

Supporting Information for:

Base Catalyzed Selective Esterification of Alcohols with Unactivated Esters

Chunyan Zhang,* Guoying Zhang,* Shizhong Luo, Chunfu Wang and Huiping Li

*Key Laboratory of Sensor Analysis of Tumor Marker, Ministry of Education; Shandong Key
Laboratory of Biochemical Analysis; Key Laboratory of Analytical Chemistry for Life Science in
Universities of Shandong; College of Chemistry and Molecular Engineering, Qingdao University of
Science and Technology, Qingdao 266042, (P. R. China)*

E-mail: qustzcy@163.com; zhanggy@qust.edu.cn

CONTENTS

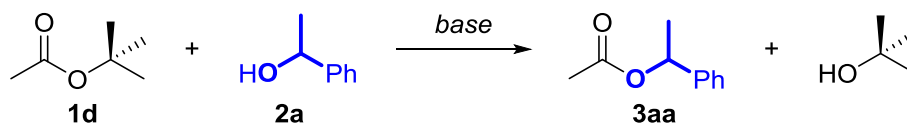
- 1 General experimental details and materials**
- 2 Optimization of the reaction conditions**
- 3 General procedure for base catalyzed selective esterification of alcohols**
- 4 Experimental characterization data for products**
- 5 Gram scale experiment and cyclic reaction experiments**
- 6 Mechanistic investigations**
- 7 Copies for ^1H NMR and ^{13}C NMR of the products**

1. General experiment details and materials

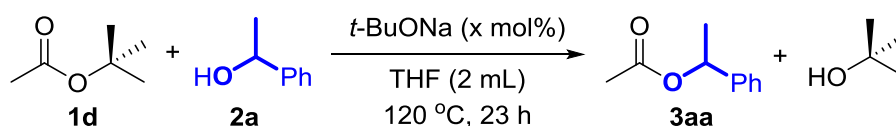
Experimental: All reactions and manipulations with air sensitive compounds being present were performed under dry argon (Ar) or nitrogen (N₂), using Schlenk and glove box techniques. Non-halogenated solvents were dried over sodium benzophenone, 2-methyltetrahydrofuran (2-Me-THF) was dried over calcium hydride, and halogenated solvents were dried over P₂O₅. Deuterated solvents were bought from Cambridge Isotope Laboratories, distilled accordingly, and stored over molecular sieves (3 Å). Other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were collected on a Varian INOVA 300 MHz spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvent signal. Coupling constants (J) are given in Hz (coupling patterns: s: singlet, s_br: broad singlet, d: doublet, t: triplet, q: quartet, m: multiplet). GC analyses were carried out using an Agilent Technologies 6890N system equipped with a Machinery-Nagel (MN) Optima 5 HT column (30 m, 320 μ m, 0.25 μ m) or an Agilent Technologies 6850 system equipped with a MN Optima 17 column (30 m, 320 μ m, 0.25 μ m). GC/MS analyses were carried out on an Agilent 7890A/MSD 5975C system equipped with a HP-5MS column (30 m, 320 μ m, 0.25 μ m). Gas mixtures were analyzed using an Agilent Technologies 6890N equipped with a TCD and an Agilent special plot and molsieve capillary column (30 m, 320 μ m, 0.25 μ m). Elemental analyses were performed using the Elementar Vario EL III. MN silica gel 60 (0.040 – 0.063 mm particle size) was used for flash column chromatography.

2. Optimization of the reaction conditions

Closed system:

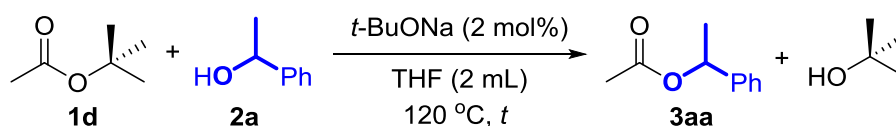


Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, base, *tert*-butyl acetate (**1d**), 1-phenylethanol (**2a**) and solvent. Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (design temperature). After design time the reaction was cooled, a small aliquot of the organic phase was analyzed by GC or GC-MS to monitor product formation. The **3aa** yield was determined by GC analysis relative to the **2a** with *n*-hexadecane as internal standard. Purification of the remainder by column chromatography on silica gel gave the corresponding product **3aa** in the reported yield.

Table S1. The amount of base *t*-BuONa loading screening ^a

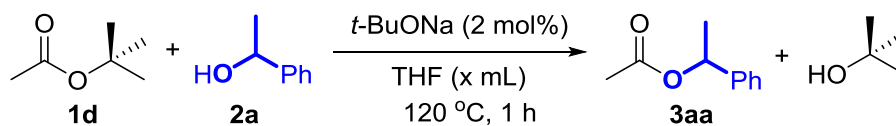
Entry	<i>t</i> -BuONa (mol %)	3aa (%)
1	0	<5
2	1	97
3	2	98
4	5	96
5	10	88
6	20	86
7	30	74
8	40	56
9	50	49
10	60	34
11	80	15
12	100	13
13	120	12

^a Reaction conditions: *t*-BuONa (x mol %), **1d** (2 mmol, 267 μ L), **2a** (1 mmol, 121 μ L), THF (2 mL), 120 °C (extern temperature), N₂, 23 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane as internal standard.

Table S2. The react time screening ^a

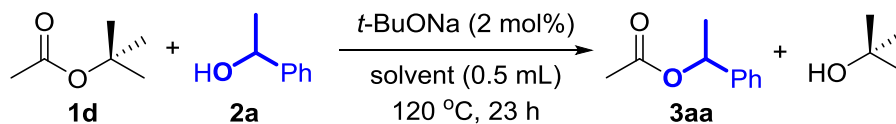
Entry	t (h)	3aa (%)
1	0	4
2	1	96
3	2	96
4	4	97
5	23	98

^a Reaction conditions: *t*-BuONa (2 mol%), **1d** (2 mmol, 267 μ L), **2a** (1 mmol, 121 μ L), THF (2 mL), 120 °C (extern temperature), N₂, x h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane as internal standard.

Table S3. The amount of THF loading screening ^a

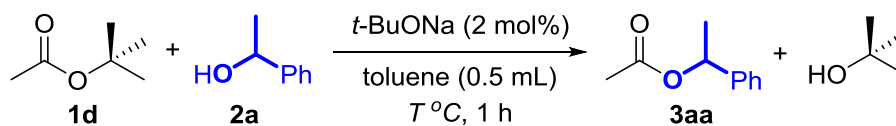
Entry	THF (mL)	3aa (%)
1	0	2.8
2	0.5	96
3	1.0	93
4	1.5	94
5	2.0	96
6	3.0	93

^a Reaction conditions: *t*-BuONa (2 mol%), **1d** (2 mmol, 267 μ L), **2a** (1 mmol, 121 μ L), THF (x mL), 120 °C (extern temperature), N₂, 1 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane as internal standard.

Table S4. The different of solvent screening ^a

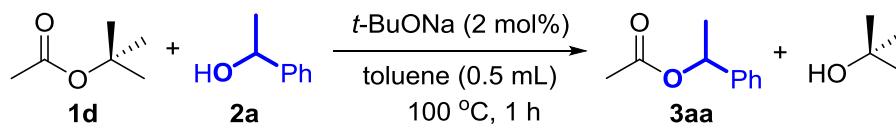
Entry	Solvent (0.5 mL)	3aa (%)
1	THF	96
2	2-MeTHF	96
3	Toluene	>99
4	<i>t</i> -BuOH	79
5	Diglyme	92
6	1,4-dioxane	98
7	DMAc	91
8	Pyridine	94

^a Reaction conditions: *t*-BuONa (2 mol%), **1d** (2 mmol, 267 μ L), **2a** (1 mmol, 121 μ L), solvent (0.5 mL), 120 °C (extern temperature), N₂, 1 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane as internal standard.

Table S5. The reaction temperature screening ^a

Entry	T (°C)	3aa (%)
1	rt	9
2	40	24
3	60	90
4	80	93
5	100	>99
6	120	>99

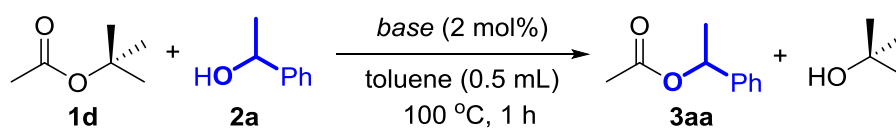
^a Reaction conditions: *t*-BuONa (2 mol%), **1d** (2 mmol, 267 μL), **2a** (1 mmol, 121 μL), toluene (0.5 mL), *T* °C (extern temperature), N₂, 1 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane as internal standard.

Table S6. The ratio of substrates screening ^a

Entry	1a	2a	3aa (%)
1	1.0	1.0	66
2	1.2	1.0	74
3	1.5	1.0	97
4	2.0	1.0	99
5	1.0	1.5	34
6	1.0	2.0	24

^a Reaction conditions: *t*-BuONa (2 mol%), **1d** (x mmol), **2a** (x mmol), toluene (0.5 mL), 100 °C (extern temperature), N₂, 1 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane as internal standard.

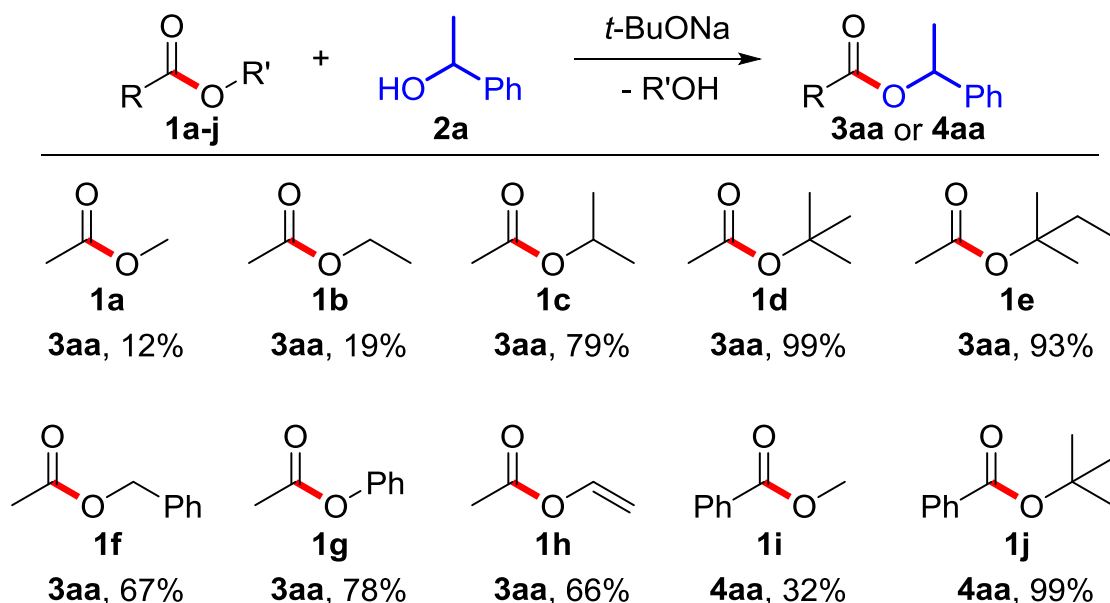
Table S7: The different base screening ^a



Entry	Base	3aa (%)
1	Et ₃ N	0
2	(<i>i</i> -Pr) ₂ NH	0
3	Pyridine	0
4	Na ₂ CO ₃	<5
5	K ₂ CO ₃	0
6	Cs ₂ CO ₃	<5
7	NaOAc	0
8	KOAc	0
9	KHCO ₃	0
10	K ₃ PO ₄	0
11	NaOCH ₂ CH ₃	16
12	<i>t</i> -BuOLi	94
13	<i>t</i> -BuONa	99(0) ^b
14	<i>t</i> -BuOK	99
15	<i>t</i> -BuOCs	12
16	LiOH	32
17	NaOH	24
18	KOH	<5
19	LiHDMS	86
20	NaHDMS	79
21	KHDMS	61
22	KH	94
23	<i>t</i> -BuONa	31 ^c

^a Reaction conditions: *base* (2 mol%), **1d** (2 mmol, 267 μL), **2a** (1 mmol, 121 μL), toluene (0.5 mL), 100 °C (extern temperature), N₂, 1 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane as internal standard. ^b H₂O (10 mol%). ^c Air

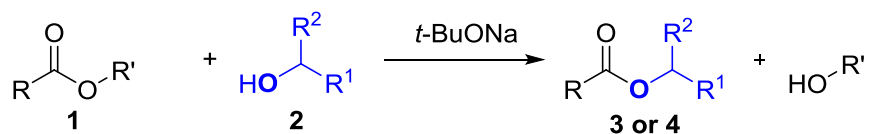
Table S8: Investigated of the different esters ^a



^a General conditions: **1a-j** (1.2 mmol), **2a** (1 mmol), *t*-BuONa (2 mol%), toluene (0.5 mL), 100 °C (extern temperature), N₂, 1 h. Yield of **3aa** or **4aa** determined by GC-analysis using *n*-dodecane as internal standard.

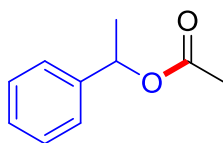
Using a nitrogen-filled glove box, an oven-dried Schlenk tube (50 mL volume) was charged with a magnetic stirring bar, *t*-BuONa (2 mol%), ester (**1**), alcohol (**2a**) and toluene (0.5 mL). Then the tube was closed tightly with a teflon cap and immersed into a pre-heated oil bath (100 °C). After design time the reaction was cooled, a small aliquot of the organic phase was analyzed by GC or GC-MS to monitor product formation. Purification of the remainder by column chromatography on silica gel gave the corresponding product **3** or **4** in the reported yield.

3. General procedure for base catalyzed selective acetylation of alcohols

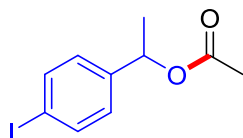


Using a nitrogen-filled glove box, an oven-dried Schlenk tube (50 mL volume) was charged with a magnetic stirring bar, *t*-BuONa (2 mol%), ester (**1**), alcohol (**2**) and toluene (0.5 mL). Then the tube was closed tightly with a teflon cap and immersed into a pre-heated oil bath (100 °C). After an hour the reaction was cooled, a small aliquot of the organic phase was analyzed by GC or GC-MS to monitor product formation. Purification of the remainder by column chromatography on silica gel gave the corresponding product **3 or 4** in the reported yield.

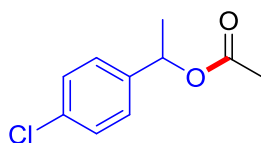
4. Experimental characterization data for products 3 or 4



1-Phenylethyl acetate (3aa):¹ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 157 mg, 96% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.56 – 7.50 (m, 4H), 7.50 – 7.40 (m, 1H), 6.06 (dd, *J* = 12.6, 6.2 Hz, 1H), 2.24 (s, 3H), 1.71 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 141.6, 128.4, 127.8, 126.0, 72.2, 22.1, 21.3. **Elemental analysis** calcd for C₁₀H₁₂O₂ (M: 164.08) [%]: C, 73.15; H, 7.37; found: C, 73.45; H, 7.87. CAS Registry Number: 93-92-5.



1-(4-Iodophenyl)ethyl acetate (3ab):² The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 272 mg, 97% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 5.80 (q, *J* = 6.6 Hz, 1H), 2.06 (s, 3H), 1.50 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 167.0, 141.2, 137.4, 127.9, 93.3, 71.5, 22.0, 21.2. **Elemental analysis** calcd for C₁₀H₁₁IO₂ (M: 289.98) [%]: C, 41.40; H, 3.82; found: C, 41.56; H, 3.92. CAS Registry Number: 90888-02-1.

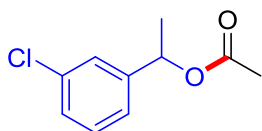


1-(4-Chlorophenyl)ethyl acetate (3ac):³ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 182 mg, 92% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.96 – 7.79 (m, 4H), 6.40 (q, *J* = 6.6 Hz, 1H), 2.62 (s, 3H), 2.07 (d, *J* = 6.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 140.1, 133.5, 128.6, 127.4, 71.5, 22.1, 21.2. **Elemental analysis** calcd for C₁₀H₁₁ClO₂ (M: 198.04) [%]: C, 60.46; H, 5.58; found: C, 60.78; H, 5.79. CAS Registry Number: 19759-43-4.

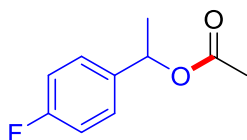
¹ A. K. Chakraborti and S. V. Chankeshwara, *J. Org. Chem.*, 2009, **74**, 1367.

² F. Hammerschmidt, B. Peric Simov, S. Schmidt, S. Schneider and I. Zolle, *Monatshefte für Chemie / Chemical Monthly*, 2005, **136**, 229.

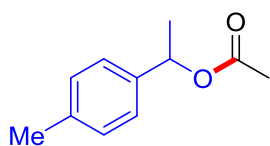
³ D. A. Powell and G. Pelletier, *Tetrahedron Lett*, 2008, **49**, 2495.



1-(3-Chlorophenyl)ethyl acetate (3ad): The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 178 mg, 90% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 9.69 (d, $J = 2.5$ Hz, 1H), 9.62 – 9.52 (m, 3H), 8.17 (q, $J = 6.6$ Hz, 1H), 4.42 (s, 3H), 3.85 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.0, 143.7, 134.3, 129.7, 127.9, 126.1, 124.2, 71.4, 22.1, 21.1. **Elemental analysis** calcd for $\text{C}_{10}\text{H}_{11}\text{ClO}_2$ (M: 198.04) [%]: C, 60.46; H, 5.58; found: C, 60.72; H, 5.56. CAS Registry Number: 19759-26-3.

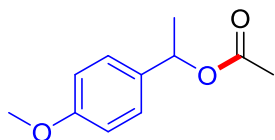


1-(4-Fluorophenyl)ethyl acetate (3ae): The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 167 mg, 92% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.54 – 7.17 (m, 2H), 7.21 – 6.82 (m, 2H), 6.06 – 5.64 (m, 1H), 2.08 (s, 3H), 1.53 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.2, 163.9, 160.6, 137.4, 127.9, 127.8, 115.4, 115.1, 71.6, 22.1, 21.2. **Elemental analysis** calcd for $\text{C}_{10}\text{H}_{11}\text{FO}_2$ (M: 182.07) [%]: C, 65.92; H, 6.09; found: C, 65.72; H, 6.59. CAS Registry Number: 2928-12-3.

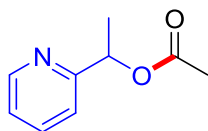


1-(p-Tolyl)ethyl acetate (3af):⁴ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 158 mg, 89% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.32 (d, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 7.9$ Hz, 2H), 5.92 (q, $J = 6.6$ Hz, 1H), 2.40 (s, 3H), 2.11 (s, 3H), 1.59 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.2, 138.6, 137.5, 129.0, 126.0, 72.1, 22.0, 21.3, 21.0. **Elemental analysis** calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2$ (M: 178.10) [%]: C, 74.13; H, 7.92; found: C, 74.25; H, 7.99. CAS Registry Number: 19759-40-1.

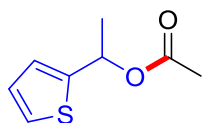
⁴ A. Fischer and G. N. Henderson, *Canadian J. Chem.*, 1981, **59**, 2314.



1-(4-Methoxyphenyl)ethyl acetate (3ag):³ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 178 mg, 92% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 5.90 (q, *J* = 6.6 Hz, 1H), 3.83 (s, 3H), 2.09 (s, 3H), 1.57 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.4, 159.3, 133.8, 127.6, 113.8, 72.0, 55.2, 22.0, 21.4. **Elemental analysis** calcd for C₁₁H₁₄O₃ (M: 194.09) [%]: C, 68.02; H, 7.27; found: C, 68.21; H, 7.34. CAS Registry Number: 945-89-1.



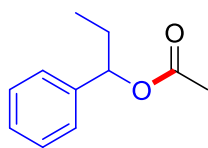
1-(Pyridin-2-yl)ethyl acetate (3ah):⁵ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 153 mg, 93% yield. ¹H NMR (300 MHz, CDCl₃) δ 8.54 (d, *J* = 4.9 Hz, 1H), 7.63 (td, *J* = 7.7, 1.7 Hz, 1H), 7.40 – 7.20 (m, 1H), 7.15 (dd, *J* = 7.5, 4.9 Hz, 1H), 5.87 (q, *J* = 6.7 Hz, 1H), 2.08 (s, 3H), 1.55 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 160.1, 149.1, 136.7, 122.6, 120.3, 72.9, 21.1, 20.6. **Elemental analysis** calcd for C₉H₁₁NO₂ (M: 165.08) [%]: C, 65.44; H, 6.71; N, 8.48; found: C, 65.72; H, 6.88; N, 8.69. CAS Registry Number: 2555-01-3.



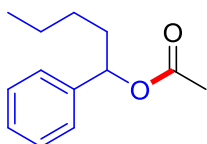
1-(Thiophen-2-yl)ethyl acetate (3ai):⁶ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 149 mg, 88% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.37 – 7.22 (m, 1H), 7.17 – 7.06 (m, 1H), 7.05 – 6.92 (m, 1H), 6.21 (q, *J* = 6.6 Hz, 1H), 2.09 (s, 3H), 1.68 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 144.5, 126.6, 125.3, 125.2, 67.6, 22.1, 21.3. **Elemental analysis** calcd for C₈H₁₀O₂S (M: 170.04) [%]: C, 56.45; H, 5.92; found: C, 56.77; H, 5.68. CAS Registry Number: 22426-23-9.

⁵ H. Jiang, H. Chen, A. Wang and X. Liu, *Chem. Comm.*, 2010, **46**, 7259.

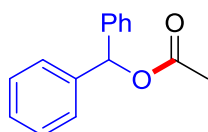
⁶ F. Fringuelli, *Org. Chem. Biochem.*, 1976, **30**, 605.



1-Phenylpropyl acetate (3aj):⁷ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 158 mg, 89% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.45 – 7.35 (m, 4H), 7.37 – 7.30 (m, 1H), 5.73 (t, *J* = 6.9 Hz, 1H), 2.12 (s, 3H), 2.01 – 1.82 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 140.4, 128.3, 128.2, 127.7, 126.4, 77.4, 29.2, 21.1, 9.8. **Elemental analysis** calcd for C₁₁H₁₄O₂ (M: 178.10) [%]: C, 74.13; H, 7.92; found: C, 74.46; H, 7.85. CAS Registry Number: 2114-29-6.



1-Phenylpentyl acetate (3ak):⁸ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 162 mg, 79% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.40 (d, *J* = 4.3 Hz, 4H), 7.37 – 7.30 (m, 1H), 5.82 (t, *J* = 7.0 Hz, 1H), 2.11 (d, *J* = 1.4 Hz, 3H), 2.05 – 1.93 (m, 1H), 1.90 – 1.80 (m, 1H), 1.44 – 1.27 (m, 4H), 0.95 (dd, *J* = 7.1, 6.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.1, 140.7, 128.2, 127.6, 126.3, 75.9, 35.9, 27.5, 22.3, 21.0, 13.7. **Elemental analysis** calcd for C₁₃H₁₈O₂ (M: 206.13) [%]: C, 75.69; H, 8.80; found: C, 75.78; H, 8.75. CAS Registry Number: 38488-01-6.

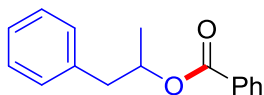


Benzhydryl acetate (3al):⁹ The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 171mg, 76% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.48 – 7.35 (m, 10H), 6.99 (s, 1H), 2.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.9, 140.1, 128.4, 127.8, 127.0, 77.4, 21.2. **Elemental analysis** calcd for C₁₅H₁₄O₂ (M: 226.10) [%]: C, 79.62; H, 6.24; found: C, 79.72; H, 6.31. CAS Registry Number: 954-67-6.

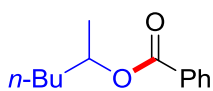
⁷ A. Berkessel, M. L. Sebastian-Ibarz and T. N. Müller, *Angew. Chem., Int. Ed.*, 2006, **45**, 6567.

⁸ V. Kumar, A. Sharma, M. Sharma, U. K. Sharma and A. K. Sinha, *Tetrahedron*, 2007, **63**, 9718.

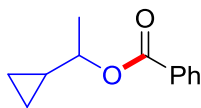
⁹ H. Baba, K. Moriyama and H. Togo, *Tetrahedron Lett*, 2011, **52**, 4303.



1-Phenylpropan-2-yl benzoate (3am):¹⁰ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 220 mg, 92% yield. ¹H NMR (300 MHz, CDCl₃) δ 8.16 – 8.01 (m, 2H), 7.60 (dd, *J* = 10.8, 4.0 Hz, 1H), 7.47 (dd, *J* = 8.0, 7.5 Hz, 2H), 7.39 – 7.20 (m, 5H), 5.42 (dd, *J* = 12.6, 6.4 Hz, 1H), 3.13 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.95 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.39 (d, *J* = 6.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 137.5, 132.7, 130.7, 129.5, 128.3, 128.3, 126.5, 72.1, 42.3, 19.5. **Elemental analysis** calcd for C₁₆H₁₆O₂ (M: 240.12) [%]: C, 79.97; H, 6.71; found: C, 79.65; H, 6.82. CAS Registry Number: 2114-33-2.



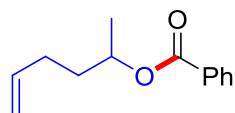
Hexan-2-yl benzoate (3an):¹¹ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 175 mg, 85% yield. ¹H NMR (300 MHz, CDCl₃) δ 8.09 – 7.96 (m, 2H), 7.60 – 7.51 (m, 1H), 7.49 – 7.39 (m, 2H), 5.27 – 5.07 (m, 1H), 1.80 – 1.69 (m, 1H), 1.61 (t, *J* = 5.1 Hz, 1H), 1.34 (dd, *J* = 6.2, 0.4 Hz, 7H), 0.91 (dd, *J* = 7.9, 6.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 132.7, 130.9, 129.5, 128.3, 71.7, 35.8, 27.6, 22.6, 20.1, 14.0. **Elemental analysis** calcd for C₁₃H₁₈O₂ (M: 206.13) [%]: C, 75.69; H, 8.80; found: C, 75.72; H, 8.63. CAS Registry Number: 5953-49-1.



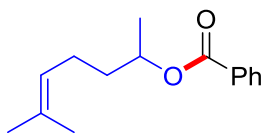
1-Cyclopropylethyl benzoate (3ao): The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 167 mg, 88% yield. ¹H NMR (300 MHz, CDCl₃) δ 8.06 (dd, *J* = 5.2, 3.8 Hz, 2H), 7.60 – 7.36 (m, 3H), 4.61 (dq, *J* = 8.3, 6.3 Hz, 1H), 1.43 (d, *J* = 6.2 Hz, 3H), 1.12 (ddt, *J* = 10.3, 8.0, 4.1 Hz, 1H), 0.52 (ddt, *J* = 12.8, 9.6, 3.6 Hz, 3H), 0.38 – 0.26 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 132.7, 130.9, 129.6, 128.3, 75.7, 20.0, 16.5, 3.7, 2.5. **Elemental analysis** calcd for C₁₂H₁₄O₂ (M: 190.10) [%]: C, 75.76; H, 7.42; found: C, 75.82; H, 7.53. CAS Registry Number: 91495-78-2.

¹⁰ R. I. Khusnutdinov, N. A. Shchadneva, L. F. Khisamova and U. M. Dzhemilev, *Russian J. Org.Chem.*, 2011, **47**, 155.

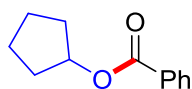
¹¹ M. Hosseini-Sarvari and E. Sodagar, *Comptes Rendus Chimie*, 2013, **16**, 229.



Hex-5-en-2-yl benzoate (3ap): The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 146 mg, 72% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.09 (d, $J = 8.3$ Hz, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 6.9$ Hz, 2H), 5.87 (ddt, $J = 16.8, 10.2, 6.6$ Hz, 1H), 5.22 (dd, $J = 12.6, 6.4$ Hz, 1H), 5.04 (dd, $J = 15.9, 14.5$ Hz, 2H), 2.21 (dd, $J = 6.7, 1.5$ Hz, 2H), 1.90 (dd, $J = 14.1, 7.4$ Hz, 1H), 1.82 – 1.70 (m, 1H), 1.40 (d, $J = 6.3$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.1, 137.7, 132.7, 130.8, 129.5, 128.2, 115.0, 71.0, 35.2, 29.7, 20.0. **Elemental analysis** calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$ (M: 204.12) [%]: C, 76.44; H, 7.90; found: C, 76.64; H, 7.68. CAS Registry Number: 54844-25-6.

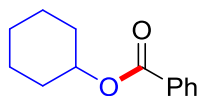


6-Methylhept-5-en-2-yl benzoate (3aq): The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 215 mg, 93% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.05 (dd, $J = 8.3, 1.2$ Hz, 2H), 7.60 – 7.49 (m, 1H), 7.46 – 7.39 (m, 2H), 5.14 (ddd, $J = 8.7, 6.3, 3.6$ Hz, 2H), 2.10 (q, $J = 7.4$ Hz, 2H), 1.80 (dd, $J = 13.8, 7.4$ Hz, 1H), 1.68 – 1.63 (m, 4H), 1.57 (s, 3H), 1.35 (d, $J = 6.3$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.2, 132.7, 132.2, 130.9, 129.5, 128.3, 123.5, 71.4, 36.1, 25.7, 24.1, 20.1, 17.6. **Elemental analysis** calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$ (M: 232.15) [%]: C, 77.55; H, 8.68; found: C, 77.69; H, 8.72. CAS Registry Number: 131225-69-9.

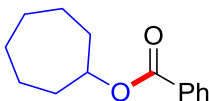


Cyclopentyl benzoate (3ar):¹² The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 155 mg, 82% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.03 (d, $J = 7.1$ Hz, 2H), 7.58 – 7.48 (m, 1H), 7.42 (t, $J = 7.7$ Hz, 2H), 5.51 – 5.31 (m, 1H), 1.97 (dt, $J = 10.3, 5.0$ Hz, 2H), 1.82 (t, $J = 12.5$ Hz, 4H), 1.72 – 1.58 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.3, 132.6, 130.8, 129.4, 128.2, 77.6, 32.7, 23.7. **Elemental analysis** calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$ (M: 190.10) [%]: C, 75.76; H, 7.42; found: C, 75.89; H, 7.67. CAS Registry Number: 32651-38-0.

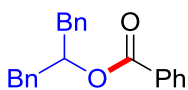
¹² J.-d. A. K. Twibanire and T. B. Grindley, *Org. Lett.*, 2011, **13**, 2988.



Cyclohexyl benzoate (3as):¹³ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 177 mg, 87% yield. ¹H NMR (300 MHz, CDCl₃) δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 5.20 – 4.86 (m, 1H), 1.93 (d, *J* = 2.7 Hz, 2H), 1.84 – 1.74 (m, 2H), 1.65 – 1.54 (m, 3H), 1.50 – 1.32 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 132.7, 131.0, 129.5, 128.3, 73.0, 31.6, 25.5, 23.7. **Elemental analysis** calcd for C₁₃H₁₆O₂ (M: 204.12) [%]: C, 76.44; H, 7.90; found: C, 76.84; H, 7.60. CAS Registry Number: 2412-73-9.



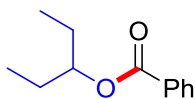
Cycloheptyl benzoate (3at):¹⁴ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 185 mg, 85% yield. ¹H NMR (300 MHz, CDCl₃) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 5.21 (dd, *J* = 7.5, 4.0 Hz, 1H), 2.00 (d, *J* = 7.4 Hz, 2H), 1.88 – 1.69 (m, 4H), 1.58 (d, *J* = 23.5 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 174.2, 132.6, 129.5, 128.3, 75.6, 33.9, 28.4, 23.0. **Elemental analysis** calcd for C₁₄H₁₈O₂ (M: 218.13) [%]: C, 77.03; H, 8.31; found: C, 77.26; H, 8.42. CAS Registry Number: 1256568-15-6.



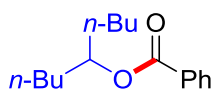
1,3-Diphenylpropan-2-yl benzoate (3au): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 271 mg, 86% yield. ¹H NMR (300 MHz, CDCl₃) δ 8.08 – 7.95 (m, 2H), 7.64 – 7.53 (m, 1H), 7.46 (dd, *J* = 11.5, 4.2 Hz, 2H), 7.38 – 7.20 (m, 10H), 5.72 – 5.50 (m, 1H), 3.12 – 2.96 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 165.9, 137.4, 132.8, 130.4, 129.5, 129.5, 128.4, 128.3, 126.5, 76.0, 39.8. **Elemental analysis** calcd for C₂₂H₂₀O₂ (M: 316.15) [%]: C, 83.52; H, 6.37; found: C, 83.68; H, 6.42. CAS Registry Number: 5565-59-3.

¹³ J. Salvadori, E. Balducci, S. Zaza, E. Petricci and M. Taddei, *J. Org. Chem.*, 2010, **75**, 1841.

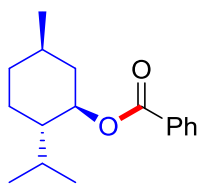
¹⁴ R. J. Kalbasi, A. R. Massah and Z. Barkhordari, *Bull. Korean Chem. Soc.*, 2010, **31**, 2361.



Pentan-3-yl benzoate (3av): The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 167 mg, 87% yield. ^1H NMR (300 MHz, CDCl_3) δ 8.07 (d, $J = 7.8$ Hz, 2H), 7.54 (t, $J = 7.3$ Hz, 1H), 7.43 (t, $J = 7.5$ Hz, 2H), 5.03 (p, $J = 6.1$ Hz, 1H), 1.70 (dd, $J = 14.2, 7.1$ Hz, 4H), 0.96 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 132.6, 130.8, 129.4, 128.2, 77.4, 26.5, 9.6. **Elemental analysis** calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$ (M: 192.12) [%]: C, 74.97; H, 8.39; found: C, 74.59; H, 8.29. CAS Registry Number: 5436-54-4.

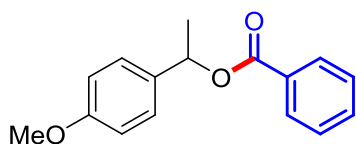


Nonan-5-yl benzoate (3aw):¹⁵ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 213 mg, 86% yield. ^1H NMR (300 MHz, CDCl_3) δ 8.06 (d, $J = 8.0$ Hz, 2H), 7.55 (t, $J = 7.3$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 5.14 (p, $J = 6.1$ Hz, 1H), 1.67 (s, 4H), 1.35 (d, $J = 2.7$ Hz, 8H), 0.90 (d, $J = 6.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 132.6, 129.5, 128.3, 75.0, 33.9, 27.5, 22.6, 14.0. **Elemental analysis** calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2$ (M: 248.18) [%]: C, 77.38; H, 9.74; found: C, 77.42; H, 9.94. CAS Registry Number: 131426-42-1.

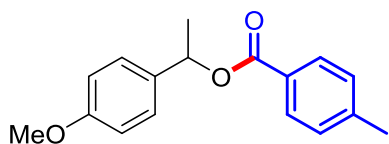


(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl benzoate (3ax):¹ The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 189 mg, 73% yield. ^1H NMR (300 MHz, CDCl_3) δ 8.06 (d, $J = 6.8$ Hz, 2H), 7.64 – 7.31 (m, 3H), 4.95 (t, $J = 10.4$ Hz, 1H), 2.14 (d, $J = 10.1$ Hz, 1H), 1.98 (s, 1H), 1.73 (d, $J = 10.6$ Hz, 2H), 1.58 (d, $J = 10.1$ Hz, 2H), 1.20 – 1.06 (m, 2H), 0.93 (d, $J = 5.6$ Hz, 6H), 0.80 (d, $J = 6.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 132.6, 130.8, 129.5, 128.2, 74.7, 47.2, 40.9, 34.3, 31.4, 26.4, 23.6, 22.0, 20.7, 16.5. **Elemental analysis** calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2$ (M: 260.18) [%]: C, 78.42; H, 9.29; found: C, 78.67; H, 9.38. CAS Registry Number: 6284-35-1.

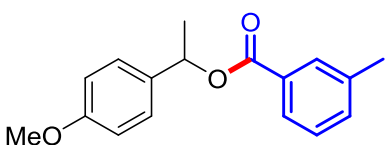
¹⁵ M. Hatano, Y. Furuya, T. Shimmura, K. Moriyama, S. Kamiya, T. Maki and K. Ishihara, *Org. Lett.*, 2011, **13**, 426.



1-(4-Methoxyphenyl)ethyl benzoate (3ga):¹⁶ The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 233 mg, 91% yield. ¹H NMR (300 MHz, CDCl₃) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 6.8 Hz, 1H), 7.42 (dd, *J* = 14.2, 7.9 Hz, 4H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.11 (q, *J* = 6.4 Hz, 1H), 3.81 (s, 3H), 1.67 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.8, 159.2, 133.8, 132.8, 130.6, 129.6, 128.2, 127.5, 113.8, 72.6, 55.2, 22.1. **Elemental analysis** calcd for C₁₆H₁₆O₃ (M: 256.11) [%]: C, 74.98; H, 6.29; found: C, 74.76; H, 6.38. CAS Registry Number: 19771-09-6.

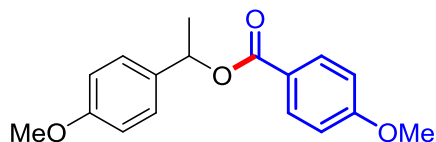


1-(4-Methoxyphenyl)ethyl 4-methylbenzoate (3gb): The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 253 mg, 94% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.10 (q, *J* = 6.5 Hz, 1H), 3.80 (s, 3H), 2.40 (s, 3H), 1.66 (d, *J* = 6.5 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 169.0, 159.0, 143.2, 133.6, 129.5, 128.8, 127.4, 113.7, 72.3, 55.1, 22.1, 21.5. **Elemental analysis** calcd for C₁₇H₁₈O₃ (M: 270.13) [%]: C, 75.53; H, 6.71; found: C, 75.48; H, 6.62.



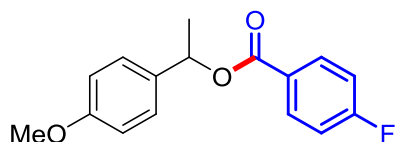
1-(4-Methoxyphenyl)ethyl 3-methylbenzoate (3gc) The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 240 mg, 89% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.09 (q, *J* = 6.6 Hz, 1H), 3.80 (d, *J* = 0.7 Hz, 3H), 1.66 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.1, 159.3, 133.5, 131.6, 131.1, 129.5, 127.9, 127.5, 113.9, 73.0, 55.2, 22.0, 21.7. **Elemental analysis** calcd for C₁₇H₁₈O₃ (M: 270.13) [%]: C, 75.53; H, 6.71; found: C, 75.69; H, 6.68.

¹⁶ M. Jereb, D. Vražič and M. Zupan, *Tetrahedron Lett*, 2009, **50**, 2347.



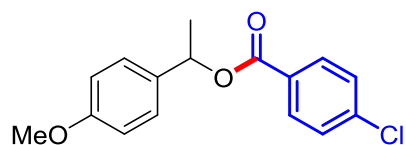
1-(4-Methoxyphenyl)ethyl 4-methoxybenzoate

(3gd): The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 263 mg, 92% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.03 (d, $J = 9.0$ Hz, 2H), 7.39 (d, $J = 8.6$ Hz, 2H), 6.94 – 6.87 (m, 4H), 6.08 (q, $J = 6.6$ Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 1.65 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.6, 163.3, 159.2, 134.1, 131.7, 127.5, 123.1, 113.9, 113.6, 72.3, 55.4, 55.3, 22.3. **Elemental analysis** calcd for $\text{C}_{17}\text{H}_{18}\text{O}_4$ (M: 286.12) [%]: C, 71.31; H, 6.34; found: C, 71.42; H, 6.55.



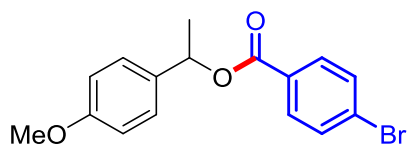
1-(4-Methoxyphenyl)ethyl 4-fluorobenzoate (3ge):

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 227 mg, 83% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.09 (dd, $J = 8.9, 5.5$ Hz, 2H), 7.40 (d, $J = 8.7$ Hz, 2H), 7.10 (dd, $J = 9.4, 8.0$ Hz, 2H), 6.92 (d, $J = 8.7$ Hz, 2H), 6.11 (q, $J = 6.6$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.3, 164.8, 163.9, 159.3, 133.6, 132.1, 132.0, 127.5, 126.8, 126.8, 115.5, 115.2, 113.8, 72.8, 55.2, 22.0. **Elemental analysis** calcd for $\text{C}_{16}\text{H}_{15}\text{FO}_3$ (M: 274.10) [%]: C, 70.06; H, 5.51; found: C, 70.22; H, 5.41.



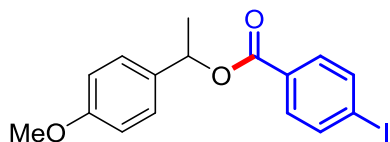
1-(4-Methoxyphenyl)ethyl 4-chlorobenzoate (3gf):

The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 240 mg, 83% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.00 (d, $J = 8.1$ Hz, 2H), 7.52 – 7.31 (m, 4H), 6.91 (d, $J = 8.2$ Hz, 2H), 6.85 (s, 1H), 6.10 (q, $J = 6.4$ Hz, 1H), 3.81 (s, 3H), 1.67 (d, $J = 6.4$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.9, 159.3, 139.2, 133.5, 131.0, 129.0, 128.6, 127.5, 113.9, 73.0, 55.2, 22.0. **Elemental analysis** calcd for $\text{C}_{16}\text{H}_{15}\text{ClO}_3$ (M: 290.07) [%]: C, 66.10; H, 5.20; found: C, 66.42; H, 5.34.



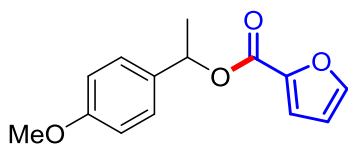
1-(4-Methoxyphenyl)ethyl 4-bromobenzoate (3gg):

The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 260 mg, 78% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.92 (d, $J = 7.7$ Hz, 2H), 7.56 (d, $J = 7.6$ Hz, 2H), 7.38 (d, $J = 8.1$ Hz, 2H), 6.90 (d, $J = 8.0$ Hz, 2H), 6.09 (q, $J = 6.6$ Hz, 1H), 3.80 (d, $J = 0.7$ Hz, 3H), 1.66 (d, $J = 6.5$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.1, 159.3, 133.5, 131.6, 131.1, 129.5, 127.9, 127.5, 113.9, 73.0, 55.2, 22.0, 21.7. **Elemental analysis** calcd for $\text{C}_{16}\text{H}_{15}\text{BrO}_3$ (M: 334.02) [%]: C, 57.33; H, 4.51; found: C, 57.33; H, 4.51.



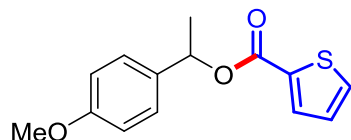
1-(4-Methoxyphenyl)ethyl 4-iodobenzoate (3gh)

The title compound was prepared according to the general procedure and purified by flash column chromatography to give a white solid, 282 mg, 74% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.90 – 7.63 (m, 4H), 7.37 (d, $J = 8.5$ Hz, 2H), 6.90 (d, $J = 8.6$ Hz, 2H), 6.19 – 5.95 (m, 1H), 3.80 (s, 3H), 1.65 (d, $J = 6.5$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.3, 159.4, 137.6, 133.5, 131.1, 130.1, 127.6, 113.9, 100.6, 73.0, 55.3, 22.1. **Elemental analysis** calcd for $\text{C}_{16}\text{H}_{15}\text{IO}_3$ (M: 382.01) [%]: C, 50.28; H, 3.96; found: C, 50.32; H, 3.78.



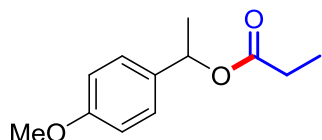
1-(4-Methoxyphenyl)ethyl furan-2-carboxylate (3gi):

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 223 mg, 91% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.56 (s, 1H), 7.37 (d, $J = 8.6$ Hz, 2H), 7.18 (d, $J = 3.3$ Hz, 1H), 6.89 (d, $J = 8.4$ Hz, 2H), 6.49 (s, 1H), 6.09 (q, $J = 6.5$ Hz, 1H), 3.80 (s, 3H), 1.65 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 146.2, 127.7, 117.8, 113.9, 111.7, 72.6, 55.3, 22.0. **Elemental analysis** calcd for $\text{C}_{14}\text{H}_{14}\text{O}_4$ (M: 246.09) [%]: C, 68.28; H, 5.73; found: C, 68.31; H, 5.75.



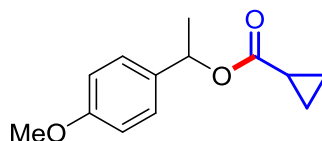
1-(4-Methoxyphenyl)ethyl thiophene-2-carboxylate

(3gj): The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 233 mg, 89% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.93 – 7.72 (m, 1H), 7.53 (d, $J = 4.9$ Hz, 1H), 7.40 (d, $J = 8.6$ Hz, 2H), 7.08 (t, $J = 4.3$ Hz, 1H), 6.92 (d, $J = 8.5$ Hz, 2H), 6.09 (q, $J = 6.5$ Hz, 1H), 3.80 (s, 3H), 1.67 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 161.4, 159.2, 134.2, 133.5, 133.2, 132.2, 127.6, 127.4, 113.8, 72.8, 55.1, 22.1. **Elemental analysis** calcd for $\text{C}_{14}\text{H}_{14}\text{O}_3\text{S}$ (M: 262.07) [%]: C, 64.10; H, 5.38; found: C, 64.17; H, 5.42.



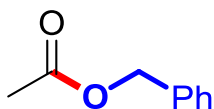
1-(4-Methoxyphenyl)ethyl propionate (3gk):

The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 189 mg, 91% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.22 (d, $J = 7.3$ Hz, 2H), 6.80 (d, $J = 7.1$ Hz, 2H), 5.78 (q, $J = 6.6$ Hz, 1H), 3.71 (s, 3H), 2.25 (q, $J = 7.5$ Hz, 2H), 1.44 (d, $J = 6.5$ Hz, 3H), 1.04 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 133.8, 127.4, 113.6, 71.6, 55.1, 27.8, 21.9, 8.9. **Elemental analysis** calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$ (M: 208.11) [%]: C, 69.21; H, 7.74; found: C, 69.32; H, 7.85. CAS Registry Number: 35279-24-4.

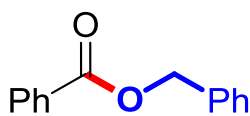


1-(4-Methoxyphenyl)ethyl cyclopropanecarboxylate

(3gl): The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 193 mg, 88% yield. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.30 (d, $J = 8.7$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 5.86 (q, $J = 6.6$ Hz, 1H), 3.80 (s, 3H), 1.67 – 1.56 (m, 1H), 1.53 (d, $J = 6.6$ Hz, 3H), 1.05 – 0.94 (m, 2H), 0.88 – 0.78 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.1, 159.1, 133.8, 127.4, 113.7, 71.84, 55.2, 22.0, 13.1, 8.3, 8.3. **Elemental analysis** calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3$ (M: 220.11) [%]: C, 70.89; H, 7.32; found: C, 70.78; H, 7.25.



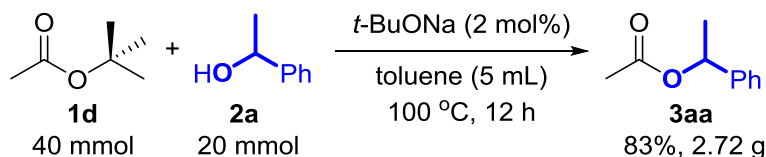
Benzyl acetate (4dm): The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 178 mg, 81% yield. ^1H NMR (300 MHz, CDCl_3) δ 7.46 – 7.28 (m, 5H), 5.12 (s, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 135.9, 128.5, 128.2, 66.3, 21.0. **Elemental analysis** calcd for $\text{C}_9\text{H}_{10}\text{O}_2$ (M: 150.18) [%]: C, 71.98; H, 6.71; found: C, 71.72; H, 6.82.



Benzyl benzoate (4jo): The title compound was prepared according to the general procedure and purified by flash column chromatography to give the colorless oil, 178 mg, 83% yield. ^1H NMR (300 MHz, CDCl_3) δ 8.12 – 8.08 (m, 2H), 7.64 – 7.51 (m, 1H), 7.49 – 7.40 (m, 6.8 Hz, 7H), 5.40 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 133.0, 130.1, 129.7, 128.6, 128.3, 128.2, 128.1, 66.7. **Elemental analysis** calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2$ (M: 212.08) [%]: C, 79.23; H, 5.70; found: C, 79.12; H, 5.82. CAS Registry Number: 19759-26-3.

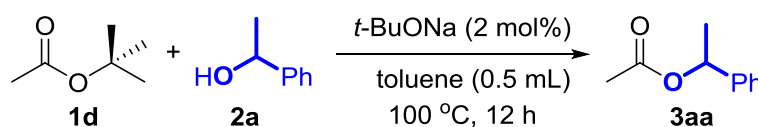
5. Gram scale experiment and recycle reaction experiment

5.1 Gram scale experiment



Using a nitrogen-filled glove box, an oven-dried Schlenk tube (100 mL volume) was charged with a magnetic stirring bar, *t*-BuONa (2 mol%, 0.4 mmol), **1d** (40 mmol), **2a** (20 mmol) and toluene (5.0 mL). The tube was sealed, taken out of the glove box and a reflux condenser was attached under argon stream. The mixture was heated at 100 °C (oil bath) for 12 hours under inert atmosphere in an open system. After cooling, a small aliquot of the organic phase was analyzed by GC to monitor product formation. Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (pentane/ethyl ether = 50/1) to give the desired product **3aa** in 83 % yield (2.72 g).

5.2 Recycle reaction experiment

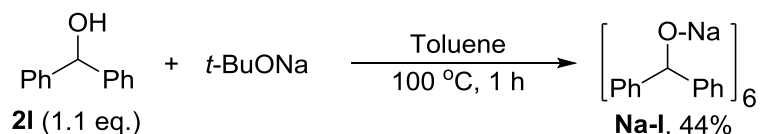


Using a nitrogen-filled glove box, an oven-dried Schlenk tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuONa (2 mol%), **1d** (2 mmol), **2a** (1.0 mmol) and toluene (0.5 mL). The tube was sealed, taken out of the glove box and a reflux condenser was attached under argon stream. The mixture was heated at 100 °C (oil bath) for an hour under inert atmosphere in an open system. A small aliquot of the organic phase was analyzed by GC to monitor product **3aa** formation. Then **1d** (2 mmol), **2a** (1.0 mmol) and toluene (0.5 mL) were added and continued to react for another an hour under inert atmosphere in an open system. A small aliquot of the organic phase was analyzed by GC to monitor product **3aa** formation. Repeat this process seven times.

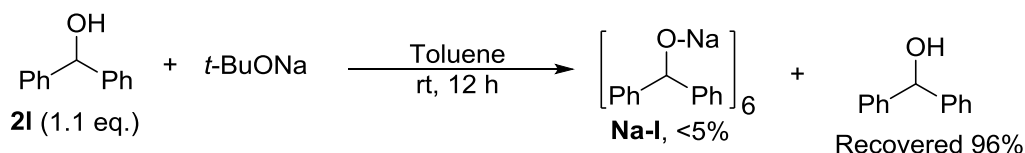
Reaction Numbers	1	2	3	4	5	6	7
3aa Yield (%)	96	94	95	93	90	91	89

6. Mechanistic investigations

6.1 Synthesis of complex Na-I

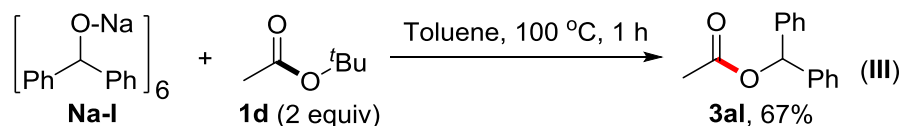


Using a nitrogen-filled glove box, an oven-dried Schlenk tube (50 mL volume) was charged with a magnetic stirring bar, *t*-BuONa (1.0 mmol, 96 mg), **2I** (1.1 mmol, 202 mg) and toluene (5.0 mL). The tube was sealed, taken out of the glove box and a reflux condenser was attached under argon stream. The mixture was heated at 100 °C (oil bath) for an hour under inert atmosphere in an open system. After cooling, the solvent was removed in vacuum and the residue recrystallized two times from cyclopentane to give white crystals **Na-I** in 44 % yield. ¹H NMR (300 MHz, THF-*d*₈) δ 7.46-7.32 (m, 4H), 7.24-7.10 (m, 4H), 7.08-7.00 (m, 2H), 6.05 (s, 1H). ¹³C NMR (100 MHz, THF-*d*₈) δ 153.4, 125.5, 124.3, 122.7, 78.9. **Elemental analysis** calcd for C₁₃H₁₁NaO (M: 206.07) [%]: C, 75.72; H, 5.38; found: C, 75.32; H, 5.49.¹⁷

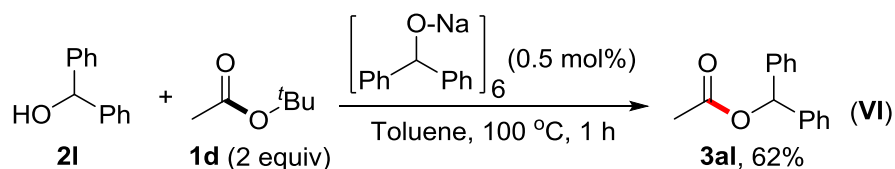


Using a nitrogen-filled glove box, an oven-dried Schlenk tube (50 mL volume) was charged with a magnetic stirring bar, *t*-BuONa (1.0 mmol, 96 mg), **2I** (1.1 mmol, 202 mg) and toluene (5.0 mL). The tube was sealed, taken out of the glove box and a reflux condenser was attached under argon stream. The mixture was stirred at room temperature for an hour under inert atmosphere in an open system. Then **2I** was recovered in 96% yield by flash column chromatography on a silica gel column.

¹⁷ J. Geier, H. Ruegger and H. Grutzmacher, *Dalton Trans*, 2006, 129-136.

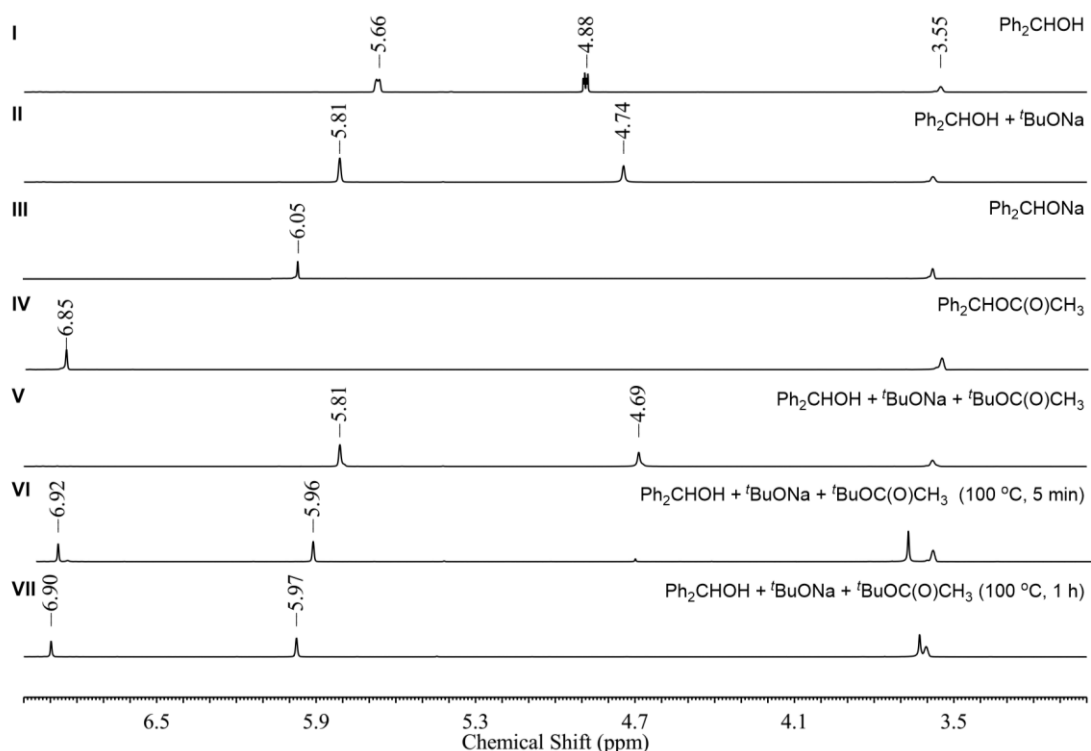


Using a nitrogen-filled glove box, an oven-dried Schlenk tube (50 mL volume) was charged with a magnetic stirring bar, **Na-I** (0.083 mmol), **1d** (1.0 mmol) and toluene (0.5 mL). The tube was sealed, taken out of the glove box and a reflux condenser was attached under argon stream. The mixture was heated at 100 °C (oil bath) for an hour under inert atmosphere in an open system. After cooling, the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (pentane/ethyl ether = 20/1) to give the desired product **3al** in 67 % yield.



Using a nitrogen-filled glove box, an oven-dried Schlenk tube (50 mL volume) was charged with a magnetic stirring bar, **Na-I** (0.5 mol%, 0.005 mmol), **1d** (2 mmol), **2l** (1.0 mmol) and toluene (0.5 mL). The tube was sealed, taken out of the glove box and a reflux condenser was attached under argon stream. The mixture was heated at 100 °C (oil bath) for an hour under inert atmosphere in an open system. After cooling, the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (pentane/ethyl ether = 20/1) to give the desired product **3al** in 62 % yield.

6.2 ^1H NMR investigations



Scheme 3 Selected part of ^1H NMR spectra of Ph_2CHOH with $t\text{-BuONa}$: (I) Ph_2CHOH in $\text{THF-}d_8$, (II) Ph_2CHOH and $t\text{-BuONa}$, (III) **Na-I** in $\text{THF-}d_8$, (IV) $\text{Ph}_2\text{CHOC(O)CH}_3$ in $\text{THF-}d_8$, (V) Ph_2CHOH , $t\text{-BuONa}$ and **1d**, (VI) Ph_2CHOH , $t\text{-BuONa}$ and **1d** after 5 min at $100\text{ }^\circ\text{C}$, (VII) Ph_2CHOH , $t\text{-BuONa}$ and **1d** after 1 h at $100\text{ }^\circ\text{C}$.

II: Using a nitrogen-filled glove box, in a Young NMR tube, Ph_2CHOH (0.12 mmol), $t\text{-BuONa}$ (30 mol%, 0.03 mmol) and $\text{THF-}d_8$ (0.5 mL) were mixed. The tube was sealed, taken out of the glove box and analyzed by NMR. ^1H NMR spectroscopy showed the presence of the characteristic peak at 5.81 ppm of CH and 4.74 ppm of OH.

V: Using a nitrogen-filled glove box, in a Young NMR tube, Ph_2CHOH (0.12 mmol), $t\text{-BuONa}$ (30 mol%, 0.03 mmol), **1d** (0.1 mmol) and $\text{THF-}d_8$ (0.5 mL) were mixed. The tube was sealed, taken out of the glove box and analyzed by NMR. ^1H NMR spectroscopy showed the presence of the characteristic peak at 5.81 ppm of CH and 4.69 ppm of OH.

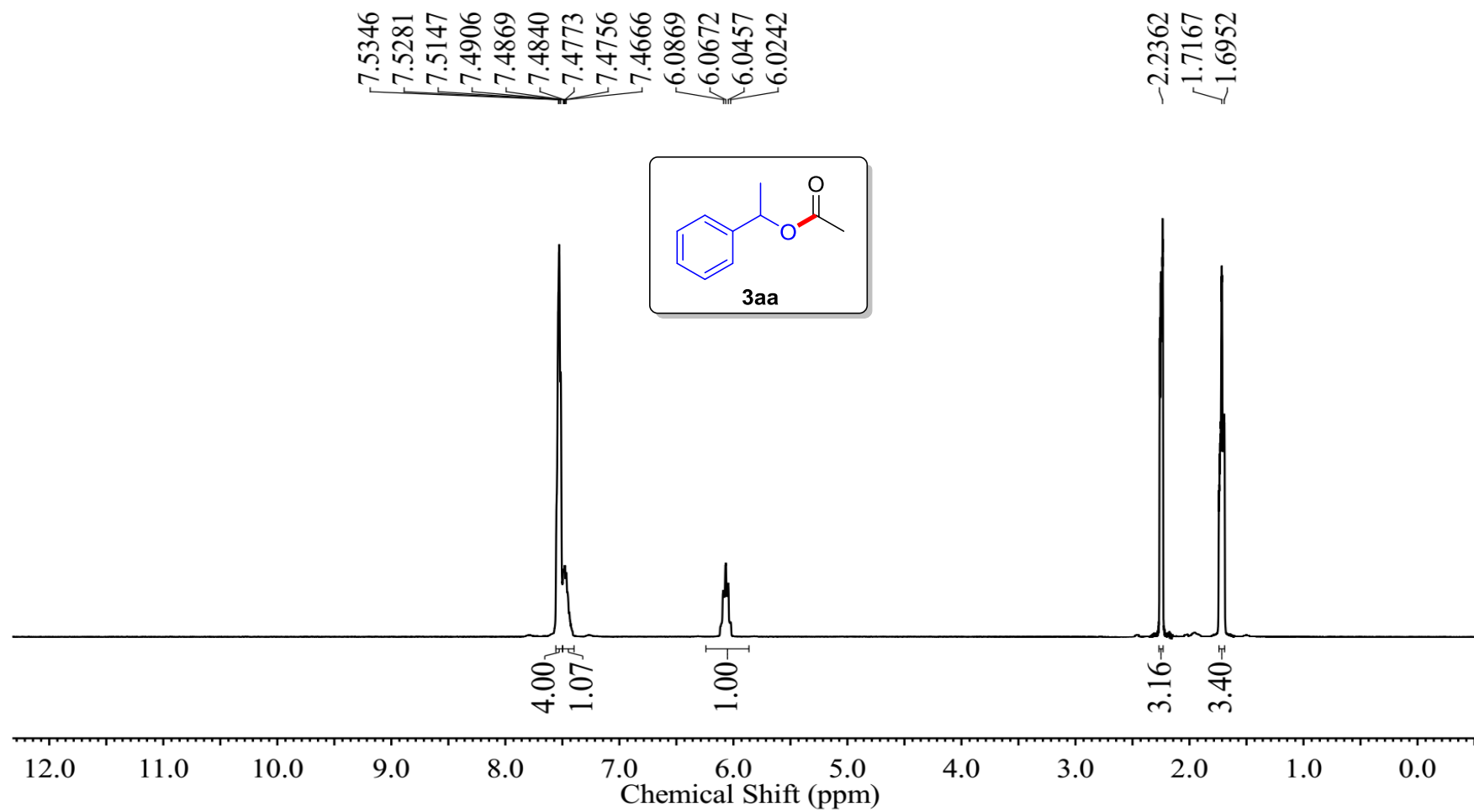
VI: Using a nitrogen-filled glove box, in a Young NMR tube, Ph_2CHOH (0.12 mmol), $t\text{-BuONa}$ (30 mol%, 0.03 mmol), **1d** (0.1 mmol) and $\text{THF-}d_8$ (0.5 mL) were mixed. The tube was sealed, taken out of the glove box. The mixture was heated at $100\text{ }^\circ\text{C}$ (oil bath) for 5 min and analyzed by NMR. ^1H NMR spectroscopy showed the

presence of the characteristic peak at 6.92 ppm of CH of product and 5.96 ppm of CH of Ph₂CHONa.

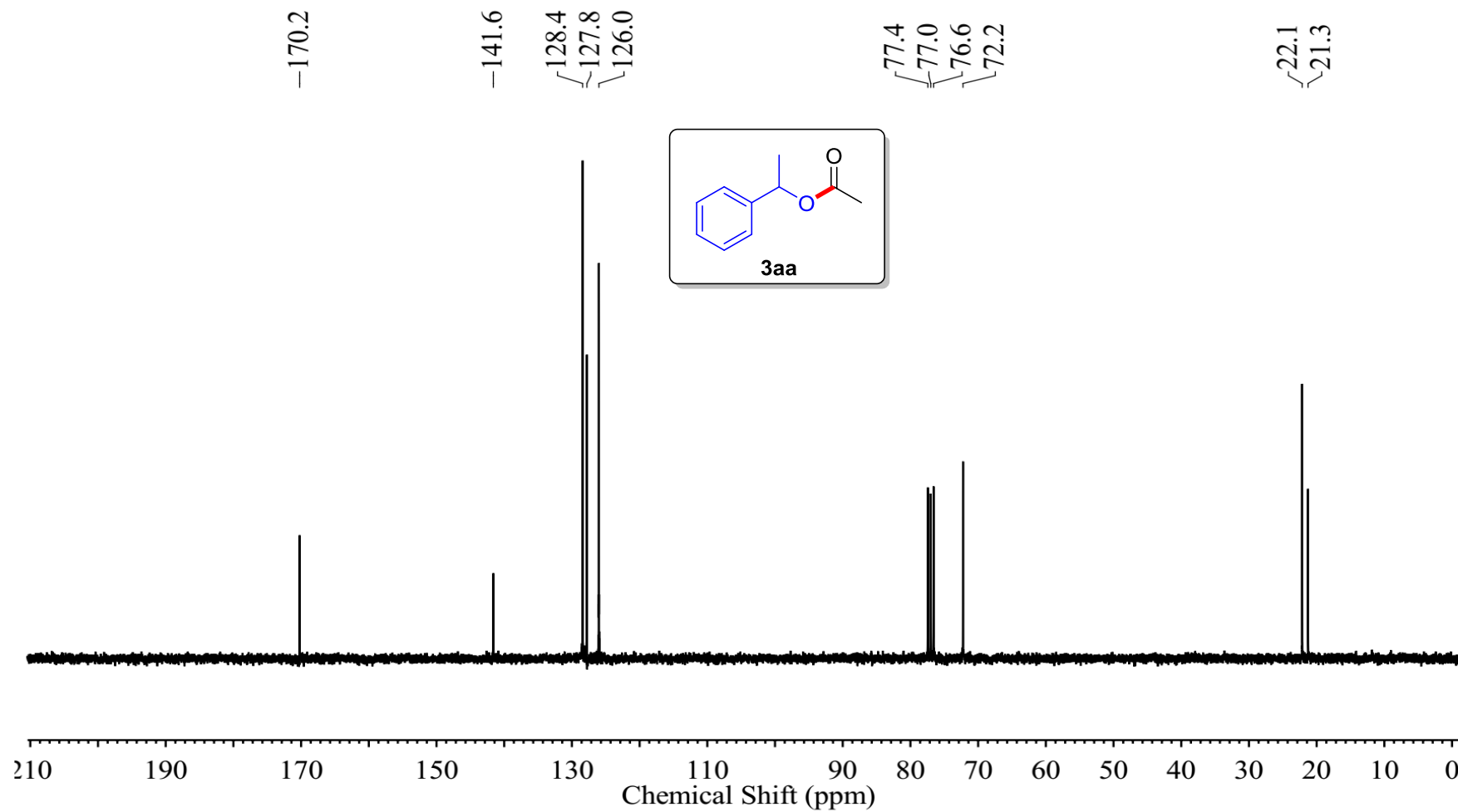
VII: Using a nitrogen-filled glove box, in a Young NMR tube, Ph₂CHOH (0.12 mmol), *t*-BuONa (30 mol%, 0.03 mmol), **1d** (0.1 mmol) and THF-*d*₈ (0.5 mL) were mixed. The tube was sealed, taken out of the glove box. The mixture was heated at 100 °C (oil bath) for an hour and analyzed by NMR. ¹H NMR spectroscopy showed the presence of the characteristic peak at 6.90 ppm of CH of product and 5.97 ppm of CH of Ph₂CHONa.

7. Copies for ¹H NMR and ¹³C NMR of the products

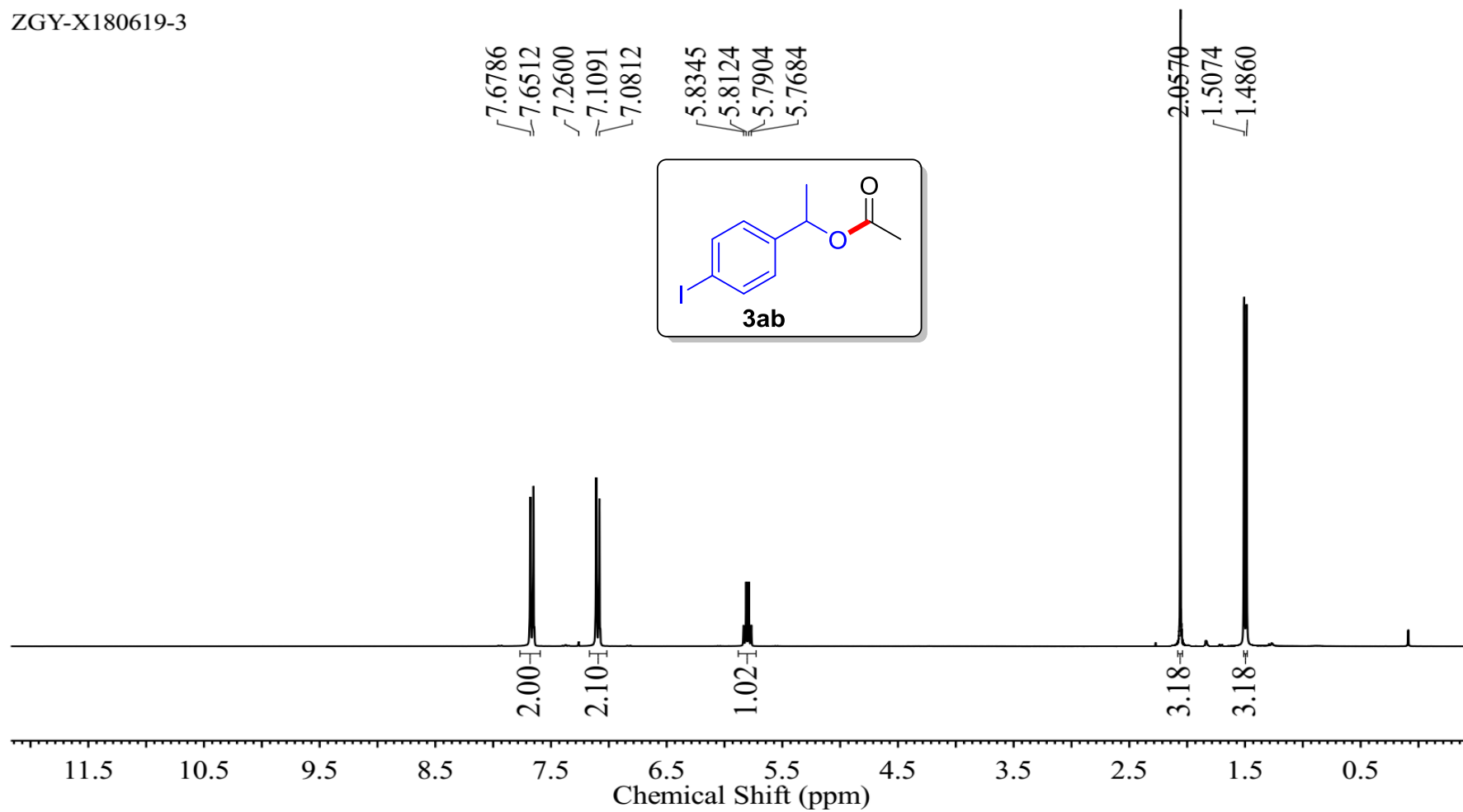
ZGY-X1806015-1



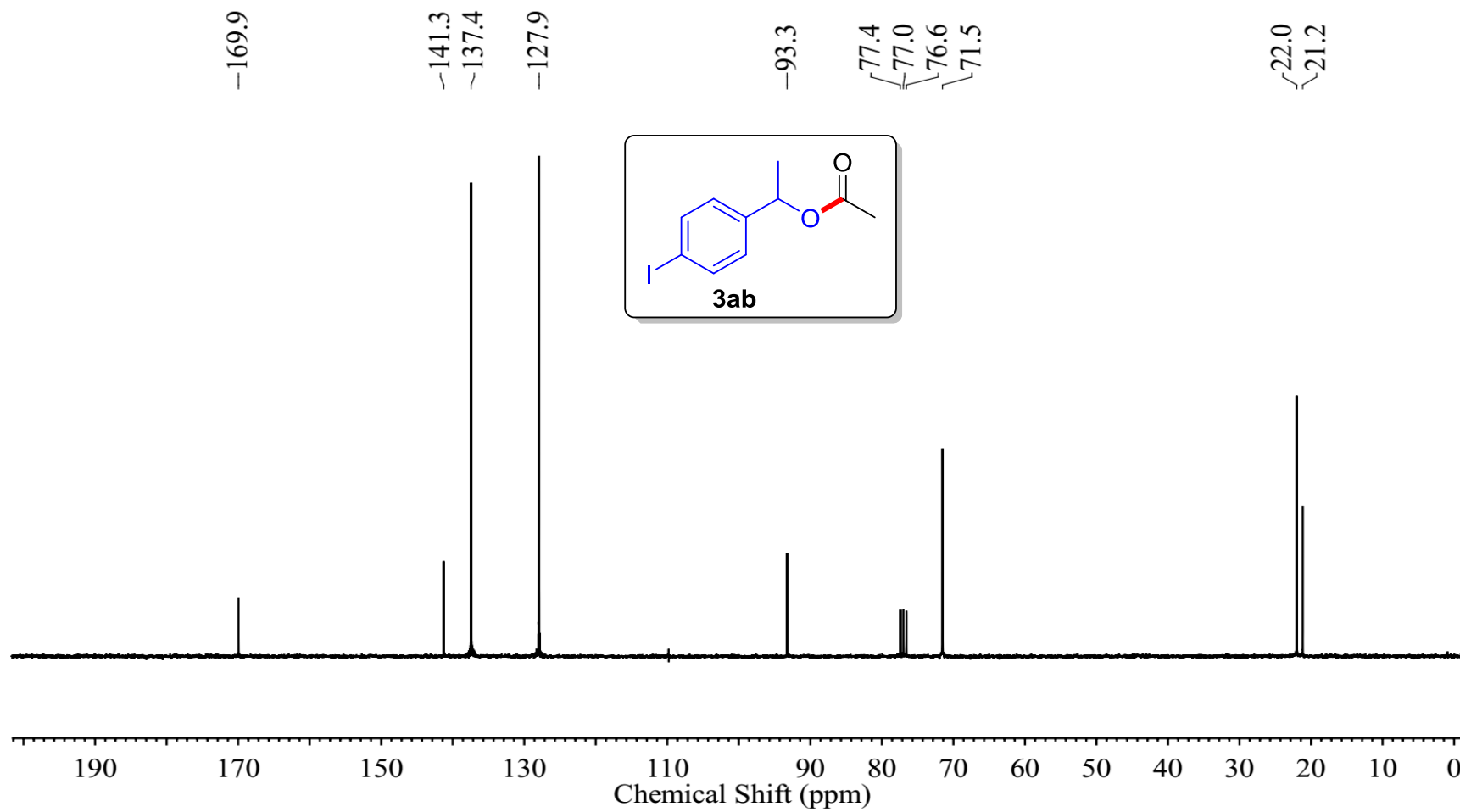
ZGY-X1806015-1



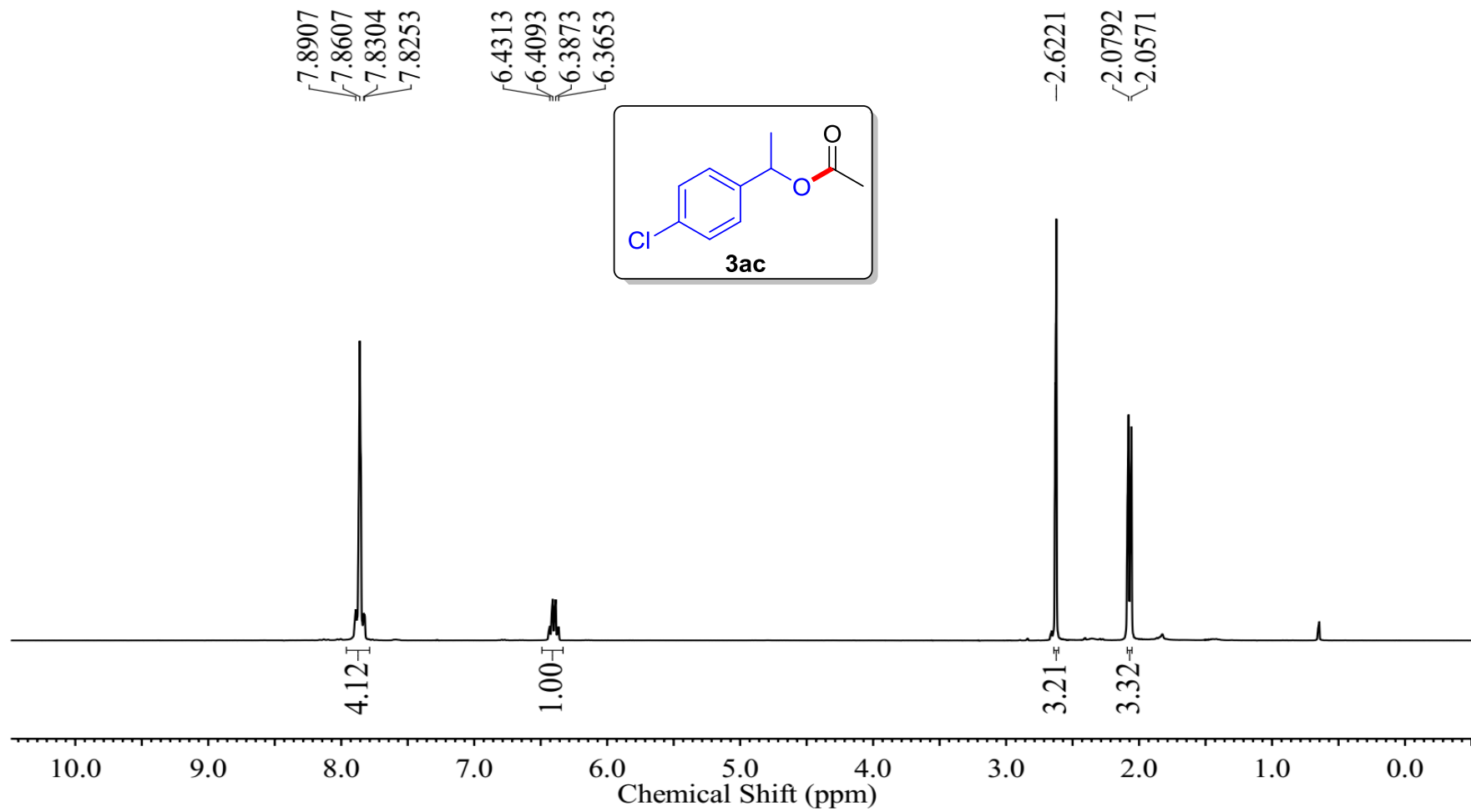
ZGY-X180619-3



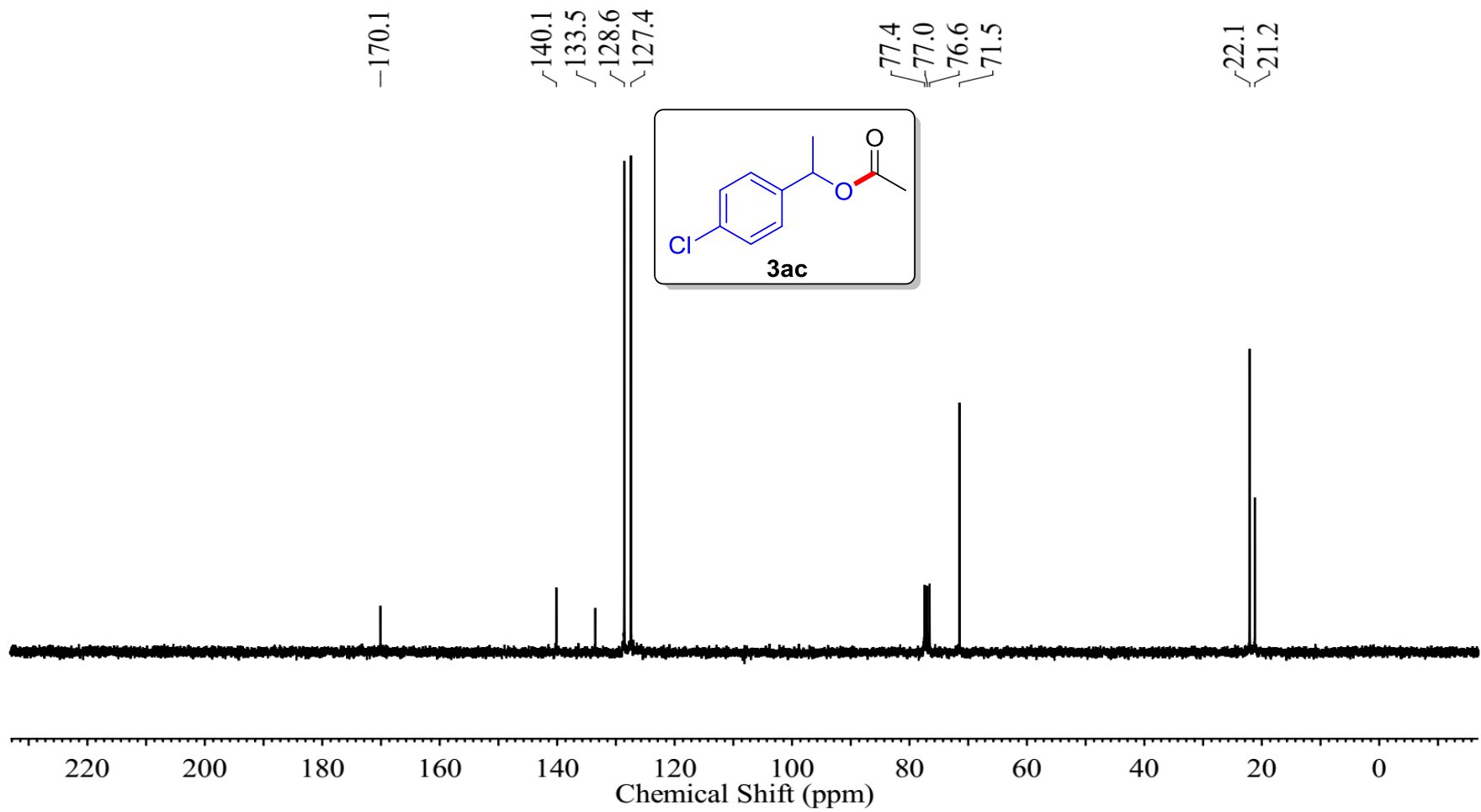
ZGY-X180619-3



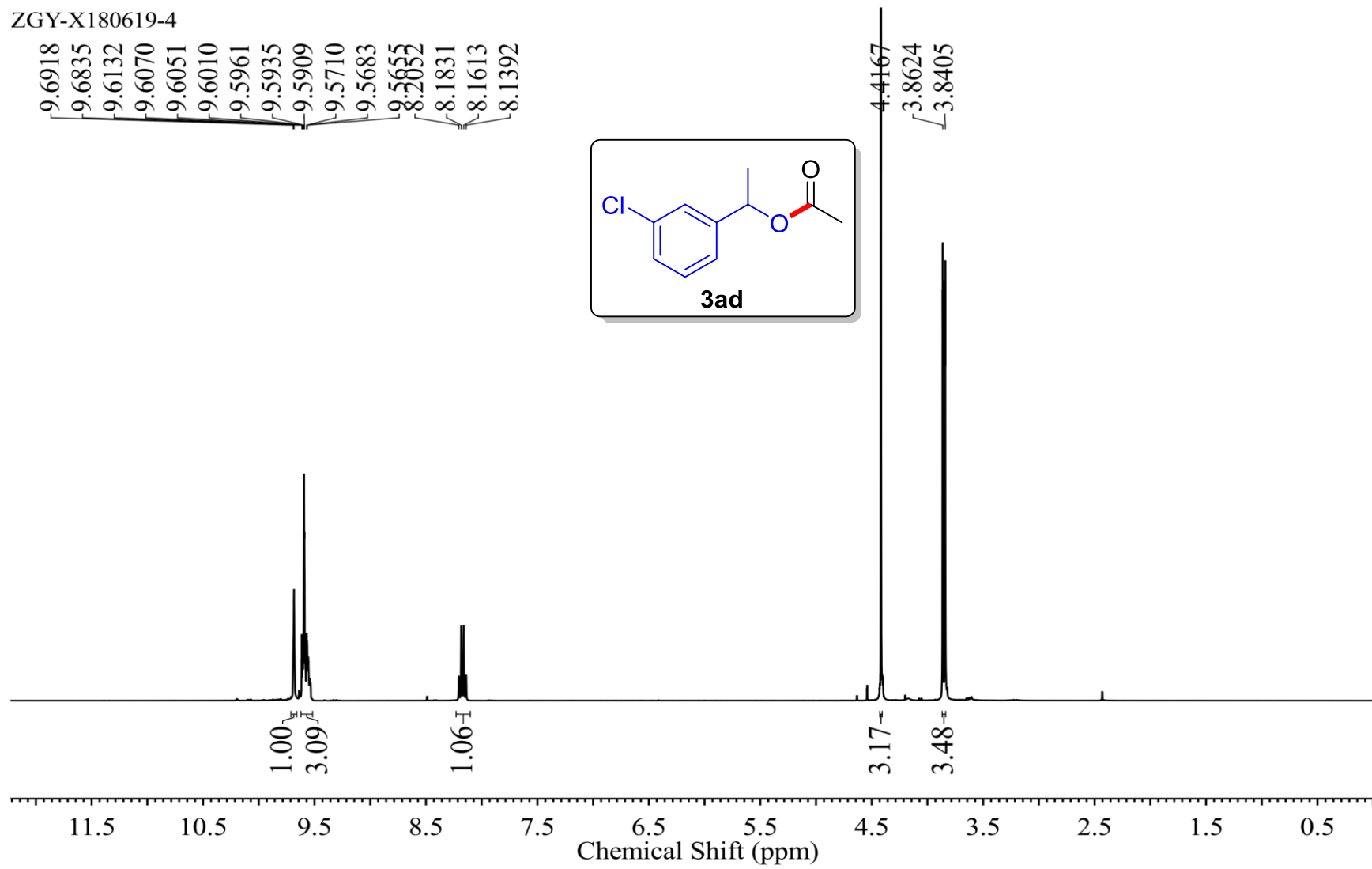
ZGY-X180616-2



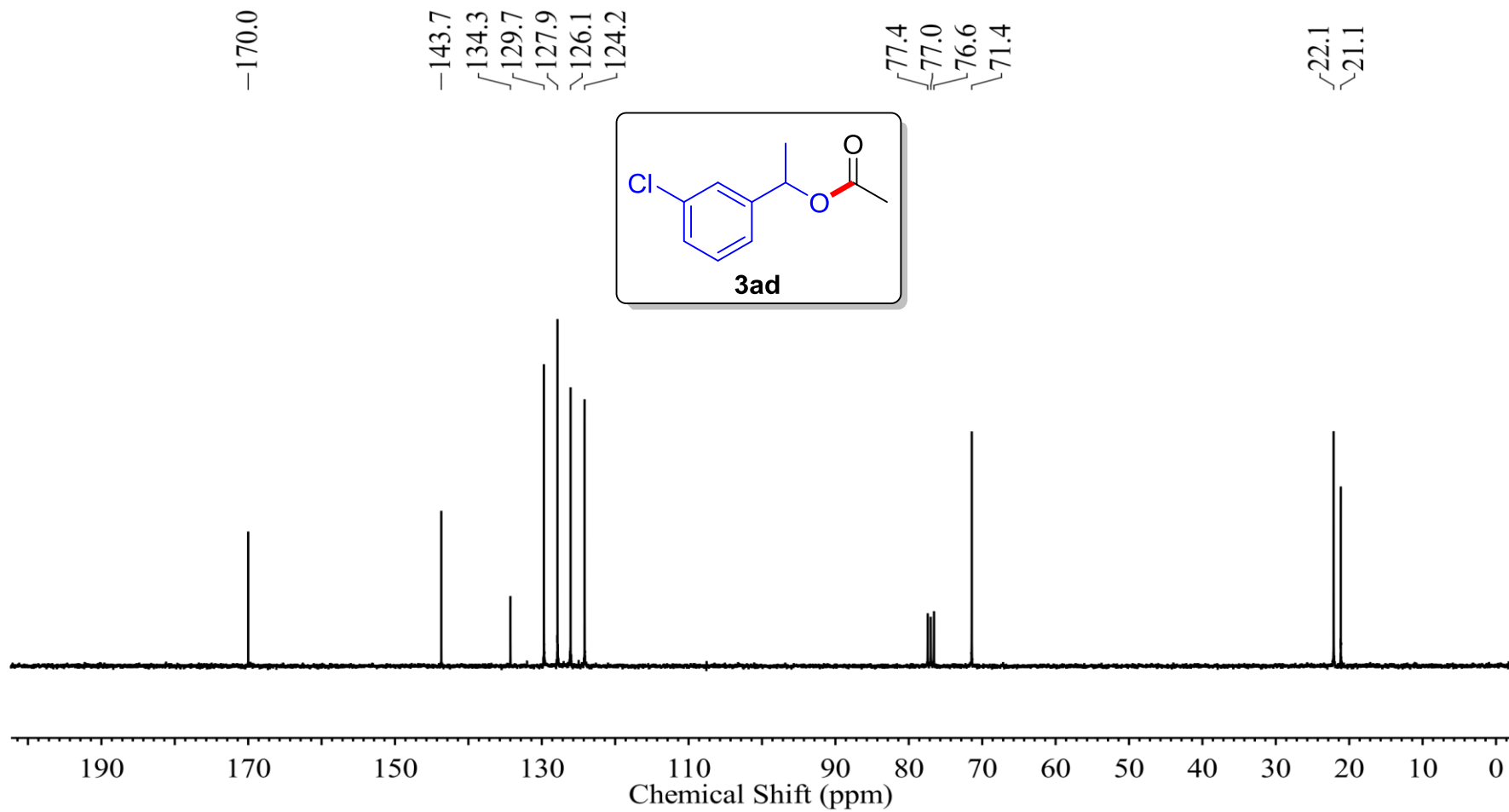
ZGY-X180616-2



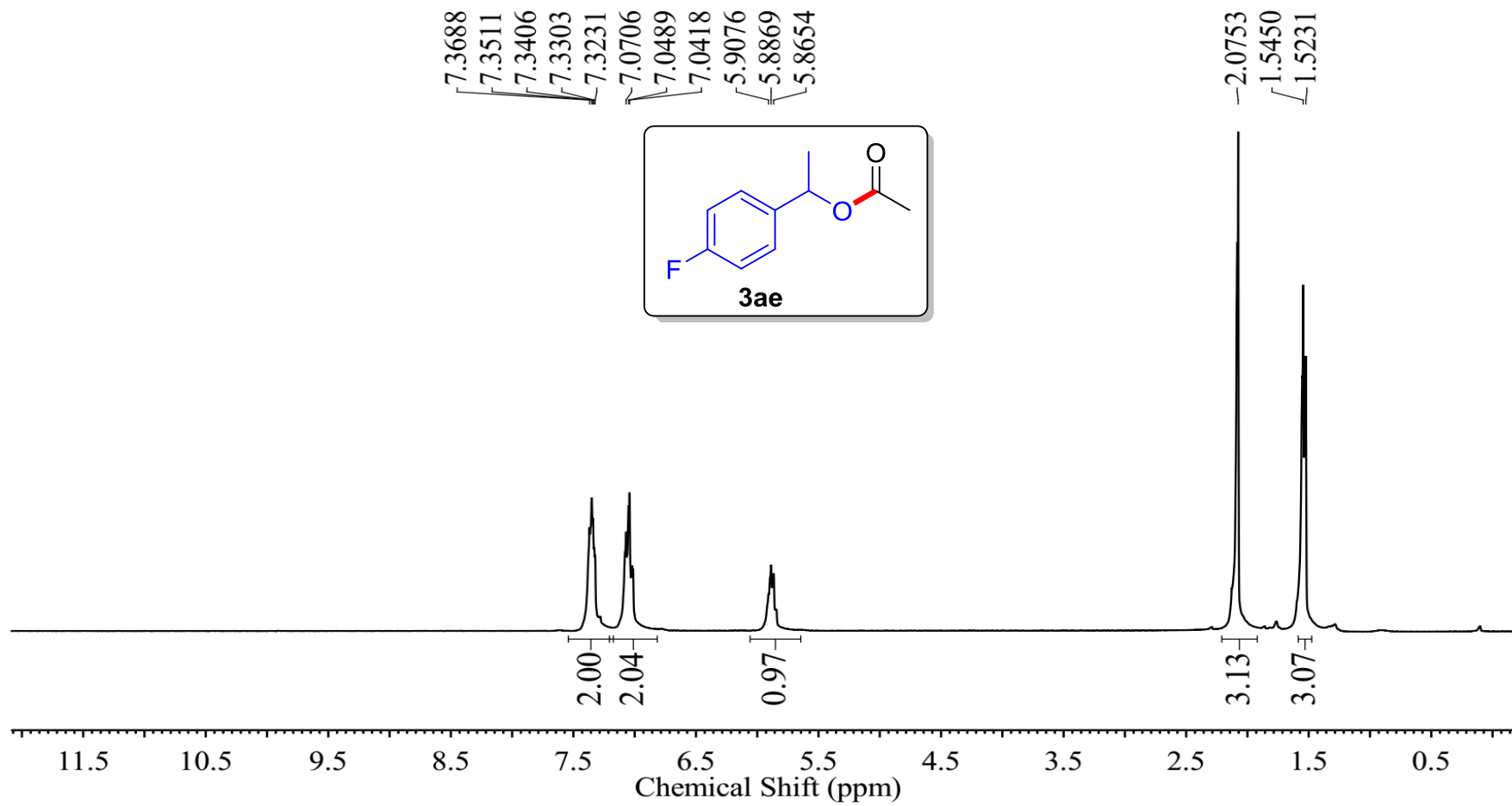
ZGY-X180619-4



ZGY-X180619-4



ZGY-X180630-4



ZGY-X180630-4

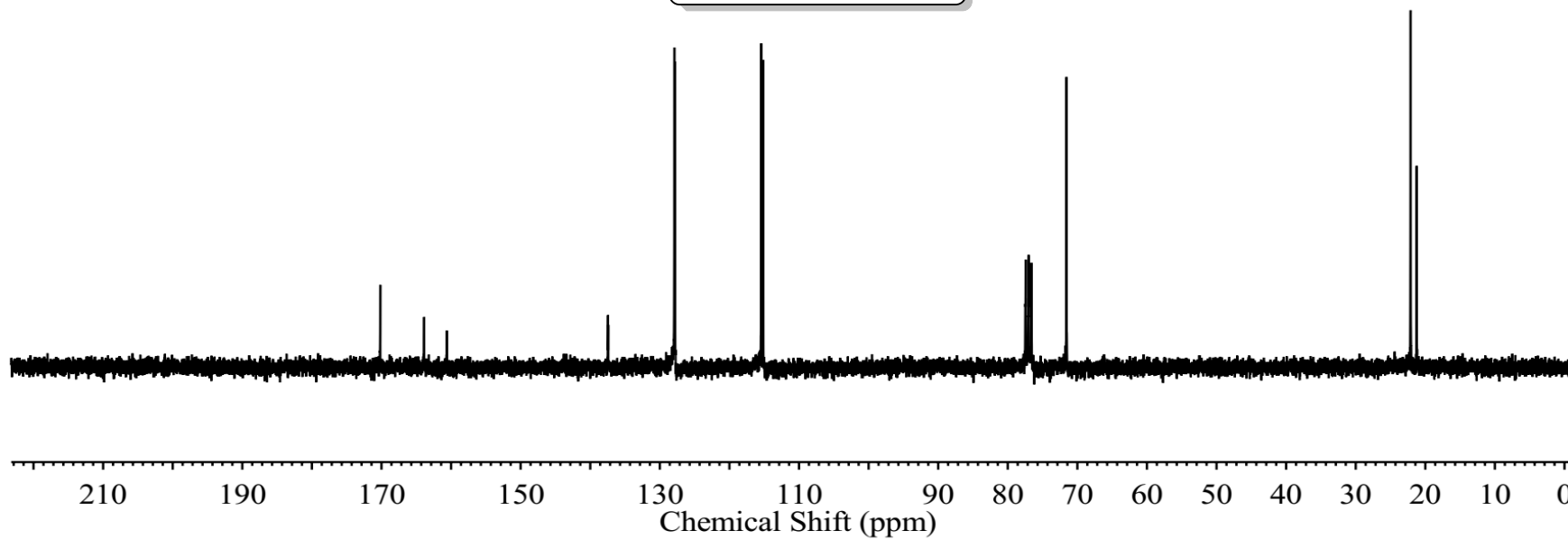
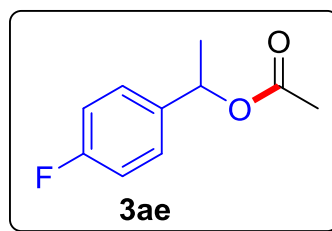
-170.2
-163.9
-160.6

-137.5
-127.9
-127.8

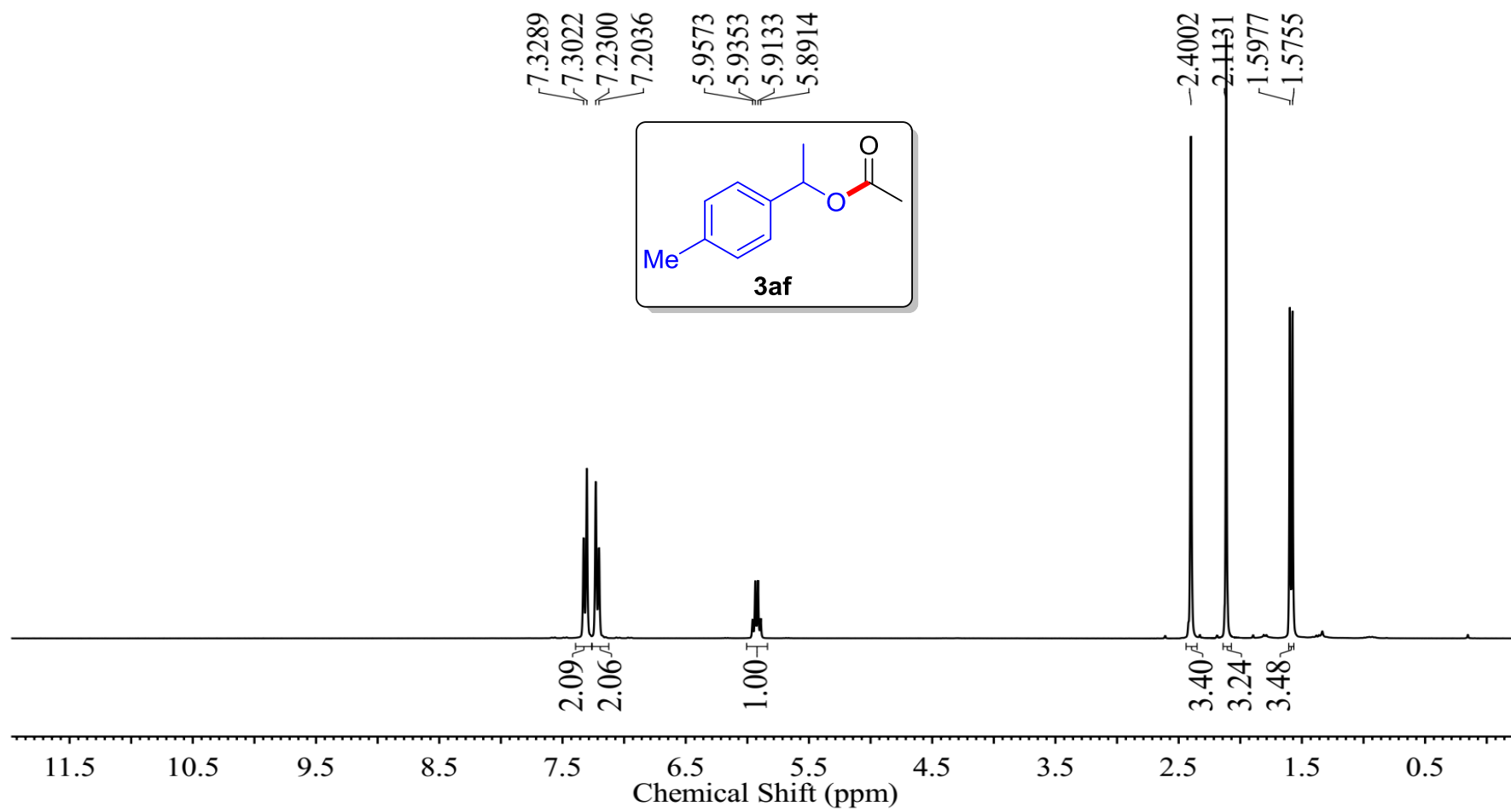
-115.4
-115.1

77.4
77.0
76.6
71.6

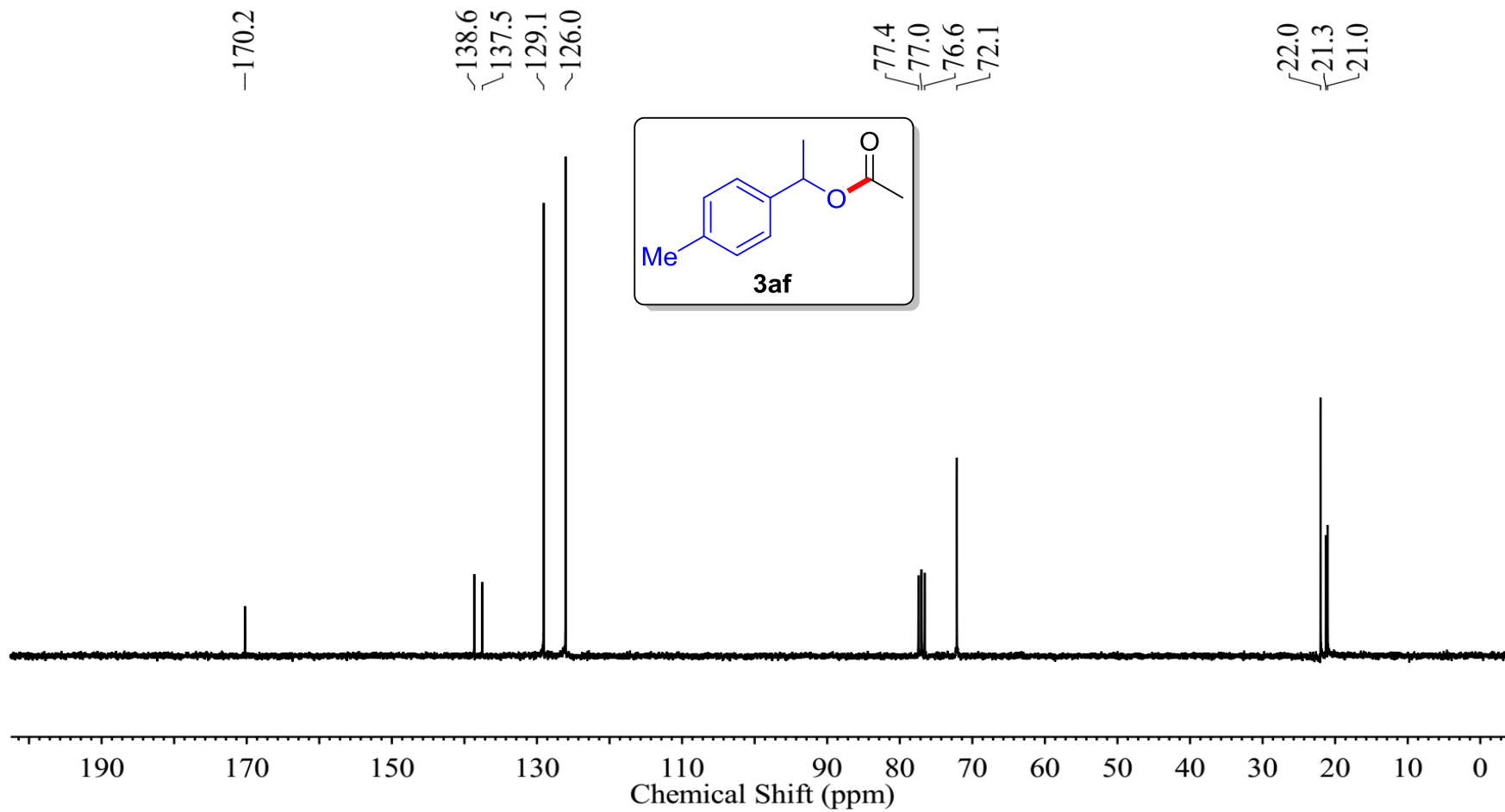
22.1
21.2



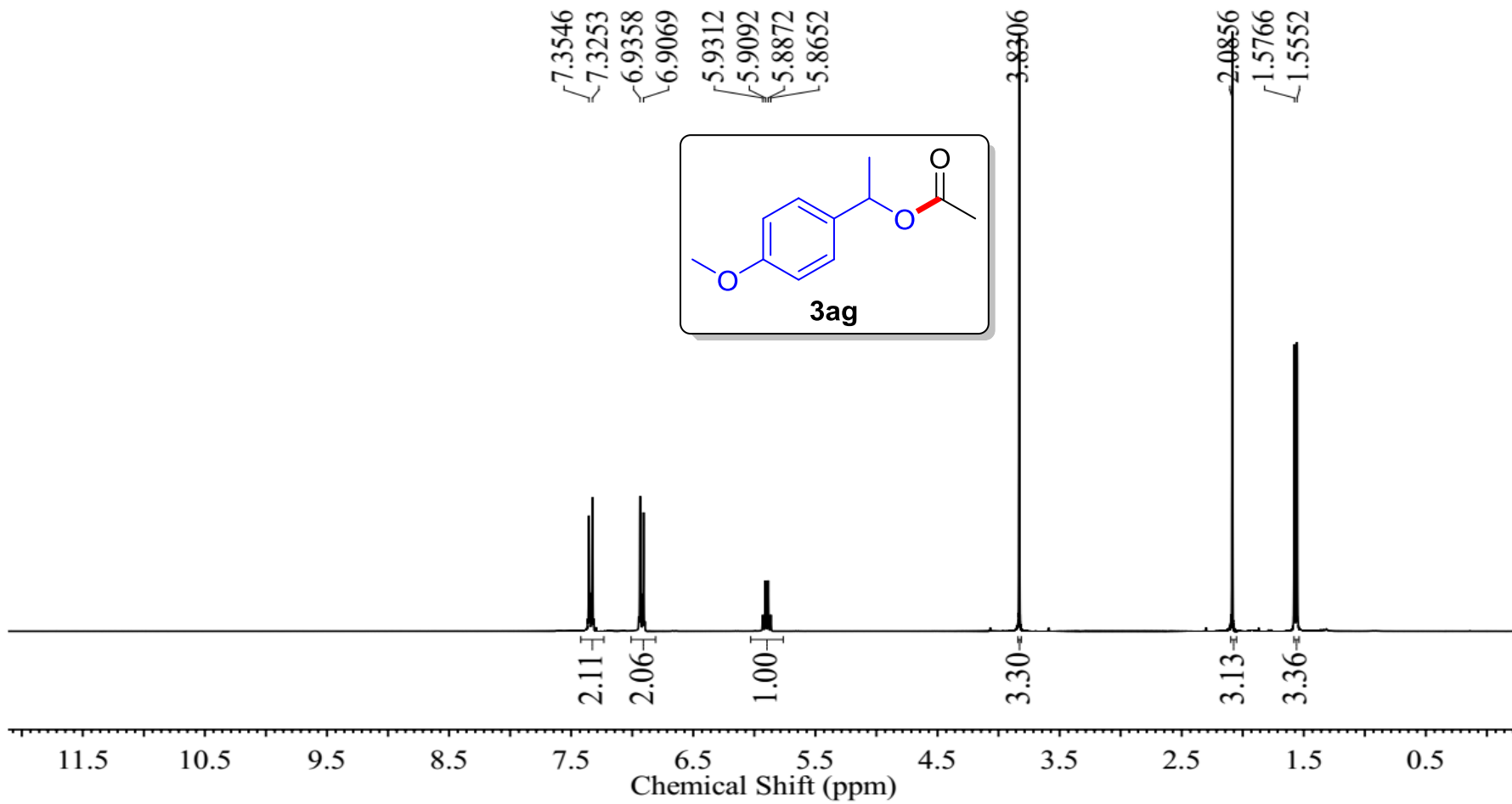
ZGY-X180618-1



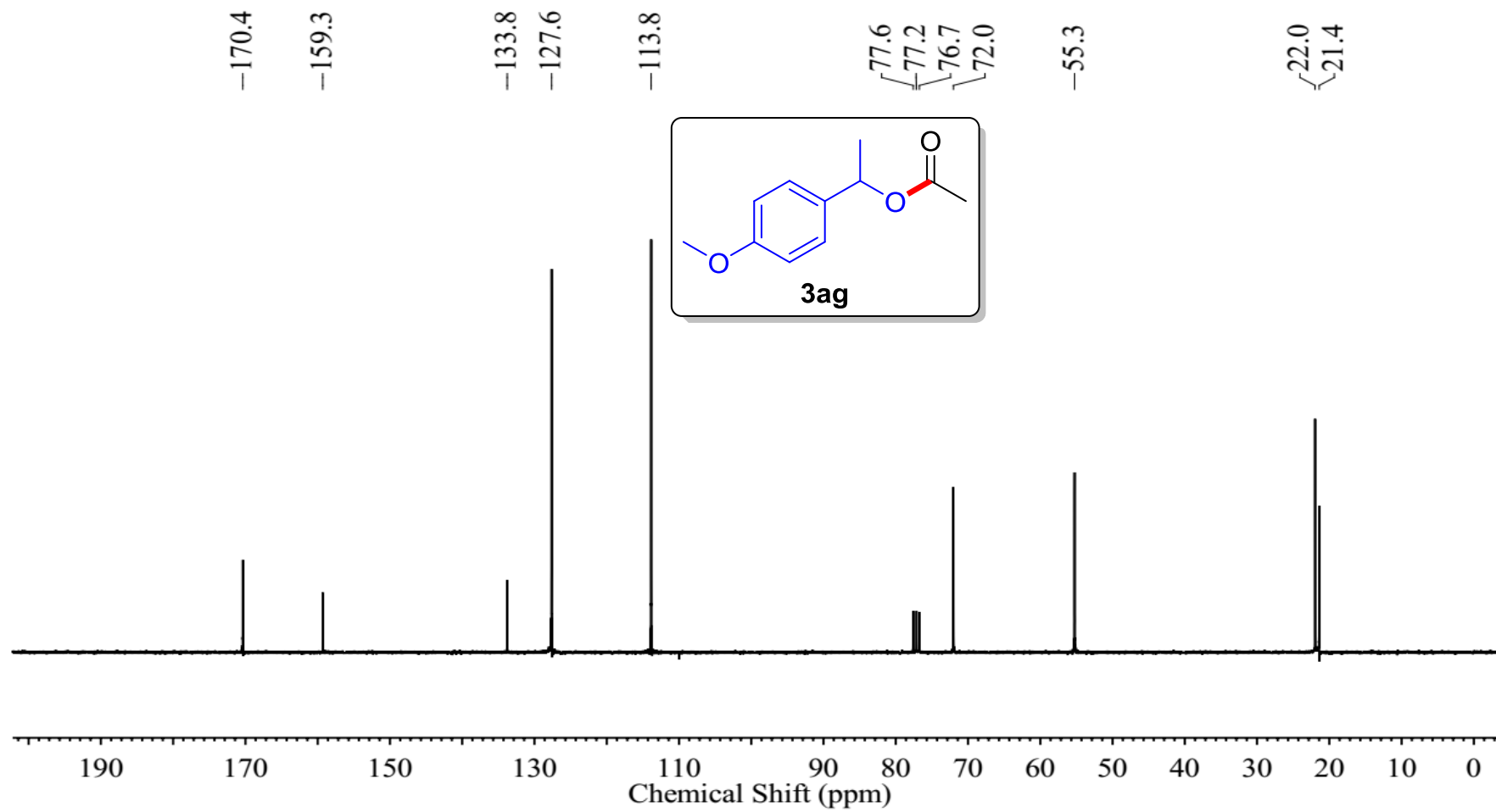
ZGY-X180618-1



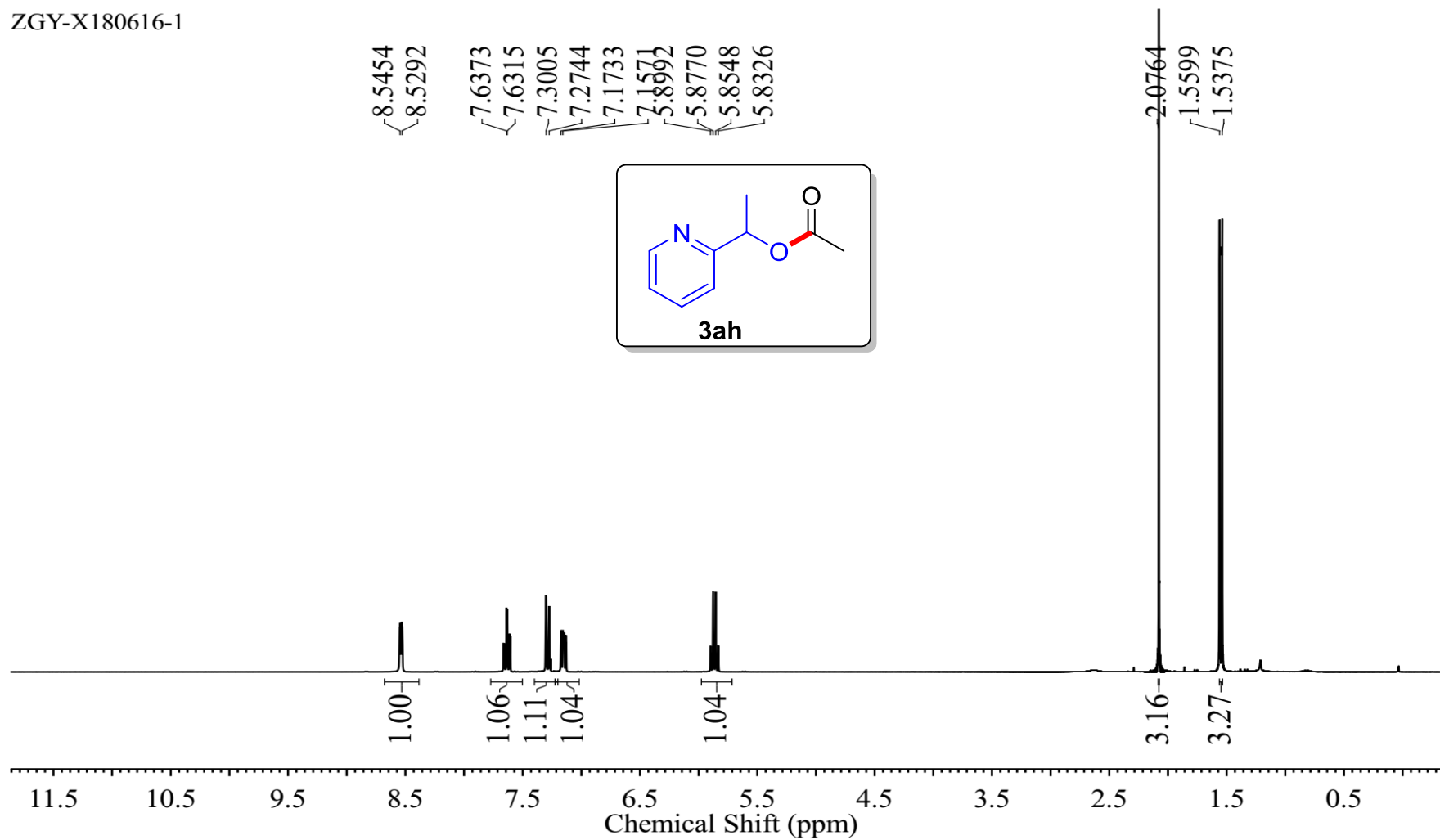
ZGY-X180619-3



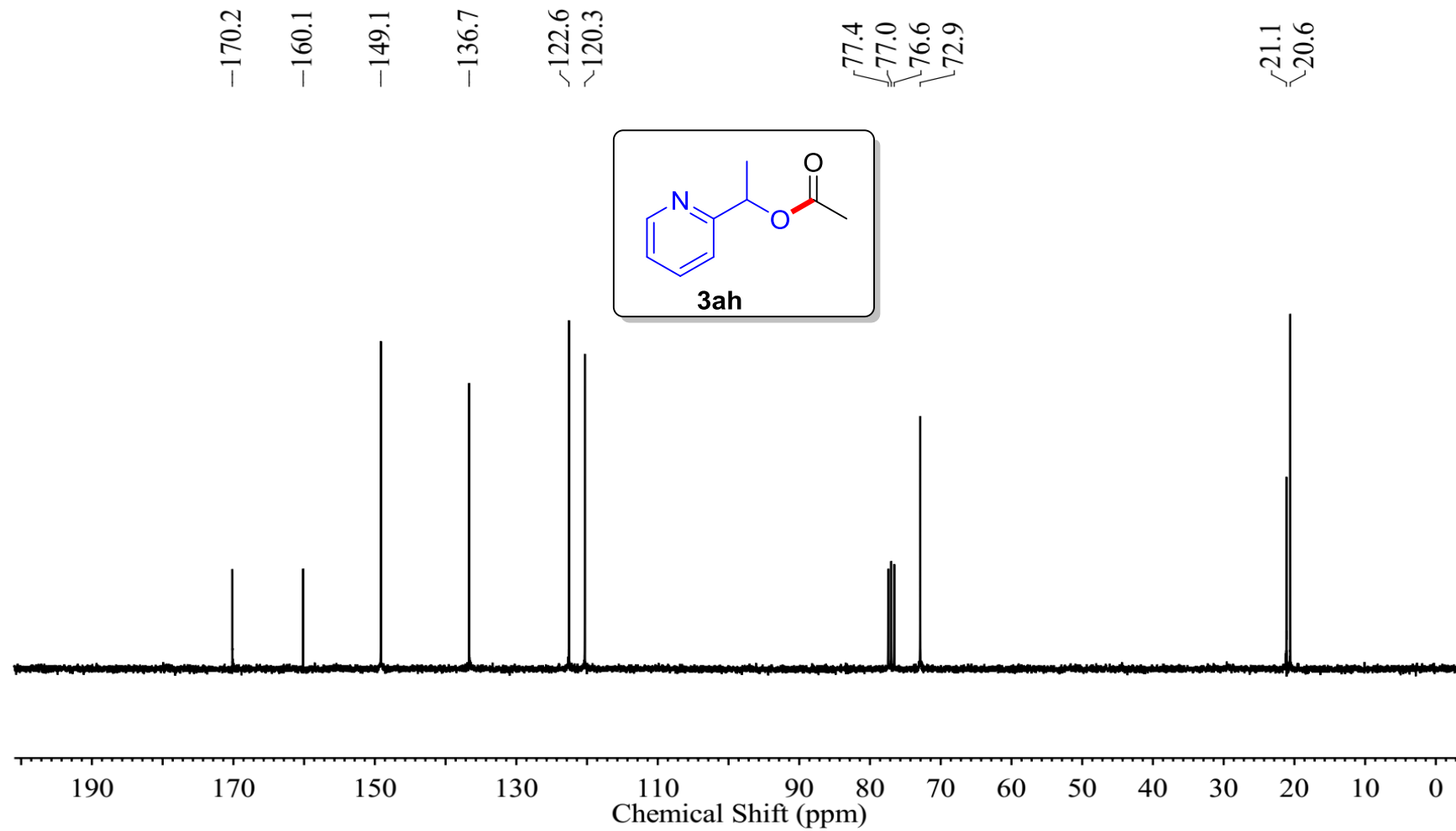
ZGY-X180619-3



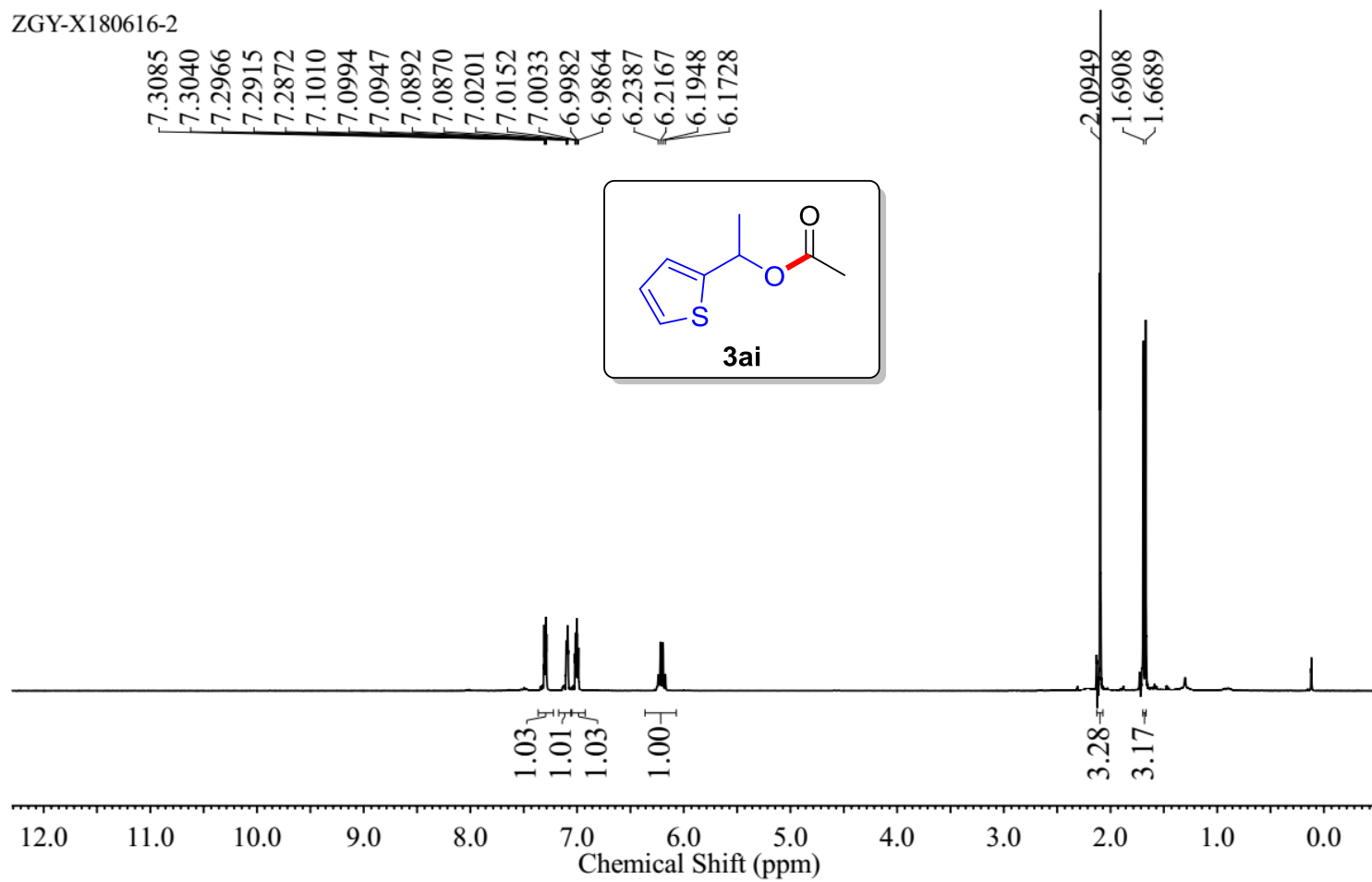
ZGY-X180616-1



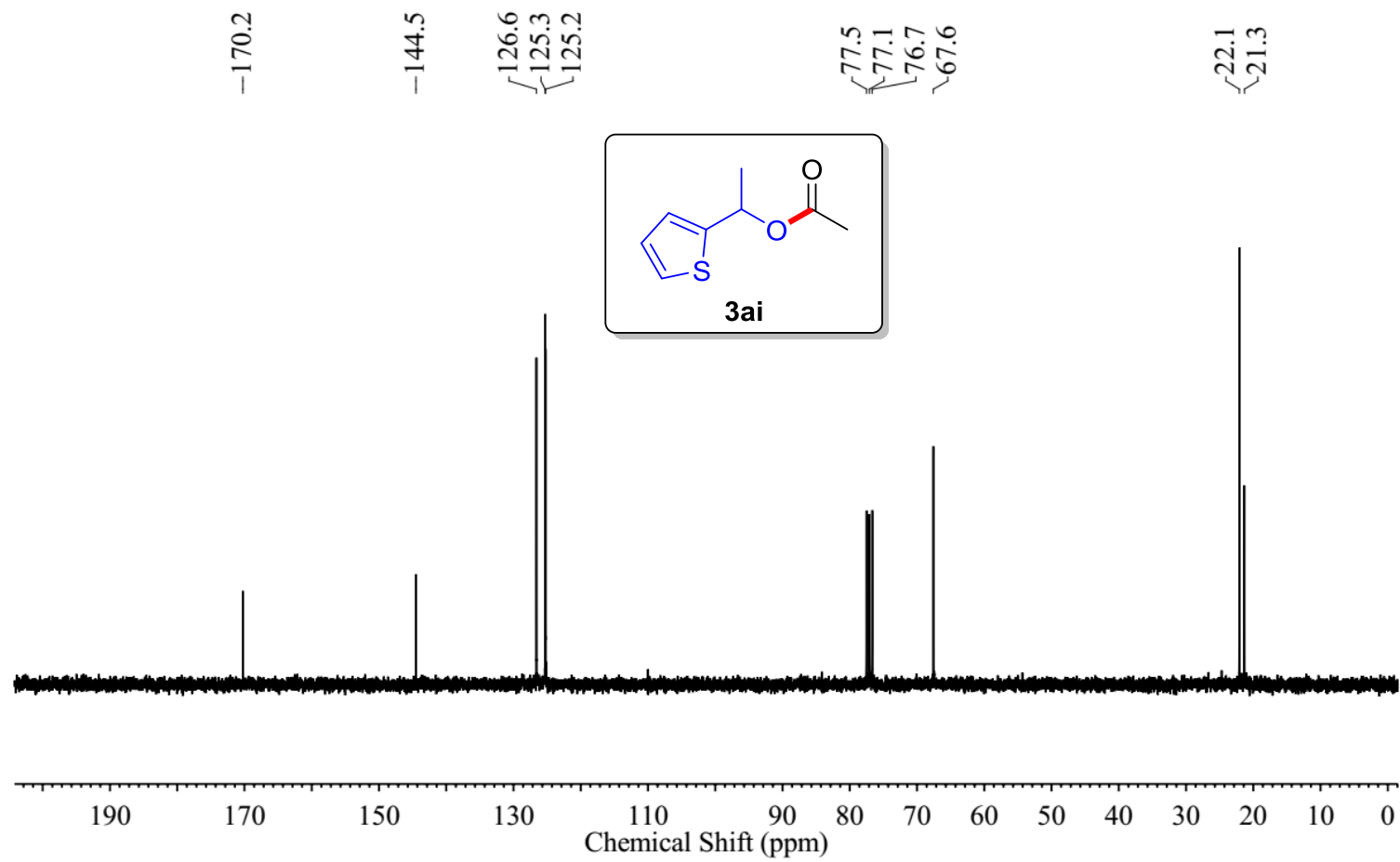
ZGY-X180616-1



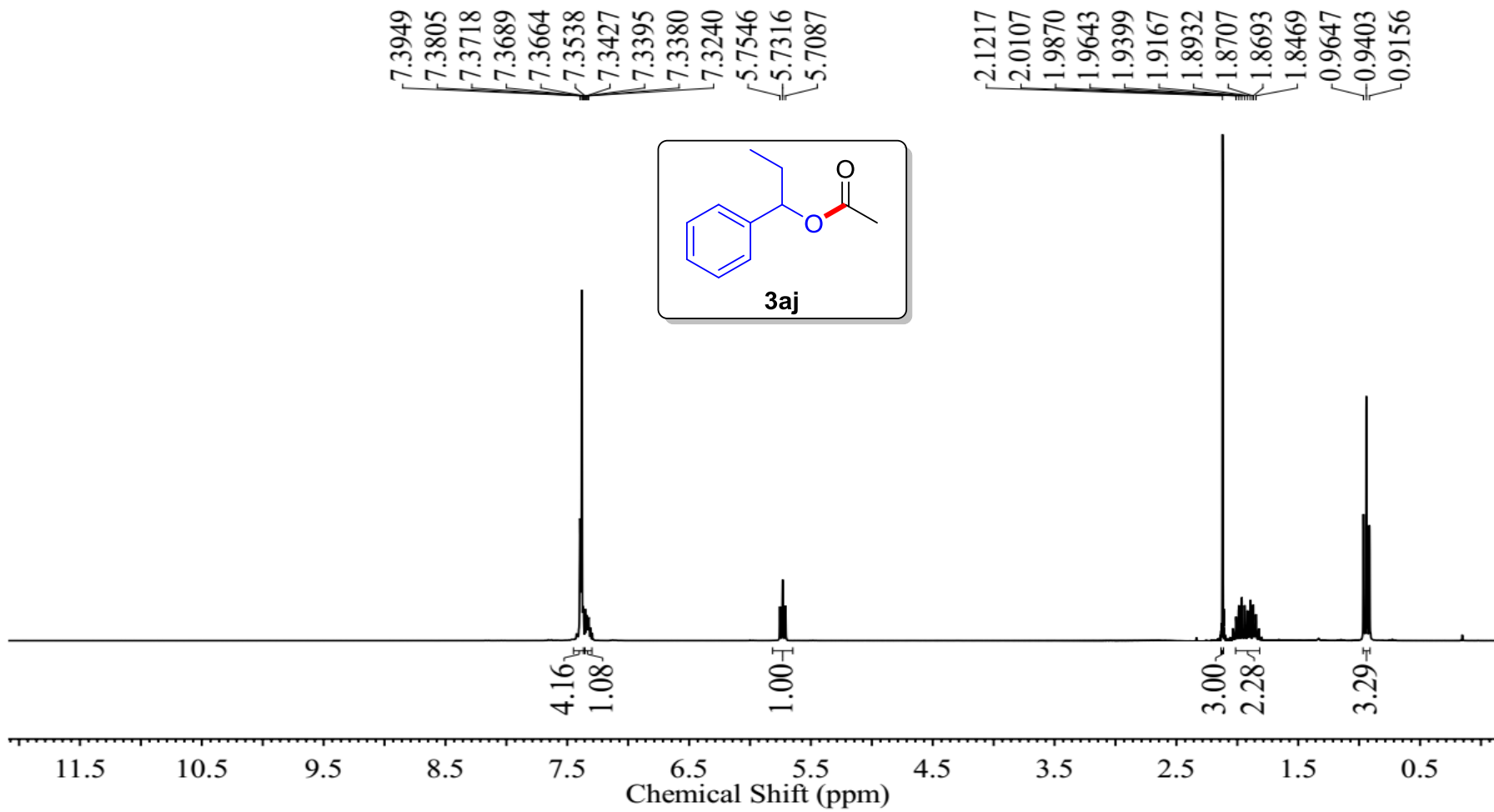
ZGY-X180616-2



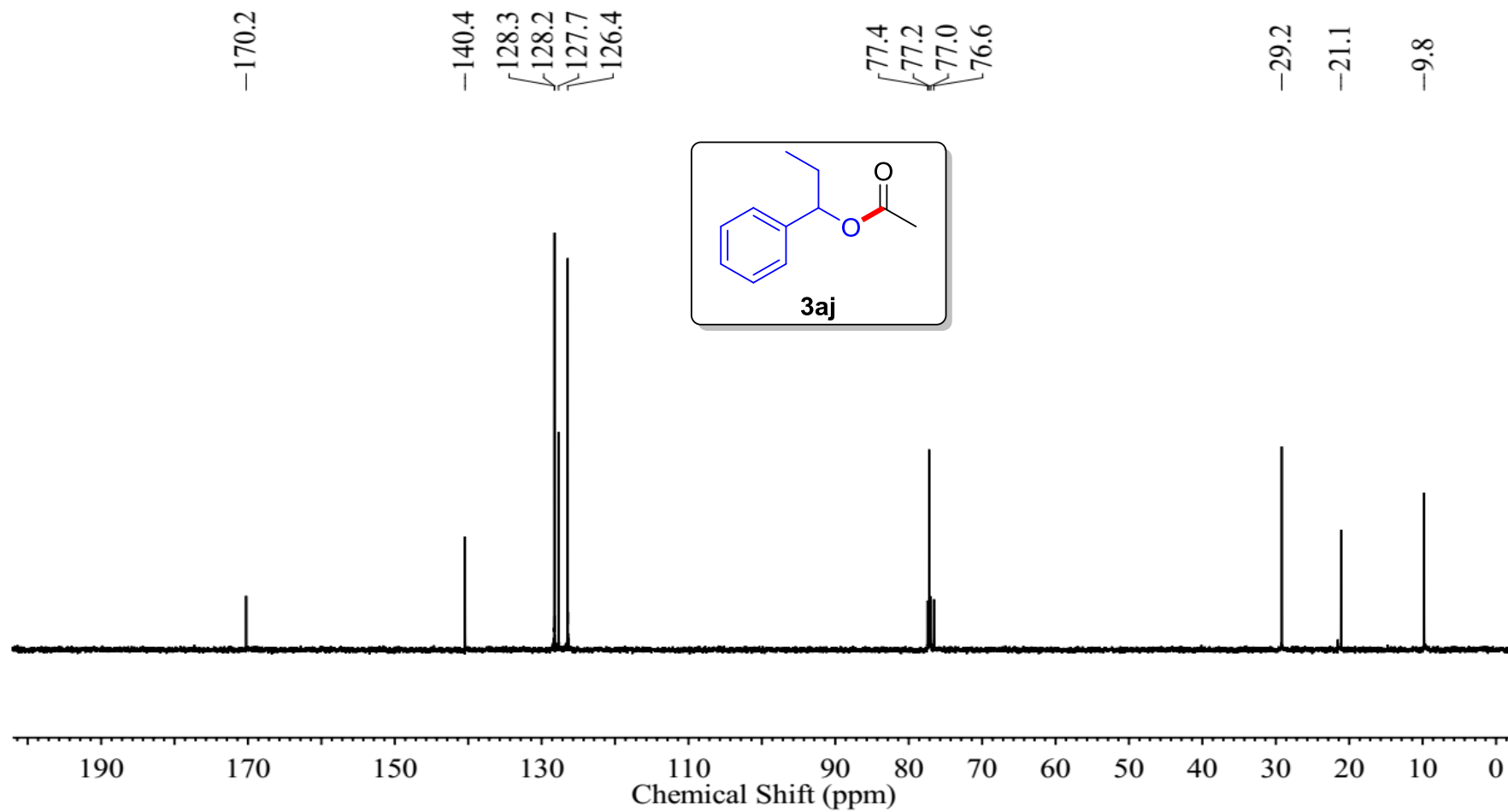
ZGY-X180616-2



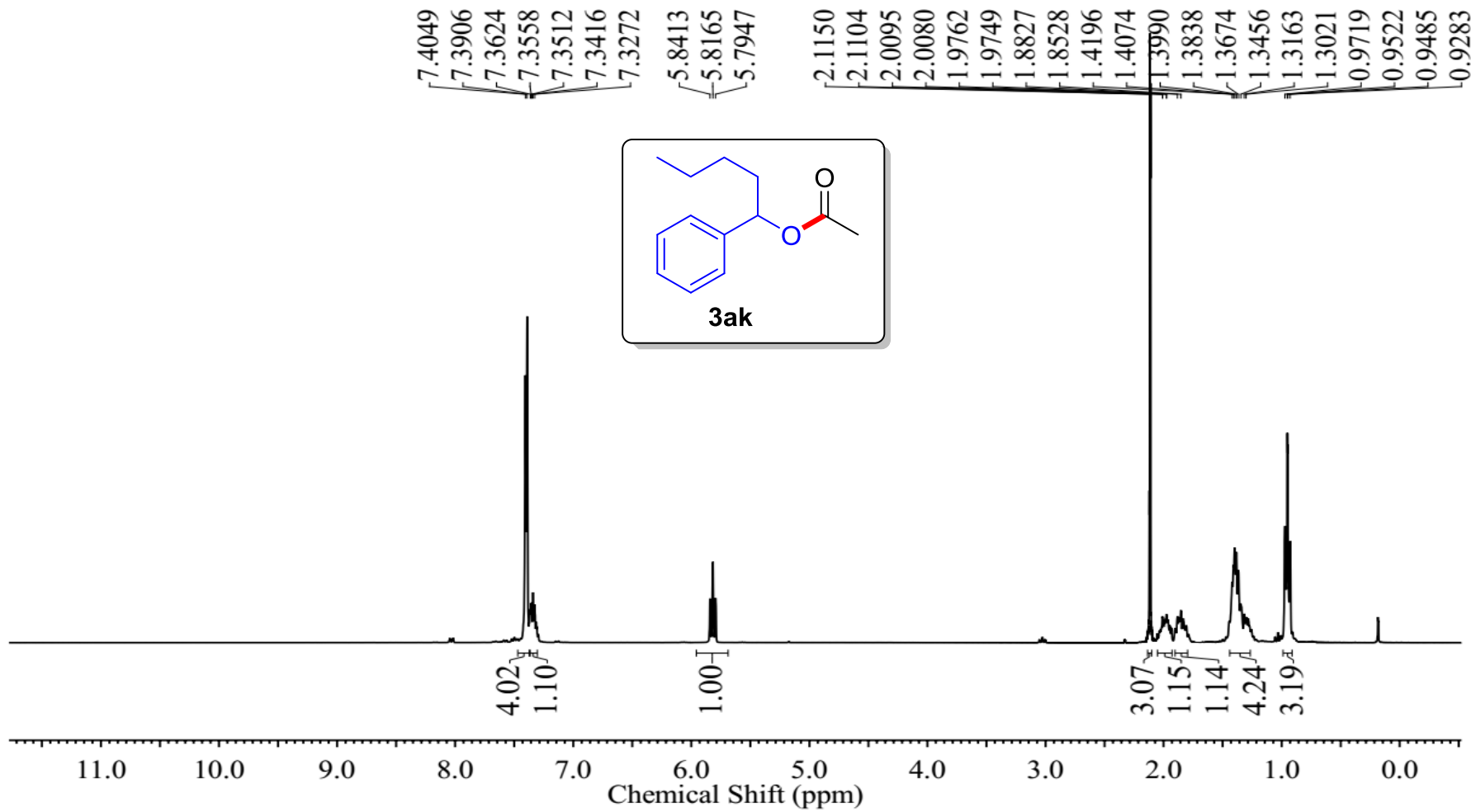
ZGY-X180619-1



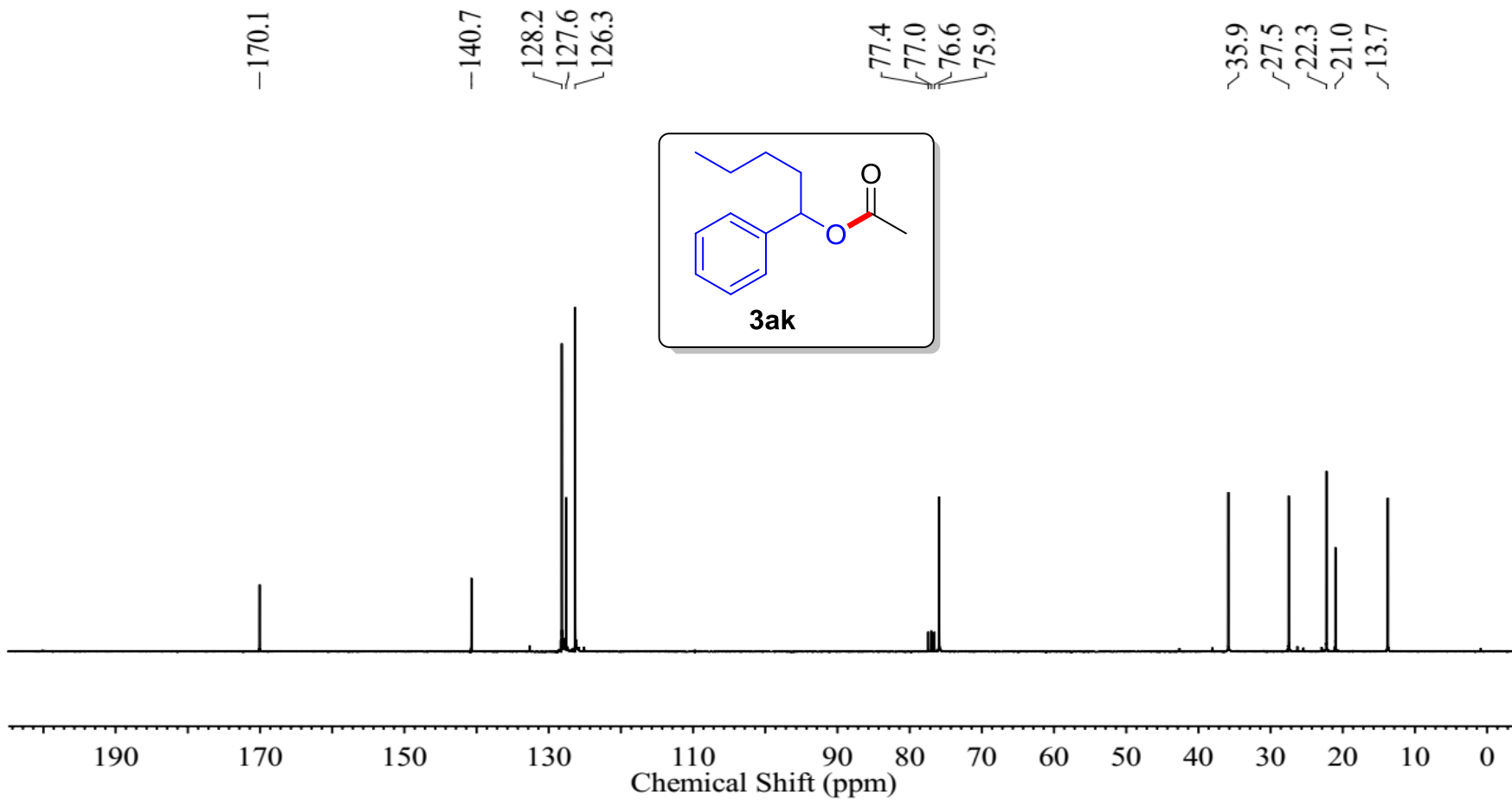
ZGY-X180619-1



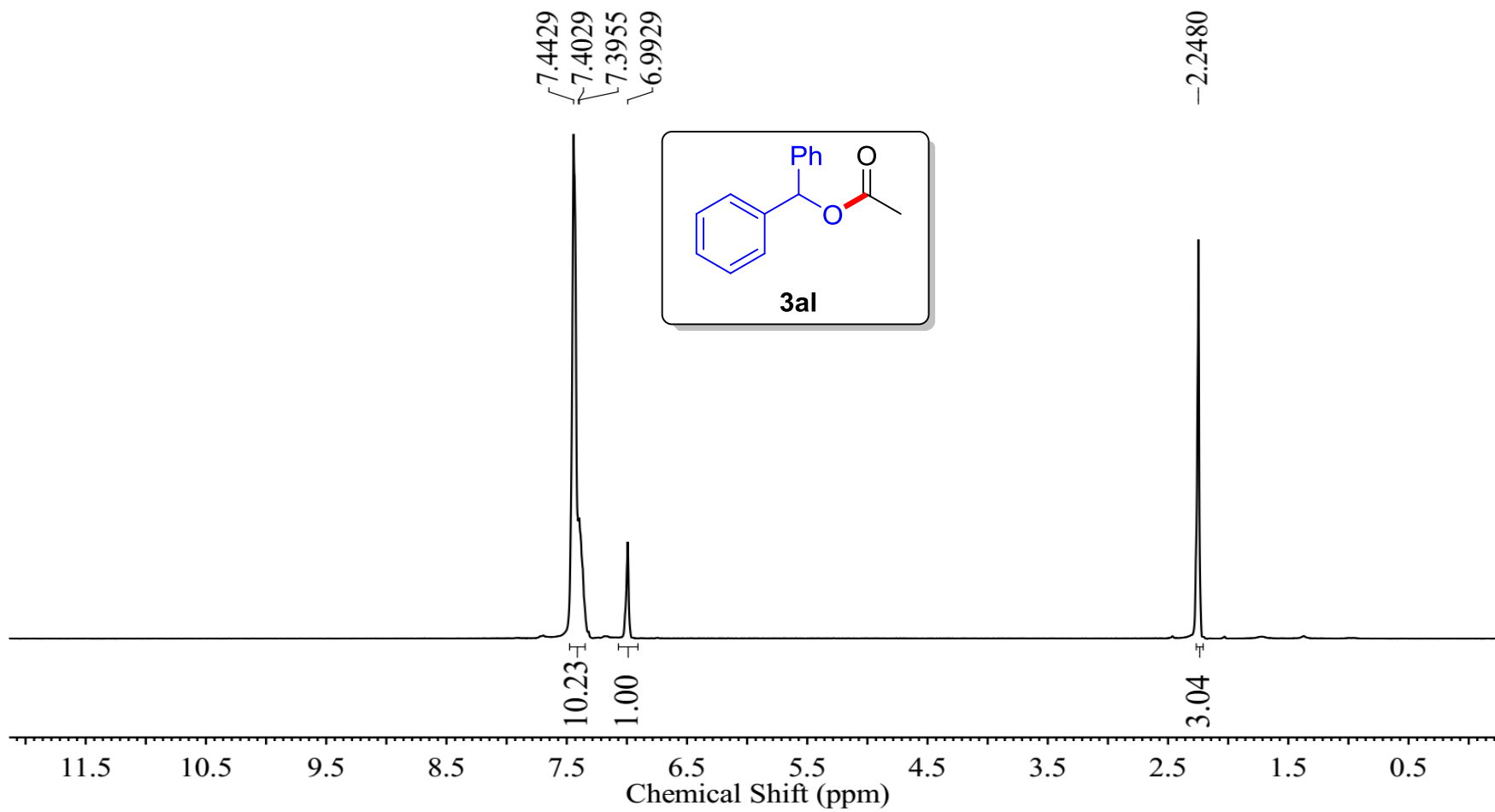
ZGY-X180618-3



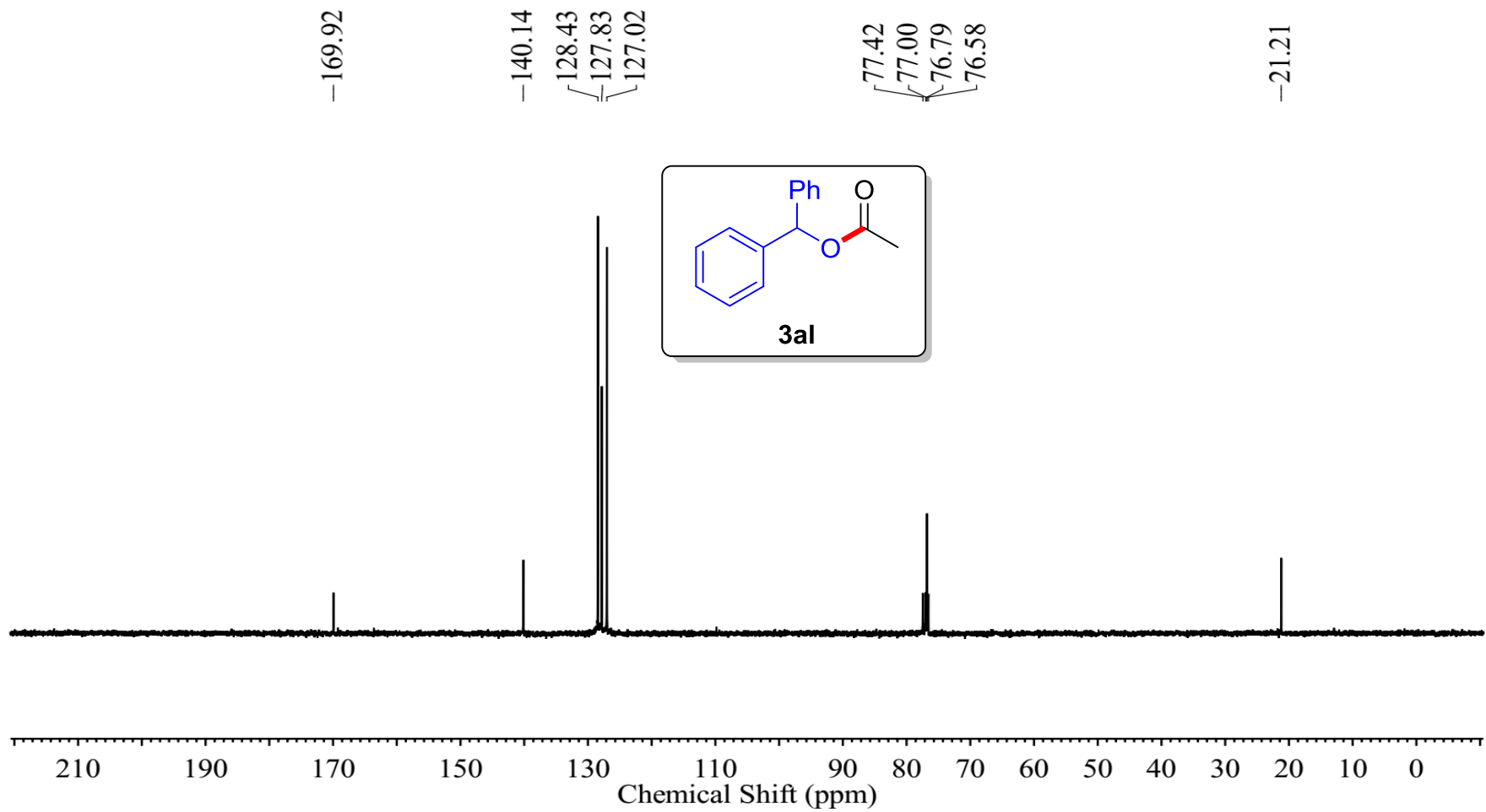
ZGY-X180618-3



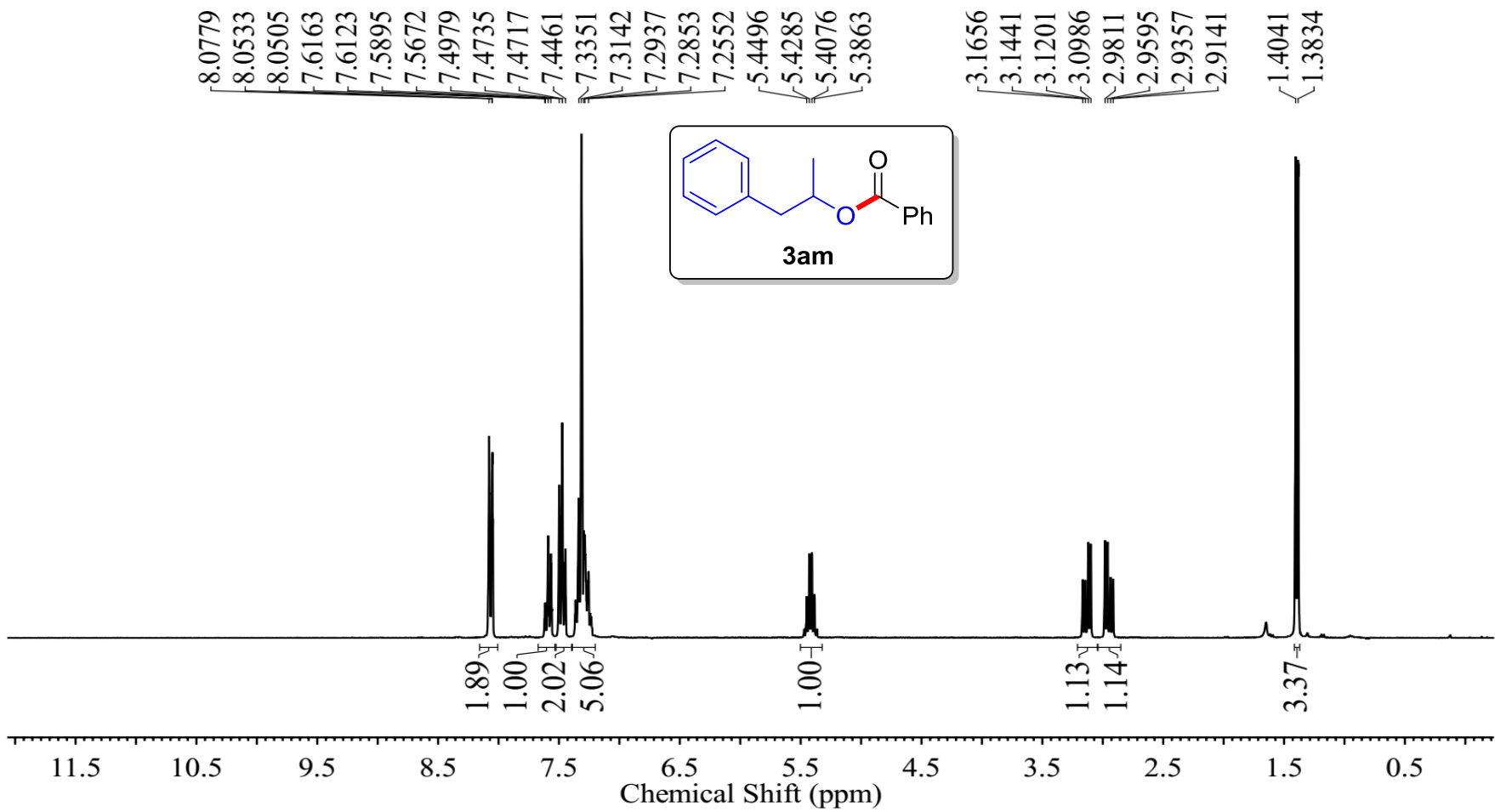
ZGY-X180705-2



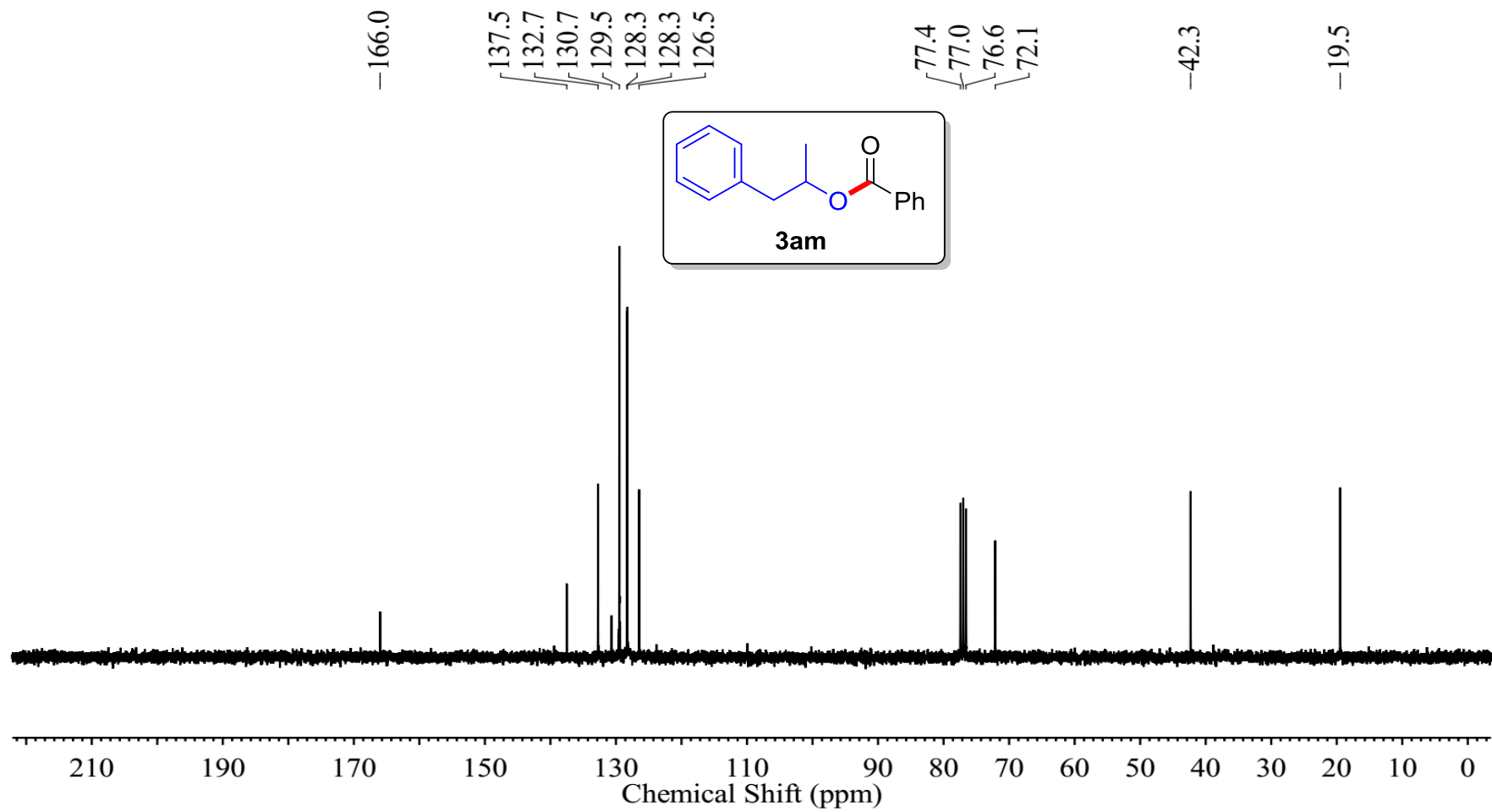
ZGY-X180705-2



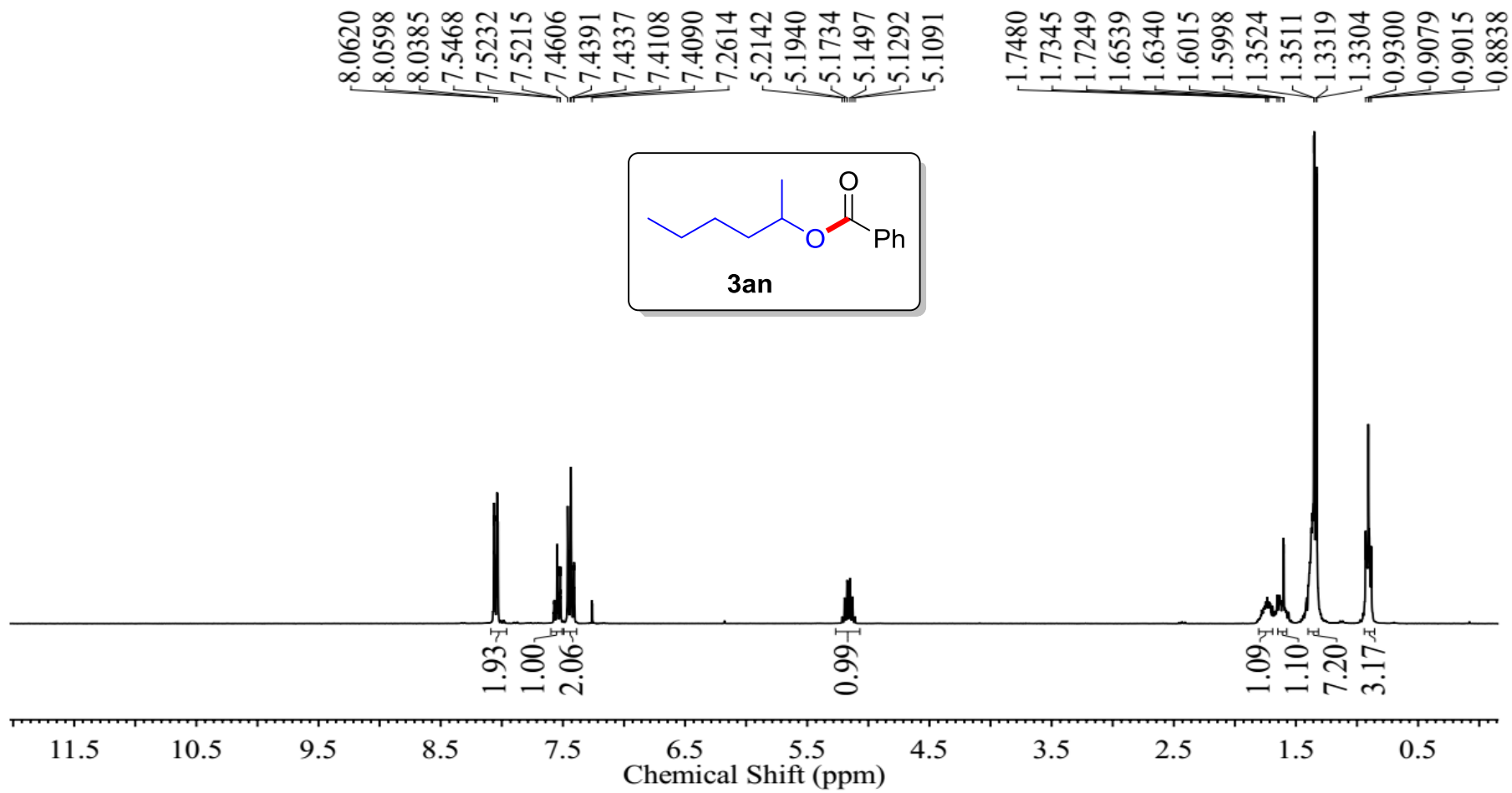
ZGY-X180625-6



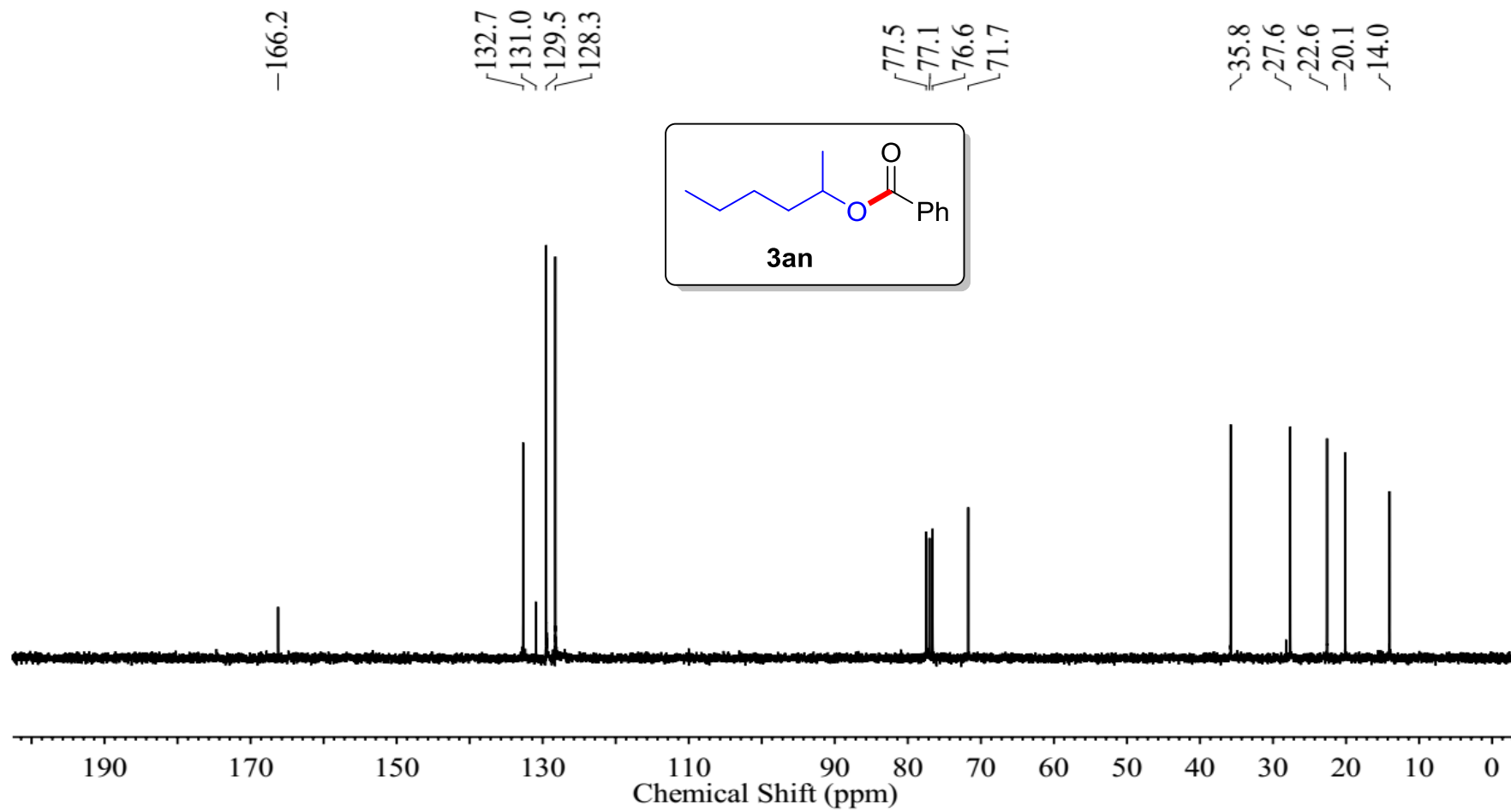
ZGY-X180625-6



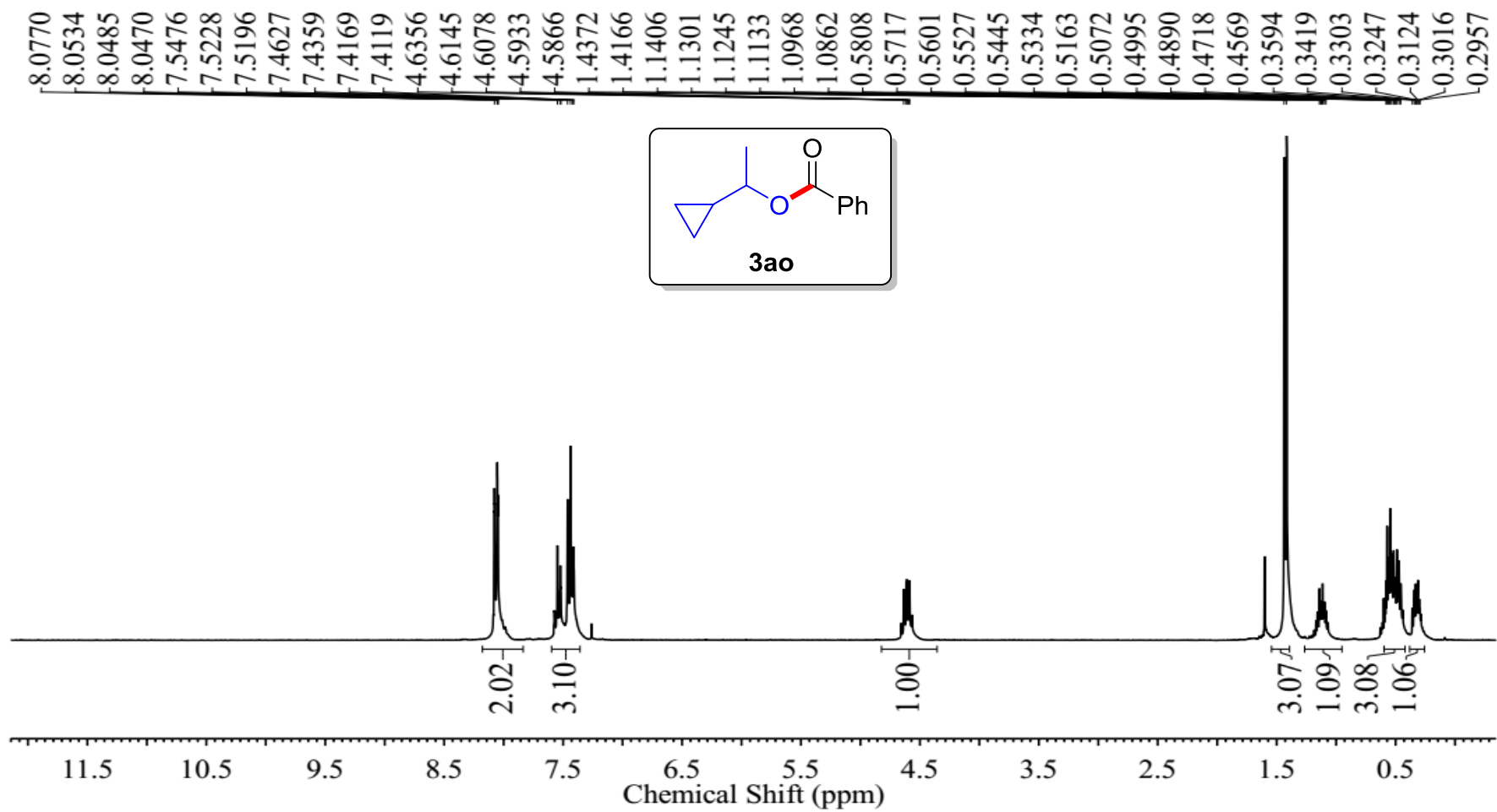
ZGY-X180625-4



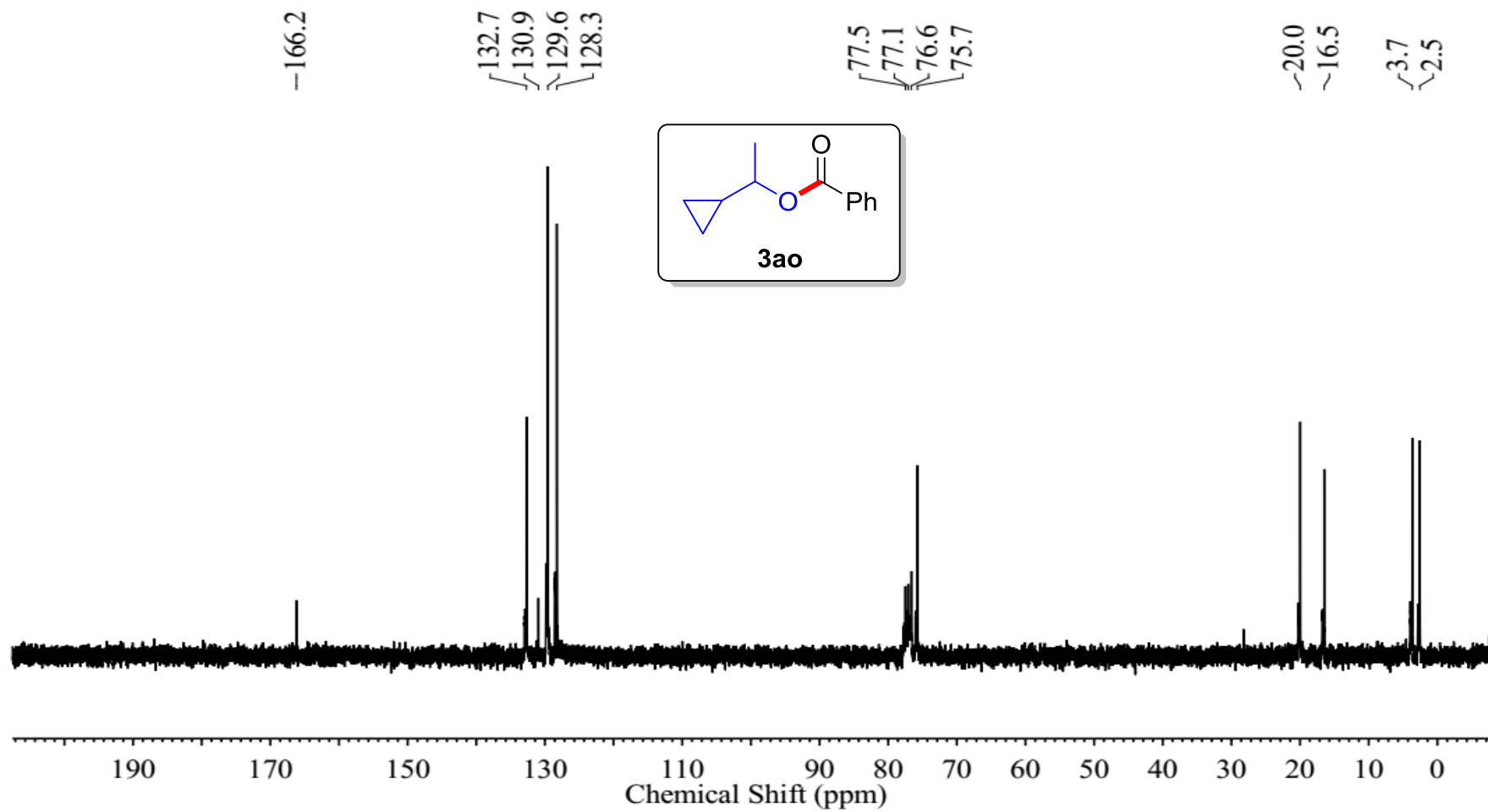
ZGY-X180625-4



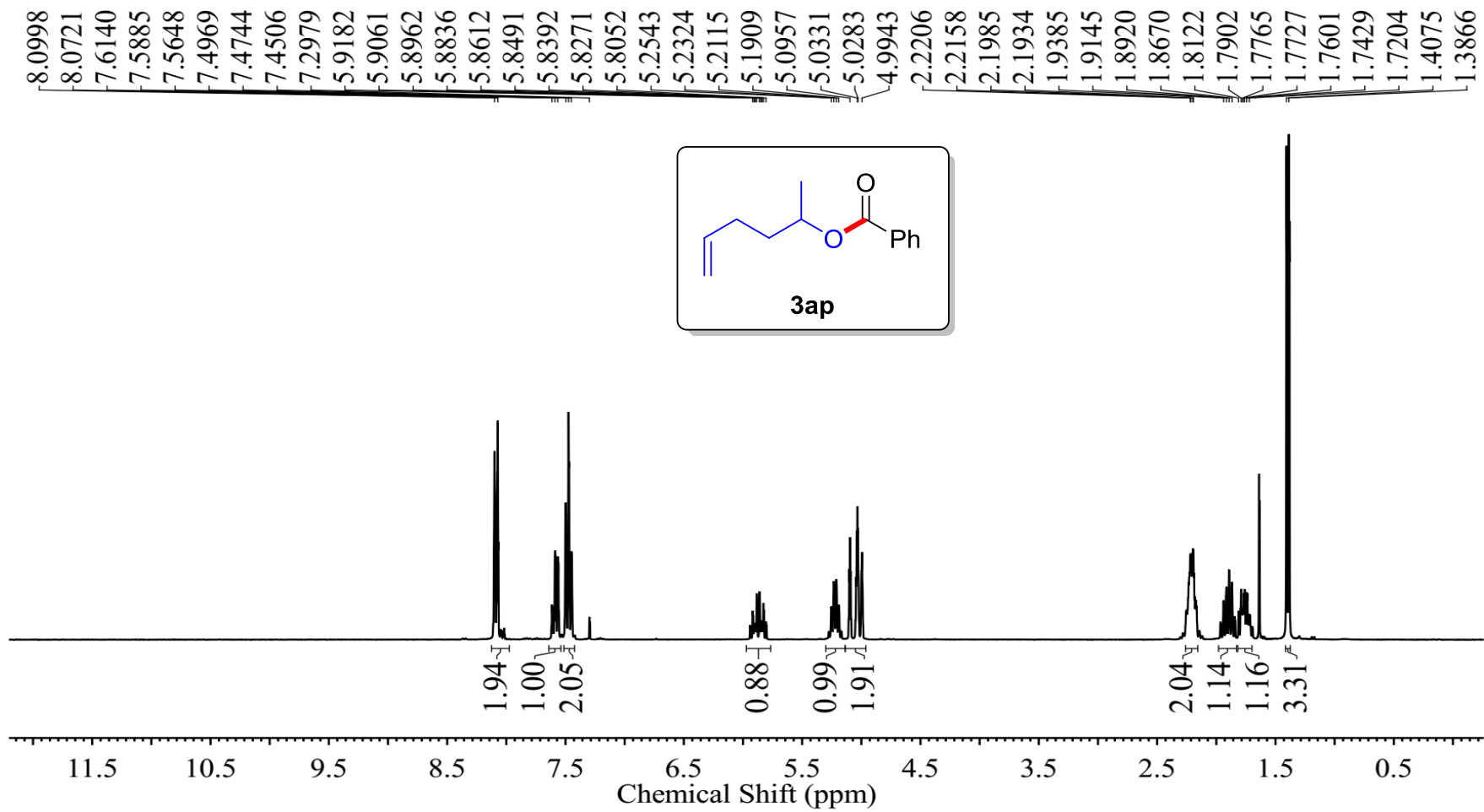
ZGY-X180625-1



ZGY-X180625-1



ZGY-X180625-3



ZGY-X180625-3

-166.1

137.7

132.7

130.8

129.5

128.2

-115.0

77.4

77.0

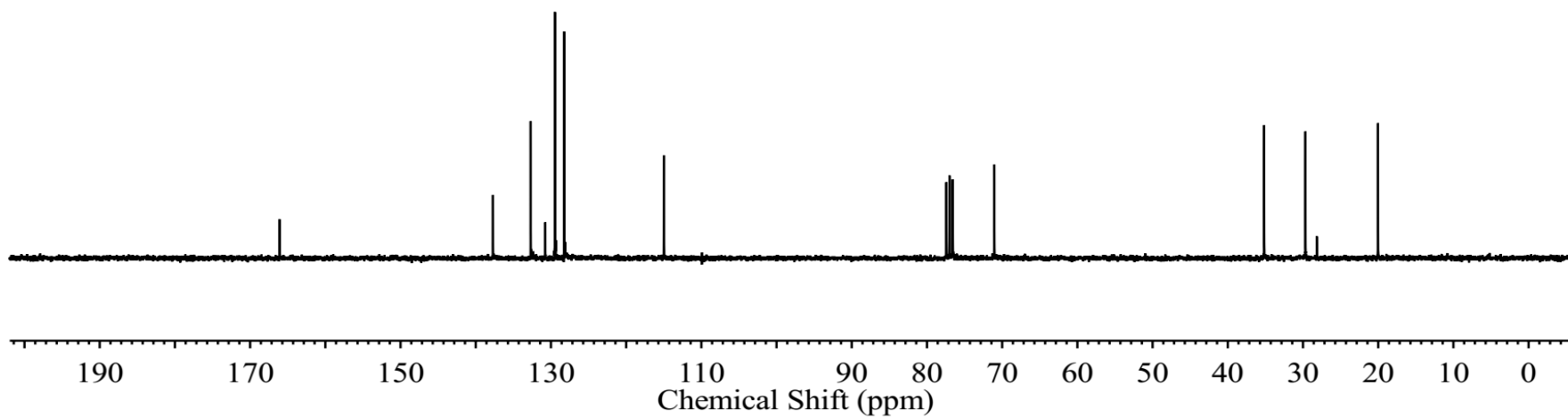
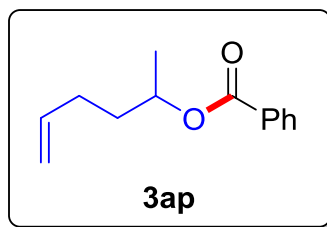
76.6

71.0

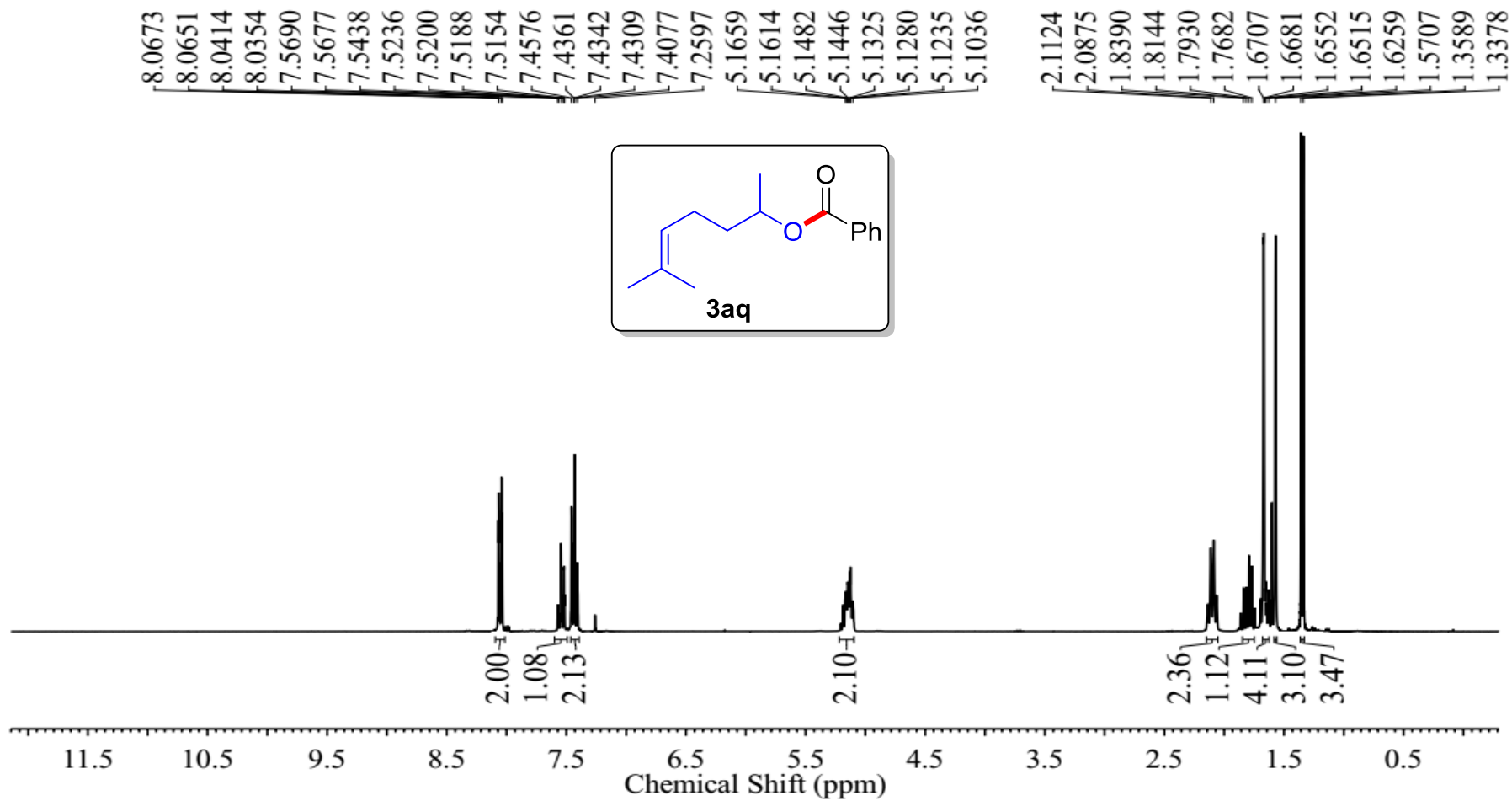
-35.2

-29.7

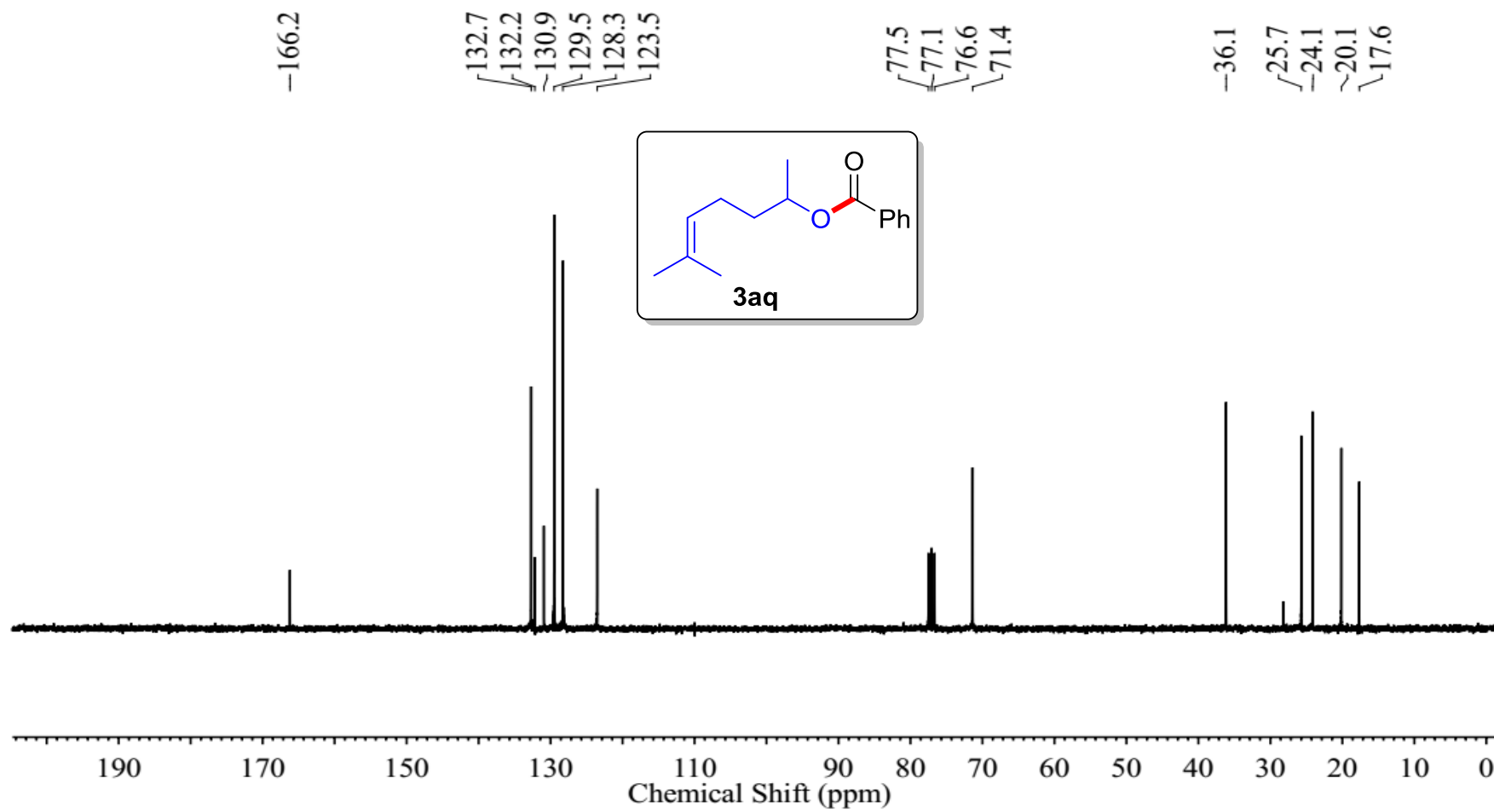
-20.0



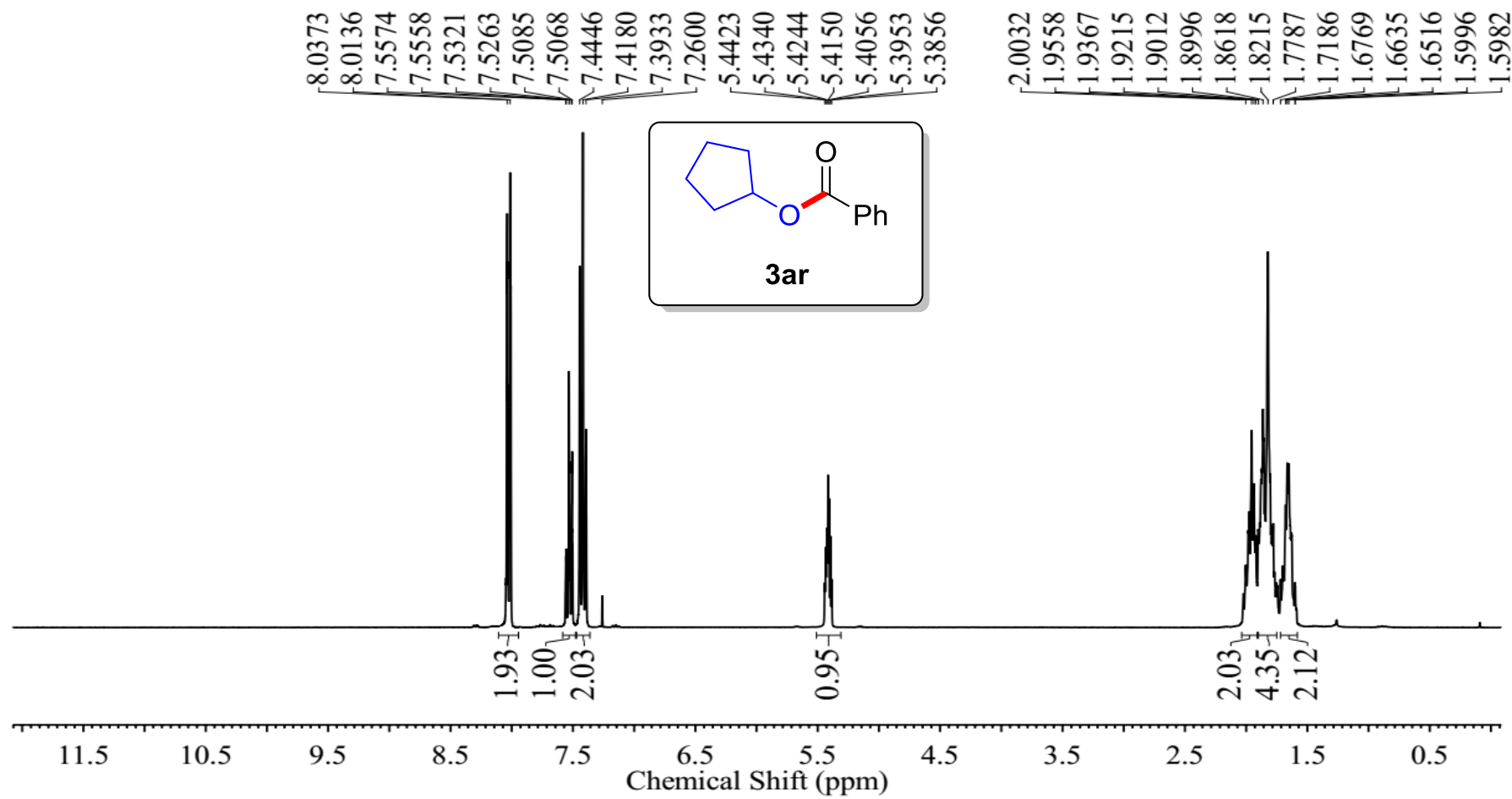
ZGU-X180625-2



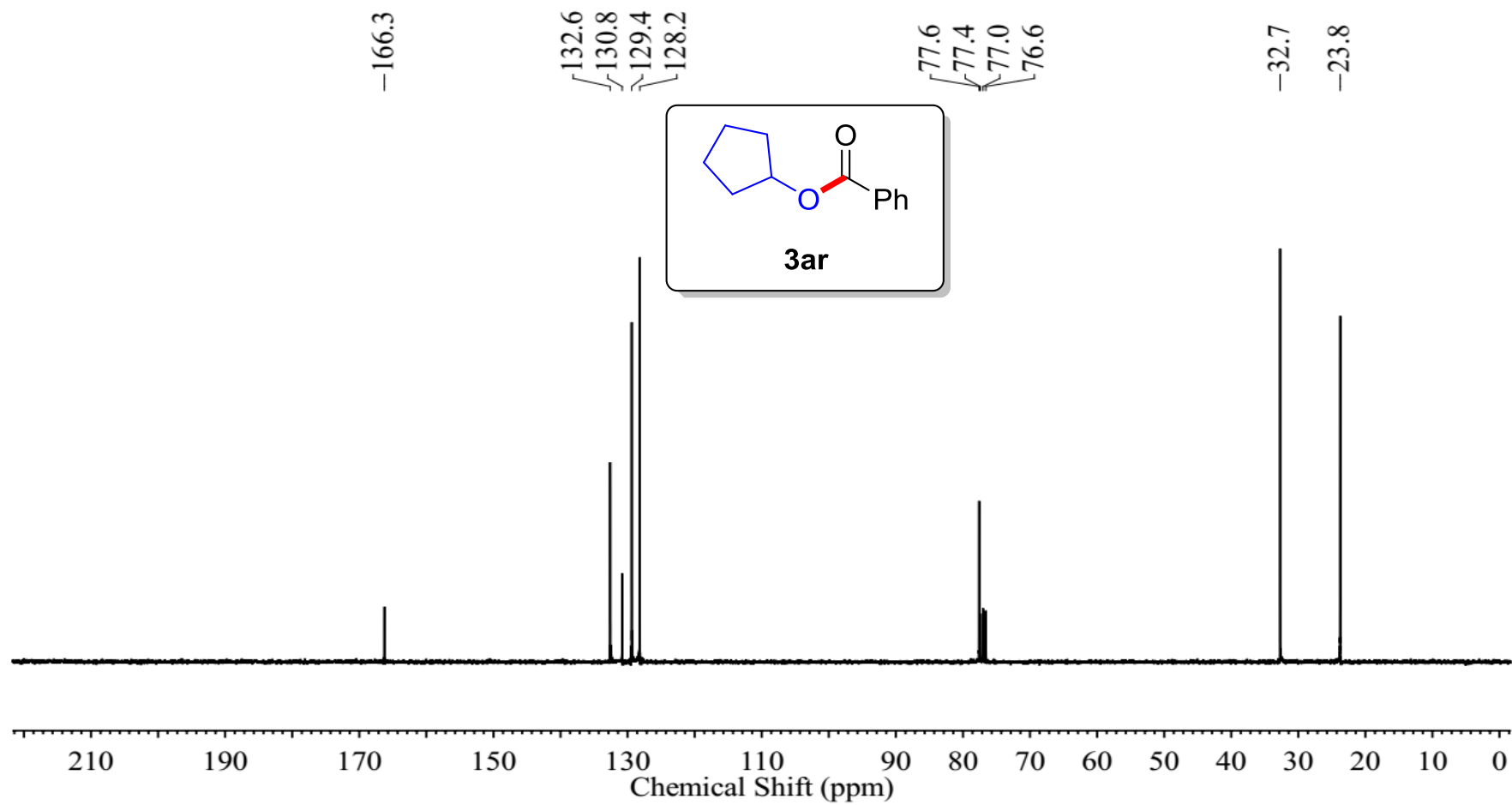
ZGU-X180625-2



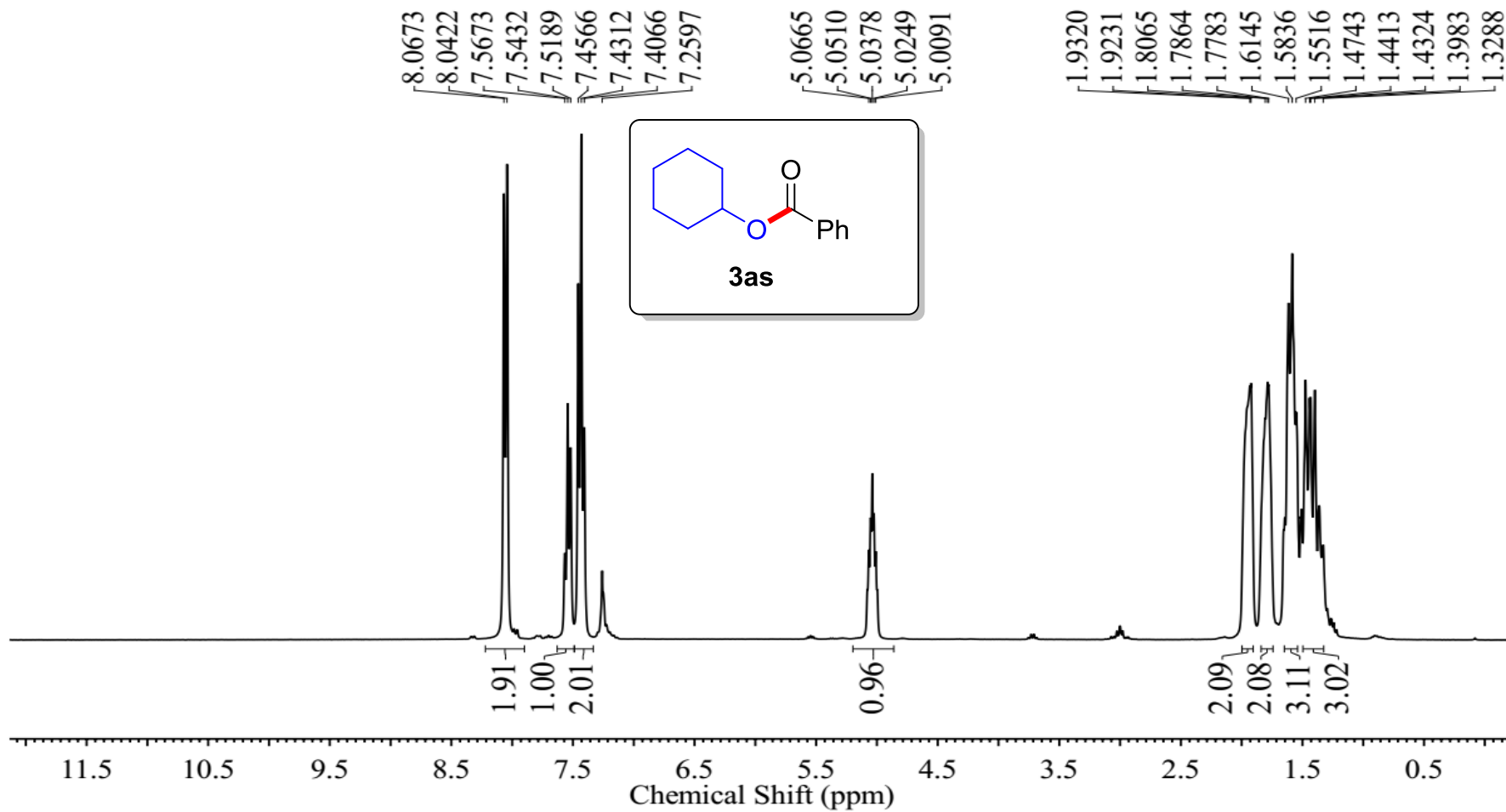
ZGY-X180625-7



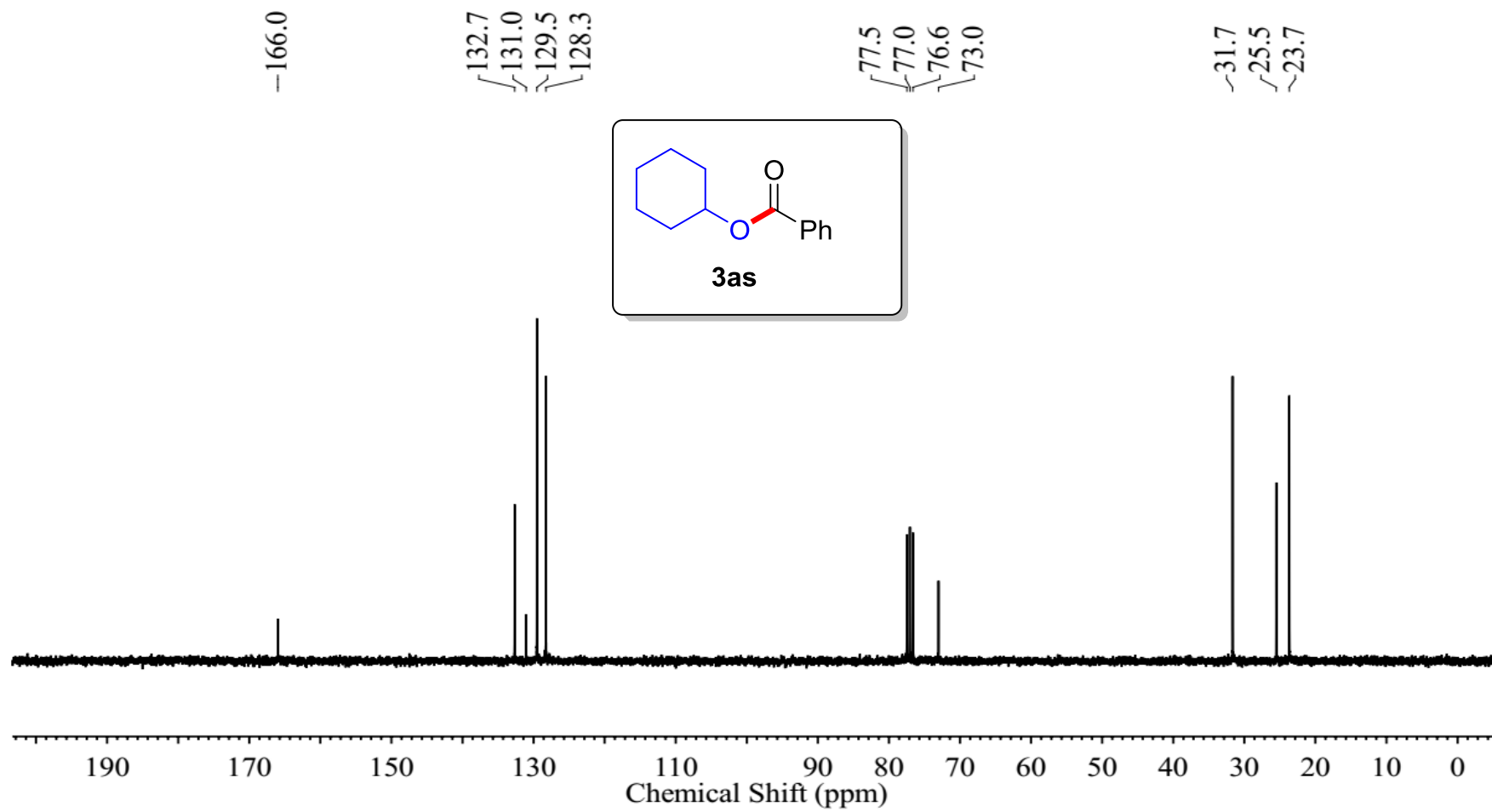
ZGY-X180625-7



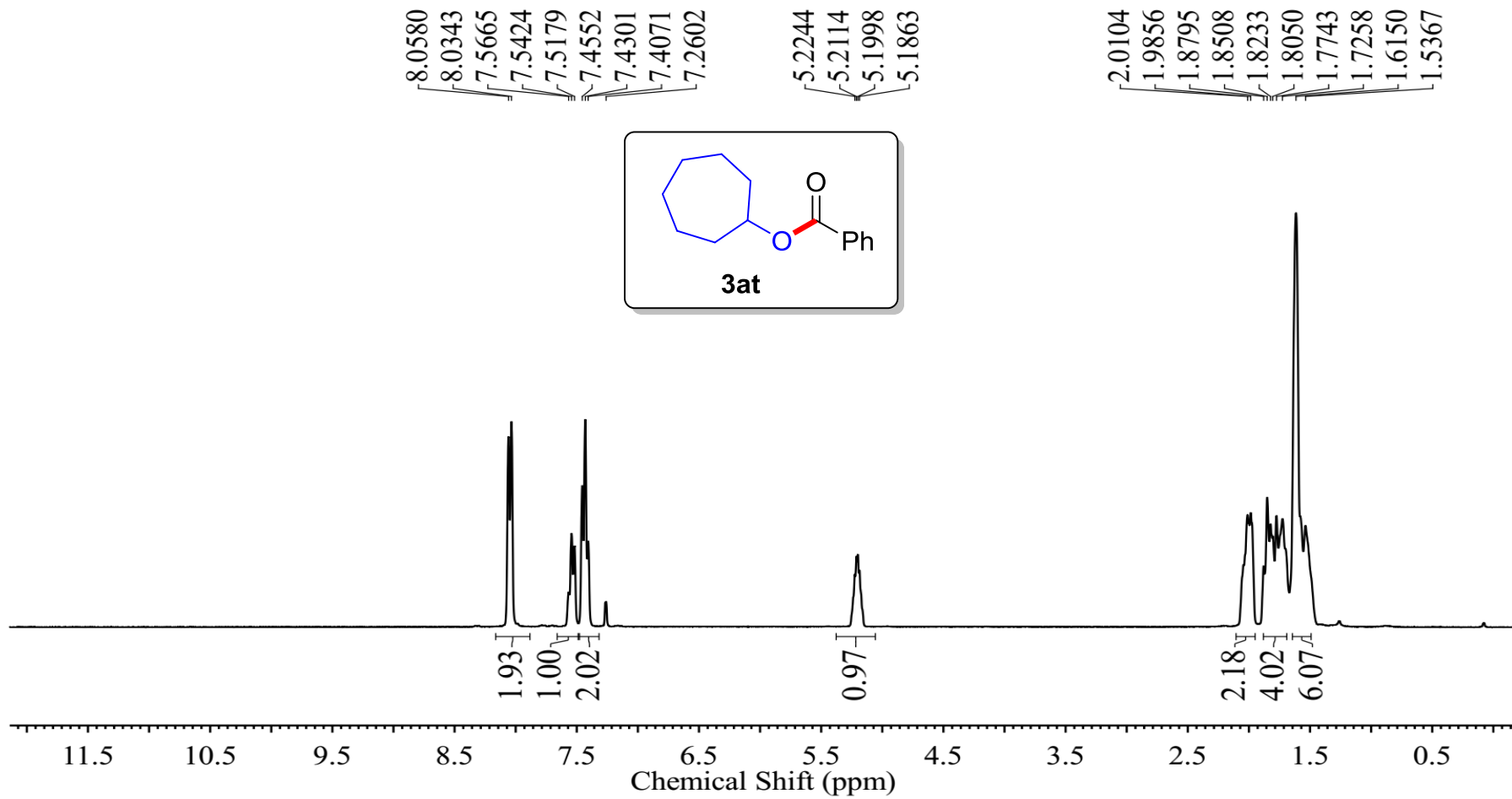
ZGY-X180626-1



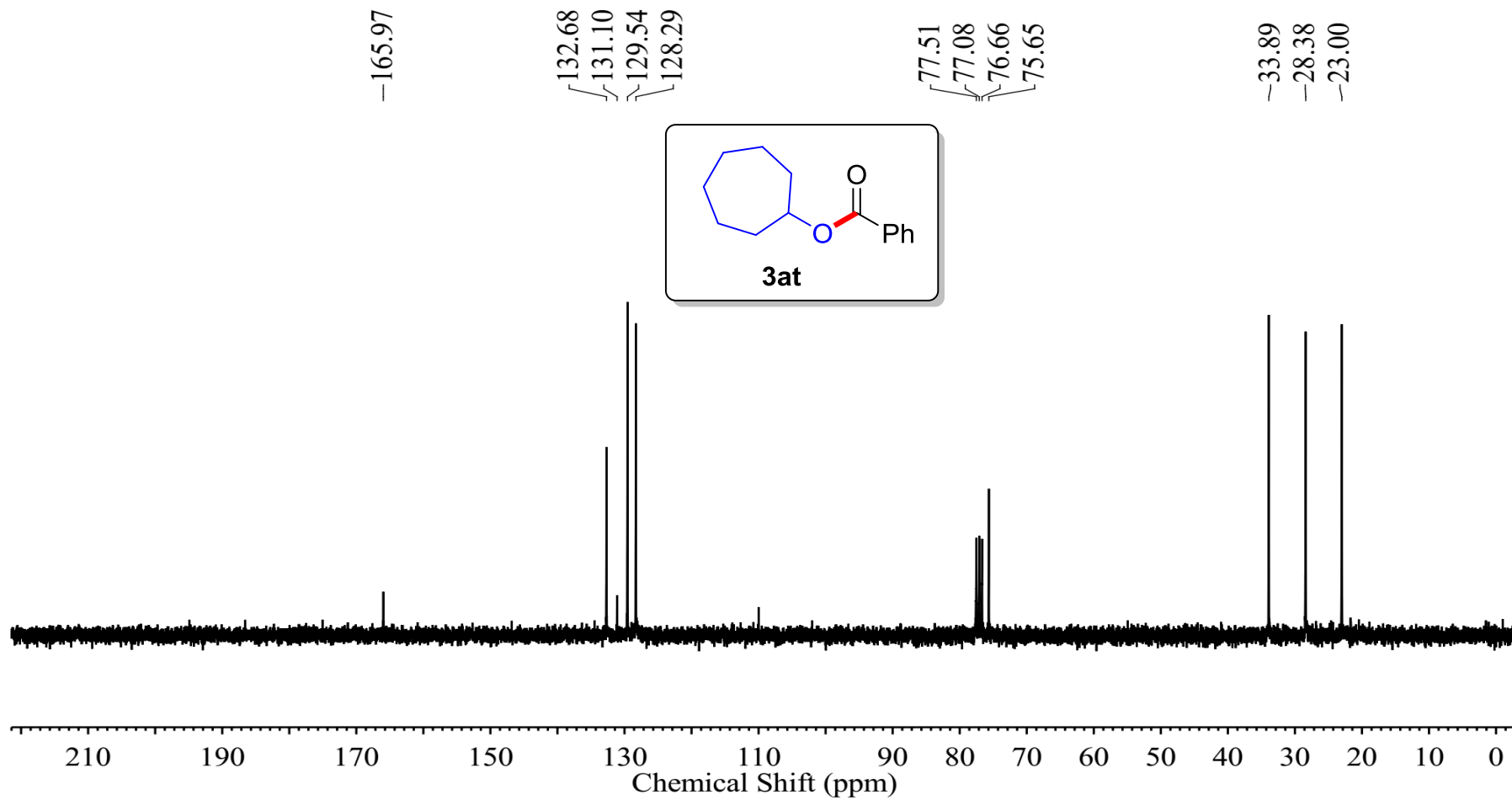
ZGY-X180626-1



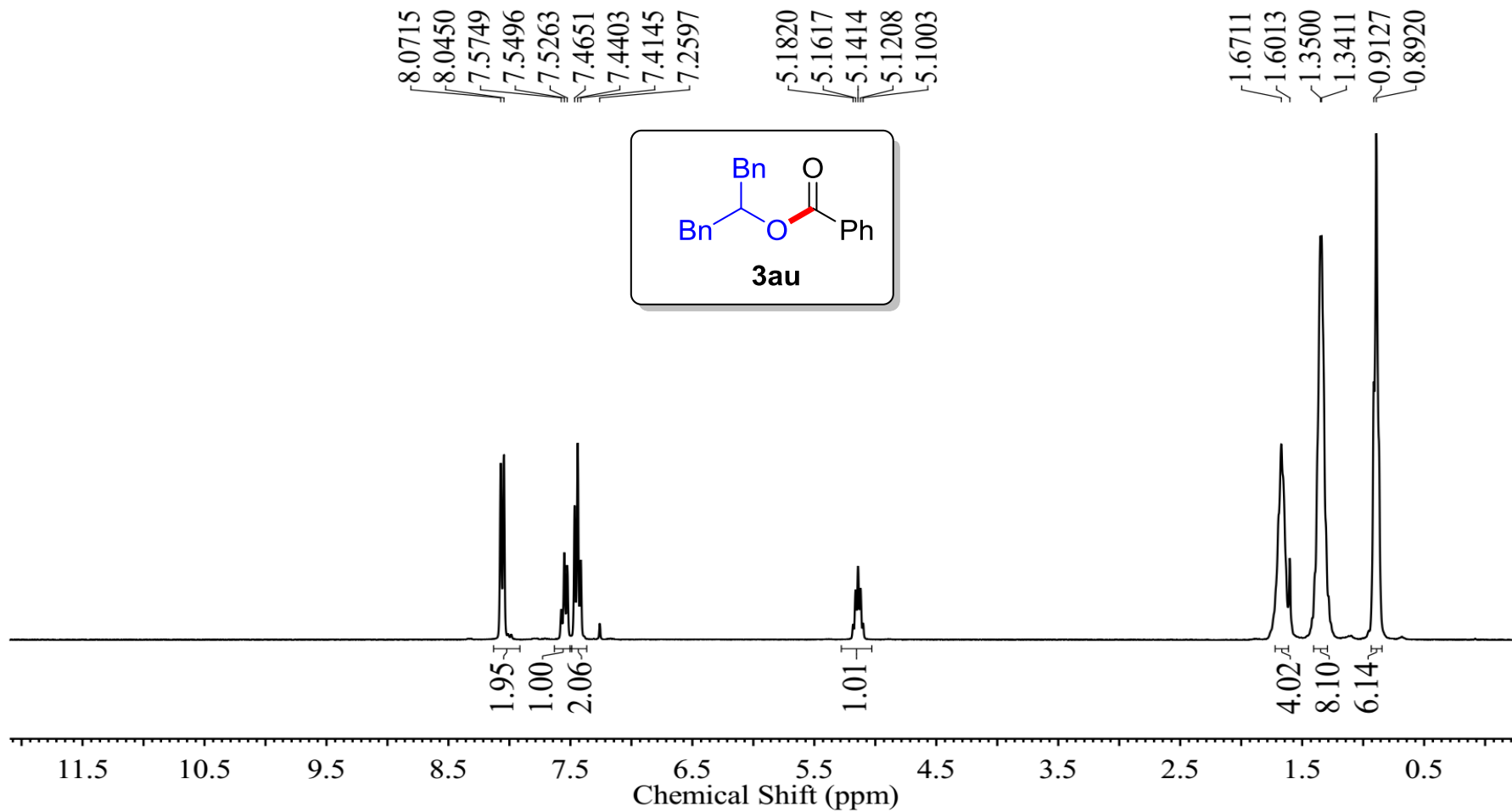
ZGY-X180629-1



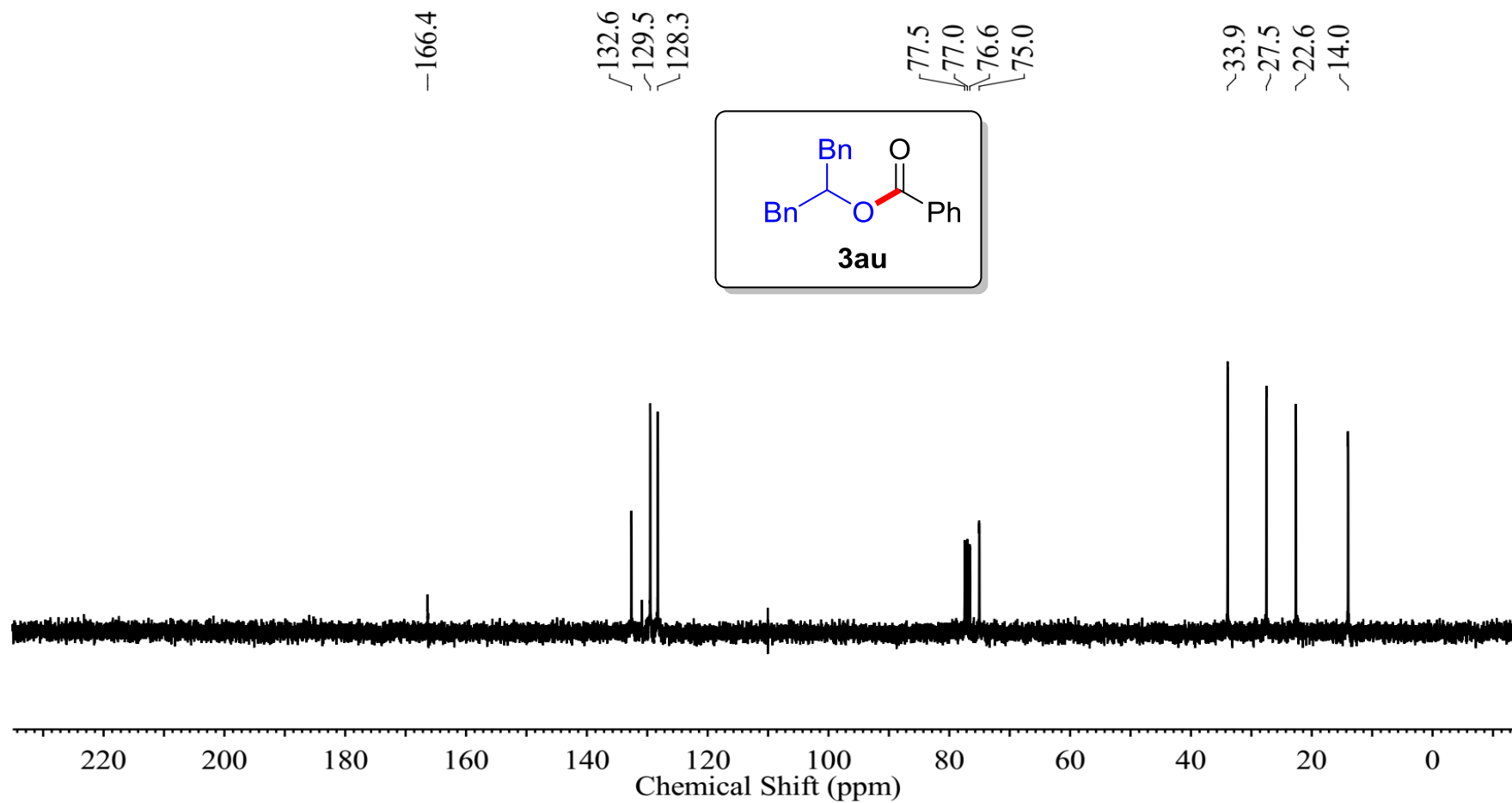
ZGY-X180705-6



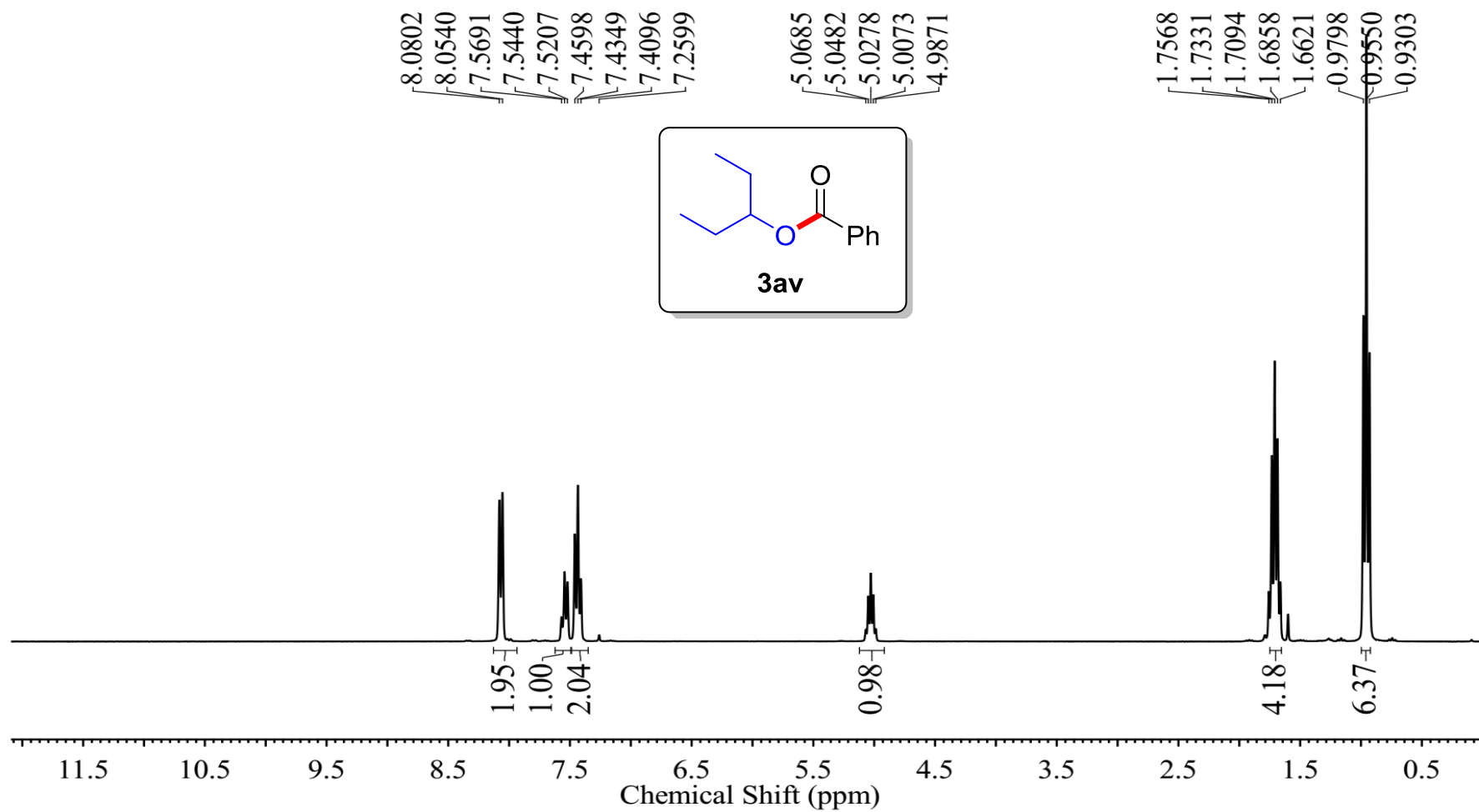
ZGY-X180630-4



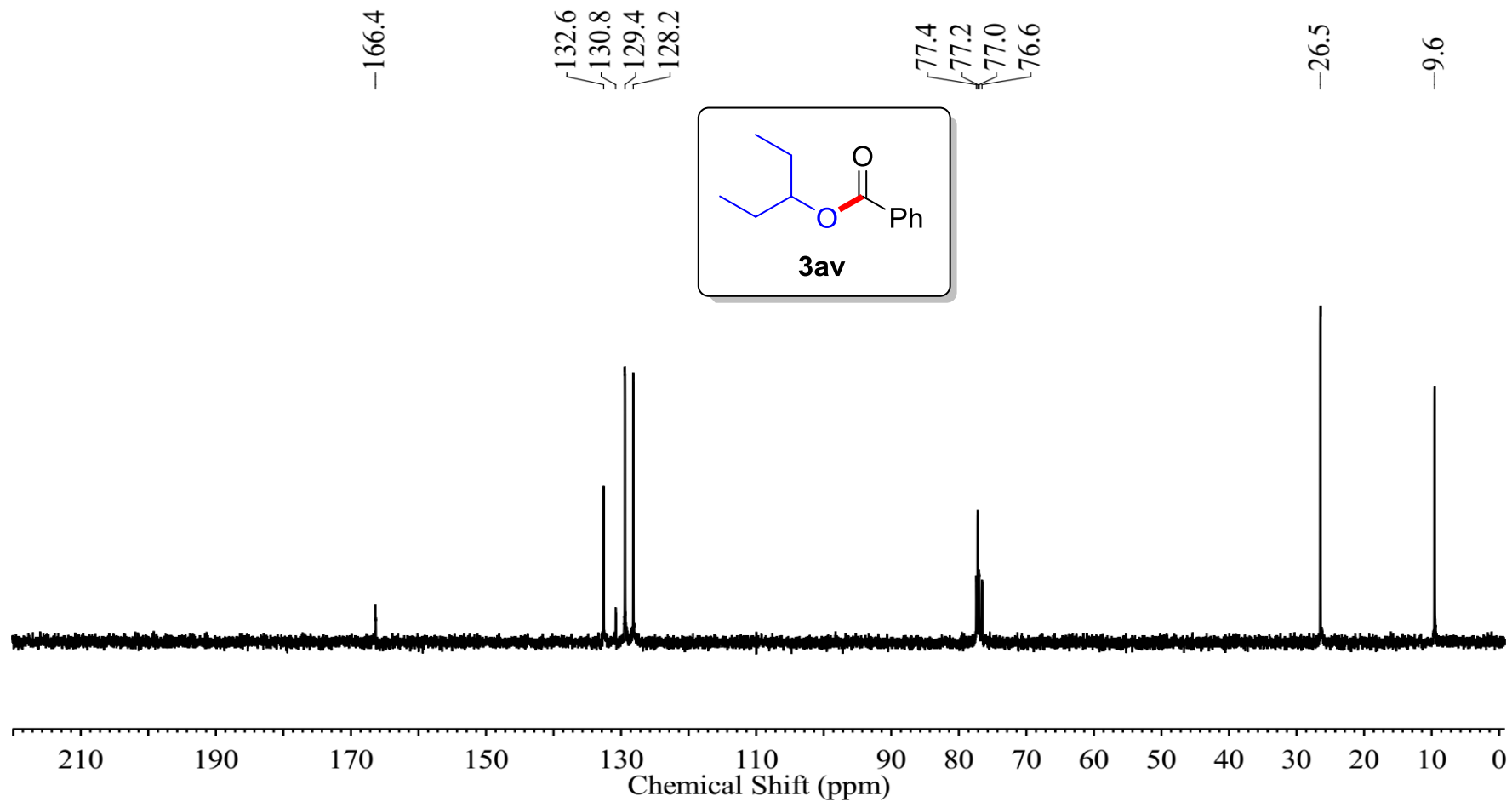
ZGY-X180630-4



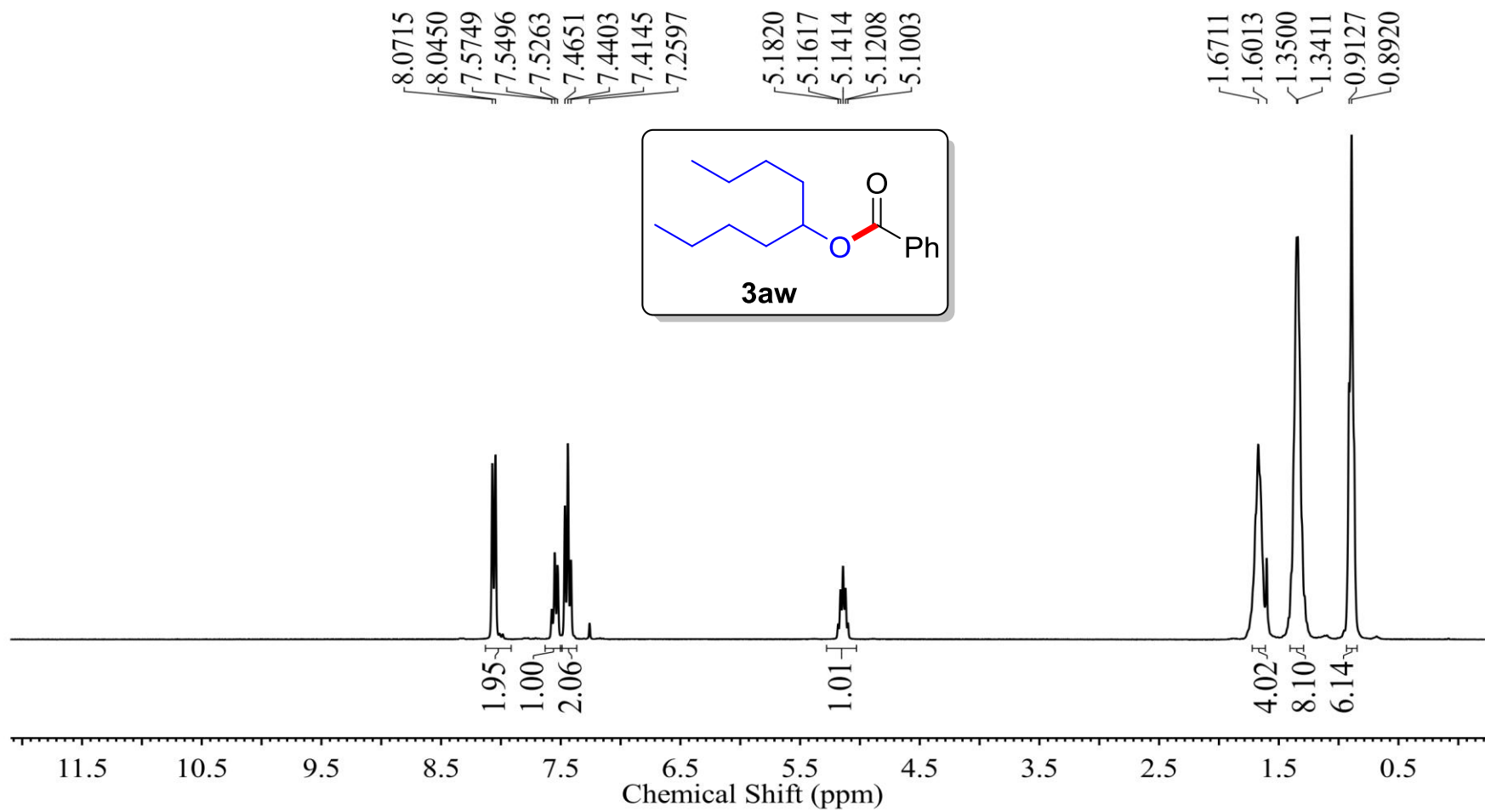
ZGY-X180630-2



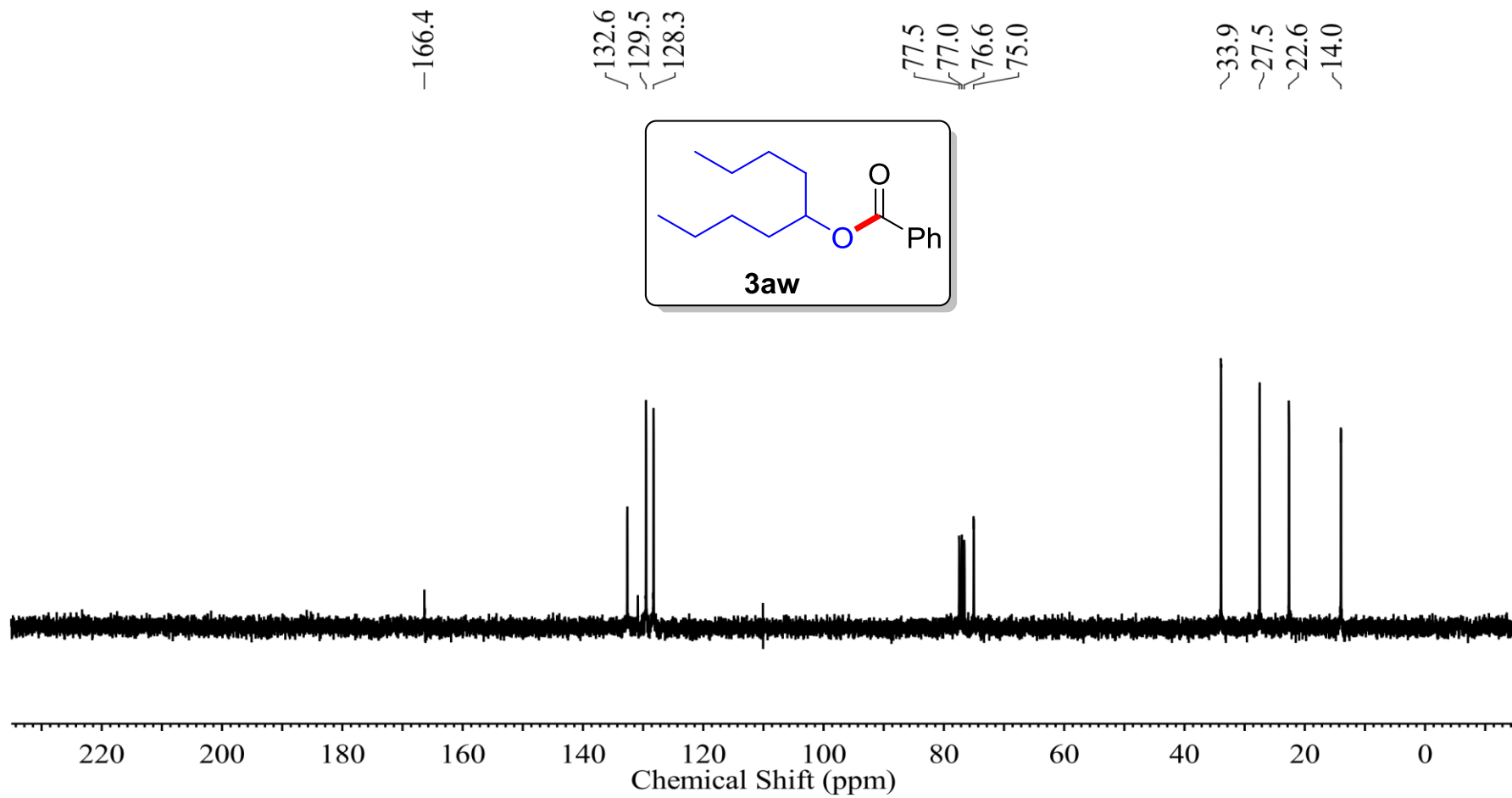
ZGY-X180630-2



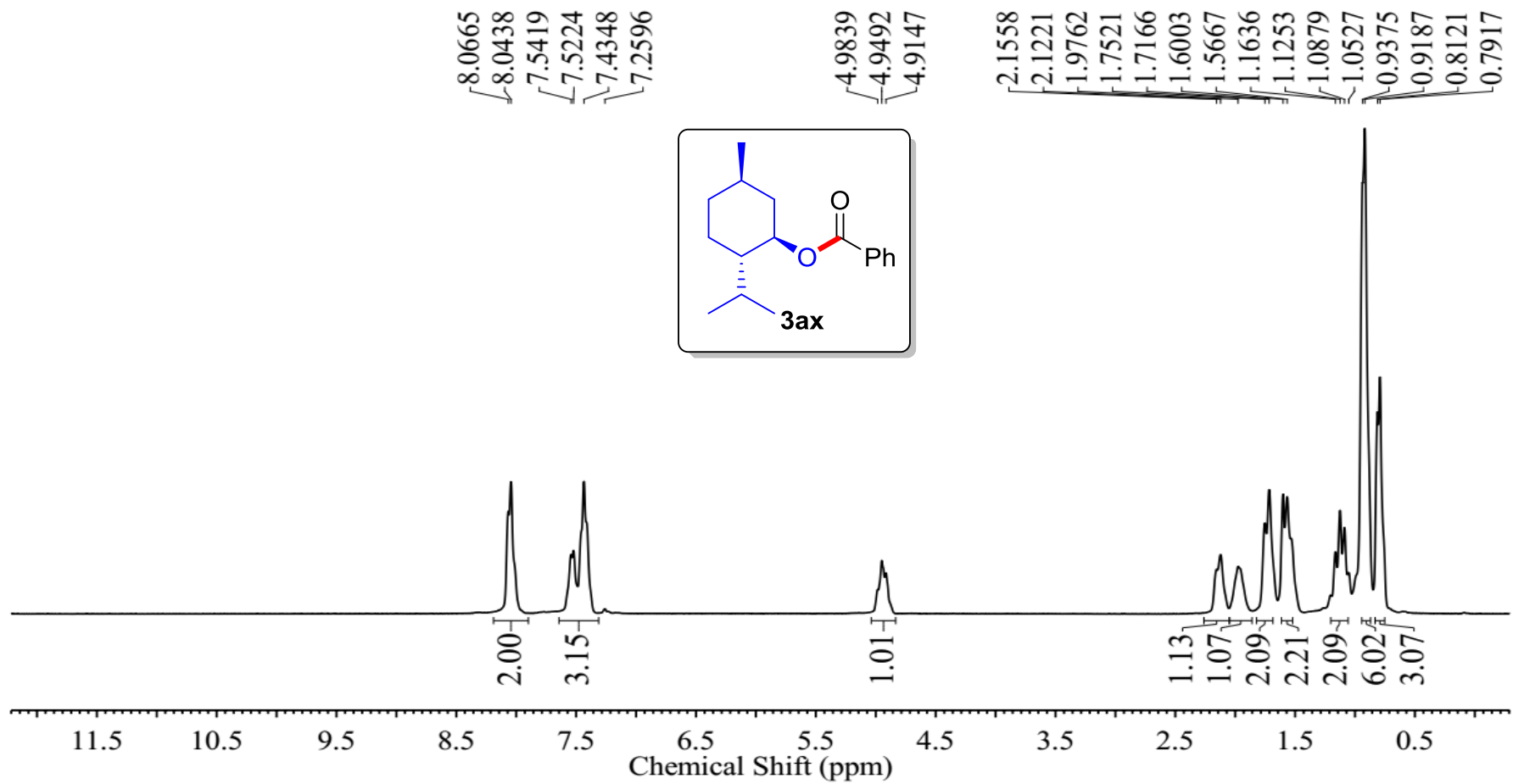
ZGY-X180630-4



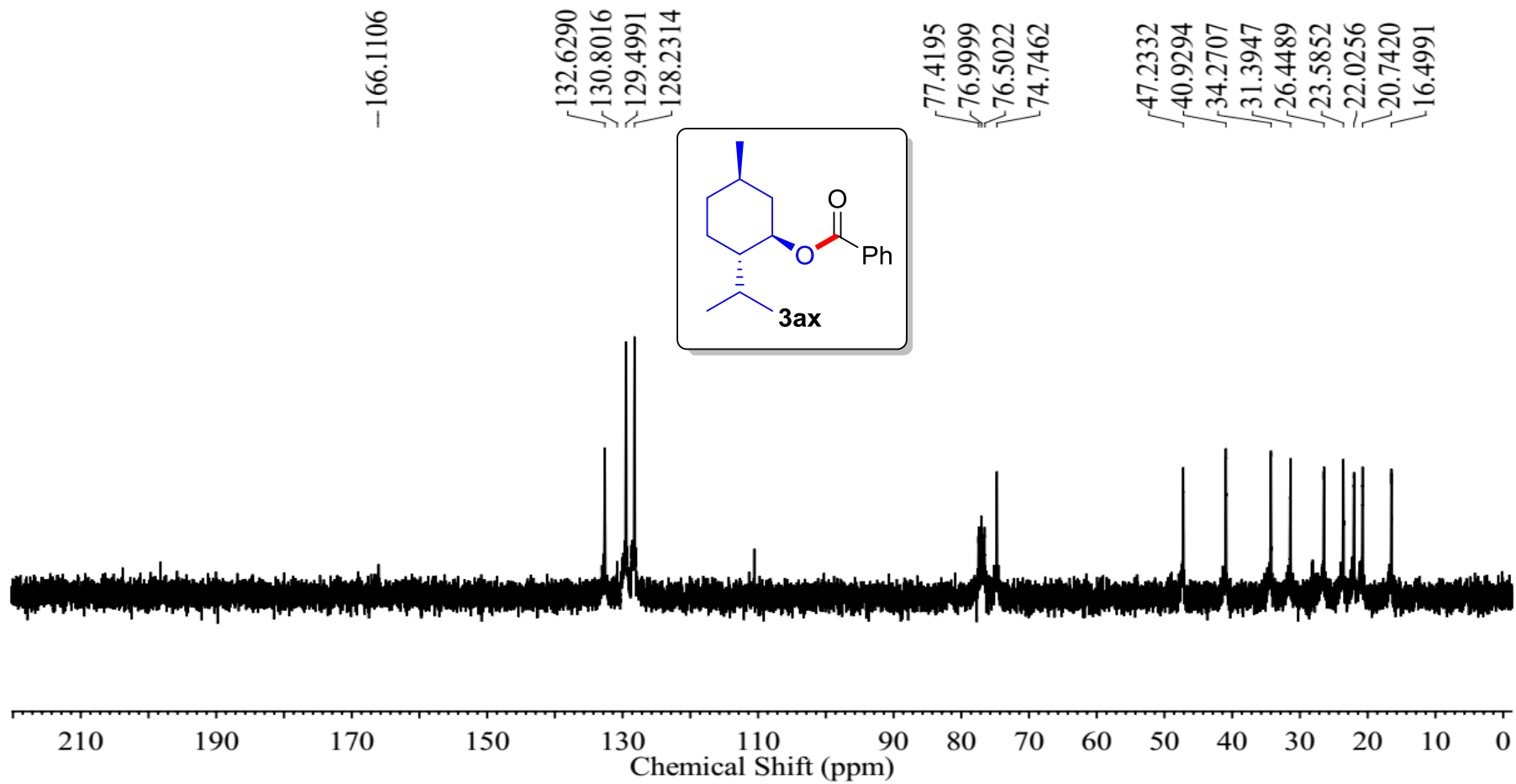
ZGY-X180630-4



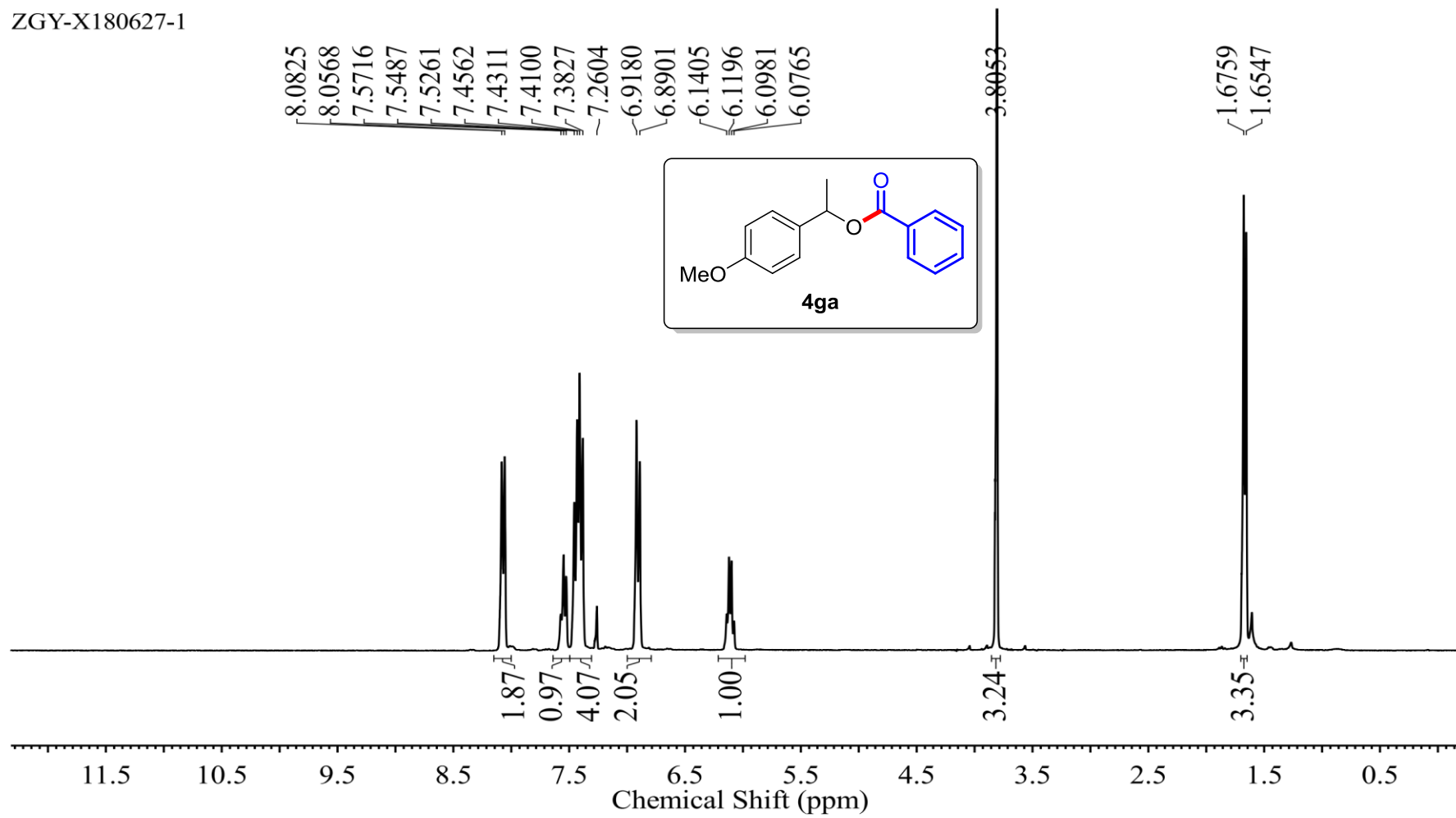
ZGY-X180630-1



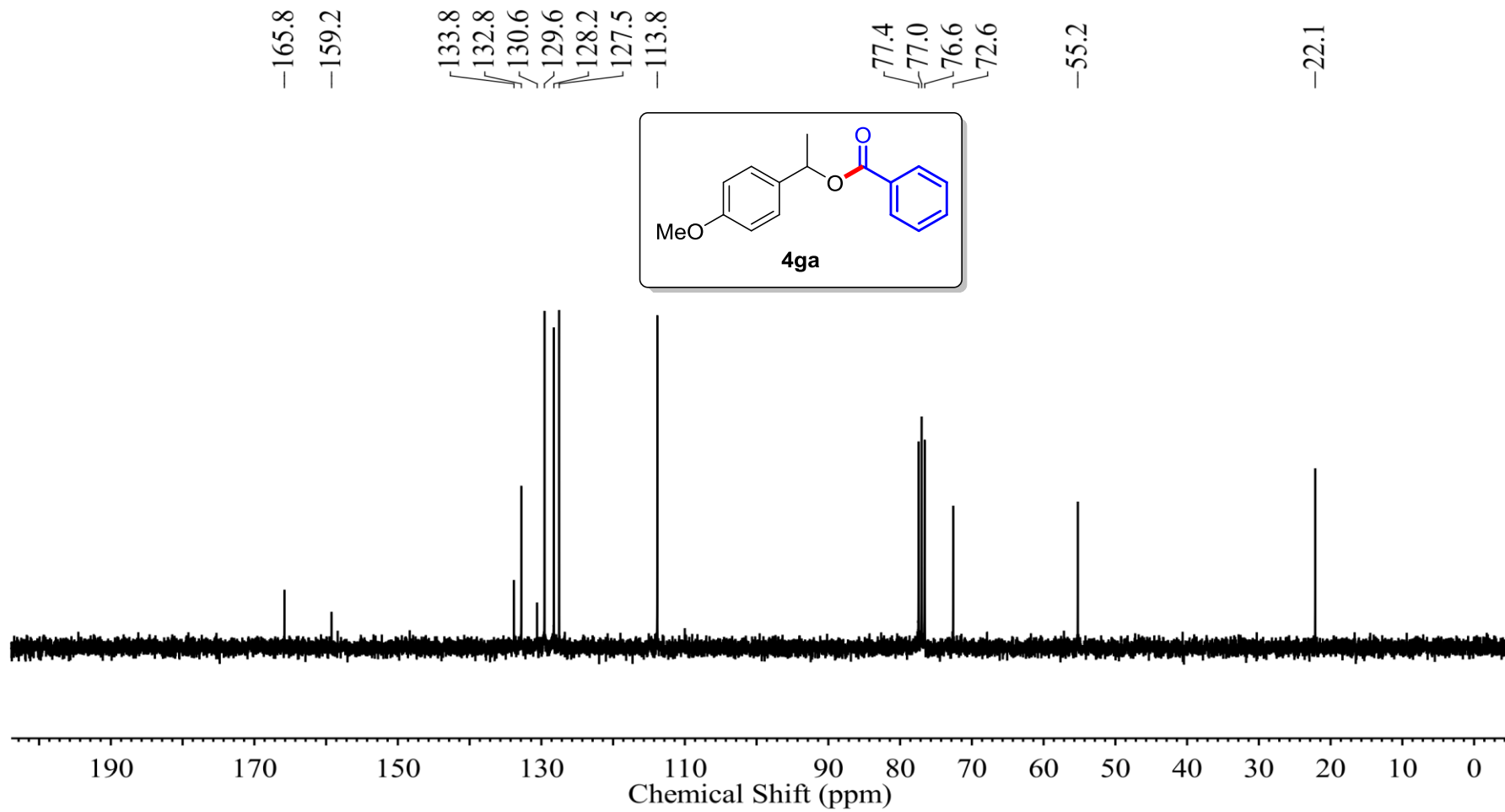
ZGY-X180630-1



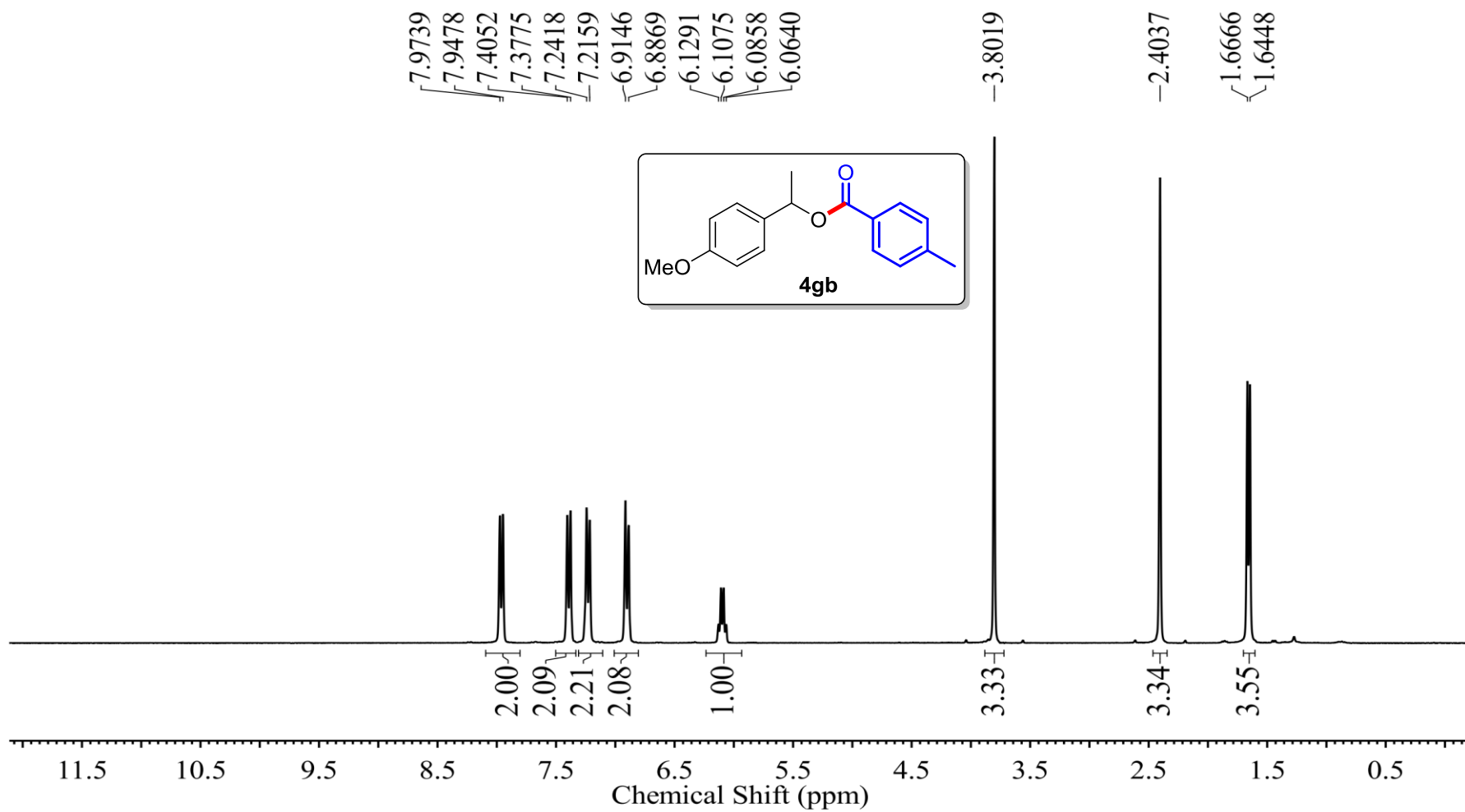
ZGY-X180627-1



ZGY-X180627-1

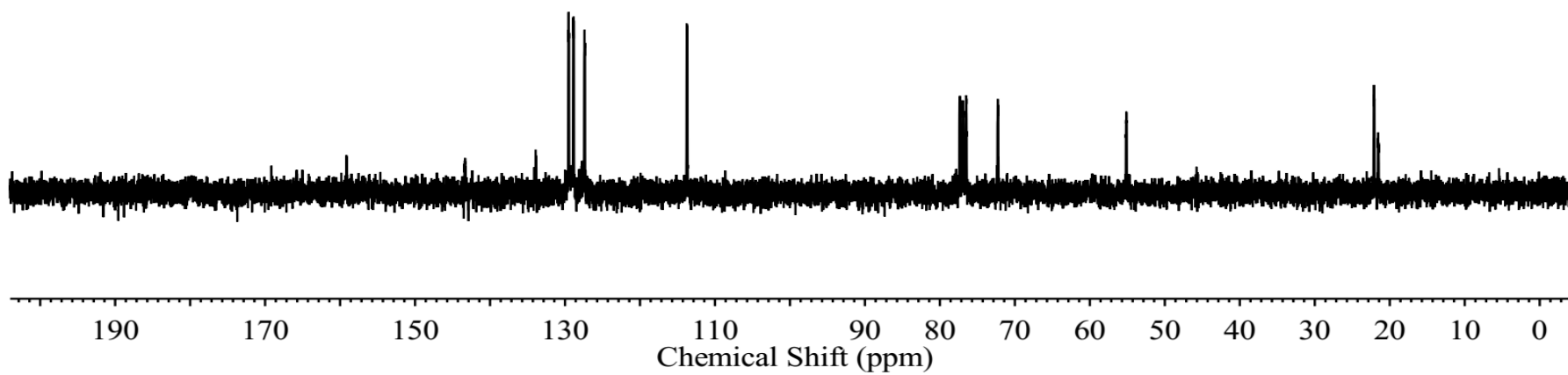
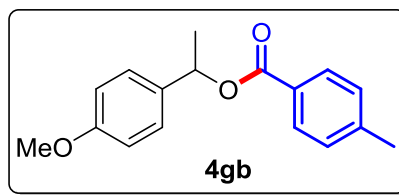


ZGY-X180627-3

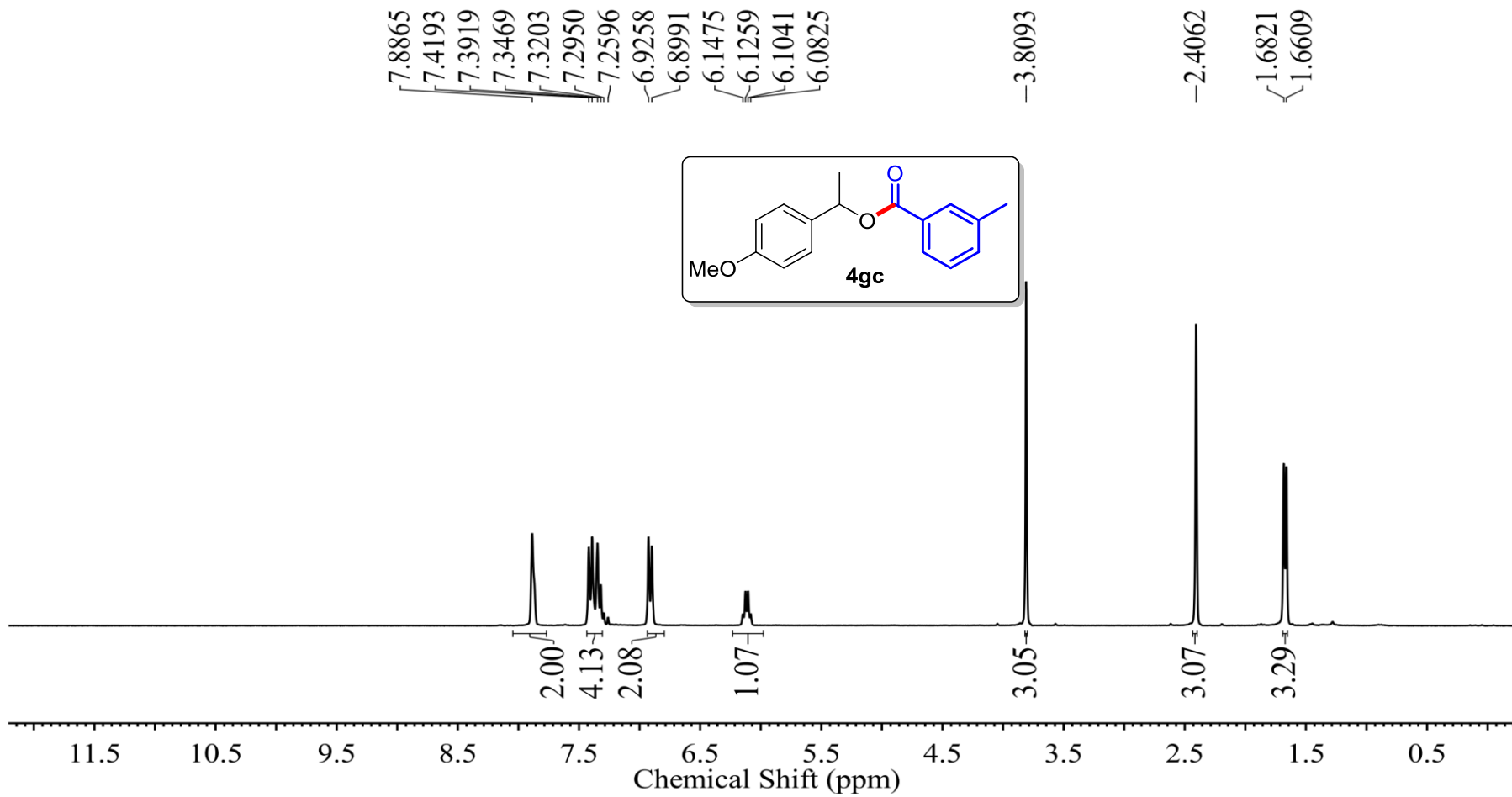


ZGY-X180627-3

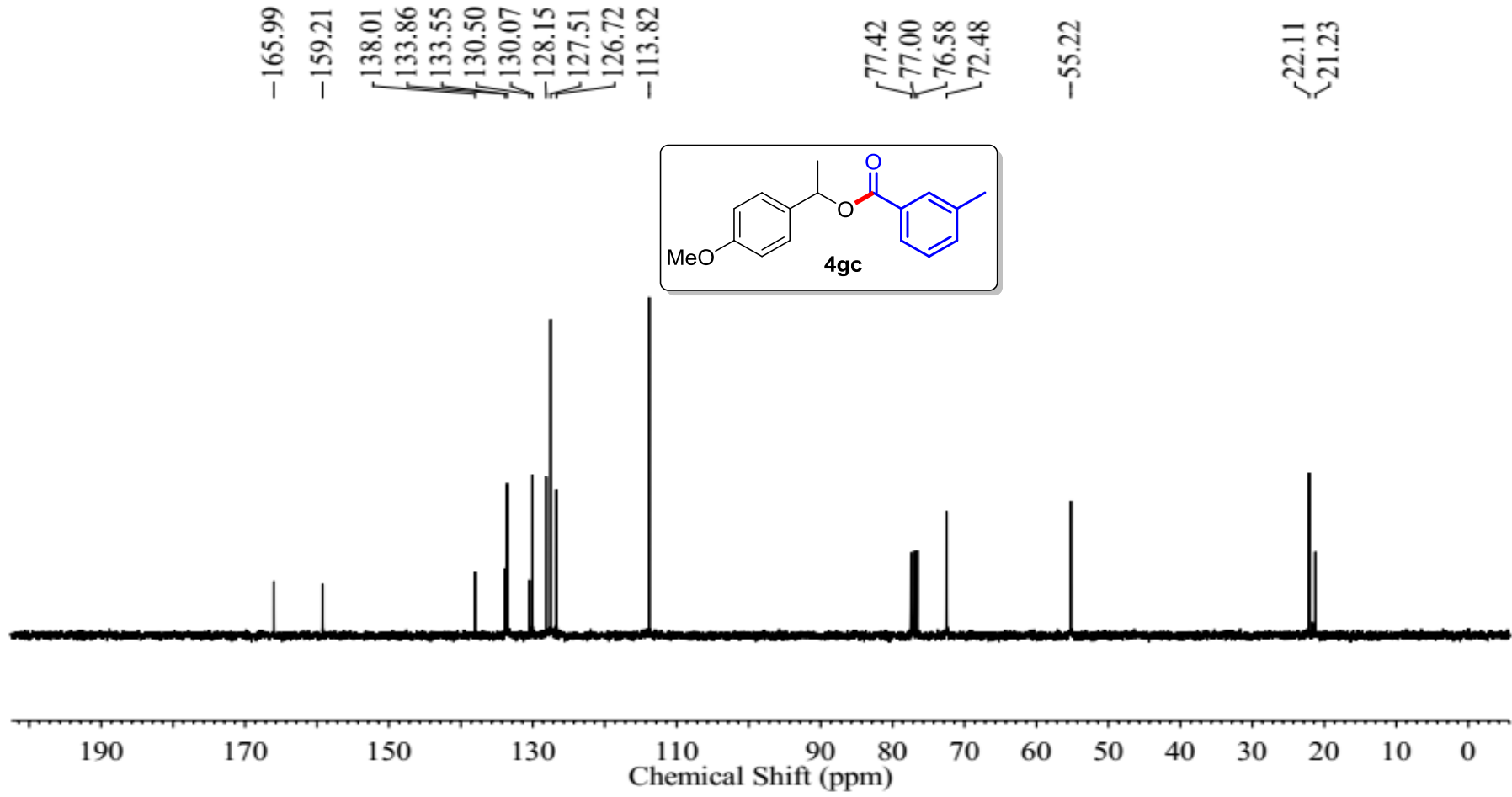
-169.0
-159.0
143.2
133.6
129.5
128.9
127.4
-113.8
77.3
77.0
76.5
72.3
-55.1
22.1
21.5



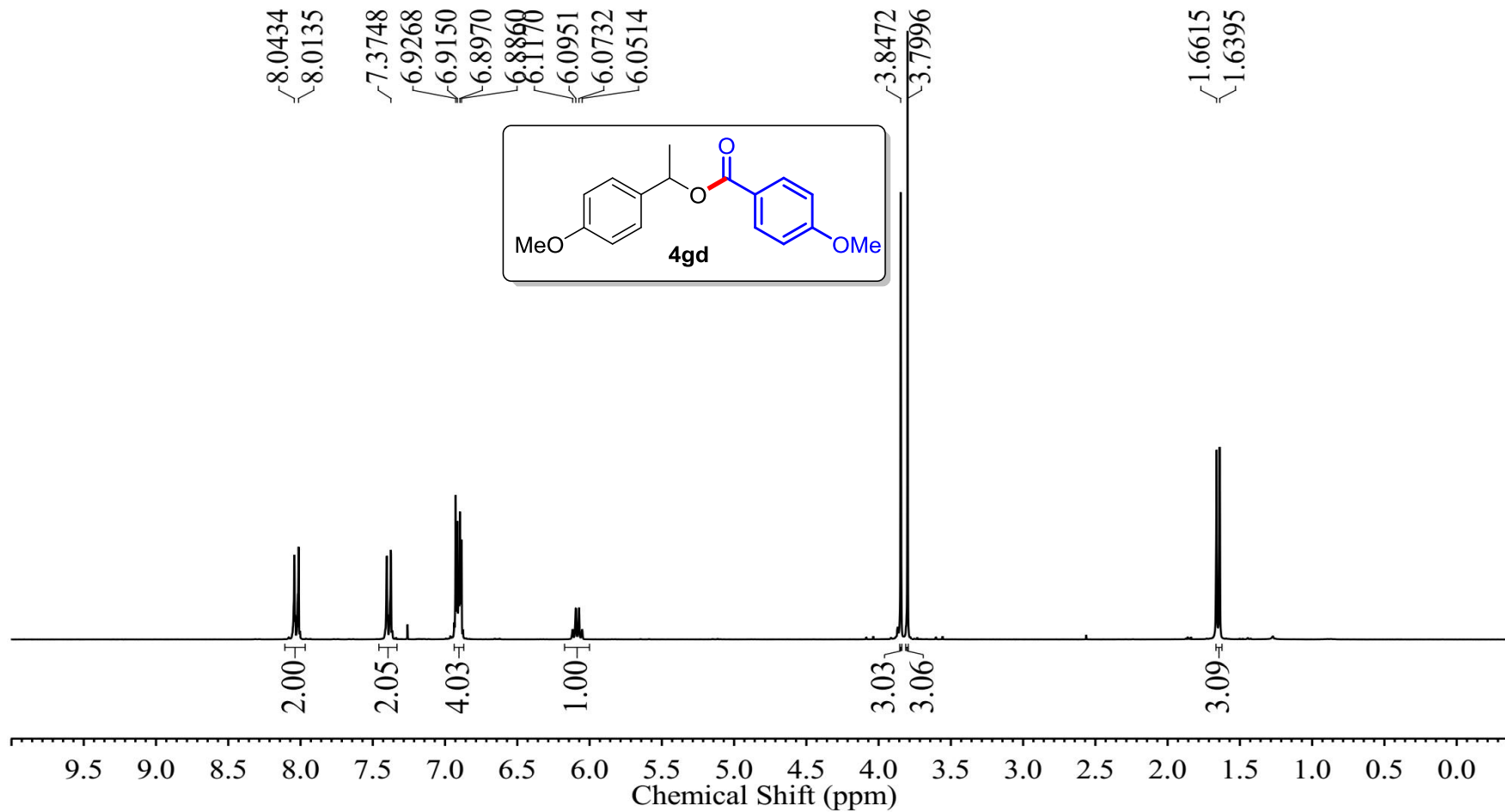
ZGY-X180715-3



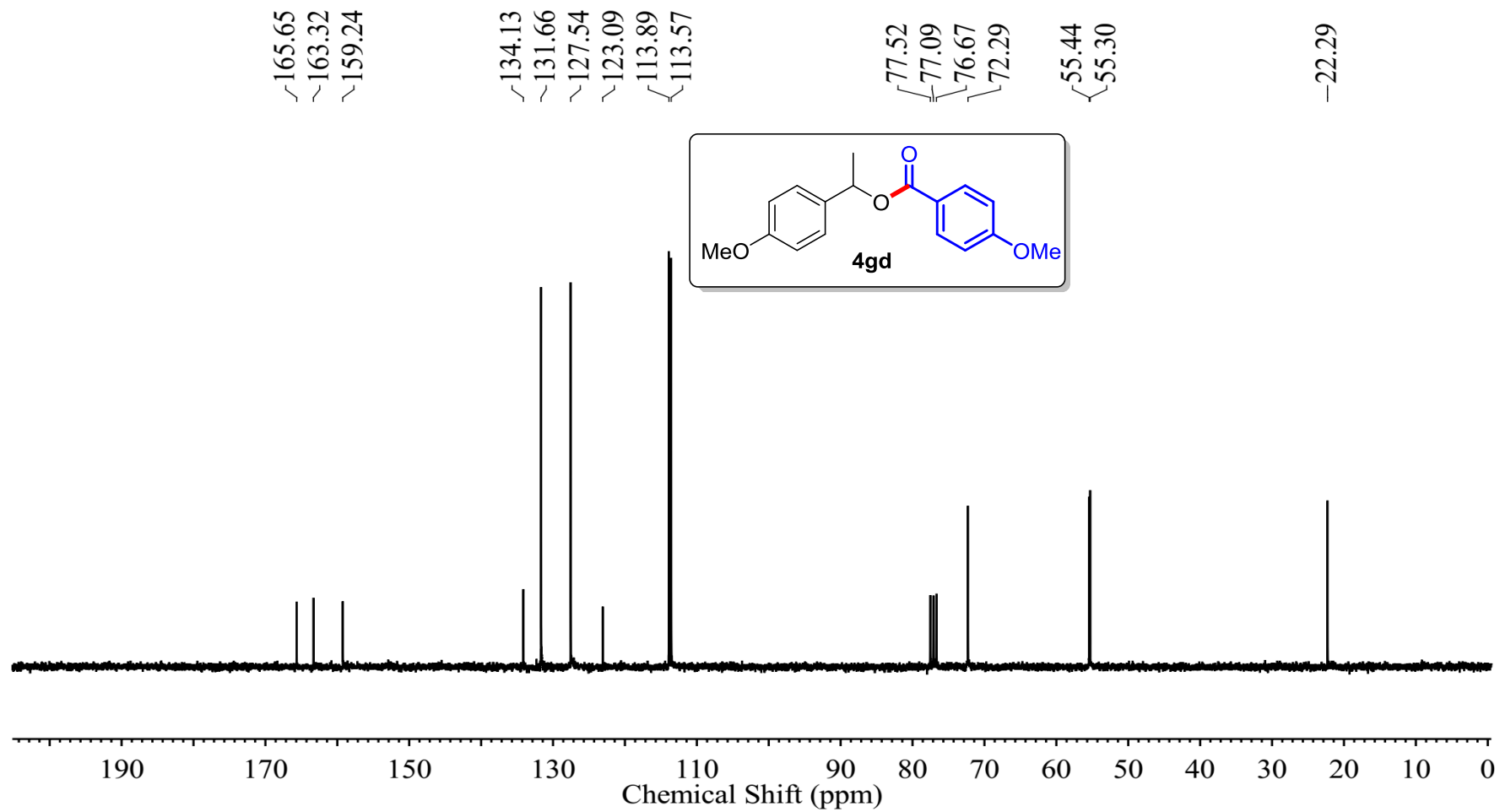
ZGY-X180715-3



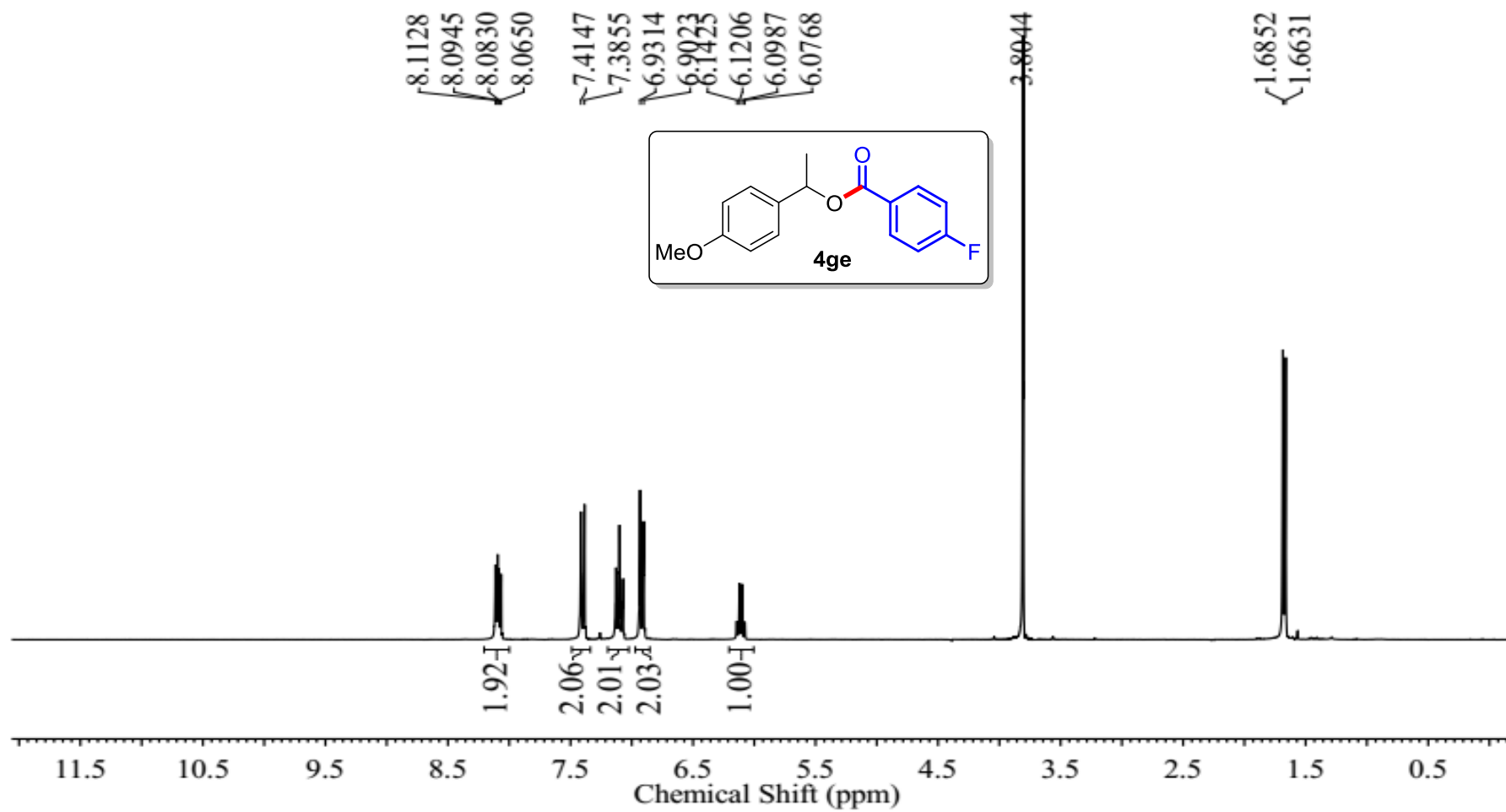
ZGY-X180721-1



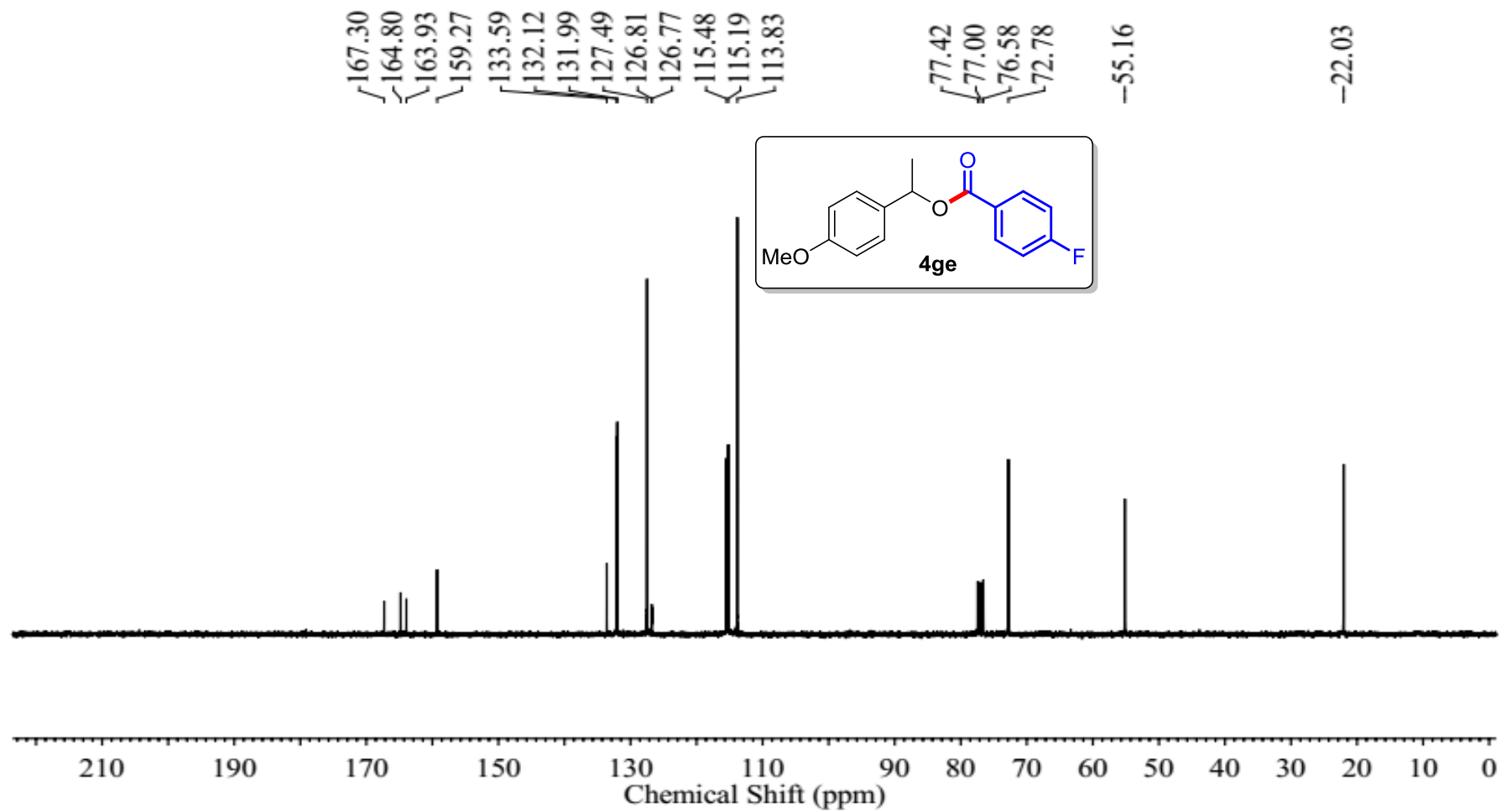
ZGY-X180721-1



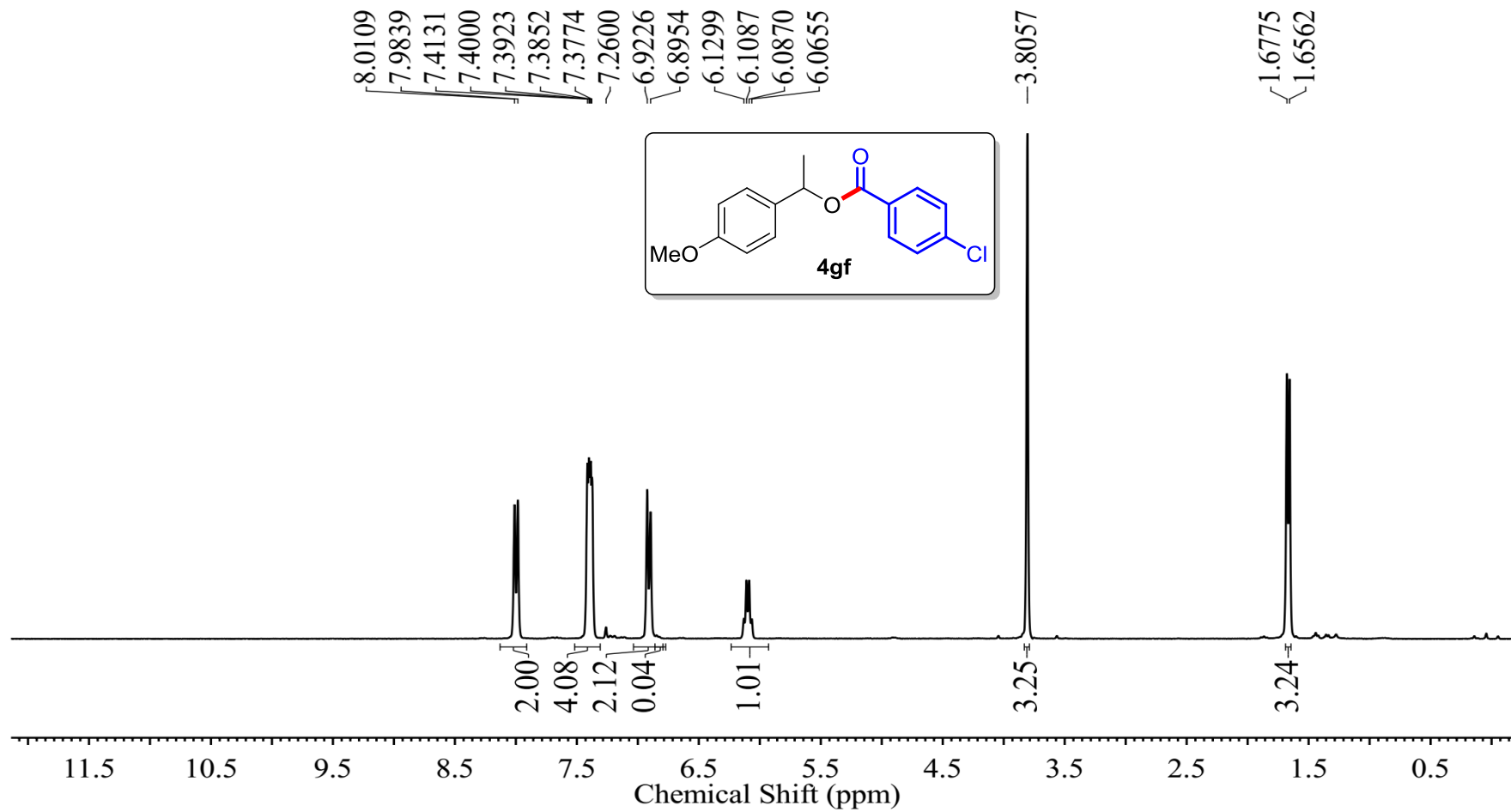
ZGY-X180705-3



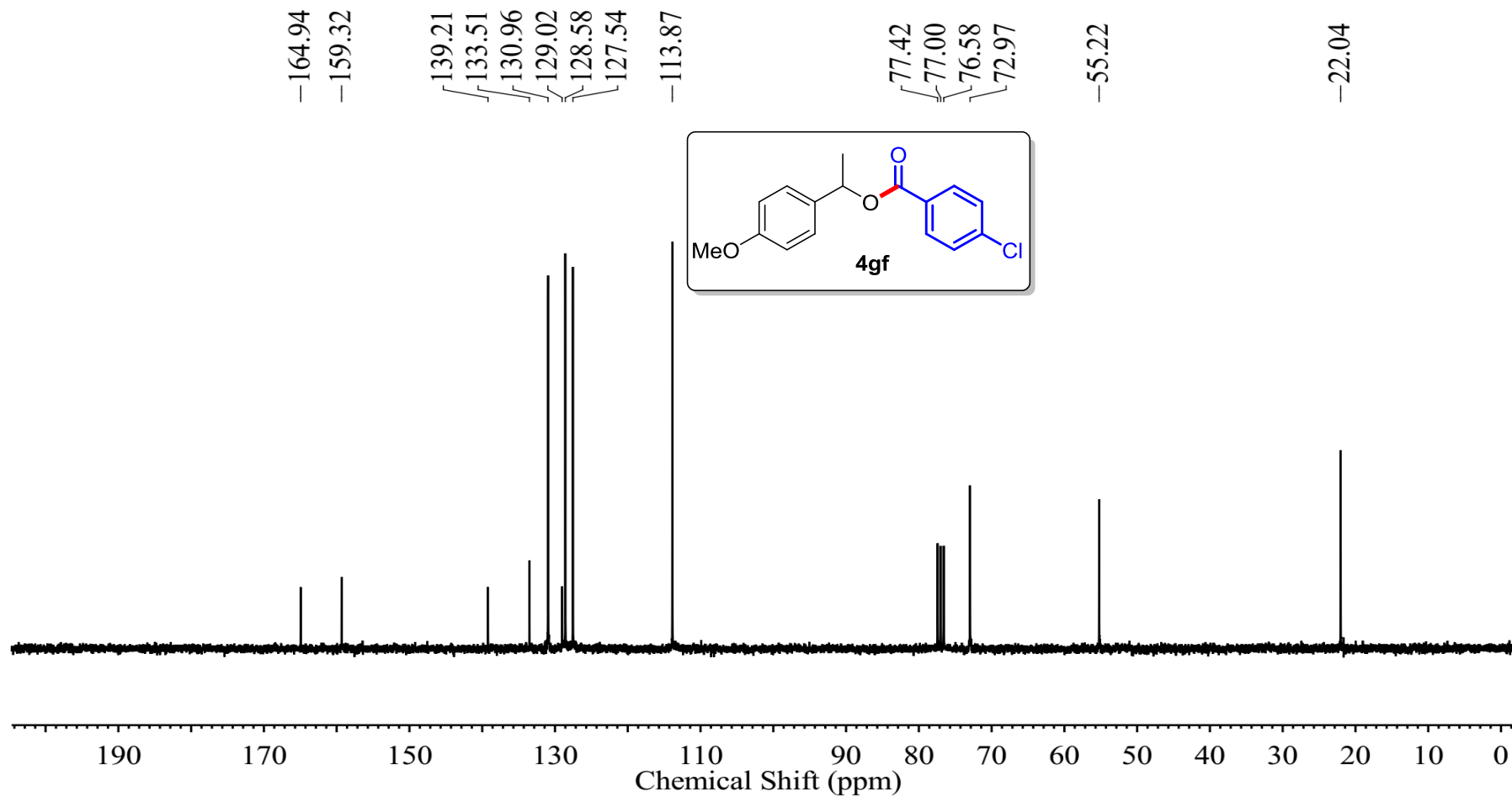
ZGY-X180705-3



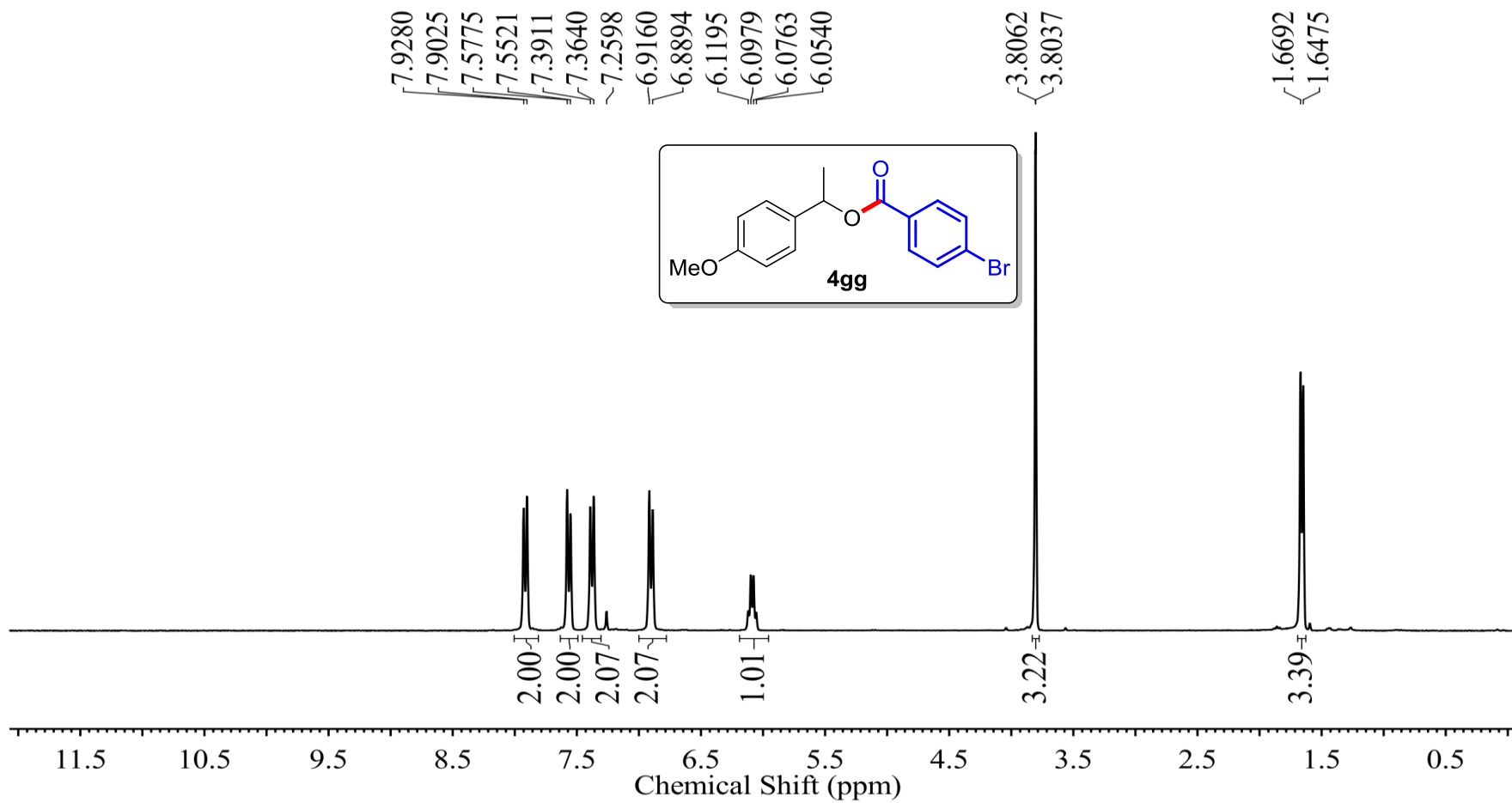
ZGY-X180715-1



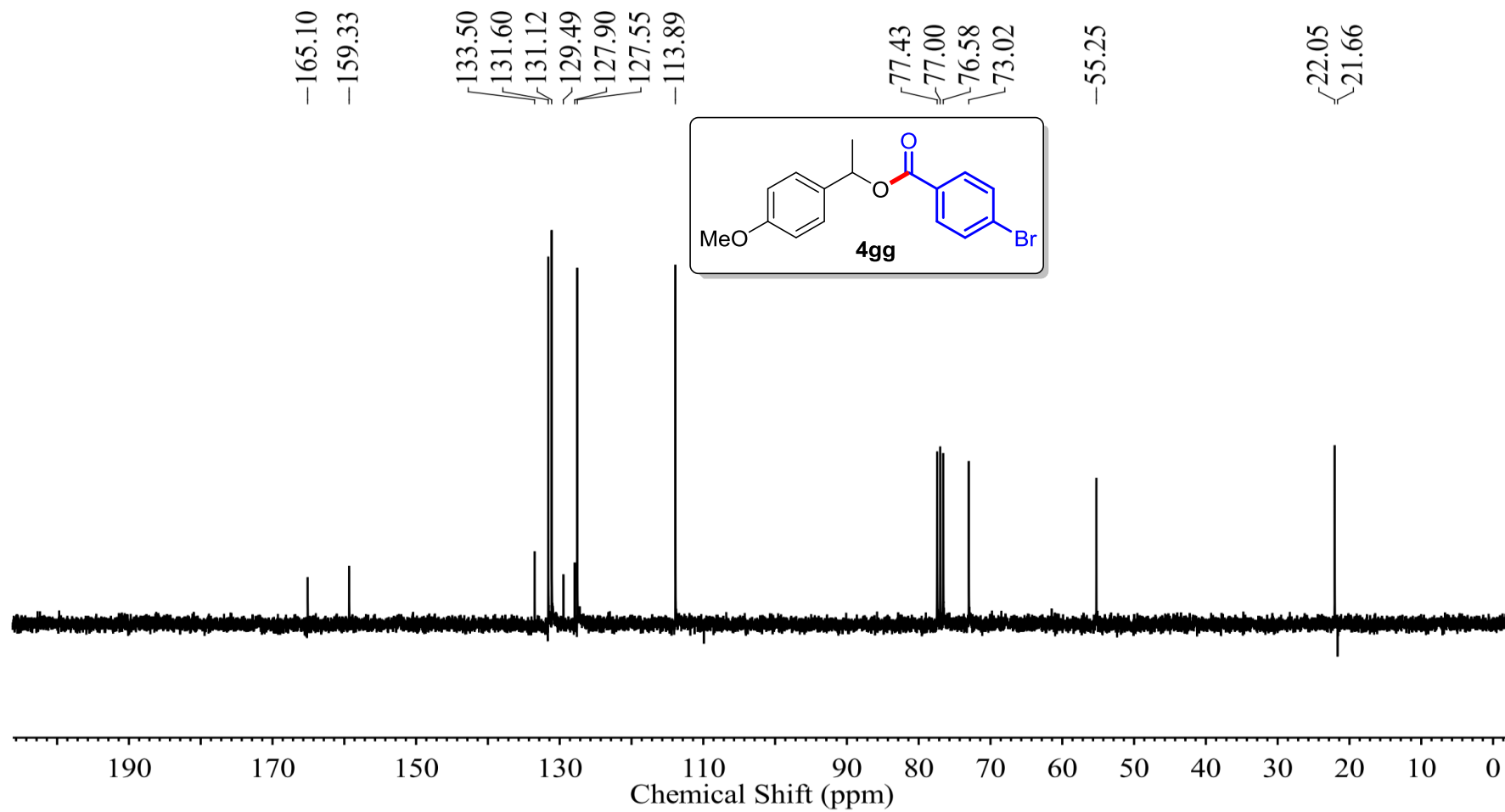
ZGY-X180715-1



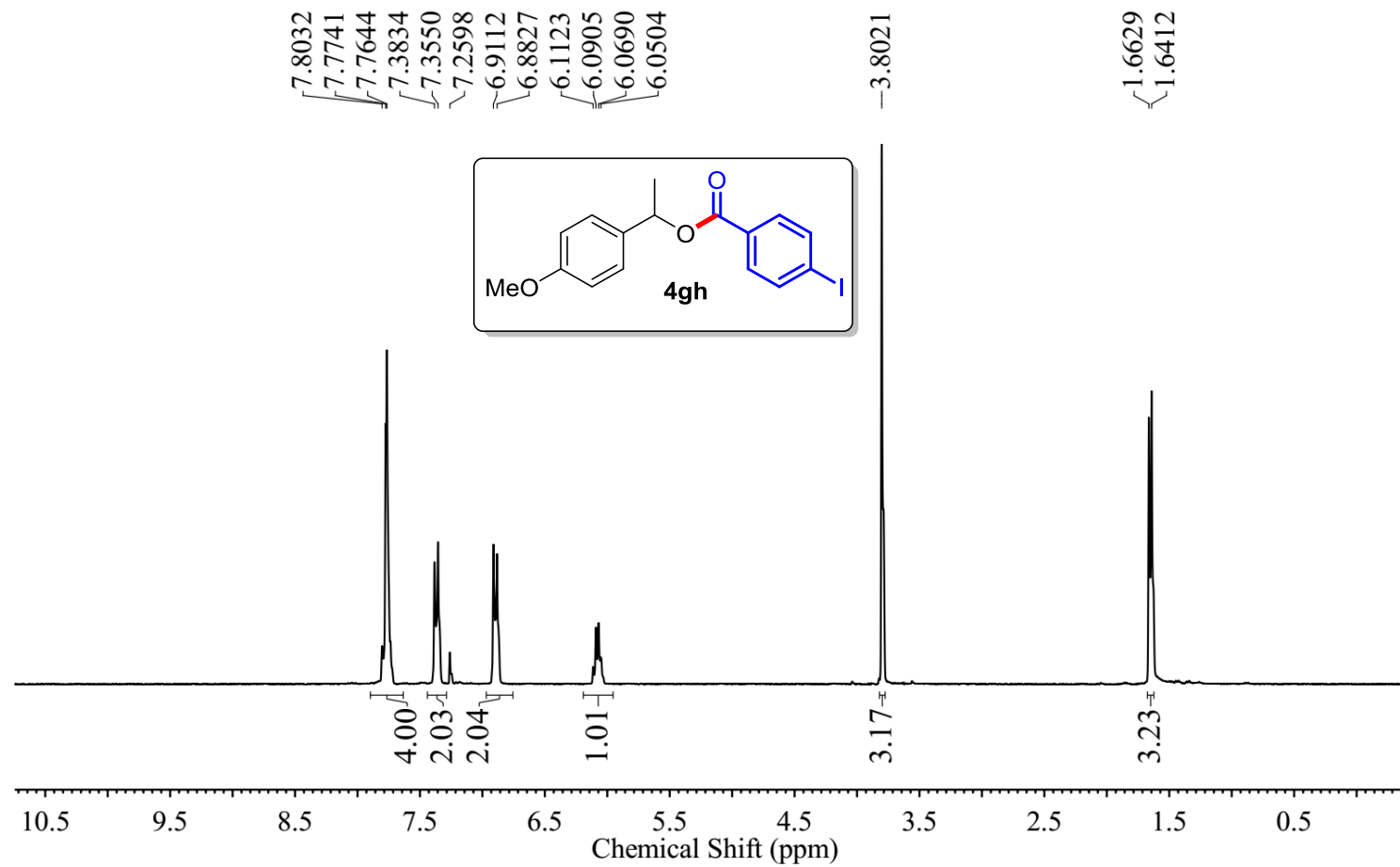
ZGY-X180715-4



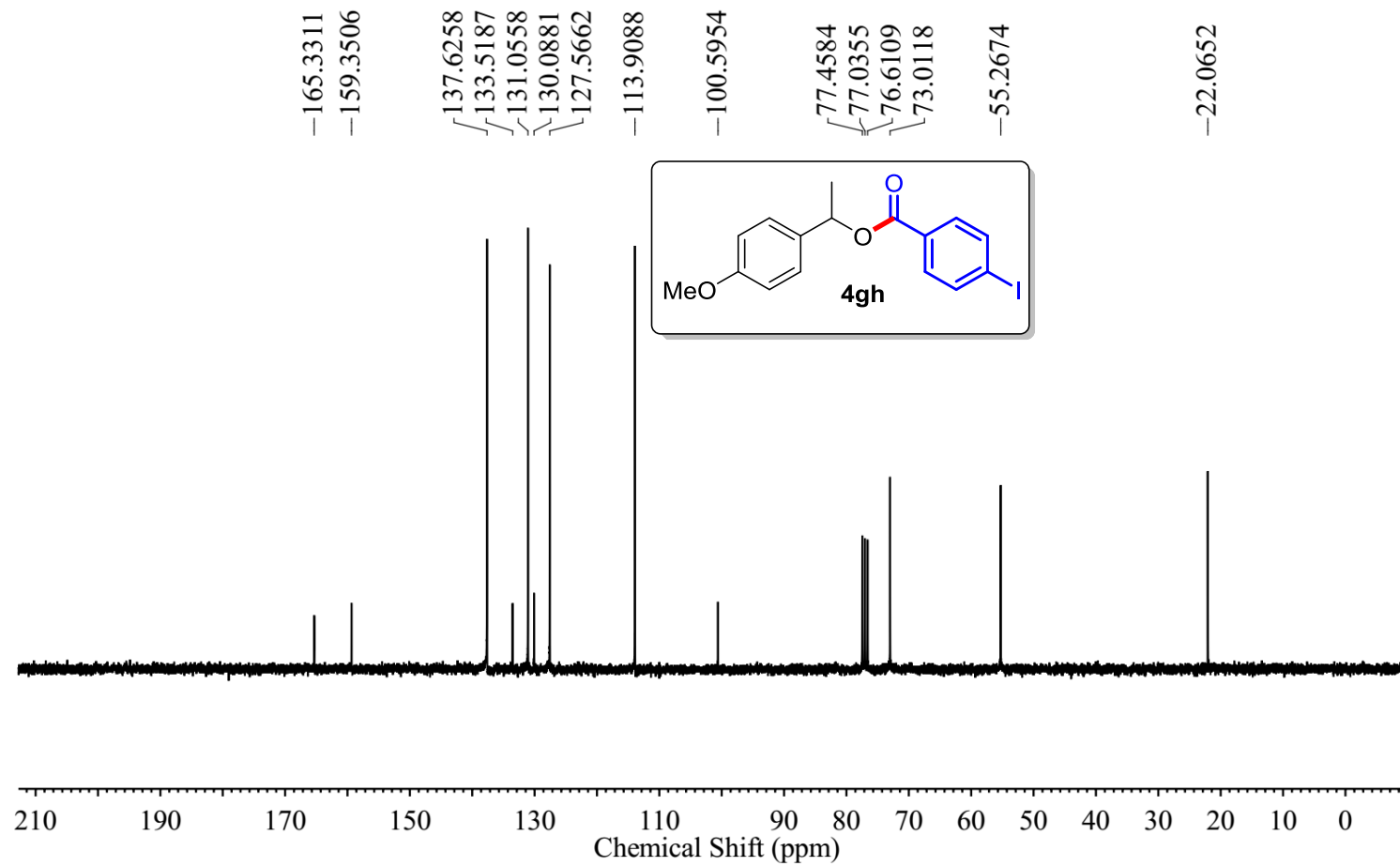
ZGY-X180715-4



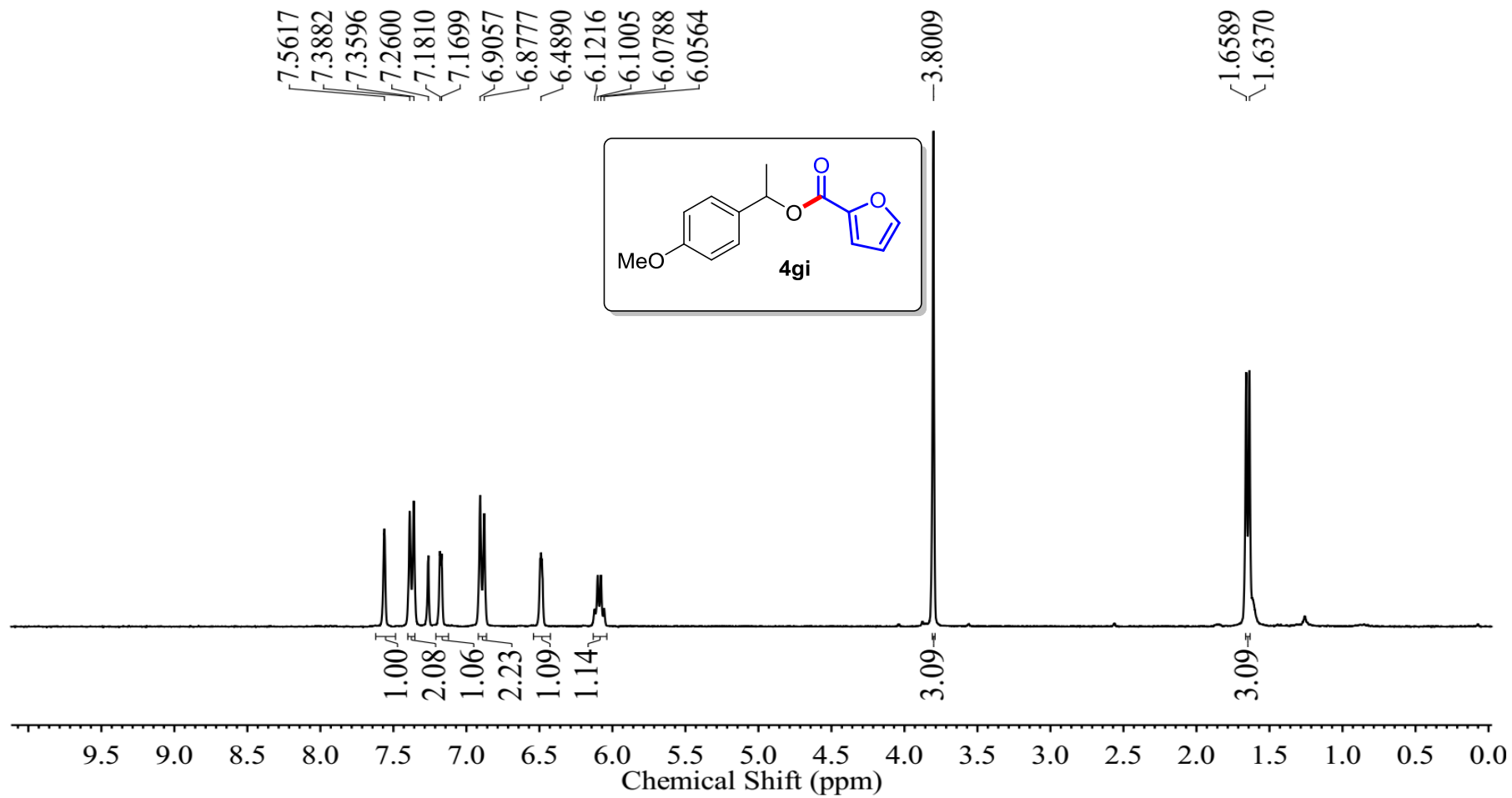
ZGY-X180921



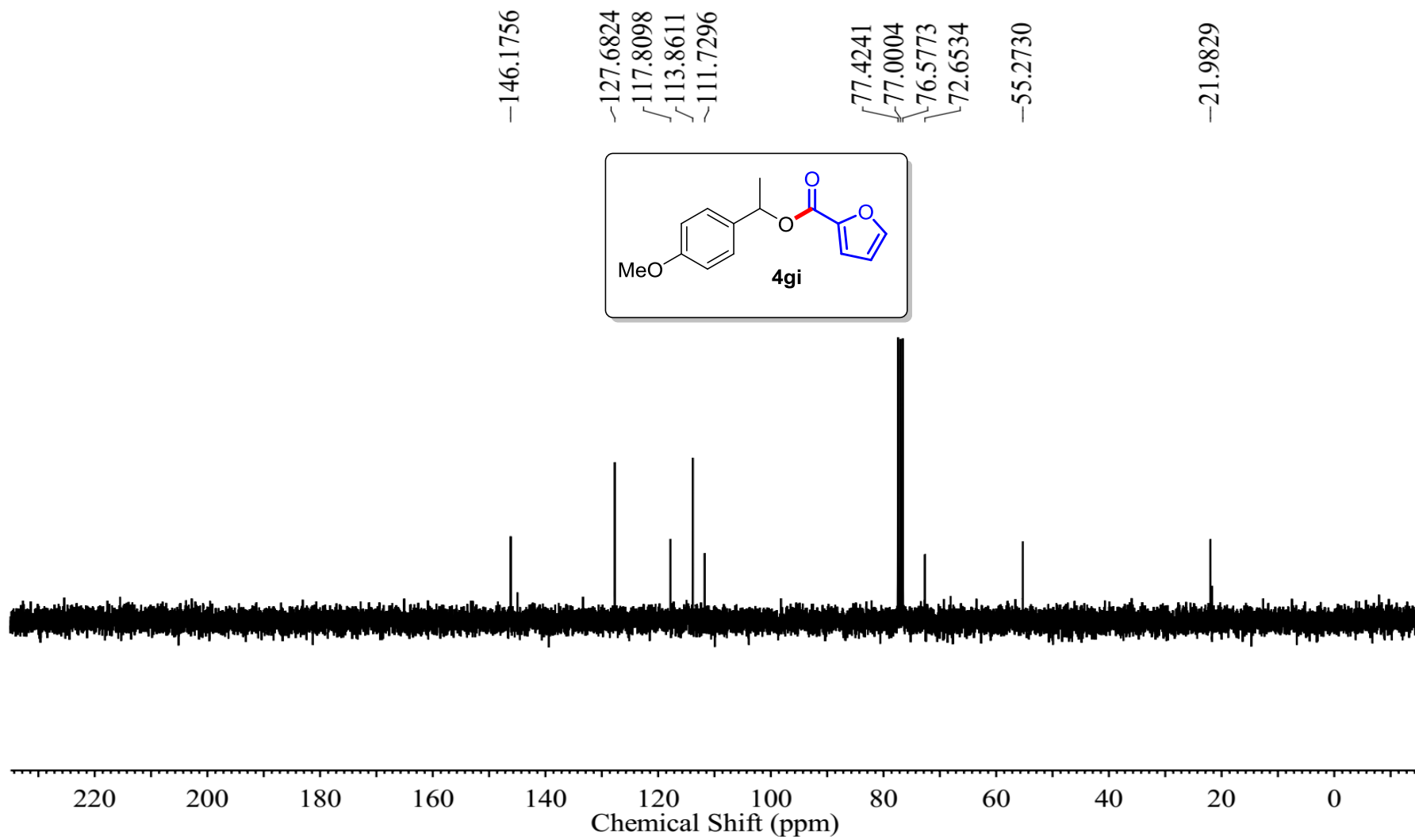
ZGY-X180921



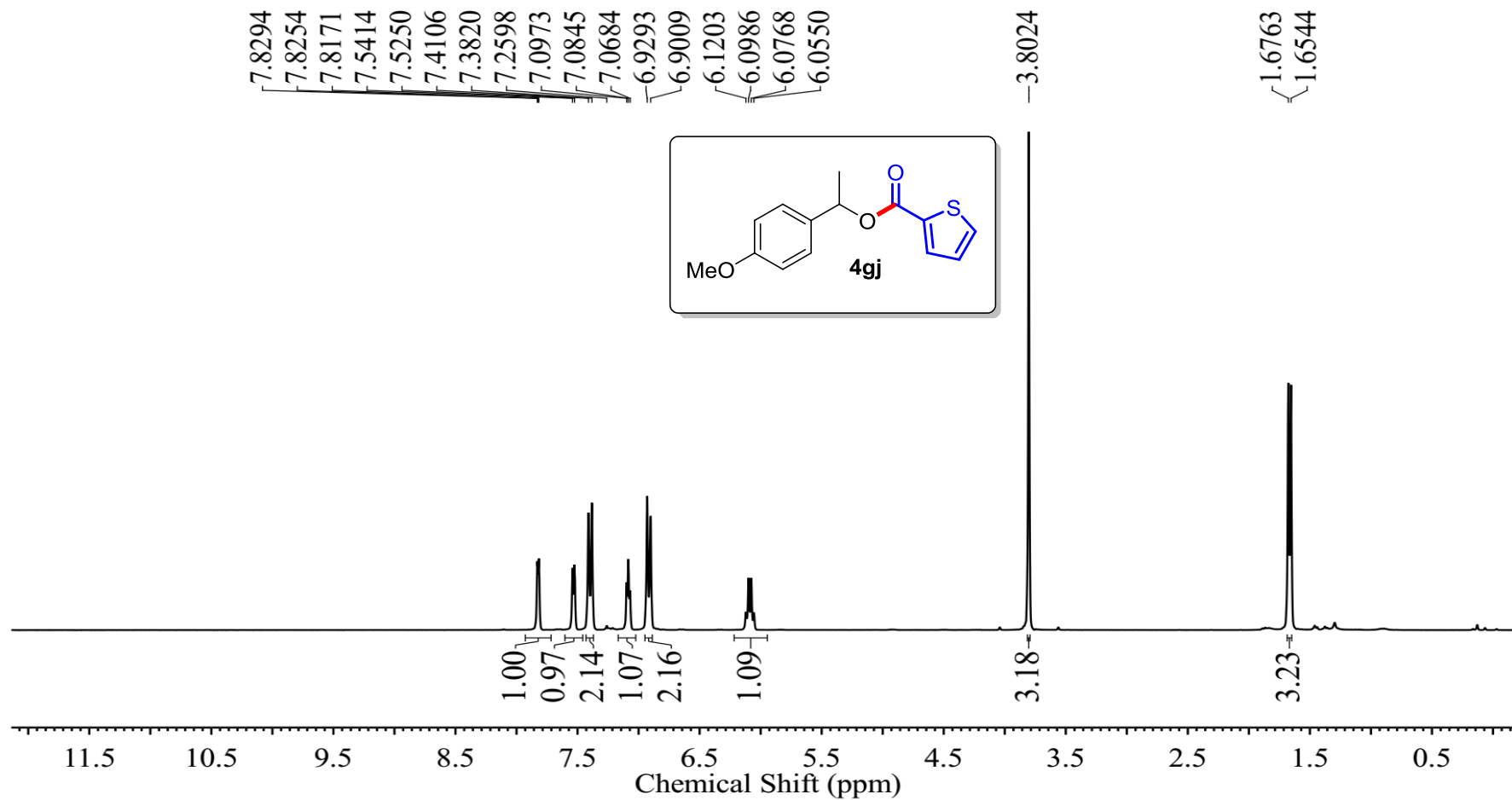
ZGY-X180715-5



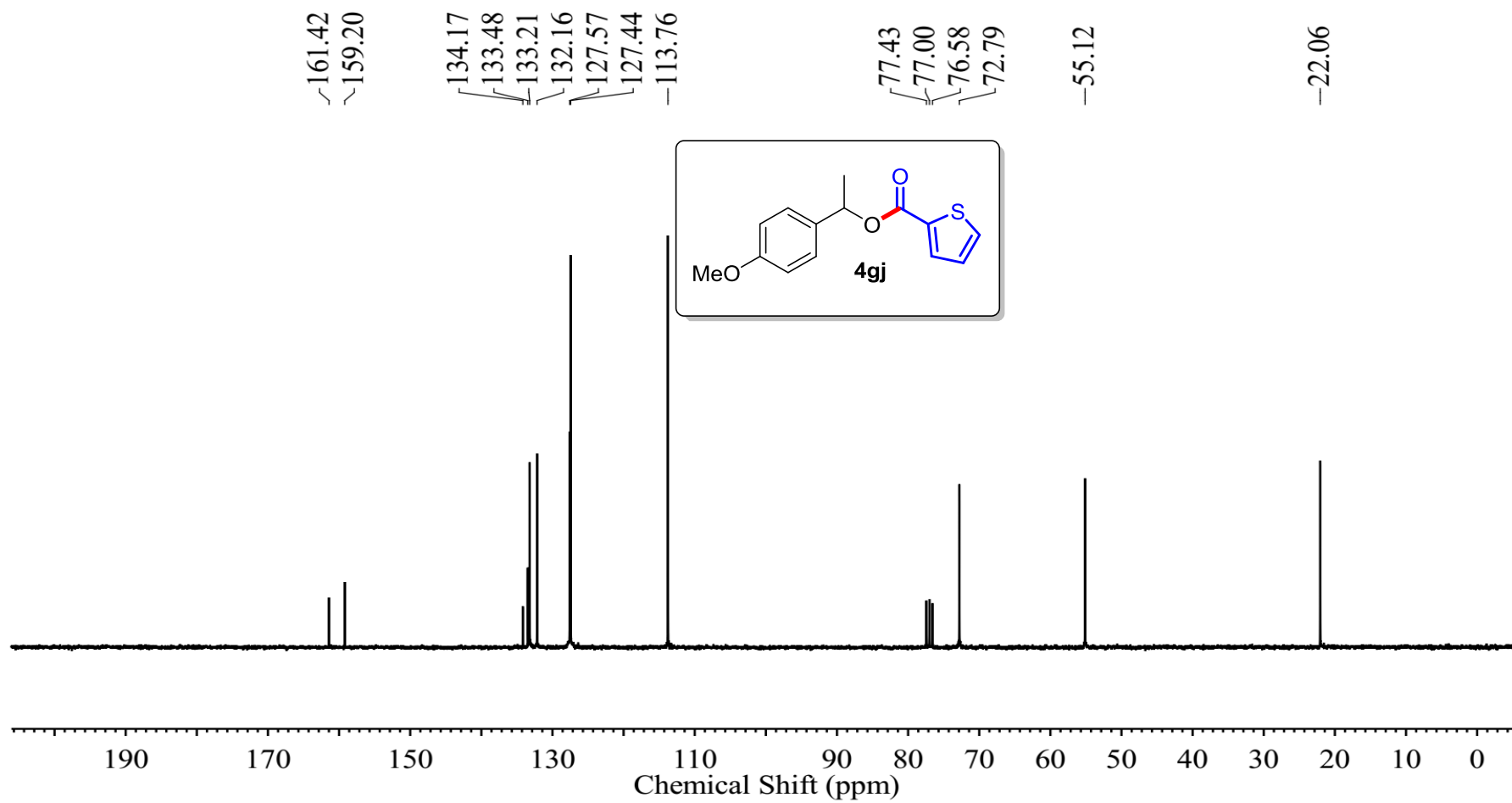
GZ201807151_CARBON_20180715_05



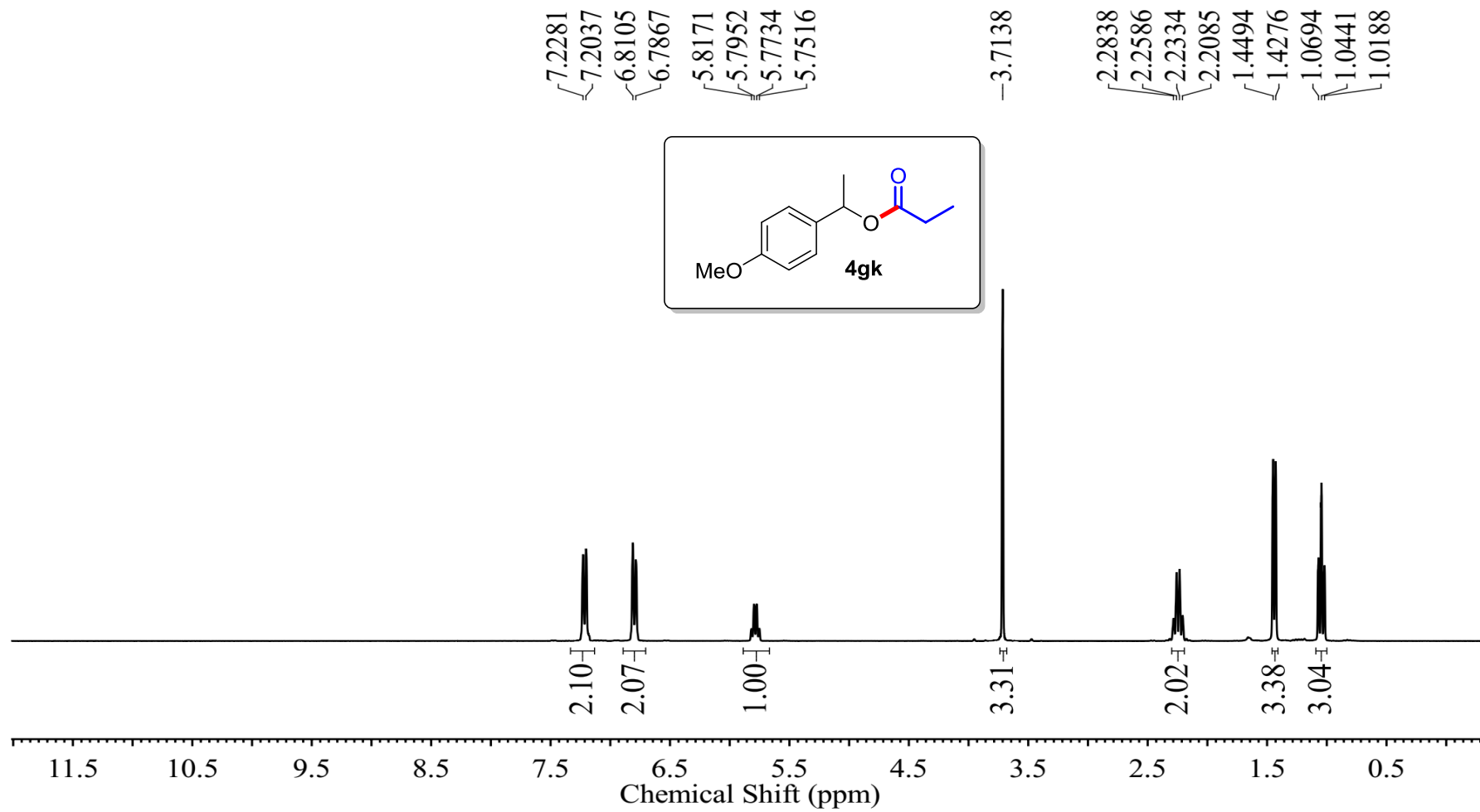
ZGY-X180715-2



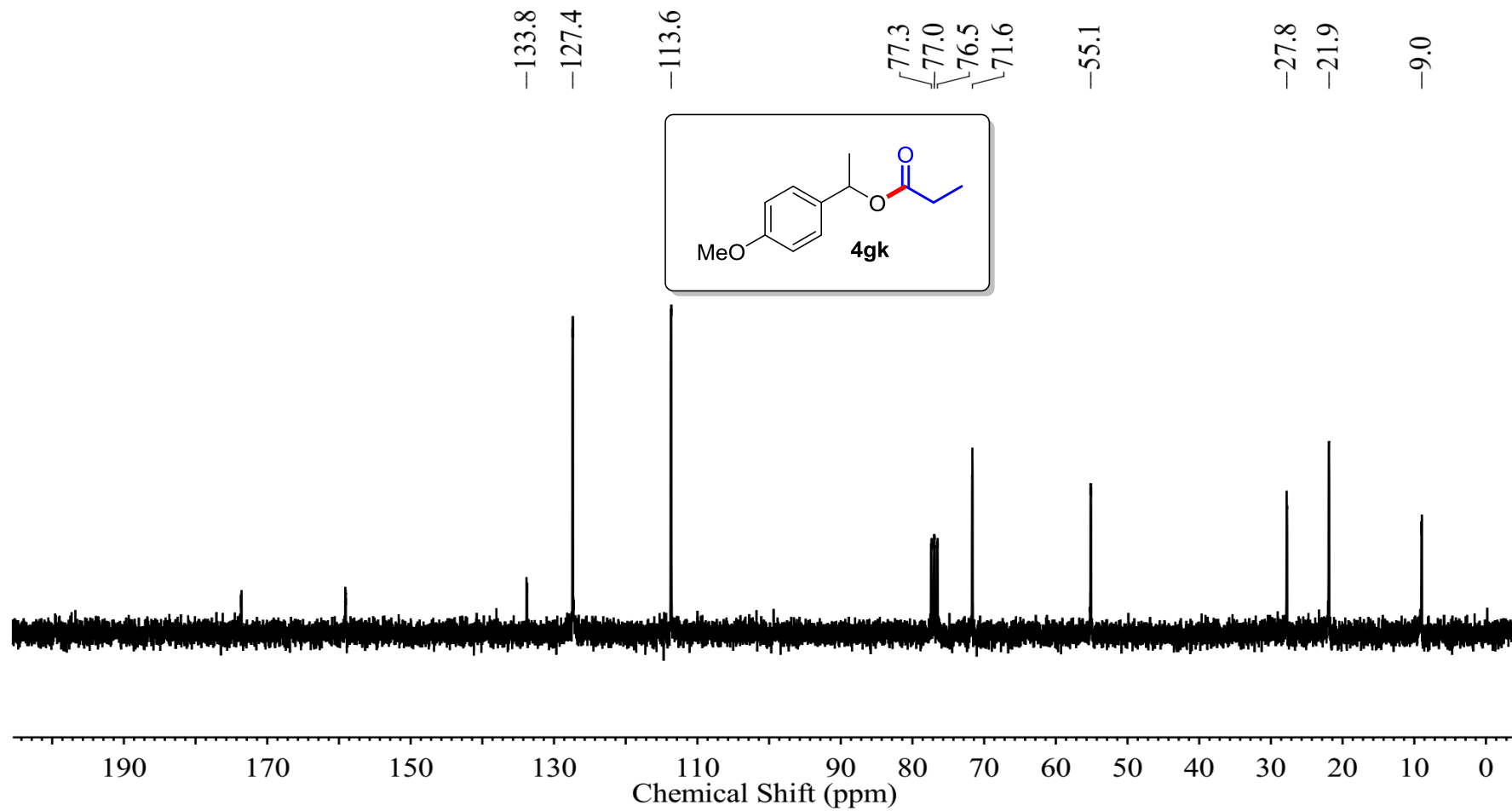
ZGY-X180715-2



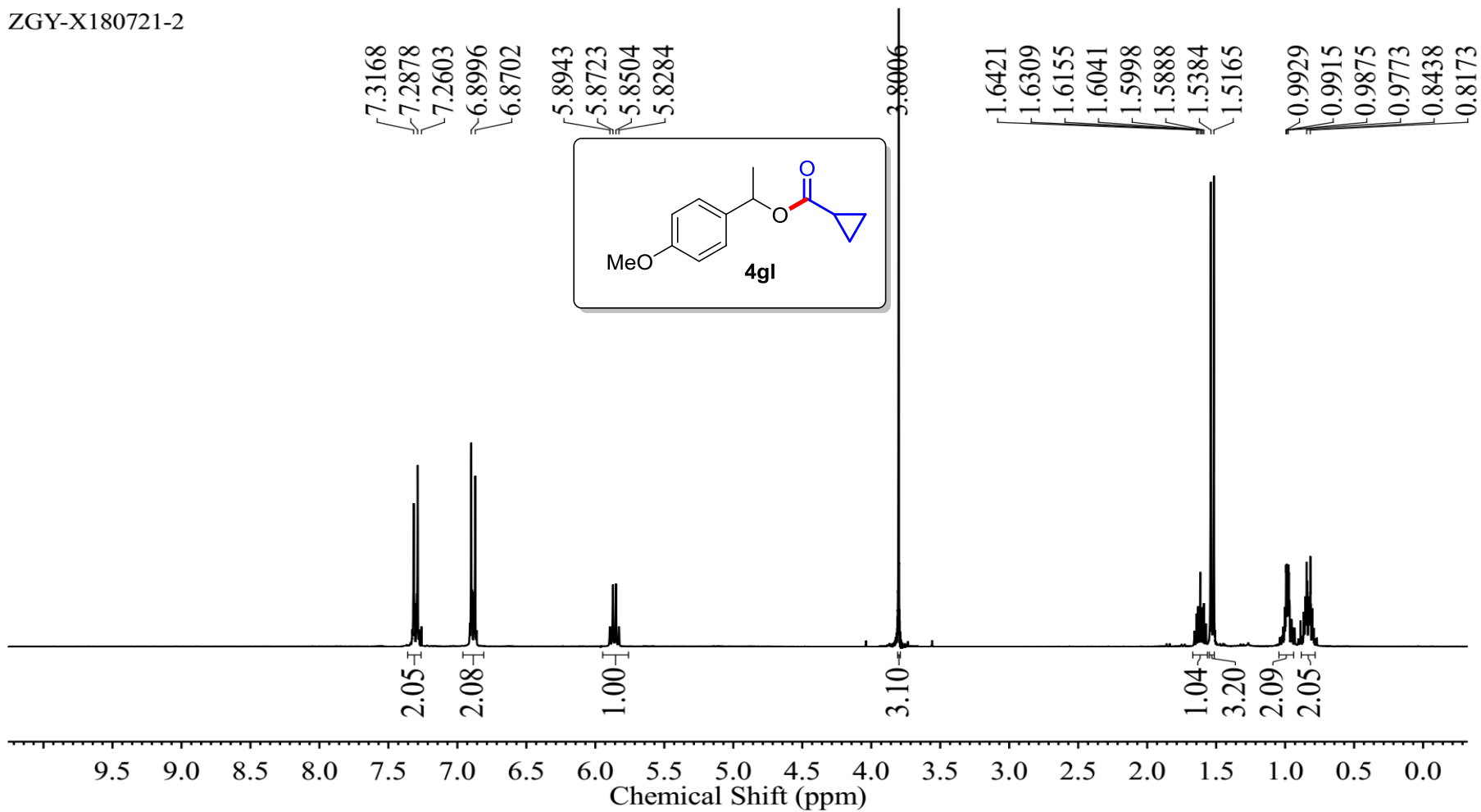
ZGY-X180627-2



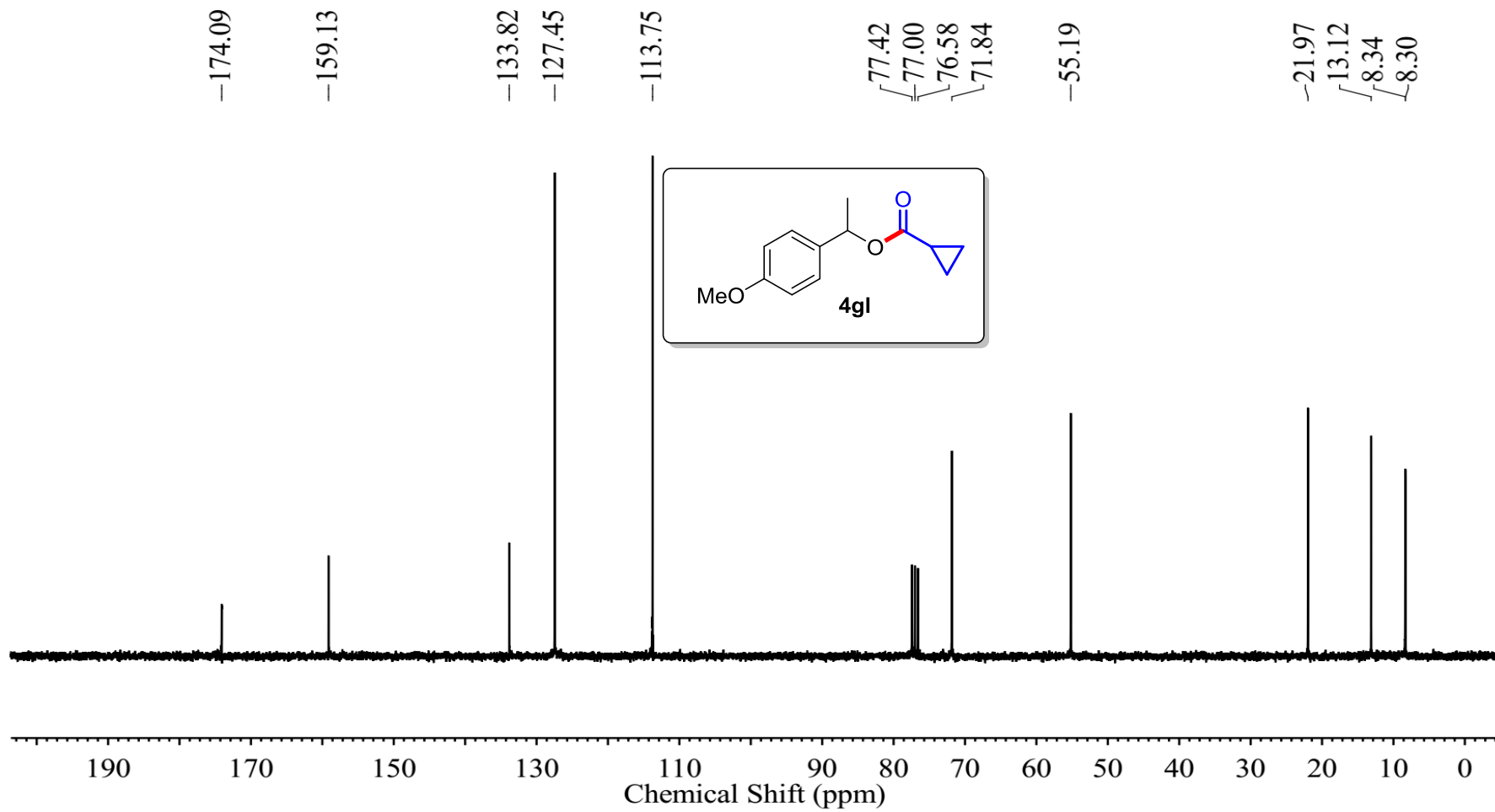
ZGY-X180627-2



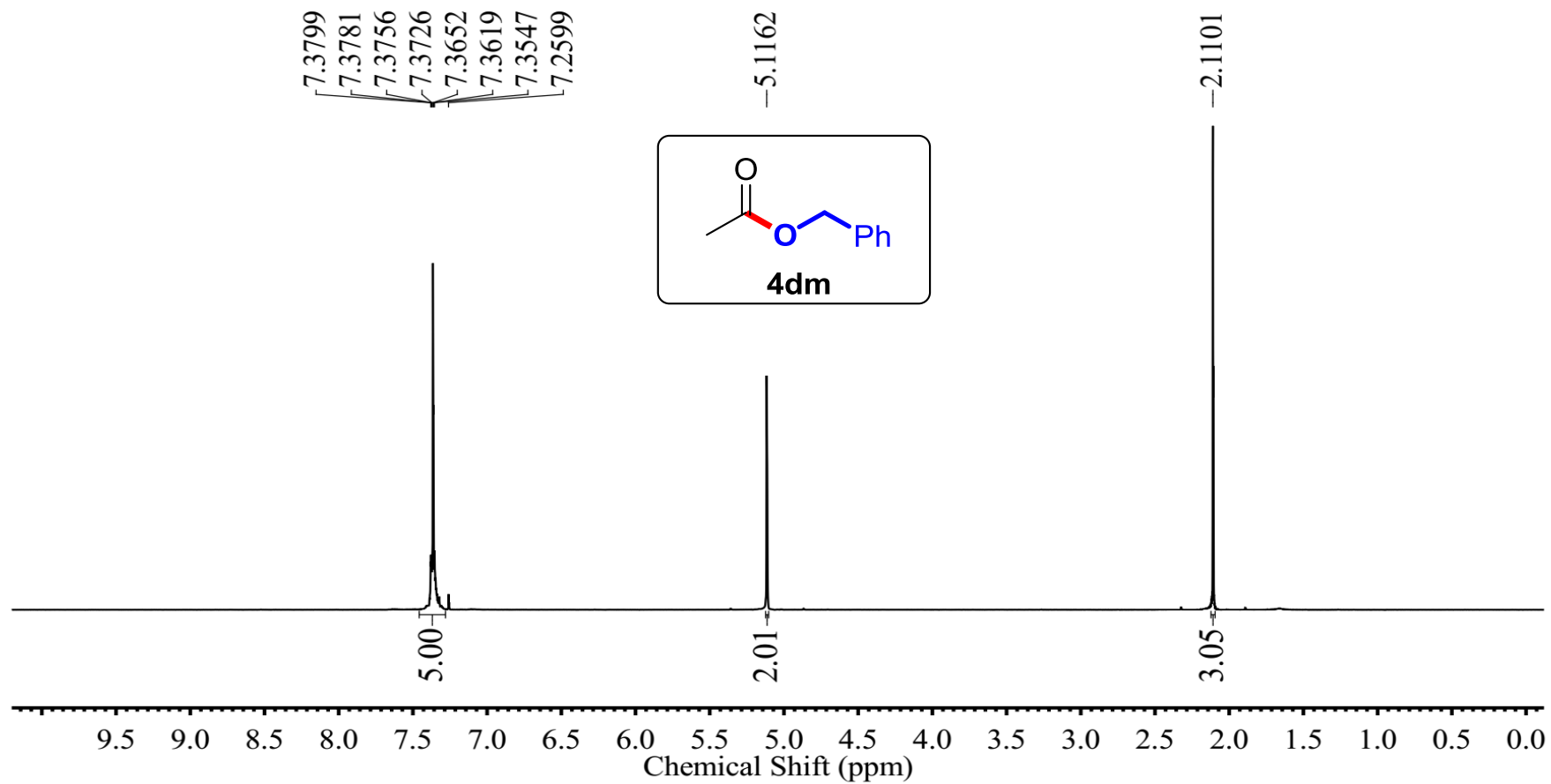
ZGY-X180721-2



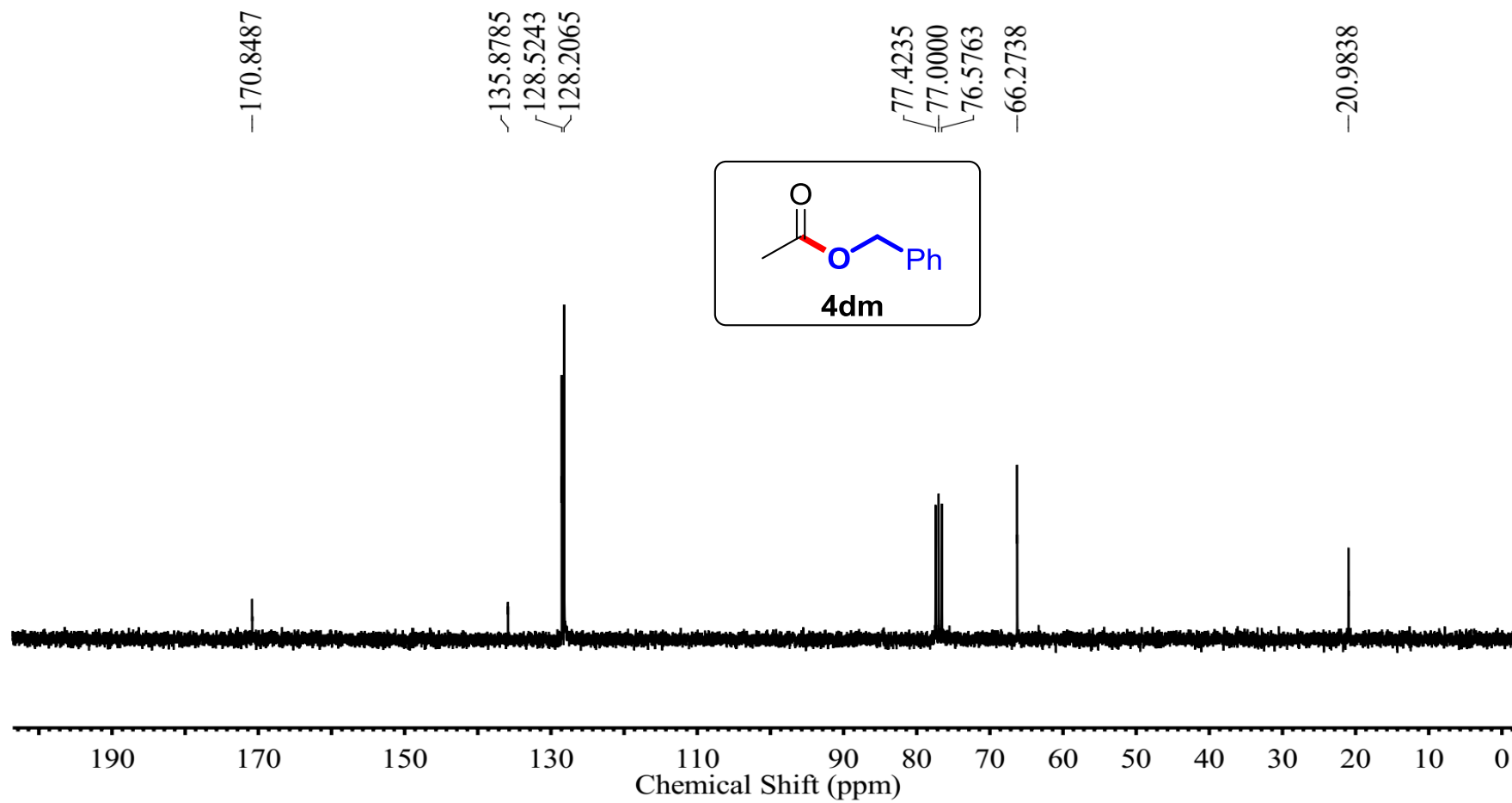
ZGY-X180721-2



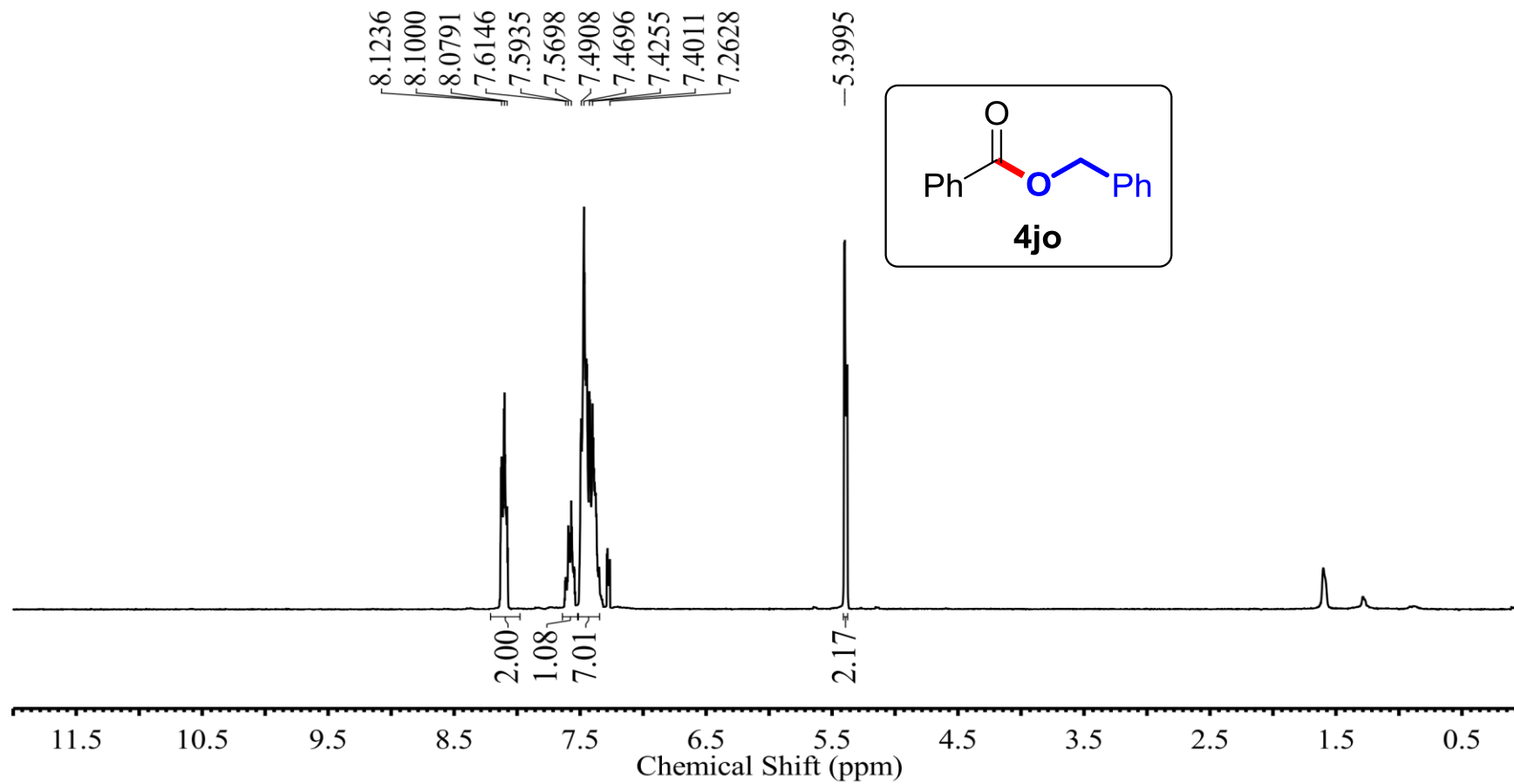
ZCY-X181017-1



ZCY-X181017-1



ZCY-X181017-3



ZCY-X181017-3

-170.8840

133.0113
130.1042
129.6842
128.5789
128.3522
128.2215
128.1458

77.4235
77.0003
76.5766
-66.6754

