Supporting Information

Access to carbamates and *o*-aminobenzoates via oxidative carbonylation of amines with CO and alcohols under rhodium/copper catalysis

Xiaoqi Chen,‡[a] Xuyao Zhong,‡[a] Lei Wang,‡[a] Houyun Teng,[a] Jingsheng Li,[b] Shuai Chen,[b] Rongjing Hu*[a,c] and Lei Yang*[a]

[a]College of Material, Chemistry and Chemical Engineering, Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Key Laboratory of Organosilicon Material Technology of Zhejiang Province, Hangzhou Normal University, Hangzhou 311121, China

[b]Kharkiv Institute at Hangzhou Normal University, Hangzhou 311121, China

[c]Library of Hangzhou Normal University, Hangzhou 311121, China

*Email: hurj@hznu.edu.cn; lyang@hznu.edu.cn; yangunibas@126.com

Table of Contents

1. General information

Techniques

All reactions involving air and water-sensitive material were carried out in pre-dried glassware under nitrogen atmosphere by using Schlenk techniques employing double-line nitrogen-vacuum lines or working in an argon-filled glove box. Analytical thin layer chromatography (TLC) was performed using pre-coated Jiangyou silica gel HSGF254 (0.2mm±0.03mm). Visualization of the developed chromatogram was performed by UV absorbance (254 nm) or TLC stains ($KMnO_4$ and Phosphomolybdic acid). Flash chromatography was performed using Nuotai Shanxi silica gel (300-400 mesh) with the indicated solvent system.

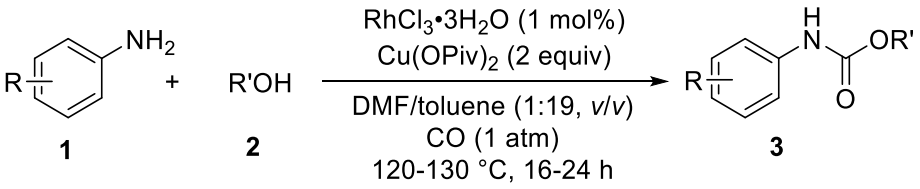
Chemicals

All chemicals were purchased from Leyan, Energy Chemical, Innochem, Bide Pharmatech, SINOPHARM, Sigma−Aldrich and used as received unless otherwise noted. Anhydrous solvents were purchased from J&K Scientific or Energy Chemical, degassed by three freeze-pump-thaw cycles and storing in single-necked flasks equipped with *J*-Young PTFE valve when necessary.

Instrumentation

GC-MS analyses were performed with Shimadzu GCMS-QP2010 SE GC-MS system. Nuclear magnetic resonance spectra were recorded on a Bruker AvanceTM III 400 MHz in deuterated chloroform unless otherwise noted. Data are reported in parts per million (ppm) as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dd = doublet of doublet and br = broad), coupling constant in Hz and integration. High resolution mass spectra were recorded on a Bruker micro QII-ESI-TOF. Melting points were recorded using a Yidianwuguang Micromelting point apparatus SGW X-5.

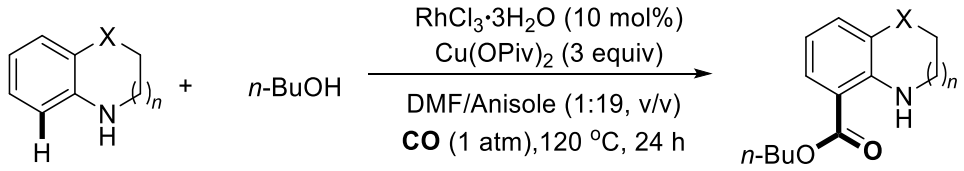
2. General procedures for oxidative carbonylation of amines



1 2 3

General procedure A

In a glovebox, $RhCl_3 \cdot 3H_2O$ (0.002 mmol, 0.01 equiv), $Cu(OPiv)_2$ (0.4 mmol, 2 equiv), were successively weighed into a dry 25 mL *J*-Young tube equipped with a magnetic stir bar. The *J*-Young tube was sealed and taken out of the glovebox. Amine **1** (0.2 mmol, 1 equiv), alcohol **2** (1 mmol, 5 equiv), dry toluene (1.9 mL) and dry DMF (0.1 mL) were added under nitrogen. The reaction mixture was then degassed by three freeze-pump-thaw cycles, backfilled with CO and heated at 120 °C or 130 °C. After indicated time, the reaction mixture was cooled to room temperature. The solvent was evaporated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel using EtOAc–petroleum ether mixture as an eluent to afford the desired compound **3**.



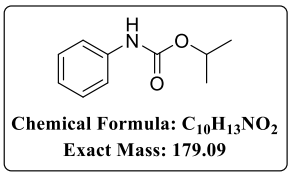
4 2b 5

General Procedure B

In a glovebox, $RhCl_3 \cdot 3H_2O$ (0.02 mmol, 0.1 equiv), $Cu(OPiv)_2$ (0.6 mmol, 3 equiv) were successively weighed into a dry 25 mL *J*-Young tube equipped with a magnetic stir bar. The *J*-Young tube was sealed and taken out of the glovebox. **4** (0.2 mmol, 1 equiv), *n*-butanol **2b** (5 equiv), dry anisole (1.9 mL) and dry DMF (0.1 mL) were added under nitrogen. The reaction mixture was then degassed by three freeze-pump-thaw cycles, backfilled with CO and heated at 120 °C. Then, the reaction mixture was cooled to room temperature. The solvent was evaporated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel using EtOAc–petroleum ether mixture as an eluent to afford the desired compound **5**.

Isopropyl phenylcarbamate (3aa)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3aa*** as a white solid (33.5 mg, 94% yield). Flash column chromatography (petroleum ether/ethyl acetate, 50:1); R_f 0.4 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[1]

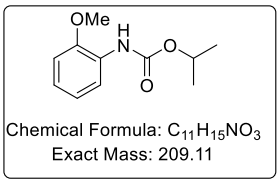


^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.40 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.73 (s, 1H), 5.03 (hept, *J* = 6.3 Hz, 1H), 1.30 (d, *J* = 6.2 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 153.4, 138.2, 129.1, 123.3, 118.7, 68.8, 22.2.

isopropyl (2-methoxyphenyl)carbamate (3ba)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ba*** as a yellow oil (33.4 mg, 80% yield). Flash column chromatography (petroleum ether/ethyl acetate, 40:1); R_f 0.3 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[2]

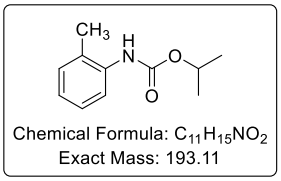


^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.02 (s, 1H), 7.11 (s, 1H), 6.93 – 6.83 (m, 2H), 6.76 (d, *J* = 9.5 Hz, 1H), 4.94 (p, *J* = 6.3 Hz, 1H), 3.77 (s, 3H), 1.22 (d, *J* = 6.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 153.3, 147.6, 128.0, 122.6, 121.2, 118.2, 110.0, 68.6, 55.7, 22.2.

isopropyl o-tolylcarbamate (3ca)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ca*** as a yellow oil (36 mg, 93% yield). Flash column chromatography (petroleum ether/ethyl acetate, 40:1); R_f 0.3 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[1]

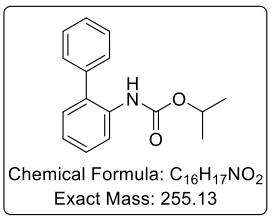


^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.82 (s, 1H), 7.25 – 7.13 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.39 (s, 1H), 5.03 (hept, *J* = 6.2 Hz, 1H), 2.25 (s, 3H), 1.31 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 153.6, 136.1, 130.4, 127.6, 126.9, 124.0, 121.1, 68.8, 22.1, 17.7.

isopropyl [1,1'-biphenyl]-2-ylcarbamate (3da)

Obtained according to the ***General procedure A*** (120 °C /24 h), to give ***3da*** as a yellow oil (31.9 mg, 63% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.4 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[3]

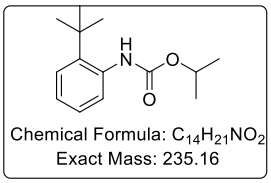


^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.16 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.40 (dd, *J* = 20.0, 6.9 Hz, 4H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.59 (s, 1H), 4.99 (h, *J* = 6.2 Hz, 1H), 1.25 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 153.4, 138.4, 135.1, 131.5, 130.3, 129.4, 129.2, 128.6, 127.9, 123.3, 119.8, 68.8, 22.1.

isopropyl (2-(*tert*-butyl)phenyl)carbamate (3ea)

Obtained according to the ***General procedure A*** (120 °C /24 h), to give ***3ea*** as a yellow oil (36.7 mg, 78% yield). Flash column chromatography (petroleum ether/ethyl acetate, 40:1); R_f 0.4 (petroleum ether/ethyl acetate, 10:1).



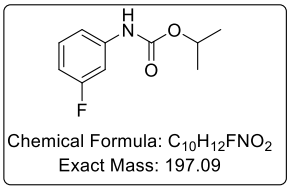
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.49 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.36 (s, 1H), 4.95 (hept, *J* = 6.3 Hz, 1H), 1.33 (s, 9H), 1.21 (d, *J* = 6.2 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 154.3, 142.0, 135.6, 126.9, 126.5, 125.5, 68.8, 34.6, 30.7, 22.3.

HRMS (ESI) m/z: Calculated for $C_{14}H_{21}NO_2$ $[M+Na]^+$: 258.1465, found: 258.1466.

isopropyl (3-fluorophenyl)carbamate (3fa)

Obtained according to the ***General procedure A*** (120 °C /24 h), to give ***3fa*** as a white solid (31.3 mg, 80% yield). Flash column chromatography (petroleum ether/ethyl acetate, 40:1); R_f 0.4 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[4]

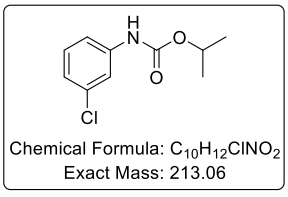


^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.26 (d, *J* = 11.4 Hz, 1H), 7.21 – 7.10 (m, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.74 – 6.59 (m, 2H), 4.94 (hept, *J* = 6.3 Hz, 1H), 1.22 (d, *J* = 6.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 163.3 (d, *J* = 244.8 Hz), 153.1, 139.9 (d, *J* = 11.3 Hz), 130.2 (d, *J* = 9.1 Hz), 113.9, 110.0 (d, *J* = 24.8 Hz), 106.1 (d, *J* = 27.2 Hz), 69.2, 22.1.

isopropyl (3-chlorophenyl)carbamate (3ga)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ga*** as a white solid (29.7 mg, 70% yield). Flash column chromatography (petroleum ether/ethyl acetate, 40:1); R_f 0.4 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[5]

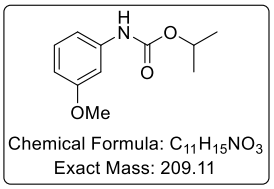


^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.51 (s, 1H), 7.24 – 7.16 (m, 2H), 7.01 (dt, *J* = 5.1, 2.2 Hz, 1H), 6.72 (s, 1H), 5.02 (h, *J* = 6.3 Hz, 1H), 1.29 (d, *J* = 6.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 153.1, 139.4, 134.8, 130.1, 123.3, 118.7, 116.6, 69.2, 22.2.

isopropyl (3-methoxyphenyl)carbamate (3ha)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ha*** as a yellow oil (33.7 mg, 81% yield). Flash column chromatography (petroleum ether/ethyl acetate, 40:1); R_f 0.3 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[6]

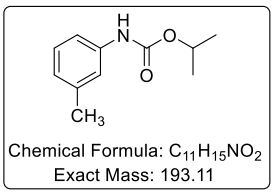


^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.13 – 7.02 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.69 (s, 1H), 6.52 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.93 (p, *J* = 6.2 Hz, 1H), 3.70 (s, 3H), 1.20 (d, *J* = 6.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 160.3, 153.3, 139.5, 129.8, 110.9, 109.2, 104.3, 68.8, 55.3, 22.2.

isopropyl m-tolylcarbamate (3ia)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ia*** as a yellow oil (33.6 mg, 87% yield). Flash column chromatography (petroleum ether/ethyl acetate, 40:1); R_f 0.3 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[1]



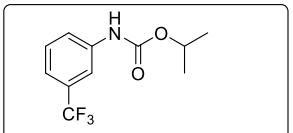
Chemical Formula: $C_{11}H_{15}NO_2$
Exact Mass: 193.11

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.24 (s, 1H), 7.16 (d, *J* = 6.6 Hz, 2H), 6.86 (d, *J* = 6.3 Hz, 1H), 6.60 (s, 1H), 5.01 (p, *J* = 6.3 Hz, 1H), 2.32 (s, 3H), 1.29 (d, *J* = 6.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 153.4, 139.0, 138.1, 128.9, 124.1, 119.3, 115.8, 68.7, 22.2, 21.6.

isopropyl (3-(trifluoromethyl)phenyl)carbamate (3ja)

Obtained according to the ***General procedure A*** (130 °C /24 h), to give ***3ja*** as a yellow oil (37.9 mg, 77% yield). Flash column chromatography (petroleum ether/ethyl acetate, 40:1); R_f 0.3 (petroleum ether/ethyl acetate, 10:1).



Chemical Formula: $C_{11}H_{12}F_3NO_2$
Exact Mass: 247.08

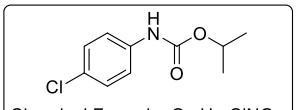
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.65 (s, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.22 – 7.17 (m, 1H), 6.88 (s, 1H), 4.94 (h, *J* = 6.3 Hz, 1H), 1.21 (d, *J* = 6.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 153.3, 138.9, 131.5 (q, *J* = 32.3 Hz), 129.6, 124.0 (q, *J* = 272.1 Hz), 121.7, 119.9 (q, *J* = 3.8 Hz), 115.4, 69.4, 22.1.

HRMS (ESI) m/z: Calculated for $C_{11}H_{12}F_3NO_2$ $[M+Na]^+$: 270.0712, found: 270.0718.

isopropyl (4-chlorophenyl)carbamate (3ka)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ka*** as a white solid (30.2 mg, 71% yield). Flash column chromatography (petroleum ether/ethyl acetate, 40:1); R_f 0.3 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported. [1]



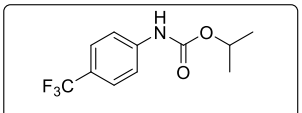
Chemical Formula: $C_{10}H_{12}ClNO_2$
Exact Mass: 213.06

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.33 (d, *J* = 8.6 Hz, 2H), 7.27 – 7.22 (m, 2H), 6.70 (s, 1H), 5.01 (p, *J* = 6.3 Hz, 1H), 1.28 (d, *J* = 6.2 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 153.3, 136.8, 129.1, 128.3, 119.9, 69.1, 22.2.

isopropyl (4-(trifluoromethyl)phenyl)carbamate (3la)

Obtained according to the ***General procedure A*** (130 °C /24 h), to give ***3la*** as a white solid (26.2 mg, 53% yield). Flash column chromatography (petroleum ether/ethyl acetate, 40:1); R_f 0.4 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[7]



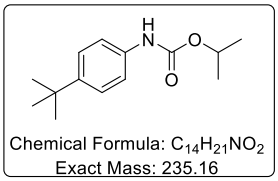
Chemical Formula: $C_{11}H_{12}F_3NO_2$
Exact Mass: 247.08

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.48 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 6.72 (s, 1H), 4.96 (hept, *J* = 6.3 Hz, 1H), 1.23 (d, *J* = 6.2 Hz, 6H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.0, 141.4, 126.3 (q, *J* = 3.8 Hz), 125.1 (q, *J* = 32.9 Hz), 124.3 (q, *J* = 271.5 Hz), 118.1, 69.5, 22.2.

isopropyl (4-(tert-butyl)phenyl)carbamate (3ma)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ma*** as a white solid (39.9 mg, 85% yield). Flash column chromatography (petroleum ether/ethyl acetate, 40:1); R_f 0.4 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[8]

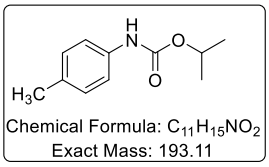


^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 4H), 6.62 (s, 1H), 5.05 – 4.99 (m, 1H), 1.30 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 146.3, 135.6, 125.9, 118.6, 68.7, 34.3, 31.5, 22.2.

isopropyl p-tolylcarbamate (3na)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3na*** as a yellow oil (34.1 mg, 88% yield). Flash column chromatography (petroleum ether/ethyl acetate, 40:1); R_f 0.4 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[9]

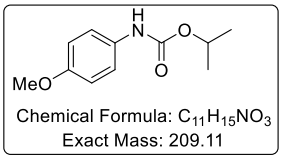


^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.57 (s, 1H), 5.01 (hept, *J* = 6.3 Hz, 1H), 2.29 (s, 3H), 1.29 (s, 6H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.5, 135.6, 132.8, 129.6, 118.8, 68.6, 22.2, 20.8.

isopropyl (4-methoxyphenyl)carbamate (3oa)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3oa*** as a yellow solid (31.1 mg, 74% yield). Flash column chromatography (petroleum ether/ethyl acetate, 40:1); R_f 0.4 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[1]

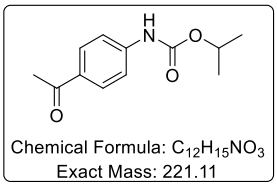


^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 2H), 6.87 – 6.81 (m, 2H), 6.51 (s, 1H), 5.00 (hept, *J* = 6.3 Hz, 1H), 3.78 (s, 3H), 1.28 (d, *J* = 6.2 Hz, 6H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.9, 153.7, 131.3, 120.7, 114.3, 68.7, 55.6, 22.2.

isopropyl (4-acetylphenyl)carbamate (3pa)

Obtained according to the ***General procedure A*** (120 °C /24 h), to give ***3pa*** as a white solid (30.9 mg, 70% yield). Flash column chromatography (petroleum ether/ethyl acetate, 8:1); R_f 0.4 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[2]

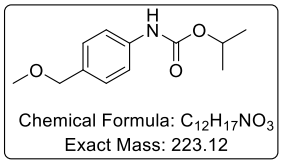


^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.93 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.14 (s, 1H), 5.04 (hept, *J* = 6.3 Hz, 1H), 2.58 (s, 3H), 1.30 (d, *J* = 6.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 197.2, 152.9, 142.9, 132.0, 130.0, 117.6, 69.3, 26.5, 22.1.

isopropyl (4-(methoxymethyl)phenyl)carbamate (3qa)

Obtained according to the ***General procedure A*** (120 °C /24 h), to give ***3qa*** as a white solid (30.9 mg, 69% yield). Flash column chromatography (petroleum ether/ethyl acetate, 10:1); R_f 0.4 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[10]

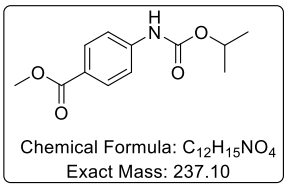


^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.76 (s, 1H), 5.02 (p, *J* = 6.3 Hz, 1H), 4.40 (s, 2H), 3.36 (s, 3H), 1.29 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 153.4, 137.8, 132.9, 128.8, 118.6, 74.4, 68.8, 58.0, 22.2.

methyl 4-((isopropoxycarbonyl)amino)benzoate (3ra)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ra*** as a white solid (32.3 mg, 68% yield). Flash column chromatography (petroleum ether/ethyl acetate, 15:1); R_f 0.2 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[11]

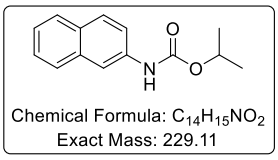


^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.03 – 7.92 (m, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.85 (s, 1H), 5.03 (p, *J* = 6.3 Hz, 1H), 3.89 (s, 3H), 1.30 (d, *J* = 6.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 166.9, 152.9, 142.6, 131.1, 124.7, 117.6, 69.4, 52.1, 22.2.

isopropyl naphthalen-2-ylcarbamate (3sa)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3sa*** as a pink solid (33.7 mg, 74% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1). R_f 0.4 (petroleum ether/ethyl acetate, 10:1).



^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.01 (s, 1H), 7.77 (d, *J* = 8.9 Hz, 3H), 7.49 – 7.42 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 6.81 (s, 1H), 5.09 (p, *J* = 6.3 Hz, 1H), 1.34 (d, *J* = 6.2 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 153.5, 135.7, 134.1, 130.2, 128.9, 127.6, 127.5, 126.6, 124.7, 119.3, 114.8, 69.0, 22.2.

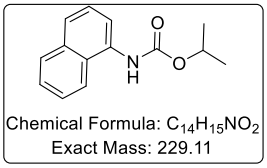
HRMS (ESI) m/z: Calculated for $C_{14}H_{15}NO_2$ $[M+Na]^+$: 252.0995, found: 252.1001.

Mp: 70-75°C.

isopropyl naphthalen-1-ylcarbamate(3ta)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ta*** as a pink solid (32 mg, 70% yield). Flash column chromatography (petroleum ether/ethyl

acetate, 30:1). R_f 0.3(petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[12]

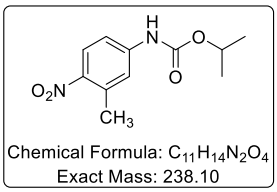


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.80 (m, 3H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.43 (m, 3H), 6.96 (s, 1H), 5.09 (hept, *J* = 6.3 Hz, 1H), 1.35 (d, *J* = 6.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.1, 134.1, 132.8, 128.8, 126.6, 126.1, 125.9, 125.9, 124.7, 120.5, 118.8, 69.1, 22.2.

isopropyl (3-methyl-4-nitrophenyl)carbamate (3ua)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ua*** as a yellow solid (24.5 mg, 51% yield). Flash column chromatography (petroleum ether/ethyl acetate, 15:1); R_f 0.4 (petroleum ether/ethyl acetate, 10:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.9 Hz, 1H), 7.39 (s, 1H), 7.35 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.93 (s, 1H), 5.02 (hept, *J* = 6.3 Hz, 1H), 2.61 (s, 3H), 1.30 (d, *J* = 6.3 Hz, 6H).

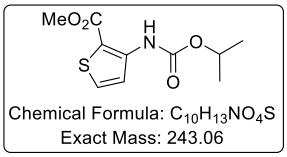
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.7, 143.6, 142.8, 136.4, 126.9, 121.0, 115.8, 69.8, 22.1, 21.6.

HRMS (ESI) m/z: Calculated for $C_{11}H_{14}N_2O_4$ $[M+Na]^+$: 261.0846, found: 261.0847.

Mp: 102-108°C.

methyl 3-((isopropoxycarbonyl)amino)thiophene-2-carboxylate (3va)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3va*** as a white solid (18.6 mg, 38% yield). Flash column chromatography (petroleum ether/ethyl acetate, 15:1); R_f 0.3 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[13]

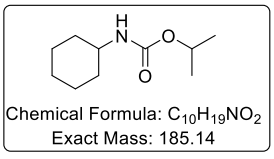


^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.89 (d, *J* = 5.4 Hz, 1H), 7.44 (d, *J* = 5.5 Hz, 1H), 5.00 (hept, *J* = 6.3 Hz, 1H), 3.87 (s, 3H), 1.30 (d, *J* = 6.2 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.7, 152.8, 145.5, 131.7, 121.4, 108.5, 69.5, 52.0, 22.1.

isopropyl cyclohexylcarbamate (3wa)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3wa*** as a white solid (27.3 mg, 74% yield). Flash column chromatography (petroleum ether/ethyl acetate, 10:1). R_f 0.5 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[14]

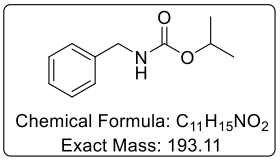


^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 (h, *J* = 6.2 Hz, 1H), 4.49 (s, 1H), 3.44 (s, 1H), 1.91 (d, *J* = 7.7 Hz, 2H), 1.68 (dt, *J* = 13.4, 3.9 Hz, 2H), 1.58 (dt, *J* = 12.8, 3.8 Hz, 1H), 1.33 (dd, *J* = 14.3, 5.1 Hz, 2H), 1.20 (d, *J* = 6.3 Hz, 6H), 1.17 – 1.04 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.6, 67.7, 49.7, 33.6, 25.6, 24.9, 22.3.

isopropyl benzylcarbamate (3xa)

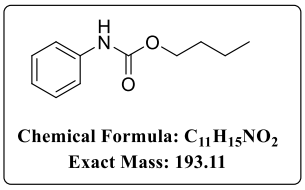
Obtained according to the **General p*rocedure A*** (120 °C /16 h), to give ***3xa*** as a white solid (18.6 mg, 48% yield). Flash column chromatography (petroleum ether/ethyl acetate, 10:1). R_f 0.4 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[15]



^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.37 – 7.25 (m, 5H), 4.98 – 4.90 (m, 2H), 4.36 (d, *J* = 5.9 Hz, 2H), 1.24 (d, *J* = 6.4 Hz, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 156.4, 138.8, 128.8, 127.7, 127.6, 68.4, 45.1, 22.3.

Butyl phenylcarbamate (3ab)

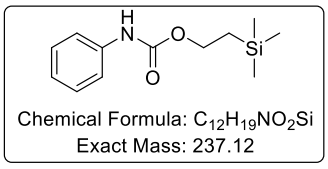
Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ab*** as a white solid (28.1 mg, 73% yield). Flash column chromatography (petroleum ether/ethyl acetate, 50:1); R_f 0.7 (petroleum ether/ethyl acetate, 5:1). Spectroscopic data are consistent with those previously reported.[16]



1H NMR (400 MHz, $CDCl_3$) *δ* 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.60 (s, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 1.66 (p, *J* = 6.9 Hz, 2H), 1.42 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 153.8, 138.1, 129.2, 123.5, 118.7, 65.3, 31.1, 19.2, 13.9.

14.3.2-(trimethylsilyl)ethyl phenylcarbamate (3ac)

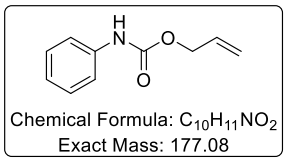
Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ac*** as a yellow solid (39.9 mg, 84% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.6 (petroleum ether/ethyl acetate, 5:1). Spectroscopic data are consistent with those previously reported.[17]



^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.33 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 6.7 Hz, 2H), 6.99 (t, *J* = 7.3 Hz, 1H), 6.62 (s, 1H), 4.25 – 4.15 (m, 2H), 1.05 – 0.94 (m, 2H), 0.00 (d, *J* = 2.6 Hz, 9H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 153.9, 138.1, 129.1, 123.4, 118.8, 63.6, 17.8, -1.4.

Allyl phenylcarbamate (3ad)

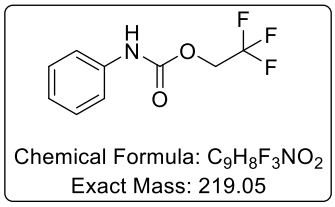
Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ad*** as a yellow solid (31.9 mg, 90% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.6 (petroleum ether/ethyl acetate, 5:1). Spectroscopic data are consistent with those previously reported.[18]



^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.40 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.77 (s, 1H), 5.97 (ddt, *J* = 16.5, 11.0, 5.7 Hz, 1H), 5.37 (d, *J* = 17.2 Hz, 1H), 5.27 (d, *J* = 10.4 Hz, 1H), 4.67 (d, *J* = 5.7 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 153.4, 137.9, 132.5, 129.2, 123.6, 118.8, 118.4, 66.0.

2,2,2-trifluoroethyl phenylcarbamate (3ae)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ae*** as a yellow solid (30.6 mg, 70% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.6 (petroleum ether/ethyl acetate, 5:1). Spectroscopic data are consistent with those previously reported.[19]



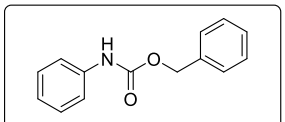
Chemical Formula: $C_9H_8F_3NO_2$
Exact Mass: 219.05

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.40 – 7.31 (m, 4H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.81 (s, 1H), 4.56 (q, *J* = 8.4 Hz, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* 151.6, 137.0, 129.3, 124.4, 123.1 (q, *J* = 278.4 Hz), 119.1, 61.1 (q, *J* = 36.4 Hz).

benzyl phenylcarbamate (3af)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3af*** as a yellow solid (42.7 mg, 94% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.6 (petroleum ether/ethyl acetate, 5:1).



Chemical Formula: $C_{14}H_{13}NO_2$
Exact Mass: 227.1

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43 – 7.27 (m, 9H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.76 (s, 1H), 5.21 (s, 2H).

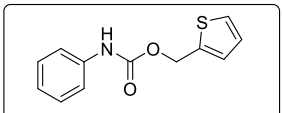
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 153.5, 137.9, 136.1, 129.2, 128.7, 128.5, 128.4, 123.6, 118.8, 67.1.

HRMS (ESI) m/z: Calculated for $C_{16}H_{17}NO_2$ $[M+Na]^+$: 250.0838, found: 250.0847.

Mp: 76-77 °C.

Thiophen-2-ylmethyl phenylcarbamate (3ag)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ag*** as a white solid (35.9 mg, 77% yield). Flash column chromatography (petroleum ether/ethyl acetate, 25:1); R_f 0.4 (petroleum ether/ethyl acetate, 5:1). Spectroscopic data are consistent with those previously reported.[20]



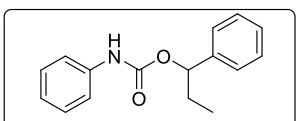
Chemical Formula: $C_{12}H_{11}NO_2S$
Exact Mass: 233.05

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.40 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.14 (d, *J* = 3.5 Hz, 1H), 7.12 – 7.05 (m, 1H), 7.01 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.80 (s, 1H), 5.35 (s, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* 153.2, 138.1, 137.7, 129.2, 128.4, 127.1, 127.0, 123.7, 118.8, 61.2.

1-phenylpropyl phenylcarbamate (3ah)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ah*** as a colorless oil (40.5 mg, 79% yield). Flash column chromatography (petroleum ether/ethyl acetate, 50:1); R_f 0.6 (petroleum ether/ethyl acetate, 5:1).



Chemical Formula: $C_{16}H_{17}NO_2$
Exact Mass: 255.13

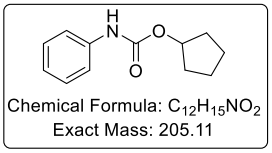
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 6H), 7.34 – 7.27 (m, 3H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.79 (s, 1H), 5.69 (t, *J* = 6.9 Hz, 1H), 2.00 (dq, *J* = 14.7, 7.3 Hz, 1H), 1.88 (dp, *J* = 14.2, 7.3 Hz, 1H), 0.95 (t, *J* = 7.4 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* 153.1, 140.6, 138.0, 129.1, 128.5, 128.0, 126.6, 123.4, 118.6, 78.5, 29.5, 10.1.

HRMS (ESI) m/z: Calculated for $C_{16}H_{17}NO_2$ $[M+Na]^+$: 278.1151, found: 278.1146.

Cyclopentyl phenylcarbamate (3ai)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ai*** as a white solid (37.4 mg, 91% yield). Flash column chromatography (petroleum ether/ethyl acetate, 25:1); R_f 0.5 (petroleum ether/ethyl acetate, 5:1). Spectroscopic data are consistent with those previously reported.[21]

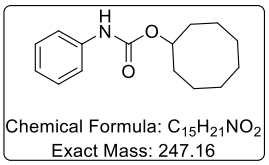


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.68 (s, 1H), 5.21 (tt, *J* = 6.1, 2.7 Hz, 1H), 1.88 (td, *J* = 12.3, 7.0 Hz, 2H), 1.82 – 1.70 (m, 4H), 1.67 – 1.57 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.6, 138.2, 129.1, 123.3, 118.6, 78.1, 32.9, 23.8.

Cyclooctyl phenylcarbamate (3aj)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3aj*** as a colorless oil (45.9 mg, 93% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.5 (petroleum ether/ethyl acetate, 5:1).



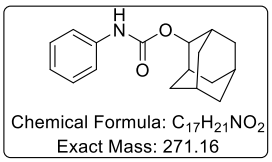
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.68 (s, 1H), 4.95 (tt, *J* = 8.4, 3.9 Hz, 1H), 1.94 – 1.55 (m, 14H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.4, 138.3, 129.1, 123.2, 118.6, 76.2, 31.7, 27.2, 25.5, 23.0.

HRMS (ESI) m/z: Calculated for $C_{15}H_{21}NO_2$ $[M+Na]^+$: 270.1464, found: 270.1465.

(1R,3S,5r,7r)-adamantan-2-yl phenylcarbamate (3ak)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ak*** as a white solid (39.8 mg, 73% yield). Flash column chromatography (petroleum ether/ethyl acetate, 50:1); R_f 0.7 (petroleum ether/ethyl acetate, 5:1). Spectroscopic data are consistent with those previously reported.[22]

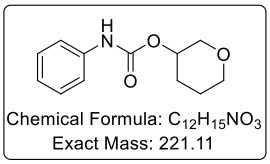


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.75 (s, 1H), 4.93 (d, *J* = 3.6 Hz, 1H), 2.11 – 2.01 (m, 4H), 1.87 – 1.73 (m, 8H), 1.59 (d, *J* = 12.4 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.4, 138.3, 129.1, 123.3, 118.6, 78.1, 37.5, 36.4, 32.1, 31.9, 27.3, 27.1.

Tetrahydro-2H-pyran-3-yl phenylcarbamate (3al)

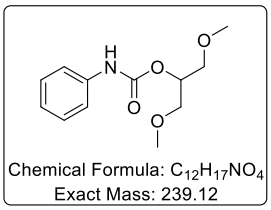
Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3al*** as a white solid (38 mg, 86% yield). Flash column chromatography (petroleum ether/ethyl acetate, 50:1); R_f 0.7 (petroleum ether/ethyl acetate, 5:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.87 (s, 1H), 4.83 (td, *J* = 5.5, 2.8 Hz, 1H), 3.83 – 3.60 (m, 4H), 2.00 – 1.83 (m, 3H), 1.62 – 1.54 (m, 1H).

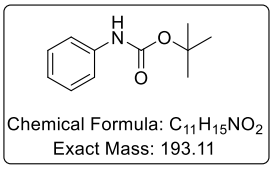
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* 153.0, 137.9, 129.2, 123.6, 118.7, 70.1, 68.8, 68.0, 28.2, 22.7.
HRMS (ESI) m/z: Calculated for $C_{12}H_{15}NO_3$ $[M+Na]^+$: 244.0944, found: 244.0945.
Mp: 122-127°C.

1,3-dimethoxypropan-2-yl phenylcarbamate (3am)
Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3am*** as a yellow oil (39.2 mg, 82% yield). Flash column chromatography (petroleum ether/ethyl acetate, 10:1 to 2:1); R_f 0.2 (petroleum ether/ethyl acetate, 5:1).



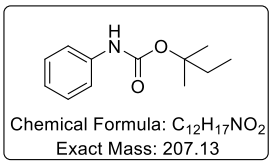
^1H NMR (400 MHz, $CDCl_3$) *δ* 7.37 (d, *J* = 7.3 Hz, 2H), 7.32 – 7.25 (m, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.93 (s, 1H), 5.13 (p, *J* = 4.9 Hz, 1H), 3.62 (d, *J* = 4.9 Hz, 4H), 3.39 (s, 6H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* 152.8, 137.9, 129.2, 123.6, 118.6, 72.1, 71.4, 59.4.
HRMS (ESI) m/z: Calculated for $C_{12}H_{17}NO_4$ $[M+Na]^+$: 262.1050, found: 262.1095.

Tert-butyl phenylcarbamate (3an)
Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3an*** as a white solid (25.7 mg, 67% yield). Flash column chromatography (petroleum ether/ethyl acetate, 50:1); R_f 0.6 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[23]



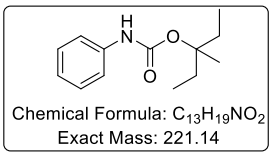
^1H NMR (400 MHz, $CDCl_3$) *δ* 7.36 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.51 (s, 1H), 1.52 (s, 9H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* 152.9, 138.4, 129.1, 123.1, 118.6, 80.6, 28.5.

Tert-pentyl phenylcarbamate (3ao)
Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ao*** as a white solid (18.6 mg, 49% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.5 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[24]



^1H NMR (400 MHz, $CDCl_3$) *δ* 7.37 (s, 2H), 7.28 (dd, *J* = 8.7, 7.2 Hz, 2H), 7.03 (tt, *J* = 7.2, 1.3 Hz, 1H), 6.52 (s, 1H), 1.85 (q, *J* = 7.5 Hz, 2H), 1.49 (s, 6H), 0.93 (t, *J* = 7.5 Hz, 3H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* 152.8, 138.5, 129.1, 123.1, 118.6, 83.1, 33.7, 25.9, 8.4.

3-methylpentan-3-yl phenylcarbamate (3ap)
Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ap*** as a yellow oil (17.1 mg, 38% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.5 (petroleum ether/ethyl acetate, 10:1).



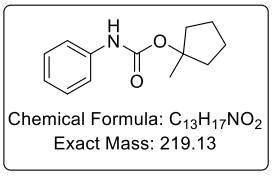
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.52 (s, 1H), 1.94 (dq, *J* = 14.9, 7.5 Hz, 2H), 1.81 (dq, *J* = 14.6, 7.4 Hz, 2H), 1.44 (s, 3H), 0.91 (t, *J* = 7.5 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.7, 138.5, 129.1, 123.1, 118.6, 85.7, 30.8, 23.2, 8.2.

HRMS (ESI) m/z: Calculated for $C_{13}H_1NO_2$ $[M+Na]^+$: 244.1308, found: 244.1298.

1-methylcyclopentyl phenylcarbamate (3aq)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3aq*** as a yellow solid (20.2 mg, 46% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.5 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[25]

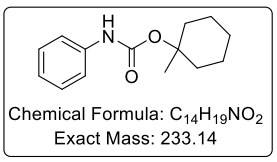


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.51 (s, 1H), 2.24 – 2.13 (m, 2H), 1.81 – 1.64 (m, 6H), 1.63 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, DMSO) δ 152.9, 139.5, 128.6, 122.0, 118.0, 88.4, 38.8, 24.4, 23.3.

1-methylcyclohexyl phenylcarbamate (3ar)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3ar*** as a yellow solid (19.4 mg, 41% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.5 (petroleum ether/ethyl acetate, 10:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.54 (s, 1H), 2.18 (d, *J* = 13.3 Hz, 2H), 1.61 – 1.40 (m, 11H).

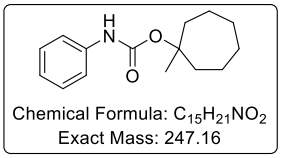
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.8, 138.5, 129.1, 123.1, 118.6, 76.8, 37.0, 25.9, 25.5, 22.3.

HRMS (ESI) m/z: Calculated for $C_{14}H_{19}NO_2$ $[M+Na]^+$: 256.1308, found: 256.1310.

Mp: 104-106 °C.

1-methylcycloheptyl phenylcarbamate (3as)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3as*** as a yellow solid (16.8 mg, 34% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.5 (petroleum ether/ethyl acetate, 10:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.9 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.51 (s, 1H), 2.18 (dd, *J* = 14.5, 8.6 Hz, 2H), 1.80 (dd, *J* = 14.7, 9.9 Hz, 2H), 1.68 – 1.59 (m, 4H), 1.57 (s, 3H), 1.56 – 1.50 (m, 2H), 1.45 (q, *J* = 7.5 Hz, 2H).

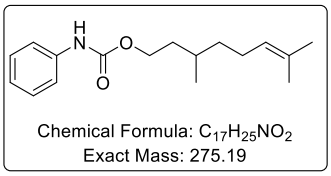
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.9, 138.5, 129.1, 123.1, 118.6, 86.6, 40.5, 29.7, 27.3, 22.8.

HRMS (ESI) m/z: Calculated for $C_{15}H_{21}NO_2$ $[M+Na]^+$: 270.1465, found: 270.1453.

Mp: 62-65 °C.

3,7-dimethyloct-6-en-1-yl phenylcarbamate (3at)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3at*** as a white oil (54.5 mg, 99% yield). Flash column chromatography (petroleum ether/ethyl acetate, 25:1); R_f 0.4 (petroleum ether/ethyl acetate, 5:1).



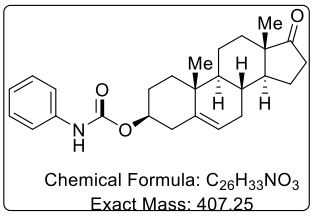
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.39 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.73 (s, 1H), 5.10 (t, *J* = 7.1 Hz, 1H), 4.27 – 4.15 (m, 2H), 2.00 (dp, *J* = 23.6, 7.5 Hz, 2H), 1.74 (dd, *J* = 11.9, 6.6 Hz, 1H), 1.69 (s, 3H), 1.61 (s, 3H), 1.60 – 1.54 (m, 1H), 1.48 (td, *J* = 13.4, 7.5 Hz, 1H), 1.43 – 1.33 (m, 1H), 1.27 – 1.15 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 153.8, 138.1, 131.5, 129.2, 124.7, 123.5, 118.7, 63.9, 37.1, 35.9, 29.5, 25.9, 25.5, 19.5, 17.8.

HRMS (ESI) m/z: Calculated for $C_{17}H_{25}NO_2$ $[M+Na]^+$: 289.1778, found: 298.1770.

(3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl phenylcarbamate (3au)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3au*** as a white solid (65.2 mg, 80% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.5 (petroleum ether/ethyl acetate, 10:1).



^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.23 (m, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.81 (s, 1H), 5.42 (d, *J* = 5.1 Hz, 1H), 4.60 (td, *J* = 11.5, 5.8 Hz, 1H), 2.52 – 2.40 (m, 2H), 2.34 (t, *J* = 11.0 Hz, 1H), 2.10 (dt, *J* = 19.0, 9.1 Hz, 2H), 1.97 (d, *J* = 13.3 Hz, 2H), 1.92 – 1.83 (m, 2H), 1.73 – 1.58 (m, 4H), 1.59 – 1.42 (m, 2H), 1.35 – 1.22 (m, 3H), 1.17 (td, *J* = 13.7, 3.7 Hz, 1H), 1.05 (s, 3H), 0.89 (s, 3H).

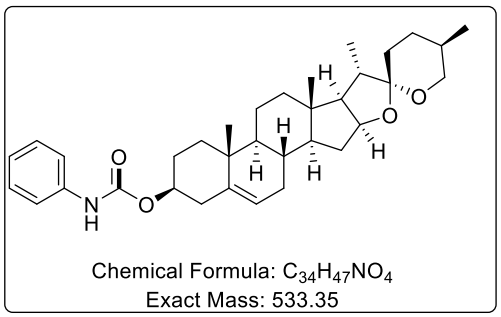
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 221.2, 153.1, 139.9, 138.1, 129.1, 123.4, 122.1, 118.7, 74.7, 51.8, 50.2, 47.6, 38.5, 36.8, 35.9, 31.6, 31.5, 30.9, 29.8, 28.1, 21.9, 20.4, 19.5, 13.7.

HRMS (ESI) m/z: Calculated for $C_{26}H_{33}NO_3$ $[M+Na]^+$: 430.2353, found: 430.2351.

Mp: 223-228 °C.

(4S,5'R,6aR,6bS,8aS,8bR,9S,10R,11aS,12aS,12bS)-5',6a,8a,9-tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-b]furan-10,2'-pyran]-4-yl phenylcarbamate (3av)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3av*** as a white solid (64 mg, 60% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.5 (petroleum ether/ethyl acetate, 10:1).



^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.38 (d, *J* = 8.1 Hz, 2H), 7.29 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.71 (s, 1H), 5.39 (d, *J* = 5.4 Hz, 1H), 4.59 (td, *J* = 11.5, 5.7 Hz, 1H), 4.42 (q, *J* = 7.6 Hz, 1H), 3.48 (dd, *J* = 10.0, 5.3 Hz, 1H), 3.38 (t, *J* = 10.9 Hz, 1H), 2.44 (dd, *J* = 13.0, 2.9 Hz, 1H), 2.33 (t, *J* = 11.0 Hz, 1H), 1.98 (td, *J* = 13.1, 5.8 Hz, 3H), 1.91 – 1.83 (m, 2H), 1.82 – 1.74 (m, 2H), 1.67 – 1.57 (m, 6H), 1.54 – 1.40 (m, 3H), 1.35 – 1.20 (m, 3H), 1.20 – 1.08 (m, 3H), 1.04 (s, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.79 (d, *J* = 6.6 Hz, 6H).

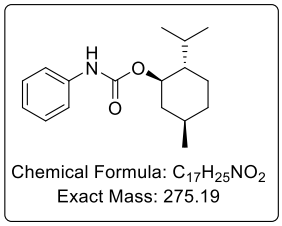
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 153.2, 139.7, 138.1, 129.2, 123.4, 122.6, 118.6, 109.4, 80.9, 74.9, 67.0, 62.2, 56.5, 50.0, 41.7, 40.4, 39.8, 38.5, 37.1, 36.8, 32.2, 32.0, 31.5, 31.5, 30.4, 28.9, 28.2, 20.9, 19.5, 17.3, 16.4, 14.7.

HRMS (ESI) m/z: Calculated for $C_{34}H_{47}NO_4$ $[M+H]^+$: 534.3578, found: 534.3551.

Mp: 210-214 °C.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl phenylcarbamate (3aw)

Obtained according to the ***General procedure A*** (120 °C /16 h), to give ***3aw*** as a white solid (54.5 mg, 99% yield). Flash column chromatography (petroleum ether/ethyl acetate, 30:1); R_f 0.5 (petroleum ether/ethyl acetate, 5:1). Spectroscopic data are consistent with those previously reported.[26]

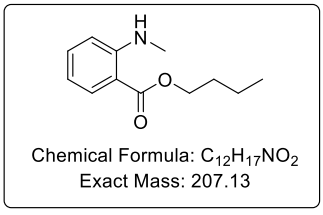


^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.69 (s, 1H), 4.67 (td, *J* = 10.9, 4.4 Hz, 1H), 2.11 (d, *J* = 11.9 Hz, 1H), 1.99 (dqd, *J* = 9.6, 7.0, 3.6 Hz, 1H), 1.69 (d, *J* = 12.1 Hz, 2H), 1.49 (ddt, *J* = 15.3, 9.4, 4.6 Hz, 1H), 1.44 – 1.23 (m, 2H), 1.15 – 0.98 (m, 2H), 0.92 (d, *J* = 6.8 Hz, 6H), 0.82 (d, *J* = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ*153.5, 138.3, 129.1, 123.3, 118.6, 75.2, 47.4, 41.5, 34.4, 31.5, 26.4, 23.6, 22.1, 20.9, 16.5.

Butyl 2-(methylamino)benzoate (5ab)

Obtained according to the ***General procedure B*** (0.2 mmol scale), to give ***5ab*** as a yellow oil (23.8 mg, 58% yield). Flash column chromatography (petroleum ether/ethyl acetate, 200:1); R_f 0.6 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[27]

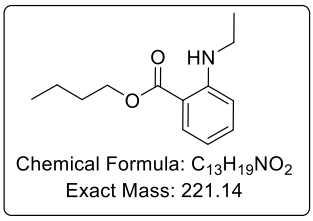


^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.91 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.67 (s, 1H), 7.40 – 7.36 (m, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.59 (t, *J* = 7.6 Hz, 1H), 4.26 (t, *J* = 6.6 Hz, 2H), 2.91 (d, *J* = 5.0 Hz, 3H), 1.79 – 1.69 (m, 2H), 1.52 – 0.99 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C{H} NMR (101 MHz, $CDCl_3$) *δ* 168.9, 152.2, 134.7, 131.6, 114.4, 110.8, 110.3, 64.2, 31.0, 29.7, 19.5, 13.9.

Butyl 2-(ethylamino)benzoate (5bb)

Obtained according to the ***General procedure B*** (0.2 mmol scale), to give ***5bb*** as a yellow oil (13.7 mg, 31% yield). Flash column chromatography (petroleum ether/ethyl acetate, 200:1); R_f 0.6 (petroleum ether/ethyl acetate, 10:1).



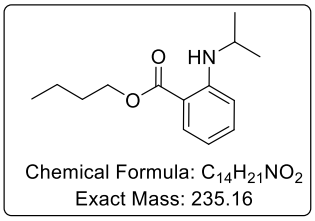
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.62 (s, 1H), 7.37 – 7.33 (m, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.61 – 6.52 (m, 1H), 4.26 (t, *J* = 6.6 Hz, 2H), 3.28 – 3.18 (m, 2H), 1.79 – 1.69 (m, 2H), 1.52 – 1.36 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C{H} NMR (101 MHz, DMSO) δ 167.8, 150.6, 134.9, 131.1, 114.3, 111.4, 109.1, 63.7, 36.7, 30.3, 18.9, 14.4, 13.7.

HRMS (ESI) m/z: Calculated for $C_{13}H_{19}NO_2$ $[M+Na]^+$: 244.1308, found: 244.1322.

Butyl 2-(isopropylamino)benzoate (5cb)

Obtained according to the ***General procedure B*** (0.2 mmol scale), to give ***5cb*** as a yellow oil (8.9 mg, 19% yield). Flash column chromatography (petroleum ether/ethyl acetate, 200:1); R_f 0.6 (petroleum ether/ethyl acetate, 10:1).



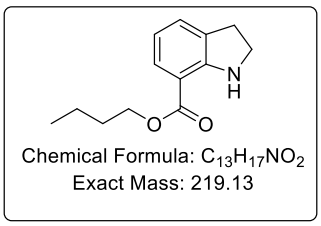
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.38 – 7.29 (m, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 6.59 – 6.50 (m, 1H), 4.25 (t, *J* = 6.6 Hz, 2H), 3.72 (h, *J* = 6.5 Hz, 1H), 1.79 – 1.68 (m, 2H), 1.48 (p, *J* = 7.4 Hz, 2H), 1.27 (d, *J* = 6.4 Hz, 6H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C{H} NMR (101 MHz, DMSO) δ 167.9, 149.9, 134.8, 131.2, 114.1, 111.9, 109.0, 63.7, 42.6, 30.3, 22.5, 18.9, 13.6.

HRMS (ESI) m/z: Calculated for $C_{14}H_{21}NO_2$ $[M+Na]^+$: 258.1465, found: 258.1461.

Butyl indoline-7-carboxylate (5db)

Obtained according to the ***General procedure B*** (0.2 mmol scale), to give ***5db*** as a yellow oil (7 mg, 16% yield). Flash column chromatography (petroleum ether/ethyl acetate, 150:1); R_f 0.6 (petroleum ether/ethyl acetate, 10:1).



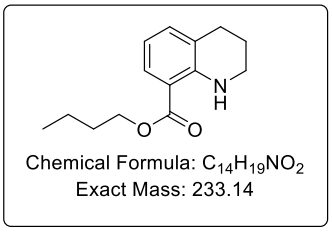
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 1H), 7.16 (d, *J* = 7.1 Hz, 1H), 6.59 – 6.52 (m, 1H), 6.08 (s, 1H), 4.27 (t, *J* = 6.6 Hz, 2H), 3.71 (t, *J* = 8.5 Hz, 2H), 3.05 (t, *J* = 8.5 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.50 – 1.43 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C{H} NMR (101 MHz, DMSO) δ 166.5, 154.1, 131.3, 128.4, 127.3, 115.3, 106.8, 63.4, 46.4, 30.4, 27.8, 18.8, 13.7.

HRMS (ESI) m/z: Calculated for $C_{13}H_{17}NO_2$ $[M+H]^+$: 220.1332, found: 220.1331.

Butyl 1,2,3,4-tetrahydroquinoline-8-carboxylate (5eb)

Obtained according to the ***General procedure B*** (0.2 mmol scale), to give ***5eb*** as a yellow oil (28.9 mg, 62% yield). Flash column chromatography (petroleum ether/ethyl acetate, 150:1); R_f 0.6 (petroleum ether/ethyl acetate, 10:1).



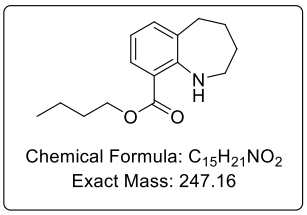
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.80 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.03 (d, *J* = 7.1 Hz, 1H), 6.44 (t, *J* = 7.6 Hz, 1H), 4.24 (t, *J* = 6.6 Hz, 2H), 3.49 – 3.36 (m, 2H), 2.78 (t, *J* = 6.3 Hz, 2H), 1.90 (p, *J* = 6.1 Hz, 2H), 1.80 – 1.67 (m, 2H), 1.47 (h, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C{H} NMR (101 MHz, $CDCl_3$) *δ* 169.0, 148.5, 133.8, 129.5, 122.1, 113.6, 108.8, 64.0, 41.30, 31.0, 27.9, 20.9, 19.5, 13.9.

HRMS (ESI) m/z: Calculated for $C_{14}H_{19}N0_2$ $[M+H]^+$: 256.1308, found: 256.1295.

Butyl 2,3,4,5-tetrahydro-1H-benzo[b]azepine-9-carboxylate (5fb)

Obtained according to the ***General procedure B*** (0.2 mmol scale), to give ***5fb*** as a yellow oil (34.5 mg, 70% yield). Flash column chromatography (petroleum ether/ethyl acetate, 150:1); R_f 0.6 (petroleum ether/ethyl acetate, 10:1).



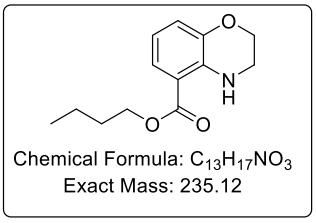
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.80 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.76 (s, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 6.67 (t, *J* = 7.6 Hz, 1H), 4.26 (t, *J* = 6.6 Hz, 2H), 3.21 (t, *J* = 5.4 Hz, 2H), 2.87 – 2.76 (m, 2H), 1.86 – 1.78 (m, 2H), 1.78 – 1.70 (m, 4H), 1.48 (dq, *J* = 14.6, 7.3 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C{H} NMR (101 MHz, $CDCl_3$) *δ* 169.1, 154.7, 135.8, 133.5, 129.4, 117.7, 115.1, 64.5, 46.9, 35.5, 30.9, 30.4, 26.3, 19.4, 13.9.

HRMS (ESI) m/z: Calculated for $C_{15}H_{21}N0_2$ $[M+H]^+$: 248.1645, found: 248.1617.

Butyl 3,4-dihydro-2H-benzo[b][1,4]oxazine-5-carboxylate (5gb)

Obtained according to the ***General procedure B*** (0.2 mmol scale), to give ***5gb*** as a yellow oil (33 mg, 70% yield). Flash column chromatography (petroleum ether/ethyl acetate, 150:1); R_f 0.6 (petroleum ether/ethyl acetate, 10:1).



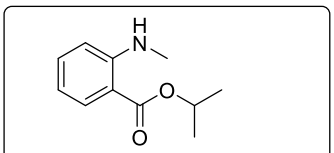
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.50 (s, 1H), 7.50-7.48 (m, 1H), 6.89 (d, *J* = 6.2 Hz, 1H), 6.50 (t, *J* = 7.9 Hz, 1H), 4.25 (t, *J* = 6.5 Hz, 2H), 4.23 – 4.19 (m, 2H), 3.53 (td, *J* = 4.5, 2.5 Hz, 2H), 1.76z – 1.69 (m, 2H), 1.51 – 1.42 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C{H} NMR (101 MHz, $CDCl_3$) *δ* 168.7, 143.5, 138.8, 123.8, 120.2, 114.8, 110.9, 64.3, 64.1, 40.0, 30.9, 19.4, 13.9.

HRMS (ESI) m/z: Calculated for $C_{13}H_{17}N0_3$ $[M+H]^+$: 236.1281, found: 236.1273.

Isopropyl 2-(methylamino)benzoate (5aa)

Obtained according to the ***General procedure B*** (0.2 mmol scale), to give **5aa** as a colorless oil (11.2 mg, 29% yield). Flash column chromatography (petroleum ether/ethyl acetate, 100:1); R_f 0.6 (petroleum ether/ethyl acetate, 10:1). Spectroscopic data are consistent with those previously reported.[27]



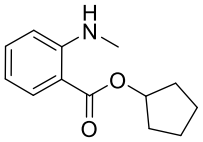
Chemical Formula: $C_{11}H_{15}NO_2$
Exact Mass: 193.11

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.91 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.69 (s, 1H), 7.40 – 7.35(m, 1H), 6.66 (d, *J* = 8.5 Hz, 1H), 6.62 – 6.51 (m, 1H), 5.19 (p, *J* = 6.2 Hz, 1H), 2.97 – 2.86 (m, 3H), 1.35 (d, *J* = 6.2 Hz, 6H).

^{13}C{H} NMR (101 MHz, $CDCl_3$) *δ* 168.4, 152.1, 134.6, 131.7, 114.3, 110.7, 110.6, 67.6, 29.7, 22.1.

Cyclopentyl 2-(methylamino)benzoate (5ai)

Obtained according to the ***General procedure B*** (0.2 mmol scale), to give **5ai** as a colorless oil (13.1 mg, 30% yield). Flash column chromatography (petroleum ether/ethyl acetate, 150:1); R_f 0.6 (petroleum ether/ethyl acetate, 10:1).



Chemical Formula: $C_{13}H_{17}NO_2$
Exact Mass: 219.1259

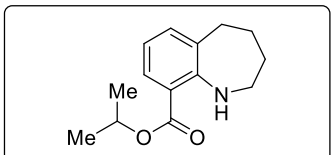
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.87 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.69 (s, 1H), 7.39 – 7.35 (m, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 6.60 – 6.56 (m, 1H), 5.36 – 5.31 (m, 1H), 2.90 (d, *J* = 3.4 Hz, 3H), 1.97 – 1.88 (m, 2H), 1.86 – 1.74 (m, 4H), 1.70 – 1.61 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 168.7, 152.1, 134.6, 131.7, 114.3, 110.8, 110.6, 77.1, 32.9, 29.7, 24.0.

HRMS (ESI) m/z: Calculated for $C_{13}H_{17}NO_2$ $[M+H]^+$: 220.1332, found: 220.1331.

Isopropyl 2,3,4,5-tetrahydro-1H-benzo[b]azepine-9-carboxylate (5fa)

Obtained according to the ***General procedure B*** (0.2 mmol scale), to give ***5fa*** as a yellow oil (42 mg, 90% yield). Flash column chromatography (petroleum ether/ethyl acetate, 150:1); R_f 0.8 (petroleum ether/ethyl acetate, 10:1).



Chemical Formula: $C_{14}H_{19}NO_2$
Exact Mass: 233.1416

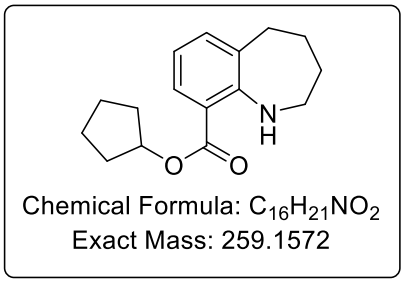
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.80 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.79 (s, 1H), 6.67 (t, *J* = 7.6 Hz, 1H), 5.25 – 5.15 (m, 1H), 3.30 – 3.14 (m, 2H), 2.91 – 2.77 (m, 2H), 1.87 – 1.78 (m, 2H), 1.78 – 1.71 (m, 2H), 1.35 (d, *J* = 6.3 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 168.5, 154.7, 135.7, 133.4, 129.4, 117.6, 115.4, 67.9, 46.9, 35.5, 30.5, 26.3, 22.1.

HRMS (ESI) m/z: Calculated for $C_{13}H_{17}NO_2$ $[M+H]^+$: 234.1489, found: 234.1483.

Cyclopentyl 2,3,4,5-tetrahydro-1H-benzo[b]azepine-9-carboxylate (5fi)

Obtained according to the ***General procedure B*** (0.2 mmol scale), to give ***5fi*** as a yellow oil (46 mg, 89% yield). Flash column chromatography (petroleum ether/ethyl acetate, 150:1); R_f 0.8 (petroleum ether/ethyl acetate, 10:1).



Chemical Formula: $C_{16}H_{21}NO_2$
Exact Mass: 259.1572

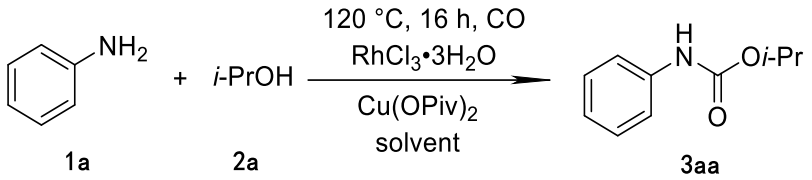
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77(s, 1H), 7.70 – 7.75 (d, 1H), 7.19 (d, J = 7.2 Hz, 1H), 6.66 (t, J = 7.6 Hz, 1H), 5.37 – 5.33 (m, 1H), 3.22 – 3.19 (m, 2H), 2.83 – 2.80 (m, 2H), 1.98 – 1.89 (m, 2H), 1.87 – 1.70 (m, 8H), 1.68 – 1.60 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.8, 154.6, 135.7, 133.4, 129.4, 117.6, 115.4, 77.4, 46.9, 35.5, 32.9, 30.5, 26.3, 24.0.

HRMS (ESI) m/z: Calculated for $C_{13}H_{17}NO_2$ $[M+H]^+$: 260.1645, found: 260.1640.

3.Optimization studies

Screening of solvents[a]

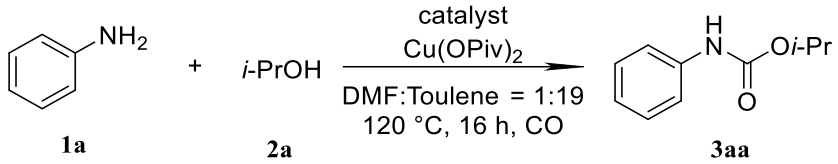


1a 2a 3aa

Entry	Solvent	Yield[b] (%)
1	toluene	84
2	mesitylene	69
3	anisole	58
4	1,4-dioxane	Trace
5	THF	Trace
6	DMF	51
7	*n*-hexane	Trace
8	CF_3Ph	79
9	DCE	ND
10	H_2O	NR
11	DMF:Anisole = 1:1	47
12	DMF:Toluene = 1:1	42
13	DMF:Anisole = 1:19	84
14	DMF:Toluene = 1:19	94
15	DMF:Toluene = 1:99	90
16	DMF:Toluene = 1:49	90

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (1 mmol, 5 equiv), $RhCl_3 \cdot 3H_2O$ (0.002 mmol, 1 mol%), $Cu(OPiv)_2$ (0.4 mmol, 2 equiv), solvent (2 mL), CO (1 atm) in a 25 mL sealed *J*-Young-tube, 16 h, 120 °C. [b]Isolated yield.

Screening of catalysts[a]

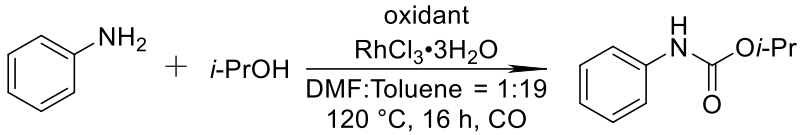


1a **2a** **3aa**

Entry	catalyst	Yield[b] (%)
1	$RhCl_3 \cdot 3H_2O$	94
2	$RhCl_3$	63
3	$[RhCp^*Cl_2]_2$	40
4	$[Rh(OAc)_2]_2$	91
5	$[Rh(CO)_2Cl]_2$	88
6	$[Rh(COD)Cl]_2$	97
7	$Pd(OAc)_2$	Trace
8	$PdCl_2$	84
9	$Pd_2(dba)_3$	Trace

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (1 mmol, 5 equiv), catalyst (0.002 mmol, 1 mol%), $Cu(OPiv)_2$ (0.4 mmol, 2 equiv), DMF/toluene (1/19, 2.0 mL), CO (1 atm) in a 25 mL sealed *J*-Young-tube, 16 h, 120 °C. [b]Isolated yield.

Screening of oxidant[a]

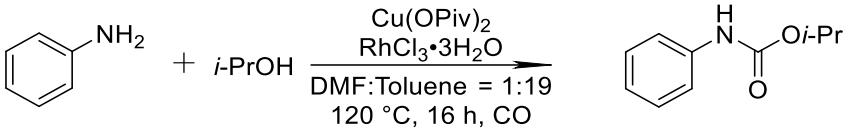


1a 2a 3aa

Entry	Oxidant	Yield[b] (%)
1	$Cu(OAc)_2$	87
2	$Cu(EtO_2)_2$	76
3	$Cu(TFA)_2 \cdot NH_2O$	trace
4	$Cu(OPiv)_2$	94
5	AgOAc	trace
6	AgOTFA	N.D.
7	AgOPiv	trace
8	Oxone	N.D.
9	BQ	N.D.
10	$K_2S_2O_8$	N.D.
11	Ag_2CO_3	N.D.
12	CuBr	Trace
13	$CuBr_2$	N.D.
14	Ag_2O	N.D.
15	$PhI(OAc)_2$	N.D.
16	(*t*-BuO)$_2$	N.D.
17	*t*-BuOOH	N.D.
18	V(CO): $V(O_2)$ = 3:1	N.D.
19	V(CO): ($V(O_2)$ = 1:1	N.D.
20[c]	V(CO): $V(O_2)$ = 3:1	Trace
21[c]	V(CO): ($V(O_2)$ = 1:1	N.D.

[a]Reaction conditions:**1a** (0.2 mmol, 1 equiv), **2a** (1 mmol, 5 equiv), $RhCl_3 \cdot 3H_2O$ (0.002 mmol, 1 mol%), oxidant (0.4 mmol, 2 equiv), DMF/toluene (1/19, 2.0 mL), CO (1 atm) in a 25 mL sealed *J*-Young-tube, 16 h, 120 °C. [b]Isolated yield. [c]$Cu(OPiv)_2$ (10 mol%) was added.

Screening of the concentration of oxidant[a]

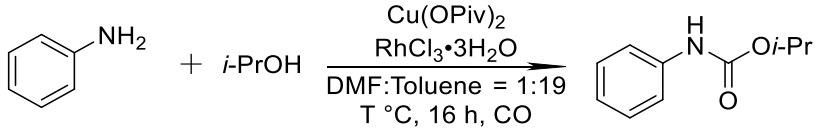


1a **2a** **3aa**

Entry	$Cu(OPiv)_2$ (x equiv)	Yield[b] (%)
1	1	55
2	1.2	74
3	1.5	81
4	2	94

[a]Reaction conditions:**1a** (0.2 mmol, 1 equiv), **2a** (1 mmol, 5 equiv), $RhCl_3 \cdot 3H_2O$ (0.002 mmol, 1 mol%), $Cu(OPiv)_2$ (x equiv), DMF/toluene (1/19, 2.0 mL), CO (1 atm) in a 25 mL sealed *J*-Young-tube, 16 h, 120 °C. [b]Isolated yield.

Screening of the reaction temperature[a]



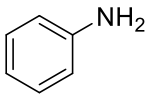
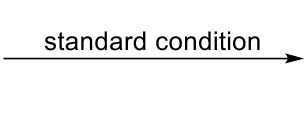
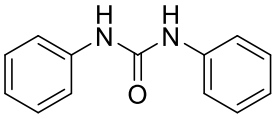
1a **2a** **3aa**

Entry	Temperature (°C)	Yield[b] (%)
1	100	41
2	110	72
3	120	94
4	130	94
5	140	88

[a]Reaction conditions:**1a** (0.2 mmol, 1 equiv), **2a** (1 mmol, 5equiv), $RhCl_3 \cdot 3H_2O$ (0.002 mmol, 1 mol%), $Cu(OPiv)_2$ (0.4 mmol, 2 equiv), DMF/toluene (1/19, 2.0 mL), CO (1 atm) in a 25 mL sealed *J*-Young-tube, 16 h, T °C. [b]Isolated yield.

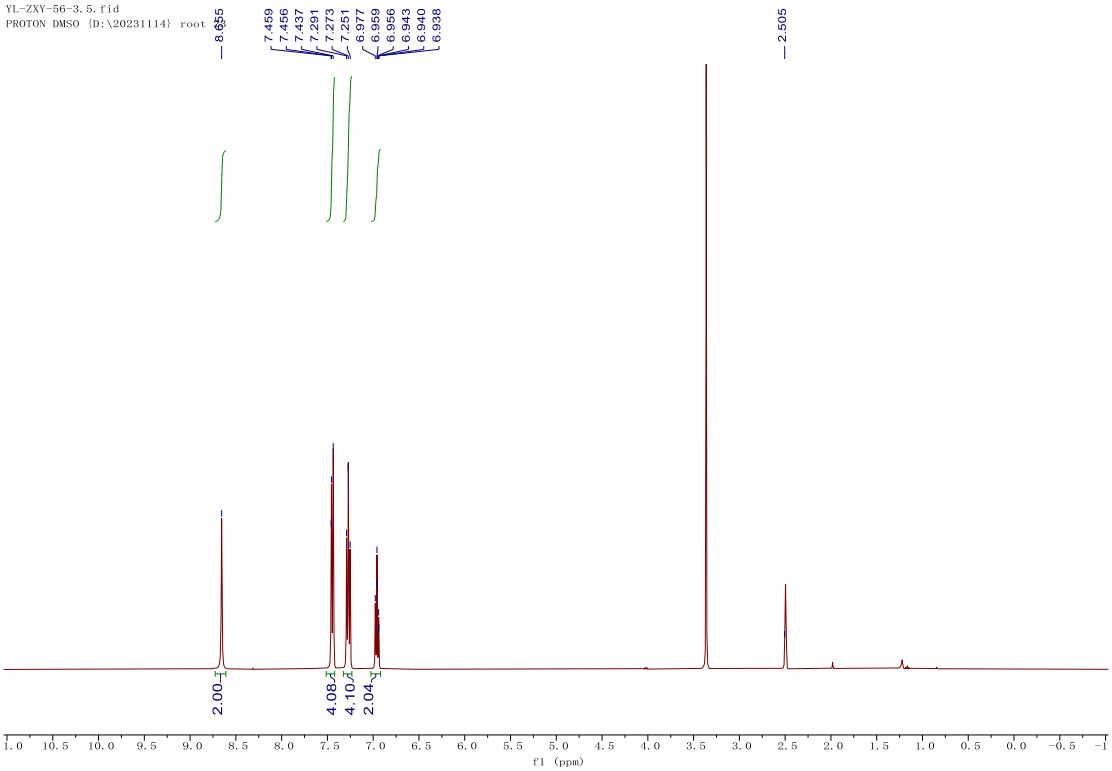
4. Preliminary mechanistic studies

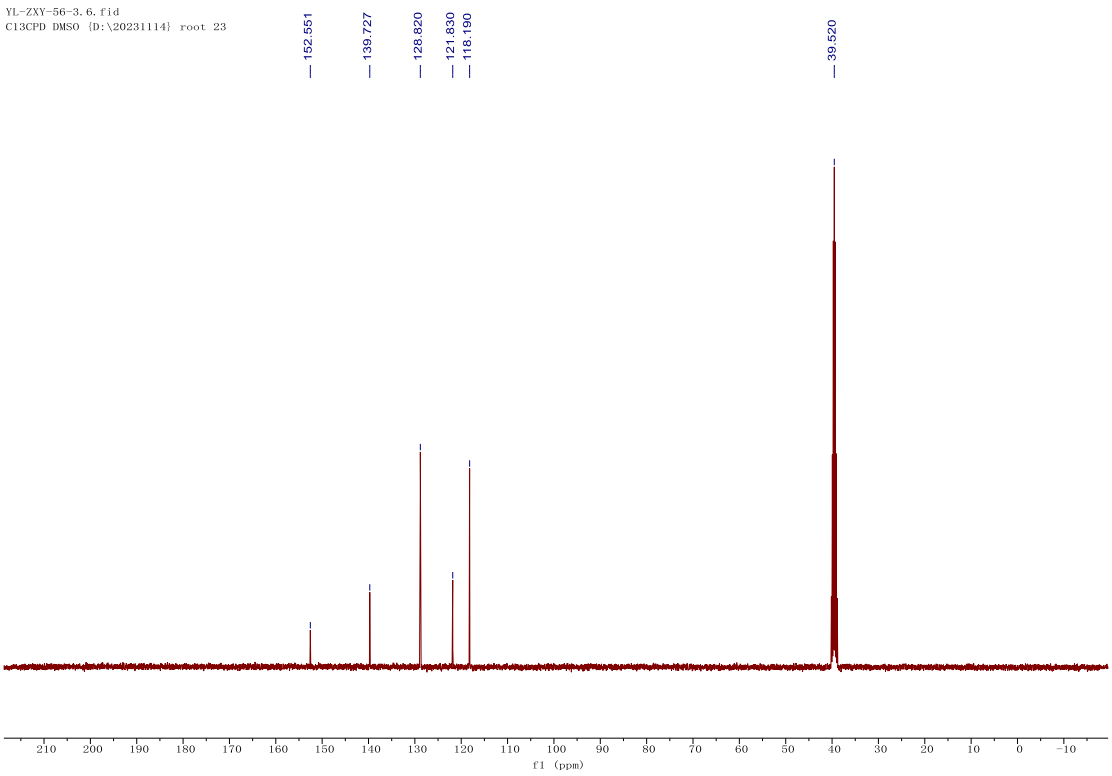
Control experiment to elucidate possible reaction intermediate

(1)  + CO  

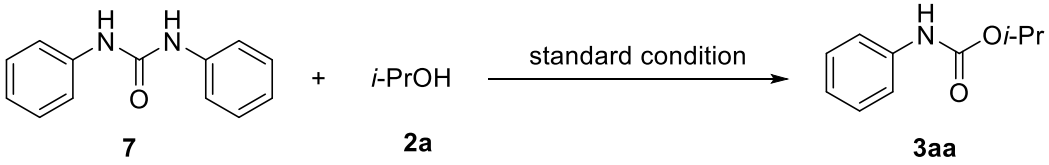
1a **7**

In a glovebox, $RhCl_3 \cdot 3H_2O$ (0.01 equiv), $Cu(OPiv)_2$ (2 equiv), were successively weighed into a dry 50 mL *J*-Young tube equipped with a magnetic stir bar. The *J*-Young tube was sealed and taken out of the glovebox. **1a** (0.8 mmol, 1 equiv), dry toluene/dry DMF (19/1, *v*/*v*, 8 mL) were added under nitrogen. The reaction mixture was then degassed by three freeze-pump-thaw cycles, backfilled with CO and heated at 120 °C for 16 h. The reaction mixture was then cooled to room temperature. The solvent was evaporated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel using EtOAc–petroleum ether mixture as an eluent to afford **7** (40.7mg, 48% yield) as a yellow solid. **^{1}H NMR (400 MHz, DMSO) *δ*** 8.66 (s, 2H), 7.51 – 7.42 (m, 4H), 7.33 – 7.23 (m, 4H), 7.02 – 6.92 (m, 2H). **^{13}C{^{1}H} NMR (101 MHz, DMSO) *δ*** 152.6, 139.7, 128.8, 121.8, 118.2. Spectroscopic data are consistent with those previously reported.[28]





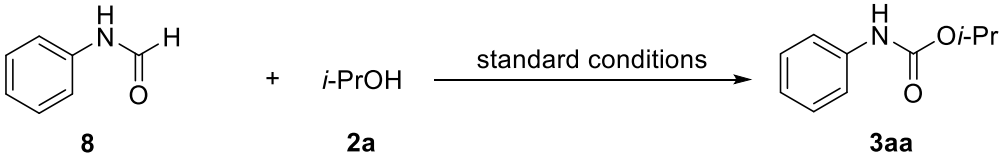
(2)



7 **2a** **3aa**

In a glovebox, $RhCl_3 \cdot 3H_2O$ (0.01 equiv), $Cu(OPiv)_2$ (2 equiv), were successively weighed into a dry 25 mL *J*-Young tube equipped with a magnetic stir bar. The *J*-Young tube was sealed and taken out of the glovebox. **7** (0.2 mmol, 1 equiv), **2a** (5 equiv), dry toluene (1.9 mL) and dry DMF (0.1 mL) were added under nitrogen. The reaction mixture was then degassed by three freeze-pump-thaw cycles, backfilled with CO and heated at 120 °C for 16h. Then, the reaction mixture was cooled to room temperature. The solvent was evaporated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel using EtOAc–petroleum ether mixture as an eluent to afford the desired compound **3aa** (30.4 mg, 85% yield).

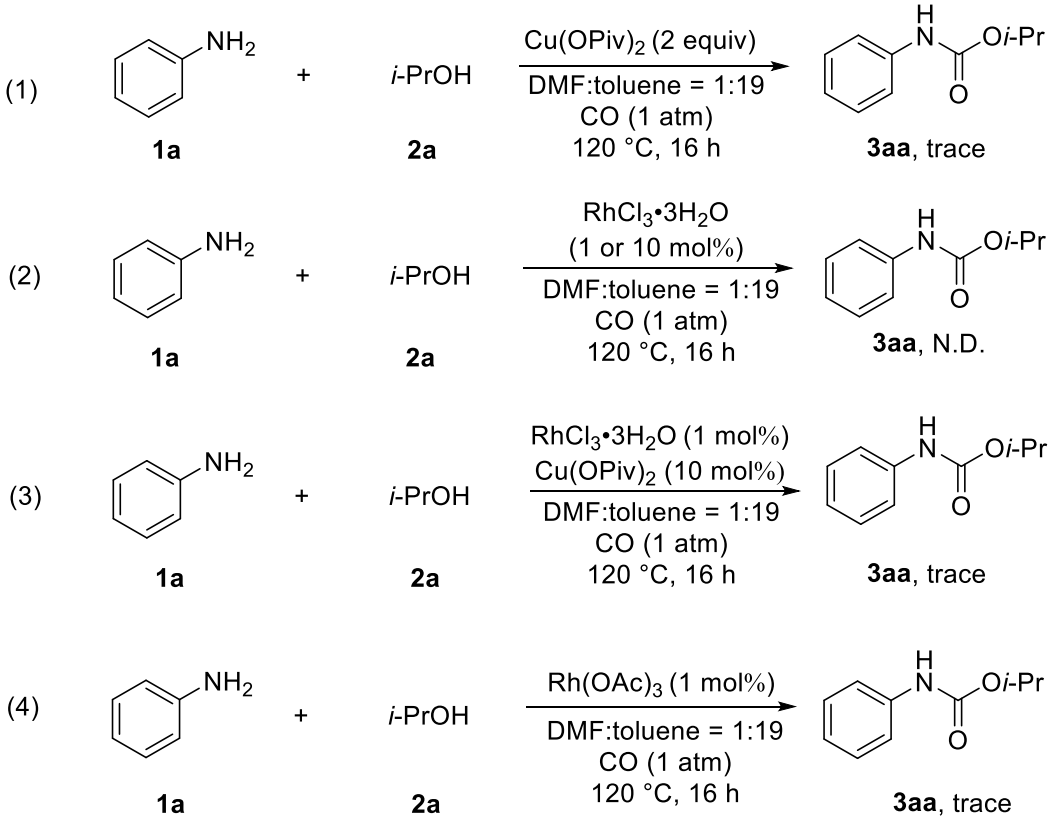
(3)



8 **2a** **3aa**

In a glovebox, $RhCl_3 \cdot 3H_2O$ (0.01 equiv), $Cu(OPiv)_2$ (2 equiv), were successively weighed into a dry 25 mL *J*-Young tube equipped with a magnetic stir bar. The *J*-Young tube was sealed and taken out of the glovebox. **8** (0.2 mmol, 1 equiv), **2a** (5 equiv), dry toluene (1.9 mL) and dry DMF (0.1 mL) were added under nitrogen. The reaction mixture was then degassed by three freeze-pump-thaw cycles, backfilled with CO and heated at 120 °C for 16 h. Then, the reaction mixture was cooled to room temperature. The solvent was evaporated under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel using EtOAc–petroleum ether mixture as an eluent to afford the desired compound **3aa** (6.8mg, 19% yield).

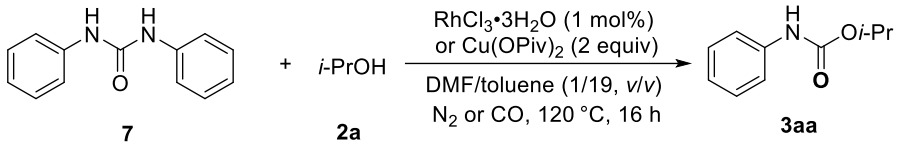
More control experiments to get insights into the effect of copper or rhodium salts



In a glovebox, [Rh] (X equiv) or/and $Cu(OPiv)_2$ (Y equiv), were successively weighed into a dry 25 mL *J*-Young tube equipped with a magnetic stir bar. The *J*-Young tube was sealed and taken out of the glovebox. **1a** (0.2 mmol, 1 equiv), **2a** (5 equiv), dry toluene (1.9 mL) and dry DMF (0.1 mL) were added under nitrogen. The reaction mixture was

then degassed by three freeze-pump-thaw cycles, backfilled with CO and heated at 120 °C for 16 h. Then, the reaction mixture was cooled to room temperature and analyzed by GC-MS and TLC.

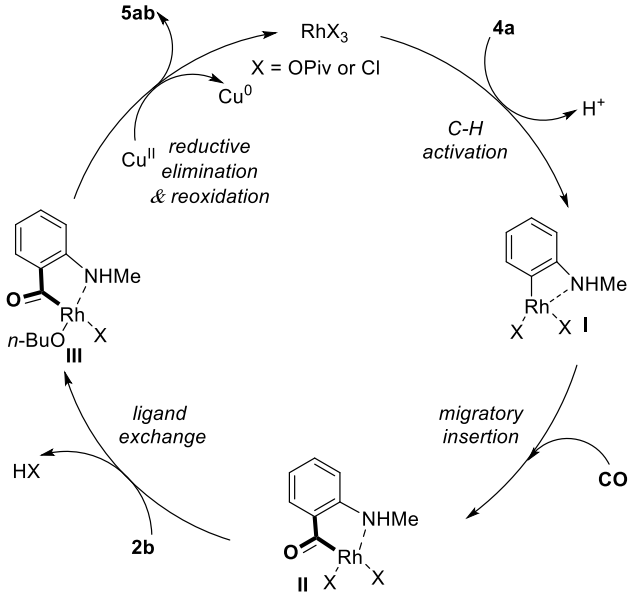
More control experiments to get insights into the formation of 3aa from 7 and 2a



Entry[a]	N_2	CO	$RhCl_3 \cdot 3H_2O$	$Cu(OPiv)_2$	Yield[b] of **3aa**
1	/	√	√	√	90%
2	/	√	√	/	14%
3	/	√	/	√	68%
4	/	√	/	/	13%
5	√	/	√	√	56%
6	√	/	√	/	16%
7	√	/	/	√	71%
8	√	/	/	/	15%

[a]Reaction conditions: **7** (0.2 mmol), **2a** (5 equiv), $Cu(OPiv)_2$ (0 or 2 equiv), $RhCl_3 \cdot 3H_2O$ (0 or 1 mol%), DMF/toluene (1/19, 2.0 mL), CO (1 atm) or N_2 in 25 mL sealed *J*-Young tube at 120 °C for 16 h. [b]Yield determined by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard

Plausible reaction mechanism for C–H alkoxycarbonylation



5. References

[1] Y. Gu, A. Miura, M. Tamura, Y. Nakagawa and K. Tomishige, Highly Efficient Synthesis of Alkyl *N*-Arylcarbamates from CO_2, Anilines, and Branched Alcohols with a Catalyst System of CeO_2 and 2-Cyanopyridine. *ACS Sustainable Chem. Eng.* 2019*,* **7***,* 16795−16802

[2] M. Usman, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, Copper-catalyzed Carbonylation of Anilines by Diisopropyl Azodicarboxylate for the Synthesis of Carbamates. *RSC Adv*. 2016, **6**, 107542–107546.

[3] N. Uhlig and C.-J. Li, Aniline Carbamates: A Versatile and Removable Motif for Palladium-Catalyzed Directed C–H Activation. *Chem. Eur. J.* 2014*,* **20***,* 12066–12070.

[4] G. C. Finger, D. R. Dickerson, D. E. Orlopp and. W. Ehrmantraut, Aromatic Fluorine Compounds. XII. *N*-(Fluorophenyl) Carbamates. *J. Med. Chem.* 1964, **7**, 572–573.

[5] D. Murzin and V. Kolesova, Synthesis of Intermediate Compounds with P-N Bond from (Thio)Carbamates and Chlorodioxaphospholanes and -Phosphorinanes and Their Reactivity. *Eur. J. Chem.* 2013, **4**, 336–342.

[6] P. C.Kearney, Influence of Physicochemical Properties on Biodegradability of Phenylcarbamate Herbicides. *J. Agr. Food Chem*. 1967, **15**, 568–571.

[7] Y. Jiang, B. Li, N. Ma, S. Shu, Y. Chen, S. Yang, Z. Huang, D. Shi and. Zhao, Photoredox-Catalyst-Enabled *para*-Selective Trifluoromethylation of *tert*-Butyl Arylcarbamates. *Angew. Chem. Int. Ed*. 2021, **60**, 19030–19034.

[8] N. V.;Reddy, K. R. Prasad, P. S. Reddy, M. L. Kantam and K. R. Reddy, Metal Free Oxidative Coupling of Aryl Formamides with Alcohols for the Synthesis of Carbamates. *Org. Biomol. Chem.* 2014, **12**, 2172–2175.

[9] Z.-H. Guan, H. Lei, M. Chen, Z.-H. Ren, Y. Bai and Y.-Y. Wang, Palladium-Catalyzed Carbonylation of Amines: Switchable Approaches to Carbamates and *N,N'*-Disubstituted Ureas. *Adv. Synth. Catal.* 2012, **354**, 489–496.

[10] Z. Shao, F. Wang, J. Shi, L. Ma and Z. Li, Synergetic Copper/TEMPO-Catalysed Benzylic C–H Imidation with *N*-Fluorobenzenesulfonimide at room Temperature and Tandem Conversions with Alcohols or Arenes. *Org. Chem. Front*. 2021, **8**, 3298–3307.

[11] N. Egger, L. Hoesch and A. S. Dreiding, Azimine. VII. Preparation by oxidation of triazanes. *Helv. Chim. Acta.* 1983, **66**, 1599–1607.

[12] X. Zhang and H. Jing, A Facile One-Pot Phosgene-Free Synthesis of Naphthalen-1-ylcarbamates by Selenium-Catalyzed Carbonylation of 1-Nitronaphthalene with Carbon Monoxide. *J. Mol. Catal. A-Chem.* 2009, **302**, 137–141.

[13] D. L. Boger, B. E. Fink and M. P. Hedrick, Chemical Total Synthesis of Distamycin A and 2640 Analogues: A Solution-Phase Combinatorial Approach to the Discovery of New, Bioactive DNA Binding Agents and Development of a Rapid, High-Throughput Screen for Determining Relative DNA Binding Affinity or DNA Binding Sequence Selectivity. *J. Am. Chem. Soc.* 2000, **122**, 6382–6639.

[14] Z. G. Hajos, D. R. Parrish and M. W. Goldberg, Synthesis and Stereochemistry of Hydrophenanthrenes. III. The Reaction of 1,3-Dicyclohexyl-1-(1,2,3,9,10,10*aβ*-hexahydro-7-methoxy-2α-phenanthrylc arbonyl)urea with Sodium Alkoxides. *J. Org. Chem.* 1965, **30**, 2849–2851.

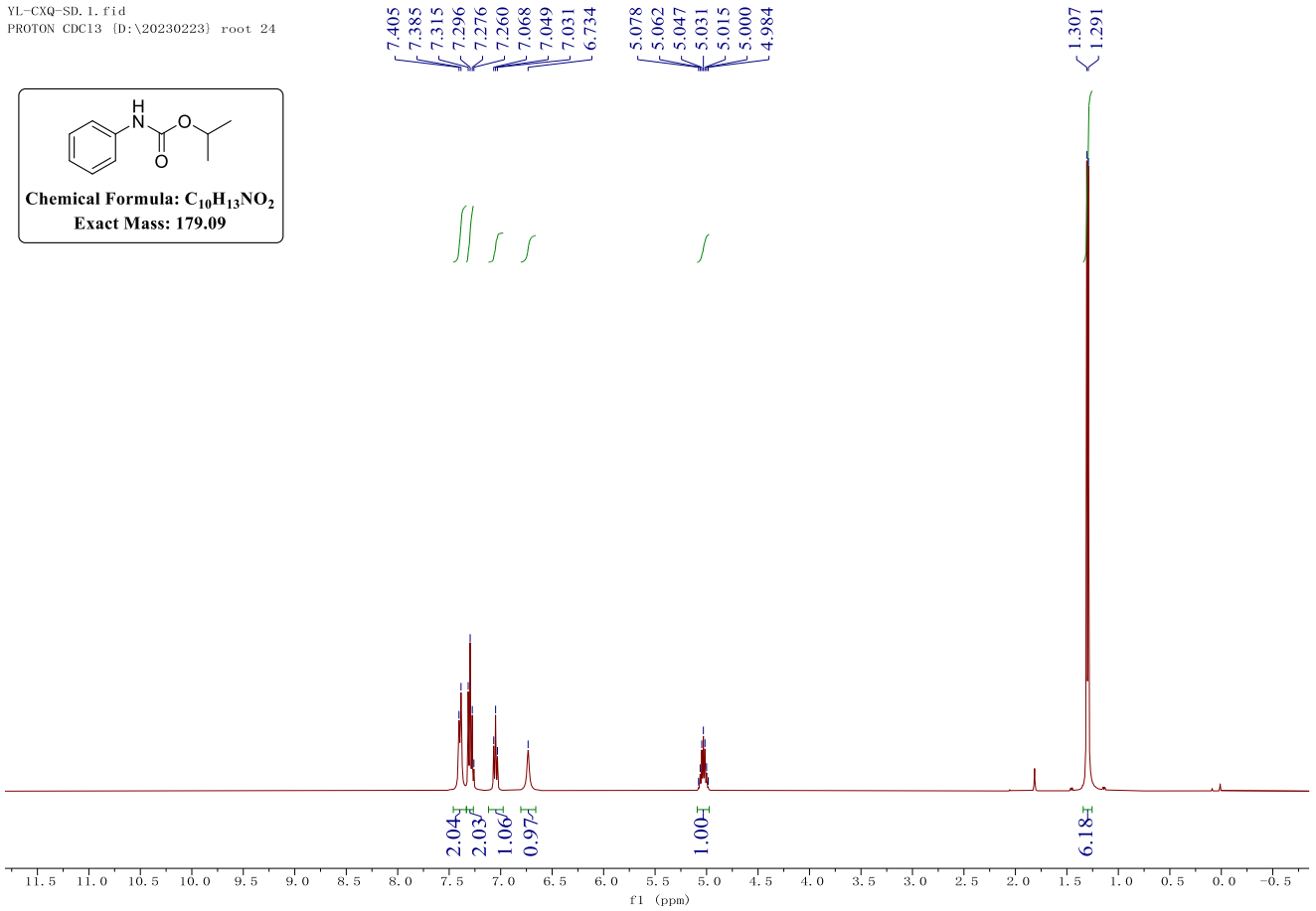
[15] M. I. Ogbu, D. M. Bassani, F. Robert and Y. Landais, Photocatalyzed Decarboxylation of Oxamic Acids under Near-Infrared Conditions. *Chem. Commun.* 2022, **58**, 8802–8805.

[16] Q. Zhang, H.-Y. Yuan, N. Fukaya, H. Yasuda and J.-C. Choi, A Simple Zinc Catalyst for Carbamate Synthesis Directly from CO_2. *ChemSusChem* 2017, **10**, 1501–1508.

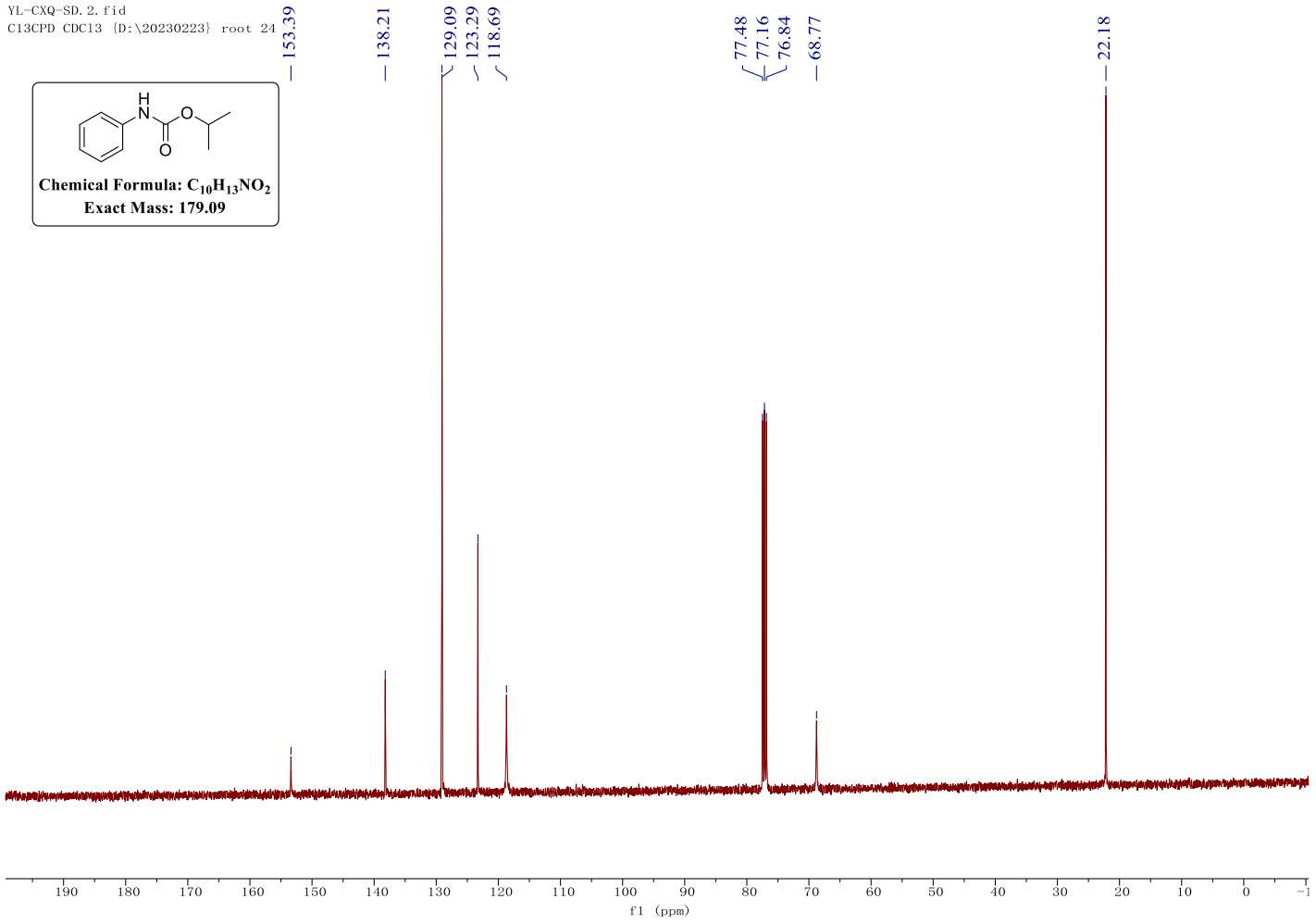
[17] M. Shimizu and M. Sodeoka, Convenient Method for the Preparation of Carbamates, Carbonates, and Thiocarbonates. *Org. Lett.* 2007, **9**, 5231–5234.
[18] J. R. Alexander and M. J. Cook, Formation of Ketenimines via the Palladium-Catalyzed Decarboxylative *π*-Allylic Rearrangement of *N*-Alloc Ynamides. *Org.Lett*. 2017, **19**, 5822–5825.
[19] Y. Matsumura, Y. Satoh, O. Onomura and T. Maki, A New Method for Synthesis of Unsymmetrical Ureas Using Electrochemically Prepared Trifluoroethyl Carbamates. *J. Org. Chem.* 2000, **65**, 1549–1551.
[20] T. Isobe and T. Ishikawa, 2-Chloro-1,3-Dimethylimidazolinium Chloride. 3. Utility for Chlorination, Oxidation, Reduction, and Rearrangement Reactions. *J. Org. Chem.* 1999, **64**, 5832–5835.
[21] N. V. Reddy, K. R. Prasad, P. S. Reddy, M. L. Kantam and K. R. Reddy, Metal Free Oxidative Coupling of Aryl Formamides with Alcohols for the Synthesis of Carbamates. *Org. Biomol. Chem.* 2014, **12**, 2172–2175.
[22] M. Hatano. S. Kamiya, K. Moriyama and K. Ishihara, Lanthanum(III) Isopropoxide Catalyzed Chemoselective Transesterification of Dimethyl Carbonate and Methyl Carbamates. *Org. Lett.* 2011, **13***,* 430–433.
[23] A. R. Sardarian, M. Zangiabadi and I. D. Inaloo, Fe_3O_4@SiO_2/Schiff Base/Pd Complex as an Efficient Heterogeneous and Recyclable Nanocatalyst for Chemoselective *N*-Arylation of *O*-Alkyl Primary Carbamates. *RSC Adv.* 2016, **6**, 92057–92064.
[24] B. Das, A. Dahiya, A. K. Sahoo and B. K. Patel, Transformable Transient Directing Group-Assisted C(sp^2)–H Activation: Synthesis and Late-Stage Functionalizations of *o*-Alkenylanilines. *J. Org. Chem.* 2022, **87**, 13383–13388.
[25] W. H. Pirkle and J. R.Hauske, Trichlorosilane-Induced Cleavage. A Mild Method for Retrieving Carbinols from Carbamates. *J. Org. Chem*. 1977, **42**, 2781–2782.
[26] J. Bruffaerts, N. von Wolff, Y. Diskin-Posner, Y. Ben-David and D. Milstein, Formamides as Isocyanate Surrogates: A Mechanistically Driven Approach to the Development of Atom-Efficient, Selective Catalytic Syntheses of Ureas, Carbamates, and Heterocycles. *J. Am. Chem. Soc*. 2019, **141**, 16486–16493.
[27] M. Chen, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, Palladium-Catalyzed Oxidative Carbonylation of Aromatic C–H Bonds of *N*-Alkylanilines with CO and Alcohols for the Synthesis of *o*-Aminobenzoates. *J. Org. Chem*. 2015, **80**, 1258–1263.
[28] K. Mao, L. Lv and Z.Li, Amine-Induced Selective C–C Bond Cleavage of 2,2,2-Trifluoroethyl Carbonyls for the Synthesis of Ureas and Amides. *J. Org. Chem*. 2023, **88**, 10137–10146.

6. NMR spectra

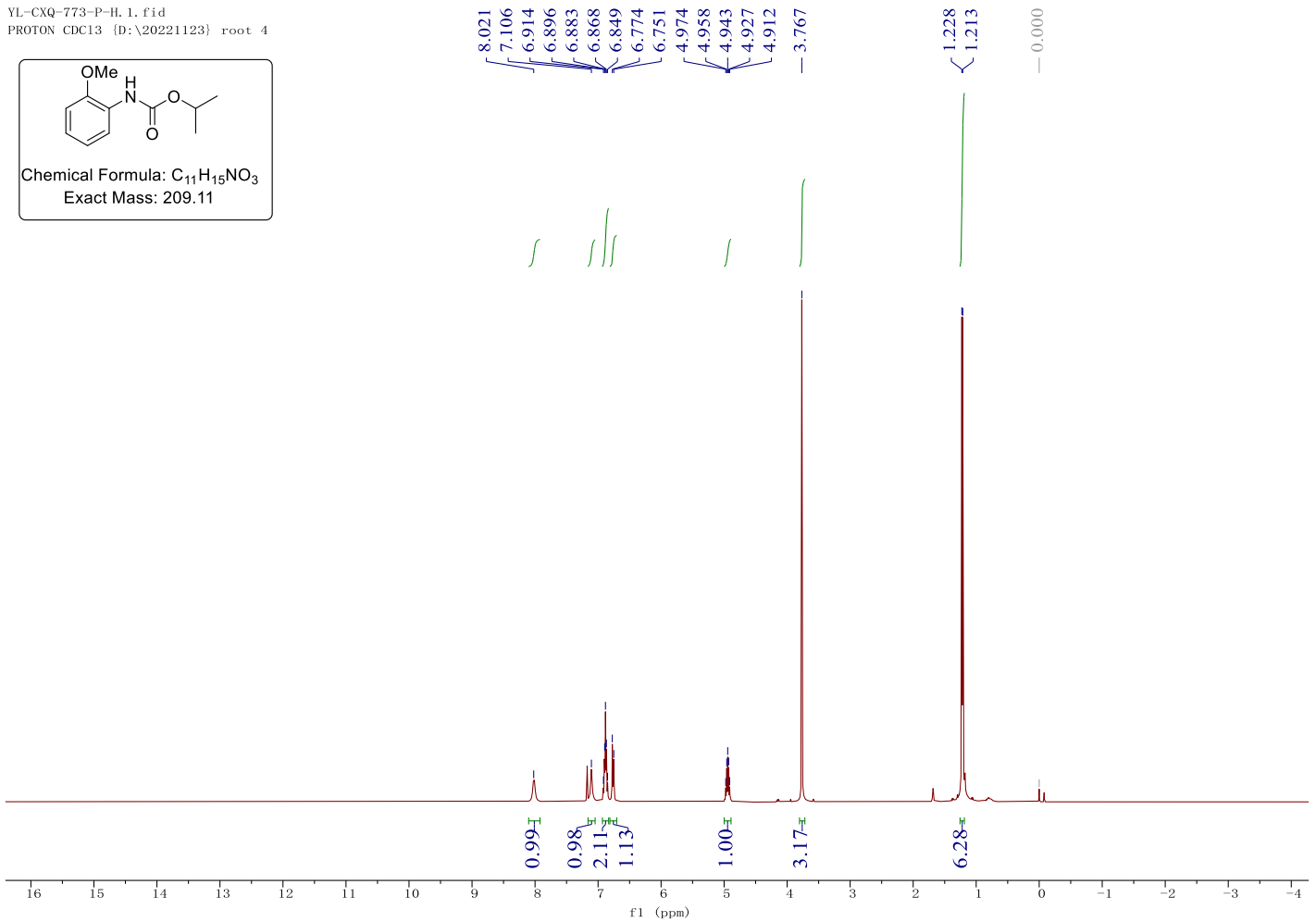
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aa.**



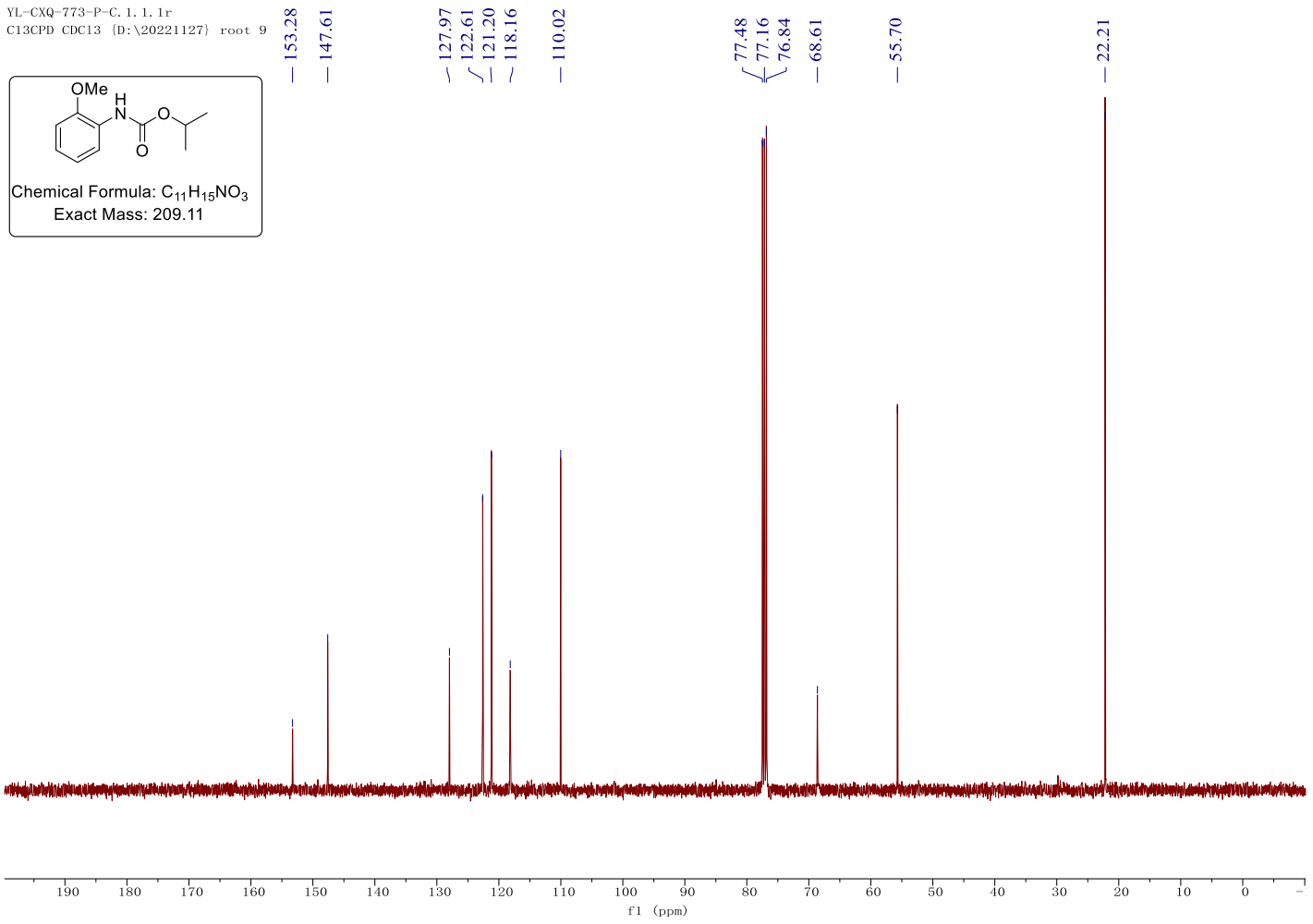
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3aa.**



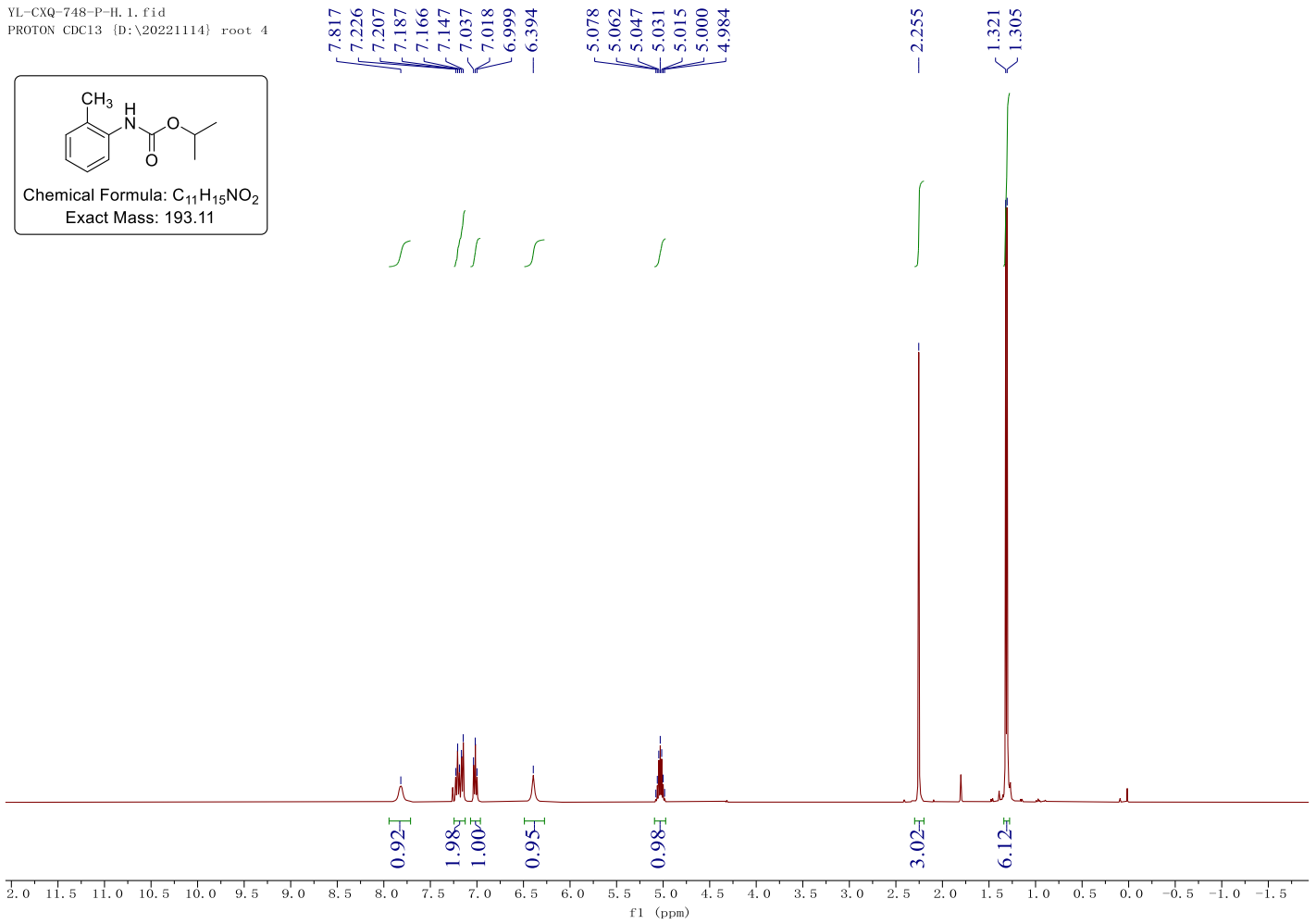
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ba.**



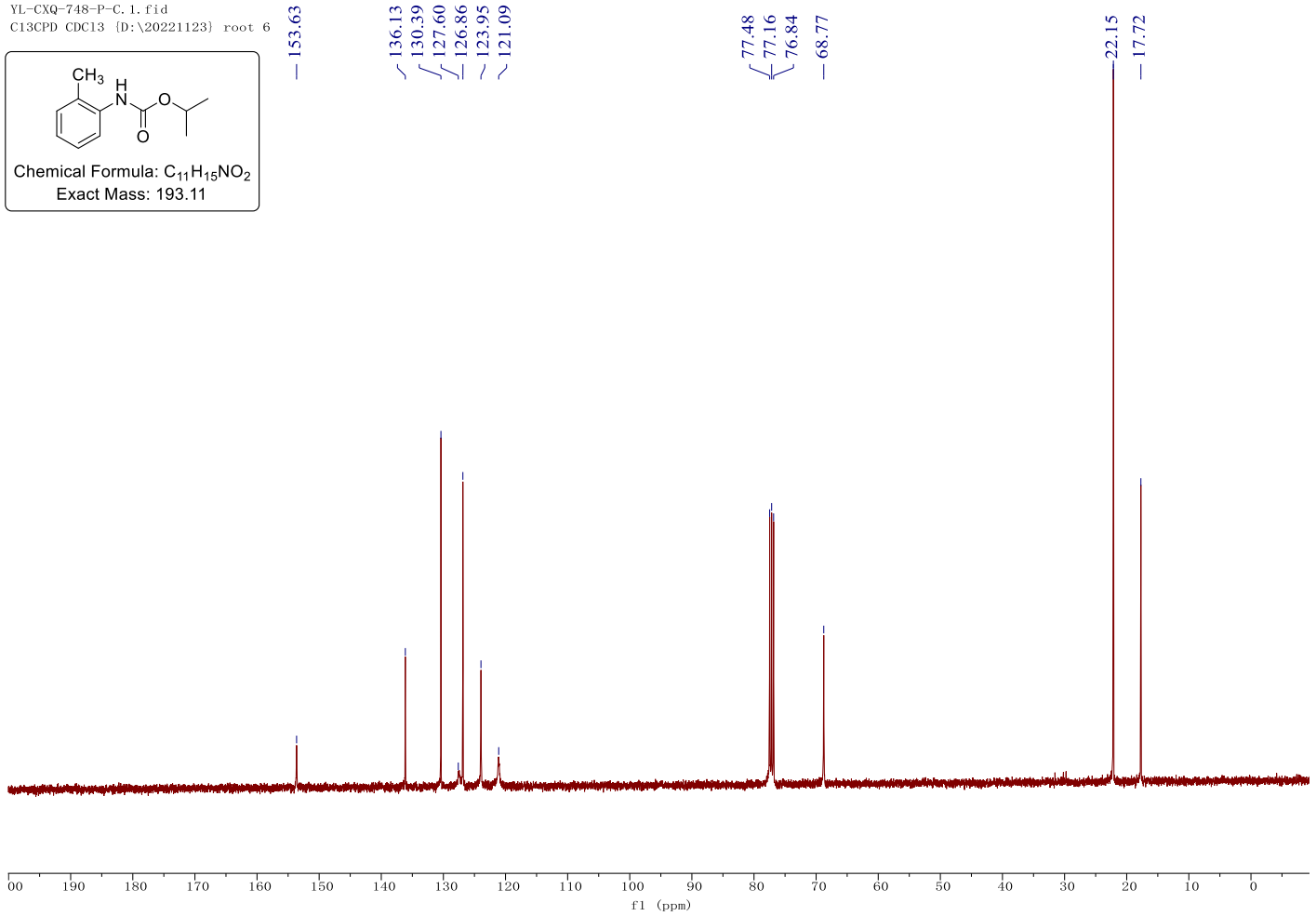
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ba.**



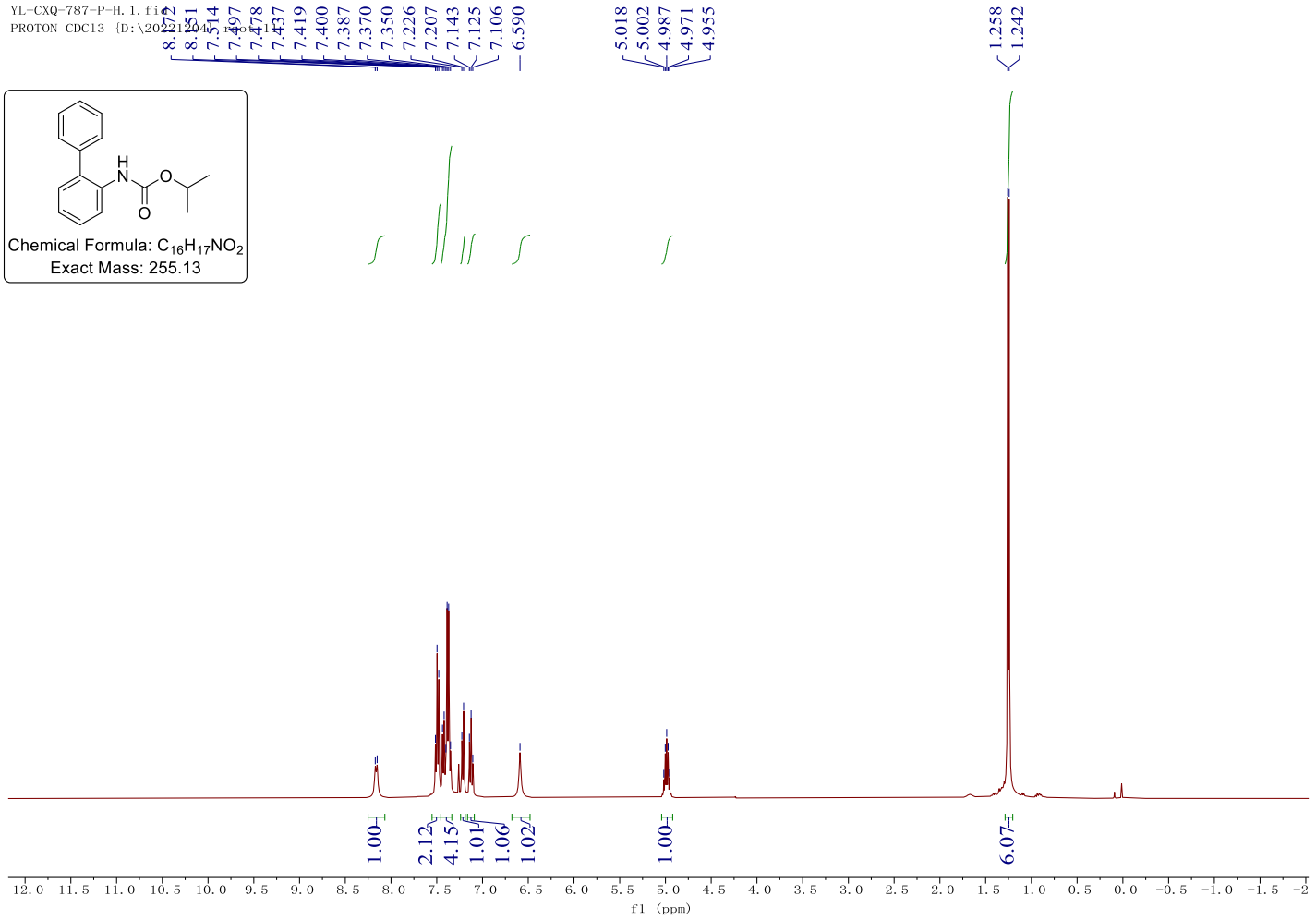
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ca.**



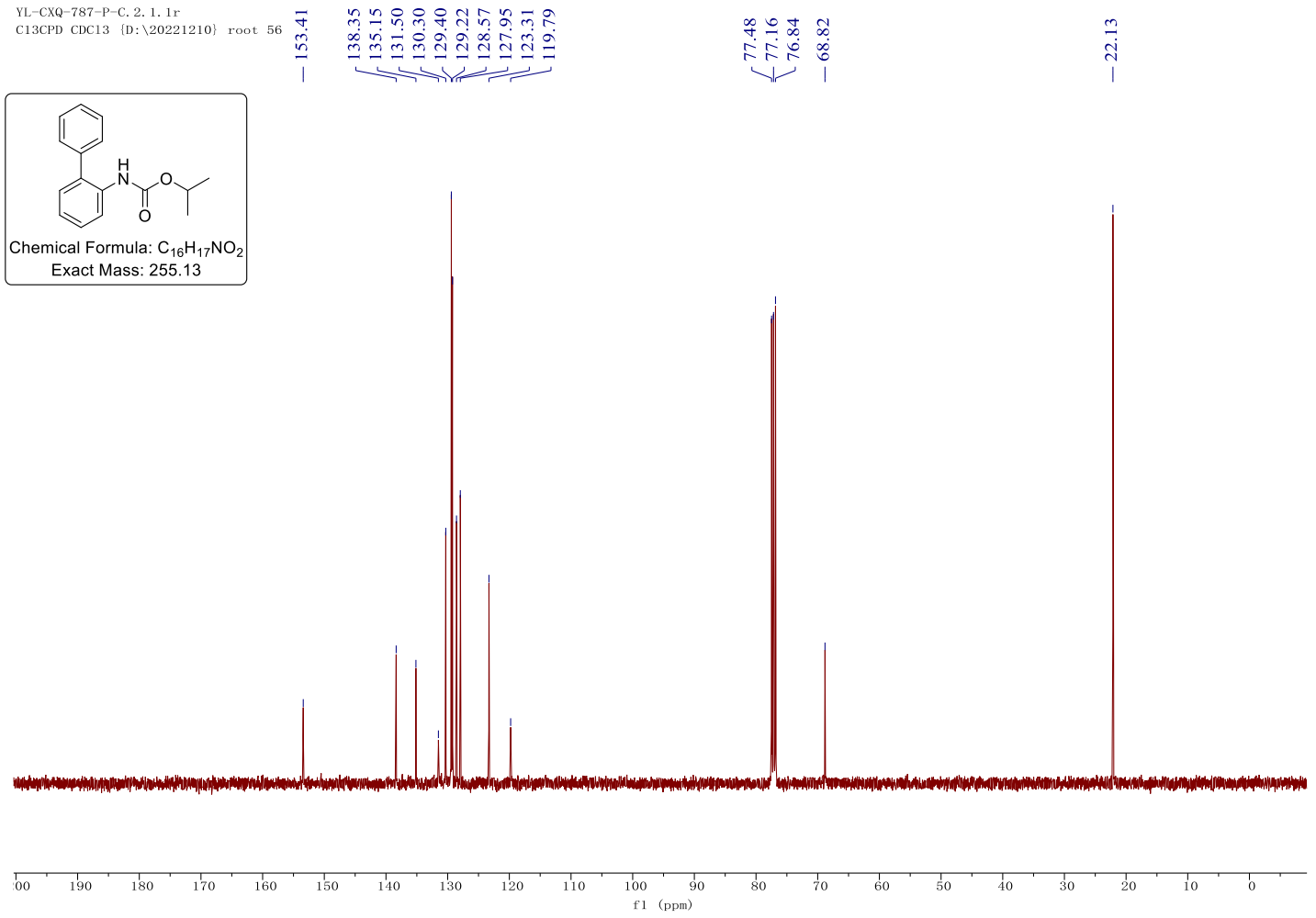
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of compound **3ca.**



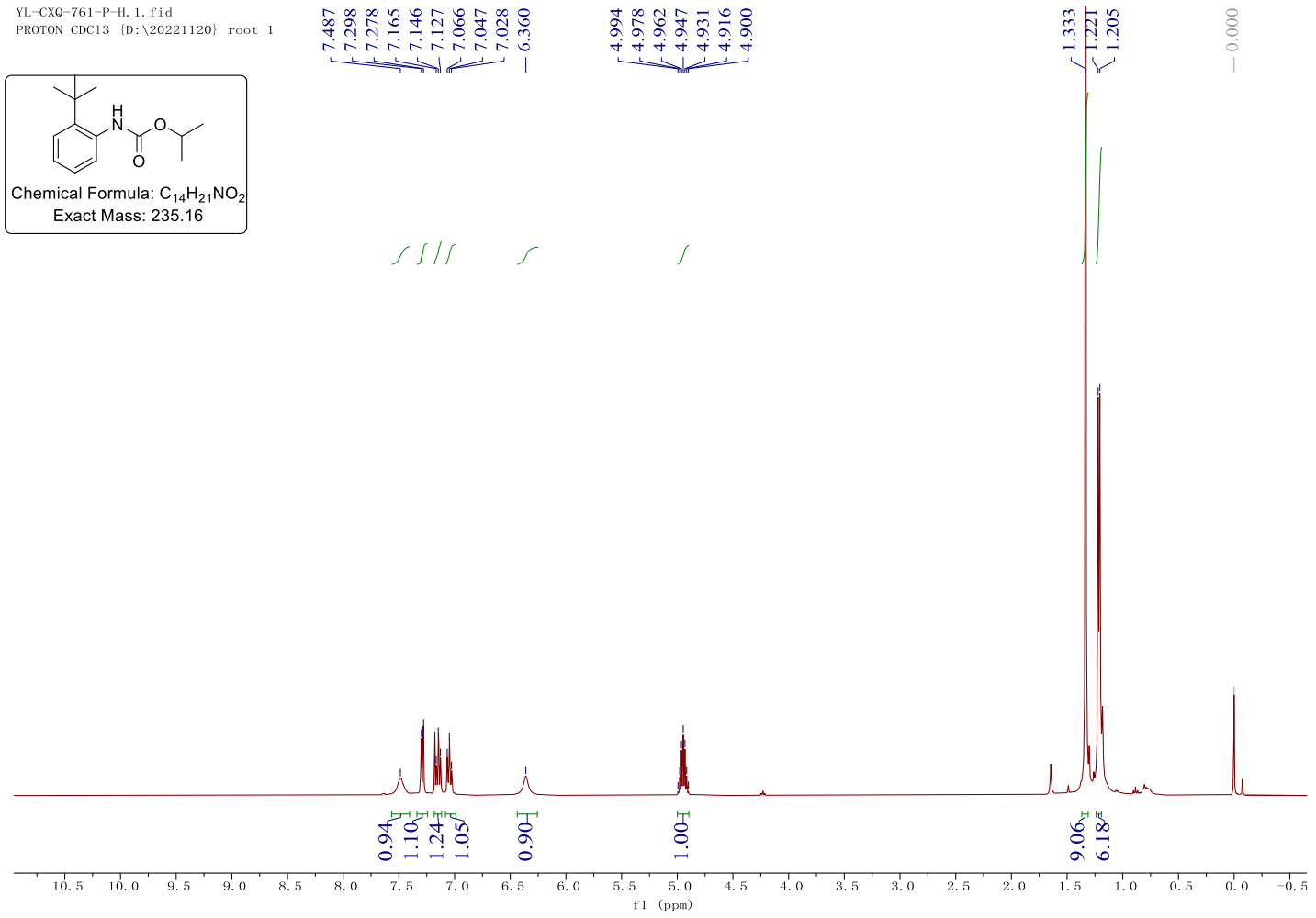
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3da.**



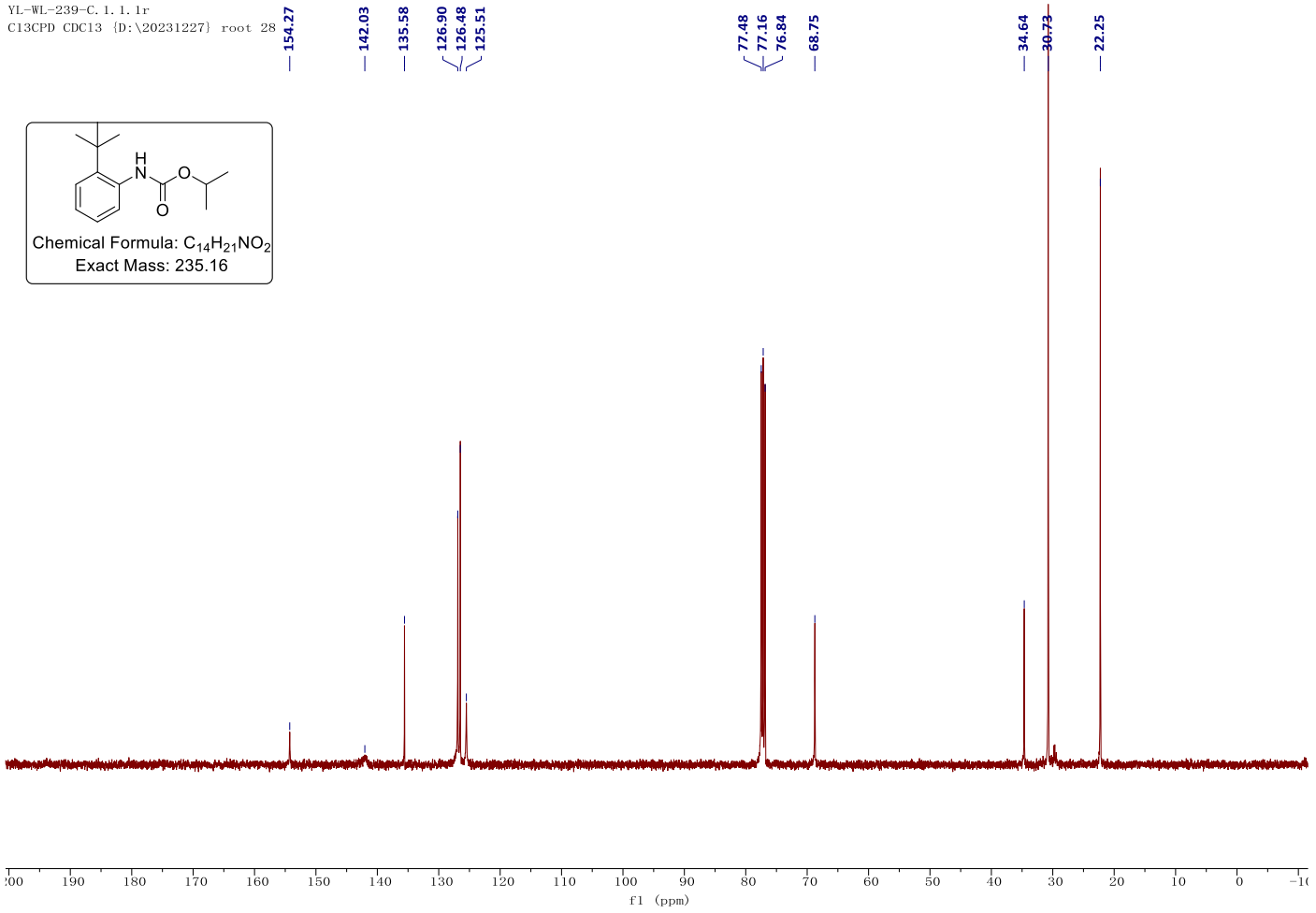
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of compound **3da.**



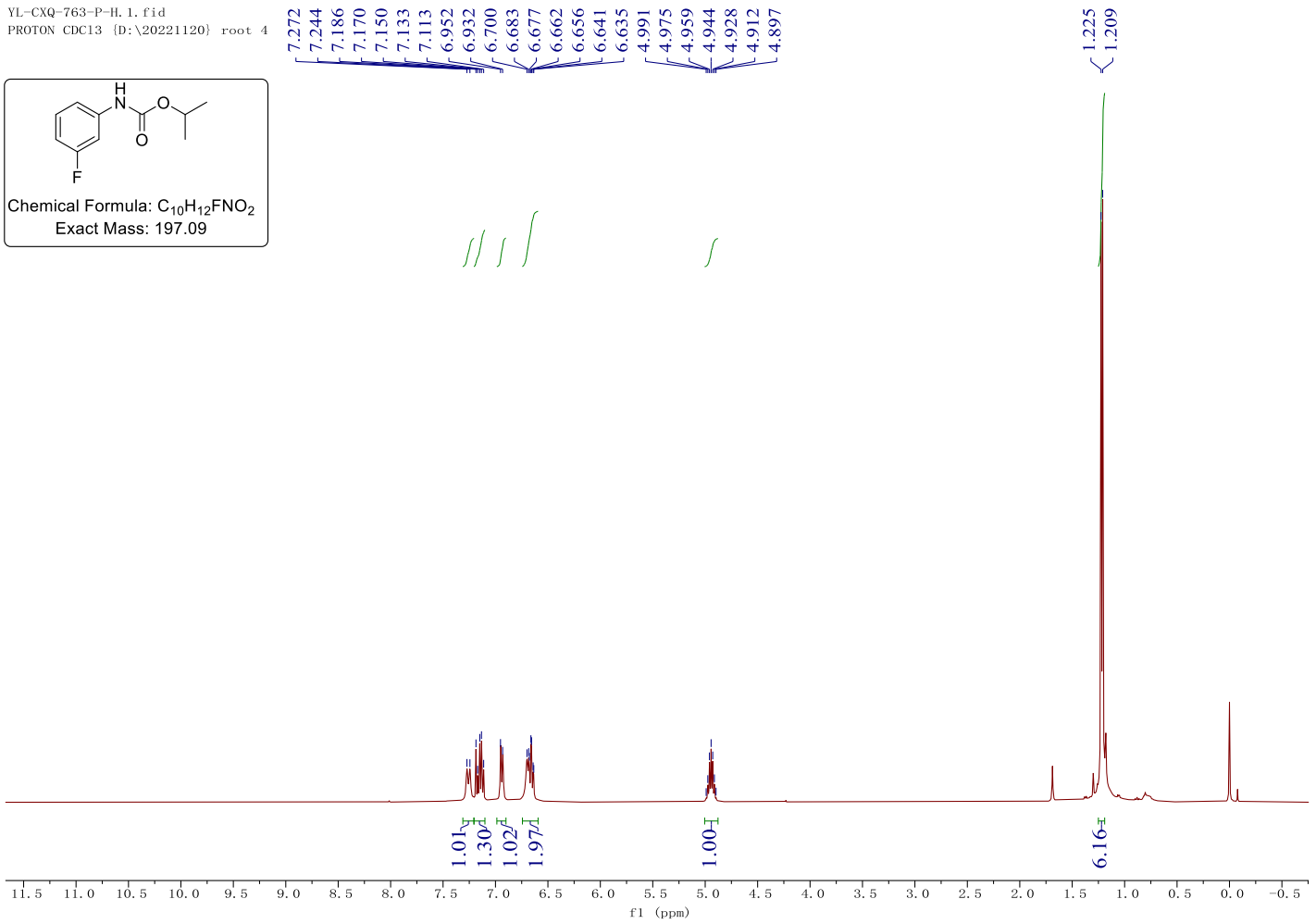
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ea.**



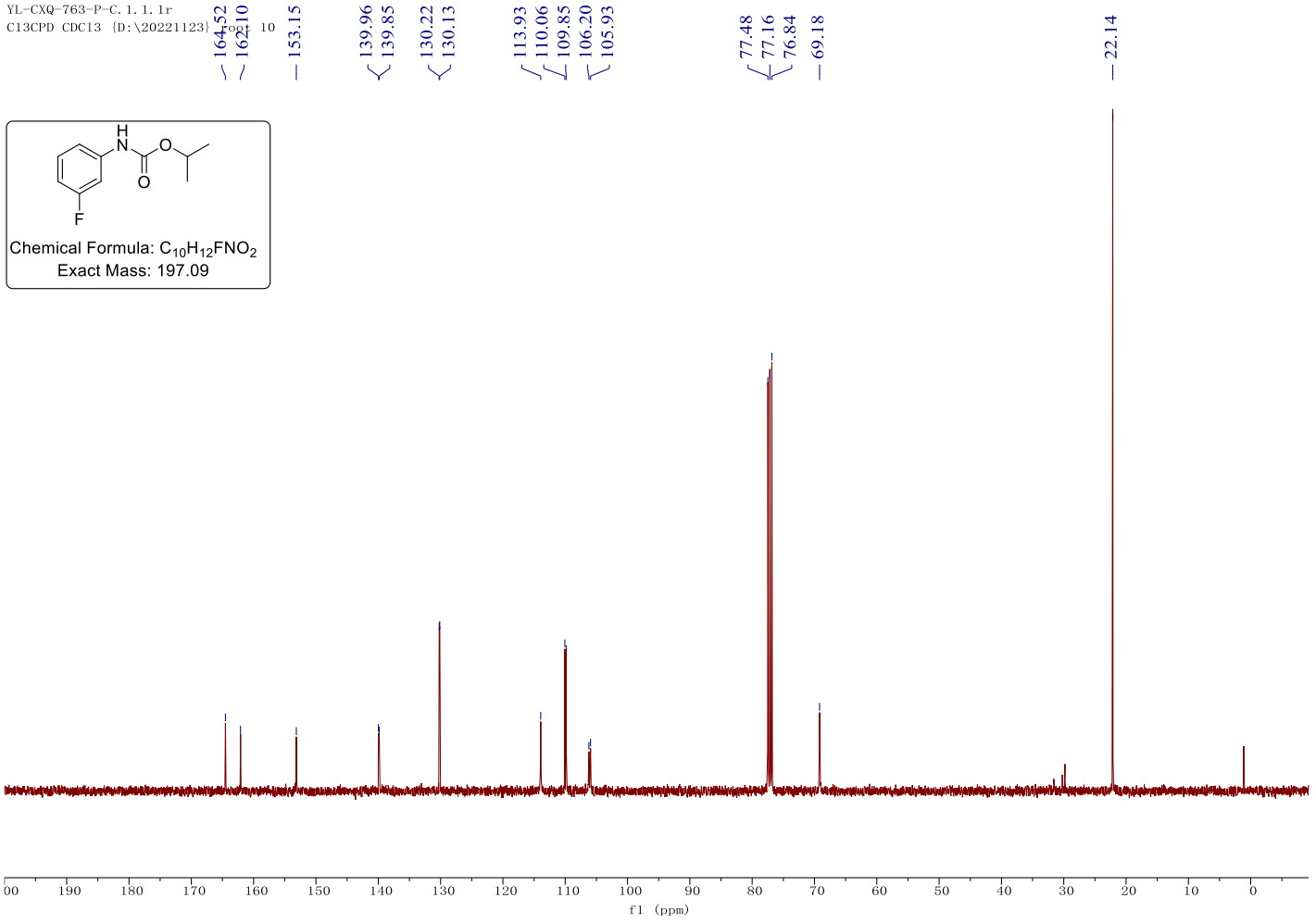
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of compound **3ea.**



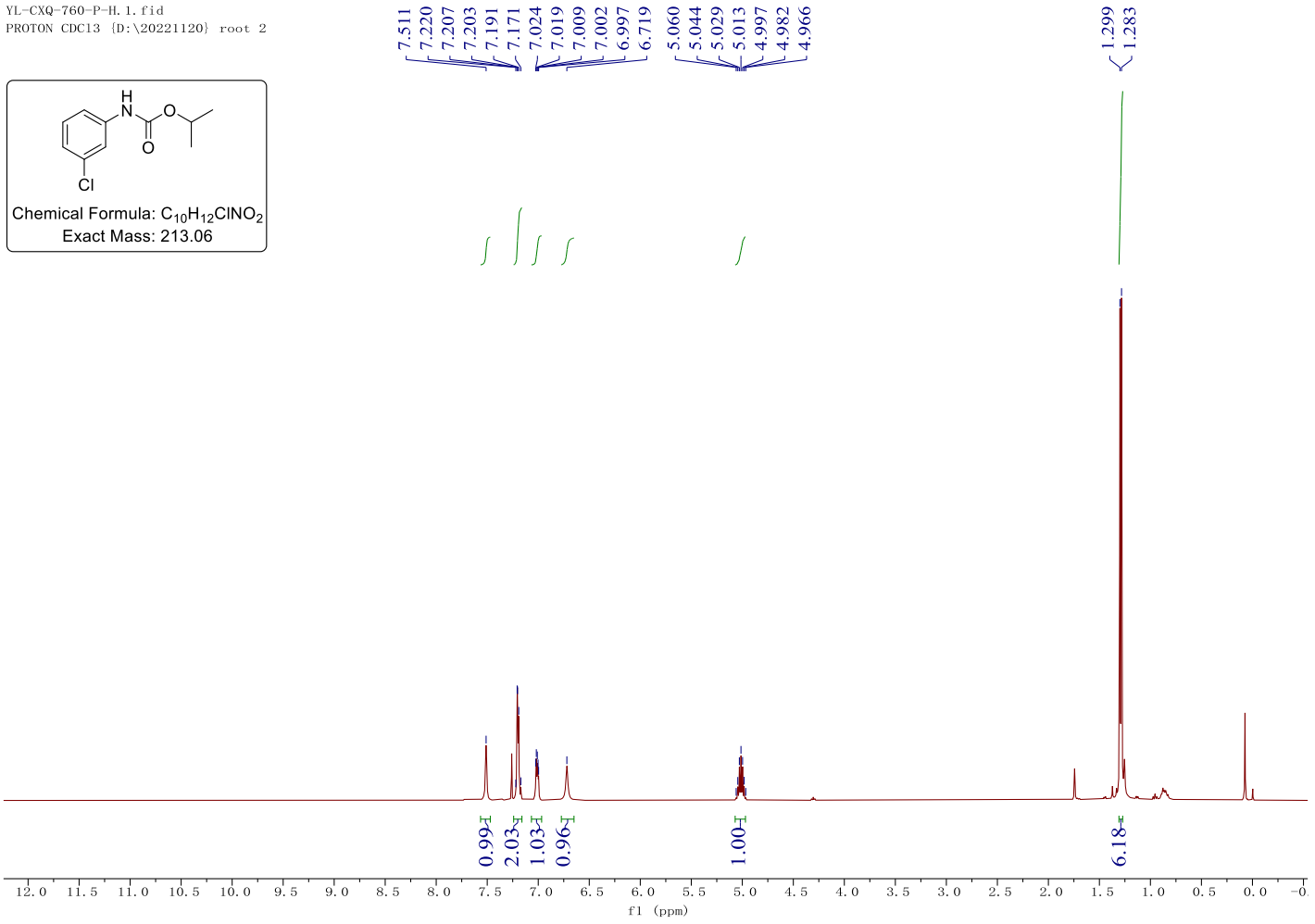
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3fa.**



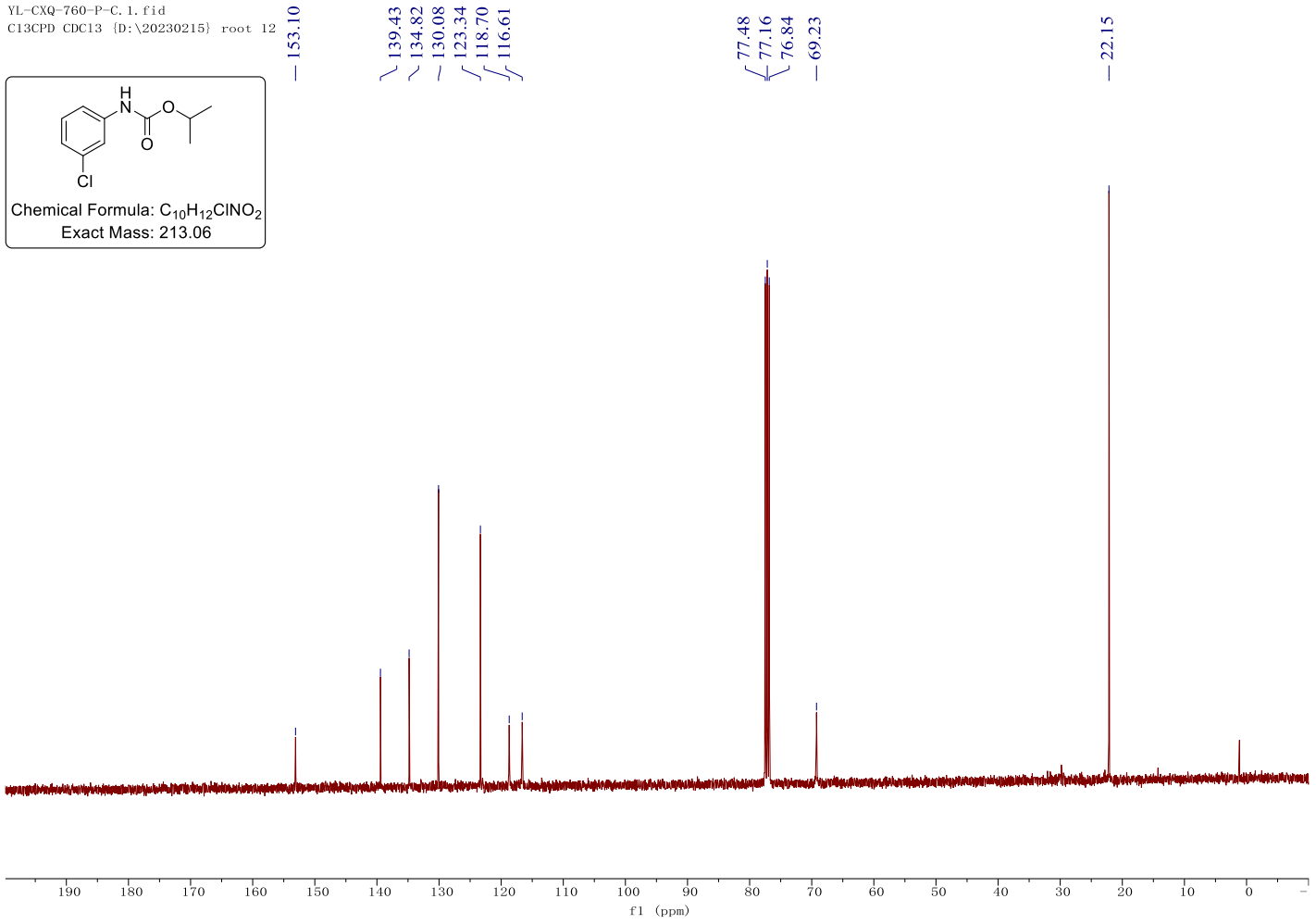
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3fa.**



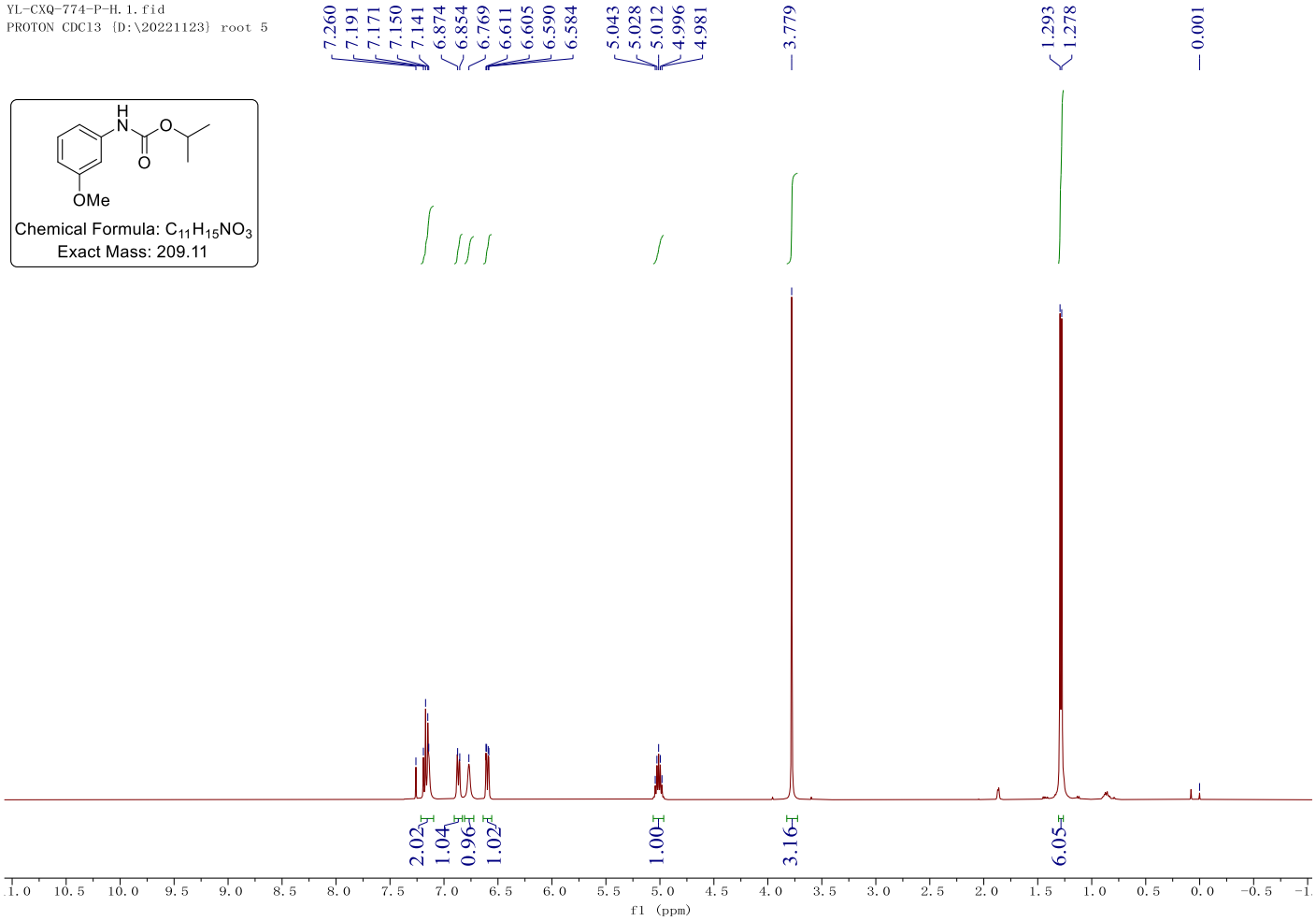
^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of compound **3ga.**



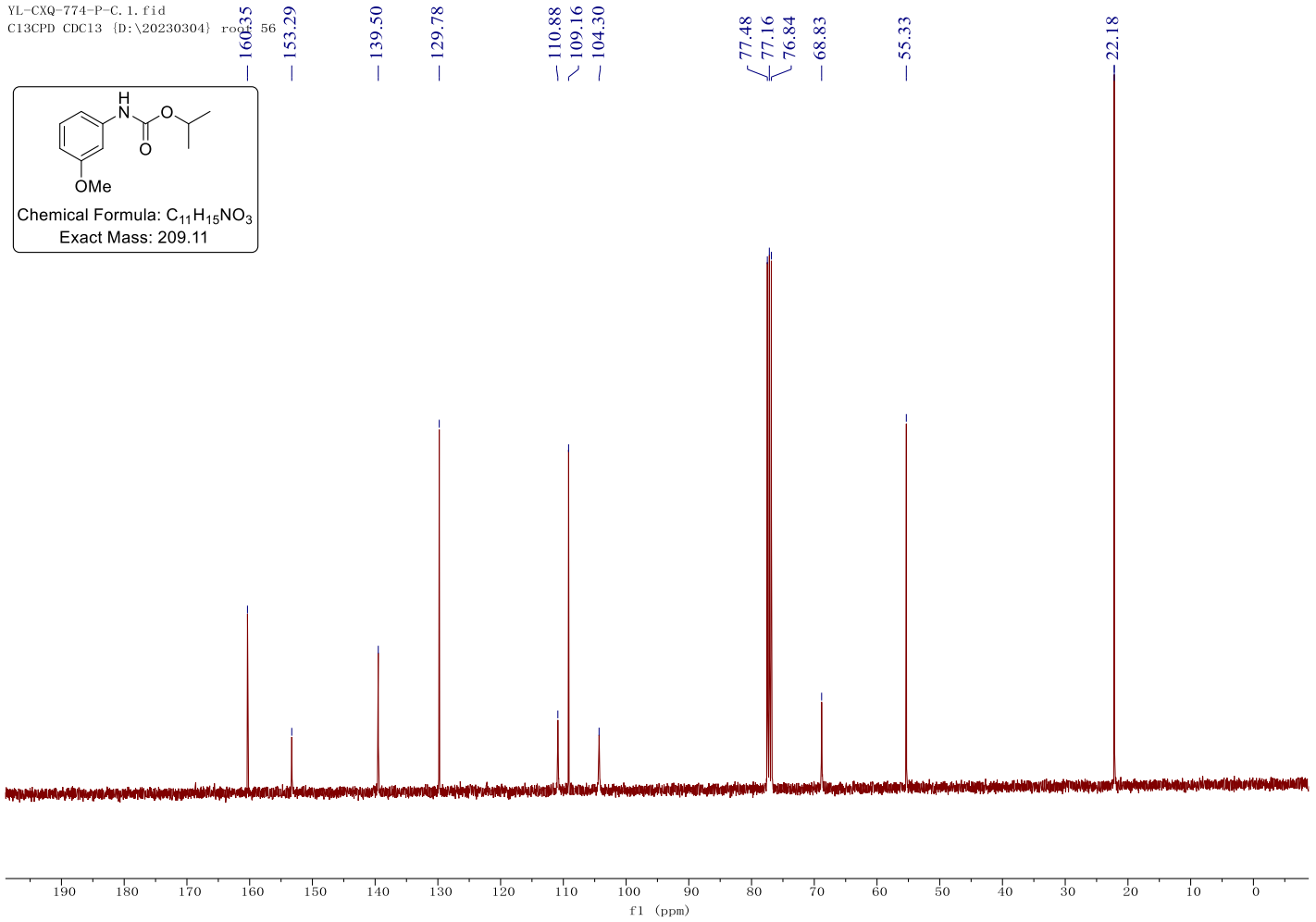
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ga.**



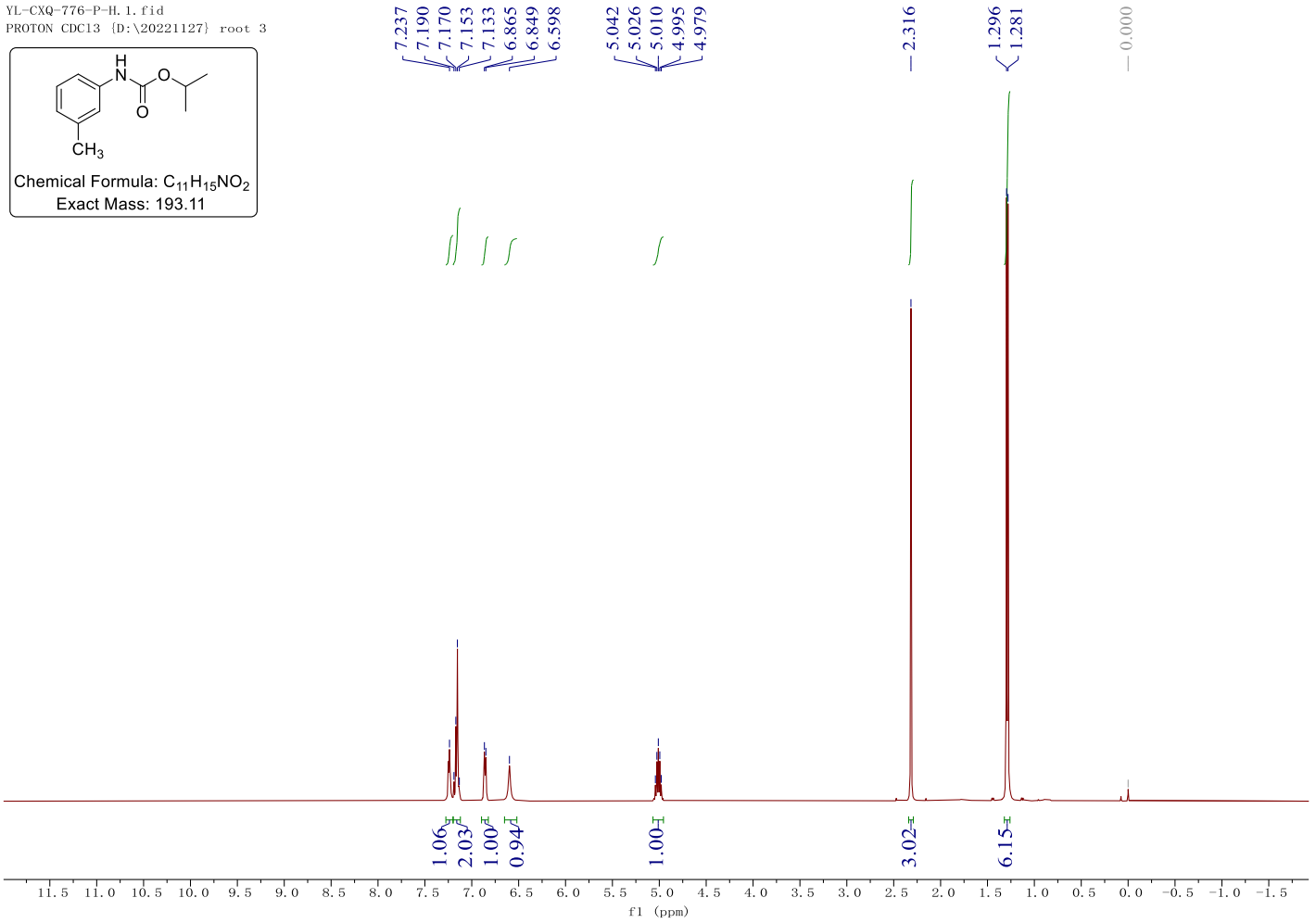
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ha.**



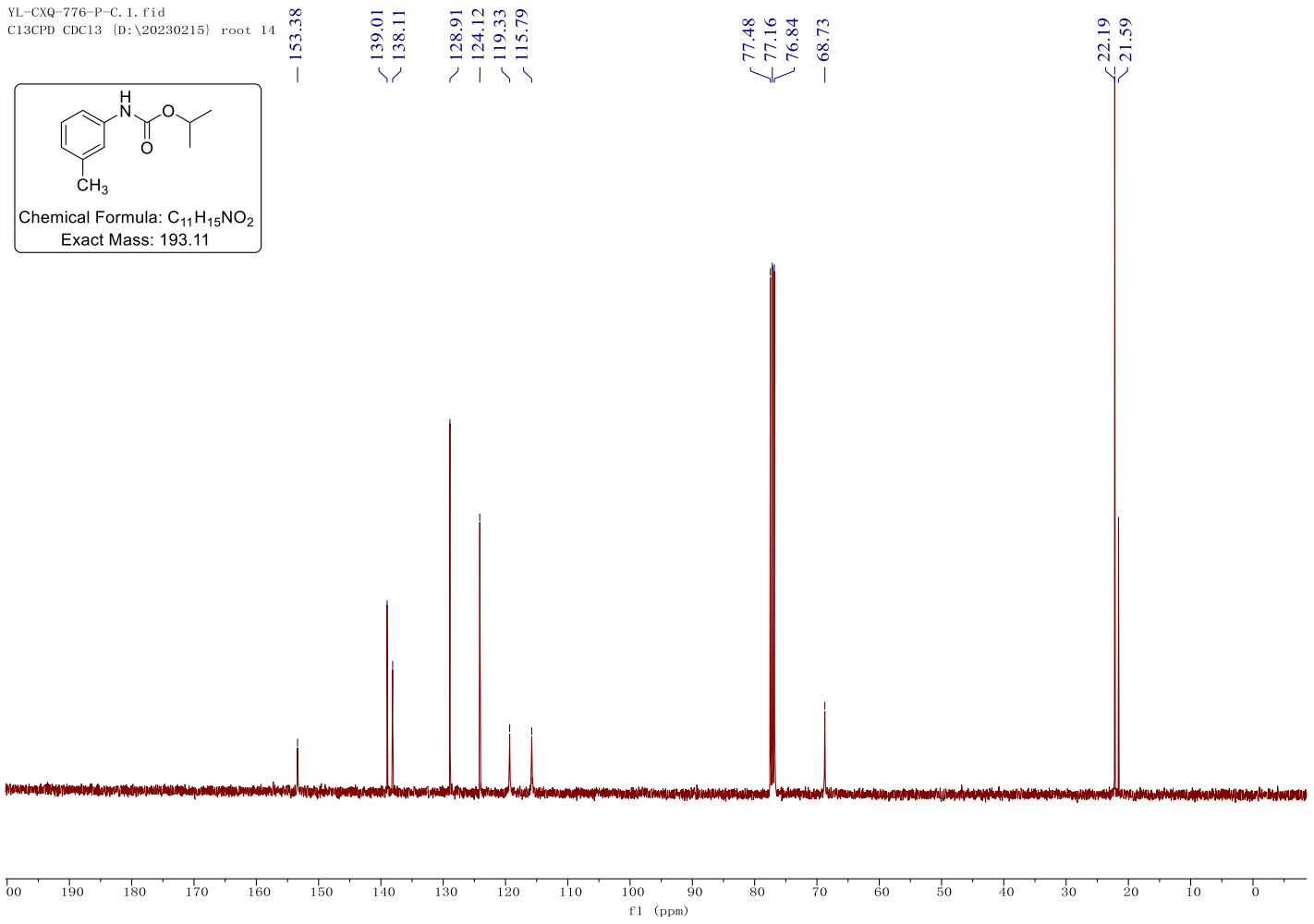
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ha.**



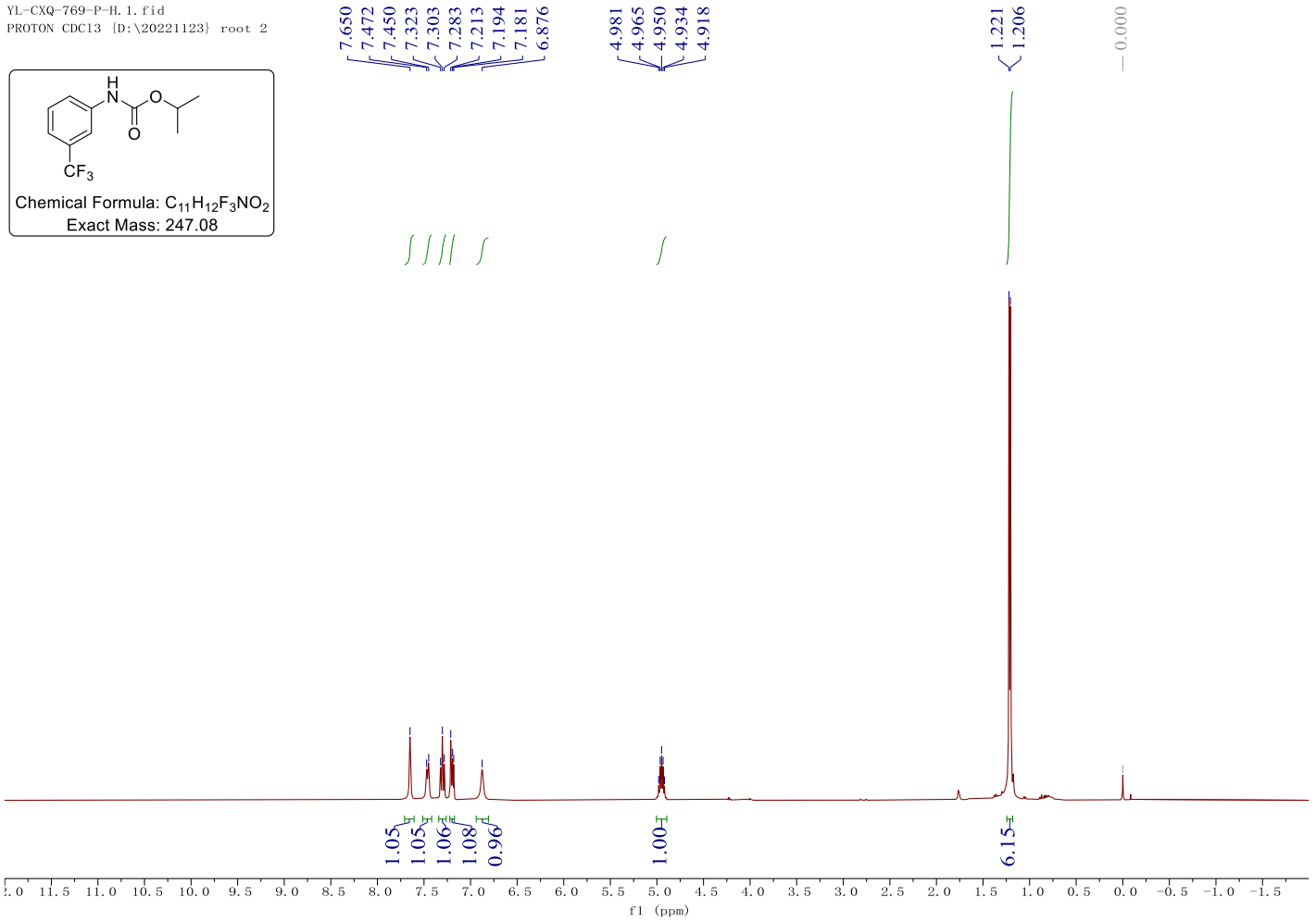
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ia.**



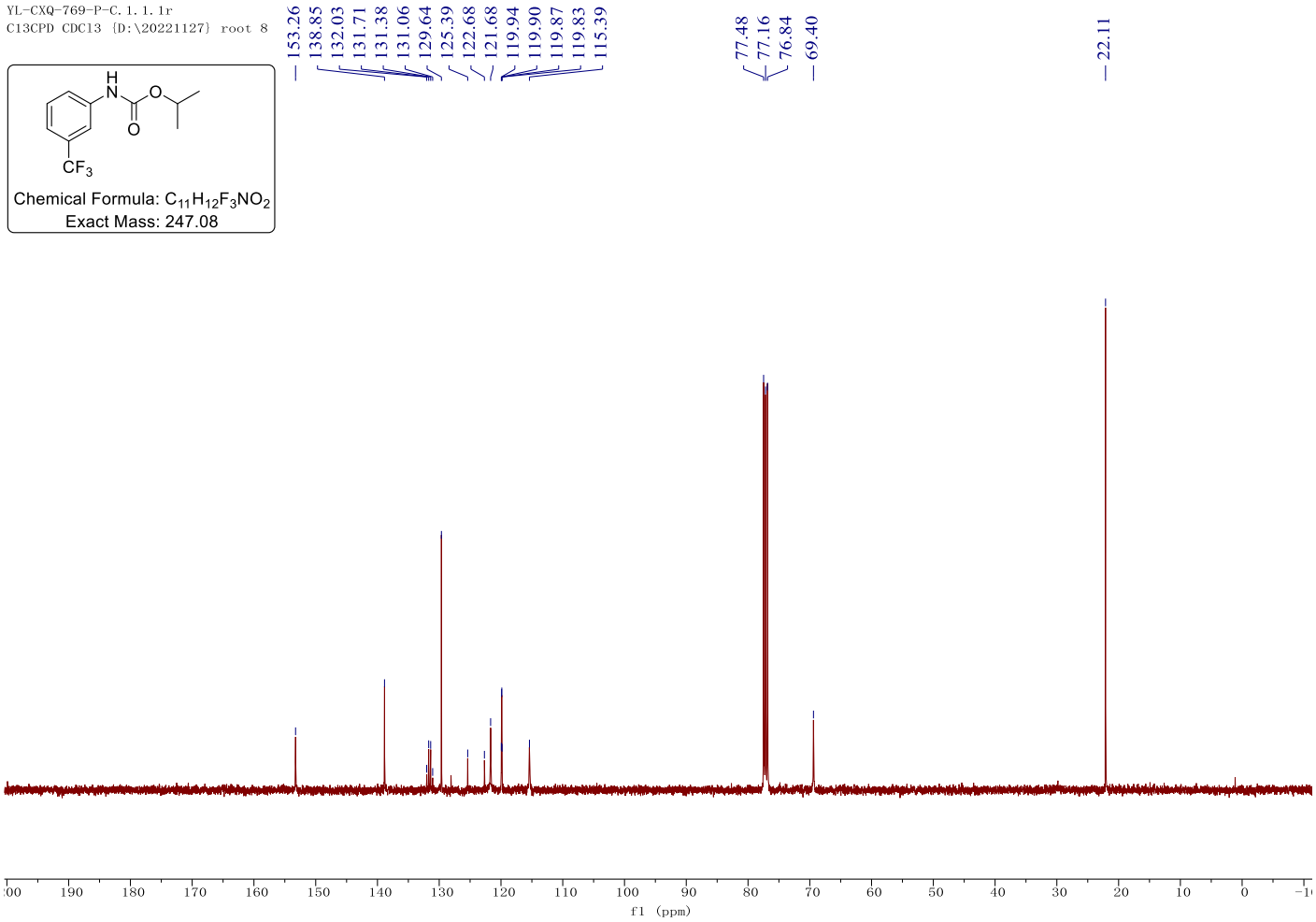
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ia.**



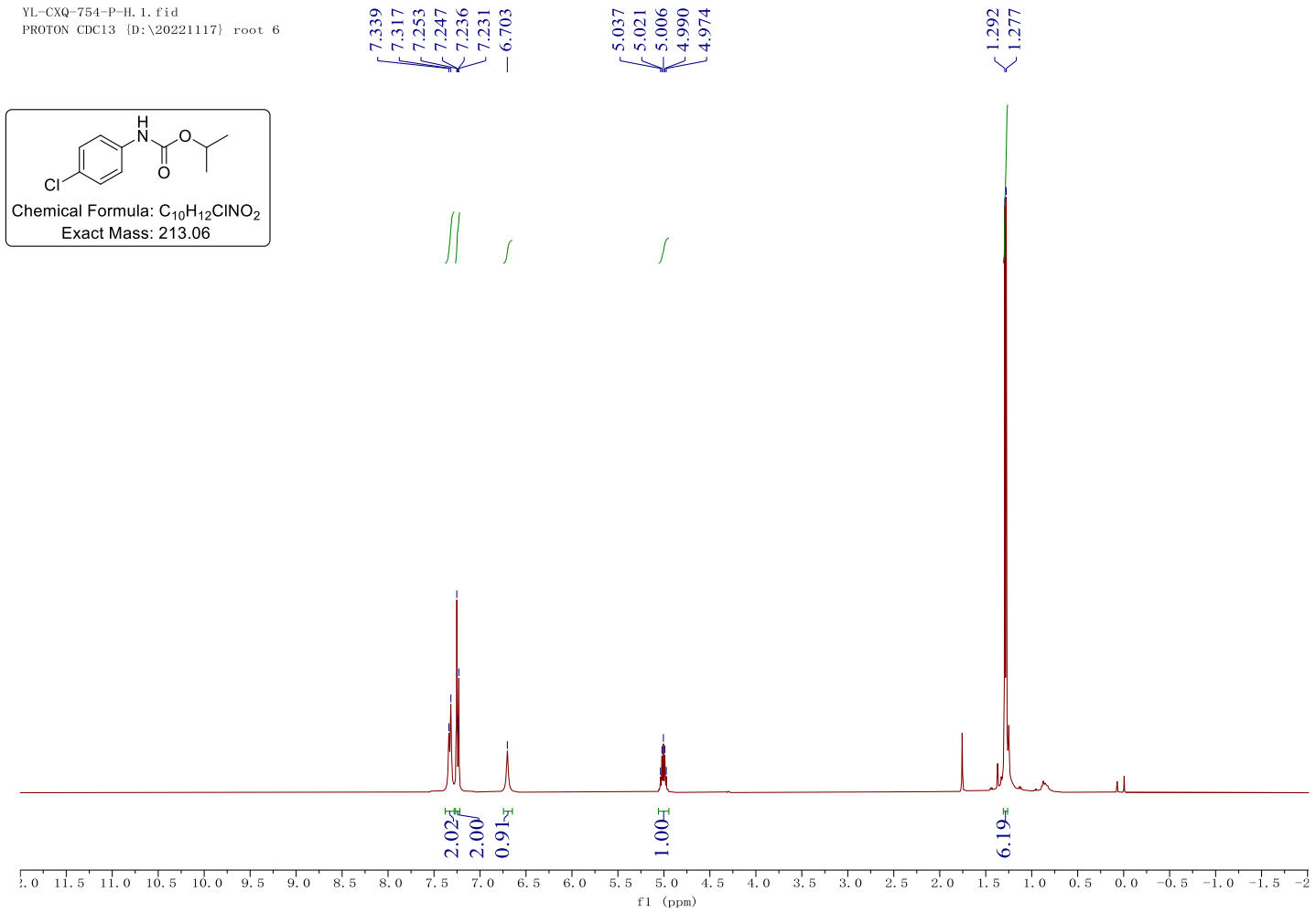
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ja.**



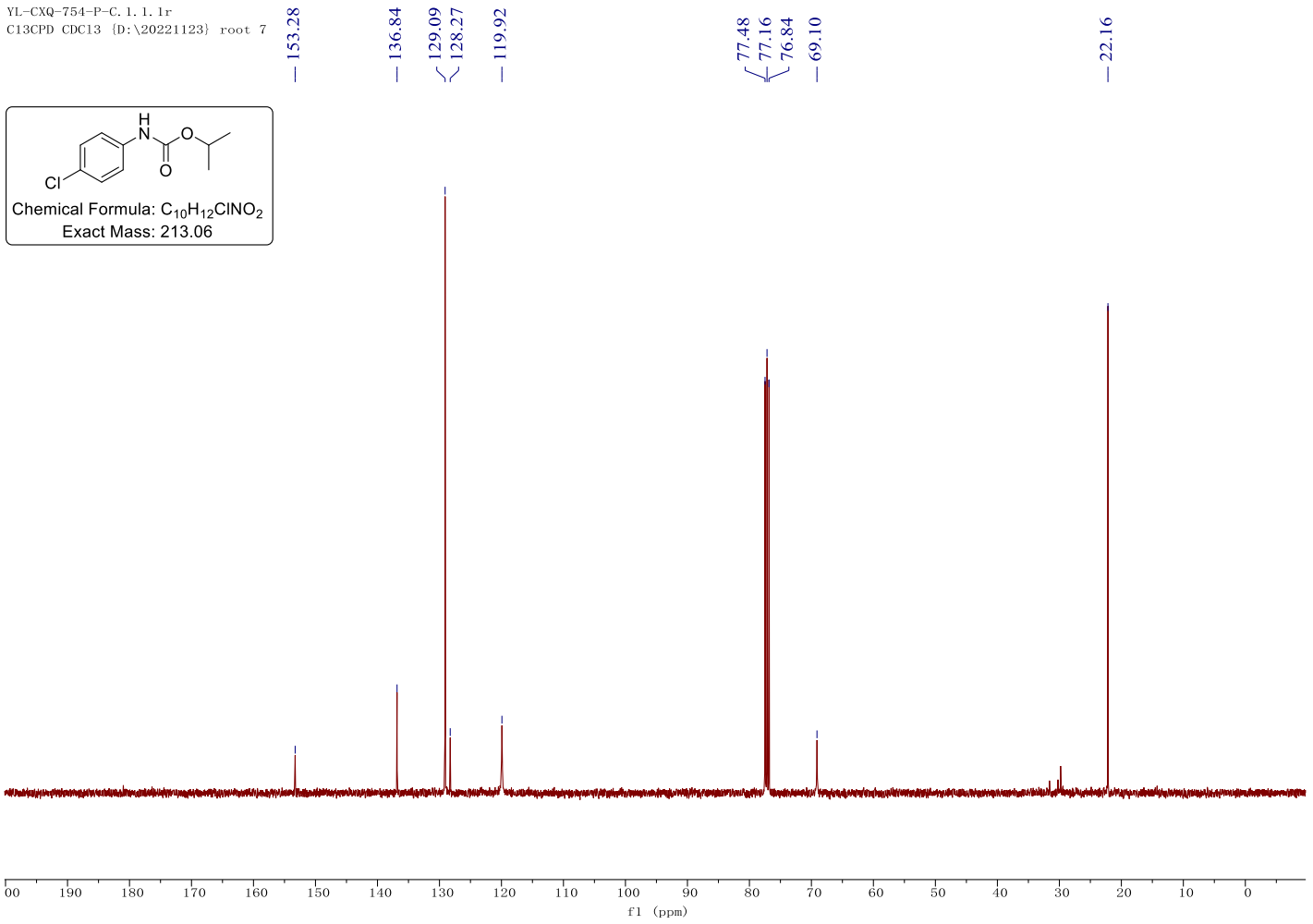
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ja.**



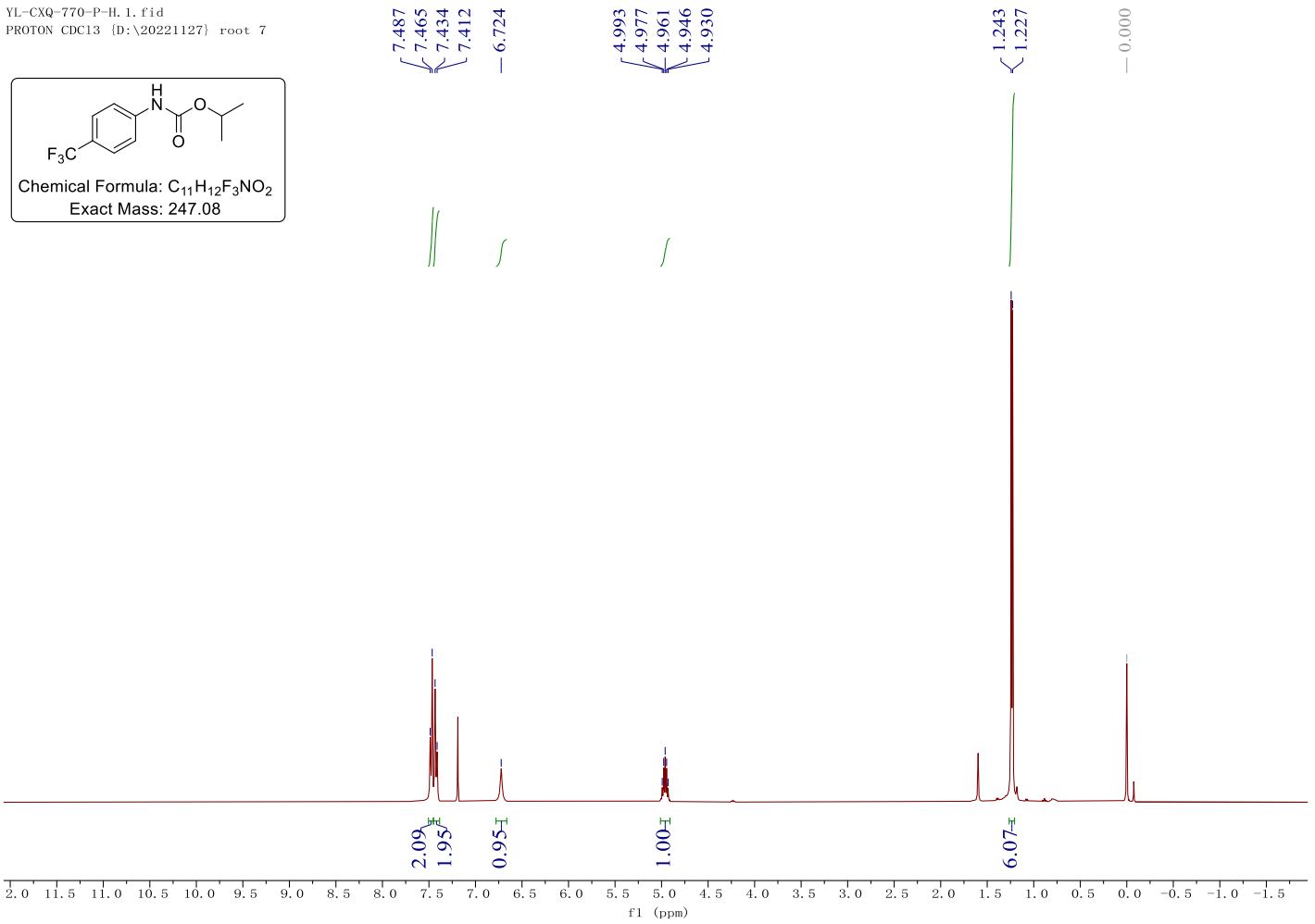
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ka.**



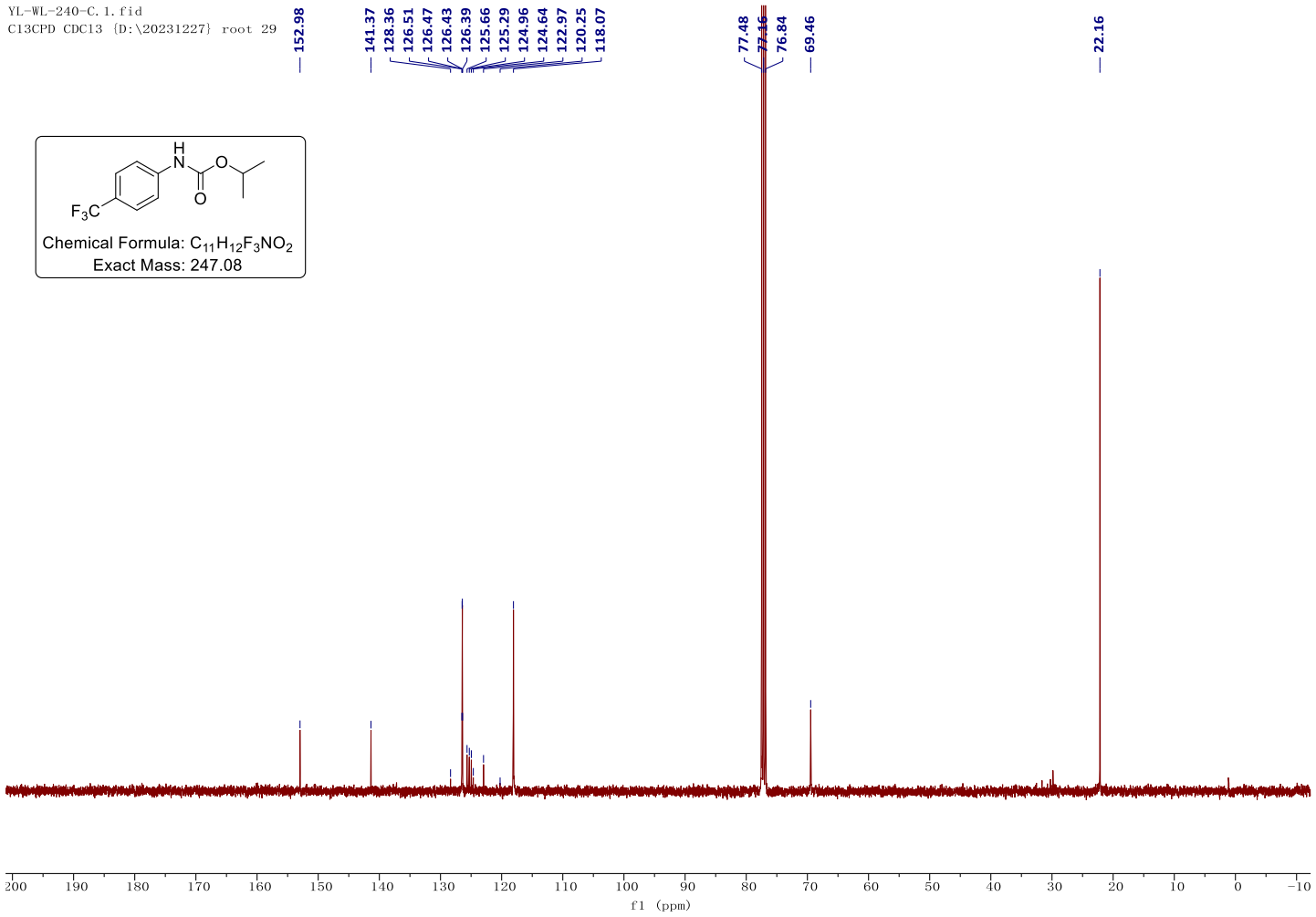
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ka.**



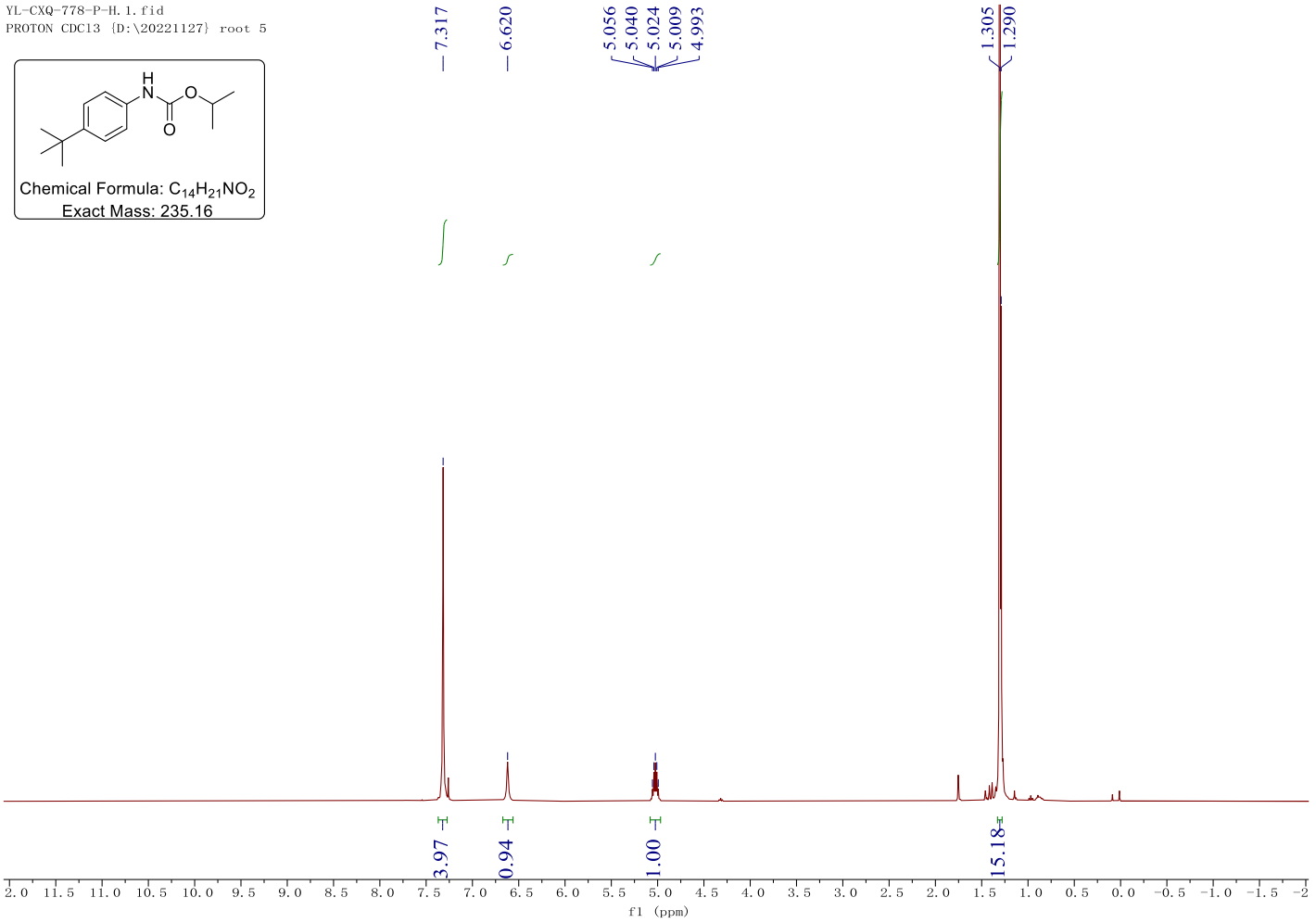
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3la.**



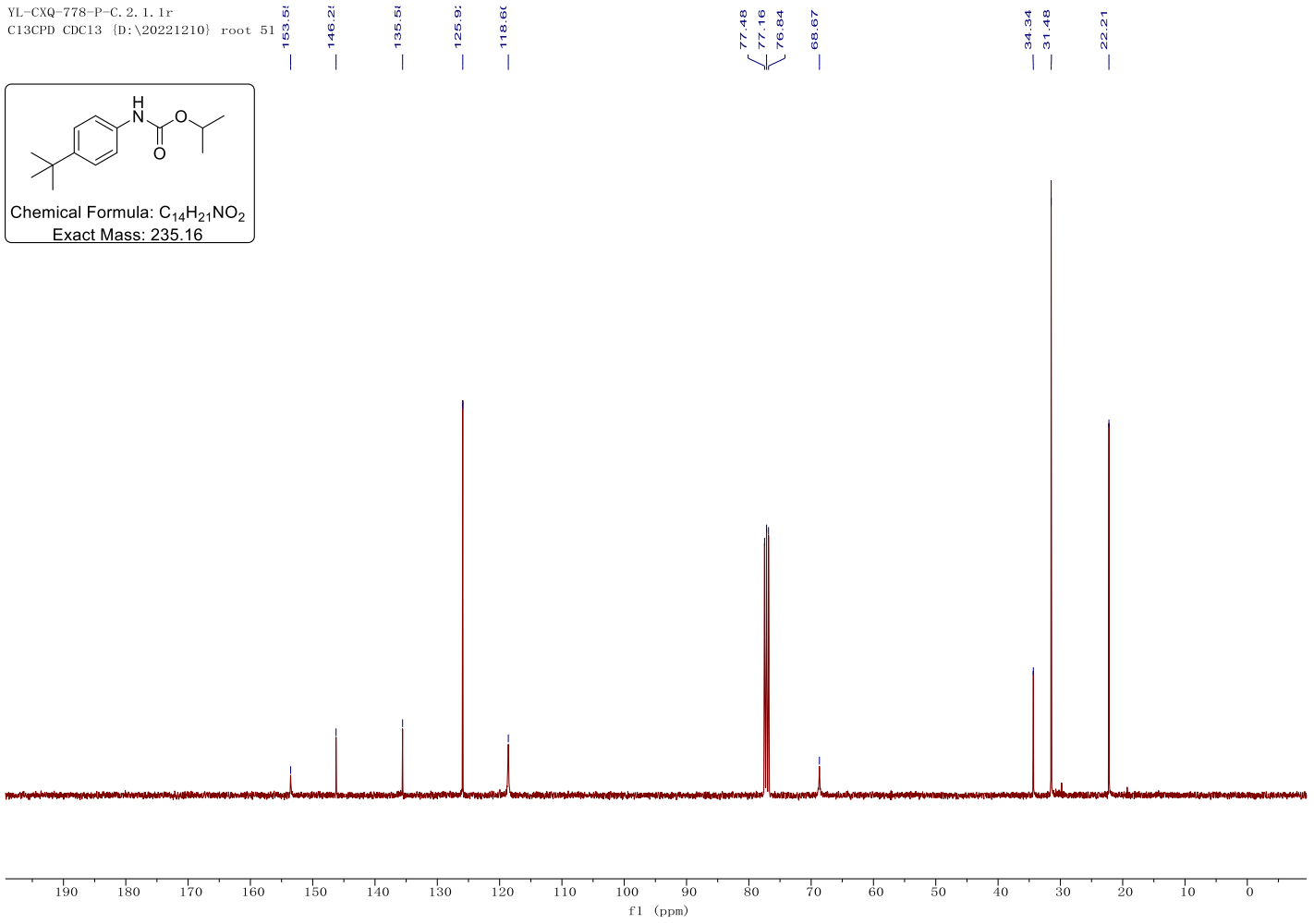
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3la.**



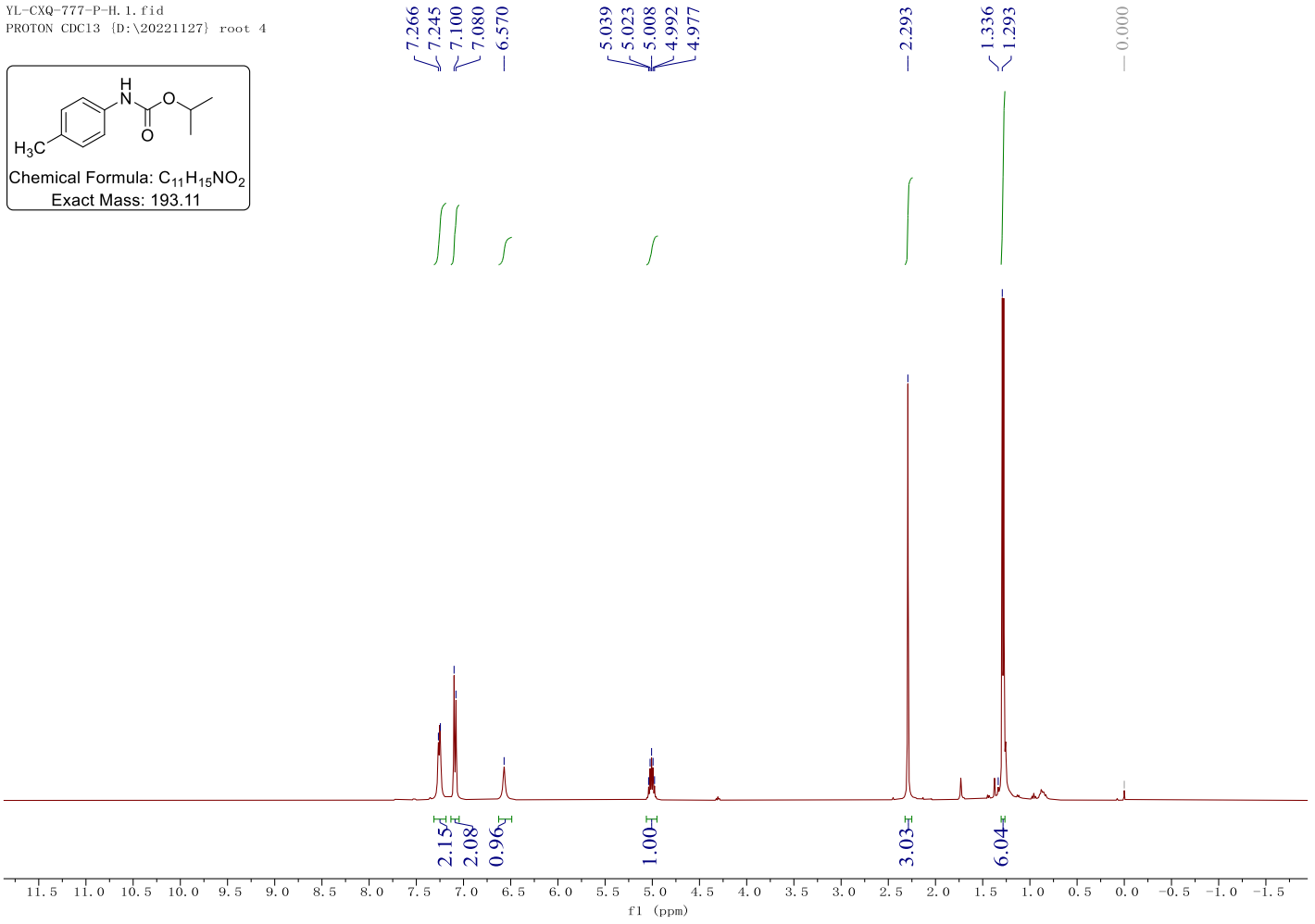
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ma.**



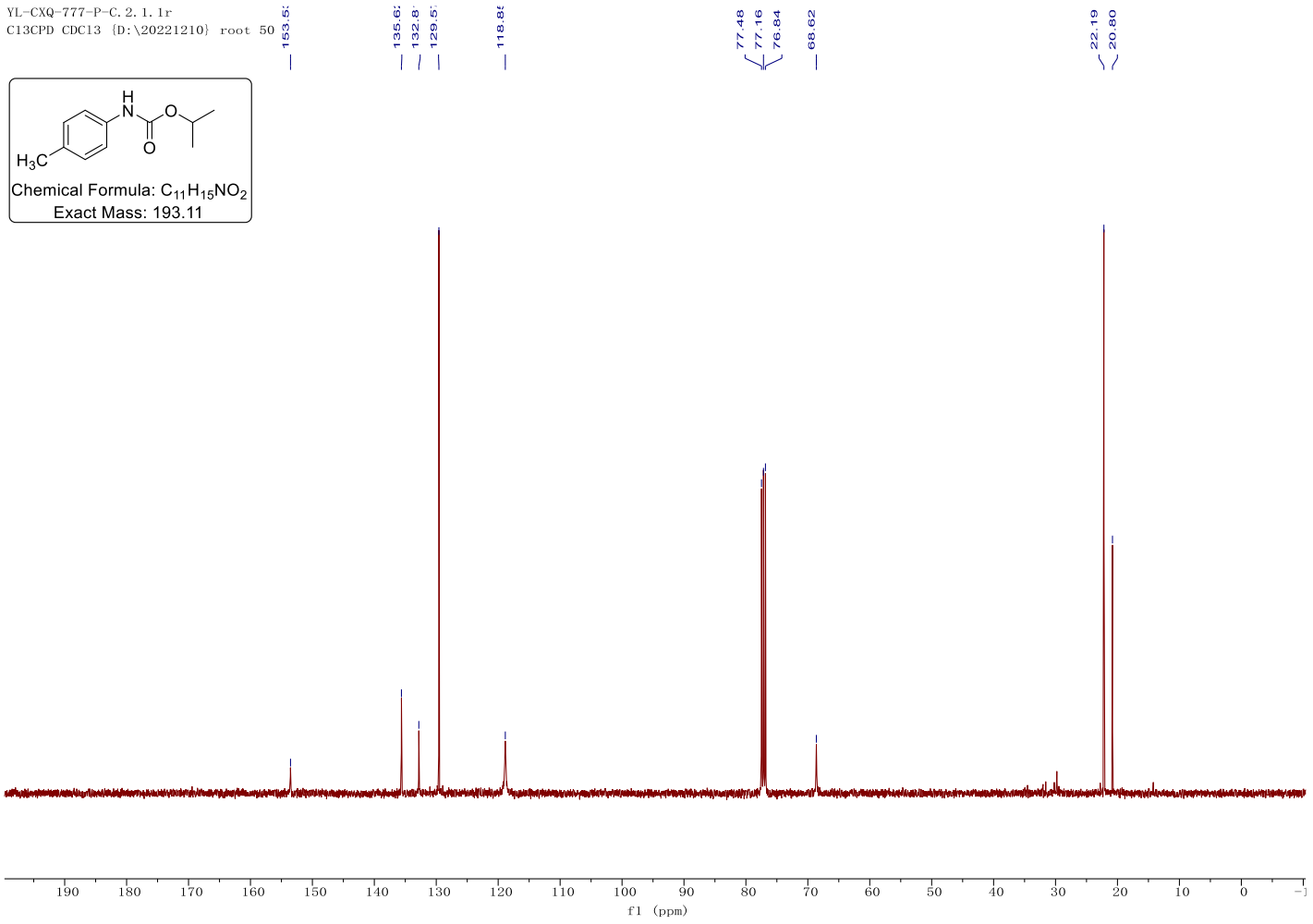
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ma.**



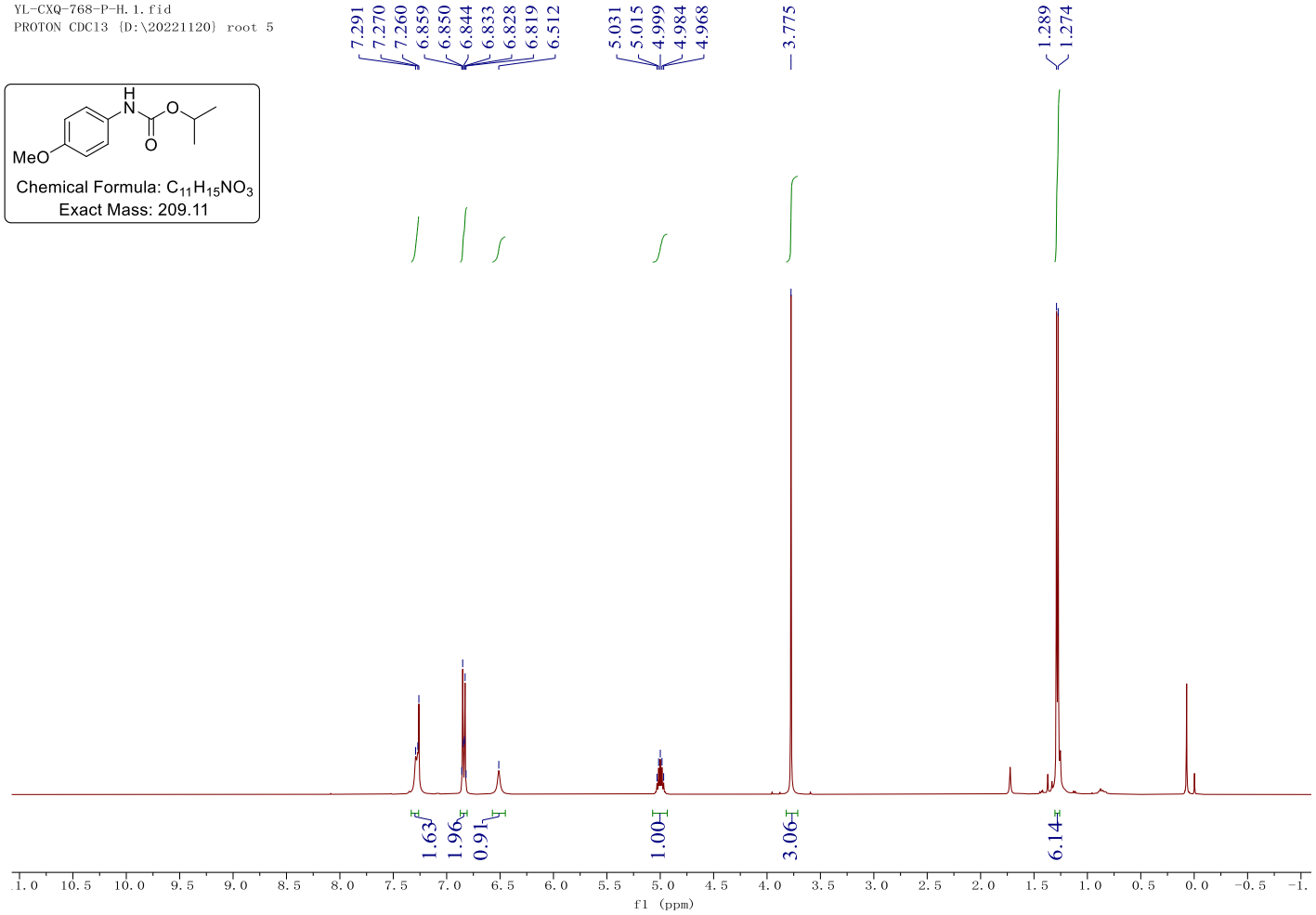
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3na.**



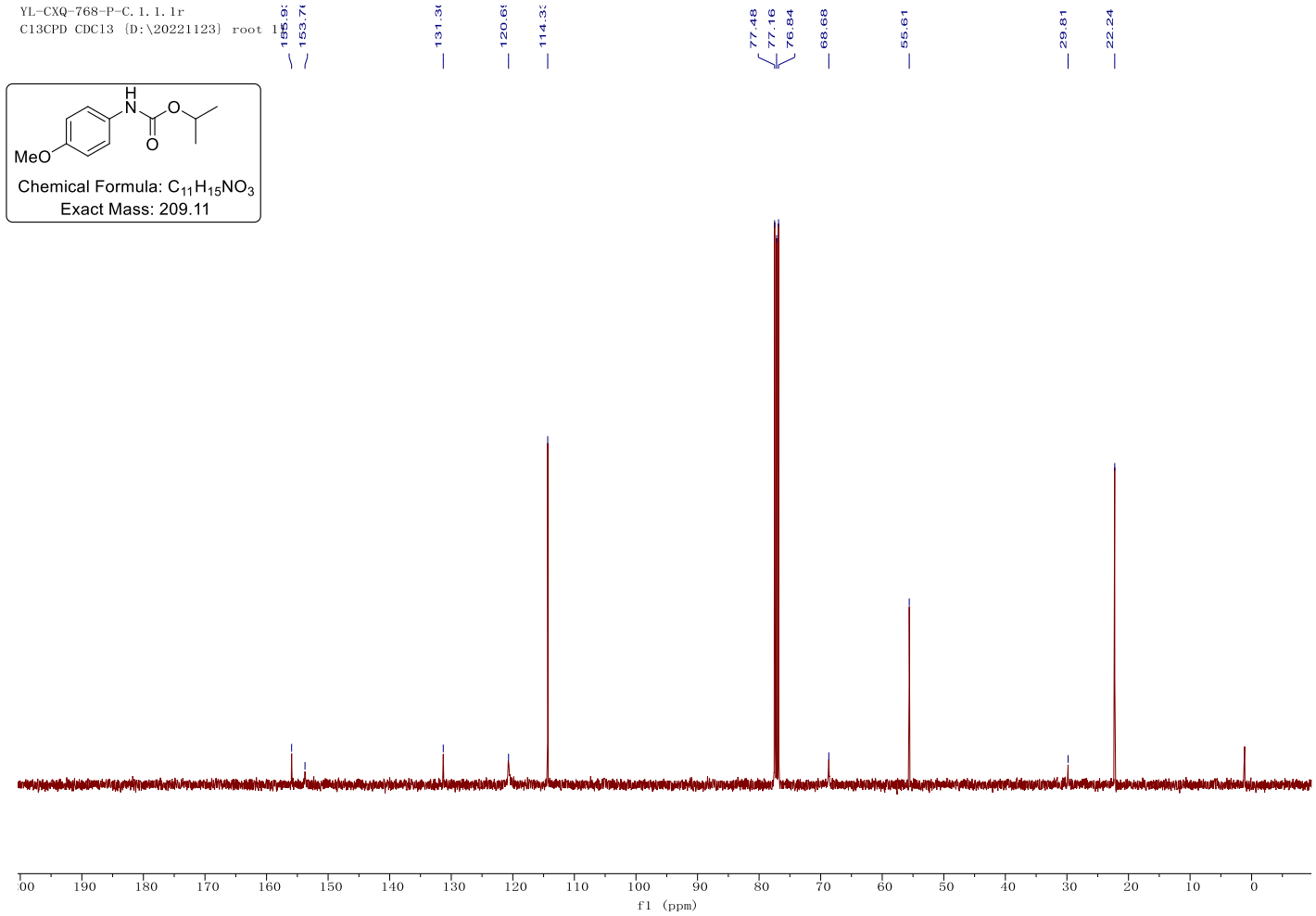
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3na.**



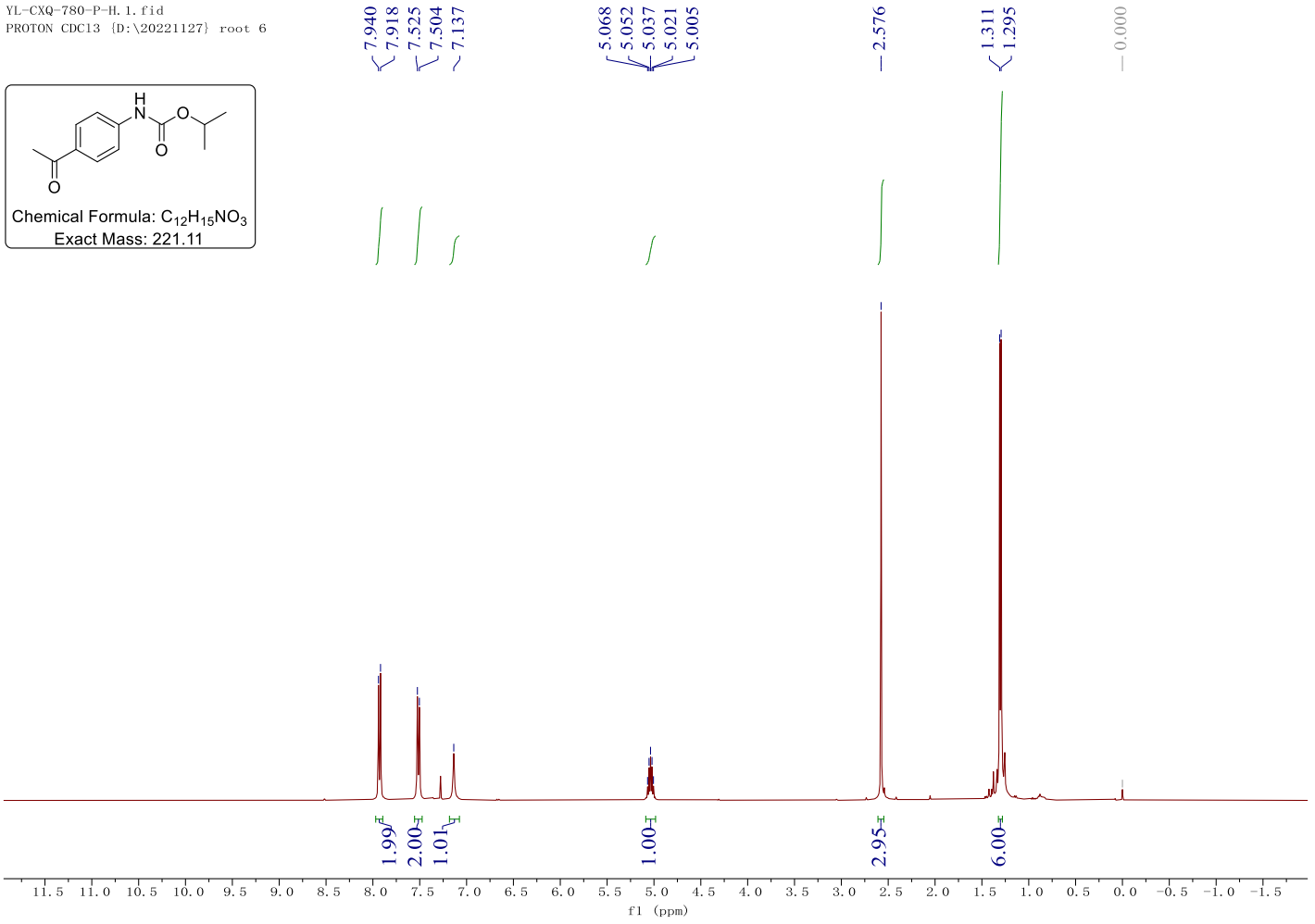
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3oa.**



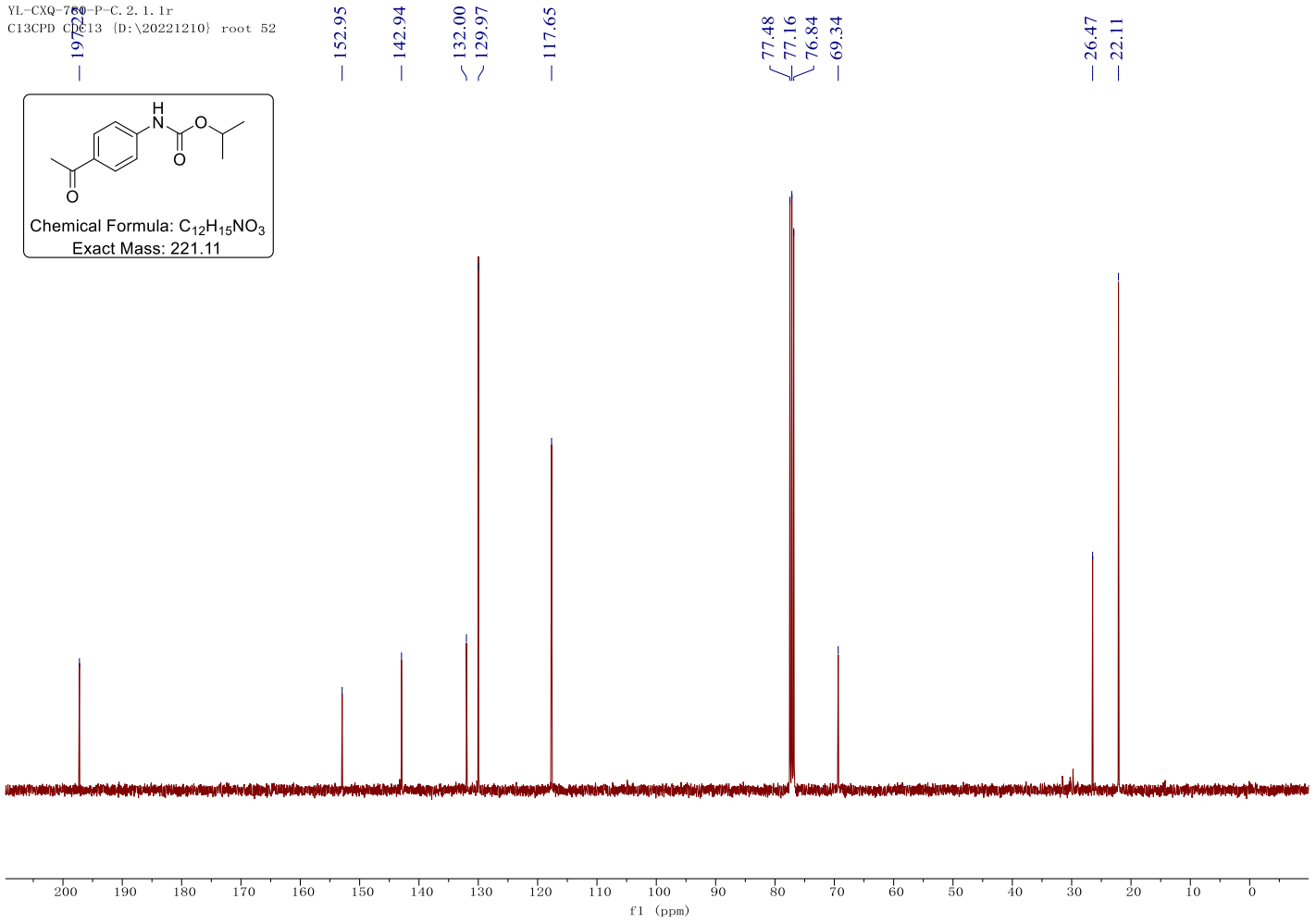
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3oa.**



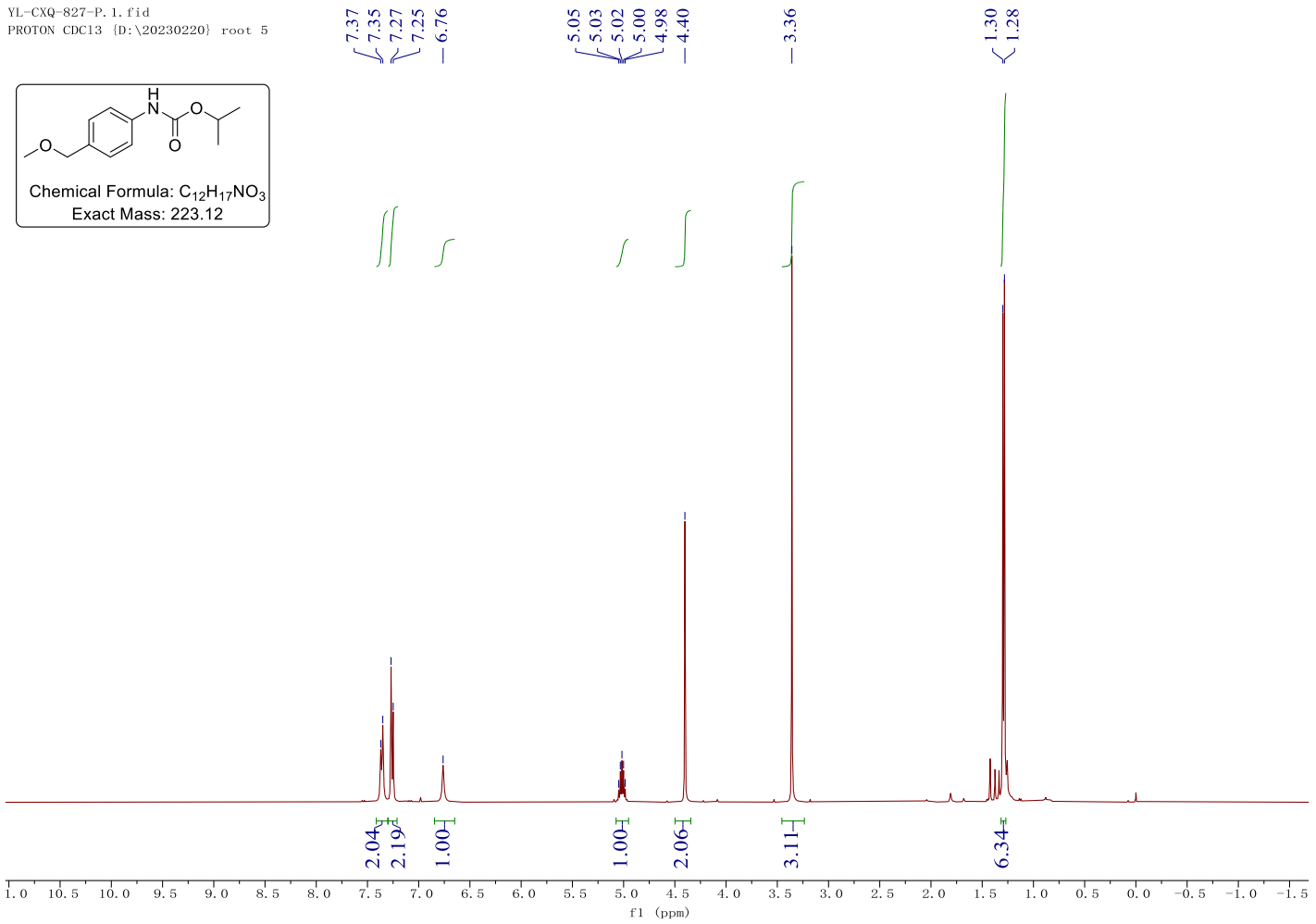
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3pa.**



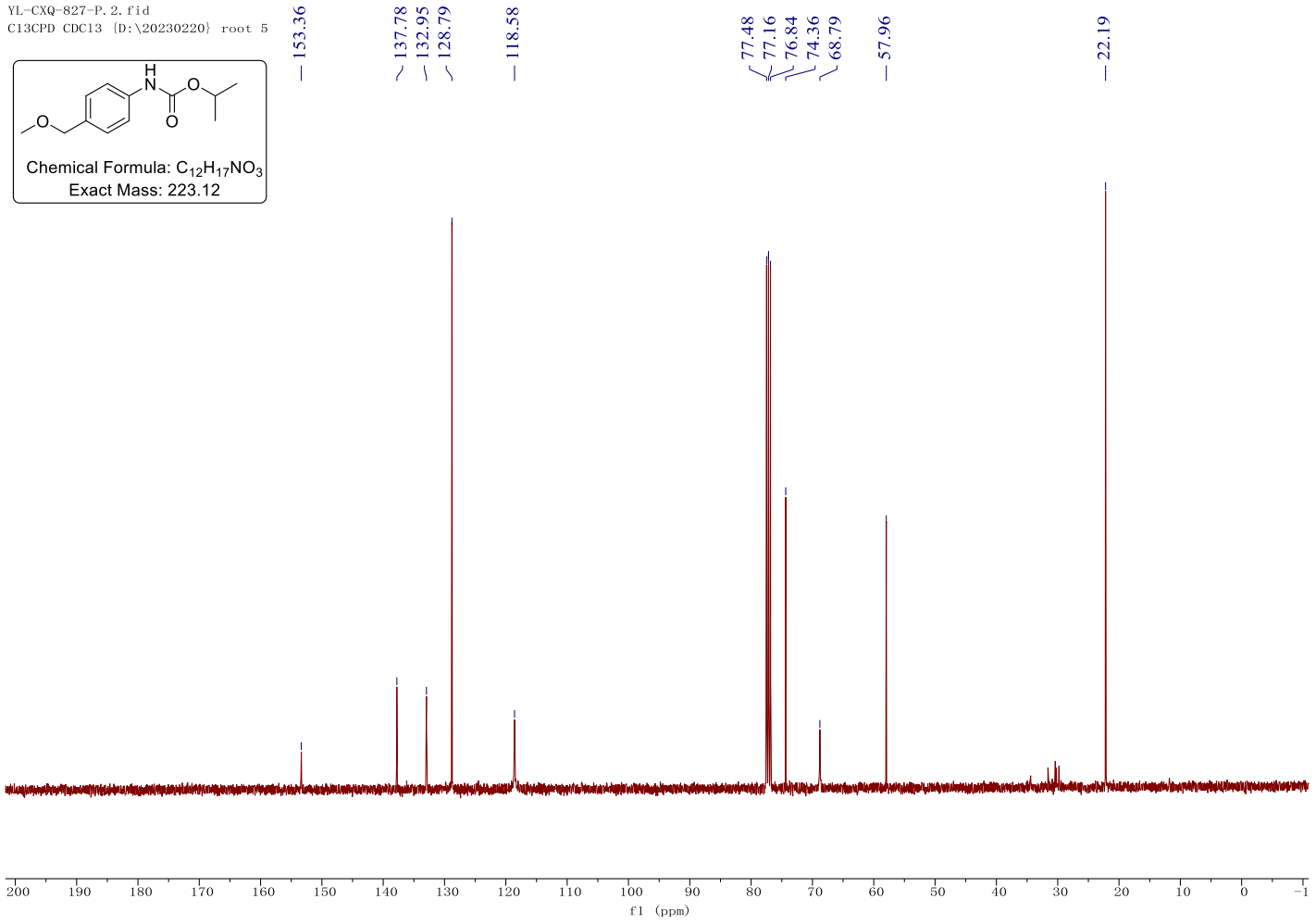
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3pa.**



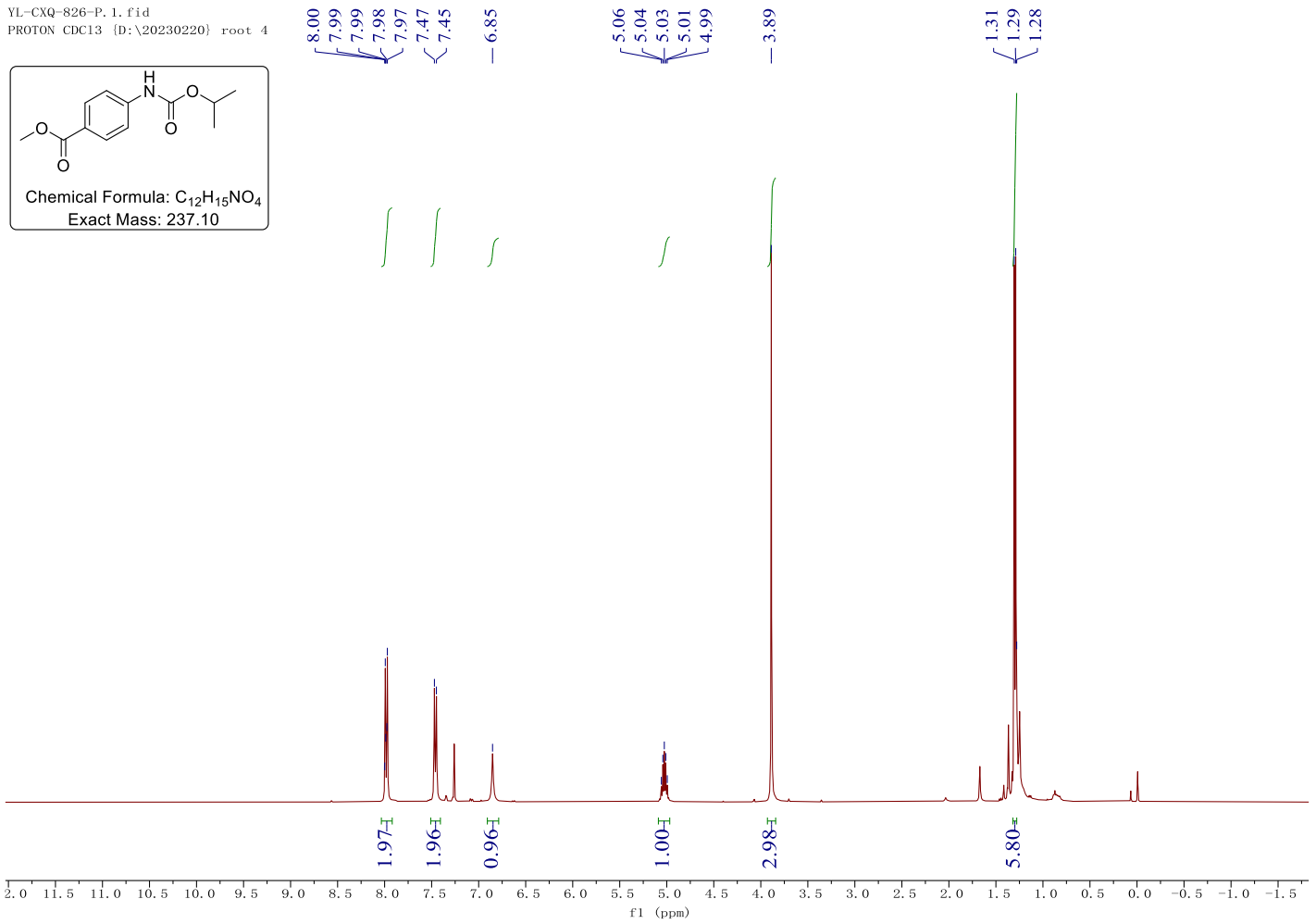
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3qa.**



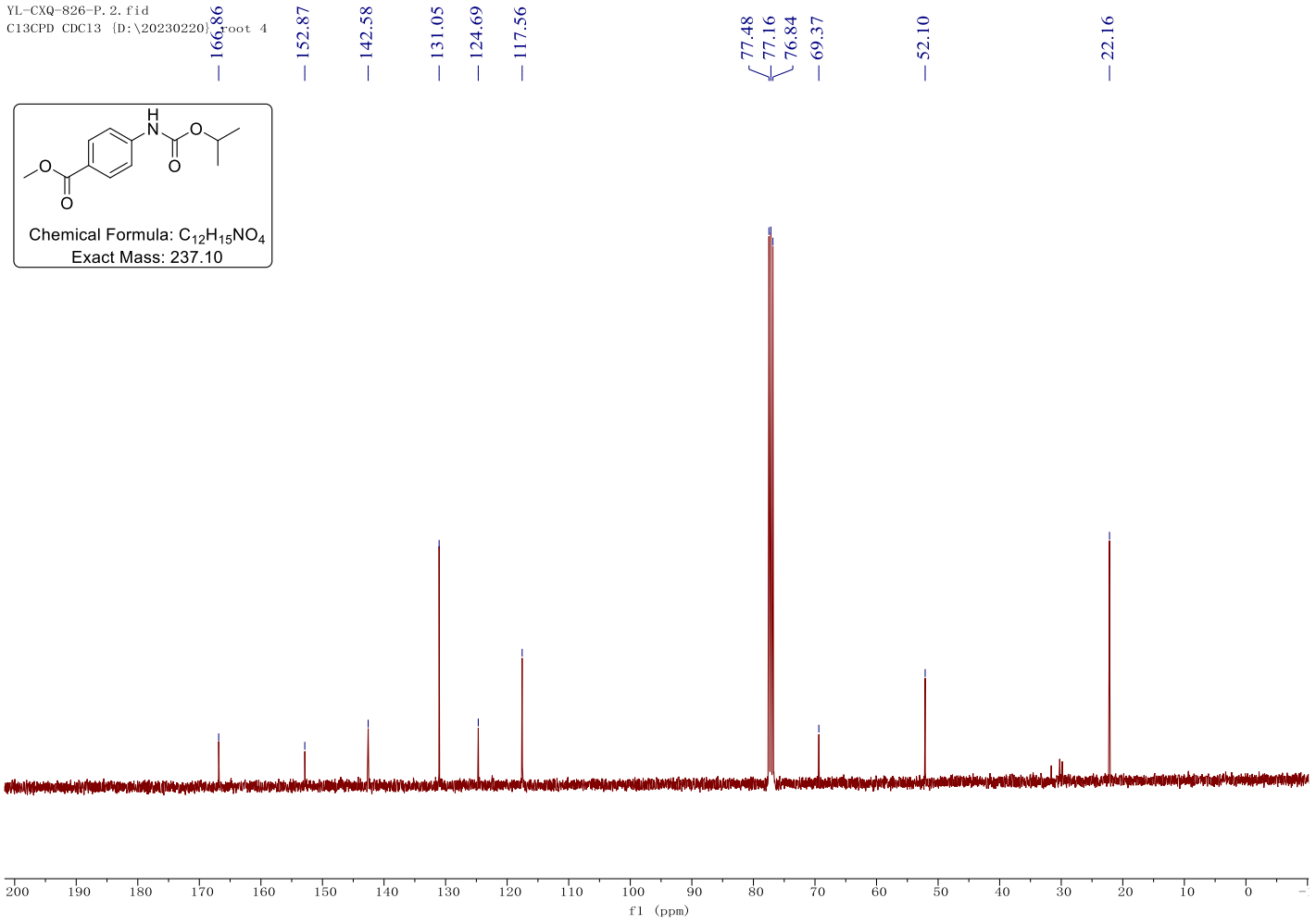
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3qa.**



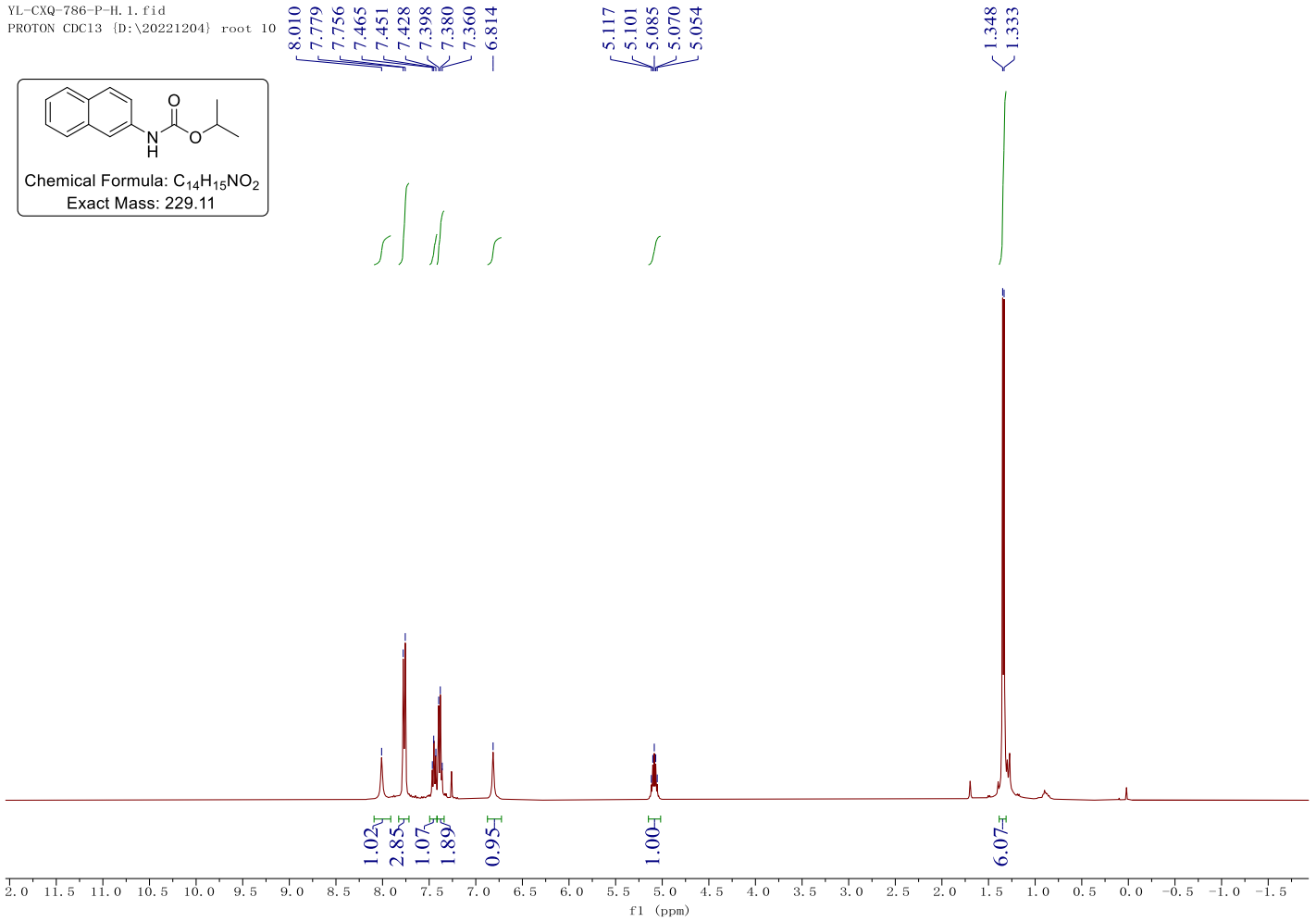
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ra.**



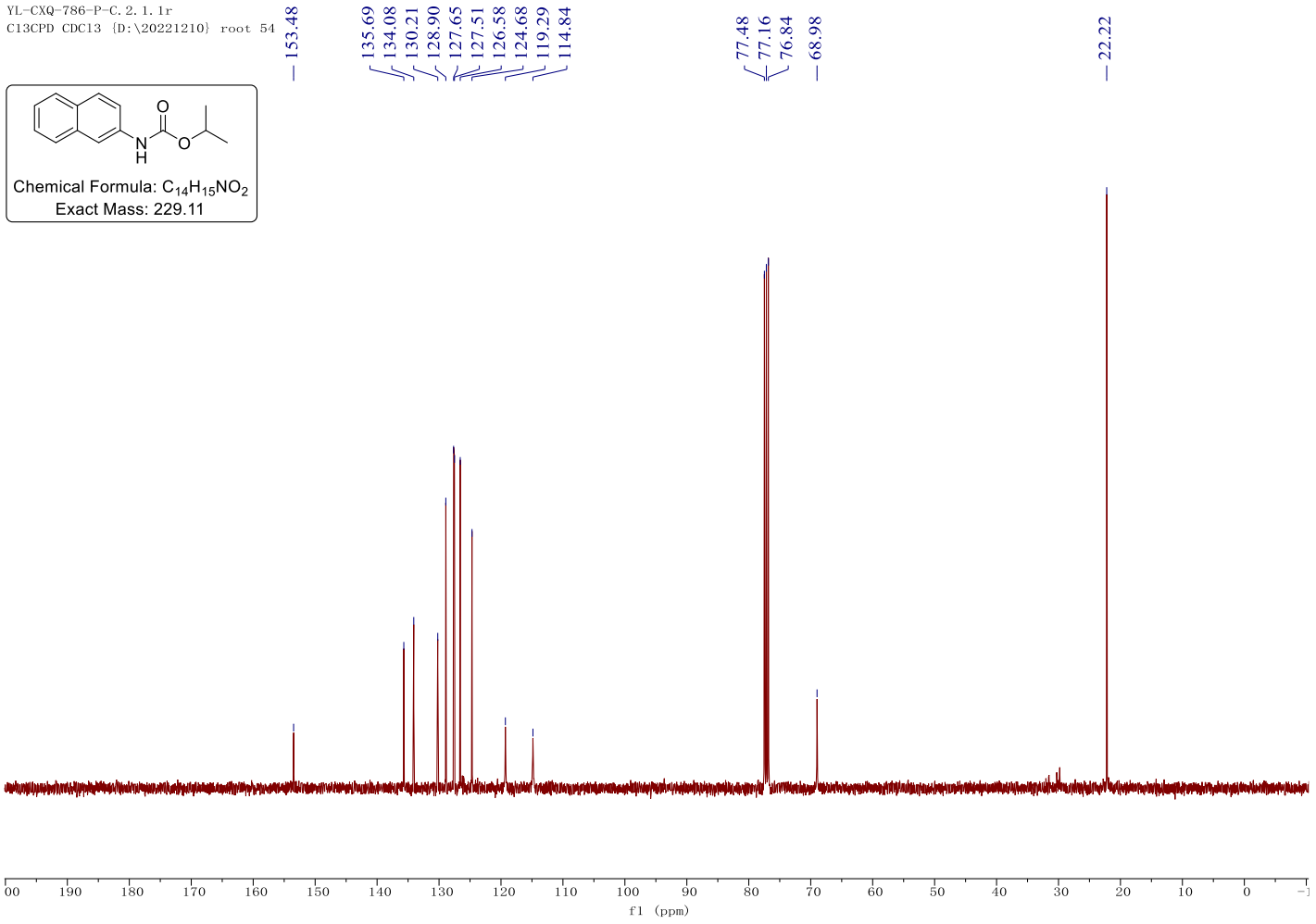
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ra.**



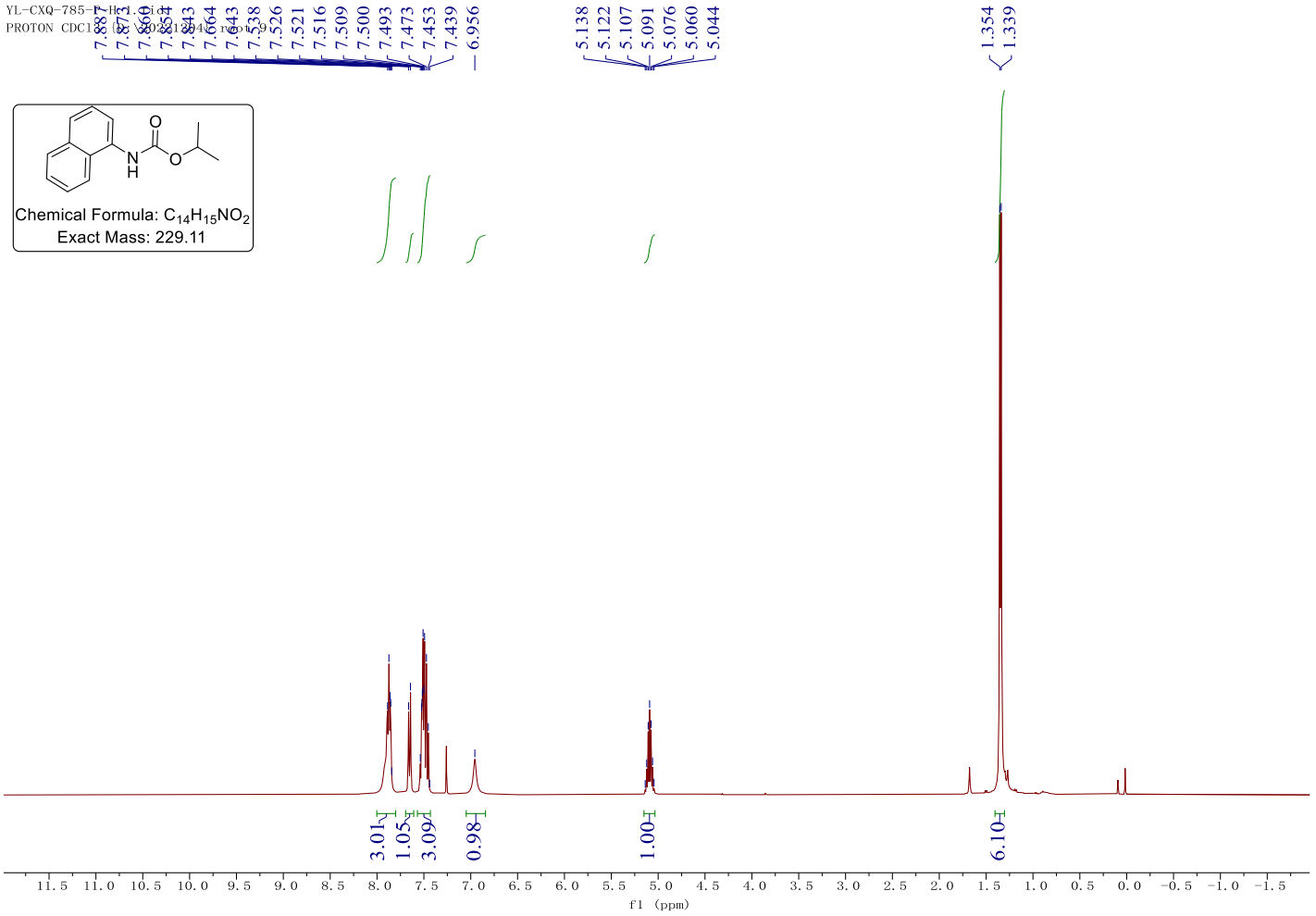
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3sa.**



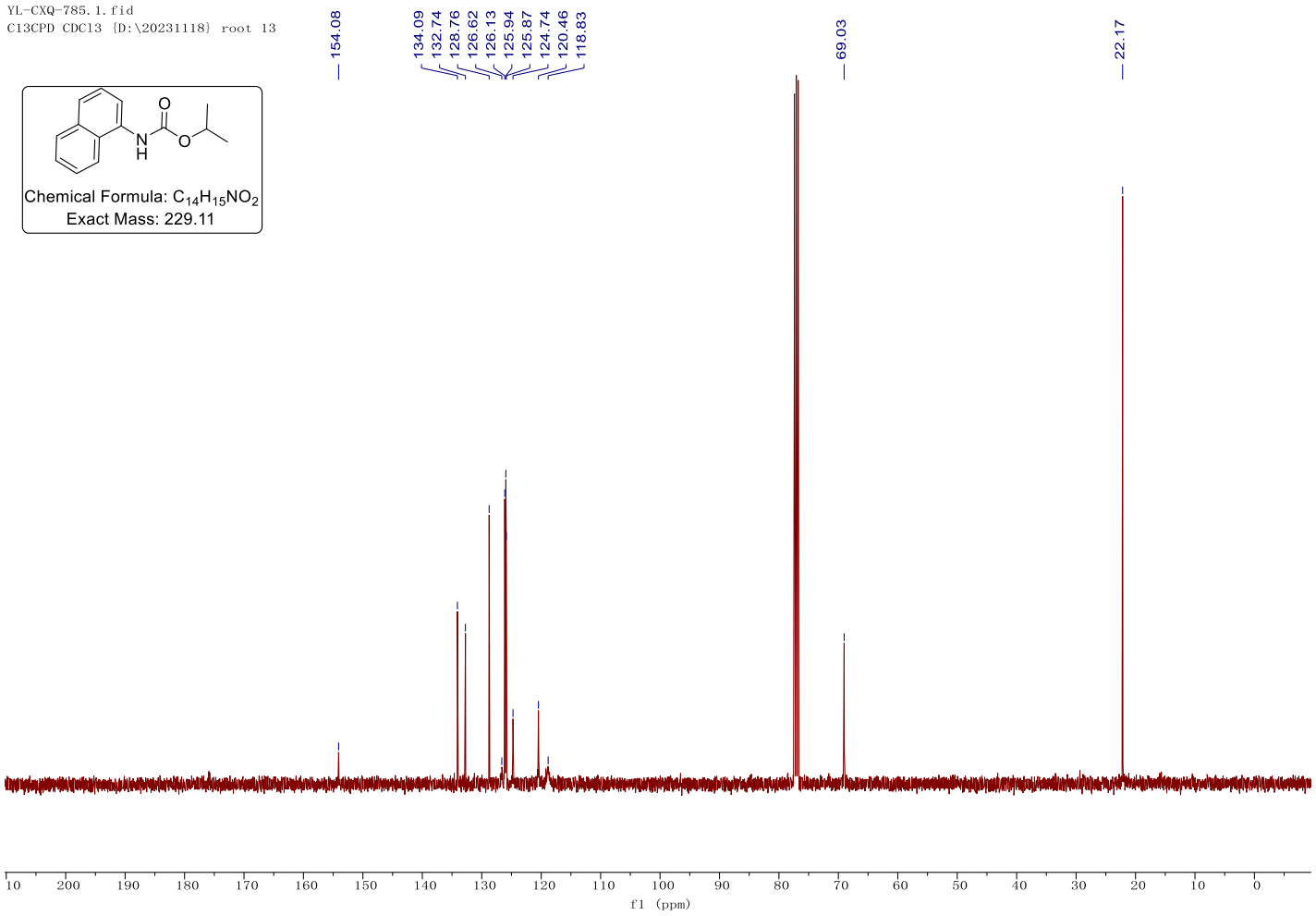
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3sa.**



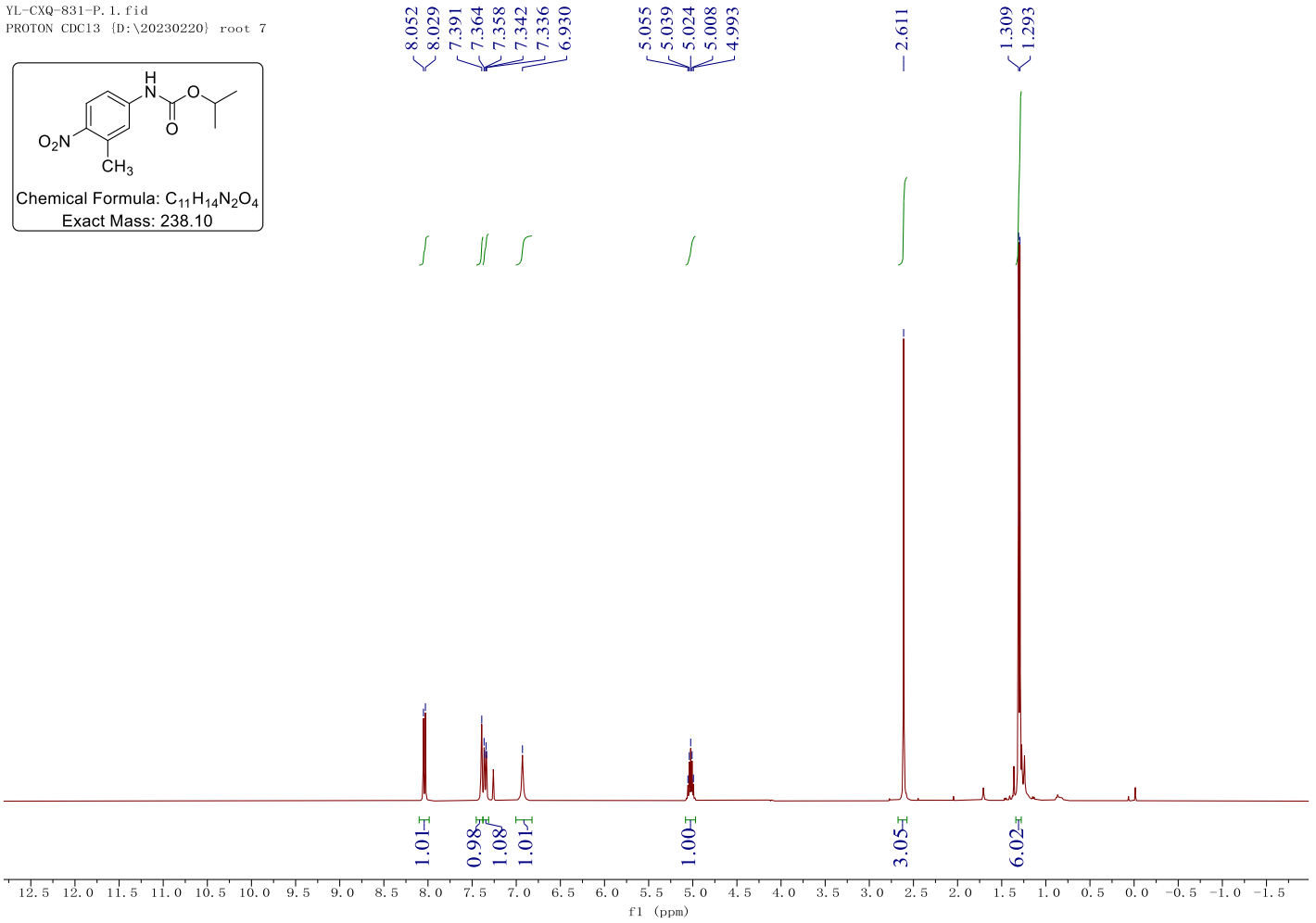
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ta.**



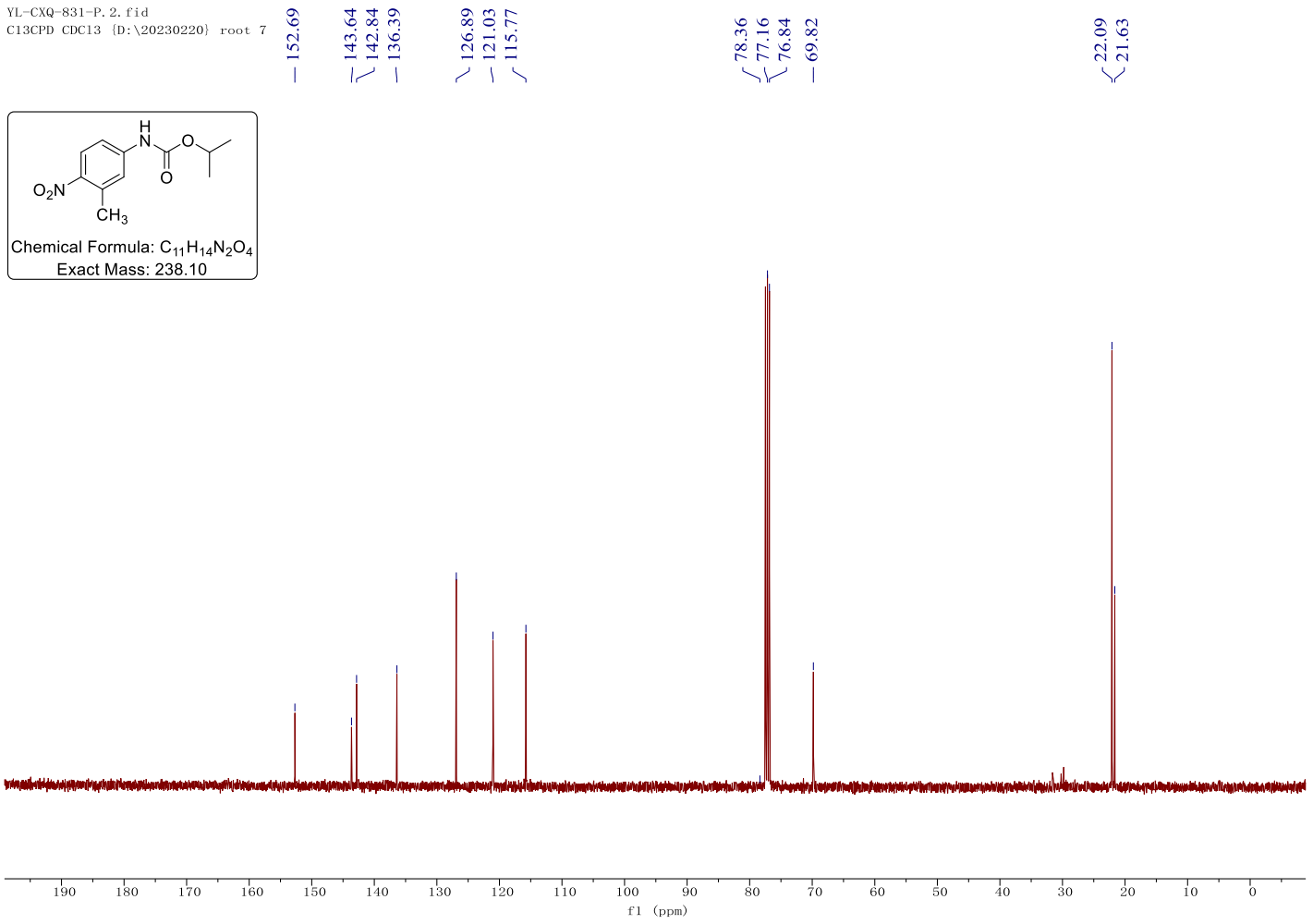
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ta.**



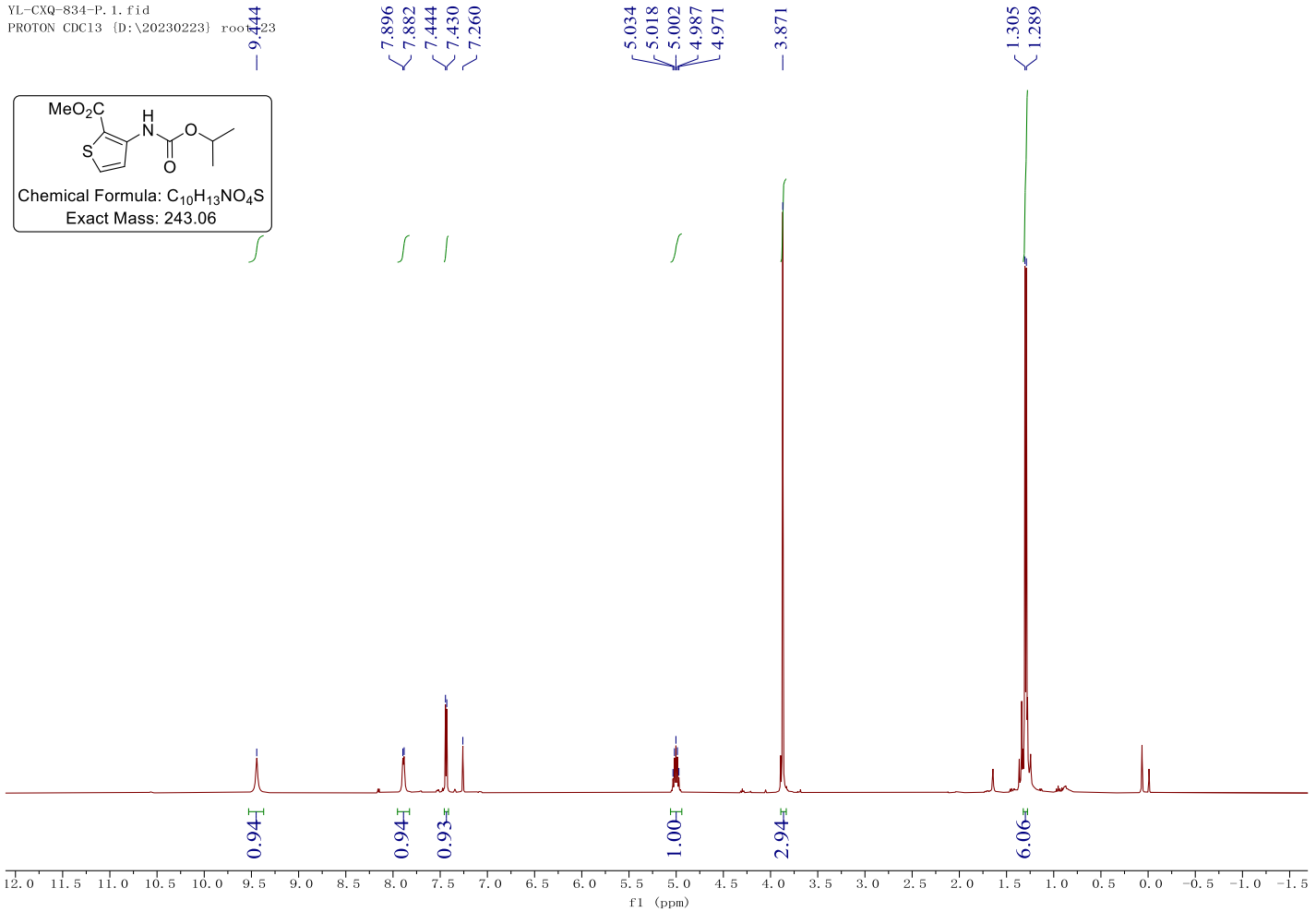
^{1}**H NMR** (400 MHz, $CDCl_3$) spectrum of compound **3ua.**



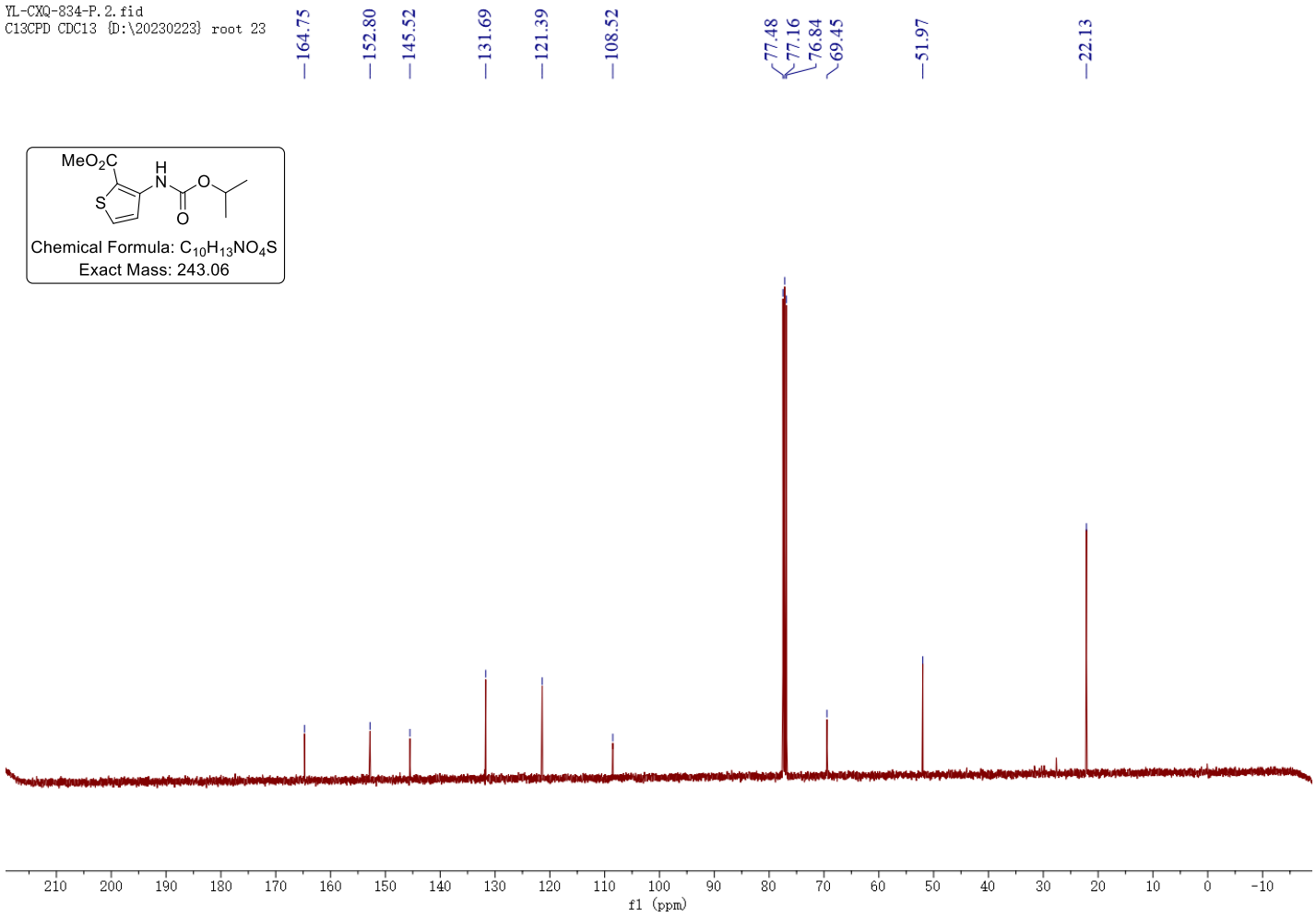
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz) spectrum of compound **3ua.**



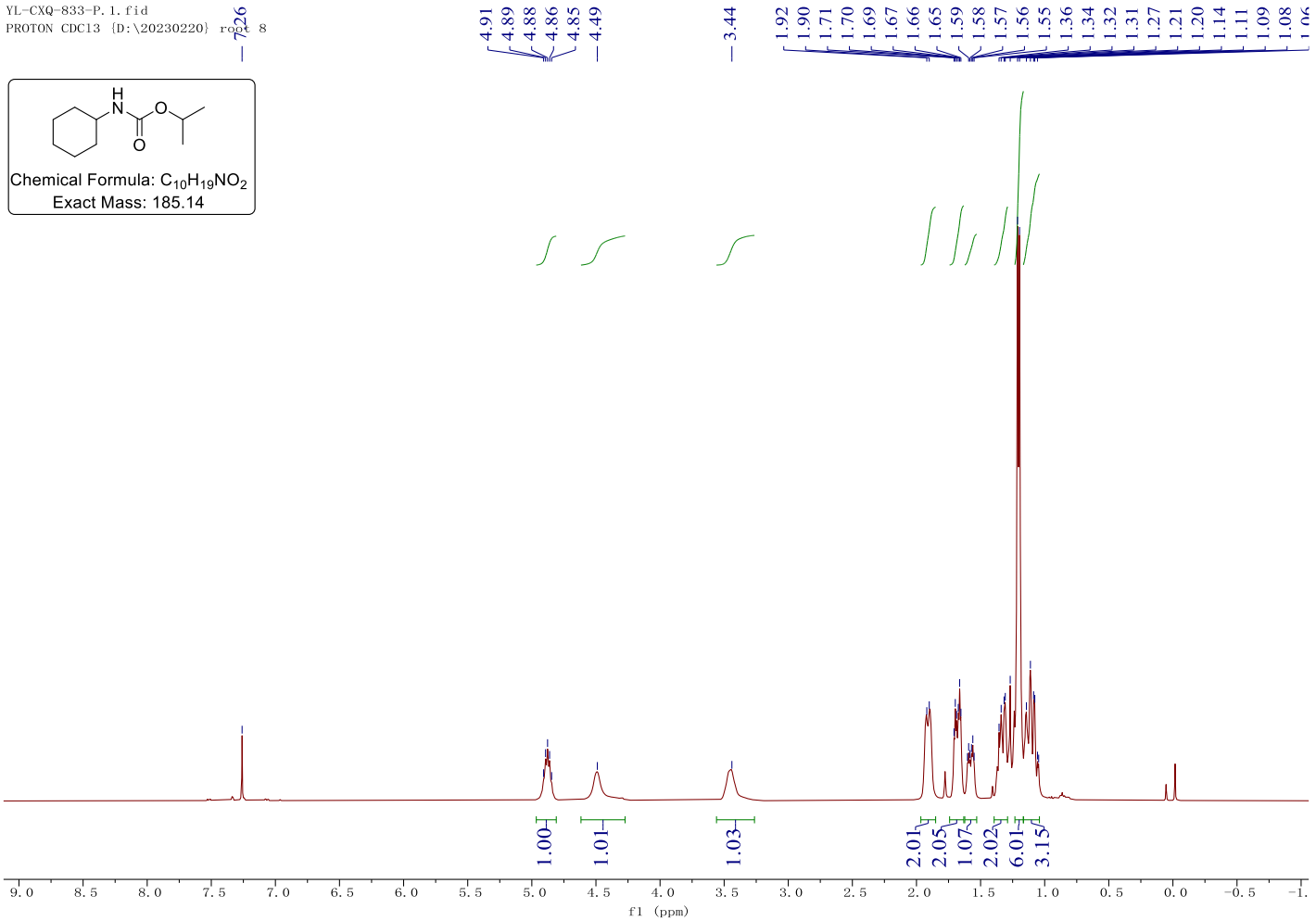
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3va.**



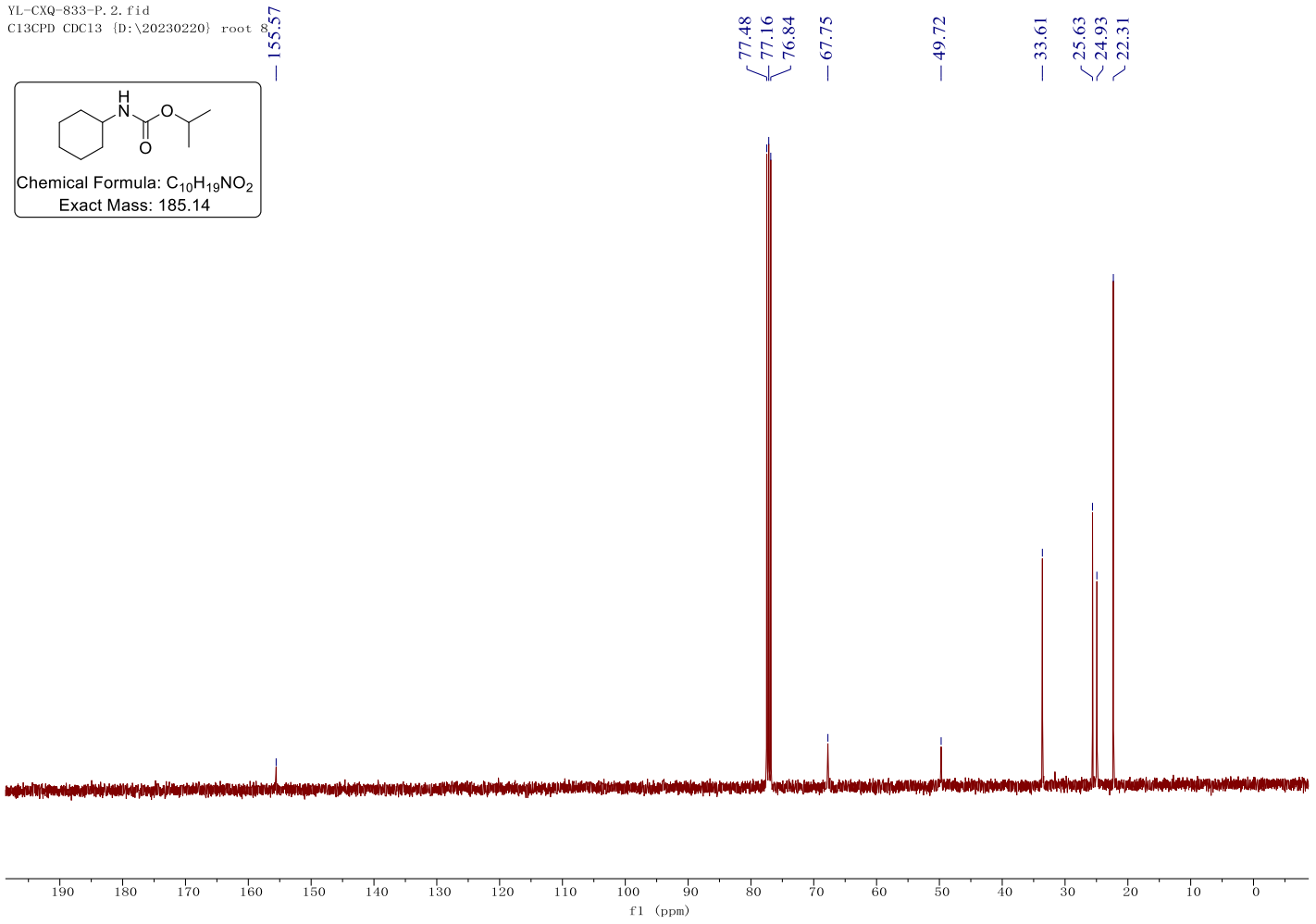
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3va.**



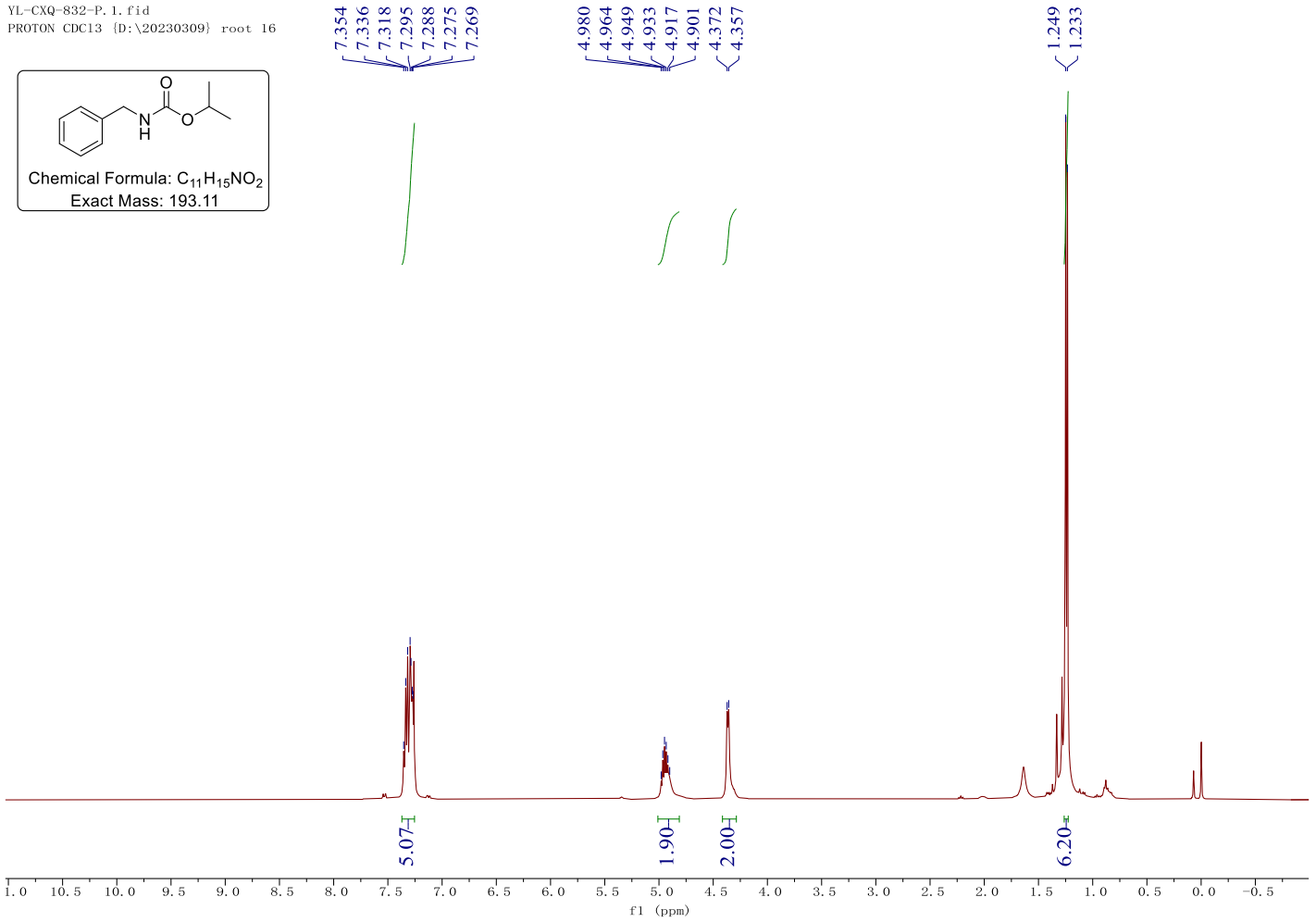
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3wa.**



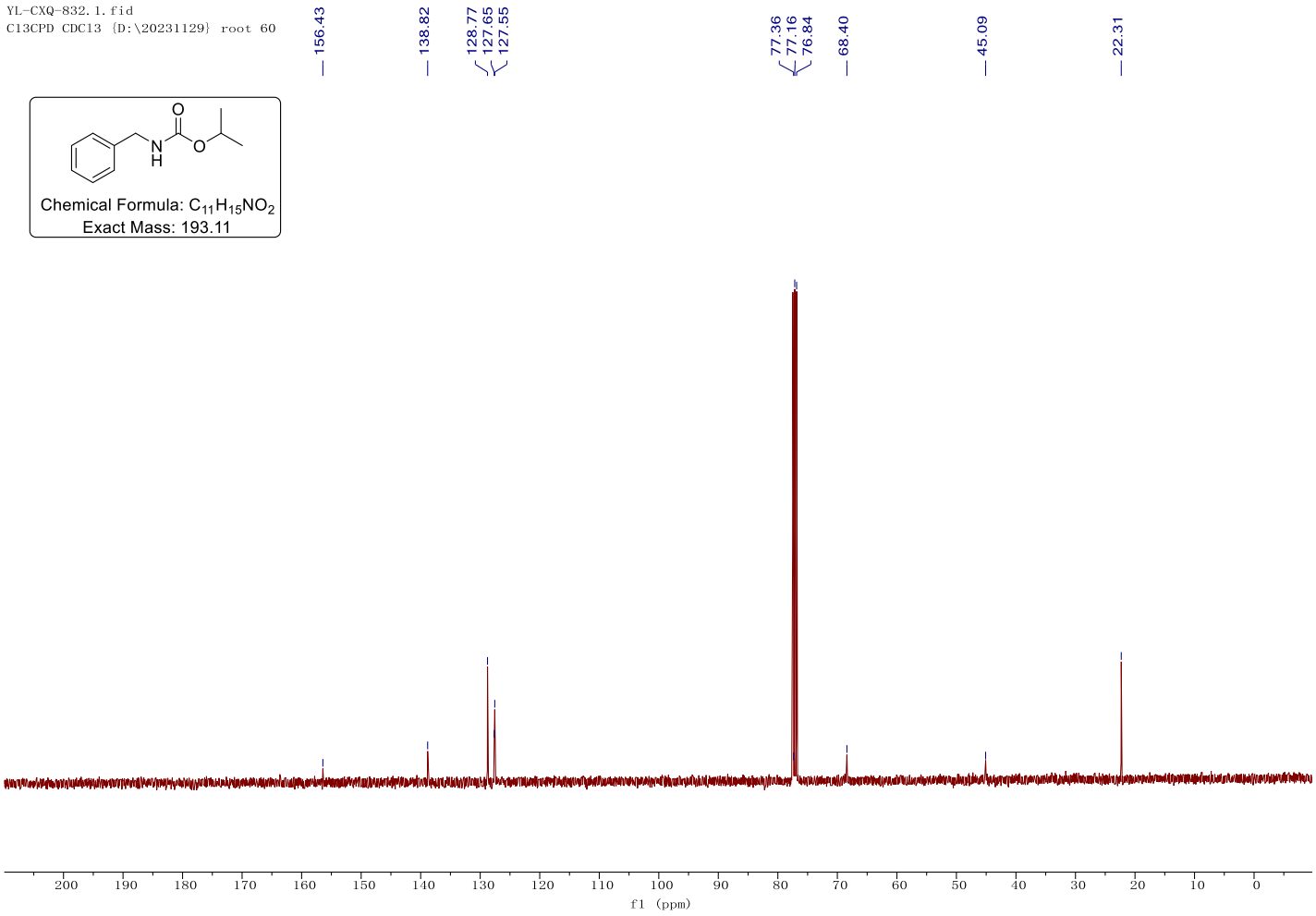
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3wa.**



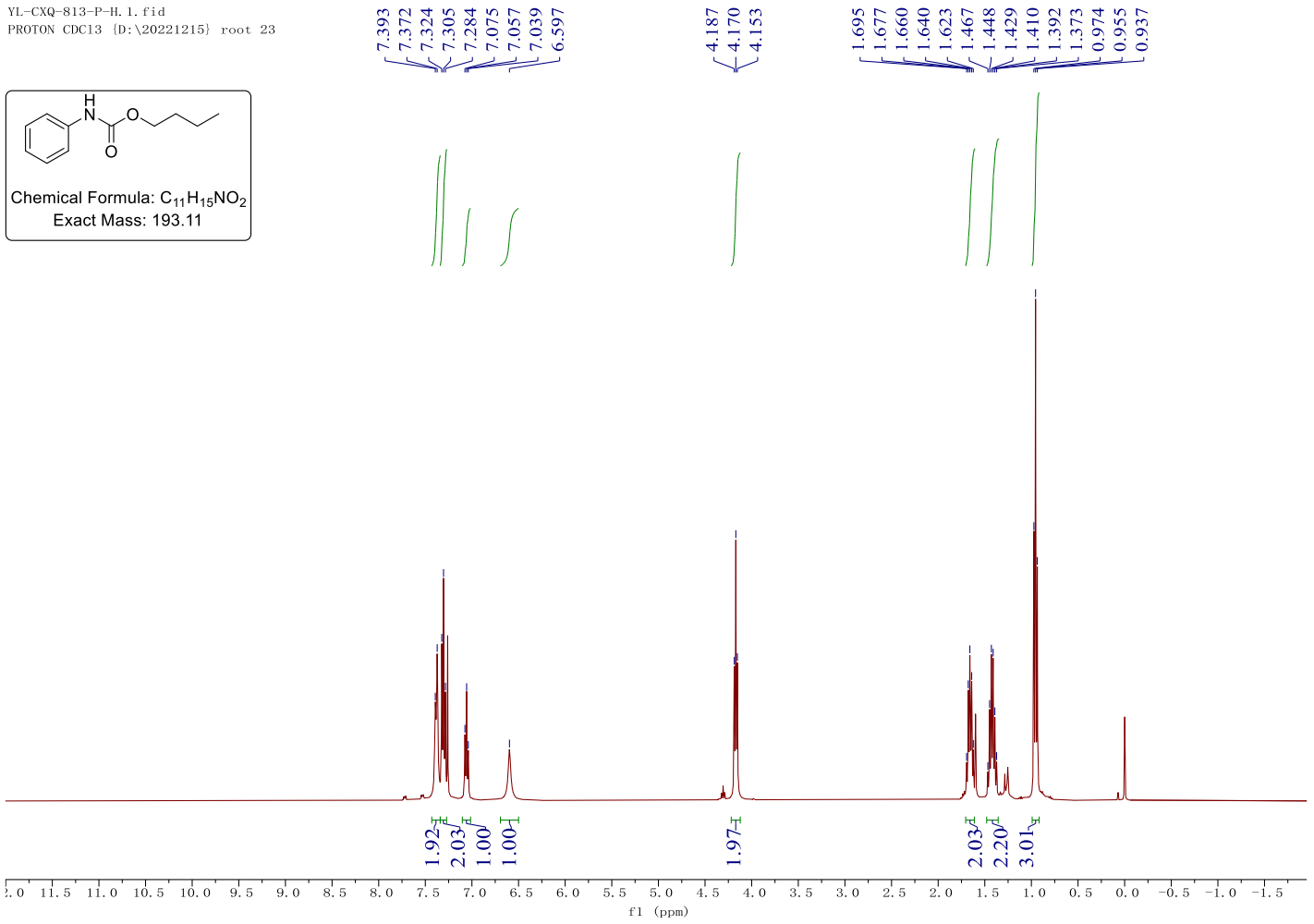
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3xa.**



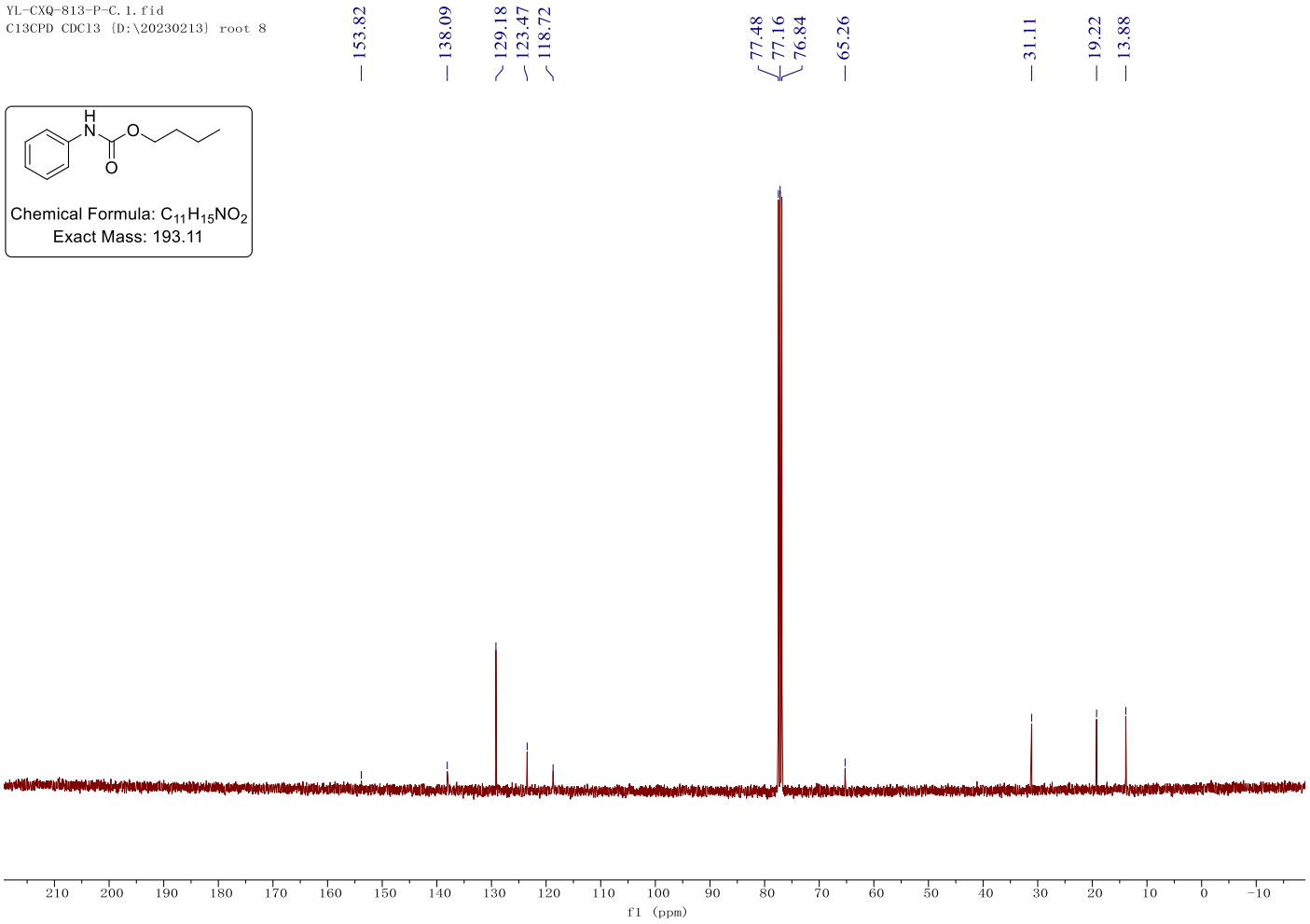
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3xa.**



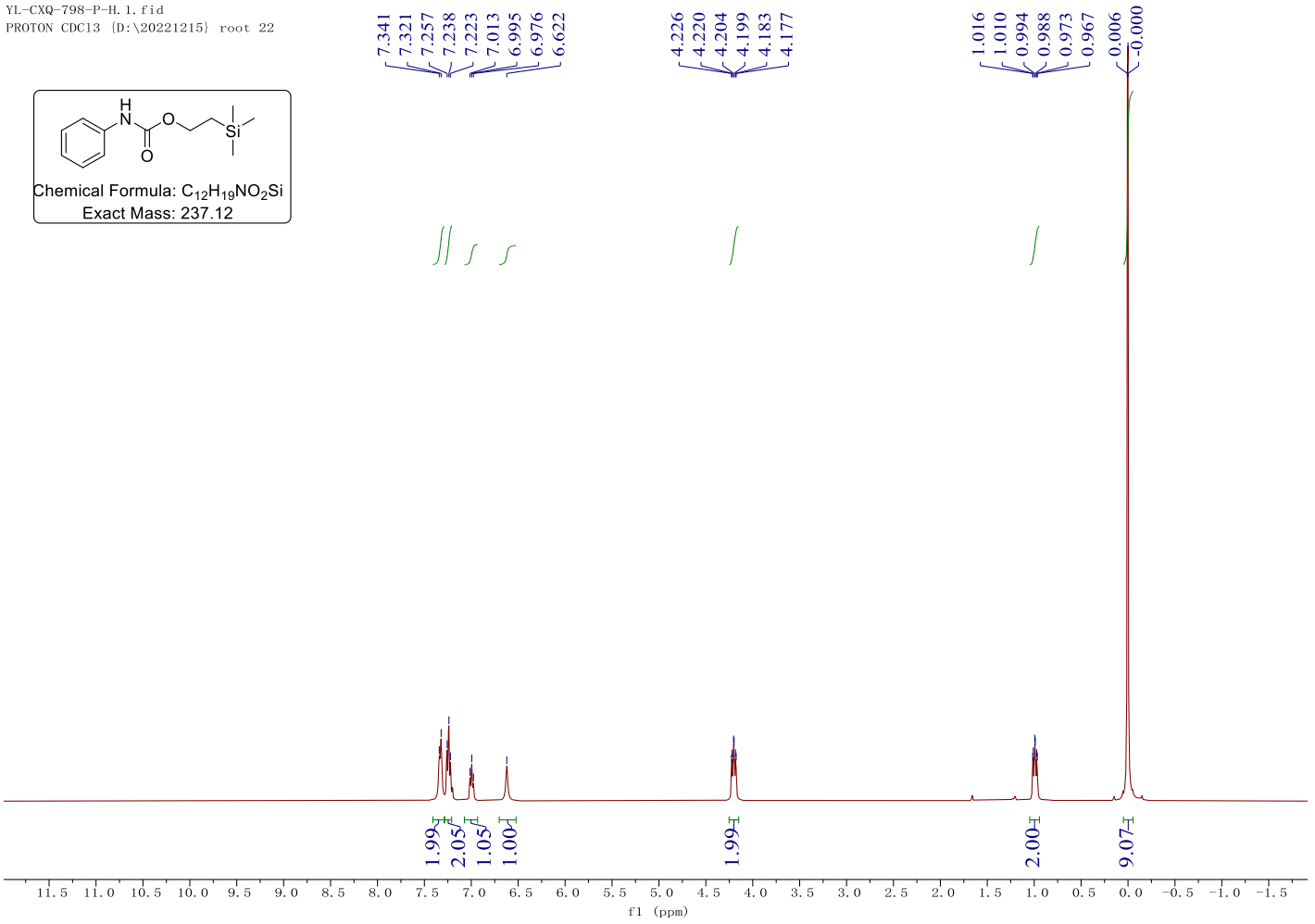
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ab.**



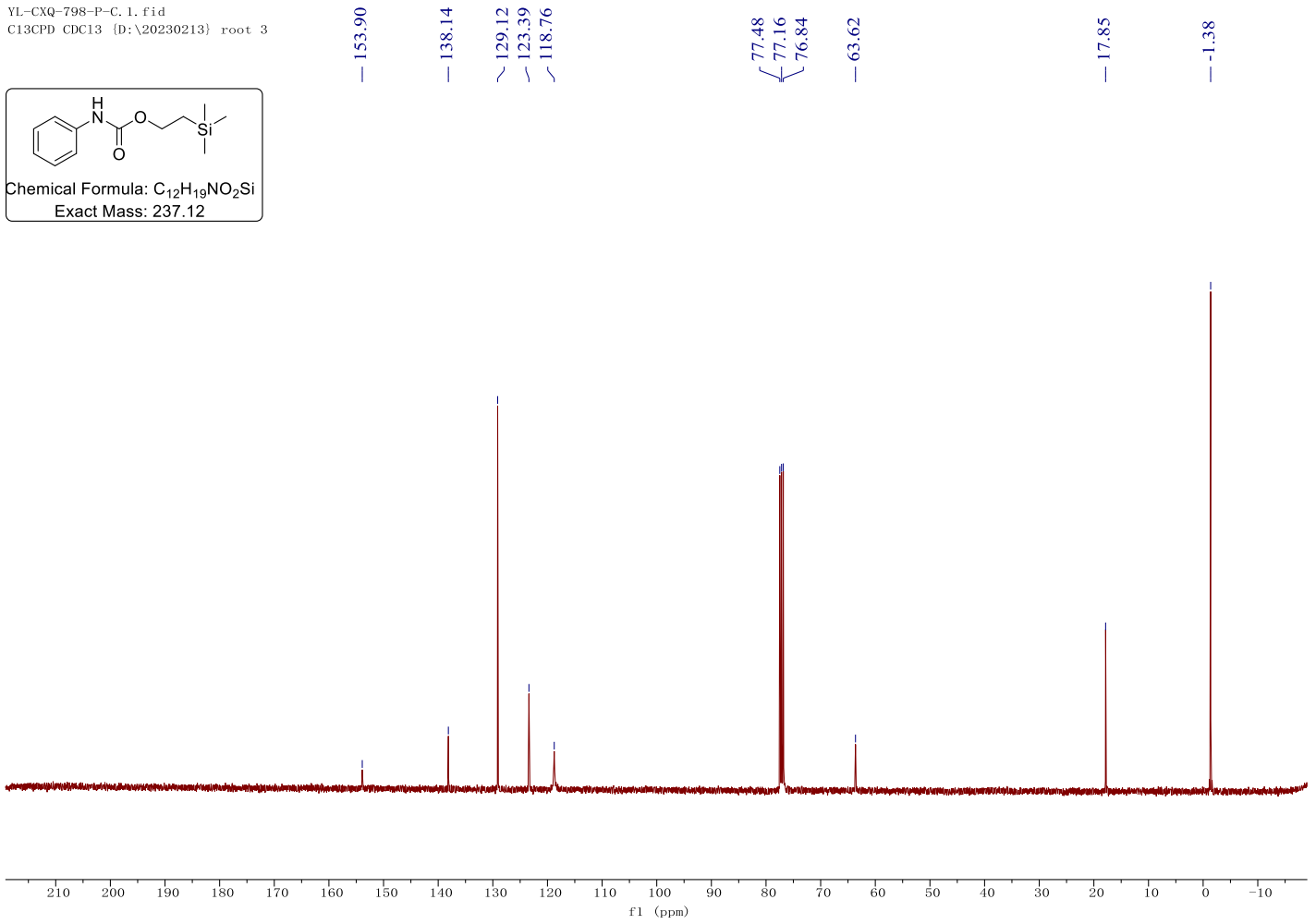
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ab.**



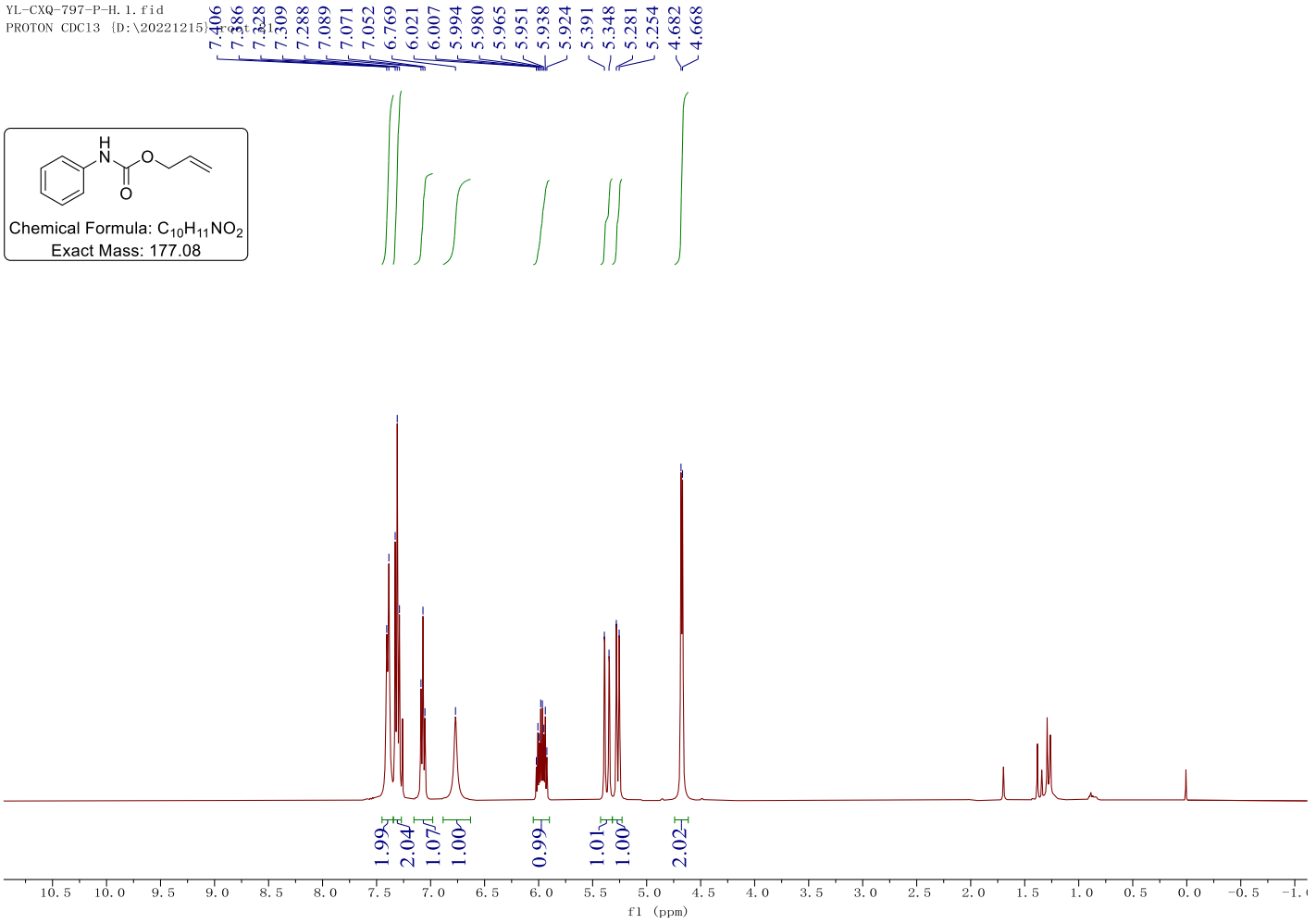
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ac.**



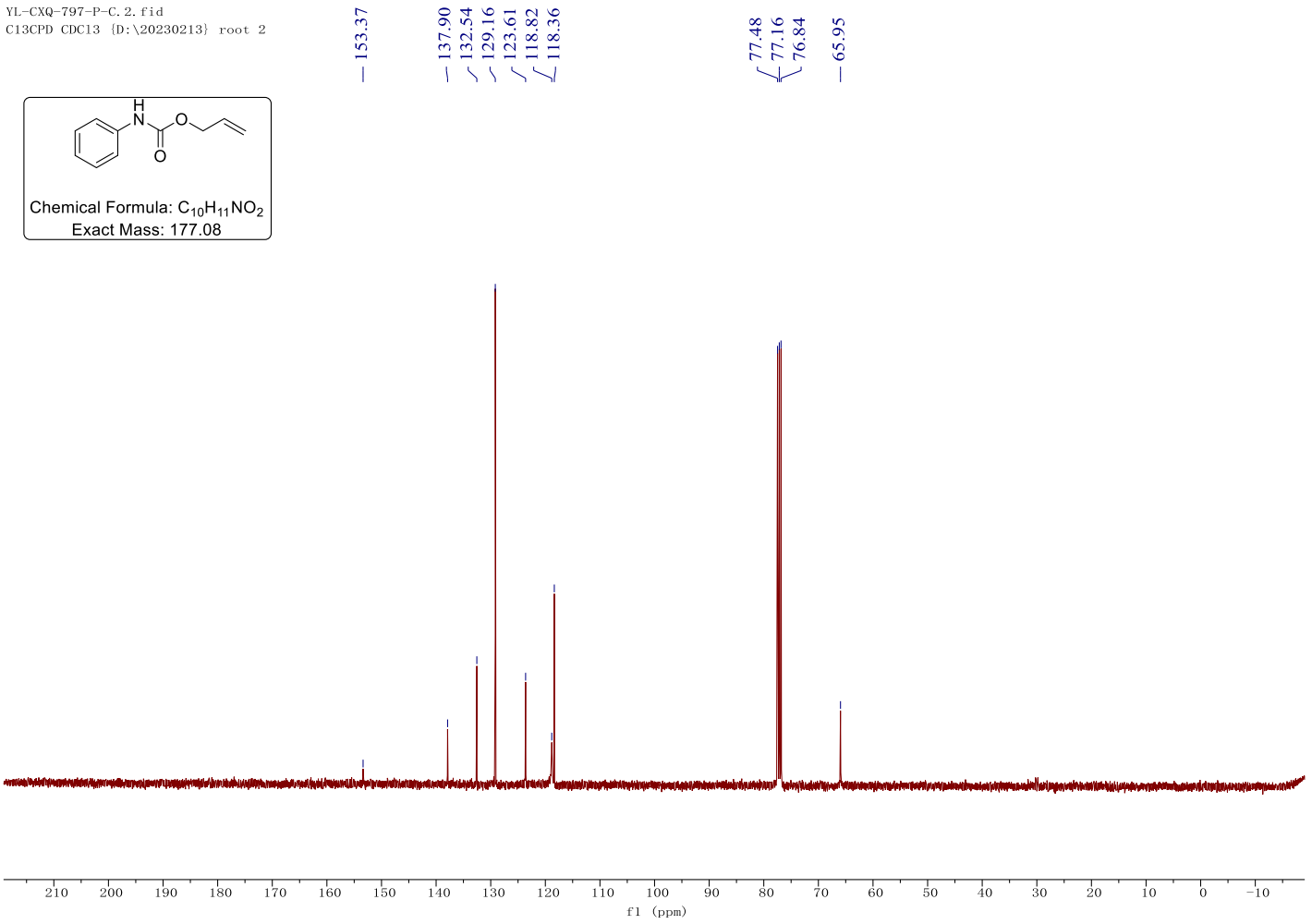
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ac.**



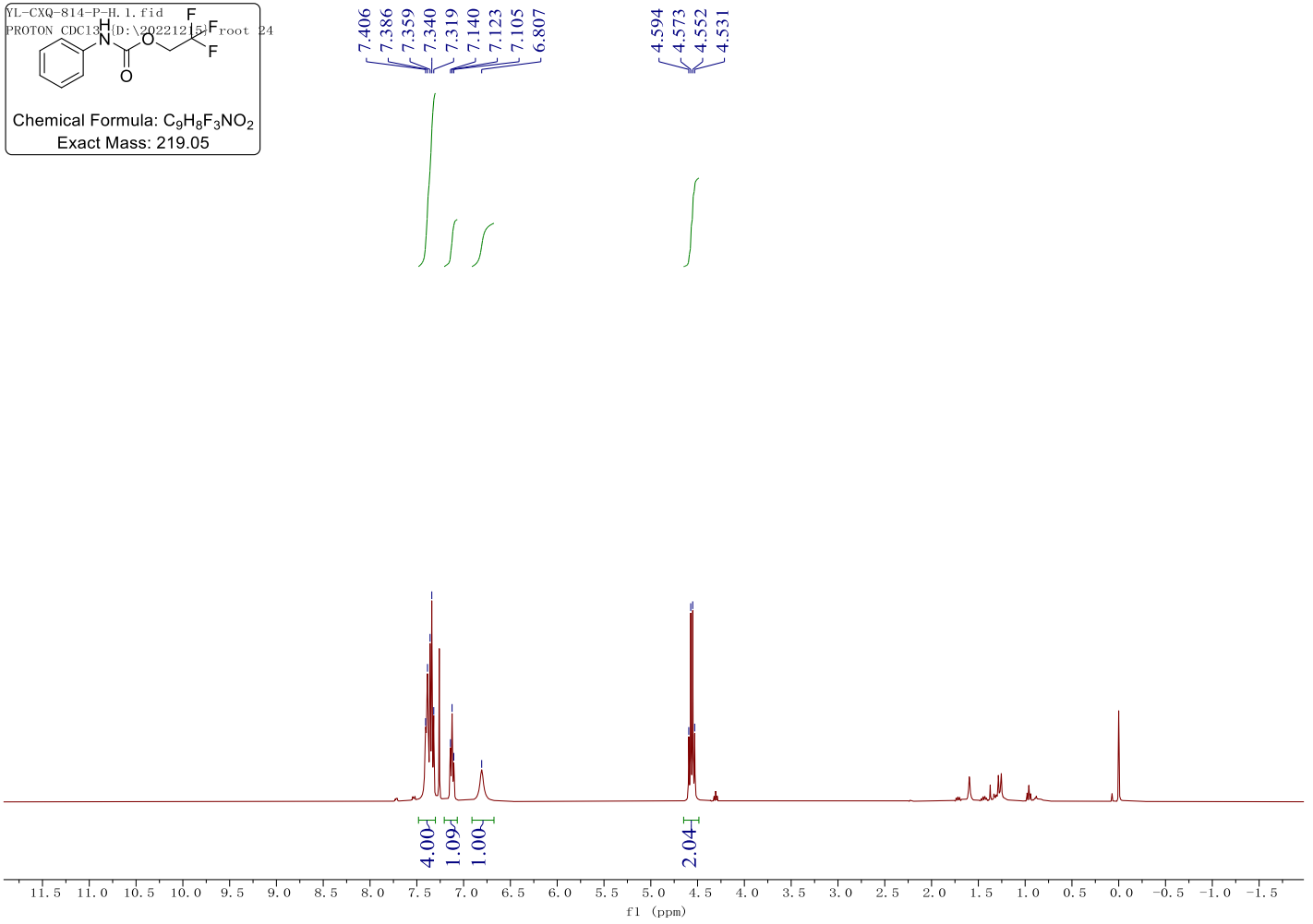
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ad.**



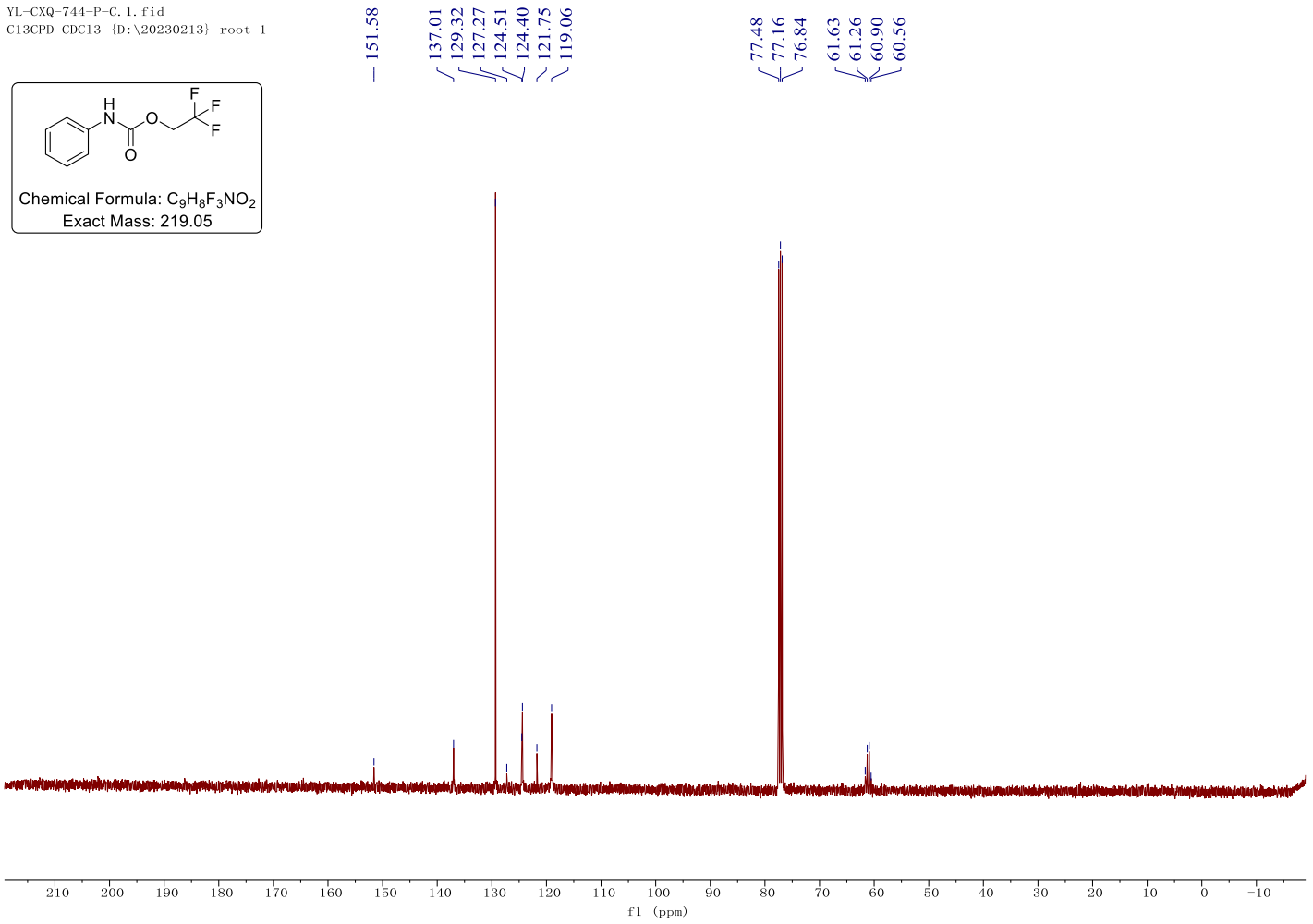
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ad.**



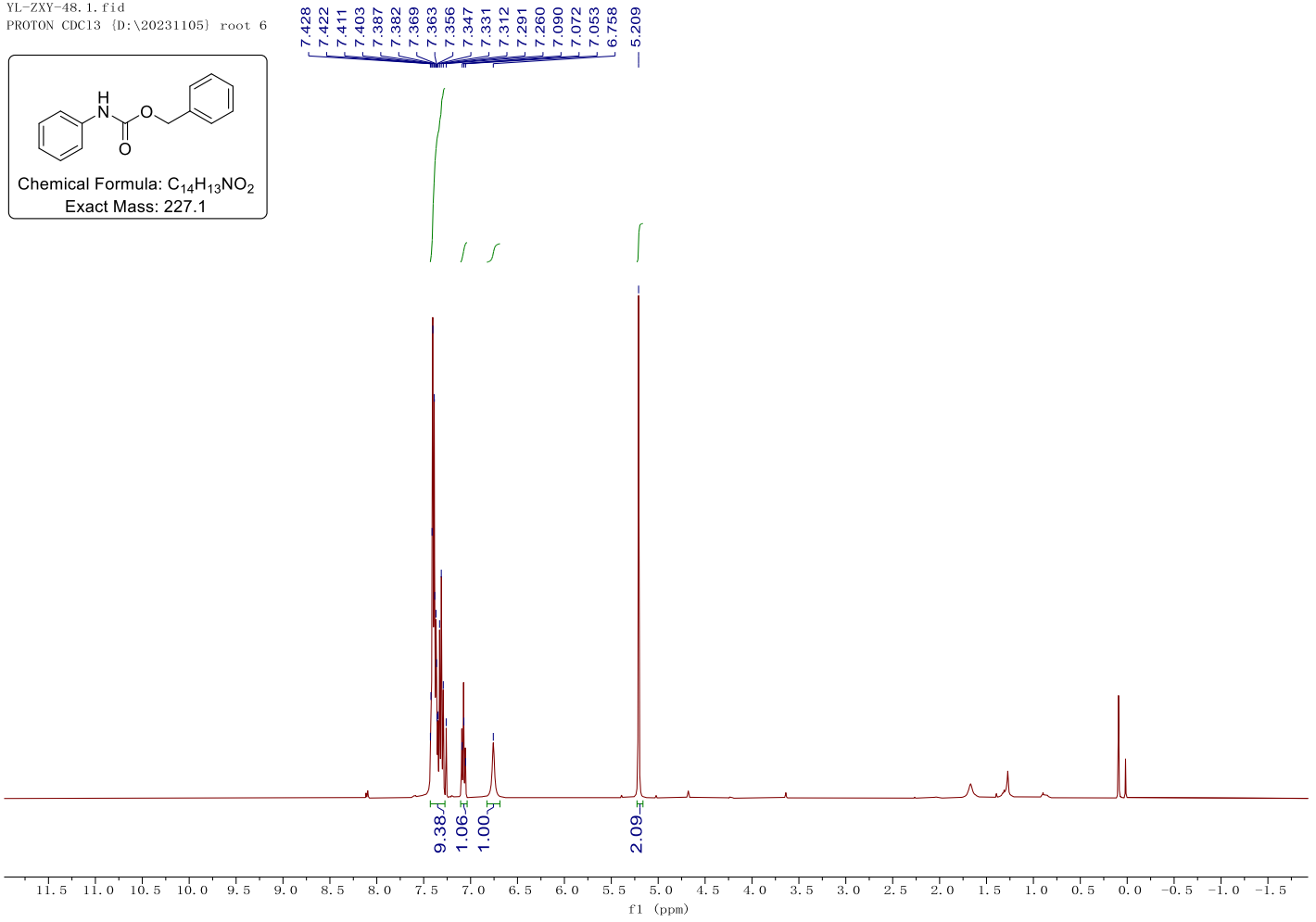
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ae.**



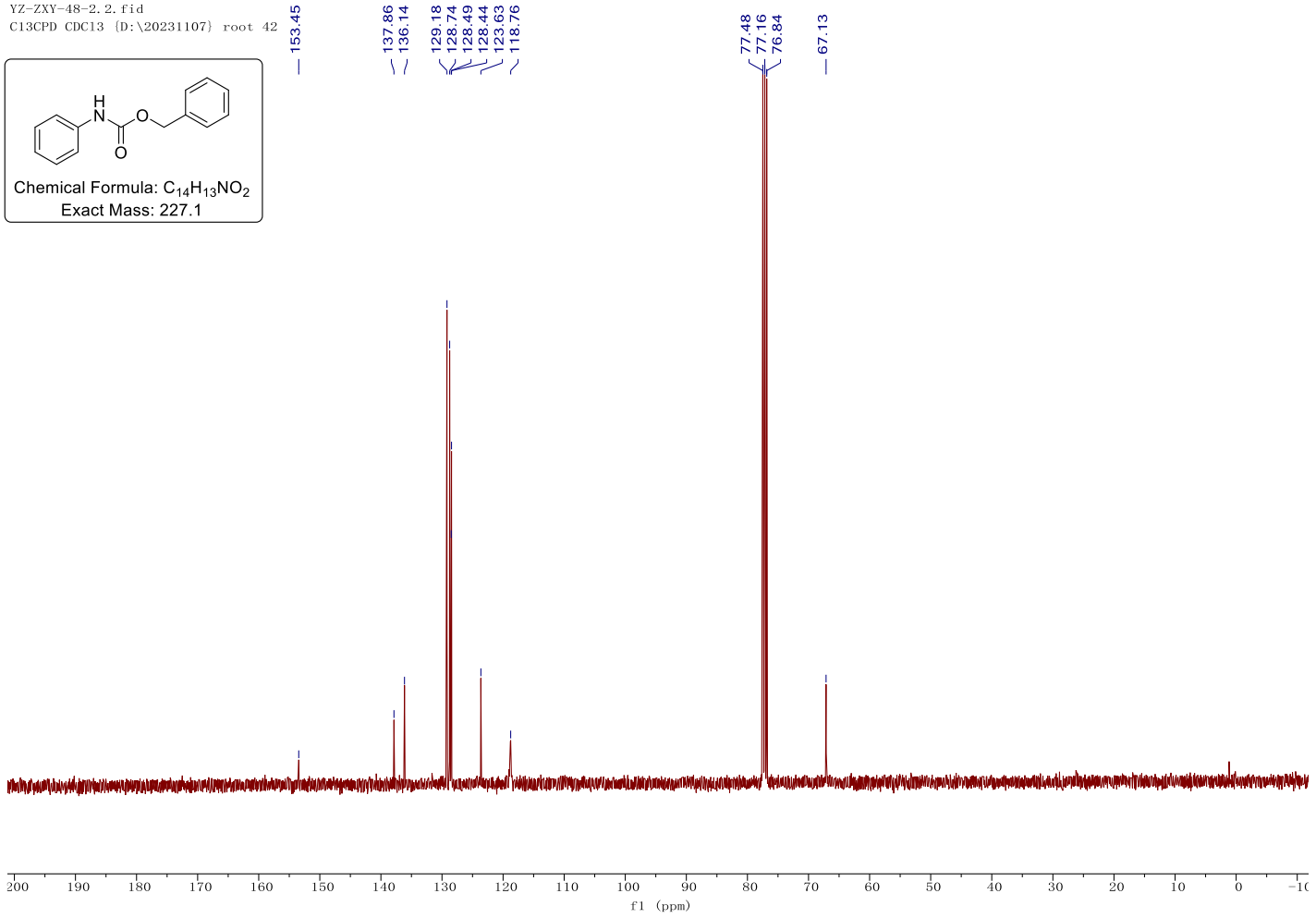
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ae.**



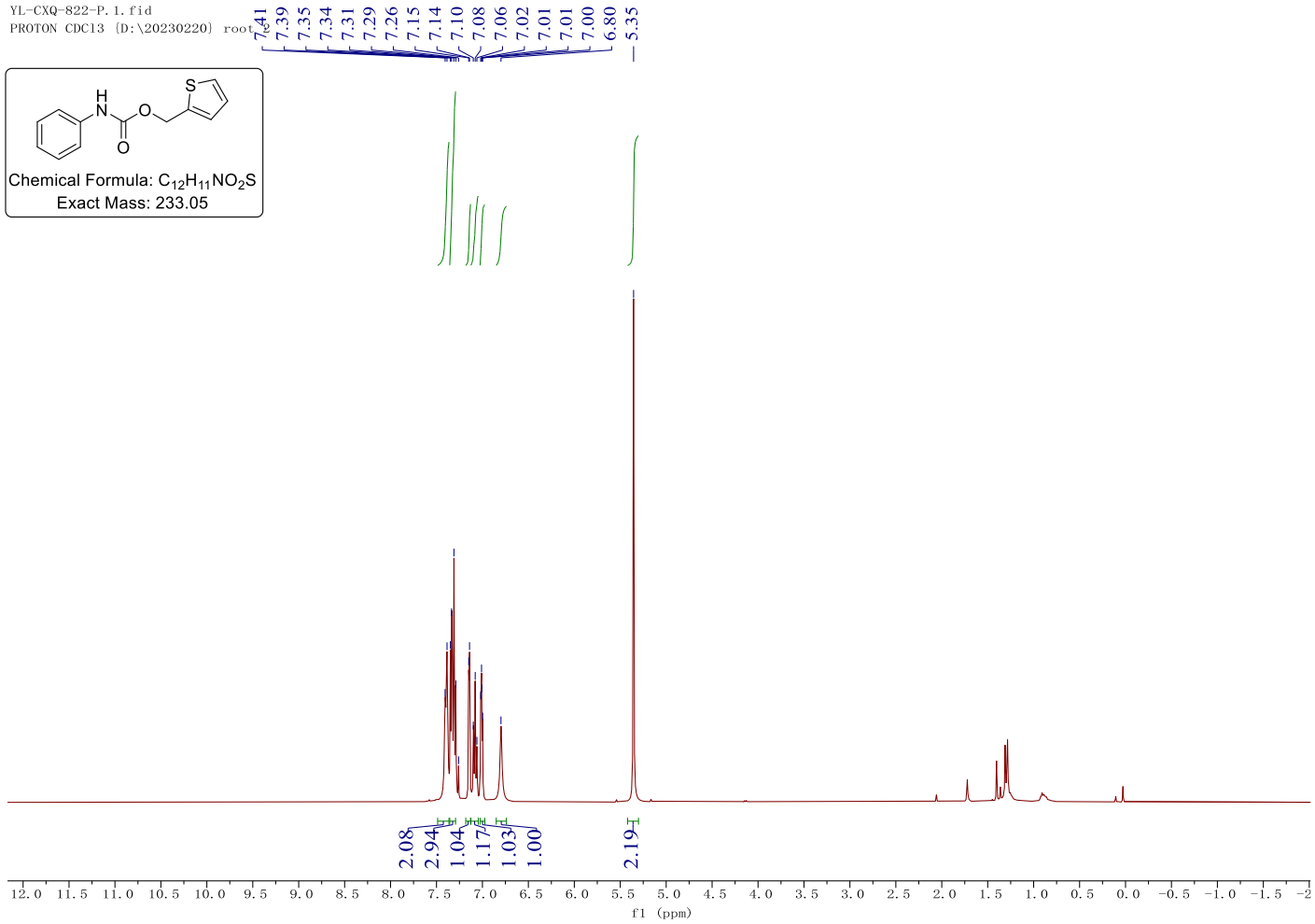
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3af.**



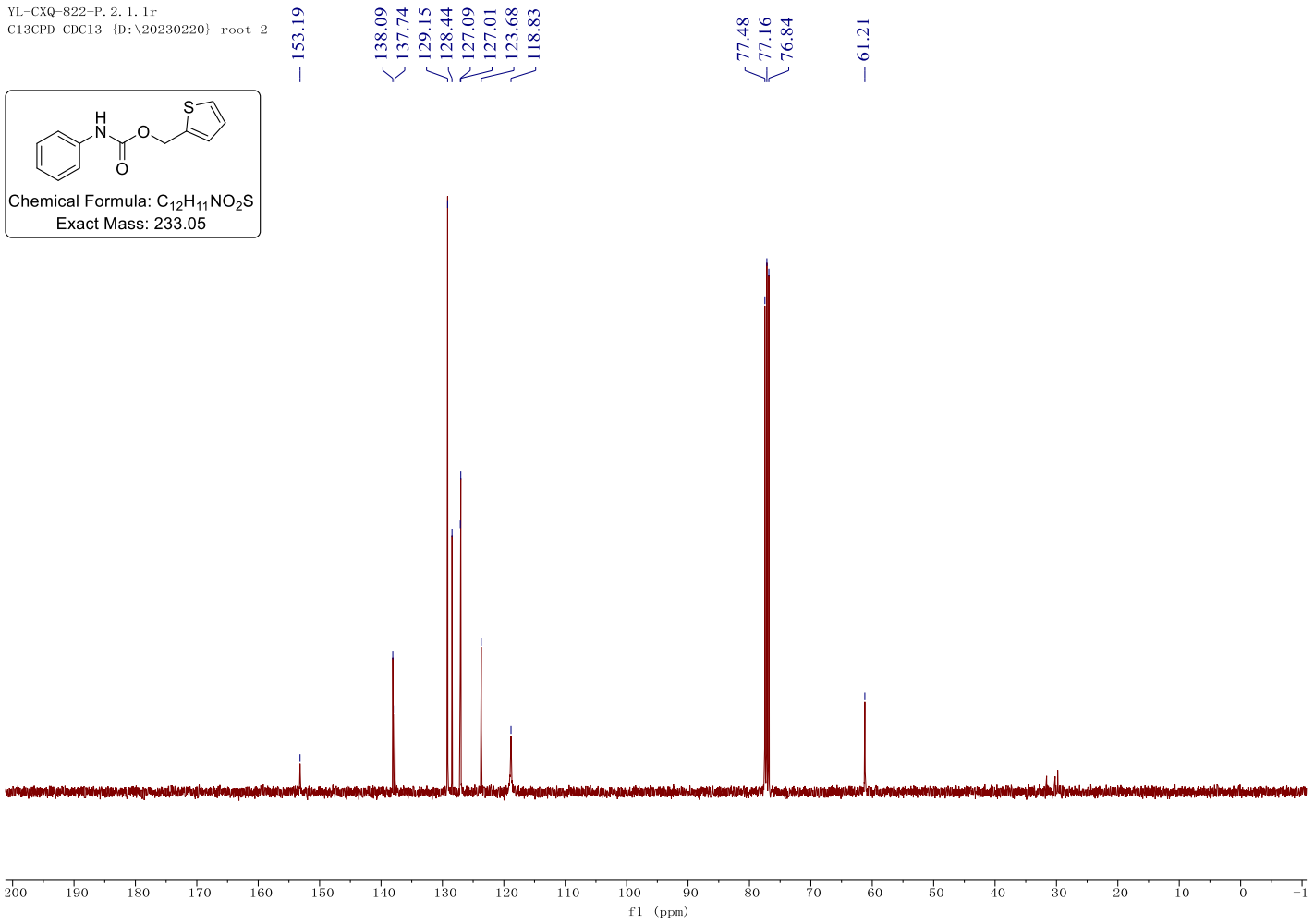
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3af.**



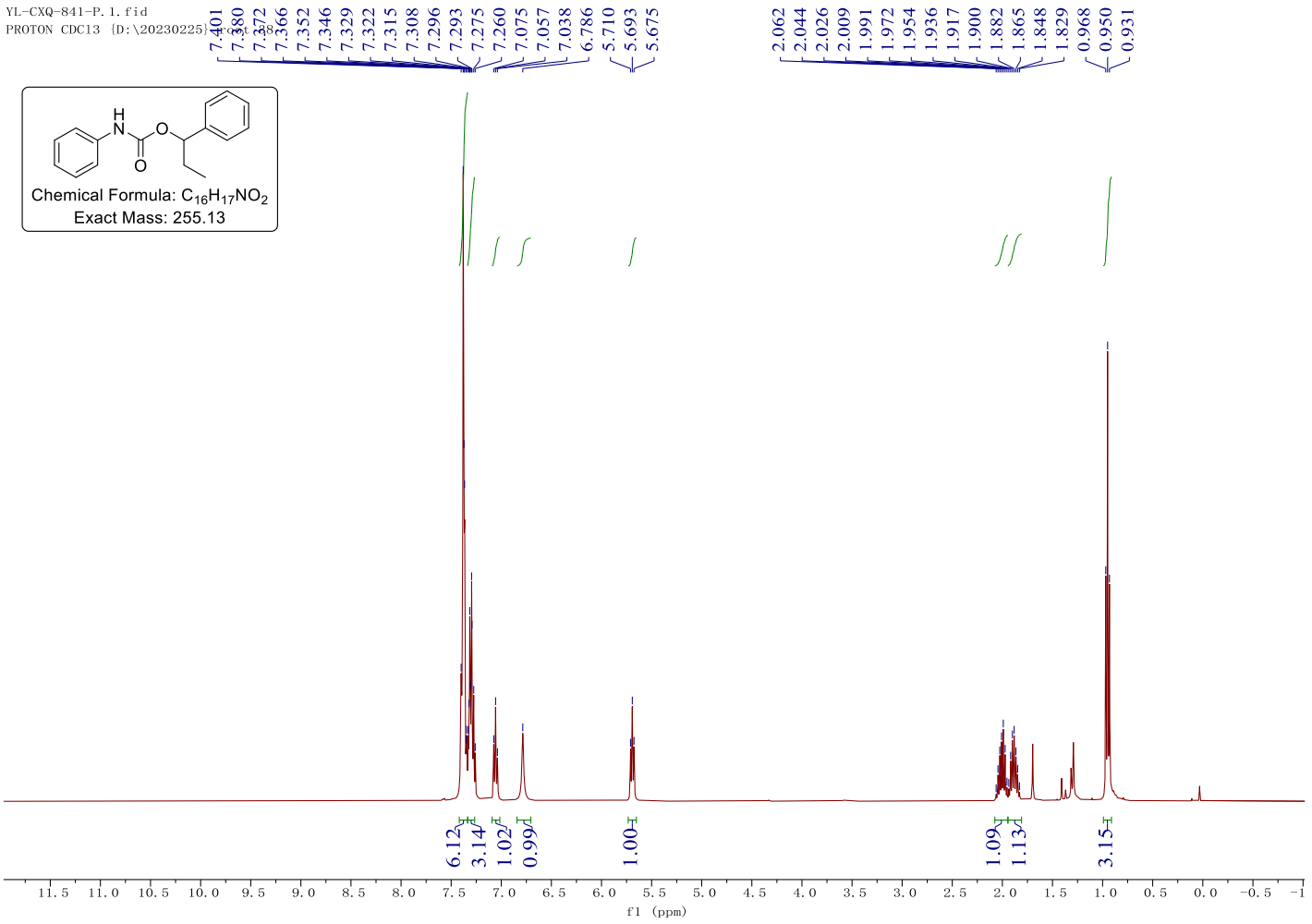
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ag.**



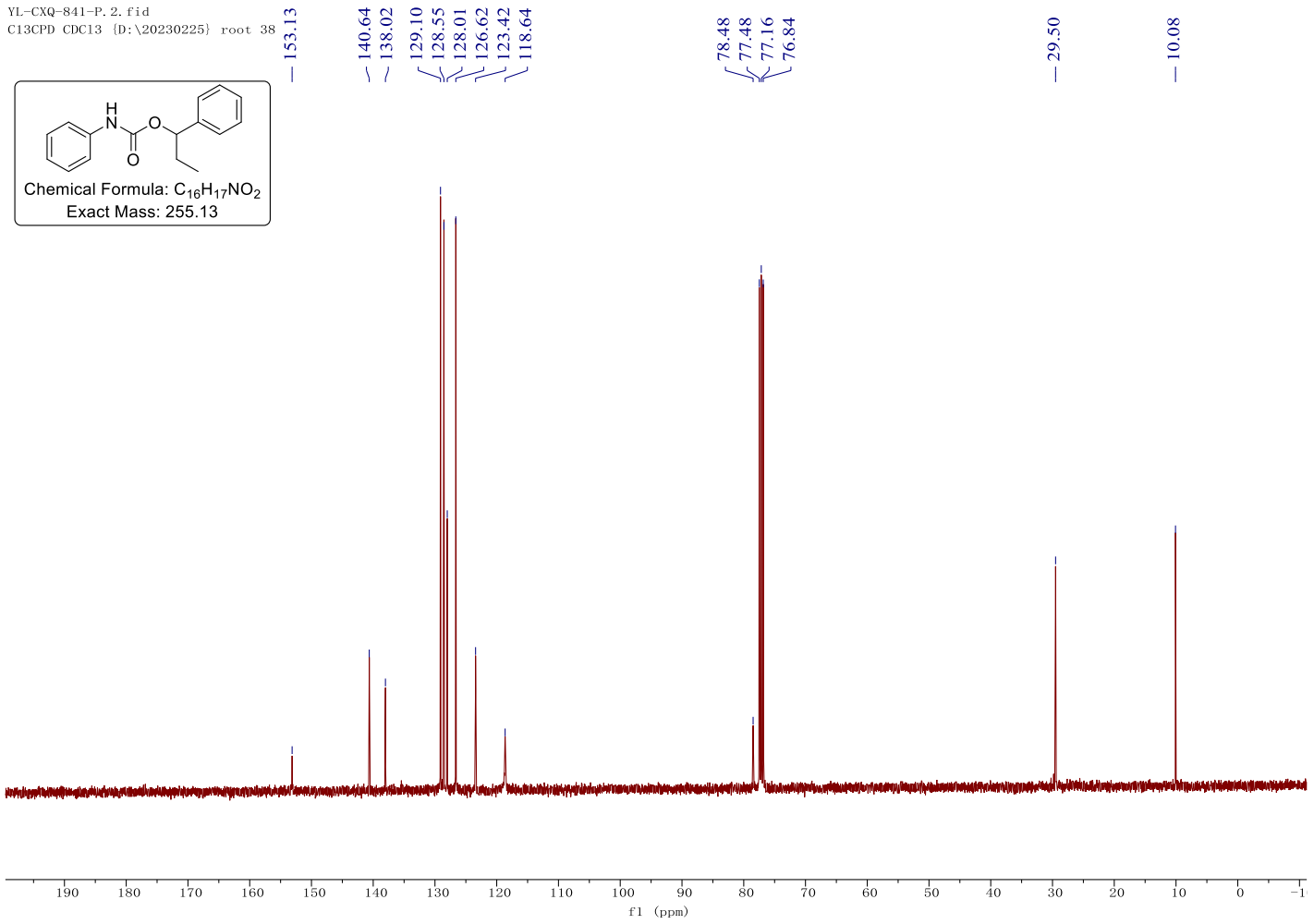
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ag.**



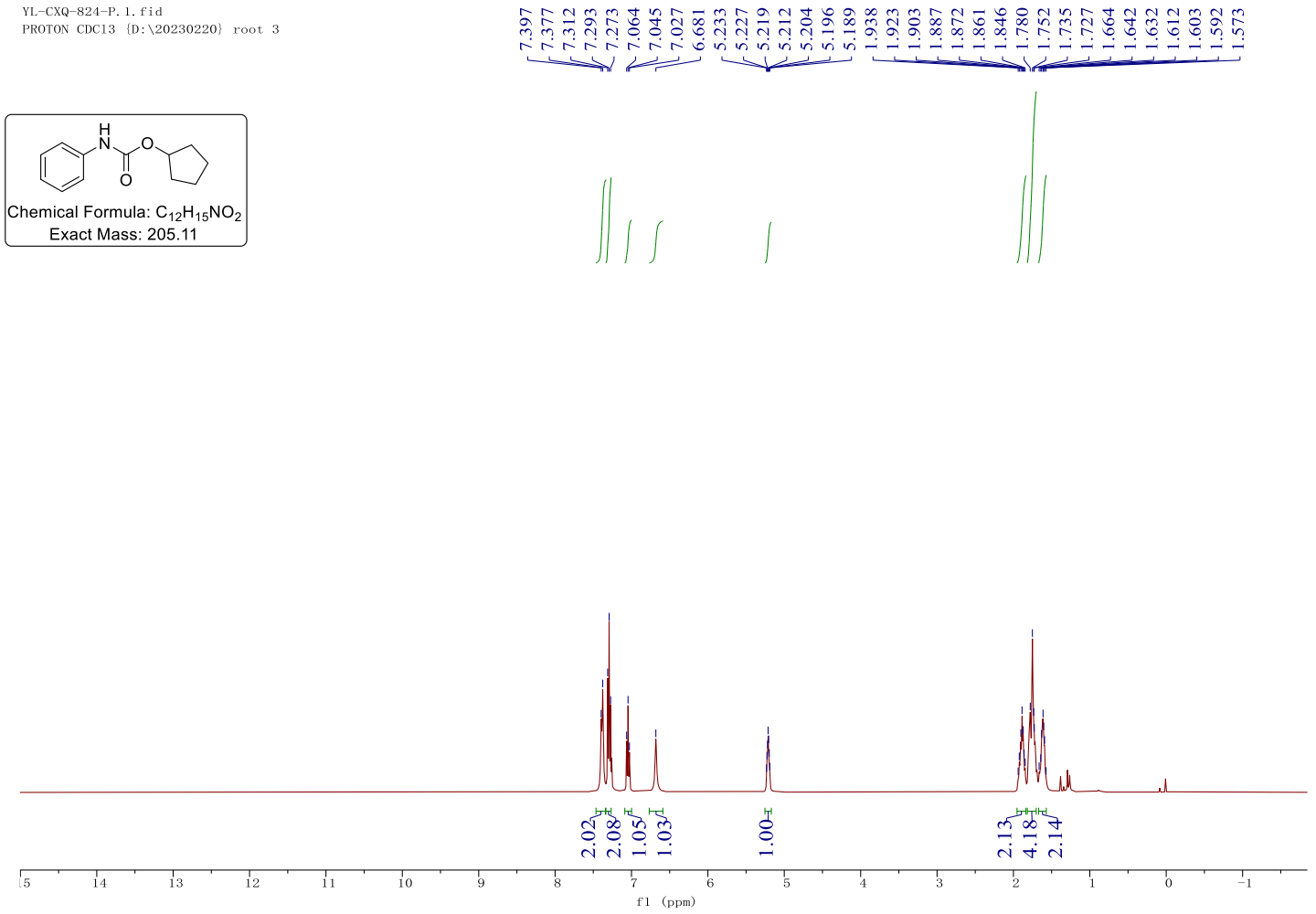
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ah.**



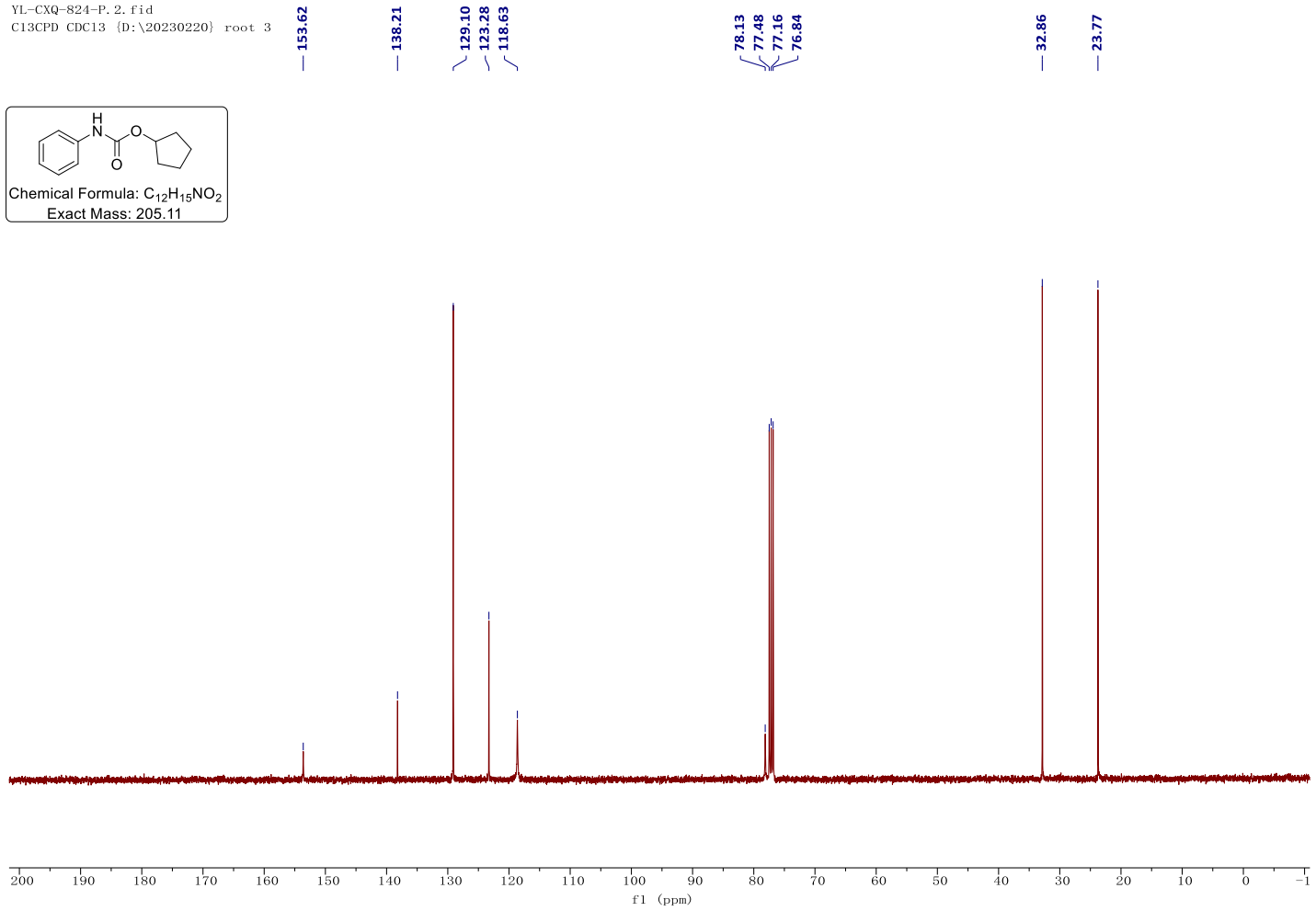
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ah.**



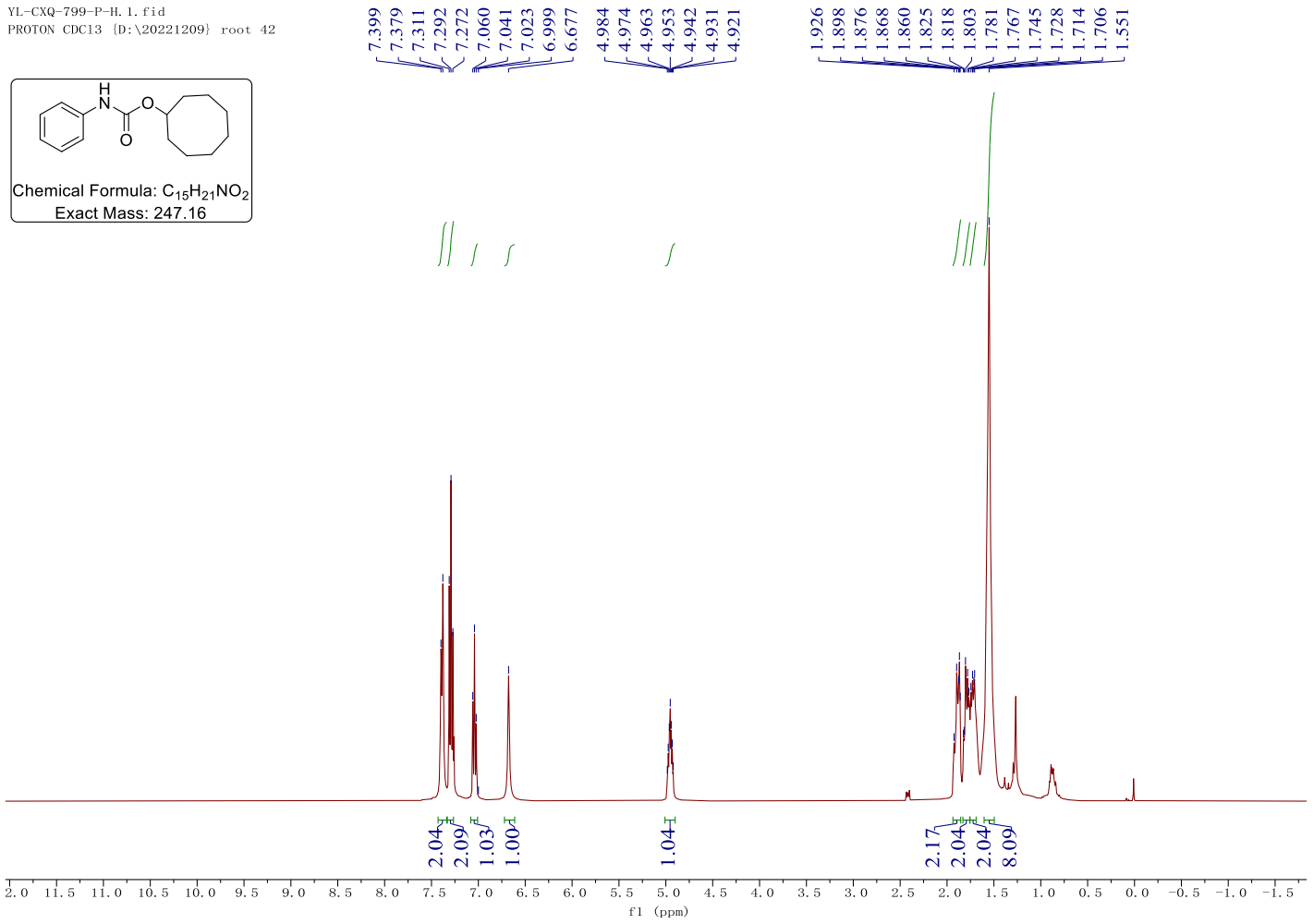
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ai.**



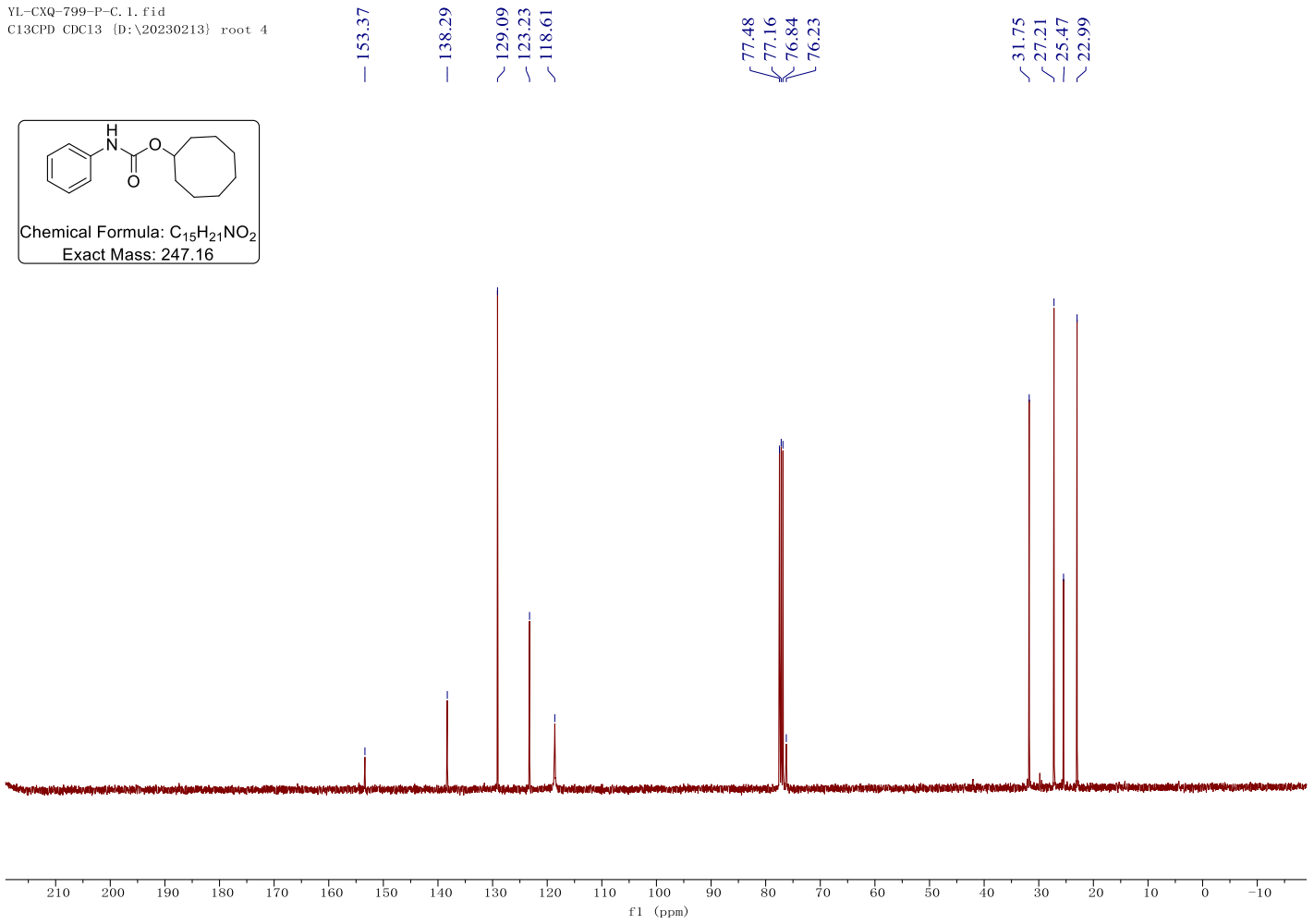
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ai.**



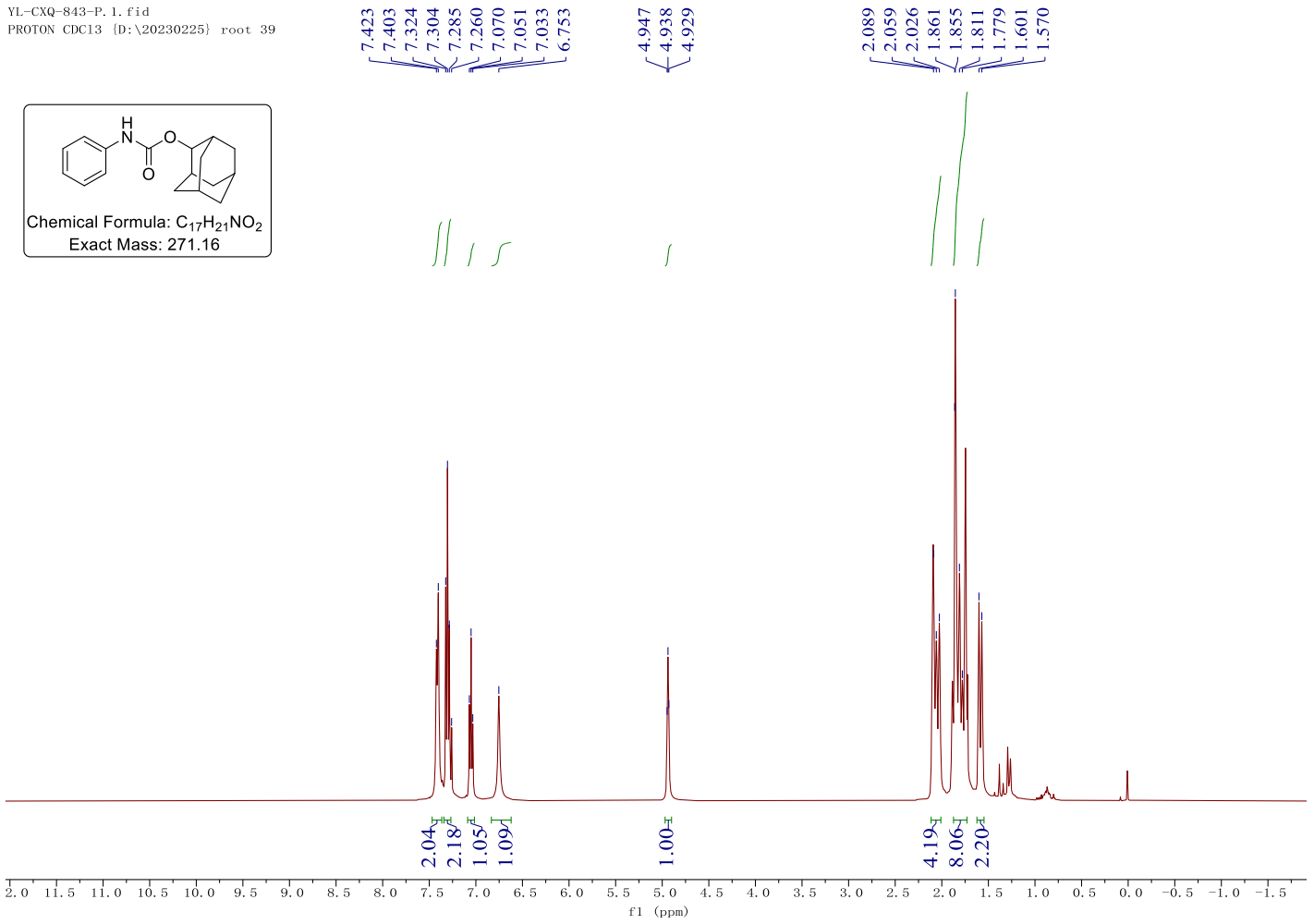
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aj.**



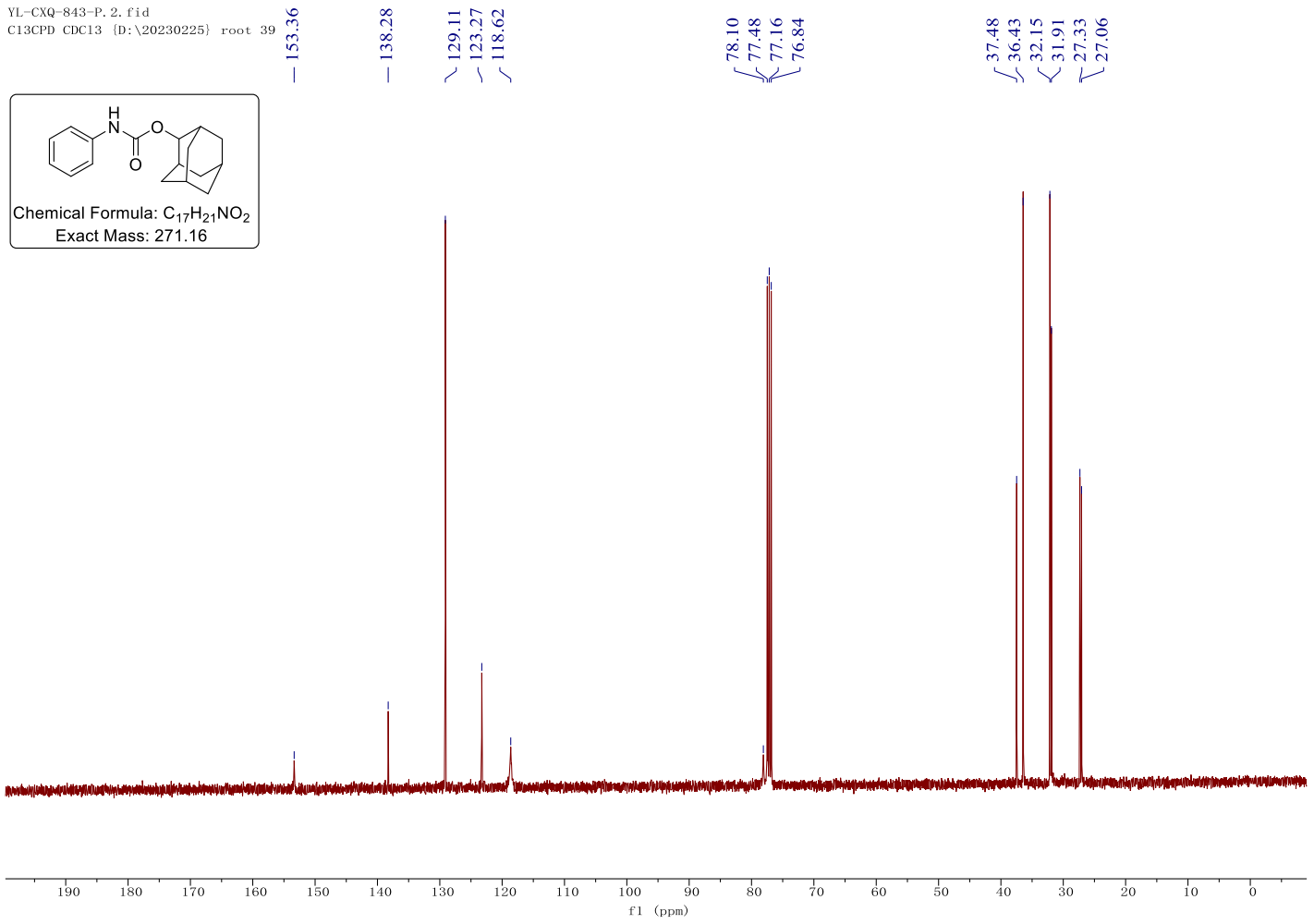
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3aj.**



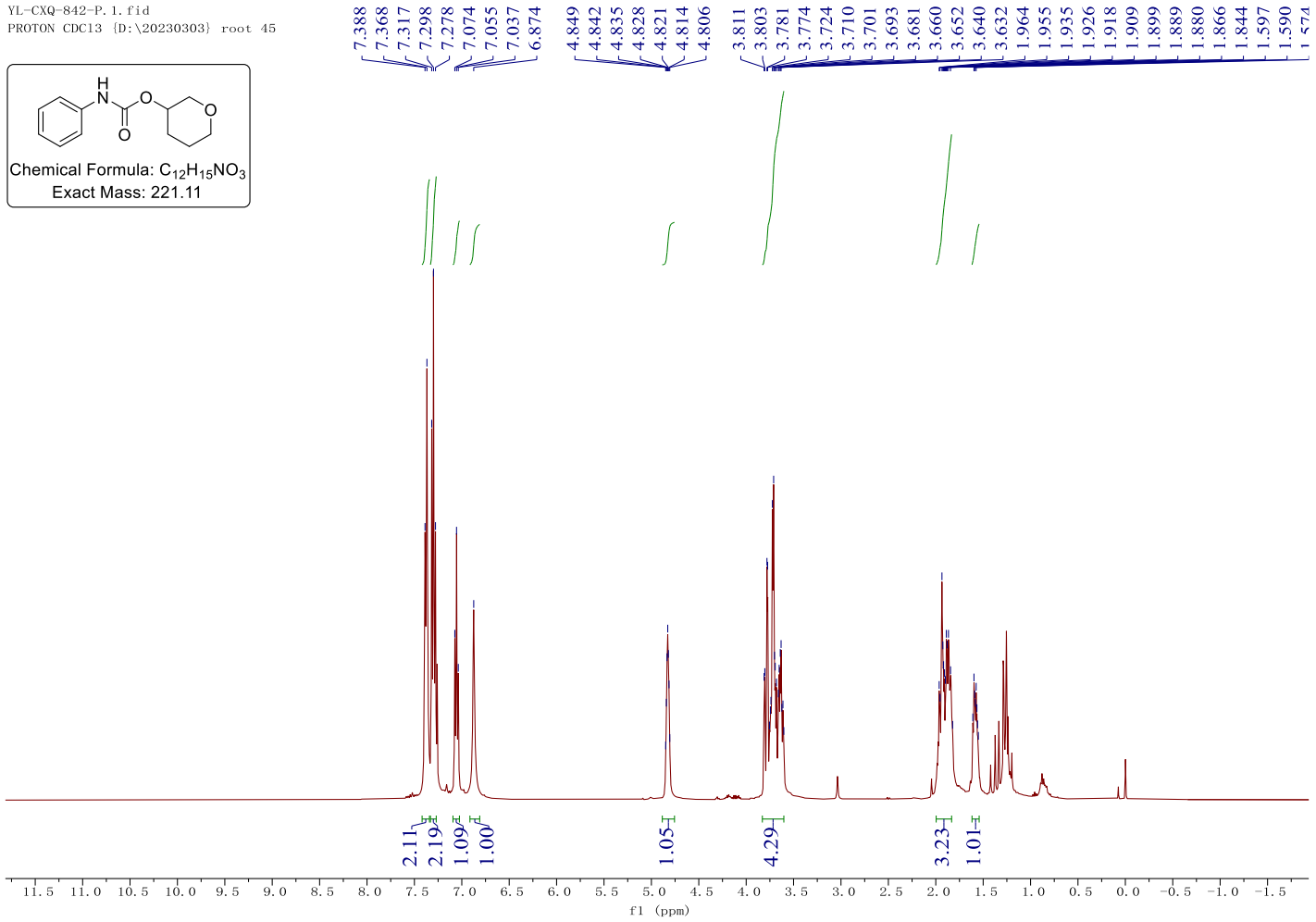
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ak.**



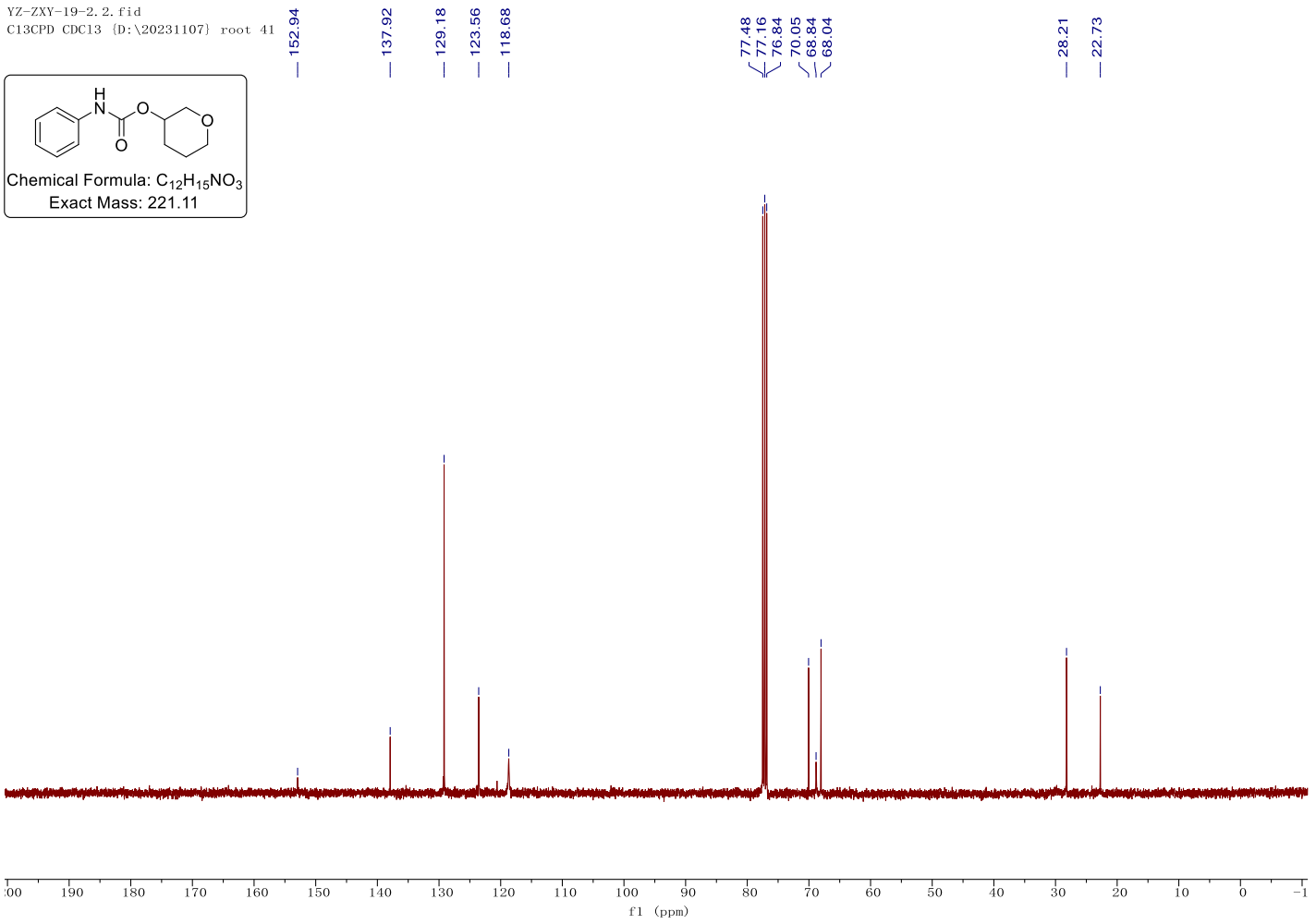
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ak.**



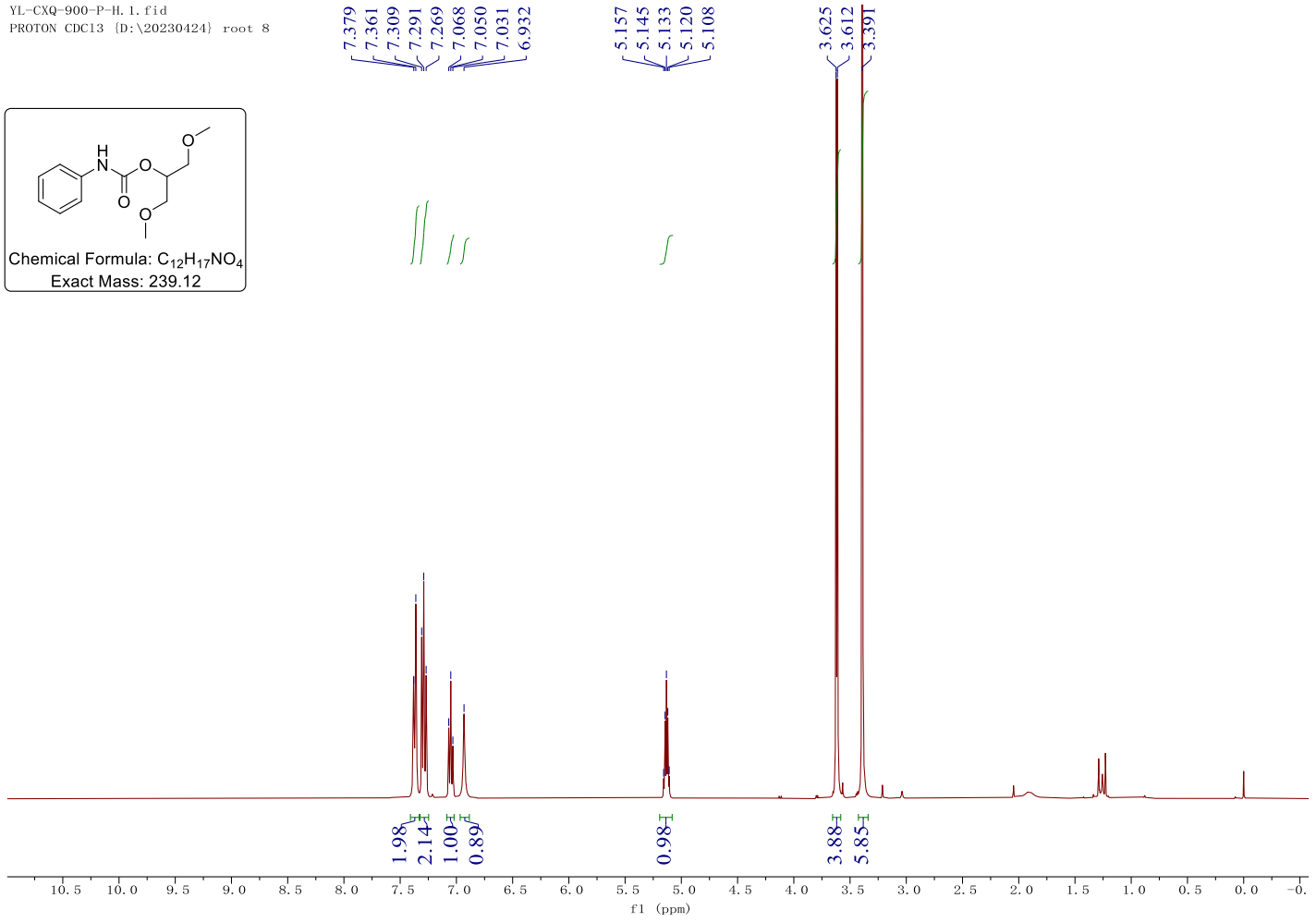
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3al.**



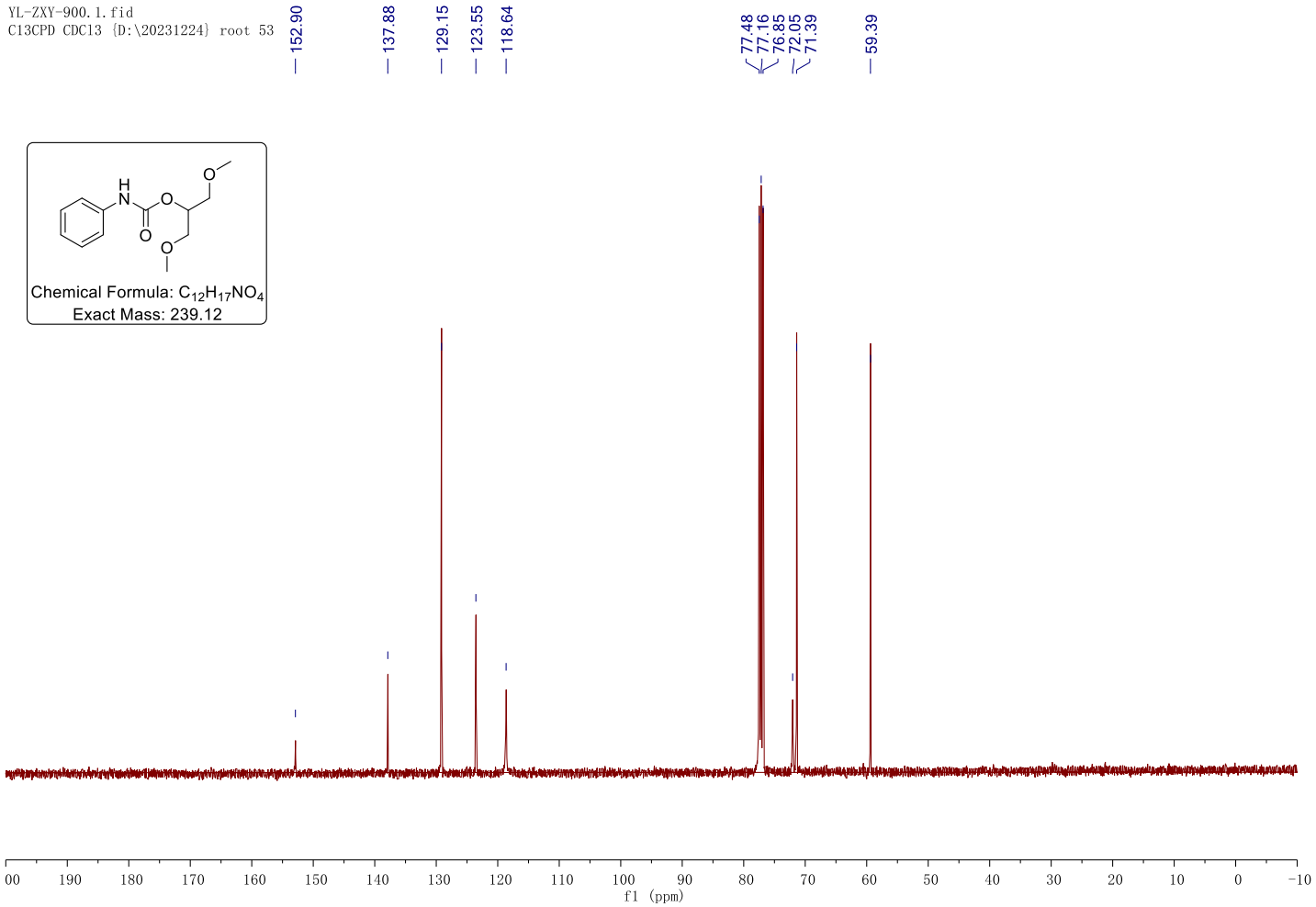
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3al.**



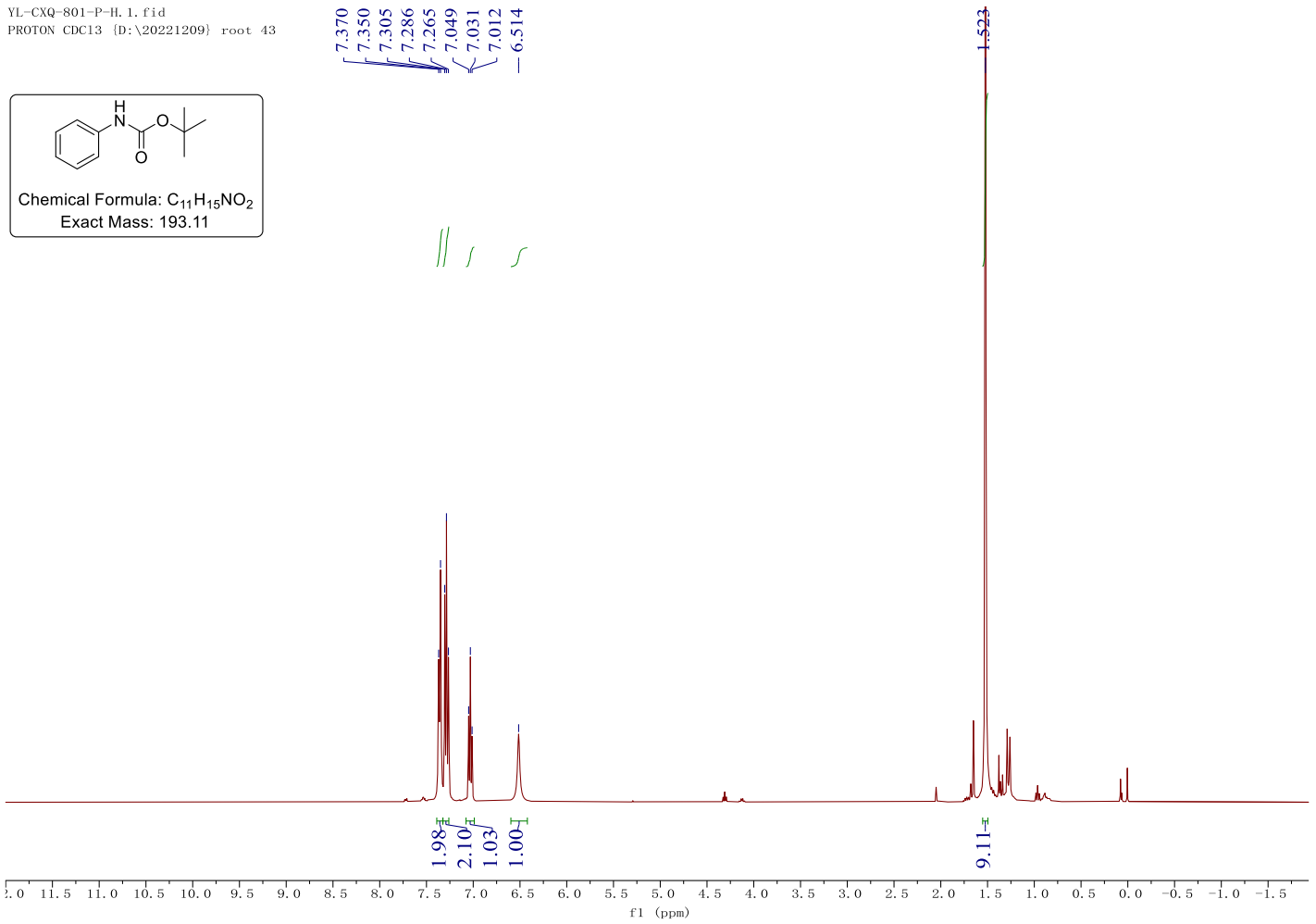
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3am.**



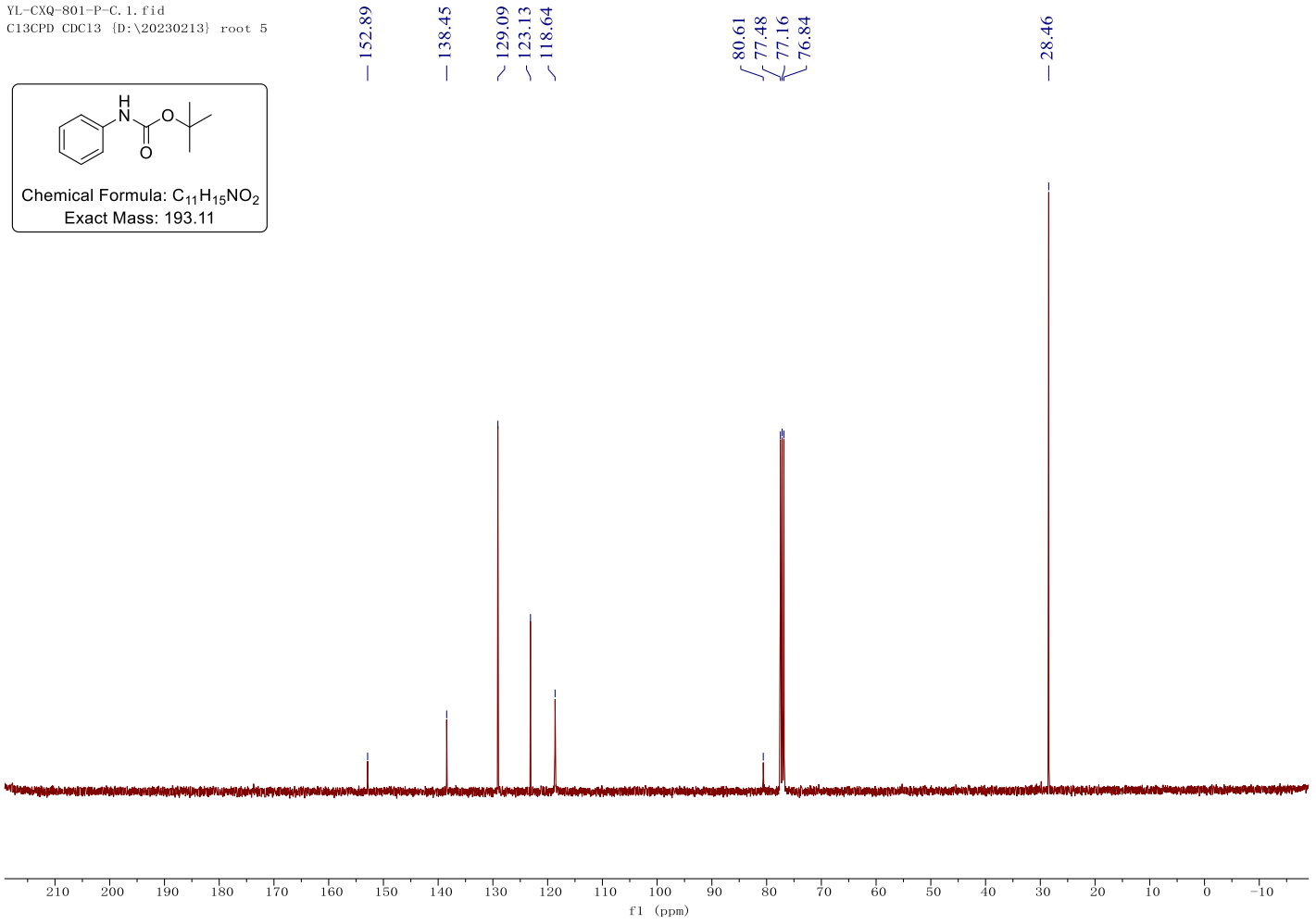
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3am.**



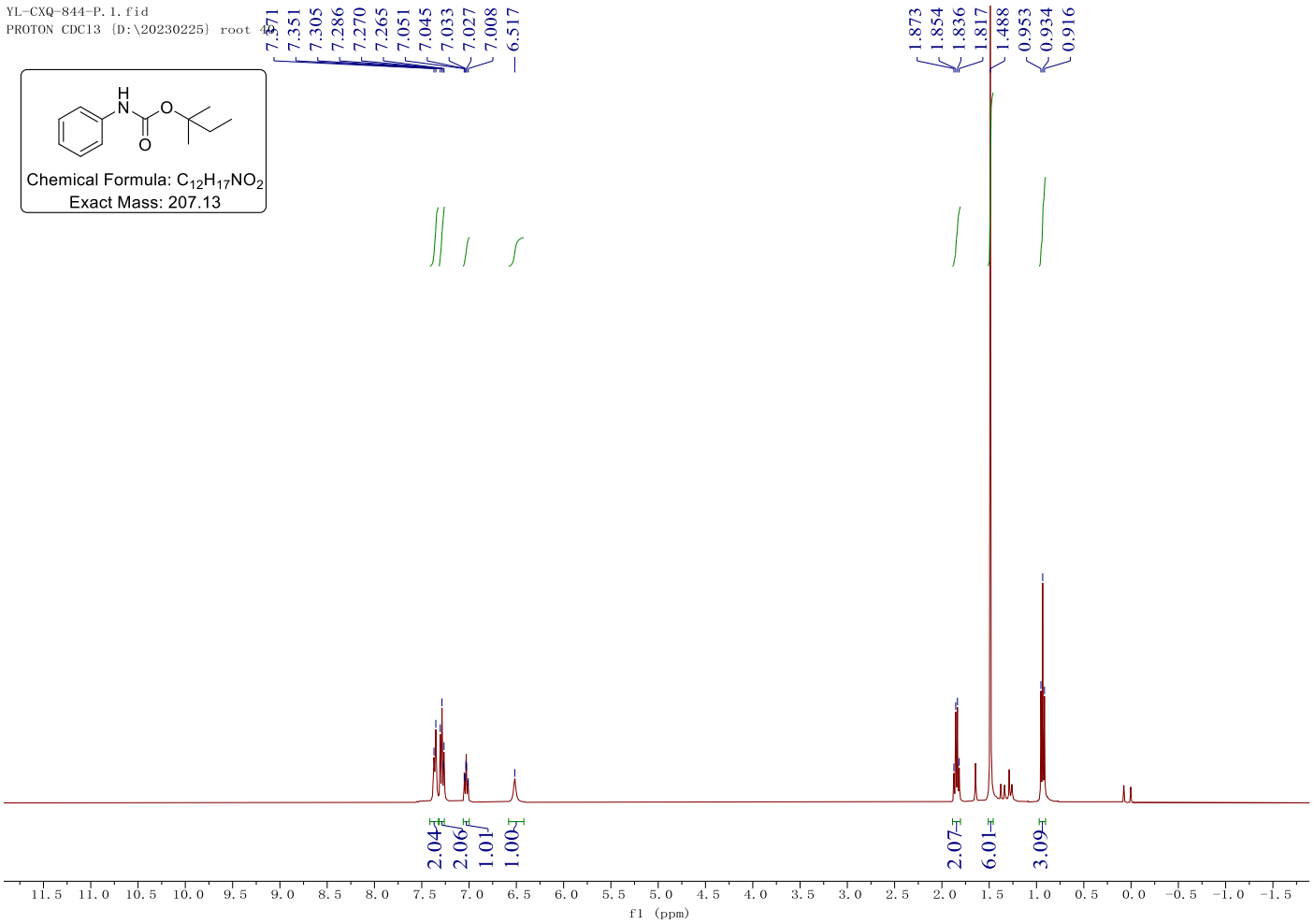
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3an.**



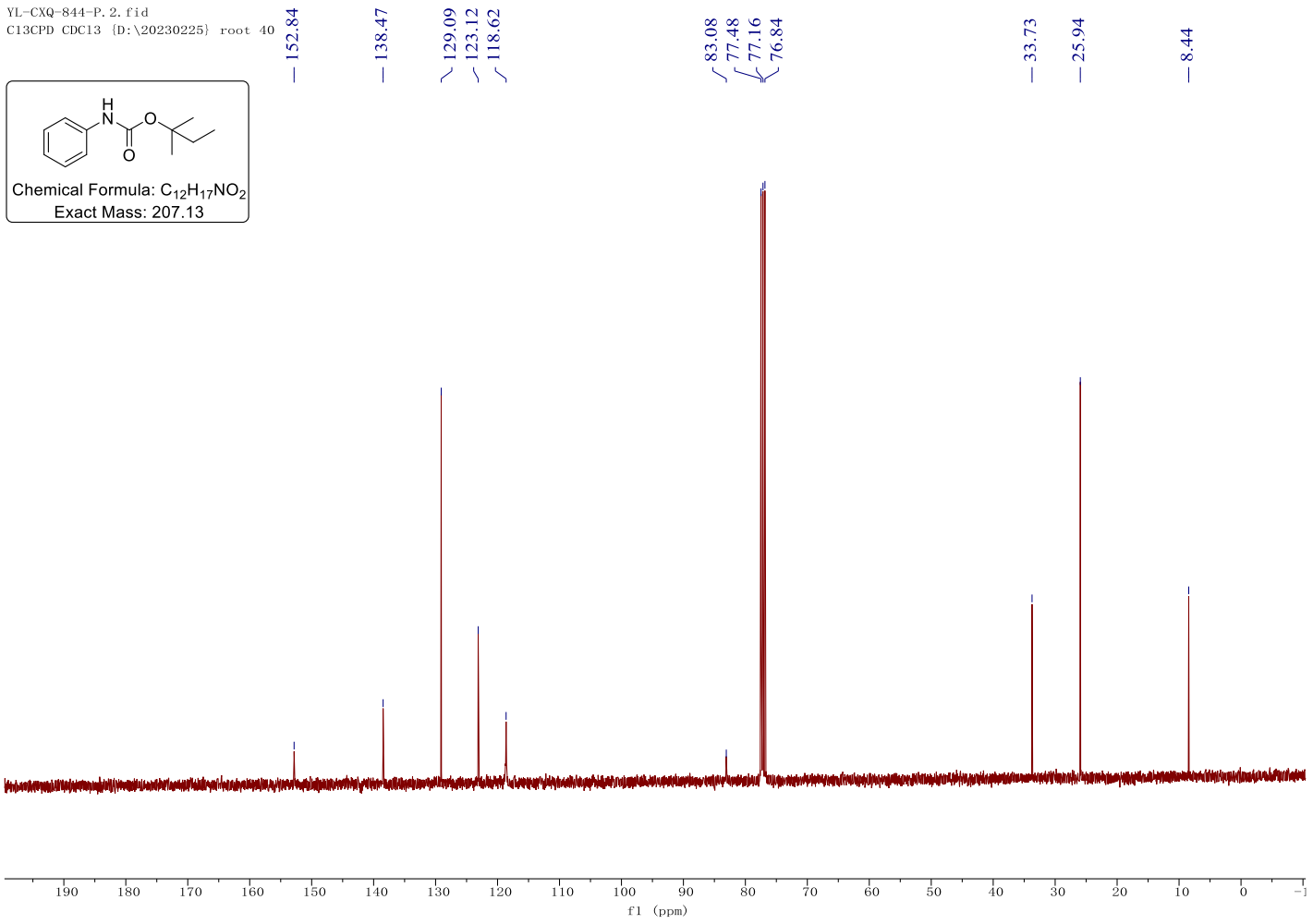
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3an.**



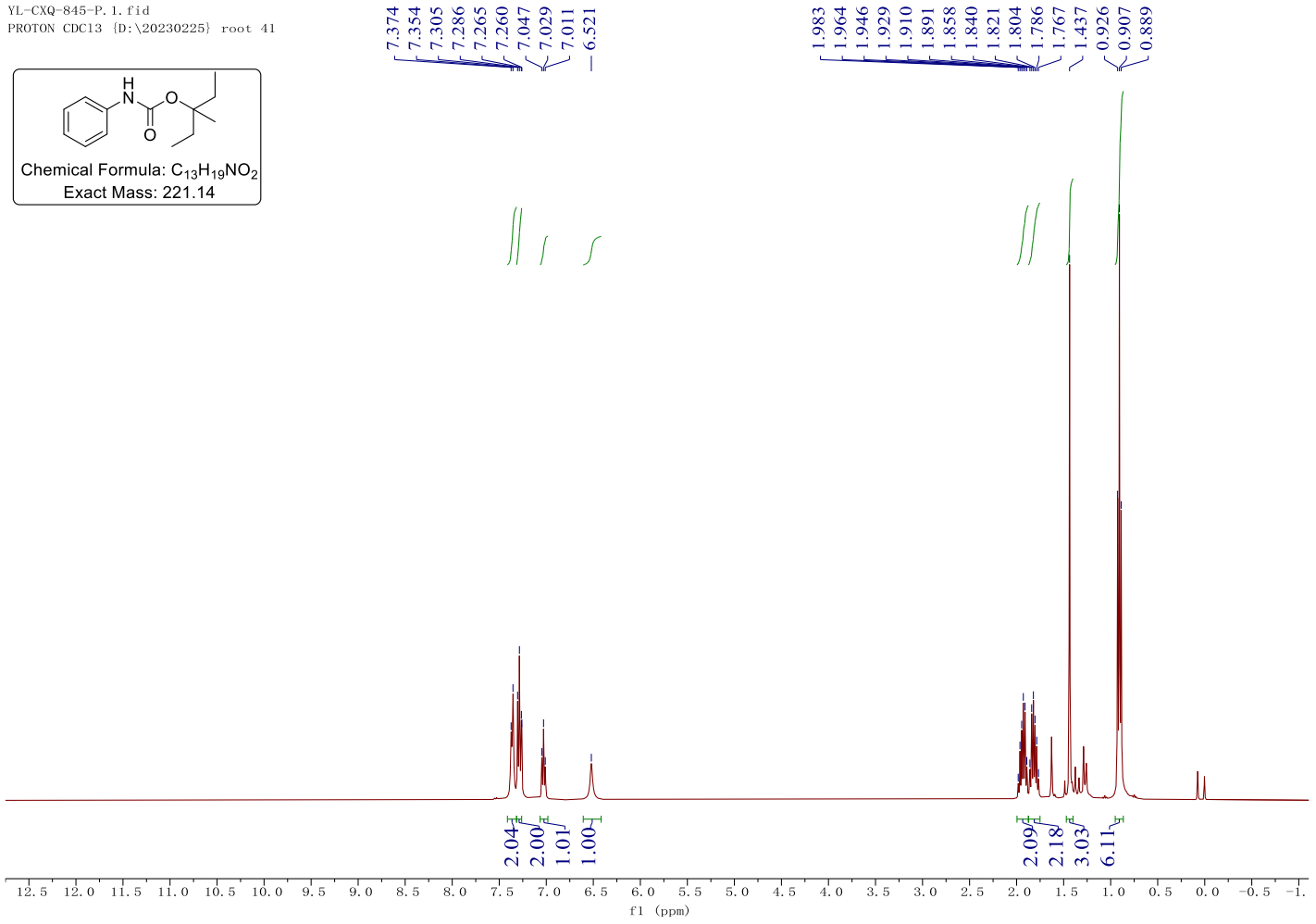
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ao.**



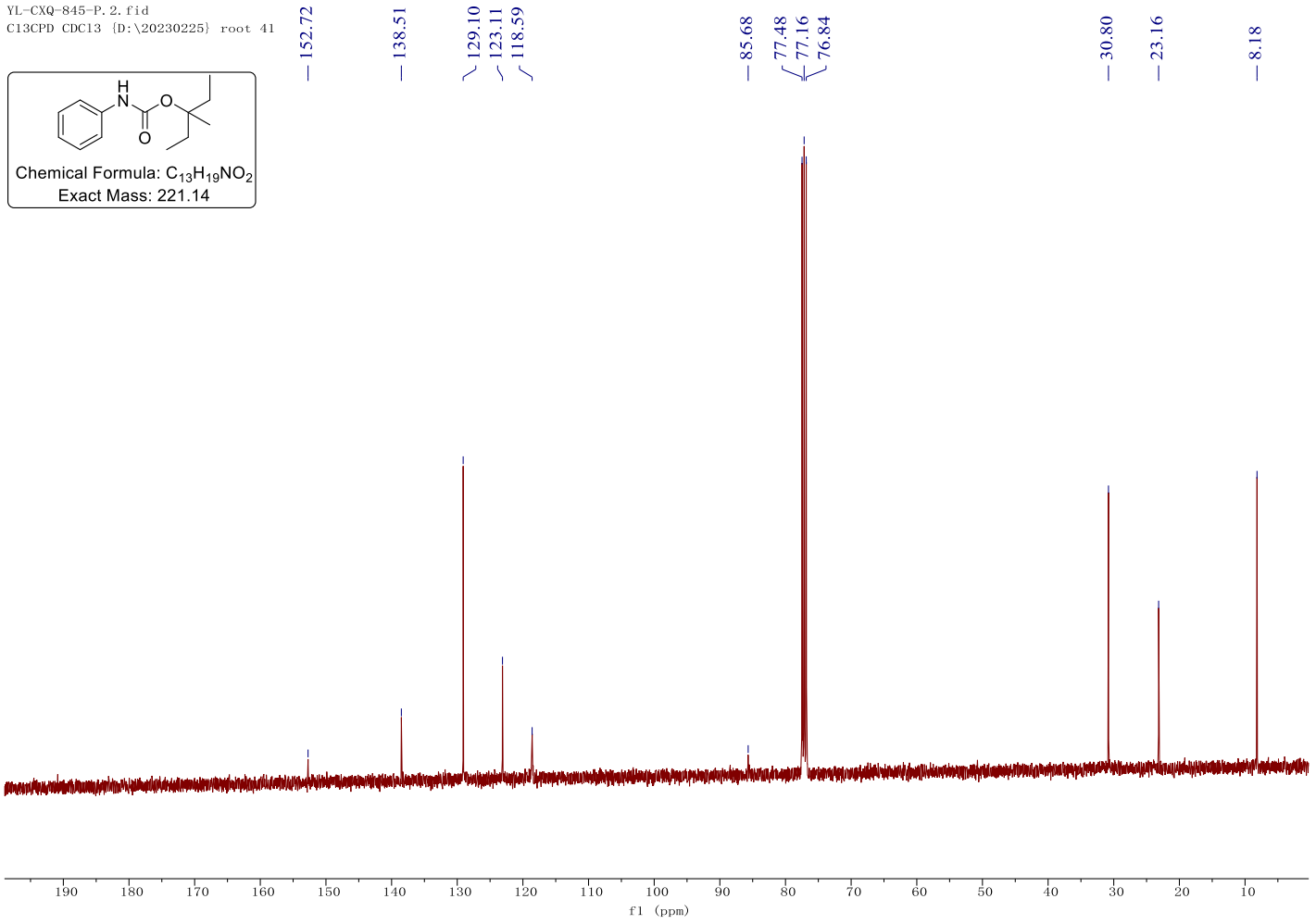
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ao.**



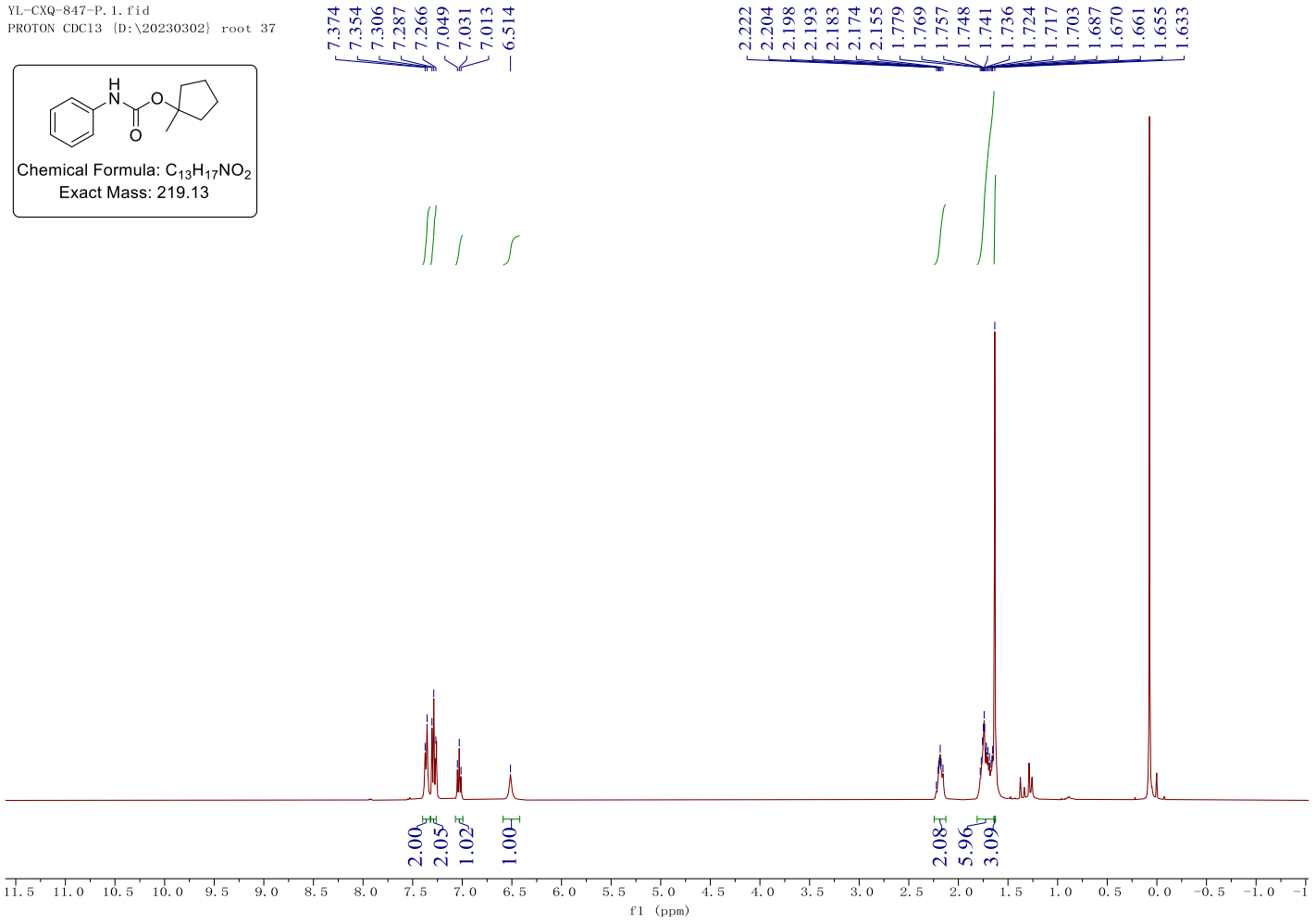
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ap.**



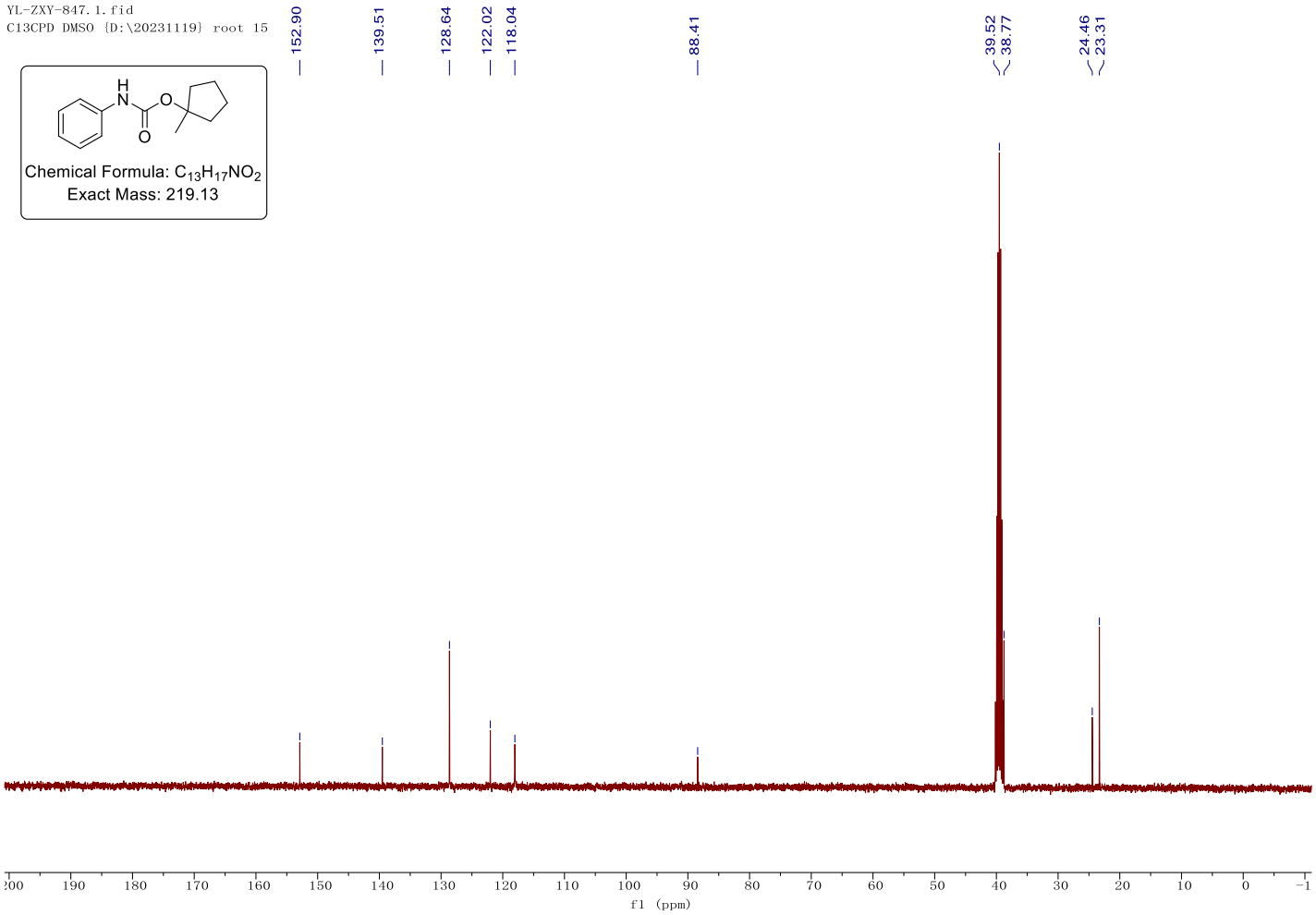
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ap.**



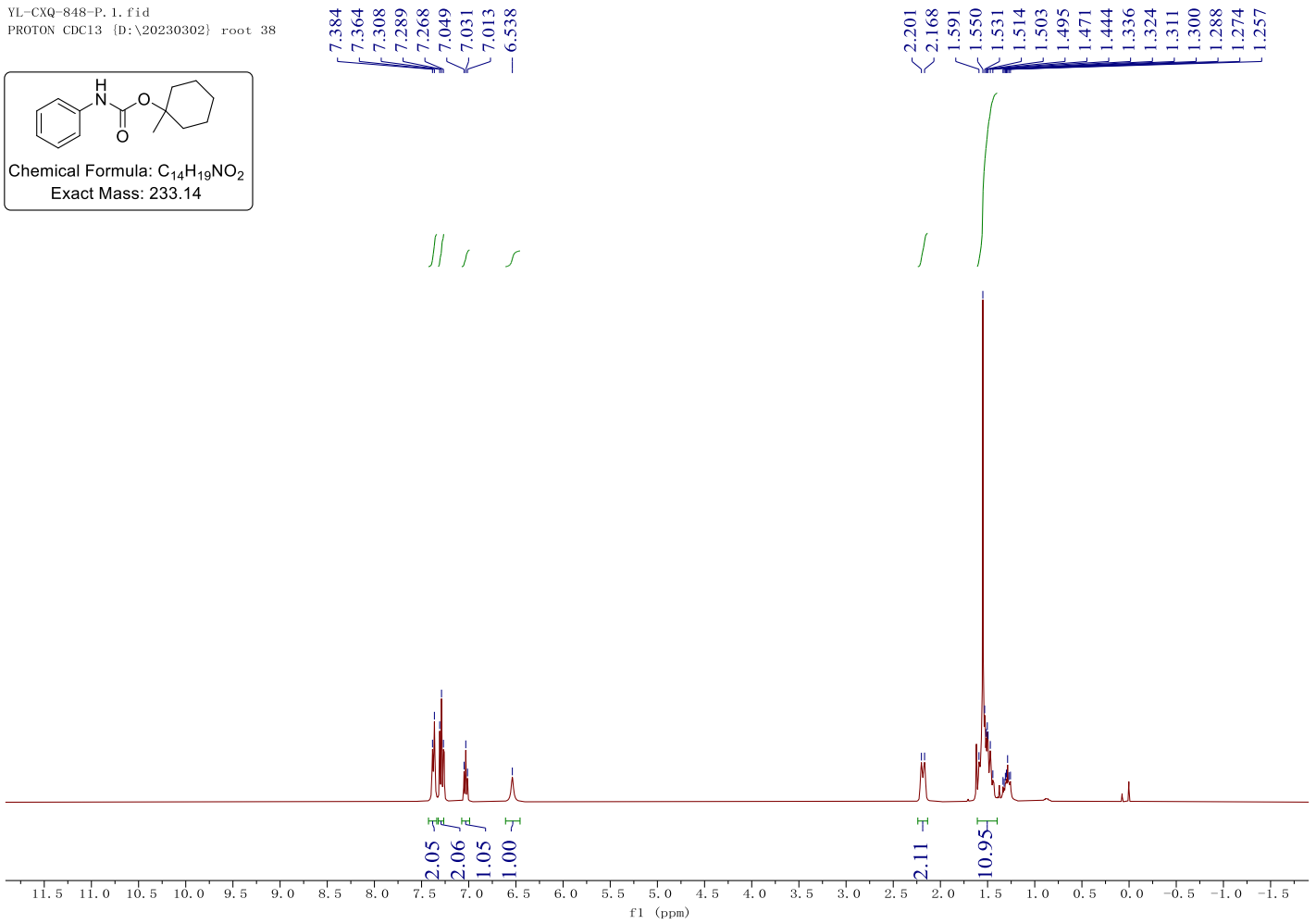
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aq.**



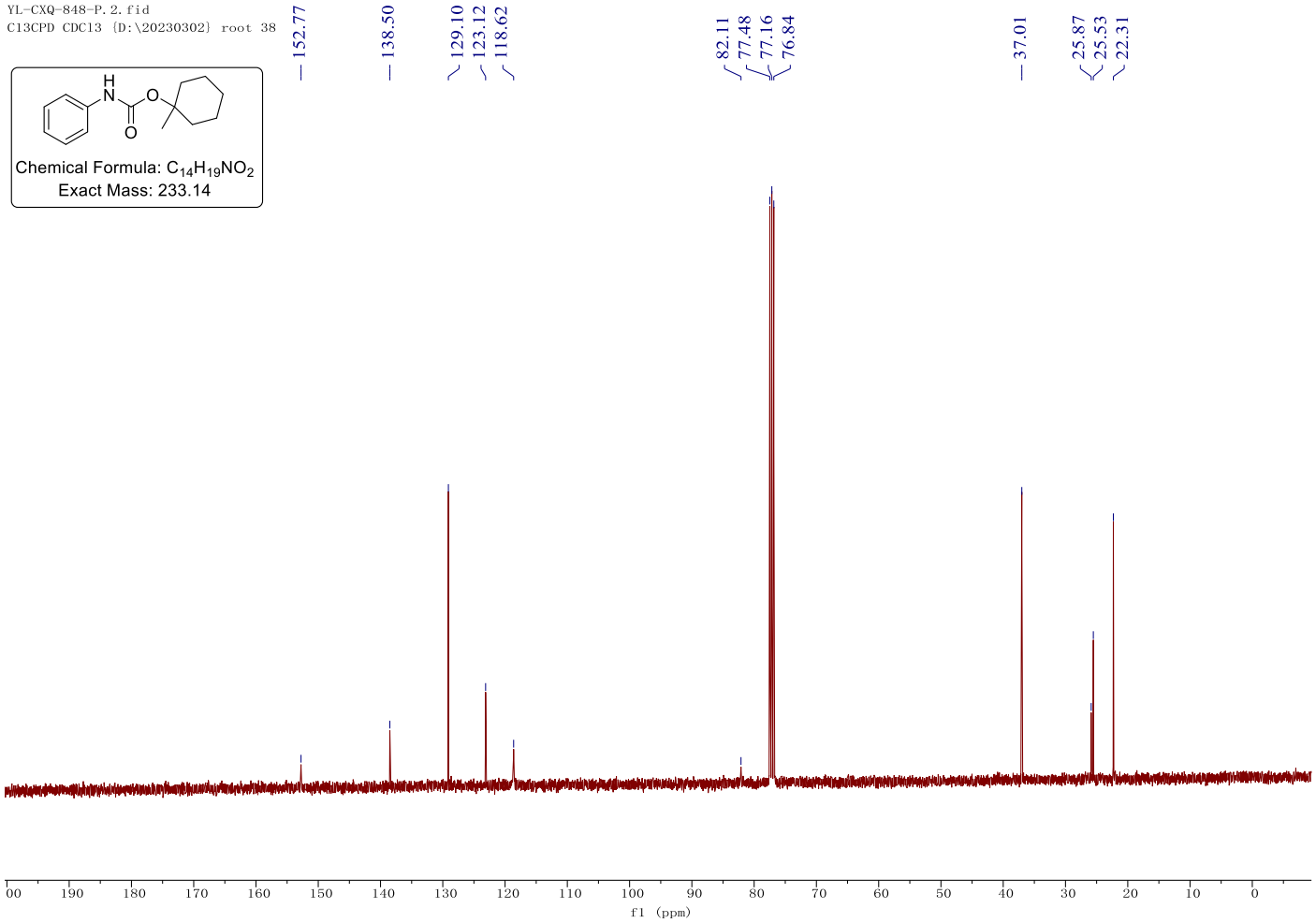
$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO) spectrum of compound **3aq.**



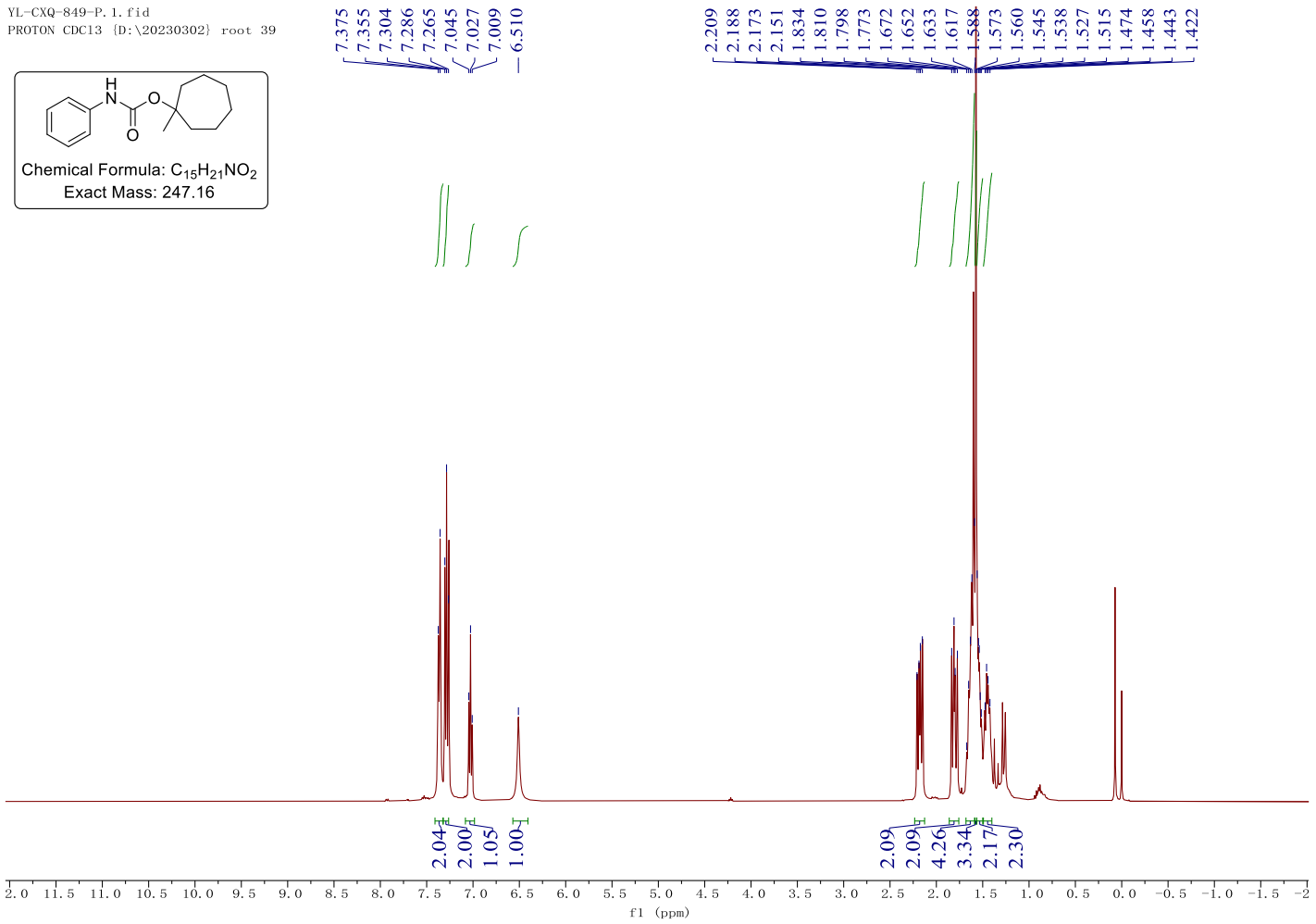
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3ar.**



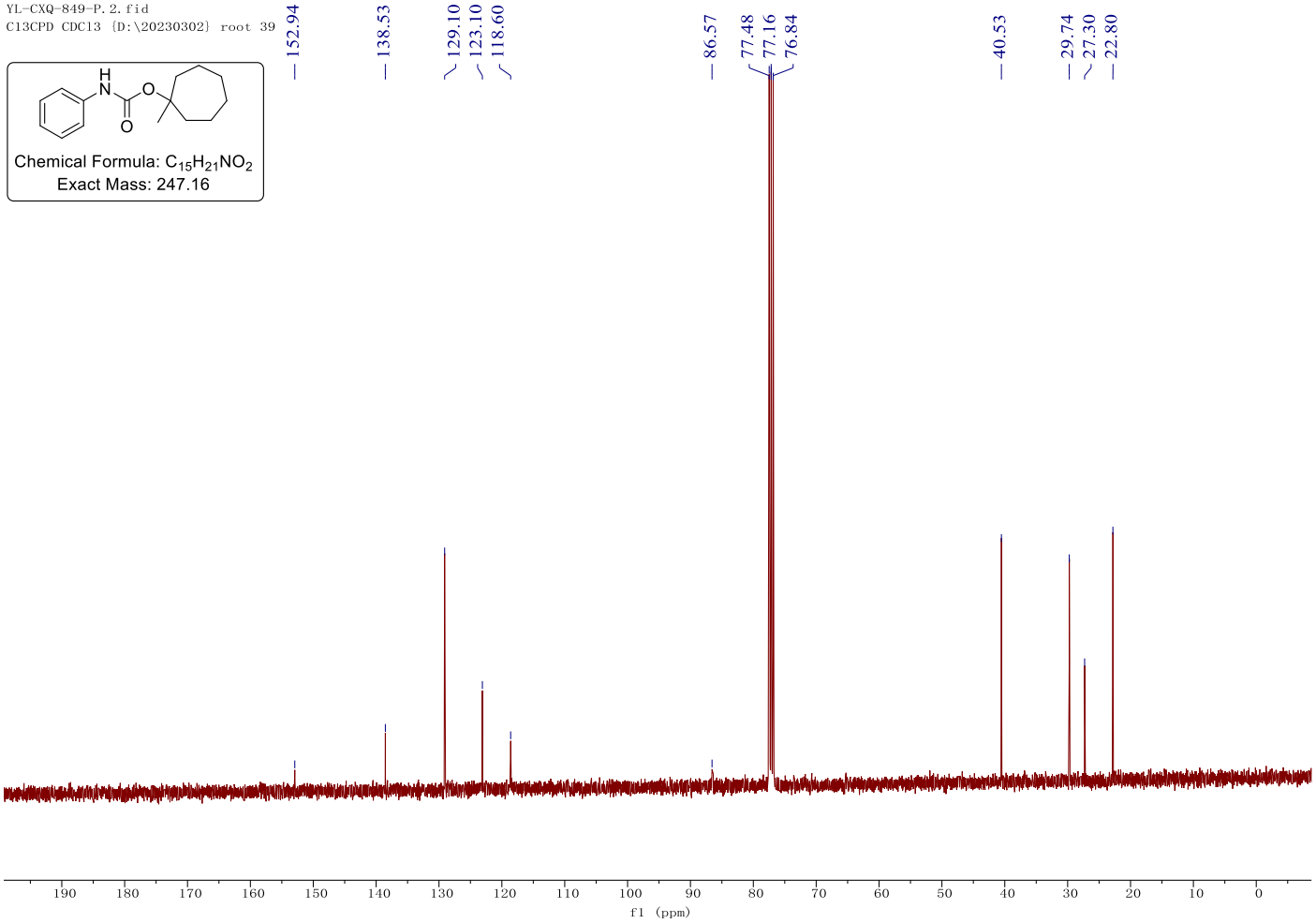
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3ar.**



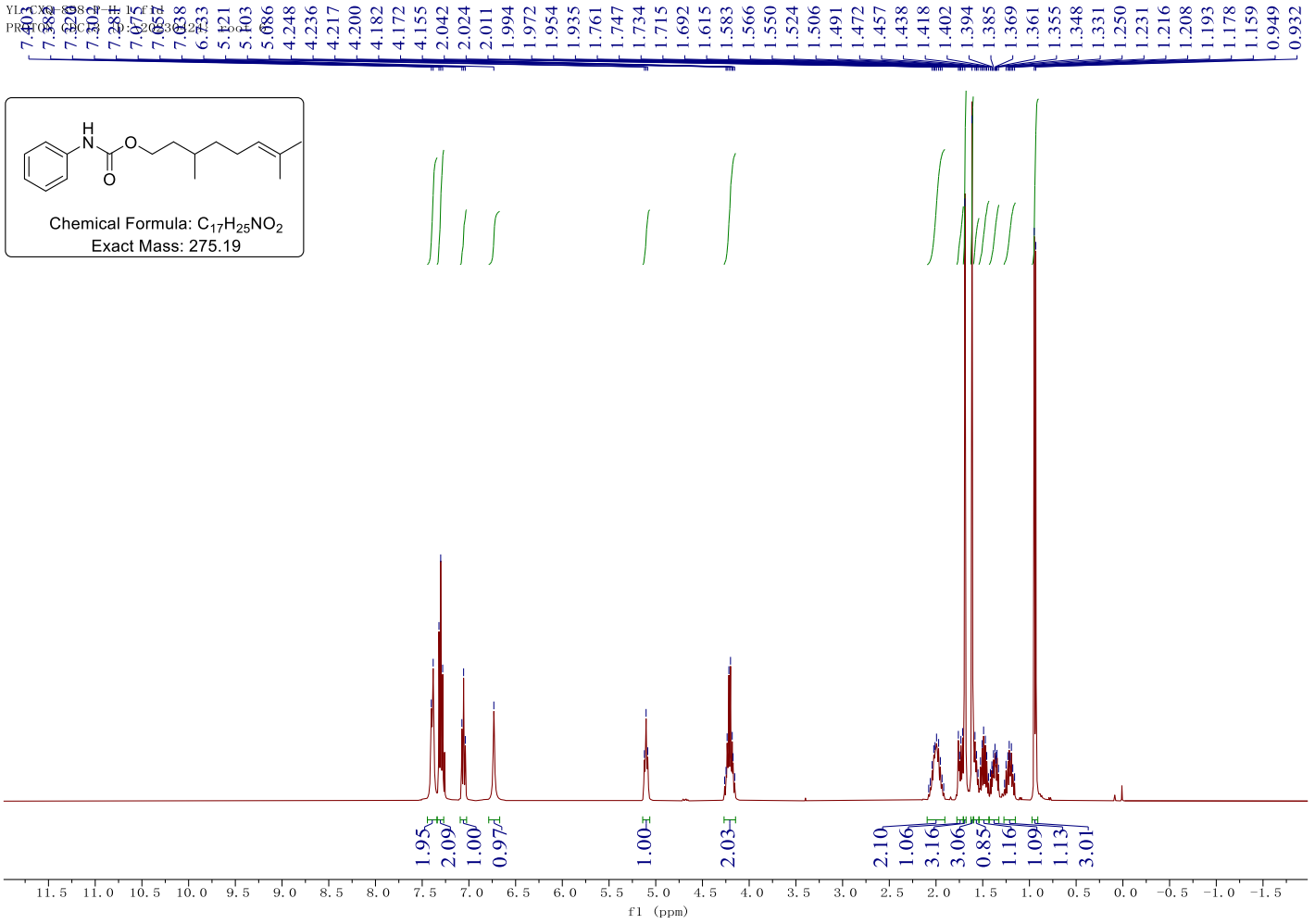
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3as.**



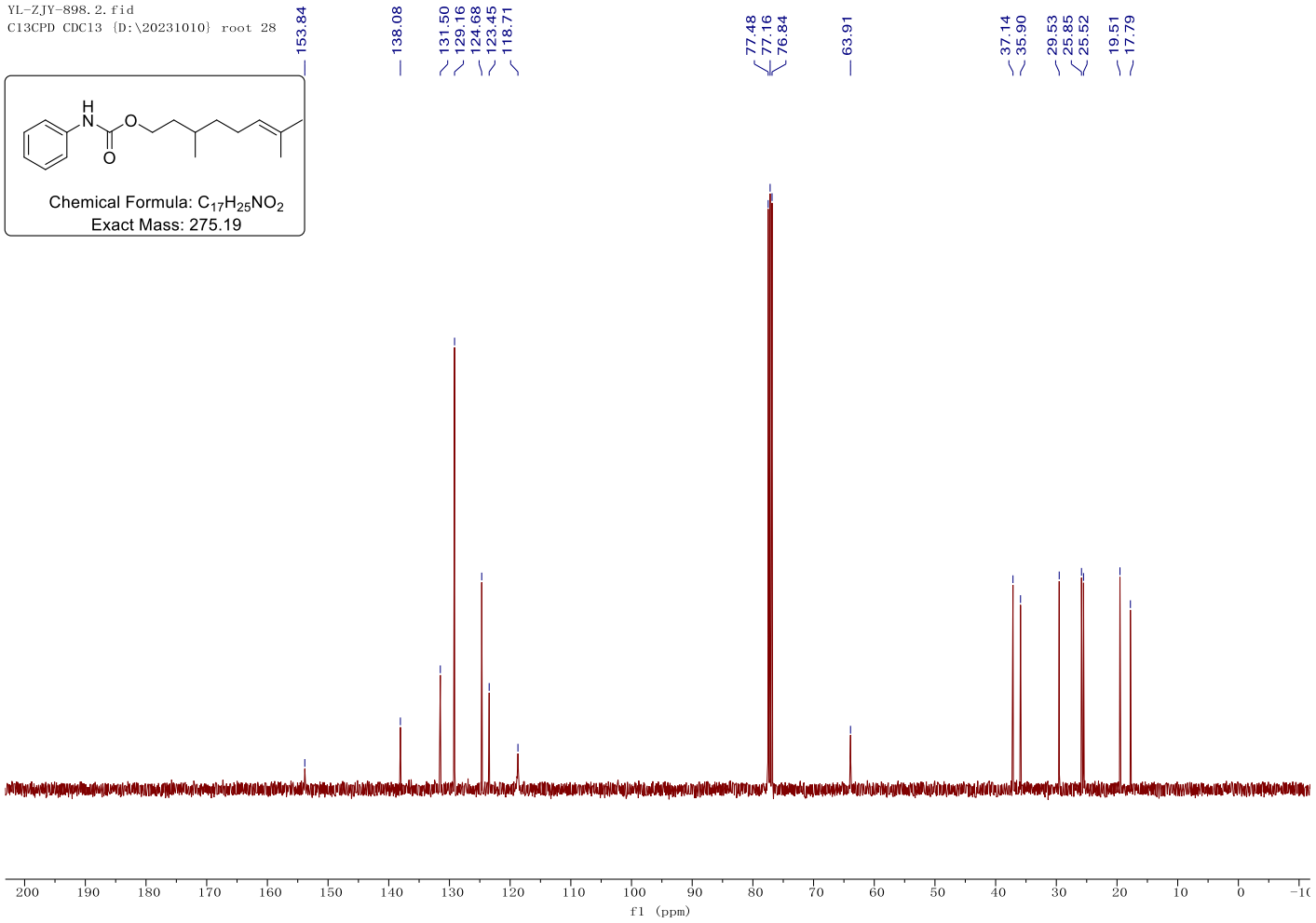
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3as.**



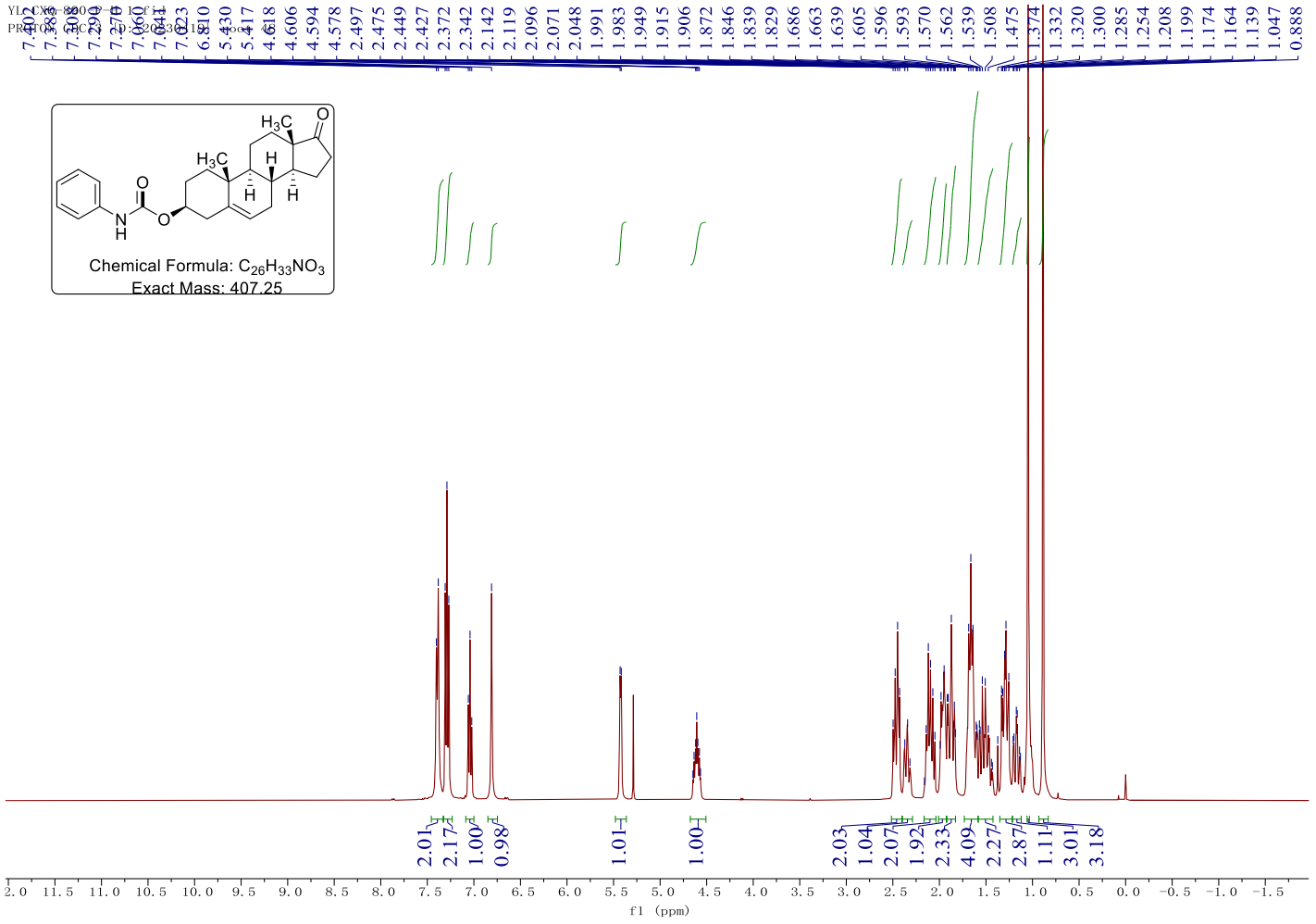
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3at.**



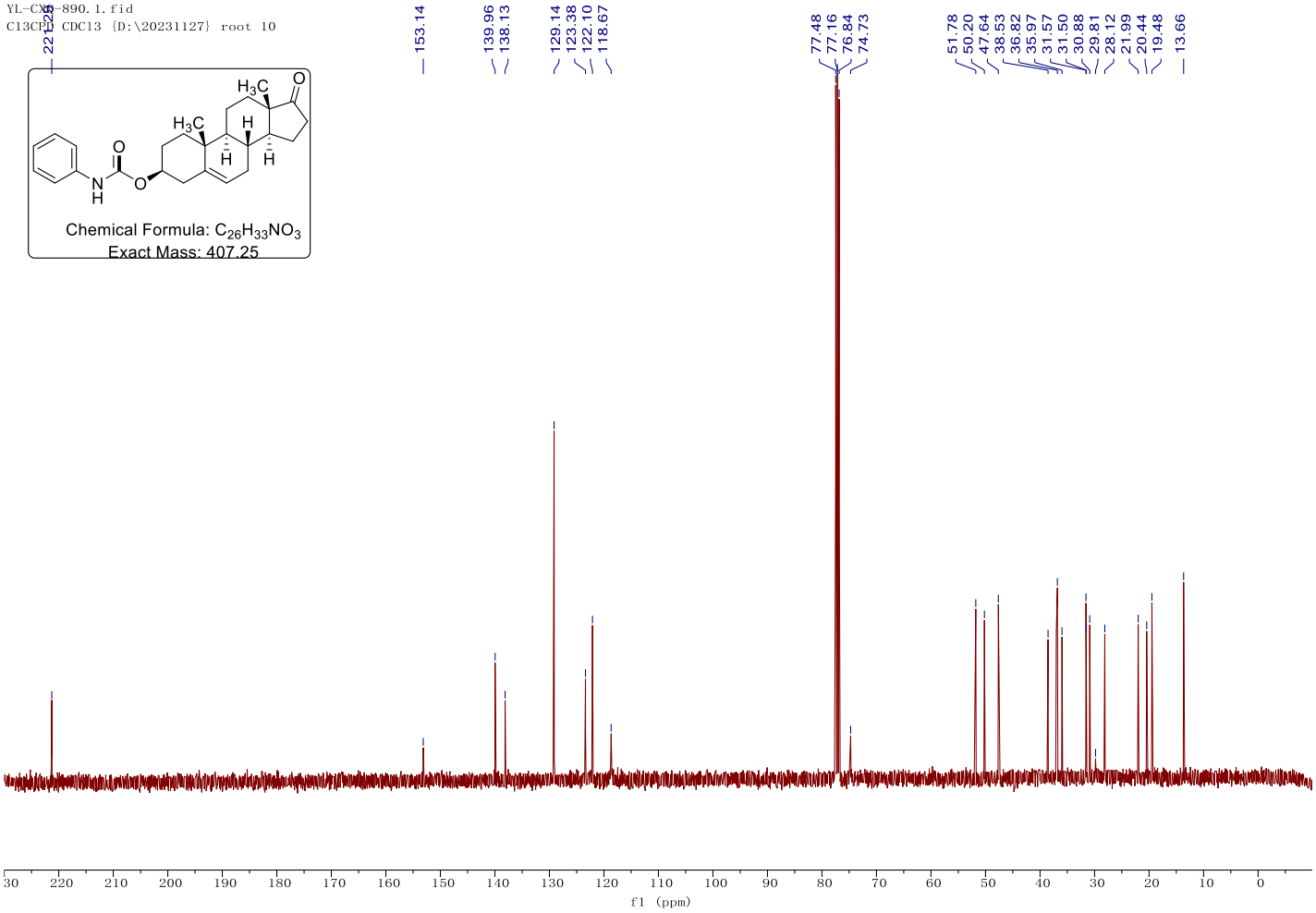
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3at.**



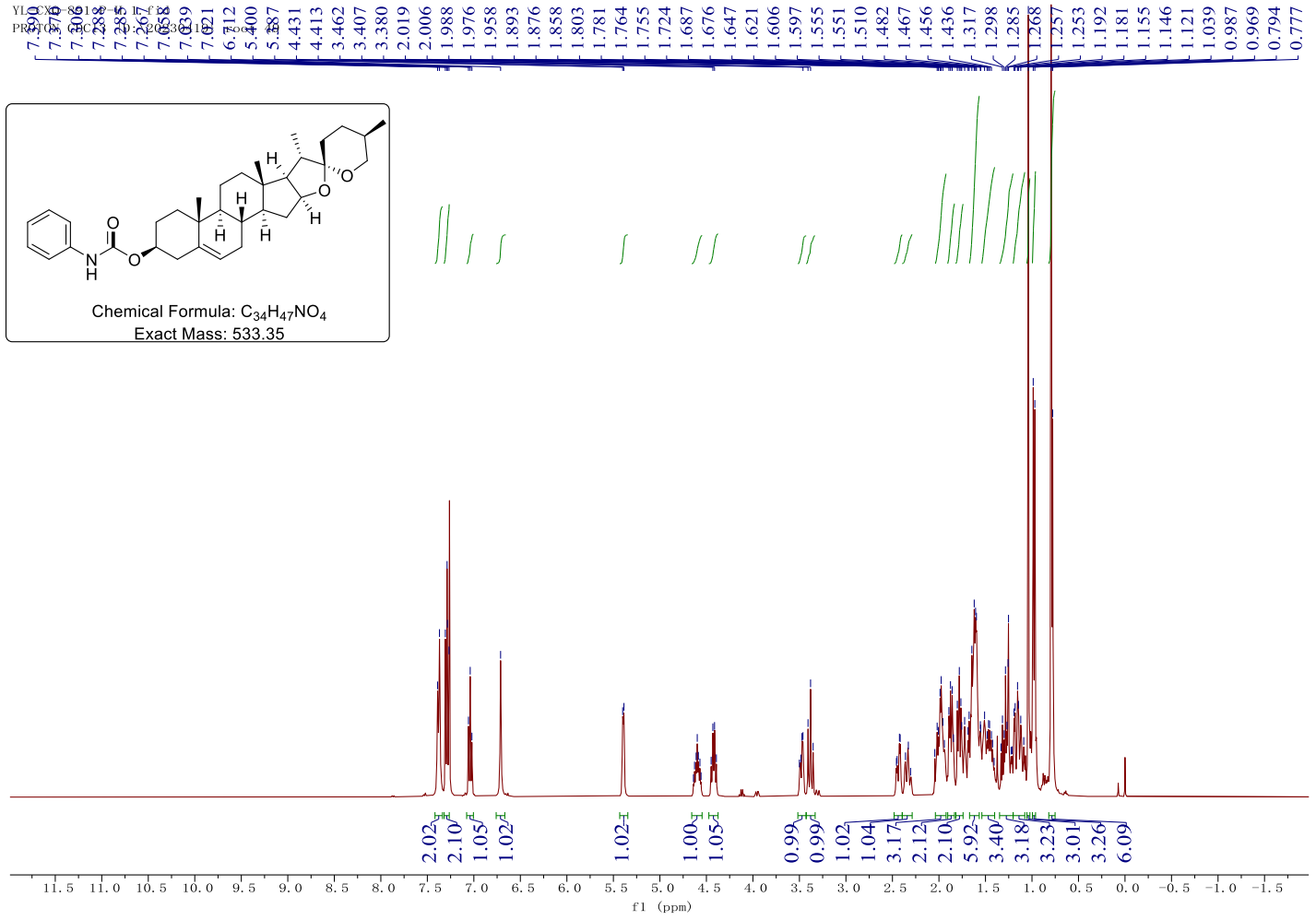
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3au.**



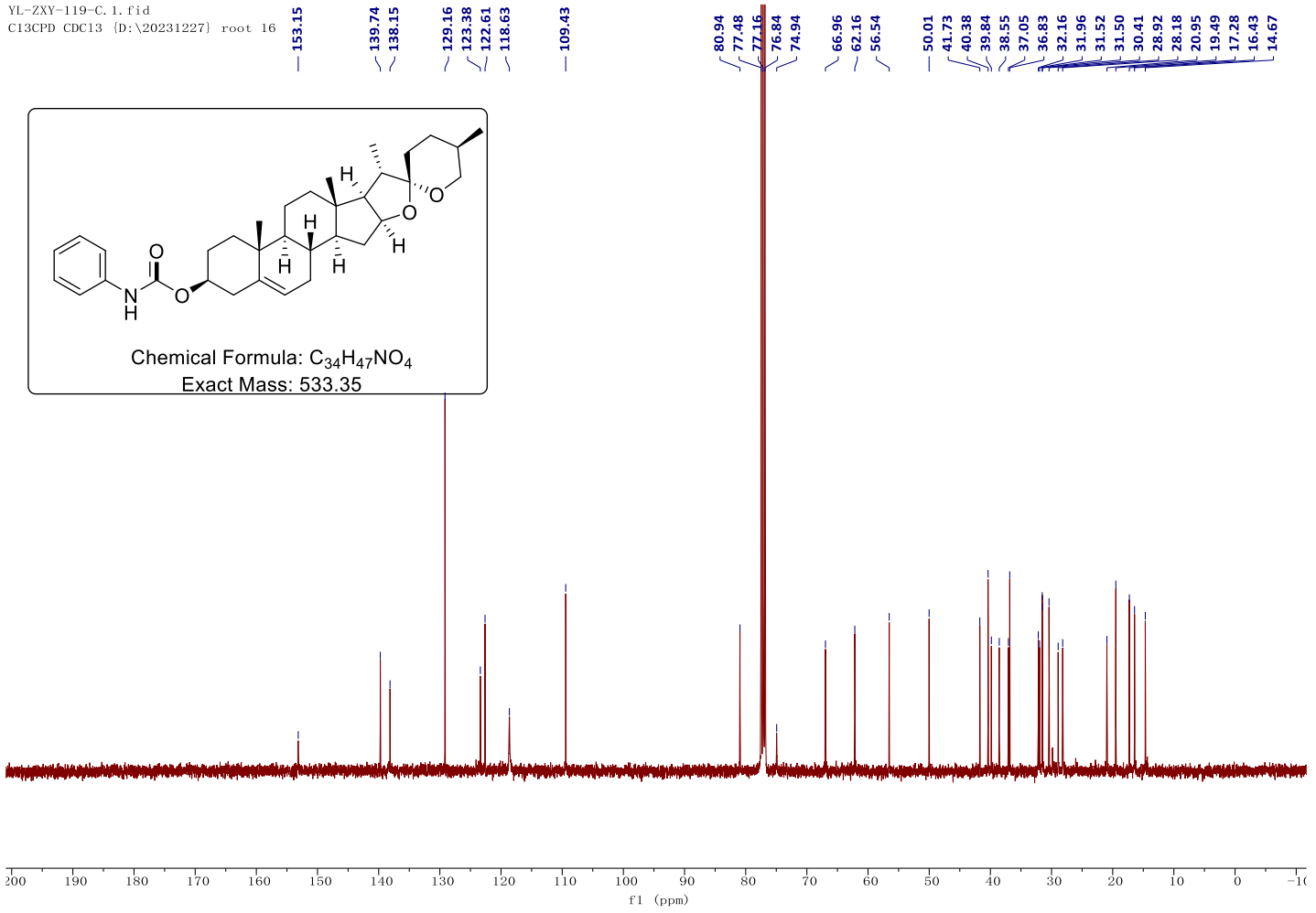
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3au.**



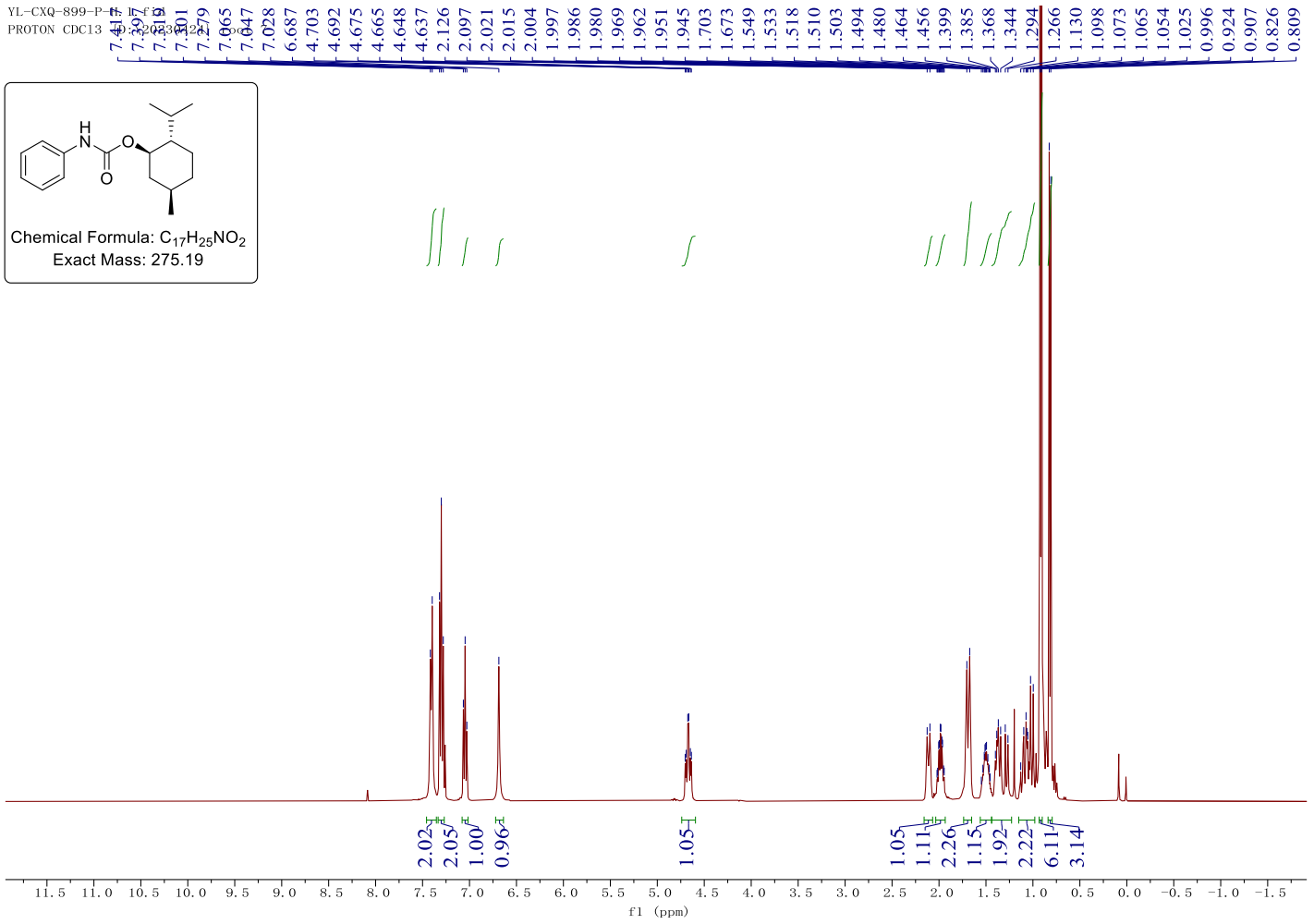
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3av.**



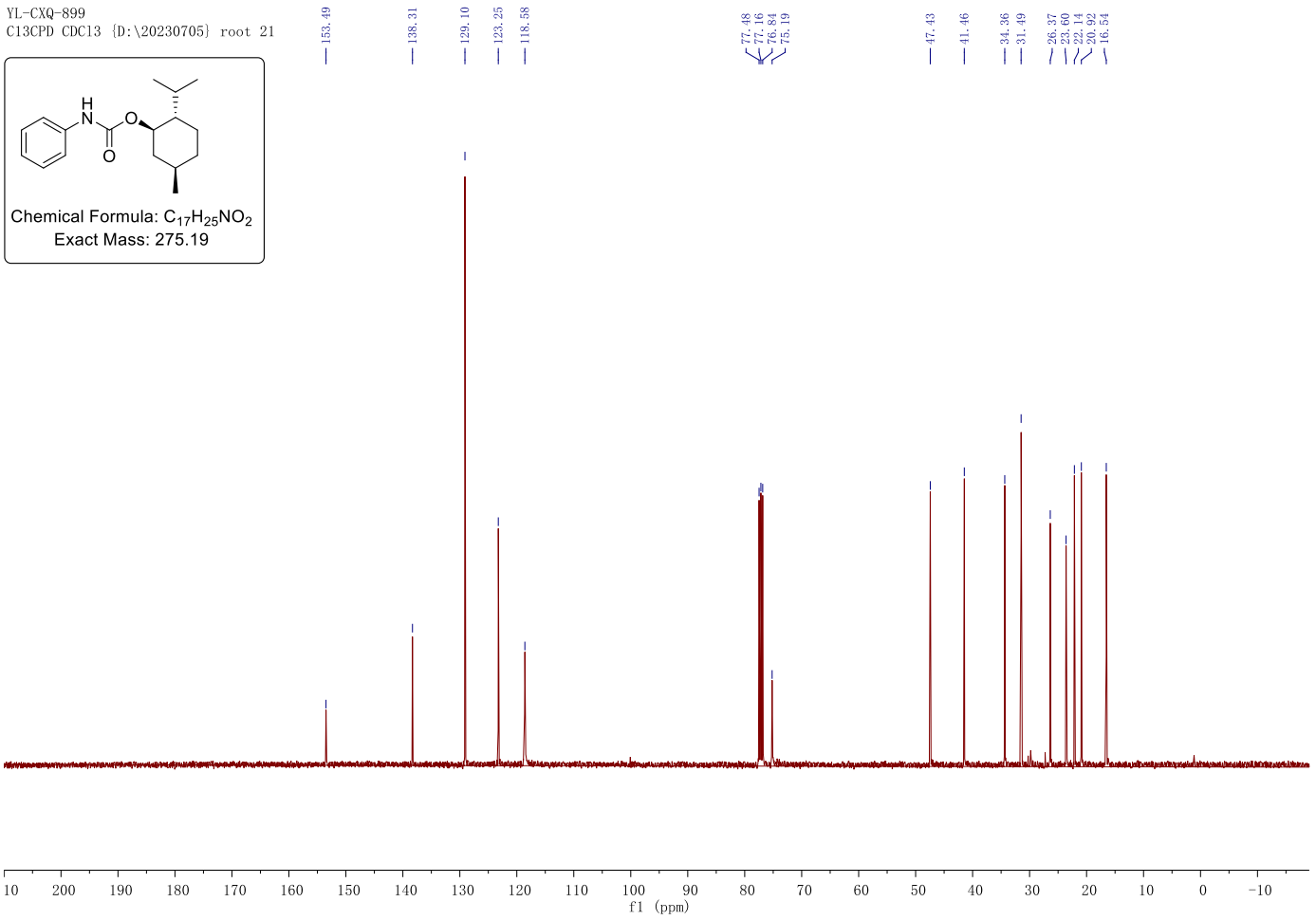
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3av.**



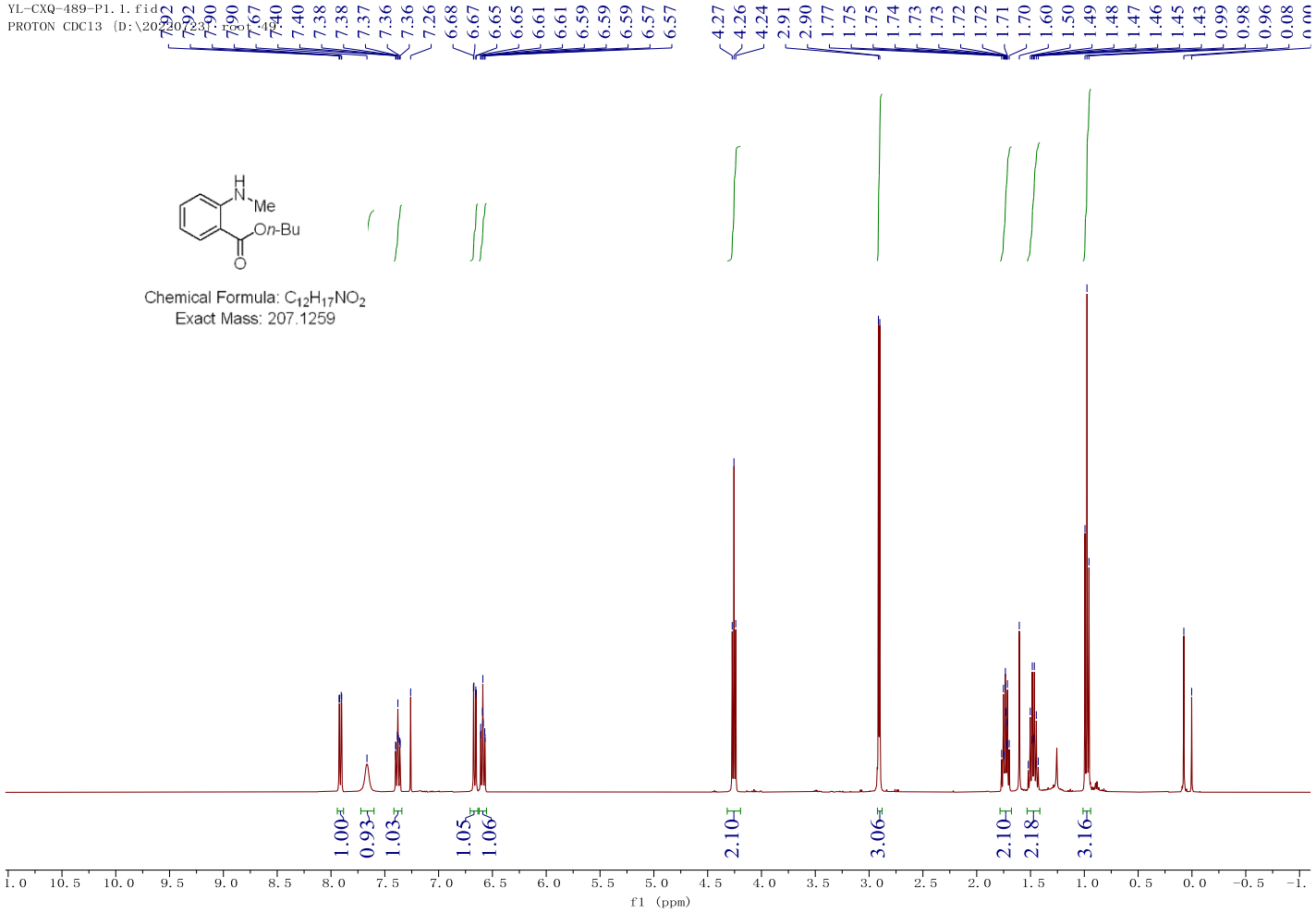
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3aw.**



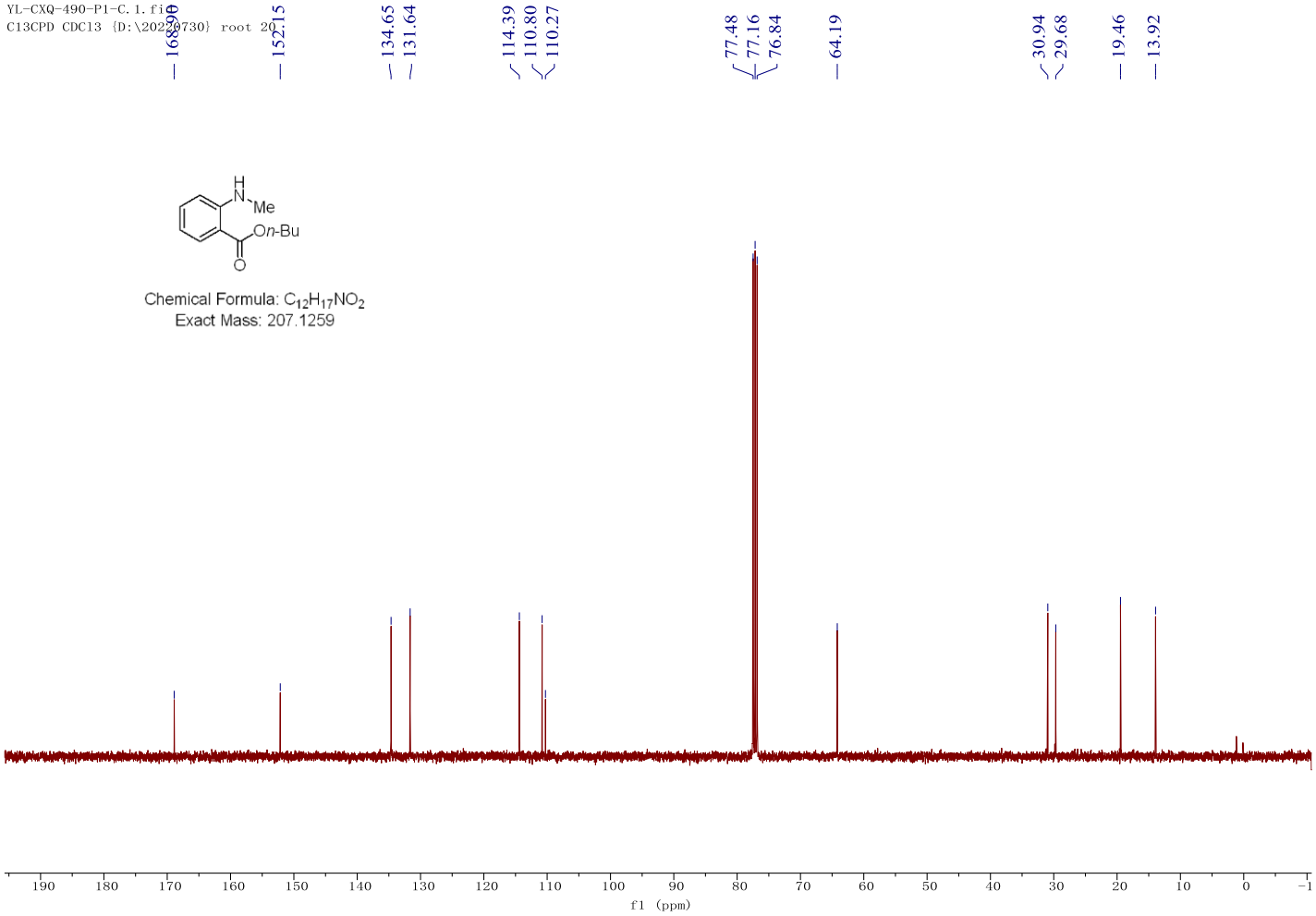
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **3aw.**



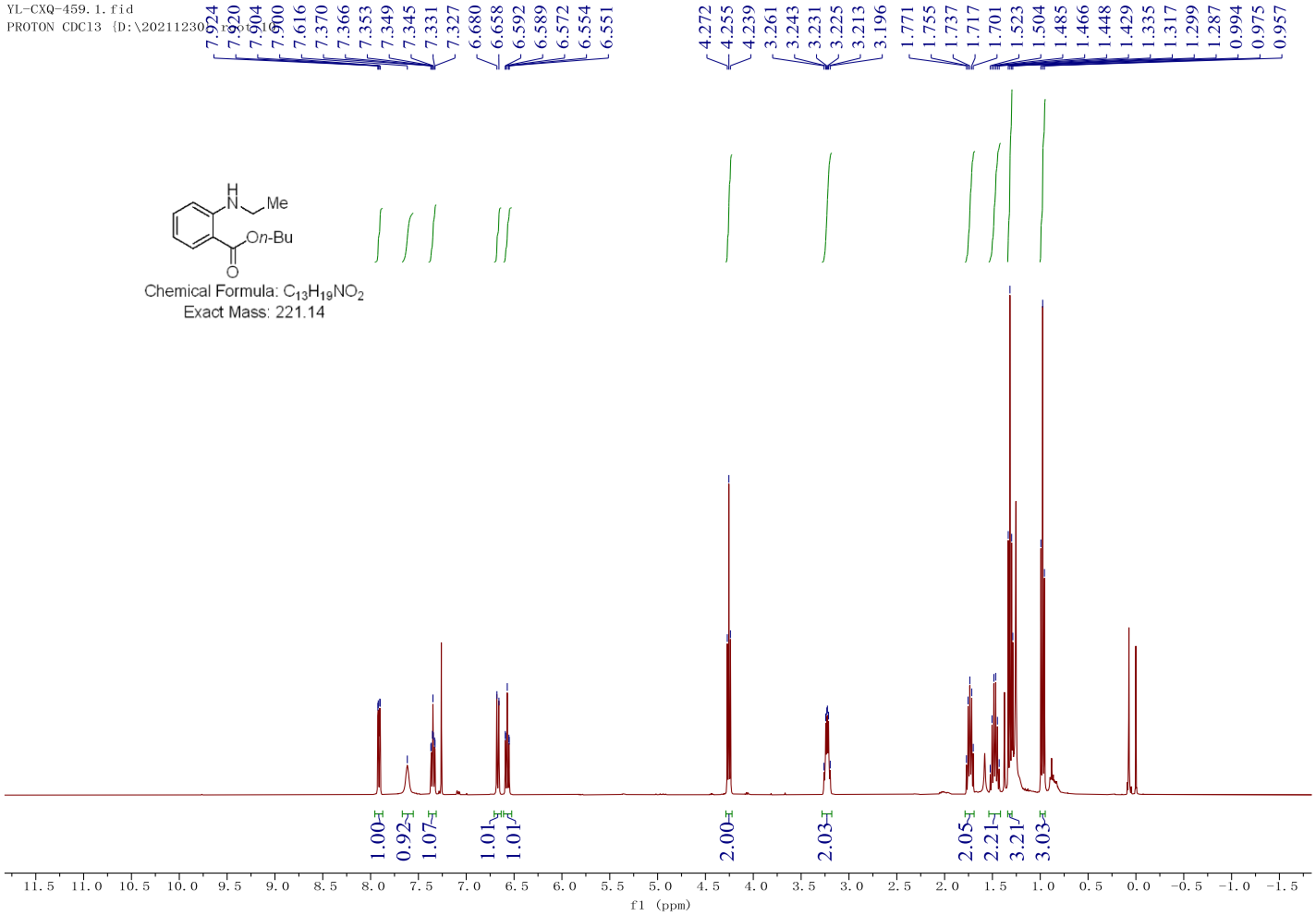
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ab.**



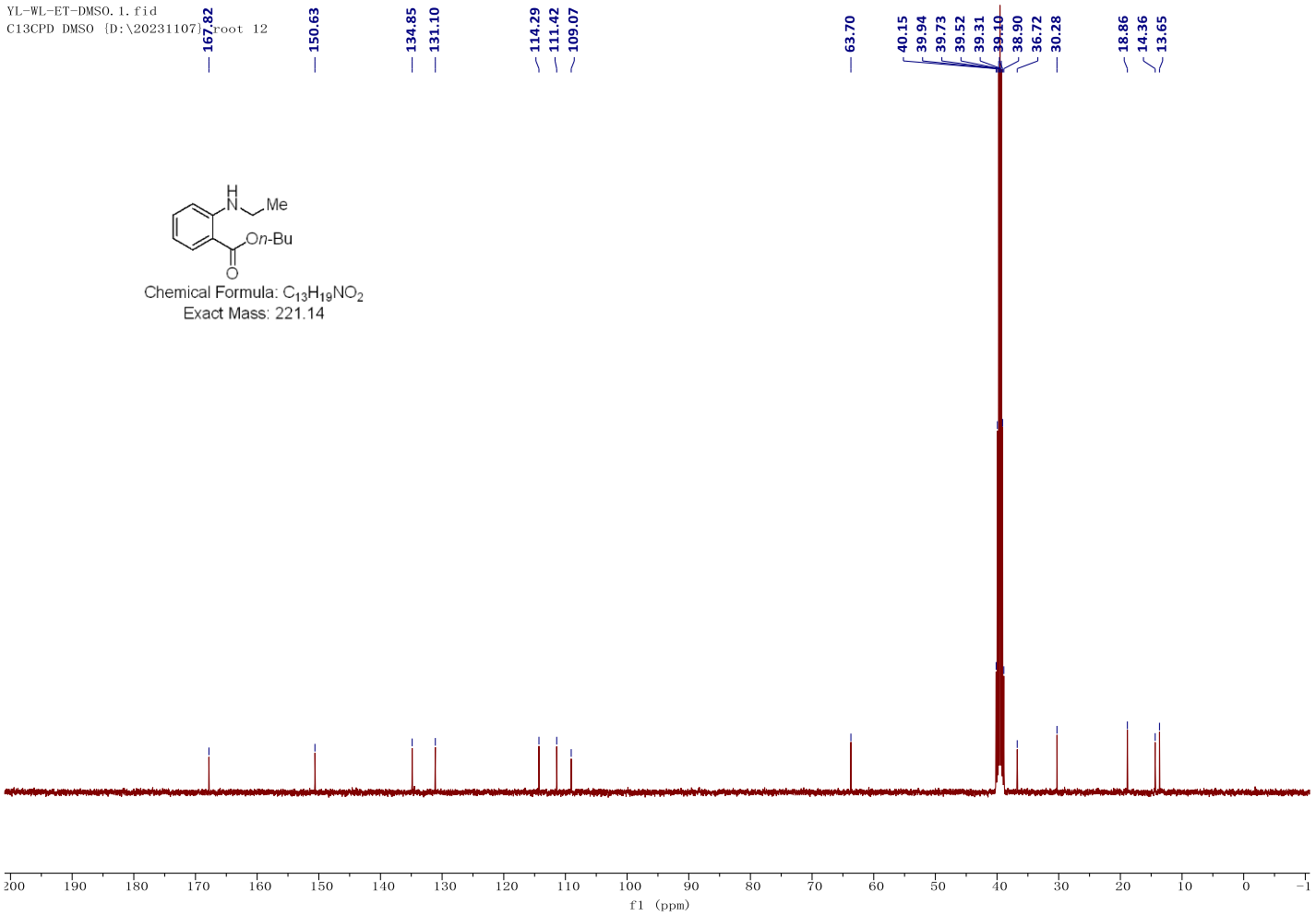
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5ab.**



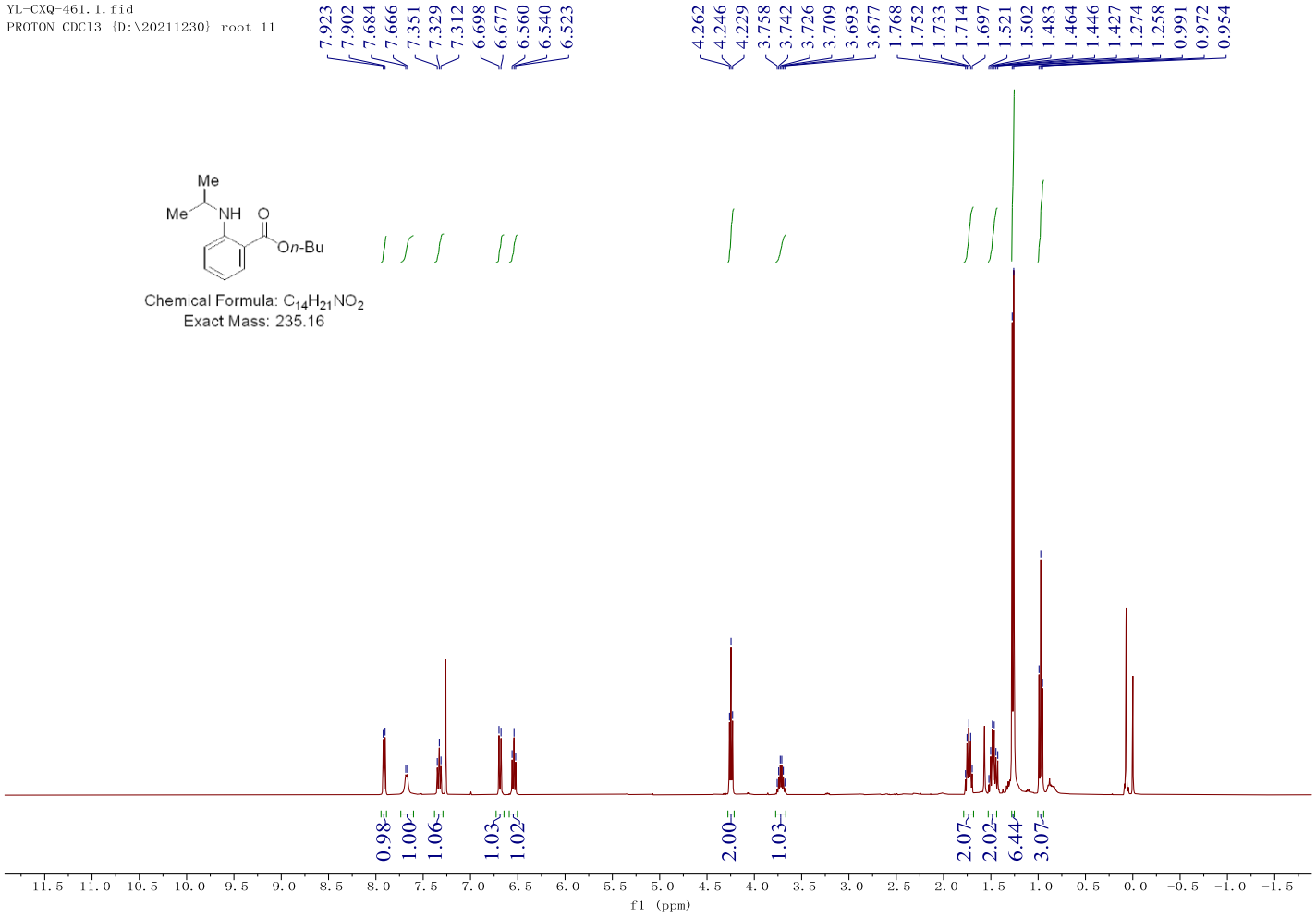
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5bb.**



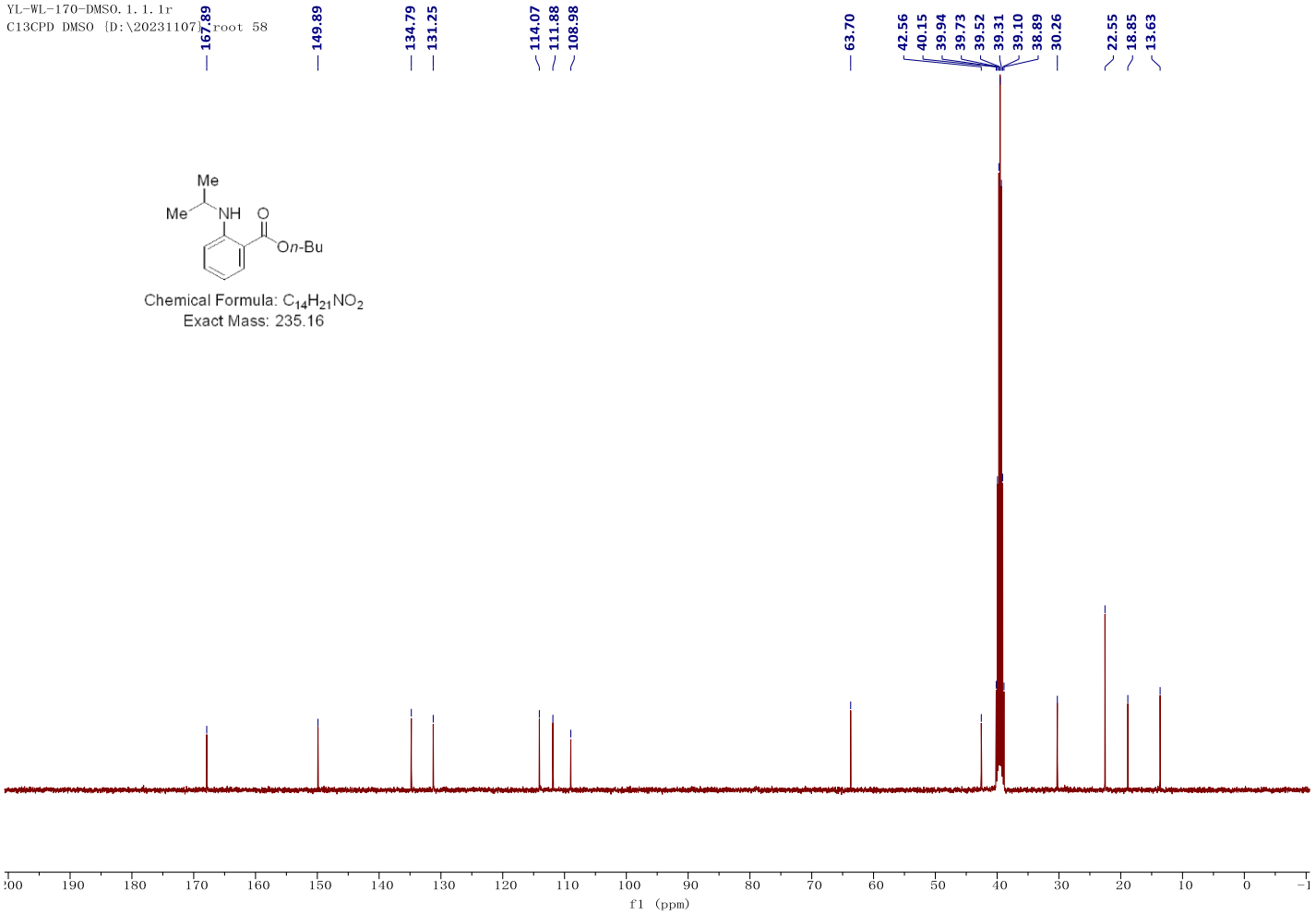
$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO) spectrum of compound **5bb.**



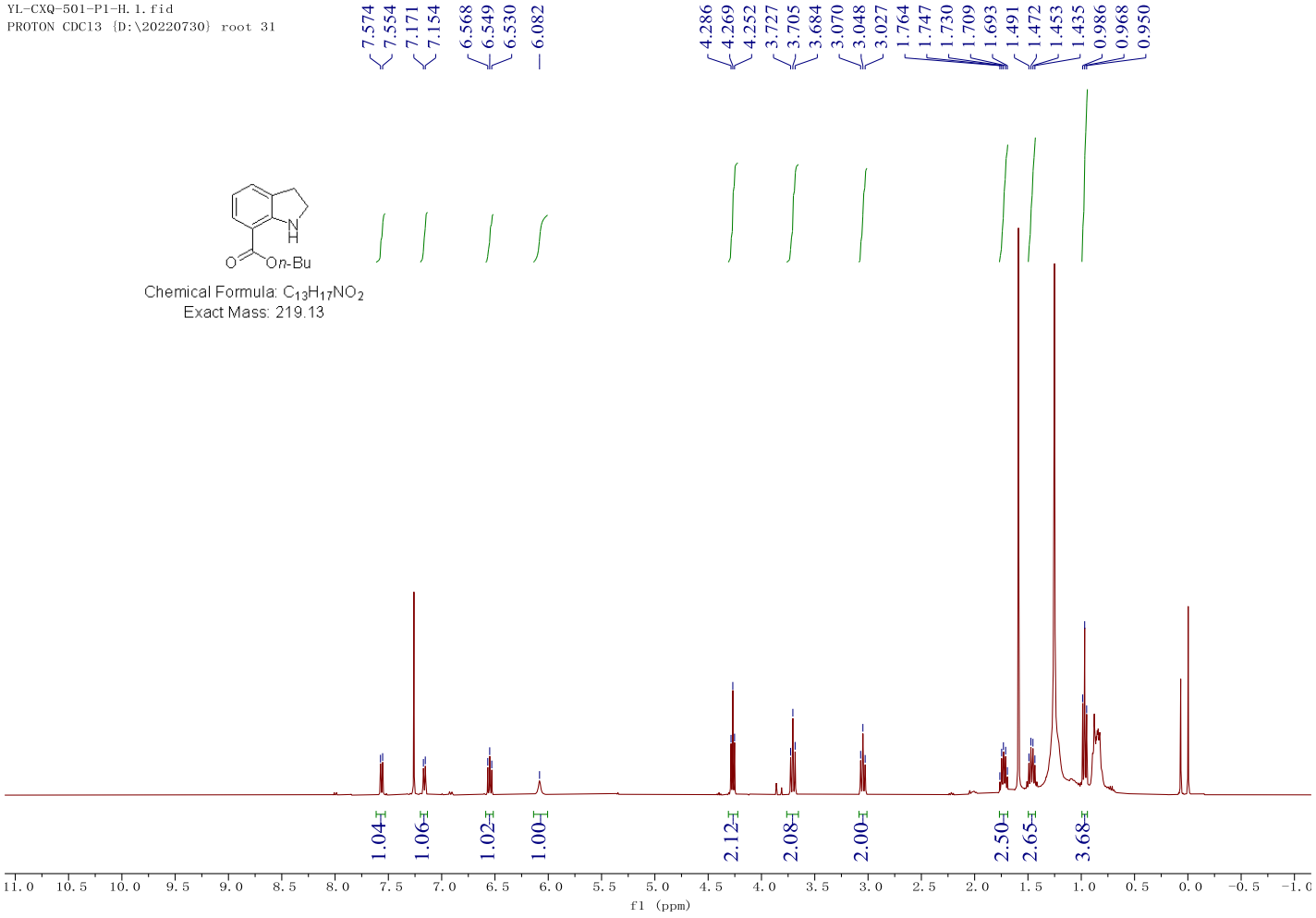
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5cb.**



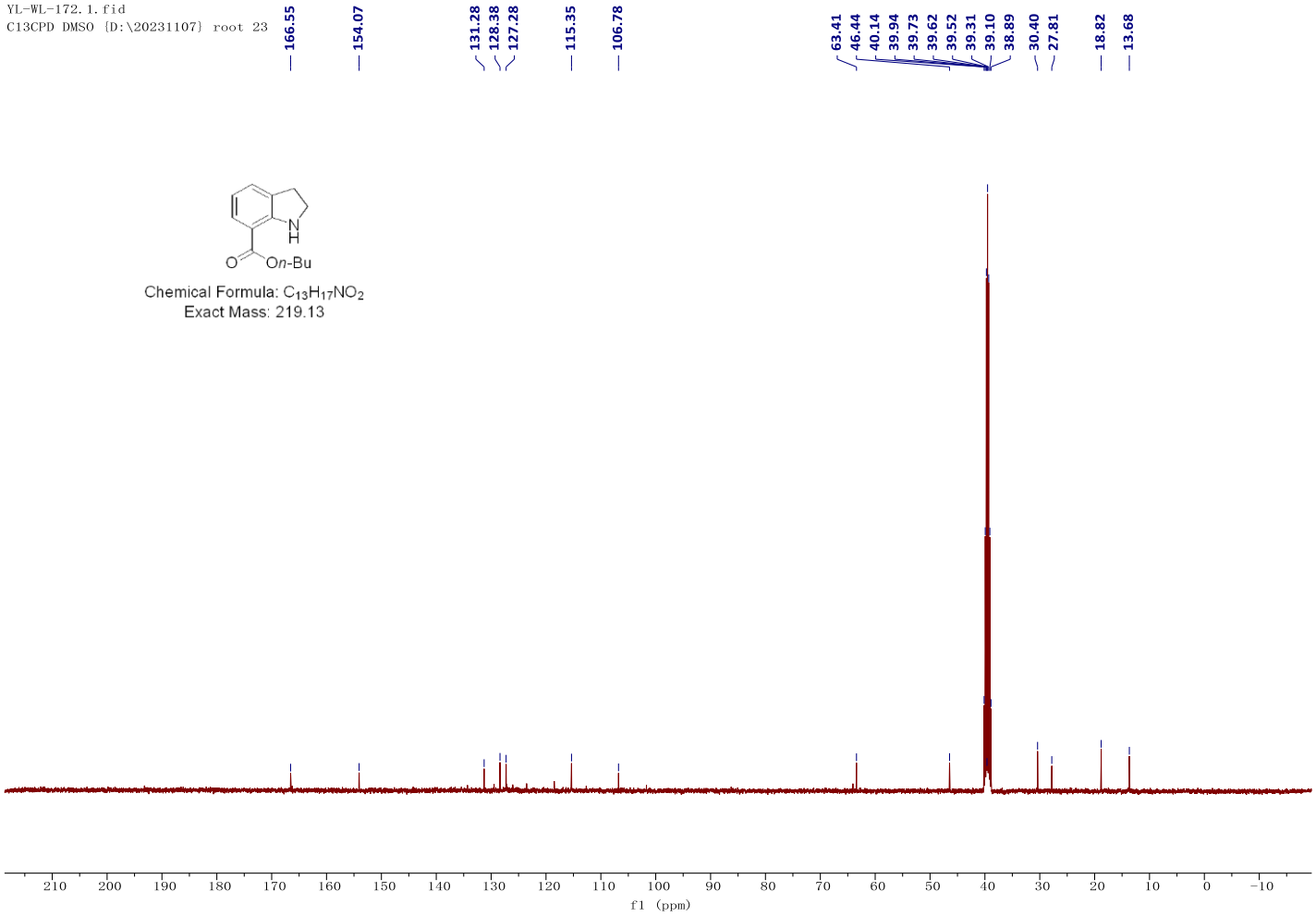
$^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO) spectrum of compound **5cb.**



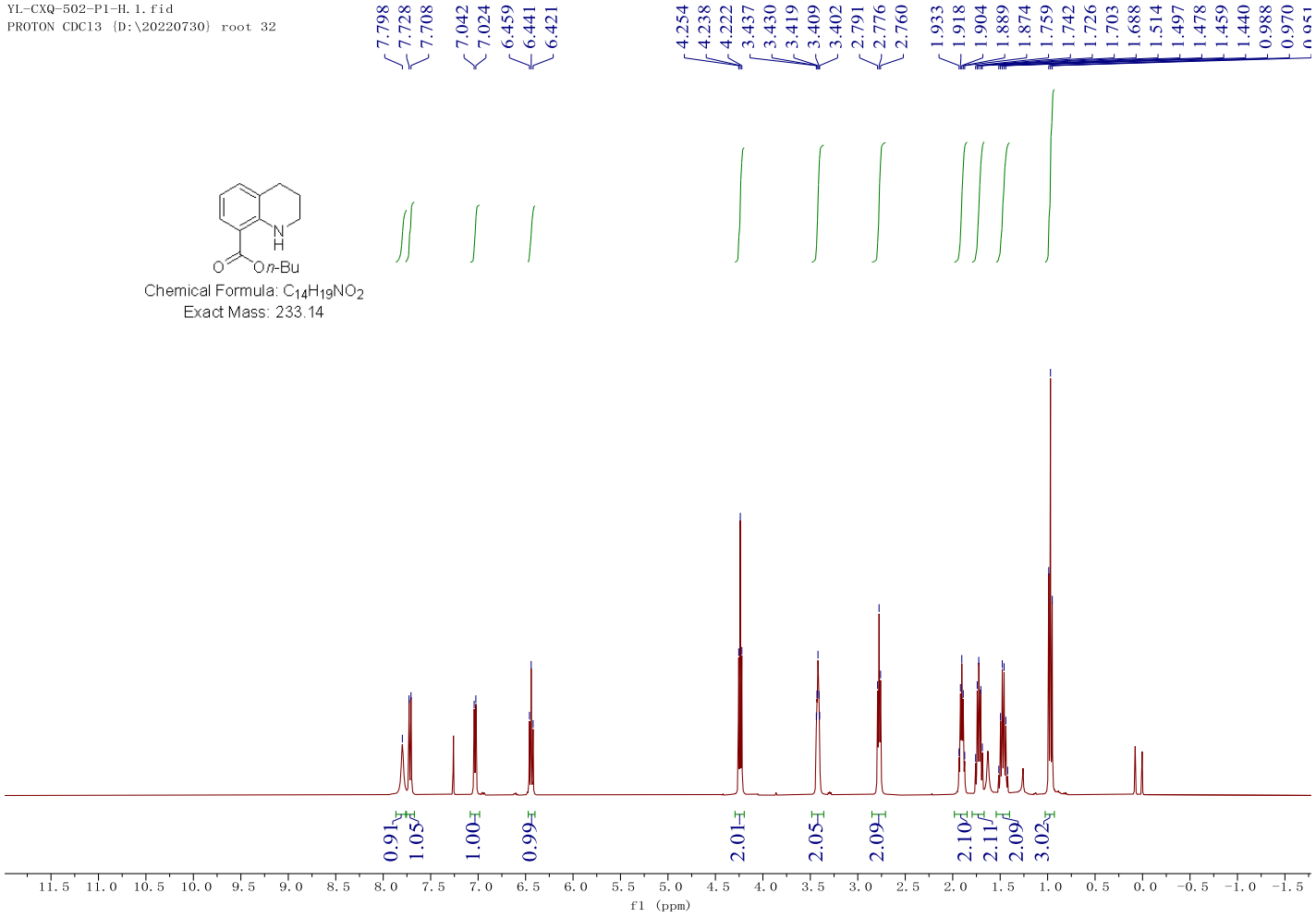
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5db.**



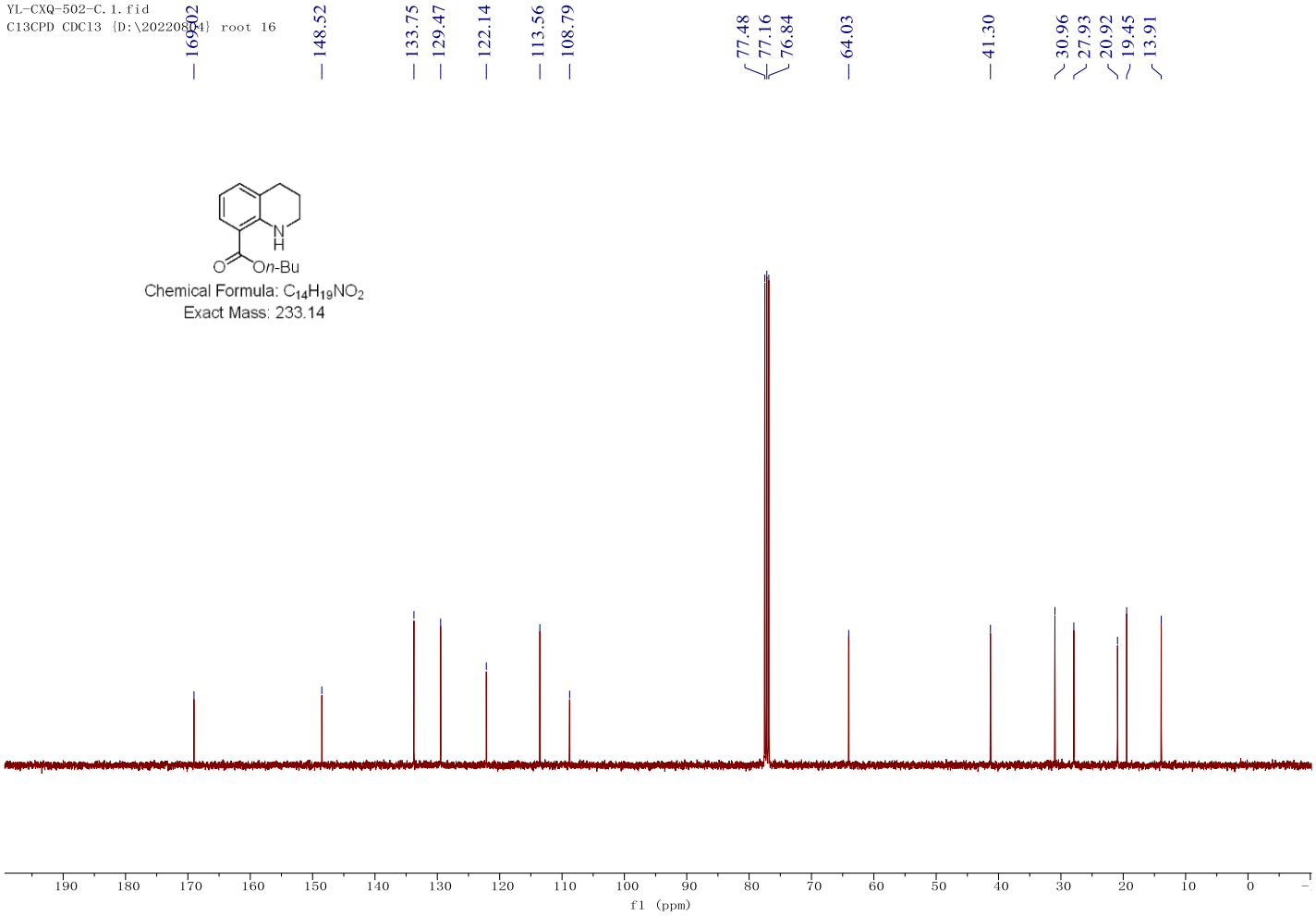
$^{13}C\{^{1}H\}$ **NMR** (101 MHz, DMSO) spectrum of compound **5db**



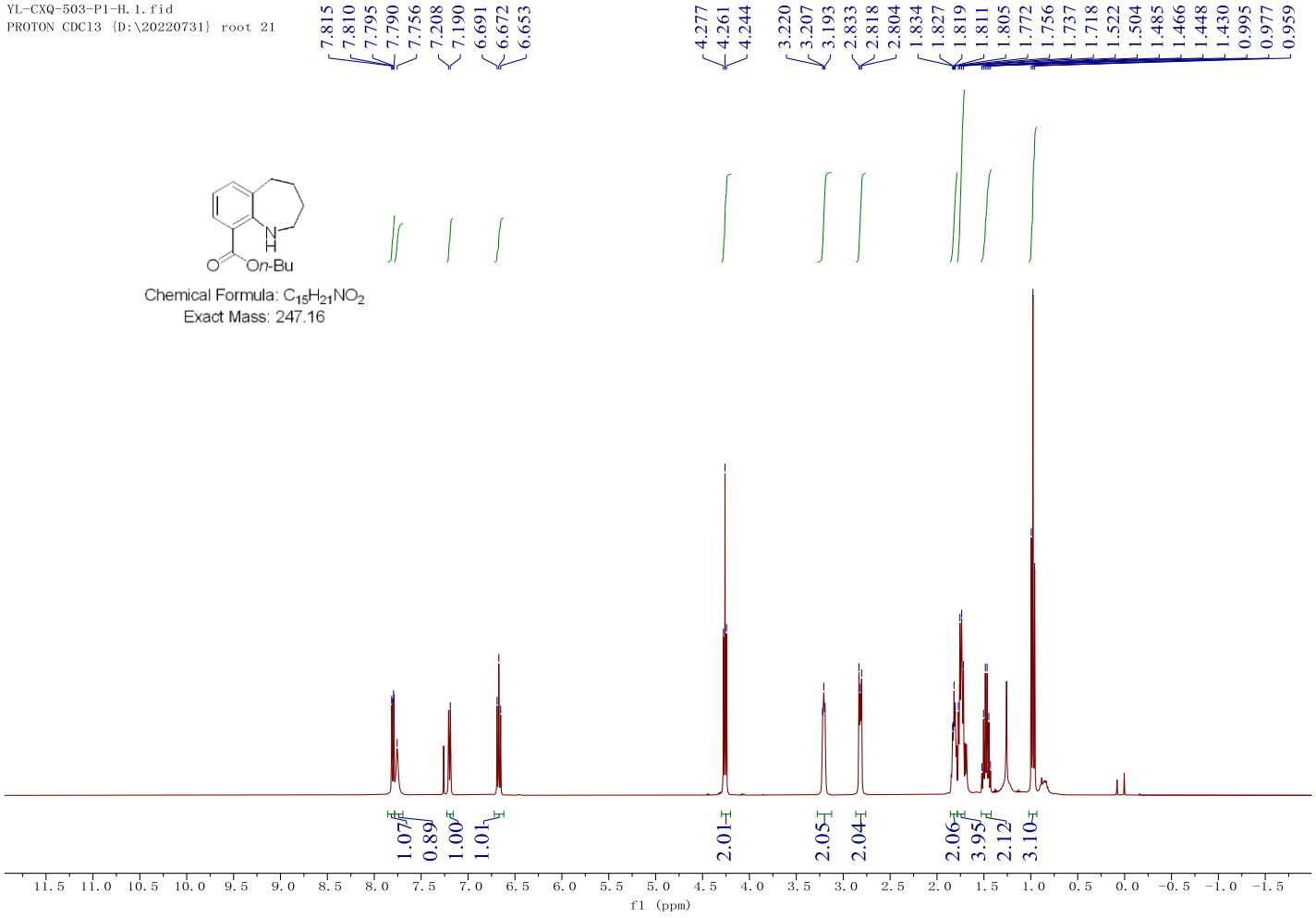
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5eb**



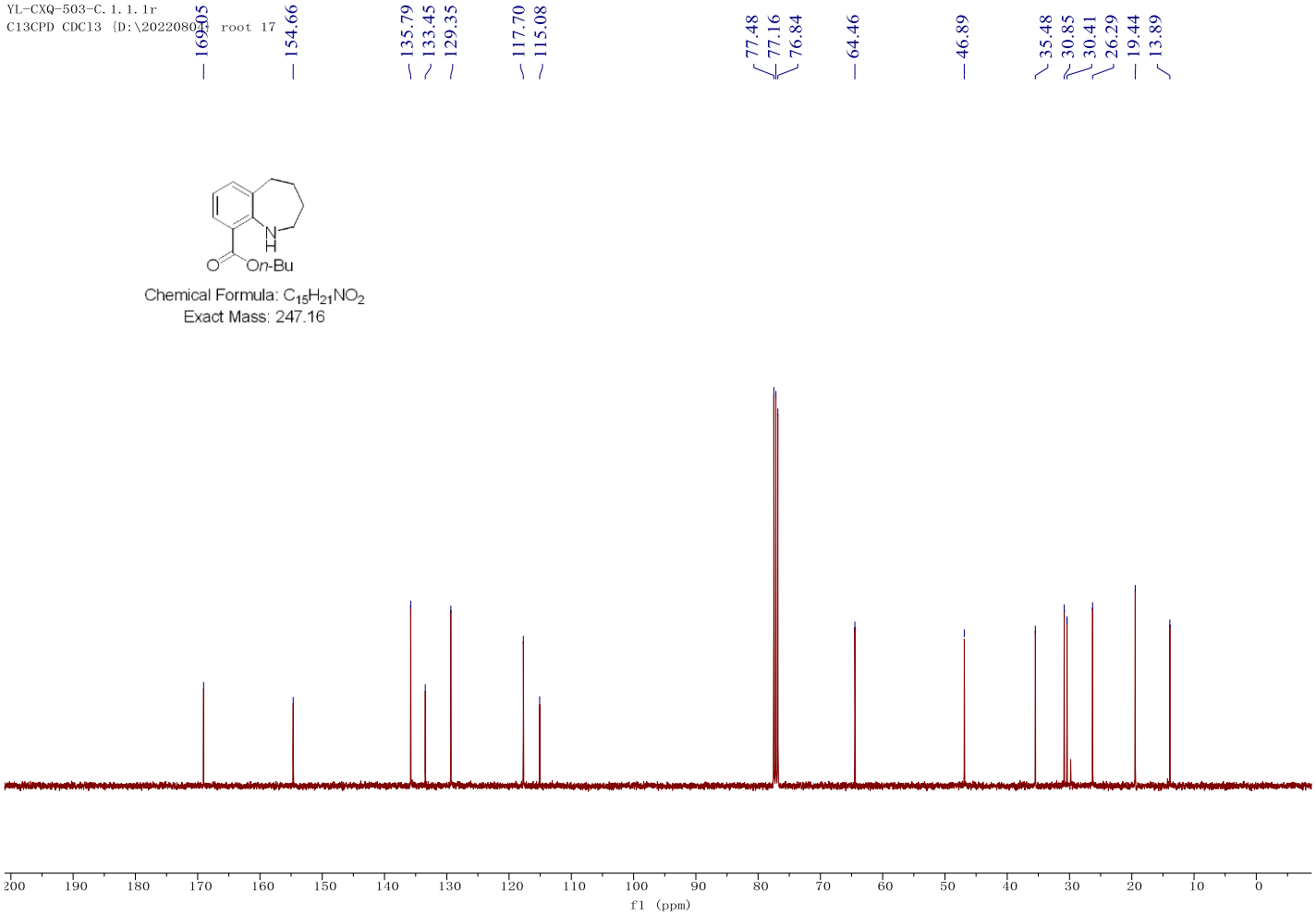
$^{13}C\{^{1}H\}$ **NMR** (101 MHz, $CDCl_3$) spectrum of compound **5eb**



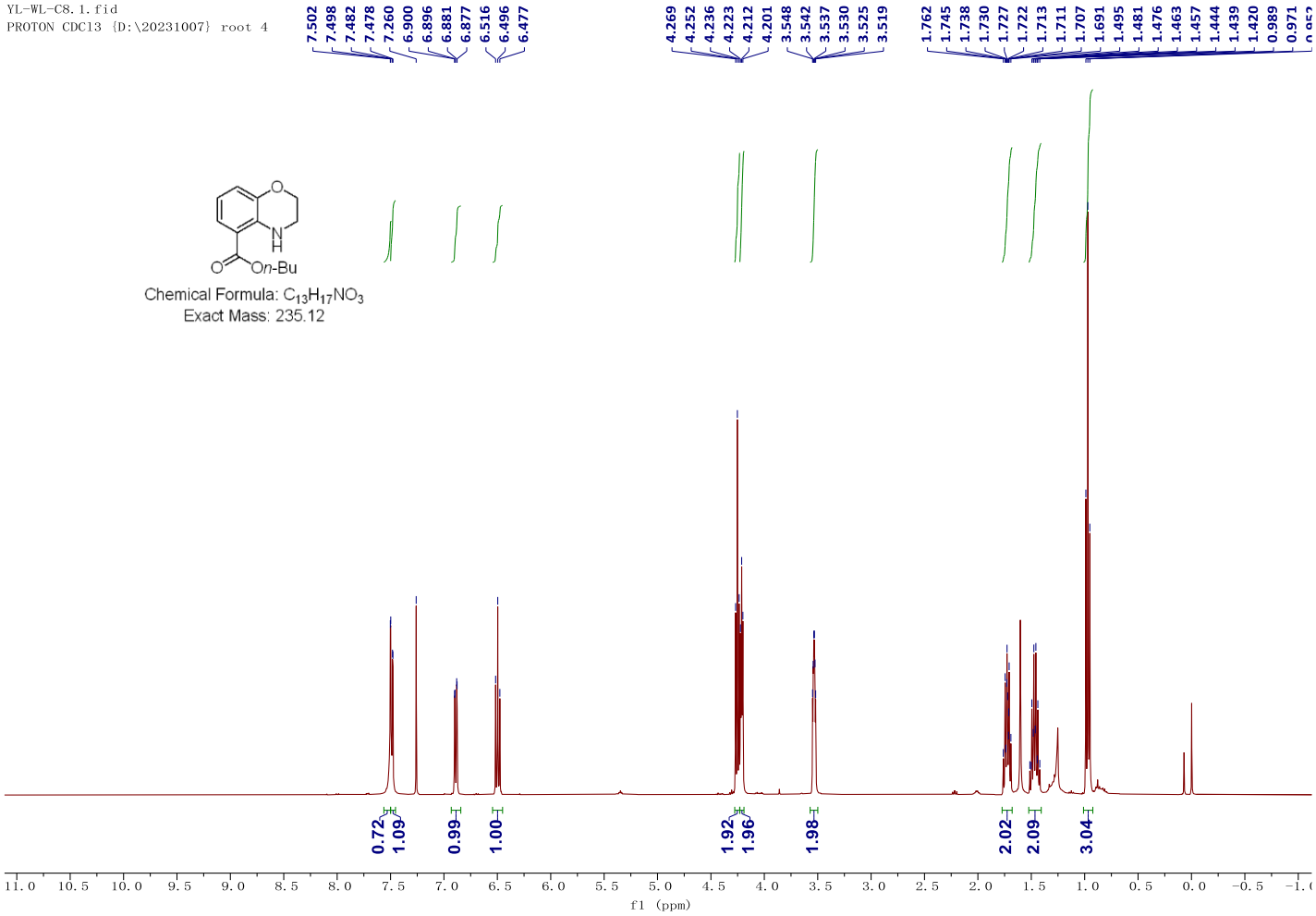
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ha**



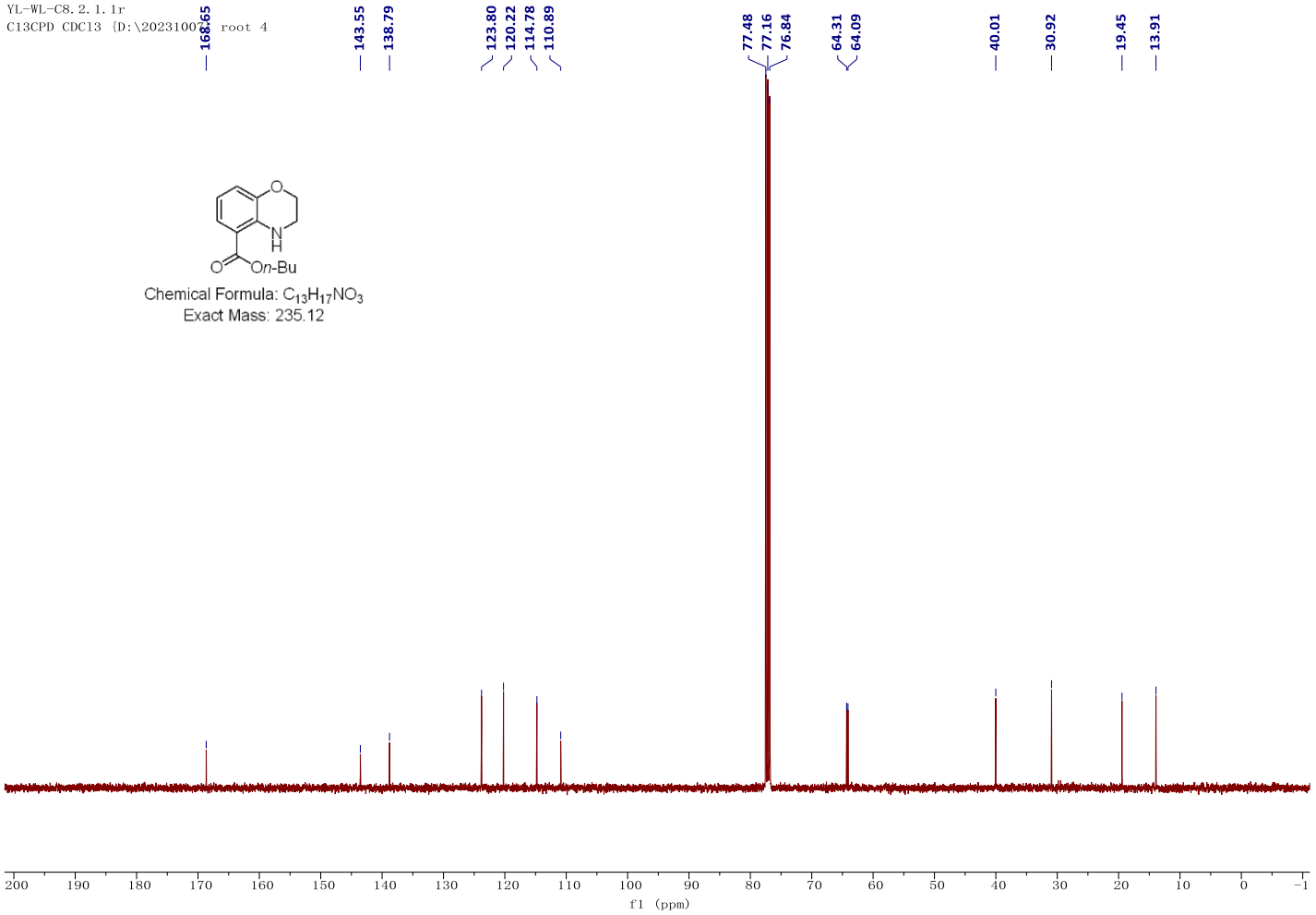
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5ha**



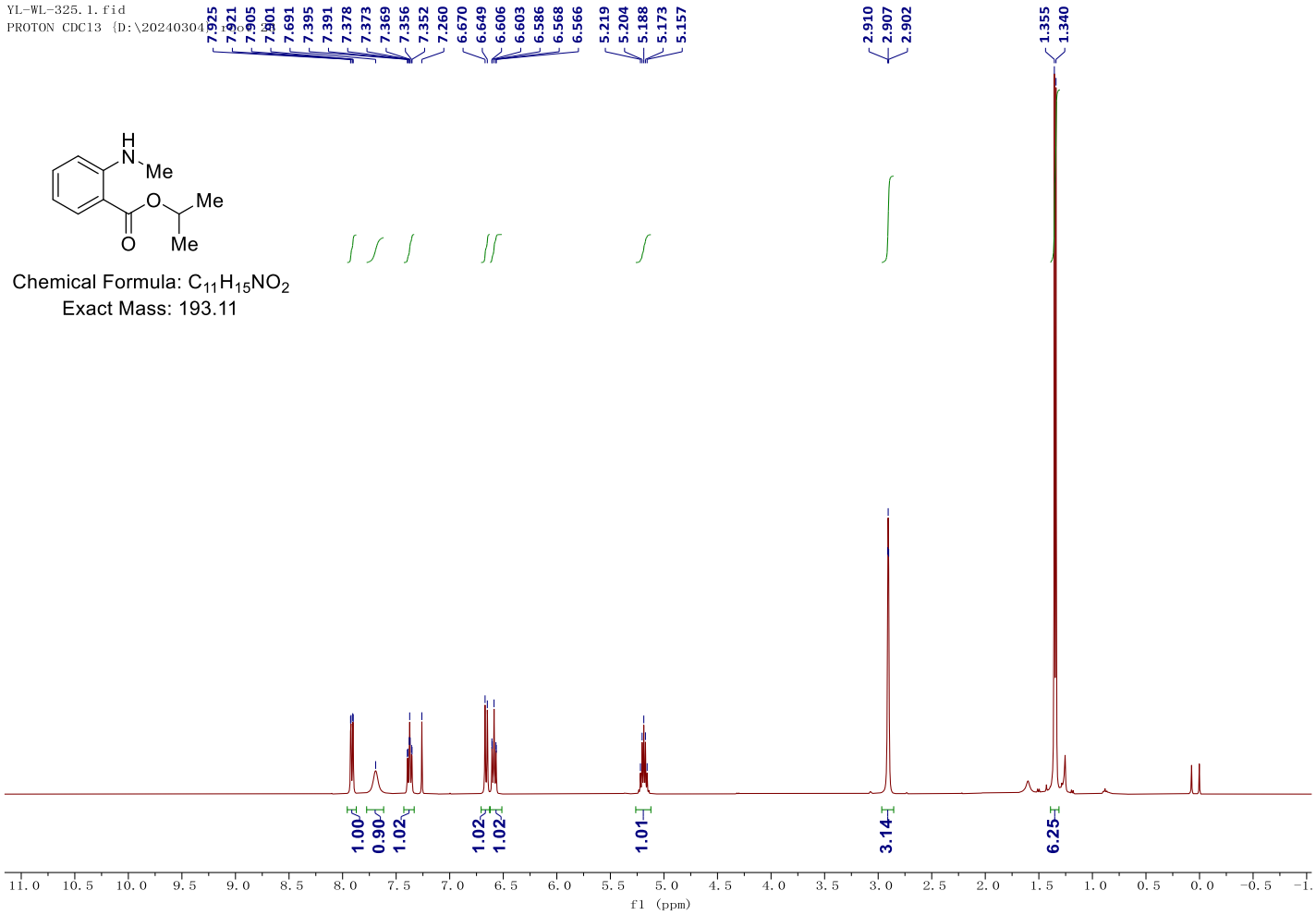
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5gb**



$^{13}C\{^{1}H\}$ **NMR** (101 MHz, $CDCl_3$) spectrum of compound **5gb**

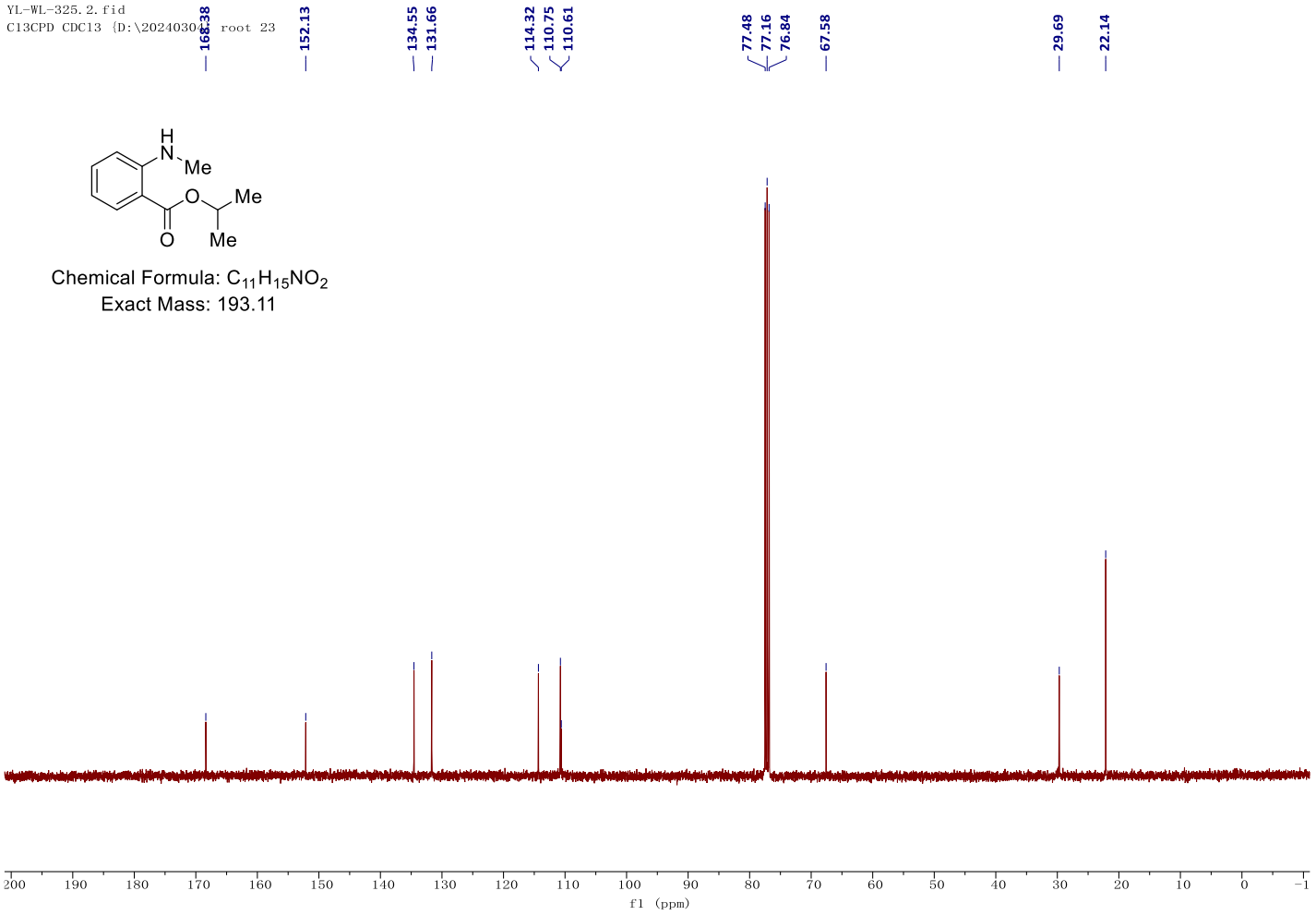


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5aa**

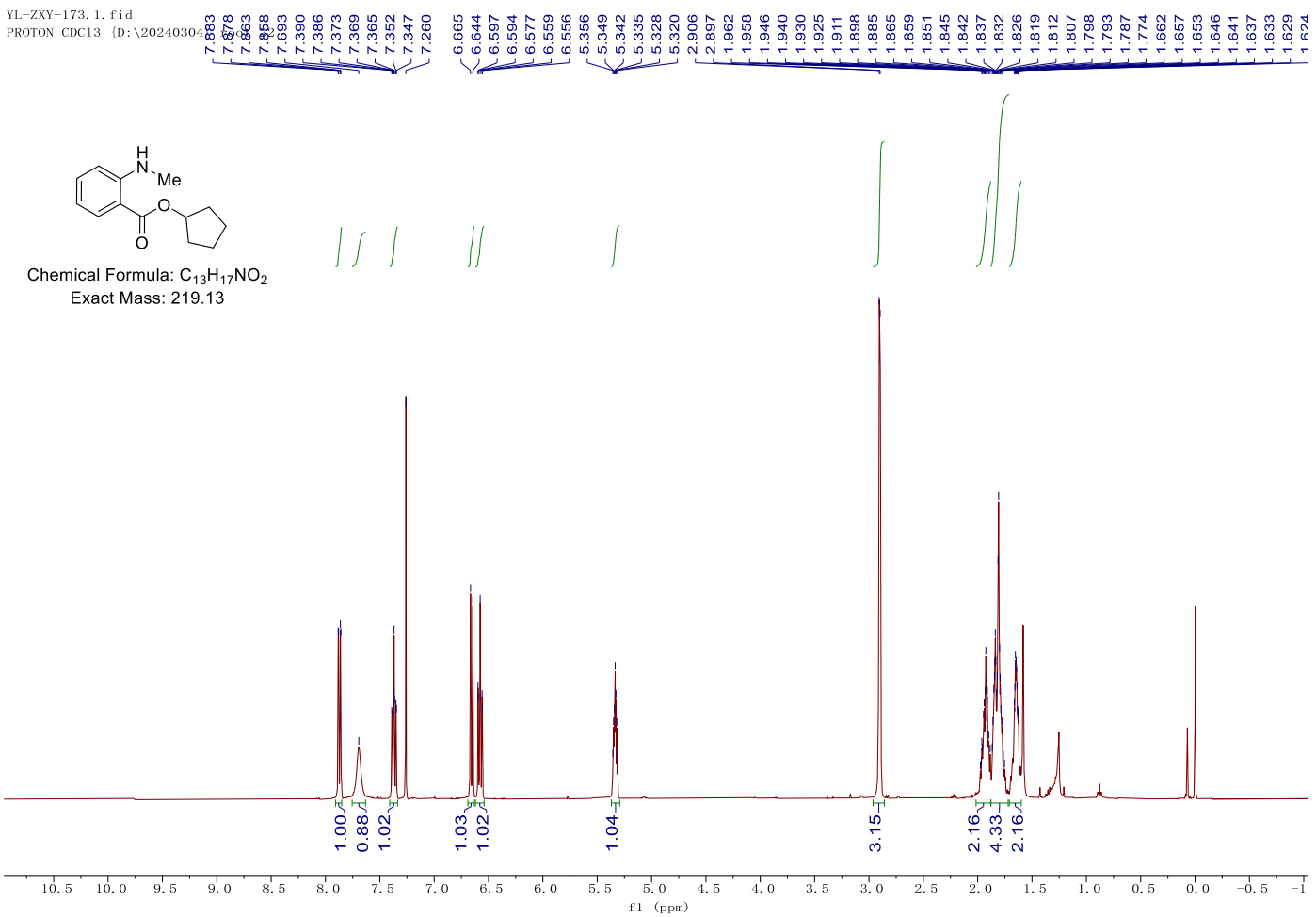


Chemical Formula: $C_{11}H_{15}NO_2$
Exact Mass: 193.11

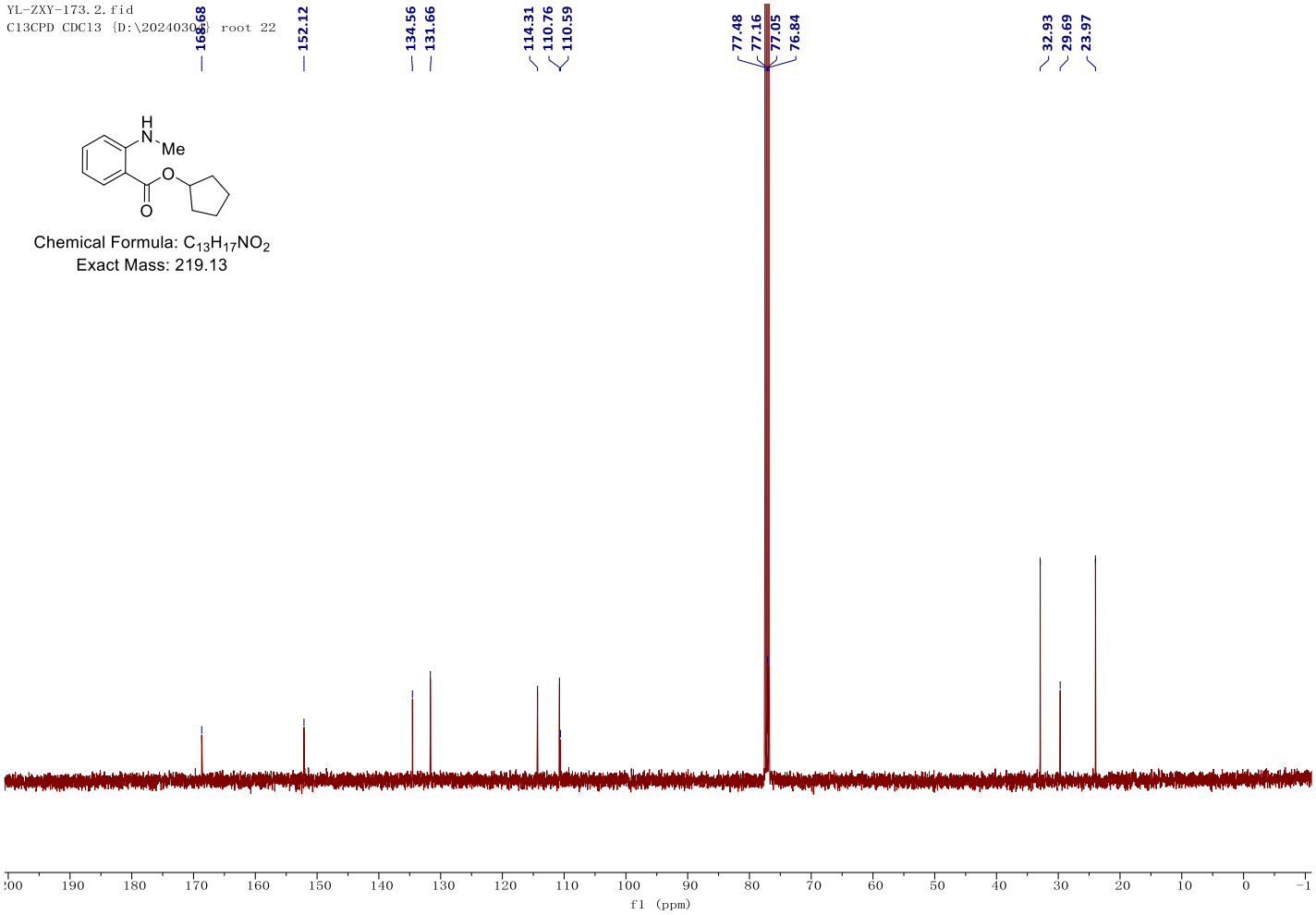
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5aa**



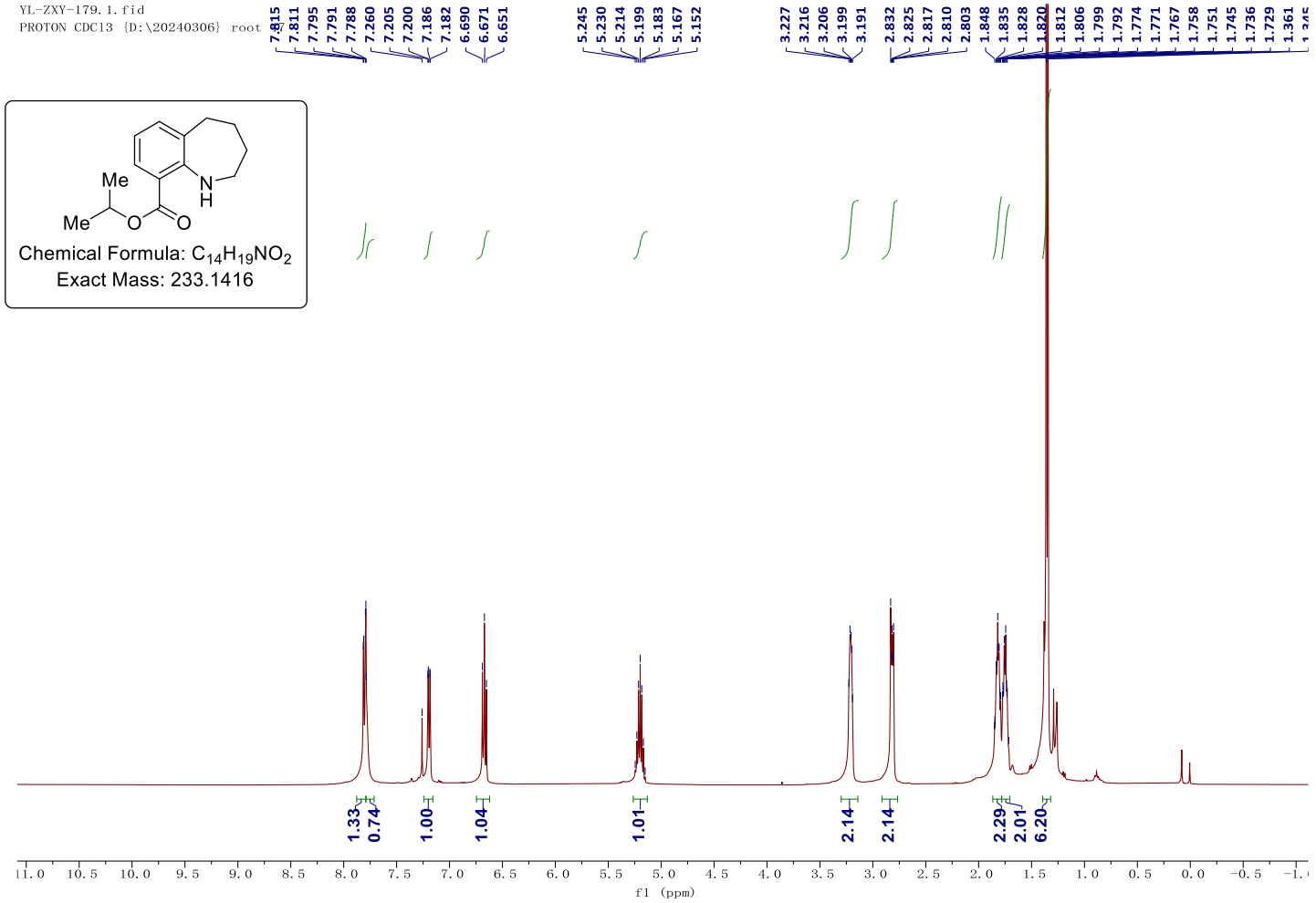
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5ai**



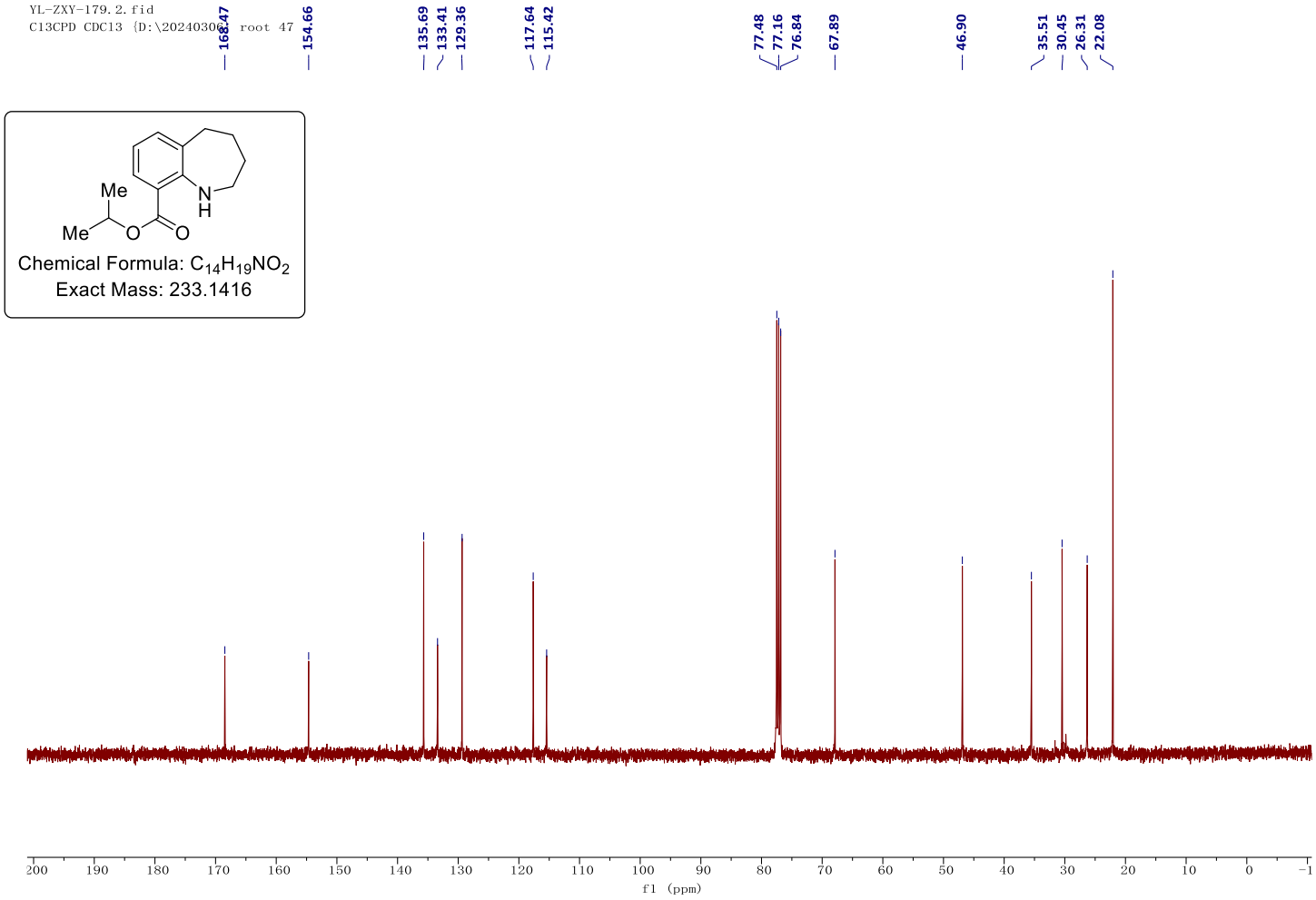
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5ai**



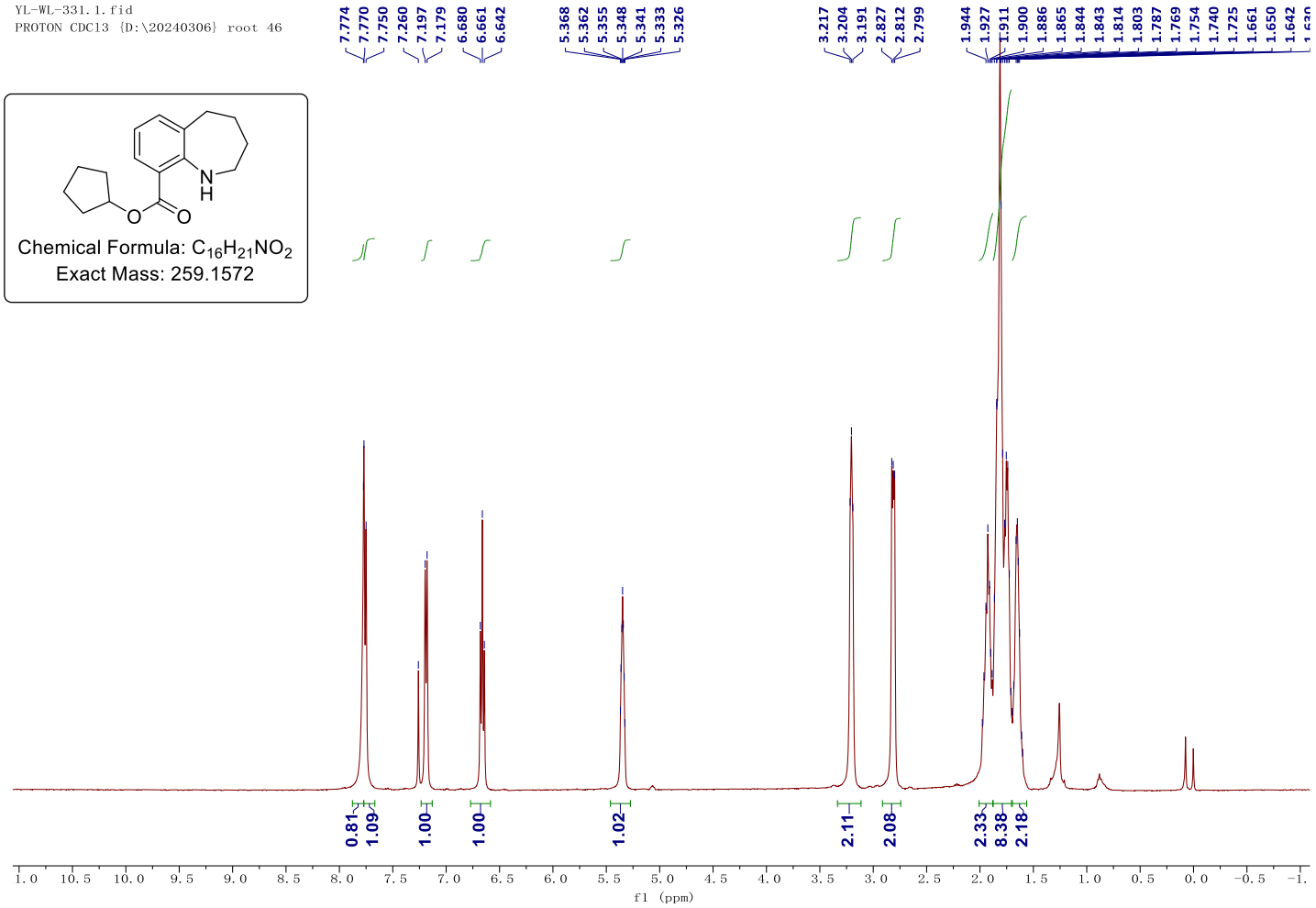
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5fa**



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5fa**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5fi**



$^{13}C\{^{1}H\}$ **NMR** (101 MHz, $CDCl_3$) spectrum of compound **5fi**