Supporting Information

Synthesis of *Z*-Alkenes from Rh(I) Catalyzed Olefin Isomerization of *β,γ*-Unsaturated Ketones

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Table of Contents

1. **Experimental Procedures and Characterization Data**

1.1 General Methods of Synthesis

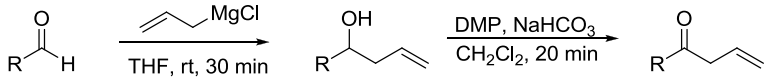
Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. THF, DME and toluene were distilled from sodium and benzophenone prior to use. CH_3CN and DCE were distilled from CaH_2 prior to use. Dichloroethane was distilled from P_2O_5 prior to use. Synthetic reagents were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds showed a single spot by analytical TLC.

NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) nuclear magnetic resonance spectrometers. Data or ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dm = doublet of multiplet, ddd = doublet of doublet of doublets, tdd = triplet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm, C_6D_6: 128.0 ppm). Infrared spectra were recorded on Mettler-Toledo React IR iC10 system with an SiComp probe and are reported in wave numbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI) using FT-ICR analyzer. Gas chromatography analyses were carried out with Agilent series 6820 GC using columns J&K Scientific CATALOG 1251017.

Abbreviations:
DCE = 1,2-dichloromethane
DCM = dichloromethane
DME = dimethoxyethane
PE = petroleum ether
EA = ethyl acetate
TBS = *tert*-butyldimethylsilyl
THF = tetrahydrofuran
TLC = thin layer chromatography
DMP = Dess–Martin periodinane

1.2 Synthesis of New Substrates

β,γ-unsaturated ketones (**1** or **3**) were prepared by following the reported procedure through allyl magnesium chloride addition to aldehydes/DMP oxidation.

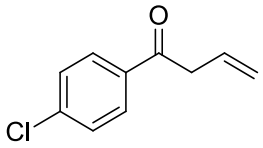


S1 **S2** **1 or 3**

A solution of allyl magnesium chloride in ether (4.1 mL, 1.7 M, 7.2 mmol) was added to a solution of aldehyde (**S1**, 5.0 mmol) in anhydrous THF (15 mL) at 0 ℃. The resulting mixture was stirred for 30 min at room temperature and then concentrated in vacuum and dissolved in 15 mL Et_2O. 5 mL saturated NH_4Cl (aq) and 5 mL water were added at 0 ˚C to the above ether solution, and then the organic layer was separated. The aqueous layer was extracted with Et_2O, and the combined organic layers were washed with saturated brine, dried over Na_2SO_4, and concentrated in vacuum. The crude product was purified by a flash silica gel eluted with PE/EA to afford the crude product **S2**.

To a solution of crude **S2** and $NaHCO_3$ (4 eq of crude **S2**) in CH_2Cl_2 (30 mL) at room temperature, DMP (1.4 eq of crude **S2**) was added. After 20 min of stirring, 5 mL saturated $Na_2S_2O_3$ (aq) and 10 mL water were added slowly at 0 ˚C. The mixture was stirred for another 20 min and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (10 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica-gel (eluted with PE/EA) to give **1**.

1-(4-chlorophenyl)but-3-en-1-one (1b)



White solid: R_f (5% EA/PE) = 0.70, 75% yield. m.p. 41-44 ˚C

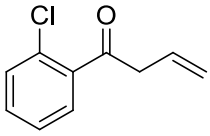
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 6.07 (ddt, J = 17.0, 10.3, 6.7 Hz, 1H), 5.28 – 5.17 (m, 2H), 3.73 (dt, J = 6.7, 1.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 139.7, 134.9, 130.7, 129.7, 129.0, 119.0, 43.4.

FT-IR (neat): ν 1687, 1590, 1400, 1211, 1091, 927 cm^{-1}

HRMS (ESI) calcd for $C_{10}H_{10}ClO$ [M+H$^+$]: 181.04147. Found: 181.04180.

1-(2-chlorophenyl)but-3-en-1-one (1c)

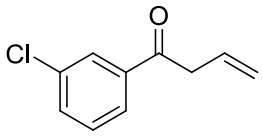


Colorless oil: R_f (5% EA/PE) = 0.70, 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.48 (m, 5H), 6.01 (ddt, J = 17.1, 10.3, 6.8 Hz, 1H), 5.25 – 5.16 (m, 2H), 3.74 (dt, J = 6.8, 1.3 Hz, 2H).

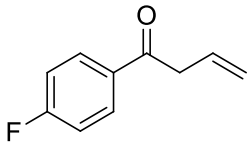
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.1, 139.1, 131.8, 130.9, 130.5, 130.2, 129.1, 126.9, 119.2, 47.5.
FT-IR (neat): v 1702, 1661, 1594, 1434, 1296, 1065, 1006, 927 cm^{-1}
HRMS (ESI) calcd for $C_{10}H_9ClNaO$ [M+Na^+]: 203.02341. Found: 203.02354.

1-(3-chlorophenyl)but-3-en-1-one (1d)



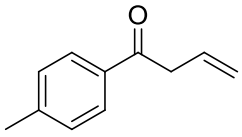
Colorless oil: R_f (5% EA/PE) = 0.70, 57% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.41 (t, J = 7.9 Hz, 1H), 6.07 (ddt, J = 17.0, 10.3, 6.7 Hz, 1H), 5.30 – 5.18 (m, 2H), 3.74 (d, J = 6.7 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 138.1, 135.0, 133.1, 130.5, 130.0, 128.4, 126.4, 119.1, 43.5.
FT-IR (neat): v 1695, 1576, 1423, 1333, 1207, 916, 793 cm^{-1}
HRMS (ESI) calcd for $C_{10}H_9ClNaO$ [M+Na^+]: 203.02341. Found: 203.02349.

1-(4-fluorophenyl)but-3-en-1-one (1e)



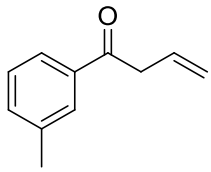
Colorless oil: R_f (5% EA/PE) = 0.70, 52% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 8.8, 5.4 Hz, 2H), 7.14 (t, J = 8.6 Hz, 2H), 6.07 (ddt, J = 17.0, 10.3, 6.7 Hz, 1H), 5.29 – 5.17 (m, 2H), 3.74 (dt, J = 6.7, 1.3 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.41 (s), 165.79 (d, J = 254.9 Hz), 132.98 (d, J = 3.0 Hz), 130.94 (d, J = 9.3 Hz), 118.89 (s), 130.85 (s), 115.74 (d, J = 21.9 Hz), 43.39 (s).
FT-IR (neat): v 1687, 1628, 1602, 1508, 1333, 1300, 1229, 1009 cm^{-1}
HRMS (ESI) calcd for $C_{10}H_{10}FO$ [M+H^+]: 165.07102. Found: 165.07119.

1-p-tolylbut-3-en-1-one (1f)



Colorless oil: R_f (5% EA/PE) = 0.75, 68% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.08 (ddt, J = 17.1, 10.4, 6.7 Hz, 1H), 5.18-5.24 (m, 2H), 3.73 (d, J = 6.7 Hz, 2H), 2.41 (s, 3H).
FT-IR (neat): v1680, 1591, 1444, 890 cm^{-1}
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 144.0, 134.1, 131.3, 129.3, 128.4, 118.6, 43.4, 21.6.
HRMS (ESI) calcd for [M+H^+]: 161.09664. Found:161.09617

1-m-tolylbut-3-en-1-one (1g)



Colorless oil: R_f (5% EA/PE) = 0.75, 68% yield.

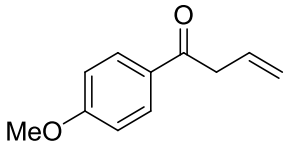
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 2H), 7.41 – 7.31 (m, 2H), 6.09 (ddt, J = 17.1, 10.4, 6.7 Hz, 1H), 5.25 – 5.22 (m, 1H), 5.18-5.24 (m, 2H), 3.75 (dt, J = 6.7, 1.4 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 138.4, 136.7, 133.9, 131.2, 128.8, 128.5, 125.5, 118.6, 43.5, 21.4.

FT-IR (neat): v 1687, 1609, 1590, 1430, 1300, 924 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{12}NaO$ [M+Na$^+$]: 183.07804. Found: 183.07818.

1-(4-methoxyphenyl)but-3-en-1-one (1h)



White solid: R_f (10% EA/PE) = 0.70, 71% yield. m.p. 40-42 ˚C

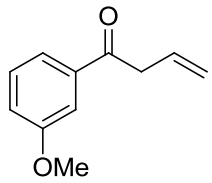
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 6.08 (ddt, J = 17.1, 10.5, 6.7 Hz, 1H), 5.18-5.21 (m, 2H), 3.87 (s, 3H), 3.71 (dt, J = 6.7, 1.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 163.6, 131.5, 130.6, 129.7, 118.5, 113.8, 55.5, 43.2.

FT-IR (neat): v1684, 1613, 1512, 1270, 1170, 1024 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{12}NaO_2$ [M+Na$^+$]: 199.07295. Found: 199.07306.

1-(3-methoxyphenyl)but-3-en-1-one (1i)



Colorless oil: R_f (5% EA/PE) = 0.75, 64% yield.

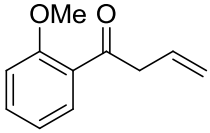
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.7 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.37 (t, J = 7.9 Hz, 1H), 7.11 (dd, J = 8.2, 2.6 Hz, 1H), 6.08 (ddt, J = 17.1, 10.4, 6.7 Hz, 1H), 5.28 – 5.16 (m, 2H), 3.85 (s, 3H), 3.74 (dt, J = 6.7, 1.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 159.9, 138.0, 131.1, 129.6, 120.9, 119.6, 118.7, 112.6, 55.4, 43.6.

FT-IR (neat): v 1687, 1583, 1486, 1438, 1248, 1028 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{12}NaO_2$ [M+Na$^+$]: 199.07295. Found: 199.07311.

1-(2-methoxyphenyl)but-3-en-1-one (1j)



Colorless oil: R_f (5% EA/PE) = 0.70, 86% yield.

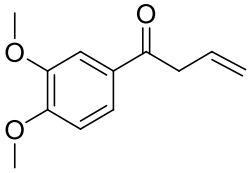
^{1}H NMR (400 MHz, C_6D_6) δ 7.86 (dd, J = 7.7, 1.4 Hz, 1H), 7.03 (tdd, J = 9.1, 4.2, 1.8 Hz, 1H), 6.70 (td, J = 7.4, 1.9 Hz, 1H), 6.37 (dd, J = 8.1, 5.3 Hz, 1H), 6.22 (ddt, J = 17.5, 10.8, 6.8 Hz, 1H), 5.02-5.06 (m, 2H), 3.67 (dd, J = 6.8, 1.3 Hz, 3H), 3.11 (d, J = 6.2 Hz, 2H).

^{13}C NMR (101 MHz, C_6D_6) δ 198.4, 158.6, 133.2, 133.1, 132.5, 130.8, 120.8, 117.3, 111.5, 54.7, 48.8.

FT-IR (neat): v 1676, 1602, 1490, 1468, 1248, 1028 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{12}NaO_2$ [M+Na$^+$]: 199.07295. Found: 199.07312.

1-(3,4-dimethoxyphenyl)but-3-en-1-one (1k)



White solid: R_f (20% EA/PE) = 0.40, 88% yield. m.p. 50-55˚C.

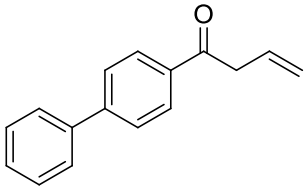
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 0.9 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.16 – 6.02 (m, 1H), 5.23 (s, 1H), 5.22 – 5.18 (m, 1H), 3.94 (s,3H), 3.96 (s,3H), 3.75 – 3.70 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 153.4, 149.1, 131.5, 129.8, 123.0, 118.43, 110.4, 110.0, 56.1, 56.0, 43.2.

FT-IR (neat): v1674, 1596, 1517, 1419, 1244, 1022 cm^{-1}

HRMS (ESI) calcd for $C_{12}H_{15}O_3$ [M+H$^+$]: 207.10157. Found: 207.10178.

1-(biphenyl-4-yl)but-3-en-1-one (1l)



White solid: R_f (5% EA/PE) = 0.75, 75% yield. m.p. 73-75 ˚C.

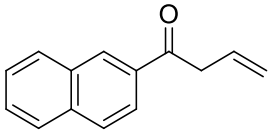
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.5 Hz, 2H), 7.62-7.67 (m, 4H), 7.38-7.49 (m, 3H), 6.11 (ddt, J = 17.1, 10.5, 6.7 Hz, 1H), 5.28 – 5.25 (m, 1H), 5.23 (dd, J = 9.3, 1.4 Hz, 1H), 3.79 (dt, J = 6.7, 1.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 145.9, 139.9, 135.3, 131.1, 129.0, 128.9, 128.3, 127.3, 118.8, 43.5.

FT-IR (neat): v1680, 1609, 1400, 1333, 1196 cm^{-1}

HRMS (ESI) calcd for $C_{16}H_{15}O$ [M+H$^+$]: 223.11174. Found: 223.11203.

1-(naphthalen-2-yl)but-3-en-1-one (1m)



Colorless oil: R_f (5% EA/PE) = 0.75, 79% yield

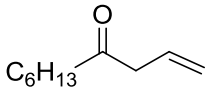
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 8.6 Hz, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.88 (t, J = 7.3 Hz, 2H), 7.63 – 7.43 (m, 3H), 6.19 – 6.04 (m, 1H), 5.30 – 5.21 (m, 2H), 3.84 (d, J = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 135.5, 134.0, 132.8, 131.2, 130.3, 128.4, 128.0, 127.8, 126.5, 125.8, 124.3, 118.8, 47.0.

FT-IR (neat): v1684, 1516, 1292, 1233, 1177, 1091, 927 cm^{-1}

HRMS (ESI) calcd for $C_{14}H_{12}NaO$ [M+Na$^+$]: 219.07804. Found: 219.07798.

dec-1-en-4-one (3a)



Colorless oil: R_f (5% EA/PE) = 0.80, 46% yield.

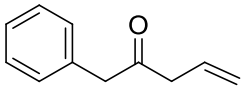
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (ddt, J = 17.2, 10.2, 7.0 Hz, 1H), 5.22 – 5.09 (m, 2H), 3.17 (d, J = 7.0 Hz, 2H), 2.43 (t, J = 7.4 Hz, 2H), 1.57 (dq, J = 14.7, 7.3 Hz, 2H), 1.26 – 1.28 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.0, 130.8, 118.6, 47.7, 42.4, 31.6, 28.9, 23.7, 22.8, 14.0.

FT-IR (neat): v1719, 1460, 700 cm^{-1}

HRMS (ESI) calcd for $C_{10}H_{19}O$ [M+H$^+$]: 155.14304. Found: 155.14319.

1-phenylpent-4-en-2-one (3b)



Colorless oil: R_f (5% EA/PE) = 0.75, 55% yield.

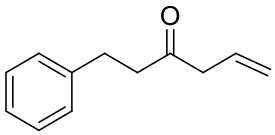
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.35 (m, 5H), 5.90 (ddt, J = 17.2, 10.2, 6.9 Hz, 1H), 5.09-5.19 (m, 2H), 3.72 (s, 2H), 3.21 (d, J = 6.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.1, 134.0, 130.4, 129.5, 128.8, 127.1, 119.0, 49.6, 46.8.

FT-IR (neat): v1720, 1499, 1458, 1333, 1056, 700 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{12}NaO$ [M+Na$^+$]: 183.07804. Found: 183.07818.

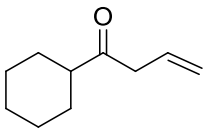
1-phenylhex-5-en-3-one (3c)



Colorless oil: R_f (5% EA/PE) = 0.75, 27% yield.

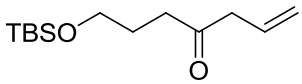
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.31 (m, 5H), 5.90 (ddt, J = 17.2, 10.2, 7.0 Hz, 1H), 5.17 (dd, J = 10.2, 1.1 Hz, 1H), 5.09-5.19 (m 1H), 3.15 (d, J = 7.0 Hz, 2H), 2.94 – 2.85 (m, 2H), 2.82 – 2.74 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 141.0, 130.5, 128.5, 128.3, 126.1, 119.0, 47.9, 43.9, 29.7.
FT-IR (neat): v1718, 1499, 700 cm^{-1}
HRMS (ESI) calcd for $C_{12}H_{14}NaO$ [M+Na$^+$]: 197.09369. Found: 197.09339.

1-cyclohexylbut-3-en-1-one (3d)



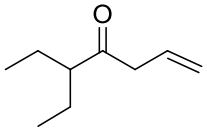
Colorless oil: R_f (5% EA/PE) = 0. 80, 46% yield.
^{1}H NMR (400 MHz, C_6D_6) δ 5.97 (ddt, J = 17.1, 10.2, 6.9 Hz, 1H), 5.02 (d, J = 9.7 Hz, 1H), 4.95 (d, J = 17.2 Hz, 1H), 2.82 (d, J = 6.8 Hz, 2H), 1.96 (ddd, J = 11.5, 7.4, 3.3 Hz, 1H), 1.65 – 1.49 (m, 4H), 1.45-1.54 (m, 1H), 1.31 – 1.15 (m, 2H), 1.43 – 1.14 (m, 3H).
^{13}C NMR (101 MHz, C_6D_6) δ 209.0, 131.9, 117.5, 50.1, 45.3, 28.4, 26.0, 25.7.
FT-IR (neat): v2934, 2858, 1709, 1450, 1149 cm^{-1}
HRMS (ESI) calcd for $C_{11}H_{12}NaO$ [M+Na$^+$]: 183.07804. Found: 183.07770.

1-(tert-butyldimethylsilyloxy)hex-5-en-3-one (3e)



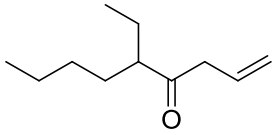
Colorless oil: R_f (5% EA/PE) = 0.75, 53% yield.
^{1}H NMR (400 MHz, C_6D_6) δ 5.86 (ddt, J = 17.2, 10.2, 7.0 Hz, 1H), 4.97 (dd, J = 10.2, 1.3 Hz, 1H), 4.89 (dd, J = 17.2, 1.5 Hz, 1H), 3.43 (t, J = 6.1 Hz, 2H), 2.74 (d, J = 7.0 Hz, 2H), 2.14 (t, J = 7.1 Hz, 2H), 1.74 – 1.66 (m, 2H), 0.93 (s, 9H), 0.02 – -0.01 (m, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 206.1, 117.8, 135.1, 62.2, 47.5, 38.2, 26.9, 26.0, 18.3, -5.4.
FT-IR (neat): v2932, 2858, 2365, 1720, 1638, 1102, 668 cm^{-1}
HRMS (ESI) calcd for $C_{13}H_{26}NaO_2Si$ [M+Na$^+$]: 265.15943. Found: 265.15941.

5-ethylhept-1-en-4-one (3f)



Colorless oil: R_f (5% EA/PE) = 0. 80, 24% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (ddt, J = 17.2, 10.2, 7.0 Hz, 1H), 5.26 – 5.05 (m, 2H), 3.19 (dt, J = 7.0, 1.3 Hz, 2H), 2.39 (tt, J = 7.9, 5.7 Hz, 1H), 1.70 – 1.56 (m, 2H), 1.54 – 1.38 (m, 2H), 0.86 (t, J = 7.4 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 212.4, 130.8, 118.5, 55.0, 47.1, 24.1, 11.8.
FT-IR (neat): v2368, 1655, 1562 cm^{-1}
HRMS (ESI) calcd for $C_9H_{16}NaO$ [M+Na$^+$]: 163.10934. Found: 163.10895.

5-ethylnon-1-en-4-one (3g)



Colorless oil: R_f (5% EA/PE) = 0. 80, 36% yield.

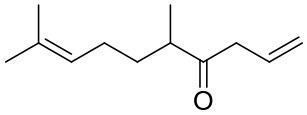
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (ddt, J = 17.2, 10.2, 7.0 Hz, 1H), 5.22 – 5.07 (m, 2H), 3.19 (d, J = 7.0 Hz, 2H), 2.51 – 2.39 (m, 1H), 1.70 – 1.53 (m, 2H), 1.38-1.46 (m, 2H), 1.34 – 1.10 (m, 4H), 0.85-0.89 (m, 6H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 212.4, 130.8, 118.4, 53.5, 47.0, 30.9, 29.6, 24.5, 22.8, 13.9, 11.8

FT-IR (neat): v 2370, 1655, 1560, cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{20}NaO$ [M+Na$^+$]: 191.14064. Found: 191.14015.

5,9-dimethyldeca-1,8-dien-4-one (3h)



Colorless oil: R_f (5% EA/PE) = 0. 80, 52% yield.

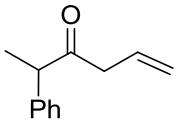
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (ddt, J = 17.2, 10.2, 6.9 Hz, 1H), 5.20 – 5.09 (m, 2H), 5.06 (t, J = 7.1 Hz, 1H), 3.21 (d, J = 6.9 Hz, 2H), 2.56 - 2.61 (m, 1H), 1.95 (q, J = 7.4 Hz, 2H), 1.77 – 1.69 (m, 1H), 1.68 (s, 3H), 1.59 (s, 3H), 1.31 – 1.39 (m, 1H), 1.08 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 212.3, 132.3, 130.9, 123.7, 118.4, 46.0, 45.4, 32.9, 25.7, 25.7, 17.7, 16.3.

FT-IR (neat): v2938, 1718, 1460, 996 cm^{-1}

HRMS (ESI) calcd for $C_{12}H_{20}NaO$ [M+Na$^+$]: 203.14064. Found: 203.14016.

2-phenylhex-5-en-3-one (3i)



Colorless oil: R_f (5% EA/PE) = 0.70, 41% yield.

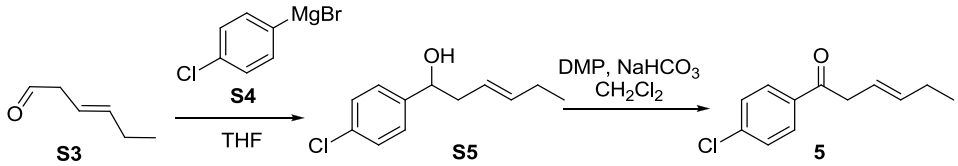
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 5H), 5.83 (ddt, J = 17.1, 10.2, 6.9 Hz, 1H), 5.11 (dd, J = 10.2, 1.4 Hz, 1H), 5.00 (dd, J = 17.1, 1.5 Hz, 1H), 3.81 (q, J = 6.9 Hz, 1H), 3.11 (dd, J = 6.9, 1.1 Hz, 2H), 1.39 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.5, 140.4, 130.8, 129.0, 128.0, 127.2, 118.6, 52.5, 45.9, 17.5.

FT-IR (neat): v1718, 1493, 1456, 702 cm^{-1}

HRMS (ESI) calcd for $C_{12}H_{14}NaO$ [M+Na$^+$]: 197.09369. Found: .197.09328.

***(E)*-1-(4-chlorophenyl)hex-3-en-1-one (5)**



A solution of **S4** in ether (3.9 mL, 1 M, 3.9 mmol) was added to a solution of aldehyde (**S3**, 2.8 mmol, 281 mg) in anhydrous THF (10 mL) at 0 ℃. The resulting mixture was stirred for 30 min at room temperature and then concentrated in vacuum and dissolved in 15 mL Et_2O. 5 mL saturated NH_4Cl (aq) and 5 mL water were added at 0 ˚C to the above ether solution, and the organic layer was separated. The aqueous layer was extracted with Et_2O, and the combined organic layers were washed with saturated brine, dried over Na_2SO_4, and concentrated in vacuum. The crude product was purified by a flash silica gel eluted with PE/EA to afford the crude **S5** (crude, yellow oil, 243 mg).

To a solution of crude **S5** and $NaHCO_3$ (4.6 mmol, 386 mg) in CH_2Cl_2 (5 mL) at room temperature, DMP (1.16 mmol, 682 mg) was added. After 20 min of stirring, 3 mL saturated $Na_2S_2O_3$ (aq) and 5 mL water were added slowly at 0 ˚C. The mixture was stirred for another 20 min and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica-gel (eluted with PE/EA = 30:1) to give **5**, 140 mg, 22% yield for two steps, as a colorless oil (R_f (5% EA/PE) = 0.65).

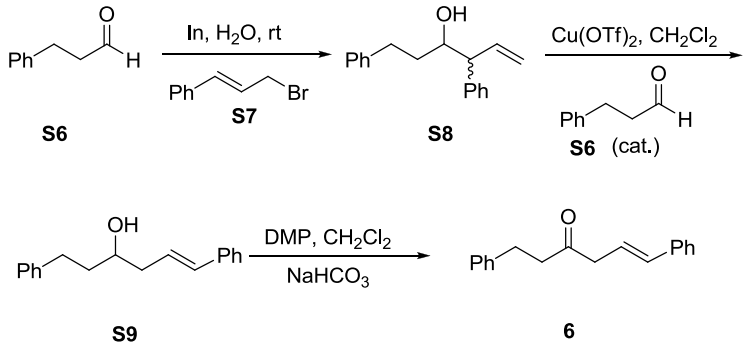
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 5.65 - 5.67 (m, 2H), 3.66 (d, J = 4.6 Hz, 2H), 2.07 (dd, J = 7.4, 4.3 Hz, 2H), 0.99 (t, J = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 139.5, 136.9, 135.0, 129.8, 128.9, 120.9, 42.5, 25.7, 13.5.

FT-IR (neat): v1634, 1607, 1500, 904 cm^{-1}

HRMS (ESI) calcd for $C_{13}H_{16}ClO$ [M+H$^+$]: 223.08842. Found: 223.08841.

(E)-1,6-diphenylhex-5-en-3-one (6)



A mixture of **S6** (5.0 mmol, 670 mg) and indium powder (7.5 mmol, 861 mg) in H_2O (5 mL) was added **S7** (6.0 mmol, 118 mg) slowly at room temperature. The reaction mixtures were stirred for 12 hours at room temperature. Ethyl ether was added to dilute the reaction mixture, followed by 1 M HCl (4 mL) to quench the reaction. The reaction mixture was then extracted with ether. The combined organic layer was washed with saturated brine, and dried over anhydrous Na_2SO_4, filtered and the solvent was removed in vacuum. The crude product of **S8**[1] was purified by flash column chromatography to get 584 mg (44%) as an oil.

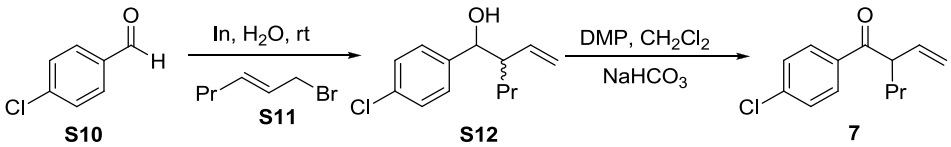
Under Ar, to a solution of crude **S8** (1.94 mmol, 490 mg) in dry CH_2Cl_2 (30 mL) at room temperature, **S6** (0.19 mmol, 38 mg) and $Cu(OTf)_2$ (0.19 mmol, 68 mg) were added. After 4 h of stirring, the reaction mixture was concentrated in vacuum. The residue was purified by column

chromatography on silica-gel (eluted with PE/EA = 20:1) to give **S9**[1], 170 mg (35%) as a colorless oil.

To a solution of **S9** (0.71 mmol, 170 mg), $NaHCO_3$ (2.84 mmol, 238 mg) in CH_2Cl_2 (8 mL) at room temperature, DMP (1.13 mmol, 481 mg) was added. After 20 min of stirring, 5 mL saturated $Na_2S_2O_3$ (aq) and 3 mL water were added slowly. The mixture was stirred for another 20 min and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica-gel (eluted with PE/EA = 30:1) to give **6**, 70 mg (41%) as a colorless oil (R_f (5% EA/PE) = 0.60).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 5H), 7.25 – 7.16 (m, 5H), 6.43 (d, J = 15.9 Hz, 1H), 6.27 (dt, J = 15.9, 7.1 Hz, 1H), 3.29 (d, J = 7.1 Hz, 2H), 2.94 – 2.88 (m, 2H), 2.85 – 2.79 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 207.7, 141.0, 136.9, 133.9, 128.6, 128.5, 128.4, 127.6, 126.3, 126.2, 121.9, 47.2, 44.0, 29.8.
FT-IR (neat): v1673, 1510, 710 cm^{-1}
HRMS (ESI) calcd for $C_{18}H_{19}O$ [M+H$^+$]: 251.14304. Found: 251.14340.

1-(4-chlorophenyl)-2-vinylpentan-1-one (7)



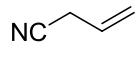
A mixture of **S10** (3 mmol, 422 mg) and indium powder (4.5 mmol, 517 mg) in H_2O (5 mL) was added **S11** (3.6 mmol, 587 mg) slowly at room temperature. The resulting reaction mixture was stirred for 16 hours at room temperature. Ethyl ether was added to dilute the reaction mixture followed by 1 M HCl (4 mL) to quench the reaction. The reaction mixture was extracted with ether. The combined organic layer was washed with saturated brine, and dried over anhydrous Na2SO4, filtered and the solvent was removed in vacuum. The crude product of **S12** was purified by flash column chromatography to get **S12** 522 mg (78%) as a yellow oil.

To a solution of crude **S12**, $NaHCO_3$ (9.28 mmol, 780 mg) in CH_2Cl_2 (30 mL) at room temperature, DMP (3.28 mmol, 1.39 g) was added. After 20 min of stirring, 10 mL saturated $Na_2S_2O_3$ (aq) and 10 mL water were added slowly at 0 ˚C. The mixture was stirred for another 20 min and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica-gel (eluted with PE/EA = 30:1) to give **7**, 503 mg (95%) as a colorless oil (R_f (5% EA/PE) = 0.65).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 5.95 – 5.82 (m, 1H), 5.17 (d, J = 1.8 Hz, 1H), 5.14 (d, J = 3.6 Hz, 1H), 3.96 - 4.02 (dd, J = 15.1, 7.5 Hz, 1H), 1.80-1.86 (m, 1H), 1.66 – 1.54 (m, 1H), 1.44 – 1.23 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 139.4, 136.9, 135.1, 129.9, 128.9, 117.7, 51.6, 34.2, 20.4, 14.0.
FT-IR (neat): v1734, 1500, 702 cm^{-1}

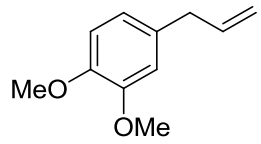
HRMS (ESI) calcd for $C_{12}H_{14}ClO$ [$M+H^+$]: 209.07277. Found:209.07311.

but-3-enenitrile (8) was synthesize by reported method[2]



8

4-allyl-1,2-dimethoxybenzene (9) is commercial available



9

1.3 Details for the Rh(I)-Catalyzed Olefin Isomerization of *β,γ*-unsaturated Ketones

General procedure for Rh(I)-catalyzed olefin isomerization of *β,γ*-unsaturated ketones. Under Ar, a solution of ligand (dppm, 0.036 mmol) and $[Rh(CO)_2Cl]_2$ (0.015 mmol) in anhydrous solvent (DCE or DME, 1.5 mL) was stirred for 30 min at room temperature. Then *β,γ*-unsaturated ketone (0.3 mmol) was added and the reaction mixture was immersed in an oil bath at the indicated temperature (65 ^oC, 75 ^oC or 85 ^oC). When GC indicated the conversion of the starting material reached 85% ~ 100%, the reaction mixture was cooled to room temperature and concentrated. The crude mixture was submitted to flash column chromatography on silica gel to afford the mixture of *β,γ*-unsaturated ketones, *Z*- and *E*-*α,β*-unsaturated ketones. The ratio was determined by integration of suitable ^1H NMR signals and the reaction's conversion and yields can be obtained. Pure *E*-*α,β*-unsaturated ketone can be obtained by further column chromatography (PE : EA = 150:1 ~ 100:1, except **1k** which used PE:EA = 10:1) on silica gel. Meanwhile, part of pure *Z*-*α,β*-unsaturated ketone can also be obtained in this further chromatography. However, the remaining mixture containing Z-*α,β*-unsaturated ketone and the starting material cannot be separated completely. This is because the R_f values of *Z*-*α,β*-ketone and the starting material are very close, while the R_f value of *E*-*α,β*-unsaturated ketone is different from those of *Z*-*α,β*-unsaturated ketone and the starting material (and *E*-*α,β*-unsaturated ketone can be separated easier).

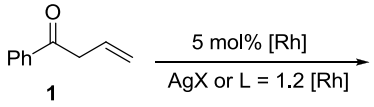
We found that, if the reaction scaled to 1.5 mmol, we can get a better separated yield. For example, in the case of isomerization of **1m**, the pure *Z*-*α,β*-unsaturated ketone can be obtained by column chromatography in 73% yield. This suggests that the present isomerization reaction can be used for synthesis if a larger scale of the reaction can be carried out.

Note 1: In some cases, the amounts of *E* isomers from the isomerization reactions were too low to get their NMR data. Therefore, we synthesized these isomers by isomerizations of the unsaturated ketones using Al_2O_3 as the catalyst (see below for details).

Note 2: The *Z*/*E* ratio of the products usually decreased with time. Therefore, we stopped the reaction when the conversion reached to 85%-100%.

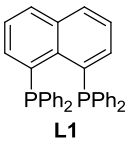
Note 3: Stereochemistry was determined by comparing the ^1H NMR shift and the coupling constants. The *α*-H of carbonyl (in olefin) in *E*-isomers is significant in the lower field with larger chemical shift than the corresponding *α*-H of carbonyl (in olefin) in *Z*-isomers. The coupling constants of olefin in *Z*-*α,β*-unsaturated ketones are usually lower than coupling constants of olefin in *E*-*α,β*-unsaturated ketones, if both can be read from the NMR data. Using either one of the above two features we can then determine the relative ratios of Z and *E* isomers of our Rh-catalyzed isomerization reactions by comparing integrations of their characteristic proton signals.

1.3.1 Additional Details of Screening Reaction Conditions



	GC 2-Z:2-E	NMR 2-Z:2-E	conv (%)	yield (%)
1, $[Rh(CO)_2Cl]_2$, AgOTf, 75 °C,DCE, 18h	0.8:1		84[a]	55[a]
2, $Rh(PPh_3)_3Cl$, 75 °C, DCE, 23h	2.8:1		67[a]	35[a]
3, $Rh(PPh_3)_3Cl$, $AgSbF_6$, 75 °C,DCE, 12h	0.2:1		92[a]	72[a]
4, $Rh(PPh_3)_3Cl$, AgOTf, 75 °C,DCE, 12h	0.1:1		82[a]	62[a]
5, $[Rh(CO)_2Cl]_2$,dppm, $AgSbF_6$, 75 °C,DCE, 13h	0.1:1		100[a]	83[a]
6, $[Rh(CO)_2Cl]_2$, dppm,75 °C,Dioxane, 23h		3.7:1	(75)[b]	(47)[b]
7, $[Rh(CO)_2Cl]_2$, dppm, 75 °C,DME, 23h		4.3:1	(94)[b]	(75)[b]
8, $[Rh(CO)_2Cl]_2$, dppm, 75 °C,Toluene, 23h		2.3:1	(95)[b]	(60)[b]
9, $[Rh(CO)_2Cl]_2$, **L1**, 75 °C,DCE, 23h	1.2:1	1.2:1	98[a](100)[b]	64[a](66)[b]
10, $[Rh(CO)_2Cl]_2$, $PPrPh_2$, 80 °C,DCE, 23h		1.4:1	(92)[b]	(75)[b]

[a] Determined by GC. [b] Determined by NMR



L1

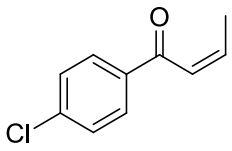
1.3.2 The Spectroscopic Data of *Z* and *E*-Unsaturated Ketones

2a-*Z*[3], **2a-*E***[3], **2b-*E***[4], **2c-*E***[4],**2c-*E***[4], **2e-*E***[5], **2f-*E***[4], **2g-*E***[5], **2h-*E***[4], **2l-*E***[5], **2m-*E***[6], **4a-*Z***[3], **4a-*E***[3], **4d-*Z***[6] and **4d-*E***[6] all are known molecules.

In some cases, the amounts of *E* isomers from our isomerization reaction were too low to get the pure products. Therefore, we synthesized these isomers by isomerizations of the unsaturated ketones using Al_2O_3 as the catalyst.[7] These new compounds are: **2i-*E***, **2j-*E***, **4d-*E***, **4e-*E***, **4f-*E***, **4g-*E***, **4h-*E*** and **4i-*E***. The general synthesis of these new compounds is given below.

General procedure for isomerization of the *β,γ*-unsaturated ketones to the corresponding *E-α,β*-unsaturated ketones.[7] To an acetone solution (1 mL) of *β,γ*-unsaturated ketone (0.2 mmol), Al_2O_3 (neutral, 0.15 g) was added, and the mixture was stirred at room temperature until TLC indicated the disappearance of the starting material. After filtration of the suspension, acetone was evaporated, and the crude mixture was submitted to flash column chromatography on silica gel to afford the *E-α,β*-unsaturated ketone.

***(Z)*-1-(4-chlorophenyl)but-2-en-1-one (2b-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.70, NMR yield of *E* and *Z* isomers, 85%

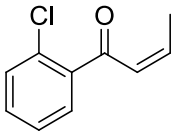
^{1}H NMR (400 MHz, C_6D_6) δ 7.35 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 6.13 (dq, J = 11.5, 1.7 Hz, 1H), 5.72 (dq, J = 11.5, 7.2 Hz, 1H), 1.82 (dd, J = 7.2, 1.8 Hz, 3H).

^{13}C NMR (101 MHz, C_6D_6) δ 189.5, 143.9, 138.7, 137.2, 129.8, 128.8, 124.8, 16.0.

FT-IR (neat): ν1672, 1620, 1694, 1233, 1099, 1017 cm^{-1}

HRMS (ESI) calcd for $C_{10}H_{10}ClO$ [M+H^+]: 181.04147. Found: 181.04181.

***(Z)*-1-(2-chlorophenyl)but-2-en-1-one (2c-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.70, NMR yield of *E* and *Z* isomers, 93%

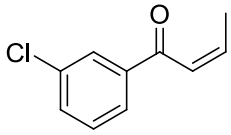
^{1}H NMR (400 MHz, C_6D_6) δ 7.12 – 7.02 (m, 1H), 6.82 (dd, *J* = 6.3, 2.8 Hz, 1H), 6.61 – 6.46 (m, 2H), 6.16 (dd, *J* = 11.4, 1.1 Hz, 1H), 5.69 (dq, *J* = 11.4, 7.3 Hz, 1H), 1.82 (dd, *J* = 7.3, 0.9 Hz, 3H).

^{13}C NMR (101 MHz, C_6D_6) δ 192.4, 144.1, 141.0, 131.1, 130.2, 129.6, 126.8, 16.0.

FT-IR (neat):*v*1676, 1616, 1430, 1270, 1222, 1076, 1013 cm^{-1}

HRMS (ESI) calcd for $C_{10}H_9ClNaO$ [M+Na^+]: 203.02341. Found: 203.02352.

***(Z)*-1-(3-chlorophenyl)but-2-en-1-one (2d-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.70, NMR yield of *E* and *Z* isomers, 75%

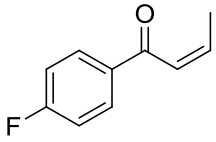
^{1}H NMR (400 MHz, C_6D_6) δ 7.66 (t, *J* = 1.8 Hz, 1H), 7.39 – 7.34 (m, 1H), 6.86 (ddd, *J* = 7.9, 1.9, 0.8 Hz, 1H), 6.52 (t, *J* = 7.9 Hz, 1H), 6.06 (dd, *J* = 11.5, 1.7 Hz, 1H), 5.68 (dq, *J* = 11.5, 7.2 Hz, 1H), 1.80 (dd, *J* = 7.3, 1.8 Hz, 3H).

^{13}C NMR (101 MHz, C_6D_6) δ 189.3, 144.4, 134.8, 132.2, 129.9, 128.5, 126.3, 124.5, 16.0.

FT-IR (neat): *v*1672, 1616, 1576, 1445, 1222 cm^{-1}

HRMS (ESI) calcd for $C_{10}H_9ClNaO$ [M+Na^+]: 203.02341. Found: 203.02349.

***(Z)*-1-(4-fluorophenyl)but-2-en-1-one (2e-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.70, NMR yield of *E* and *Z* isomers, 79%

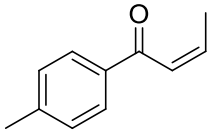
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.8, 5.5 Hz, 2H), 6.53 (t, *J* = 8.7 Hz, 2H), 6.24 (dd, *J* = 11.5, 1.7 Hz, 1H), 5.80 (dq, *J* = 11.6, 7.2 Hz, 1H), 1.88 (dd, *J* = 7.2, 1.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.99 (s), 164.21 (d, *J* = 253.0 Hz), 142.22 (s), 134.07 (d, *J* = 2.9 Hz), 129.70 (d, *J* = 9.1 Hz), 123.60 (s), 114.17 (d, *J* = 21.8 Hz), 14.74 (s).

FT-IR (neat): *v*1676, 1620, 1605, 1441, 1209, 1044cm^{-1}

HRMS (ESI) calcd for $C_{10}H_{10}FO$ [M+H^+]: 165.07102. Found: 165.07123.

***(Z)*-1-p-tolylbut-2-en-1-one (2f-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.75, NMR yield of *E* and *Z* isomers, 80%

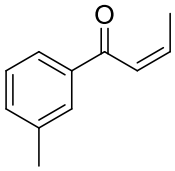
^{1}H NMR (400 MHz, C_6D_6) δ 7.67 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 6.38 (dq, *J* = 11.5, 1.7 Hz, 1H), 5.75 (dq, *J* = 11.5, 7.2 Hz, 1H), 1.88 (dd, *J* = 7.2, 1.8 Hz, 3H), 1.79 (s, 3H).

^{13}C NMR (101 MHz, C_6D_6) δ 189.3, 141.6, 141.4, 135.5, 128.0, 127.4, 124.1, 19.9, 14.8.

FT-IR (neat): *v*1676, 1609, 1237, 1021 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{13}O$ [M+H$^+$]: 161.09609. Found: 161.09618.

***(Z)*-1-m-tolylbut-2-en-1-one(2g-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.75, NMR yield of *E* and *Z* isomers, 65%

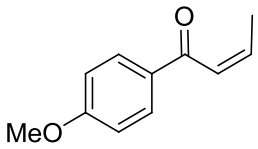
^{1}H NMR (400 MHz, C_6D_6) δ 7.60 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.37 (dq, *J* = 11.5, 1.8 Hz, 1H), 5.75 (dq, *J* = 11.5, 7.2 Hz, 1H), 1.87 (dd, *J* = 7.2, 1.8 Hz, 3H), 1.82 (s, 3H).

^{13}C NMR (101 MHz, C_6D_6) δ 189.9, 141.7, 136.9, 131.9, 127.8, 127.2, 124.5, 124.2, 19.7, 14.8.

FT-IR (neat): *v*1676, 1617, 1240 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{13}O$ [M+H$^+$]: 161.09609. Found: 161.09624.

***(Z)*-1-(4-methoxyphenyl)but-2-en-1-one (2h-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.70, NMR yield of *E* and *Z* isomers, 74%

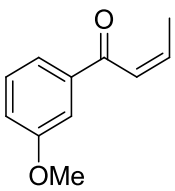
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 8.9 Hz, 2H), 6.65 (dq, *J* = 11.5, 1.7 Hz, 1H), 6.03 (dq, *J* = 11.5, 7.2 Hz, 1H), 3.24 (s, 3H), 2.16 (dd, *J* = 7.2, 1.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5, 163.1, 142.0, 132.1, 130.6, 125.3, 113.7, 54.6, 15.9.

FT-IR (neat): *v*1684, 1613, 1270, 1222, 1170, 1024 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{12}NaO2$ [M+Na$^+$]: 199.07295. Found: 199.09124.

***(Z)*-1-(3-methoxyphenyl)but-2-en-1-one (2i-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.75, NMR yield of *E* and *Z* isomers, 67%

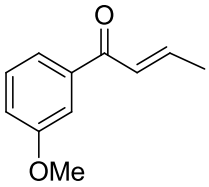
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.10 (td, J = 7.9, 1.4 Hz, 1H), 6.93-6.96 (m 1H), 6.63 (d, J = 11.5 Hz, 1H), 6.08 – 5.97 (m, 1H), 3.35 (s, 3H), 2.13 (dt, J = 7.2, 1.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 160.2, 143.1, 140.4, 129.4, 125.2, 120.9, 119.1, 112.5, 54.5, 15.9.

FT-IR (neat): v1669, 1583, 1270, 1207, 1028 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{12}NaO2$ [M+Na$^+$]: 199.07295. Found: 199.07336.

_(E)_-1-(3-methoxyphenyl)but-2-en-1-one (2i-*E*)



(from isomerization of the β,γ-unsaturated ketone by Al_2O_3, see section 1.3.2)

Colorless oil: R_f (5% EA/PE) = 0.65, 67%

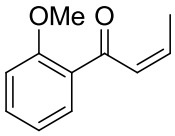
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.51 (m, 2H), 7.34-7.38 (m, 1H), 7.14 – 7.02 (m, 1H), 6.89 (dd, J = 15.3, 1.4 Hz, 1H), 3.85 (s, 3H), 1.99 (dd, J = 6.8, 0.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 159.8, 145.1, 139.3, 129.5, 127.5, 121.1, 119.1, 112.8, 55.4, 18.6.

FT-IR (neat): v1674, 1569, 1439, 1296, 1035, 778 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{13}O_2$ [M+H$^+$]: 177.09101. Found: 177.09128.

_(Z)_-1-(2-methoxyphenyl)but-2-en-1-one (2j-*Z*)



Colorless oil: R_f (5% EA/PE) = 0.70, NMR yield of *E* and *Z* isomers, 66%

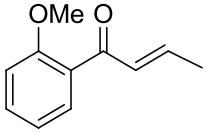
^{1}H NMR (400 MHz, C_6D_6) δ 7.82 (dd, J = 7.6, 1.6 Hz, 1H), 7.07 – 6.99 (m, 1H), 6.72-6.81 (s, 1H), 6.77 – 6.69 (m, 1H), 6.39 (d, J = 8.3 Hz, 1H), 5.95 (dq, J = 11.4, 7.3 Hz, 1H), 3.16 (s, 3H), 2.16 (dd, J = 7.3, 1.7 Hz, 3H).

^{13}C NMR (101 MHz, C_6D_6) δ 192.5, 158.1, 141.3, 132.5, 131.1, 130.9, 129.8, 120.9, 111.6, 54.9, 16.2.

FT-IR (neat): v1669, 1583, 1270, 1207, 1028 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{12}NaO_2$ [M+Na$^+$]: 199.07295. Found: 199.07316.

_(E)_-1-(2-methoxyphenyl)but-2-en-1-one (2j-*E*)



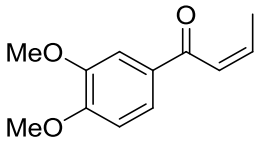
(from isomerization of the β,γ-unsaturated ketone by Al_2O_3, see section 1.3.2)

Colorless oil: R_f (5% EA/PE) = 0.65, 56%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 7.5, 1.5 Hz, 1H), 7.46 – 7.38 (m, 1H), 6.94-7.01 (m, 2H), 6.86 (dq, J = 13.6, 6.8 Hz, 1H), 6.67 – 6.71 (m, 1H), 3.85 (s, 3H), 1.93 (d, J = 6.8 Hz, 3H).

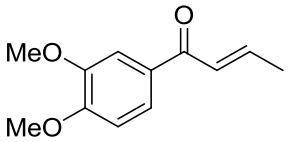
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 157.8, 144.2, 132.4, 132.3, 129.9, 129.2, 120.5, 111.5, 55.7, 18.4.
FT-IR (neat): v1657, 1620, 1486, 1437, 1324, 1244, 1026cm^{-1}
HRMS (ESI) calcd for $C_{11}H_{13}O_2$ [M+H$^+$]: 177.09101. Found: 177.09125.

(*Z*)-1-(3,4-dimethoxyphenyl)but-2-en-1-one(2k-*Z*)



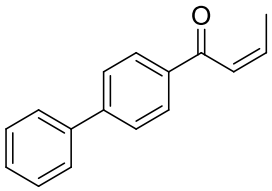
yellow oil: R_f (5% EA/PE) = 0.70, NMR yield of *E* and *Z* isomers, 90%
^{1}H NMR (400 MHz, C_6D_6) δ 7.70 (d, J = 1.4 Hz, 1H), 7.48 (dd, J = 8.3, 1.9 Hz, 1H), 6.69 (dd, J = 11.5, 1.8 Hz, 1H), 6.43 (d, J = 8.3 Hz, 1H), 6.00 (dq, J = 11.6, 7.2 Hz, 1H), 3.35 (s, 3H), 3.29 (s, 3H), 2.11 (dd, J = 7.2, 1.4 Hz, 3H).
^{13}C NMR (101 MHz, C_6D_6) δ 189.8, 153.8, 150.0, 142.0, 132.3, 125.5, 122.7, 111.3, 110.4, 55.2, 55.2, 16.1.
FT-IR (neat): v1584, 1514, 1266, 1206, 1167, 1024 cm^{-1}
HRMS (ESI) calcd for $C_{12}H_{15}O_3$ [M+H$^+$]: 207.10157. Found: 207.10189.

(*E*)-1-(3,4-dimethoxyphenyl)but-2-en-1-one (2k-*E*)



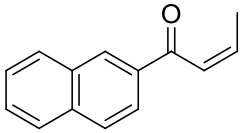
yellow oil: R_f (5% EA/PE) = 0.70, NMR yield of *E* and *Z* isomers, 90%
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 2H), 7.12-7.03 (dq, J = 13.4, 6.7 Hz, 1H), 6.98 – 6.87 (m, 2H), 3.95 (s, 6H), 2.00 (dd, J = 6.7, 1.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 153.1, 149.1, 144.0, 131.0, 126.9, 123.0, 110.8, 109.9, 56.1, 56.0, 18.6.
FT-IR (neat): v1657, 1620, 1486, 1437, 1324, 1244, 1244, 1026 cm^{-1}
HRMS (ESI) calcd for $C_{12}H_{15}O_3$ [M+H$^+$]: 207.10157. Found: 207.10175.

(*Z*)-1-(biphenyl-4-yl)but-2-en-1-one (2l-*Z*)



White solid: R_f (5% EA/PE) = 0.75, NMR yield of *E* and *Z* isomers, 82%. m.p. 51-55 ˚C.
^{1}H NMR (400 MHz, C_6D_6) δ 7.76 (d, J = 8.3 Hz, 2H), 7.25 – 7.14 (m, 4H), 7.06 – 6.91 (m, 3H), 6.40 (dq, J = 11.5, 1.7 Hz, 1H), 5.80 (dq, J = 11.5, 7.2 Hz, 1H), 1.90 (dd, J = 7.2, 1.8 Hz, 3H).
^{13}C NMR (101 MHz, C_6D_6) δ 189.2, 143.9, 142.0, 139.0, 136.6, 127.8, 127.7, 126.8, 126.2, 126.0, 124.0, 14.8.
FT-IR (neat): v1665, 1620, 1427, 1248 cm^{-1}
HRMS (ESI) calcd for $C_{16}H_{15}O$ [M+H$^+$]: 223.11174. Found: 223.11206.

***(Z)*-1-(naphthalen-2-yl)but-2-en-1-one (2m-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.70, NMR yield of *E* and *Z* isomers, 78%

When we scaled our reaction to 1.5 mmol, we can get 94% conversion and 81% yield (by NMR), with the *Z*:*E* =13:1. The isolated yield of **2m-*Z*** is 73% in column chromatography (PE : EA = 120:1).

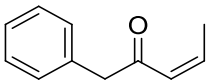
^{1}H NMR (400 MHz, C_6D_6) δ 8.68 (d, J = 8.6 Hz, 1H), 7.43 – 7.32 (m, 3H), 7.19-7.14 (m, 1H), 7.07 – 6.99 (m, 1H), 6.96 (s, 1H), 6.86-6.90 (m, 1H), 6.20 (dq, J = 11.5, 1.7 Hz, 1H), 5.72 (dq, J = 11.5, 7.3 Hz, 1H), 1.83 (dd, J = 7.3, 1.7 Hz, 3H).

^{13}C NMR (101 MHz, C_6D_6) δ 194.7, 142.9, 138.0, 134.2, 132.0, 130.8, 129.1, 128.5, 127.9, 126.4, 126.3, 124.5, 16.0.

FT-IR (neat): v1672, 1616, 1434, 1237, 11284, 1106, 793 cm^{-1}

HRMS (ESI) calcd for $C_{14}H_{13}O$ [M+H$^+$]: 197.09609. Found: 197.09631.

***(Z)*-1-phenylpent-3-en-2-one (4b-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.75, NMR yield of *E* and *Z* isomers, 88%

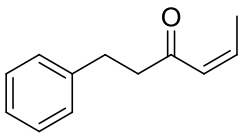
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 6.96 (m, 5H), 5.82 (dd, J = 11.3, 1.6 Hz, 1H), 5.65 (dq, J = 11.3, 7.2 Hz, 1H), 3.35 (s, 2H), 1.96 (dd, J = 7.2, 1.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 141.9, 133.8, 128.4, 127.5, 125.6, 125.6, 50.1, 14.4.

FT-IR (neat): v1687, 1618, 1439, 1076, 700 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{12}NaO$ [M+Na$^+$]: 183.07804. Found: 183.07769.

***(Z)*-1-phenylhex-4-en-3-one (4c-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.75, NMR yield of *E* and *Z* isomers, 73%

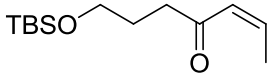
^{1}H NMR (400 MHz, C_6D_6) δ 7.17-7.21 (m, 2H), 7.08-7.13 (m, 3H), 5.82 – 5.70 (m, 2H), 2.90 (t, J = 7.6 Hz, 2H), 2.44 (t, J = 7.6 Hz, 2H), 2.09 (d, J = 6.1 Hz, 3H).

^{13}C NMR (101 MHz, C_6D_6) δ 198.9, 141.8, 141.6, 128.4, 128.4, 127.5, 125.9, 45.6, 29.9, 15.6.

FT-IR (neat): v1694, 1620, 1454 cm^{-1}

HRMS (ESI) calcd for $C_{12}H_{14}NaO$ [M+Na$^+$]: 197.09369. Found: 197.09338.

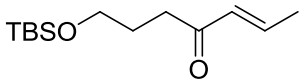
***(Z)*-1-(tert-butyldimethylsilyloxy)hex-4-en-3-one (4e-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.75, NMR yield of *E* and *Z* isomers, 67%

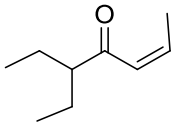
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (dd, J = 11.4, 1.5 Hz, 1H), 5.74 – 5.64 (m, 1H), 3.47 (t, J = 6.2 Hz, 2H), 2.27 (t, J = 7.1 Hz, 2H), 2.01 (dd, J = 7.2, 1.6 Hz, 3H), 1.78 (p, J = 6.6 Hz, 2H), 0.93 (s, 9H), 0.00 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 140.3, 126.6, 61.0, 39.1, 25.9, 24.7, 17.1, 14.4, 0.0, -6.6.
FT-IR (neat): v2932, 2860, 1698, 1257, 1102, 728 cm^{-1}
HRMS (ESI) calcd for $C_{13}H_{26}NaO_2Si$ [M+Na$^+$]: 265.15943. Found: 265.15939.

***(E)*-1-(tert-butyldimethylsilyloxy)hex-4-en-3-one (4e-*E*)**



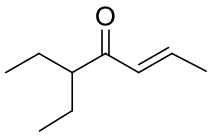
(from isomerization of the β,γ-unsaturated ketone by Al_2O_3, see section 1.3.2)
Colorless oil: R_f (5% EA/PE) = 0.70, 60%
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (dq, J = 13.7, 6.8 Hz, 1H), 6.09 (dd, J = 15.8, 1.5 Hz, 1H), 3.59 (t, J = 6.1 Hz, 2H), 2.57 (t, J = 7.3 Hz, 2H), 1.86 (dd, J = 6.8, 1.4 Hz, 3H), 1.83 – 1.73 (m, 2H), 0.85 (s, 9H), -0.00 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 142.3, 132.1, 62.2, 36.2, 27.2, 25.9, 18.3, 18.2, -5.35.
FT-IR (neat): v2134, 1702, 1560, 1257, 1102, 836 cm^{-1}
HRMS (ESI) calcd for $C_{13}H_{26}NaO_2Si$ [M+Na$^+$]: 265.15943. Found:265.15919.

***(Z)*-5-ethylhept-2-en-4-one (4f-*Z*)**



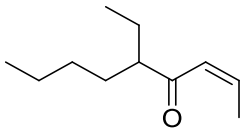
Colorless oil: R_f (5% EA/PE) = 0.80, NMR yield of *E* and *Z* isomers, 69%
^{1}H NMR (400 MHz, C_6D_6) δ 5.88-5.92 (m, 1H), 5.73-5.81 (m, 1H), 2.05 (dd, J = 7.1, 1.5 Hz, 3H), 2.13-2.09 (m, 1H), 1.53-1.62 (m, 2H), 1.35 – 1.23 (m, 2H), 0.78 (t, J = 7.4 Hz, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 202.4, 140.9, 126.3, 54.8, 23.1, 10.6.
FT-IR (neat): v1655, 1507, 1207 cm^{-1}
HRMS (ESI) calcd for $C_9H_{16}NaO$ [M+Na$^+$]: 163.10934. Found: 163.10908.

***(E)*-5-ethylhept-2-en-4-one (4f-*E*)**



(from isomerization of the β,γ-unsaturated ketone by Al_2O_3, see section 1.3.2)
Colorless oil: R_f (5% EA/PE) = 0.75, 65%
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (dq, J = 13.7, 6.9 Hz, 1H), 6.14 (dd, J = 15.6, 1.5 Hz, 1H), 2.46 (dq, J = 8.1, 5.6 Hz, 1H), 1.83 (dd, J = 6.9, 1.5 Hz, 3H), 1.63 – 1.50 (m, 2H), 1.46 – 1.33 (m, 2H), 0.77 (t, J = 7.4 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 141.2, 130.4, 51.8, 23.5, 17.2, 10.8.
FT-IR (neat): v1655, 1560, 1262 cm^{-1}
HRMS (ESI) calcd for $C_9H_{16}NaO$ [M+Na$^+$]: 163.10934. Found:163.10956.

***(Z)*-5-ethylnon-2-en-4-one (4g-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.80, NMR yield of *E* and *Z* isomers, 75%

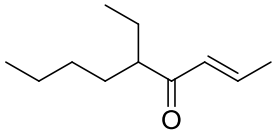
^{1}H NMR (400 MHz, C_6D_6) δ 5.93 (dd, *J* = 11.4, 1.6 Hz, 1H), 5.78 (dq, *J* = 11.4, 7.2 Hz, 1H), 2.22 (tt, *J* = 8.3, 5.3 Hz, 1H), 2.07 (dd, *J* = 7.2, 1.7 Hz, 3H), 1.69 – 1.55 (m, 2H), 1.39 – 1.25 (m, 2H), 1.26 – 1.11 (m, 4H), 0.85-0.80 (m, 6H).

^{13}C NMR (101 MHz, C_6D_6) δ 203.8, 142.2, 127.5, 54.6, 31.3, 29.9, 24.9, 23.1, 15.8, 14.0, 11.9.

FT-IR (neat): *v*1655, 1560 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{20}NaO$ [M+Na$^+$]: 191.14064. Found: 191.14015.

***(E)*-5-ethylnon-2-en-4-one(4g-*E*)**



(from isomerization of the *β,γ*-unsaturated ketone by Al_2O_3, see section 1.3.2)

Colorless oil: R_f (5% EA/PE) = 0.75, 77%

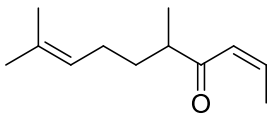
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (dq, *J* = 20.8, 6.9 Hz, 1H), 6.21 (dd, *J* = 15.6, 1.6 Hz, 1H), 2.58 (tt, *J* = 8.2, 5.5 Hz, 1H), 1.90 (dd, *J* = 6.9, 1.5 Hz, 3H), 1.57-1.67 (m, 2H), 1.55 – 1.35 (m, 3H), 1.34 – 1.25 (m, 2H), 1.25 – 1.14 (m, 3H), 0.93 – 0.80 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 142.2, 131.3, 51.3, 31.3, 29.7, 24.9, 22.9, 18.3, 13.9, 11.9.

FT-IR (neat): *v*2934, 1629, 1462, 970 cm^{-1}

HRMS (ESI) calcd for $C_{11}H_{21}O$ [M+H$^+$]: 169.15865. Found:.169.15899.

***(Z)*-5,9-dimethyldeca-2,8-dien-4-one (4h-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.80, NMR yield of *E* and *Z* isomers, 70%

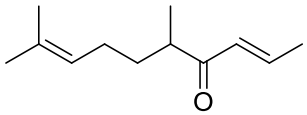
^{1}H NMR (400 MHz, C_6D_6) δ 5.71 (dd, *J* = 11.4, 1.5 Hz, 1H), 5.35 – 5.63 (m, 1H), 4.97 – 4.89 (m, 1H), 2.13-2.19 (m, 1H), 1.88 (dd, *J* = 7.1, 1.6 Hz, 3H), 1.79 (q, *J* = 7.4 Hz, 2H), 1.66 – 1.54 (m, 1H), 1.45 (s, 3H), 1.32 (s, 3H), 1.15 – 1.06 (m, 2H), 0.80 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, C_6D_6) δ 203.5, 142.4, 131.6, 127.1, 124.6, 46.5, 33.2, 30.1, 26.0, 25.7, 17.5, 16.2, 15.8.

FT-IR (neat): *v*2919, 2815, 2283, 1692, 1622, 1331, 812 cm^{-1}

HRMS (ESI) calcd for $C_{12}H_{20}NaO$ [M+Na$^+$]: 203.14064. Found: 203.14023.

***(E)*-5,9-dimethyldeca-2,8-dien-4-one (4h-*E*)**



(from isomerization of the *β,γ*-unsaturated ketone by Al_2O_3, see section 1.3.2)

Colorless oil: R_f (5% EA/PE) = 0.75, 52%

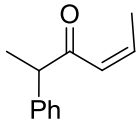
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 6.81 (dq, *J* = 13.7, 6.8 Hz, 1H), 6.11 (dd, *J* = 15.6, 1.4 Hz, 1H), 5.00 (t, *J* = 7.1 Hz, 1H), 2.66 (d, *J* = 6.9 Hz, 1H), 1.93 – 1.86 (m, 2H), 1.83 (dd, *J* = 6.8, 1.3 Hz, 3H), 1.71 – 1.62 (m, 1H), 1.60 (s, 3H), 1.50 (s, 3H), 1.29 (td, *J* = 14.2, 7.3 Hz, 1H), 1.01 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 203.8, 142.2, 132.1, 130.6, 124.0, 43.2, 33.2, 25.7, 25.7, 18.2, 17.7, 16.6.

FT-IR (neat): *v*2932, 1698, 1631, 1560, 1460, 1378, 974 cm^{-1}

HRMS (ESI) calcd for $C_{12}H_{20}NaO$ [M+Na^+]: 203.14064. Found:.203.14086.

***(Z)*-2-phenylhex-4-en-3-one (4i-*Z*)**



Colorless oil: R_f (5% EA/PE) = 0.70, NMR yield of *E* and *Z* isomers, 70%

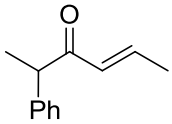
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.19 – 7.11 (m, 4H), 7.05 – 7.10 (m, 1H), 5.92 (dd, *J* = 11.4, 1.7 Hz, 1H), 5.71 (dq, *J* = 11.4, 7.2 Hz, 1H), 3.48 (q, *J* = 6.9 Hz, 1H), 2.10 (dd, *J* = 7.2, 1.6 Hz, 3H), 1.44 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, C_6D_6) *δ* 198.4, 141.5, 140.2, 127.7, 126.9, 125.8, 125.7, 52.5, 16.3, 14.5.

FT-IR (neat): *v*1698, 1565, 1460 cm^{-1}

HRMS (ESI) calcd for $C_{12}H_{14}NaO$ [M+Na^+]: 197.09369. Found: .197.09333.

***(E)*-2-phenylhex-4-en-3-one (4i-*E*)**



(from isomerization of the *β,γ*-unsaturated ketone by Al_2O_3, see section 1.3.2)

Colorless oil: R_f (5% EA/PE) = 0.65, 61%

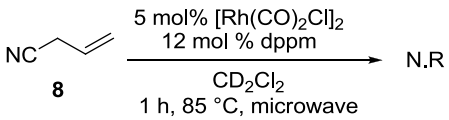
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.37 – 7.17 (m, 5H), 6.89 (dq, *J* = 13.8, 6.9 Hz, 1H), 6.10 (dd, *J* = 15.5, 1.6 Hz, 1H), 3.91 (q, *J* = 6.9 Hz, 1H), 1.79 (dd, *J* = 6.9, 1.6 Hz, 3H), 1.41 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 142.8, 140.9, 130.1, 128.9, 128.0, 127.0, 51.1, 18.2, 17.8.

FT-IR (neat): *v*1698, 1631, 1452, 702 cm^{-1}

HRMS (ESI) calcd for $C_{12}H_{14}NaO$ [M+Na^+]: 197.09369. Found: 197.09413.

1.3.3 Additional Detail of Rh(I)-Catalyzed Olefin Isomerization of But-3-enenitrile (8).



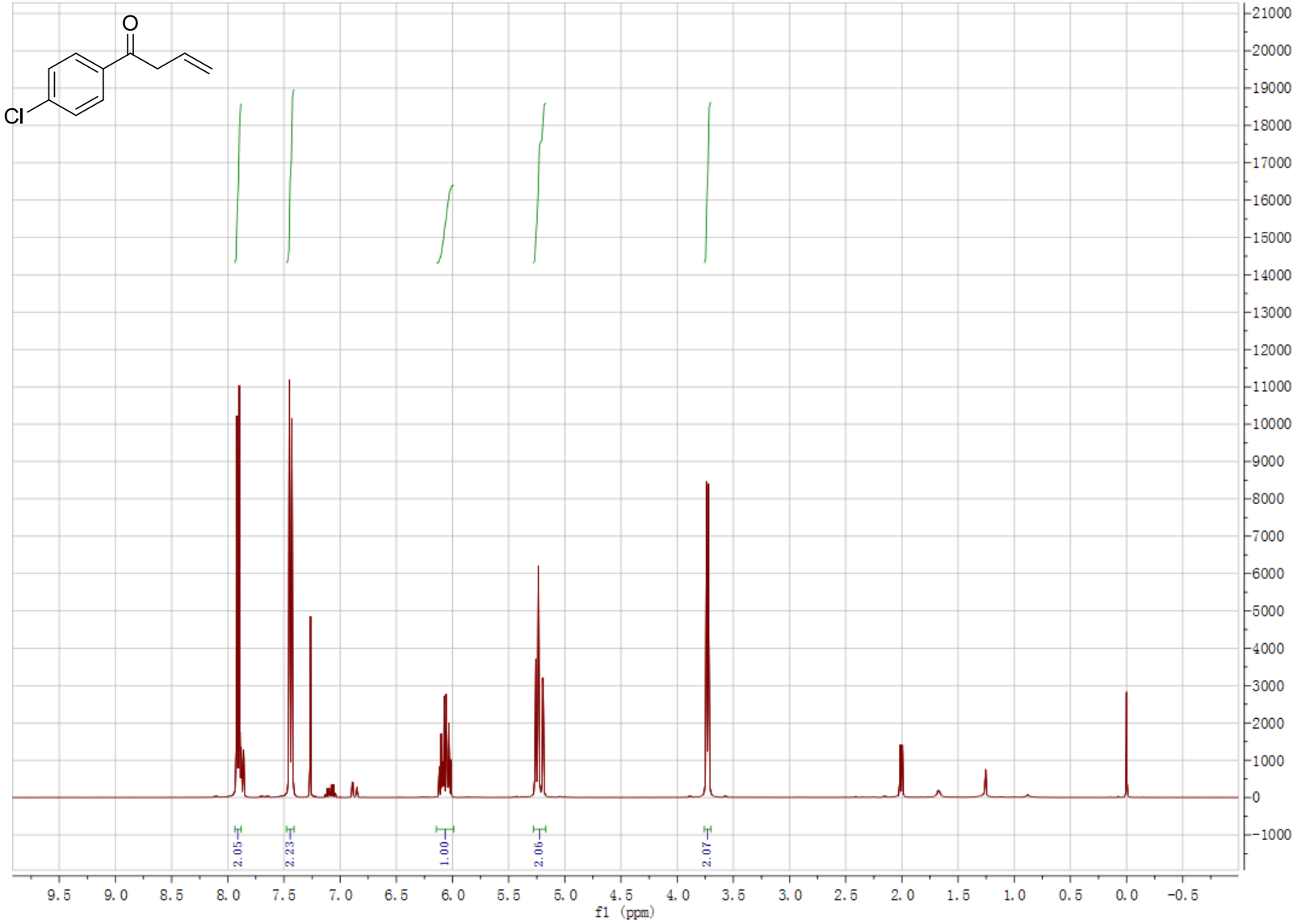
Under Ar, a solution of dppm (0.036 mmol, 13.8 mg) and $[Rh(CO)_2Cl]_2$ (0.015 mmol, 5.6 mg) in CD_2Cl_2 (1.5 mL) was stirred for 50 min at room temperature. Then but-3-enenitrile **8** [2] (0.3 mmol, 20.1 mg) was added and the reaction mixture was immersed in microwave at 85 ^{o}C. After 1 h, the reaction mixture was cooled to room temperature. The crude mixture was used for ^{1}H NMR analysis directly, showing that no new product was observed.

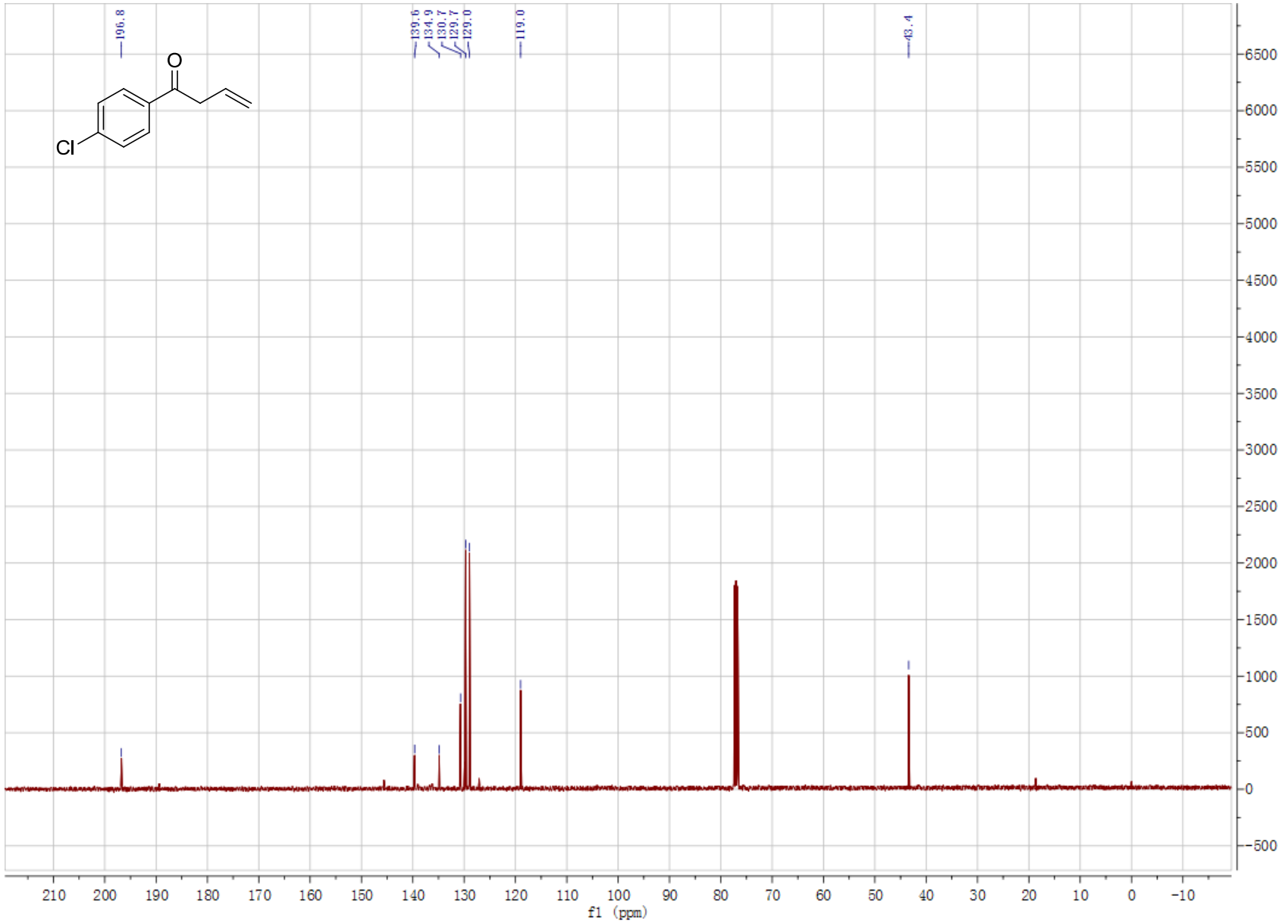
1.4 References

(1) Sumida, S.; Ohga, M.; Mitani, J.; Nokami, J. *J. Am. Chem. Soc.* **2000**, *122*, 1310.
(2) Supniewski, J. V.; Salzberg. P. L. *Org. Synth.* **1941**, *1*, 46.
(3) Egi, M.; Yamaguchi, Y.; Fujiwara, N.; Akai, S. *Org. Lett.* **2008**, *10*, 1867.
(4) Provencher, B. A.; Bartelson, K. J.; Liu, Y.; Foxman, B. M.; Deng, L. *Angew. Chem. Int. Ed.* **2011**, *50*, 10565.
(5) Manjolinho, F.; Grunberg, M. F.; Rodriguez, N.; Goossen, L. J. *Eur. J. Org. Chem.* **2012**, 4680.
(6) Snowden, R. L.; Linder, S. M.; Muller, B. L.; Schulte-Elte, K. H. *Helv. Chim. Acta* **1987**, *70*, 1858.
(7) Kurono, N.; Nii, N.; Sakaguchi, Y.; Uemura, M.; Ohkuma, T. *Angew. Chem. Int. Ed.* **2011**, *50*, 5541.

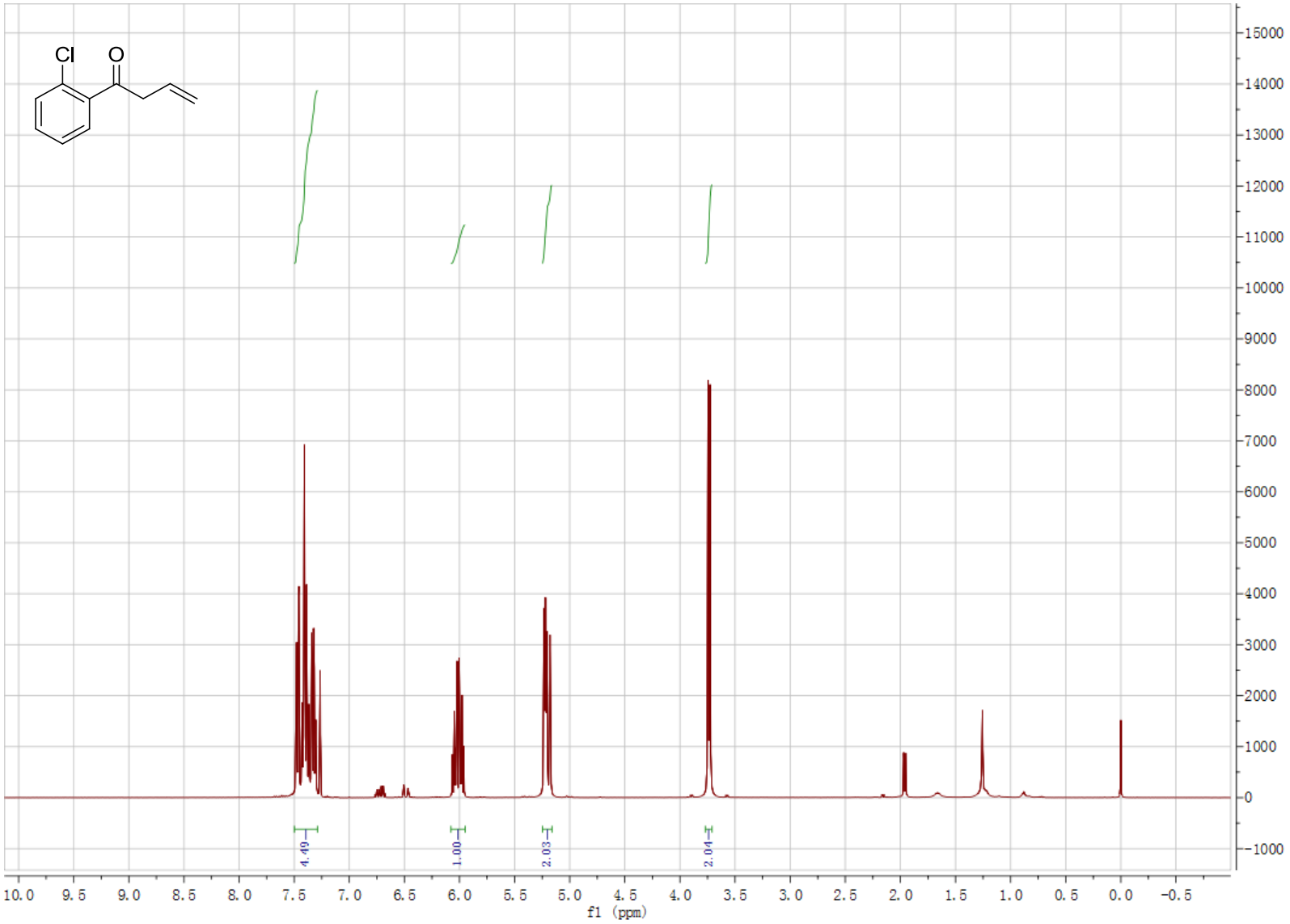
2. **NMR Spectra**

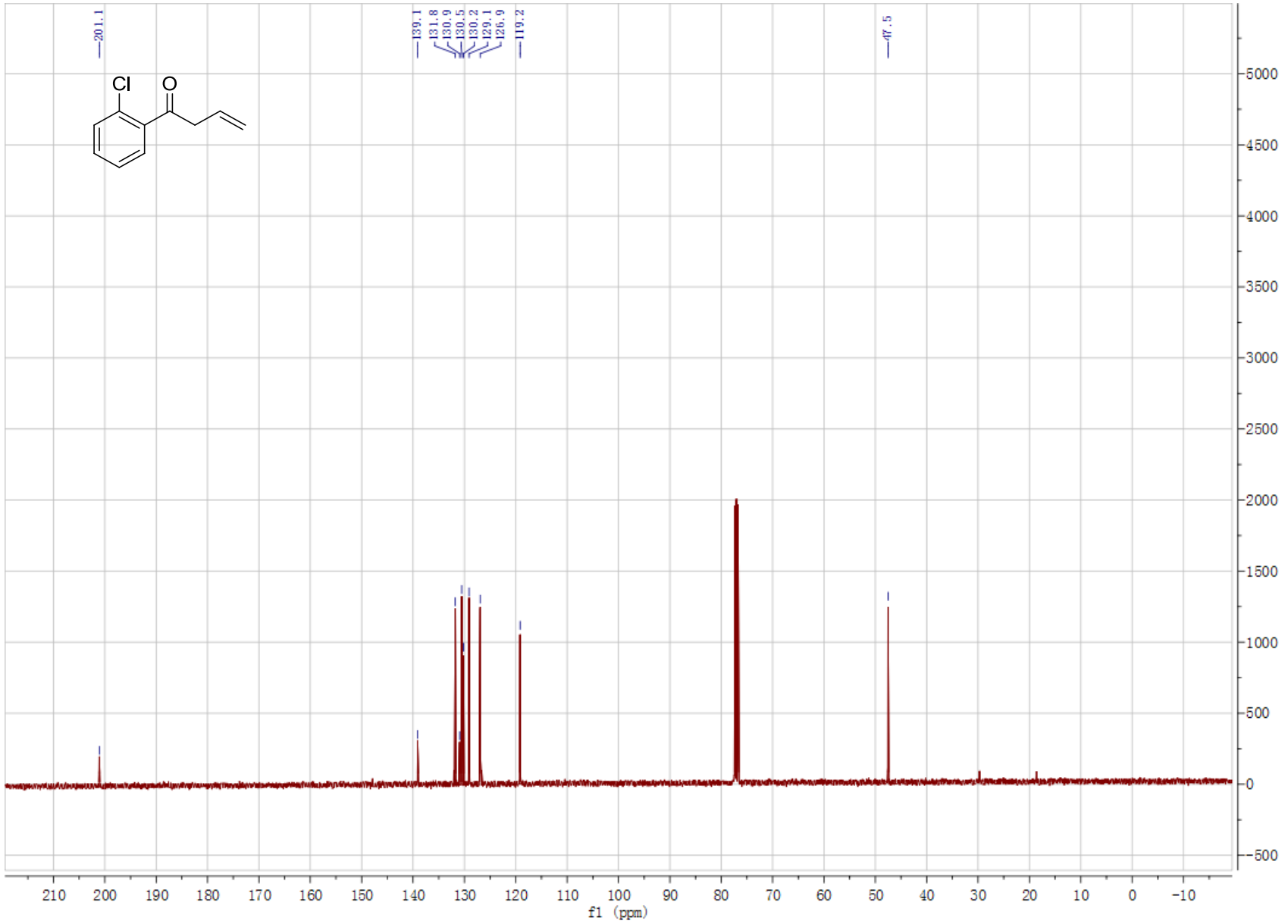
1-(4-chlorophenyl)but-3-en-1-one (1b, mixture with trace of 2b-*E*)



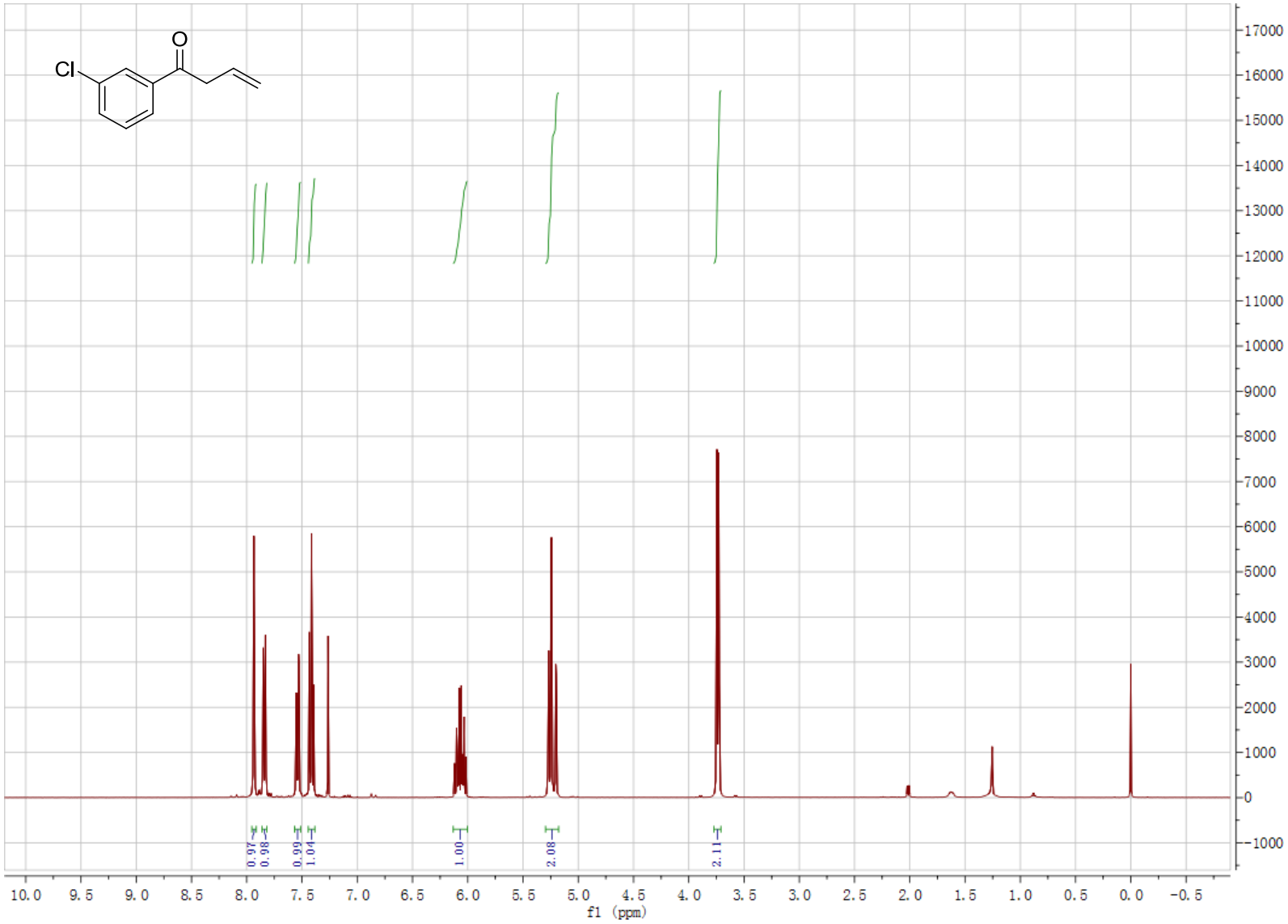

196.8
139.6
134.9
130.7
129.7
129.0
119.0
43.4
O
Cl
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

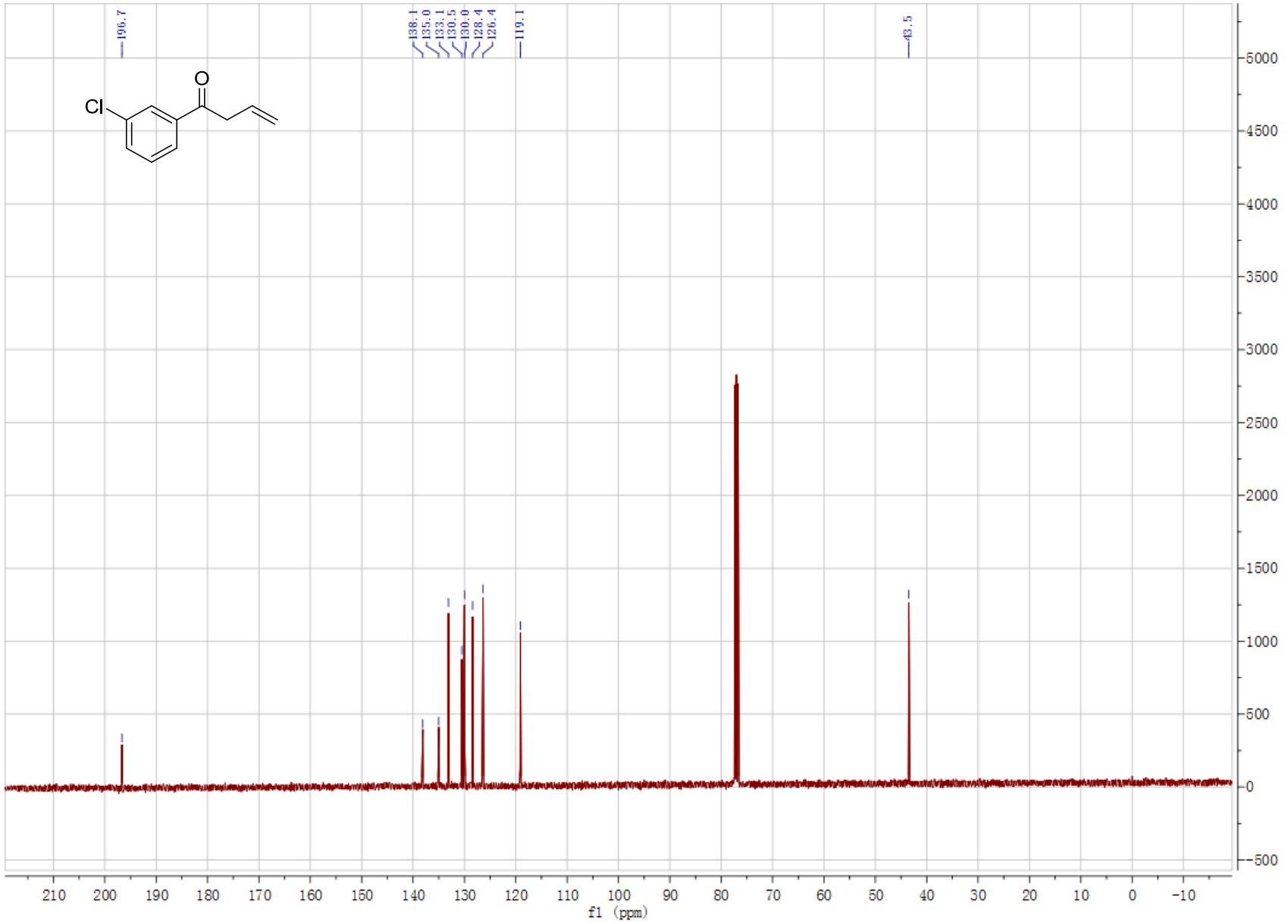
1-(2-chlorophenyl)but-3-en-1-one (1c,mixture with trace of 2c-*E*)



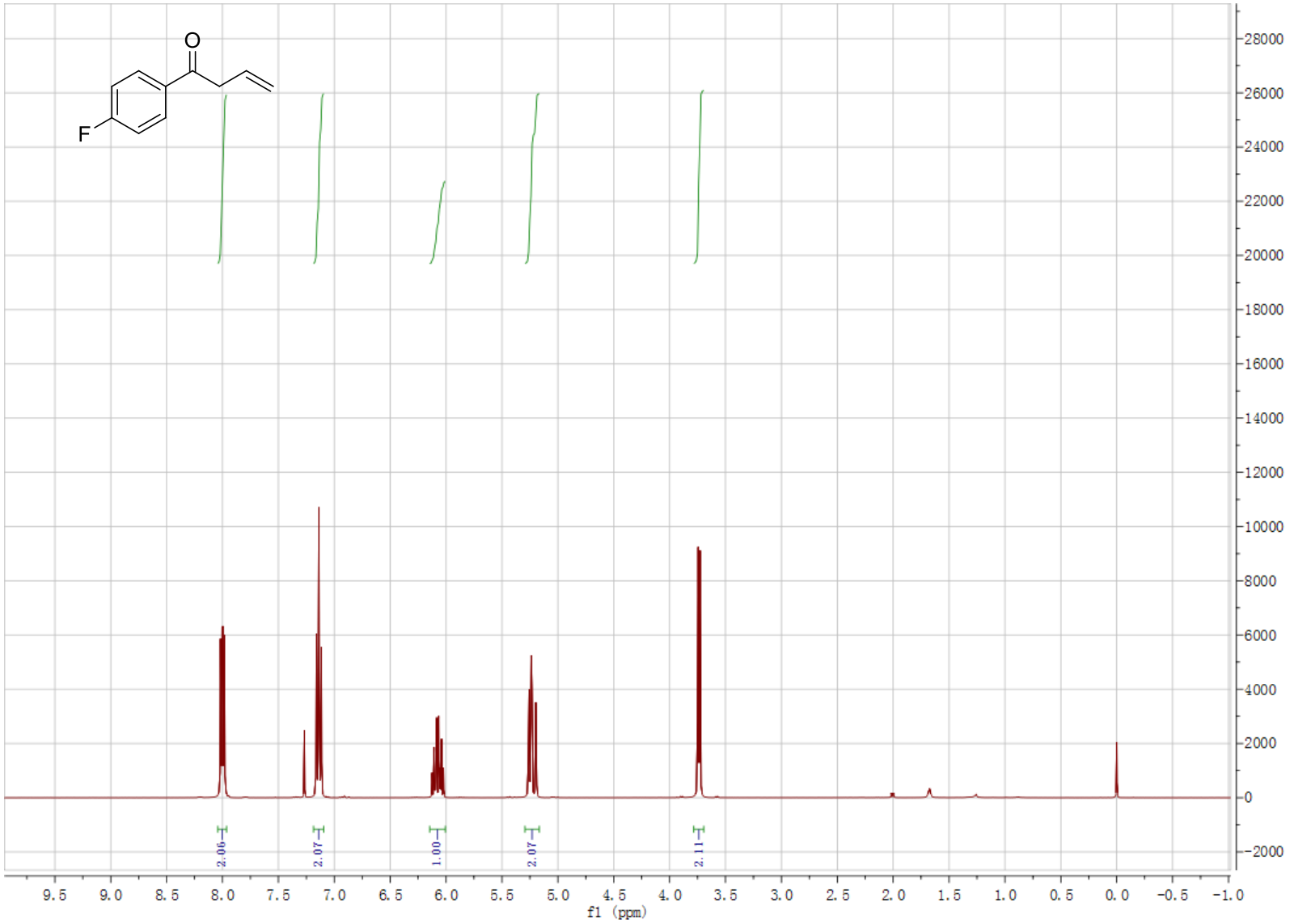

201.1
139.1
131.8
130.9
130.5
130.2
129.1
126.9
119.2
47.5
Cl
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

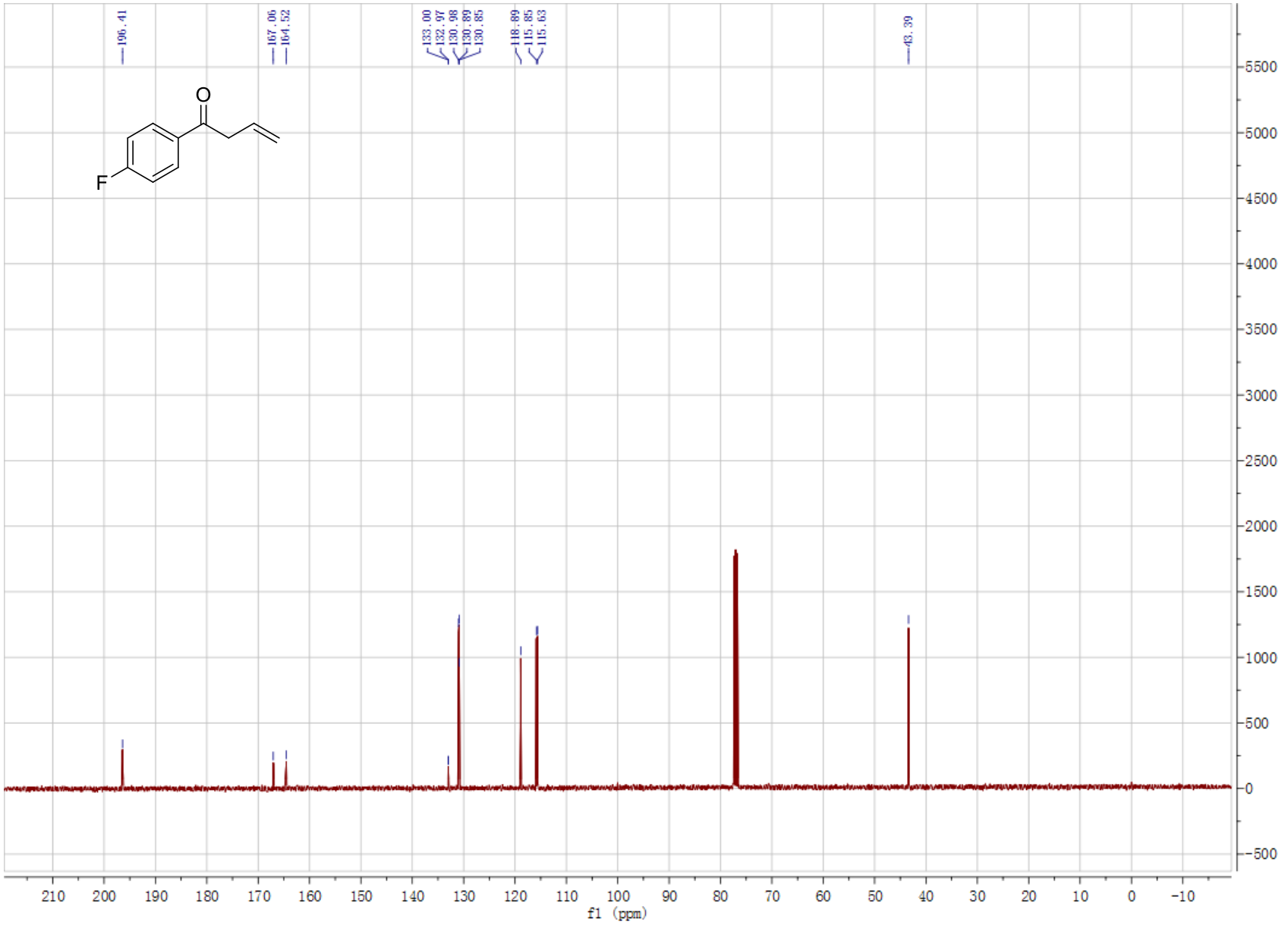
1-(3-chlorophenyl)but-3-en-1-one (1d)



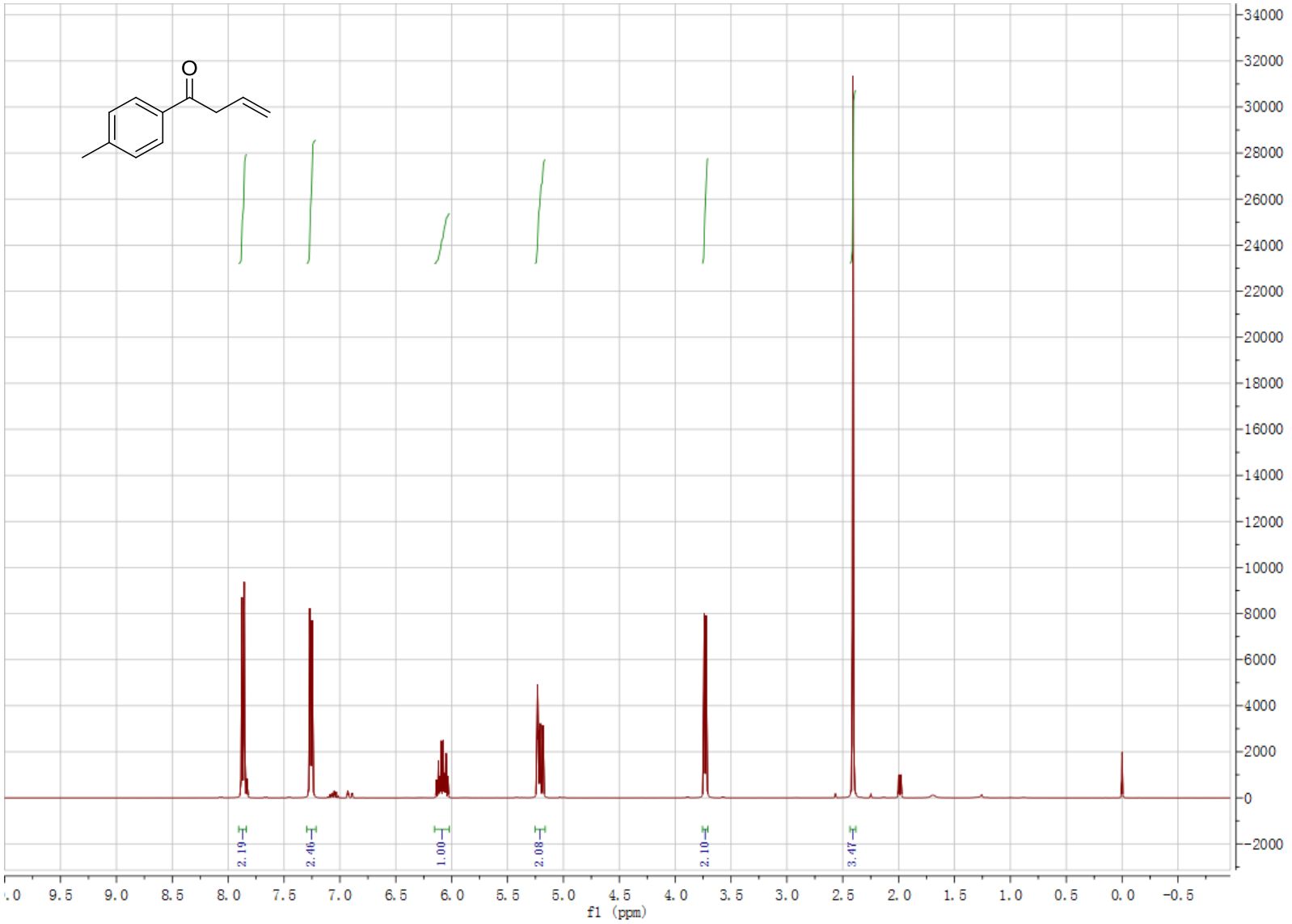

196.7
138.1
135.0
133.1
130.5
130.0
128.4
126.4
119.1
43.5
Cl
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

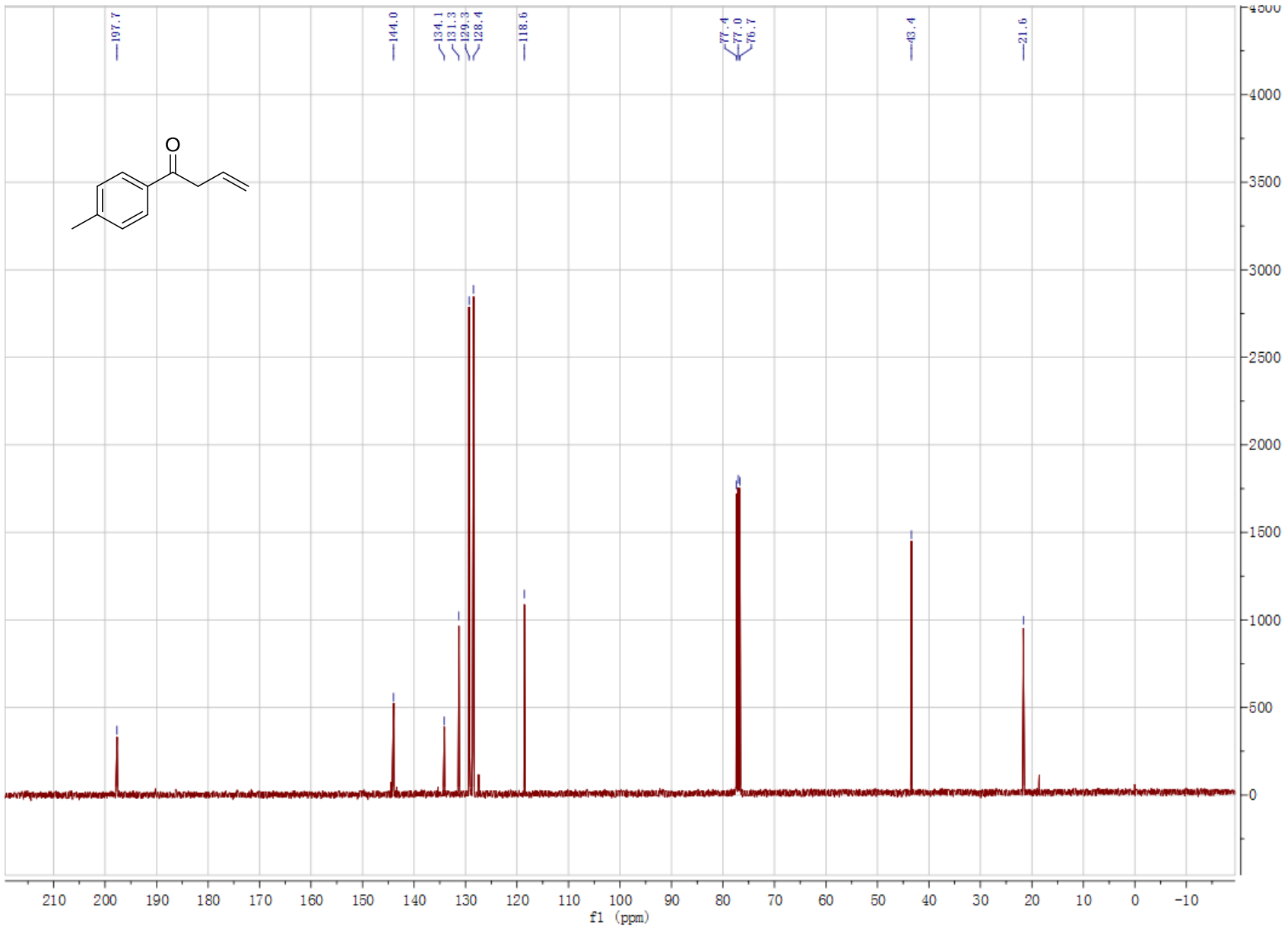
1-(4-fluorophenyl)but-3-en-1-one (1e)



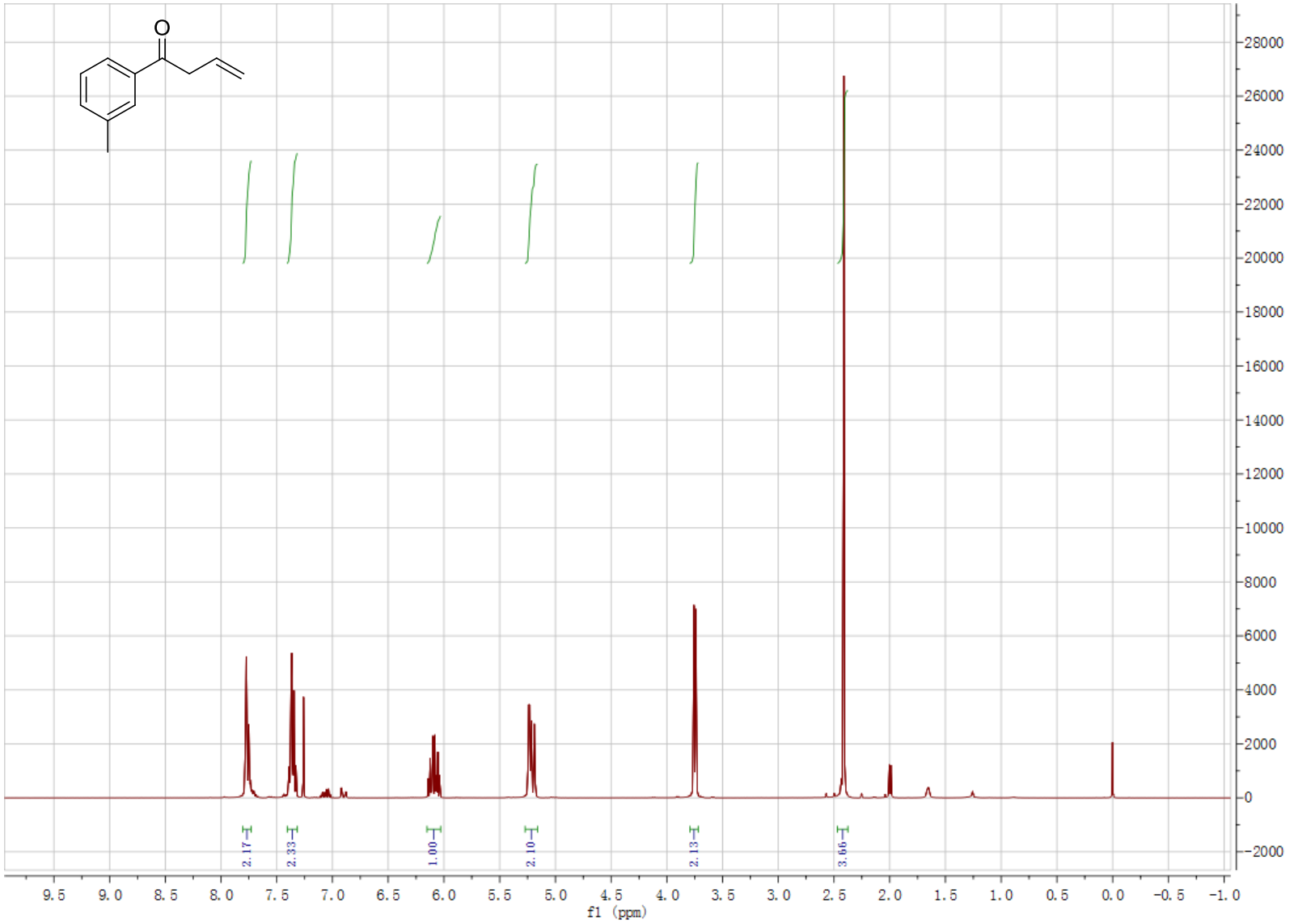

196.41
167.06
164.52
133.00
132.97
130.98
130.89
130.85
118.89
115.85
115.63
43.39
O
F
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

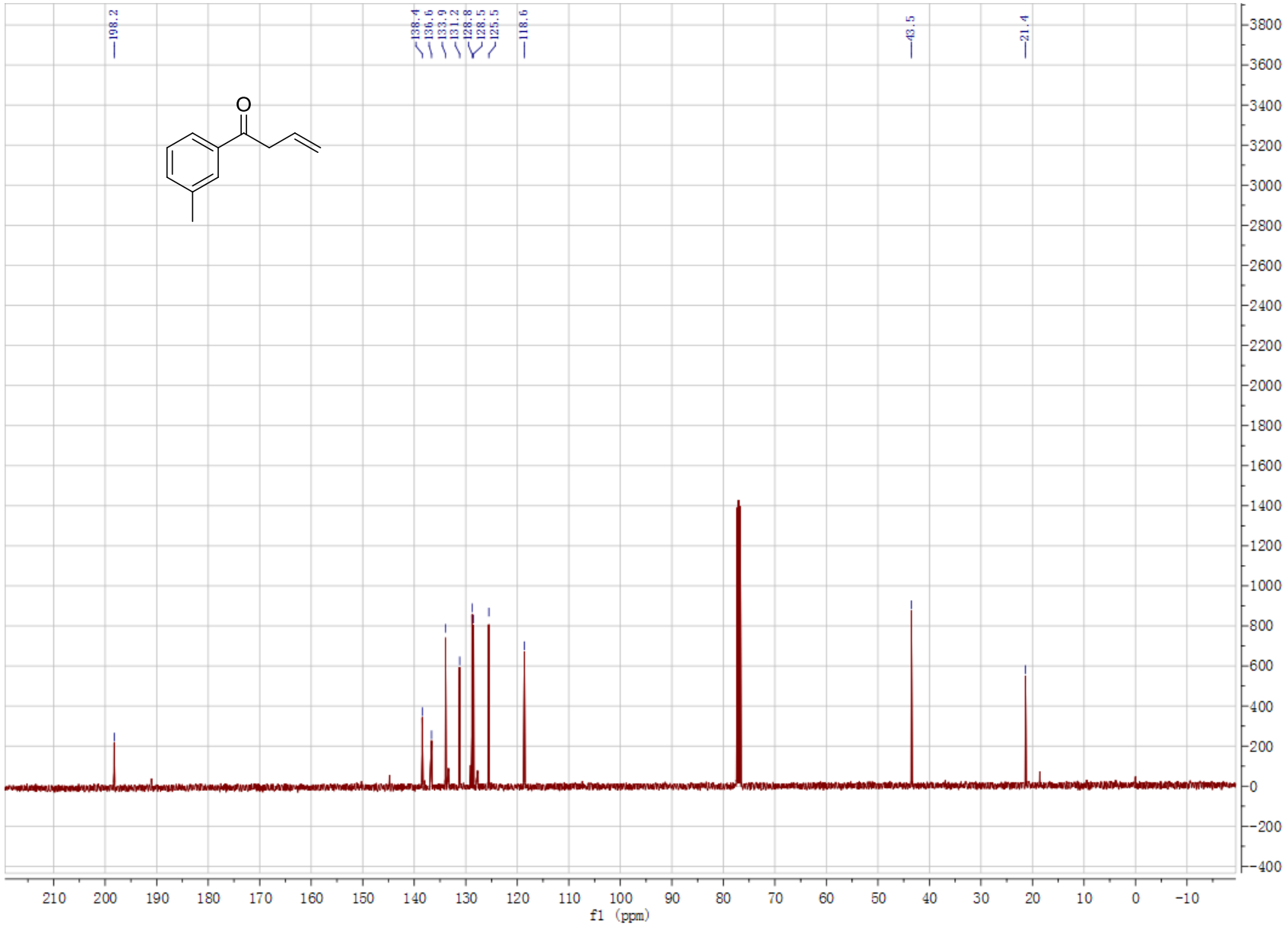
1-p-tolylbut-3-en-1-one (1f,mixture with trace of 2f-*E*)



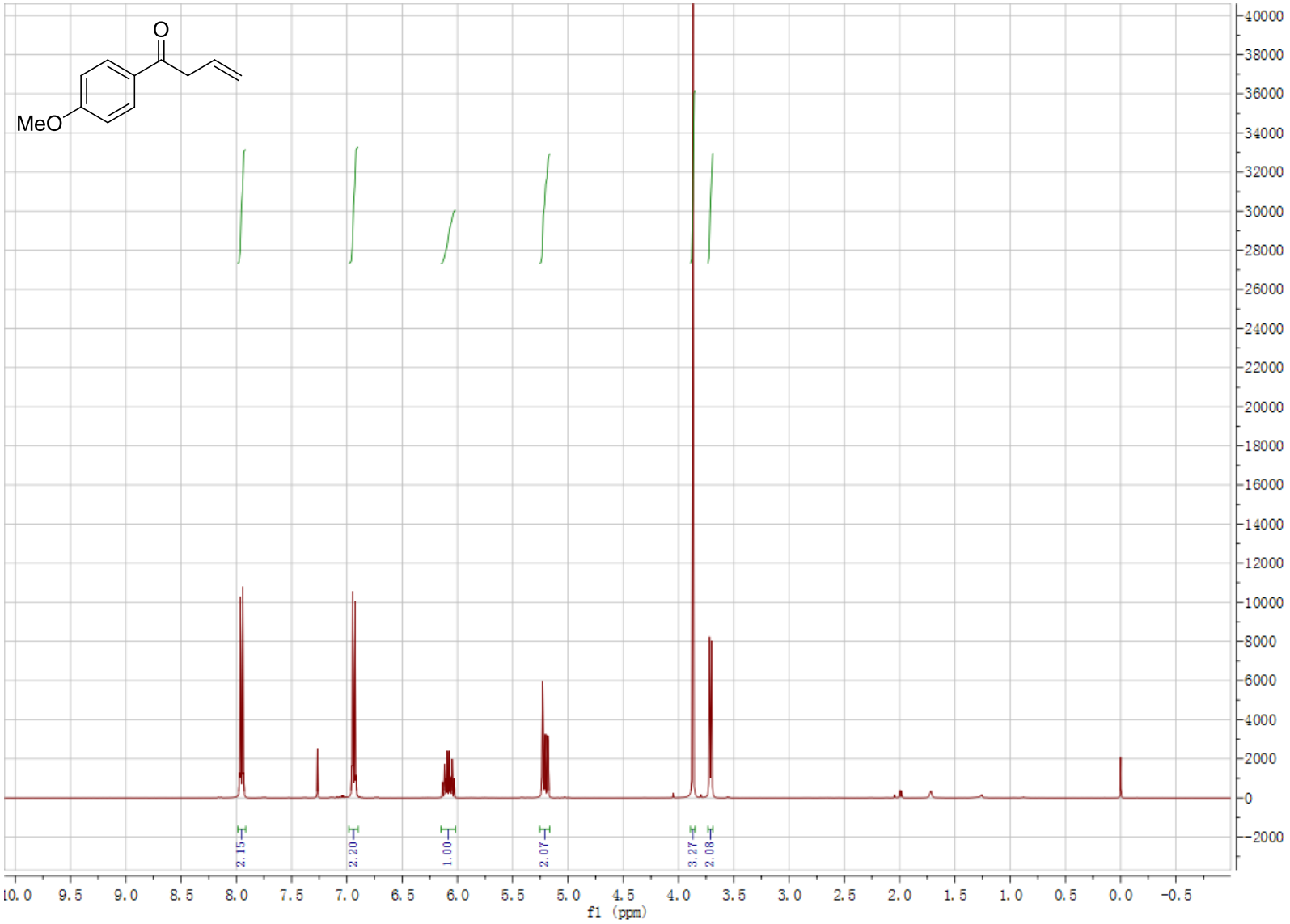

197.7
144.0
134.1
131.3
129.3
128.4
118.6
77.4
77.0
76.7
43.4
21.6
O
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

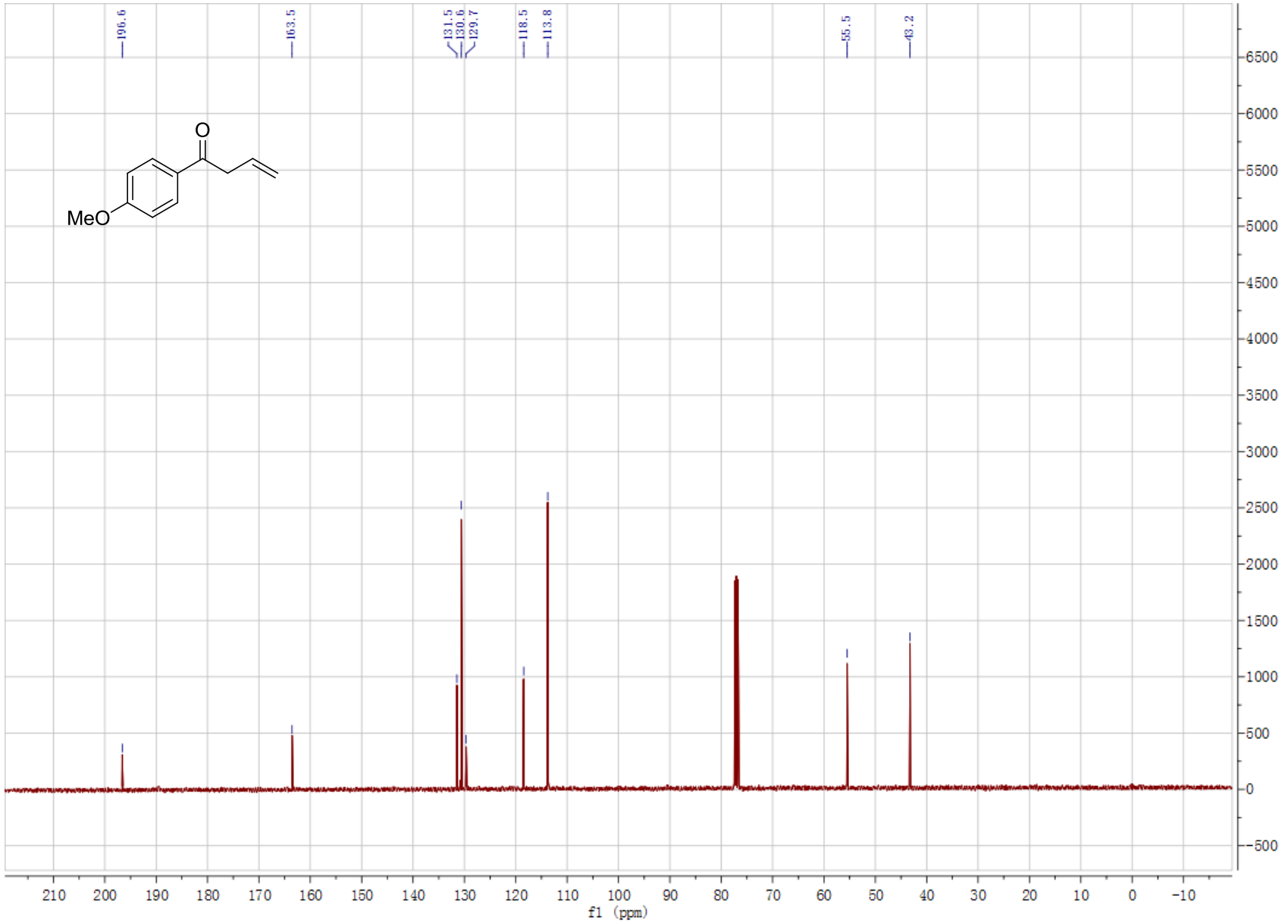
1-m-tolylbut-3-en-1-one (1g, mixture with trace of 2g-*E*)



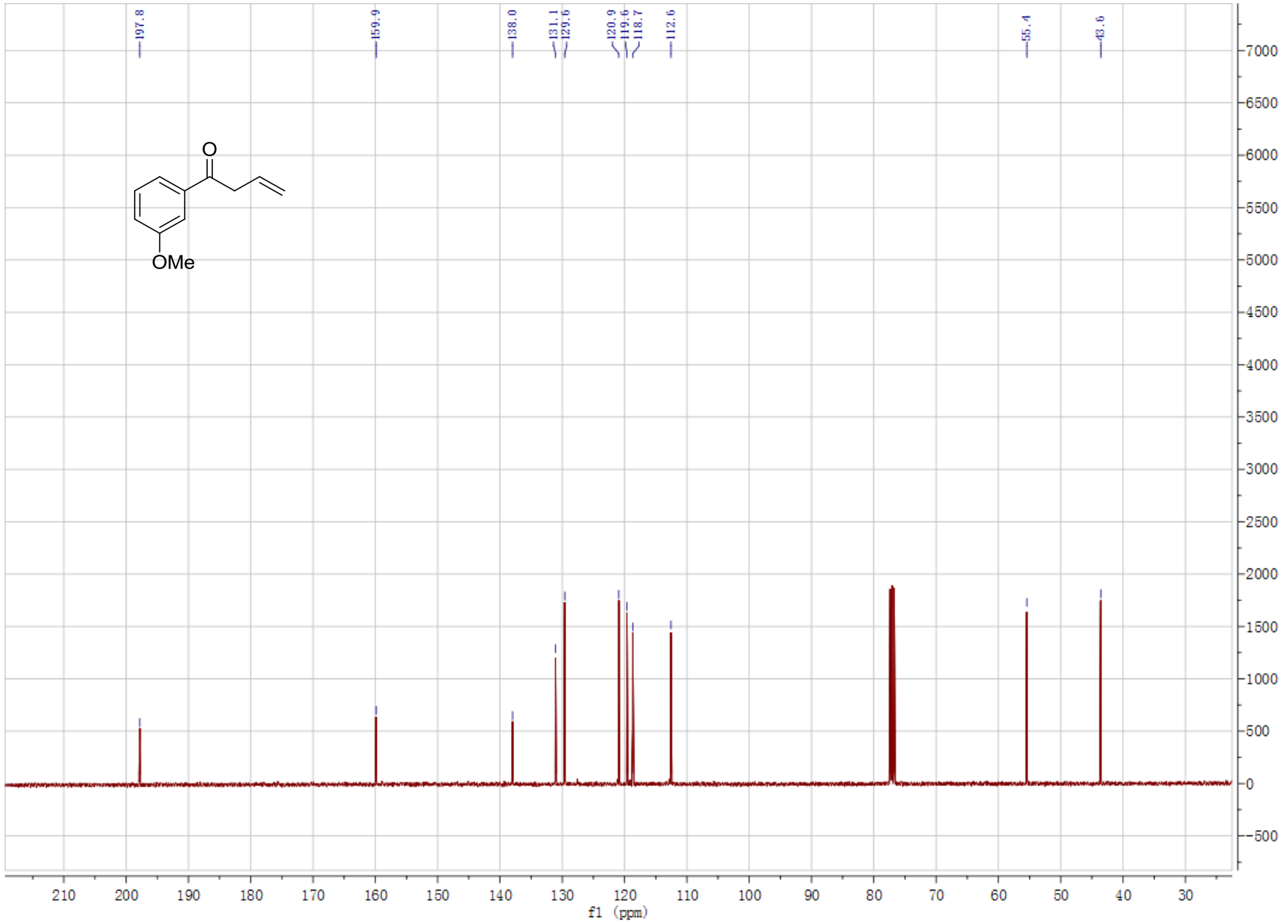

198.2
138.4
136.6
133.9
131.2
128.8
128.5
125.5
118.6
43.5
21.4
O
f1 (ppm)

1-(4-methoxyphenyl)but-3-en-1-one (1h)

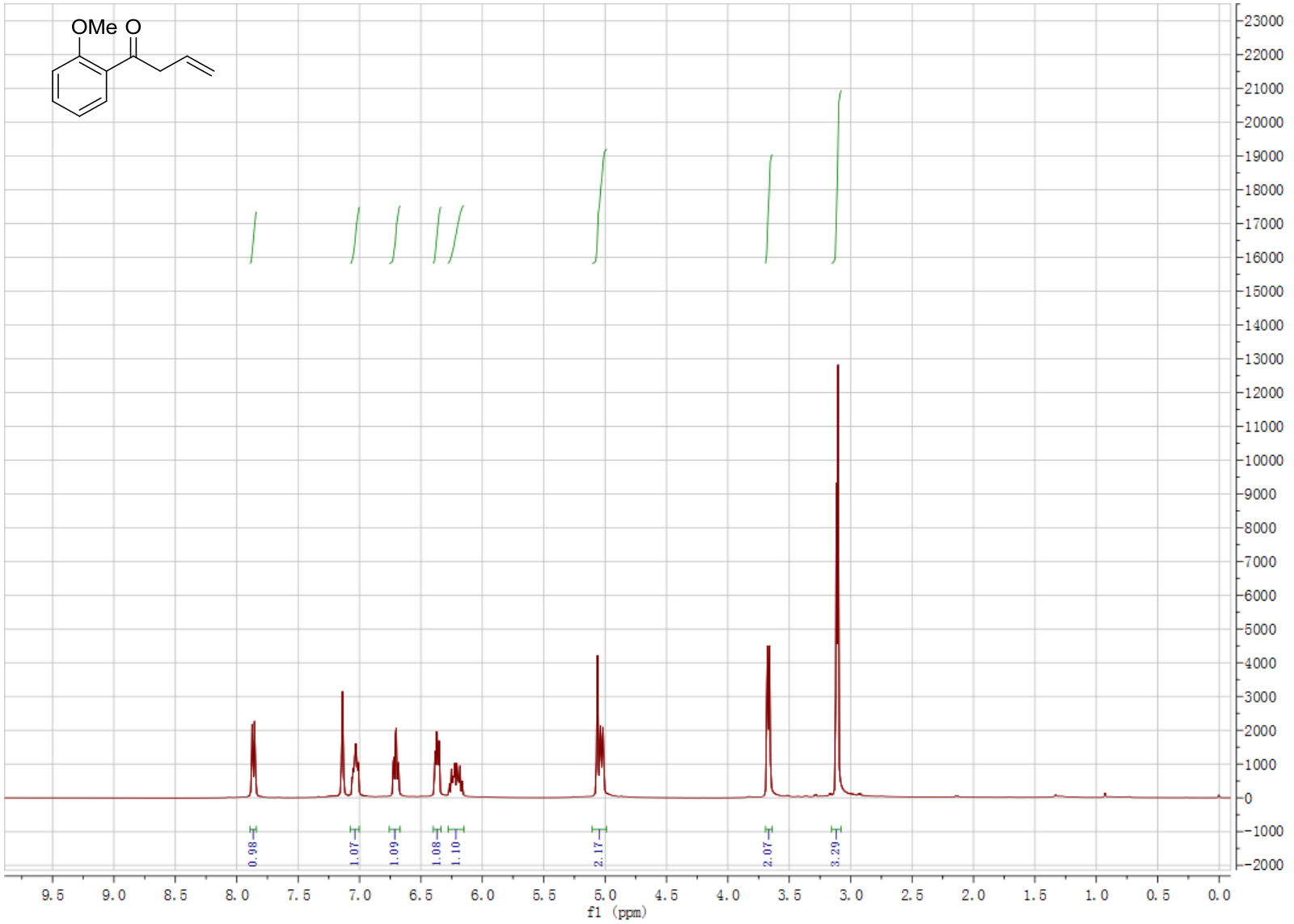


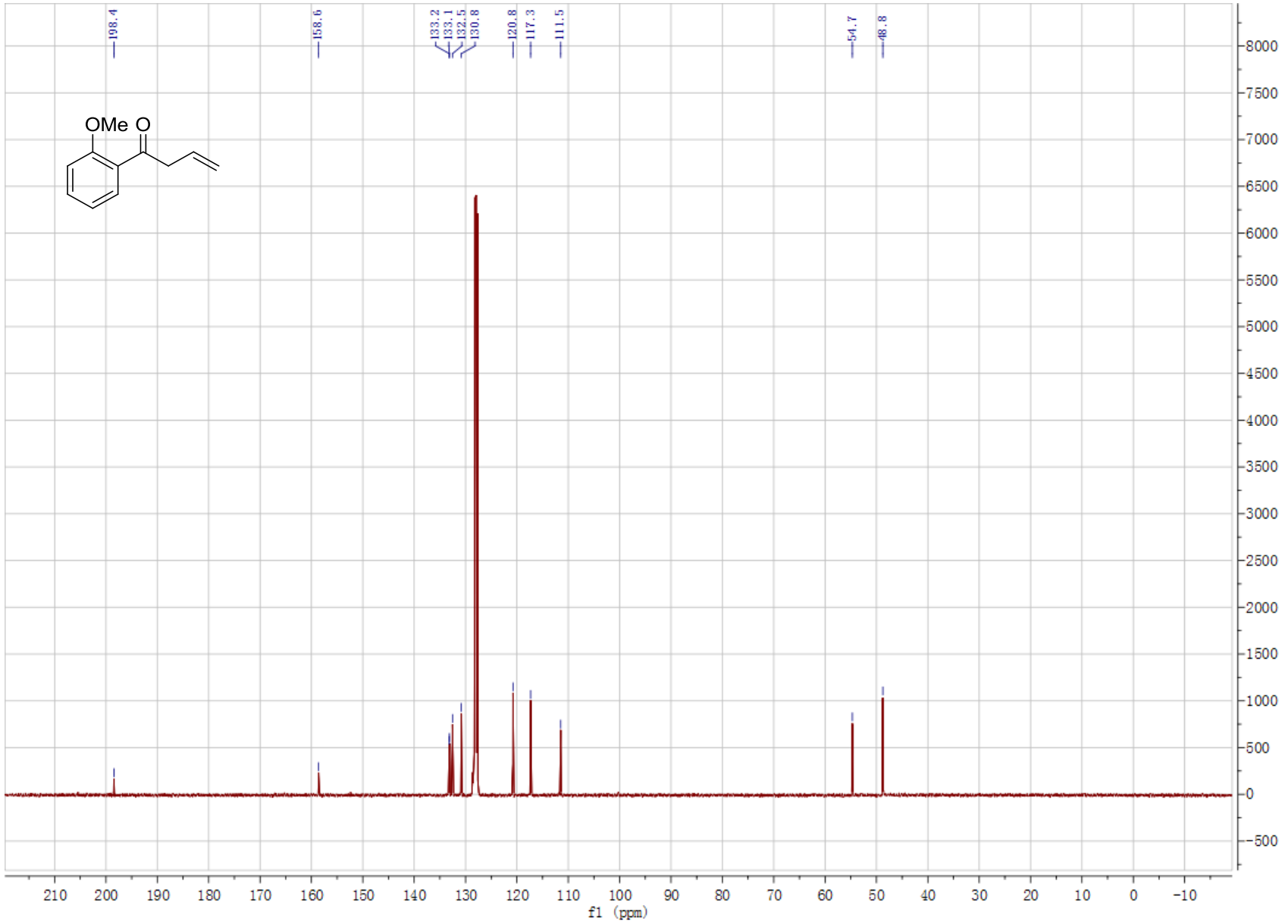

196.6
163.5
131.5
130.6
129.7
118.5
113.8
55.5
43.2
O
MeO
f1 (ppm)

1-(3-methoxyphenyl)but-3-en-1-one (1i)

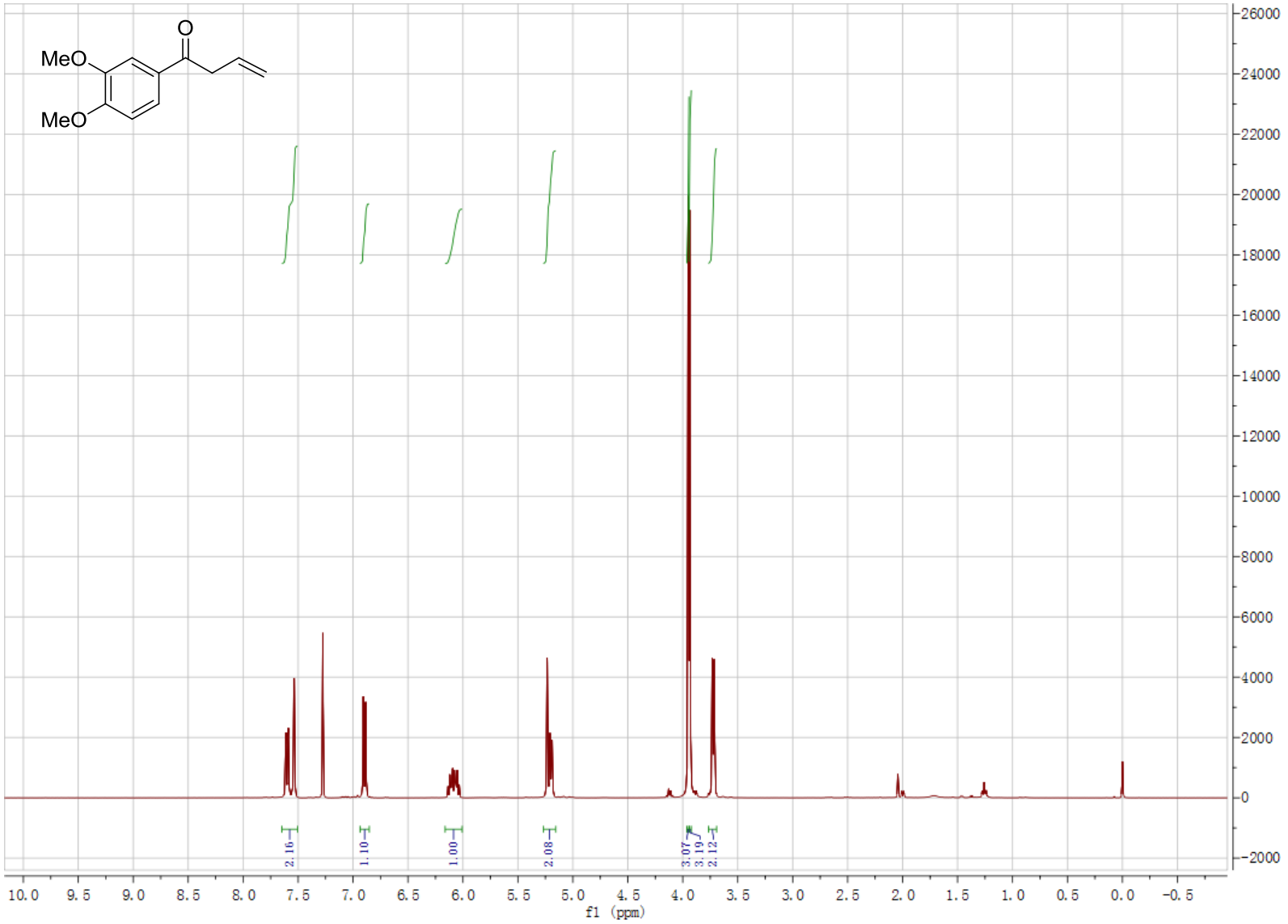

197.8
159.9
138.0
131.1
129.6
120.9
119.6
118.7
112.6
55.4
43.6
O
OMe
f1 (ppm)

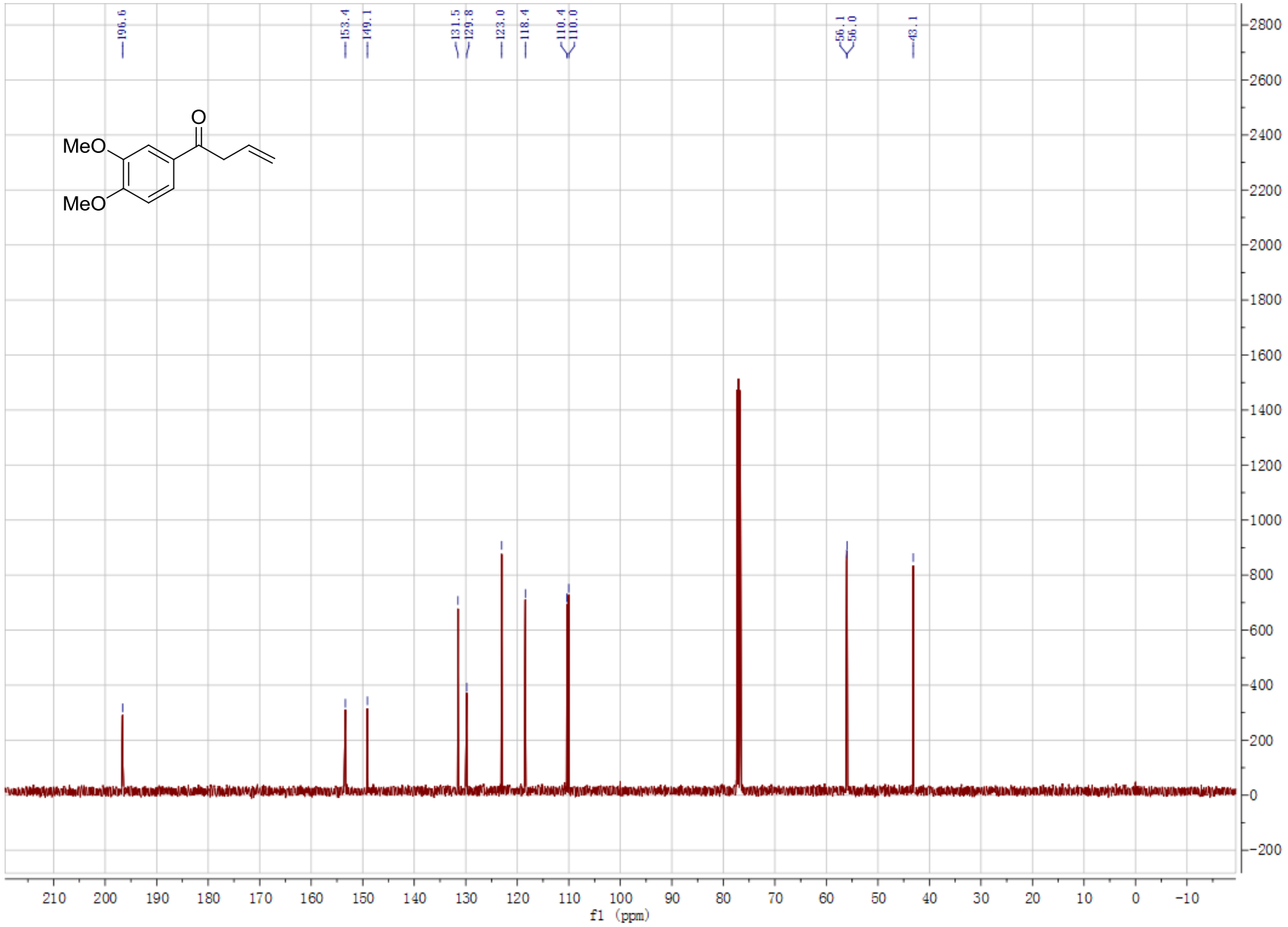
1-(2-methoxyphenyl)but-3-en-1-one (1j)



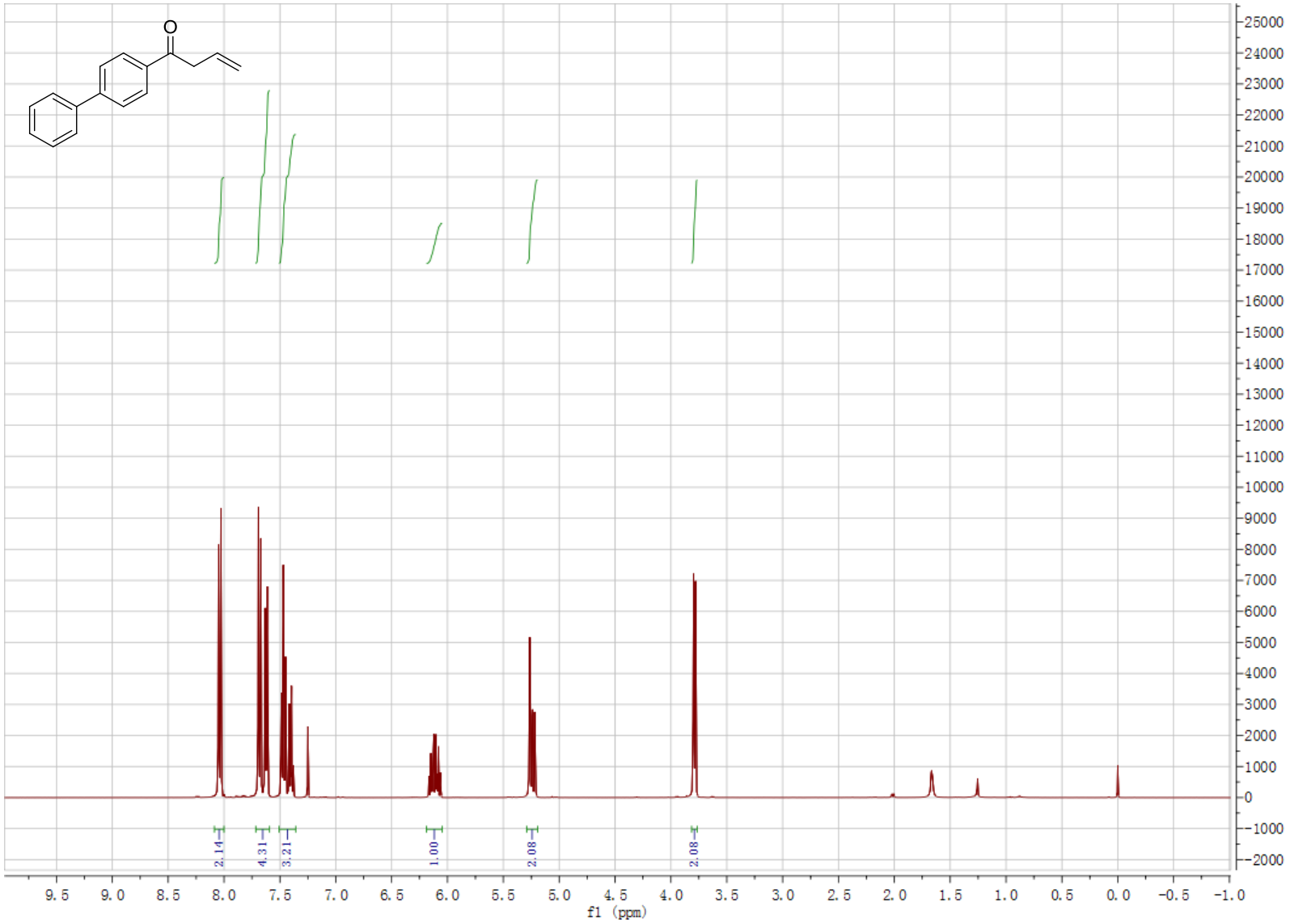

198.4
158.6
133.2
133.1
132.5
130.8
120.8
117.3
111.5
54.7
48.8
OMe O
f1 (ppm)

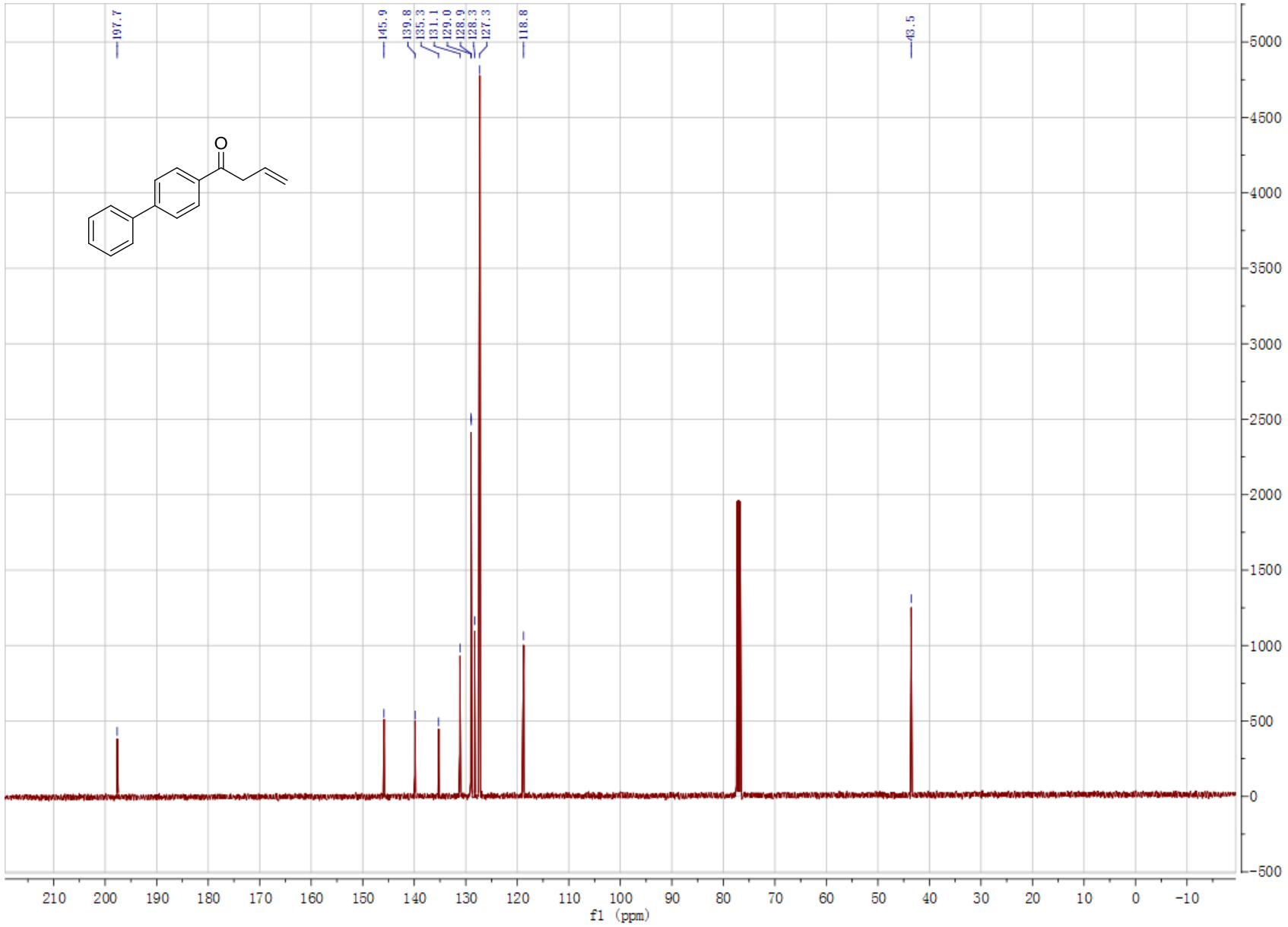
1-(3,4-dimethoxyphenyl)but-3-en-1-one (1k)



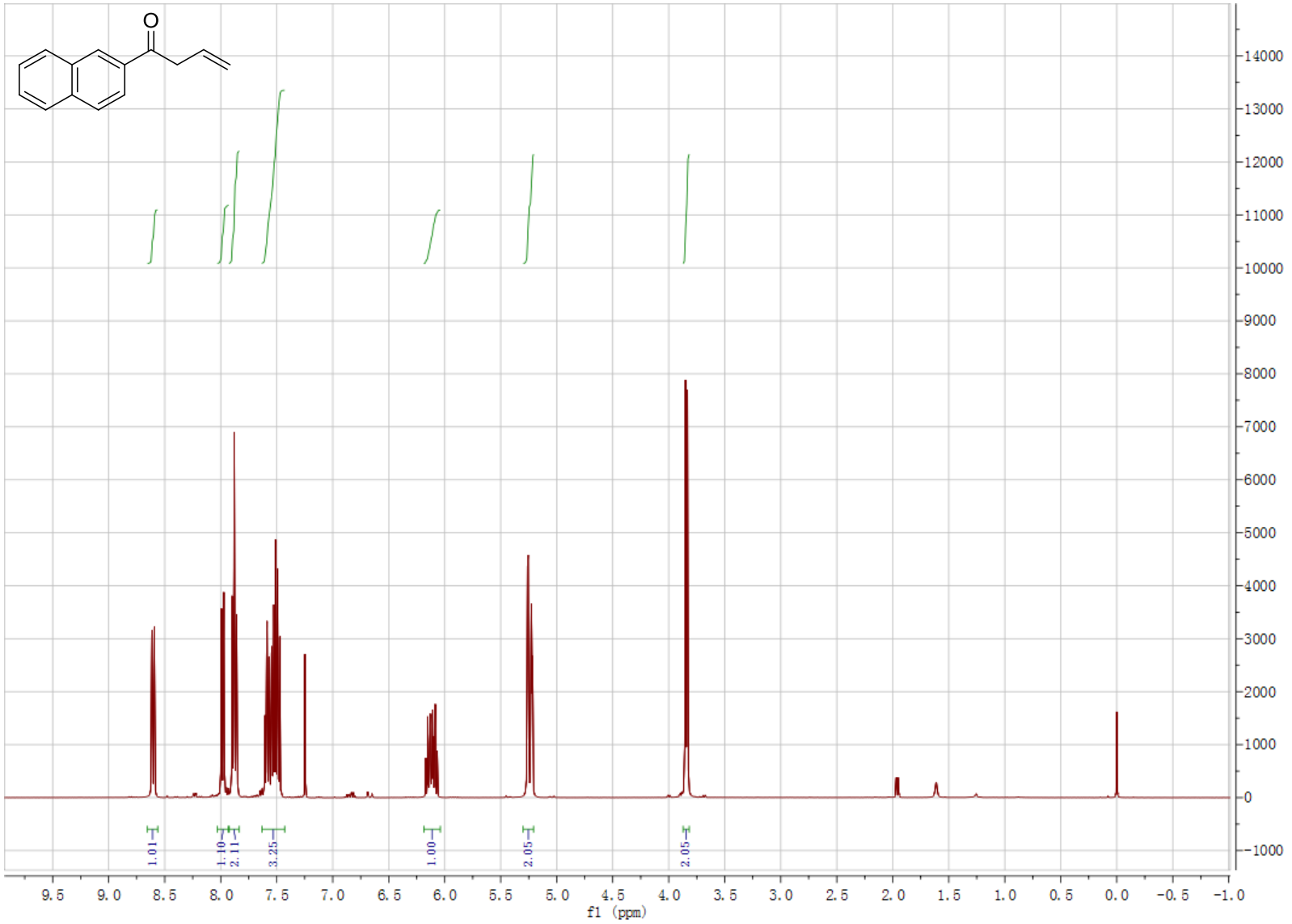

196.6
153.4
149.1
131.5
129.8
123.0
118.4
110.4
110.0
56.1
56.0
43.1
MeO
MeO
O
f1 (ppm)

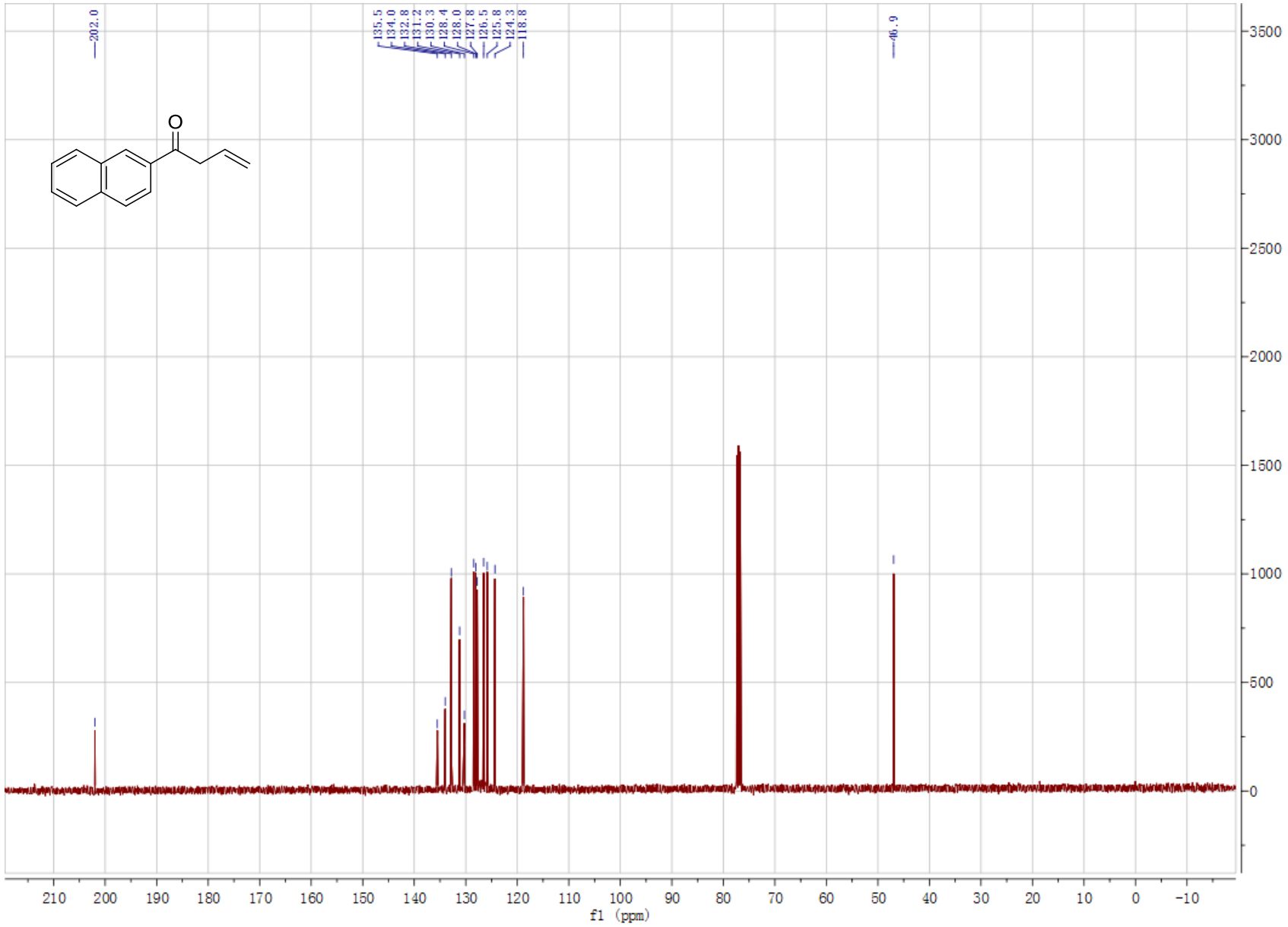
1-(biphenyl-4-yl)but-3-en-1-one (1l)



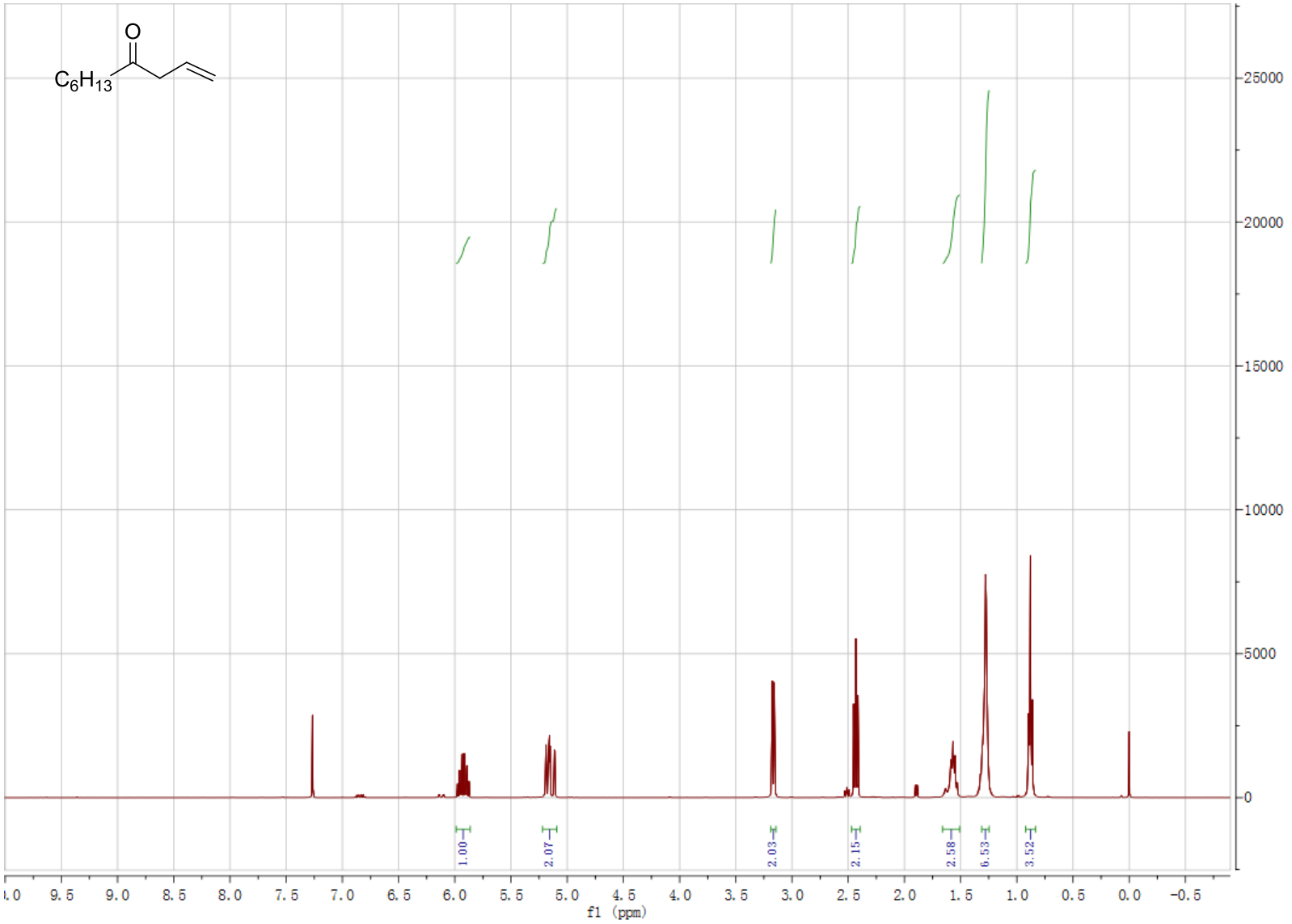

197.7
145.9
139.8
135.3
131.1
129.0
128.9
128.3
127.3
118.8
43.5
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

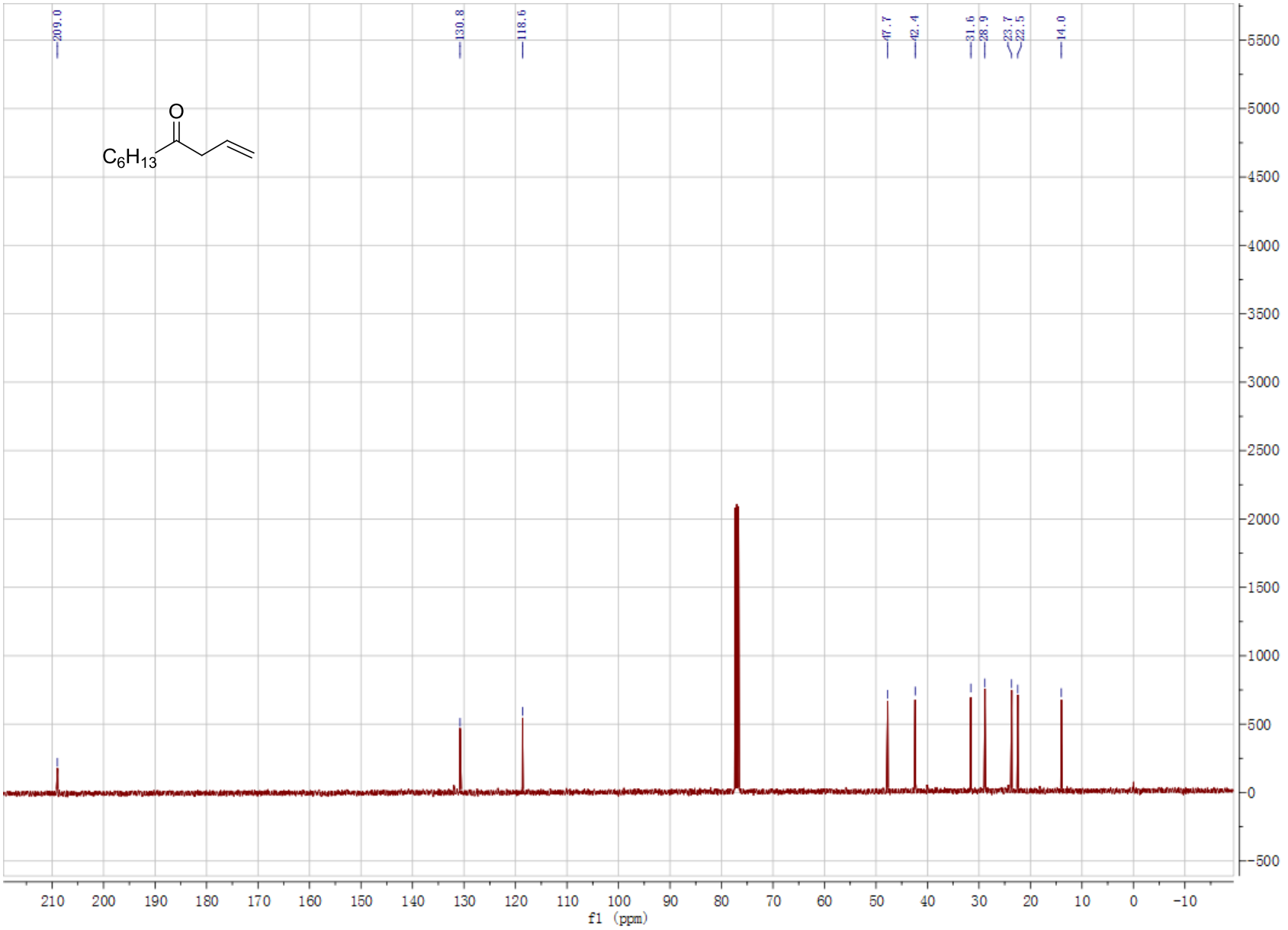
1-(naphthalen-2-yl)but-3-en-1-one (1m)



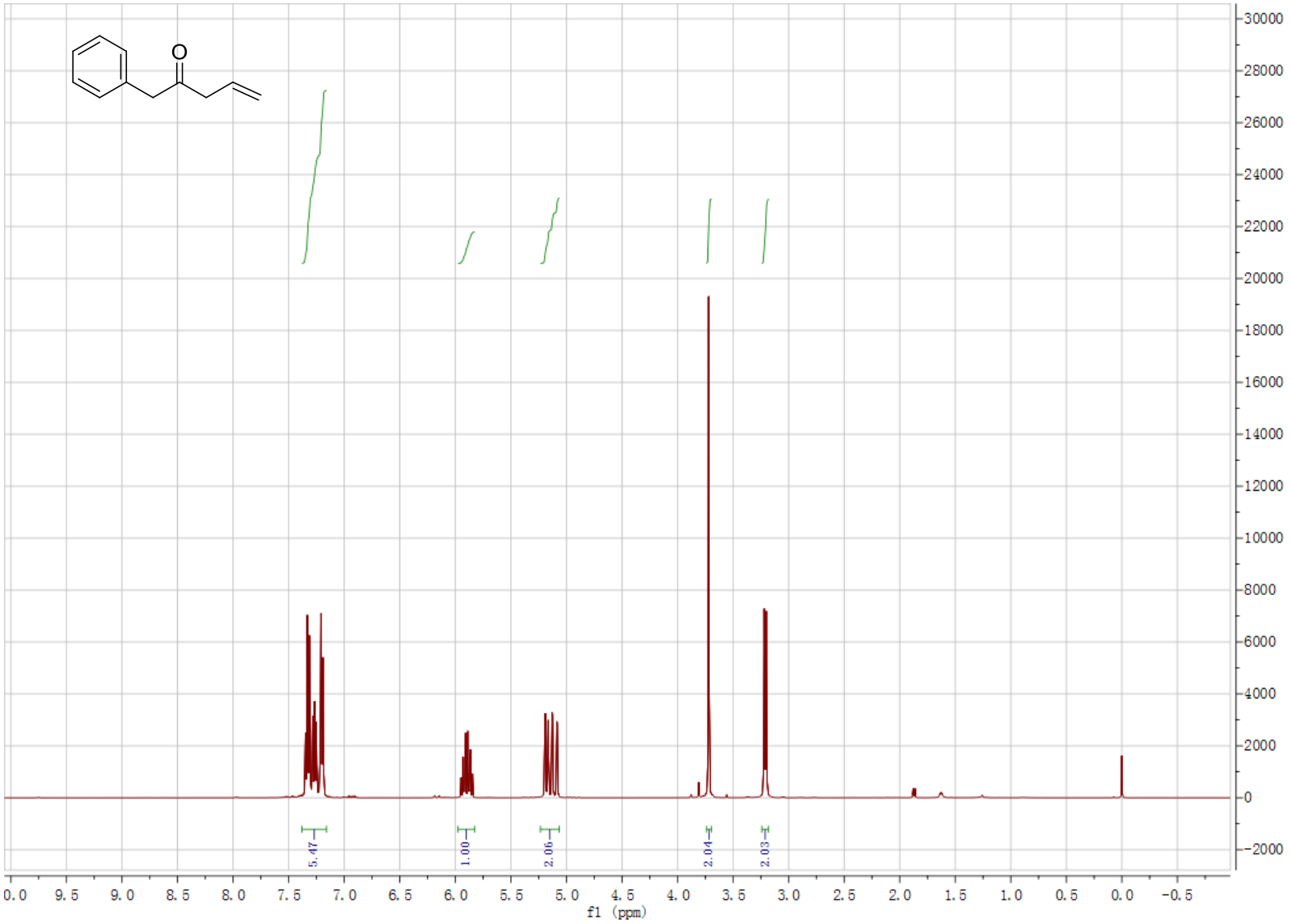

202.0
135.5
134.0
132.8
131.2
130.3
128.4
128.0
127.8
126.5
125.8
124.3
118.8
46.9
O
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

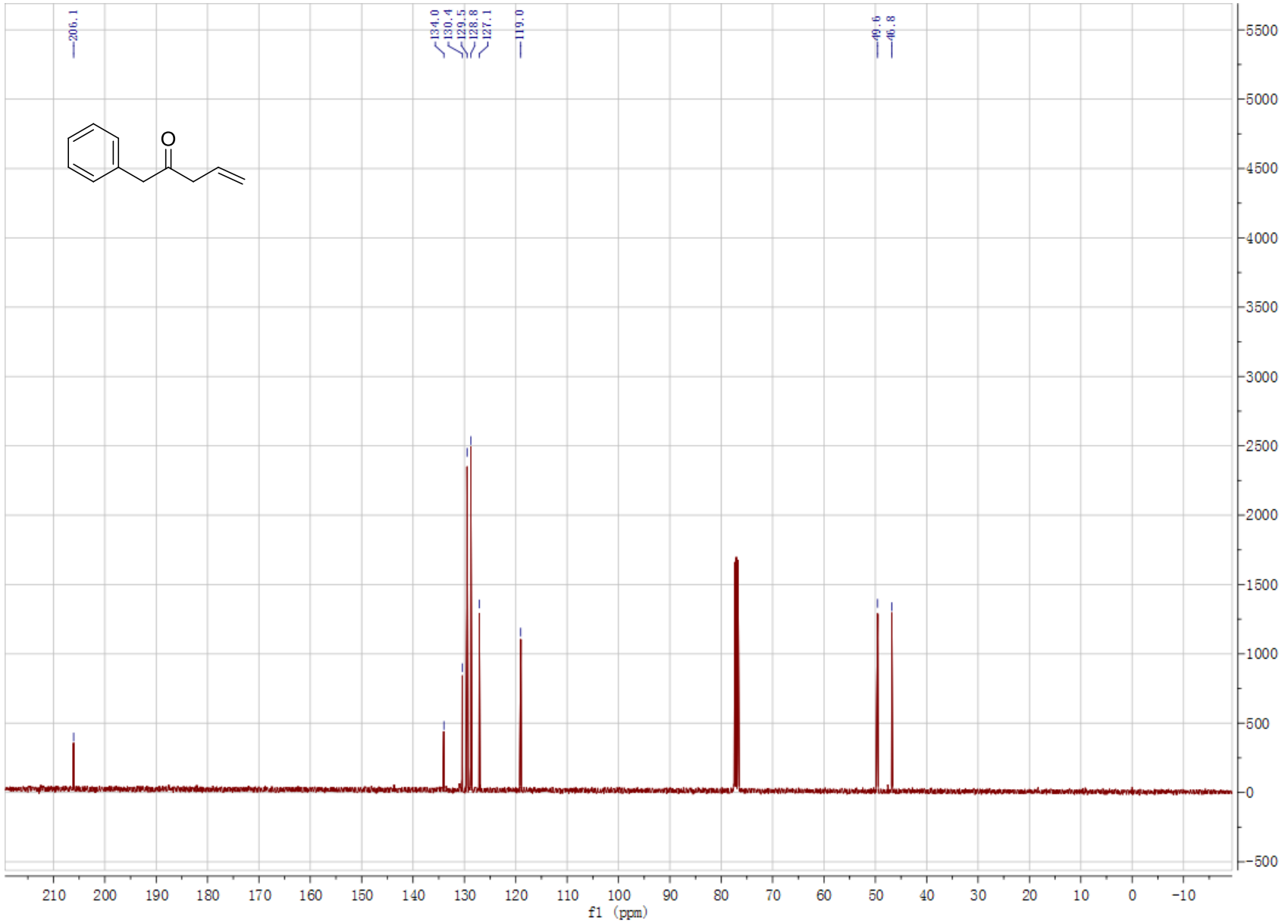
dec-1-en-4-one (3a)



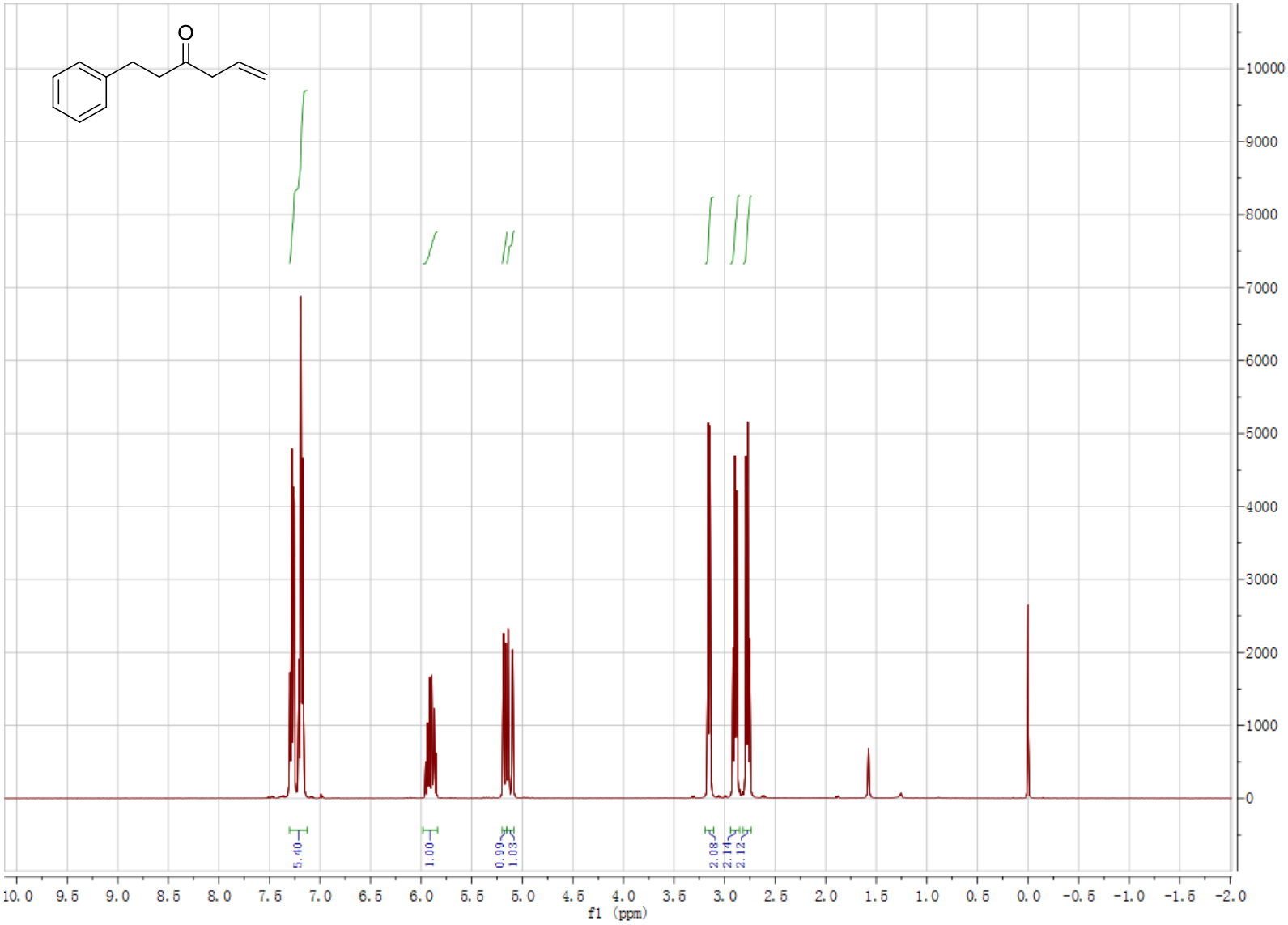

209.0
130.8
118.6
47.7
42.4
31.6
28.9
23.7
22.5
14.0
O
C6H13
f1 (ppm)

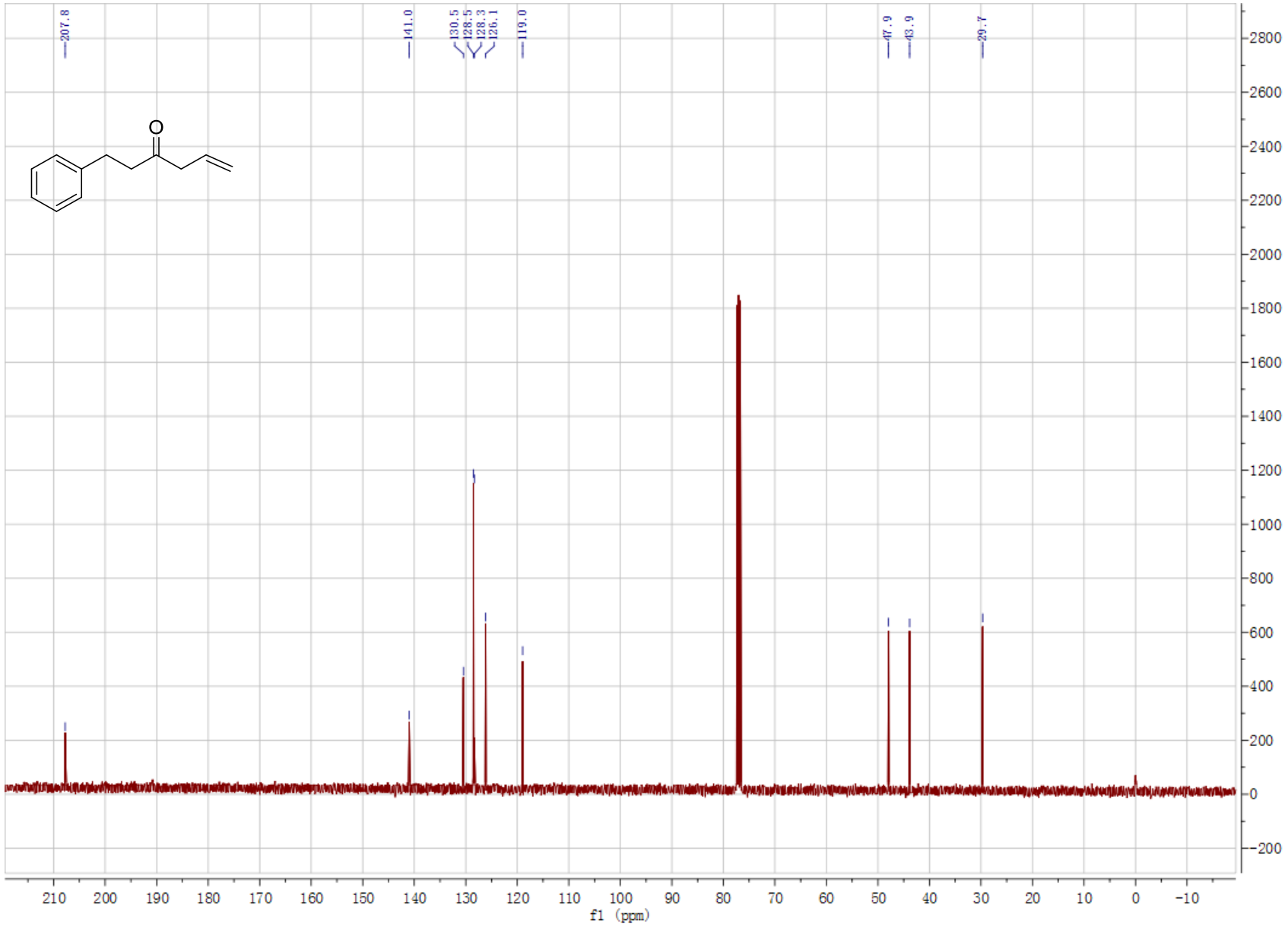
1-phenylpent-4-en-2-one (3b)



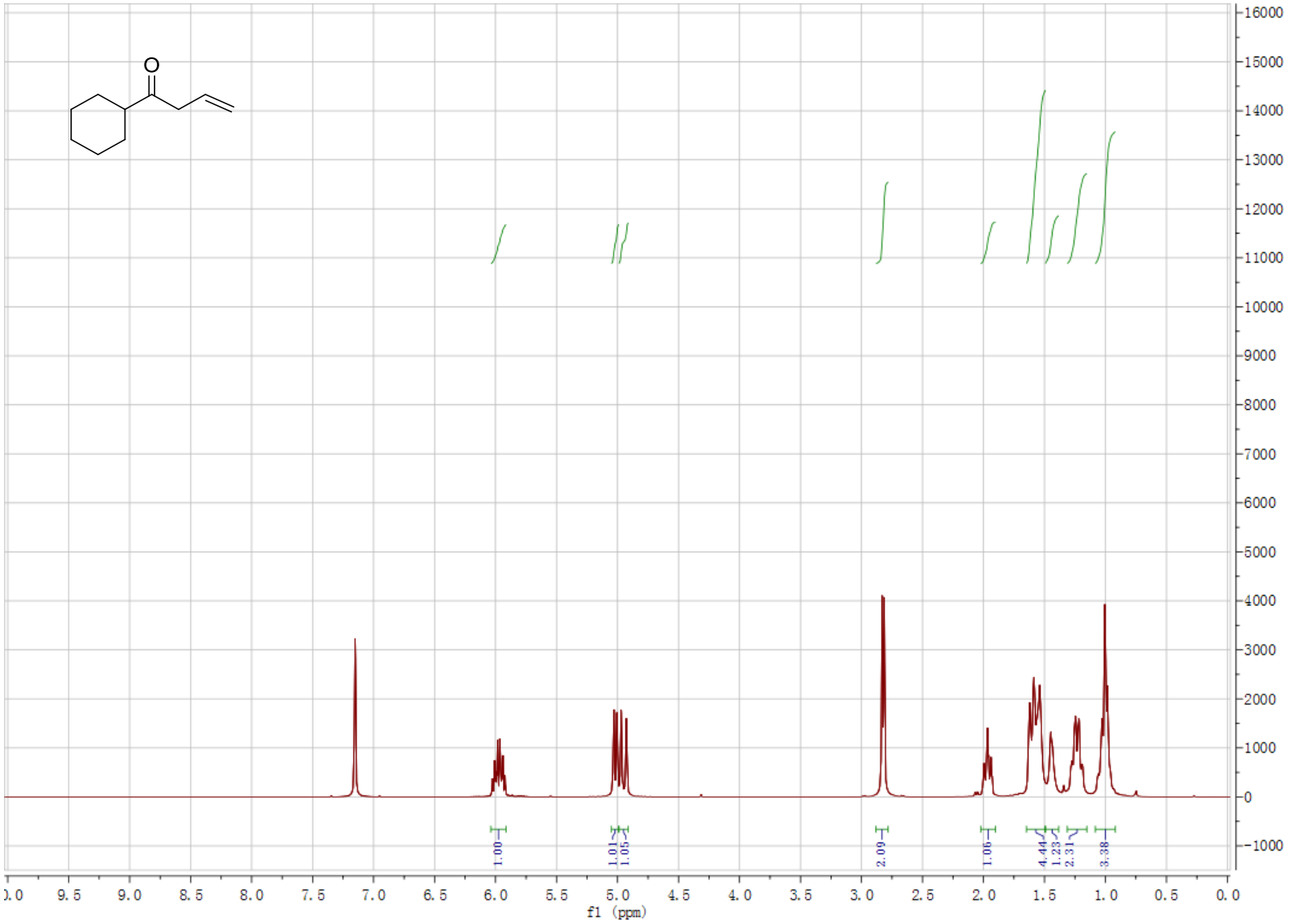

206.1
134.0
130.4
129.5
128.8
127.1
119.0
49.6
46.8
O
f1 (ppm)

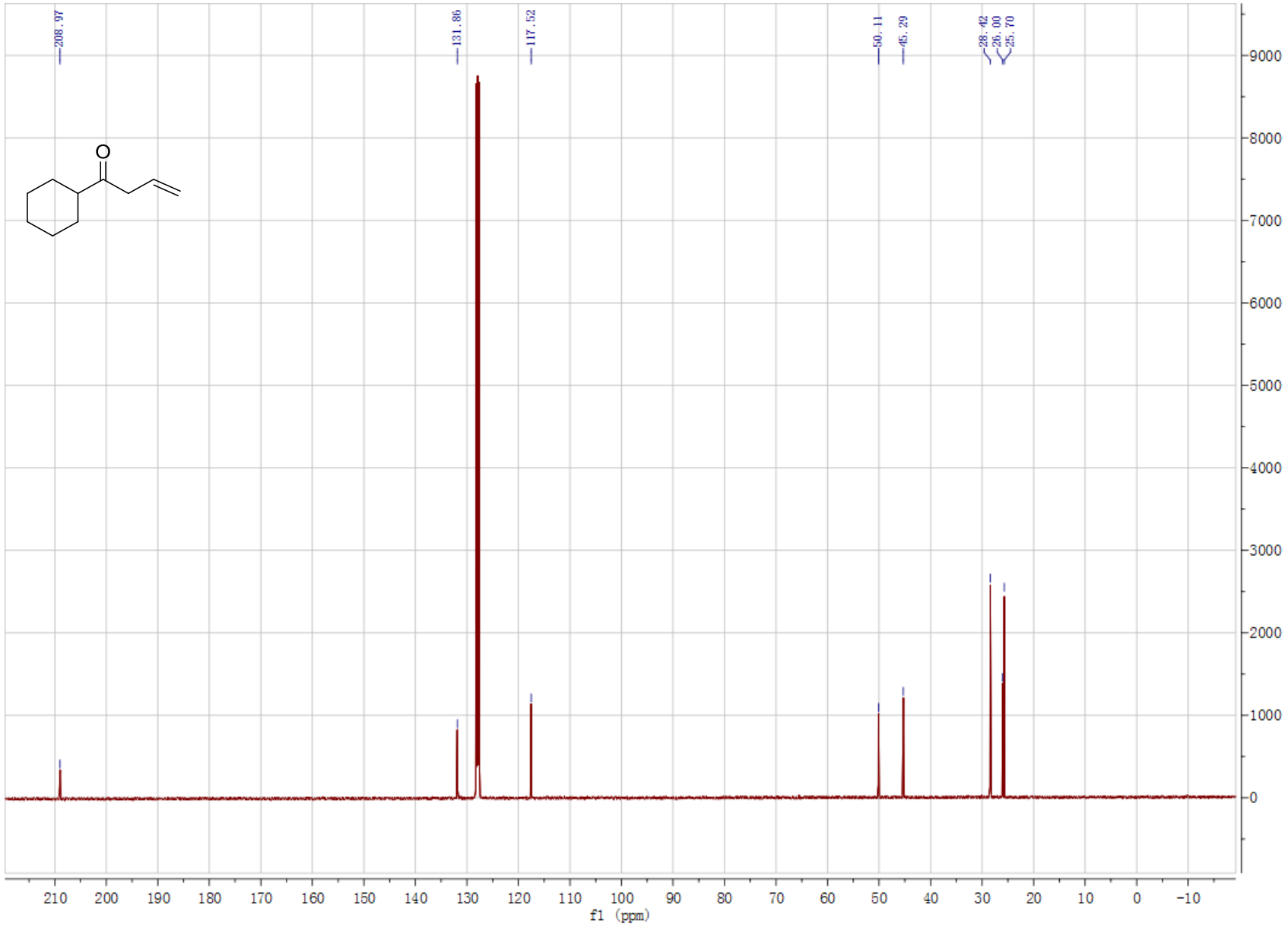
1-phenylhex-5-en-3-one (3c)



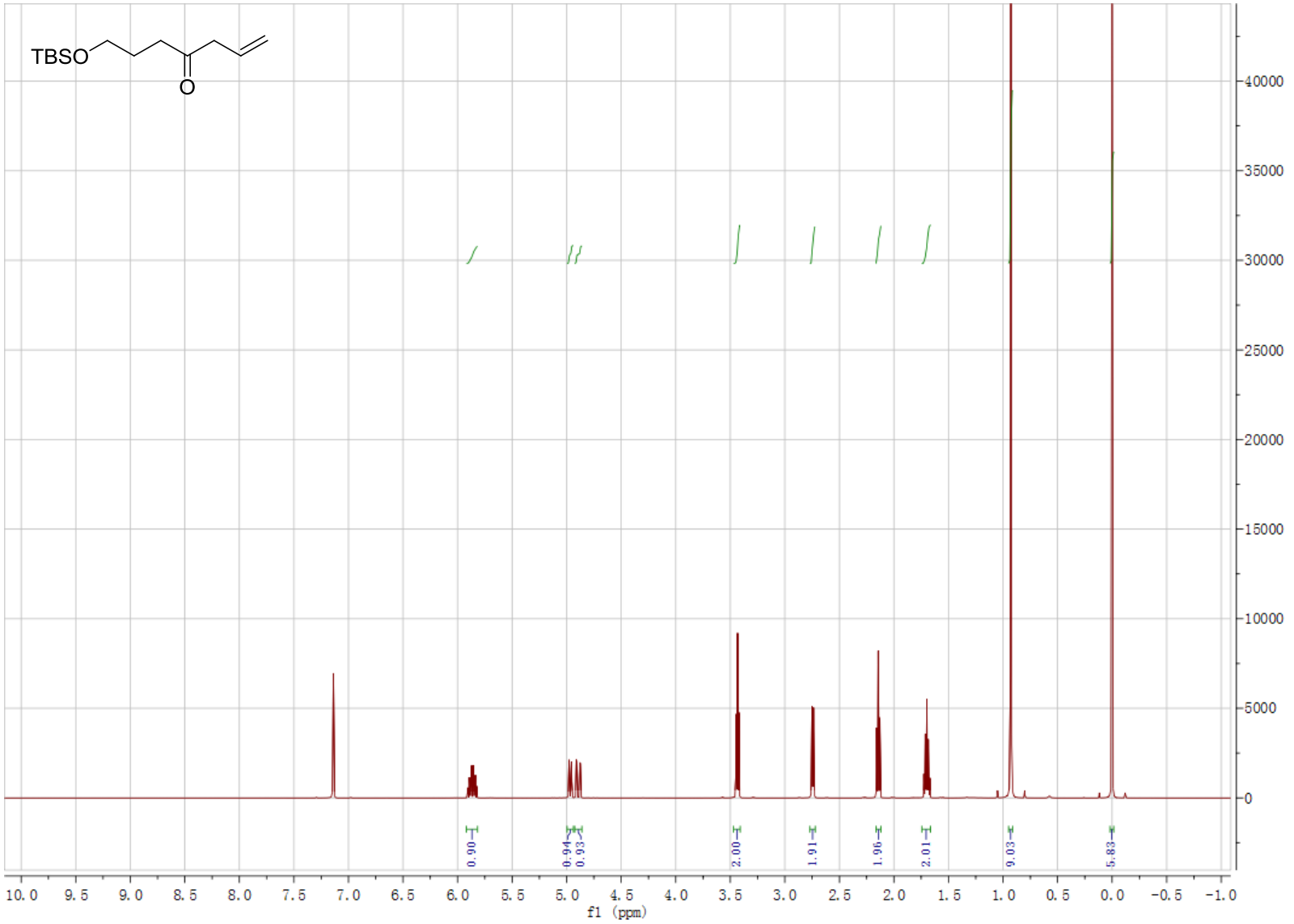

207.8
141.0
130.5
128.5
128.3
126.1
119.0
47.9
43.9
29.7
O
f1 (ppm)

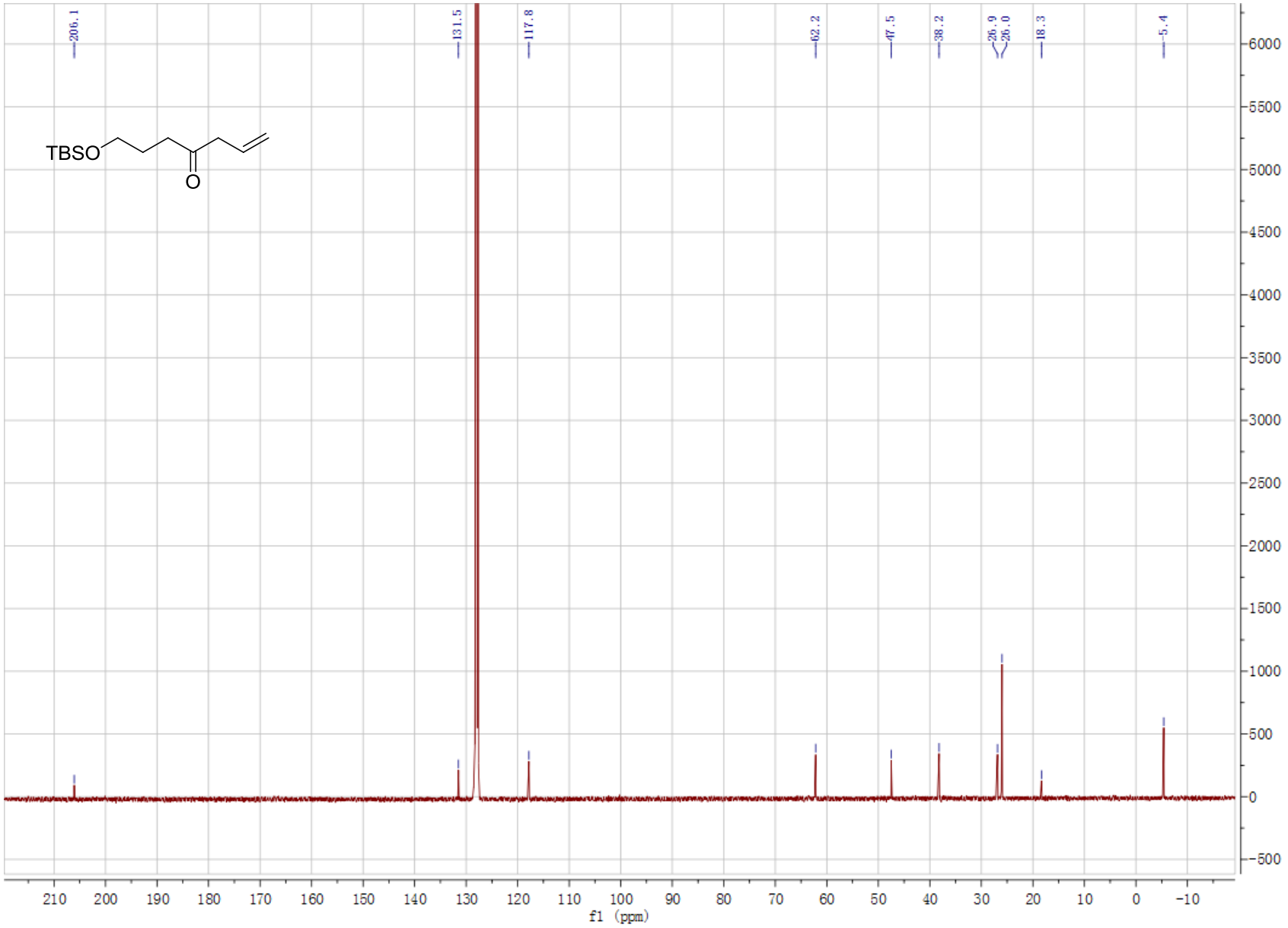
1-cyclohexylbut-3-en-1-one (3d)



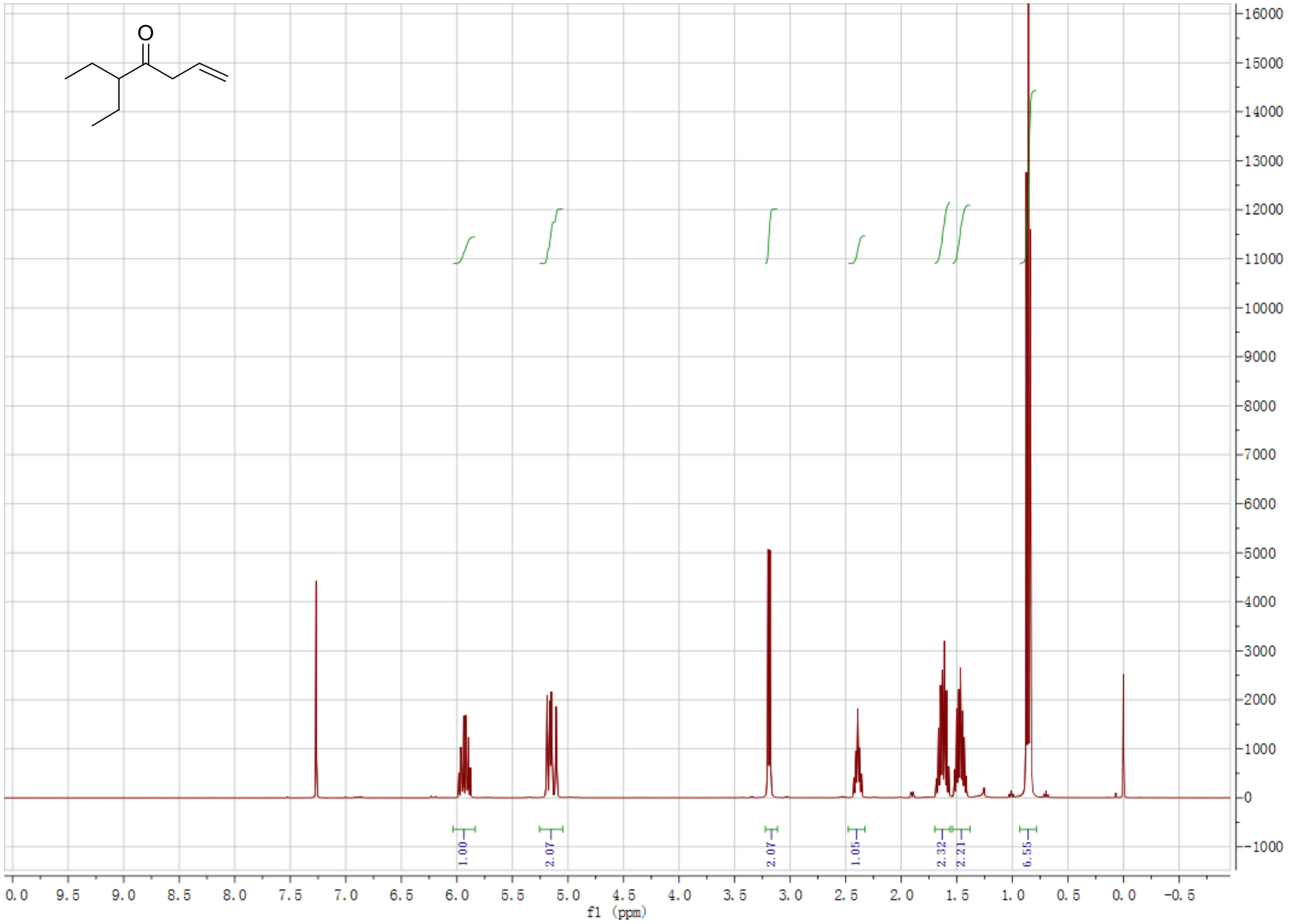

208.97
131.86
117.52
50.11
45.29
28.42
26.00
25.70
O
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

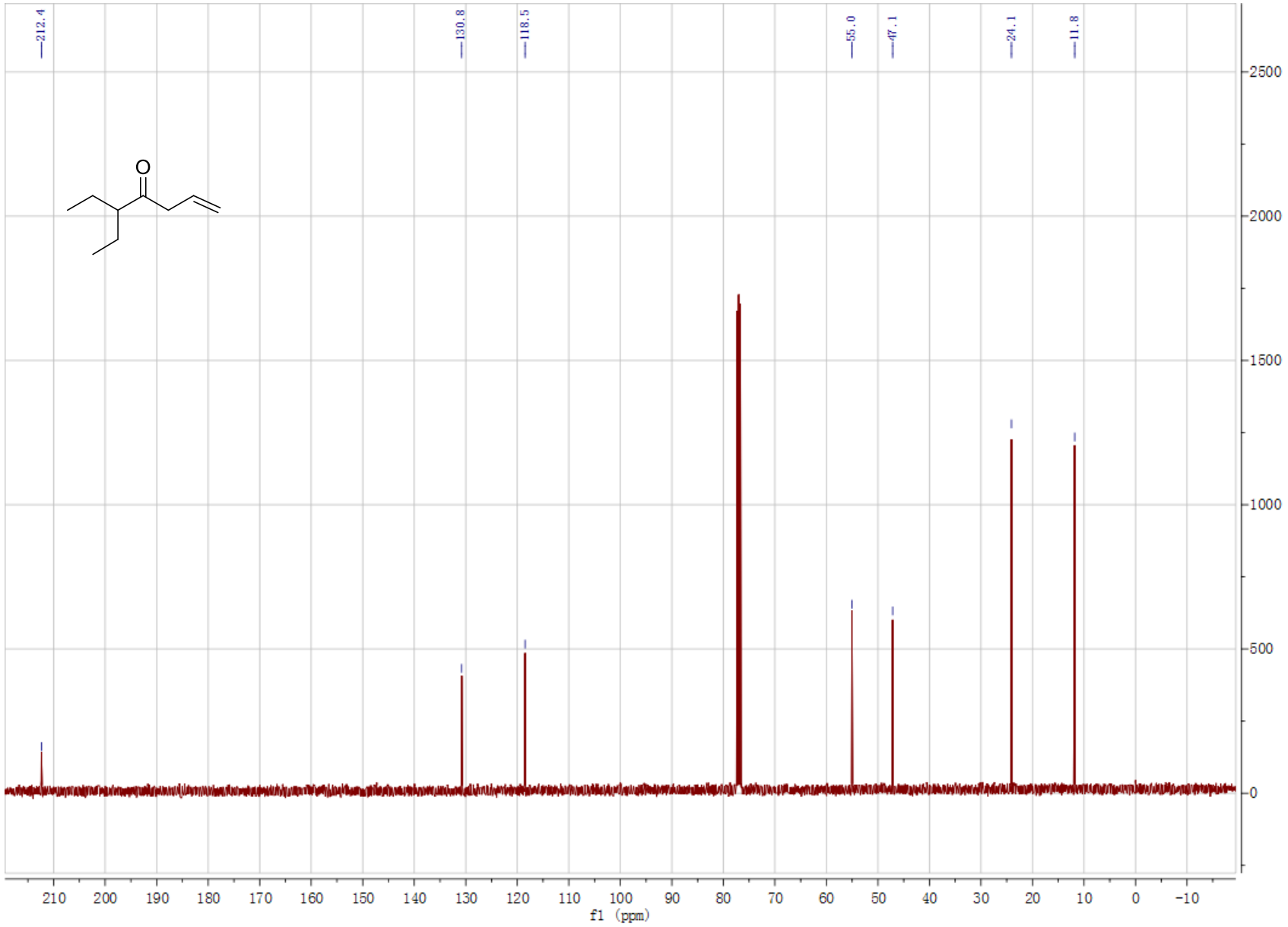
1-(tert-butyldimethylsilyloxy)hex-5-en-3-one (3e)



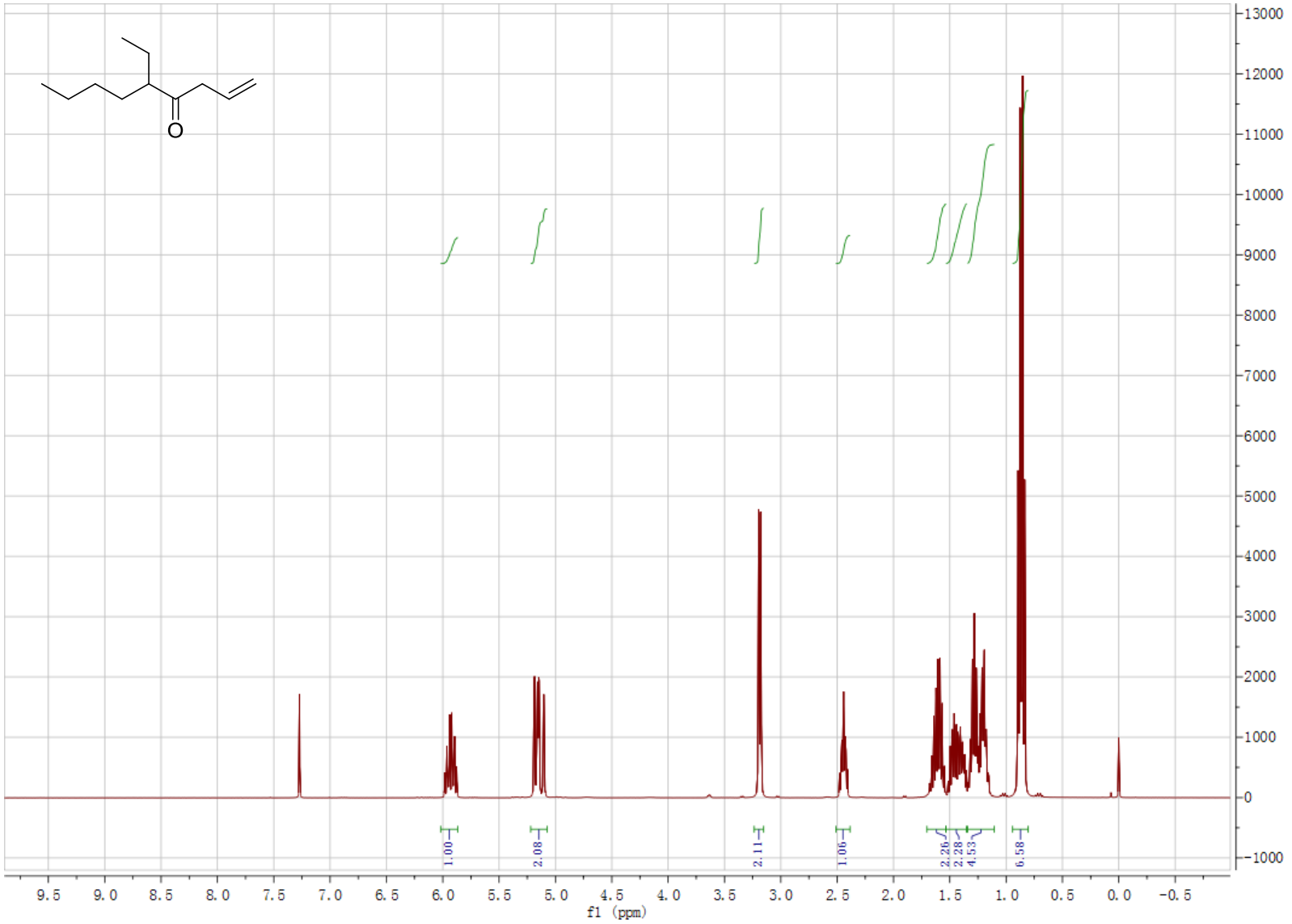

206.1
131.5
117.8
62.2
47.5
38.2
26.9
26.0
18.3
-5.4
TBSO
O
f1 (ppm)

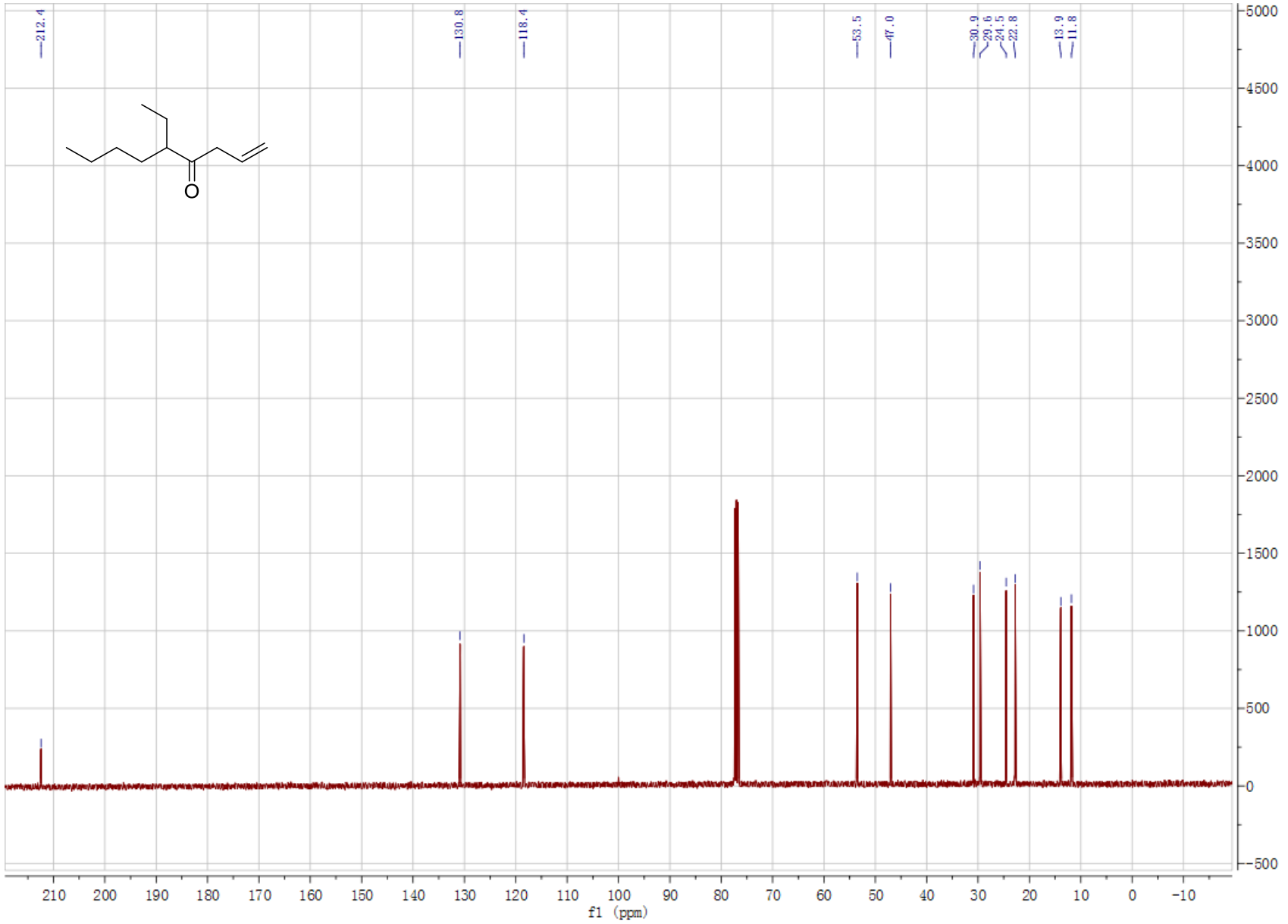
5-ethylhept-1-en-4-one (3f)



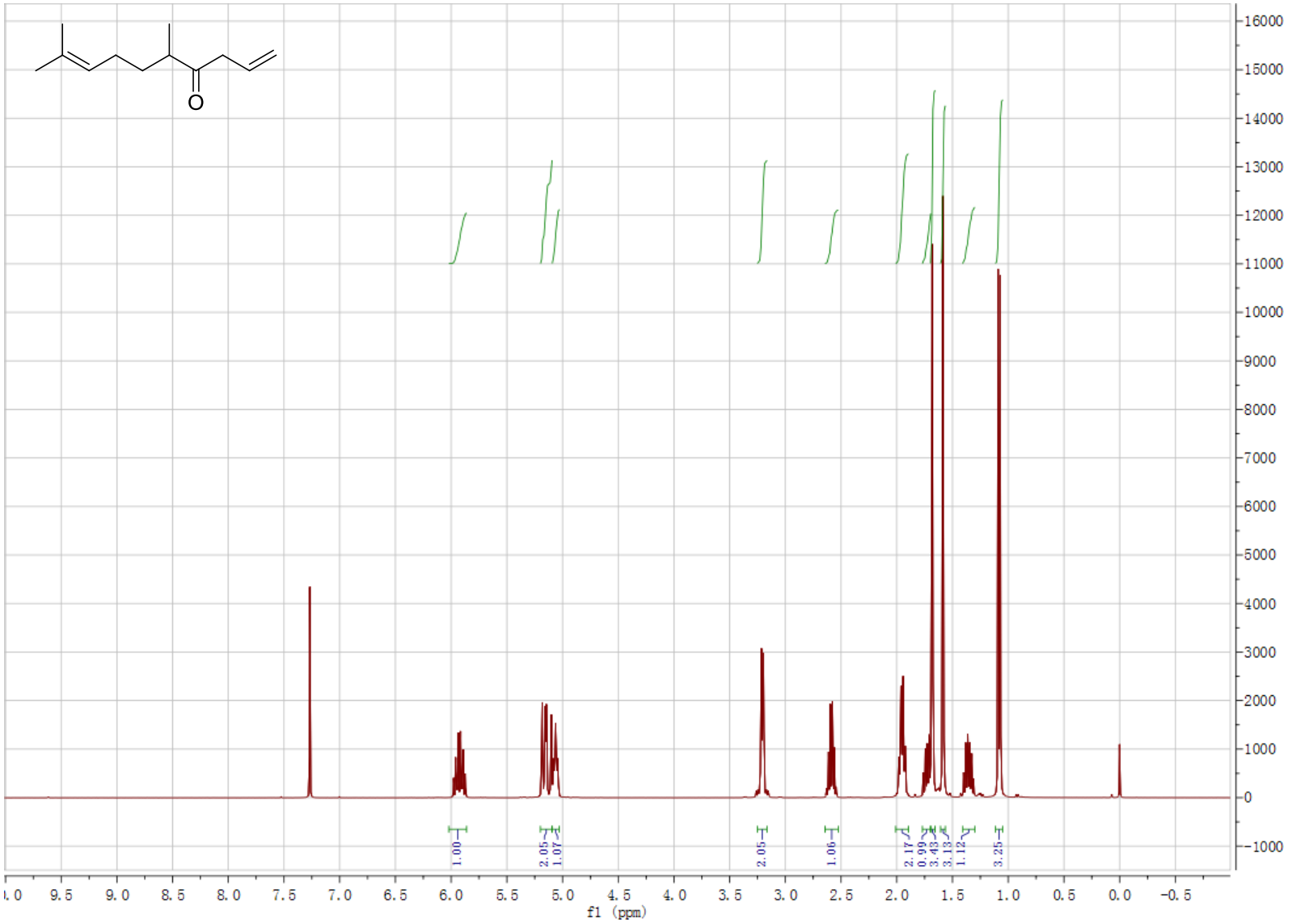

212.4
130.8
118.5
55.0
47.1
24.1
11.8
O
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

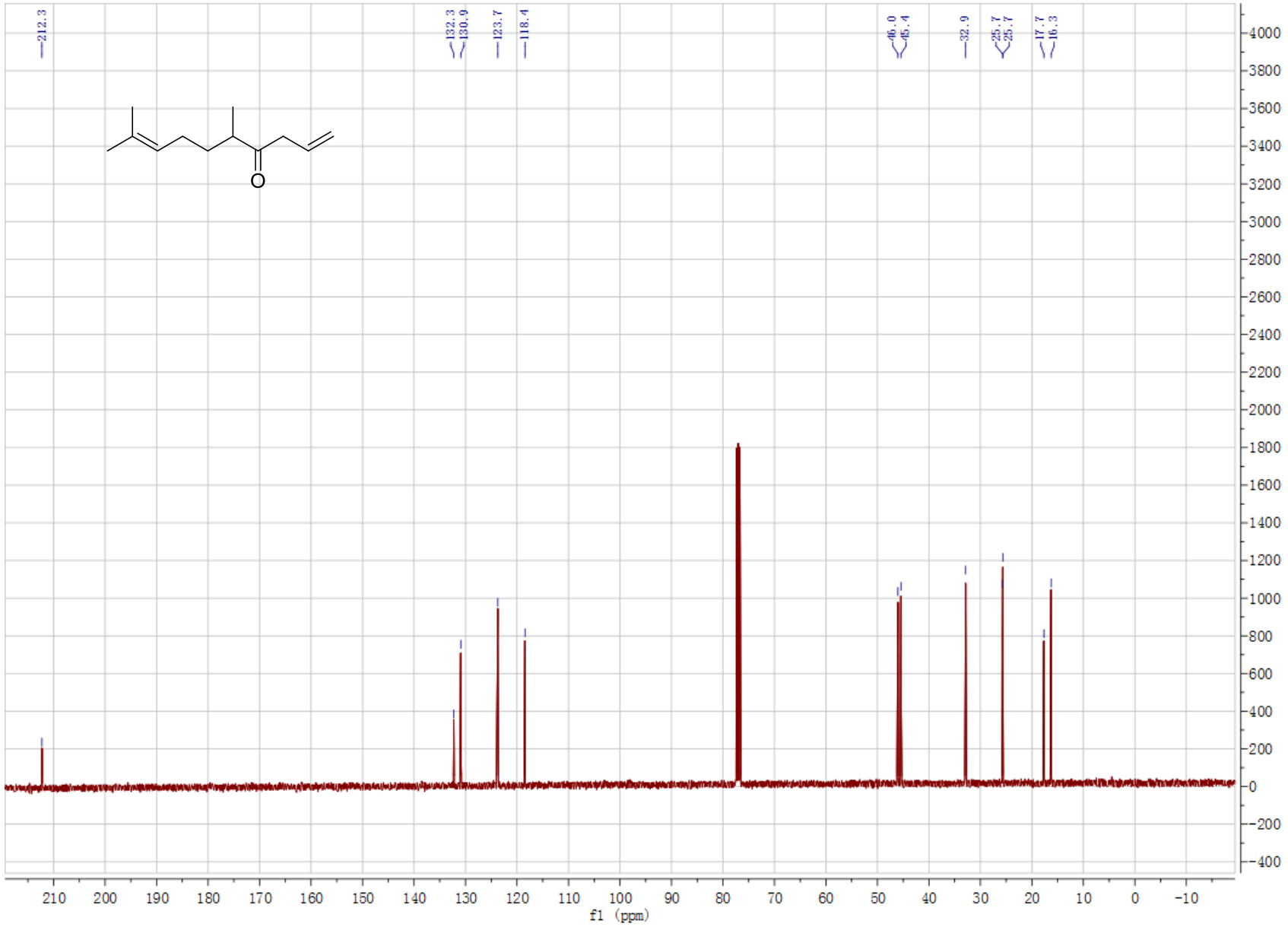
5-ethylnon-1-en-4-one (3g)



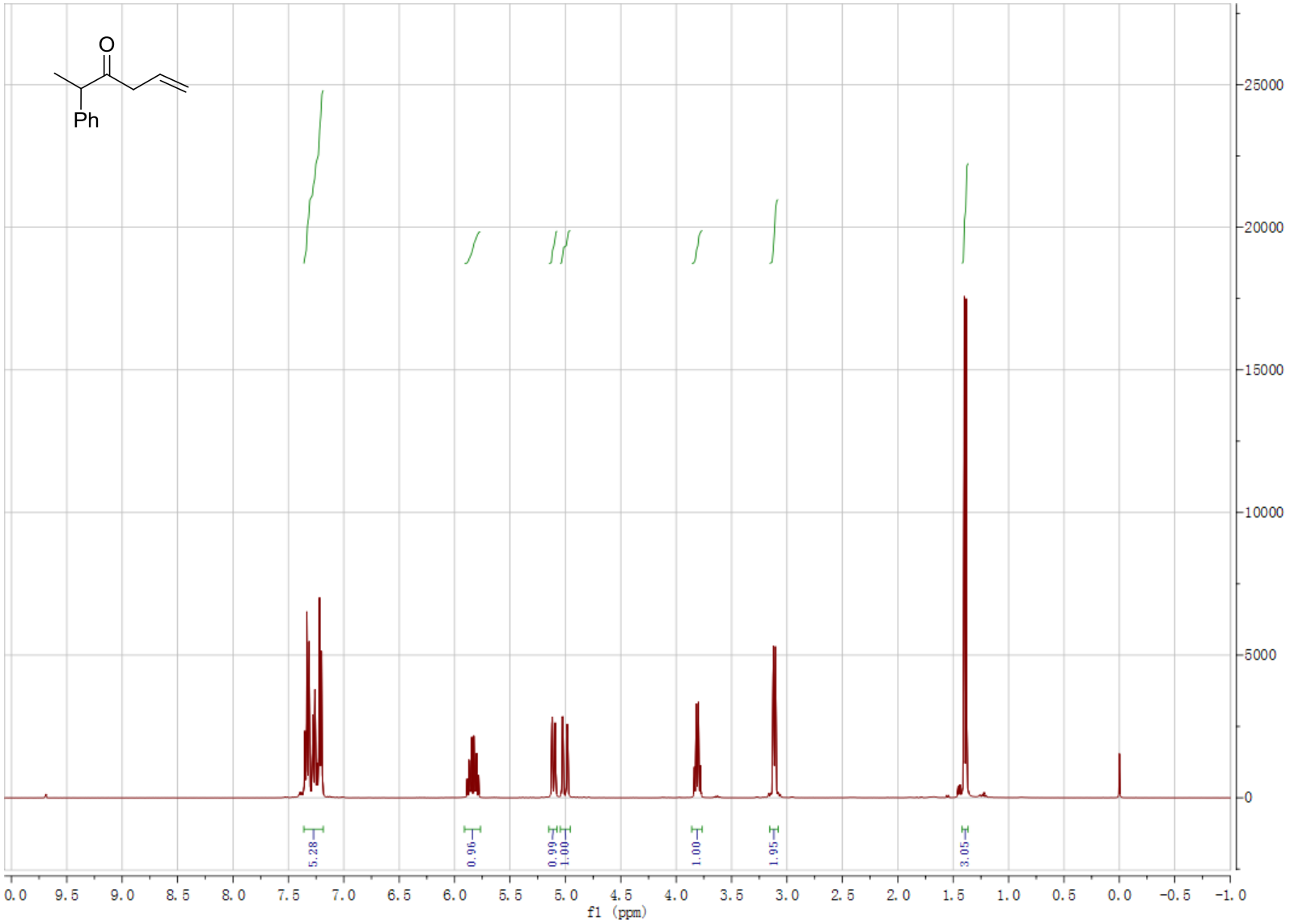

212.4
130.8
118.4
53.5
47.0
30.9
29.6
24.5
22.8
13.9
11.8
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

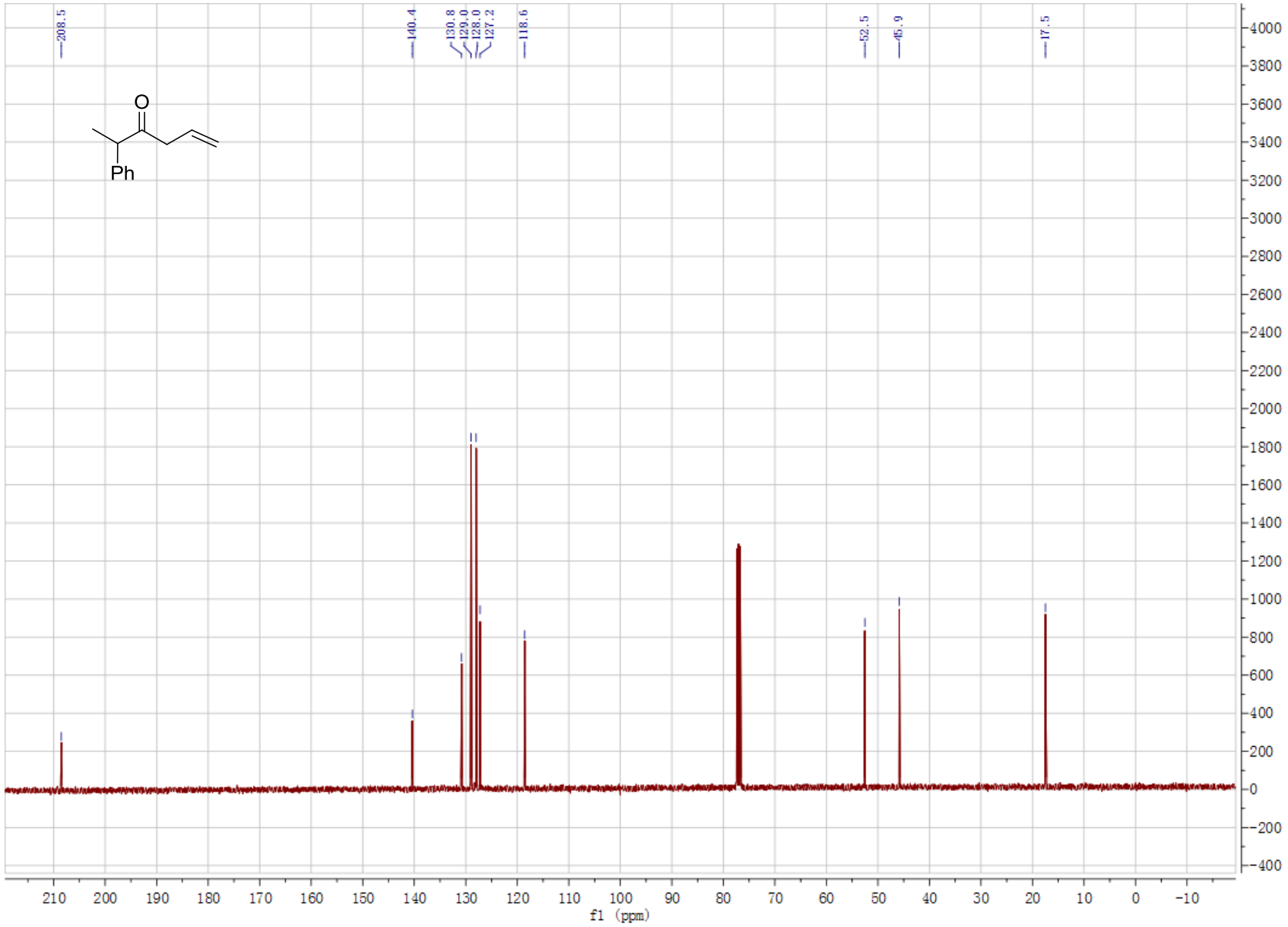
5,9-dimethyldeca-1,8-dien-4-one (3h)



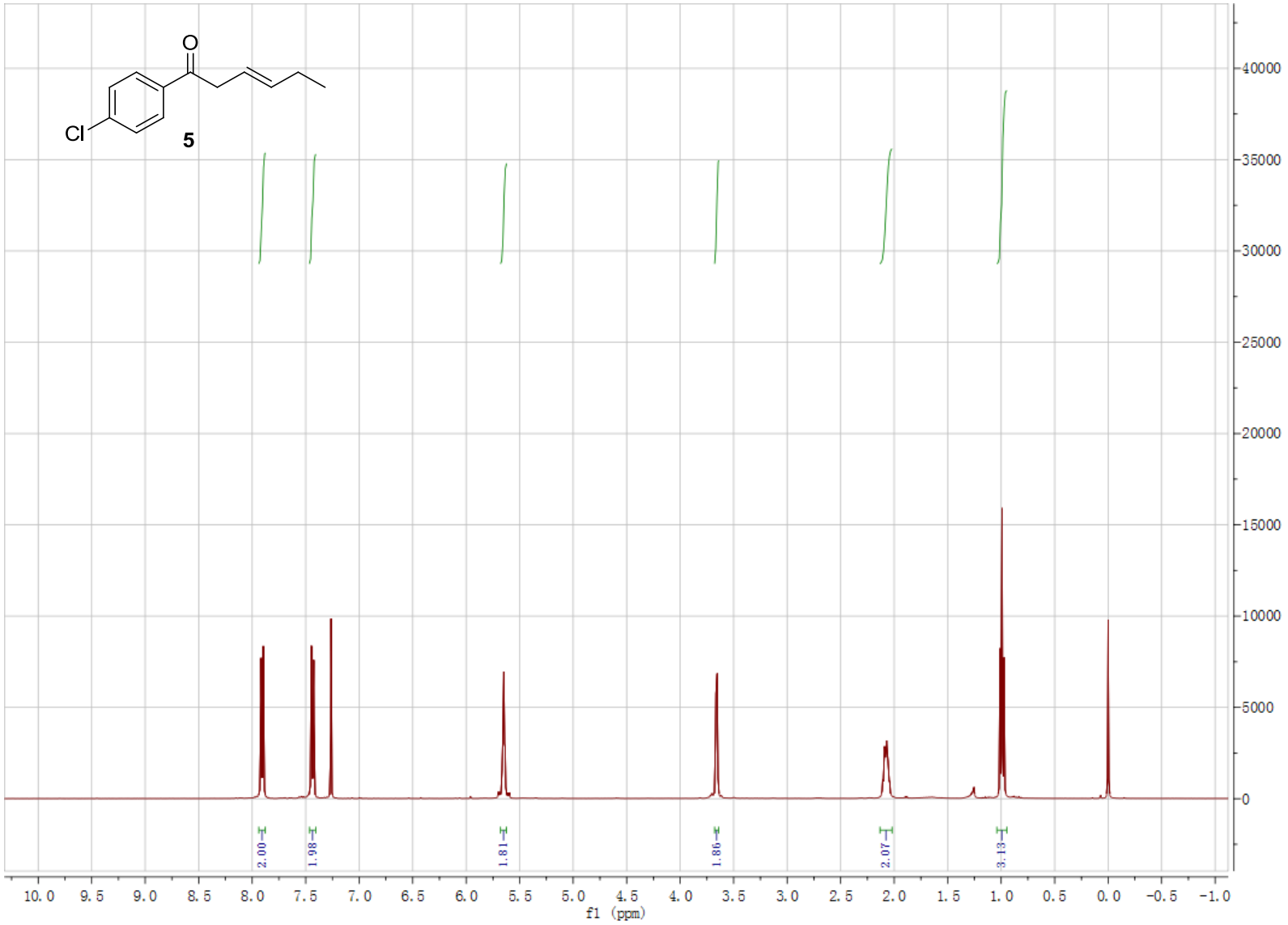

212.3
132.3
130.9
123.7
118.4
46.0
45.4
32.9
25.7
25.7
17.7
16.3
O
f1 (ppm)

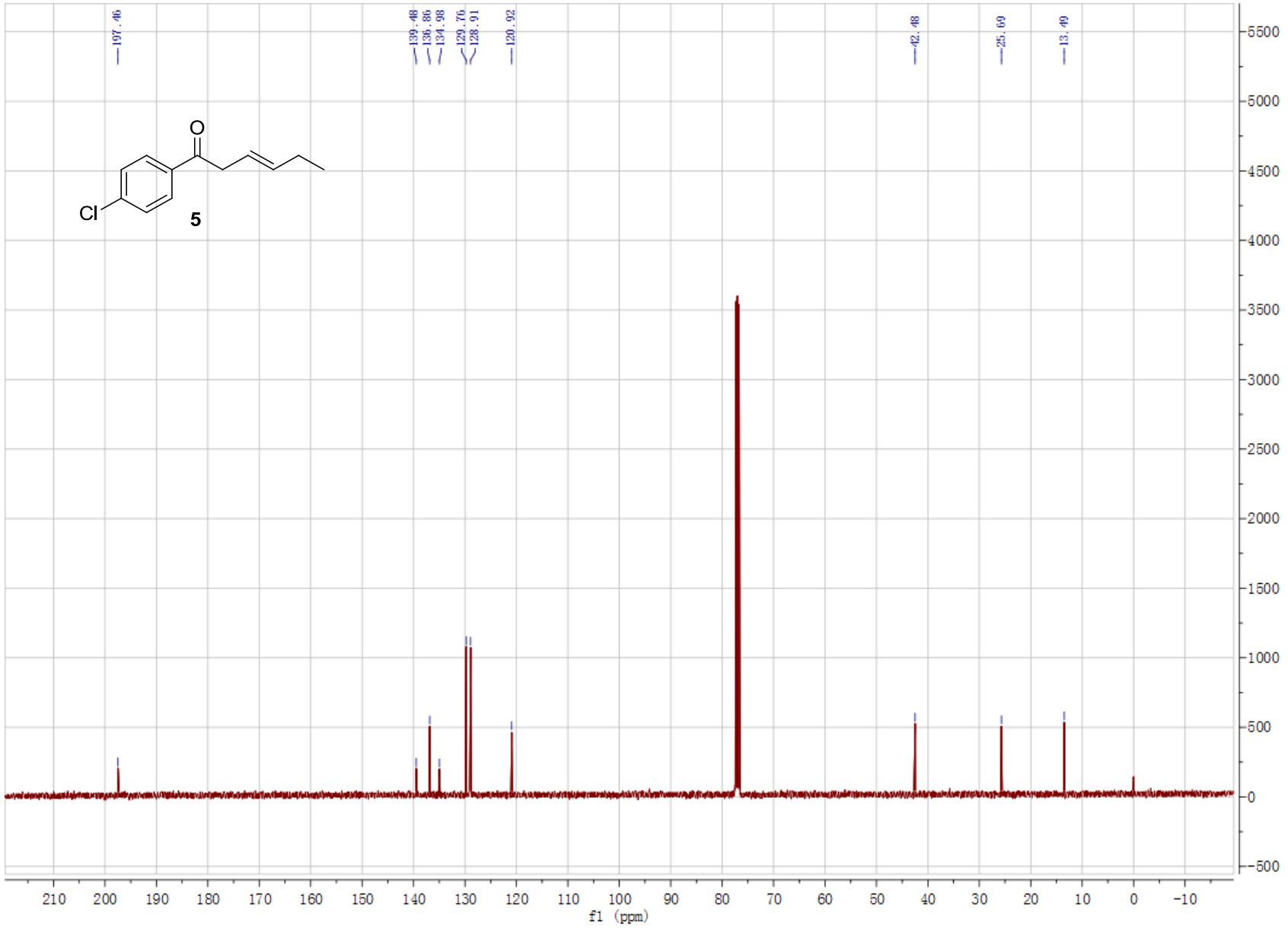
2-phenylhex-5-en-3-one (3i)



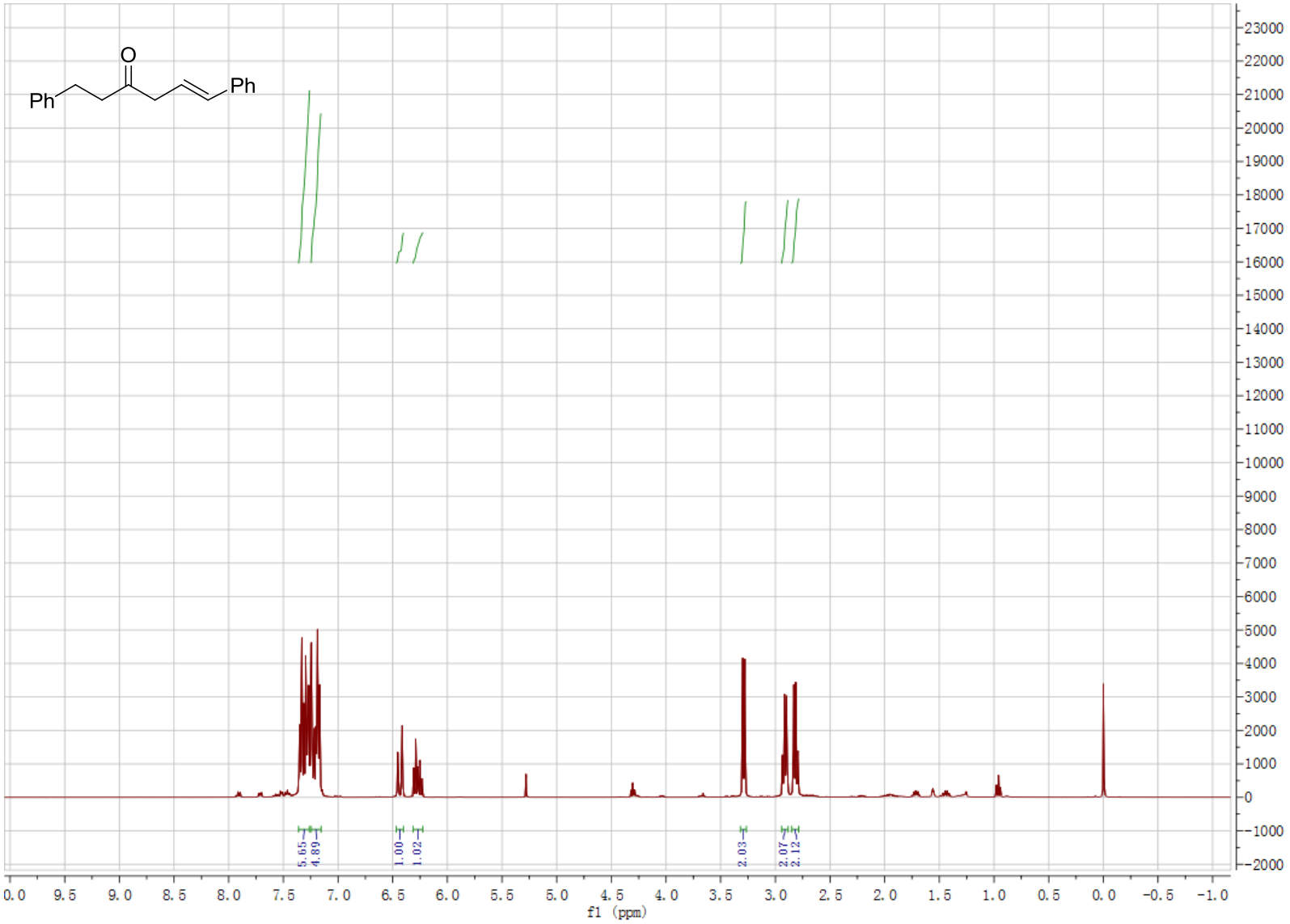

208.5
140.4
130.8
129.0
128.0
127.2
118.6
52.5
45.9
17.5
O
Ph
f1 (ppm)

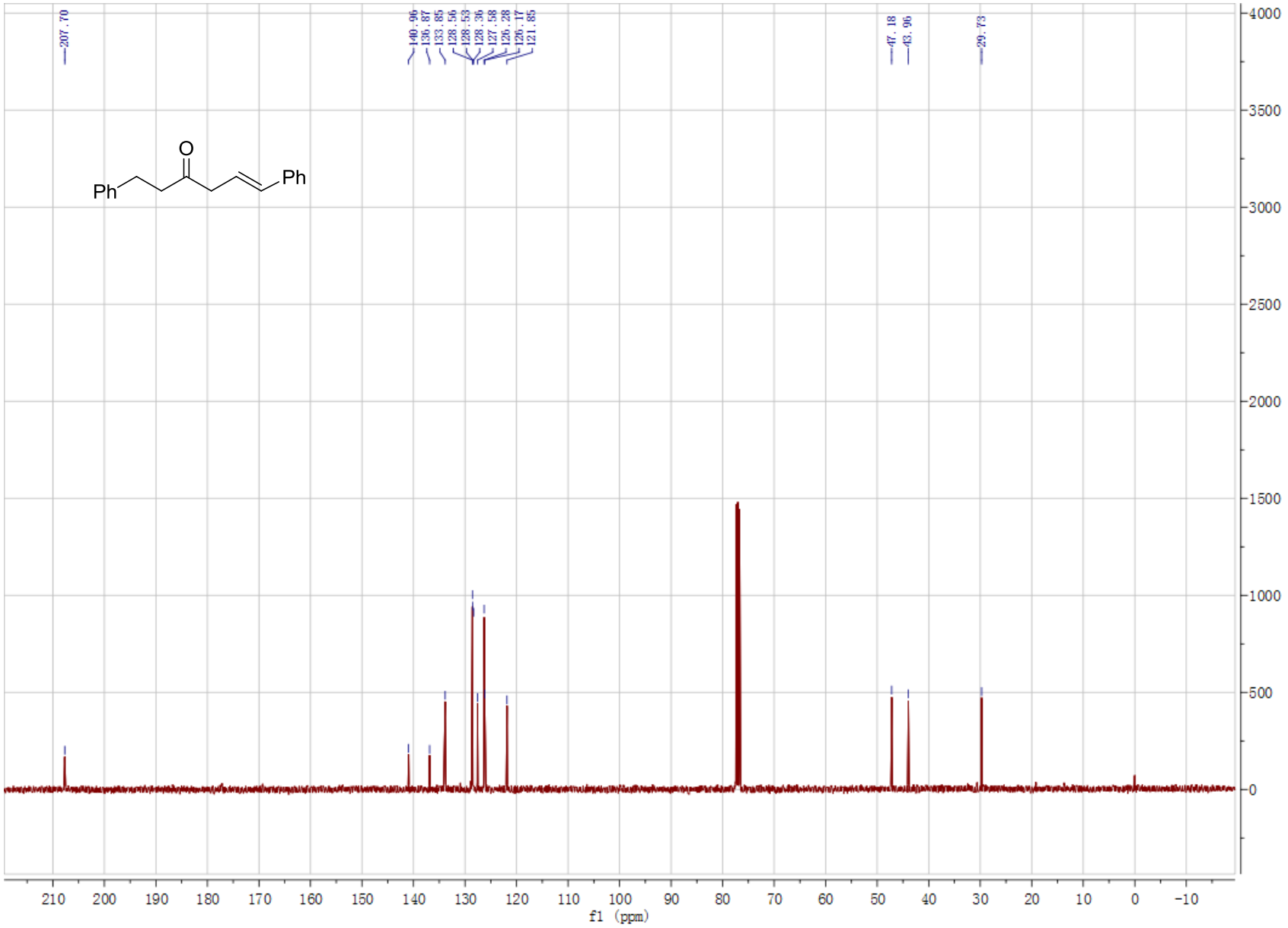
***(E)*-1-(4-chlorophenyl)hex-3-en-1-one (5)**



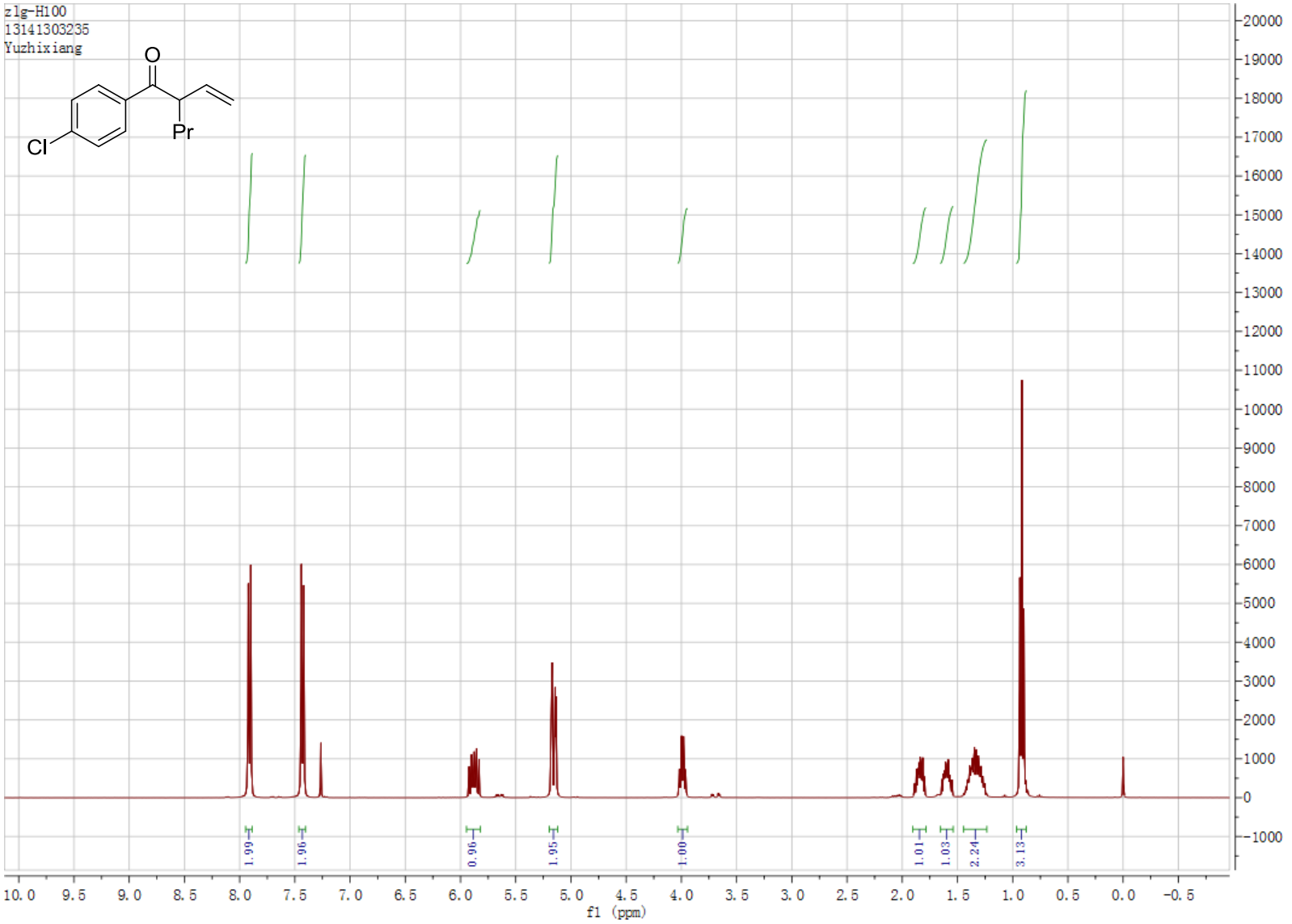

197.46
139.48
136.86
134.98
129.76
128.91
120.92
42.48
25.69
13.49
O
Cl
5
f1 (ppm)

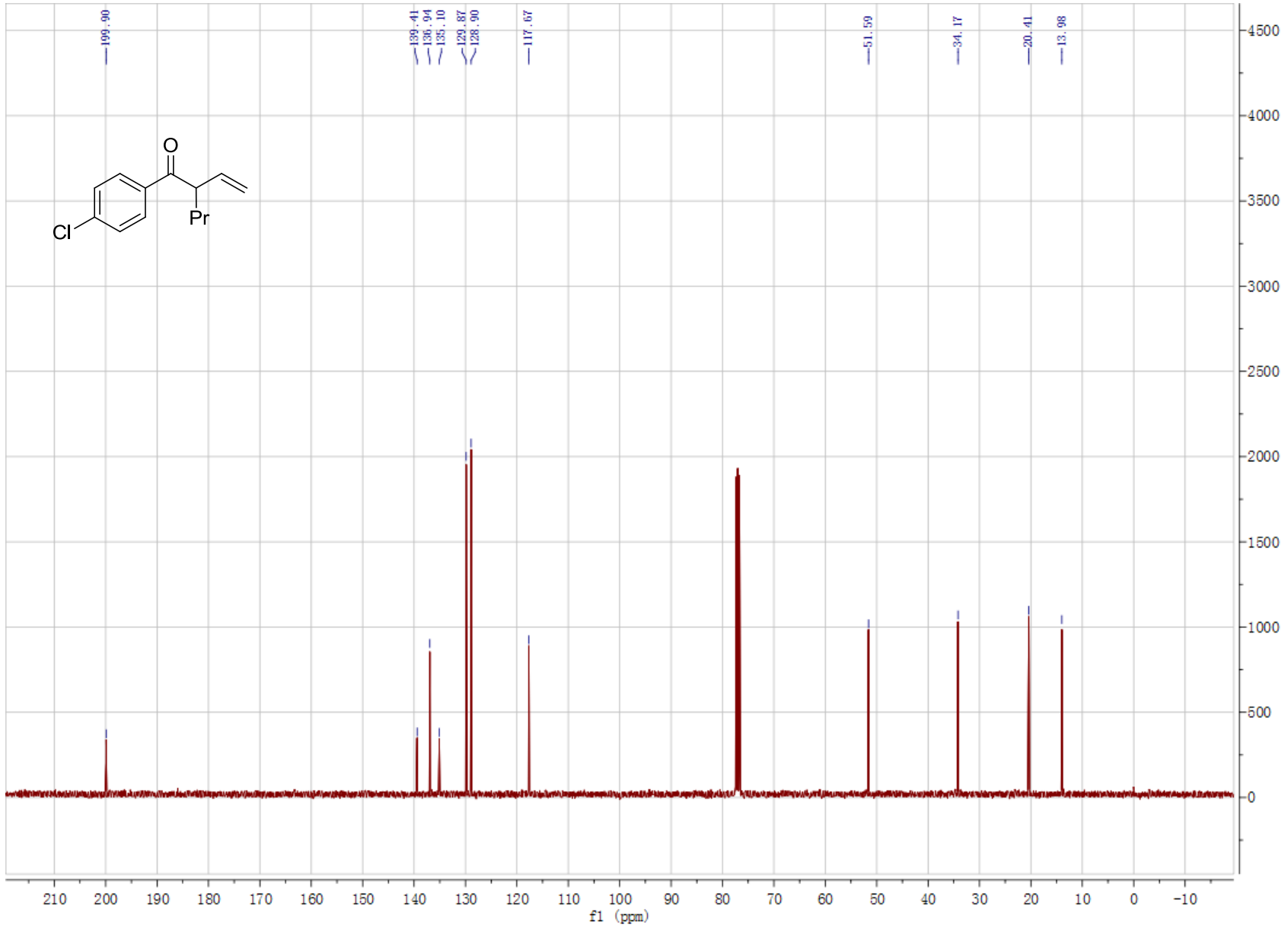
***(E)*-1,6-diphenylhex-5-en-3-one (6)**



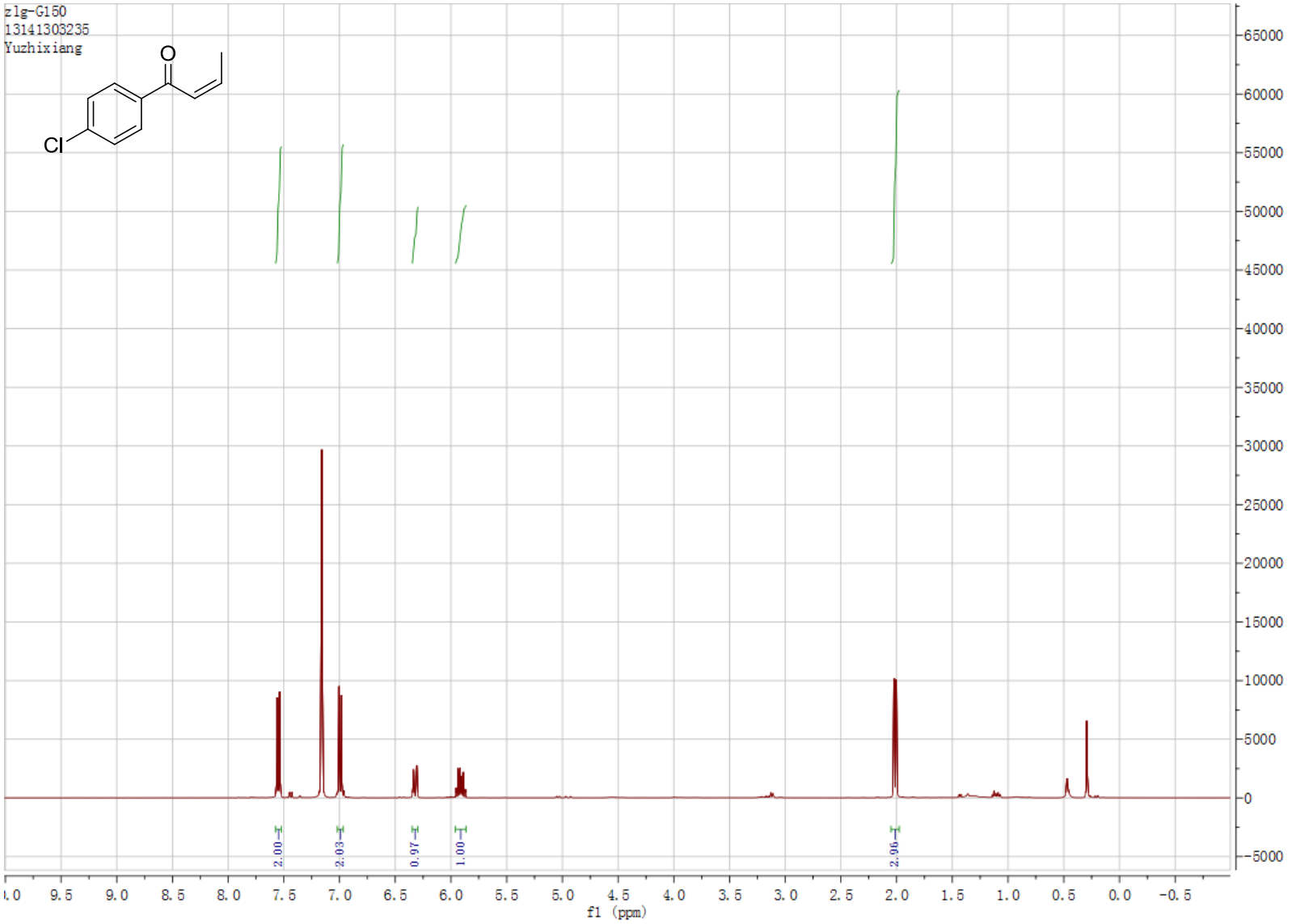

207.70
140.96
136.87
133.85
128.56
128.53
128.36
127.58
126.28
126.17
121.85
47.18
43.96
29.73
O
Ph
Ph
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

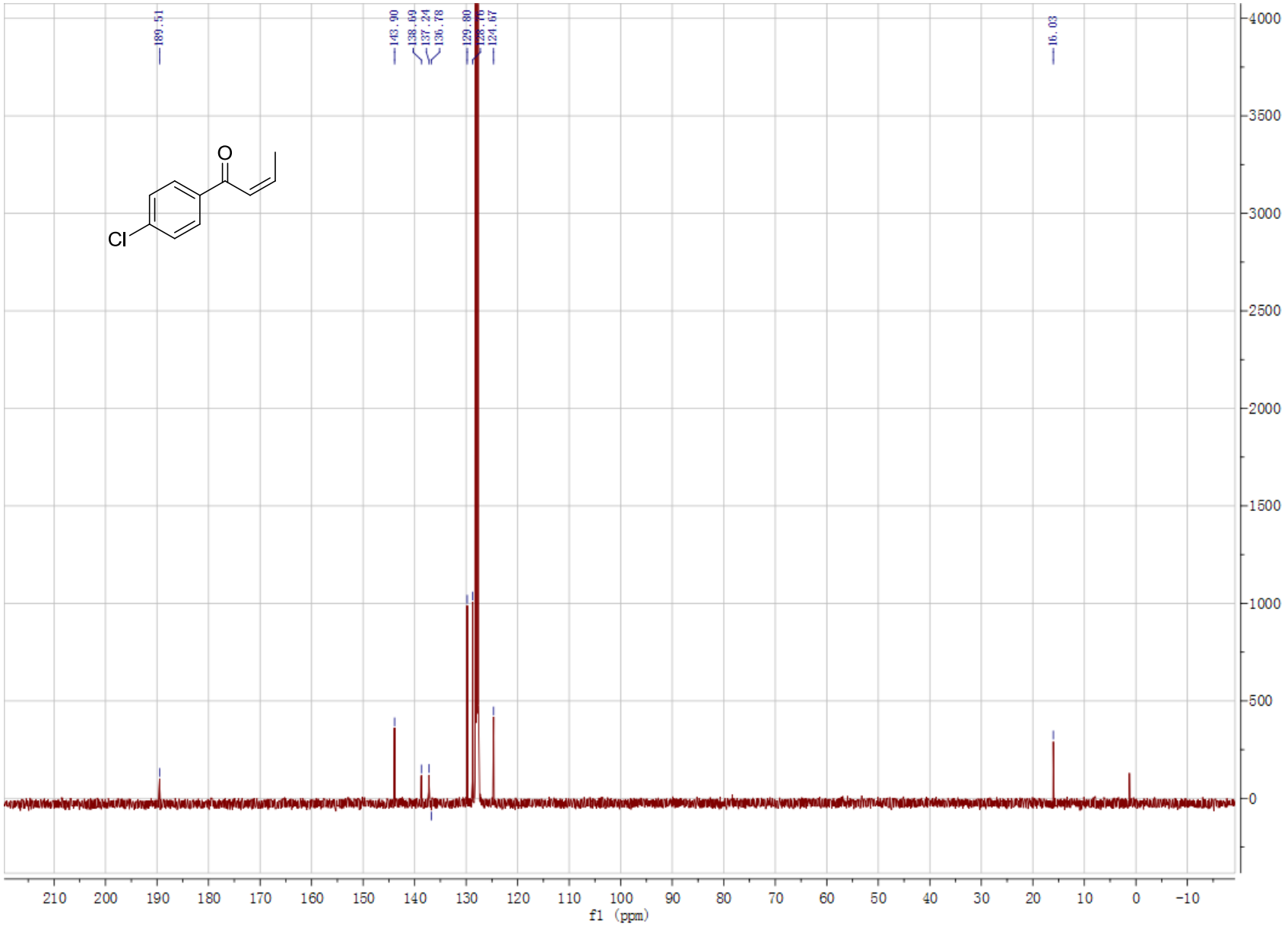
1-(4-chlorophenyl)-2-vinylpentan-1-one (7)



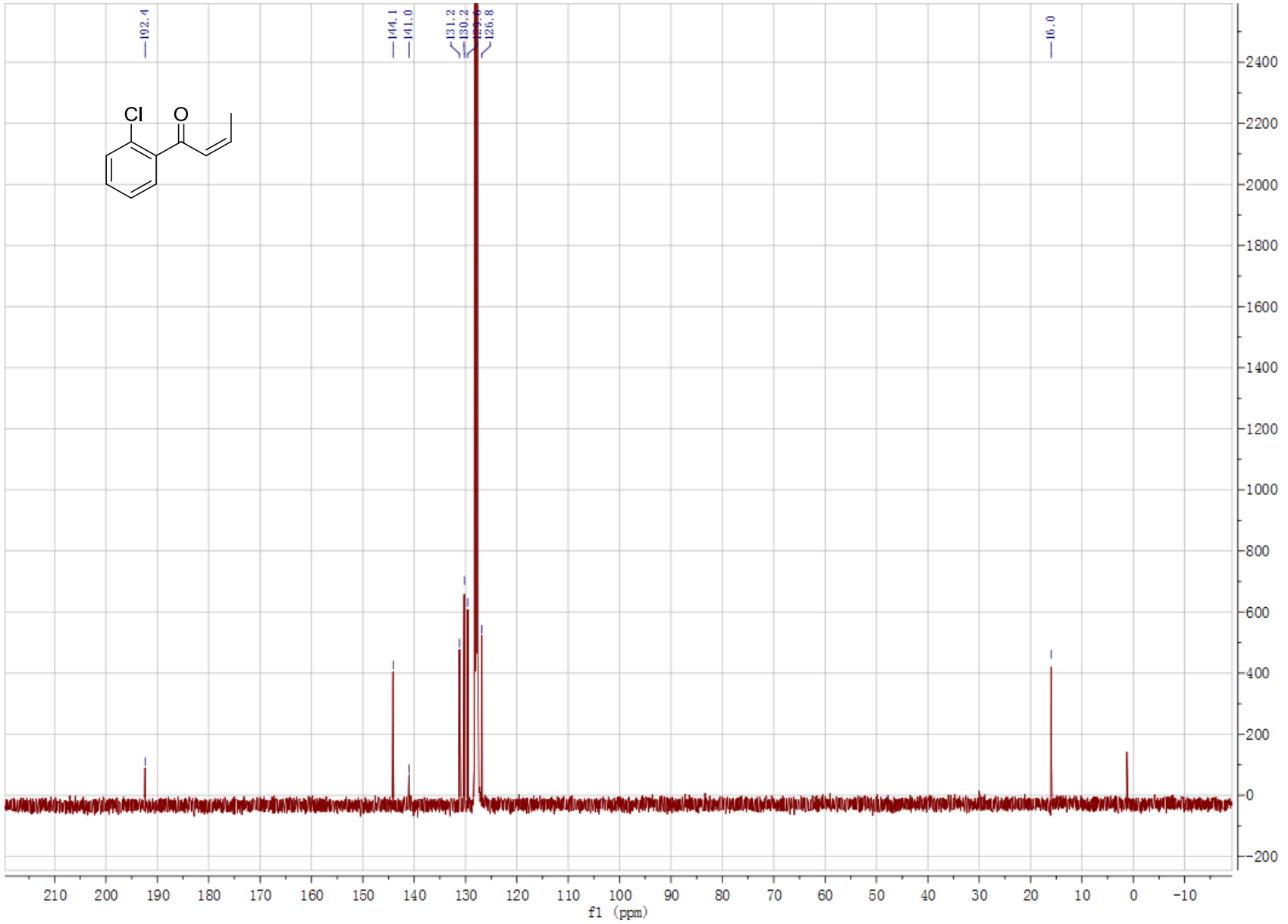

199.90
139.41
136.94
135.10
129.87
128.90
117.67
51.59
34.17
20.41
13.98
O
Cl
Pr
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

(*Z*)-1-(4-chlorophenyl)but-2-en-1-one (2b-*Z*)

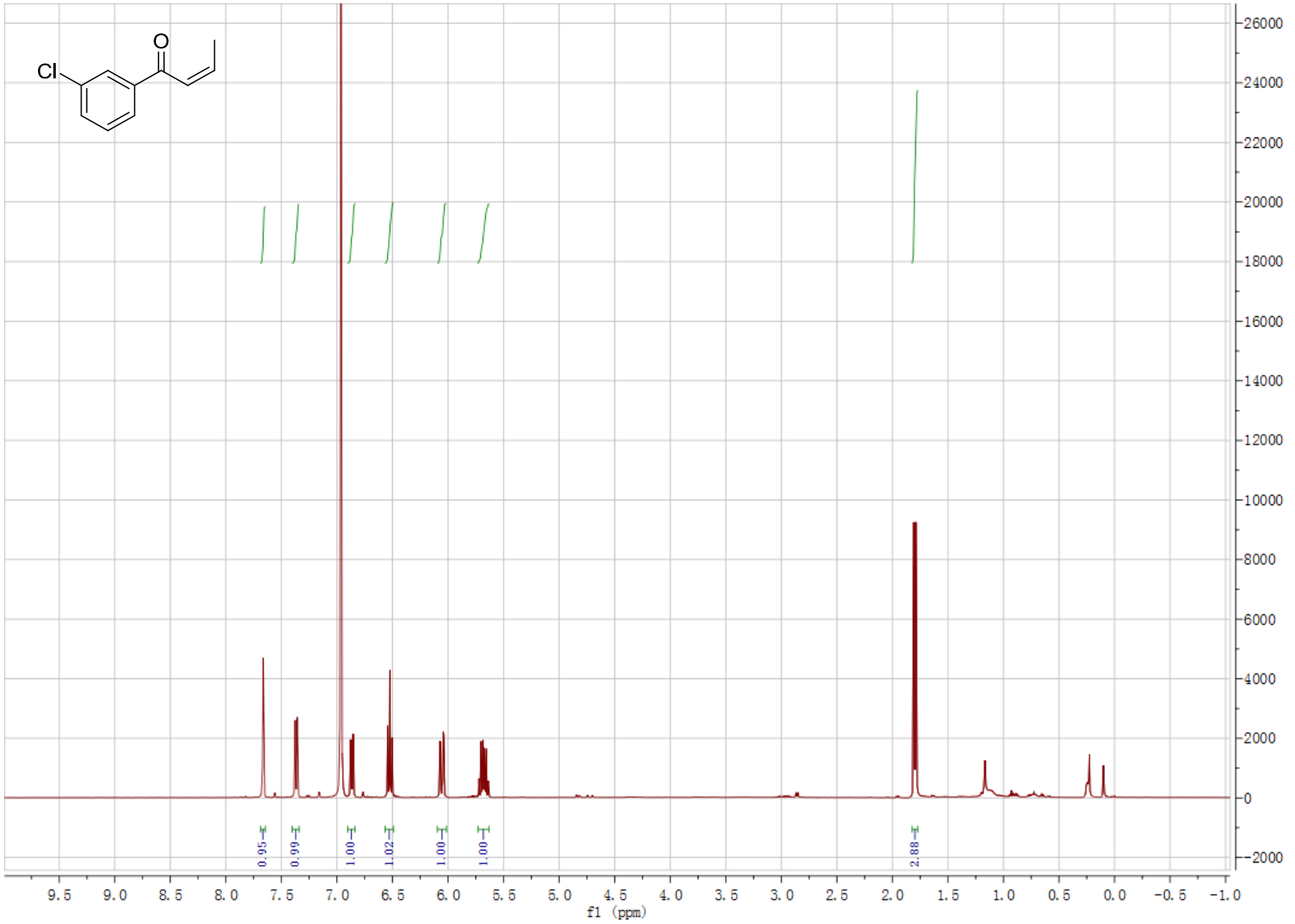


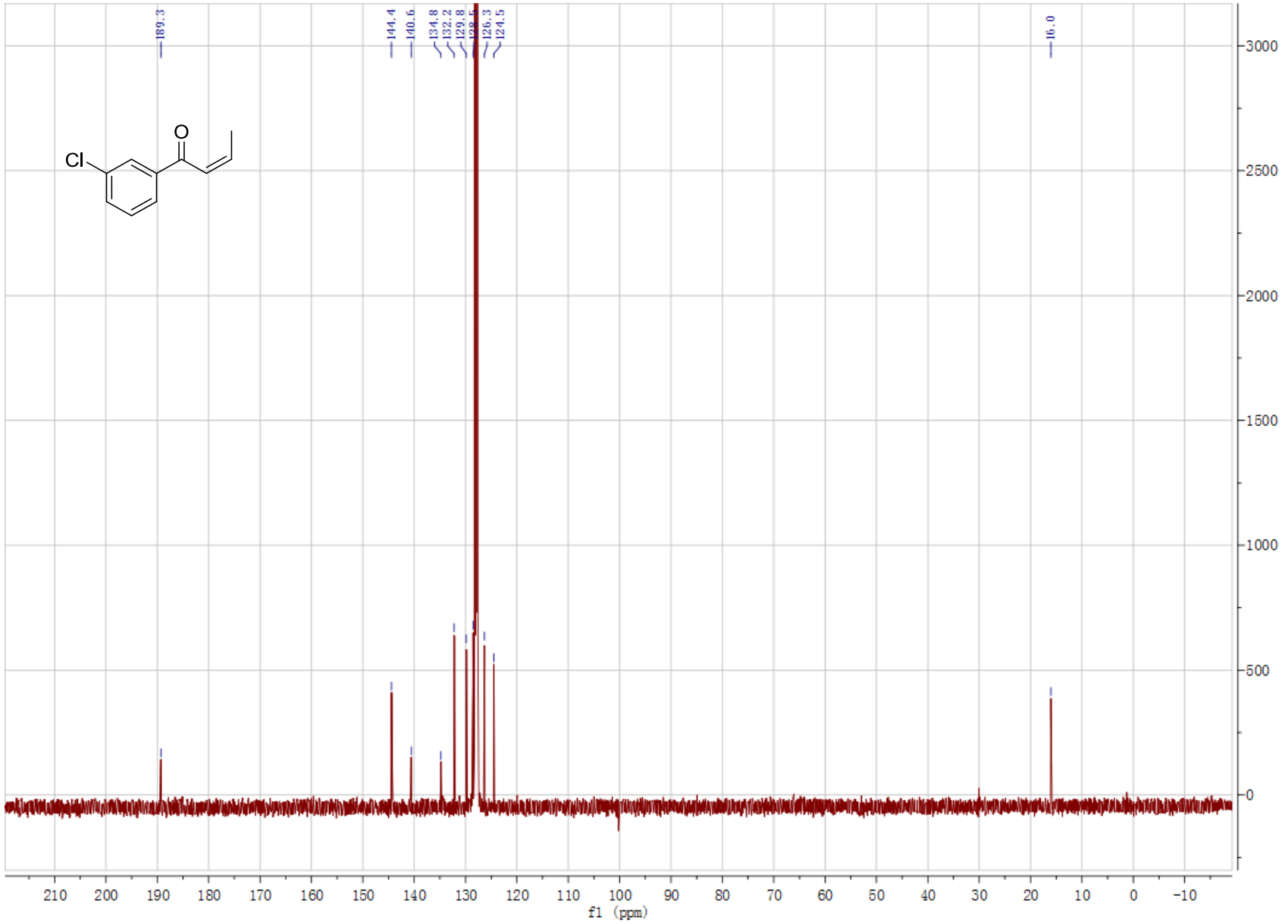

189.51
143.90
138.69
137.24
136.78
129.80
128.16
124.67
16.03
O
Cl
4000
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

***(Z)*-1-(2-chlorophenyl)but-2-en-1-one (2c-*Z*)**

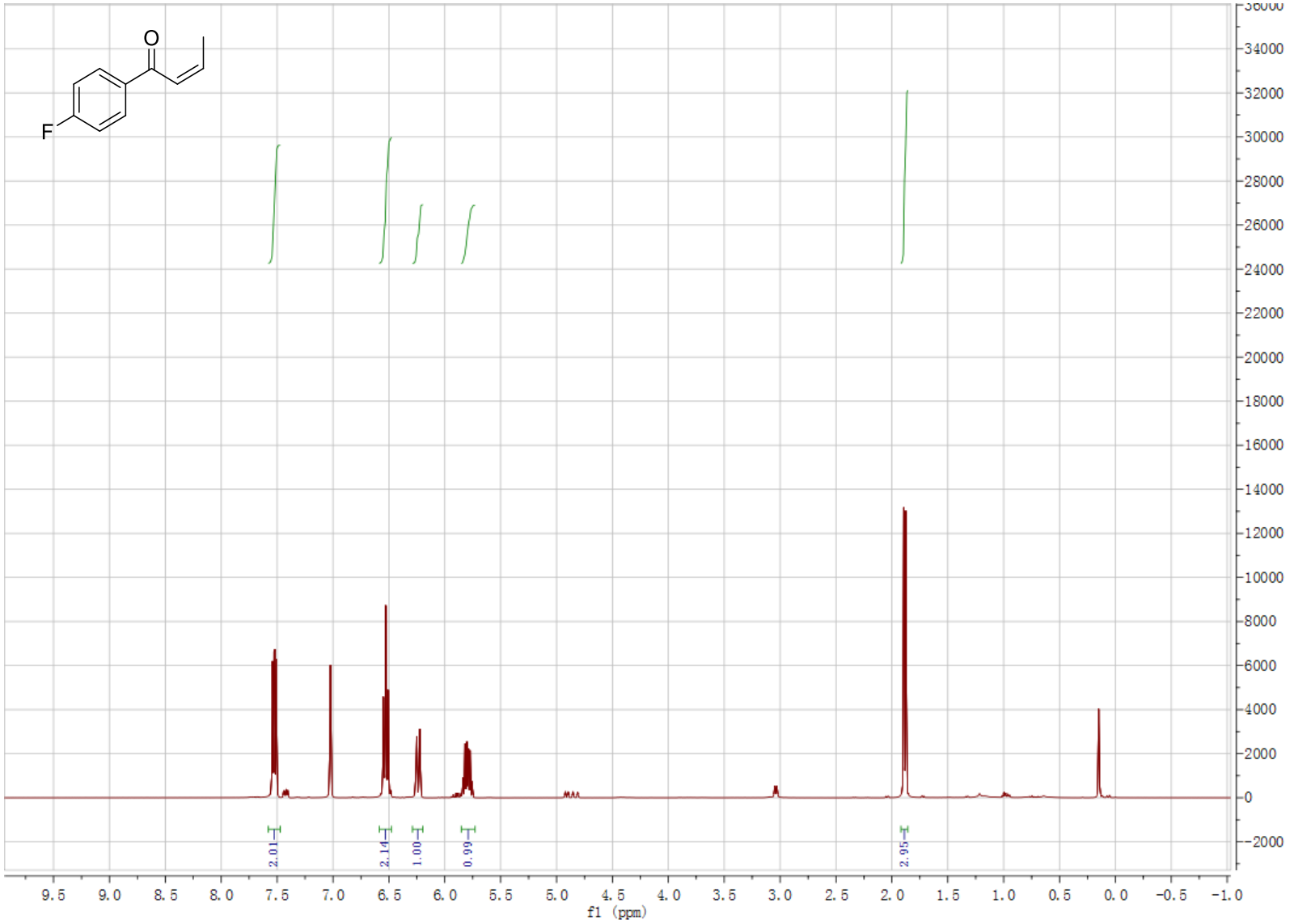

192.4
144.1
141.0
131.2
130.2
129.6
126.8
16.0
Cl
O
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

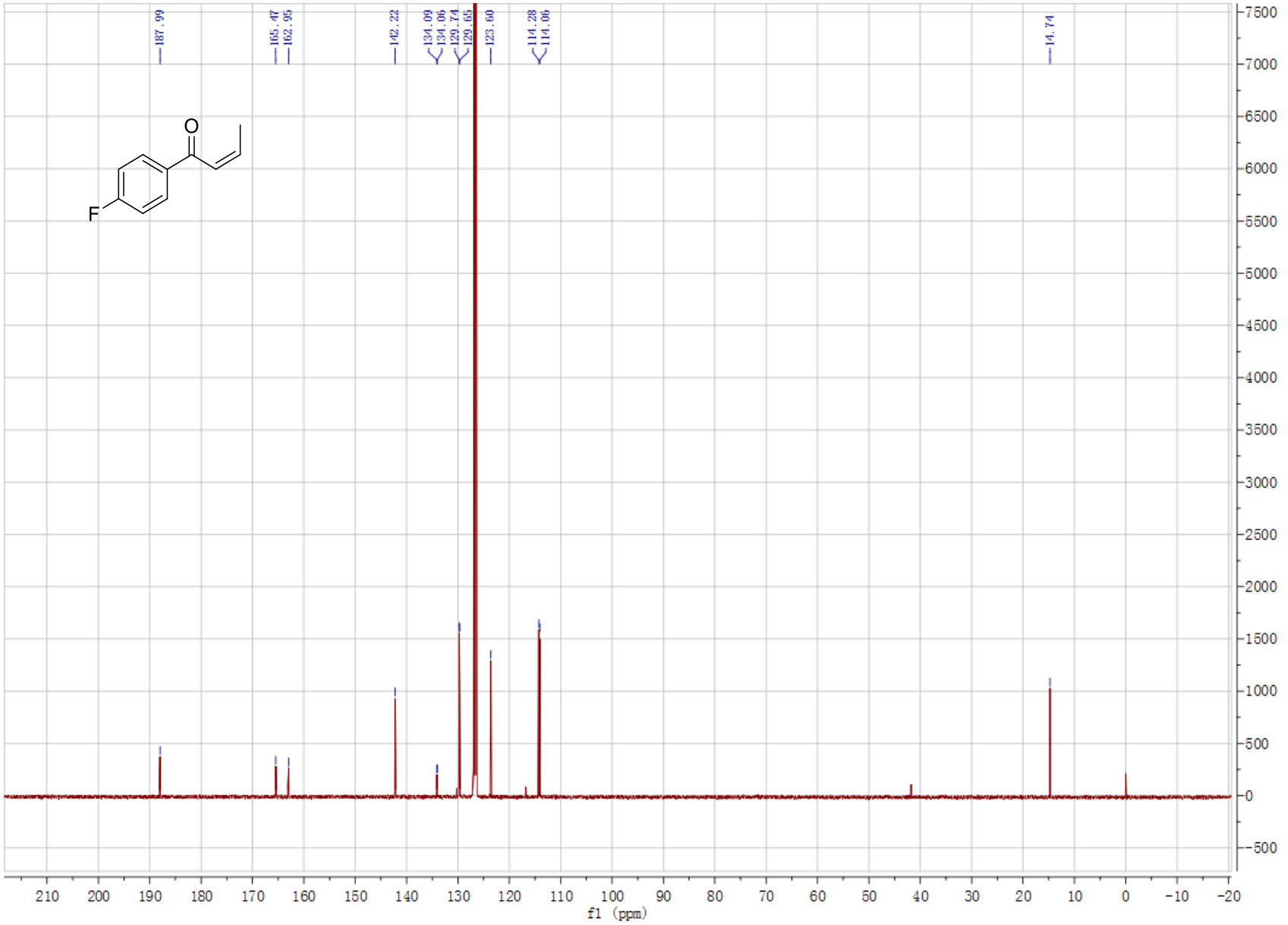
(*Z*)-1-(3-chlorophenyl)but-2-en-1-one (2d-*Z*)



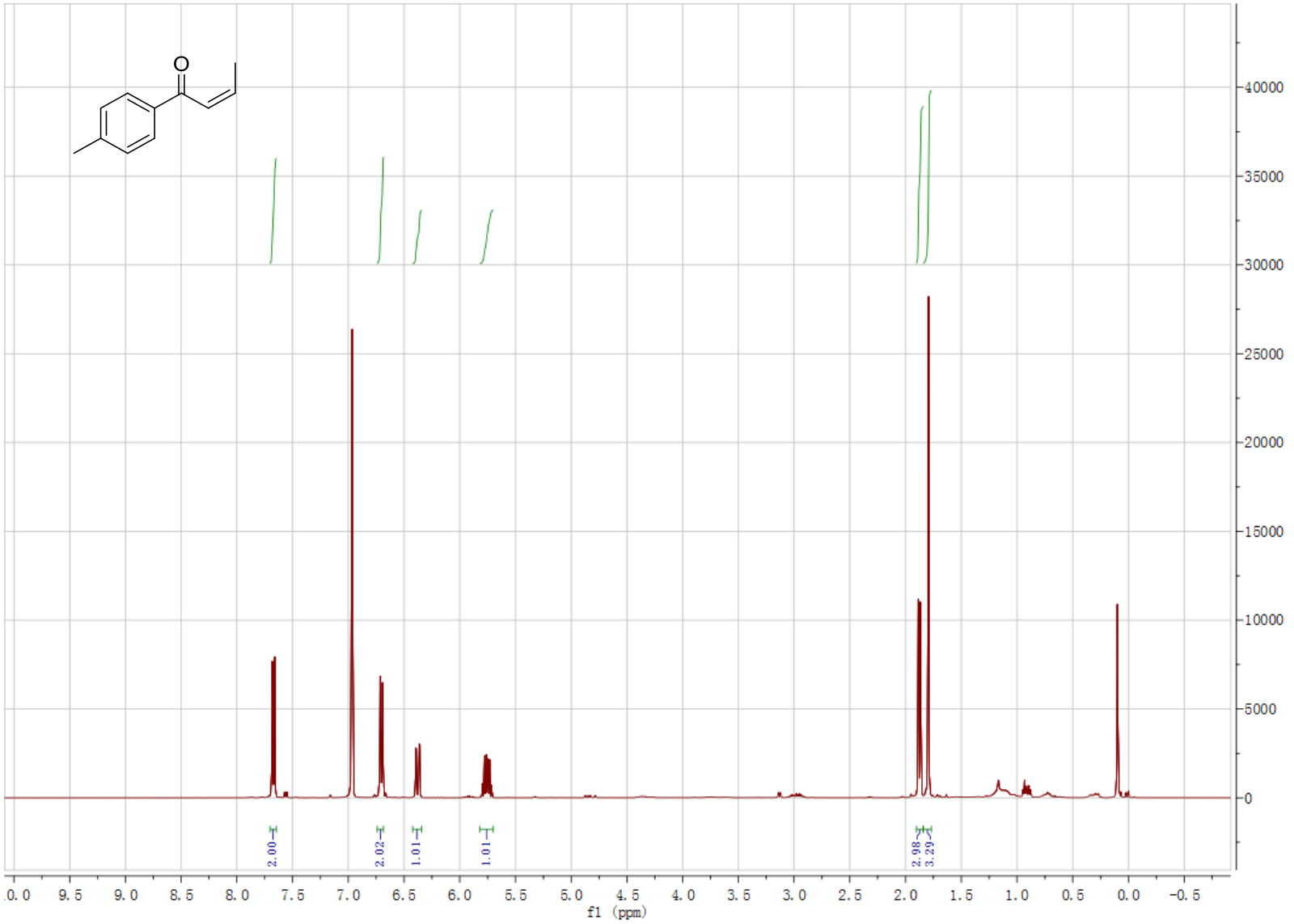

189.3
144.4
140.6
134.8
132.2
129.8
128.5
126.3
124.5
16.0
Cl
O
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

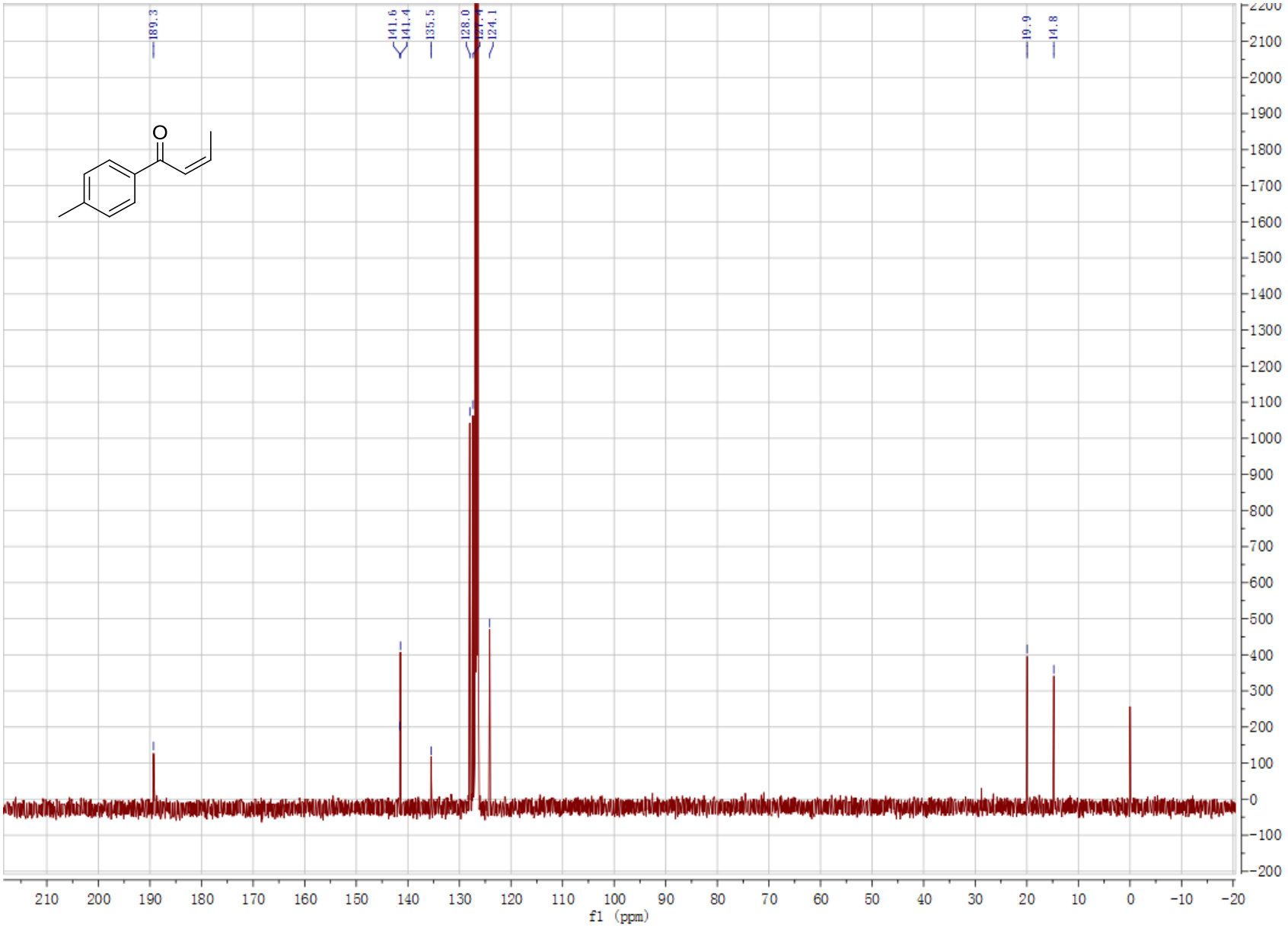
***(Z)*-1-(4-fluorophenyl)but-2-en-1-one (2e-*Z*)**



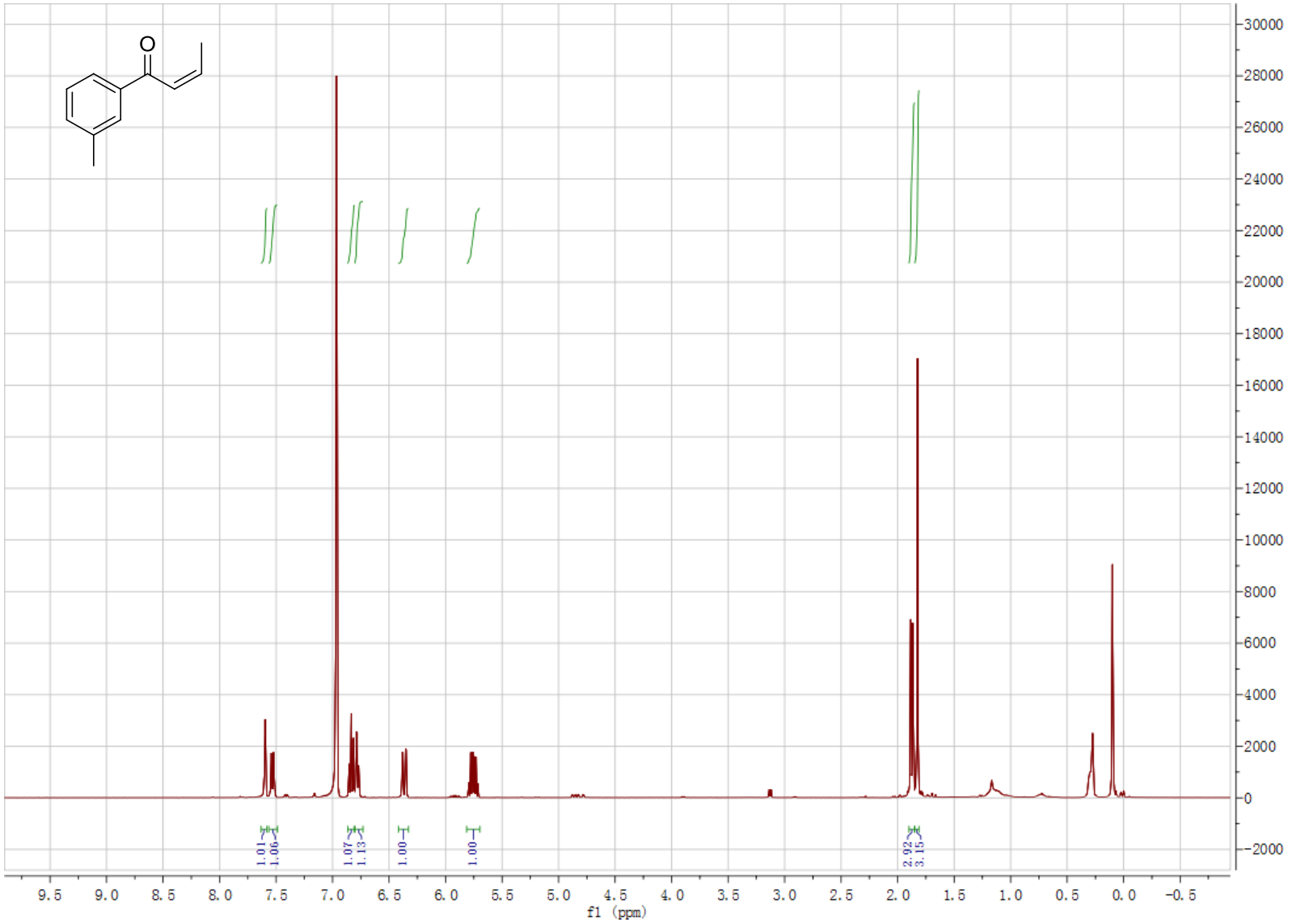

187.99
165.47
162.95
142.22
134.09
134.06
129.74
129.65
123.60
114.28
114.06
14.74
O
F
f1 (ppm)

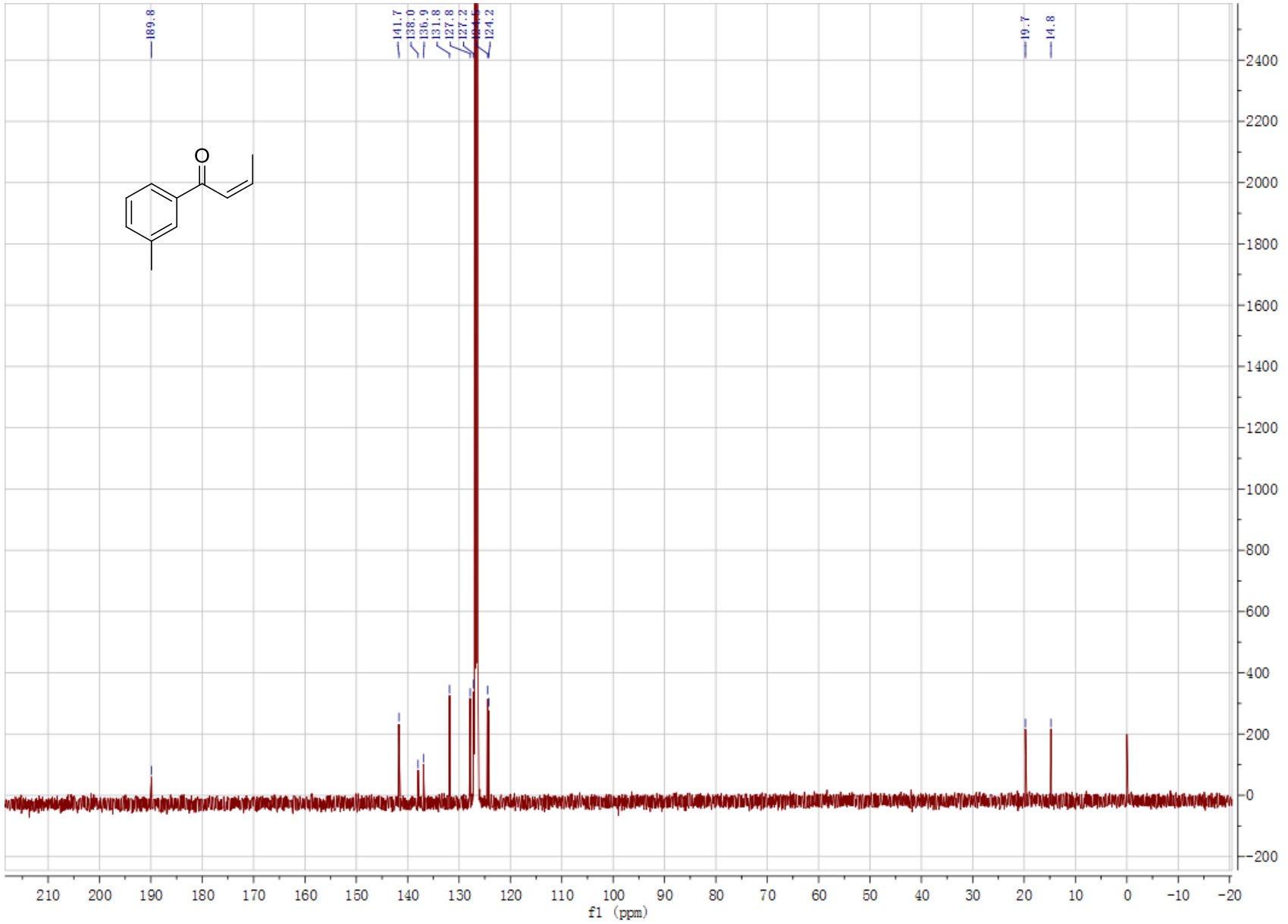
***(Z)*-1-p-tolylbut-2-en-1-one (2f-*Z*)**



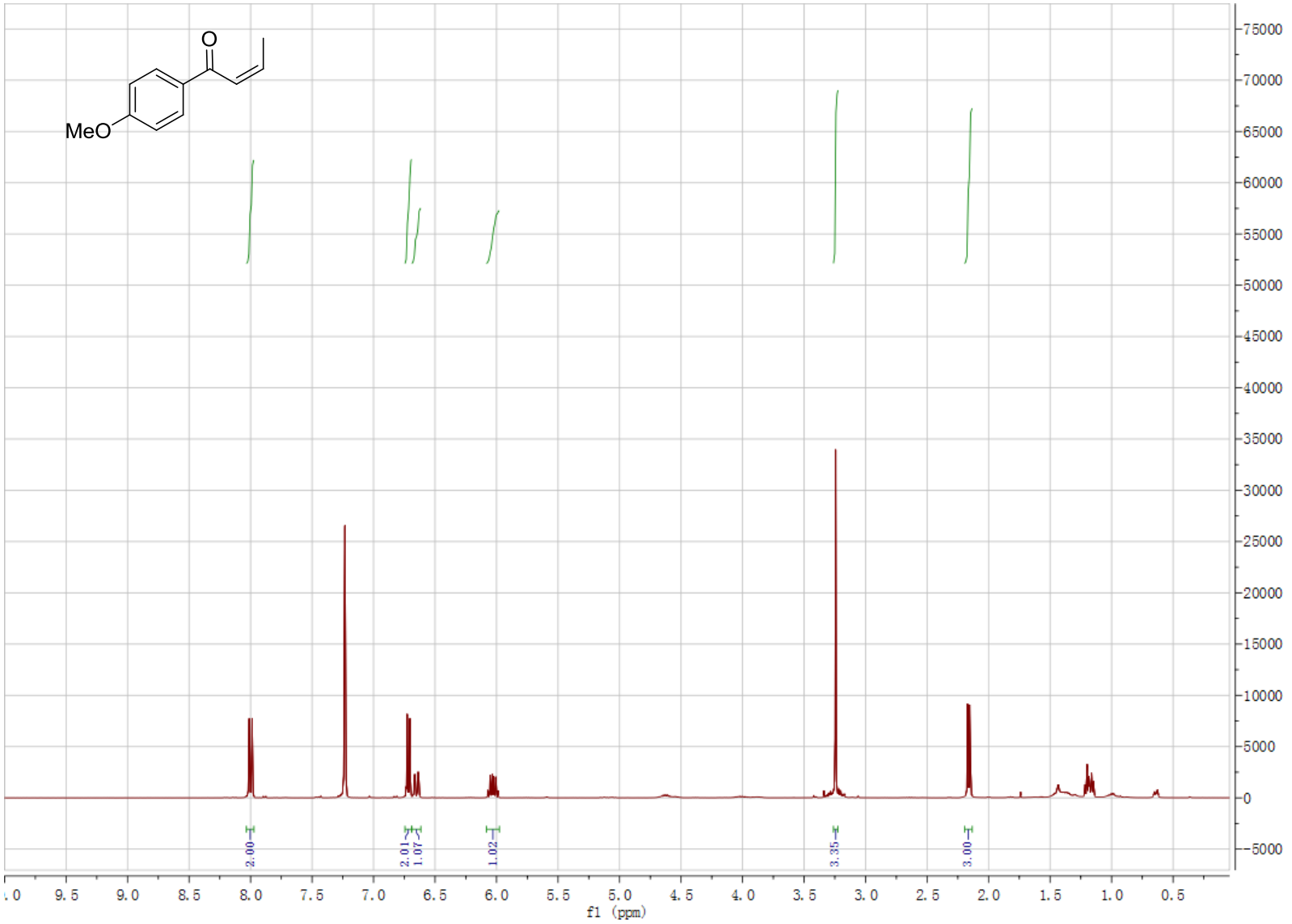

189.3
141.6
141.4
135.5
128.0
124.1
19.9
14.8
O
f1 (ppm)

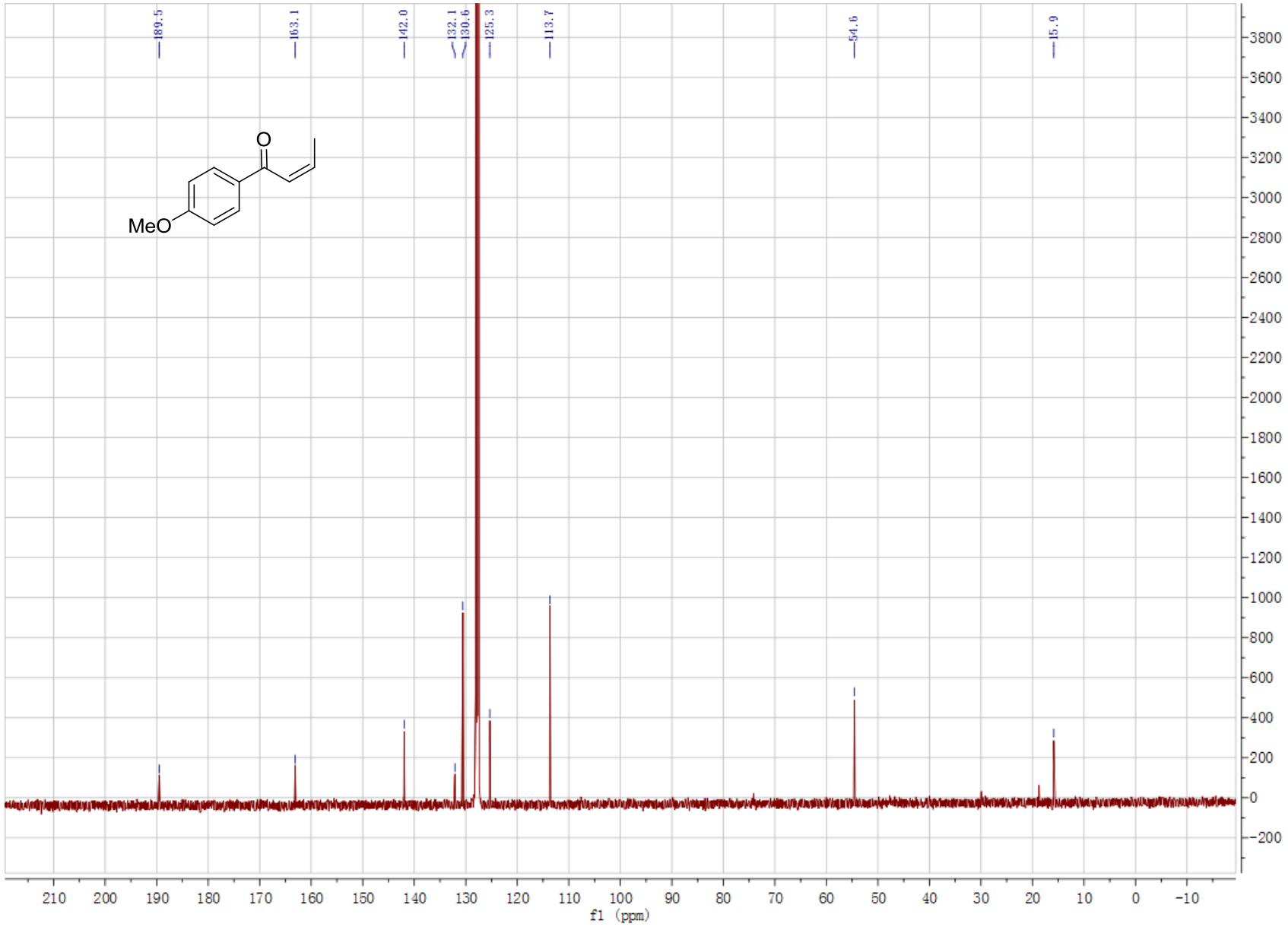
***(Z)*-1-m-tolylbut-2-en-1-one(2g-*Z*)**



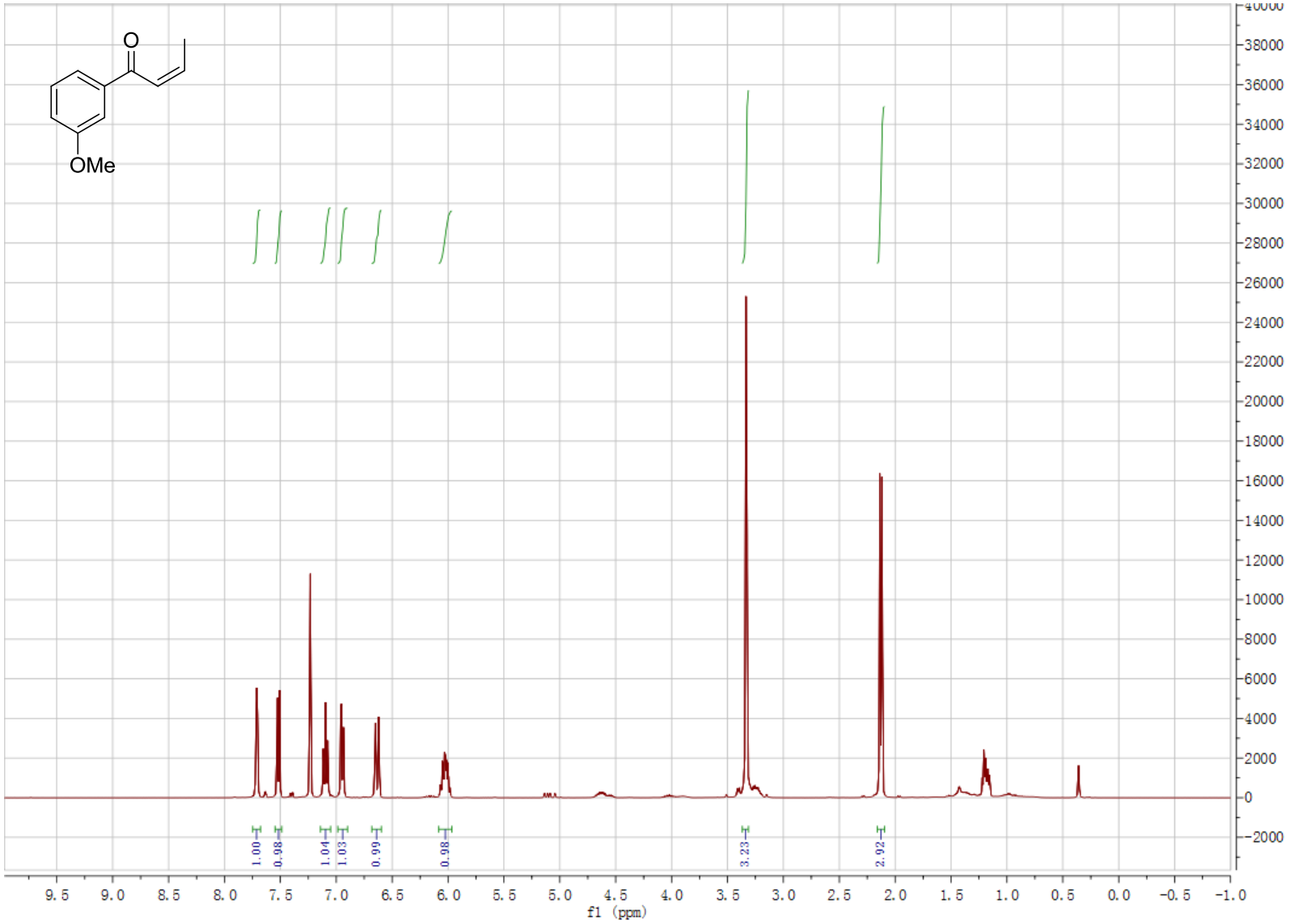

189.8
141.7
138.0
136.9
131.8
127.8
127.2
124.2
19.7
14.8
O
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

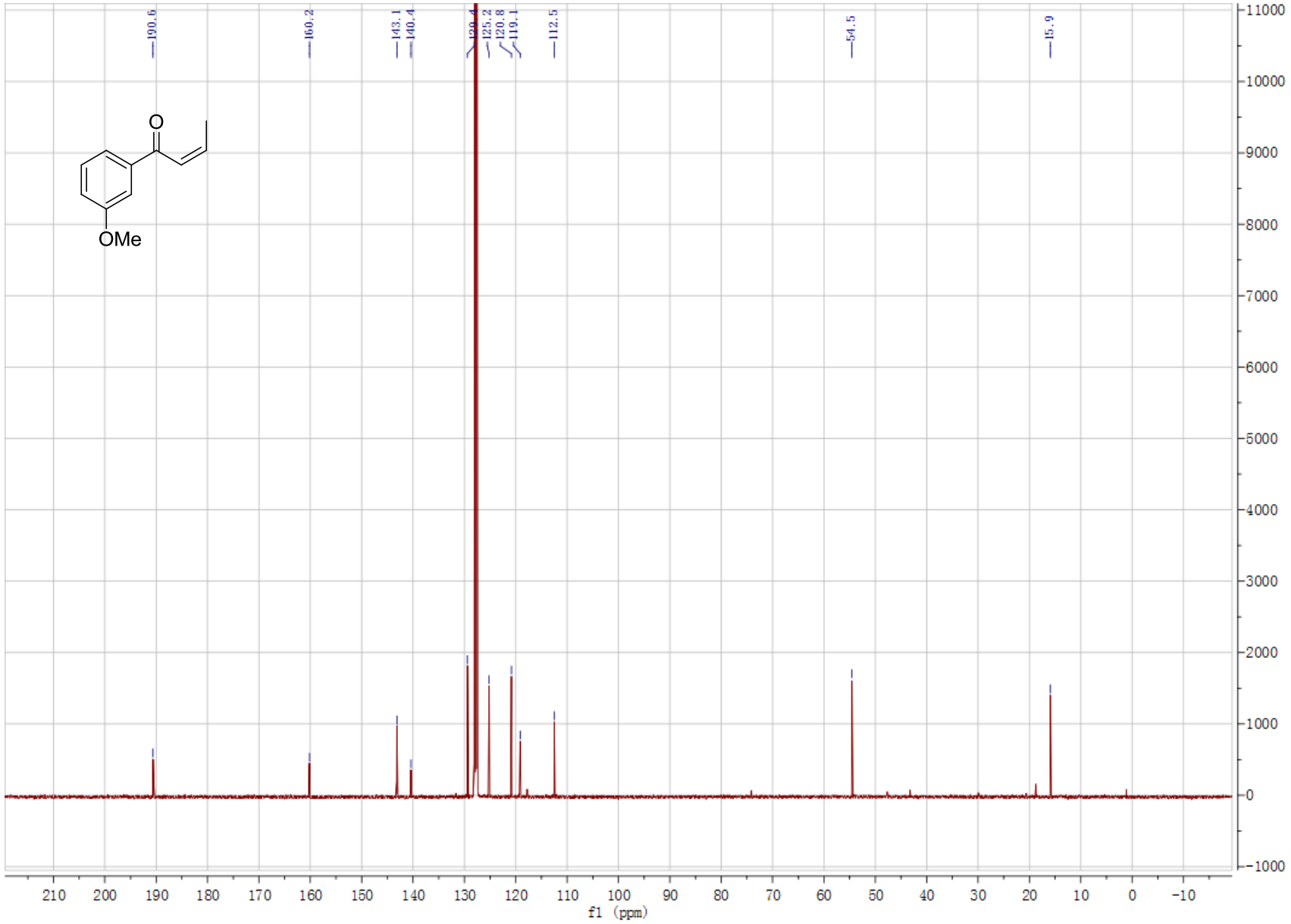
(*Z*)-1-(4-methoxyphenyl)but-2-en-1-one (2h-*Z*)



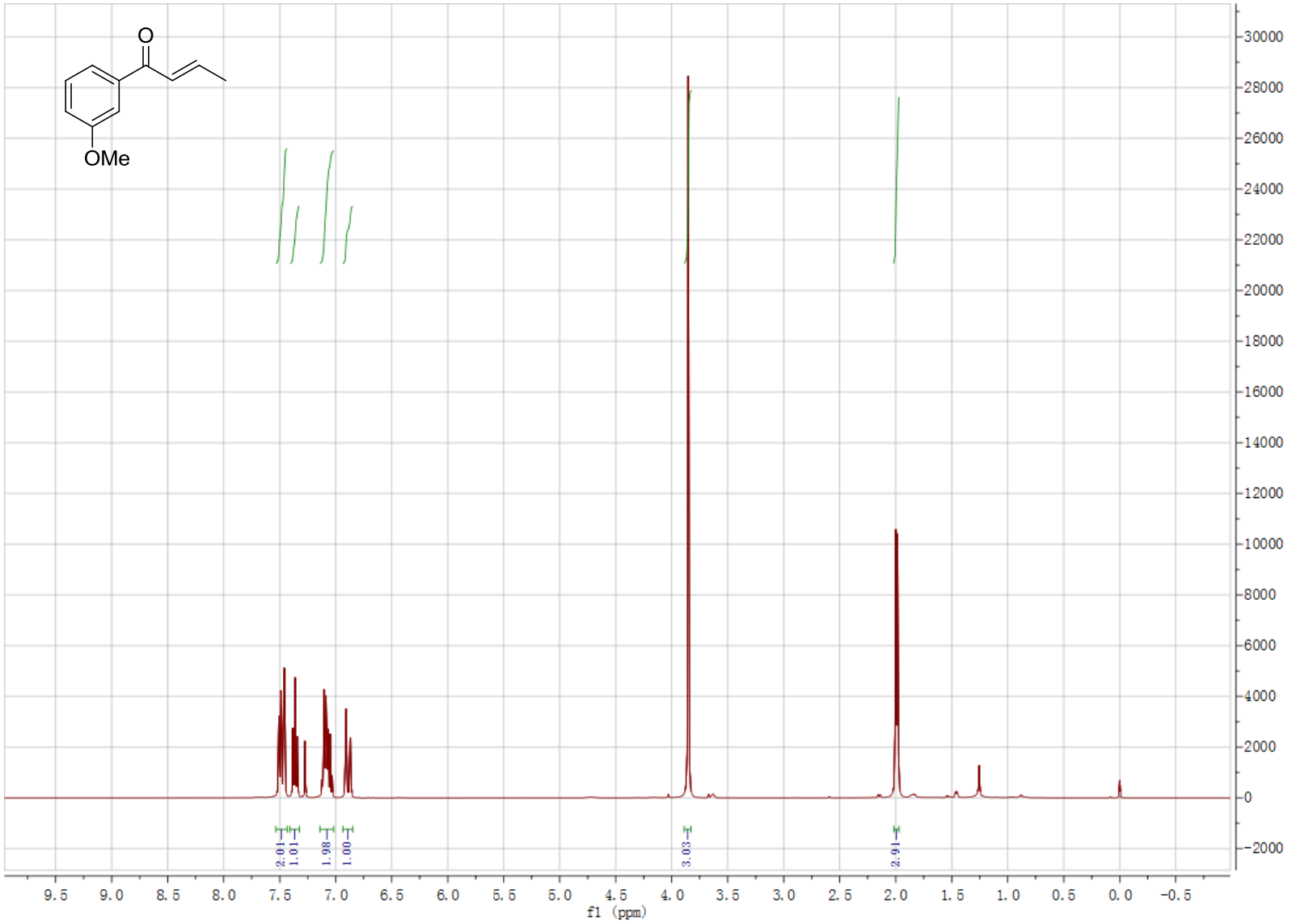

189.5
163.1
142.0
132.1
130.6
125.3
113.7
54.6
15.9
O
MeO
f1 (ppm)

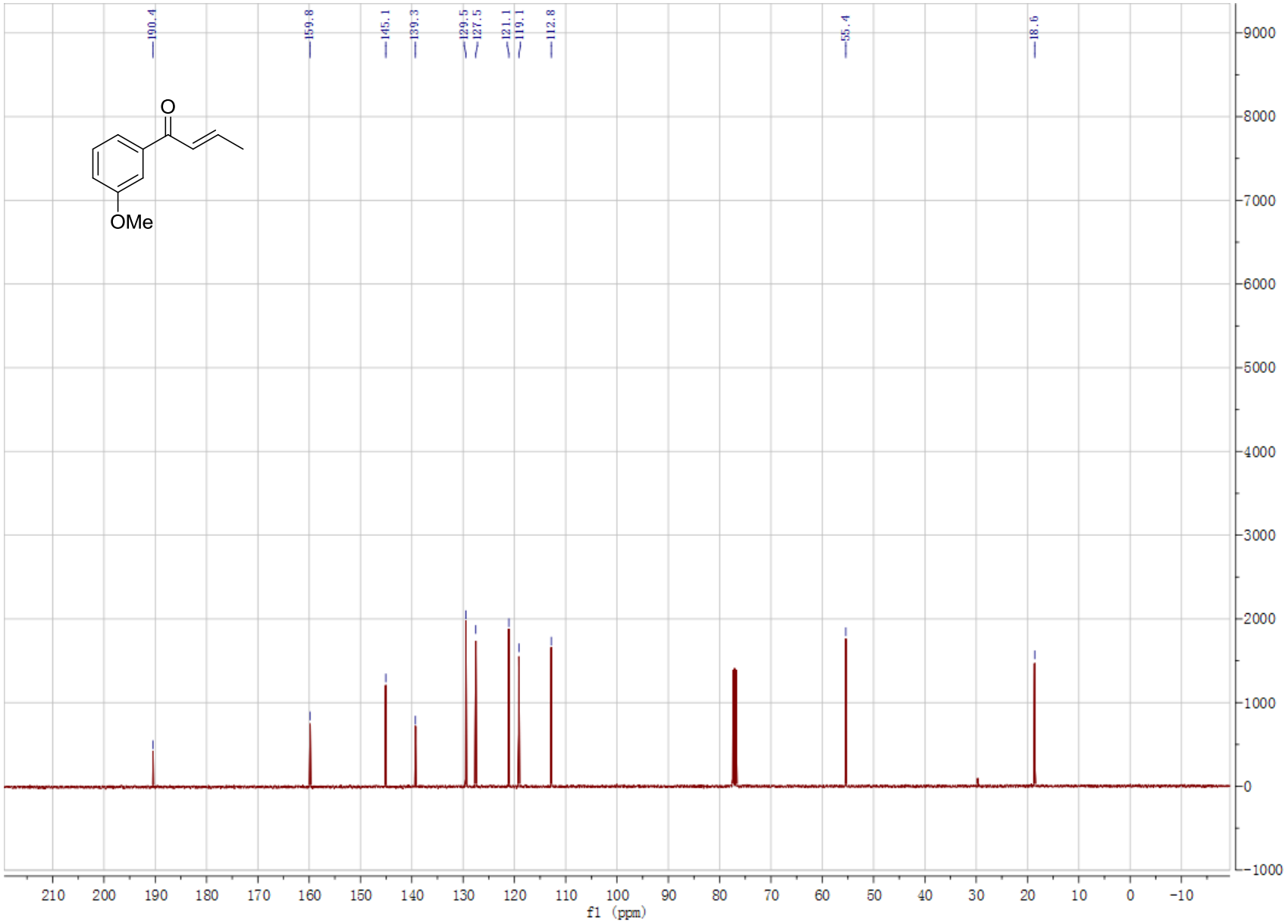
***(Z)*-1-(3-methoxyphenyl)but-2-en-1-one (2i-*Z*)**



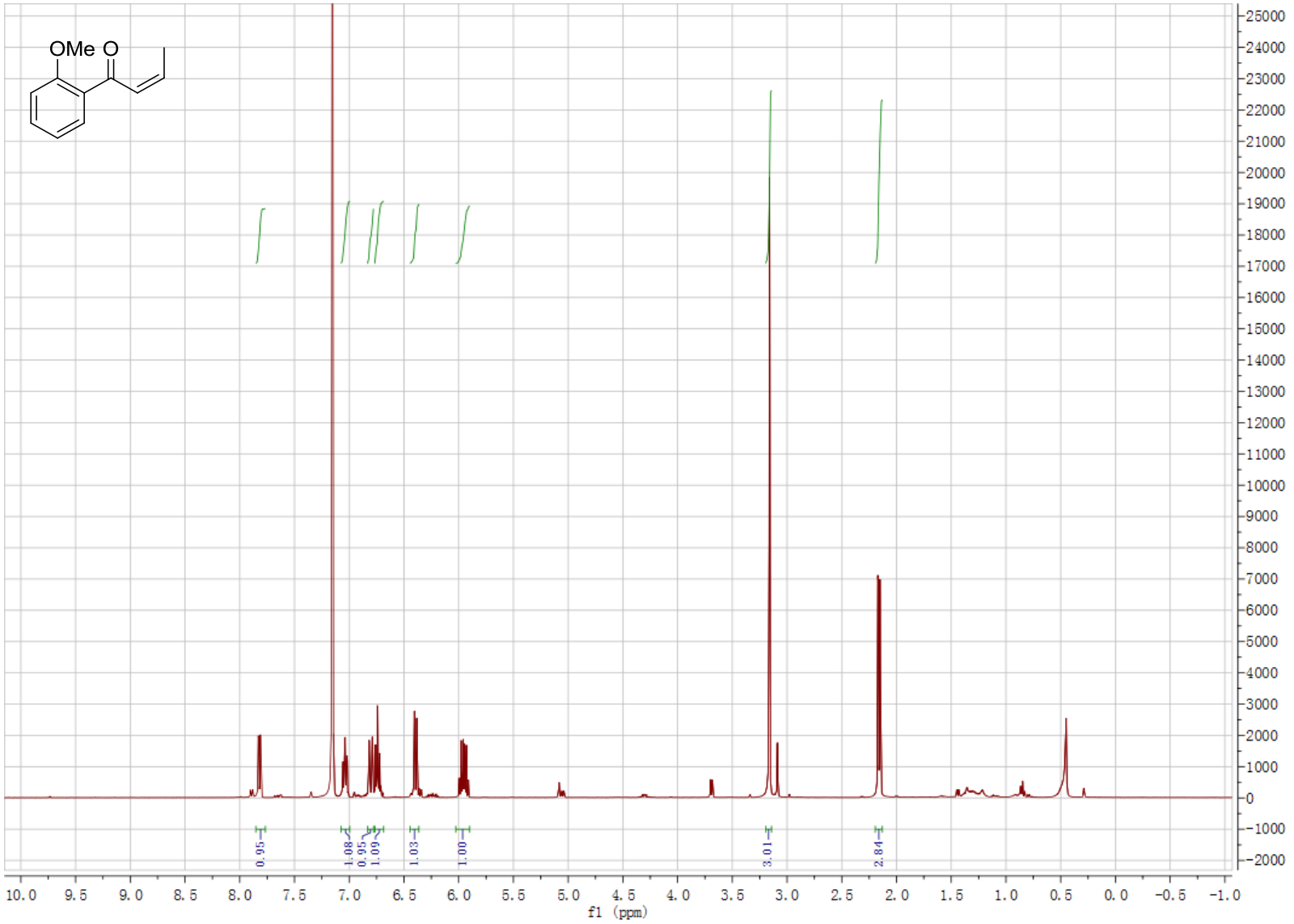

190.6
160.2
143.1
140.4
129.4
125.2
120.8
119.1
112.5
54.5
15.9
O
OMe
f1 (ppm)

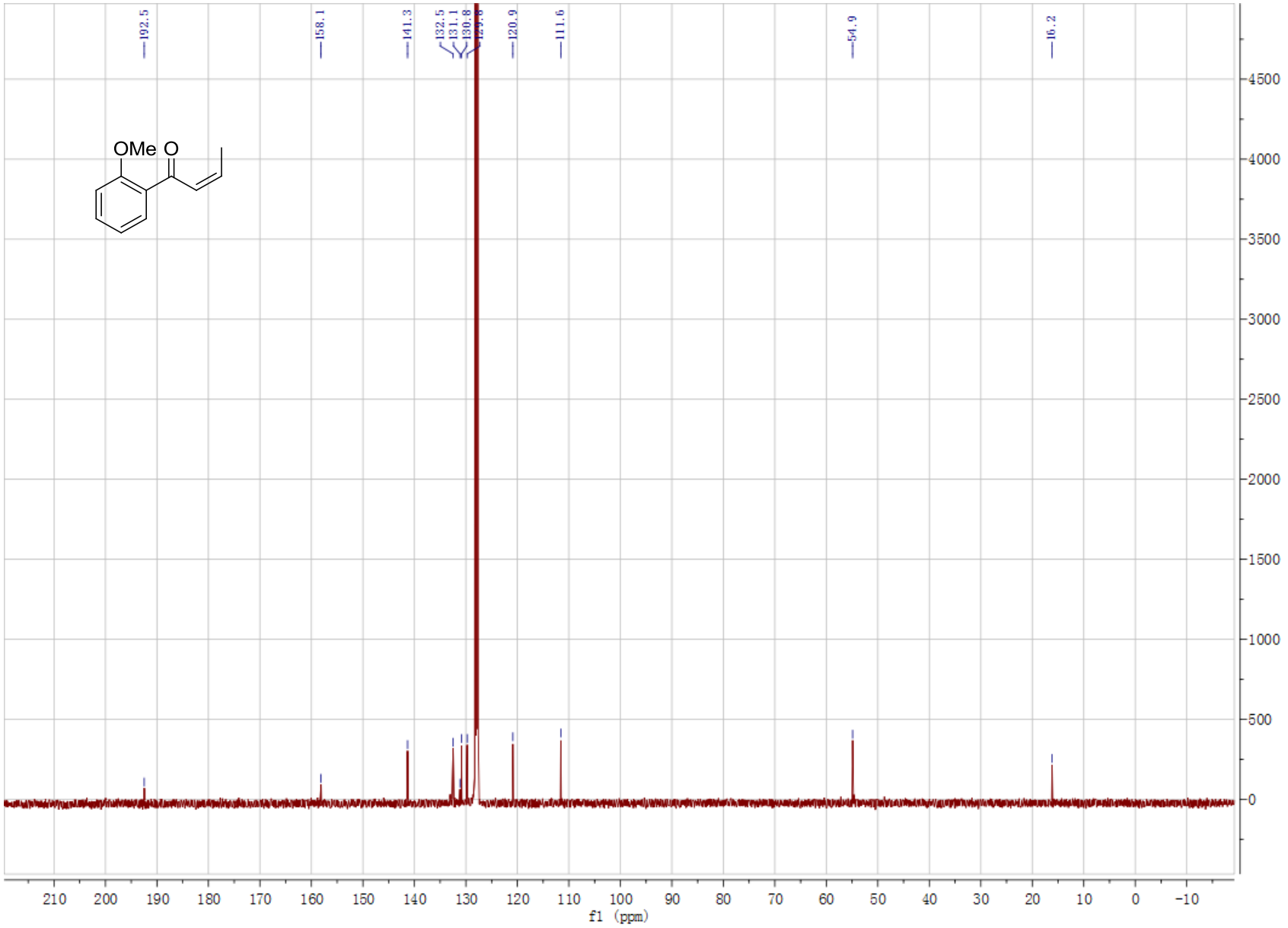
***(E)*-1-(3-methoxyphenyl)but-2-en-1-one (2i-*E*)**



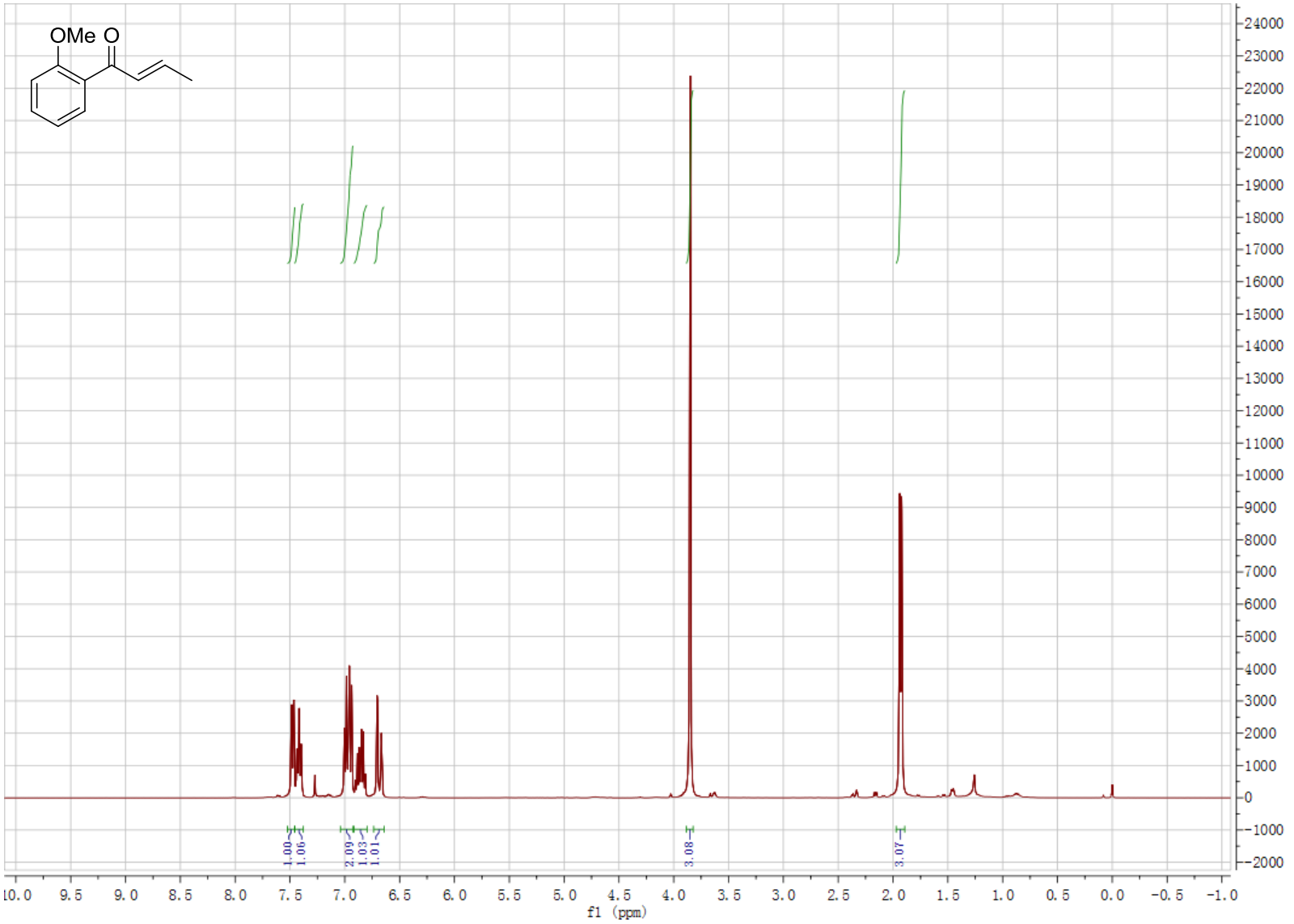

190.4
159.8
145.1
139.3
129.5
127.5
121.1
119.1
112.8
55.4
18.6
O
OMe
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

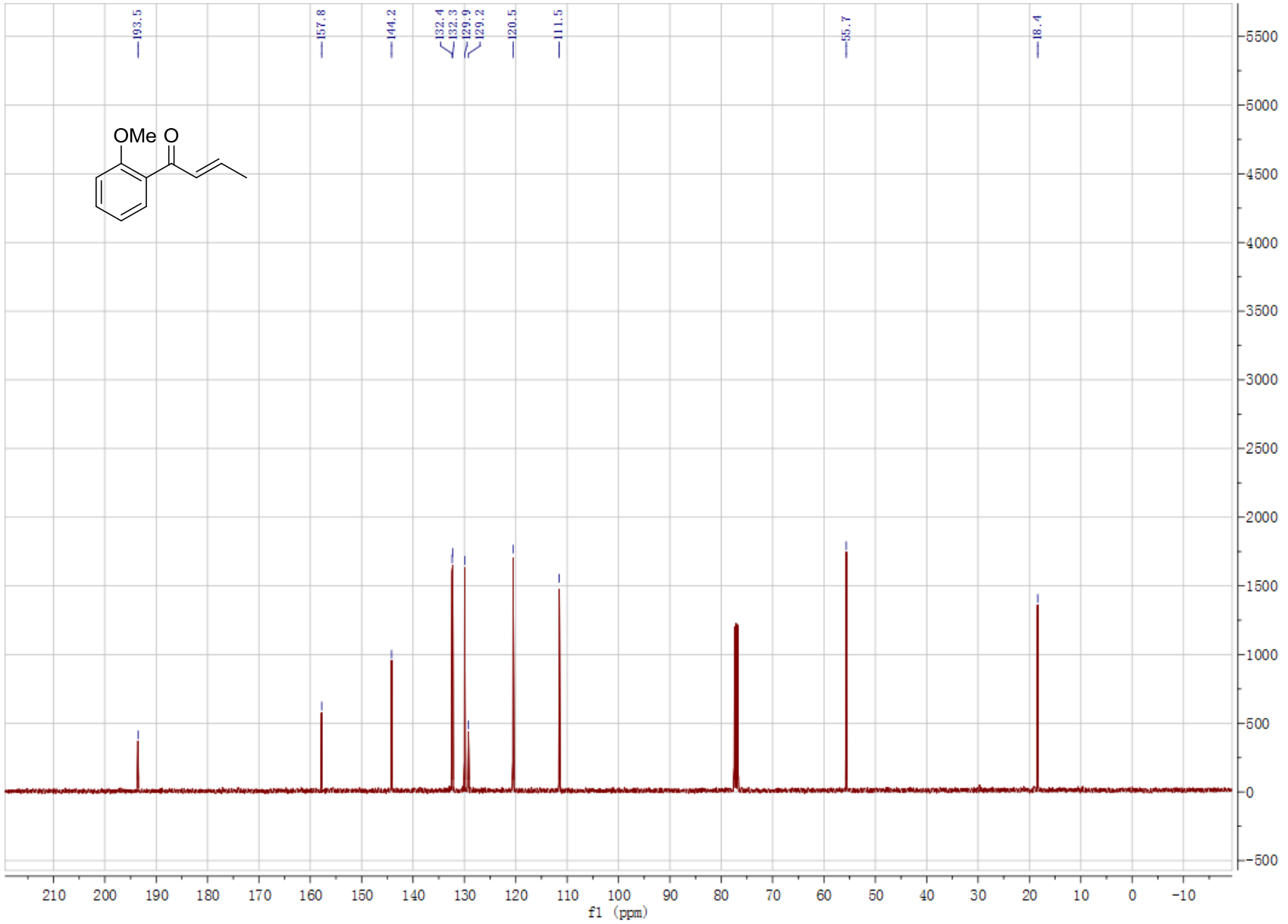
(*Z*)-1-(2-methoxyphenyl)but-2-en-1-one (2j-*Z*)



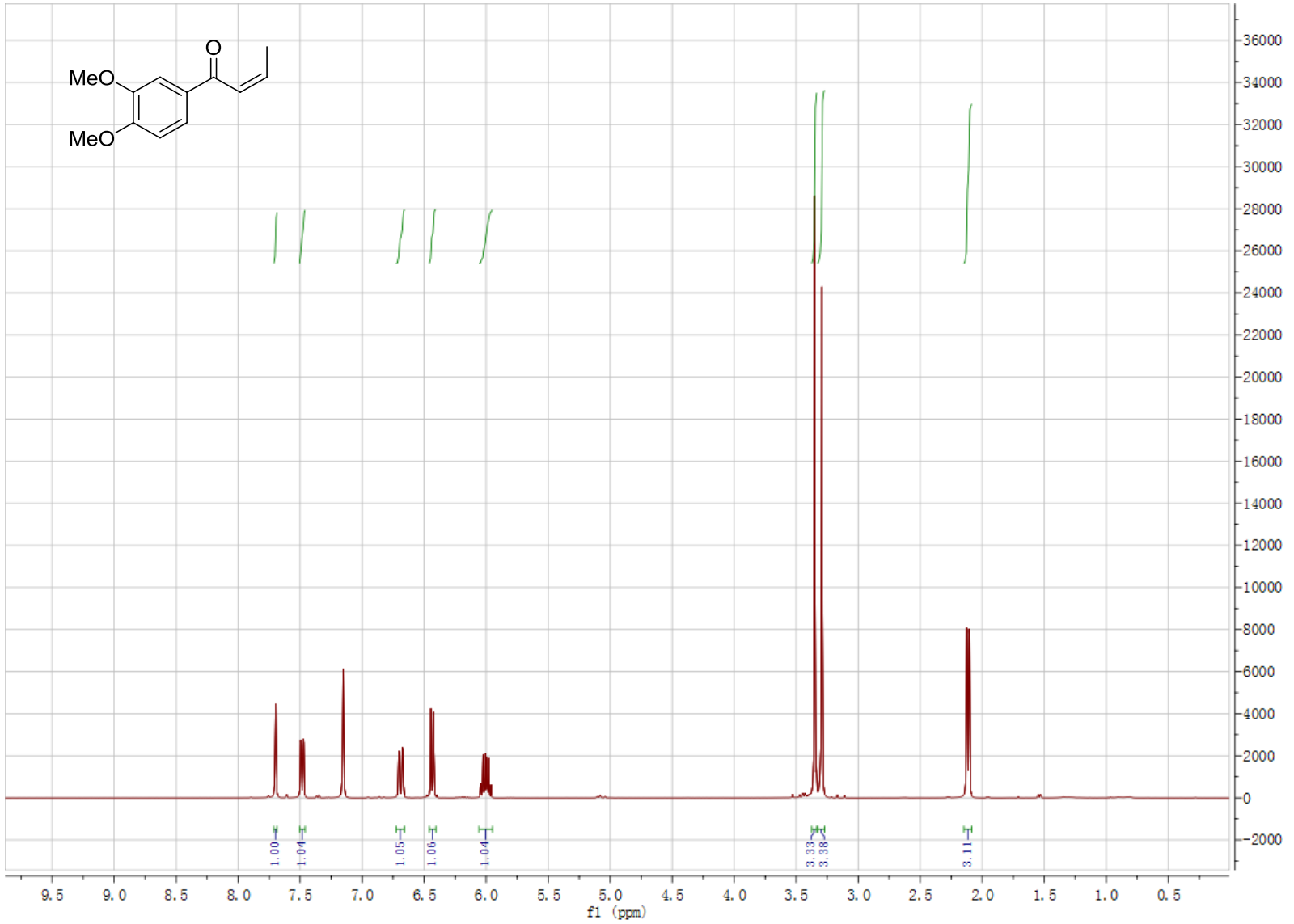

192.5
158.1
141.3
132.5
131.1
130.8
129.8
120.9
111.6
54.9
16.2
OMe O
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

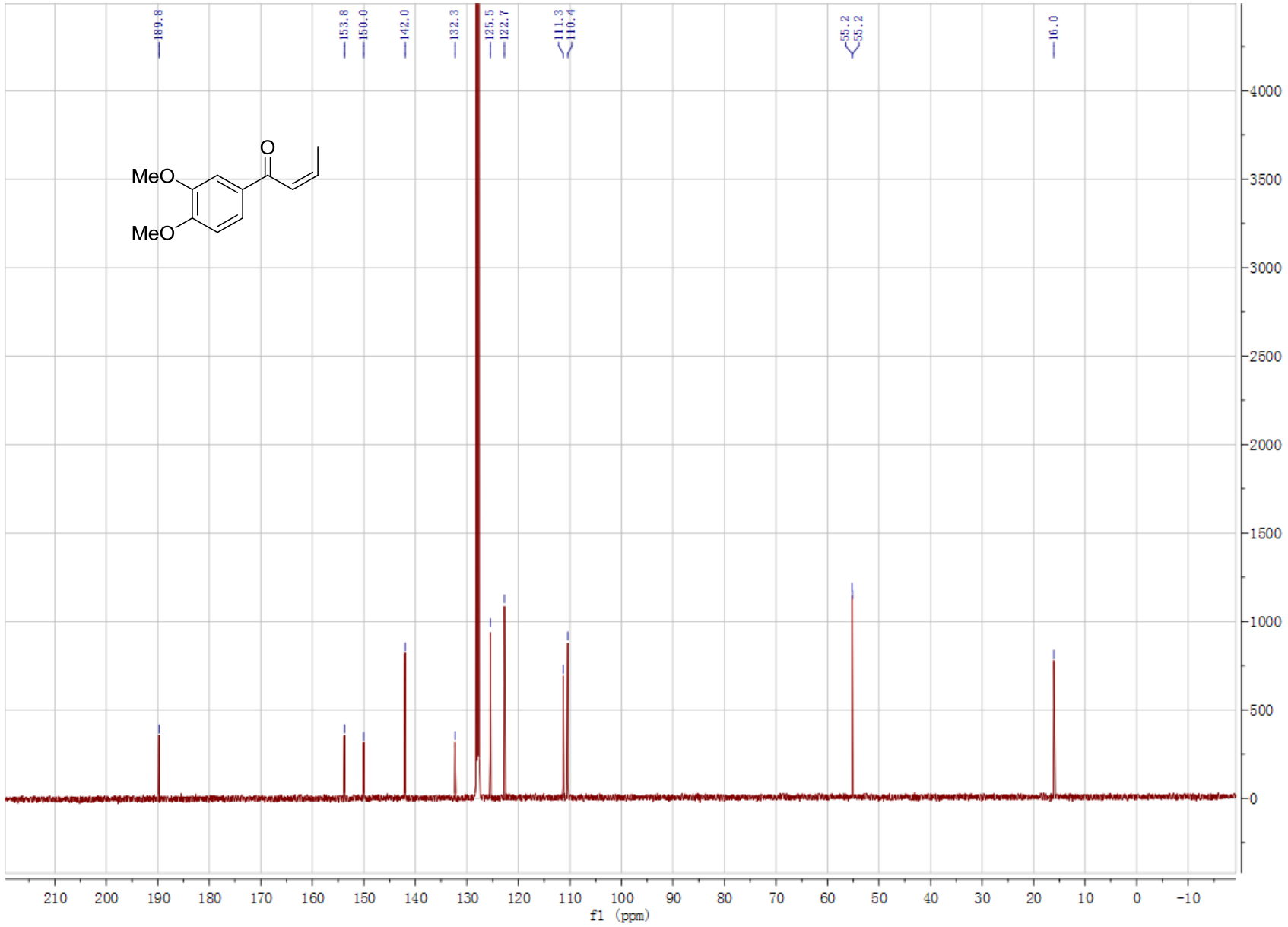
***(E)*-1-(2-methoxyphenyl)but-2-en-1-one (2j-*E*)**



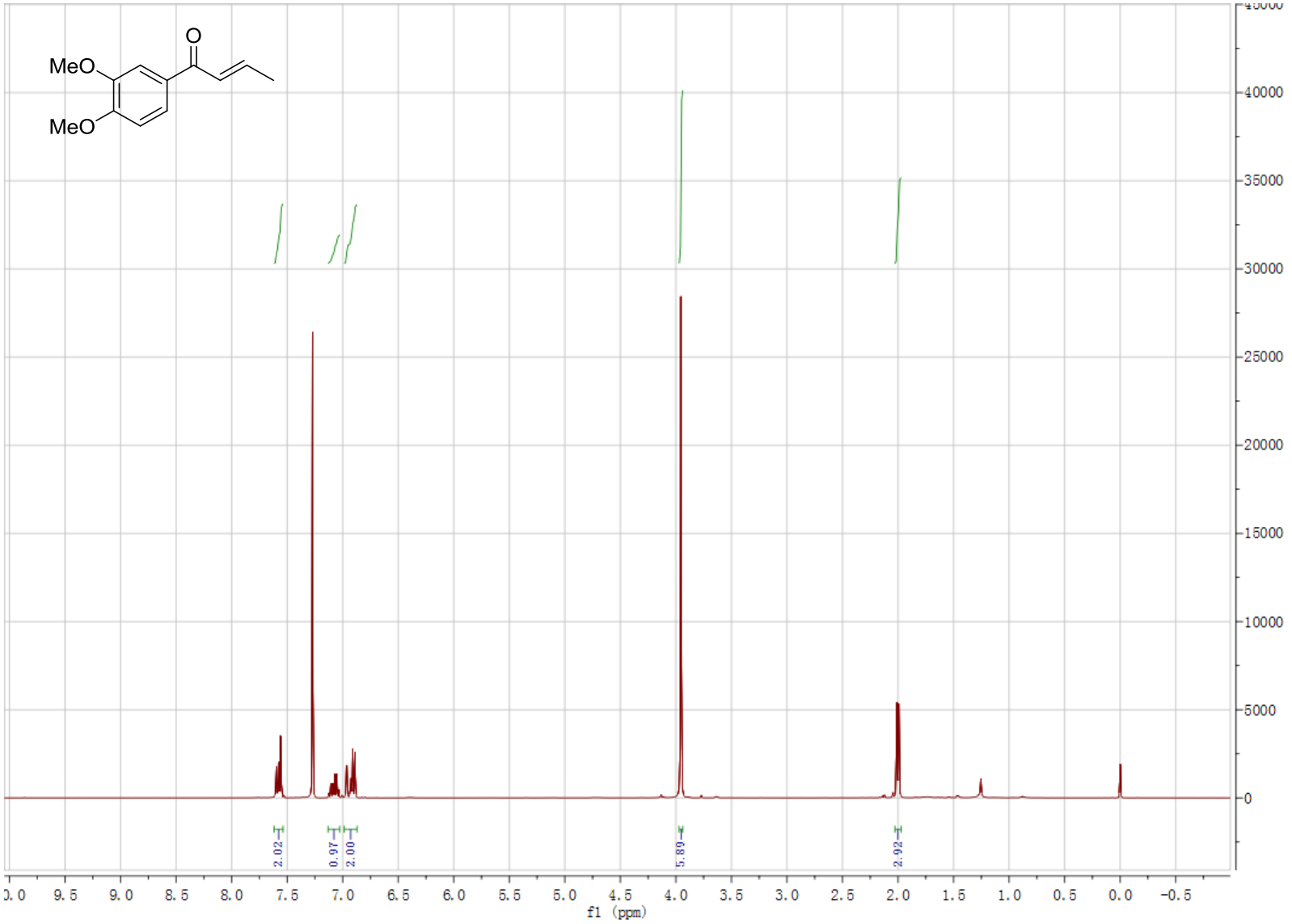

193.5
157.8
144.2
132.4
132.3
129.9
129.2
120.5
111.5
55.7
18.4
OMe
O
f1 (ppm)

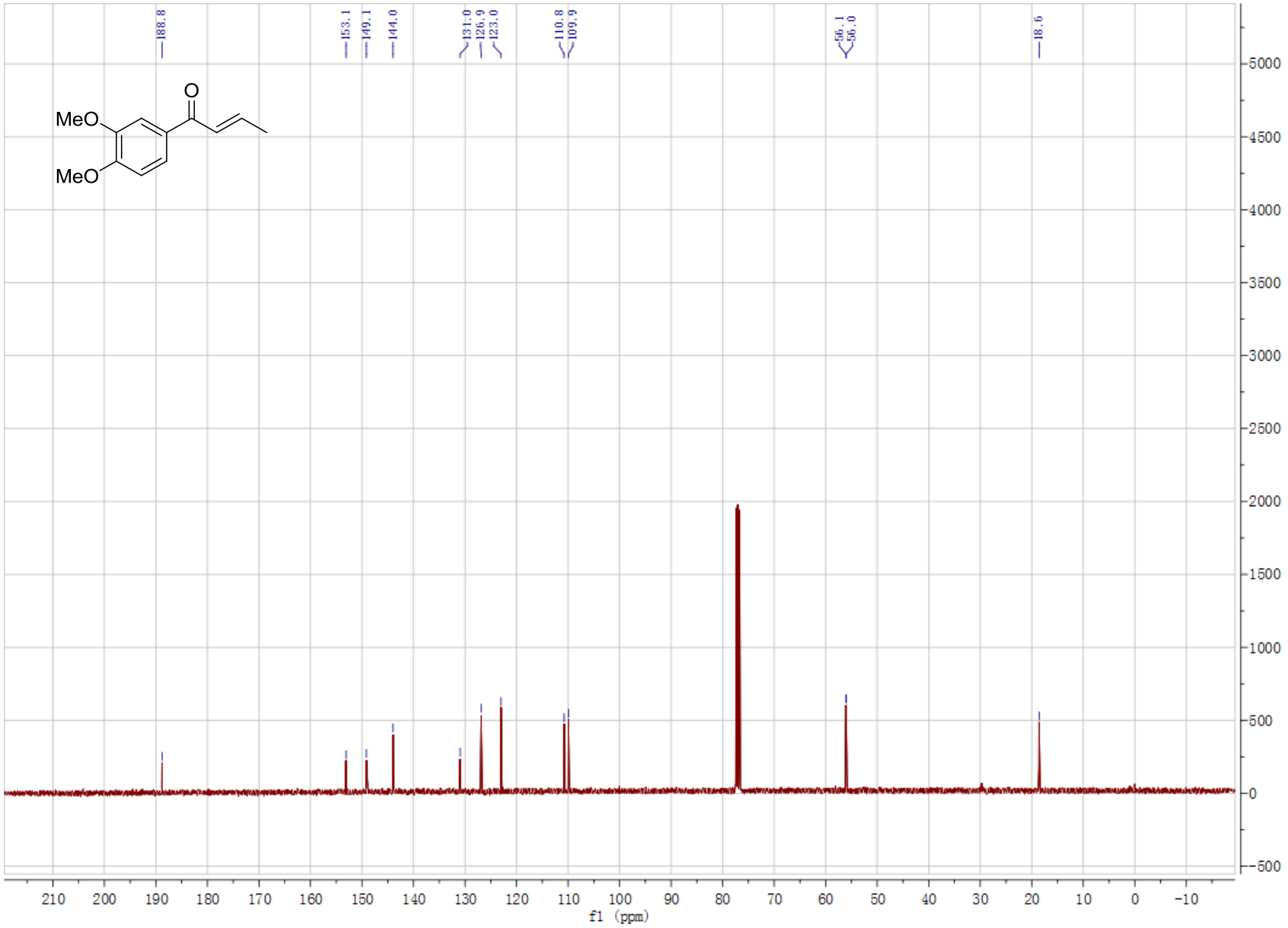
***(Z)*-1-(3,4-dimethoxyphenyl)but-2-en-1-one(2k-*Z*)**



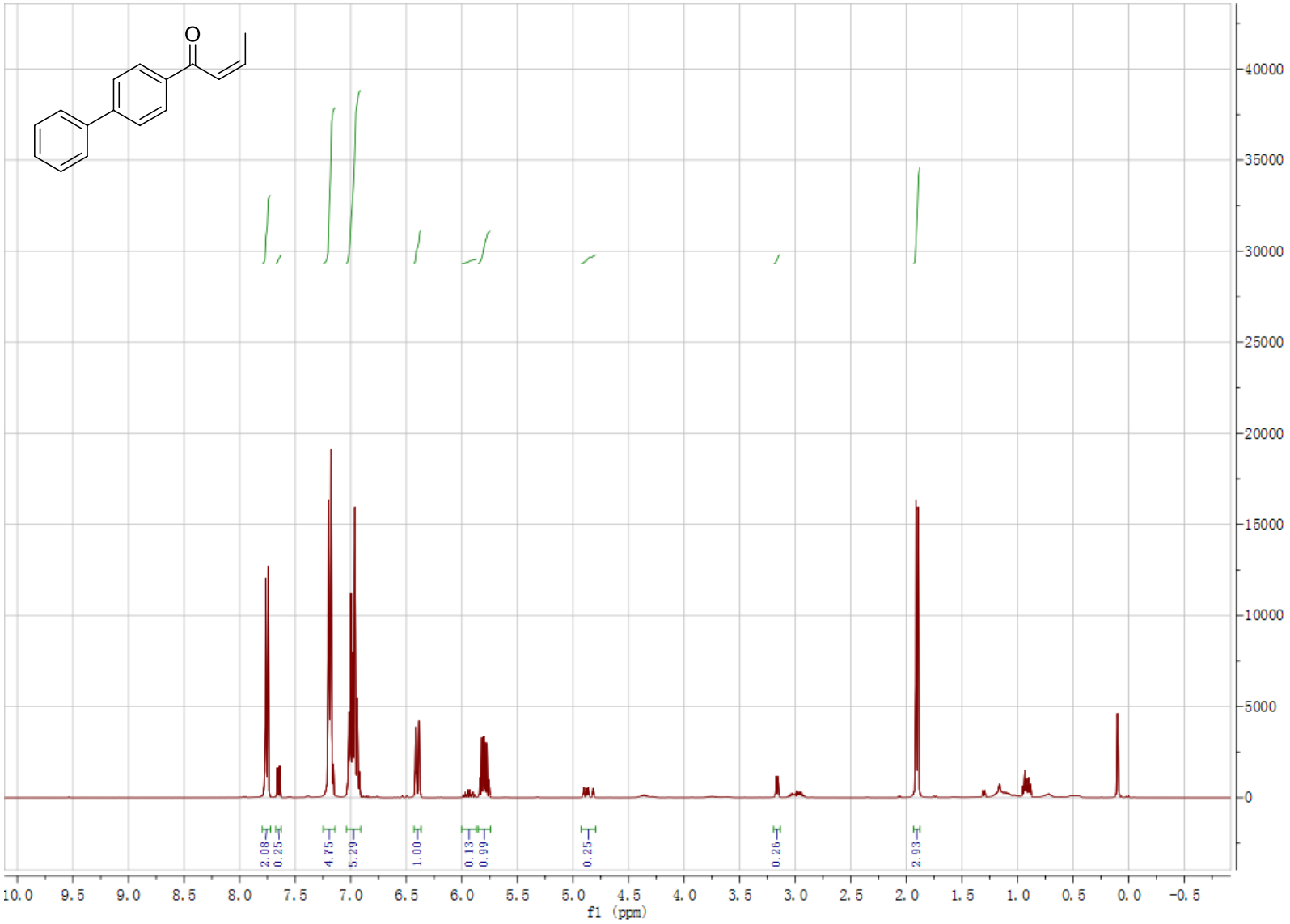

189.8
153.8
150.0
142.0
132.3
125.5
122.7
111.3
110.4
55.2
55.2
16.0
MeO
MeO
O
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

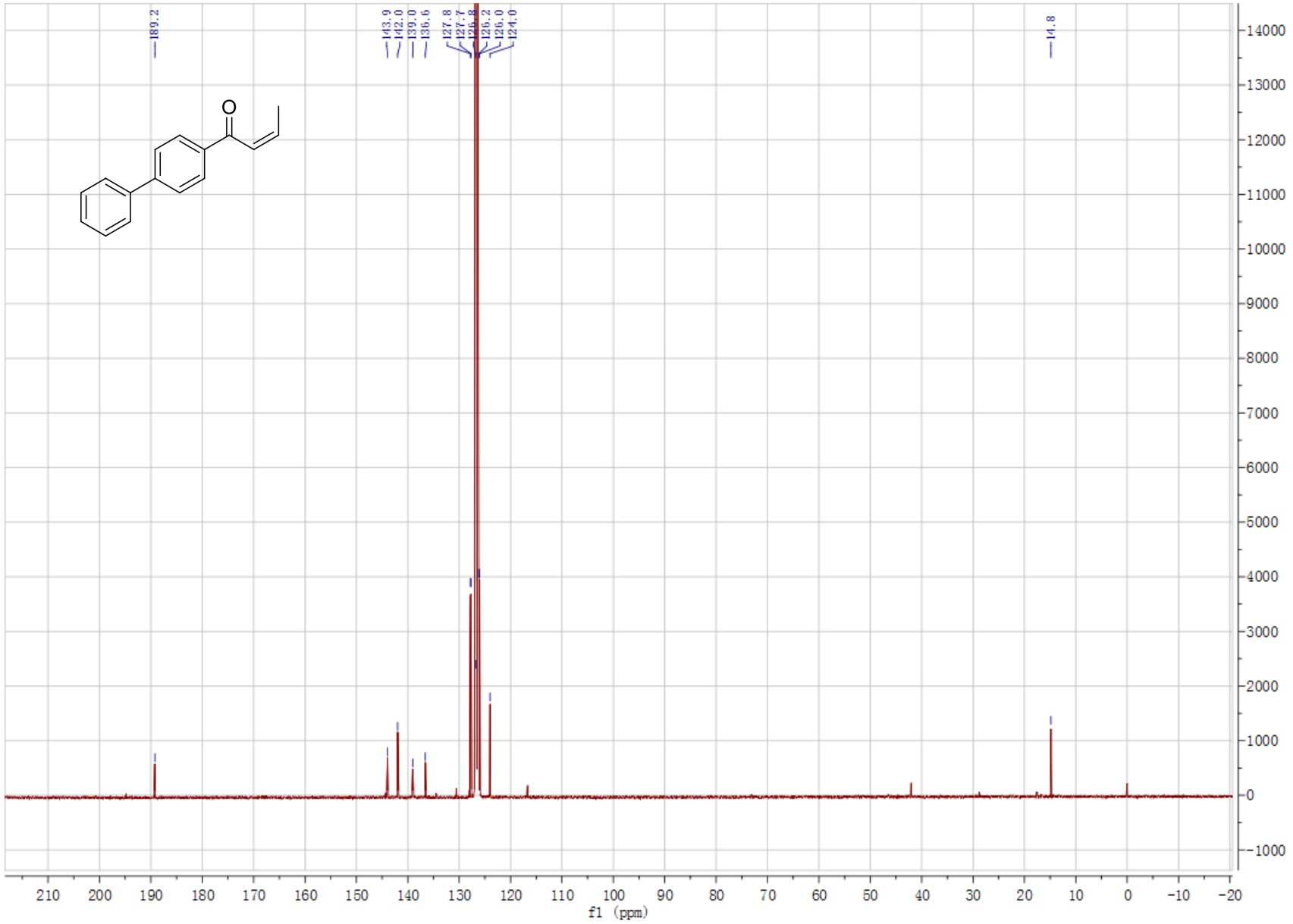
***(E)*-1-(3,4-dimethoxyphenyl)but-2-en-1-one (2k-*E*)**



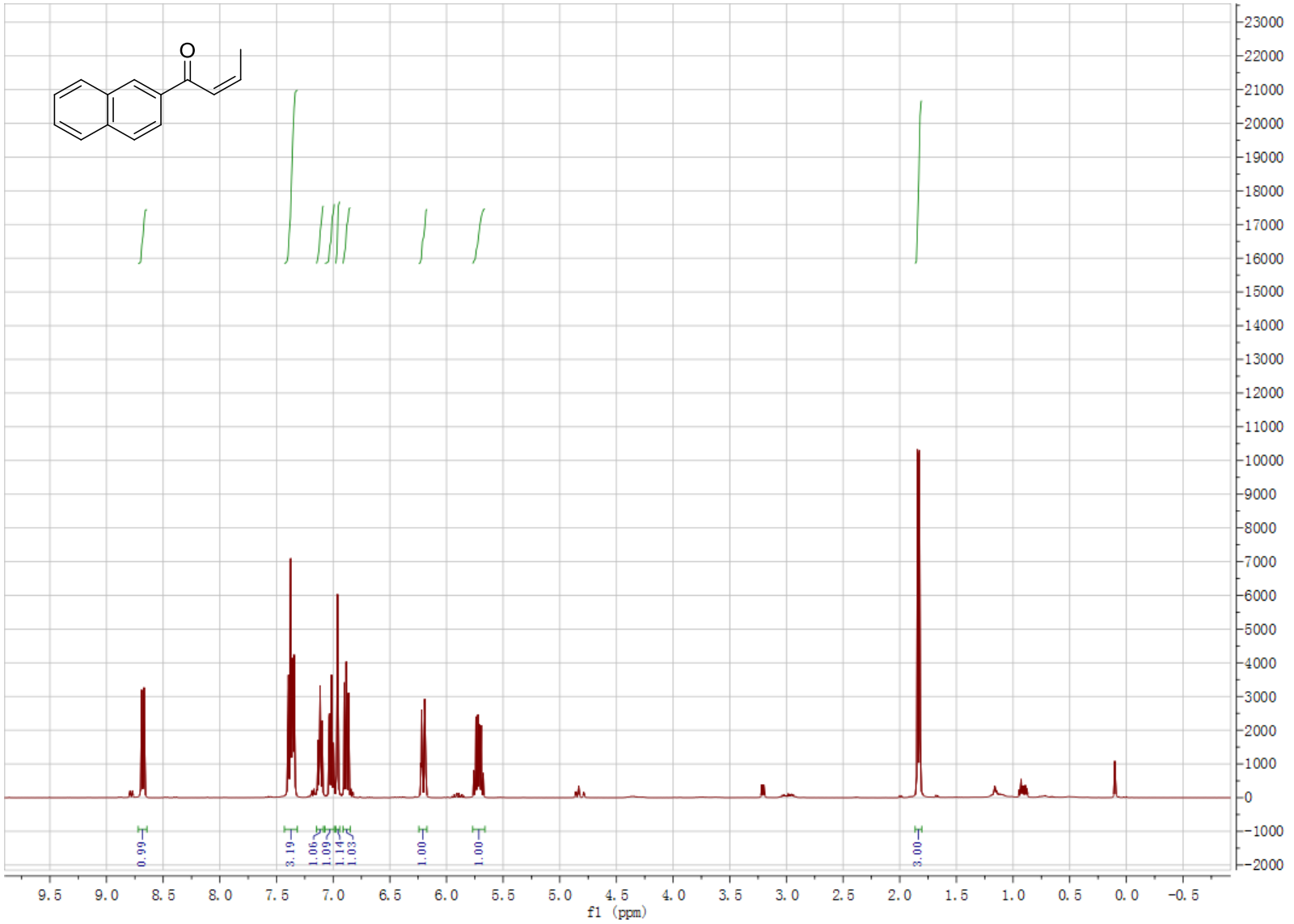

188.8
153.1
149.1
144.0
131.0
126.9
123.0
110.8
109.9
56.1
56.0
18.6
MeO
MeO
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

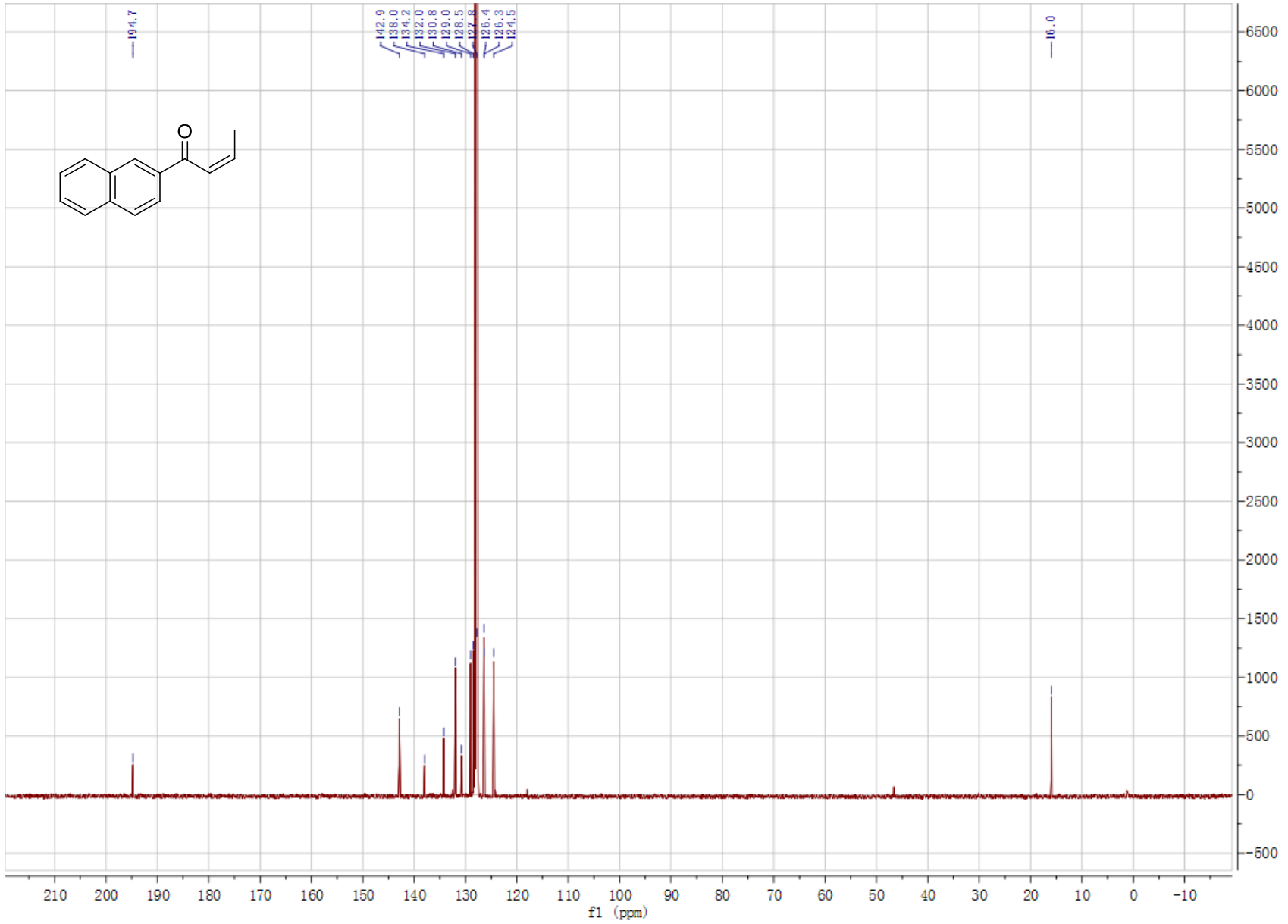
(*Z*)-1-(biphenyl-4-yl)but-2-en-1-one (2l-*Z*) (mixture with minor *E*-isomer)



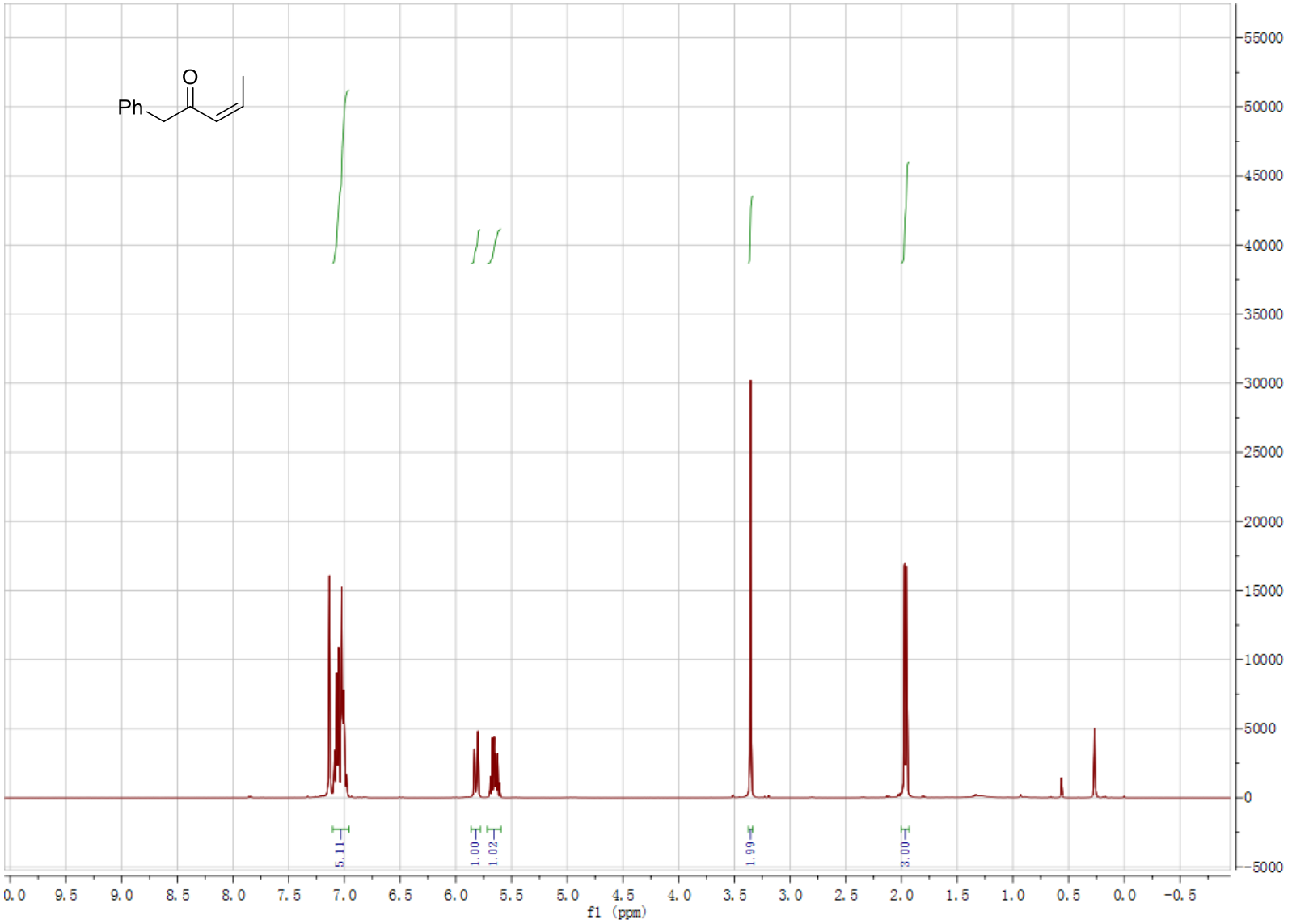

189.2
143.9
142.0
139.0
136.6
127.8
127.7
126.8
126.2
126.0
124.0
14.8
O
f1 (ppm)

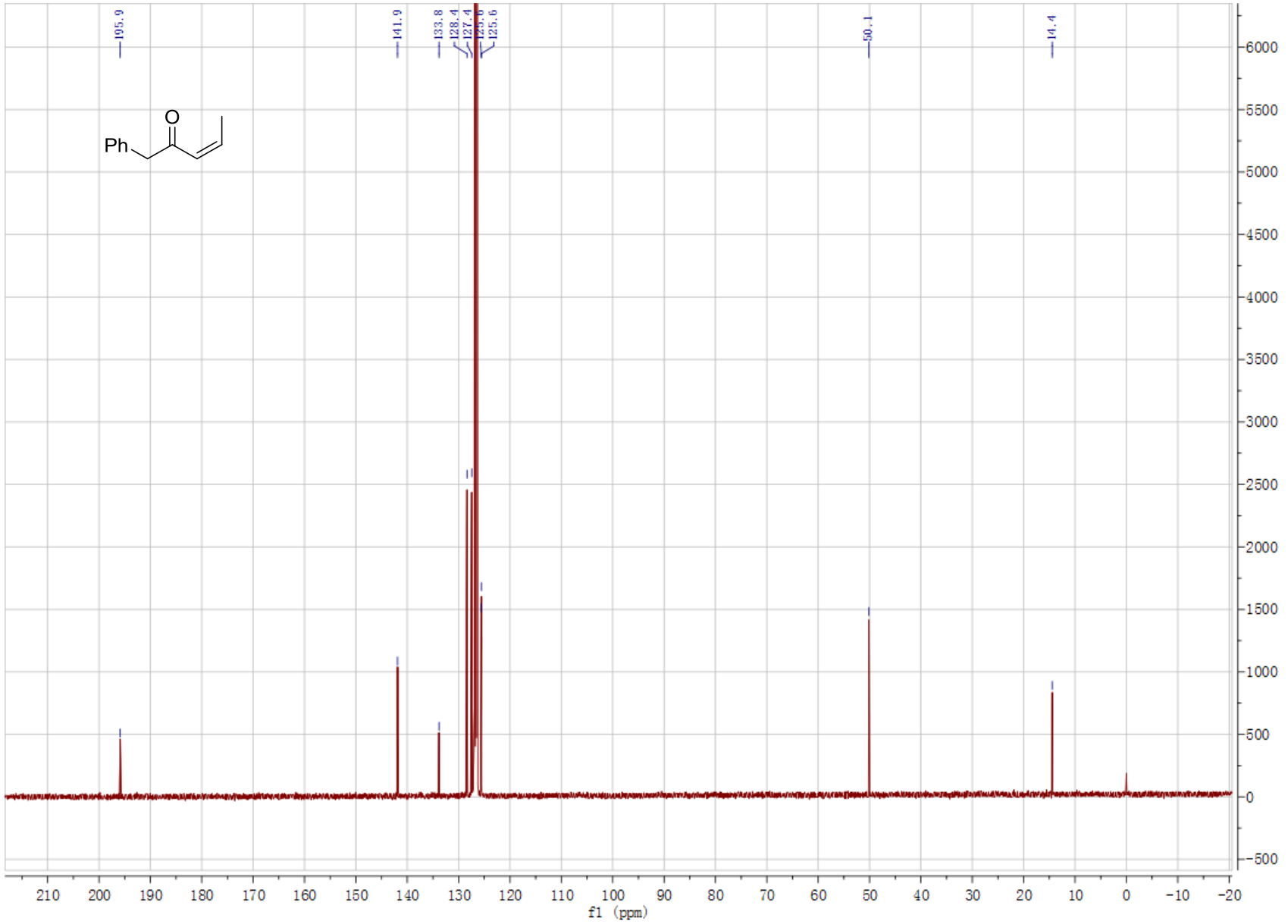
***(Z)*-1-(naphthalen-2-yl)but-2-en-1-one (2m-*Z*)**



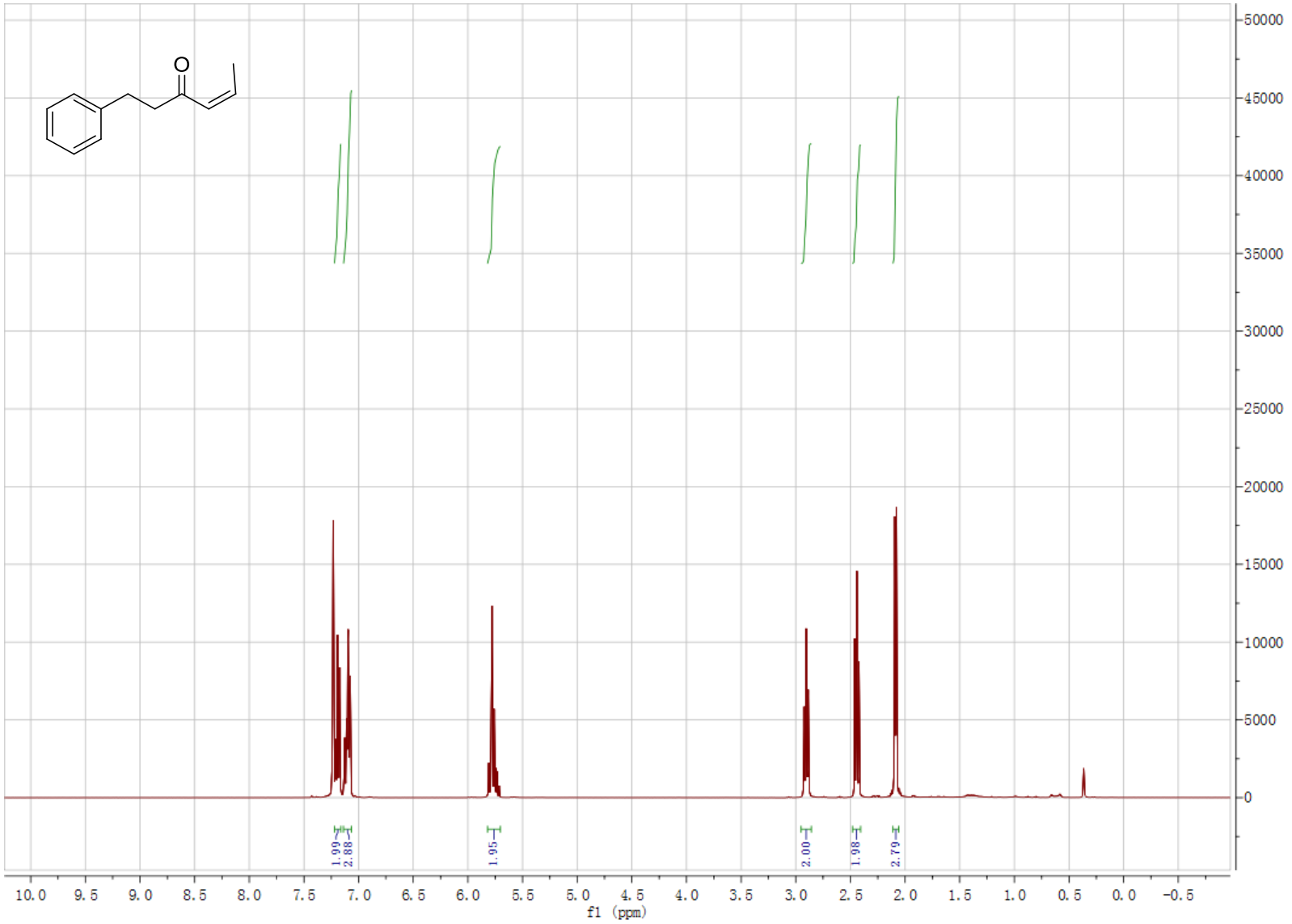

194.7
142.9
138.0
134.2
132.0
130.8
129.0
128.5
127.8
126.4
126.3
124.5
16.0
O
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

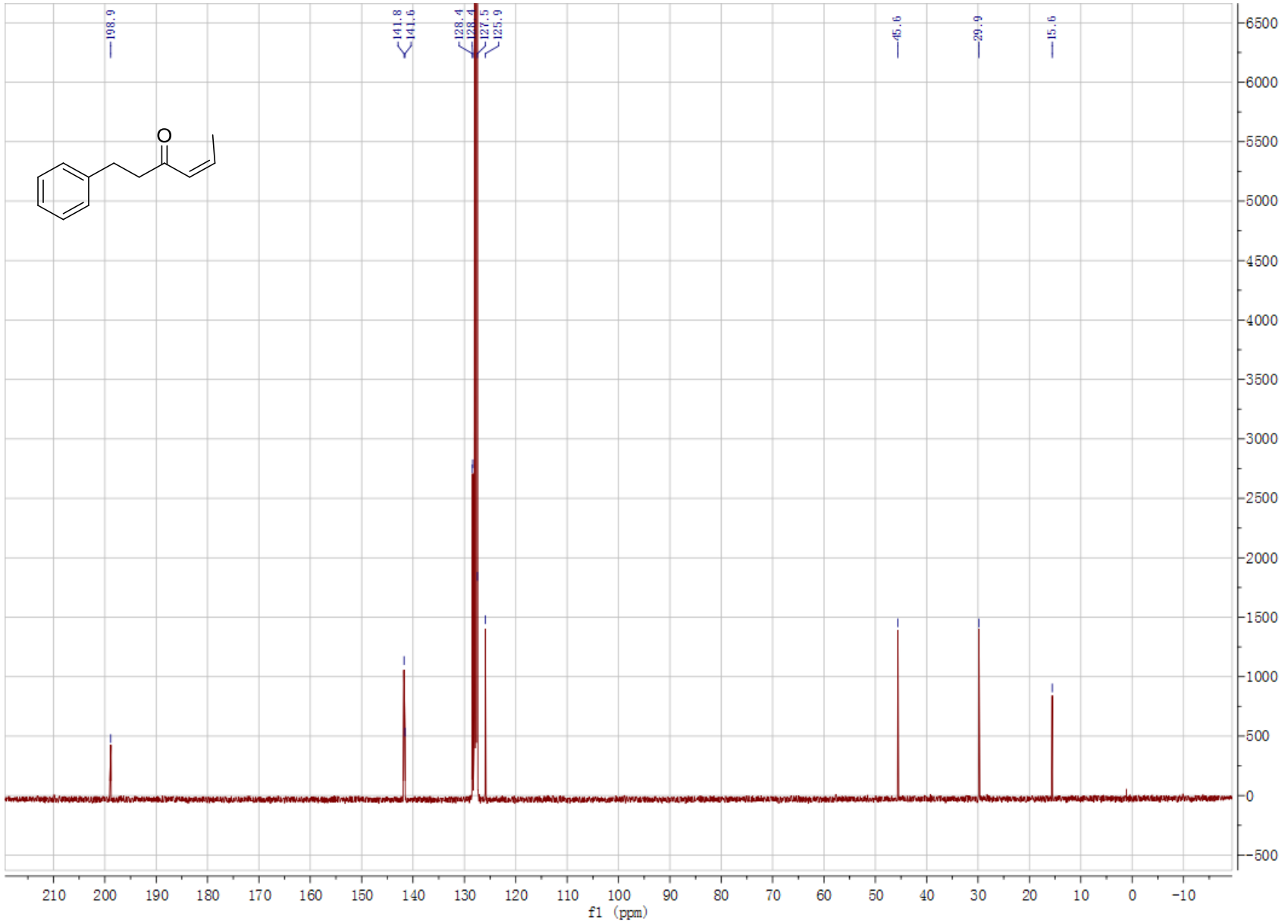
***(Z)*-1-phenylpent-3-en-2-one (4b-*Z*)**



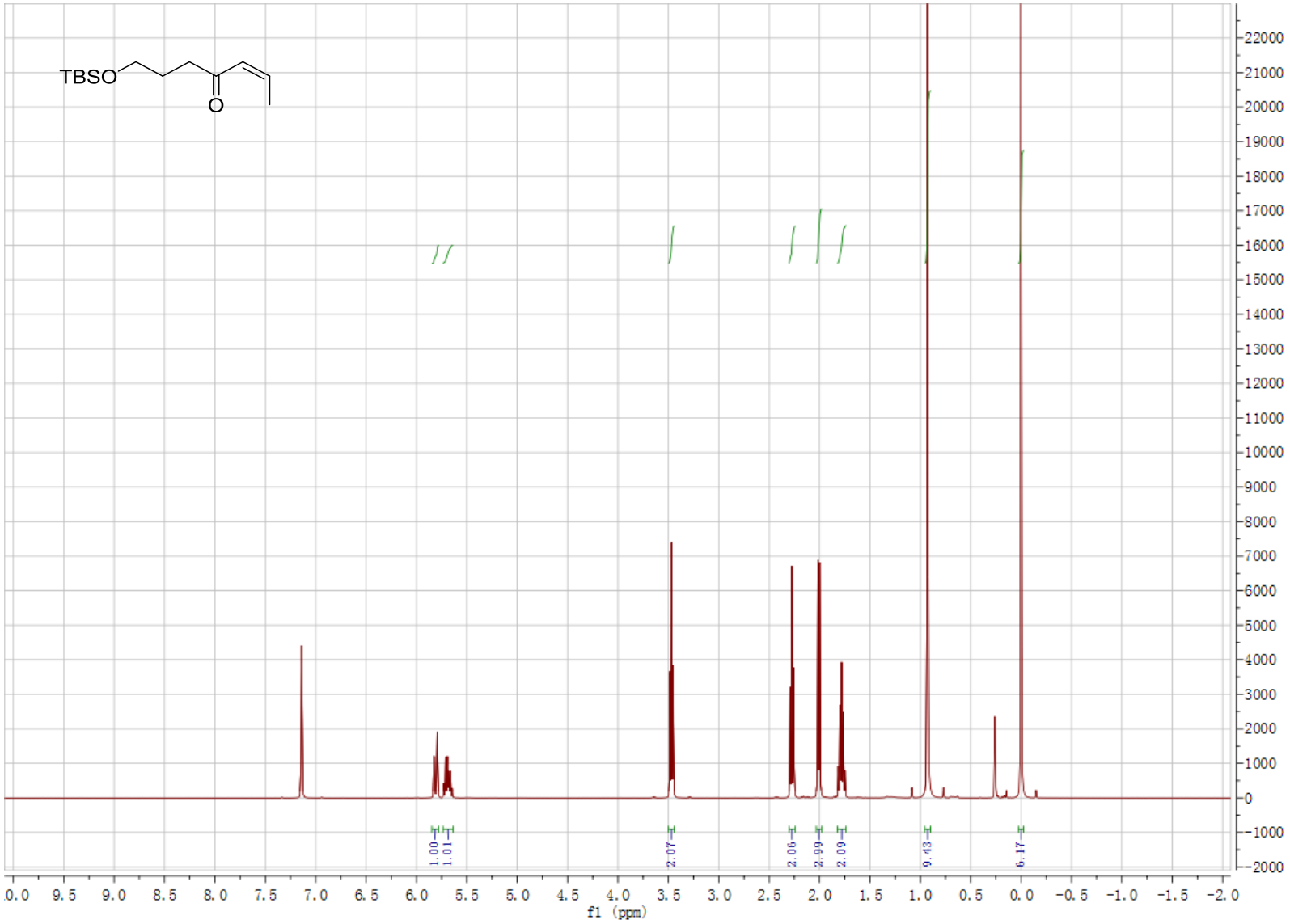

195.9
141.9
133.8
128.4
127.4
125.8
125.6
50.1
14.4
O
Ph
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

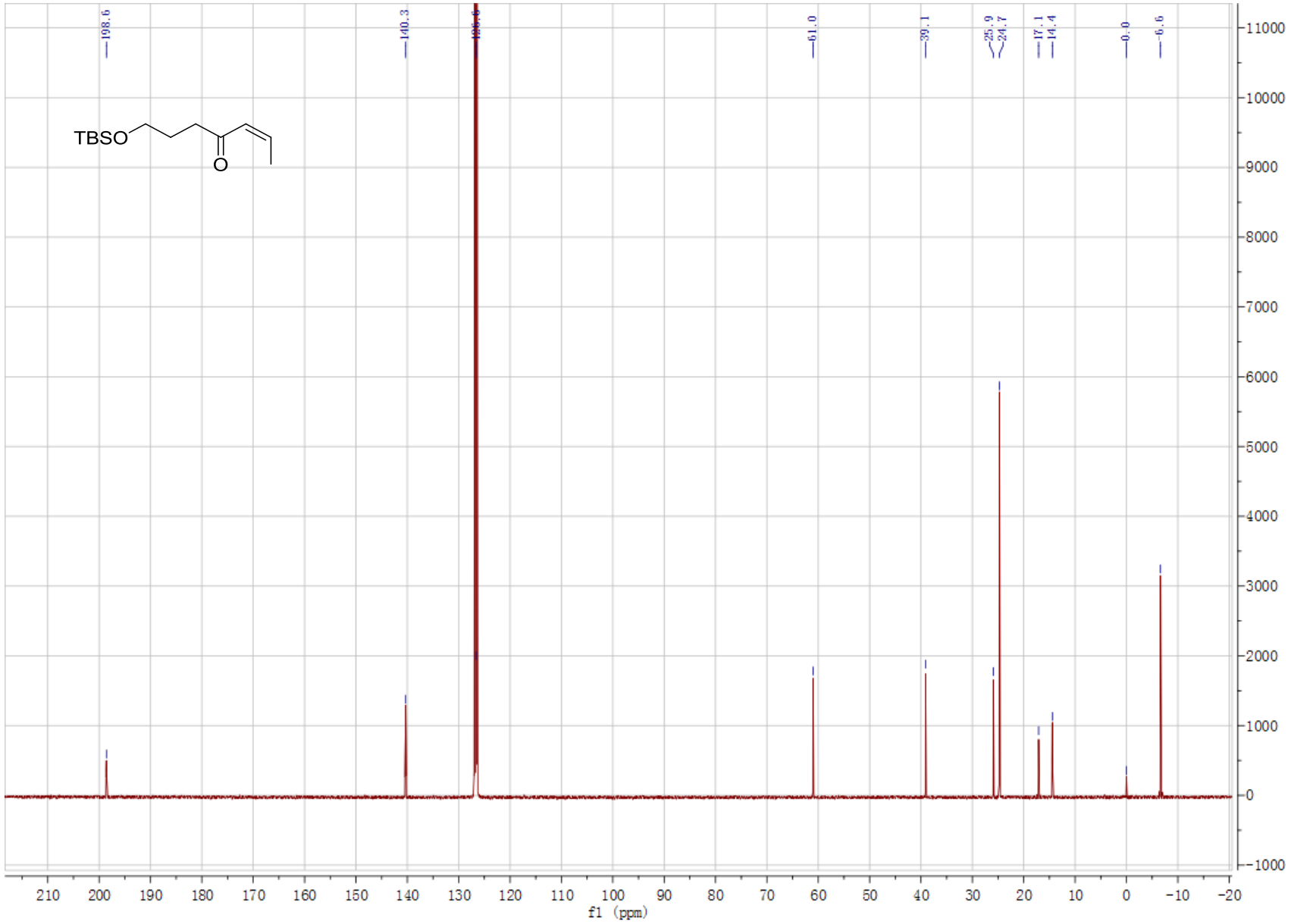
***(Z)*-1-phenylhex-4-en-3-one (4c-*Z*)**



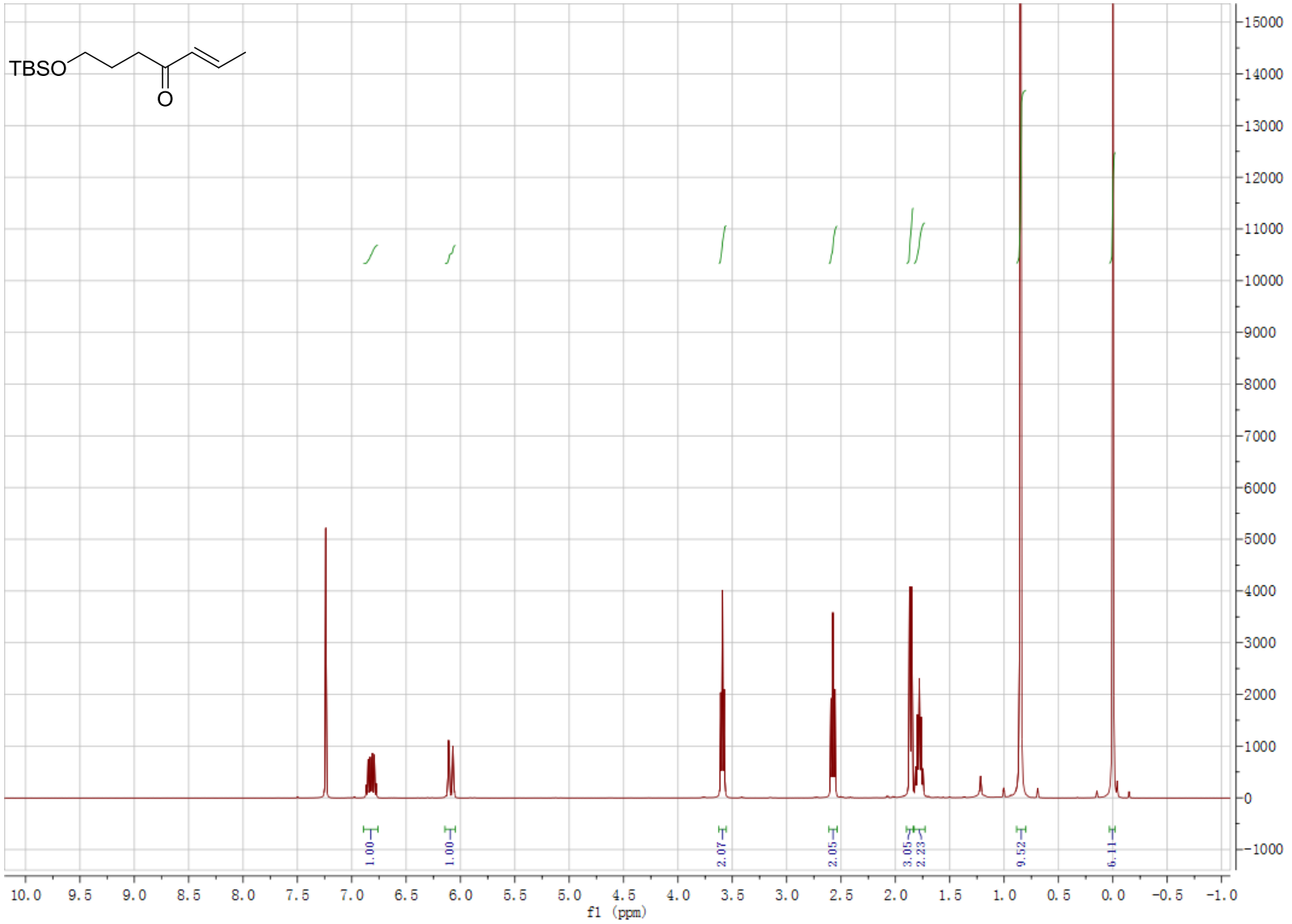

198.9
141.8
141.6
128.4
128.4
127.5
125.9
45.6
29.9
15.6
O
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

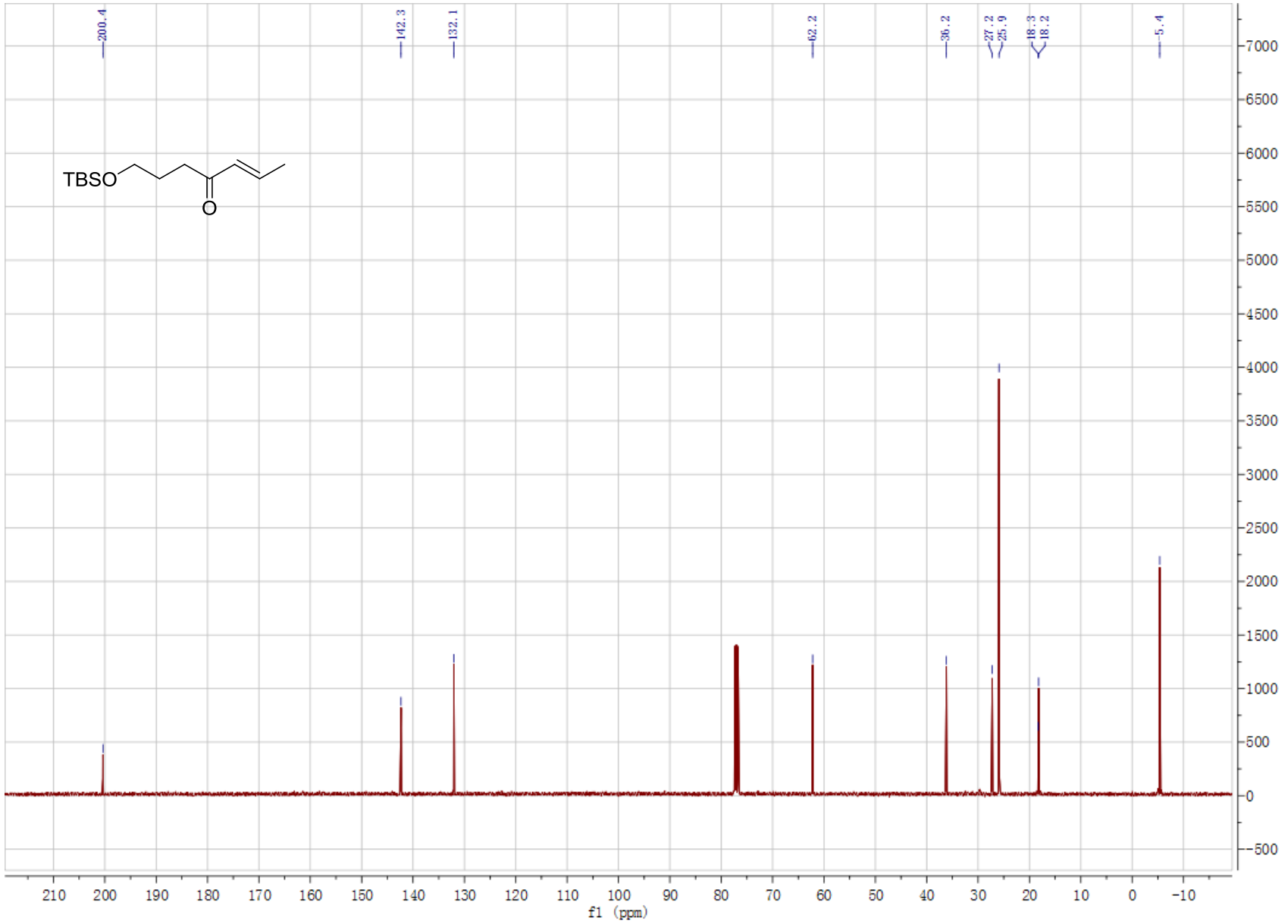
***(Z)*-1-(tert-butyldimethylsilyloxy)hex-4-en-3-one (4e-*Z*)**



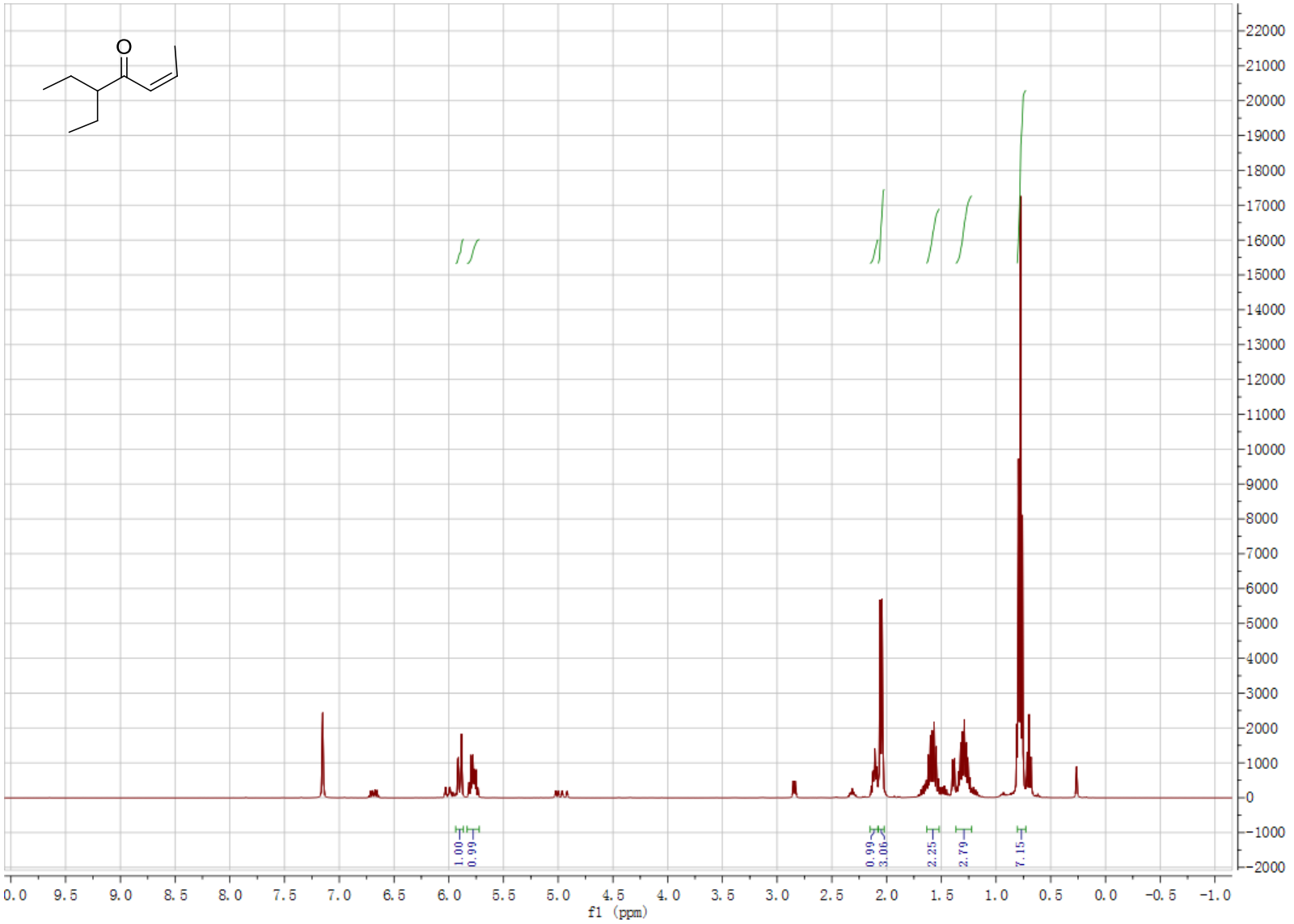

198.6
140.3
136.6
61.0
39.1
25.9
24.7
17.1
14.4
0.0
-6.6
TBSO
O
f1 (ppm)

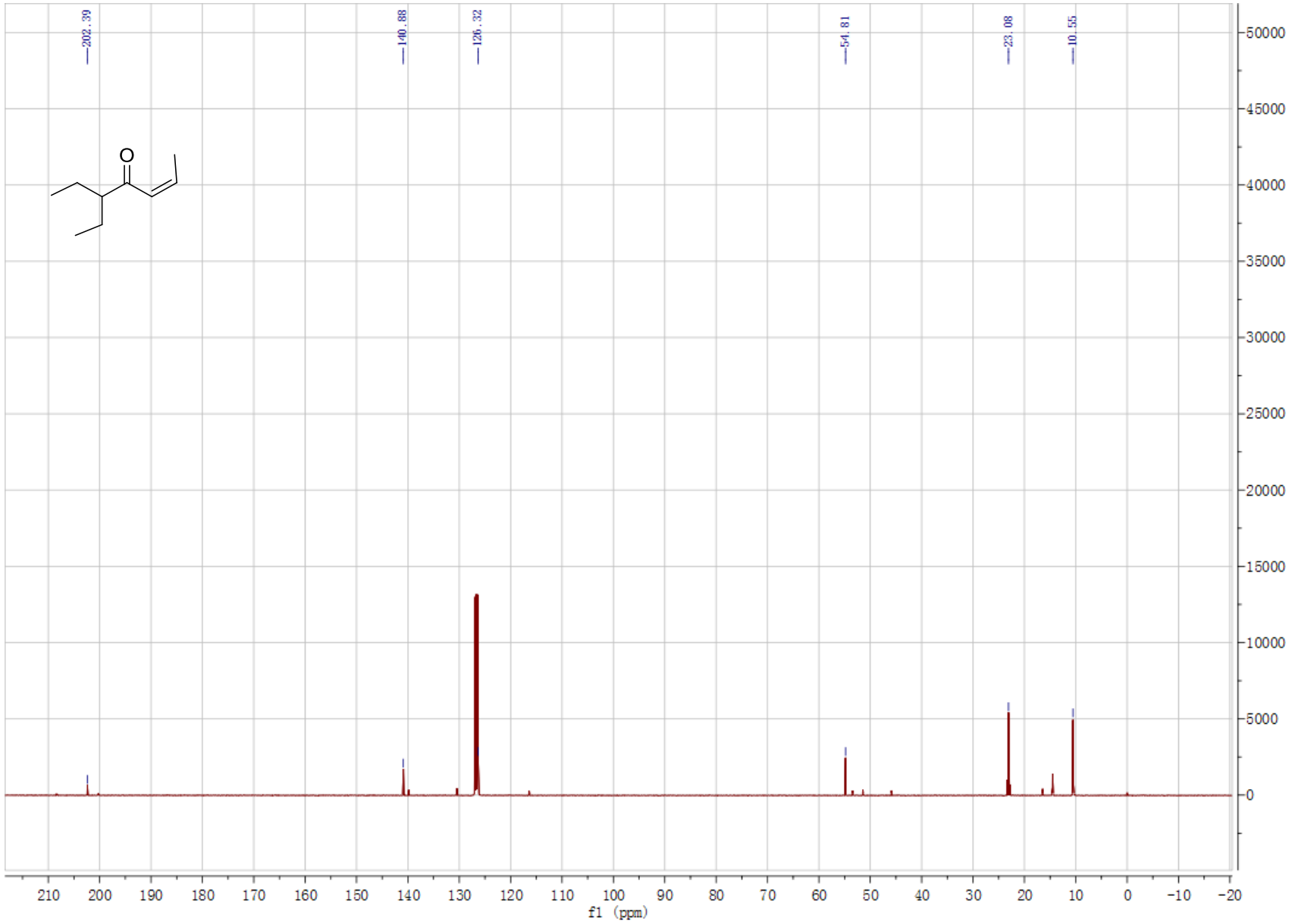
***(E)*-1-(tert-butyldimethylsilyloxy)hex-4-en-3-one (4e-*E*)**



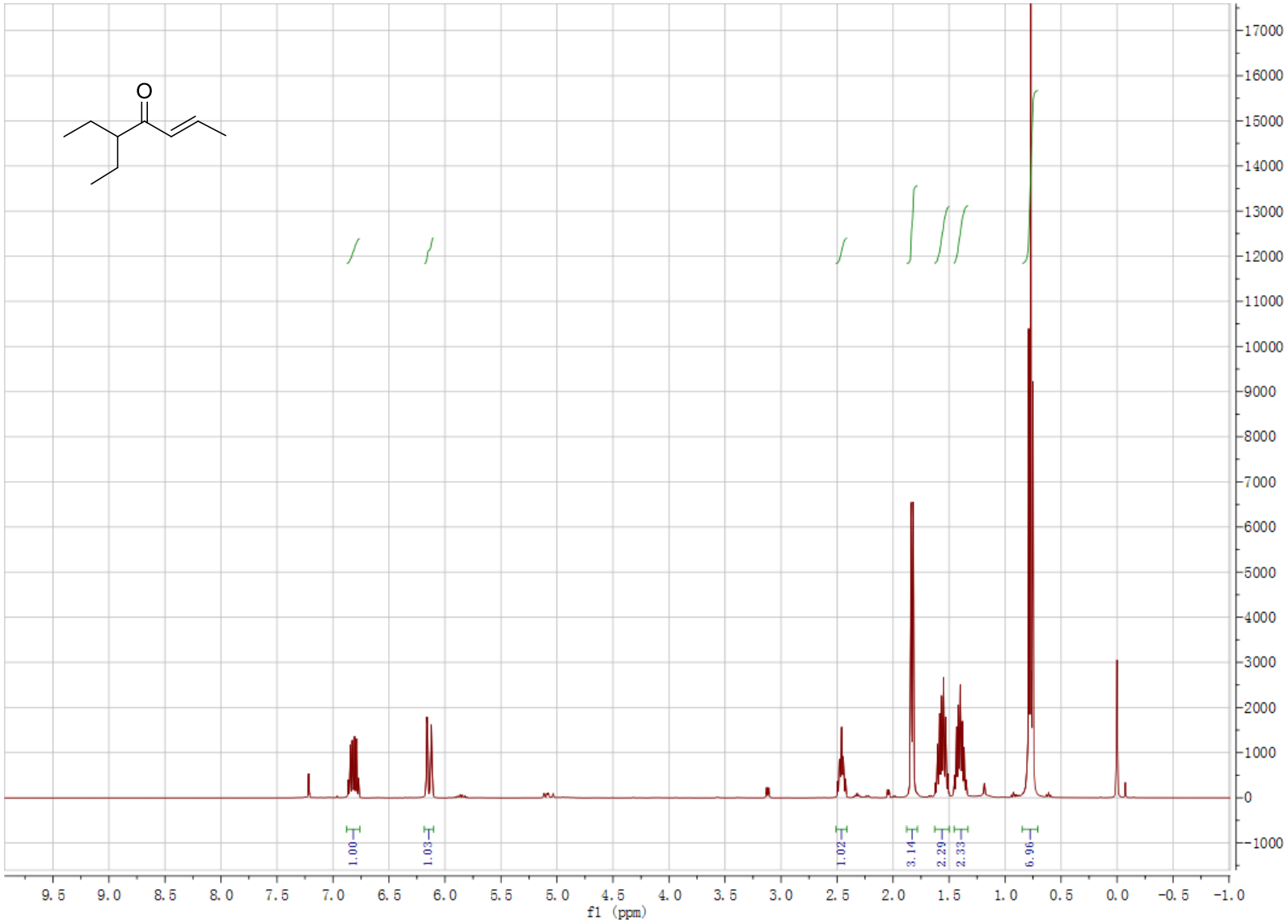

200.4
142.3
132.1
62.2
36.2
27.2
25.9
18.3
18.2
-5.4
TBSO
O
f1 (ppm)

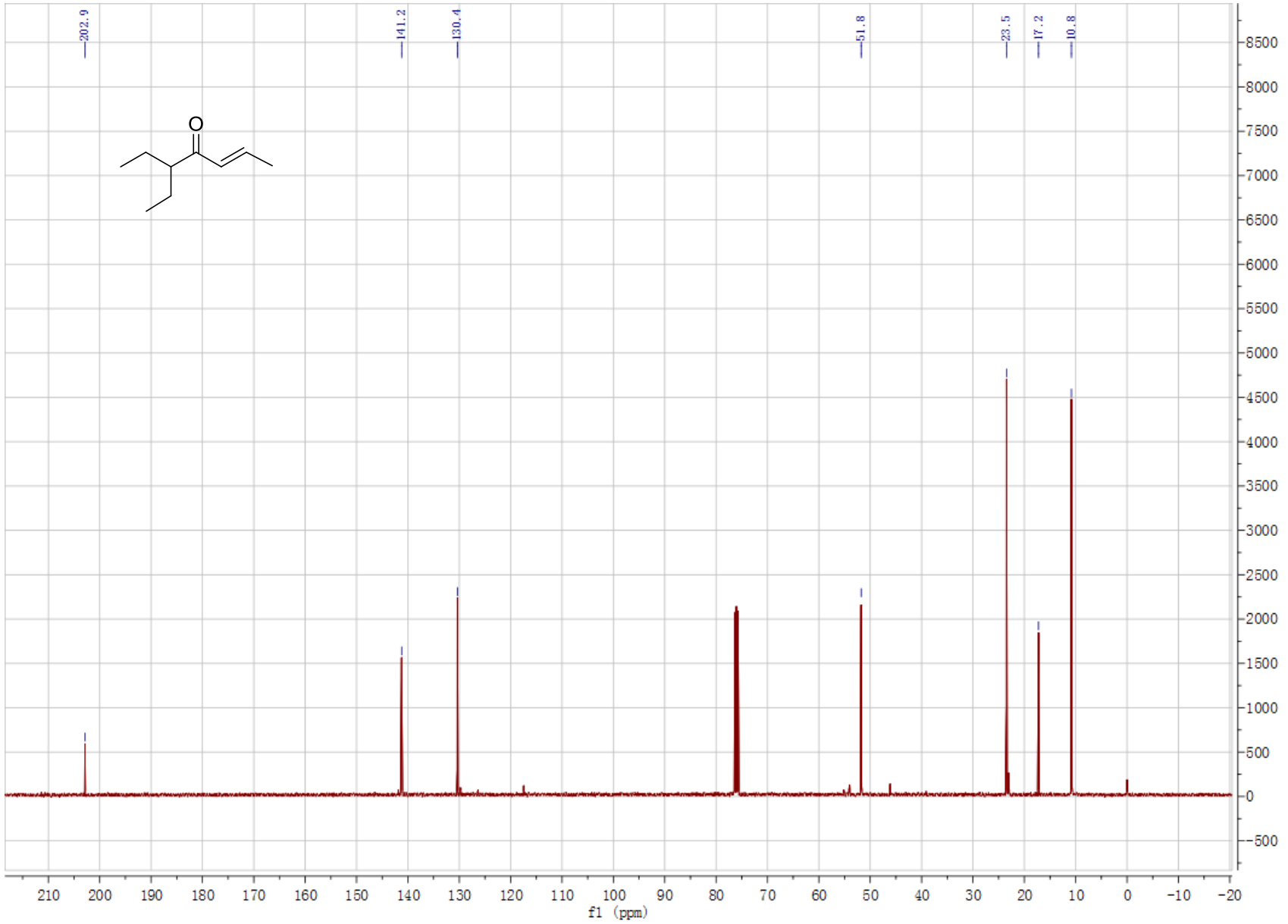
***(Z)*-5-ethylhept-2-en-4-one (4f-*Z*) (mixture with minor *E*-isomer)**



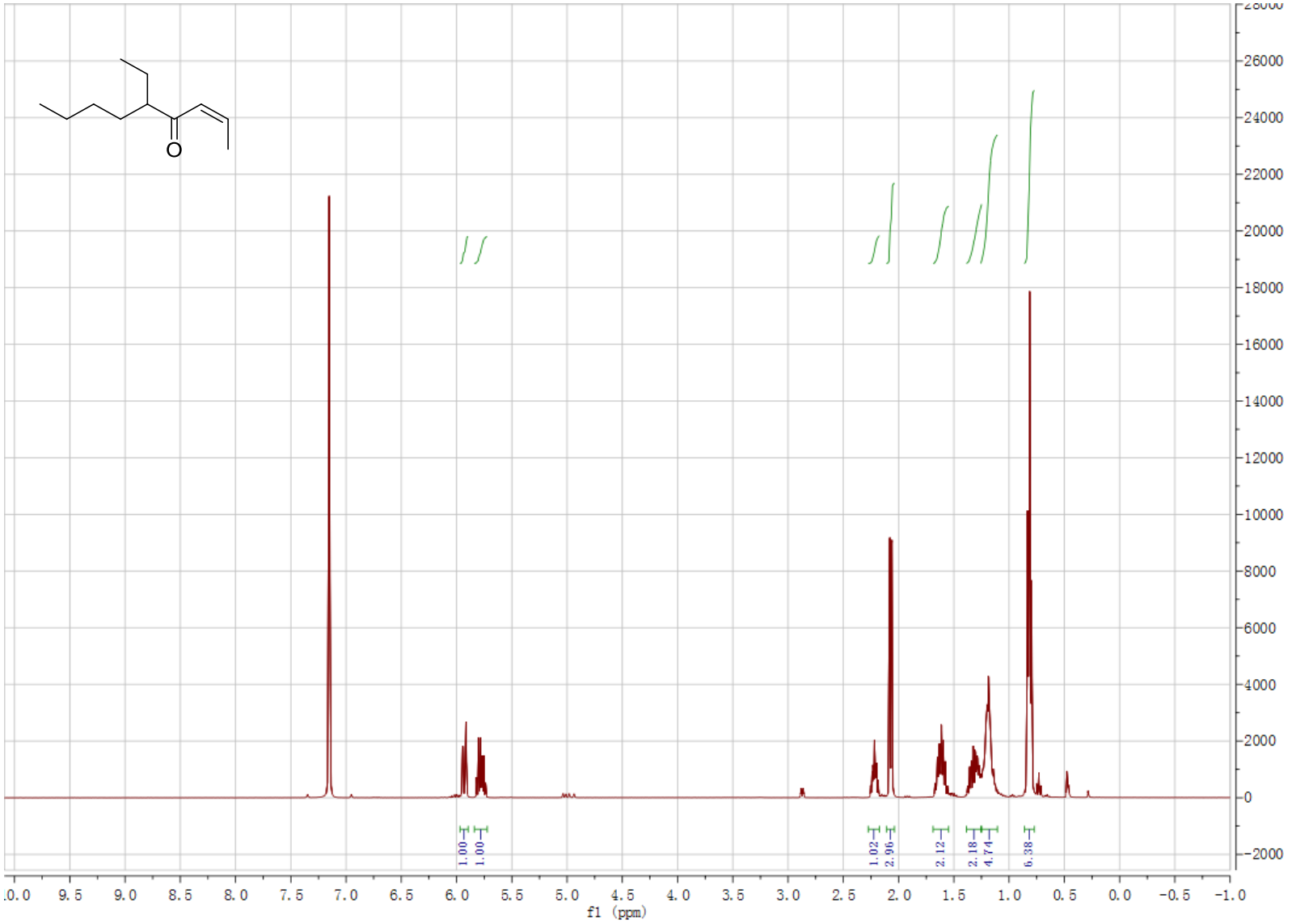

202.39
140.88
126.32
54.81
23.08
10.55
O
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

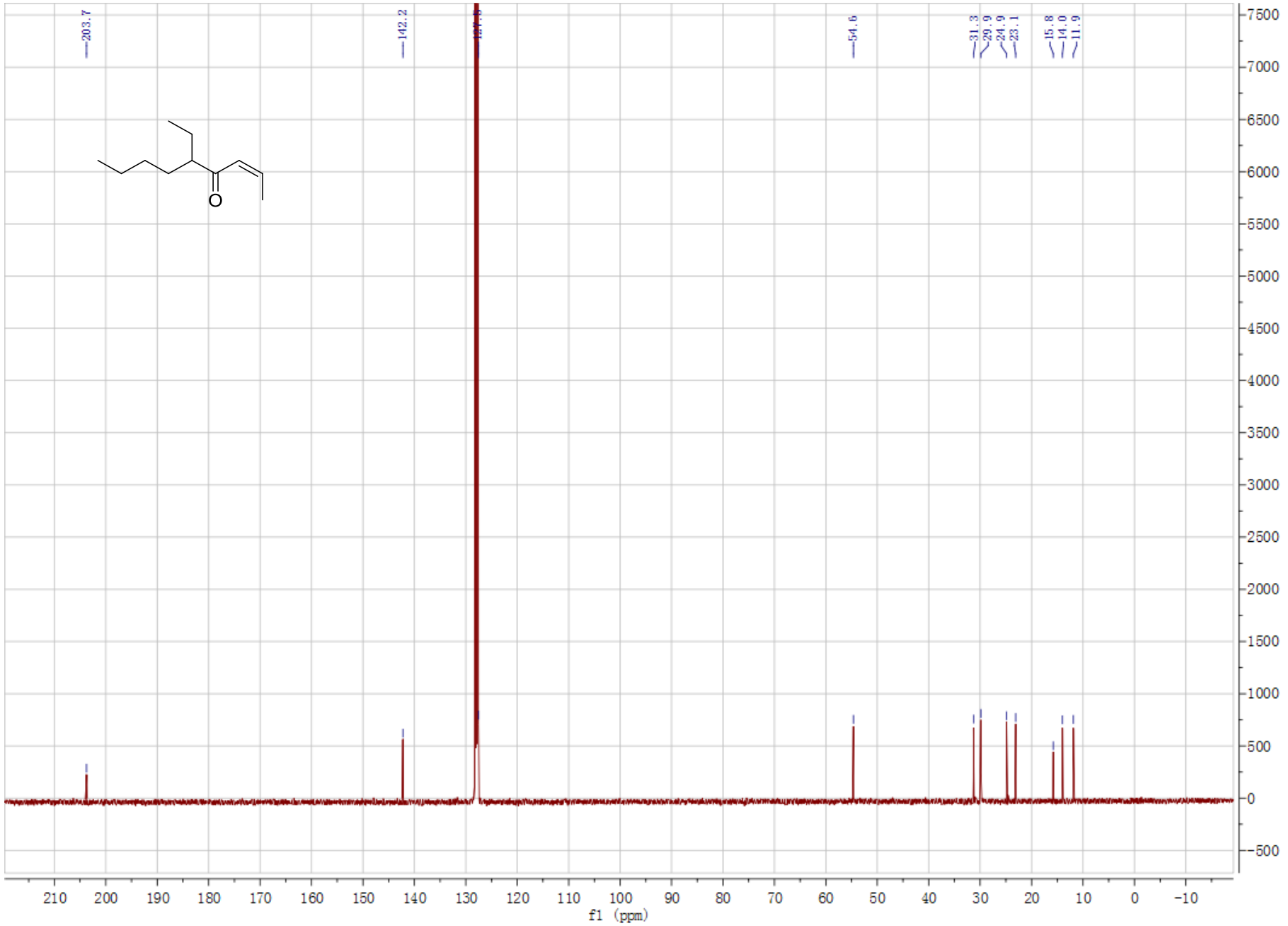
***(E)*-5-ethylhept-2-en-4-one (4f-*E*)**



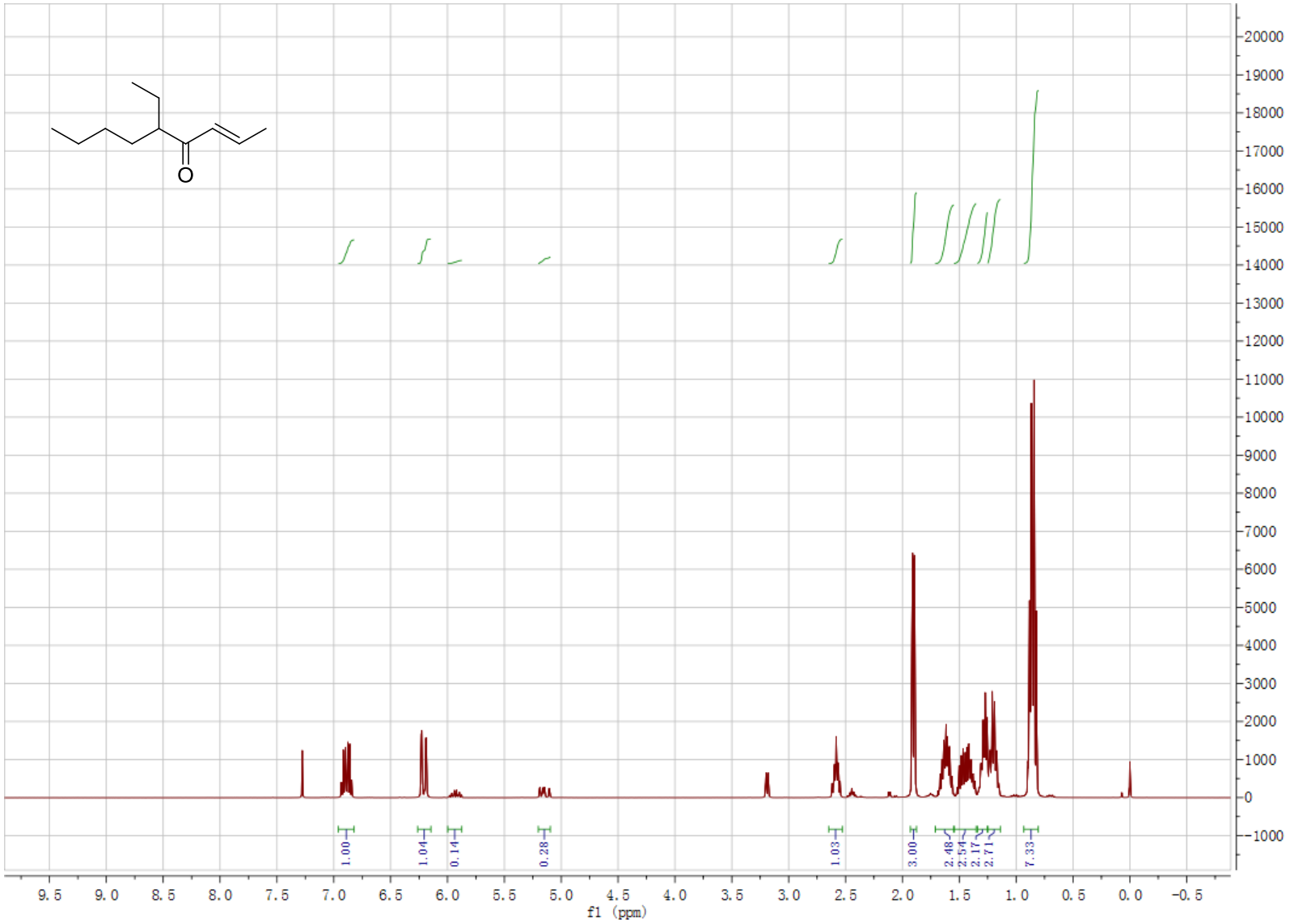

202.9
141.2
130.4
51.8
23.5
17.2
10.8
O
f1 (ppm)

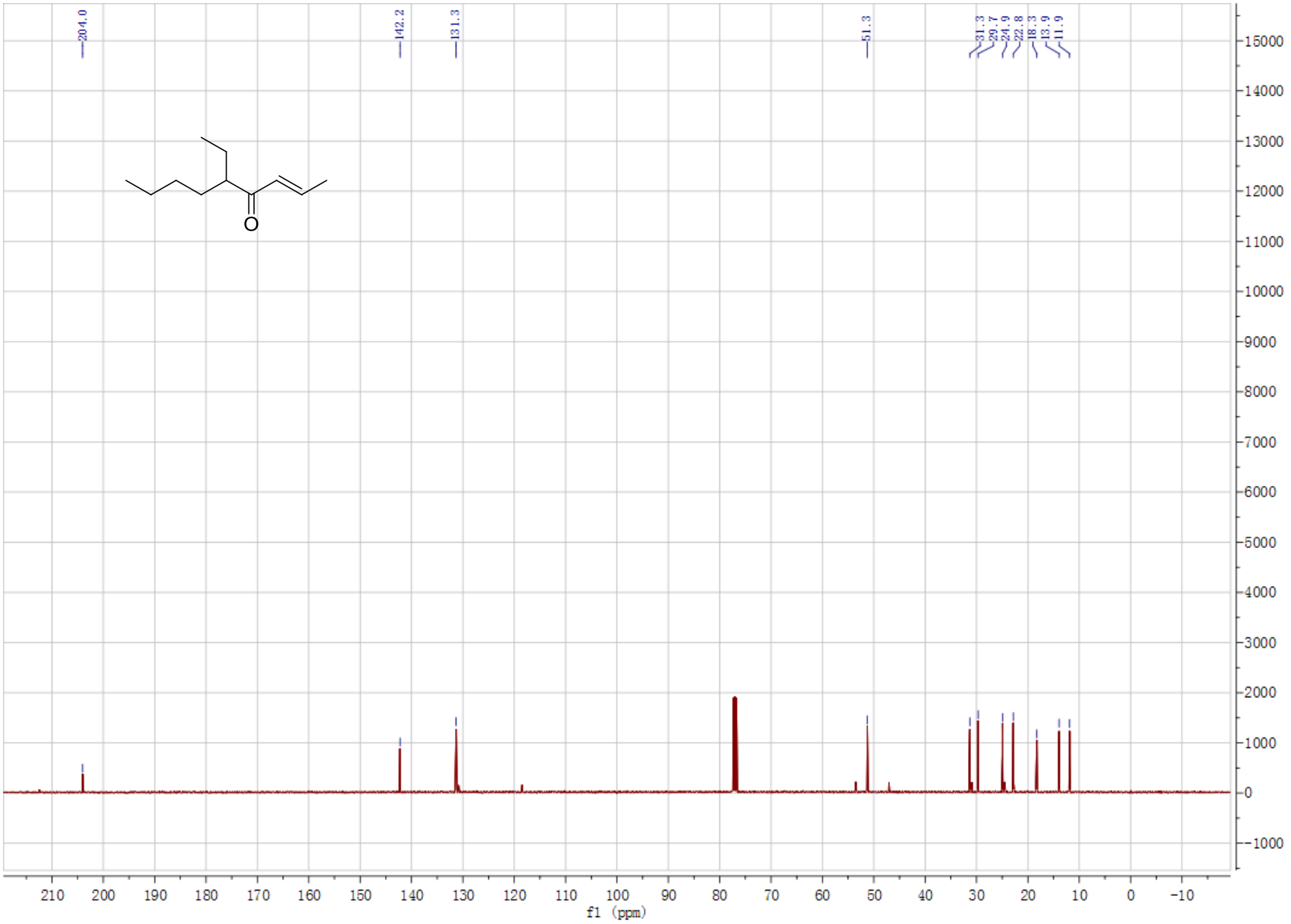
(*Z*)-5-ethylnon-2-en-4-one(4g-*Z*)



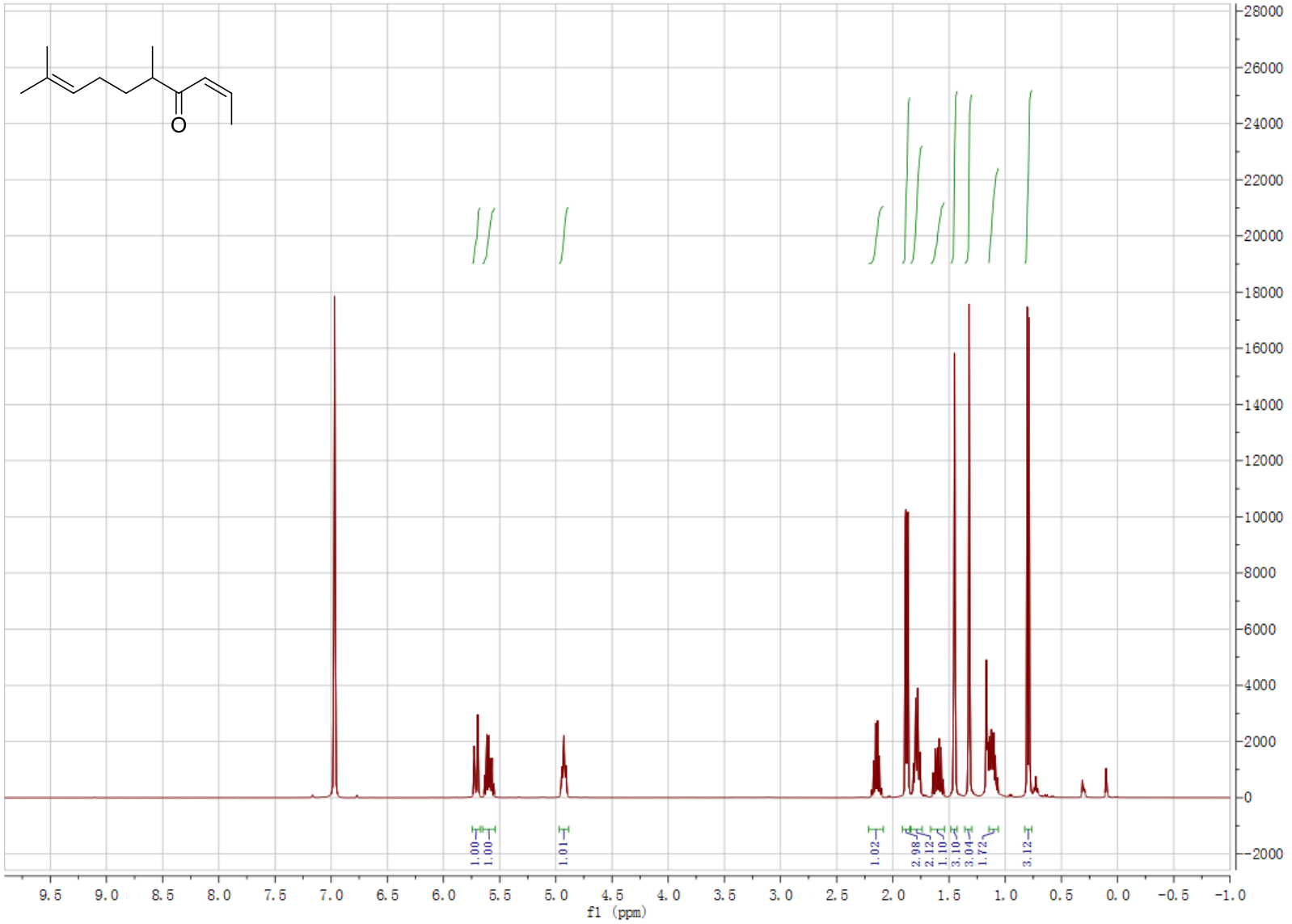

203.7
142.2
127.6
54.6
31.3
29.9
24.9
23.1
15.8
14.0
11.9
O
f1 (ppm)

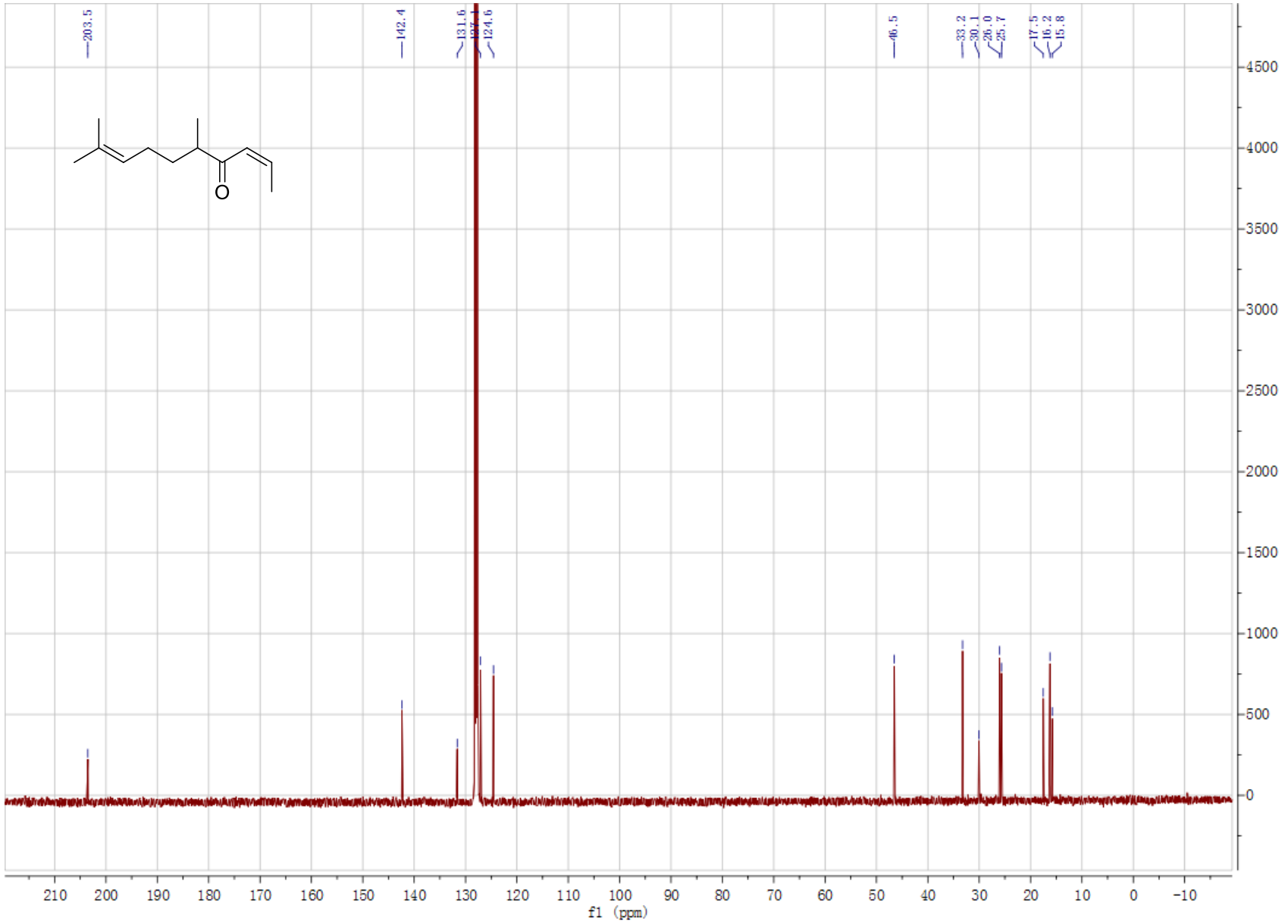
***(E)*-5-ethylnon-2-en-4-one(4g-*E*) (mixture with 3g)**



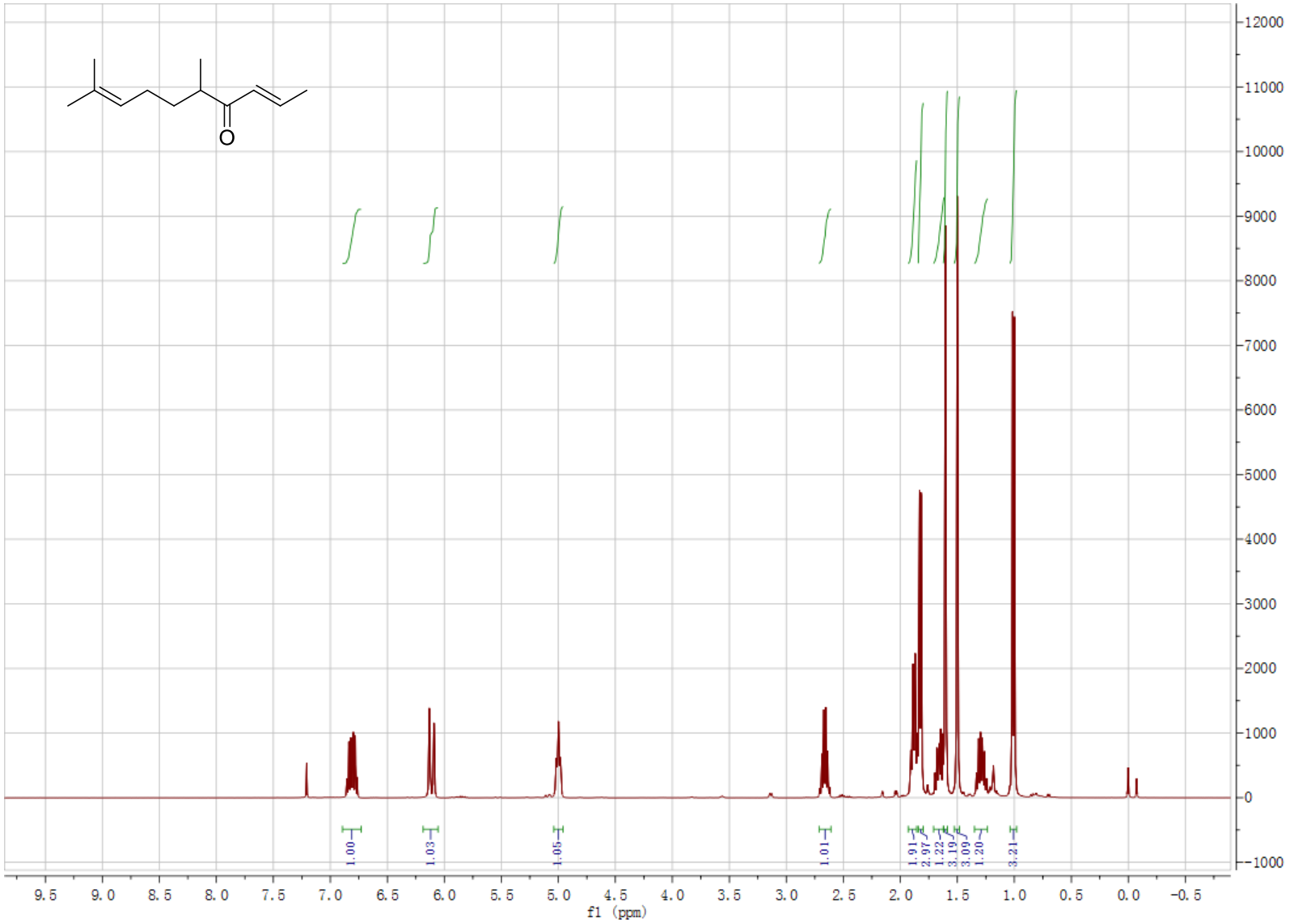

204.0
142.2
131.3
51.3
31.3
29.7
24.9
22.8
18.3
13.9
11.9
O
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

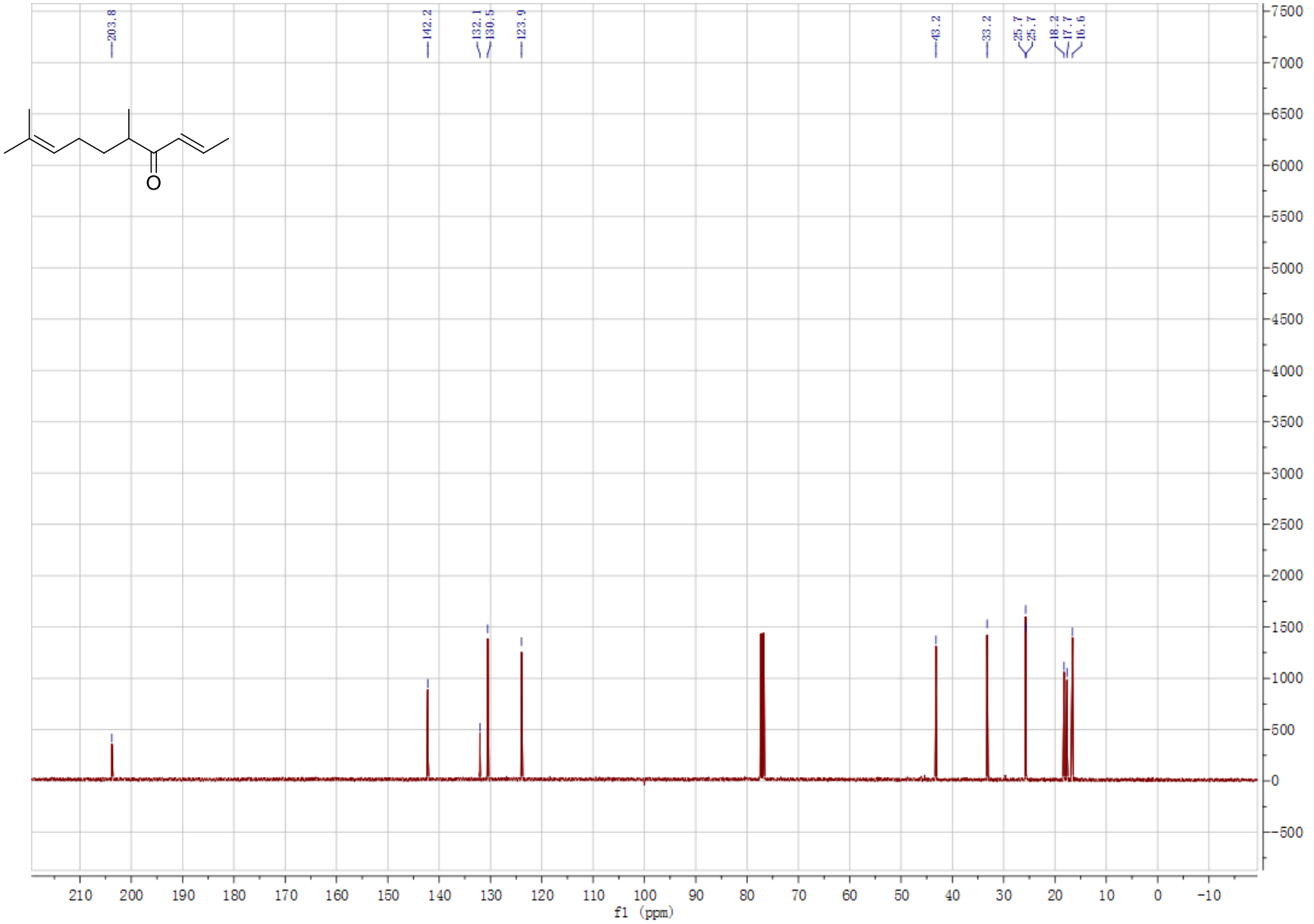
***(Z)*-5,9-dimethyldeca-2,8-dien-4-one (4h-*Z*)**



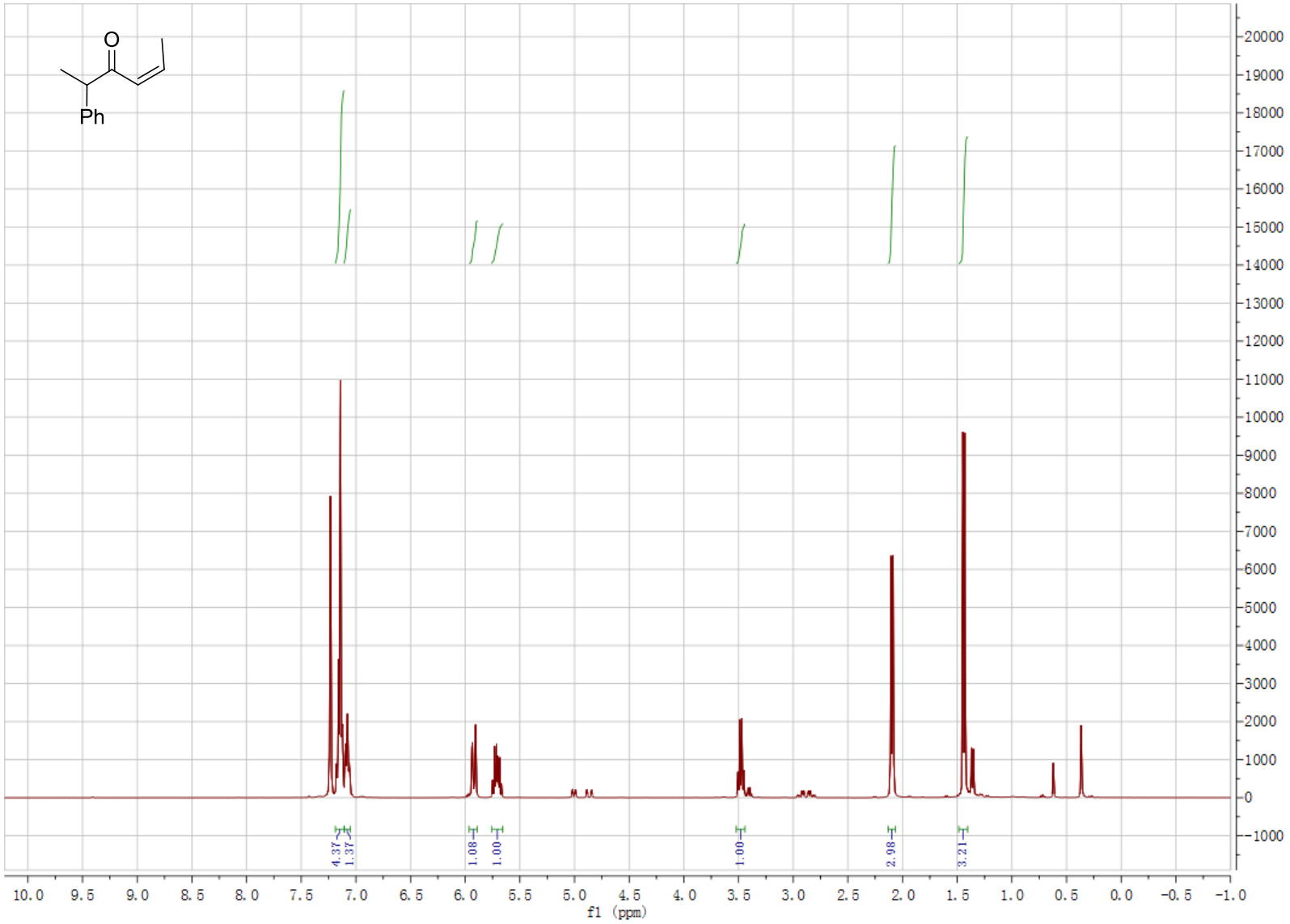

203.5
142.4
131.6
127.1
124.6
46.5
33.2
30.1
26.0
25.7
17.5
16.2
15.8
O
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

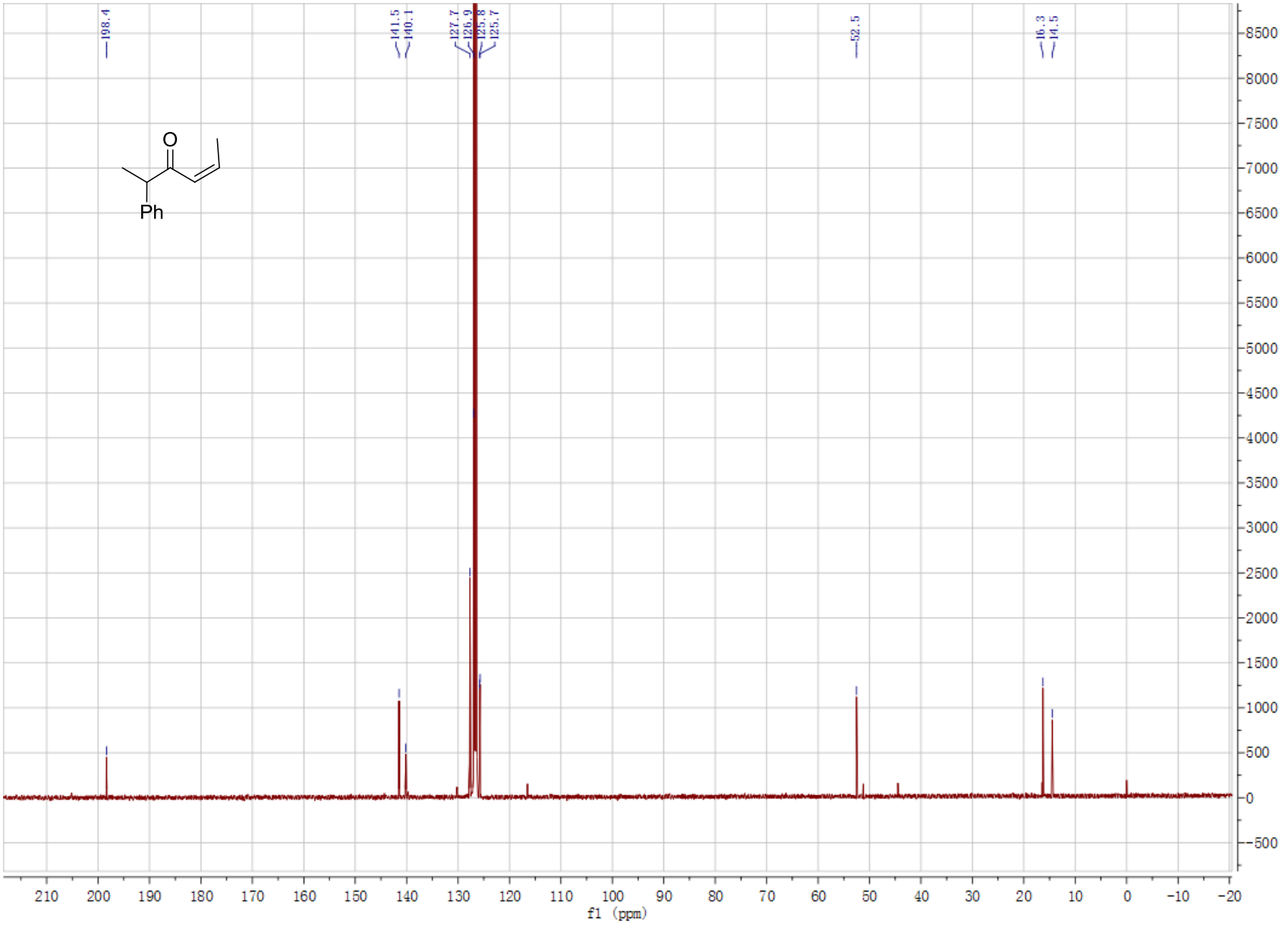
***(E)*-5,9-dimethyldeca-2,8-dien-4-one (4h-*E*)**



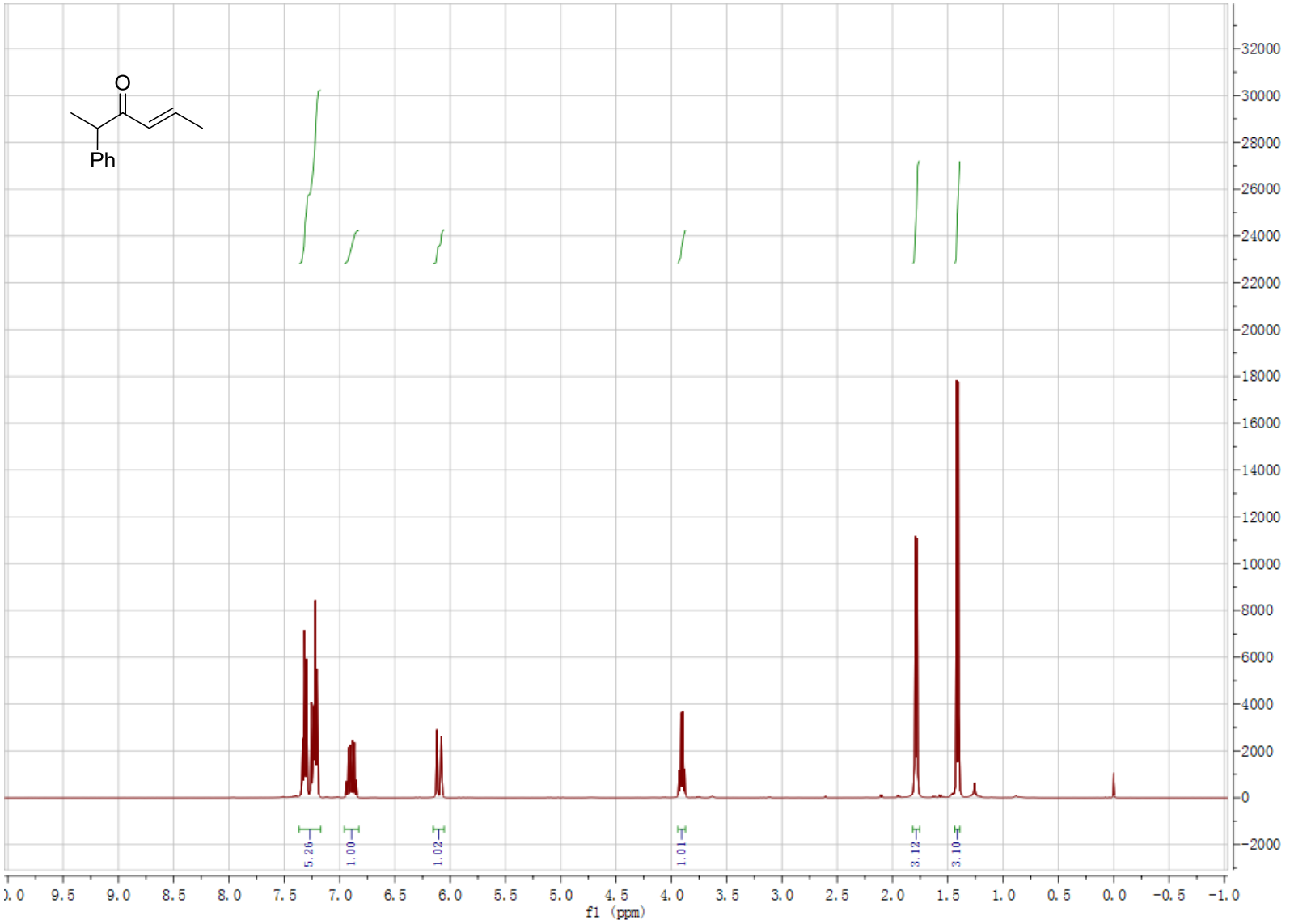

203.8
142.2
132.1
130.5
123.9
43.2
33.2
25.7
25.7
18.2
17.7
16.6
O
f1 (ppm)

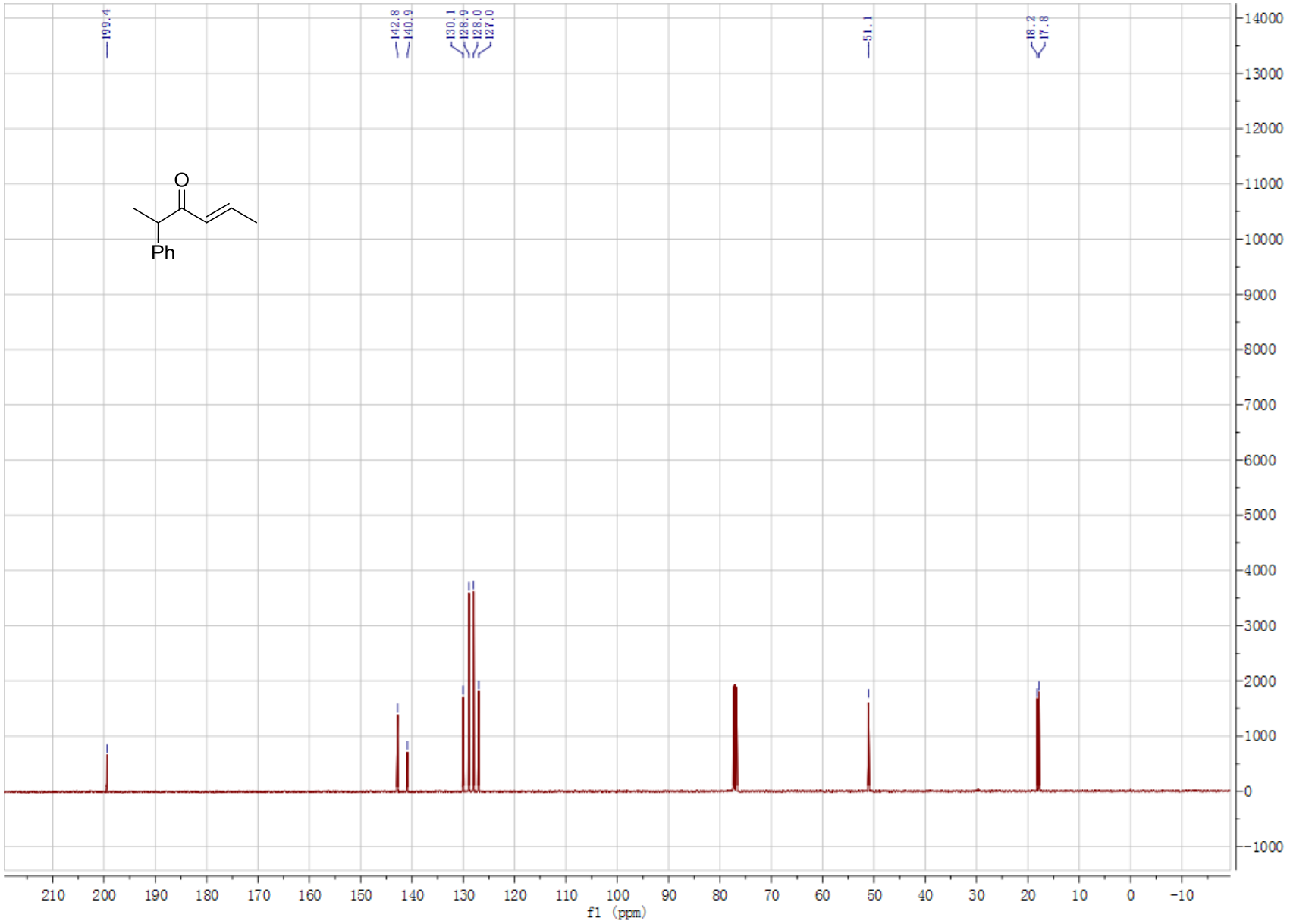
***(Z)*-2-phenylhex-4-en-3-one (4i-*Z*)**




198.4
141.5
140.1
127.7
126.9
125.8
125.7
52.5
16.3
14.5
O
Ph
f1 (ppm)

***(E)*-2-phenylhex-4-en-3-one (4i-*E*)**




199.4
142.8
140.9
130.1
128.9
128.0
127.0
51.1
18.2
17.8
O
Ph
f1 (ppm)