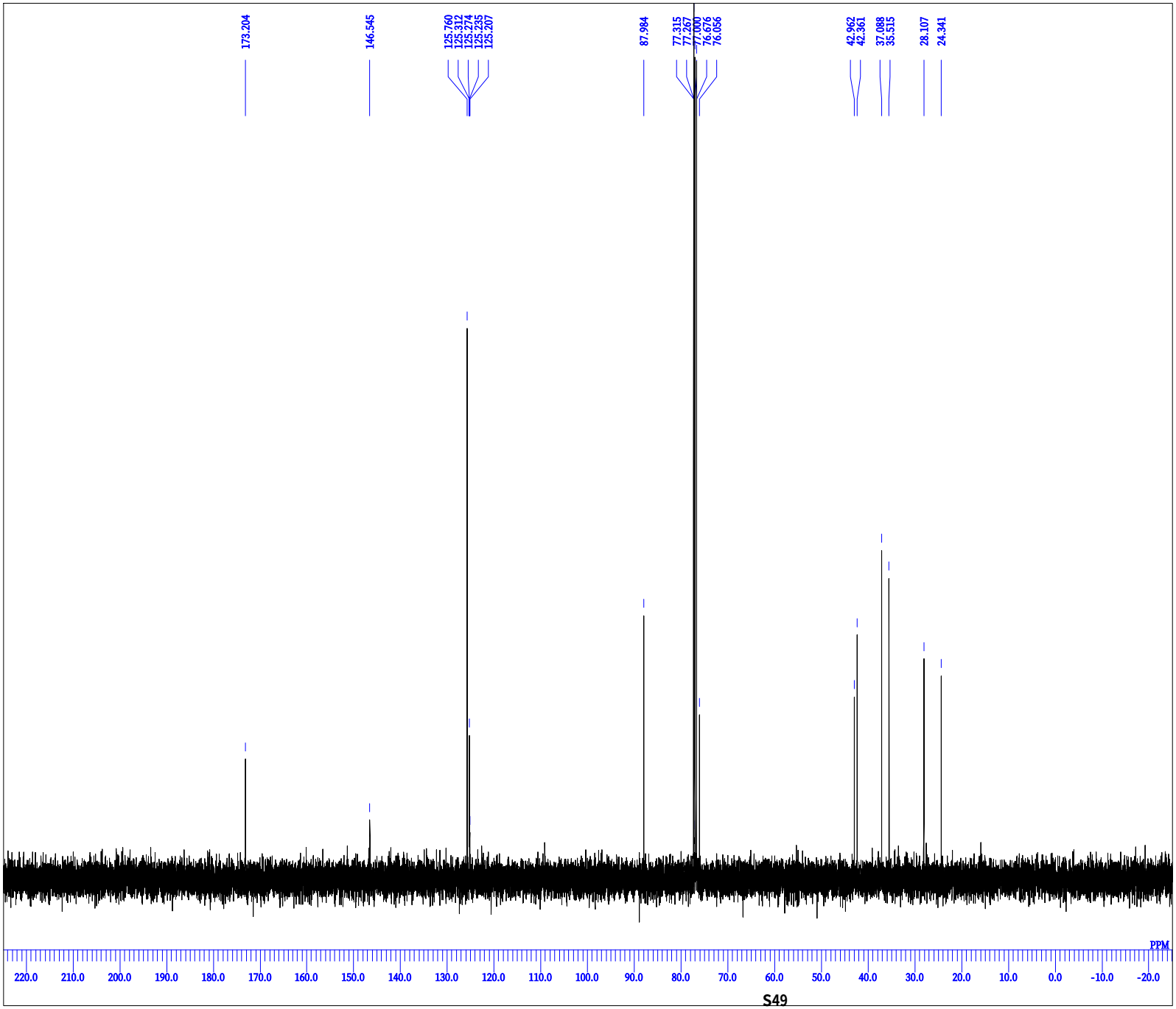
***syn*-4d**



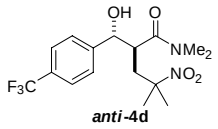
DFILE amide 4-CF3 sita n-1.als
COMNT
DATIM 2020-11-12 10:50:11
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 50



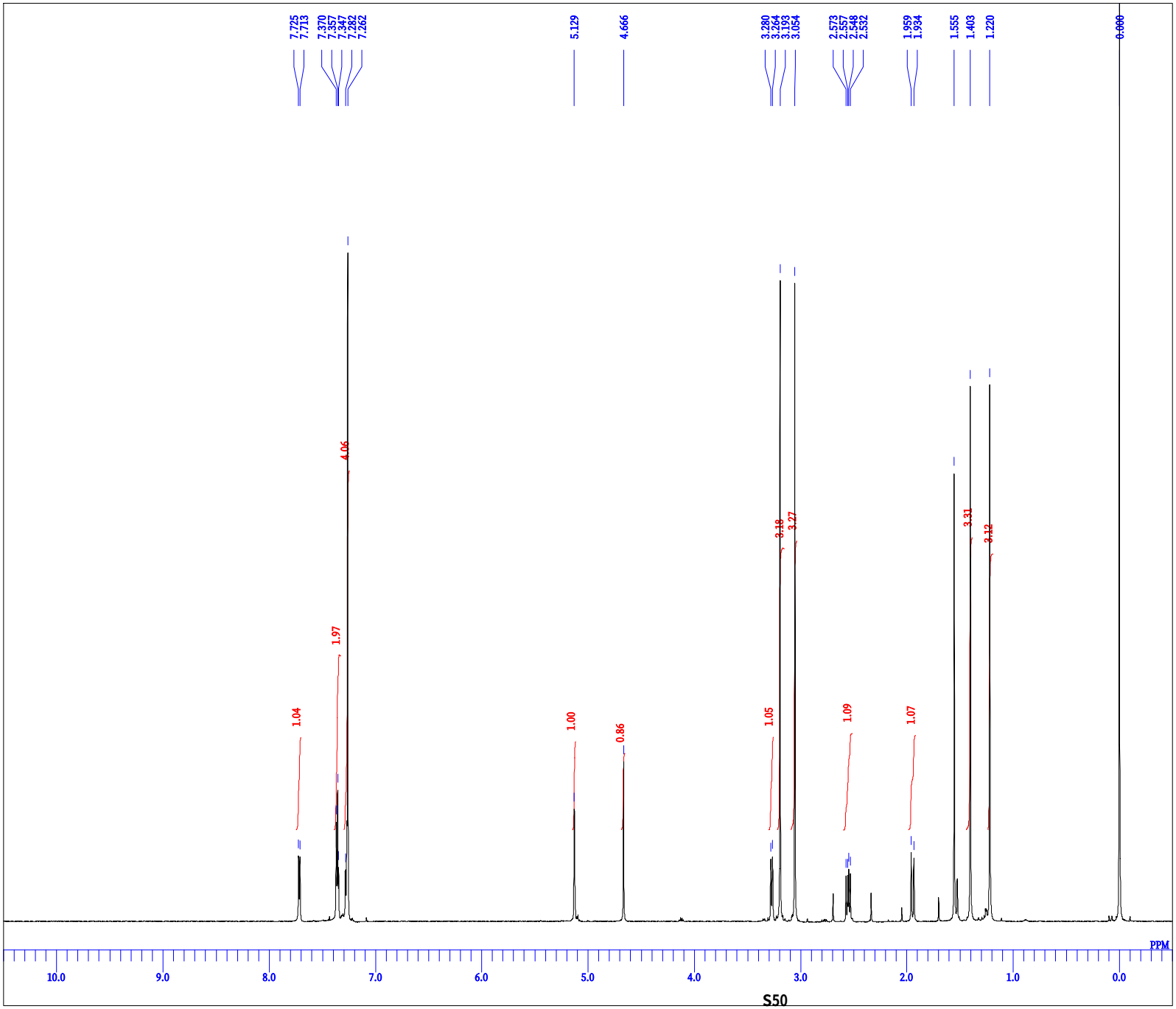
anti-4d



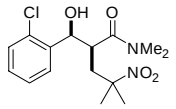
DFILE	4-CF3 sita 13C-1.als
COMNT	
DATIM	2020-10-28 02:07:04
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	101
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.6 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



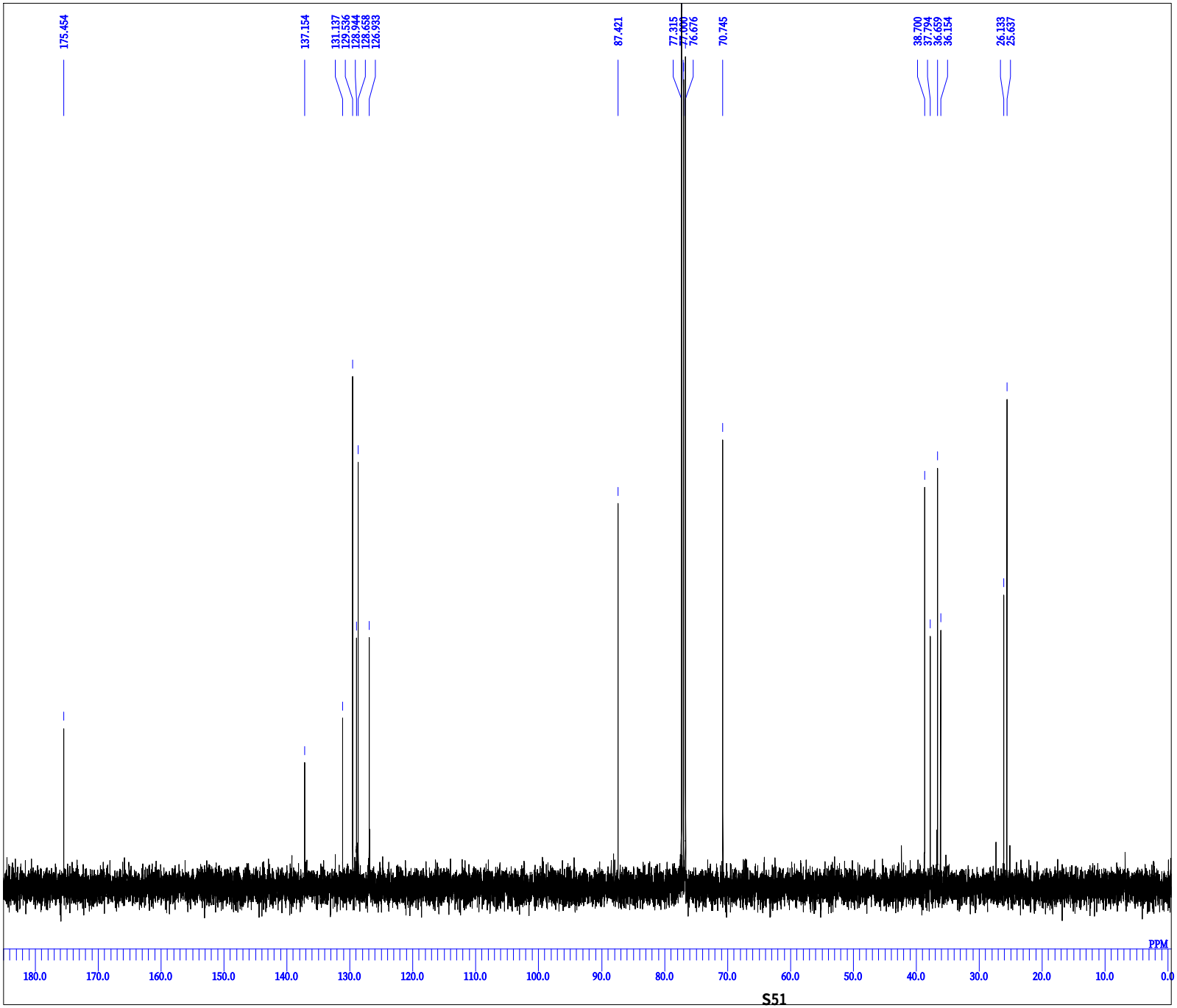
***anti*-4d**



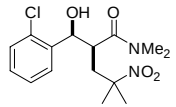
DFILE	amide 2-Cl ue-1.als
COMNT	
DATIM	2020-11-10 20:22:60
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	26214
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	2.0000 sec
PW1	6.90 usec
IRNUC	1H
CTEMP	19.8 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	1.40 Hz
RGAIN	54



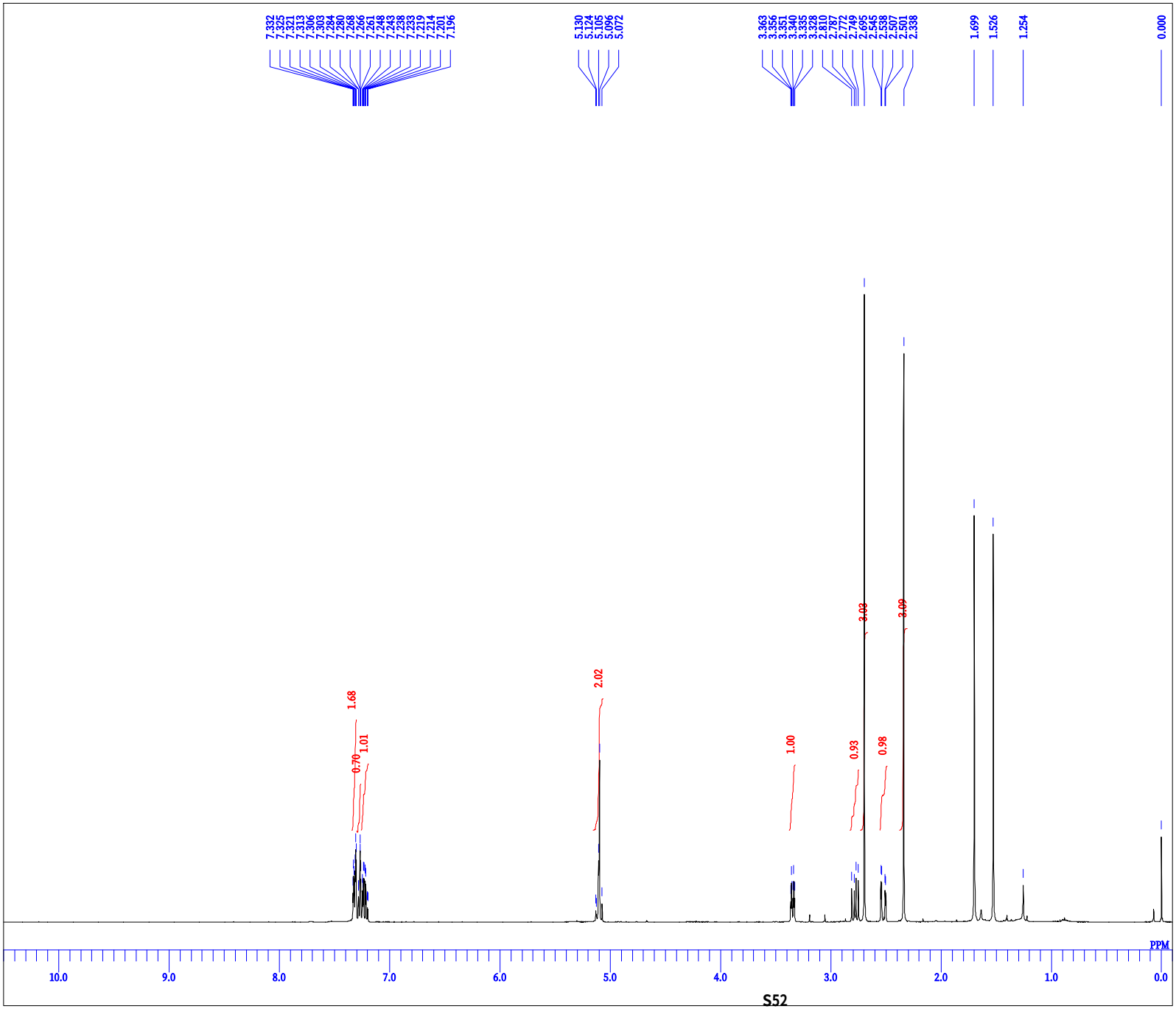
syn-4e



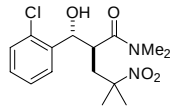
DFILE	2-Cl ue 13C-1.als
COMNT	
DATIM	2020-10-27 23:03:19
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	101
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.6 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



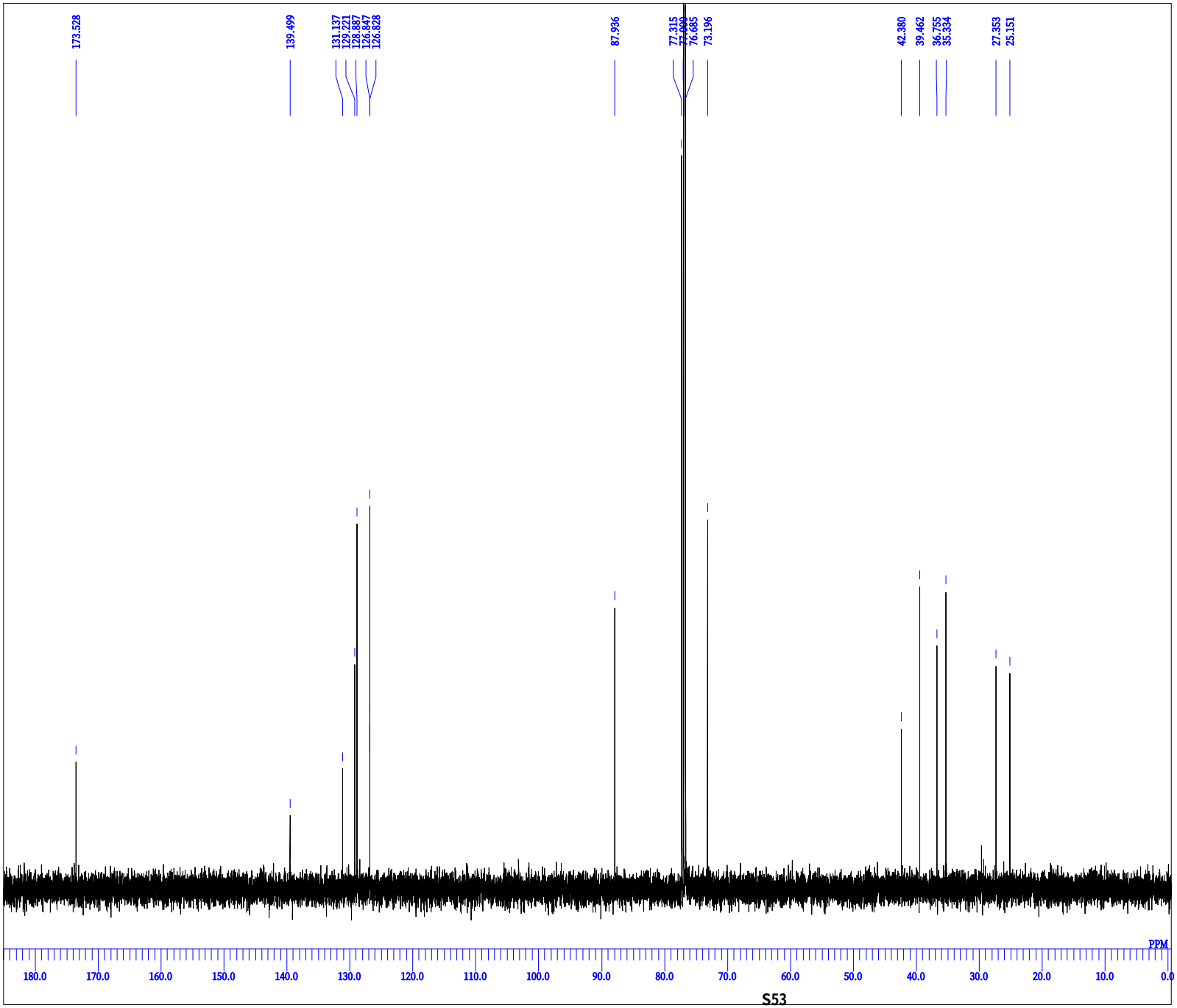
syn-4e



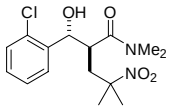
DFILE 2-Cl sita-1.als
COMNT
DATIM 2020-10-27 23:08:48
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 21.3 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.25 Hz
RGAIN 38



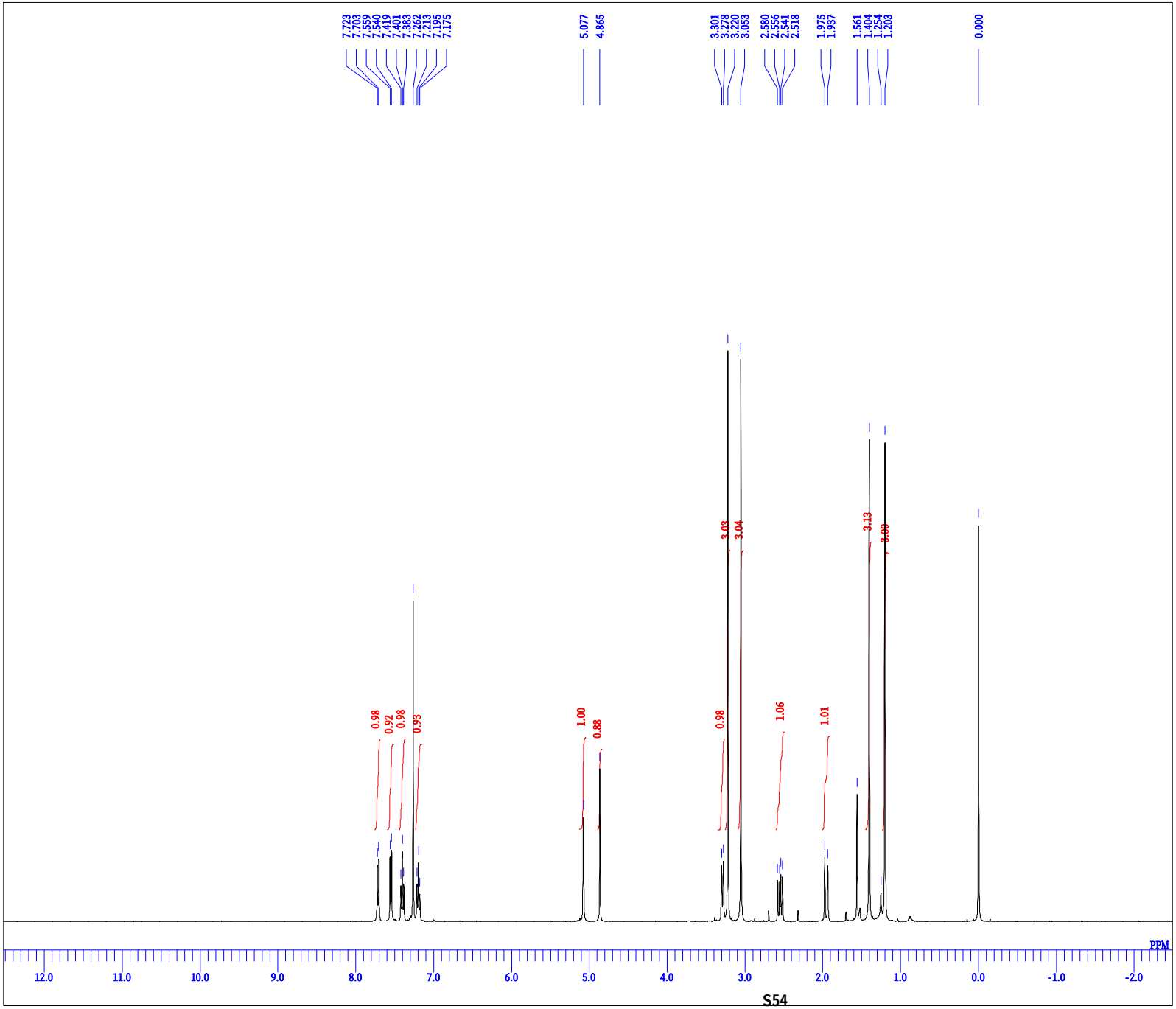
anti-4e



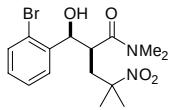
DFILE	2-Cl sita 13C-1.als
COMNT	
DATIM	2020-10-27 23:14:11
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	131
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



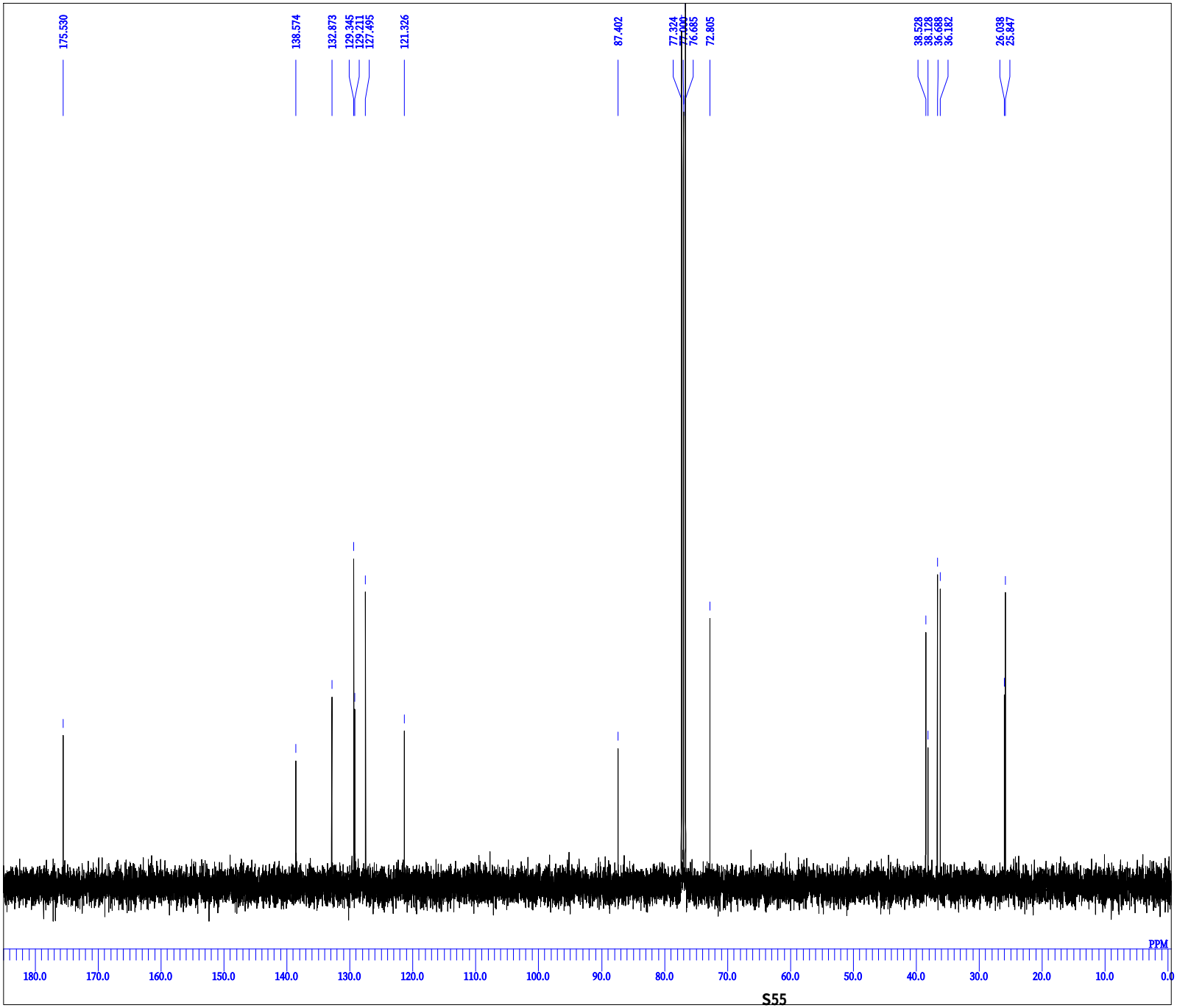
anti-4e



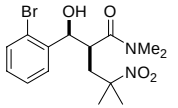
DFILE	amide 2-Br ue n-1.als
COMNT	
DATIM	2020-11-18 14:33:35
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	21.2 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	1.40 Hz
RGAIN	48



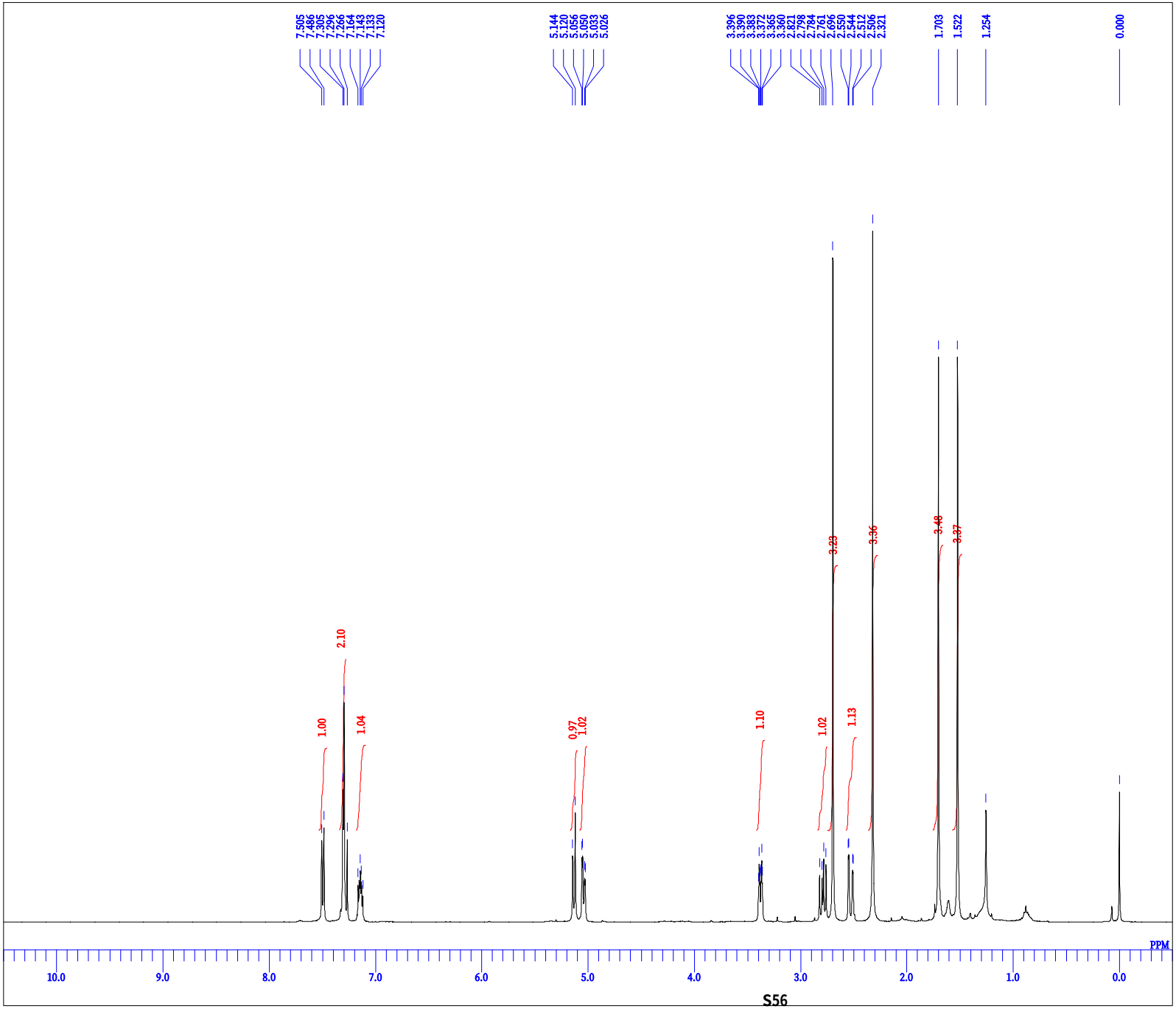
syn-4f



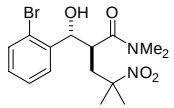
DFILE	2-Br ue 13C-1.als
COMNT	
DATIM	2020-10-28 00:45:25
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	102
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



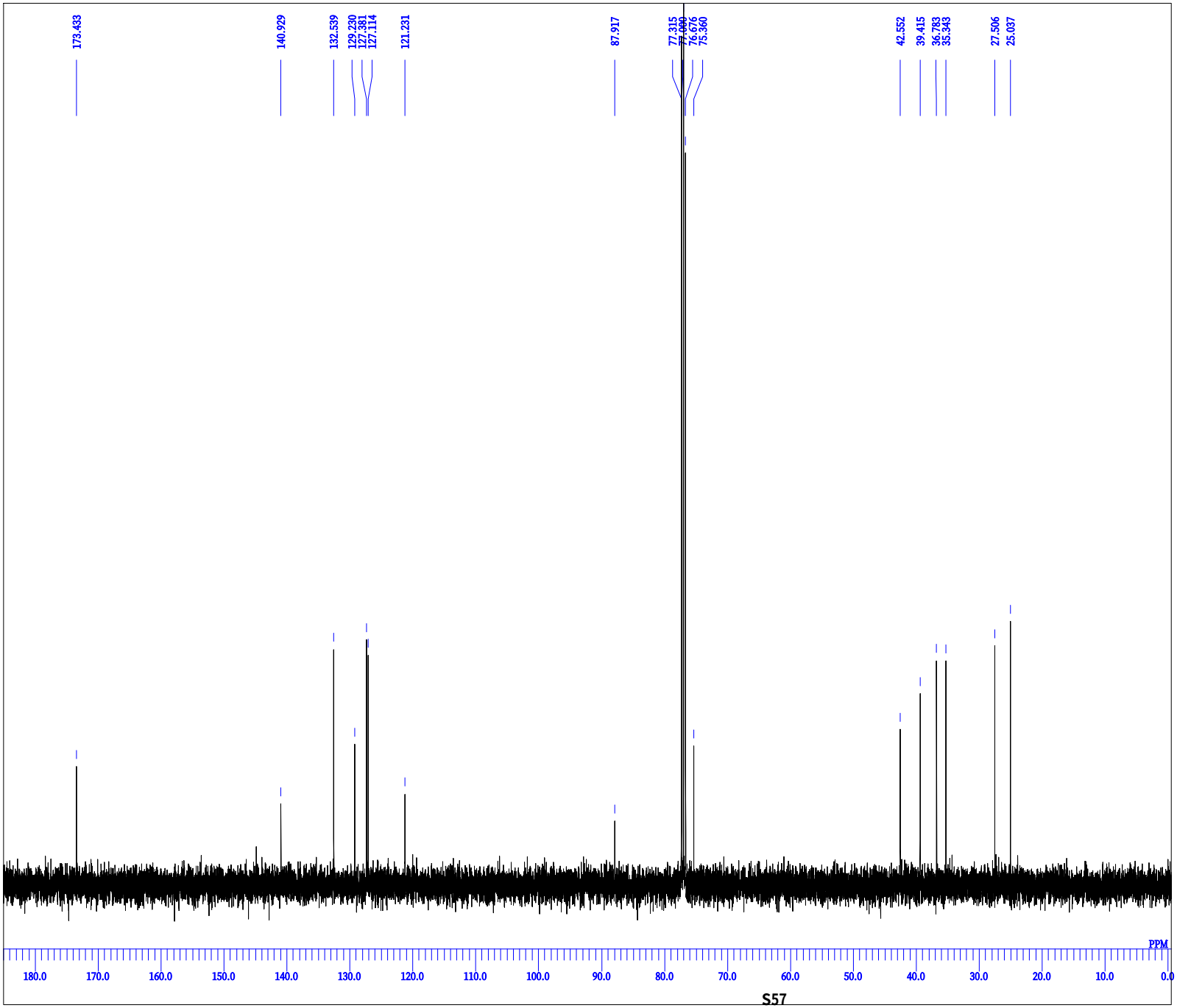
syn-4f



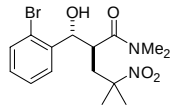
DFILE 2-Br sita-1.als
COMNT
DATIM 2020-10-28 00:50:44
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 40



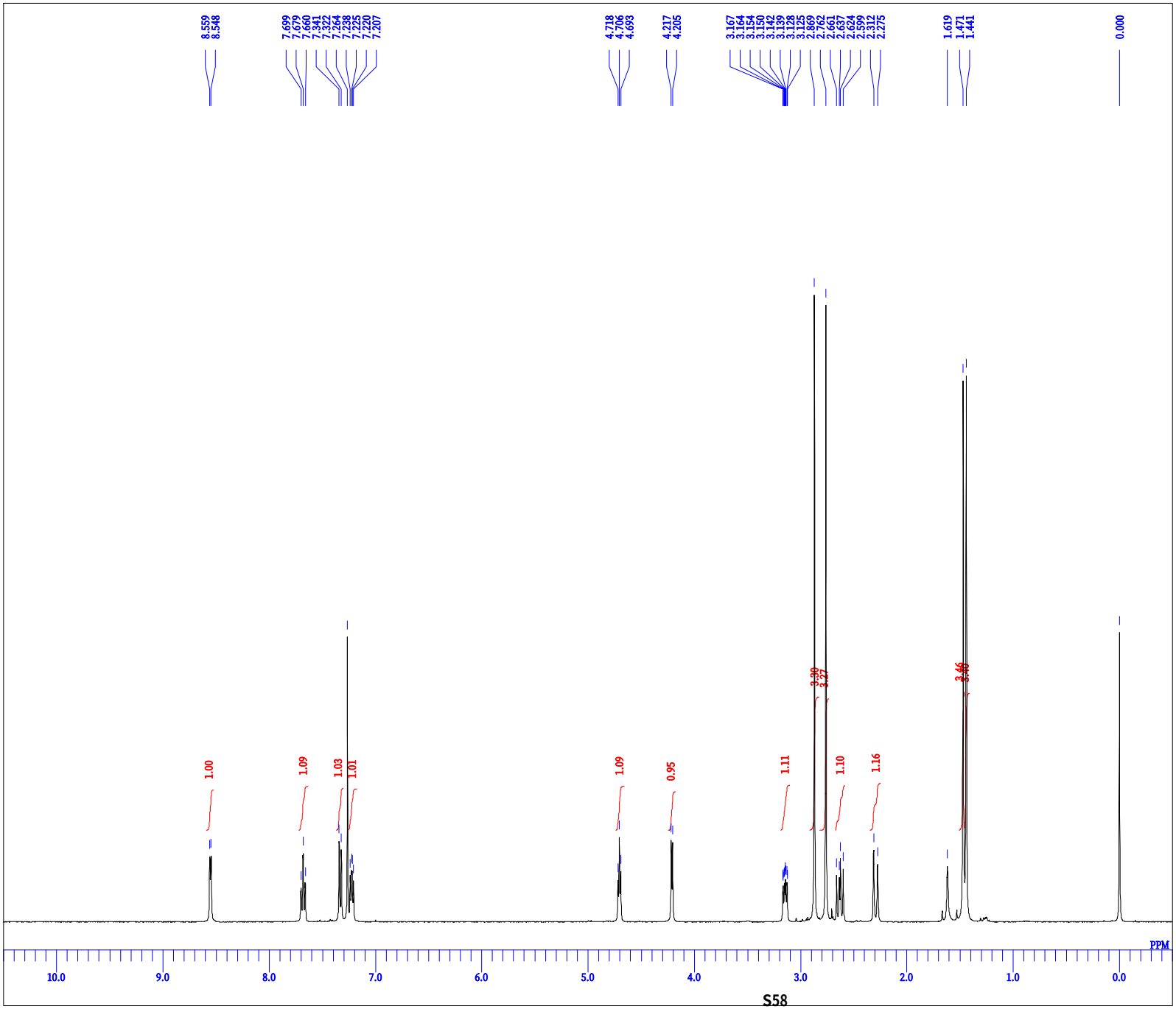
anti-4f



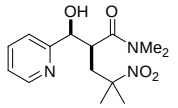
DFILE	2-Br sita 13C-1.als
COMNT	
DATIM	2020-10-28 00:55:16
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	106
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



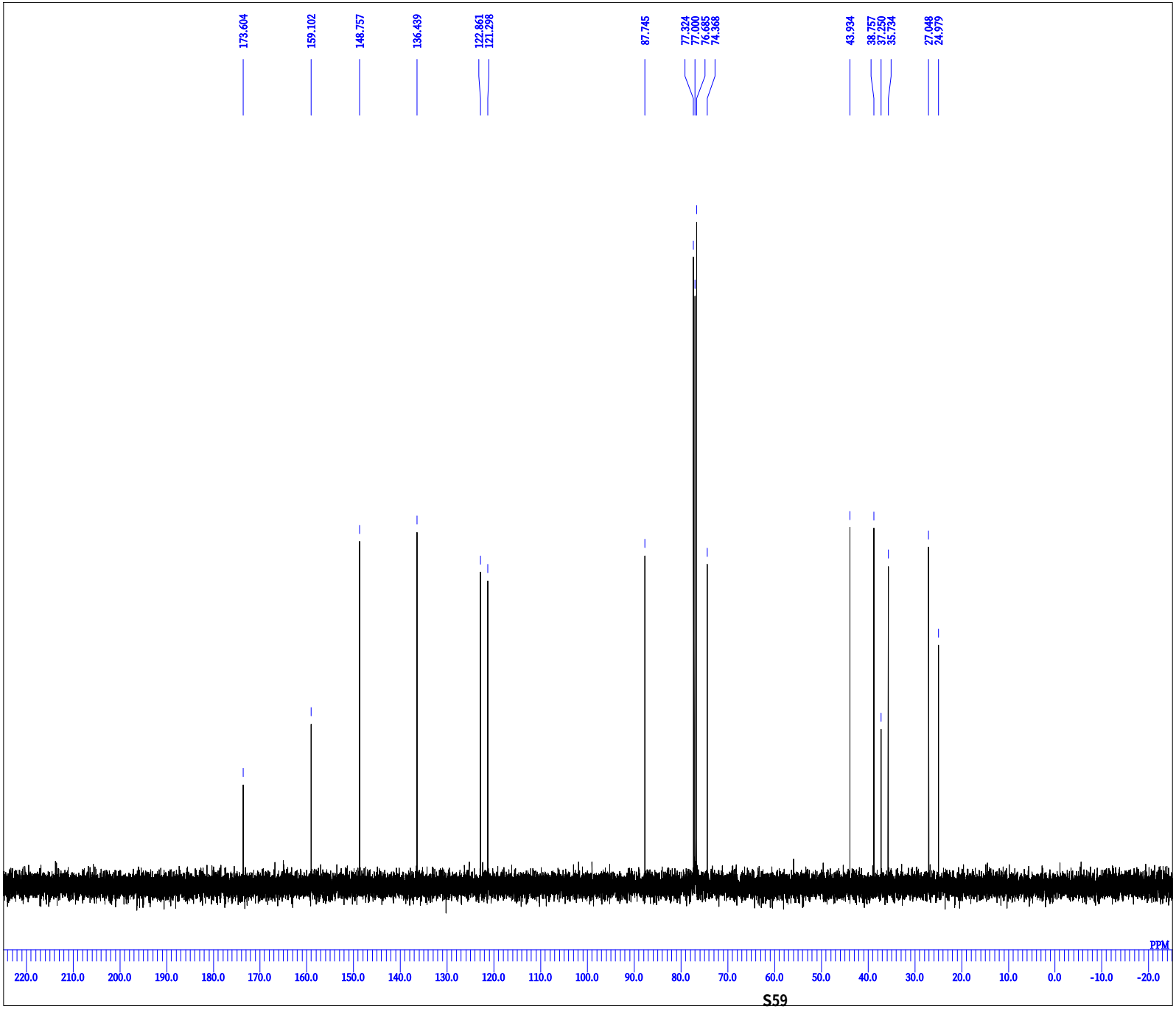
anti-4f



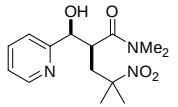
DFILE	amide 2-py ue n-1.als
COMNT	
DATIM	2020-11-18 14:12:36
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	1.40 Hz
RGAIN	46



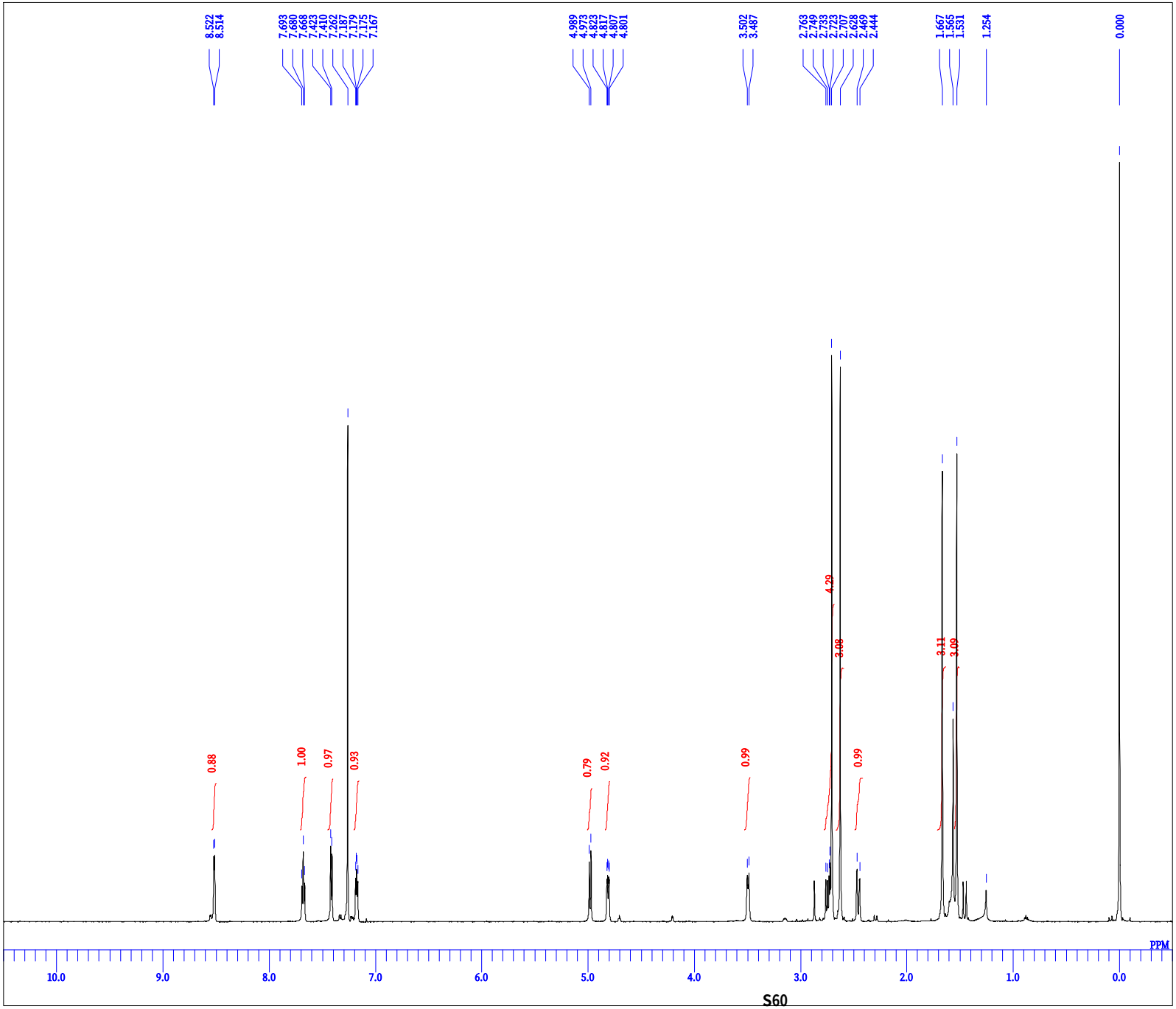
syn-4g



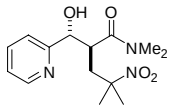
DFILE 2-pyridyl syn 13C-1.jdf
COMNT
DATIM 2020-10-04 16:21:19
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32768
FREQU 31407.03 Hz
SCANS 102
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.98 usec
IRNUC 1H
CTEMP 22.0 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.20 Hz
RGAIN 60



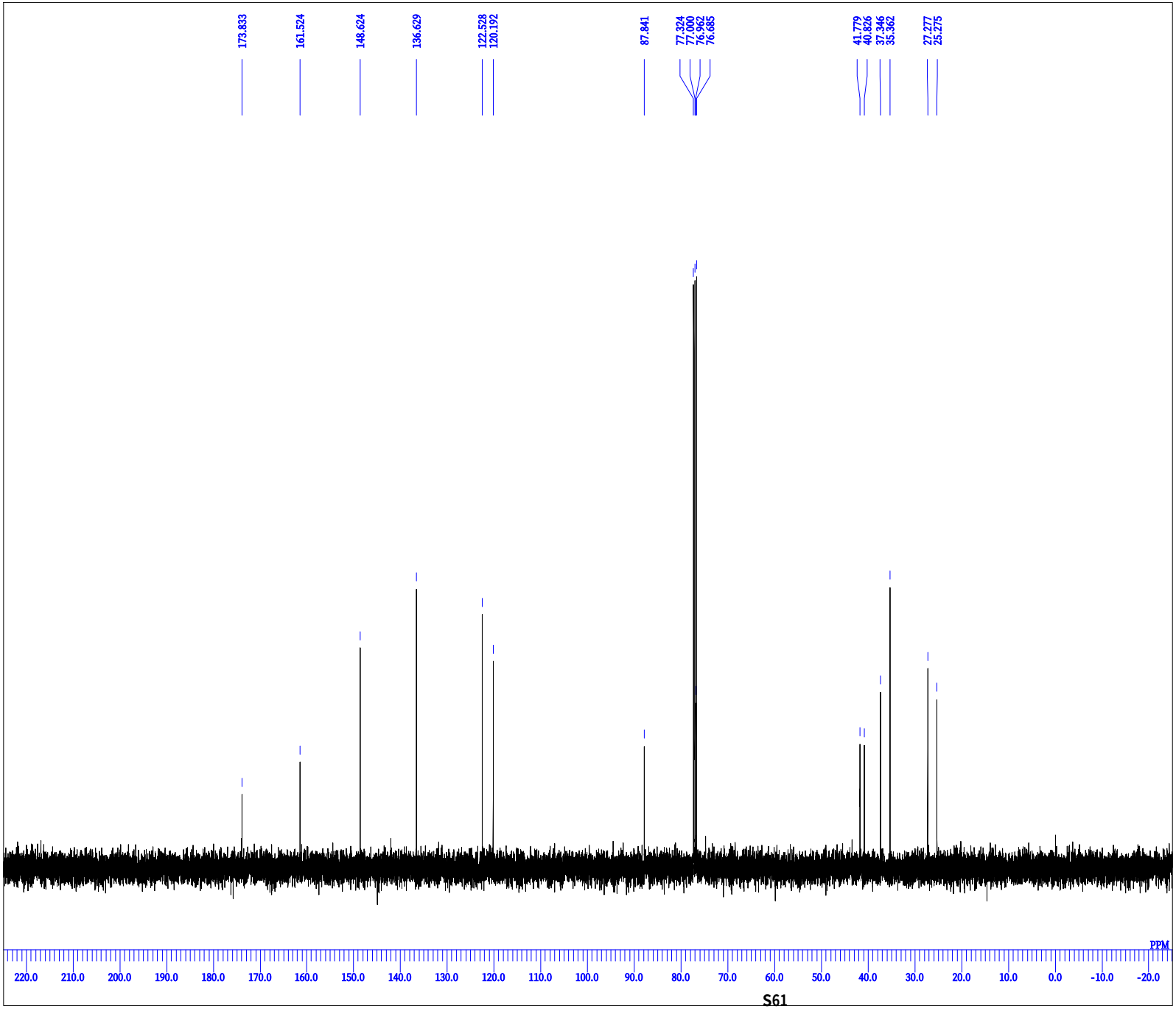
syn-4g



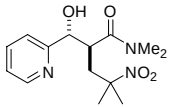
DFILE 2-Py sita 600MHz-1.als
COMNT
DATIM 2020-11-12 21:16:09
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 26214
FREQU 9008.87 Hz
SCANS 8
ACQTM 2.9098 sec
PD 2.0000 sec
PW1 6.90 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 54



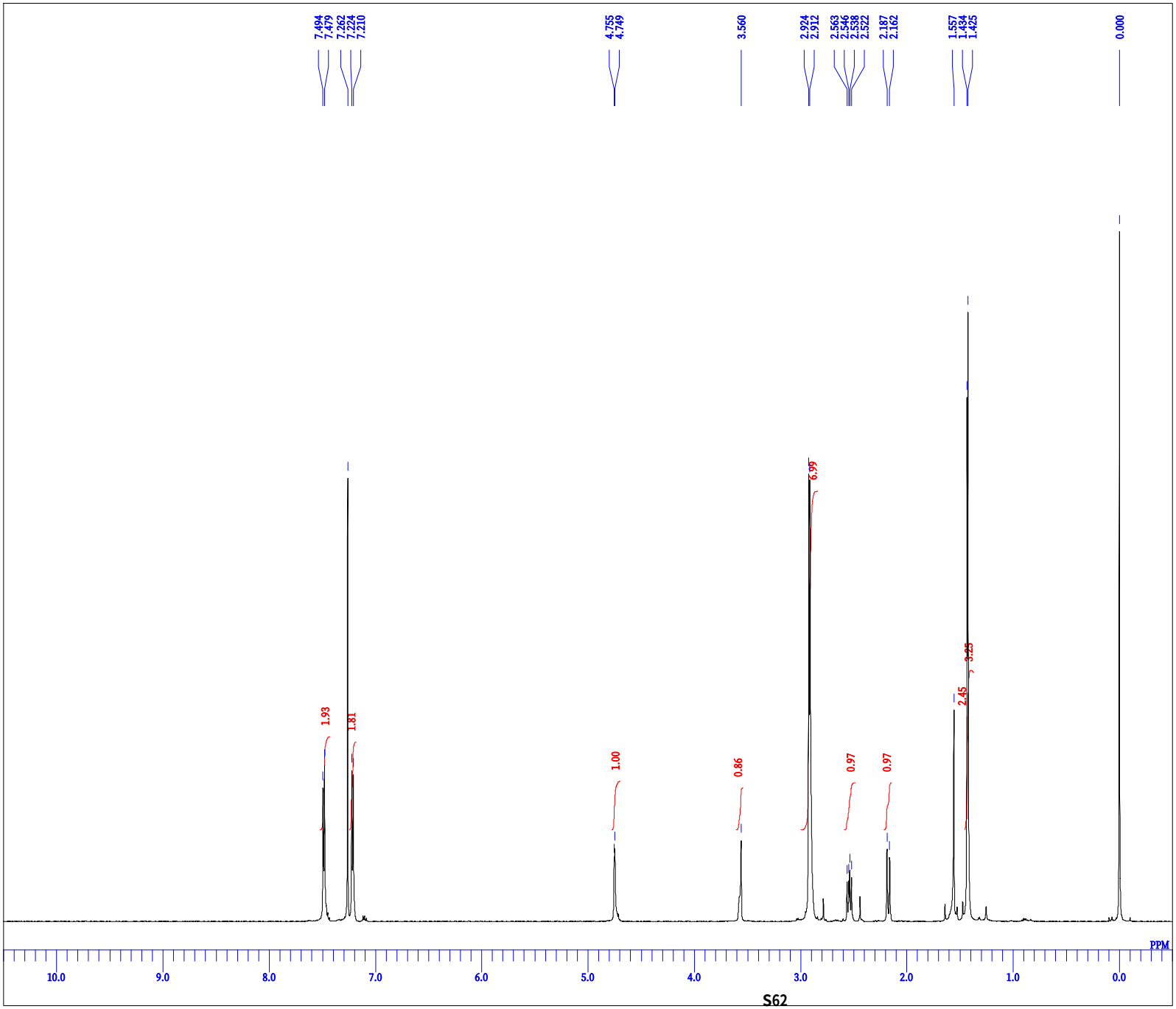
anti-**4g**



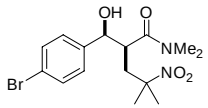
DFILE 2-pyridyl anti 13C-1.jdf
COMNT
DATIM 2020-10-04 16:31:37
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32768
FREQU 31407.03 Hz
SCANS 107
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.98 usec
IRNUC 1H
CTEMP 21.9 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.20 Hz
RGAIN 60



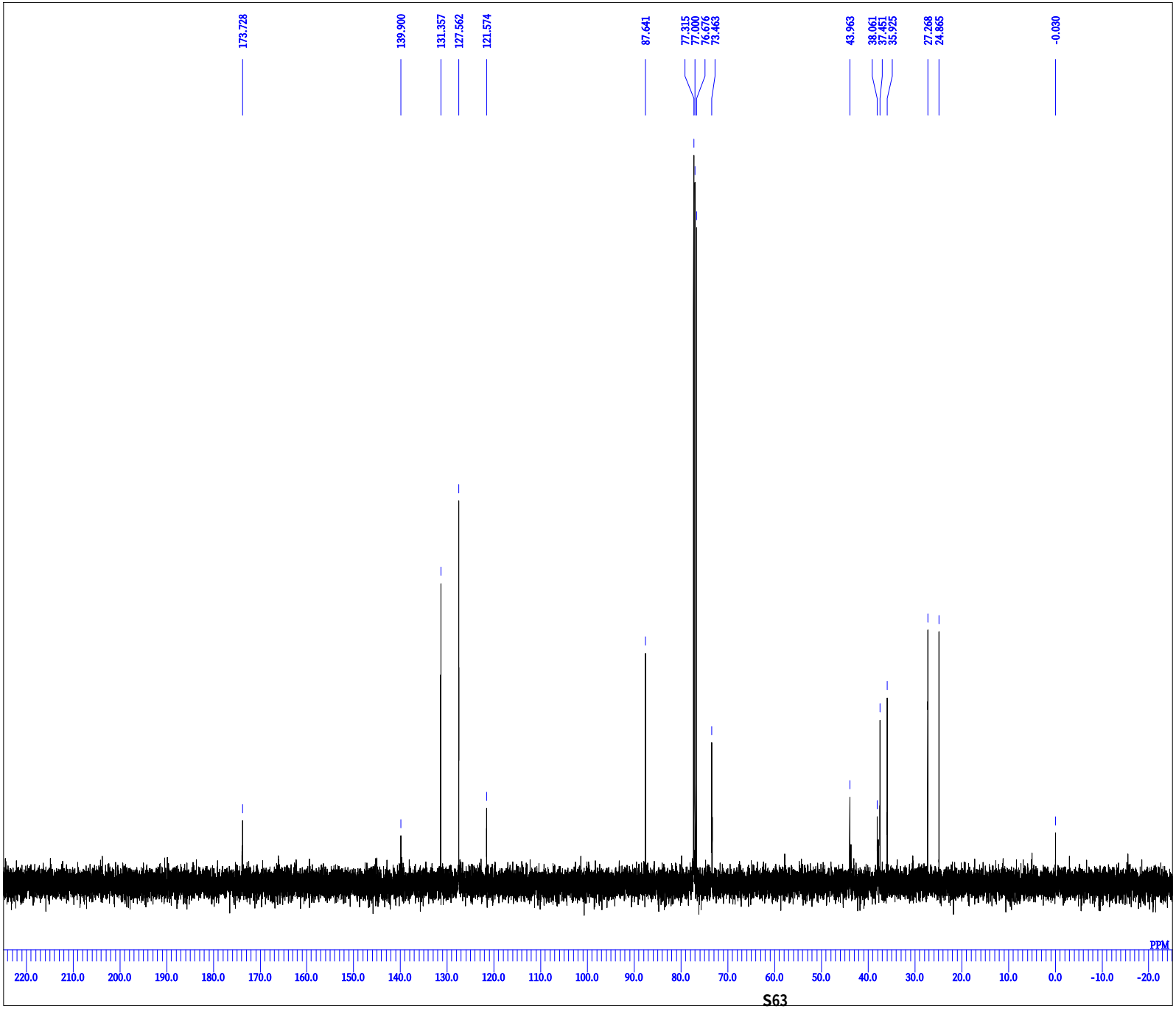
anti-4g



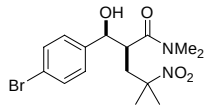
DFILE 4-Br ue 600MHz-1.als
COMNT
DATIM 2020-11-12 20:41:24
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 26214
FREQU 9008.87 Hz
SCANS 8
ACQTM 2.9098 sec
PD 2.0000 sec
PW1 6.90 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 54



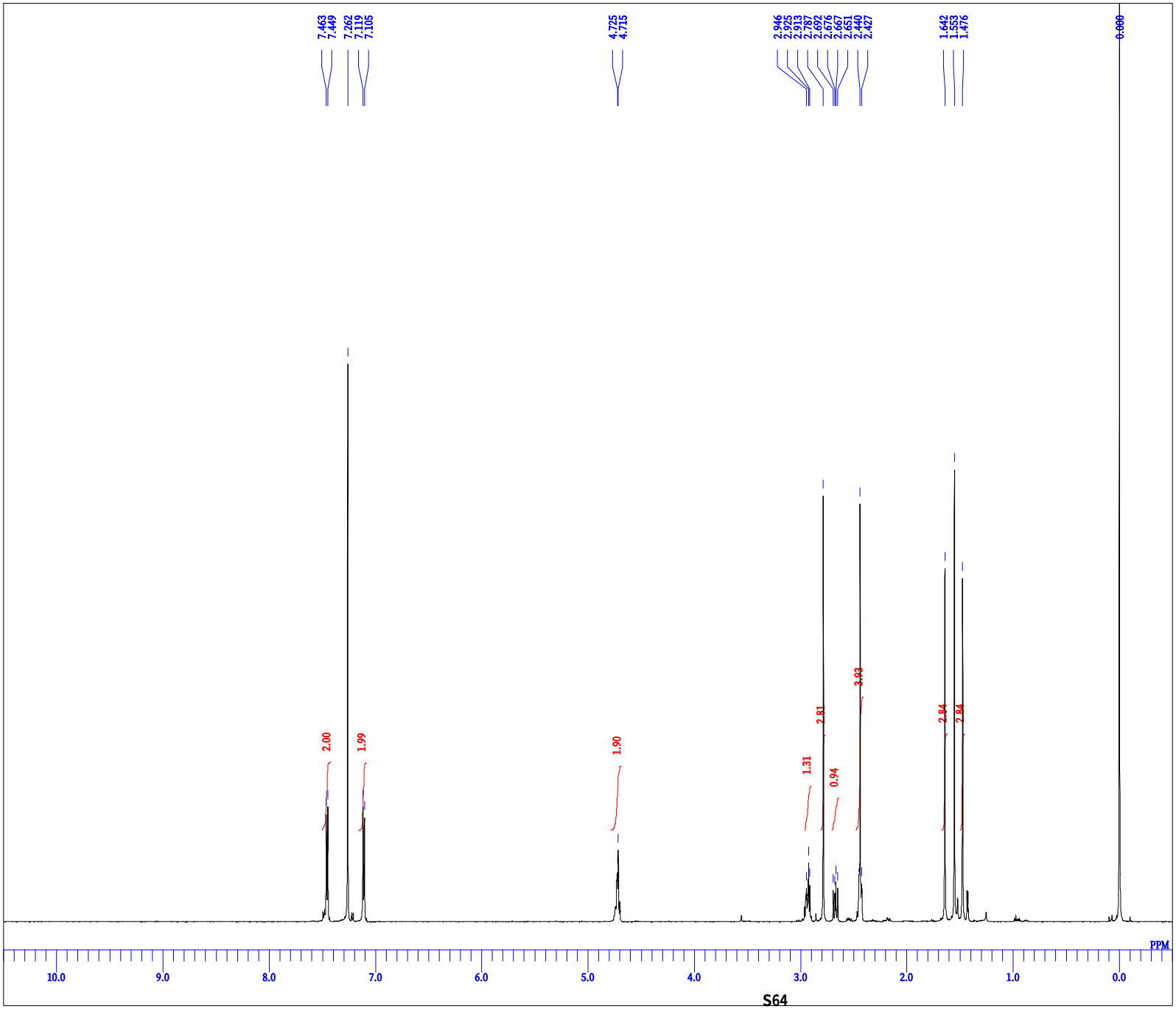
syn-4h



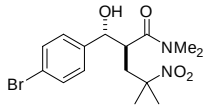
DFILE	p-Br syn 13C-1.jdf
COMNT	
DATIM	2020-10-04 16:01:48
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	296
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	22.1 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



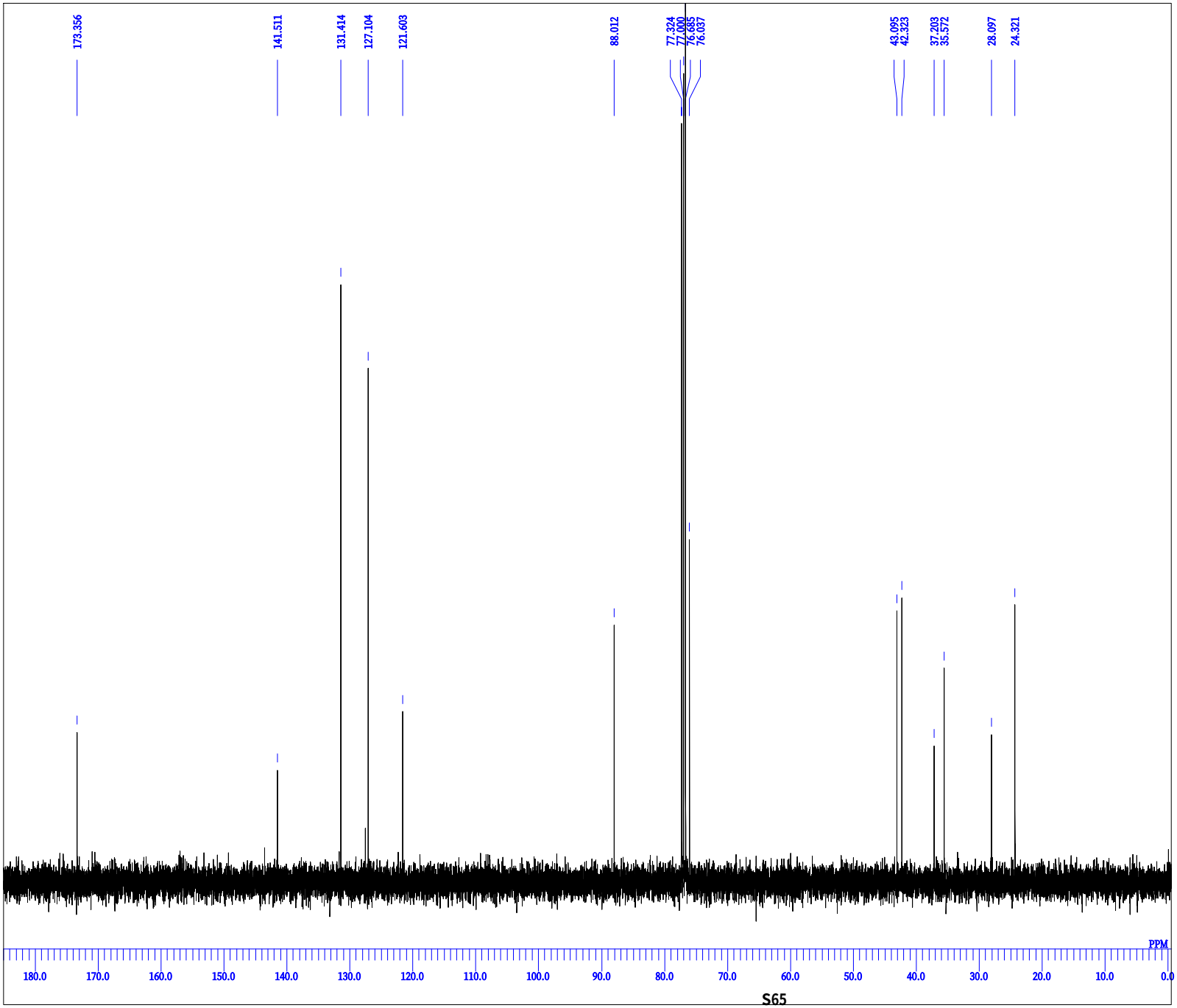
syn-4h



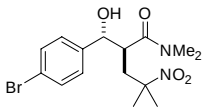
DFILE	4-Br sita 600MHz-1.als
COMNT	
DATIM	2020-11-12 20:47:10
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	32768
FREQU	11261.26 Hz
SCANS	8
ACQTM	2.9098 sec
PD	2.0000 sec
PW1	6.90 usec
IRNUC	1H
CTEMP	20.3 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	1.40 Hz
RGAIN	56



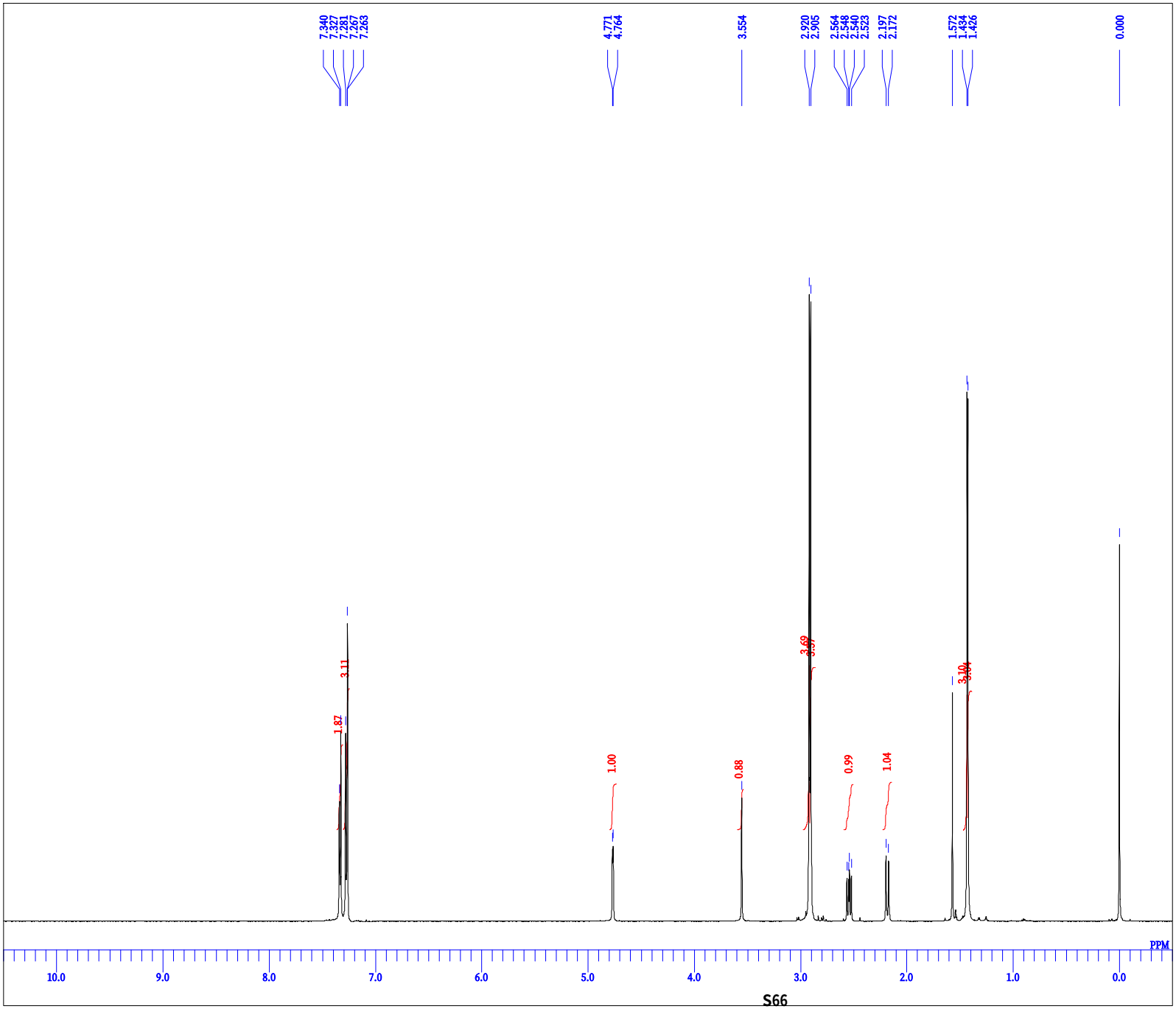
anti-4h



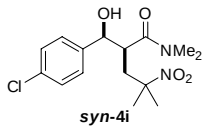
DFILE	p-Br anti 13C-1.als
COMNT	
DATIM	2020-10-04 16:11:28
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	101
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



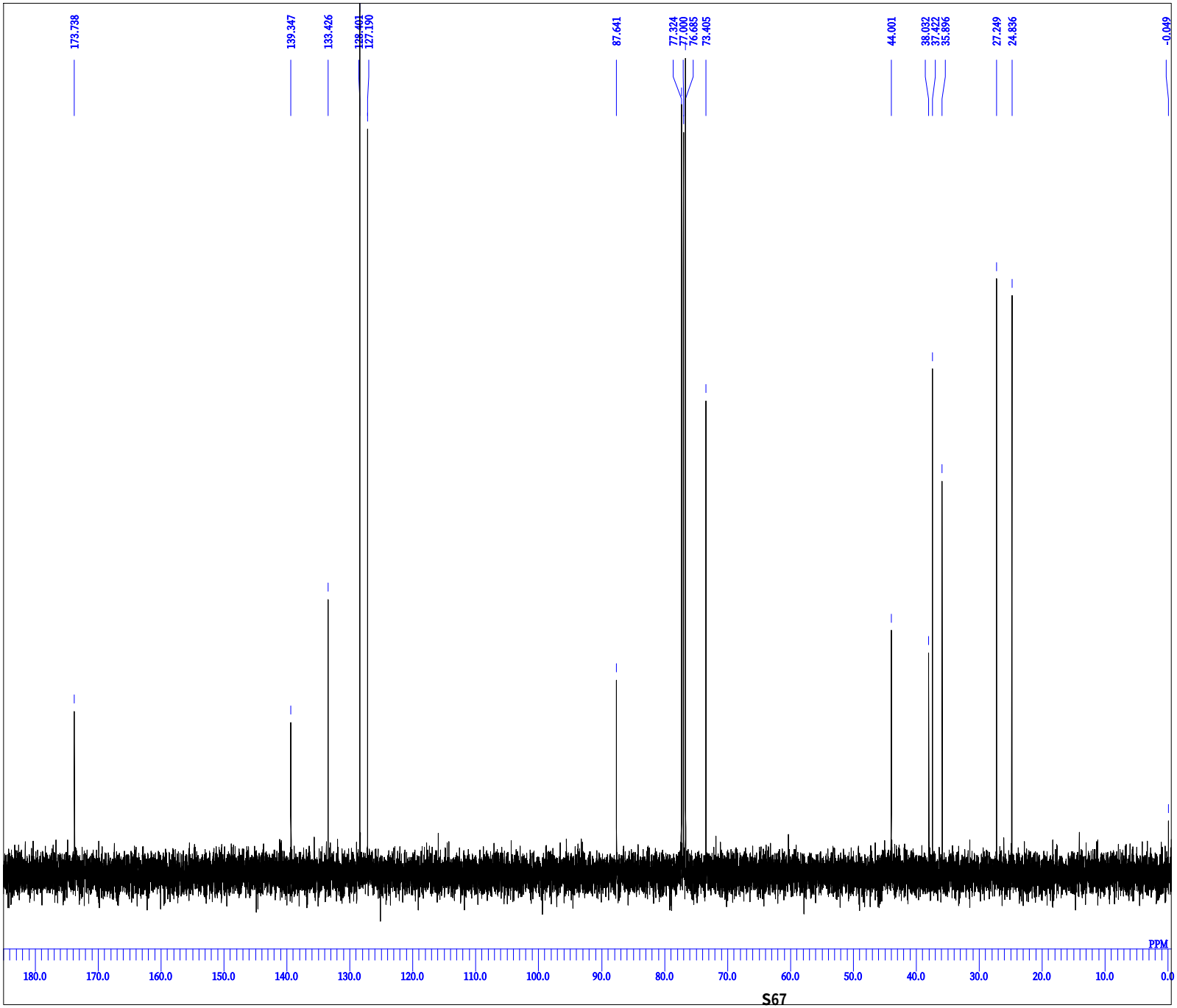
anti-4h



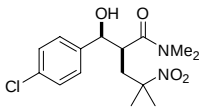
DFILE 4-Cl ue 600MHz-1.als
COMNT
DATIM 2020-11-12 20:52:49
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 26214
FREQU 9008.87 Hz
SCANS 8
ACQTM 2.9098 sec
PD 2.0000 sec
PW1 6.90 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 52



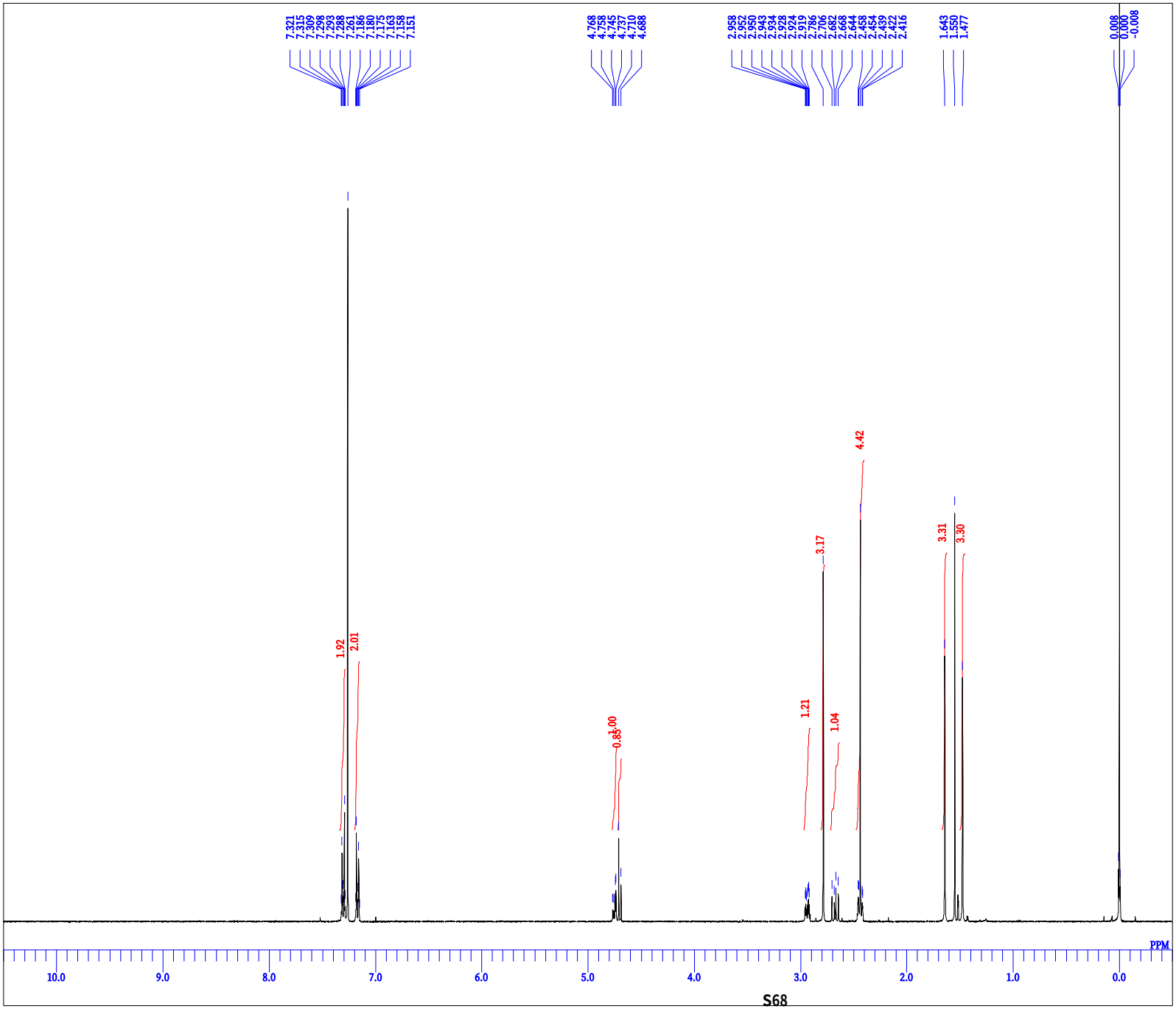
syn-4i



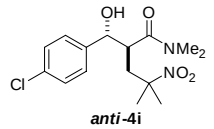
DFILE	4-Cl 13C-1.als
COMNT	
DATIM	2020-10-05 21:04:10
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	52
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.9 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



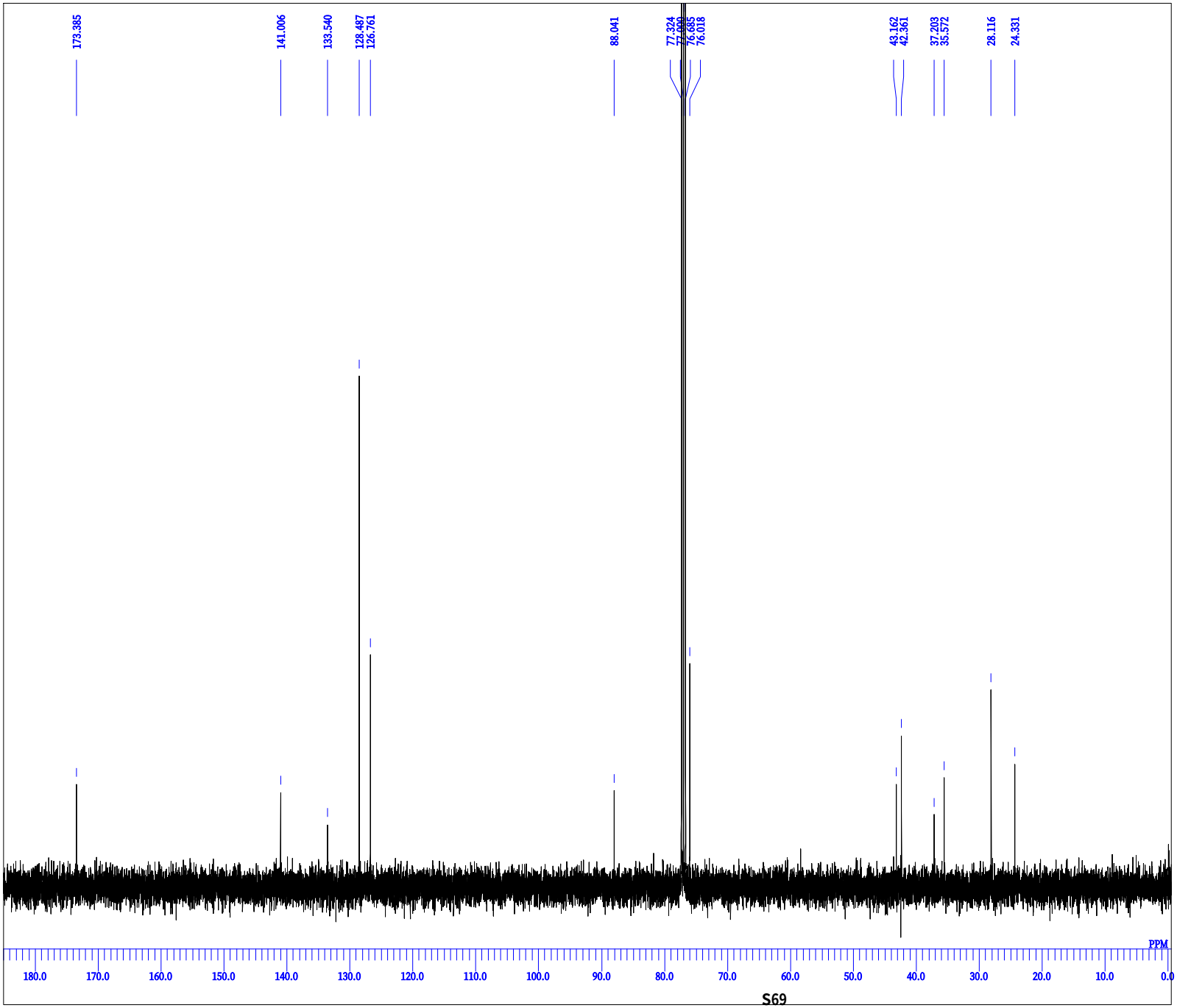
syn-4i



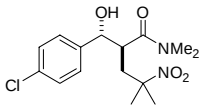
DFILE	4-Cl sita n-1.als
COMNT	
DATIM	2020-11-19 16:28:35
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	21.2 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	0.20 Hz
RGAIN	52



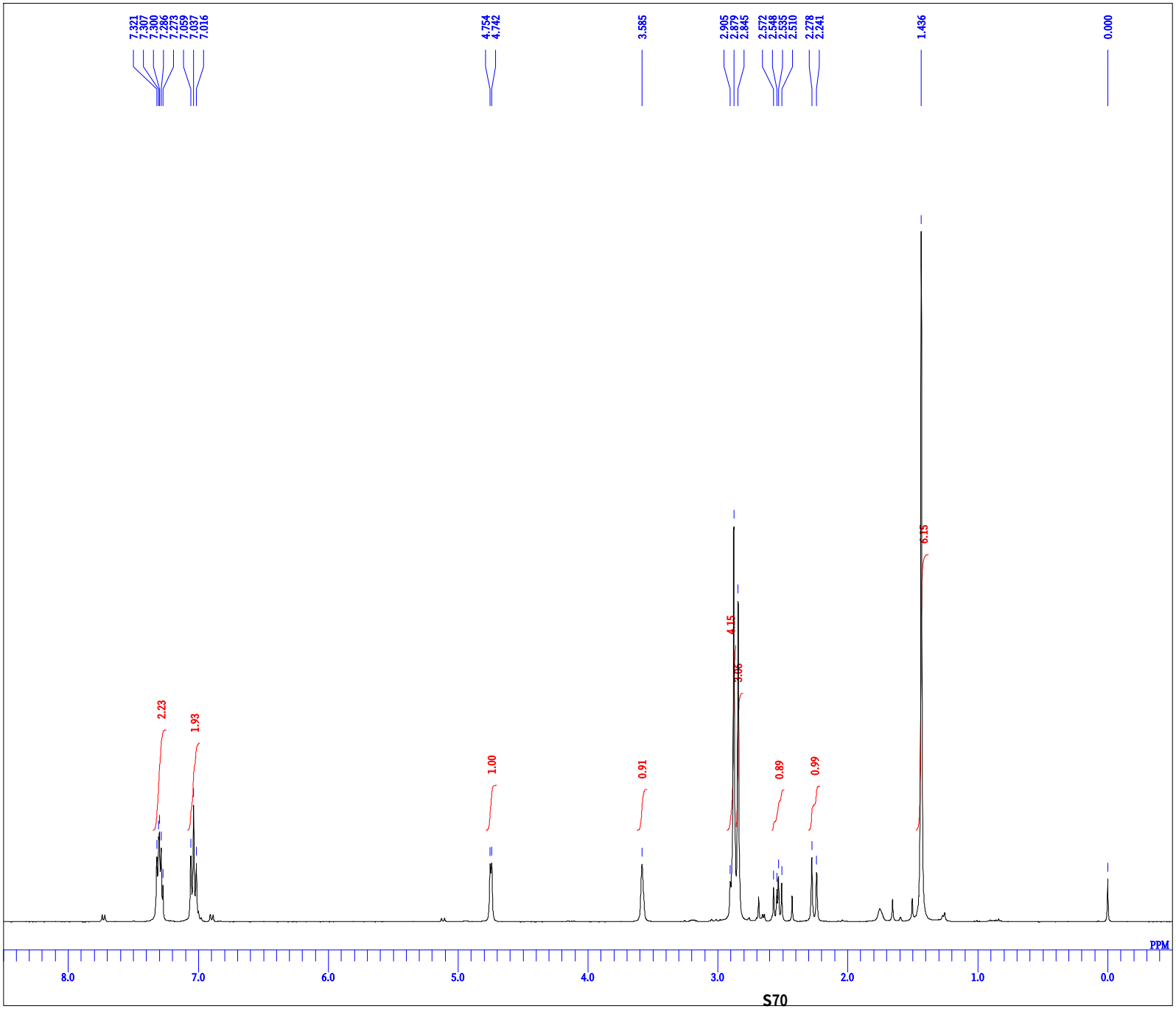
***anti*-4i**



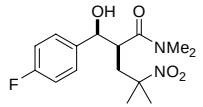
DFILE	4-Cl sita 13C-1.als
COMNT	
DATIM	2020-10-05 21:17:35
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	202
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	22.1 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



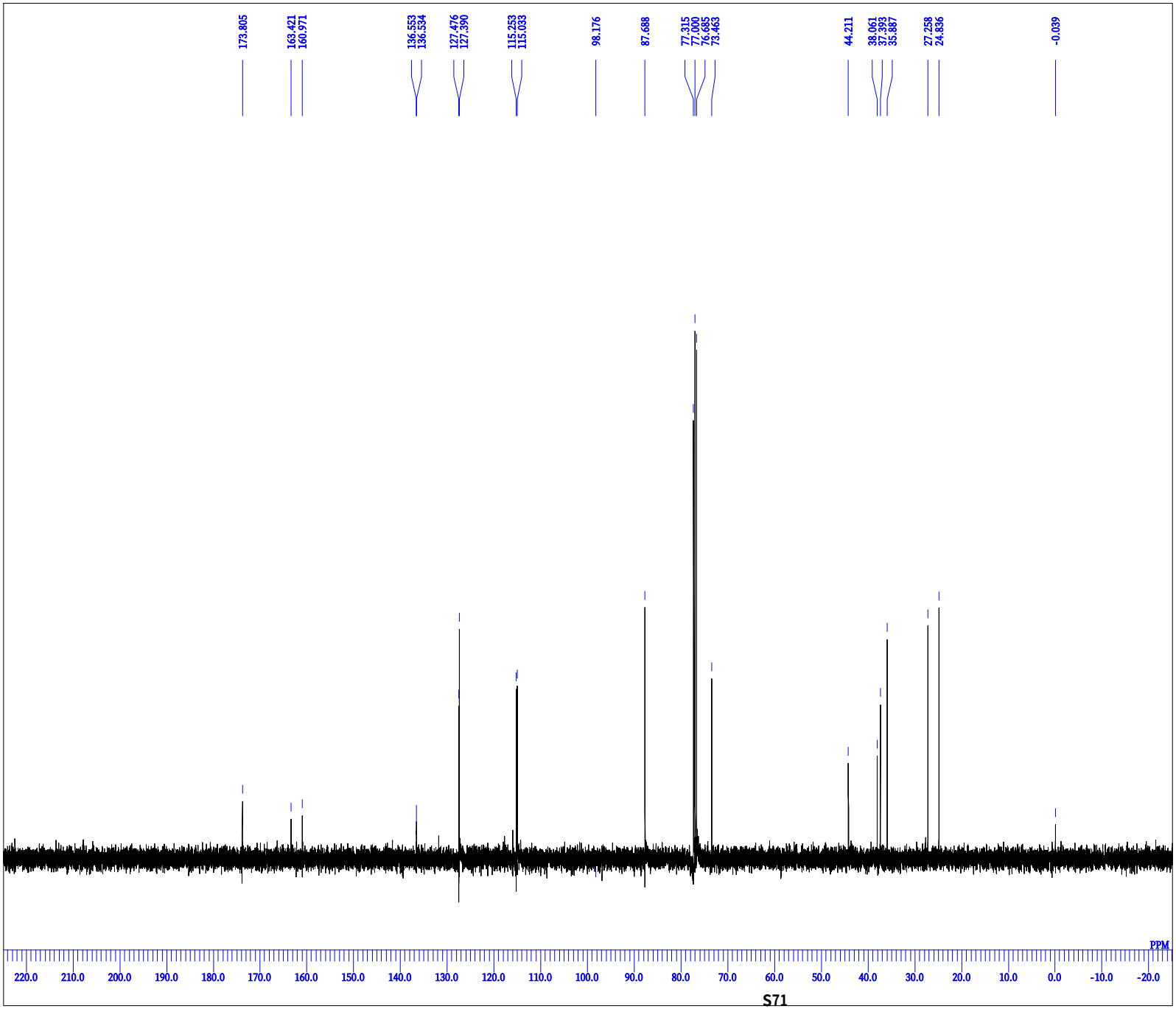
anti-4i



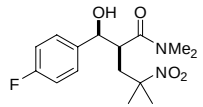
DFILE 4-F ue-1.als
COMNT
DATIM 2020-10-28 03:14:16
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 21.2 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 34



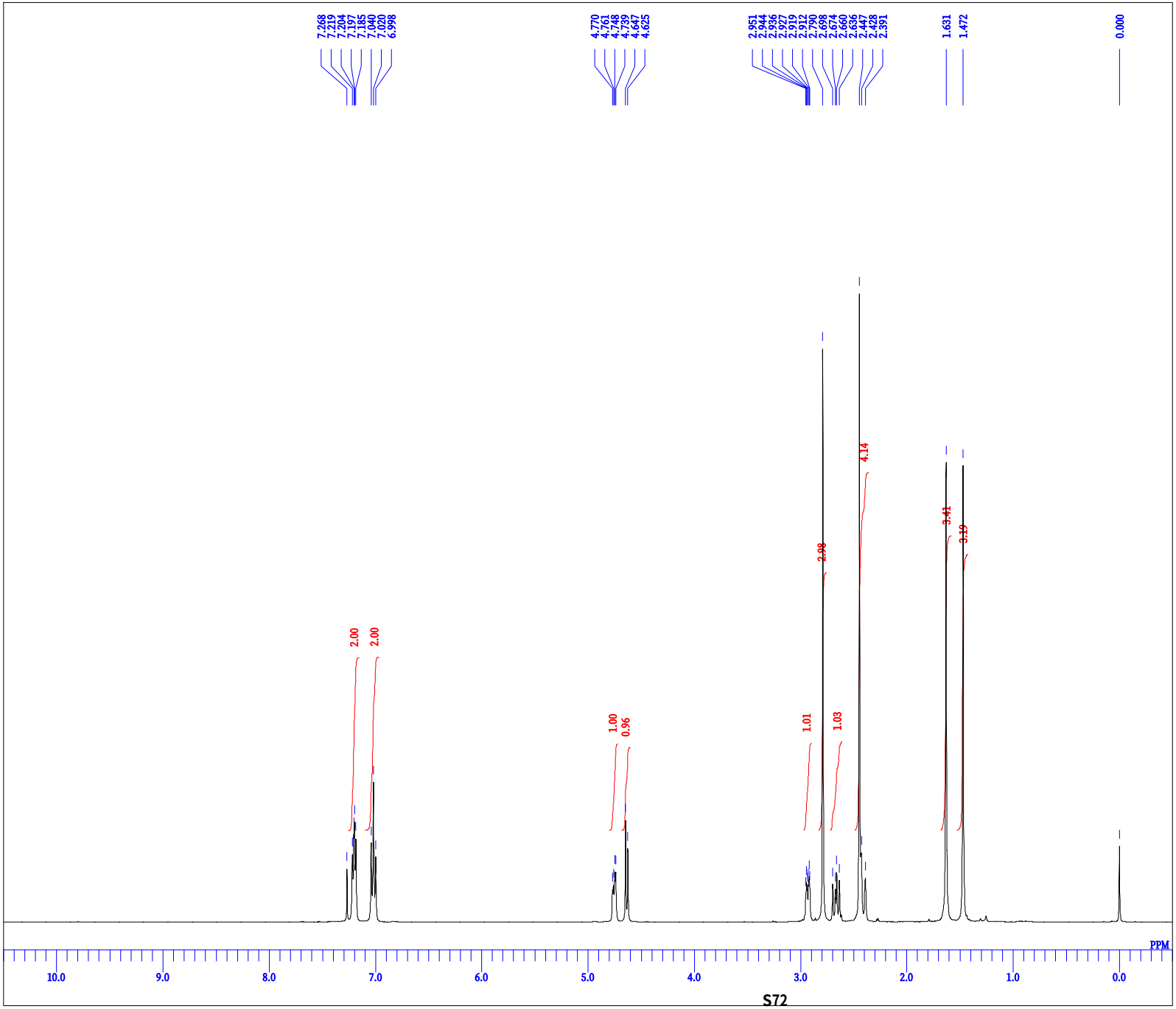
syn-4j



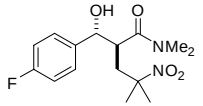
DFILE	4-F ue 13C-1.als
COMNT	
DATIM	2020-10-28 03:18:58
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	110
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



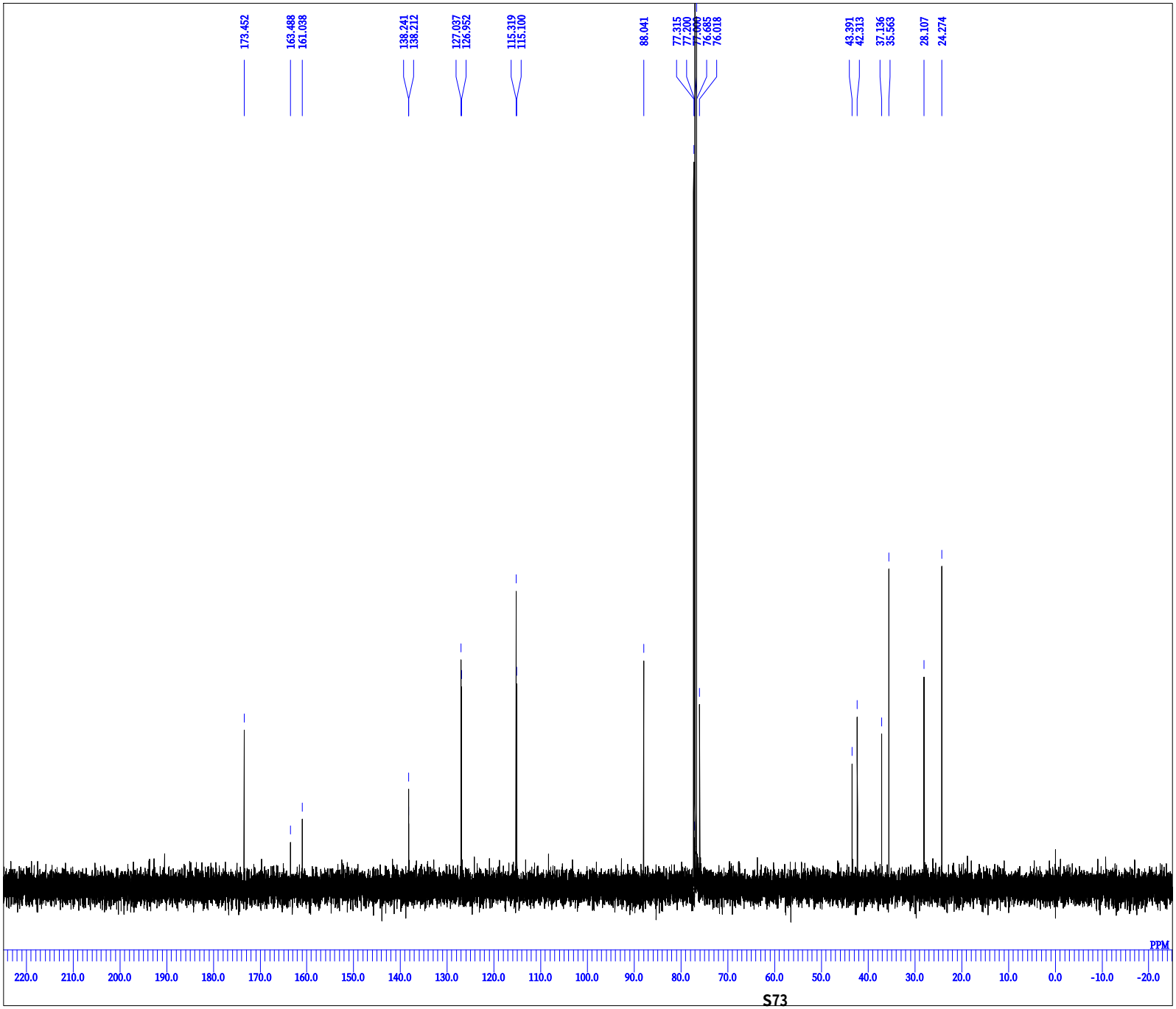
syn-4j



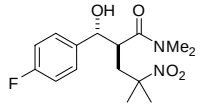
DFILE 4-F sita-1.als
COMNT
DATIM 2020-10-28 03:32:22
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 38



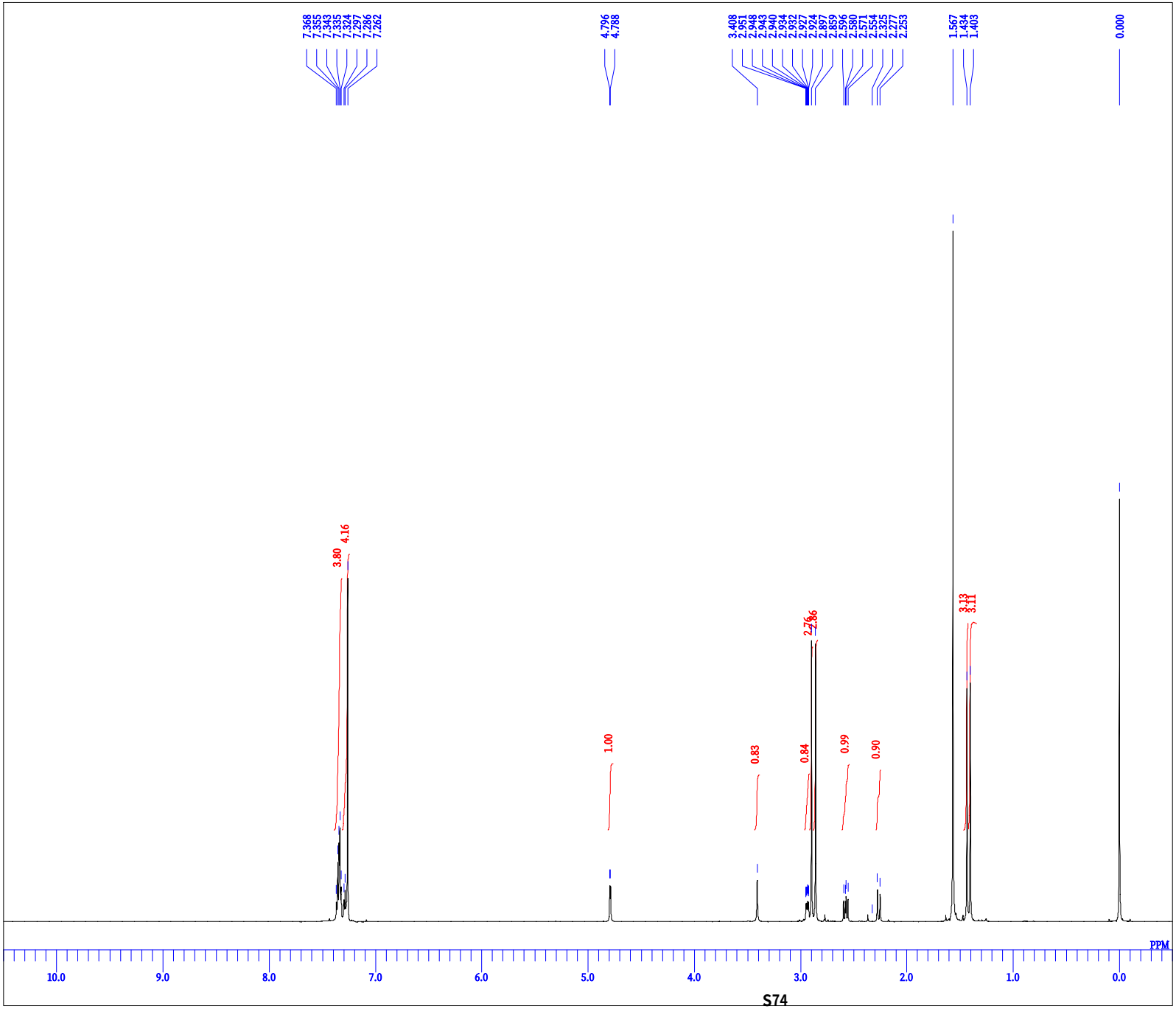
anti-4j



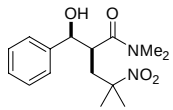
DFILE 4-F sita 13C-1.jdf
COMNT
DATIM 2020-10-28 03:37:13
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32768
FREQU 31407.03 Hz
SCANS 113
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.98 usec
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.20 Hz
RGAIN 60



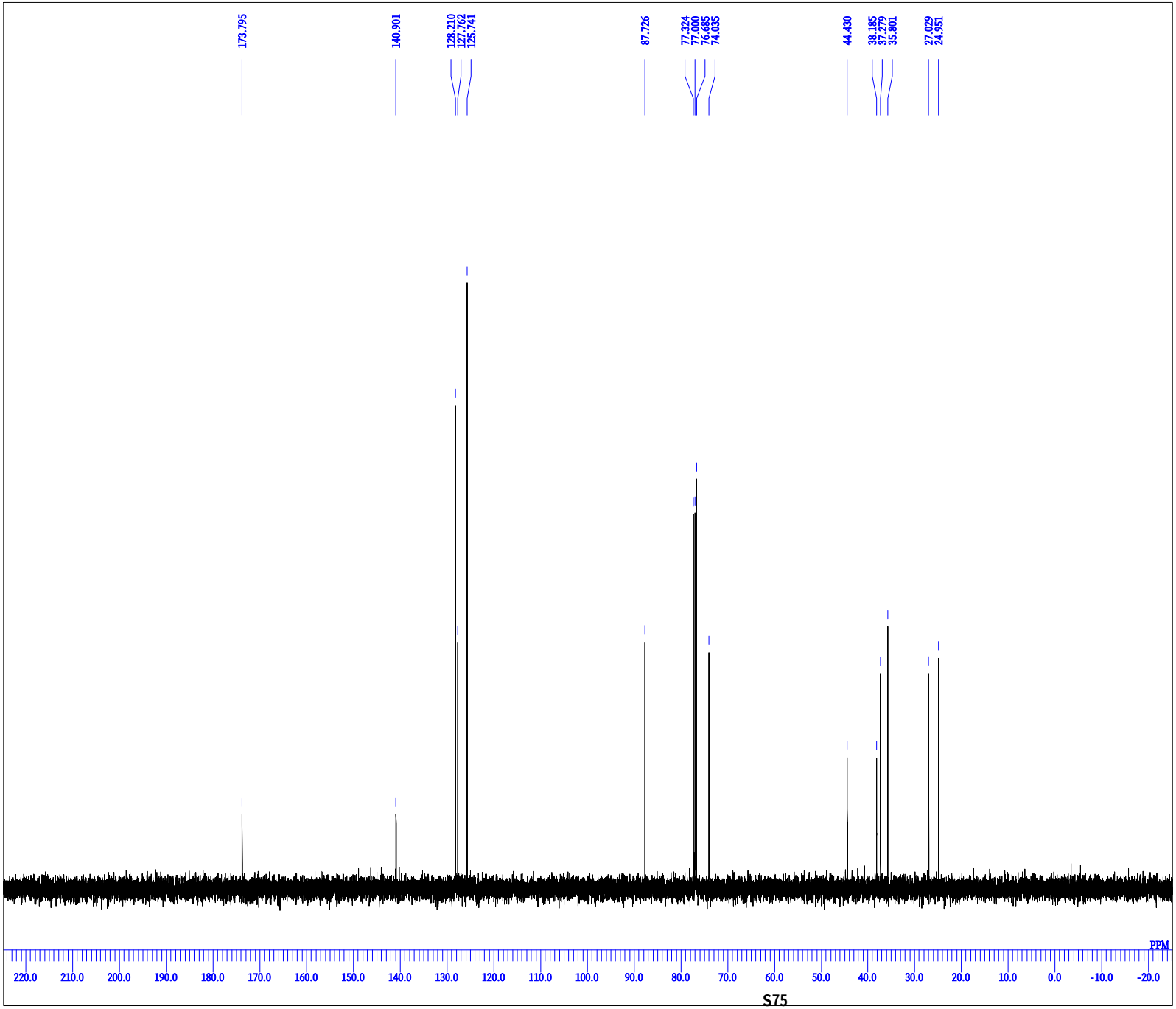
anti-4j



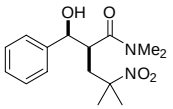
DFILE	amide H ue 1H-1.als
COMNT	
DATIM	2020-11-09 20:36:54
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	26214
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	2.0000 sec
PW1	6.90 usec
IRNUC	1H
CTEMP	19.8 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	1.40 Hz
RGAIN	56



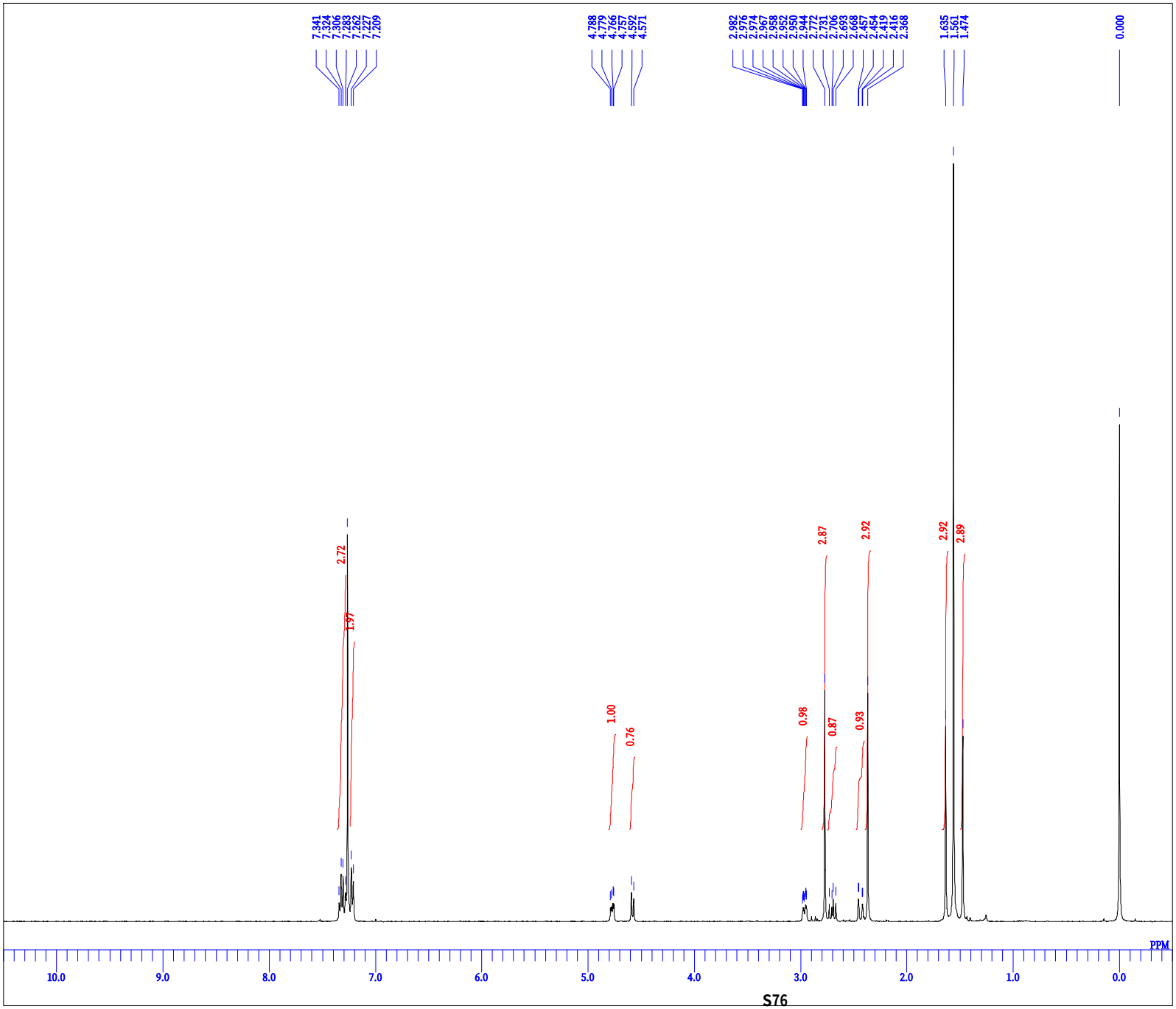
***syn*-4k**



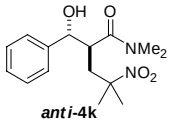
DFILE	amide H ue 13C-1.jdf
COMNT	
DATIM	2020-11-07 10:10:26
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	47
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.4 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



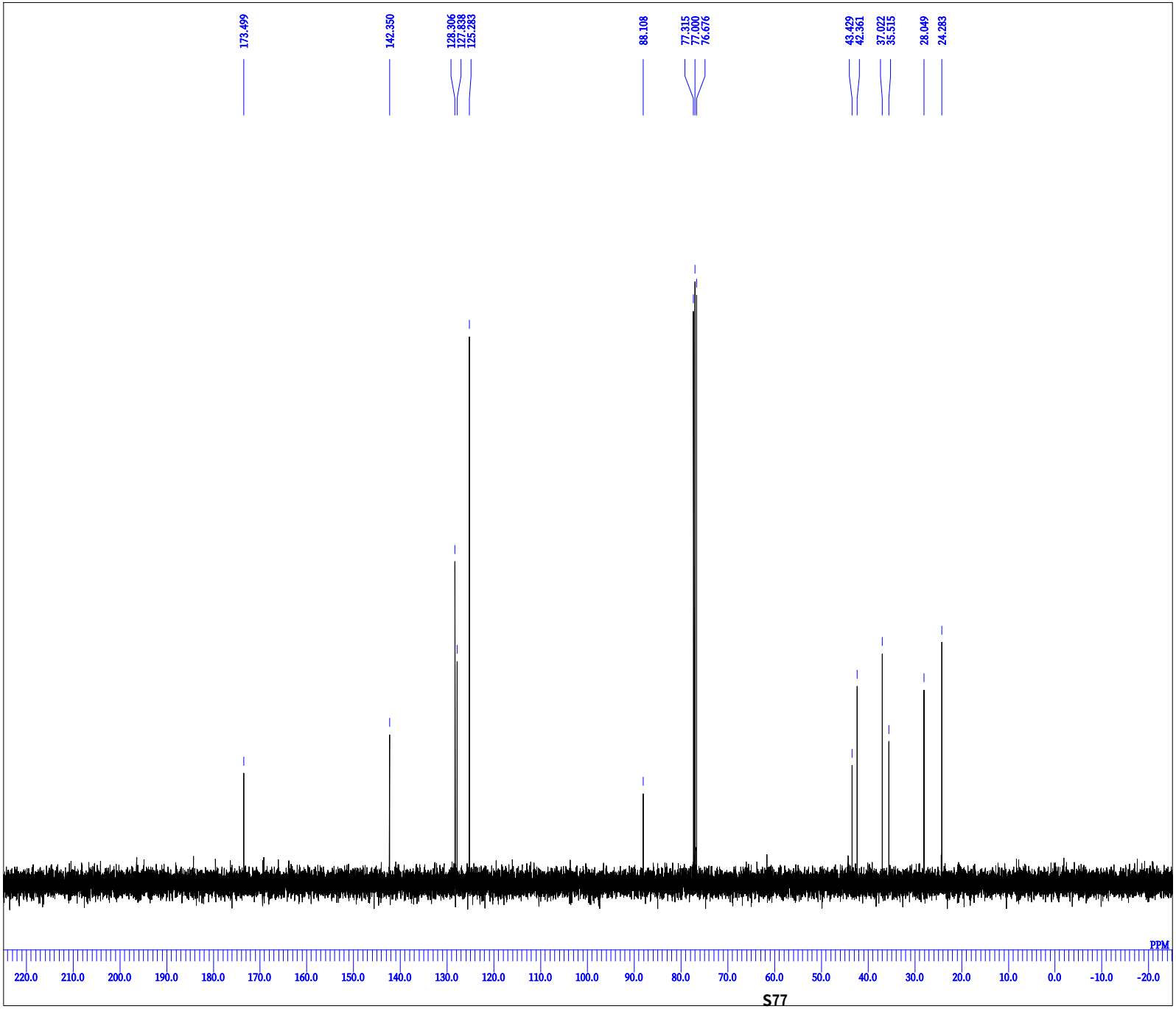
***syn*-4k**



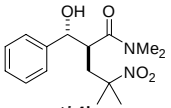
DFILE amide H sita-1.als
COMNT
DATIM 2020-11-09 08:25:08
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 21.3 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 54



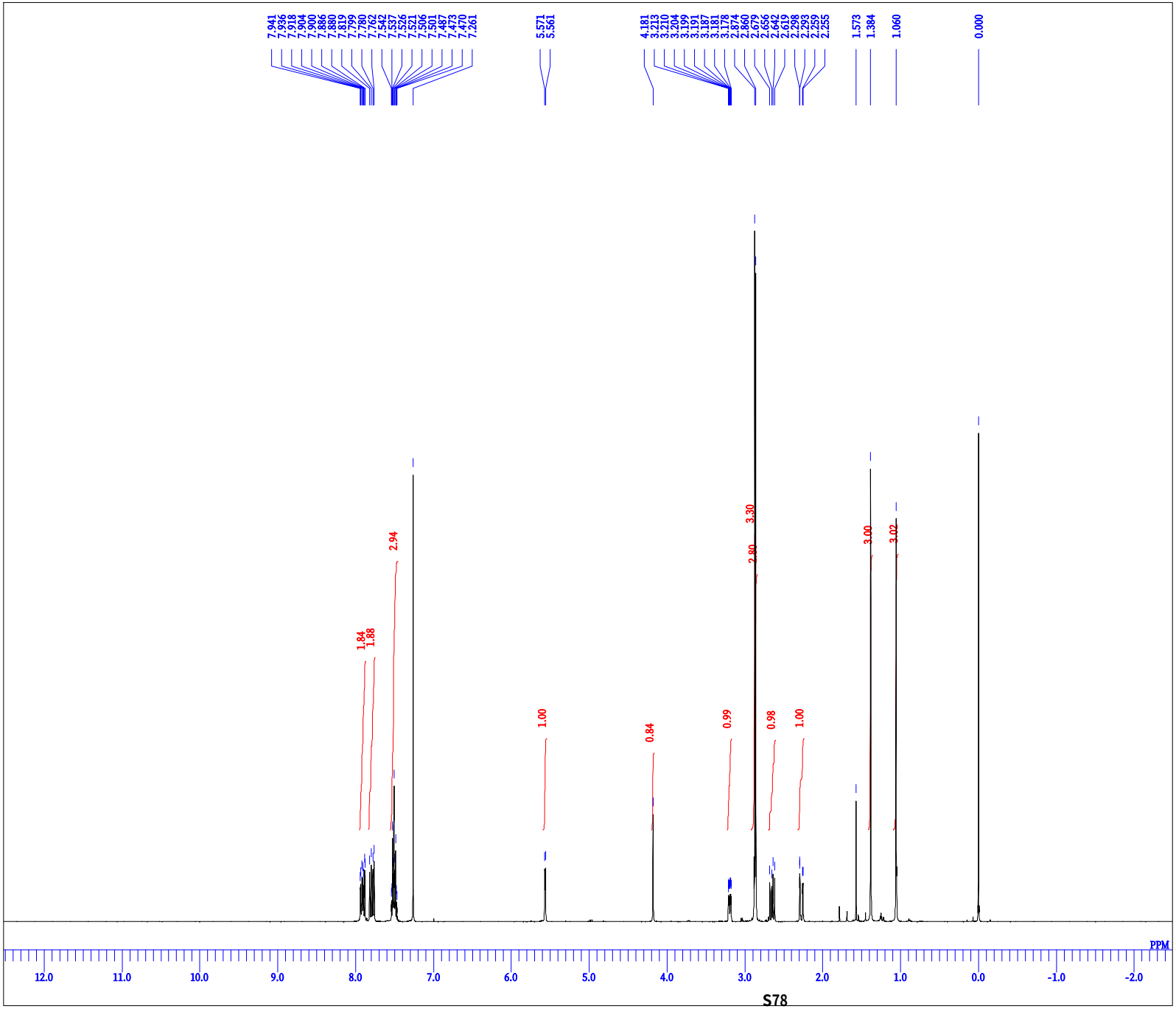
anti-4k



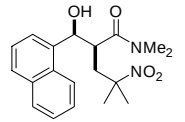
DFILE	H sita 13C-1.jdf
COMNT	
DATIM	2020-11-24 22:43:32
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	75
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



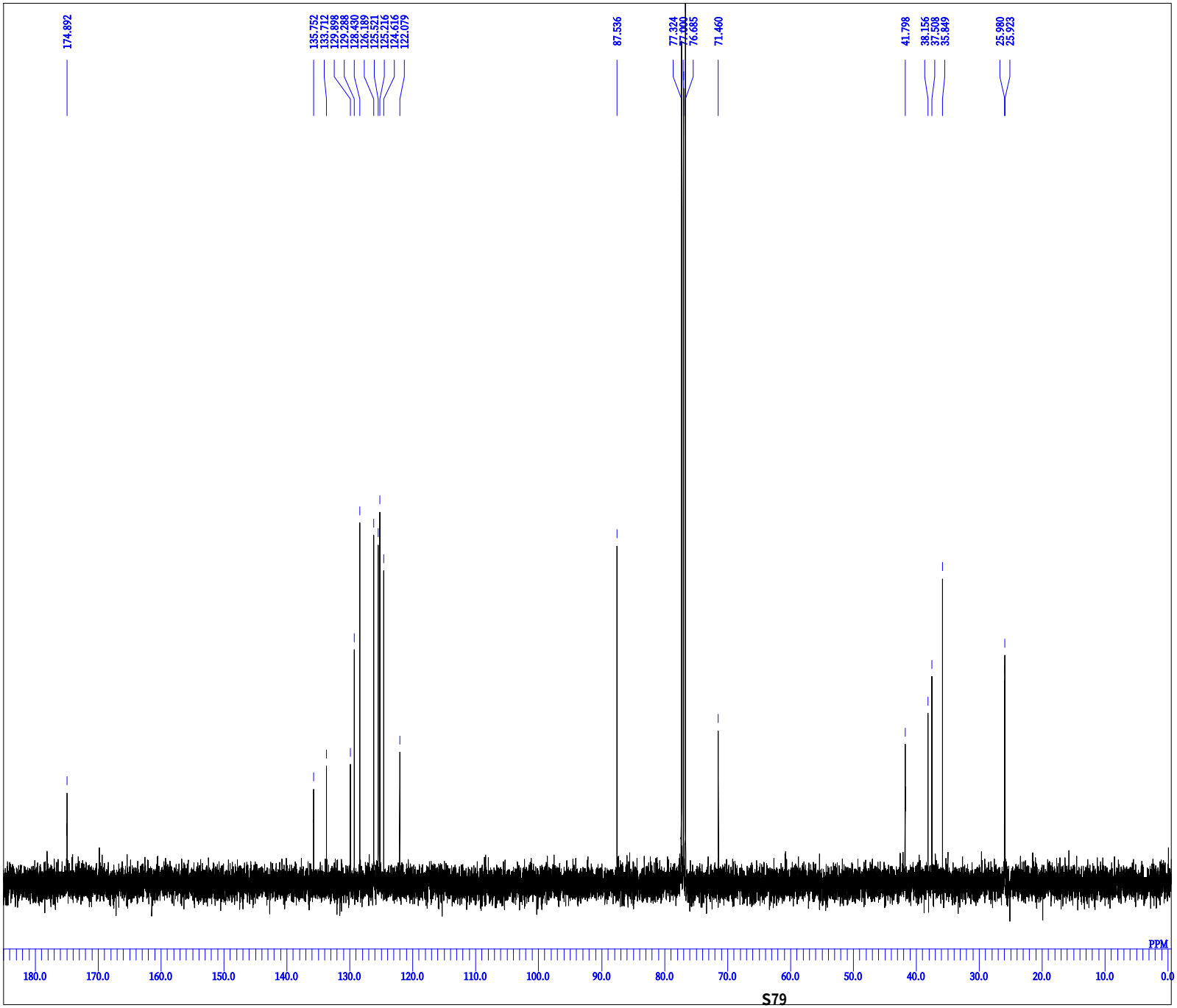
anti-4k



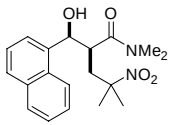
DFILE	amide 1-naph ue n-1.als
COMNT	
DATIM	2020-11-18 14:17:53
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	0.20 Hz
RGAIN	46



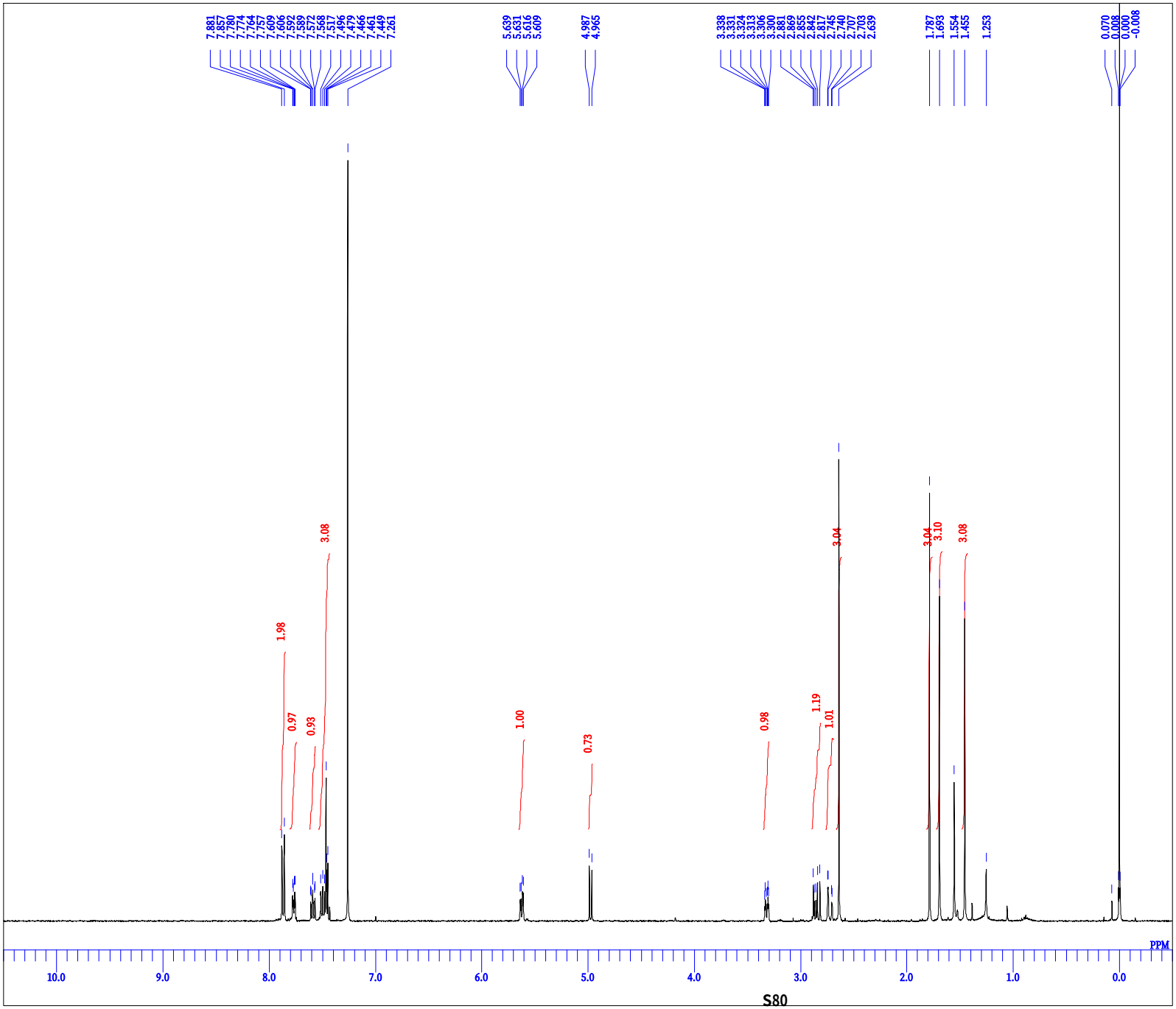
syn-4l



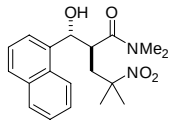
DFILE	1-Naphthyl 1 13C-1.als
COMNT	
DATIM	2020-10-18 15:00:46
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	109
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	22.1 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



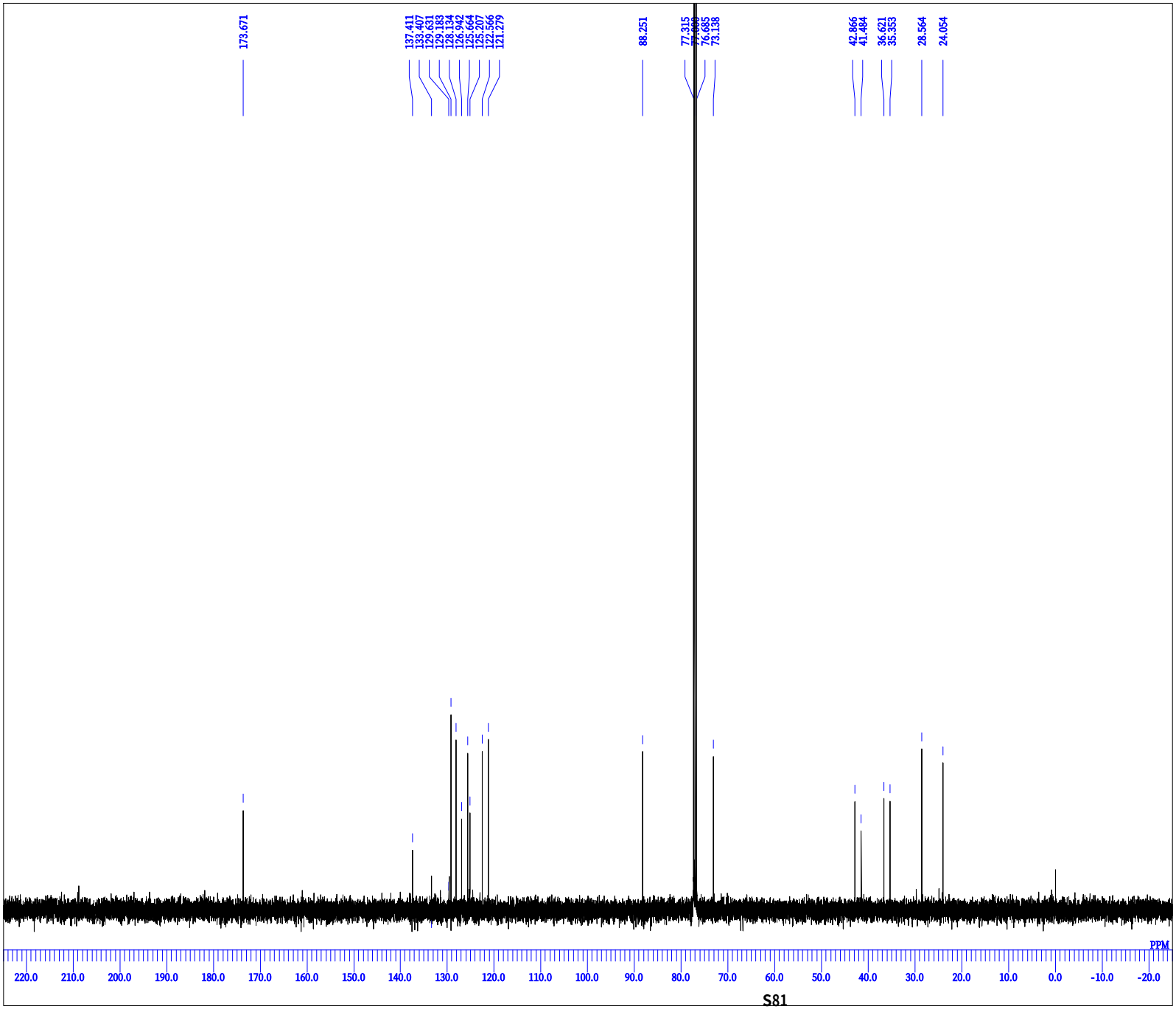
***syn*-4l**



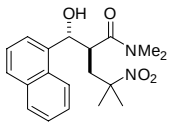
DFILE	amide 1-naph sita n-1.als
COMNT	
DATIM	2020-11-18 14:22:57
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	0.20 Hz
RGAIN	50



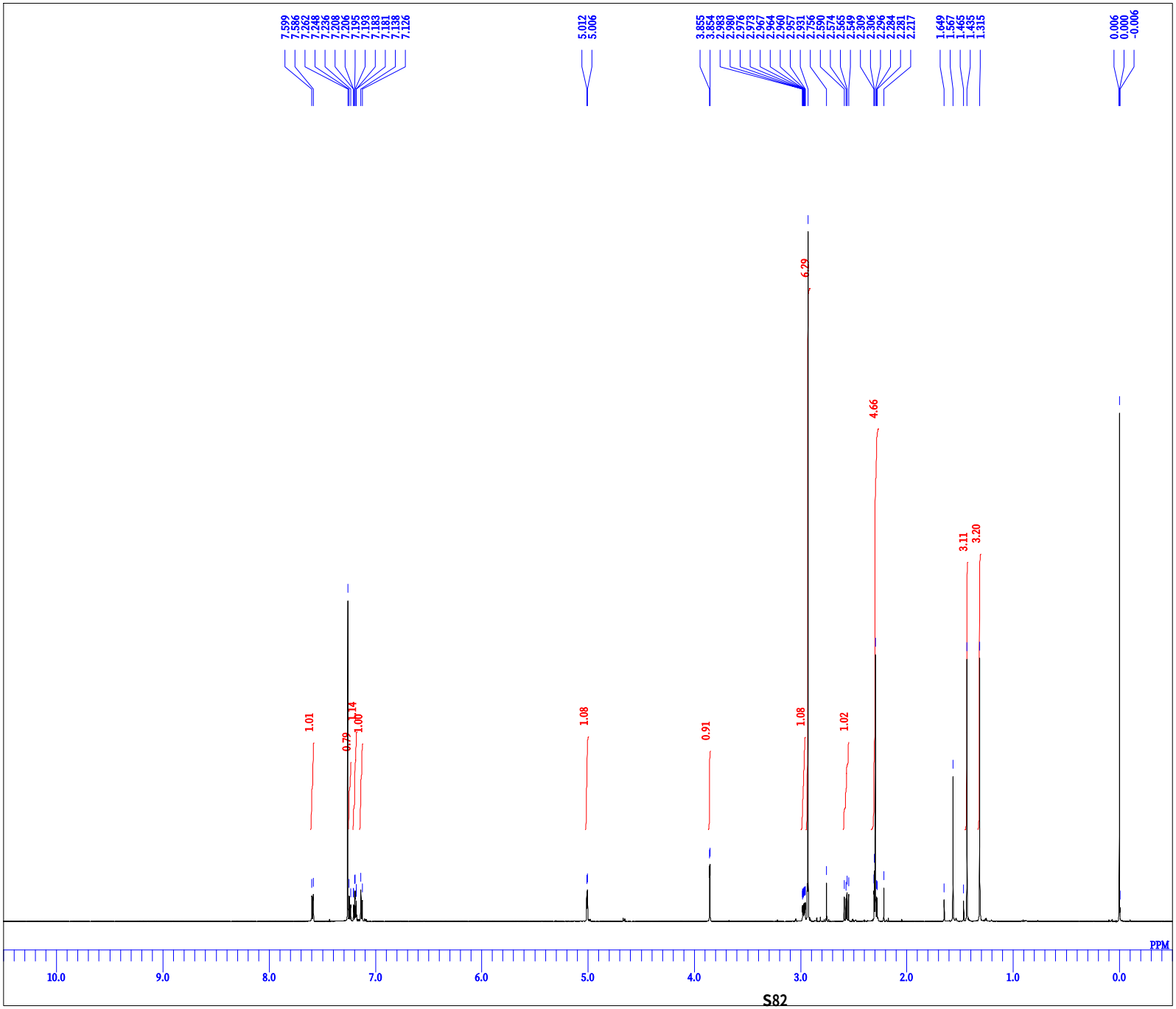
anti-4l



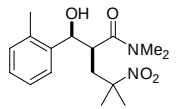
DFILE	1-Naphthyl 2 13C-1.als
COMNT	
DATIM	2020-10-18 15:43:22
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	977
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	22.4 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



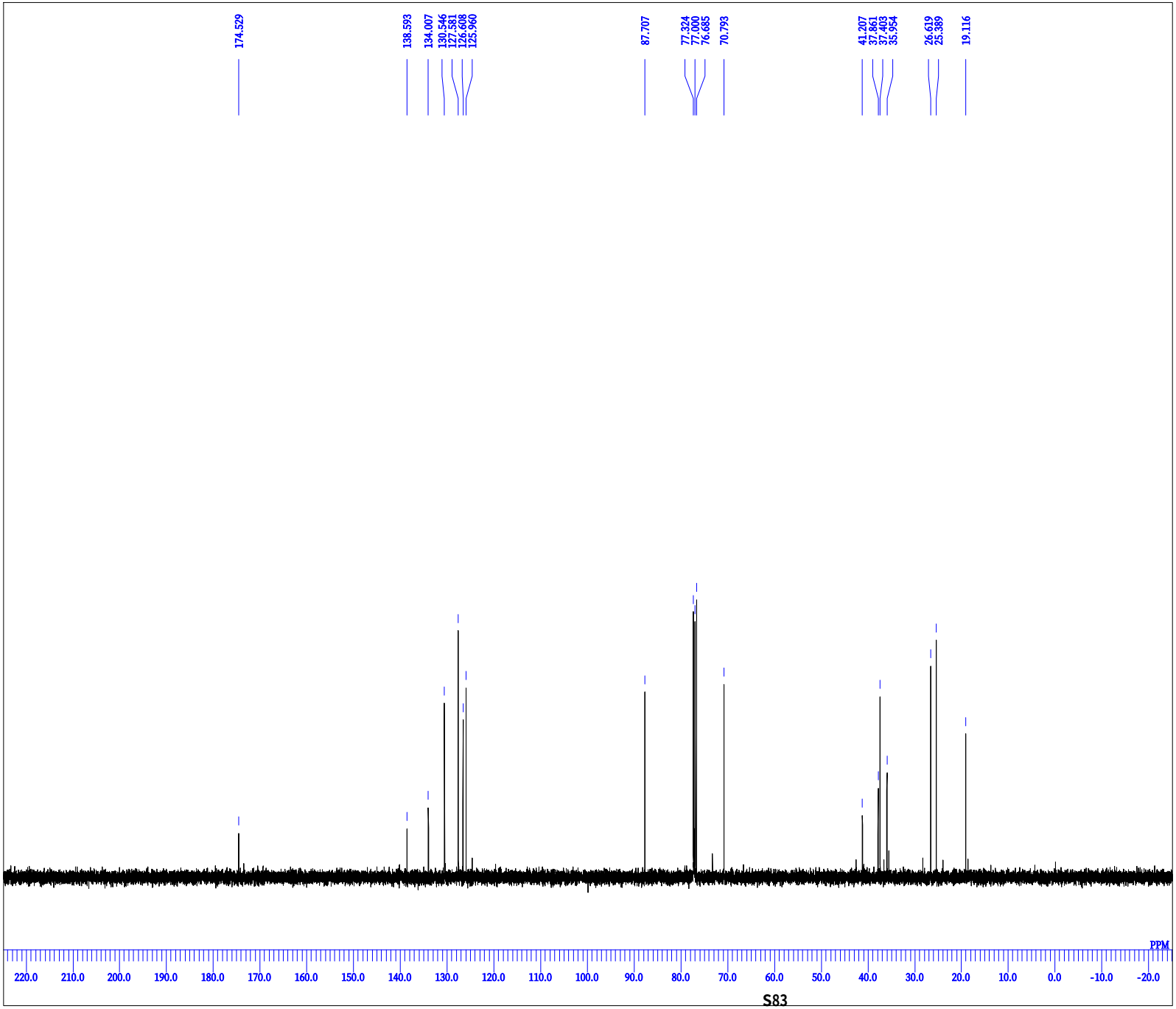
anti-4l



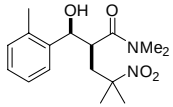
DFILE 2-Me ue 600MHz-1.als
COMNT
DATIM 2020-11-12 20:29:29
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 26214
FREQU 9008.87 Hz
SCANS 8
ACQTM 2.9098 sec
PD 2.0000 sec
PW1 6.90 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 52



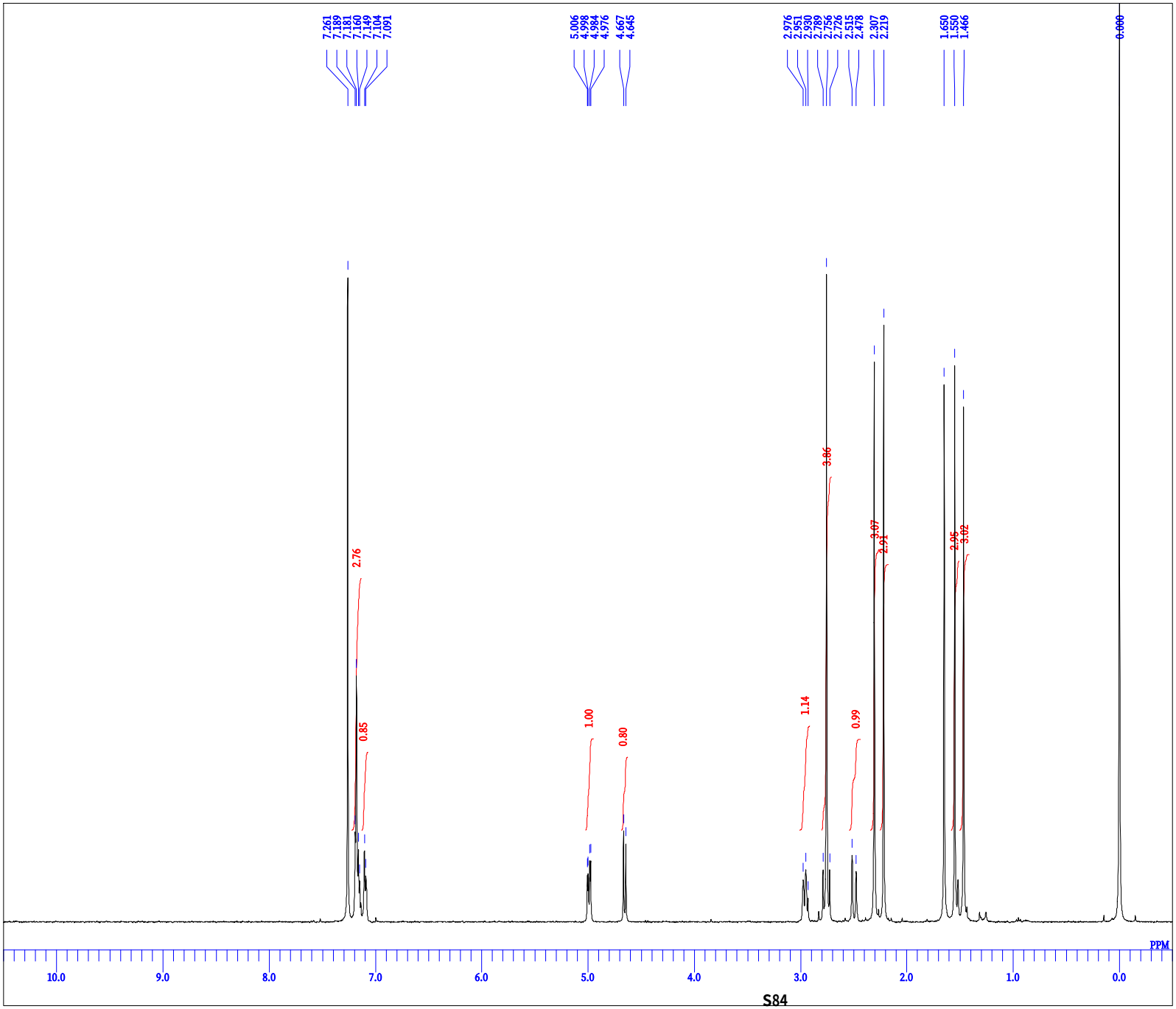
syn-4m



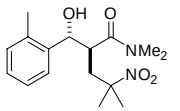
DFILE	2-Me ue 13C-1.als
COMNT	
DATIM	2020-11-24 22:15:23
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	85
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.0 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



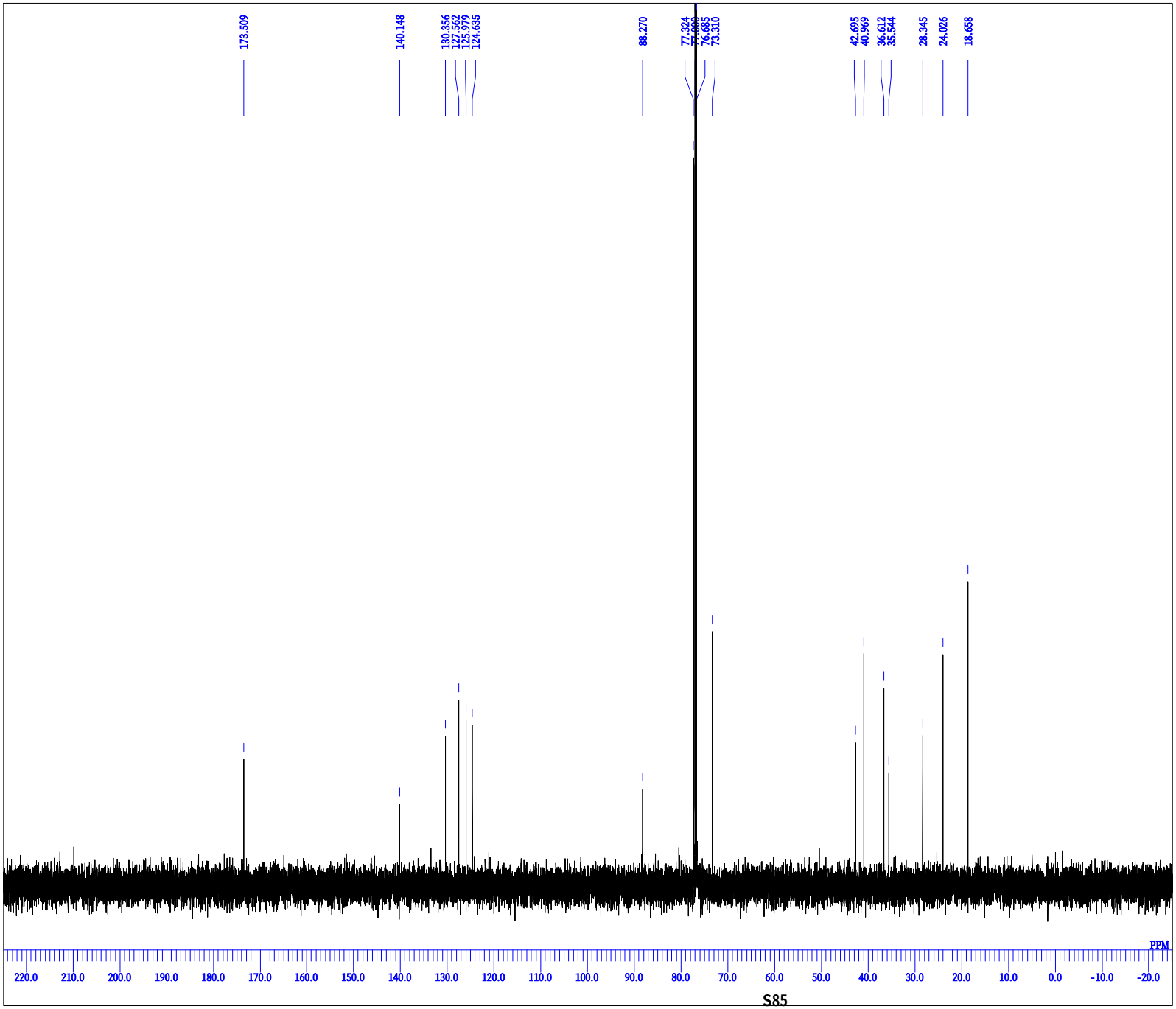
***syn*-4m**



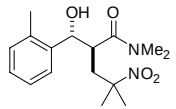
DFILE sm 1531 column 10-13-1.als
COMNT
DATIM 2020-09-24 17:28:55
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 54



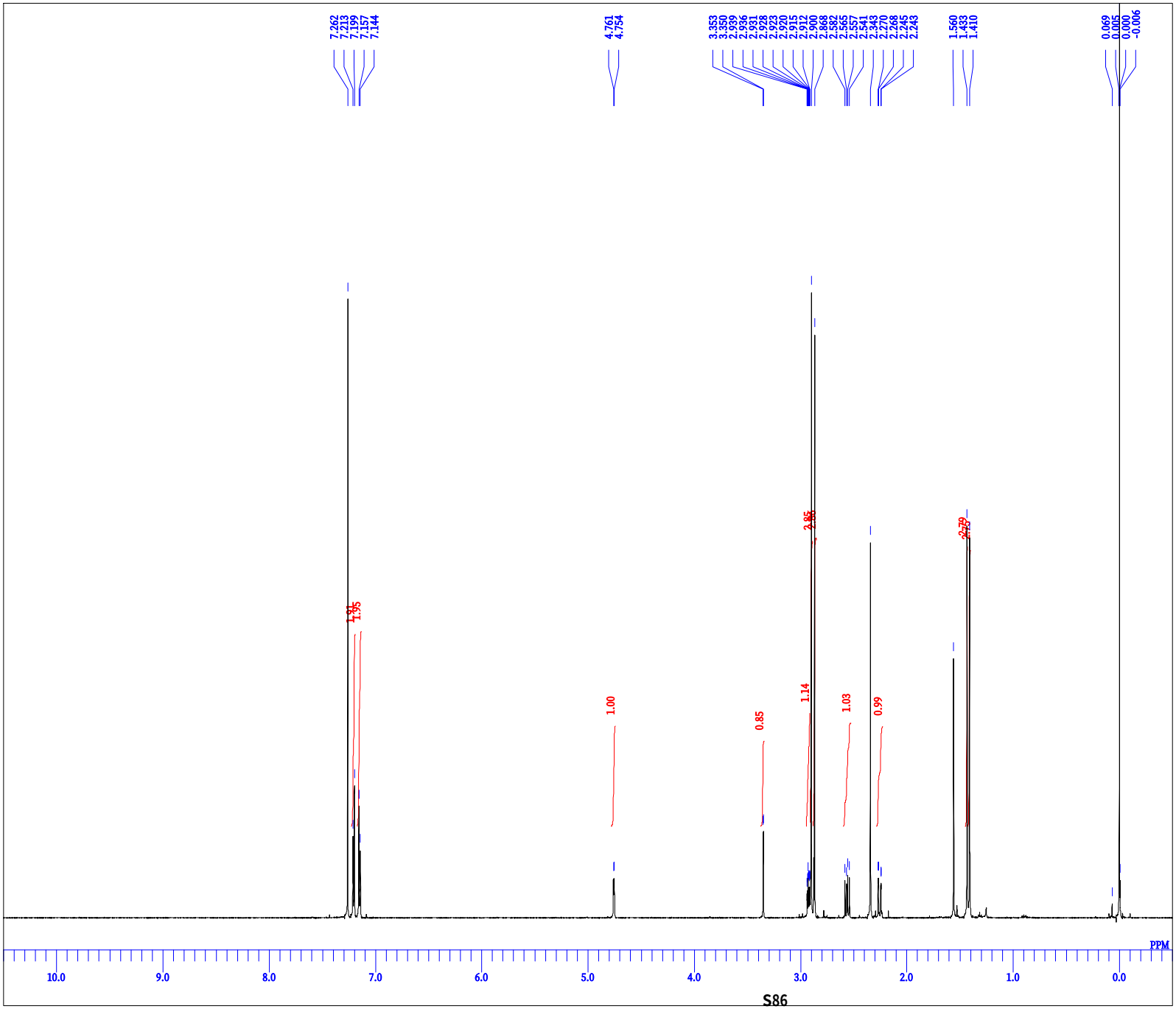
anti-4m



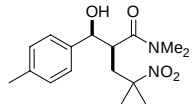
DFILE	2-Me sita 13C-1.als
COMNT	
DATIM	2020-11-24 22:25:14
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	103
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.0 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



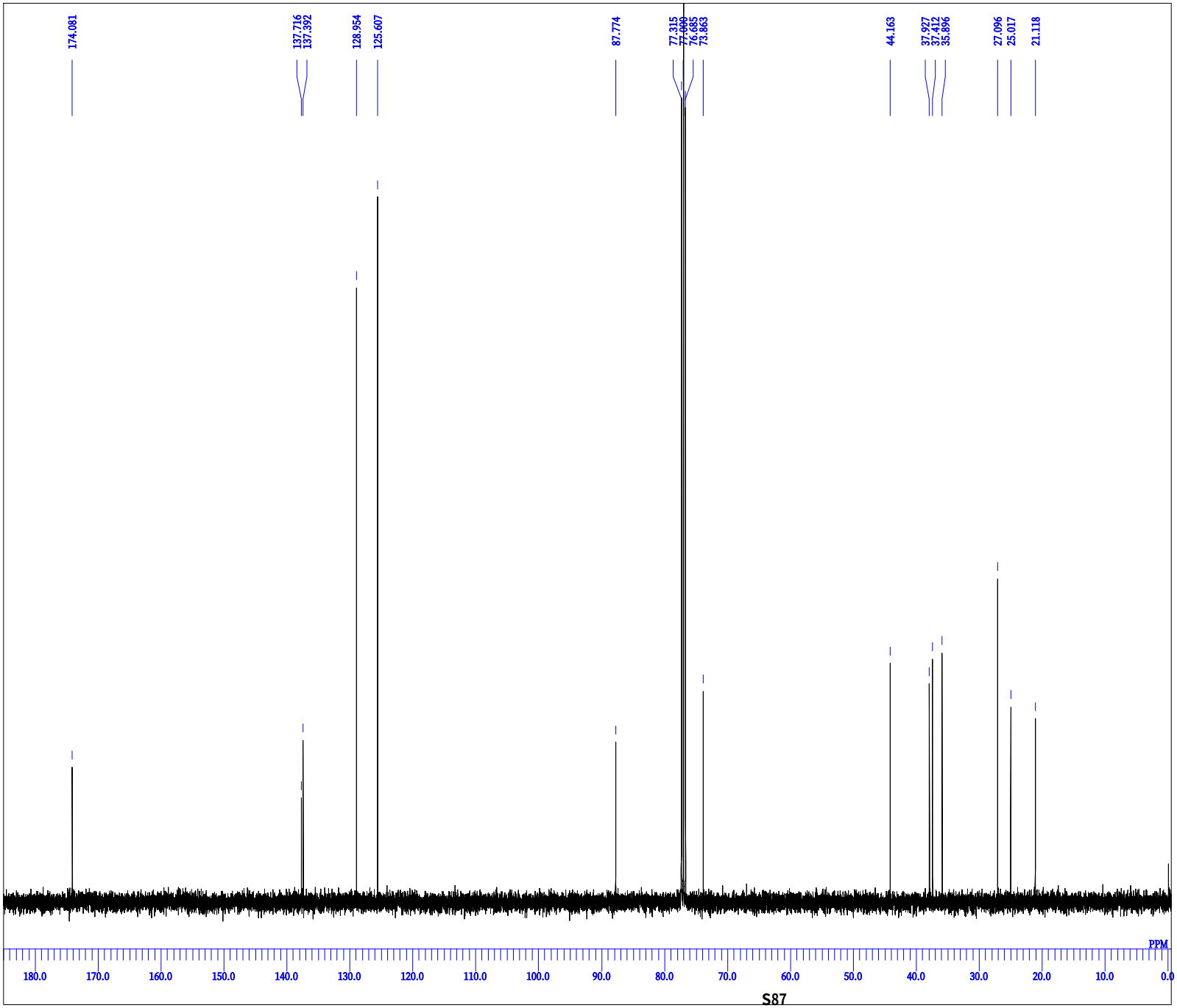
anti-4m



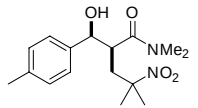
DFILE 4-Me ue 600MHz-1.als
COMNT
DATIM 2020-11-12 20:35:11
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 32768
FREQU 11261.26 Hz
SCANS 8
ACQTM 2.9098 sec
PD 2.0000 sec
PW1 6.90 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 54



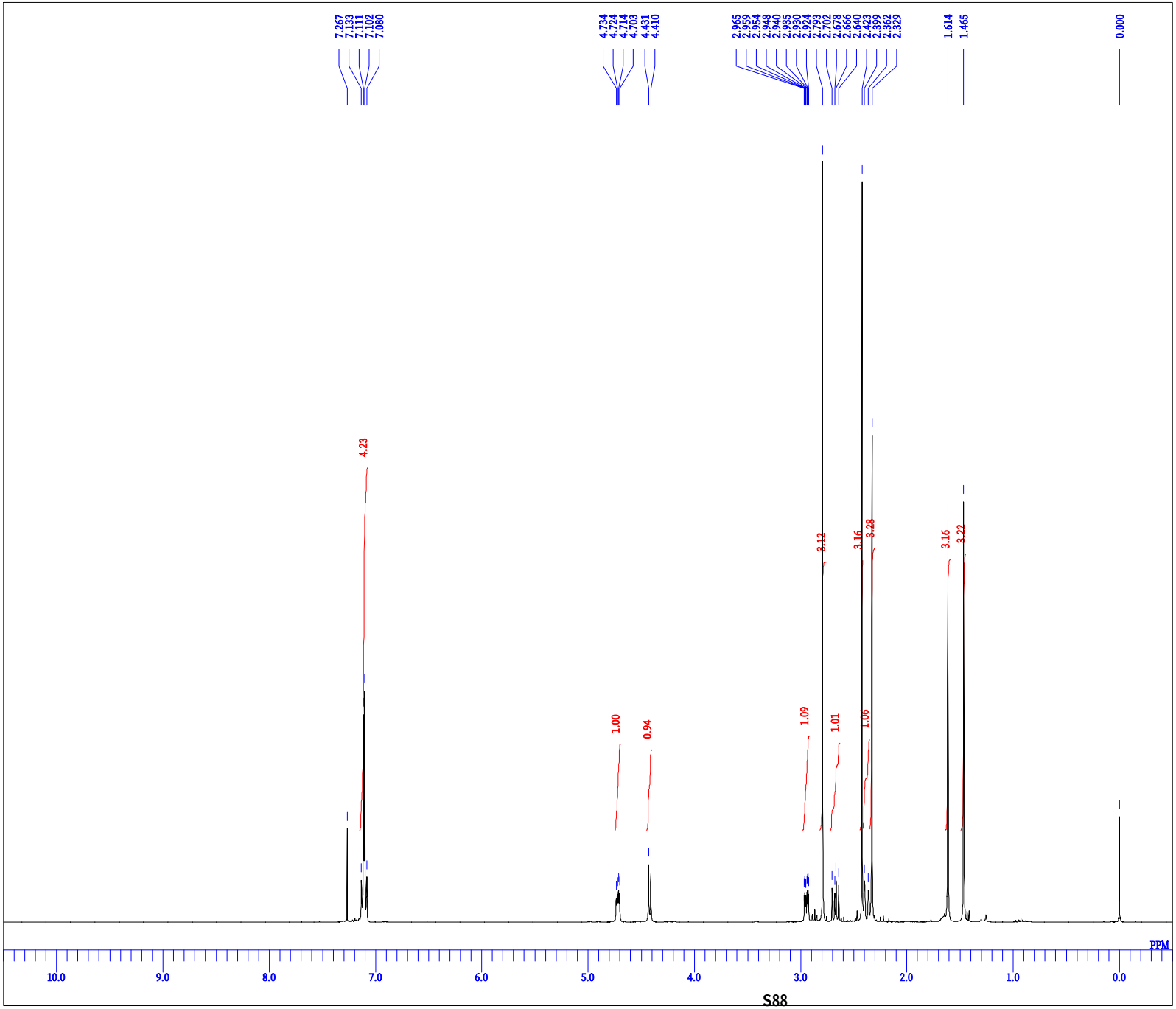
syn-4n



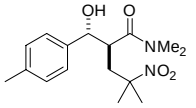
DFILE	p-Me 1 13C-1.als
COMNT	
DATIM	2020-10-18 14:12:07
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	390
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	22.3 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



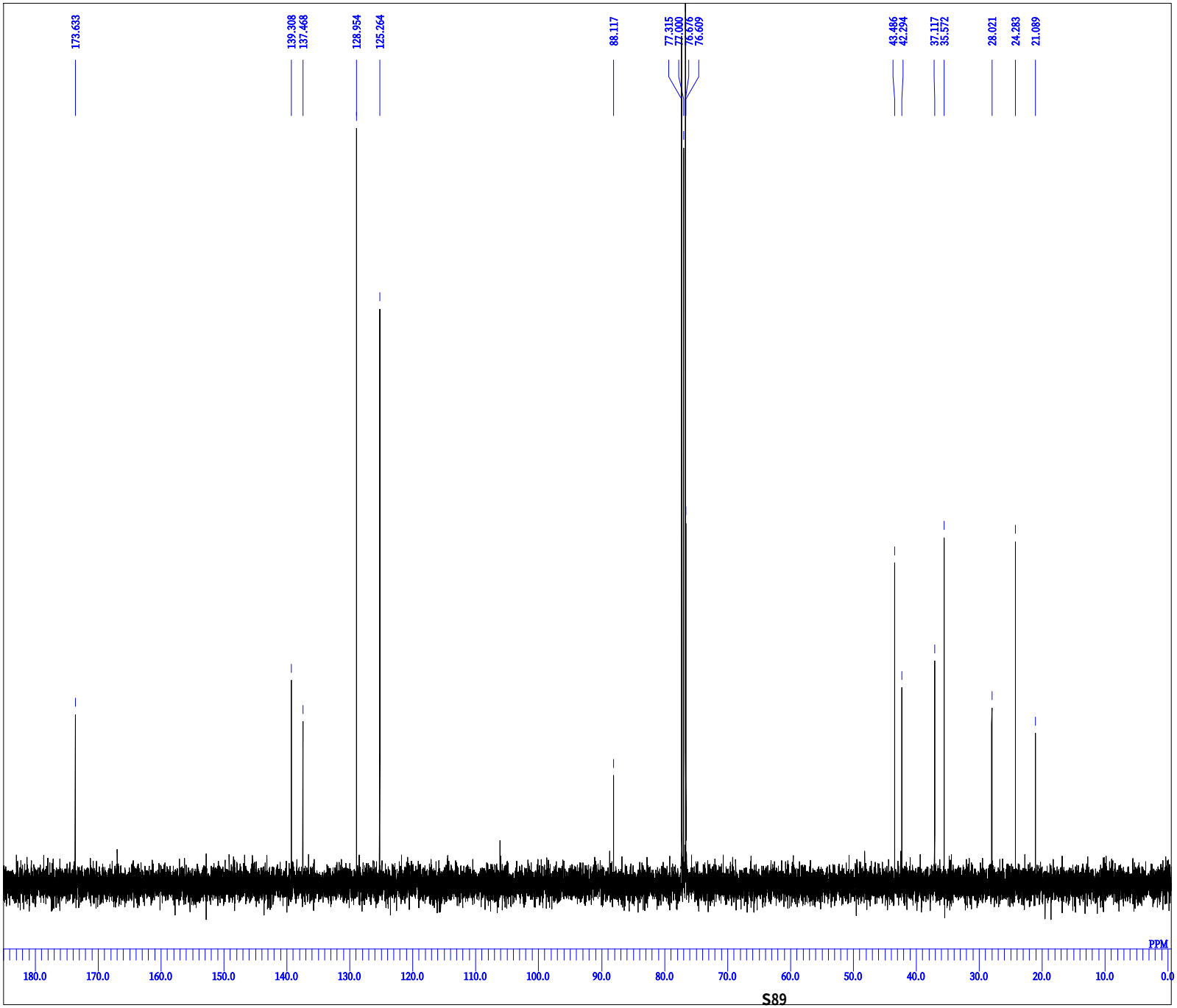
***syn*-4n**



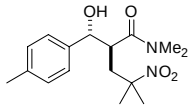
DFILE	4-Me sita-1.als
COMNT	
DATIM	2020-10-28 02:12:30
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	0.20 Hz
RGAIN	36



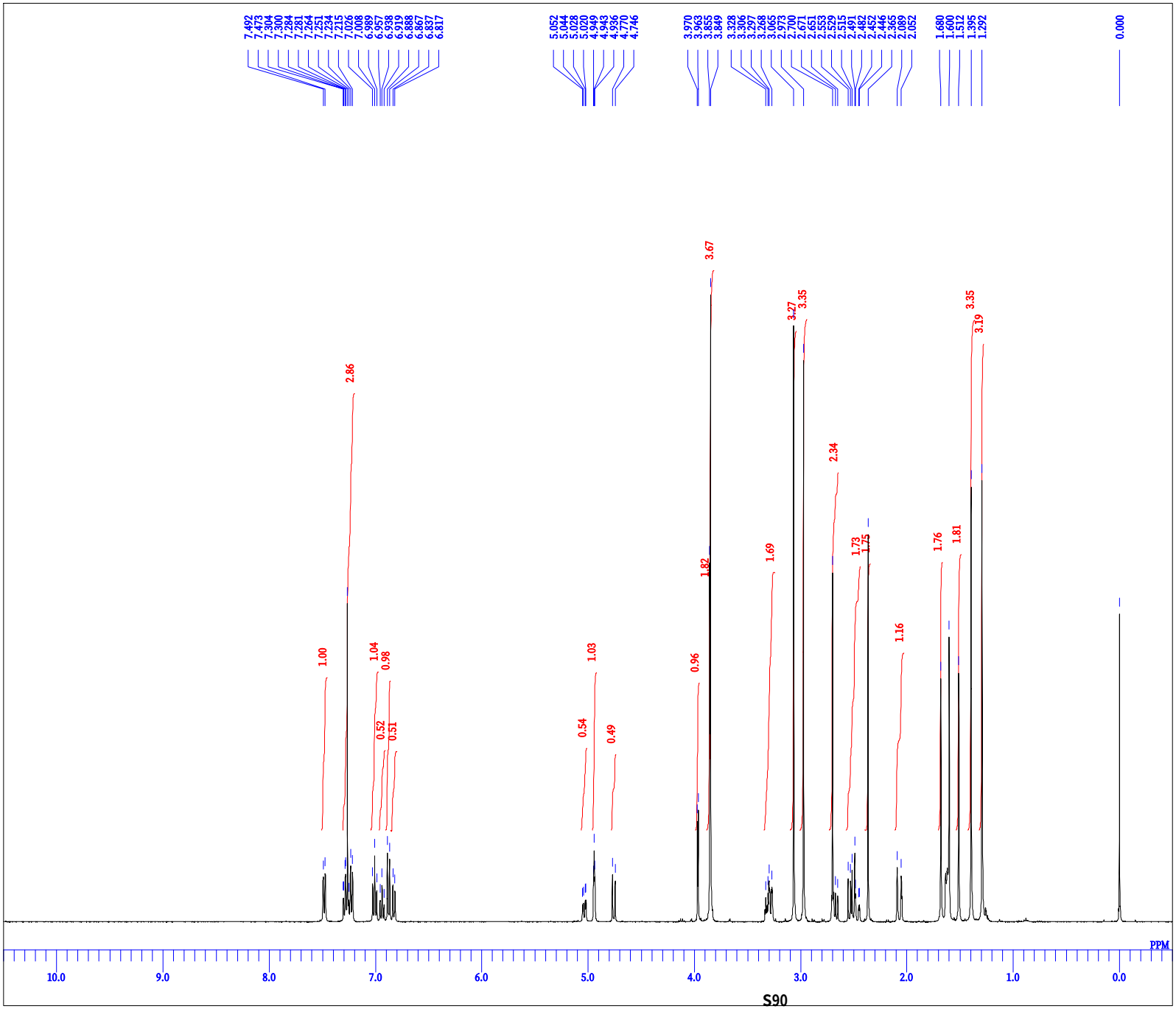
anti-4n



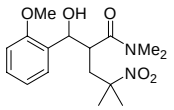
DFILE	4-Me sita 13C-1.als
COMNT	
DATIM	2020-10-28 02:16:56
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	103
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



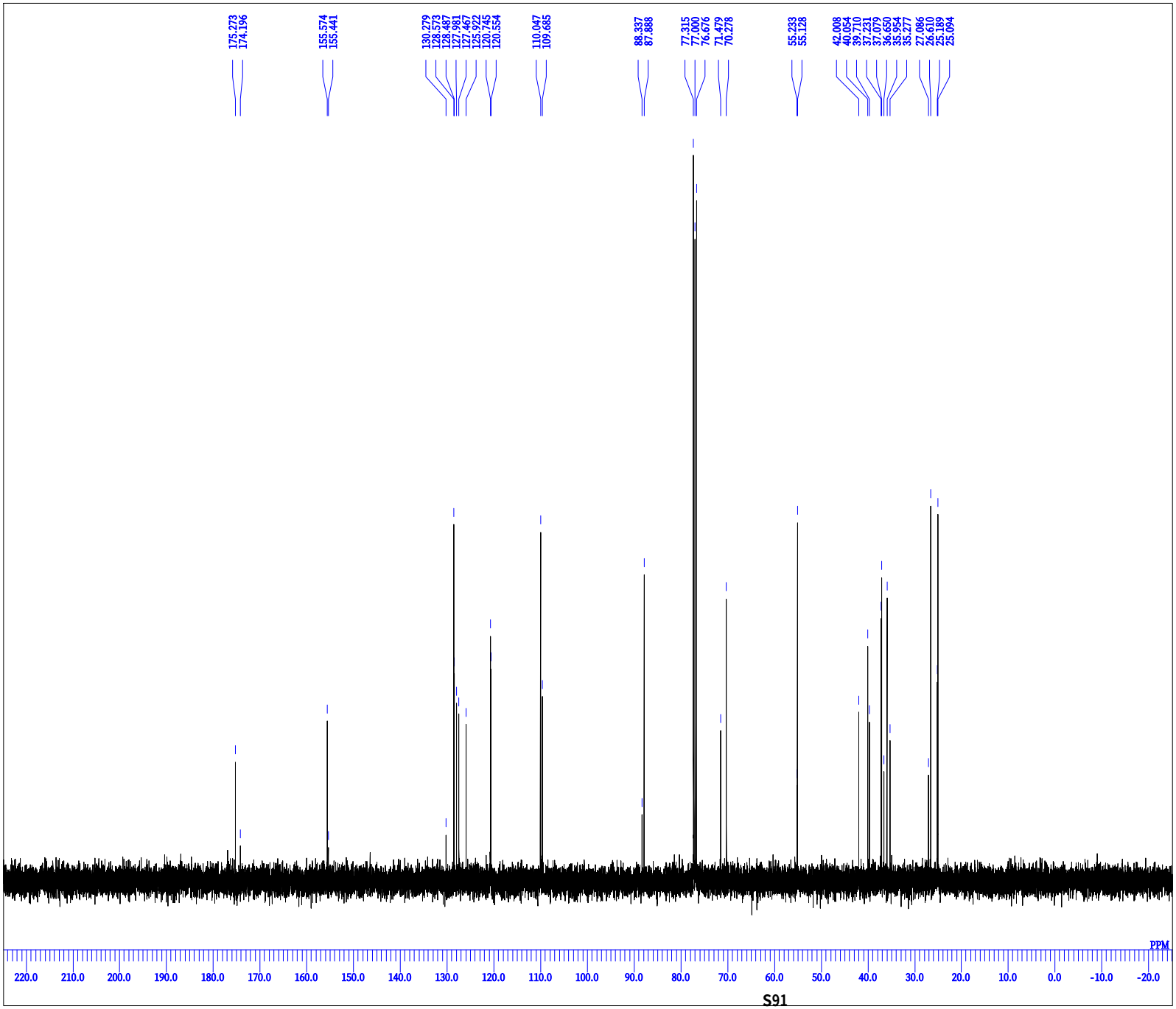
anti-4n



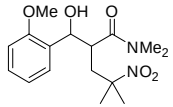
DFILE sm 1521 column 2-1.als
COMNT
DATIM 2020-09-18 19:15:02
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 22.0 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 44



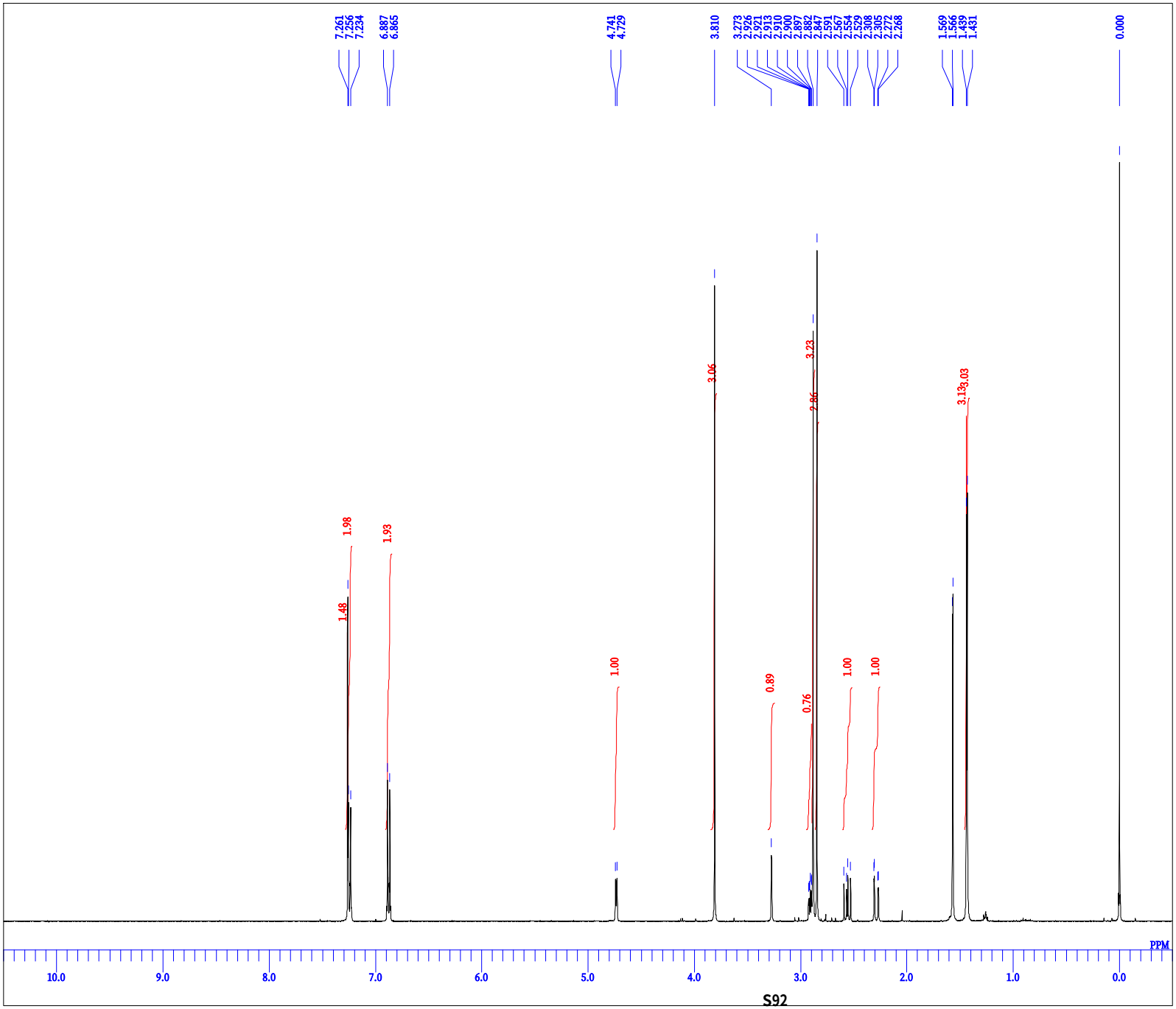
4o



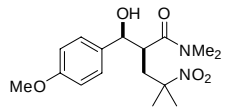
DFILE	2-OMe 13C-1.als
COMNT	
DATIM	2020-11-24 22:34:45
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	103
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.0 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



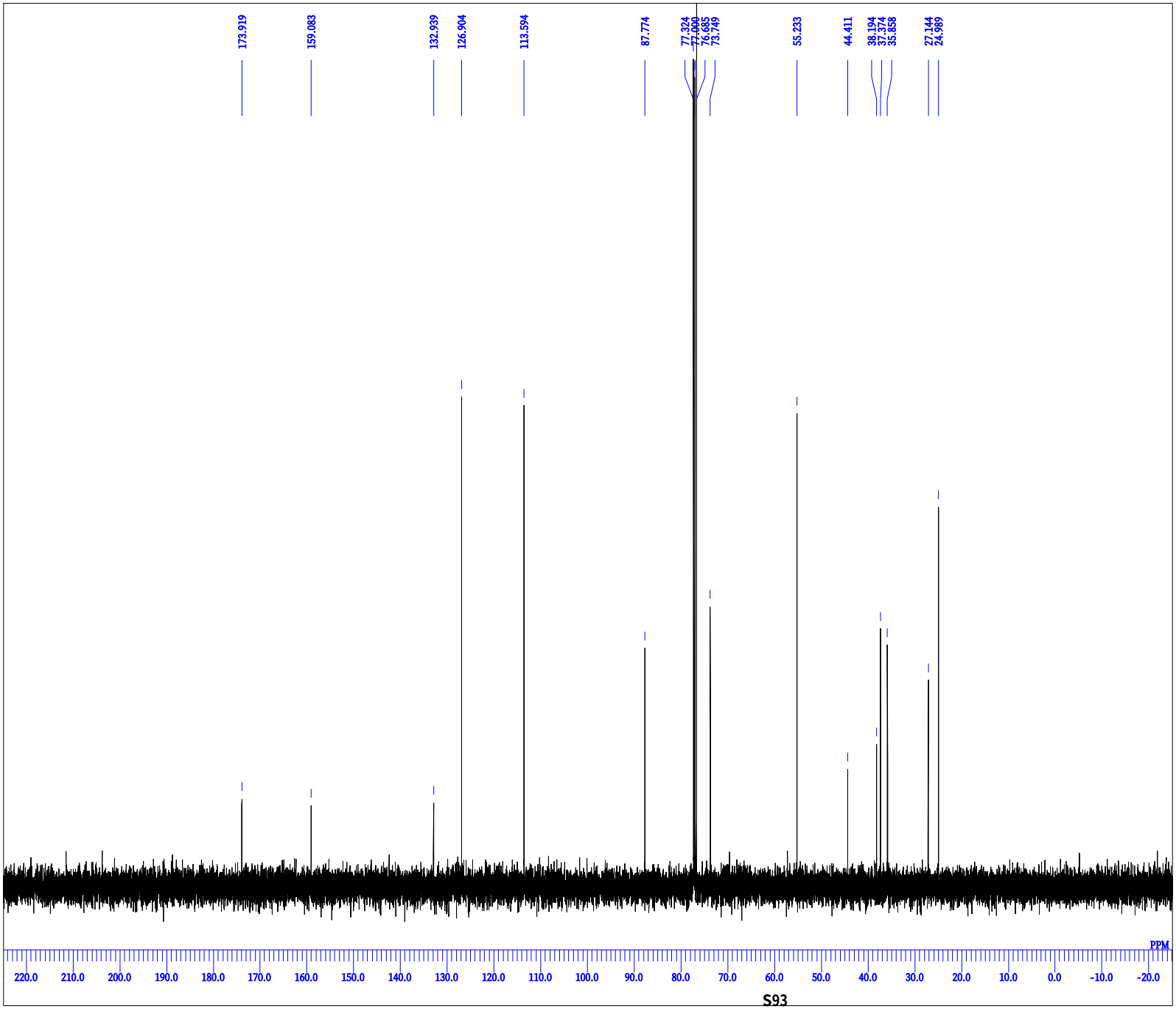
4o



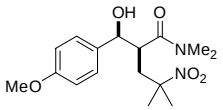
DFILE sm 1469 column 14-19-1 ue.als
COMNT
DATIM 2020-08-11 21:58:53
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 50



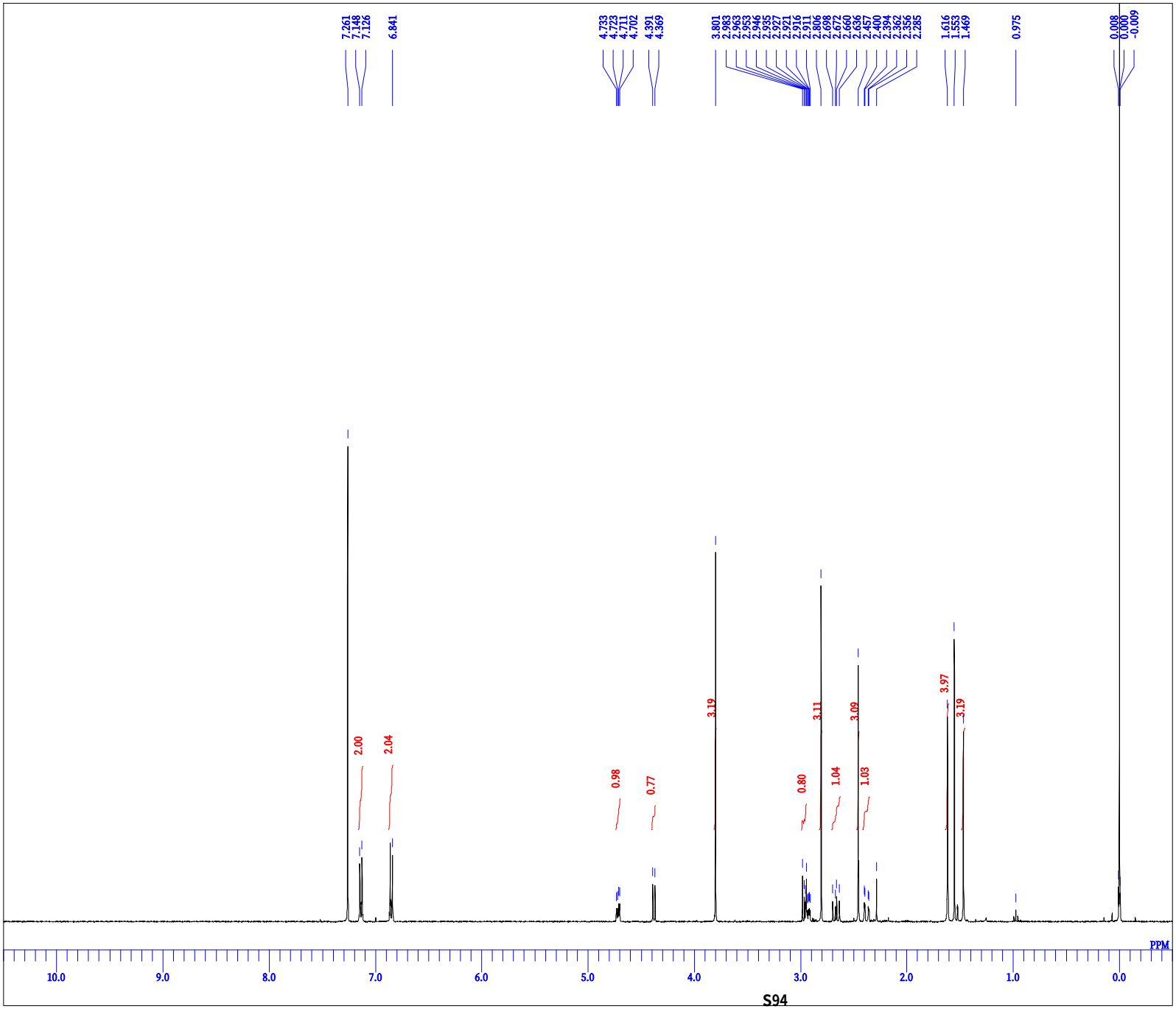
***syn*-4p**



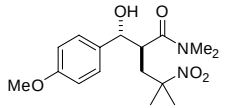
DFILE	amide 4-OMe ue 13C-1.jdf
COMNT	
DATIM	2020-11-16 21:15:29
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	105
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



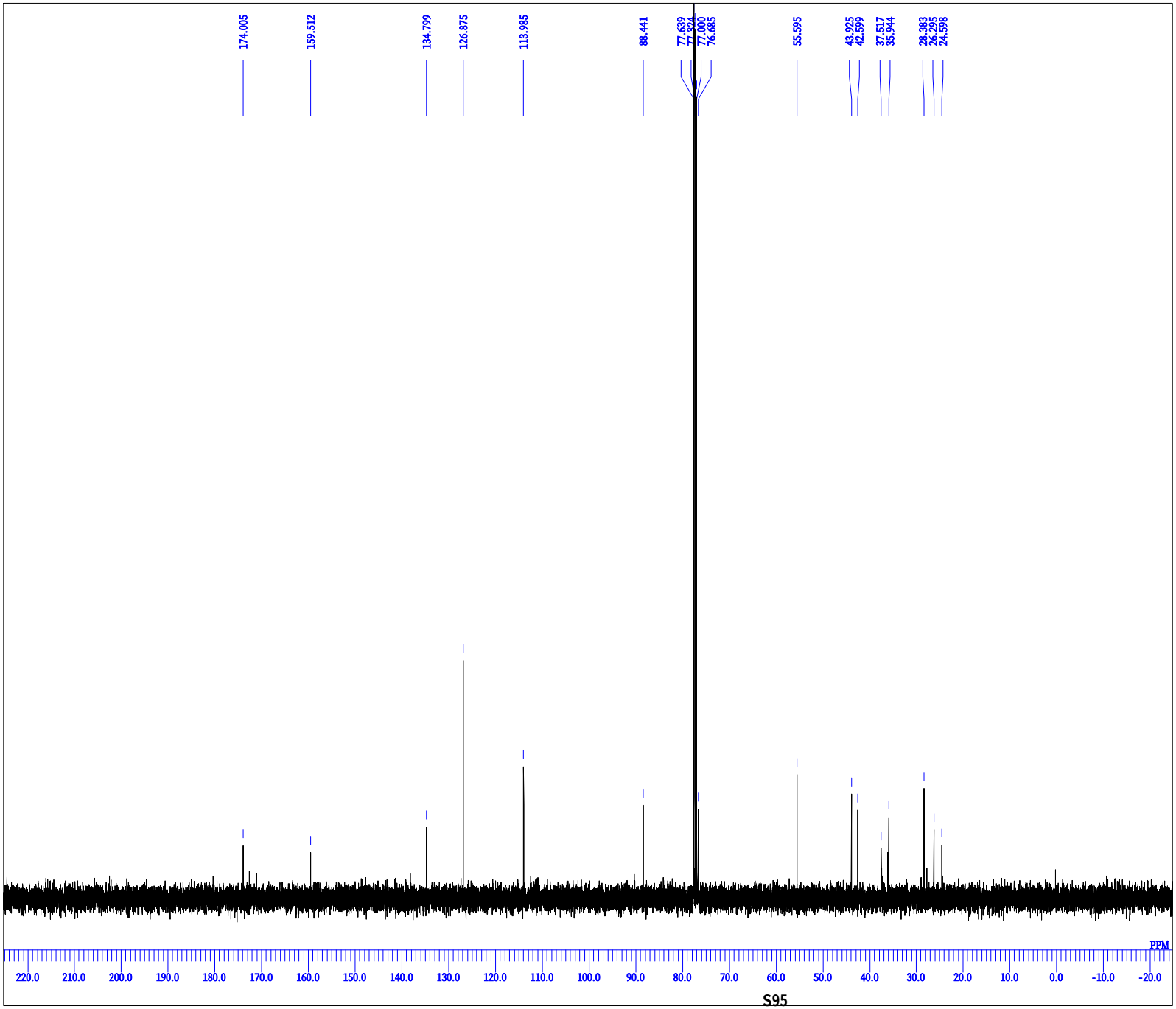
***syn*-4p**



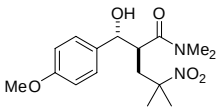
DFILE 4-OMe sita n-1.als
COMNT
DATIM 2020-11-19 16:33:54
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 21.3 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 52



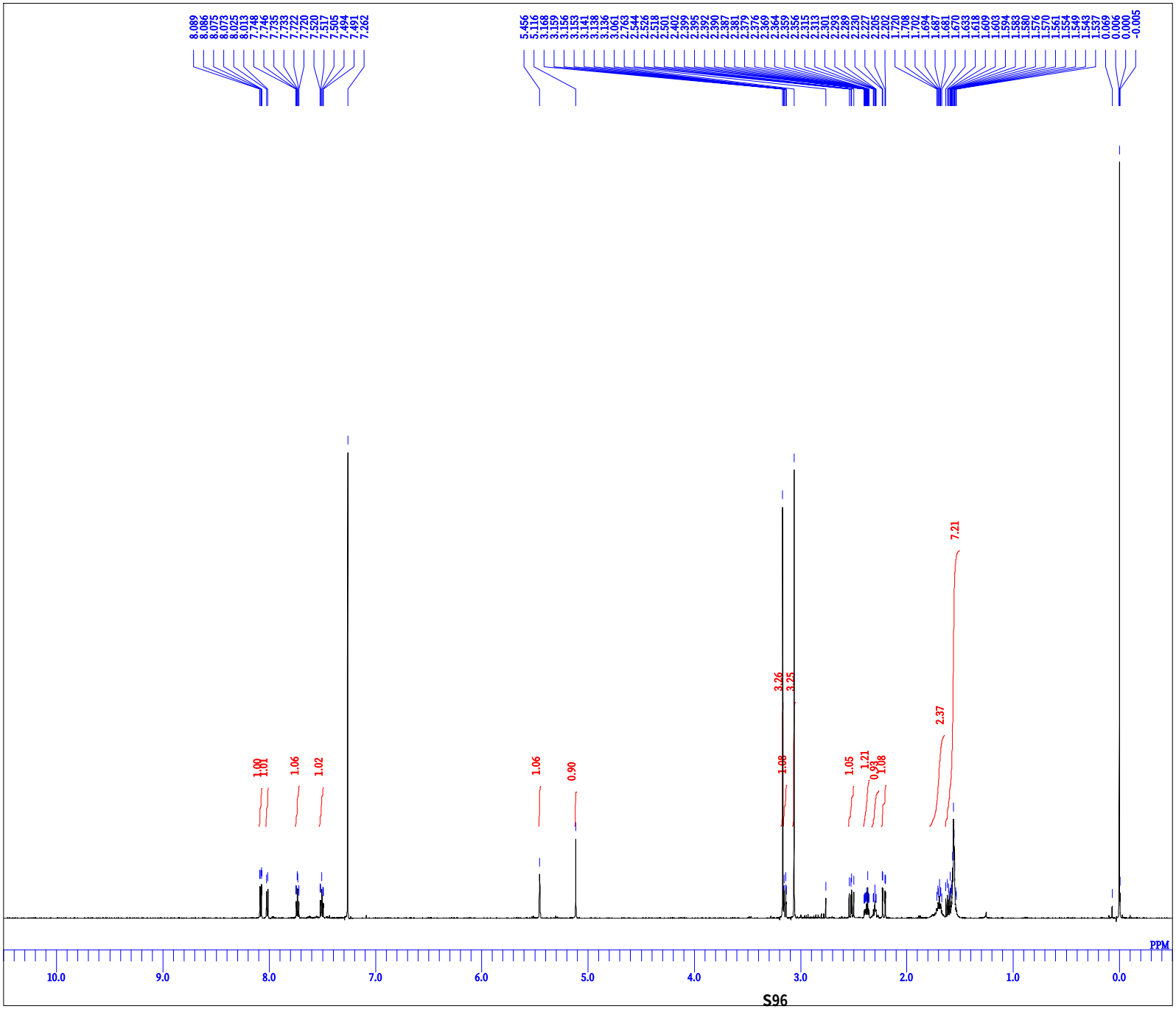
anti-4p



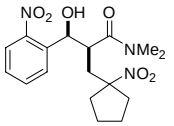
DFILE	amide 4-OMe sita 13C-1.jdf
COMNT	
DATIM	2020-11-16 21:28:34
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	204
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.6 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



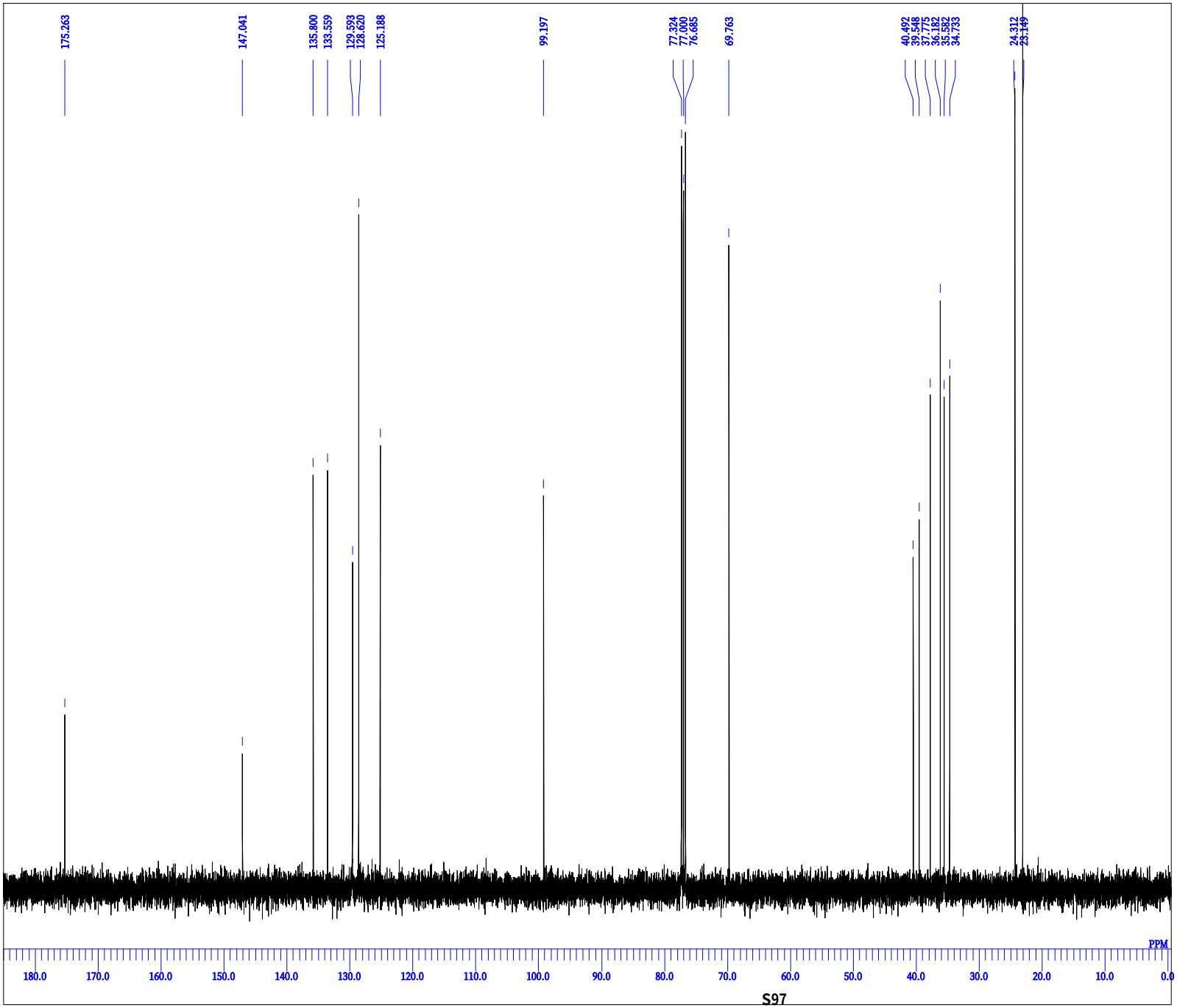
***anti*-4p**



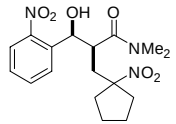
DFILE 5-Cy ue 600MHz-1.als
COMNT
DATIM 2020-11-12 21:04:26
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 26214
FREQU 9008.87 Hz
SCANS 8
ACQTM 2.9098 sec
PD 2.0000 sec
PW1 6.90 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 54



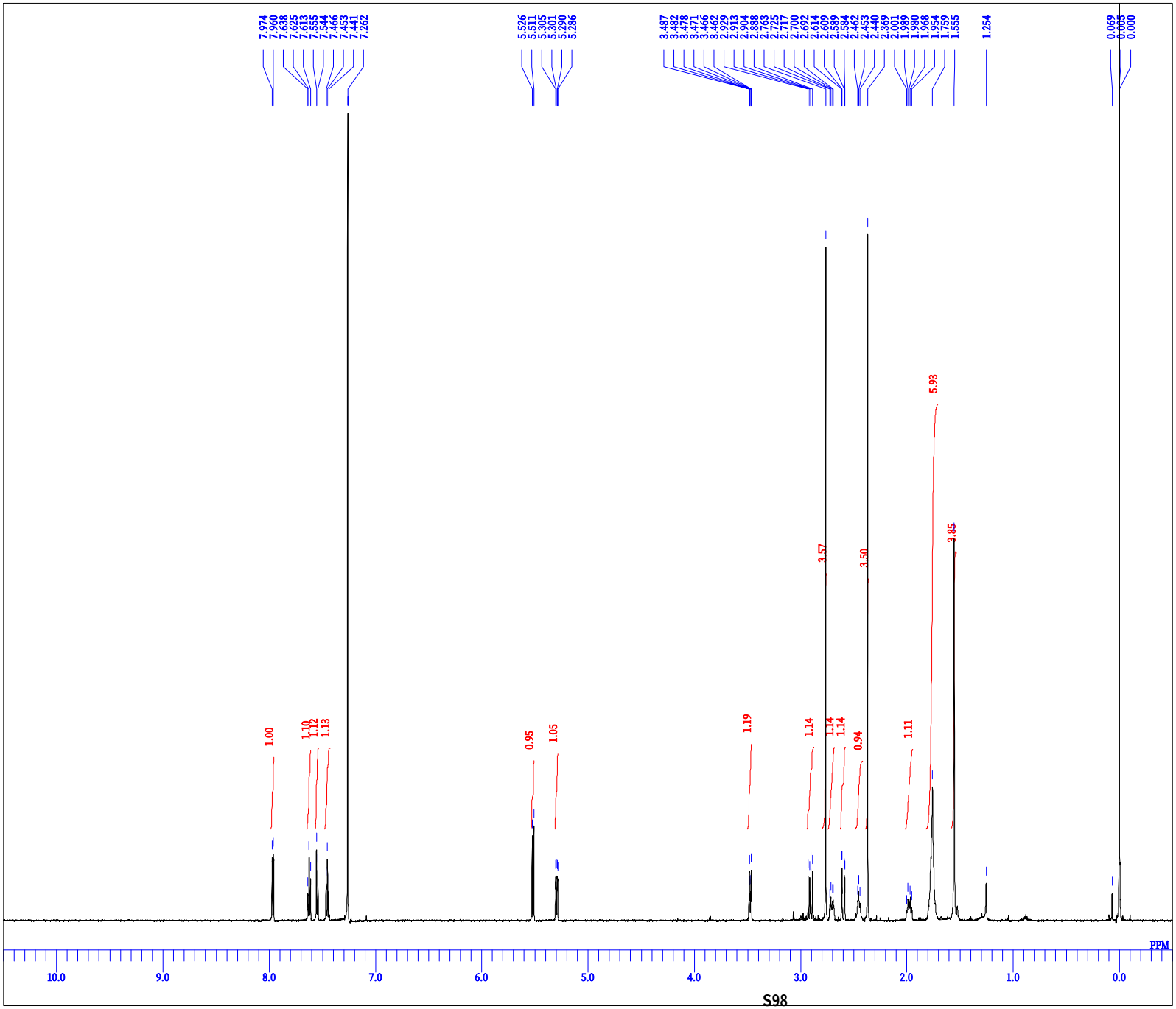
syn-4q



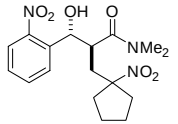
DFILE	5-cy ue 13C-1.als
COMNT	
DATIM	2020-10-27 21:48:11
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	101
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



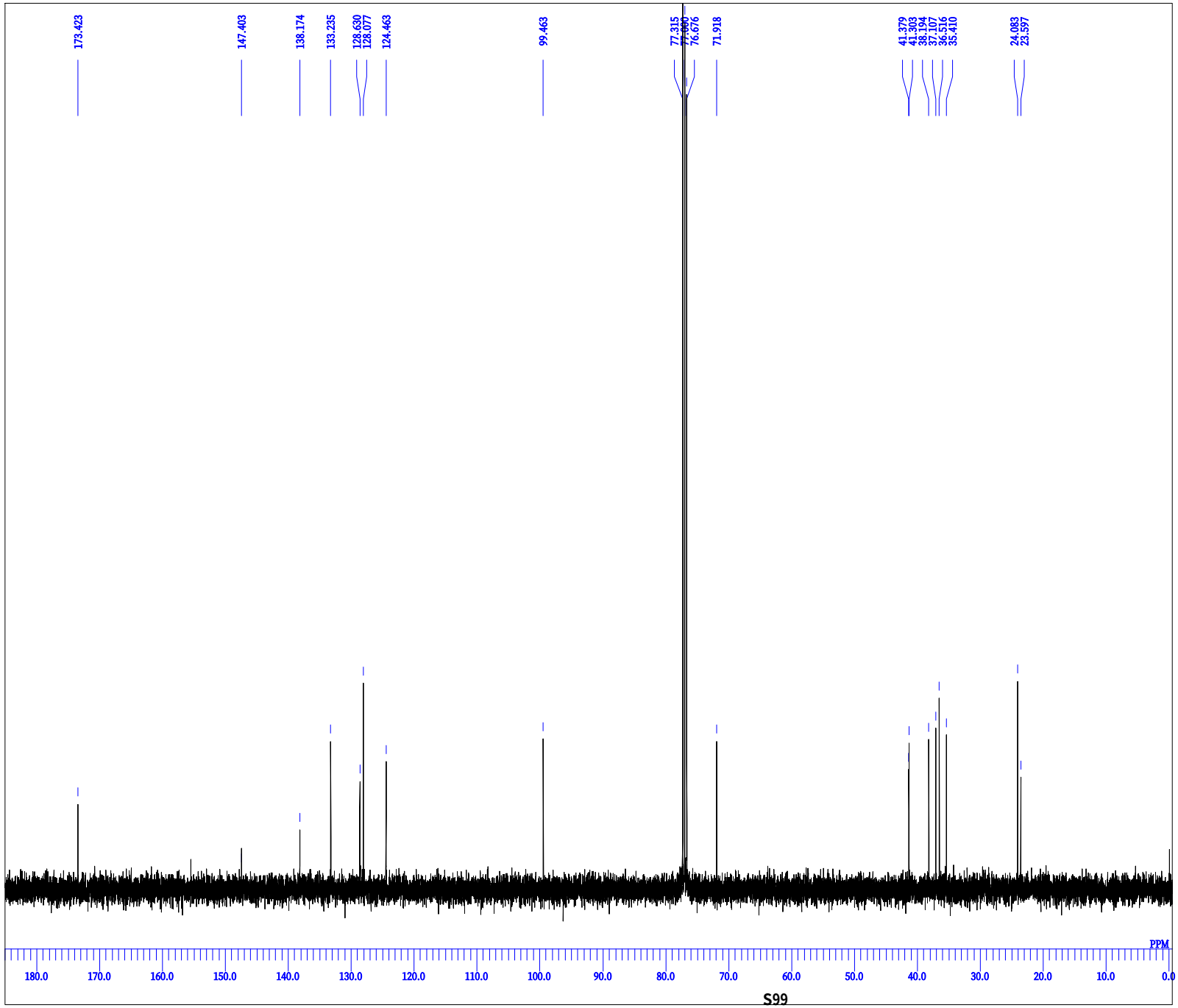
syn-4q



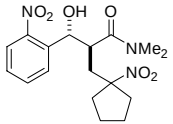
DFILE 5-Cy sita 1H 600MHz-1.als
COMNT
DATIM 2020-11-02 19:43:50
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 26214
FREQU 9008.87 Hz
SCANS 8
ACQTM 2.9098 sec
PD 2.0000 sec
PW1 6.90 usec
IRNUC 1H
CTEMP 20.6 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 54



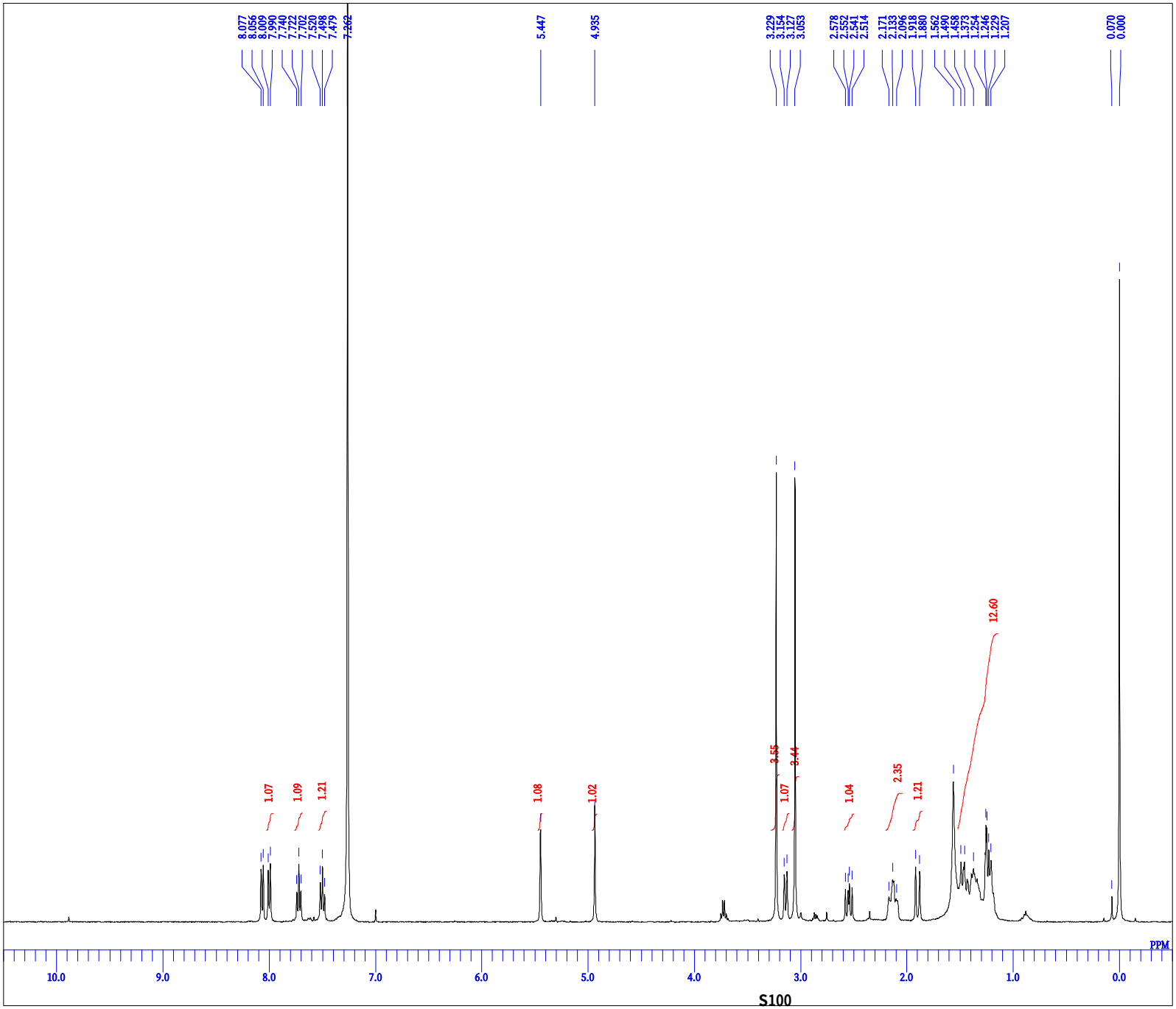
anti-4q



DFILE	5-cy sita 13C-1.als
COMNT	
DATIM	2020-10-27 22:02:02
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	206
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60

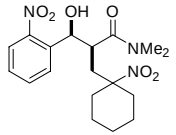


anti-4q

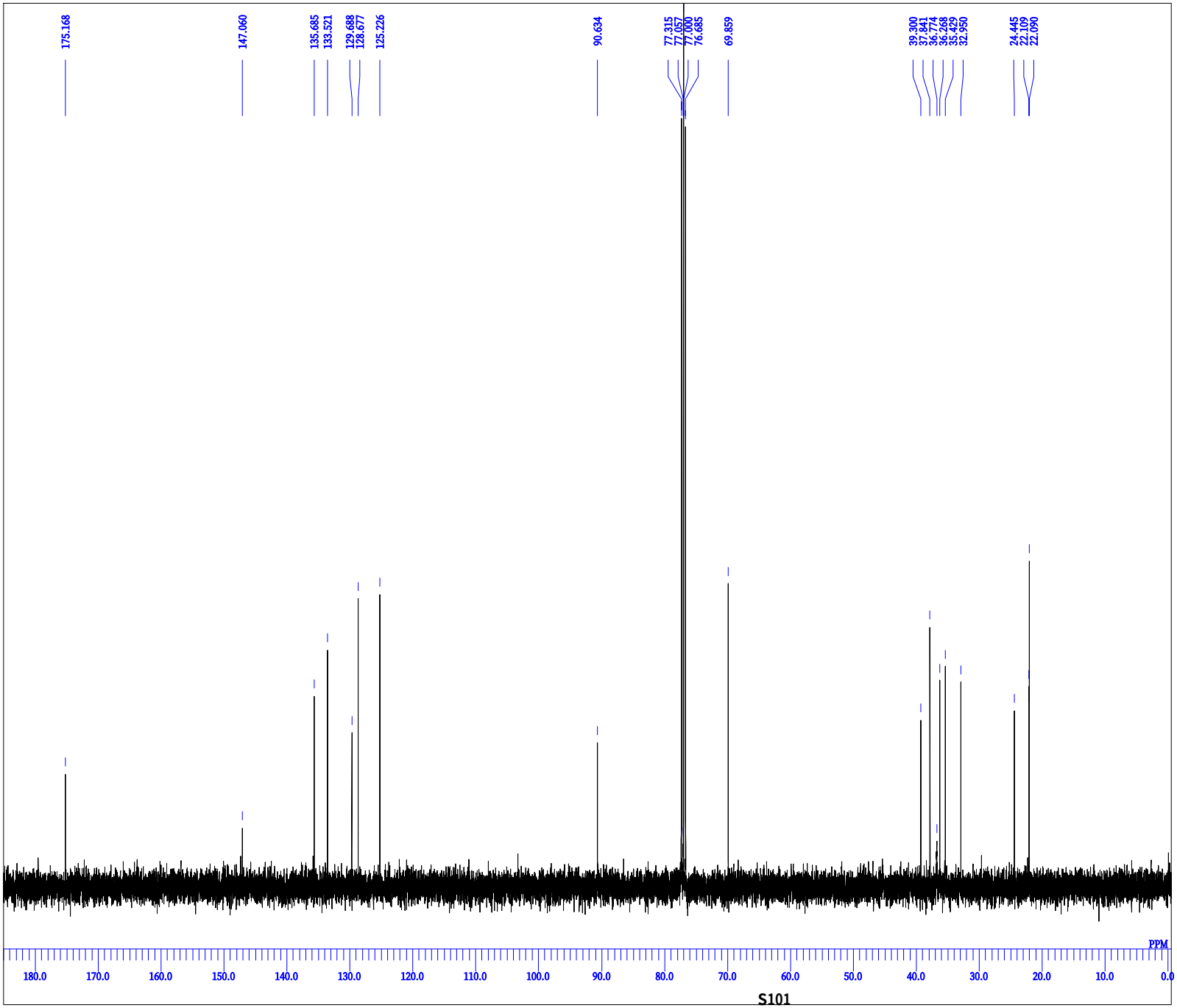


S100

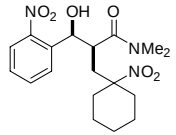
DFILE	6-cy ue nn-1.als
COMNT	
DATIM	2020-11-27 19:33:44
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	21.0 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	1.40 Hz
RGAIN	48



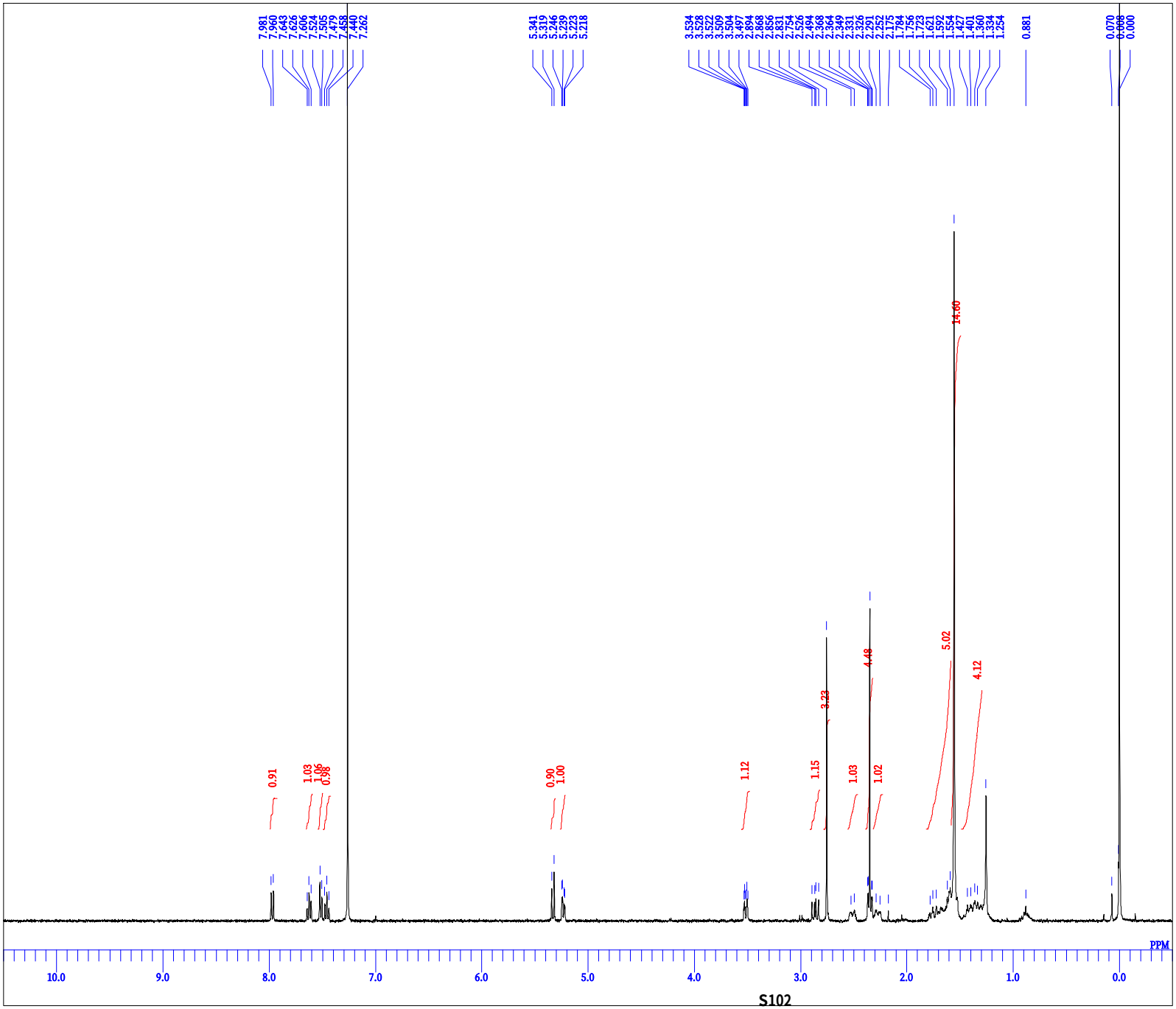
syn-4r



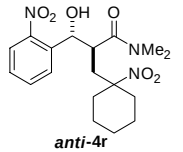
DFILE	6-cy ue 13C-1.als
COMNT	
DATIM	2020-10-27 23:23:59
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	102
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.6 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



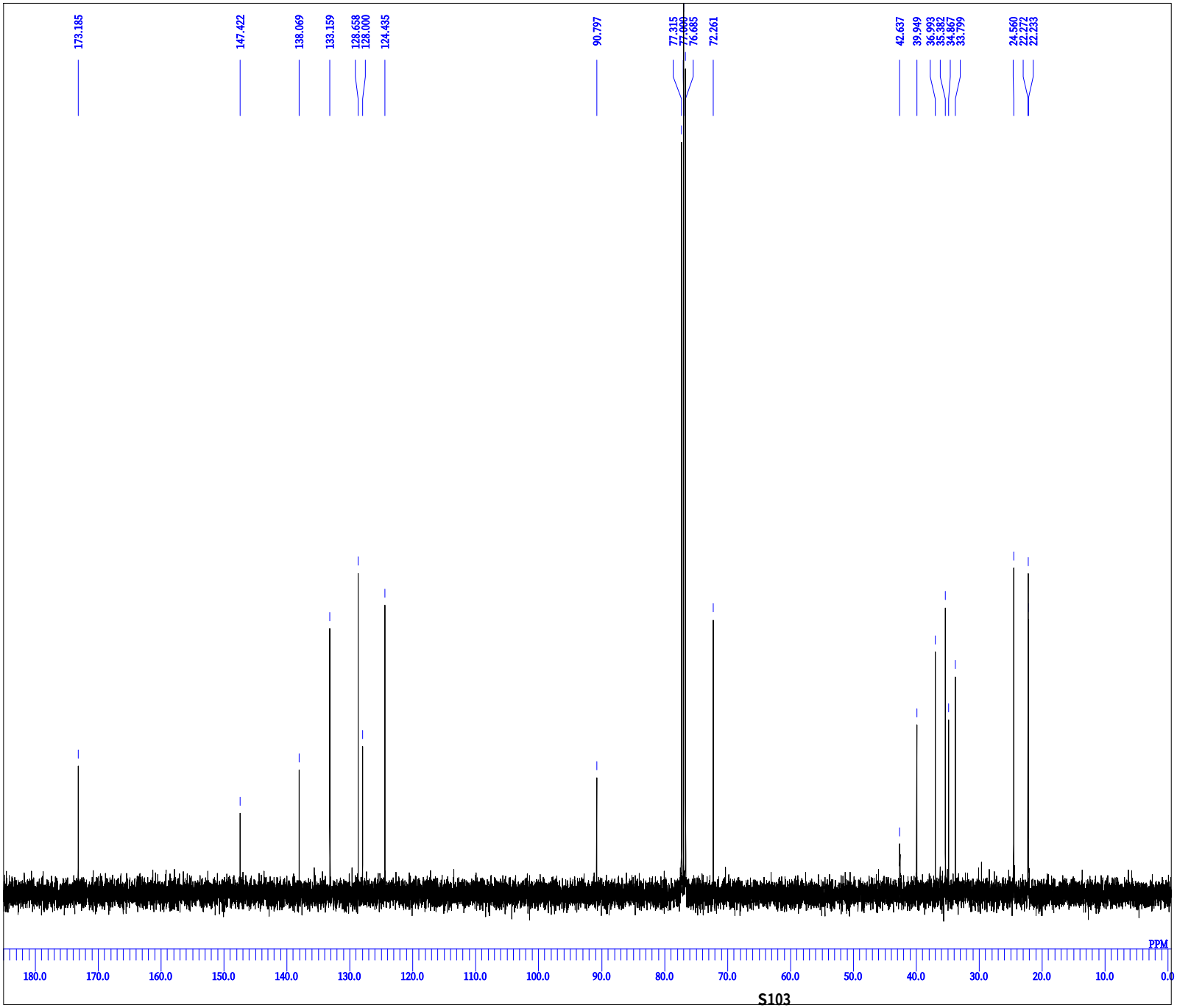
syn-4r



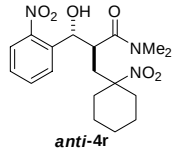
DFILE 6-Cy sita nn2-1.als
COMNT
DATIM 2020-11-29 15:25:53
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 52



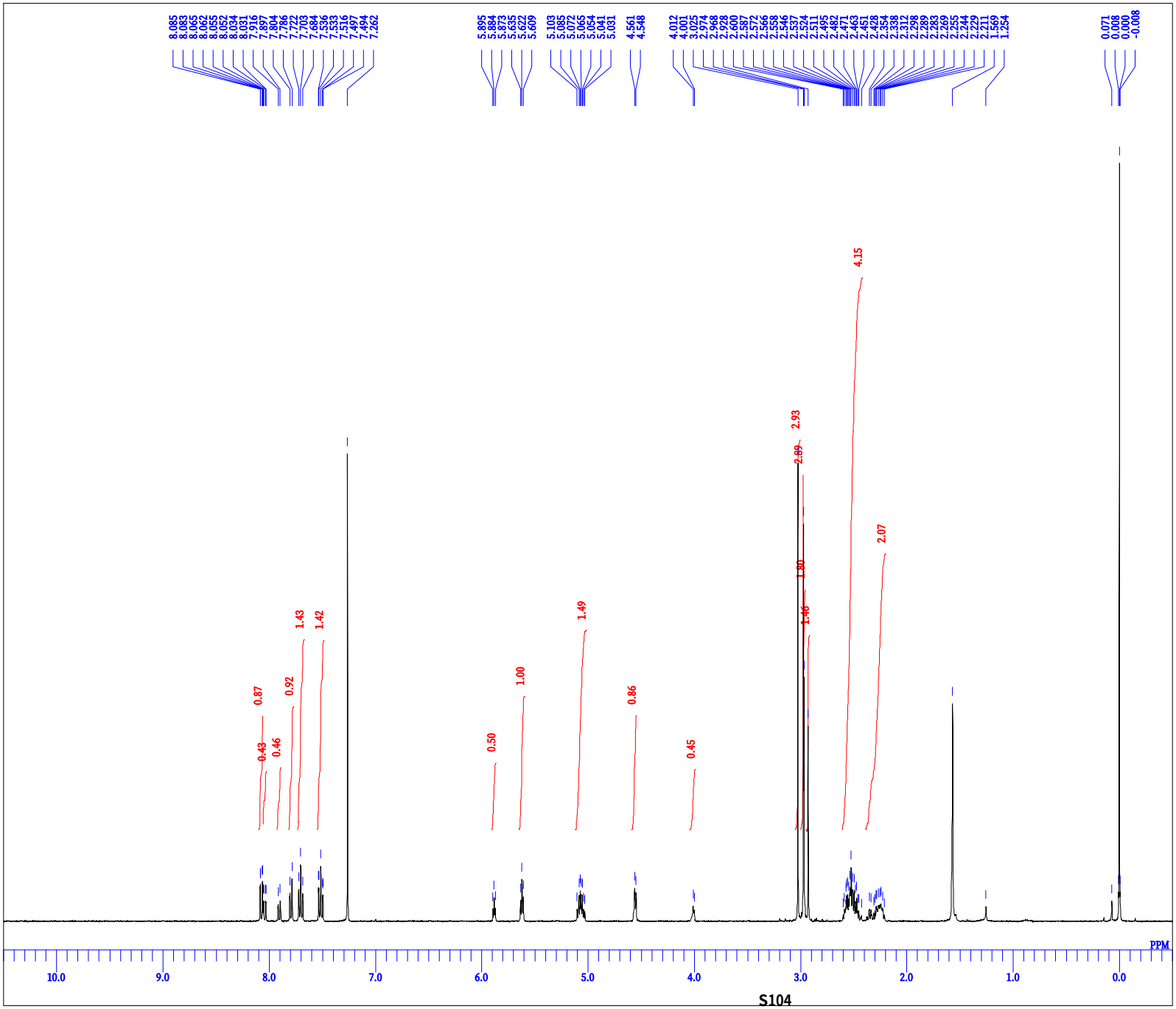
anti-4r



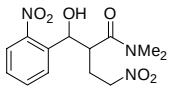
DFILE 6-cy sita 13C-1.als
COMNT
DATIM 2020-10-27 23:34:19
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 108
ACQTM 1.0433 sec
PD 1.2000 sec
PW1 2.98 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.20 Hz
RGAIN 60



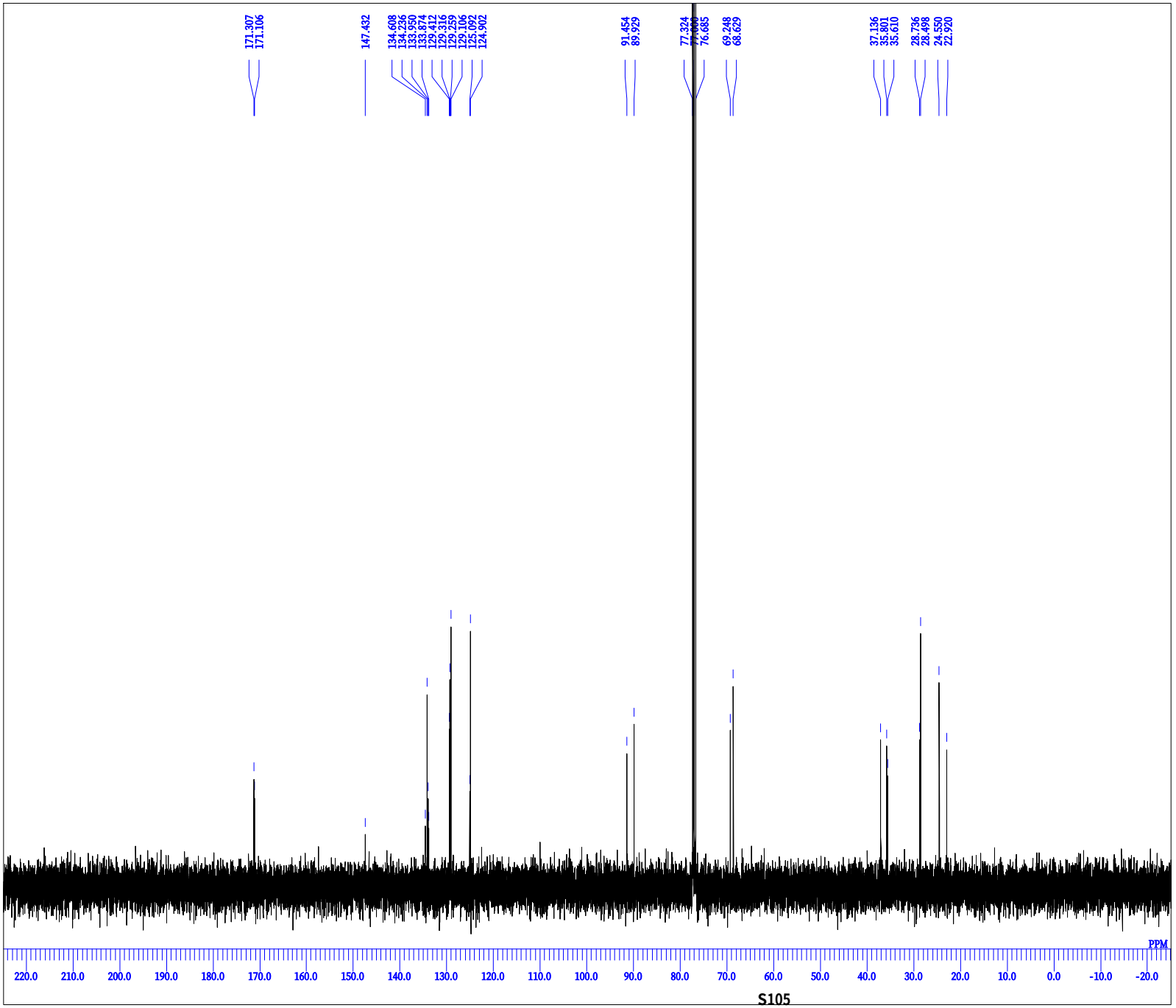
anti-4r



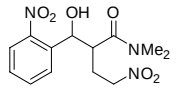
DFILE	an-59-column-1-2.als
COMNT	
DATIM	2020-11-04 14:09:06
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	0.20 Hz
RGAIN	50



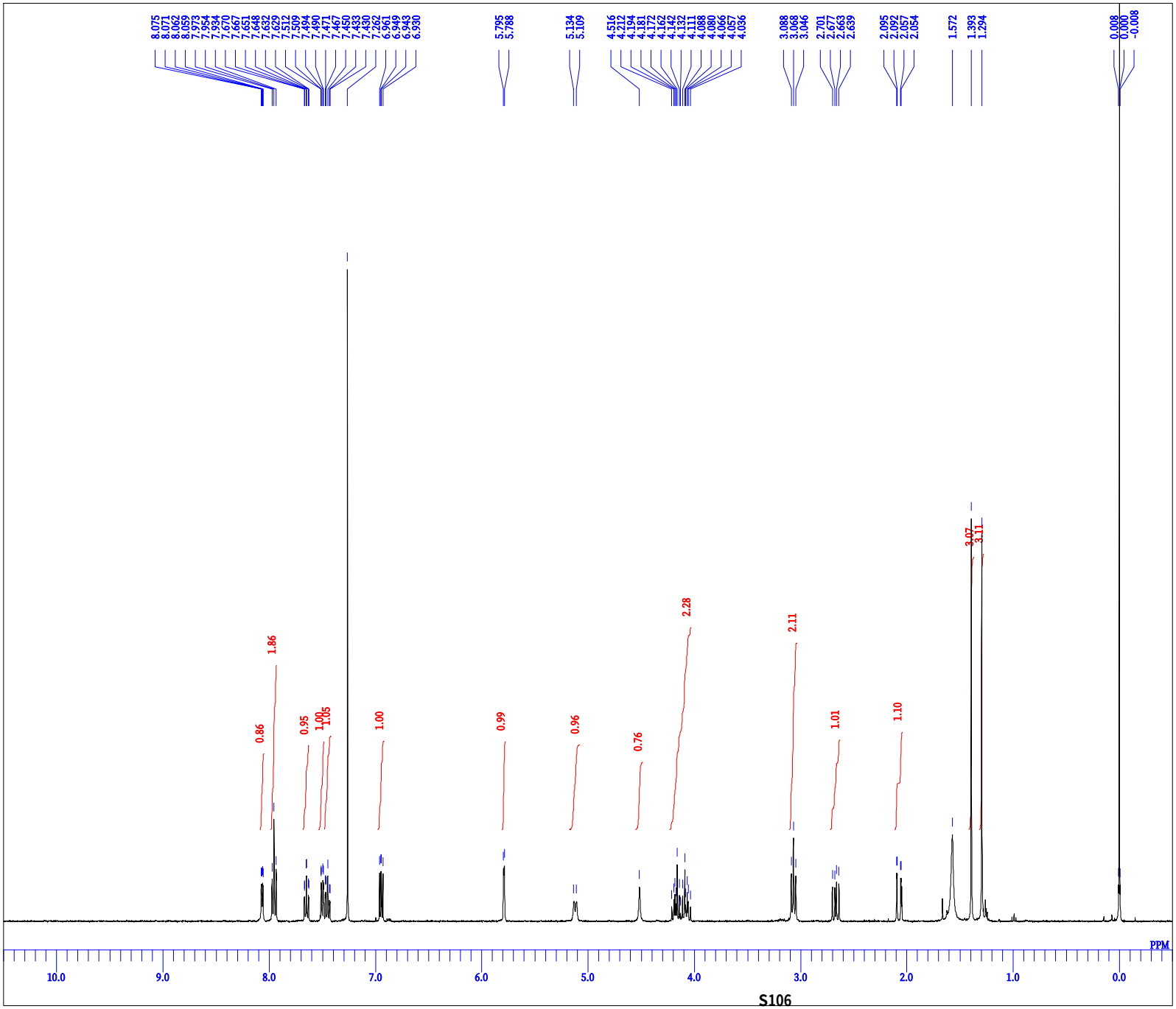
4s



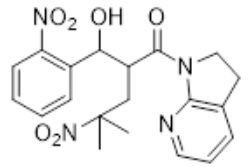
DFILE	MeNO2 13C-1.als
COMNT	
DATIM	2020-11-23 19:51:04
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	154
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



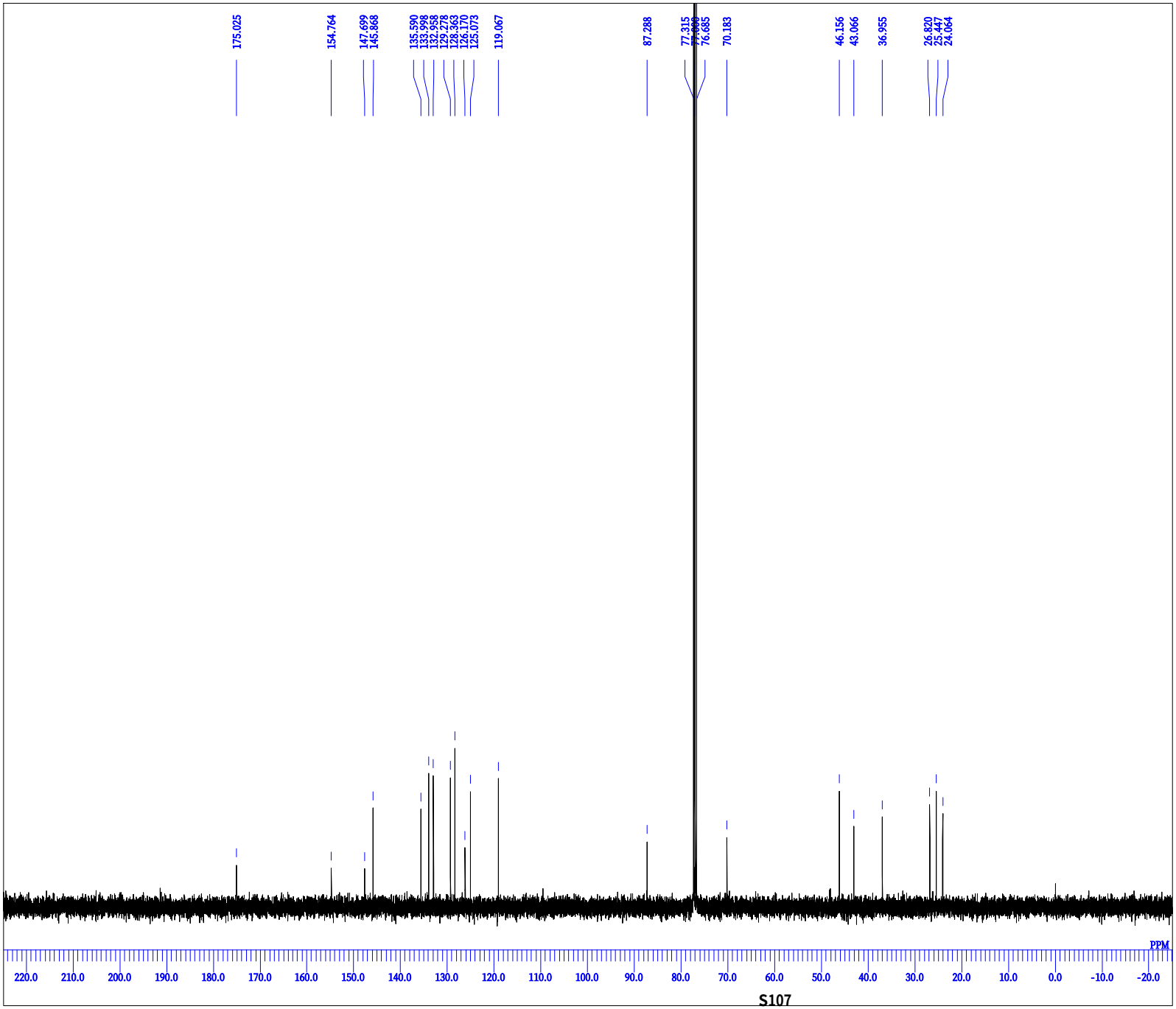
4s



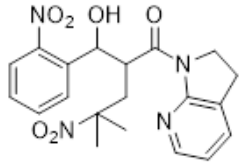
DFILE	azaindo ue-1.als
COMNT	
DATIM	2020-11-16 13:57:13
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	21.4 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	0.20 Hz
RGAIN	50



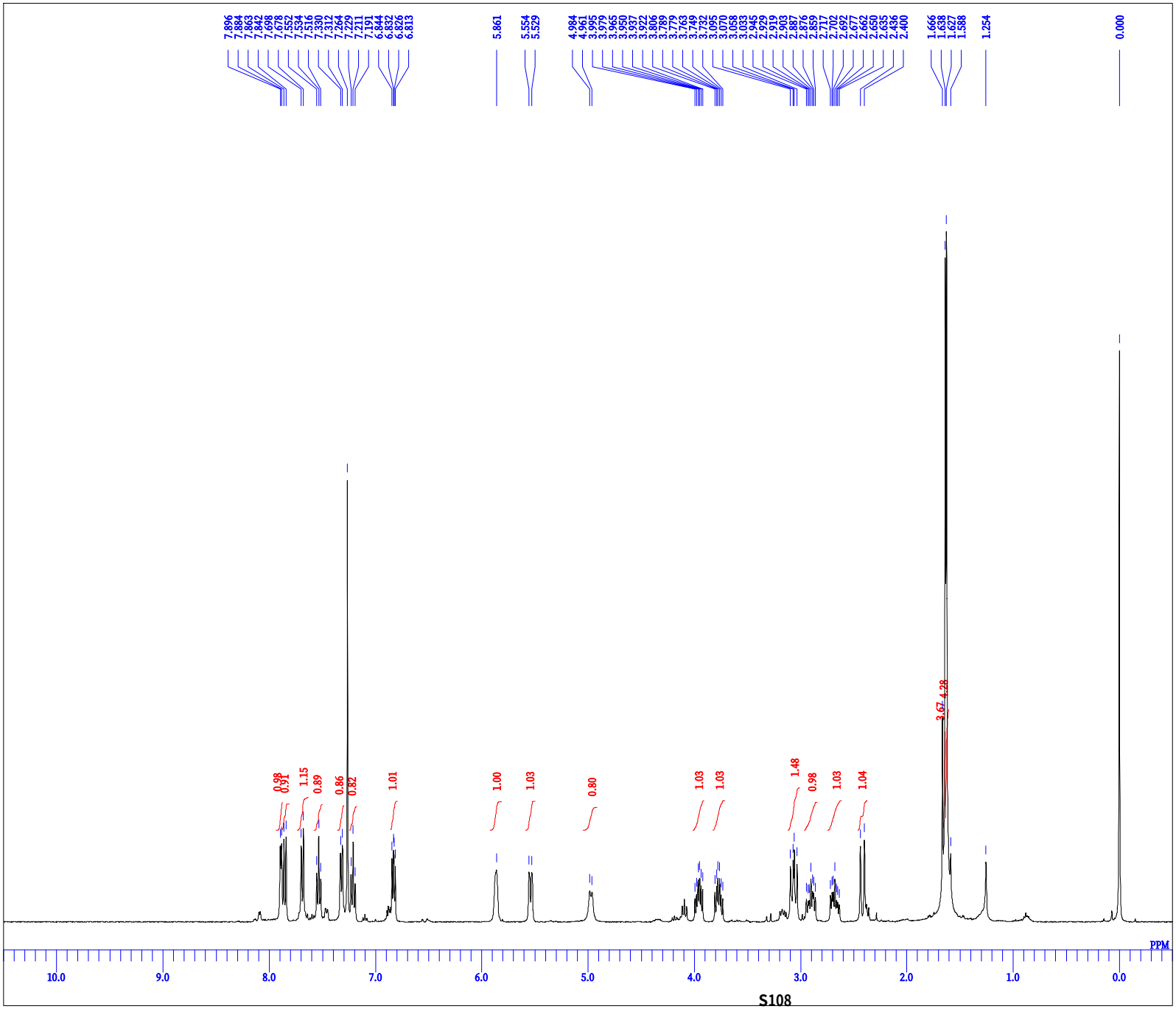
the minor isomer of **4t**



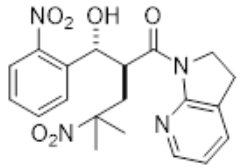
DFILE	azaindole ue 13_C-1.jdf
COMNT	
DATIM	2020-11-16 22:01:01
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	722
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



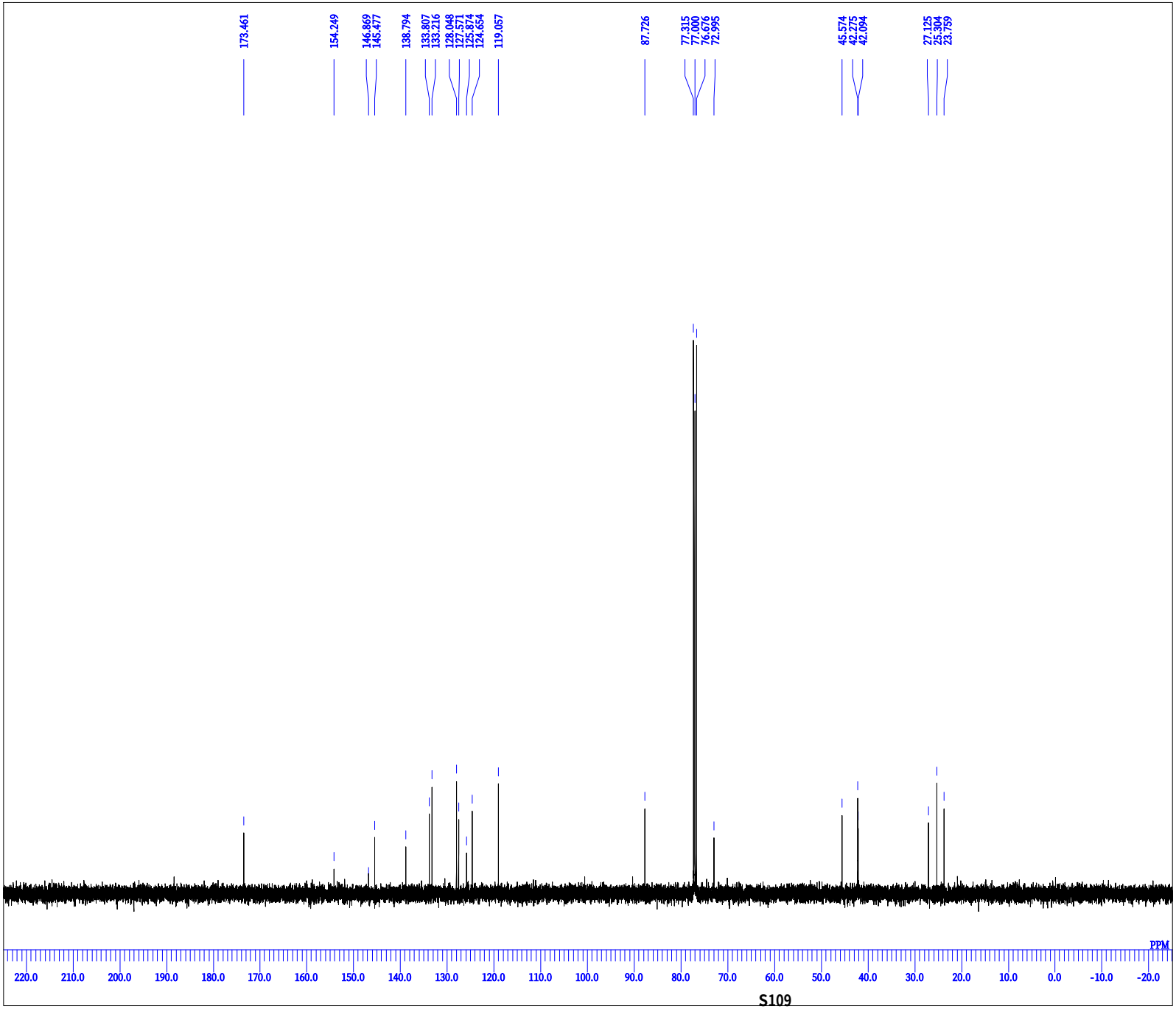
the minor isomer of **4t**



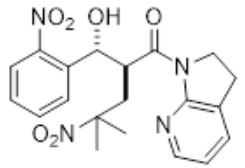
DFILE azin sita nnn-1.als
COMNT
DATIM 2020-11-28 15:33:10
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 1.40 Hz
RGAIN 46



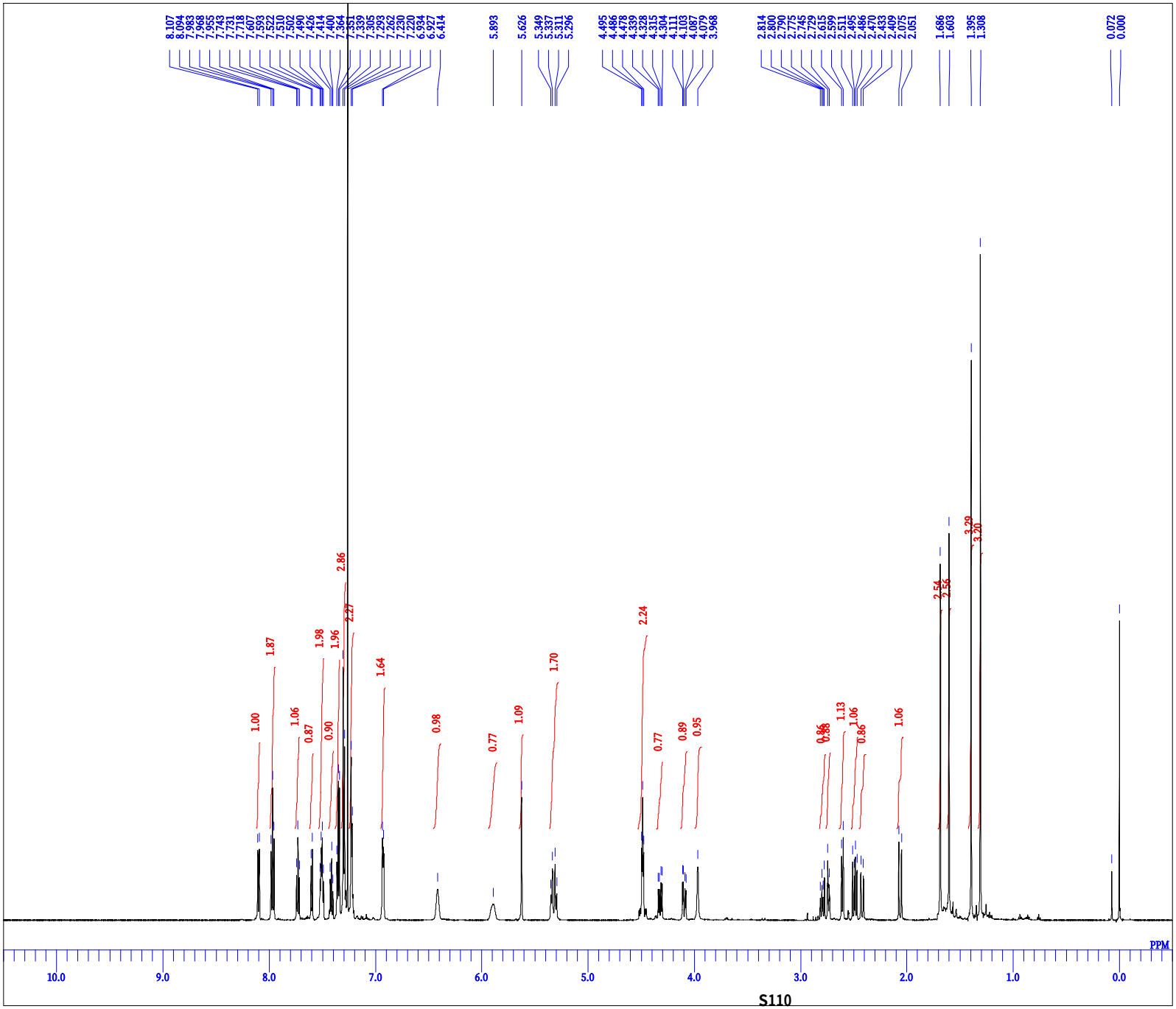
the major isomer of **4t**



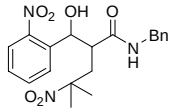
DFILE	anaindo sita 13C-1.jdf
COMNT	
DATIM	2020-11-24 22:57:04
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	204
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



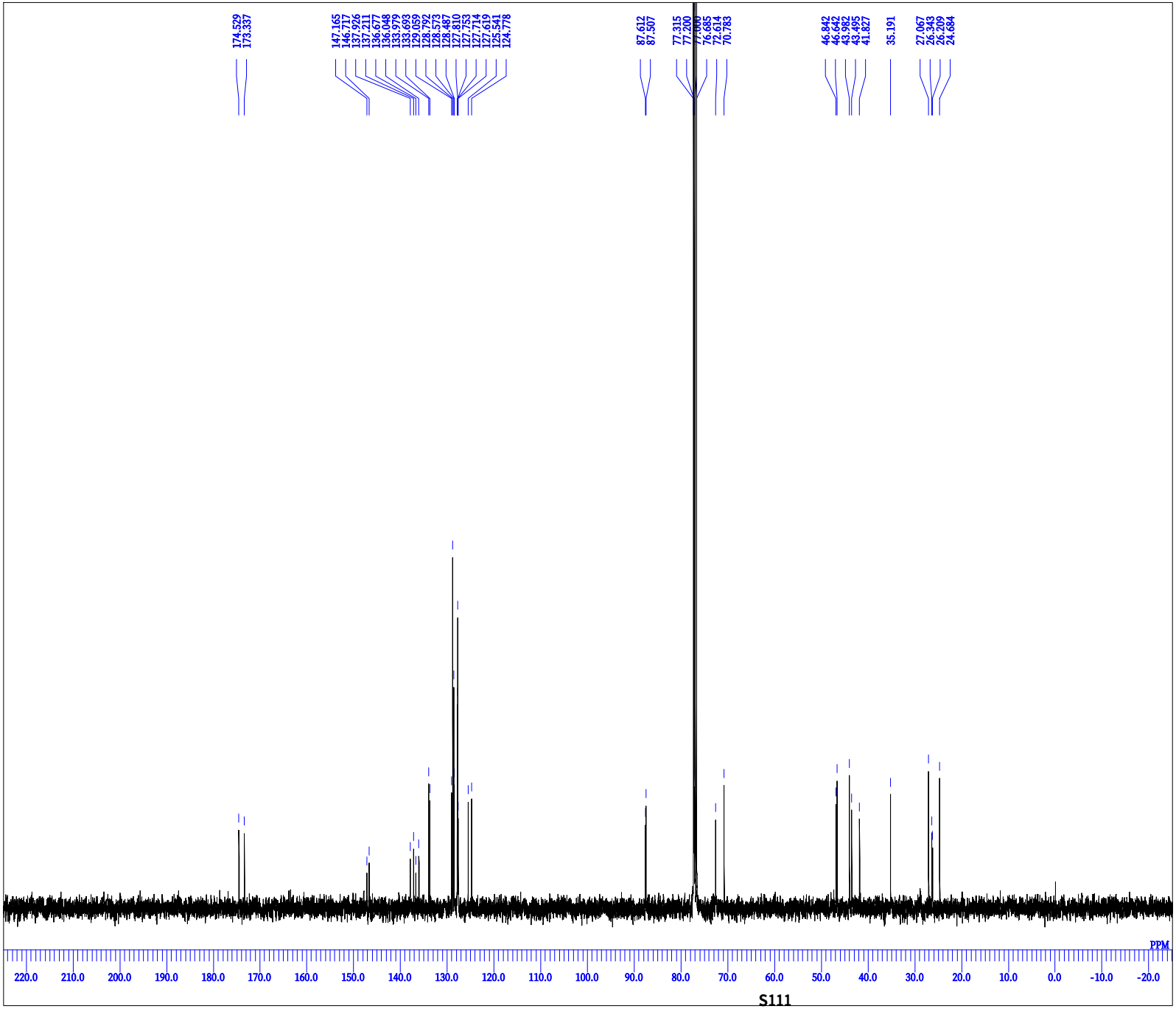
the major isomer of **4t**



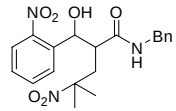
DFILE N-Bn-1.jdf
COMNT
DATIM 2020-11-23 12:12:31
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 32768
FREQU 11261.26 Hz
SCANS 8
ACQTM 2.9098 sec
PD 2.0000 sec
PW1 6.90 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 42



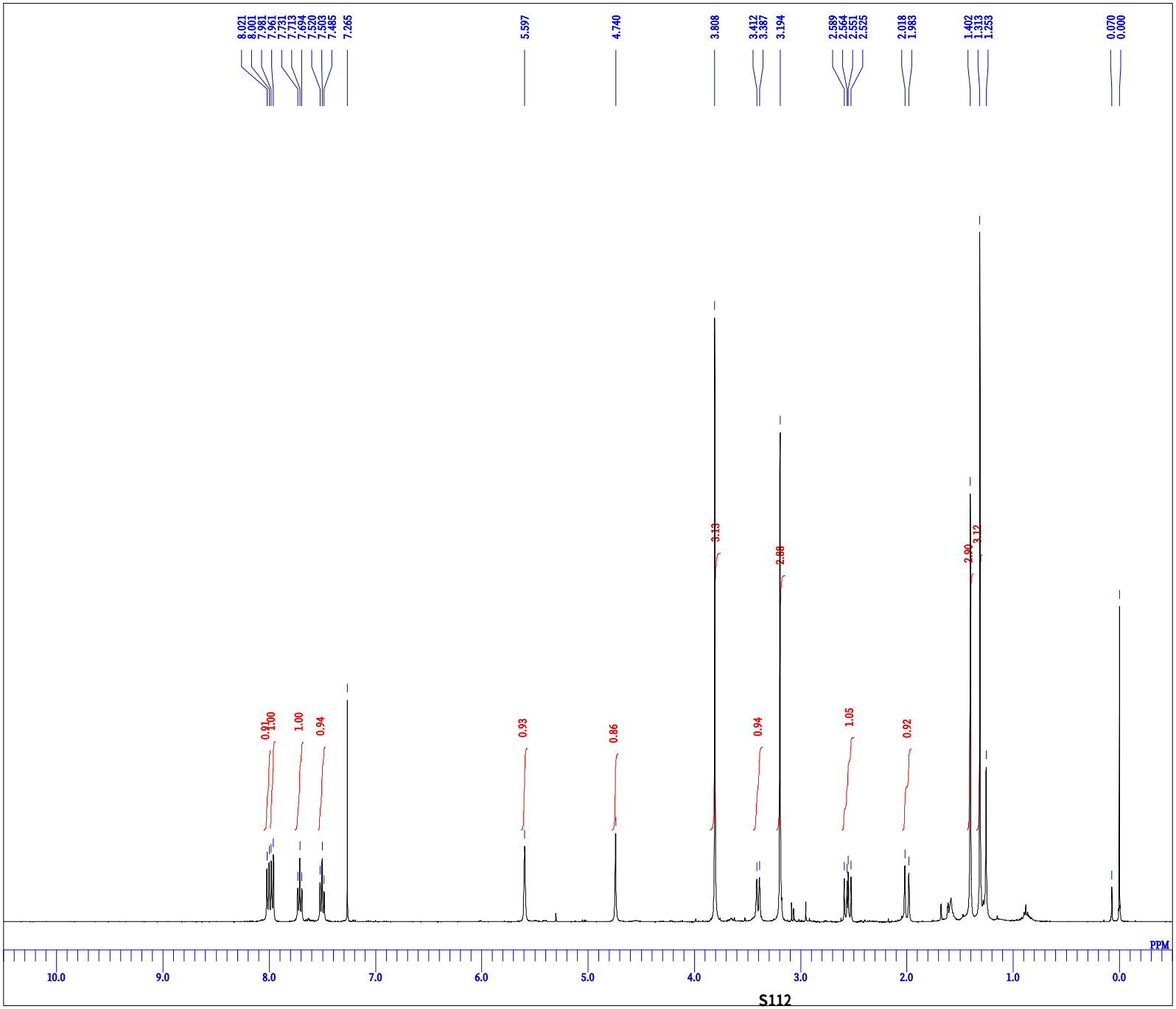
4u



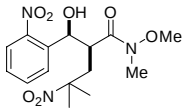
DFILE	N-Bn 13C-1.als
COMNT	
DATIM	2020-11-23 20:07:08
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	307
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60



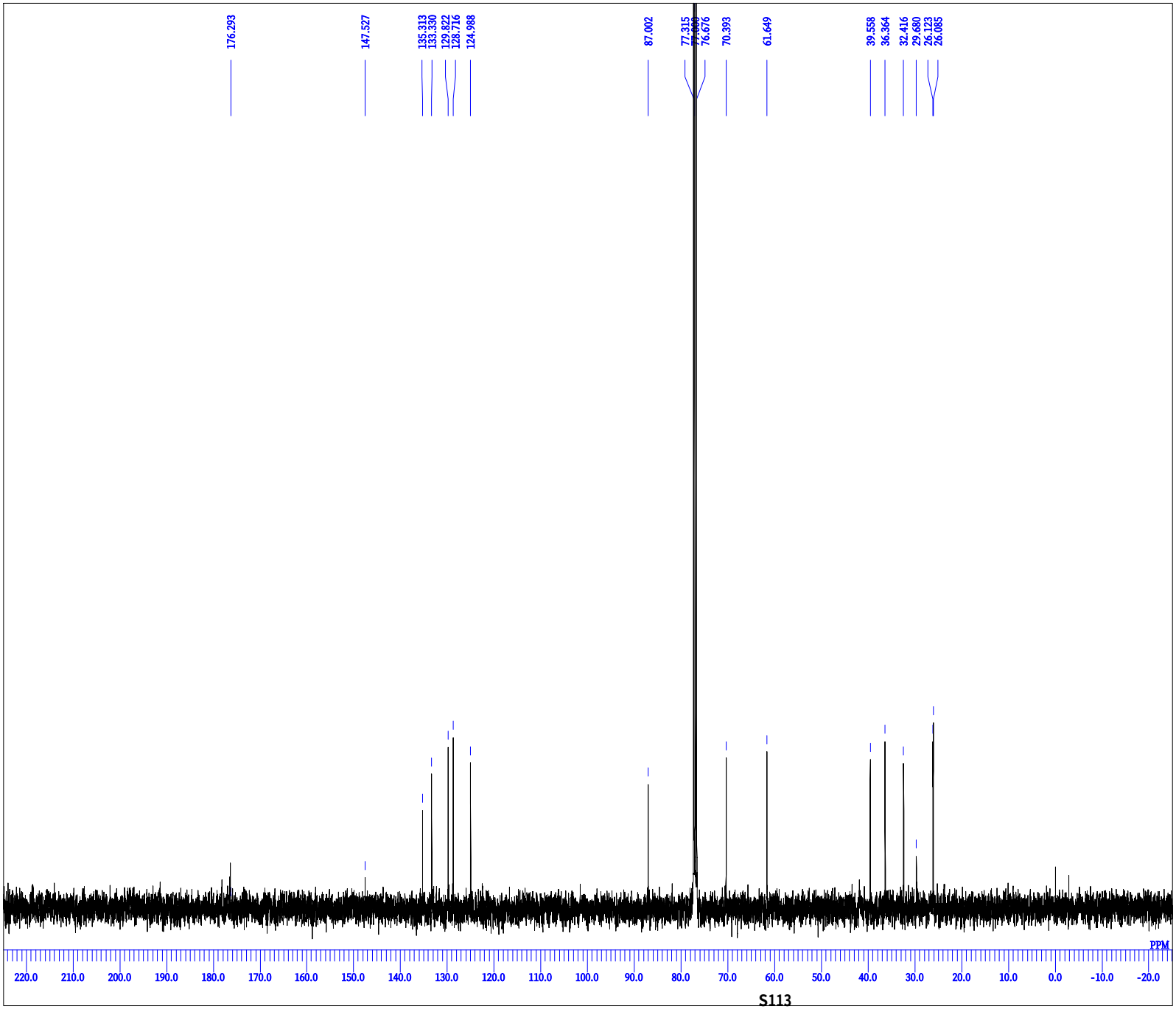
4u



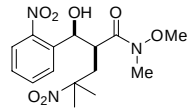
DFILE N-OMeme ue-1.als
COMNT
DATIM 2020-11-21 18:29:01
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 21.3 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 42



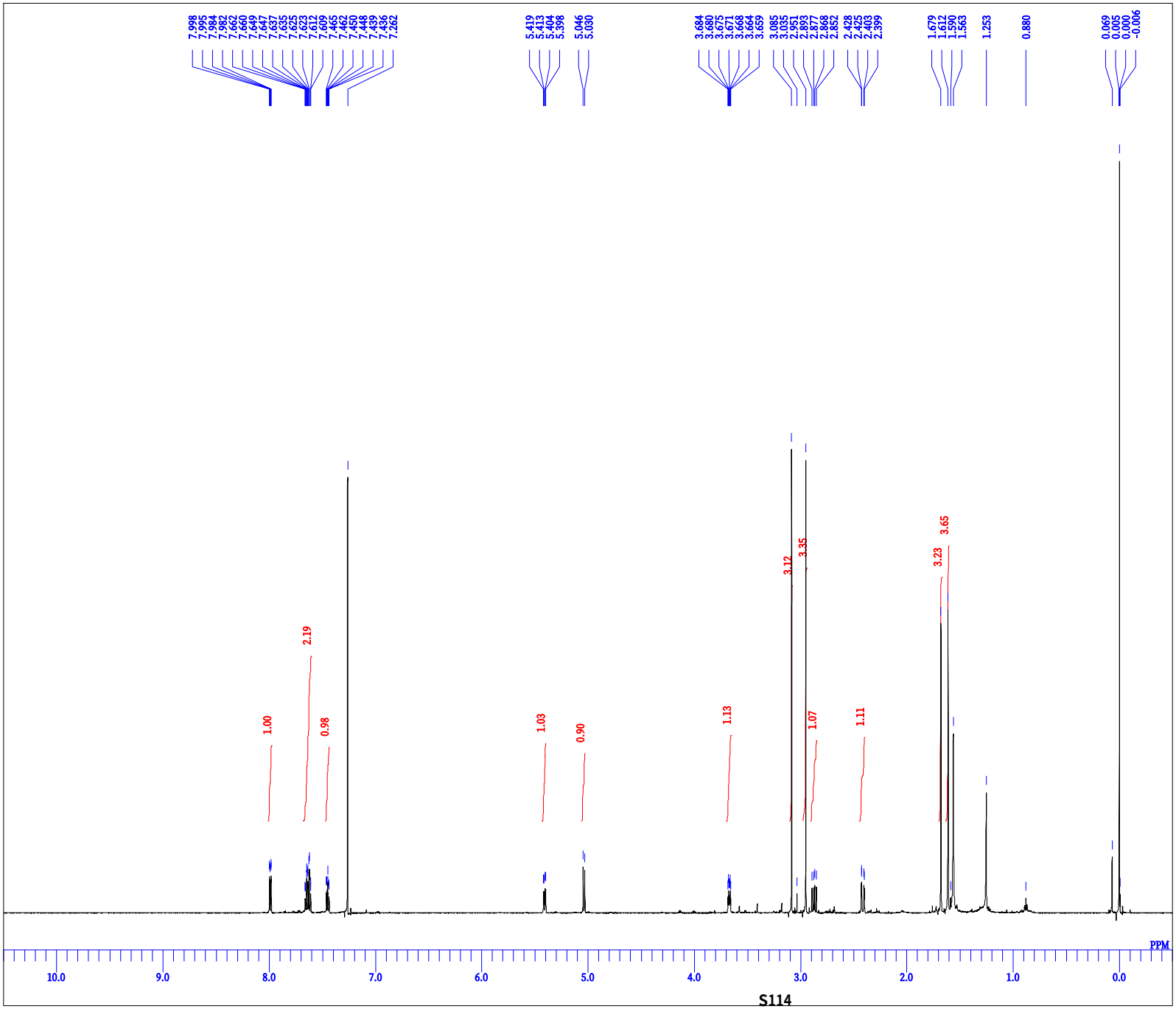
syn-4v



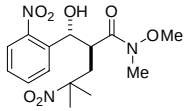
DFILE	N-OMeme ue 13C-1.als
COMNT	
DATIM	2020-11-21 18:43:42
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	380
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.6 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	1.40 Hz
RGAIN	60



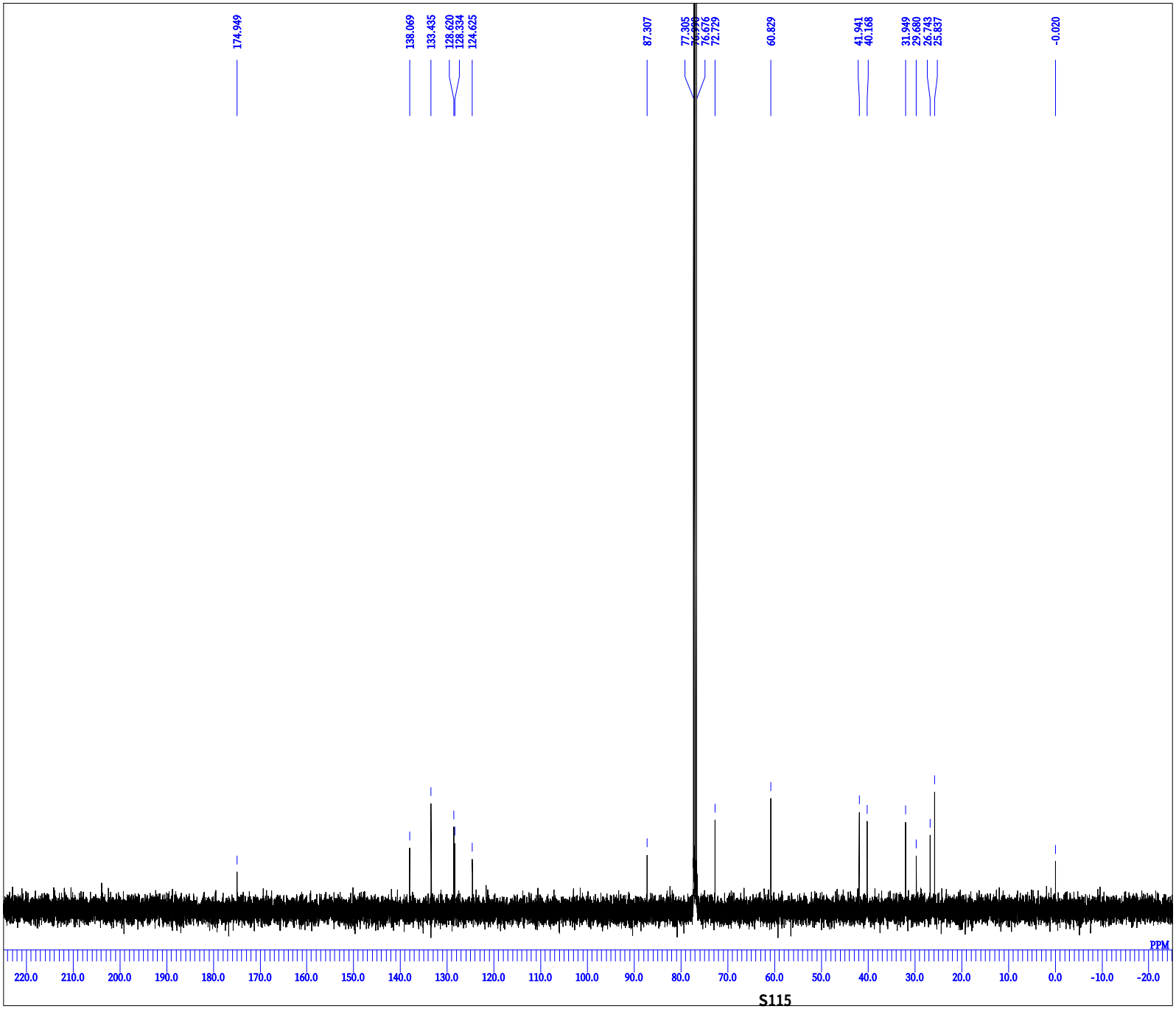
syn-4v



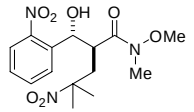
DFILE N-OMeme sita-1.als
COMNT
DATIM 2020-11-23 12:18:31
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 26214
FREQU 9008.87 Hz
SCANS 8
ACQTM 2.9098 sec
PD 2.0000 sec
PW1 6.90 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 52



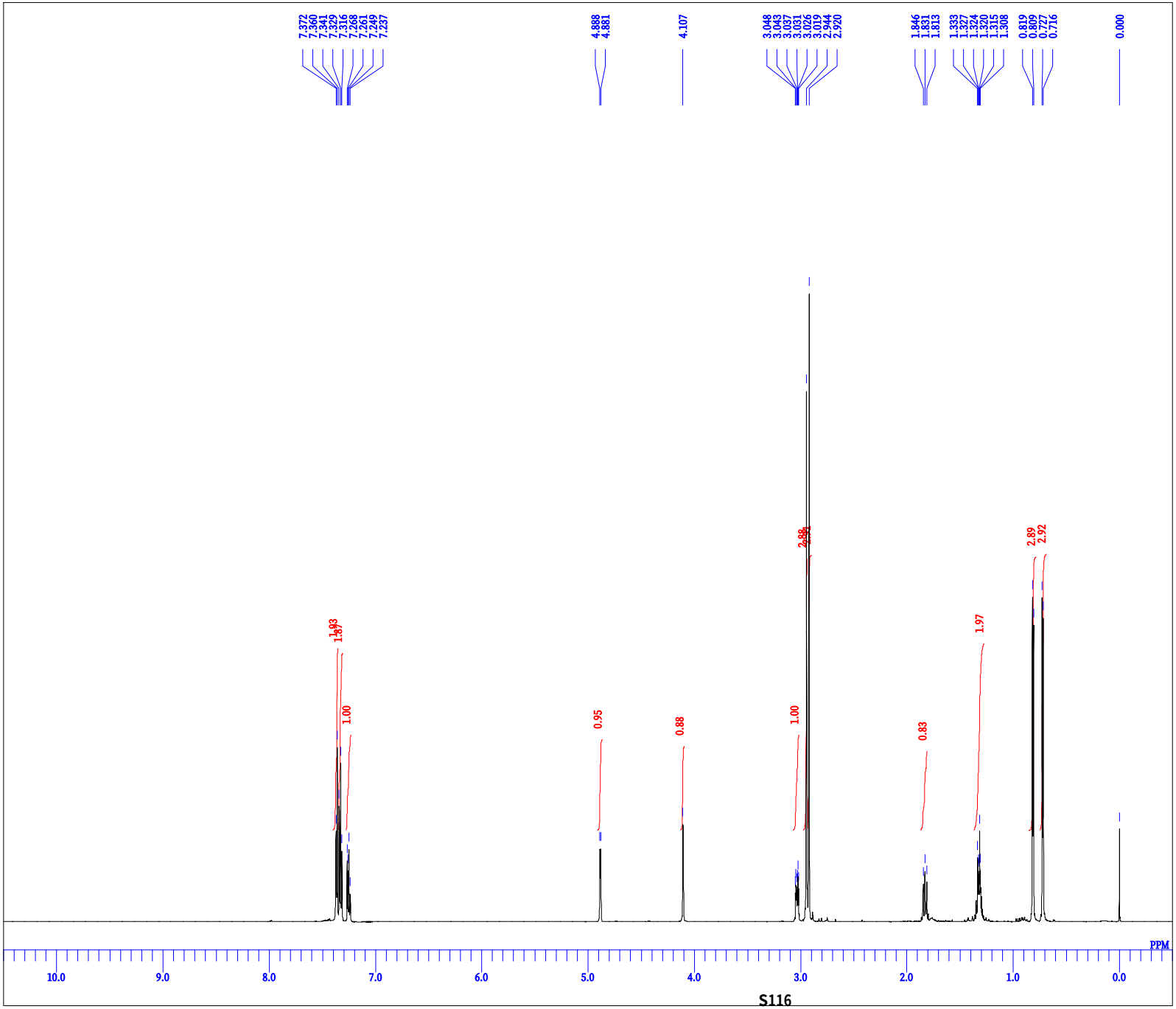
anti-4v



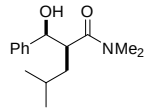
DFILE	N-OMeMe sita 13C-1.jdf
COMNT	
DATIM	2020-11-23 21:20:05
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	1820
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.0 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



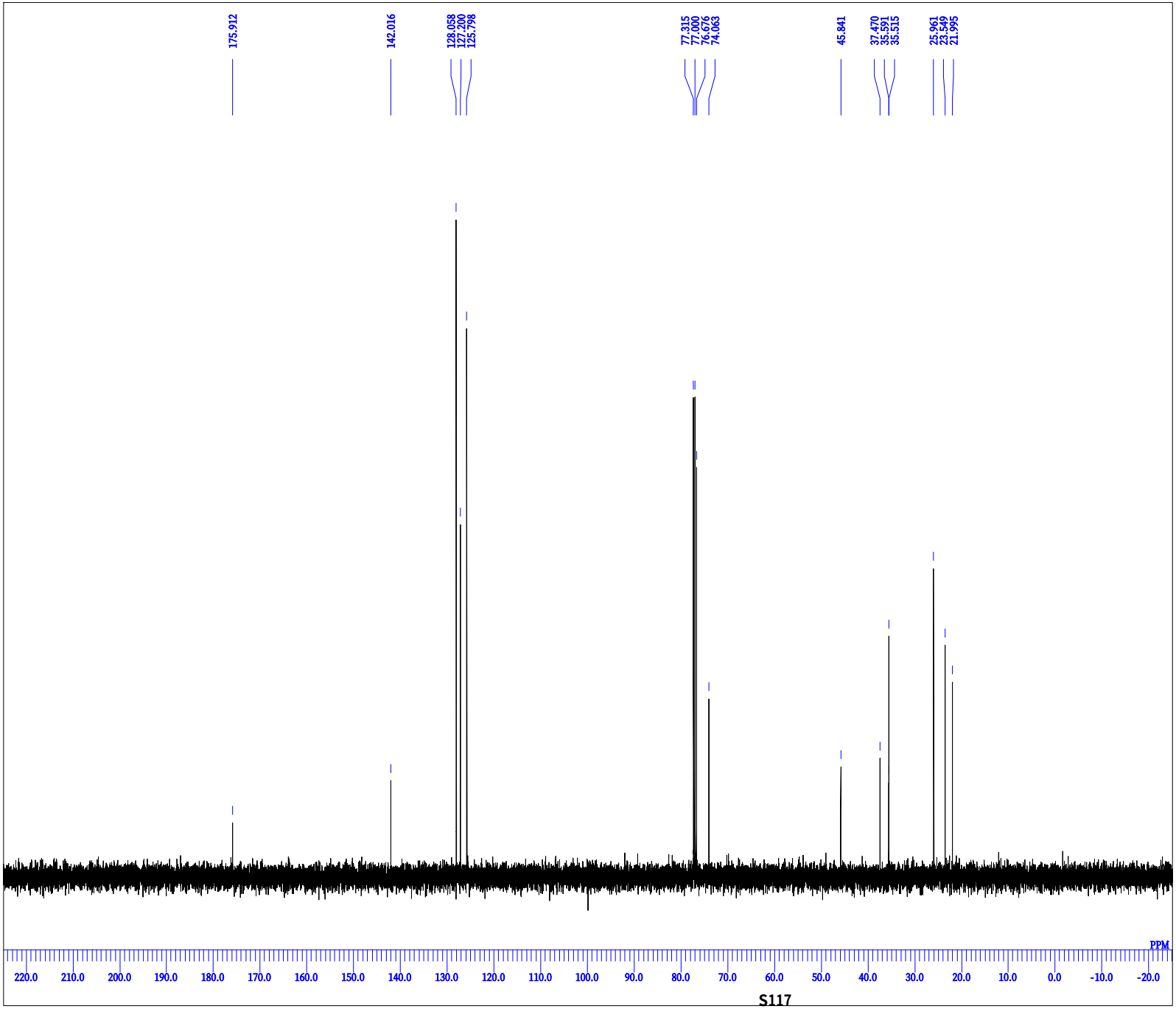
***anti*-4v**



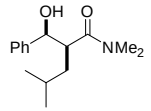
DFILE	No-NO2 ue-1.als
COMNT	
DATIM	2020-11-23 12:25:01
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	26214
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	2.0000 sec
PW1	6.90 usec
IRNUC	1H
CTEMP	20.3 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	0.20 Hz
RGAIN	38



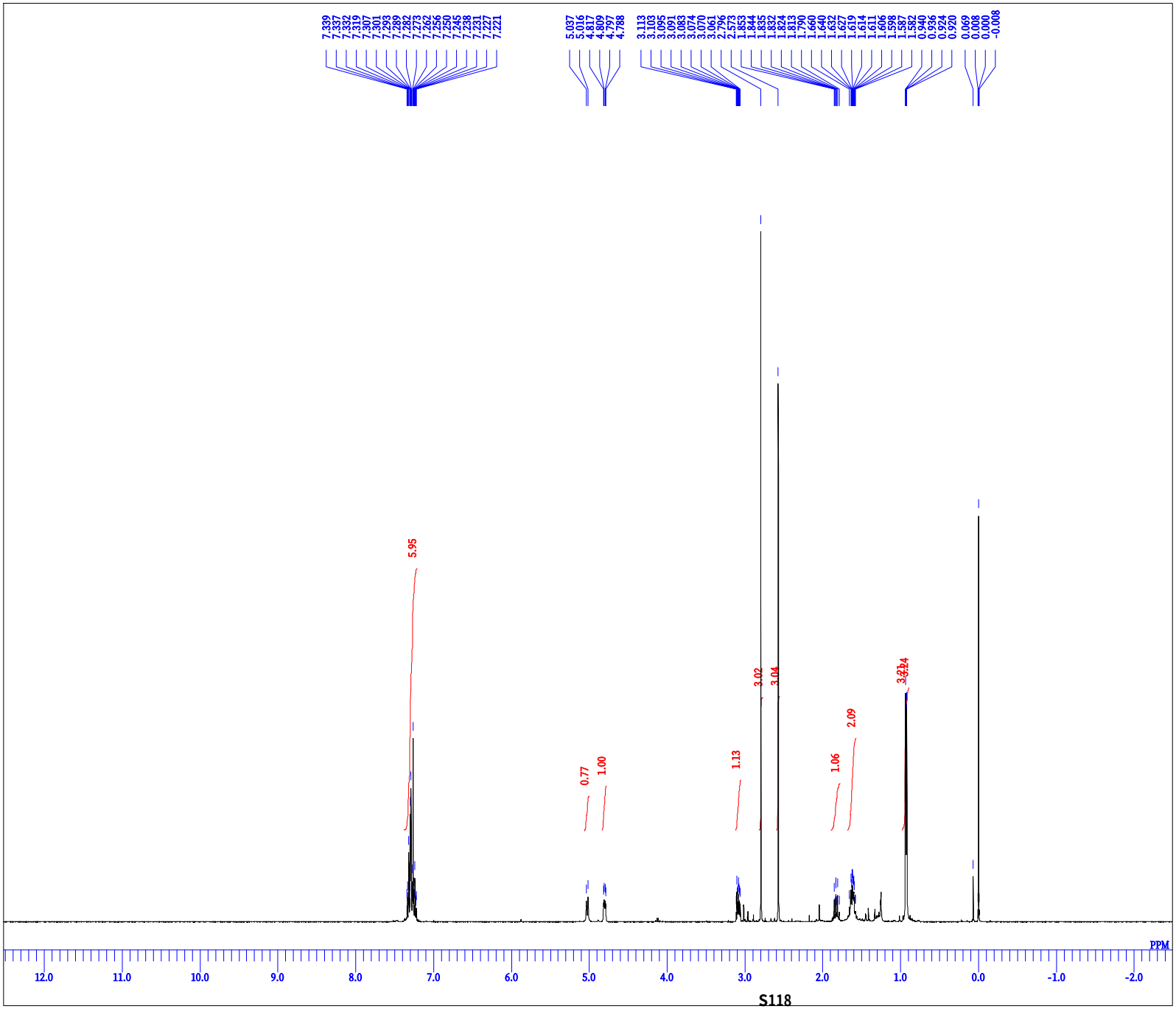
***syn*-13**



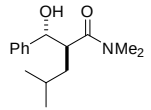
DFILE	No-NO2 ue 13C-1.als
COMNT	
DATIM	2020-11-23 21:26:57
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	54
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	20.8 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



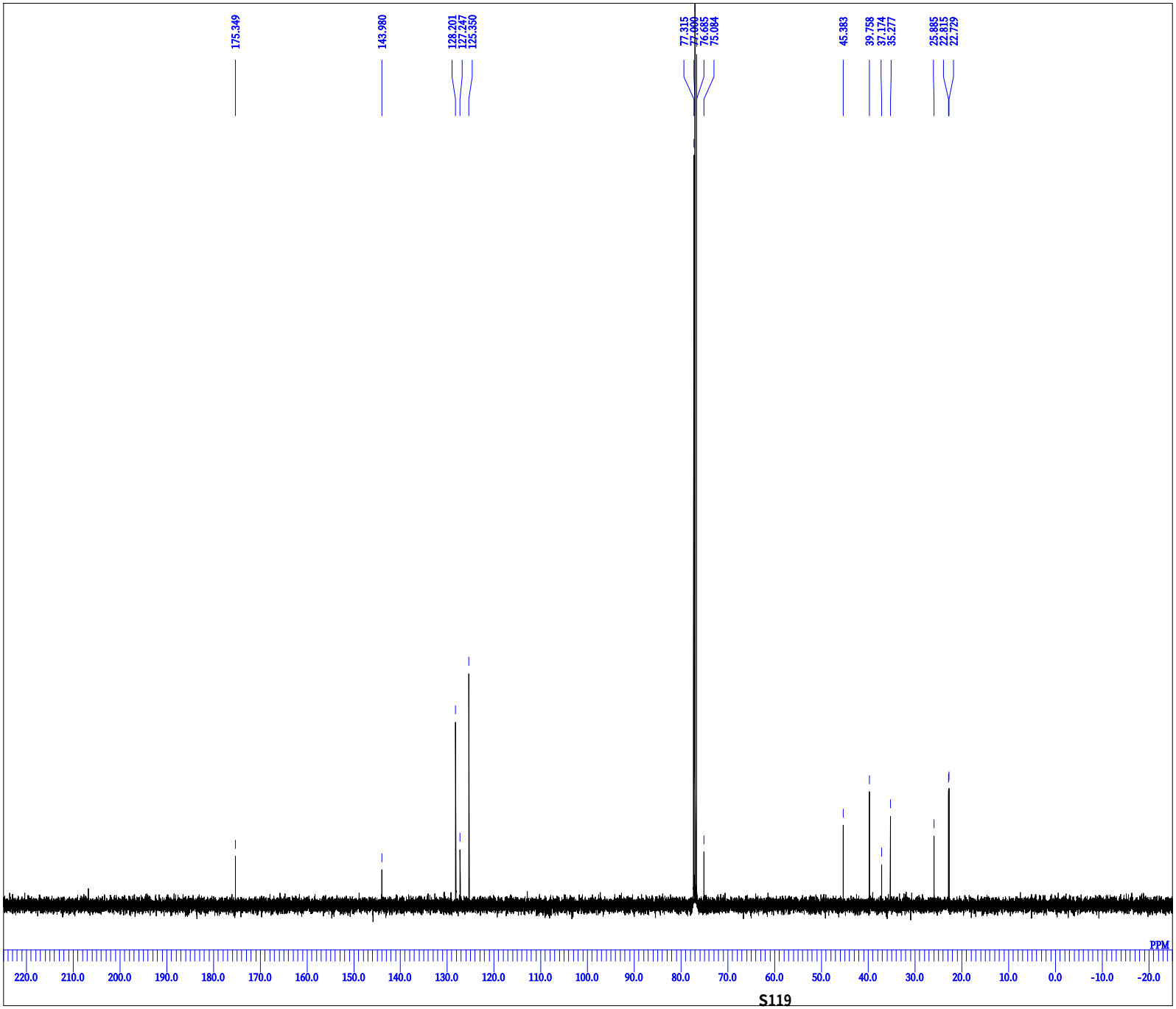
***syn*-13**



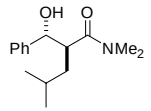
DFILE	No NO2 sita-1.als
COMNT	
DATIM	2020-11-24 23:03:38
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCl3
EXREF	0.00 ppm
BF	0.20 Hz
RGAIN	46



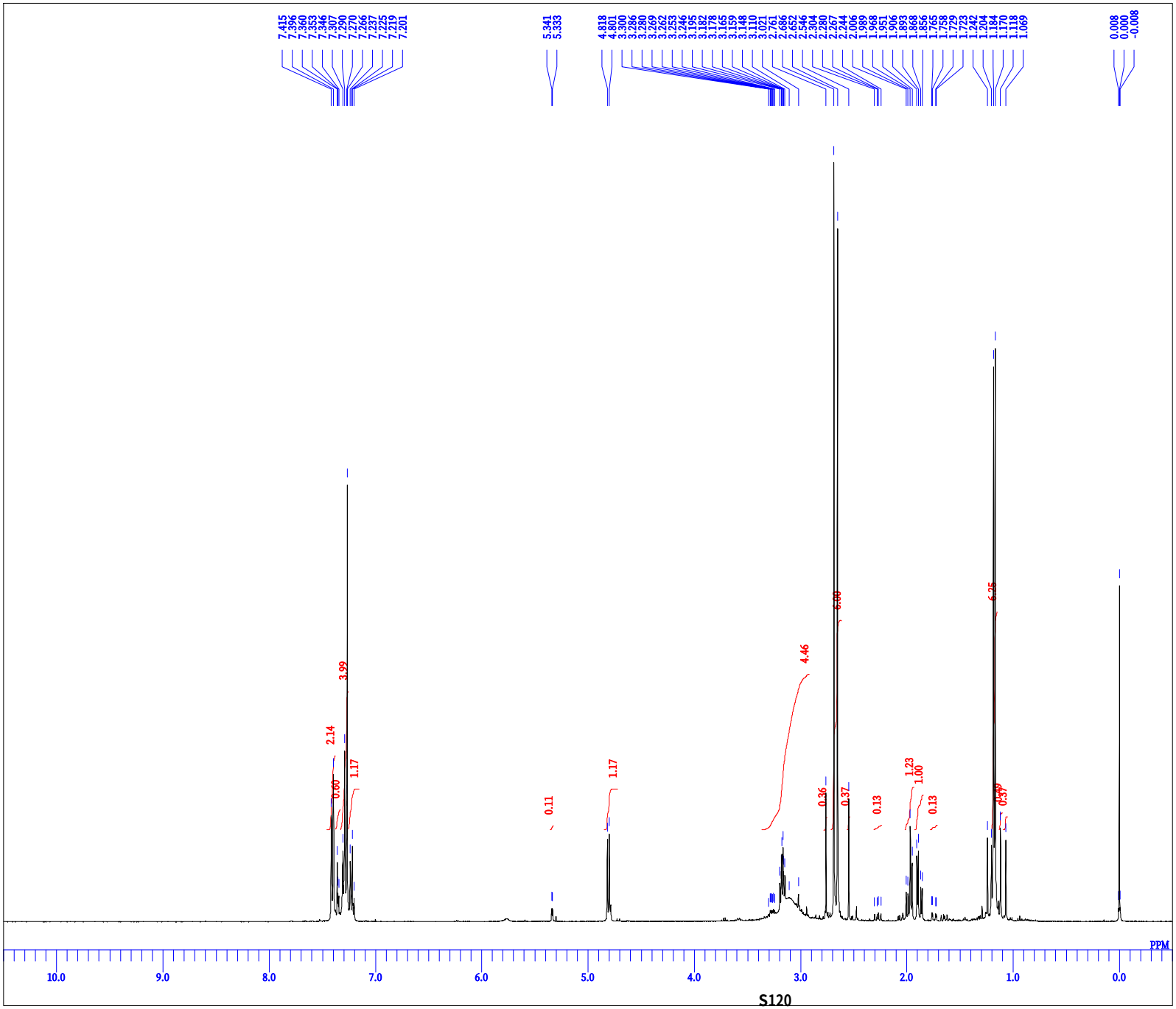
anti-13



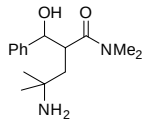
DFILE	No NO2 sita 13C-1.als
COMNT	
DATIM	2020-11-24 23:33:29
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	780
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



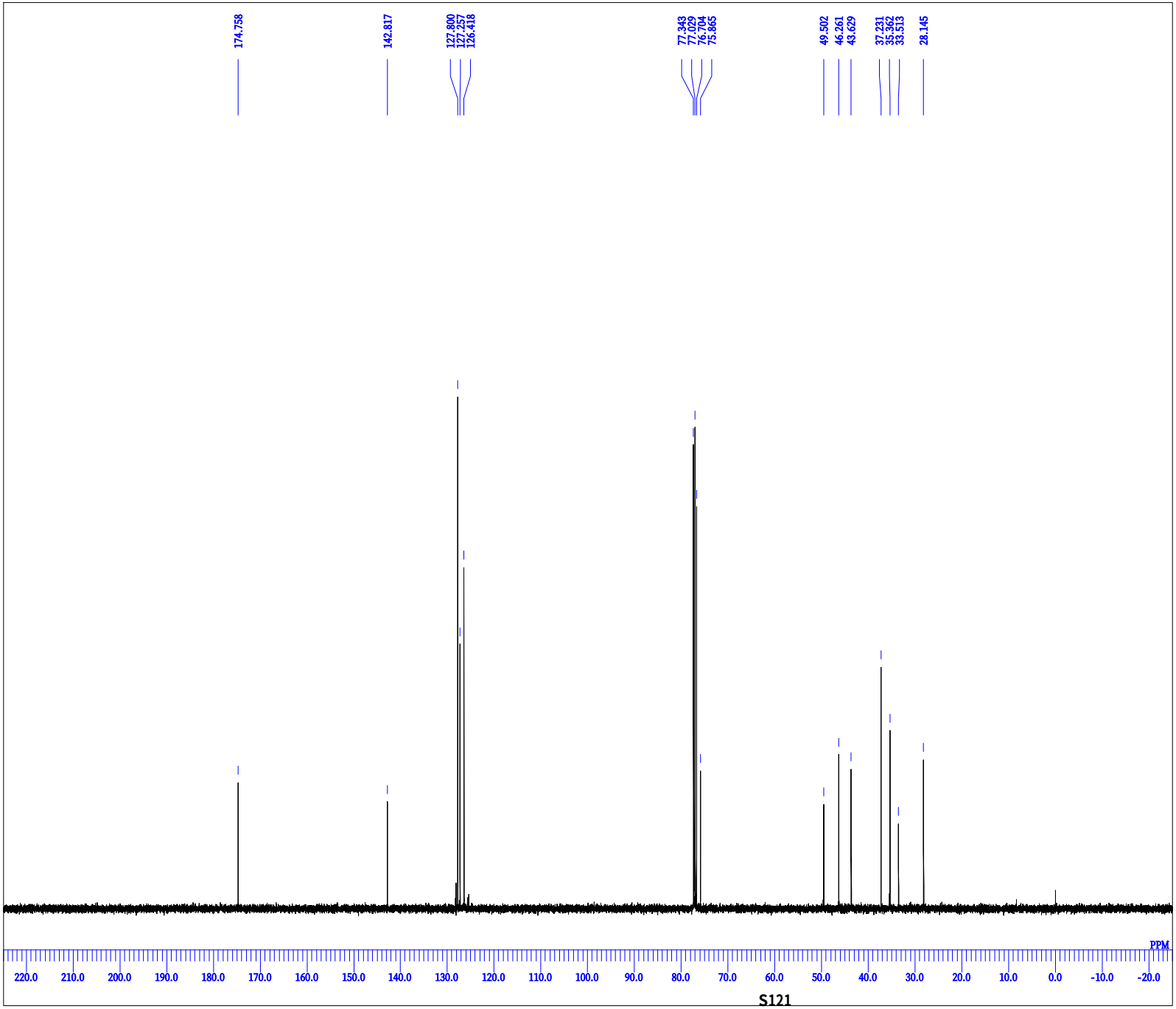
anti-13



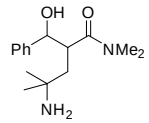
DFILE sm 1586 column 7-12 n-1.als
COMNT
DATIM 2020-11-05 22:23:24
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.31 Hz
SCANS 8
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.20 Hz
RGAIN 44



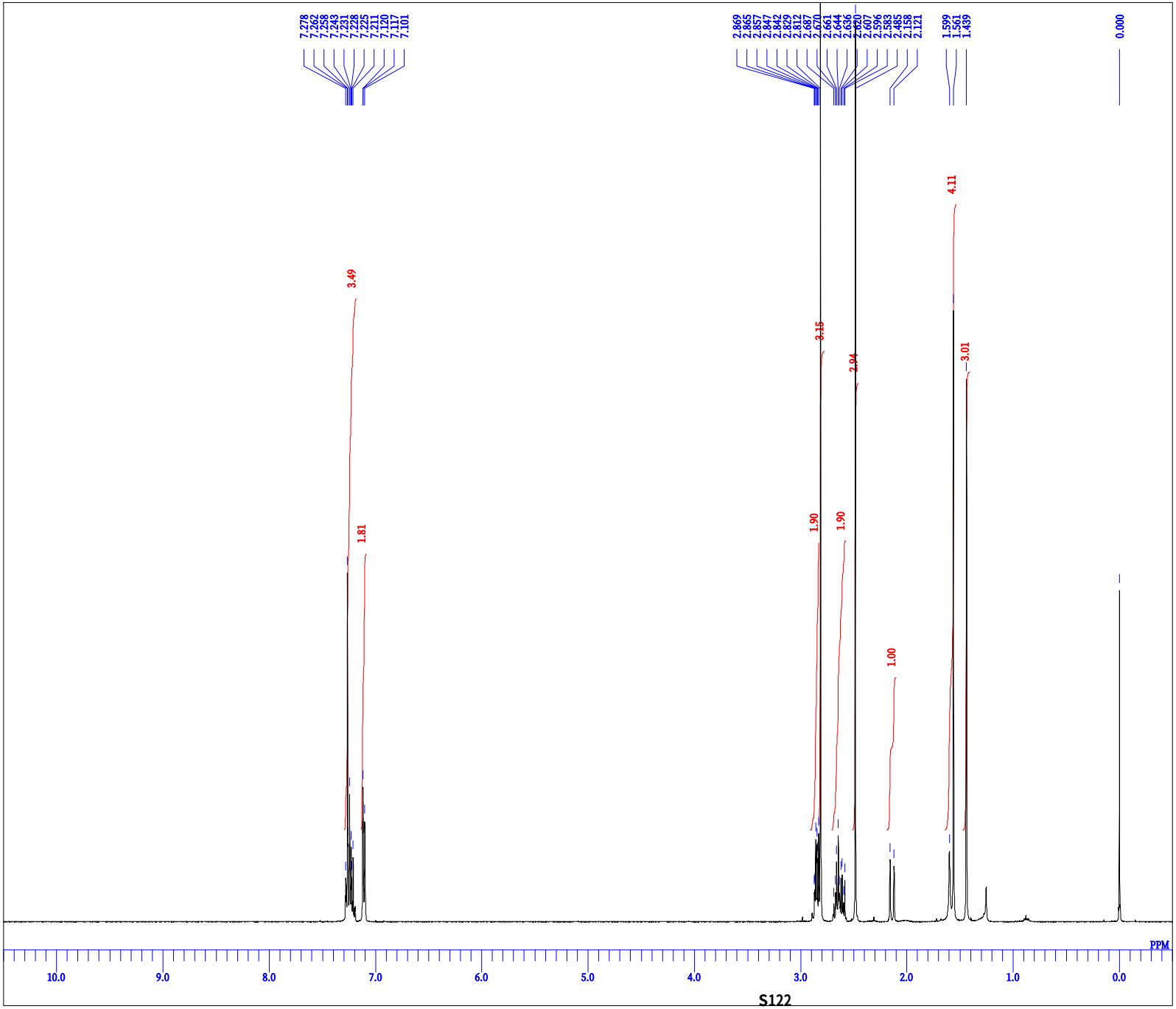
14



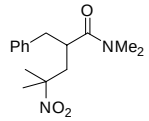
DFILE	NH2 n 13C-1.als
COMNT	
DATIM	2020-11-25 00:15:32
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	965
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



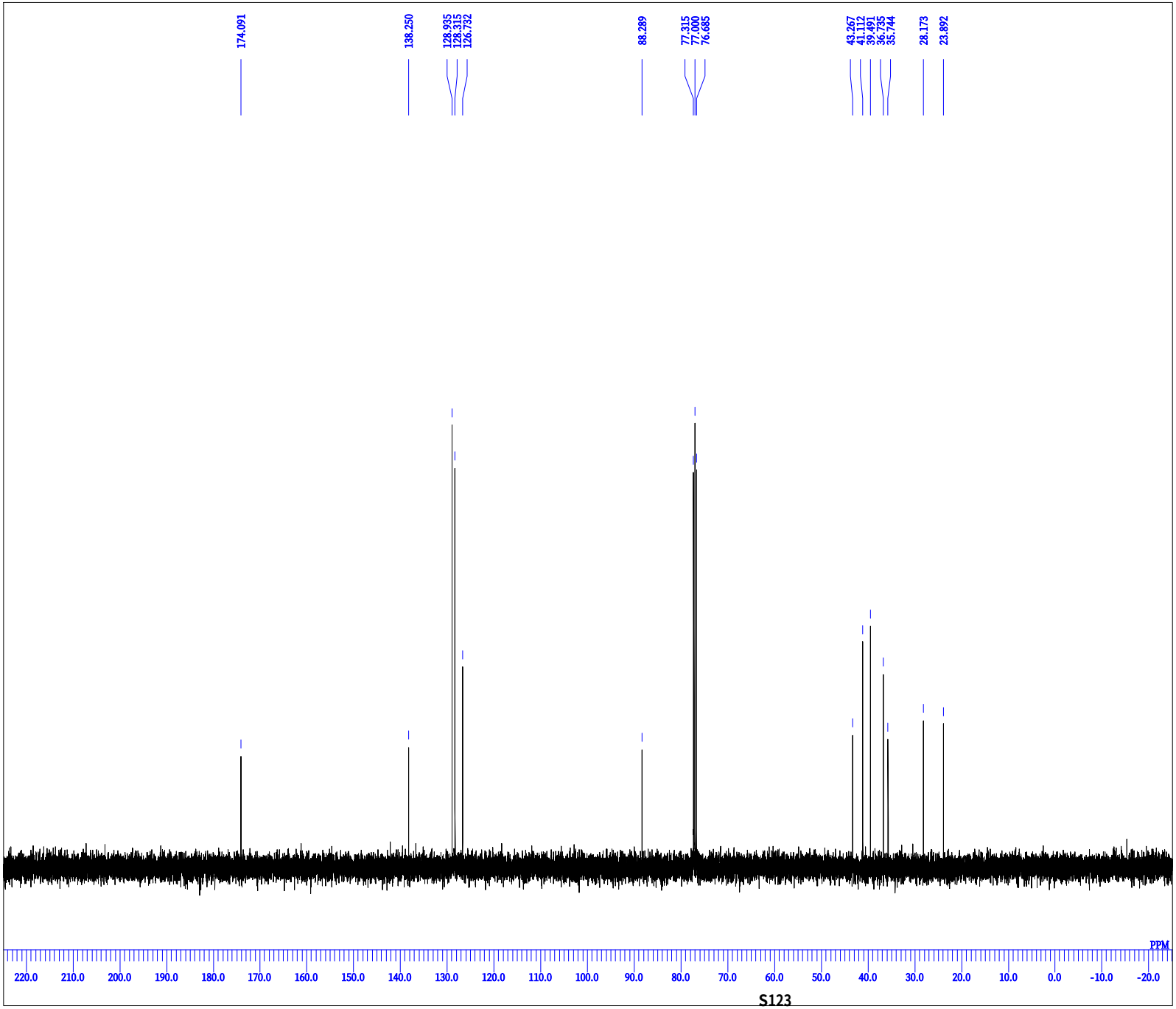
14



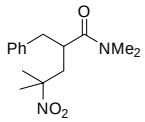
DFILE	sm 1591 column-1.jdf
COMNT	
DATIM	2020-11-02 17:23:44
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	16384
FREQU	7503.00 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.20 Hz
RGAIN	48



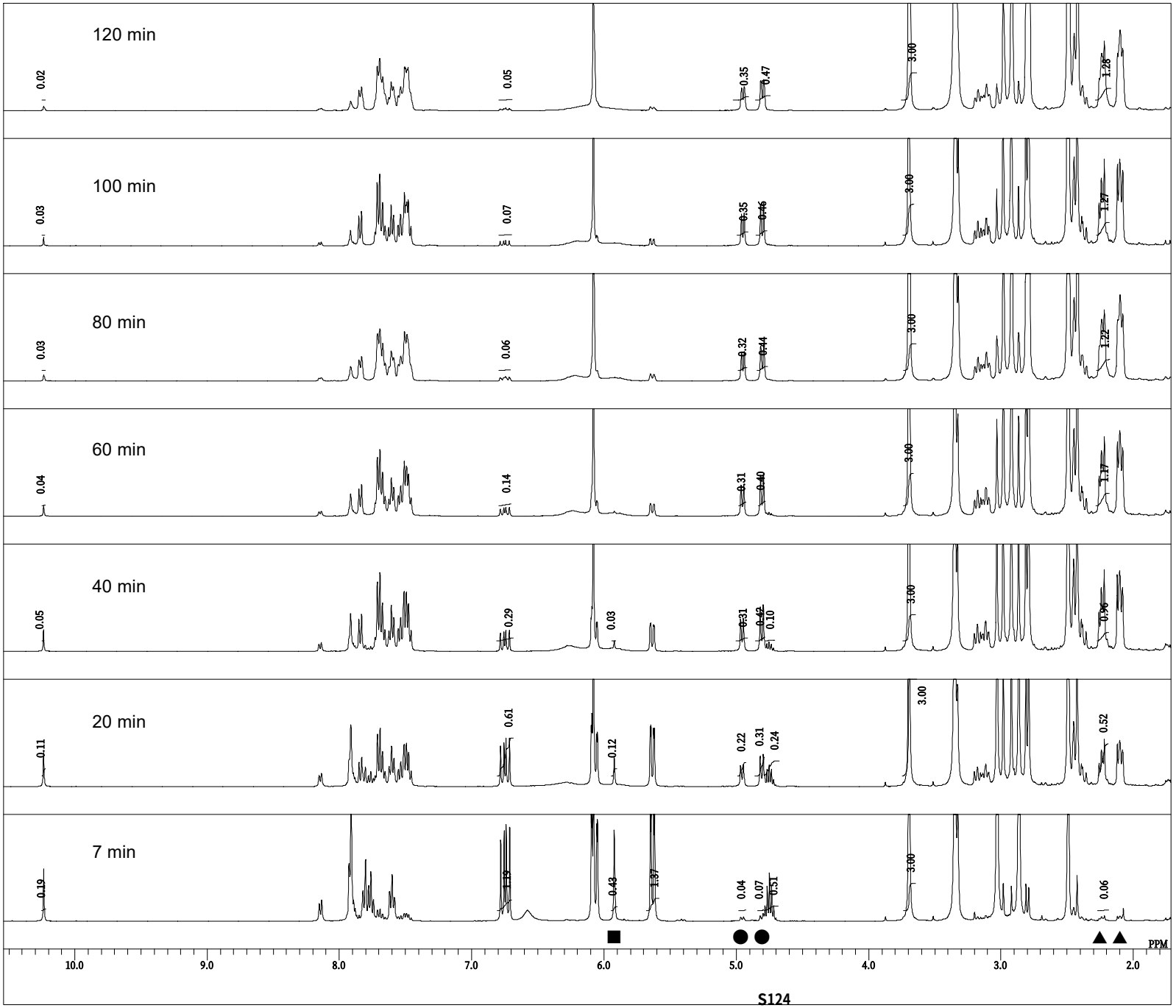
15



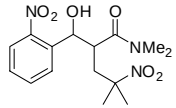
DFILE	No OH 13C-1.als
COMNT	
DATIM	2020-11-21 18:51:09
OBNUC	13C
EXMOD	single_pulse.dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32768
FREQU	31407.03 Hz
SCANS	43
ACQTM	1.0433 sec
PD	1.2000 sec
PW1	2.98 usec
IRNUC	1H
CTEMP	21.4 c
SLVNT	CDCl3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60



15



DFILE	sm 1622 crude 1n-1.als
COMNT	
DATIM	2021-01-14 21:51:43
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	8
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	20.4 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	1.40 Hz
RGAIN	30



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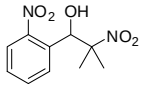
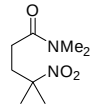


5a ■



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