Supporting Information for:

Palladium-Catalyzed Regiodivergent Hydroaminocarbonylation of Alkenes to Primary Amides with Ammonium Chloride

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1. General experiment details and materials

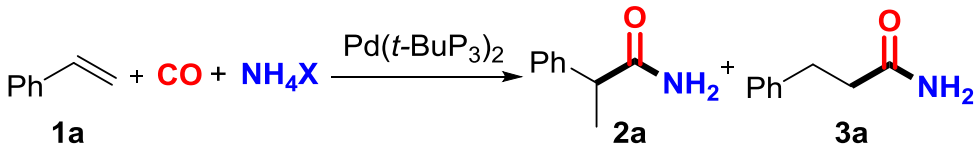
Experimental: All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before use were dried and degassed by standard methods and stored under nitrogen atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avence III 400 MHz spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) were reported in Hz and refered to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass (ESI). GC analysis were performed on Agilent 7890B with Hp-5 column. GS-MS analysis were performed with Agilent 7890B/5975B GC-MS system. Styrenes (**1a-1t**, **4a**, **4m-4p**) purchased from Alfa Aesar or Sigma Aldrich. Alkenes (**4b-4l**)[1], estrone derivative alkene[2] and aliphatic alkenes containing heteroatom[3] were known compounds and synthesized according to the reported methods.

2. Optimization of the reaction conditions

2.1 Effects of ammonium salts on the hydroaminocarbonylation of alkenes

In a glove box, a mixture of NH_4X (2.0 mmol), Pd(*t*-$Bu_3P)_2$ (25.5 mg, 0.05 mmol, 5 mol%) and NMP (5.0 mL) was added into a dry glass vessel. The resulting mixture was stirred for 10 minutes at room temperature and then styrene (114 uL, 1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 120 ºC for 24 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The regioselectivity and yield were measured by GC and GC-MS using *n*-cetane as the internal standard, respectively.

Table S1. Effects of ammonium salts on the hydroaminocarbonylation [a]



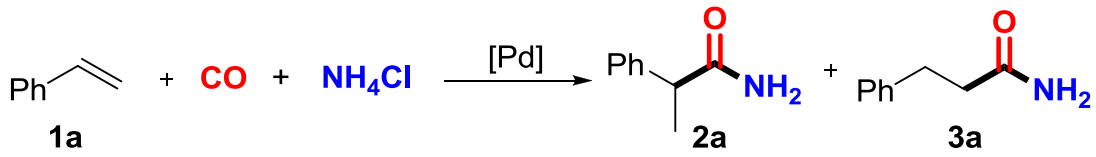
entry	NH_4X	**2a+3a** (%)	**2a:3a**
1	NH_4Cl	95	96:4
2	NH_4F	0	-
3	NH_4Br	<5	-
4	NH_4I	6	-
5	NH_4OAc	0	-
6	NH_4Bz	0	-
7	NH_4PF_6	0	
8	NH_4HF_2	0	-
9	NH_4HCO_3	0	-
10[b]	$(NH_4)_2CO_3$	0	-
11[b]	$(NH_4)_2S_2O_8$	0	-
12[b]	$(NH_4)_2SO_4$	0	-
13	-	0	-
14[c]	NH_4Cl	<5	-

[a] Reaction conditions: **1a** (1.0 mmol), NH_4X (2.0 mmol), Pd(*t*-$Bu_3P)_2$ (0.05 mmol), NMP (5 mL), CO (30 atm), 120 °C, 24 h. [b] NH_4X (1.0 mmol). [c] CO (1.0 atm).Yields and ratios of **2a** and **3a** were determined by GC and GC-MS analysis using *n*-cetane as the internal standard.

2.2 Effects of ligands on the hydroaminocarbonylation of alkenes

In a glove box, a mixture of NH_4Cl (106.8 mg, 2.0 mmol), [Pd] and NMP was added into a dry glass vessel. The resulting mixture was stirred for 10 minutes at room temperature and then styrene (114 uL, 1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from glove box. The autoclave was purged and charged with CO. The reaction mixture was stirred at 120 °C for 24 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The regioselectivity and yield were measured by GC and GC-MS using *n*-cetane as the internal standard, respectively.

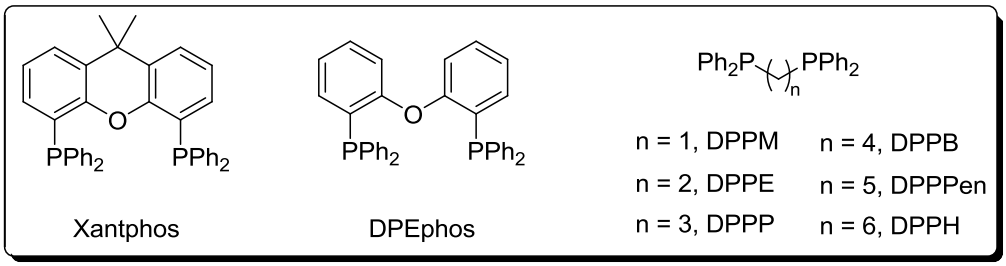
Table S2. Effects of ligands on the hydroaminocarbonylation of alkenes [a]



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

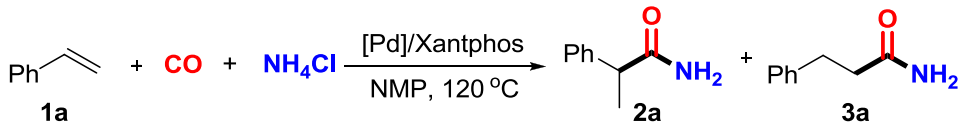
Entry	[Pd]	Ligand	CO (atm)	Yield **2a+3a** (%)	**2a:3a**
1	**Pd(*t*-$Bu_3P)_2$**	**-**	**30**	**95**	**96:4**
2	Pd(*t*-$Bu_3P)_2$	-	20	96	88:12
3	Pd(*t*-$Bu_3P)_2$	-	10	82	85:15
4[b]	Pd(*t*-$Bu_3P)_2$	-	30	84	96:4
5	$Pd(PPh_3)_4$	-	30	90	81:19
6[c]	PdI_2	Xantphos	30	86	17:83
7[c]	PdI_2	DPEphos	30	34	22:78
8[c]	PdI_2	DPPF	30	25	36:64
9[c]	PdI_2	DPPH	30	27	51:49
10[c]	PdI_2	DPPPen	30	23	21:79
11c	PdI_2	DPPB	30	<5	-
12[c]	PdI_2	DPPP	30	<5	-
13[c]	PdI_2	DPPE	30	<5	-
14[c]	PdI_2	DPPM	30	<5	-
15[c]	PdI_2	PPh_3	30	56	30:70
16[c]	PdI_2	P(2-MePh)$_3$	30	13	68:32

17[c]	PdI_2	$P(4\text{-}MePh)_3$	30	41	31:69
18[c]	PdI_2	PCy_3	30	40	52:48
19[c]	PdI_2	Ruphos	30	58	35:65
20[c]	PdI_2	Dave Phos	30	46	48:52
21[c]	PdI_2	Xphos	30	47	42:58
22[c]	-	Xantphos	30	20	32:68



[a] Reaction conditions: **1a** (1.0 mmol), NH_4Cl (2.0 mmol), Pd(*t*-$Bu_3P)_2$ (0.05 mmol), NMP (5 mL), CO (30 atm), 120 °C, 24 h. [b] 15 h, isolated yield. [c]PdI_2 (0.02 mmol), bidentate phosphine ligand (0.025 mmol) or monodentate phosphine ligand (0.05 mmol), CO (30 atm), NMP (3.0 mL), 24 h. Yields and ratios of **2a** and **3a** were determined by GC and GC-MS analysis using *n*-cetane as the internal standard.

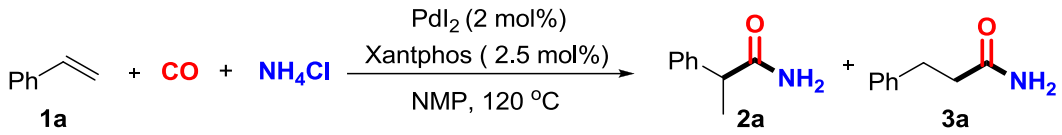
Table S3. Screening of catalyst precursors for linear amide [a]



Entry	[Pd]	Ligand	Yield **2a+3a** (%)	**2a:3a**
1	PdI_2	Xantphos	**86**	**17:83**
2	$PdCl_2$	Xantphos	68	25:75
3	$PdBr_2$	Xantphos	86	24:76
4	$Pd_2(dba)_3$	Xantphos	61	22:78
5	$Pd(OAc)_2$	Xantphos	67	27:73
6	$Pd(TFA)_2$	Xantphos	68	24:76
7	$Pd(COD)Cl_2$	Xantphos	74	25:75
8	$Pd(COD)Br_2$	Xantphos	64	29:71
9	$Pd(CH_3CN)_2Cl$	Xantphos	62	24:76
10	-	Xantphos	20	32:68

[a] Reaction conditions: **1a** (1.0 mmol), NH_4Cl (2.0 mmol), [Pd] (0.02 mmol), Xantphos (0.025 mmol), CO (30 atm), NMP (3.0 mL), 24 h. Yields and ratios of **2a** and **3a** were determined by GC and GC-MS analysis using *n*-cetane as the internal standard.

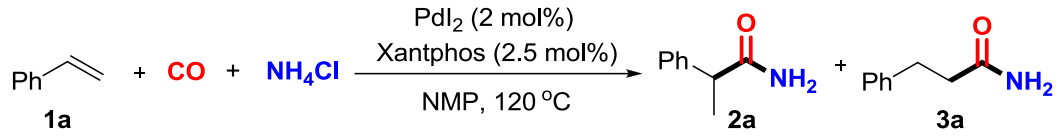
Table S4. Screening of reaction time for linear amide [a]



Entry	t (h)	Yield **2a**+**3a** (%)	**2a:3a**
1	24	86	17:83
2	12	87	17:83
3	6	88	18:82
4	4	90	17:83
5	2	61	16:84

[a] Reaction conditions: **1a** (1.0 mmol), NH_4Cl (2.0 mmol), PdI_2 (0.02 mmol), Xantphos (0.025 mmol), CO (30 atm), NMP (3 mL), 120 °C. Yields and ratios of **2a** and **3a** were determined by GC and GC-MS analysis using *n*-cetane as the internal standard.

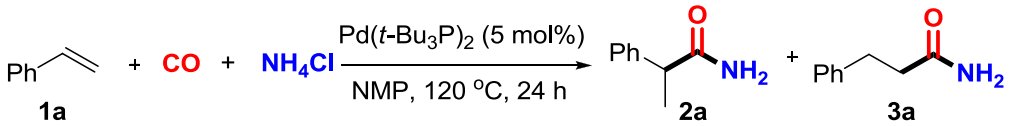
Table S5. Screening of the pressure of CO for linear amide [a]



Entry	CO (atm)	Yield **2a**+**3a** (%)	**2a:3a**
1	30	90	17:83
2	20	65	17:83
3	10	60	17:83

[a] Reaction conditions: **1a** (1.0 mmol), NH_4Cl (2.0 mmol), PdI_2 (0.02 mmol), Xantphos (0.025 mmol), CO, NMP (3 mL), 4 h. Yields and ratios of **2a** and **3a** were determined by GC and GC-MS analysis using *n*-cetane as the internal standard.

Table S6. Effect of concentration for synthesis of branched amide [a]

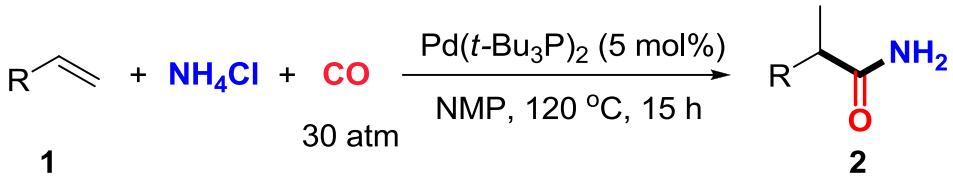


Entry	NMP (mL)	Yield **2a**+**3a** (%)	**2a:3a**
1	1 mL	68	59:41
2	2 mL	76	74:26
3	3 mL	80	85:15
4	4 mL	91	91:9
5	5 mL	95	96:4

[a] Reaction condition: **1a** (1.0 mmol), NH_4Cl (2.0 mmol), Pd(*t*-$Bu_3P)_2$ (0.05 mmol), NMP (5 mL), CO (30 atm), 120 °C, 24 h. Yields and ratios of **2a** and **3a** were determined by GC and GC-MS analysis using *n*-cetane as the internal standard.

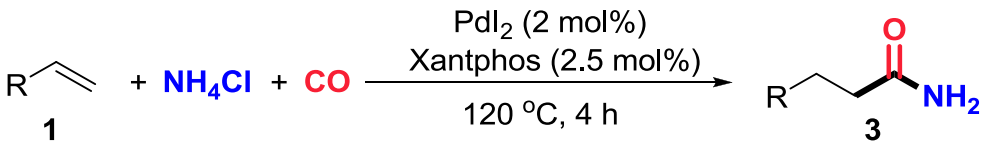
3. General procedure for the hydroaminocarbonylation reaction

3.1 Reaction condition A:



In a glove box, a mixture of NH_4Cl (106.8 mg, 2.0 mmol), Pd(*t*-$Bu_3P)_2$ (25.5 mg, 0.05 mmol) and NMP (5.0 mL) was added into a dry glass vessel. The resulting mixture was stirred for 10 minutes at room temperature and then alkenes **1** (1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from the glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 120 °C for 15 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The regioselectivity was measured by GC and GC-MS, respectively. Then the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1 - 1/1) to give the desired products **2**.

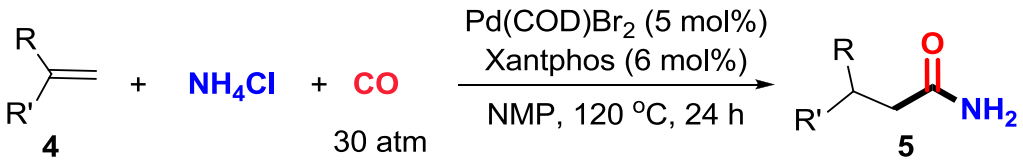
3.2 Reaction condition B:



In a glove box, a mixture of NH_4Cl (106.8 mg, 2.0 mmol), PdI_2 (7.2 mg, 0.02 mmol), Xantphos (14.5 mg, 0.025 mmol) and NMP (3.0 mL) was added into a dry glass vessel. The resulting mixture was stirred for 10 minutes at room temperature and then alkenes (1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from the glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 120 °C for 4 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The regioselectivity was measured

by GC and GC-MS, respectively. Then the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1 - 1/1) to give the desired products **3**.

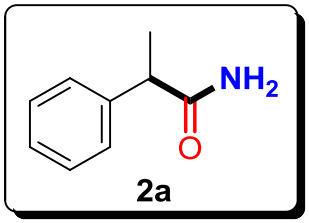
3.3 Reaction condition C:



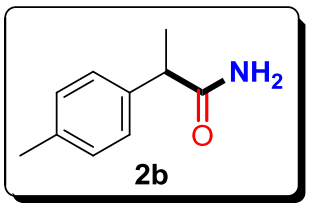
In a glove box, a mixture of NH_4Cl (106.8 mg, 2.0 mmol), $Pd(COD)Br_2$ (18.7 mg, 0.05 mmol), Xantphos (34.7 mg, 0.06 mmol) and NMP (5.0 mL) was added into a dry glass vessel. The resulting mixture was stirred for 10 minutes at room temperature and then alkenes **4** (1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from the glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 120 °C for 24 or 48 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The regioselectivity was measured by GC and GC-MS, respectively. Then the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1 - 1/1) to give the desired products **5**.

4. Experimental characterization data for products

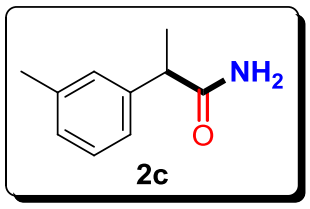
2-phenylpropanamide (2a): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 124.8 mg, 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.39 (d, *J* = 7.2 Hz, 3H), 3.46 (q, *J* = 7.2 Hz, 1H), 5.53 (br, 1H), 6.27 (br, 1H), 7.15-7.25 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.4, 46.5, 127.3, 127.6, 128.9, 141.3, 177.3; **HRMS** (ESI) calcd. for $C_9H_{11}NONa$ [M+Na]: 172.0733, found: 172.0733.



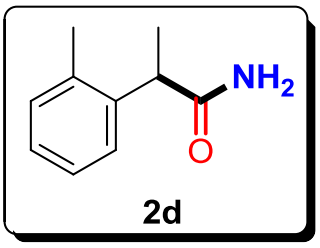
2-*p*-tolylpropanamide (2b): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 130.7 mg, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.48 (d, *J* = 7.2 Hz, 3H), 2.33 (s, 3H), 3.52 (q, *J* = 7.2 Hz, 1H), 5.45 (br, 1H), 6.05 (br, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.3, 21.0, 46.2, 127.5, 129.6, 137.0, 138.3, 177.3; **HRMS** (ESI) calcd. for $C_{10}H_{13}NONa$ [M+Na]: 186.0889, found: 186.0889.



2-*m*-tolylpropanamide (2c): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 125.6 mg, 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.49 (d, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 3.53 (q, *J* = 7.2 Hz, 1H), 5.44 (br, 1H), 6.02 (br, 1H), 7.07-7.11 (m, 3H), 7.21-7.26 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.3, 21.4, 46.5, 124.6, 128.1, 128.3, 128.8, 138.7, 141.2, 177.1; **HRMS** (ESI) calcd. for $C_{10}H_{13}NONa$ [M+Na]: 186.0889, found: 186.0897.

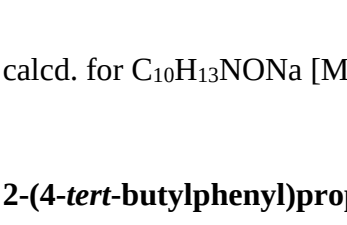


2-*o*-tolylpropanamide (2d): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 126.9



mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.50 (d, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 3.76 (q, *J* = 7.2 Hz, 1H), 5.32 (br, 1H), 6.11 (br, 1H), 7.17-7.24 (m, 3H), 7.29-7.30 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 17.6, 19.6, 43.1, 126.8, 126.8, 127.3, 130.8, 136.3, 139.3, 177.4; **HRMS** (ESI) calcd. for $C_{10}H_{13}NONa$ [M+Na]: 186.0889, found: 186.0894.

2-(4-*tert*-butylphenyl)propanamide (2e): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 160.8 mg, 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.31 (s, 9H), 1.51 (d, *J* = 7.2 Hz, 3H), 3.55 (q, *J* = 7.2 Hz, 1H), 5.37 (br, 1H), 5.72 (br, 1H), 7.22-7.26 (m, 2H), 7.36-7.38 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.2, 31.3, 34.5, 46.1, 125.9, 127.3, 138.1, 150.3, 177.0; **HRMS** (ESI) calcd. for $C_{13}H_{20}NO$ [M+H]: 206.1539, found: 206.1546.



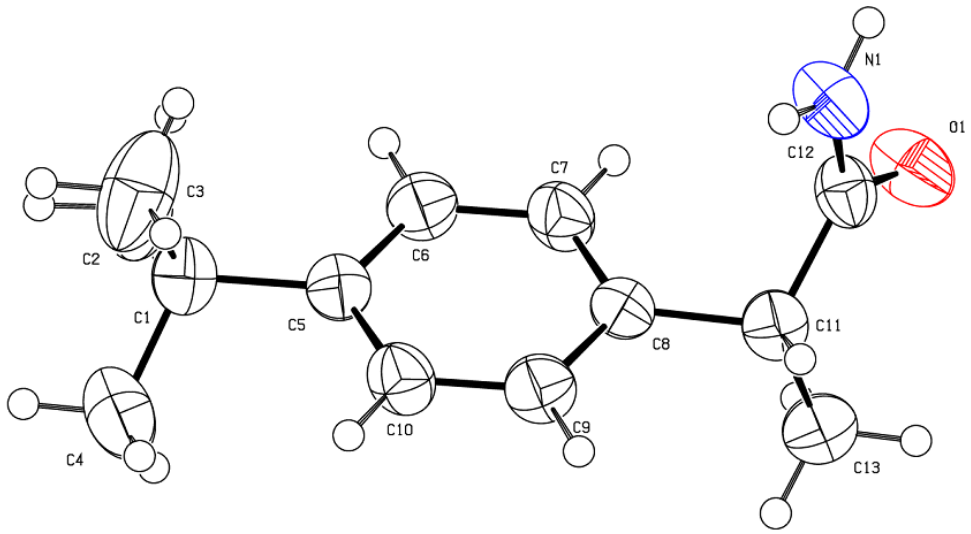
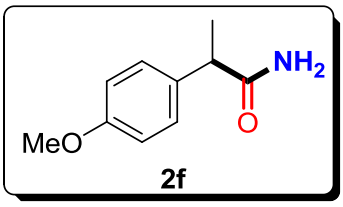


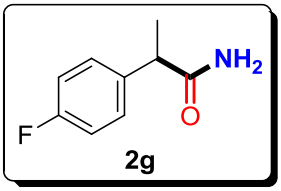
Figure S1. ORTEP drawing of product **2e**

2-(4-methoxyphenyl)propanamide (2f): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid,

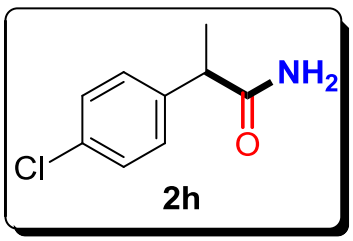


146.8 mg, 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.38 (d, *J* = 7.2 Hz, 3H), 3.43 (q, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 5.50 (br, 1H), 6.21 (br, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.4, 45.7, 55.3, 114.3, 128.6, 133.4, 158.8, 177.6; **HRMS** (ESI) calcd. for $C_{13}H_{19}NONa$ [M+Na]: 202.0838, found: 202.0838.

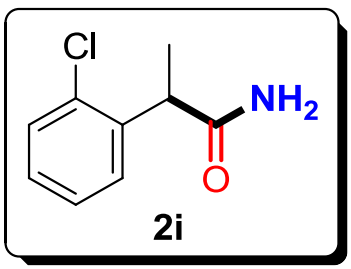
2-(4-fluorophenyl)propanamide (2g): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 149.3 mg, 89% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.46 (d, *J* = 7.2 Hz, 3H), 3.54 (q, *J* = 7.2 Hz, 1H), 5.65 (br, 1H), 6.42 (br, 1H), 6.99-7.04 (m, 2H), 7.24-7.29 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.6, 45.7, 115.6, 115.8, 129.1, 129.1, 137.0, 137.0, 160.7, 163.2, 177.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.37; **HRMS** (ESI) calcd. for $C_9H_{10}FNONa$ [M+Na]: 190.0639, found: 190.0643.



2-(4-chlorophenyl)propanamide (2h): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 138.7 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.46 (d, *J* = 7.2 Hz, 3H), 3.53 (q, *J* = 7.2 Hz, 1H), 5.58 (br, 1H), 6.27 (br, 1H), 7.22-7.25 (m, 2H), 7.28-7.31 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.5, 45.9, 128.9, 129.0, 133.1, 139.7, 176.6; **HRMS** (ESI) calcd. for $C_9H_{11}ClNO$ [M+H]: 184.0524, found: 184.0521.

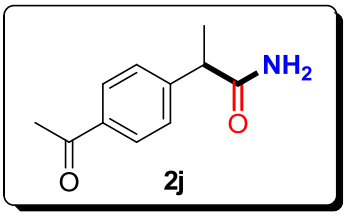


2-(2-chlorophenyl)propanamide (2i): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 135.2 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.48 (d, *J* = 7.2 Hz, 3H), 4.08 (q, *J* = 7.2 Hz, 1H), 5.54 (br, 1H), 6.15

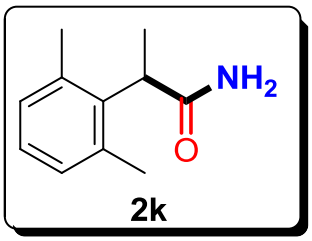


(br, 1H), 7.18-7.29 (m, 2H), 7.37-7.43 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 17.3, 42.5, 127.5, 128.5, 129.7, 133.6, 138.7, 175.9; **HRMS** (ESI) calcd. for $C_9H_{10}ClNONa$ [M+Na]: 206.0343, found: 206.0350.

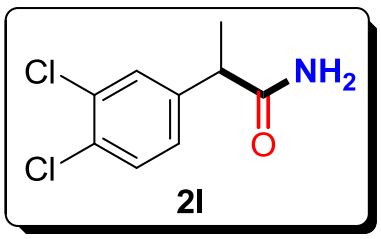
2-(4-acetylphenyl)propanamide (2j): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 146.3 mg, 77% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 1.33 (d, J = 6.8 Hz, 3H), 2.56 (s, 3H), 3.65 (q, J = 7.2 Hz, 1H), 6.92 (br, 1H), 7.45-7.47 (m, 3H), 7.89 (d, J = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 18.2, 26.6, 44.9, 127.5, 128.2, 135.2, 147.8, 174.6, 197.5; **HRMS** (ESI) calcd. for $C_{11}H_{13}NO_2Na$ [M+Na]: 214.0838, found: 214.0831.



2-(2,6-dimethylphenyl)propanamide (2k): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 148.2 mg, 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.50 (d, J = 7.2 Hz, 3H), 2.30-2.31 (m, 6H), 3.74 (q, J = 7.2 Hz, 1H), 5.29 (br, 1H), 5.84 (br, 1H), 6.99-7.00 (m, 1H),7.06-7.10 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 17.6, 19.1, 21.1, 43.0, 127.5, 128.0, 130.7, 133.0, 136.2, 139.1, 177.3; **HRMS** (ESI) calcd. for $C_{11}H_{15}NONa$ [M+Na]: 200.1046, found: 200.1041.

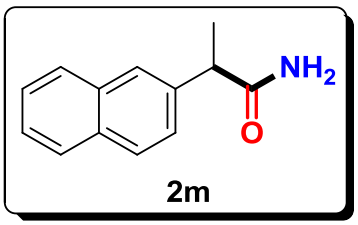


2-(3,4-dichlorophenyl)propanamide (2l): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 148.7 mg, 69% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.48 (d, J = 7.2 Hz, 3H), 3.52 (q, J = 7.2 Hz, 1H), 5.57 (br, 1H), 6.12 (br, 1H), 7.15-7.18 (m, 1H), 7.40-7.42 (m,

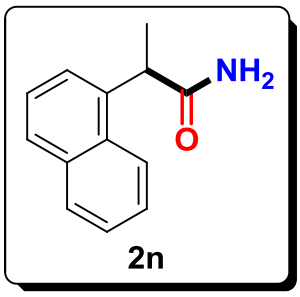


2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.5, 45.7, 127.0, 129.6, 130.8, 131.4, 132.8, 141.3, 175.7; **HRMS** (ESI) calcd. for $C_9H_{10}Cl_2NO$ [M+H]: 218.0134, found: 218.0145.

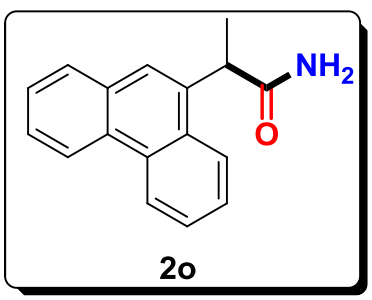
2-(naphthalen-2-yl)propanamide (2m): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 141.3 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.58 (d, *J* = 7.2 Hz, 3H), 3.71 (q, *J* = 7.2 Hz, 1H), 5.45 (br, 1H), 5.97 (br, 1H), 7.25-7.50 (m, 3H), 7.74-7.82 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.3, 46.7, 125.7, 126.0, 126.3, 126.4, 127.7, 127.7, 128.8, 132.6, 133.5, 138.7, 176.8; **HRMS** (ESI) calcd. for $C_{13}H_{13}NONa$ [M+Na]: 222.0889, found: 222.0896.



2-(naphthalen-1-yl)propanamide (2n): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 135.2 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.63 (d, *J* = 7.2 Hz, 3H), 4.24 (q, *J* = 7.2 Hz, 1H), 5.37 (br, 1H), 6.09 (br, 1H), 7.24-7.52 (m, 4H), 7.75-7.77 (m, 1H), 7.83-7.85 (m, 1H), 8.00-8.02 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 17.9, 43.2, 123.3, 124.8, 125.7, 125.9, 126.6, 128.1, 129.0, 131.5, 134.1, 137.1, 177.5; **HRMS** (ESI) calcd. for $C_{13}H_{13}NONa$ [M+Na]: 222.0889, found: 222.0890.

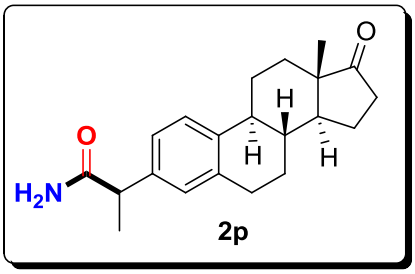


2-(phenanthren-9-yl)propanamide (2o): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 169.0 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.78 (d, *J* = 7.2 Hz, 3H), 4.30 (q, *J* = 7.2 Hz, 1H), 5.37 (br, 1H), 5.51

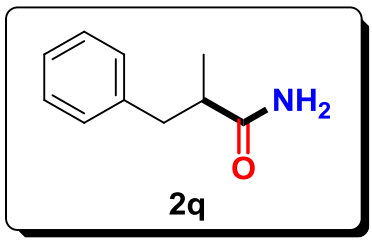


(br, 1H), 7.61-7.69 (m, 4H), 7.77 (s, 1H), 7.87-7.89 (m, 1H), 8.09-8.12 (m, 1H), 8.66-8.68 (m, 1H), 8.74-8.76 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 17.6, 44.0, 122.5, 123.4, 124.1, 125.9, 126.8, 127.0, 127.0, 127.2, 128.6, 130.1, 130.4, 130.9, 131.4, 135.2, 177.1; **HRMS** (ESI) calcd. for $C_{17}H_{15}NONa$ [M+Na]: 272.1046, found: 272.1041.

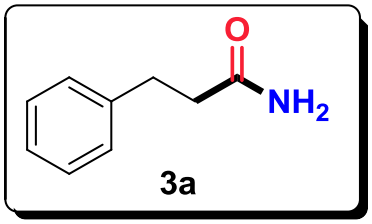
3-(1-carbamoylethyl)estrone (2p): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 145.1 mg, 45% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.91 (s, 3H), 1.39-1.68 (m, 9H), 1.95-2.19 (m, 4H), 2.27-2.31 (m, 1H), 2.40-2.54 (m, 2H), 2.89-2.92 (m, 2H), 3.51 (q, *J* = 7.2 Hz, 1H), 5.51 (br, 1H), 6.00 (br, 1H), 7.05 (s, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.9, 18.4, 21.6, 25.7, 26.5, 29.4, 31.6, 35.9, 38.1, 44.3, 46.1, 48.0, 50.5, 125.0, 125.0, 125.9, 128.1, 128.2, 137.1, 138.8, 138.9, 177.2, 221.0; **HRMS** (ESI) calcd. for $C_{21}H_{27}NO_2Na$ [M+Na]: 348.1934, found: 348.1933.



2-methyl-3-phenylpropanamide (2q): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 169.0 mg, 68% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.18 (d, *J* = 6.8 Hz, 3H), 2.51-2.56 (m, 1H), 2.65-2.70 (m, 1H), 2.96-3.01 (m, 1H), 5.34 (br, 1H), 5.67 (br, 1H), 7.18-7.22 (m, 3H), 7.26-7.30 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 17.6, 40.3, 42.9, 126.4, 128.5, 129.0, 139.7, 178.3; **HRMS** (ESI) calcd. for $C_{10}H_{13}NONa$ [M+Na]: 186.0899, found: 186.0895.

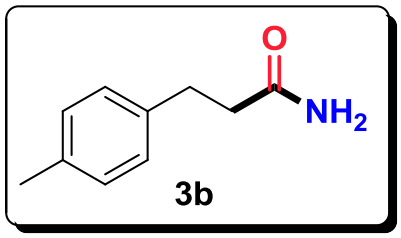


3-phenylpropanamide (3a): The title compound was prepared according to the

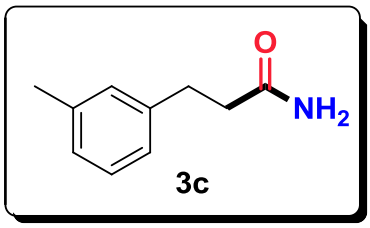


general procedure and purified by column chromatography to give a white solid, 107.6 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.51 (t, *J* = 7.6 Hz, 2H), 2.95 (t, *J* = 8.0 Hz, 2H), 5.59 (br, 1H), 6.03 (br, 1H), 7.19-7.21 (m, 3H), 7.26-7.30 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 31.4, 37.5, 126.3, 128.3, 128.6, 140.7, 174.9; **HRMS** (ESI) calcd. for $C_9H_{11}NONa$ [M+Na]: 172.0733, found: 172.0734.

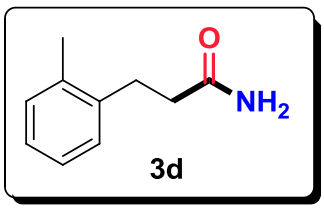
3-*p*-tolylpropanamide (3b): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 118.6 mg, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.49 (t, *J* = 7.2 Hz, 2H), 2.91 (t, *J* = 8.0 Hz, 2H), 5.56 (br, 1H), 5.99 (br, 1H), 7.09 (s, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.0, 31.0, 37.7, 128.2, 128.5, 129.3, 135.8, 137.6, 175.0; **HRMS** (ESI) calcd. for $C_{10}H_{13}NONa$ [M+Na]: 186.0889, found: 186.0895.



3-*m*-tolylpropanamide (3c): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 112.5 mg, 69% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.49 (t, *J* = 7.6 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 5.68 (br, 1H), 6.18 (br, 1H), 6.98-7.01 (m, 3H), 7.15-7.18 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.4, 31.4, 37.6, 125.3, 127.0, 128.5, 129.1, 138.2, 140.7, 175.2; **HRMS** (ESI) calcd. for $C_{10}H_{13}NONa$ [M+Na]: 186.0889, found: 186.0893.

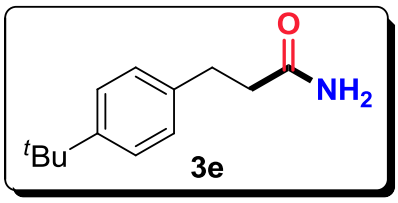


3-*o*-tolylpropanamide (3d): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 140.2 mg, 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.46 (dd, J_1 = 8.0 Hz, J_2 =

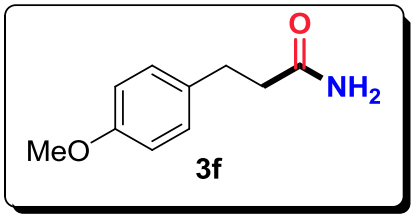


10.0 Hz, 2H), 2.92 (dd, J_1 = 8.0 Hz, J_2 = 10.0 Hz, 2H), 5.70 (br, 1H), 6.22 (br, 1H), 7.10-7.15 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.3, 28.7, 36.2, 126.2, 126.4, 128.5, 130.4, 136.0 138.9, 175.3; **HRMS** (ESI) calcd. for $C_{10}H_{13}NONa$ [M+Na]: 186.0889, found: 186.0893.

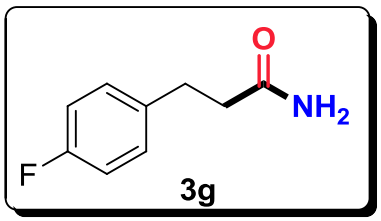
3-(4-*tert*-butylphenyl)propanamide (3e): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 158.1 mg, 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.30 (s, 9H), 2.49-2.53 (m, 2H), 2.92 (t, J = 8.0 Hz, 2H), 5.69 (br, 1H), 6.18 (br, 1H), 7.13 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 30.9, 31.4, 34.4, 37.5, 125.5, 128.0, 137.6, 149.1, 175.3; **HRMS** (ESI) calcd. for $C_{13}H_{19}NONa$ [M+Na]: 228.1359, found: 228.1364.



3-(4-methoxyphenyl)propanamide (3f): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 124.0 mg, 69% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.49 (t, J = 8.0 Hz, 2H), 2.90 (t, J = 8.0 Hz, 2H), 3.78 (s, 3H), 5.49 (br, 1H), 5.80 (br, 1H), 6.82 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 30.6, 37.8, 55.3, 114.0, 129.3, 132.7, 158.1, 174.9; **HRMS** (ESI) calcd. for $C_{10}H_{13}NO_2Na$ [M+Na]: 202.0838, found: 202.0837.

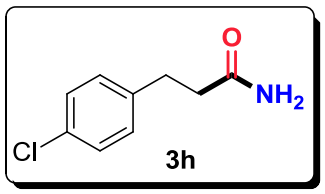


3-(4-fluorophenyl)propanamide (3g): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 112.3 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.40 (t, J = 8.0



Hz, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 5.68 (br, 1H), 6.12 (br, 1H), 6.85-6.90 (m, 2H), 7.04-7.08 (m 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 30.5, 37.5, 115.2, 115.4, 129.7, 129.8, 136.4, 136.4, 160.2, 162.7, 174.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.0; **HRMS** (ESI) calcd. for $C_9H_{11}FNONa$ [M+Na]: 168.0819, found: 168.0827.

3-(4-chlorophenyl)propanamide (3h): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 123.2 mg, 67% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.50 (t, *J* = 8.0 Hz, 2H), 2.93 (t, *J* = 8.0 Hz, 2H), 5.54 (br, 1H), 6.01 (br, 1H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.24-7.27 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 30.6, 37.3, 128.7, 129.7, 132.1, 139.1, 174.6; **HRMS** (ESI) calcd. for $C_9H_{10}ClNONa$ [M+Na]: 206.0343, found: 206.0350.



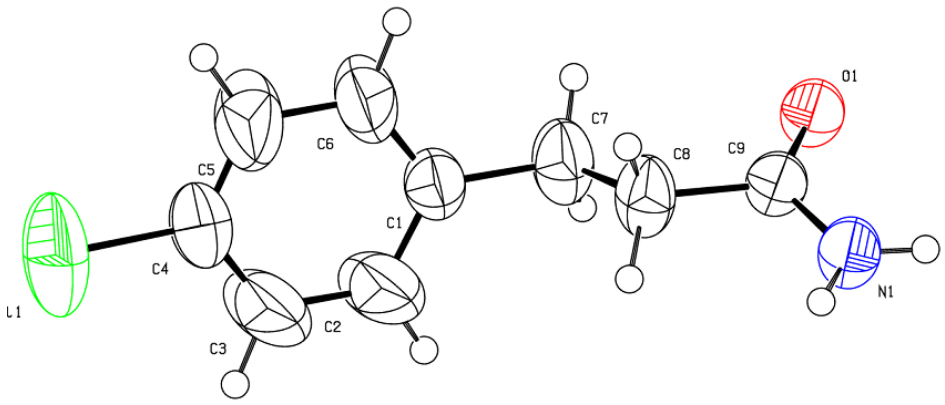
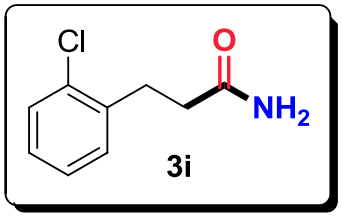


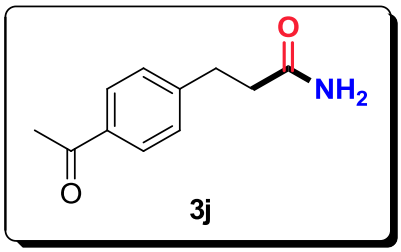
Figure S2. ORTEP drawing of product **3h**

3-(2-chlorophenyl)propanamide (3i): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 141.5 mg, 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.53 (t, *J* = 8.0 Hz,

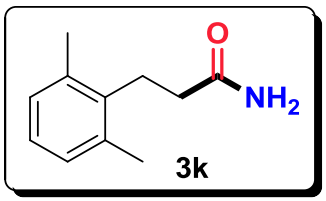


2H), 3.06 (t, J = 8.0 Hz, 2H), 5.65 (br, 1H), 6.02 (br, 1H), 7.13-7.20 (m, 2H), 7.24-7.27 (m, 1H), 7.32-7.34 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 29.4, 35.5, 127.0, 127.9, 129.5, 130.6, 133.8, 138.2, 174.6; **HRMS** (ESI) calcd. for $C_9H_{10}ClNONa$ [M+Na]: 206.0343, found: 206.0351.

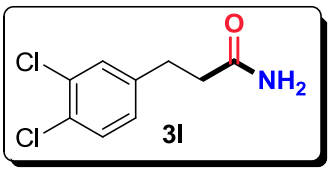
3-(4-acetylphenyl)propanamide (3j): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 138.9 mg, 73% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 2.39 (t, J = 7.6 Hz, 2H), 2.55 (s, 3H), 2.88 (t, J = 7.6 Hz, 2H), 6.80 (br, 1H), 7.32 (br, 1H), 7.35 (d, J = 7.6 Hz, 2H), 7.86 (d, J = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 26.6, 30.7, 36.1, 128.3, 128.5, 134.8, 147.3, 173.1, 197.5; **HRMS** (ESI) calcd. for $C_{11}H_{13}NO_2Na$ [M+Na]: 214.0838, found: 214.0834.



3-(2,6-dimethylphenyl)propanamide (3k): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 150.5 mg, 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.27-2.28 (m, 6H), 2.44 (dd, J_1 = 8.0 Hz, J_2 = 10.0 Hz, 2H), 2.88 (dd, J_1 = 8.0 Hz, J_2 = 10.0 Hz, 2H), 5.59 (br, 1H), 6.09 (br, 1H), 6.92-6.96 (m, 2H), 7.02-7.04 (d, J = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.8, 21.0, 28.7, 36.3, 127.1, 129.4, 130.3, 132.8, 135.6, 138.6, 175.2; **HRMS** (ESI) calcd. for $C_{11}H_{16}NO$ [M+H]: 178.1233, found: 178.1236.

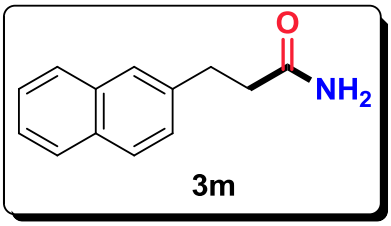


3-(3,4-dichlorophenyl)propanamide (3l): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 149.2 mg, 69% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.50 (t, J = 8.0 Hz,

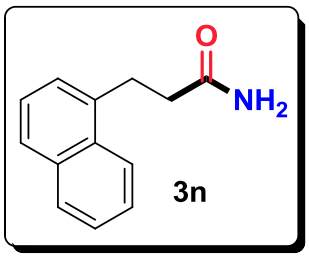


2H), 2.91 (t, J = 8.0 Hz, 2H), 5.58 (br, 1H), 5.99 (br, 1H), 7.03-7.06 (m, 1H), 7.27-7.35 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 30.3, 36.8, 127.9, 130.3, 130.3, 130.4, 132.3, 141.0, 174.0; **HRMS** (ESI) calcd. for $C_9H_{10}Cl_2NO$ [M+H]: 218.0134, found: 218.0140.

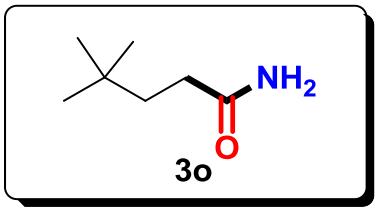
3-(naphthalen-2-yl)propanamide (3m): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 154.3 mg, 78% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 2.45-2.51 (m, 2H), 2.99 (t, J = 8.0 Hz, 2H), 6.82 (br, 1H), 7.35 (br, 1H), 7.40-7.50 (m, 3H), 7.70 (s, 1H), 7.82-7.87 (m, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 31.0, 36.6, 125.2, 125.9, 126.0, 127.2, 127.3, 127.4, 127.6, 131.6, 133.1, 139.1, 173.4; **HRMS** (ESI) calcd. for $C_{13}H_{14}NO$ [M+H]: 200.1070, found: 200.1077.



3-(naphthalen-1-yl)propanamide (3n): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 162.7 mg, 82% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 2.48 (t, J = 8.0 Hz, 2H), 3.28 (t, J = 8.0 Hz, 2H), 6.85 (br, 1H), 7.37-7.45 (m, 3H), 7.50-7.59 (m, 2H), 7.77-7.79 (m, 1H), 7.92-7.94 (m, 1H), 8.08-8.10 (m, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 27.9, 36.1, 123.5, 125.5, 125.6, 125.7, 126.0, 126.5, 128.6, 131.2, 133.4, 137.5, 173.4; **HRMS** (ESI) calcd. for $C_{13}H_{14}NO$ [M+H]: 200.1070, found: 200.1077.

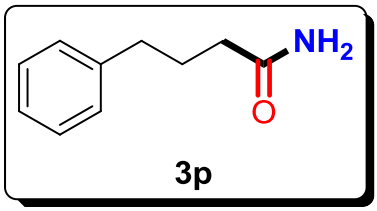


4,4-dimethylpentanamide (3o): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 95.1 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.91 (s, 9H),

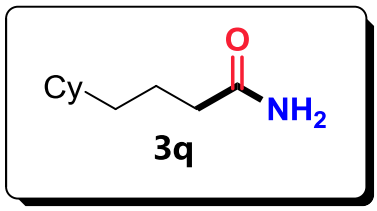


1.53-1.57 (m, 2H), 2.17-2.21 (m, 2H), 5.71 (br, 1H), 6.20 (br, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 29.1, 30.1, 31.6, 39.3, 176.7; **HRMS** (ESI) calcd. for $C_7H_{15}NONa$ [M+Na]: 152.1046, found: 152.1049.

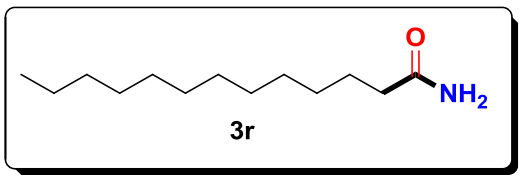
4-phenylbutanamide (3p): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 87.5 mg, 54% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.92-1.99 (m, 2H), 2.20 (t, *J* = 7.2 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 5.61 (br, 1H), 6.13 (br, 1H), 7.16-7.20 (m, 3H), 7.26-7.29 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 26.9, 35.0, 35.1, 126.0, 128.4, 128.5, 141.4, 175.7; **HRMS** (ESI) calcd. for $C_{10}H_{13}NONa$ [M+Na]: 186.0889, found: 186.0887.



4-cyclohexylbutanamide (3q): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 93.8 mg, 56% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.82-0.91 (m, 2H), 1.07-1.25 (m, 6H), 1.61-1.80 (m, 7H), 2.00-2.24 (m, 2H), 5.43 (br, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 22.9, 26.3, 26.6, 33.3, 36.2, 37.0, 37.4, 175.6; **HRMS** (ESI) calcd. for $C_{10}H_{19}NONa$ [M+Na]: 192.1359, found: 192.1359.

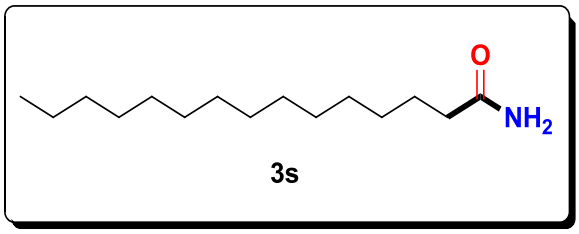


tridecanamide (3r): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 124.8 mg, 59% yield. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ 0.86 (t, *J* = 6.8 Hz, 3H), 1.24-1.30 (m, 18H), 1.44-1.50 (m, 2H), 2.01 (t, *J* = 7.6 Hz, 2H), 6.68 (br, 1H), 7.22 (br, 1H); **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 13.9, 22.1, 25.1, 28.7, 28.8, 28.9, 29.0, 29.0,

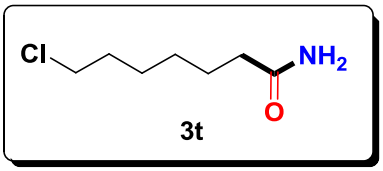


31.3, 35.1, 174.3; **HRMS** (ESI) calcd. for $C_{13}H_{27}NONa$ [M+Na]: 236.1985, found: 236.1982.

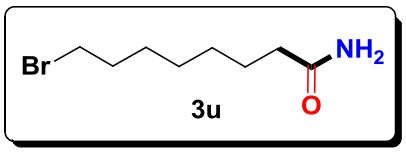
Pentadecanamide (3s): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 135.3 mg, 56% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 0.86 (t, J = 6.8 Hz, 3H), 1.24-1.29 (m, 22H), 1.44-1.48 (m, 2H), 2.01 (t, J = 7.6 Hz, 2H), 6.68 (br, 1H), 7.23 (br, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 13.9, 22.1, 25.1, 28.7, 28.8, 28.9, 29.0, 29.0, 31.3, 35.1, 174.4; **HRMS** (ESI) calcd. for $C_{15}H_{31}NONa$ [M+Na]: 264.2298, found: 264.2299.



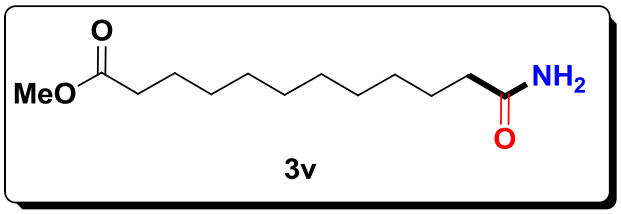
7-chloroheptanamide (3t): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 103.5 mg, 63% yield. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 1.31-1.39 (m, 2H), 1.41-1.49 (m, 2H), 1.56-1.63 (m, 2H), 1.73-1.80 (m, 2H), 2.17 (t, J = 7.2 Hz, 2H), 3.60 (t, J = 6.8 Hz, 2H), 6.26 (br, 1H), 6.76 (br, 1H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 25.2, 26.4, 28.3, 32.4, 35.1, 44.9, 174.3; **HRMS** (ESI) calcd. for $C_7H_{14}NOClNa$ [M+Na]: 186.0656, found: 186.0651.



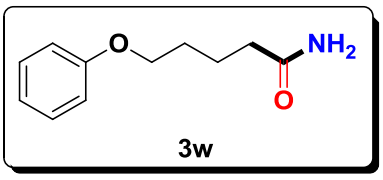
8-bromooctanamide (3u): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 112.5 mg, 51% yield. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 1.33-1.46 (m, 6H), 1.57-1.60 (m, 2H), 1.73-1.80 (m, 2H), 2.16 (t, J = 7.2 Hz, 2H), 3.60 (t, J = 6.4 Hz, 2H), 6.14 (br, 1H), 6.71 (br, 1H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 25.3, 26.5, 28.5, 32.5, 35.2, 44.9, 174.2; **HRMS** (ESI) calcd. for $C_{18}H_{16}NOBrNa$ [M+Na]: 244.0307, found: 244.0302.



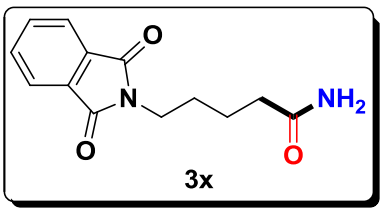
Methyl 12-amino-12-oxododecanoate (3v): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 134.7 mg, 55% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 1.24 (m, 12H), 1.44-1.52 (m, 4H), 2.01 (t, J = 7.2 Hz, 2H), 2.28 (t, J = 7.2 Hz, 2H), 3.58 (s, 3H), 6.68 (br, 1H), 7.22 (br, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 24.9, 25.6, 28.9, 29.1, 29.2, 29.3, 29.3, 29.4, 33.7, 35.6, 51.6, 173.8, 174.8; **HRMS** (ESI) calcd. for $C_{13}H_{25}NO_3Na$ [M+Na]: 266.1727, found: 266.1731.



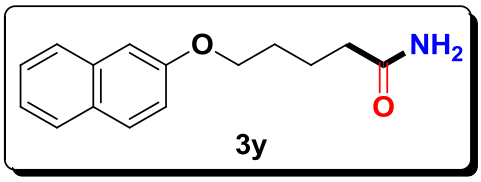
5-phenoxypentanamide (3w): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 121.3 mg, 63% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 1.61-1.71 (m, 4H), 2.11 (t, J = 7.6 Hz, 2H), 3.95 (t, J = 6.0 Hz, 2H), 6.75 (br, 1H), 6.89-6.93 (m, 3H), 7.25-7.29 (m, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 22.9, 28.1, 35.0, 37.7, 123.4, 132.0, 134.8, 168.4, 174.4; **HRMS** (ESI) calcd. for $C_{11}H_{15}NO_2Na$ [M+Na]: 216.0995, found: 216.0993.



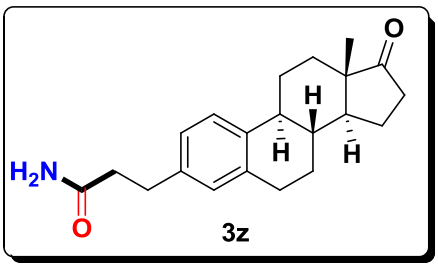
5-(1,3-dioxoisoindolin-2-yl)pentanamide (3x): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 131.2 mg, 53% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 1.45-1.62 (m, 4H), 2.08 (t, J = 7.2 Hz, 2H), 3.57 (t, J = 6.8 Hz, 2H), 6.74 (br, 1H), 7.26 (br, 1H), 7.82-7.88 (m, 4H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 22.9, 28.1, 35.0, 37.7, 123.4, 132.0, 134.8, 168.4, 174.4; **HRMS** (ESI) calcd. for $C_{13}H_{14}N_2O_3Na$ [M+Na]: 269.0897, found: 269.0889.



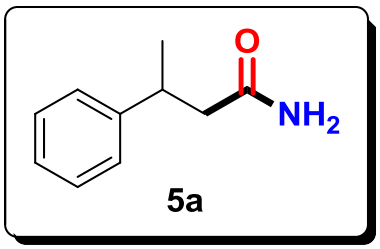
5-(Naphthalen-2-yloxy)pentanamide (3y): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 171.1 mg, 70% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 1.65-1.73 (m, 2H), 1.75-1.82 (m, 2H), 2.15 (t, J = 7.2 Hz, 2H), 4.09 (t, J = 6.4 Hz, 2H), 6.78 (br, 1H), 7.15-7.18 (m, 1H), 7.31-7.36 (m, 3H), 7.44-7.47 (m, 1H), 7.79-7.83 (m, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 22.3, 28.7, 35.2, 67.7, 107.0, 119.2, 123.9, 126.8, 127.1, 128.0, 128.9, 129.7, 134.8, 157.0, 174.6; **HRMS** (ESI) calcd. for $C_{15}H_{17}NO_2Na$ [M+Na]: 266.1151, found: 266.1162.



3-(2-carbamoylethyl)estrone (3z): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 210.2 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.90 (s, 3H), 1.37-1.67 (m, 6H), 1.93-2.18 (m, 4H), 2.24-2.28 (m, 1H), 2.38-2.41 (m, 1H), 2.47-2.54 (m, 3H), 2.88-2.92 (m, 4H), 5.69 (br, 1H), 5.99 (br, 1H), 6.95 (s, 1H), 6.99 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.9, 21.6, 25.8, 26.6, 29.4, 30.9, 31.6, 35.9, 37.5, 38.2, 44.3, 48.0, 50.5, 125.6, 125.7, 129.0, 136.7, 137.7, 138.2, 175.0, 221.1; **HRMS** (ESI) calcd. for $C_{21}H_{27}NO_2Na$ [M+Na]: 348.1934, found: 348.1918.

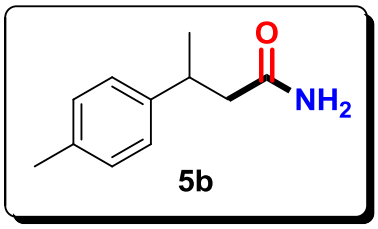


3-phenylbutanamide (5a): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 132.9 mg, 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.29 (d, J = 8.0 Hz, 3H), 2.37-2.42 (m, 1H), 2.46-2.52 (m, 1H), 3.20-3.29 (m,

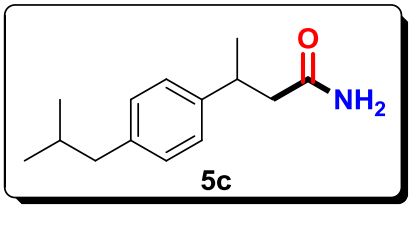


1H), 5.68 (br, 1H), 6.16 (br, 1H), 7.17-7.22 (m, 3H), 7.25-7.30 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.8, 36.7, 44.7, 126.5, 126.8, 128.6, 145.9, 174.7; **HRMS** (ESI) calcd. for $C_{10}H_{14}NO$ [M+H]: 164.1073, found: 164.1070.

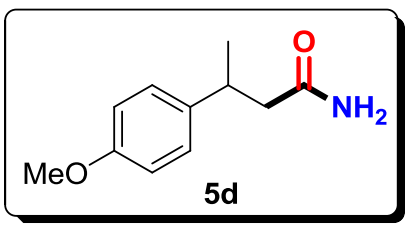
3-*p*-tolylbutanamide (5b): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 125.3 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.28 (d, *J* = 6.8 Hz, 3H), 2.31 (s, 3H), 2.36-2.42 (m, 1H), 2.46-2.51 (m, 1H), 3.17-3.26 (m, 1H), 5.52 (br, 1H), 6.00 (br, 1H), 7.09-7.13 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.0, 21.9, 36.4, 44.9, 126.6, 129.3, 136.0, 142.8, 174.7; **HRMS** (ESI) calcd. for $C_{11}H_{16}NO$ [M+H]: 178.1226, found: 178.1233.



3-(4-isobutylphenyl)butanamide (5c): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 161.2 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.81 (d, *J* = 6.8 Hz, 6H), 1.23 (d, *J* = 6.8 Hz, 3H), 1.71-1.81 (m, 1H), 2.31-2.37 (m, 3H), 2.41-2.46 (m, 1H), 3.12-3.21 (m, 1H), 5.26 (br, 1H), 5.57 (br, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.8, 22.4, 30.2, 36.4, 45.0, 45.0, 126.4, 129.3, 139.8, 143.0, 174.4; **HRMS** (ESI) calcd. for $C_{14}H_{21}NONa$ [M+Na]: 242.1515, found: 242.1517.

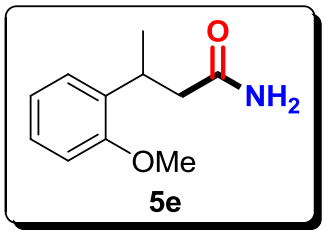


3-(4-methoxyphenyl)butanamide (5d): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 173.1 mg, 90% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.29 (d, *J* = 6.8 Hz, 3H), 2.37-2.50 (m, 2H), 3.20-3.25 (m, 1H), 3.78 (s, 3H), 5.38 (br, 1H), 5.73 (br, 1H), 6.83-6.85 (m, 2H), 7.14-7.16 (m, 2H);

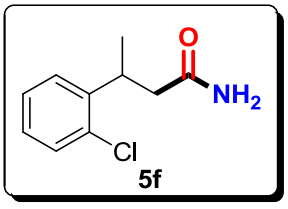


^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 36.0, 45.1, 55.2, 114.0, 127.7, 137.8, 158.1, 174.4; **HRMS** (ESI) calcd. for $C_{11}H_{15}NO_2Na$ [M+Na]: 216.0995, found: 216.1000.

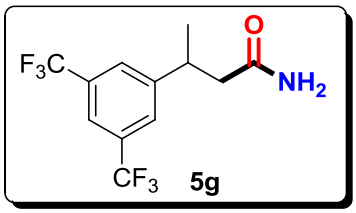
3-(2-methoxyphenyl)butanamide (5e): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 154.1 mg, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.28 (d, *J* = 6.8 Hz, 3H), 2.35-2.41 (m, 1H), 2.59-2.64 (m, 1H), 3.57-3.66 (m, 1H), 3.83 (s, 3H), 5.60 (br, 1H), 5.90 (br, 1H), 6.85-6.94 (m, 2H), 7.17-7.21 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.2, 30.2, 43.4, 55.4, 110.7, 120.8, 126.9, 127.4, 133.7, 156.7, 175.0; **HRMS** (ESI) calcd. for $C_{11}H_{15}NO_2Na$ [M+Na]: 216.0995, found: 216.1001.



3-(2-chlorophenyl)butanamide (5f): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 139.8 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.32 (d, *J* = 6.8 Hz, 3H), 2.34-2.40 (m, 1H), 2.60-2.65 (m, 1H), 3.71-3.80 (m, 1H), 5.61 (br, 1H), 6.05 (br, 1H), 7.12-7.16 (m, 1H), 7.21-7.28 (m, 2H), 7.34-7.36 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.1, 33.0, 43.0, 127.2, 127.6, 129.8, 133.5, 142.7, 174.1; **HRMS** (ESI) calcd. for $C_{10}H_{13}NClO$ [M+H]: 198.0680, found: 198.0686.

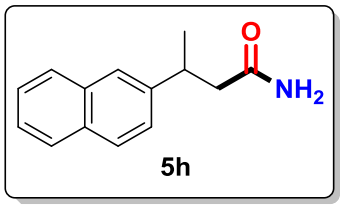


3-(3,5-bis(trifluoromethyl)phenyl)butanamide (5g): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 218.3 mg, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.36 (d, *J* = 6.8 Hz, 3H), 2.50-2.52 (m, 2H), 3.46-3.52 (m, 1H), 5.52 (br, 1H), 5.94 (br, 1H), 7.69 (s, 2H), 7.73 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.3, 36.2, 43.9, 119.3, 120.5, 120.5, 120.6, 122.0,

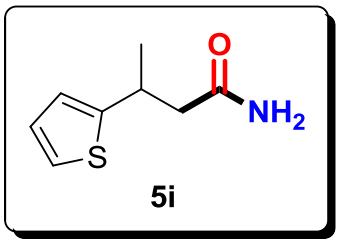


124.7, 127.2, 127.4, 131.2, 131.6, 131.9, 132.2, 148.4, 173.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.86; **HRMS** (ESI) calcd. for $C_{12}H_{11}F_6NONa$ [M+Na]: 322.0637, found: 322.0636.

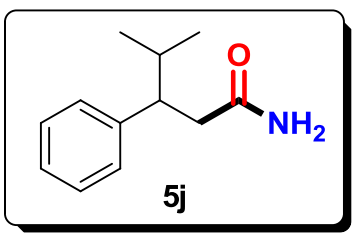
3-(naphthalen-2-yl)butanamide (5h): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 151.4 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.46 (d, *J* = 6.8 Hz, 3H), 2.45-2.51 (m, 1H), 2.73-2.78 (m, 1H), 4.16-4.21 (m, 1H), 5.34 (br, 1H), 5.50 (br, 1H), 7.38-7.56 (m, 4H), 7.72-7.74 (m, 1H), 7.85-7.87 (m, 1H), 8.20-8.22 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.1, 30.9, 44.1, 122.4, 123.1, 125.5, 125.6, 126.2, 127.0, 129.0, 131.2, 134.0, 141.8, 174.1; **HRMS** (ESI) calcd. for $C_{14}H_{16}NO$ [M+H]: 214.1226, found: 214.1226.



3-(thiophen-2-yl)butanamide (5i): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 87.9 mg, 52% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.40 (d, *J* = 6.8 Hz, 3H), 2.43-2.49 (m, 1H), 2.55-2.60 (m, 1H), 3.58-3.66 (m, 1H), 5.40 (br, 1H), 5.63 (br, 1H), 6.86-6.87 (m, 1H), 6.91-6.94 (m, 1H), 7.14-7.15 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 22.7, 32.3, 45.7, 123.1, 123.2, 126.7, 149.8, 173.6; **HRMS** (ESI) calcd. for $C_8H_{11}SNONa$ [M+Na]: 192.0454, found: 192.0451.

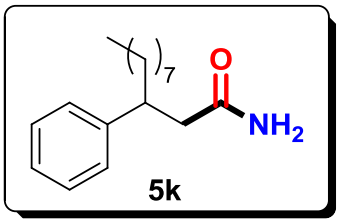


4-methyl-3-phenylpentanamide (5j): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 131.7 mg, 69% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.67 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H), 1.75-1.83 (m, 1H),

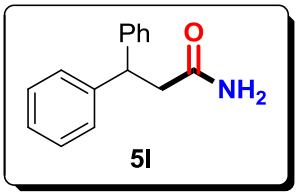


2.34-2.41 (m, 1H), 2.58-2.62 (m, 1H), 2.74-2.79 (m, 1H), 5.26 (br, 1H), 5.64 (br, 1H), 7.07-7.14 (m, 3H), 7.18-7.22 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.3, 20.8, 33.1, 40.3, 49.3, 126.5, 128.2, 128.3, 142.9, 174.9; **HRMS** (ESI) calcd. for $C_{12}H_{18}NO$ [M+H]: 192.1383, found: 192.1388.

3,3-diphenylpropanamide (5k): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 114.3 mg, 51% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.76-0.80 (m, 3H), 1.03-1.21 (m, 12H), 1.50-1.64 (m, 2H), 2.34-2.47 (m, 2H), 2.95-3.02 (m, 1H), 5.17 (br, 1H), 5.47 (br, 1H), 7.11-7.15 (m, 3H), 7.19-7.24 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.1, 22.6, 27.4, 29.2, 29.4, 29.5, 31.8, 36.3, 42.7, 43.8, 126.5, 127.5, 128.6, 144.3, 174.3; **HRMS** (ESI) calcd. for $C_{17}H_{28}NO$ [M+H]: 262.2165, found: 262.2166.



3,3-diphenylpropanamide (5l): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 144.3 mg, 51% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.92 (d, *J* = 6.8 Hz, 2H), 4.54 (t, *J* = 6.8 Hz, 1H), 5.35 (br, 1H), 5.57 (br, 1H), 7.16-7.30 (m, 10H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 41.4, 46.1, 125.6, 126.7, 127.6, 142.6, 172.5; **HRMS** (ESI) calcd. for $C_{15}H_{15}NONa$ [M+Na]: 248.1046, found: 248.1051.



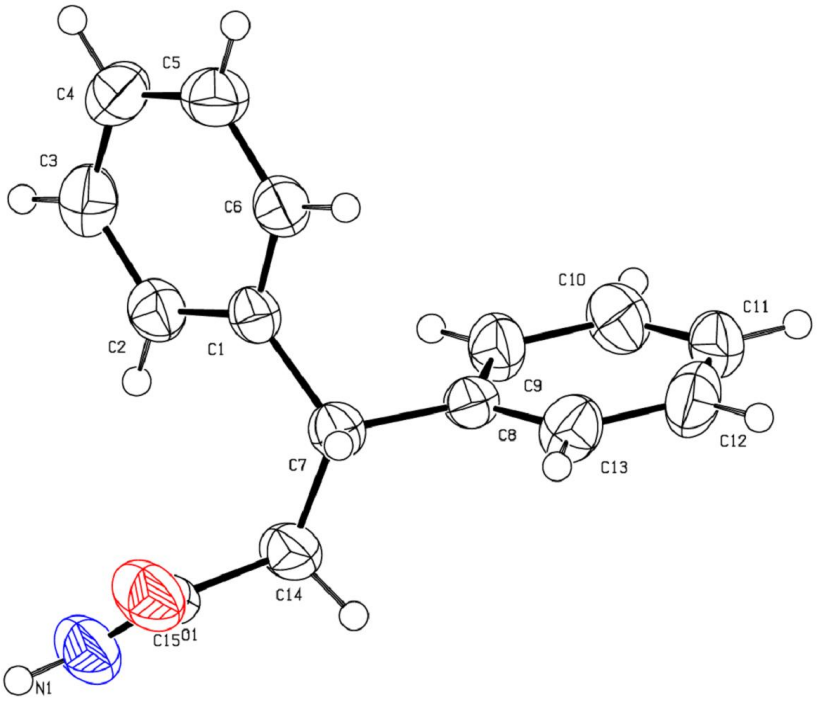
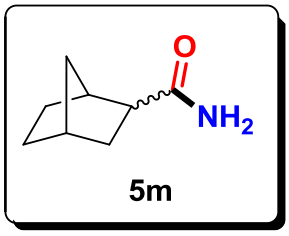
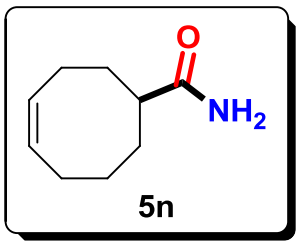


Figure S3. ORTEP drawing of product **5l**

Bicyclo[2.2.1]heptane-2-carboxamide (5m): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 106.8 mg, 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.16-1.26 (m, 3H), 1.38-1.67 (m, 4H), 1.83-1.89 (m, 1H), 2.17-2.21 (m, 0.83H), 2.27-2.30 (m, 1H), 2.35-2.43 (m, 1H), 2.66-2.72 (m, 0.15H), 5.47 (br, 1H), 5.71 (br, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 24.3, 28.6, 29.2, 29.7, 31.4, 34.3, 35.9, 36.5, 40.5, 40.9, 41.4, 47.4, 178.4; **HRMS** (ESI) calcd. for $C_{11}H_{13}NONa$ [M+Na]: 162.0889, found: 162.0891.

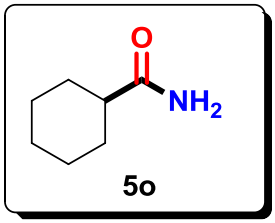


Cyclooct-4-enecarboxamide (5n): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 94.9 mg, 62% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 1.30-1.40 (m, 1H), 1.44-1.54 (m, 2H), 1.59-1.66 (m, 2H), 1.74-1.78 (m, 1H), 2.01-2.06 (m, 1H), 2.08-2.12 (m, 2H), 2.14-2.21 (m, 1H), 2.29-2.33 (m, 1H),

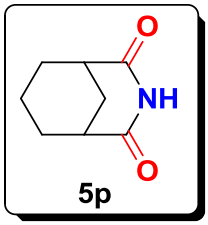


5.62-5.65 (m, 2H), 5.68 (br, 1H), 6.56 (br, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 24.0, 25.4, 27.5, 29.8, 32.0, 43.7, 129.9, 178.9; **HRMS** (ESI) calcd. for $C_9H_{15}NONa$ [M+Na]: 176.1046, found: 176.1052.

Cyclohexanecarboxamide (5o): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 101.3 mg, 79% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.19-1.34 (m, 3H), 1.38-1.48 (m, 2H), 1.66-1.70 (m, 1H), 1.78-1.82 (m, 2H), 1.88-1.92 (m, 2H), 2.11-2.19 (m, 1H), 5.50 (br, 1H), 5.68 (br, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 25.7, 25.7, 29.7, 44.8, 178.7; **HRMS** (ESI) calcd. for $C_7H_{14}NO$ [M+H]: 128.1070, found: 128.1071.



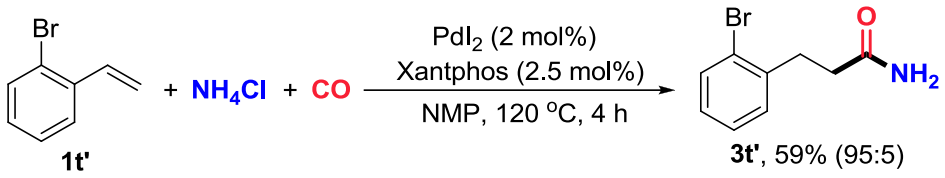
3-Azabicyclo[3.3.1]nonane-2,4-dione (5p): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 90.0 mg, 65% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.47-1.57 (m, 1H), 1.67-1.82 (m, 4H), 2.00-2.05 (m, 2H), 2.21-2.26 (m, 1H), 2.83 (m, 2H), 8.13 (br, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.5, 28.0, 29.0, 37.8, 175.9; **HRMS** (ESI) calcd. for $C_8H_{11}NO_2Na$ [M+Na]: 176.0682, found: 176.0677.



5. Application of primary amides

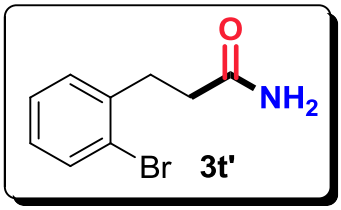
5.1 Synthesis of the antibacterial drug of 3,4-dihydroquinolin-2(1H)-one

5.1.1 Synthesis of 3-(2-bromophenyl)propanamide (3t')

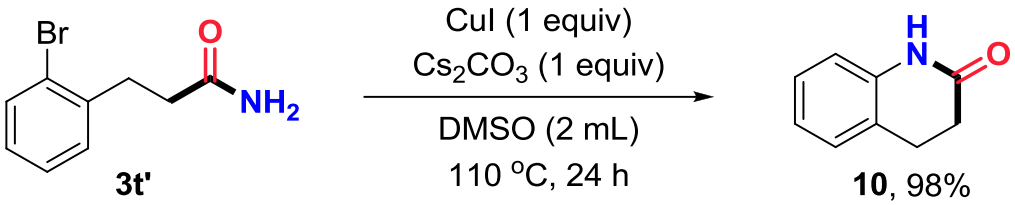


Following our general procedure: In the glove box, a mixture of NH_4Cl (106.8 mg, 2.0 mmol), PdI_2 (7.2 mg, 0.02 mmol), Xantphos (14.5 mg, 0.025 mmol) and NMP (3.0 mL) was added into a dry glass vessel. The resulting mixture was stirred for 10 minutes at room temperature and then 1-bromo-2-vinylbenzene **1t'** (183mg, 1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from the glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 120 °C for 4 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The regioselectivity were measured by GC and GC-MS, respectively. Then the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1 - 1/1) to give the desired products **3-(2-bromophenyl)propanamide (3t')**.

3-(2-bromophenyl)propanamide (3t'): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 135.1 mg, 59% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.54 (t, *J* = 8.0 Hz, 2H), 3.07 (t, *J* = 8.0 Hz, 2H), 5.56 (br, 1H), 5.92 (br, 1H), 7.06-7.10 (m, 1H), 7.21-7.28 (m, 2H), 7.52-7.54 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 31.9, 35.7, 124.3, 127.7, 128.1, 130.7, 132.9, 139.9, 174.4; **HRMS** (ESI) calcd. for $C_9H_{11}BrNO$ [M+H]: 228.0019, found: 228.0025.

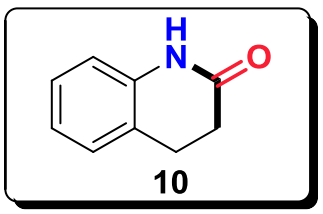


5.1.2 Synthesis of 3,4-dihydroquinolin-2(1H)-one (10)

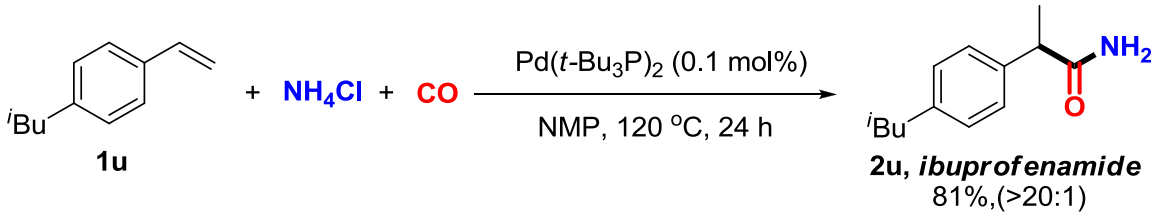


A mixture of 3-(2-bromophenyl)propanamide **3t'** (45.6 mg, 0.2 mmol), CuI (38.0 mg, 0.2 mmol), $CsCO_3$ (77.2 mg, 0.4 mmol) and DMSO (2.0 mL) was added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and then stirred at 110 °C for 24 hours. After cooling to room temperature, the solvents were evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel and eluted with petroleum ethers/ethyl acetate (10:1 - 1:1) to afford the desired product **10** as a white solid.

3,4-dihydroquinolin-2(1H)-one (10): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 28.8 mg, 98% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.57 (t, *J* = 6.8 Hz, 2H), 2.89 (t, *J* = 6.8 Hz, 2H), 6.77 (d, *J* = 7.2 Hz, 1H), 6.89-6.93 (m, 1H), 7.07-7.11 (m, 2H), 9.25 (br, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 25.3, 30.7, 115.6, 123.1, 123.6, 127.5, 127.9, 137.4, 172.3; **HRMS** (ESI) calcd. for C_9H_9NONa [M+Na]: 170.0576, found: 170.0587.



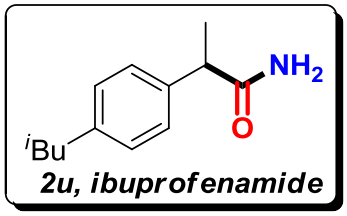
5.2 Synthesis of ibuprofenamide (2u)



Following our general procedure: In the glove box, a mixture of NH_4Cl (106.8 mg, 2.0 mmol), Pd(*t*-$Bu_3P)_2$ (0.5 mg, 0.001 mmol, 0.1 mol%) and NMP (5.0 mL) was added into a dry glass vessel. The resulting mixture was stirred for 10 minutes at room

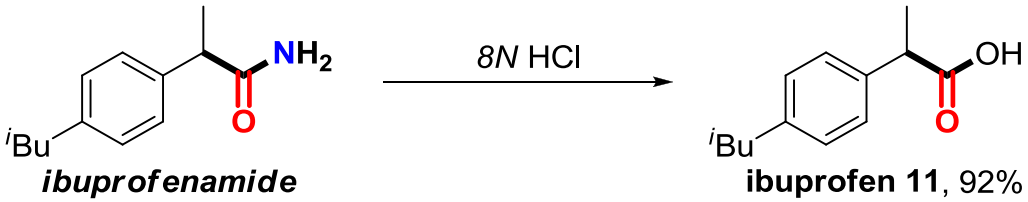
temperature and then 1-isobutyl-4-vinylbenzene (**1u**) (160 mg, 1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from the glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 120 °C for 24 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The regioselectivity were measured by GC and GC-MS, respectively. Then the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1 - 1/1) to give the desired products **ibuprofenamide (2u)**.

Ibuprofenamide: The title compound was prepared according to the above procedure



and purified by column chromatography to give a white solid, 165.8 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.88 (d, *J* = 6.8 Hz, 6H), 1.47 (d, *J* = 7.2 Hz, 3H), 1.79 (m, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 3.53 (q, *J* = 7.2 Hz, 1H), 5.55 (br, 1H), 6.37 (br, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.3, 22.4, 30.2, 31.8, 45.0, 46.2, 127.3, 129.6, 138.5, 140.7, 177.5; **HRMS** (ESI) calcd. for $C_{13}H_{20}NO$ [M+H]: 206.1539, found: 206.1543.

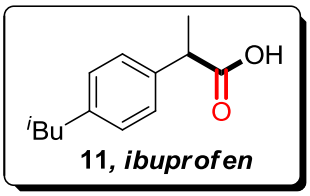
5.3 Synthesis of ibuprofen



A mixture of ibuprofenamide (**2u**) (41.0 mg, 0.2 mmol), HCl (8N, 2.0 mL) and DCM (1.0 mL) was added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and then stirred at 90 °C for 24 hours. After cooling to room temperature, the reaction mixture was quenched with H_2O (10.0 mL) and the residue was extracted with DCM (10 mL x 3). The organic layer extract was dried over anhydrous Na_2SO_4. Then the solvents were evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel

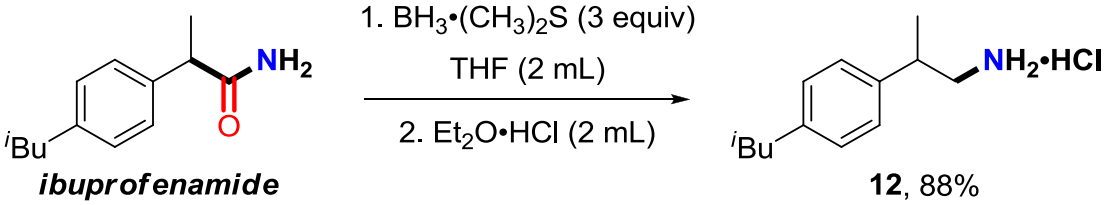
and eluted with petroleum ethers/ethyl acetate (50:1 - 10:1) to afford the desired product **ibuprofen (11)**.

Ibuprofen: The title compound was prepared according to the above procedure and purified by column chromatography to give a white solid, 37.8 mg, 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.81 (d, *J* = 6.8 Hz, 6H), 1.40 (d, *J* = 7.2 Hz, 3H), 1.73 (m, 1H), 2.35 (d, *J* = 7.2 Hz, 2H), 3.59 (q, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H) 11.05 (br, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.1, 22.4, 30.2, 45.0, 45.1, 127.3, 129.4, 137.0, 140.9, 181.2. **HRMS** (ESI) calcd. for $C_{13}H_{18}O_2Na$ [M+Na]: 229.1199, found: 229.1195.



11, *ibuprofen*

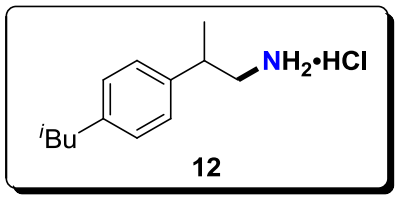
5.4 Synthesis of 2-(4-isobutylphenyl)propan-1-aminium chloride



ibuprofenamide **12**, 88%

A mixture of ibuprofenamide (**2u**) (102.5 mg, 0.5 mmol), THF (2.0 mL) and BH_3•$(CH_3)_2S$ (1.5 mmol, 0.75 mL) was added to a 25 mL flame-dried Young-type tube and stirred at 50 °C for 24 hours. After cooling to room temperature, the mixture was quenched with CH_3OH (1.0 mL) at 0 °C. Then the residue was extracted with DCM (10 mL x 3) and Et_2O•HCl (2M, 2 mL) was added into the mixture. The solvent was removed under reduced pressure and concentrated under reduced pressure to afford the desired product **2-(4-isobutylphenyl)propan-1-aminium chloride (12)**

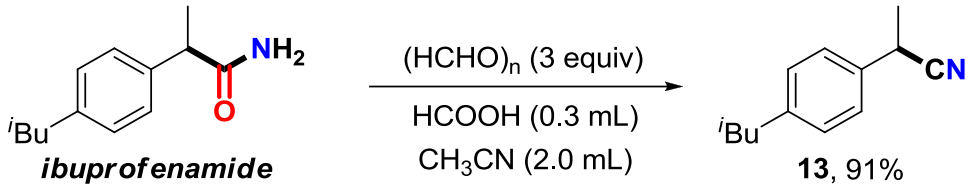
2-(4-isobutylphenyl)propan-1-aminium chloride (12): The title compound was prepared according to the above procedure and afforded the white solid, 100.5 mg, 88% yield. **^{1}H NMR** (400 MHz, D_2O) δ 0.75-0.77 (m, 6H), 1.21 (d, *J* = 7.2 Hz, 3H), 1.70 (m, 1H), 2.35 (d, *J* = 7.2 Hz, 2H), 3.00-3.16 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, D_2O) δ 18.6, 21.7, 29.7, 37.3, 44.3, 45.7, 127.1, 129.8, 139.3, 141.2.



12

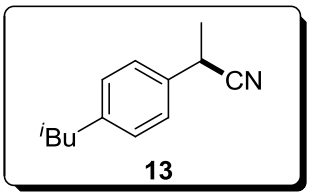
HRMS (ESI) calcd. for $C_{13}H_{22}N$ [M+H]: 192.1747, found: 192.1750.

5.5 Synthesis of 2-(4-isobutylphenyl)propanenitrile

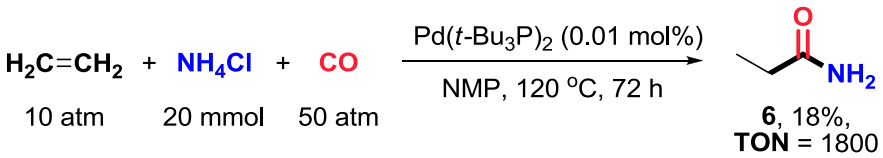


A mixture of ibuprofenamide (**2u**) (102.5 mg, 0.5 mmol), $(HCHO)_n$ (75.0 mg, 1.5 mmol), HCOOH (0.3 mL) and CH_3CN (2.0 mL) was added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and then stirred at 85 °C for 24 hours. After cooling to room temperature, the solvents were evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel and eluted with petroleum ethers/ethyl acetate (50:1 - 10:1) to afford the desired product **2-(4-isobutylphenyl)propanenitrile (13)**.

2-(4-isobutylphenyl)propanenitrile (13): The title compound was prepared according to the above procedure and purified by column chromatography to give the colorless liquid, 85.2 mg, 91% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.82 (s, 3H), 0.83 (s, 3H), 1.55 (d, *J* = 7.2 Hz, 3H), 1.73-1.83 (m, 1H), 2.39 (d, *J* = 7.2 Hz, 2H), 3.77 (q, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.4, 22.3, 30.2, 30.9, 45.0, 121.8, 126.4, 129.8, 134.3, 141.7. **HRMS** (ESI) calcd. for $C_{13}H_{17}NNa$ [M+Na]: 210.1253, found: 210.1246.



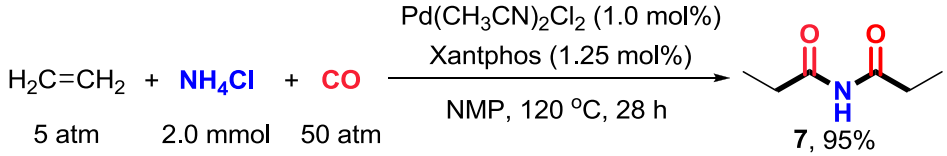
5.6 Synthesis of propionamide (TON experiment)



A mixture of NH_4Cl (1.068 g, 20.0 mmol), Pd(*t*-$Bu_3P)_2$ (0.002 mmol, 0.01 mol%) and NMP (30 mL) was added into a glass tube which was placed in an autoclave (350 mL). Then the autoclave was purged and charged with ethylene (10 atm) and CO (50 atm). The reaction mixture was stirred at 120 °C for 72 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The yield was determined by GC using *n*-Cetane as the

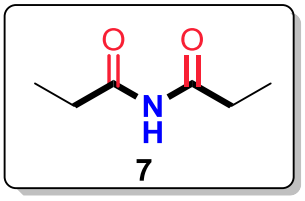
internal standard (18%, TON = 1800).

5.7 Synthesis of 2-(4-isobutylphenyl)propanenitrile



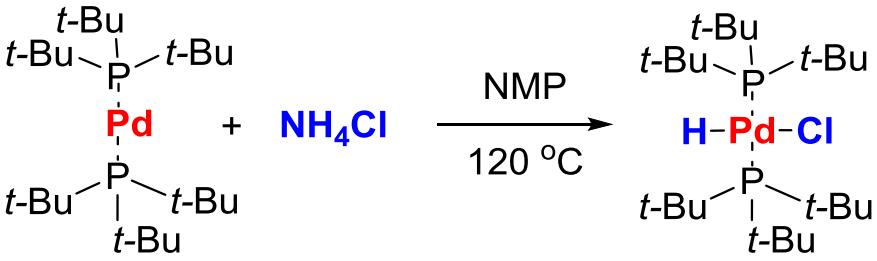
A mixture of NH_4Cl (106.8 mg, 2.0 mmol), $Pd(CH_3CN)_2Cl_2$ (5.2 mg, 0.02 mmol, 1 mol%), Xantphos (14.5 mg, 0.025 mmol, 1.25 mol%) and NMP (5.0 mL) was added into a dry glass tube which was placed in an autoclave. Then the autoclave was purged and charged with ethylene (5 atm) and CO (50 atm). The reaction mixture was stirred at 120 °C for 28 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. Then the corresponding reaction mixture was purified by flash column chromatography on silica gel column and eluted with petroleum ether/ethyl acetate (100/1 – 1/1) to give the desired product ***N*-propionylpropionamide (7)**.

***N*-propionylpropionamide (7):** The title compound was prepared according to the above procedure and purified by column chromatography to give a white solid, 243.1 mg, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.2 Hz, 6H), 2.62 (q, *J* = 7.2 Hz, 4H), 9.08 (br, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 8.4, 30.7, 175.4; **HRMS** (ESI) calcd. for $C_6H_{11}NONa$ [M+Na]: 152.0682, found: 152.0686.



6. Mechanistic studies

6.1 NMR studies for monitoring the HPdCl(*t*-Bu$_3$P)$_2$



In the glove box, a mixture of NH_4Cl (10.7 mg, 0.2 mmol), Pd(*t*-Bu$_3$P)$_2$ (51.0 mg, 0.1 mmol) and NMP (0.6 mL) was added into a J-Young-type NMR tube (containing 0.1 mL DMF-d_7). The mixture was stirred at 120^{o}C for designed time and the mixture was characterized by ^{1}H NMR and ^{31}P NMR (Figure S4 and S5).

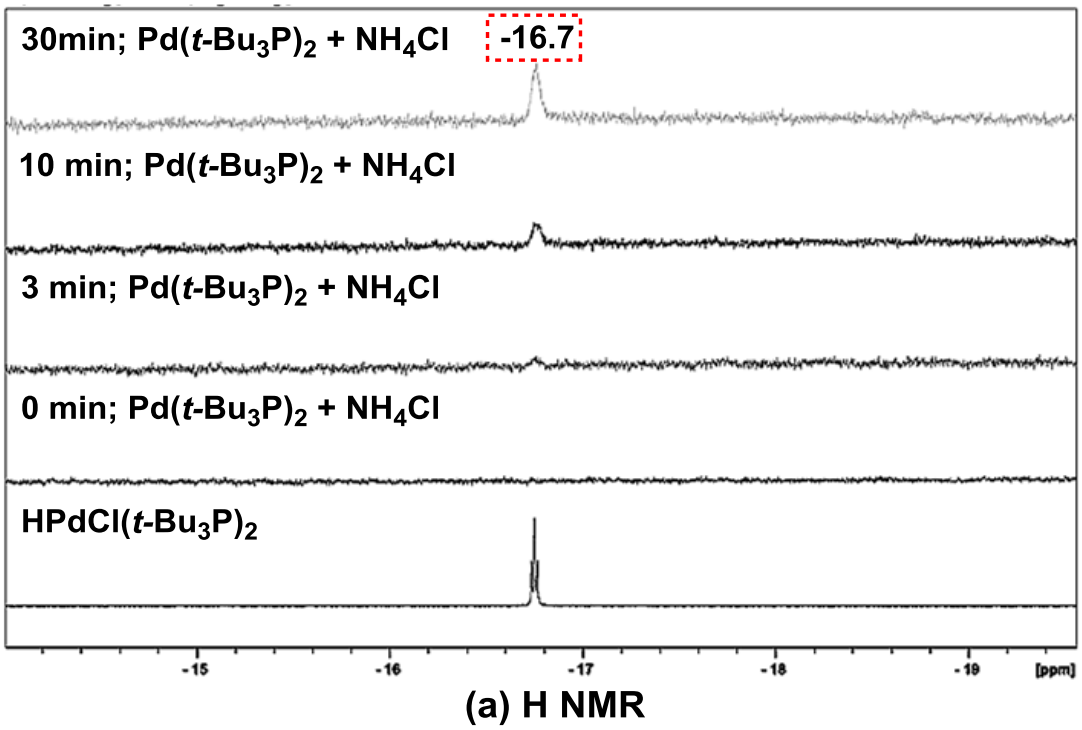


Figure S4. ^{1}H NMR spectra of the reaction mixture as the time goes on

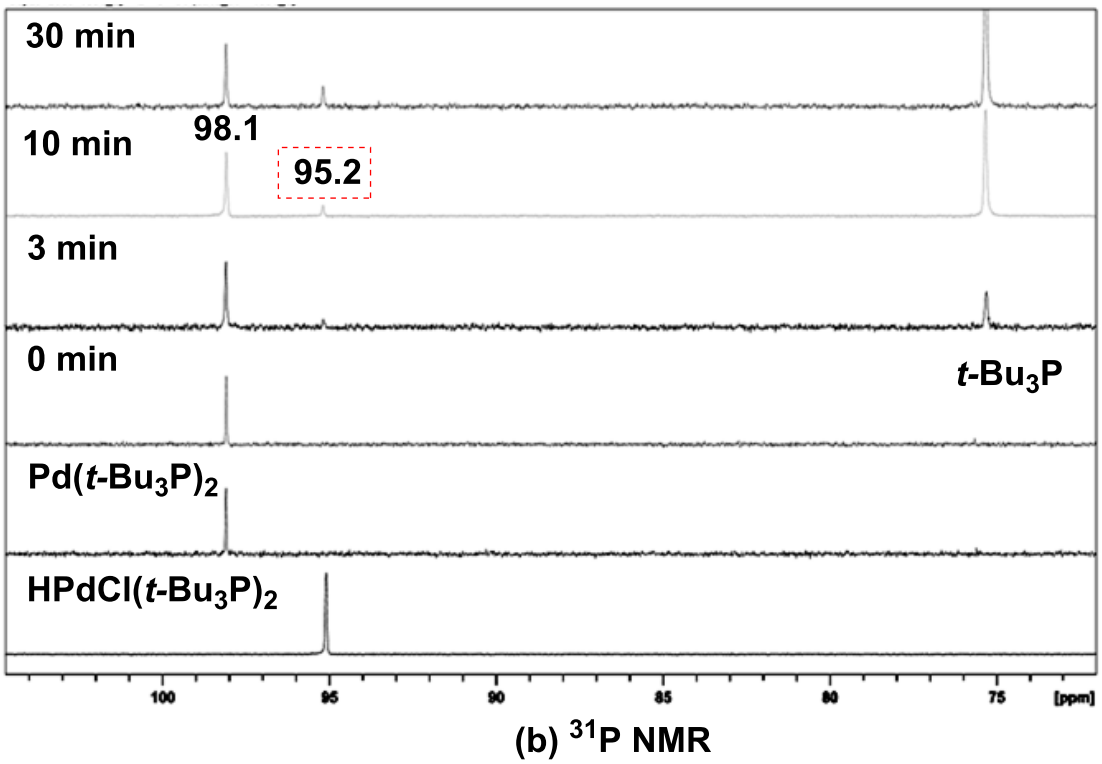
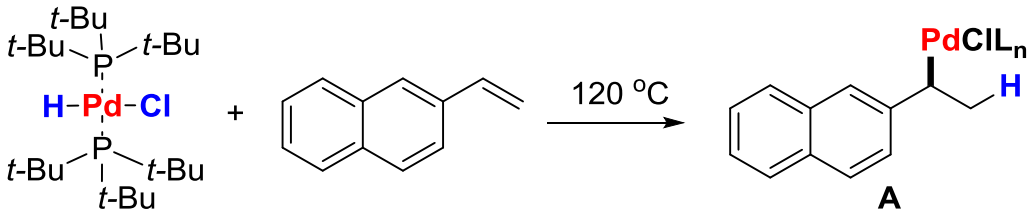


Figure S5. ^{31}P NMR spectra of the reaction mixture as the time goes on

6.2 NMR studies for monitoring the complex A



In the glove box, a mixture of 2-vinylnaphthalene (3.1 mg, 0.022 mmol), HPdCl(*t*-Bu$_3$P)$_2$[4] (10.2 mg, 0.02 mmol) and DMF-d_7 (0.6 mL) was added into a J-Young-type NMR tube. The mixture was stirred at 120 °C for designed time and the mixture was characterized by ^{1}H NMR and ^{31}P NMR (Figure S6 and S7).

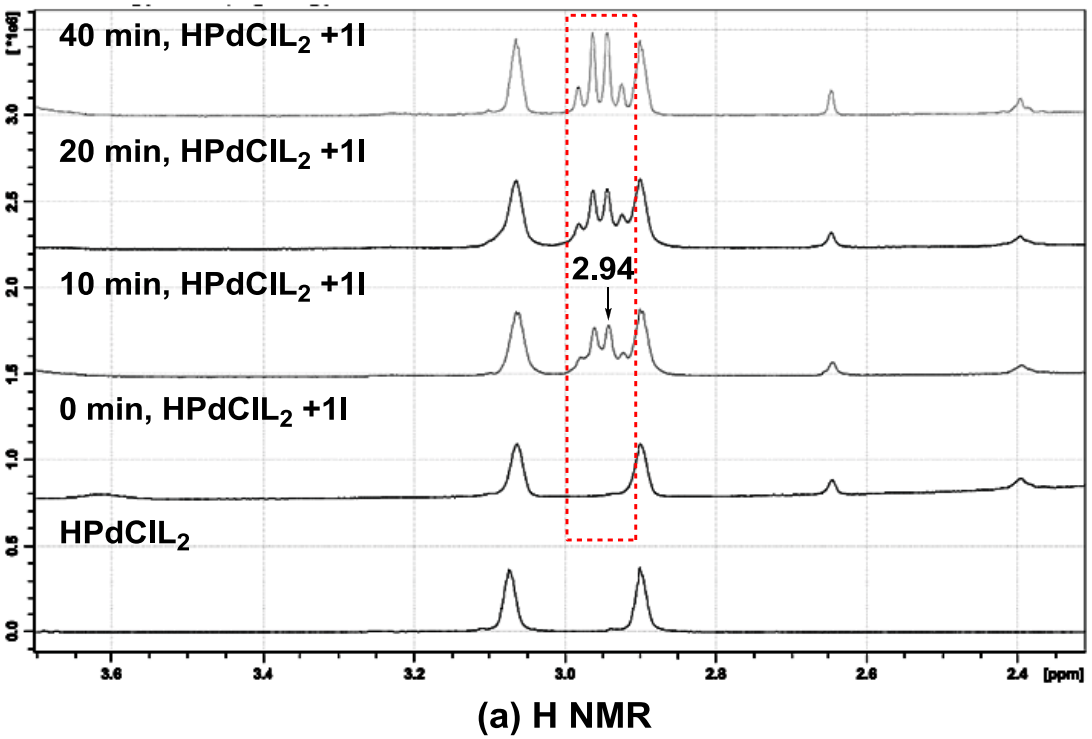


Figure S6. ^{1}H NMR spectra of the reaction mixture as the time goes on

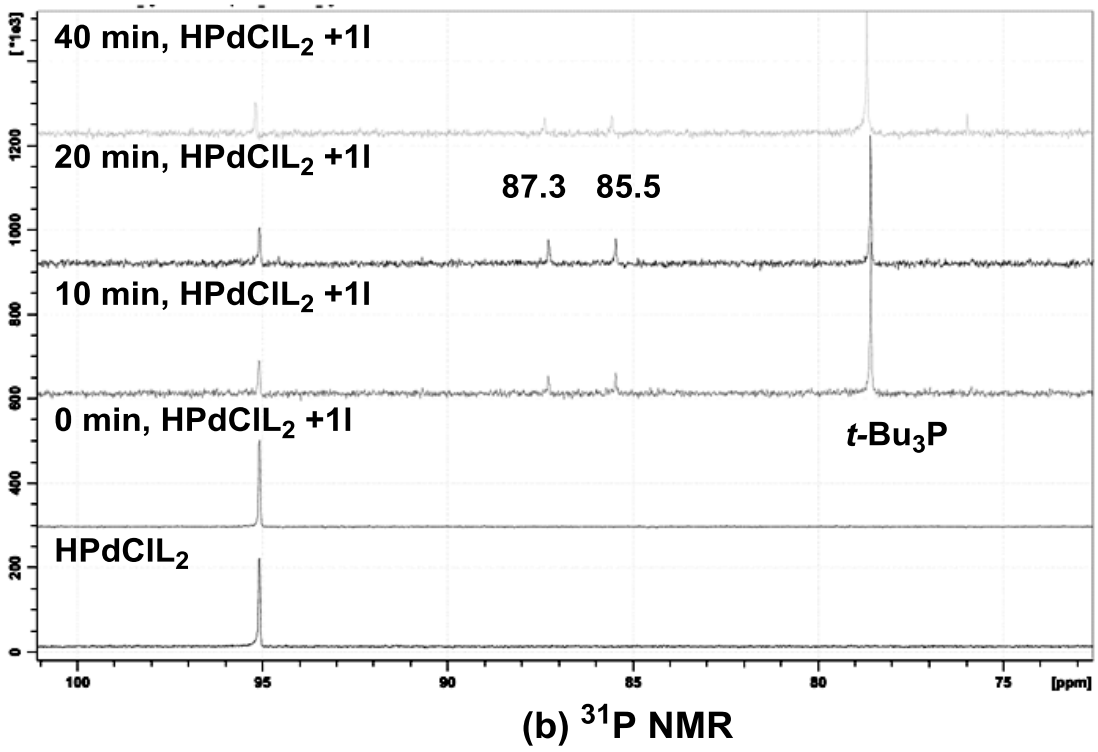
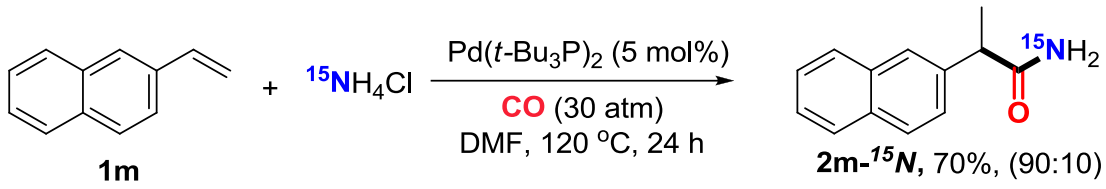


Figure S7. ^{31}P NMR spectra of the reaction mixture as the time goes on

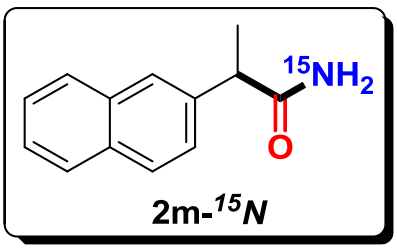
6.3 ^{15}N-Labeled experiments: $^{15}NH_4Cl$



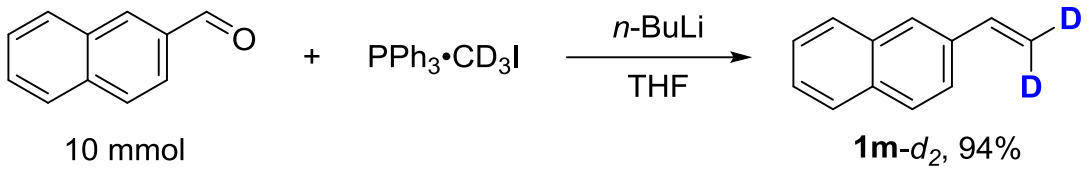
1m **2m-*15N*, 70%, (90:10)**

Following our general procedure: In the glove box, a mixture of 2-vinylnaphthalene (**1m**) (154.0 mg, 1.0 mmol), $^{15}NH_4Cl$ (108.8 mg, 2.0 mmol), Pd(*t*-$Bu_3P)_2$ (25.5 mg, 0.05 mmol, 5 mol%) and NMP (5.0 mL) was added into a dry glass vessel. The resulting mixture was stirred for 10 minutes at room temperature and then 2-vinylnaphthalene (**1m**) (154.0 mg, 1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from the glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 120 °C for 24 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The regioselectivity was measured by GC and GC-MS, respectively. Then the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1 - 1/1) to give the desired product **2m-*15N* (**140.2 mg, 70% yield**)**.

2-(naphthalen-2-yl)propanamide (2m-*15N*): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 140.2 mg, 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.60 (d, *J* = 7.2 Hz, 3H), 3.73 (q, *J* = 7.2 Hz, 1H), 5.28 (br, 0.5H), 5.50 (br, 0.5H), 5.63 (br, 0.5H), 5.85 (br, 0.5H), 7.41-7.51 (m, 3H), 7.75-7.84 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.3, 46.7, 46.8, 125.7, 126.0, 126.3, 126.4, 127.7, 127.7, 128.8, 132.6, 133.5, 138.7, 176.5, 176.7; **HRMS** (ESI) calcd. for $C_{13}H_{13}{}^{15}NONa$ [M+Na]: 223.0860, found: 223.0859.



6.4 Labeling experiments: 2-vinylnaphthalene (1m-d_2)



To the solution of $PPh_3 \cdot CD_3I$ (4.86 g, 12.0 mmol) in 30 mL of dry THF, *n*-Butyl lithium (4.8 mL of 2.5 M in hexane, 12 mmol,) was added dropwise at room temperature under nitrogen. After stirring for 30 minutes, 2-naphthaldehyde (1.5 g, 10.2 mmol) was added into the reaction mixture. Then the reaction mixture was stirred for another 17 hours at the room temperature under nitrogen. After the mixture was quenched with 1.0 mL of H_2O at the 0 ^oC, the reaction mixture was diluted with 20 mL of ethyl acetate and washed with 20 mL of brine. The organic layer was dried with anhydrous Na_2SO_4 and concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1/100 ~ 1/50) to afford the desired product **1m**-d_2 as a white solid (1.5 g, 94%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.31-5.33 (m, 0.06H), 5.84-5.88 (m, 0.06H), 6.87 (s, 1H), 7.42-7.48 (m, 2H), 7.62-7.65 (m, 1H), 7.75 (s, 1H), 7.78-7.81 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 123.2, 125.9, 126.2, 126.4, 127.7, 128.1, 128.2, 133.2, 133.6, 135.0, 136.8.

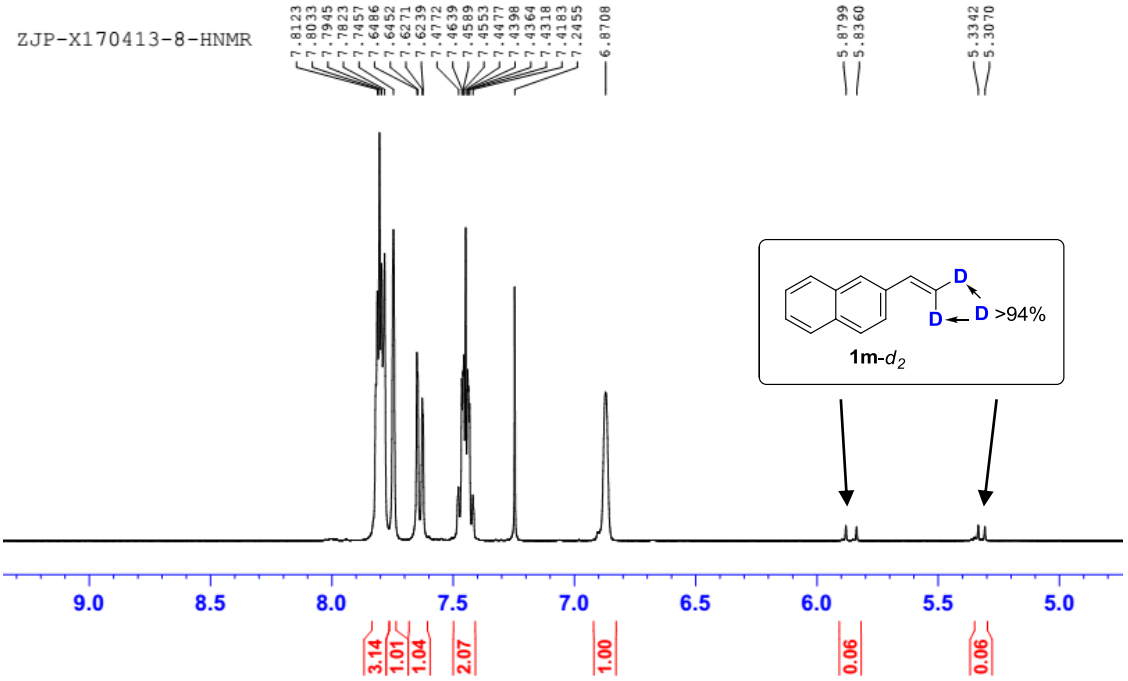
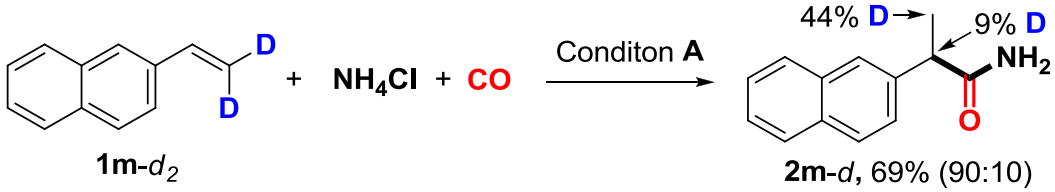


Figure S8. ^{1}H NMR spectra of **2m-*d***

6.5 Labeling experiments: 2-vinylnaphthalene (1m-d_2)



Following our general procedure: In the glove box, a mixture of 2-vinylnaphthalene (**1m-*d*$_2$**) (156.0 mg, 1.0 mmol), NH_4Cl (106.8 mg, 2.0 mmol), Pd(*t*-$Bu_3P)_2$ (25.5 mg, 0.05 mmol, 5 mol%) and NMP (5.0 mL) was added into a glass vessel. The resulting mixture was stirred for 10 minutes at room temperature and then 2-vinylnaphthalene (**1m-*d*$_2$**) (156.0 mg, 1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from the glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 120 ^{o}C for 24 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The regioselectivity were measured by GC and GC-MS, respectively. Then the mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1 - 1/1) to give the desired product **2m-*d*** **(**137.4 mg, 69%

yield**)**.

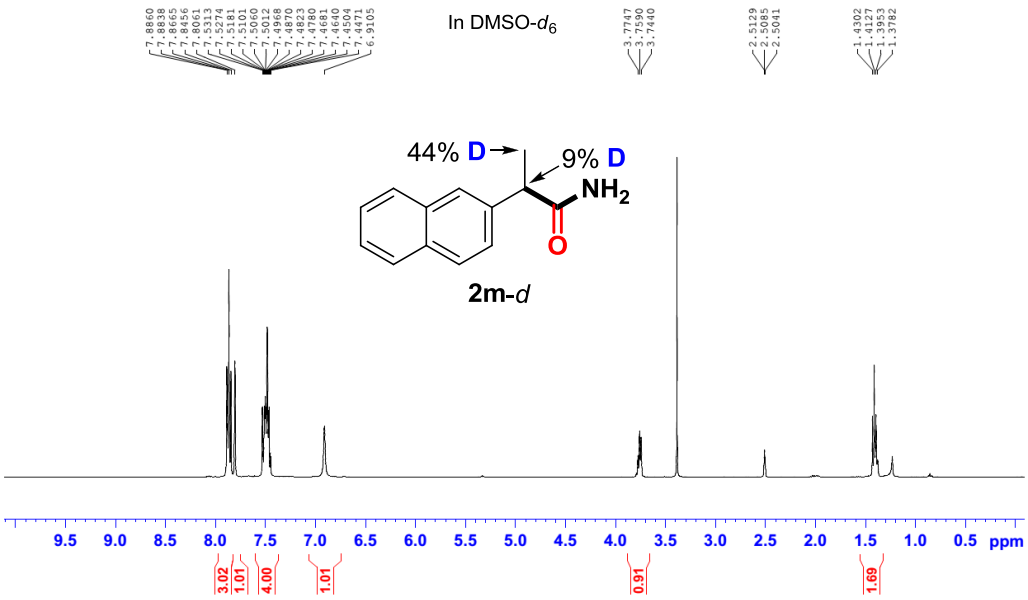
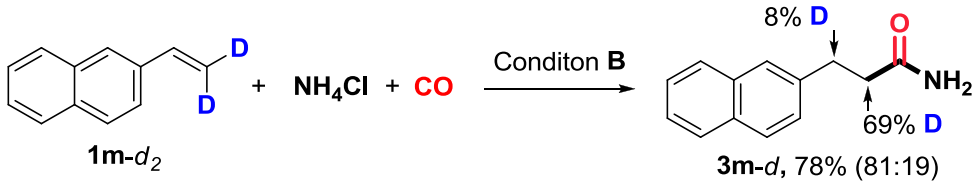


Figure S9. ^{1}H NMR spectra of **2m-*d***

6.6 Labeling experiments: 2-vinylnaphthalene (1m-d_2)



Following our general procedure: In the glove box, a mixture of NH_4Cl (106.8 mg, 2.0 mmol), PdI_2 (7.2 mg, 0.02 mmol), Xantphos (14.6 mg, 0.025 mmol) and NMP (3.0 mL) was added into a dry glass vessel. The resulting mixture was stirred for 10 minutes at room temperature and then 2-vinylnaphthalene (**1m-*d*$_2$**) (156.0 mg, 1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from the glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 120 ^{o}C for 4 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The regioselectivity was measured by GC and GC-MS, respectively. Then the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1 - 1/1) to give the desired product **3m-*d*** (154.3 mg, 78% yield，L:B = 81:19).

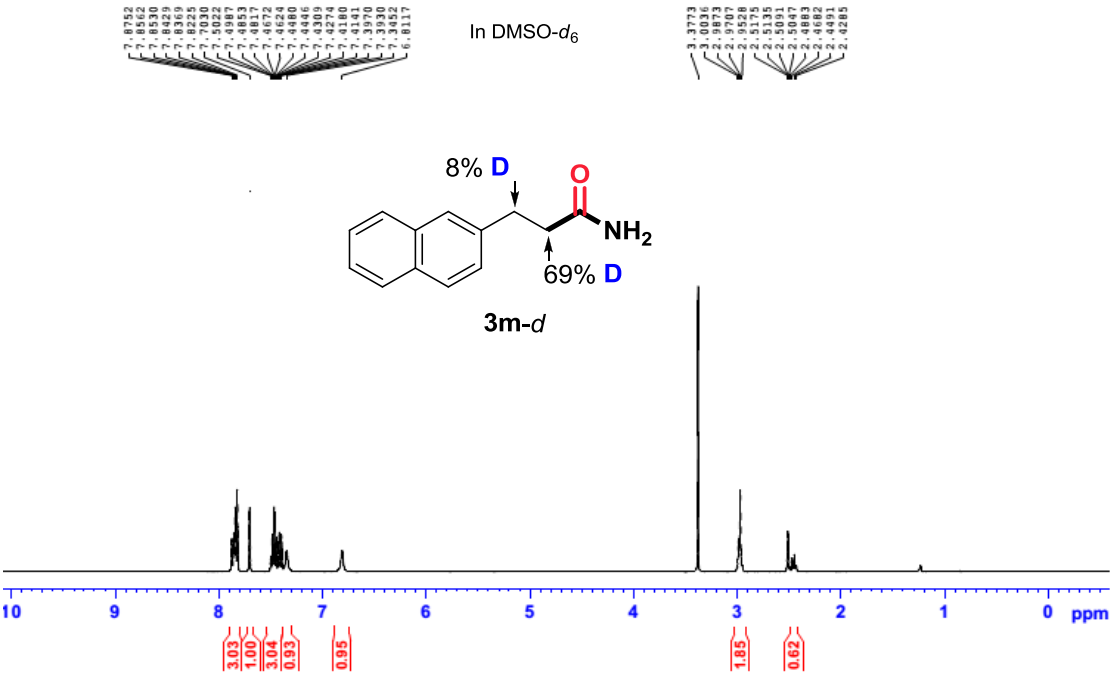
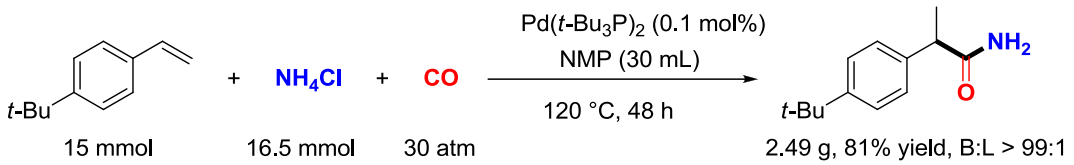


Figure S10. ^{1}H NMR spectra of **3m-*d***

6.7 Gram-scale experiments

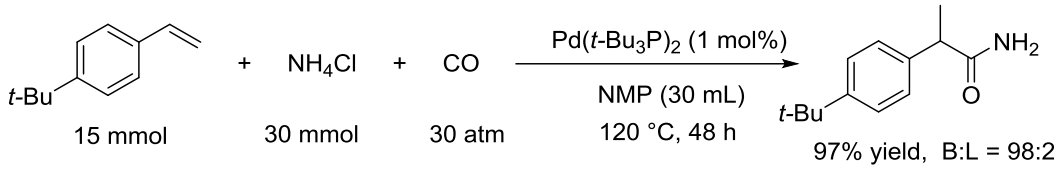


In a glove box, a mixture of NH_4X (0.88 g, 16.5 mmol), Pd(*t*-$Bu_3P)_2$ (7.7 mg, 0.015 mmol) and NMP (30 mL) was added into a round-bottomed flask. The resulting mixture was stirred for 10 minutes at room temperature and then 4-*tert*-butylstyrene (2.4 g, 15 mmol) was added into the reaction mixture. The flask was put into an autoclave and then taken out from the glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 120 ^{o}C for 48 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood, and then the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1 - 1/1) to give the desired product 2.29 g, 81% yield (B:L>99:1).

6.8 The experiments for investigate the fate of HCl released from the reaction

To investigate the fate of the produced HCl, a series of control experiments have been conducted. We assumed that there are three possible existential states for the produced HCl may exist:

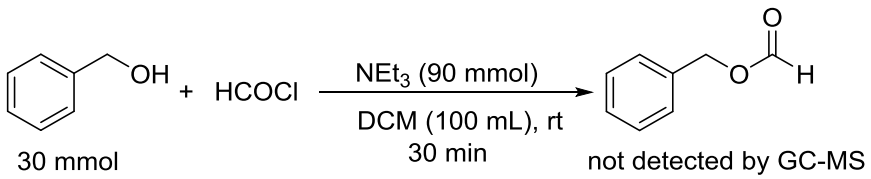
(1) To invesitage whether it existed as a gas in the reaction system:



We use the above reaction as the model reaction which was conducted in a large scale (15 mmol). Once the reaction was finished, the remaining gas was carefully released from the autoclave and absorbed by deionized water either at 120 ^{o}C or cooling down to room temperature. The resulting solution was titrated by NaOH (0.1 mol/L NaOH standard solution) to test the acidity and $AgNO_3$ (0.1 mol/L standard solution) to test the concentration of Cl^-. The results demonstrated that no HCl was found in the resulting solution, which indicated that HCl did not exist as HCl-gas in the reaction system.

(2) To invesitage whether it convert to HCOCl

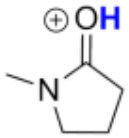
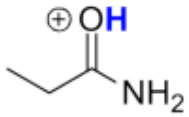
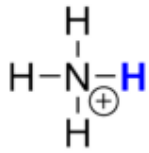
After the reaction finished and released the remaining gas, we brought the autoclave to the glovebox. After opening the autoclave in the glovebox, benzyl alcohol (30 mmol), Et_3N (90 mmol) and CH_2Cl_2 (100 mL) were introduced into the reaction mixture. The resulting mixture was stirred at room temperature for 30 minutes and then examined by GC-MS. The GC-MS analysis demonstrated that no benzyl formate was detected. These results suggested that HCOCl was not formed in the reaction system.



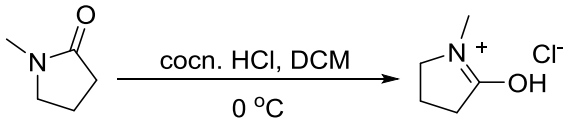
(3) To invesitage whether it bound to NMP.

After the reaction finished and released the remaining gas, the resulting reaction mixture was poured into deionized water (100 mL), and the resulting reaction mixture was stirred at room temperature for 30 minutes. The desired amide was precipitated from the reaction mixture. The mixture was filtrated, washed with deionized water. The resulting filtrate (200 mL) was collected and titrated with $AgNO_3$ (0.1 mol/L) to exam the content of Cl^-. The titration was repeated for three times and the results demonstrated that the total Cl^- is 29.7 mmol (very close to 30 mmol, the amount of HCl= 29.7 mmol-15 mmol = 14.7 mmol (0.0735 mol/L)). The pH of the filtrate solution was 2.20 (which was tested by pH meter). These results suggested that the released HCl was indeed existed in the reaction solvent, but it was not existed as free-state (the pH value of these dissociative HCl (0.0735 mol/L) should be 1.13).

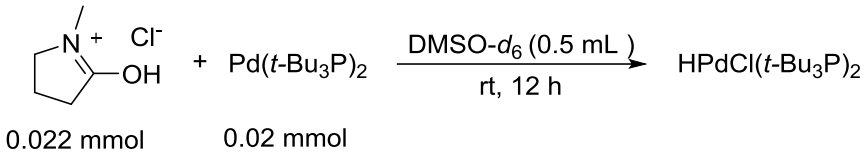
Table S7. The pKa value for different hydrochloride salts [a]

Structure	Solvent	pK_a	Method
	H_2O	-0.72	SM
	H_2O	-0.86	NMR
	H2O	9.27	PTM

We have checked the pKa of protonated NMP, primary amide and NH_4^+ (*J. Chem. Soc., Perkin Trans. 2*, **1991**, 373-376; *J. Chem. Soc., Perkin Trans. 2*, **1993**, 1091-1098*; J. Am. Chem. Soc.*, **1957**, *79*, 796–800), which has been shown in the Table S7. Comparing the corresponding pKa of these compounds, we thought that the HCl was most likely bounded to NMP to form the N-methyl-2-pyrrolidone hydrochloride.



We have also synthesized the N-methyl-2-pyrrolidone hydrochloride according to the reported method (Sebastian Herler; Peter Mayer; Axel Schulz; Alexander Villinger. *Acta Cryst.* **2007**, *E63*, o3991). The Pd(*t*-Bu$_3$P)$_2$ was treated with N-methyl-2-pyrrolidone hydrochloride at room temperature in DMSO-d_6 and monitored by NMR. After 12 hours, the signal at δ = -16.77 (*t*) (which was assigned as HPd(*t*-Bu$_3$P)$_2$Cl) was observed by ^{1}H-NMR, indicating that N-methyl-2-pyrrolidone hydrochloride could react with Pd(0) to form HPdCl species.



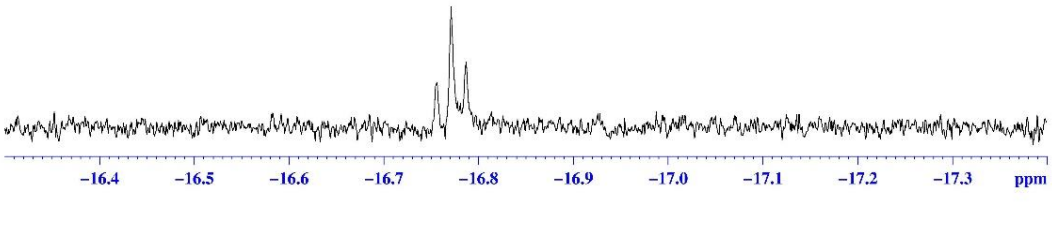
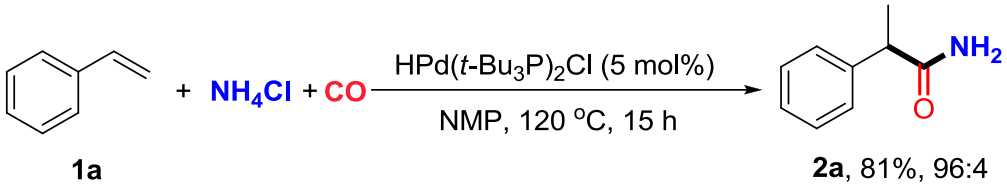


Figure S11. ^{1}H NMR spectra of **HPdCl(*t*-Bu$_3$P)$_2$**

The above experiments suggested that the HCl released from NH_4Cl was most likely captured by NMP to drive the reaction.

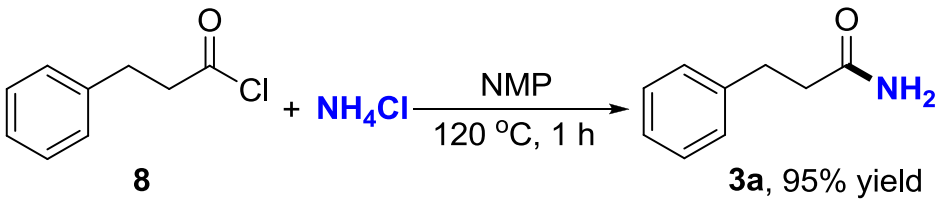
6.9 The experiments of acyl palladium complex

6.9.1 The catalytic reaction of HPd(*t*-$Bu_3P)_2Cl$ with 1a



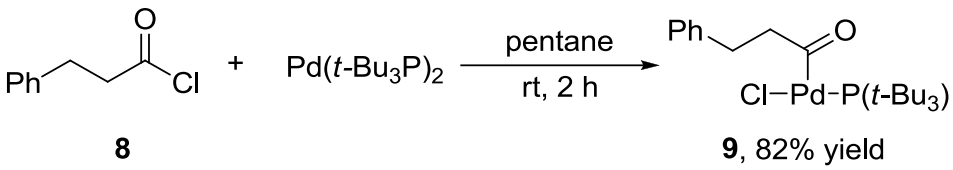
In a glove box, a mixture of NH_4Cl (106.8 mg, 2.0 mmol), HPd(*t*-$Bu_3P)_2Cl$ (27.3 mg, 0.05 mmol)[4] and NMP (5.0 mL) was added into a dry glass vessel. The resulting mixture was stirred for 10 minutes at room temperature and then styrene (114 uL, 1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from the glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 120 °C for 15 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The regioselectivity was measured by GC and GC-MS, respectively. Then the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1 - 1/1) to give the desired products **2a** (120.9 mg, 81% yield, B:L = 96:4).

6.9.2 The reaction of 3-phenylpropionyl chloride and NH_4Cl



In a glove box, a mixture of 3-phenylpropionyl chloride (148.5 uL, 1.0 mmol), NH_4Cl (107 mg, 2.0 mmol), NMP (5 mL) were added to a 25 mL flame-dried Young-type tube. The tube was taken out from glove box and stirred at 120 °C for 1 hours. After the reaction finished, the corresponding reaction mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (100/1 - 1/1) to give the desired product **3a** (142 mg, 95% yield).

6.9.3 Synthesis of palladium complex [$PhCH_2CH_2COPd$(*t*-Bu_3P)Cl][5]



8 **9**, 82% yield

In a glove box, a mixture of Pd(*t*-$Bu_3P)_2$ (511 mg, 1.0 mmol), 3-phenylpropionyl chloride (297 uL, 2.0 mmol) and pentane (15 mL) was added to a 25 mL flame-dried Schlenk flask. The yellow homogeneous mixture is allowed to stand, precipitating a yellow solid after 15 minutes. After 2 hours, the yellow solid is filtered and washed with pentane (3 × 5 mL) to afford the pure complex **9** (390 mg, 82% yield). ^{1}H NMR (400 MHz, C_6D_6) δ 0.99 (d, *J* = 12.8 Hz, 27H), 2.90 (t, *J* = 7.6 Hz, 2H), 3.72 (t, *J* = 7.6 Hz, 2H), 6.98-7.08 (m, 5H); ^{31}P NMR (162 MHz, C_6D_6) 73.98; ^{13}C NMR (100 MHz, $CDCl_3$) 30.6, 32.1 (32.1), 39.2 (d, *J* = 16.2 Hz), 55.7 (d, *J* = 32.4 Hz), 126.5, 128.6, 128.8, 139.7, 203.5.

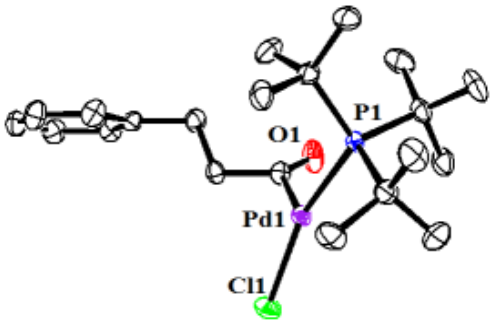
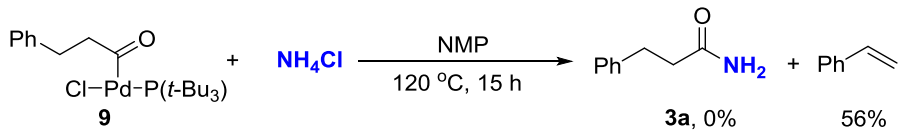


Figure S12. ORTEP drawing of palladium complex **9**

6.9.4 Stoichiometric reaction of palladium complex 9 and NH_4Cl

In the absence of CO:

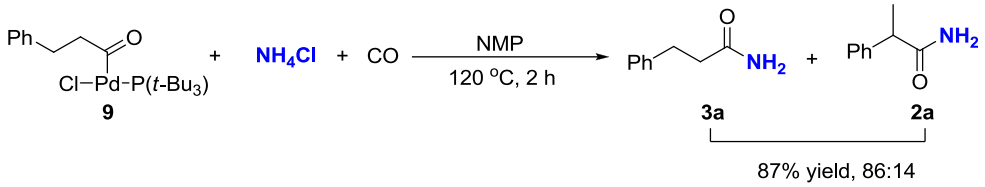


9 **3a**, 0% 56%

In a glove box, a mixture of [$PhCH_2CH_2COPd$(*t*-Bu_3P)Cl] **9** (47.6 mg, 0.1 mmol), NH_4Cl (10.7 mg, 0.2 mmol) and NMP (1 mL) were added to a 25 mL flame-dried Young-type tube. The tube was taken out from glove box and stirred at 120 °C for 15 hours. The tube was cooled to room temperature and the reaction mixture was

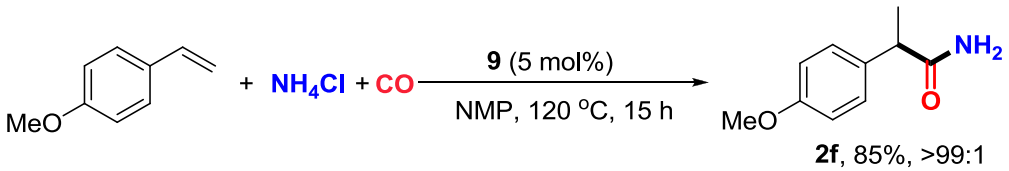
examined by GC and GC-MS and showed that no desired product **3a** was produced, however, 56% styrene could be detected by GC and GC-MS using *n*-cetane as the internal standard.

In the presence of CO:



In a glove box, a mixture of [$PhCH_2CH_2COPd(t\text{-}Bu_3P)Cl$] **9** (47.6 mg, 0.1 mmol), NH_4Cl (10.7 mg, 0.2 mmol) and NMP (1 mL) was added into a dry glass vessel. The glass vessel was put into an autoclave and then taken out from the glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 120 °C for 2 hour. The autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The regioselectivity and the yield was measured by GC and GC-MS using *n*-cetane as the internal standard. The desired amides were obtained in 87% yield with L:B = 86:14.

6.9.5 The catalytic reaction of complex 9 with 4-methoxystyrene



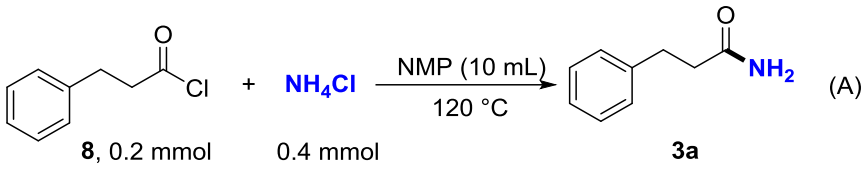
In a glove box, a mixture of NH_4Cl (106.8 mg, 2.0 mmol), [$PhCH_2CH_2COPd(t\text{-}Bu_3P)Cl$] **9** (23.8 mg, 0.05 mmol) and NMP (5.0 mL) was added into a dry glass vessel. The resulting mixture was stirred at room temperature for 10 minutes and then 4-methoxystyrene (134 mg, 1.0 mmol) was added into the reaction mixture. The glass vessel was put into an autoclave and then taken out from the glove box. The autoclave was purged and charged with CO (30 atm). The reaction mixture was stirred at 120 °C for 15 hours. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released in the fume hood. The regioselectivity was measured by GC and GC-MS, respectively. Then the corresponding reaction mixture was purified by flash column chromatography on silica

gel and eluted with petroleum ether/ethyl acetate (100/1 - 1/1) to give the desired products **2f** (152.5 mg, 85% yield, >99:1).

6.10 The kinetic experiments

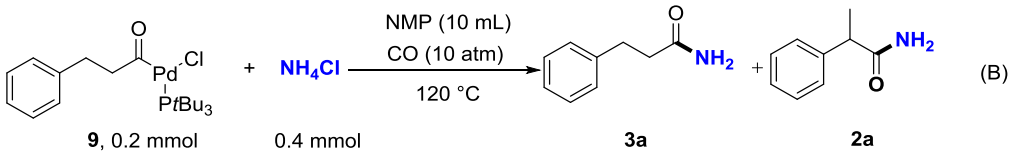
6.10.1 Kinetic reaction profiles of 8 or 9 under 120 °C.

Reaction A:



In a glove box, a mixture of 3-phenylpropanoyl chloride **8** (33.7 mg, 0.2 mmol), NH_4Cl (21.4 mg, 0.4 mmol) and NMP (10.0 mL) was added into a 50 ml Young-type tube. The reaction mixture was stirred at 120 °C. At each sampling time 0.2 mL reaction mixture was extracted and examined by gas chromatography (Agilent 7890B). The yield of **3a** was determined by GC analysis using *n*-tetradecane as internal standard (Figure S13).

Reaction B:



In a glove box, a mixture of acyl palladium **9** (95.4 mg, 0.2 mmol), NH_4Cl (21.4 mg, 0.4 mmol) and NMP (10.0 mL) was added into a teflon tube which was placed in an autoclave (50 mL). The autoclave was purged and charged with CO (10 atm) after taken out from the glove box. The reaction mixture was stirred at 120 °C. At each sampling time 0.2 mL reaction mixture was extracted and examined by gas chromatography (Agilent 7890B). The yield of (**2a**+**3a**) was determined using *n*-tetradecane as internal standard by GC analysis (Figure S13).

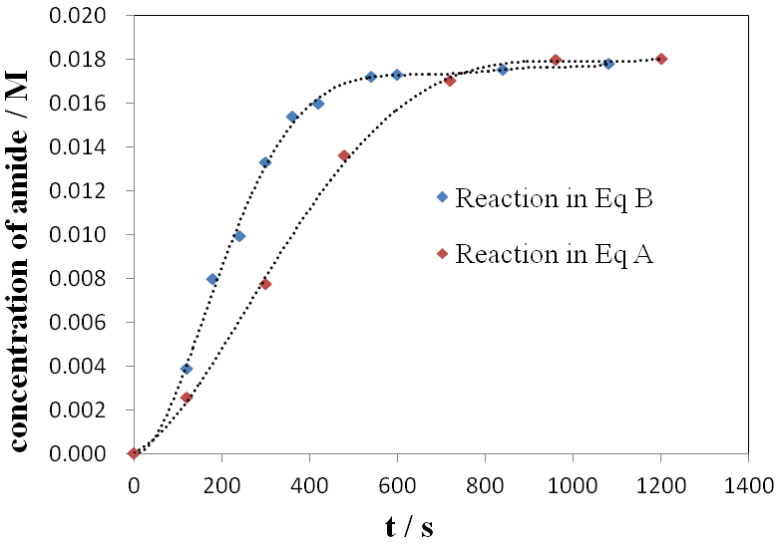


Figure S13. Reaction profiles of **8** (Eq A) and **9** (Eq B) under 120 °C.

Reference:

(1) (a) Li, S.; Huang, K.; Cao, B.; Zhang, J.; Wu, W.; Zhang, X. *Angew. Chem. Int. Ed.* **2012**, *51*, 8573. (b) Monfette, S.; Turner, Z. R.; Semproni, S. P.; Chirik, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 4561. (c) Müller, D. S.; Marek, I. *J. Am. Chem. Soc.* **2015**, *137*, 15414.

(2) Guo, R.; Yang, H.; Tang, P. *Chem. Commun.* **2015**, *51*, 8829.

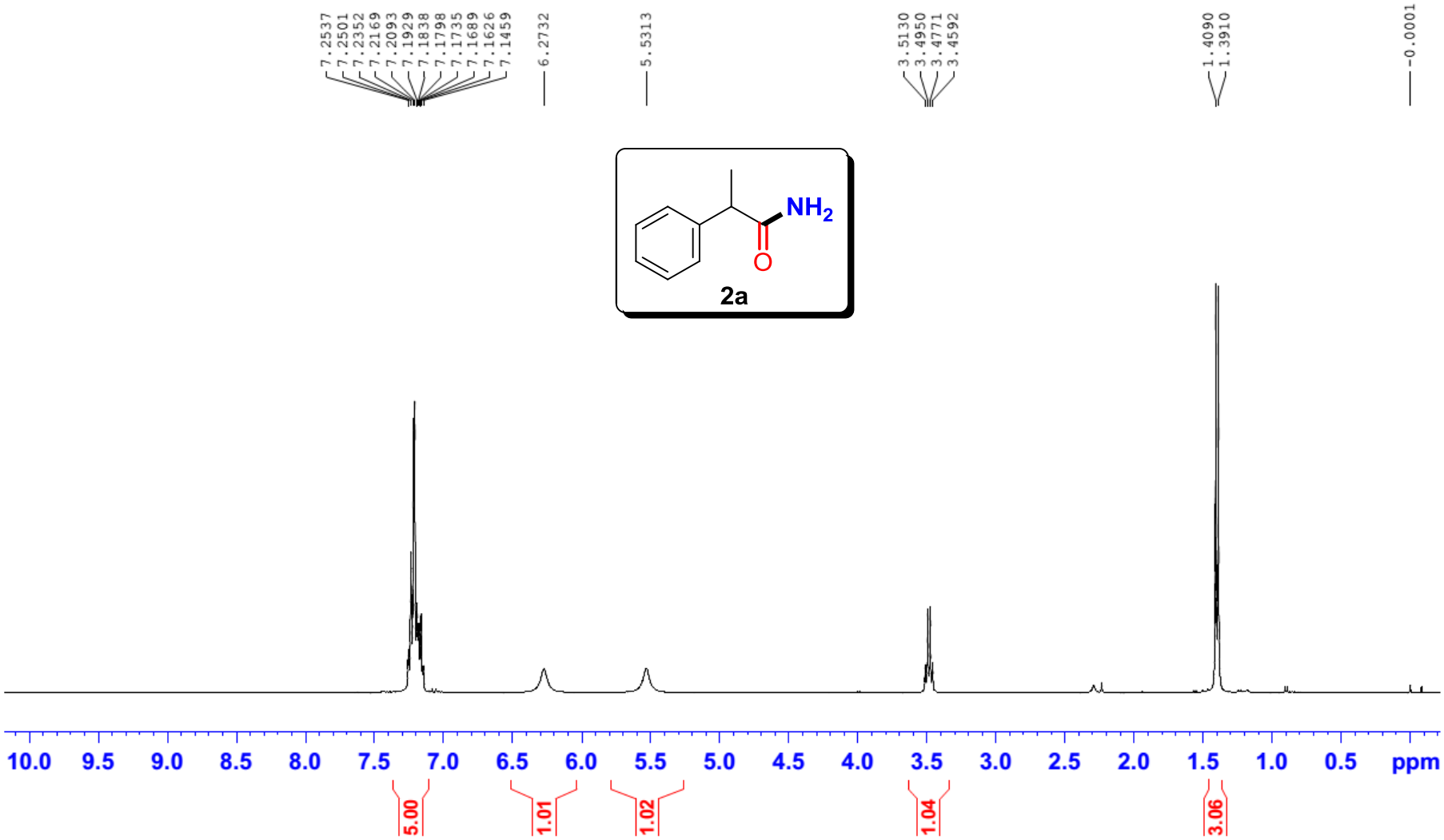
(3) (a) Lipshutz, B. H.; Ghorai, S.; Leong, W. W. Y. *J. Org. Chem.* **2009**, *74*, 2854. (b) Li, S.; Li, F.; Gong, J.; Yang, Z. *Org.Lett*. **2015**, *17*, 1240. (c) Chen, X.-M.; Ning, X.-S.; Kang, Y.-B. *Org. Lett.* **2016**, *18*, 5368.

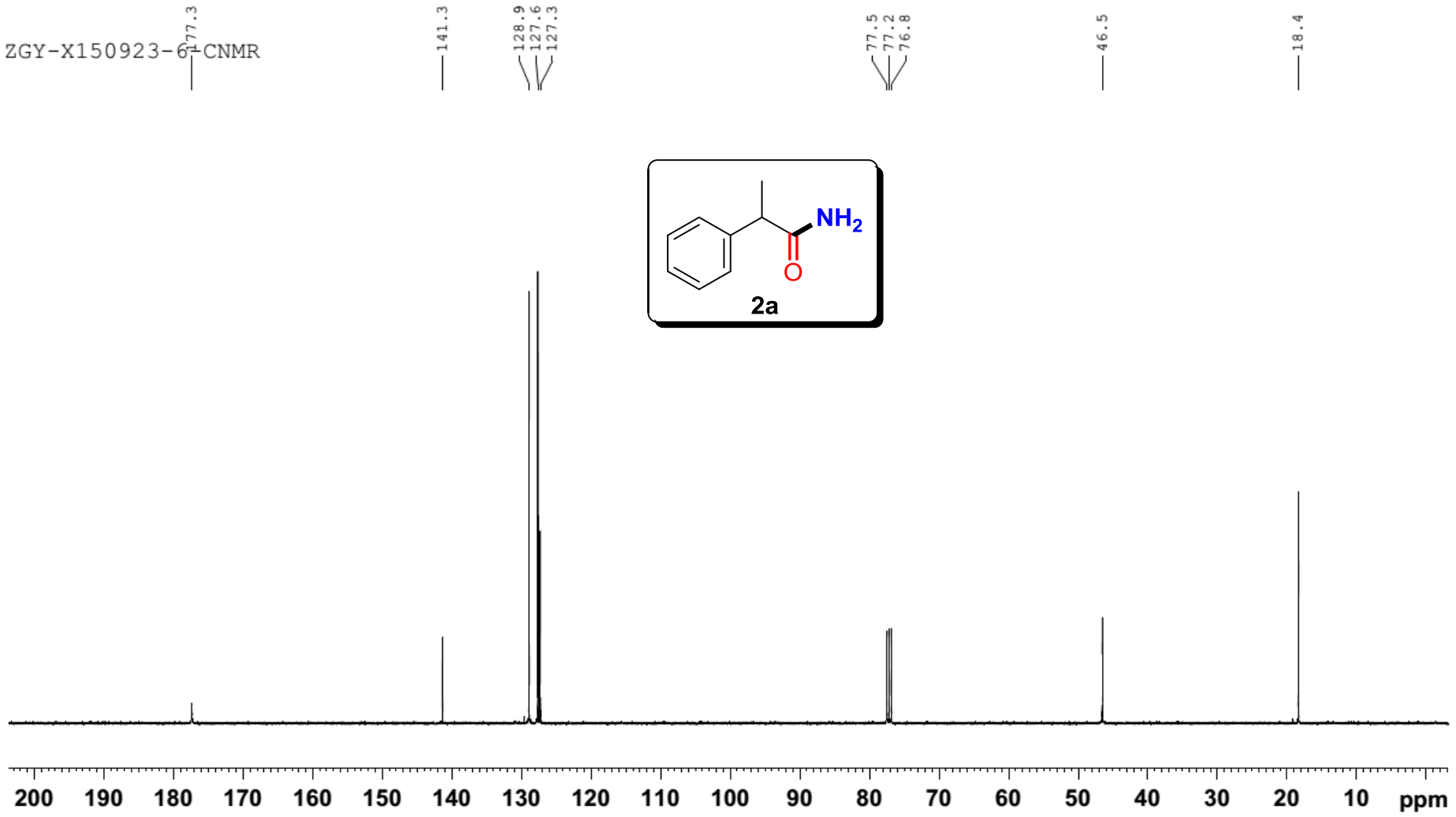
(4) (a) Hills, I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 13178. (b) Hu, Y.; Shen, Z.; Huang, H. *ACS Catal.* **2016**, *6*, 6785.

(5) Quesnel, J. S.; Arndtsen, B. A. *J. Am. Chem. Soc.* **2013**, *135*, 16841.

7. Copies for ^{1}H NMR and ^{13}C NMR of the amides

ZGY-X150922-3 HNMR

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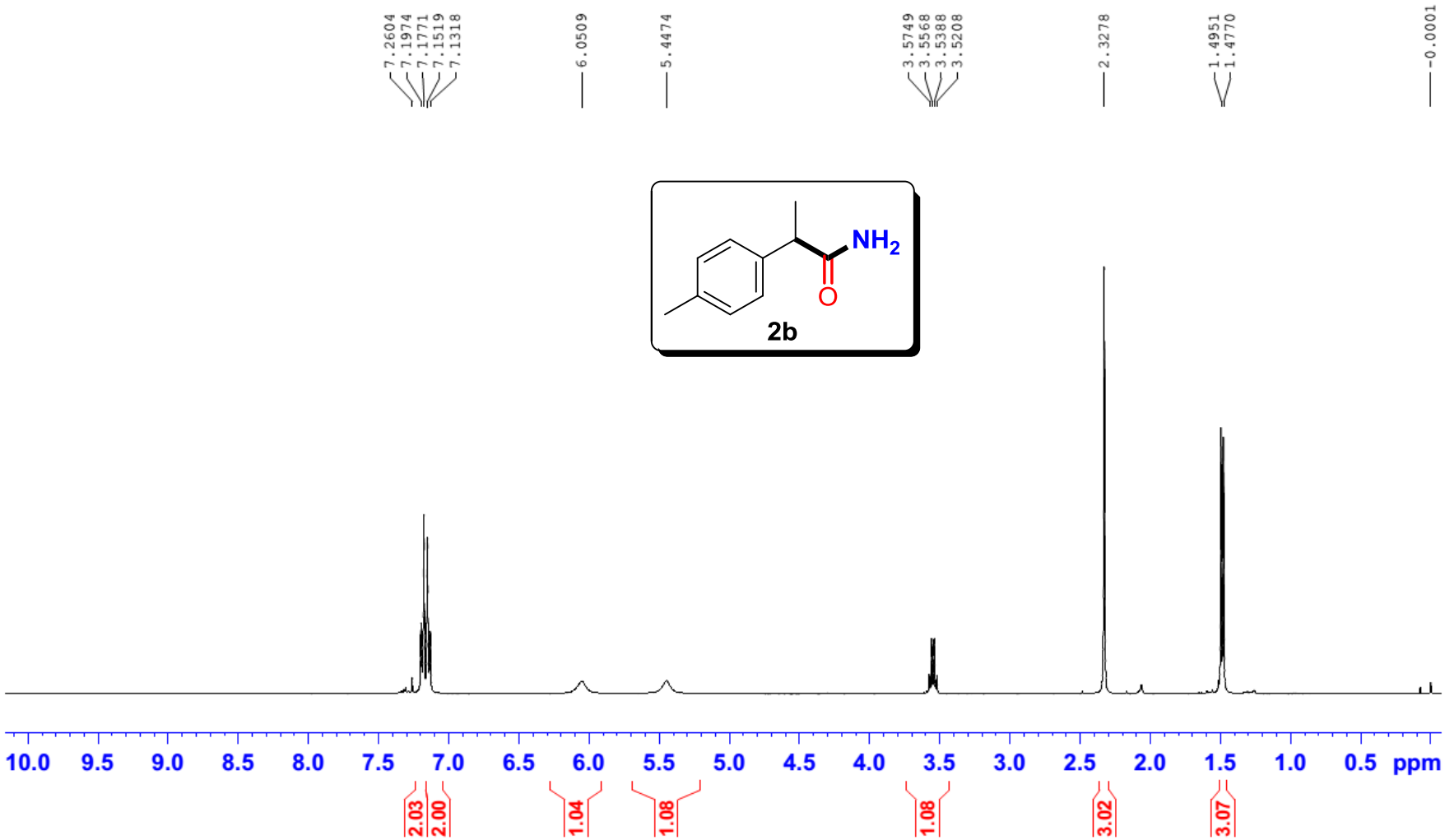
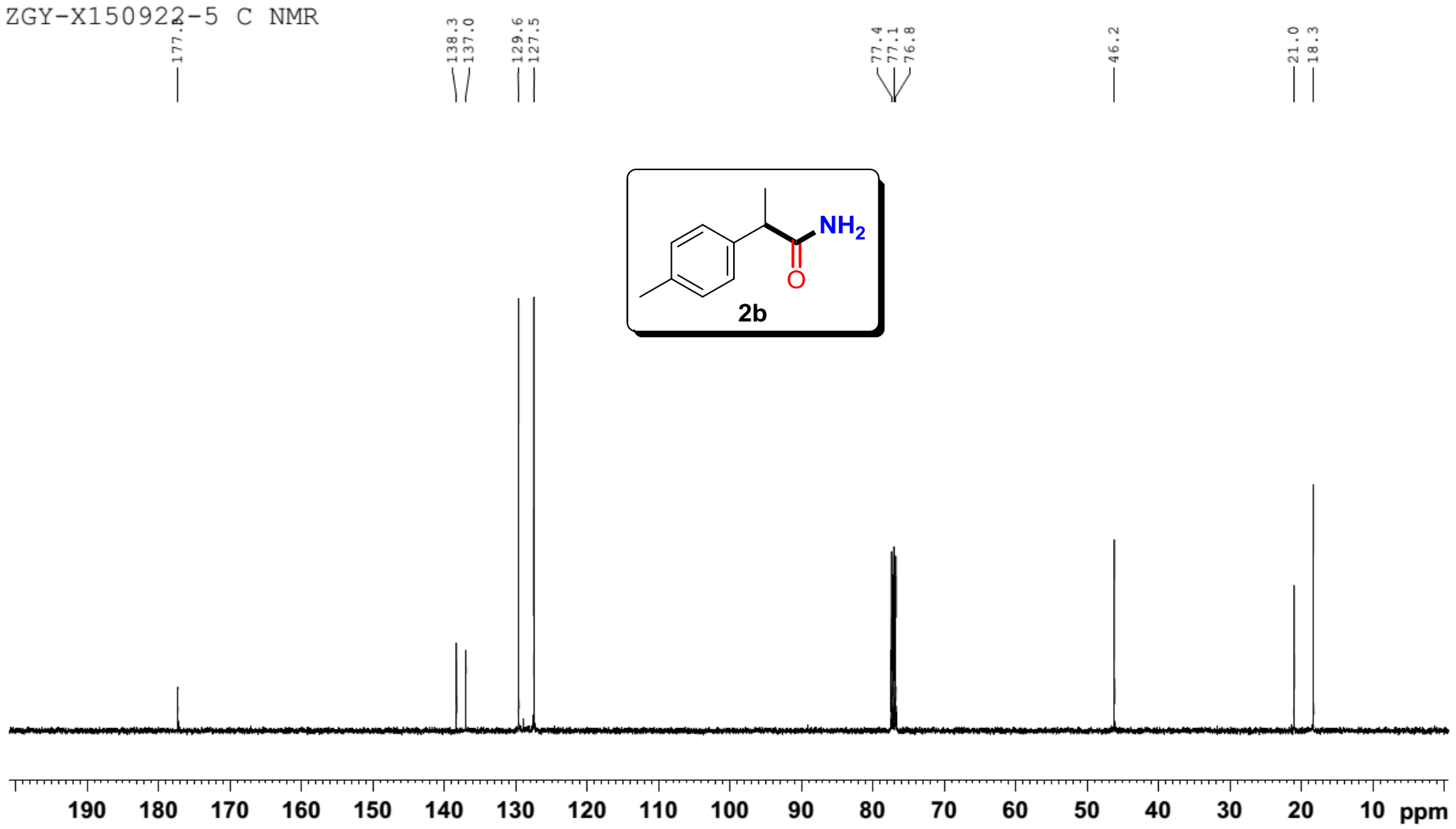
177.3
141.3
128.9
127.6
127.3
77.5
77.2
76.8
46.5
18.4
NH2
O
2a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

ZGY-X150926-4 H NMR

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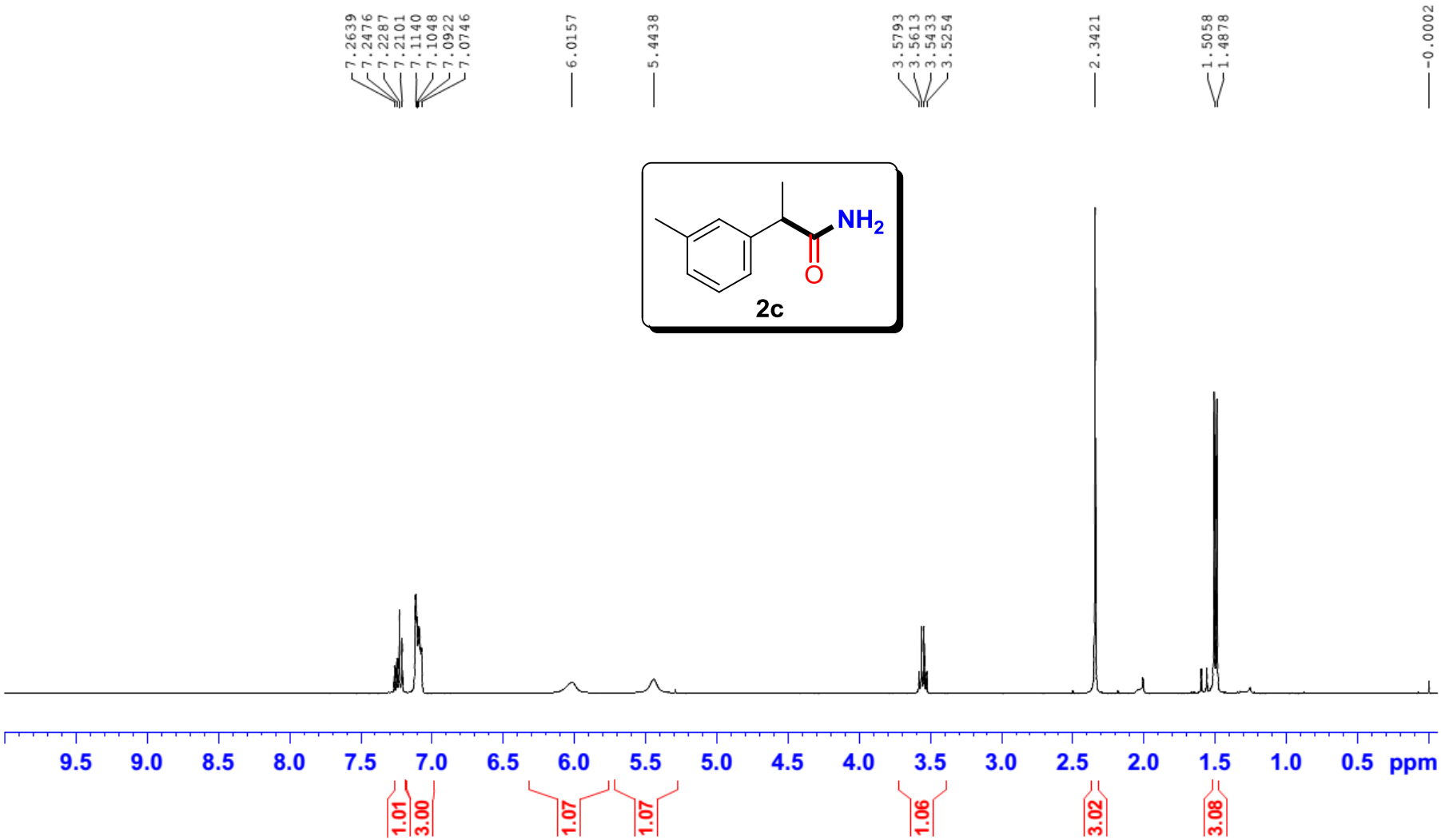
137.0
129.6
127.5
77.4
77.1
76.8
46.2
21.0
18.3
NH2
O
2b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

ZGY-X150927-5-HNMR



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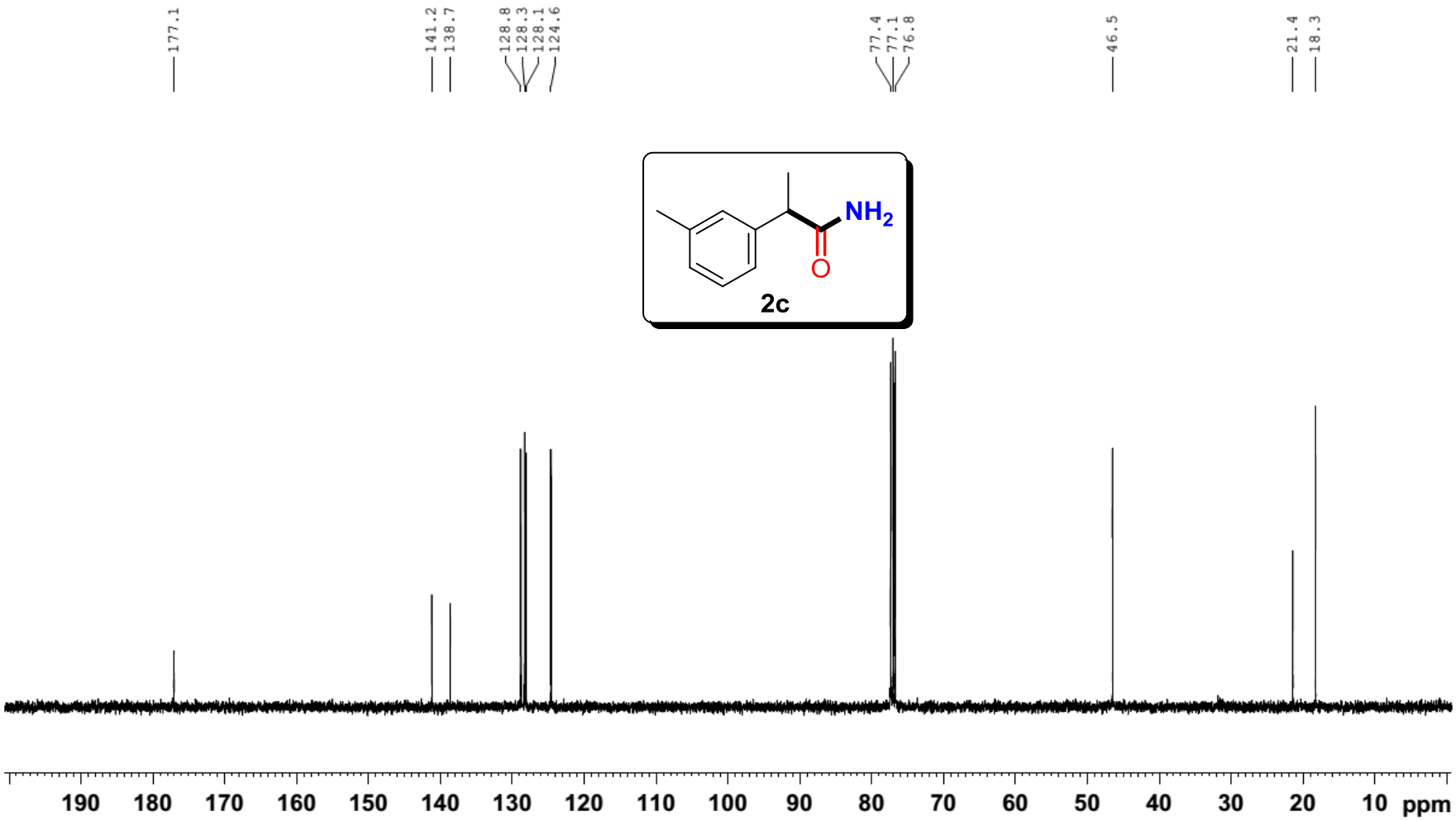

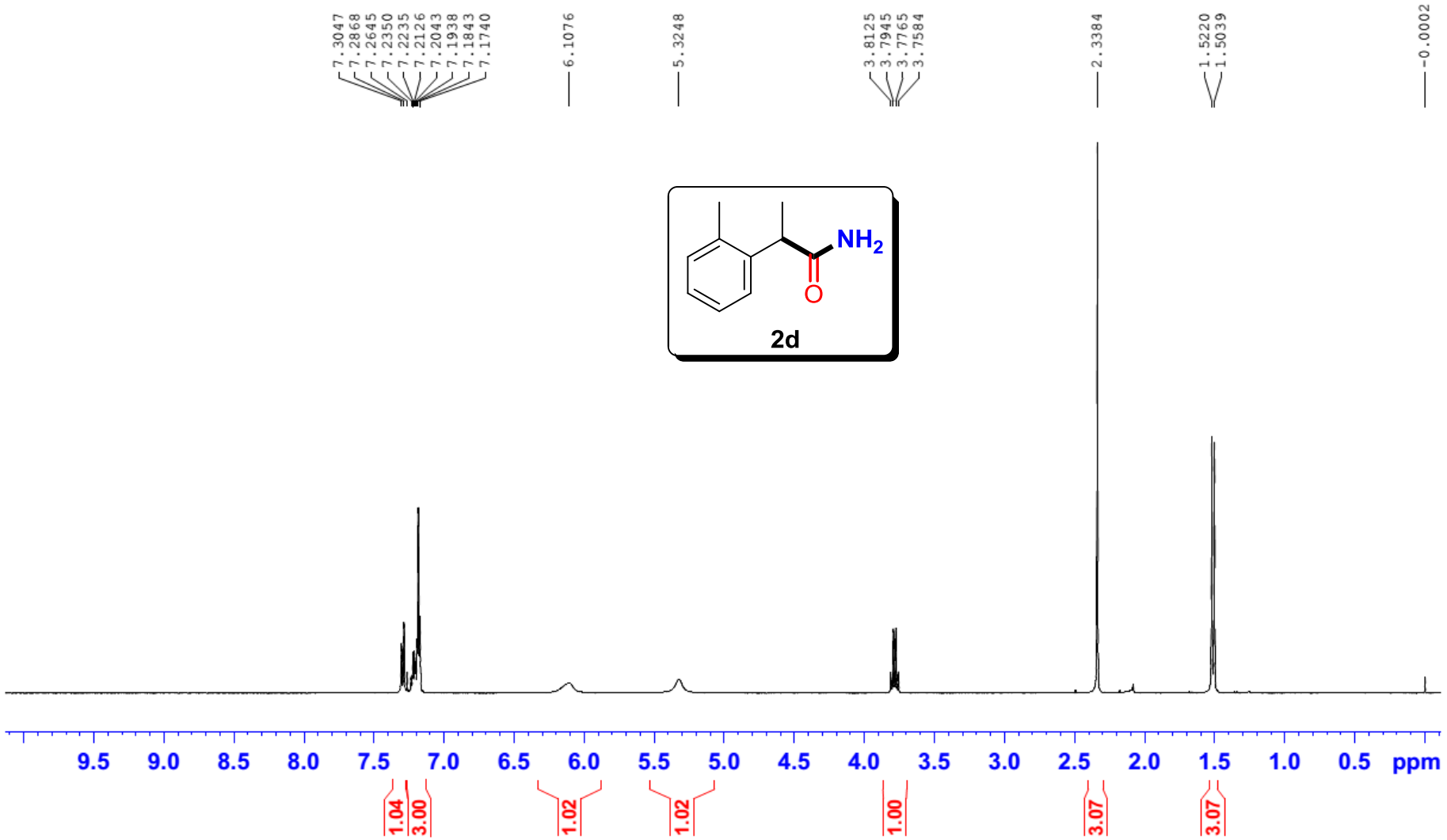
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7.2126
7.2043
7.1938
7.1843
7.1740
6.1076
5.3248
3.8125
3.7945
3.7765
3.7584
2.3384
1.5220
1.5039
-0.0002
NH2
O
2d
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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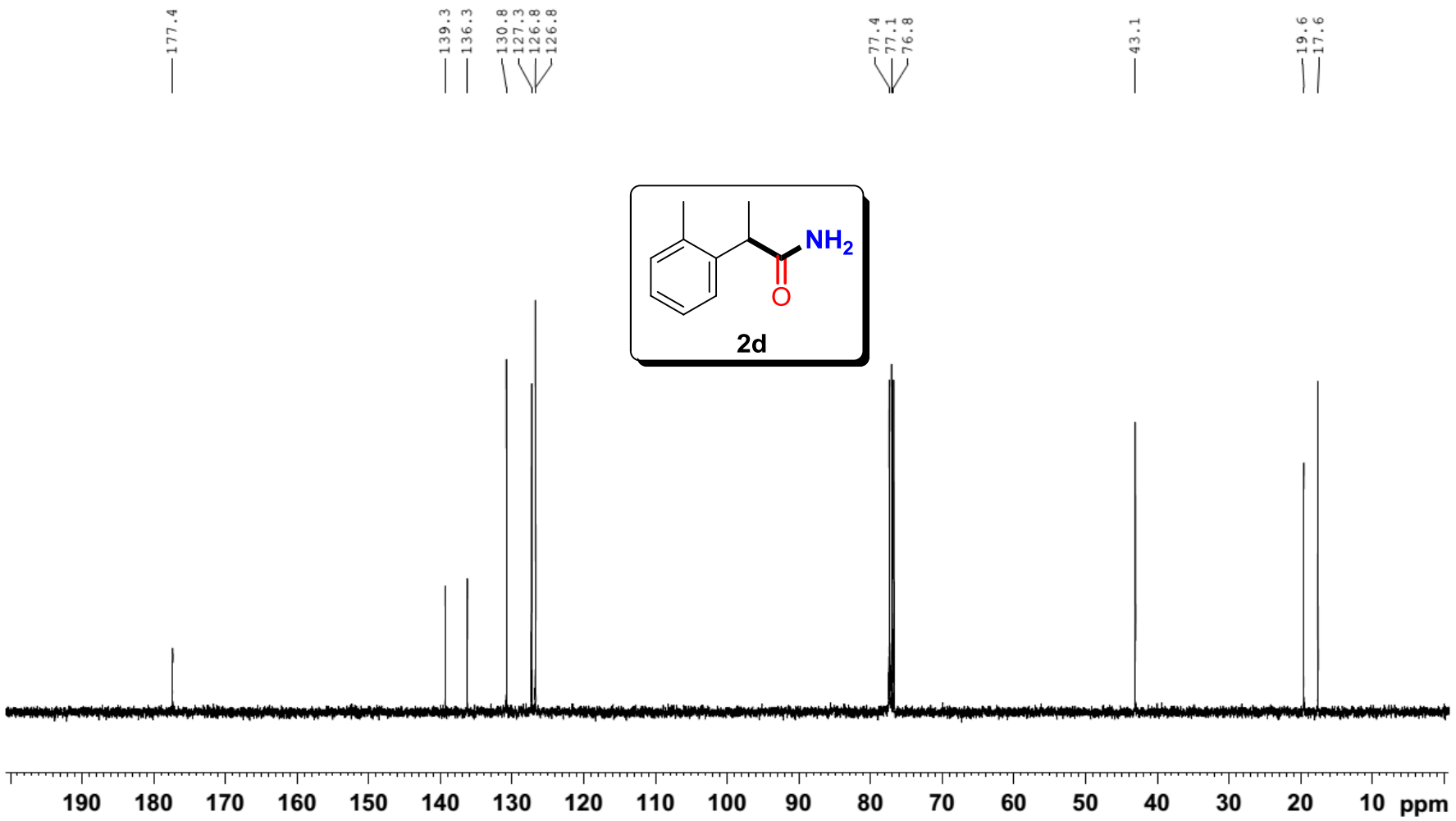
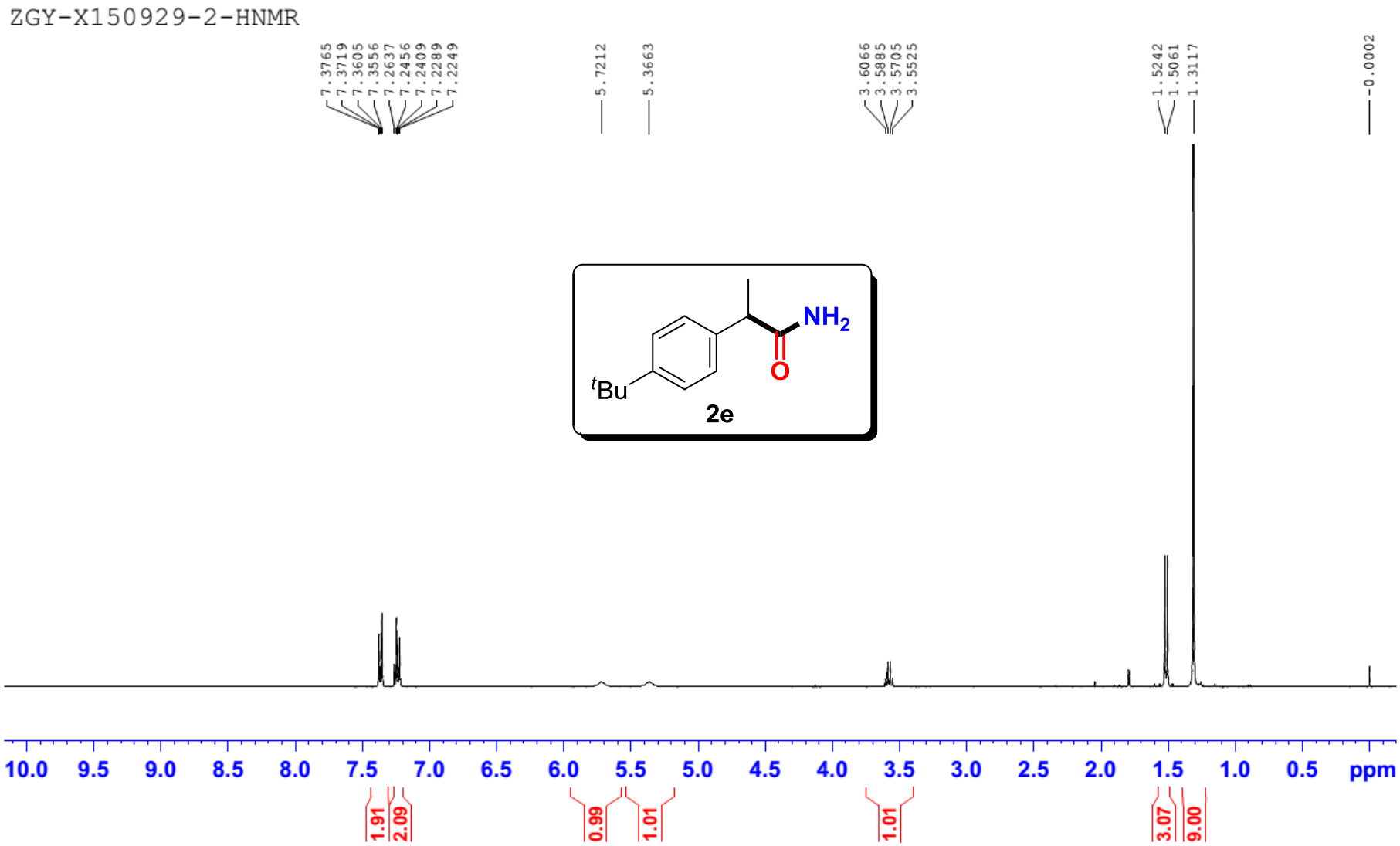
3.00
1.02
1.02
1.00
3.07
3.07

ZGY-X150927-7-CNMR

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7.2456
7.2409
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7.2249
5.7212
5.3663
3.6066
3.5885
3.5705
3.5525
1.5242
1.5061
1.3117
0.0002
NH2
O
tBu
2e
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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ppm
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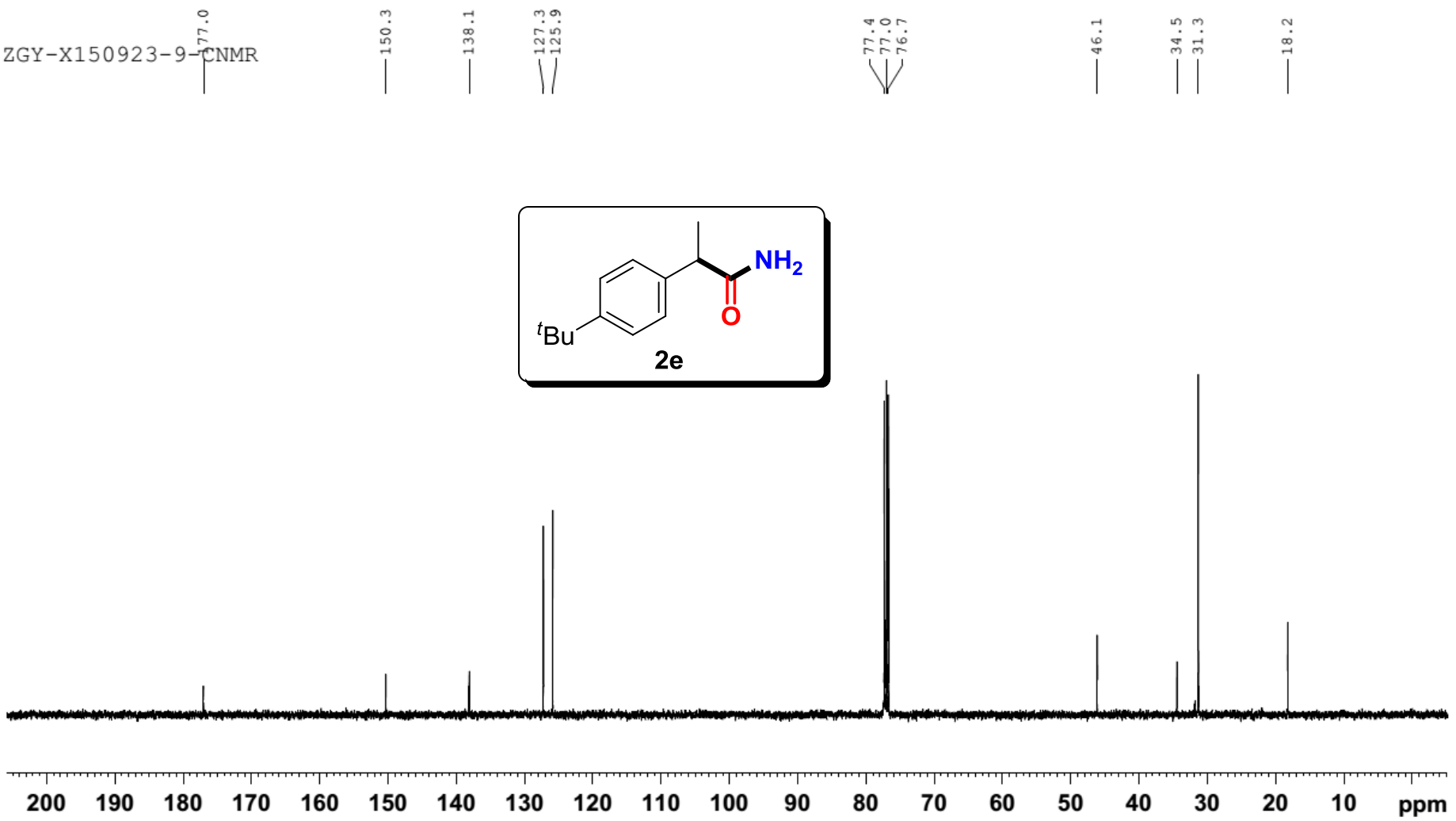
0.99
1.01
1.01
3.07
9.00


ZGY-X150923-9-CNMR
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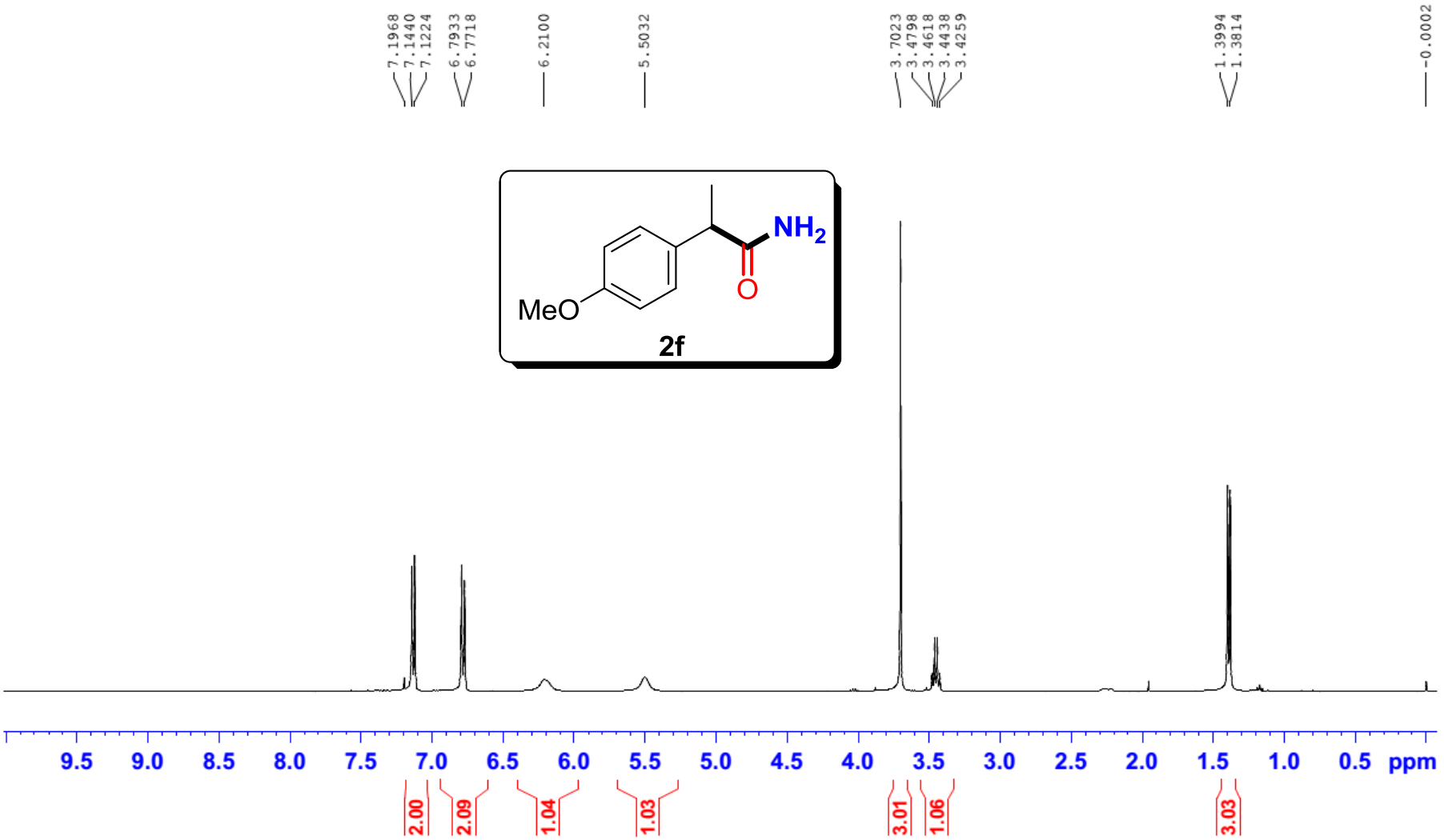
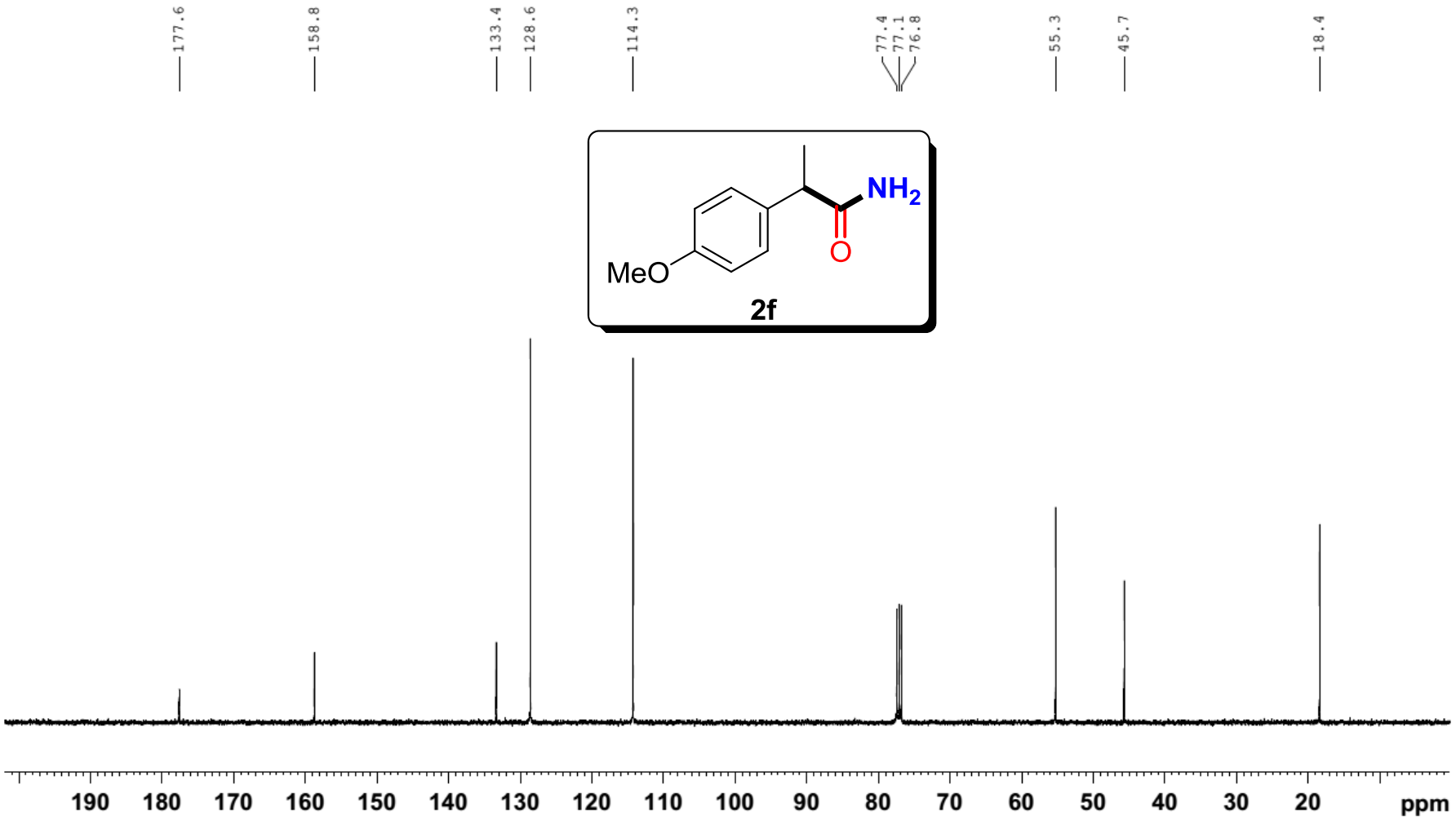
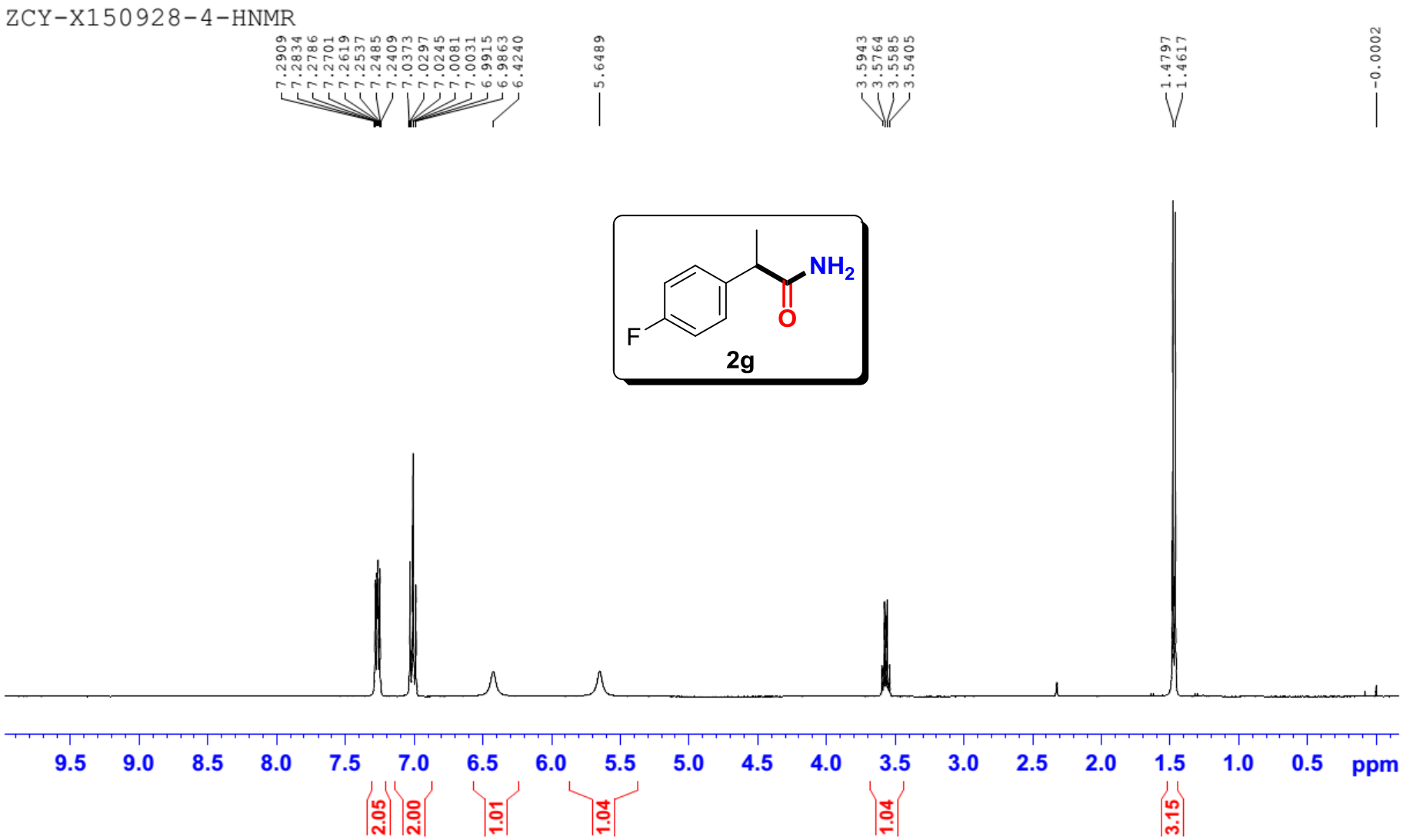
138.1
127.3
125.9
77.4
77.0
76.7
46.1
34.5
31.3
18.2
NH2
O
tBu
2e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

ZGY-X150927-6-HNMR

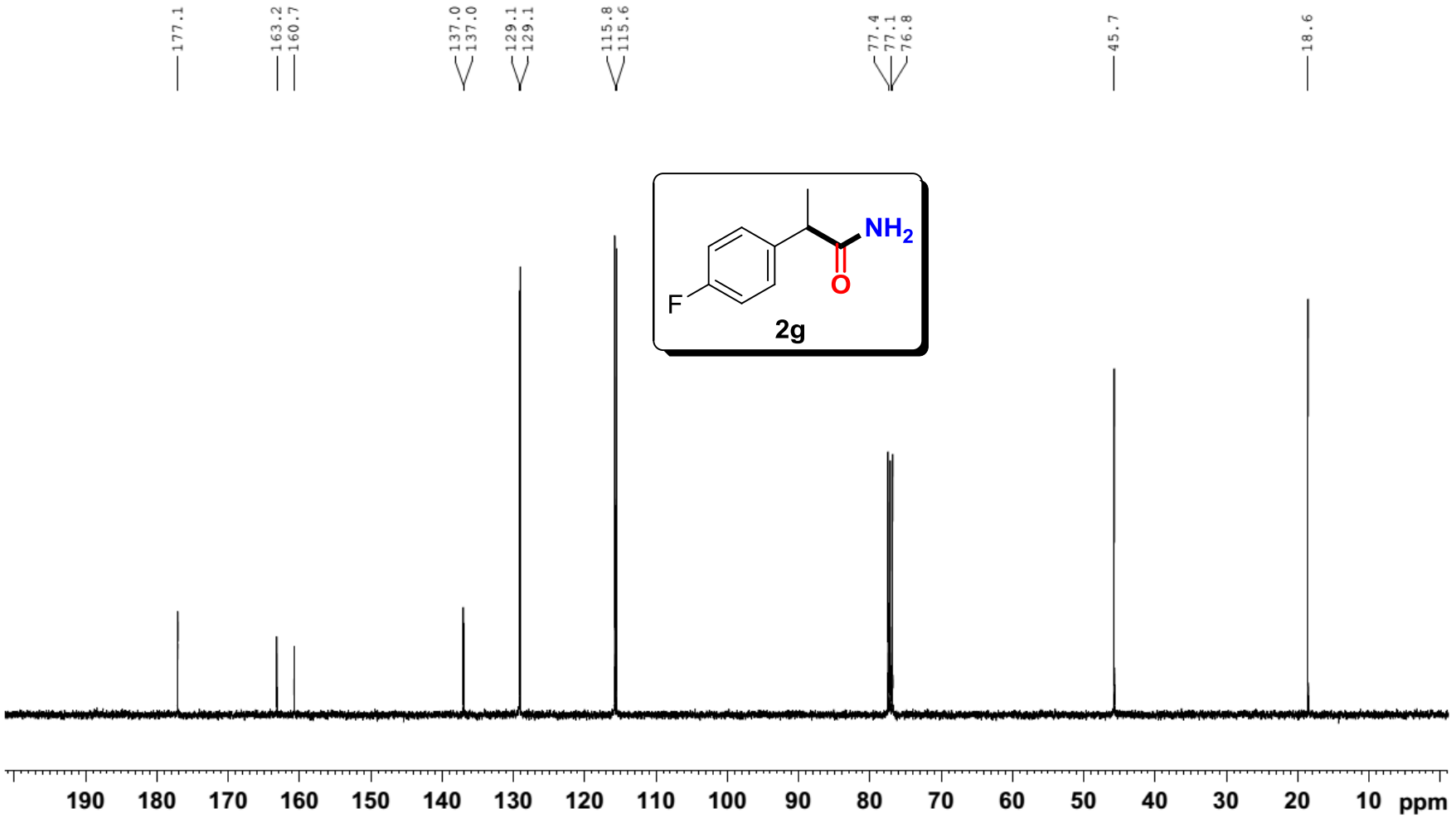


ZGY-X150927-6-CNMR

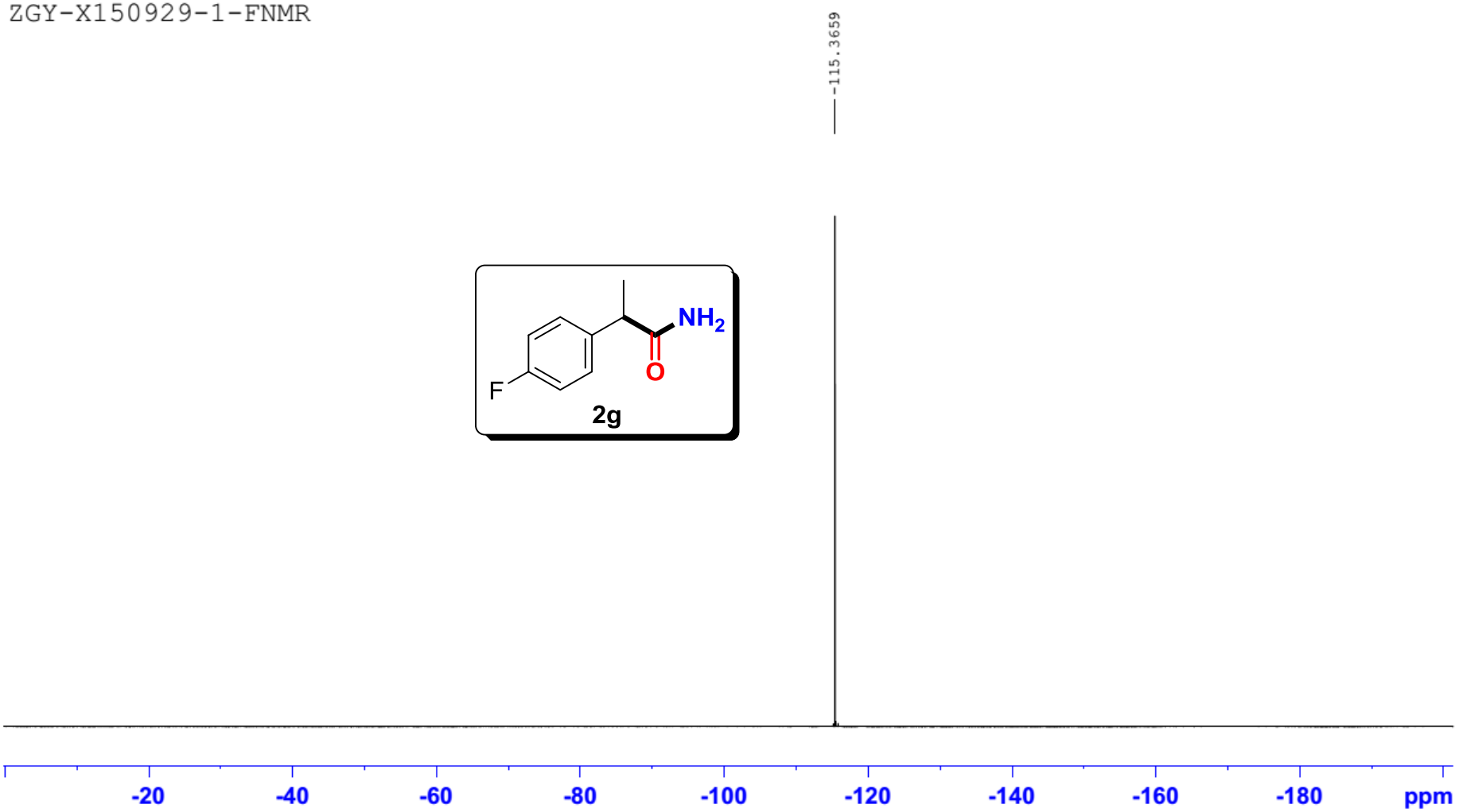


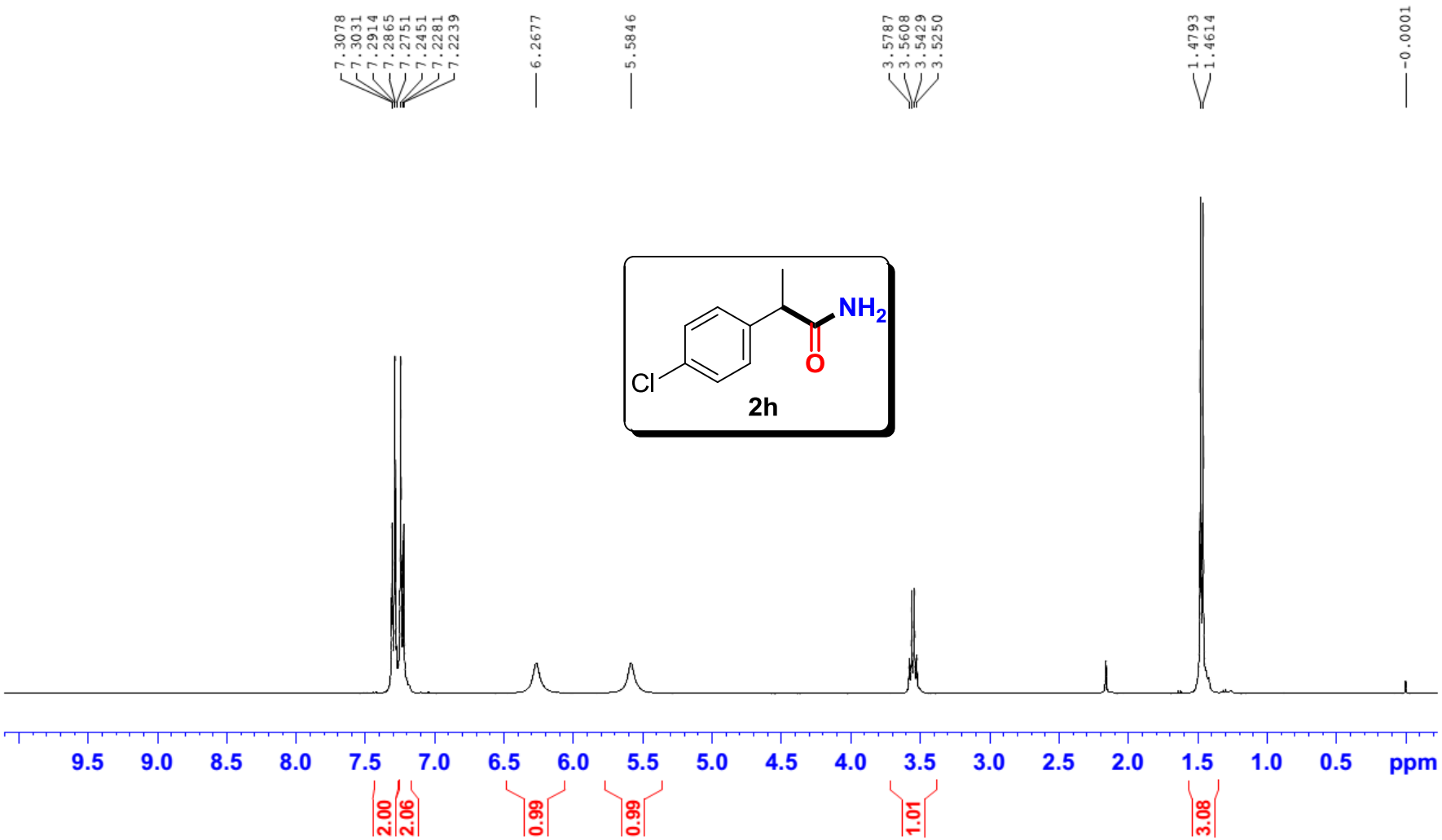

ZCY-X150928-4-HNMR
7.2909
7.2834
7.2786
7.2701
7.2619
7.2537
7.2485
7.2409
7.0373
7.0297
7.0245
7.0081
7.0031
6.9915
6.9863
6.4240
5.6489
3.5943
3.5764
3.5585
3.5405
1.4797
1.4617
-0.0002
NH2
O
F
2g
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.05
2.00
1.01
1.04
1.04
3.15

ZCY-X150928-4-CNMR



ZGY-X150929-1-FNMR




N CDCl3 {E:\data} R
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7.3031
7.2914
7.2865
7.2751
7.2451
7.2281
7.2239
6.2677
5.5846
3.5787
3.5608
3.5429
3.5250
1.4793
1.4614
-0.0001
NH2
O
Cl
2h
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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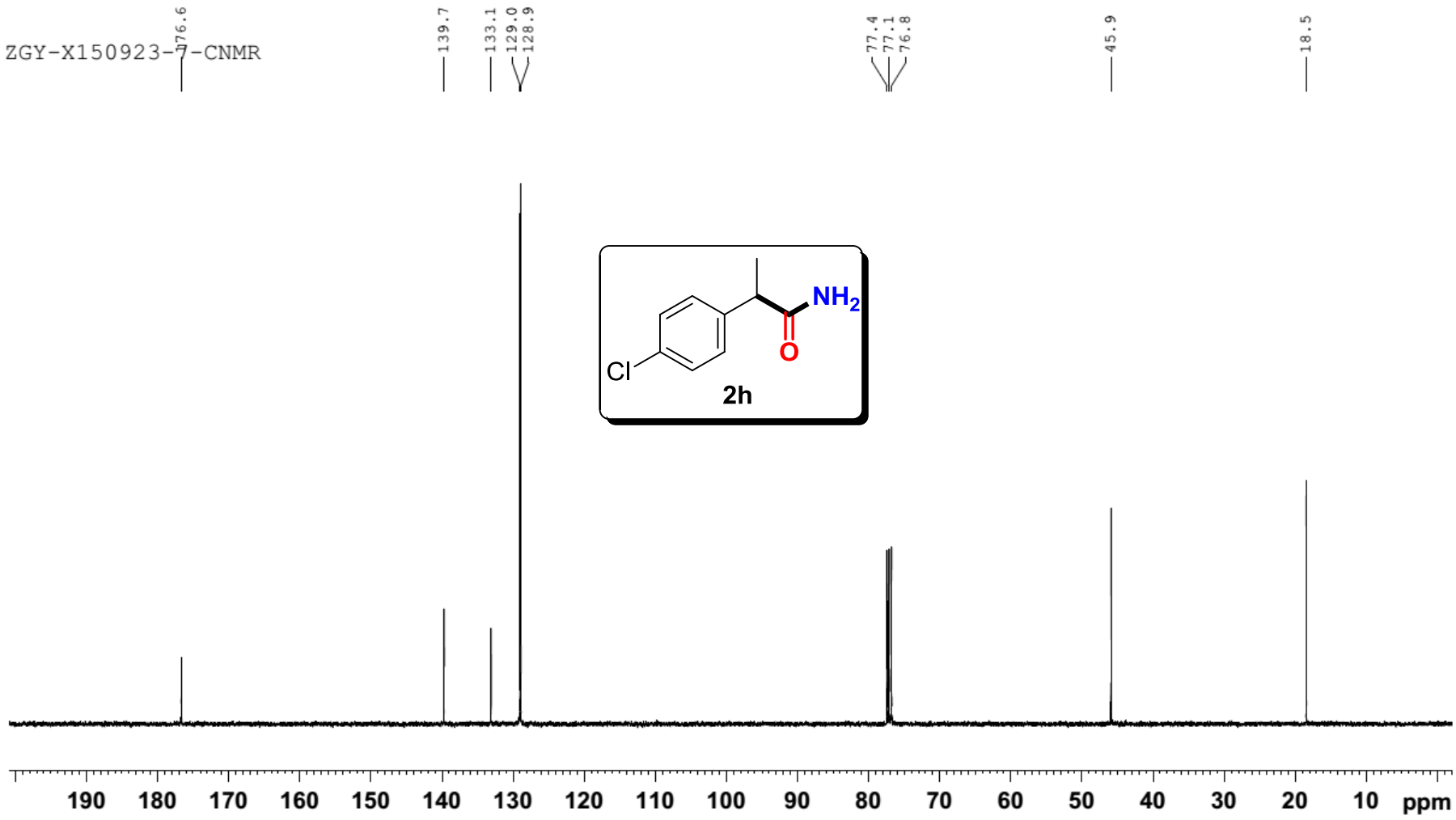
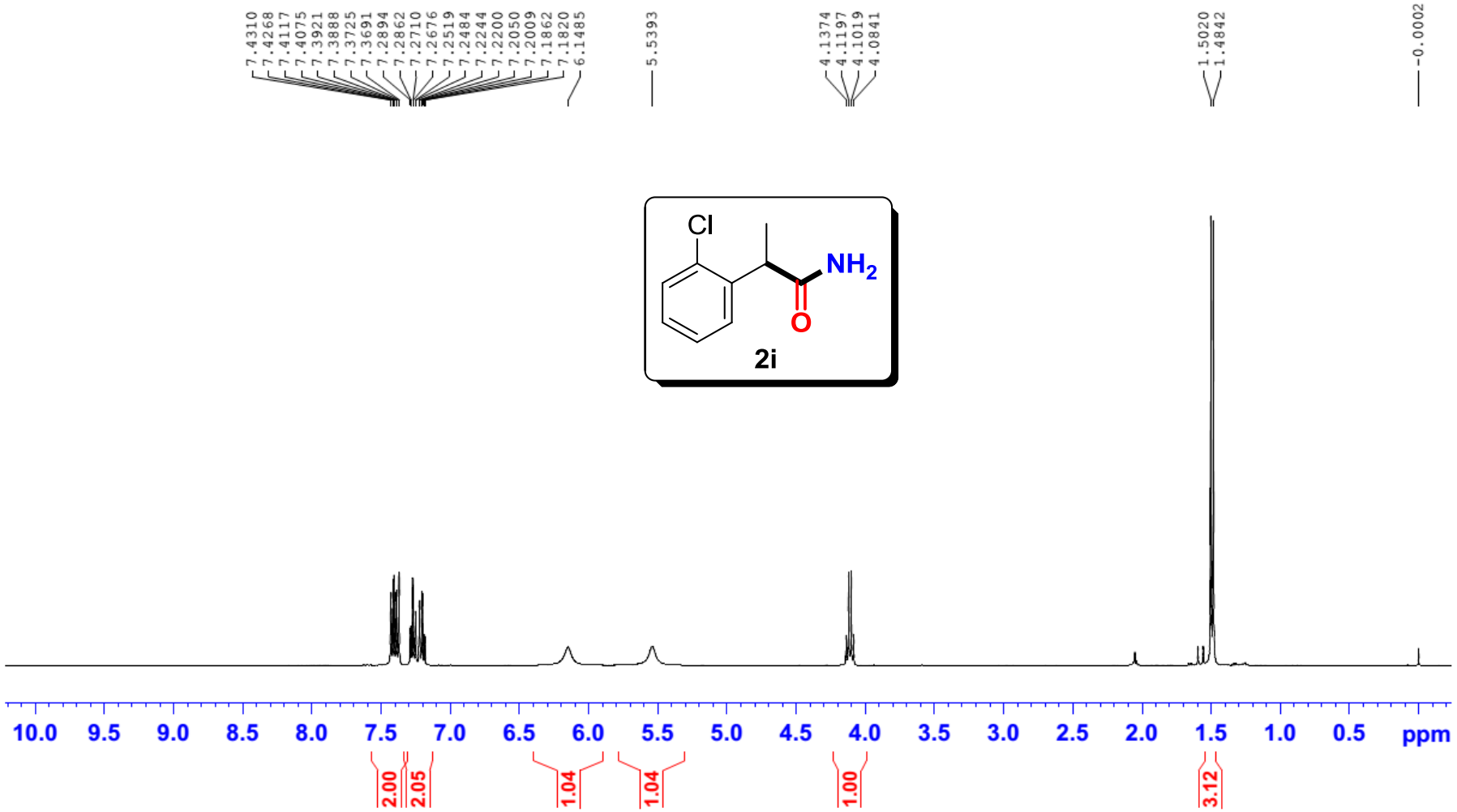
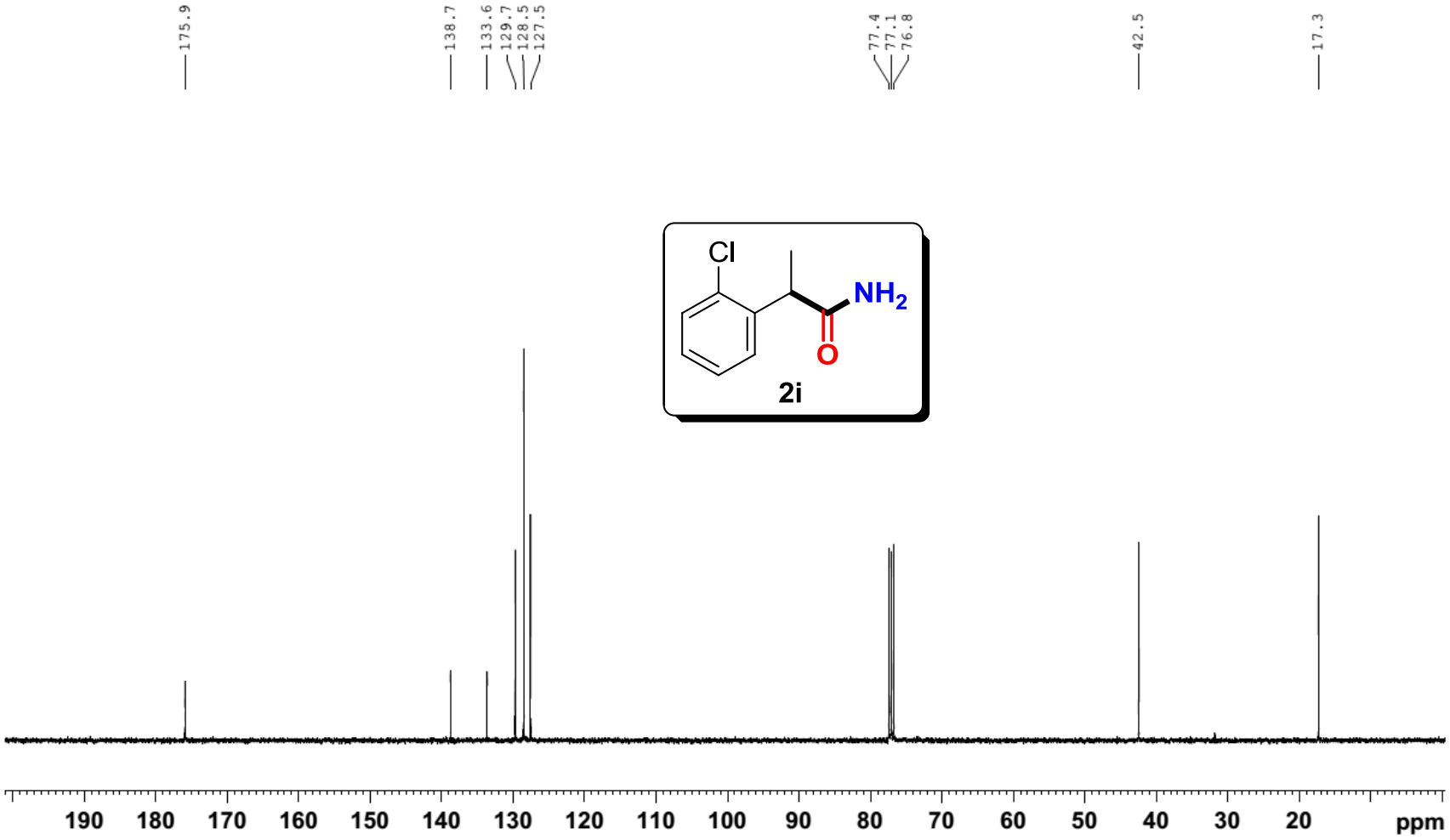
1.5
1.0
0.5
ppm
2.00
2.06
0.99
0.99
1.01
3.08


ZGY-X150923-7-CNMR
176.6
139.7
133.1
129.0
128.9
77.4
77.1
76.8
45.9
18.5
NH2
O
Cl
2h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

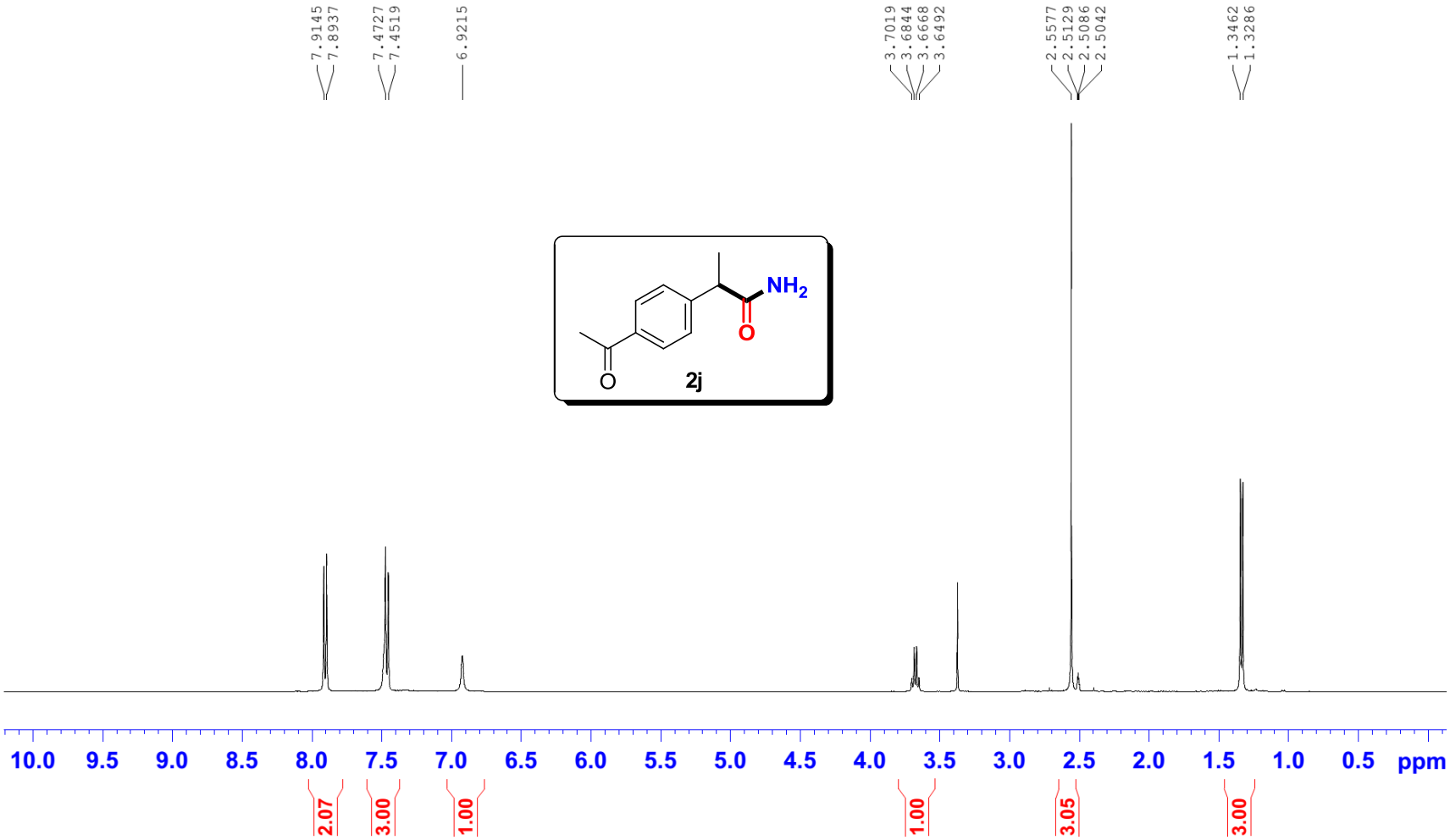
ZGY-X15X15-1-HNMR



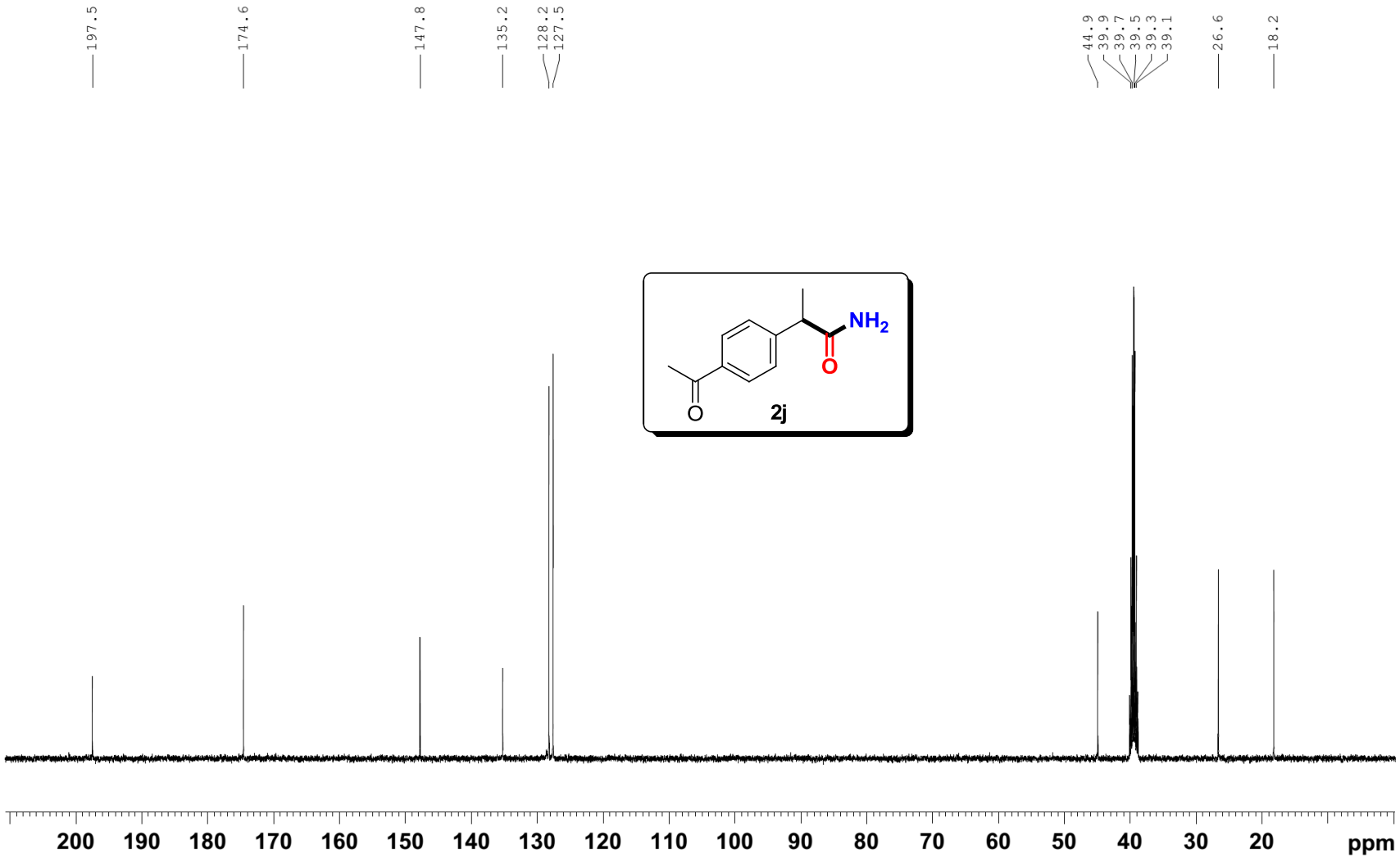
ZGY-X15X15-1-CNMR



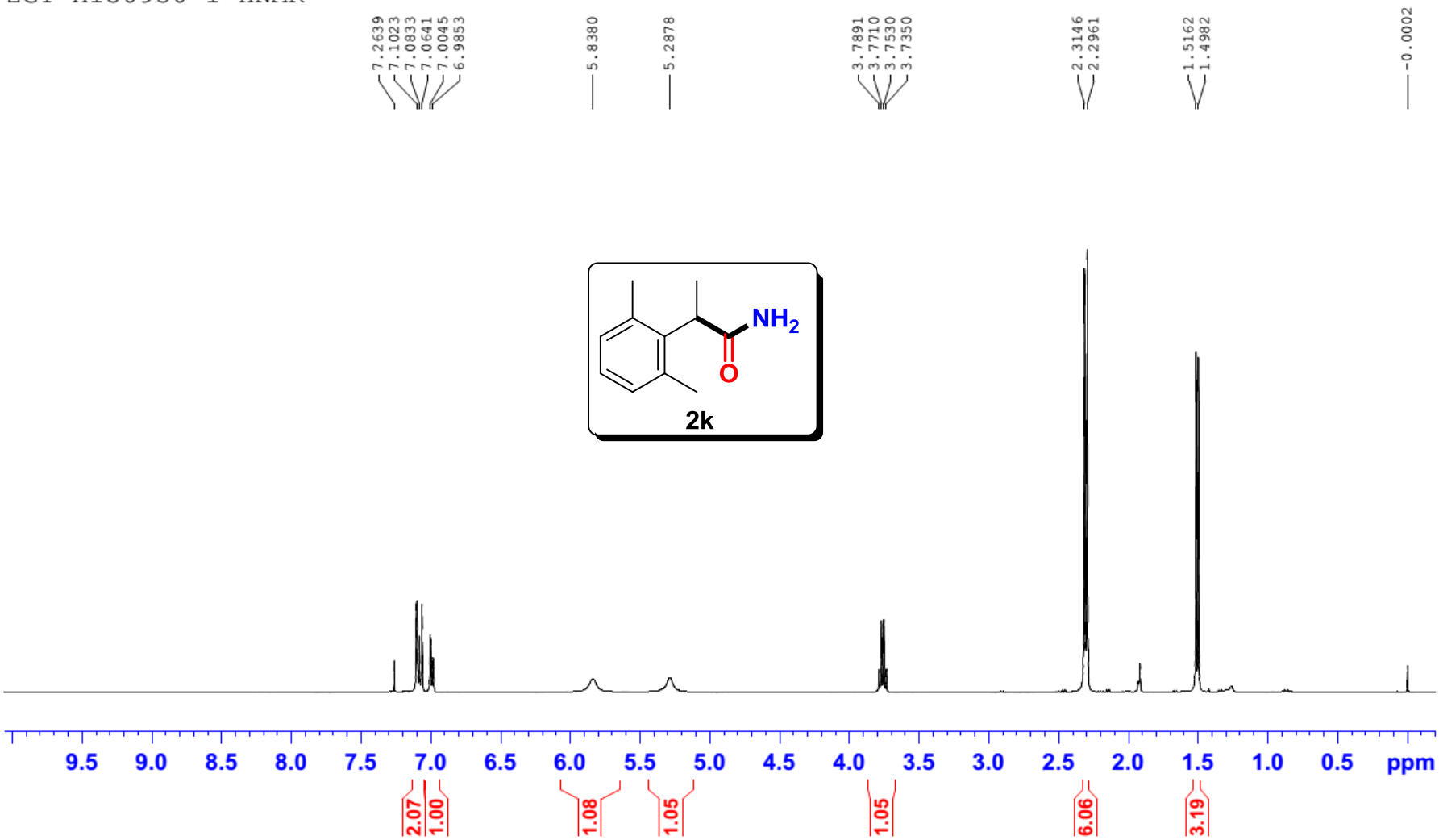
ZJP-X160113-1-HNMR



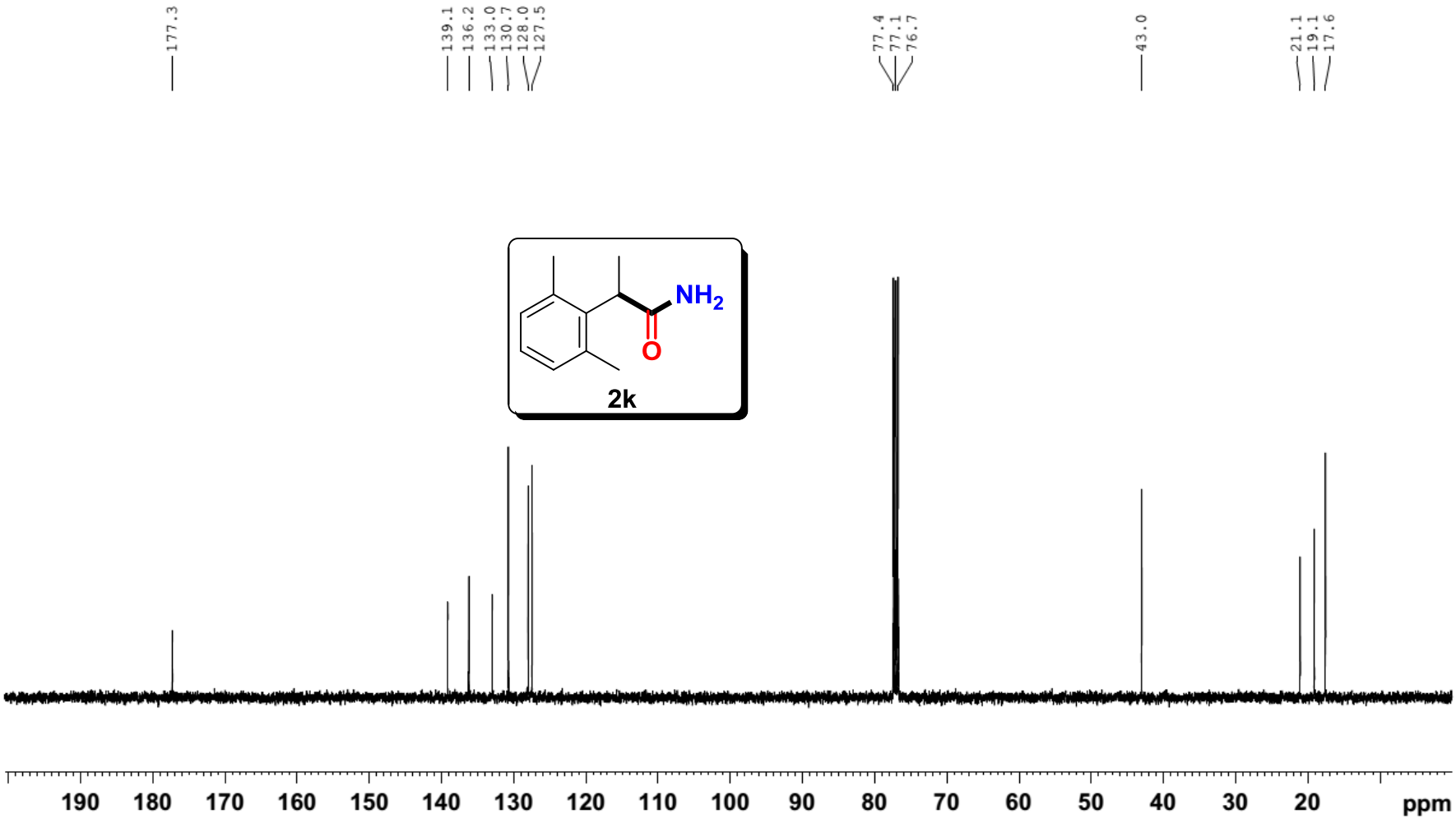
ZJP-X160113-1-CNMR



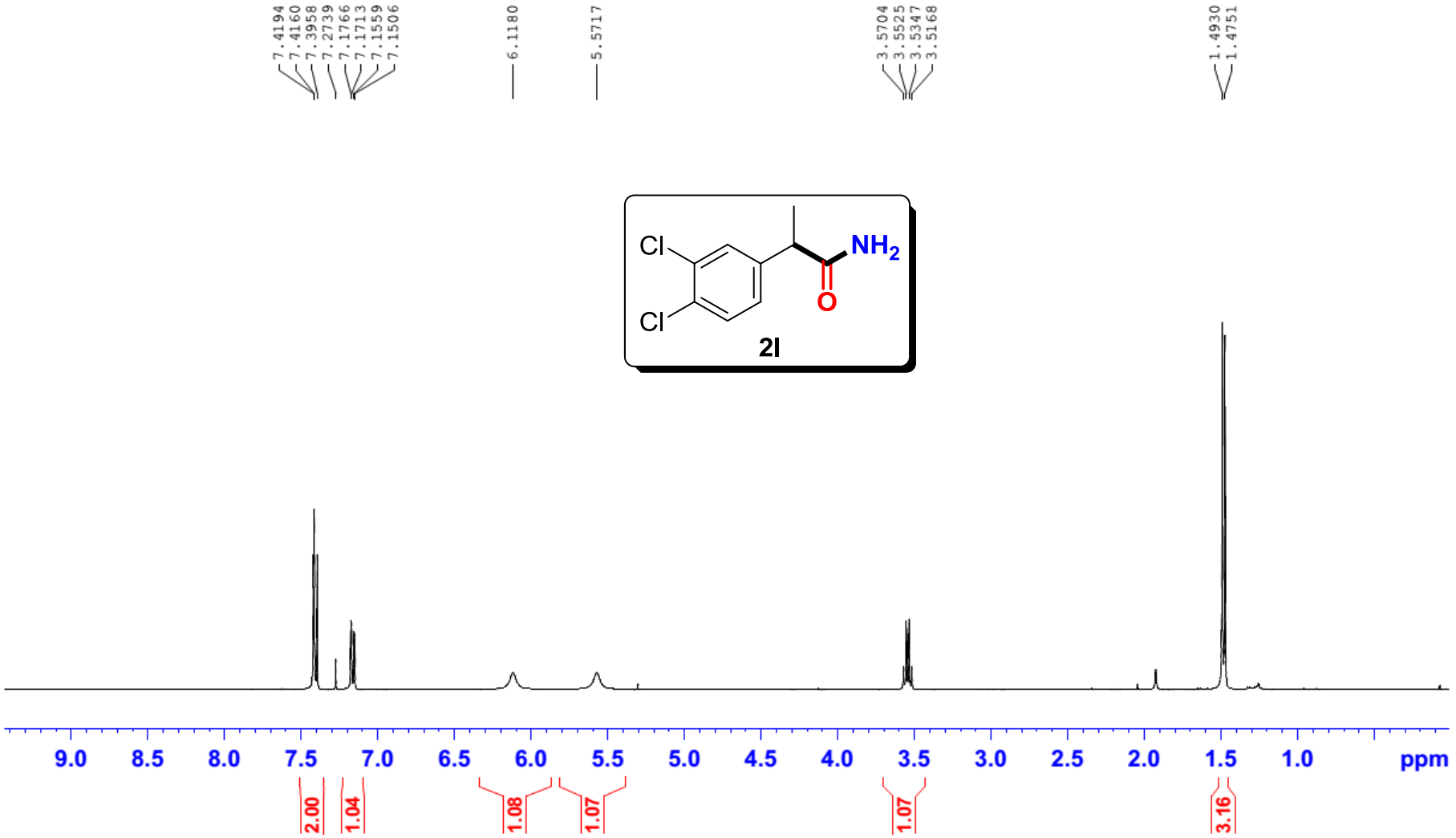
ZGY-X150930-1-HNMR



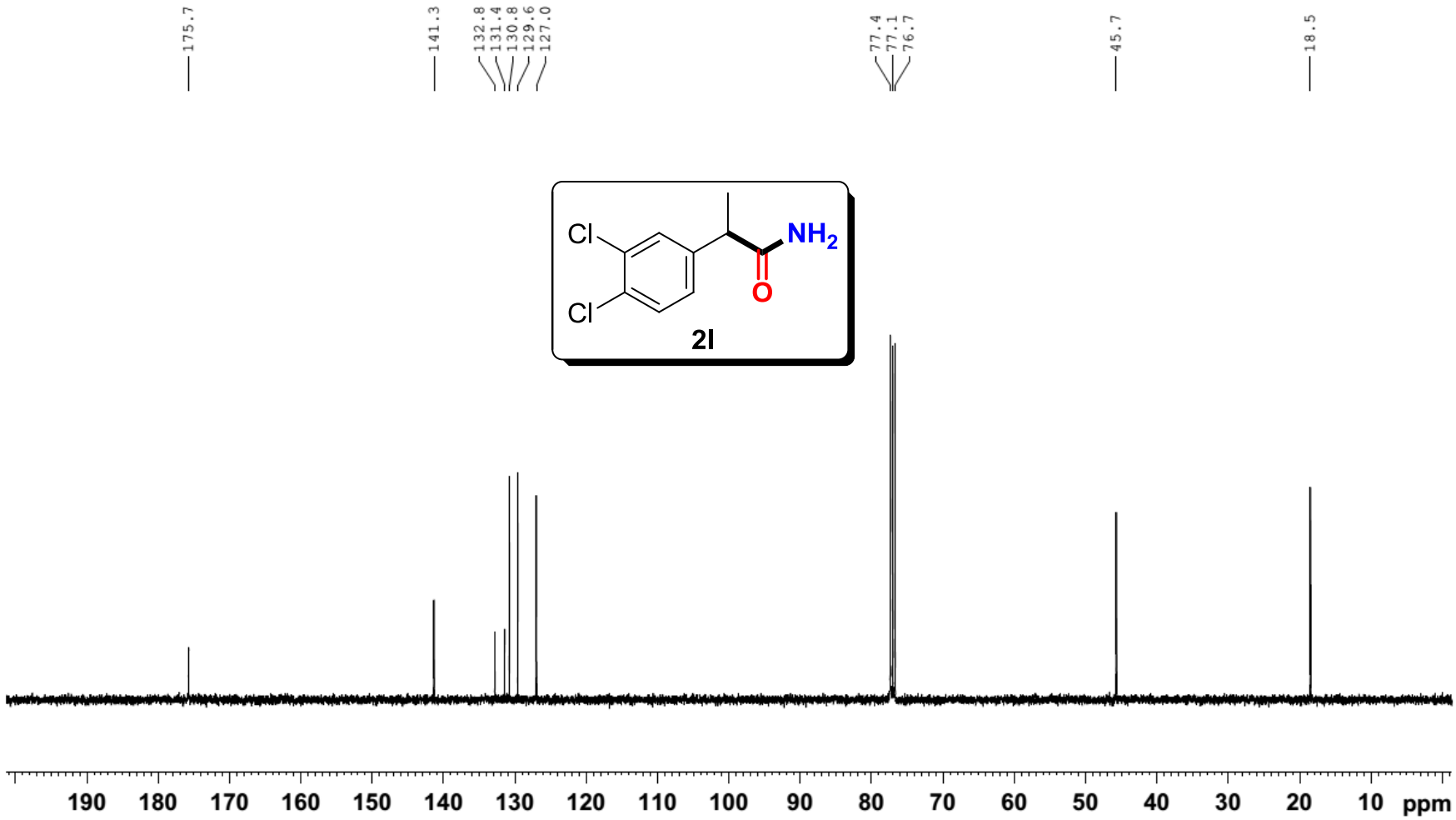
ZGY-X150930-1-CNMR



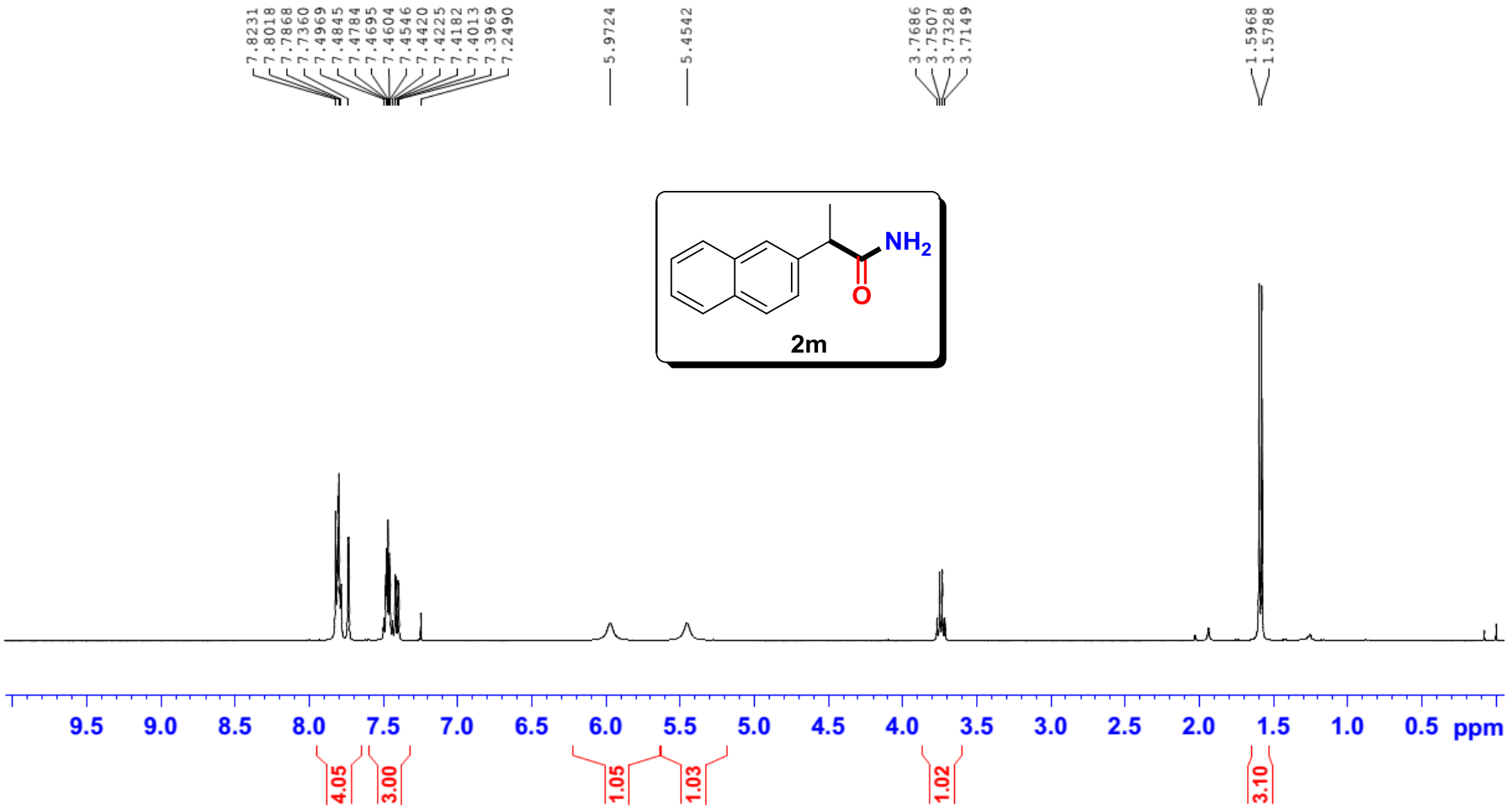
ZGY-X150927-4-HNMR



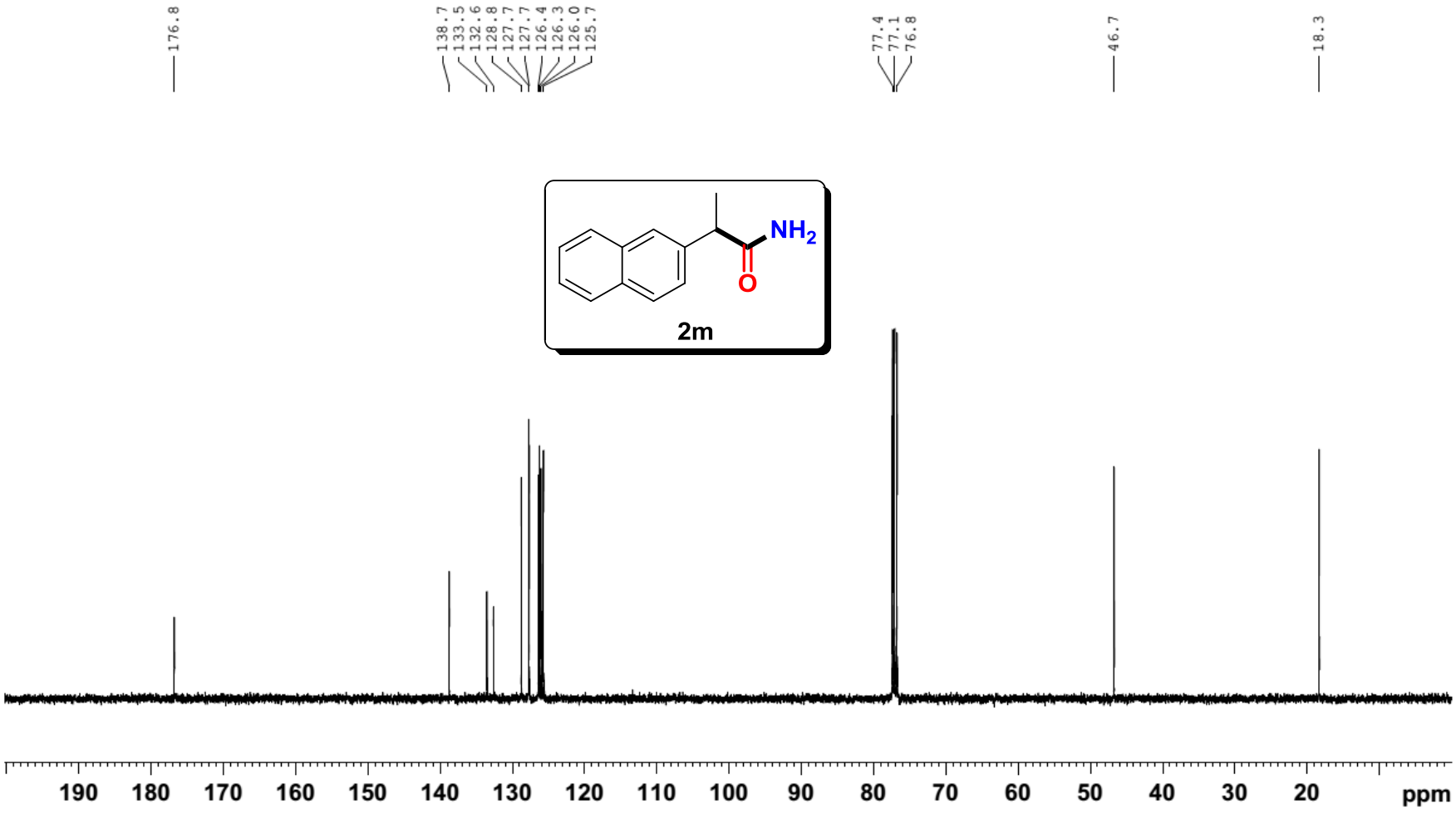
ZGY-X150927-4-CNMR



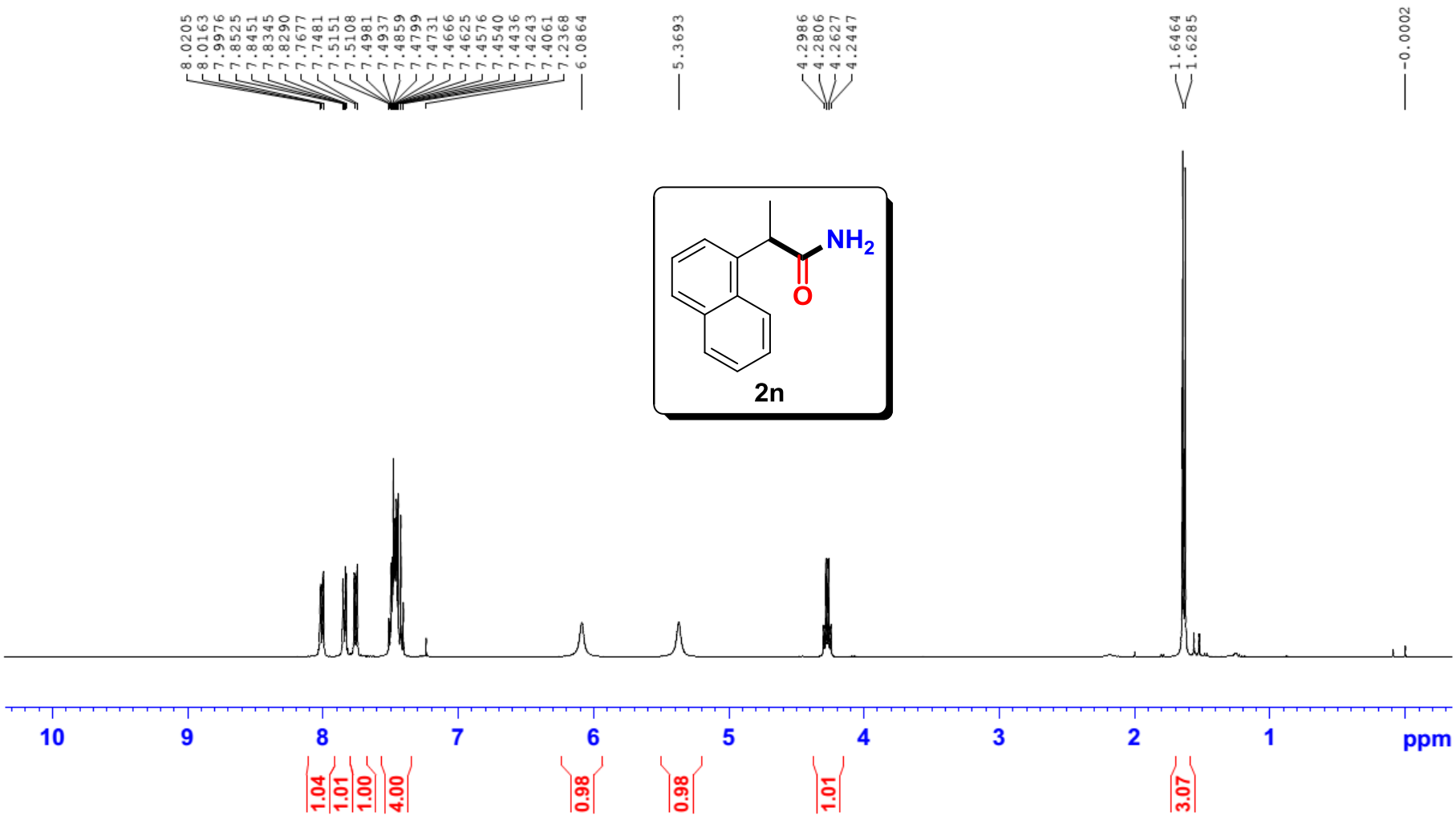
ZGY-X15X28-3-HNMR



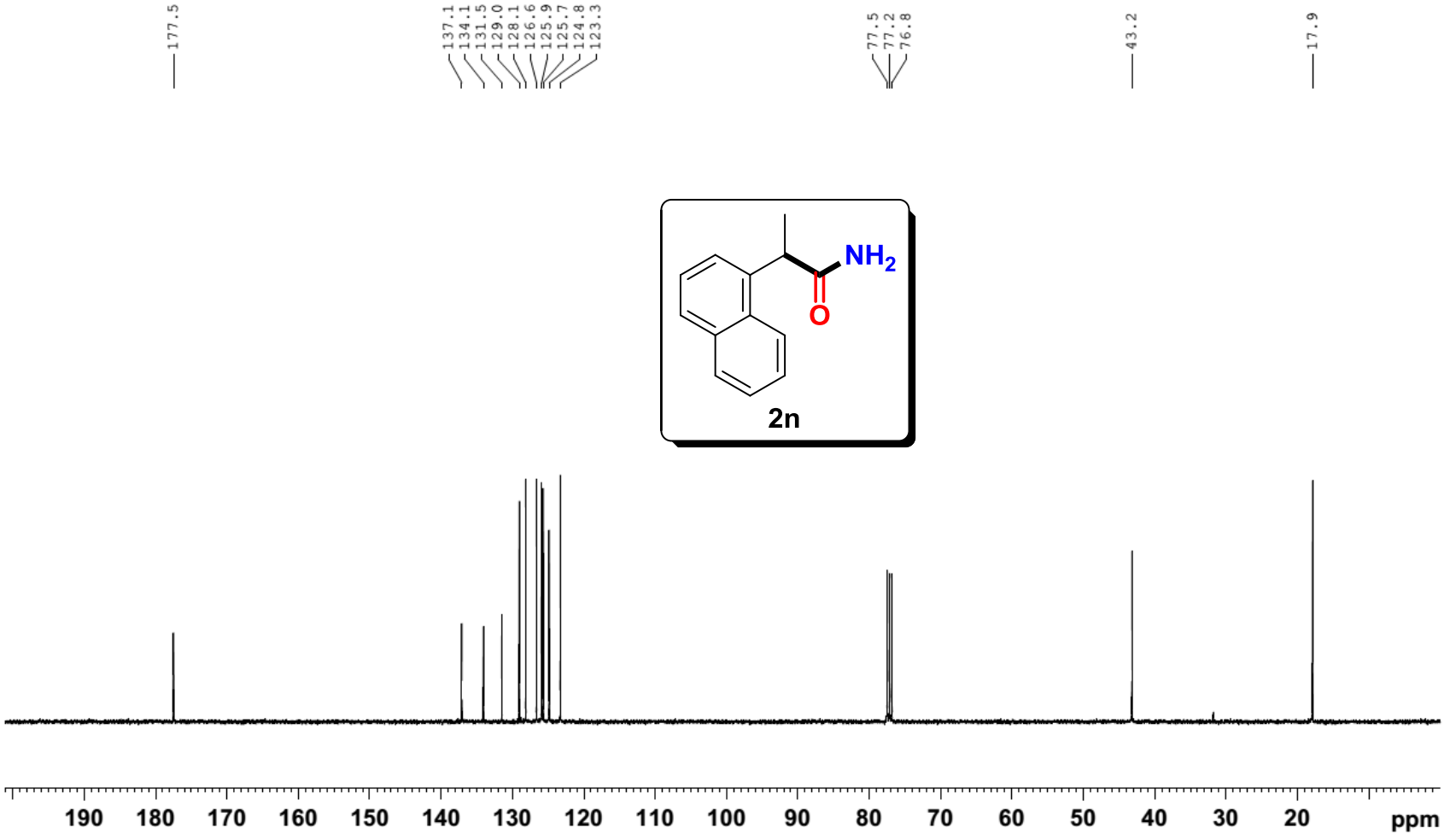
ZGY-X15X28-3-CNMR

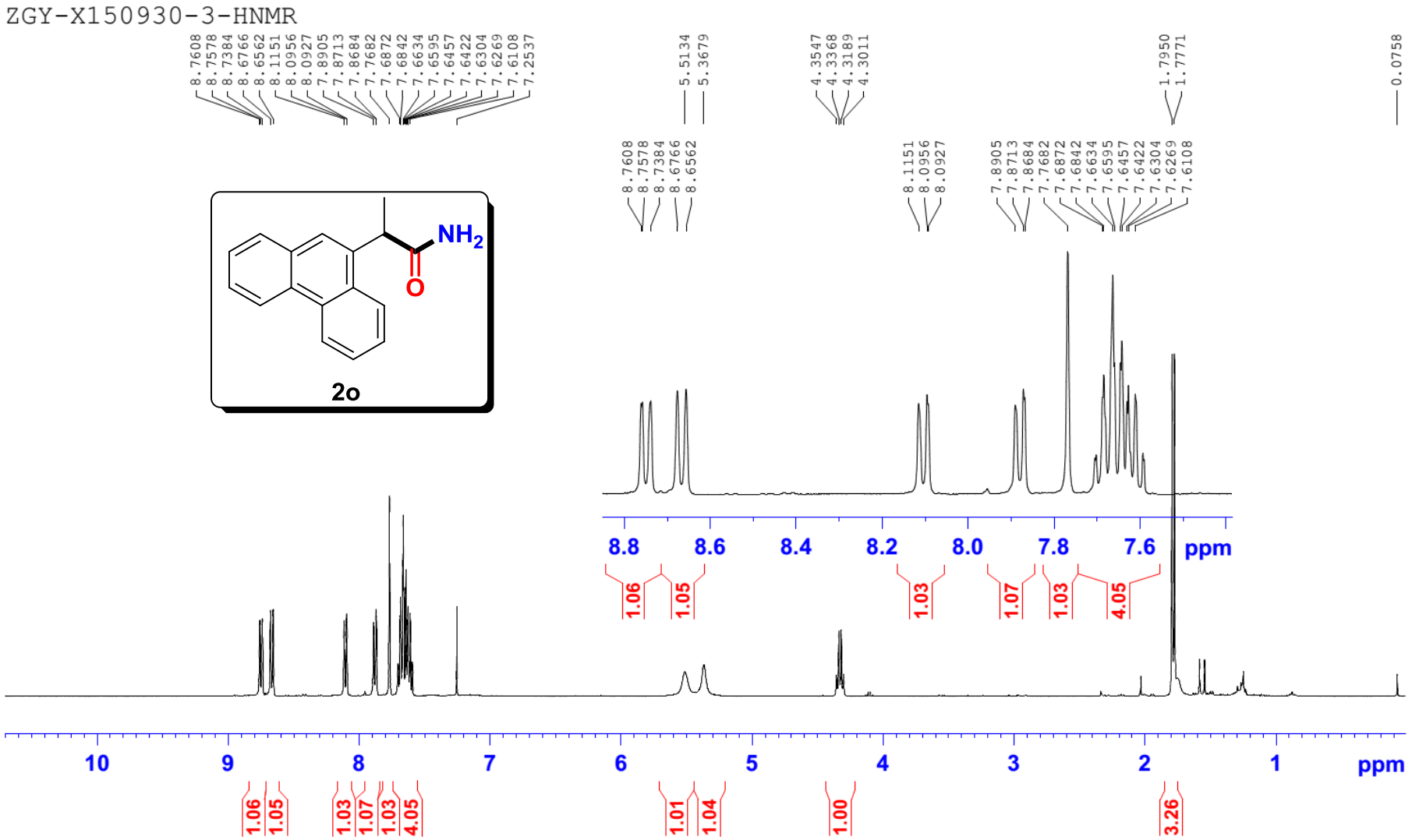


ZGY-X15X19-1-HNMR

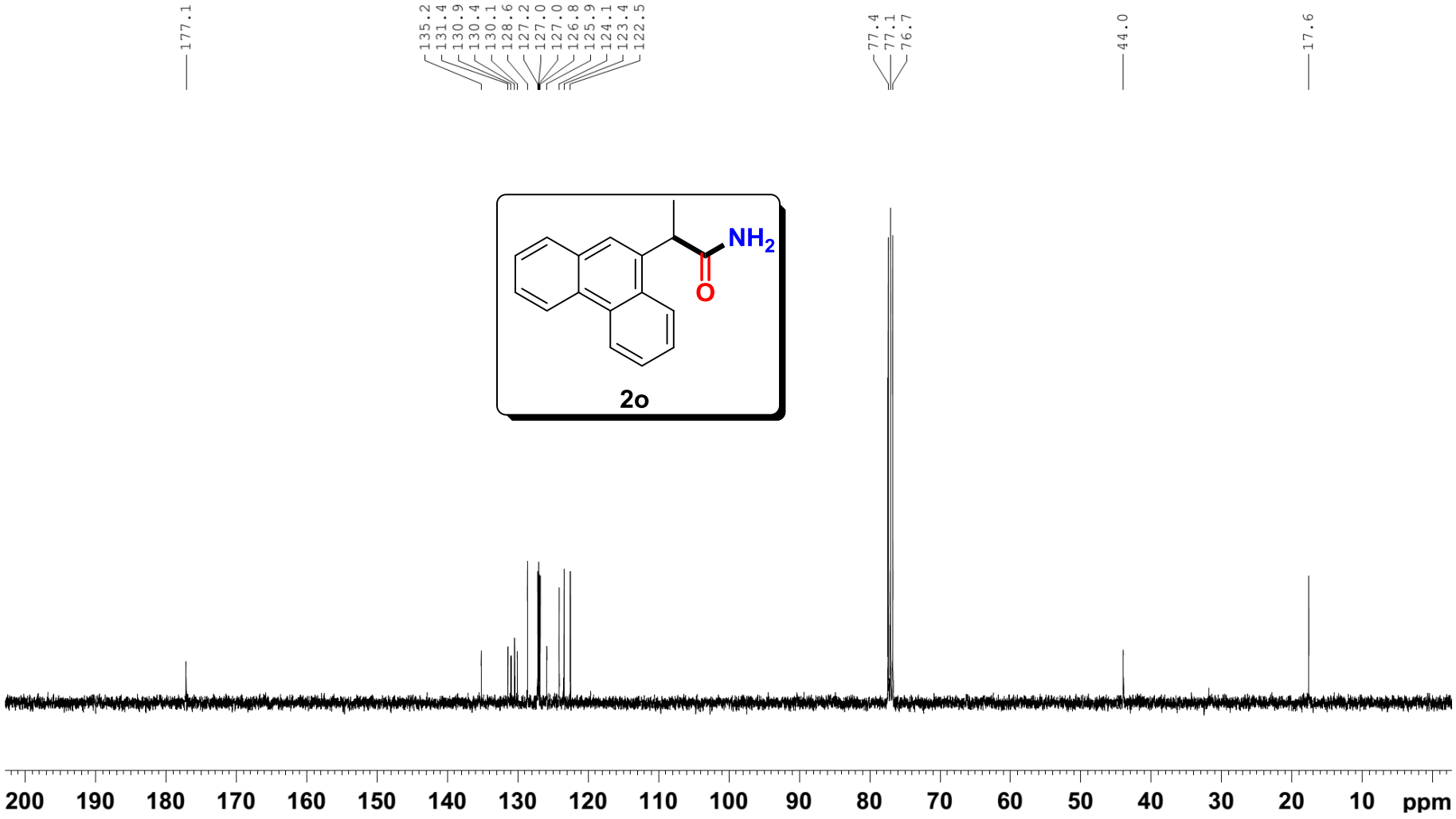


ZGY-X15X19-1-CNMR

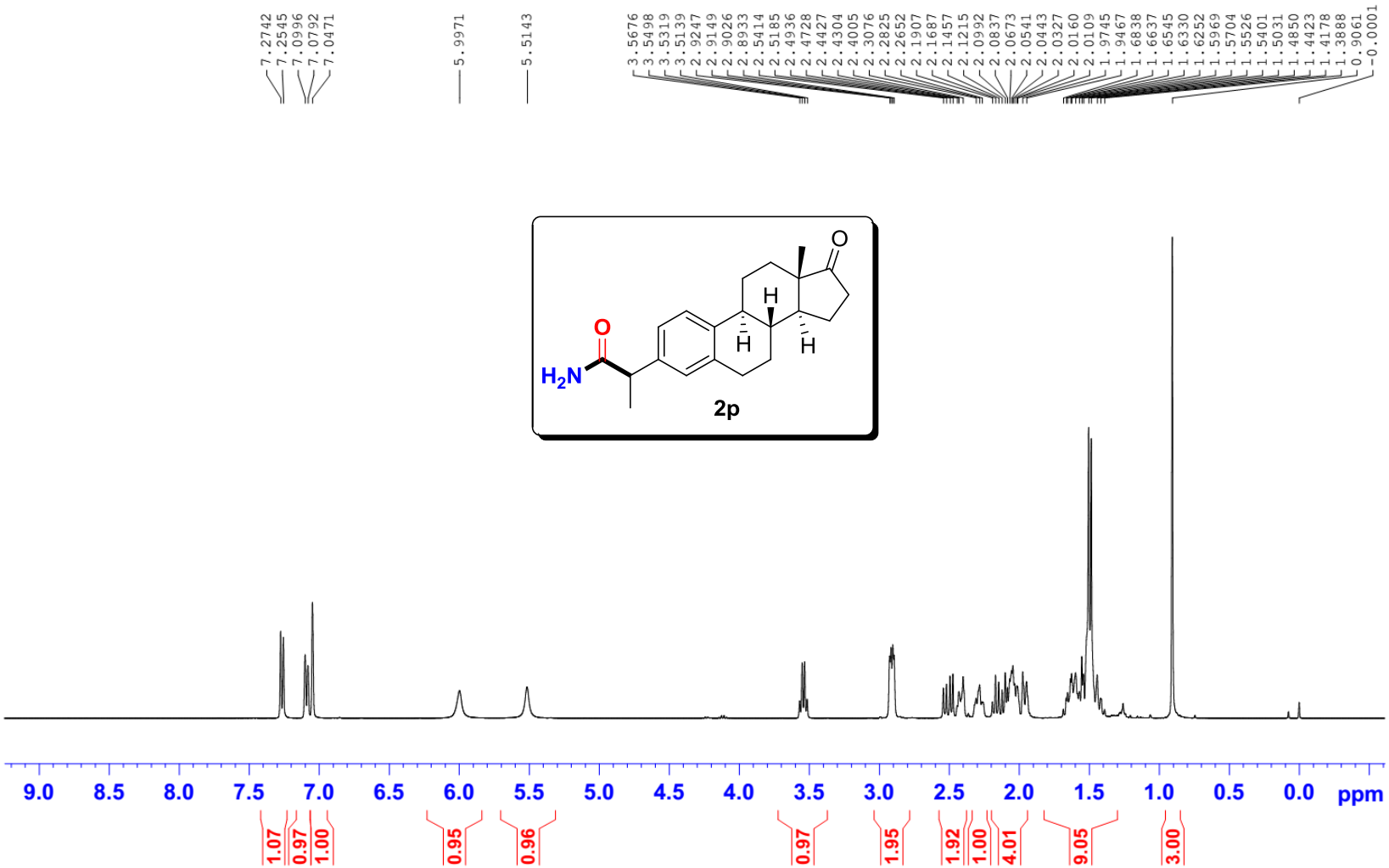



ZGY-X150930-3-HNMR
8.7608
8.7578
8.7384
8.6766
8.6562
8.1151
8.0956
8.0927
7.8905
7.8713
7.8684
7.7682
7.6872
7.6842
7.6634
7.6595
7.6457
7.6422
7.6304
7.6269
7.6108
7.2537
5.5134
5.3679
4.3547
4.3368
4.3189
4.3011
1.7950
1.7771
0.0758
NH2
O
2o
8.8
8.6
8.4
8.2
8.0
7.8
7.6
ppm
1.06
1.05
1.03
1.07
1.03
4.05
10
9
8
7
6
5
4
3
2
1
ppm
1.06
1.05
1.03
1.07
1.03
4.05
1.01
1.04
1.00
3.26

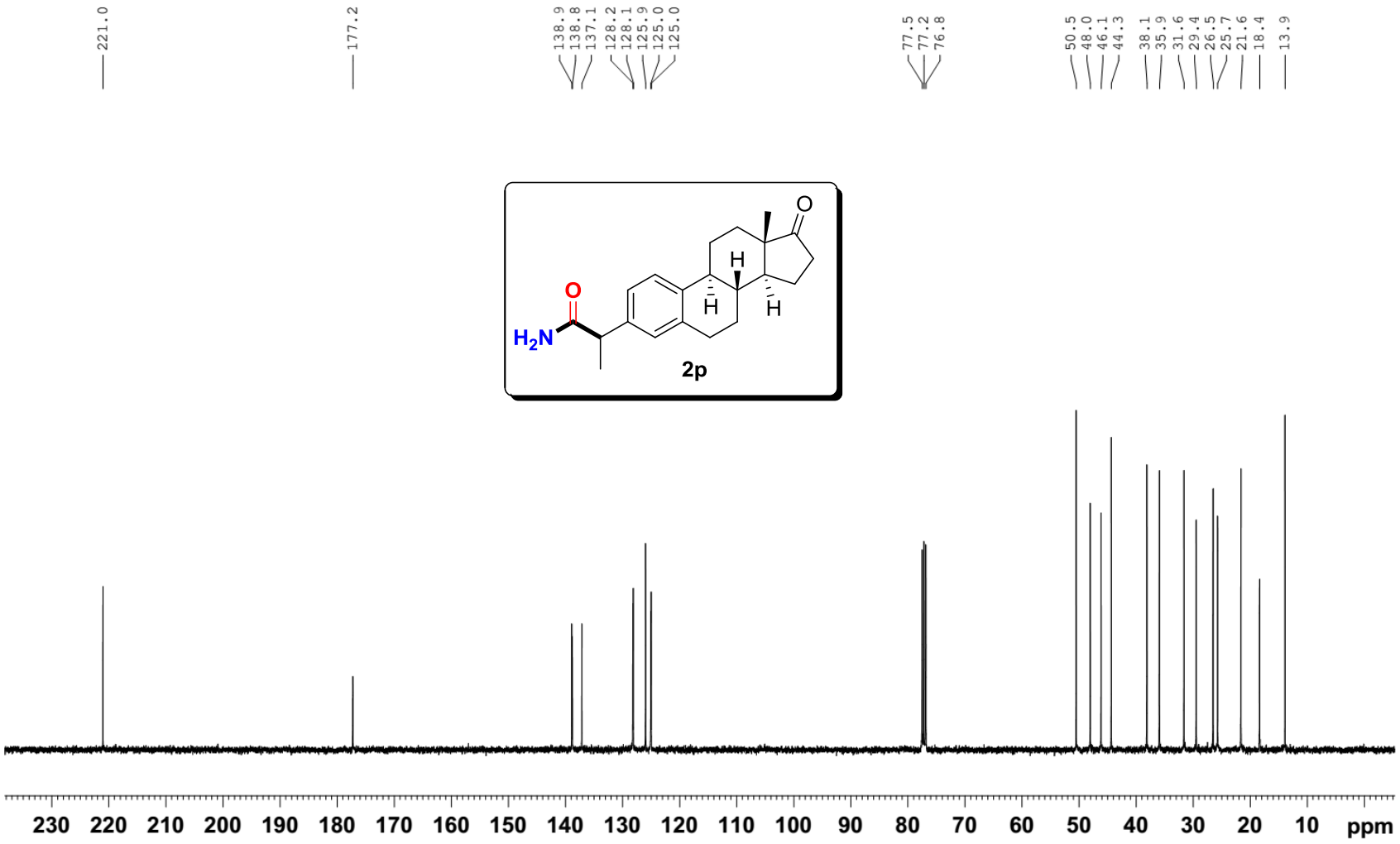
ZGY-X150930-3-CNMR



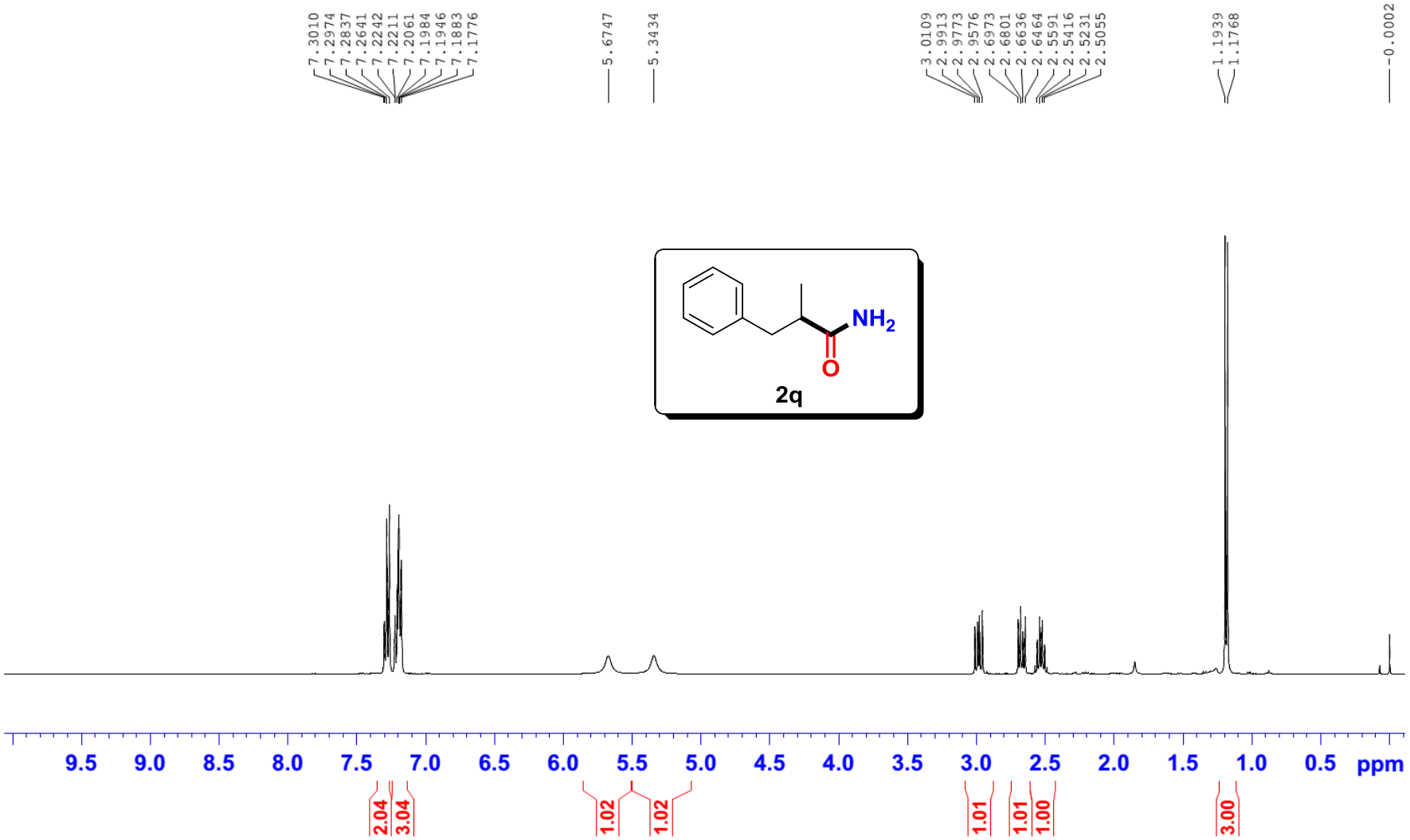
GB-X170220-1-2-HNMR



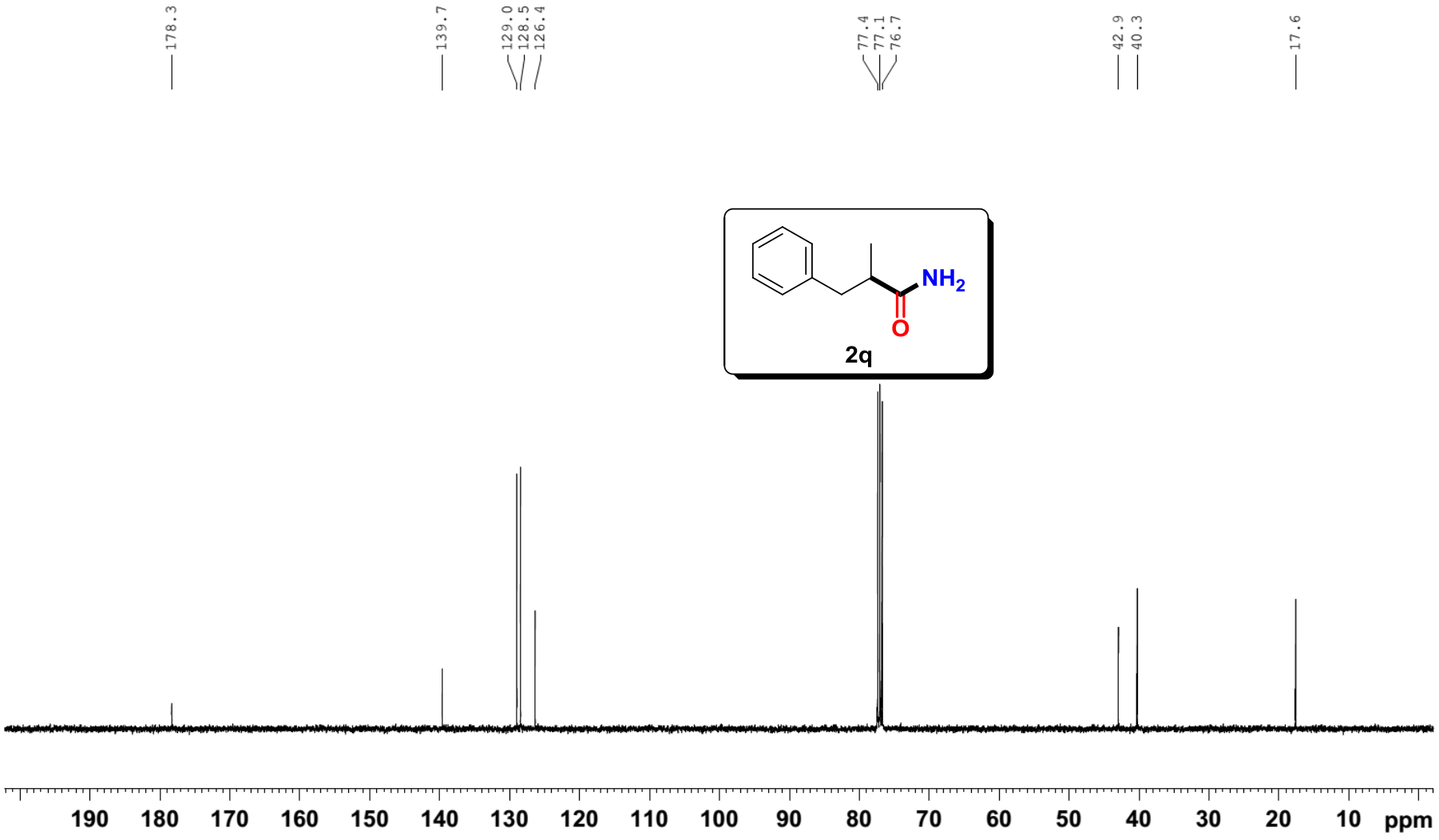
GB-X170220-1-2-CNMR



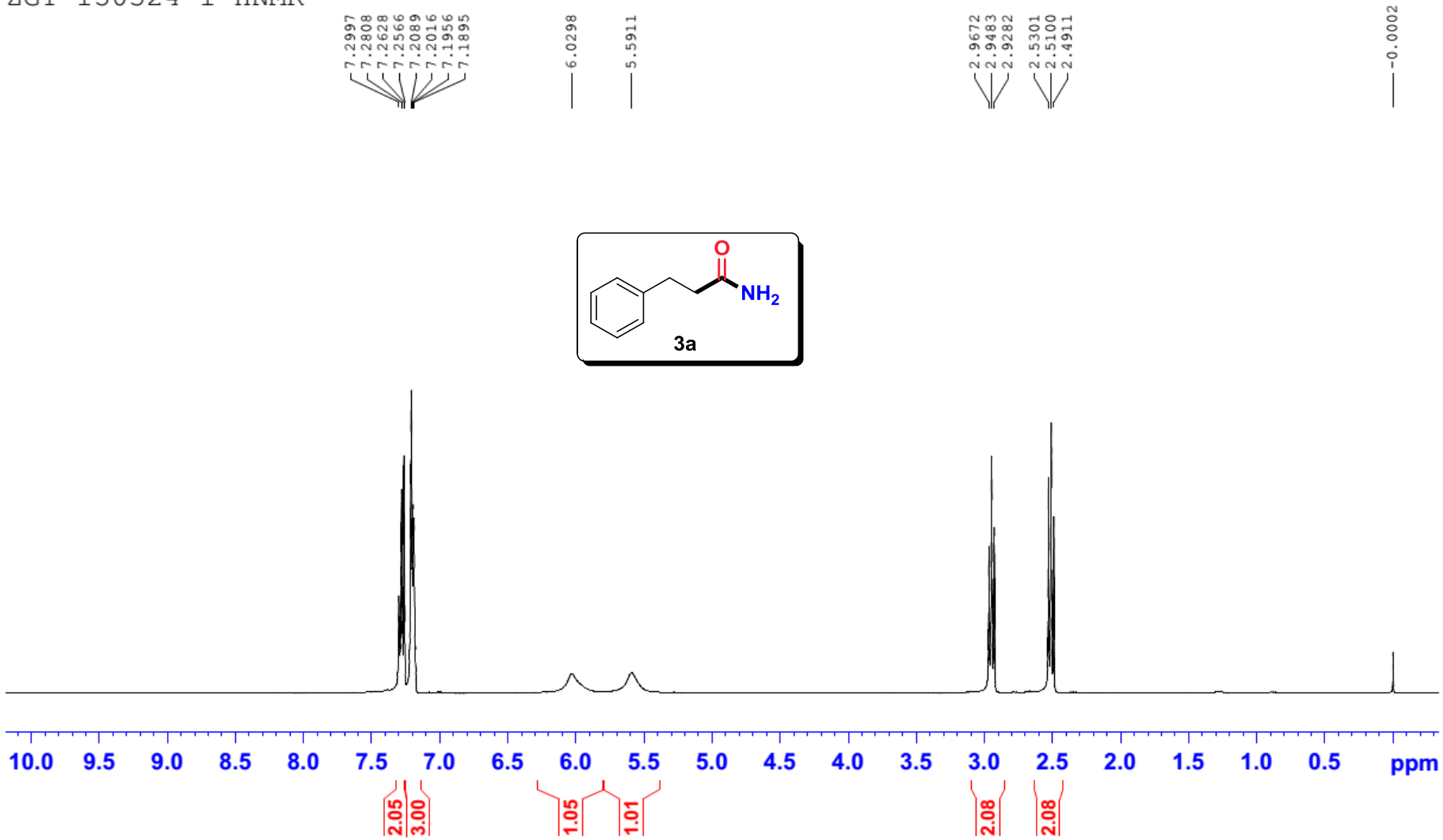
ZGY-X15X07-2-HNMR



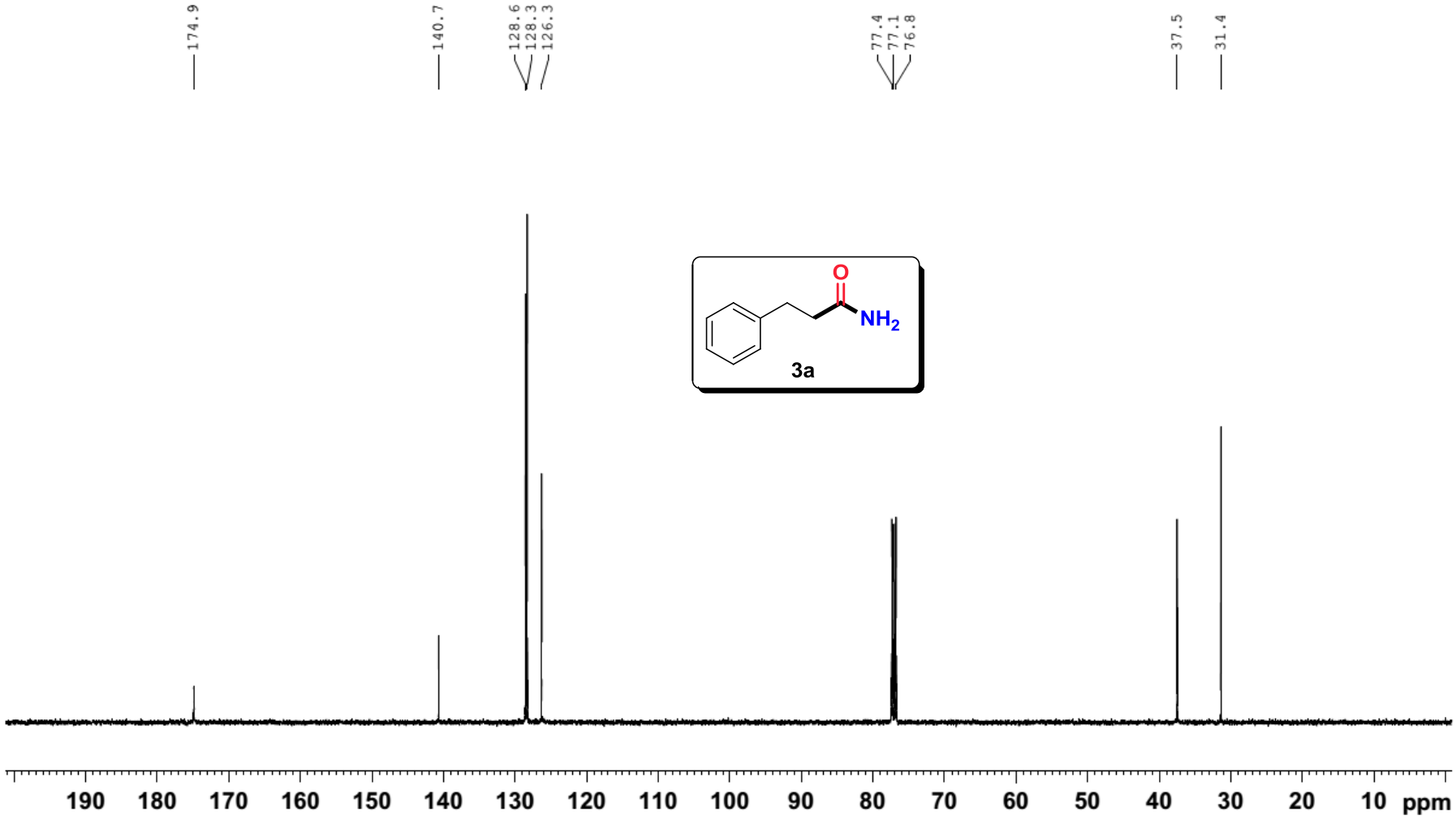
ZGY-X15X07-2-CNMR

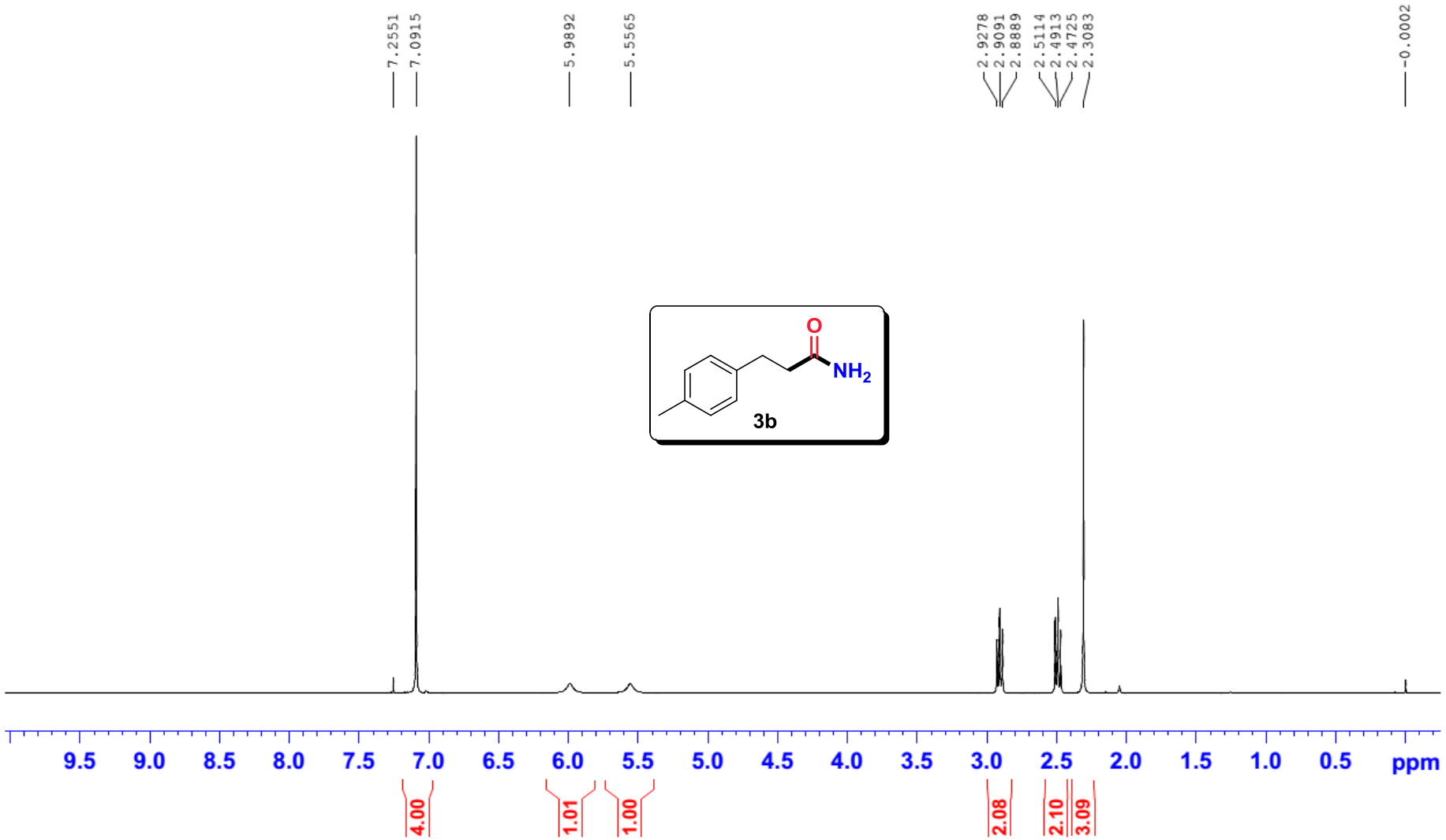


ZGY-150324-1-HNMR



ZGY-150324-1-CNMR




ZCY-X150928-5-HNMR
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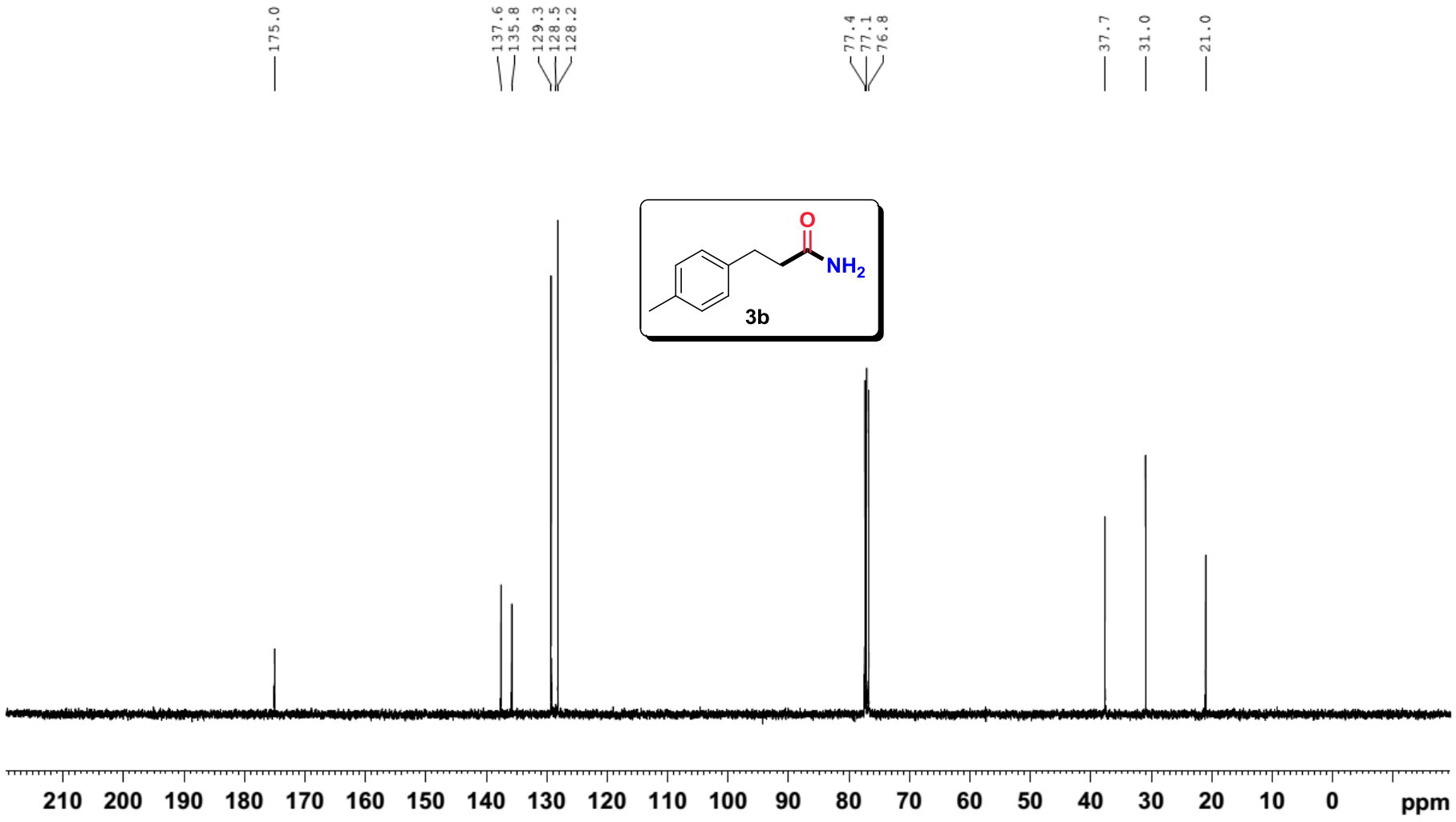
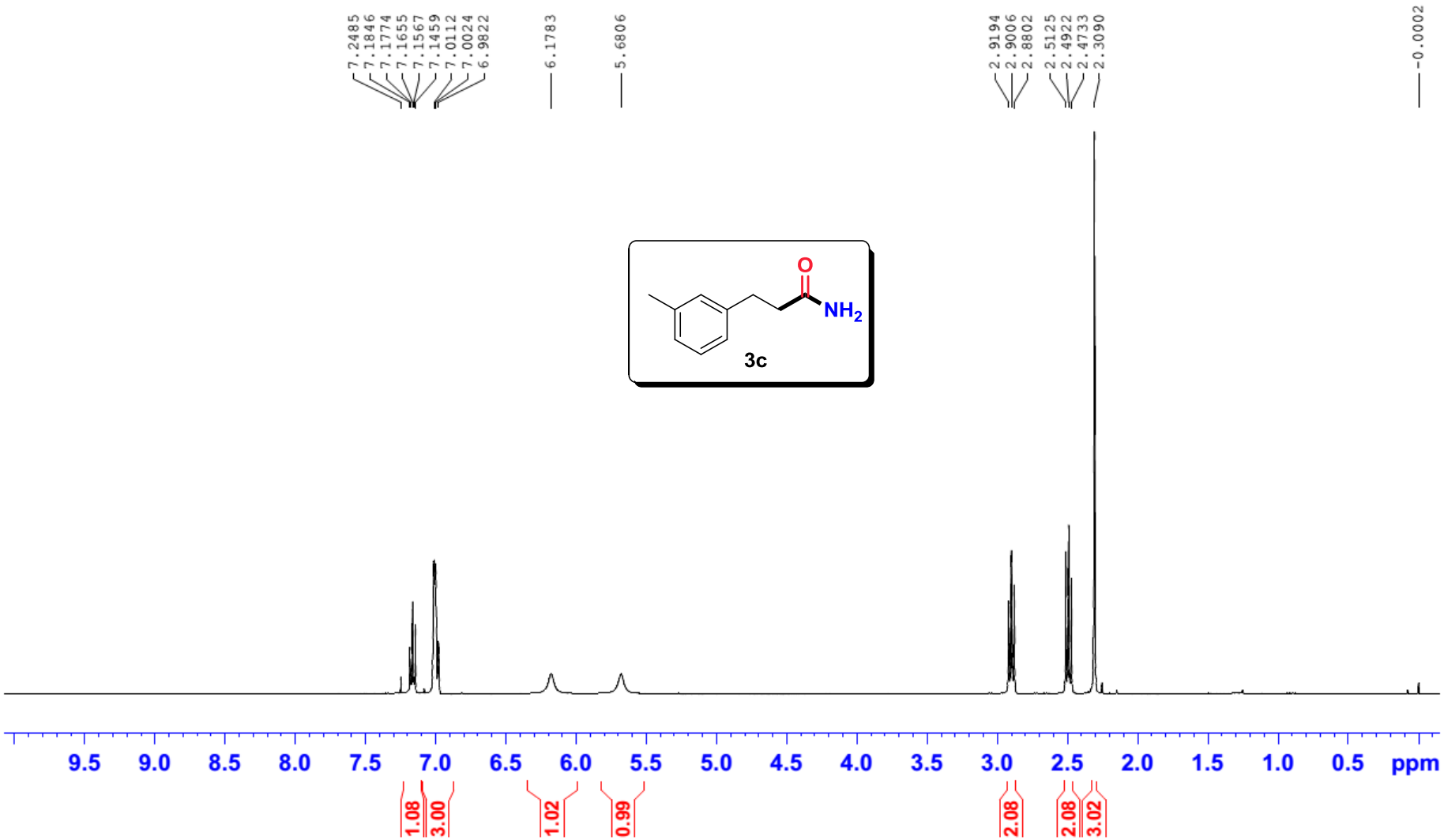
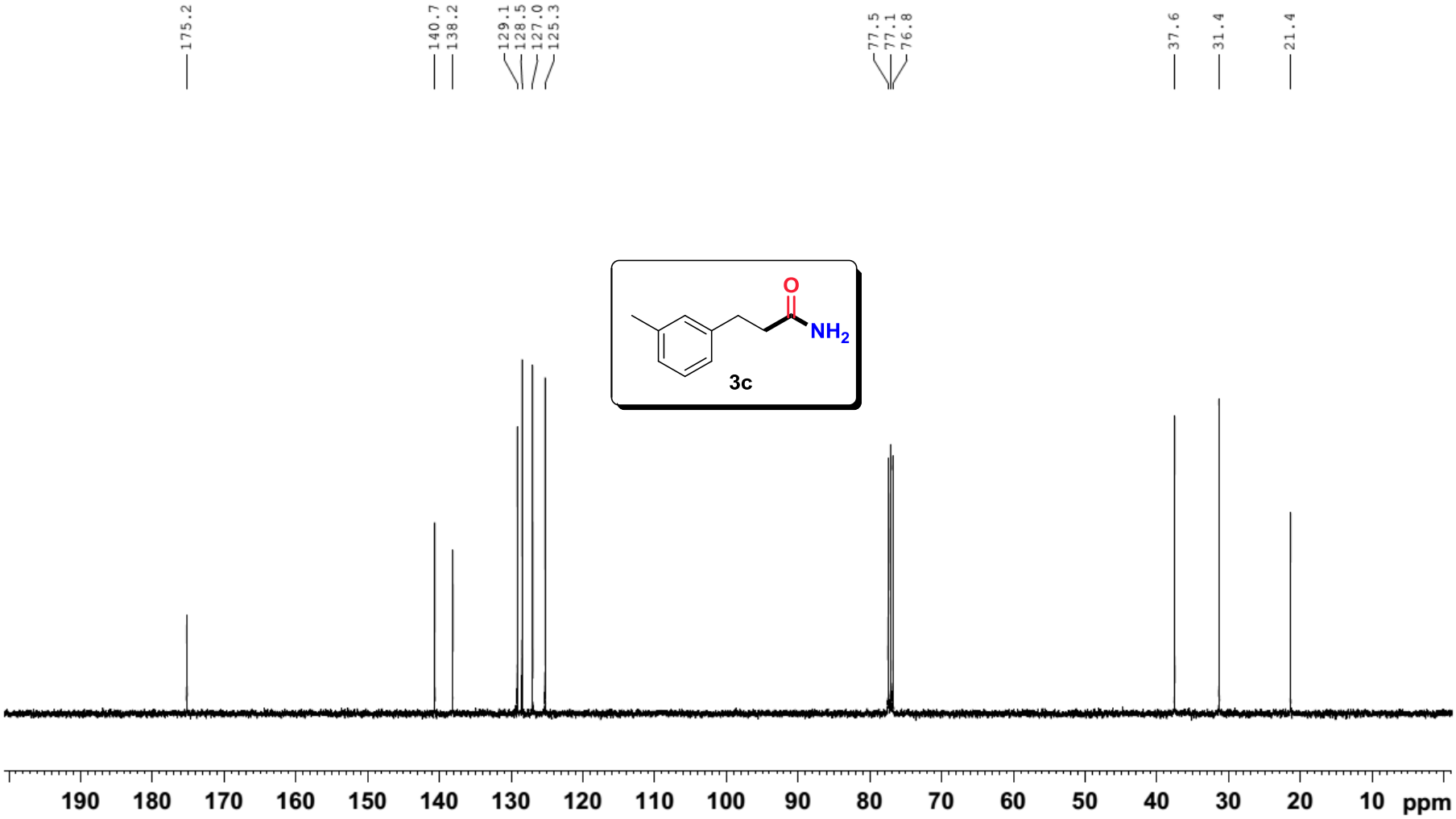
5.9892
5.5565
2.9278
2.9091
2.8889
2.5114
2.4913
2.4725
2.3083
-0.0002
O
NH2
3b
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.00
1.01
1.00
2.08
2.10
3.09

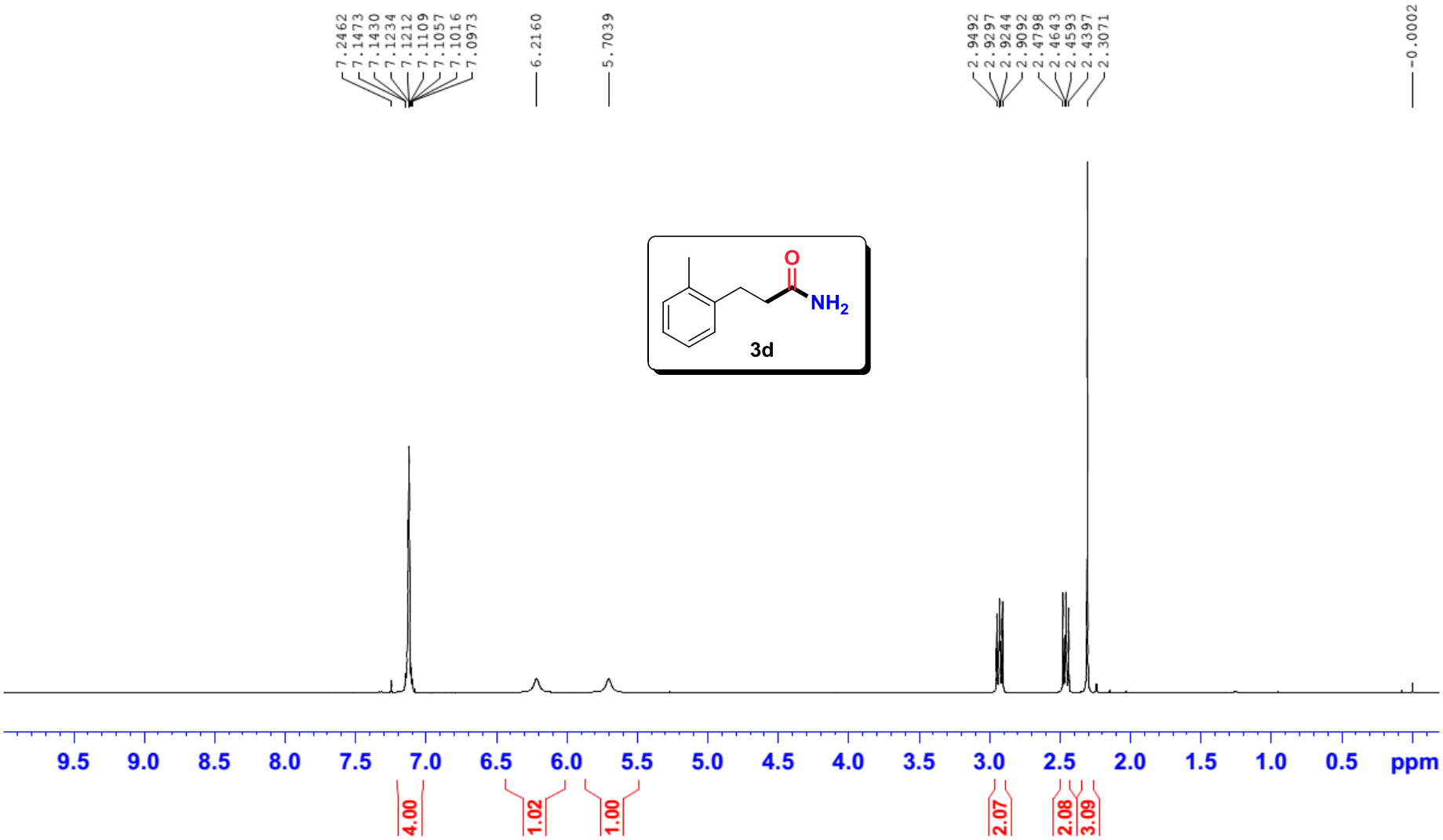
ZCY-X150928-5-CNMR



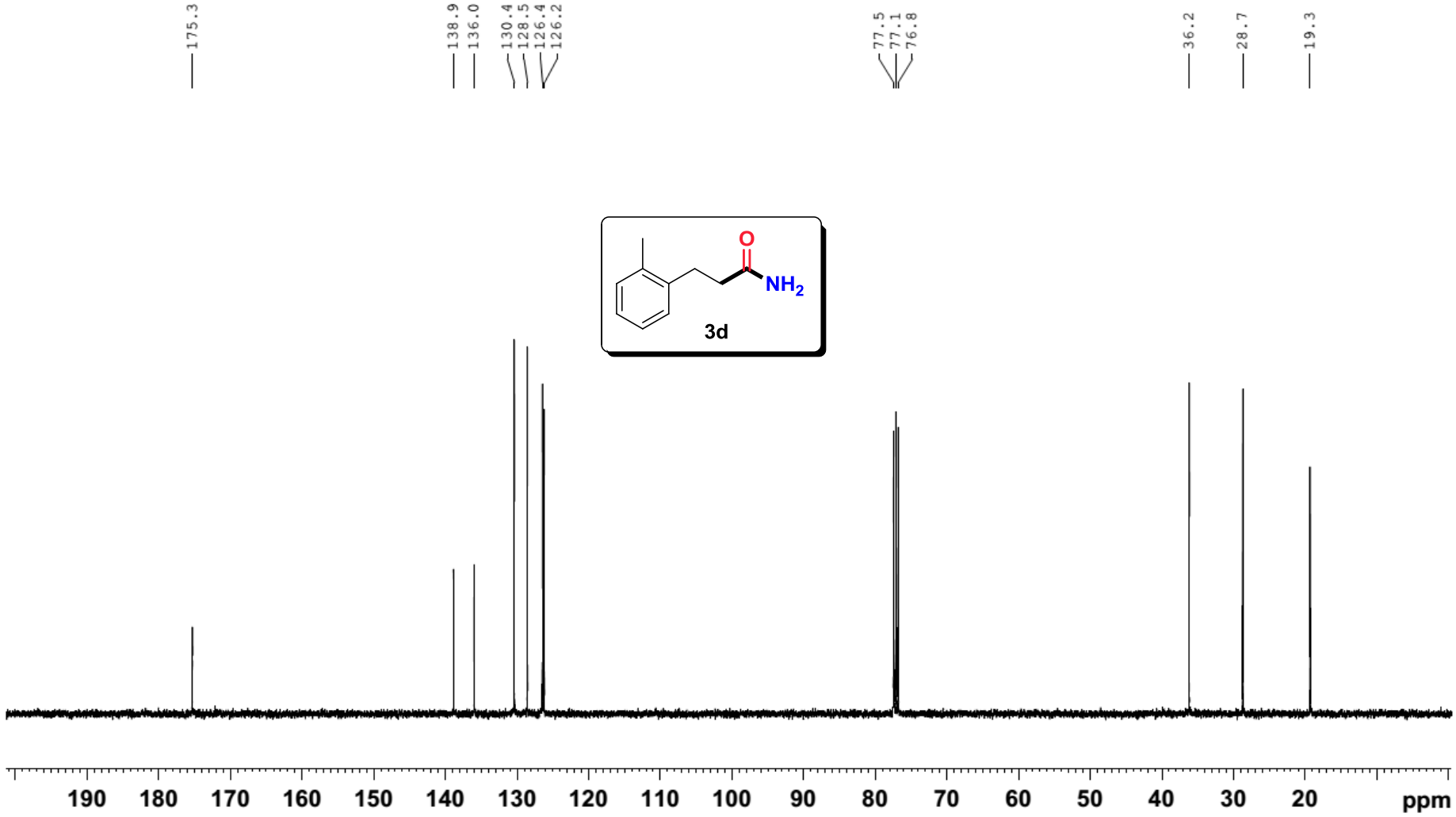

ZCY-X150928-3-HNMR
7.2485
7.1846
7.1774
7.1655
7.1567
7.1459
7.0112
7.0024
6.9822
6.1783
5.6806
2.9194
2.9006
2.8802
2.5125
2.4922
2.4733
2.3090
-0.0002
O
NH2
3c
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.08
3.00
1.02
0.99
2.08
2.08
3.02

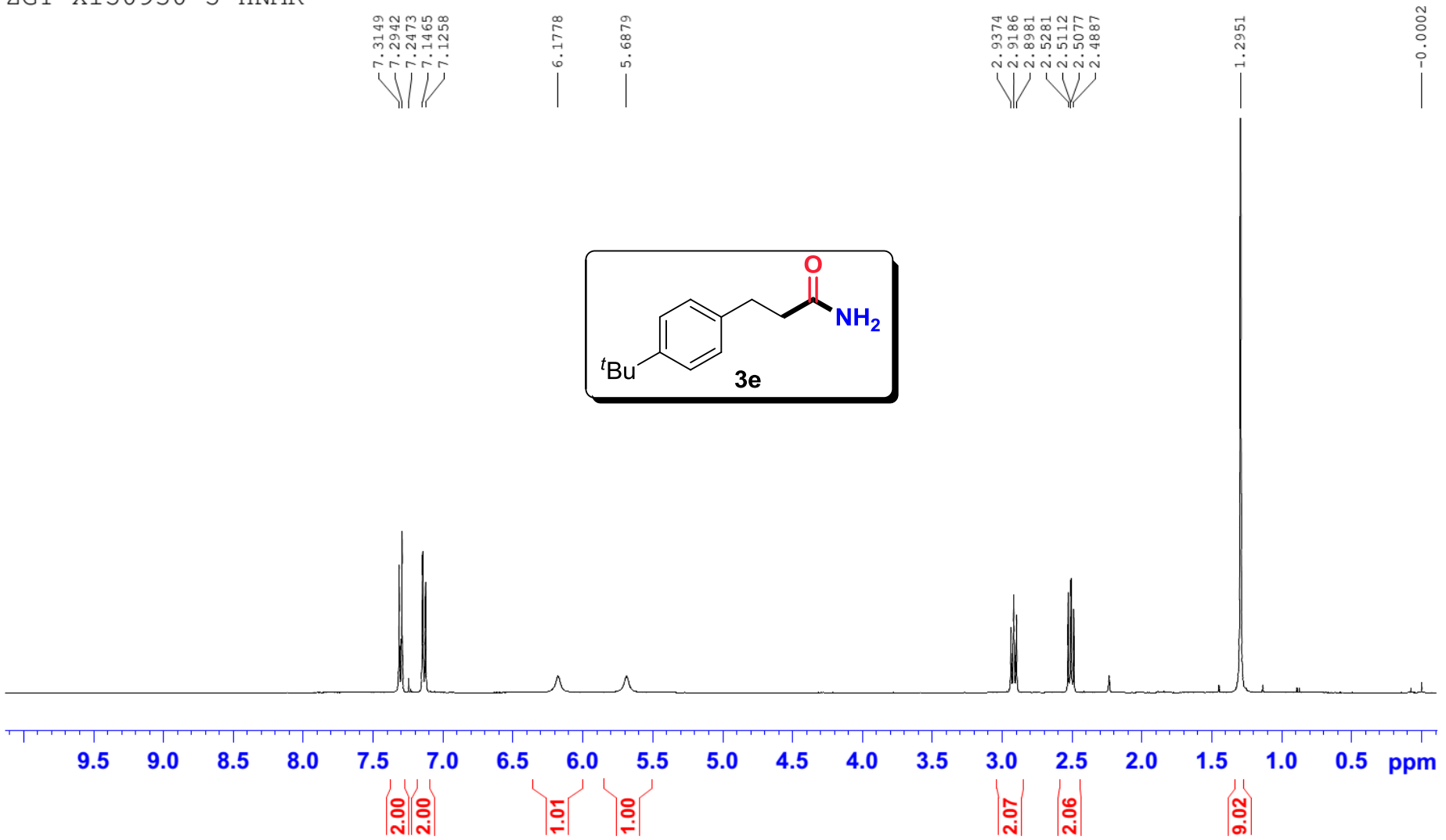
ZCY-X150928-3-CNMR




ZCY-X150928-2-HNMR
7.2462
7.1473
7.1430
7.1234
7.1212
7.1109
7.1057
7.1016
7.0973
6.2160
5.7039
2.9492
2.9297
2.9244
2.9092
2.4798
2.4643
2.4593
2.4397
2.3071
-0.0002
O
NH2
3d
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.00
1.02
1.00
2.07
2.08
3.09

ZCY-X150928-2-CNMR




ZGY-X150930-5-HNMR
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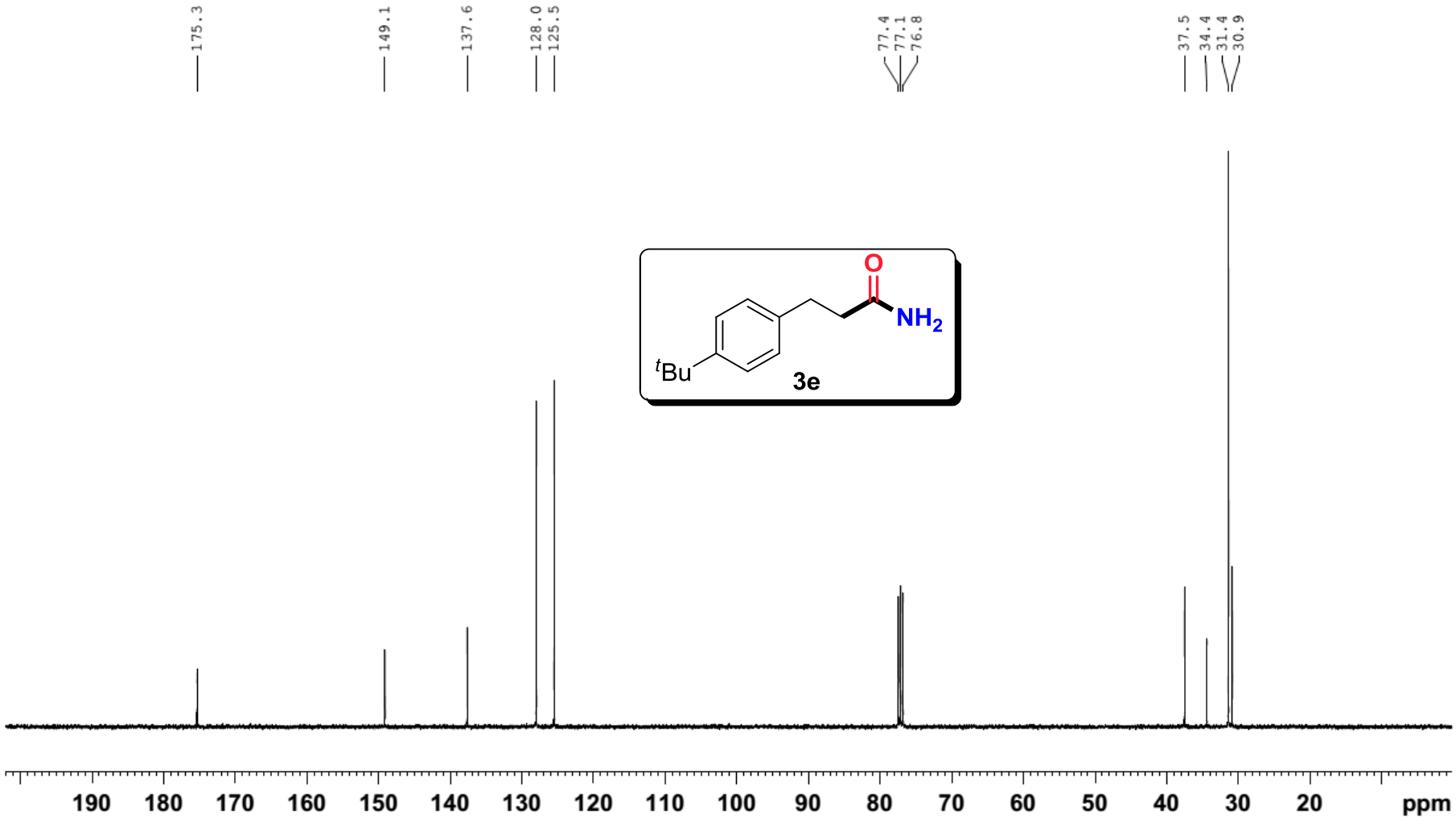
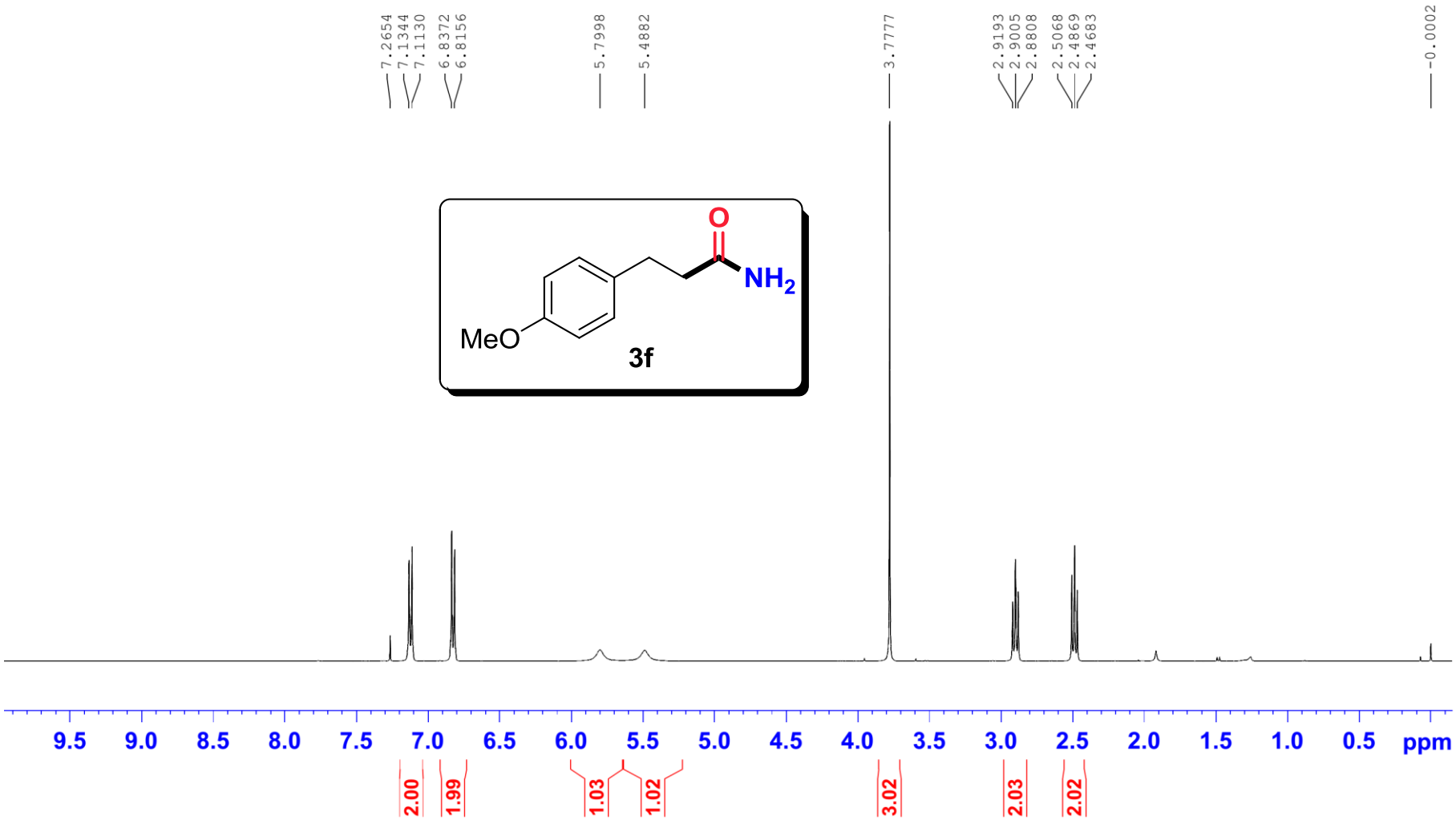
7.2473
7.1465
7.1258
6.1778
5.6879
2.9374
2.9186
2.8981
2.5281
2.5112
2.5077
2.4887
1.2951
-0.0002
O
NH2
tBu
3e
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.00
1.01
1.00
2.07
2.06
9.02

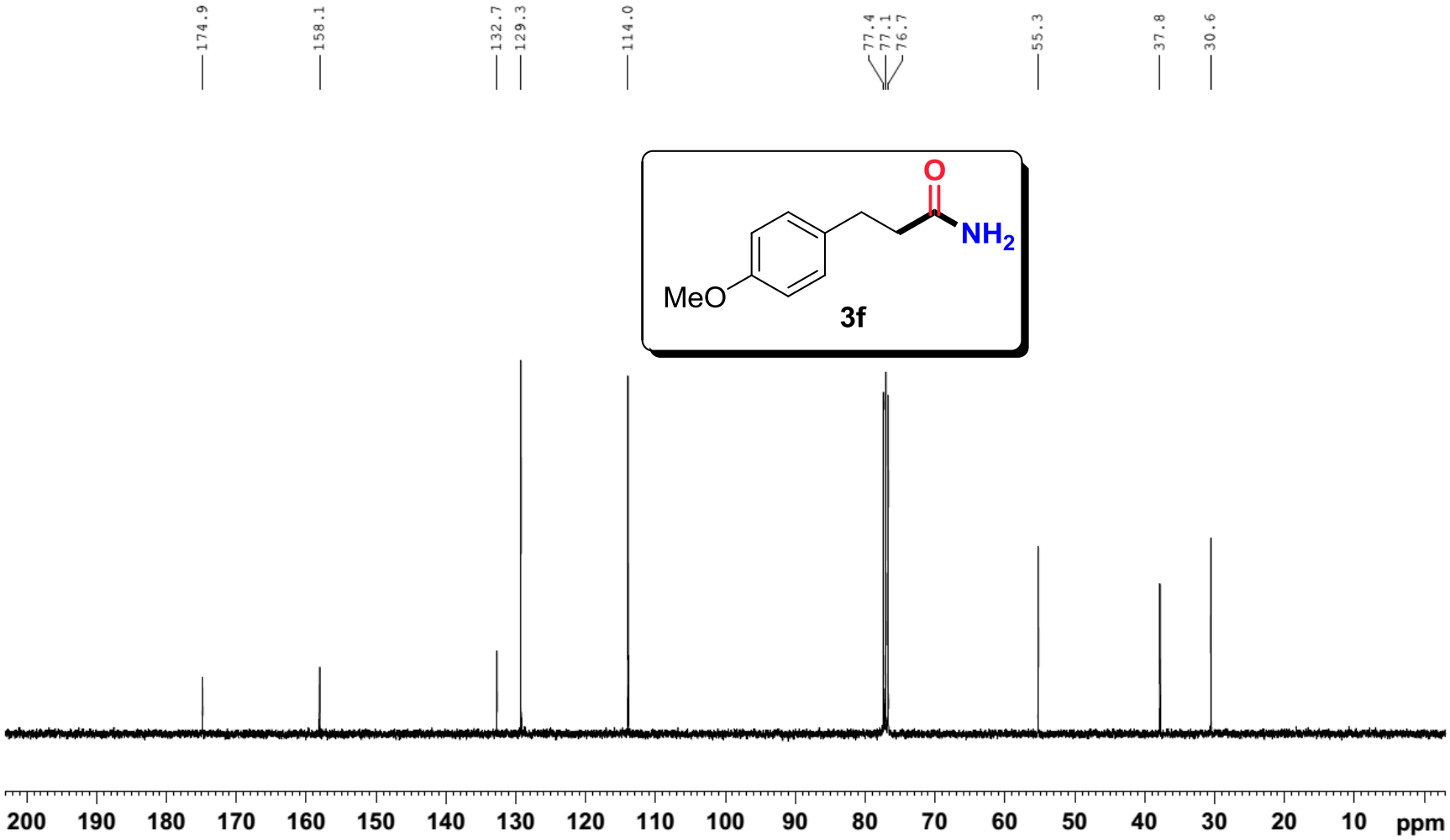
ZGY-X150930-5-CNMR



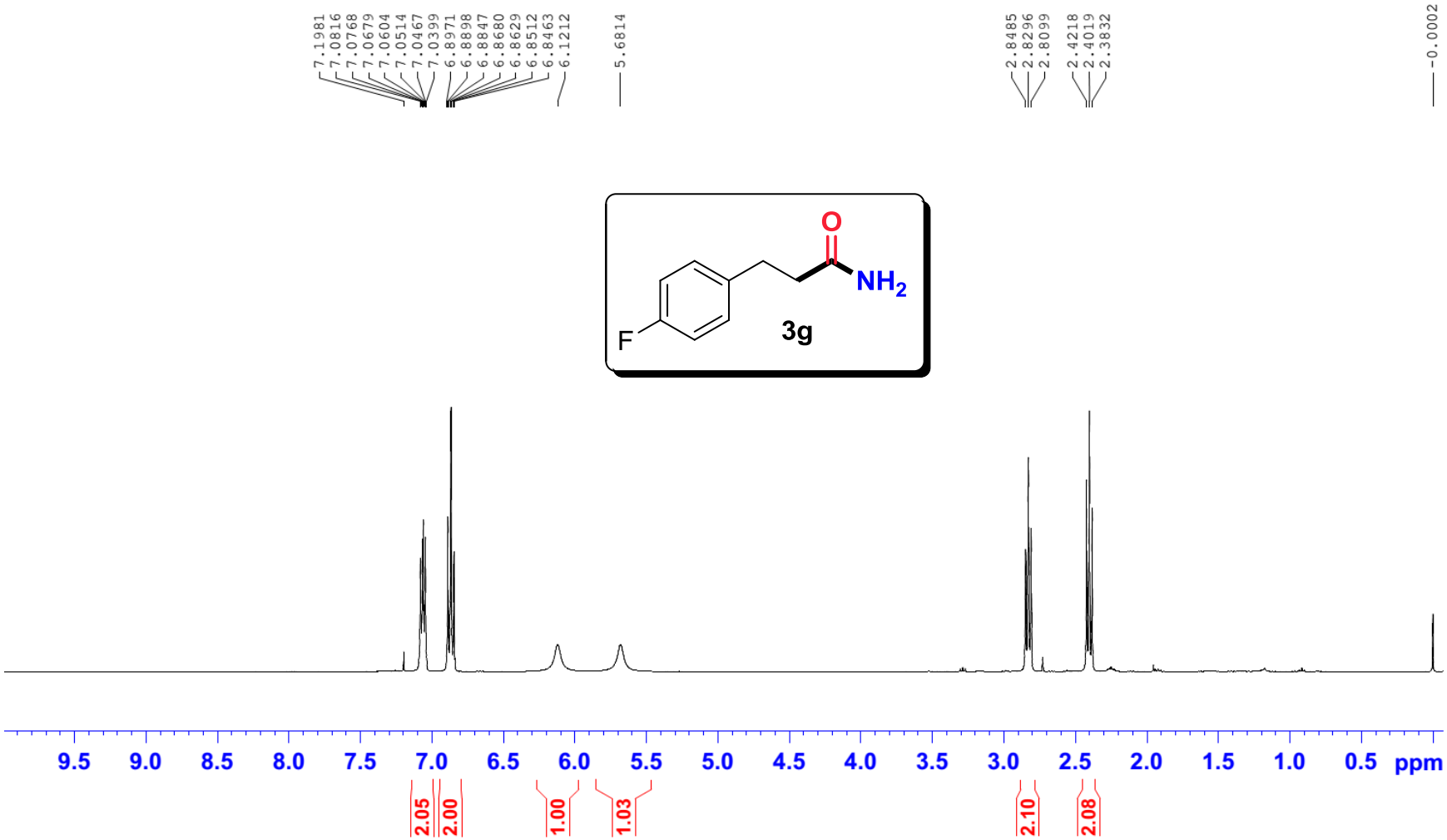
ZGY-X15X19-4-HNMR



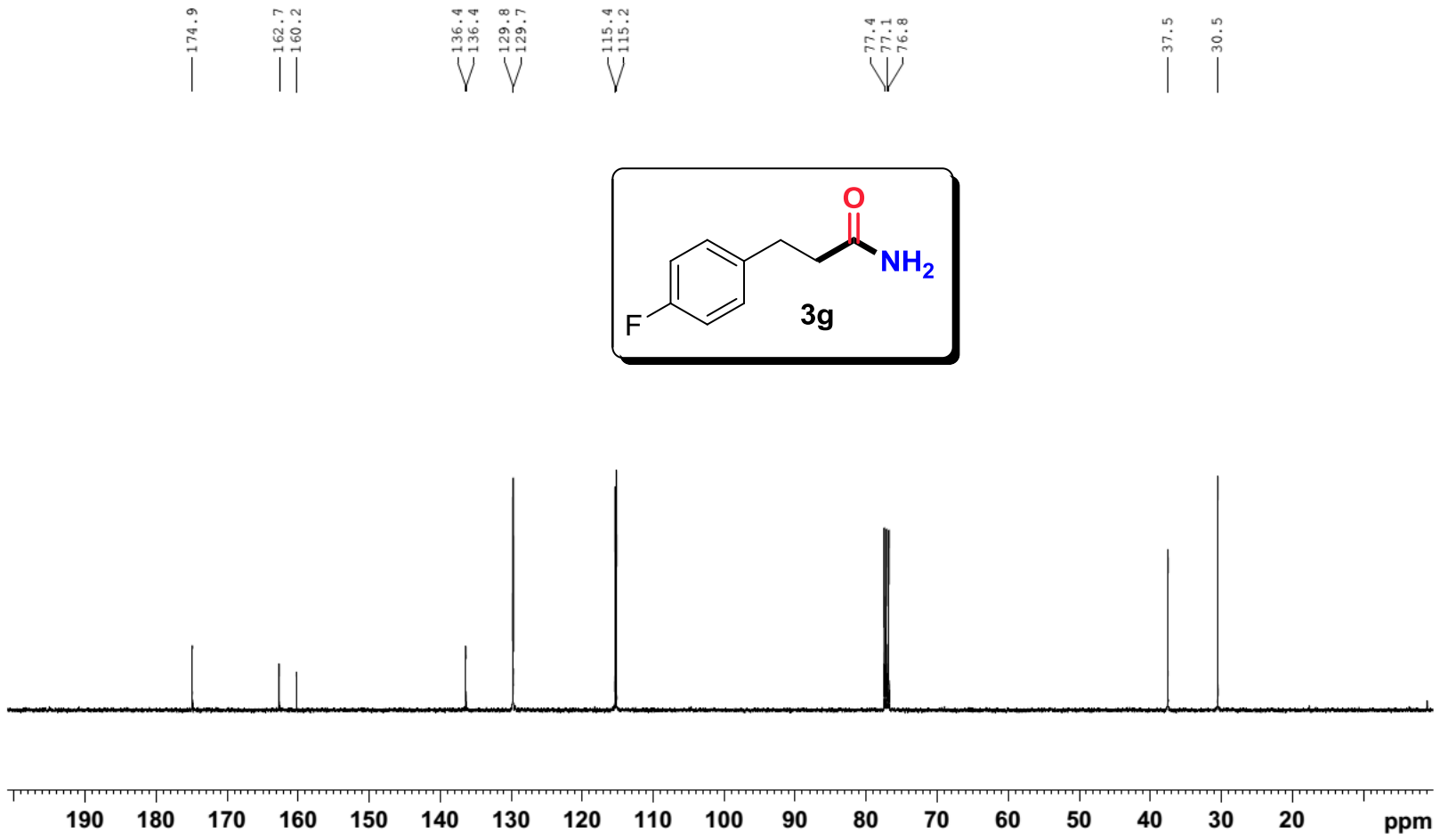
ZGY-X15X19-4-CNMR



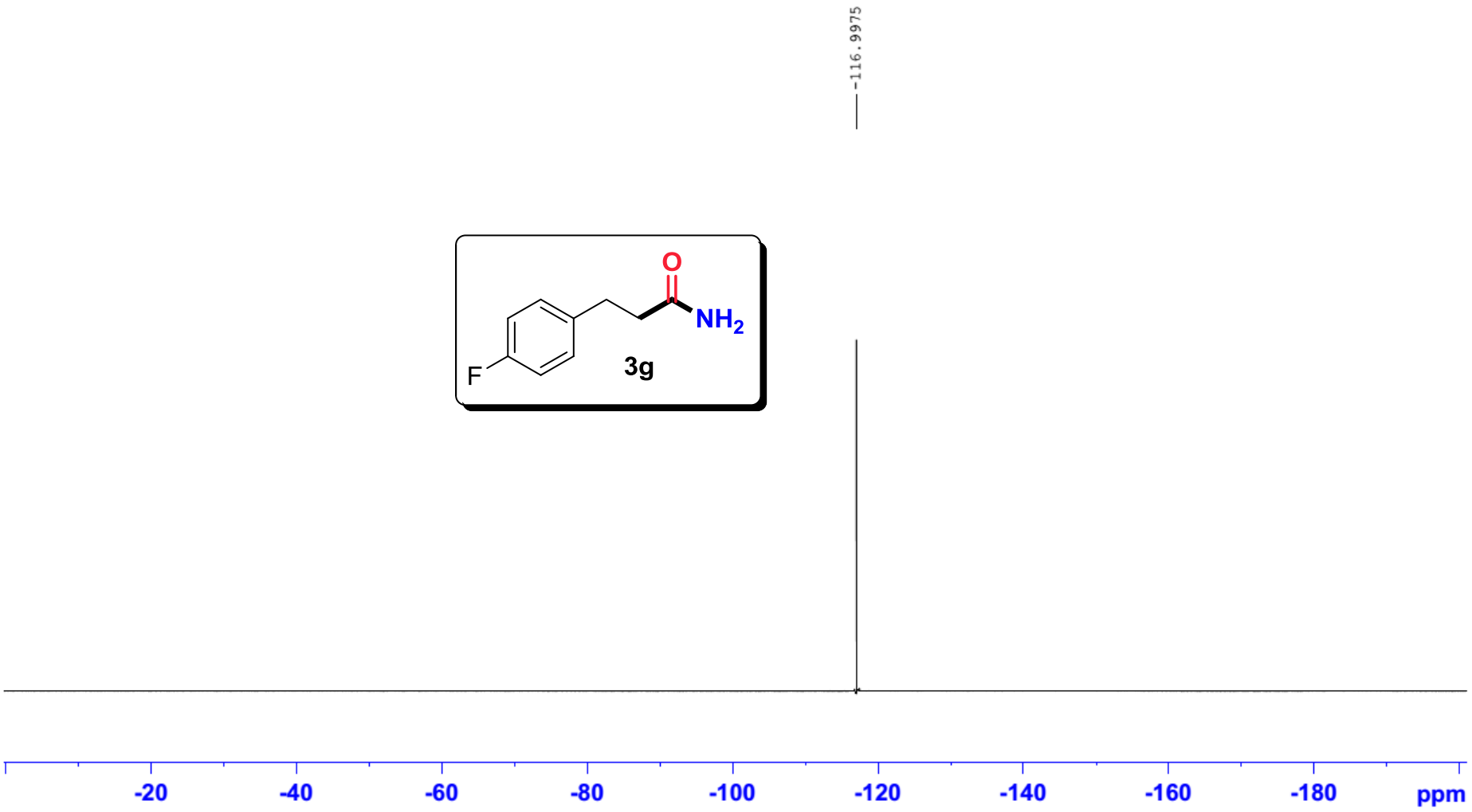
ZGY-X15Y10-1-HNMR



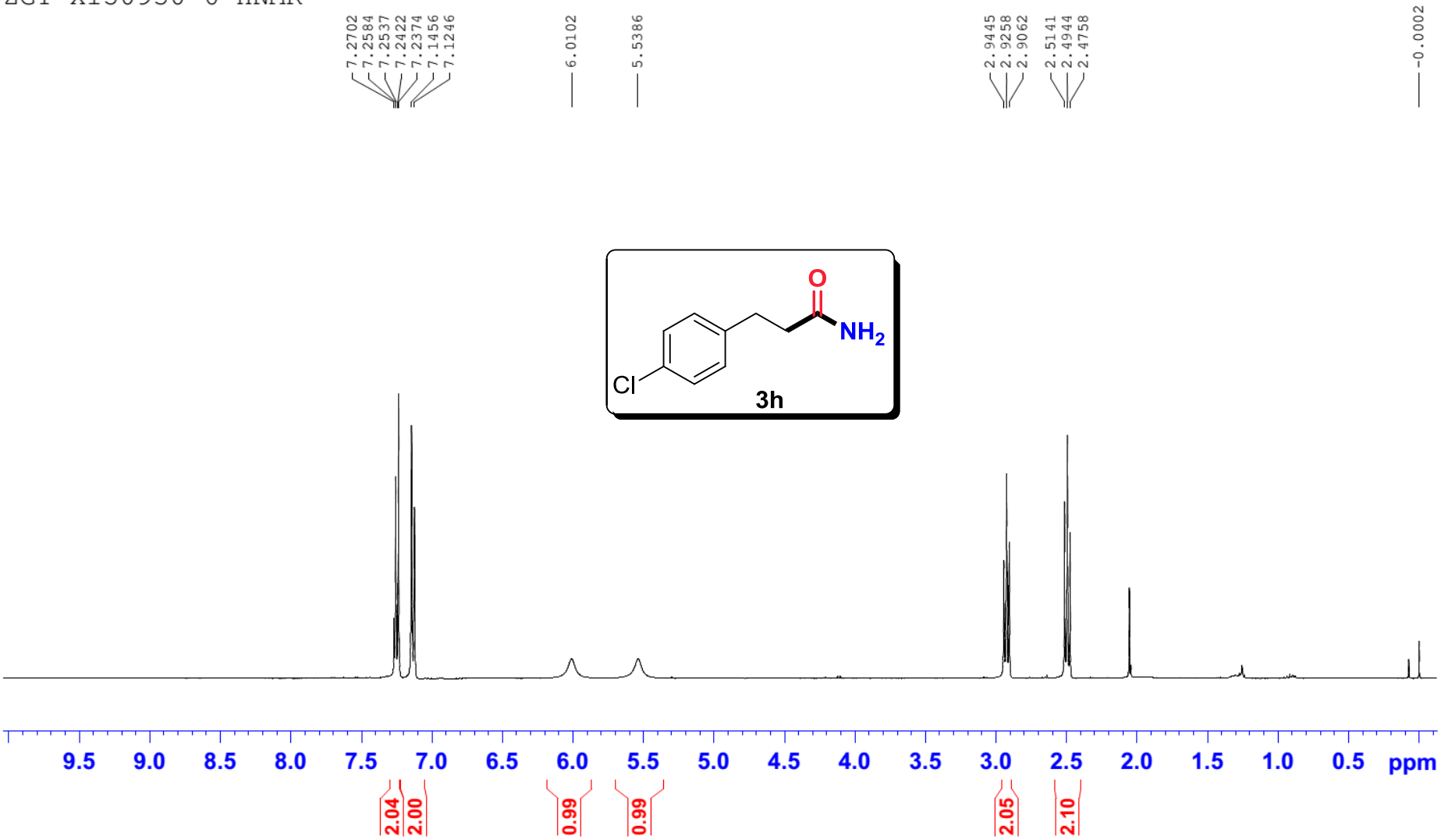
ZGY-X15Y10-1-CNMR



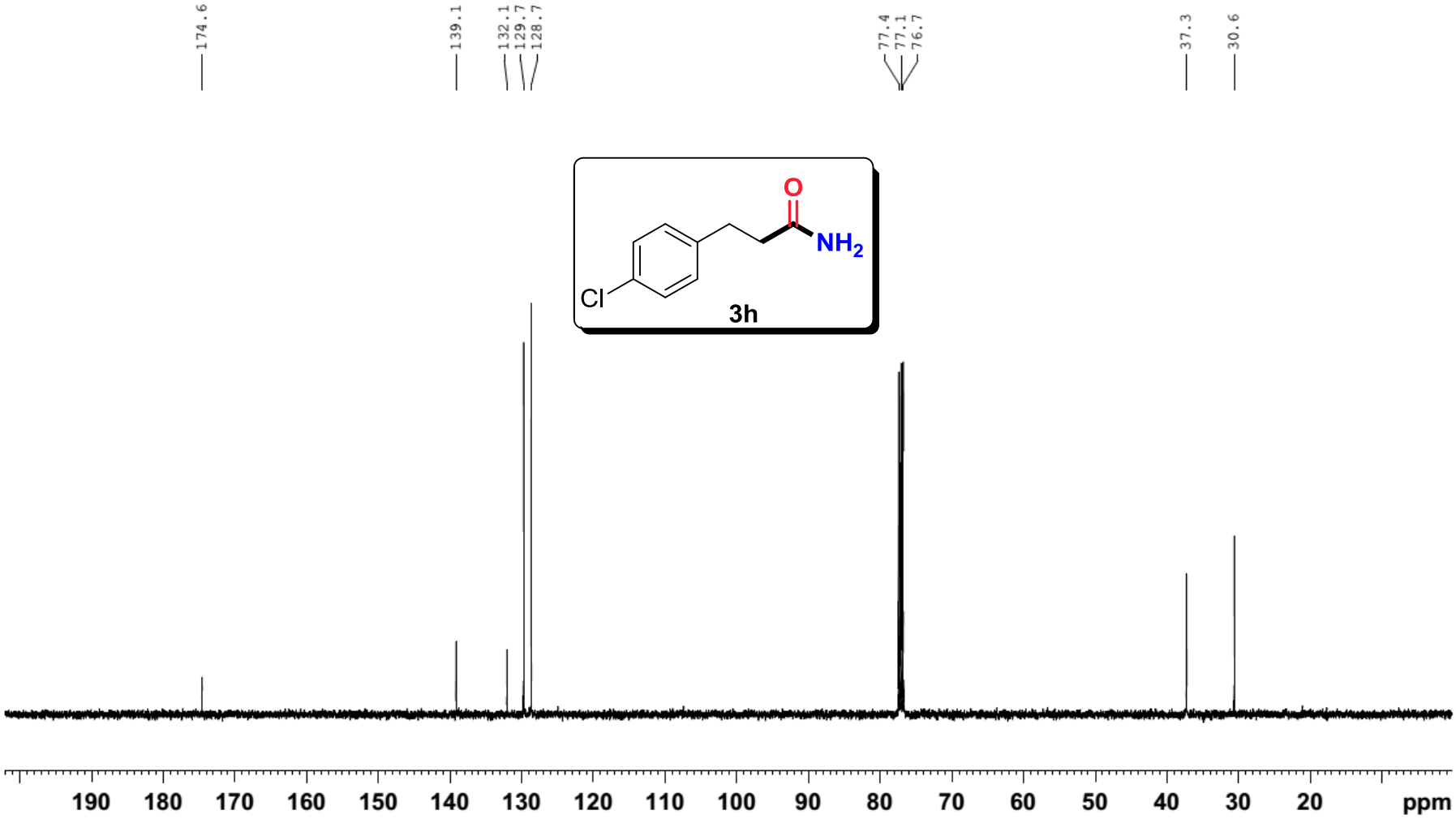
ZGY-X15Y10-1-FNMR



ZGY-X150930-6-HNMR



ZGY-X150930-6-CNMR



ZGY-X15X14-2 H NMR

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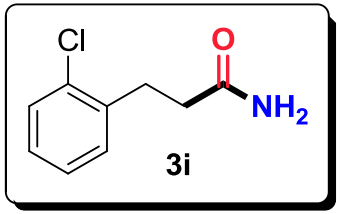
7.3206
7.2700
7.2670
7.2612
7.2487
7.2437
7.1991
7.1948
7.1808
7.1764
7.1684
7.1632
7.1583
7.1498
7.1446
7.1313
6.0183
5.6477
3.0822
3.0633
3.0431
2.5485
2.5284
2.5093
0.0758



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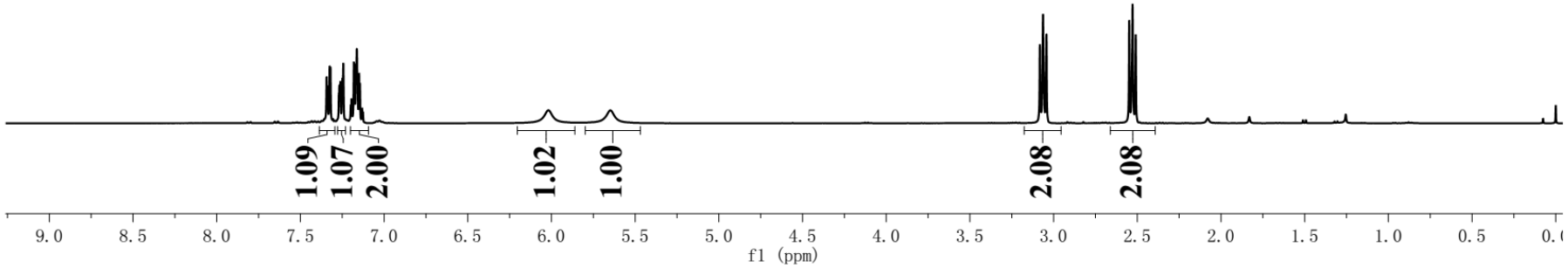
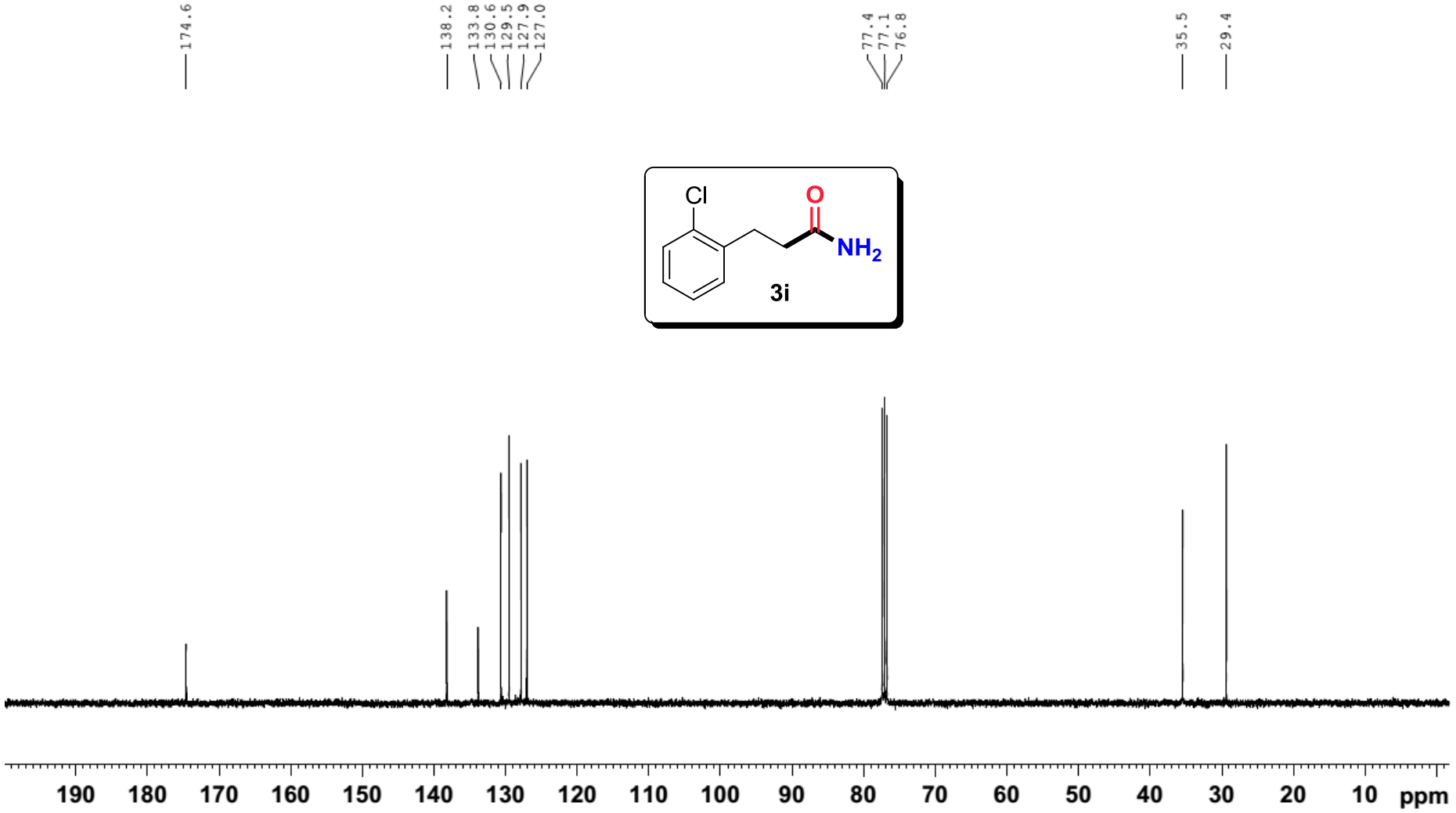
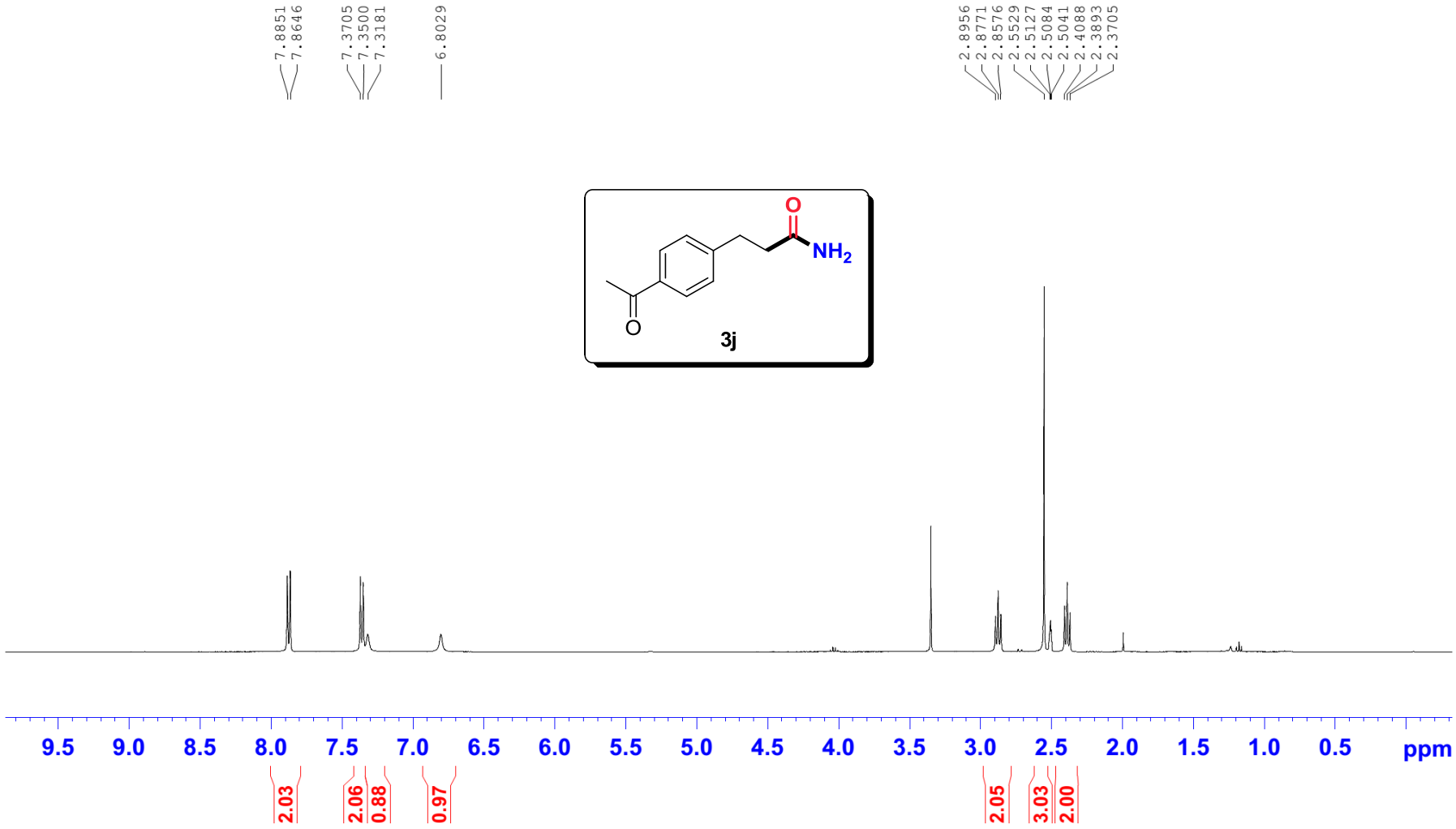
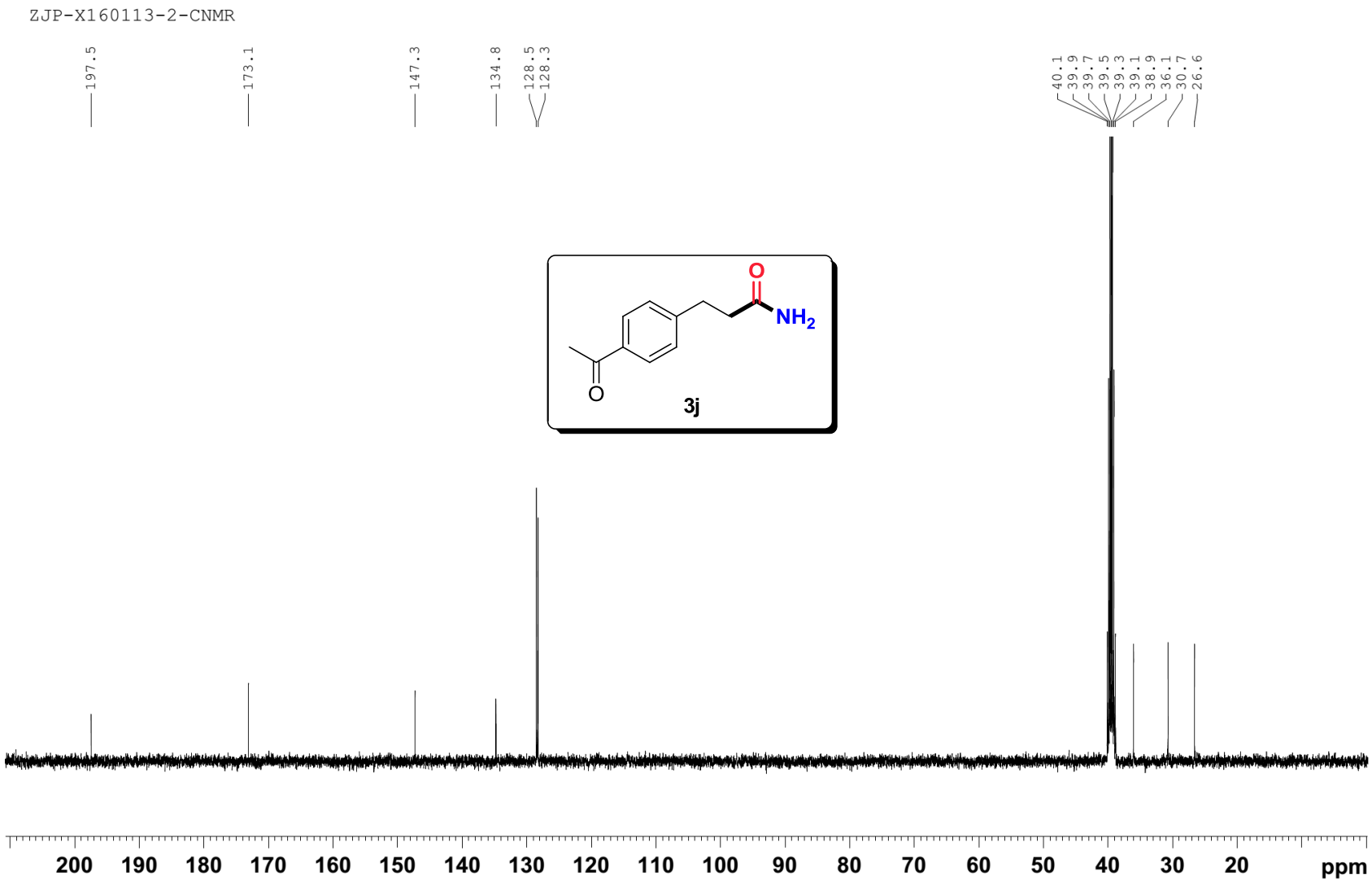


ZGY-X15X13-2-CNMR

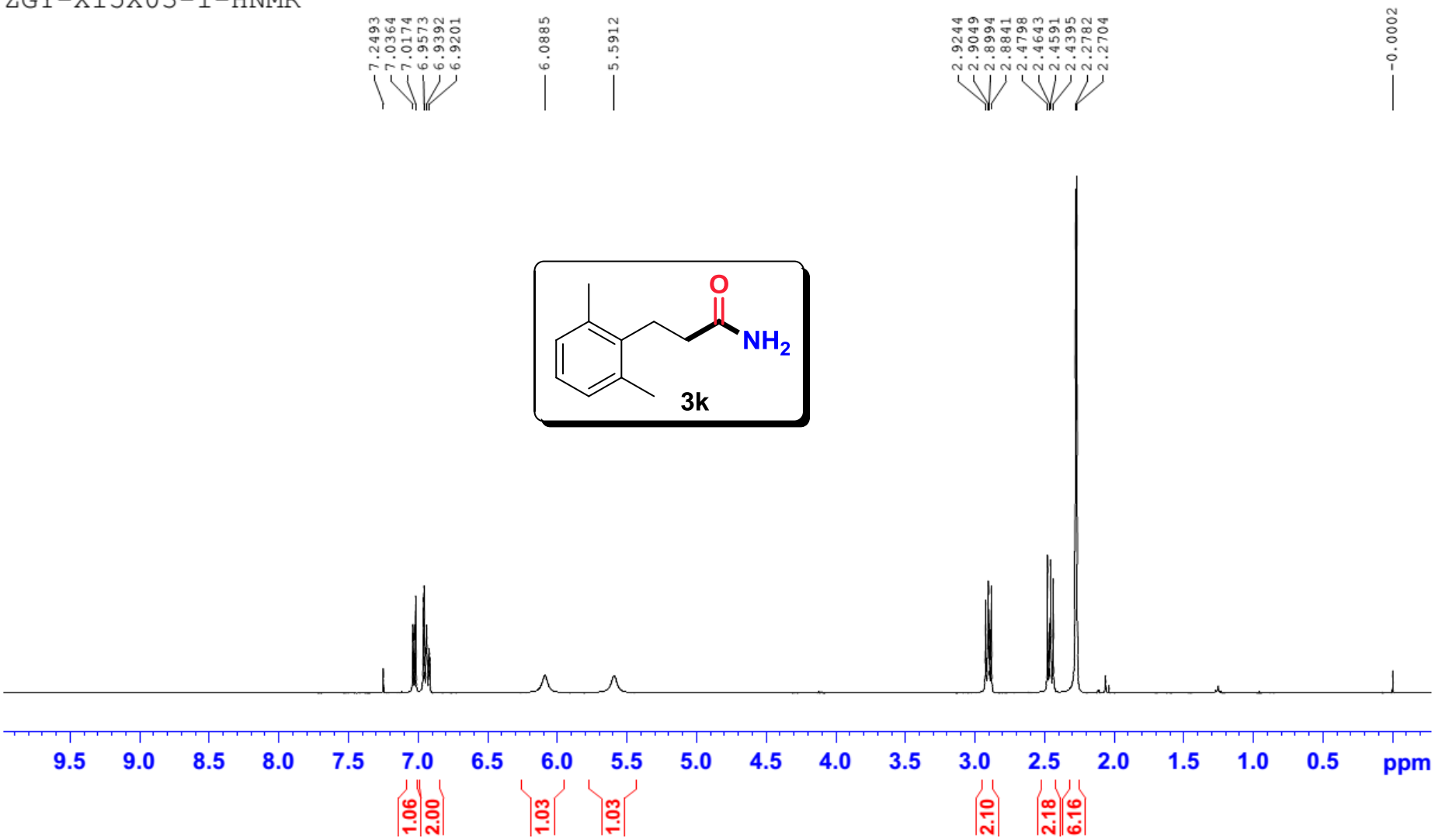


ZJP-X160113-2-HNMR

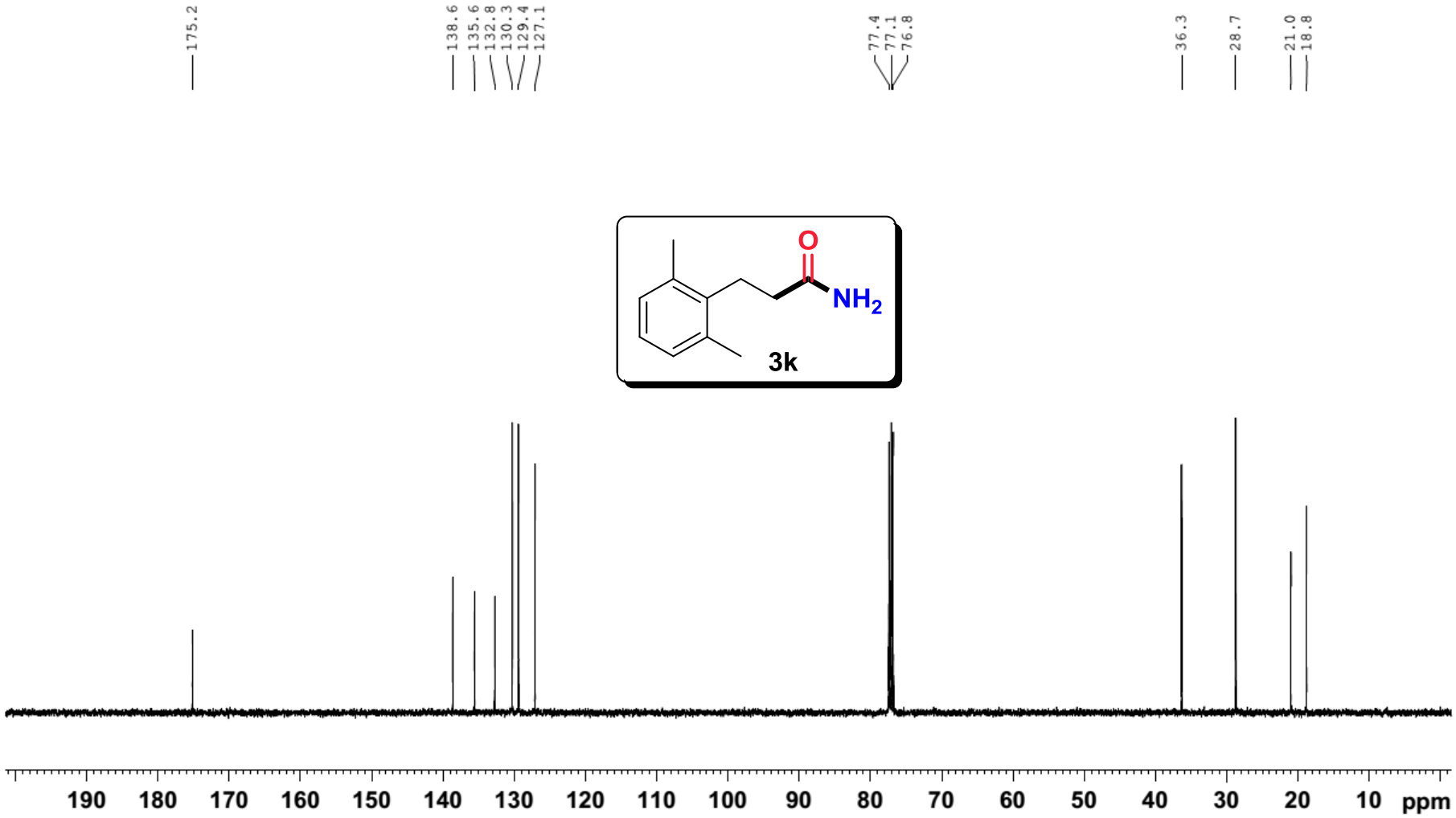


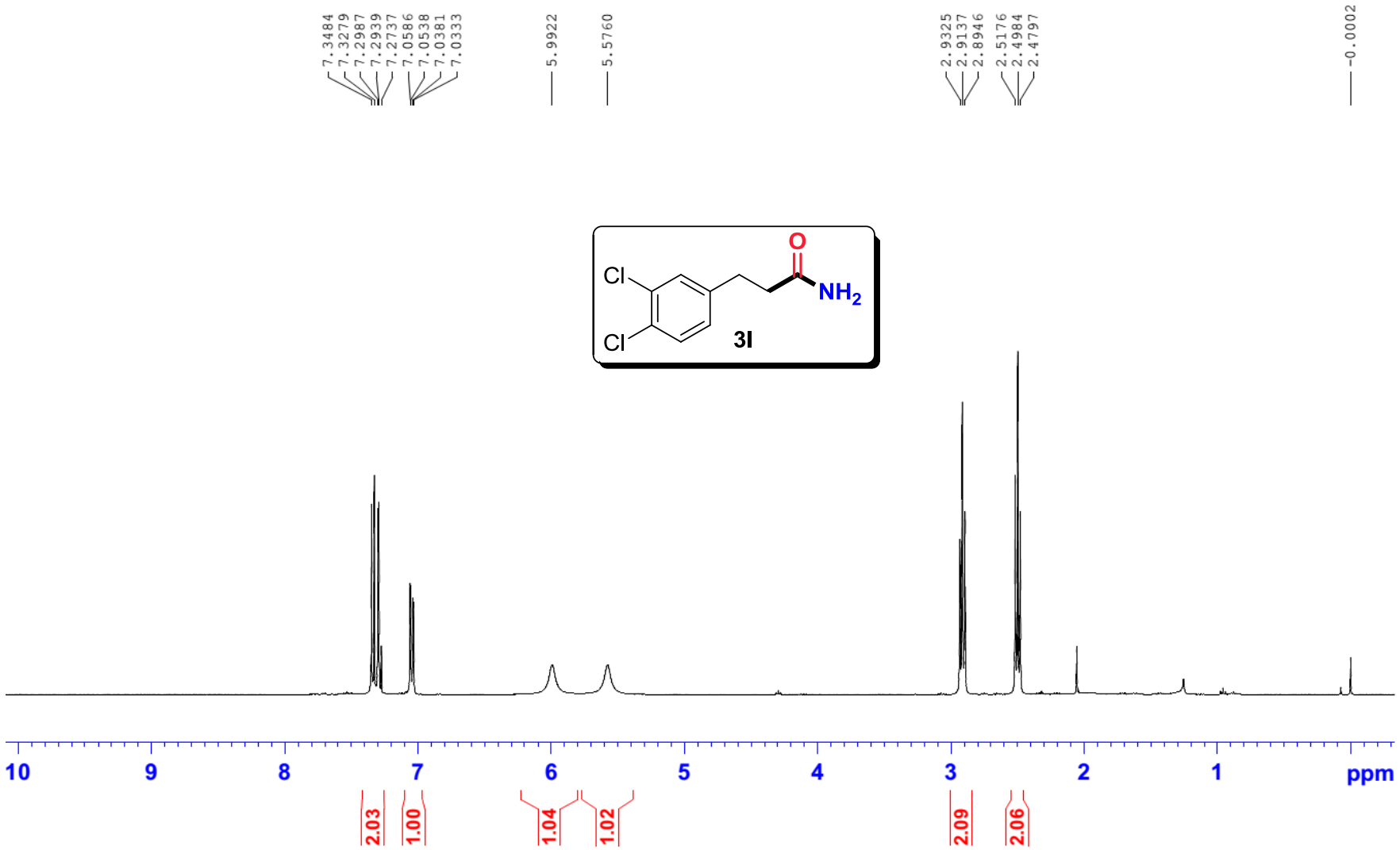

ZJP-X160113-2-CNMR
197.5
173.1
147.3
134.8
128.5
128.3
40.1
39.9
39.7
39.5
39.3
39.1
38.9
36.1
30.7
26.6
O
NH2
O
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

ZGY-X15X03-1-HNMR

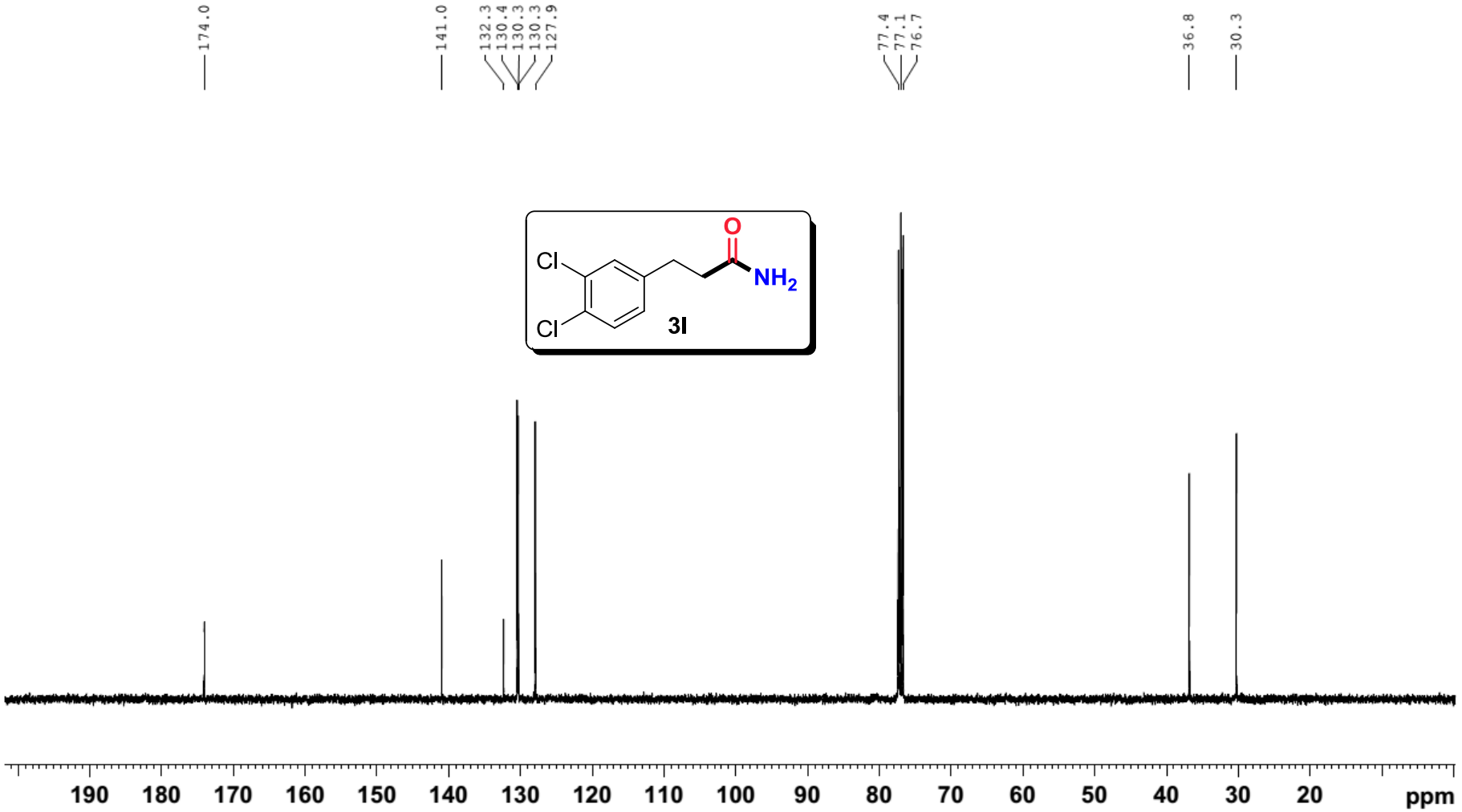


ZGY-X15X03-1-CNMR

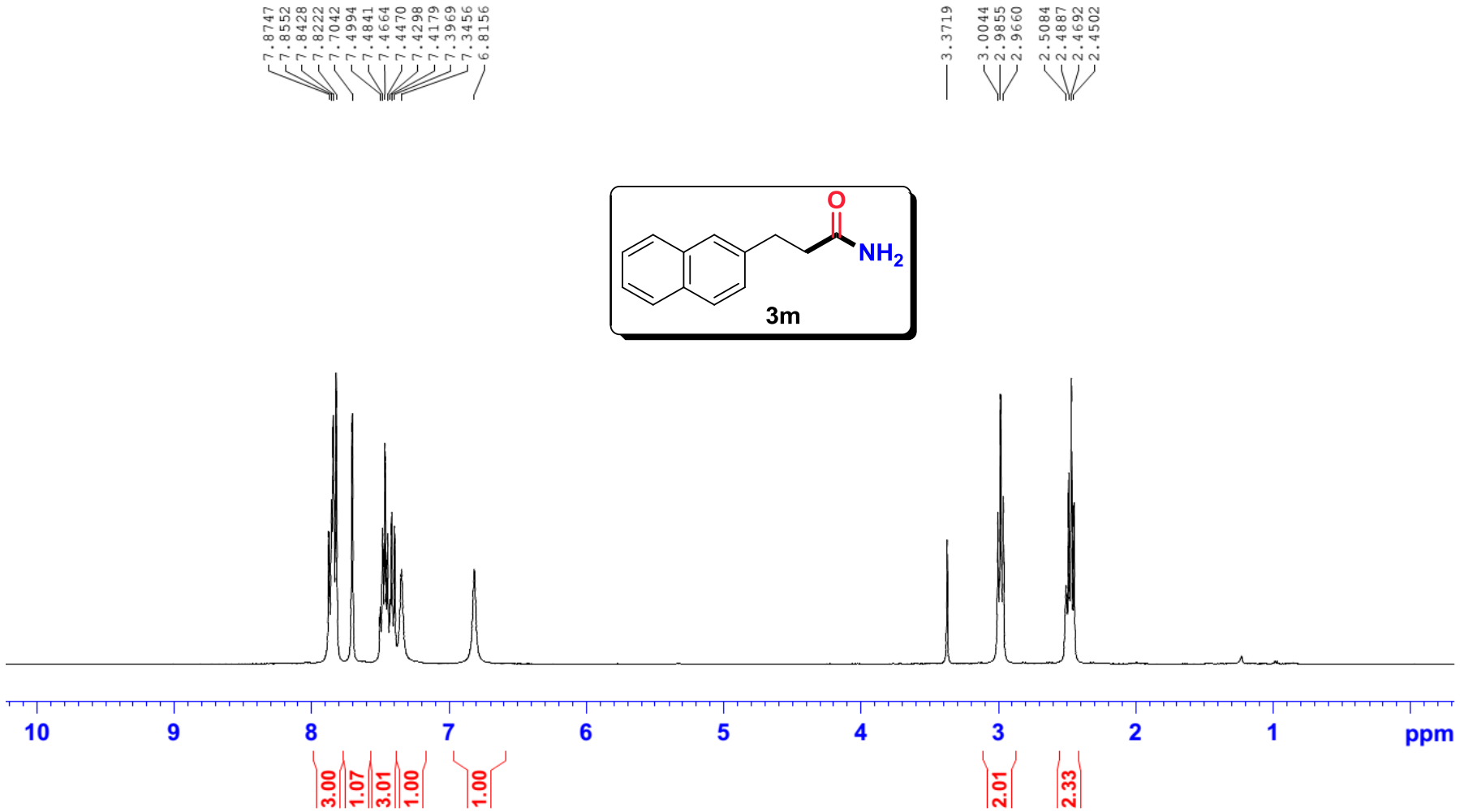



ZGY-X15X12-1-HNMR
7.3484
7.3279
7.2987
7.2939
7.2737
7.0586
7.0538
7.0381
7.0333
5.9922
5.5760
2.9325
2.9137
2.8946
2.5176
2.4984
2.4797
-0.0002
Cl
Cl
O
NH2
3l
10
9
8
7
6
5
4
3
2
1
ppm
2.03
1.00
1.04
1.02
2.09
2.06

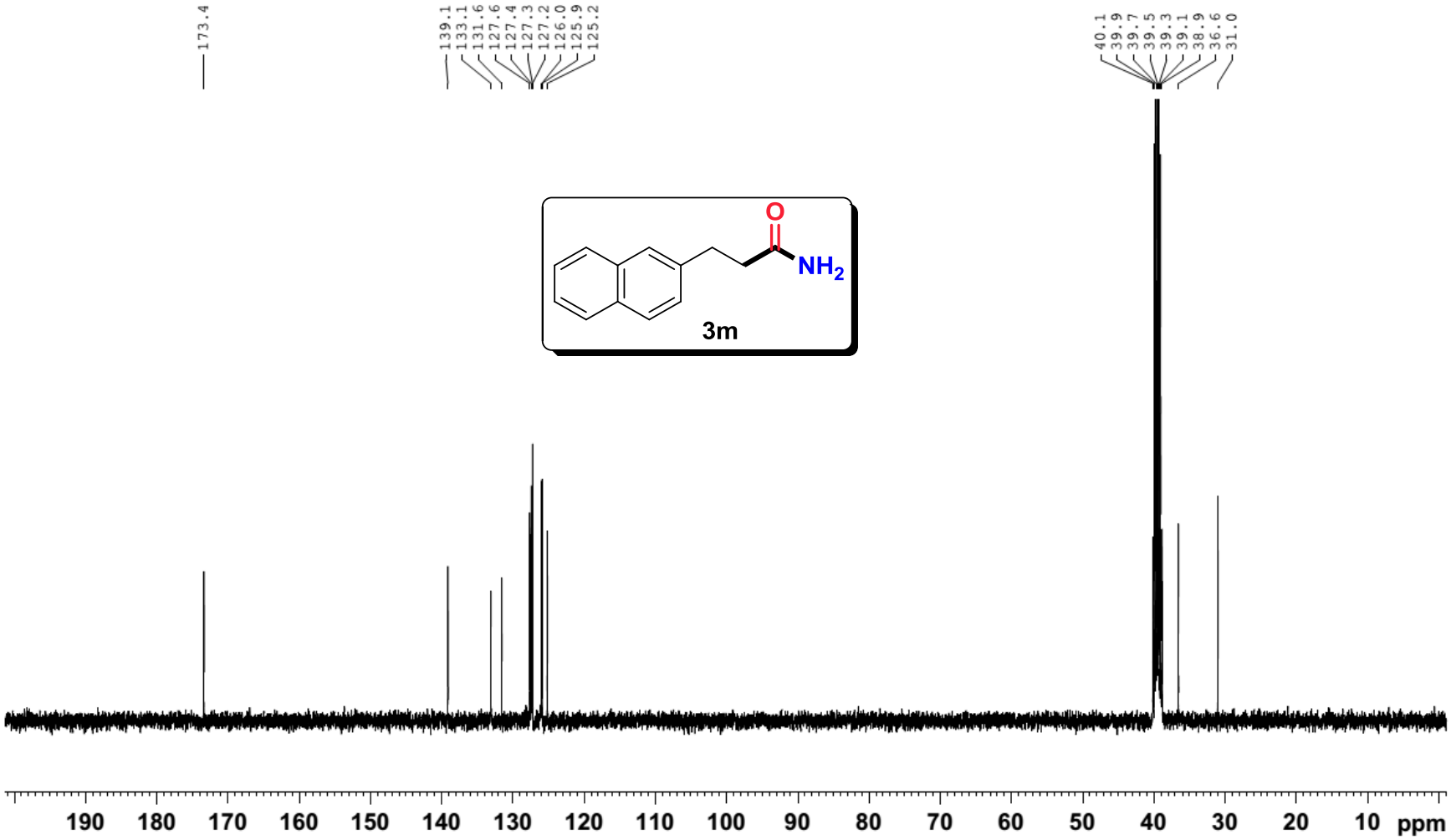
ZGY-X15X12-1-CNMR



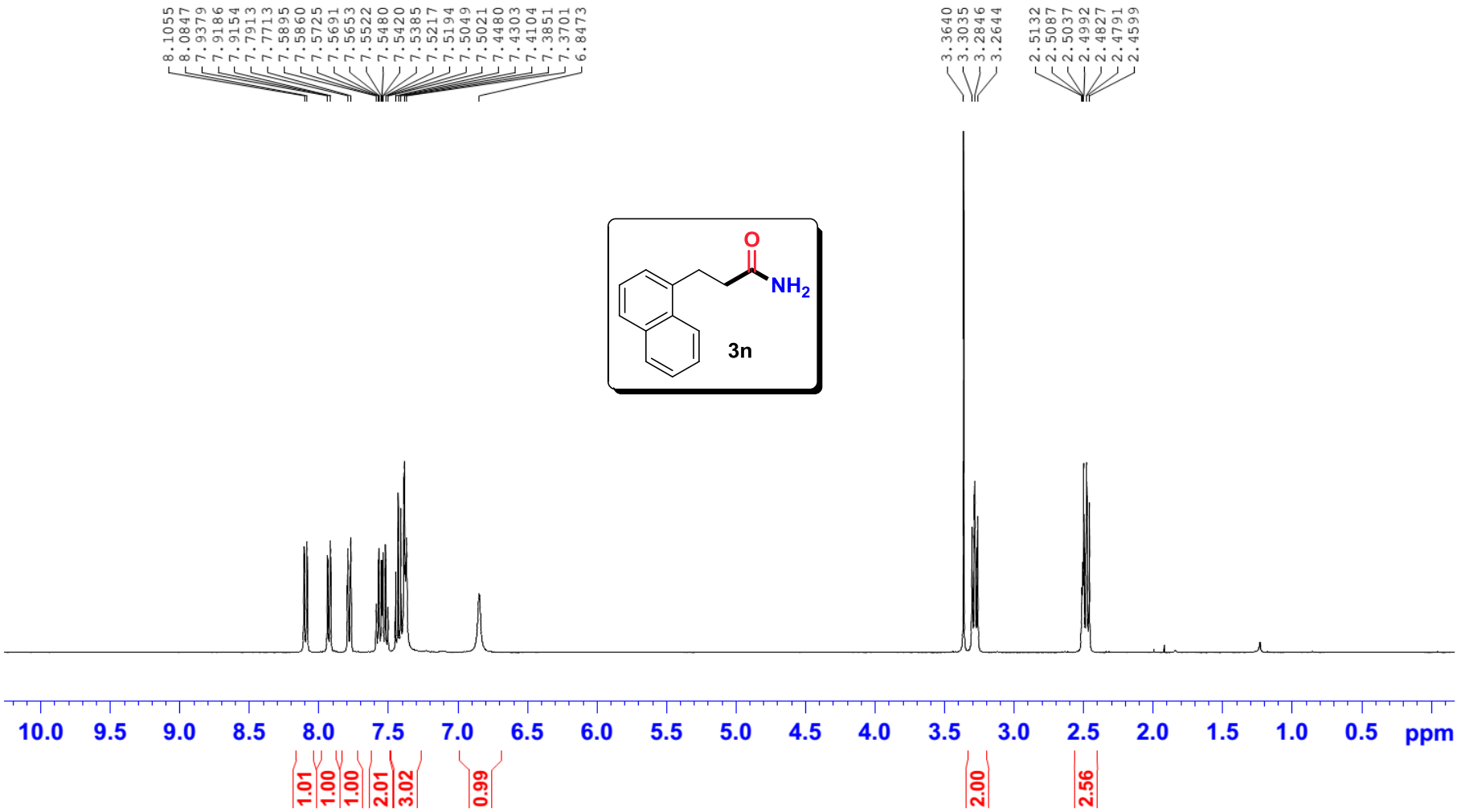
ZGY-X15X15-4-HNMR

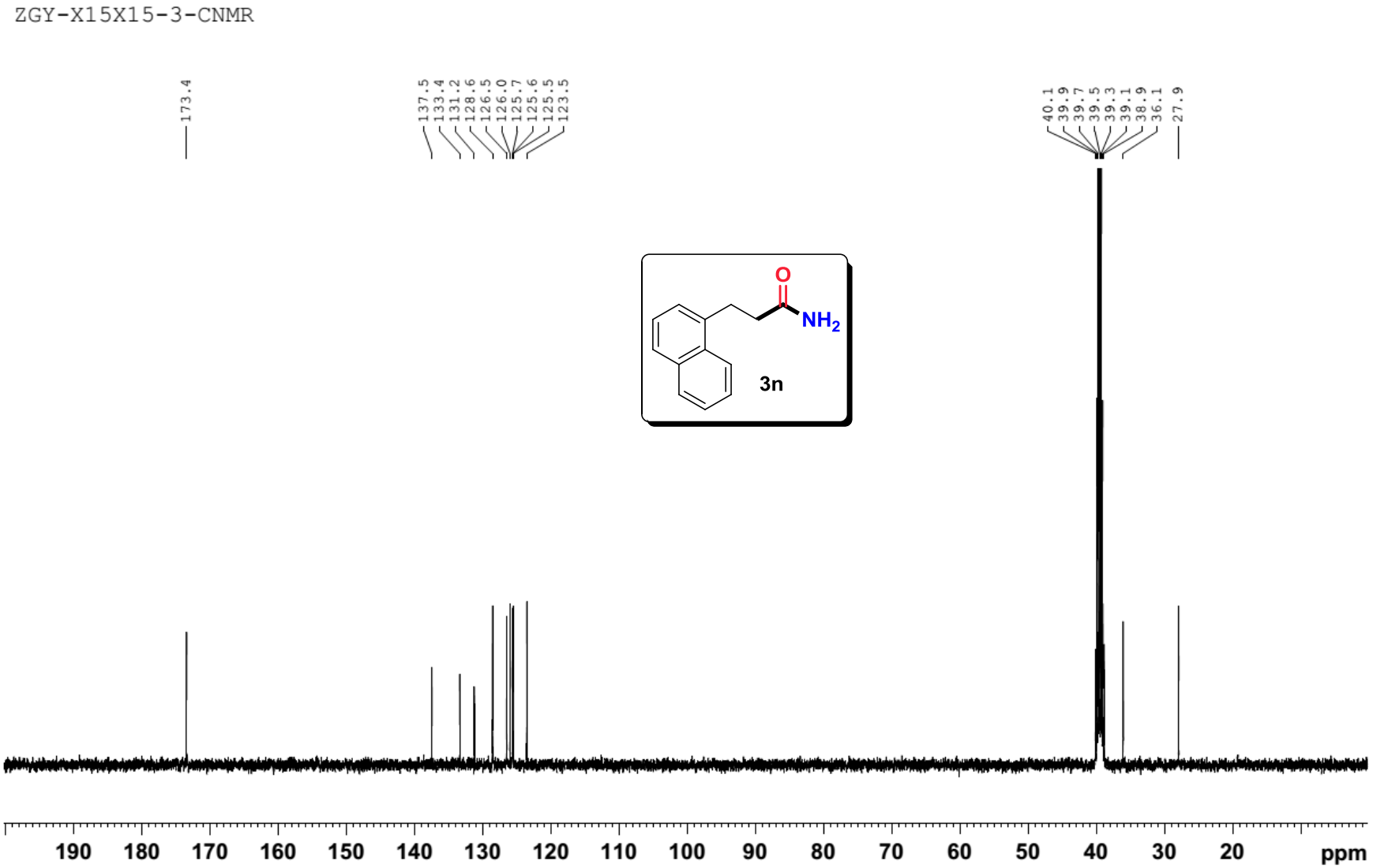


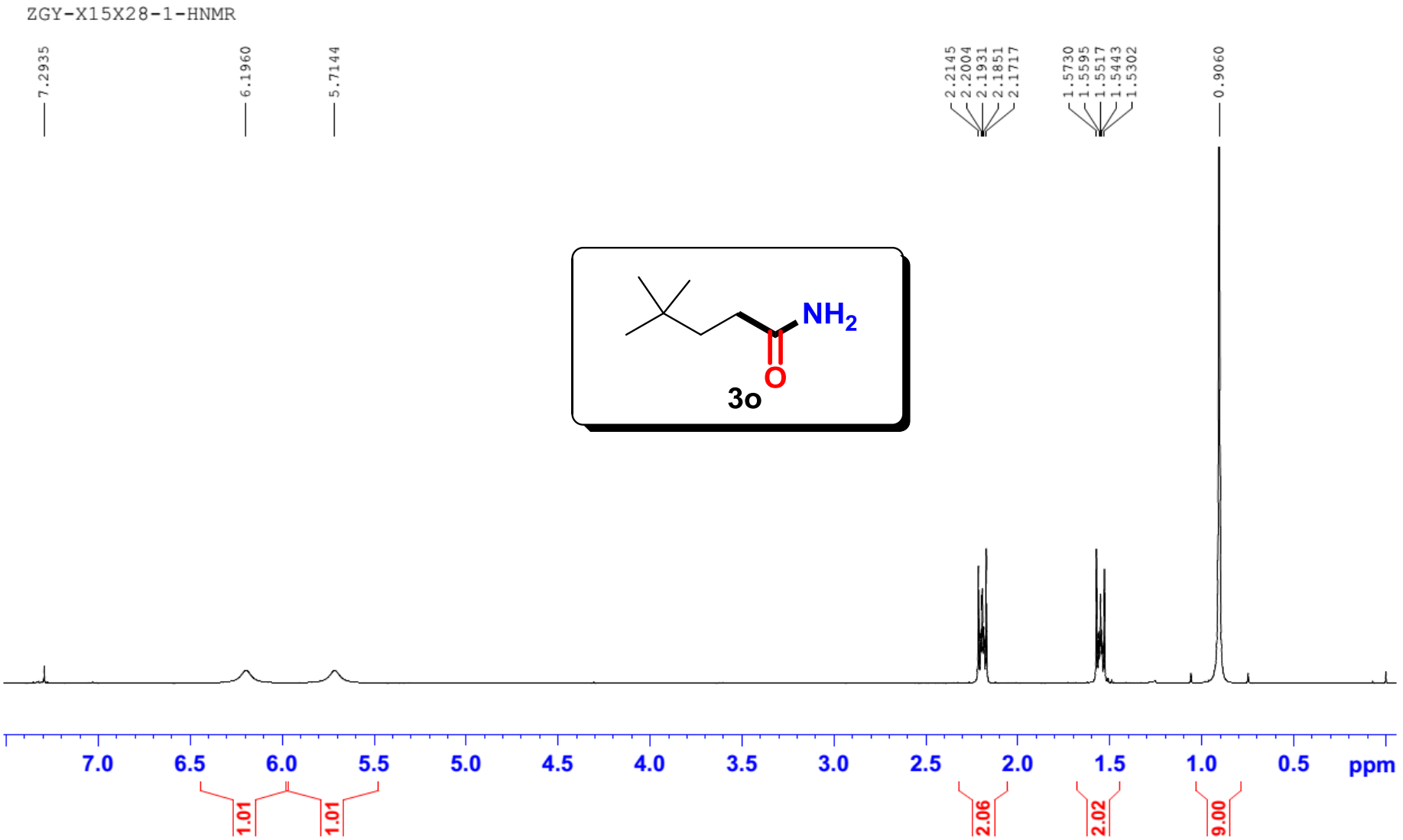
ZGY-X15X15-2-CNMR



ZGY-X15X15-3-HNMR




ZGY-X15X15-3-CNMR
173.4
137.5
133.4
131.2
128.6
126.5
126.0
125.7
125.6
125.5
123.5
40.1
39.9
39.7
39.5
39.3
39.1
38.9
36.1
27.9
O
NH2
3n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


ZGY-X15X28-1-HNMR
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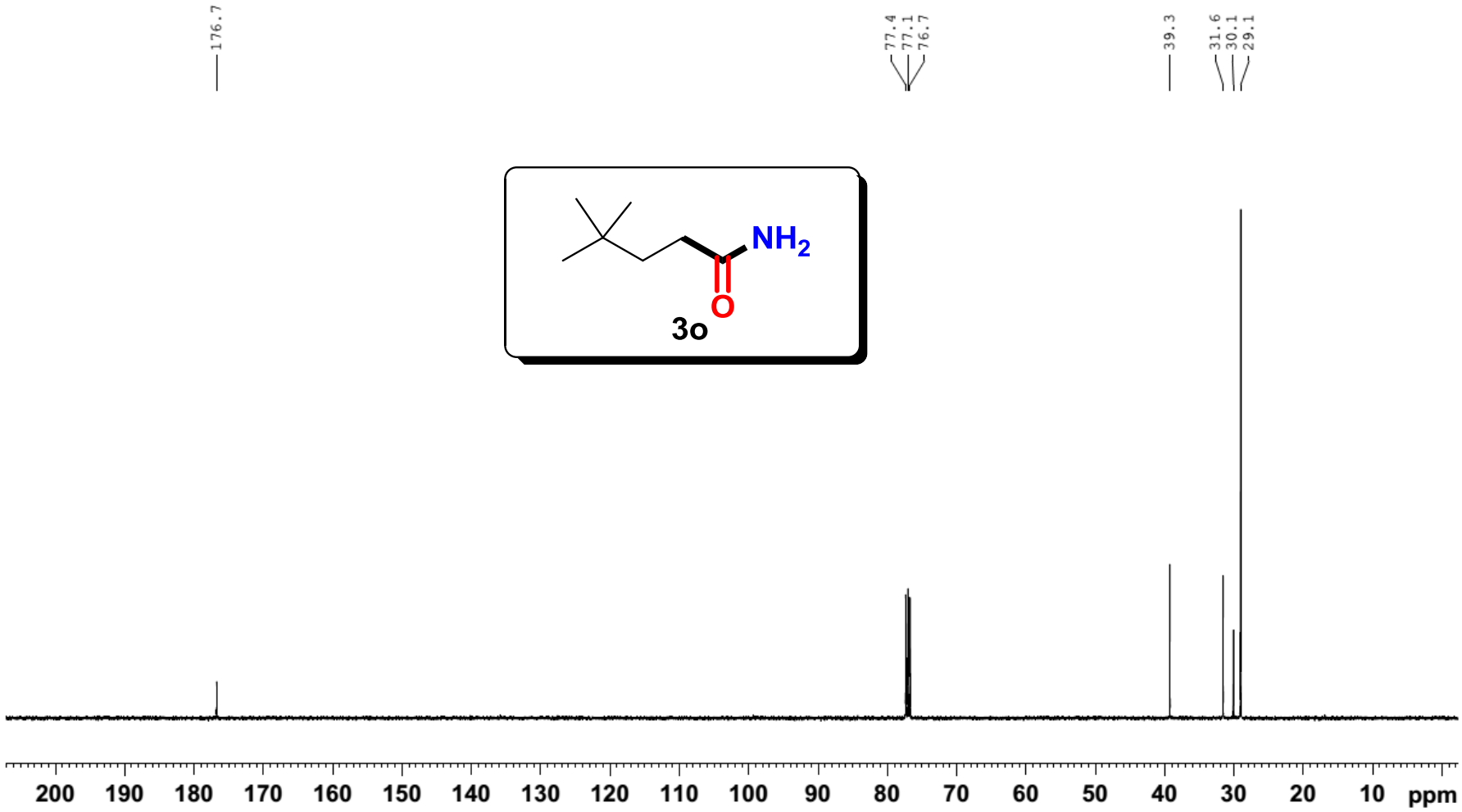
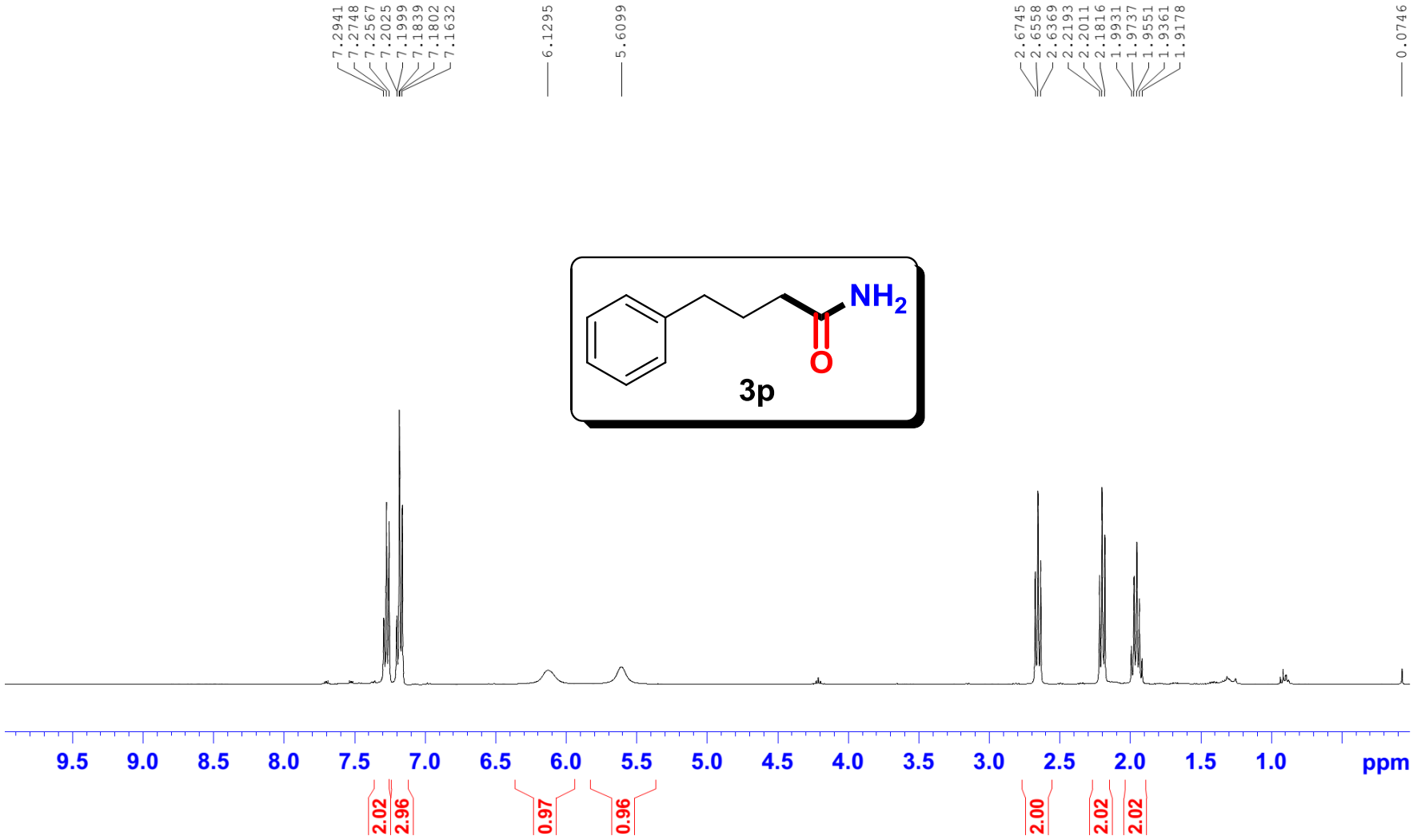
6.1960
5.7144
2.2145
2.2004
2.1931
2.1851
2.1717
1.5730
1.5595
1.5517
1.5443
1.5302
0.9060
NH2
O
3o
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.01
1.01
2.06
2.02
9.00

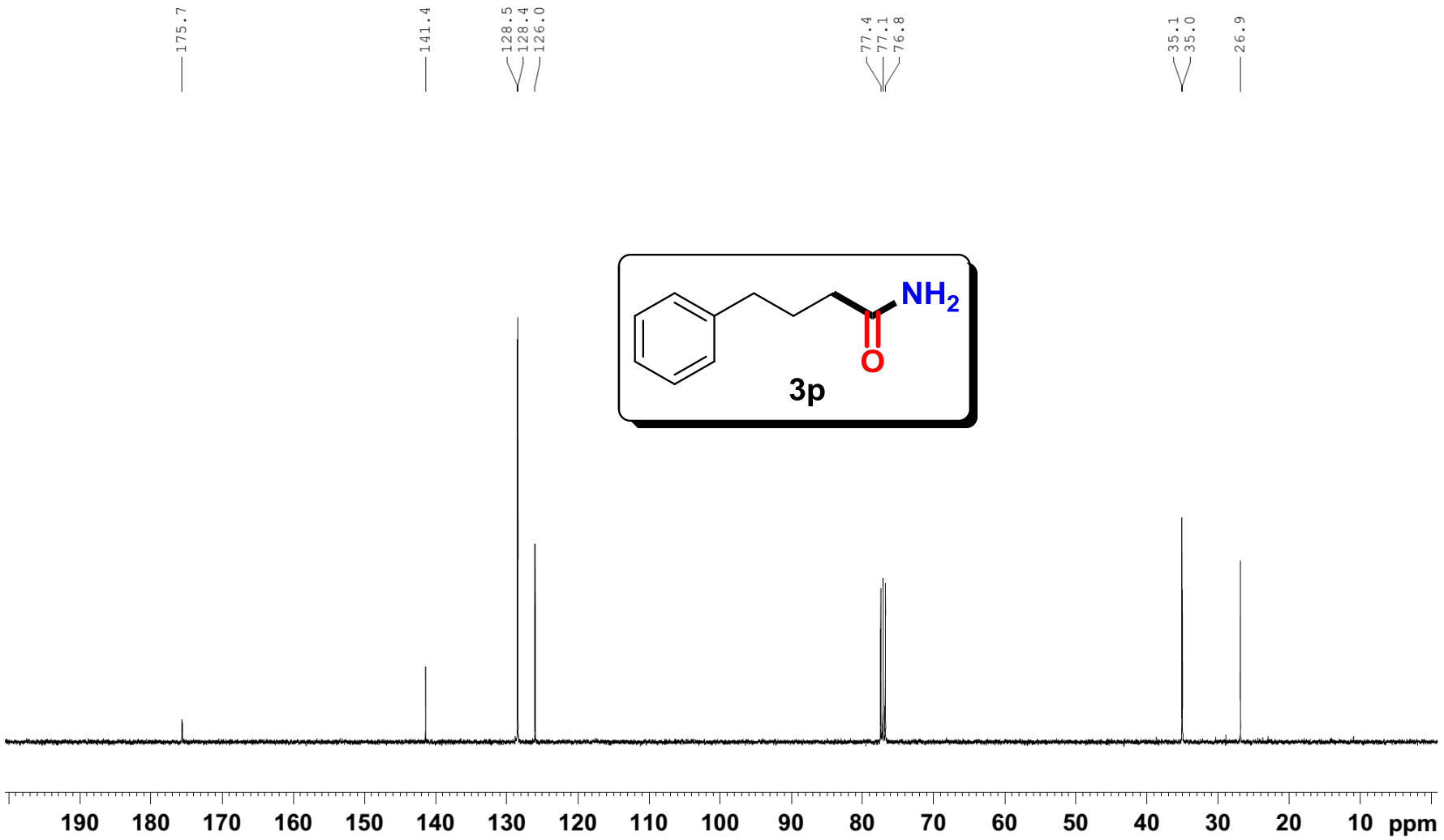
ZGY-X15X28-1-CNMR



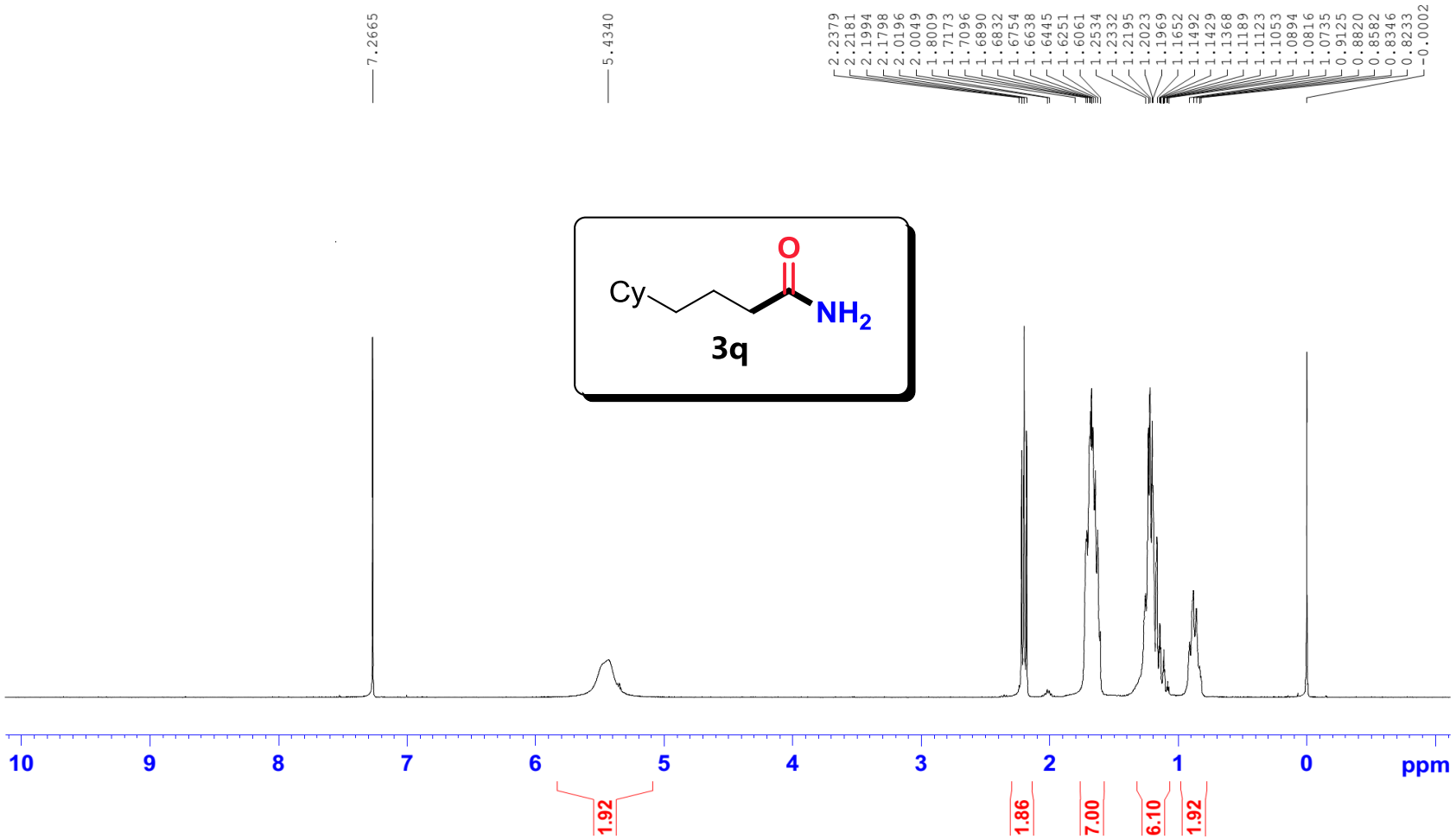
ZGY-X15X07-1-HNMR



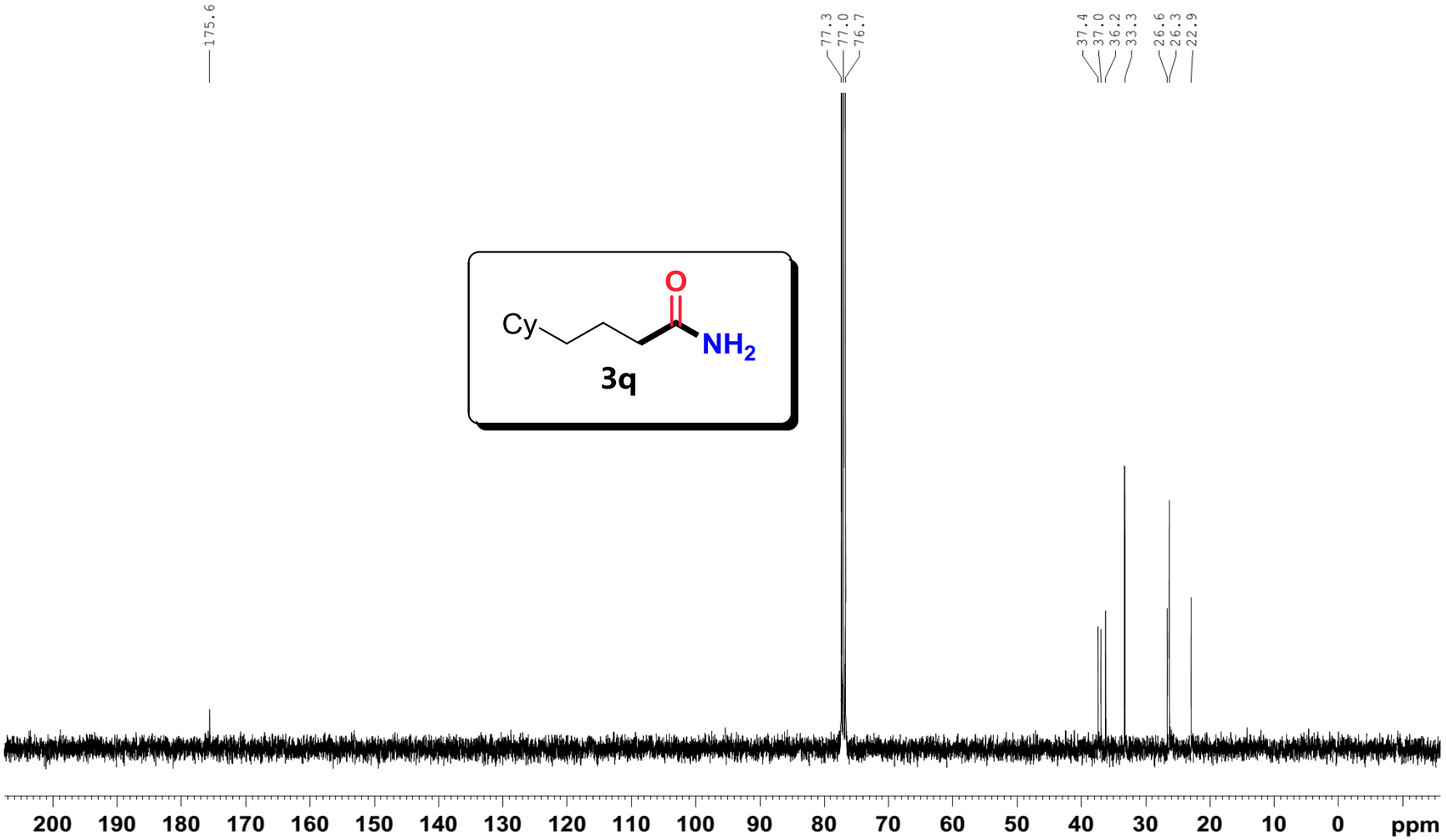
ZGY-X15X07-1-CNMR



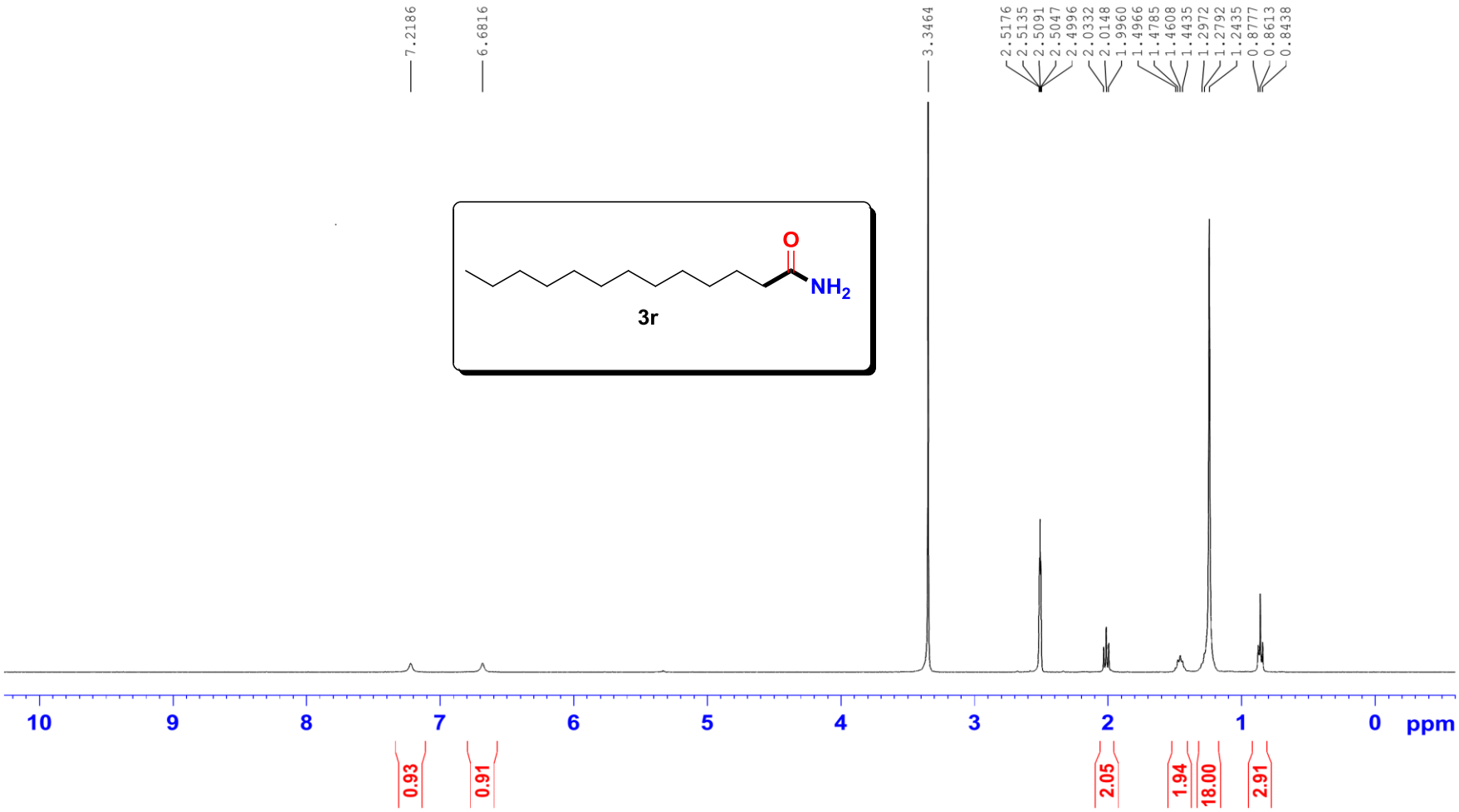
ZJP-X160914-3-HNMR



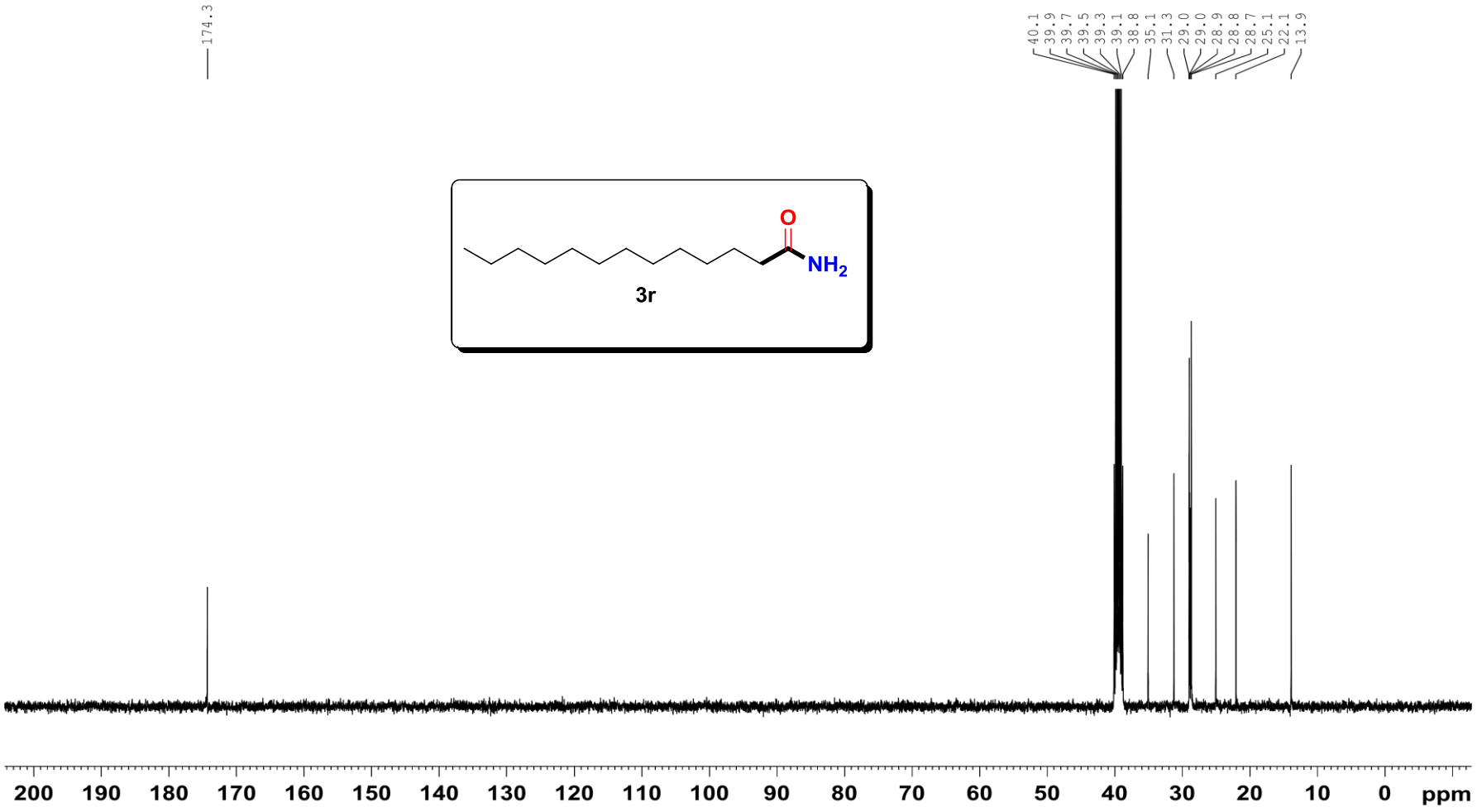
ZJP-X160914-3-CNMR



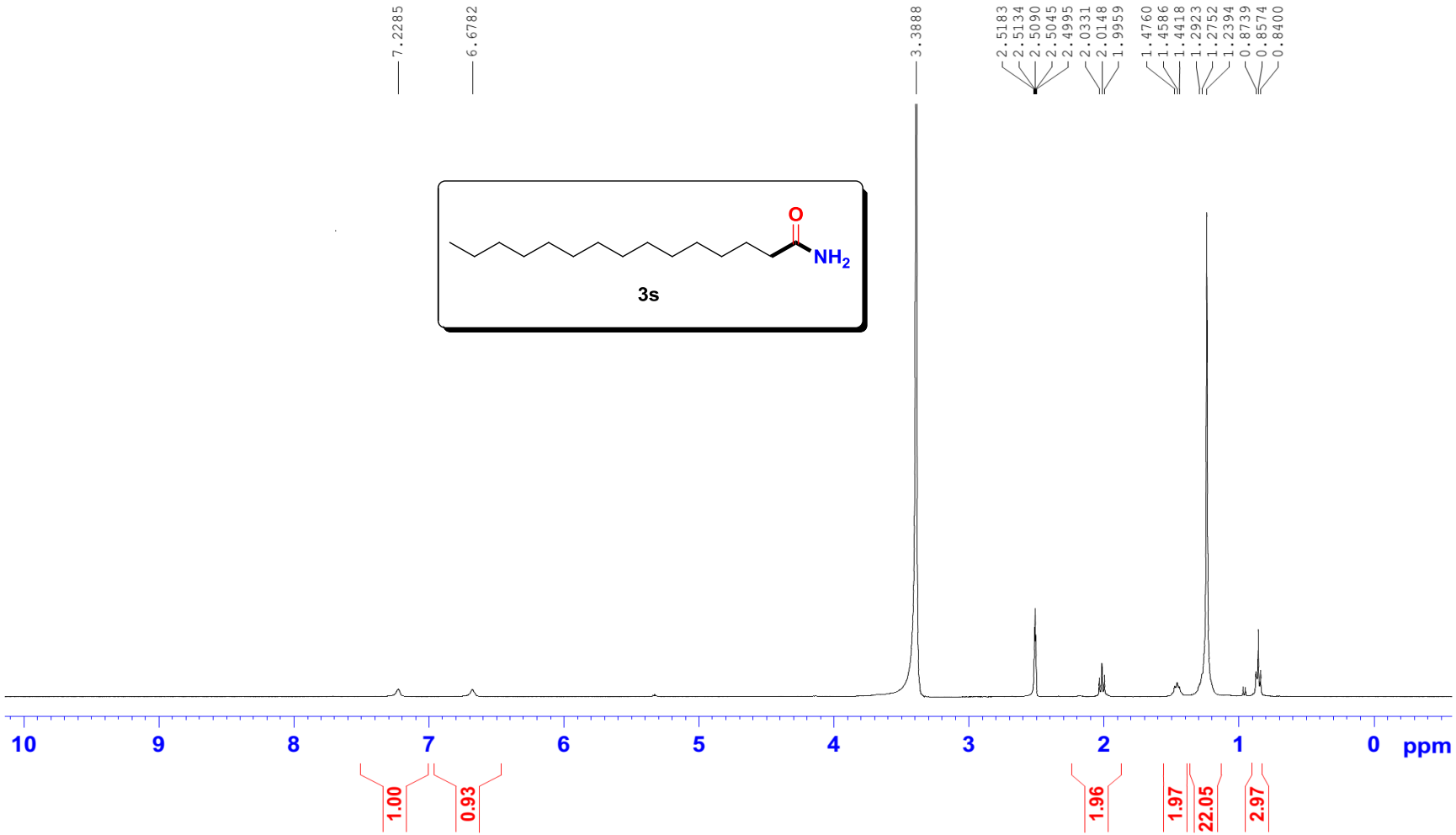
ZJP-X160914-2-HNMR-d6-DMSO



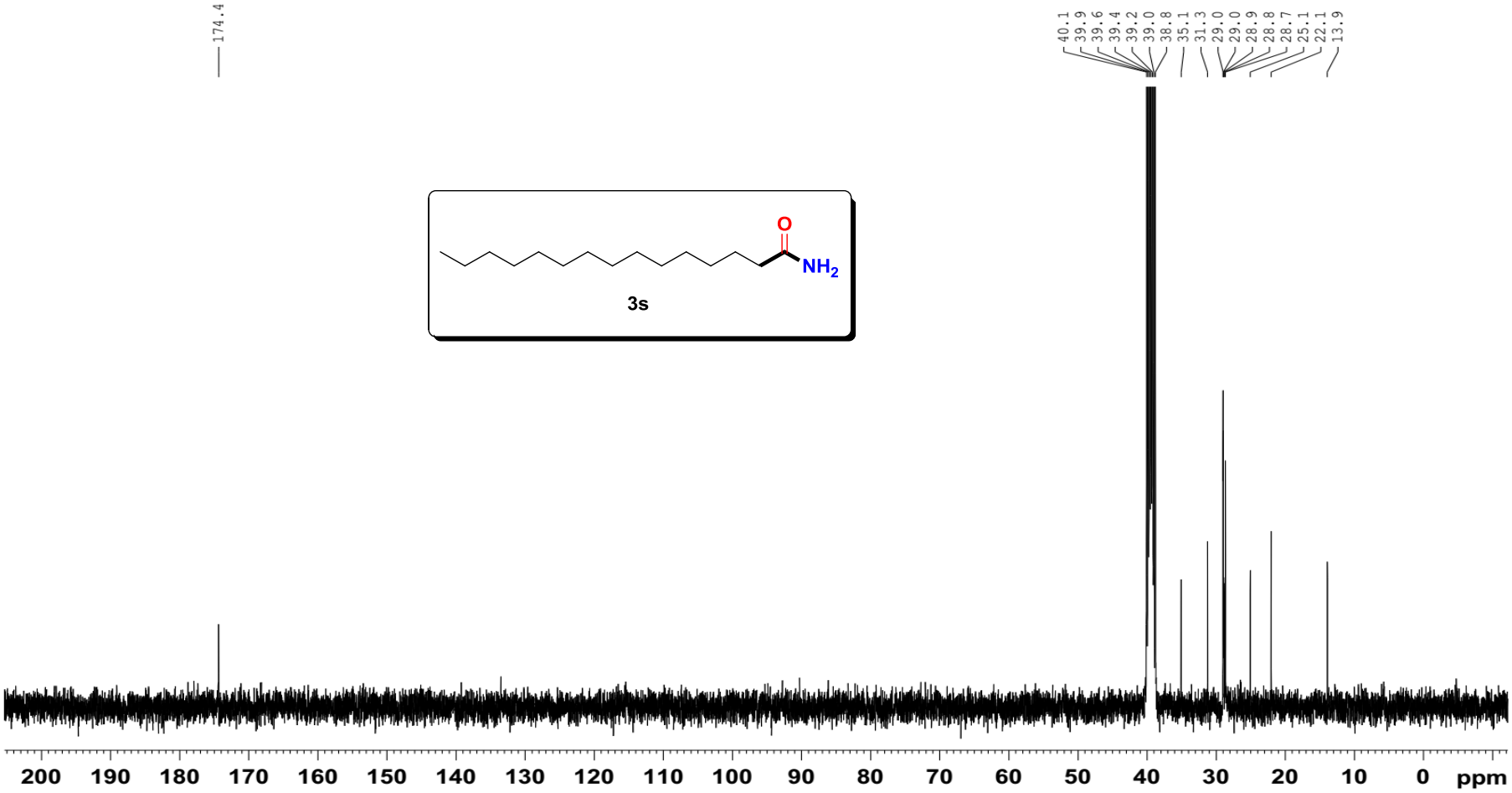
ZJP-X160926-2-CNMR-d6-DMSO



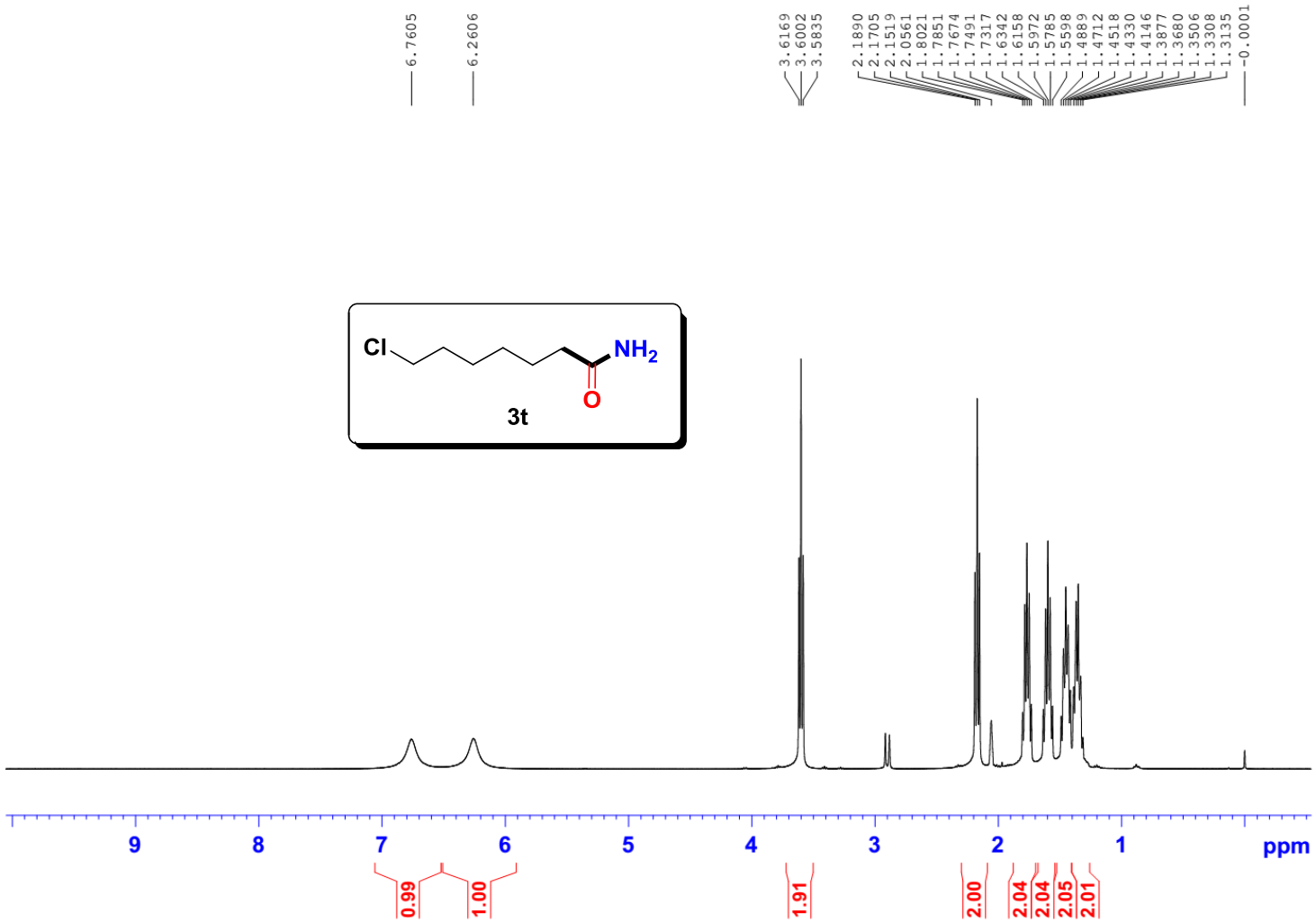
ZJP-X16X19-1-HNMR-d6-DMSO



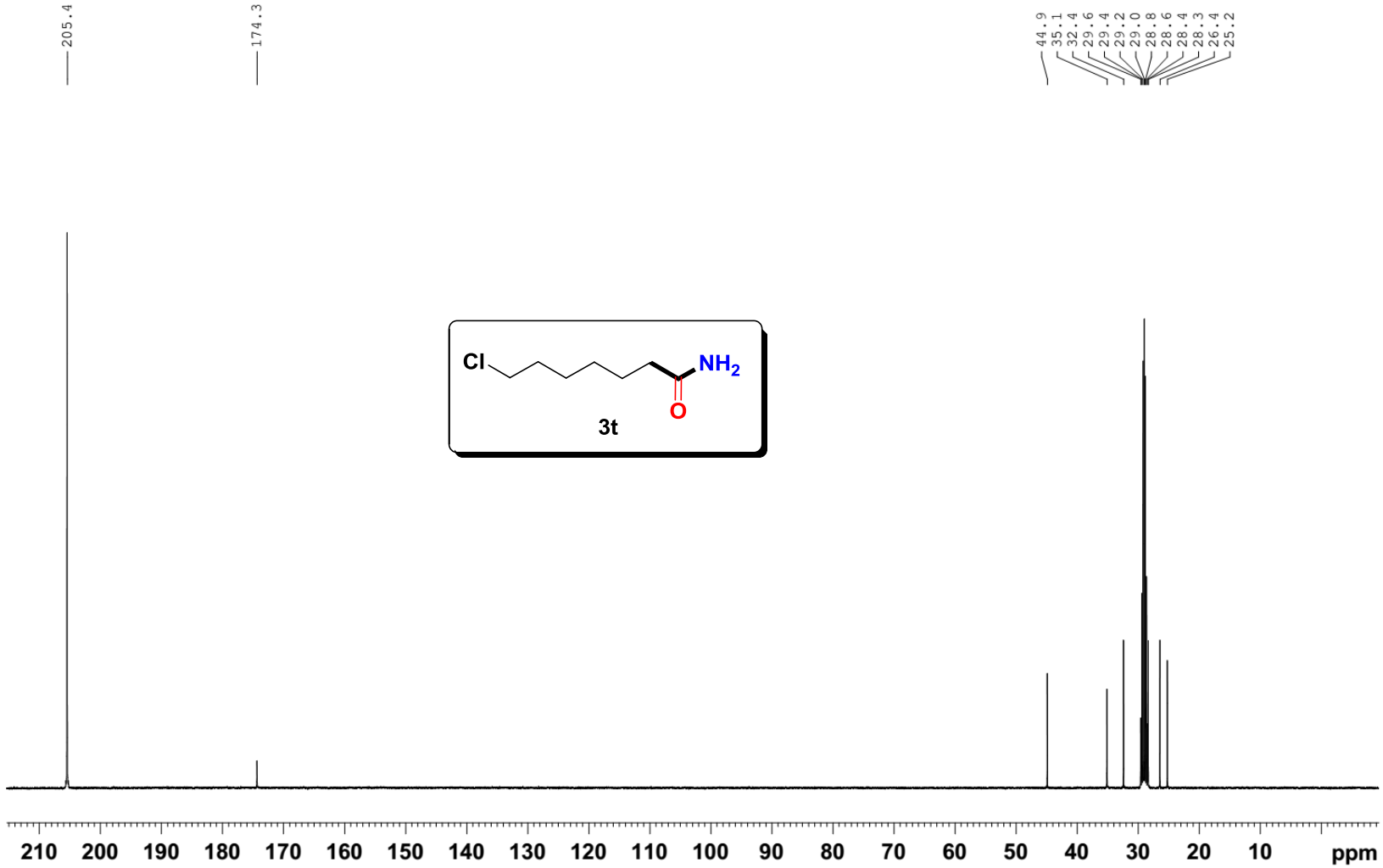
ZJP-X16X26-1-CNMR-d6-DMSO



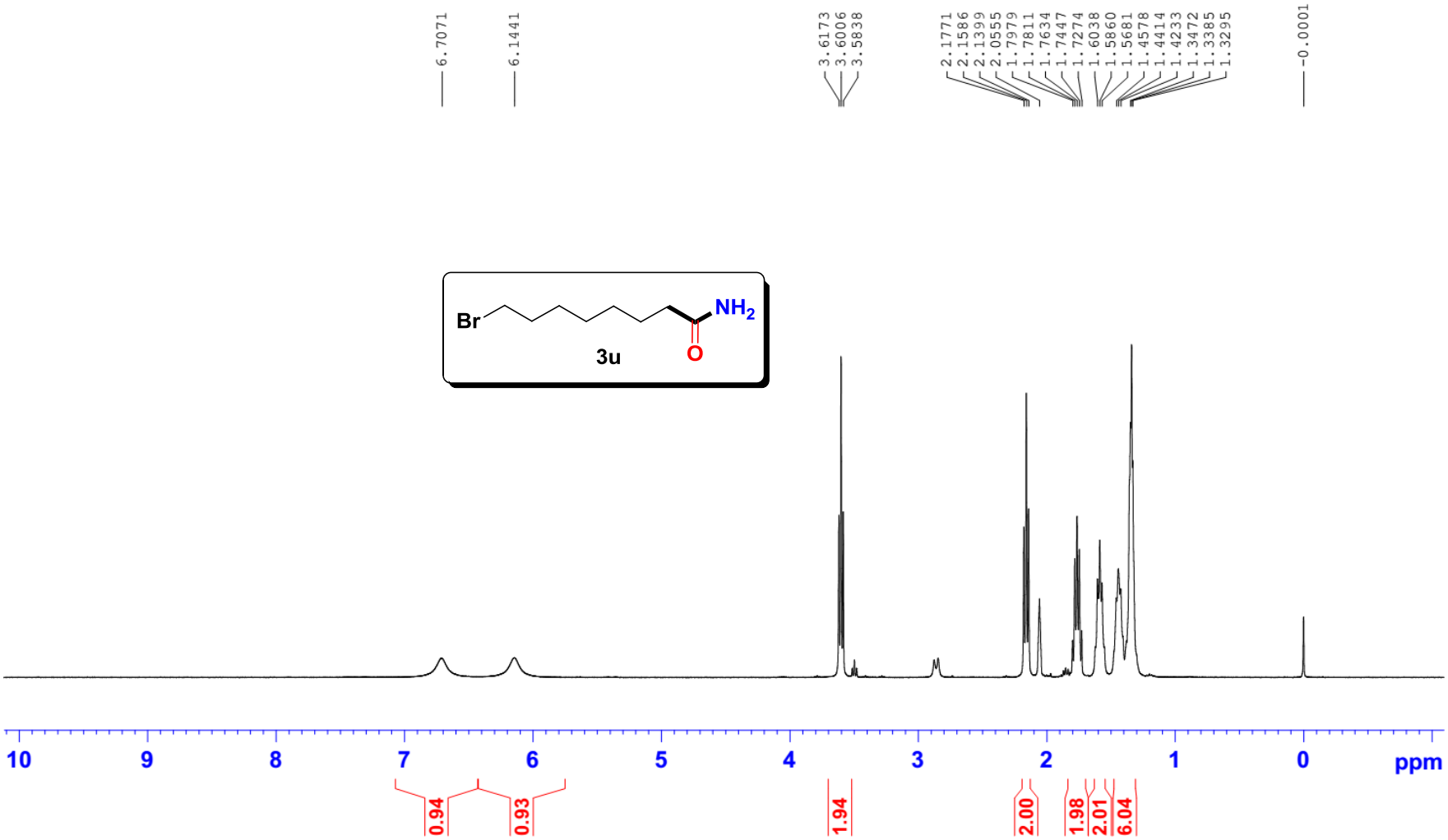
GB-X170301-1-4-HNMR in Acetone-d_6



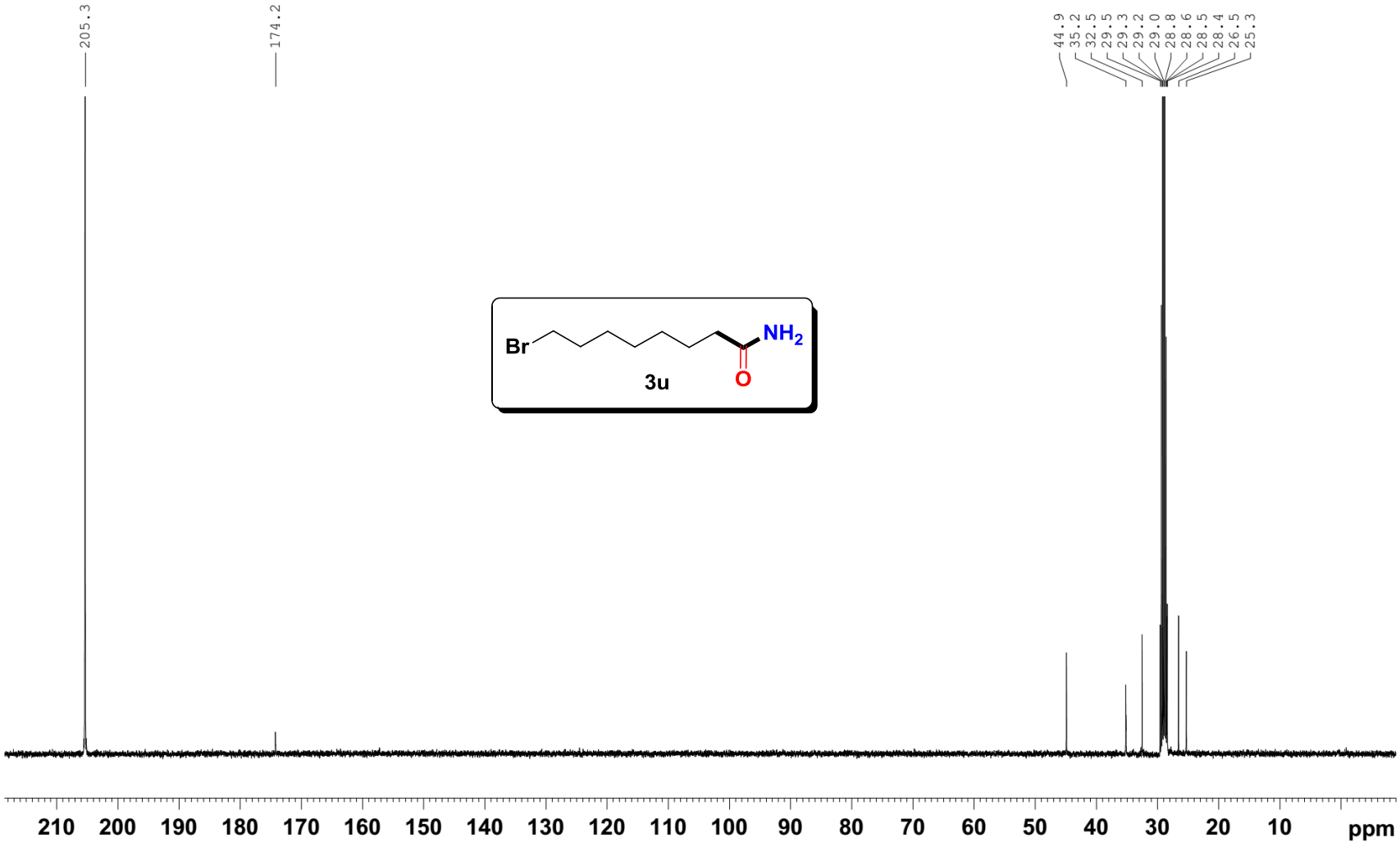
GB-X170301-1-4-CNMR in Acetone-d_6



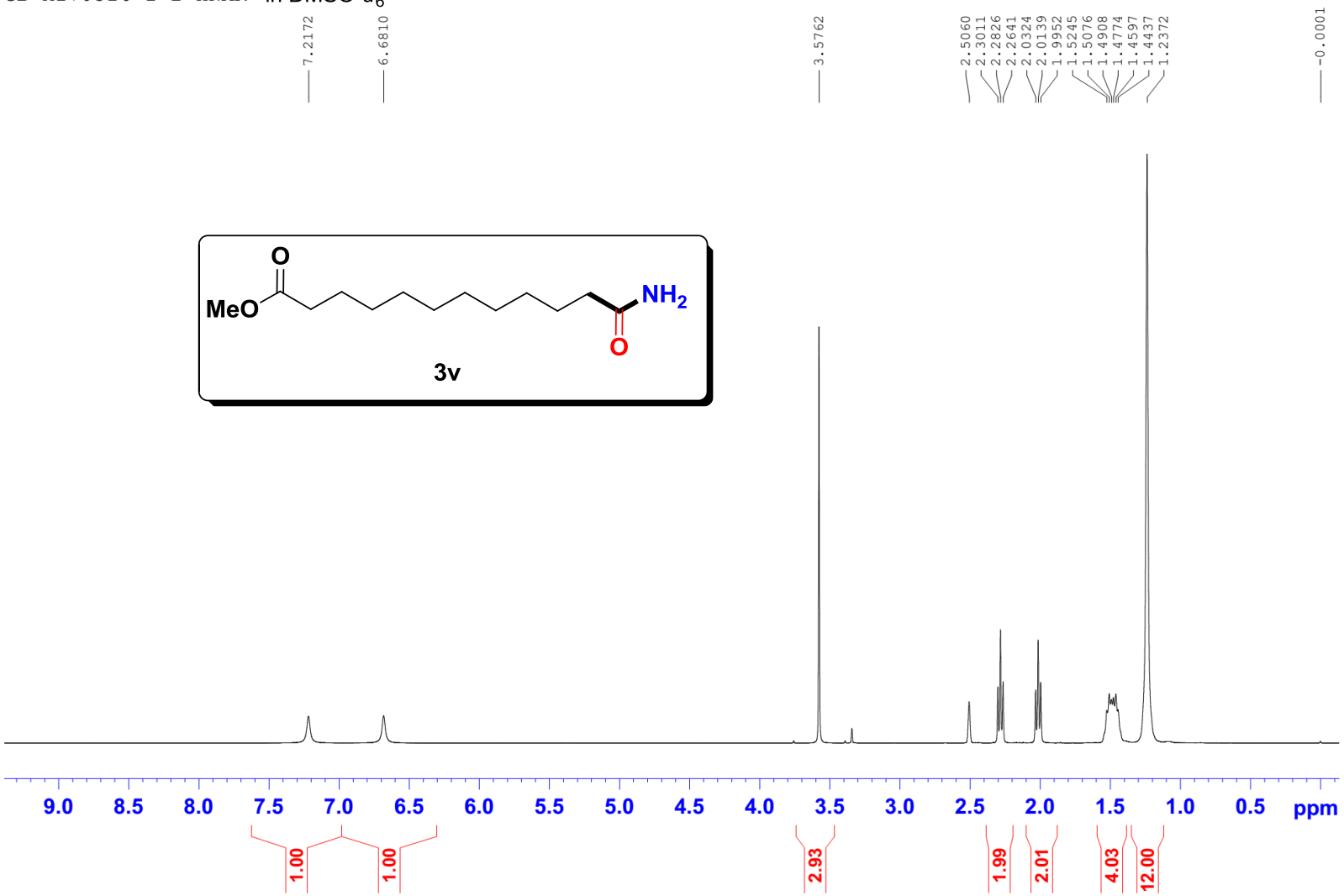
GB-X170301-1-3-HNMR in Acetone-d_6



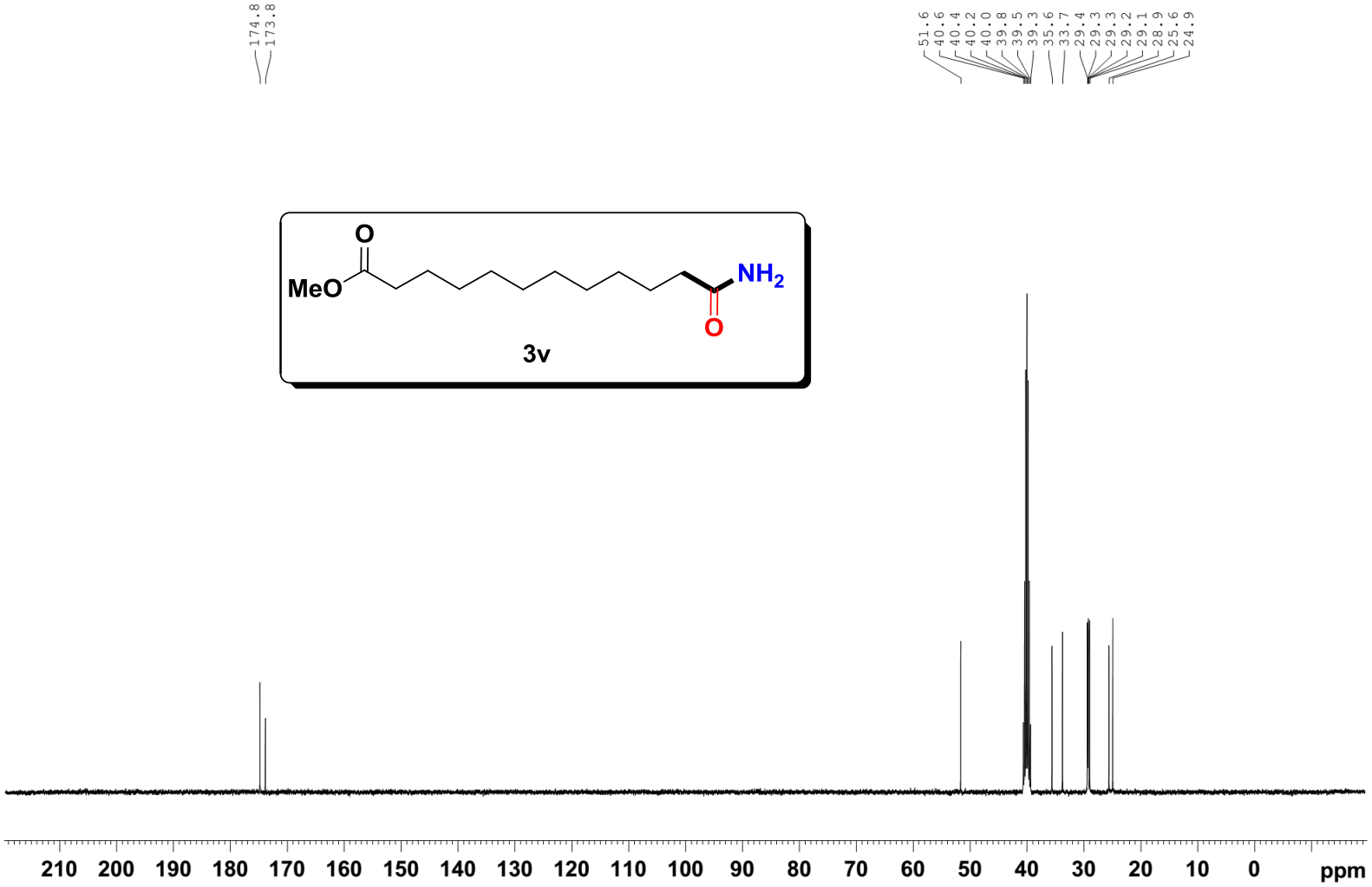
GB-X170301-1-3-CNMR in Acetone-d_6



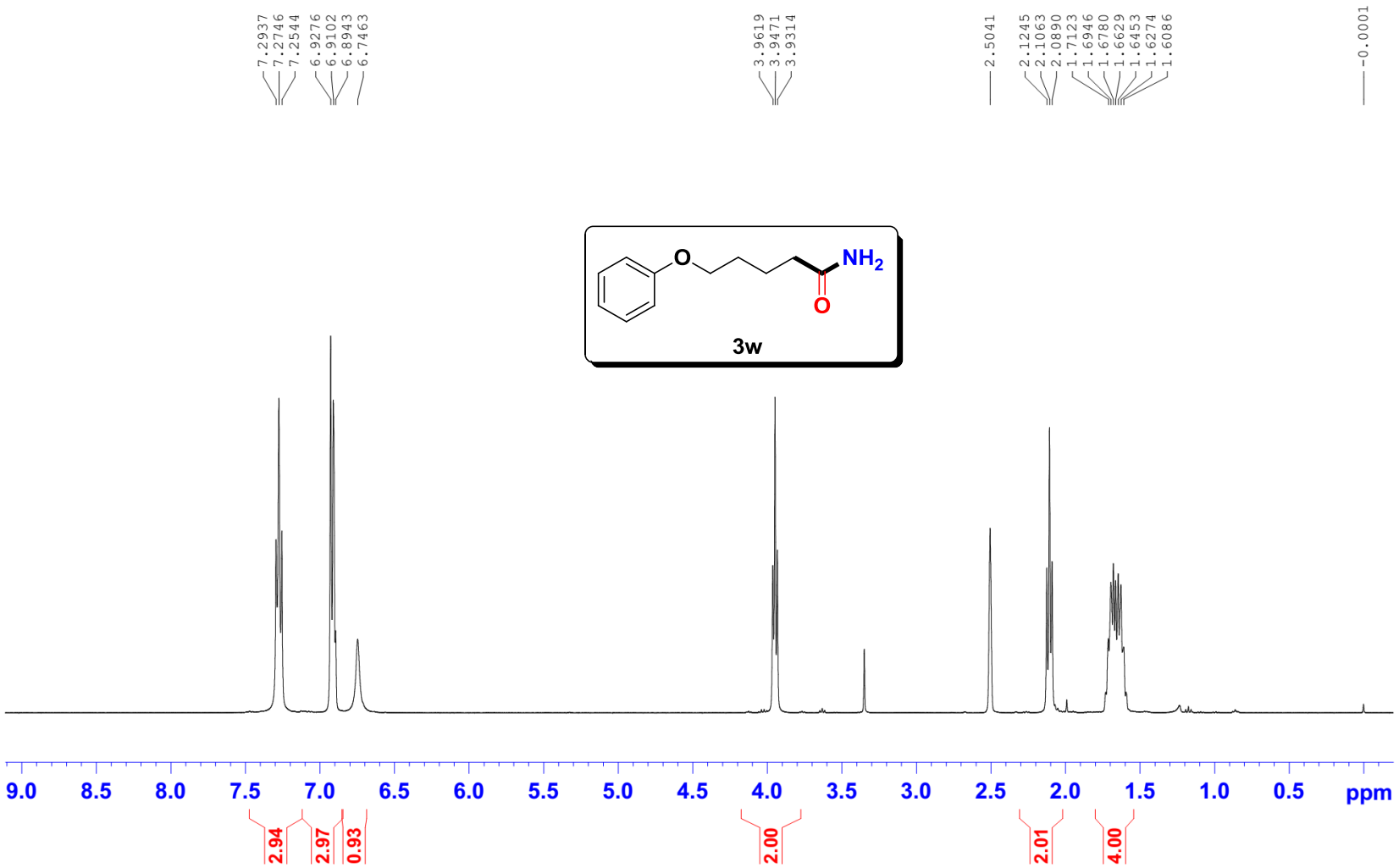
GB-X170316-1-2-HNMR in DMSO-d_6



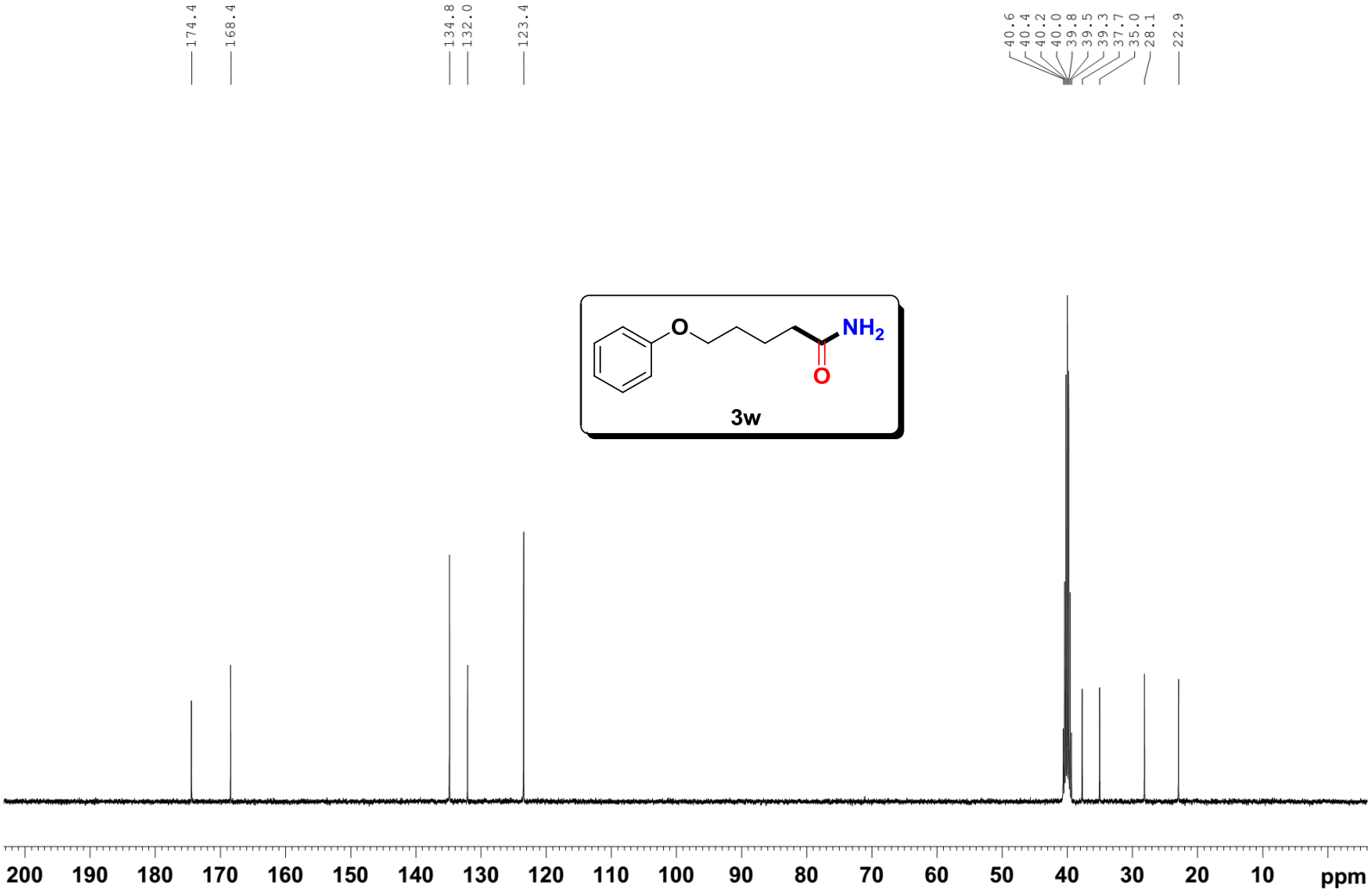
GB-X170316-1-2-CNMR in DMSO-d_6



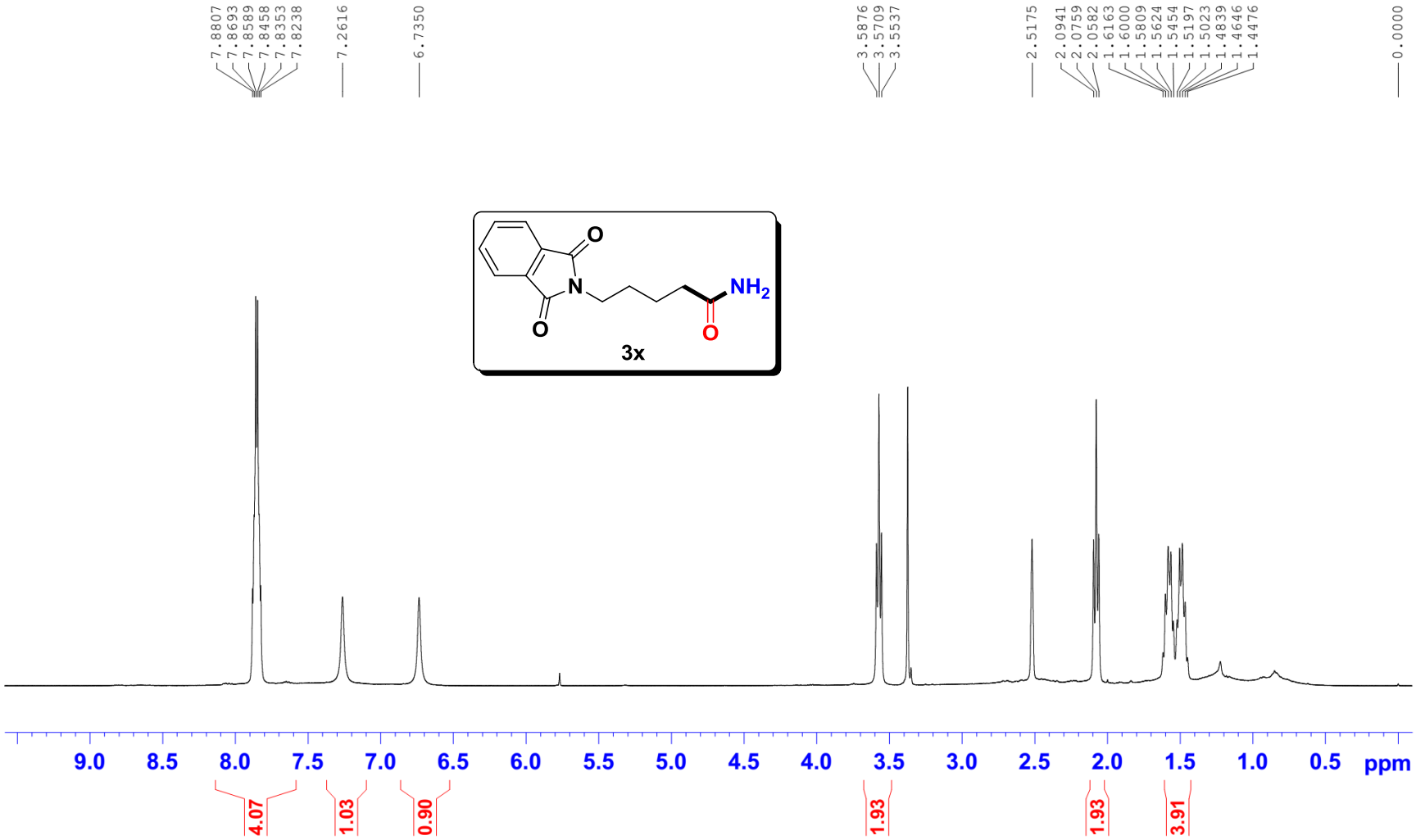
GB-X170228-1-5-HNMR in DMSO-d_6



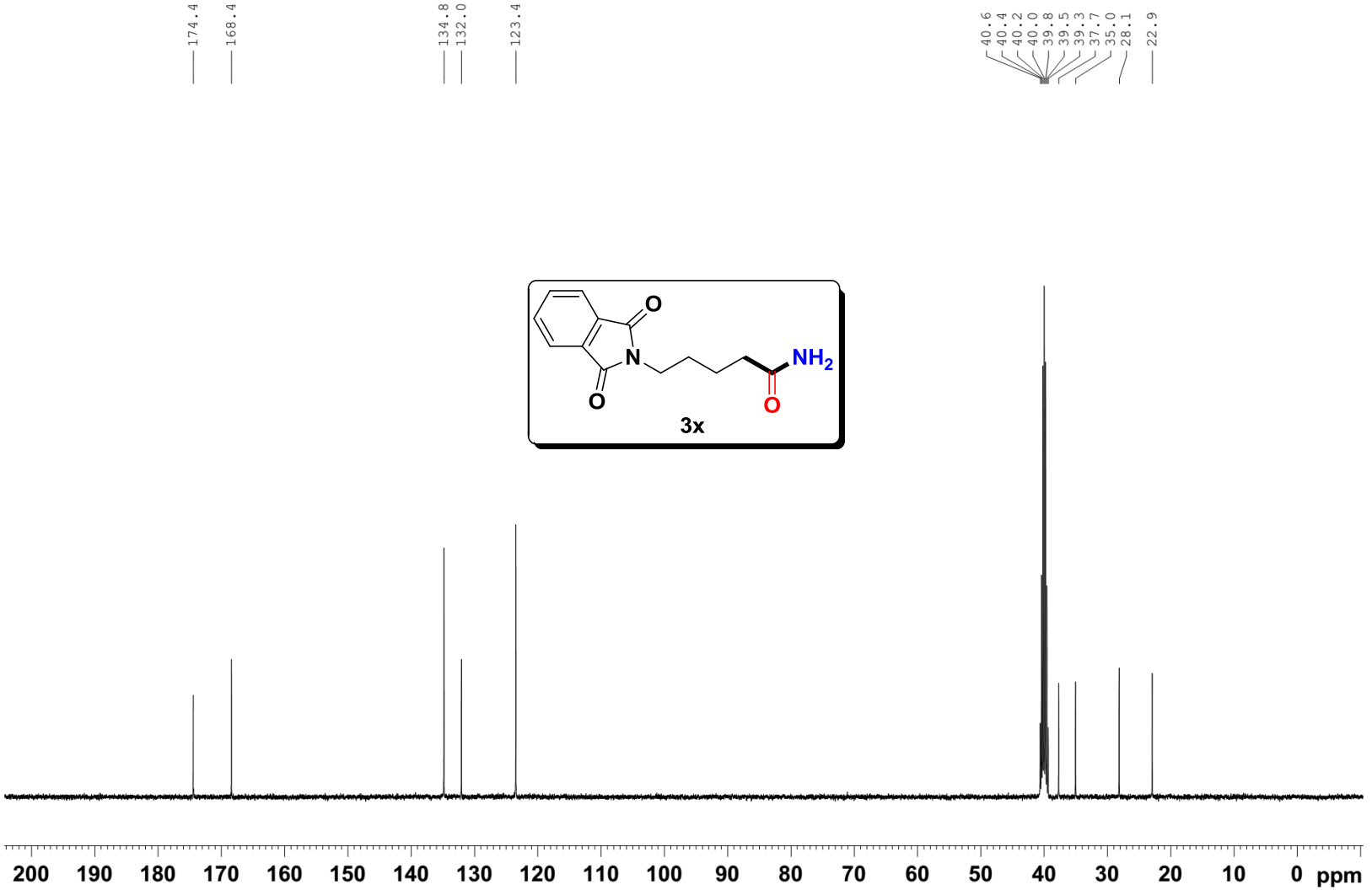
GB-X170228-1-5-CNMR in DMSO-d_6



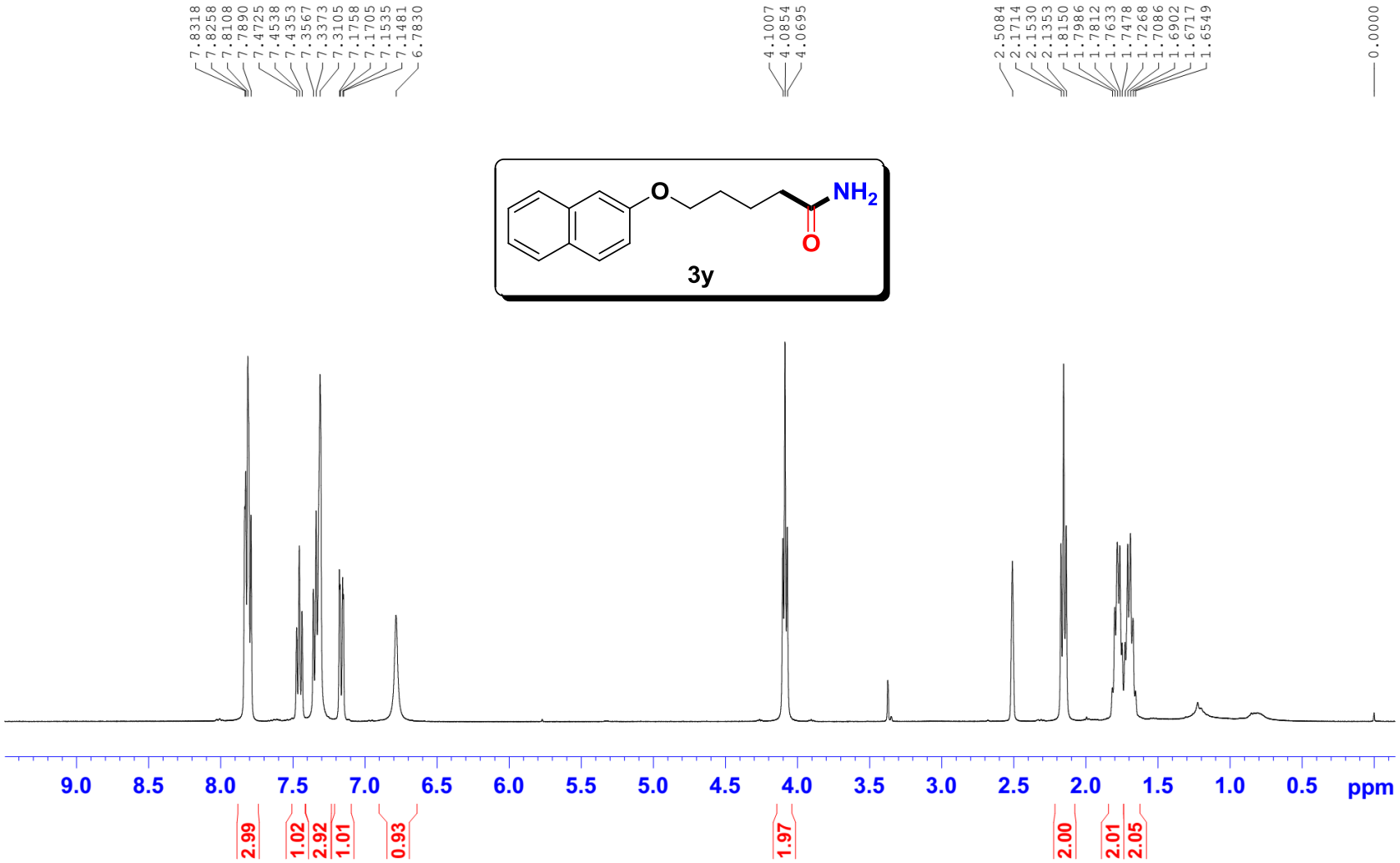
GB-X170228-1-3-HNMR in DMSO-d_6



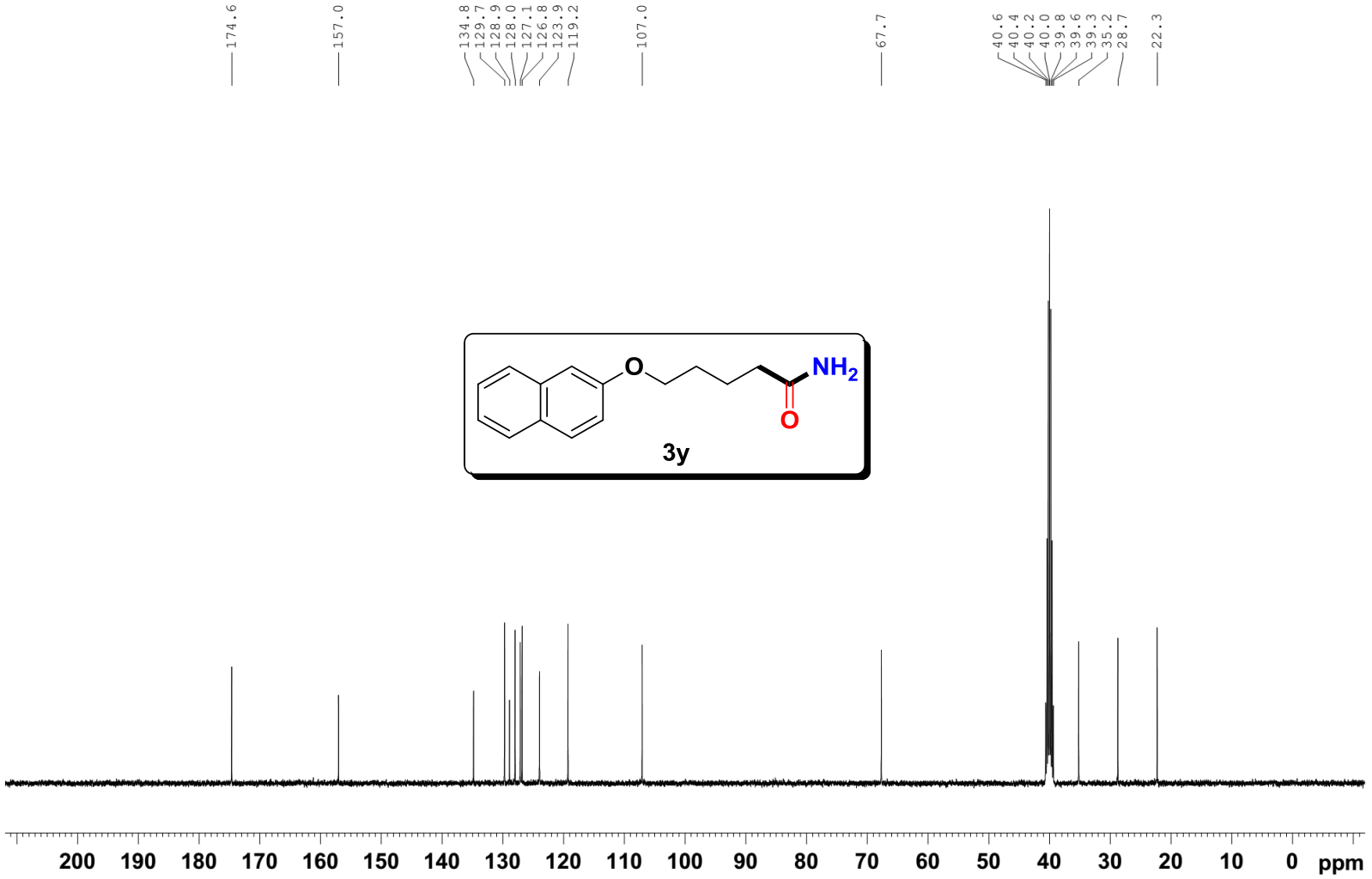
GB-X170228-1-3-CNMR in DMSO-d_6



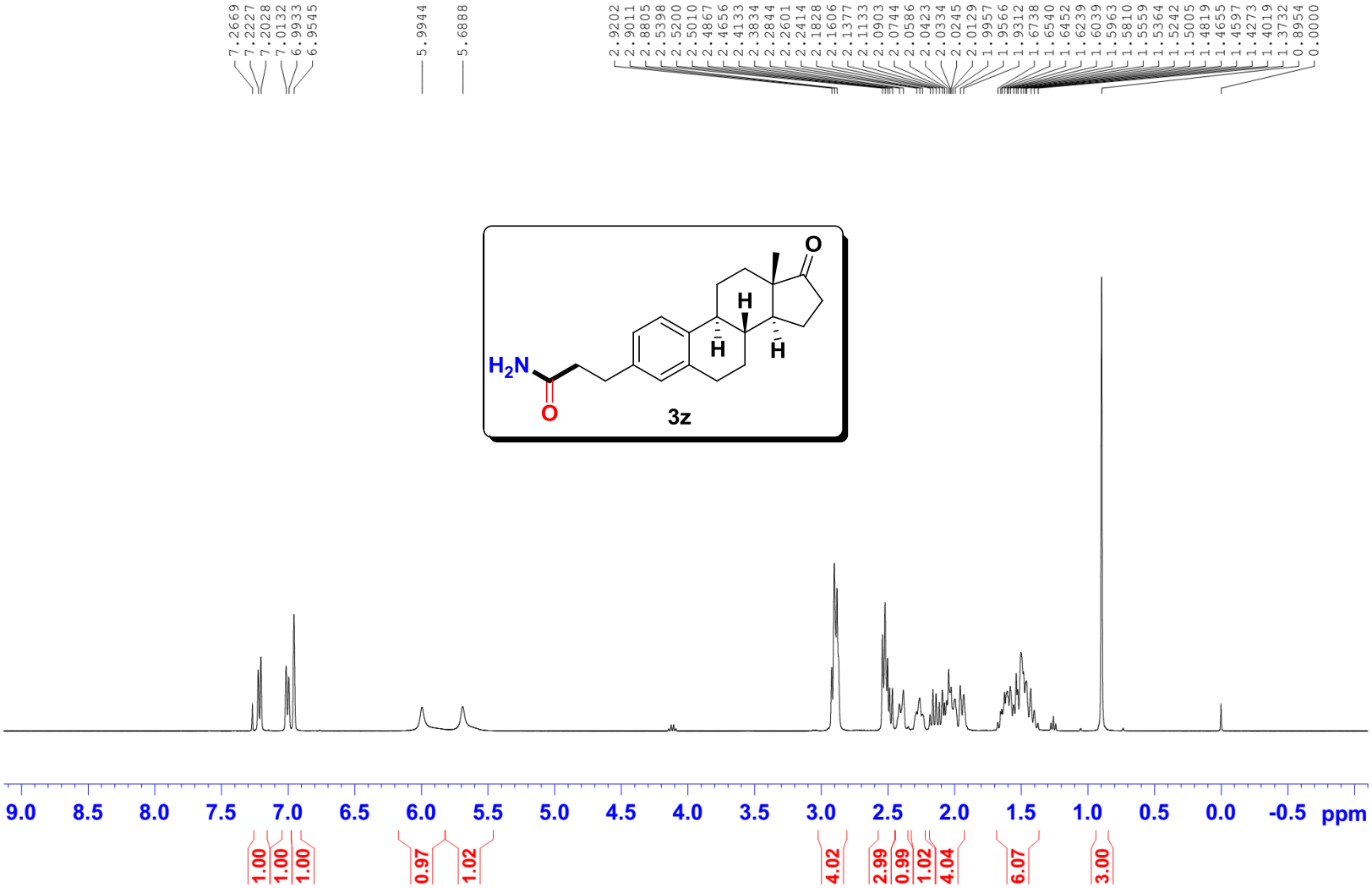
GB-X170228-1-6-HNMR in DMSO-d_6



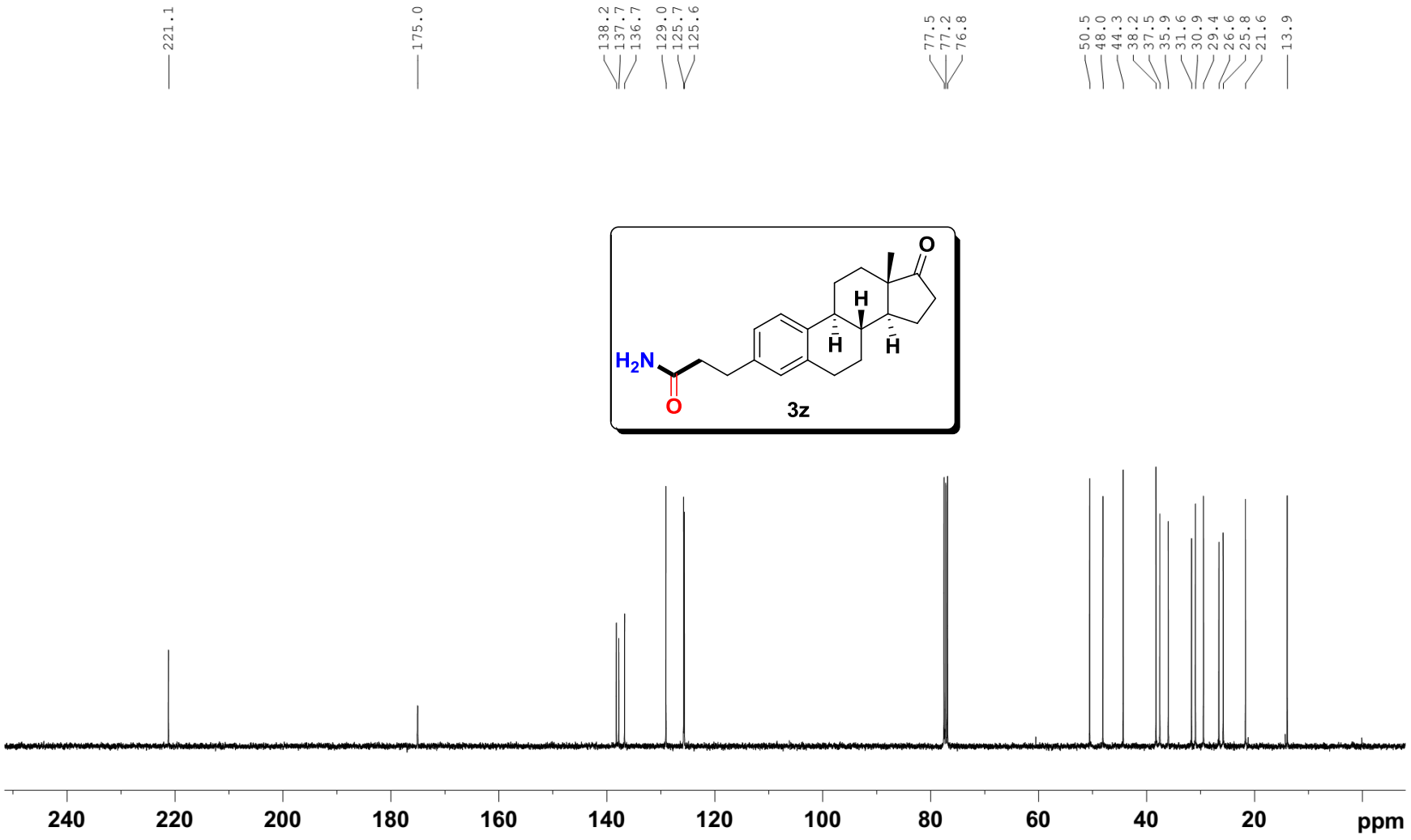
GB-X170228-1-6-CNMR in DMSO-d_6



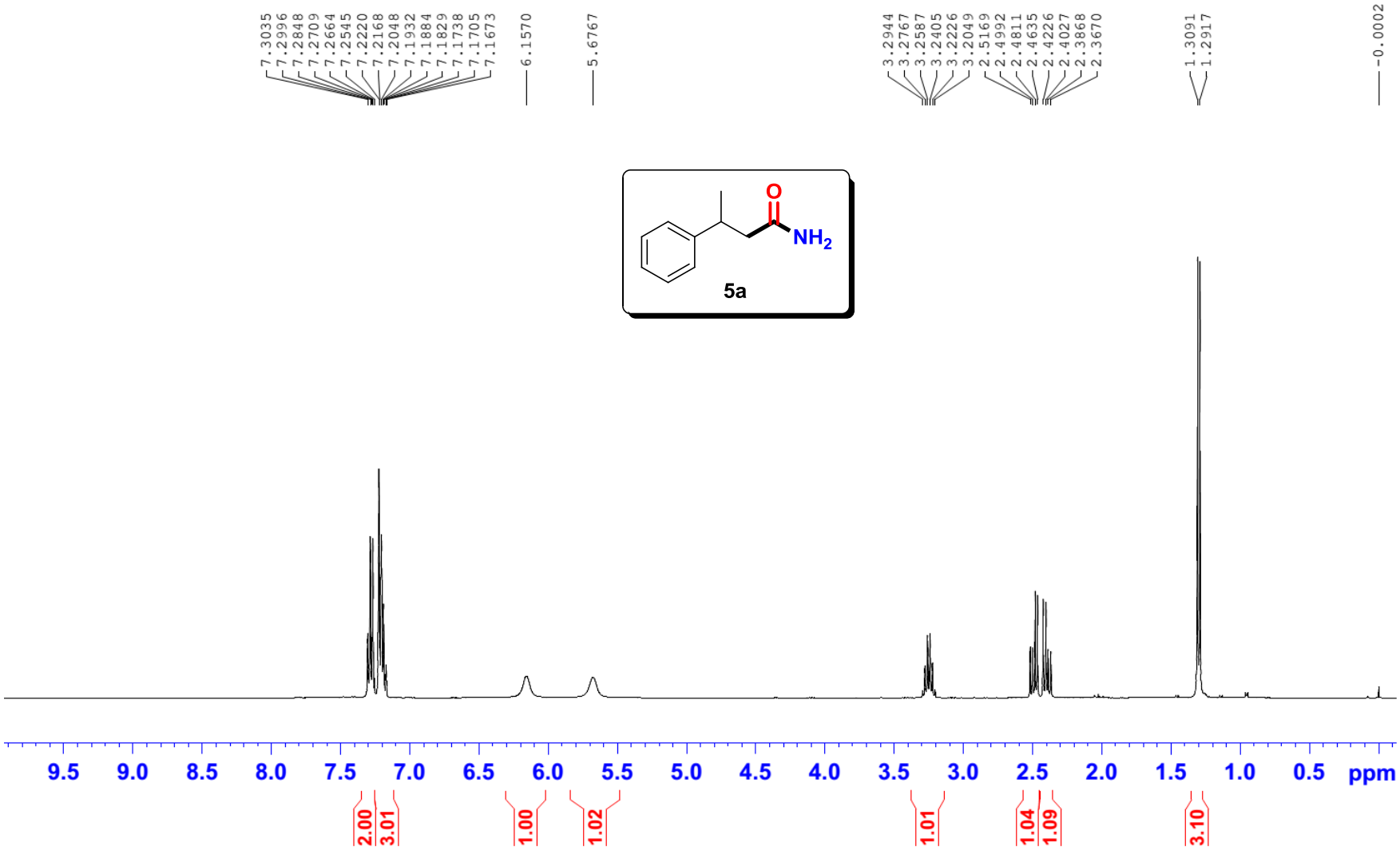
GB-X170223-1-2-HNMR



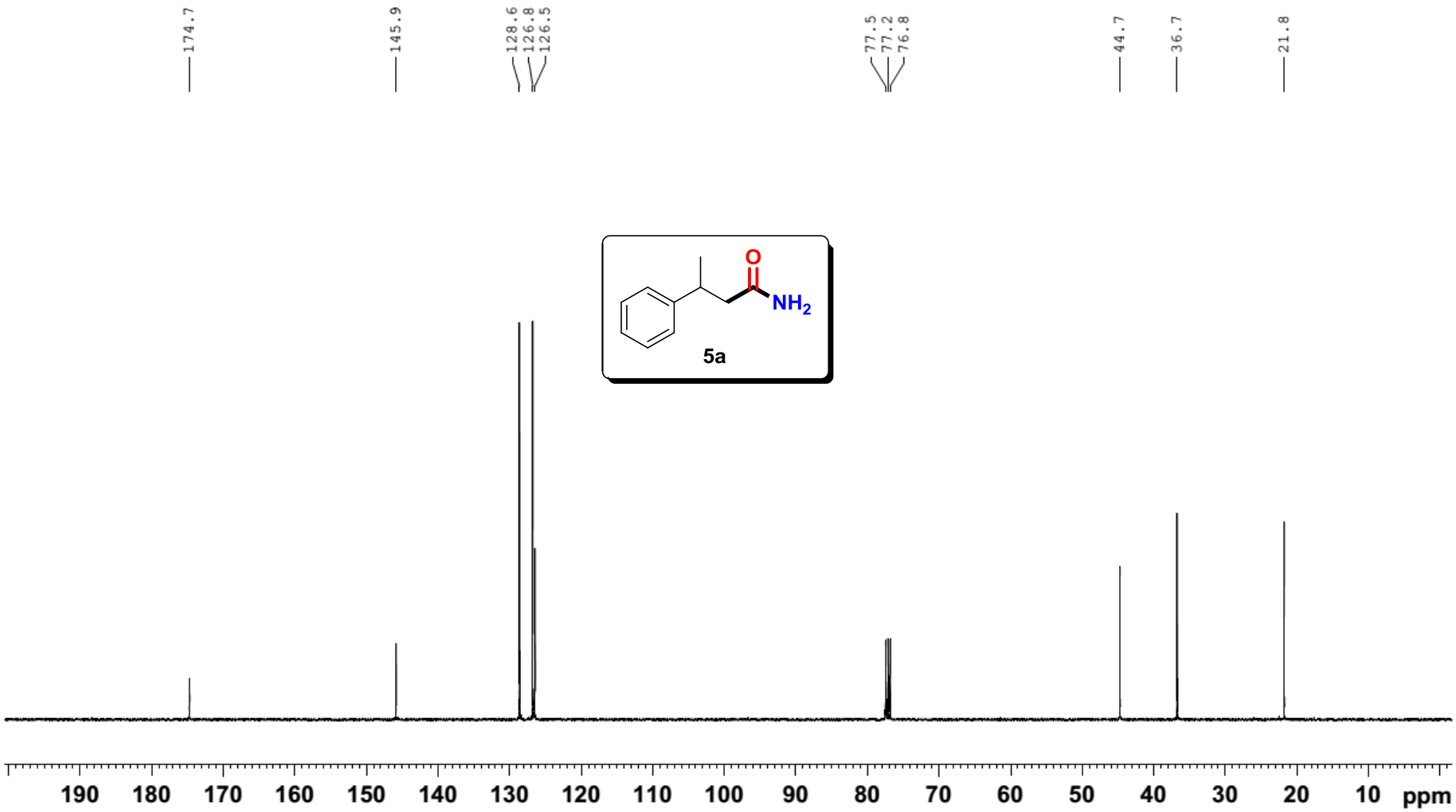
GB-X170223-1-2-CNMR



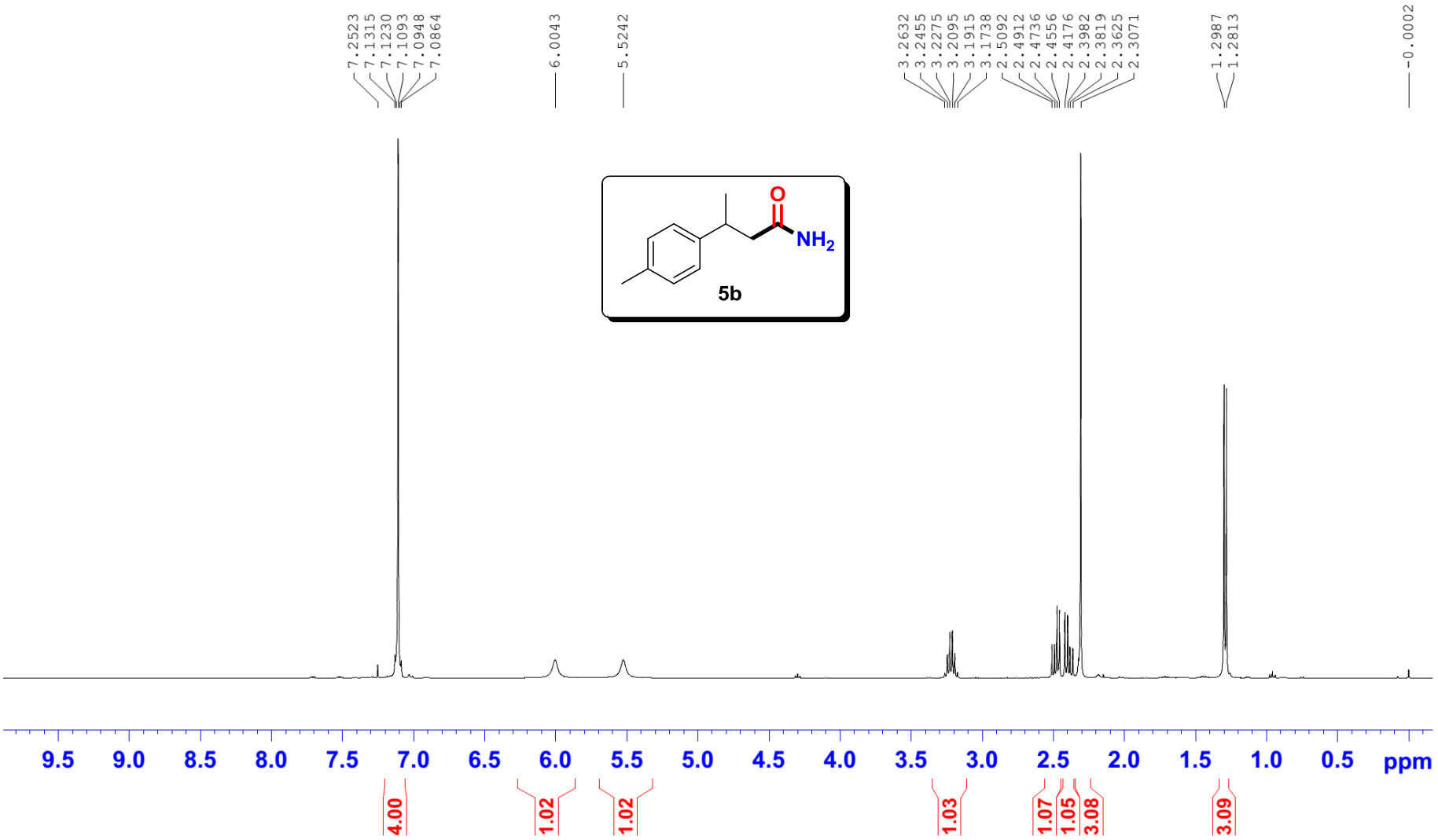
ZGY-X15X12-3-HNMR

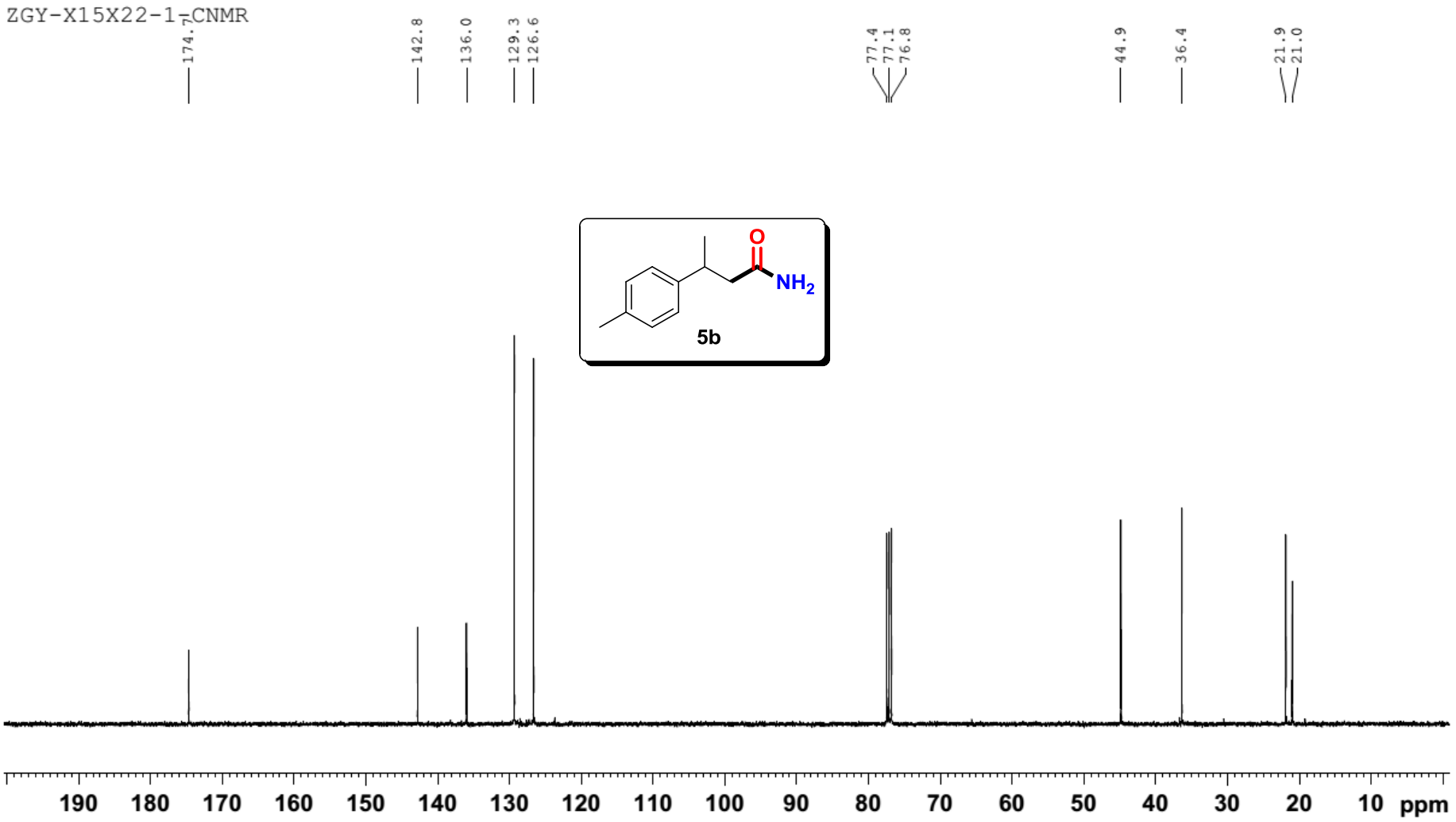


ZGY-X15X12-3-CNMR

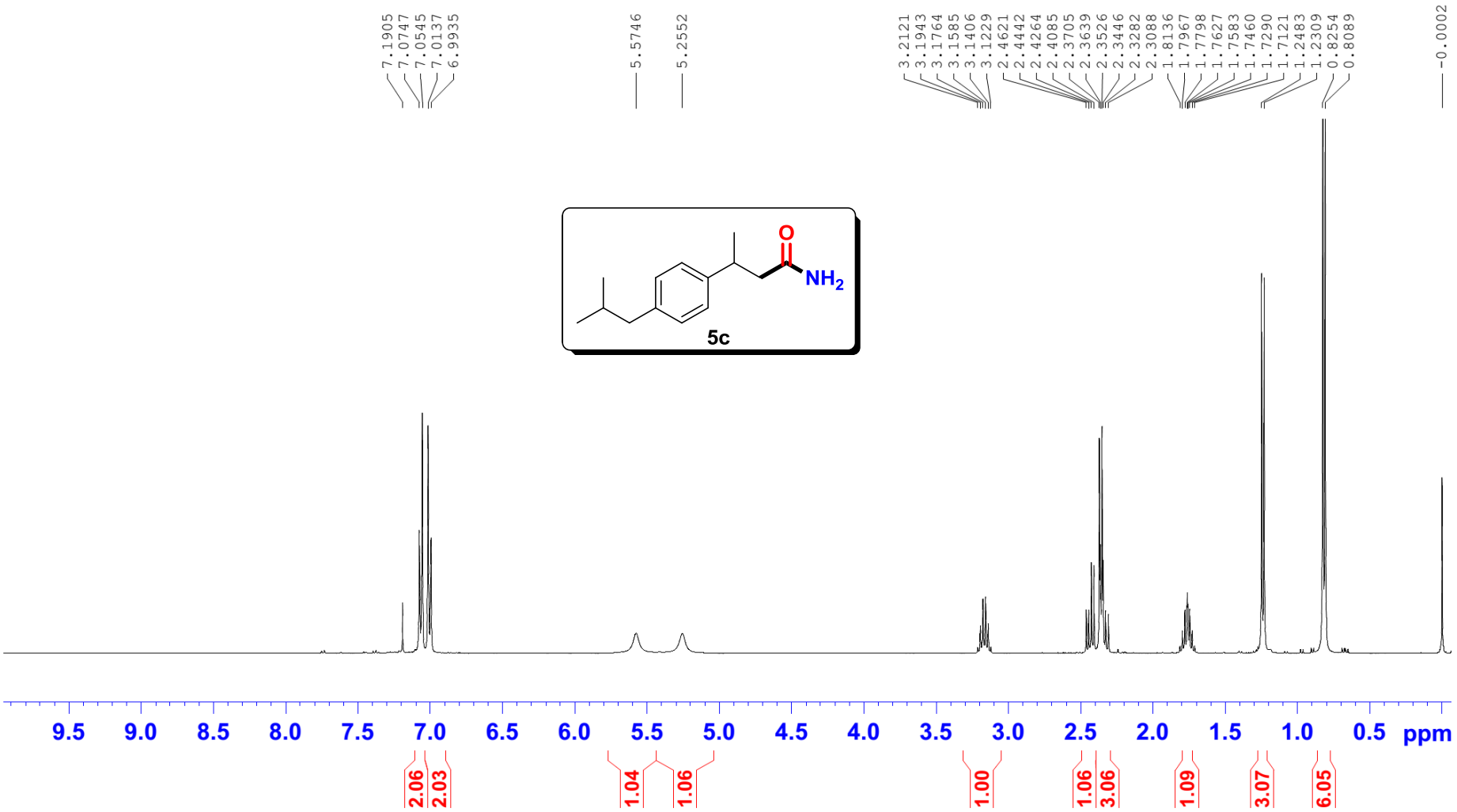


ZGY-X15X22-1-HNMR

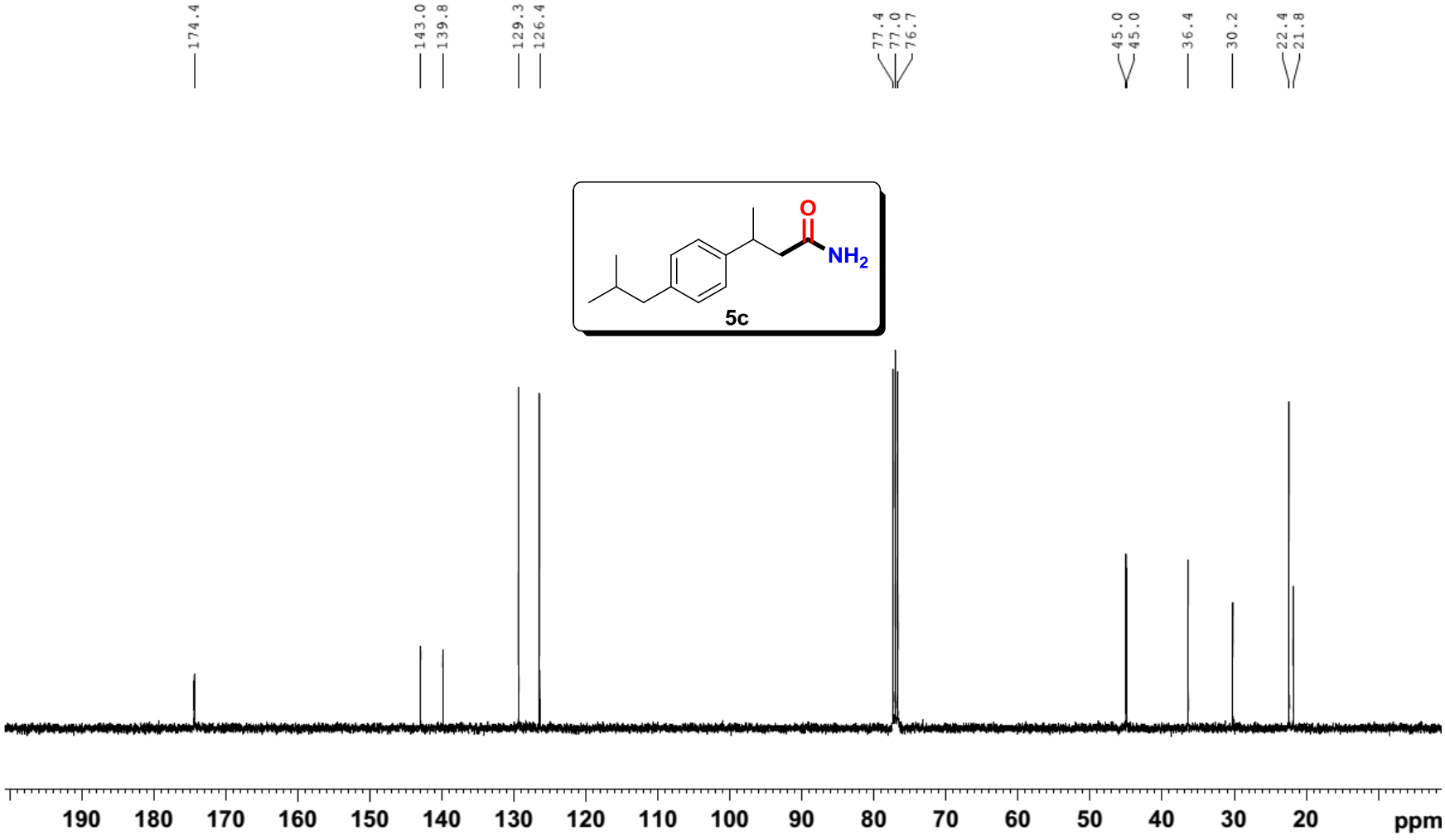



ZGY-X15X22-1-CNMR
174.7
142.8
136.0
129.3
126.6
77.4
77.1
76.8
44.9
36.4
21.9
21.0
O
NH2
5b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

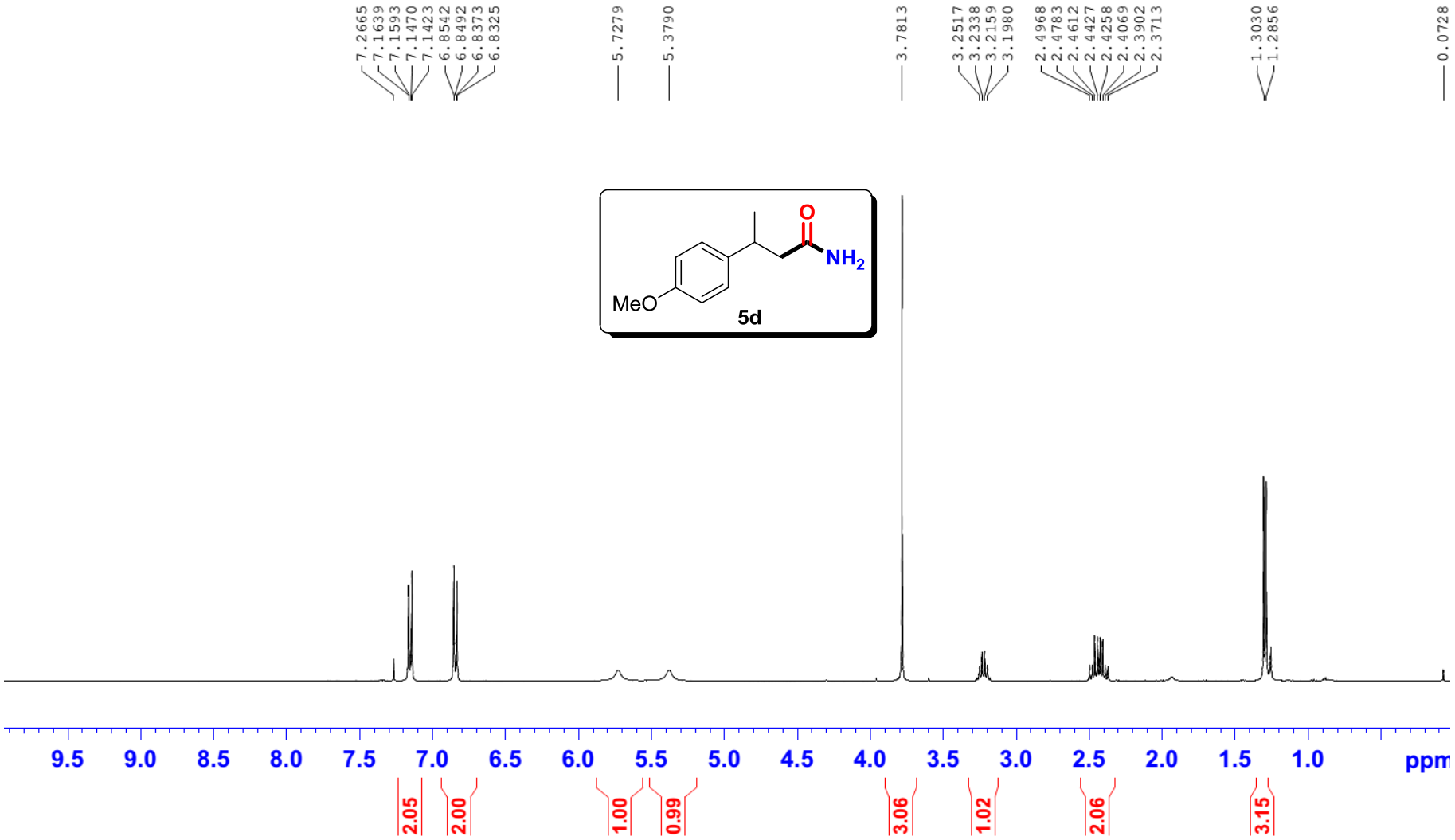
ZGY-X15X21-5-HNMR



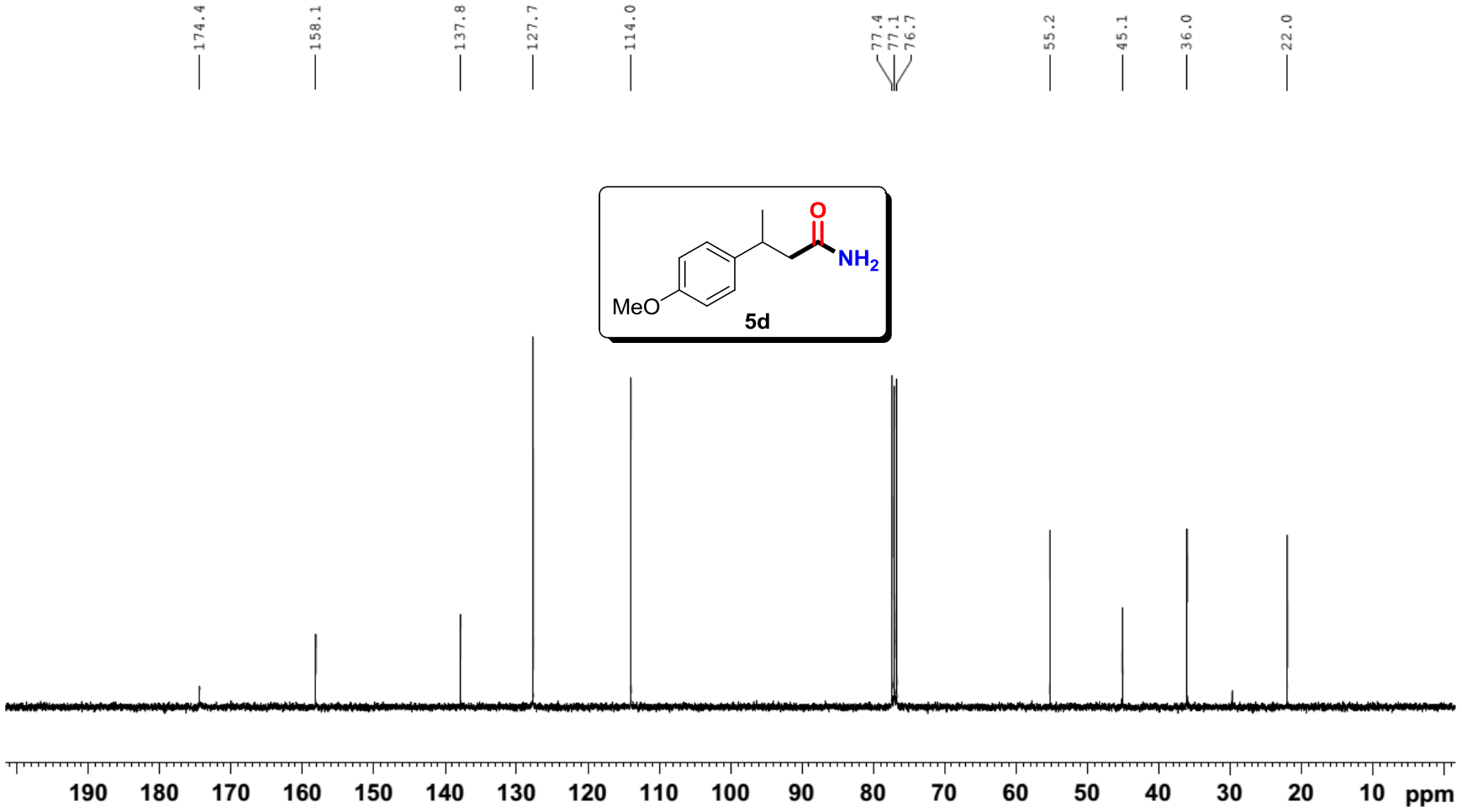
ZGY-X15X21-5-CNMR



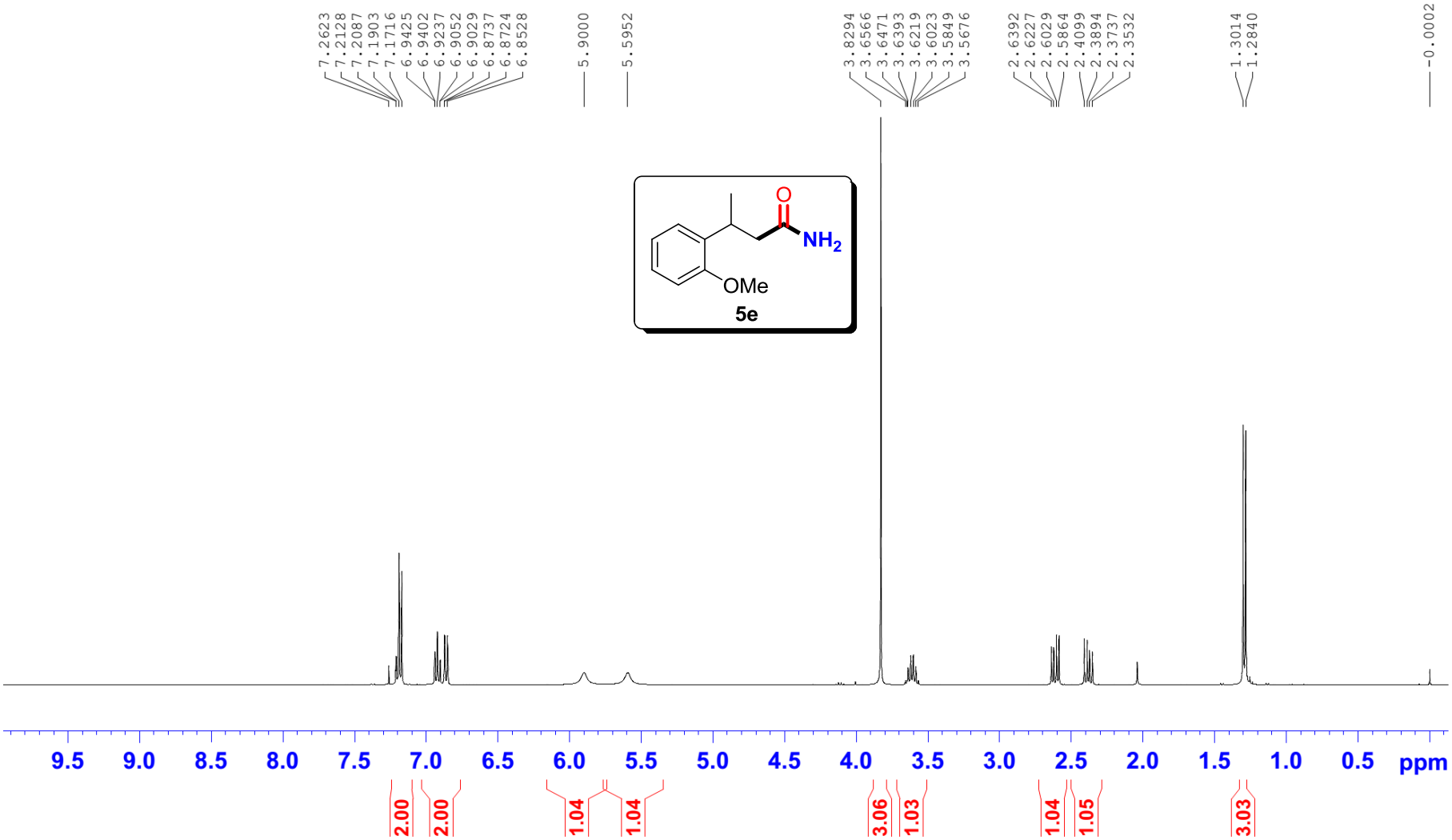
ZGY-X15X26-2-HNMR



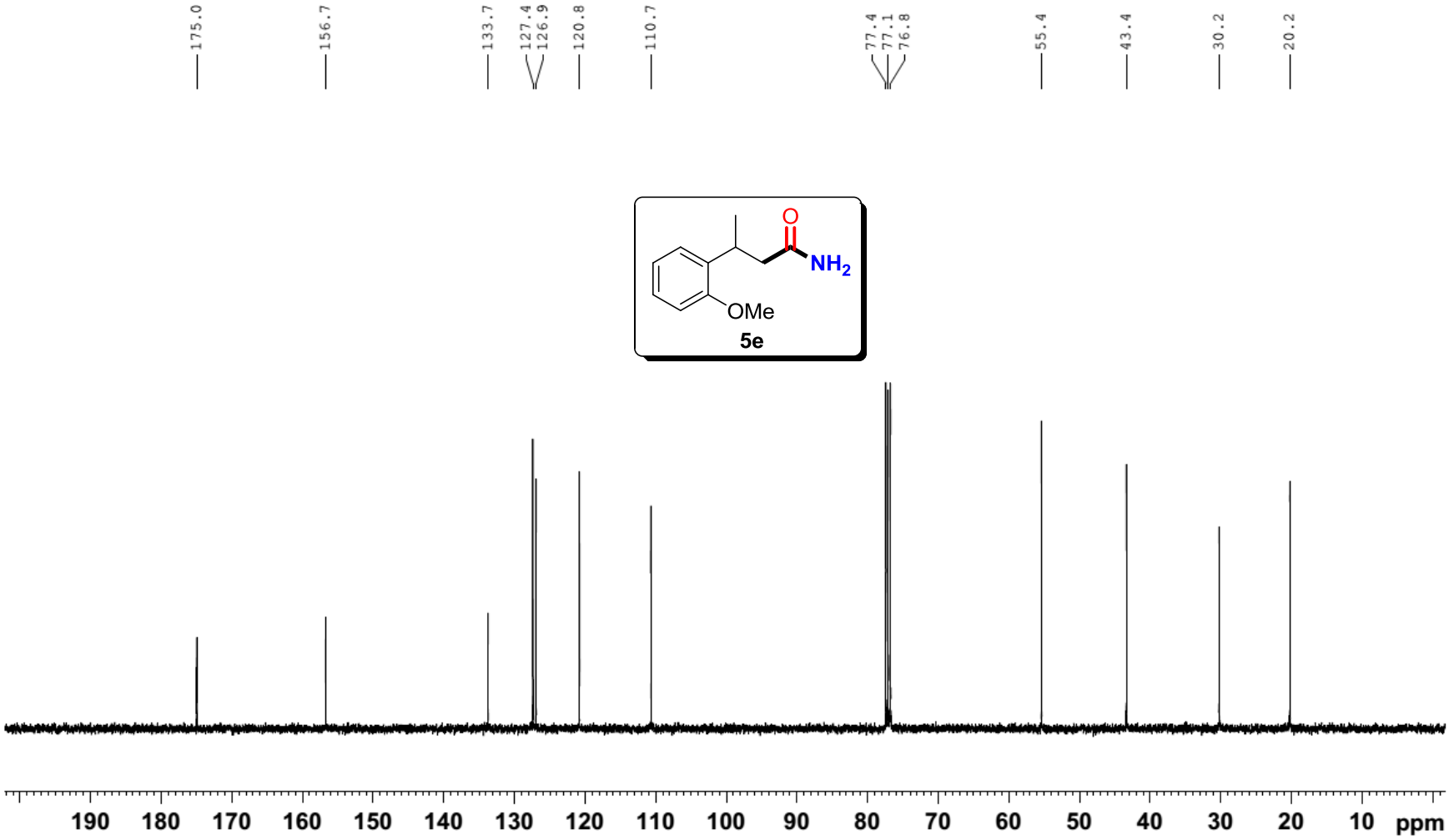
ZGY-X15X26-2-CNMR



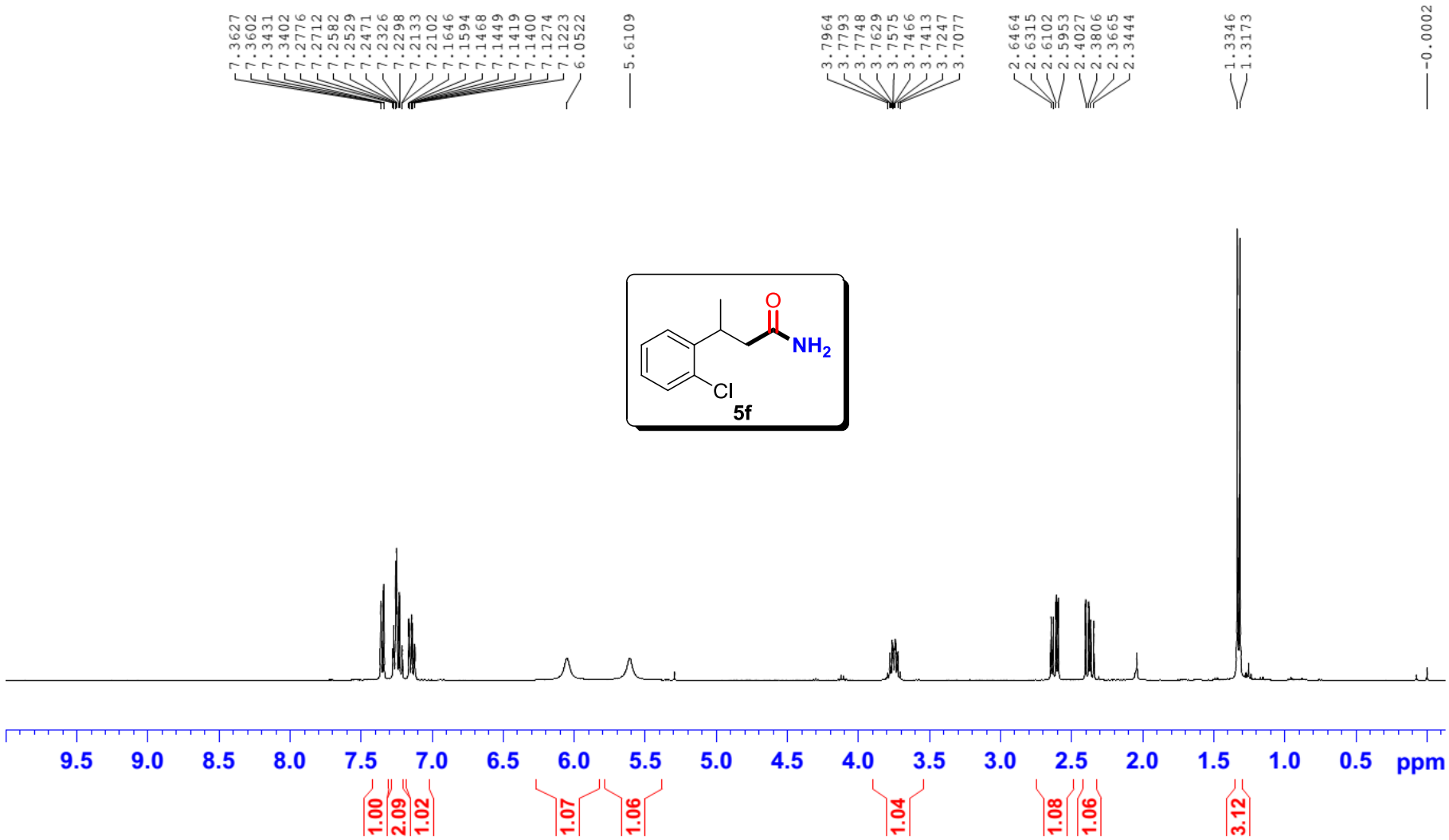
ZGY-X15X21-1-HNMR



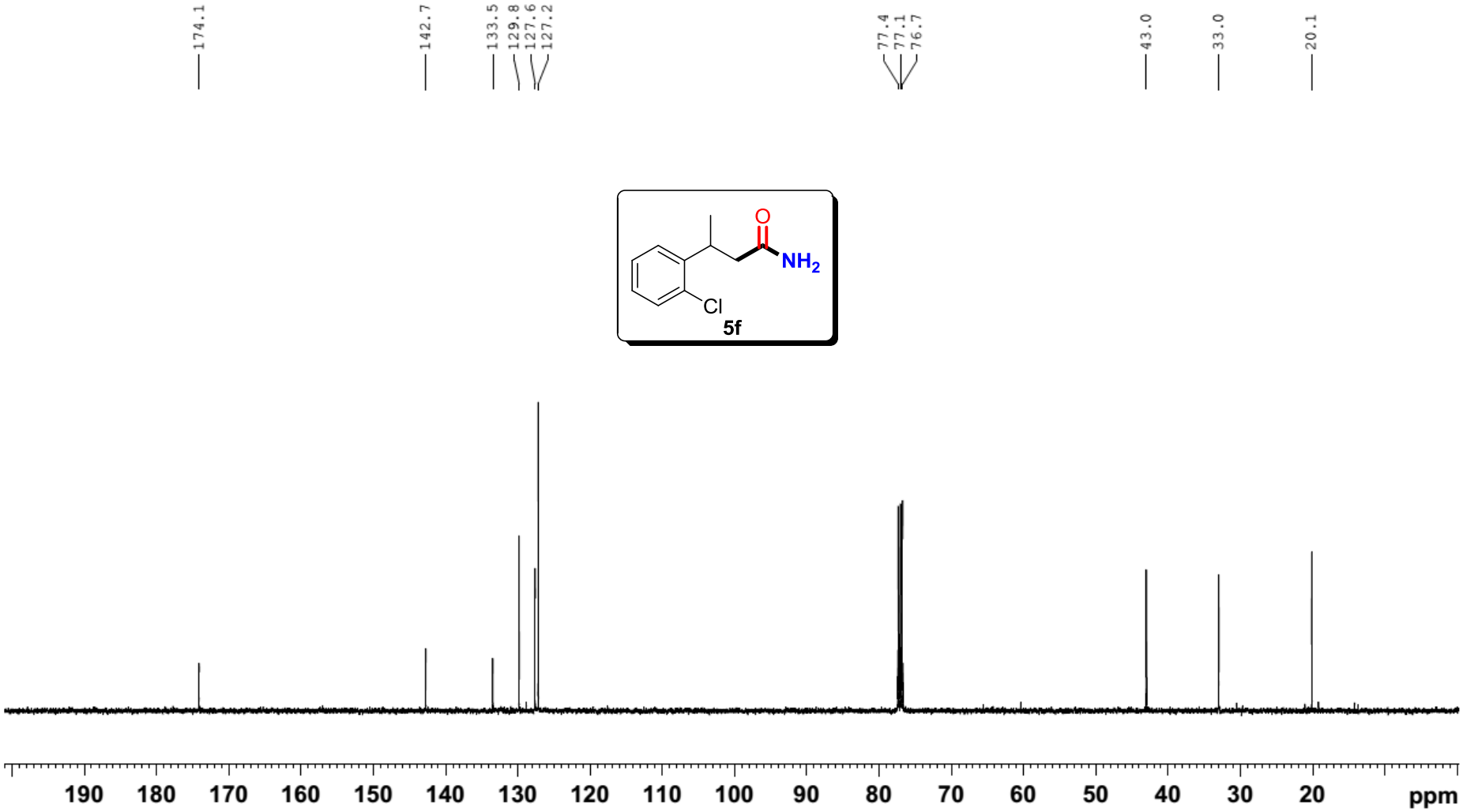
ZGY-X15X21-1-CNMR



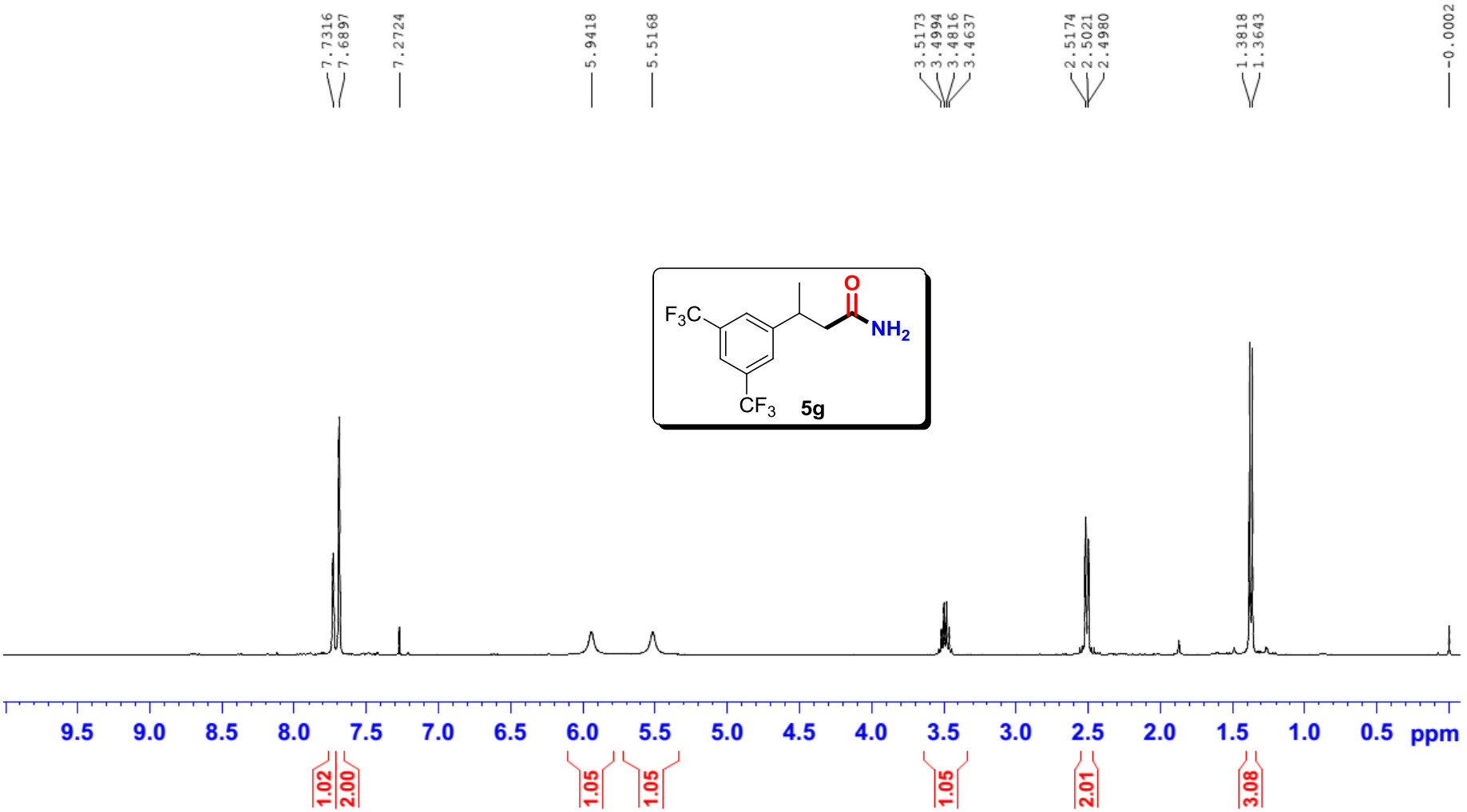
ZGY-X15X27-3-HNMR



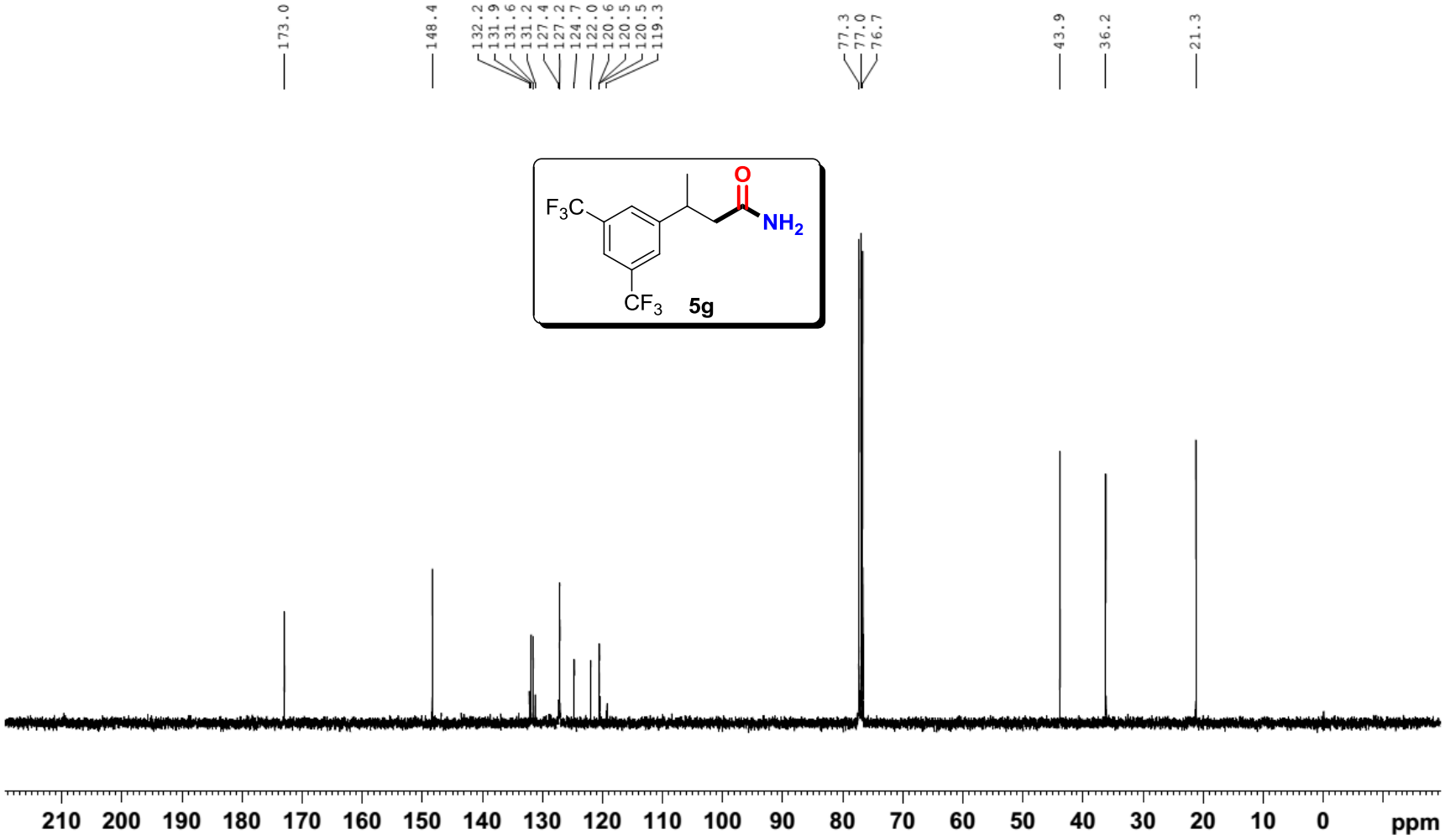
ZGY-X15X21-4-CNMR



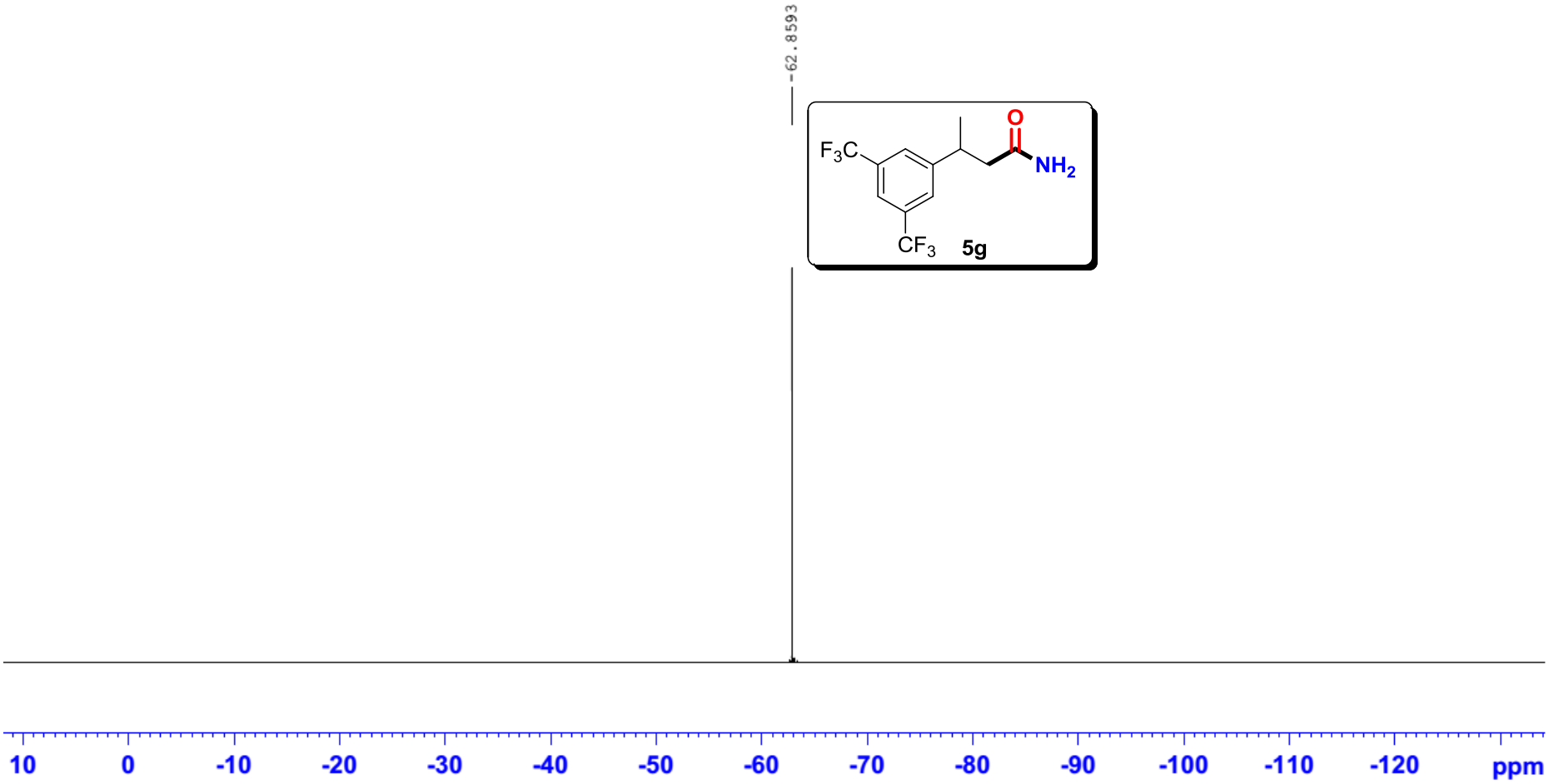
ZGY-X15Y10-2-HNMR



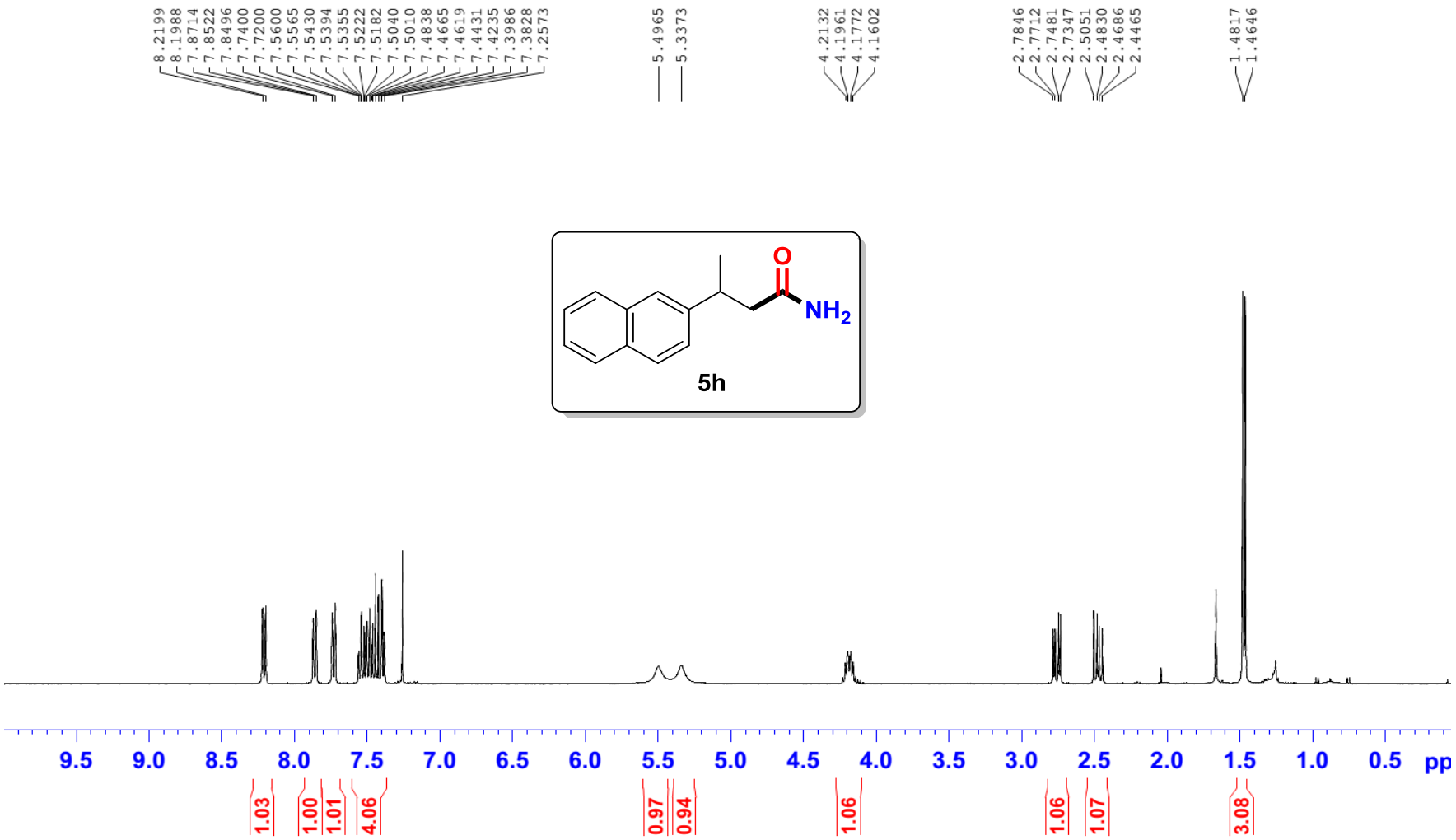
ZGY-X15Y10-2-CNMR



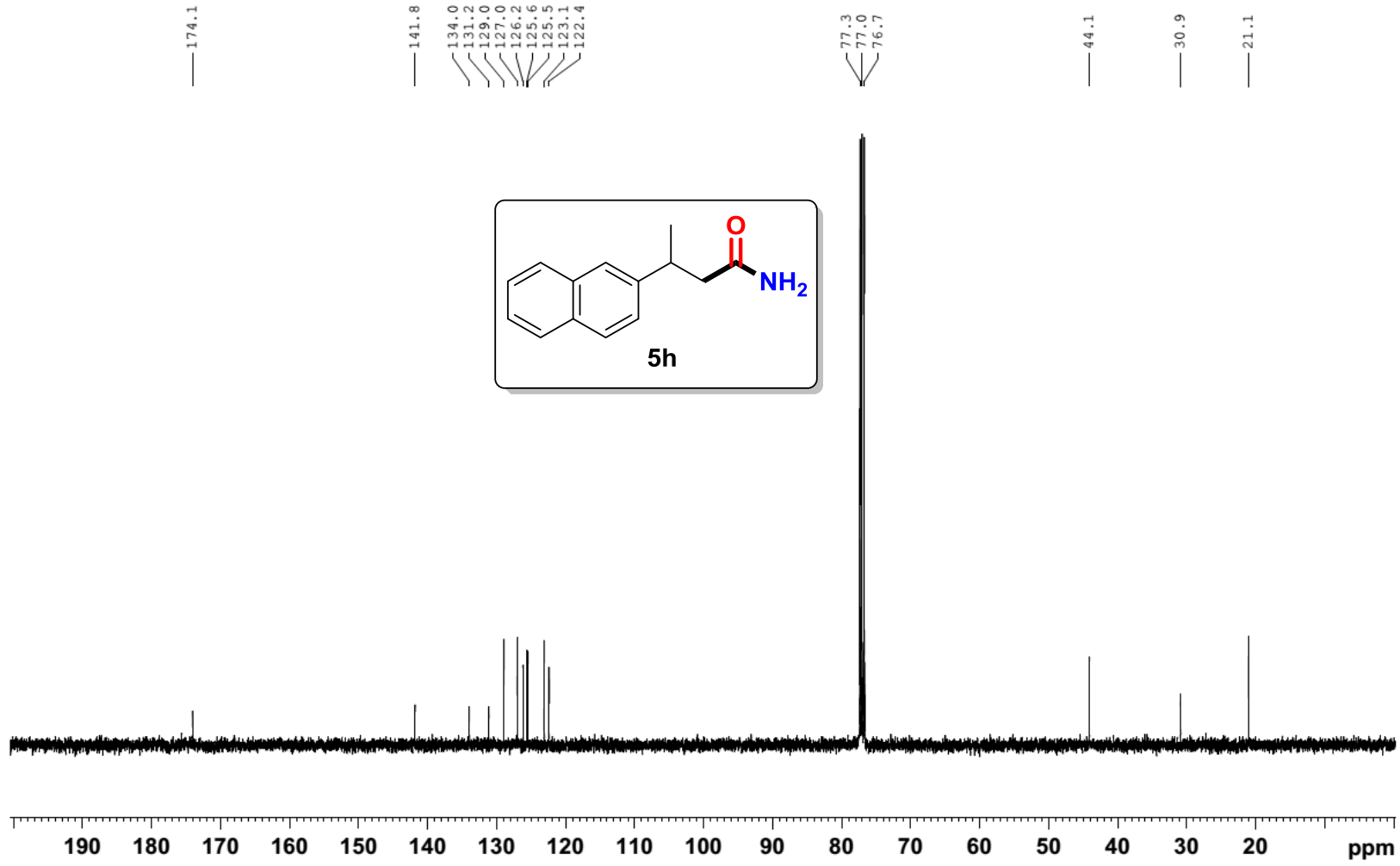
ZGY-X15Y04-1-FNMR



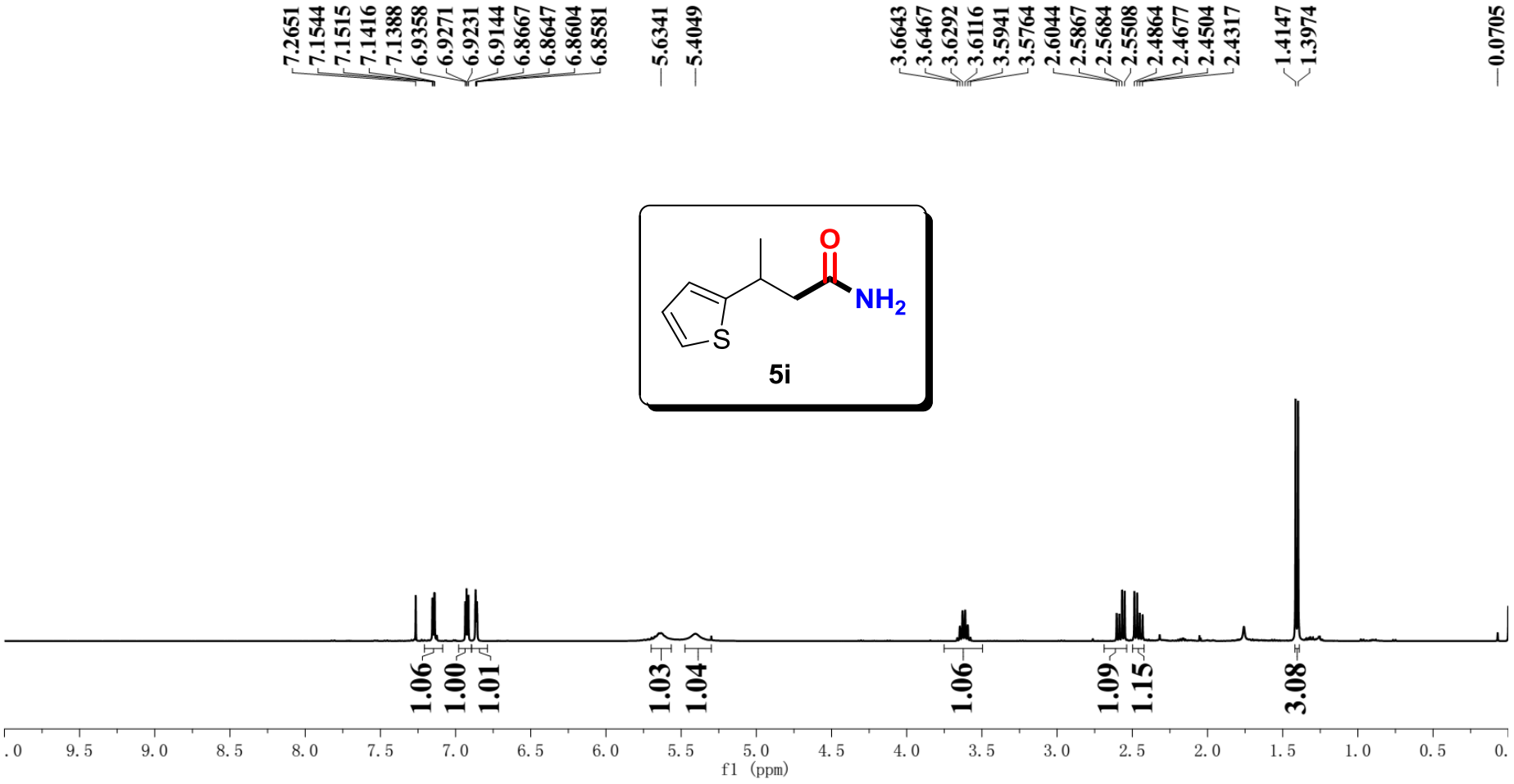
ZGY-X15Y09-4-HNMR



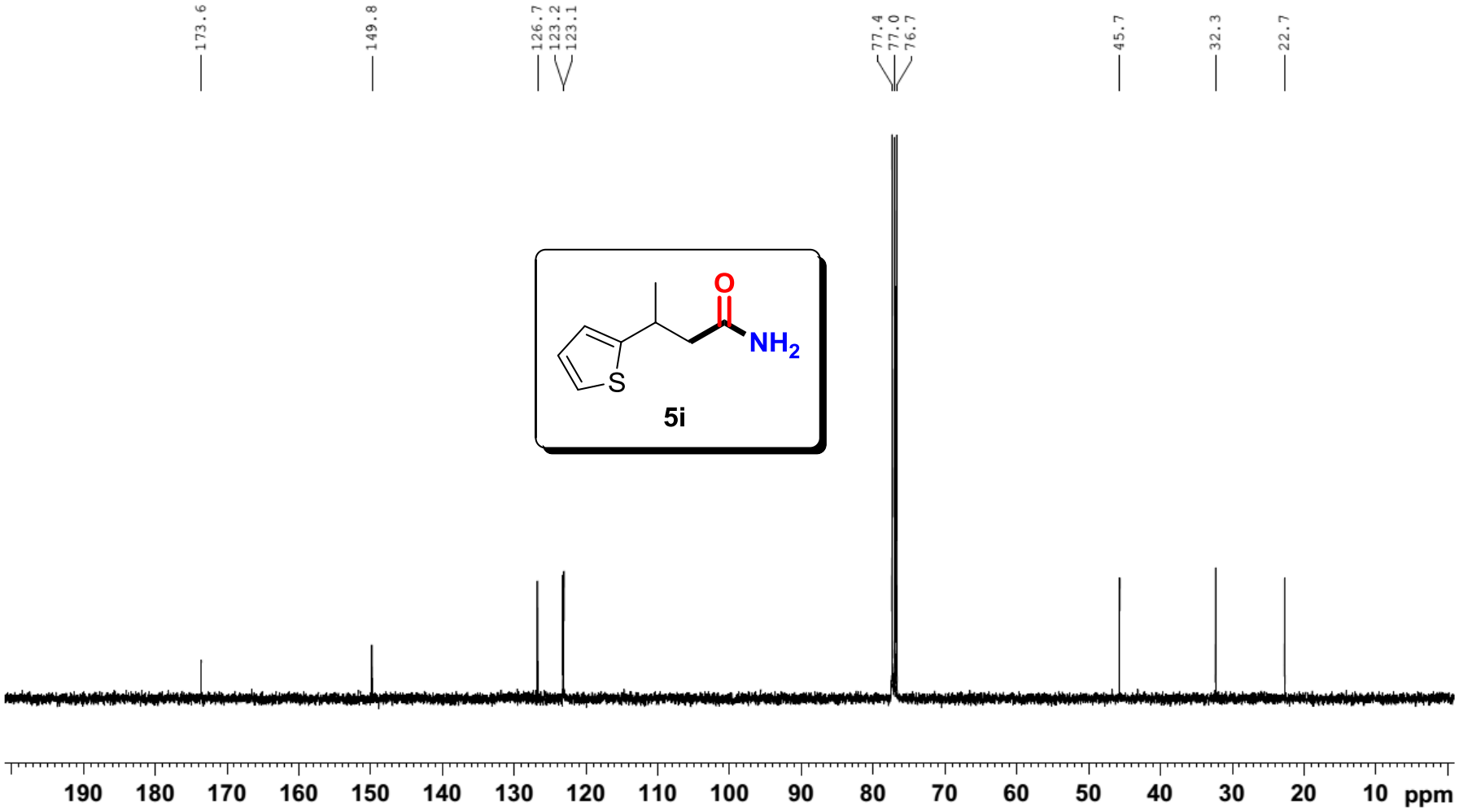
ZGY-X15Y09-4-CNMR



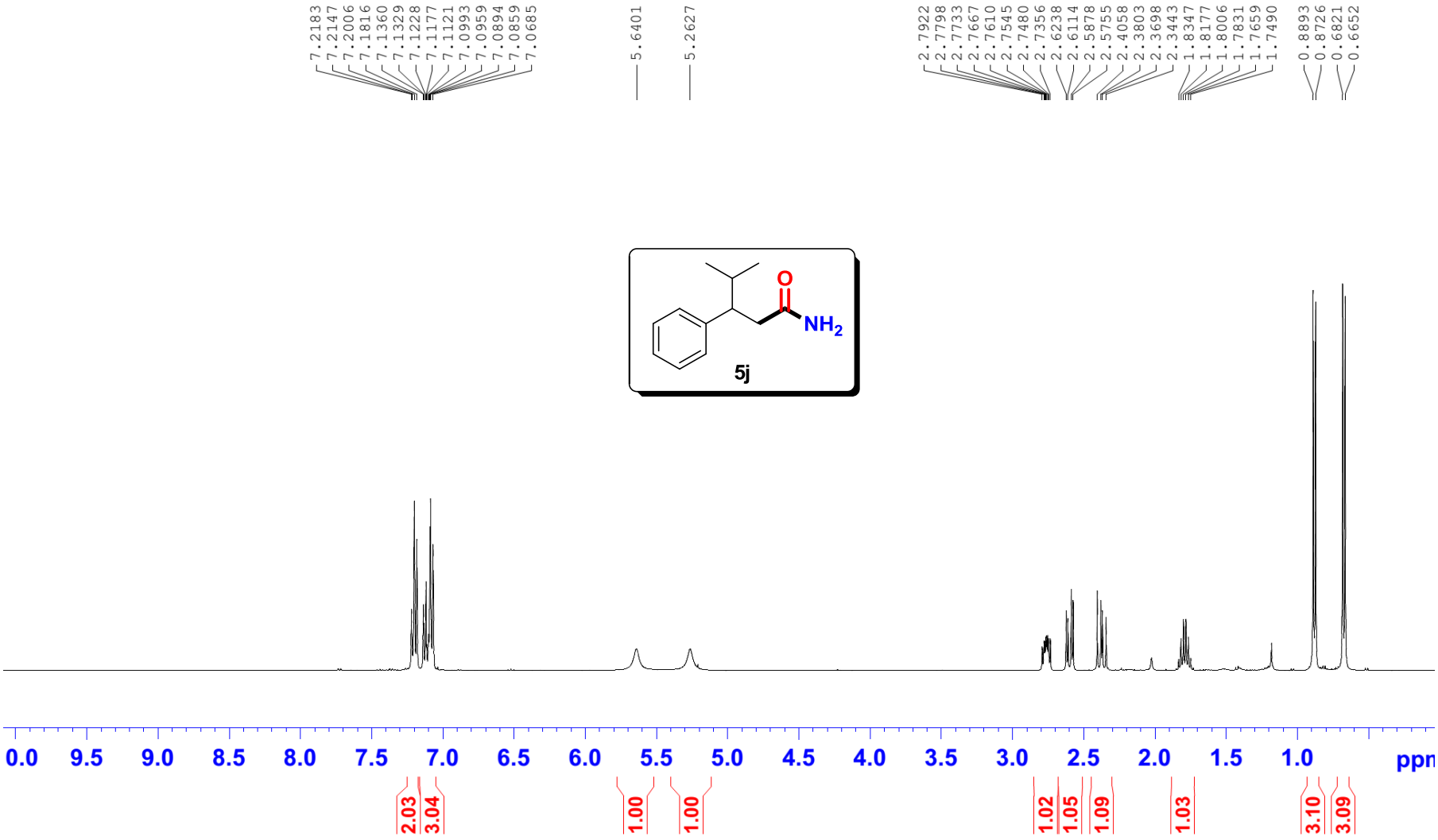
ZGY-X15X28-2 H NMR



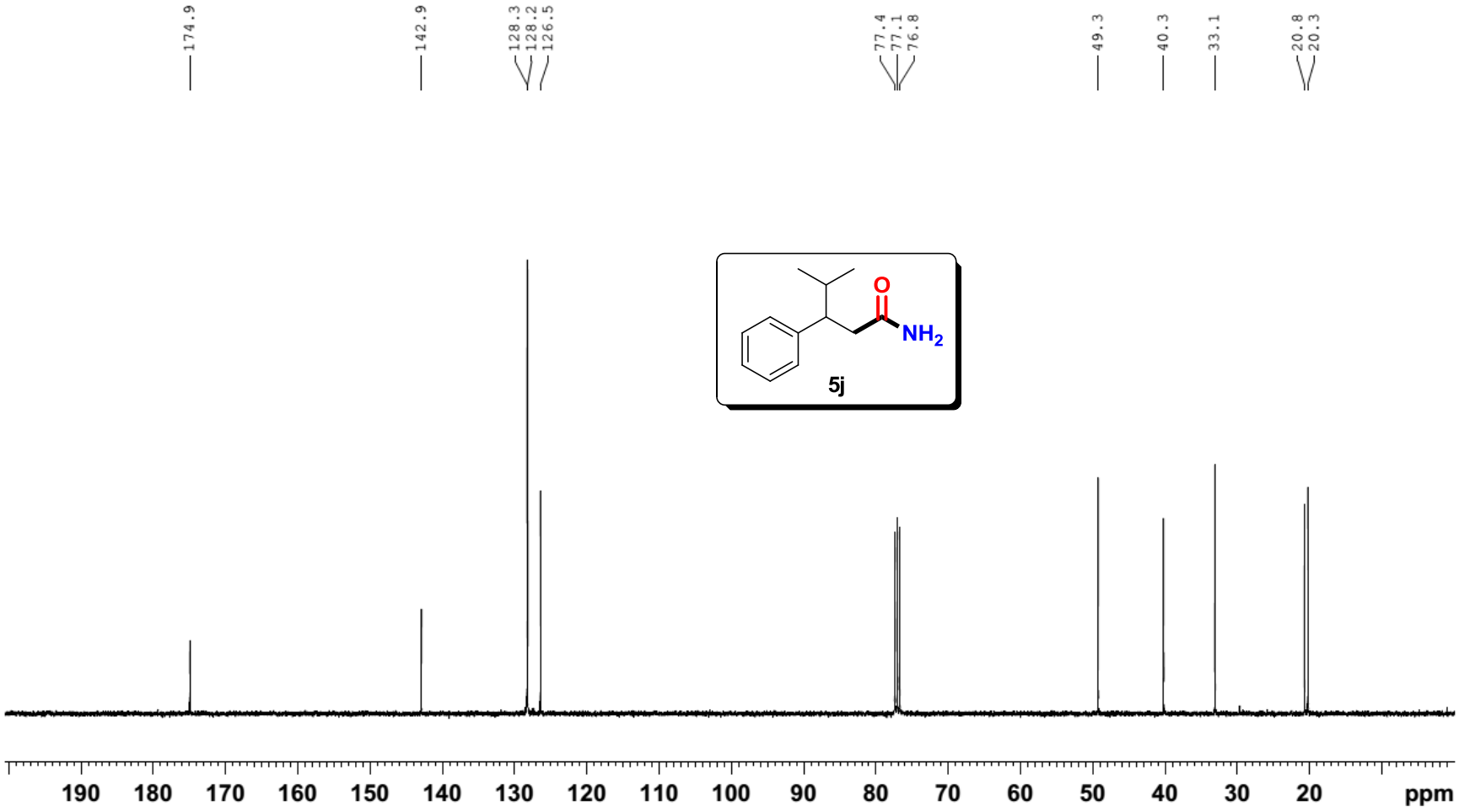
ZGY-X15X28-2-CNMR



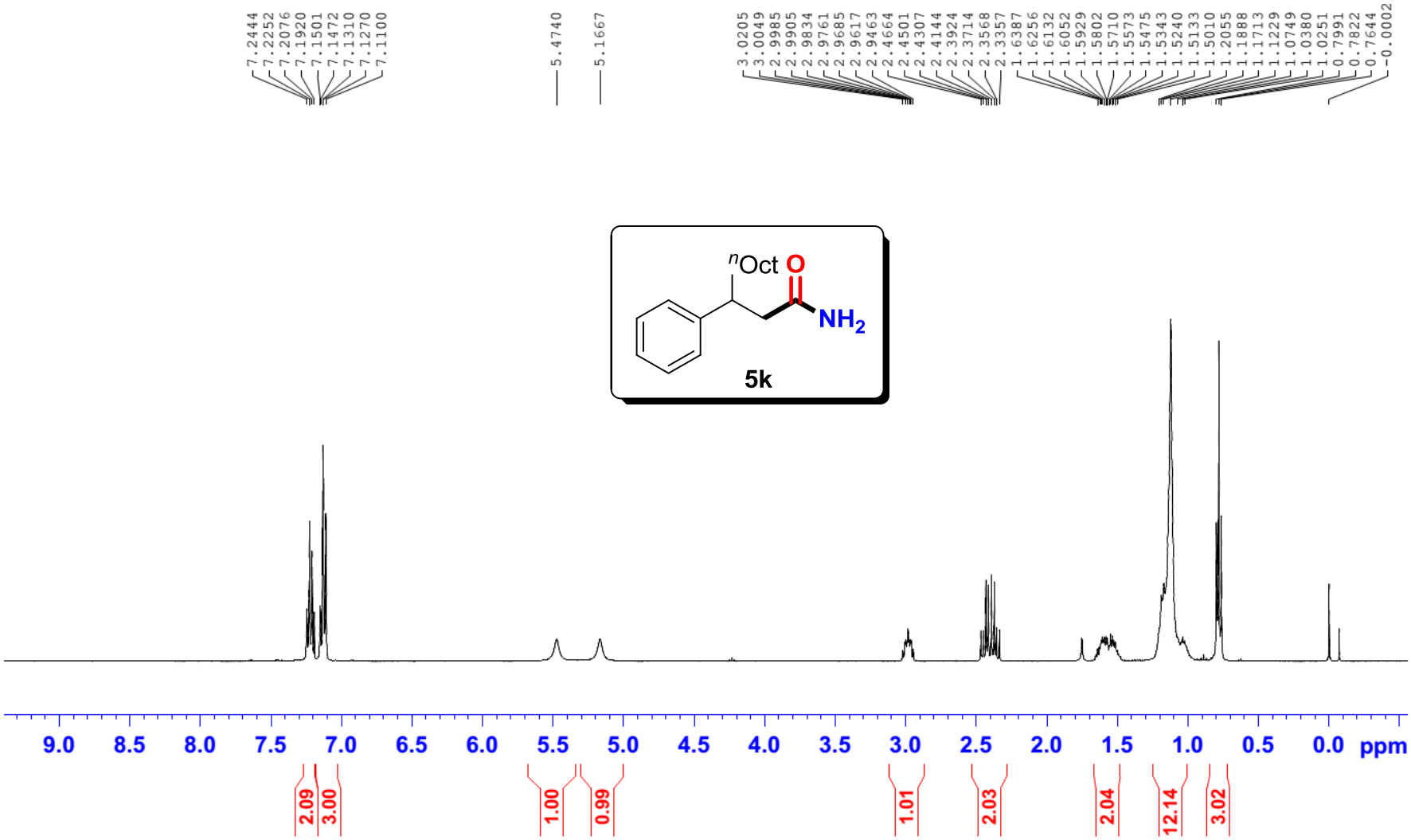
ZGY-X15X27-4-HNMR



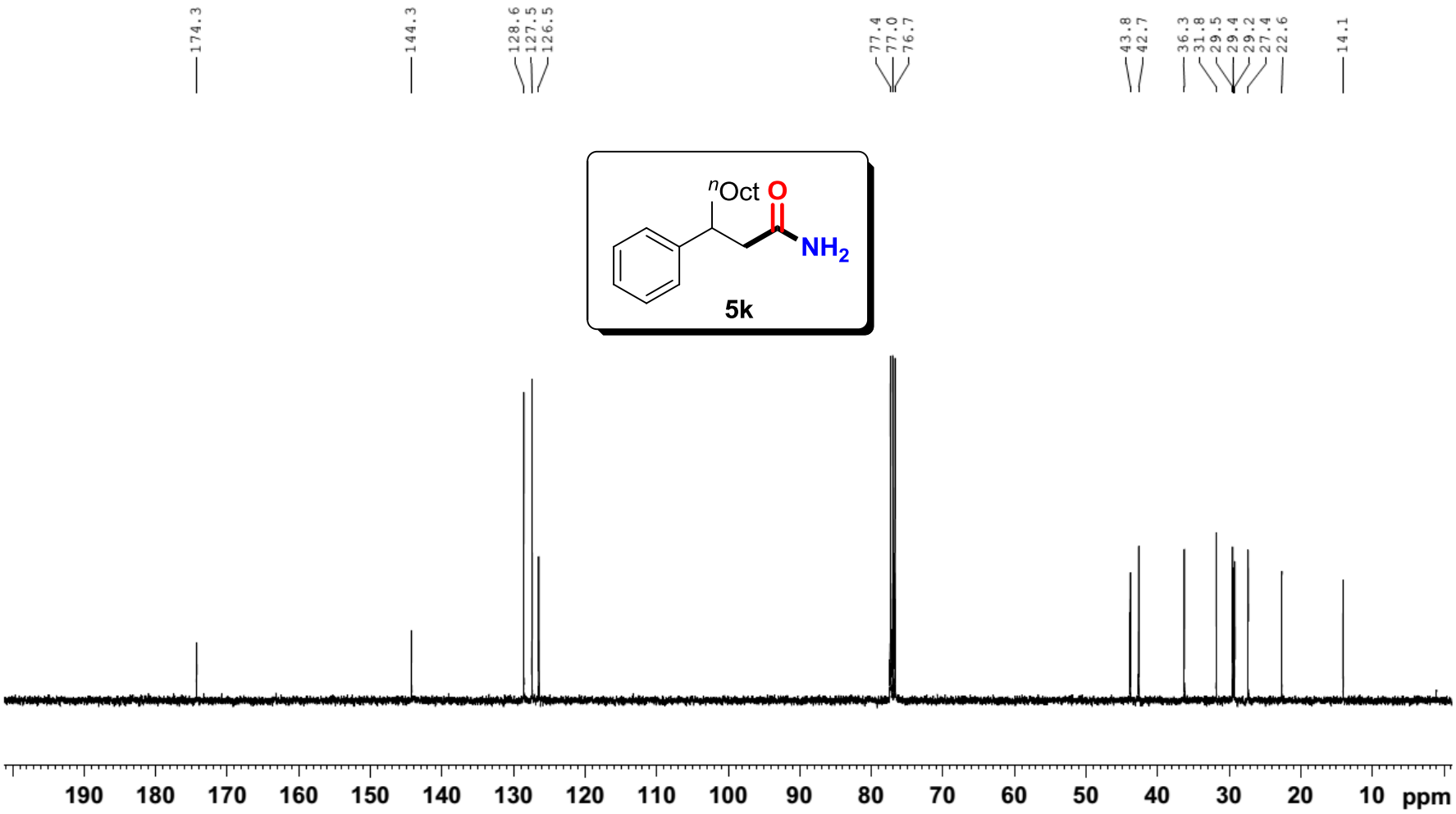
ZGY-X15X27-4-CNMR



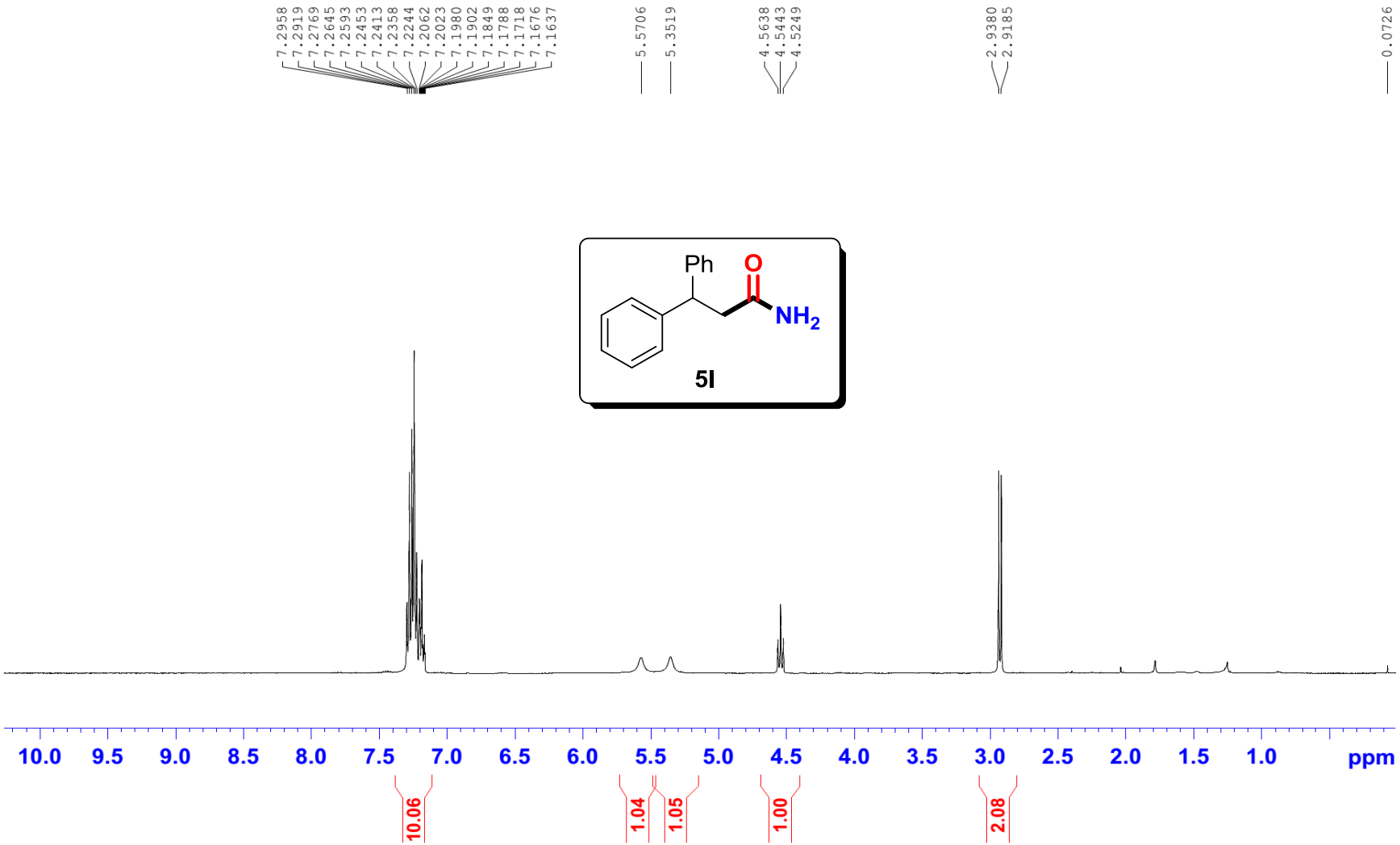
ZGY-X15X26-4-HNMR



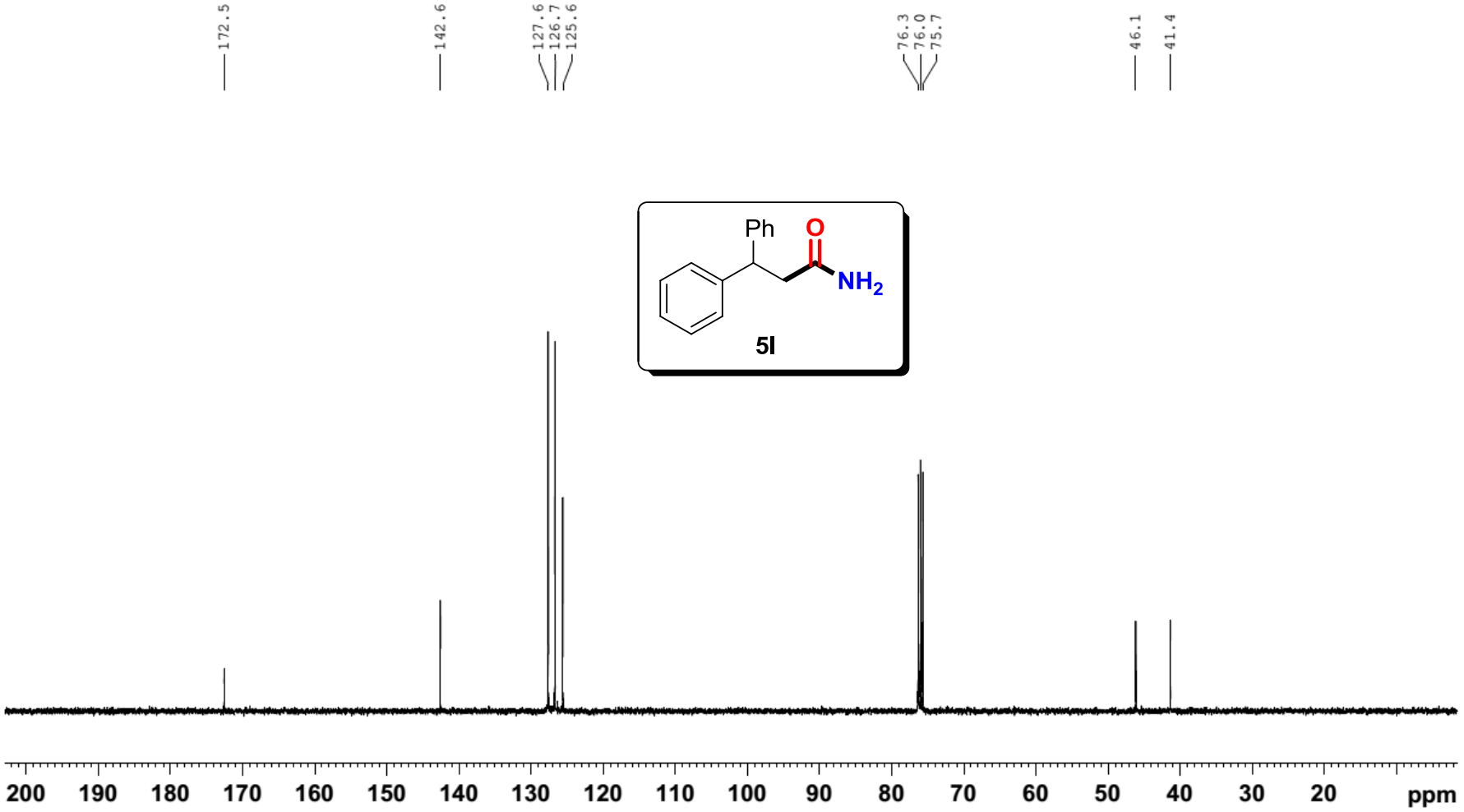
ZGY-X15X26-4-CNMR

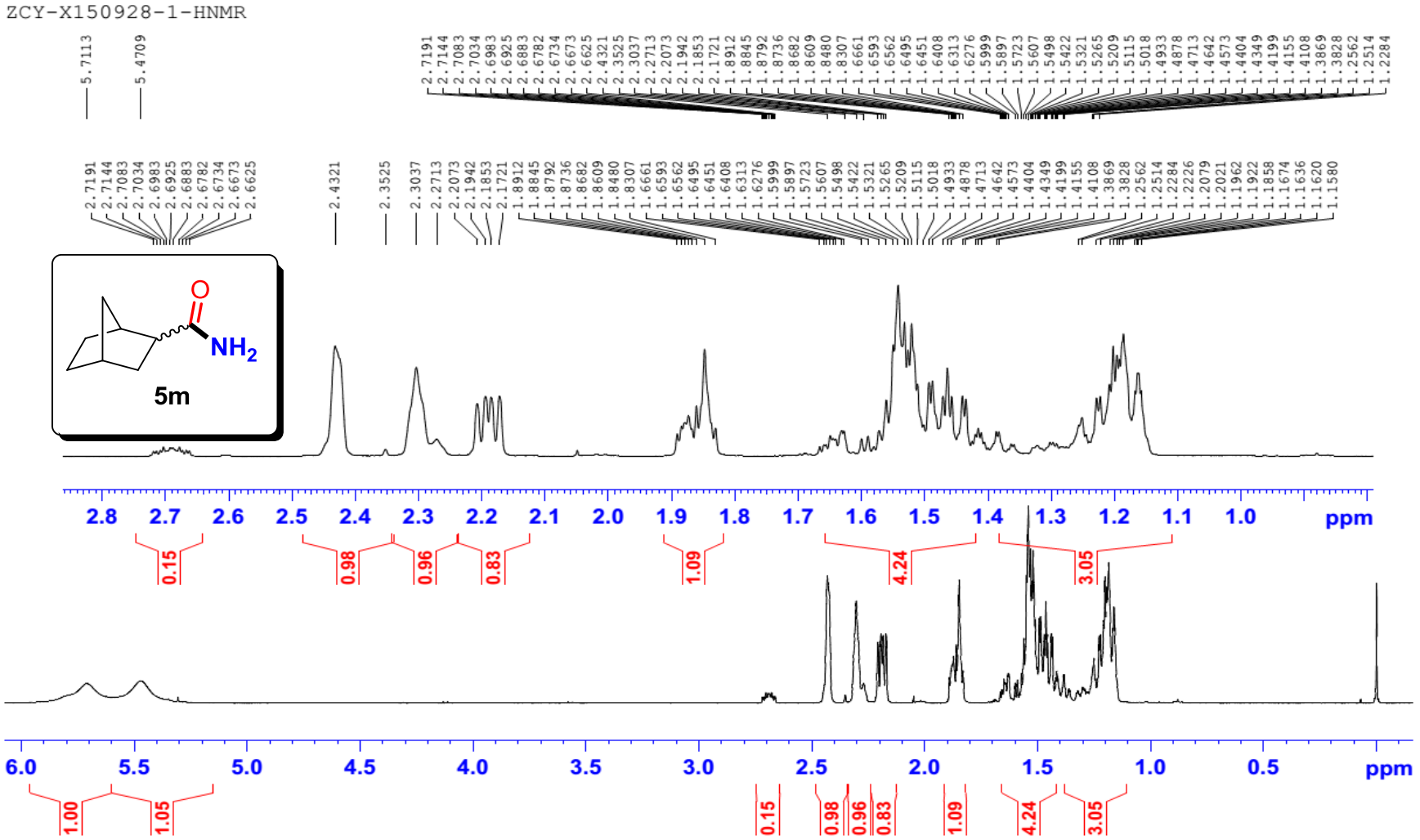


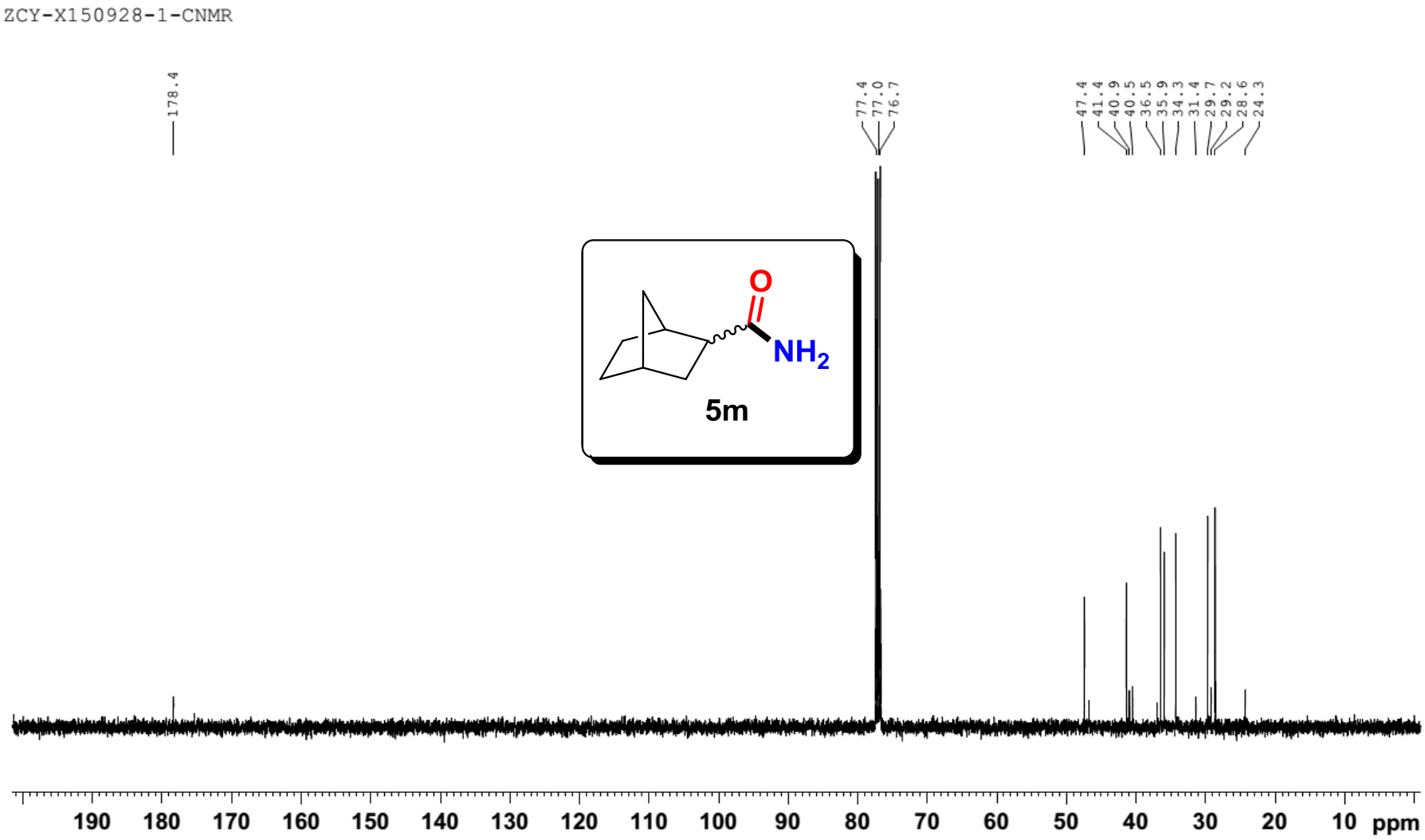
ZGY-X160111-4-HNMR

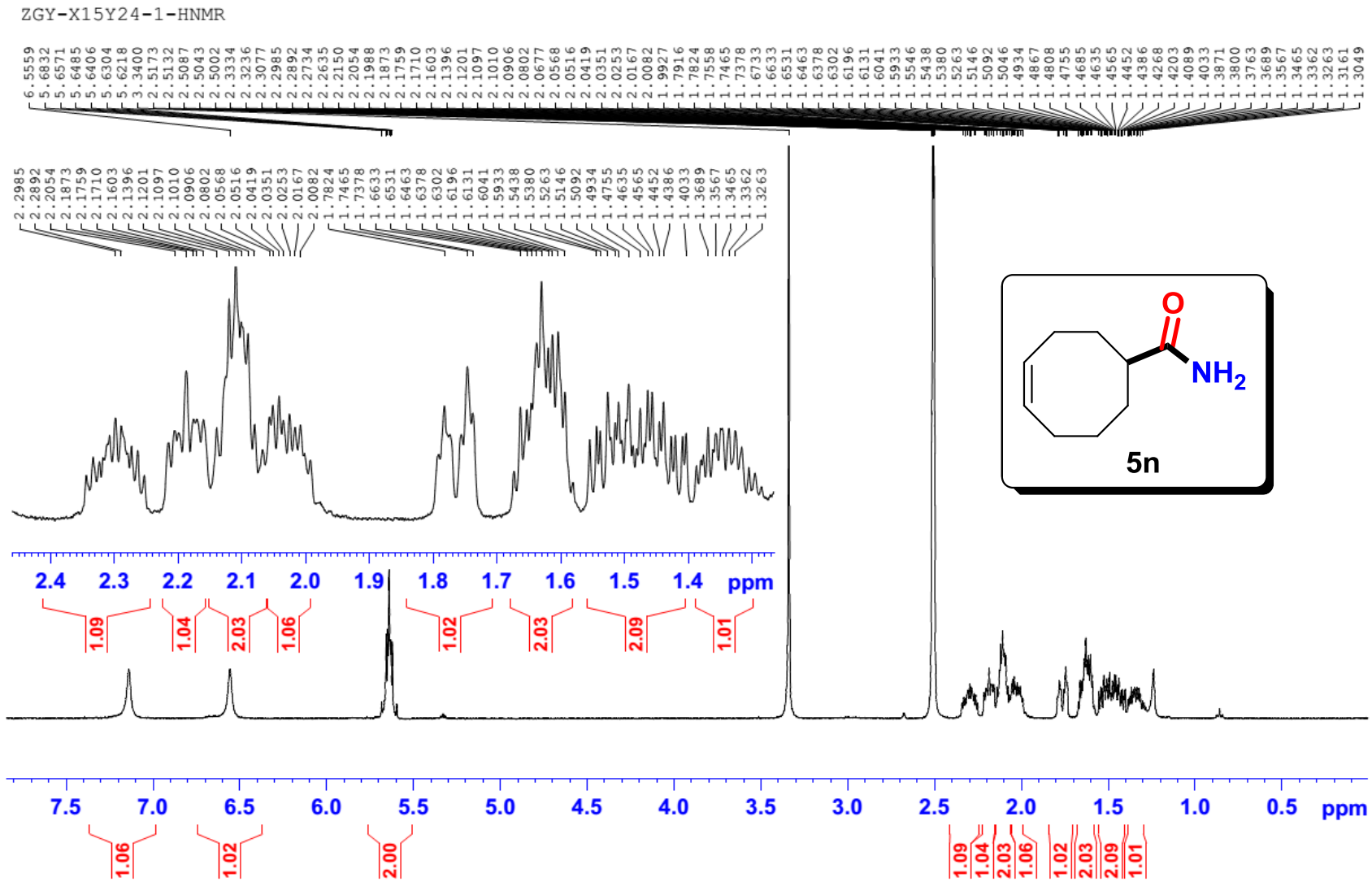


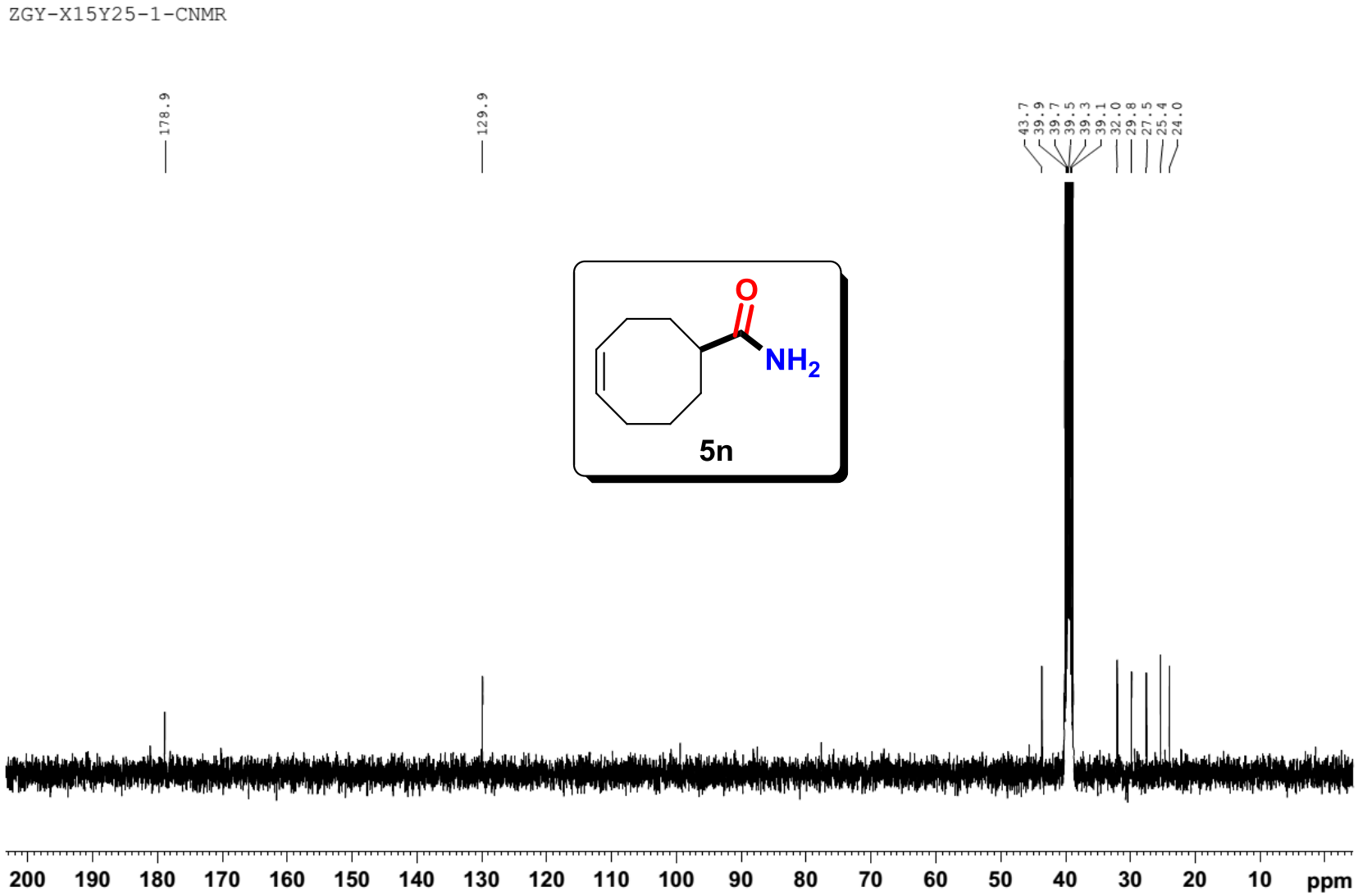
ZGY-X15X02-4-CNMR

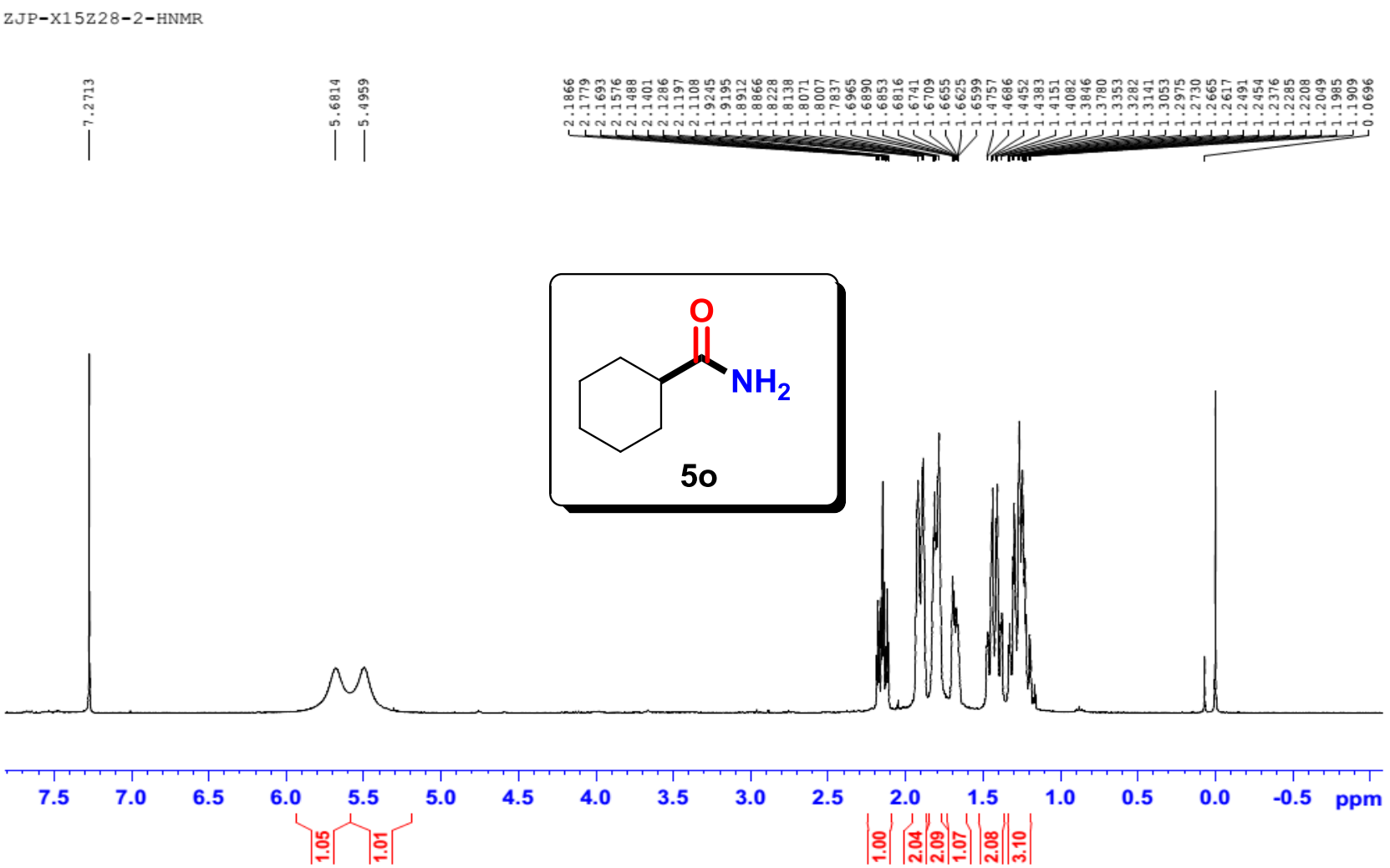


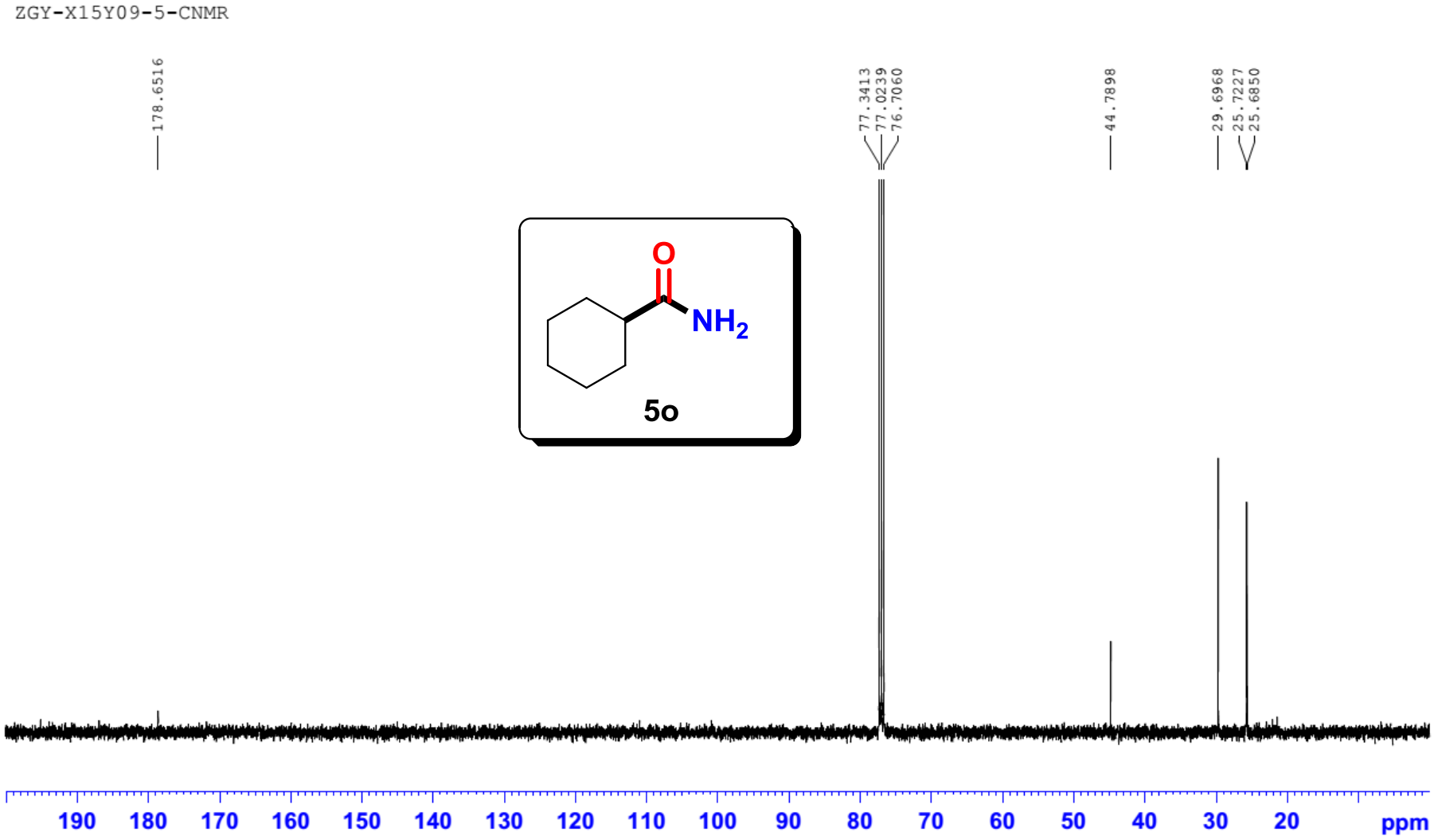

ZCY-X150928-1-HNMR
5m
NH2
ppm


ZCY-X150928-1-CNMR
178.4
77.4
77.0
76.7
47.4
41.4
40.9
40.5
36.5
35.9
34.3
31.4
29.7
29.2
28.6
24.3
O
NH2
5m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

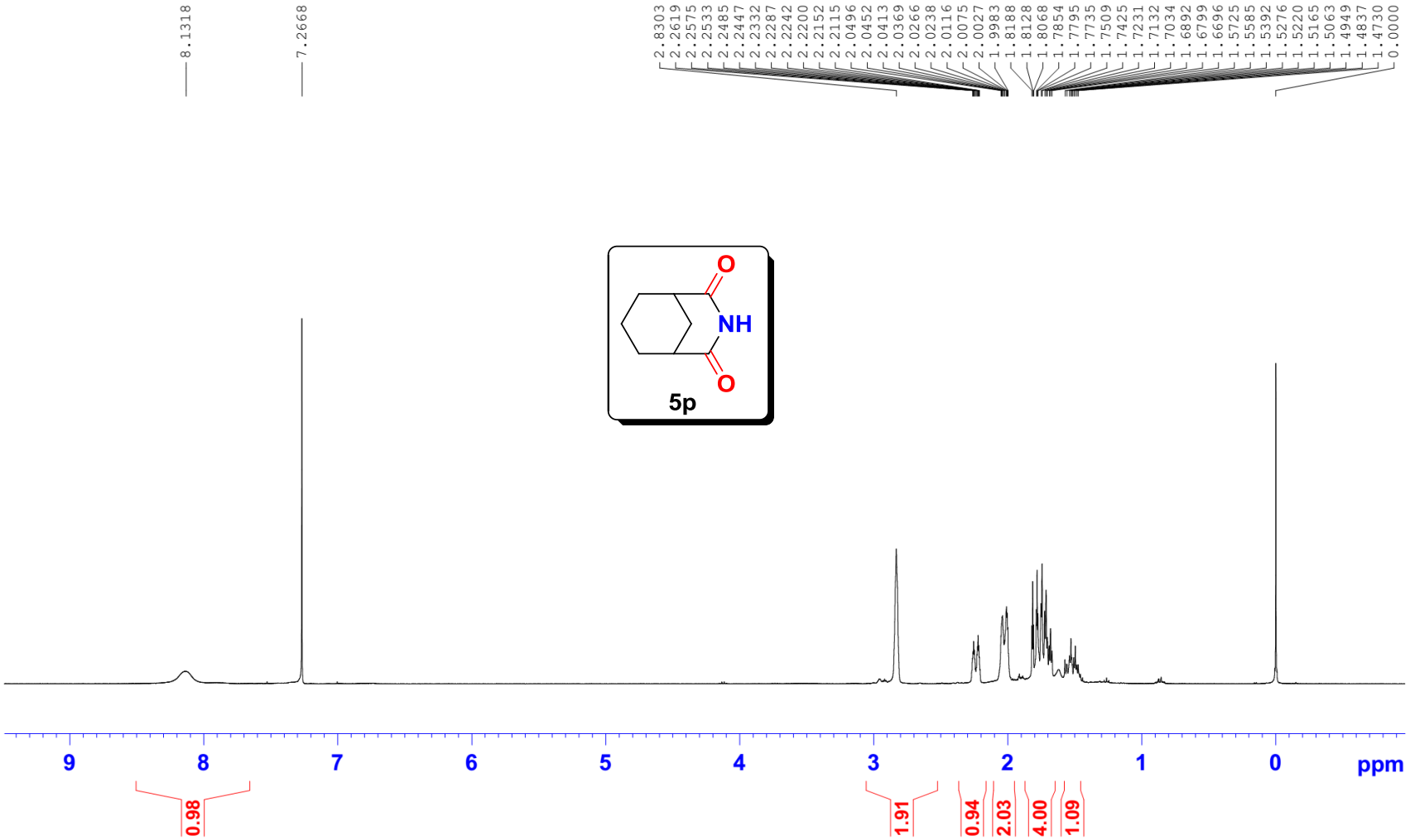

ZGY-X15Y24-1-HNMR
O
NH2
5n
ppm


ZGY-X15Y25-1-CNMR
178.9
129.9
43.7
39.9
39.7
39.5
39.3
39.1
32.0
29.8
27.5
25.4
24.0
O
NH2
5n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

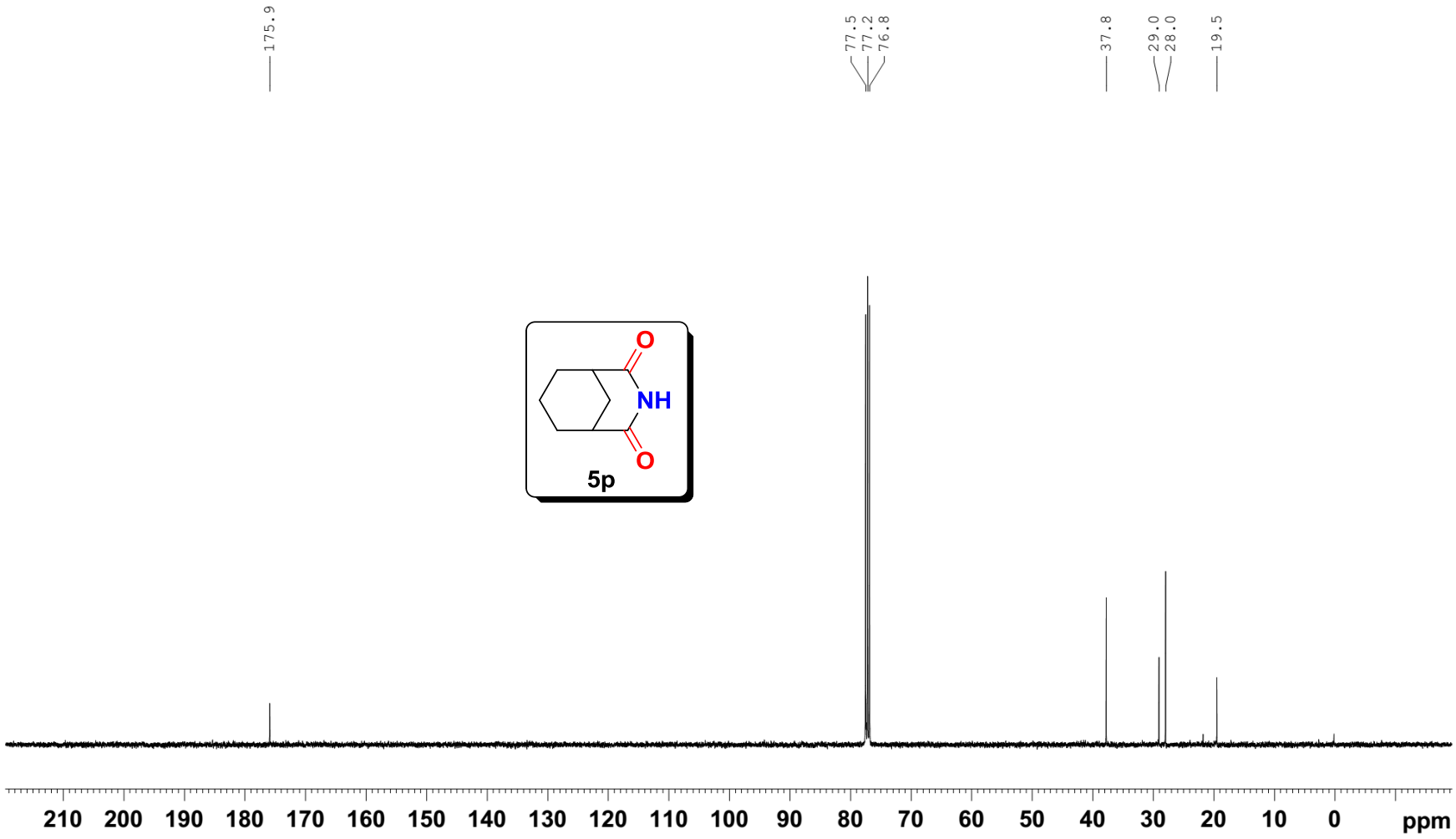

ZJP-X15Z28-2-HNMR
7.2713
5.6814
5.4959
2.1866
2.1779
2.1693
2.1576
2.1488
2.1401
2.1286
2.1197
2.1108
1.9245
1.9195
1.8912
1.8866
1.8228
1.8138
1.8071
1.8007
1.7837
1.6965
1.6890
1.6853
1.6816
1.6741
1.6709
1.6655
1.6625
1.6599
1.4757
1.4686
1.4452
1.4383
1.4151
1.4082
1.3846
1.3780
1.3353
1.3282
1.3141
1.3053
1.2975
1.2730
1.2665
1.2617
1.2491
1.2454
1.2376
1.2285
1.2208
1.2049
1.1985
1.1909
0.0696
O
NH2
5o
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
1.05
1.01
1.00
2.04
2.09
1.07
2.08
3.10

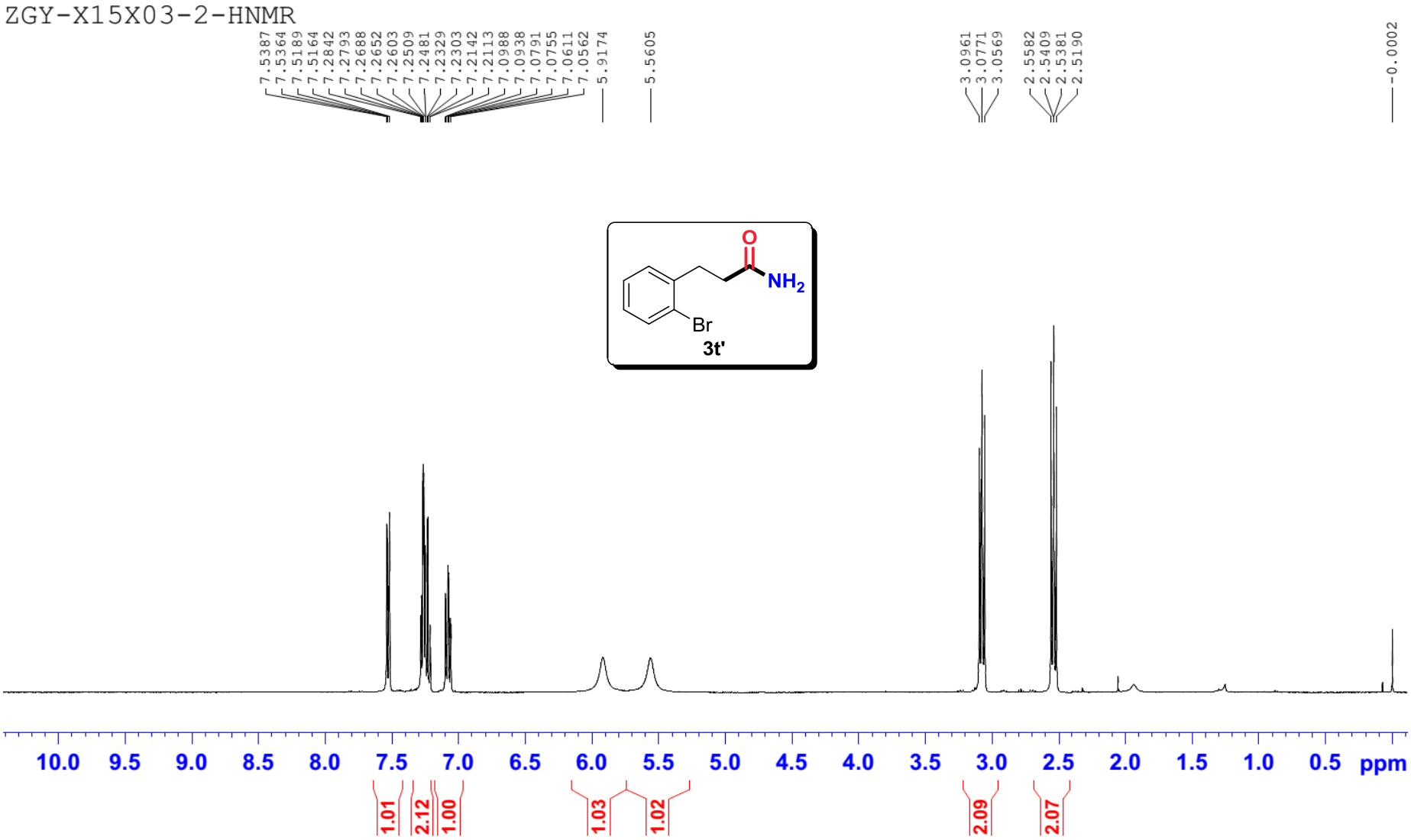

ZGY-X15Y09-5-CNMR
178.6516
77.3413
77.0239
76.7060
44.7898
29.6968
25.7227
25.6850
O
NH2
5o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

GB-X170223-1-7-HNMR

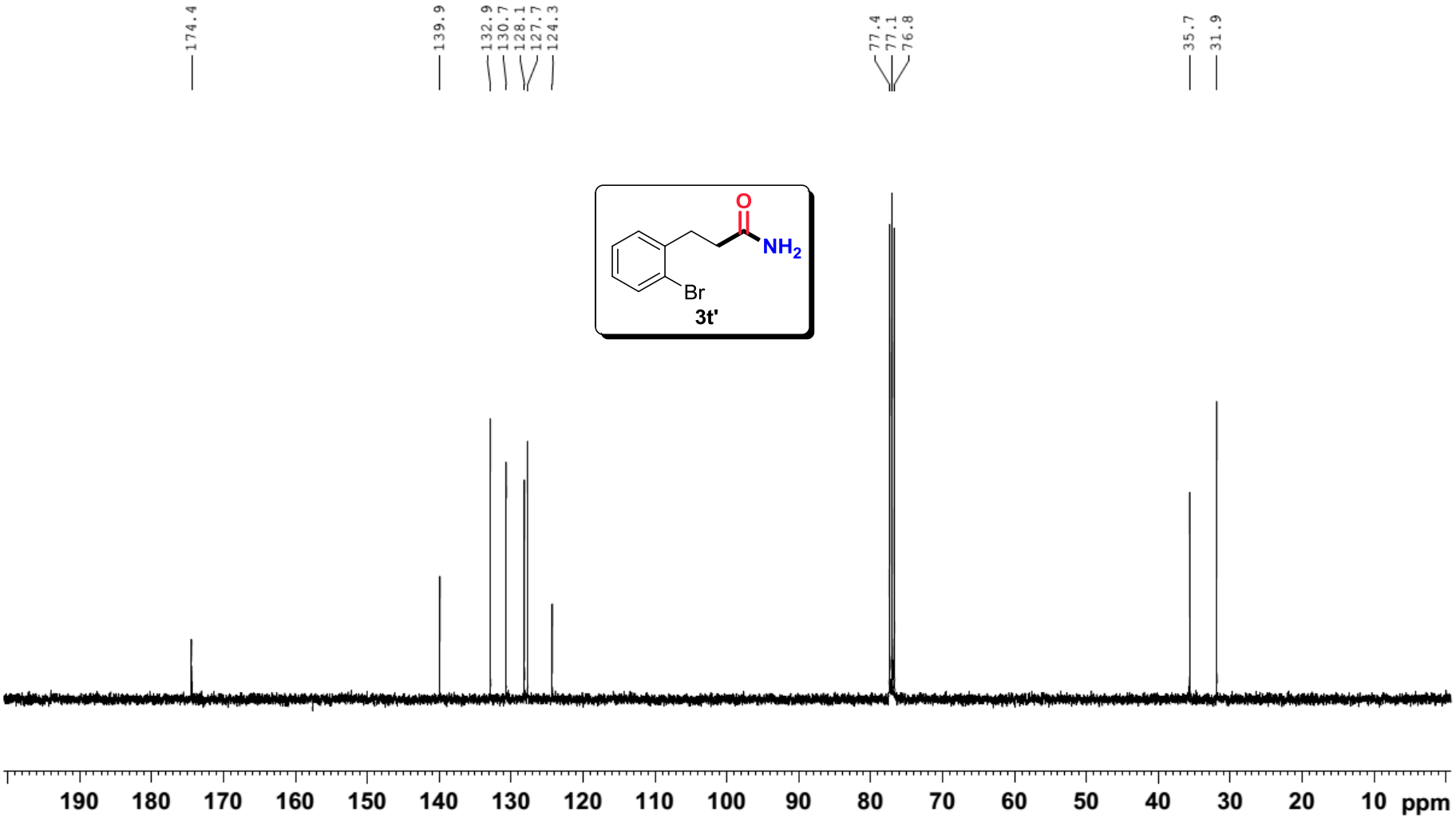


GB-X170223-1-7-CNMR

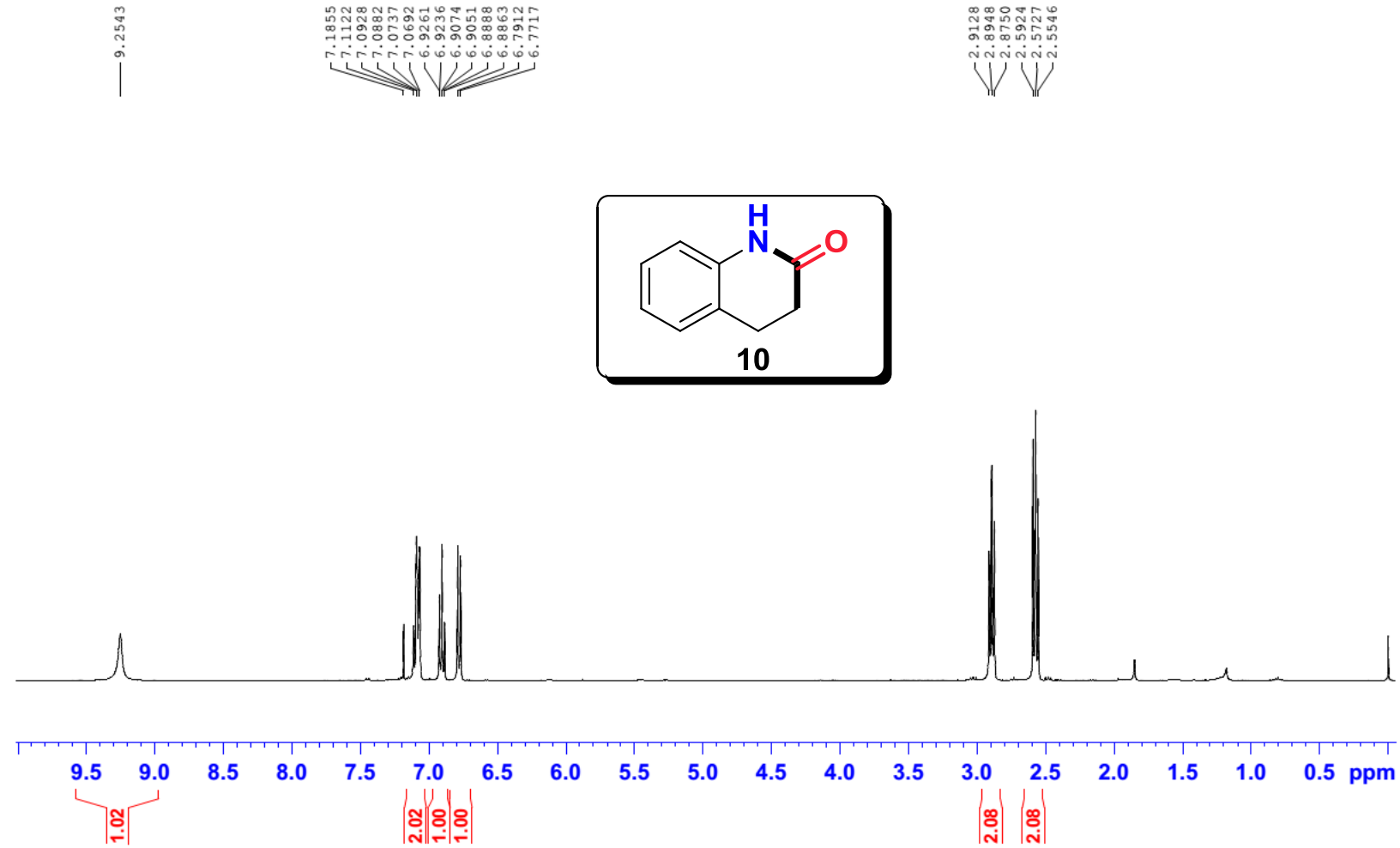



ZGY-X15X03-2-HNMR
7.5387
7.5364
7.5189
7.5164
7.2842
7.2793
7.2688
7.2652
7.2603
7.2509
7.2481
7.2329
7.2303
7.2142
7.2113
7.0988
7.0938
7.0791
7.0755
7.0611
7.0562
5.9174
5.5605
3.0961
3.0771
3.0569
2.5582
2.5409
2.5381
2.5190
0.0002
O
NH2
Br
3t'
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.01
2.12
1.00
1.03
1.02
2.09
2.07

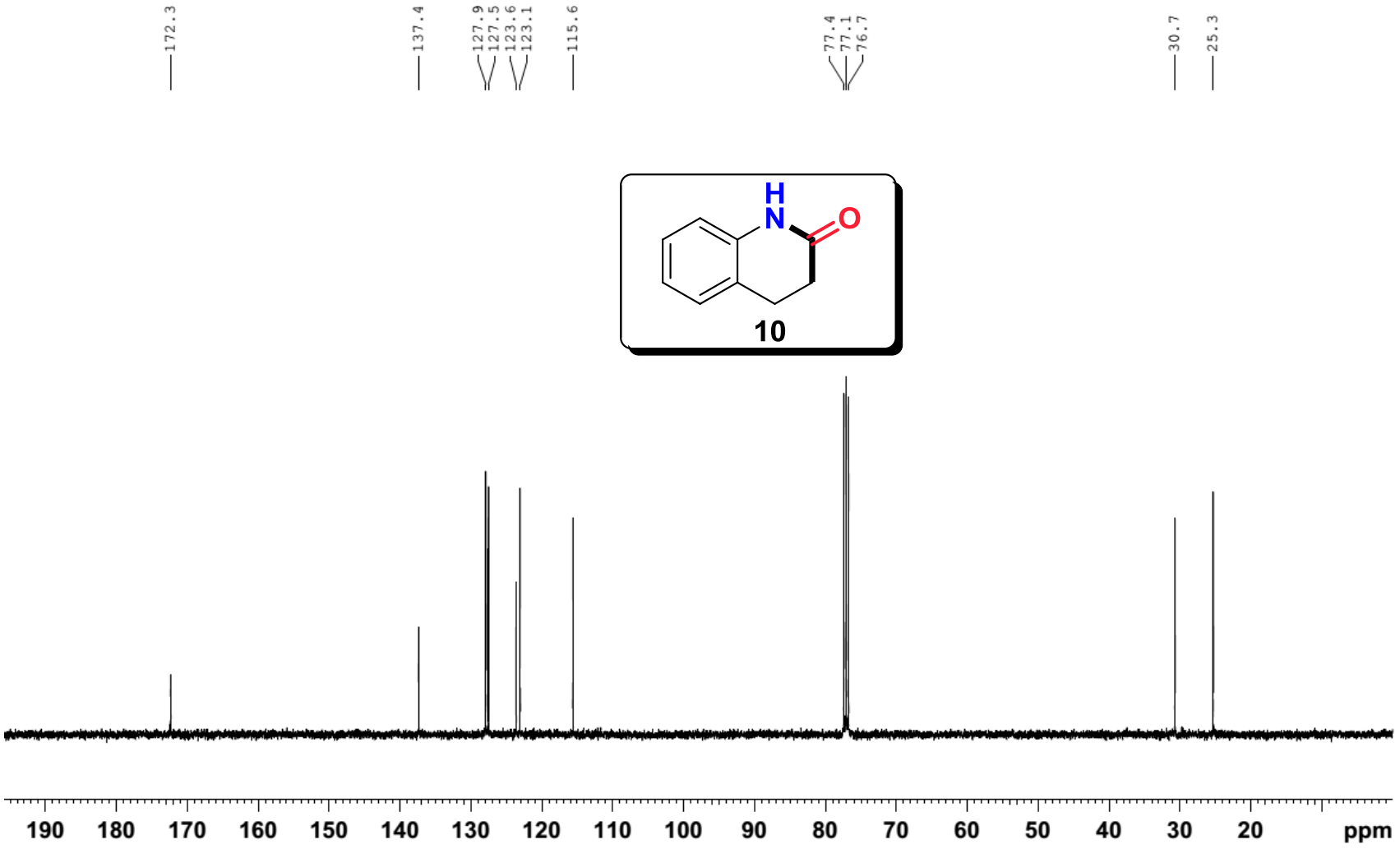
ZGY-X15X03-2-CNMR

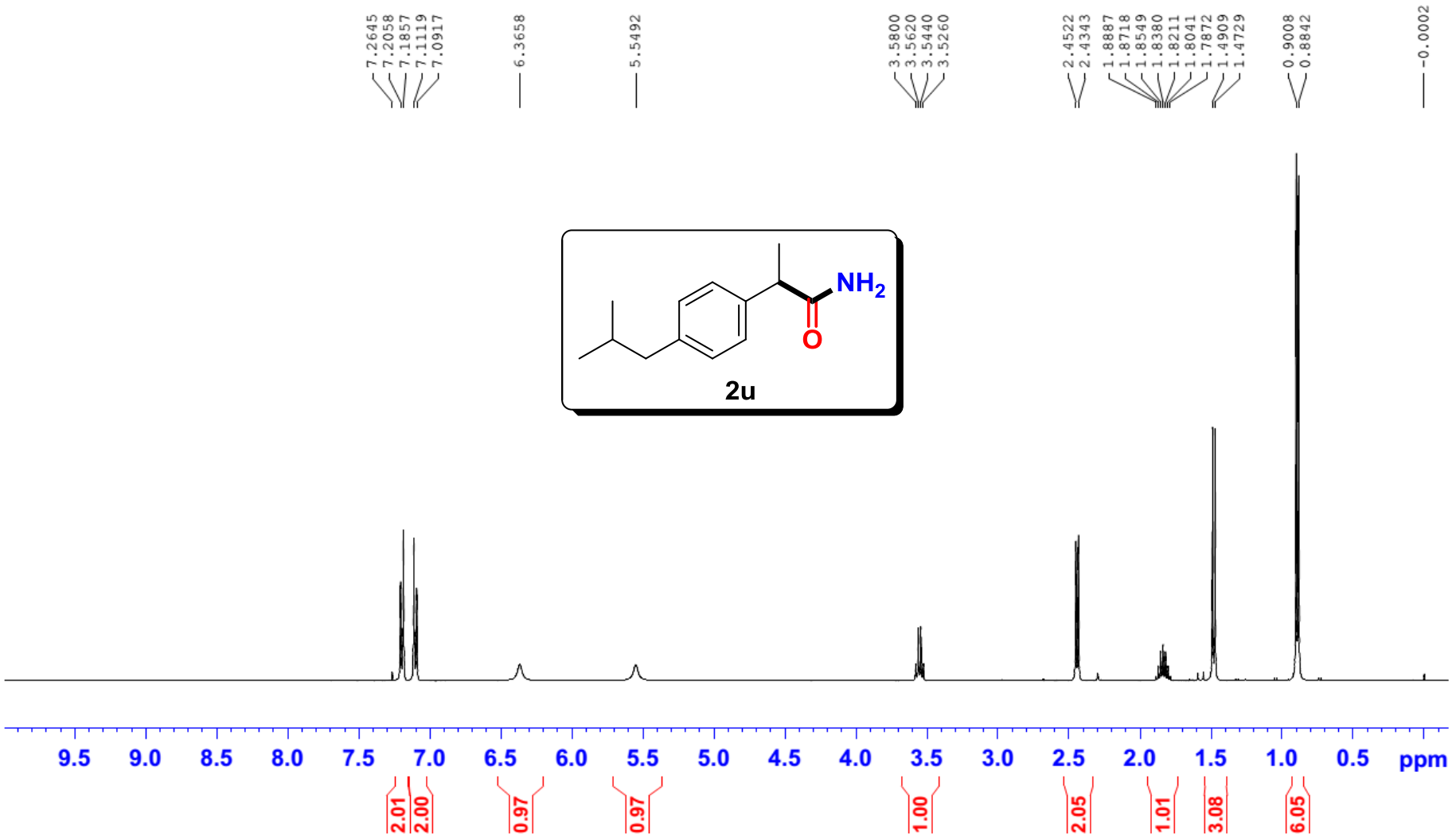


ZGY-X15Y16-4-HNMR

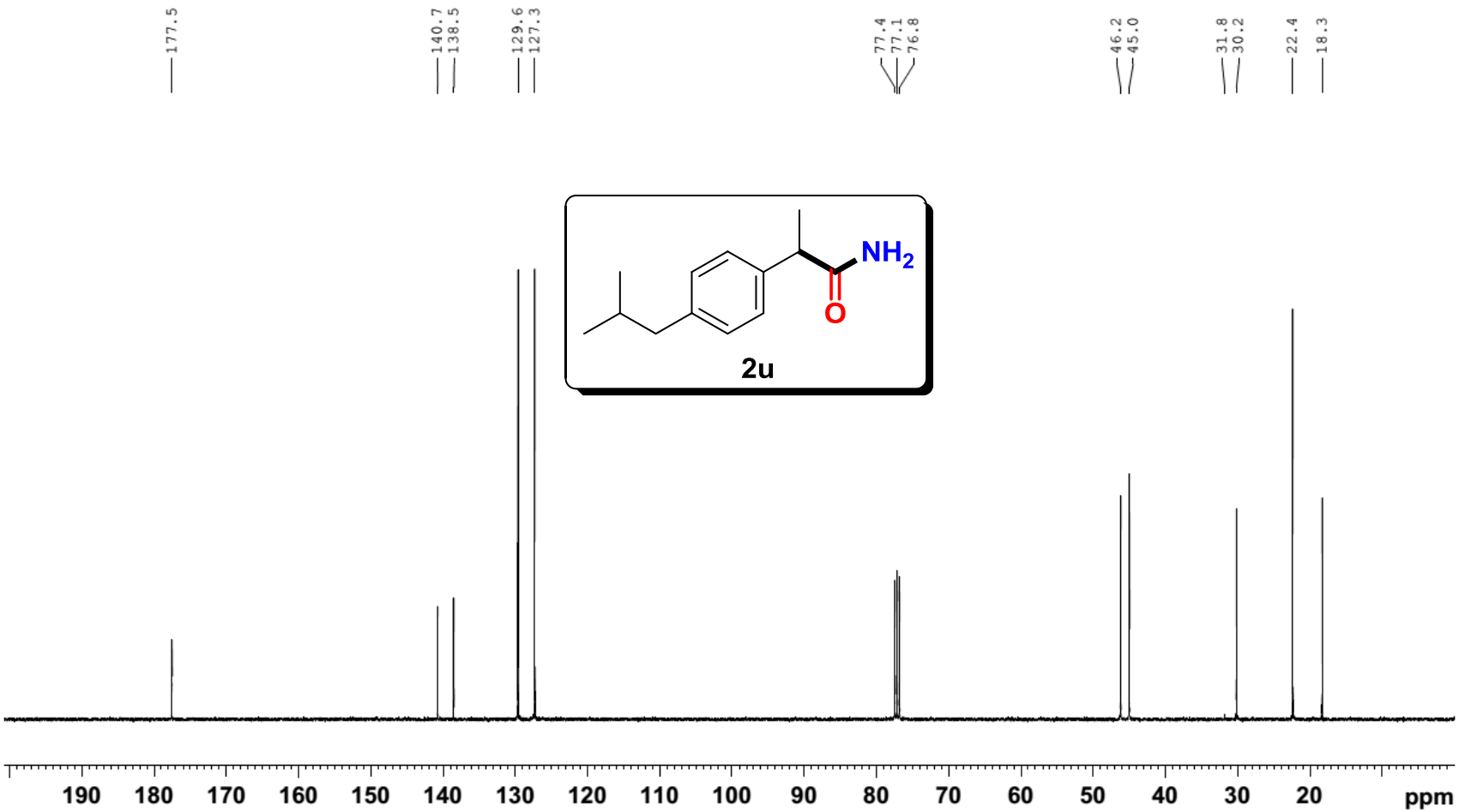


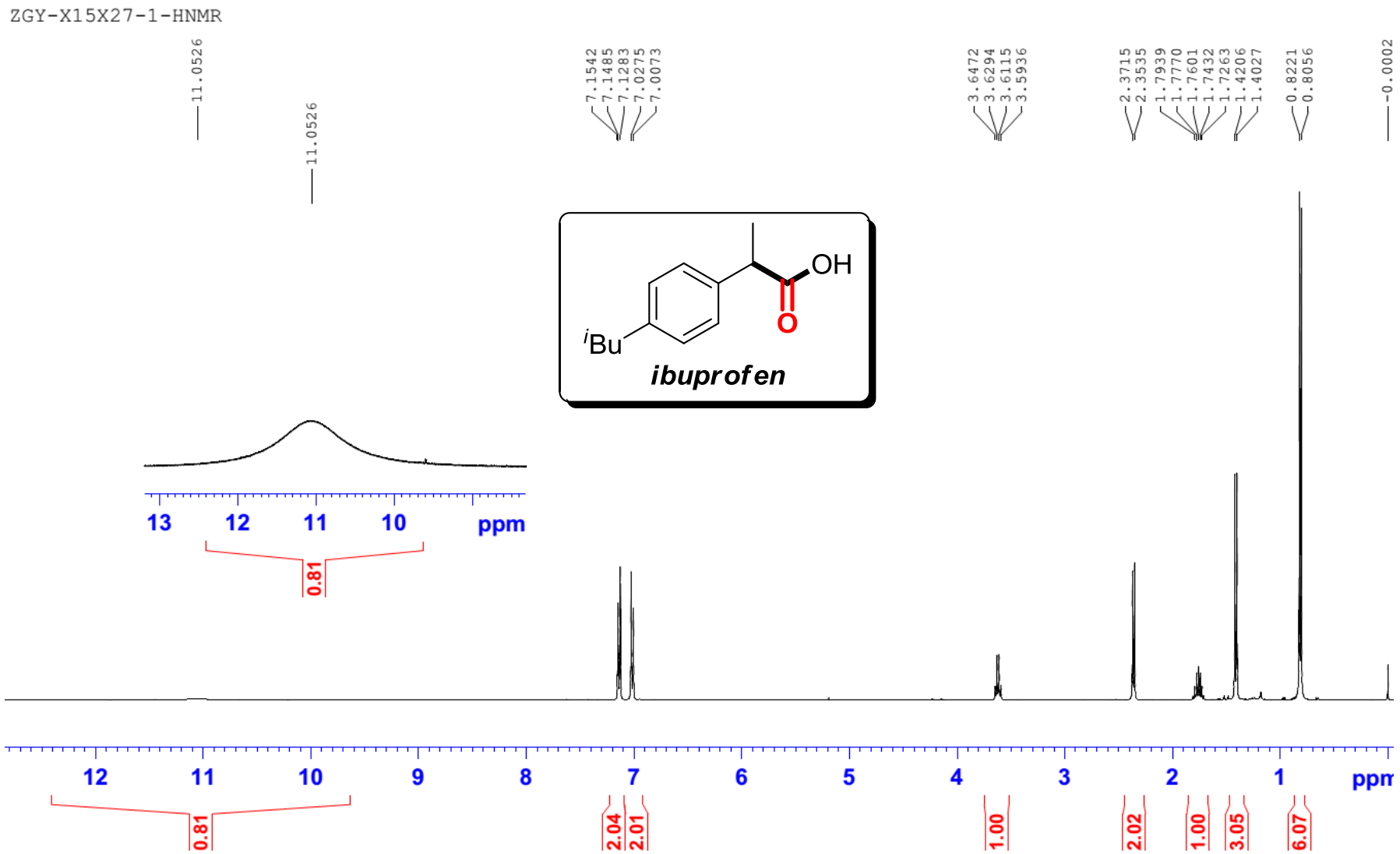
ZGY-X15Y16-4-CNMR



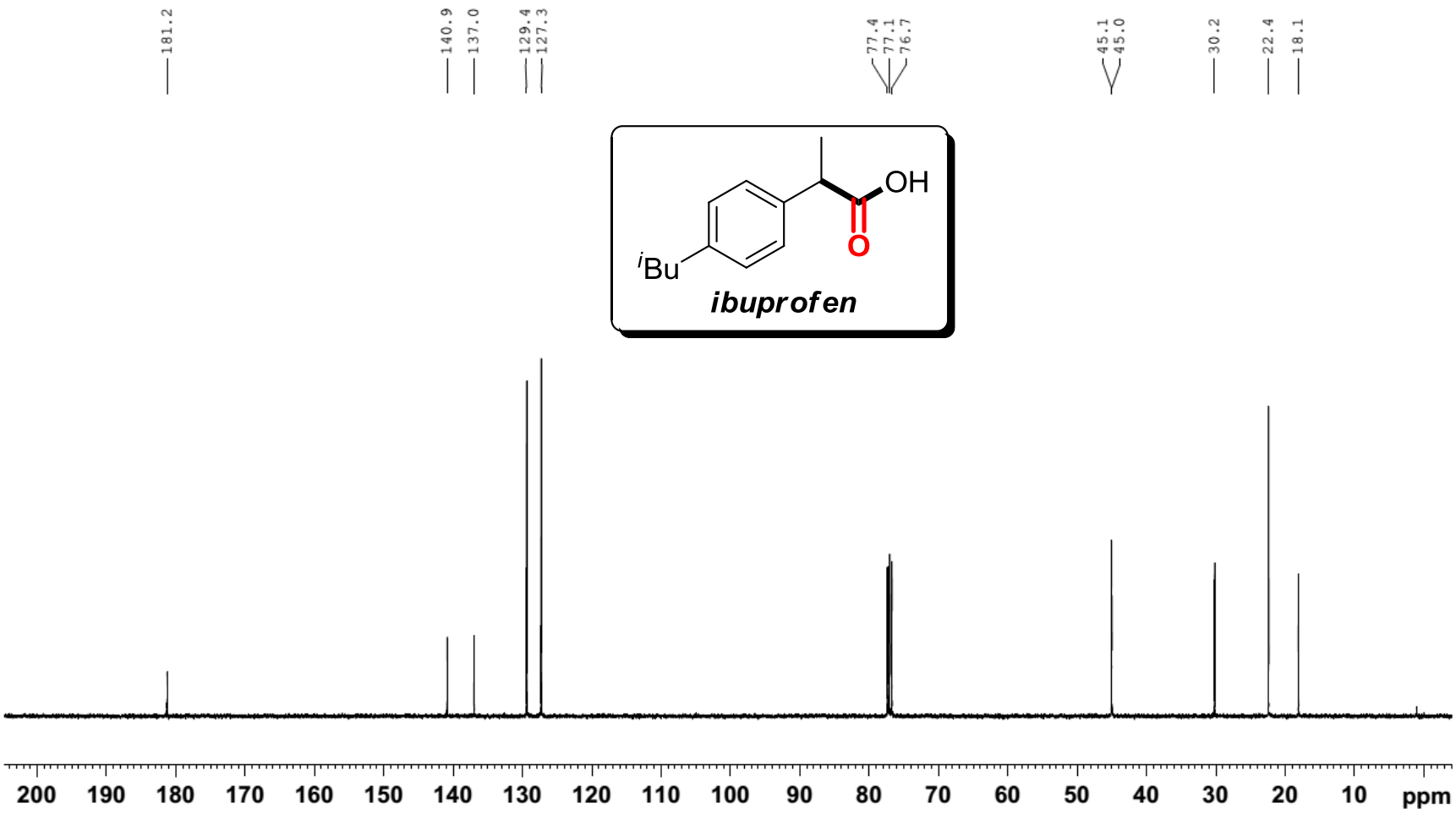

ZGY-X15X26-3-HNMR
7.2645
7.2058
7.1857
7.1119
7.0917
6.3658
5.5492
3.5800
3.5620
3.5440
3.5260
2.4522
2.4343
1.8887
1.8718
1.8549
1.8380
1.8211
1.8041
1.7872
1.4909
1.4729
0.9008
0.8842
-0.0002
NH2
O
2u
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.01
2.00
0.97
0.97
1.00
2.05
1.01
3.08
6.05

ZGY-X15X26-3-CNMR

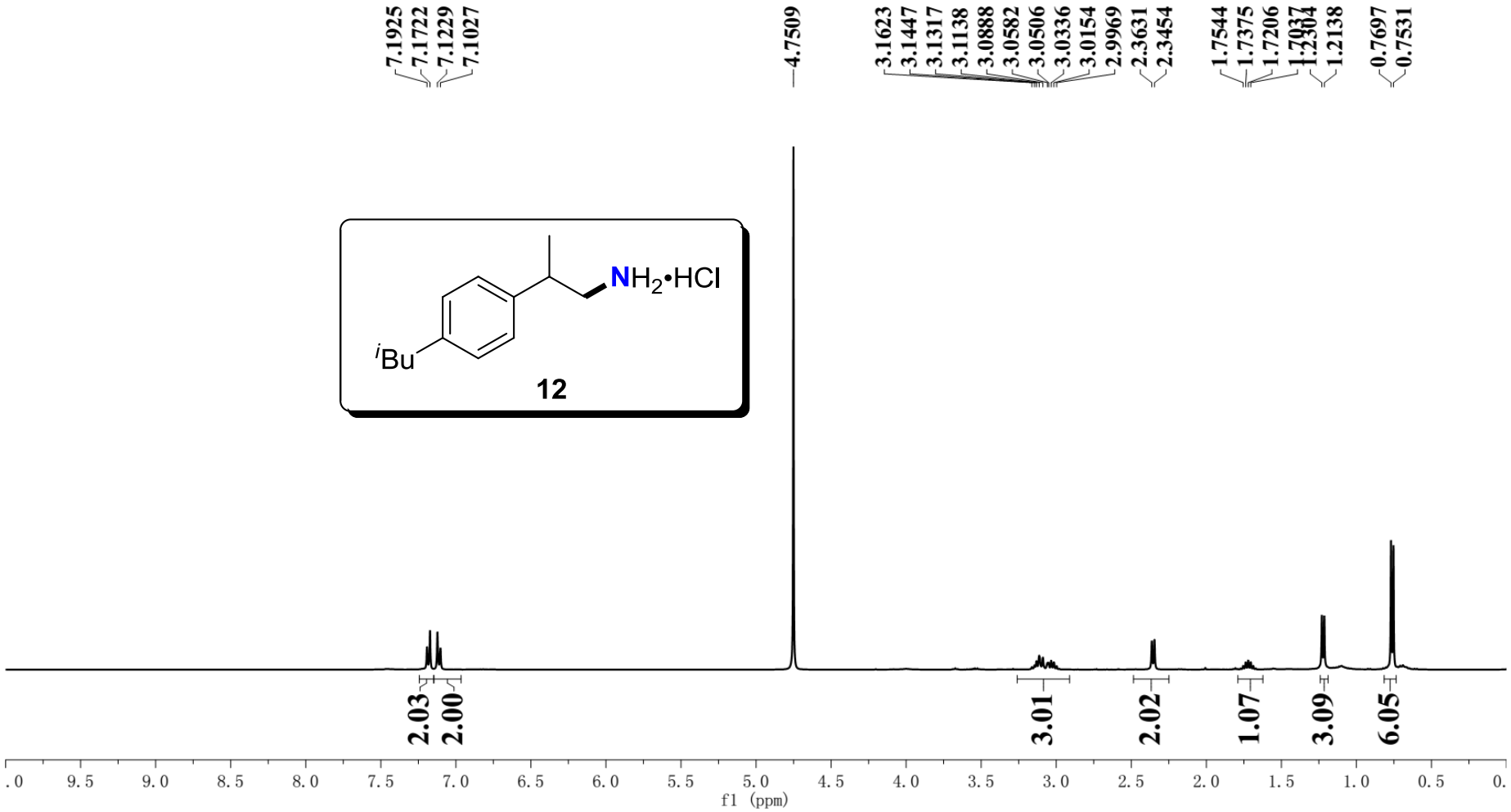


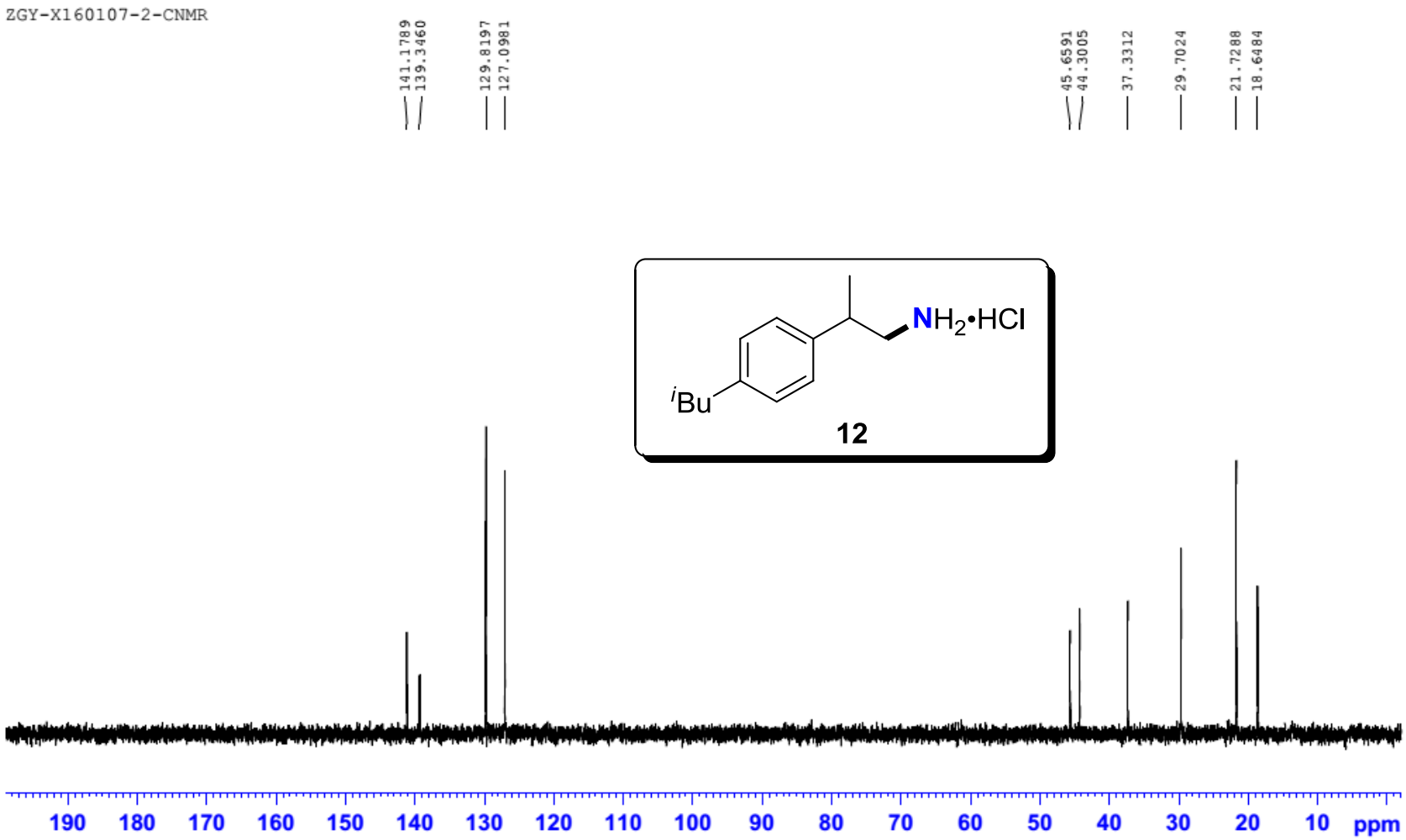

ZGY-X15X27-1-HNMR
11.0526
11.0526
7.1542
7.1485
7.1283
7.0275
7.0073
3.6472
3.6294
3.6115
3.5936
2.3715
2.3535
1.7939
1.7770
1.7601
1.7432
1.7263
1.4206
1.4027
0.8221
0.8056
-0.0002
OH
O
iBu
ibuprofen
13
12
11
10
ppm
0.81
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.81
2.04
2.01
1.00
2.02
1.00
3.05
6.07

ZGY-X15X27-1-CNMR

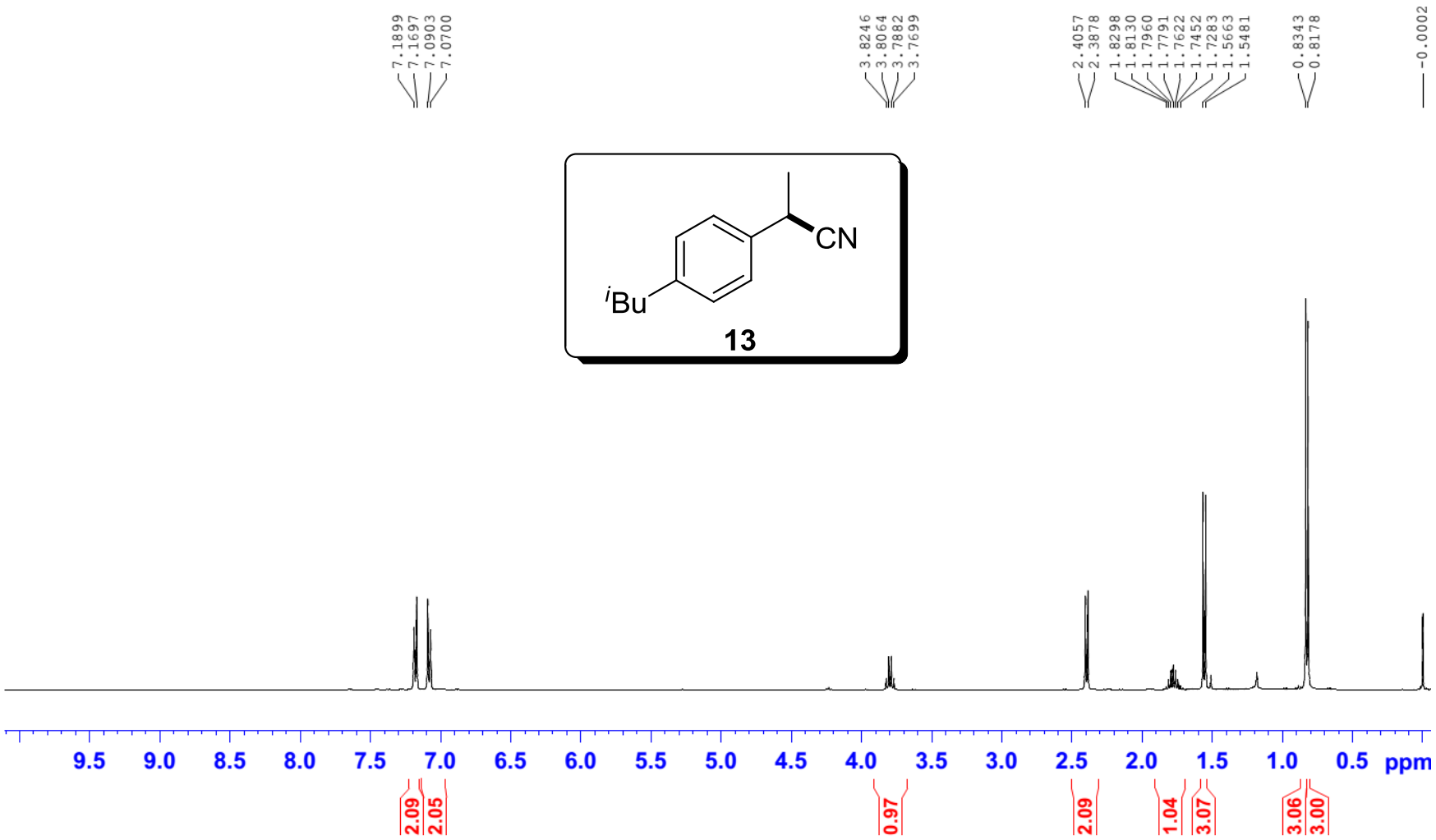


ZGY-X160107-2 H NMR

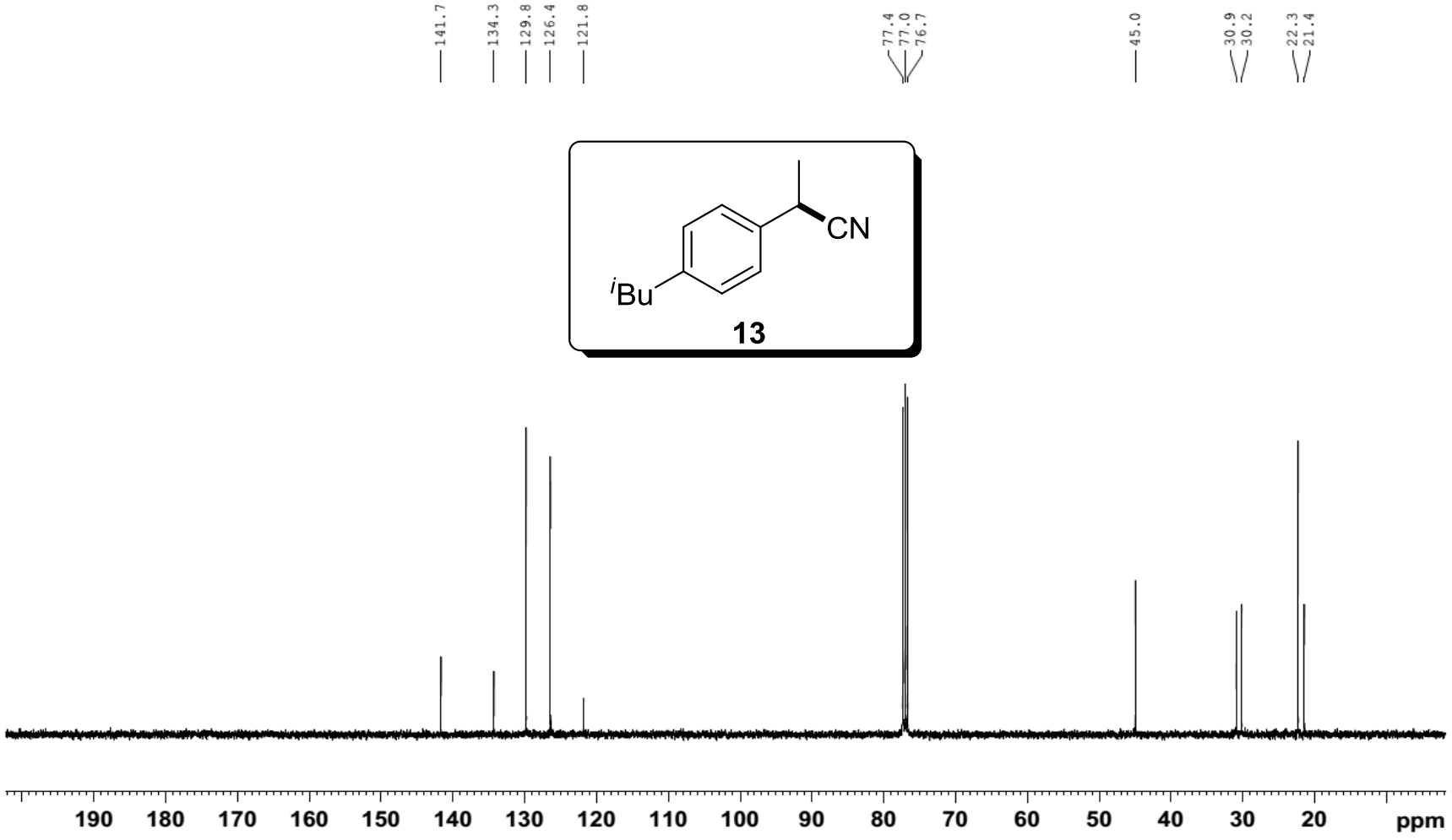



ZGY-X160107-2-CNMR
141.1789
139.3460
129.8197
127.0981
45.6591
44.3005
37.3312
29.7024
21.7288
18.6484
NH2•HCl
iBu
12
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

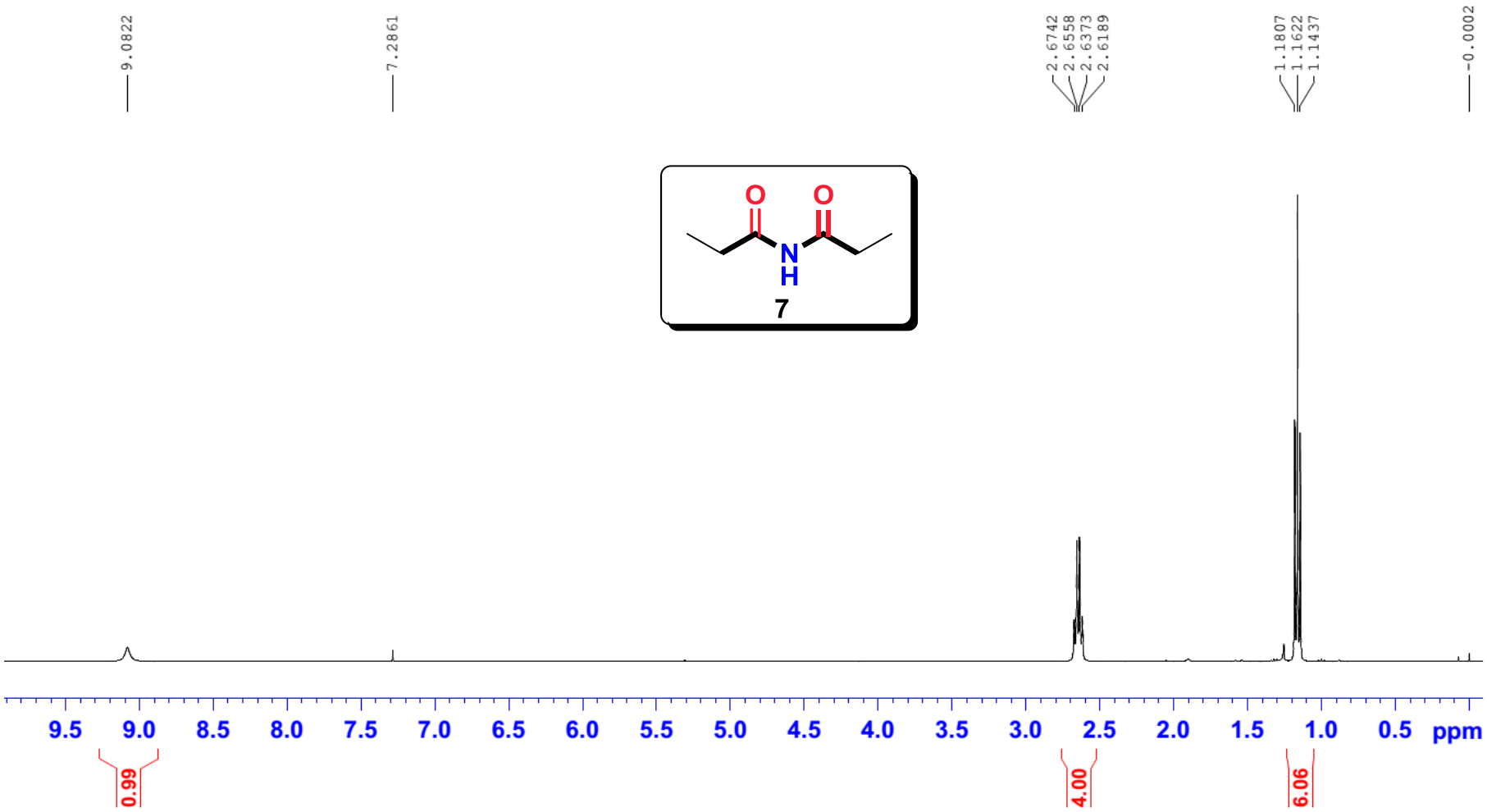
ZGY-X15Y09-2-HNMR



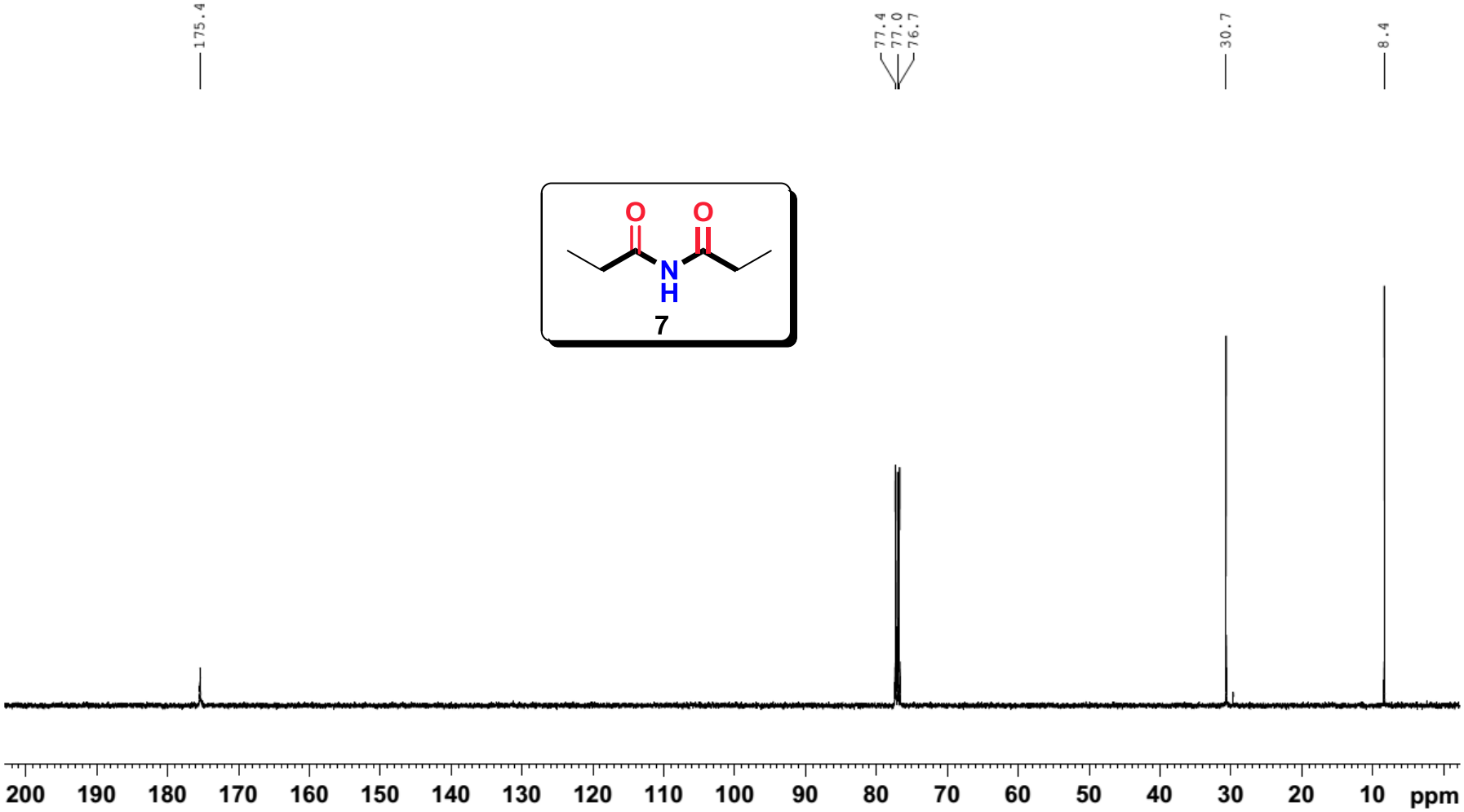
ZGY-X15Y09-2-CNMR



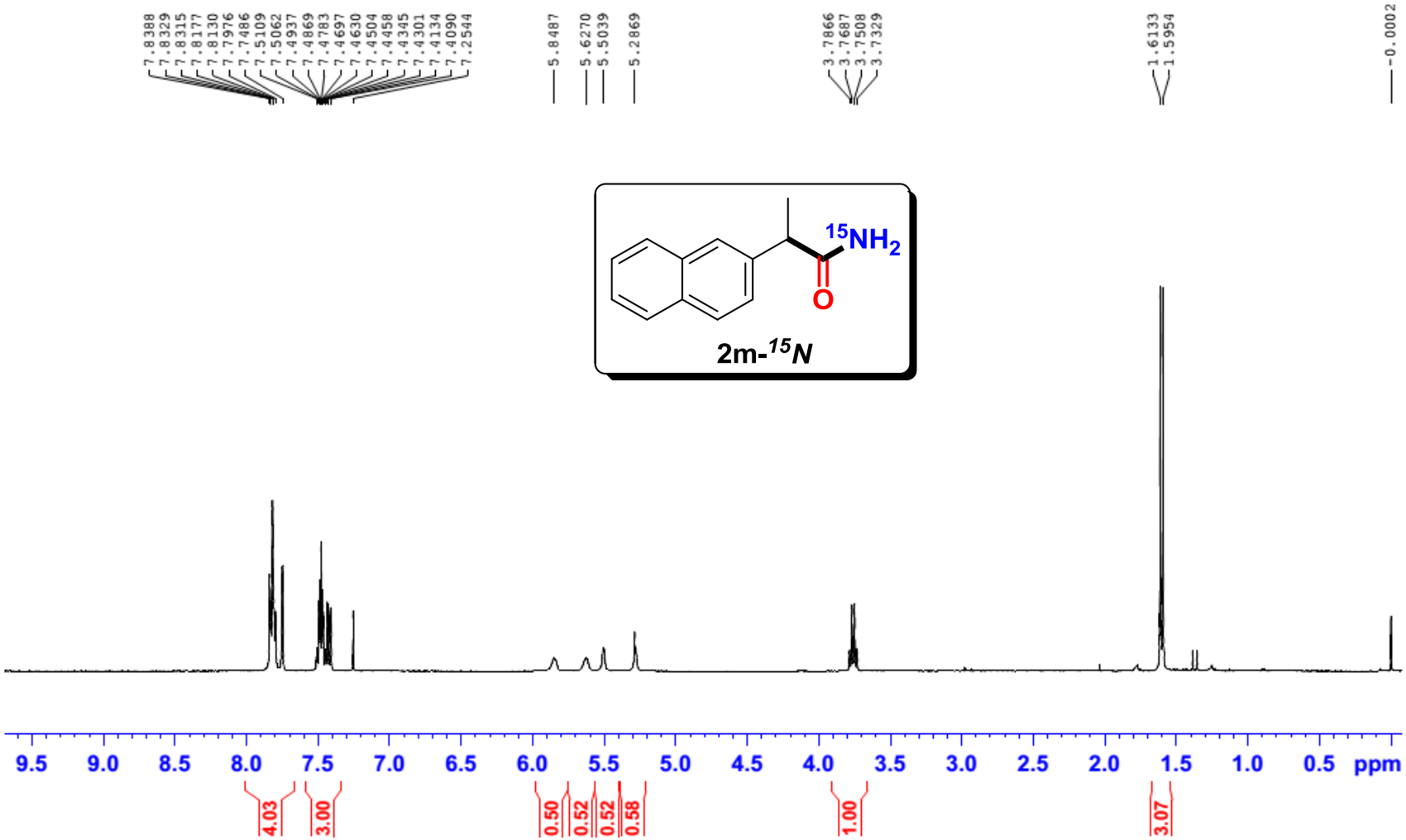
ZGY-X15X02-3-HNMR

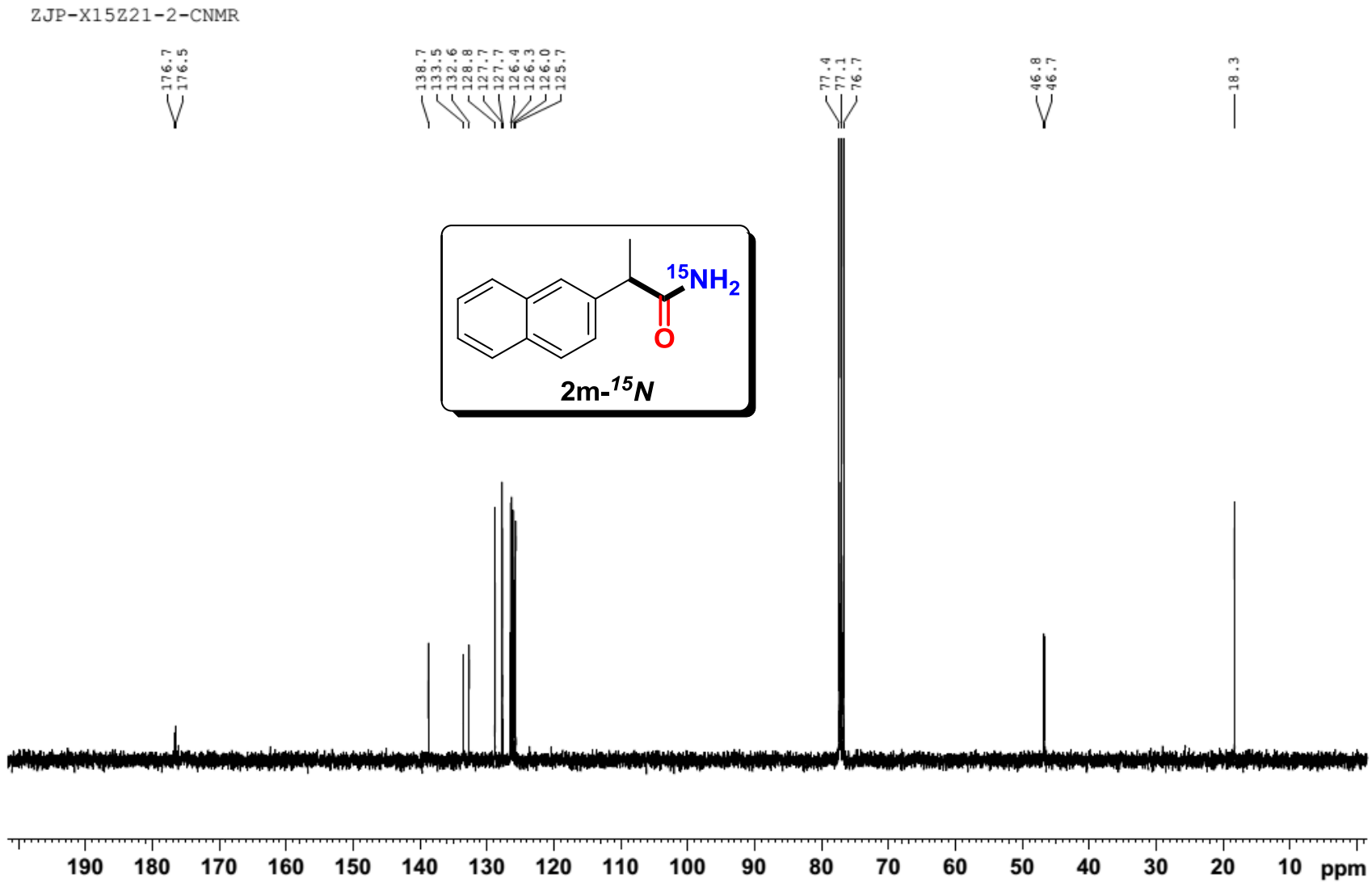


ZGY-X15X02-3-CNMR

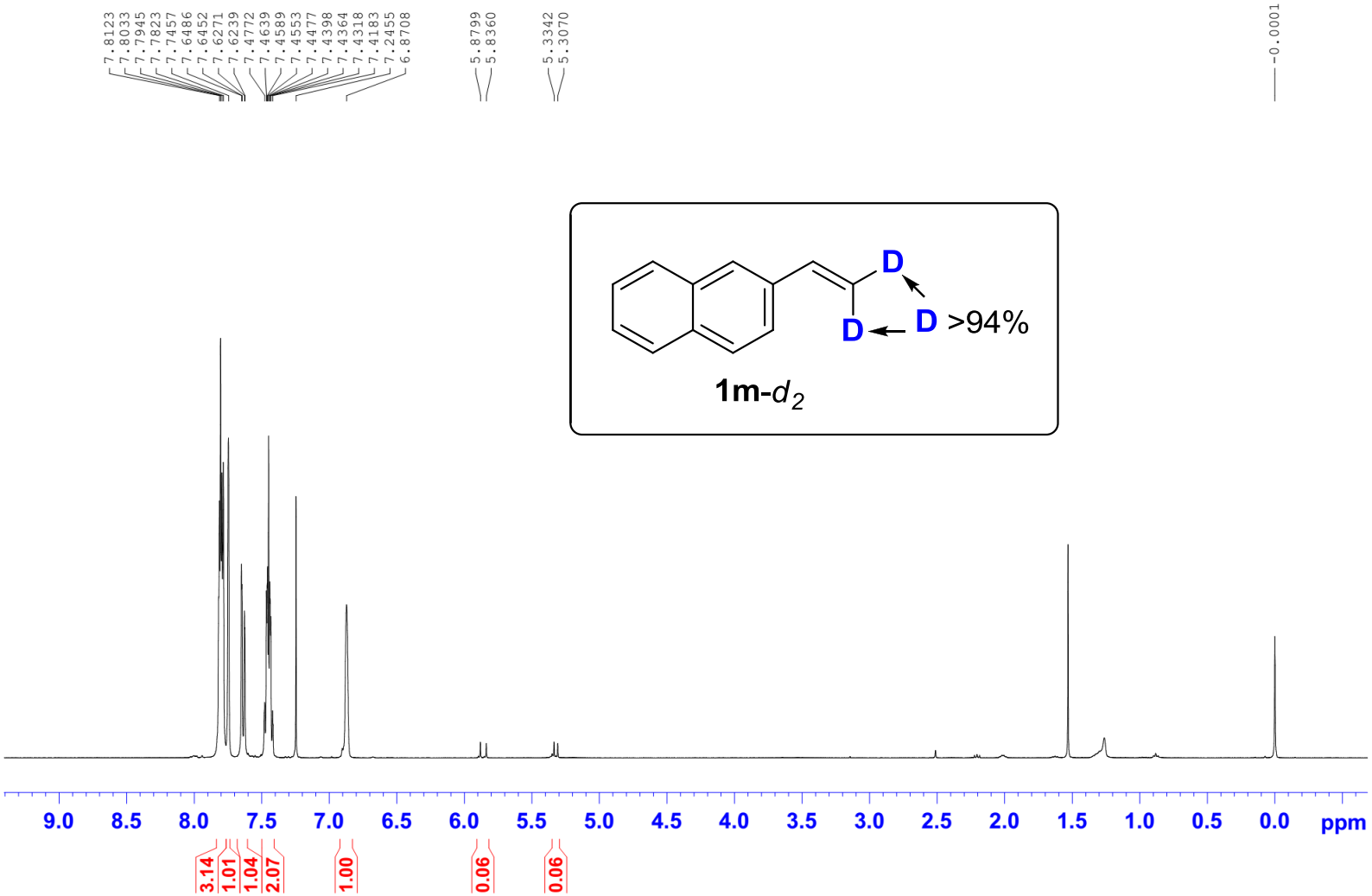


ZJP-X15Z21-2-HNMR

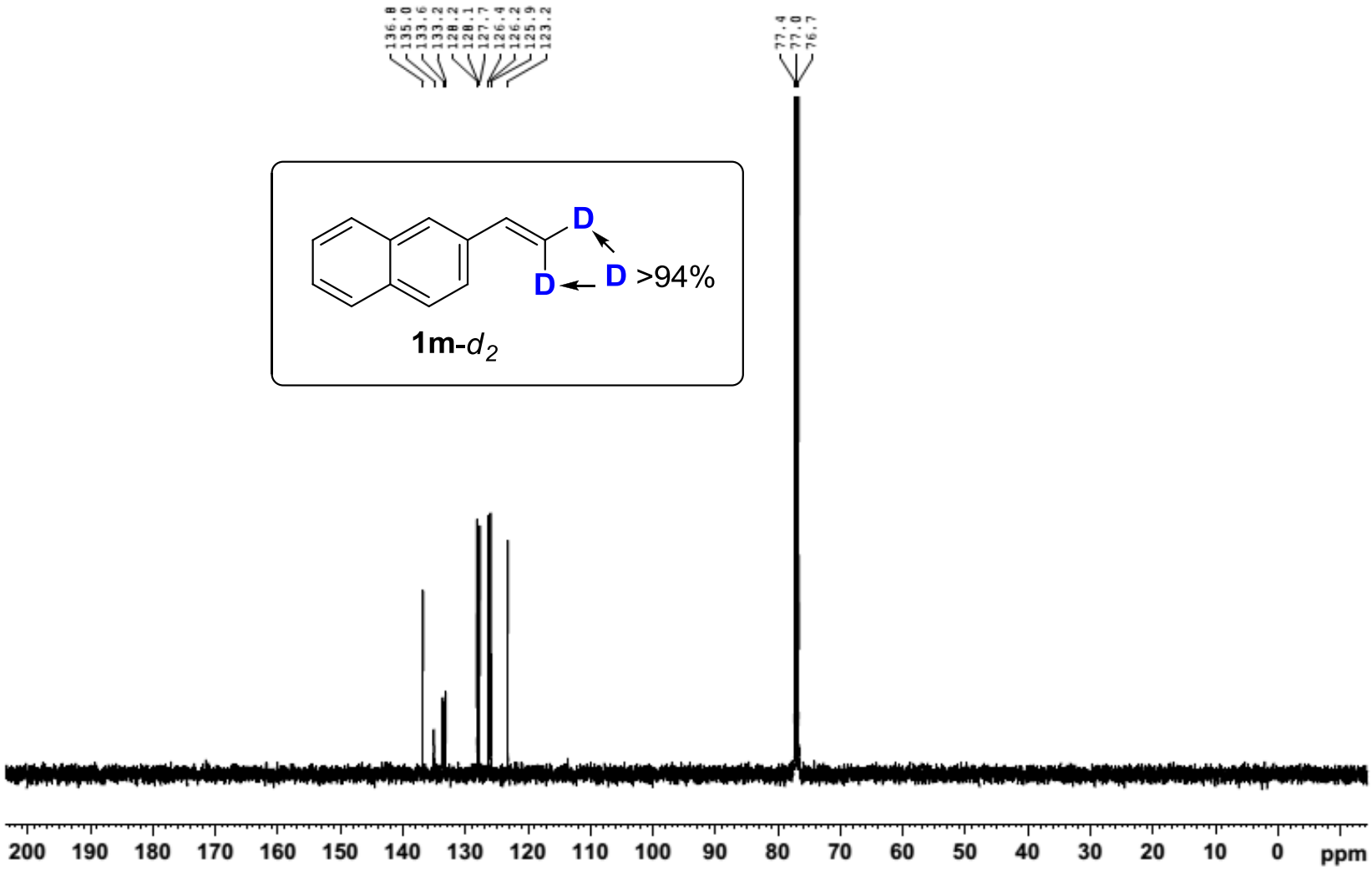



ZJP-X15Z21-2-CNMR
176.7
176.5
138.7
133.5
132.6
128.8
127.7
127.7
126.4
126.3
126.0
125.7
77.4
77.1
76.7
46.8
46.7
18.3
15NH2
O
2m-15N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

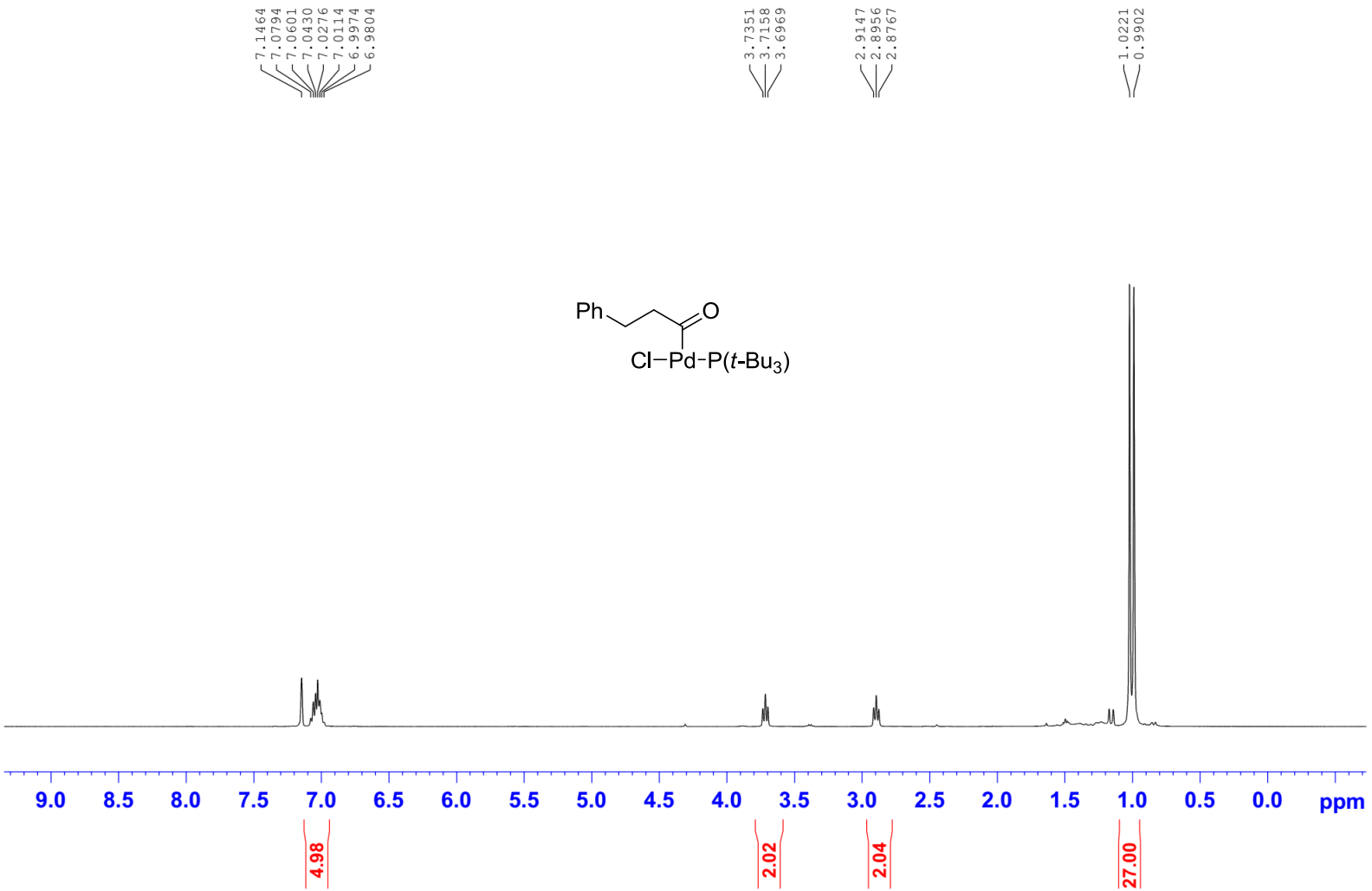
ZJP-X170413-8-HNMR



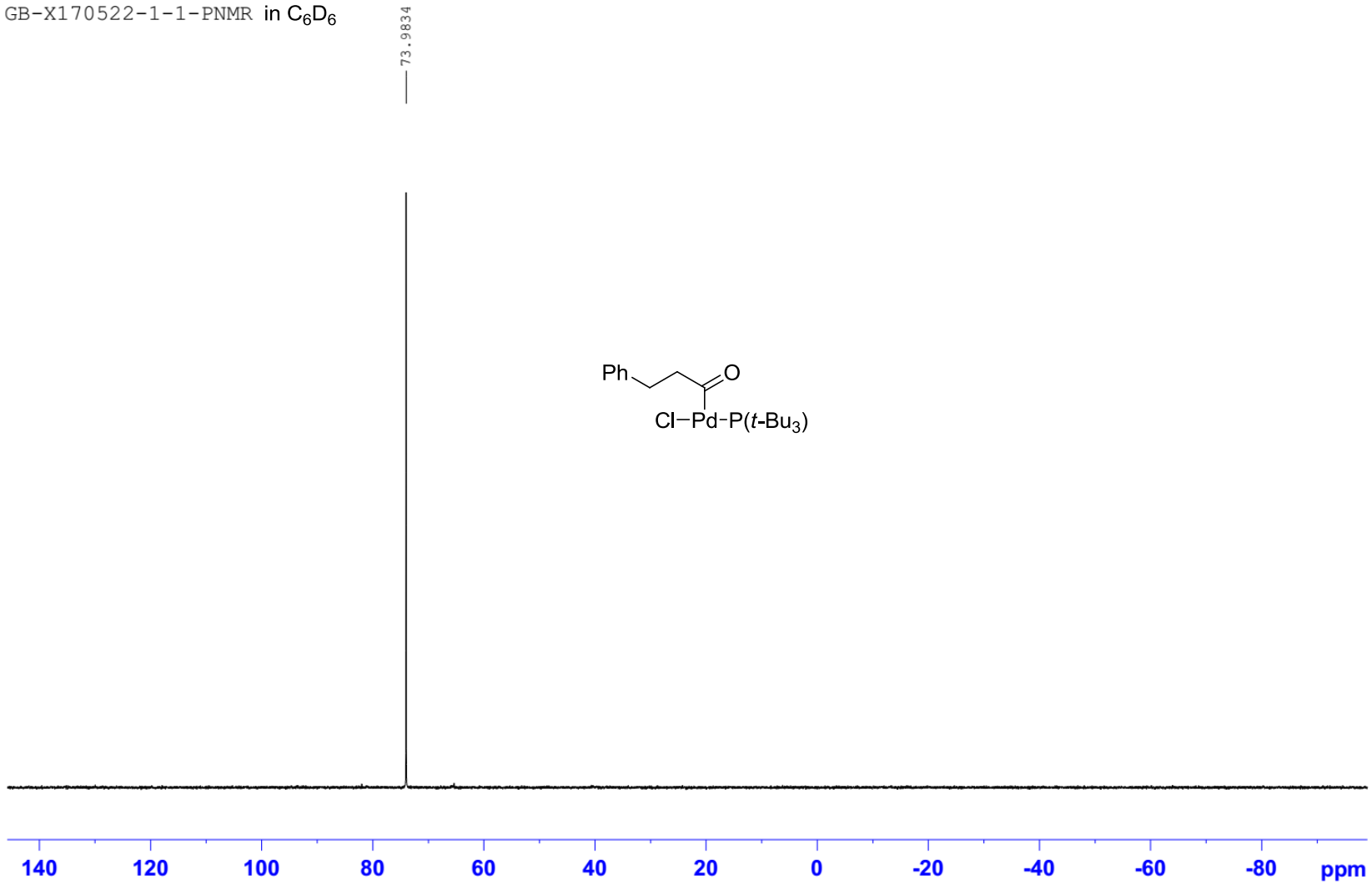
ZJP-X170418-1-CNMR



GB-X170522-1-1-HNMR in C_6D_6



GB-X170522-1-1-PNMR in C_6D_6



GB-X170522-1-CNMR in $CDCl_3$