Supporting Information for:

Palladium-Catalyzed Highly Regioselective Hydroaminocarbonyltion of Aromatic Alkenes to Branched Amides

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CONTENTS

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 7890 with OV-225 column or Hp-5 column. GS-MS analysis were performed with Agilent 7890A/5975C GC-MS system. Styrenes and amines were purchased from Energy Chemical except 2-(vinyloxy)naphthalene (**3si**) which was known compounds and synthesized according to the reported methods.[1]

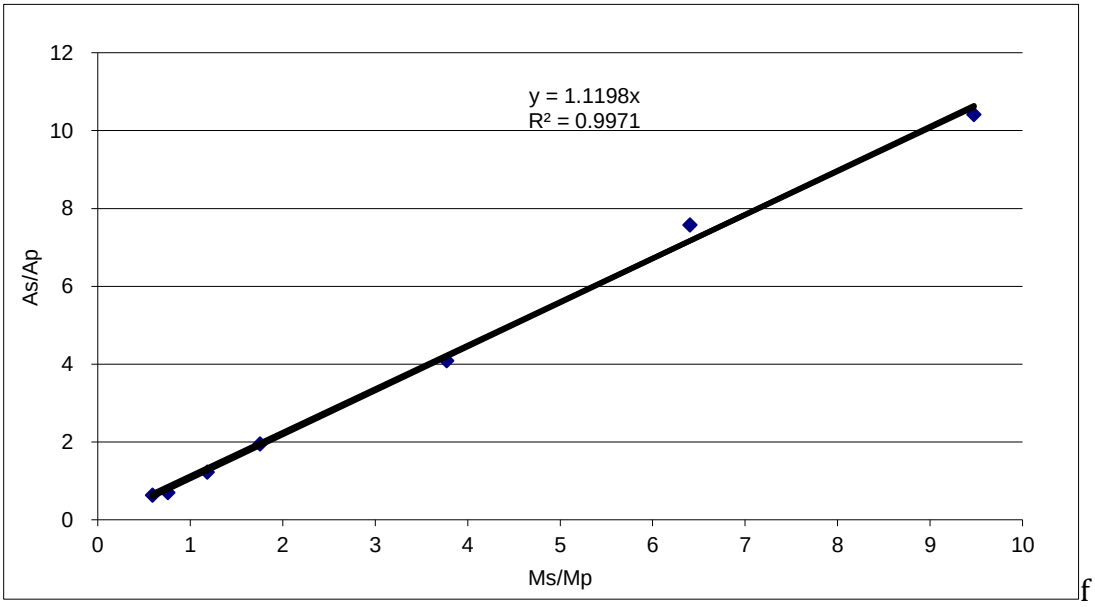
2. Standard curve for determining the yield of 3aa by GC

n-Hexadecane was selected as the internal standard and the quantitative correction factor was determined.

Table S1. Determination of quantitative correction factor

entry	Ms(mg)	Mp(mg)	Ms/Mp	As(g/s)	Ap(g/s)	As/Ap
1	2	1.14	1.754386	492.6	252.9	1.947805
2	2.7	2.28	1.184211	668	545.5	1.224565
3	2.6	3.42	0.760234	520.8	746.1	0.69803
4	2.7	4.56	0.592105	716	1138.6	0.628842
5	4.3	1.14	3.77193	1124.1	275.2	4.084666
6	7.3	1.14	6.403509	1985.5	262	7.578244
7	10.8	1.14	9.473684	2672.3	256.5	10.41832

ps: Ms means the quality of *n*-hexadecane. Mp means the quality of **3aa**. As means the peak area of *n*-hexadecane. Ap means the peak area of **3aa**. **3aa** was treated as solution of 0.087M



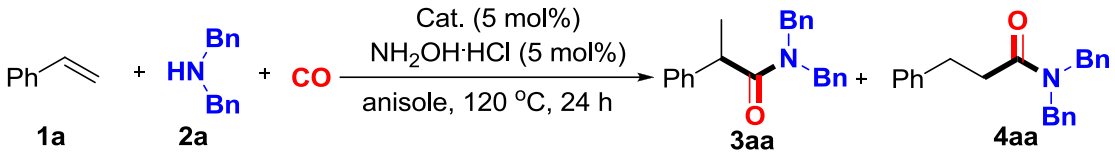
$$f = \frac{As/Ap}{Ms/Mp} = 1.1198$$

3. Optimization of the reaction conditions

A mixture of styrene **1a** (91 μl, 0.8 mmol), dibenzylamine **2a** (78.8 mg, 0.4 mmol), [Pd] (0.02 mmol), additive (0.02 mmol) and anisole (1.0 mL) were added into a glass tube which was placed in an autoclave. Then the autoclave was purged and charged with CO at the designed pressure. 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. The regioselectivity was measured by GC and GC-MS using *n*-hexadecane as the internal standard, respectively. Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (petroleum ether/ethyl acetate = 10/1 – 2/1) to give the desired product **3aa**.

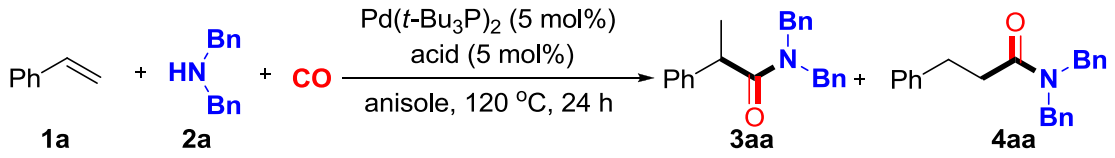
Table S2. Screening of the catalysts [a]



Entry	Cat. (5 mol%)	**3aa** + **4aa** (%)[b]	**3aa**/**4aa**[c]
1	$PdCl_2$	NR	-
2	$Pd(OAc)_2$	NR	-
3	$[Pd(allyl)Cl]_2$	NR	-
4	$PdCl_2(PPh_3)_2$	15.2	>20:1
5	$PdCl_2$(xantphos)	13.7	34:66
6	$Pd(PPh_3)_4$	11.1	>20:1
7	$Pd(t\text{-}Bu_3P)_2$	>99(95)[d]	>20:1

[a] General conditions: **1a** (0.8 mmol), **2a** (0.4 mmol), catalyst (0.02 mmol), $NH_2OH{\cdot}HCl$ (0.02 mmol), anisole (1.0 mL), CO (20 atm), 120 °C, 24 h. [b] Yields were based on amine and determined by GC analysis using *n*-hexadecane as the internal standard. [c] The ratios of **3aa** and **4aa** were determined by GC analysis. [d] Isolated yield was given in parenthesis.

Table S3. Screening of the additives [a]

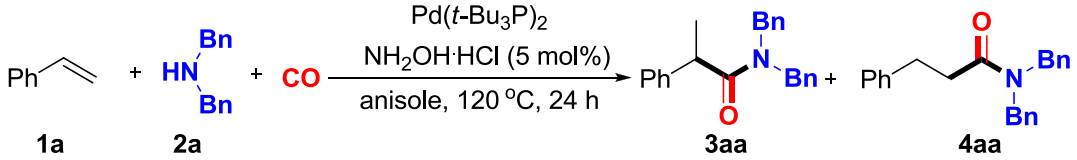


Entry	Acid (5 mol%)	**3aa** + **4aa** (%)[b]	**3aa**/**4aa**[c]
1	$NH_2OH{\cdot}HCl$	>99(95)[d]	>20:1
2	$NH_2CH_2CO_2Me{\cdot}HCl$	>99	>20:1
3	$NH_2CH_2CO_2iPr{\cdot}HCl$	42.7	>20:1
4	$NH_2CH_2CO_2H{\cdot}HCl$	55.4	>20:1
5	$NH_2CH(Ph)CO_2Me{\cdot}HCl$	>99	>20:1
6	$NEt_3{\cdot}HCl$	>99	>20:1
7	PhCOOH	<5	>20:1
8	CH_3COOH	NR	-
9	$PhB(OH)_2$	39.2	>20:1

10	TsOH	<5	>20:1
11	TsOH	<5	>20:1

[a] General conditions: **1a** (0.8 mmol), **2a** (0.4 mmol), Pd(*t*-$Bu_3P)_2$ (0.02 mmol), acid (0.02 mmol), anisole (1.0 mL), CO (20 atm), 120 °C, 24 h. [b] Yields were based on amine and determined by GC analysis using *n*-hexadecane as the internal standard. [c] The ratios of **3aa** and **4aa** were determined by GC analysis. [d] Isolated yield was given in parenthesis.

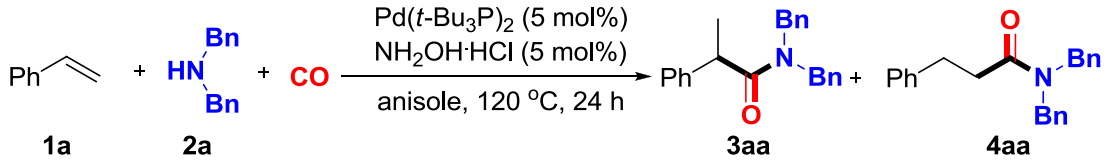
Table S4. Screening of the loadings of catalyst [a]



Entry	Pd(*t*-$Bu_3P)_2$ (mol%)	**3aa** + **4aa** (%)[b]	**3aa**/**4aa**[c]
1	0.5	<5	>20:1
2	1.0	<5	>20:1
3	2.0	22.5	>20:1
4	3.0	34.1	>20:1
5	4.0	63.9	>20:1
6	5.0	>99(95)[d]	>20:1

[a] General conditions: **1a** (0.8 mmol), **2a** (0.4 mmol), Pd(*t*-$Bu_3P)_2$, $NH_2OH{\cdot}HCl$ (0.02 mmol), anisole (1.0 mL), CO (20 atm), 120 °C, 24 h. [b] Yields were based on amine and determined by GC analysis using *n*-hexadecane as the internal standard. [c] The ratios of **3aa** and **4aa** were determined by GC analysis. [d] Isolated yield was given in parenthesis.

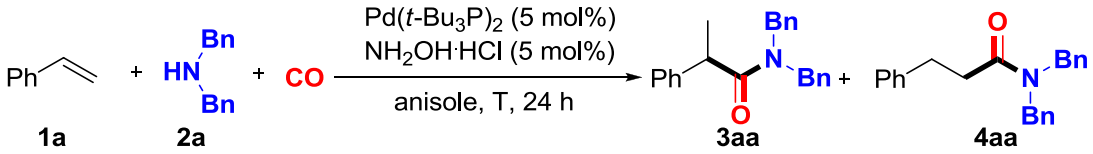
Table S5. Screening of the ratio of 2a/1a[a]



Entry	**2a**/**1a**	**3aa** + **4aa** (%)[b]	**3aa**/**4aa**[c]
1	1:1	40.7	>20:1
2	1:1.25	52.1	>20:1
3	1:1.5	94.3	>20:1
4	1:2	>99(95)[d]	>20:1
5	1:2.5	>99	>20:1

[a] General conditions: **1a**, **2a** (0.4 mmol), Pd(*t*-$Bu_3P)_2$ (0.02 mmol), $NH_2OH{\cdot}HCl$ (0.02 mmol), anisole (1.0 mL), CO (20 atm), 120 °C, 24 h. [b] Yields were based on amine and determined by GC analysis using *n*-hexadecane as the internal standard. [c] The ratios of **3aa** and **4aa** were determined by GC analysis. [d] Isolated yield was given in parenthesis.

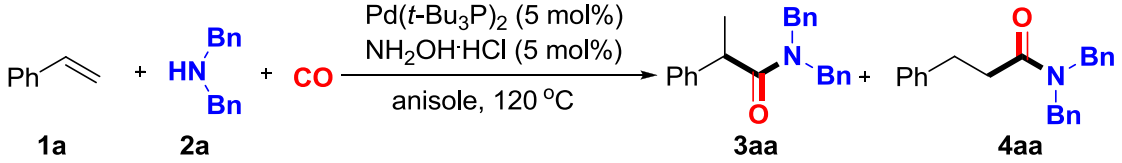
Table S6. Screening of the temperature [a]



Entry	T (°C)	**3aa** + **4aa** (%)[b]	**3aa**/**4aa**[c]
1	120	>99(95)[d]	>20:1
2	100	65.6	>20:1
3	80	9.1	>20:1

[a] General conditions: **1a** (0.8 mmol), **2a** (0.4 mmol), Pd(t-Bu$_3$P)$_2$ (0.02 mmol), NH$_2$OH·HCl (0.02 mmol), anisole (1.0 mL), CO (20 atm), 24 h. [b] Yields were based on amine and determined by GC analysis using *n*-hexadecane as the internal standard. [c] The ratios of **3aa** and **4aa** were determined by GC analysis. [d] Isolated yield was given in parenthesis.

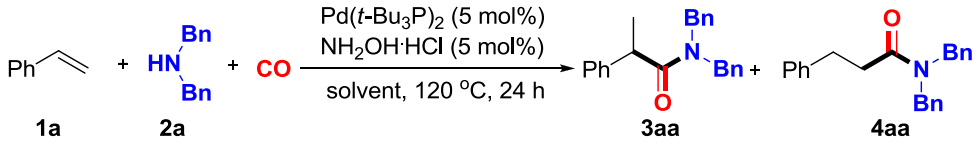
Table S7. Screening of the reaction time [a]



Entry	t (h)	**3aa** + **4aa** (%)[b]	**3aa**/**4aa**[c]
1	24	>99(95)[d]	>20:1
2	18	65.6	>20:1
3	12	59.6	>20:1

[a] General conditions: **1a** (0.8 mmol), **2a** (0.4 mmol), Pd(*t*-Bu$_3$P)$_2$ (0.02 mmol), NH$_2$OH·HCl (0.02 mmol), anisole (1.0 mL), CO (20 atm), 120 °C. [b] Yields were based on amine and determined by GC analysis using *n*-hexadecane as the internal standard. [c] The ratios of **3aa** and **4aa** were determined by GC analysis. [d] Isolated yield was given in parenthesis.

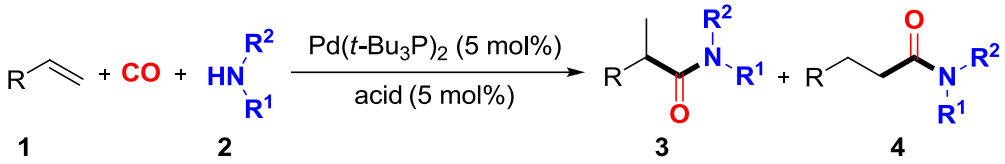
Table S8. Screening of the solvent [a]



Entry	solvent	**3aa** + **4aa** (%)[b]	**3aa**/**4aa**[c]
1	anisole	>99(95)[d]	>20:1
2	THF	98.8	94:6
3	toluene	38.2	>20:1
4	MeCN	8.1	>20:1

[a] General conditions: **1a** (0.8 mmol), **2a** (0.4 mmol), Pd(*t*-Bu$_3$P)$_2$ (0.02 mmol), NH$_2$OH·HCl (0.02 mmol), solvent (1.0 mL), CO (20 atm), 120 °C, 24 h. [b] Yields were based on amine and determined by GC analysis using *n*-hexadecane as the internal standard. [c] The ratios of **3aa** and **4aa** were determined by GC analysis. [d] Isolated yield was given in parenthesis.

4. General procedure for the hydroaminocarbonylation of aromatic alkenes

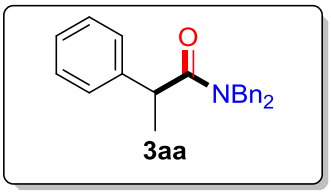


1 2 3 4

A mixture of alkenes **1** (0.8 mmol), amines **2** (0.4 mmol), Pd(*t*-$Bu_3P)_2$ (10.2 mg, 0.02 mmol), NH_2OH ·HCl (1.4 mg, 0.02 mmol) and anisole (1.0 mL) were added into a glass tube which was placed in an autoclave. Then the autoclave was purged and charged with CO at 20 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. The regioselectivity were measured by GC and GC-MS, respectively. Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (petroleum ether/ethyl acetate = 10/1 – 2/1) to give the desired products **3**.

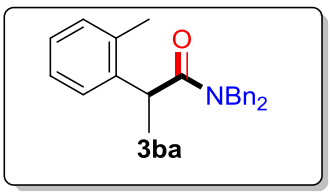
5. Experimental characterization data for products

***N,N*-Dibenzyl-2-phenylpropanamide (3aa):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 125.0 mg, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.48 (d, *J* = 6.8 Hz, 3H), 3.85 (q, *J* = 6.8 Hz, 1H), 4.09-4.17 (m, 2H), 4.52 (d, *J* = 16.8 Hz, 1H), 5.09 (d, *J* = 14.8 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 2H), 7.11 (d, *J* = 7.2 Hz, 2H), 7.20-7.34 (m, 11H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.1, 43.4, 48.5, 49.7, 126.4, 127.0, 127.3, 127.4, 127.6, 128.2, 128.6, 129.0, 136.8, 137.5, 141.9, 174.4; **HRMS** (ESI) calcd. for $C_{23}H_{24}NO$ [M+H]: 330.1852, found: 330.1855.



3aa

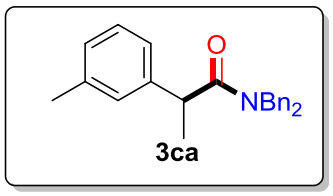
***N,N*-Dibenzyl-2-(*o*-tolyl)propanamide (3ba):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 102.9 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.33 (d, *J* = 6.8 Hz, 3H), 2.11 (s, 3H), 3.86-3.95 (m, 3H), 4.20 (d, *J* = 17.2 Hz,



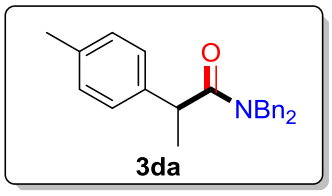
3ba

1H), 5.17 (d, *J* = 14.8 Hz, 1H), 6.94 (d, *J* = 6.8 Hz, 2H), 7.03-7.28 (m, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.0, 19.4, 39.8, 48.3, 49.3, 126.2, 126.5, 126.9, 127.0, 127.3, 127.5, 128.2, 128.5, 128.9, 130.7, 134.4, 136.7, 137.5, 140.3, 174.8; **HRMS** (ESI) calcd. for $C_{24}H_{25}NONa$ [M+Na]: 366.1828, found: 366.1836.

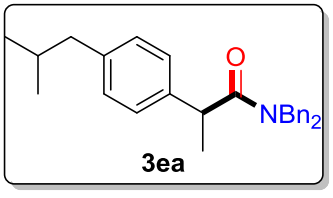
***N,N*-Dibenzyl-2-(*m*-tolyl)propanamide (3ca):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 127 mg, 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.40 (d, *J* = 6.8 Hz, 3H), 2.23 (s, 3H), 3.74 (q, *J* = 6.8 Hz, 1H), 3.96-4.06 (m, 2H), 4.45 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 14.8 Hz, 1H), 6.96-7.01 (m, 5H), 7.06-7.28 (m, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.1, 21.5, 43.4, 48.5, 49.7, 124.6, 126.4, 127.3, 127.6, 127.7, 127.9, 128.2, 128.6, 128.9 ,129.0, 136.8, 137.6, 138.6, 141.8, 174.4; **HRMS** (ESI) calcd. for $C_{24}H_{25}NONa$ [M+Na]: 366.1828, found: 366.1840.



***N,N*-Dibenzyl-2-(*p*-tolyl)propanamide (3da):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 124.5mg, 91% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.38 (d, *J* = 6.8 Hz, 3H), 2.23 (s, 3H), 3.73 (q, *J* = 6.8 Hz, 1H), 3.97-4.07 (m, 2H), 4.45 (d, *J* = 17.2 Hz, 1H), 5.05 (d, *J* = 14.8 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 2H), 7.02-7.27 (m, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.1, 21.2, 43.0, 48.4, 49.6, 126.3, 127.2, 127.3, 127.5, 128.2, 128.5, 128.9, 129.6, 136.6 , 136.8, 137.5, 138.8, 174.5; **HRMS** (ESI) calcd. for $C_{24}H_{25}NONa$ [M+Na]: 366.1828, found: 366.1840.

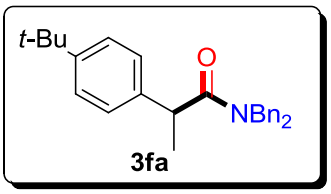


***N,N*-Dibenzyl-2-(4-isobutylphenyl)propanamide (3ea):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 141.7 mg, 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.89 (d, *J* = 6.4 Hz, 6H), 1.48 (d, *J* = 6.8 Hz, 3H), 1.79-1.89 (m, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 3.84 (q, *J* = 6.8 Hz, 1H), 4.15-4.21 (m, 2H), 4.52 (d, *J* = 16.8 Hz, 1H), 5.02 (d, *J* = 15.2 Hz, 1H), 7.01 (d, *J* = 6.4 Hz, 2H); 7.07-7.11 (m, 4H), 7.18-7.34

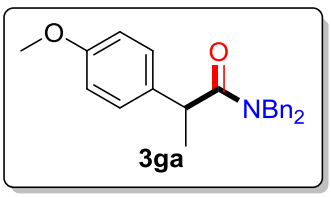


(m, 8H), **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.0, 22.4, 22.4, 30.2, 43.0, 45.0, 48.2, 49.6, 126.4, 127.1, 127.2, 127.5, 128.1, 128.5, 128.9, 129.6, 136.8, 137.5, 139.0, 140.4, 174.6; **HRMS** (ESI) calcd. for $C_{27}H_{31}NONa$ [M+Na]: 408.2298, found: 408.2299.

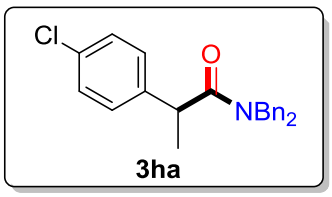
***N,N*-Dibenzyl-2-(4-(tert-butyl)phenyl)propanamide (3fa):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 150.3 mg, 98% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.31 (s, 9H) 1.48 (d, *J* = 6.8 Hz, 3H), 3.85 (q, *J* = 6.8 Hz, 1H), 4.20 (d, *J* = 15.2 Hz, 2H), 4.51 (d, *J* = 17.2 Hz, 1H), 4.96 (d, *J* = 14.8 Hz, 1H), 6.98 (d, *J* = 6.8 Hz, 2H), 7.11-7.13 (m, 2H), 7.20-7.32 (m, 10H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.0, 31.4, 34.5, 42.8, 48.3, 49.7, 125.8, 126.4, 127.1, 127.2, 127.5, 128.2, 128.5, 128.9, 136.8, 137.6, 138.7, 149.8, 174.6; **HRMS** (ESI) calcd. for $C_{27}H_{31}NONa$ [M+Na]: 408.2298, found: 408.2312.



***N,N*-Dibenzyl-2-(4-methoxyphenyl)propanamide (3ga):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 41 mg, 29% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.45 (d, *J* = 6.8 Hz, 3H), 3.78 (s, 3H), 3.81 (q, *J* = 6.8 Hz, 1H), 4.09-4.18 (m, 2H), 4.54 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 14.8 Hz , 1H), 6.83-6.85 (m, 2H), 7.05 (d, *J* = 7.2 Hz, 2H), 7.11-7.13 (m, 2H), 7.18-7.36 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.2, 42.5, 48.4, 49.6, 55.3, 114.3, 126.3, 127.3, 127.5, 128.1, 128.4, 128.5, 128.9, 133.9, 136.8, 137.5, 158.6, 174.7; **HRMS** (ESI) calcd. for $C_{24}H_{25}NO_2Na$ [M+Na]: 382.1778, found: 382.1783.

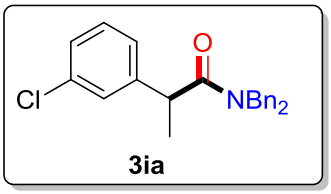


***N,N*-Dibenzyl-2-(4-chlorophenyl)propanamide (3ha):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 137.5 mg, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.46 (d, *J* = 6.8 Hz, 3H), 3.83 (q, *J* = 6.8 Hz, 1H), 4.15-4.22 (m, 2H), 4.49 (d, *J* = 17.2 Hz, 1H), 5.04 (d, *J* = 14.8 Hz, 1H), 7.04 (d, *J* = 6.8 Hz, 2H), 7.12-7.14 (m,



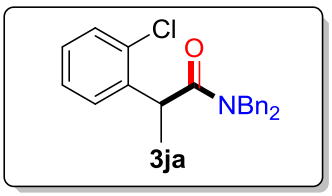
2H), 7.19-7.37 (m, 10H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.0, 42.6, 48.6, 49.7, 126.2, 127.4, 127.7, 128.1, 128.6, 128.8, 129.0, 132.8, 136.5, 137.3, 140.2, 174.0; **HRMS** (ESI) calcd. for $C_{23}H_{23}ClNO$ [M+H]: 386.1284, found: 386.1290.

***N,N*-Dibenzyl-2-(3-chlorophenyl)propanamide (3ia):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 121.3 mg, 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.39 (d, *J* = 6.8 Hz, 3H), 3.75 (q, *J* = 6.8 Hz, 1H), 4.06-4.12 (m, 2H), 4.41 (d, *J* = 17.2 Hz, 1H), 5.00 (d, *J* = 14.8 Hz, 1H), 6.97 (d, *J* = 6.8 Hz, 2H), 7.05-7.08 (m, 3H), 7.11-7.29 (m, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.9, 42.9, 48.7, 49.7, 125.6, 126.2, 127.2, 127.4, 127.6, 127.7, 128.1, 128.6, 129.0, 130.1, 134.7, 136.5, 137.3, 143.7, 173.8; **HRMS** (ESI) calcd. for $C_{23}H_{23}ClNO$ [M+H]: 386.1284, found: 386.1290.



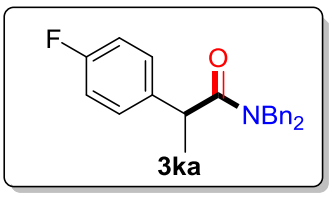
3ia

***N,N*-Dibenzyl-2-(2-chlorophenyl)propanamide (3ja):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 103.6 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.44 (d, *J* = 6.8 Hz, 3H), 4.12 (d, *J* = 15.2 Hz, 2H), 4.38-4.45 (m, 2H), 5.07 (d, *J* = 14.8 Hz, 1H), 7.02-7.04 (m, 2H), 7.12-7.33 (m, 11H), 7.50-7.52 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.3, 39.5, 48.2, 49.5, 126.5, 127.3, 127.5, 127.5, 128.1, 128.3, 128.5, 128.5, 128.8, 129.6, 132.7, 136.5, 137.3, 139.3, 174.0; **HRMS** (ESI) calcd. for $C_{23}H_{23}ClNO$ [M+H]: 386.1284, found: 386.1290.



3ja

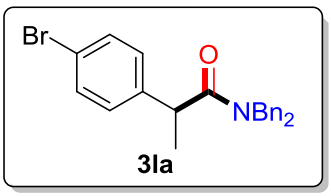
***N,N*-Dibenzyl-2-(4-fluorophenyl)propanamide (3ka):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 128.0 mg, 92% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.46 (d, *J* = 6.8 Hz, 3H), 3.85 (q, *J* = 6.8 Hz, 1H), 4.17-4.23 (m, 2H), 4.50 (d, *J* = 17.2 Hz, 1H), 5.02 (d, *J* = 14.8 Hz, 1H), 6.96-7.00 (m, 2H), 7.04-7.13 (m, 4H), 7.22-7.36 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.1, 42.4, 48.6, 49.7, 115.6 (d, *J* = 21.2 Hz), 126.2, 127.4 (d, *J* = 27.1 Hz), 128.1, 128.6, 128.9, 129.0, 129.0, 136.6, 137.4,



3ka

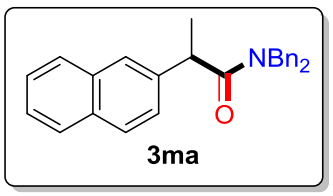
137.5 (d, *J* = 3.0 Hz), 160.6 (d, *J* = 243.9 Hz), 174.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.77; **HRMS** (ESI) calcd. for $C_{23}H_{22}FNONa$ [M+Na]: 370.1578, found: 370.1572.

***N,N*-Dibenzyl-2-(4-bromophenyl)propanamide (3la):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 23.1 mg, 14% yield. **^{1}H NMR** (400 MHz, CDCl3) δ 1.46 (d, *J* = 6.8 Hz, 3H), 3.81 (q, *J* = 6.8 Hz, 1H), 4.14-4.22 (m, 2H), 4.48 (d, *J* = 17.2 Hz, 1H), 5.04 (d, *J* = 14.8 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.12-2.16(m, 4H), 7.24-7.37 (m, 6H), 7.40-7.43 (m, 2H); **^{13}C NMR** (100 MHz, CDCl3) δ 21.0, 42.7, 48.7, 49.7, 120.9, 126.2, 127.4, 127.4, 127.7, 128.1, 128.6, 128.9, 129.0, 129.2, 132.0, 136.5, 137.3, 140.8, 173.9; **HRMS** (ESI) calcd. for $C_{23}H_{22}BrNONa$ [M+Na]: 430.0777, found: 430.0792.



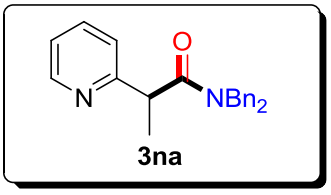
3la

***N,N*-Dibenzyl-2-(naphthalen-2-yl)propanamide (3ma):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 143.9mg, 95% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.56 (d, *J* = 7.2 Hz, 3H), 4.01-4.11 (m, 3H), 4.59 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 14.8 Hz, 1H), 7.06 (d, *J* = 6.8 Hz, 2H), 7.14-7.16 (m, 2H), 7.19-7.34 (m, 6H), 7.41-7.47 (m, 3H), 7.66 (s, 1H), 7.72-7.74 (m, 1H), 7.79-7.81 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.1, 43.5, 48.6, 49.8, 125.7, 125.8, 125.9, 126.3, 126.3, 127.3, 127.6, 127.7, 127.7, 128.2, 128.6, 128.8, 129.0, 132.5, 133.7, 136.8, 137.5, 139.3, 174.3; **HRMS** (ESI) calcd. for $C_{27}H_{25}NONa$ [M+Na]: 402.1828, found: 402.1841.



3ma

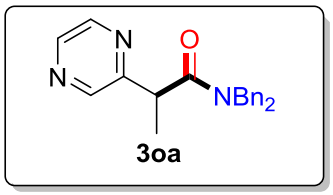
***N,N*-Dibenzyl-2-(pyridin-2-yl)propanamide (3na):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 113.6 mg, 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.57 (d, *J* = 6.8 Hz, 3H), 4.15-4.27 (m, 3H), 4.75 (d, *J* = 17.2 Hz, 1H), 5.03 (d, *J* = 14.8 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 2H), 7.12-7.14 (m, 3H), 7.20-7.32 (m, 6H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.62-7.66 (m, 1H), 8.46 (dd, J_1 = 0.8 Hz, J_2 = 4.0 Hz, 1H); **^{13}C NMR**



3na

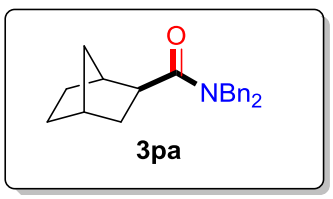
(100 MHz, $CDCl_3$) δ 18.5, 43.6, 48.7, 49.9, 126.2, 127.5, 127.7, 128.2, 128.6, 129.0, 136.3, 137.1, 143.0, 143.8, 143.9, 156.6, 172.9; **HRMS** (ESI) calcd. for $C_{22}H_{23}N_2O$ [M+H]: 331.1805, found: 331.1801.

***N,N*-Dibenzyl-2-(pyrazin-2-yl)propanamide (3oa):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 79.6 mg, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.61 (d, *J* = 6.8 Hz, 3H), 4.23 (q, *J* = 7.2 Hz, 1H), 4.33-4.37 (m, 2H), 4.64 (d, *J* = 17.2 Hz, 1H), 4.93 (d, *J* = 14.8 Hz, 1H), 7.07 (d, *J* = 6.8 Hz, 2H), 7.16-7.18 (m, 2H), 7.24-7.36 (m, 6H), 8.44 (s, 2H), 8.67 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.5, 43.6, 48.7, 49.9, 126.2, 127.5, 127.7, 128.2, 128.6, 129.0, 136.3, 137.1, 143.0, 143.8, 143.9, 156.6, 172.9; **HRMS** (ESI) calcd. for $C_{21}H_{22}N_3O$ [M+H]: 332.1757, found: 332.1769.



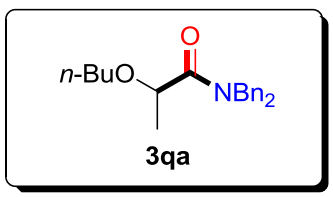
3oa

***N,N*-Dibenzylbicyclo[2.2.1]heptane-2-carboxamide (3pa):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 105.0 mg, 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.13-1.15 (m, 2H), 1.20-1.26 (m, 1H), 1.40-1.53 (m, 3H), 1.74-1.77 (m, 1H), 1.99-2.02 (m, 1H), 2.32 (s, 1H), 2.44-2.50 (m, 2H), 4.38-4.44 (m, 2H), 4.51 (d, *J* = 17.2 Hz, 1H), 4.71 (d, *J* = 14.8 Hz, 1H), 7.14-7.18 (m, 4H), 7.22-7.38 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 28.8, 29.7, 35.3, 36.1, 36.7, 41.3, 44.0, 47.8, 49.6, 126.6, 127.3, 127.6, 128.1, 128.6, 128.9, 136.9, 137.9, 176.1; **HRMS** (ESI) calcd. for $C_{22}H_{26}NO$ [M+H]: 320.2009, found: 320.2018.



3pa

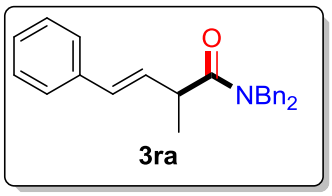
***N,N*-Dibenzyl-2-butoxypropanamide (3qa):** The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 37.5 mg, 29% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.25-1.35 (m, 2H), 1.42-1.51 (m, 5H), 3.33-3.38 (m, 1H), 3.45-3.50 (m, 1H), 4.29 (q, *J* = 6.8 Hz, 1H), 4.43 (d, *J* = 14.8 Hz, 1H), 4.59 (s, 2H), 4.71 (d, *J* = 14.4 Hz, 1H), 7.16-7.21 (m, 4H), 7.26-7.38 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$)



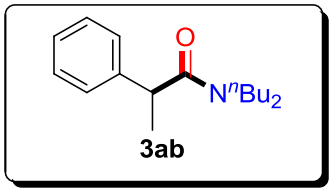
3qa

δ 13.8, 17.9, 19.3, 31.8, 48.1, 49.0, 69.0, 74.9, 126.7, 127.4, 127.5, 128.3, 128.6, 128.8, 136.7, 137.2, 172.9; **HRMS** (ESI) calcd. for $C_{21}H_{28}NO_2$ [M+H]: 326.2115, found: 326.2116.

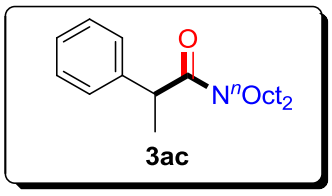
***N,N*-Dibenzylheptadecanamide (3ra):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 24.9 mg, 18% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.37 (d, *J* = 6.8 Hz, 3H), 3.51-3.58 (m, 1H), 4.36-4.43 (m, 2H), 4.62 (d, *J* = 17.2 Hz, 1H), 4.87 (d, *J* = 14.8 Hz, 1H), 6.29-6.40 (m, 2H), 7.16-7.39 (m, 15H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.9, 40.5, 48.5, 49.8, 126.3, 126.3, 127.4, 127.5, 127.6, 128.3, 128.5, 128.6, 128.7, 129.0, 130.2, 130.8, 136.8, 136.9, 137.5, 174.8; **HRMS** (ESI) calcd. for $C_{25}H_{25}NONa$ [M+Na]: 378.1828, found: 378.1825.



***N,N*-Dibutyl-2-phenylpropanamide (3ab):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 59.7 mg, 57% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.86-0.92 (m, 6H), 1.19-1.32 (m, 5H), 1.40-1.51 (m, 6H), 2.93-3.01 (m, 1H), 3.08-3.15 (m, 1H), 3.22-3.29 (m, 1H), 3.44-3.52 (m, 1H), 3.79 (q, *J* = 6.8 Hz, 1H), 7.20-7.32 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13.8, 13.9, 20.1, 20.2, 21.0, 29.7, 31.2, 43.2, 45.9, 47.4, 126.6, 127.3, 128.7, 142.5, 173.1; **HRMS** (ESI) calcd. for $C_{17}H_{27}NONa$ [M+Na]: 284.1985, found: 284.1973.

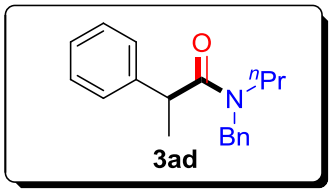


***N,N*-Dioctyl-2-phenylpropanamide (3ac):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 90.2 mg, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.85-0.91 (m, 6H), 1.17-1.32 (m, 21H), 1.42-1.49 (m, 6H), 2.93-3.00 (m, 1H), 3.06-3.14 (m, 1H), 3.20-3.28 (m, 1H), 3.44-3.51 (m, 1H), 3.79 (q, *J* = 6.8 Hz, 1H), 7.20-7.32 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.1, 21.0, 22.6, 22.6, 26.9, 27.0, 27.6, 29.1, 29.2, 29.3, 29.4, 31.8, 31.8, 43.2, 46.1, 47.6, 126.6, 127.3, 128.7, 142.5, 173.1;



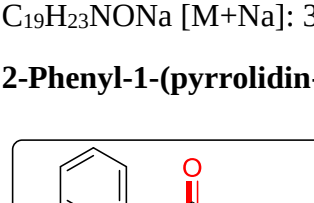
HRMS (ESI) calcd. for $C_{25}H_{44}NO$ [M+H]: 374.3417, found: 374.3426.

***N*-Benzyl-2-phenyl-*N*-propylpropanamide (3ad):** The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 80.5 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.76-0.84 (m, 3H), 1.30-1.34 (m, 0.5H), 1.41 (d, *J* = 6.8 Hz, 1.5H), 1.45-1.56 (m, 3H), 2.92-3.00(m, 1H), 3.18-3.23 (m, 0.5H), 3.67-3.79 (m, 1H), 3.90 (q, *J* = 6.8 Hz, 0.5H), 4.19 (d, *J* = 17.2 Hz, 0.5H), 4.40 (d, *J* = 15.2 Hz, 0.5H), 4.58 (d, *J* = 17.2 Hz, 0.5H), 4.79 (d, *J* = 14.8 Hz, 0.5H), 7.06 (d, *J* = 6.8 Hz, 1H), 7.13 (d, *J* = 6.8 Hz, 1H), 7.20-7.35 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 11.2, 11.3, 20.6, 21.0, 21.1, 21.8, 43.2, 43.4, 48.2, 48.3, 48.4, 50.6, 126.1, 126.8, 126.9, 127.1, 127.3, 127.4, 127.8, 128.4, 128.8, 128.9, 128.9, 137.3, 138.0, 142.2, 173.8, 174.0; **HRMS** (ESI) calcd. for $C_{19}H_{23}NONa$ [M+Na]: 304.1672, found: 304.1672.



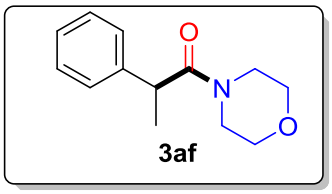
3ad

2-Phenyl-1-(pyrrolidin-1-yl)propan-1-one (3ae): The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 67.7 mg, 83% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.44 (d, *J* = 6.8 Hz, 3H), 1.73-1.90 (m, 4H), 3.13-3.18 (m, 1H), 3.38-3.57 (m, 3H), 3.71 (q, *J* = 6.8 Hz, 1H) , 7.21-7.24 (m, 1H), 7.28-7.33 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.3, 24.2, 26.1, 45.0, 46.0, 46.2, 126.7, 127.6, 128.7, 141.8, 172.2; **HRMS** (ESI) calcd. for $C_{13}H_{17}NONa$ [M+Na]: 226.1202, found: 226.1201.



3ae

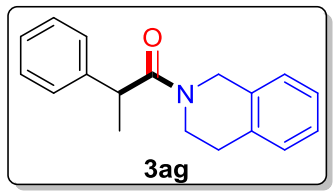
1-Morpholino-2-phenylpropan-1-one (3af): The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 78.6 mg, 90% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.45 (d, *J* = 6.8 Hz, 3H), 3.07-3.13 (m, 1H), 3.27-3.32 (m, 1H), 3.36-3.42 (m, 1H), 3.46-3.55 (m, 3H), 3.63-3.68 (m, 1H), 3.77-3.87 (m, 2H), 7.22-7.27 (m, 3H) , 7.30-7.34 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.6, 42.4, 43.3, 46.0, 66.3, 66.8, 126.9, 127.2, 129.0, 141.9, 172.2; **HRMS** (ESI) calcd. for $C_{13}H_{17}NO_2Na$ [M+Na]: 242.1151, found:



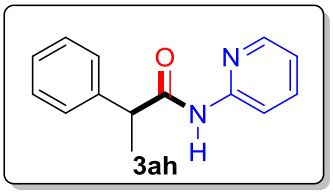
3af

242.1157.

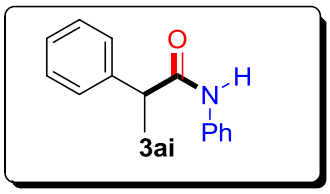
1-(3,4-Dihydroisoquinolin-2(1H)-yl)-2-phenylpropan-1-one (3ag): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 75.4 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.47 (dd, J_1 = 2.4 Hz, J_2= 4.4 Hz, 3H), 2.31-2.38 (m, 0.65H), 2.62-2.69 (m, 0.64H), 2.75-2.89(m, 0.72H), 3.56-3.59 (m, 1.30H), 3.67-3.73 (m, 0.38H), 3.93-4.01 (m, 1.35H), 4.32 (d, *J* = 16.0 Hz, 0.35H), 4.61 (d, *J* = 16.0 Hz, 0.36H), 4.68 (d, *J* = 17.2 Hz, 0.64H), 4.81 (d, *J* = 17.2 Hz, 0.65H), 6.88 (d, *J* = 7.2 Hz, 0.36H), 7.00 (d, *J* = 7.2 Hz, 0.64H), 7.10-7.33 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.7, 20.8, 28.5, 29.1, 40.2, 43.0, 43.8, 43.8, 44.6, 47.3, 125.9, 126.2, 126.4, 126.5, 126.7, 126.8, 126.8, 127.3, 127.3, 128.3, 128.7, 128.9, 129.0, 132.7, 133.5, 134.1, 135.1, 141.8, 142.0, 172.5, 172.6; **HRMS** (ESI) calcd. for $C_{18}H_{19}NONa$ [M+Na]: 288.1359, found: 288.1349.



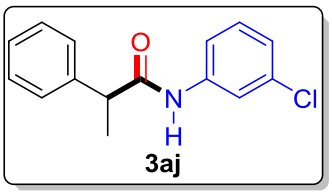
2-Phenyl-*N*-(pyridin-2-yl)propanamide (3ah): The title compound was prepared according to the general procedure and purified by column chromatography to give the colorless oil, 63.9 mg, 71% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.58 (d, *J* = 7.2 Hz, 3H), 3.69 (q, *J* = 7. 2 Hz, 1H), 6.97-7.01 (m, 1H), 7.26-7.37 (m, 5H), 7.65-7.69 (m, 1H), 8.09 (br, 1H), 8.17-8.19(m, 1H), 8.22 (d, *J* = 8.4 Hz, 1H);**^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.5, 48.2, 113.9, 119.7, 127.6, 129.2, 138.4, 140.5, 147.7, 151.4, 172.7; **HRMS** (ESI) calcd. for $C_{14}H_{15}N_2O$ [M+H]: 227.1179, found: 227.1187.



***N*,2-Diphenylpropanamide (3ai):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 85.7 mg, 95% yield. **^{1}H NMR** (400 MHz, CDCl3) δ 1.59 (d, *J* = 7.2 Hz, 3H), 3.69 (q, *J* = 7.2 Hz, 1H), 7.04-7.10 (m, 2H), 7.24-7.35 (m, 3H), 7.36-7.42 (m, 6H); **^{13}C NMR** (100 MHz, CDCl3) δ 18.6, 48.1, 119.7, 124.3, 127.6, 127.7, 128.9, 129.2, 137.9, 140.9, 172.4; **HRMS** (ESI) calcd. for $C_{15}H_{16}NO$ [M+H]: 226.1226, found: 226.1222.

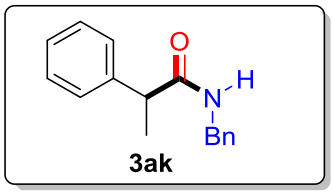


***N*-(3-Chlorophenyl)-2-phenylpropanamide (3aj):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 83.9 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.57 (d, *J* = 7.2 Hz, 3H), 3.68 (q, *J* = 6.8 Hz, 1H), 7.01-7.03 (m, 1H), 7.13-7.17 (m, 1H), 7.23-7.39 (m, 7H), 7.54 (d, *J* = 1.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.5, 48.1, 117.8, 119.9, 124.3, 127.7, 127.7, 129.2, 129.9, 134.6, 139.0, 140.6, 172.6; **HRMS** (ESI) calcd. for $C_{15}H_{15}ClNO$ [M+H]: 260.0837, found: 260.0825.



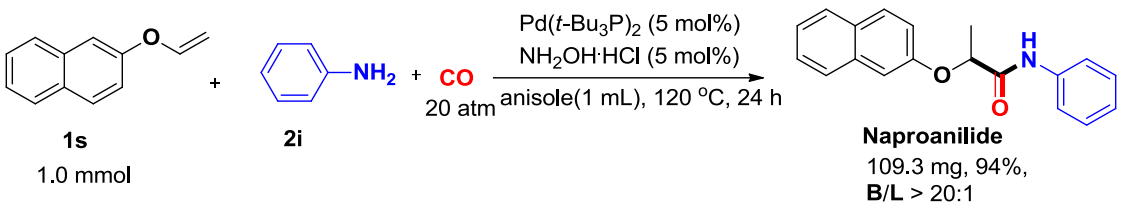
3aj

***N*-Benzyl-2-phenylpropanamide (3ak):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 15.8 mg, 17% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.54 (d, *J* = 7.2 Hz, 3H), 3.57 (q, *J* = 7.2 Hz, 1H), 4.33-4.43 (m, 2H), 5.69 (br, 1H), 7.13-7.15 (m, 2H), 7.21-7.36 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.6, 43.6, 47.2, 127.3, 127.4, 127.5, 127.7, 128.6, 129.0, 138.3, 141.3, 174.1; **HRMS** (ESI) calcd. for $C_{16}H_{18}NO$ [M+H]: 240.1383, found: 240.1394.



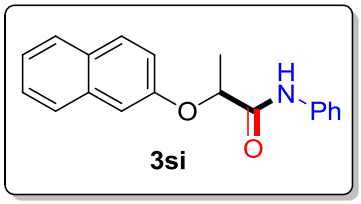
3ak

6. Synthesis of naproanilide



A mixture of **1s** (136 mg, 0.8 mmol), **2i** (37 mg, 0.4 mmol), Pd(*t*-$Bu_3P)_2$ (10.2 mg, 0.02 mmol), $NH_2OH·HCl$ (1.4 mg, 0.02 mmol) and anisole (1.0 mL) were added into a glass tube which was placed in an autoclave. Then the autoclave was purged and charged with CO (20 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. Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (petroleum ether/ethyl acetate = 50/1 - 10/1) to give the desired products naproanilide in 94 % yield (109.3 g) with excellent regioselectivity (**B/L** > 20:1).

Naproanilide (3si): The title compound was prepared according to the above procedure



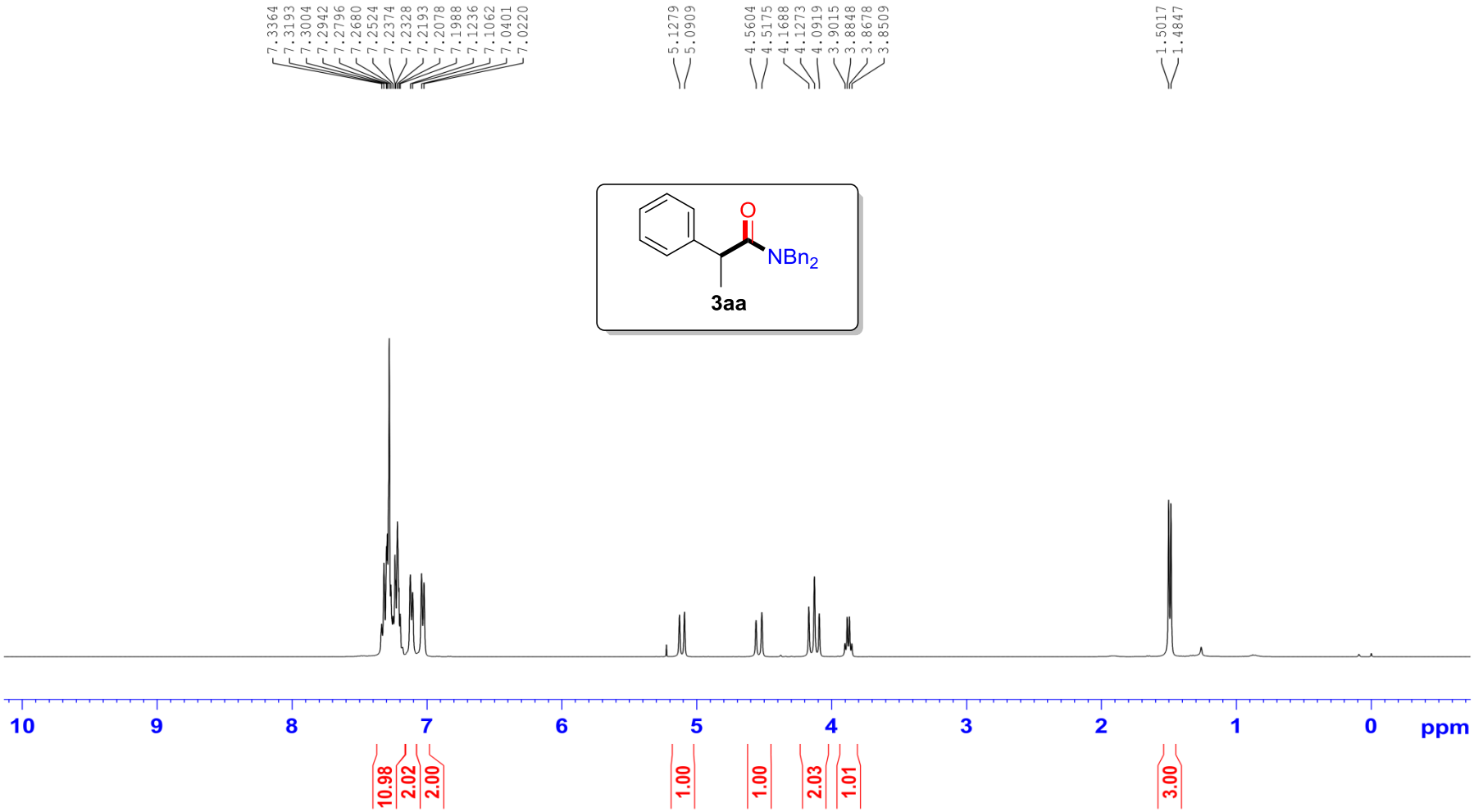
and purified by column chromatography to give a white solid, 109.3 mg, 94% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.71 (d, *J* = 6.8 Hz, 3H), 4.90 (q, *J* = 6.8 Hz, 1H), 7.08-7.12 (m, 1H), 7.22-7.28 (m, 2H), 7.30-7.32 (m, 2H), 7.35-7.39 (m, 1H), 7.42-7.46 (m, 1H), 7.53 (d, *J* = 0.8 Hz, 2H), 7.55 (d, *J* = 1.2 Hz, 1H), 7.71-7.81 (m, 2H), 5.69 (br, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.8, 75.6, 109.2, 118.5, 120.0, 124.6, 124.8, 126.8, 127.1, 127.7, 129.1, 129.7, 130.1, 134.3, 137.1, 154.5, 170.3; **HRMS** (ESI) calcd. for $C_{19}H_{17}NO_2Na$ [M+Na]: 314.1151, found: 314.1156.

7. References

1. B. A. Trofimov, L. A. Oparina, N. A. Kolyvanov, O. V. Vysotskaya, and N. K. Gusarova, *Russ. J. Org. Chem.*, 2015, **51**, 2.

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

ZJP-X160316-1-HNMR(7)



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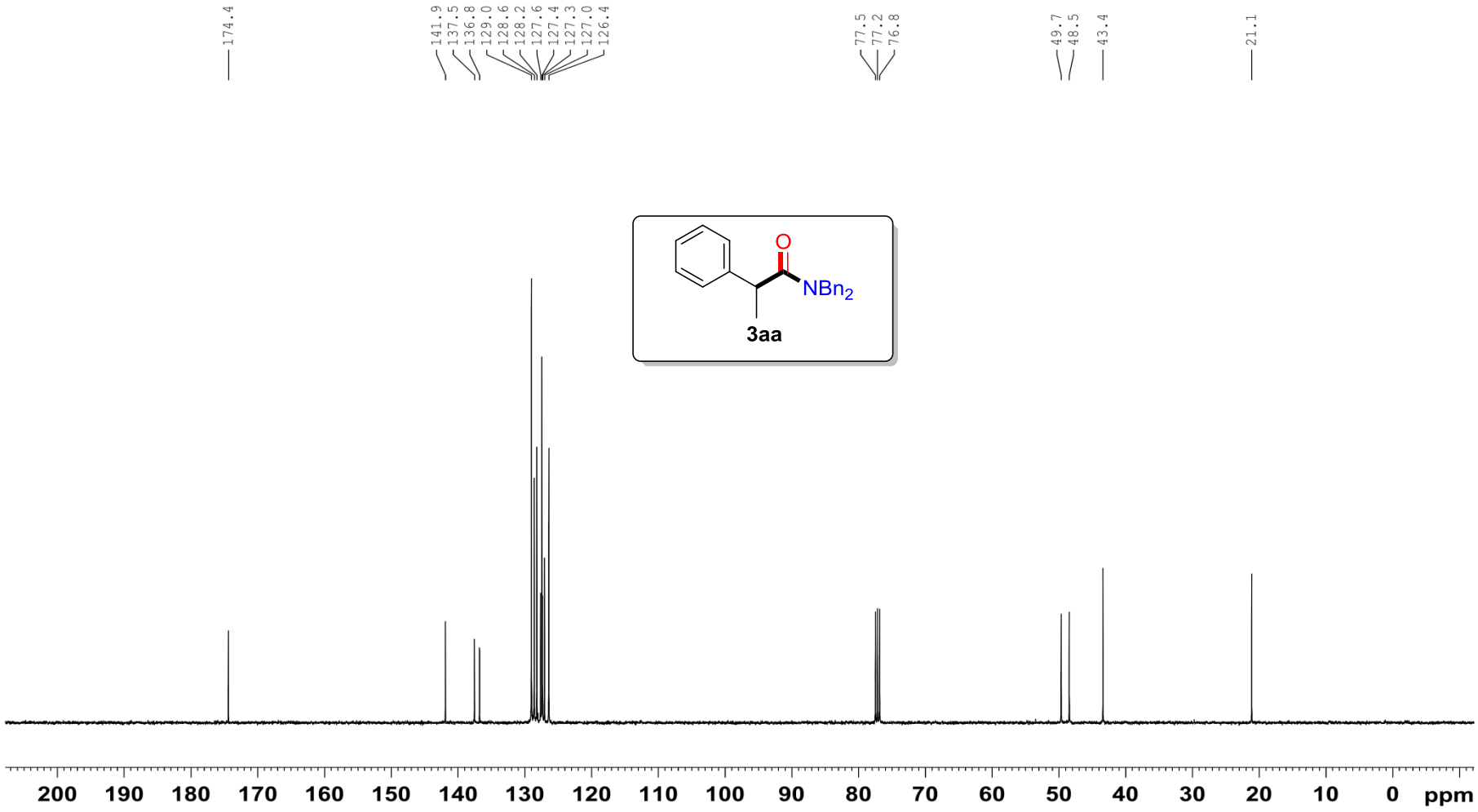

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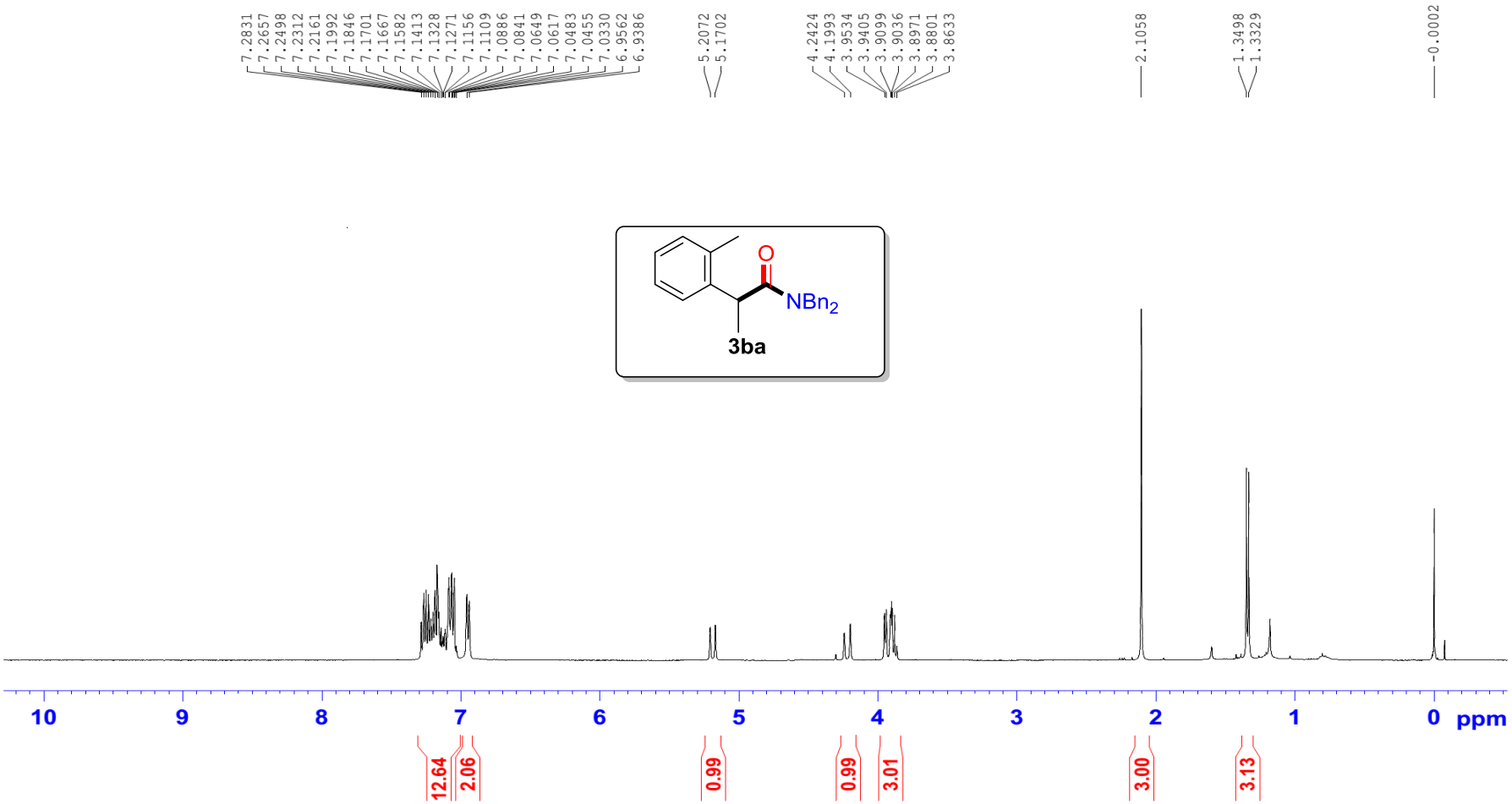

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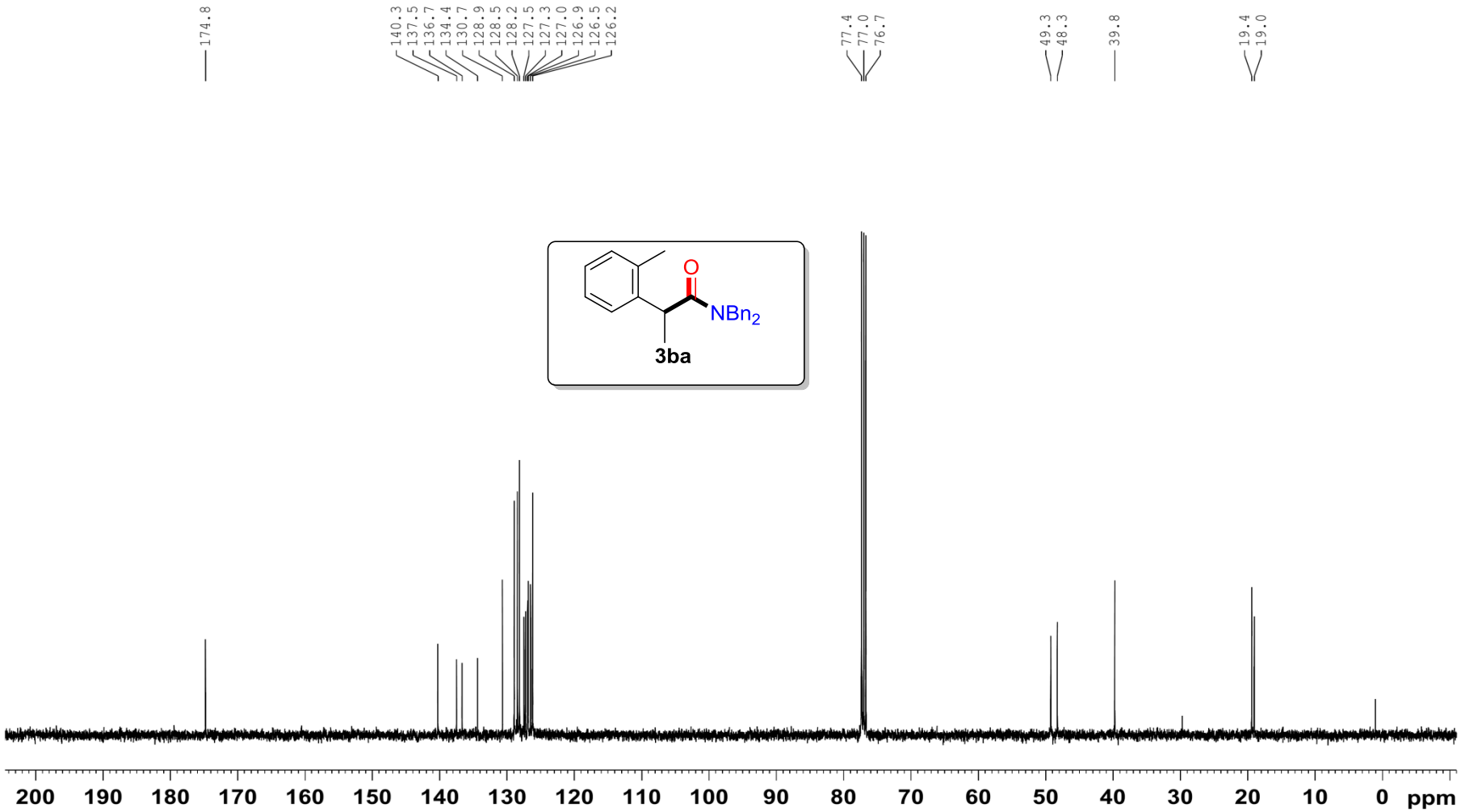

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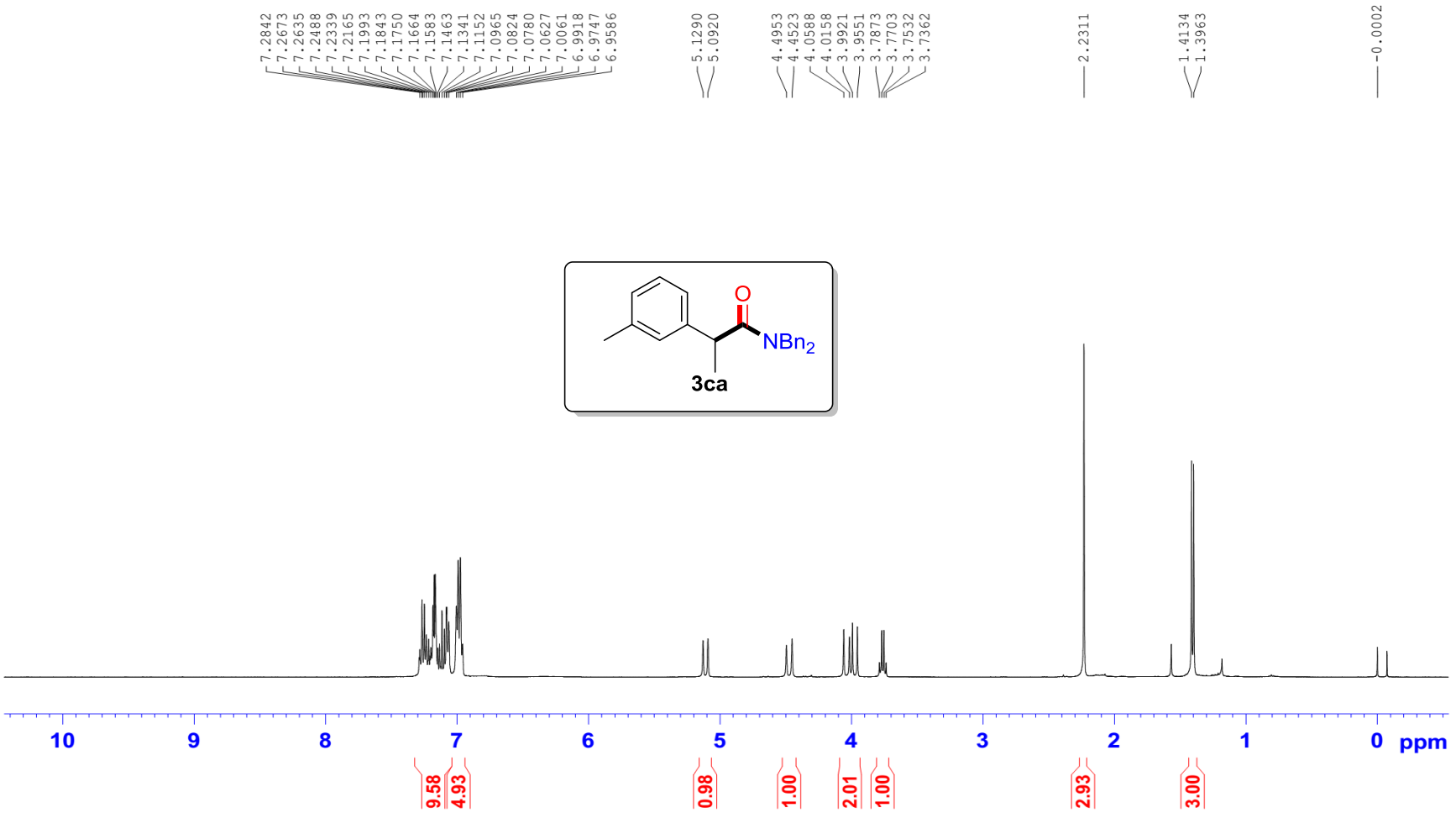

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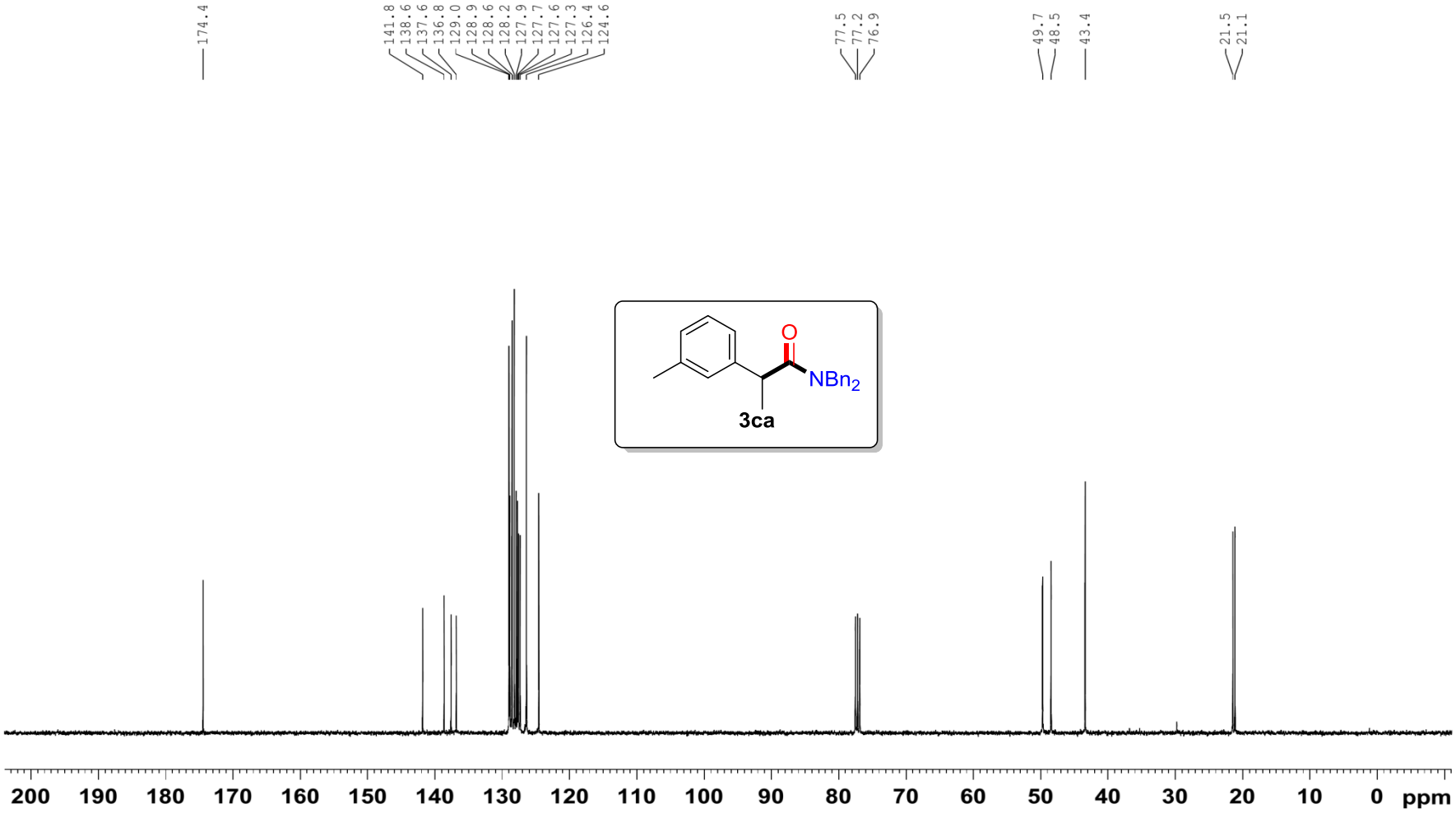

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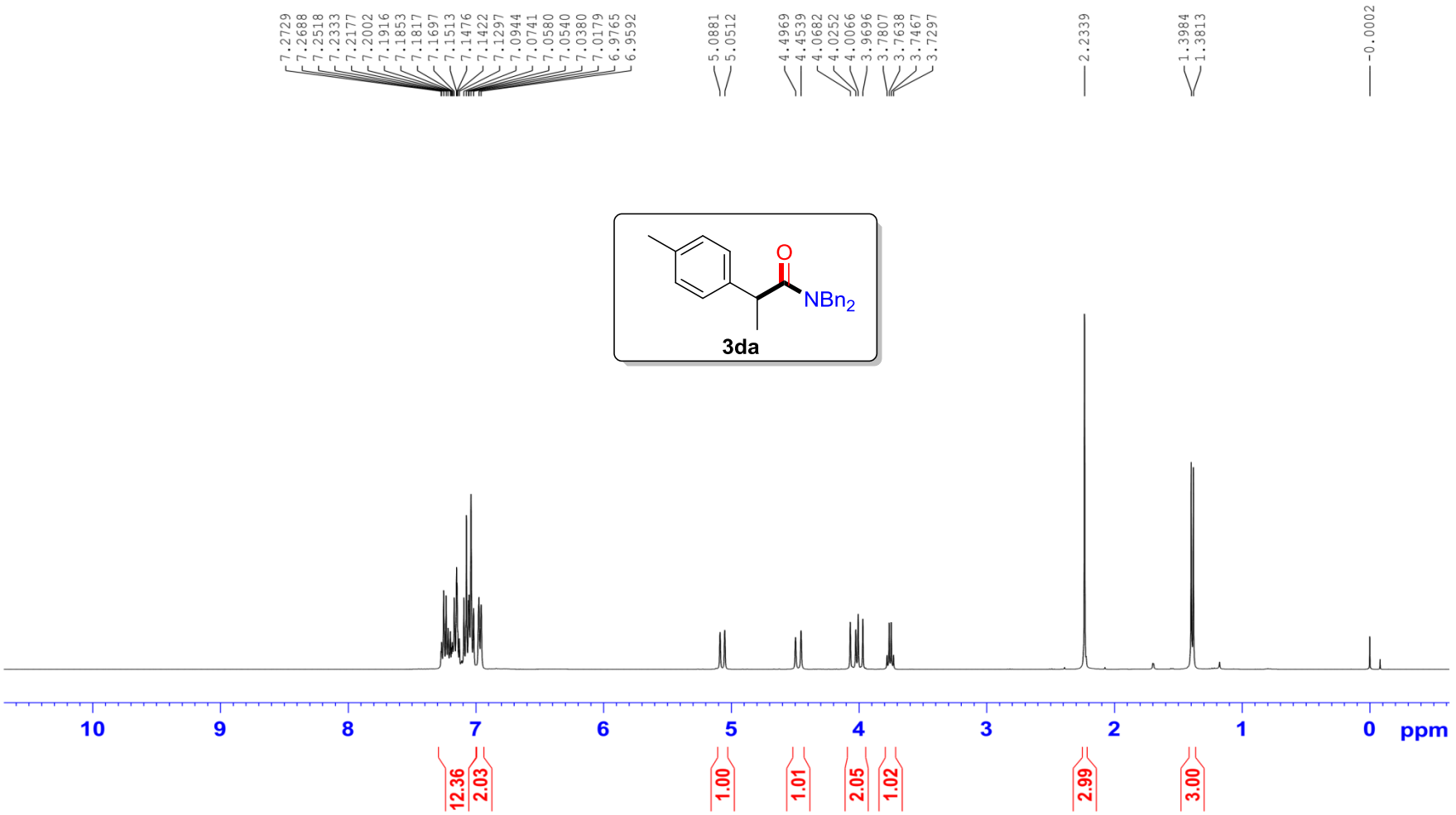

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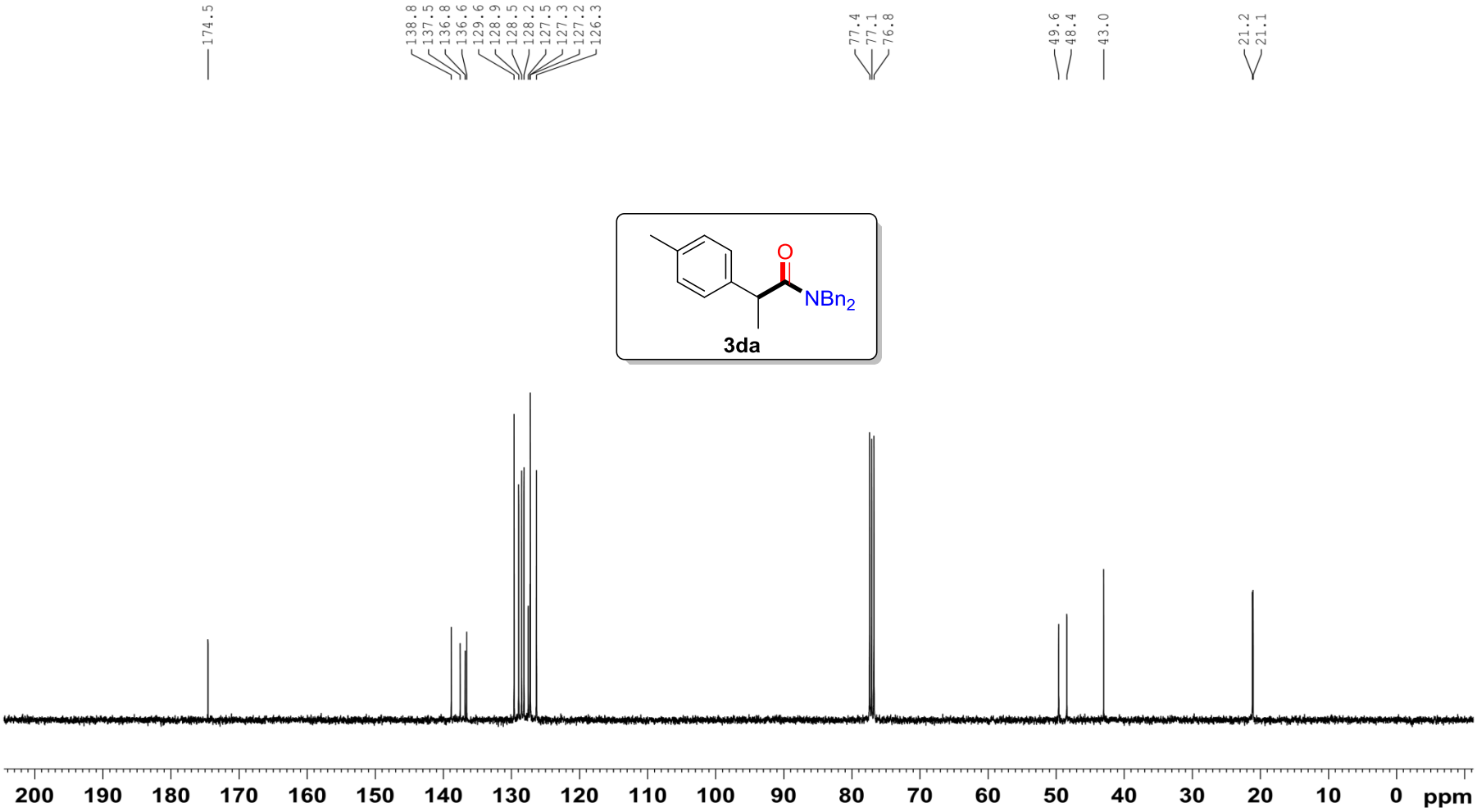

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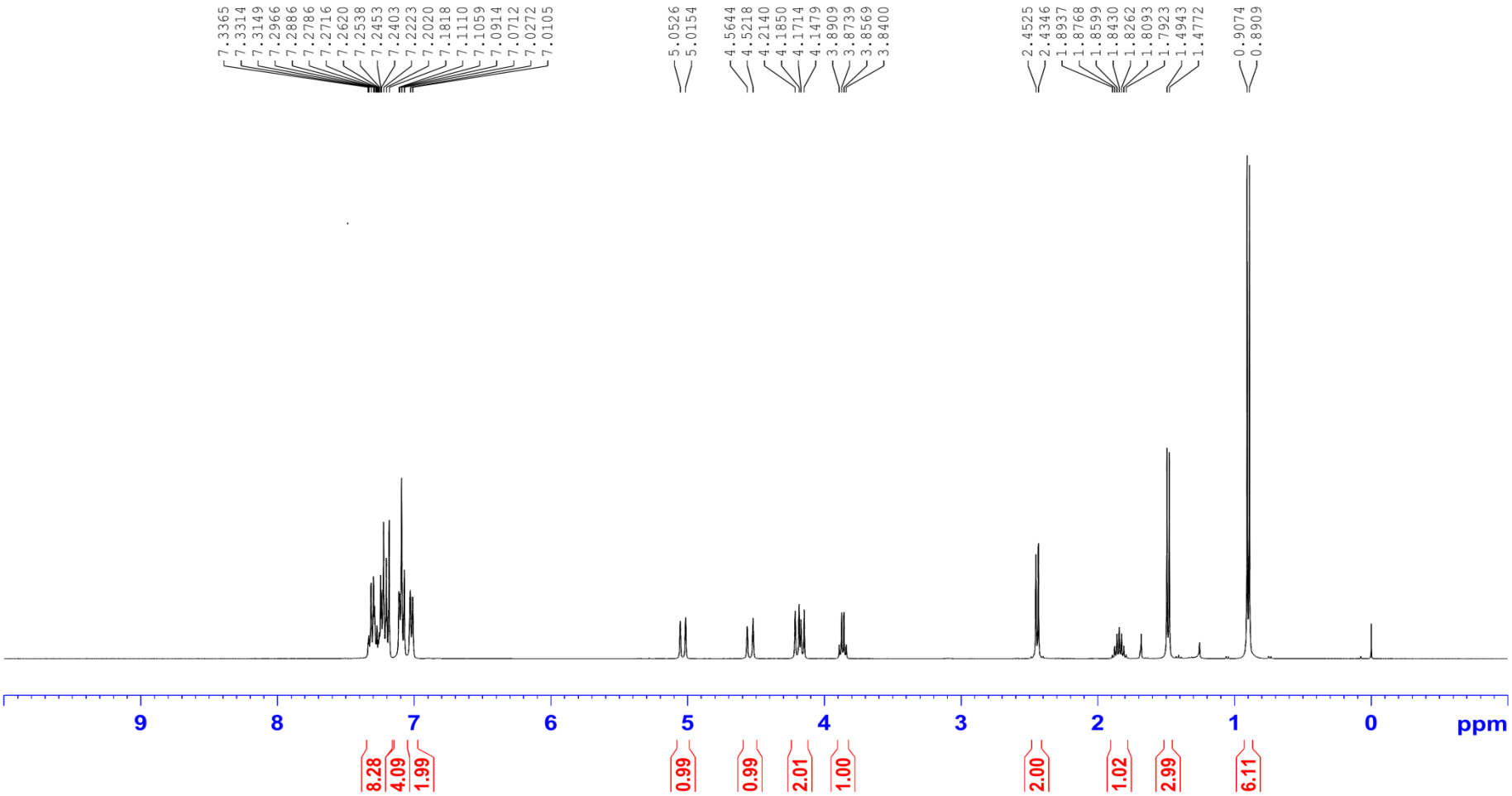

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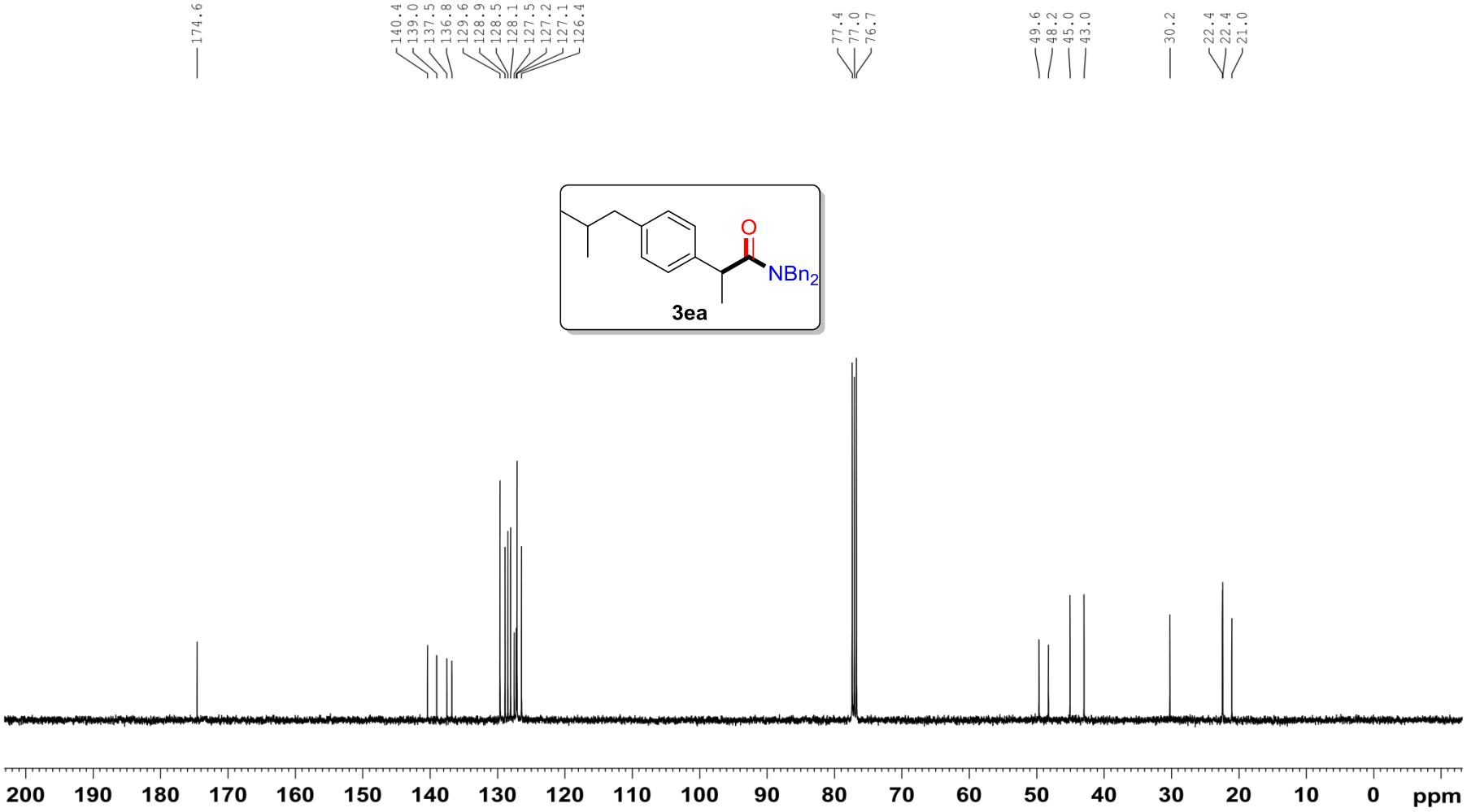

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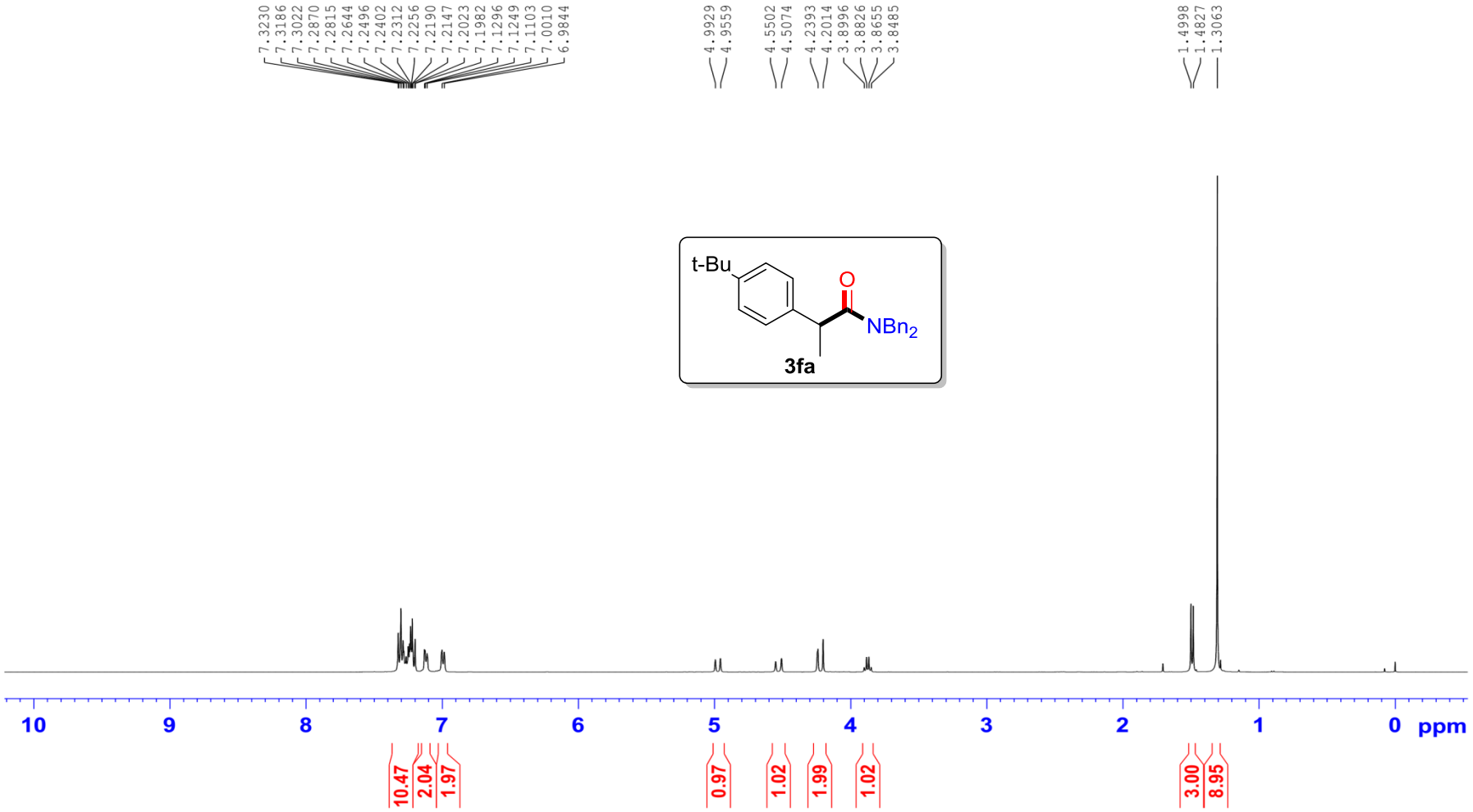

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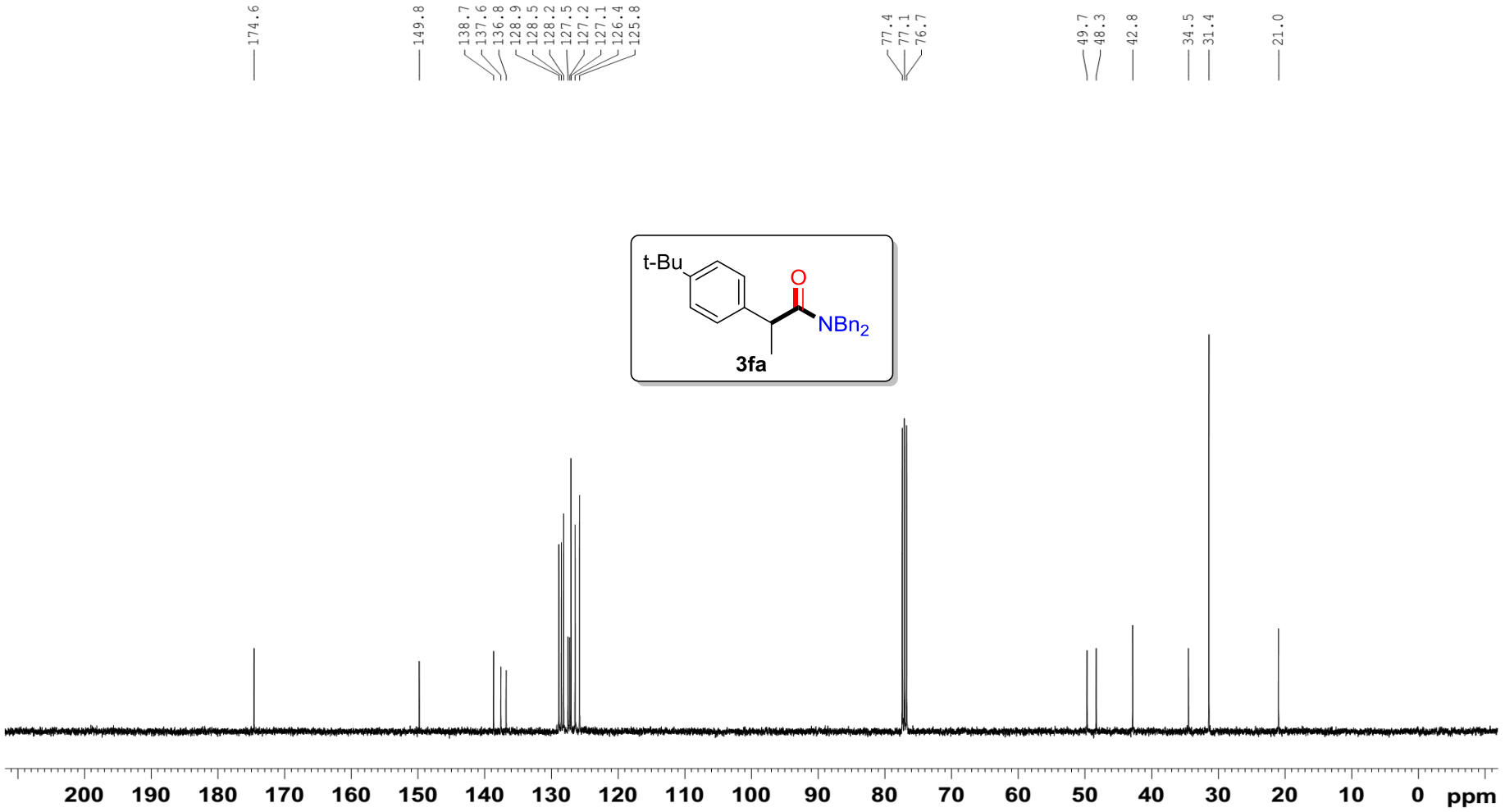

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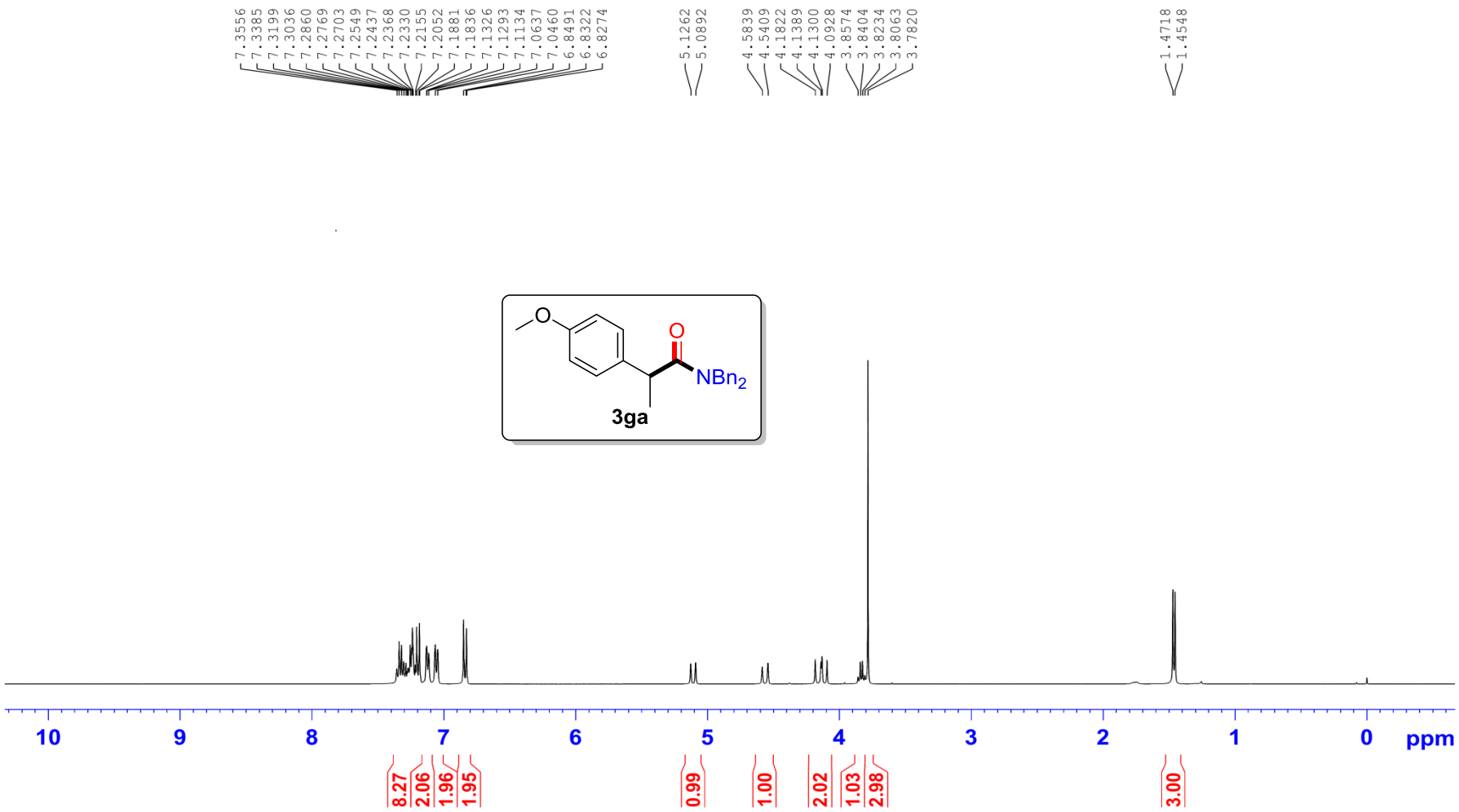

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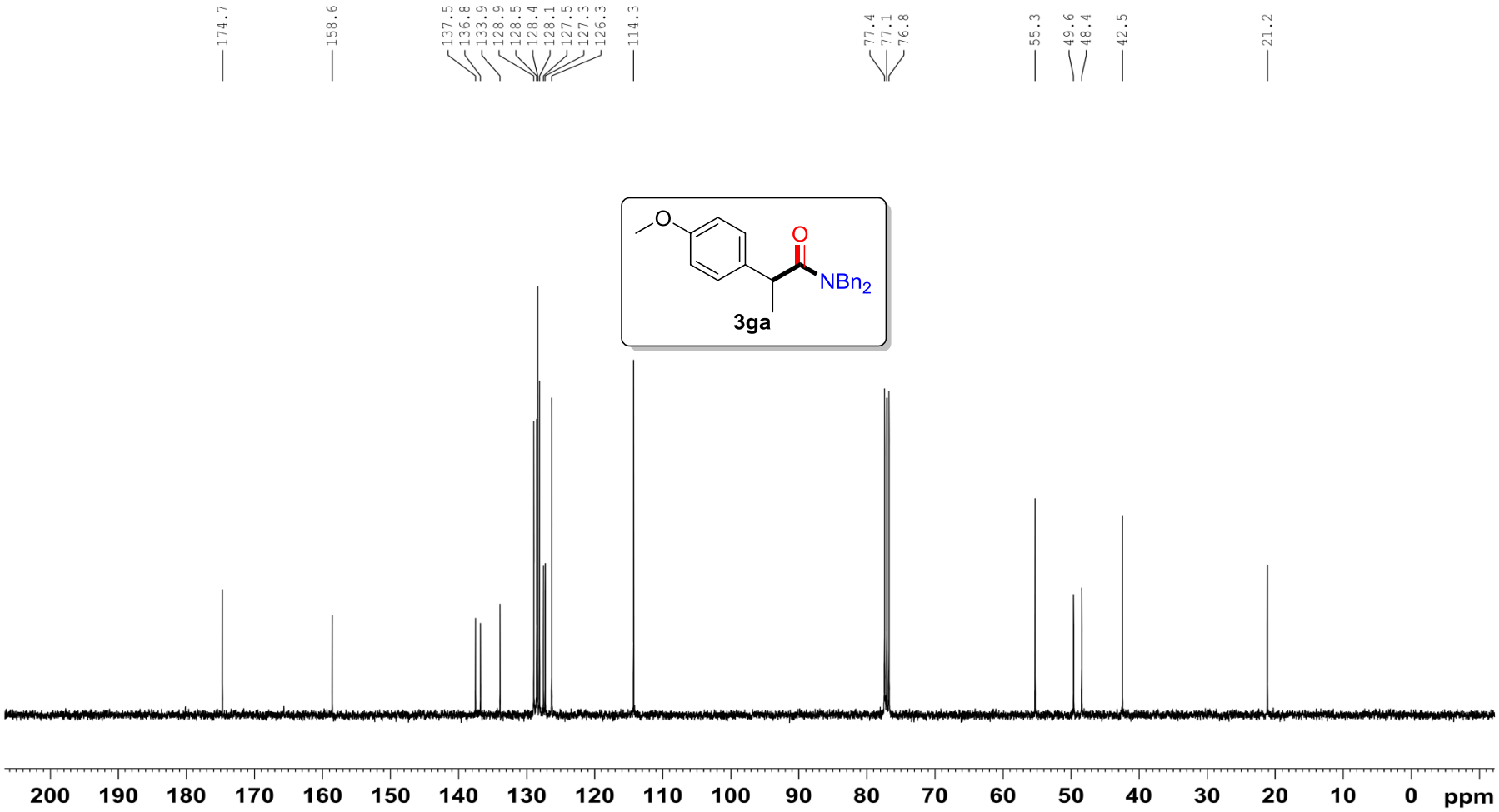

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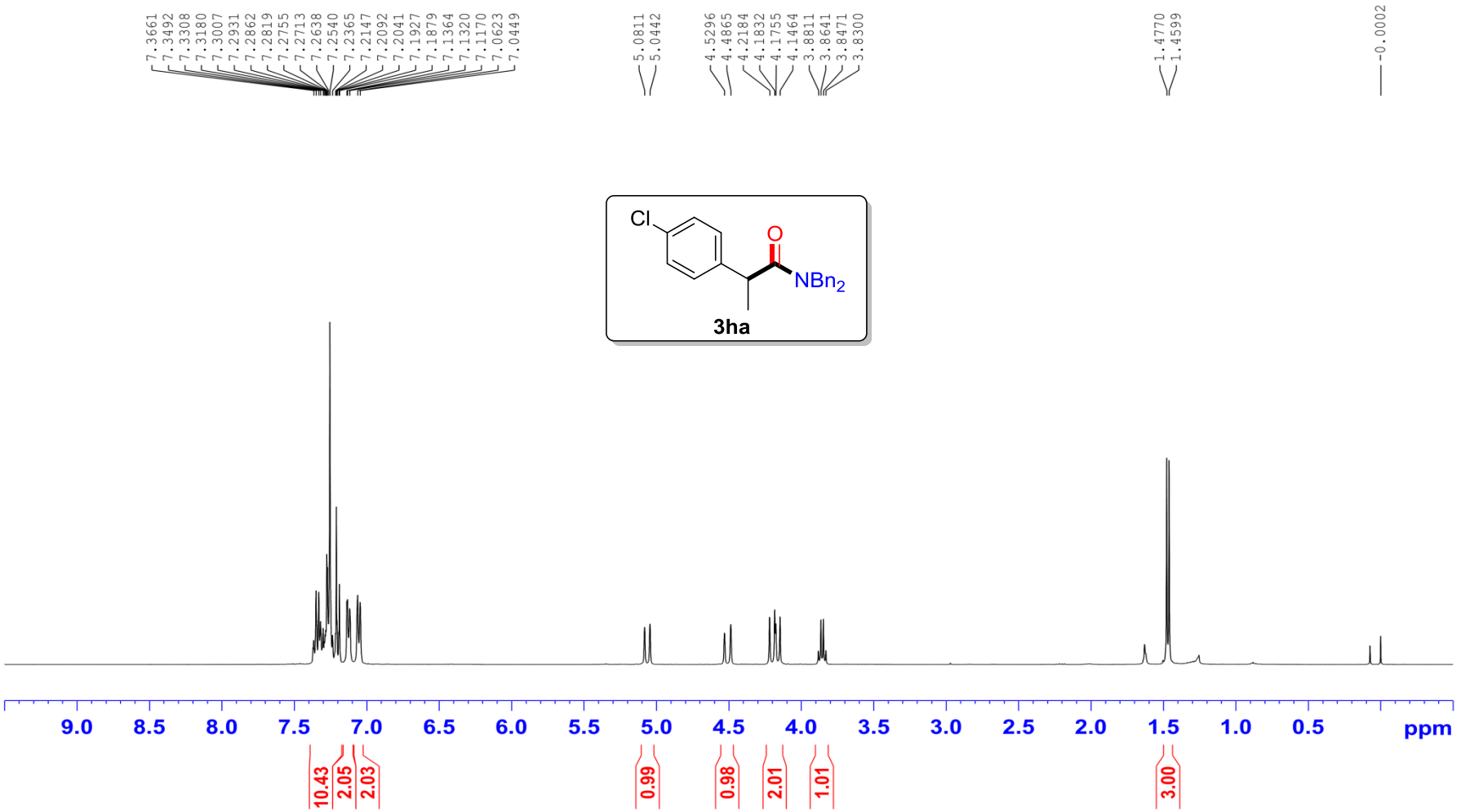

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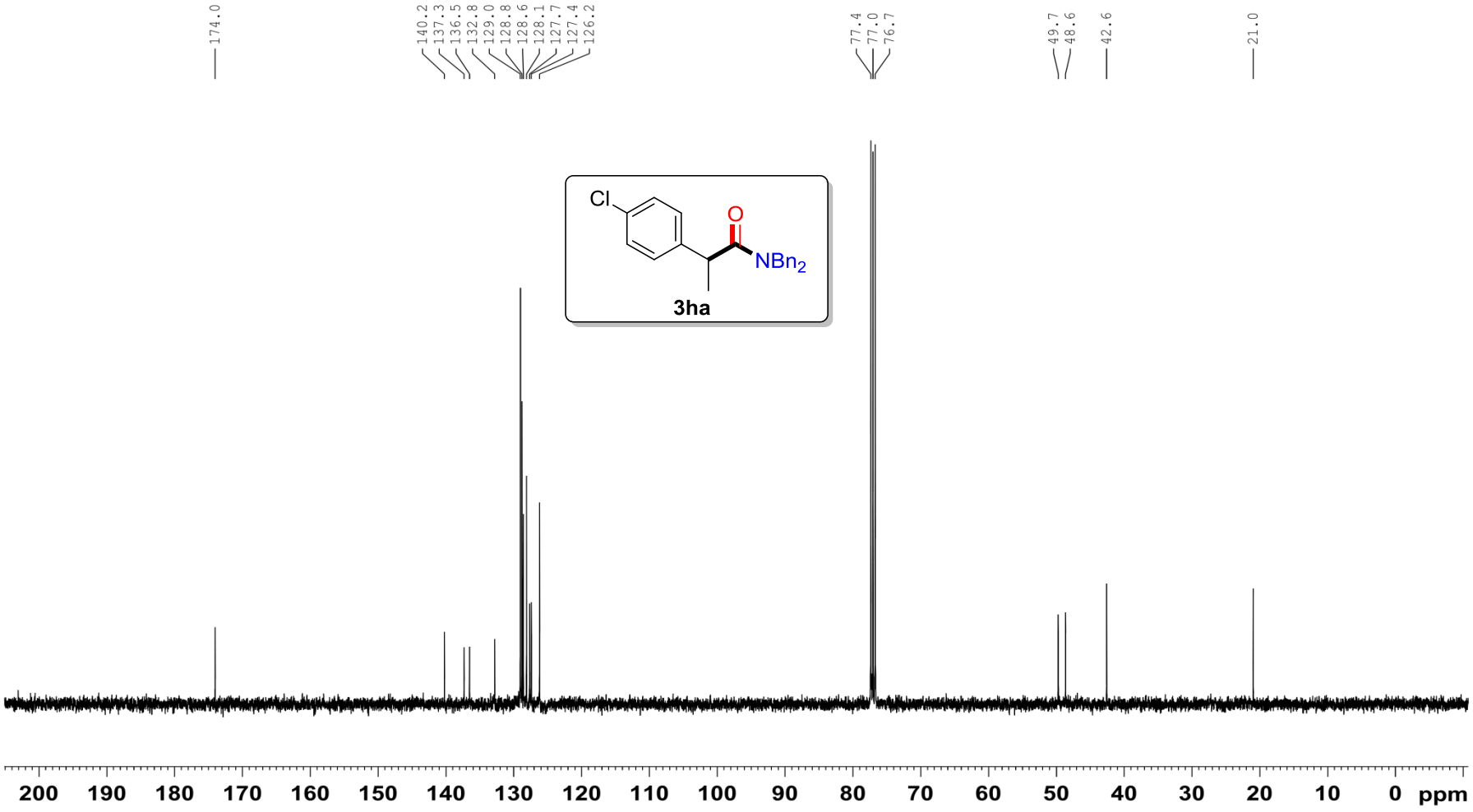

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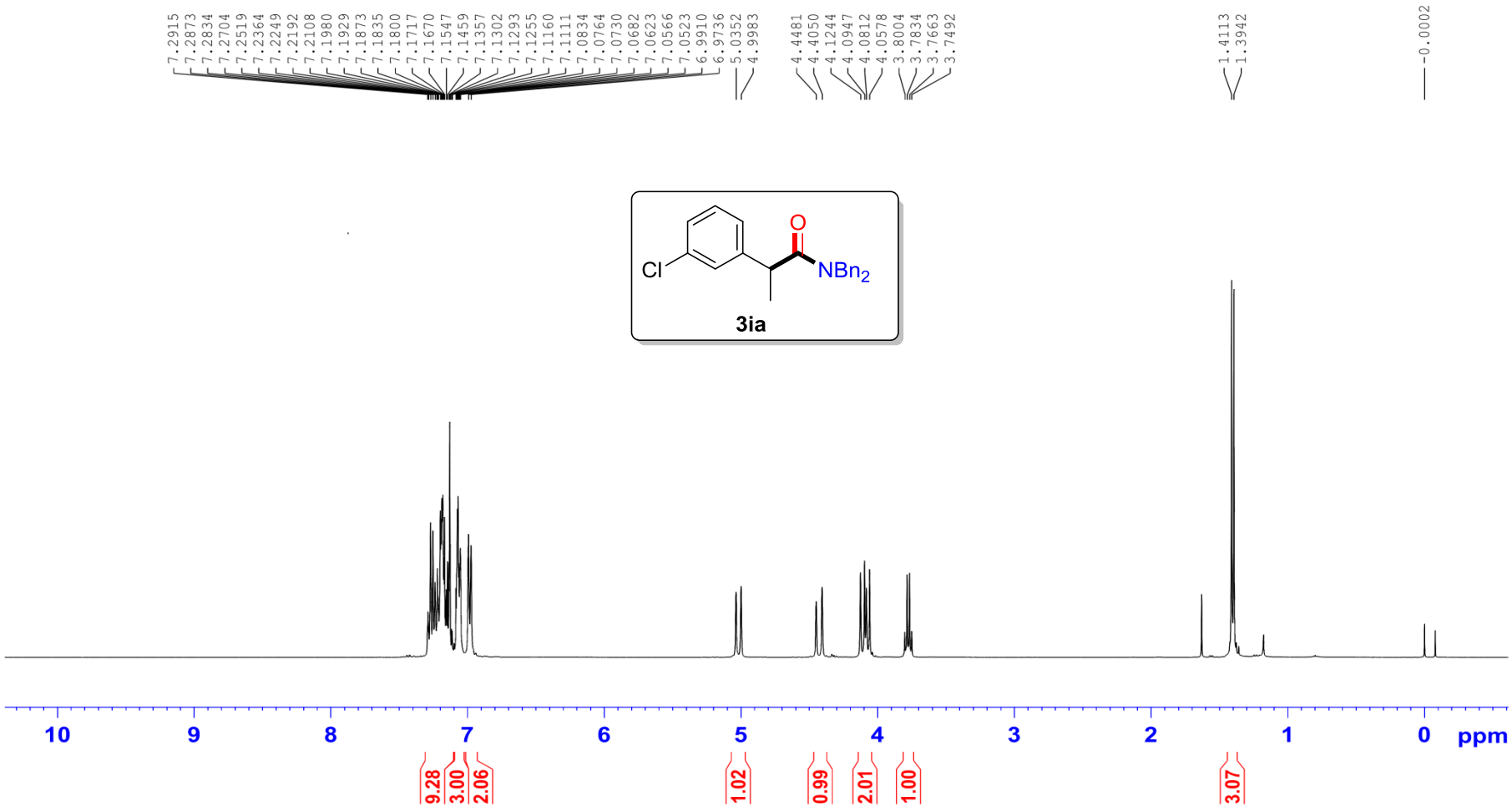

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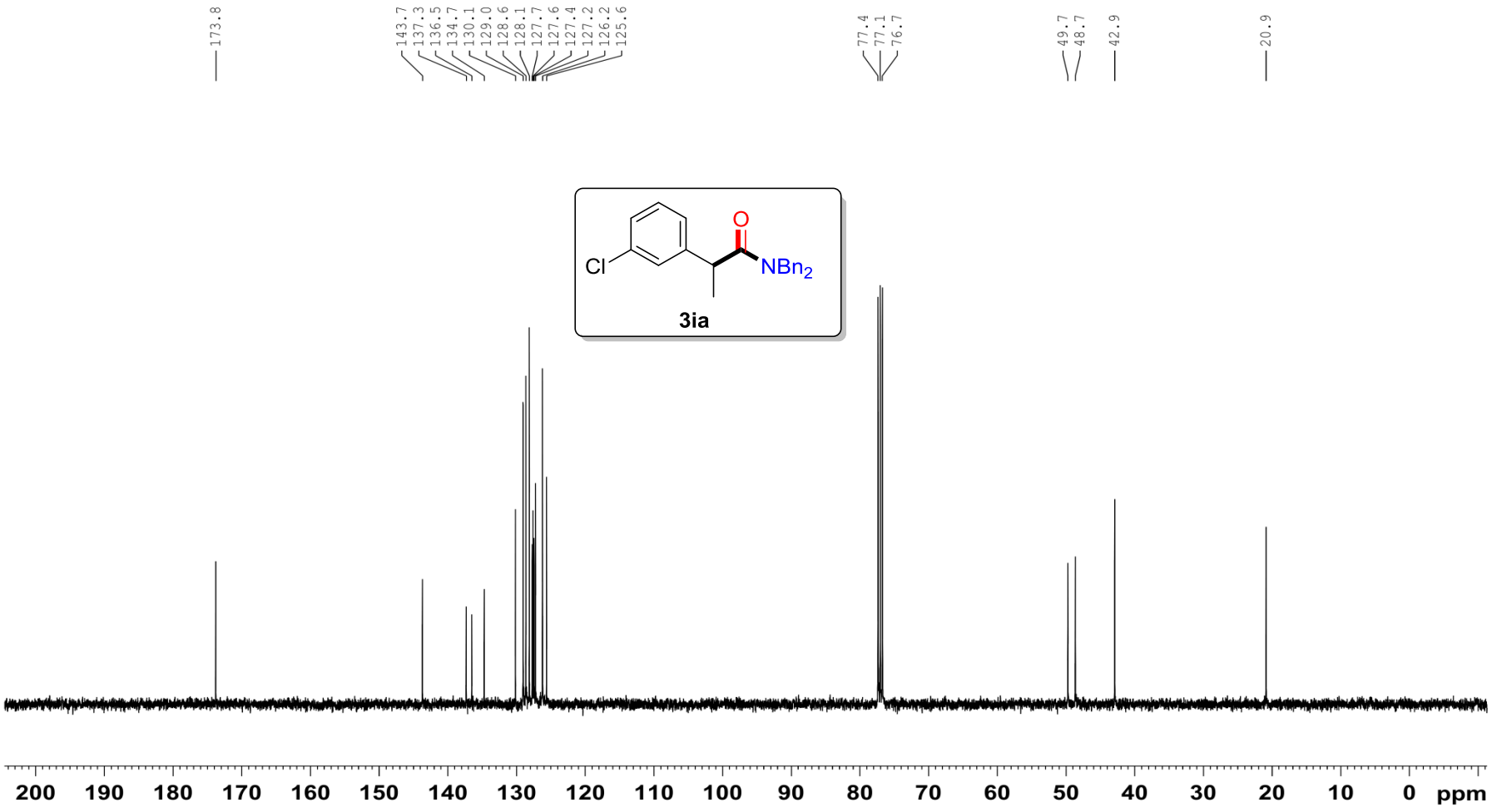

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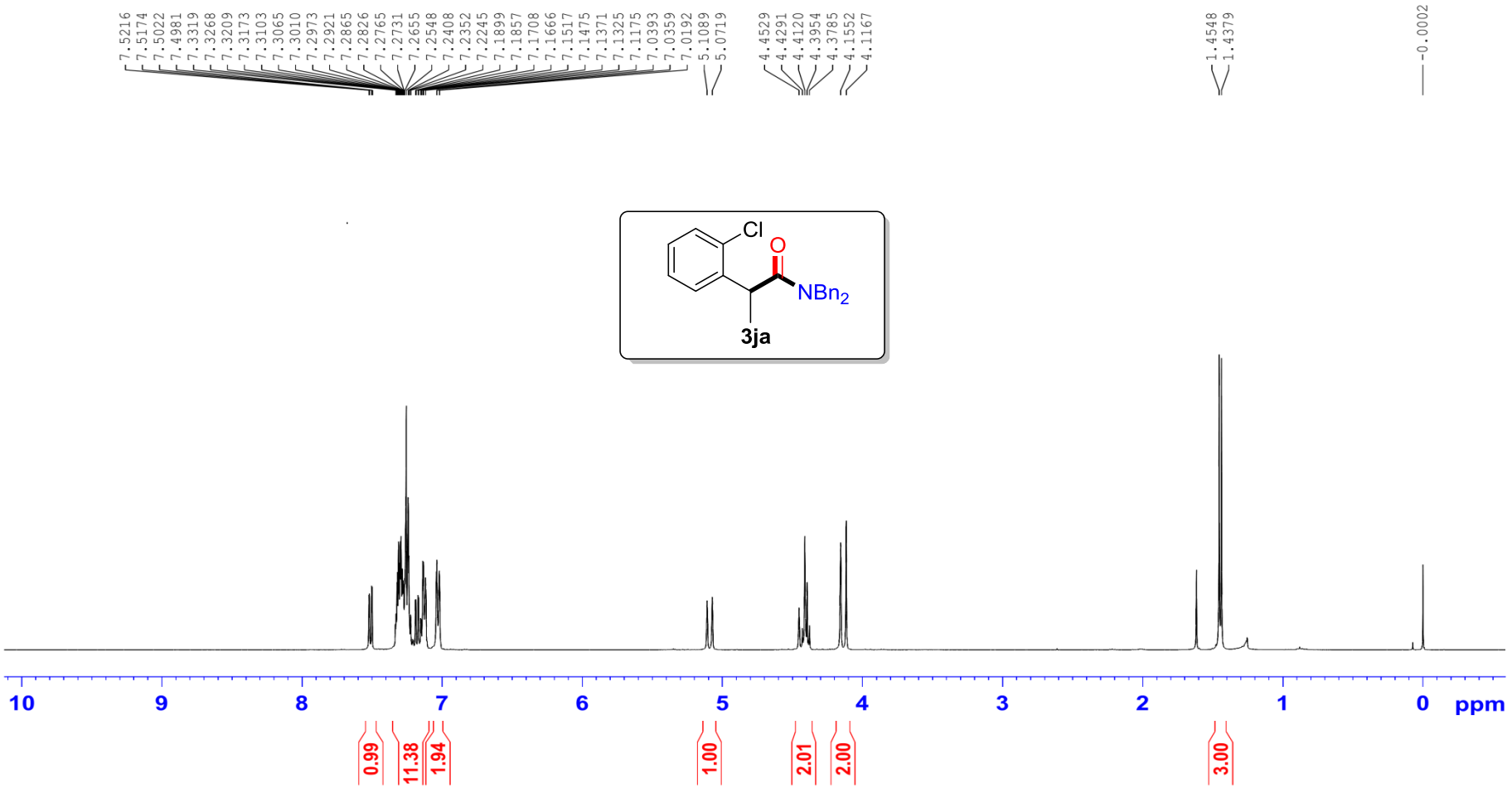

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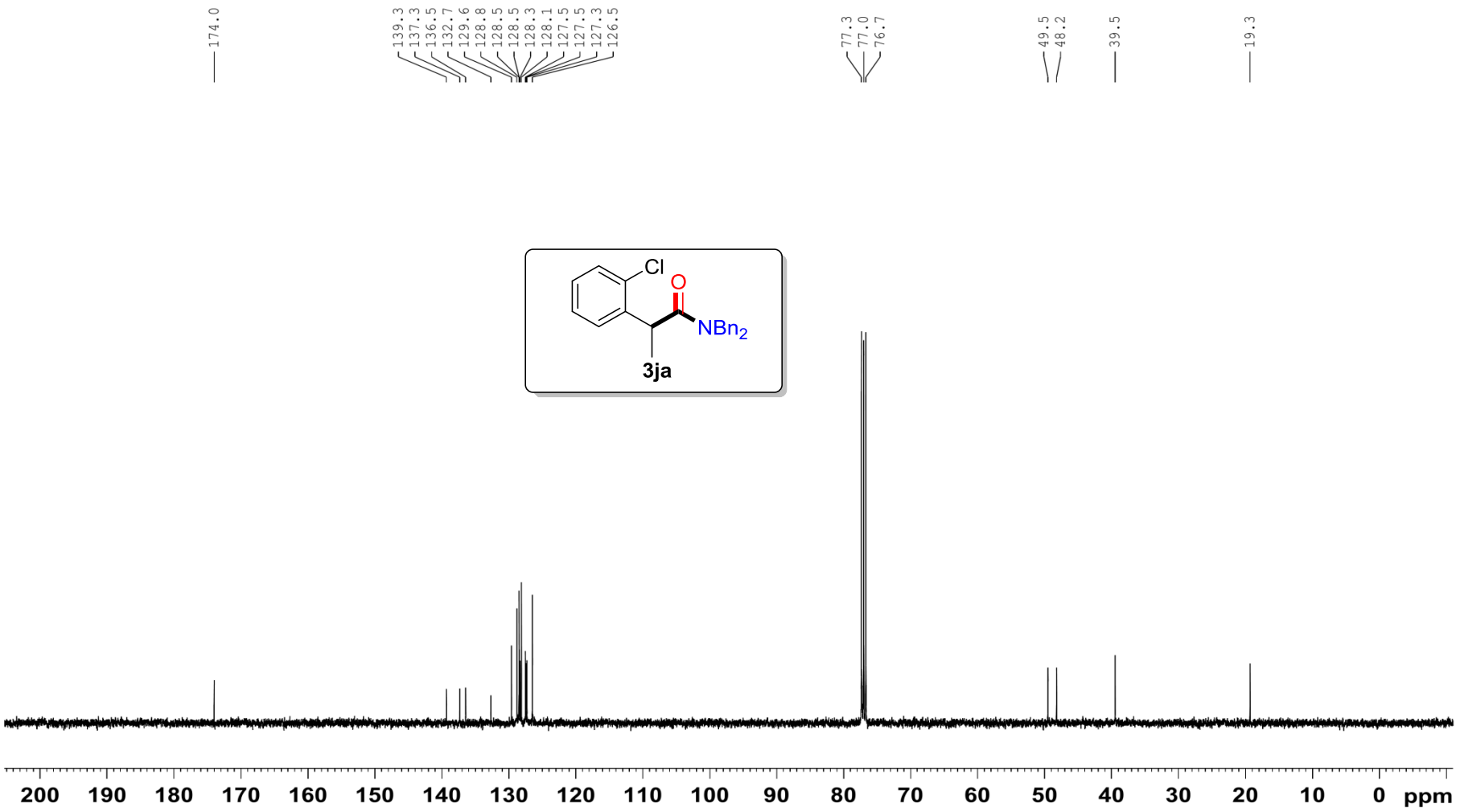

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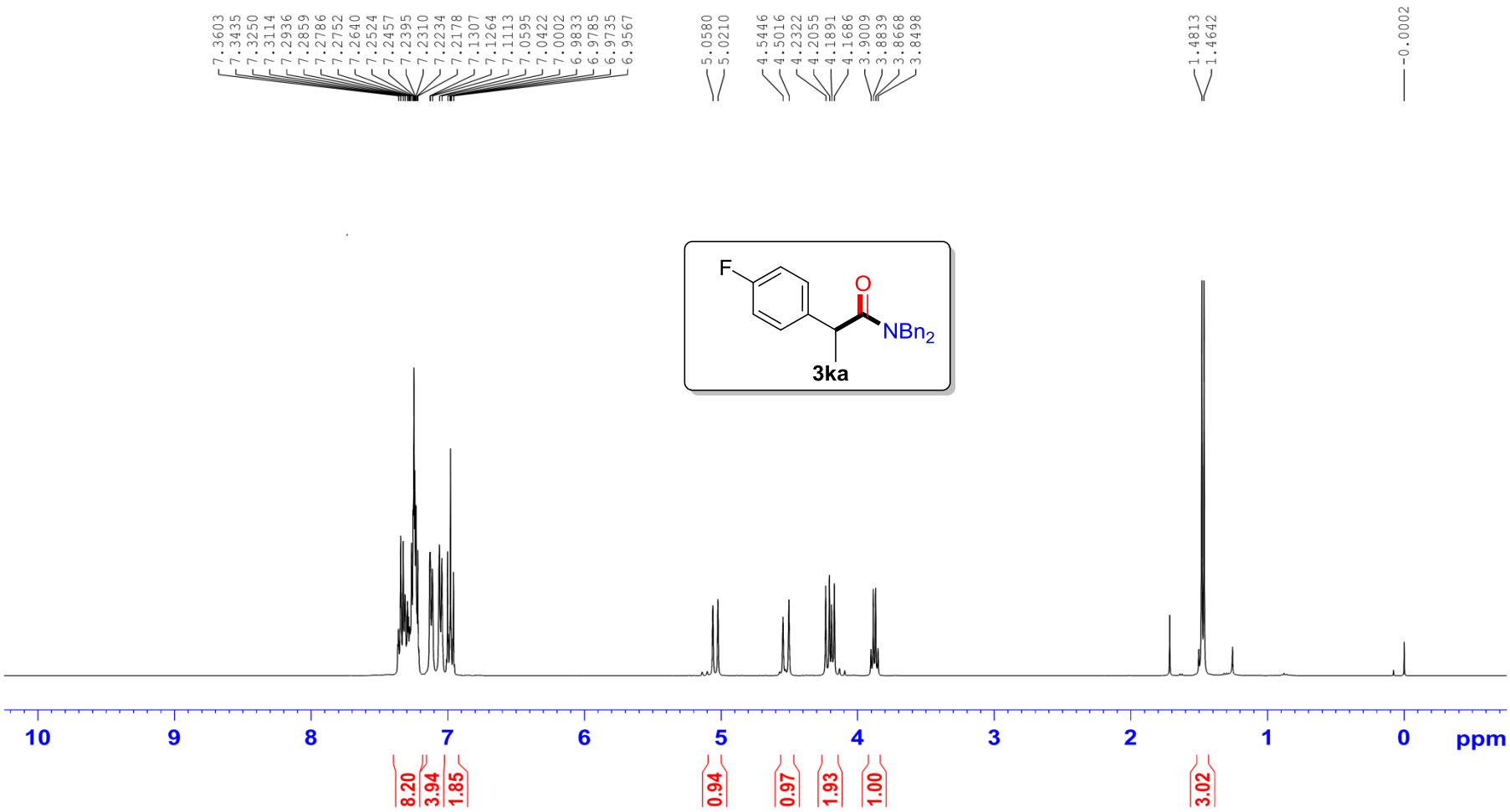

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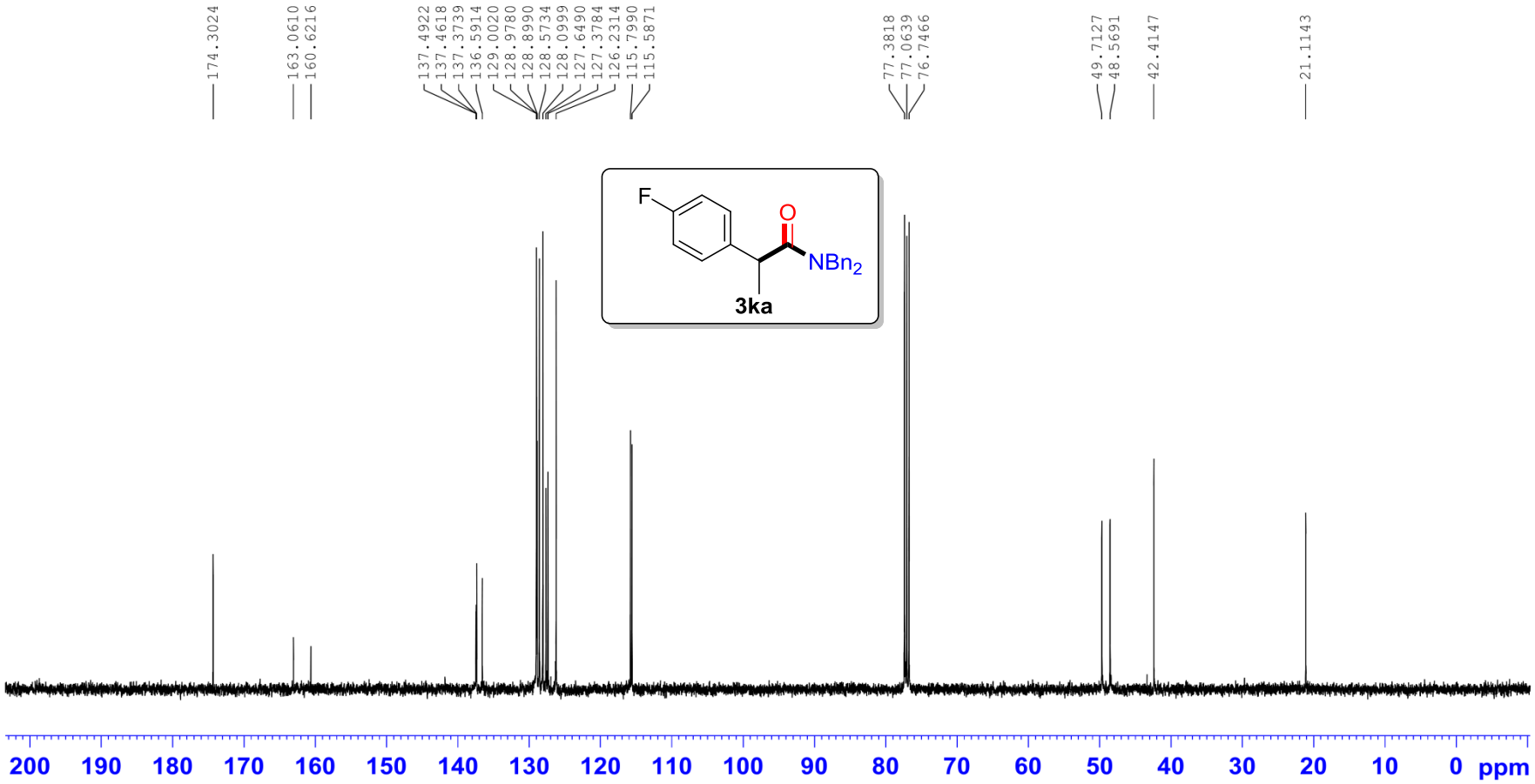

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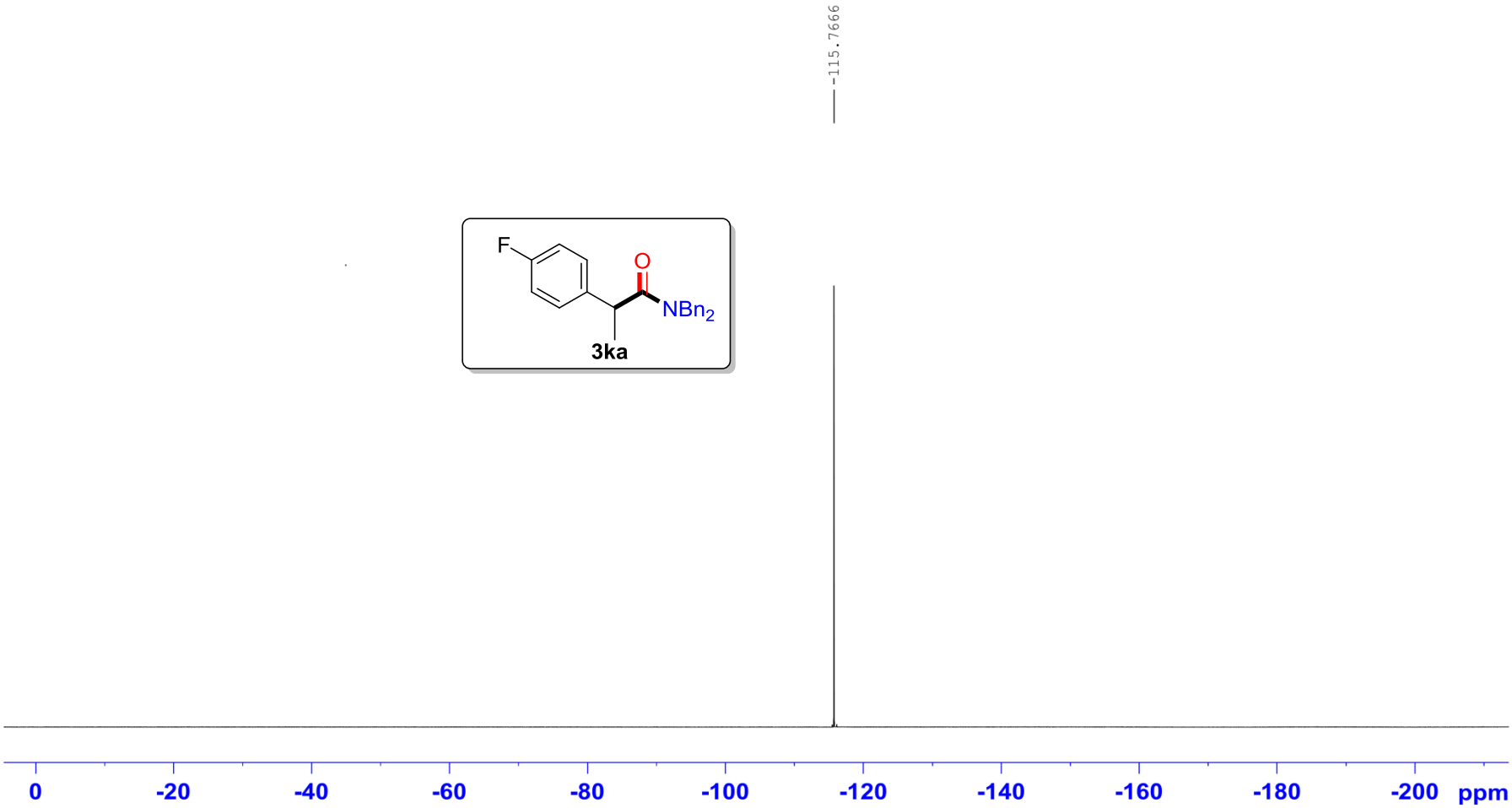

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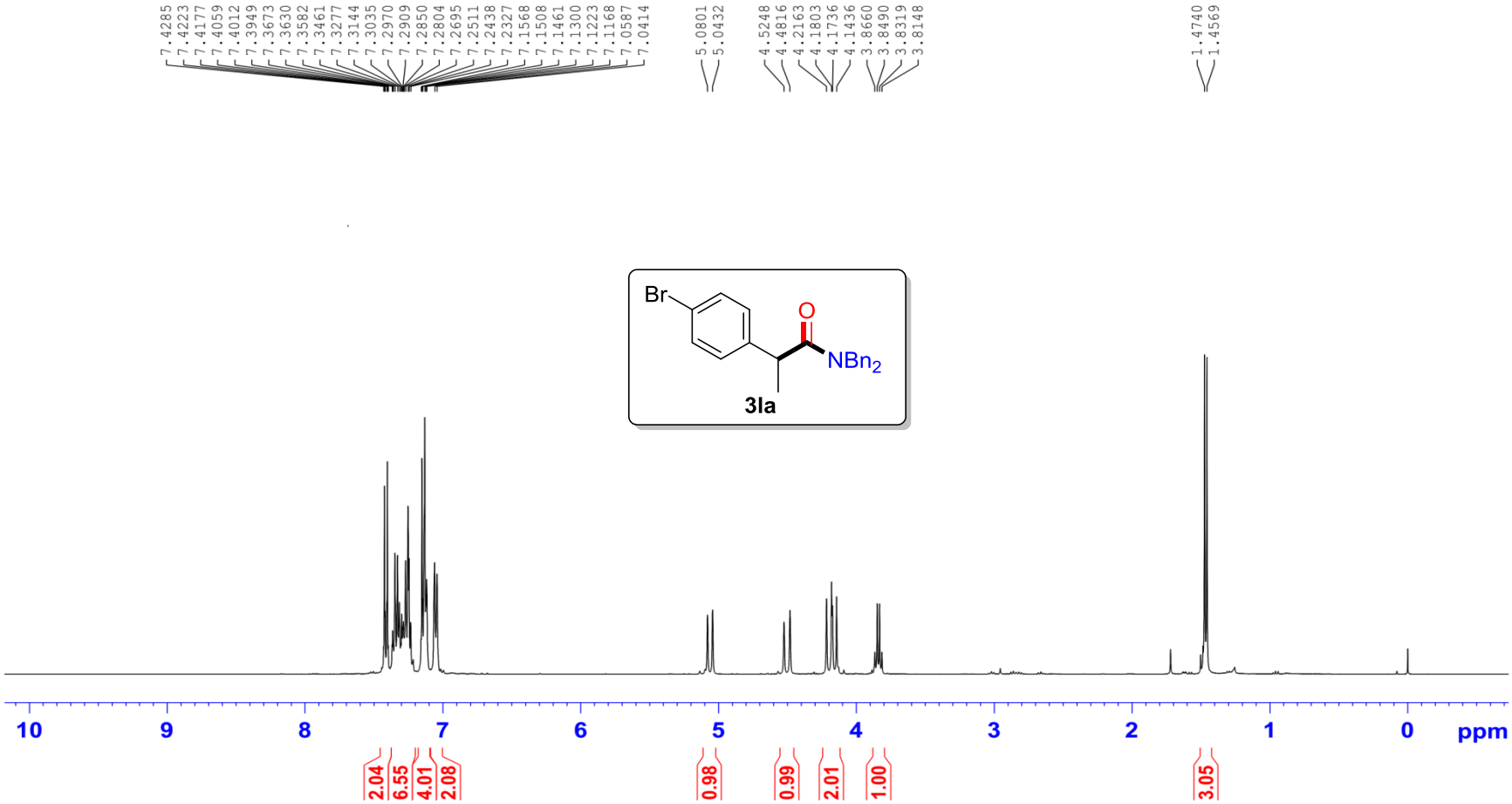

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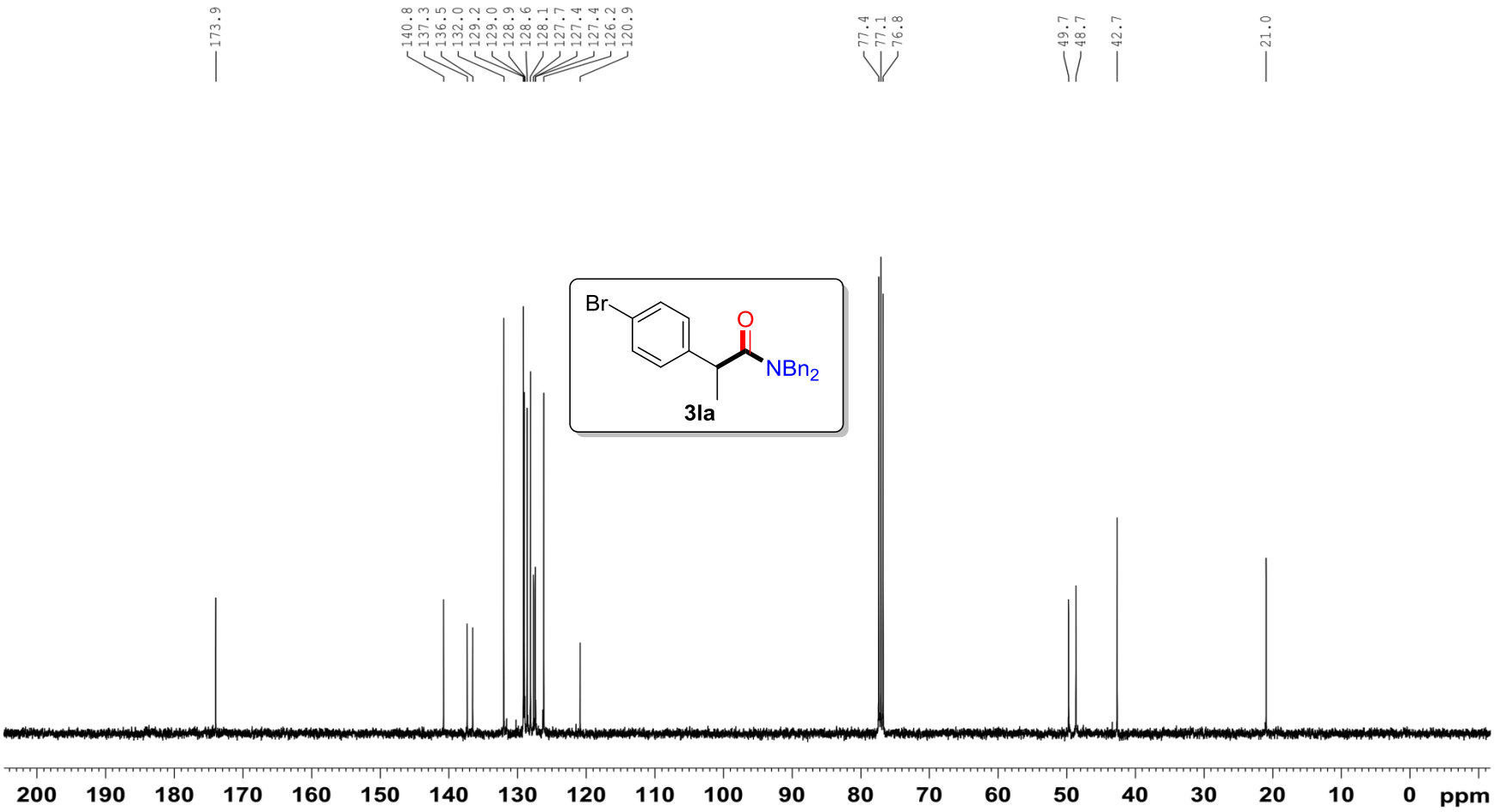

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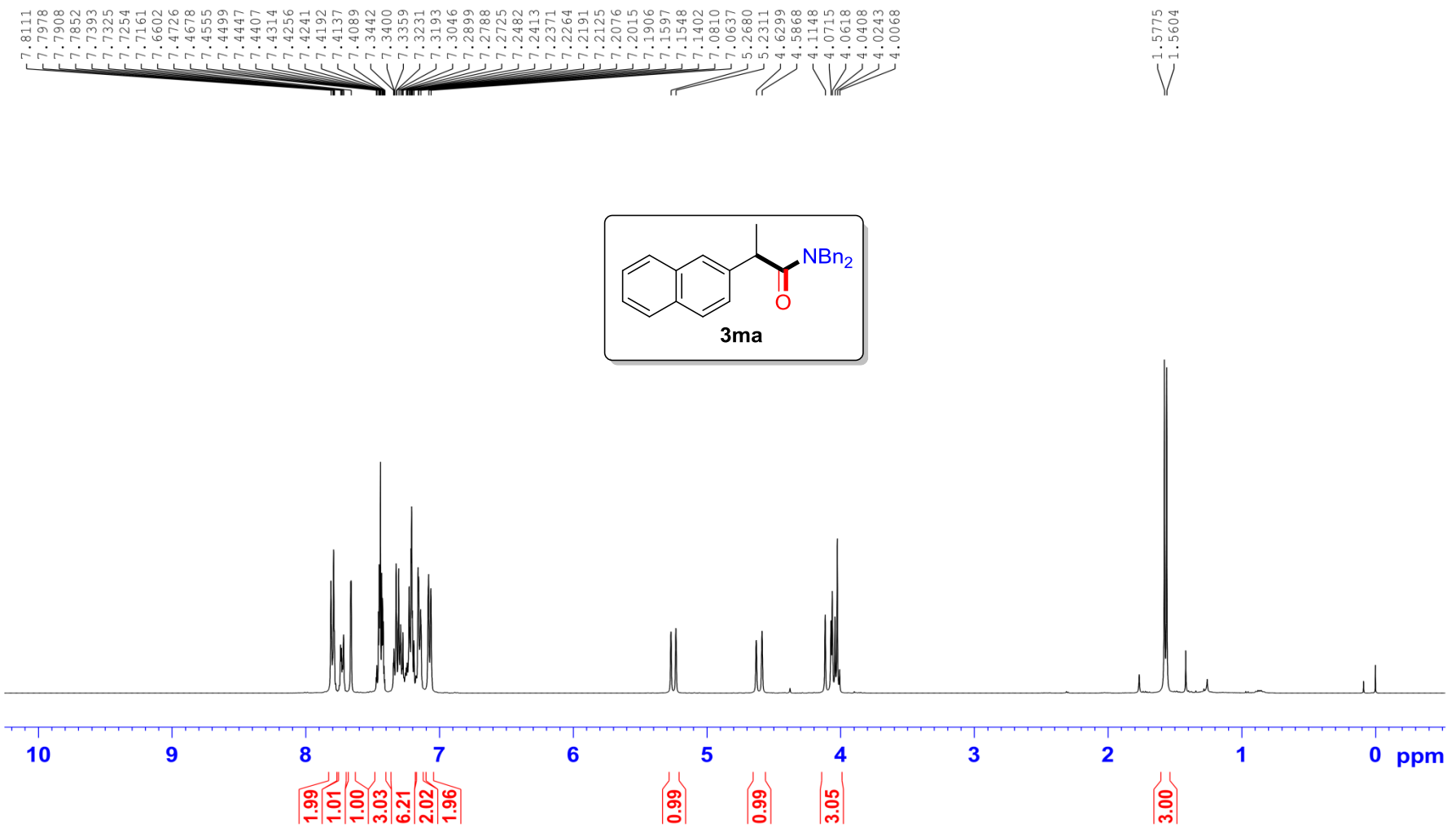

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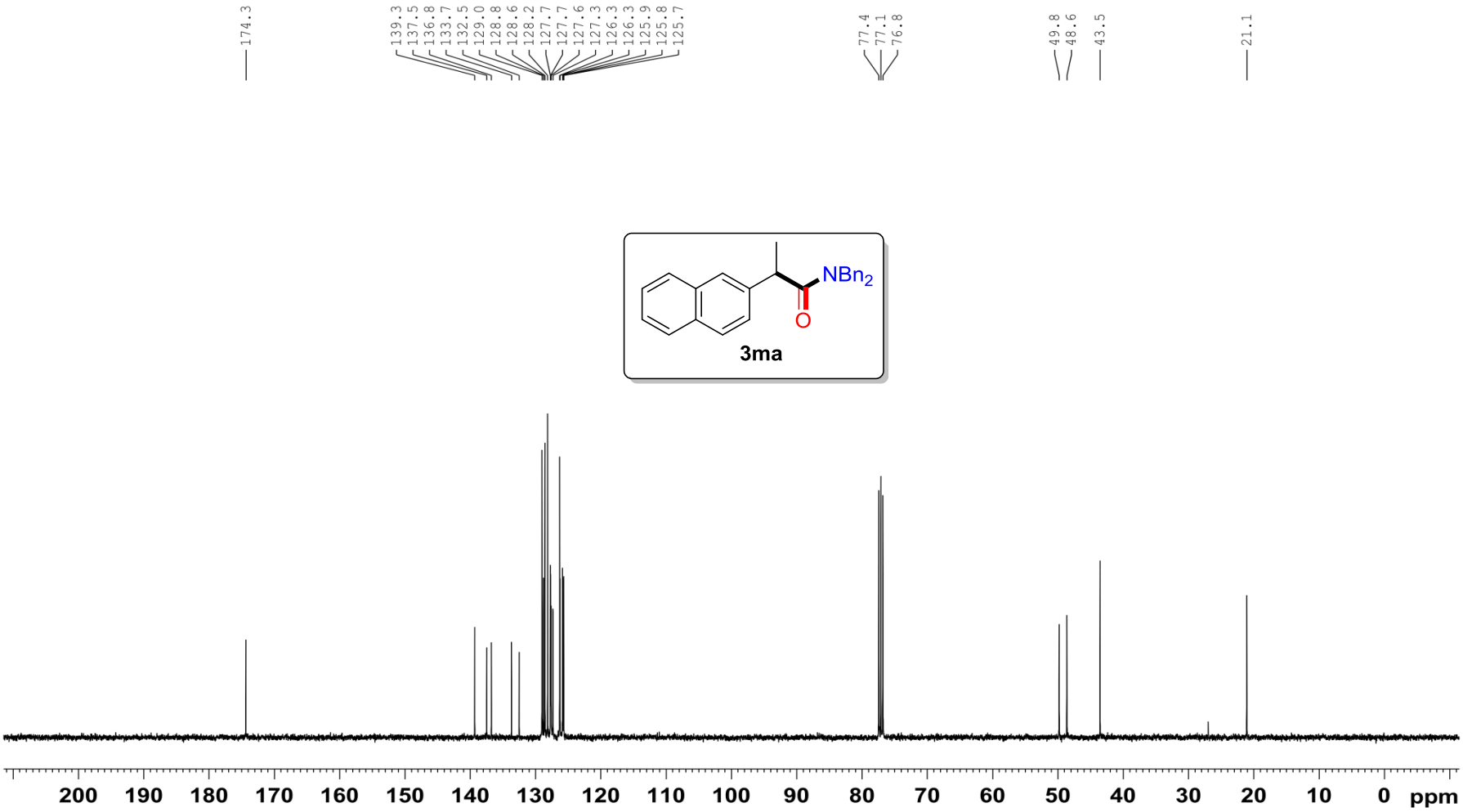

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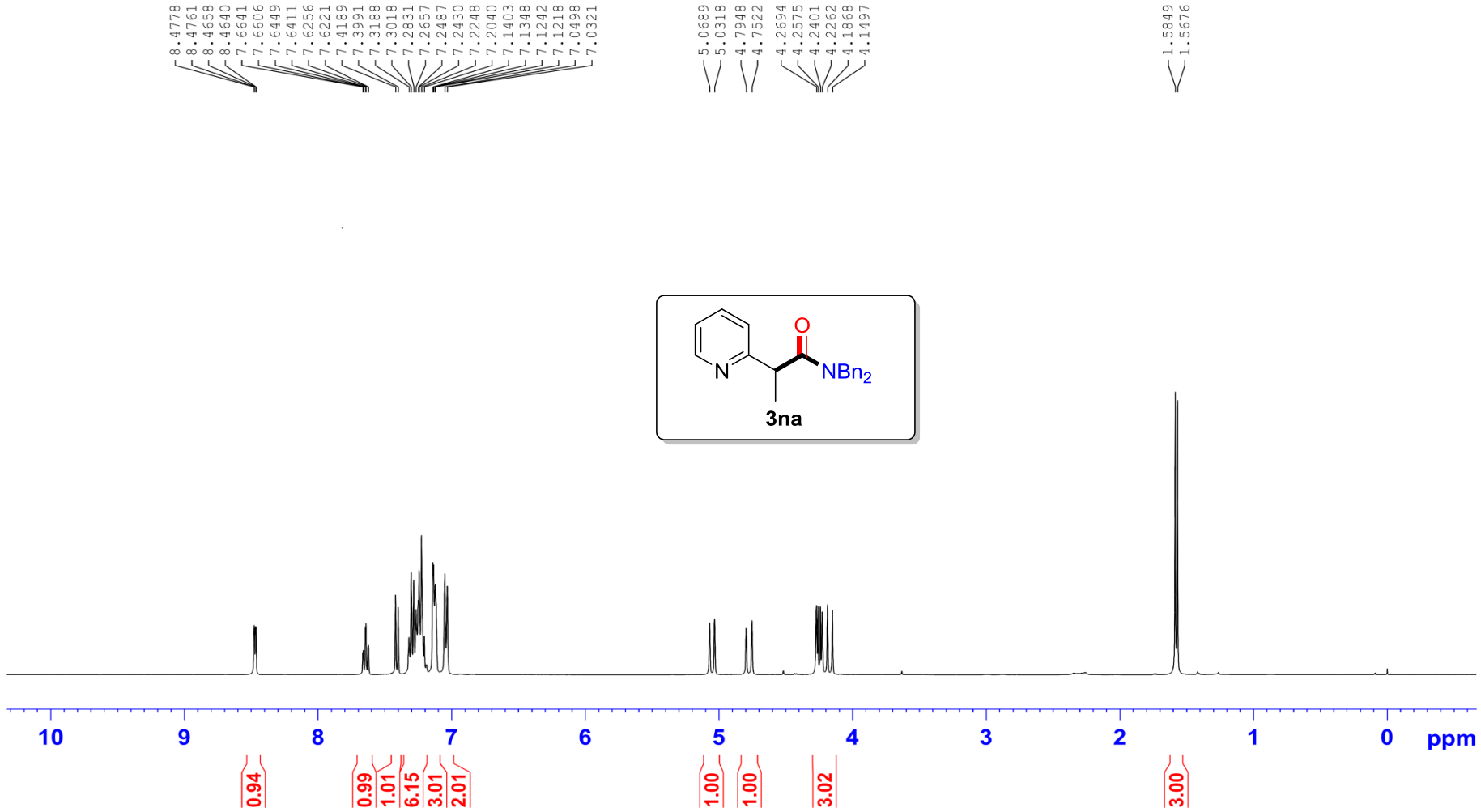

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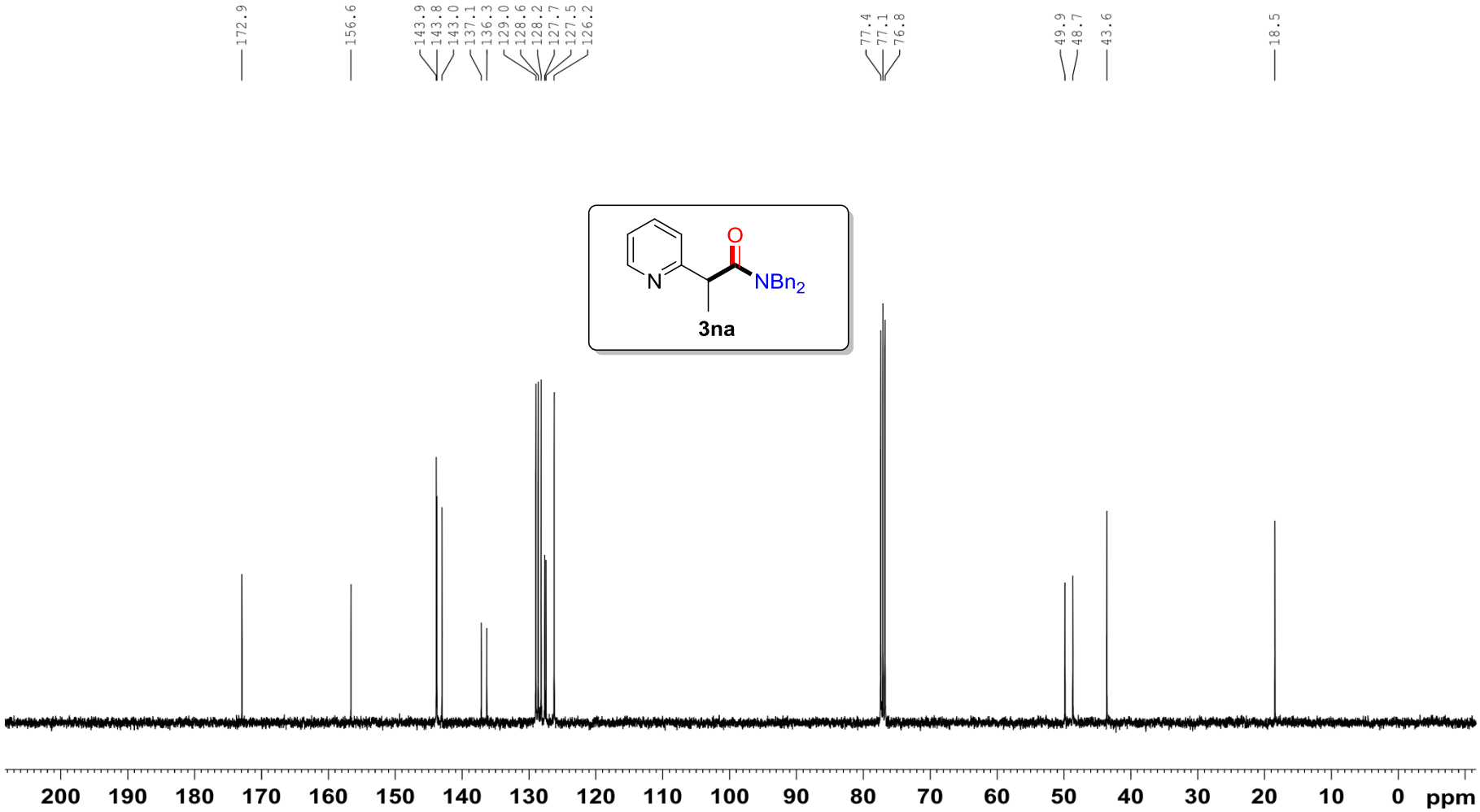

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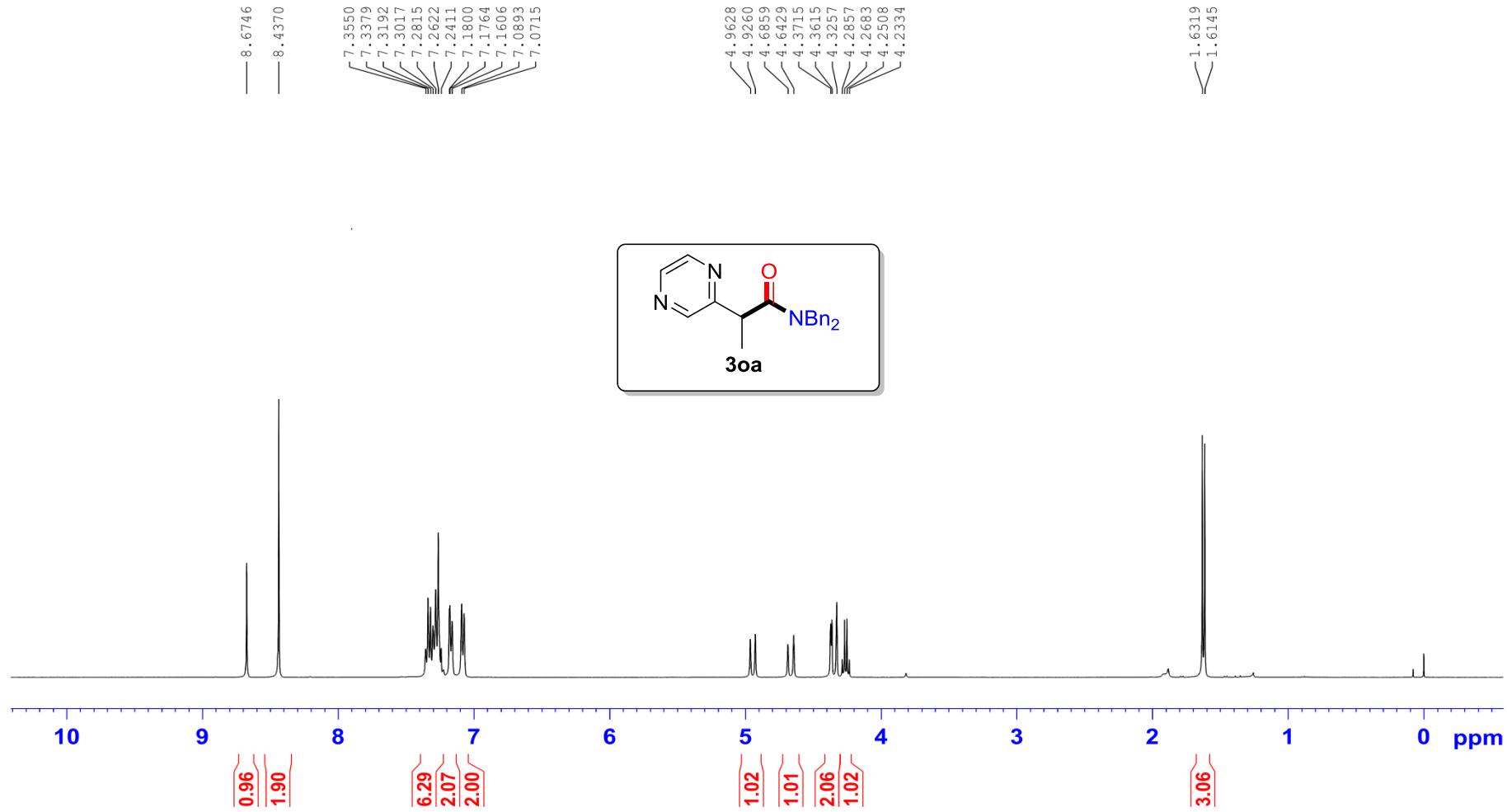

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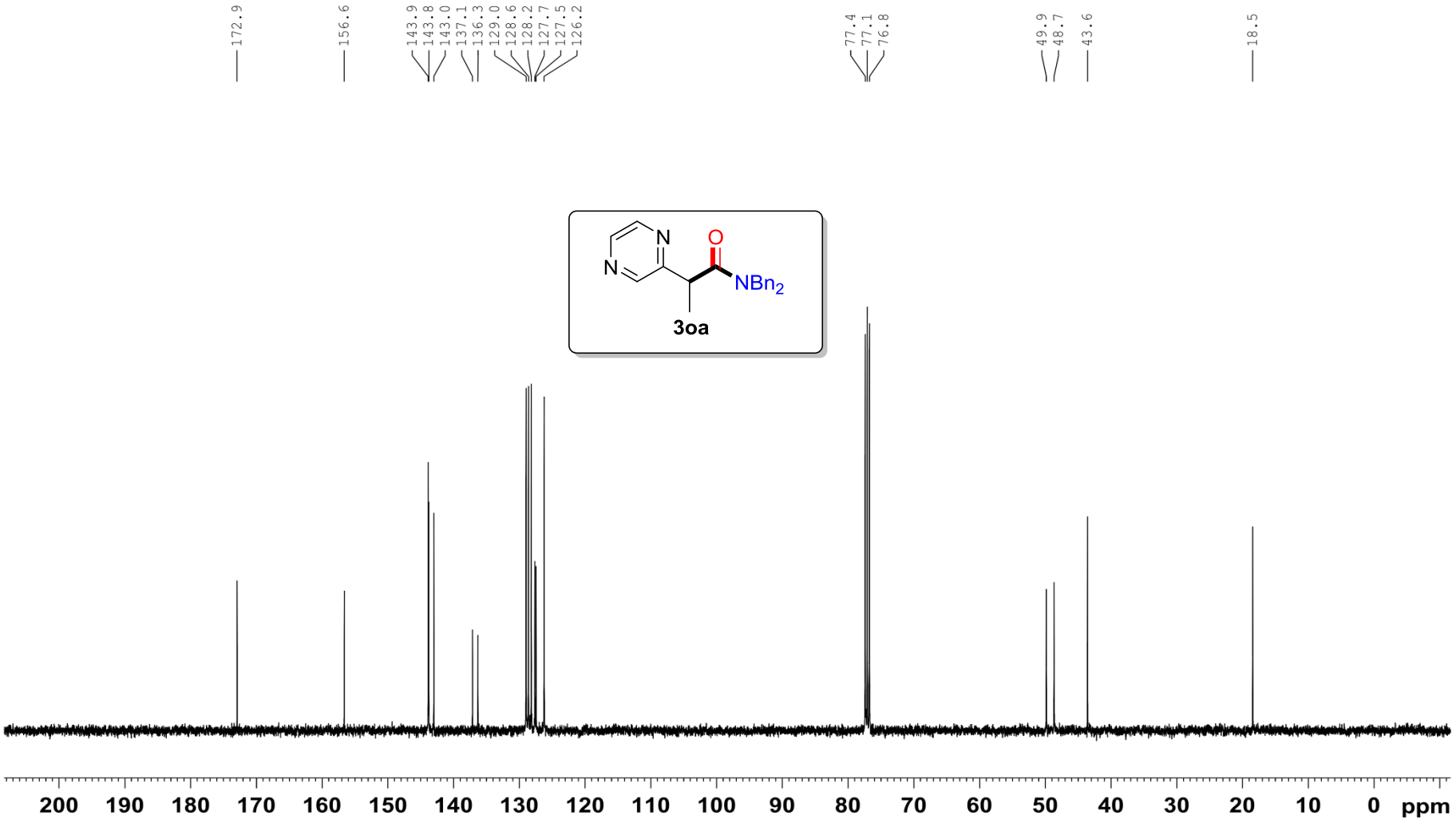

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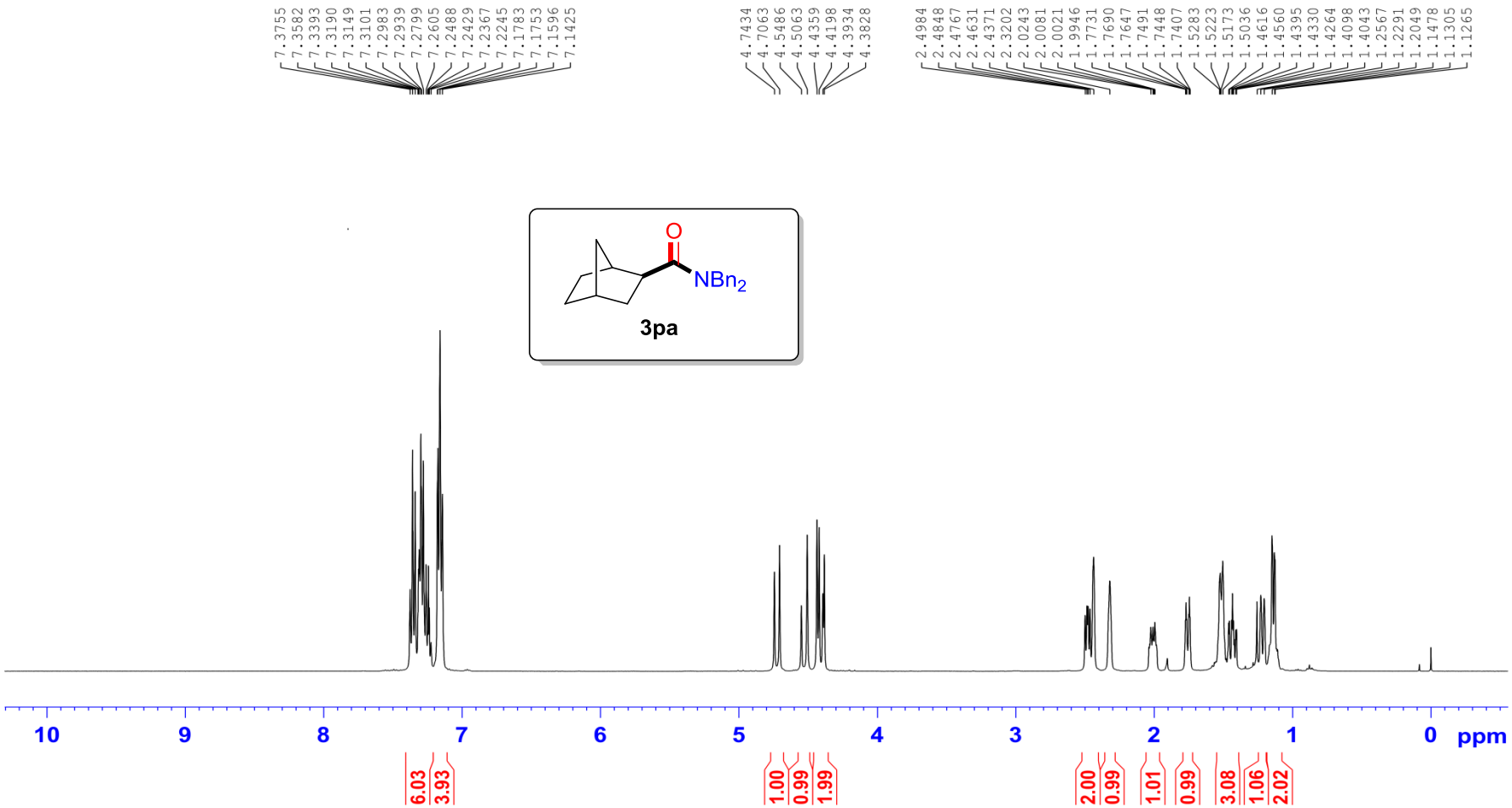

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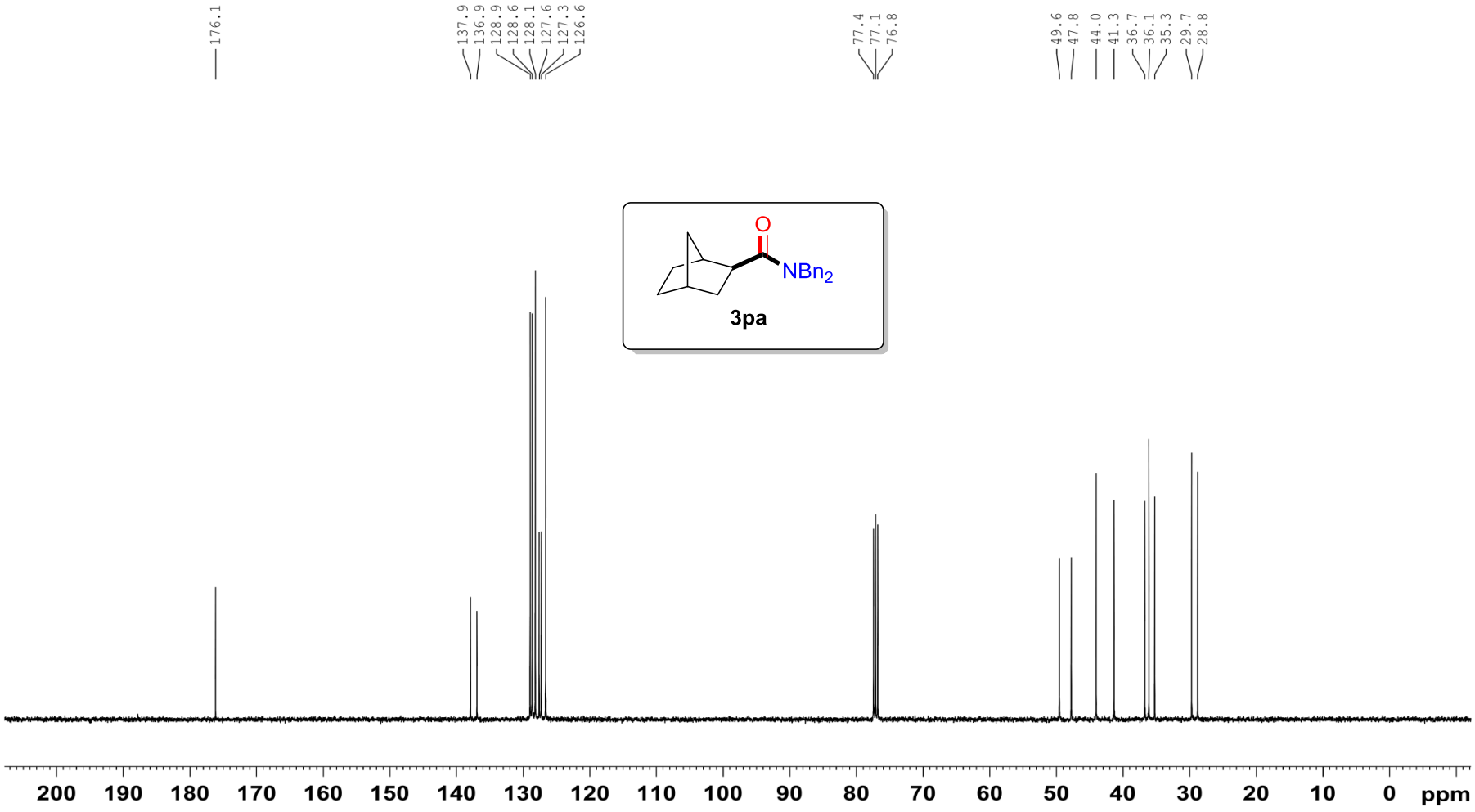
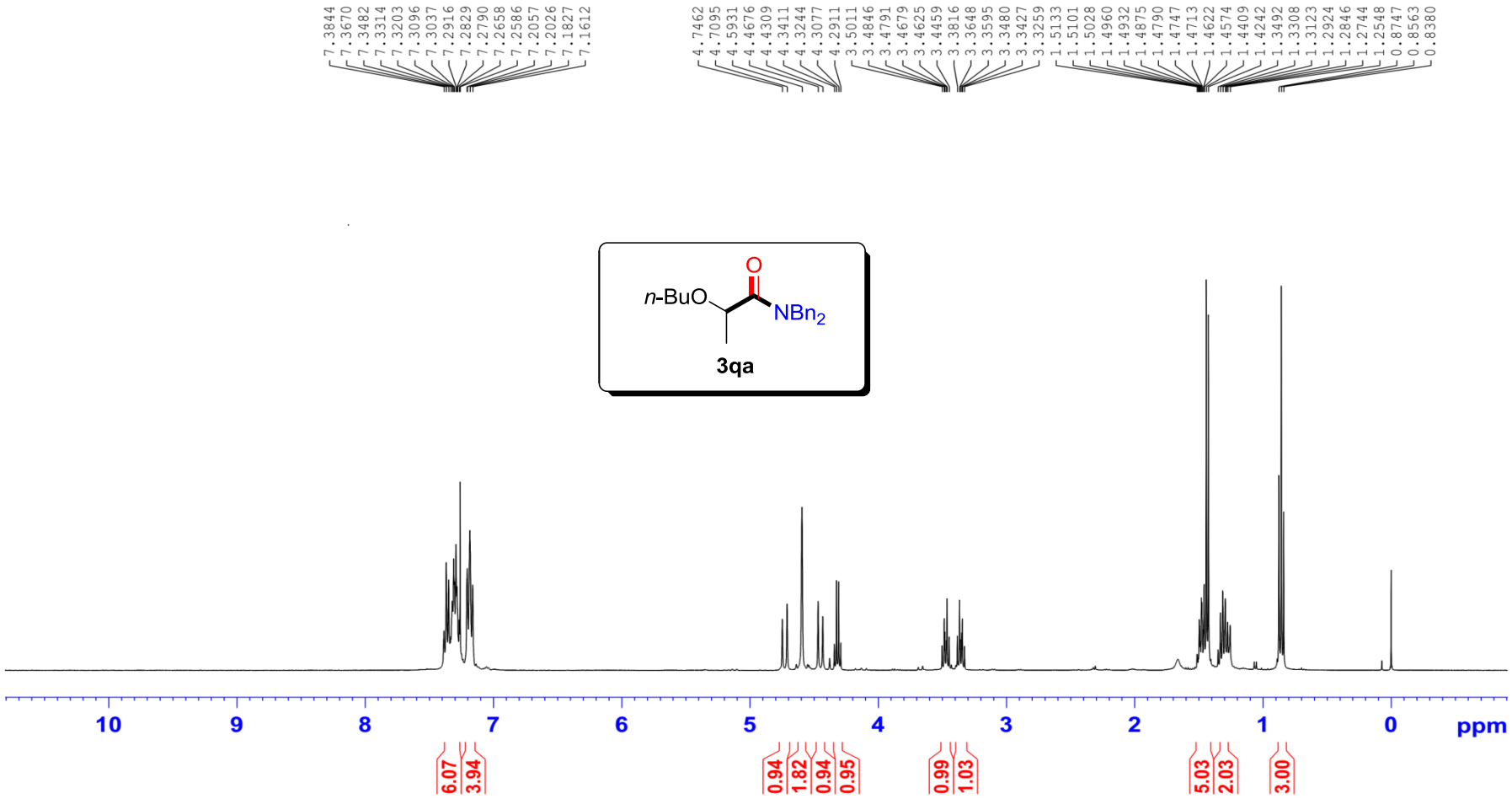
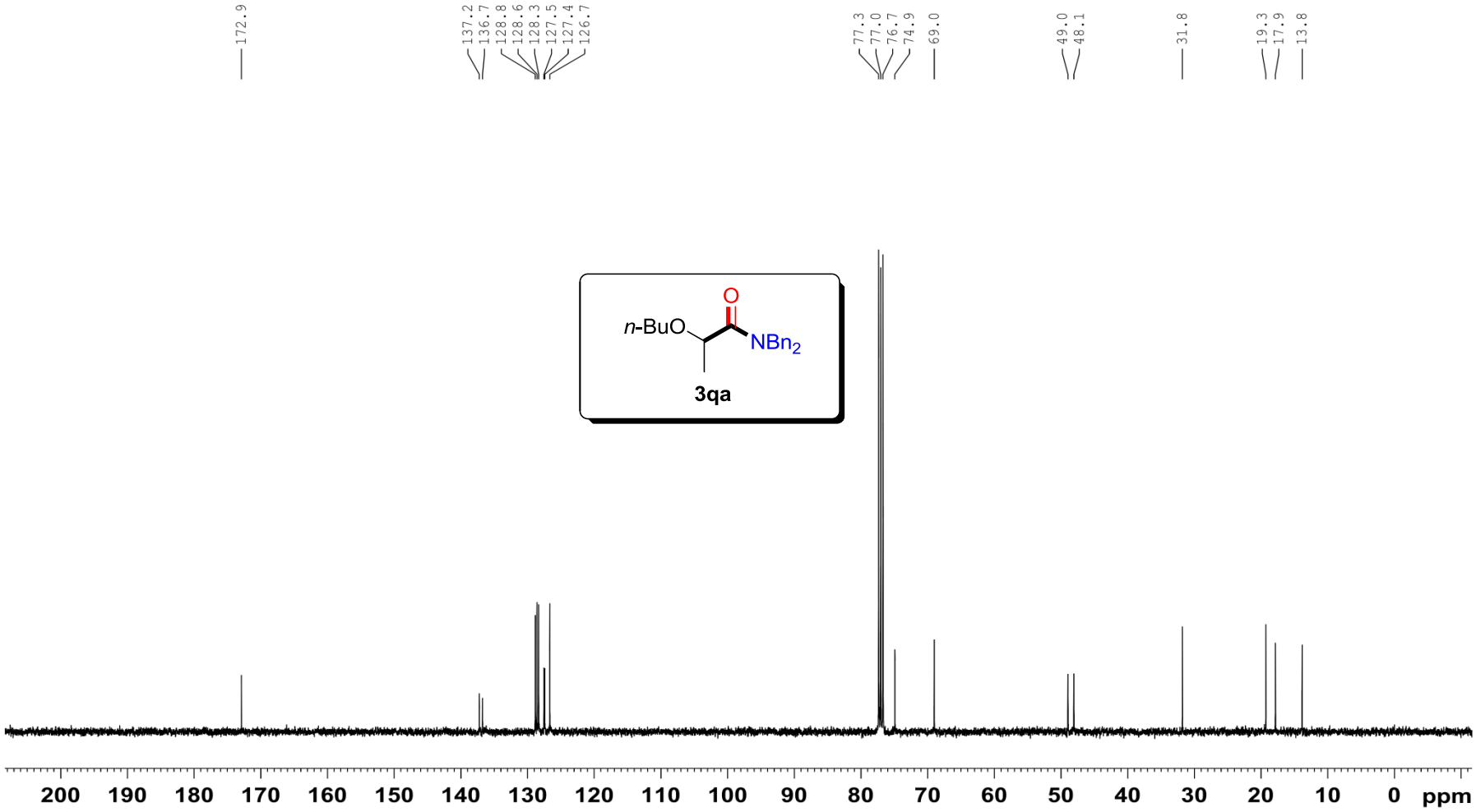


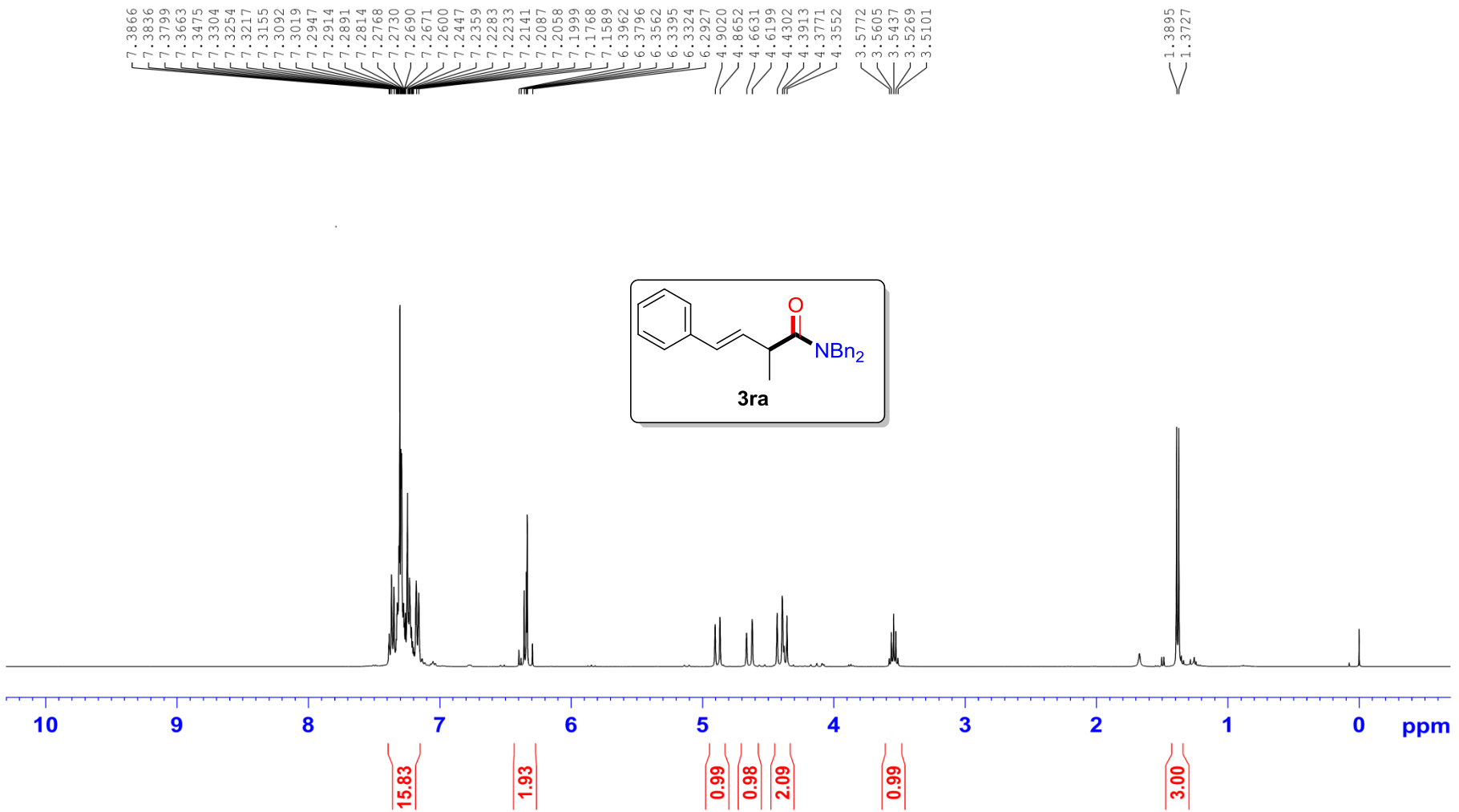
ZJP-X160411-6-HNMR(12)



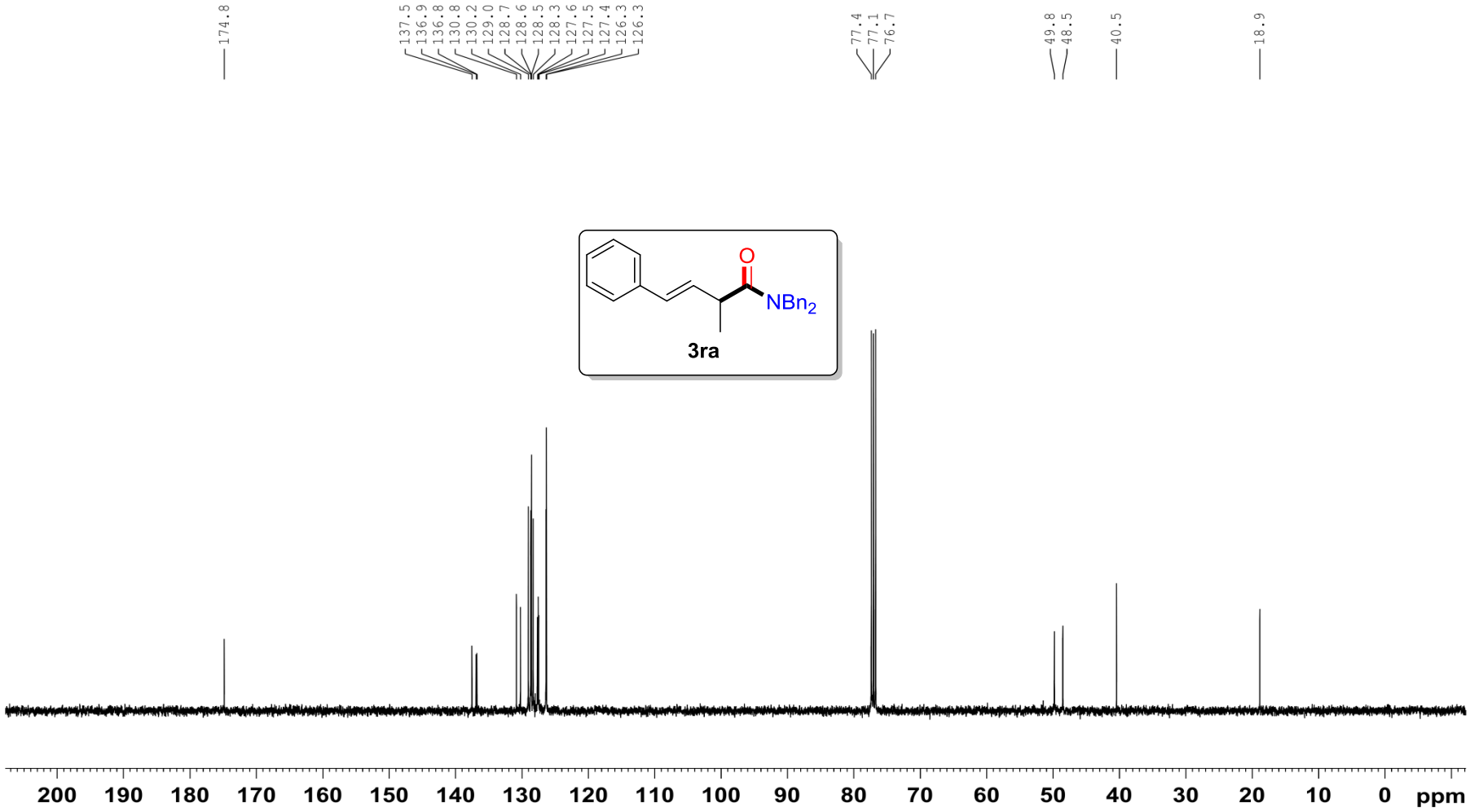
ZJP-X160524-3-CNMR(17)



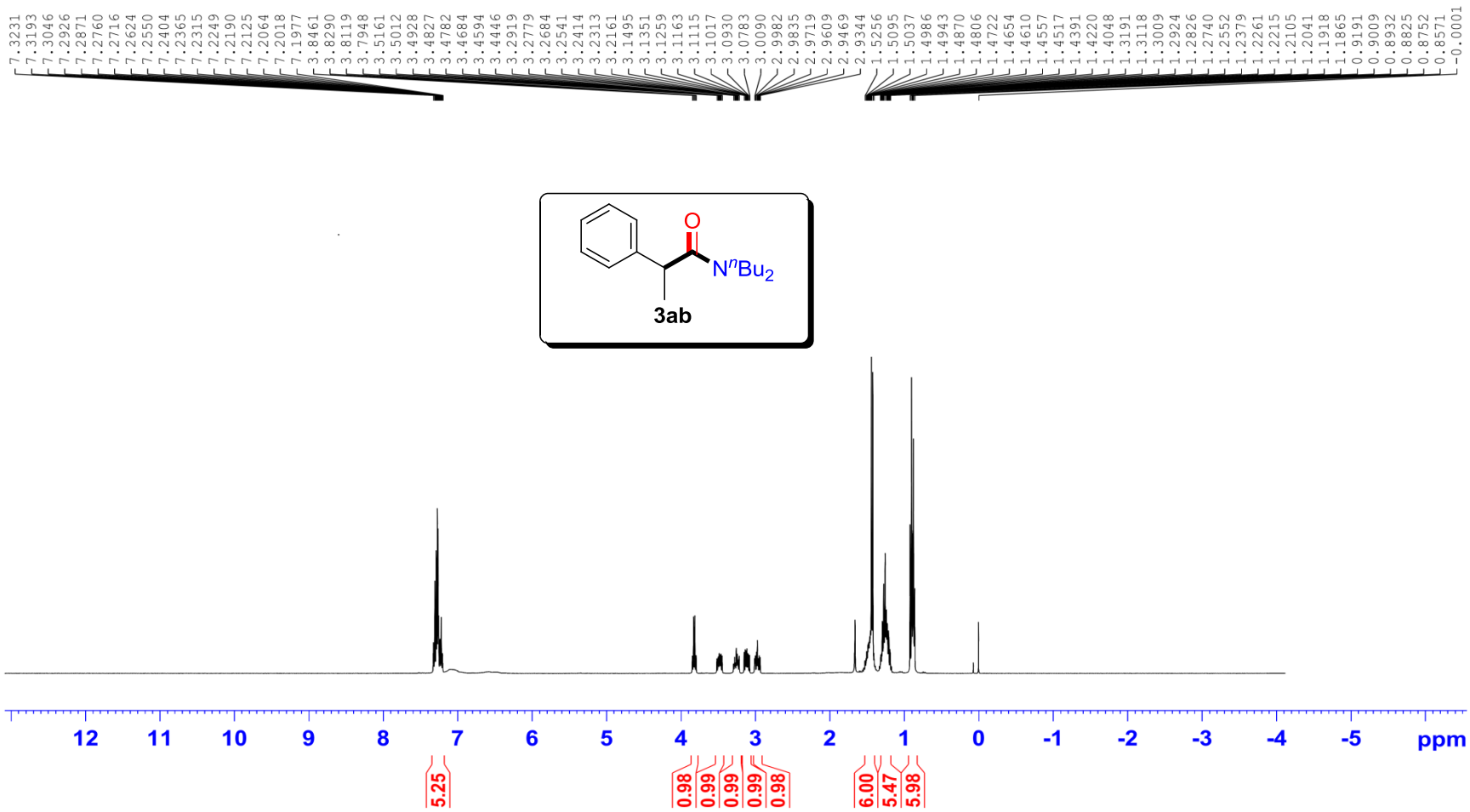
ZJP-X160517-7-HNMR(27)



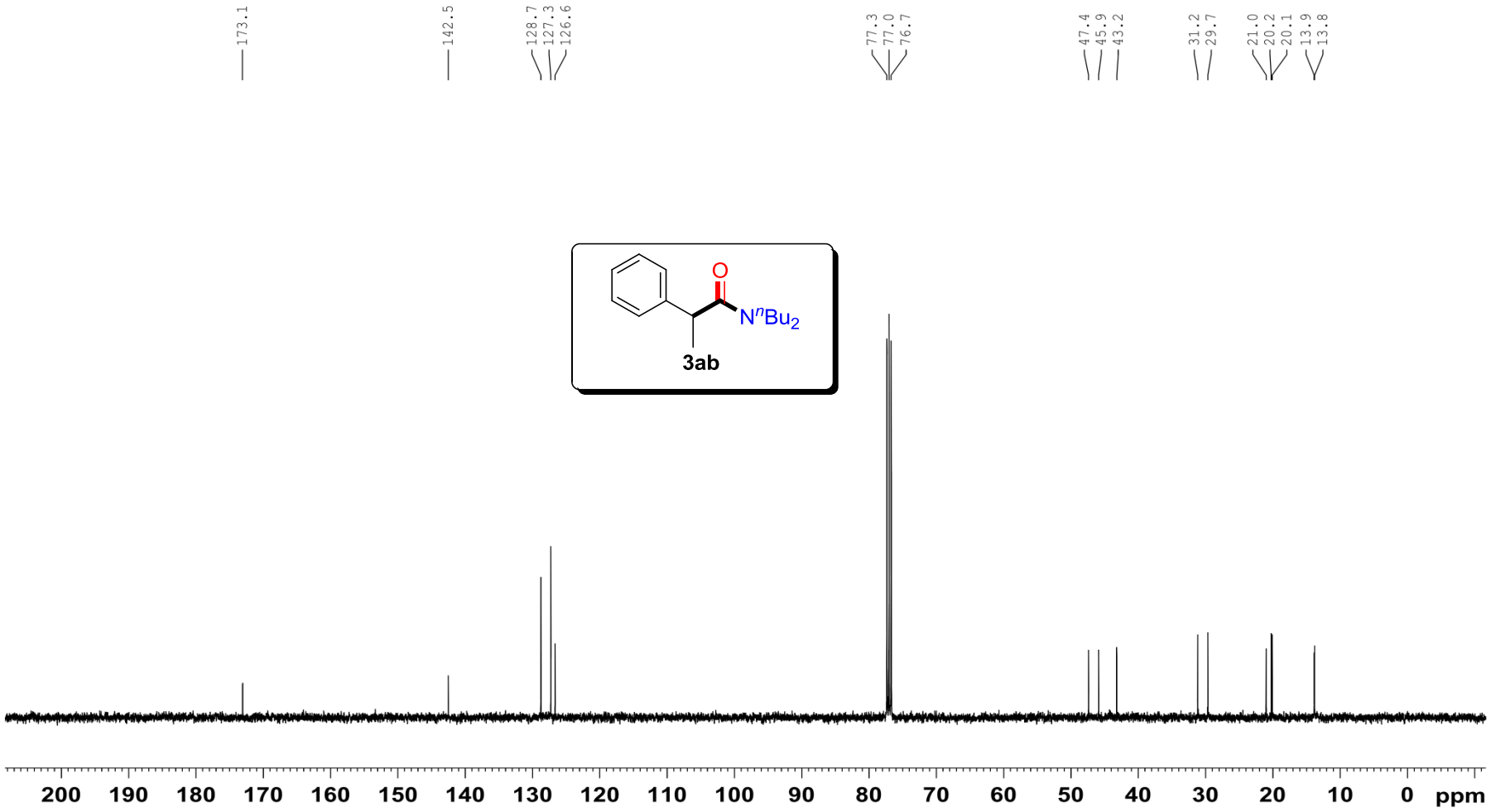
ZJP-X160518-5-CNMR(13)



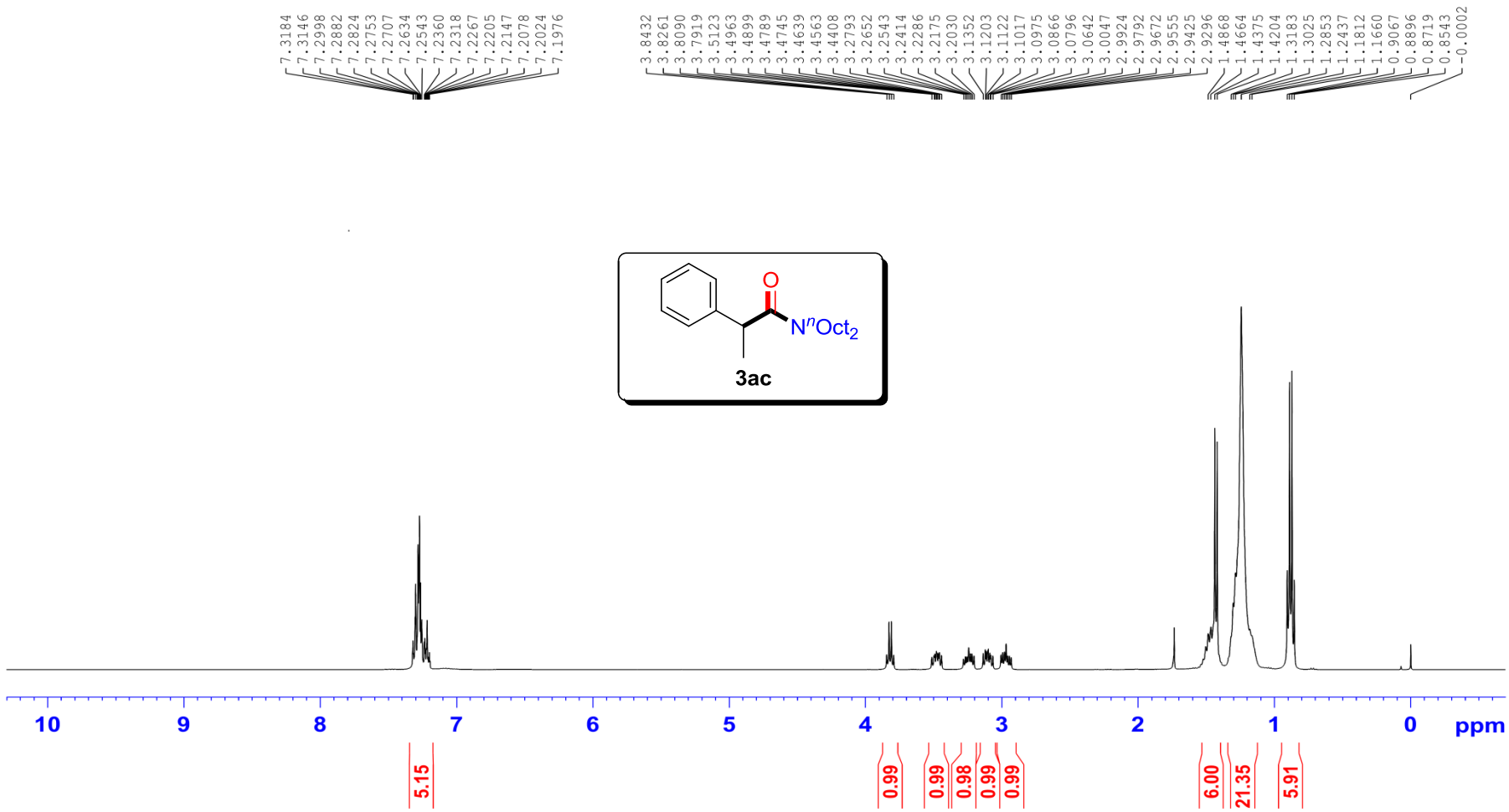
ZJP-X160517-3-HNMR(23)



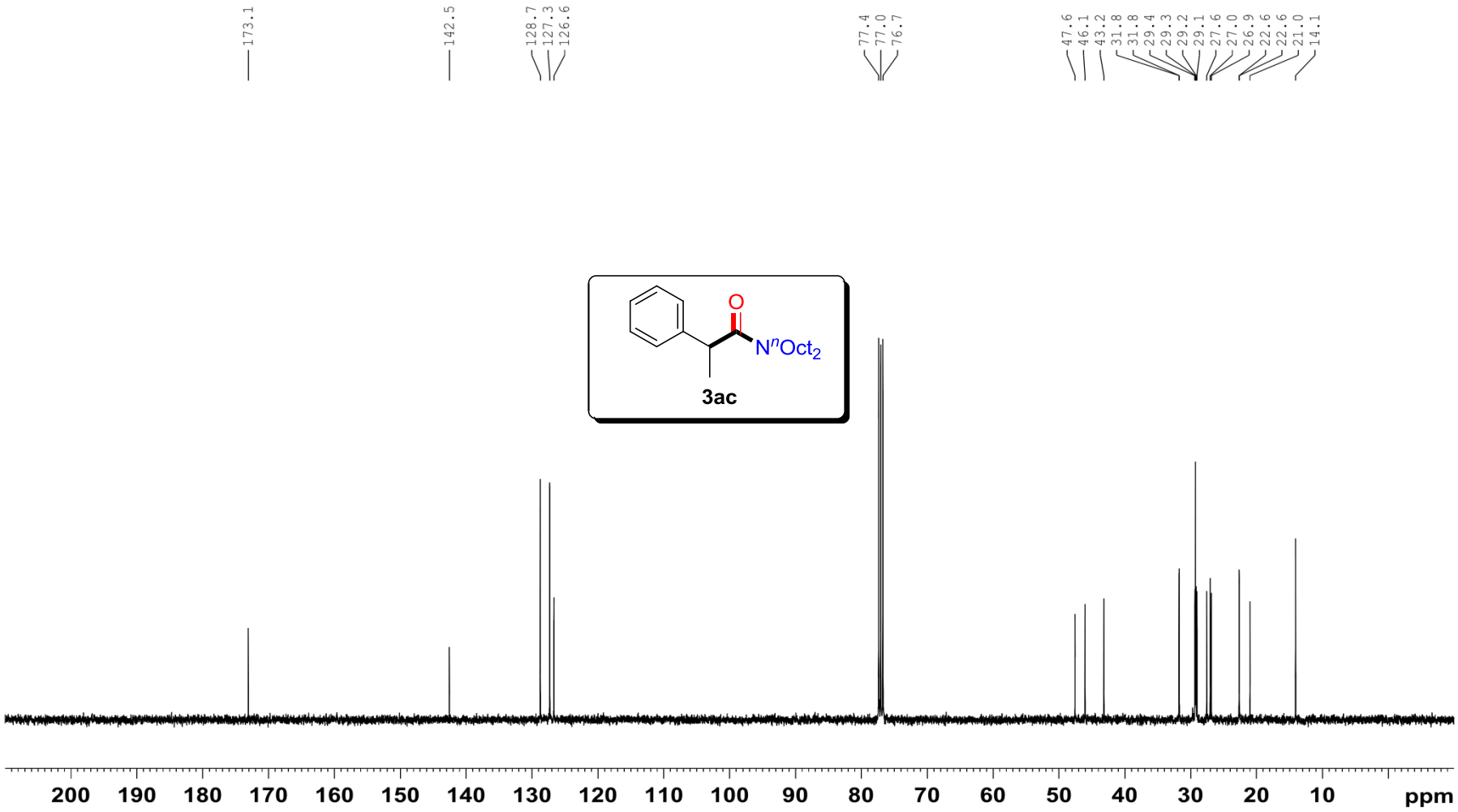
ZJP-X160518-1-CNMR(37)



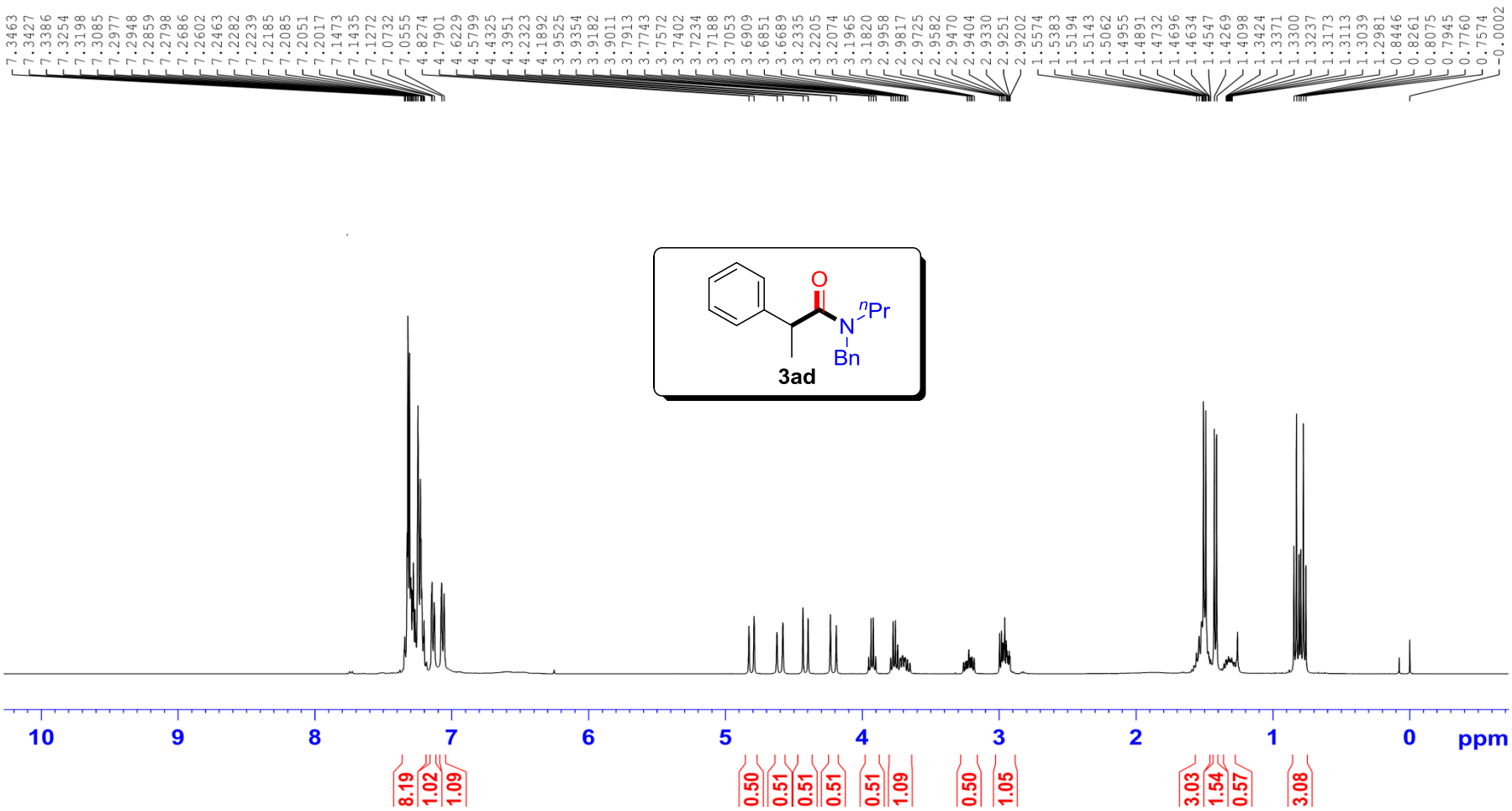
ZJP-X160517-4-HNMR(24)



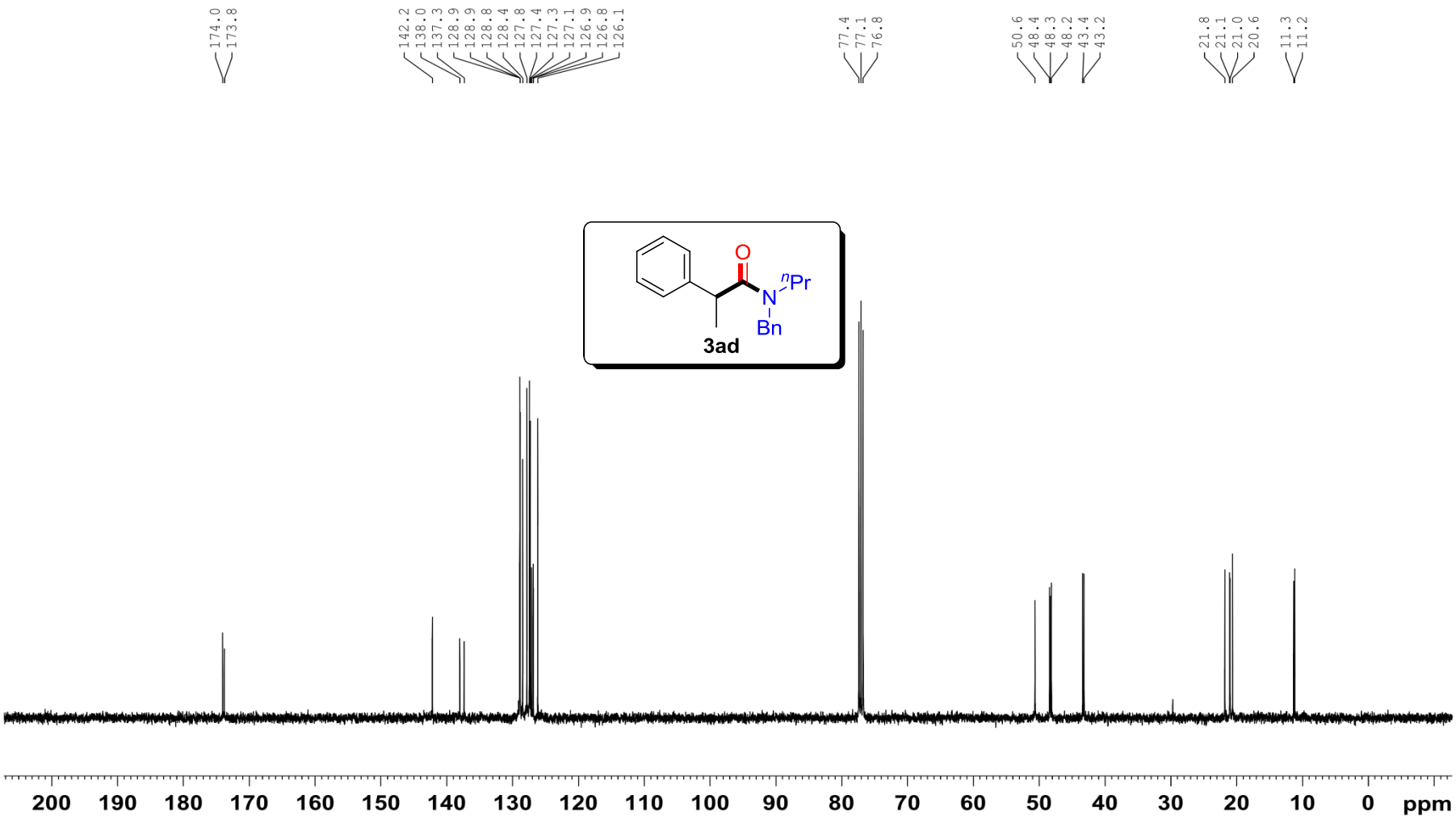
ZJP-X160518-2-CNMR(10)



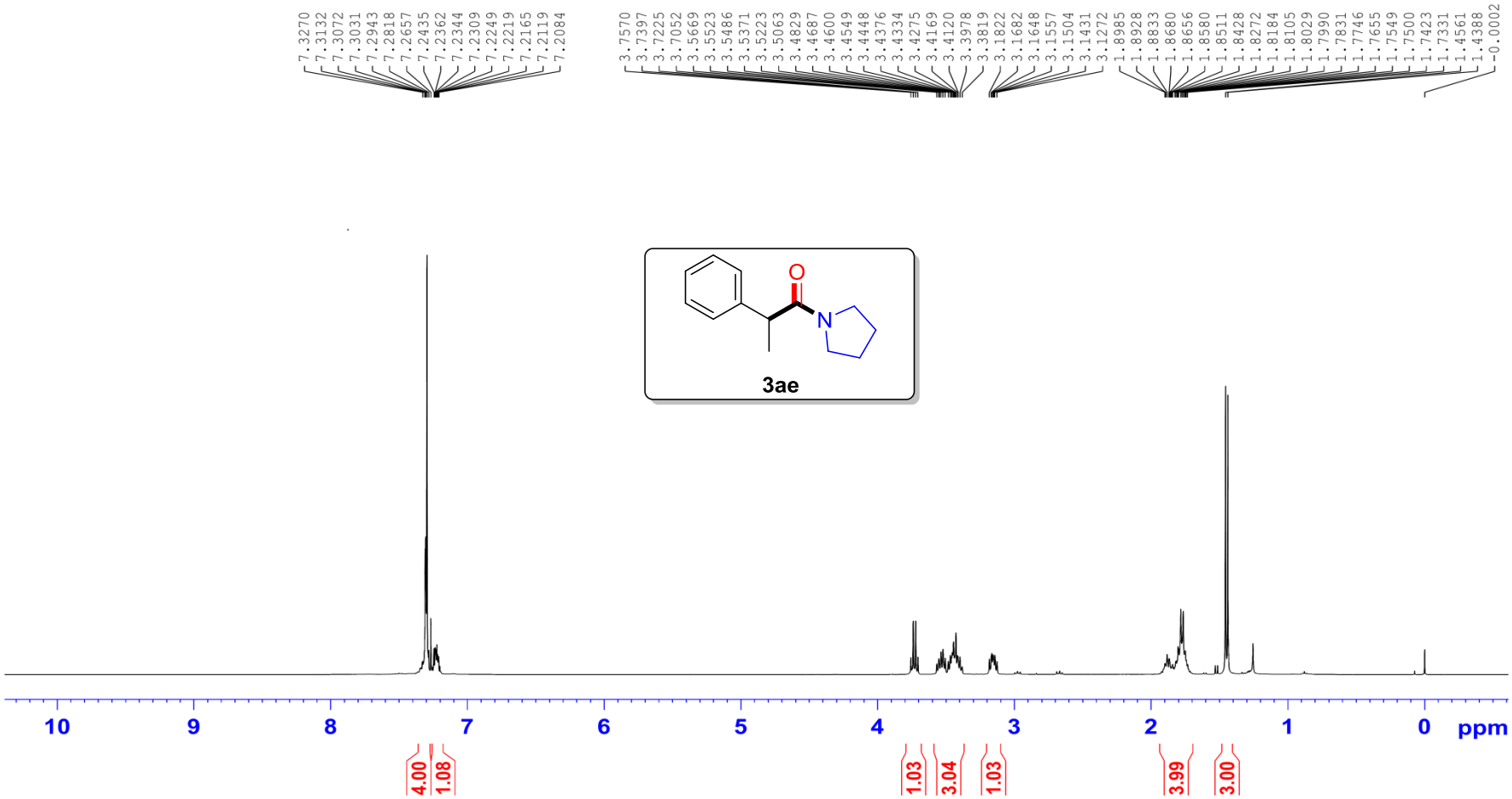
ZJP-X160517-5-HNMR(25)



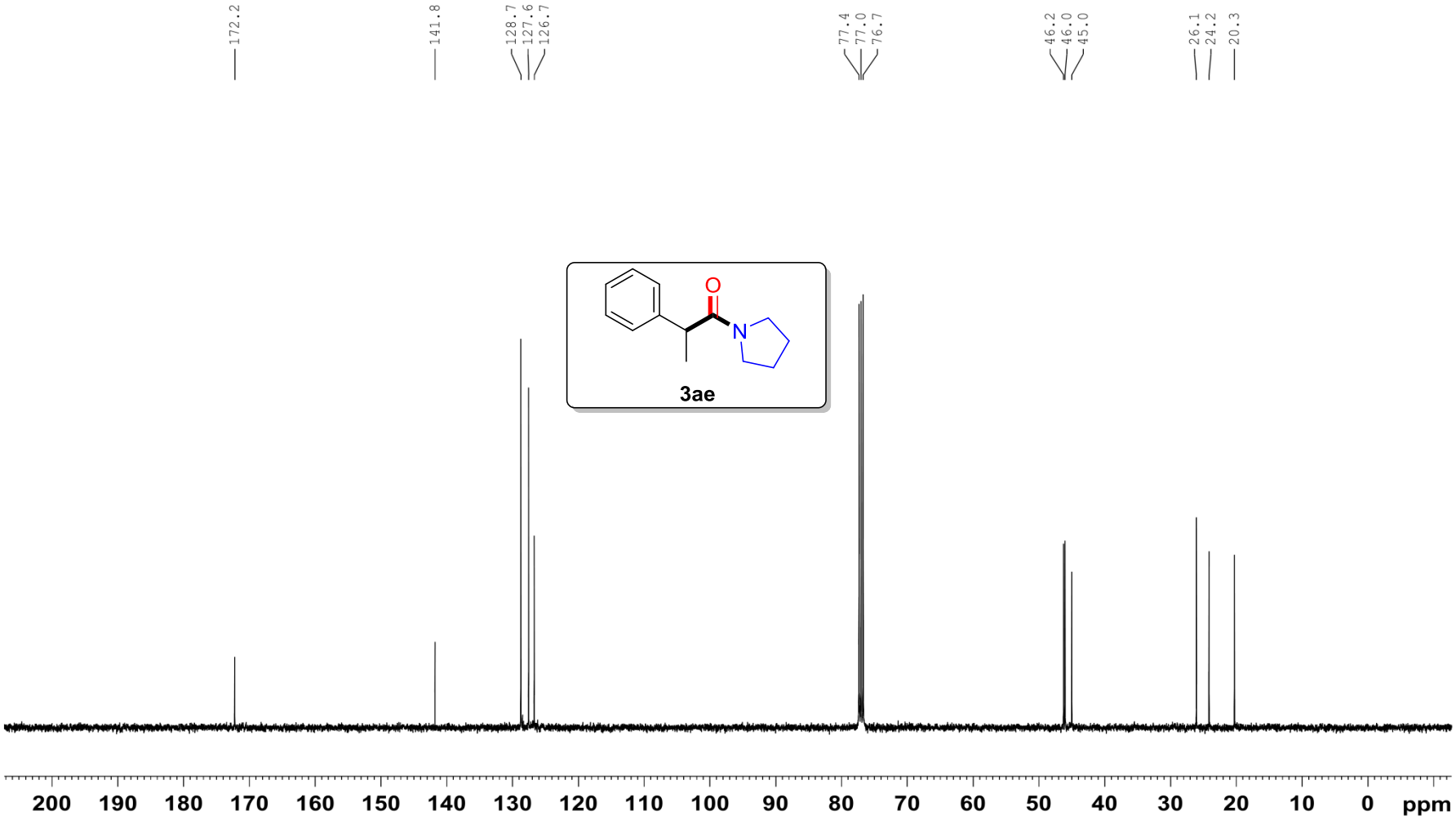
ZJP-X160518-3-CNMR(11)



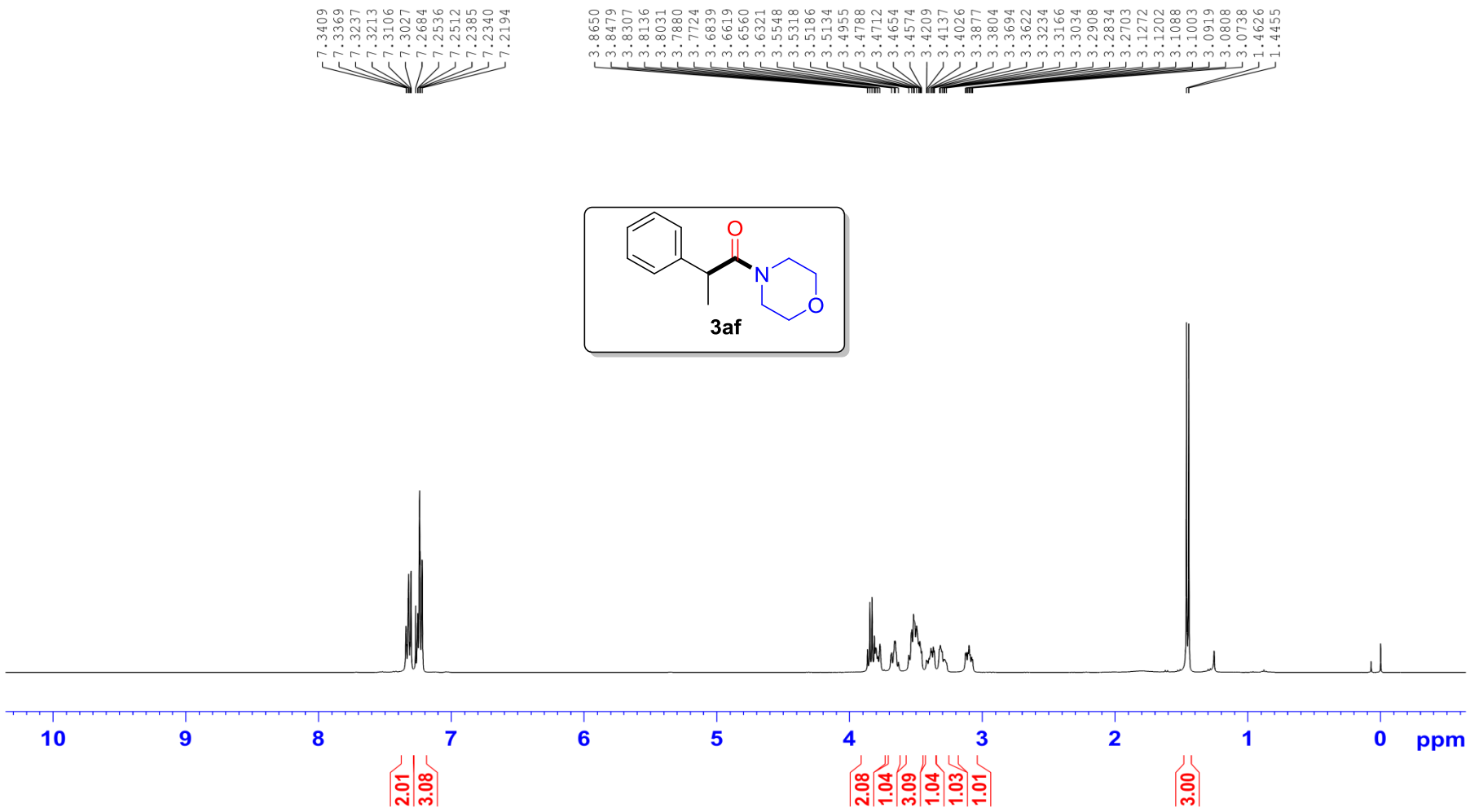
ZJP-X160504-2-HNMR(13)



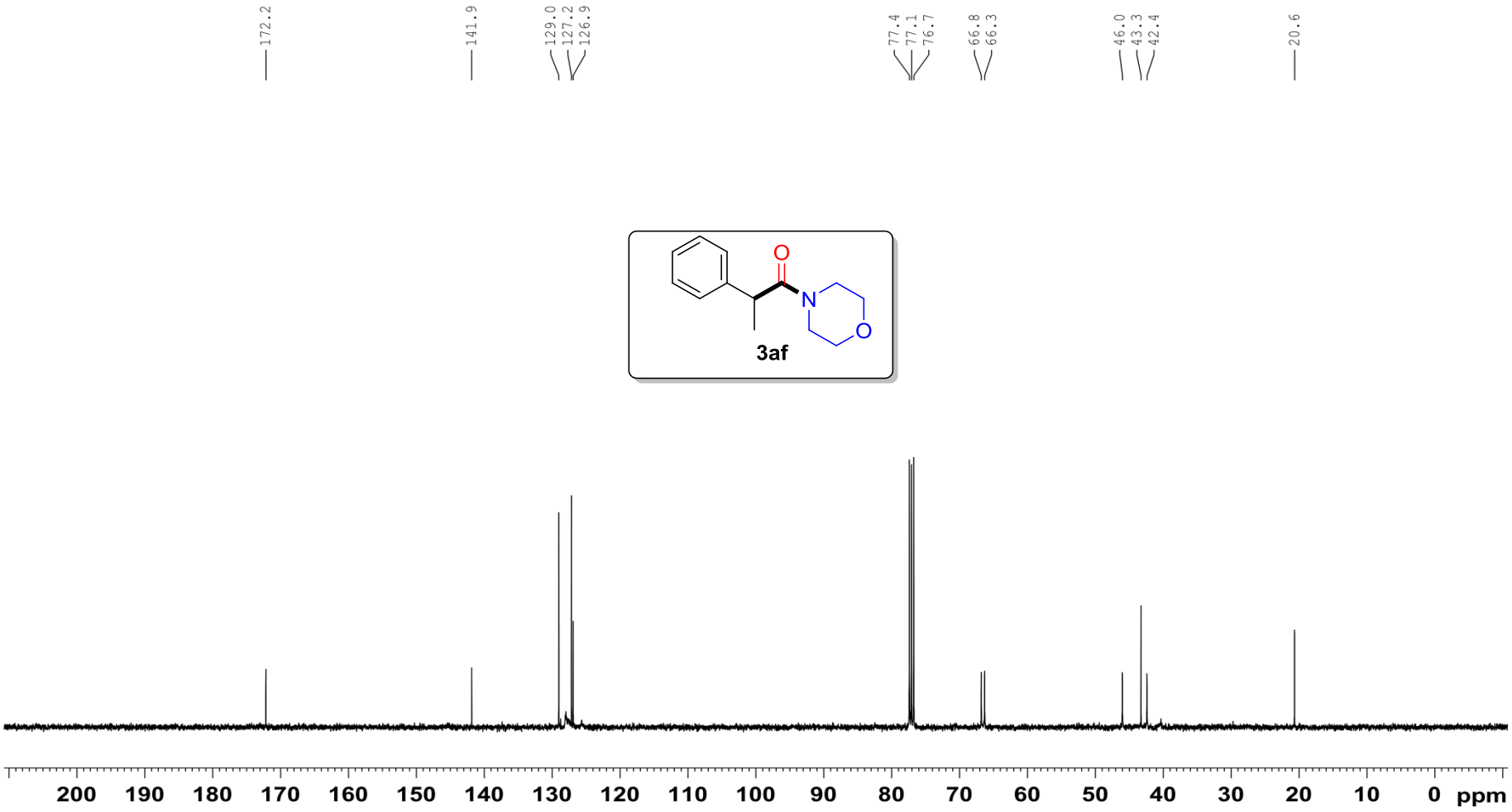
ZJP-X160524-2-CNMR(16)



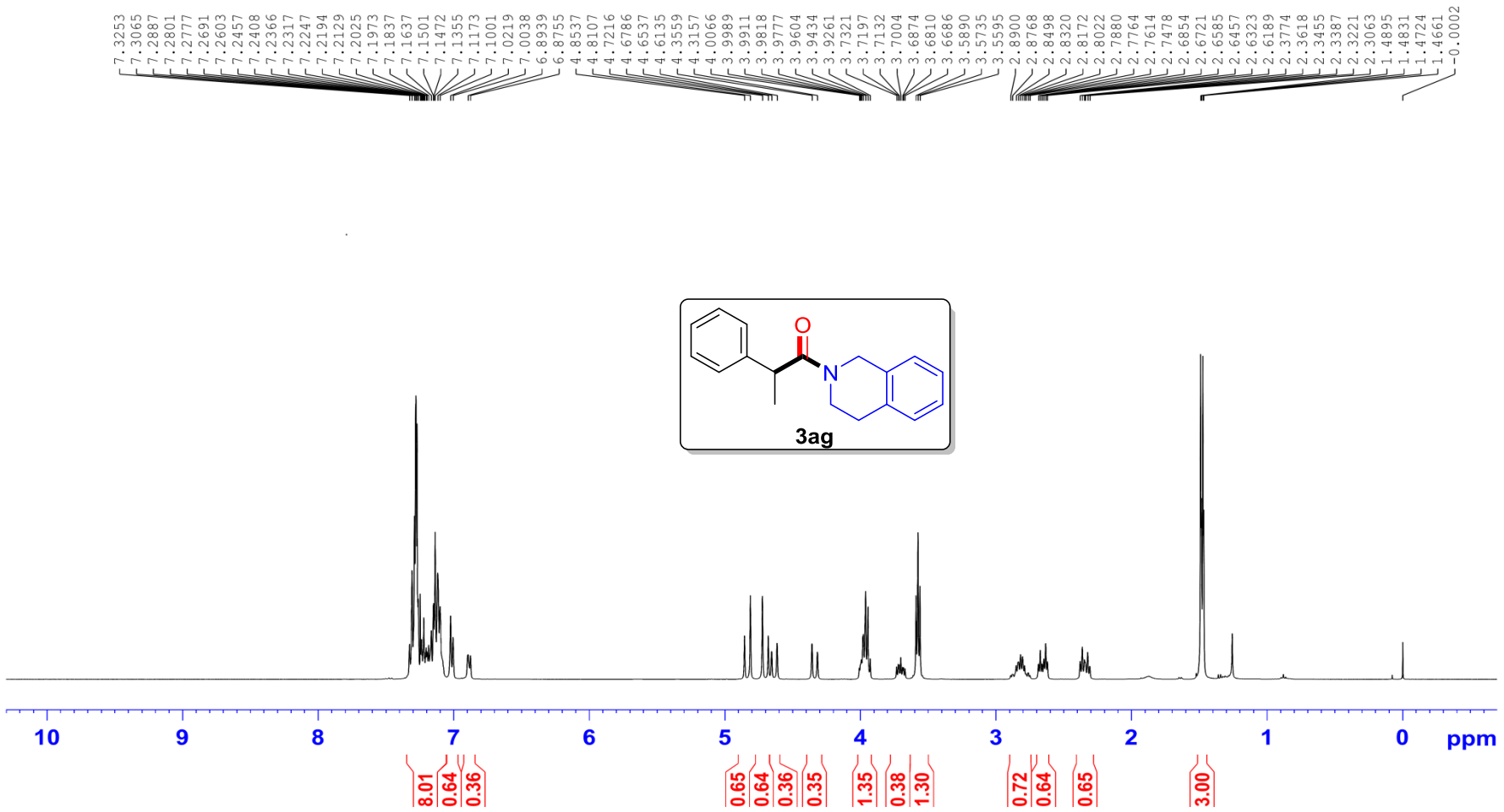
ZJP-X160518-6-HNMR(3)



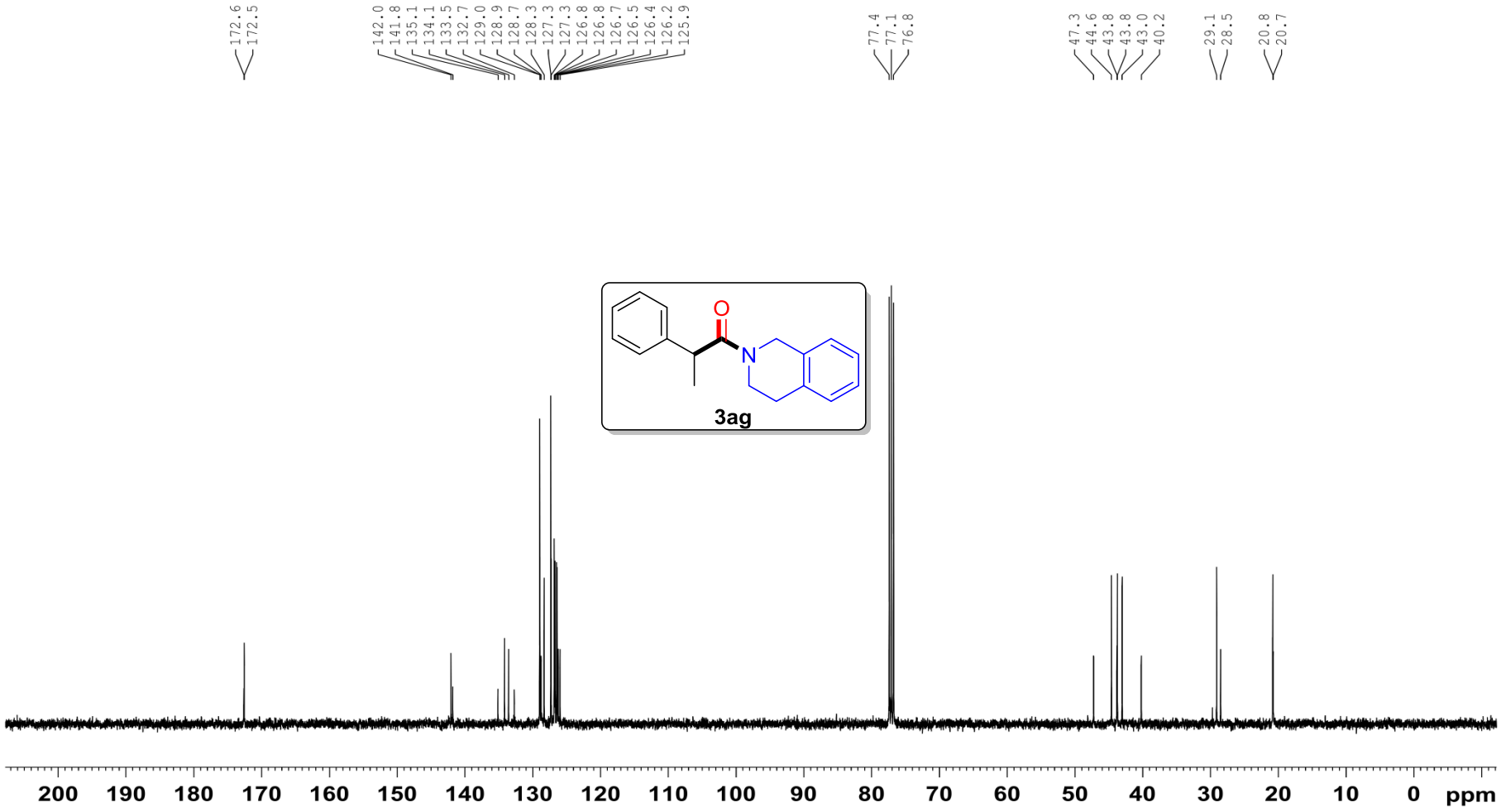
ZJP-X160405-3-CNMR(15)



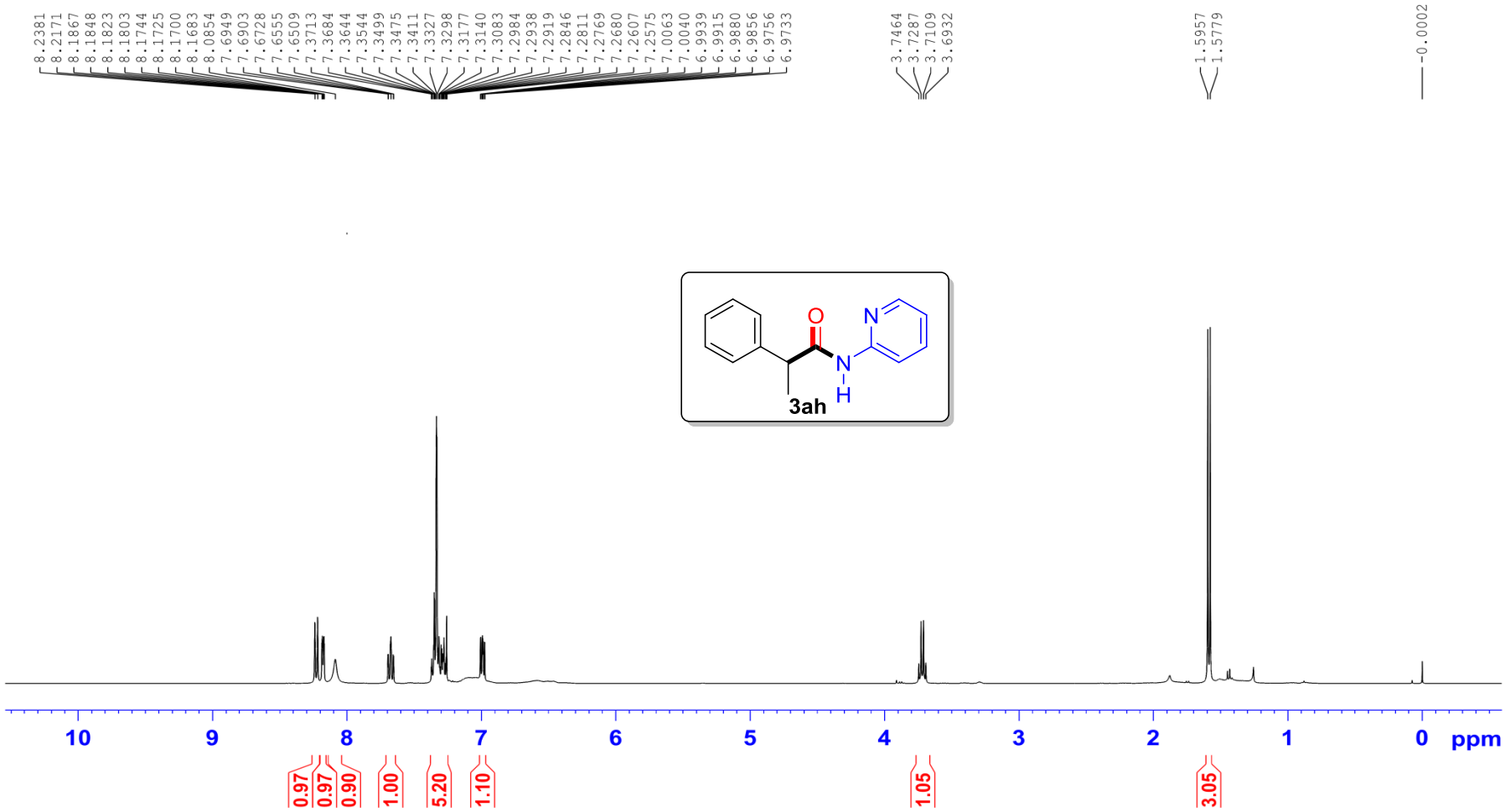
ZJP-X160517-6-HNMR(26)



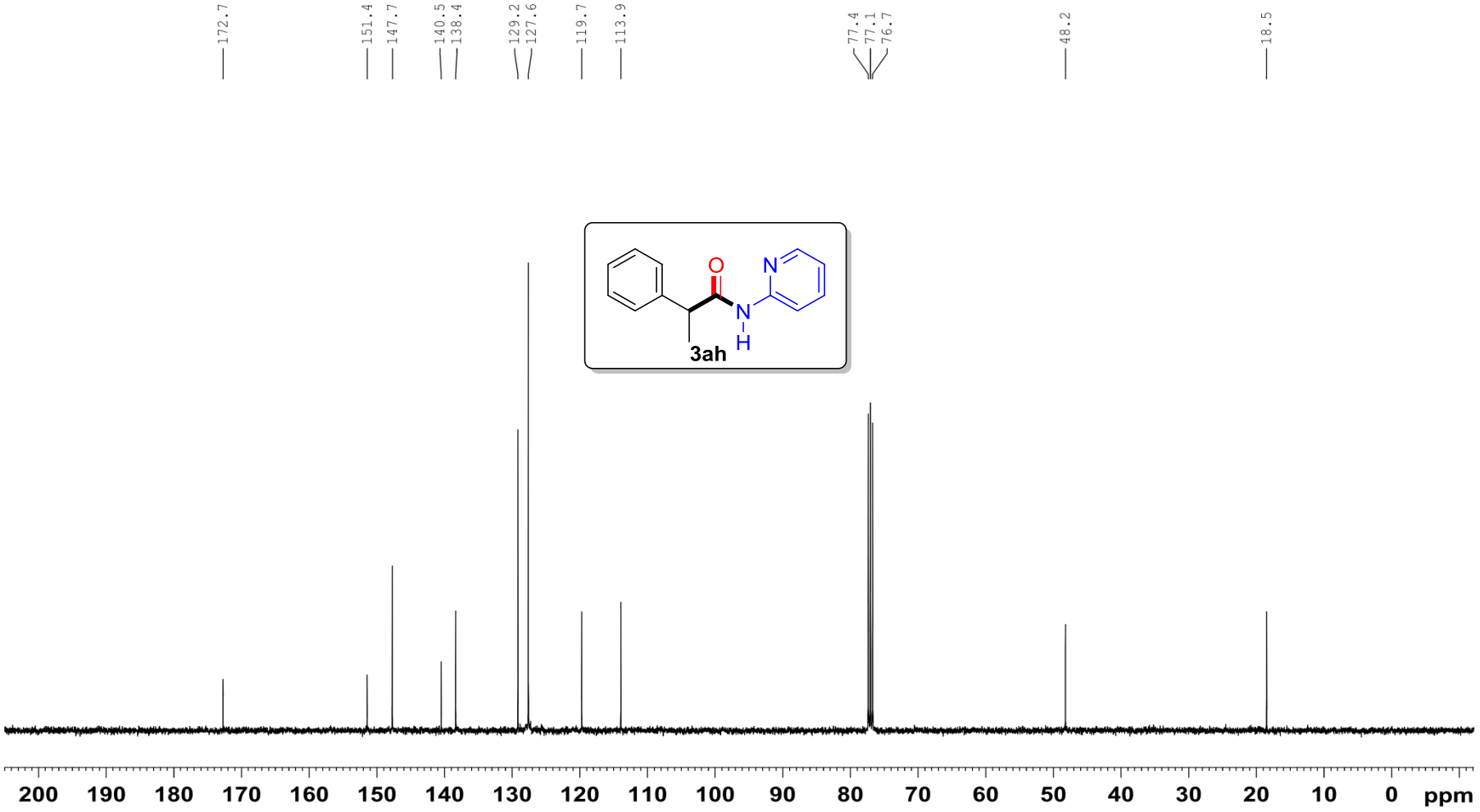
ZJP-X160518-4-CNMR(12)



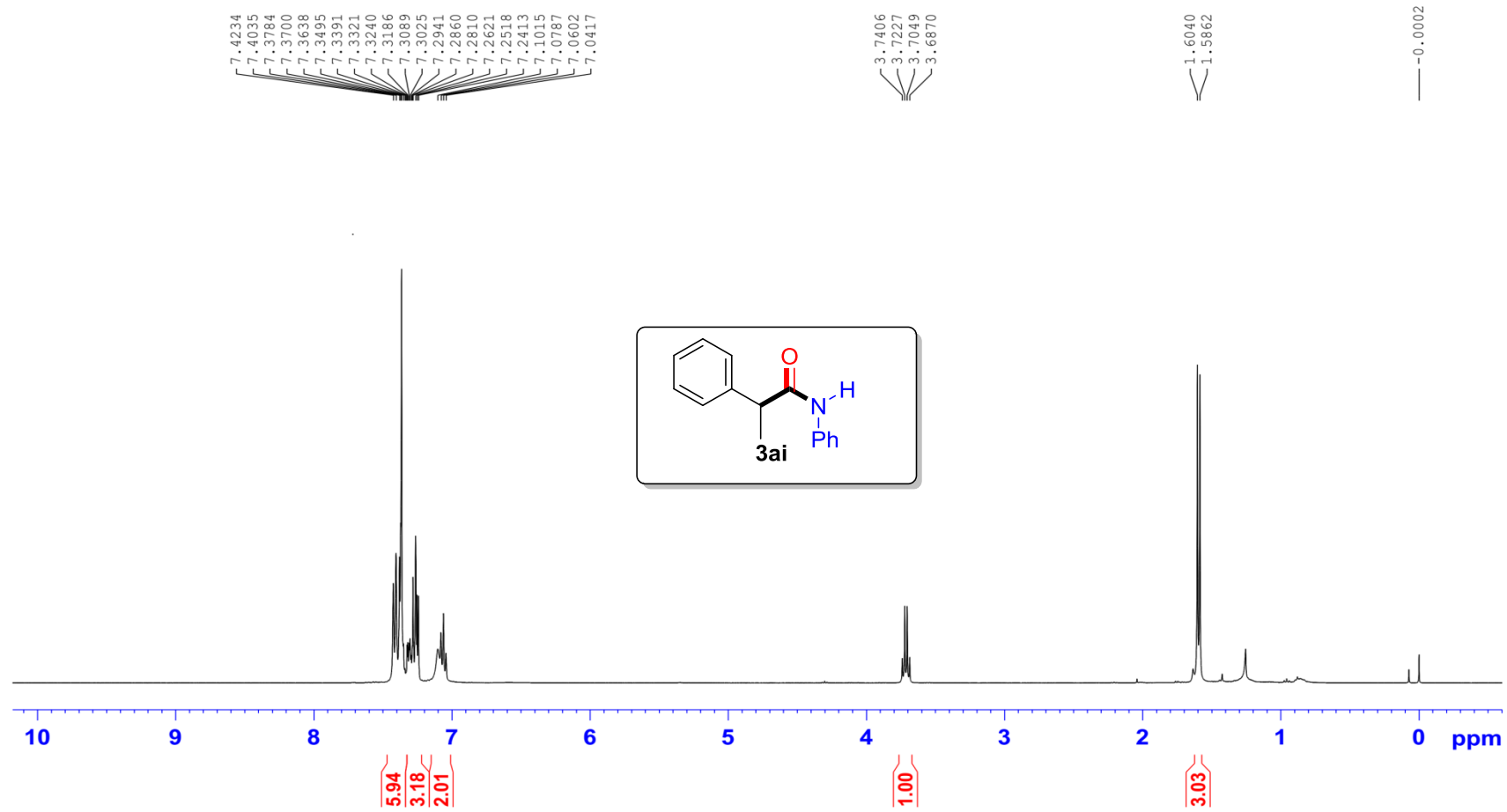
ZJP-X160420-2-HNMR(6)



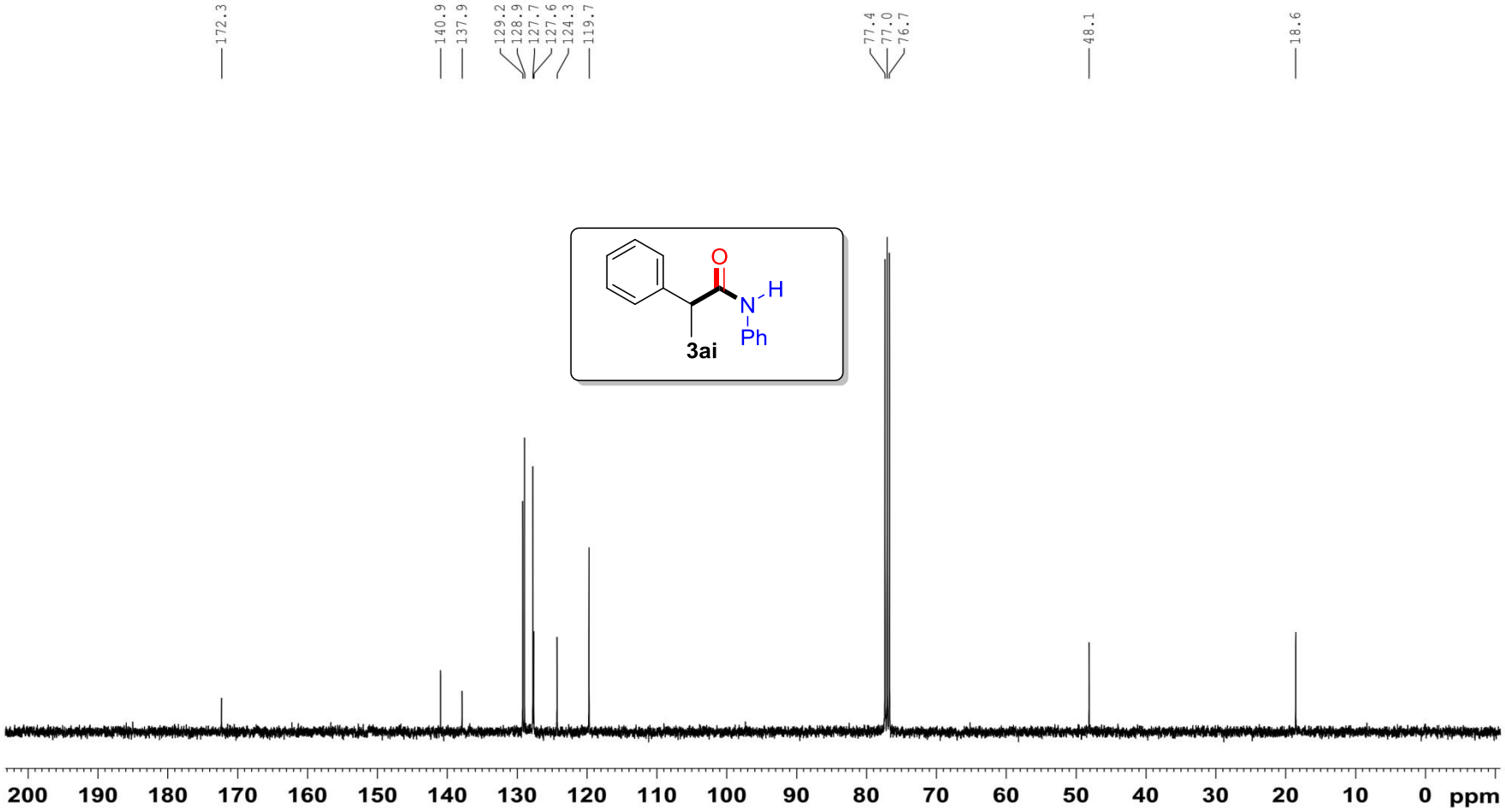
ZJP-X160420-2-CNMR(7)



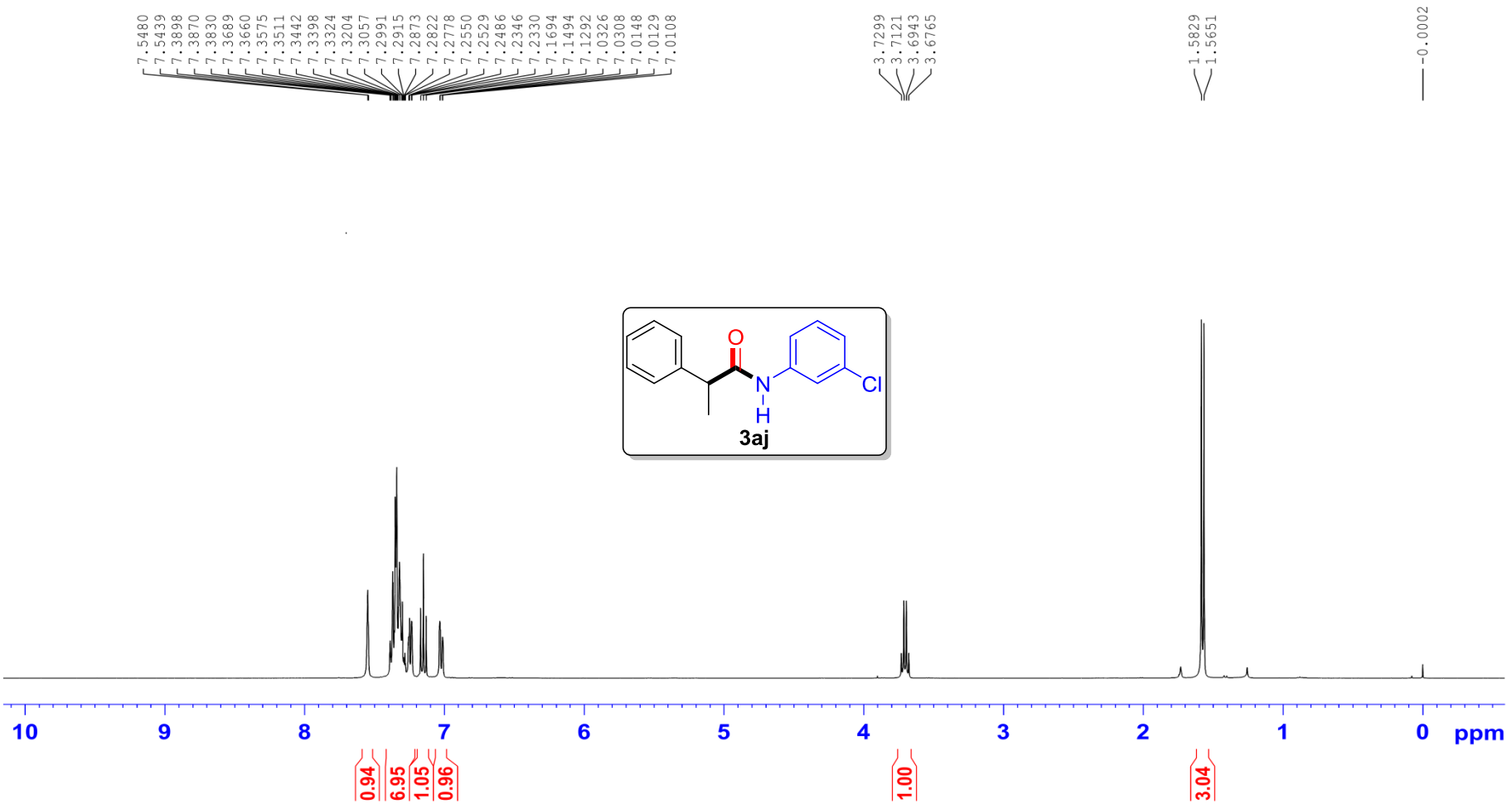
ZJP-X170224-1-HNMR



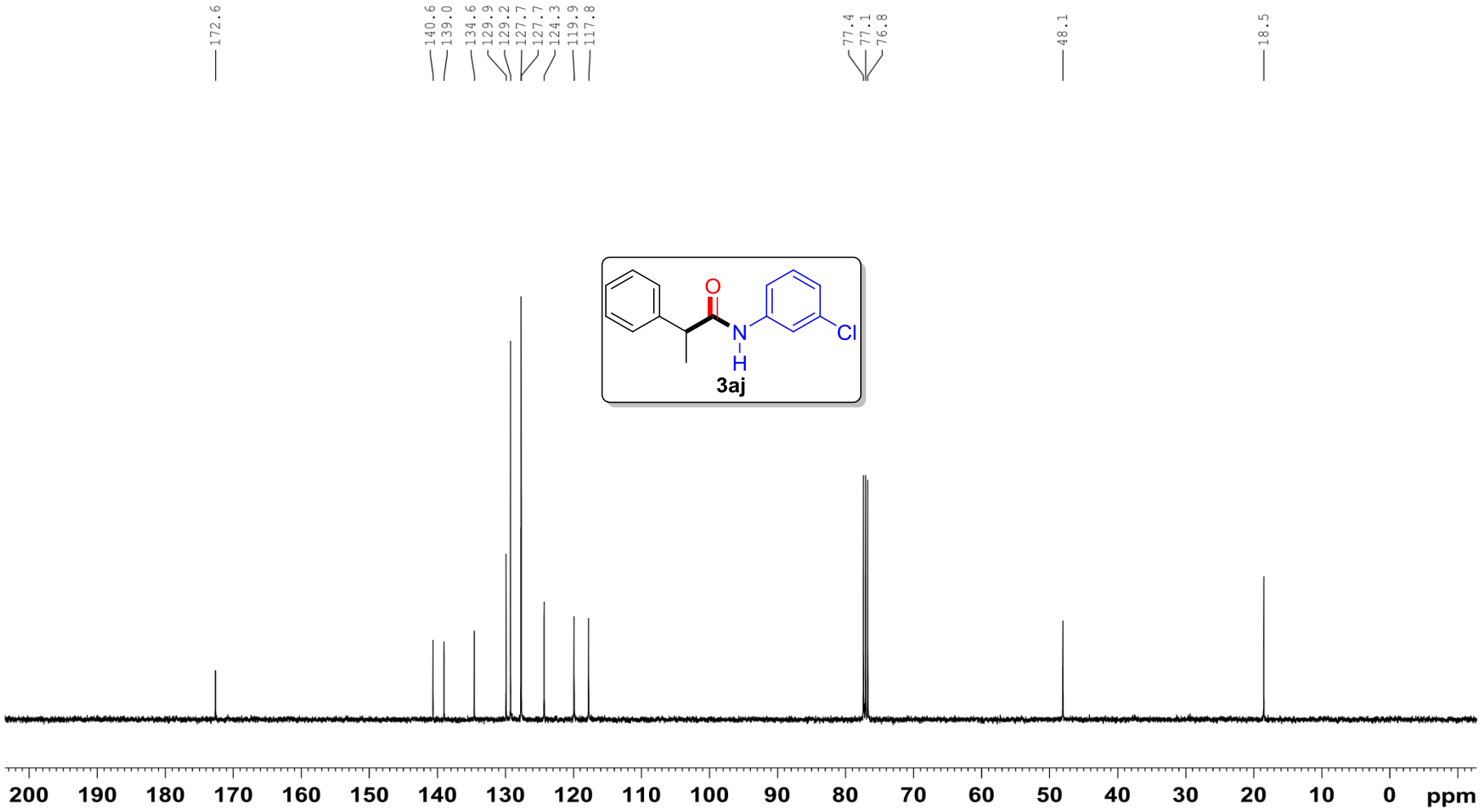
ZJP-X170224-1-CNMR



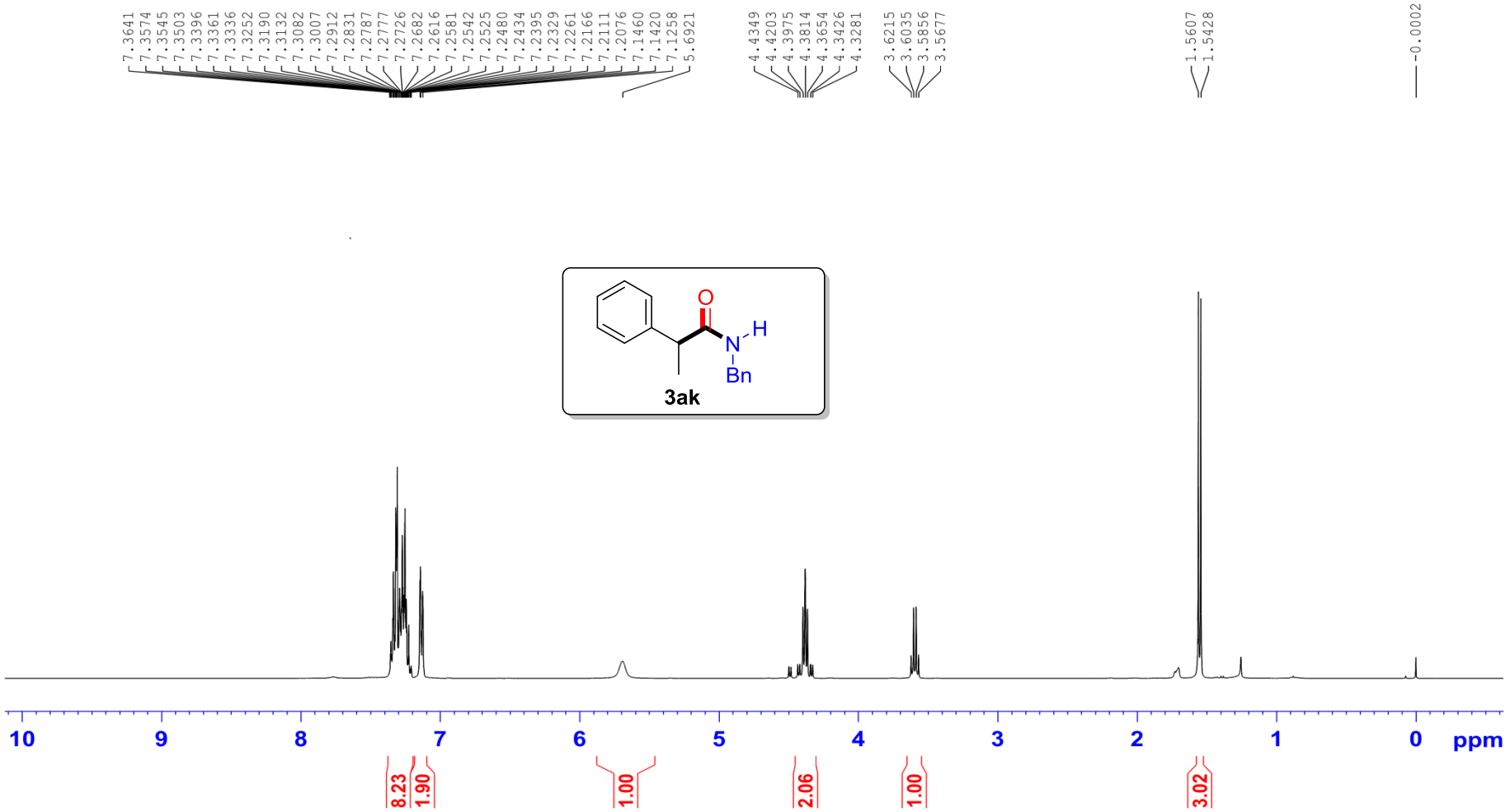
ZJP-X160420-1-HNMR(4)



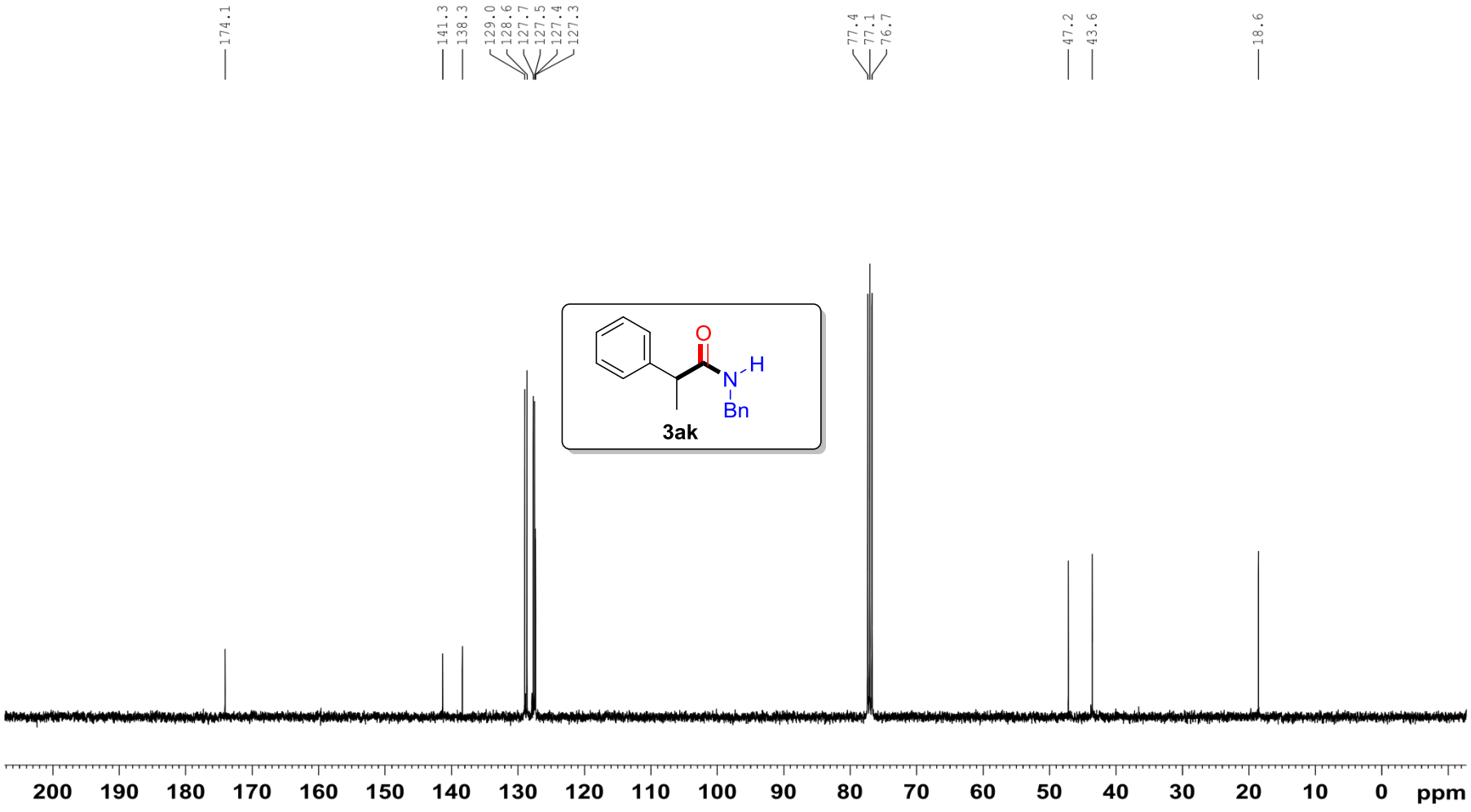
ZJP-X160420-1-CNMR(5)



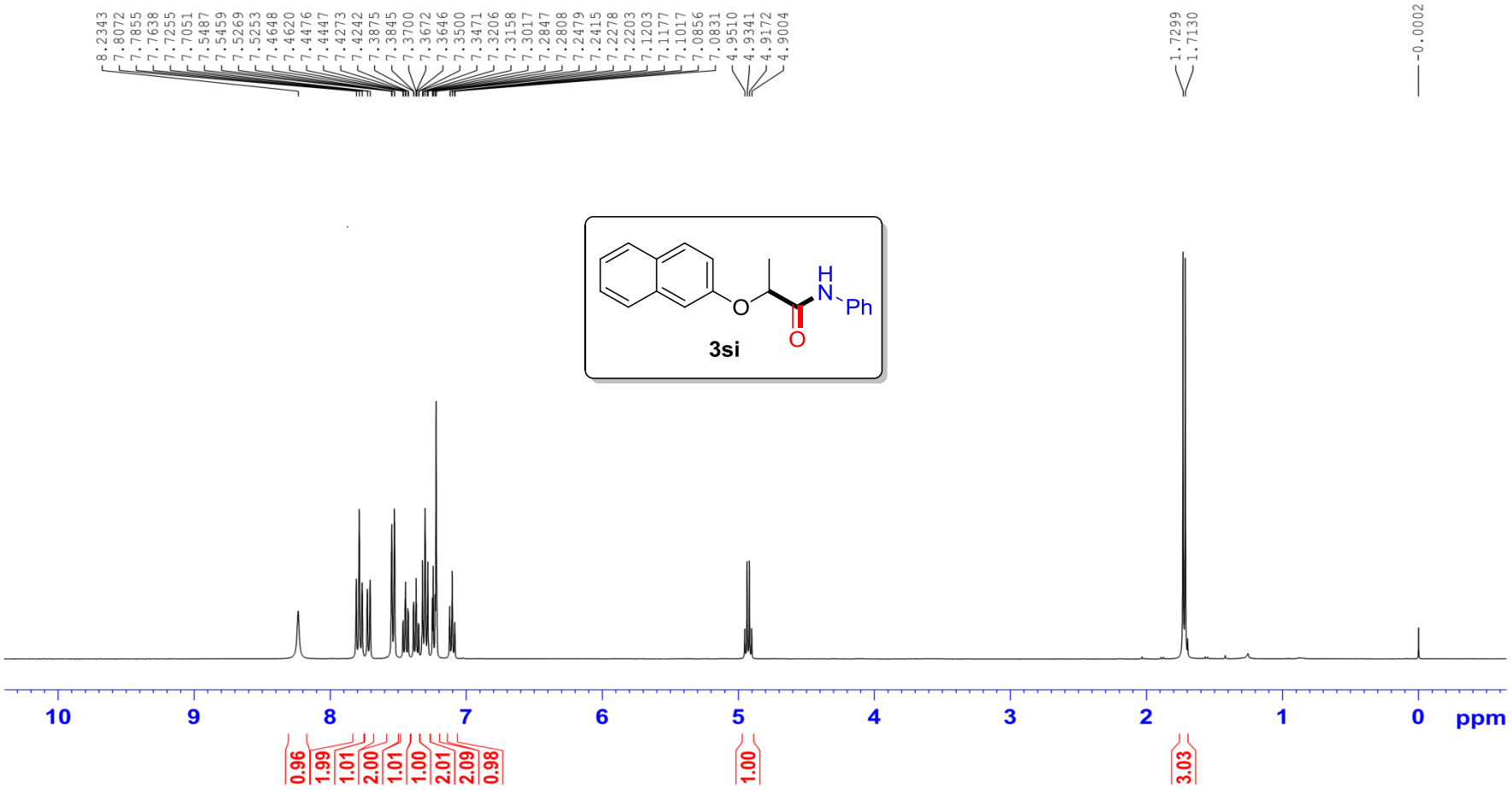
ZJP-X160518-7-HNMR(4)



ZJP-X160519-2-CNMR(13)



ZJP-X170227-2-HNMR



ZJP-X170227-2-CNMR