Supporting information

for

One-Pot Reaction of Carboxylic Acids, Ynol Ethers and *m*-CPBA for Synthesis of α-Carbonyloxy Esters

Linwei Zeng,[†] Hironao Sajiki,[*,‡] and Sunliang Cui[*,†]

[†]Institute of Drug Discovery and Design, College of Pharmaceutical Sciences, Zhejiang University, Hangzhou 310058, China

[‡]Laboratory of Organic Chemistry, Gifu Pharmaceutical University, Gifu 501-1196, Japan

Email: sajiki@gifu-pu.ac.jp; slcui@zju.edu.cn

Contents

1	General Information	*S2*
2	Starting Materials	*S3*
3	Typical Procedure for the Synthesis of **3a**	*S4*
4	Gram-Scale Synthesis of **3a**	*S4*
5	Stepwise Reaction	*S5*
6	X-ray Crystallographic Analysis of **3u**	*S5-S6*
7	Characterization of Compounds	*S7-S29*
8	References	*S29*
9	Copies of NMR Spectra	*S30– S125*

1. General Information

The reaction temperatures are reported corresponding to the oil bath temperature. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Column chromatography was performed over silica gel (200–300mesh).

Melting points were measured with X–4 micro melting point apparatus.

HRMS were performed on Waters GCT premier time of flight mass spectrometer (EI).

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a *Bruker AV-600* spectrometer or a WNMR-I-400 spectrometer in chloroform-*d* (contain internal TMS). Chemical shifts of ^{1}H NMR spectra were reported in ppm with the internal TMS signal at 0 ppm as a standard, and chemical shifts of ^{13}C NMR spectra were reported in ppm with the chloroform signal at 77.16 ppm as a standard.[1] The data is being reported as (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dt = double of triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration).

Solvents, such as ethyl acetate (EA), petroleum ether (PE), 1,2-dichloroethane (DCE), *N, N*-dimethylformamide (DMF), tetrahydrofuran (THF) were obtained commercially and used without further purification unless otherwise noted.

Anhydrous solvents were purified according to standard methods.[2]

2. Starting Materials

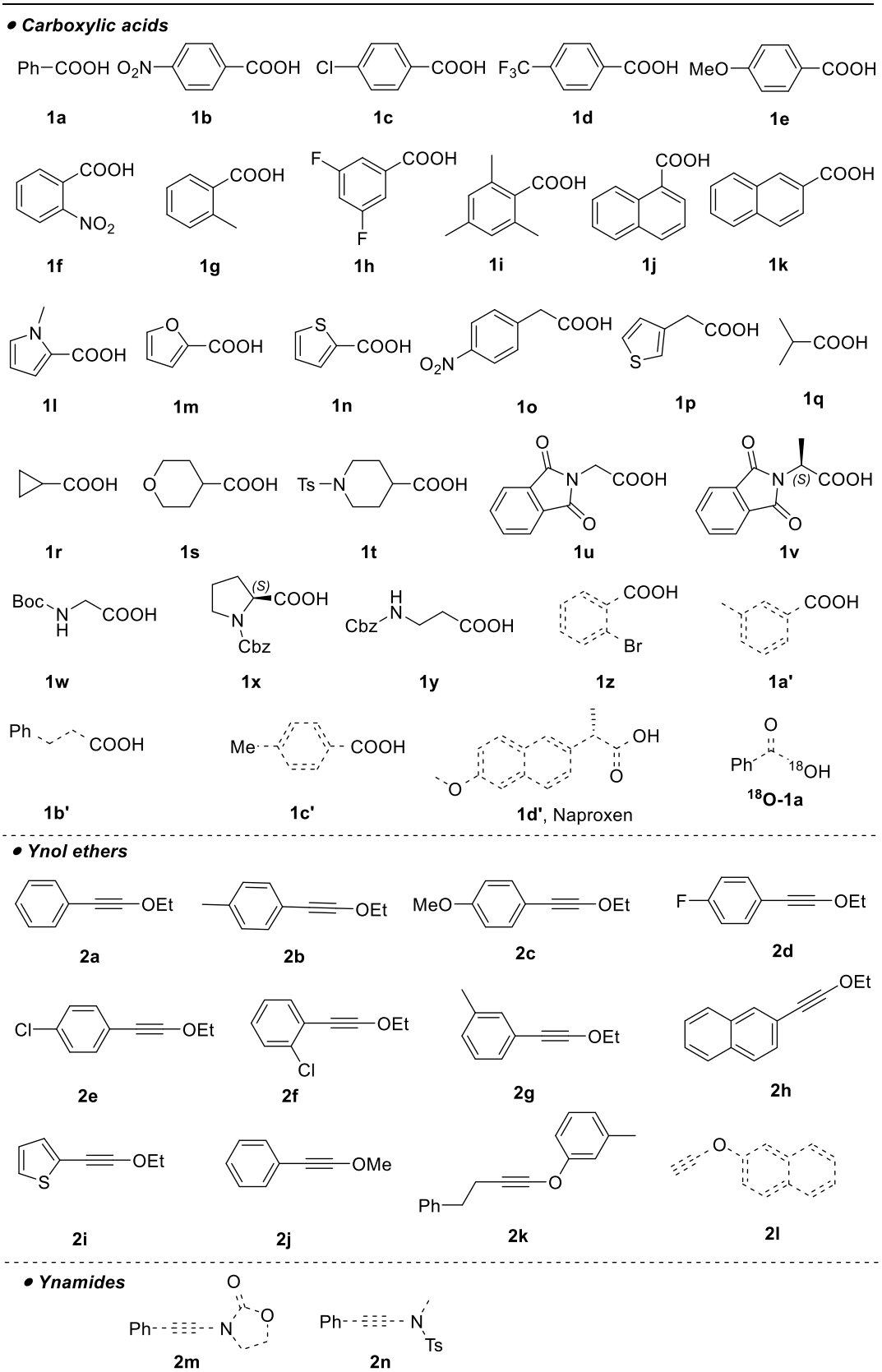
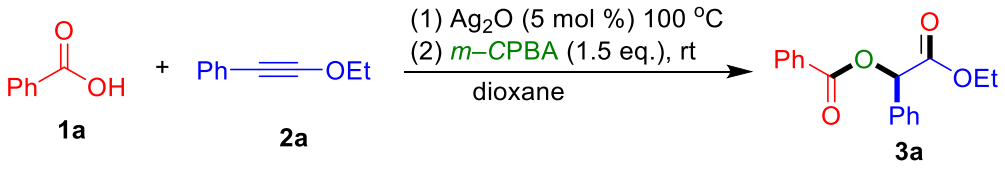


Figure S1 starting carboxylic acids, ynol ethers and ynamides

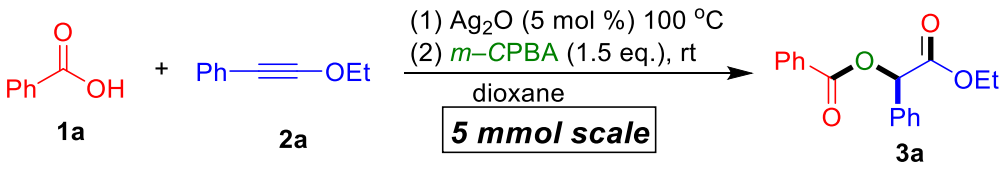
Carboxylic acids **1t**, **1u**, **1v**, **1y** and **^{18}O-1a** were prepared according to the reported methods.[3] Besides these, all of starting carboxylic acids are commercial available. Ynol ethers **2a** – **2l** were synthesized according to the literature.[4] Ynamides **2m** and **2n** were synthesized according to the literature.[5]

3. Typical Procedure for the Synthesis of 3a



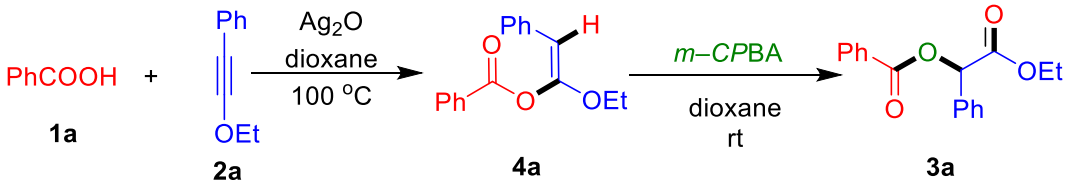
An oven-dried Schlenk tube equipped with magnetic stirrer bar was charged with benzoic acid **1a** (30.5 mg, 0.25 mmol) and silver oxide (Ag_2O, 2.9 mg, 5 mol %), then evacuated and purged with argon three times. Ynol ether **2a** (37 mg, 0.25 mmol) was dissolved in 2 mL anhydrous dioxane and added by a syringe. The mixture was stirred at 100°C for 5 hours and cooled to room temperature. *m*-CPBA (85% purity, 76 mg, 0.375 mmol) was added and the reaction was stirred for another 12 hours at room temperature. Na_2SO_3 (aq.) was added and the mixture was extracted with ethyl acetate (3×10 mL). The combined organic phase was washed by $NaHCO_3$ (aq.) and brine, dried over anhydrous Na_2SO_4, filtered. The filtrate was concentrated under vacuum and the residue was purified by silica gel column chromatography using ethyl acetate/petroleum ether (v/v, 1:20) as eluent to give 2-ethoxy-2-oxo-1-phenylethyl benzoate **3a** (59 mg, 83% yield) as a colorless oil.

4. Gram-Scale Synthesis of 3a



An oven-dried two-neck flask equipped with magnetic stirrer bar was charged with benzoic acid **1a** (610 mg, 5 mmol) and silver oxide (Ag_2O, 57.5 mg, 5 mol %), then evacuated and purged with argon three times. Ynol ether **2a** (730 mg, 5 mmol) was dissolved in 40 mL anhydrous dioxane and added by a syringe. The mixture was stirred at 100°C until starting ynol ether was consumed completely (TLC). Then the reaction was cooled to room temperature followed by added *m*-CPBA (85% purity, 1.53 g, 7.5 mmol). The reaction was stirred at room temperature until the reaction complete. Dioxane was removed under vacuum and Na_2SO_3 (aq.) was added. The mixture was extracted with ethyl acetate (3×30 mL). The combined organic phase was washed by $NaHCO_3$ (aq.) and brine, dried over anhydrous Na_2SO_4, filtered. The filtrate was concentrated under vacuum to obtain residue, which was purified by silica gel column chromatography using ethyl acetate/petroleum ether (v/v, 1:20) as eluent to give 2-ethoxy-2-oxo-1-phenylethyl benzoate **3a** (1.2 g, 84% yield) as a colorless oil.

5. Stepwise Reaction



An oven-dried Schlenk tube equipped with magnetic stirrer bar was charged with benzoic acid **1a** (34 mg, 0.27 mmol) and silver oxide (Ag_2O, 2.8 mg, 5 mol %), then evacuated and purged with argon three times. Ynol ether **2a** (37 mg, 0.25 mmol) was dissolved in 2 mL anhydrous dioxane and added by a syringe. The mixture was stirred at 100°C for 5h. Solvent was removed under vacuum and the residue was purified by silica gel column chromatography using ethyl acetate/petroleum ether (v/v, 1:50) as eluent to give (*Z*)-1-ethoxy-2-phenylvinyl benzoate **4a** (64 mg, 95% yield) as a colorless oil, which was further transformed to a colorless crystal.

An oven-dried Schlenk tube equipped with magnetic stirrer bar was charged with **4a** (64 mg, 0.235 mmol) and *m*-CPBA (85% purity, 72 mg, 0.35 mmol), 2 mL anhydrous dioxane was added as solvent and the reaction was stirred at room temperature for 12h. Dioxane was removed under vacuum and Na_2SO_3 (aq.) was added. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phase was washed by $NaHCO_3$ (aq.) and brine, dried over anhydrous Na_2SO_4, filtered. The filtrate was concentrated under vacuum and the residue was purified by silica gel column chromatography using ethyl acetate/petroleum ether (v/v, 1:20) as eluent to give 2-ethoxy-2-oxo-1-phenylethyl benzoate **3a** (58 mg, 86% yield) as a colorless oil.

6. X-ray Crystallographic Analysis of 3u

Crystals suitable for X-ray diffraction experiments were obtained by following methods: Compound **3u** was crystallized from mixed solvent of hexane/choroform; Intensity data for compound **3u** were collected on 'Bruke Apex2' diffractometer.

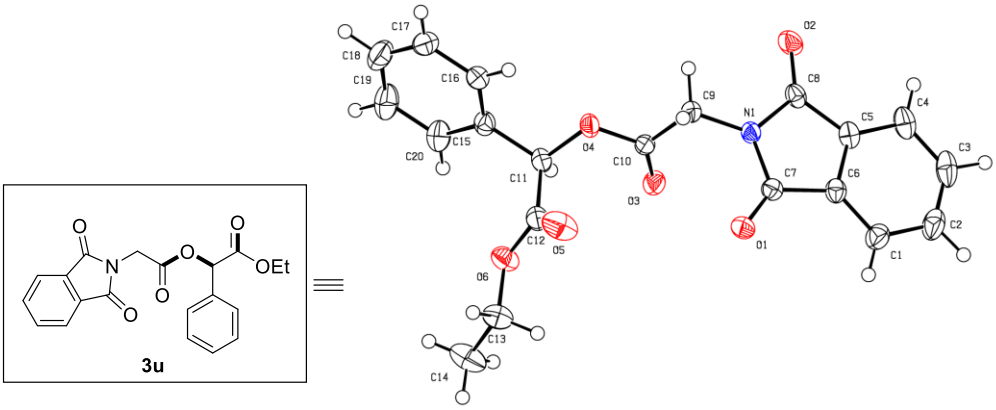
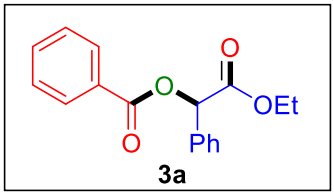


Figure S2. X-ray crystallographic structure **3u** (ORTEP view with 50% thermal ellipsoid contour probability, **CCDC 1916376**)

Table S1. Crystal data and structure refinements for **3u**

Empirical formula	$C_{20}H_{17}NO_6$
Formula weight	367.35
Crystal system	triclinic
Space group	P-1
Hall group	-p 1
a/Å	8.5599(3)
b/Å	9.2365(3)
c/Å	12.4679(4)
α/°	107.9080(10)
β/°	103.1070(10)
γ/°	94.5610(10)
Volume	1782.9(6)
Z	2
Temperature/K	170(2)
X-ray wavelength/Å	0.71073
2θ range for data collection/°	2.48 to 27.10
Crystal color	colourless
ρ_{Calcd} g/m^3	1.353
μ/mm^{-1}	0.101
Max. transmission	0.983
Min. transmission	0.952
F_000	384
Crystal_size/mm^3	0.489 x 0.383 x 0.166
Radiation	MoK\α
Independent reflections I > 2σ (I)	3610
Independent reflections	3933
Index ranges	–10≦h≦10, –10≦k≦11, –15≦l≦15
Data/restraints/parameters	3933/0/245
Final R indexes R [I>2σ (I)]gt	R1 = 0.0389, wR2 = 0.0951
Final R indexes R [all data]	R1 = 0.0421, wR2 = 0.0976
Goodness-of-fit on F^2	1.036
Largest peak/deepest hole eÅ^{-3}	0.286/-0.202

7. Characterization of Compounds



3a

2-ethoxy-2-oxo-1-phenylethyl benzoate

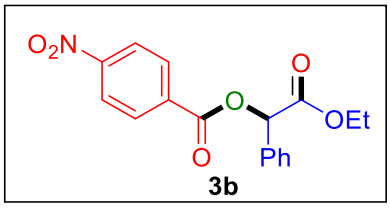
Colorless oil, (59 mg, 83% yield).

TLC: Rf = 0.3 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 – 8.09 (m, 2H), 7.61 – 7.55 (m, 3H), 7.47 – 7.38 (m, 5H), 6.15 (s, 1H), 4.28 – 4.14 (m, 2H), 1.22 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.89, 165.99, 134.21, 133.54, 130.06, 129.42, 129.31, 128.92, 128.54, 127.72, 75.10, 61.84, 14.11.

HRMS (EI) Calcd for $C_{17}H_{16}O_4$ $(M)^+$: 284.1049; Found: 284.1045.



3b

2-ethoxy-2-oxo-1-phenylethyl 4-nitrobenzoate

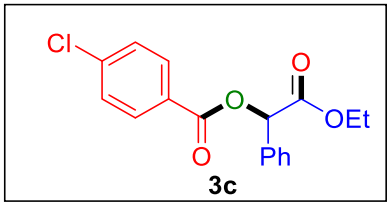
Yellowish oil, (62 mg, 75% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 – 8.27 (m, 4H), 7.61 – 7.55 (m, 2H), 7.48 – 7.41 (m, 3H), 6.17 (s, 1H), 4.32 – 4.16 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.40, 164.16, 150.95, 134.82, 133.57, 131.21, 129.68, 129.10, 127.83, 123.74, 75.79, 62.15, 14.12.

HRMS (EI) Calcd for $C_{17}H_{15}NO_6$ $(M)^+$: 329.0899; Found: 329.0894.



3c

2-ethoxy-2-oxo-1-phenylethyl 4-chlorobenzoate

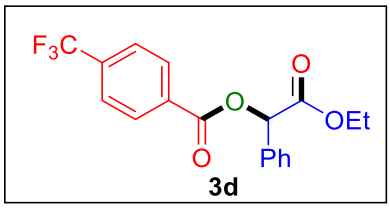
Colorless oil, (63 mg, 79% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.01 (m, 2H), 7.58 – 7.54 (m, 2H), 7.47 – 7.39 (m, 5H), 6.13 (s, 1H), 4.28 – 4.15 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.76, 165.17, 140.11, 134.03, 131.48, 129.46, 129.01, 128.97, 127.92, 127.78, 75.29, 61.97, 14.15.

HRMS (EI) Calcd for $C_{17}H_{15}ClO_4$ $(M)^+$: 318.0659; Found: 318.0657.



3d

2-ethoxy-2-oxo-1-phenylethyl 4-(trifluoromethyl)benzoate

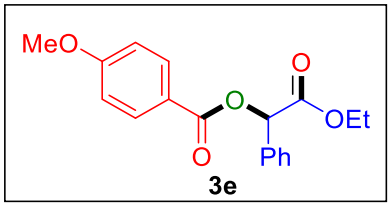
Colorless oil, (63 mg, 72% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.47 – 7.40 (m, 3H), 6.16 (s, 1H), 4.30 – 4.14 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.60, 164.84, 135.03 (q, *J* = 32.7 Hz), 133.84, 132.71, 130.49, 129.56, 129.05, 127.80, 125.63 (q, *J* = 3.8 Hz), 123.70 (q, *J* = 272.8 Hz), 75.54, 62.05, 14.13.

HRMS (EI) Calcd for $C_{18}H_{15}F_3O_4$ $(M)^+$: 352.0922; Found: 352.0919.



3e

2-ethoxy-2-oxo-1-phenylethyl 4-methoxybenzoate

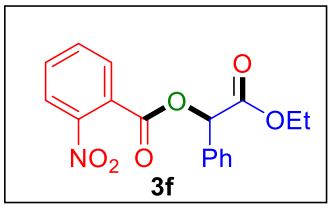
Colorless oil, (54 mg, 69% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.45 – 7.38 (m, 3H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.11 (s, 1H), 4.31 – 4.10 (m, 2H), 3.86 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.11, 165.73, 163.88, 134.38, 132.20, 129.26, 128.91, 127.73, 121.75, 113.82, 74.88, 61.82, 55.59, 14.15.

HRMS (EI) Calcd for $C_{18}H_{18}O_5$ $(M)^+$: 314.1154; Found: 314.1159.



2-ethoxy-2-oxo-1-phenylethyl 2-nitrobenzoate

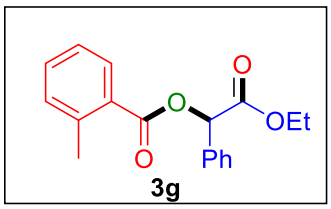
Yellow oil, (68 mg, 83% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.80 (m, 2H), 7.69 – 7.58 (m, 2H), 7.54 – 7.46 (m, 2H), 7.43 – 7.33 (m, 3H), 6.17 (s, 1H), 4.29 – 4.16 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.16, 164.54, 148.09, 133.07, 132.99, 132.27, 130.20, 129.46, 128.85, 127.66, 126.52, 123.93, 76.03, 61.98, 13.95.

HRMS (EI) Calcd for $C_{17}H_{15}NO_6$ $(M)^+$: 329.0899; Found: 2329.0894.



2-ethoxy-2-oxo-1-phenylethyl 2-methylbenzoate

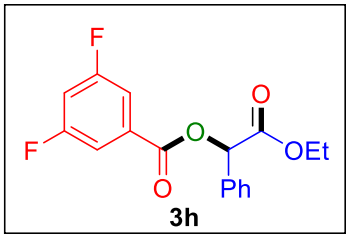
Colorless oil, (61 mg, 82% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.46 – 7.38 (m, 4H), 7.30 – 7.24 (m, 2H), 6.12 (s, 1H), 4.41 – 4.08 (m, 2H), 2.64 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.10, 166.97, 140.80, 134.21, 132.58, 131.82, 131.15, 129.30, 128.93, 128.82, 127.81, 125.93, 75.12, 61.90, 21.87, 14.17.

HRMS (EI) Calcd for $C_{18}H_{18}O_4$ $(M)^+$: 298.1205; Found: 298.1207.



2-ethoxy-2-oxo-1-phenylethyl 3,5-difluorobenzoate

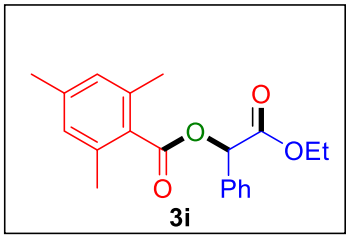
Yellowish oil, (56 mg, 70% yield).

TLC: Rf = 0.3 (Petroleum ether/EtOAc = 15/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.58 – 7.53 (m, 2H), 7.48 – 7.41 (m, 3H), 7.08 – 7.00 (m, 1H), 6.12 (s, 1H), 4.32 – 4.11 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.47, 164.15 (d, *J* = 11.7 Hz), 163.89, 161.66 (d, *J* = 11.9 Hz), 133.63, 132.59 (t, *J* = 9.2 Hz), 129.63, 129.09, 127.80, 113.25 (d, *J* = 7.4 Hz), 113.06 (d, *J* = 7.4 Hz), 109.08 (t, *J* = 25.3 Hz), 75.67, 62.11, 14.14.

HRMS (EI) Calcd for $C_{17}H_{14}F_2O_4$ $(M)^+$: 320.0860; Found: 320.0865.



2-ethoxy-2-oxo-1-phenylethyl 2,4,6-trimethylbenzoate

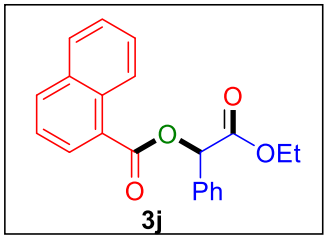
Colorless oil, (66 mg, 81% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.41 – 7.34 (m, 3H), 6.85 (s, 2H), 6.12 (s, 1H), 4.30 – 4.16 (m, 2H), 2.36 (s, 6H), 2.27 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.43, 168.93, 139.94, 136.19, 133.88, 129.62, 129.26, 128.85, 128.67, 127.81, 75.25, 61.88, 21.25, 20.08, 14.14.

HRMS (EI) Calcd for $C_{20}H_{22}O_4$ $(M)^+$: 326.1518; Found: 326.1515.



2-ethoxy-2-oxo-1-phenylethyl 1-naphthoate

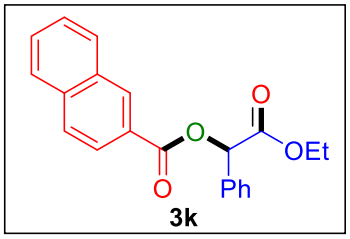
White solid, 79 – 81℃ (72 mg, 86% yield).

TLC: Rf = 0.4 (Petroleum ether/EtOAc = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 7.2 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.65 – 7.58 (m, 3H), 7.54 – 7.46 (m, 2H), 7.44 – 7.36 (m, 3H), 6.26 (s, 1H), 4.35 – 4.12 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.08, 166.88, 134.14, 133.96, 133.87, 131.52, 130.90, 129.31, 128.94, 128.64, 128.04, 127.77, 126.40, 126.28, 125.82, 124.61, 75.25, 61.92, 14.15.

HRMS (EI) Calcd for $C_{21}H_{18}O_4$ $(M)^+$: 334.1205; Found: 334.1209.



2-ethoxy-2-oxo-1-phenylethyl 2-naphthoate

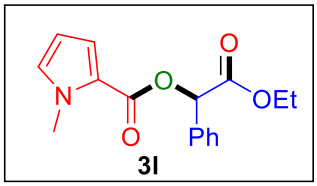
Colorless oil, (58 mg, 70% yield).

TLC: Rf = 0.4 (Petroleum ether/EtOAc = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.16 – 8.09 (m, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.69 – 7.62 (m, 2H), 7.61 – 7.50 (m, 2H), 7.48 – 7.40 (m, 3H), 6.22 (s, 1H), 4.34 – 4.10 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.95, 166.17, 135.85, 134.23, 132.51, 131.75, 129.54, 129.36, 128.97, 128.58, 128.36, 127.88, 127.81, 126.81, 126.59, 125.41, 75.24, 61.88, 14.13.

HRMS (EI) Calcd for $C_{21}H_{18}O_4$ $(M)^+$: 334.1205; Found: 334.1205.



2-ethoxy-2-oxo-1-phenylethyl 1-methyl-1H-pyrrole-2-carboxylate

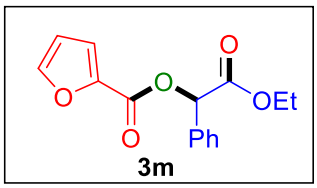
Colorless oil, (41 mg, 57% yield).

TLC: Rf = 0.3 (Petroleum ether/EtOAc = 15/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.43 – 7.35 (m, 3H), 7.11 (dd, J_1 = 4.0 Hz, J_2 = 1.6 Hz, 1H), 6.81 (t, J = 2.0 Hz, 1H), 6.12 (dd, J = 4.0 Hz, J_2 = 2.4 Hz, 1H), 6.05 (s, 1H), 4.27 – 4.11 (m, 2H), 3.92 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.27, 160.35, 134.49, 130.32, 129.12, 128.83, 127.65, 121.64, 119.27, 108.29, 74.16, 61.72, 36.96, 14.13.

HRMS (EI) Calcd for $C_{16}H_{17}NO_4$ $(M)^+$: 287.1158; Found: 287.1152.



2-ethoxy-2-oxo-1-phenylethyl furan-2-carboxylate

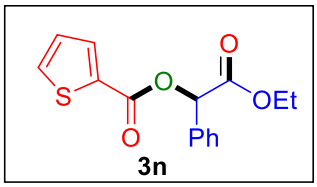
Yellow solid, 85 – 87°C. (36 mg, 53% yield).

TLC: Rf = 0.4 (Petroleum ether/EtOAc = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 1H), 7.58 – 7.52 (m, 2H), 7.46 – 7.38 (m, 3H), 7.31 (d, J = 3.5 Hz, 1H), 6.53 (dd, J = 3.5, 1.7 Hz, 1H), 6.12 (s, 1H), 4.31 – 4.11 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.65, 157.92, 147.09, 143.95, 133.83, 129.42, 128.96, 127.80, 119.30, 112.13, 74.83, 62.00, 14.13.

HRMS (EI) Calcd for $C_{15}H_{14}O_5$ $(M)^+$: 274.0841; Found: 274.0847.



2-ethoxy-2-oxo-1-phenylethyl thiophene-2-carboxylate

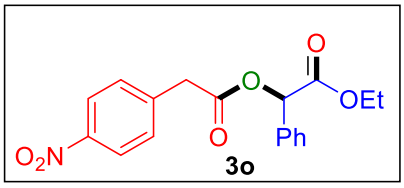
Colorless oil, (66 mg, 91% yield).

TLC: Rf = 0.3 (Petroleum ether/EtOAc = 15/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 7.60 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.45 – 7.38 (m, 3H), 7.12 (dd, J = 4.8 Hz, J_2 = 4.0 Hz, 1H), 6.11 (s, 1H), 4.31 – 4.09 (m, 2H), 1.23 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.73, 161.54, 134.47, 133.96, 133.34, 132.73, 129.34, 128.92, 127.99, 127.69, 75.09, 61.92, 14.13.

HRMS (EI) Calcd for $C_{15}H_{14}O_4S$ $(M)^+$: 290.0613; Found: 290.0610.



ethyl 2-(2-(4-nitrophenyl)acetoxy)-2-phenylacetate

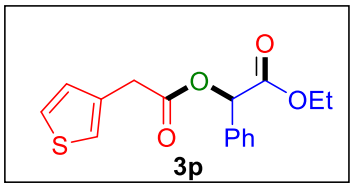
Yellowish solid, 62 – 64℃. (53 mg, 62% yield).

TLC: Rf = 0.1 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.45 – 7.36 (m, 5H), 5.93 (s, 1H), 4.25 – 4.06 (m, 2H), 3.93 (d, J = 16.0 Hz, 1H), 3.86 (d, J = 16.0 Hz, 1H), 1.19 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.74, 168.54, 147.40, 140.81, 133.47, 130.56, 129.56, 129.00, 127.72, 123.91, 75.35, 62.05, 40.67, 14.10.

HRMS (EI) Calcd for $C_{18}H_{17}NO_6$ $(M)^+$: 343.1056; Found: 343.1051.



ethyl 2-phenyl-2-(2-(thiophen-3-yl)acetoxy)acetate

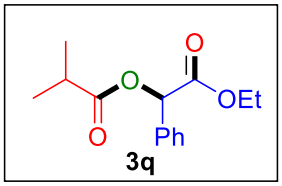
Colorless oil, (60 mg, 79% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.35 (m, 5H), 7.28 (dd, J = 4.8 Hz, J_2 = 2.8 Hz, 1H), 7.24 – 7.17 (m, 1H), 7.07 (dd, J = 4.8 Hz, J_2 = 1.2 Hz, 1H), 5.93 (s, 1H), 4.28 – 4.06 (m, 2H), 3.84 (d, J = 16.4 Hz, 1H), 3.79 (d, J = 16.4 Hz, 1H), 1.19 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.58, 168.76, 133.82, 132.99, 129.33, 128.88, 128.64, 127.67, 125.85, 123.27, 75.01, 61.87, 35.54, 14.07.

HRMS (EI) Calcd for $C_{16}H_{16}O_4S$ $(M)^+$: 304.0769; Found: 304.0766.



2-ethoxy-2-oxo-1-phenylethyl isobutyrate

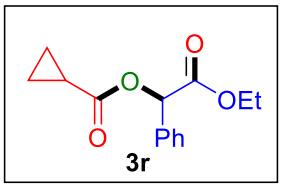
Colorless oil, (32 mg, 51% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 15/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.41 – 7.36 (m, 3H), 5.90 (s, 1H), 4.23 – 4.11 (m, 2H), 2.77 – 2.66 (m, 1H), 1.28 (d, J = 7.0 Hz, 3H), 1.23 – 1.20 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.58, 169.05, 134.25, 129.21, 128.86, 127.64, 74.46, 61.76, 33.94, 19.10, 18.85, 14.12.

HRMS (EI) Calcd for $C_{14}H_{18}O_4$ $(M)^+$: 250.1205; Found: 250.1200.



2-ethoxy-2-oxo-1-phenylethyl cyclopropanecarboxylate

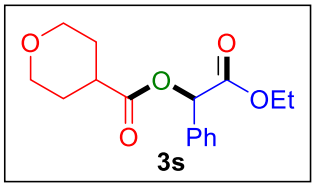
White solid, 48 – 50℃. (30 mg, 49% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 15/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.42 – 7.36 (m, 3H), 5.91 (s, 1H), 4.27 – 4.10 (m, 2H), 1.83 – 1.75 (m, 1H), 1.21 (t, J = 7.2 Hz, 3H), 1.13 – 1.07 (m, 2H), 0.99 – 0.90 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.33, 169.03, 134.18, 129.24, 128.87, 127.70, 74.60, 61.76, 14.11, 12.95, 9.13, 9.06.

HRMS (EI) Calcd for $C_{14}H_{16}O_4$ $(M)^+$: 248.1049; Found: 248.1042.



3s

2-ethoxy-2-oxo-1-phenylethyl tetrahydro-2H-pyran-4-carboxylate

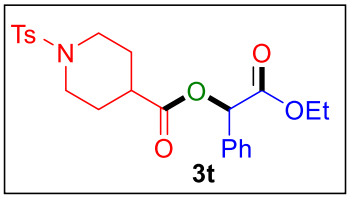
Colorless oil, (43 mg, 59% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.42 – 7.35 (m, 3H), 5.92 (s, 1H), 4.23 – 4.12 (m, 2H), 4.01 – 3.93 (m, 2H), 3.50 – 3.42 (m, 2H), 2.75 – 2.67 (m, 1H), 2.00 – 1.94 (m, 1H), 1.93 – 1.82 (m, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.89, 168.82, 133.97, 129.30, 128.88, 127.62, 74.58, 67.09, 66.99, 61.83, 39.91, 28.71, 28.49, 14.09.

HRMS (EI) Calcd for $C_{16}H_{20}O_5$ $(M)^+$: 292.1311; Found: 292.1314.



3t

2-ethoxy-2-oxo-1-phenylethyl 1-tosylpiperidine-4-carboxylate

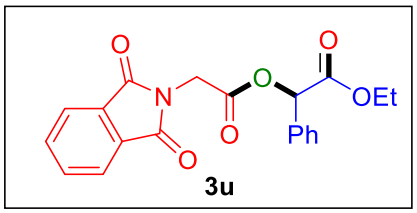
White solid, 73 – 75°C. (73 mg, 66% yield).

TLC: Rf = 0.1 (Petroleum ether/EtOAc = 4/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.35 (m, 5H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.86 (s, 1H), 4.21 – 4.06 (m, 2H), 3.67 – 3.55 (m, 2H), 2.58 – 2.50 (m, 2H), 2.47 – 2.44 (m, 1H), 2.43 (s, 3H), 2.12 – 2.05 (m, 1H), 2.03 – 1.97 (m, 1H), 1.96 – 1.85 (m, 2H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.33, 168.64, 143.67, 133.74, 133.29, 129.78, 129.37, 128.90, 127.79, 127.58, 74.69, 61.86, 45.35, 45.28, 39.82, 27.53, 27.33, 21.64, 14.07.

HRMS (EI) Calcd for $C_{23}H_{27}NO_6S$ $(M)^+$: 445.1559; Found: 445.1551.



ethyl 2-(2-(1,3-dioxoisoindolin-2-yl)acetoxy)-2-phenylacetate

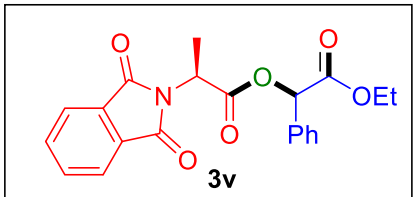
White solid, 107 – 109°C. (68 mg, 74% yield).

TLC: Rf = 0.1 (Petroleum ether/EtOAc = 4/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.77 – 7.72 (m, 2H), 7.48 – 7.43 (m, 2H), 7.41 – 7.36 (m, 3H), 5.98 (s, 1H), 4.68 (d, *J* = 17.4 Hz, 1H), 4.54 (d, *J* = 17.4 Hz, 1H), 4.28 – 4.10 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.07, 167.38, 166.94, 134.38, 133.38, 132.11, 129.53, 128.94, 127.72, 123.77, 75.69, 62.06, 38.87, 14.06.

HRMS (EI) Calcd for $C_{20}H_{17}NO_6$ $(M)^+$: 367.1056; Found: 367.1059.



dr 53:47

2-ethoxy-2-oxo-1-phenylethyl (2S)-2-(1,3-dioxoisoindolin-2-yl)propanoate

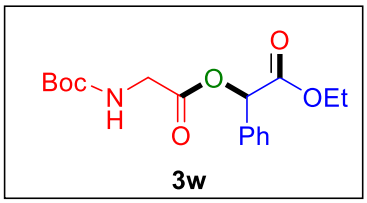
Colorless oil, (77 mg, 81% yield).

TLC: Rf = 0.1 (Petroleum ether/EtOAc = 4/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 2H), 7.77 – 7.69 (m, 2H), 7.44 – 7.29 (m, 5H), 5.99 (s, 0.53H), 5.94 (s, 0.47H), 5.23 – 5.11 (m, 1H), 4.24 – 4.06 (m, 2H), 1.82 (d, *J* = 7.2 Hz, 1.41H), 1.78 (d, *J* = 7.2 Hz, 1.59H), 1.23 (t, *J* = 7.2 Hz, 1.41H), 1.17 (t, *J* = 7.2 Hz, 1.59H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.26, 169.14, 168.19, 168.13, 167.38, 134.26, 134.25, 133.55, 133.48, 131.98, 131.90, 129.31, 129.26, 128.83, 128.76, 127.49, 127.44, 123.59, 123.57, 75.56, 75.53, 61.94, 61.88, 47.68, 47.65, 15.30, 15.21, 14.01, 13.99.

HRMS (EI) Calcd for $C_{21}H_{19}NO_6$ $(M)^+$: 381.1212; Found: 381.1219.



ethyl 2-(((tert-butoxycarbonyl)glycyl)oxy)-2-phenylacetate

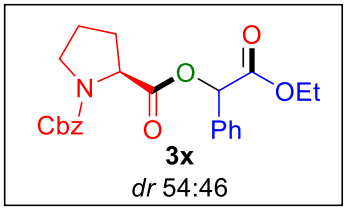
Colorless oil, (62 mg, 73% yield).

TLC: Rf = 0.15 (Petroleum ether/EtOAc = 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.42 – 7.36 (m, 3H), 5.96 (s, 1H), 5.03 (t, *J* = 6.0 Hz, 1H), 4.28 – 4.01 (m, 4H), 1.44 (s, 9H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.04, 168.52, 155.76, 133.48, 129.51, 128.95, 127.77, 80.23, 75.24, 62.03, 42.47, 28.42, 14.11.

HRMS (EI) Calcd for $C_{17}H_{23}NO_6$ $(M)^+$: 337.1525; Found: 337.1521.



1-benzyl 2-(2-ethoxy-2-oxo-1-phenylethyl) (2S)-pyrrolidine-1,2-dicarboxylate

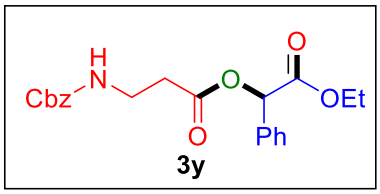
Colorless oil, (79 mg, 77% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 3/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.17 (m, 10H), 5.97 (s, 0.18H), 5.95 (s, 0.29H), 5.83 (s,0.53H), 5.18 – 4.99 (m, 2H), 4.58 – 4.52 (m, 0.46H), 4.51 – 4.46 (m, 0.54H), 4.22 – 4.05 (m, 2H), 3.71 – 3.60 (m, 1H), 3.56 – 3.42 (m, 1H), 2.40 – 1.88 (m, 4H), 1.21 – 1.14 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.07, 171.86, 171.85, 171.68, 168.62, 168.38, 168.36, 168.28, 154.83, 154.71, 154.16, 136.65, 136.50, 133.81, 133.49, 133.41, 133.37, 129.21, 129.17, 129.10, 128.99, 128.71, 128.67, 128.64, 128.40, 128.36, 128.26, 128.26, 127.89, 127.82, 127.77, 127.73, 127.60, 127.59, 127.53, 127.51, 127.21, 127.16, 74.84, 74.69, 74.56, 66.94, 66.89, 66.84, 66.80, 61.69, 61.68, 61.65, 61.63, 59.44, 59.03, 58.86, 58.47, 46.92, 46.90, 46.40, 30.85, 30.61, 29.80, 29.60, 24.17, 24.11, 23.36, 23.32, 13.90, 13.89.

HRMS (EI) Calcd for $C_{23}H_{25}NO_6$ $(M)^+$: 411.1682; Found: 411.1688.



3y

2-ethoxy-2-oxo-1-phenylethyl 3-(((benzyloxy)carbonyl)amino)propanoate

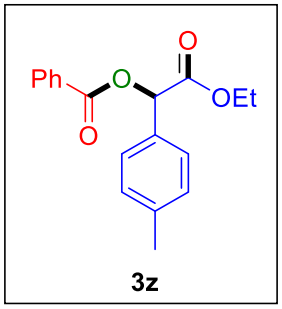
Colorless oil, (69 mg, 72% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 3/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.26 (m, 10H), 5.94 (s, 1H), 5.59 (s, 1H), 5.18 – 5.05 (m, 2H), 4.27 – 4.06 (m, 2H), 3.62 – 3.49 (m, 2H), 2.78 – 2.60 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.74, 169.01, 156.46, 136.65, 133.53, 129.44, 128.93, 128.58, 128.14, 128.10, 127.70, 74.82, 66.76, 62.08, 36.90, 34.76, 14.06.

HRMS (EI) Calcd for $C_{21}H_{23}NO_6$ $(M)^+$: 385.1525; Found: 385.1520.



3z

2-ethoxy-2-oxo-1-(*p*-tolyl)ethyl benzoate

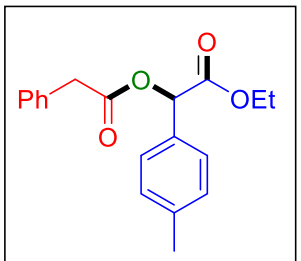
Colorless oil, (57 mg, 76% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 15/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.2 Hz, 2H), 7.62 – 7.53 (m, 1H), 7.51 – 7.41 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.10 (s, 1H), 4.30 – 4.10 (m, 2H), 2.38 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.05, 166.05, 139.31, 133.50, 131.23, 130.06, 129.62, 129.46, 128.52, 127.73, 75.01, 61.79, 21.38, 14.14.

HRMS (EI) Calcd for $C_{18}H_{18}O_4$ $(M)^+$: 298.1205; Found: 298.1201.



3a'

ethyl 2-(2-phenylacetoxy)-2-(*p*-tolyl)acetate

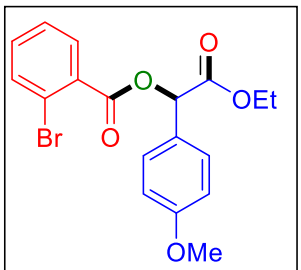
Colorless oil, (49 mg, 63% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 7H), 7.19 (d, J = 7.6Hz, 2H), 5.88 (s, 1H), 4.21 – 4.05 (m, 2H), 3.80 (d, J = 15.6 Hz, 1H), 3.74 (d, J = 15.6 Hz, 1H), 2.35 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.13, 168.92, 139.27, 133.53, 130.92, 129.54, 129.52, 128.65, 127.64, 127.28, 74.90, 61.75, 40.94, 21.35, 14.06.

HRMS (EI) Calcd for $C_{19}H_{20}O_4$ $(M)^+$: 312.1362; Found: 312.1361.



3b'

2-ethoxy-1-(4-methoxyphenyl)-2-oxoethyl 2-bromobenzoate

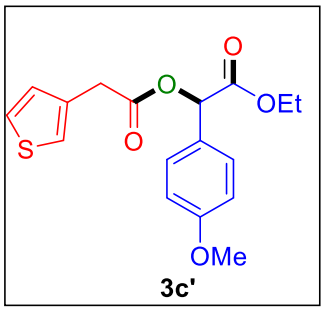
Colorless oil, (73 mg, 74% yield).

TLC: Rf = 0.1 (Petroleum ether/EtOAc = 15/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 1H), 7.67 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H), 7.49 (d, J = 8.8 Hz, 2H), 7.40 – 7.31 (m, 2H), 6.94 (d, J = 8.8 Hz, 2H), 6.10 (s, 1H), 4.32 – 4.13 (m, 2H), 3.82 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.89, 165.39, 160.46, 134.59, 133.14, 132.11, 131.13, 129.36, 127.32, 125.79, 122.25, 114.32, 75.29, 61.92, 55.43, 14.16.

HRMS (EI) Calcd for $C_{18}H_{17}BrO_5$ $(M)^+$: 392.0259; Found: 392.0251.



3c'

ethyl 2-(4-methoxyphenyl)-2-(2-(thiophen-3-yl)acetoxy)acetate

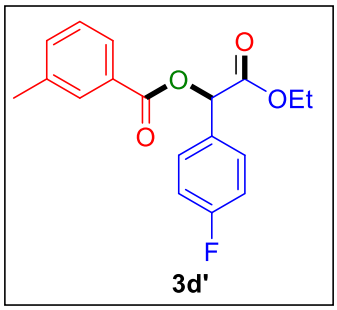
Colorless oil, (59 mg, 71% yield).

TLC: Rf = 0.1 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.23 – 7.17 (m, 1H), 7.07 (d, *J* = 5.2 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.87 (s, 1H), 4.26 – 4.08 (m, 2H), 3.86 – 3.75 (m, 5H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.65, 169.00, 160.39, 133.06, 129.18, 128.65, 125.91, 125.80, 123.22, 114.28, 74.70, 61.78, 55.42, 35.54, 14.09.

HRMS (EI) Calcd for $C_{17}H_{18}O_5S$ $(M)^+$: 334.0875; Found: 334.0870.



3d'

2-ethoxy-1-(4-fluorophenyl)-2-oxoethyl 3-methylbenzoate

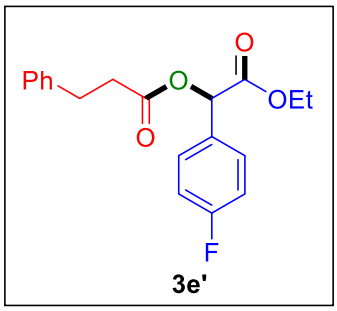
Colorless oil, (61 mg, 77% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.86 (m, 2H), 7.59 – 7.54 (m, 2H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.13 – 7.08 (m, 2H), 6.12 (s, 1H), 4.30 – 4.12 (m, 2H), 2.40 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.81, 166.10, 163.31 (d, *J* = 248.3 Hz), 138.42, 134.43, 130.52, 130.21 (d, *J* = 3.6 Hz), 129.66 (d, *J* = 8.6 Hz), 129.21, 128.49, 127.23, 115.97 (d, *J* = 21.9 Hz), 74.35, 61.94, 21.37, 14.12.

HRMS (EI) Calcd for $C_{18}H_{17}FO_4$ $(M)^+$: 316.1111; Found: 316.1115.



3e'

2-ethoxy-1-(4-fluorophenyl)-2-oxoethyl 3-phenylpropanoate

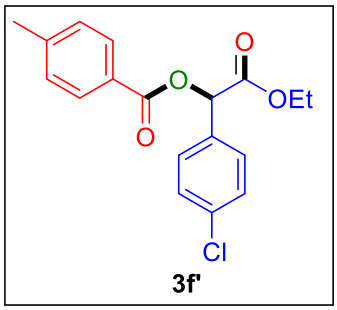
Colorless oil, (40 mg, 49% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.32 – 7.24 (m, 2H), 7.24 – 7.17 (m, 3H), 7.07 (t, *J* = 8.6 Hz, 2H), 5.89 (s, 1H), 4.30 – 4.04 (m, 2H), 3.05 – 2.96 (m, 2H), 2.89 – 2.70 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.24, 168.76, 163.23 (d, *J* = 248.3 Hz), 140.25, 129.89 (d, *J* = 2.1 Hz), 129.59 (d, *J* = 8.4 Hz), 128.62, 128.40, 126.44, 115.88 (d, *J* = 21.8 Hz), 73.94, 61.93, 35.58, 30.79, 14.09.

HRMS (EI) Calcd for $C_{19}H_{19}FO_4$ $(M)^+$: 330.1267; Found: 330.1269.



3f'

1-(4-chlorophenyl)-2-ethoxy-2-oxoethyl 4-methylbenzoate

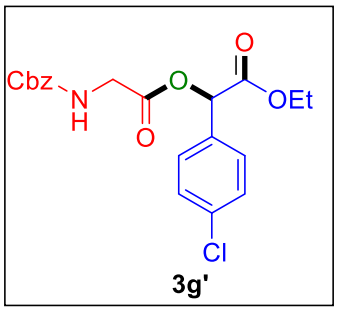
White solid, 59 – 61℃. (54 mg, 65% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 15/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.10 (s, 1H), 4.27 – 4.14 (m, 2H), 2.40 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.59, 165.84, 144.45, 135.23, 132.82, 130.04, 129.28, 129.09, 129.01, 126.42, 74.18, 61.94, 21.79, 14.07.

HRMS (EI) Calcd for $C_{18}H_{17}ClO_4$ $(M)^+$: 332.0815; Found: 332.0810.



3g'

ethyl 2-((((benzyloxy)carbonyl)glycyl)oxy)-2-(4-chlorophenyl)acetate

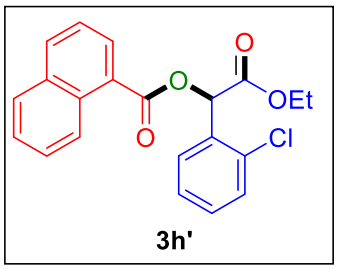
Colorless oil, (77 mg, 76% yield).

TLC: Rf = 0.1 (Petroleum ether/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 9H), 5.93 (s, 1H), 5.30 (t, *J* = 5.4 Hz, 1H), 5.12 (s, 2H), 4.25 – 4.08 (m, 4H), 1.21 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.51, 168.07, 156.35, 136.25, 135.59, 131.92, 129.20, 129.05, 128.66, 128.35, 128.23, 74.53, 67.31, 62.24, 42.77, 14.07.

HRMS (EI) Calcd for $C_{20}H_{20}ClNO_6$ $(M)^+$: 405.0979; Found: 405.0971.



3h'

1-(2-chlorophenyl)-2-ethoxy-2-oxoethyl 1-naphthoate

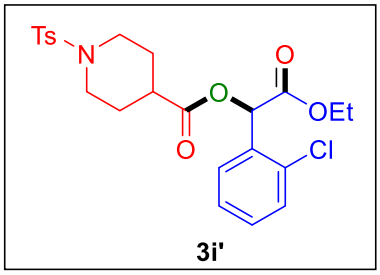
Colorless oil, (76 mg, 83% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 15/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.54 – 7.43 (m, 3H), 7.37 – 7.29 (m, 2H), 6.81 (s, 1H), 4.36 – 4.19 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.63, 166.58, 134.41, 134.00, 133.86, 132.49, 131.53, 130.94, 130.63, 130.17, 129.77, 128.64, 128.06, 127.38, 126.42, 126.12, 125.83, 124.61, 71.82, 62.15, 14.17.

HRMS (EI) Calcd for $C_{21}H_{17}ClO_4$ $(M)^+$: 368.0815; Found: 368.0811.



3i'

1-(2-chlorophenyl)-2-ethoxy-2-oxoethyl 1-tosylpiperidine-4-carboxylate

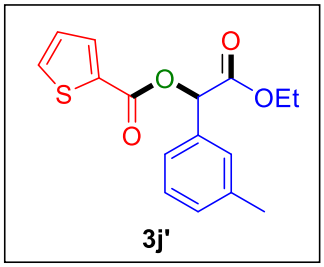
Colorless oil, (63 mg, 53% yield).

TLC: Rf = 0.1 (Petroleum ether/EtOAc = 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.23 (m, 6H), 6.39 (s, 1H), 4.26 – 4.07 (m, 2H), 3.69 – 3.48 (m, 2H), 2.61 – 2.38 (m, 6H), 2.11 – 1.84 (m, 4H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.05, 168.19, 143.68, 134.31, 133.18, 132.02, 130.69, 130.13, 129.77, 129.48, 127.77, 127.31, 71.30, 62.08, 45.30, 45.24, 39.72, 27.46, 27.29, 21.63, 14.07.

HRMS (EI) Calcd for $C_{23}H_{26}ClNO_6S$ $(M)^+$: 479.1169; Found: 479.1165.



3j'

2-ethoxy-2-oxo-1-(m-tolyl)ethyl thiophene-2-carboxylate

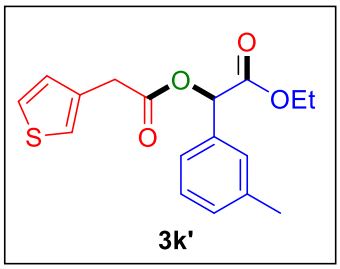
Colorless oil, (62 mg, 82% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 4.2 Hz, J_2 = 1.2 Hz, 1H), 7.58 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.10 (dd, J_1 = 4.8 Hz, J_2 = 4.2 Hz, 1H), 6.07 (s, 1H), 4.29 – 4.22 (m, 1H), 4.21 – 4.13 (m, 1H), 2.38 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.80, 161.55, 138.67, 134.39, 133.82, 133.28, 132.78, 130.12, 128.78, 128.35, 127.94, 124.81, 75.14, 61.84, 21.51, 14.10.

HRMS (EI) Calcd for $C_{16}H_{16}O_4S$ $(M)^+$: 304.0769; Found: 304.0765.



ethyl 2-(2-(thiophen-3-yl)acetoxy)-2-(m-tolyl)acetate

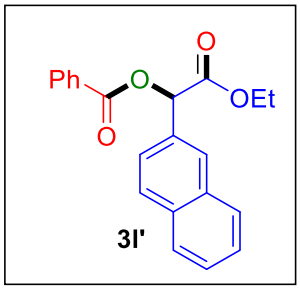
Colorless oil, (56 mg, 71% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 4H), 7.21 – 7.15 (m, 2H), 7.07 (d, *J* = 4.8 Hz, 1H), 5.89 (s, 1H), 4.23 – 4.09 (m, 2H), 3.82 (d, *J* = 16.2 Hz, 1H), 3.77 (d, *J* = 16.2 Hz, 1H), 2.35 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.54, 168.82, 138.64, 133.70, 133.02, 130.08, 128.73, 128.63, 128.28, 125.77, 124.78, 123.22, 75.03, 61.78, 35.50, 21.45, 14.05.

HRMS (EI) Calcd for $C_{17}H_{18}O_4S$ $(M)^+$: 318.0926; Found: 318.0921.



2-ethoxy-1-(naphthalen-2-yl)-2-oxoethyl benzoate

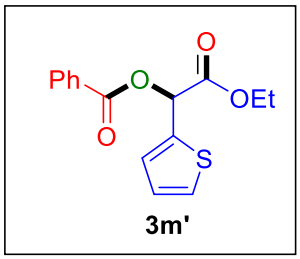
Colorless oil, (67 mg, 80% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 15/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.6 Hz, 2H), 8.06 (s, 1H), 7.92 – 7.83 (m, 3H), 7.69 (dd, J_1= 8.8 Hz, J_2 = 1.6 Hz, 1H), 7.60 – 7.42 (m, 5H), 6.31 (s, 1H), 4.30 – 4.12 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.93, 166.04, 133.68, 133.59, 133.22, 131.53, 130.10, 129.42, 128.86, 128.58, 128.37, 127.88, 127.55, 126.90, 126.67, 124.84, 75.31, 61.95, 14.15.

HRMS (EI) Calcd for $C_{21}H_{18}O_4$ $(M)^+$: 334.1205; Found: 334.1200.



3m'

2-ethoxy-1-(furan-2-yl)-2-oxoethyl benzoate

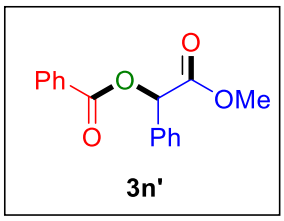
Colorless oil, (50 mg, 69% yield).

TLC: Rf = 0.15 (Petroleum ether/EtOAc = 15/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 – 8.10 (m, 2H), 7.61 – 7.55 (m, 1H), 7.48 – 7.44 (m, 2H), 7.38 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.26 (d, J = 3.6 Hz, 1H), 7.04 (dd, J_1 = 4.8 Hz, J_2 = 3.6 Hz, 1H), 6.42 (s, 1H), 4.31 – 4.20 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.05, 165.76, 135.82, 133.67, 130.15, 129.13, 128.58, 127.81, 127.21, 127.11, 70.91, 62.20, 14.12.

HRMS (EI) Calcd for $C_{15}H_{14}O_4S$ $(M)^+$: 290.0613; Found: 290.0611.



3n'

2-methoxy-2-oxo-1-phenylethyl benzoate

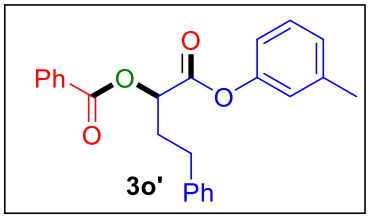
Colorless oil, (53 mg, 79% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.09 (m, 2H), 7.61 – 7.56 (m, 2H), 7.52 – 7.45 (m, 1H), 7.41 – 7.31 (m, 5H), 6.18 (s, 1H), 3.65 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.10, 165.63, 133.85, 133.35, 129.76, 129.17, 129.07, 128.74, 128.33, 127.51, 74.75, 52.39.

HRMS (EI) Calcd for $C_{16}H_{14}O_4$ $(M)^+$: 270.0892; Found: 270.0897.



3o'

1-oxo-4-phenyl-1-(m-tolyloxy)butan-2-yl benzoate

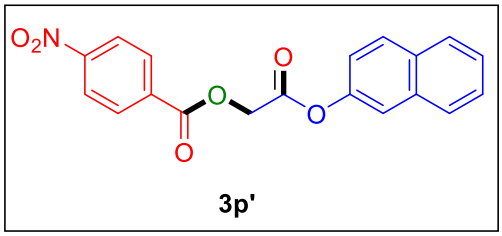
Colorless oil, (42 mg, 45% yield).

TLC: Rf = 0.3 (Petroleum ether/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 – 8.05 (m, 2H), 7.61 – 7.55 (m, 1H), 7.51 – 7.44 (m, 2H), 7.34 – 7.30 (m, 2H), 7.28 – 7.21 (m, 4H), 7.03 (d, J = 7.8 Hz, 1H), 6.93 – 6.86 (m, 2H), 5.41 (dd, J_1 = 7.8 Hz, J_2 = 4.8 Hz, 1H), 2.99 – 2.91 (m, 2H), 2.52 – 2.44 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.01, 166.22, 150.34, 140.42, 139.87, 133.61, 130.05, 129.39, 129.31, 128.80, 128.64, 128.62, 127.08, 126.52, 122.02, 118.37, 72.37, 33.00, 31.66, 21.39.

HRMS (EI) Calcd for $C_{24}H_{22}O_4$ $(M)^+$: 374.1518; Found: 374.1517.



3p'

2-(naphthalen-2-yloxy)-2-oxoethyl 4-nitrobenzoate

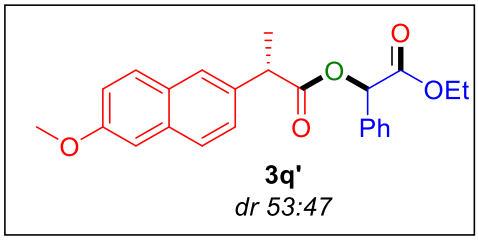
Yellowish solid, 144 – 146℃. (43 mg, 49% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 10/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 – 8.29 (m, 4H), 7.87 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 1.8 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.27 (dd, J = 8.9, 2.3 Hz, 1H), 5.20 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.15, 164.34, 151.05, 147.72, 134.49, 133.77, 131.79, 131.29, 129.83, 127.95, 127.84, 126.96, 126.20, 123.83, 120.57, 118.54, 61.85.

HRMS (EI) Calcd for $C_{19}H_{13}NO_6$ $(M)^+$: 351.0743; Found: 351.0747.



2-ethoxy-2-oxo-1-phenylethyl (2S)-2-(6-methoxynaphthalen-2-yl)propanoate

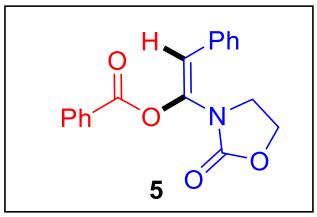
Colorless oil, (83 mg, 85% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 3H), 7.50 – 7.28 (m, 6H), 7.15 – 7.08 (m, 2H), 5.91 (s, 0.53H), 5.89 (s, 0.47H), 4.22 – 3.98 (m, 3H), 3.90 (s, 1.59H), 3.89 (s, 1.41H), 1.66 (d, *J* = 7.2 Hz, 1.41H), 1.64 (d, *J* = 7.2 Hz, 1.59H), 1.18 (t, *J* = 7.2 Hz, 1.41H), 1.06 (t, *J* = 7.2 Hz, 1.59H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.16, 174.03, 168.89, 168.65, 157.76, 157.76, 135.15, 135.08, 134.06, 133.93, 133.88, 133.86, 129.45, 129.42, 129.18, 129.11, 129.05, 129.00, 128.80, 128.74, 127.58, 127.49, 127.24, 127.16, 126.61, 126.49, 126.35, 126.26, 119.04, 119.01, 105.72, 105.68, 74.98, 74.88, 61.79, 61.67, 55.40, 55.39, 45.32, 45.26, 18.82, 18.55, 14.08, 13.94.

HRMS (EI) Calcd for $C_{24}H_{24}O_5$ $(M)^+$: 392.1624; Found: 392.1629.



(E)-1-(2-oxooxazolidin-3-yl)-2-phenylvinyl benzoate

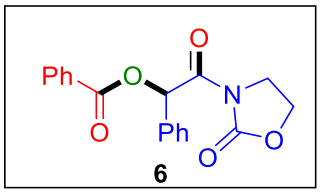
Colorless oil, (71 mg, 92% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.2 Hz, 2H), 7.66 – 7.60 (m, 1H), 7.53 – 7.46 (m, 2H), 7.41 – 7.35 (m, 4H), 7.34 – 7.27 (m, 1H), 6.39 (s, 1H), 4.47 – 4.26 (m, 2H), 3.91 – 3.65 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.30, 155.66, 137.68, 134.13, 132.13, 130.44, 128.88, 128.75, 128.47, 128.27, 128.22, 116.59, 63.25, 44.61.

HRMS (EI) Calcd for $C_{18}H_{15}NO_4$ $(M)^+$: 309.1001; Found: 309.1005.



2-oxo-2-(2-oxooxazolidin-3-yl)-1-phenylethyl benzoate

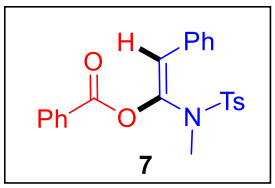
Colorless oil, (21 mg, 32% yield, *0.2 mmol scale*).

TLC: Rf = 0.15 (Petroleum ether/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.71 – 7.65 (m, 2H), 7.59 – 7.54 (m, 1H), 7.47 – 7.40 (m, 5H), 7.30 (s, 1H), 4.49 – 4.42 (m, 1H), 4.38 – 4.32 (m, 1H), 4.17 – 4.10 (m, 1H), 3.95 – 3.88 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.94, 166.41, 153.06, 133.58, 133.02, 130.04, 129.69, 129.24, 129.17, 128.90, 128.52, 73.97, 62.67, 42.60.

HRMS (EI) Calcd for $C_{18}H_{15}NO_5$ $(M)^+$: 325.0950; Found: 325.0953.



(E)-1-((N,4-dimethylphenyl)sulfonamido)-2-phenylvinyl benzoate

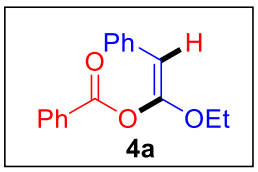
White solid, 63 – 65℃. (92 mg, 90% yield).

TLC: Rf = 0.3 (Petroleum ether/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.57 (m, 3H), 7.42 – 7.35 (m, 4H), 7.32 – 7.28 (m, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.34 (s, 1H), 3.13 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.70, 143.79, 140.01, 136.13, 133.82, 131.99, 130.16, 129.54, 128.74, 128.72, 128.50, 128.44, 127.68, 119.46, 36.73, 21.46.

HRMS (EI) Calcd for $C_{23}H_{21}NO_4S$ $(M)^+$: 407.1191; Found: 407.1188.



(*Z*)-1-ethoxy-2-phenylvinyl benzoate

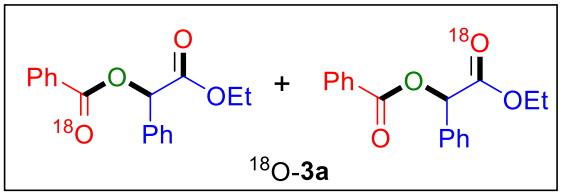
Colorless crystal, 98 – 99°C. (64 mg, 95% yield).

TLC: Rf = 0.4 (Petroleum ether/EtOAc = 30/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.68 – 7.58 (m, 1H), 7.54 – 7.44 (m, 2H), 7.34 – 7.26 (m, 2H), 7.23 – 7.14 (m, 2H), 7.12 – 7.03 (m, 1H), 5.39 (s, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.48, 152.77, 134.29, 134.07, 130.49, 128.80, 128.53, 127.46, 125.80, 91.54, 65.56, 14.50.

HRMS (EI) Calcd for $C_{17}H_{16}O_3$ $(M)^+$: 268.1099; Found: 268.1094.



2-ethoxy-2-oxo-1-phenylethyl ^{18}O-benzoate

Colorless oil, (59 mg, 82% yield).

TLC: Rf = 0.2 (Petroleum ether/EtOAc = 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.53 (m, 3H), 7.48 – 7.37 (m, 5H), 6.14 (s, 1H), 4.33 – 4.07 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.90, 168.87, 166.00, 165.97, 134.20, 133.56, 130.07, 129.40, 129.32, 128.93, 128.55, 127.72, 75.11, 61.86, 14.12.

HRMS (EI) Calcd for $C_{17}H_{16}O_3{}^{18}O$ $(M)^+$: 286.1091; Found: 286.1093.

8. References

1. Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, 62, 7512.

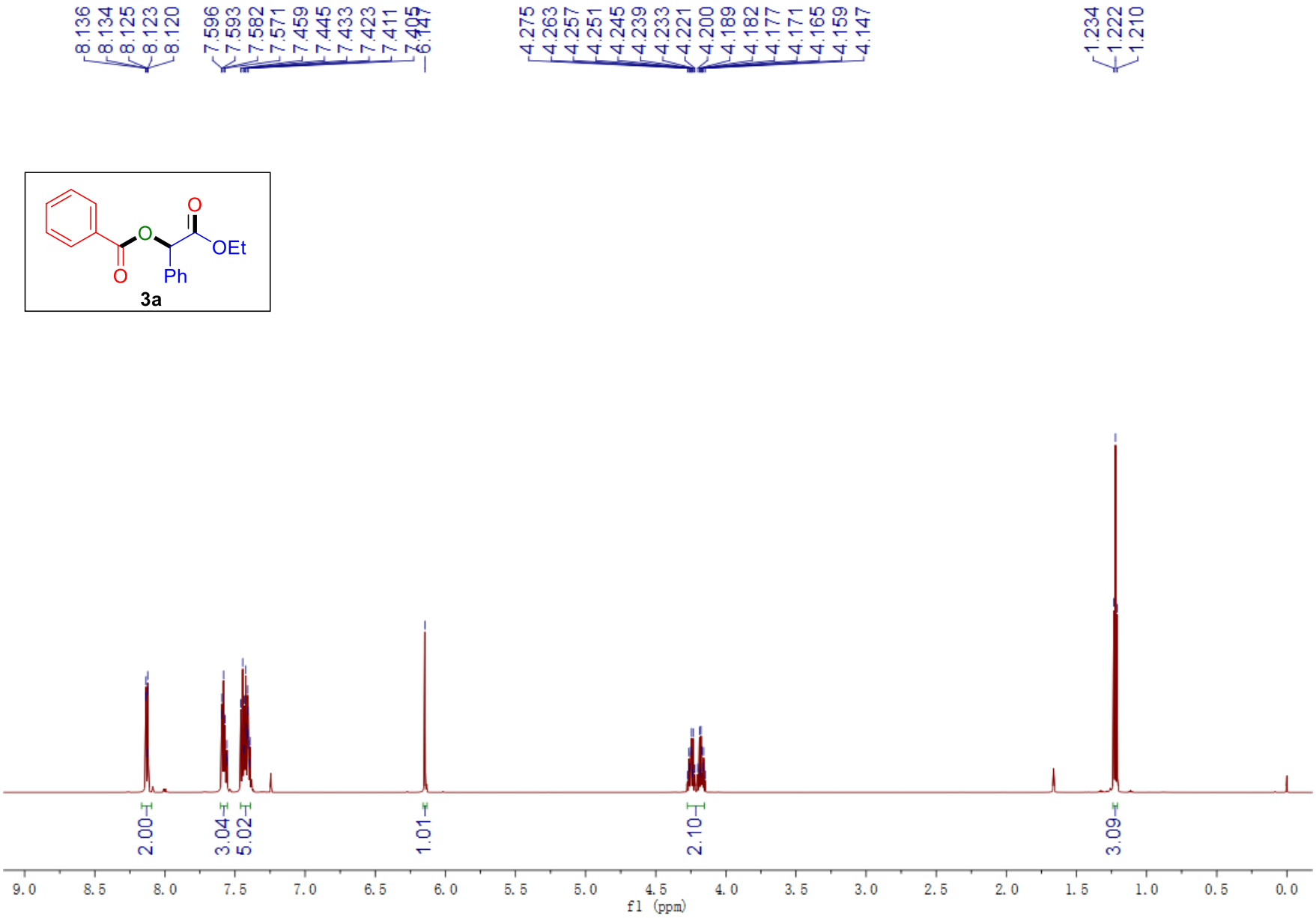
2. Armarego, W. L. F.; Chai, C. L. L. *Purification of laboratory chemical*, 6th ed.; Elsevier: Burlington, 2009; Chapter 4.

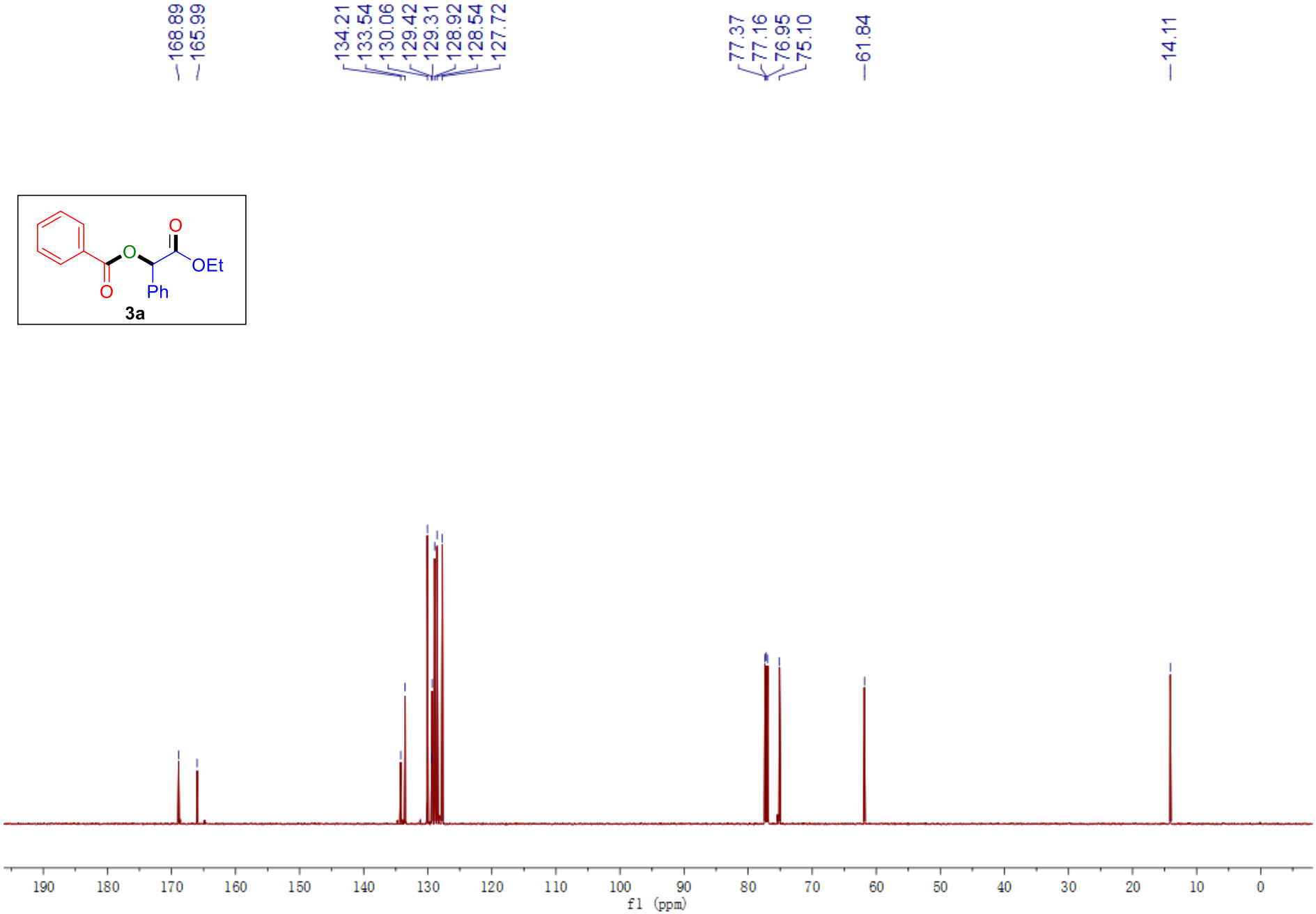
3. (a) Zhang, C. W., Li, Z. D., Zhu, L., Yu, L. M., Wang, Z. T., Li, C. Z. *J. Am. Chem. Soc.* **2013**, *135*, 14082. (b) Nyfeler, E., Renaud, P. *Org. Lett.* **2008**, *10*, 985. (c) Mallik, A. K., Qiu, H. D., Kuwahara, Y., Takafuji, M., Ihara, H. *Chem. Commun.* **2015**, *51*, 14243. (d) Huang, B.; Zeng, L. W.; Shen, Y. Y.; Cui, S. L. *Angew. Chem., Int. Ed.* **2017,** *56*, 4565.

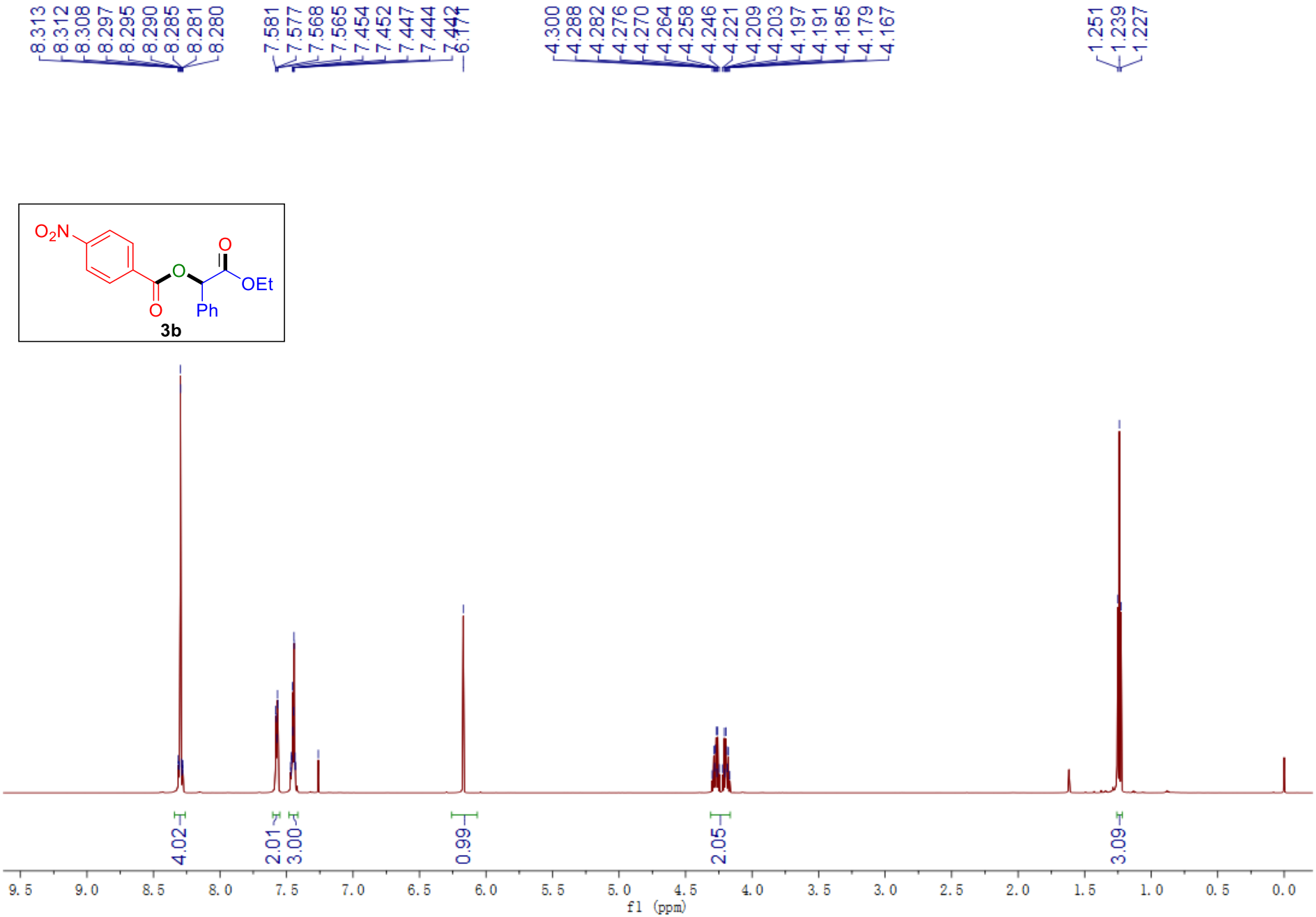
4. (a) Zhu, X. Q.; Yuan, H.; Sun, Q.; Zhou, B.; Han, X. Q.; Zhang, Z. X.; Lu, X.; Ye, L. W. *Green Chem.* **2018**, *20*, 4287. (b) Graf, K.; Ruhl, C. L.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2013**, *52*, 12727. (c) Jouvin, K.; Bayle, A.; Legrand, F.; Evano, G. *Org. Lett.* **2012**, *14*, 1652.

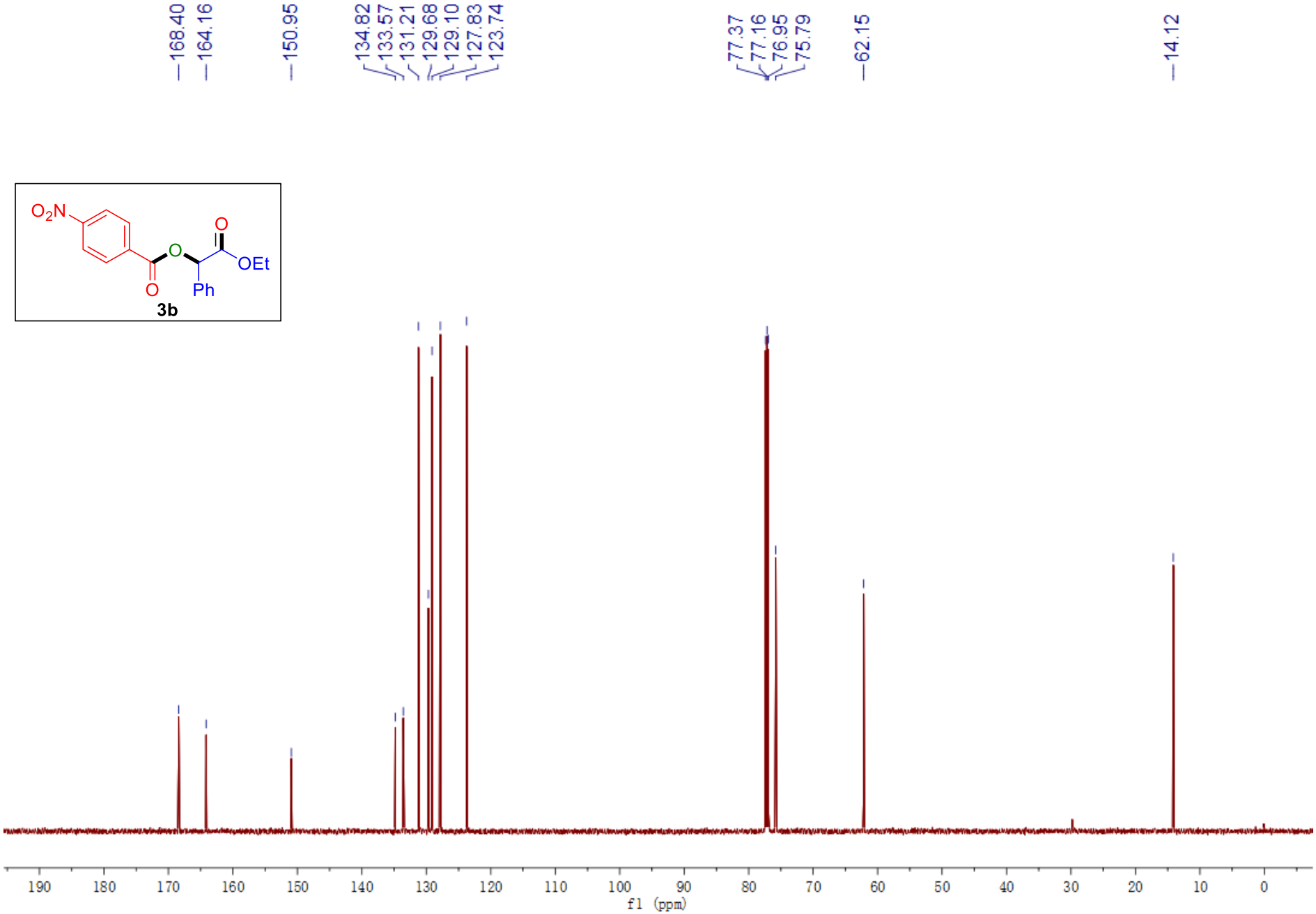
5. Zhang, X. J.; Zhang, Y. S.; Huang, J.; Hsung, R. P.; Kurtz, K. C. M.; Oppenheimer, J.; Petersen, M. E.; Sagamanova, I. K.; Shen, L. C.; Tracey, M. R. *J. Org. Chem.* **2006**, *71*, 4170.

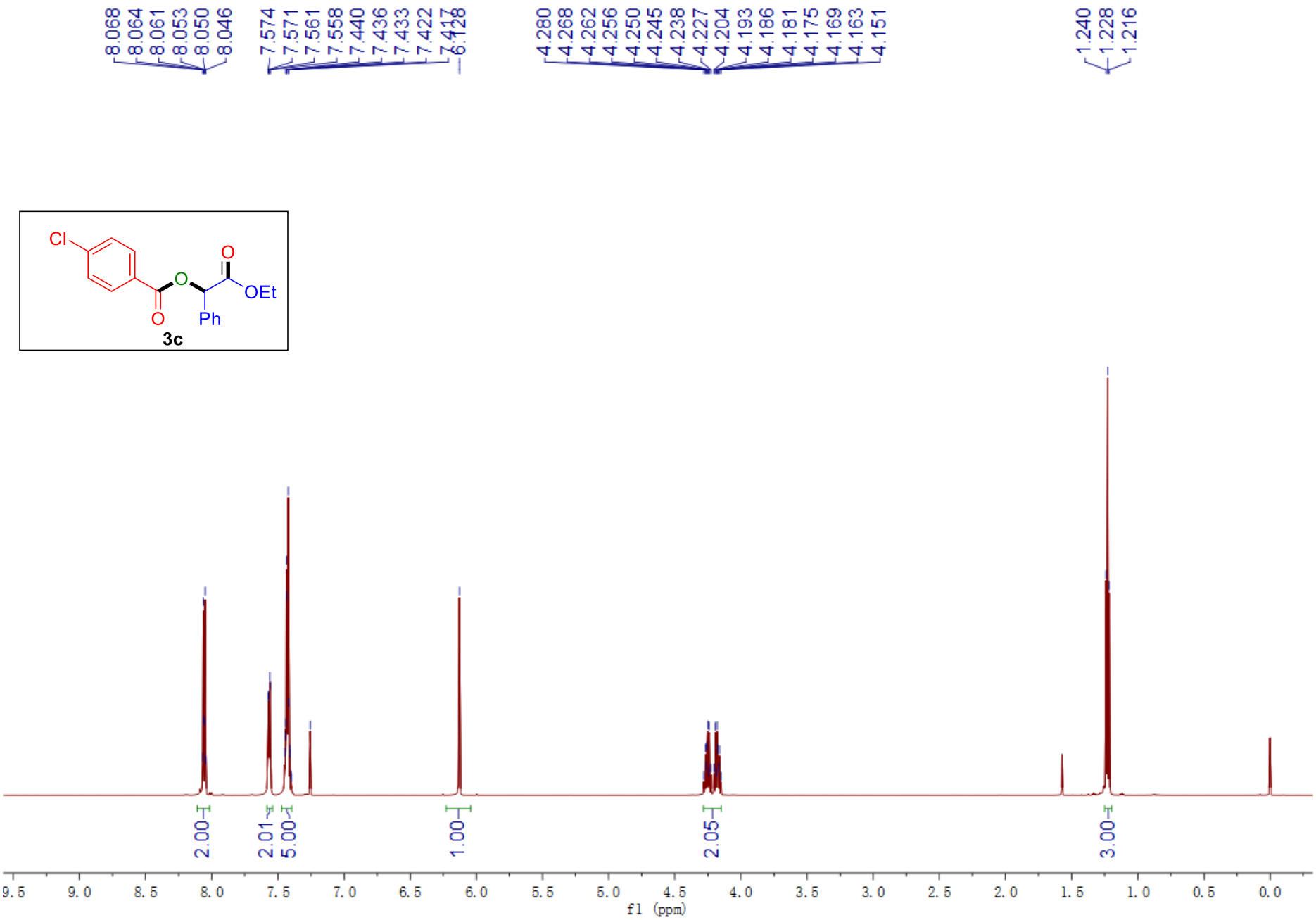
9. Copies of NMR spectrum

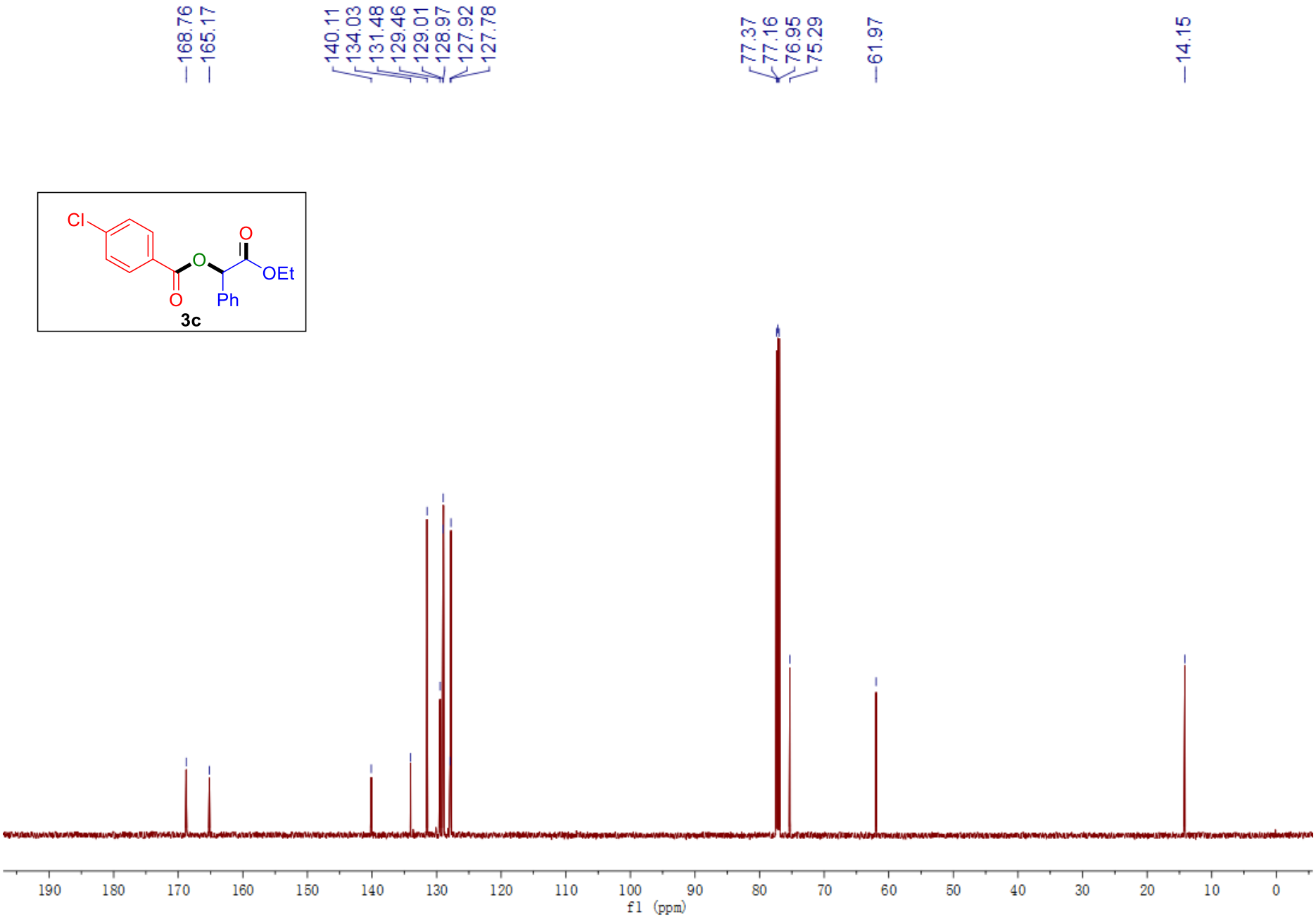


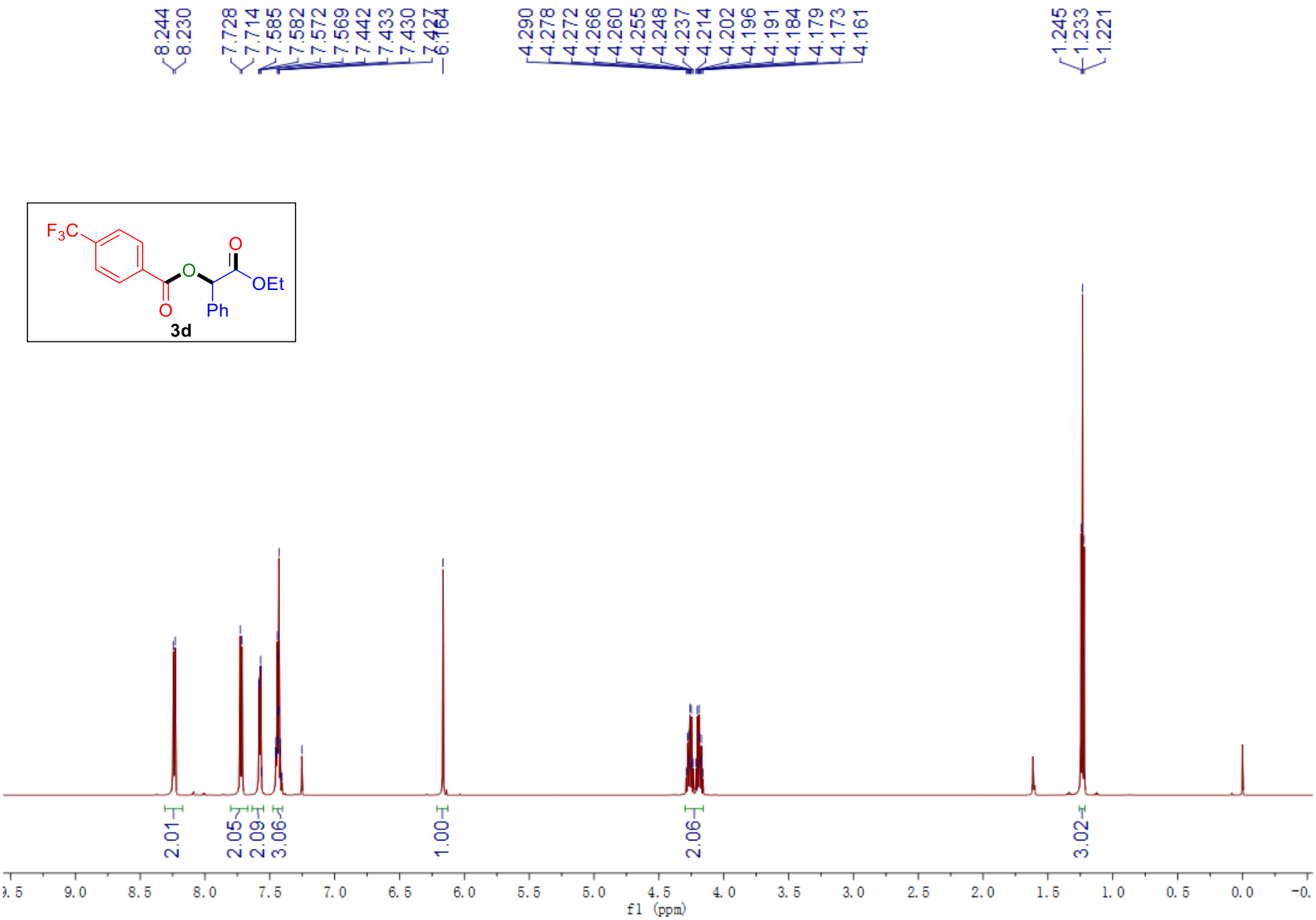

168.89
165.99
134.21
133.54
130.06
129.42
129.31
128.92
128.54
127.72
77.37
77.16
76.95
75.10
61.84
14.11
O
O
O
OEt
Ph
3a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

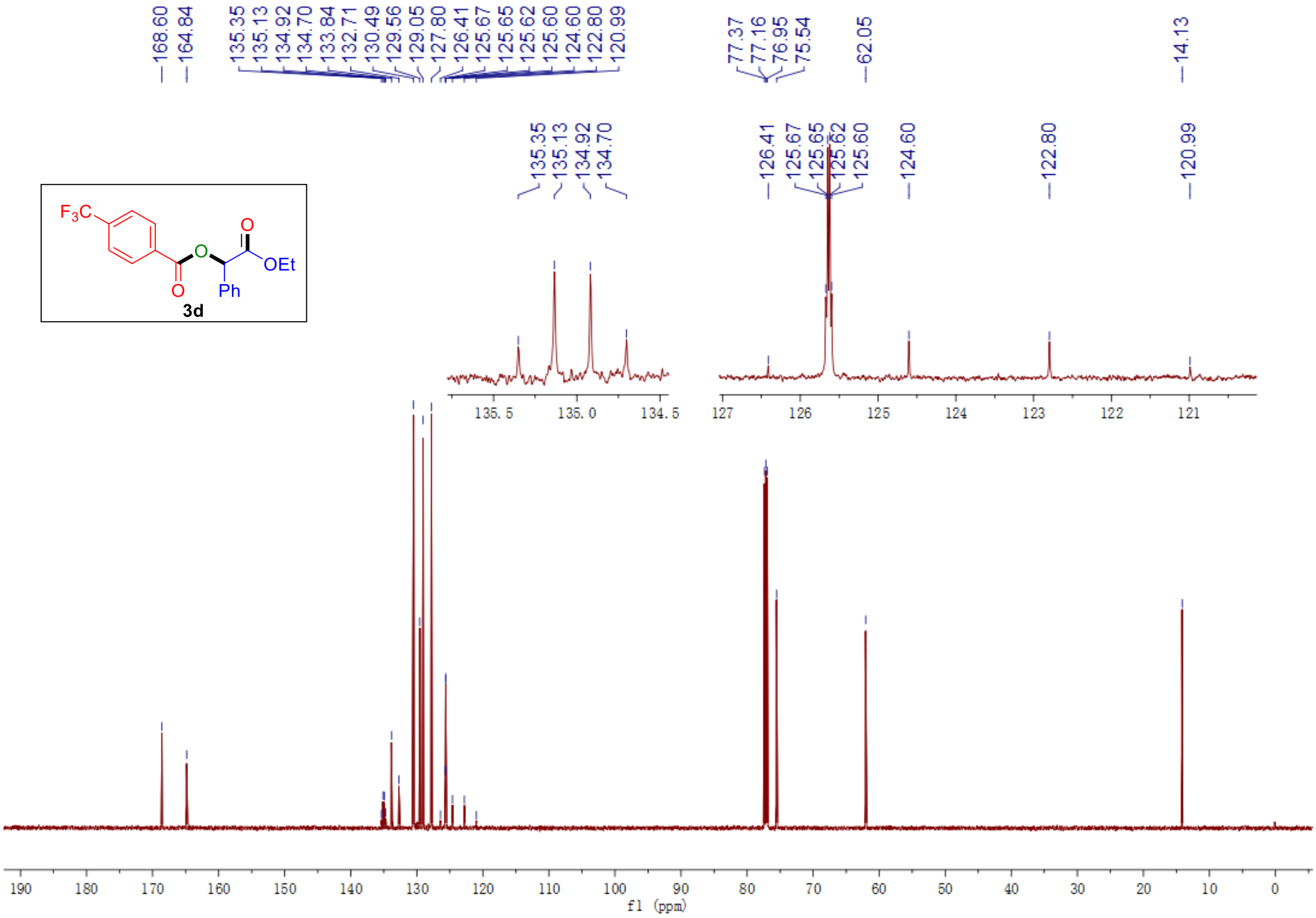

8.313
8.312
8.308
8.297
8.295
8.290
8.285
8.281
8.280
7.581
7.577
7.568
7.565
7.454
7.452
7.447
7.444
7.442
6.171
4.300
4.288
4.282
4.276
4.270
4.264
4.258
4.246
4.221
4.209
4.203
4.197
4.191
4.185
4.179
4.167
1.251
1.239
1.227
O2N
O
O
OEt
O
Ph
3b
4.02
2.01
3.00
0.99
2.05
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

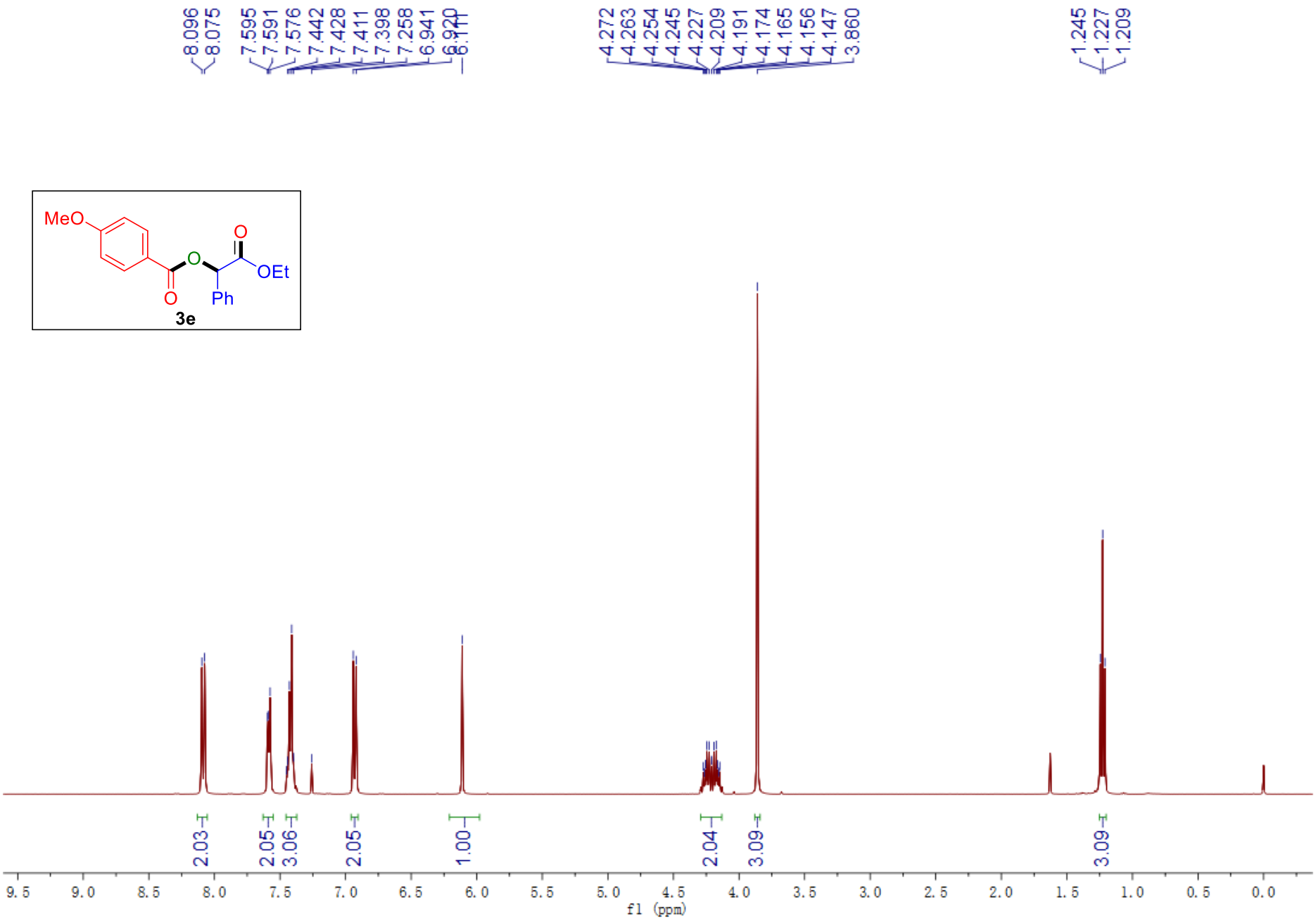

168.40
164.16
150.95
134.82
133.57
131.21
129.68
129.10
127.83
123.74
77.37
77.16
76.95
75.79
62.15
14.12
O2N
O
O
OEt
O
Ph
3b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

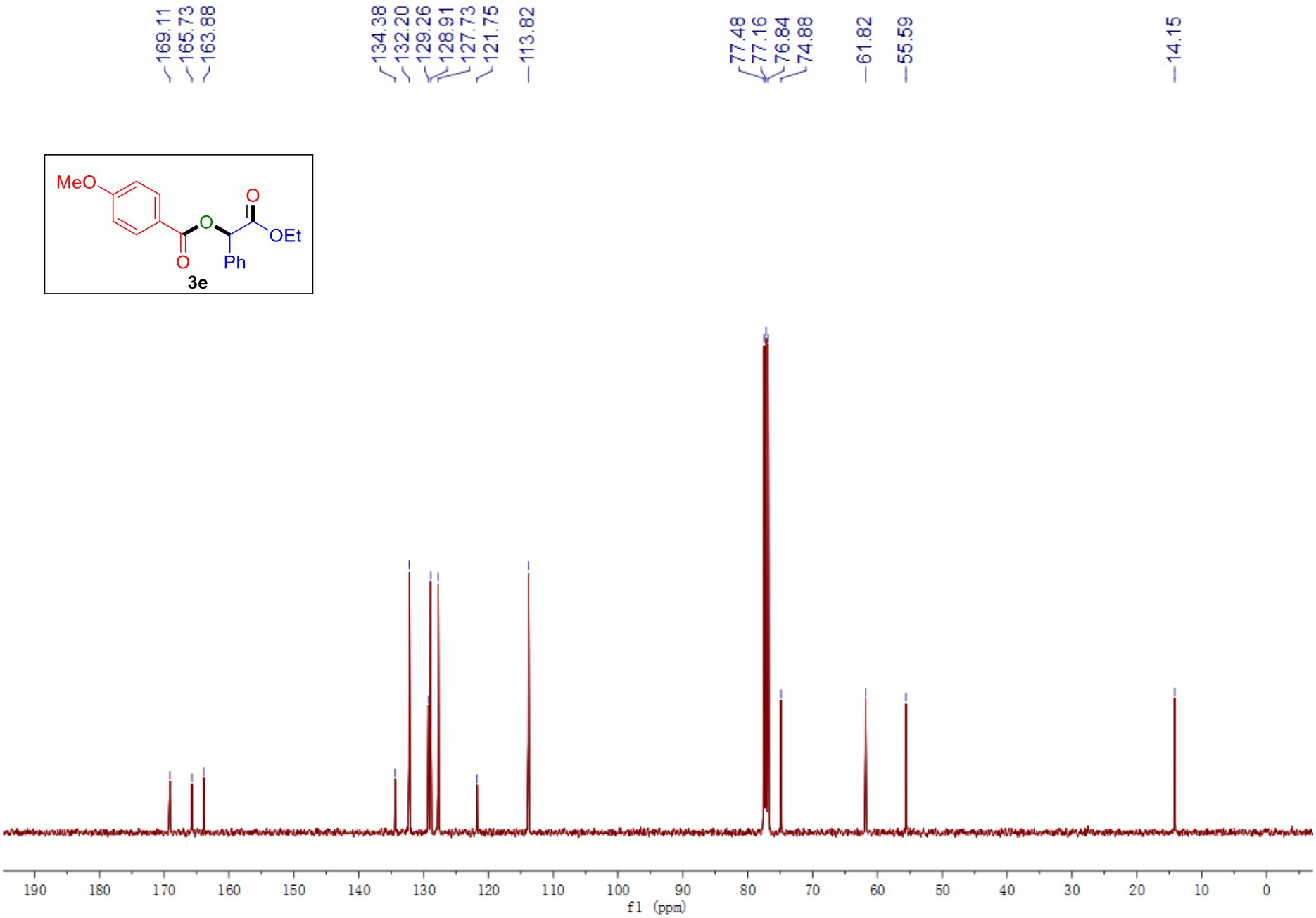

8.068
8.064
8.061
8.053
8.050
8.046
7.574
7.571
7.561
7.558
7.440
7.436
7.433
7.422
7.417
6.128
4.280
4.268
4.262
4.256
4.250
4.245
4.238
4.227
4.204
4.193
4.186
4.181
4.175
4.169
4.163
4.151
1.240
1.228
1.216
Cl
O
O
O
OEt
Ph
3c
2.00
2.01
5.00
1.00
2.05
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

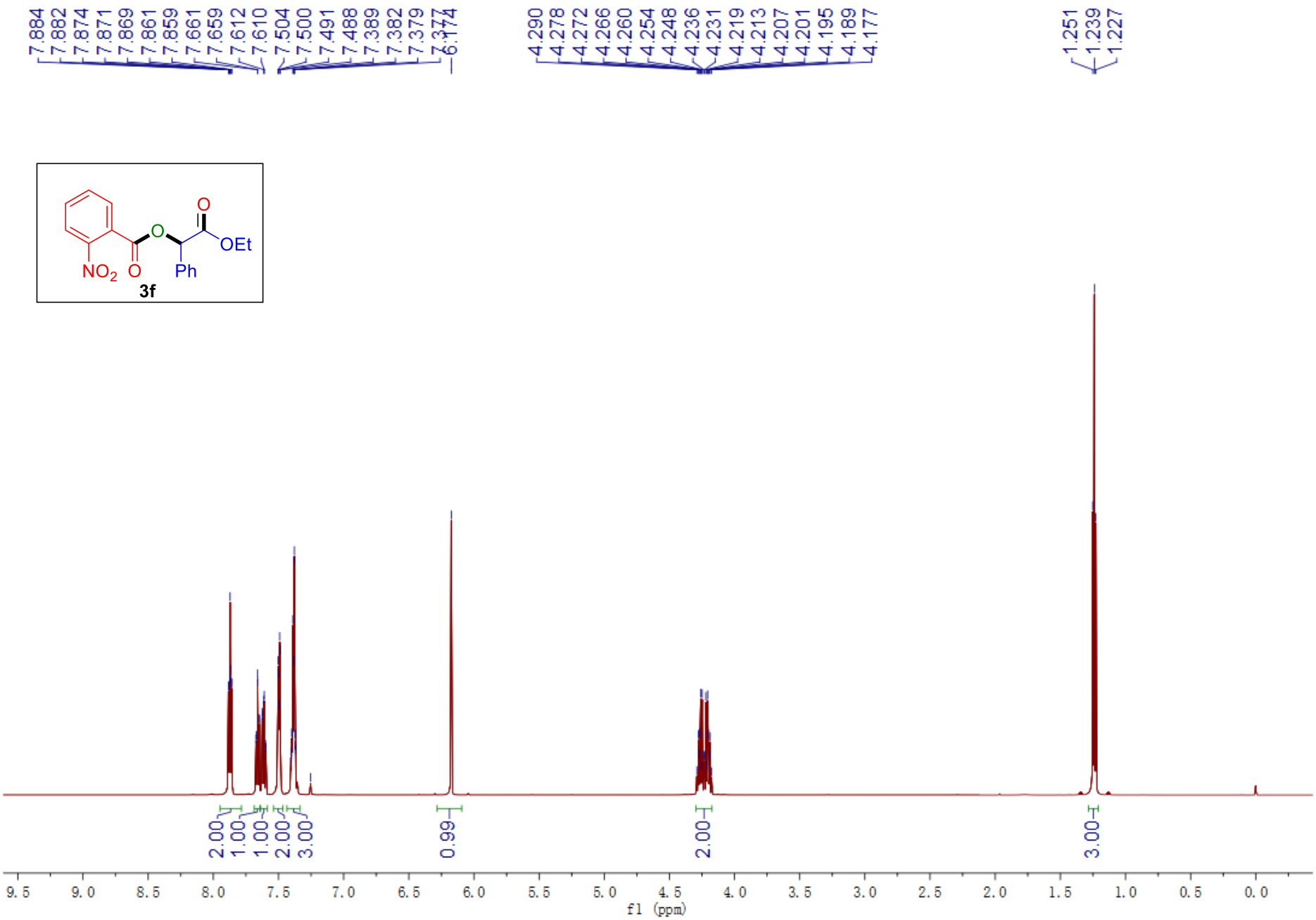

168.76
165.17
140.11
134.03
131.48
129.46
129.01
128.97
127.92
127.78
77.37
77.16
76.95
75.29
61.97
14.15
Cl
O
O
O
OEt
Ph
3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

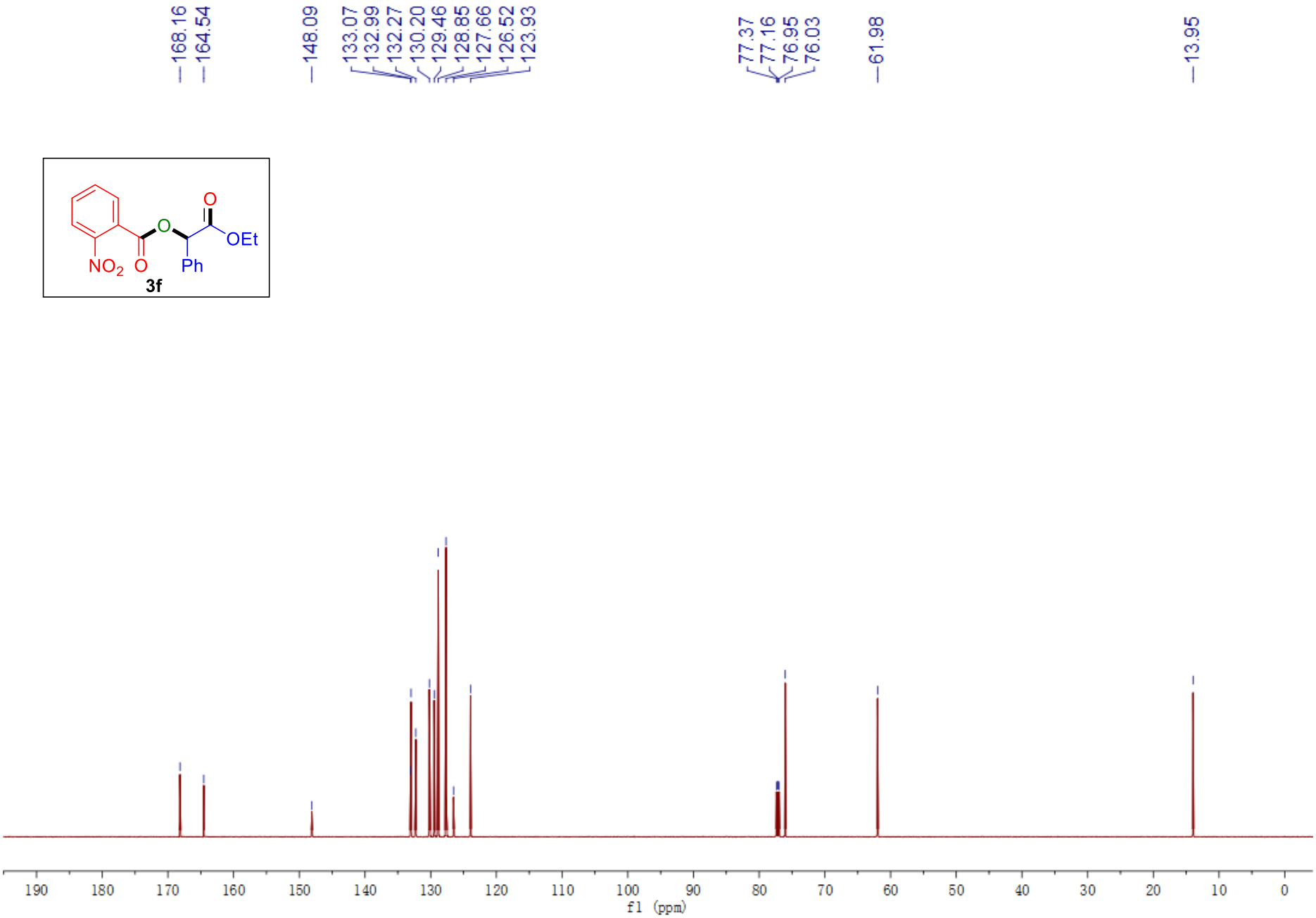

8.244
8.230
7.728
7.714
7.585
7.582
7.572
7.569
7.442
7.433
7.430
7.427
6.164
4.290
4.278
4.272
4.266
4.260
4.255
4.248
4.237
4.214
4.202
4.196
4.191
4.184
4.179
4.173
4.161
1.245
1.233
1.221
F3C
O
O
OEt
O
Ph
3d
2.01
2.05
2.09
3.06
1.00
2.06
3.02
f1 (ppm)

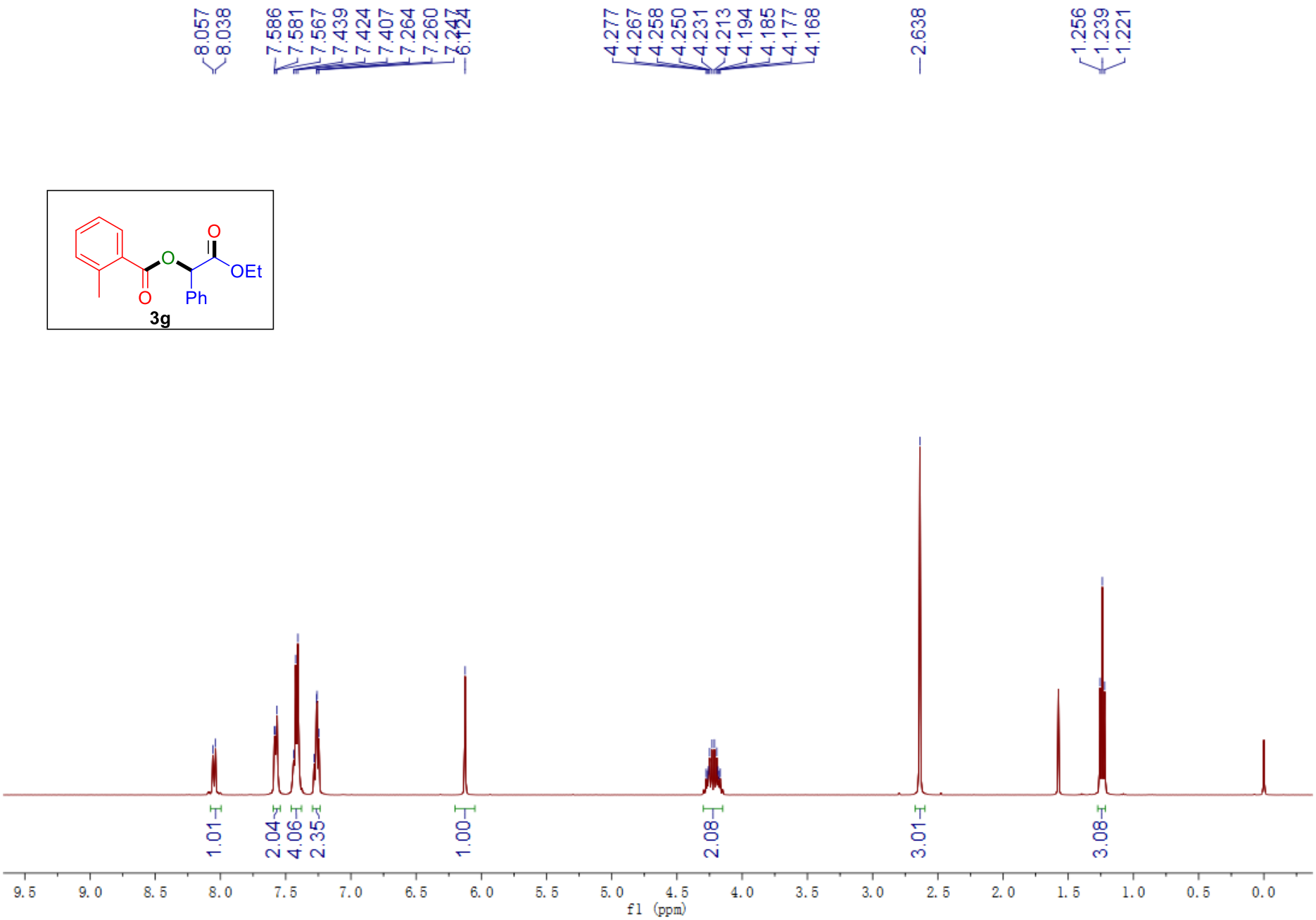

168.60
164.84
135.35
135.13
134.92
134.70
133.84
132.71
130.49
129.56
129.05
127.80
126.41
125.67
125.65
125.62
125.60
124.60
122.80
120.99
77.37
77.16
76.95
75.54
62.05
14.13
F3C
O
O
O
OEt
Ph
3d
f1 (ppm)

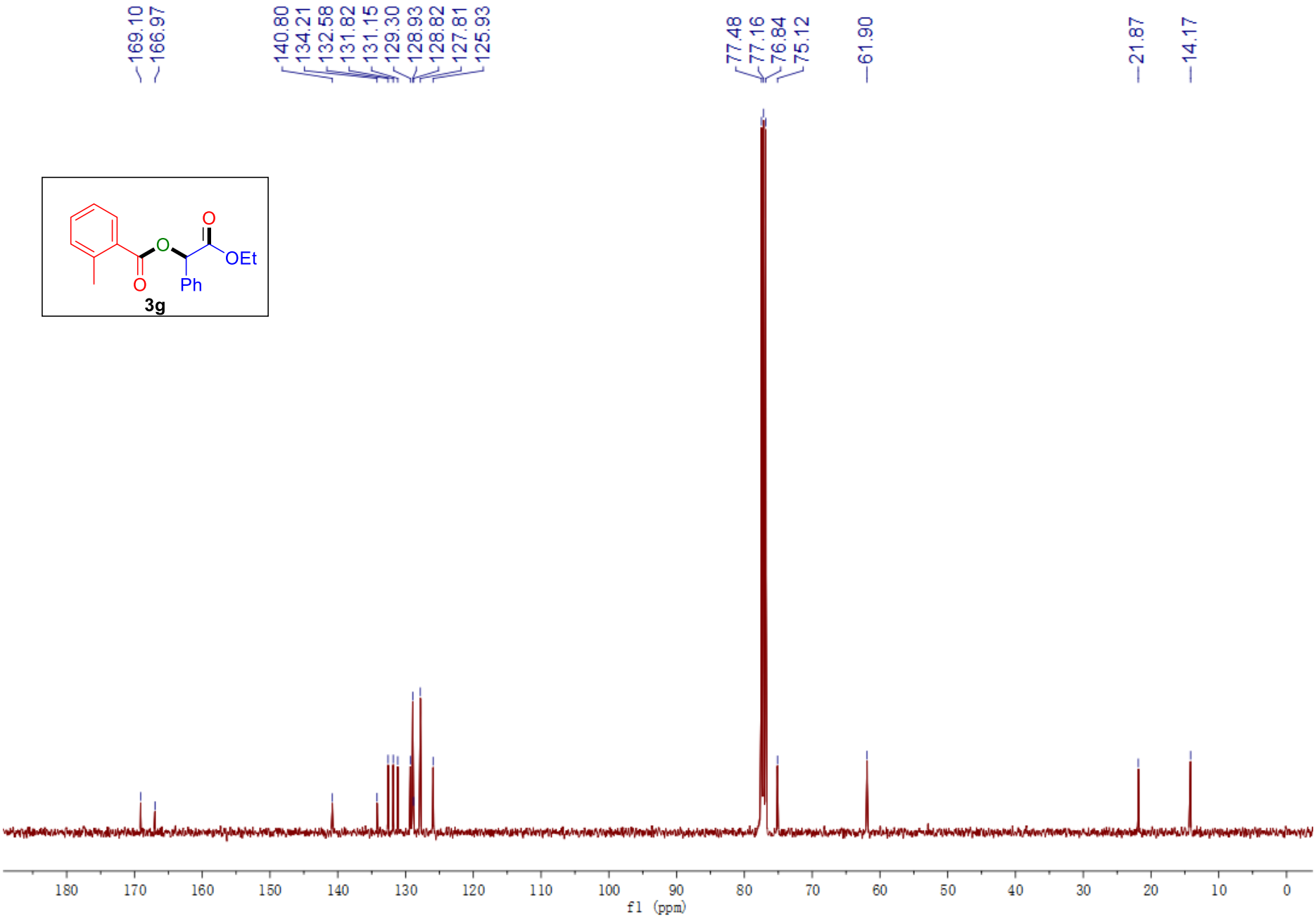

8.096
8.075
7.595
7.591
7.576
7.442
7.428
7.411
7.398
7.258
6.941
6.920
6.911
4.272
4.263
4.254
4.245
4.227
4.209
4.191
4.174
4.165
4.156
4.147
3.860
1.245
1.227
1.209
MeO
O
O
O
OEt
Ph
3e
2.03
2.05
3.06
2.05
1.00
2.04
3.09
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

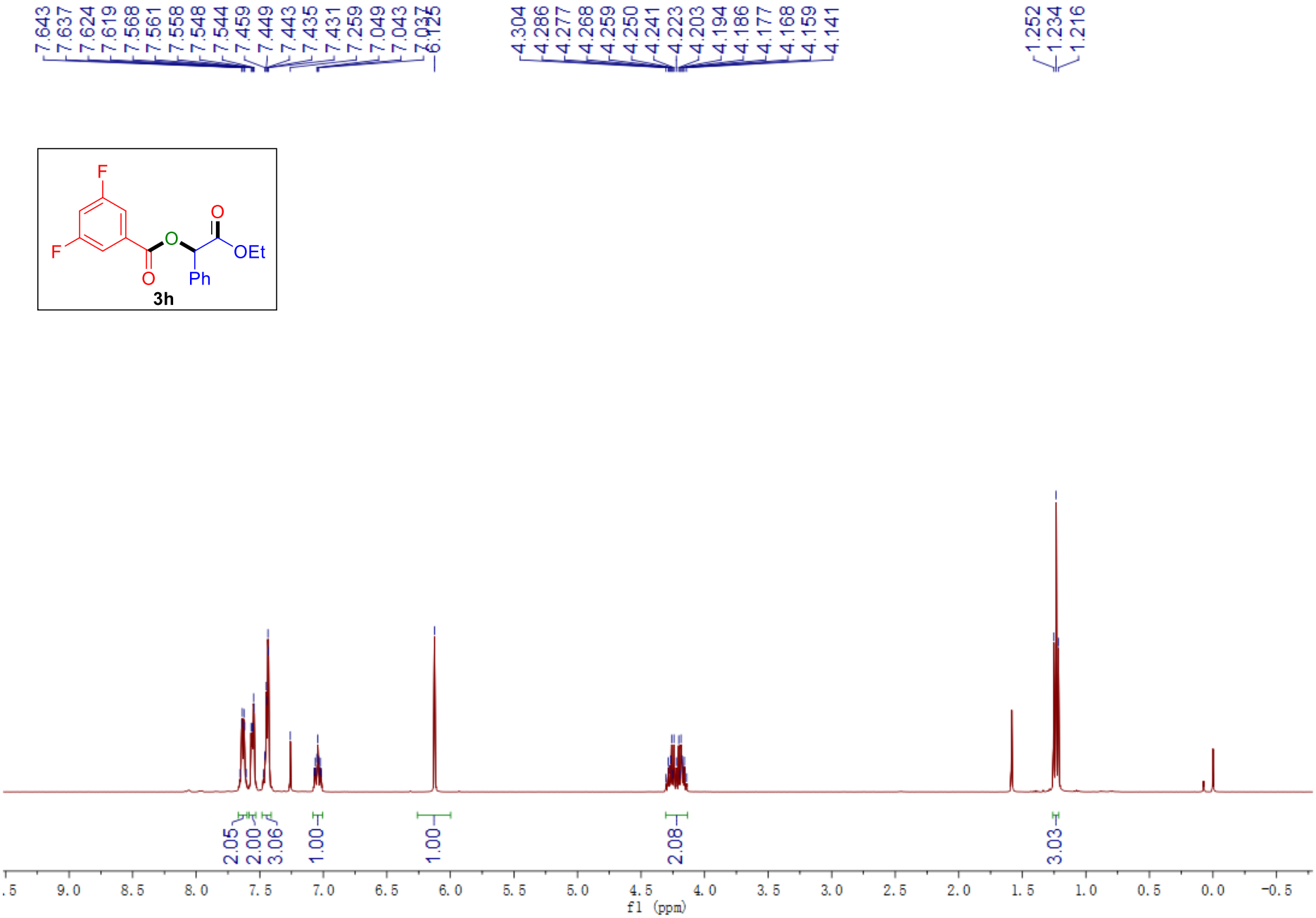

169.11
165.73
163.88
134.38
132.20
129.26
128.91
127.73
121.75
113.82
77.48
77.16
76.84
74.88
61.82
55.59
14.15
MeO
O
O
O
OEt
Ph
3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

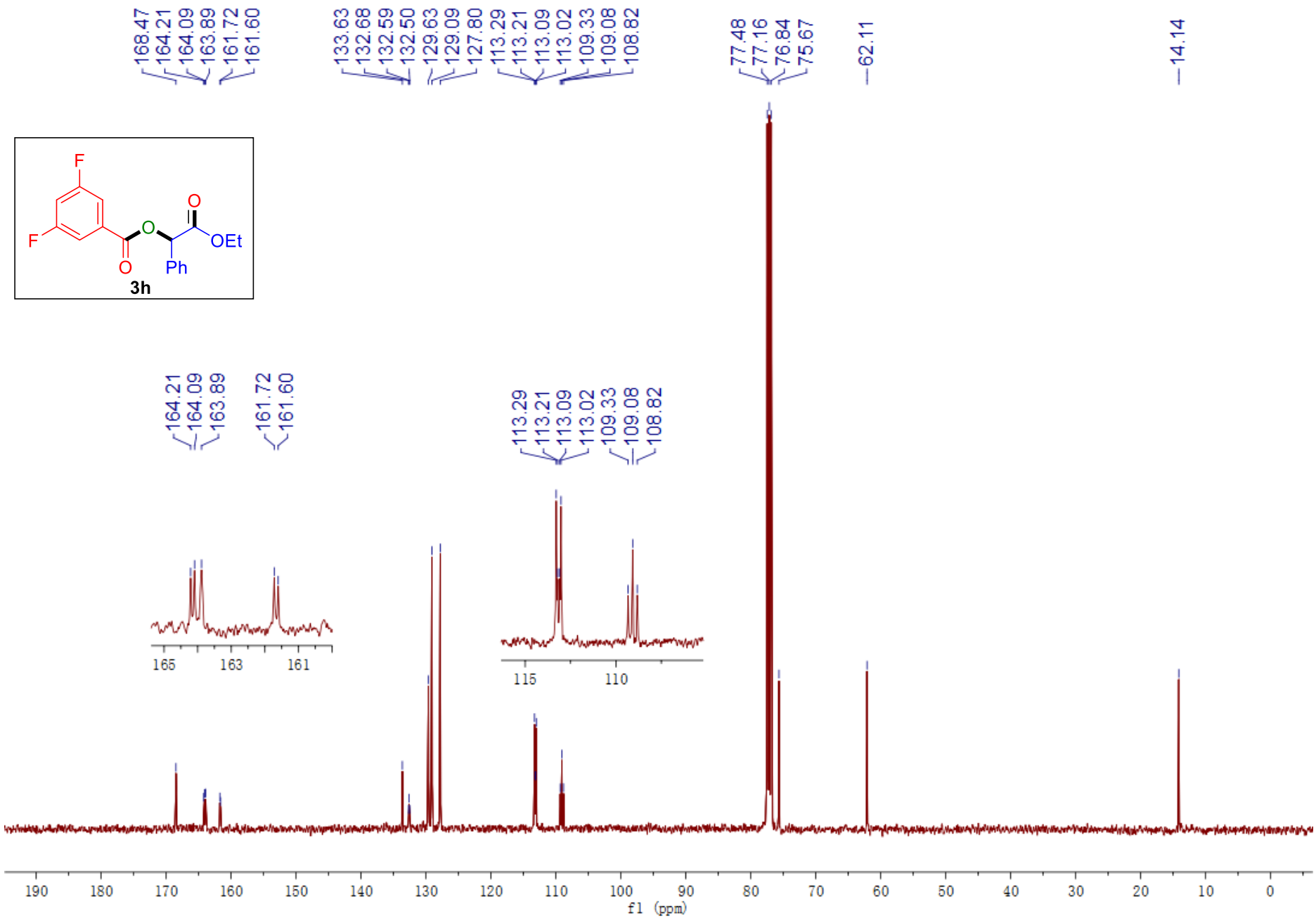

7.884
7.882
7.874
7.871
7.869
7.861
7.859
7.661
7.659
7.612
7.610
7.504
7.500
7.491
7.488
7.389
7.382
7.379
7.377
7.174
4.290
4.278
4.272
4.266
4.260
4.254
4.248
4.236
4.231
4.219
4.213
4.207
4.201
4.195
4.189
4.177
1.251
1.239
1.227
O
O
OEt
NO2
O
Ph
3f
2.00
1.00
1.00
2.00
3.00
0.99
2.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

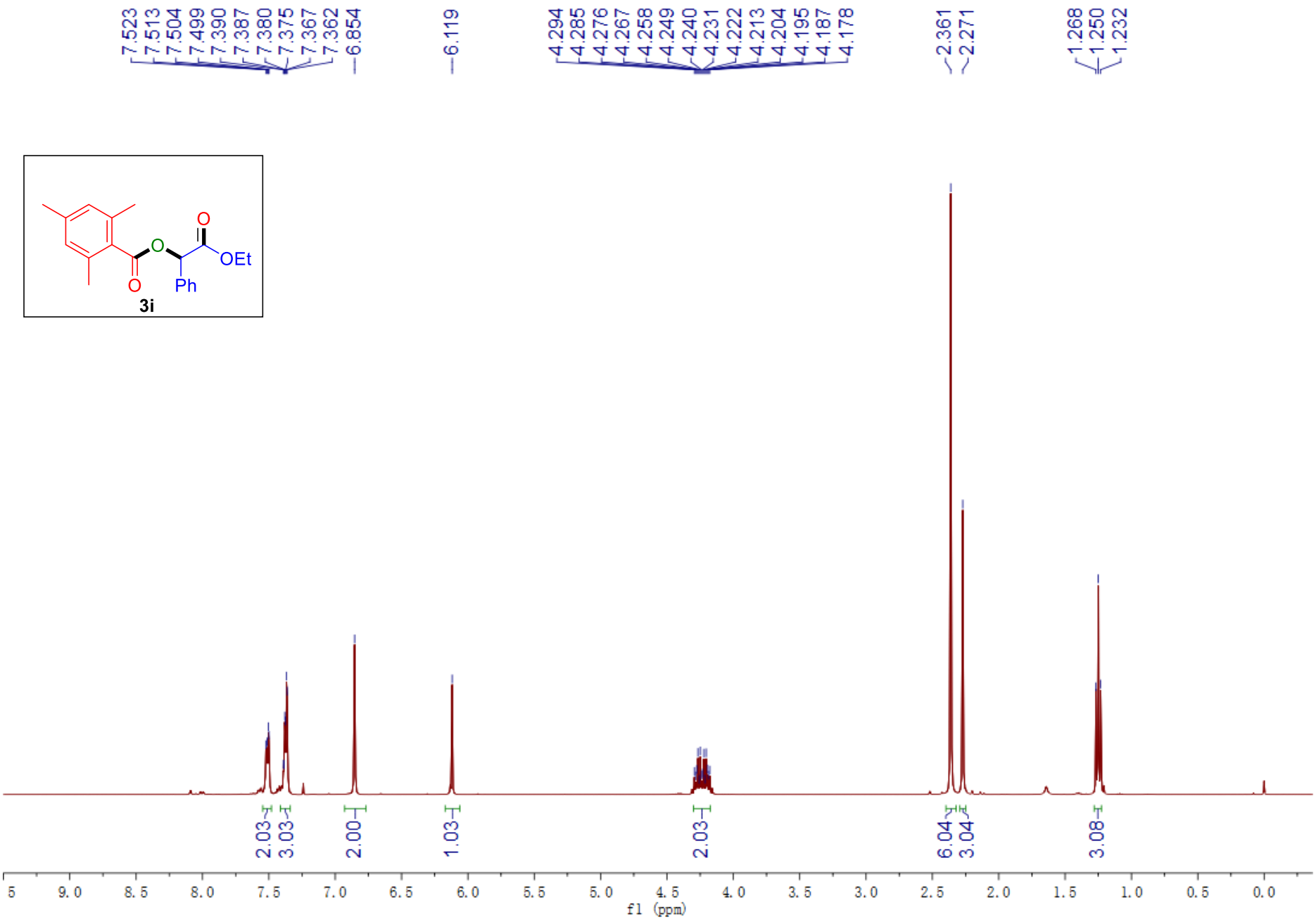

168.16
164.54
148.09
133.07
132.99
132.27
130.20
129.46
128.85
127.66
126.52
123.93
77.37
77.16
76.95
76.03
61.98
13.95
O
O
OEt
NO2
O
Ph
3f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

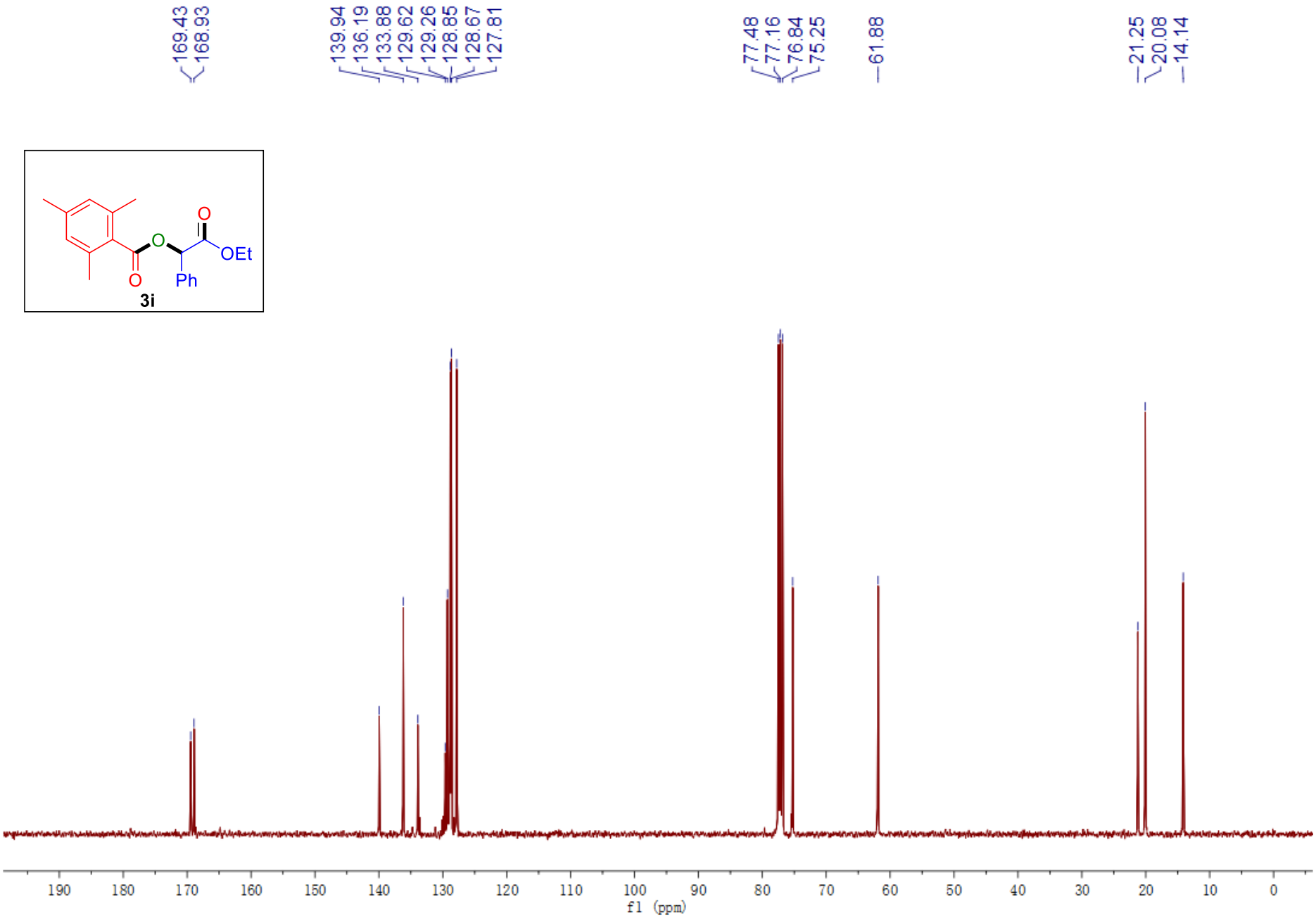

8.057
8.038
7.586
7.581
7.567
7.439
7.424
7.407
7.264
7.260
6.124
4.277
4.267
4.258
4.250
4.231
4.213
4.194
4.185
4.177
4.168
2.638
1.256
1.239
1.221
O
O
OEt
O
Ph
3g
1.01
2.04
4.06
2.35
1.00
2.08
3.01
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

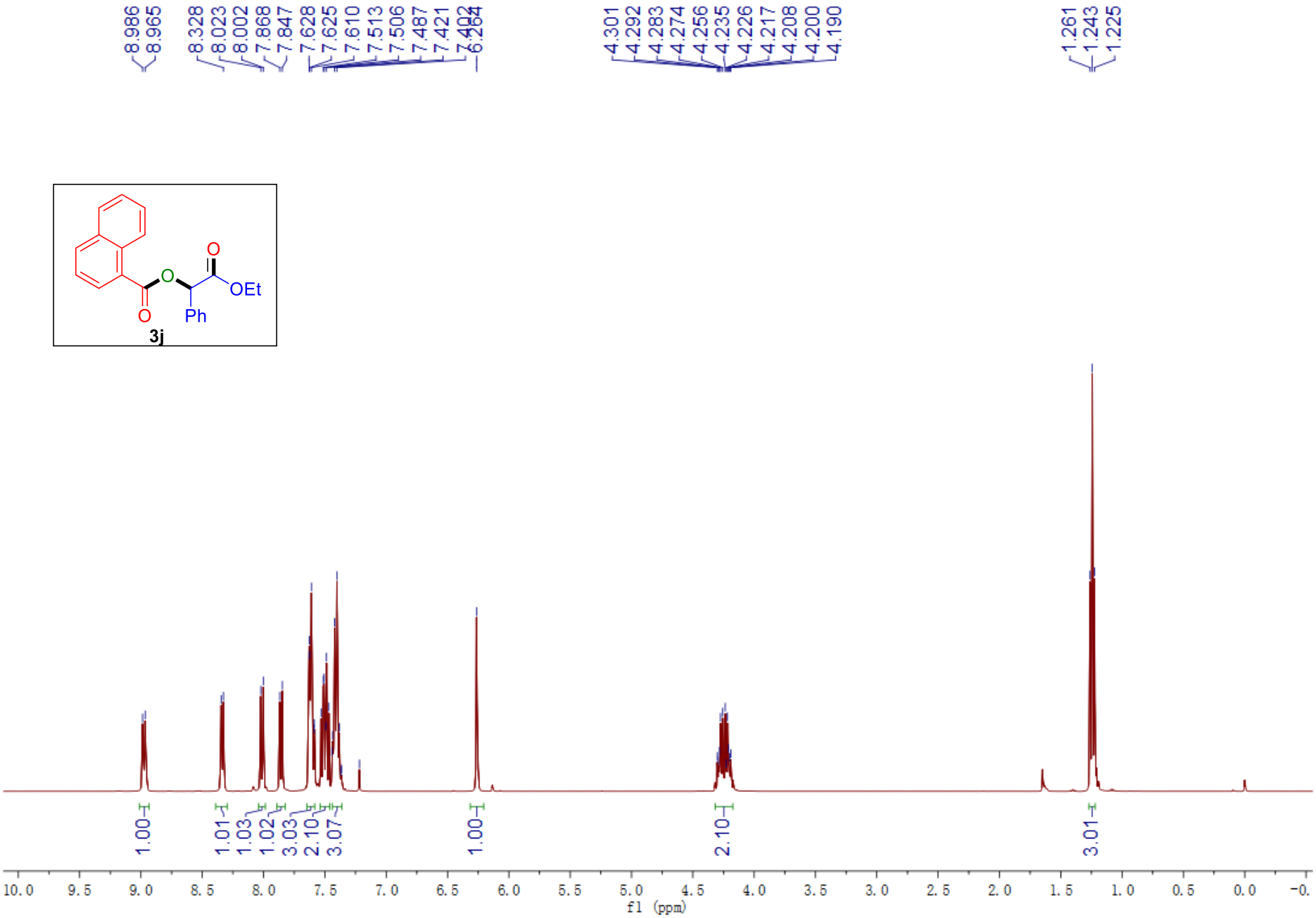

169.10
166.97
140.80
134.21
132.58
131.82
131.15
129.30
128.93
128.82
127.81
125.93
77.48
77.16
76.84
75.12
61.90
21.87
14.17
O
O
OEt
O
Ph
3g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

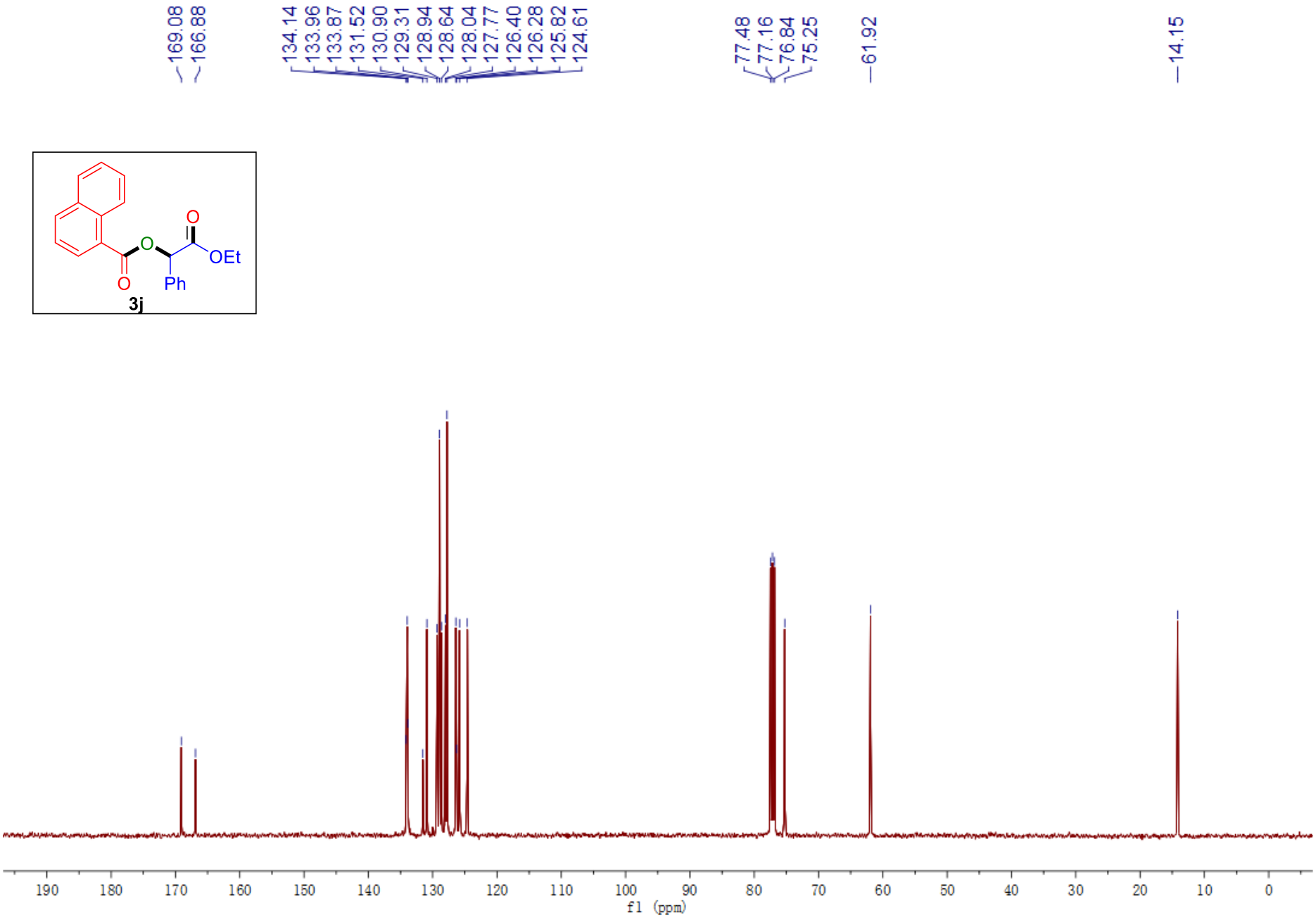

7.643
7.637
7.624
7.619
7.568
7.561
7.558
7.548
7.544
7.459
7.449
7.443
7.435
7.431
7.259
7.049
7.043
7.037
6.125
4.304
4.286
4.277
4.268
4.259
4.250
4.241
4.223
4.203
4.194
4.186
4.177
4.168
4.159
4.141
1.252
1.234
1.216
F
F
O
O
O
OEt
Ph
3h
2.05
2.00
3.06
1.00
1.00
2.08
3.03
f1 (ppm)

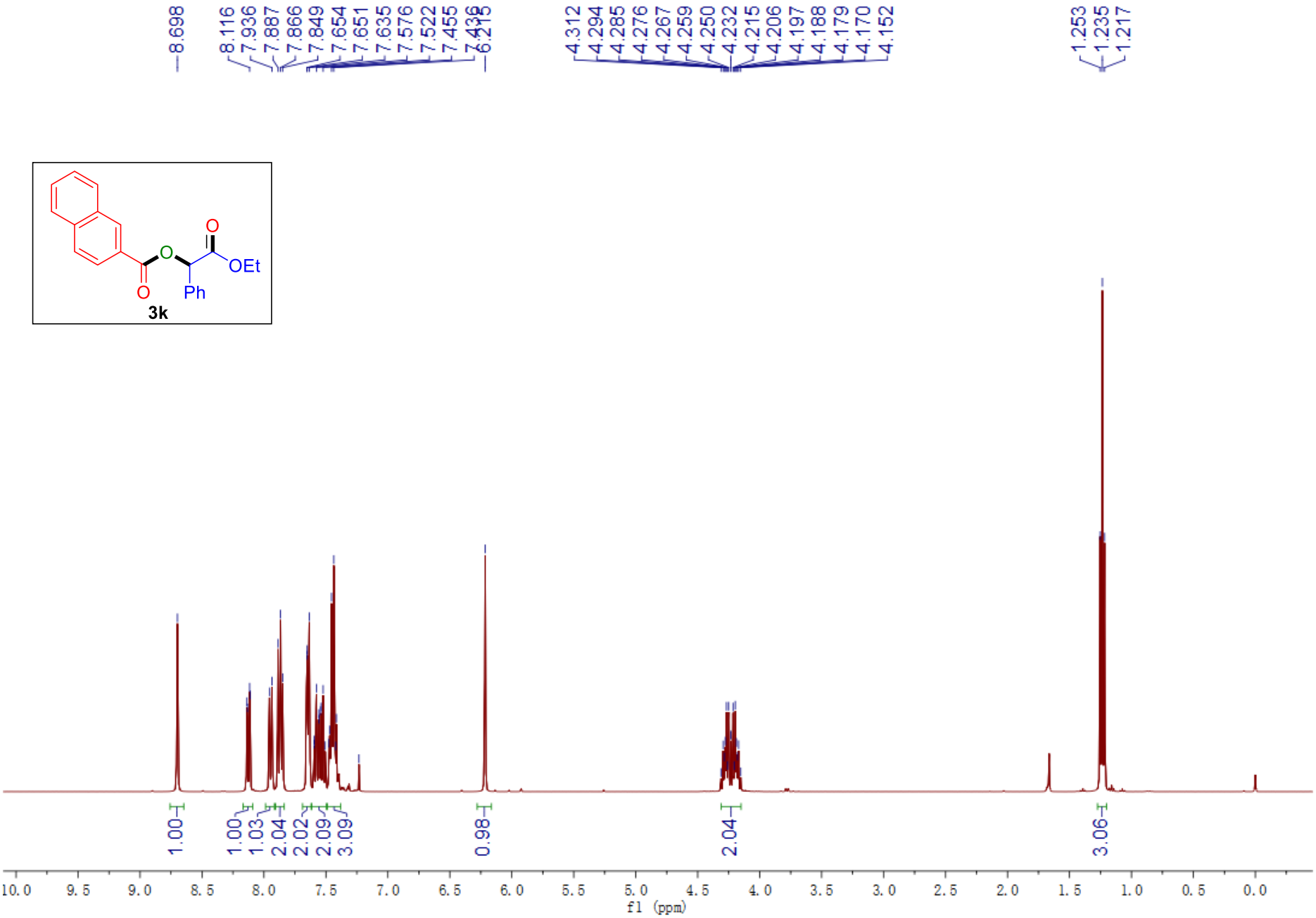

168.47
164.21
164.09
163.89
161.72
161.60
133.63
132.68
132.59
132.50
129.63
129.09
127.80
113.29
113.21
113.09
113.02
109.33
109.08
108.82
77.48
77.16
76.84
75.67
62.11
14.14
F
F
O
O
O
OEt
Ph
3h
165
163
161
115
110
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

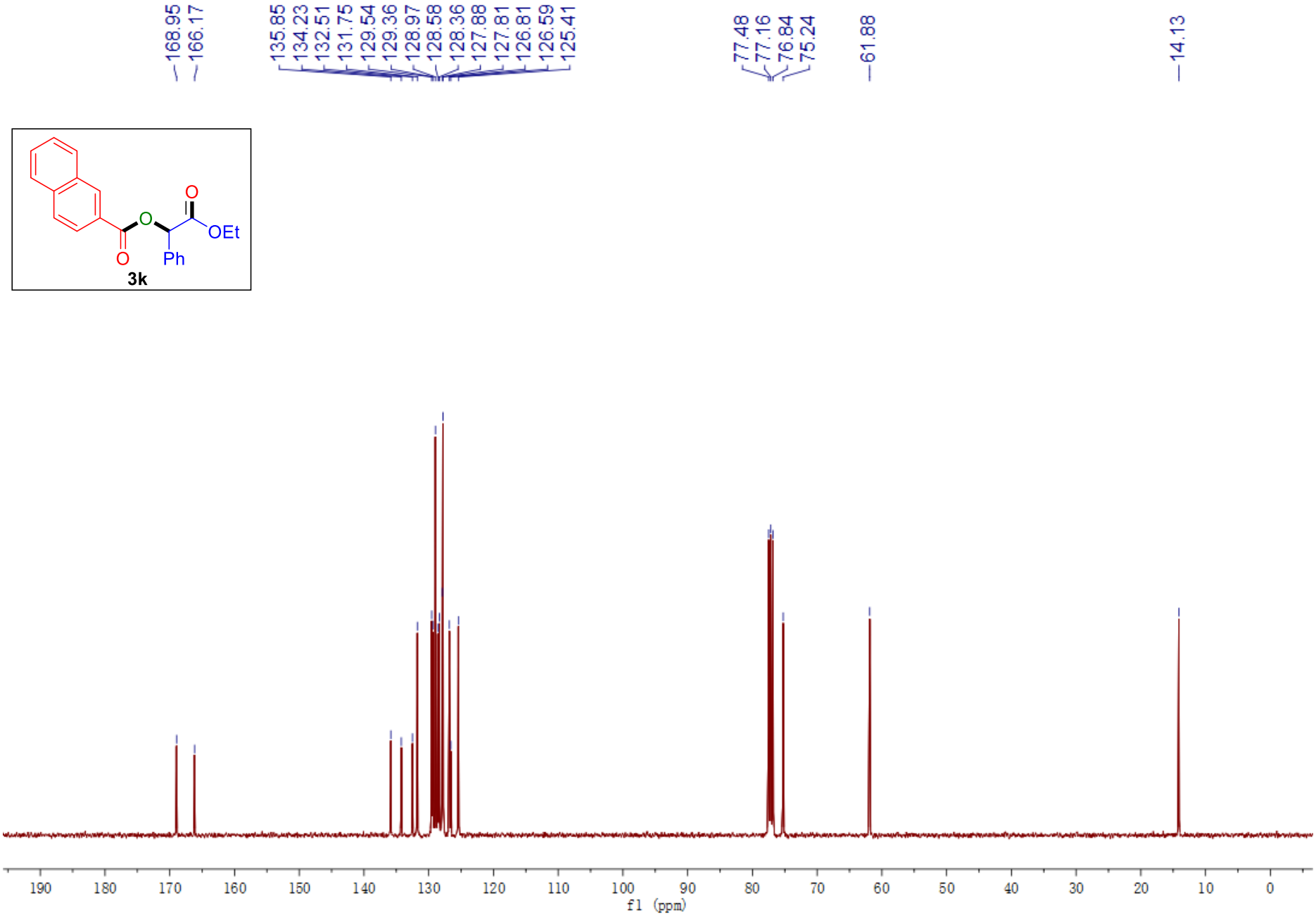

7.523
7.513
7.504
7.499
7.390
7.387
7.380
7.375
7.367
7.362
6.854
6.119
4.294
4.285
4.276
4.267
4.258
4.249
4.240
4.231
4.222
4.213
4.204
4.195
4.187
4.178
2.361
2.271
1.268
1.250
1.232
O
O
OEt
O
Ph
3i
2.03
3.03
2.00
1.03
2.03
6.04
3.04
3.08
f1 (ppm)

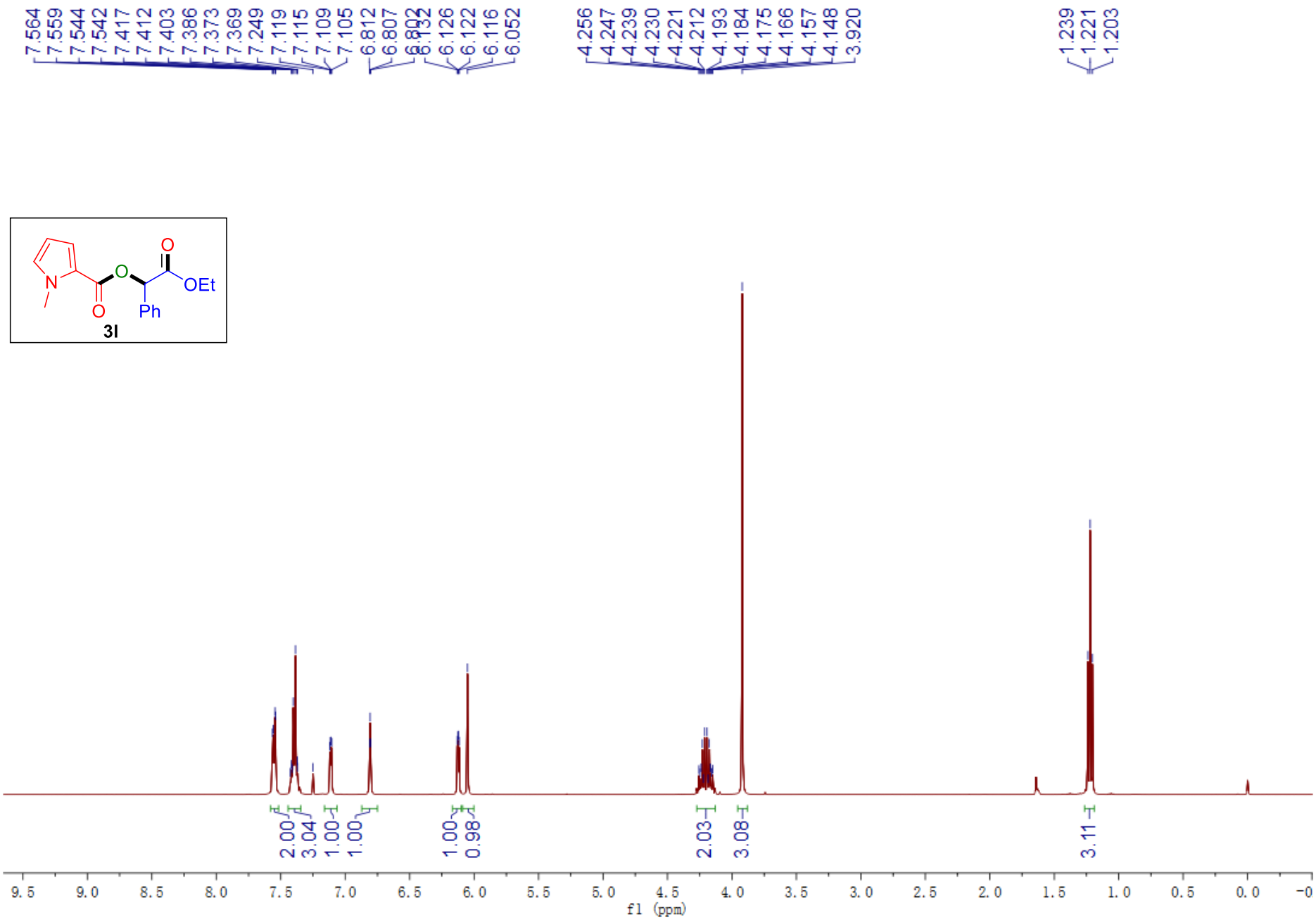

169.43
168.93
139.94
136.19
133.88
129.62
129.26
128.85
128.67
127.81
77.48
77.16
76.84
75.25
61.88
21.25
20.08
14.14
O
O
OEt
O
Ph
3i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.986
8.965
8.328
8.023
8.002
7.868
7.847
7.628
7.625
7.610
7.513
7.506
7.487
7.421
7.402
6.264
4.301
4.292
4.283
4.274
4.256
4.235
4.226
4.217
4.208
4.200
4.190
1.261
1.243
1.225
O
O
OEt
O
Ph
3j
1.00
1.01
1.03
1.02
3.03
2.10
3.07
1.00
2.10
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


169.08
166.88
134.14
133.96
133.87
131.52
130.90
129.31
128.94
128.64
128.04
127.77
126.40
126.28
125.82
124.61
77.48
77.16
76.84
75.25
61.92
14.15
O
O
OEt
O
Ph
3j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

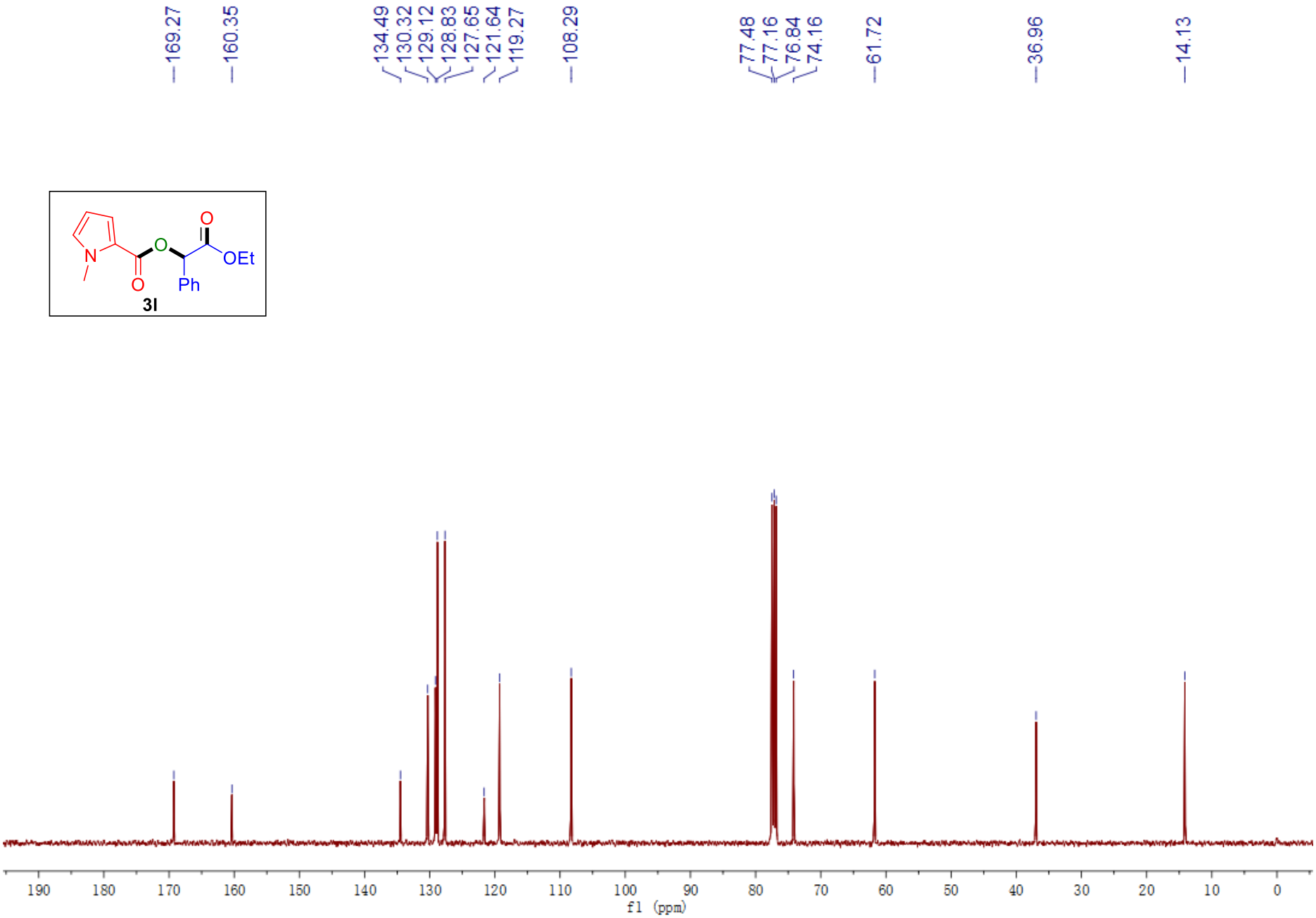

8.698
8.116
7.936
7.887
7.866
7.849
7.654
7.651
7.635
7.576
7.522
7.455
7.436
7.215
4.312
4.294
4.285
4.276
4.267
4.259
4.250
4.232
4.215
4.206
4.197
4.188
4.179
4.170
4.152
1.253
1.235
1.217
O
O
OEt
O
Ph
3k
1.00
1.00
1.03
2.04
2.02
2.09
3.09
0.98
2.04
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

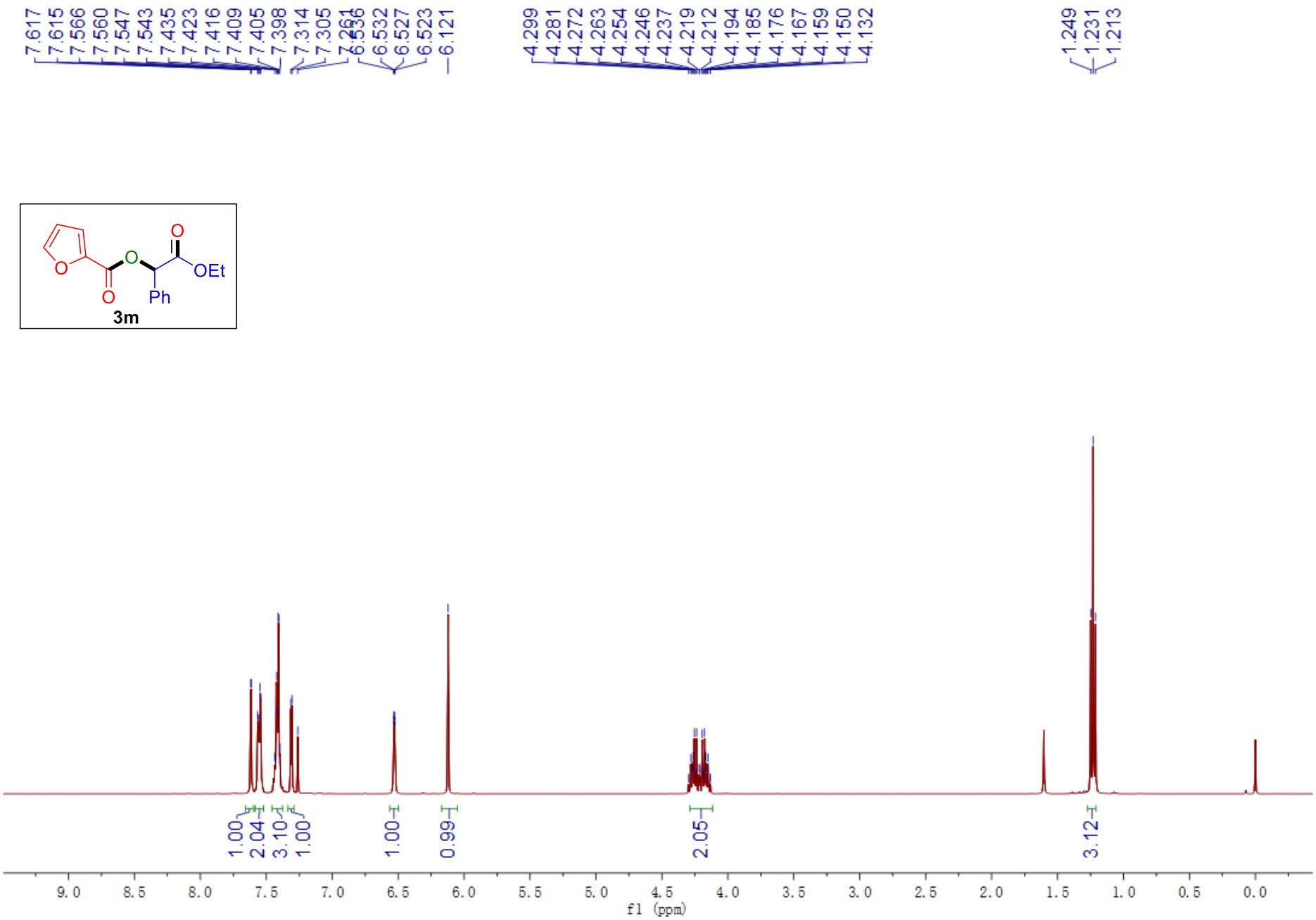

168.95
166.17
135.85
134.23
132.51
131.75
129.54
129.36
128.97
128.58
128.36
127.88
127.81
126.81
126.59
125.41
77.48
77.16
76.84
75.24
61.88
14.13
O
O
OEt
O
Ph
3k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

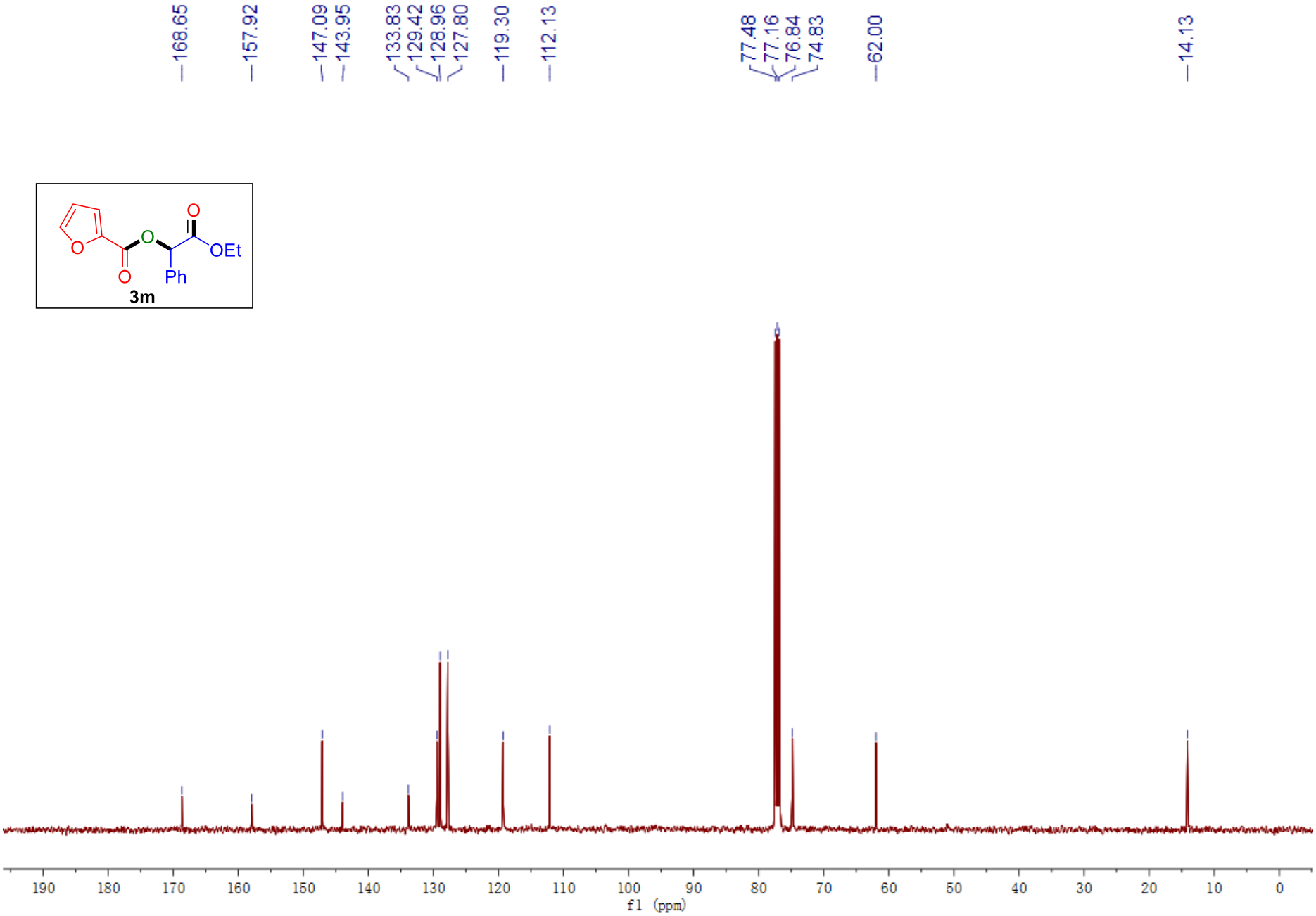

7.564
7.559
7.544
7.542
7.417
7.412
7.403
7.386
7.373
7.369
7.249
7.119
7.115
7.109
7.105
6.812
6.807
6.126
6.122
6.116
6.052
4.256
4.247
4.239
4.230
4.221
4.212
4.193
4.184
4.175
4.166
4.157
4.148
3.920
1.239
1.221
1.203
N
O
O
O
OEt
Ph
3l
2.00
3.04
1.00
1.00
1.00
0.98
2.03
3.08
3.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

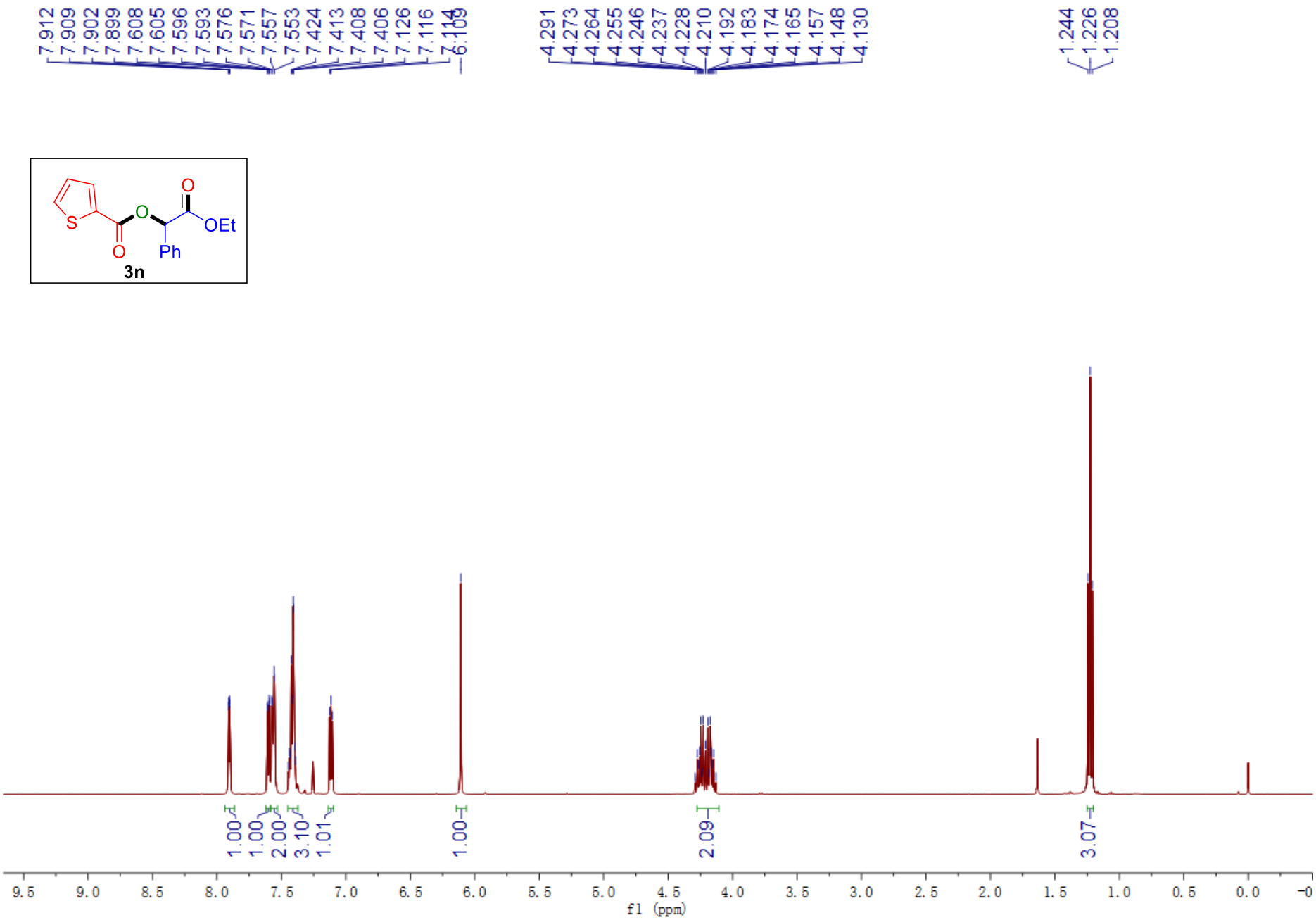
N
O
O
O
OEt
Ph

3l

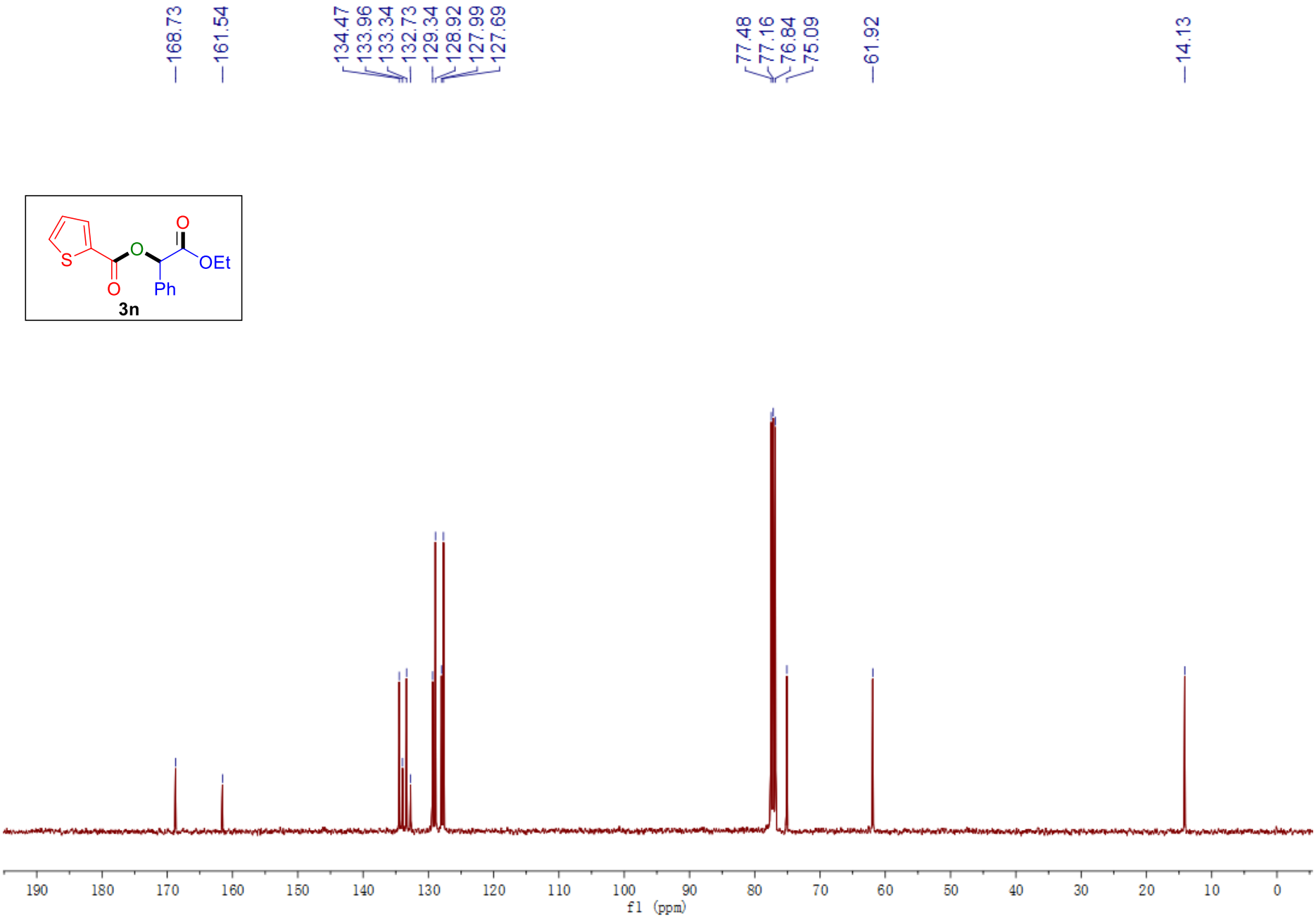

169.27
160.35
134.49
130.32
129.12
128.83
127.65
121.64
119.27
108.29
77.48
77.16
76.84
74.16
61.72
36.96
14.13
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

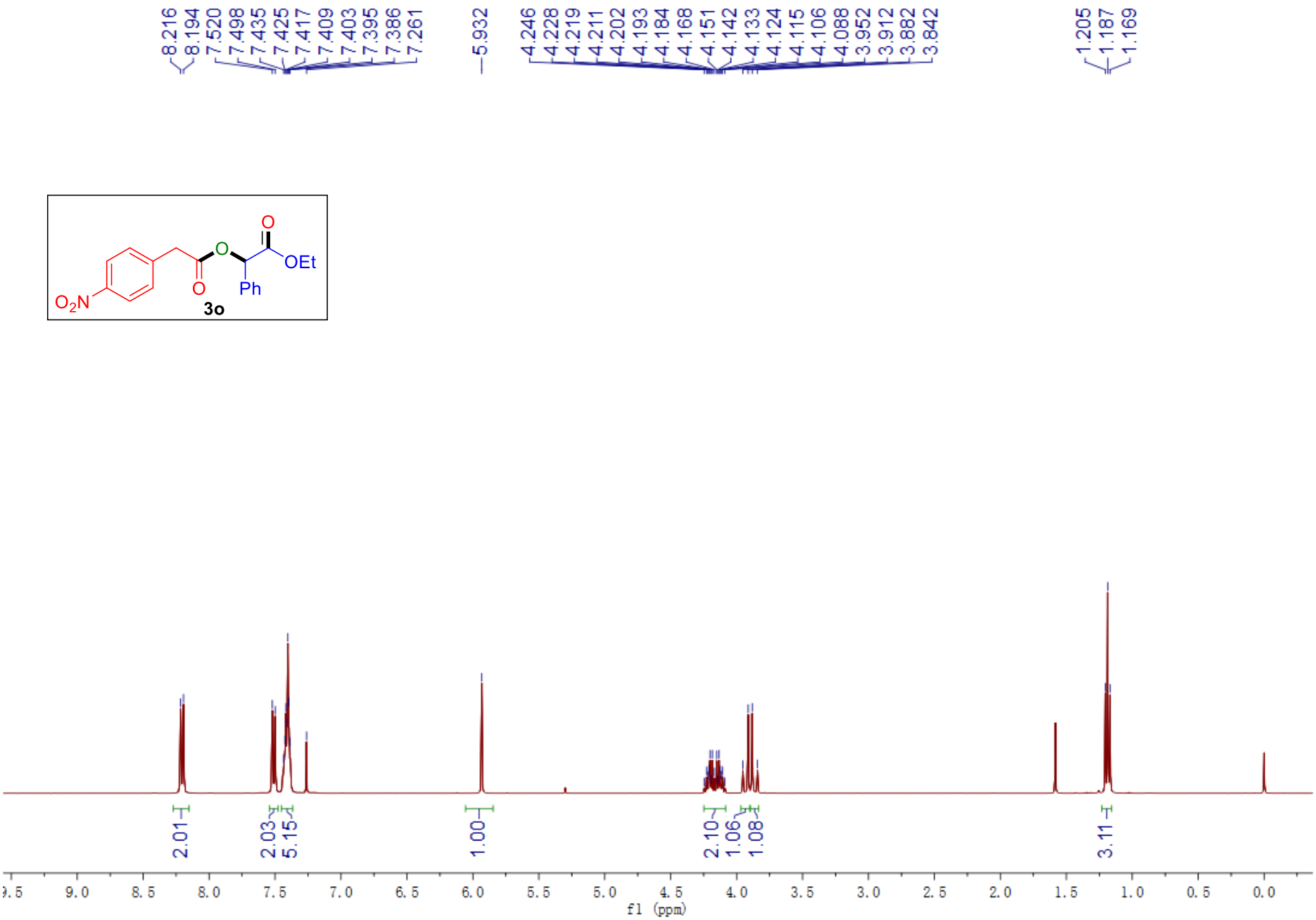

7.617
7.615
7.566
7.560
7.547
7.543
7.435
7.423
7.416
7.409
7.405
7.398
7.314
7.305
7.261
6.536
6.532
6.527
6.523
6.121
4.299
4.281
4.272
4.263
4.254
4.246
4.237
4.219
4.212
4.194
4.185
4.176
4.167
4.159
4.150
4.132
1.249
1.231
1.213
O
O
O
O
OEt
Ph
3m
1.00
2.04
3.10
1.00
1.00
0.99
2.05
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

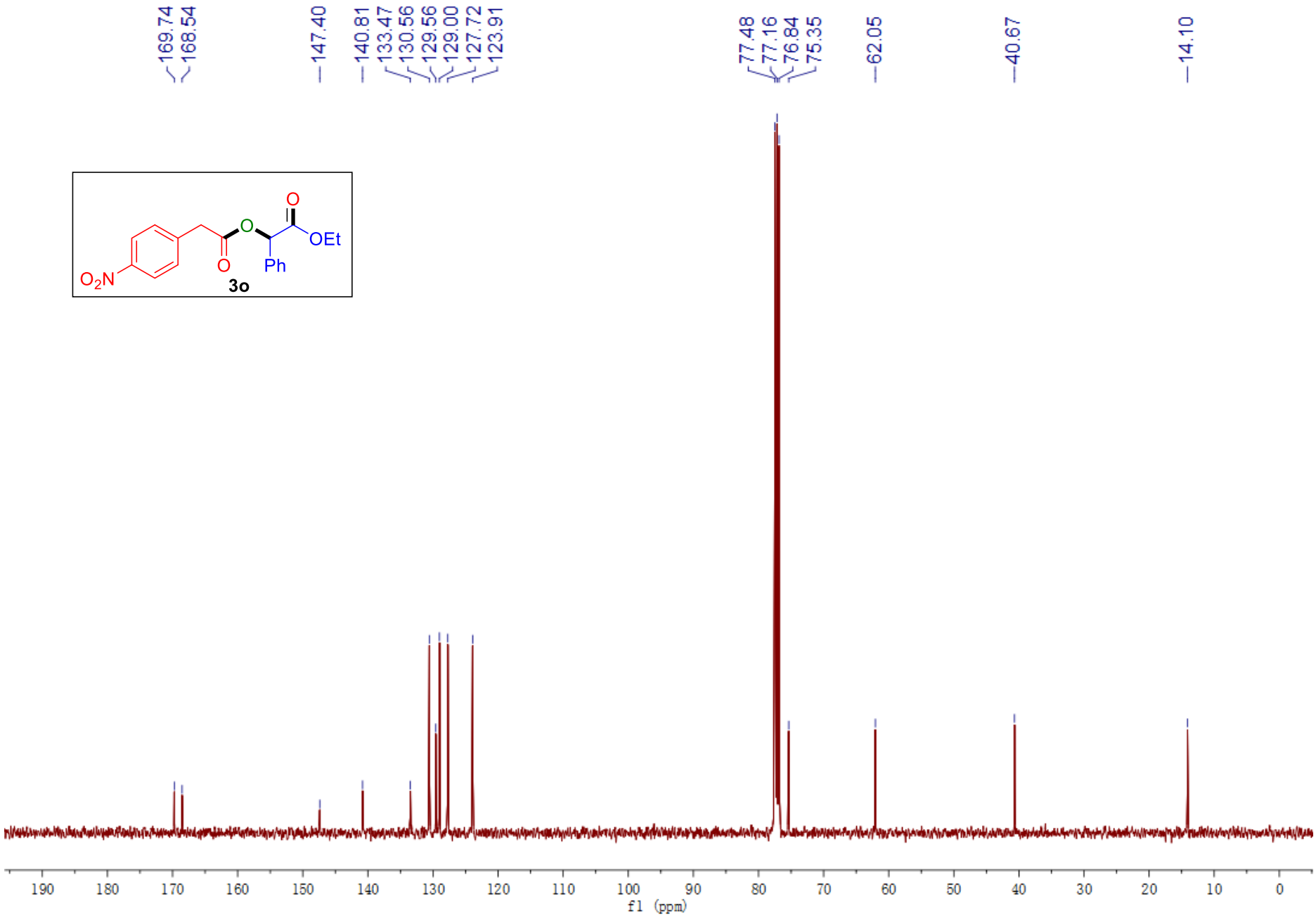

168.65
157.92
147.09
143.95
133.83
129.42
128.96
127.80
119.30
112.13
77.48
77.16
76.84
74.83
62.00
14.13
O
O
O
OEt
Ph
3m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

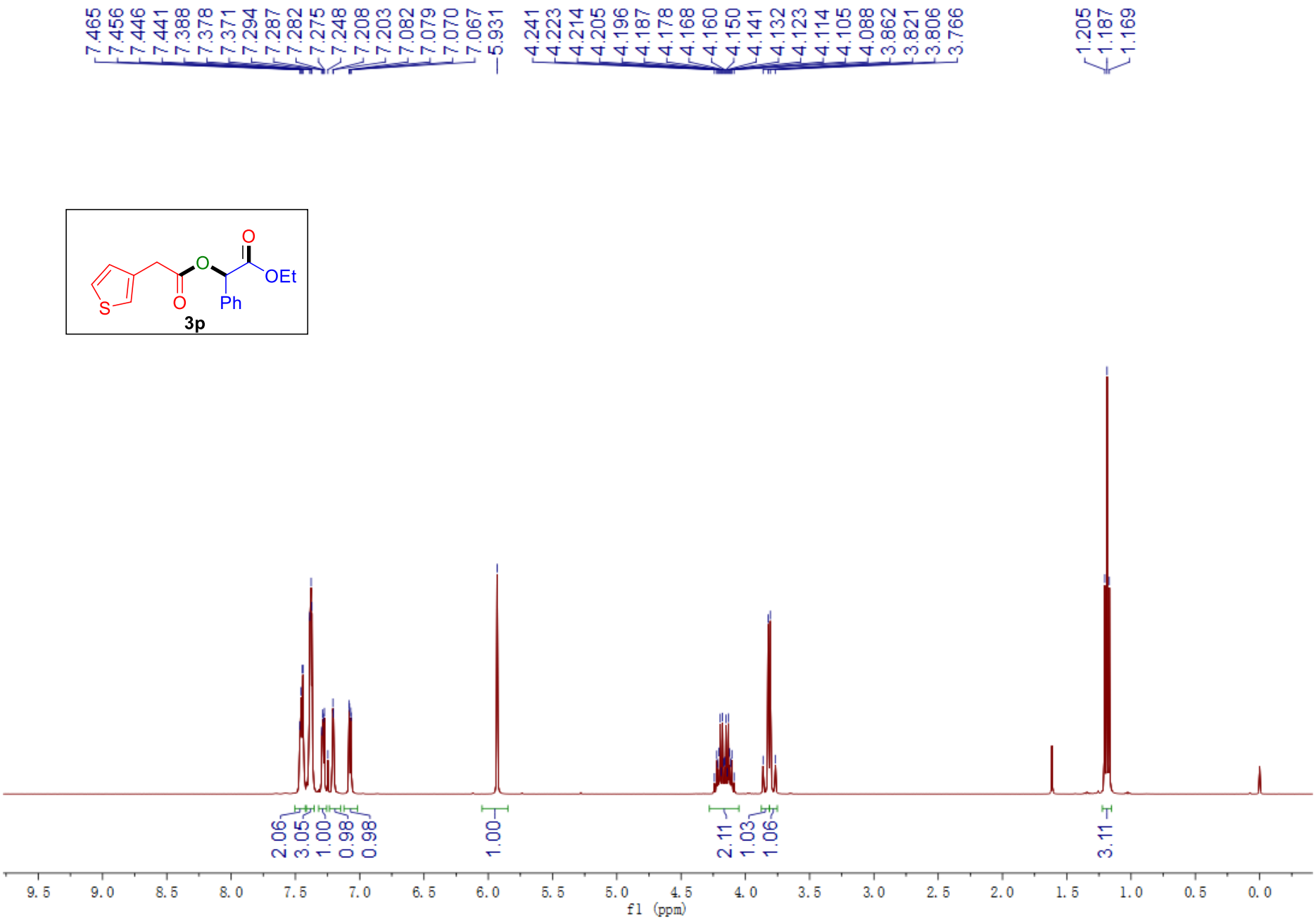

7.912
7.909
7.902
7.899
7.608
7.605
7.596
7.593
7.576
7.571
7.557
7.553
7.424
7.413
7.408
7.406
7.126
7.116
7.114
6.109
4.291
4.273
4.264
4.255
4.246
4.237
4.228
4.210
4.192
4.183
4.174
4.165
4.157
4.148
4.130
1.244
1.226
1.208
S
O
O
O
OEt
Ph
3n
1.00
1.00
2.00
3.10
1.01
1.00
2.09
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

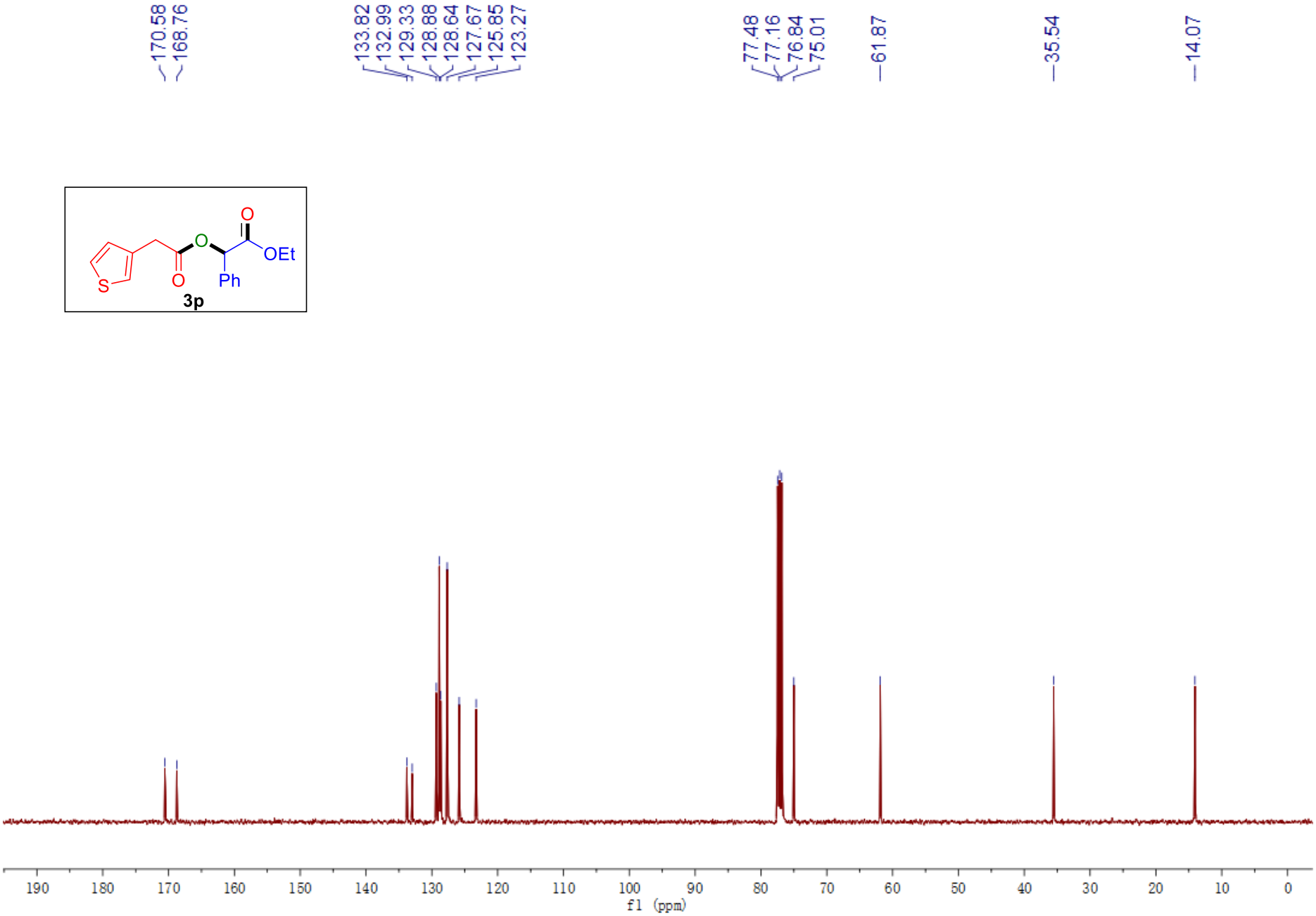
S
O
O
O
OEt
Ph
3n

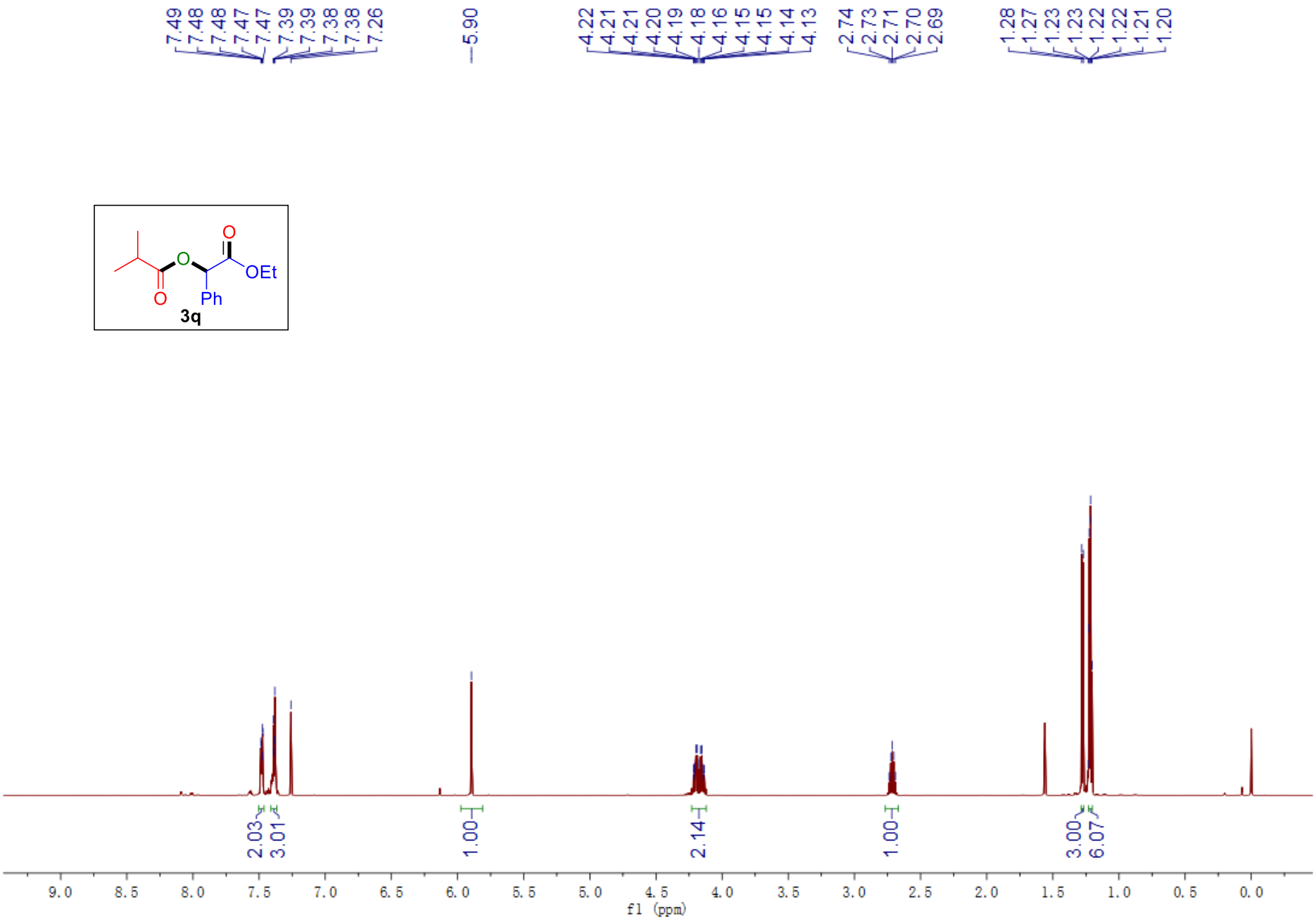

168.73
161.54
134.47
133.96
133.34
132.73
129.34
128.92
127.99
127.69
77.48
77.16
76.84
75.09
61.92
14.13
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

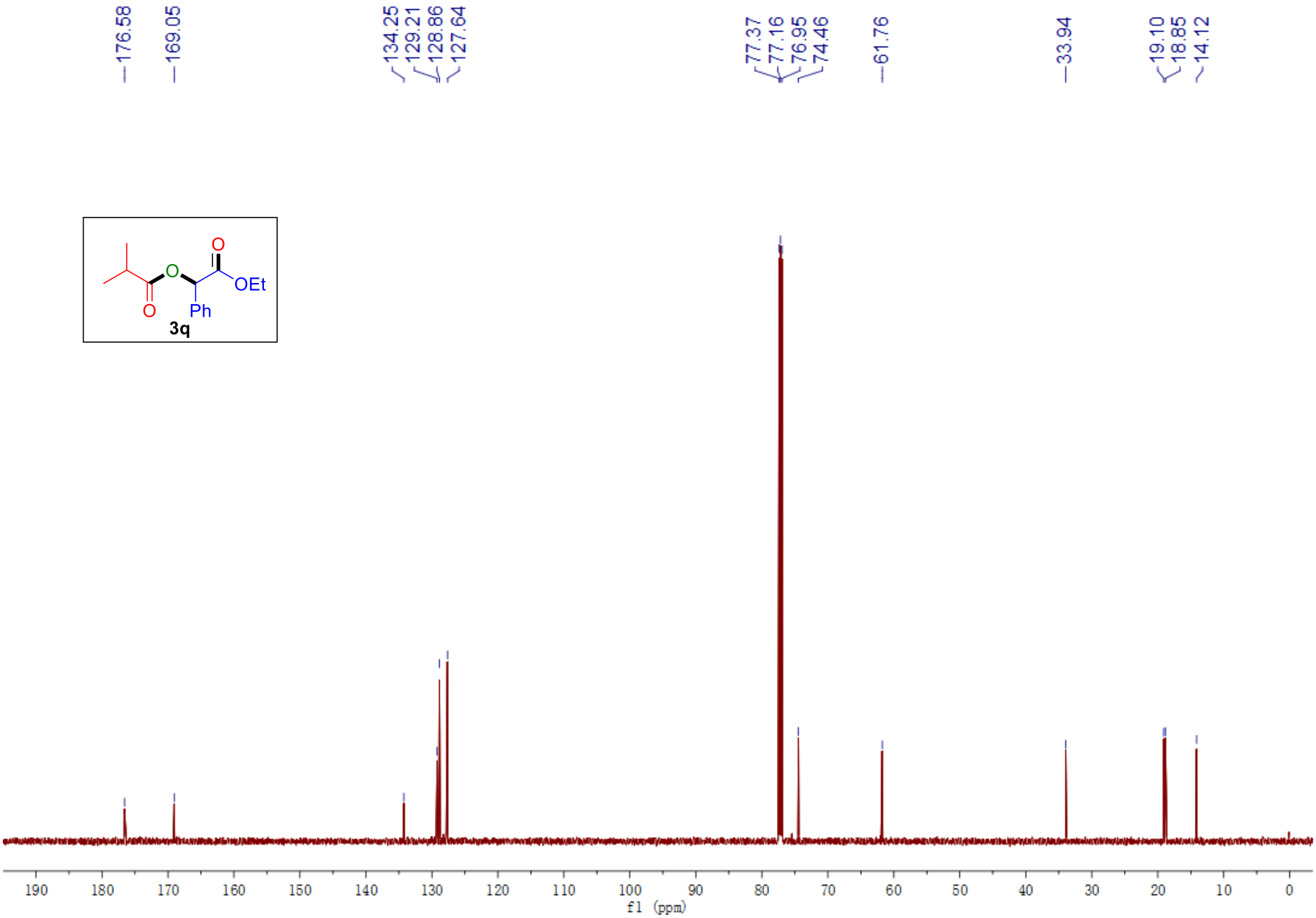

8.216
8.194
7.520
7.498
7.435
7.425
7.417
7.409
7.403
7.395
7.386
7.261
5.932
4.246
4.228
4.219
4.211
4.202
4.193
4.184
4.168
4.151
4.142
4.133
4.124
4.115
4.106
4.088
3.952
3.912
3.882
3.842
1.205
1.187
1.169
O
O
OEt
O
Ph
O2N
3o
2.01
2.03
5.15
1.00
2.10
1.06
1.08
3.11
f1 (ppm)

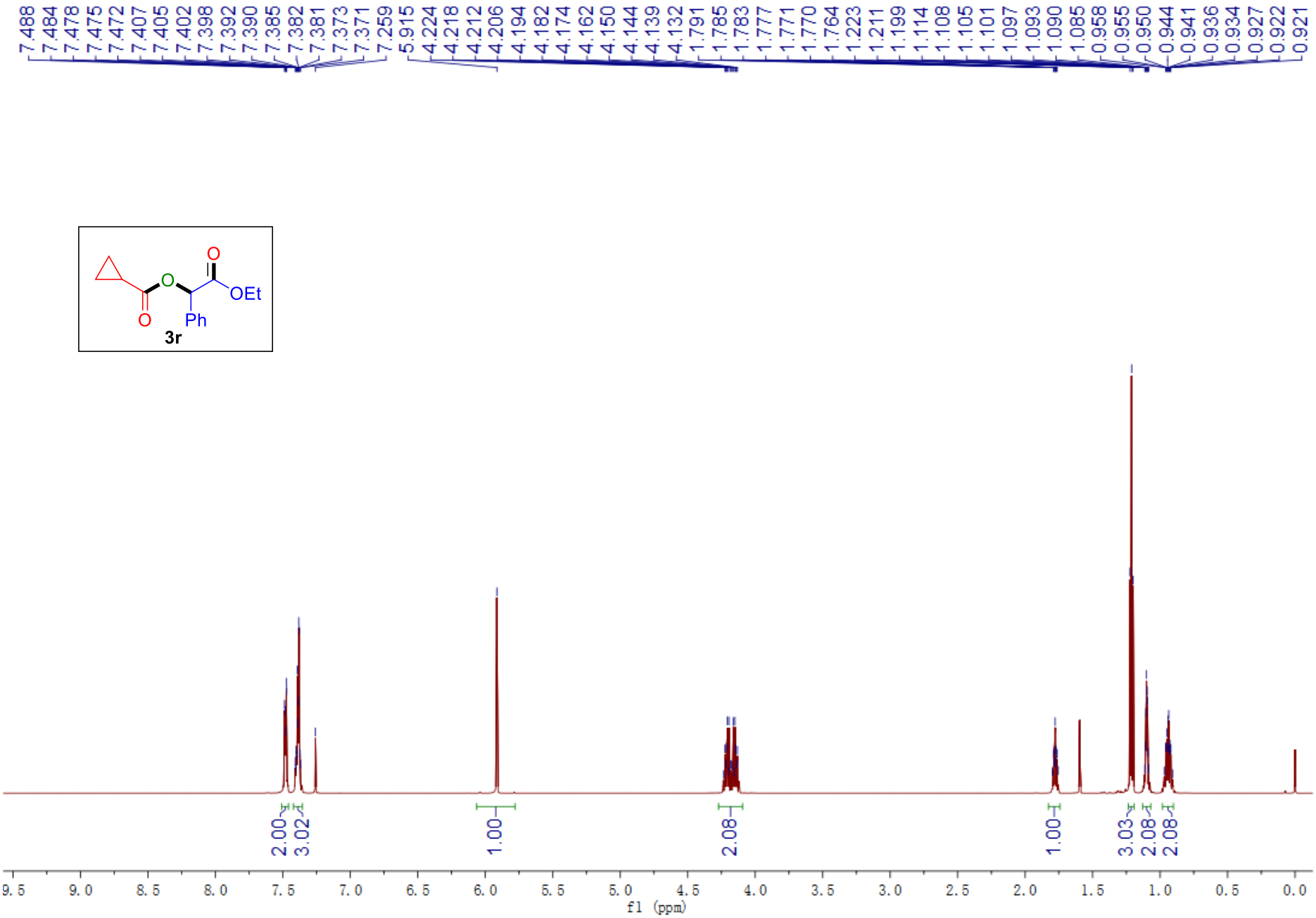

169.74
168.54
147.40
140.81
133.47
130.56
129.56
129.00
127.72
123.91
77.48
77.16
76.84
75.35
62.05
40.67
14.10
O
O
OEt
O
Ph
O_2N
3o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

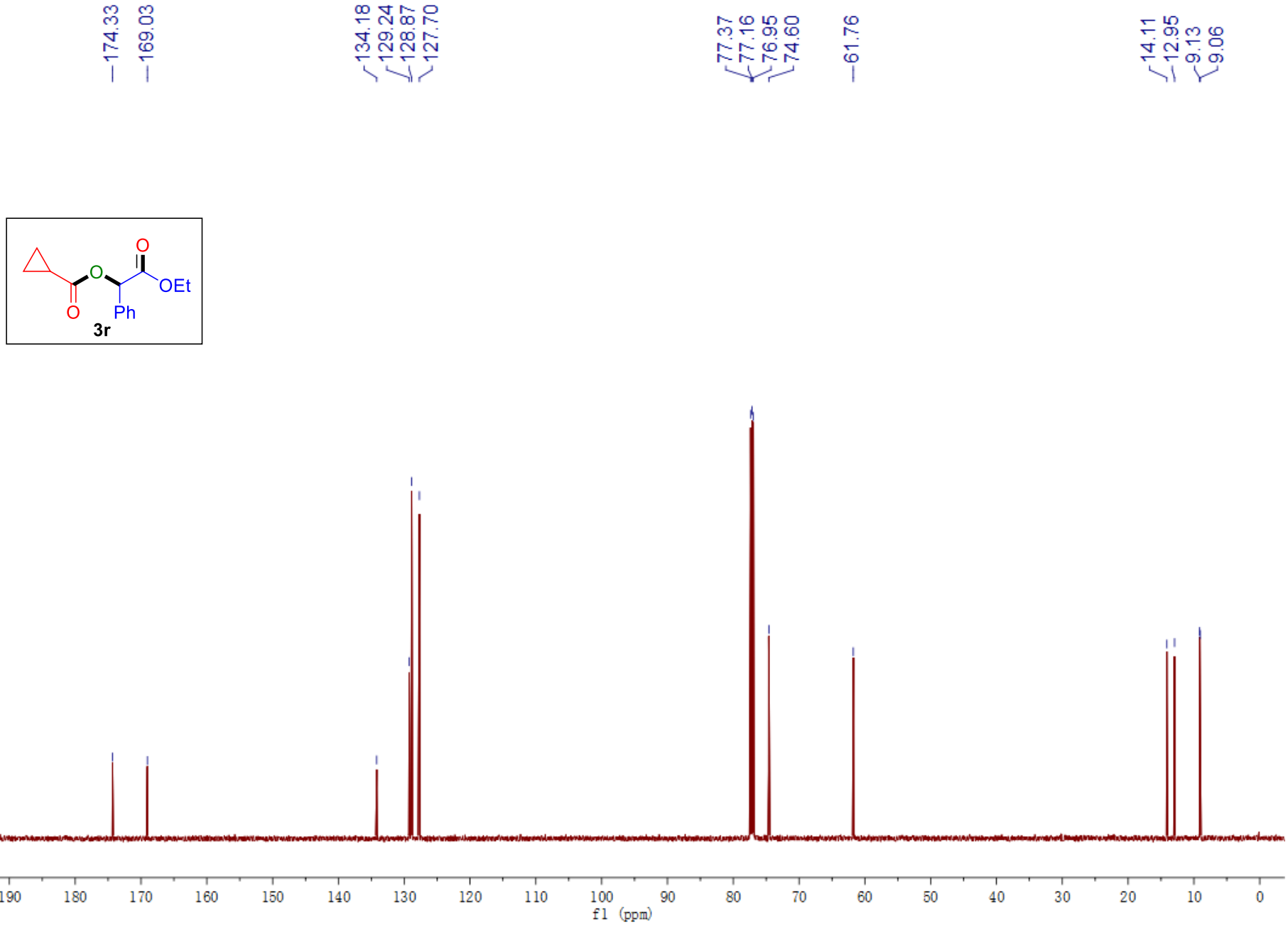

7.465
7.456
7.446
7.441
7.388
7.378
7.371
7.294
7.287
7.282
7.275
7.248
7.208
7.203
7.082
7.079
7.070
7.067
5.931
4.241
4.223
4.214
4.205
4.196
4.187
4.178
4.168
4.160
4.150
4.141
4.132
4.123
4.114
4.105
4.088
3.862
3.821
3.806
3.766
1.205
1.187
1.169
O
O
OEt
S
O
Ph
3p
2.06
3.05
1.00
0.98
0.98
1.00
2.11
1.03
1.06
3.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

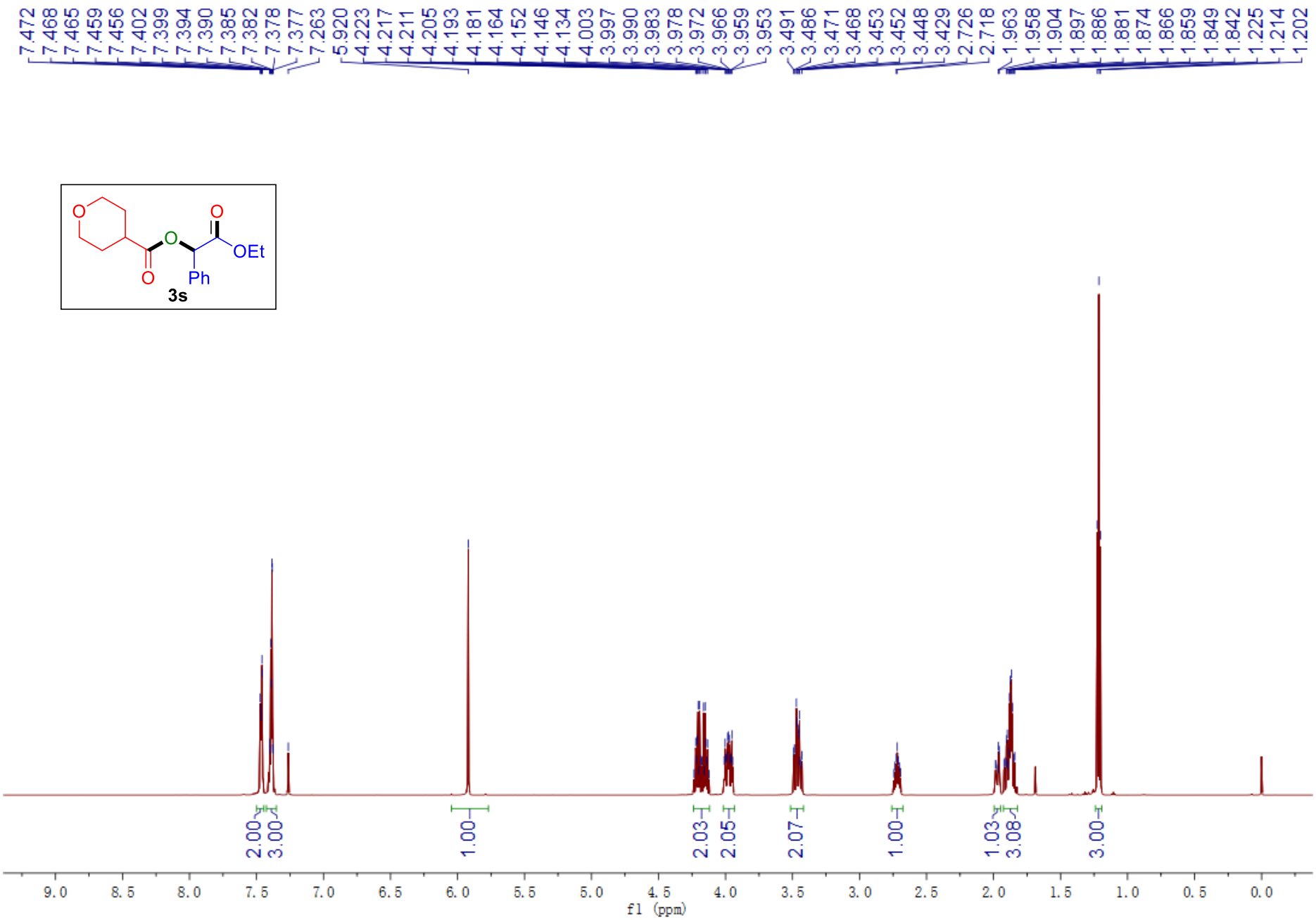

170.58
168.76
133.82
132.99
129.33
128.88
128.64
127.67
125.85
123.27
77.48
77.16
76.84
75.01
61.87
35.54
14.07
O
O
OEt
S
O
Ph
3p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

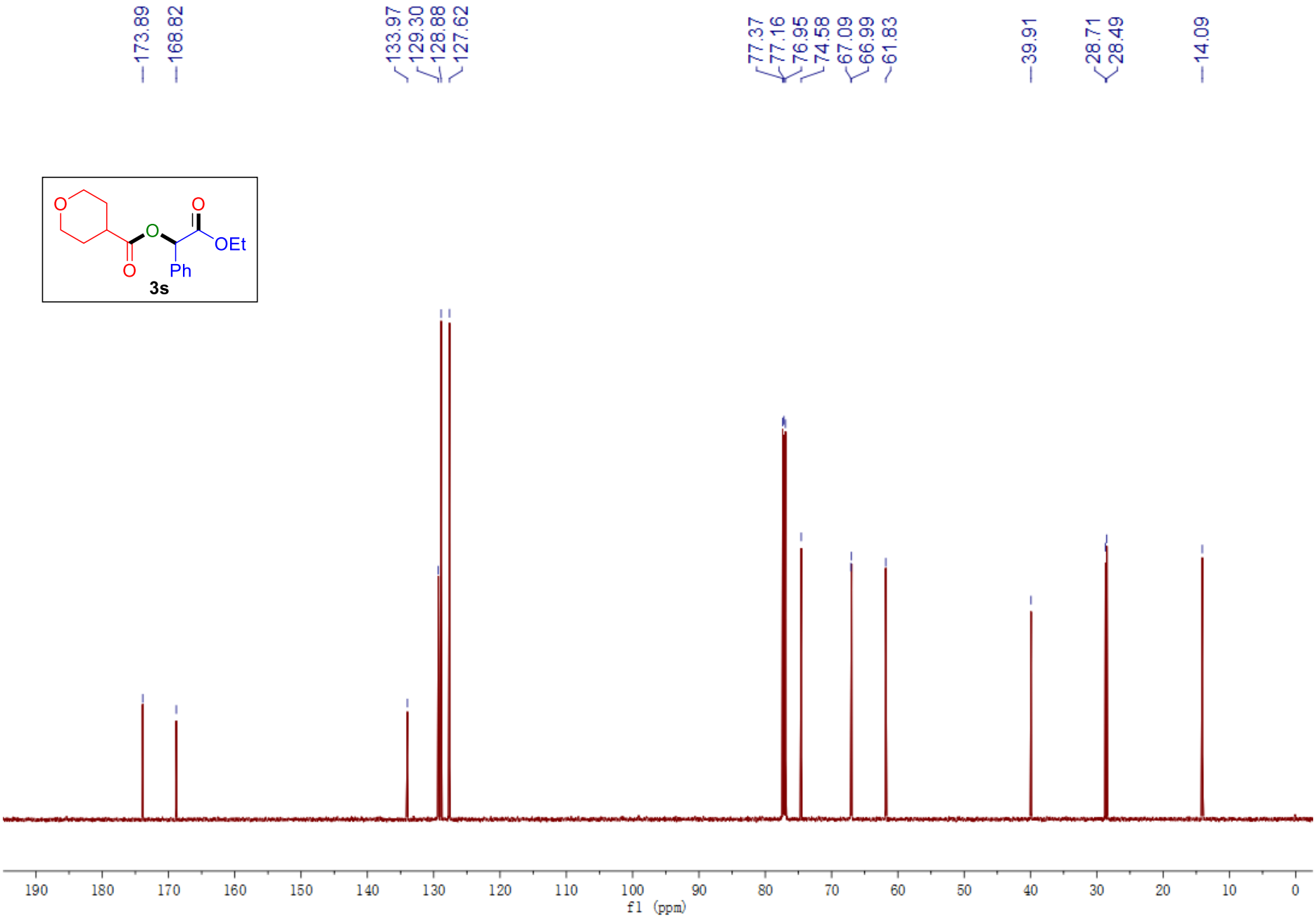

7.49
7.48
7.48
7.47
7.47
7.39
7.39
7.38
7.38
7.26
5.90
4.22
4.21
4.21
4.20
4.19
4.18
4.16
4.15
4.15
4.14
4.13
2.74
2.73
2.71
2.70
2.69
1.28
1.27
1.23
1.23
1.22
1.22
1.21
1.20
O
O
OEt
O
Ph
3q
2.03
3.01
1.00
2.14
1.00
3.00
6.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

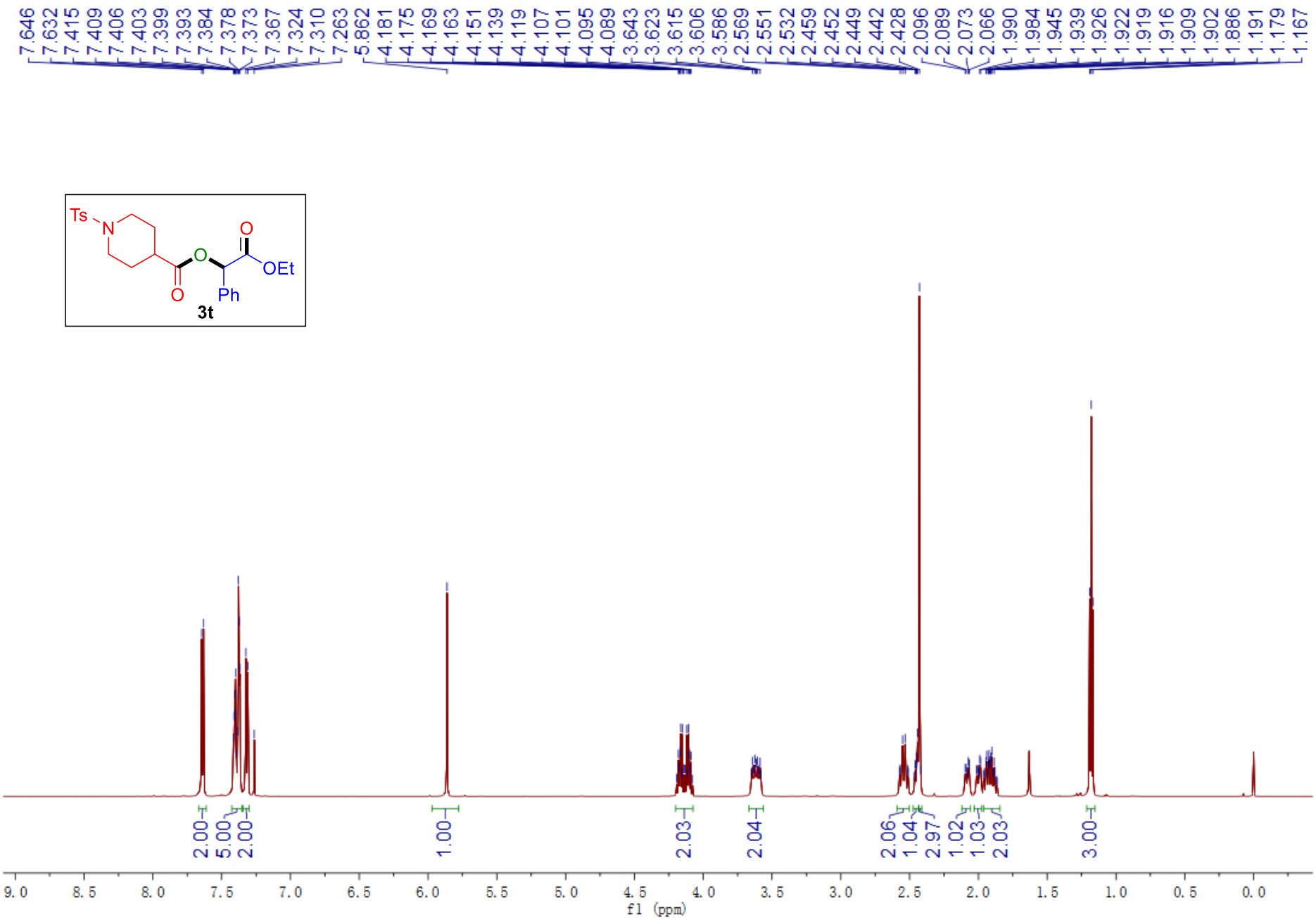

176.58
169.05
134.25
129.21
128.86
127.64
77.37
77.16
76.95
74.46
61.76
33.94
19.10
18.85
14.12
O
O
OEt
O
Ph
3q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

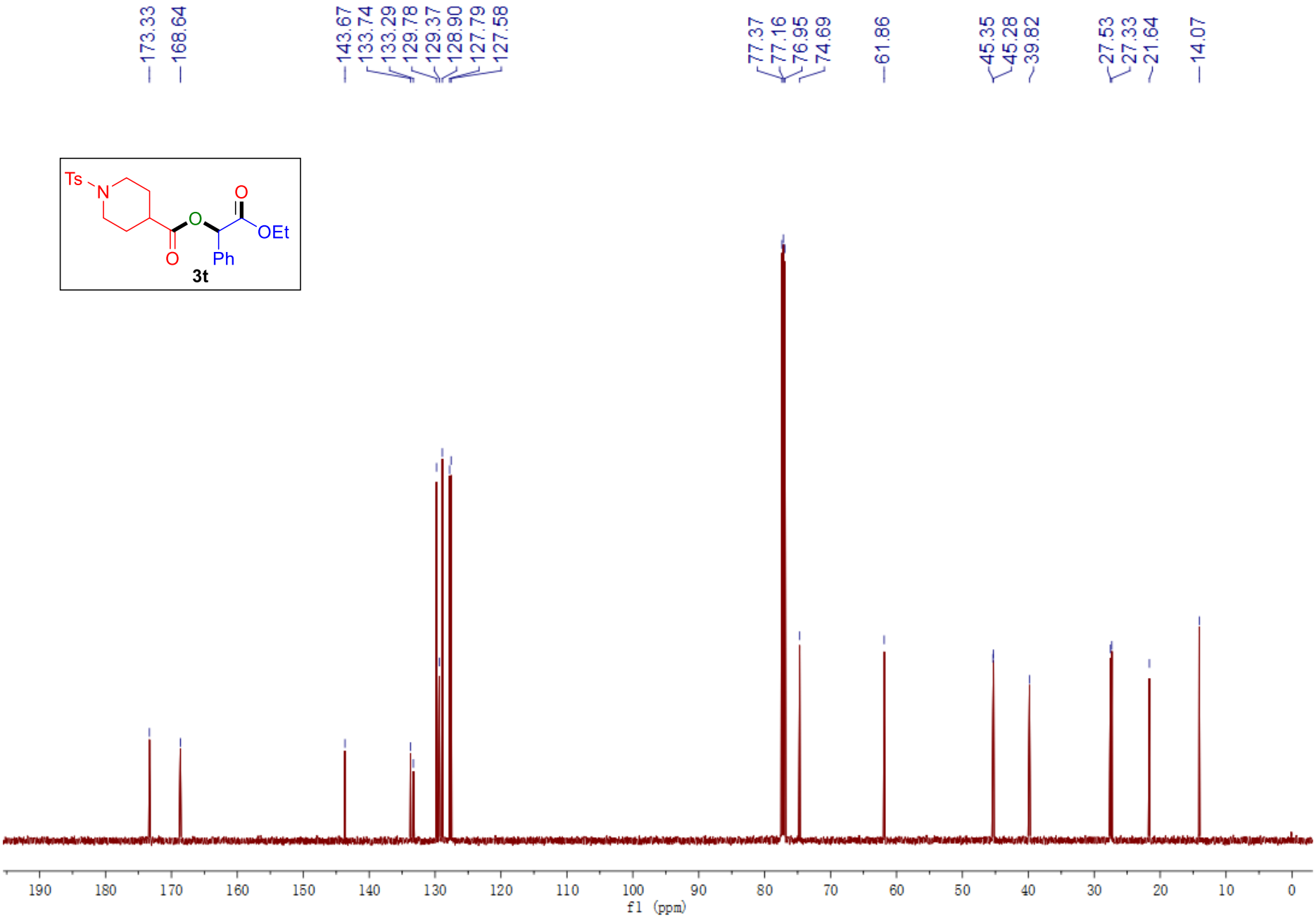

7.488
7.484
7.478
7.475
7.472
7.407
7.405
7.402
7.398
7.392
7.390
7.385
7.382
7.381
7.373
7.371
7.259
5.915
4.224
4.218
4.212
4.206
4.194
4.182
4.174
4.162
4.150
4.144
4.139
4.132
1.791
1.785
1.783
1.777
1.771
1.770
1.764
1.223
1.211
1.199
1.114
1.108
1.105
1.101
1.097
1.093
1.090
1.085
0.958
0.955
0.950
0.944
0.941
0.936
0.934
0.927
0.922
0.921
O
O
OEt
O
Ph
3r
2.00
3.02
1.00
2.08
1.00
3.03
2.08
2.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

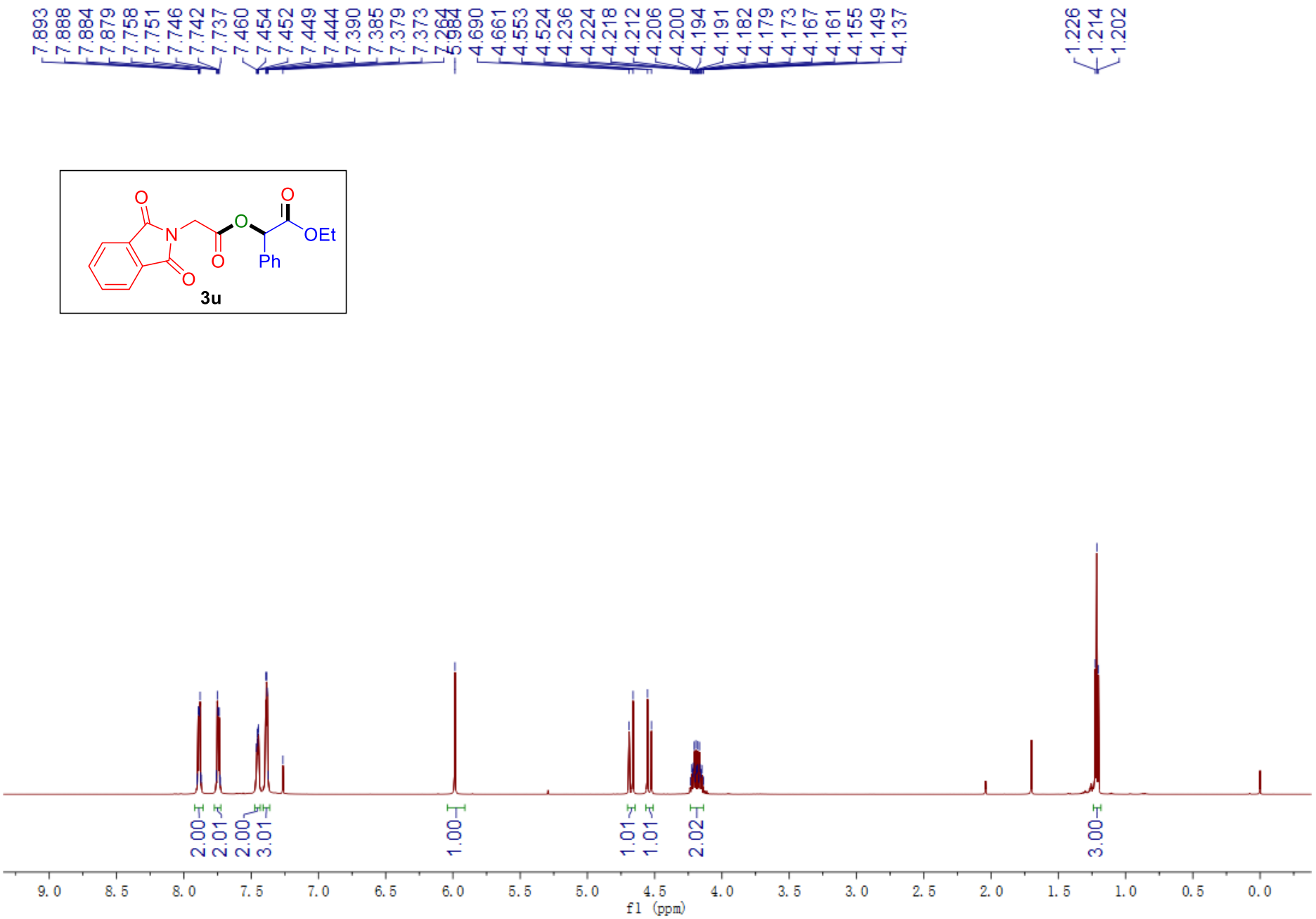

174.33
169.03
134.18
129.24
128.87
127.70
77.37
77.16
76.95
74.60
61.76
14.11
12.95
9.13
9.06
O
O
OEt
O
Ph
3r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

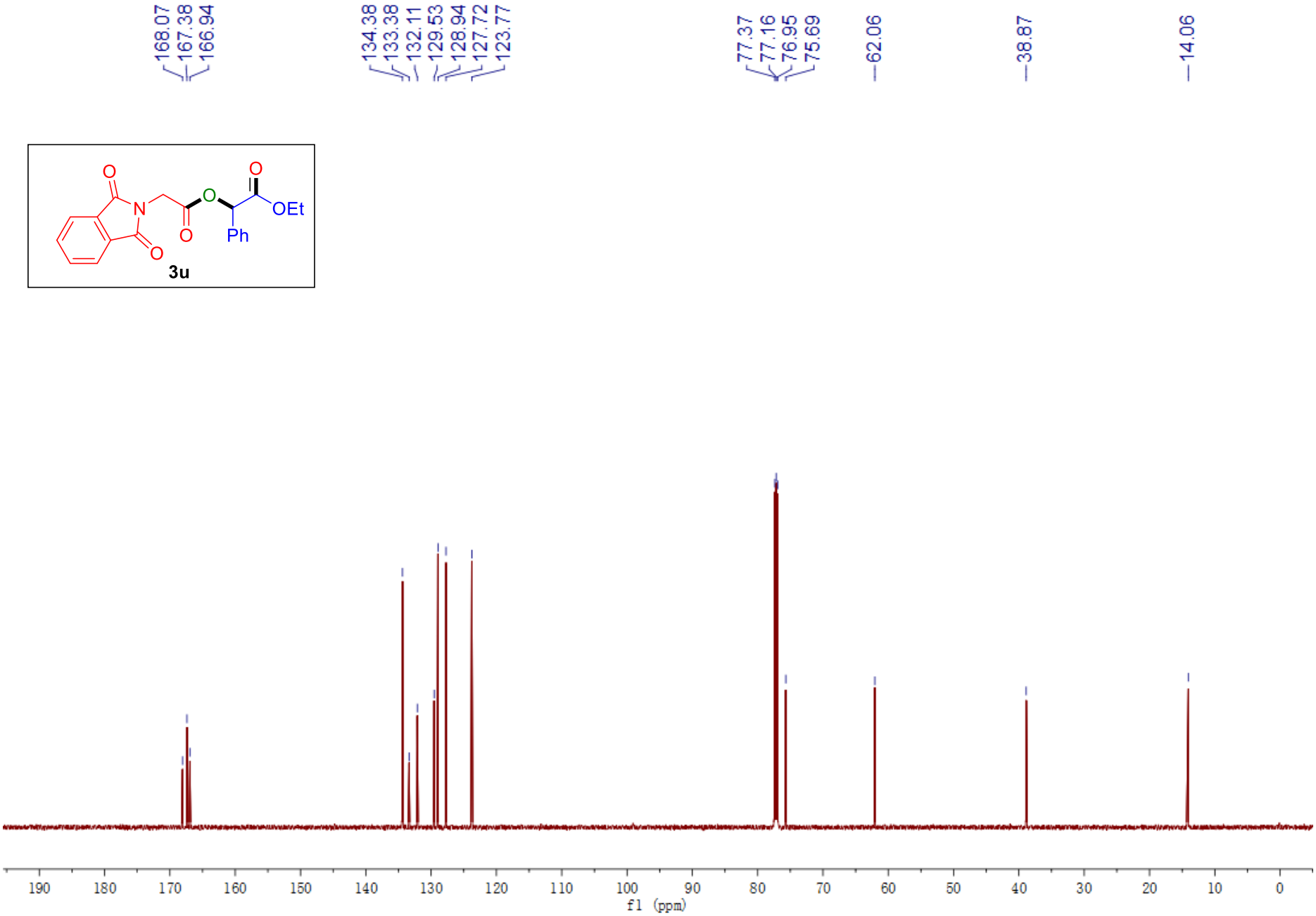

7.472
7.468
7.465
7.459
7.456
7.402
7.399
7.394
7.390
7.385
7.382
7.378
7.377
7.263
5.920
4.223
4.217
4.211
4.205
4.193
4.181
4.164
4.152
4.146
4.134
4.003
3.997
3.990
3.983
3.978
3.972
3.966
3.959
3.953
3.491
3.486
3.471
3.468
3.453
3.452
3.448
3.429
2.726
2.718
1.963
1.958
1.904
1.897
1.886
1.881
1.874
1.866
1.859
1.849
1.842
1.225
1.214
1.202
O
O
O
O
OEt
Ph
3s
2.00
3.00
1.00
2.03
2.05
2.07
1.00
1.03
3.08
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

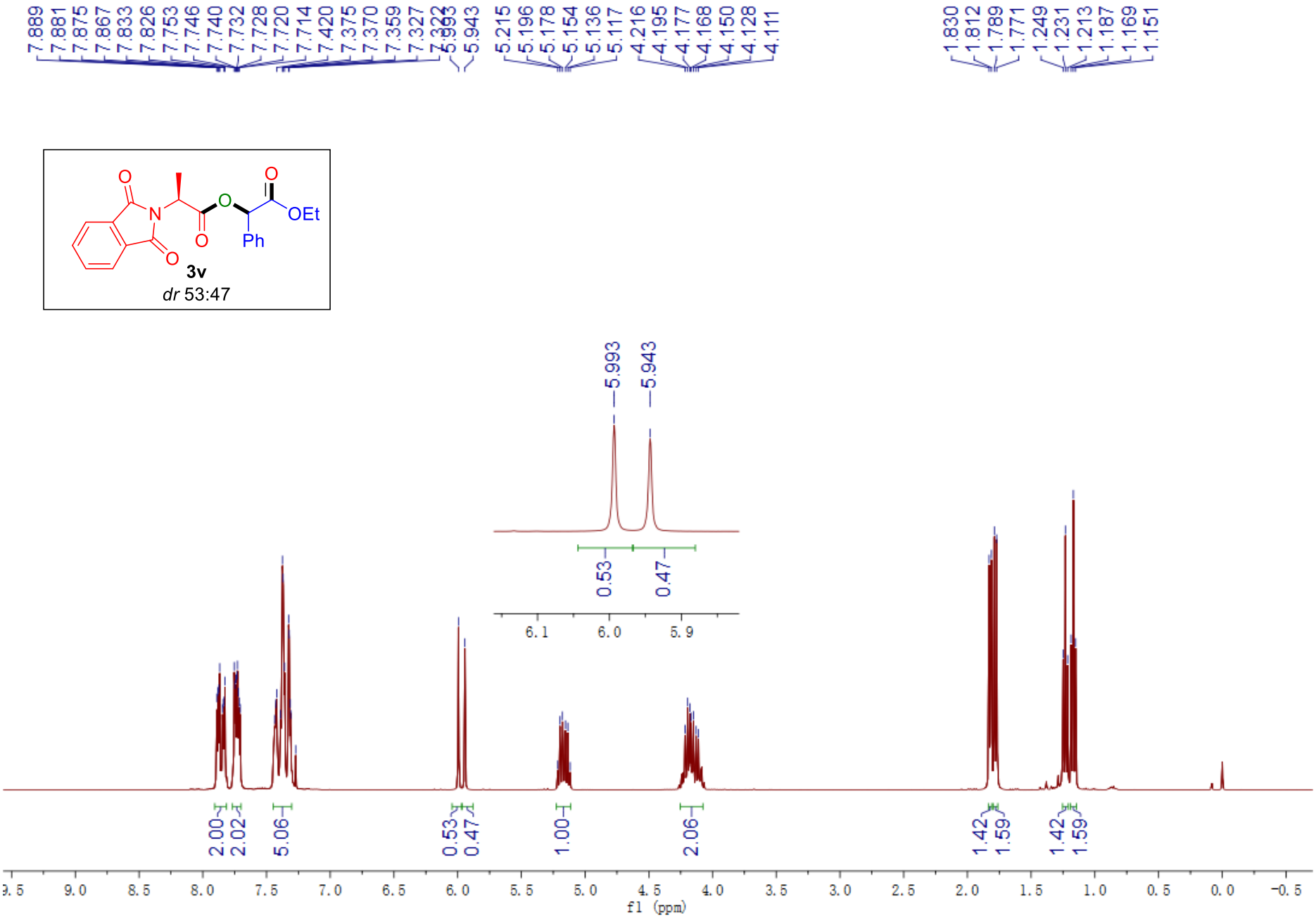

173.89
168.82
133.97
129.30
128.88
127.62
77.37
77.16
76.95
74.58
67.09
66.99
61.83
39.91
28.71
28.49
14.09
O
O
O
O
OEt
Ph
3s
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

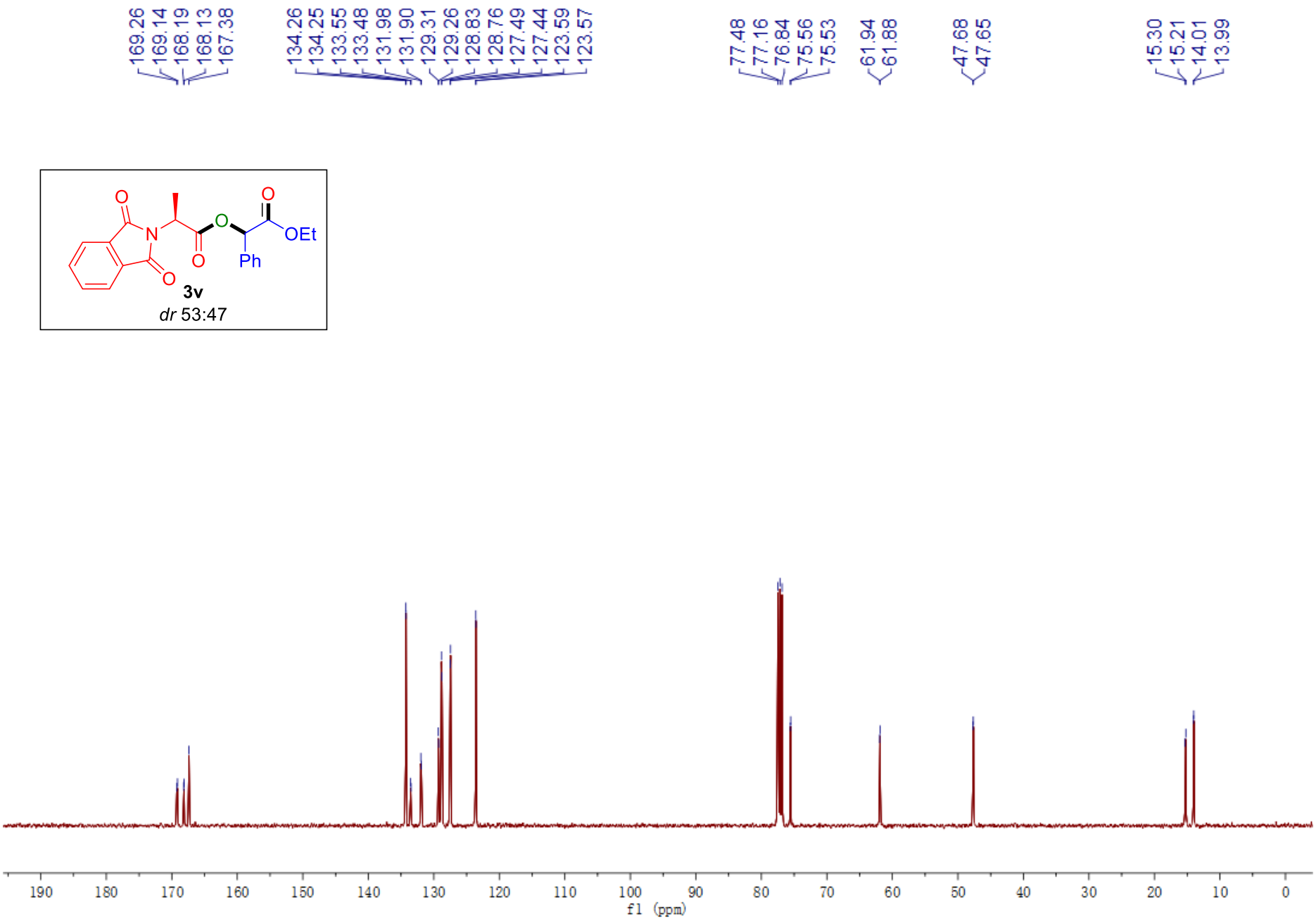

7.646 7.632 7.415 7.409 7.406 7.403 7.399 7.393 7.384 7.378 7.373 7.367 7.324 7.310 7.263 5.862 4.181 4.175 4.169 4.163 4.151 4.139 4.119 4.107 4.101 4.095 4.089 3.643 3.623 3.615 3.606 3.586 2.569 2.551 2.532 2.459 2.452 2.449 2.442 2.428 2.096 2.089 2.073 2.066 1.990 1.984 1.945 1.939 1.926 1.922 1.919 1.916 1.909 1.902 1.886 1.191 1.179 1.167
Ts
N
O
O
O
OEt
Ph
3t
2.00
5.00
2.00
1.00
2.03
2.04
2.06
1.04
2.97
1.02
1.03
2.03
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


173.33
168.64
143.67
133.74
133.29
129.78
129.37
128.90
127.79
127.58
77.37
77.16
76.95
74.69
61.86
45.35
45.28
39.82
27.53
27.33
21.64
14.07
Ts
N
O
O
O
OEt
Ph
3t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

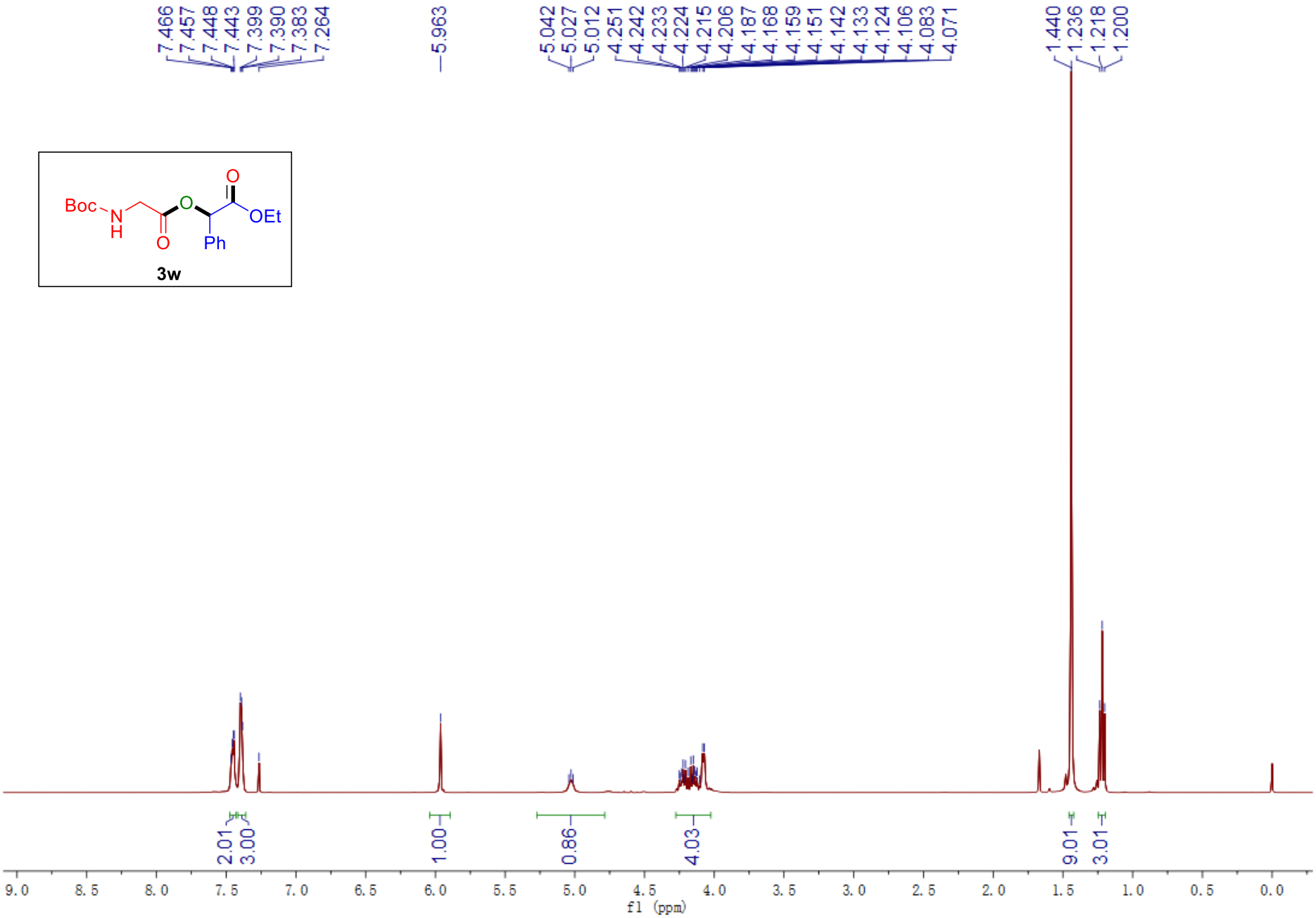

7.893
7.888
7.884
7.879
7.758
7.751
7.746
7.742
7.737
7.460
7.454
7.452
7.449
7.444
7.390
7.385
7.379
7.373
7.264
5.984
4.690
4.661
4.553
4.524
4.236
4.224
4.218
4.212
4.206
4.200
4.194
4.191
4.182
4.179
4.173
4.167
4.161
4.155
4.149
4.137
1.226
1.214
1.202
O
N
O
O
O
O
OEt
Ph
3u
2.00
2.01
2.00
3.01
1.00
1.01
1.01
2.02
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

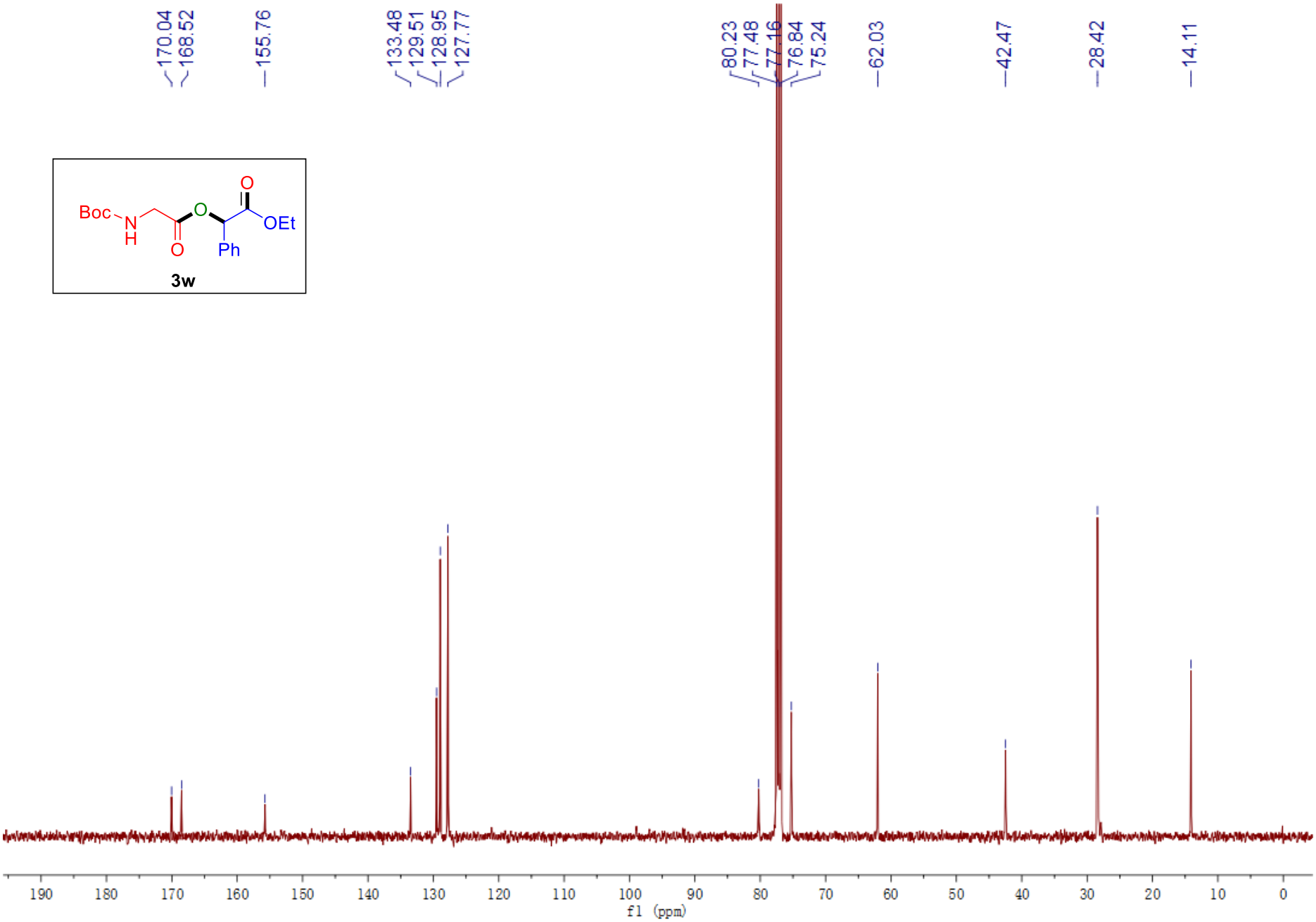

168.07
167.38
166.94
134.38
133.38
132.11
129.53
128.94
127.72
123.77
77.37
77.16
76.95
75.69
62.06
38.87
14.06
O
N
O
O
O
O
OEt
Ph
3u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

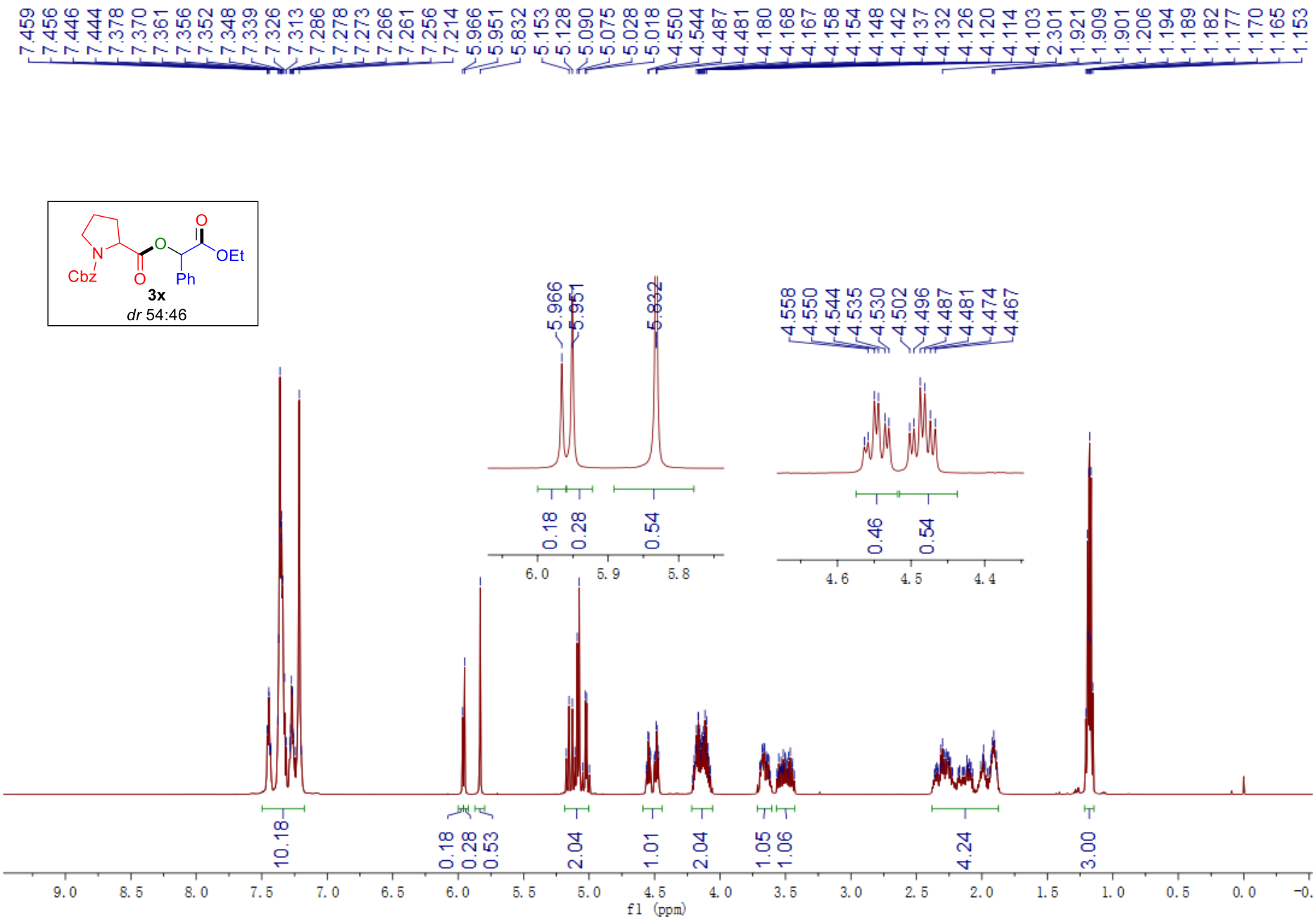

7.889
7.881
7.875
7.867
7.833
7.826
7.753
7.746
7.740
7.732
7.728
7.720
7.714
7.420
7.375
7.370
7.359
7.327
5.993
5.943
5.215
5.196
5.178
5.154
5.136
5.117
4.216
4.195
4.177
4.168
4.150
4.128
4.111
1.830
1.812
1.789
1.771
1.249
1.231
1.213
1.187
1.169
1.151
O
N
O
O
O
O
OEt
Ph
3v
dr 53:47
5.993
5.943
0.53
0.47
6.1
6.0
5.9
2.00
2.02
5.06
0.53
0.47
1.00
2.06
1.42
1.59
1.42
1.59
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

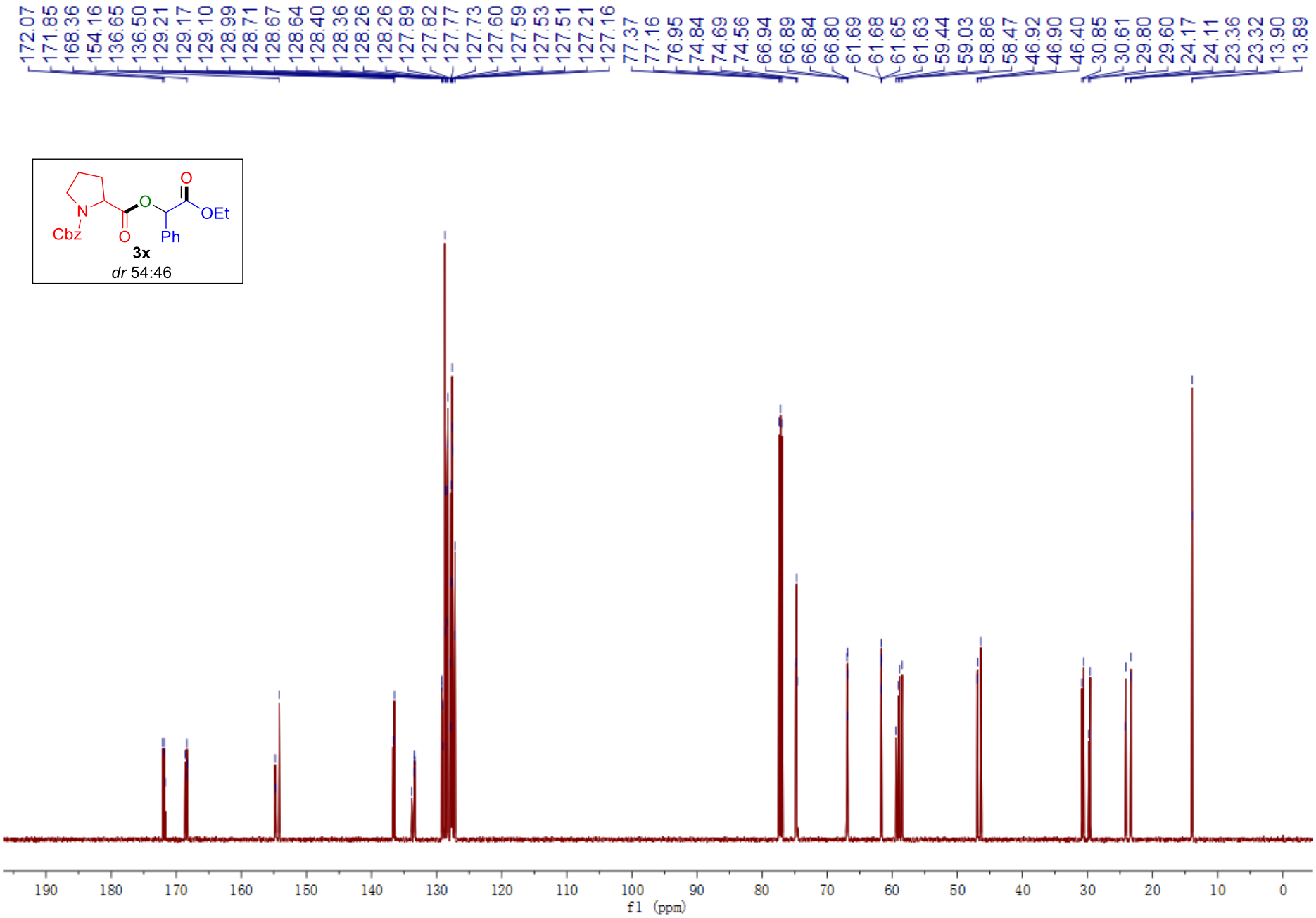

169.26
169.14
168.19
168.13
167.38
134.26
134.25
133.55
133.48
131.98
131.90
129.31
129.26
128.83
128.76
127.49
127.44
123.59
123.57
77.48
77.16
76.84
75.56
75.53
61.94
61.88
47.68
47.65
15.30
15.21
14.01
13.99
O
N
O
O
O
O
OEt
Ph
3v
dr 53:47
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

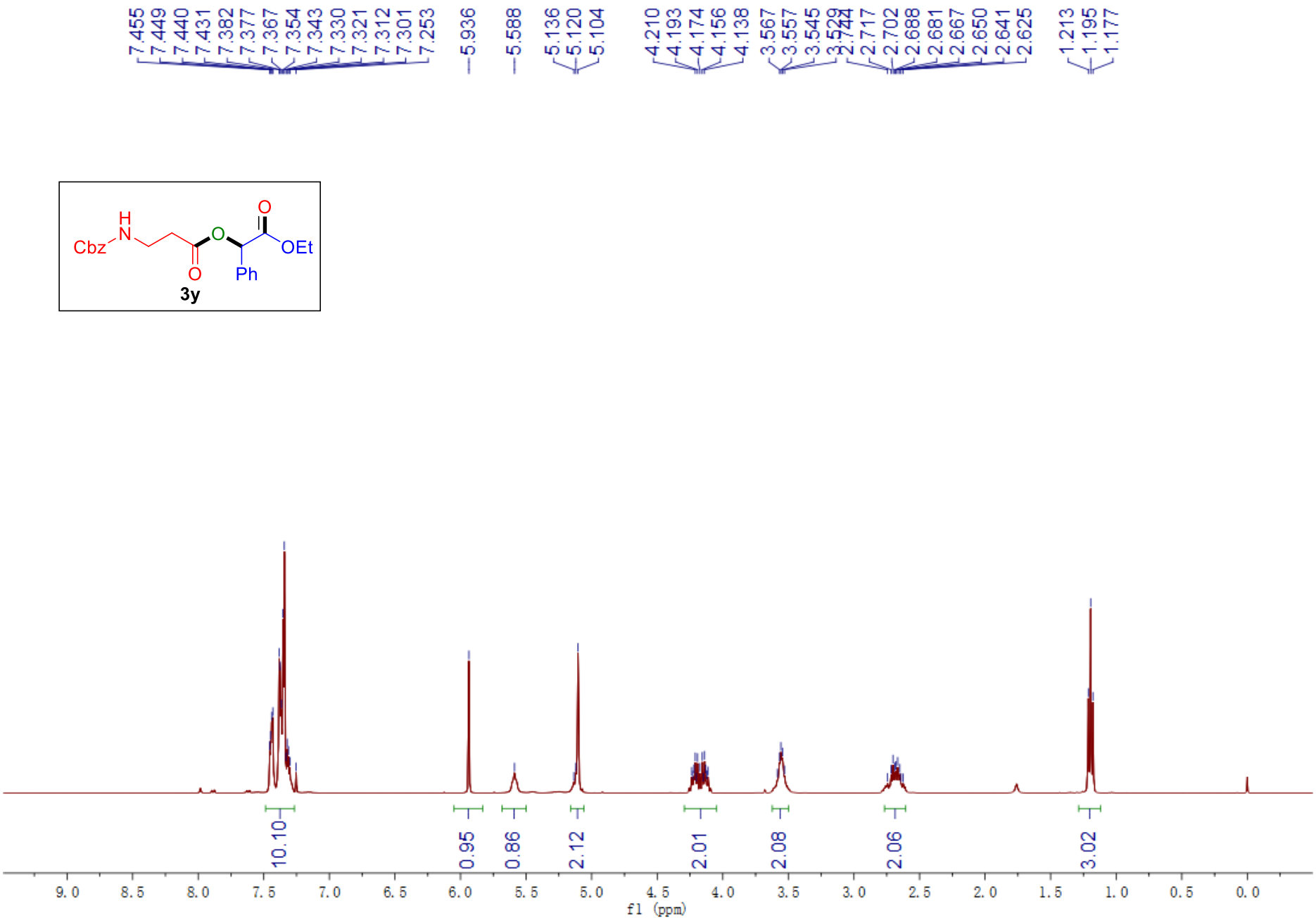
Boc
N
H
O
O
O
OEt
Ph
3w

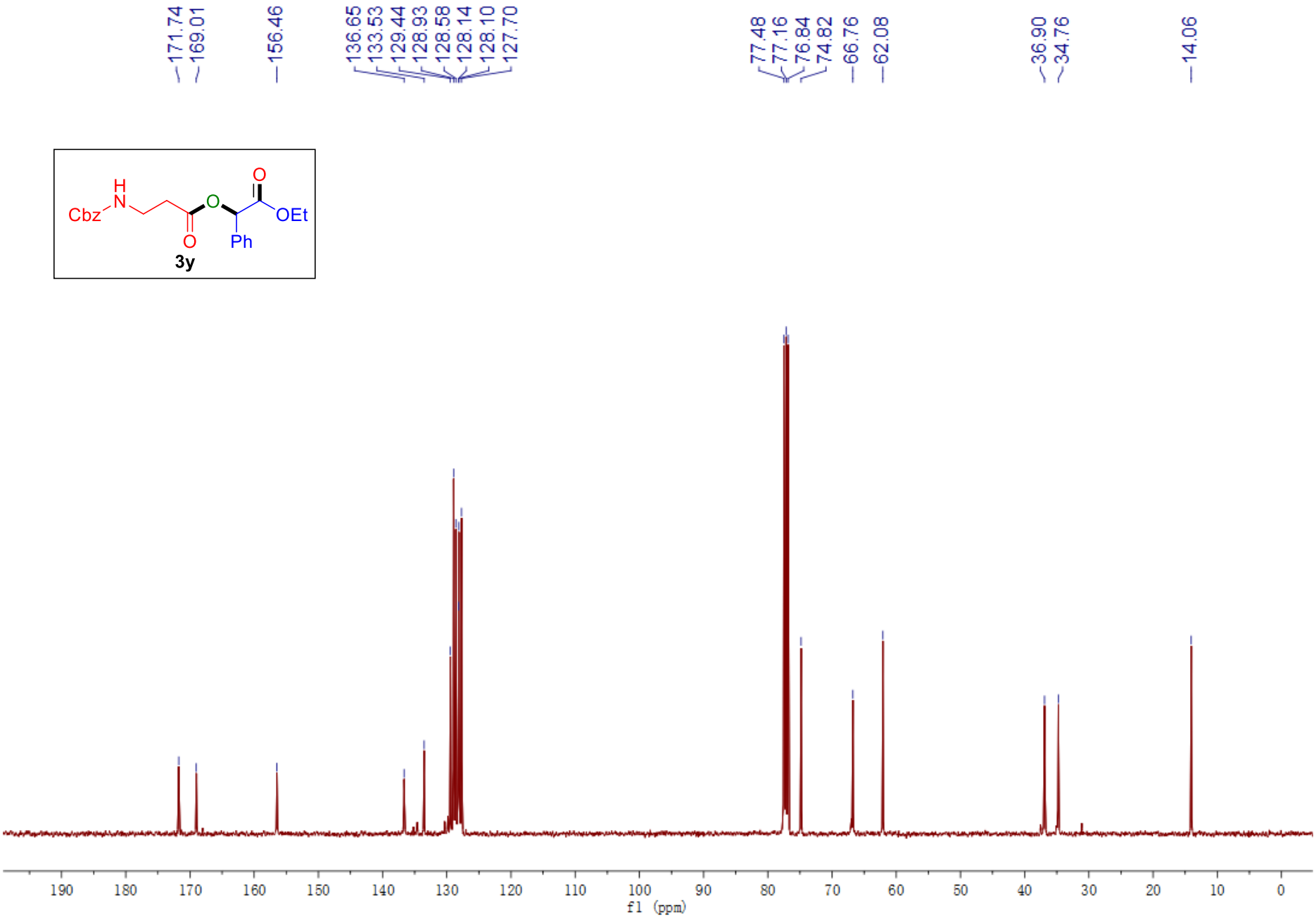

7.466
7.457
7.448
7.443
7.399
7.390
7.383
7.264
5.963
5.042
5.027
5.012
4.251
4.242
4.233
4.224
4.215
4.206
4.187
4.168
4.159
4.151
4.142
4.133
4.124
4.106
4.083
4.071
1.440
1.236
1.218
1.200
2.01
3.00
1.00
0.86
4.03
9.01
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

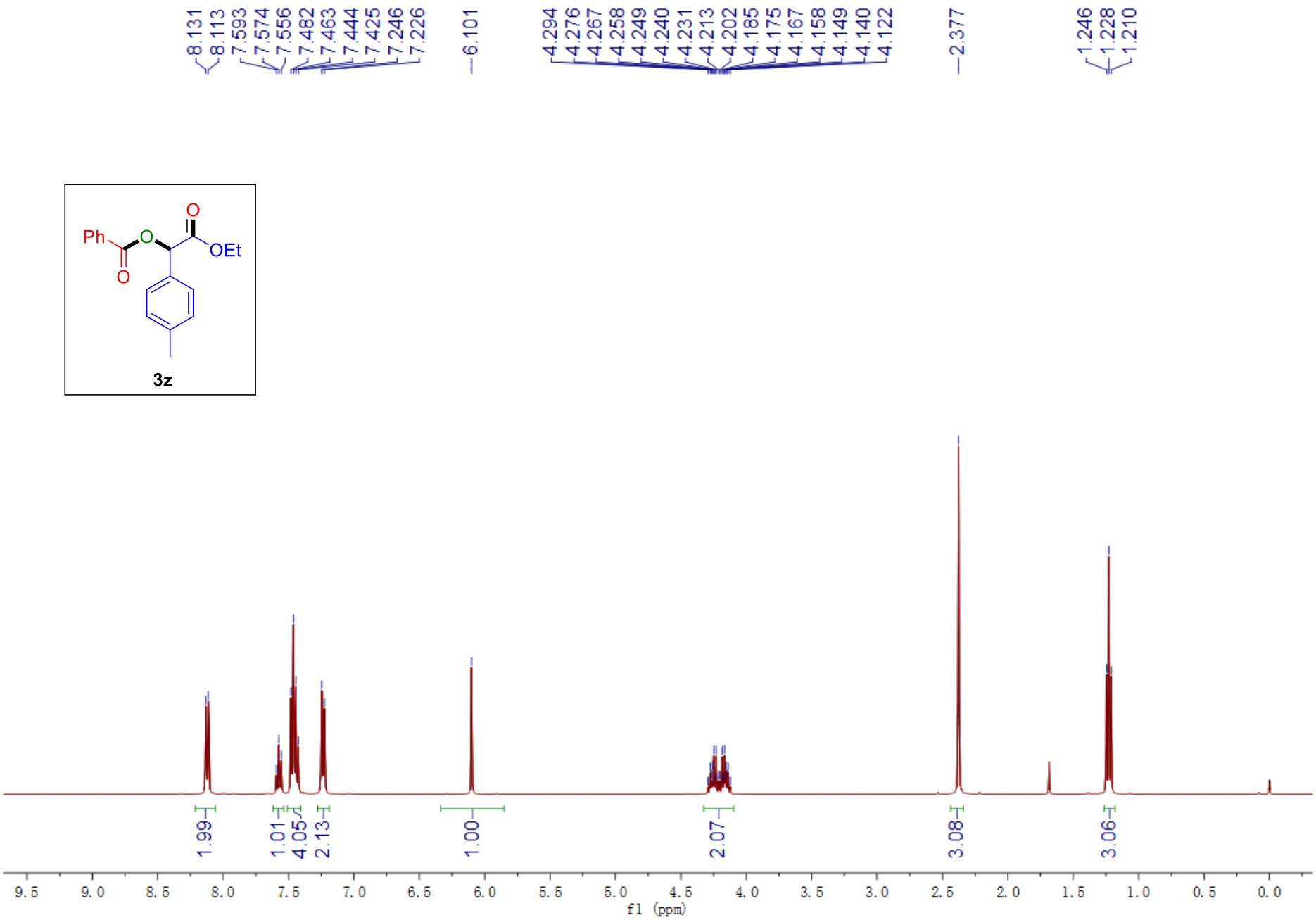

170.04
168.52
155.76
133.48
129.51
128.95
127.77
80.23
77.48
77.16
76.84
75.24
62.03
42.47
28.42
14.11
Boc
N
H
O
O
O
OEt
Ph
3w
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.459 7.456 7.446 7.444 7.378 7.370 7.361 7.356 7.352 7.348 7.339 7.326 7.313 7.286 7.278 7.273 7.266 7.261 7.256 7.214 5.966 5.951 5.832 5.153 5.128 5.090 5.075 5.028 5.018 4.550 4.544 4.487 4.481 4.180 4.168 4.167 4.158 4.154 4.148 4.142 4.137 4.132 4.126 4.120 4.114 4.103 2.301 1.921 1.909 1.901 1.206 1.194 1.189 1.182 1.177 1.170 1.165 1.153
Cbz
N
O
O
O
OEt
Ph
3x
dr 54:46
5.966 5.951 5.832
0.18 0.28 0.54
6.0 5.9 5.8
4.558 4.550 4.544 4.535 4.530 4.502 4.496 4.487 4.481 4.474 4.467
0.46 0.54
4.6 4.5 4.4
10.18 0.18 0.28 0.53 2.04 1.01 2.04 1.05 1.06 4.24 3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

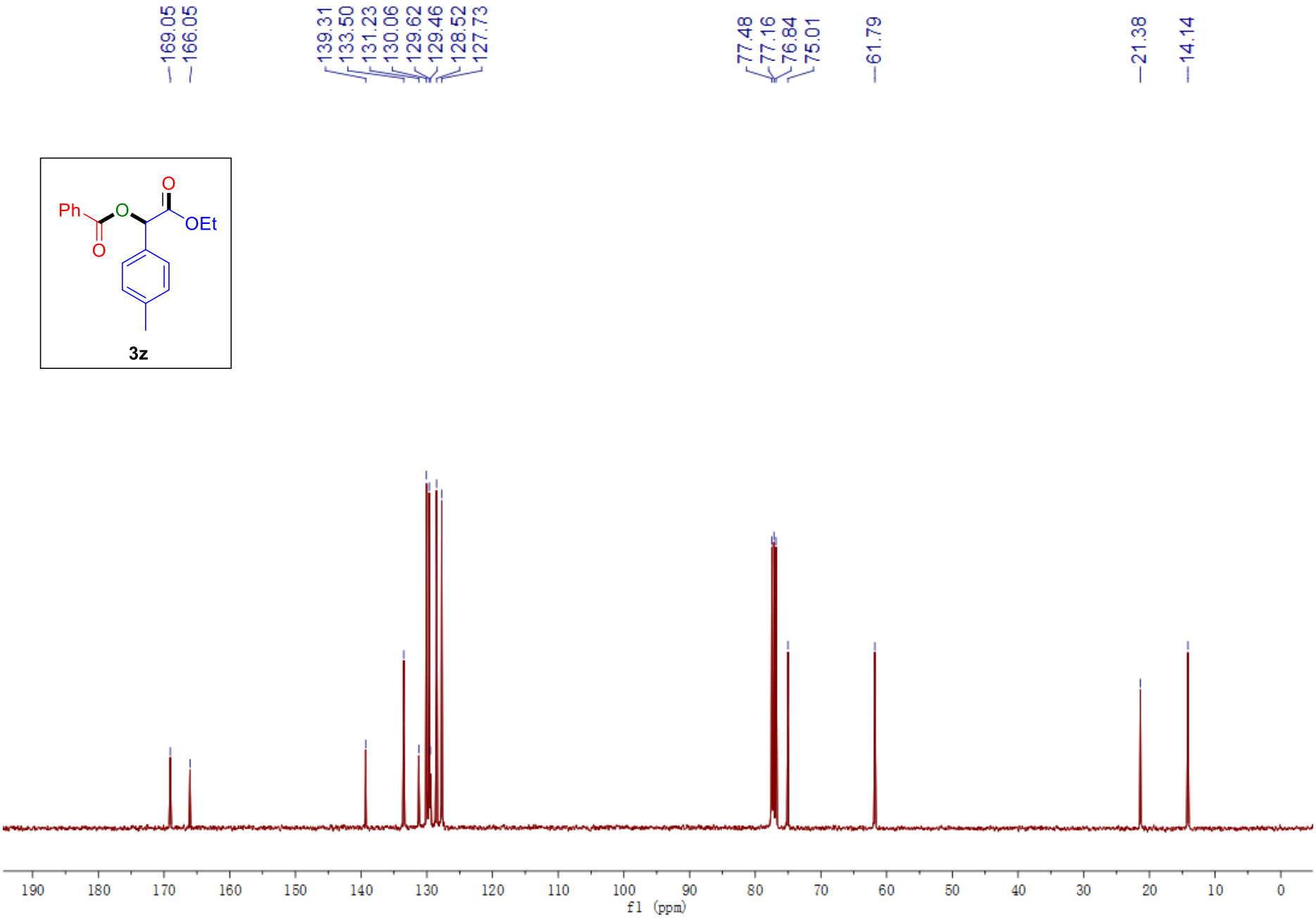

172.07
171.85
168.36
154.16
136.65
136.50
129.21
129.17
129.10
128.99
128.71
128.67
128.64
128.40
128.36
128.26
128.26
127.89
127.82
127.77
127.73
127.60
127.59
127.53
127.51
127.21
127.16
77.37
77.16
76.95
74.84
74.69
74.56
66.94
66.89
66.84
66.80
61.69
61.68
61.65
61.63
59.44
59.03
58.86
58.47
46.92
46.90
46.40
30.85
30.61
29.80
29.60
24.17
24.11
23.36
23.32
13.90
13.89
N
Cbz
O
O
O
Ph
O
OEt
3x
dr 54:46
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

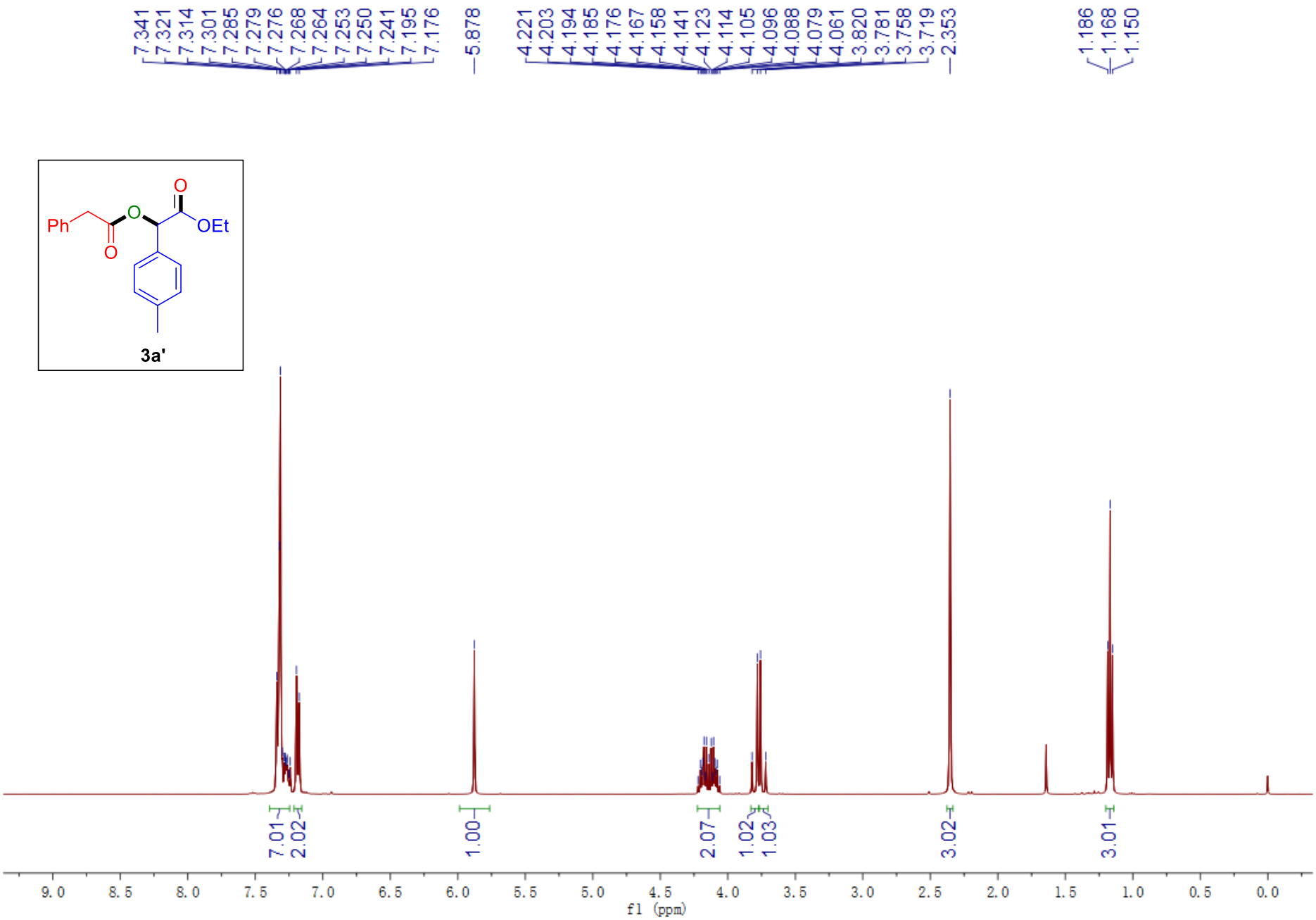

7.455
7.449
7.440
7.431
7.382
7.377
7.367
7.354
7.343
7.330
7.321
7.312
7.301
7.253
5.936
5.588
5.136
5.120
5.104
4.210
4.193
4.174
4.156
4.138
3.567
3.557
3.545
3.529
2.717
2.702
2.688
2.681
2.667
2.650
2.641
2.625
1.213
1.195
1.177
Cbz
H
N
O
O
O
OEt
Ph
3y
10.10
0.95
0.86
2.12
2.01
2.08
2.06
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

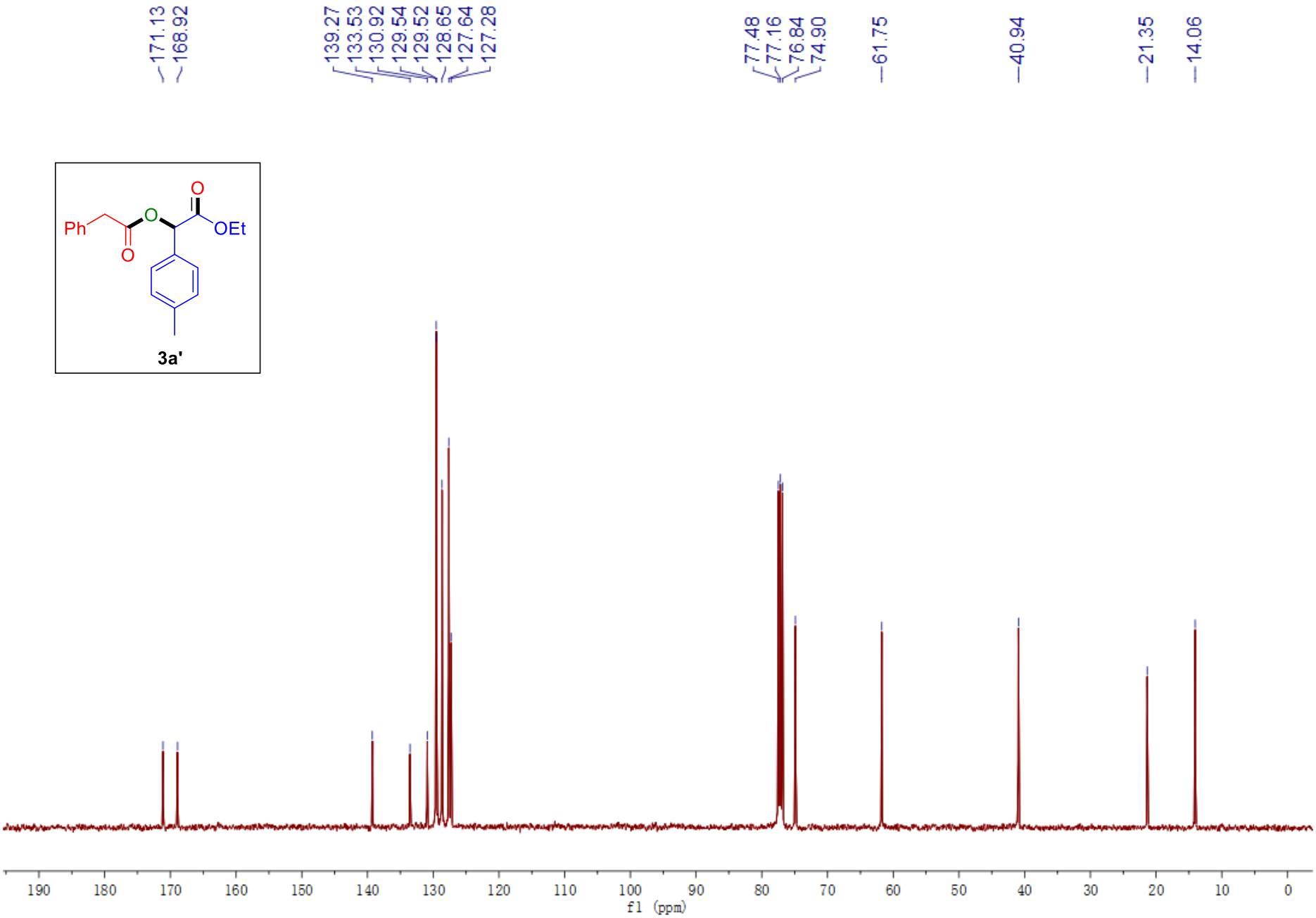

171.74
169.01
156.46
136.65
133.53
129.44
128.93
128.58
128.14
128.10
127.70
77.48
77.16
76.84
74.82
66.76
62.08
36.90
34.76
14.06
Cbz
H
N
O
O
O
OEt
Ph
3y
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

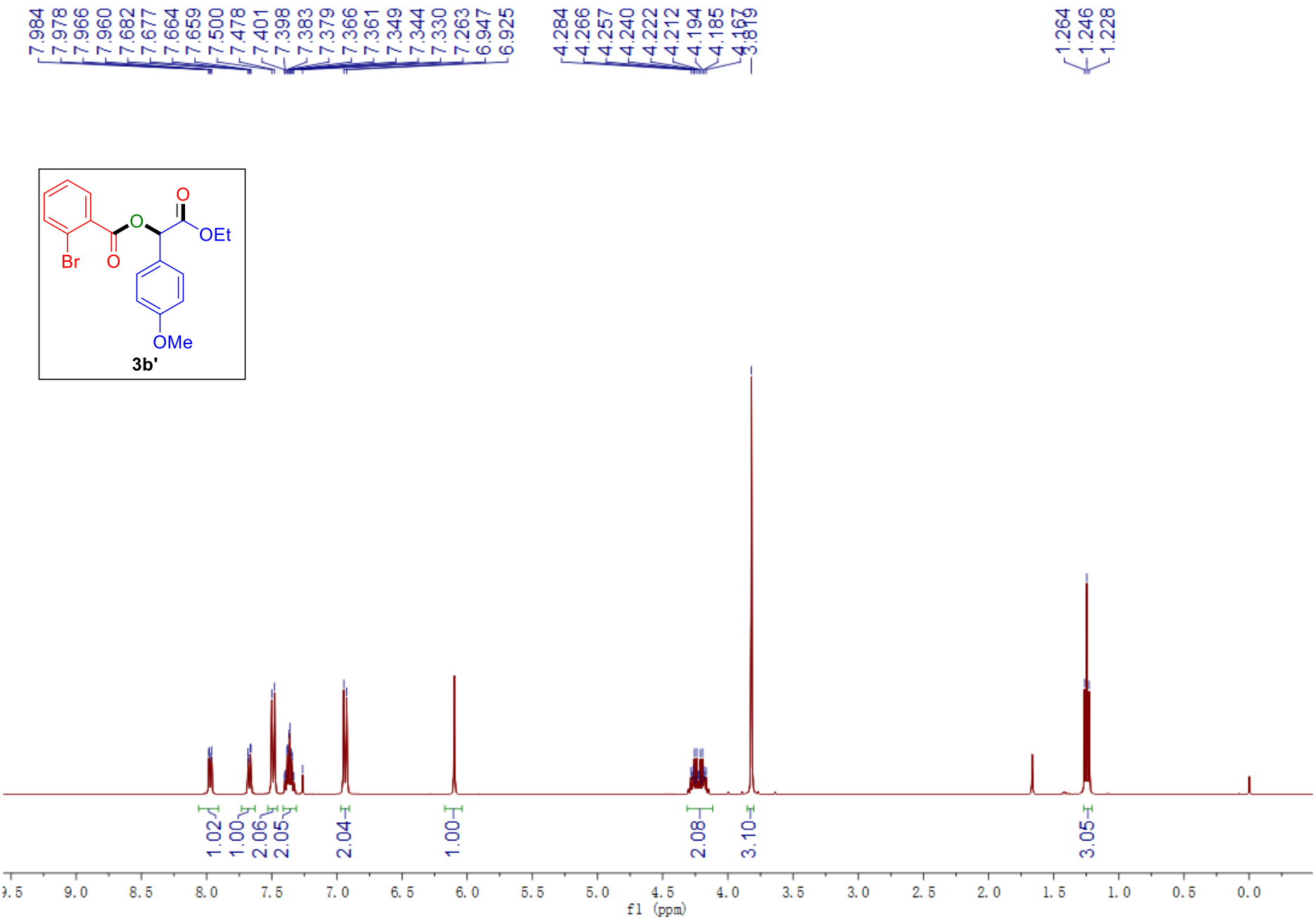

8.131
8.113
7.593
7.574
7.556
7.482
7.463
7.444
7.425
7.246
7.226
6.101
4.294
4.276
4.267
4.258
4.249
4.240
4.231
4.213
4.202
4.185
4.175
4.167
4.158
4.149
4.140
4.122
2.377
1.246
1.228
1.210
Ph
O
O
O
OEt
3z
1.99
1.01
4.05
2.13
1.00
2.07
3.08
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

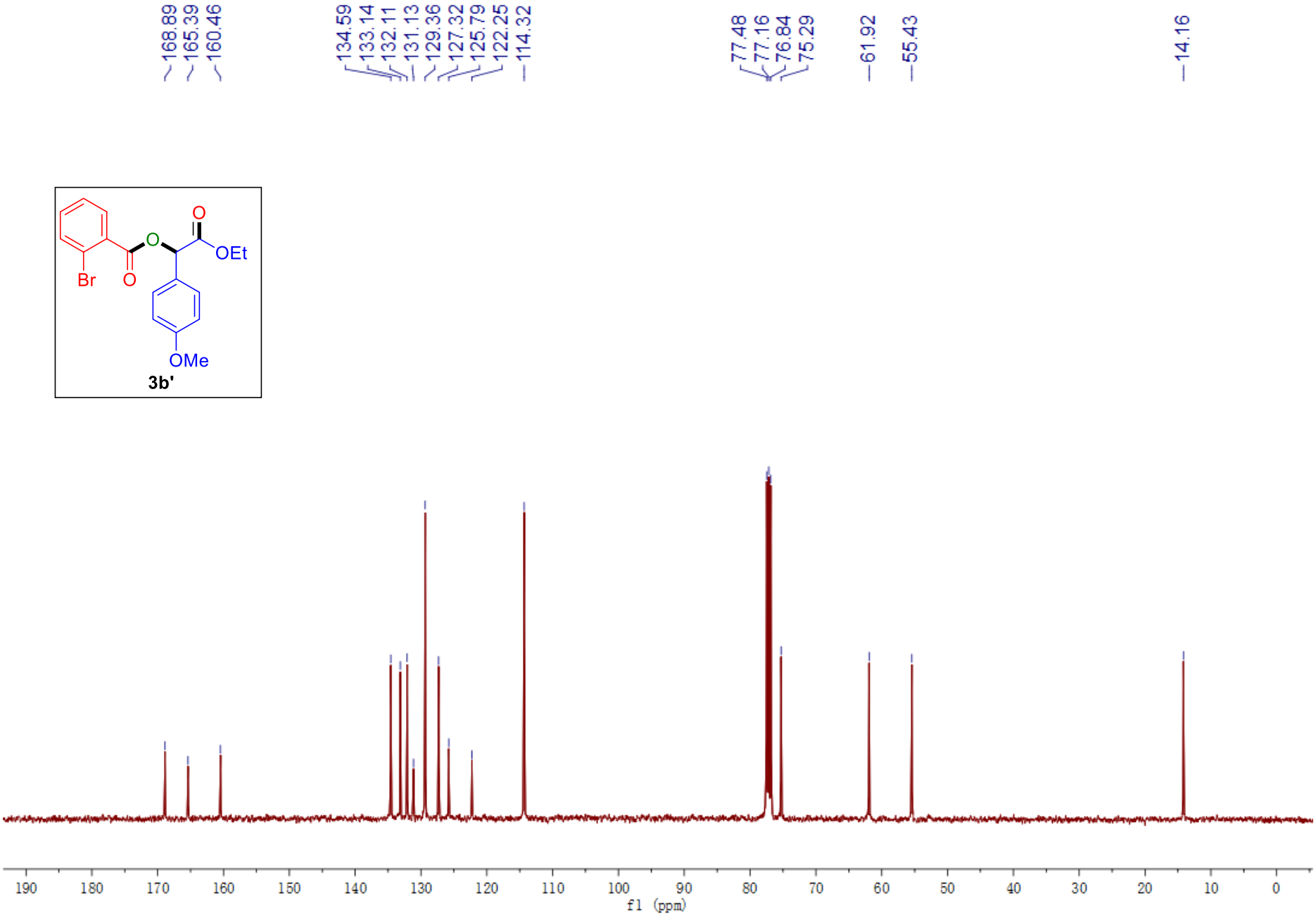
Ph
O
O
O
OEt
3z

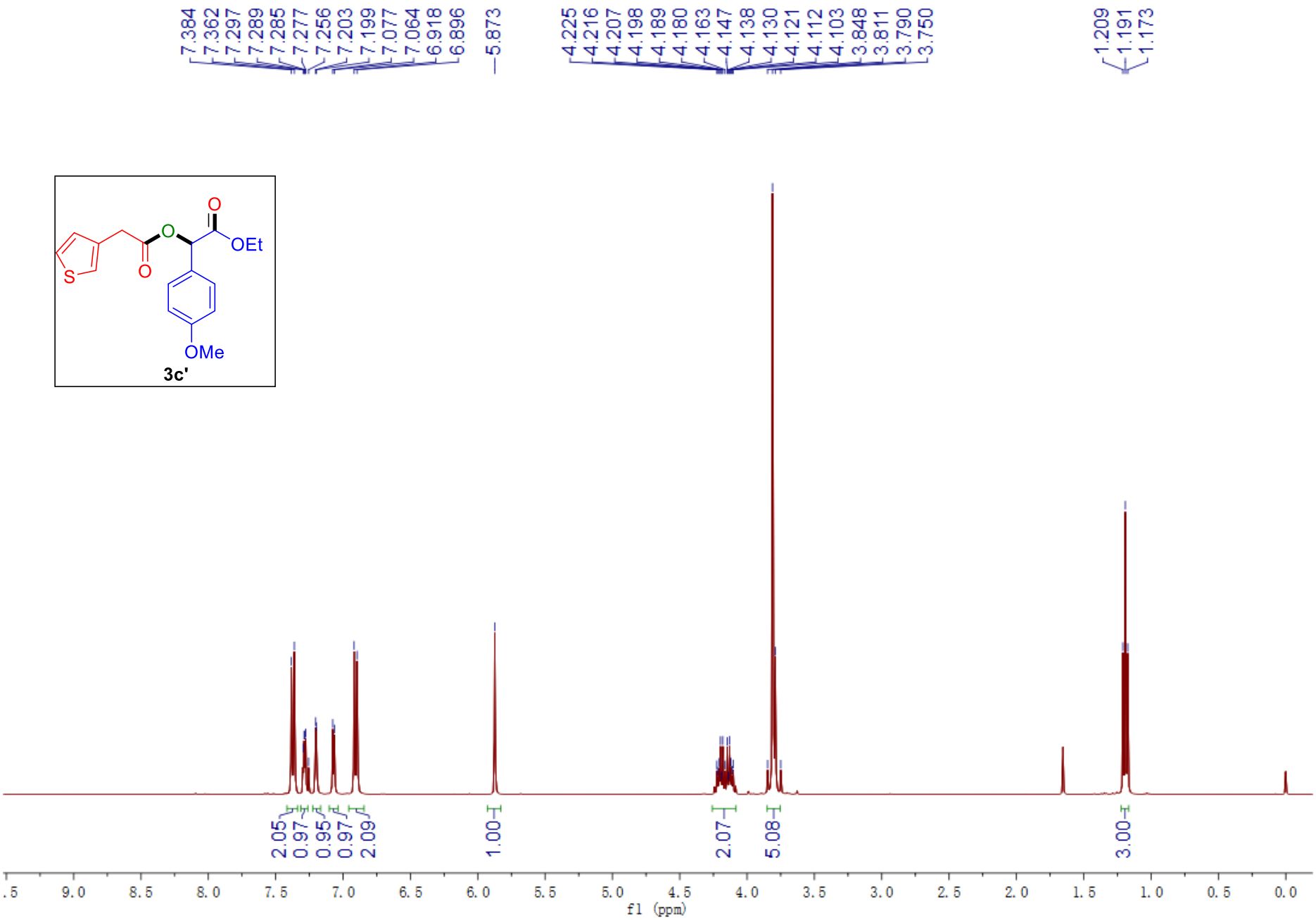

169.05
166.05
139.31
133.50
131.23
130.06
129.62
129.46
128.52
127.73
77.48
77.16
76.84
75.01
61.79
21.38
14.14
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

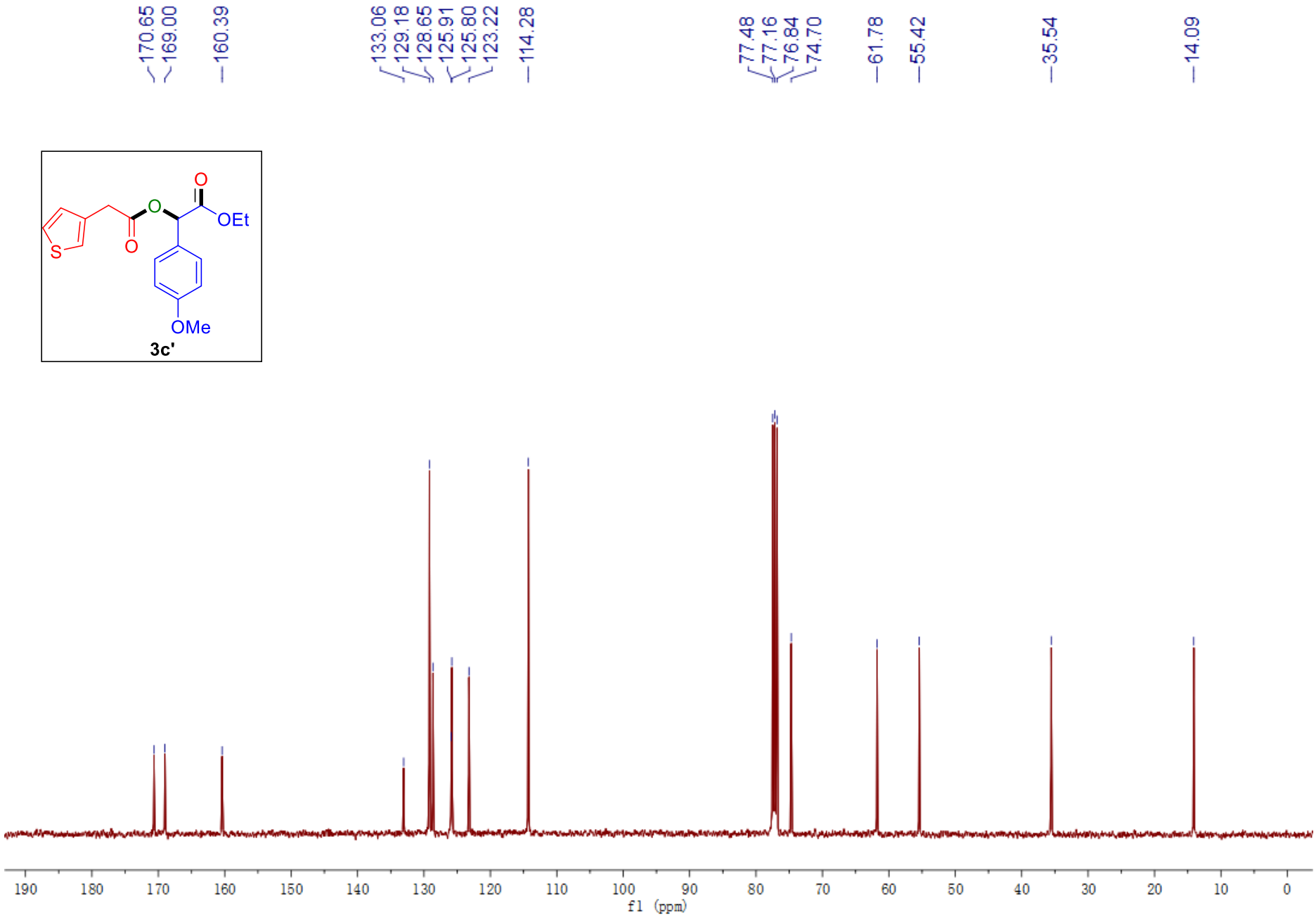

7.341
7.321
7.314
7.301
7.285
7.279
7.276
7.268
7.264
7.253
7.250
7.241
7.195
7.176
5.878
4.221
4.203
4.194
4.185
4.176
4.167
4.158
4.141
4.123
4.114
4.105
4.096
4.088
4.079
4.061
3.820
3.781
3.758
3.719
2.353
1.186
1.168
1.150
Ph
O
O
O
OEt
3a'
7.01
2.02
1.00
2.07
1.02
1.03
3.02
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

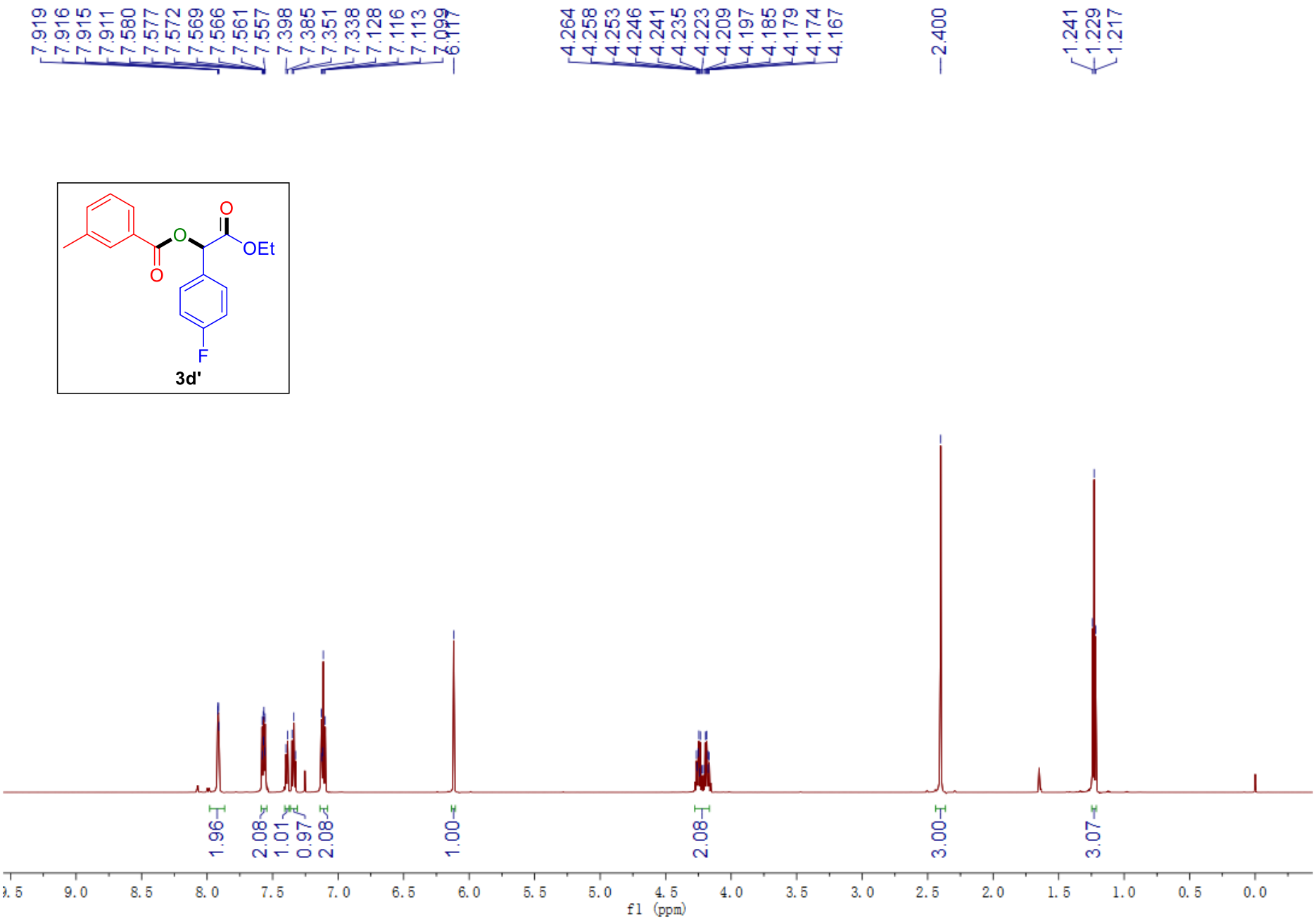

171.13
168.92
139.27
133.53
130.92
129.54
129.52
128.65
127.64
127.28
77.48
77.16
76.84
74.90
61.75
40.94
21.35
14.06
Ph
O
O
O
OEt
3a'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

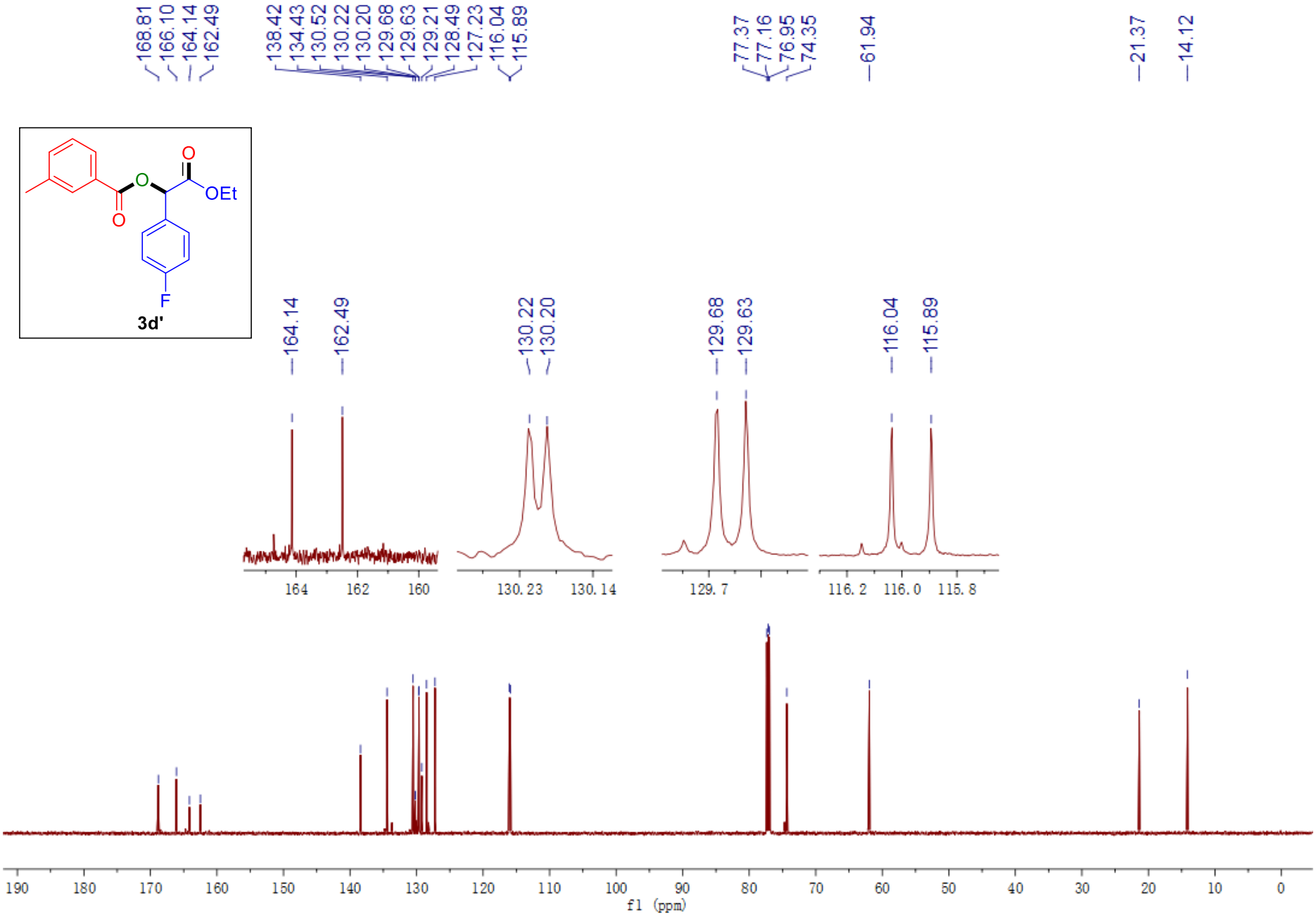

7.984
7.978
7.966
7.960
7.682
7.677
7.664
7.659
7.500
7.478
7.401
7.398
7.383
7.379
7.366
7.361
7.349
7.344
7.330
7.263
6.947
6.925
4.284
4.266
4.257
4.240
4.222
4.212
4.194
4.185
4.167
3.819
1.264
1.246
1.228
Br
O
O
O
OEt
OMe
3b'
1.02
1.00
2.06
2.05
2.04
1.00
2.08
3.10
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

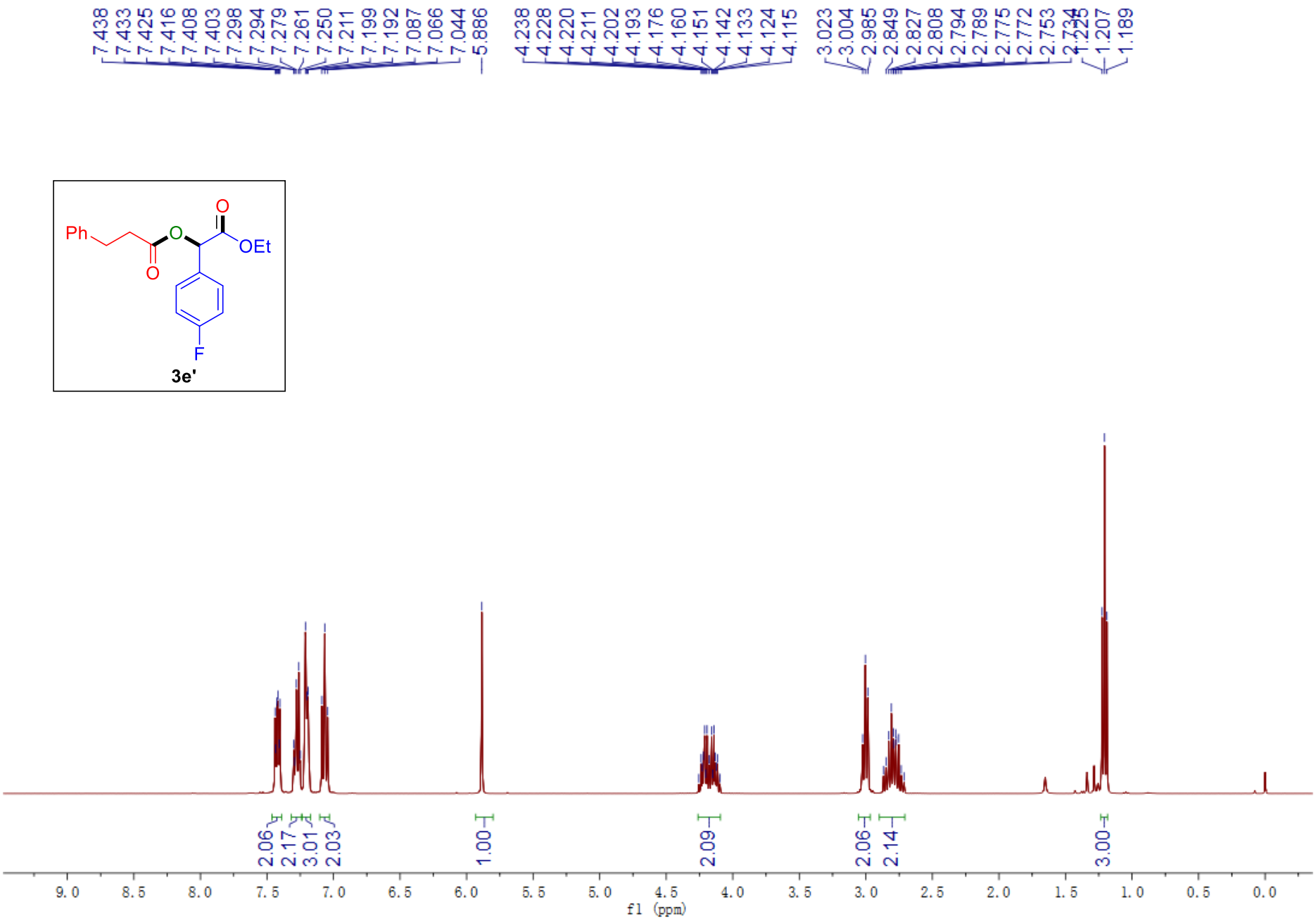

168.89
165.39
160.46
134.59
133.14
132.11
131.13
129.36
127.32
125.79
122.25
114.32
77.48
77.16
76.84
75.29
61.92
55.43
14.16
Br
O
O
O
OEt
OMe
3b'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

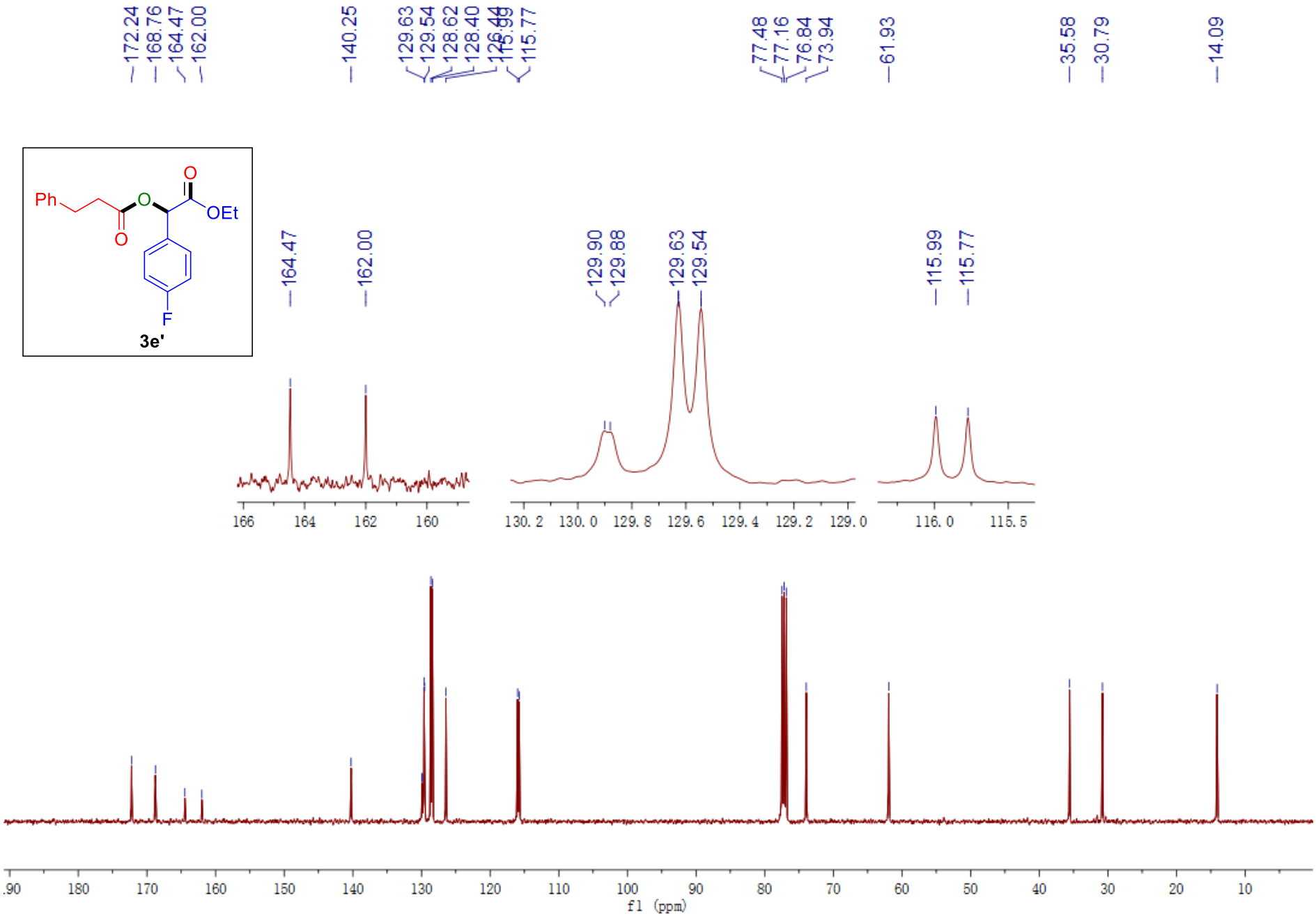

7.384
7.362
7.297
7.289
7.285
7.277
7.256
7.203
7.199
7.077
7.064
6.918
6.896
5.873
4.225
4.216
4.207
4.198
4.189
4.180
4.163
4.147
4.138
4.130
4.121
4.112
4.103
3.848
3.811
3.790
3.750
1.209
1.191
1.173
O
O
OEt
S
O
OMe
3c'
2.05
0.97
0.95
0.97
2.09
1.00
2.07
5.08
3.00
f1 (ppm)

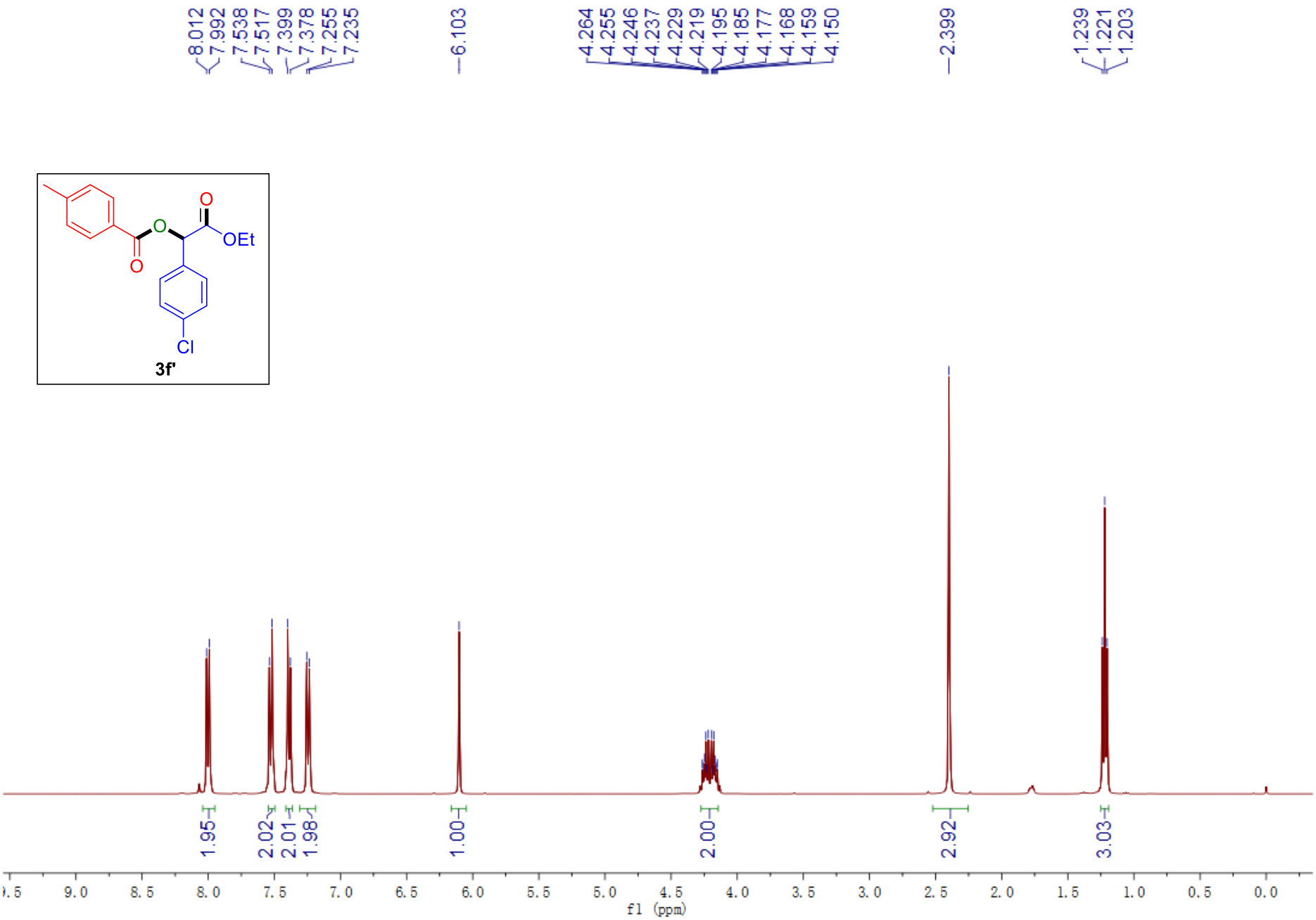

170.65
169.00
160.39
133.06
129.18
128.65
125.91
125.80
123.22
114.28
77.48
77.16
76.84
74.70
61.78
55.42
35.54
14.09
O
O
OEt
O
S
OMe
3c'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

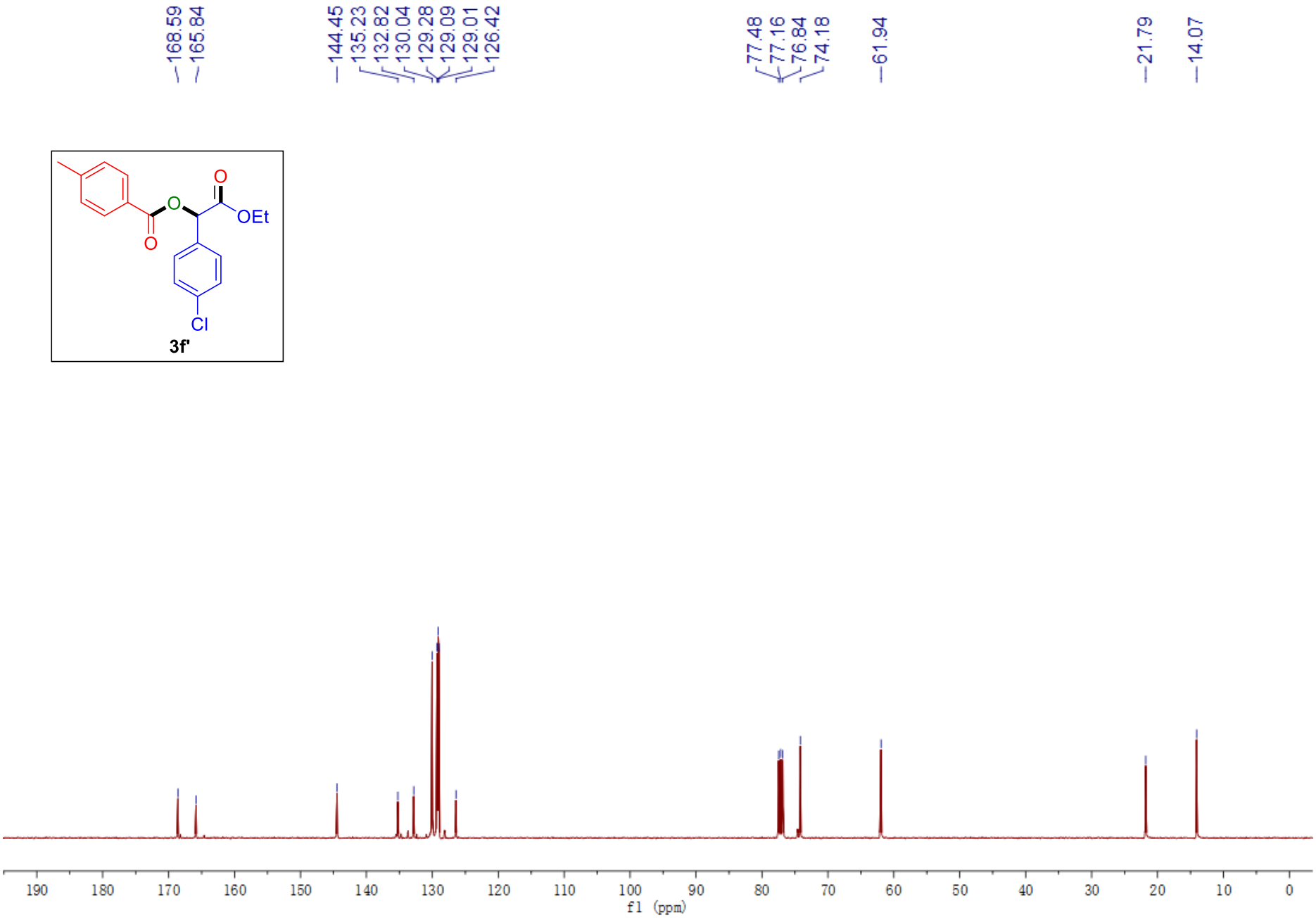

7.919
7.916
7.915
7.911
7.580
7.577
7.572
7.569
7.566
7.561
7.557
7.398
7.385
7.351
7.338
7.128
7.116
7.113
7.099
6.117
4.264
4.258
4.253
4.246
4.241
4.235
4.223
4.209
4.197
4.185
4.179
4.174
4.167
2.400
1.241
1.229
1.217
O
O
OEt
O
F
3d'
1.96
2.08
1.01
0.97
2.08
1.00
2.08
3.00
3.07
f1 (ppm)

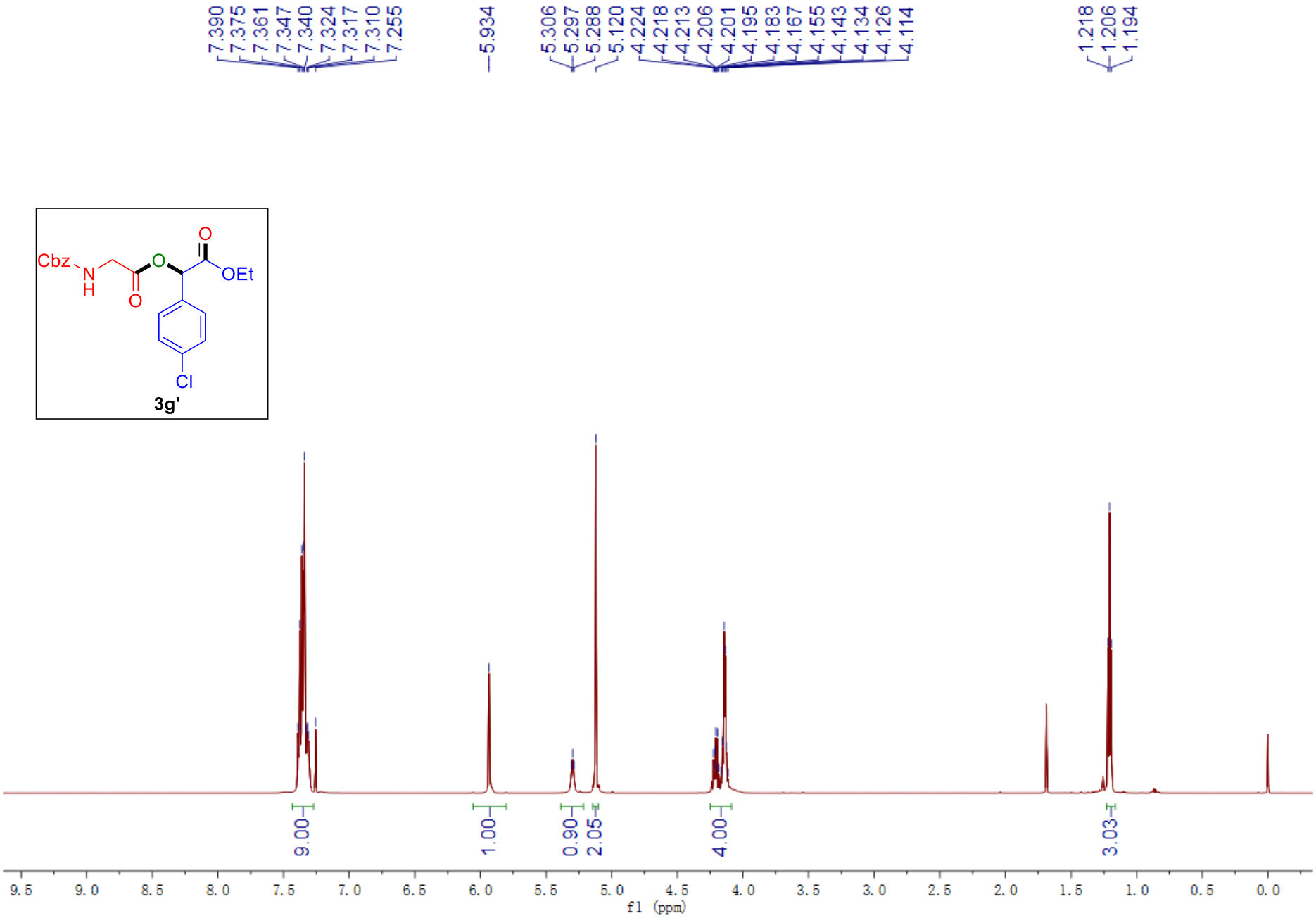

168.81
166.10
164.14
162.49
138.42
134.43
130.52
130.22
130.20
129.68
129.63
129.21
128.49
127.23
116.04
115.89
77.37
77.16
76.95
74.35
61.94
21.37
14.12
O
O
O
OEt
F
3d'
164.14
162.49
130.22
130.20
129.68
129.63
116.04
115.89
164
162
160
130.23
130.14
129.7
116.2
116.0
115.8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

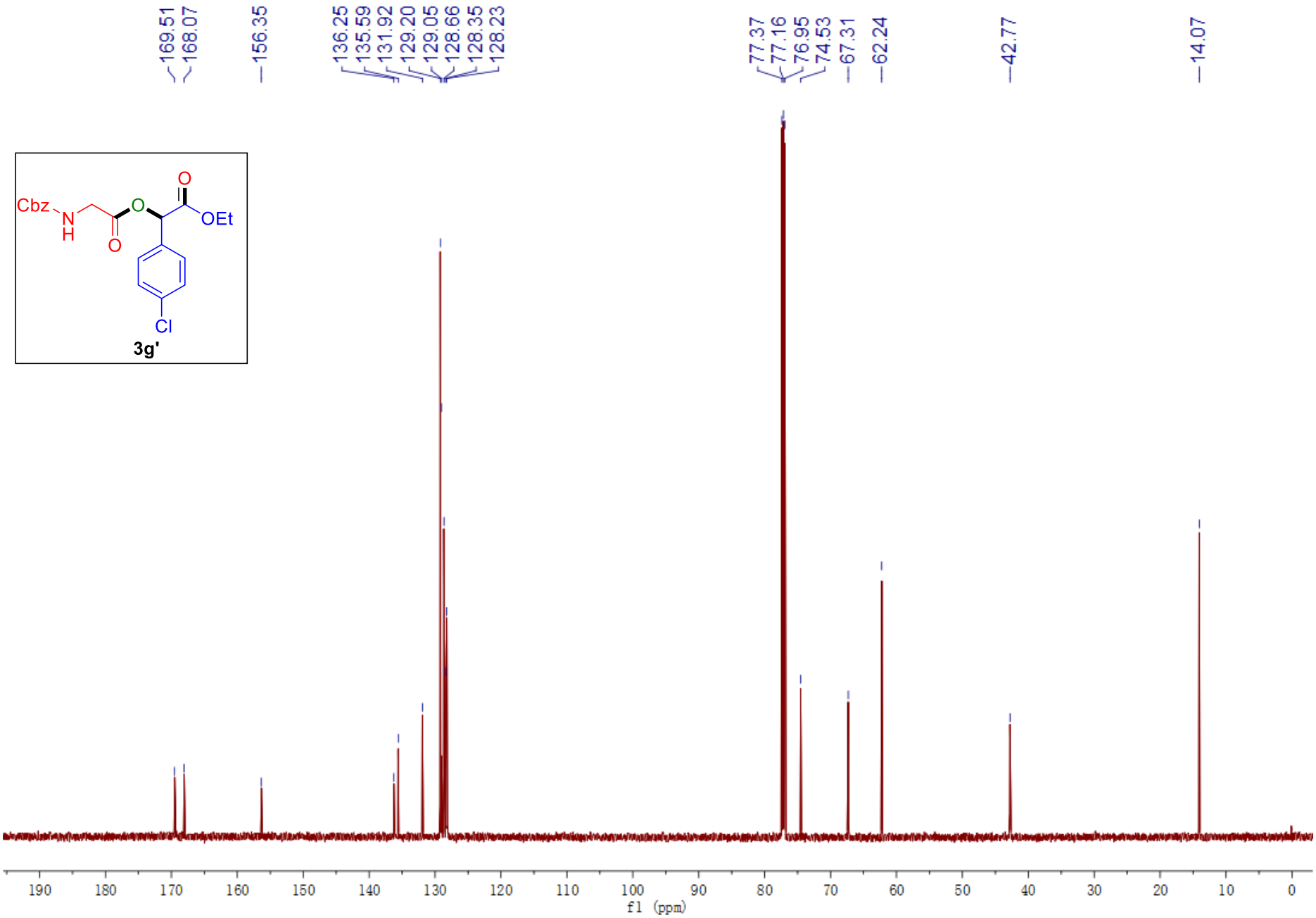

7.438
7.433
7.425
7.416
7.408
7.403
7.298
7.294
7.279
7.261
7.250
7.211
7.199
7.192
7.087
7.066
7.044
5.886
4.238
4.228
4.220
4.211
4.202
4.193
4.176
4.160
4.151
4.142
4.133
4.124
4.115
3.023
3.004
2.985
2.849
2.827
2.808
2.794
2.789
2.775
2.772
2.753
1.207
1.189
Ph
O
O
O
OEt
F
3e'
2.06
2.17
3.01
2.03
1.00
2.09
2.06
2.14
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

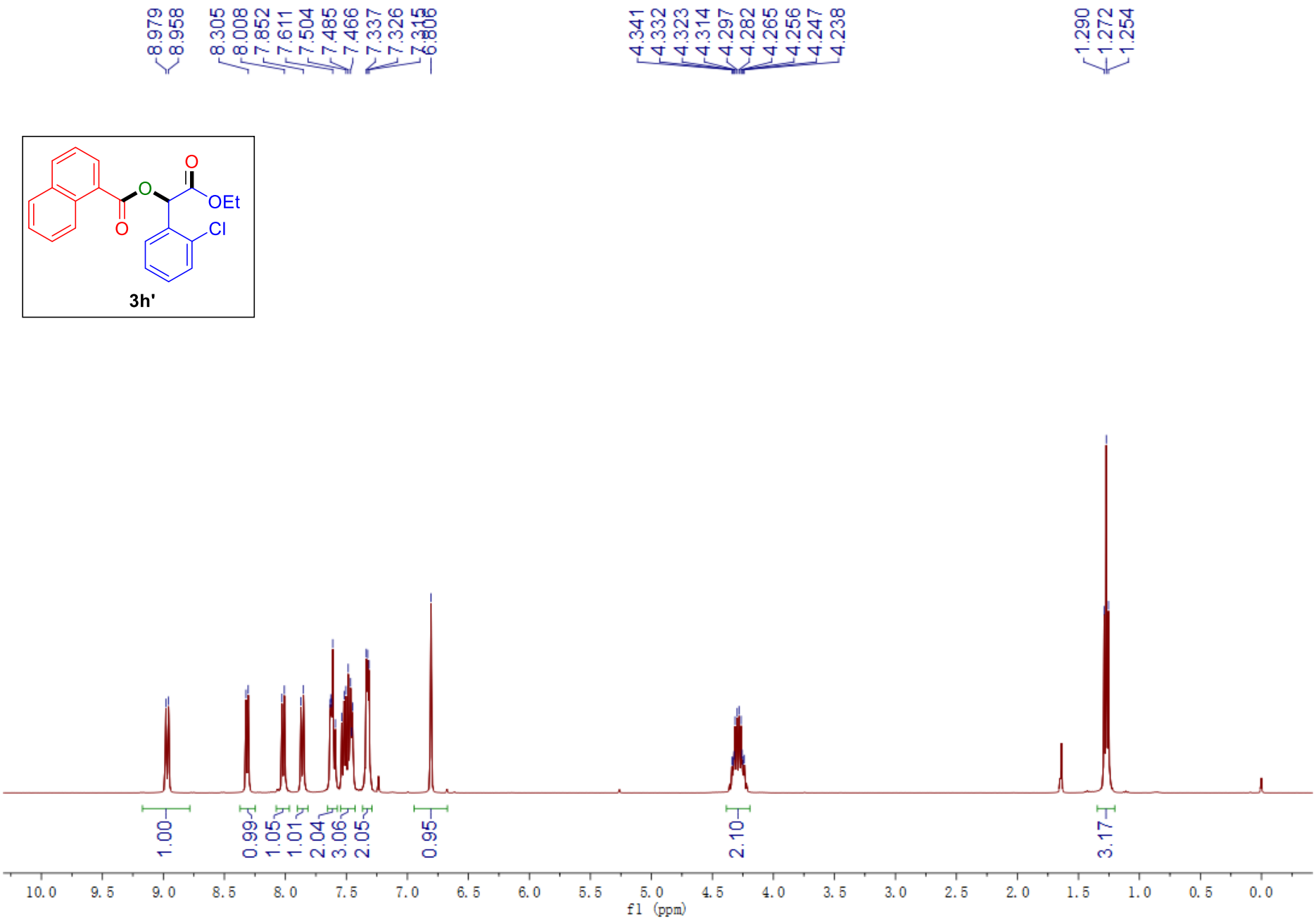

172.24
168.76
164.47
162.00
140.25
129.63
129.54
128.62
128.40
126.44
115.99
115.77
77.48
77.16
76.84
73.94
61.93
35.58
30.79
14.09
Ph
O
O
O
OEt
F
3e'
164.47
162.00
129.90
129.88
129.63
129.54
115.99
115.77
166
164
162
160
130.2
130.0
129.8
129.6
129.4
129.2
129.0
116.0
115.5
.90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.012
7.992
7.538
7.517
7.399
7.378
7.255
7.235
6.103
4.264
4.255
4.246
4.237
4.229
4.219
4.195
4.185
4.177
4.168
4.159
4.150
2.399
1.239
1.221
1.203
O
O
OEt
O
Cl
3f'
1.95
2.02
2.01
1.98
1.00
2.00
2.92
3.03
f1 (ppm)

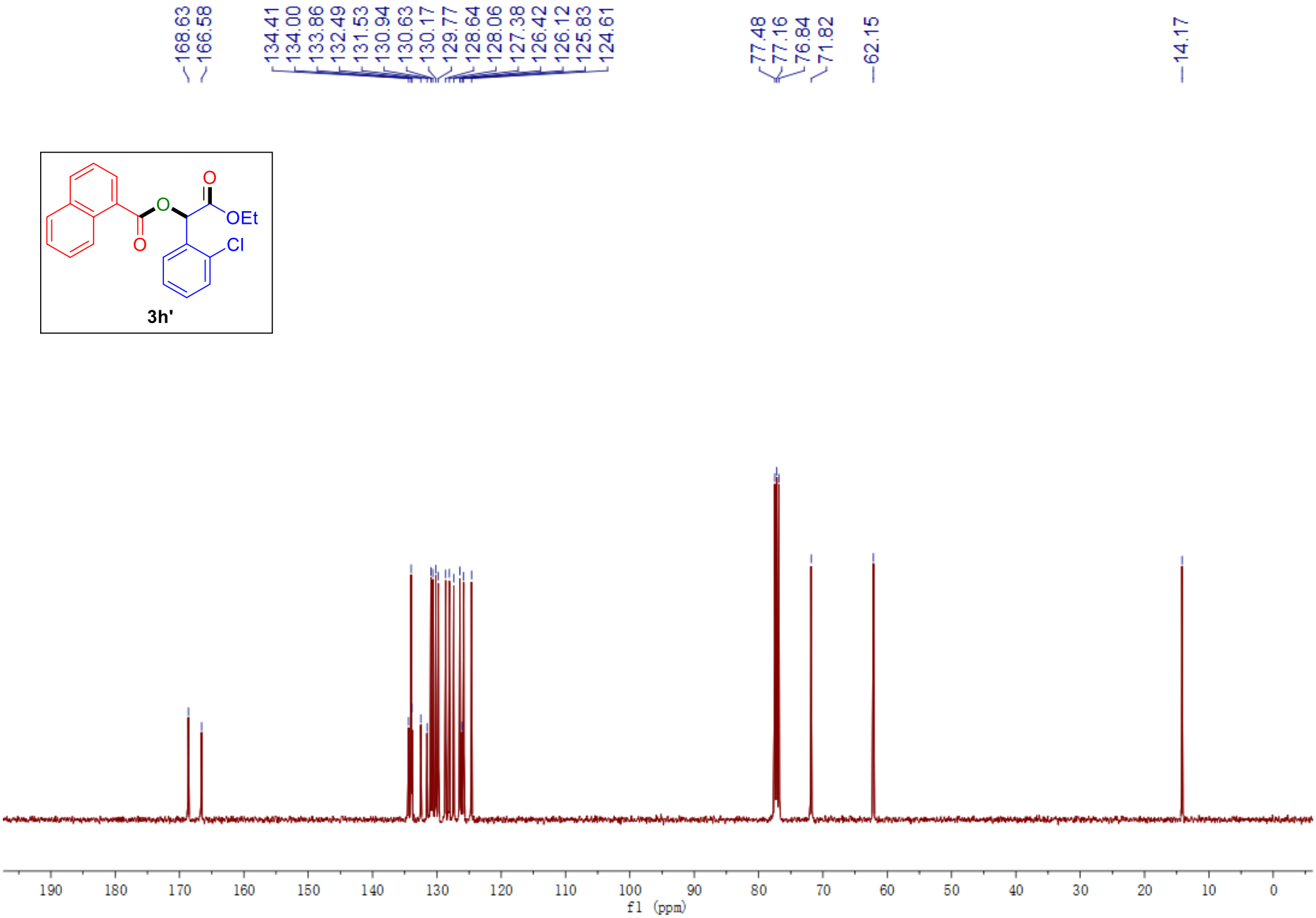

168.59
165.84
144.45
135.23
132.82
130.04
129.28
129.09
129.01
126.42
77.48
77.16
76.84
74.18
61.94
21.79
14.07
O
O
O
OEt
Cl
3f'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

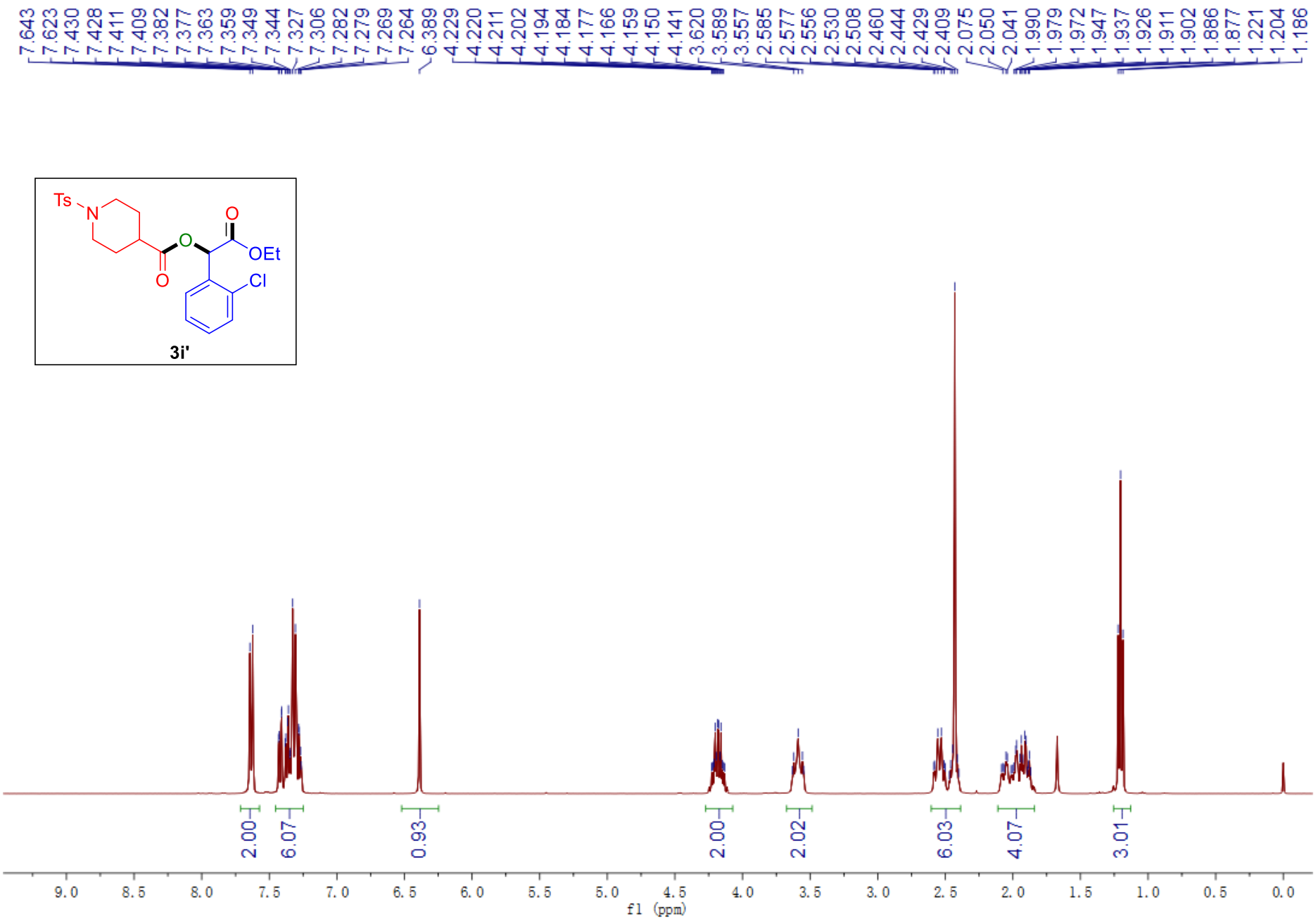

7.390
7.375
7.361
7.347
7.340
7.324
7.317
7.310
7.255
5.934
5.306
5.297
5.288
5.120
4.224
4.218
4.213
4.206
4.201
4.195
4.183
4.167
4.155
4.143
4.134
4.126
4.114
1.218
1.206
1.194
Cbz
N
H
O
O
O
OEt
Cl
3g'
9.00
1.00
0.90
2.05
4.00
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

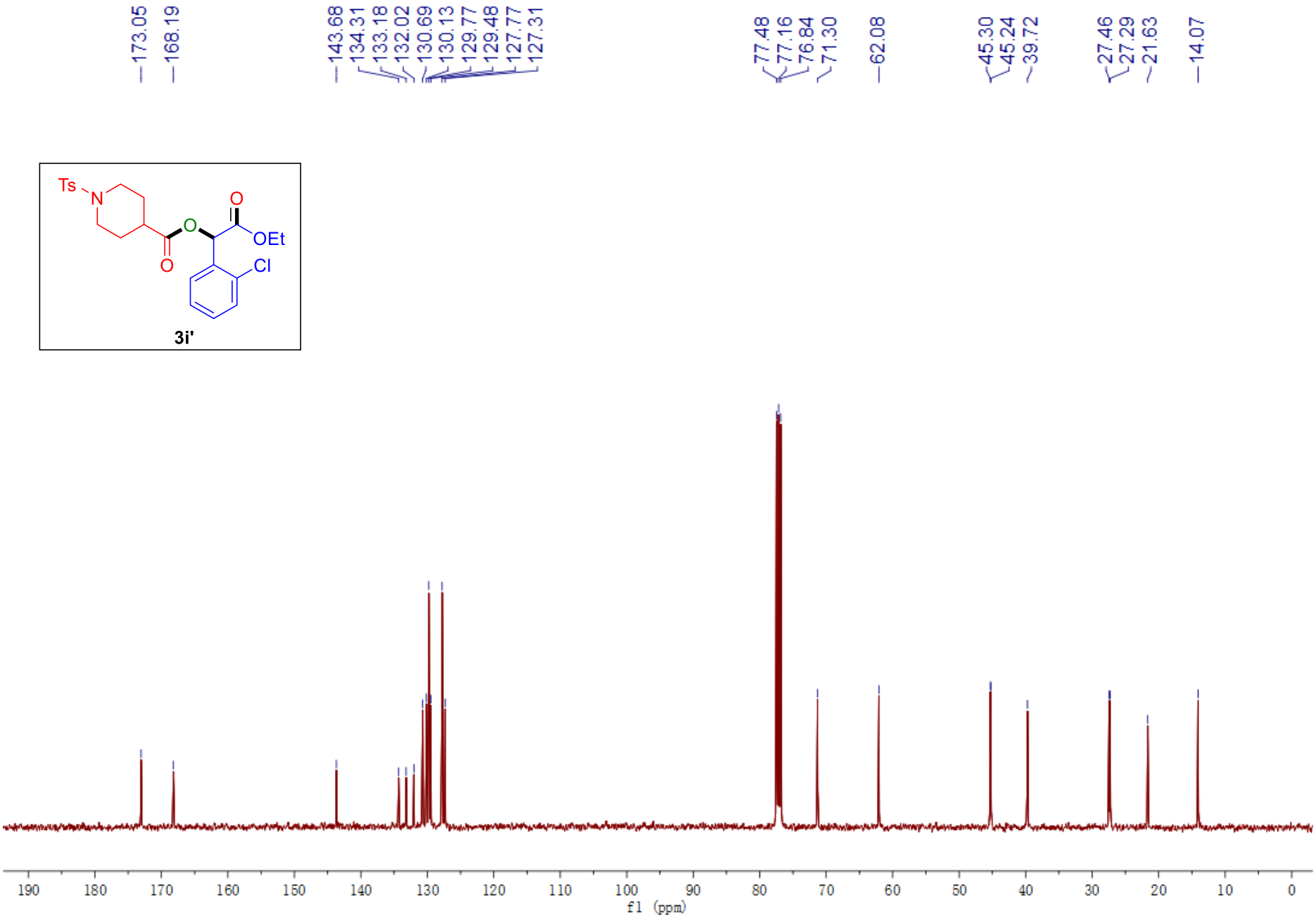

169.51
168.07
156.35
136.25
135.59
131.92
129.20
129.05
128.66
128.35
128.23
77.37
77.16
76.95
74.53
67.31
62.24
42.77
14.07
Cbz
N
H
O
O
O
OEt
Cl
3g'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

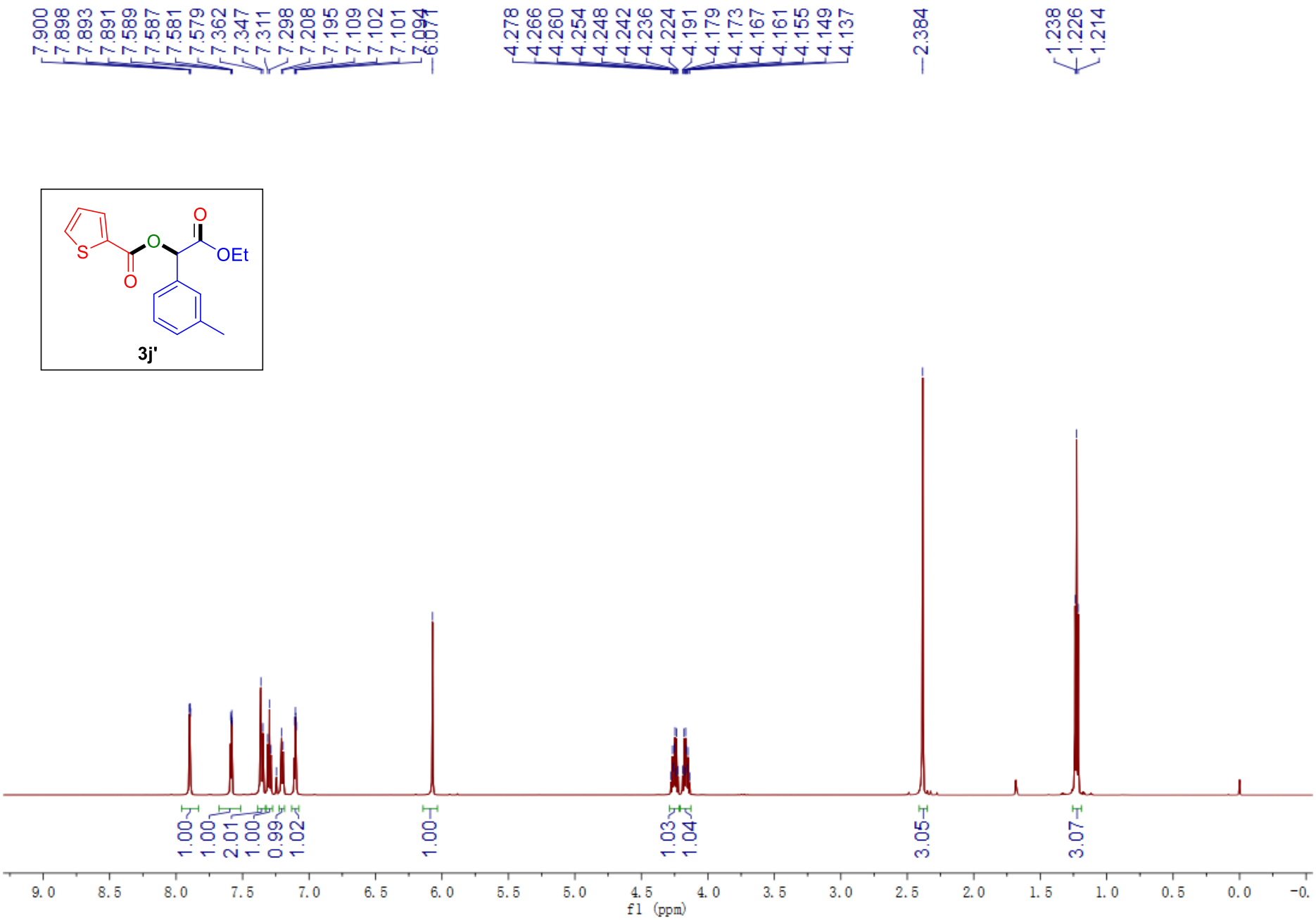

8.979
8.958
8.305
8.008
7.852
7.611
7.504
7.485
7.466
7.337
7.326
7.315
6.806
4.341
4.332
4.323
4.314
4.297
4.282
4.265
4.256
4.247
4.238
1.290
1.272
1.254
O
O
O
OEt
Cl
3h'
1.00
0.99
1.05
1.01
2.04
3.06
2.05
0.95
2.10
3.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

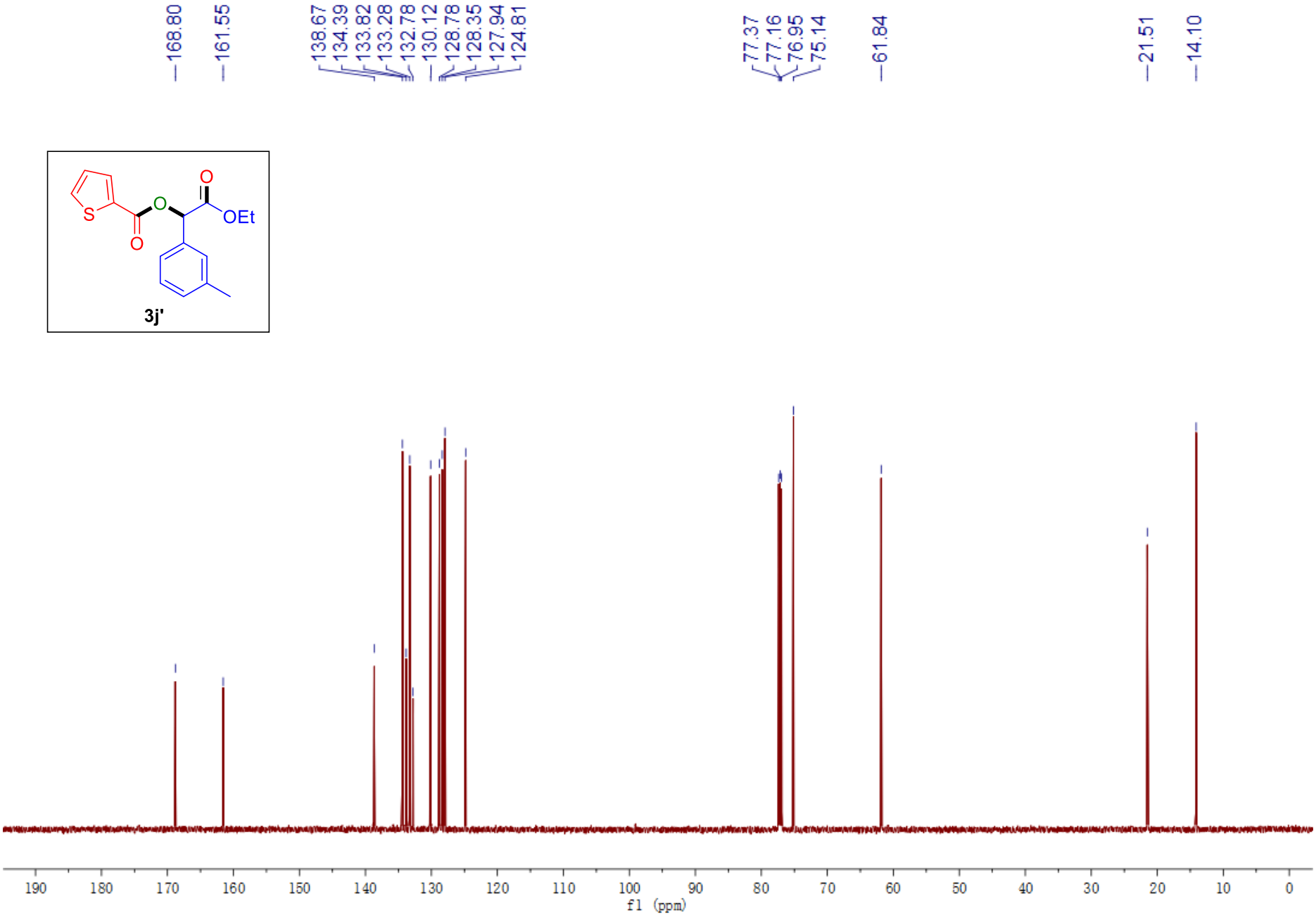
O
O
OEt
O
Cl
3h'

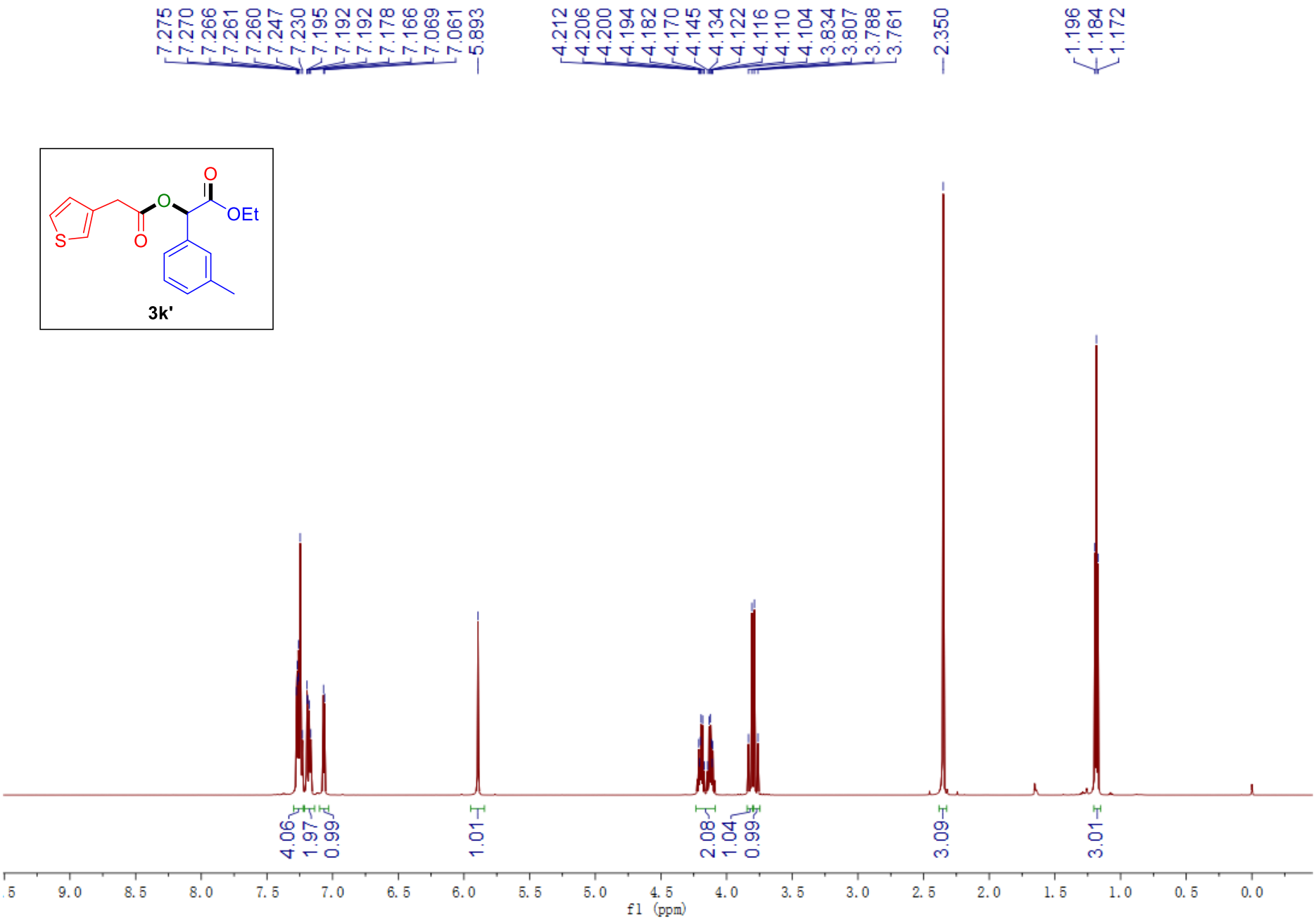

168.63
166.58
134.41
134.00
133.86
132.49
131.53
130.94
130.63
130.17
129.77
128.64
128.06
127.38
126.42
126.12
125.83
124.61
77.48
77.16
76.84
71.82
62.15
14.17
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

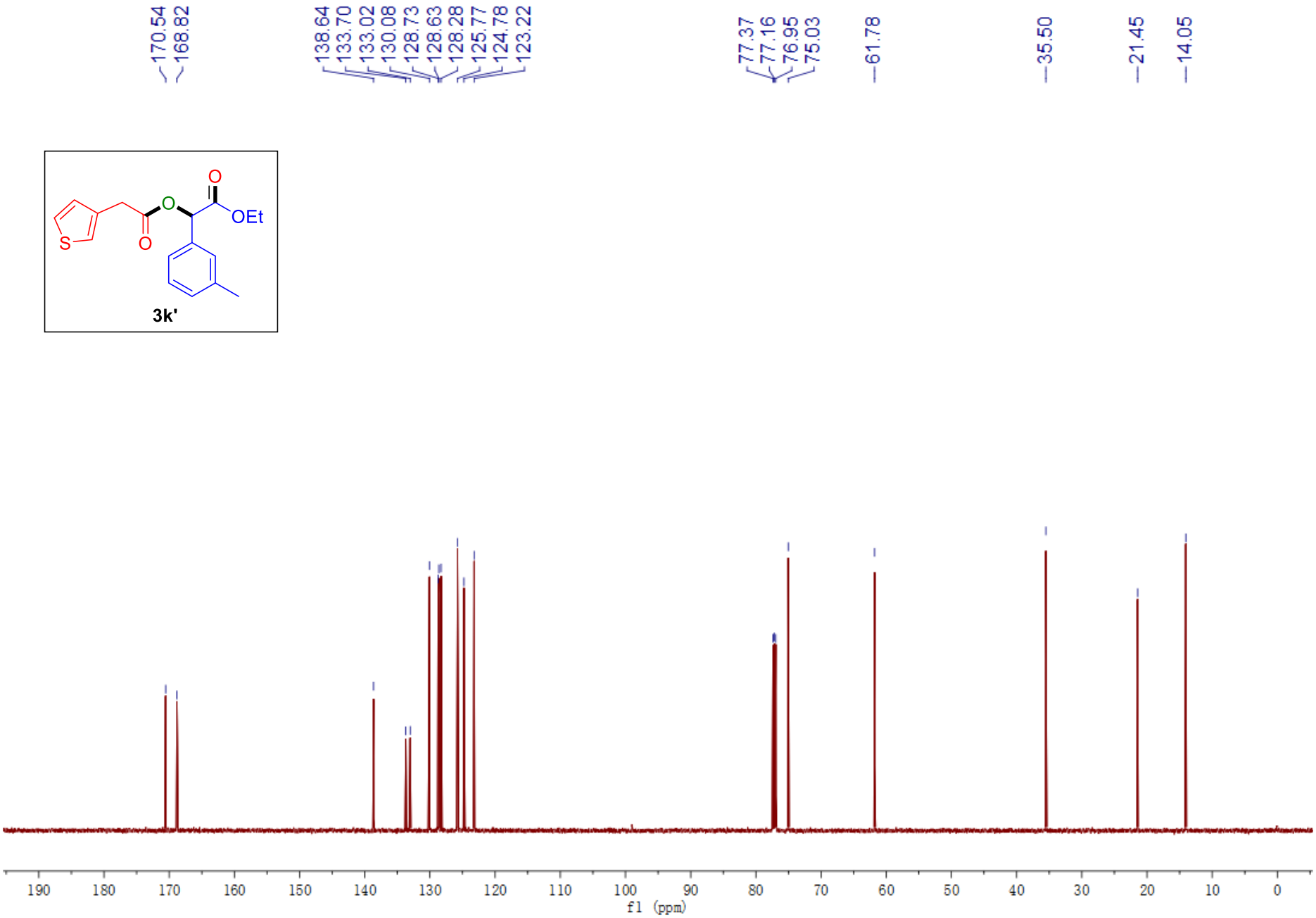

7.643 7.623 7.430 7.428 7.411 7.409 7.382 7.377 7.363 7.359 7.349 7.344 7.327 7.306 7.282 7.279 7.269 7.264 6.389 4.229 4.220 4.211 4.202 4.194 4.184 4.177 4.166 4.159 4.150 4.141 3.620 3.589 3.557 2.585 2.577 2.556 2.530 2.508 2.460 2.444 2.429 2.409 2.075 2.050 2.041 1.990 1.979 1.972 1.947 1.937 1.926 1.911 1.902 1.886 1.877 1.221 1.204 1.186
Ts
N
O
O
O
OEt
Cl
3i'
2.00
6.07
0.93
2.00
2.02
6.03
4.07
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

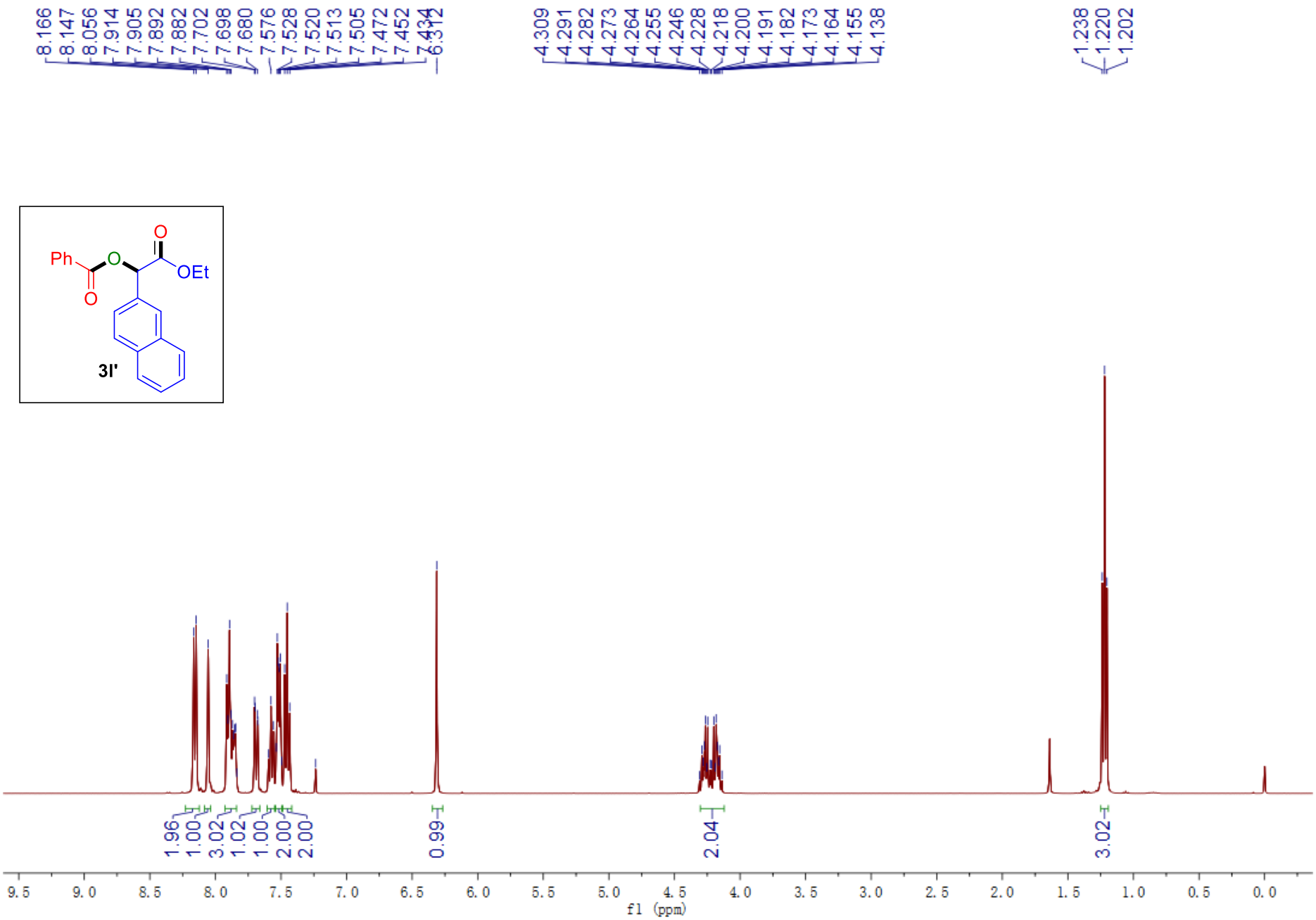

173.05
168.19
143.68
134.31
133.18
132.02
130.69
130.13
129.77
129.48
127.77
127.31
77.48
77.16
76.84
71.30
62.08
45.30
45.24
39.72
27.46
27.29
21.63
14.07
Ts
N
O
O
O
OEt
Cl
3i'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

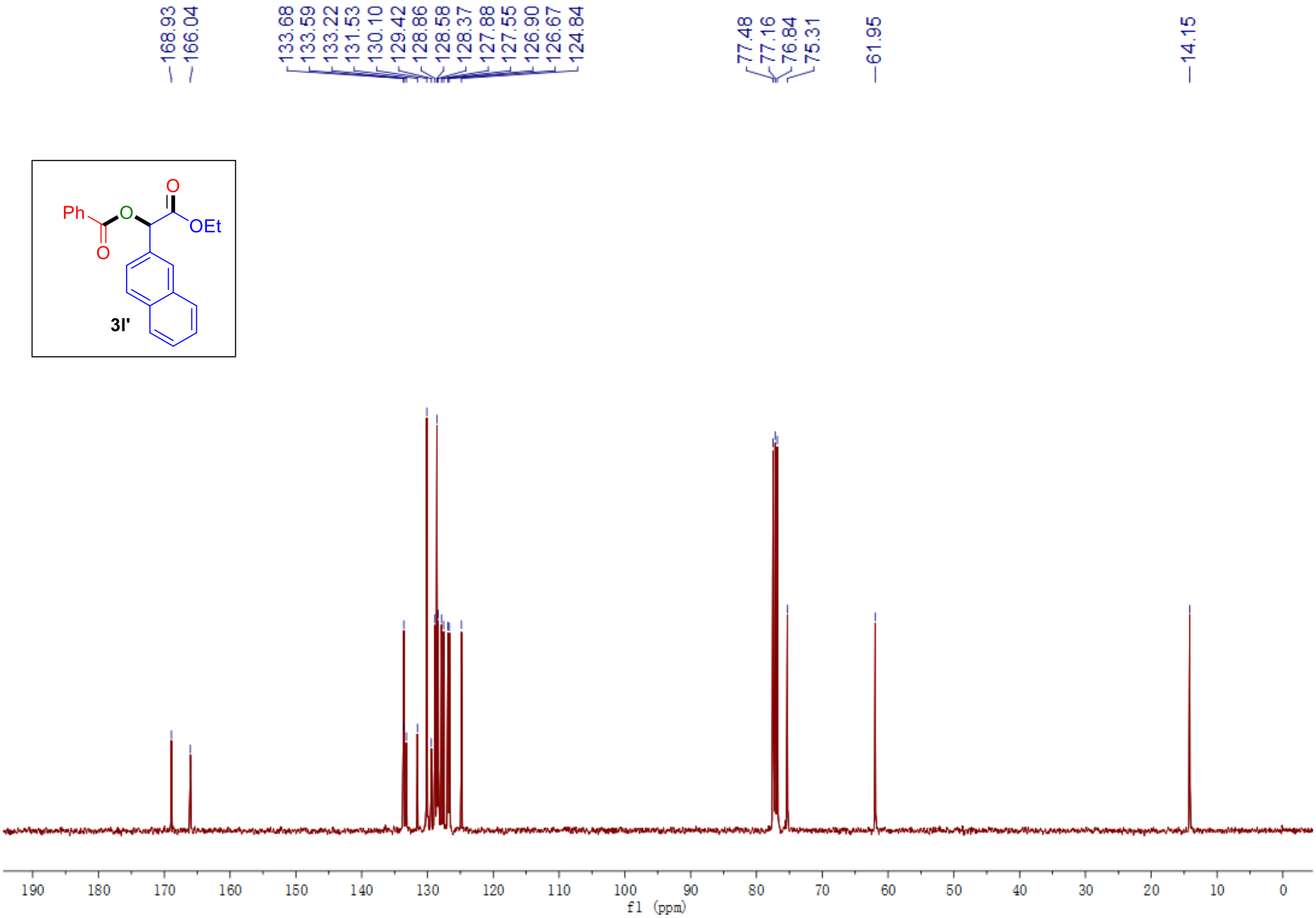

7.900
7.898
7.893
7.891
7.589
7.587
7.581
7.579
7.362
7.347
7.311
7.298
7.208
7.195
7.109
7.102
7.101
7.094
6.071
4.278
4.266
4.260
4.254
4.248
4.242
4.236
4.224
4.191
4.179
4.173
4.167
4.161
4.155
4.149
4.137
2.384
1.238
1.226
1.214
S
O
O
O
OEt
3j'
1.00
1.00
2.01
1.00
0.99
1.02
1.00
1.03
1.04
3.05
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

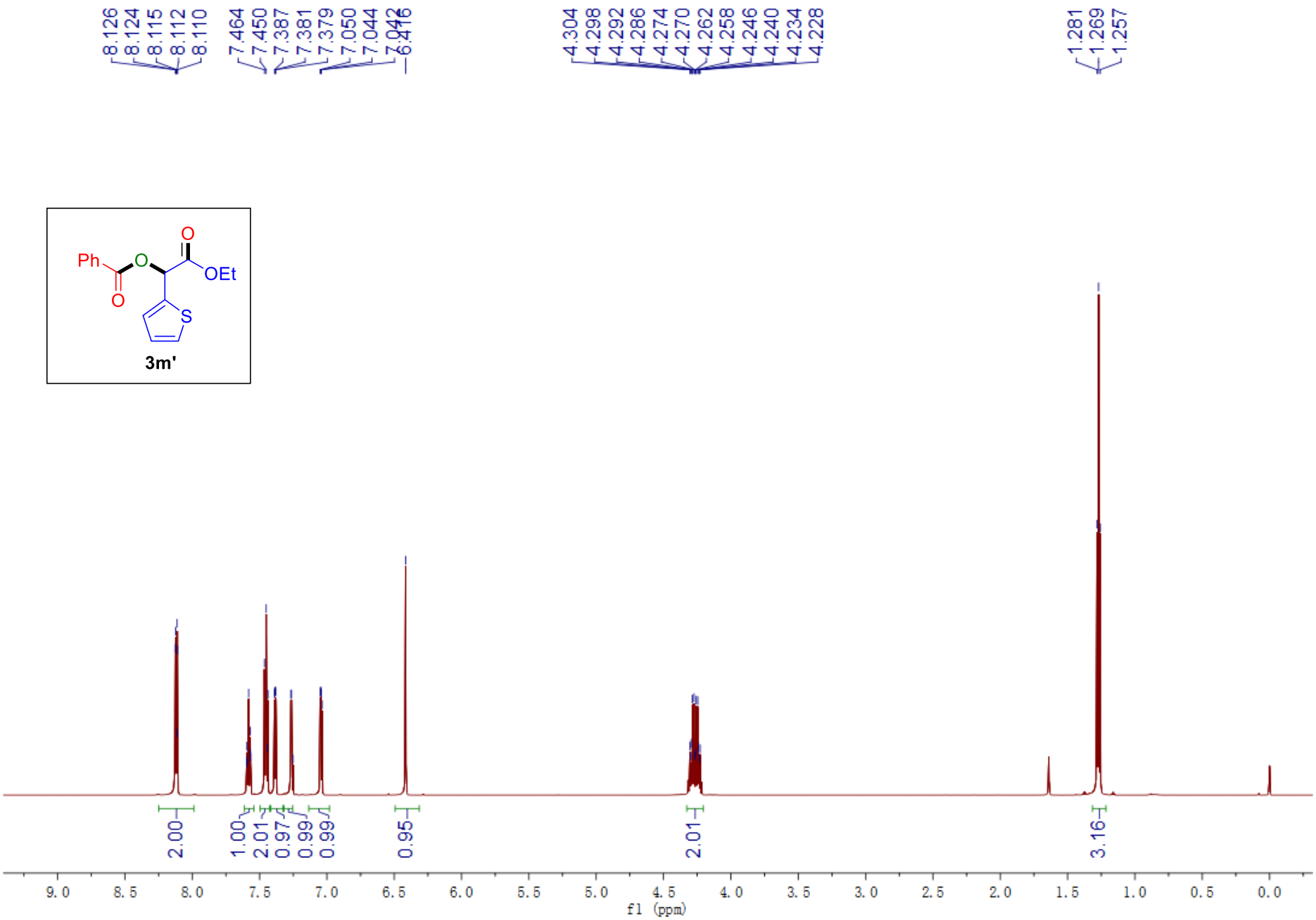

168.80
161.55
138.67
134.39
133.82
133.28
132.78
130.12
128.78
128.35
127.94
124.81
77.37
77.16
76.95
75.14
61.84
21.51
14.10
S
O
O
O
OEt
3j'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

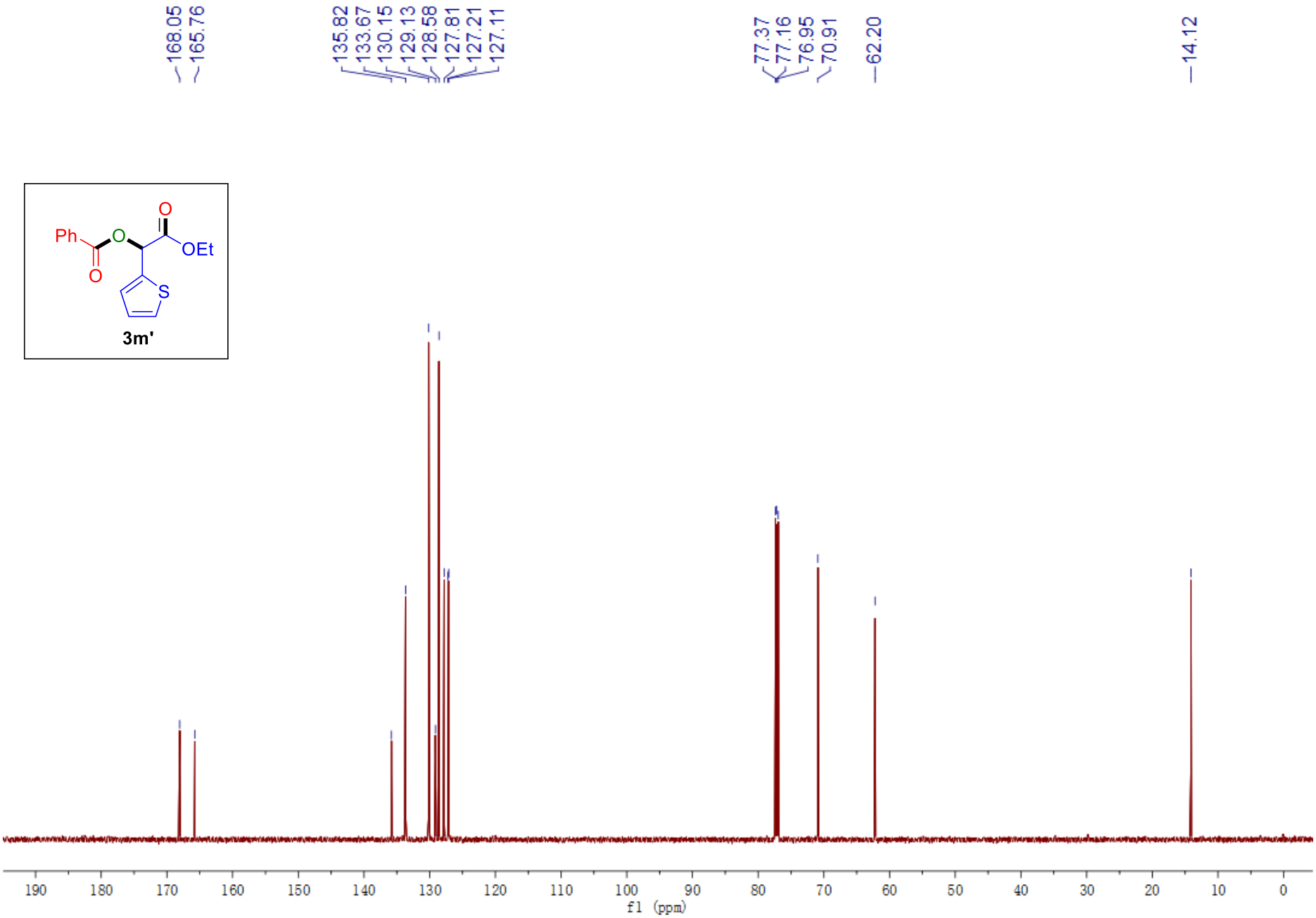

7.275
7.270
7.266
7.261
7.260
7.247
7.230
7.195
7.192
7.192
7.178
7.166
7.069
7.061
5.893
4.212
4.206
4.200
4.194
4.182
4.170
4.145
4.134
4.122
4.116
4.110
4.104
3.834
3.807
3.788
3.761
2.350
1.196
1.184
1.172
O
O
OEt
S
O
3k'
4.06
1.97
0.99
1.01
2.08
1.04
0.99
3.09
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

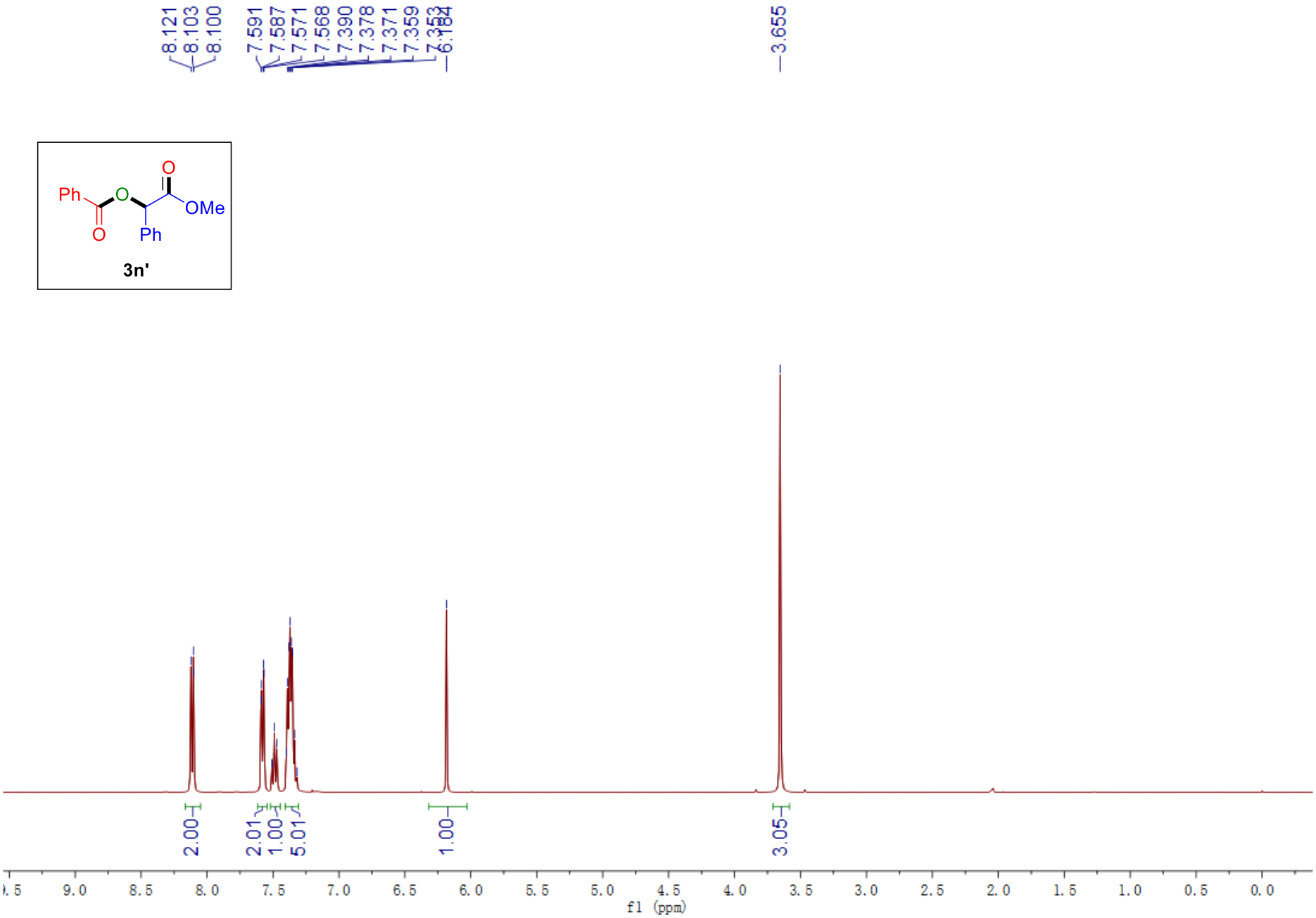

170.54
168.82
138.64
133.70
133.02
130.08
128.73
128.63
128.28
125.77
124.78
123.22
77.37
77.16
76.95
75.03
61.78
35.50
21.45
14.05
O
O
OEt
S
O
3k'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

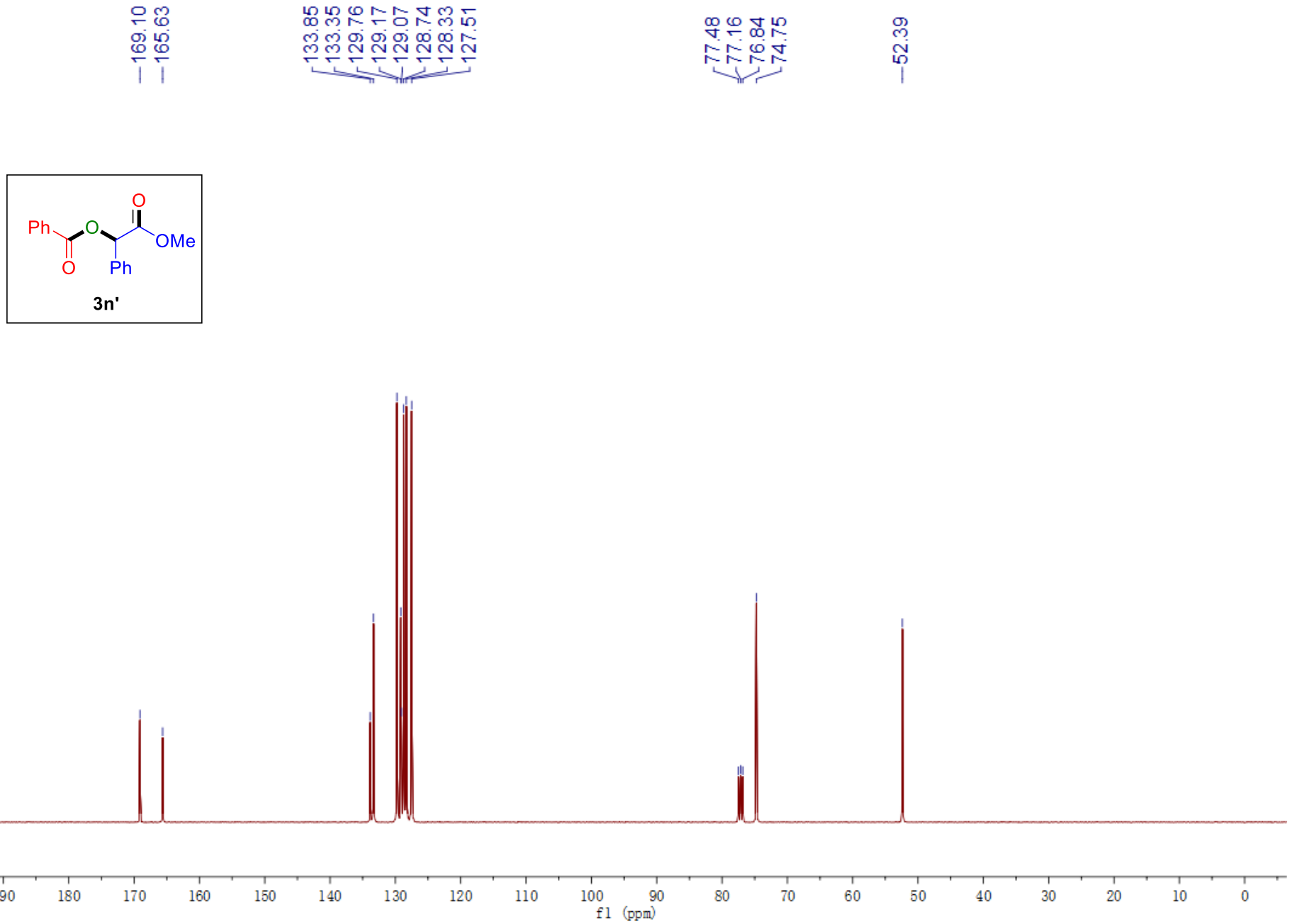

8.166
8.147
8.056
7.914
7.905
7.892
7.882
7.702
7.698
7.680
7.576
7.528
7.520
7.513
7.505
7.472
7.452
7.434
6.312
4.309
4.291
4.282
4.273
4.264
4.255
4.246
4.228
4.218
4.200
4.191
4.182
4.173
4.164
4.155
4.138
1.238
1.220
1.202
Ph
O
O
O
OEt
3l'
1.96
1.00
3.02
1.02
1.00
2.00
2.00
0.99
2.04
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

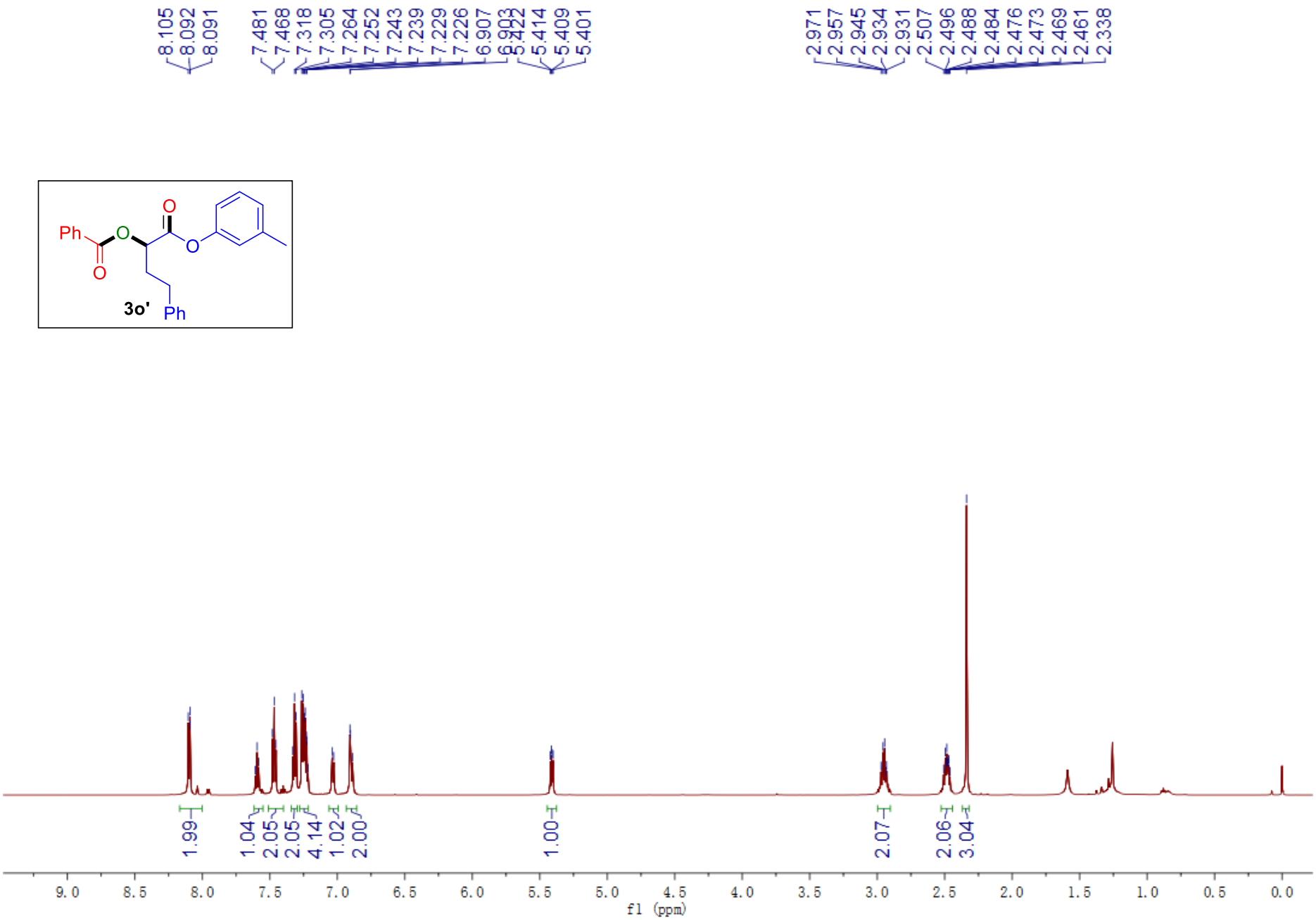

168.93
166.04
133.68
133.59
133.22
131.53
130.10
129.42
128.86
128.58
128.37
127.88
127.55
126.90
126.67
124.84
77.48
77.16
76.84
75.31
61.95
14.15
Ph
O
O
O
OEt
3l'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

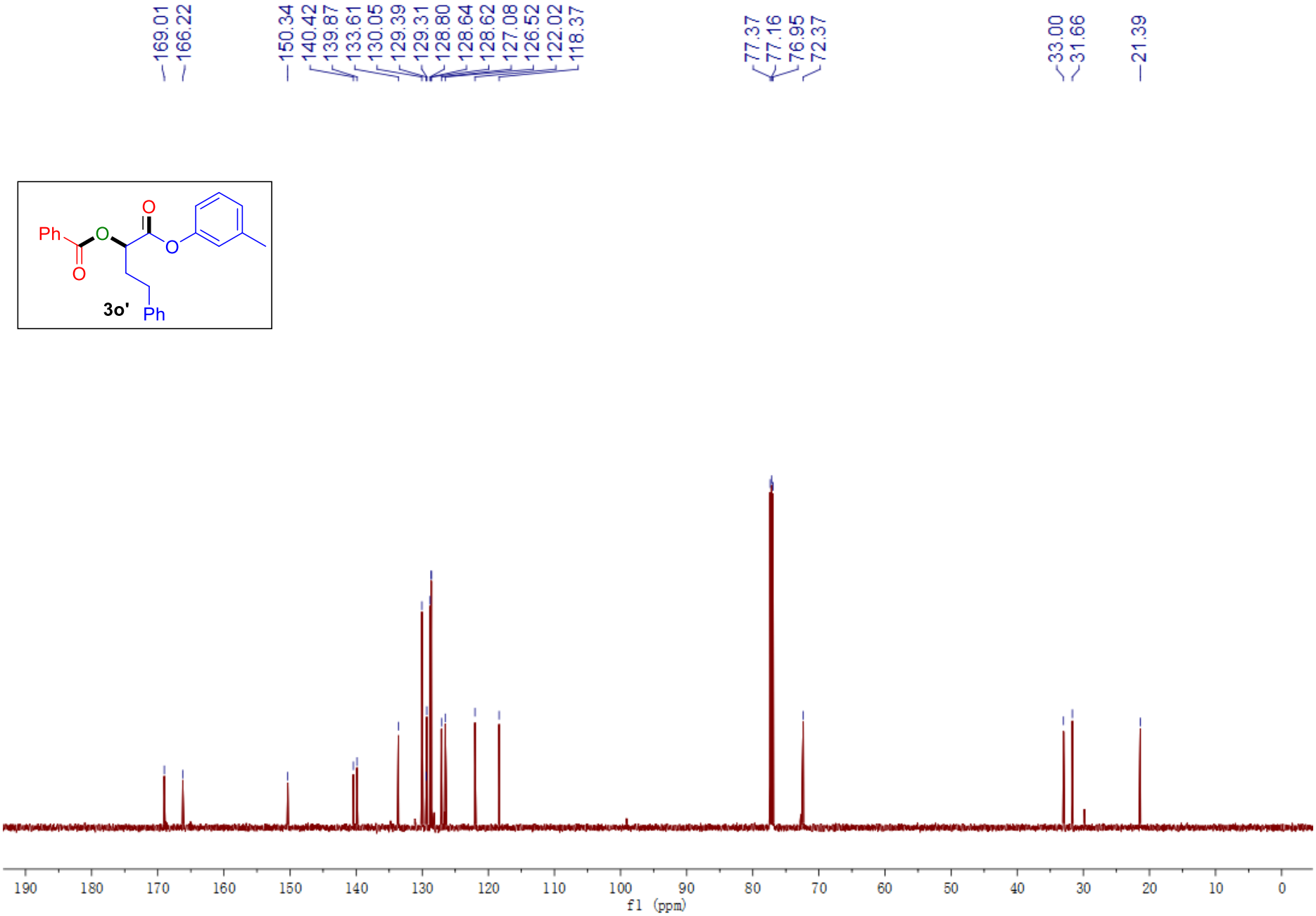

8.126
8.124
8.115
8.112
8.110
7.464
7.450
7.387
7.381
7.379
7.050
7.044
7.042
6.416
4.304
4.298
4.292
4.286
4.274
4.270
4.262
4.258
4.246
4.240
4.234
4.228
1.281
1.269
1.257
Ph
O
O
O
OEt
S
3m'
2.00
1.00
2.01
0.97
0.99
0.99
0.95
2.01
3.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

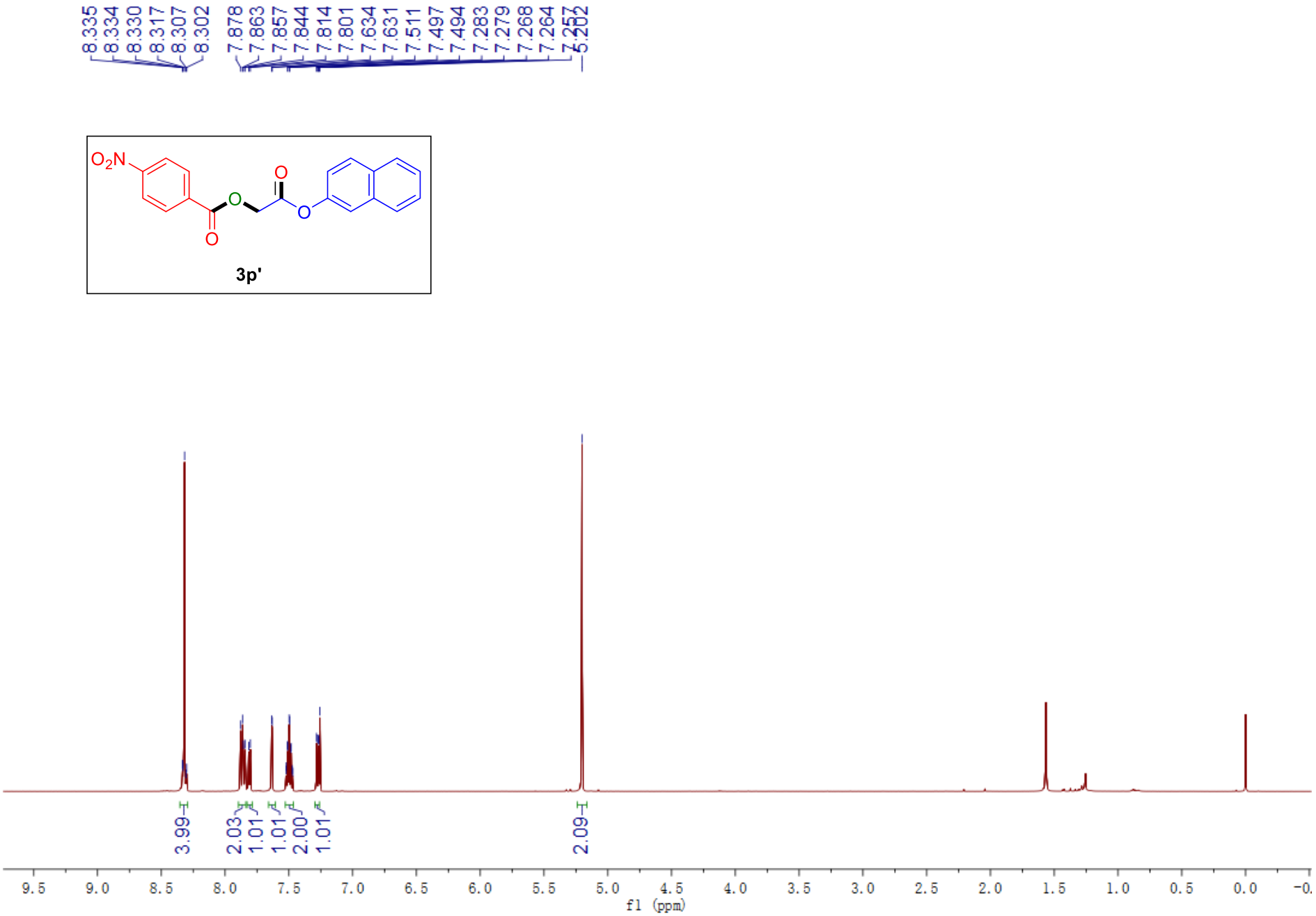

168.05
165.76
135.82
133.67
130.15
129.13
128.58
127.81
127.21
127.11
77.37
77.16
76.95
70.91
62.20
14.12
Ph
O
O
O
OEt
S
3m'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

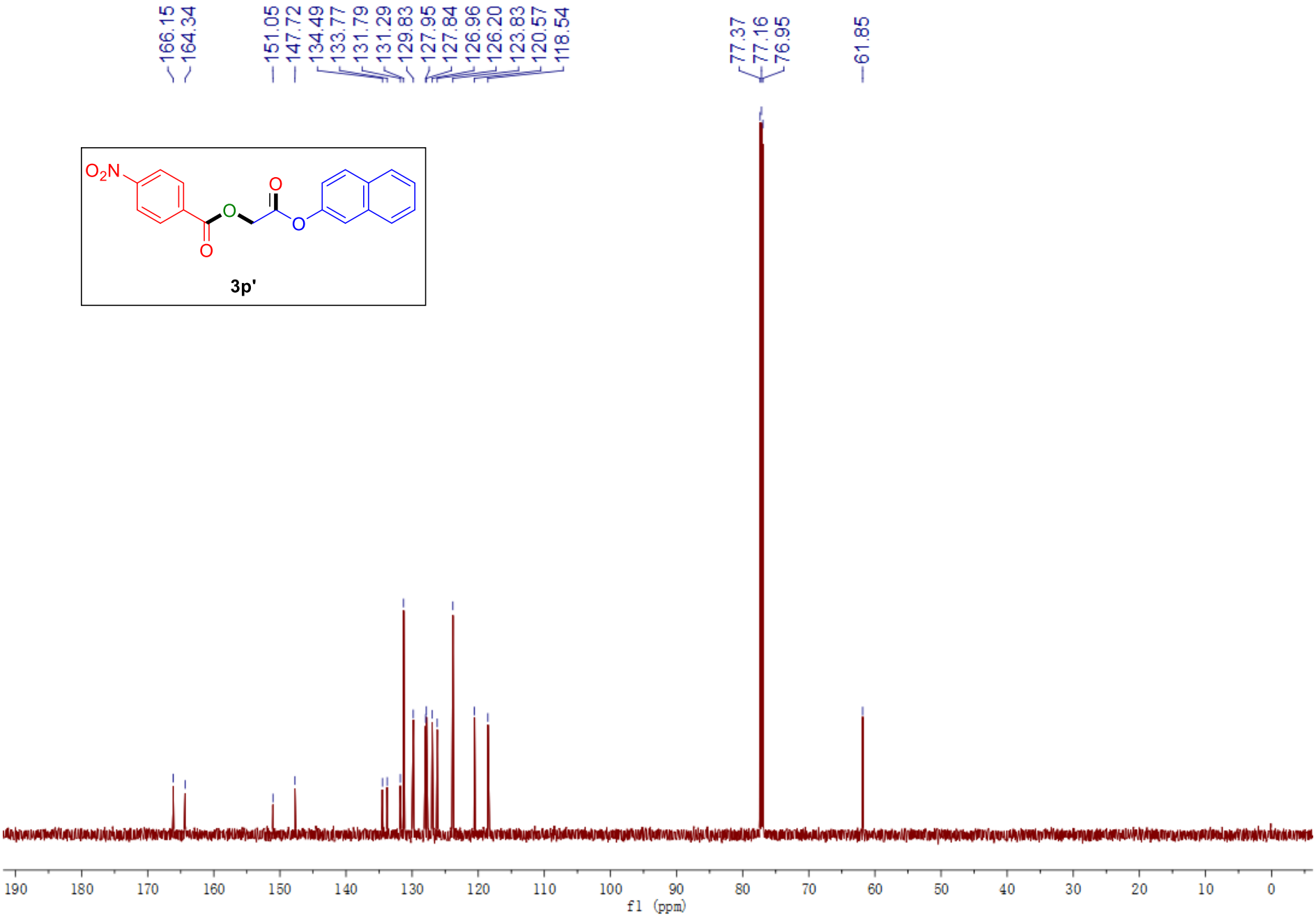

8.121
8.103
8.100
7.591
7.587
7.571
7.568
7.390
7.378
7.371
7.359
7.353
6.184
3.655
Ph
O
O
O
OMe
Ph
3n'
2.00
2.01
1.00
5.01
1.00
3.05
f1 (ppm)

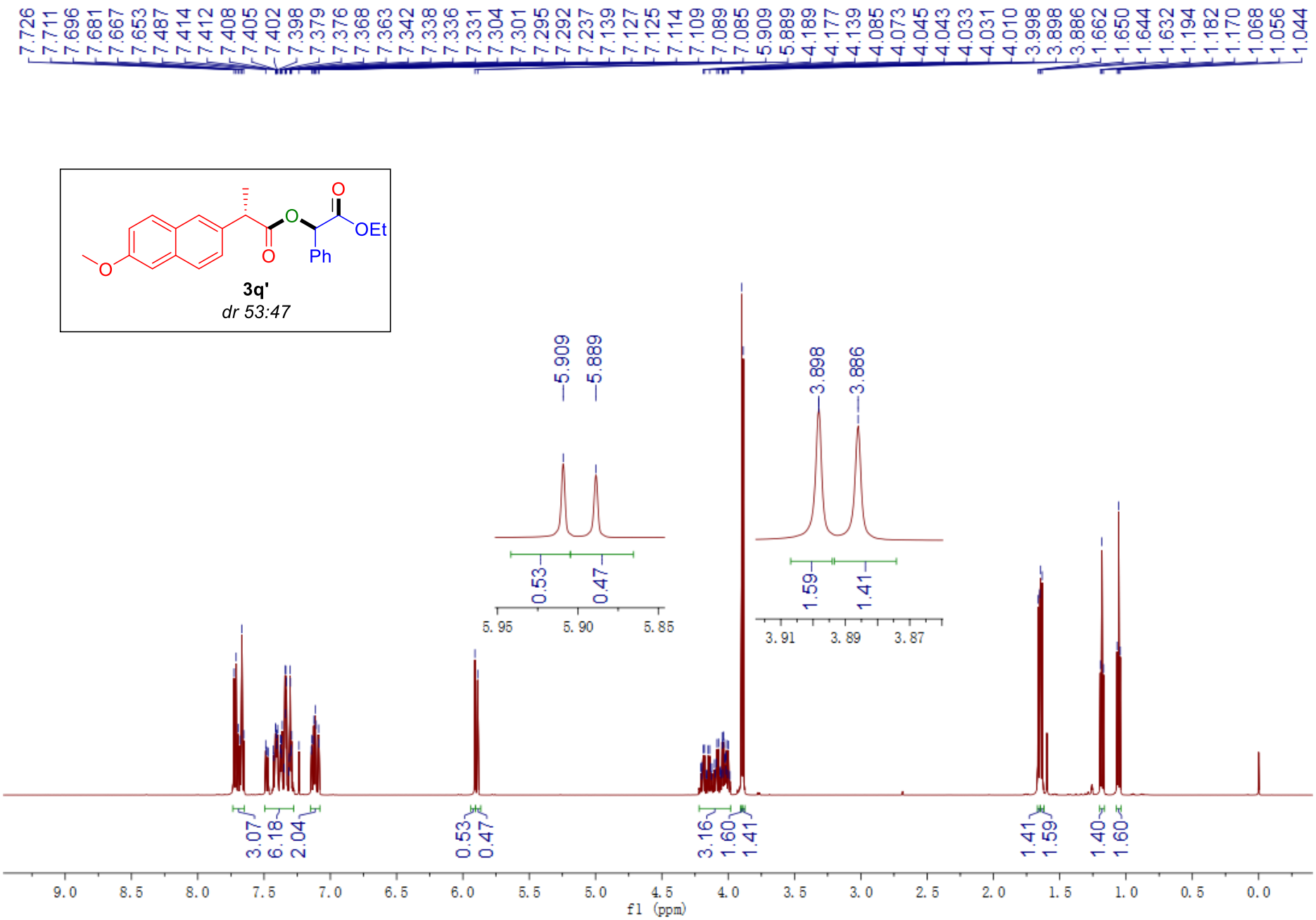

169.10
165.63
133.85
133.35
129.76
129.17
129.07
128.74
128.33
127.51
77.48
77.16
76.84
74.75
52.39
Ph
O
O
O
OMe
Ph
3n'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

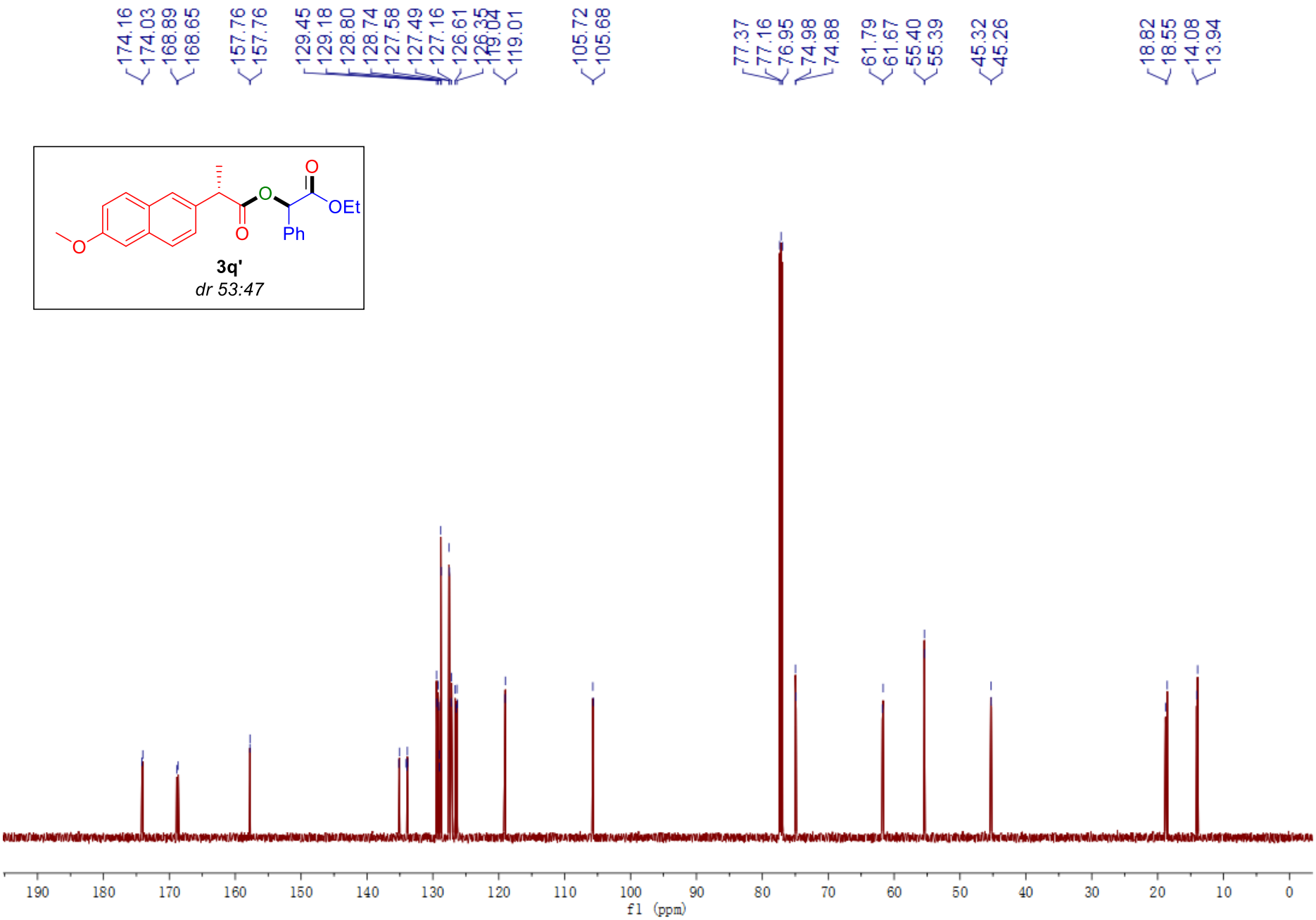

8.105
8.092
8.091
7.481
7.468
7.318
7.305
7.264
7.252
7.243
7.239
7.229
7.226
6.907
6.903
5.422
5.414
5.409
5.401
2.971
2.957
2.945
2.934
2.931
2.507
2.496
2.488
2.484
2.476
2.473
2.469
2.461
2.338
Ph
O
O
O
O
3o'
Ph
1.99
1.04
2.05
2.05
4.14
1.02
2.00
1.00
2.07
2.06
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

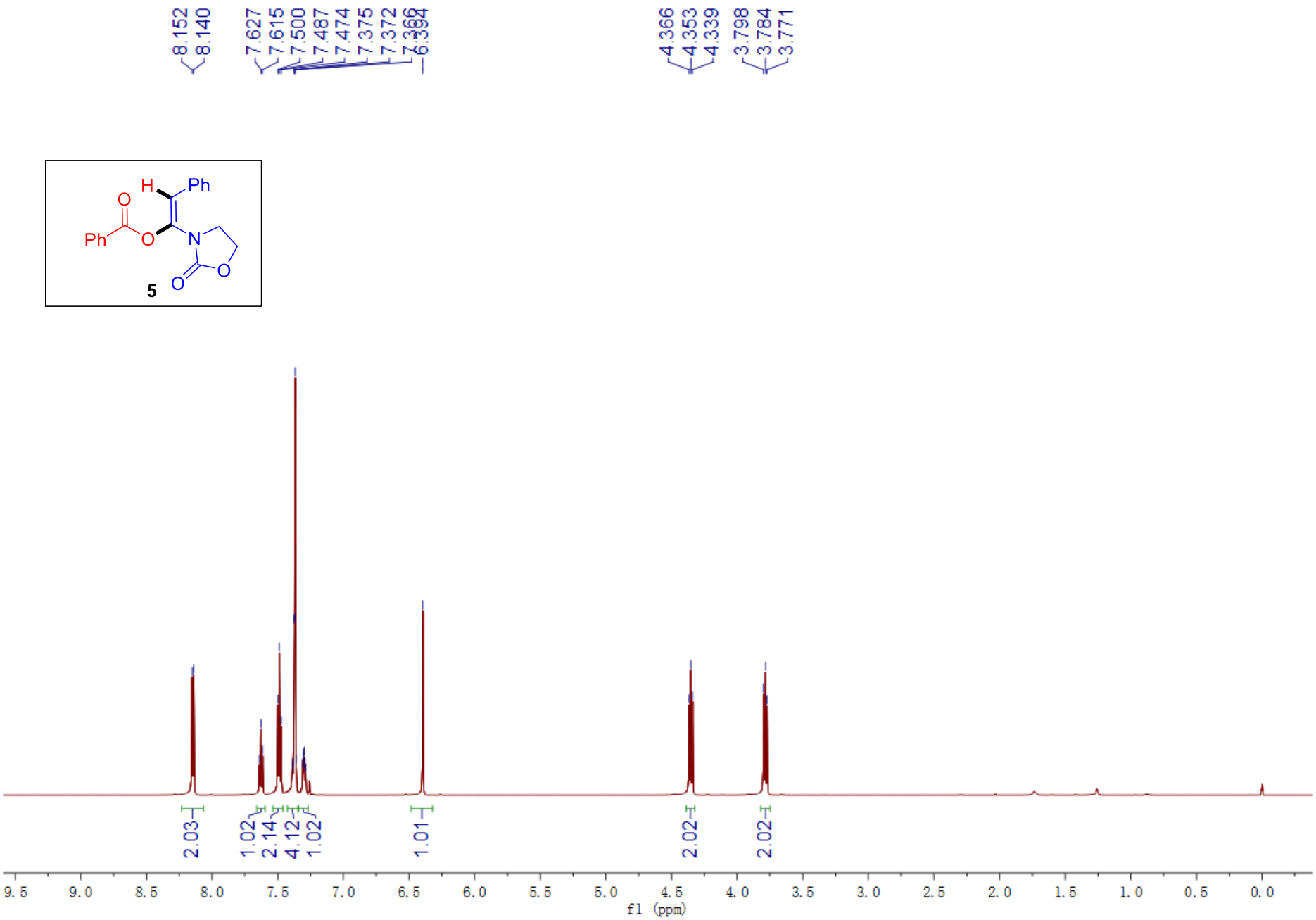

169.01
166.22
150.34
140.42
139.87
133.61
130.05
129.39
129.31
128.80
128.64
128.62
127.08
126.52
122.02
118.37
77.37
77.16
76.95
72.37
33.00
31.66
21.39
Ph
O
O
O
O
3o'
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

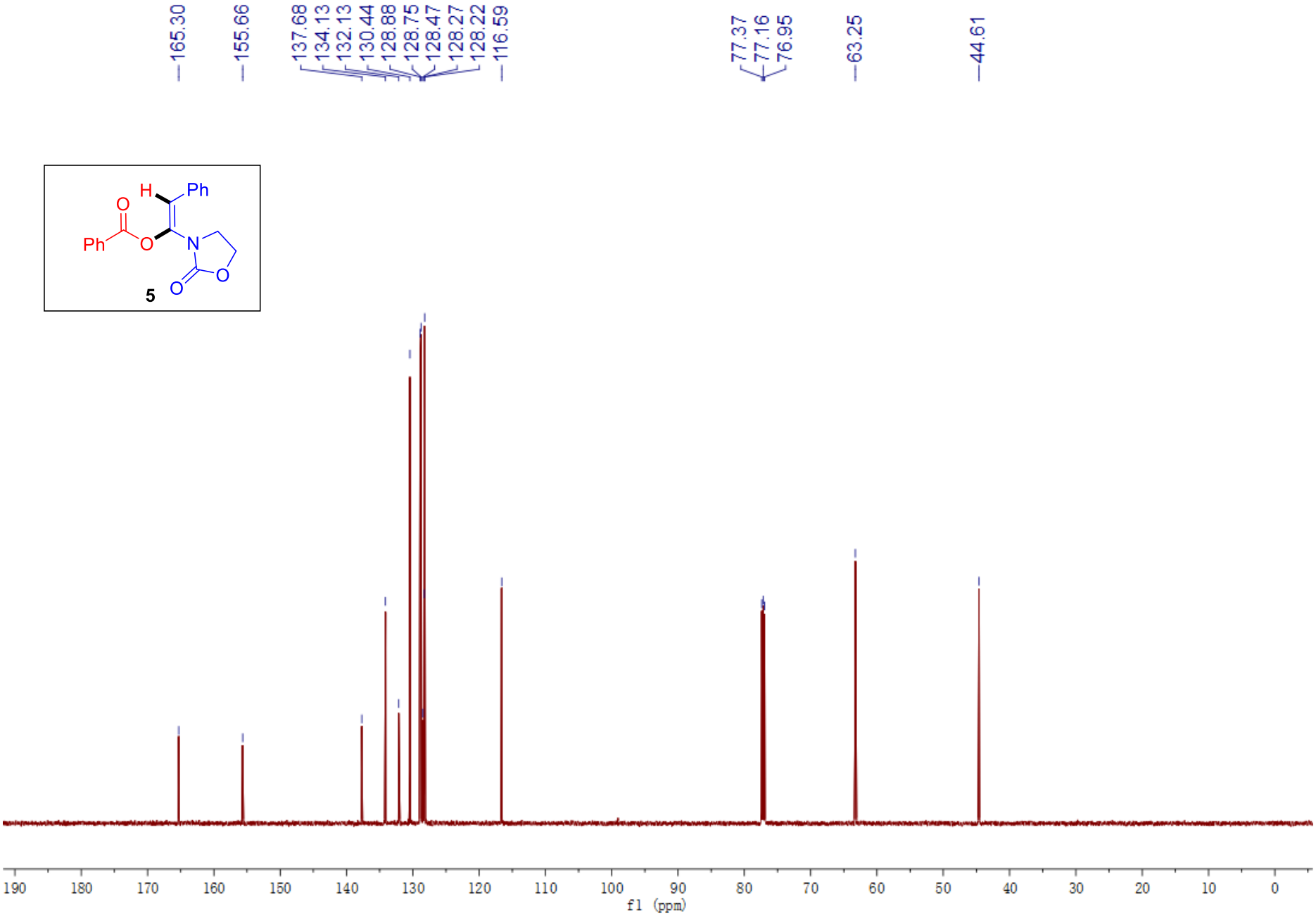

8.335
8.334
8.330
8.317
8.307
8.302
7.878
7.863
7.857
7.844
7.814
7.801
7.634
7.631
7.511
7.497
7.494
7.283
7.279
7.268
7.264
5.202
O2N
O
O
O
O
3p'
3.99
2.03
1.01
1.01
2.00
1.01
2.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.15
164.34
151.05
147.72
134.49
133.77
131.79
131.29
129.83
127.95
127.84
126.96
126.20
123.83
120.57
118.54
77.37
77.16
76.95
61.85
O2N
O
O
O
O
3p'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

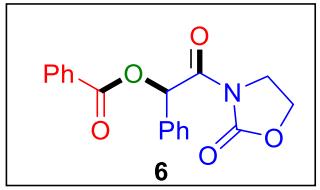

7.726 7.711 7.696 7.681 7.667 7.653 7.487 7.414 7.412 7.408 7.405 7.402 7.398 7.379 7.376 7.368 7.363 7.342 7.338 7.336 7.331 7.304 7.301 7.295 7.292 7.237 7.139 7.127 7.125 7.114 7.109 7.089 7.085 5.909 5.889 4.189 4.177 4.139 4.085 4.073 4.045 4.043 4.033 4.031 4.010 3.998 3.898 3.886 1.662 1.650 1.644 1.632 1.194 1.182 1.170 1.068 1.056 1.044
O
O
OEt
O
Ph
O
3q'
dr 53:47
5.909
5.889
0.53
0.47
5.95
5.90
5.85
3.898
3.886
1.59
1.41
3.91
3.89
3.87
3.07
6.18
2.04
0.53
0.47
3.16
1.60
1.41
1.41
1.59
1.40
1.60
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

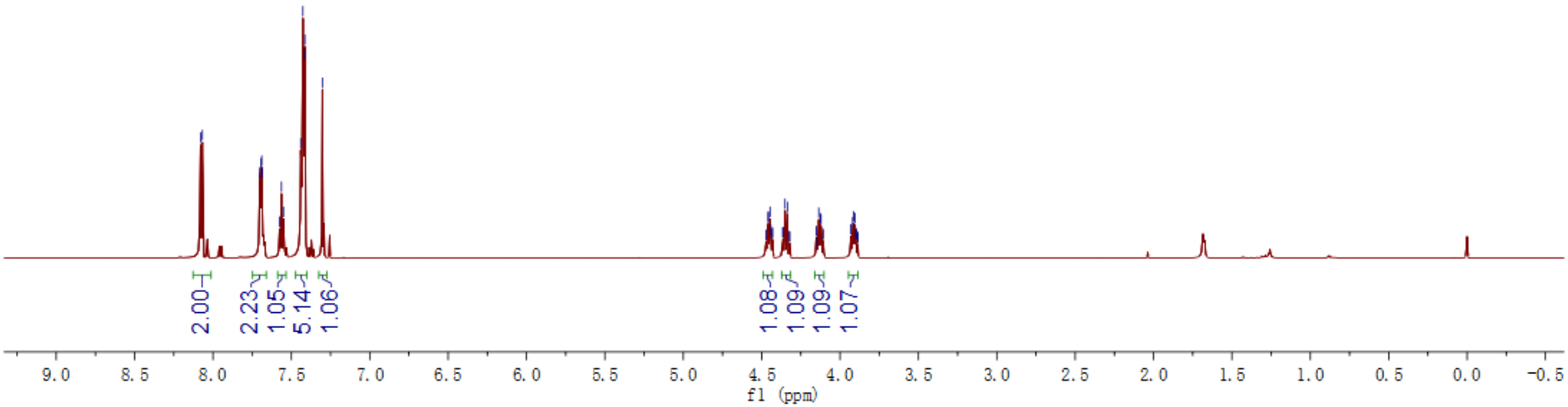

174.16
174.03
168.89
168.65
157.76
157.76
129.45
129.18
128.80
128.74
127.58
127.49
127.16
126.61
126.35
119.04
119.01
105.72
105.68
77.37
77.16
76.95
74.98
74.88
61.79
61.67
55.40
55.39
45.32
45.26
18.82
18.55
14.08
13.94
O
O
OEt
O
Ph
O
3q'
dr 53:47
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

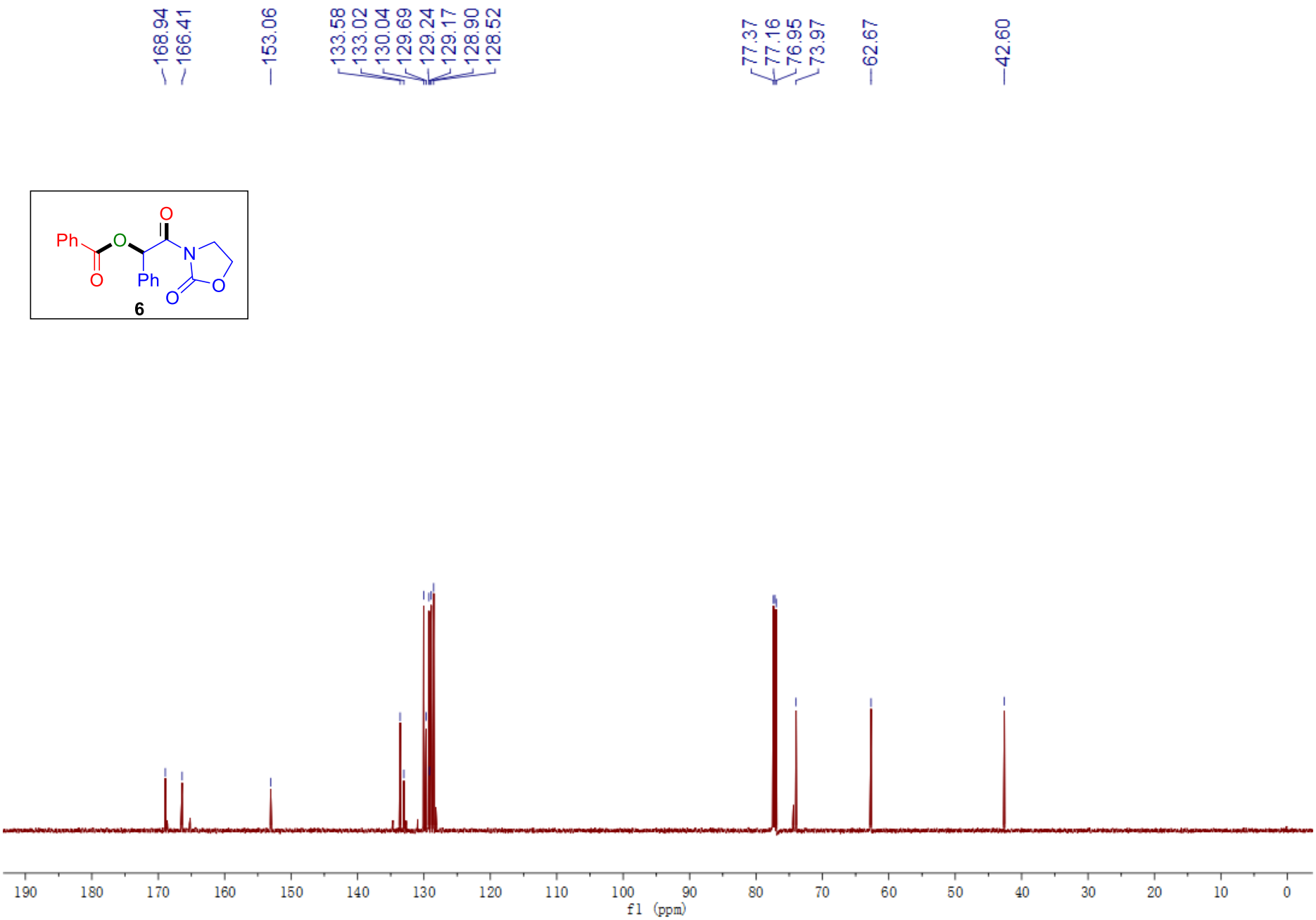

8.152
8.140
7.627
7.615
7.500
7.487
7.474
7.375
7.372
4.366
4.353
4.339
3.798
3.784
3.771
H
Ph
O
Ph
O
N
O
O
5
2.03
1.02
2.14
4.12
1.02
1.01
2.02
2.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

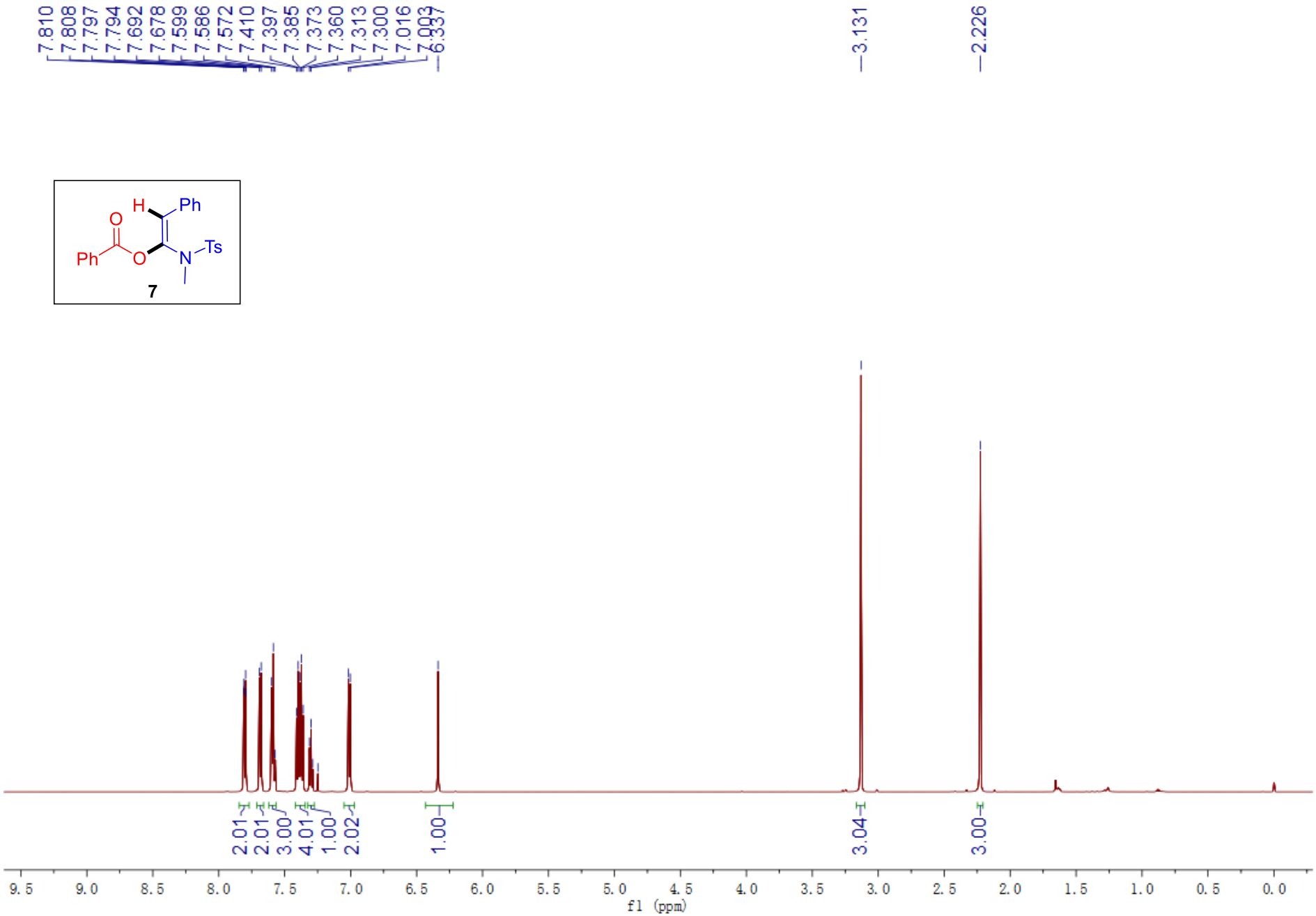

165.30
155.66
137.68
134.13
132.13
130.44
128.88
128.75
128.47
128.27
128.22
116.59
77.37
77.16
76.95
63.25
44.61
H
Ph
O
Ph
O
N
O
O
5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

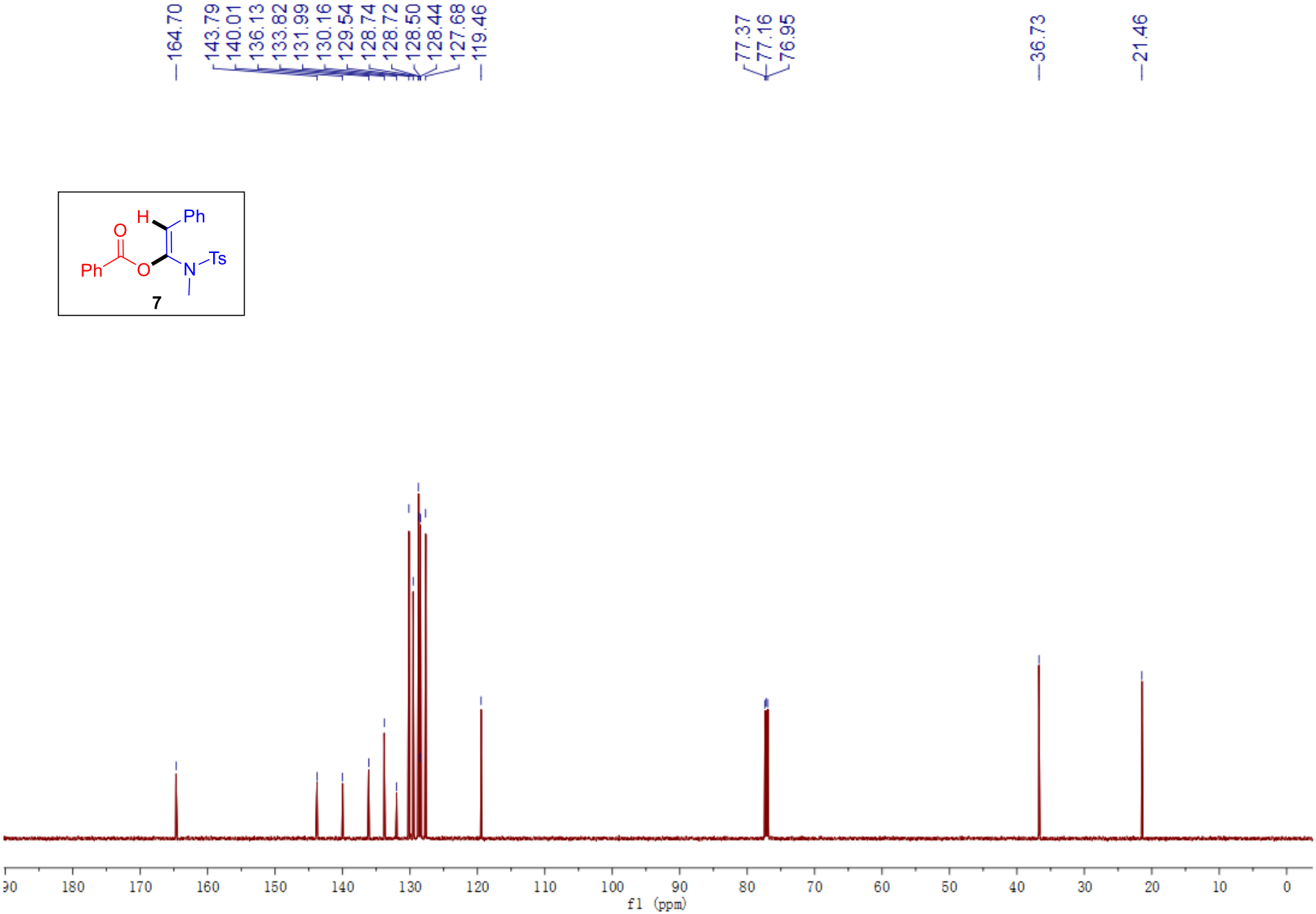
8.080
8.068
7.701
7.695
7.689
7.686
7.563
7.551
7.440
7.426
7.417
7.414
7.392
4.472
4.459
4.457
4.446
4.441
4.433
4.431
4.366
4.363
4.351
4.336
4.323
4.321
4.152
4.147
4.136
4.124
4.121
4.107
3.931
3.920
3.914
3.904
3.899
3.897
3.887
3.886

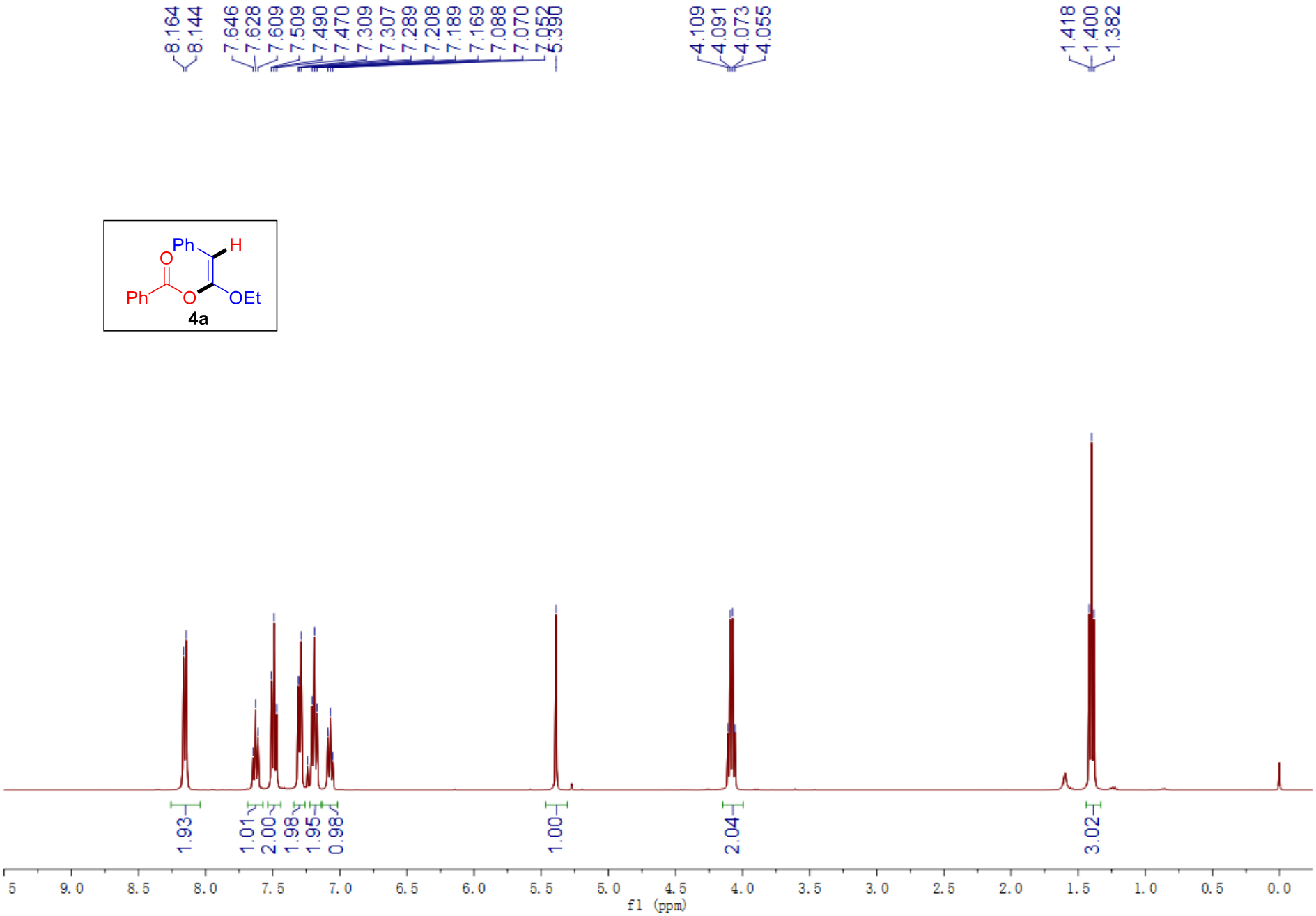

Ph
O
O
O
N
Ph
O
O
6

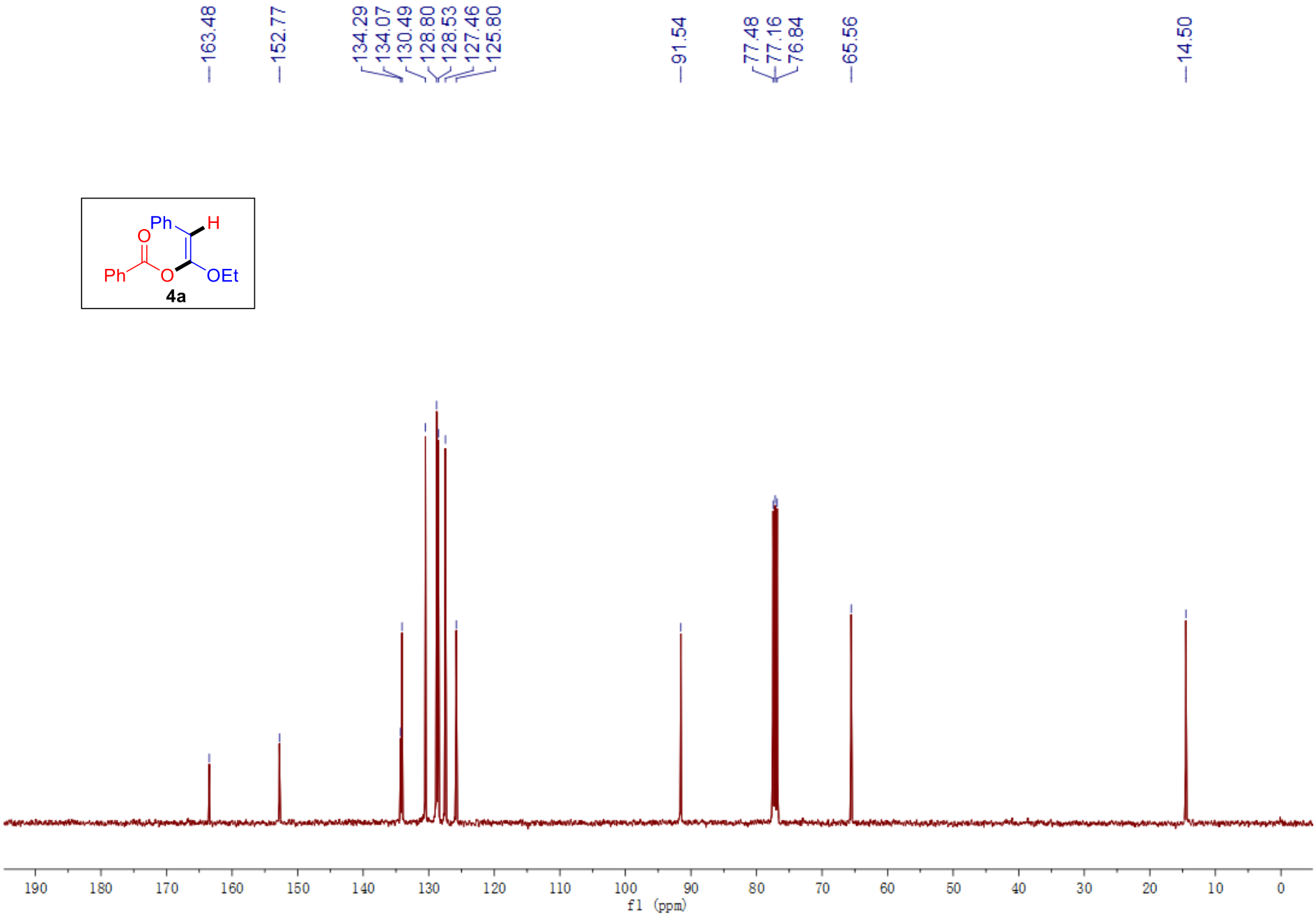

2.00
2.23
1.05
5.14
1.06
1.08
1.09
1.09
1.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

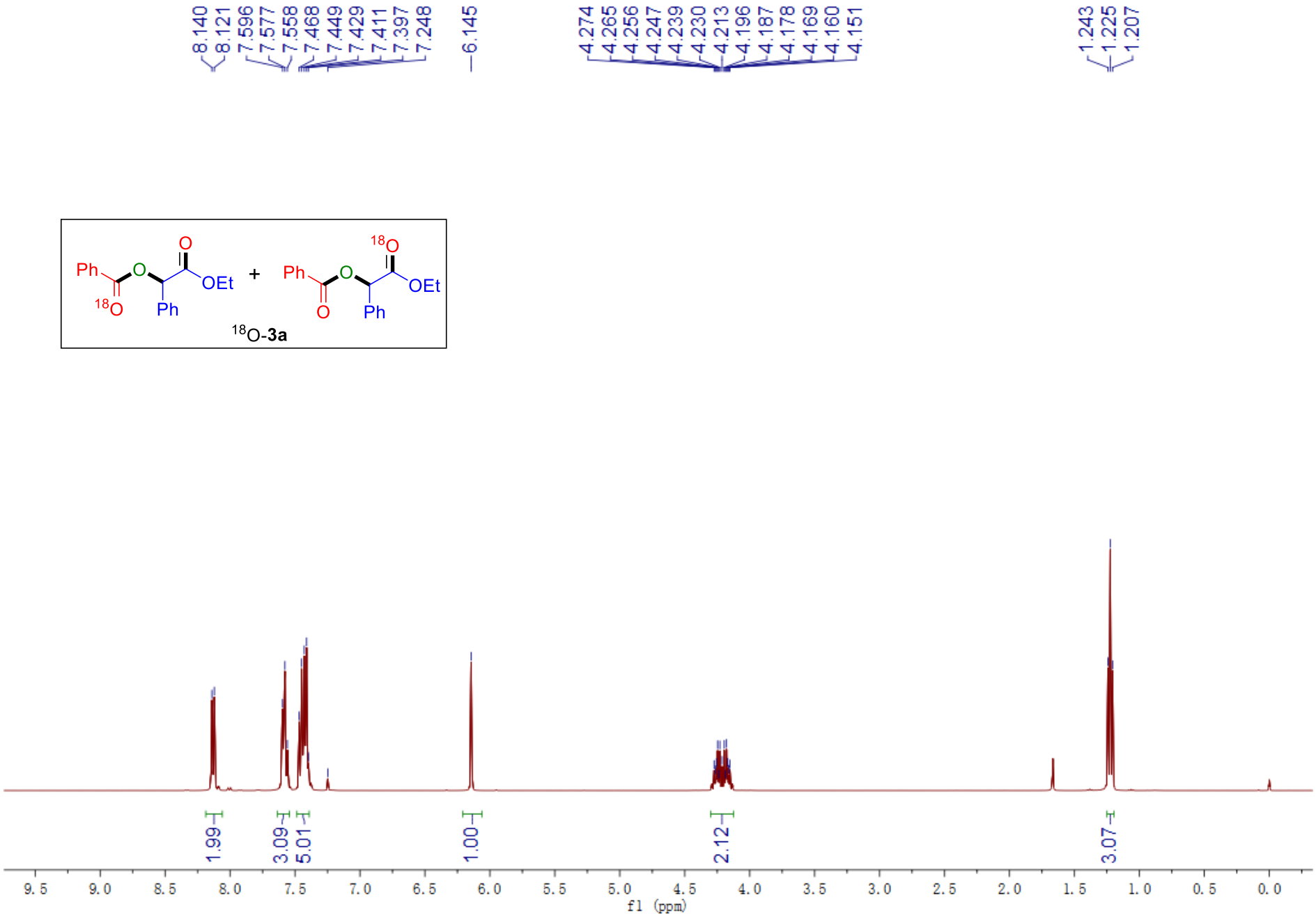

168.94
166.41
153.06
133.58
133.02
130.04
129.69
129.24
129.17
128.90
128.52
77.37
77.16
76.95
73.97
62.67
42.60
Ph
O
O
O
N
Ph
O
O
6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

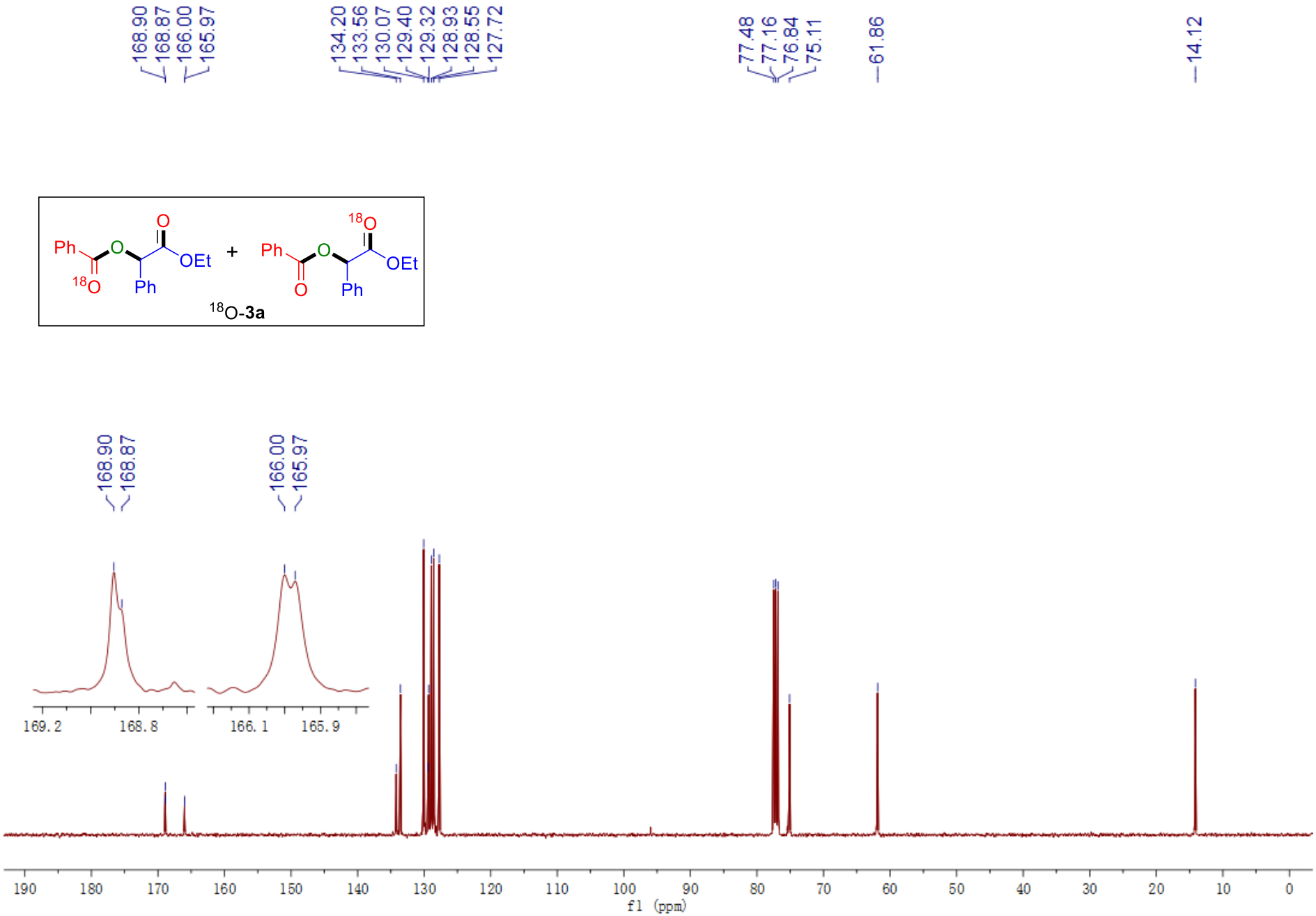

7.810
7.808
7.797
7.794
7.692
7.678
7.599
7.586
7.572
7.410
7.397
7.385
7.373
7.360
7.313
7.300
7.016
7.003
6.337
3.131
2.226
H
Ph
O
Ph
O
N
Ts
7
2.01
2.01
3.00
4.01
1.00
2.02
1.00
3.04
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.70
143.79
140.01
136.13
133.82
131.99
130.16
129.54
128.74
128.72
128.50
128.44
127.68
119.46
77.37
77.16
76.95
36.73
21.46
H
Ph
O
Ph
O
N
Ts
7
f1 (ppm)


8.164
8.144
7.646
7.628
7.609
7.509
7.490
7.470
7.309
7.307
7.289
7.208
7.189
7.169
7.088
7.070
7.052
5.390
4.109
4.091
4.073
4.055
1.418
1.400
1.382
Ph
H
O
Ph
O
OEt
4a
1.93
1.01
2.00
1.98
1.95
0.98
1.00
2.04
3.02
f1 (ppm)


163.48
152.77
134.29
134.07
130.49
128.80
128.53
127.46
125.80
91.54
77.48
77.16
76.84
65.56
14.50
Ph
H
O
Ph
O
OEt
4a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.140
8.121
7.596
7.577
7.558
7.468
7.449
7.429
7.411
7.397
7.248
6.145
4.274
4.265
4.256
4.247
4.239
4.230
4.213
4.196
4.187
4.178
4.169
4.160
4.151
1.243
1.225
1.207
Ph
O
OEt
18O
Ph
+
18O
Ph
O
OEt
O
Ph
18O-3a
1.99
3.09
5.01
1.00
2.12
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.90
168.87
166.00
165.97
134.20
133.56
130.07
129.40
129.32
128.93
128.55
127.72
77.48
77.16
76.84
75.11
61.86
14.12
Ph
O
OEt
Ph
18O
+
18O
Ph
O
OEt
Ph
O
18O-3a
169.2
168.8
166.1
165.9
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)