Supporting information

Access to (*E*)-δ-Vinyl-Homoallylic Alcohols/Ethers/Pyrazoles by Ring-opening Nucleophilic Substitution of cyclopropyl allylic alcohols

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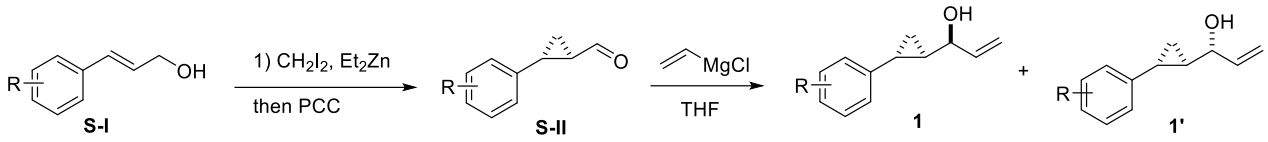
General information

All reactions were carried out using oven-dried tube with magnetic stirring under argon atmosphere unless otherwise noted. Anhydrous solvents were dried prior to use. Reagents were purchased from Energy Chemical and used without further purification. For column chromatography, 200-300 mesh silica gel was used. Thin layer chromatography (TLC) was performed on Silicycle 250μm silica gel 60Å plates. Visualization was accomplished with UV light (254 nm), Iodine, or Potassium Permanganate.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 MHz (300 MHz for ^{1}H; 282 MHz for ^{19}F; 75 MHz for ^{13}C) spectrometers at ambient temperature. The chemical shifts (δ) are given in parts per million relative to $CDCl_3$ (7.26 ppm for ^{1}H) or TMS (0 ppm for ^{1}H) and $CDCl_3$ (77.16 ppm for ^{13}C). Coupling constants (*J*) are reported in Hz, and multiplicity is described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, or combinations thereof. HRMS were performed on Agilent 6540 Q-TOF mass spectrometer (ESI).

All pyrazoles/alcohols **2/4** are commercially available, purchased from Energy Chemical and used directly without further purification. All known vinyl cyclopropyl alcohols **1** were prepared according to the reported literatures.[1] The configuration of **1p** was determined by comparing the NMR spectra with the reported literature.[2] All new compounds have been characterized by ^{1}H NMR, ^{13}C NMR and HRMS.

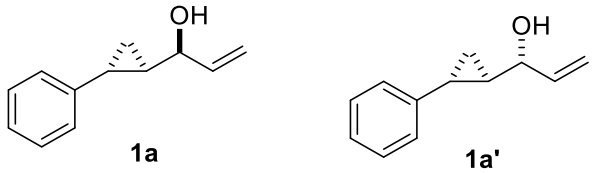
General procedure for the preparation of the substrates 1



To a dried 250 mL flask were added CH_2I_2 (20.0 mmol, 2.0 eq.) and CH_2Cl_2 (100 mL). After cooling to 0 °C, Et_2Zn (1 M in hexane, 12.5 mmol, 1.25 eq.) was added. The resulting mixture was stirred at this temperature for 30 min. To another flask were added compound **S-I** (10.0 mmol, 1.0 eq.) and CH_2Cl_2 (30 mL). After cooling to 0 °C, Et_2Zn (1 M in hexane, 12.5 mmol, 1.25 eq.) was added. The resulting mixture was stirred at this temperature for 30 min. This reaction mixture was then added to the reaction mixture in the 250 mL flask. After stirred at 0 °C for 30 min, the resulting mixture was allowed to warm to room temperature and then stirred for 18 h. Then, the reaction mixture was quenched with sat. aq. NH_4Cl and 1 M aq. HCl. The organic layer was separated. The aqueous layer was then extracted with CH_2Cl_2 (2*100 mL). The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was direct used without further purification. To a solution of compound (10.0 mmol) in CH_2Cl_2 (25 mL) was added PCC (15.0 mmol, 1.5 eq.) at room temperature under Ar atmosphere. After 1 h, the reaction mixture was filtered through a pad of Celite and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford aldehyde **S-II** as colorless oil.

To a flame dried flask was cooled to 0 °C and charged with compound **S-II** and dry THF (100 mL), the flask was backfilled with argon gas. Then, vinylmagnesium chloride (1.0 M in THF solution, 20.0 mmol, 2.0 eq.) was slowly added to the above solution of compound **S-II**. Then, the mixture was stirred at 0 °C for 1 h (monitored by TLC) and quenched with saturated aq. NH_4Cl (50 mL). The aqueous layer was extracted with EtOAc (50*3) and the organic phase was dried with Na_2SO_4, filtered and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel to give the diastereoisomer **1**/**1'** = 1:1. The new compounds as listed below:

1-(2-Phenylcyclopropyl)prop-2-en-1-ol (1a+1a')



The title compound was prepared from the general procedure A, 3-phenylprop-2-en-1-ol (1.34 g, 10.0 mmol, 1.0 eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1a** (696.4 mg, 40% yield over two steps) and **1a'** (696.0 mg, 40% yield over two steps) as colorless oil.

NMR data of **1a**:

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.00 (m, 5H), 6.12-5.87 (m, 1H), 5.28 (d, J = 17.2 Hz, 1H), 5.14 (d, J = 10.5 Hz, 1H), 3.76 (t, J = 6.6 Hz, 1H), 1.87 (dt, J = 8.7, 5.0 Hz, 1H), 1.78 (s, 1H), 1.40-1.27 (m, 1H), 1.12-0.94 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 139.4, 128.5, 126.0, 125.8, 115.2, 76.1, 28.9, 21.3, 13.0.

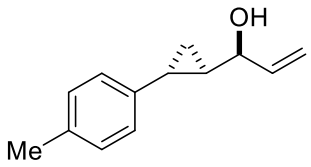
NMR data of **1a'**:

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-6.97 (m, 5H), 6.10-5.85 (m, 1H), 5.30 (d, J = 17.2 Hz, 1H), 5.15 (d, J = 10.5 Hz, 1H), 3.77 (t, J = 6.7 Hz, 1H), 1.96 (dt, J = 8.5, 5.1 Hz, 1H), 1.76 (s, 1H), 1.41-1.29 (m, 1H), 1.04-0.90 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 139.6, 128.5, 126.1, 125.8, 115.2, 76.1, 28.7, 20.5, 13.7.

HRMS (ESI) m/z calculated for $C_{12}H_{15}O$ $[M+H]^+$: 175.1117, found: 175.1119.

1-(2(-p-Tolyl)cyclopropyl)prop-2-en-1-ol (1b)



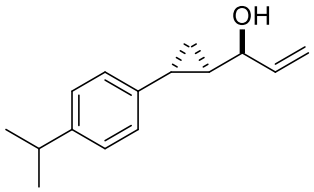
The title compound was prepared from the general procedure A, 3-(p-tolyl)prop-2-en-1-ol (1.48 g, 10.0 mmol, 1eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1b** (790.1 mg, 42% yield over two steps) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.08-5.85 (m, 1H), 5.25 (d, *J* = 17.3 Hz, 1H), 5.10 (d, *J* = 10.5 Hz, 1H), 3.69 (t, *J* = 6.7 Hz, 1H), 2.37 (s, 1H), 2.28 (s, 3H), 1.80 (dt, *J* = 9.5, 5.0 Hz, 1H), 1.33-1.21 (m, 1H), 1.07-0.88 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 139.2, 135.1, 129.0, 125.9, 114.9, 76.0, 28.4, 21.0, 20.1, 13.5.

HRMS (ESI) m/z calculated for $C_{13}H_{17}O$ $[M+H]^+$: 189.1274, found: 189.1273.

1-(2-(4-Isopropylphenyl)cyclopropyl)prop-2-en-1-ol (1c)



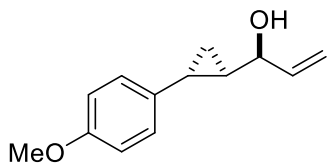
The title compound was prepared from the general procedure A, 3-(4-isopropylphenyl)prop-2-en-1-ol (1.76 g, 10.0 mmol, 1eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1c** (864.6 mg, 40% yield over two steps) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.04-5.80 (m, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.06 (d, *J* = 10.4 Hz, 1H), 3.67 (t, *J* = 6.8 Hz, 1H), 2.79 (p, *J* = 7.0 Hz, 1H), 1.78 (dt, *J* = 9.5, 5.1 Hz, 1H), 1.62 (s, 1H), 1.30-1.20 (m, 1H), 1.16 (s, 3H), 1.14 (s, 3H), 1.02-0.82 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5, 139.61, 139.57, 126.5, 126.1, 115.2, 76.3, 33.8, 28.6, 24.2, 20.2, 13.6.

HRMS (ESI) m/z calculated for $C_{15}H_{21}O$ $[M+H]^+$: 217.1587, found: 217.1580.

1-(2-(4-Methoxyphenyl)cyclopropyl)prop-2-en-1-ol (1d)



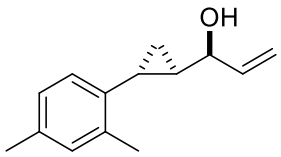
The title compound was prepared from the general procedure A, 3-(4-methoxyphenyl)prop-2-en-1-ol (1.64 g, 10.0 mmol, 1eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1d** (898.1 mg, 44% yield over two steps) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.08-5.88 (m, 1H), 5.27 (d, *J* = 17.3 Hz, 1H), 5.13 (d, *J* = 9.9 Hz, 1H), 3.80-3.69 (m, 1H), 3.76 (s, 3H), 2.00-1.87 (m, 1H), 1.87-1.76 (m, 1H), 1.33-1.16 (m, 1H), 1.07-0.80 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 139.6, 134.2, 127.2, 115.1, 113.9, 76.3, 55.4, 28.3, 19.8, 13.3.

HRMS (ESI) m/z calculated for $C_{13}H_{17}O_2$ $[M+H]^+$: 205.1223, found: 205.1225.

1-(2-(2,4-Dimethylphenyl)cyclopropyl)prop-2-en-1-ol (1e)



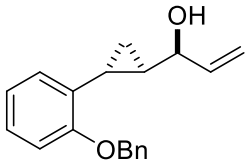
The title compound was prepared from the general procedure A, 3-(2,4-dimethylphenyl)prop-2-en-1-ol (1.62 g, 10.0 mmol, 1eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1e** (849.0 mg, 42% yield over two steps) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02-6.64 (m, 3H), 6.09-5.76 (m, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 5.04 (d, *J* = 10.5 Hz, 1H), 3.66 (t, *J* = 6.9 Hz, 1H), 2.38-2.03 (m, 1H), 2.25 (s, 3H), 2.17 (s, 3H),1.74 (d, *J* = 8.5 Hz, 1H), 1.28-1.07 (m, 1H), 0.99-0.69 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.8, 137.3, 136.7, 135.4, 130.6, 126.5, 125.6, 115.1, 76.3, 26.9, 20.9, 19.8, 18.1, 11.8.

HRMS (ESI) m/z calculated for $C_{14}H_{19}O$ $[M+H]^+$: 203.1430, found: 203.1437.

1-(2-(2-(Benzyloxy)phenyl)cyclopropyl)prop-2-en-1-ol (1f)



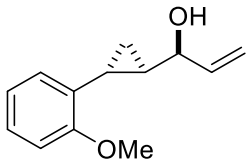
The title compound was prepared from the general procedure A, 3-(2-(benzyloxy)phenyl)prop-2-en-1-ol (2.40 g, 10.0 mmol, 1eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1f** (1.15 g, 41% yield over two steps) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.22 (m, 5H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.91-6.75 (m, 3H), 5.86-5.68 (m, 1H), 5.18-4.91 (m, 4H), 3.85 (t, *J* = 6.2 Hz, 1H), 2.12-1.84 (m, 2H), 1.24-1.09 (m, 1H), 1.02-0.81 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 138.9, 137.1, 130.6, 128.7, 128.2, 127.7, 126.9, 126.4, 121.0, 115.0, 111.7, 74.8, 70.4, 27.7, 14.3, 11.0.

HRMS (ESI) m/z calculated for $C_{19}H_{21}O_2$ $[M+H]^+$: 281.1536, found: 281.1539.

1-(2-(2-Methoxyphenyl)cyclopropyl)prop-2-en-1-ol (1g)



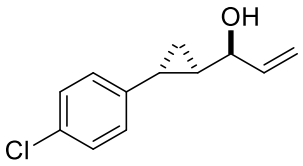
The title compound was prepared from the general procedure A, 3-(2-methoxyphenyl)prop-2-en-1-ol (1.64 g, 10.0 mmol, 1eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1g** (714.4 mg, 35% yield over two steps) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15-7.02 (m, 1H), 6.91-6.71 (m, 3H), 5.96-5.73 (m, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.07 (d, *J* = 10.3 Hz, 1H), 3.94 (t, *J* = 6.3 Hz, 1H), 3.78 (s, 3H), 2.28 (s, 1H), 1.96 (dt, *J* = 8.8, 5.5 Hz, 1H), 1.24-1.11 (m, 1H), 0.99-0.84 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3, 138.9, 130.2, 127.0, 126.5, 120.7, 115.1, 110.2, 74.7, 55.5, 27.2, 14.1, 11.1.

HRMS (ESI) m/z calculated for $C_{13}H_{17}O_2$ $[M+H]^+$: 205.1223, found: 205.1225.

1-(2-(4-Chlorophenyl)cyclopropyl)prop-2-en-1-ol (1h)



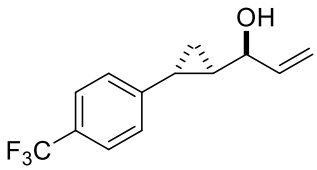
The title compound was prepared from the general procedure A, 3-(4-chlorophenyl)prop-2-en-1-ol (1.68 g, 10.0 mmol, 1eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1h** (811.5 mg, 39% yield over two steps) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.17 (m, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.07-5.88 (m, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.17 (d, *J* = 10.4 Hz, 1H), 3.78 (t, *J* = 6.7 Hz, 1H), 1.95 (dt, *J* = 9.3, 5.0 Hz, 1H), 1.67 (s, 1H), 1.34-1.24 (m, 1H), 1.05-0.86 (m, 2H).

^{13}C NMR (75 MHz, CDCl3) δ 141.1, 139.3, 131.4, 128.5, 127.4, 115.4, 75.9, 28.9, 20.8, 13.0.

HRMS (ESI) m/z calculated for $C_{12}H_{14}ClO$ $[M+H]+$: 209.0728, found: 209.0723.

1-(2-(4-(Trifluoromethyl)phenyl)cyclopropyl)prop-2-en-1-ol (1i)



The title compound was prepared from the general procedure A, 3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (2.02 g, 1eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1i** (798.9 mg, 33% yield over two steps) as colorless oil.

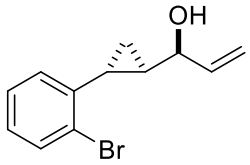
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.11-5.86 (m, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.16 (d, *J* = 10.4 Hz, 1H), 3.83 (t, *J* = 6.6 Hz, 1H), 1.93 (dt, *J* = 9.4, 5.0 Hz, 1H), 1.77 (s, 1H), 1.46-1.30 (m, 1H), 1.22-0.99 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.7, 139.3, 128.1 (q, *J* = 32.4 Hz), 126.2, 125.40 (q, *J* = 3.8 Hz), 122.6, 115.6, 75.6, 29.4, 20.3, 14.2.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.3.

HRMS (ESI) m/z calculated for $C_{13}H_{14}F_3O$ $[M+H]^+$: 243.0991, found: 243.0994.

1-(2-(2-Bromophenyl)cyclopropyl)prop-2-en-1-ol (1j)



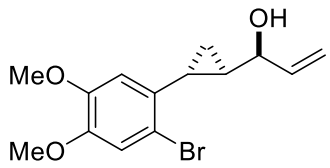
The title compound was prepared from the general procedure A, 3-(2-bromophenyl)prop-2-en-1-ol (2.12 g, 10.0 mmol, 1eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1j** (806.4 mg, 32% yield over two steps) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.36-6.80 (m, 3H), 6.24-5.85 (m, 1H), 5.32 (d, *J* = 17.2 Hz, 1H), 5.16 (d, *J* = 10.5 Hz, 1H), 3.96 (t, *J* = 6.3 Hz, 1H), 2.39-1.90 (m, 2H), 1.42-1.19 (m, 1H), 1.19-0.89 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0, 139.4, 132.6, 127.5, 127.4, 126.8, 125.8, 115.3, 75.0, 28.2, 20.8, 12.2.

HRMS (ESI) m/z calculated for $C_{12}H_{14}BrO$ $[M+H]^+$: 253.0223, found: 253.0227.

1-(2-(2-Bromo-4,5-dimethoxyphenyl)cyclopropyl)prop-2-en-1-ol (1k)



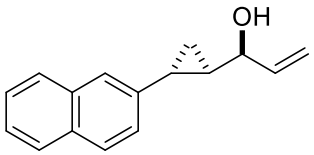
The title compound was prepared from the general procedure A, 3-(2-bromo-4,5-dimethoxyphenyl)prop-2-en-1-ol (2.72 g, 10.0 mmol, 1eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1k** (1.06 g, 34% yield over two steps) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.45 (s, 1H), 6.12-5.94 (m, 1H), 5.32 (d, *J* = 17.2 Hz, 1H), 5.17 (d, *J* = 10.5 Hz, 1H), 3.97 (t, *J* = 6.3 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.11 (dt, *J* = 8.5, 5.2 Hz, 1H), 2.01 (s, 1H), 1.32-1.20 (m, 1H), 1.15-1.02 (m, 1H), 1.01-0.90 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 147.9, 139.4, 132.9, 115.6, 115.5, 115.3, 110.1, 74.9, 56.3, 56.1, 28.0, 20.5, 12.0.

HRMS (ESI) m/z calculated for $C_{14}H_{18}BrO_3$ $[M+H]^+$: 313.0434, found: 313.0437.

1-(2-(Naphthalen-2-yl)cyclopropyl)prop-2-en-1-ol (1l)



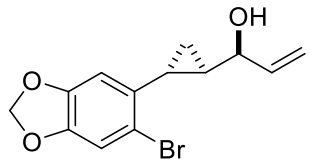
The title compound was prepared from the general procedure A, 3-(naphthalen-2-yl)prop-2-en-1-ol (1.84 g, 10.0 mmol, 1eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1l** (851.7 mg, 38% yield over two steps) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.68 (m, 3H), 7.56-7.34 (m, 3H), 7.17 (d, *J* = 8.5 Hz, 1H), 6.11-5.91 (m, 1H), 5.30 (d, *J* = 16.3 Hz, 1H), 5.15 (d, *J* = 10.8 Hz, 1H), 3.80 (t, *J* = 6.7 Hz, 1H), 2.09-1.98 (m, 1H), 1.86 (s, 1H), 1.50-1.35 (m, 1H), 1.21-1.04 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.8, 139.5, 133.6, 132.1, 128.1, 127.7, 127.4, 126.2, 125.2, 124.9, 124.2, 115.3, 76.1, 28.8, 20.7, 13.7.

HRMS (ESI) m/z calculated for $C_{16}H_{17}O$ $[M+H]^+$: 225.1274, found: 225.1279.

1-(2-(6-Bromobenzo[d][1,3]dioxol-5-yl)cyclopropyl)prop-2-en-1-ol (1m)



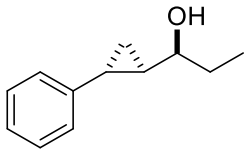
The title compound was prepared from the general procedure A, 3-(6-bromobenzo[d][1,3]dioxol-5-yl)prop-2-en-1-ol (2.56 g, 10.0 mmol, 1eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1m** (1.27 g, 43% yield over two steps) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.46 (s, 1H), 6.07-5.92 (m, 1H), 5.93 (s, 2H), 5.32 (dt, *J* = 17.3, 1.5 Hz, 1H), 5.17 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.04-3.86 (m, 1H), 2.09 (dt, *J* = 8.8, 5.2 Hz, 1H), 1.81 (d, *J* = 4.4 Hz, 1H), 1.30-1.17 (m, 1H), 1.14-1.01 (m, 1H), 0.95-0.84 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.5, 146.6, 139.3, 134.2, 115.9, 115.4, 112.7, 107.2, 101.7, 75.0, 28.1, 20.9, 12.1.

HRMS (ESI) m/z calculated for $C_{13}H_{14}BrO_3$ $[M+H]^+$: 297.0121, found: 297.0118.

1-(2-Phenylcyclopropyl)propan-1-ol (1p)



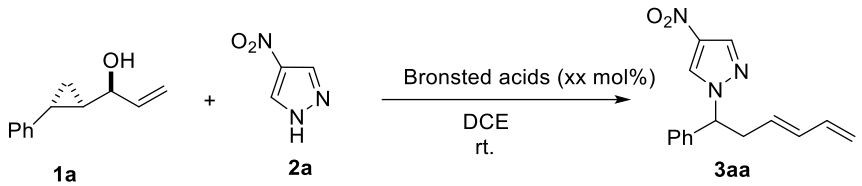
The title compound was prepared from the general procedure A, 3-phenylprop-2-en-1-ol (1.34 g, 10.0 mmol, 1eq.), CH_2I_2 (5.36 g, 20.0 mmol, 2.0 eq.), Et_2Zn (1 M in hexane, 12.5 mL, 1.25 eq.), vinylmagnesium chloride (1.0 M in THF, 20.0 mL, 2eq.) was used. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1p** (845.4 mg, 48% yield over two steps) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.21 (m, 2H), 7.20-7.11 (m, 1H), 7.11-7.00 (m, 2H), 3.08 (dt, *J* = 8.1, 6.3 Hz, 1H), 1.82 (dt, *J* = 9.2, 5.0 Hz, 1H), 1.74-1.61 (m, 3H), 1.30-1.17 (m, 1H), 1.06-0.91 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 128.5, 125.9, 125.7, 77.2, 30.4, 29.5, 21.3, 13.3, 10.3.

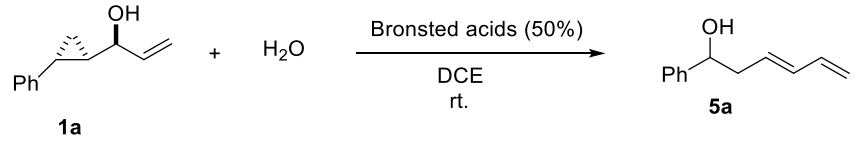
The NMR data was consistent with the reported literture.[2]

Table S1. Screening of the Bronsted acids to **3aa**



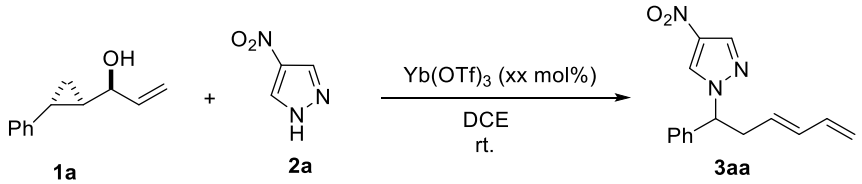
entry	Cat. (mol%)	Yield (%)
1	TfOH (1eq.)	15%
2	TfOH(50 mol%)	trace
3	HBr (50 mol%)	trace
4	AcOH (50 mol%)	0%
5	$PhCO_2H$ (50 mol%)	0%
6	TsOH (50 mol%)	50%
7	TsOH (1eq.)	61%
8	TFA (50 mol%)	45%

Table S2. Screening of the Bronsted acids to **5a**



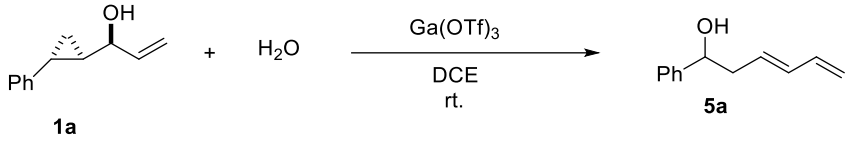
entry	Cat. (mol%)	Yield (%)
1	TfOH (1eq.)	55%
2	TfOH(50 mol%)	30%
3	HBr (50 mol%)	12%
4	AcOH (50 mol%)	trace
5	$PhCO_2H$ (50 mol%)	trace
6	TsOH (1 eq.)	51
7	TFA (1 eq.)	46

Table S3. Testing of the loading of catalyst for the synthesis of **3aa**



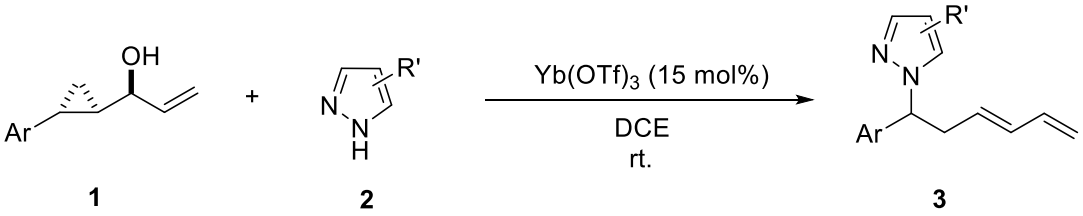
entry	$Yb(OTf)_3$ (xx mol%)	Yield (%)
1	10 mol%, 24 h	80
2	15 mol%, 24 h	82
3	20 mol%, 12 h	82
4	50 mol%, 6 h	82

Table S4. Testing of the loading of catalyst for the synthesis of **5a**



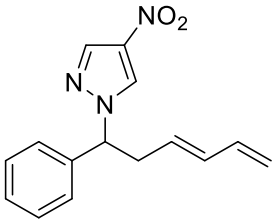
entry	$Ga(OTf)_3$ (xx mol%)	Yield of **5a** (%)
1	10 mol%, 24 h	20%
2	20 mol%, 24 h	42%
3	30 mol%, 24 h	65%
4	50 mol%, 12 h	65%
5	60 mol%, 12 h	64%

General procedure B for synthesis of 3aa-3na, 3ab-3aj



General procedure B: A 10 mL dry tube equipped with a stir bar was charged with allylic alcohols **1** (0.1 mmol, 1.0 eq.), pyrazoles **2** (0.15 mmol, 1.5 eq.), $Yb(OTf)_3$ (15 mol%.) and dry DCE (2.0 mL). The reaction mixture was stirred at room temperature for 12 hours. After completion of the reaction, the reaction mixture was concentrated under reduced pressure, then 2.0 ml of water was added, and the reaction solution was extracted with ethyl acetate (3 x 5 mL), the combined organic layers were dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. The remaining residue was purified by column chromatography on silica gel to afford the corresponding products (**3aa-3na**, **3ab-3aj**).

(E)-4-Nitro-1-(1-phenylhexa-3,5-dien-1-yl)-1H-pyrazole (3aa)



The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3aa** (22.1 mg, 82%

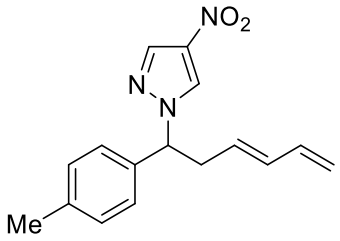
yield) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (s, 1H), 8.02 (s, 1H), 7.38-7.21 (m, 5H), 6.23-5.95 (m, 2H), 5.42 (dt, *J* = 14.3, 7.1 Hz, 1H), 5.23 (t, 1H), 5.14-4.88 (m, 2H), 3.17 (dt, *J* = 15.6, 8.1 Hz, 1H), 2.89 (dt, *J* = 14.2, 6.8 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.9, 136.3, 135.9, 135.8, 135.1, 129.3, 129.1, 128.1, 127.9, 127.2, 117.4, 67.8, 38.0.

HRMS (ESI) m/z calculated for $C_{15}H_{16}N_3O_2$ $[M+H]^+$: 270.1237, found: 270.1238.

(E)-4-Nitro-1-(1-(p-tolyl)hexa-3,5-dien-1-yl)-1H-pyrazole (3ba)



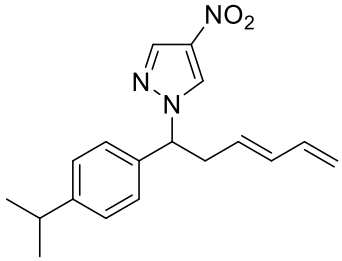
The title compound was prepared from **1b** (18.8 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3ba** (22.7 mg, 80% yield) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.05 (s, 1H), 7.26-7.16 (m, 4H), 6.33-6.01 (m, 2H), 5.48 (dt, *J* = 14.4, 7.2 Hz, 1H), 5.27 (t, 1H), 5.12 (d, *J* = 16.1 Hz, 1H), 5.03 (d, *J* = 10.4 Hz, 1H), 3.22 (dt, *J* = 15.1, 8.0 Hz, 1H), 3.03-2.88 (m, 1H), 2.35 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 136.4, 135.9, 135.0, 134.8, 130.0, 128.1, 127.9, 127.2, 117.4, 67.5, 37.9, 21.3.

HRMS (ESI) m/z calculated for $C_{16}H_{18}N_3O_2$ $[M+H]^+$: 280.1394, found: 280.1390.

(E)-1-(1-(4-Isopropylphenyl)hexa-3,5-dien-1-yl)-4-nitro-1H-pyrazole (3ca)



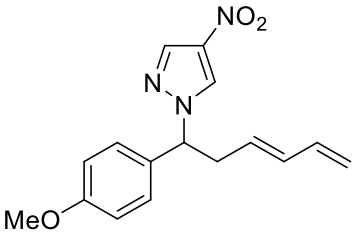
The title compound was prepared from **1c** (21.6 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:15) furnished **3ca** (24.0 mg, 77% yield) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.2 Hz, 2H), 7.17 (s, 4H), 6.26-5.93 (m, 2H), 5.51-5.32 (m, 1H), 5.21 (t, 1H), 5.04 (d, *J* = 16.2 Hz, 1H), 4.95 (d, *J* = 10.3 Hz, 1H), 3.15 (dt, *J* = 15.7, 8.1 Hz, 1H), 2.97-2.75 (m, 2H), 1.17 (d, *J* = 7.0 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 136.4, 135.8, 135.2, 135.0, 128.1, 128.0, 127.34, 127.29, 127.2, 117.3, 67.6, 37.9, 33.9, 24.0.

HRMS (ESI) m/z calculated for $C_{18}H_{22}N_3O_2$ $[M+H]^+$: 312.1707, found: 312.1710.

(E)-1-(1-(4-Methoxyphenyl)hexa-3,5-dien-1-yl)-4-nitro-1H-pyrazole (3da)



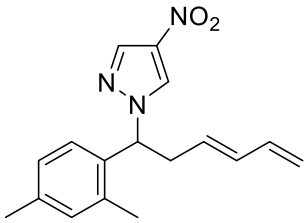
The title compound was prepared from **1d** (20.4 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3da** (21.2 mg, 71% yield) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.04 (s, 1H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.34-5.98 (m, 2H), 5.48 (dt, *J* = 14.3, 7.1 Hz, 1H), 5.25 (t, *J* = 7.7 Hz, 1H), 5.12 (d, *J* = 16.5 Hz, 1H), 5.03 (d, *J* = 10.4 Hz, 1H), 3.81 (s, 3H), 3.22 (dt, *J* = 15.2, 7.9 Hz, 1H), 2.94 (dt, *J* = 14.3, 7.0 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 136.4, 135.9, 135.0, 129.7, 128.8, 128.7, 128.1, 127.8, 117.4, 114.6, 67.2, 55.5, 38.0.

HRMS (ESI) m/z calculated for $C_{16}H_{18}N_3O_3$ $[M+H]^+$: 300.1343, found: 300.1348.

(E)-1-(1-(2,4-Dimethylphenyl)hexa-3,5-dien-1-yl)-4-nitro-1H-pyrazole (3ea)



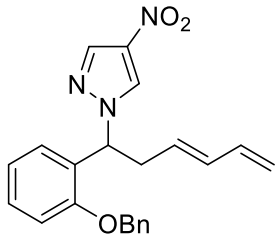
The title compound was prepared from **1e** (20.2 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3ea** (21.4 mg, 72% yield) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.93 (s, 1H), 7.33-7.24 (m, 1H), 7.13-7.01 (m, 2H), 6.32-6.04 (m, 2H), 5.64-5.45 (m, 2H), 5.13 (d, *J* = 15.6 Hz, 1H), 5.03 (d, *J* = 8.9 Hz, 1H), 3.18 (dt, *J* = 15.3, 7.8 Hz, 1H), 2.93 (dt, *J* = 14.5, 7.0 Hz, 1H), 2.32 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 136.5, 136.4, 135.7, 134.9, 132.3, 132.2, 128.2, 127.7, 127.6, 126.3, 117.3, 63.5, 37.7, 21.2, 19.3.

HRMS (ESI) m/z calculated for $C_{17}H_{20}N_3O_2$ $[M+H]^+$: 298.1550, found: 298.1557.

(E)-1-(1-(2-(Benzyloxy)phenyl)hexa-3,5-dien-1-yl)-4-nitro-1H-pyrazole (3fa)



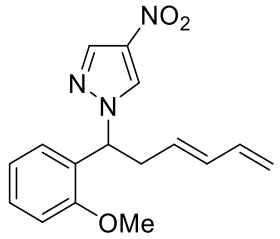
The title compound was prepared from **1f** (28.0 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3fa** (29.3 mg, 78% yield) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.01 (s, 1H), 7.51-7.31 (m, 7H), 7.12-6.98 (m, 2H), 6.33-6.00 (m, 2H), 5.74 (dd, *J* = 9.1, 6.1 Hz, 1H), 5.51 (dt, *J* = 14.5, 7.1 Hz, 1H), 5.18-4.96 (m, 4H), 3.25 (dt, *J* = 15.9, 8.3 Hz, 1H), 2.98 (dt, *J* = 14.0, 6.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 136.4, 136.1, 135.8, 135.1, 134.8, 130.2, 129.1, 129.0, 128.6, 128.5, 127.9, 127.7, 126.1, 121.3, 117.1, 112.2, 70.6, 61.1, 36.2.

HRMS (ESI) m/z calculated for $C_{22}H_{22}N_3O_3$ $[M+H]^+$: 376.1656, found: 376.1659.

(E)-1-(1-(2-Methoxyphenyl)hexa-3,5-dien-1-yl)-4-nitro-1H-pyrazole (3ga)



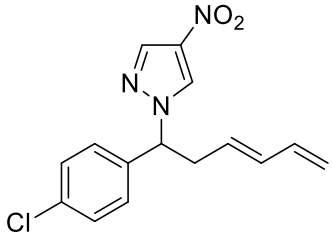
The title compound was prepared from **1g** (20.4 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3ga** (20.3 mg, 68% yield) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.99 (s, 1H), 7.36-7.21 (m, 2H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.23-5.93 (m, 2H), 5.69 (dd, *J* = 9.2, 6.2 Hz, 1H), 5.44 (dt, *J* = 14.4, 7.1 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 4.94 (d, *J* = 9.6 Hz, 1H), 3.77 (s, 3H), 3.17 (dt, *J* = 15.9, 8.4 Hz, 1H), 2.86 (dt, *J* = 14.0, 6.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7, 136.5, 135.8, 134.7, 130.2, 128.7, 128.6, 127.6, 126.0, 121.1, 117.1, 111.0, 60.9, 55.7, 36.5.

HRMS (ESI) m/z calculated for $C_{16}H_{18}N_3O_3$ $[M+H]^+$: 300.1343, found: 300.1348.

(E)-1-(1-(4-Chlorophenyl)hexa-3,5-dien-1-yl)-4-nitro-1H-pyrazole (3ha)



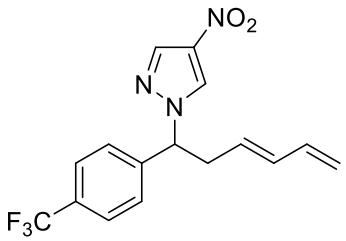
The title compound was prepared from **1h** (20.8 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3ha** (16.7 mg, 55% yield) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.10 (s, 1H), 7.47-7.22 (m, 4H), 6.47-5.88 (m, 2H), 5.62-5.32 (m, 1H), 5.36-4.93 (m, 3H), 3.34-3.08 (m, 1H), 3.05-2.83 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 136.5, 136.2, 136.1, 135.4, 135.1, 129.5, 128.6, 128.0, 127.4, 117.7, 67.1, 38.0.

HRMS (ESI) m/z calculated for $C_{15}H_{15}ClN_3O_2$ $[M+H]^+$: 304.0847, found: 304.0851.

(E)-4-Nitro-1-(1-(4-(trifluoromethyl)phenyl)hexa-3,5-dien-1-yl)-1H-pyrazole (3ia)



The title compound was prepared from **1i** (24.2 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **3ia** (15.5 mg, 46% yield) as yellow oil.

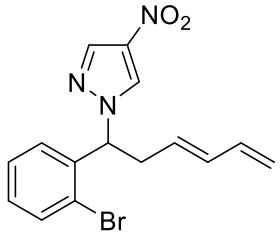
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.13 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 6.34-5.99 (m, 2H), 5.47 (dt, *J* = 14.3, 7.2 Hz, 1H), 5.41-5.27 (m, 1H), 5.24-4.99 (m, 2H), 3.25 (dt, *J* = 15.7, 8.2 Hz, 1H), 2.97 (dt, *J* = 14.1, 6.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 136.2, 136.1, 135.6, 128.2, 127.6, 127.5, 127.1, 126.3 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 245.2 Hz), 120.1, 118.0, 67.3, 38.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.8.

HRMS (ESI) m/z calculated for $C_{16}H_{15}F_3N_3O_2$ $[M+H]^+$: 338.1111, found: 338.1115.

(E)-1-(1-(2-Bromophenyl)hexa-3,5-dien-1-yl)-4-nitro-1H-pyrazole (3ja)



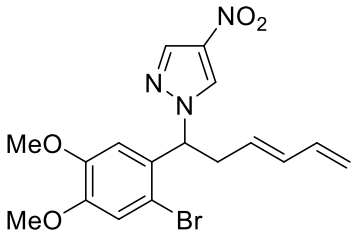
The title compound was prepared from **1j** (25.2 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0. 5 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3ja** (17.7 mg, 51% yield) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.12 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.54-7.16 (m, 3H), 6.40-5.94 (m, 2H), 5.80 (t, 1H), 5.53 (dt, *J* = 14.4, 7.3 Hz, 1H), 5.29-4.89 (m, 2H), 3.25 (dt, *J* = 16.5, 8.2 Hz, 1H), 3.07-2.82 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 136.3, 136.2, 135.3, 133.5, 130.5, 129.1, 128.4, 127.6, 117.6, 66.0, 37.2.

HRMS (ESI) m/z calculated for $C_{15}H_{15}BrN_3O_2$ $[M+H]^+$: 348.0342, found: 348.0340.

(E)-1-(1-(2-Bromo-4,5-dimethoxyphenyl)hexa-3,5-dien-1-yl)-4-nitro-1H-pyrazole (3ka)



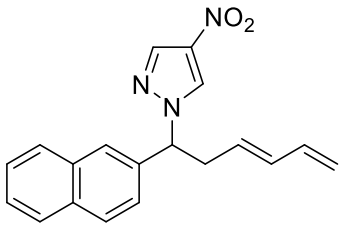
The title compound was prepared from **1k** (31.2 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3ka** (26.1 mg, 64% yield) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.12 (s, 1H), 7.03 (s, 2H), 6.34-6.01 (m, 2H), 5.79-5.65 (m, 1H), 5.60-5.41 (m, 1H), 5.13 (d, *J* = 16.3 Hz, 1H), 5.04 (d, *J* = 8.6 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.37-3.15 (m, 1H), 3.02-2.81 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 149.1, 136.3, 136.1, 135.6, 135.2, 129.02, 128.96, 127.7, 117.5, 115.5, 114.1, 110.7, 65.7, 56.34, 56.30, 37.5.

HRMS (ESI) m/z calculated for $C_{17}H_{19}BrN_3O_4$ $[M+H]^+$: 408.0553, found: 408.0558.

(E)-1-(1-(Naphthalen-2-yl)hexa-3,5-dien-1-yl)-4-nitro-1H-pyrazole (3la)



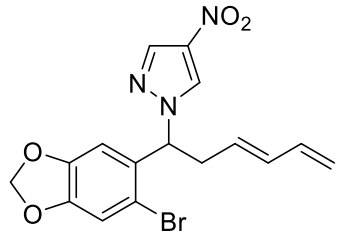
The title compound was prepared from **1l** (22.4 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:15) furnished **3la** (19.2 mg, 60% yield) as yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.11 (s, 1H), 7.96-7.73 (m, 4H), 7.52 (dd, *J* = 6.3, 3.3 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 6.39-5.99 (m, 2H), 5.63-5.40 (m, 2H), 5.13 (d, *J* = 15.3 Hz, 1H), 5.03 (d, *J* = 10.2 Hz, 1H), 3.34 (dt, *J* = 15.5, 8.0 Hz, 1H), 3.08 (dt, *J* = 14.0, 6.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3, 135.9, 135.2, 133.4, 133.3, 129.4, 128.3, 128.1, 127.9, 127.0, 126.9, 126.7, 124.4, 117.5, 67.9, 37.9.

HRMS (ESI) m/z calculated for $C_{19}H_{18}N_3O_2$ $[M+H]^+$: 320.1394, found: 320.1390.

(E)-1-(1-(6-Bromobenzo[d][1,3]dioxol-5-yl)hexa-3,5-dien-1-yl)-4-nitro-1H-pyrazole (3ma)



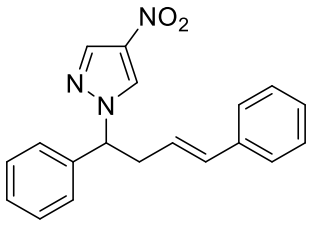
The title compound was prepared from **1m** (29.6 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3ma** (25.4 mg, 65% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.11 (s, 1H), 7.02 (s, 1H), 6.98 (s, 1H), 6.34-6.06 (m, 2H), 6.01 (d, *J* = 13.5 Hz, 2H), 5.72 (dd, *J* = 9.1, 6.0 Hz, 1H), 5.49 (dt, *J* = 14.5, 7.2 Hz, 1H), 5.14 (d, *J* = 16.6 Hz, 1H), 5.05 (d, *J* = 9.9 Hz, 1H), 3.20 (dt, *J* = 15.8, 8.1 Hz, 1H), 2.87 (dt, *J* = 13.9, 6.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 148.2, 136.3, 136.1, 135.6, 135.2, 130.2, 128.9, 127.5, 117.6, 114.6, 113.0, 107.9, 102.4, 65.8, 37.4.

HRMS (ESI) m/z calculated for $C_{16}H_{15}BrN_3O_4$ $[M+H]^+$: 392.0240, found: 392.0245.

(E)-1-(1,4-Diphenylbut-3-en-1-yl)-4-nitro-1H-pyrazole (3na)



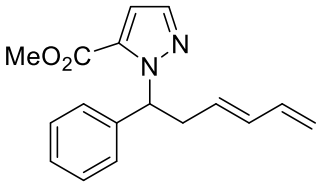
The title compound was prepared from **1n** (22.4 mg, 0.1 mmol, 1 eq.) and **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:20) furnished **3na** (15.0 mg, 47% yield) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.40-7.23 (m, 5H), 7.23-7.11 (m, 5H), 6.40 (d, *J* = 15.8 Hz, 1H), 5.93 (dt, *J* = 16.1, 7.1 Hz, 1H), 5.31 (dd, *J* = 8.6, 6.7 Hz, 1H), 3.30 (dt, *J* = 15.5, 8.0 Hz, 1H), 3.02 (dt, *J* = 14.1, 6.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 136.8, 135.9, 134.3, 129.3, 129.2, 128.7, 128.1, 127.9, 127.2, 126.3, 123.9, 68.0, 38.4.

HRMS (ESI) m/z calculated for $C_{19}H_{18}N_3O_2$ $[M+H]^+$: 320.1394, found: 320.1399.

Methyl (E)-1-(1-phenylhexa-3,5-dien-1-yl)-1H-pyrazole-3-carboxylate (3ab)



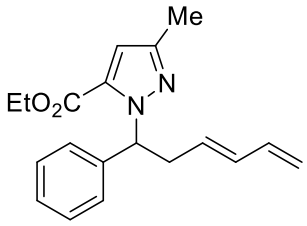
The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **2b** (18.9 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3ab** (14.7 mg, 52% yield) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.32 (d, *J* = 7.3 Hz, 2H), 7.29-7.15 (m, 3H), 6.75 (s, 1H), 6.40 (dd, *J* = 9.5, 6.0 Hz, 1H), 6.21-5.90 (m, 2H), 5.45 (dt, *J* = 14.4, 7.1 Hz, 1H), 4.99 (d, *J* = 16.3 Hz, 1H), 4.88 (d, *J* = 9.5 Hz, 1H), 3.76 (s, 3H), 3.26 (dt, *J* = 15.9, 8.2 Hz, 1H), 2.85 (dt, *J* = 13.9, 6.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 140.7, 138.4, 137.0, 133.9, 132.4, 130.1, 128.6, 127.9, 127.3, 116.2, 111.8, 63.3, 52.0, 38.9.

HRMS (ESI) m/z calculated for $C_{17}H_{19}N_2O_2$ $[M+H]^+$: 283.1441, found: 283.1443.

Ethyl (E)-3-methyl-1-(1-phenylhexa-3,5-dien-1-yl)-1H-pyrazole-5-carboxylate (3ac)



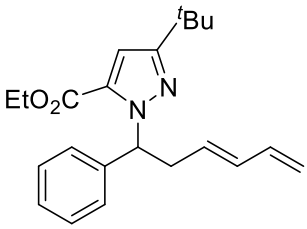
The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **2c** (23.1 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3ac** (20.2 mg, 65% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.19 (m, 5H), 6.60 (s, 1H), 6.38 (dd, *J* = 9.3, 6.2 Hz, 1H), 6.28-5.96 (m, 2H), 5.52 (dt, *J* = 14.6, 7.1 Hz, 1H), 5.06 (d, *J* = 16.7 Hz, 1H), 4.95 (d, *J* = 10.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.29 (dt, *J* = 15.5, 8.2 Hz, 1H), 2.91 (dt, *J* = 14.0, 6.8 Hz, 1H), 2.30 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 147.4, 141.1, 137.1, 133.7, 133.2, 130.6, 128.5, 127.7, 127.3, 115.9, 111.1, 62.9, 60.9, 38.9, 14.3, 13.8.

HRMS (ESI) m/z calculated for $C_{19}H_{23}N_2O_2$ $[M+H]^+$: 311.1754, found: 311.1750.

Ethyl (E)-5-(tert-butyl)-1-(1-phenylhexa-3,5-dien-1-yl)-1H-pyrazole-3-carboxylate (3ad)



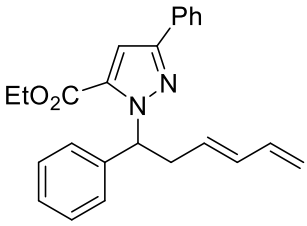
The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **2d** (29.4 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3ad** (21.1 mg, 60% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.2 Hz, 2H), 7.32-7.21 (m, 3H), 6.65 (s, 1H), 6.34 (dd, *J* = 9.9, 5.6 Hz, 1H), 6.28-5.97 (m, 2H), 5.52 (dt, *J* = 14.8, 7.2 Hz, 1H), 5.04 (d, *J* = 16.8 Hz, 1H), 4.93 (d, *J* = 9.9 Hz, 1H), 4.36-4.17 (m, 2H), 3.35 (dt, *J* = 14.3, 8.6 Hz, 1H), 2.81 (dt, *J* = 13.6, 6.4 Hz, 1H), 1.33 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 141.5, 137.1, 133.9, 132.4, 130.7, 128.4, 127.6, 127.3, 126.3, 115.8, 107.6, 63.3, 60.8, 39.6, 32.3, 30.60, 30.57, 14.4.

HRMS (ESI) m/z calculated for $C_{22}H_{29}N_2O_2$ $[M+H]^+$: 353.2224, found: 353.2227.

Ethyl (E)-5-phenyl-1-(1-phenylhexa-3,5-dien-1-yl)-1H-pyrazole-3-carboxylate (3ae)



The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **2e** (32.4 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3ae** (23.1 mg, 62%

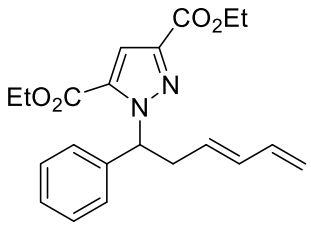
yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.82 (m, 2H), 7.49-7.37 (m, 4H), 7.36-7.21 (m, 4H), 7.13 (s, 1H), 6.45 (dd, *J* = 9.4, 5.9 Hz, 1H), 6.28-6.04 (m, 2H), 5.58 (dt, *J* = 14.5, 7.1 Hz, 1H), 5.05 (d, *J* = 15.6 Hz, 1H), 4.94 (d, *J* = 9.1 Hz, 1H), 4.38-4.24 (m, 2H), 3.43 (dt, 1H), 2.95 (dt, 1H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 149.9, 140.9, 137.0, 133.9, 133.1, 130.5, 128.8, 128.6, 128.1, 127.8, 127.4, 125.8, 116.1, 108.5, 63.8, 61.1, 39.3, 14.4.

HRMS (ESI) m/z calculated for $C_{24}H_{25}N_2O_2$ $[M+H]^+$: 373.1911, found: 373.1910.

Diethyl (E)-1-(1-phenylhexa-3,5-dien-1-yl)-1H-pyrazole-3,5-dicarboxylate (3af)



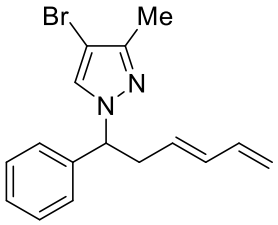
The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **2f** (31.8 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3af** (25.8 mg, 70% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.6 Hz, 2H), 7.36-7.21 (m, 4H), 6.50 (dd, *J* = 9.1, 6.3 Hz, 1H), 6.26-6.02 (m, 2H), 5.51 (dt, *J* = 14.5, 7.1 Hz, 1H), 5.07 (d, *J* = 15.8 Hz, 1H), 4.96 (d, *J* = 9.0 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 4.37-4.24 (m, 2H), 3.40 (dt, *J* = 15.6, 8.2 Hz, 1H), 2.98 (dt, *J* = 14.1, 6.8 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 159.3, 142.5, 139.8, 136.8, 134.2, 133.9, 129.7, 128.6, 128.1, 127.5, 116.3, 114.4, 64.5, 61.4, 61.2, 38.8, 14.5, 14.2.

HRMS (ESI) m/z calculated for $C_{21}H_{25}N_2O_4$ $[M+H]^+$: 369.1809, found: 369.1807.

(E)-4-Bromo-3-methyl-1-(1-phenylhexa-3,5-dien-1-yl)-1H-pyrazole (3ag)



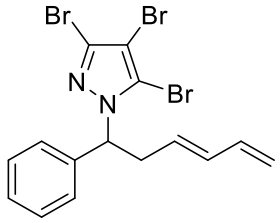
The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **2g** (24.0 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3ag** (23.7 mg, 75% yield) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.12 (m, 6H), 6.25-5.95 (m, 2H), 5.43 (dt, *J* = 14.4, 7.1 Hz, 1H), 5.19-5.08 (m, 1H), 5.03 (d, *J* = 15.6 Hz, 1H), 4.92 (d, *J* = 9.5 Hz, 1H), 3.09 (dt, *J* = 15.2, 7.8 Hz, 1H), 2.82 (dt, *J* = 14.5, 7.0 Hz, 1H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 139.7, 136.7, 134.3, 129.3, 129.0, 128.9, 128.3, 127.0, 116.6, 93.8, 66.6, 38.2, 12.2.

HRMS (ESI) m/z calculated for $C_{16}H_{18}BrN_2$ $[M+H]^+$: 317.0648, found: 317.0647.

(E)-3,4,5-Tribromo-1-(1-phenylhexa-3,5-dien-1-yl)-1H-pyrazole (3ah)



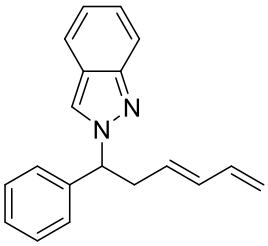
The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **2h** (45.3 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **3ah** (36.6 mg, 80% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.26 (m, 5H), 6.33-6.02 (m, 2H), 5.60-5.34 (m, 2H), 5.12 (d, *J* = 16.4 Hz, 1H), 5.02 (d, *J* = 9.9 Hz, 1H), 3.29 (dt, *J* = 15.5, 8.2 Hz, 1H), 2.91 (dt, *J* = 13.8, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 136.6, 134.6, 128.93, 128.90, 128.6, 128.4, 127.1, 116.9, 116.8, 99.9, 65.8, 38.1.

HRMS (ESI) m/z calculated for $C_{15}H_{14}Br_3N_2$ $[M+H]^+$: 458.8702, found: 458.8699.

(E)-1-(1-Phenylhexa-3,5-dien-1-yl)-1H-indazole (3ai)



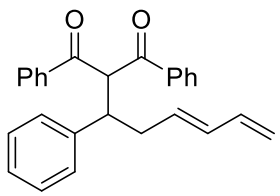
The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **2i** (17.7 mg, 0.15 mmol, 1.5 eq.) via general procedure B. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:15) furnished **3ai** (19.7 mg, 72% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.42-7.21 (m, 6H), 7.13-7.00 (m, 1H), 6.32-6.00 (m, 2H), 5.61 (dd, *J* = 8.7, 6.7 Hz, 1H), 5.52 (dt, *J* = 14.4, 7.0 Hz, 1H), 5.09 (d, *J* = 16.0 Hz, 1H), 4.97 (d, *J* = 9.3 Hz, 1H), 3.42 (dt, *J* = 15.1, 7.6 Hz, 1H), 3.09 (dt, *J* = 14.2, 7.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 139.6, 136.7, 134.3, 129.3, 128.9, 128.4, 127.1, 126.0, 122.2, 121.8, 121.7, 120.4, 117.9, 116.7, 67.8, 38.6.

HRMS (ESI) m/z calculated for $C_{19}H_{19}N_2$ $[M+H]^+$: 275.1543, found: 275.1545.

(E)-1,3-Diphenyl-2-(1-phenylhexa-3,5-dien-1-yl)propane-1,3-dione (3aj)



The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **2j** (44.8 mg, 0.2mmol, 2.0 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:20) furnished **3aj** (19.0 mg, 50% yield)

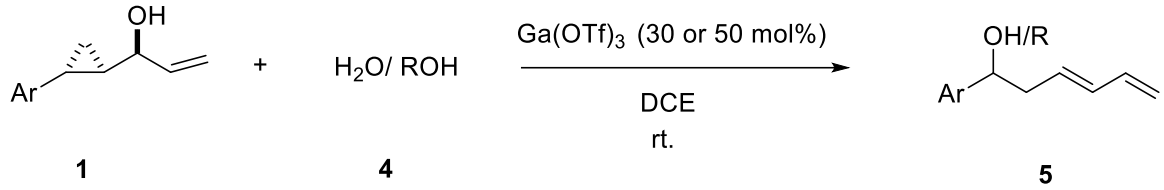
as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.60-7.38 (m, 4H), 7.33-7.05 (m, 7H), 6.11 (dt, *J* = 17.0, 10.2 Hz, 1H), 5.88 (dd, *J* = 15.1, 10.4 Hz, 1H), 5.69 (d, *J* = 10.3 Hz, 1H), 5.40 (dt, *J* = 14.8, 7.2 Hz, 1H), 5.12-4.69 (m, 2H), 4.05 (dt, 1H), 2.52 (t, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9, 194.5, 140.9, 137.2, 137.0, 136.9, 133.7, 133.3, 133.2, 131.5, 129.0, 128.8, 128.6, 128.5, 128.4, 126.8, 115.7, 63.9, 47.1, 37.3.

HRMS (ESI) m/z calculated for $C_{27}H_{25}O_2$ $[M+H]^+$: 381.1849, found: 381.1850.

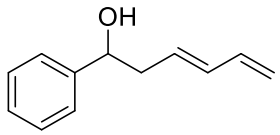
General procedure C for synthesis of 5a-5k



1 **4** **5**

General procedure C: A 10 mL dry tube equipped with a stir bar was charged with compound **1** (0.1 mmol, 1.0 eq.), **water** (0.5 mmol) or alcohols **4** (0.2 mmol, 2.0 eq.), $Ga(OTf)_3$ (30 mol% for the synthesis of **5a**-**5b**, **5e** and **5h**-**5k**; 50 mol% for the synthesis of **5c**-**5d**, **5f**-**5g**) and dry DCE (2.0 mL). The reaction mixture was stirred at room temperature for 12 hours. After completion of the reaction, the reaction mixture was concentrated under reduced pressure, then 2.0 ml of water was added, and the reaction solution was extracted with ethyl acetate (3 x 5 mL), the combined organic layers were dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. The remaining residue was purified by column chromatography on silica gel to afford the corresponding products (**5a-5k**).

(E)-1-Phenylhexa-3,5-dien-1-ol (5a)



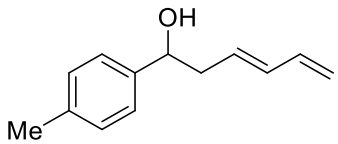
The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **4a** (3.6 mg, 0.2mmol, 2.0 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **5a** (11.3 mg, 65% yield) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.26 (m, 5H), 6.49-6.04 (m, 2H), 5.69 (dt, *J* = 14.8, 7.3 Hz, 1H), 5.15 (d, *J* = 16.6 Hz, 1H), 5.03 (d, *J* = 9.9 Hz, 1H), 4.74 (t, *J* = 6.5 Hz, 1H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.00 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 136.8, 134.6, 130.2, 128.6, 127.8, 125.9, 116.5, 73.8, 42.8.

HRMS (ESI) m/z calculated for $C_{12}H_{15}O$ $[M+H]^+$: 175.1117, found: 175.1120.

(E)-1-(p-Tolyl)hexa-3,5-dien-1-ol (5b)



The title compound was prepared from **1b** (18.8 mg, 0.1 mmol, 1 eq.) and **4a** (3.6 mg, 0.2mmol, 2.0 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **5b** (12.4 mg, 66% yield)

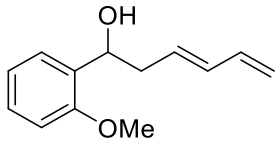
as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.14 (m, 4H), 6.53-6.03 (m, 2H), 5.68 (dt, *J* = 14.8, 7.0 Hz, 1H), 5.15 (d, *J* = 16.2 Hz, 1H), 5.03 (d, *J* = 10.2 Hz, 1H), 4.85-4.61 (m, 1H), 2.53 (t, *J* = 6.7 Hz, 2H), 2.35 (s, 3H), 1.96 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0, 137.4, 136.9, 134.4, 130.4, 129.3, 125.9, 116.3, 73.6, 42.7, 21.3.

The NMR data was similar with the reported literature.[3]

(E)-1-(2-Methoxyphenyl)hexa-3,5-dien-1-ol (5c)



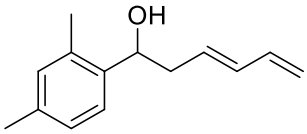
The title compound was prepared from **1d** (19.2 mg, 0.1 mmol, 1 eq.) and **4a** (3.6 mg, 0.2mmol, 2.0 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **5c** (11.5 mg, 60% yield) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.28-7.21 (m, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.32 (dt, *J* = 16.9, 10.3 Hz, 1H), 6.15 (dd, *J* = 15.1, 10.4 Hz, 1H), 5.74 (dt, *J* = 14.9, 7.3 Hz, 1H), 5.12 (d, *J* = 16.8 Hz, 1H), 5.04-4.91 (m, 2H), 3.85 (s, 3H), 2.67-2.48 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 137.1, 133.8, 131.8, 131.2, 128.5, 126.9, 120.8, 115.8, 110.5, 70.2, 55.4, 40.7.

The NMR data was similar with the reported literature.[3]

(E)-1-(2,4-Dimethylphenyl)hexa-3,5-dien-1-ol (5d)



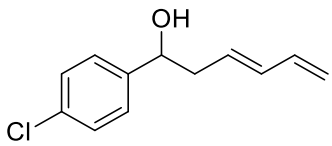
The title compound was prepared from **1e** (20.2 mg, 0.1 mmol, 1 eq.) and **4a** (3.6 mg, 0.2mmol, 2.0 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **5d** (12.3 mg, 61% yield) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.96 (s, 1H), 6.48-6.06 (m, 2H), 5.73 (dt, *J* = 14.8, 7.3 Hz, 1H), 5.15 (d, *J* = 15.9 Hz, 1H), 5.02 (d, *J* = 9.9 Hz, 1H), 4.94 (dd, *J* = 7.7, 5.1 Hz, 1H), 2.57-2.40 (m, 2H), 2.32 (s, 3H), 2.30 (s, 3H), 1.88 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 137.0, 136.9, 134.4, 134.3, 131.3, 130.7, 127.1, 125.3, 116.3, 70.1, 41.6, 21.1, 19.1.

HRMS (ESI) m/z calculated for $C_{14}H_{19}O$ $[M+H]^+$: 203.1430, found: 203.1433.

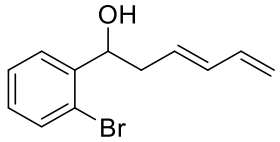
(E)-1-(4-Chlorophenyl)hexa-3,5-dien-1-ol (5e)



The title compound was prepared from **1h** (20.8 mg, 0.1 mmol, 1 eq.) and **4a** (3.6 mg, 0.2mmol, 2.0 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **5e** (11.0 mg, 53% yield) as colorless oil.

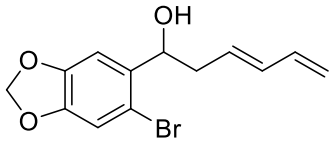
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.24 (m, 4H), 6.41-6.23 (m, 1H), 6.22-6.07 (m, 1H), 5.64 (dt, *J* = 14.8, 7.4 Hz, 1H), 5.15 (d, *J* = 16.1 Hz, 1H), 5.04 (d, *J* = 9.9 Hz, 1H), 4.71 (t, *J* = 6.5 Hz, 1H), 2.59-2.41 (m, 2H), 2.08 (s, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 136.7, 134.9, 133.3, 129.6, 128.7, 127.3, 116.7, 73.0, 42.8.
The NMR data was similar with the reported literature.[3]

(E)-1-(2-Bromophenyl)hexa-3,5-dien-1-ol (5f)



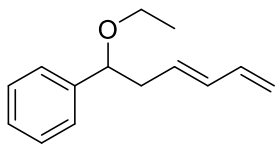
The title compound was prepared from **1j** (25.2 mg, 0.1 mmol, 1 eq.) and **4a** (3.6 mg, 0.2mmol, 2.0 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **5f** (12.6 mg, 50% yield) as yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.46 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.64-5.97 (m, 2H), 5.77 (dt, *J* = 14.8, 7.3 Hz, 1H), 5.35-4.90 (m, 3H), 2.76-2.58 (m, 1H), 2.38 (dt, *J* = 15.2, 8.2 Hz, 1H), 2.13 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 136.8, 134.8, 132.8, 130.0, 129.0, 127.8, 127.4, 121.9, 116.6, 72.3, 41.0.
HRMS (ESI) m/z calculated for $C_{12}H_{14}BrO$ $[M+H]^+$: 253.0223, found: 253.0220.

(E)-1-(6-Bromobenzo[d][1,3]dioxol-5-yl)hexa-3,5-dien-1-ol (5g)



The title compound was prepared from **1m** (29.6 mg, 0.1 mmol, 1 eq.) and **4a** (3.6 mg, 0.2mmol, 2.0 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **5g** (16.0 mg, 54% yield) as yellow oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (s, 1H), 6.96 (s, 1H), 6.50-6.07 (m, 2H), 5.97 (s, 2H), 5.74 (dt, *J* = 14.9, 7.3 Hz, 1H), 5.19 (d, 1H), 5.14-4.94 (m, 2H), 2.67-2.49 (m, 1H), 2.34 (dt, *J* = 15.1, 8.2 Hz, 1H), 2.10 (s, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 136.8, 136.3, 134.7, 130.0, 116.6, 112.6, 112.1, 107.3, 101.9, 72.2, 41.2.
HRMS (ESI) m/z calculated for $C_{13}H_{14}BrO_3$ $[M+H]^+$: 297.0121, found: 297.0125.

(E)-(1-Ethoxyhexa-3,5-dien-1-yl)benzene (5h)

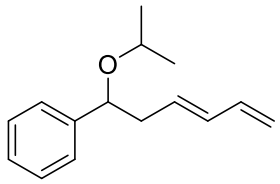


The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **4b** (9.2 mg, 0.2mmol, 2.0 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:20) furnished **5h** (17.0 mg, 84% yield) as colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.21 (m, 5H), 6.29 (dt, *J* = 17.0, 10.3 Hz, 1H), 6.18-5.96 (m, 1H), 5.66 (dt, *J* = 14.8, 7.2 Hz, 1H), 5.08 (d, *J* = 17.0 Hz, 1H), 4.97 (d, *J* = 10.1 Hz, 1H), 4.25 (dd, *J* = 7.6, 5.8 Hz, 1H), 3.46-3.21 (m, 2H), 2.60 (dt, *J* = 14.5, 7.3 Hz, 1H), 2.41 (dt, *J* = 13.6, 6.6 Hz, 1H), 1.17 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 137.2, 133.1, 131.2, 128.5, 127.6, 126.7, 115.6, 82.0, 64.3, 41.6, 15.4.

HRMS (ESI) m/z calculated for $C_{14}H_{19}O$ $[M+H]^+$: 203.1430, found: 203.1433.

(E)-(1-Isopropoxyhexa-3,5-dien-1-yl)benzene (5i)



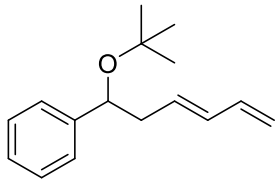
The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **4c** (12.0 mg, 0.2mmol, 2.0 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:20) furnished **5i** (15.8 mg, 73% yield) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.24 (m, 5H), 6.40-6.17 (m, 1H), 6.06 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.66 (dt, *J* = 14.8, 7.2 Hz, 1H), 5.08 (d, *J* = 17.1 Hz, 1H), 4.96 (d, *J* = 10.1 Hz, 1H), 4.35 (dd, *J* = 7.8, 5.7 Hz, 1H), 3.58-3.37 (m, 1H), 2.54 (dt, *J* = 14.6, 7.4 Hz, 1H), 2.38 (dt, *J* = 13.8, 6.5 Hz, 1H), 1.14 (d, *J* = 6.0 Hz, 3H), 1.08 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 137.3, 133.0, 131.4, 128.4, 127.5, 126.7, 115.5, 79.3, 69.1, 42.0, 23.5, 21.4.

HRMS (ESI) m/z calculated for $C_{15}H_{21}O$ $[M+H]^+$: 217.1587, found: 217.1591.

(E)-(1-(tert-Butoxy)hexa-3,5-dien-1-yl)benzene (5j)



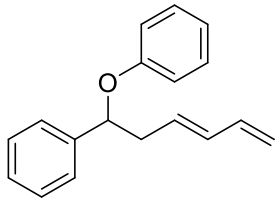
The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **4d** (14.8 mg, 0.2mmol, 2.0 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:20) furnished **5j** (13.8 mg, 60% yield) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.26 (m, 5H), 6.30 (dt, *J* = 16.9, 10.2 Hz, 1H), 6.05 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.67 (dt, *J* = 14.9, 7.3 Hz, 1H), 5.09 (d, *J* = 17.0 Hz, 1H), 4.97 (d, *J* = 10.1 Hz, 1H), 4.46 (dd, *J* = 8.1, 5.3 Hz, 1H), 2.54-2.24 (m, 2H), 1.11 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 137.4, 133.0, 132.1, 128.2, 126.8, 126.2, 115.4, 74.6, 74.5, 43.7, 28.8.

HRMS (ESI) m/z calculated for $C_{16}H_{23}O$ $[M+H]^+$: 231.1743, found: 231.1745.

(E)-(1-Phenoxyhexa-3,5-dien-1-yl)benzene (5k)



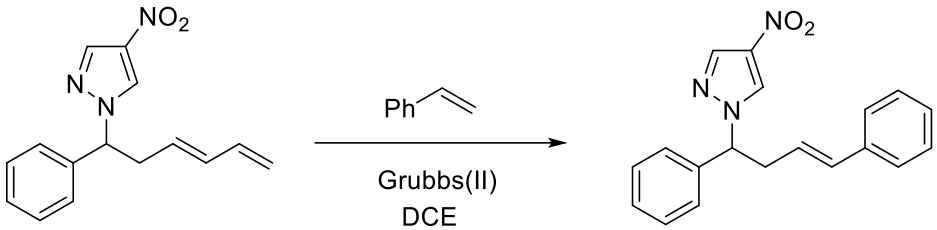
The title compound was prepared from **1a** (17.4 mg, 0.1 mmol, 1 eq.) and **4e** (18.8 mg, 0.2mmol, 2.0 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:20) furnished **5k** (16.5 mg, 66% yield) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 6.8 Hz, 4H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.17 (t, *J* = 7.9 Hz, 2H), 6.96-6.75 (m, 3H), 6.29 (dt, *J* = 16.9, 10.2 Hz, 1H), 6.12 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.74 (dt, *J* = 14.8, 7.2 Hz, 1H), 5.18-5.06 (m, 2H), 4.99 (d, *J* = 10.0 Hz, 1H), 2.78 (dt, *J* = 14.7, 7.4 Hz, 1H), 2.60 (dt, *J* = 13.8, 6.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 141.5, 137.1, 133.8, 130.2, 129.5, 129.4, 128.7, 127.7, 126.1, 120.9, 116.1, 80.0, 41.9.

HRMS (ESI) m/z calculated for $C_{18}H_{19}O$ $[M+H]^+$: 251.1430, found: 251.1437.

The preparation of the compound 6



3aa **6**

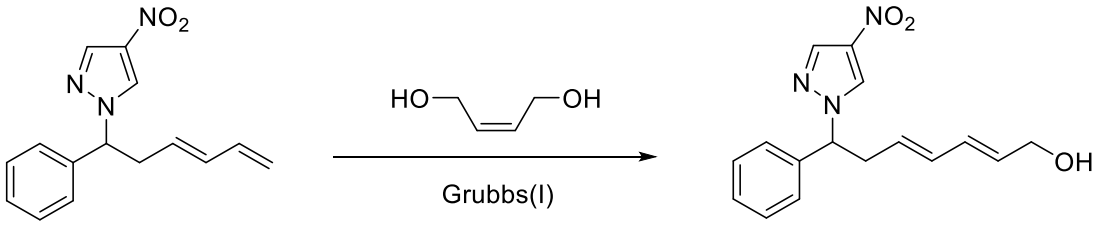
The compound **3aa** (26.9 mg, 0.1 mmol) was dissolved in the solvent of DCE (2.0 mL), then styrene (8.0 equiv.) and the Grubbs II catalyst (15 mol %) was added. The reaction was heated to 100 ℃ stirred for 12 h, until the substrate was fully consumed (monited by TLC). After complete consumption of the starting material, the mixture solution was quenched by H_2O (2 mL) and extracted with EtOAc (3 * 2 mL). The combined organic layer was washed with brine solution and dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified by silica gel column chromatography (EtOAc/PE = 1:10) to give (E)-1-(1,4-diphenylbut-3-en-1-yl)-4-nitro-1H-pyrazole **6** (23.0 mg, 72% yield) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (s, 2H), 7.58-7.09 (m, 10H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.00 (dt, *J* = 15.3, 7.2 Hz, 1H), 5.38 (t, *J* = 7.7 Hz, 1H), 3.37 (dt, *J* = 15.6, 8.1 Hz, 1H), 3.10 (dt, *J* = 14.1, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 136.7, 135.9, 134.2, 129.3, 129.2, 128.73, 128.70, 128.1, 127.8, 127.2, 126.3, 123.9, 67.9, 38.4.

HRMS (ESI) m/z calculated for $C_{19}H_{18}N_3O_2$ $[M+H]^+$: 320.1394, found: 320.1399.

The preparation of the compound 7



3aa **7**

The compound **3aa** (26.9 mg, 0.1 mmol) was dissolved in the solvent of THF (2.0 mL), then 2-Butene-1,4-diol (8.0 equiv.) and the Grubbs I catalyst (15 mol %) was added. The reaction was heated to 100 ℃ stirred for 12 h, until the substrate was fully consumed (monited by TLC). After complete consumption of the starting material, the mixture solution was quenched by H_2O (2 mL) and extracted with EtOAc (3 * 2 mL). The combined organic layer was washed with brine solution and dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified by silica gel column

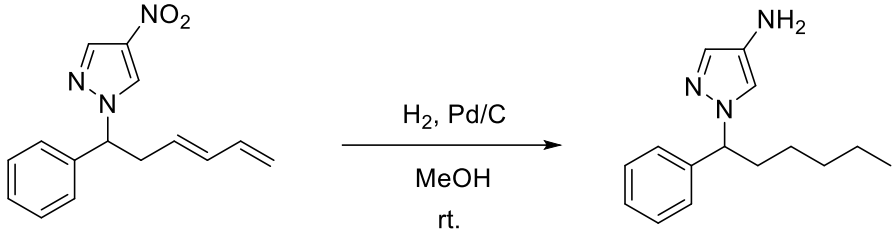
chromatography (EtOAc/PE = 1:5) to give (2E,4E)-7-(4-nitro-1H-pyrazol-1-yl)-7-phenylhepta-2,4-dien-1-ol **7** (17.3 mg, 58% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.09 (s, 1H), 7.46-7.26 (m, 5H), 6.31-5.96 (m, 2H), 5.88-5.65 (m, 1H), 5.60-5.42 (m, 1H), 5.30 (t, *J* = 7.7 Hz, 1H), 4.15 (d, *J* = 5.6 Hz, 2H), 3.24 (dt, *J* = 15.6, 8.1 Hz, 1H), 2.97 (dt, *J* = 14.2, 6.8 Hz, 1H), 1.40 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 135.9, 133.7, 132.2, 130.5, 129.3, 129.2, 128.0, 127.8, 127.2, 67.8, 63.3, 38.0.

HRMS (ESI) m/z calculated for $C_{16}H_{18}N_3O_3$ $[M+H]^+$: 300.1343, found: 300.1340.

The preparation of the compound 8



3aa **8**

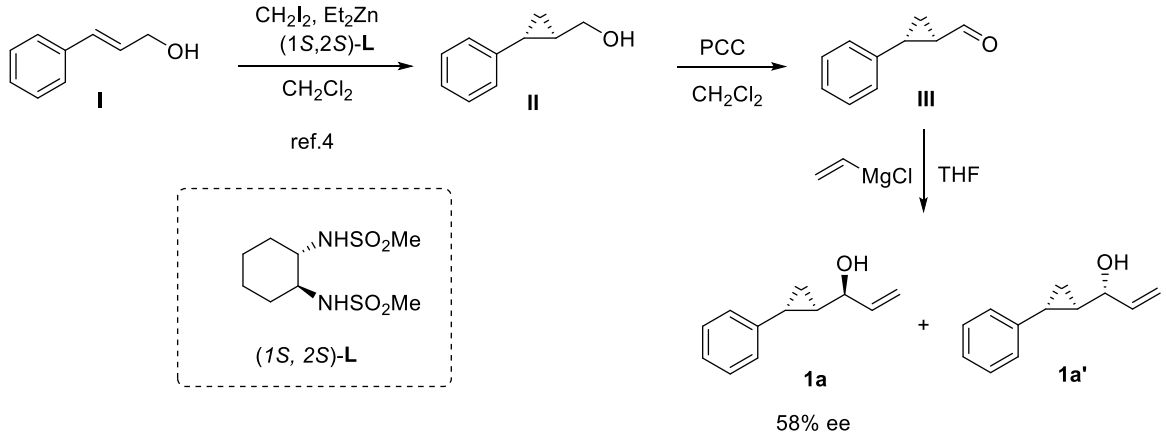
The compound **3aa** (26.9 mg, 0.1 mmol) was dissolved in the solvent of methanol (4.0 mL), Pd/C (15%wt, 5.5 mg) was added to the mixture solution, and the solution was then purged with hydrogen balloon and went 24 h under hydrogen balloon. Then, the reaction was filtered over a short path of Celite, concentrated in vacuo, and the crude mixture was purified by flash column chromatography (EtOAc/PE = 1/3) to give 1-(1-phenylhexyl)-1H-pyrazol-4-amine **8** (14.8 mg, 61% yield) as dark red oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.09 (m, 6H), 7.03 (s, 1H), 5.12 (t, *J* = 7.7 Hz, 1H), 2.63 (s, 2H), 2.43-2.25 (m, 1H), 2.16-2.01 (m, 1H), 1.28 (d, *J* = 12.0 Hz, 6H), 0.85 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 131.1, 128.8, 128.7, 127.8, 126.7, 117.6, 66.4, 35.2, 31.6, 26.3, 22.6, 14.1.

HRMS (ESI) m/z calculated for $C_{15}H_{22}N_3$ $[M+H]^+$: 244.1808, found: 244.1814.

Synthesis method of enantioenriched vinyl cyclopropyl alcohol 1a



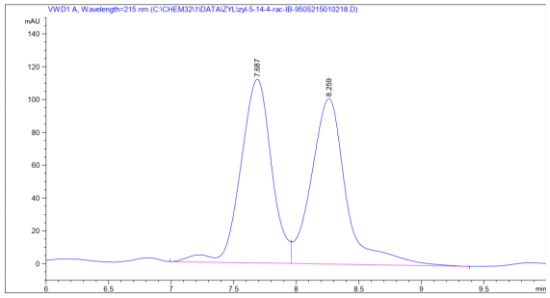
58% ee

According to the procedure of reported literature,[4] to a dried 250 mL flask were added CH_2I_2 (20.0 mmol, 2.0 eq.) and CH_2Cl_2 (100 mL). After cooling to 0 °C, Et_2Zn (1 M in hexane, 12.5 mmol, 1.25 eq.) was added. The resulting mixture was stirred at this temperature for 30 min. To another flask were added 3-Phenyl-2-propen-1-ol (**I**) (1.34 g, 10.0 mmol, 1.0 eq.), (1*S*,2*S*)-**L** (270.4 mg, 1.0 mmol, 0.1 eq.) and CH_2Cl_2 (30 mL). After cooling to 0 °C, Et_2Zn (1 M in hexane, 12.5

mmol, 1.25 eq.) was added. The resulting mixture was stirred at this temperature for 30 min. This reaction mixture was then added to the reaction mixture in the 250 mL flask. After stirred at 0 °C for 30 min, the resulting mixture was allowed to warm to room temperature and then stirred for 18 h. Then, the reaction mixture was quenched with sat. aq. NH_4Cl and 1 M aq. HCl. The organic layer was separated. The aqueous layer was then extracted with CH_2Cl_2 (2*100 mL). The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was direct used without further purification. To a solution of compound (10.0 mmol) in CH_2Cl_2 (25 mL) was added PCC (15.0 mmol, 1.5 eq.) at room temperature under Ar atmosphere. After 1 h, the reaction mixture was filtered through a pad of Celite and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford **III** as colorless oil.

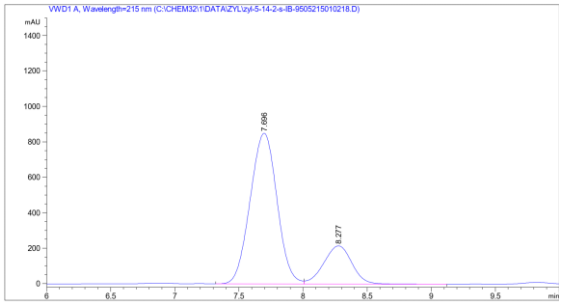
To a flame dried flask was cooled to 0 °C and charged with **III** (1.24g, 8.5 mmol, 1.0 eq.) and dry THF, the flask was backfilled with argon gas. Then, vinylmagnesium chloride (1.0 M in THF solution, 17.0 mmol, 2.0 eq.) was slowly added to the above solution. Then, the mixture was stirred at 0 °C for 1 h (monitored by TLC) and quenched with saturated aq. NH_4Cl (30 mL). The aqueous layer was extracted with EtOAc and the organic phase was dried with Na_2SO_4, filtered and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel to give the enantioen-riched diastereoisomer **1a**/**1a'** = 1:1. Compound **1a** (591.6 mg, 40% yield) and **1a'** (591.6 mg, 40% yield) as colorless oil.

HPLC spectra of chiral **1a (**Daicel Chiralpak IB column (hexane/iPrOH = 95:5), flow rate: 1.0 mL/min, λ= 215 nm, t_R(major) = 7.70 min, t_R (minor) = 8.28 min. ee = 58%)



Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	7.687	VV R	0.2597	1923.05945	111.99230	49.8778
2	8.259	VB	0.2886	1932.48340	100.83273	50.1222

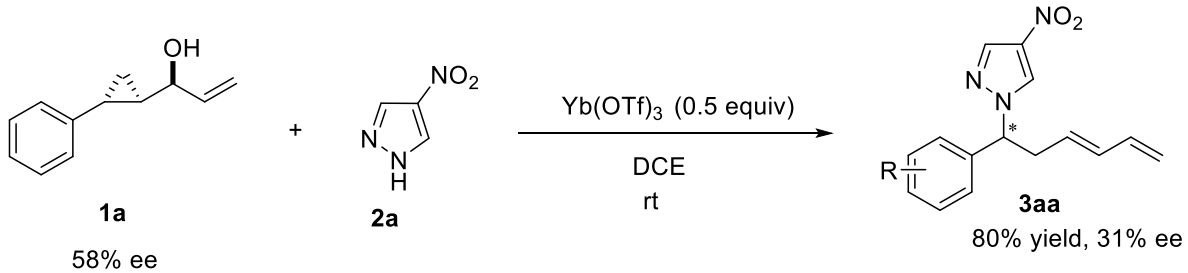
Rac-**1a**



Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	7.696	BV	0.2298	1.23717e4	850.12811	78.9960
2	8.277	VB	0.2383	3289.46387	215.21815	21.0040

Chiral-**1a**

Stereospecific reaction with enantioenriched vinyl cyclopropyl alcohol 1a with 2a



1a

58% ee

2a

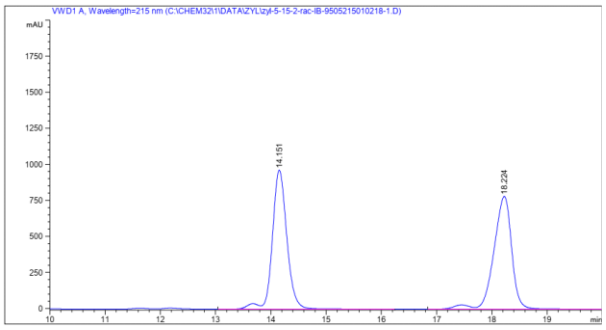
3aa

80% yield, 31% ee

The compound chiral **1a** (17.5 mg, 0.1 mmol, 58% ee) was dissolved in dry DCE (2 mL), and then the 3-nitropyrazole **2a** (17.0 mg, 0.15 mmol, 1.5 eq.) and $Yb(OTf)_3$ (50 mol%, 0.5 eq.) were added to the solution. The reaction mixture was stirred at room temperature for 12 hours. After completion of the reaction, the reaction mixture was concentrated under reduced pressure, then 2.0 ml of water was added, and the reaction solution was extracted with ethyl acetate (3 * 5 mL), the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The

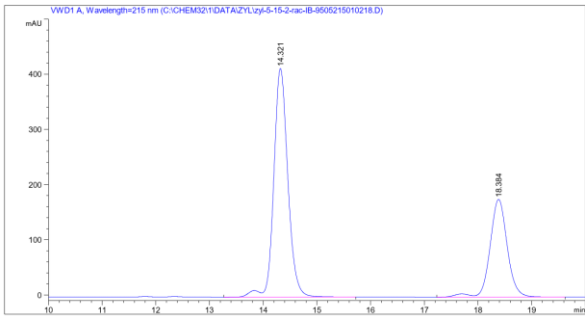
remaining residue was purified by column chromatography on silica gel to afford the corresponding products chiral **3aa** in 80% yield. ^{1}H NMR was similar with the compound **3aa**.

HPLC spectra of **3aa (**Daicel Chiralpak IB column (hexane/iPrOH) = 95:5, flow rate: 1.0 mL/min, λ= 215 nm, t_R(major) = 14.32 min, t_R (minor) = 18.38 min. ee = 31%)



Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	14.151	VB R	0.2723	1.75550e4	962.76953	49.9793
2	18.224	VB R	0.3372	1.75695e4	780.72186	50.0207

Rac-**3aa**

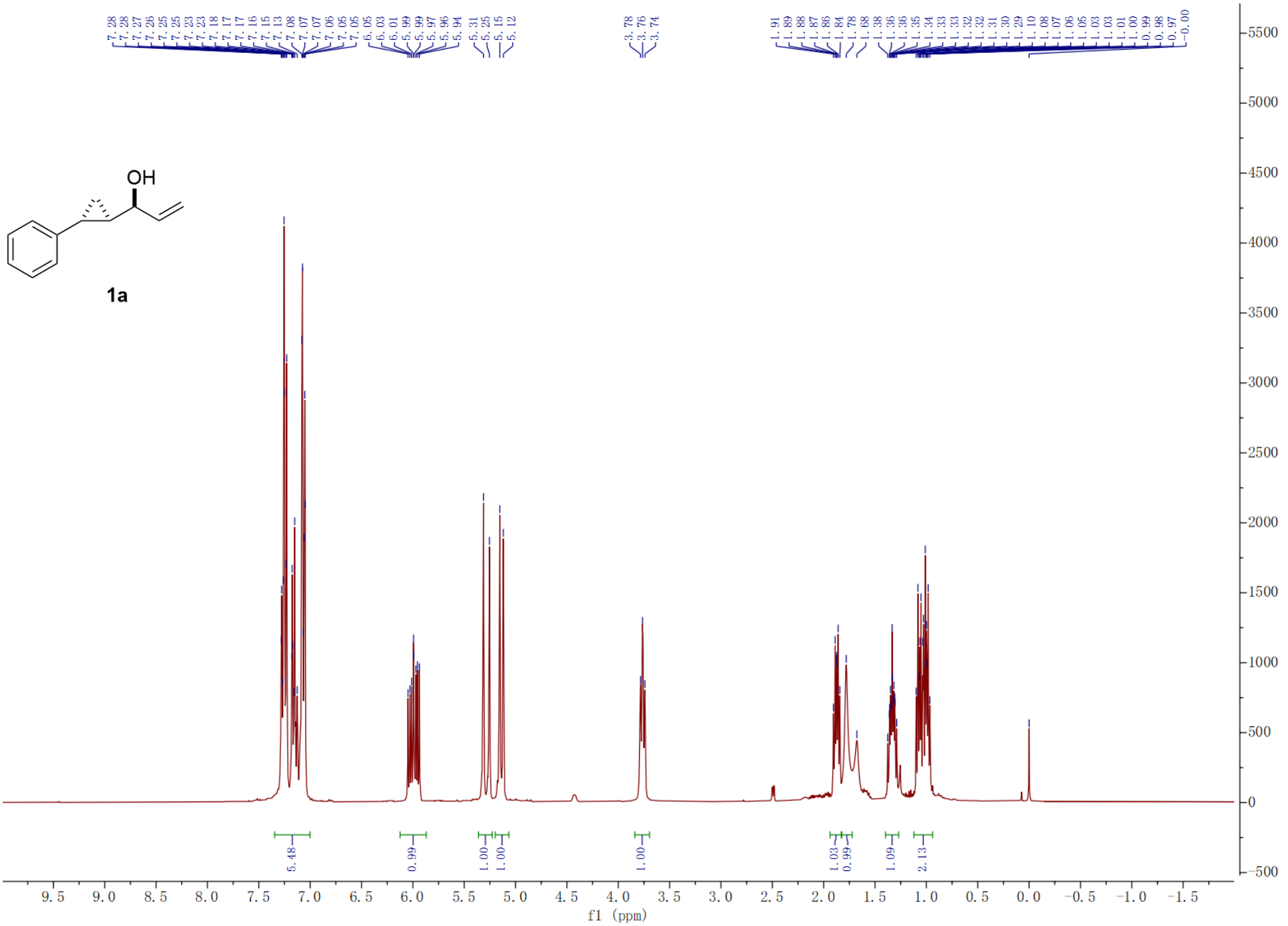


Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	14.321	VB R	0.2756	7577.15625	414.42847	65.6356
2	18.384	VB R	0.3349	3967.11499	177.14307	34.3644

Chiral-**3aa**

References

1. a) Qu, Z.; Shi, W.; Wang, J. *Chin. Chem. Lett.* **2002**, 13, 1033-1036. b) Toy, P. H.; Newcomb, M.; Hollenberg, P. F. *J. Am. Chem. Soc.* **1998**, *120*, 7719-7729. c) Kim, H. Y.; Salvi, L.; Carroll, P. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2010**, *132*, 402-412.
2. a) H. Y. Kim, L. Salvi, P. J. Carroll, P. J. Walsh, *J. Am. Chem. Soc.* **2010**, 132, 402-412. b) R. Infante, J. Nieto, C. Andrés, *Org. Biomol. Chem.*, **2014**, 12, 345-354.
3. J. Liu, B. Su, M. Chen. *Org. Lett.* **2021**, *23*, 6035-6040.
4. S. E. Denmark and S. P. O'Connor, *J. Org. Chem.* **1997**, 62, 3390-3401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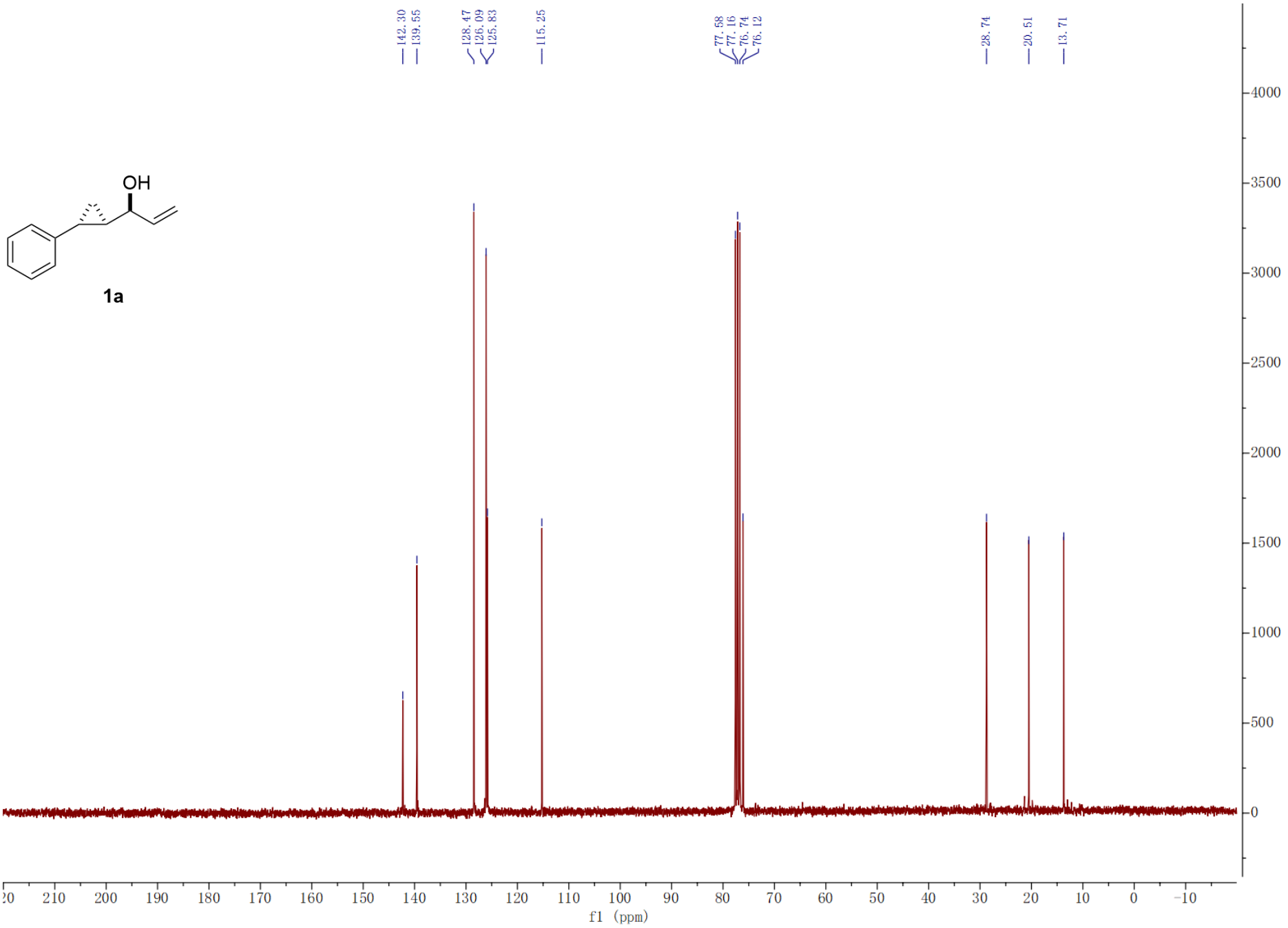
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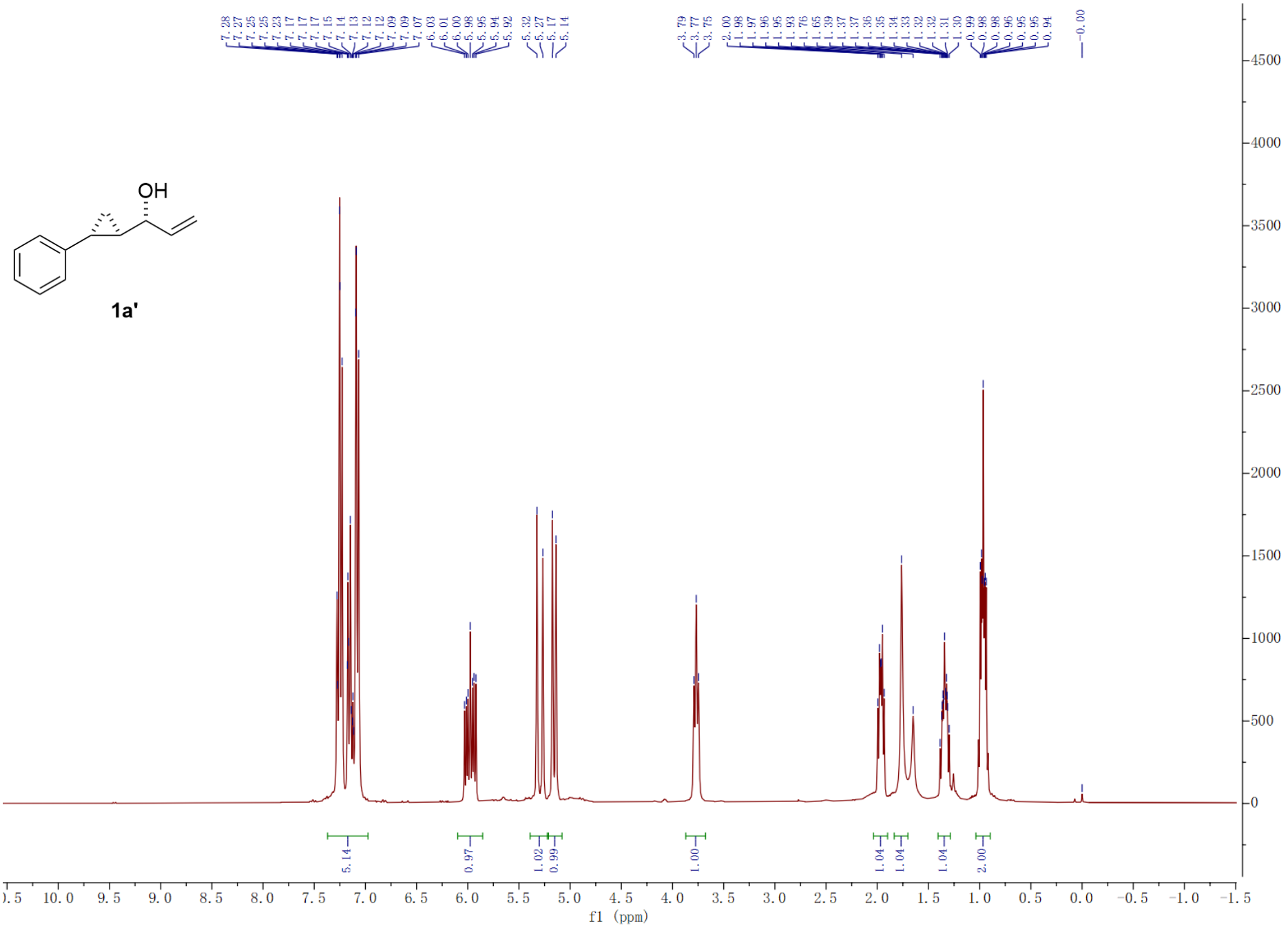
1000
500
0
f1 (ppm)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7.12
7.09
7.09
7.07
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6.01
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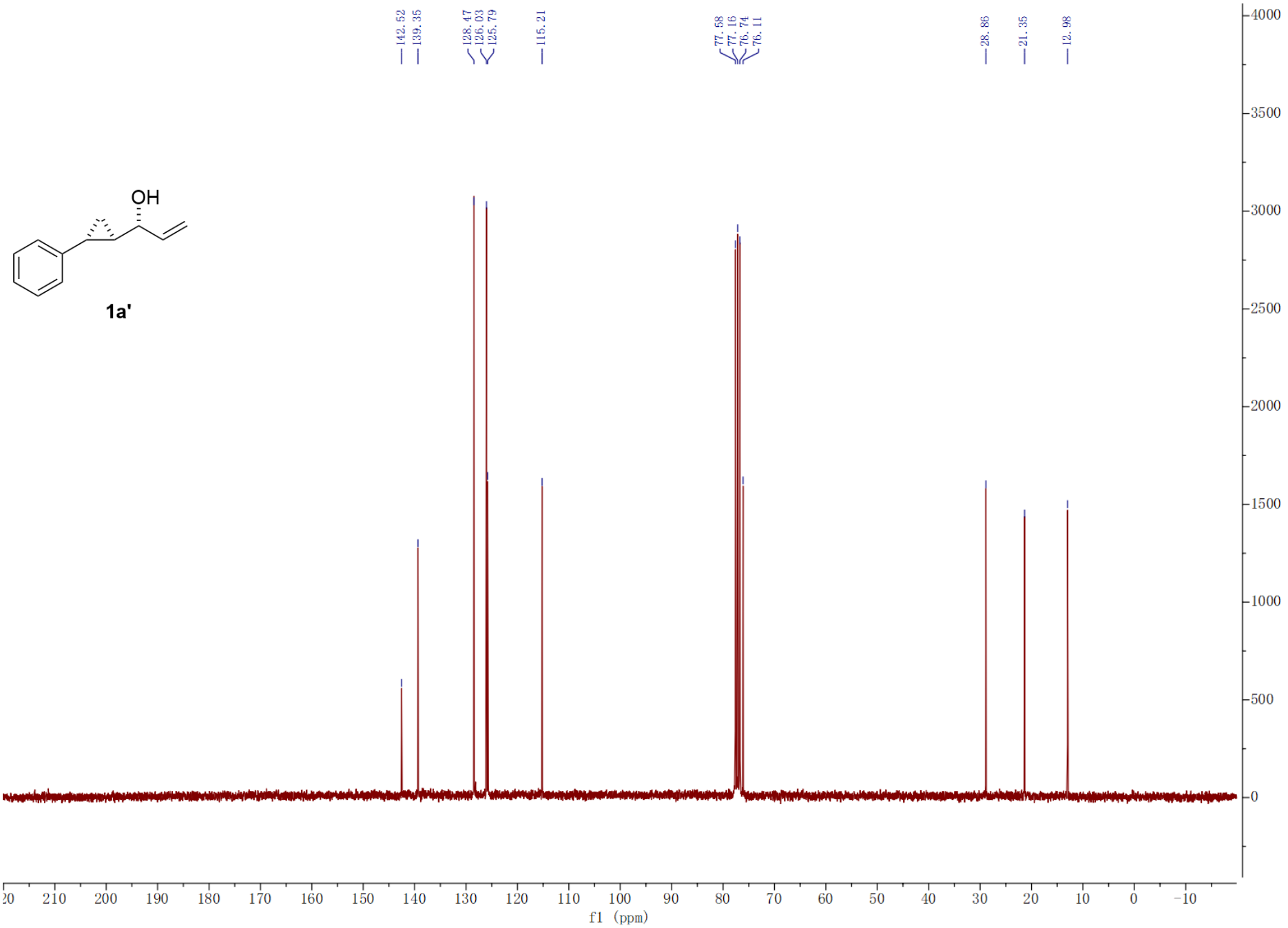
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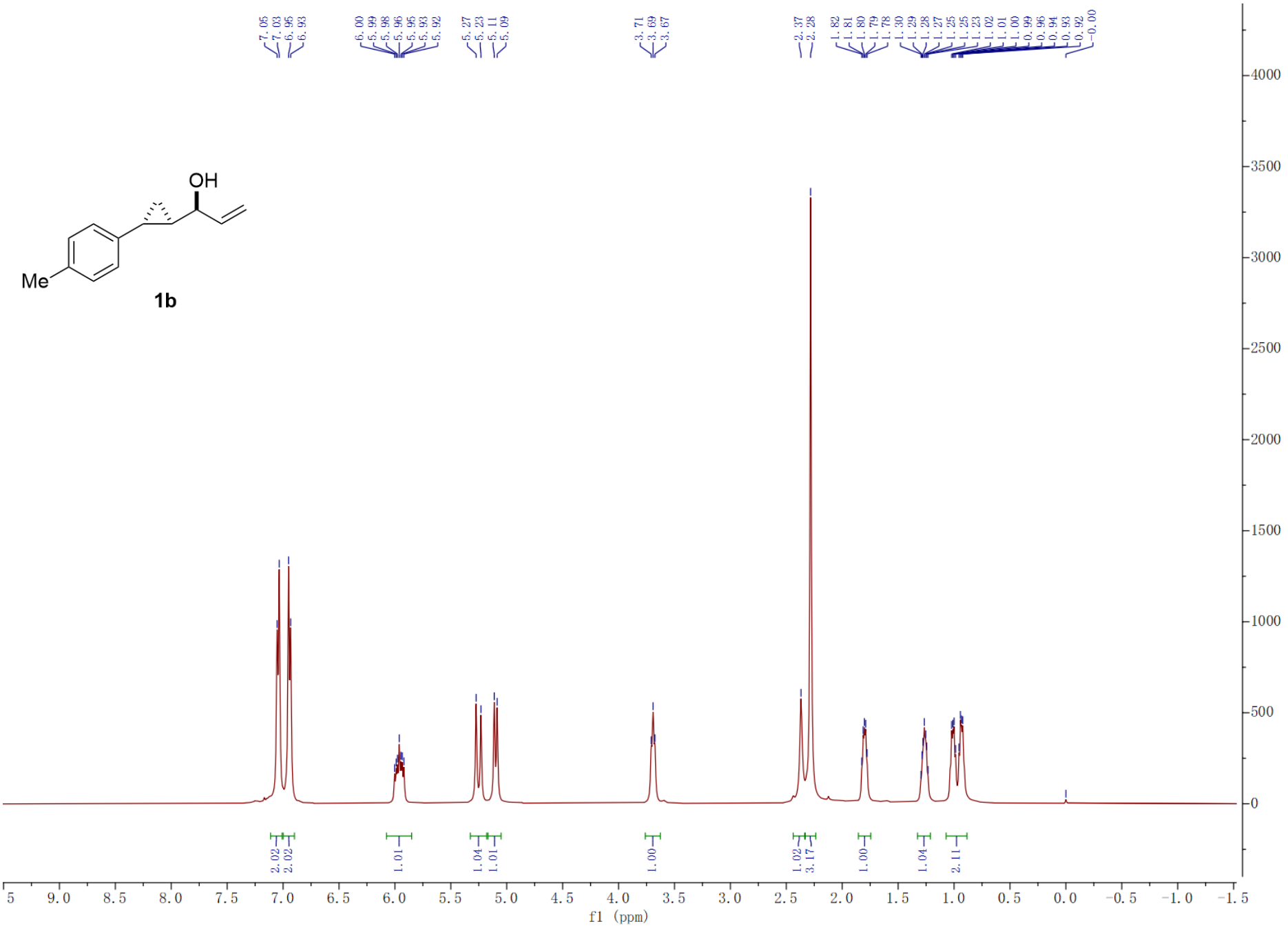
f1 (ppm)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1.80
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1.23
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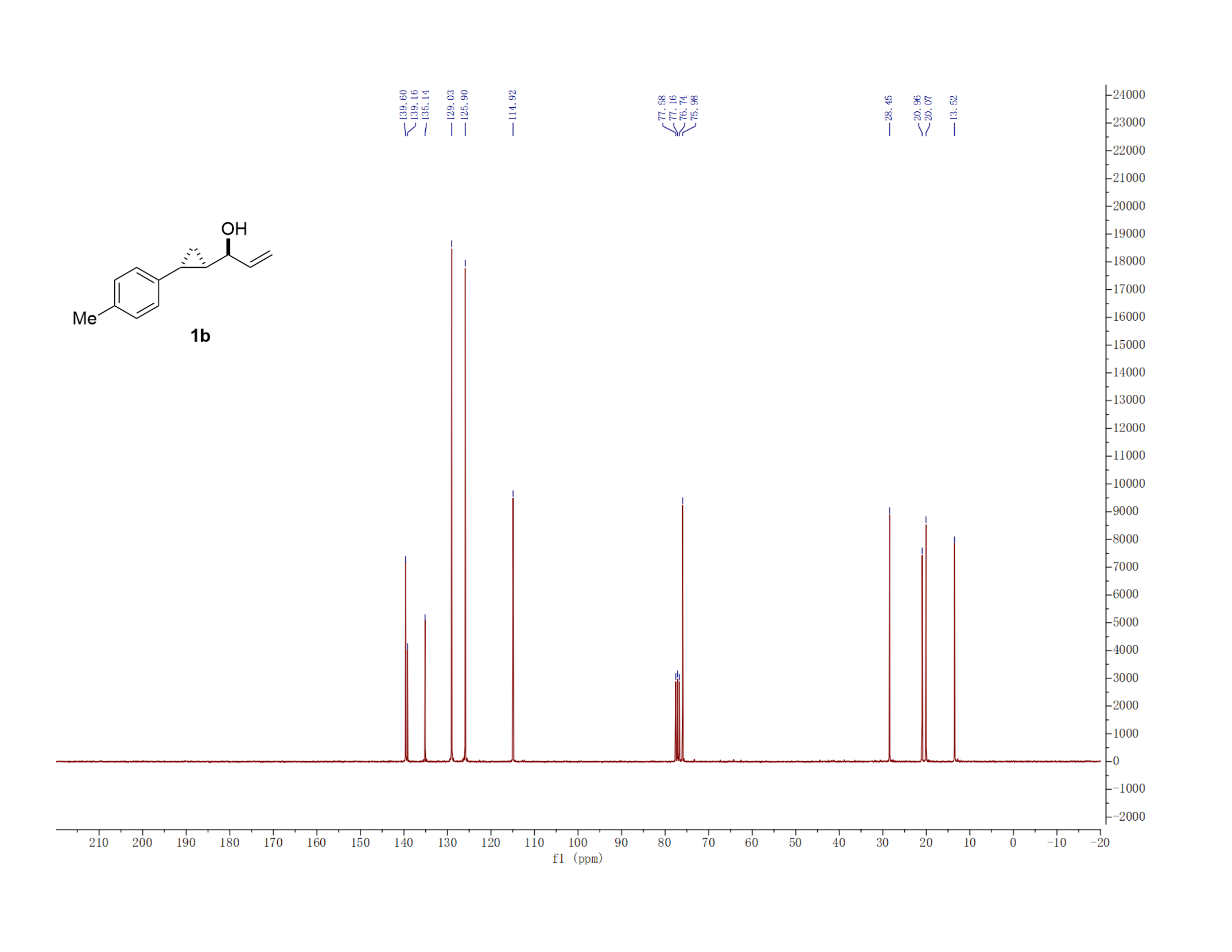
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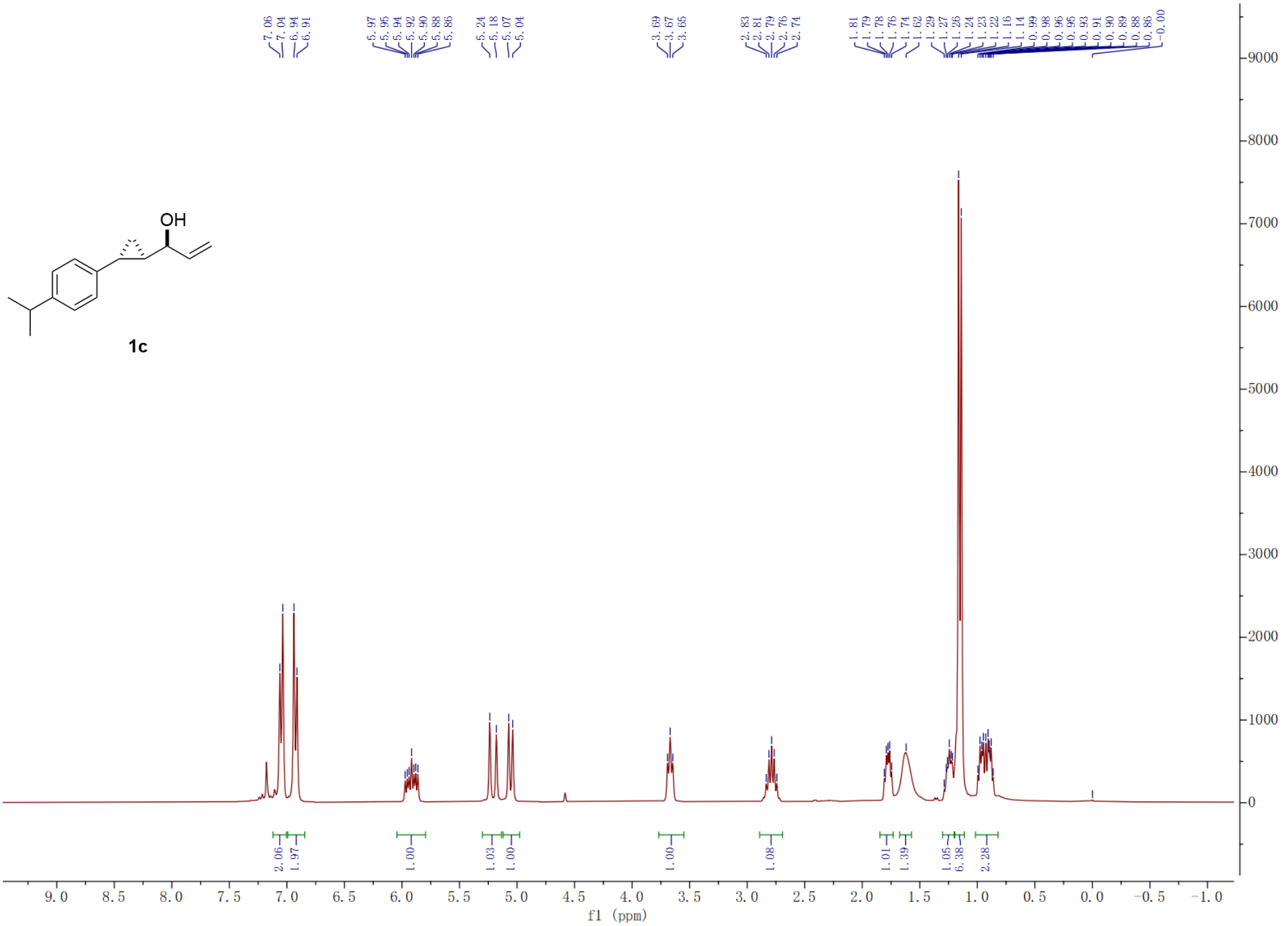
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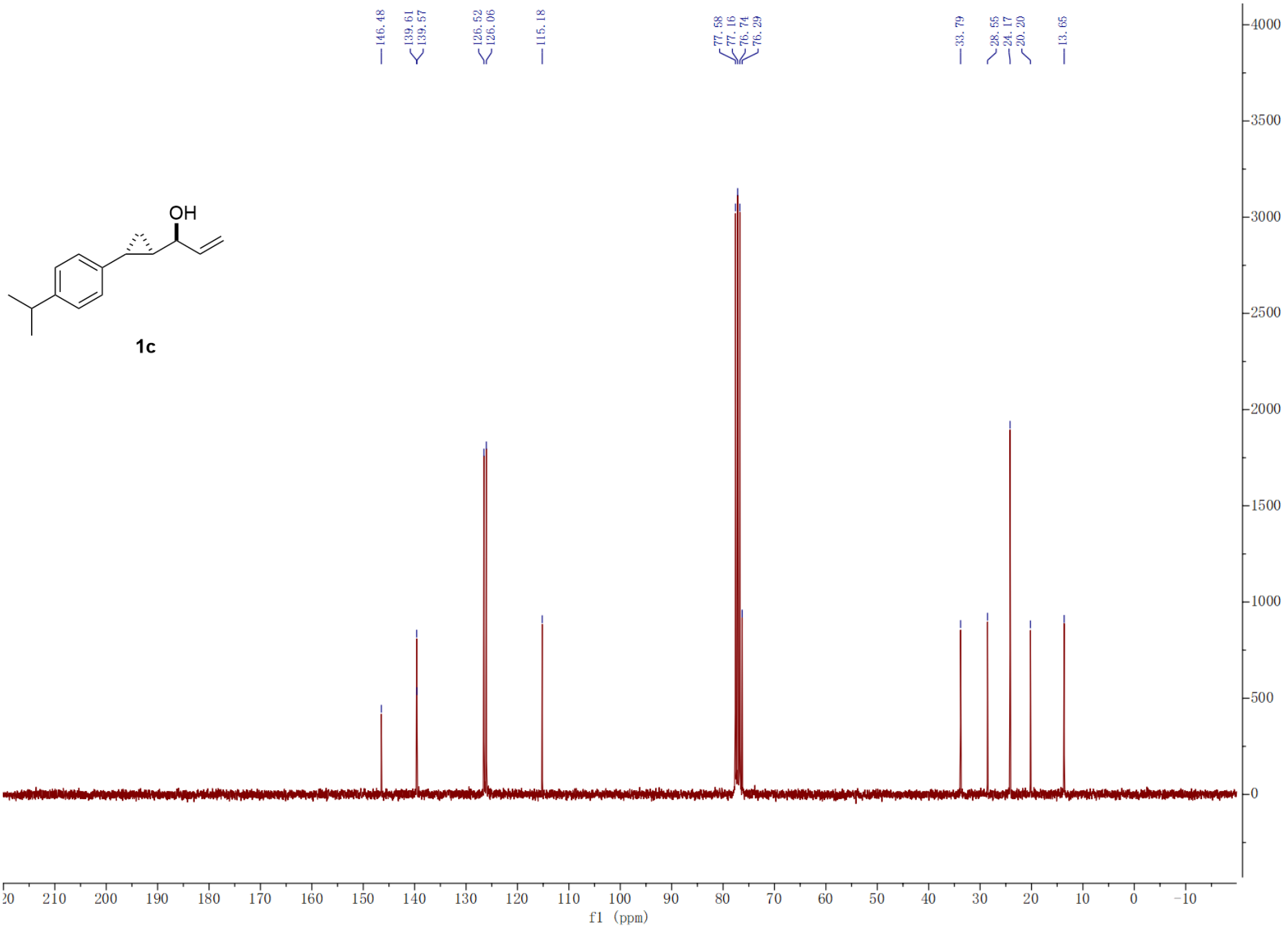
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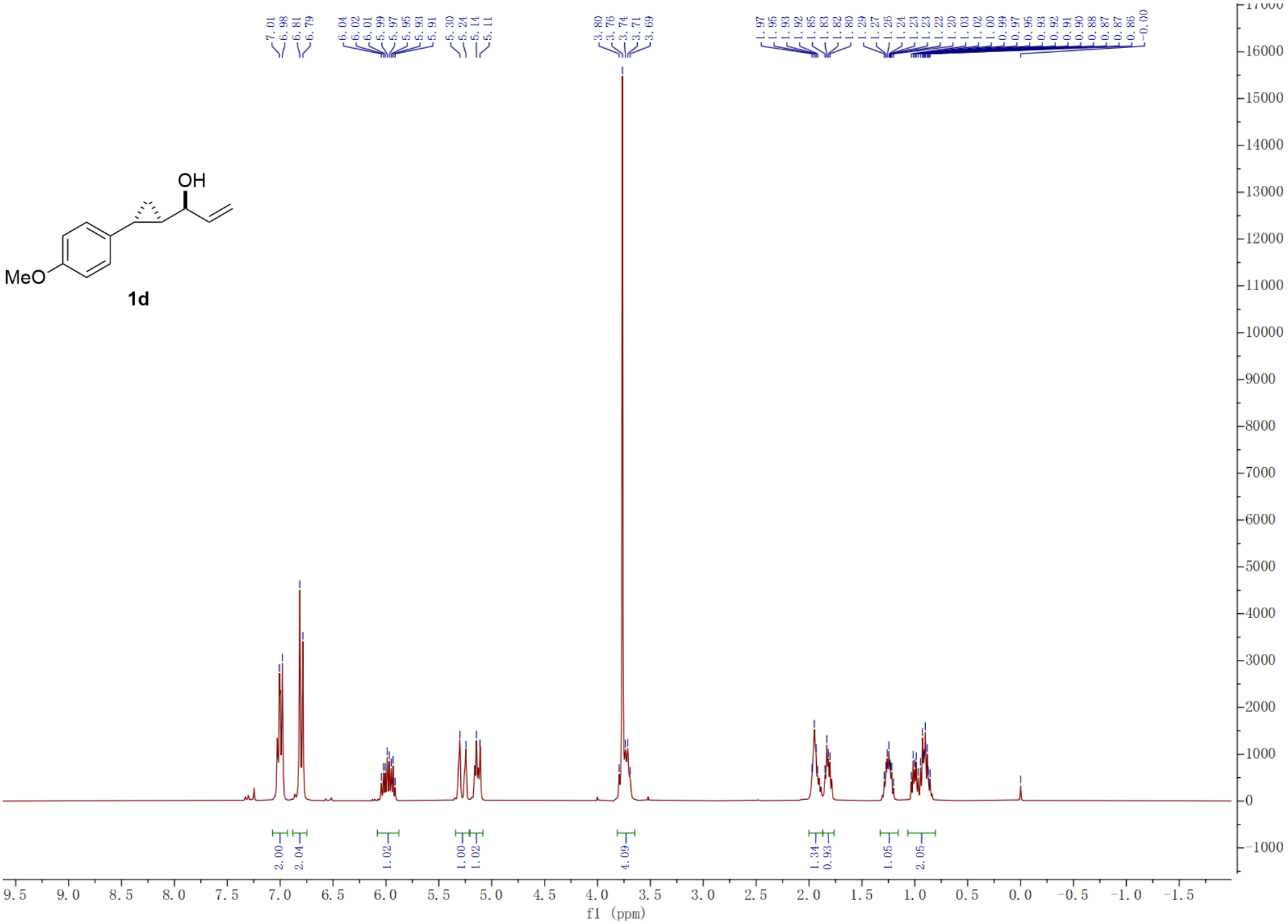
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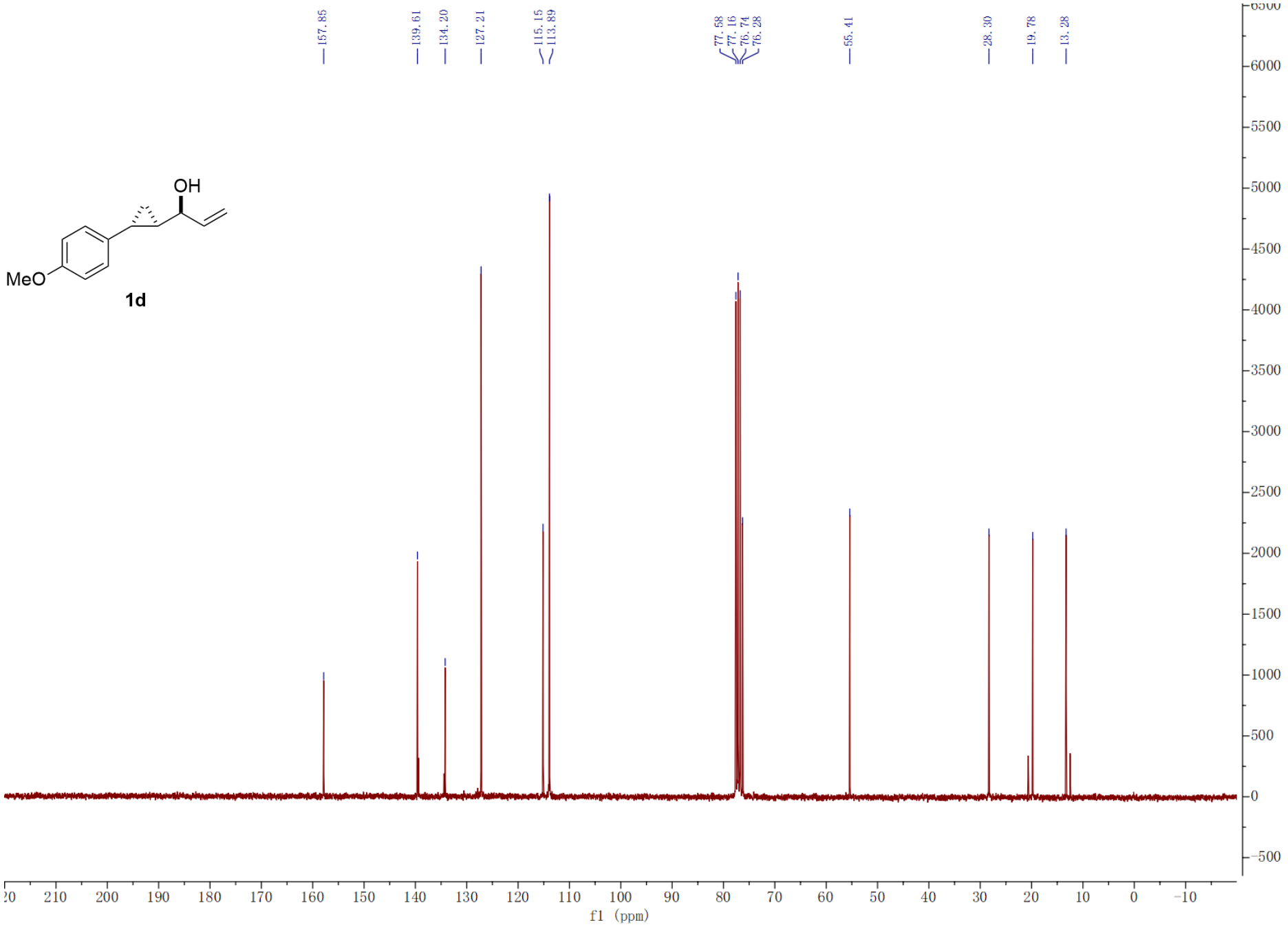
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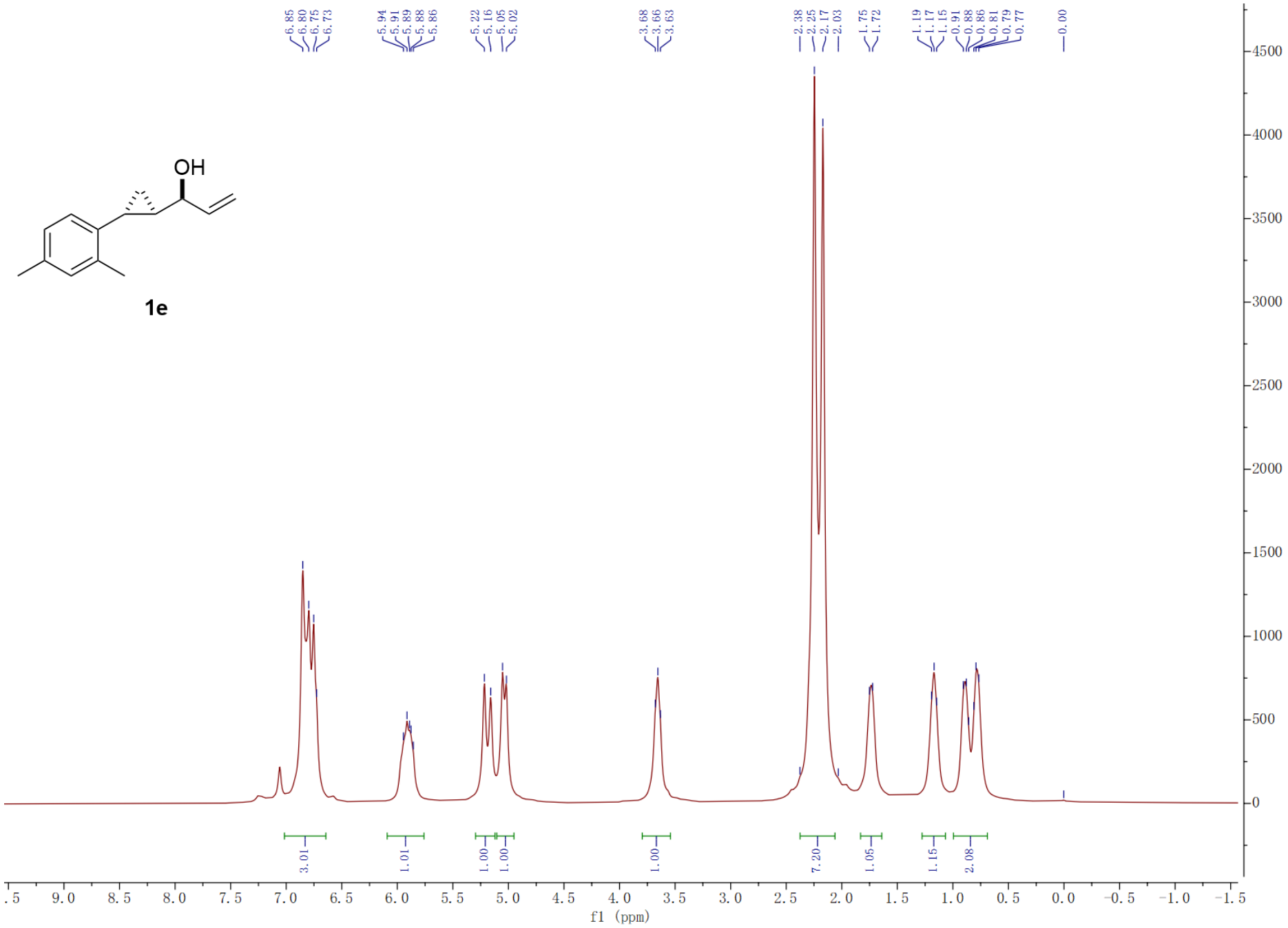
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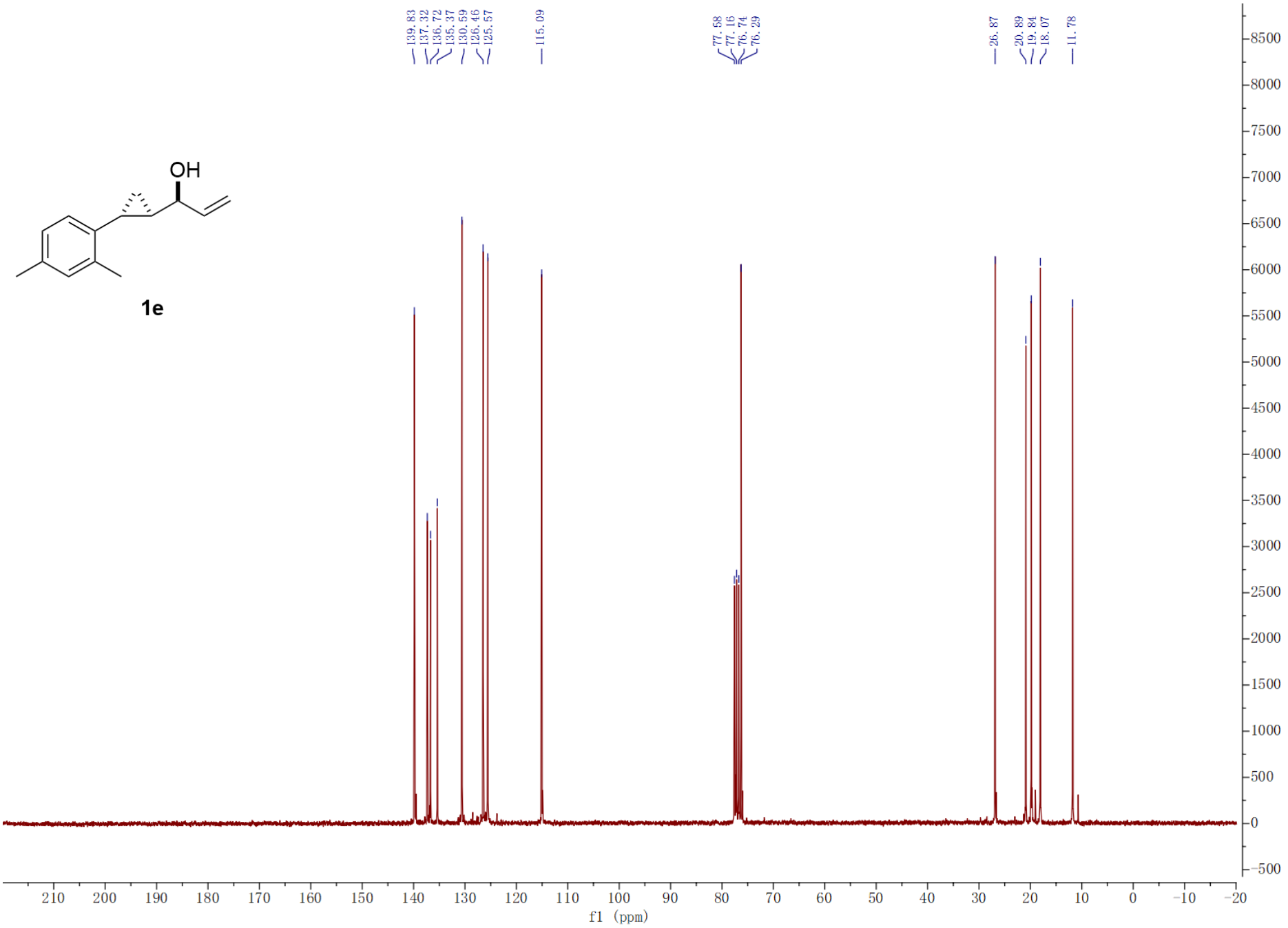
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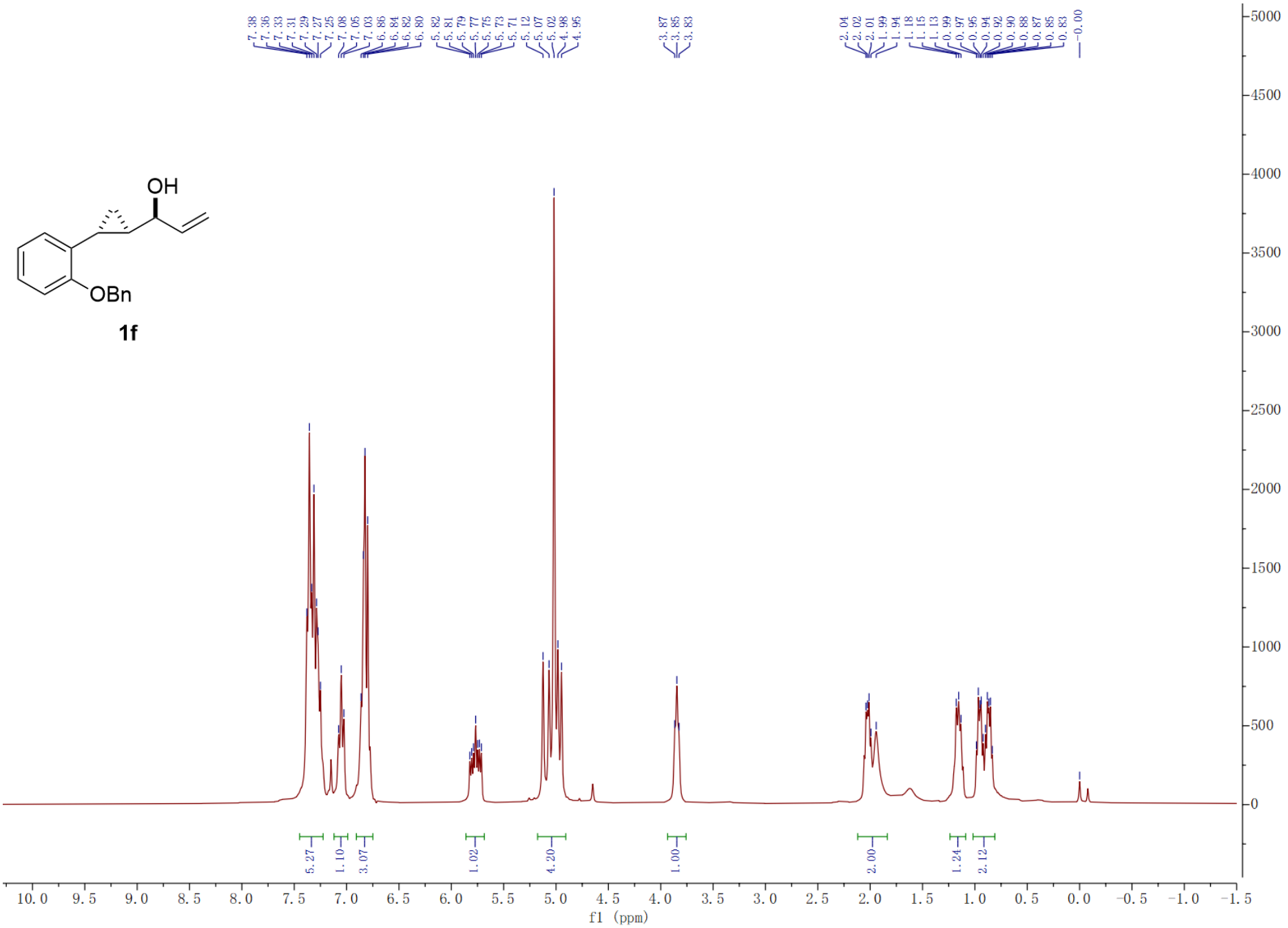
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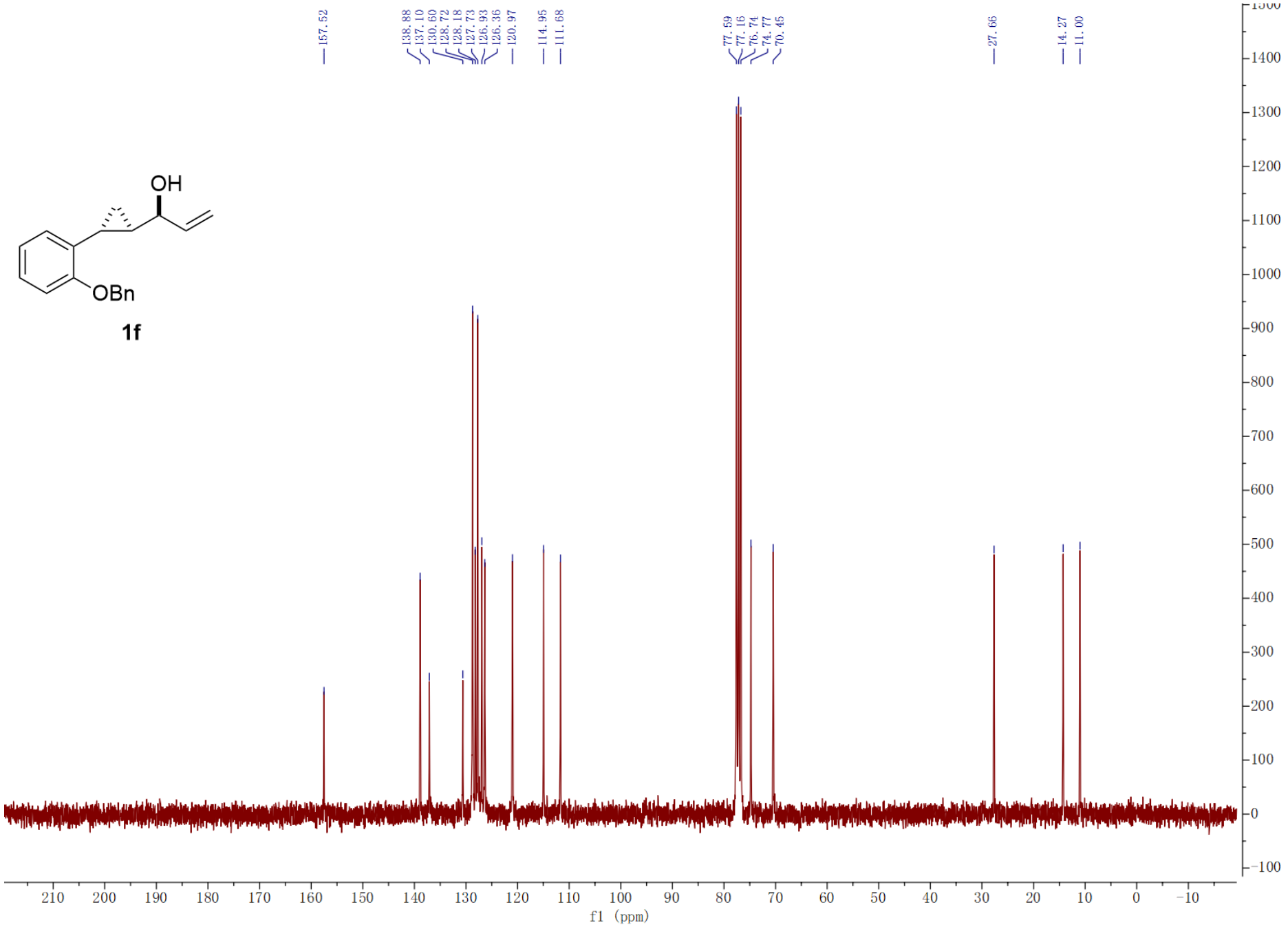
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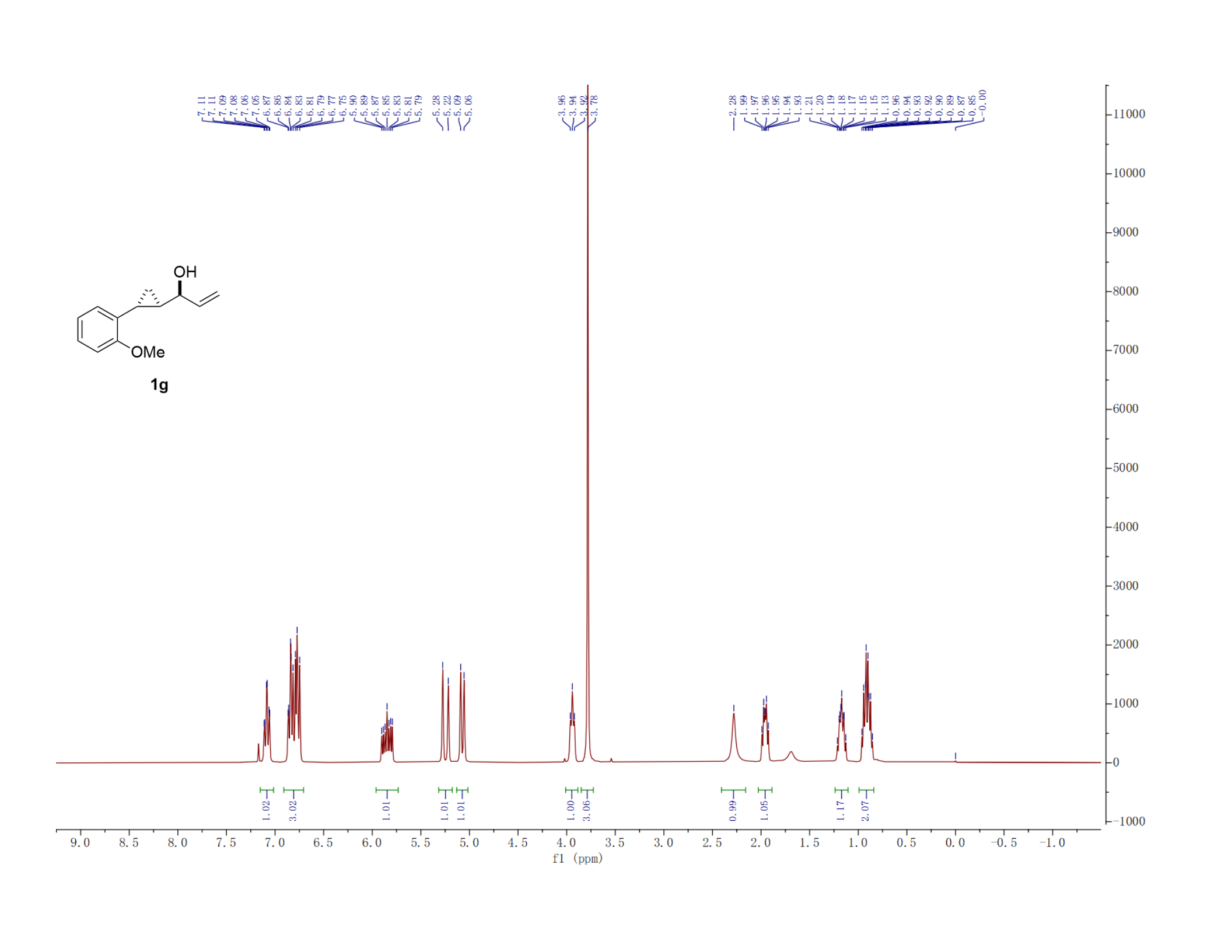
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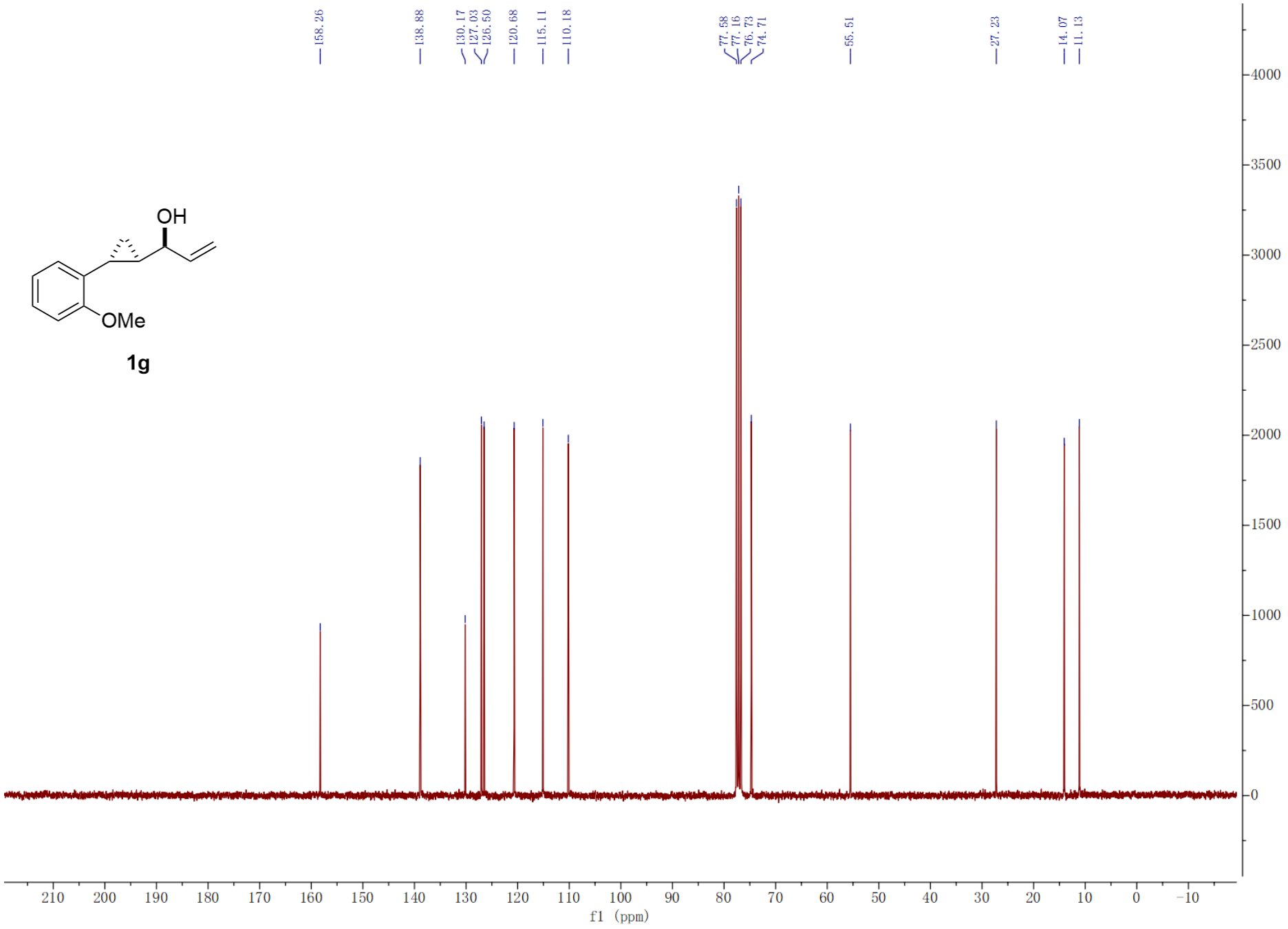
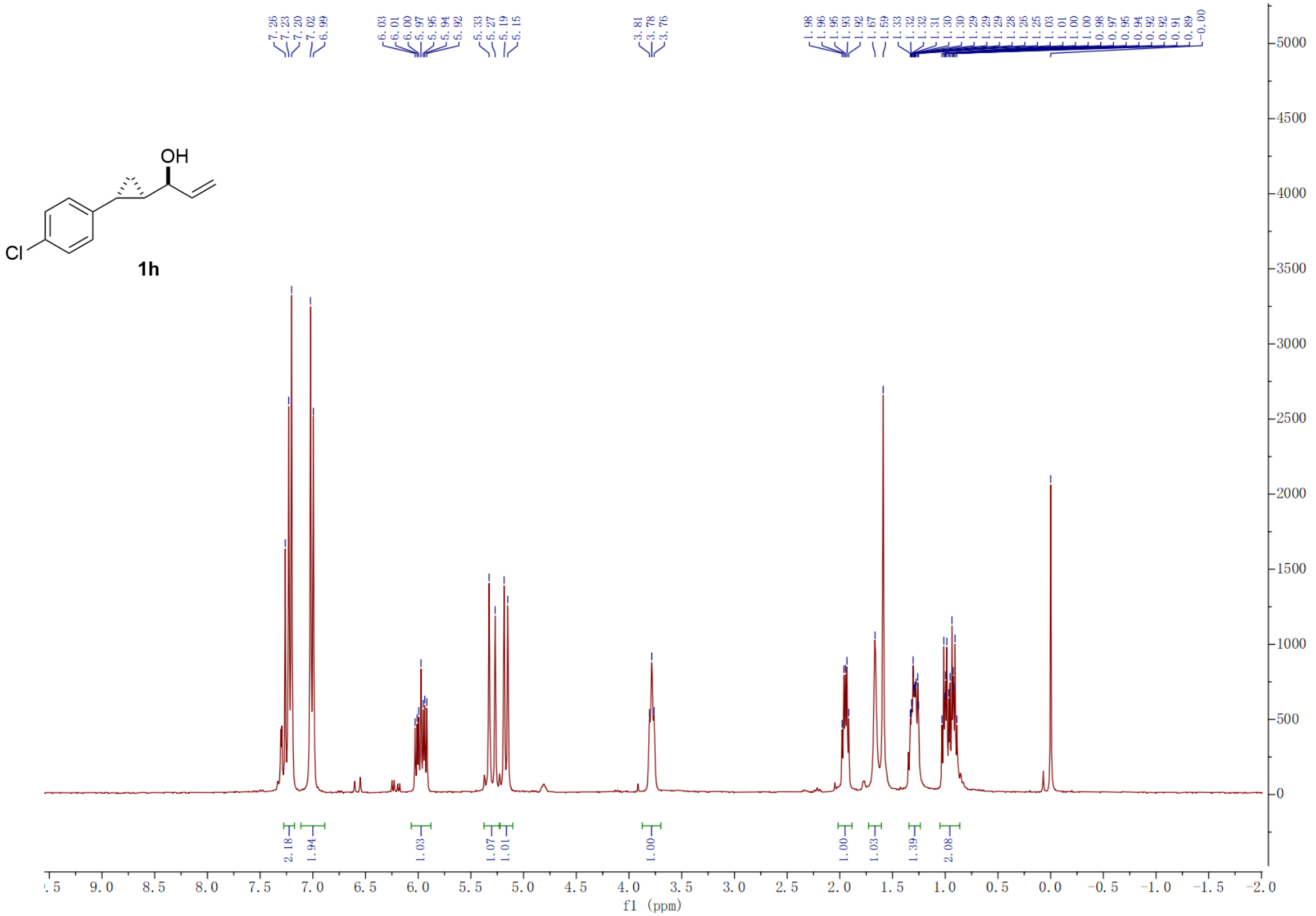
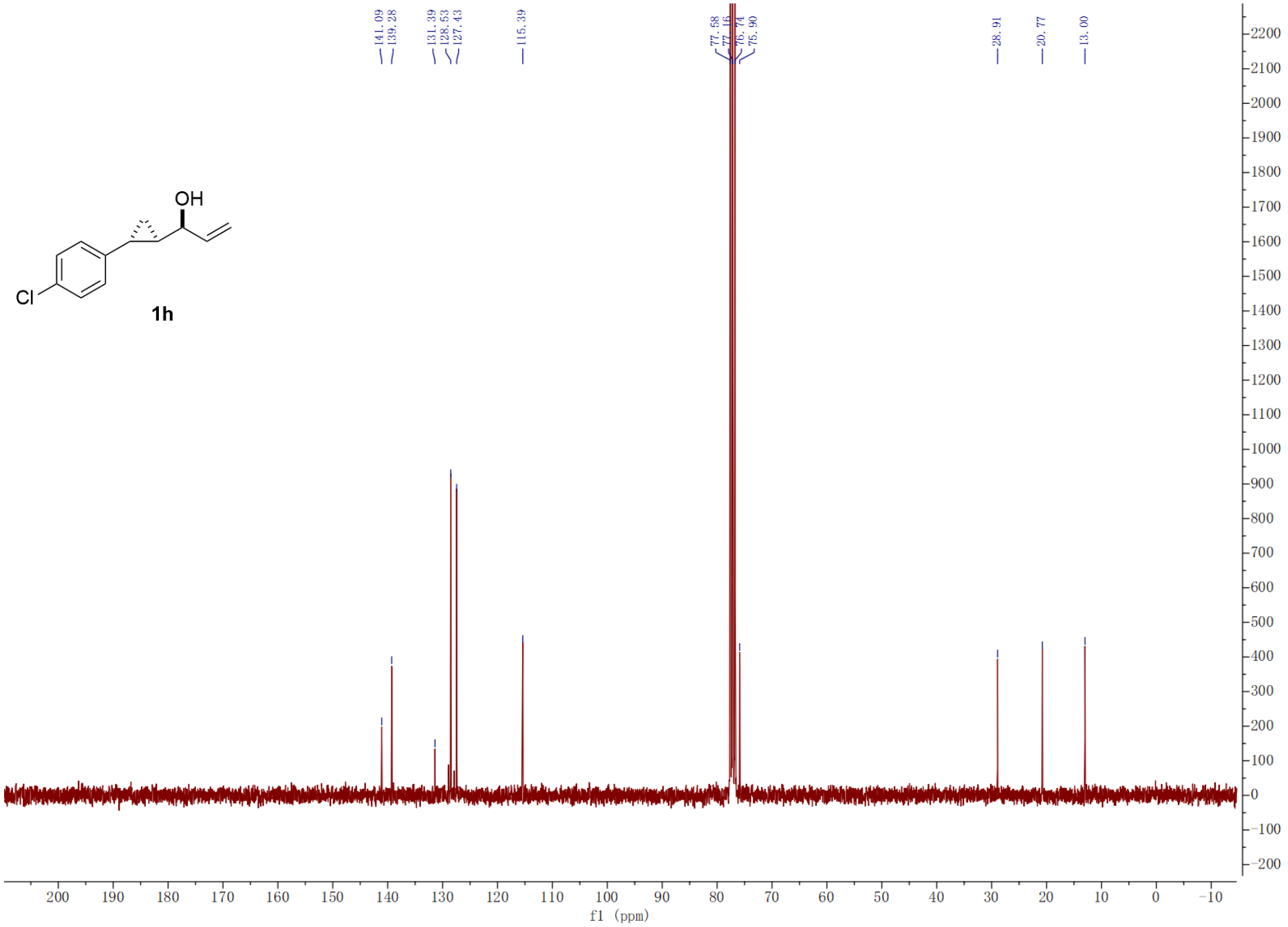
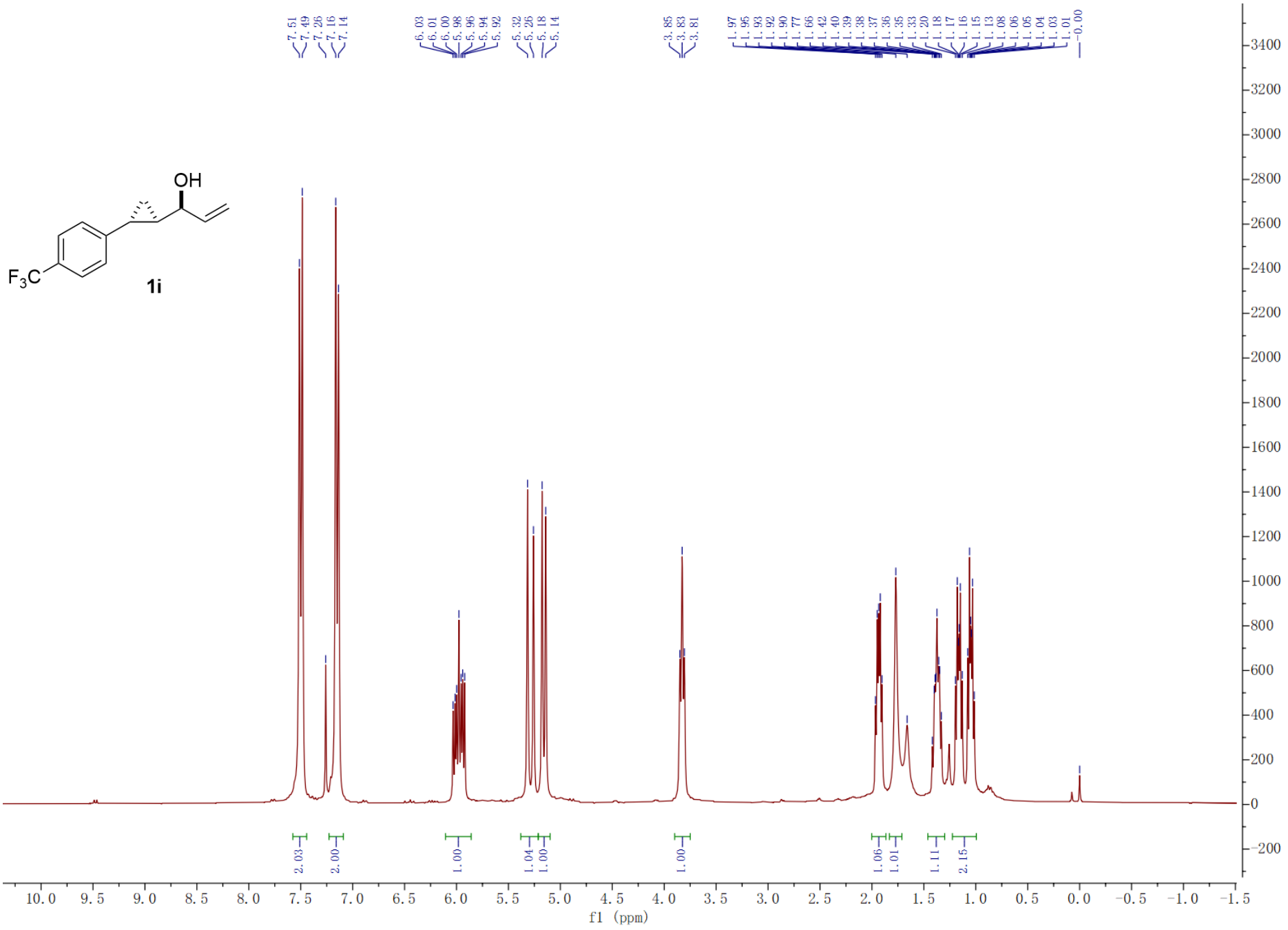
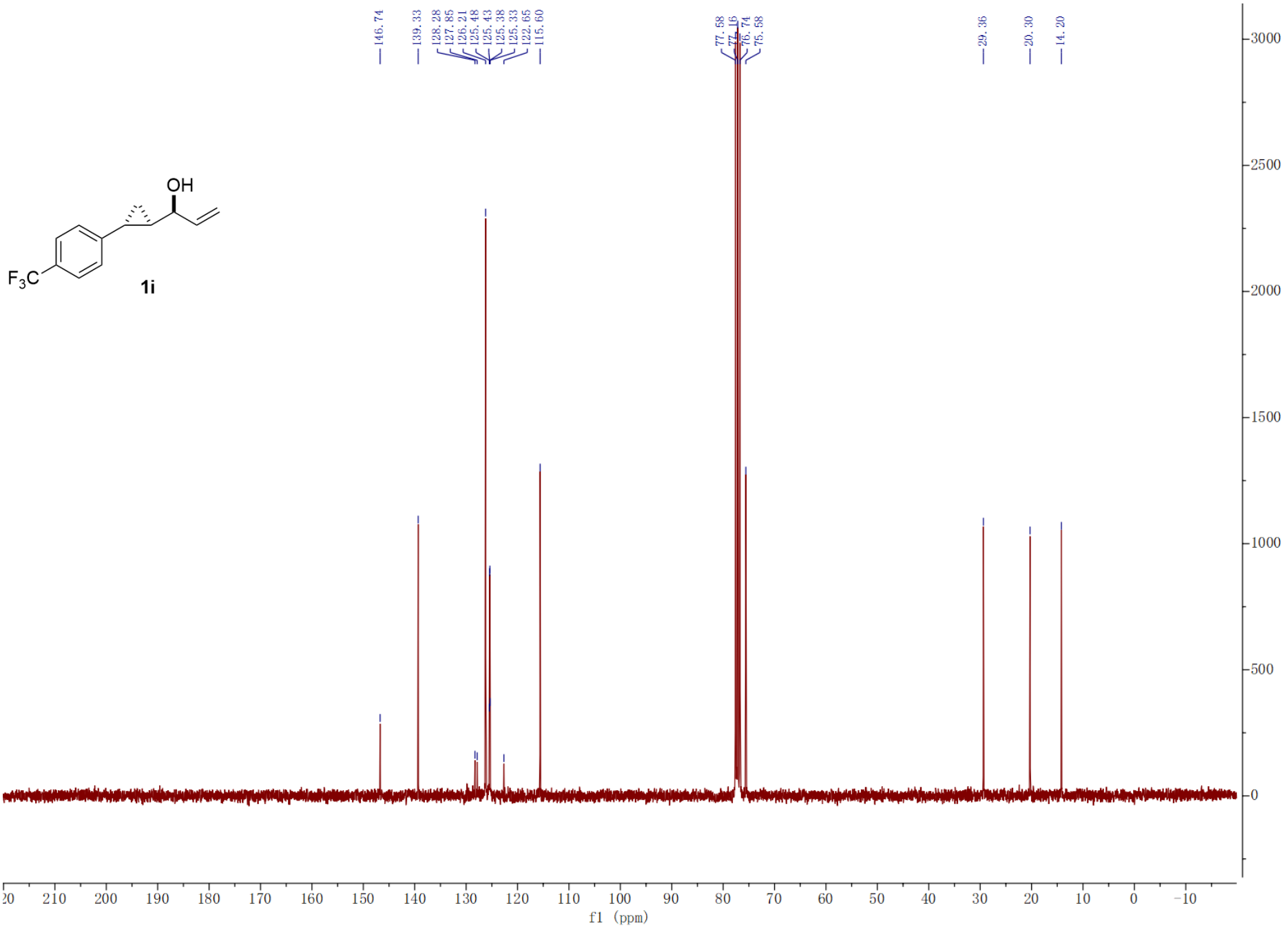
1g
f1 (ppm)

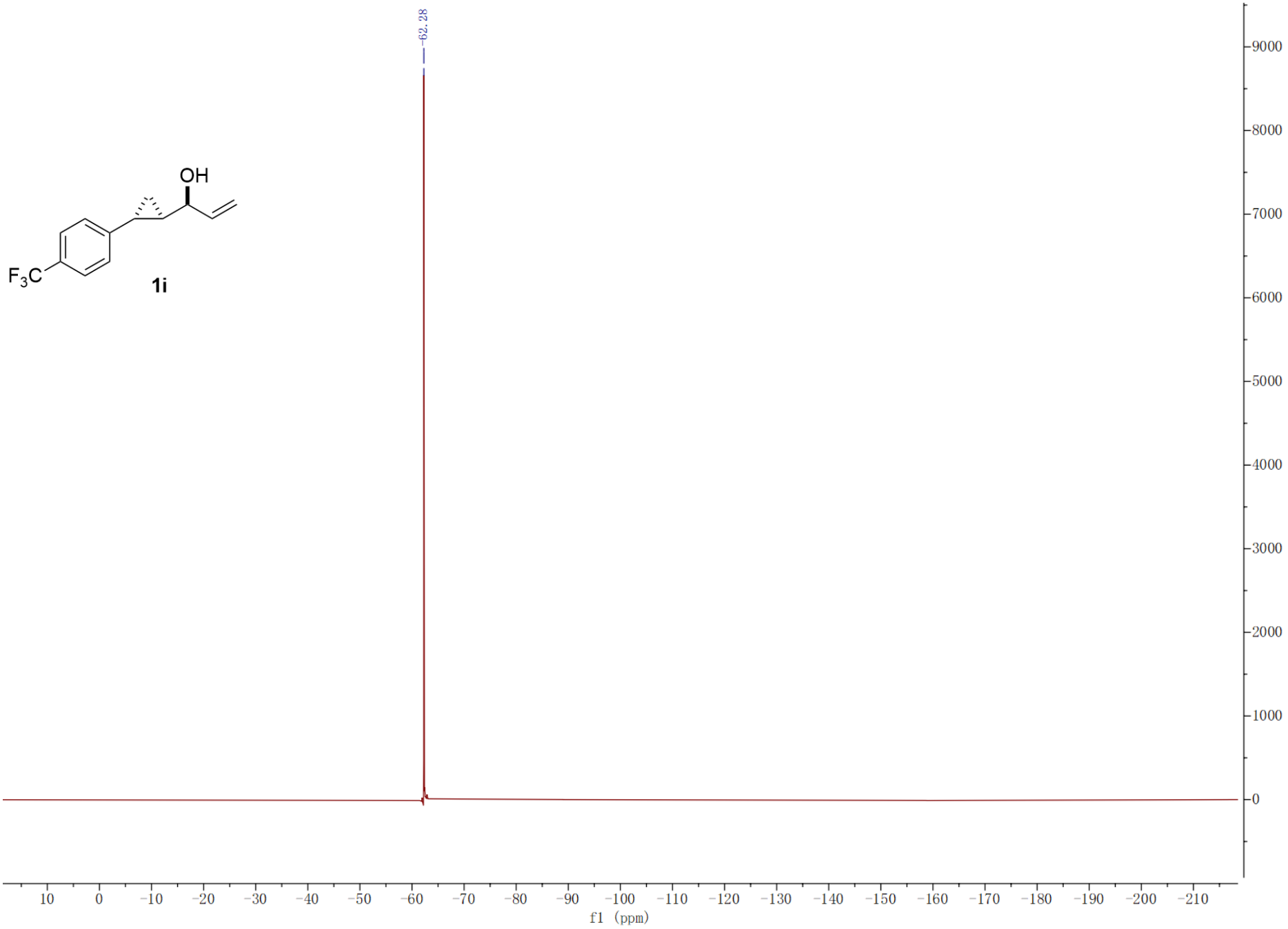

158.26
138.88
130.17
127.03
126.50
120.68
115.11
110.18
77.58
77.16
76.73
74.71
55.51
27.23
14.07
11.13
OH
OMe
1g
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

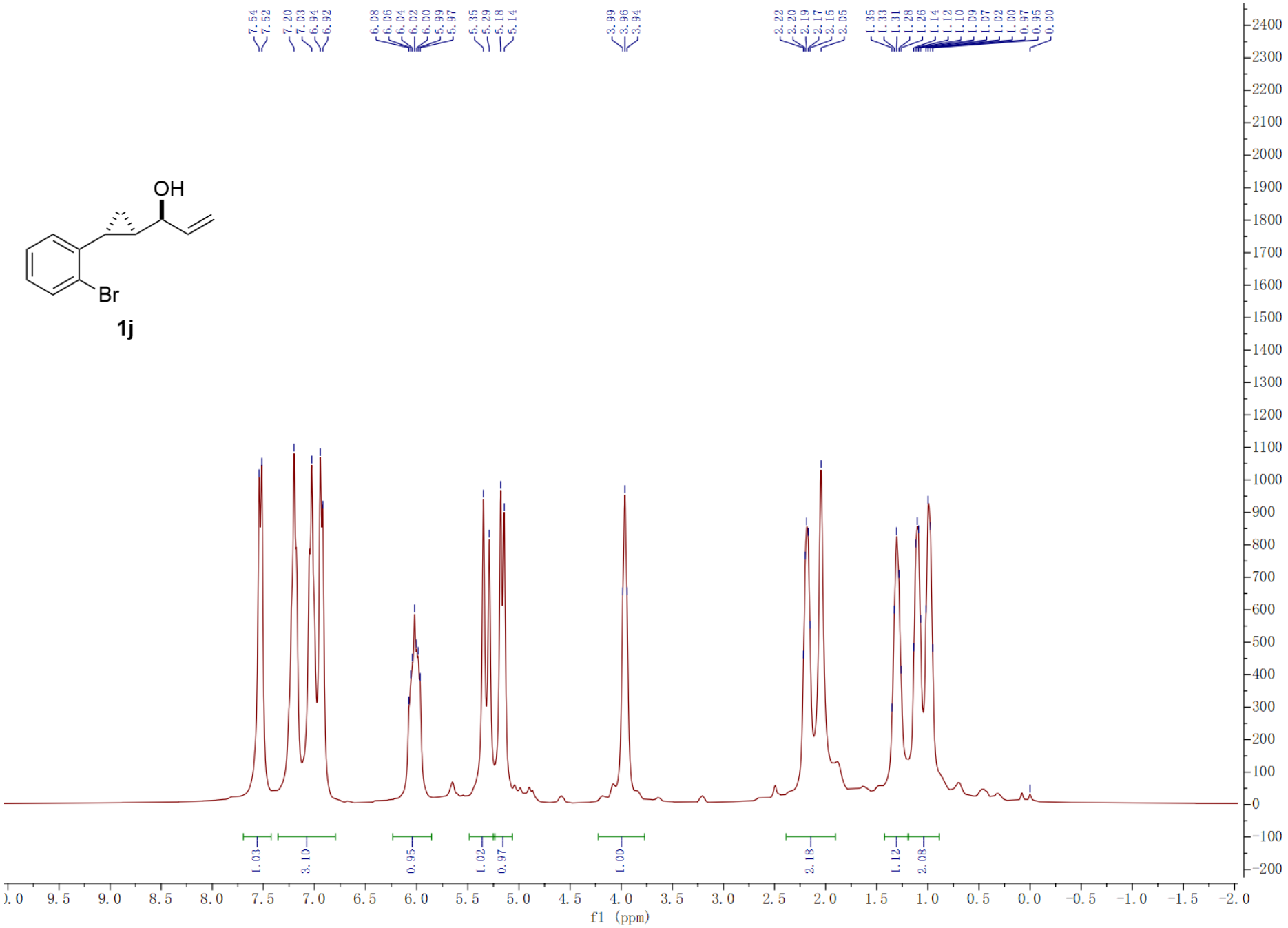

OH
Cl
1h
7.26
7.23
7.20
7.02
6.99
6.03
6.01
6.00
5.97
5.95
5.94
5.92
5.33
5.27
5.19
5.15
3.81
3.78
3.76
1.98
1.96
1.95
1.93
1.92
1.67
1.59
1.33
1.32
1.32
1.31
1.30
1.30
1.29
1.29
1.29
1.28
1.26
1.25
1.03
1.01
1.00
1.00
0.98
0.97
0.95
0.94
0.92
0.92
0.91
0.89
0.00
2.18
1.94
1.03
1.07
1.01
1.00
1.00
1.03
1.39
2.08
f1 (ppm)

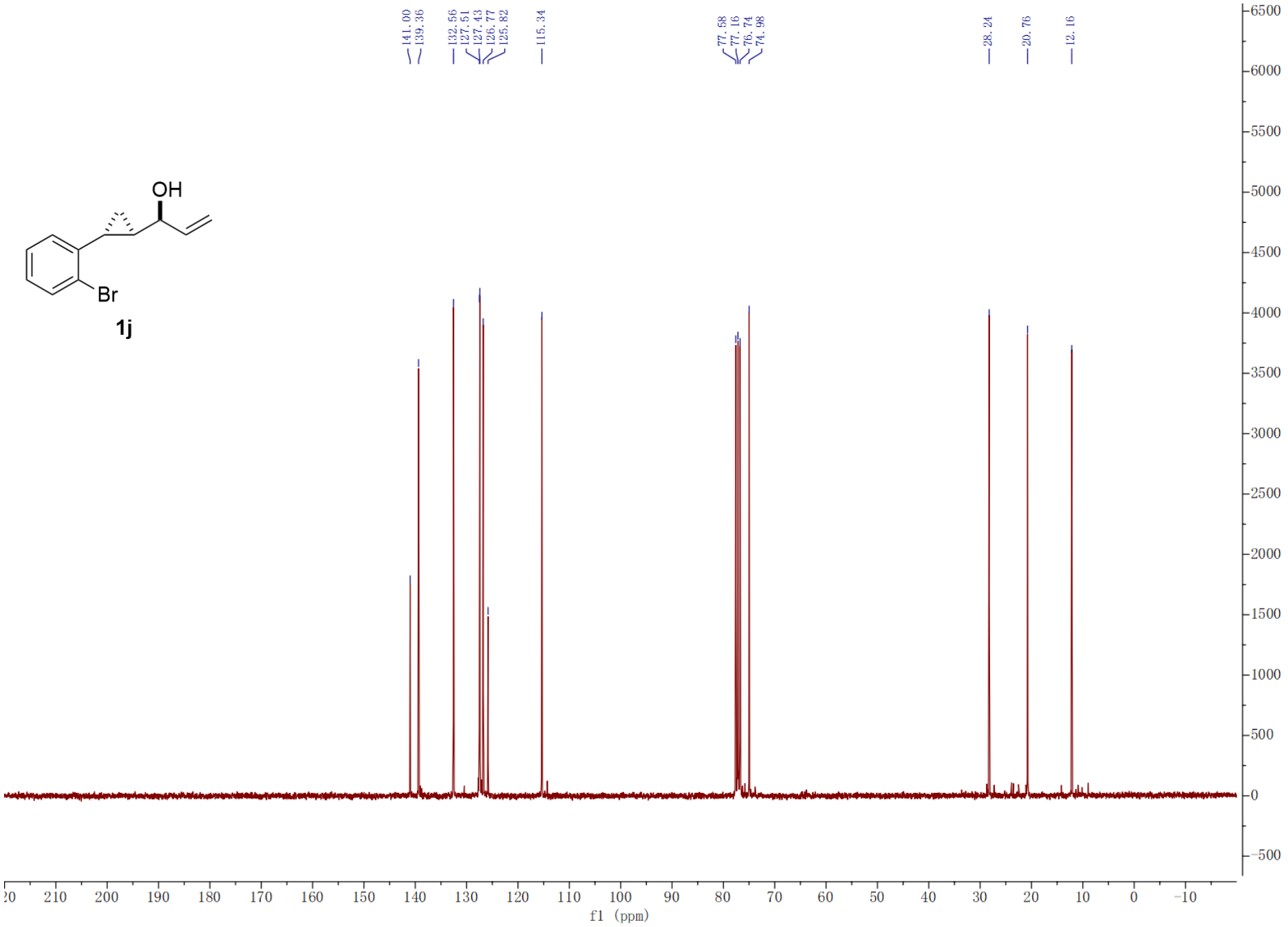

141.09
139.28
131.39
128.53
127.43
115.39
77.58
77.16
76.74
75.90
28.91
20.77
13.00
OH
Cl
1h
f1 (ppm)

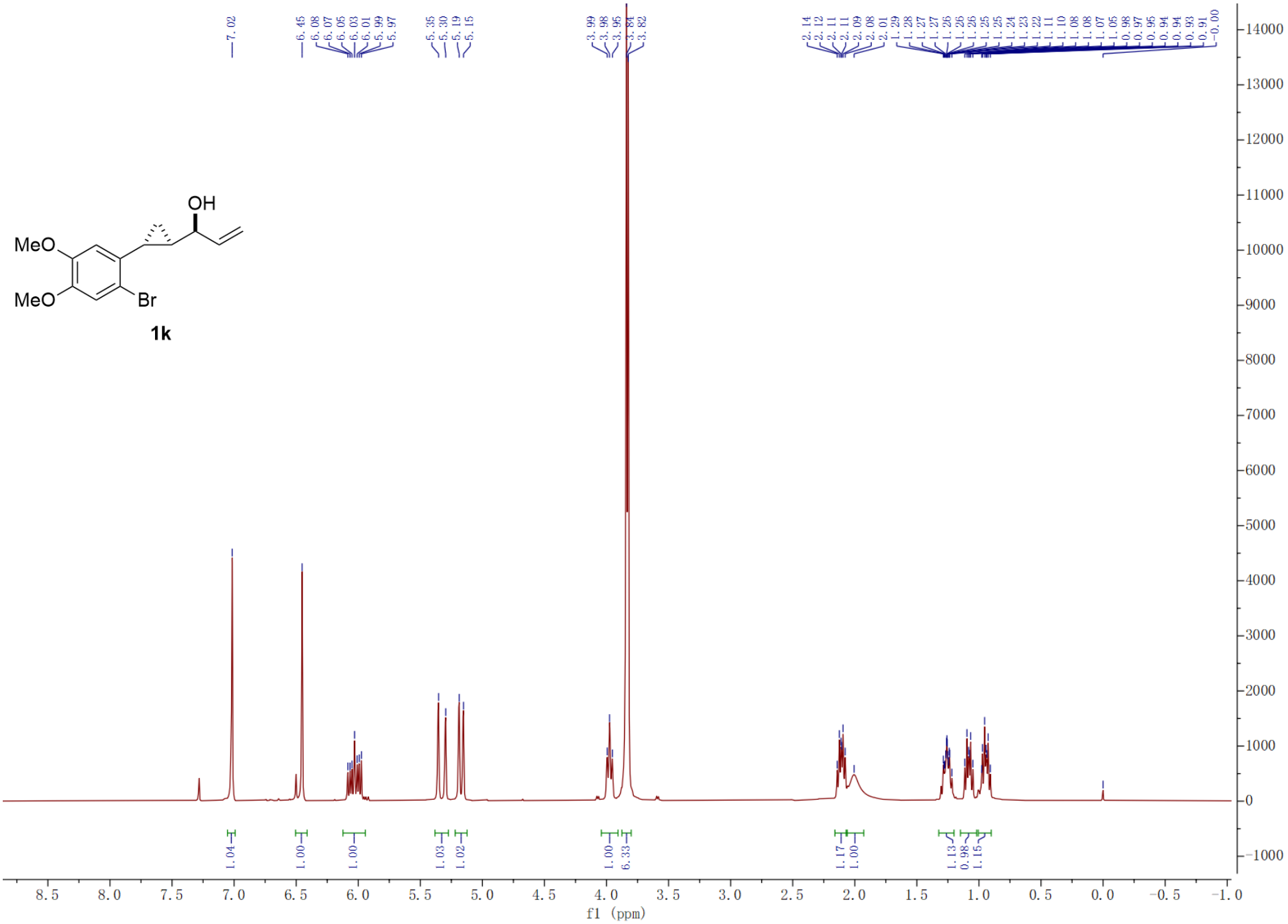

7.51
7.49
7.26
7.16
7.14
6.03
6.01
6.00
5.98
5.96
5.94
5.92
5.32
5.26
5.18
5.14
3.85
3.83
3.81
1.97
1.95
1.93
1.92
1.90
1.77
1.66
1.42
1.40
1.39
1.38
1.37
1.36
1.35
1.33
1.20
1.18
1.17
1.16
1.15
1.13
1.08
1.06
1.05
1.04
1.03
1.01
-0.00
OH
F3C
1i
2.03
2.00
1.00
1.04
1.00
1.00
1.06
1.01
1.11
2.15
f1 (ppm)

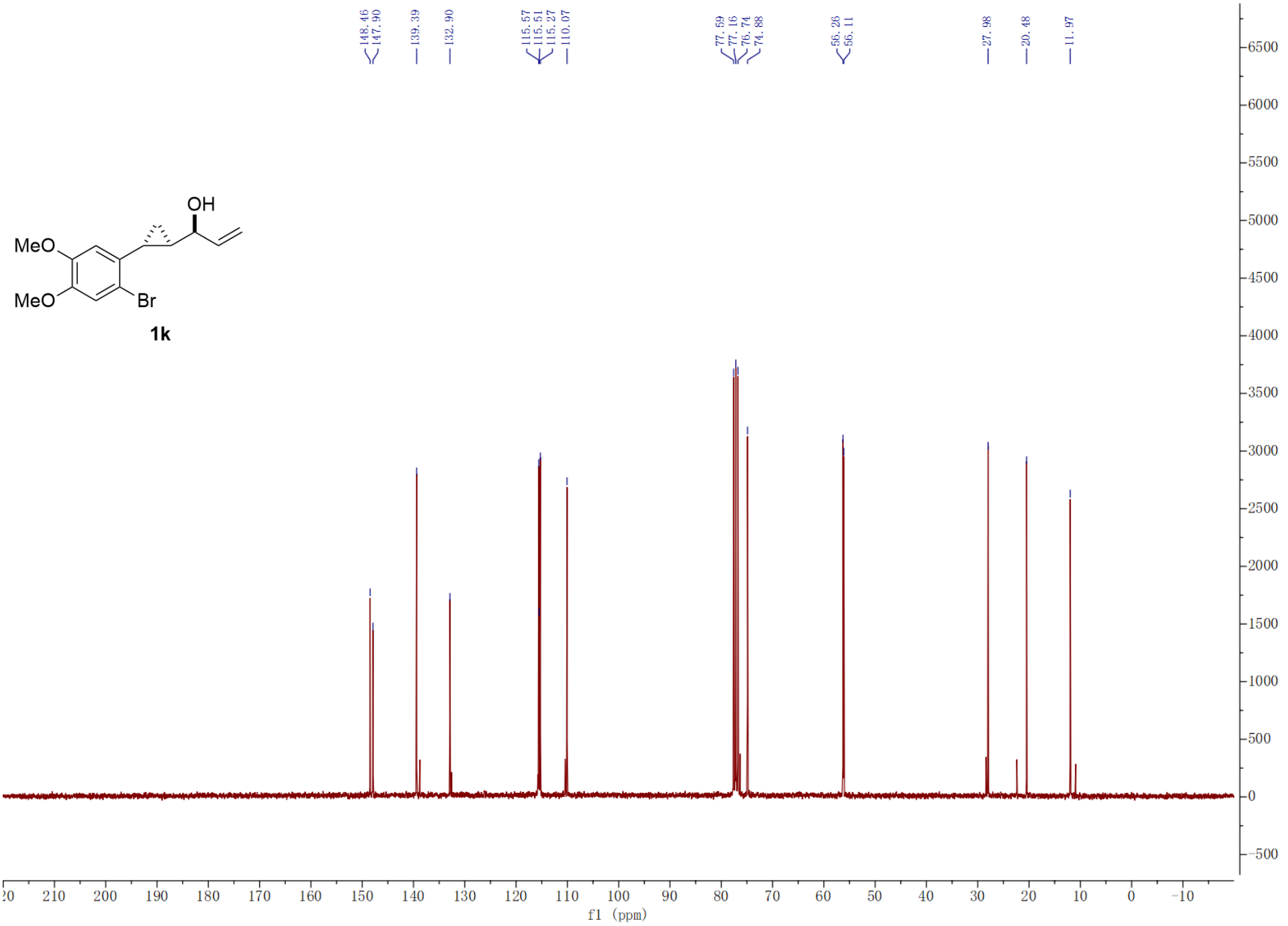

146.74
139.33
128.28
127.85
126.21
125.48
125.43
125.38
125.33
122.65
115.60
77.58
77.16
76.74
75.58
29.36
20.30
14.20
OH
F3C
1i
3000
2500
2000
1500
1000
500
0
f1 (ppm)

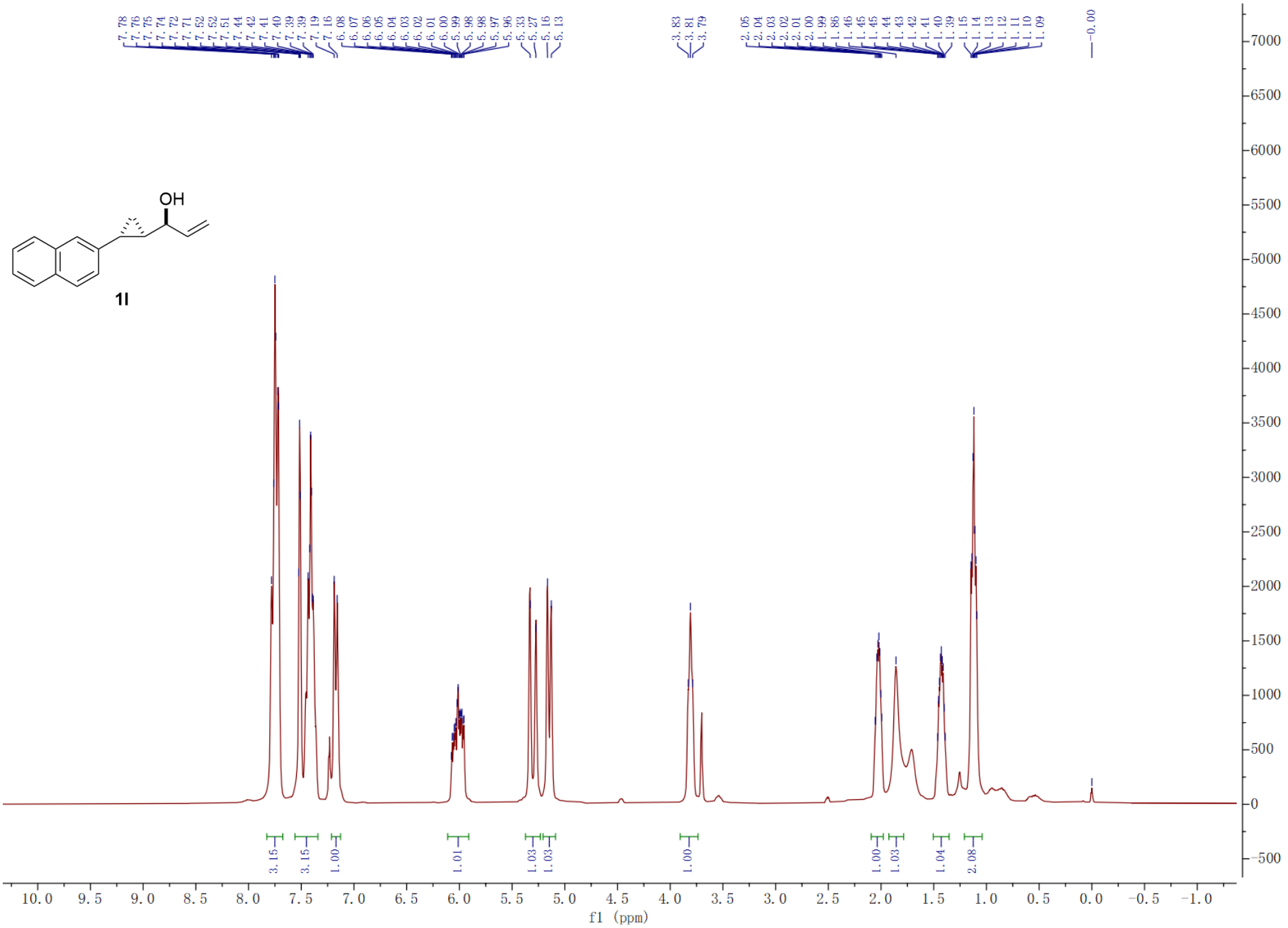

OH
F3C
1i
-62.28
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

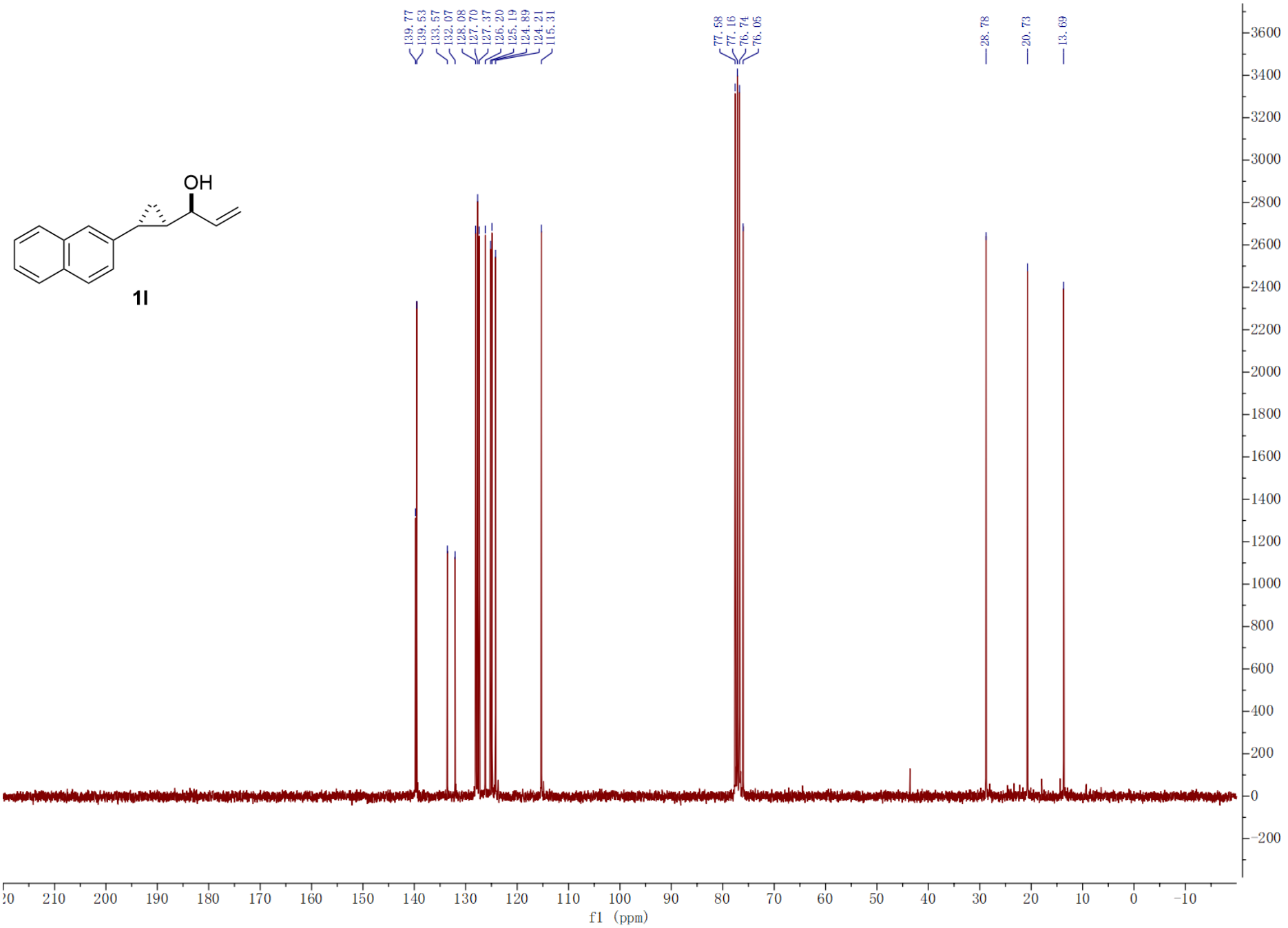

7.54
7.52
7.20
7.03
6.94
6.92
6.08
6.06
6.04
6.02
6.00
5.99
5.97
5.35
5.29
5.18
5.14
3.99
3.96
3.94
2.22
2.20
2.19
2.17
2.15
2.05
1.35
1.33
1.31
1.28
1.26
1.14
1.12
1.10
1.09
1.07
1.02
1.00
0.97
0.95
0.00
OH
Br
1j
1.03
3.10
0.95
1.02
0.97
1.00
2.18
1.12
2.08
f1 (ppm)


141.00
139.36
132.56
127.51
127.43
126.77
125.82
115.34
77.58
77.16
76.74
74.98
28.24
20.76
12.16
OH
Br
1j
f1 (ppm)


OH
MeO
MeO
Br
1k
7.02
6.45
6.08
6.07
6.05
6.03
6.01
5.99
5.97
5.35
5.30
5.19
5.15
3.99
3.98
3.95
3.84
3.82
2.14
2.12
2.11
2.11
2.09
2.08
2.01
1.29
1.28
1.27
1.27
1.26
1.26
1.26
1.25
1.25
1.24
1.23
1.22
1.11
1.10
1.08
1.08
1.07
1.05
0.98
0.97
0.95
0.94
0.94
0.93
0.91
0.00
1.04
1.00
1.00
1.03
1.02
1.00
6.33
1.17
1.00
1.13
0.98
1.15
f1 (ppm)


148.46
147.90
139.39
132.90
115.57
115.51
115.27
110.07
77.59
77.16
76.74
74.88
56.26
56.11
27.98
20.48
11.97
OH
MeO
MeO
Br
1k
f1 (ppm)


7.78
7.76
7.75
7.74
7.72
7.71
7.52
7.52
7.51
7.44
7.42
7.41
7.40
7.39
7.39
7.19
7.16
6.08
6.07
6.06
6.05
6.04
6.03
6.02
6.01
6.00
5.99
5.98
5.98
5.97
5.96
5.33
5.27
5.16
5.13
3.83
3.81
3.79
2.05
2.04
2.03
2.02
2.01
2.00
1.99
1.86
1.46
1.45
1.45
1.44
1.43
1.42
1.41
1.40
1.39
1.15
1.14
1.13
1.12
1.11
1.10
1.09
-0.00
OH
1l
3.15
3.15
1.00
1.01
1.03
1.03
1.00
1.00
1.03
1.04
2.08
f1 (ppm)


OH
1l
139.77
139.53
133.57
132.07
128.08
127.70
127.37
126.20
125.19
124.89
124.21
115.31
77.58
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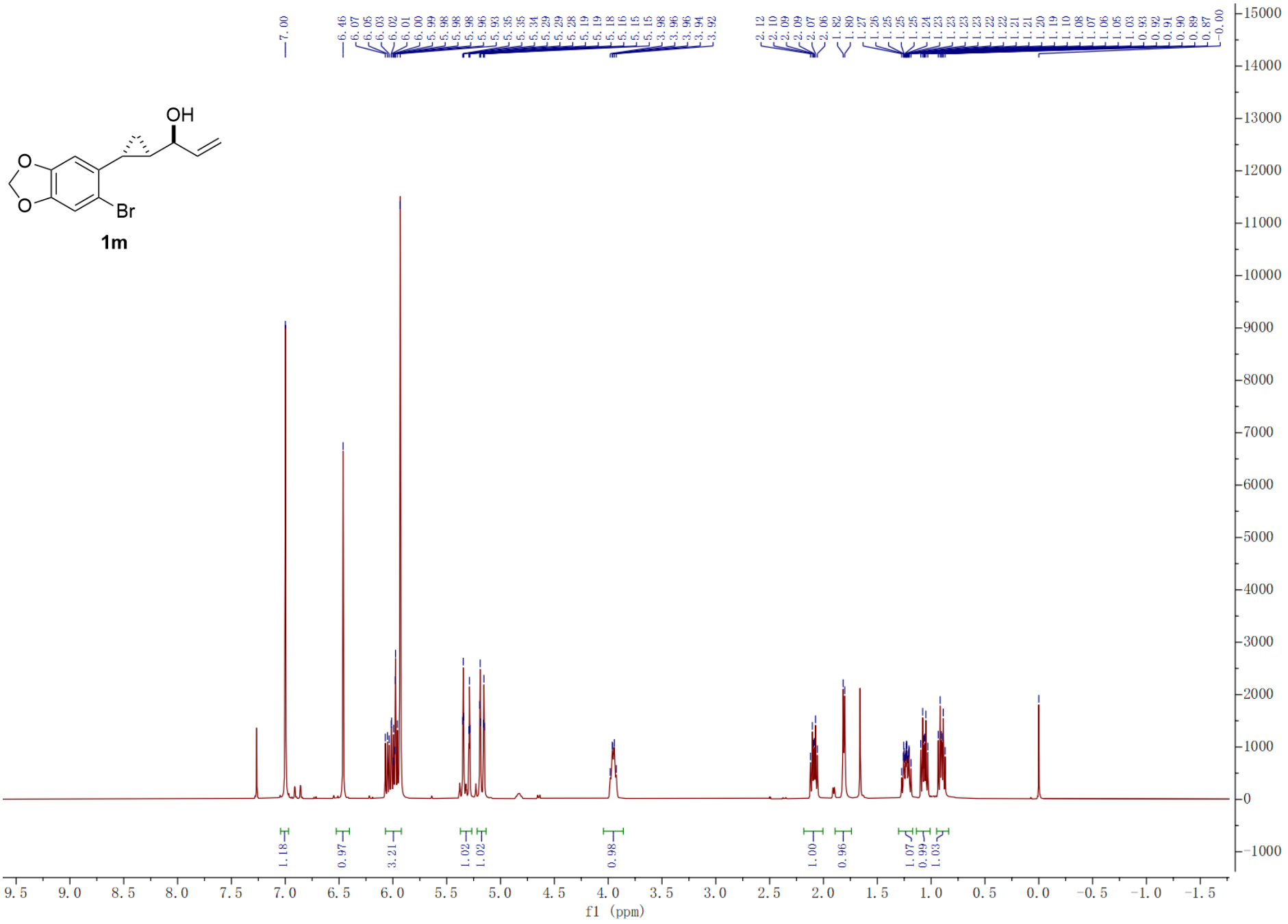
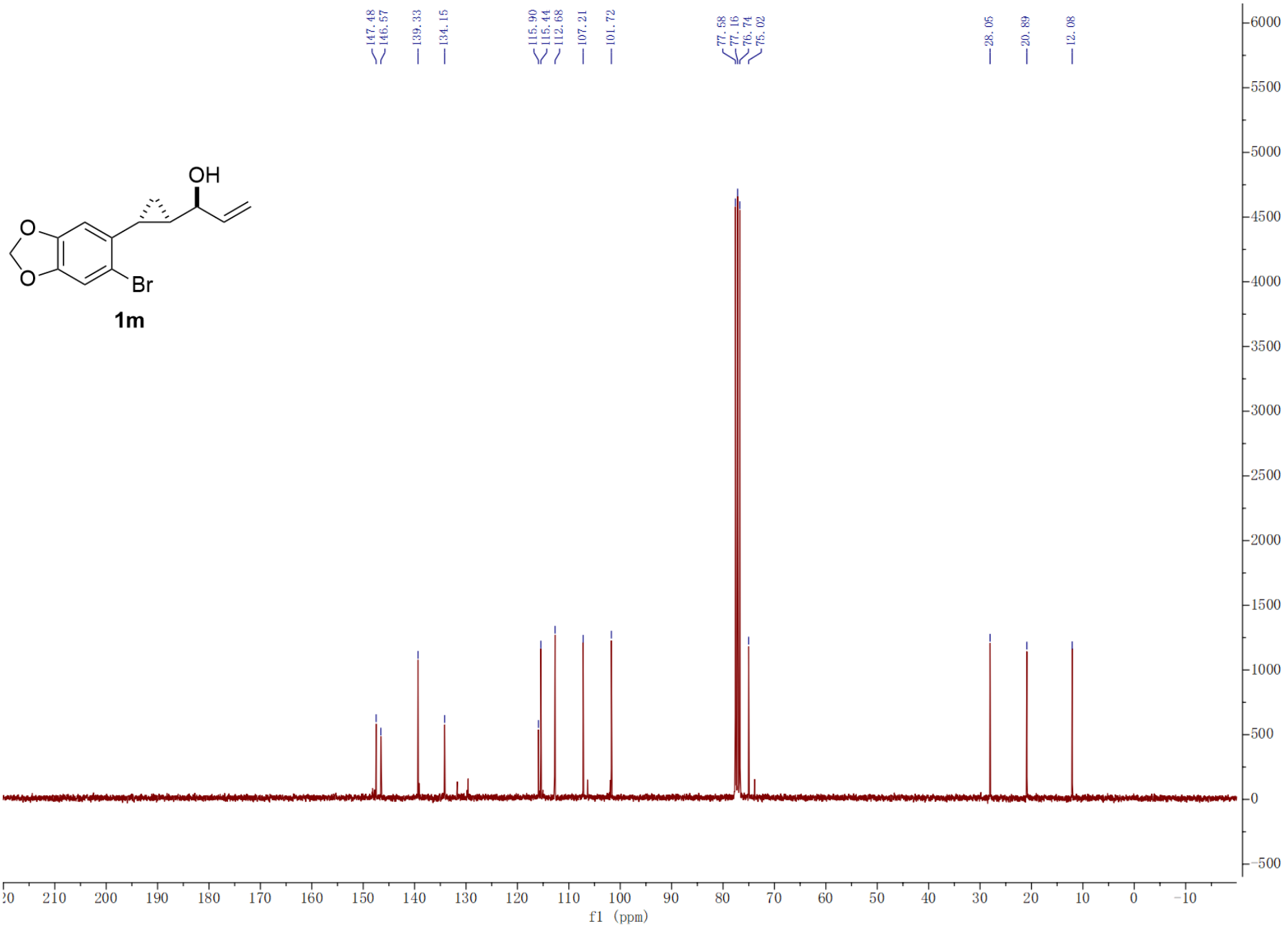
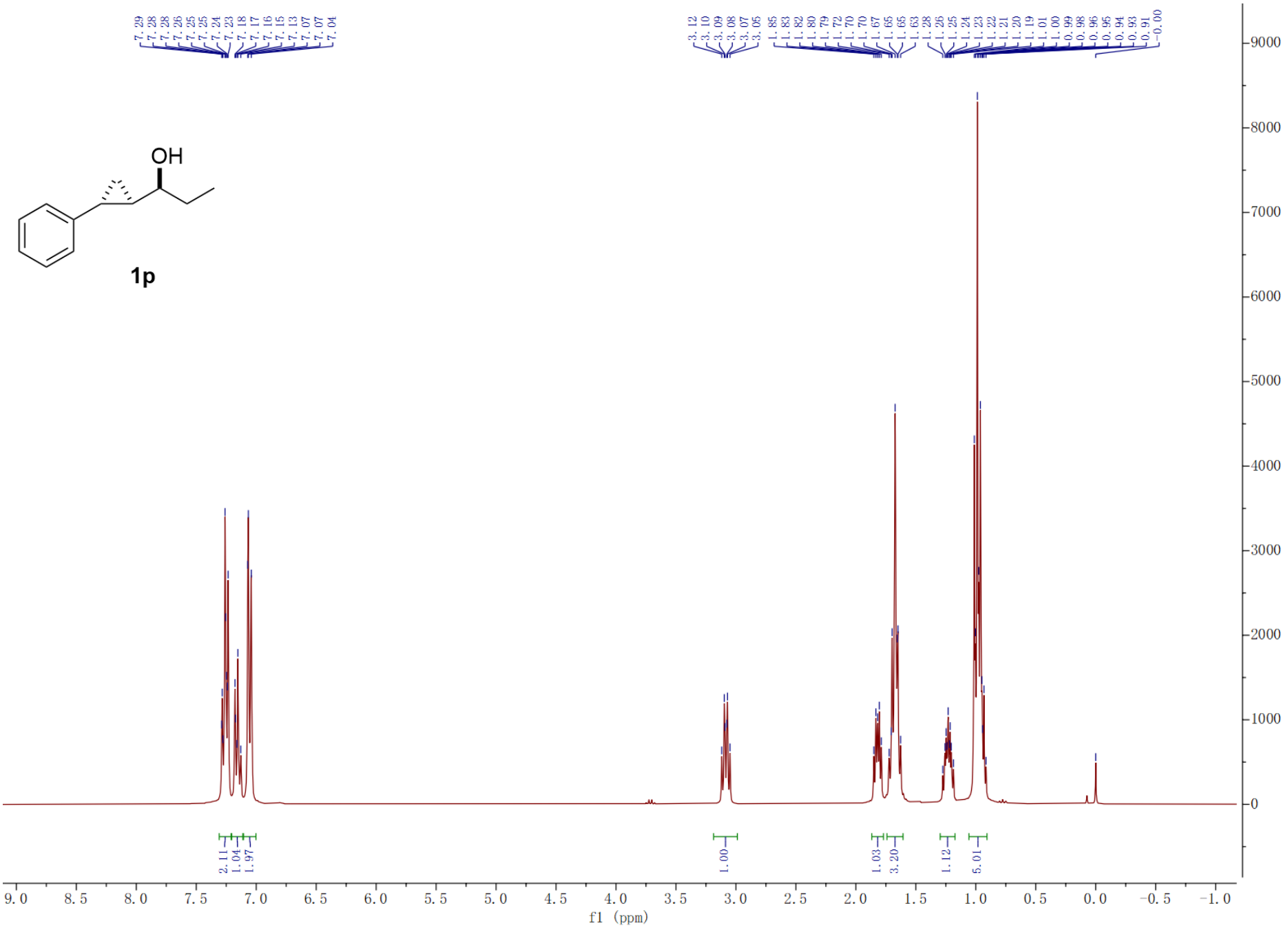
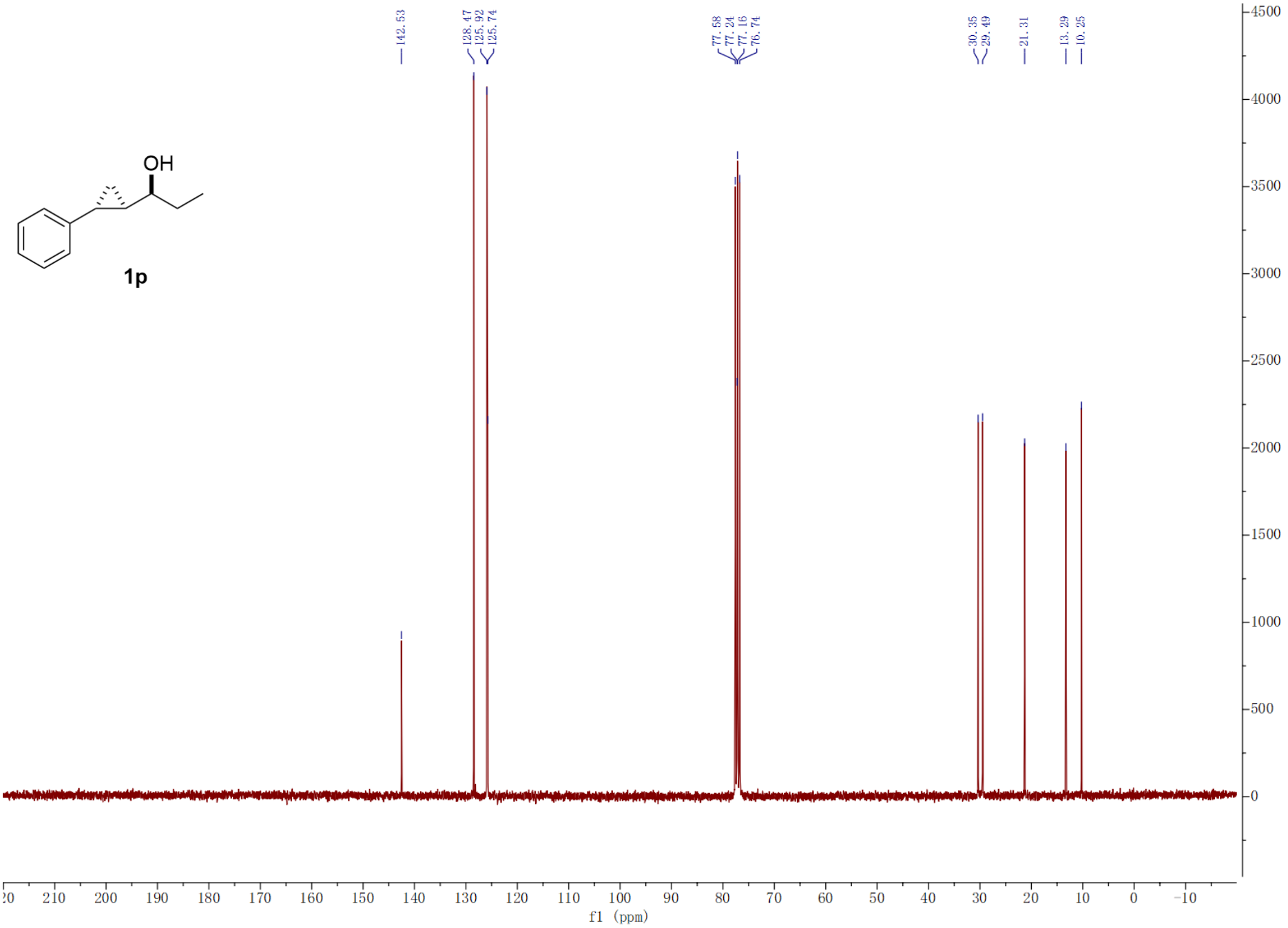
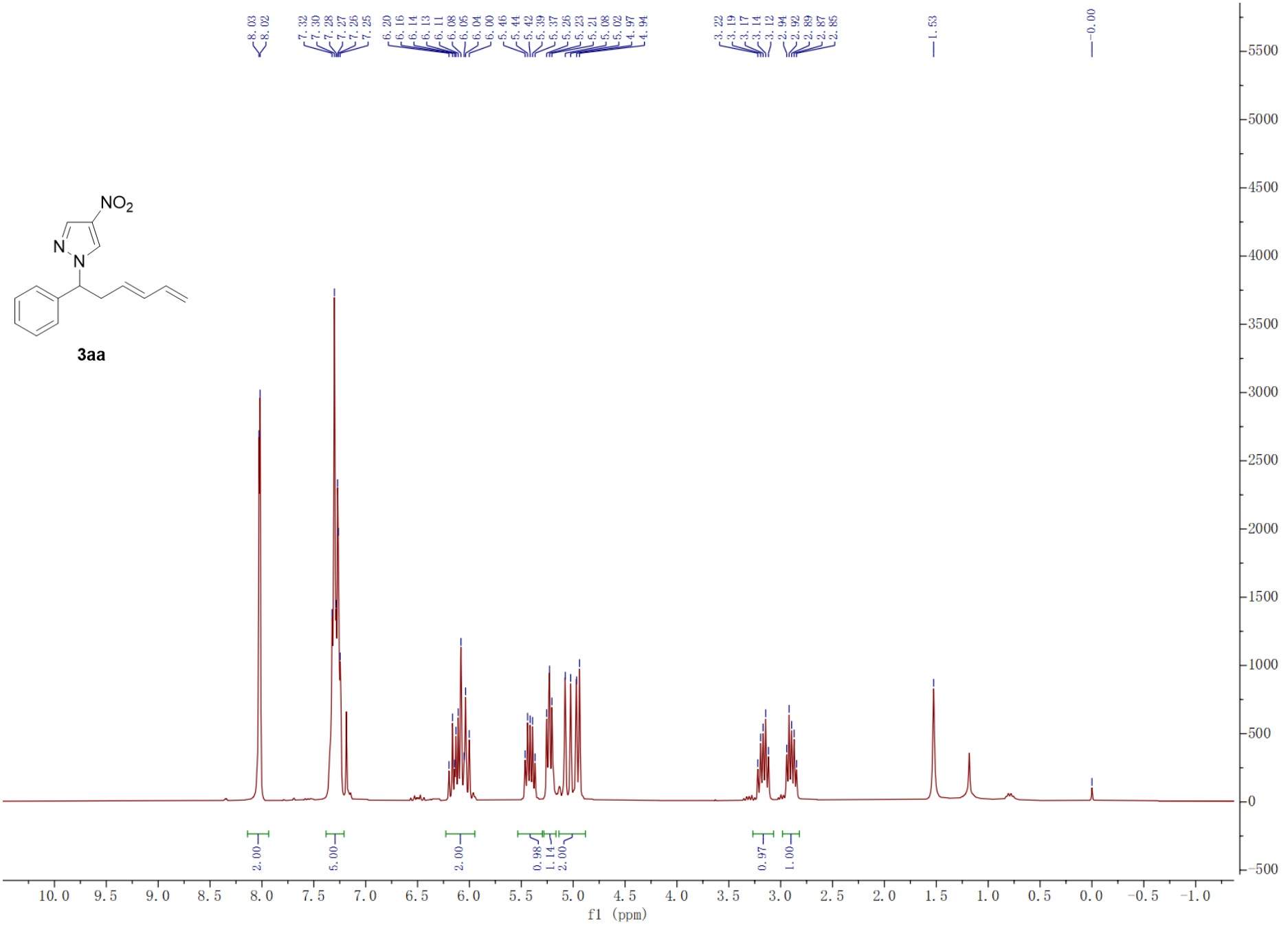
76.74
76.05
28.78
20.73
13.69
f1 (ppm)

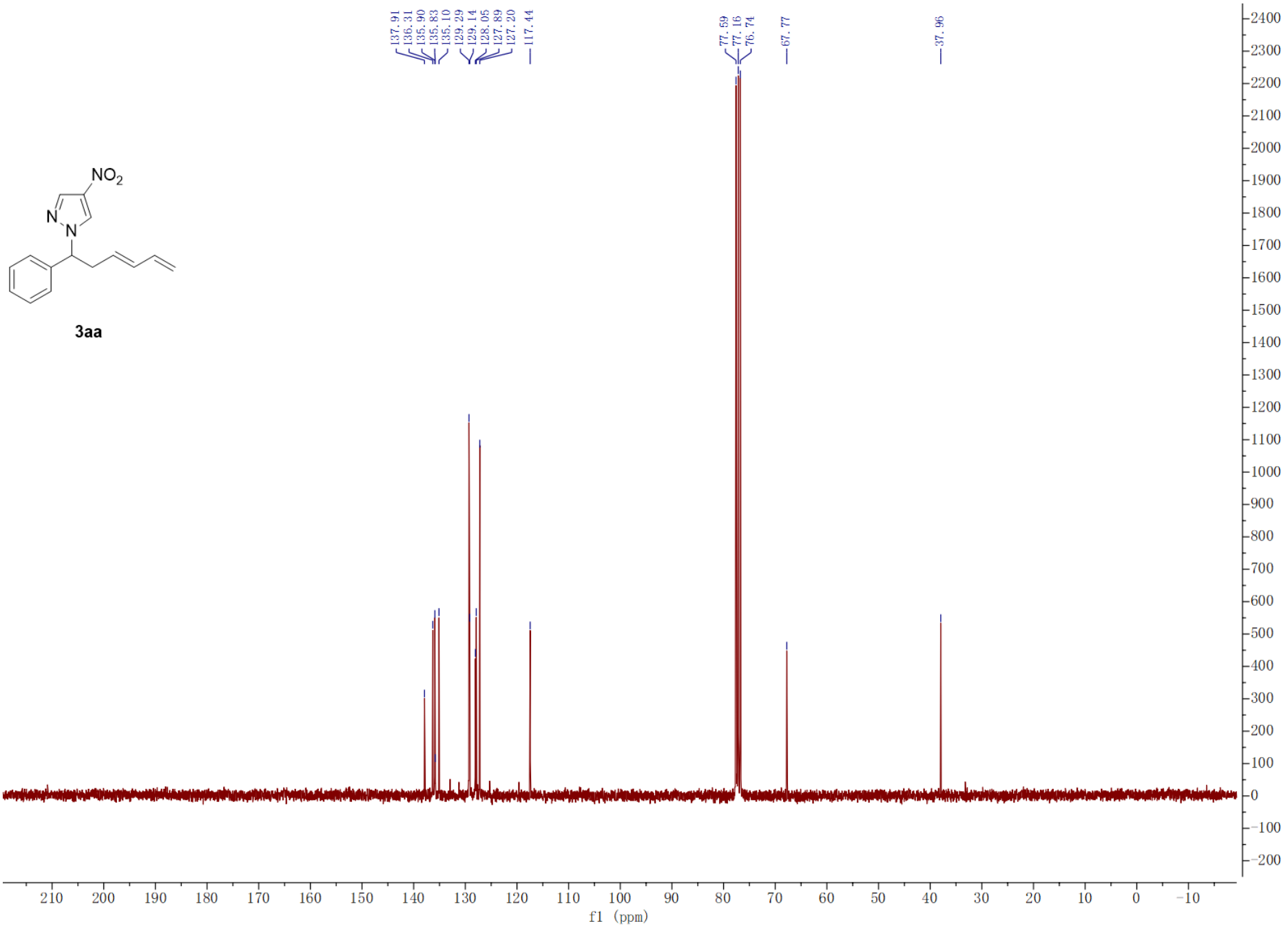

OH
O
O
Br
1m
7.00
6.46
6.07
6.05
6.03
6.02
6.01
6.00
5.99
5.98
5.98
5.98
5.96
5.93
5.35
5.35
5.34
5.29
5.29
5.28
5.19
5.19
5.18
5.16
5.15
5.15
3.98
3.96
3.96
3.94
3.92
2.12
2.10
2.09
2.09
2.07
2.06
1.82
1.80
1.27
1.26
1.25
1.25
1.25
1.24
1.23
1.23
1.23
1.22
1.22
1.21
1.21
1.20
1.19
1.10
1.08
1.07
1.06
1.05
1.03
0.93
0.92
0.91
0.90
0.89
0.87
0.00
1.18
0.97
3.21
1.02
1.02
0.98
1.00
0.96
1.07
0.99
1.03
f1 (ppm)

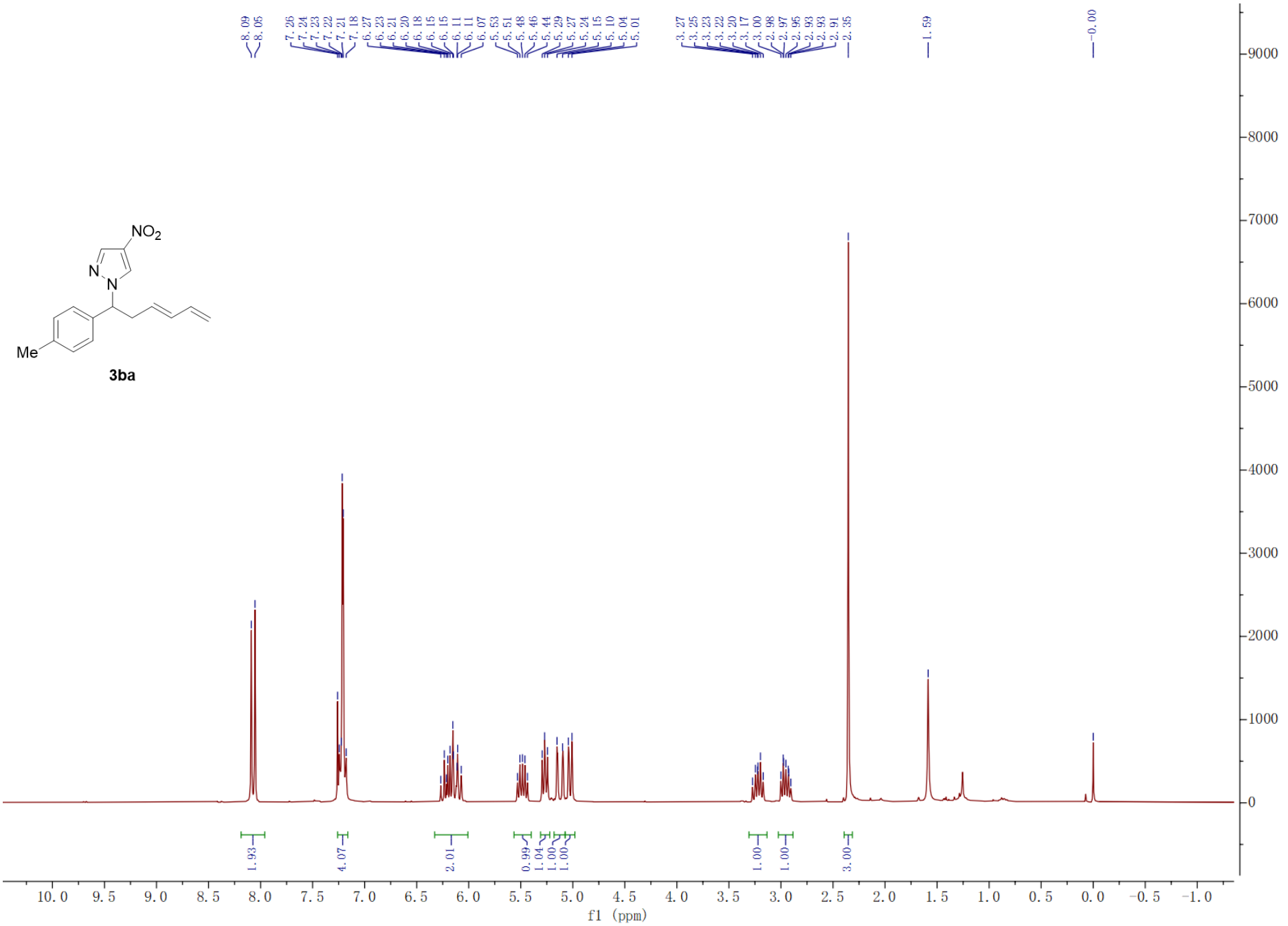

147.48
146.57
139.33
134.15
115.90
115.44
112.68
107.21
101.72
77.58
77.16
76.74
75.02
28.05
20.89
12.08
OH
O
O
Br
1m
f1 (ppm)

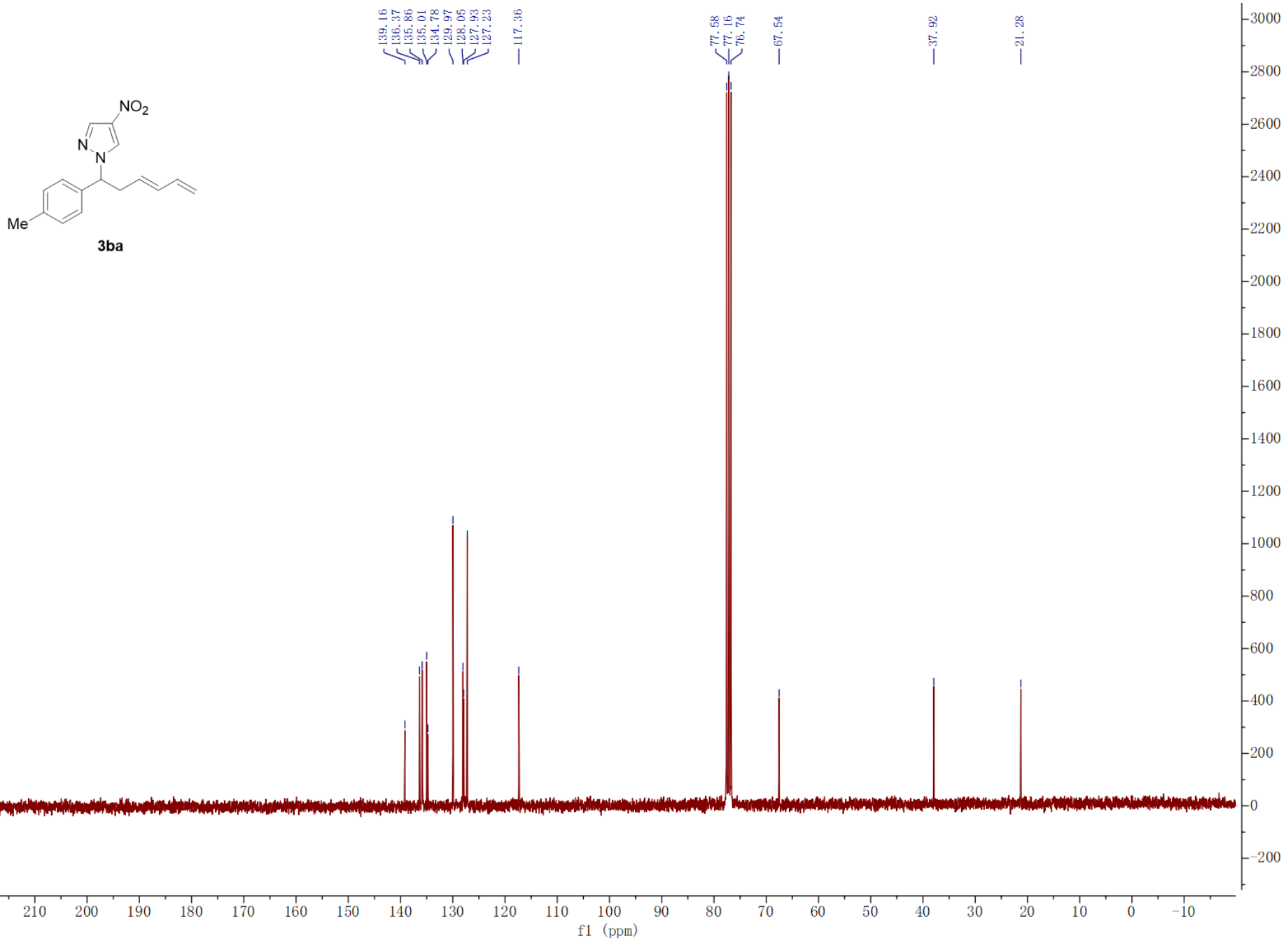

OH
1p
7.29
7.28
7.28
7.26
7.25
7.25
7.24
7.23
7.18
7.17
7.16
7.15
7.13
7.07
7.07
7.04
3.12
3.10
3.09
3.08
3.07
3.05
1.85
1.83
1.82
1.80
1.79
1.72
1.70
1.70
1.67
1.65
1.65
1.63
1.28
1.26
1.25
1.24
1.23
1.22
1.21
1.20
1.19
1.01
1.00
0.99
0.98
0.96
0.95
0.94
0.93
0.91
-0.00
2.11
1.04
1.97
1.00
1.03
3.20
1.12
5.01
f1 (ppm)

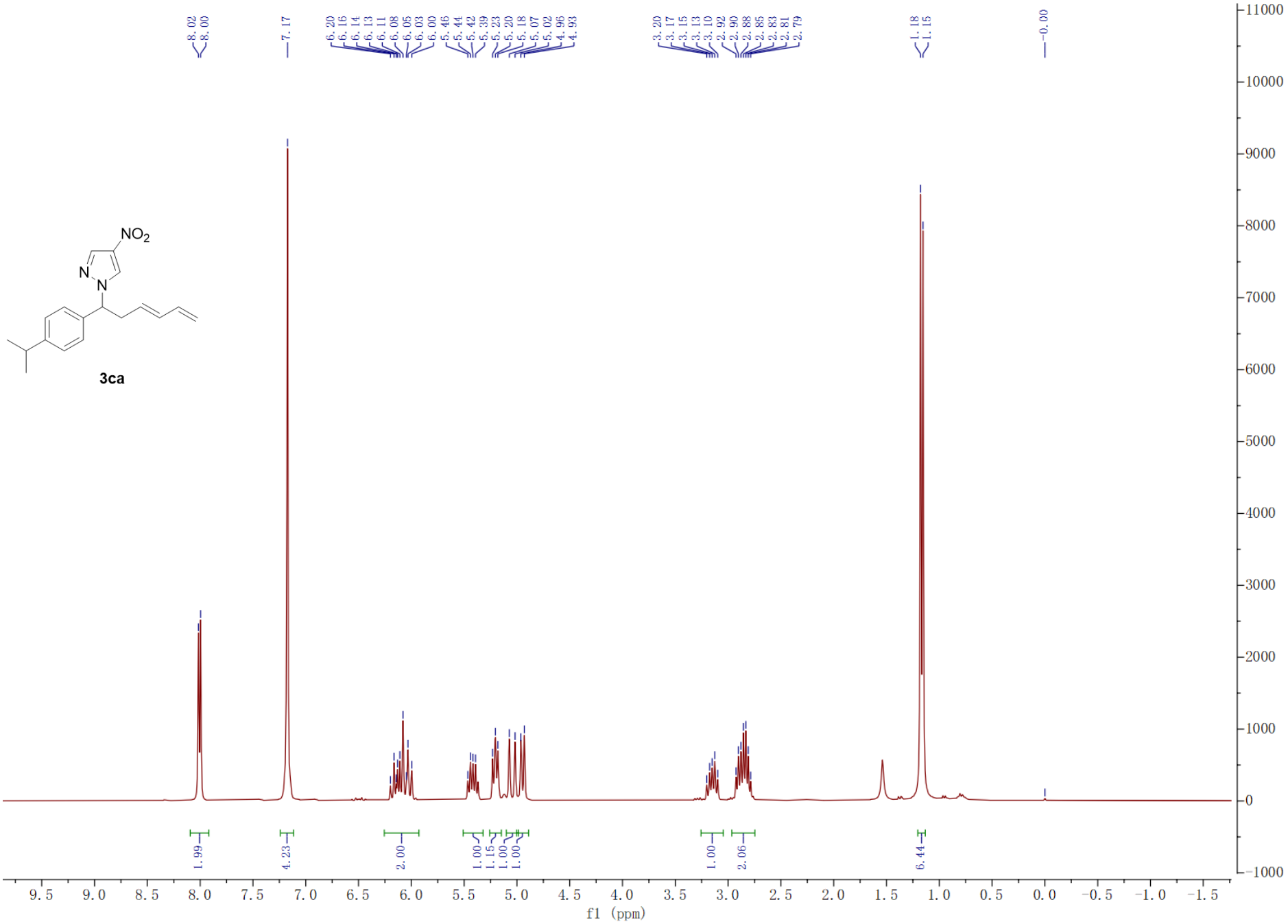

OH
1p
142.53
128.47
125.92
125.74
77.58
77.24
77.16
76.74
30.35
29.49
21.31
13.29
10.25
f1 (ppm)

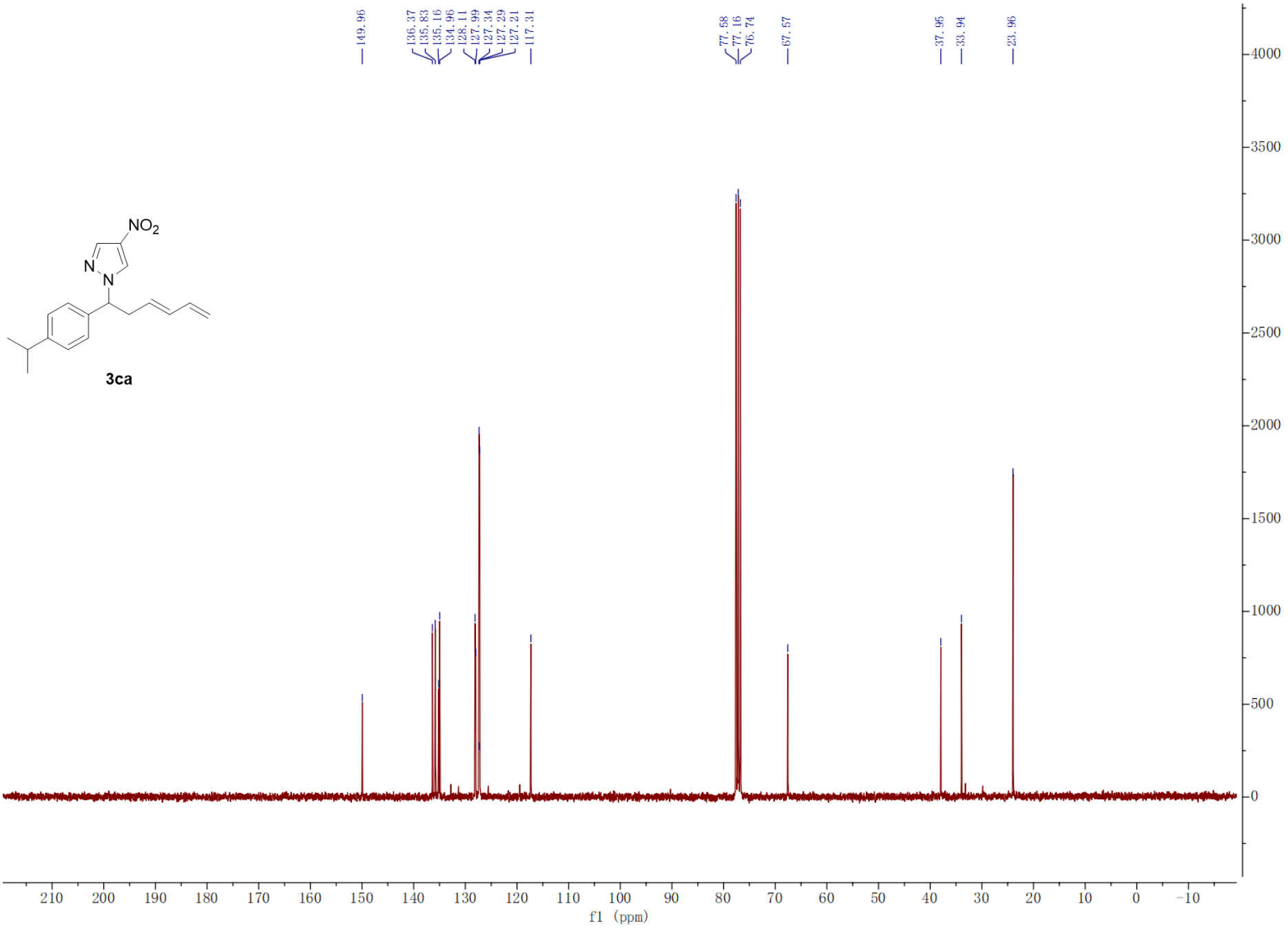

8.03
8.02
7.32
7.30
7.28
7.27
7.26
7.25
6.20
6.16
6.14
6.13
6.11
6.08
6.05
6.04
6.00
5.46
5.44
5.42
5.39
5.37
5.26
5.23
5.21
5.08
5.02
4.97
4.94
3.22
3.19
3.17
3.14
3.12
2.94
2.92
2.89
2.87
2.85
1.53
0.00
NO2
N
N
3aa
2.00
5.00
2.00
0.98
1.14
2.00
0.97
1.00
f1 (ppm)

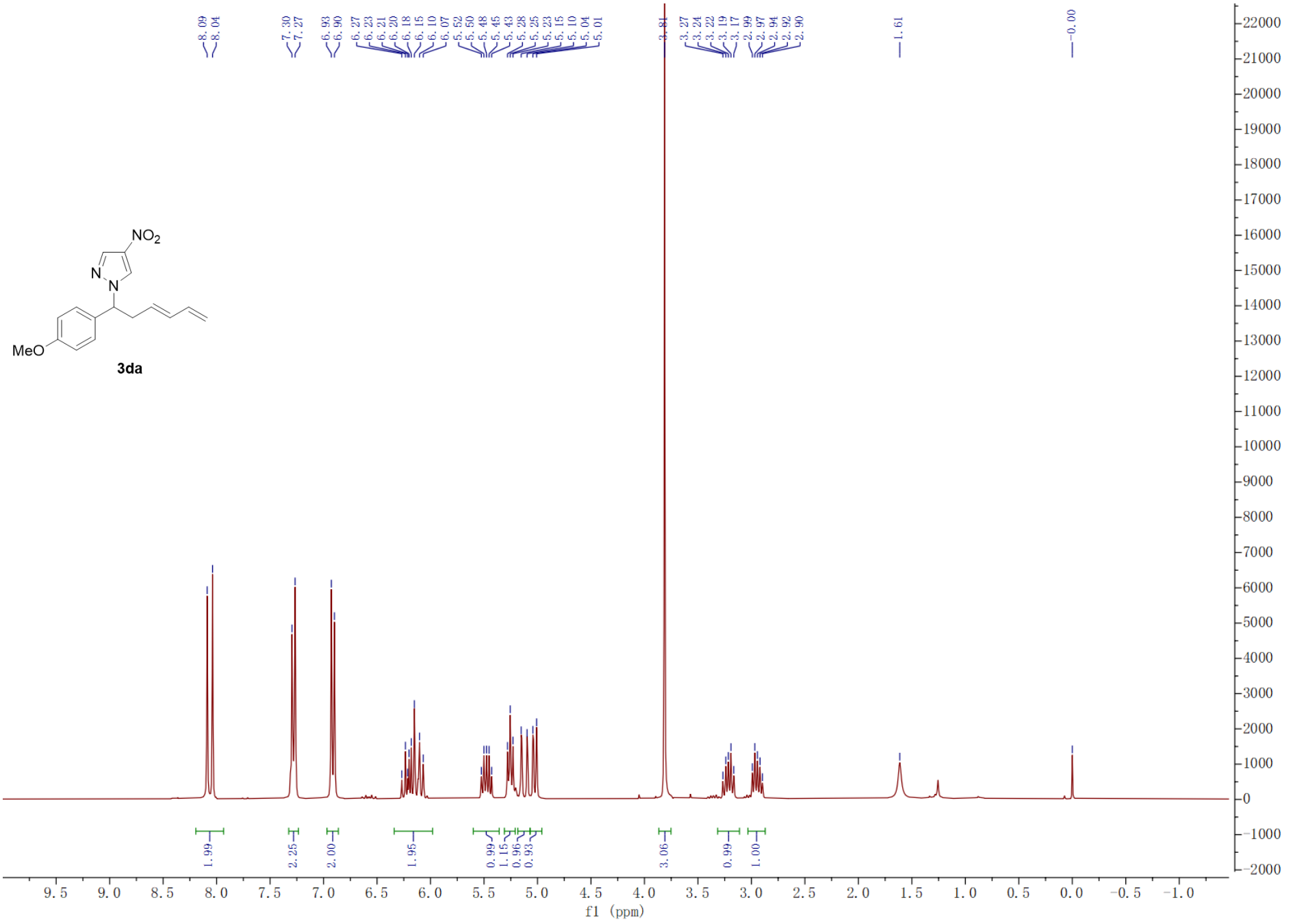

137.91
136.31
135.90
135.83
135.10
129.29
129.14
128.05
127.89
127.20
117.44
77.59
77.16
76.74
67.77
37.96
NO2
N
N
3aa
f1 (ppm)

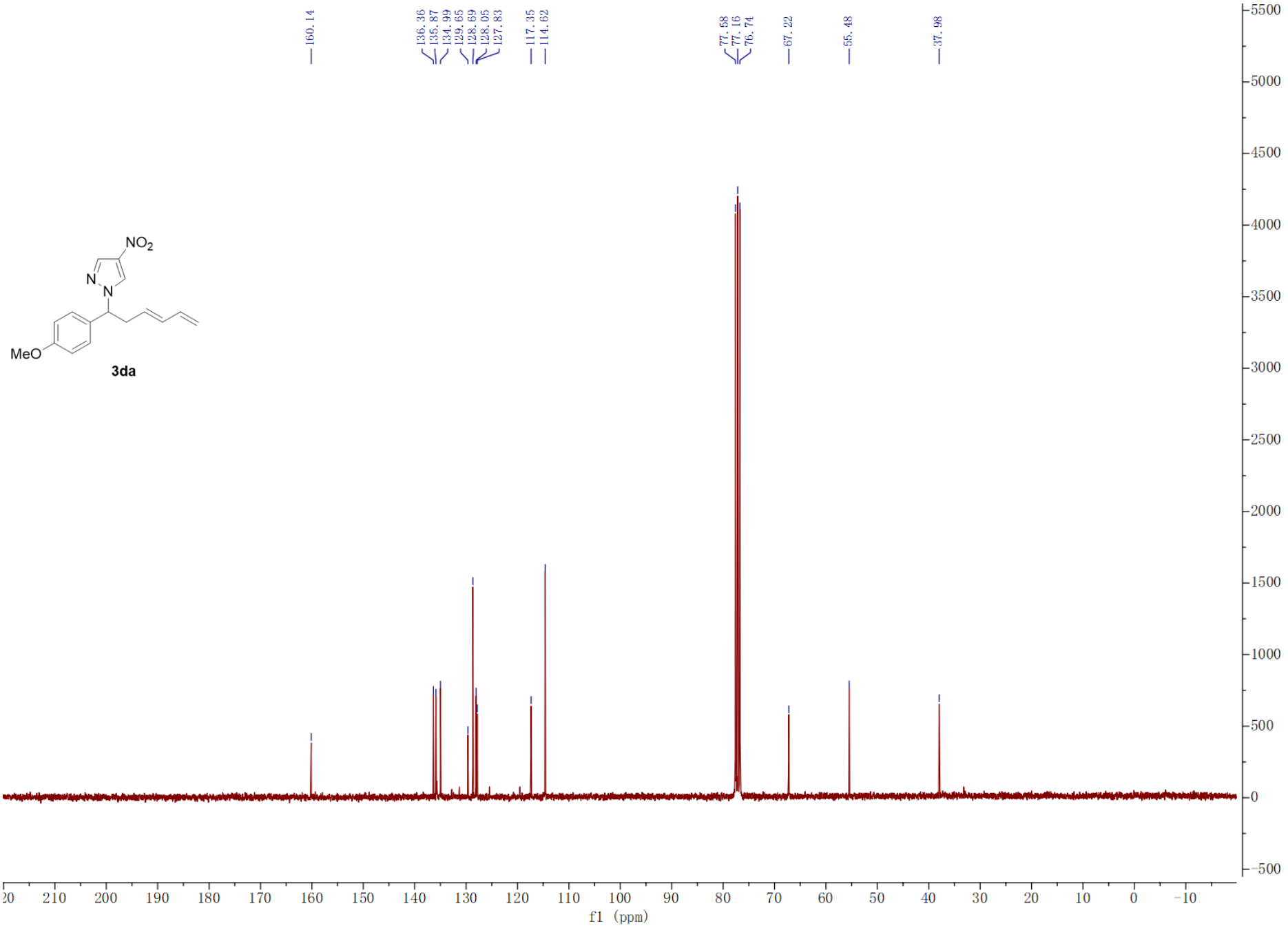

8.09
8.05
7.26
7.24
7.23
7.22
7.21
7.18
6.27
6.23
6.21
6.20
6.18
6.15
6.15
6.11
6.11
6.07
5.53
5.51
5.48
5.46
5.44
5.29
5.27
5.24
5.15
5.10
5.04
5.01
3.27
3.25
3.23
3.22
3.20
3.17
3.00
2.98
2.97
2.95
2.93
2.93
2.91
2.35
1.59
-0.00
NO2
N
N
Me
3ba
1.93
4.07
2.01
0.99
1.04
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

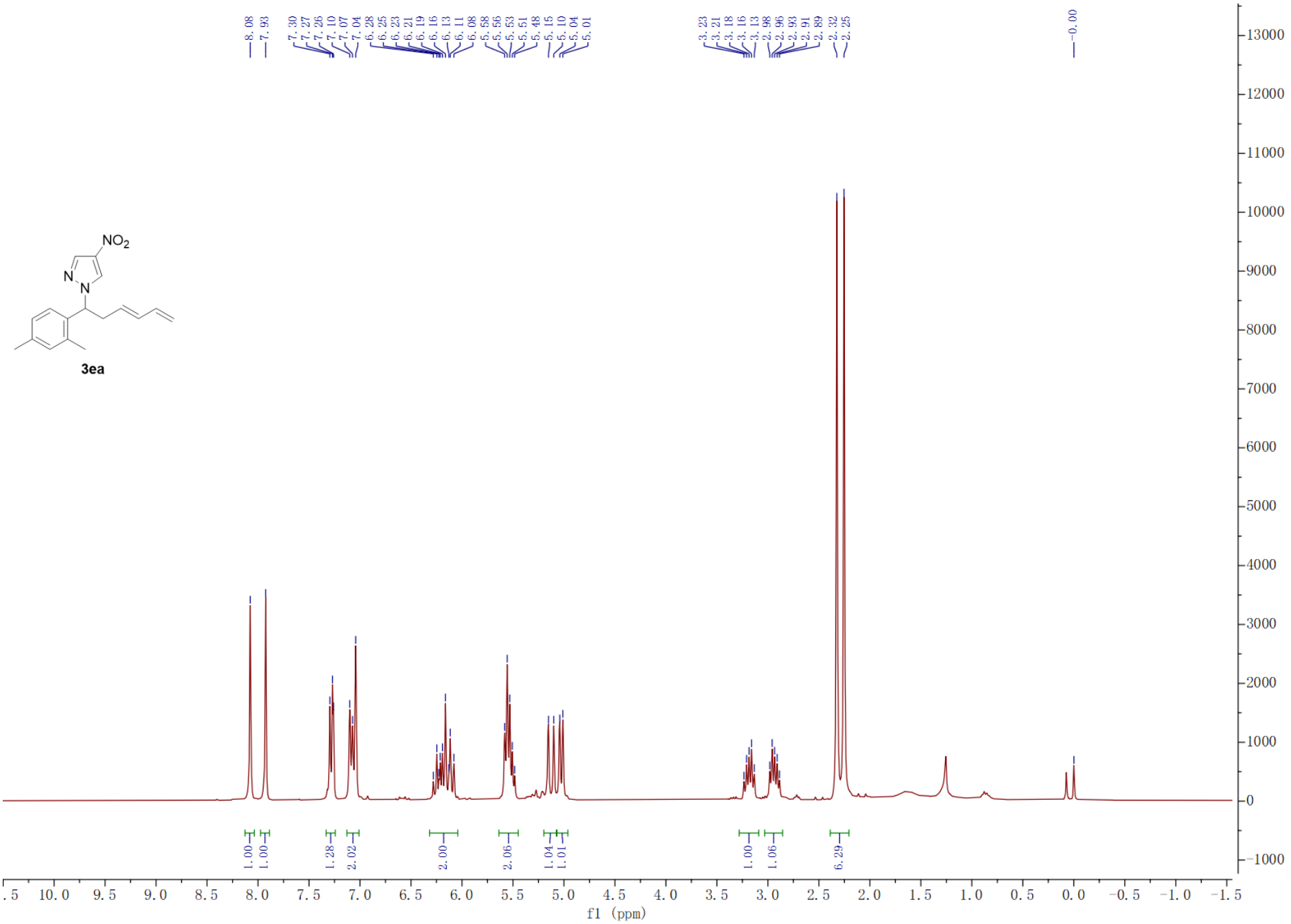

NO2
N
N
Me
3ba
139.16
136.37
135.86
135.01
134.78
129.97
128.05
127.93
127.23
117.36
77.58
77.16
76.74
67.54
37.92
21.28
f1 (ppm)


8.02
8.00
7.17
6.20
6.16
6.14
6.13
6.11
6.08
6.05
6.03
6.00
5.46
5.44
5.42
5.39
5.23
5.20
5.18
5.07
5.02
4.96
4.93
3.20
3.17
3.15
3.13
3.10
2.92
2.90
2.88
2.85
2.83
2.81
2.79
1.18
1.15
0.00
NO2
N
N
3ca
1.99
4.23
2.00
1.00
1.15
1.00
1.00
1.00
2.06
6.44
f1 (ppm)


149.96
136.37
135.83
135.16
134.96
128.11
127.99
127.34
127.29
127.21
117.31
77.58
77.16
76.74
67.57
37.95
33.94
23.96
NO2
N
N
3ca
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)


8.09
8.04
7.30
7.27
6.93
6.90
6.27
6.23
6.21
6.20
6.18
6.15
6.10
6.07
5.52
5.50
5.48
5.45
5.43
5.28
5.25
5.23
5.15
5.10
5.04
5.01
3.81
3.27
3.24
3.22
3.19
3.17
2.99
2.97
2.94
2.92
2.90
1.61
0.00
NO2
N
N
MeO
3da
1.99
2.25
2.00
1.95
0.99
1.15
0.96
0.93
3.06
0.99
1.00
f1 (ppm)


160.14
136.36
135.87
134.99
129.65
128.69
128.05
127.83
117.35
114.62
77.58
77.16
76.74
67.22
55.48
37.98
NO2
N
N
MeO
3da
f1 (ppm)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7.10
7.07
7.04
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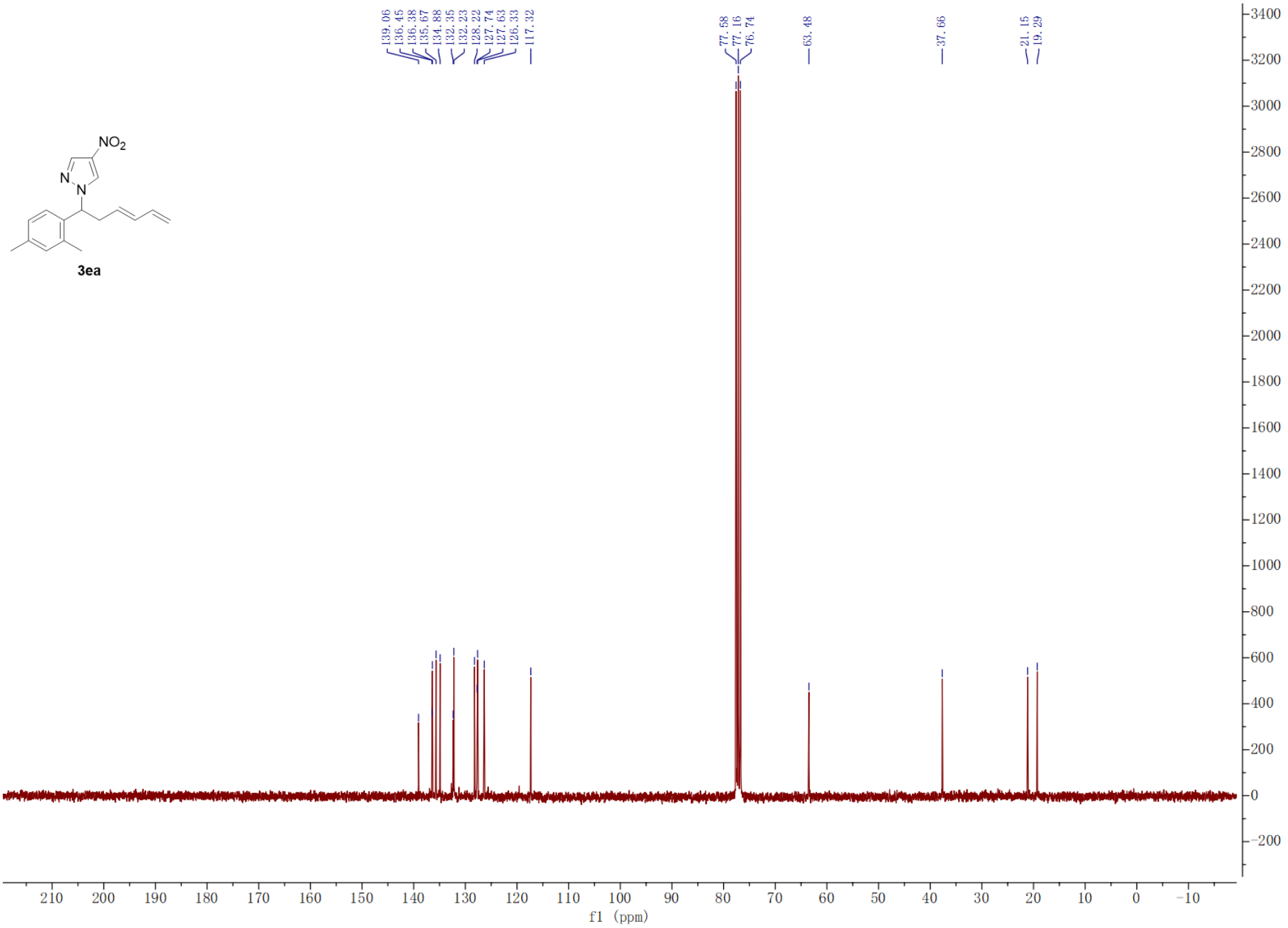
6.25
6.23
6.21
6.19
6.16
6.13
6.11
6.08
5.58
5.56
5.53
5.51
5.48
5.15
5.10
5.04
5.01
3.23
3.21
3.18
3.16
3.13
2.98
2.96
2.93
2.91
2.89
2.32
2.25
-0.00
NO2
N
N
3ea
1.00
1.00
1.28
2.02
2.00
2.06
1.04
1.01
1.00
1.06
6.29
f1 (ppm)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136.45
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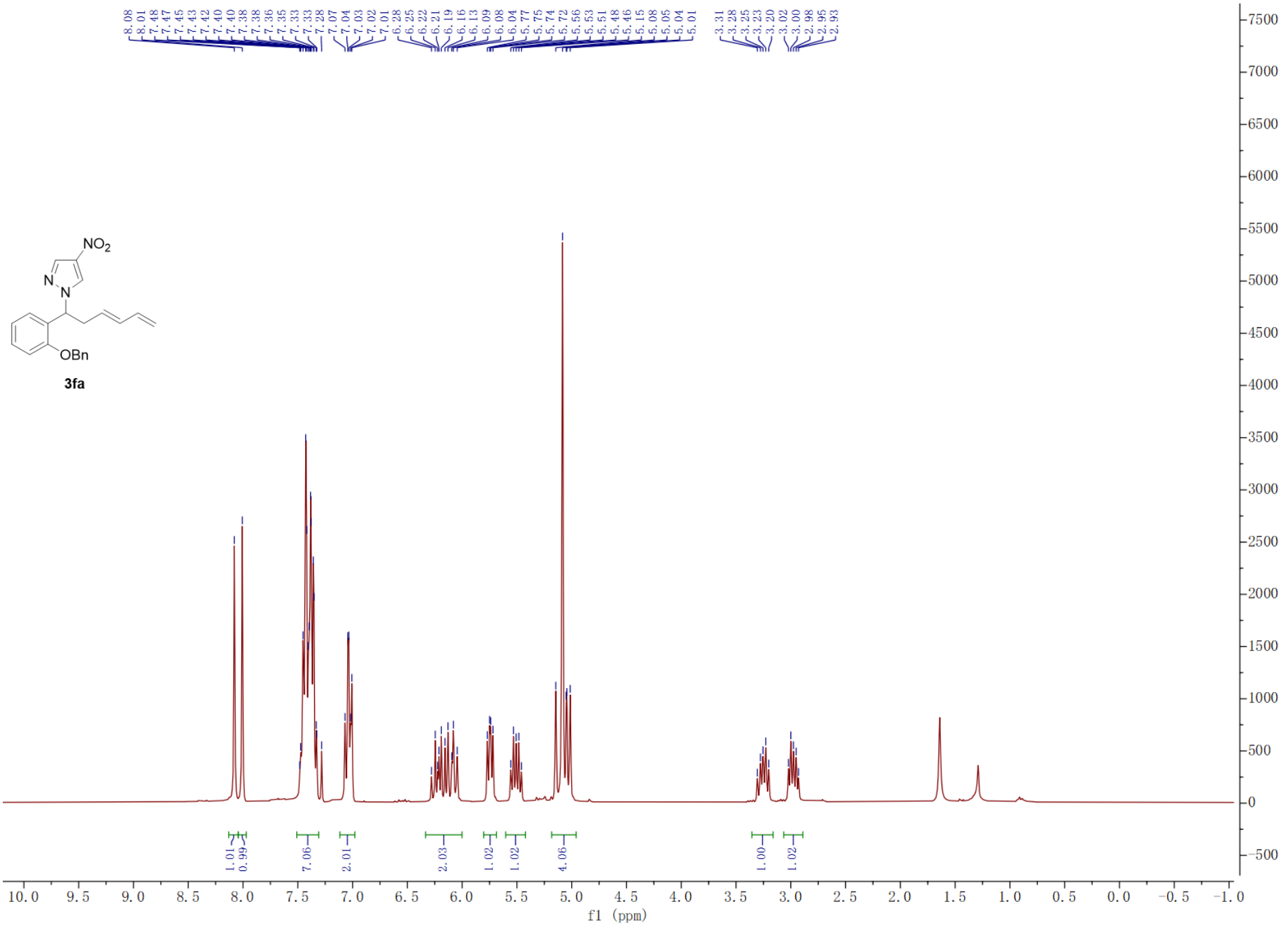
134.88
132.35
132.23
128.22
127.74
127.63
126.33
117.32
77.58
77.16
76.74
63.48
37.66
21.15
19.29
NO2
N
N
3ea
f1 (ppm)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7.38
7.36
7.35
7.33
7.33
7.28
7.07
7.04
7.03
7.02
7.01
6.28
6.25
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6.21
6.19
6.16
6.13
6.09
6.08
6.04
5.77
5.75
5.74
5.72
5.56
5.53
5.51
5.48
5.46
5.15
5.08
5.05
5.04
5.01
3.31
3.28
3.25
3.23
3.20
3.02
3.00
2.98
2.95
2.93
NO2
N
N
OBn
3fa
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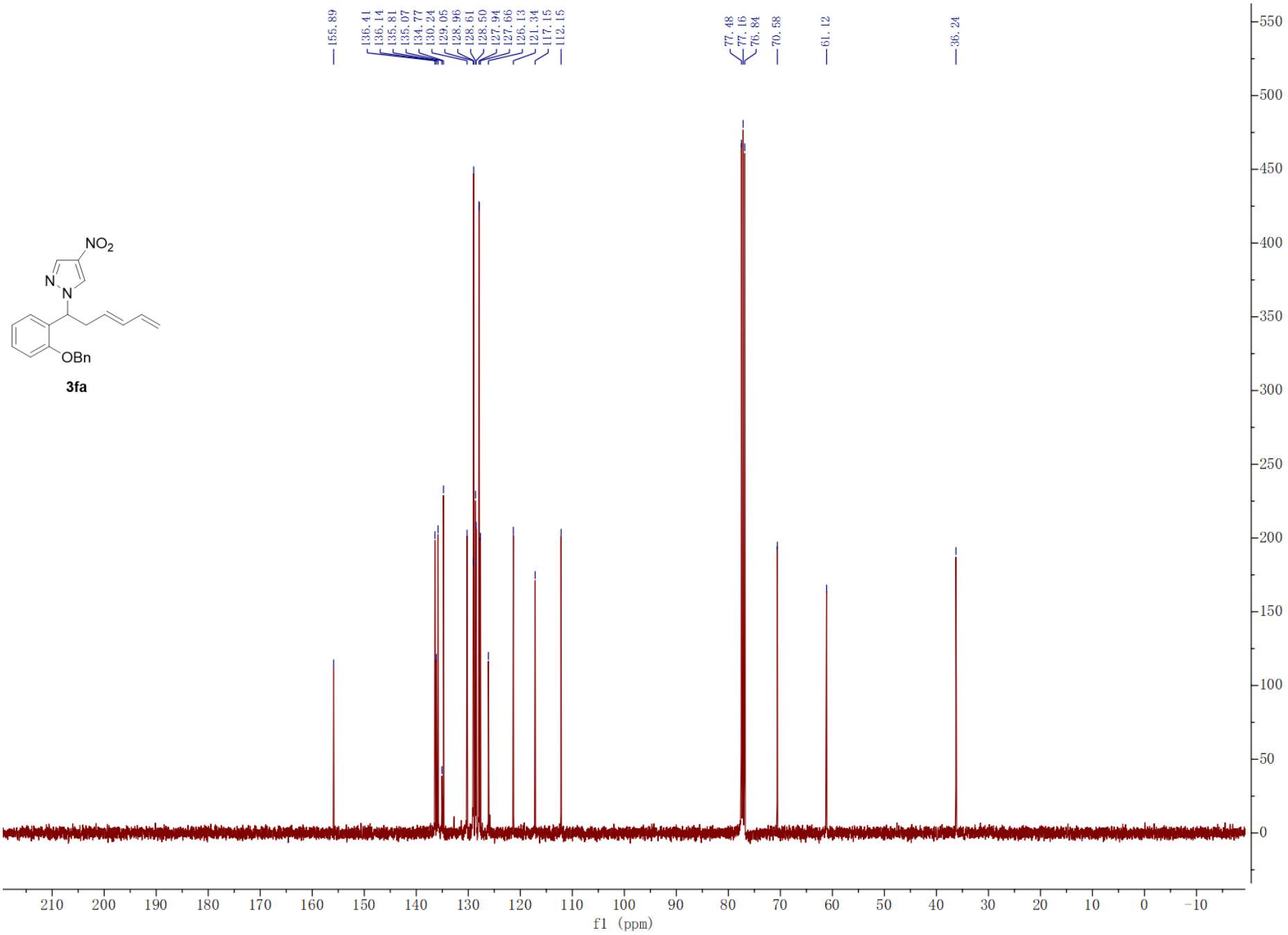
7.06
2.01
2.03
1.02
1.02
4.06
1.00
1.02
f1 (ppm)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129.05
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128.61
128.50
127.94
127.66
126.13
121.34
117.15
112.15
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77.16
76.84
70.58
61.12
36.24
NO2
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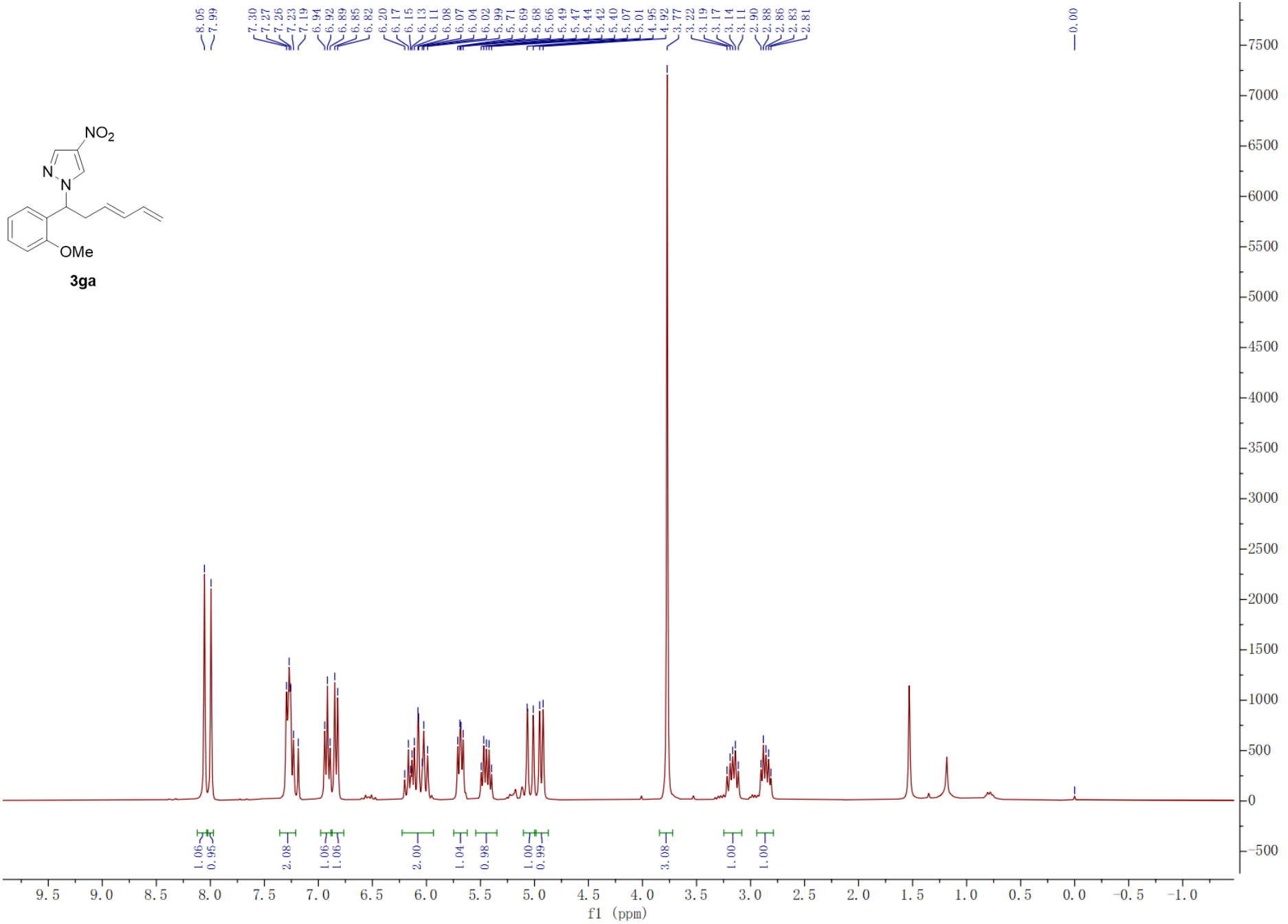
N
OBn
3fa
f1 (ppm)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N
OMe
3ga
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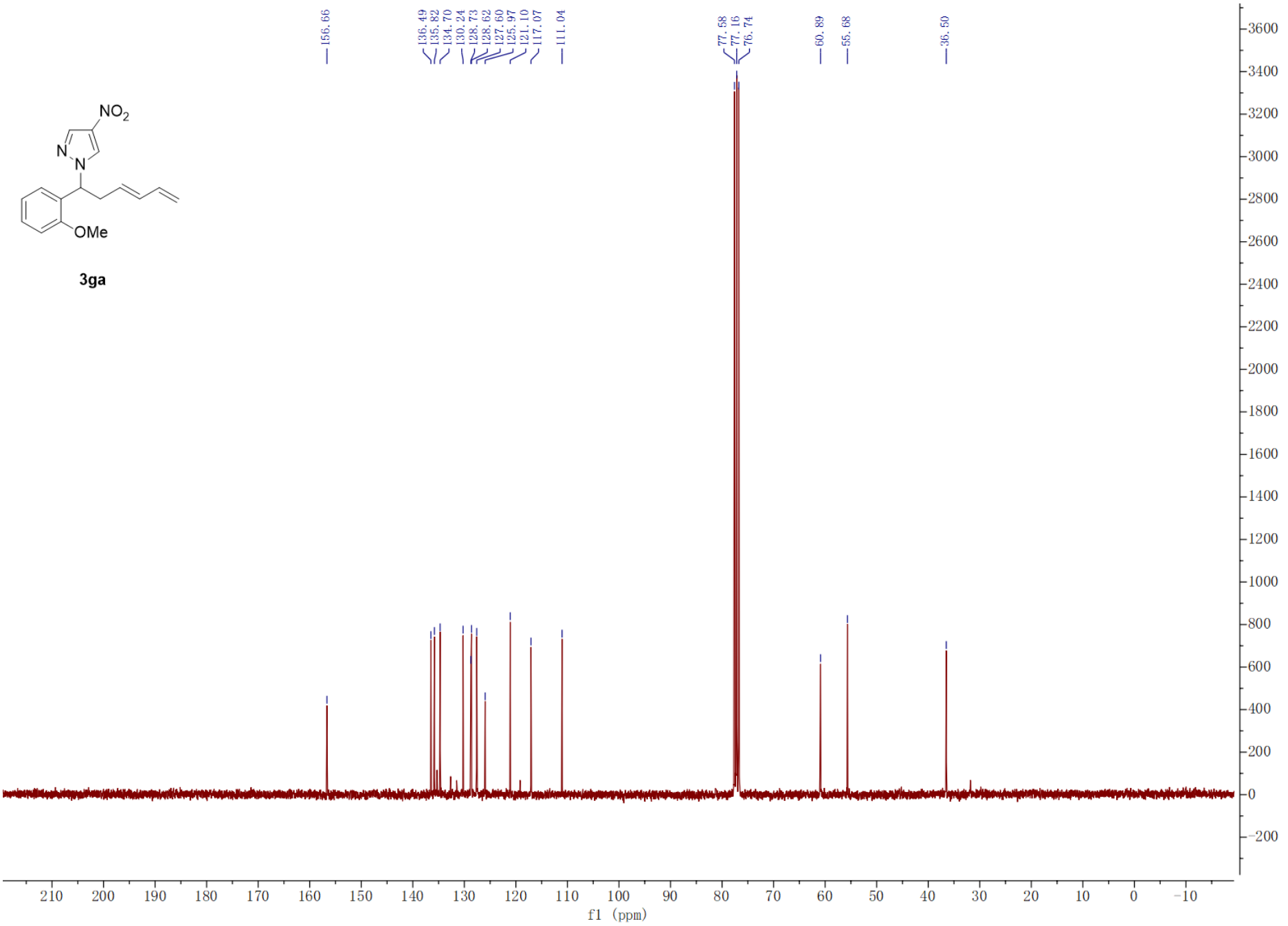
7.19
6.94
6.92
6.89
6.85
6.82
6.20
6.17
6.15
6.13
6.11
6.08
6.07
6.04
6.02
5.99
5.71
5.69
5.68
5.66
5.49
5.47
5.44
5.42
5.40
5.07
5.01
4.95
4.92
3.77
3.22
3.19
3.17
3.14
3.11
2.90
2.88
2.86
2.83
2.81
0.00
1.06
0.95
2.08
1.06
1.06
2.00
1.04
0.98
1.00
0.99
3.08
1.00
1.00
f1 (ppm)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128.62
127.60
125.97
121.10
117.07
111.04
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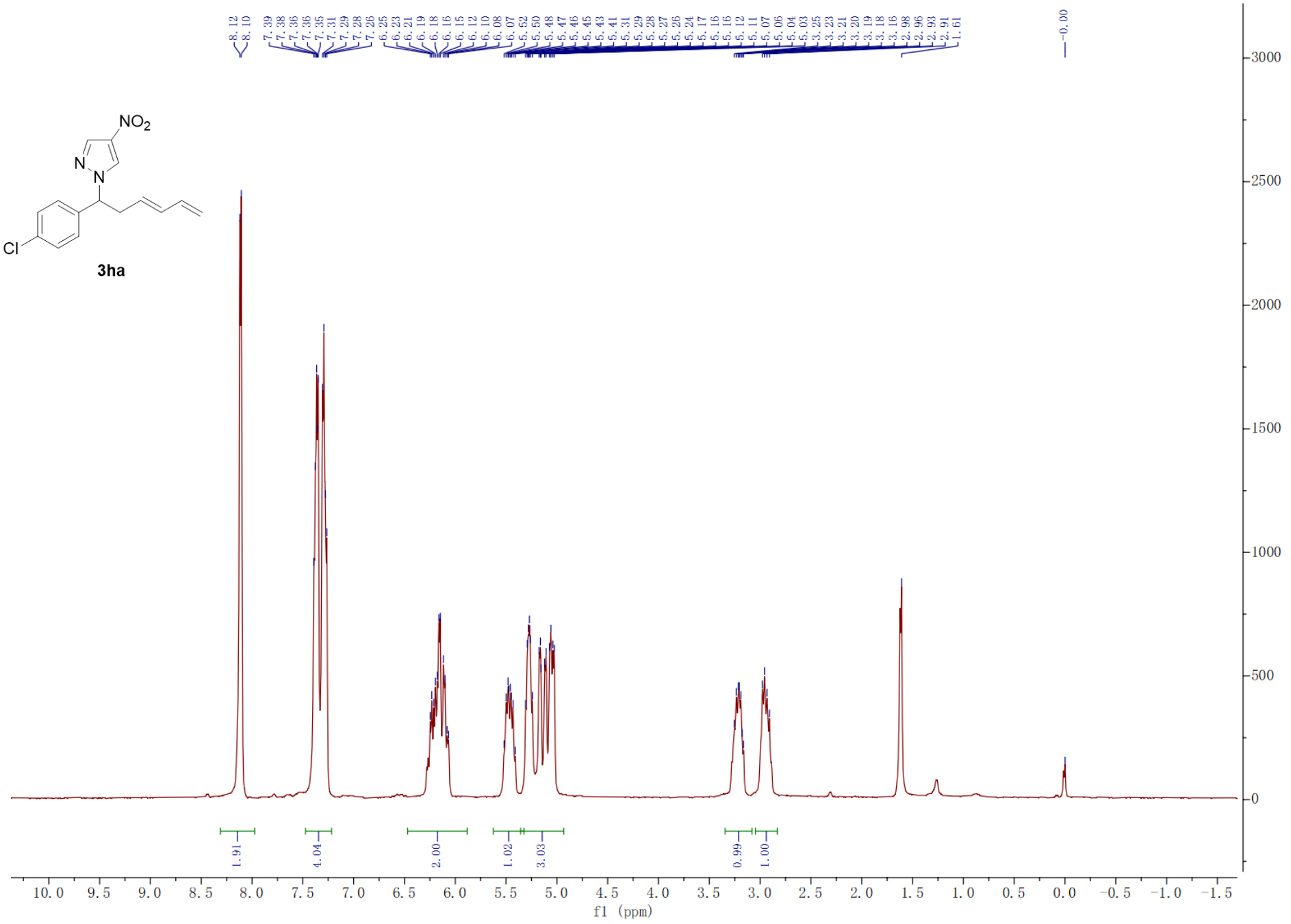
77.16
76.74
60.89
55.68
36.50
NO2
N
N
OMe
3ga
f1 (ppm)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7.35
7.31
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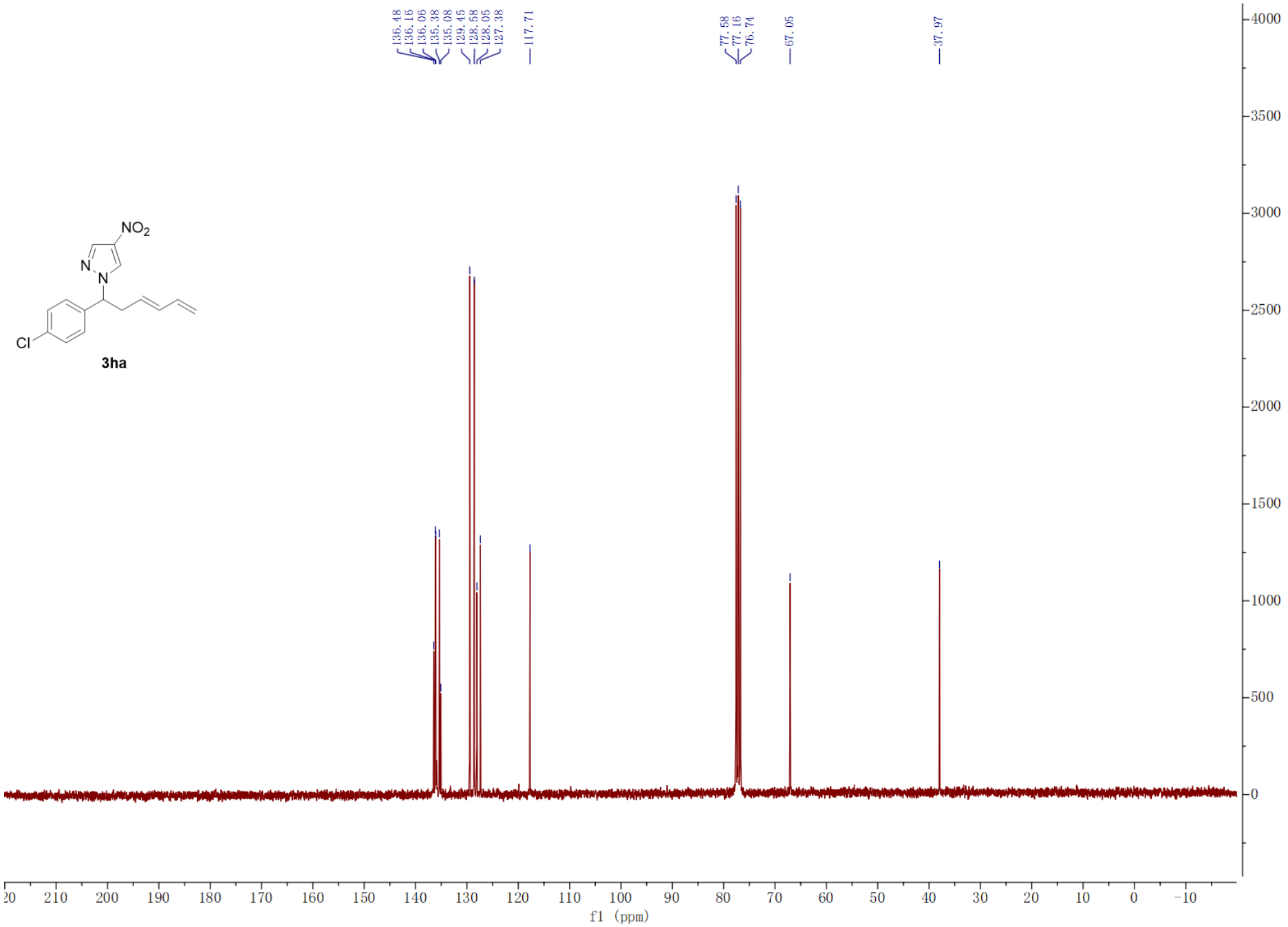
7.28
7.26
6.25
6.23
6.21
6.19
6.18
6.16
6.15
6.12
6.10
6.08
6.07
5.52
5.50
5.48
5.47
5.46
5.45
5.43
5.41
5.31
5.29
5.28
5.27
5.26
5.24
5.17
5.16
5.16
5.12
5.11
5.07
5.06
5.04
5.03
3.25
3.23
3.21
3.20
3.19
3.18
3.16
2.98
2.96
2.93
2.91
1.61
-0.00
NO2
N
N
Cl
3ha
3000
2500
2000
1500
1000
500
0
1.91
4.04
2.00
1.02
3.03
0.99
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)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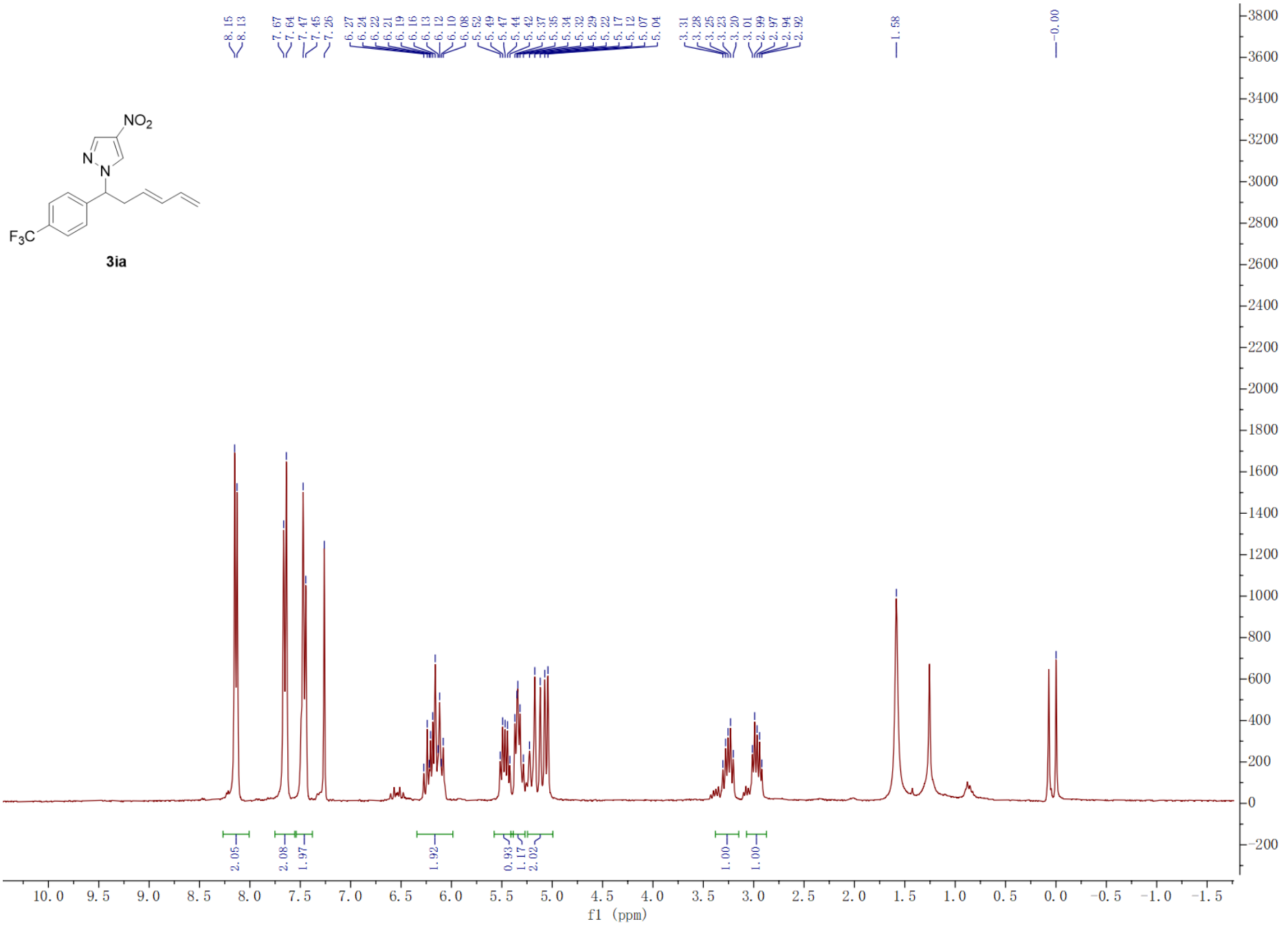
136.16
136.06
135.38
135.08
129.45
128.58
128.05
127.38
117.71
77.58
77.16
76.74
67.05
37.97
NO2
N
N
Cl
3ha
4000
3500
3000
2500
2000
1500
1000
500
0
f1 (ppm)


8.15
8.13
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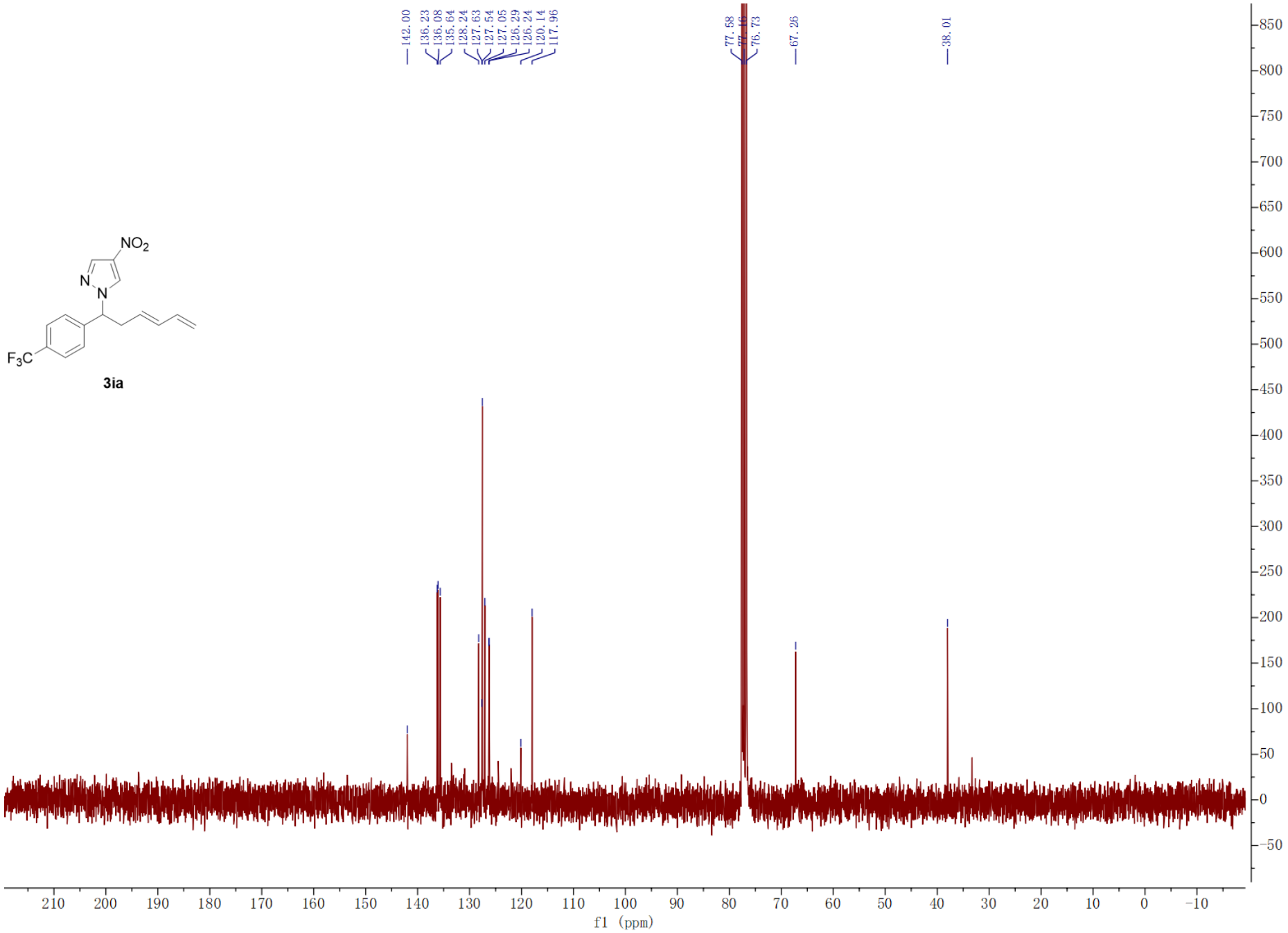
7.45
7.26
6.27
6.24
6.22
6.21
6.19
6.16
6.13
6.12
6.10
6.08
5.52
5.49
5.47
5.44
5.42
5.37
5.35
5.34
5.32
5.29
5.22
5.17
5.12
5.07
5.04
3.31
3.28
3.25
3.23
3.20
3.01
2.99
2.97
2.94
2.92
1.58
-0.00
NO2
N
N
F3C
3ia
2.05
2.08
1.97
1.92
0.93
1.17
2.02
1.00
1.00
f1 (ppm)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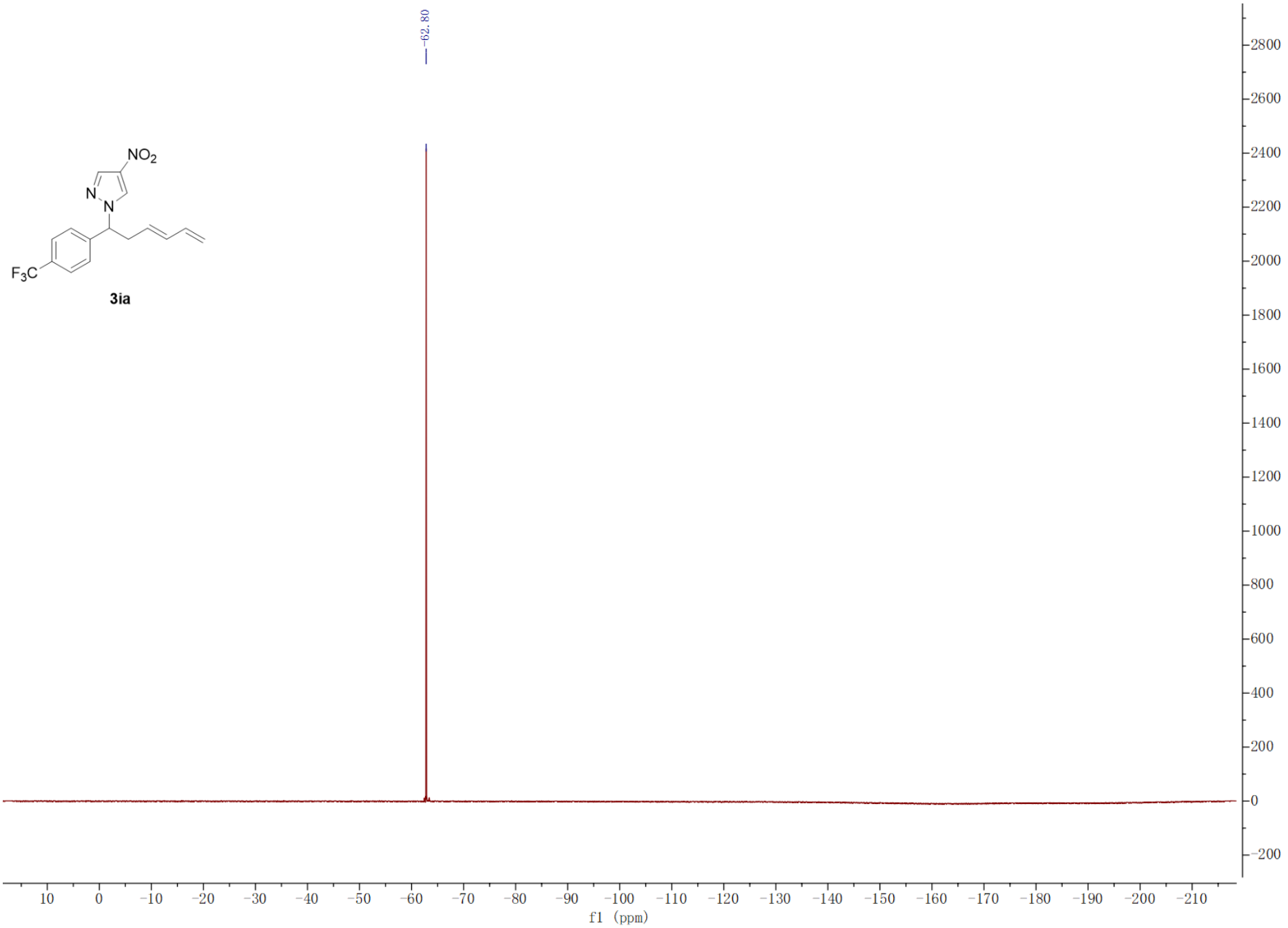
136.23
136.08
135.64
128.24
127.63
127.54
127.05
126.29
126.24
120.14
117.96
77.58
77.16
76.73
67.26
38.01
NO2
N
N
F3C
3ia
f1 (ppm)


−62.80
NO2
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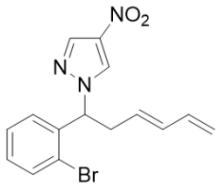
N
F3C
3ia
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


NO2
N
N
Br

3ja

8.19
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7.62
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7.46
7.44
7.38
7.36
7.33
7.26
7.25
7.22
7.20
6.29
6.25
6.22
6.20
6.17
6.13
6.09
5.83
5.80
5.78
5.57
5.55
5.53
5.50
5.48
5.17
5.11
5.06
5.03
3.30
3.27
3.25
3.22
3.19
2.99
2.97
2.94
2.92
1.58
0.00
1.96
1.00
3.24
1.94
1.00
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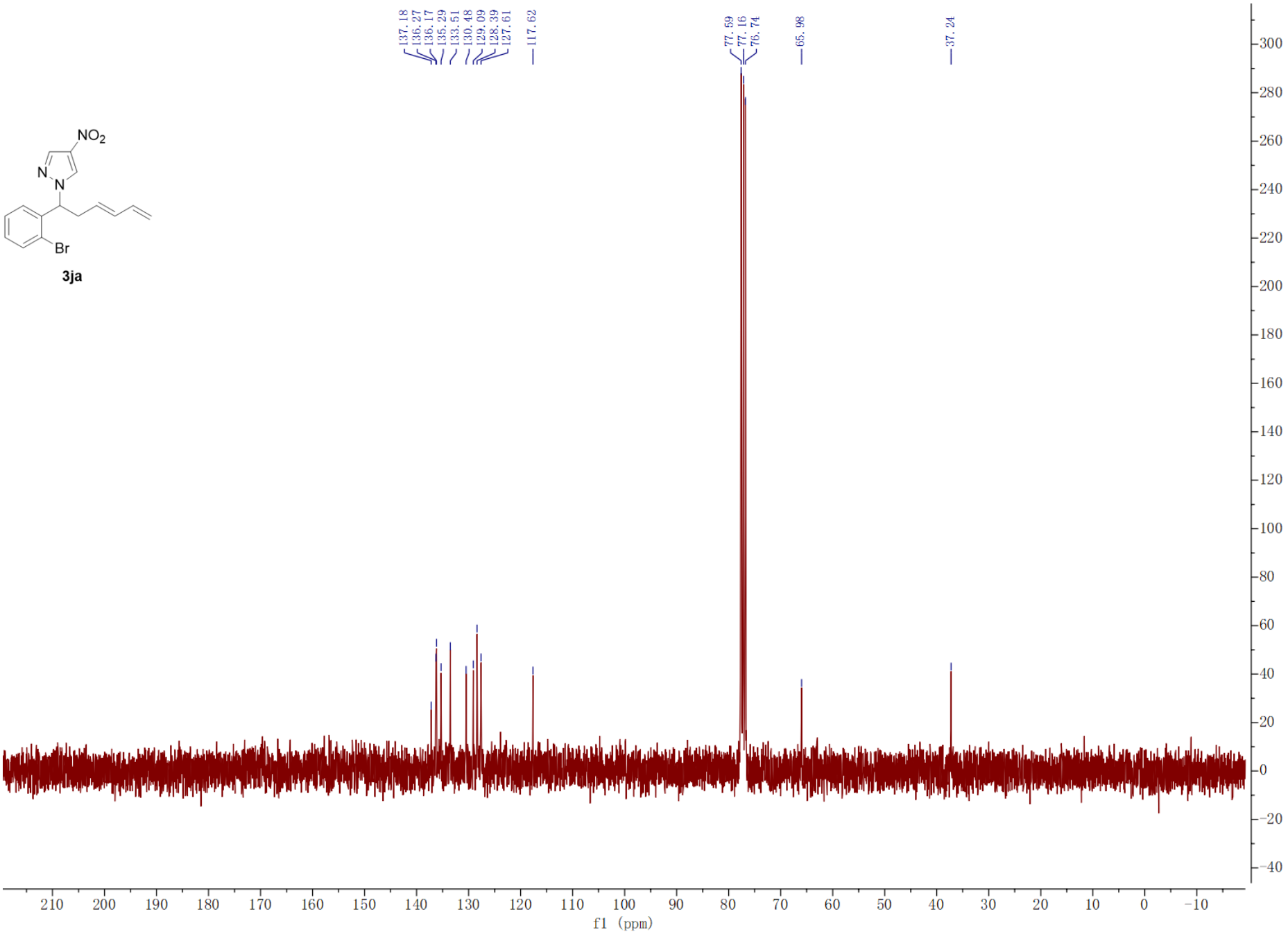
2.04
1.00
1.00
f1 (ppm)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128.39
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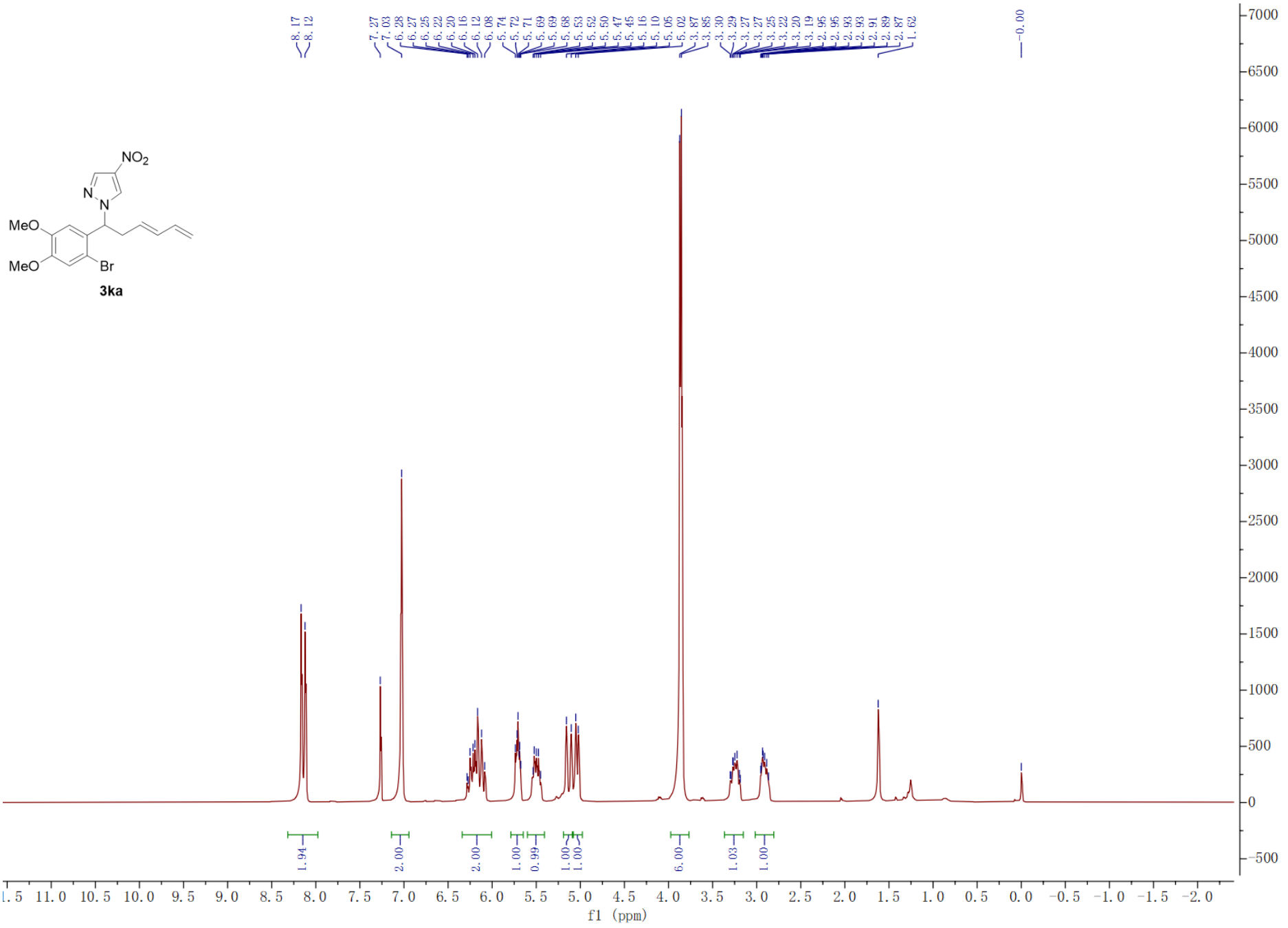
77.59
77.16
76.74
65.98
37.24
NO2
N
N
Br
3ja
f1 (ppm)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8.12
7.27
7.03
6.28
6.27
6.25
6.22
6.20
6.16
6.12
6.08
5.74
5.72
5.71
5.69
5.69
5.68
5.53
5.52
5.50
5.47
5.45
5.16
5.10
5.05
5.02
3.87
3.85
3.30
3.29
3.27
3.27
3.25
3.22
3.20
3.19
2.95
2.95
2.93
2.93
2.91
2.89
2.87
1.62
-0.00
NO2
N
N
MeO
MeO
Br
3ka
1.94
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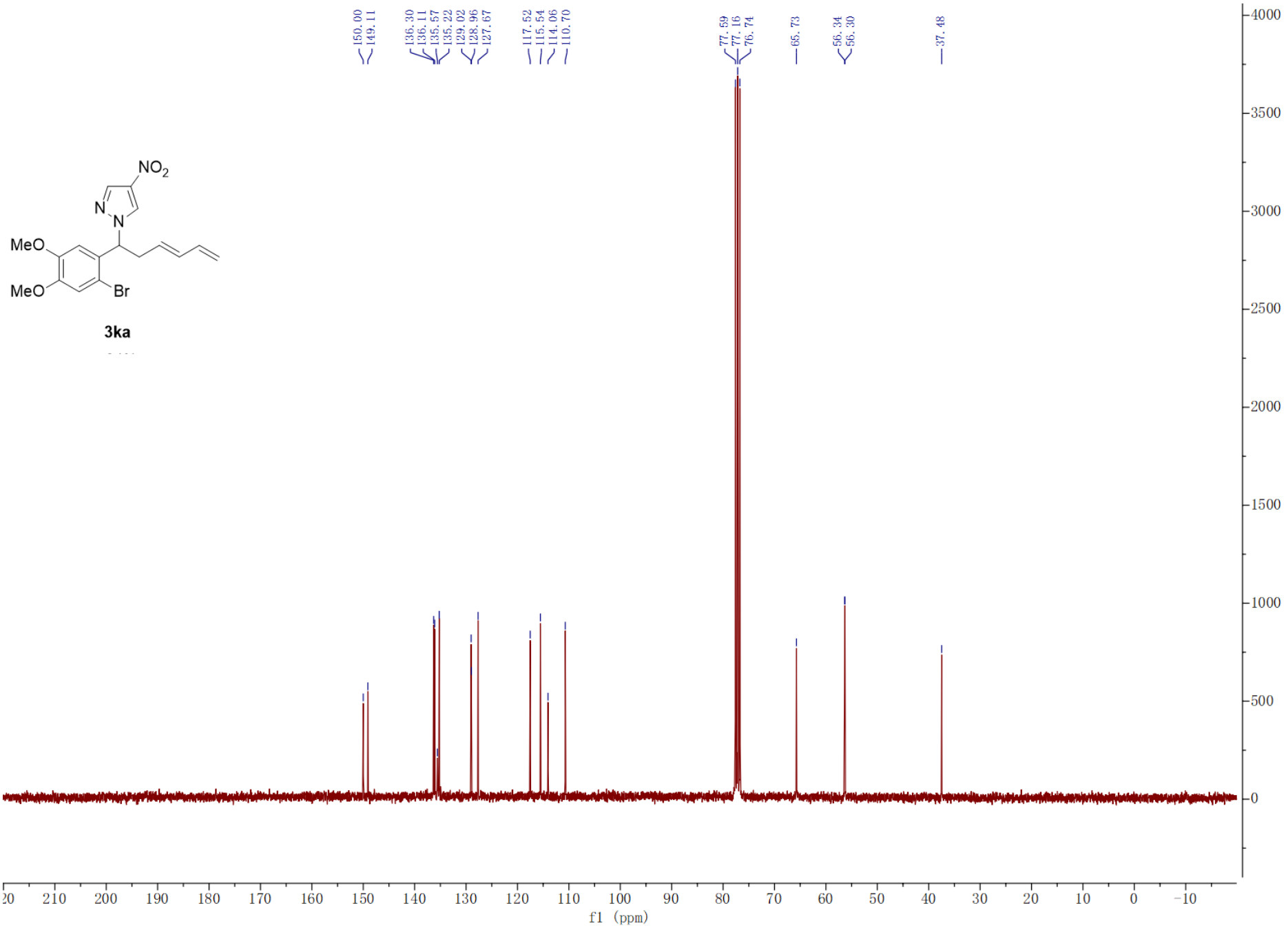
2.00
1.00
0.99
1.00
1.00
6.00
1.03
1.00
f1 (ppm)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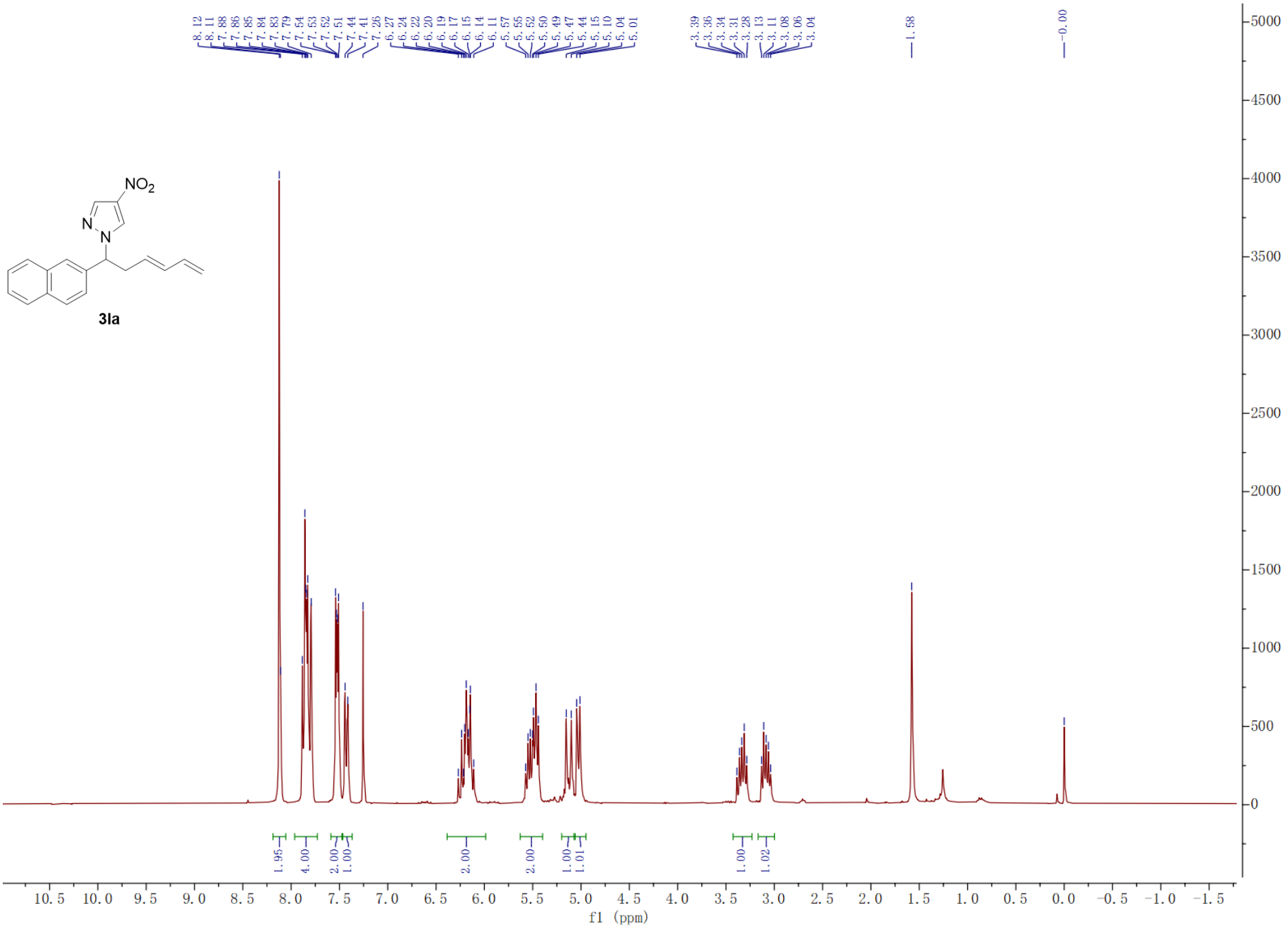
128.96
127.67
117.52
115.54
114.06
110.70
77.59
77.16
76.74
65.73
56.34
56.30
37.48
NO2
N
N
MeO
MeO
Br
3ka
4000
3500
3000
2500
2000
1500
1000
500
0
f1 (ppm)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7.84
7.83
7.79
7.54
7.53
7.52
7.51
7.44
7.41
7.26
6.27
6.24
6.22
6.20
6.19
6.17
6.15
6.14
6.11
5.57
5.55
5.52
5.50
5.49
5.47
5.44
5.15
5.10
5.04
5.01
3.39
3.36
3.34
3.31
3.28
3.13
3.11
3.08
3.06
3.04
1.58
0.00
NO2
N
N
3la
1.95
4.00
2.00
1.00
2.00
2.00
1.00
1.01
1.00
1.02
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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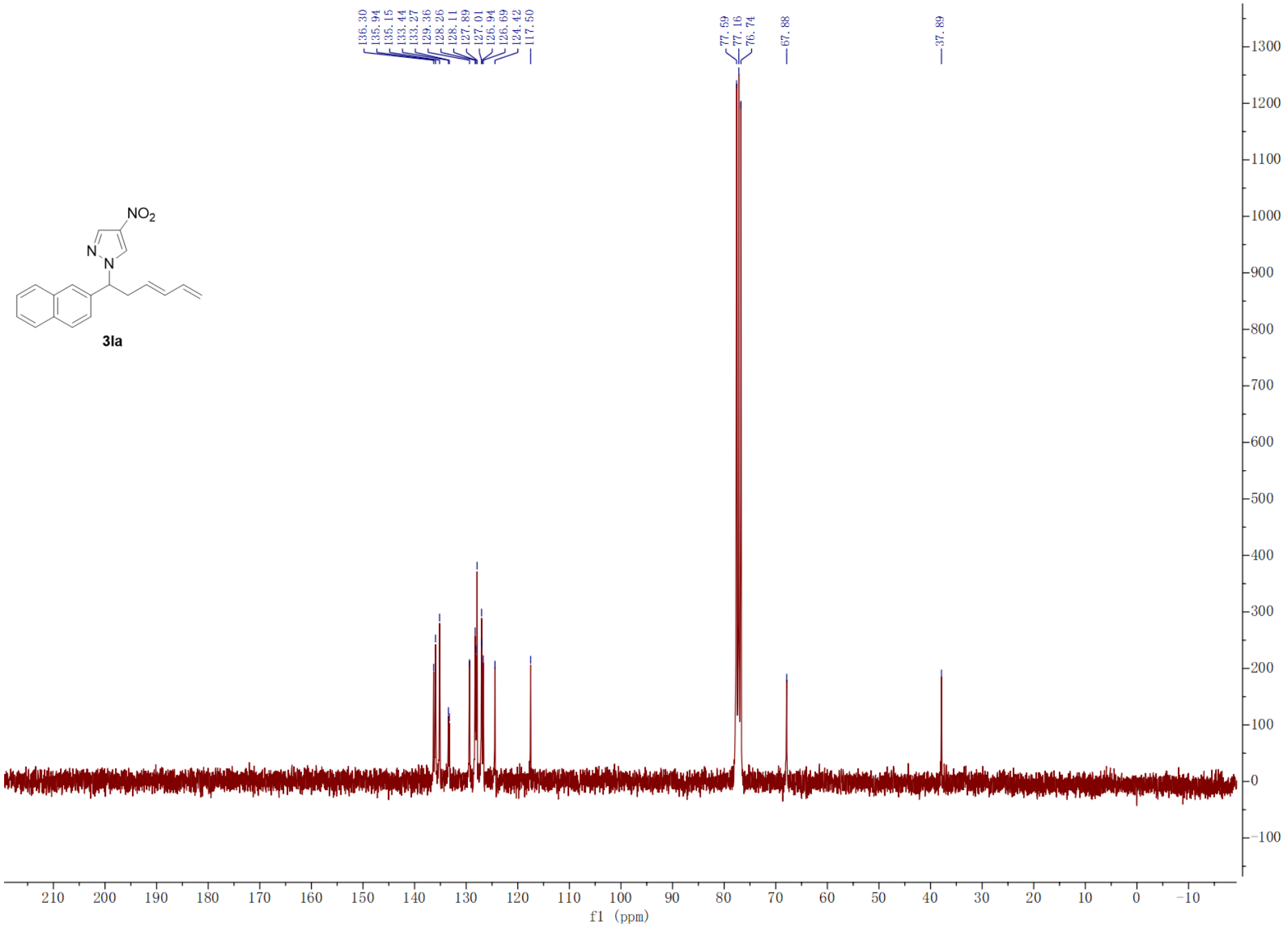
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)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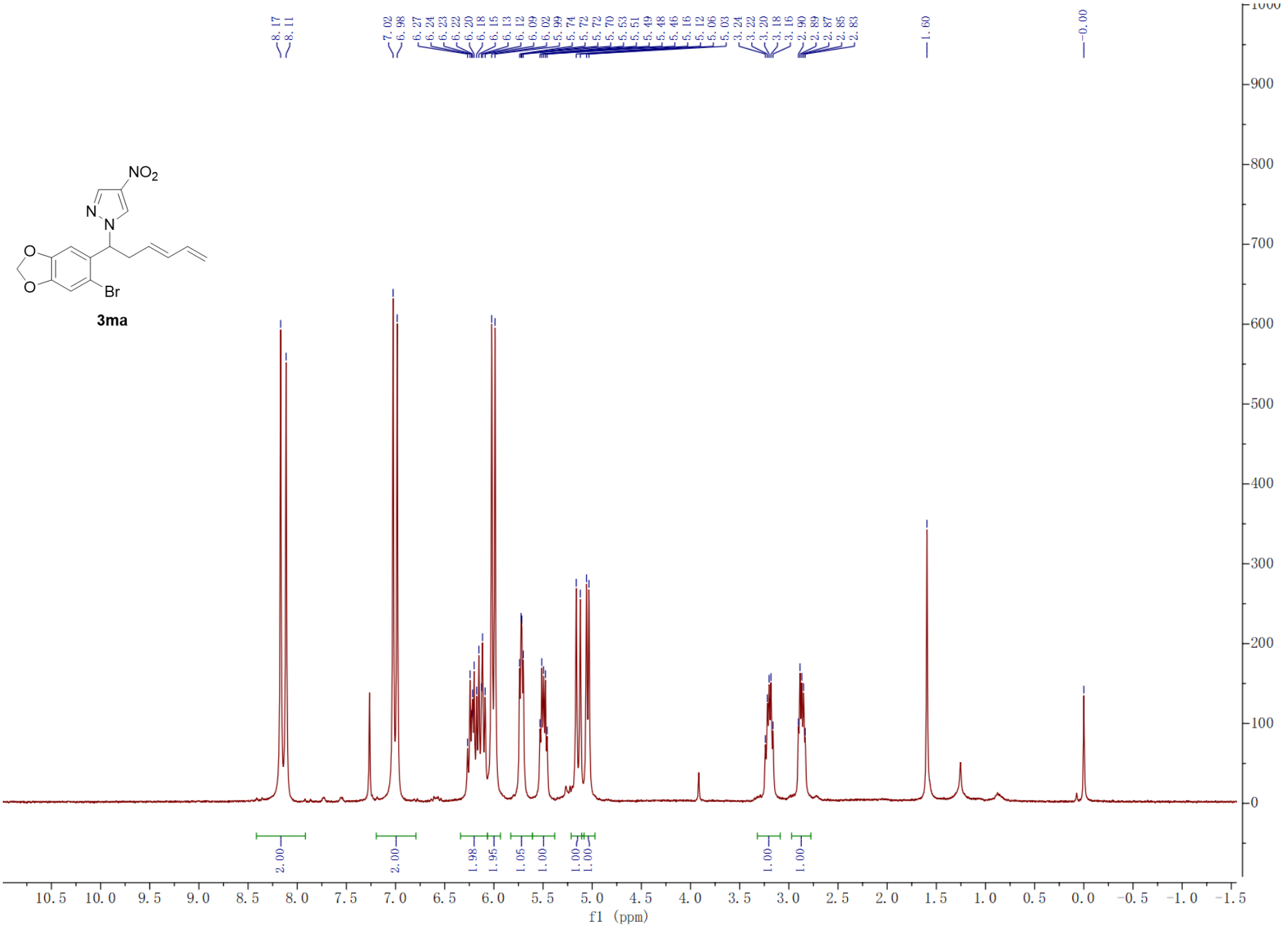
133.27
129.36
128.26
128.11
127.89
127.01
126.94
126.69
124.42
117.50
77.59
77.16
76.74
67.88
37.89
NO2
N
N
3la
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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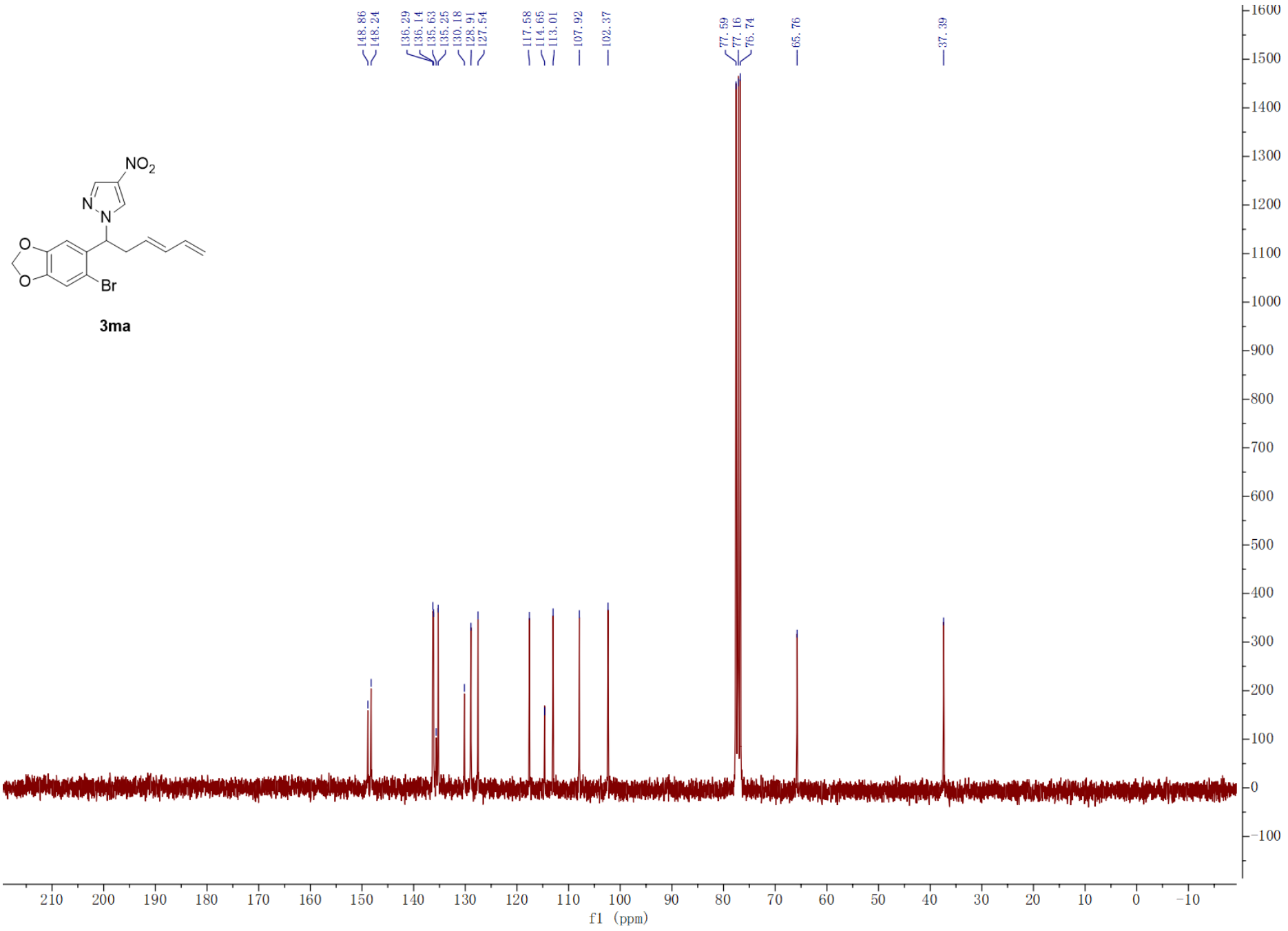
6.27
6.24
6.23
6.22
6.20
6.18
6.15
6.13
6.12
6.09
6.02
5.99
5.74
5.72
5.70
5.53
5.51
5.49
5.48
5.46
5.16
5.12
5.06
5.03
3.24
3.22
3.20
3.18
3.16
2.90
2.89
2.87
2.85
2.83
1.60
-0.00
NO2
N
N
O
O
Br
3ma
2.00
2.00
1.98
1.95
1.05
1.00
1.00
1.00
1.00
1.00
f1 (ppm)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148.24
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136.14
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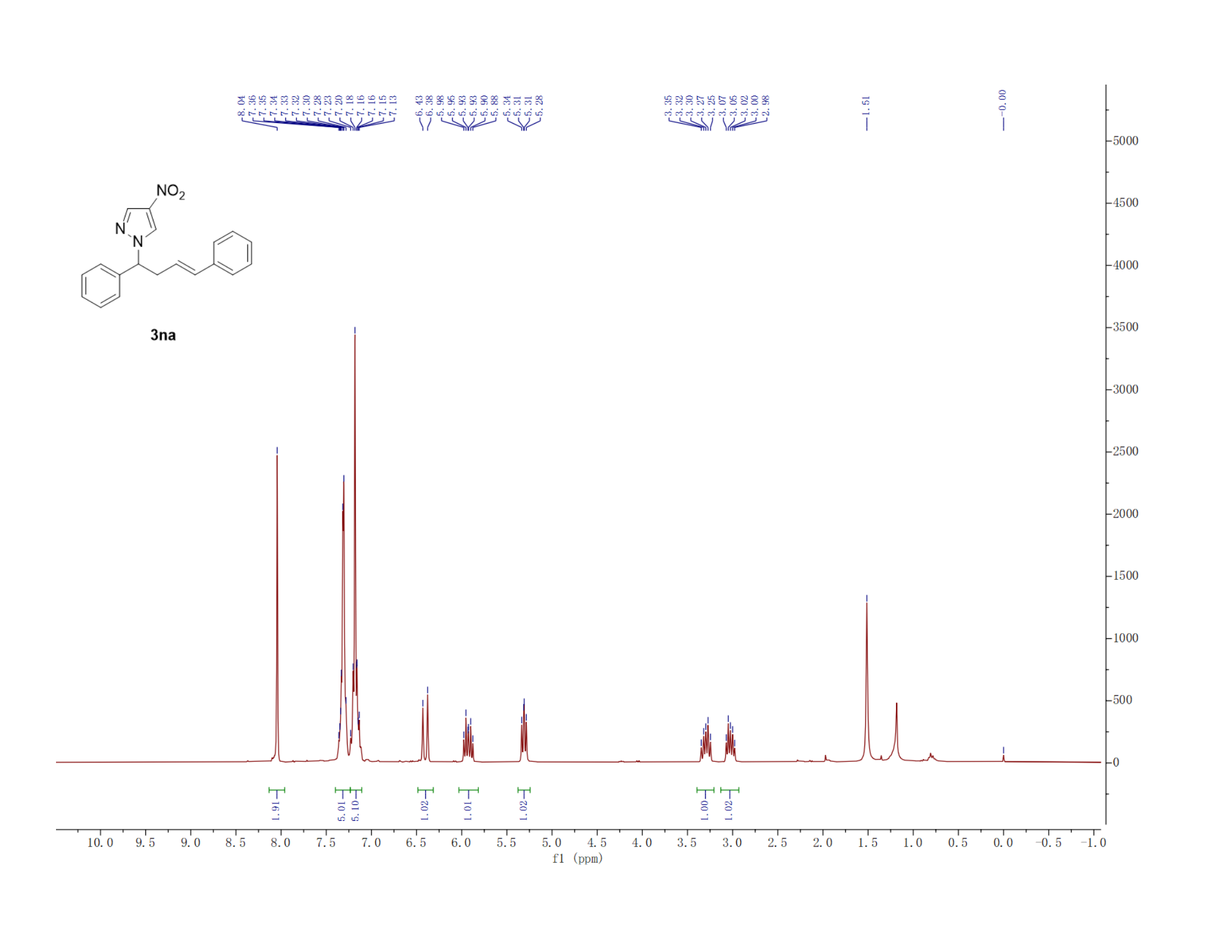
135.25
130.18
128.91
127.54
117.58
114.65
113.01
107.92
102.37
77.59
77.16
76.74
65.76
37.39
NO2
N
N
O
O
Br
3ma
f1 (ppm)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7.32
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7.28
7.23
7.20
7.18
7.16
7.16
7.15
7.13
6.43
6.38
5.98
5.95
5.93
5.93
5.90
5.88
5.34
5.31
5.31
5.28
3.35
3.32
3.30
3.27
3.25
3.07
3.05
3.02
3.00
2.98
1.51
-0.00
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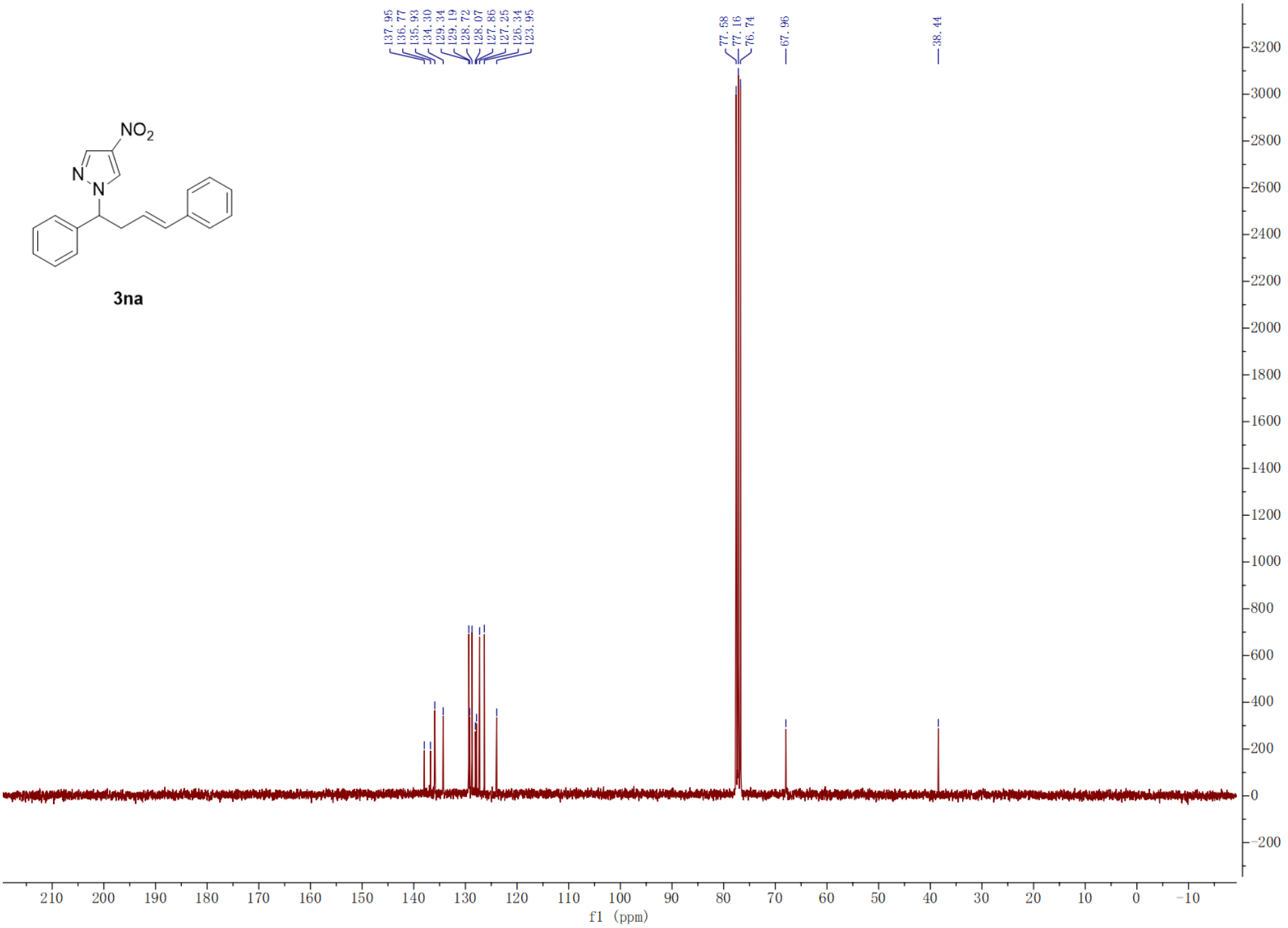
1.91
5.01
5.10
1.02
1.01
1.02
1.00
1.02
f1 (ppm)


137.95
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129.34
129.19
128.72
128.07
127.86
127.25
126.34
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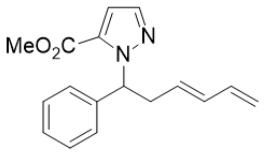
77.58
77.16
76.74
67.96
38.44
NO2
N
N
3na
f1 (ppm)


MeO2C
N
N

3ab

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7.19
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7.14
6.75
6.43
6.41
6.39
6.37
6.18
6.15
6.13
6.11
6.09
6.06
6.04
6.00
5.99
5.95
5.49
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5.42
5.40
5.02
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4.89
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2.83
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1.04
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1.00
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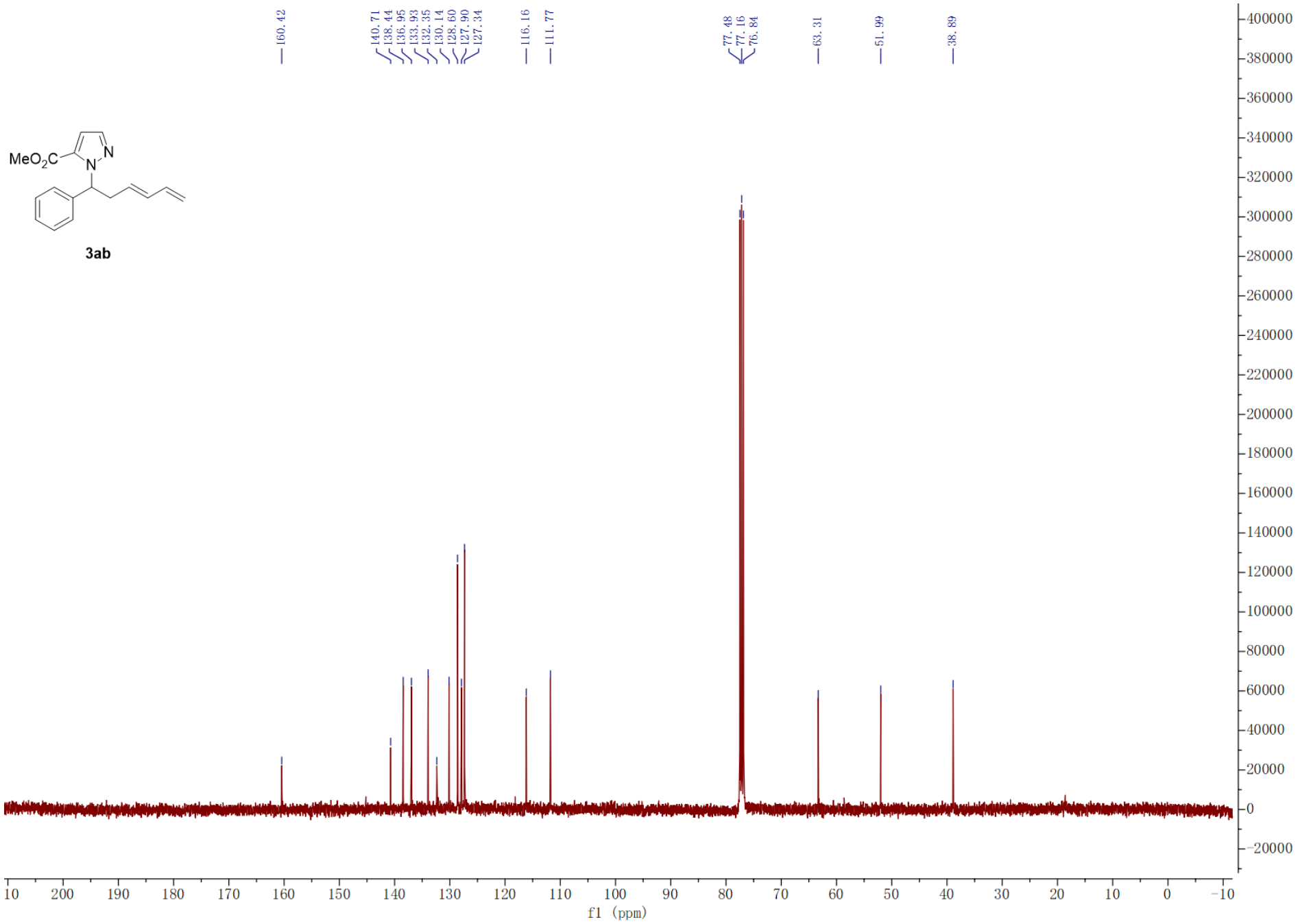
1.00
f1 (ppm)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133.93
132.35
130.14
128.60
127.90
127.34
116.16
111.77
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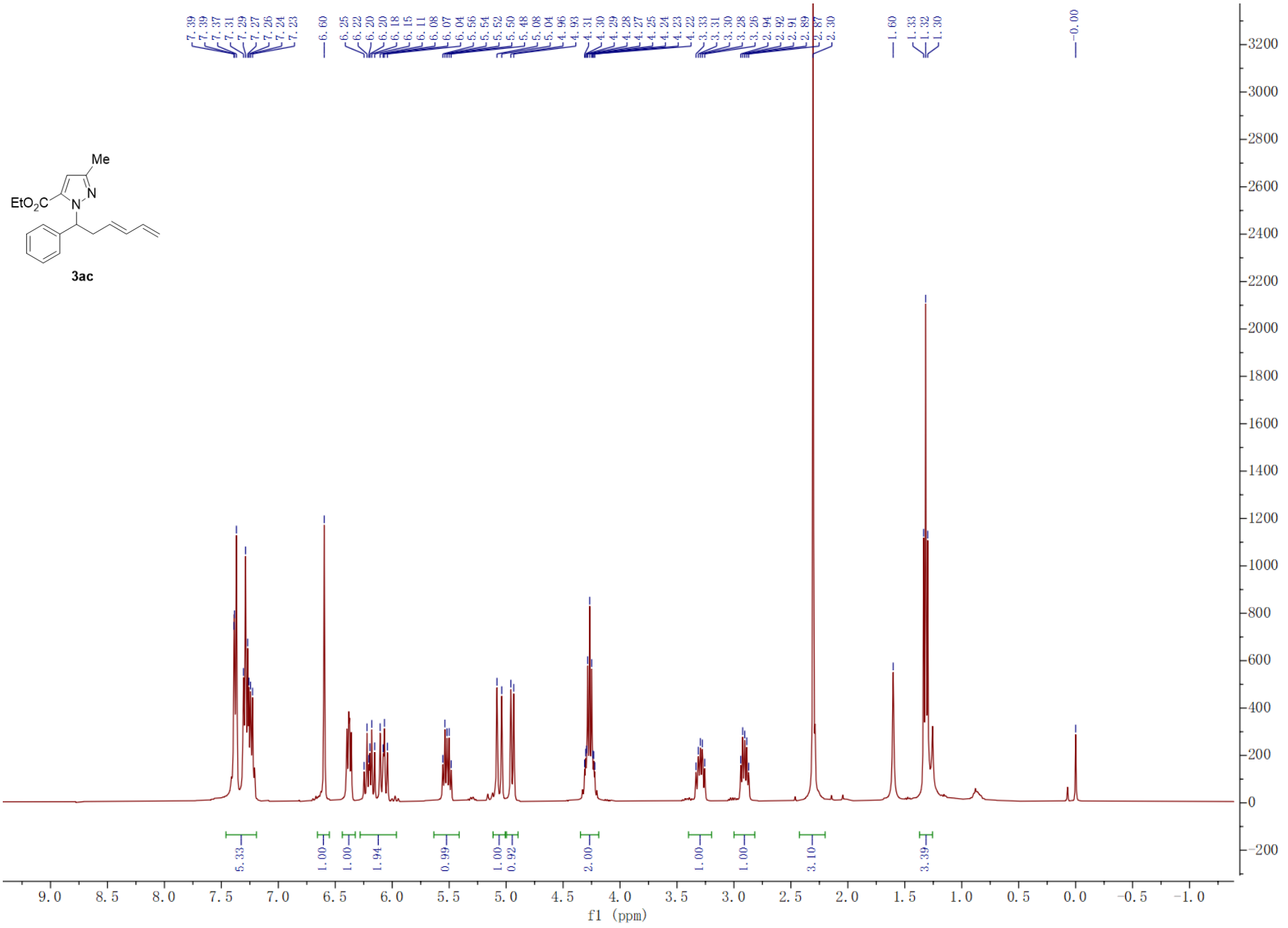
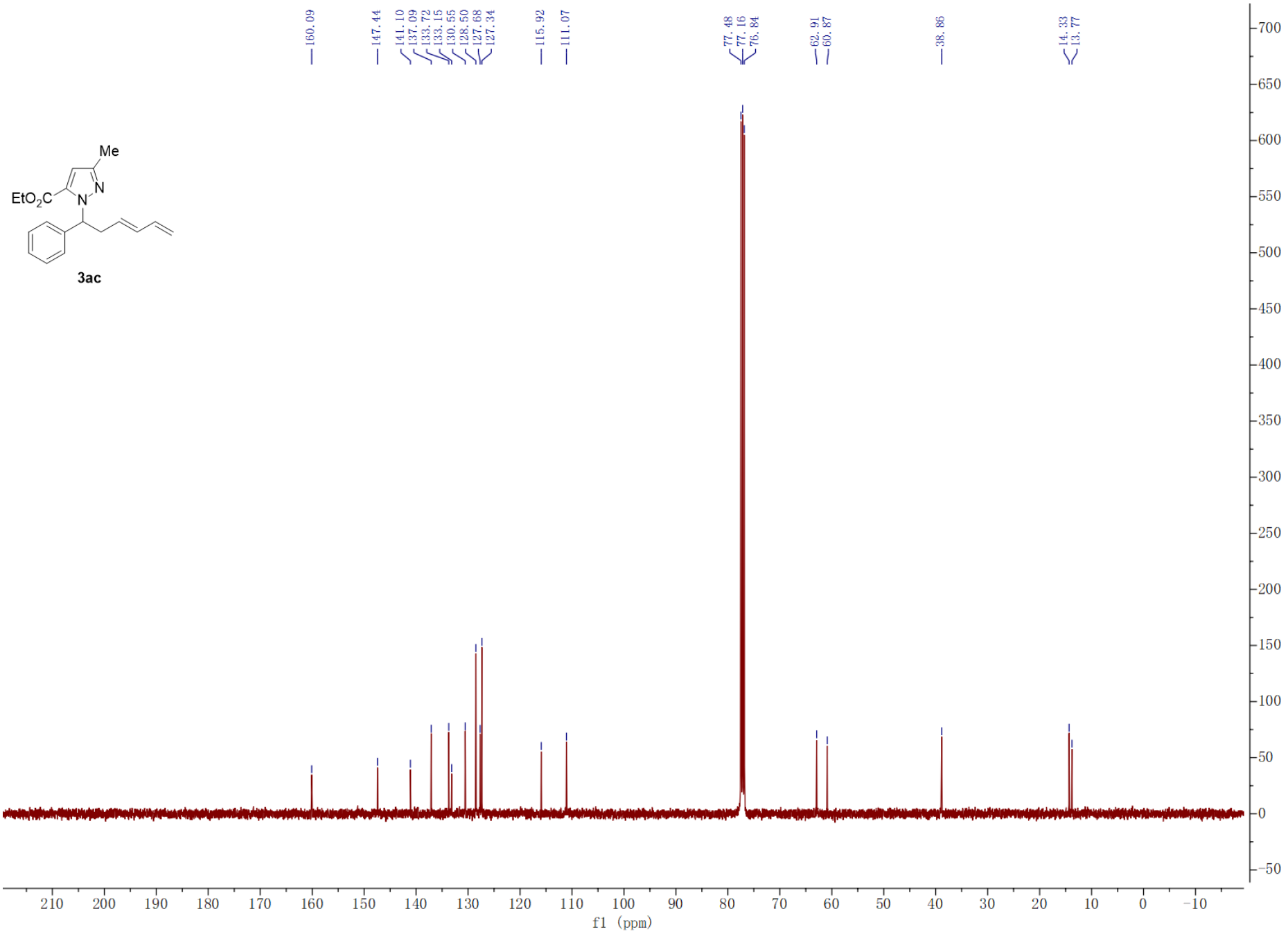
77.16
76.84
63.31
51.99
38.89
MeO2C
N
N
3ab
f1 (ppm)


Me
EtO2C
N
N
3ac
7.39
7.39
7.37
7.31
7.29
7.27
7.26
7.24
7.23
6.60
6.25
6.22
6.20
6.20
6.18
6.15
6.11
6.08
6.07
6.04
5.56
5.54
5.52
5.50
5.48
5.08
5.04
4.96
4.93
4.31
4.30
4.29
4.28
4.27
4.25
4.24
4.23
4.22
3.33
3.31
3.30
3.28
3.26
2.94
2.92
2.91
2.89
2.87
2.30
1.60
1.33
1.32
1.30
-0.00
5.33
1.00
1.00
1.94
0.99
1.00
0.92
2.00
1.00
1.00
3.10
3.39
f1 (ppm)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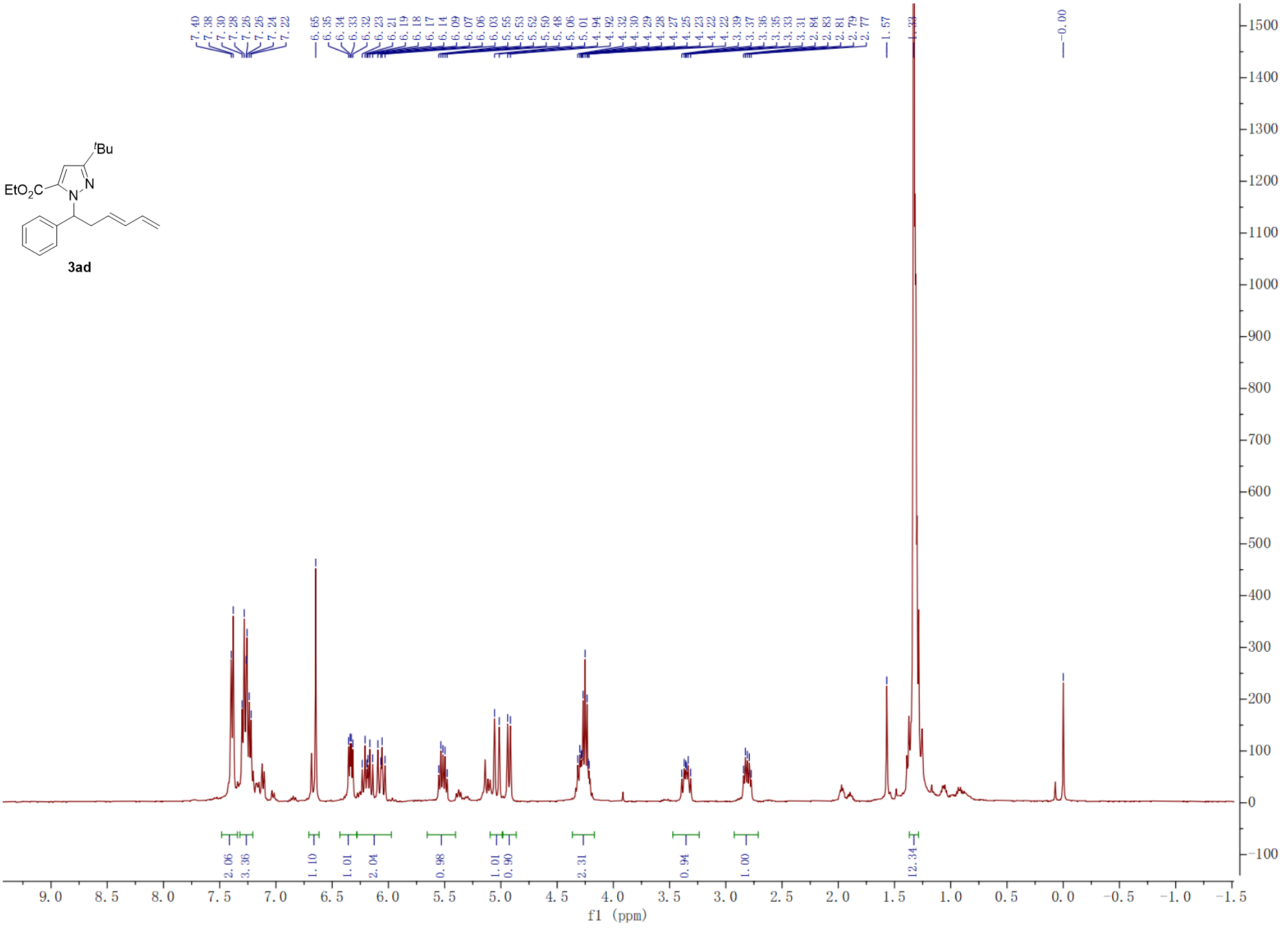
133.15
130.55
128.50
127.68
127.34
115.92
111.07
77.48
77.16
76.84
62.91
60.87
38.86
14.33
13.77
Me
N
N
EtO2C
3ac
f1 (ppm)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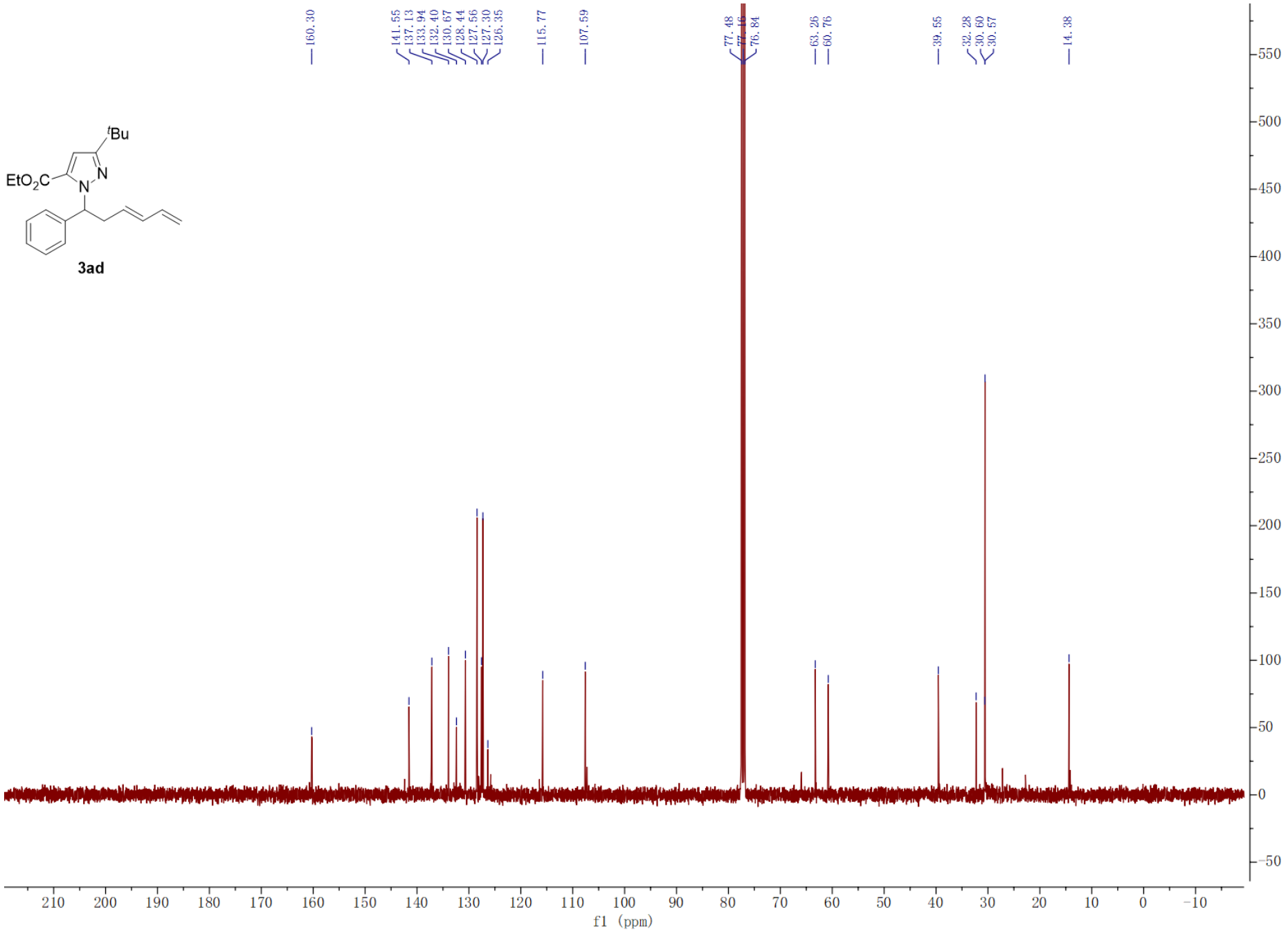
7.38
7.30
7.28
7.26
7.26
7.24
7.22
6.65
6.35
6.34
6.33
6.32
6.23
6.21
6.19
6.18
6.17
6.14
6.09
6.07
6.06
6.03
5.55
5.53
5.52
5.50
5.48
5.06
5.01
4.94
4.92
4.32
4.30
4.29
4.28
4.27
4.25
4.23
4.22
4.22
3.39
3.37
3.36
3.35
3.33
3.31
2.84
2.83
2.81
2.79
2.77
1.57
1.33
0.00
tBu
EtO2C
N
N
3ad
2.06
3.36
1.10
1.01
2.04
0.98
1.01
0.90
2.31
0.94
1.00
12.34
f1 (ppm)


160.30
141.55
137.13
133.94
132.40
130.67
128.44
127.56
127.30
126.35
115.77
107.59
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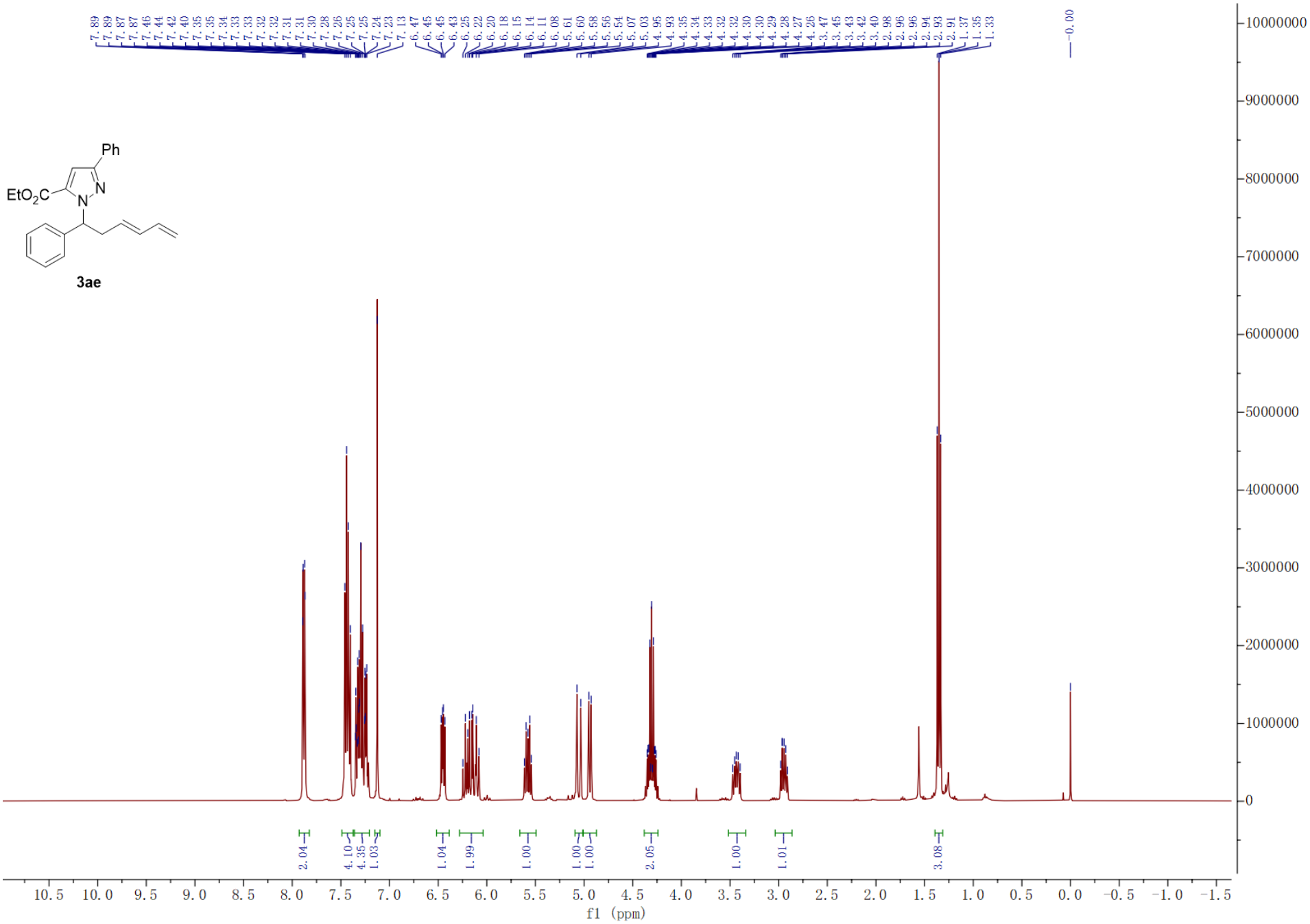
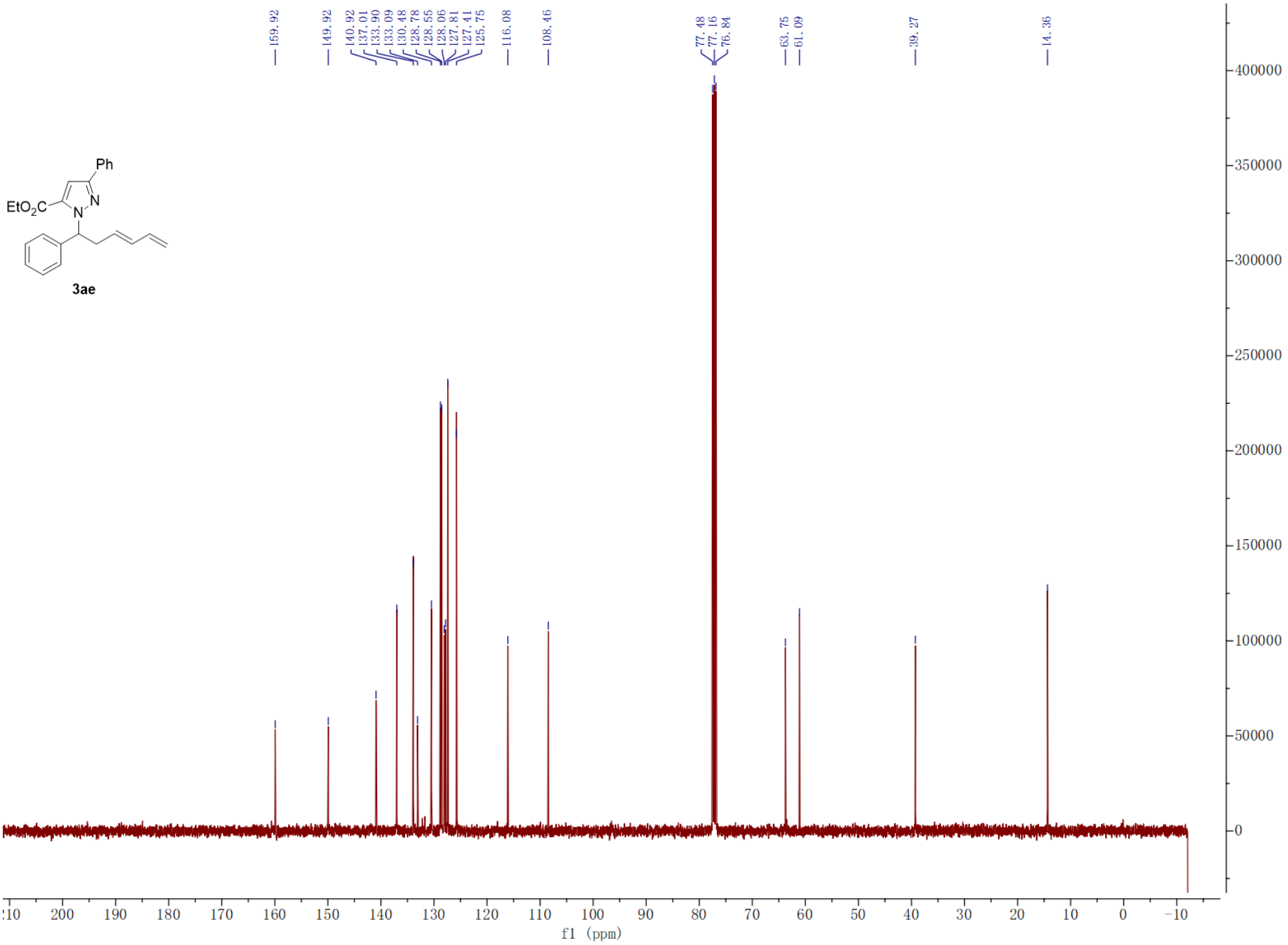
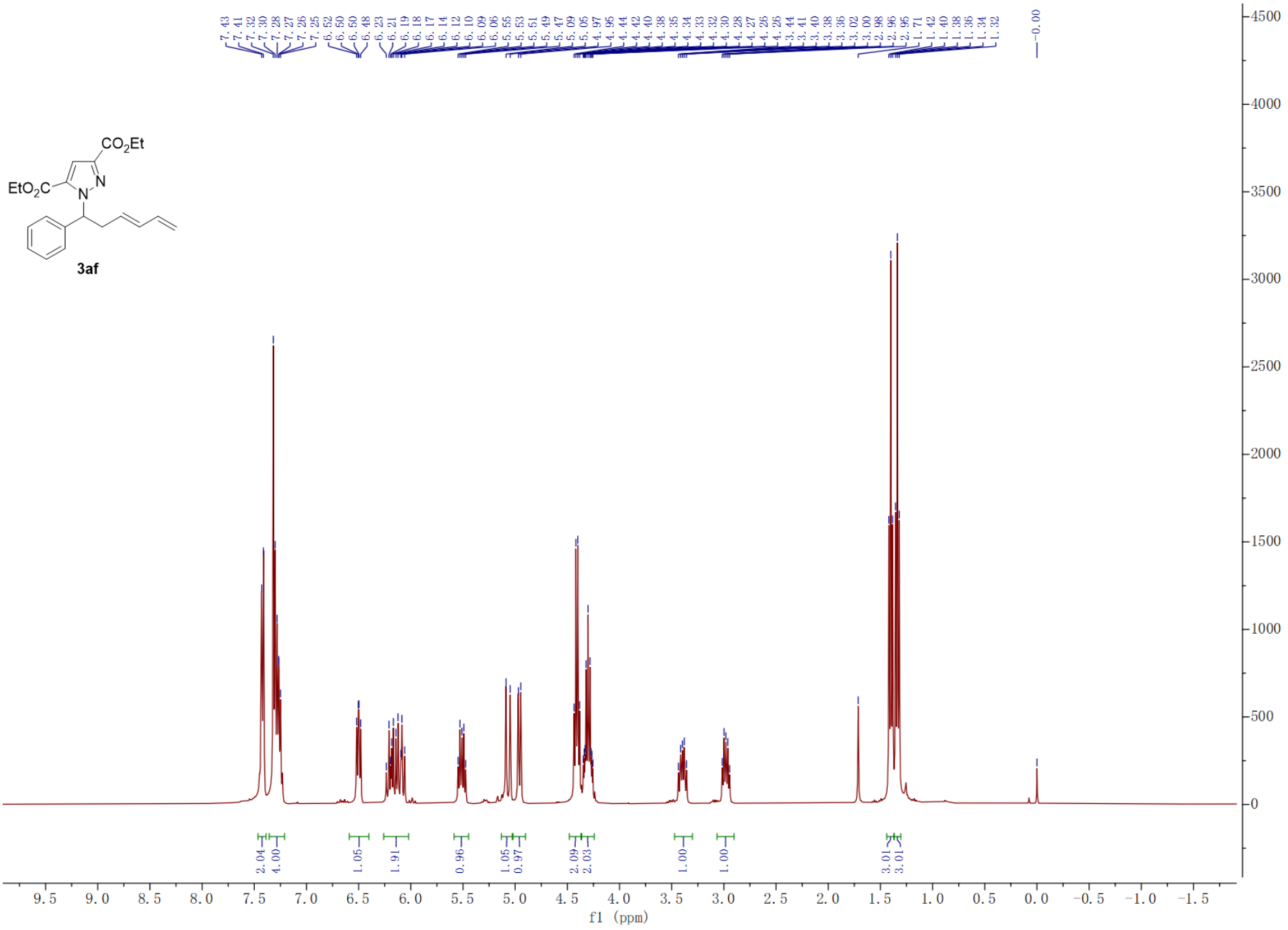
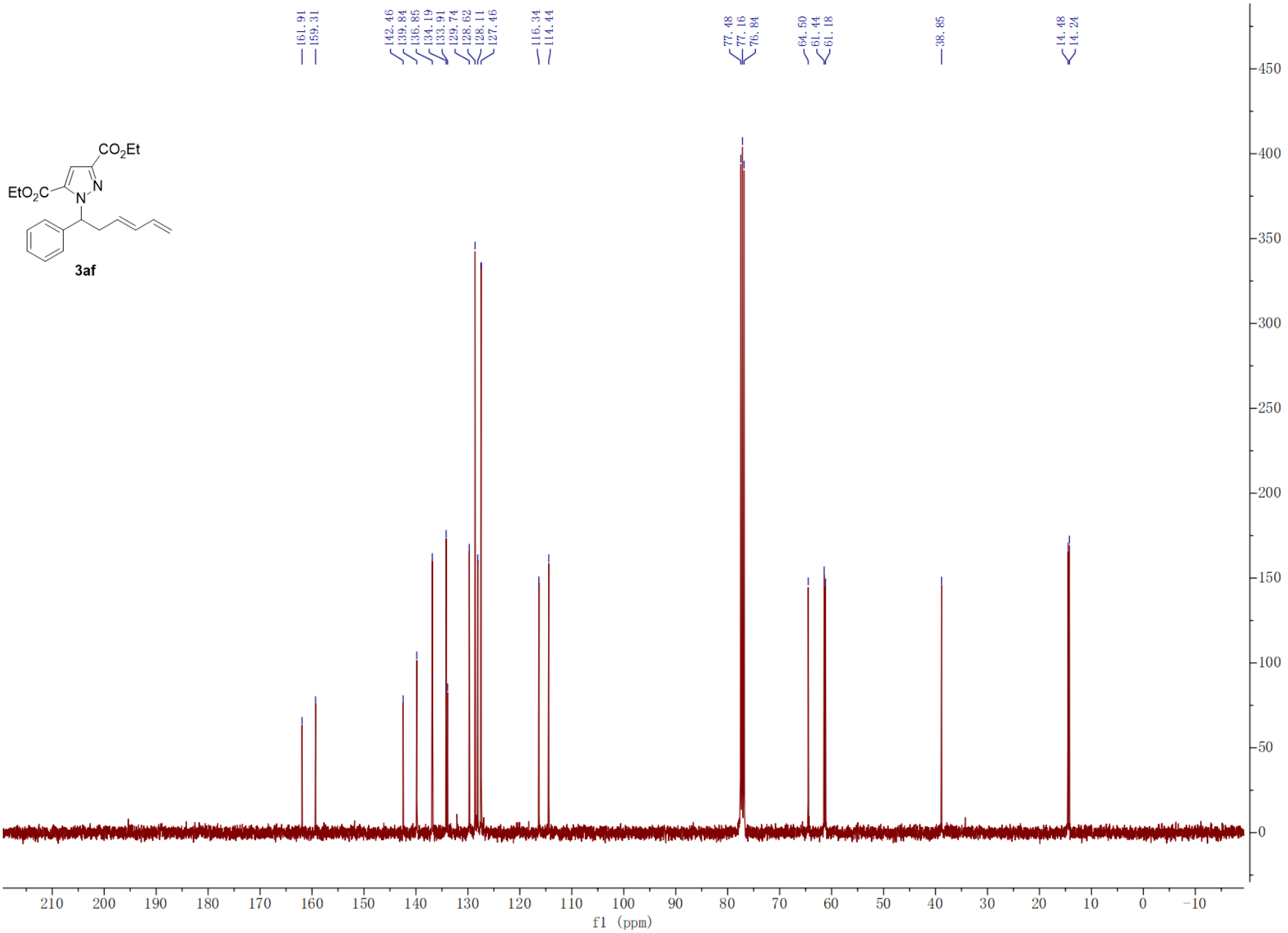
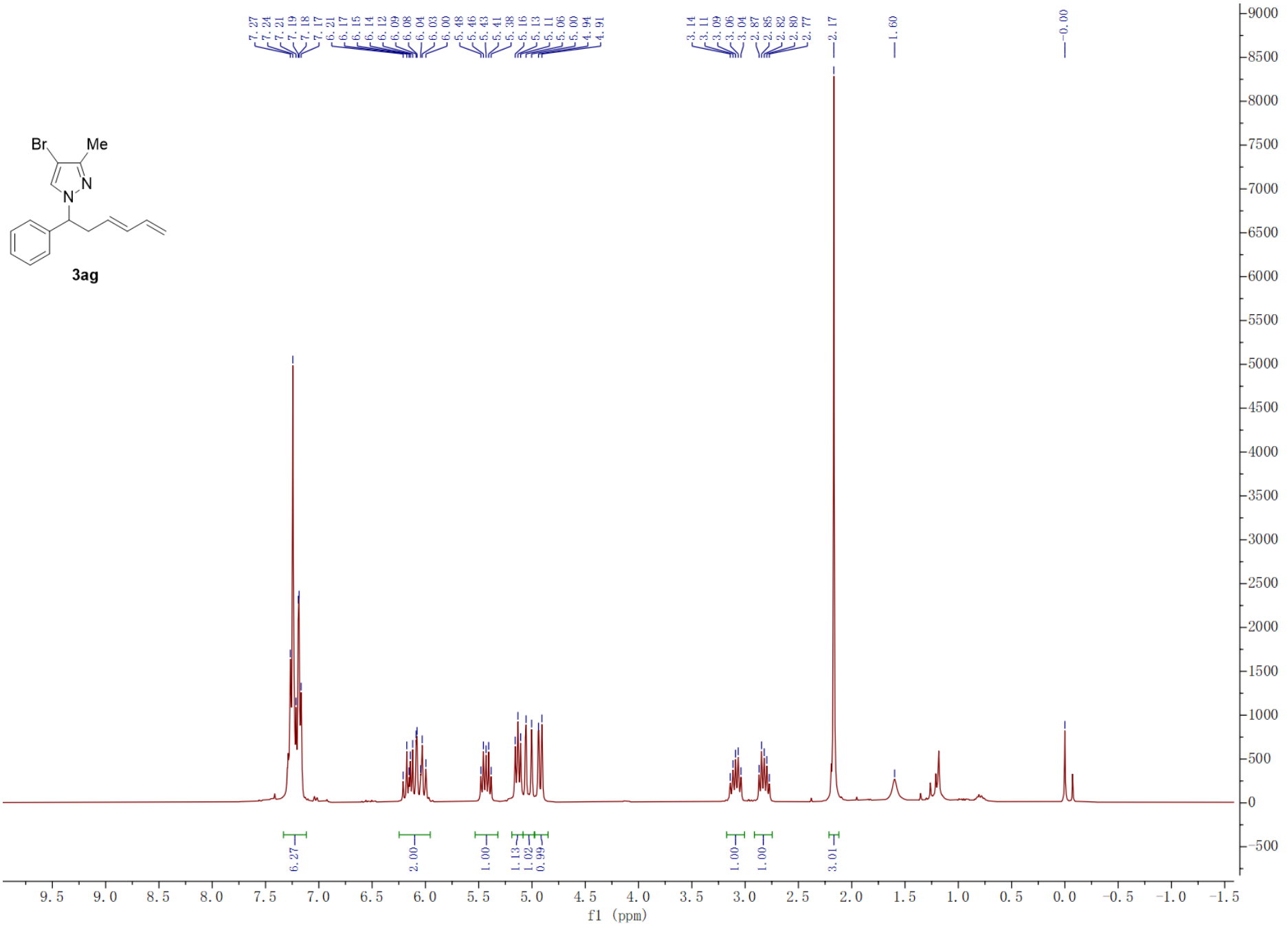
77.16
76.84
63.26
60.76
39.55
32.28
30.60
30.57
14.38
tBu
EtO2C
N
N
3ad
550
500
450
400
350
300
250
200
150
100
50
0
−50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

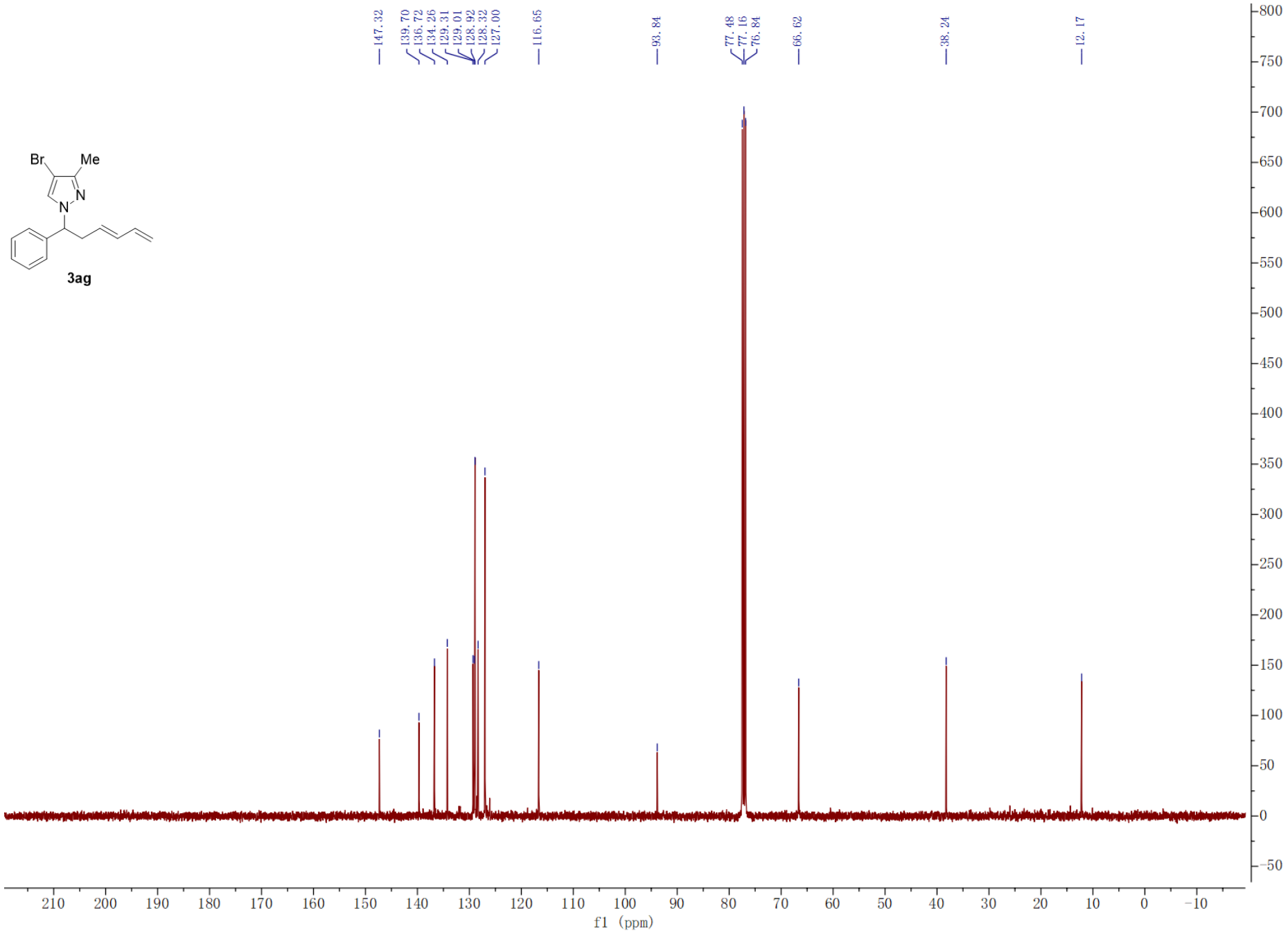

Ph
EtO2C
N
N
3ae
7.89 7.89 7.87 7.87 7.46 7.44 7.42 7.40 7.35 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.28 7.26 7.25 7.25 7.24 7.23 7.13 6.47 6.45 6.45 6.43 6.25 6.22 6.20 6.18 6.15 6.14 6.11 6.08 5.61 5.60 5.58 5.56 5.54 5.07 5.03 4.95 4.93 4.35 4.34 4.33 4.32 4.32 4.30 4.30 4.29 4.28 4.27 4.26 3.47 3.45 3.43 3.42 3.40 2.98 2.96 2.96 2.94 2.93 2.91 1.37 1.35 1.33
0.00
2.04 4.10 4.35 1.03 1.04 1.99 1.00 1.00 1.00 2.05 1.00 1.01 3.08
10000000 9000000 8000000 7000000 6000000 5000000 4000000 3000000 2000000 1000000 0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


159.92
149.92
140.92
137.01
133.90
133.09
130.48
128.78
128.55
128.06
127.81
127.41
125.75
116.08
108.46
77.48
77.16
76.84
63.75
61.09
39.27
14.36
Ph
EtO2C
N
N
3ae
400000
350000
300000
250000
200000
150000
100000
50000
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)


7.43 7.41 7.32 7.30 7.28 7.27 7.26 7.25 6.52 6.50 6.50 6.48 6.23 6.21 6.19 6.18 6.17 6.14 6.12 6.10 6.09 6.06 5.55 5.53 5.51 5.49 5.47 5.09 5.05 4.97 4.95 4.44 4.42 4.40 4.38 4.35 4.34 4.33 4.32 4.30 4.28 4.27 4.26 4.26 3.44 3.41 3.40 3.38 3.36 3.02 3.00 2.98 2.96 2.95 1.71 1.42 1.40 1.38 1.36 1.34 1.32
0.00
CO2Et
EtO2C
N
N
3af
2.04 4.00 1.05 1.91 0.96 1.05 0.97 2.09 2.03 1.00 1.00 3.01 3.01
f1 (ppm)


161.91
159.31
142.46
139.84
136.85
134.19
133.91
129.74
128.62
128.11
127.46
116.34
114.44
77.48
77.16
76.84
64.50
61.44
61.18
38.85
14.48
14.24
CO2Et
EtO2C
N
N
3af
450
400
350
300
250
200
150
100
50
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)


Br
Me
N
N
3ag
7.27
7.24
7.21
7.19
7.18
7.17
6.21
6.17
6.15
6.14
6.12
6.09
6.08
6.04
6.03
6.00
5.48
5.46
5.43
5.41
5.38
5.16
5.13
5.11
5.06
5.00
4.94
4.91
3.14
3.11
3.09
3.06
3.04
2.87
2.85
2.82
2.80
2.77
2.17
1.60
0.00
6.27
2.00
1.00
1.13
1.02
0.99
1.00
1.00
3.01
f1 (ppm)


147.32
139.70
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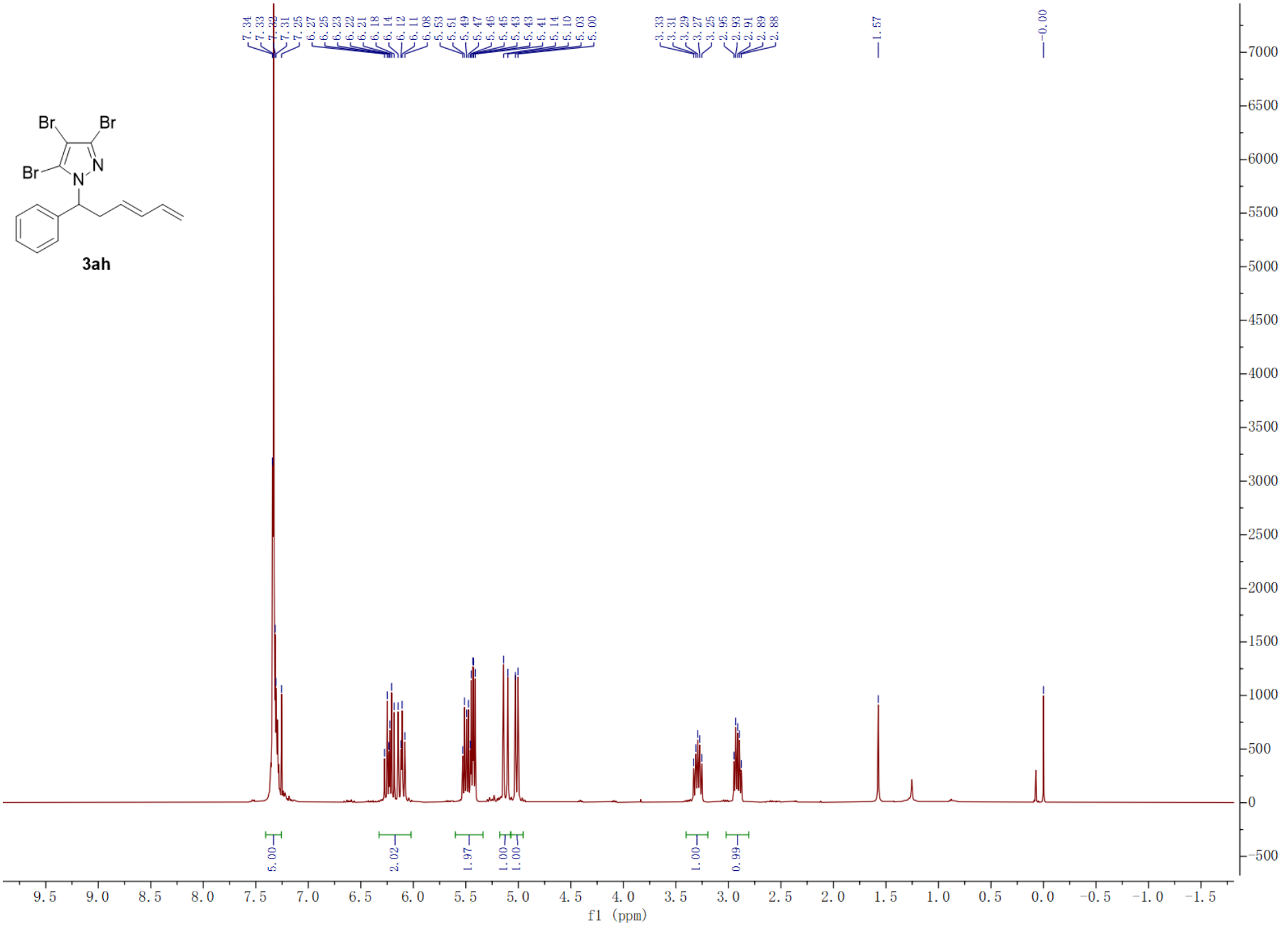
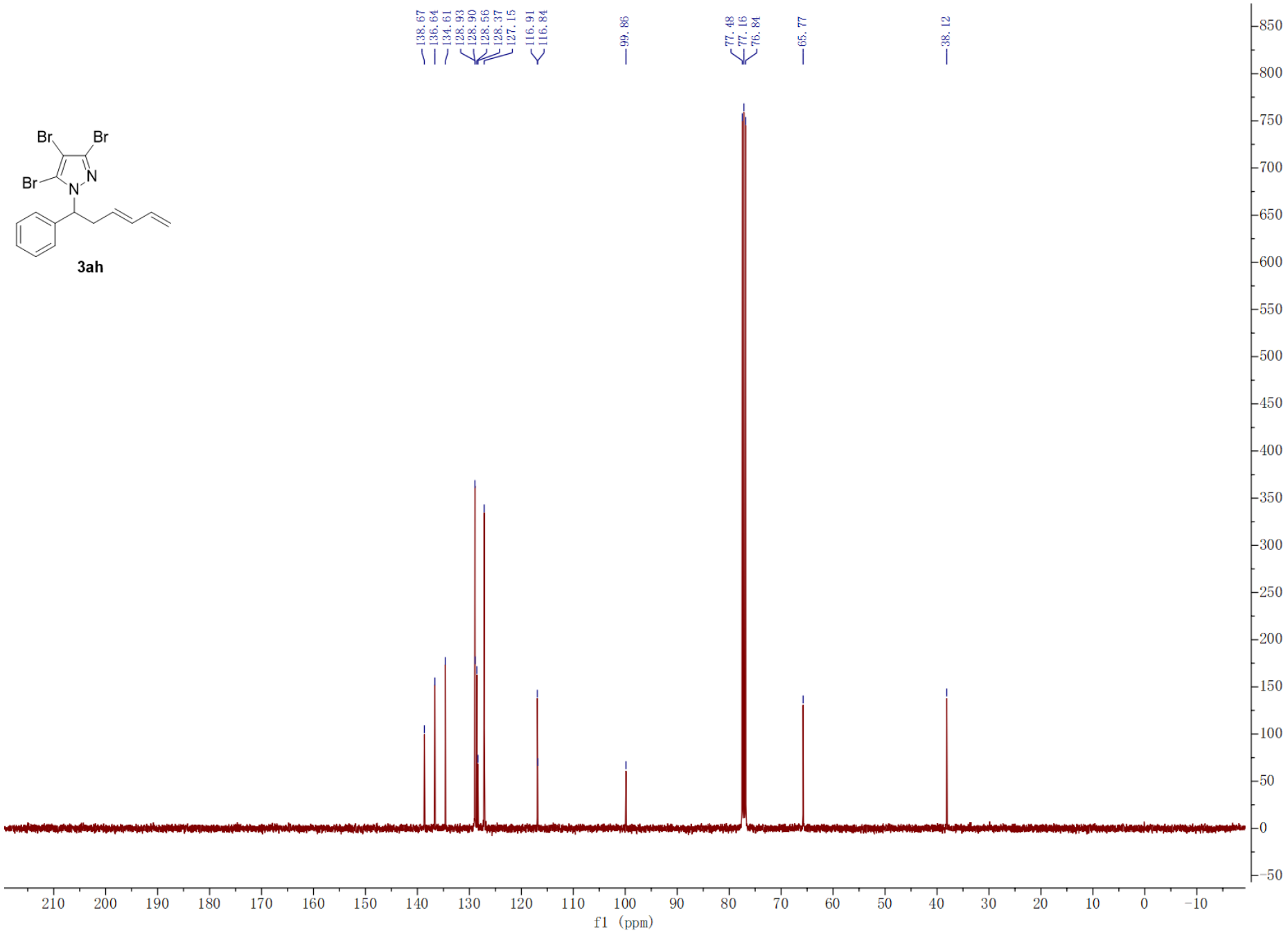
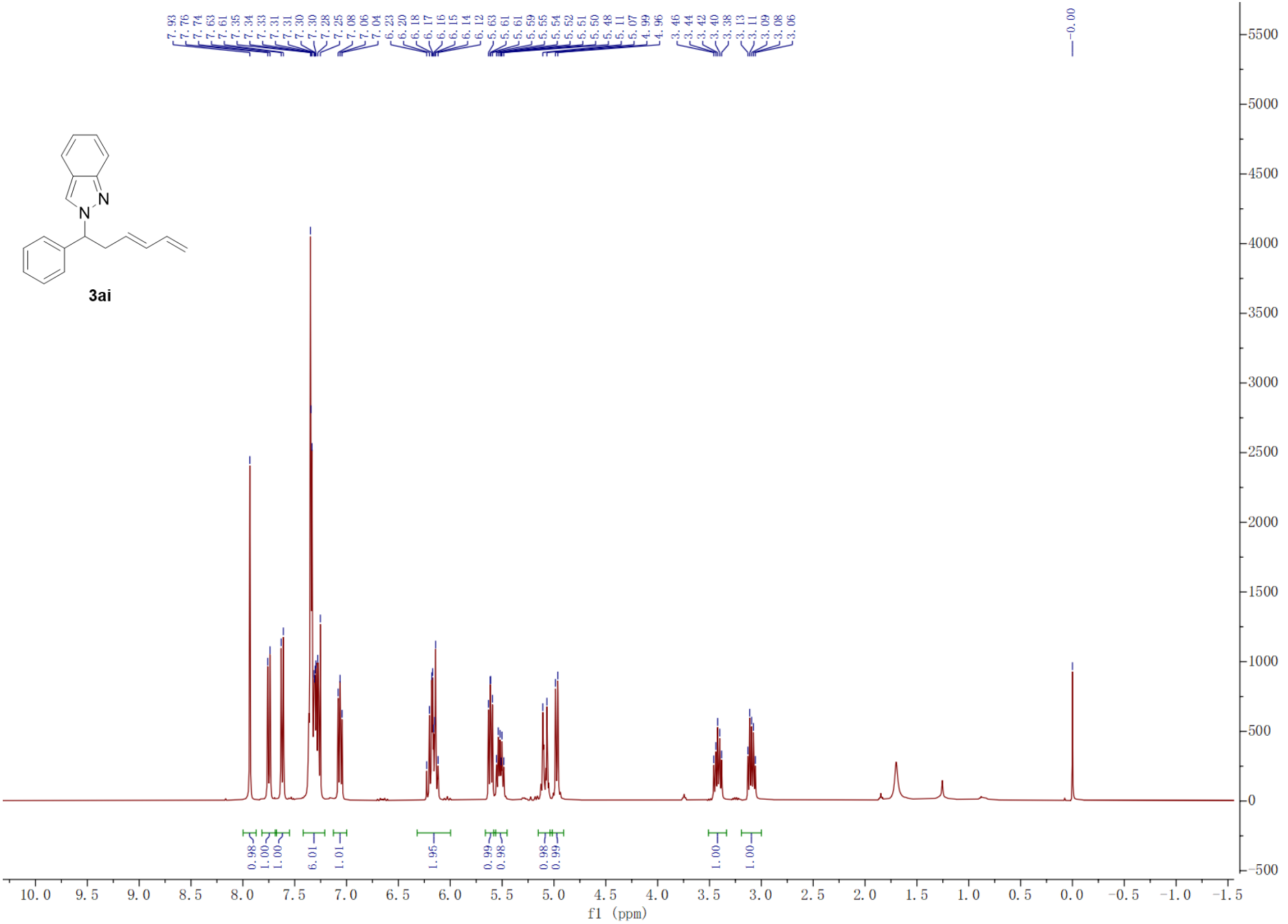
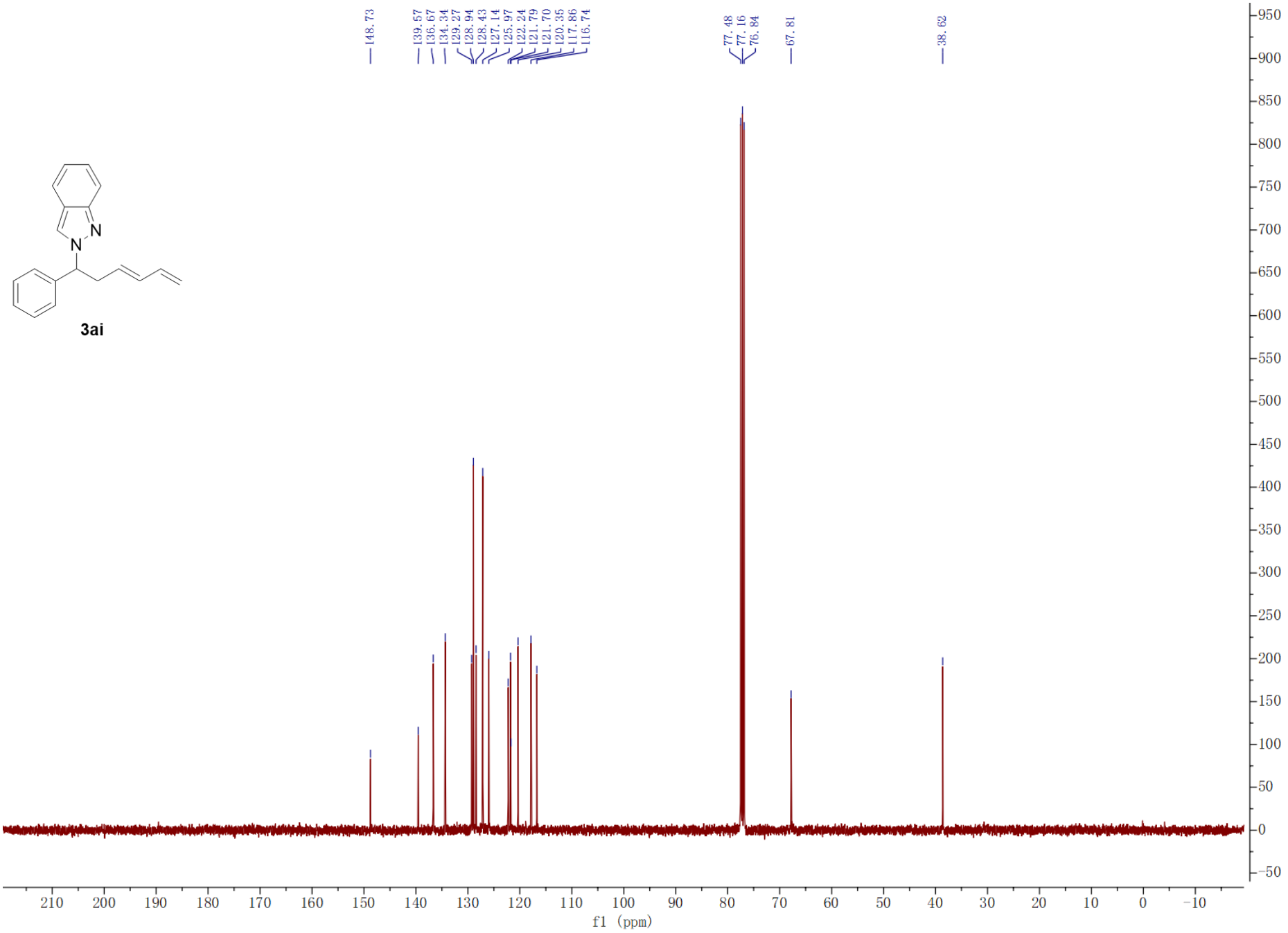
134.26
129.31
129.01
128.92
128.32
127.00
116.65
93.84
77.48
77.16
76.84
66.62
38.24
12.17
Br
Me
N
N
3ag
f1 (ppm)

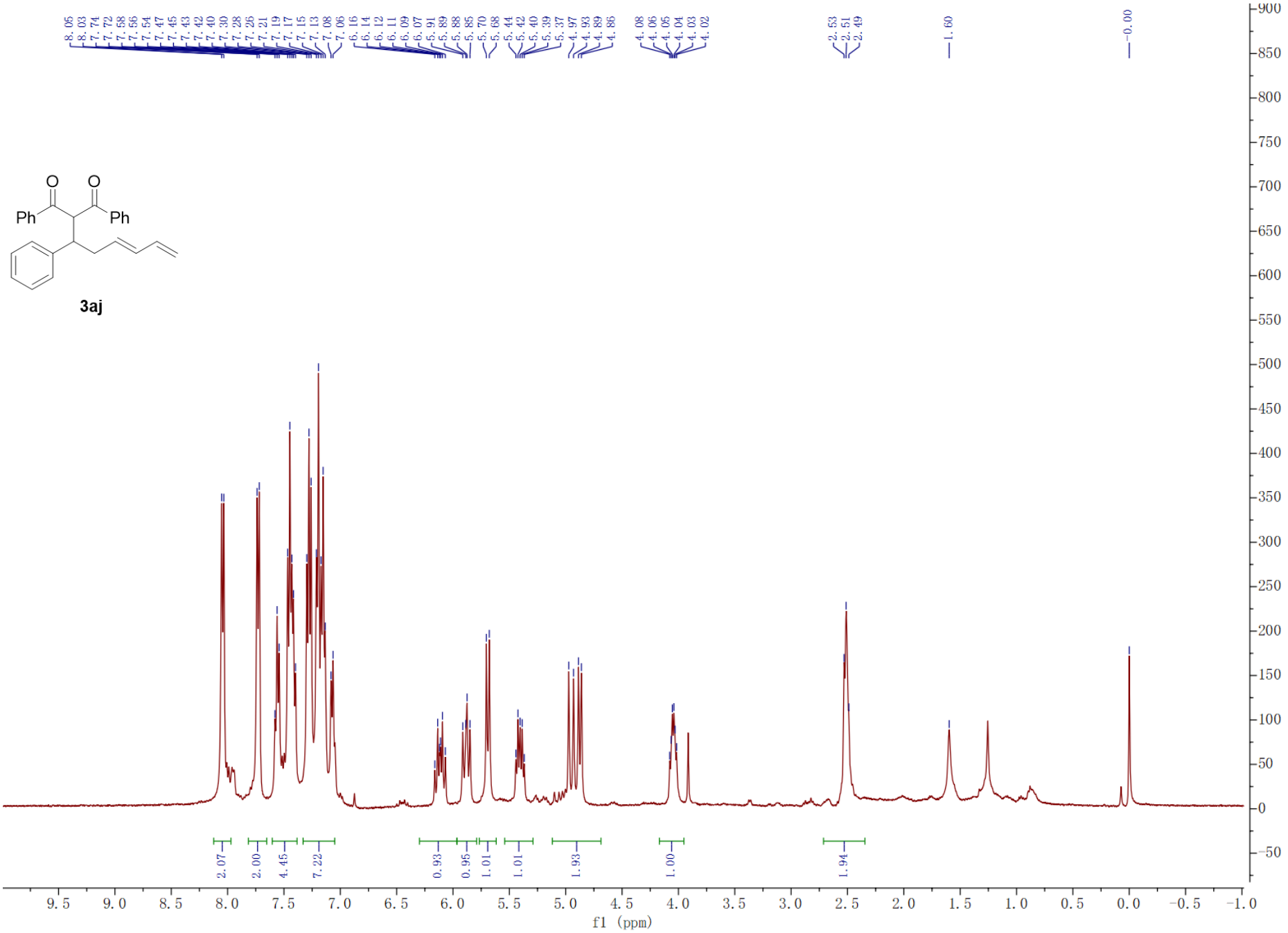

Br
Br
Br
N
N
3ah
7.34
7.33
7.32
7.31
7.25
6.27
6.25
6.23
6.22
6.21
6.18
6.14
6.12
6.11
6.08
5.53
5.51
5.49
5.47
5.46
5.45
5.43
5.41
5.14
5.10
5.03
5.00
3.33
3.31
3.29
3.27
3.25
2.95
2.93
2.91
2.89
2.88
1.57
0.00
5.00
2.02
1.97
1.00
1.00
1.00
0.99
f1 (ppm)

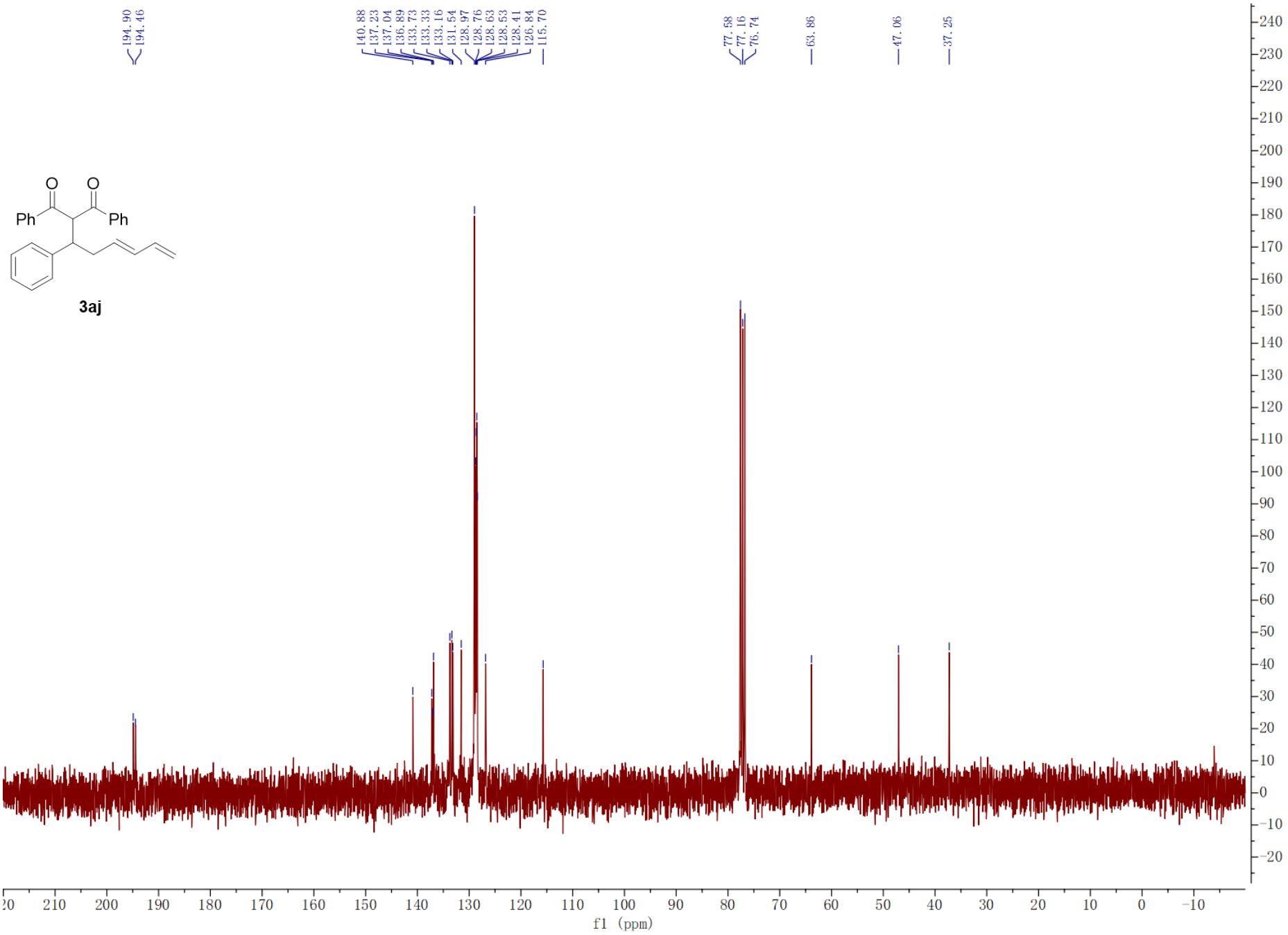

138.67
136.64
134.61
128.93
128.90
128.56
128.37
127.15
116.91
116.84
99.86
77.48
77.16
76.84
65.77
38.12
Br
Br
Br
N
N
3ah
f1 (ppm)


7.93
7.76
7.74
7.63
7.61
7.35
7.34
7.33
7.31
7.31
7.30
7.30
7.28
7.25
7.08
7.06
7.04
6.23
6.20
6.18
6.17
6.16
6.15
6.14
6.12
5.63
5.61
5.61
5.59
5.55
5.54
5.52
5.51
5.50
5.48
5.11
5.07
4.99
4.96
3.46
3.44
3.42
3.40
3.38
3.13
3.11
3.09
3.08
3.06
0.00
3ai
0.98
1.00
1.00
6.01
1.01
1.95
0.99
0.98
0.98
0.99
1.00
1.00
f1 (ppm)


148.73
139.57
136.67
134.34
129.27
128.94
128.43
127.14
125.97
122.24
121.79
121.70
120.35
117.86
116.74
77.48
77.16
76.84
67.81
38.62
f1 (ppm)

3ai


8.05
8.03
7.74
7.72
7.58
7.56
7.54
7.47
7.45
7.43
7.42
7.40
7.30
7.28
7.26
7.21
7.19
7.17
7.15
7.13
7.08
7.06
6.16
6.14
6.12
6.11
6.09
6.07
5.91
5.89
5.88
5.85
5.70
5.68
5.44
5.42
5.40
5.39
5.37
4.97
4.93
4.89
4.86
4.08
4.06
4.05
4.04
4.03
4.02
2.53
2.51
2.49
1.60
0.00
O
O
Ph
Ph
3aj
2.07
2.00
4.45
7.22
0.93
0.95
1.01
1.01
1.93
1.00
1.94
f1 (ppm)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194.46
140.88
137.23
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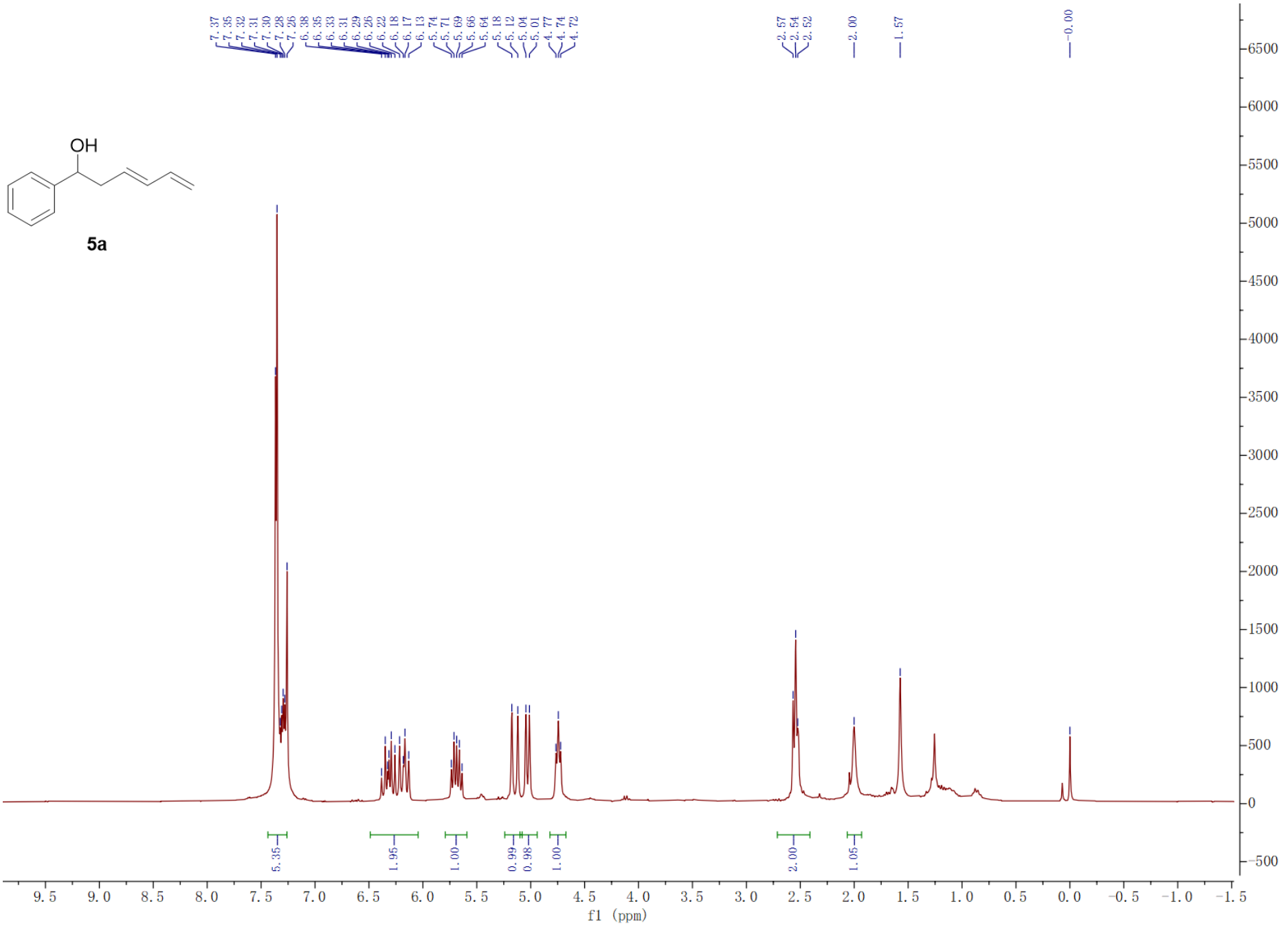
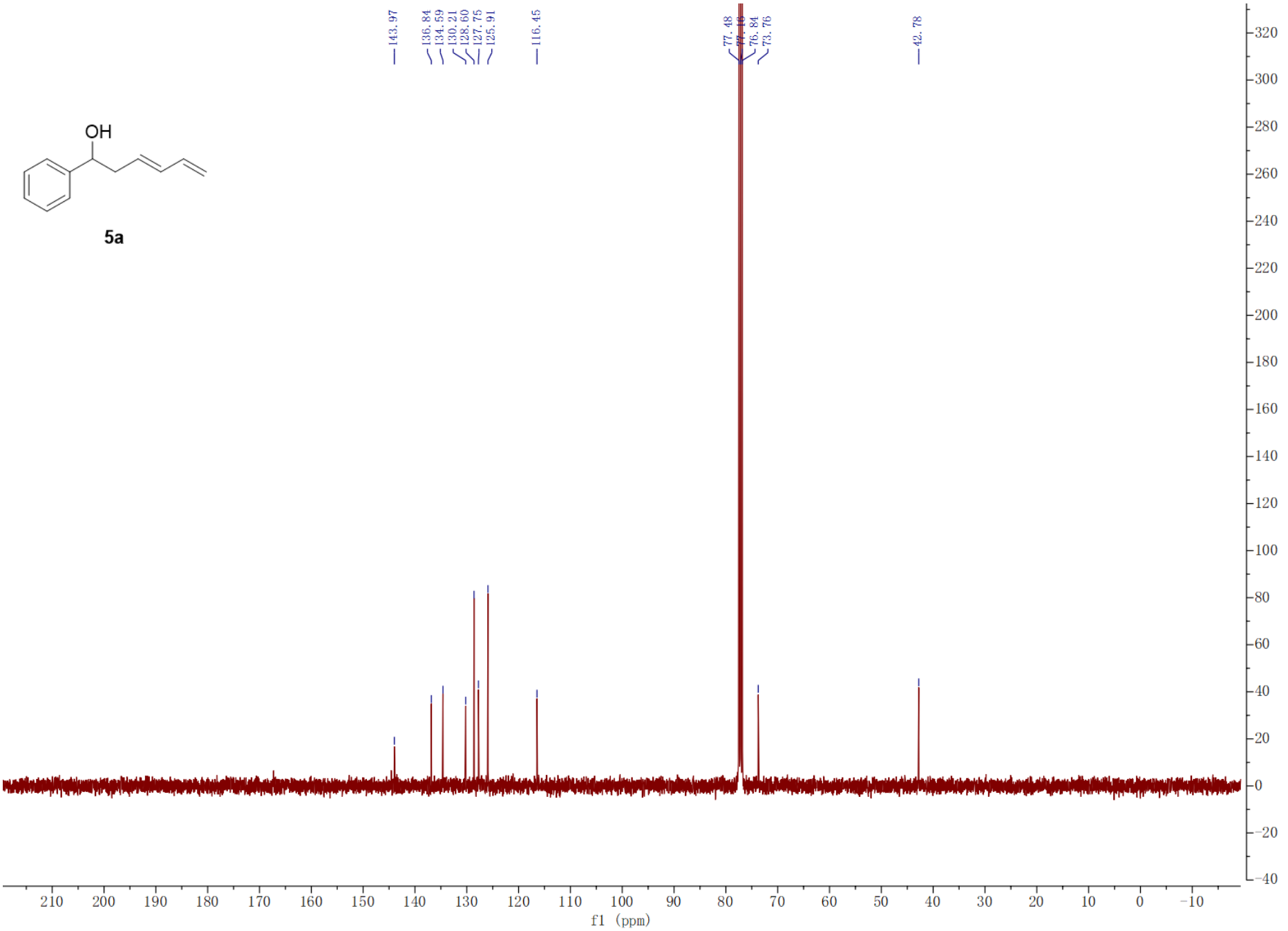
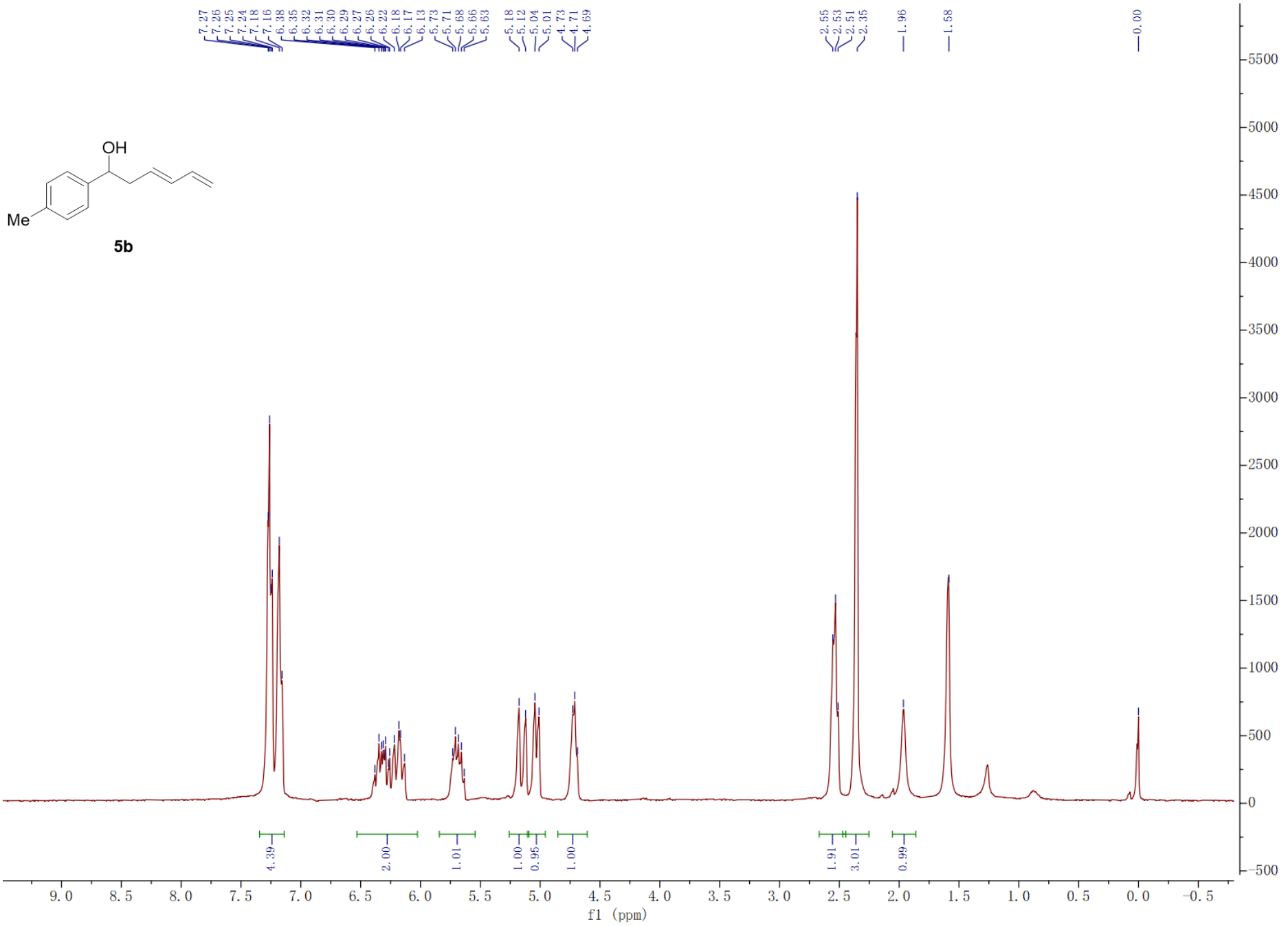
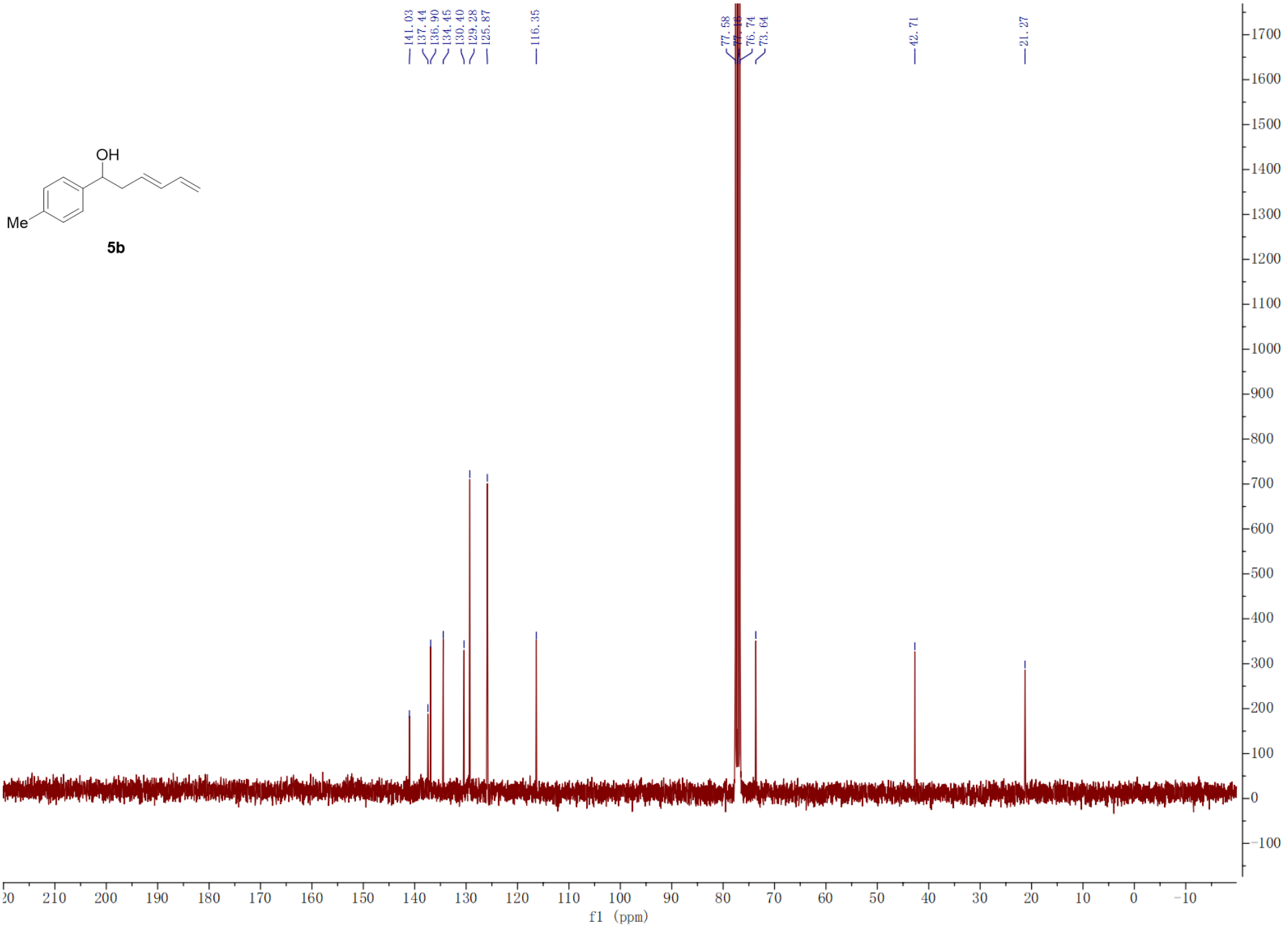
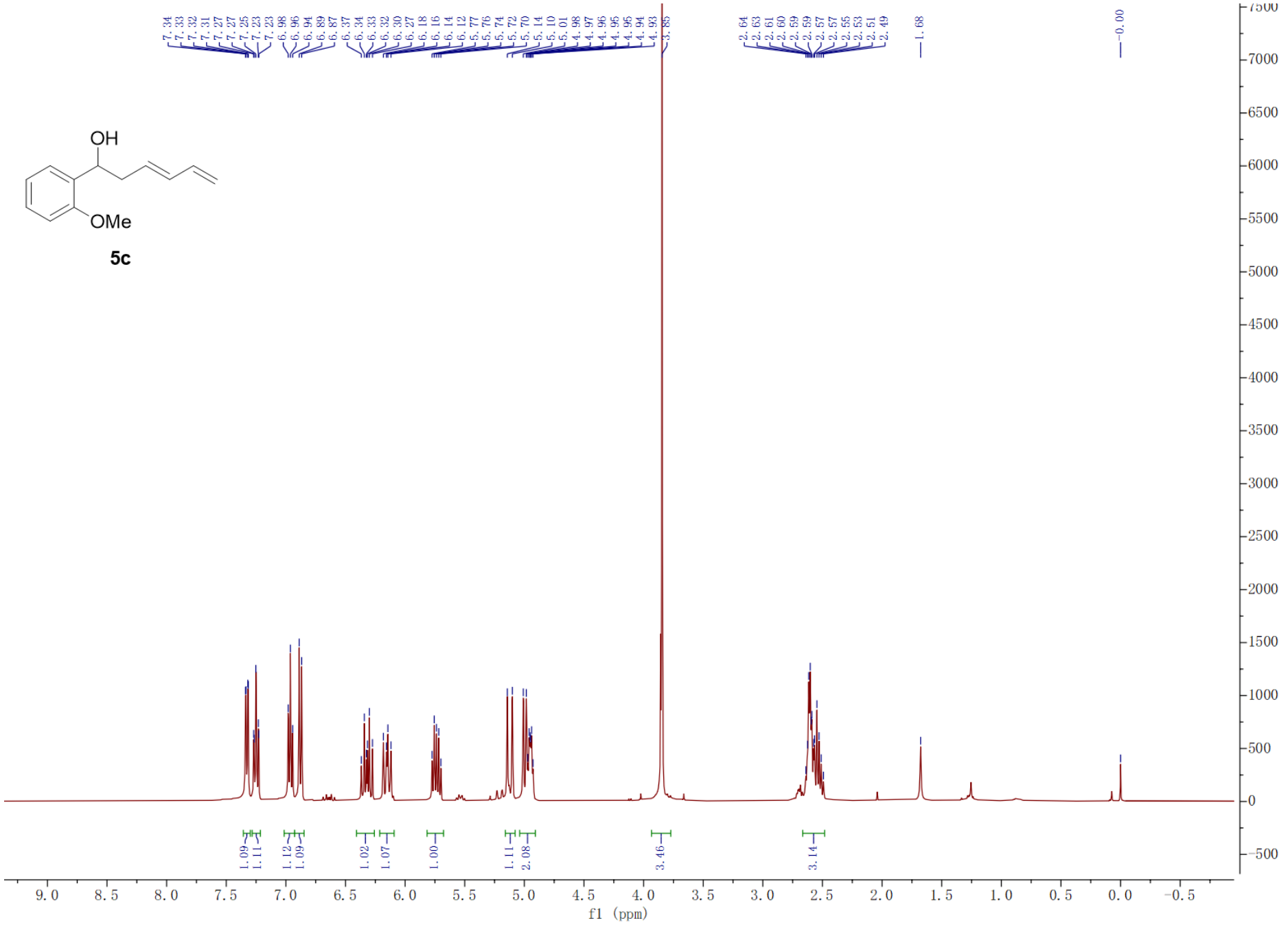
136.89
133.73
133.33
133.16
131.54
128.97
128.76
128.63
128.53
128.41
126.84
115.70
77.58
77.16
76.74
63.86
47.06
37.25
O
O
Ph
Ph
3aj
f1 (ppm)

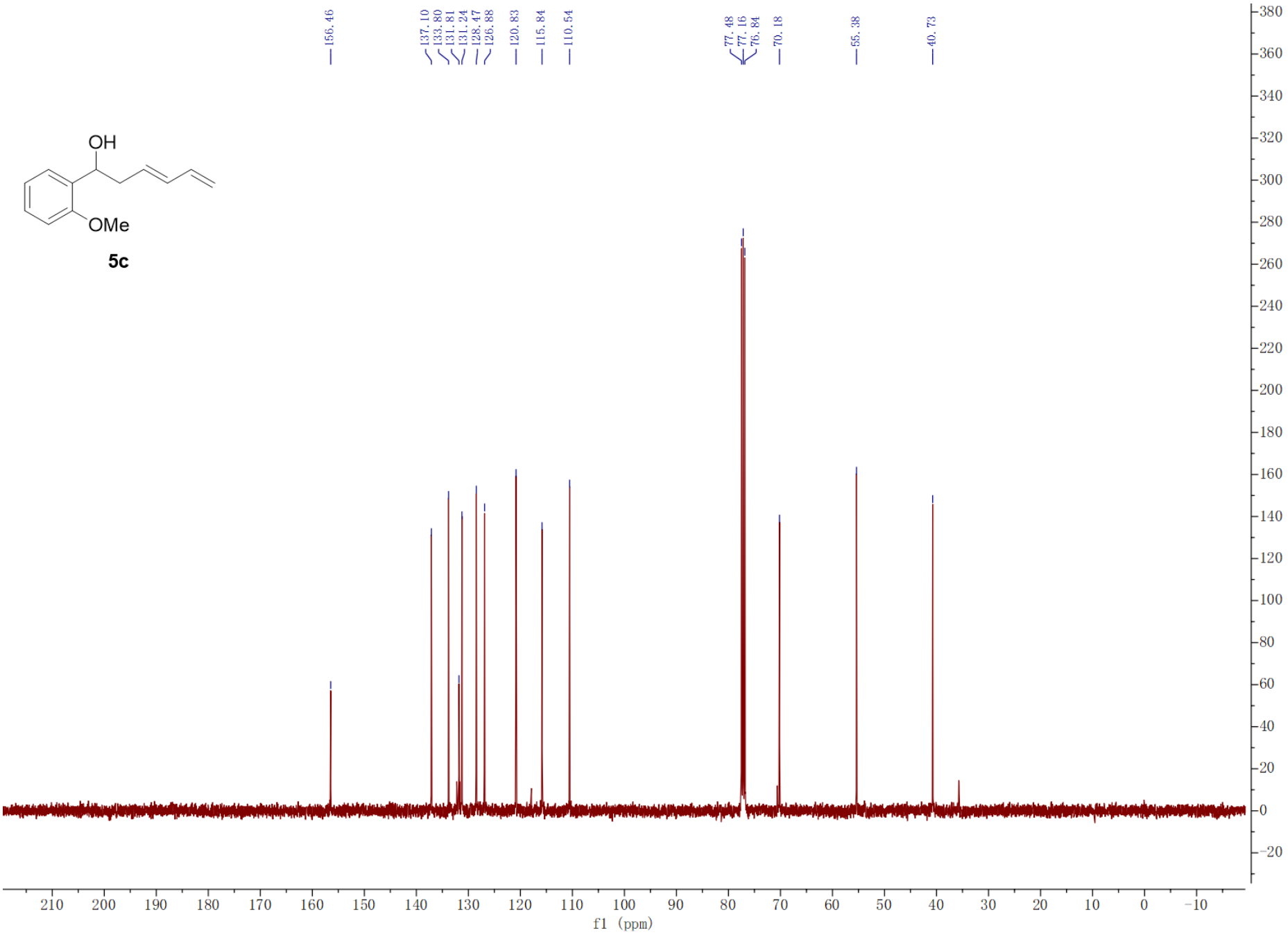

7.37
7.35
7.32
7.31
7.30
7.28
7.26
6.38
6.35
6.33
6.31
6.29
6.26
6.22
6.18
6.17
6.13
5.74
5.71
5.69
5.66
5.64
5.18
5.12
5.04
5.01
4.77
4.74
4.72
2.57
2.54
2.52
2.00
1.57
0.00
OH
5a
5.35
1.95
1.00
0.99
0.98
1.00
2.00
1.05
f1 (ppm)

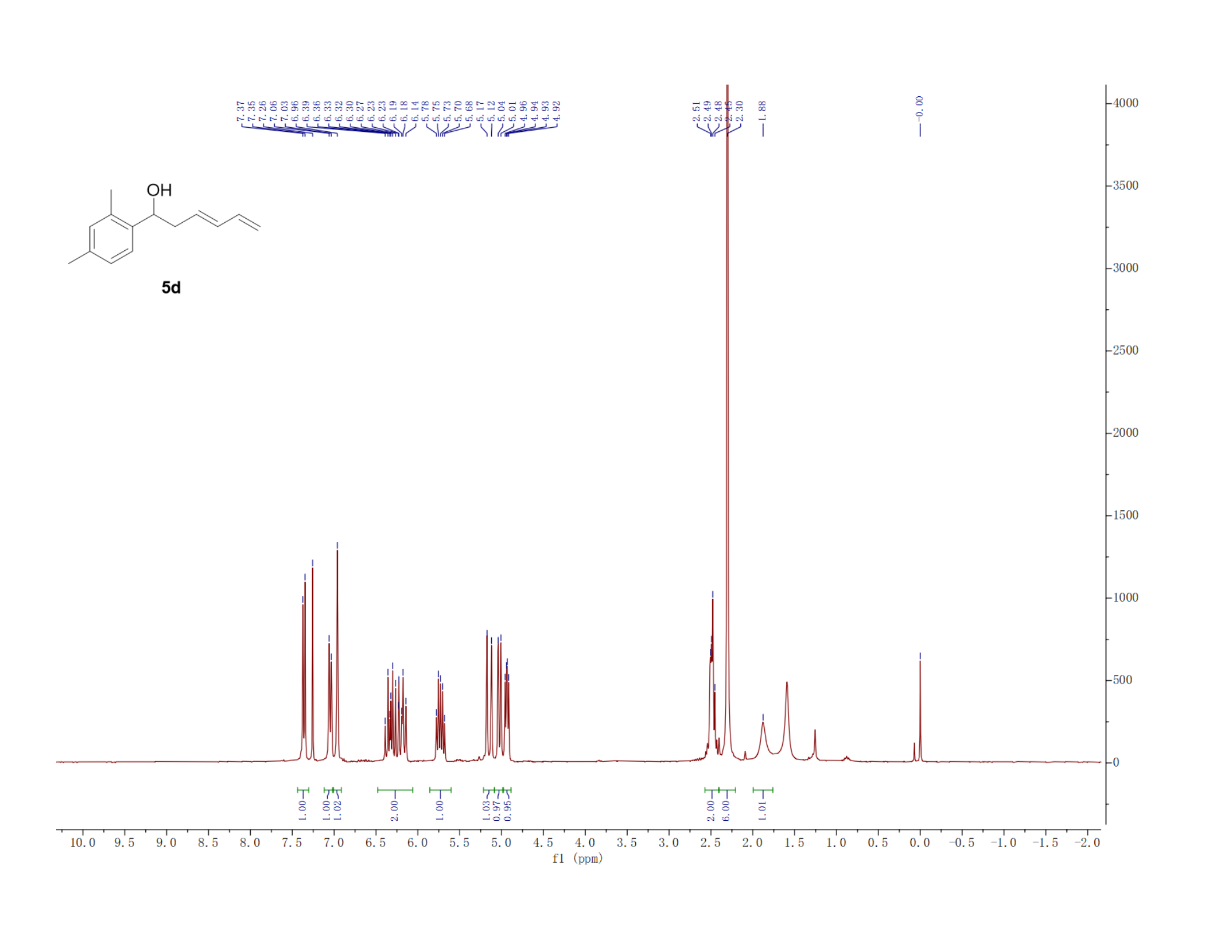

OH
5a
143.97
136.84
134.59
130.21
128.60
127.75
125.91
116.45
77.48
76.84
73.76
42.78
f1 (ppm)

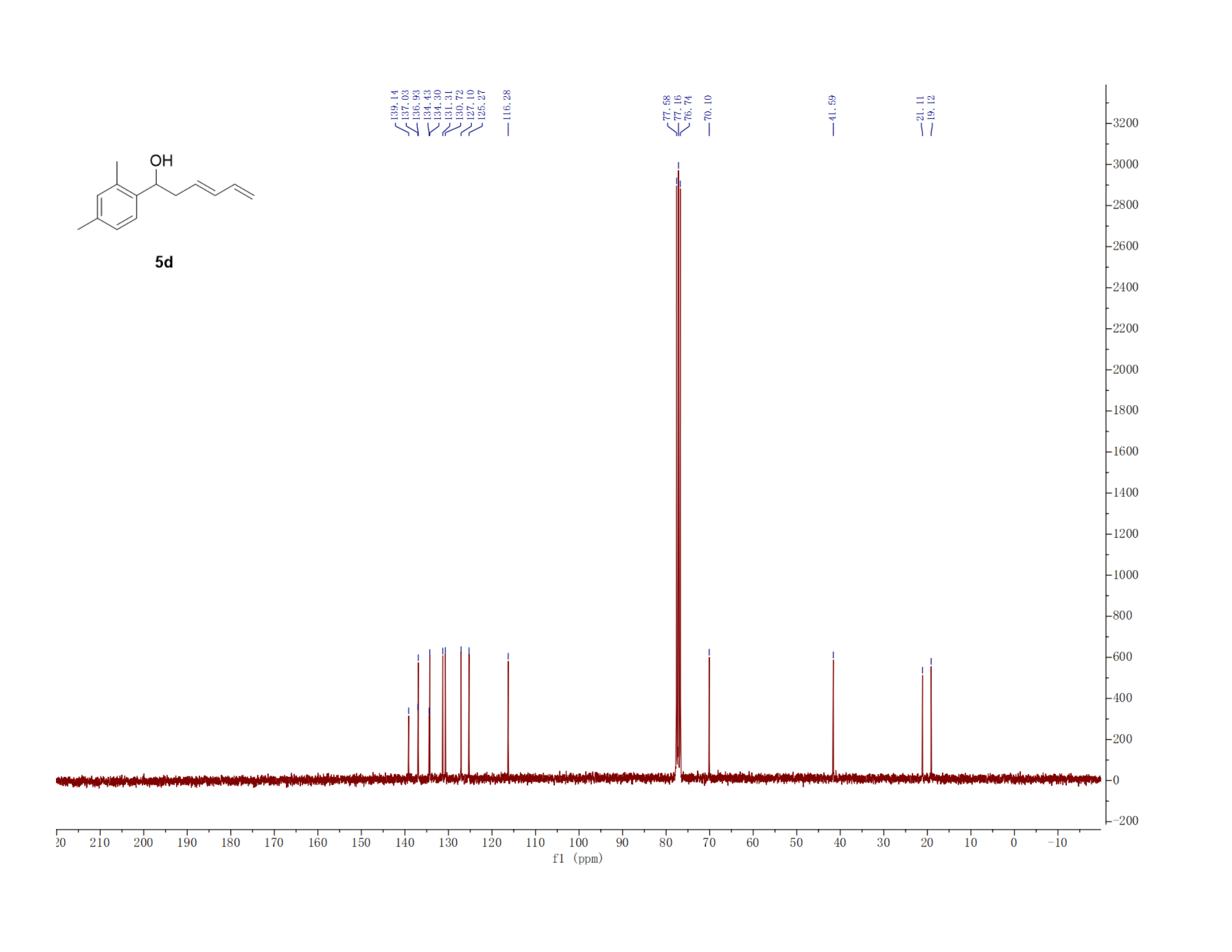

7.27
7.26
7.25
7.24
7.18
7.16
6.38
6.35
6.32
6.31
6.30
6.29
6.27
6.26
6.22
6.18
6.17
6.13
5.73
5.71
5.68
5.66
5.63
5.18
5.12
5.04
5.01
4.73
4.71
4.69
2.55
2.53
2.51
2.35
1.96
1.58
0.00
OH
Me
5b
4.39
2.00
1.01
1.00
0.95
1.00
1.91
3.01
0.99
f1 (ppm)

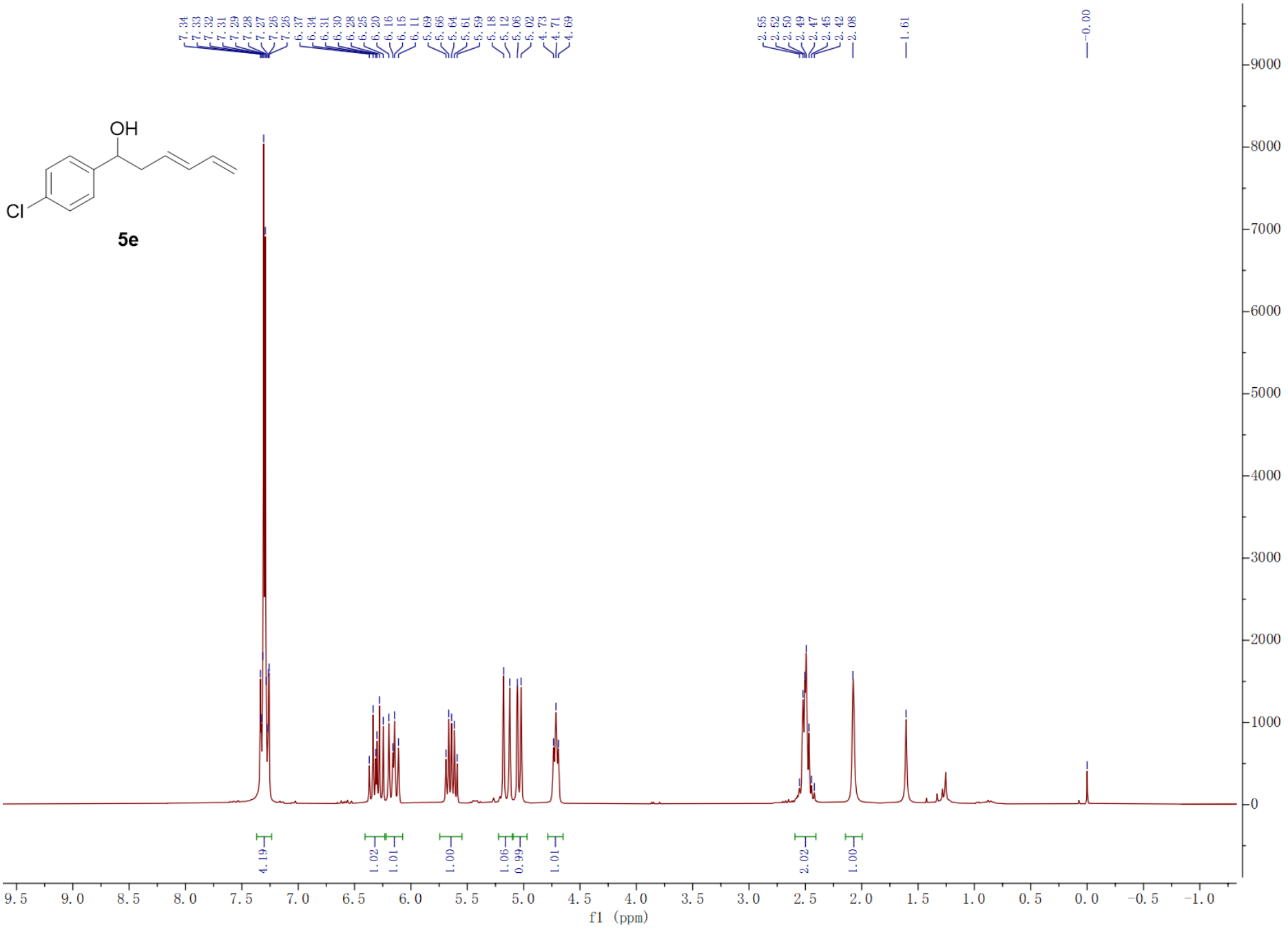

141.03
137.44
136.90
134.45
130.40
129.28
125.87
116.35
77.58
76.74
73.64
42.71
21.27
OH
Me
5b
f1 (ppm)


OH
OMe
5c
f1 (ppm)


156.46
137.10
133.80
131.81
131.24
128.47
126.88
120.83
115.84
110.54
77.48
77.16
76.84
70.18
55.38
40.73
OH
OMe
5c
f1 (ppm)


OH
5d
7.37
7.35
7.26
7.06
7.03
6.96
6.39
6.36
6.33
6.32
6.30
6.27
6.23
6.23
6.19
6.18
6.14
5.78
5.75
5.73
5.70
5.68
5.17
5.12
5.04
5.01
4.96
4.94
4.93
4.92
2.51
2.49
2.48
2.45
2.30
1.88
0.00
1.00
1.00
1.02
2.00
1.00
1.03
0.97
0.95
2.00
6.00
1.01
f1 (ppm)


OH
5d
139.14
137.03
136.93
134.43
134.30
131.31
130.72
127.10
125.27
116.28
77.58
77.16
76.74
70.10
41.59
21.11
19.12
f1 (ppm)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6.28
6.25
6.20
6.16
6.15
6.11
5.69
5.66
5.64
5.61
5.59
5.18
5.12
5.06
5.02
4.73
4.71
4.69
2.55
2.52
2.50
2.49
2.47
2.45
2.42
2.08
1.61
0.00
OH
Cl
5e
4.19
1.02
1.01
1.00
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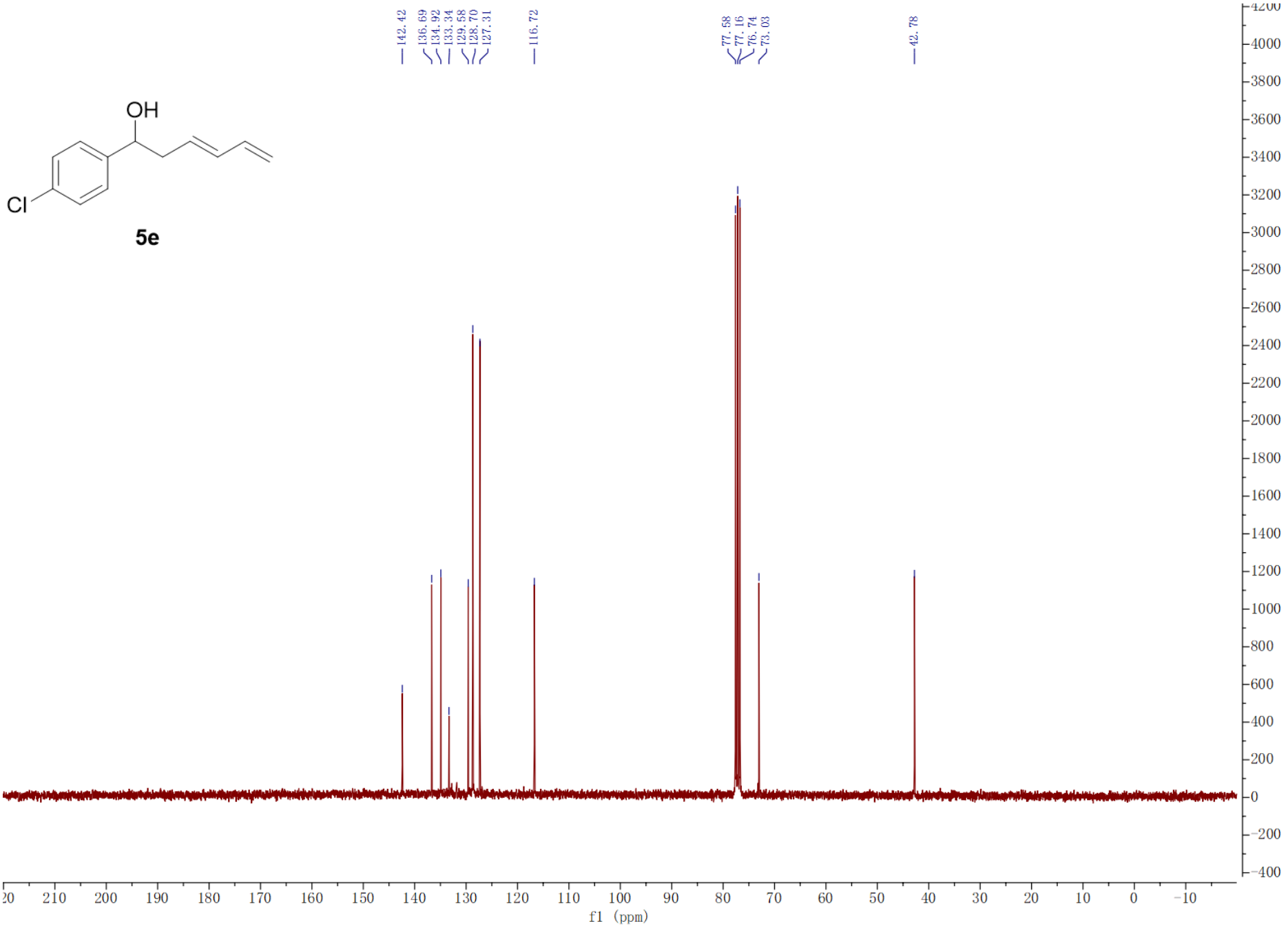
1.01
2.02
1.00
f1 (ppm)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76.74
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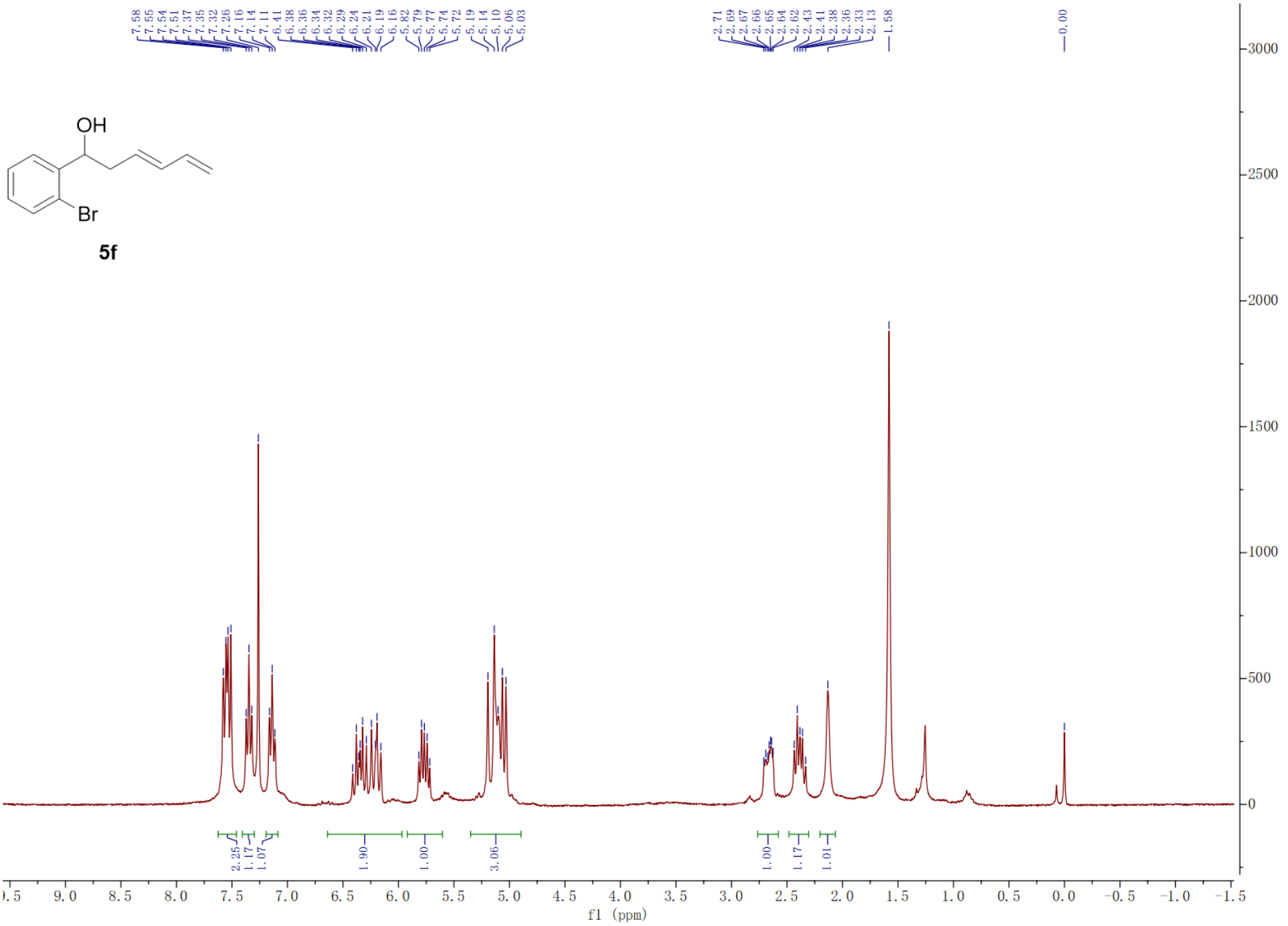
42.78
OH
Cl
5e
f1 (ppm)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7.14
7.11
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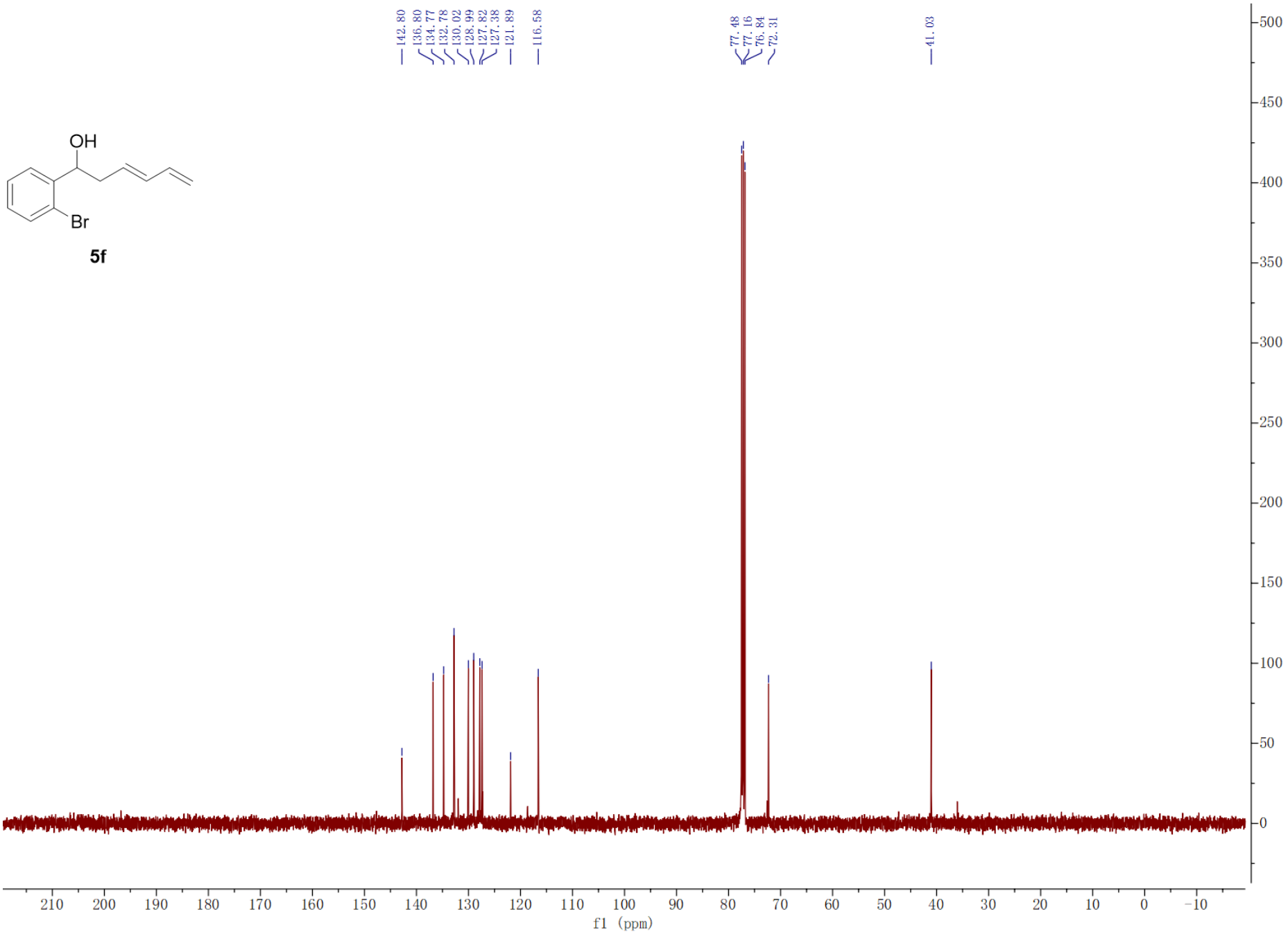
6.38
6.36
6.34
6.32
6.29
6.24
6.21
6.19
6.16
5.82
5.79
5.77
5.74
5.72
5.19
5.14
5.10
5.06
5.03
2.71
2.69
2.67
2.66
2.65
2.64
2.62
2.43
2.41
2.38
2.36
2.33
2.13
1.58
0.00
OH
Br
5f
3000
2500
2000
1500
1000
500
0
2.25
1.17
1.07
1.90
1.00
3.06
1.00
1.17
1.01
f1 (ppm)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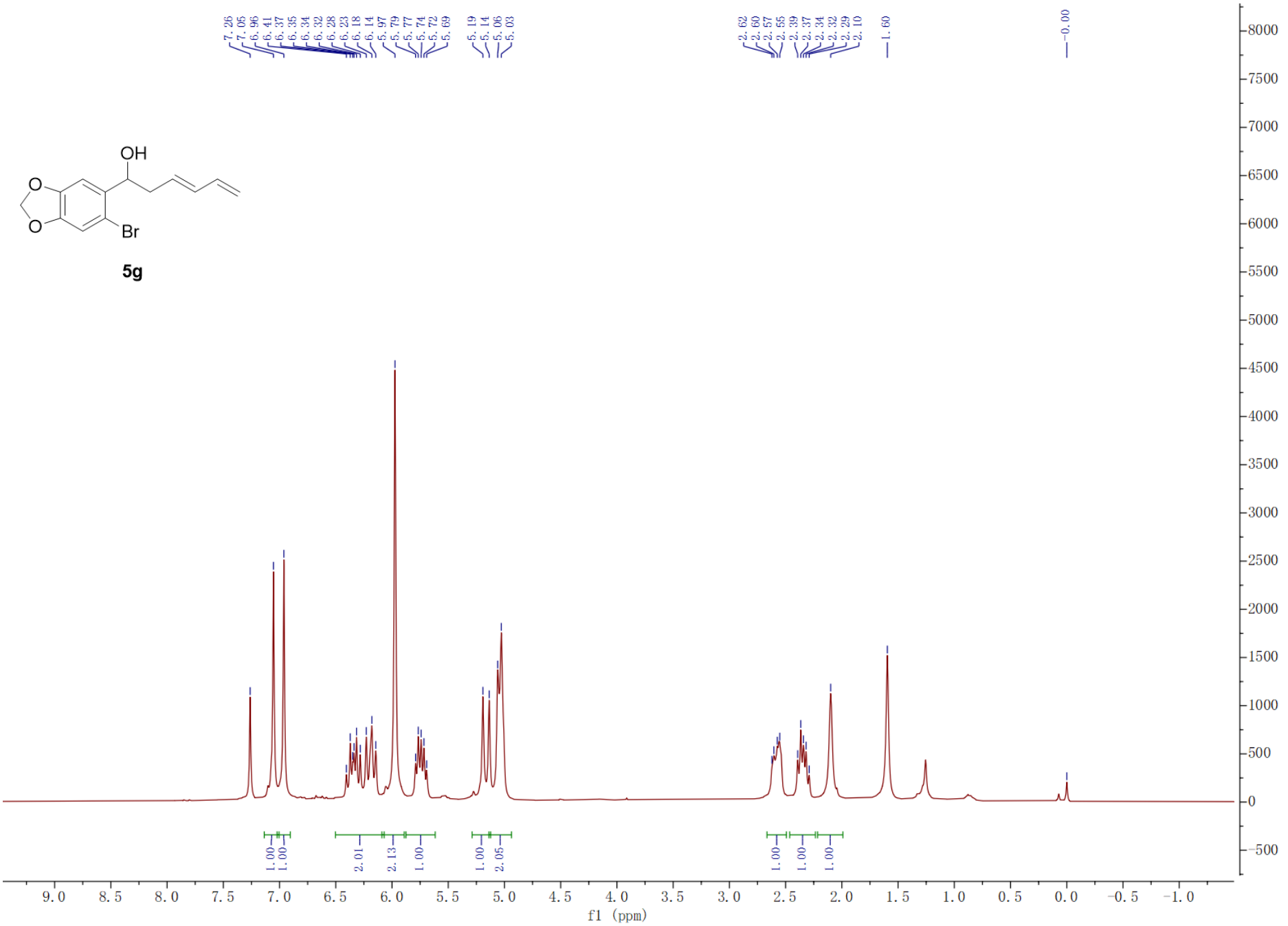
41.03
OH
Br
5f
f1 (ppm)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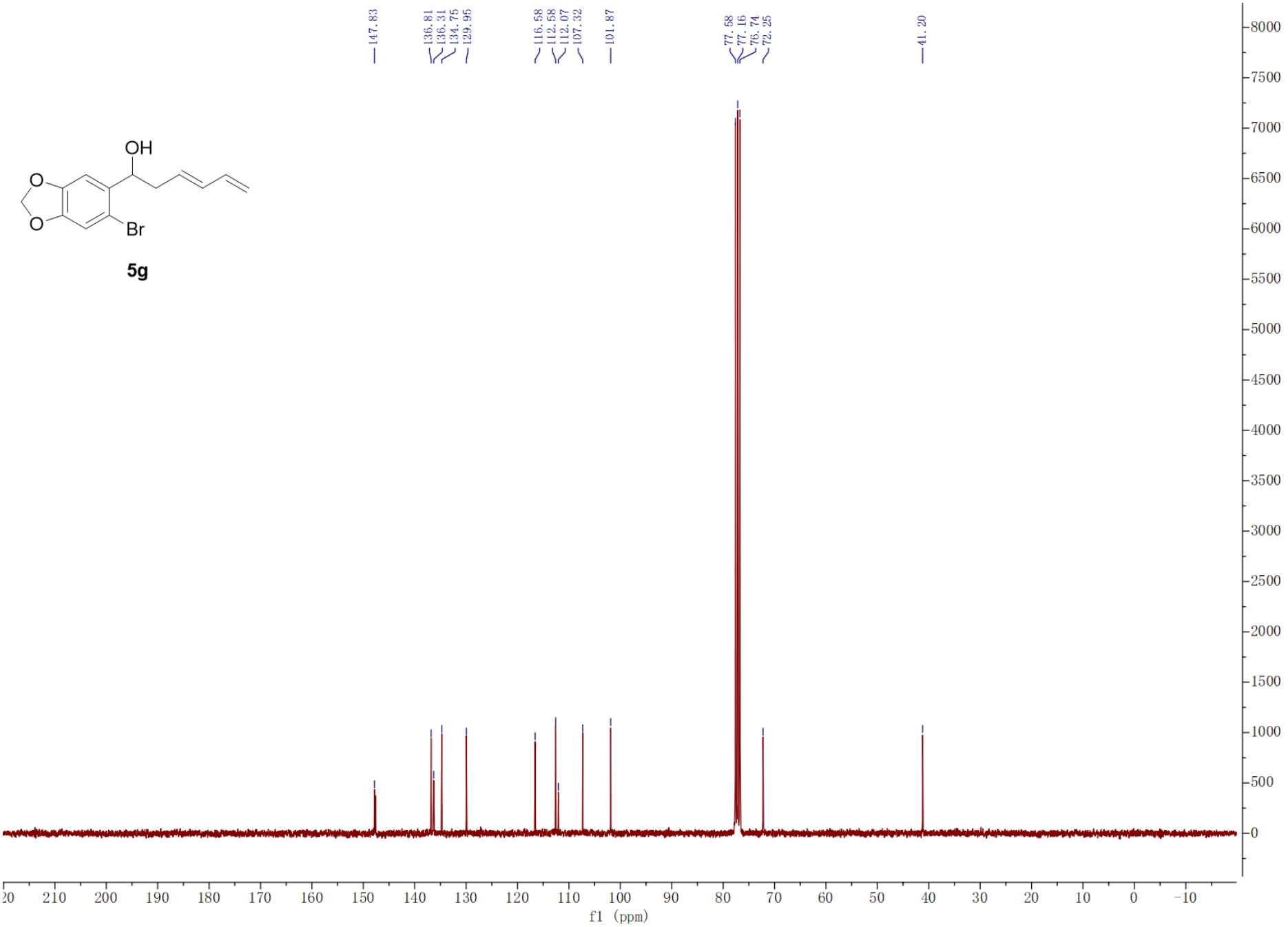
6.23
6.18
6.14
5.97
5.79
5.77
5.74
5.72
5.69
5.19
5.14
5.06
5.03
2.62
2.60
2.57
2.55
2.39
2.37
2.34
2.32
2.29
2.10
1.60
0.00
OH
O
O
Br
5g
1.00
1.00
2.01
2.13
1.00
1.00
2.05
1.00
1.00
1.00
f1 (ppm)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129.95
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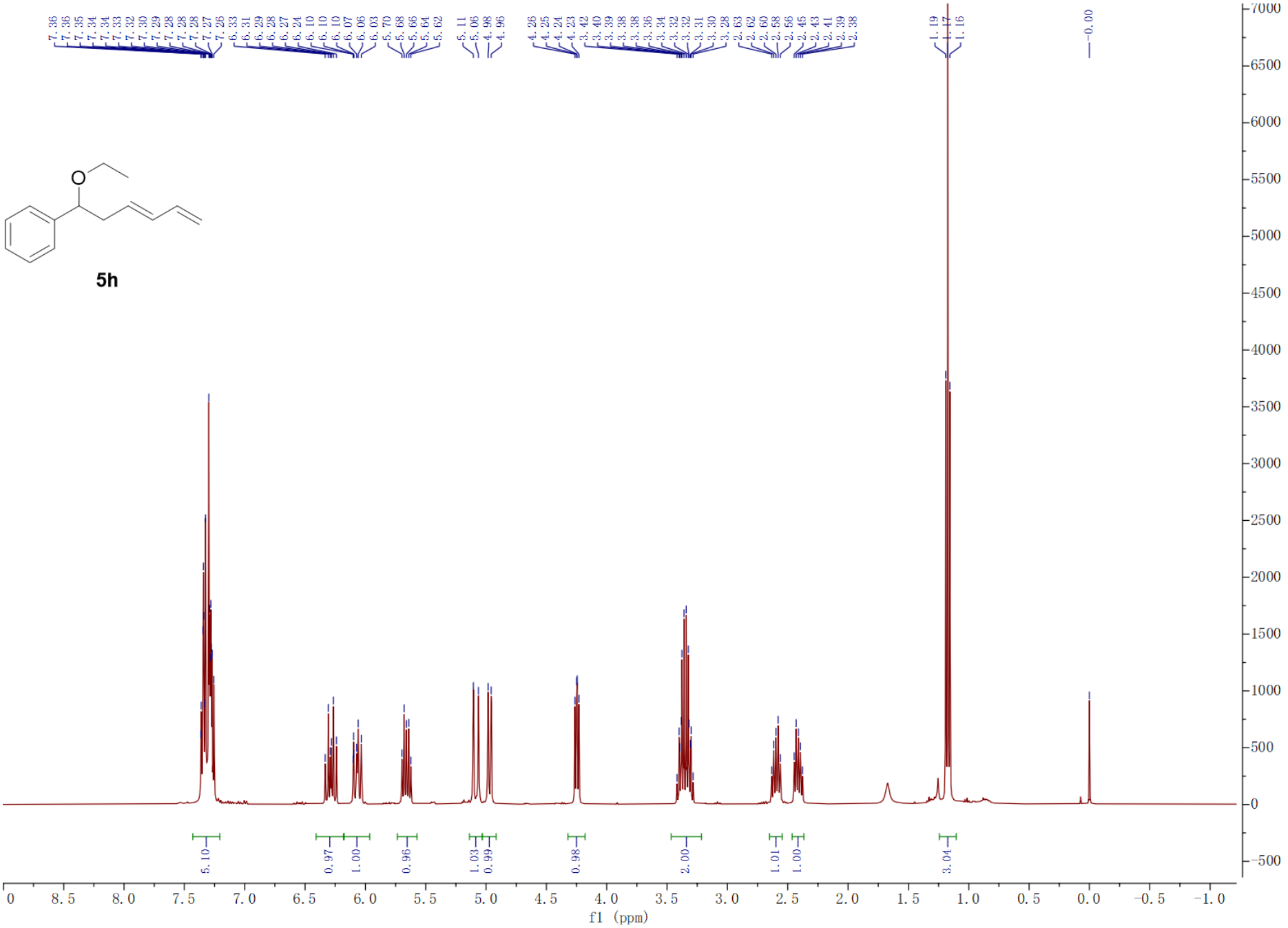
77.58
77.16
76.74
72.25
41.20
OH
O
O
Br
5g
f1 (ppm)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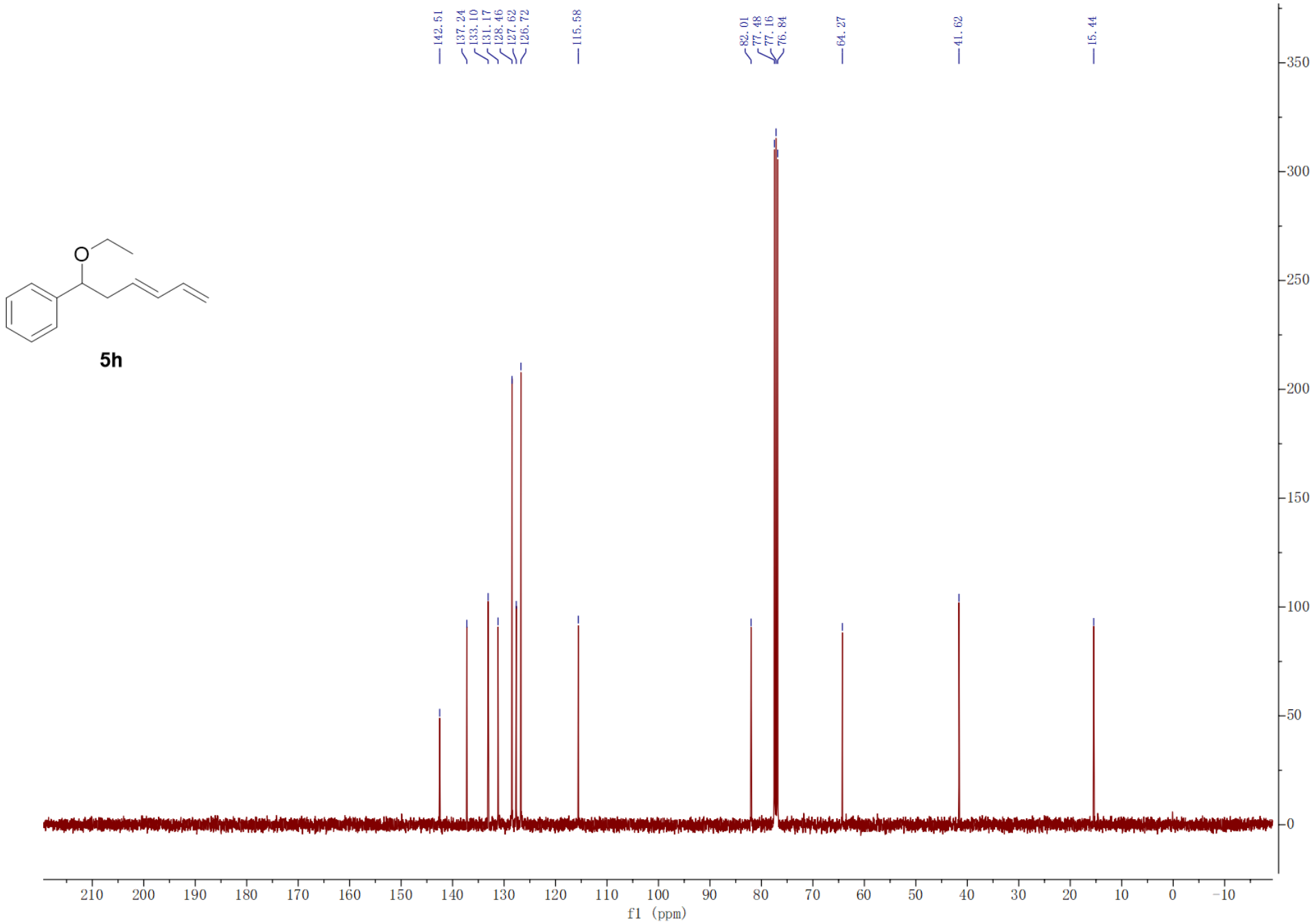
6.31
6.29
6.28
6.27
6.24
6.10
6.10
6.10
6.07
6.06
6.03
5.70
5.68
5.66
5.64
5.62
5.11
5.06
4.98
4.96
4.26
4.25
4.24
4.23
3.42
3.40
3.39
3.38
3.38
3.36
3.34
3.32
3.32
3.31
3.30
3.28
2.63
2.62
2.60
2.58
2.56
2.45
2.43
2.41
2.39
2.38
1.19
1.17
1.16
0.00
O
5h
5.10
0.97
1.00
0.96
1.03
0.99
0.98
2.00
1.01
1.00
3.04
f1 (ppm)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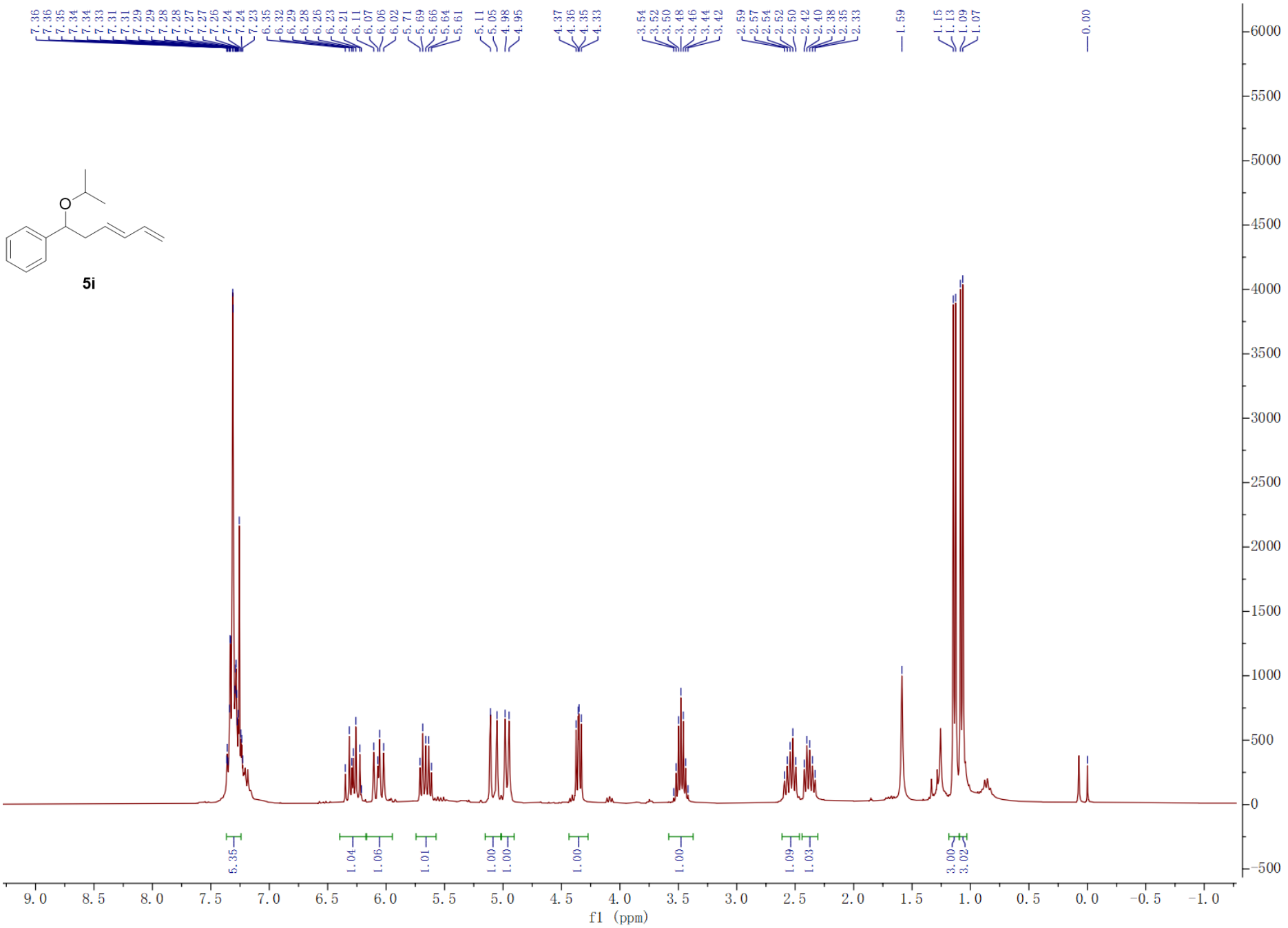
115.58
82.01
77.48
77.16
76.84
64.27
41.62
15.44
5h
f1 (ppm)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7.27
7.26
7.24
7.24
7.23
6.35
6.32
6.29
6.28
6.25
6.23
6.21
6.11
6.07
6.06
6.02
5.71
5.69
5.66
5.64
5.61
5.11
5.05
4.98
4.95
4.37
4.36
4.35
4.33
3.54
3.52
3.50
3.48
3.46
3.44
3.42
2.59
2.57
2.54
2.52
2.50
2.42
2.40
2.38
2.35
2.33
1.59
1.15
1.13
1.09
1.07
0.00
O
5i
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
5.35
1.04
1.06
1.01
1.00
1.00
1.00
1.00
1.09
1.03
3.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
1.5
1.0
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0.0
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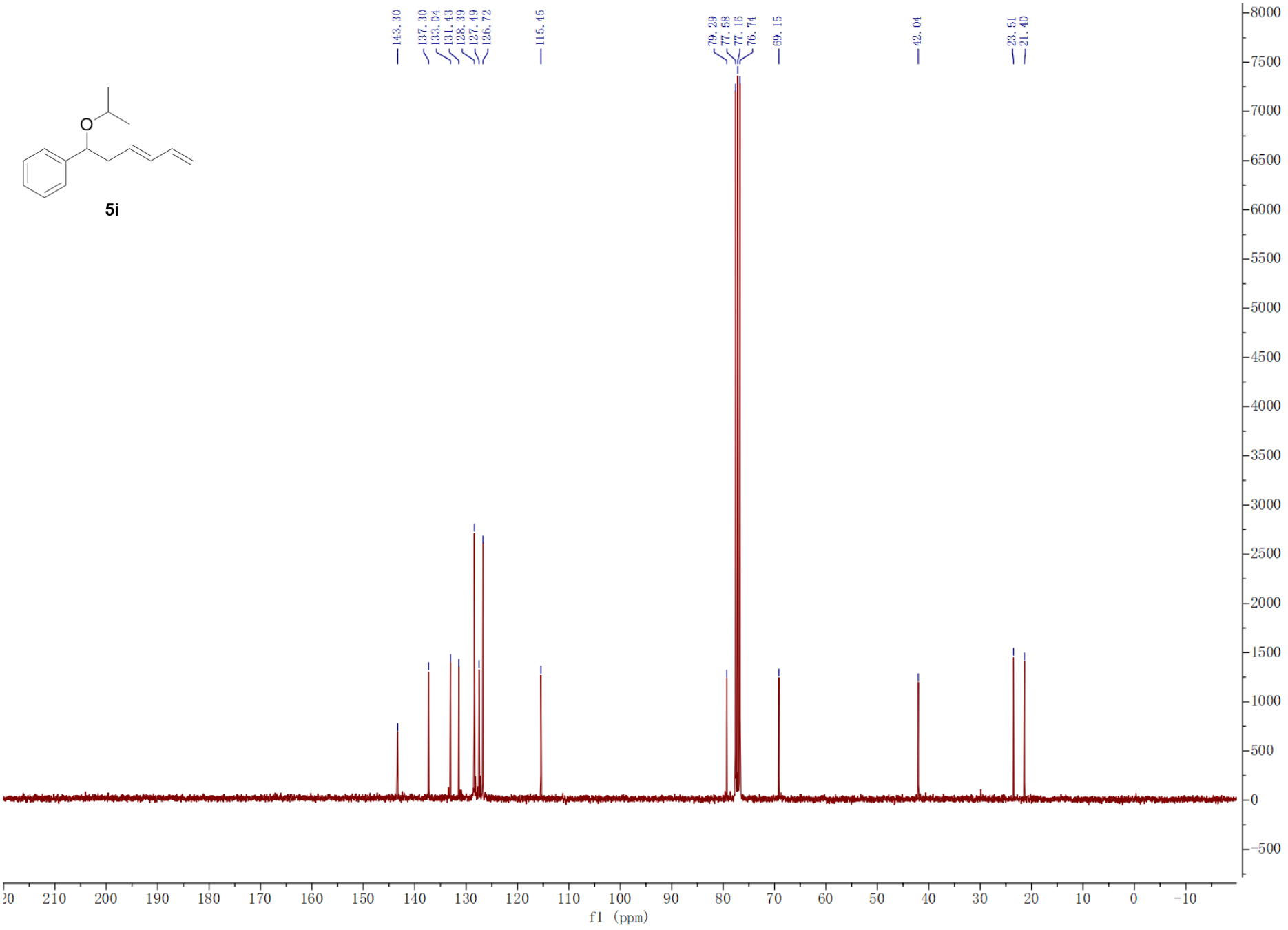
−1.0
f1 (ppm)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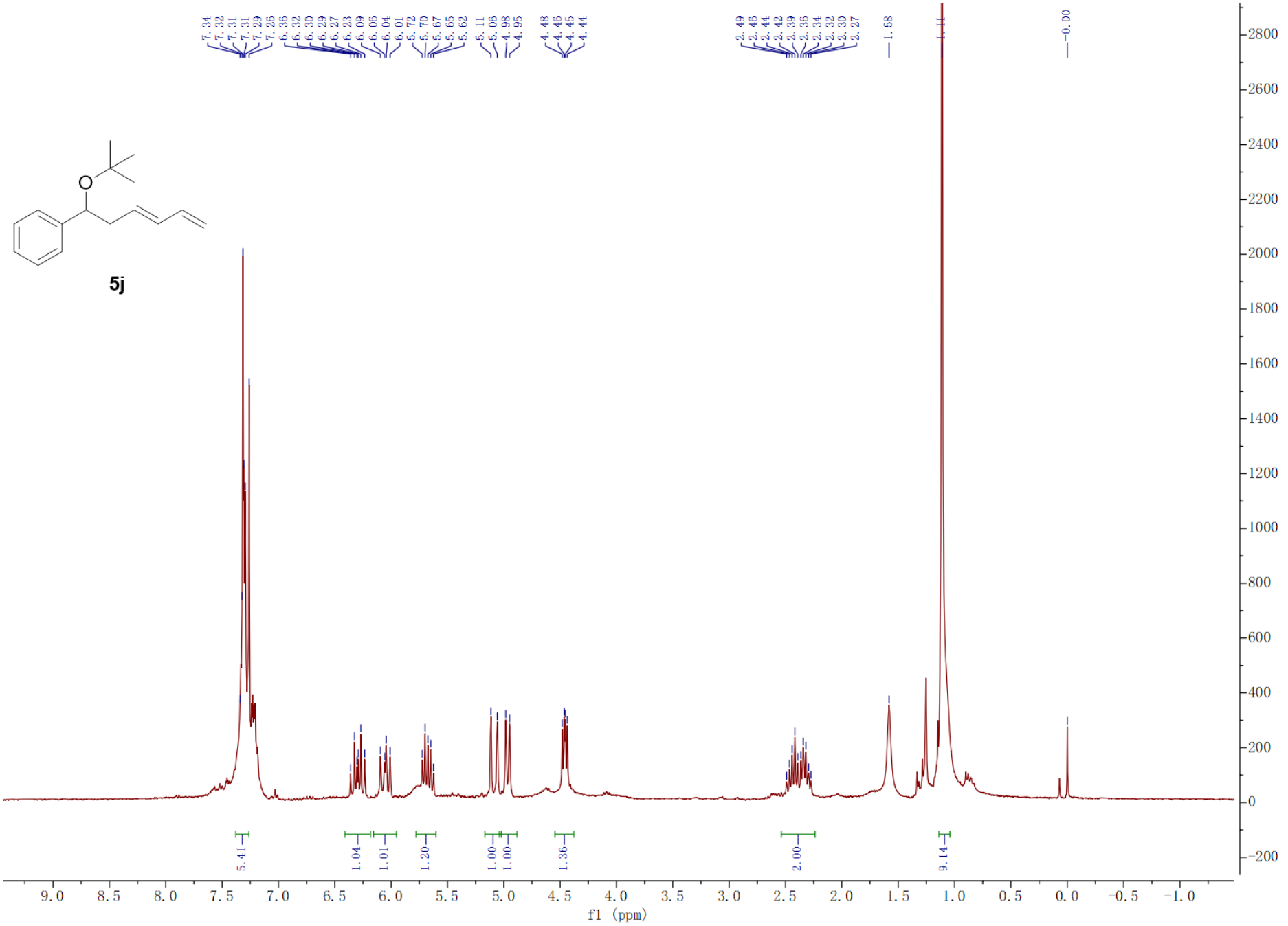
127.49
126.72
115.45
79.29
77.58
77.16
76.74
69.15
42.04
23.51
21.40
5i
f1 (ppm)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7.31
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7.26
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6.32
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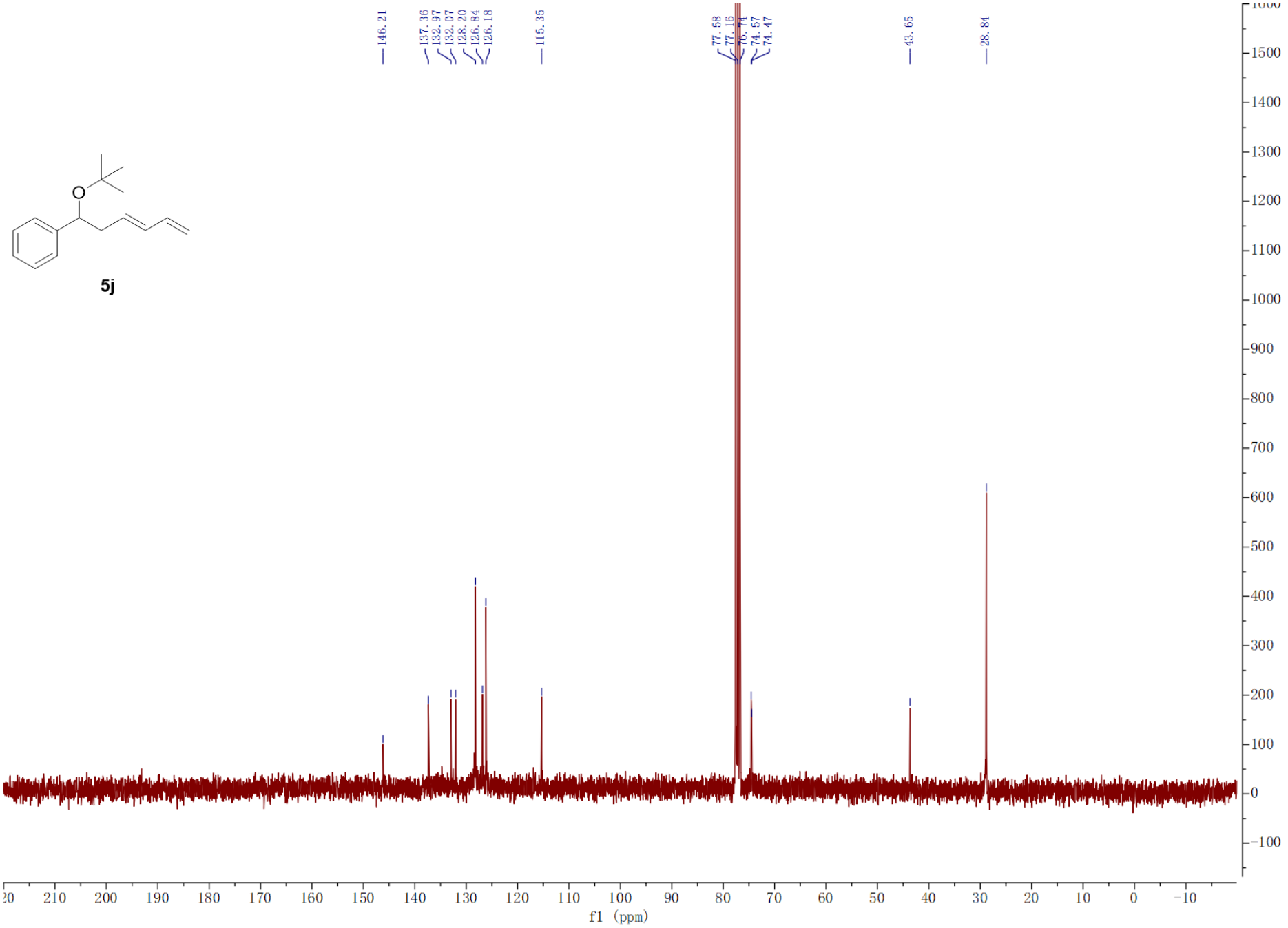
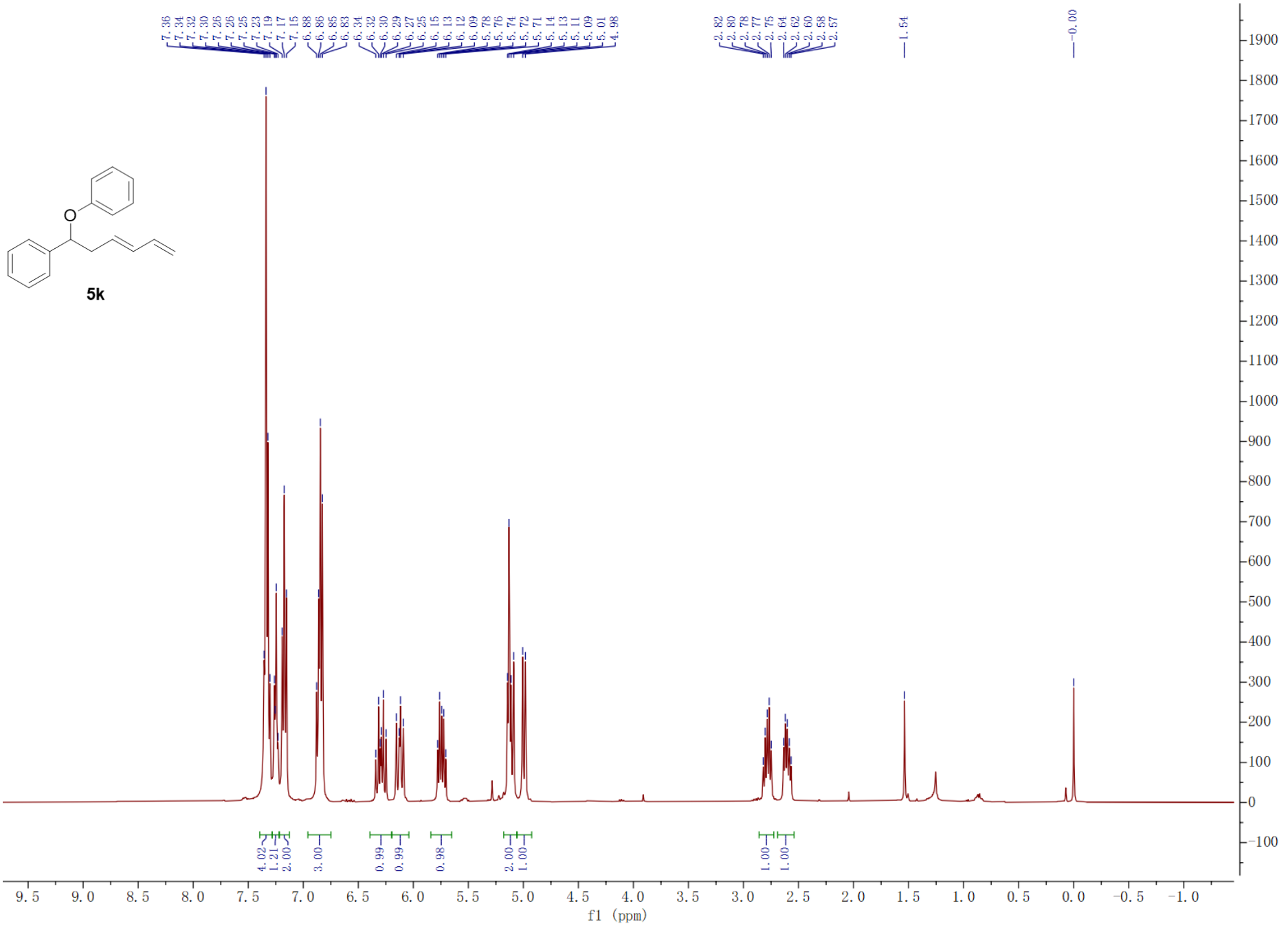
6.29
6.27
6.23
6.09
6.06
6.04
6.01
5.72
5.70
5.67
5.65
5.62
5.11
5.06
4.98
4.95
4.48
4.46
4.45
4.44
2.49
2.46
2.44
2.42
2.39
2.36
2.34
2.32
2.30
2.27
1.58
1.11
0.00
5.41
1.04
1.01
1.20
1.00
1.00
1.36
2.00
9.14
f1 (ppm)

5j


146.21
137.36
132.97
132.07
128.20
126.84
126.18
115.35
77.58
77.16
76.74
74.57
74.47
43.65
28.84
f1 (ppm)

5j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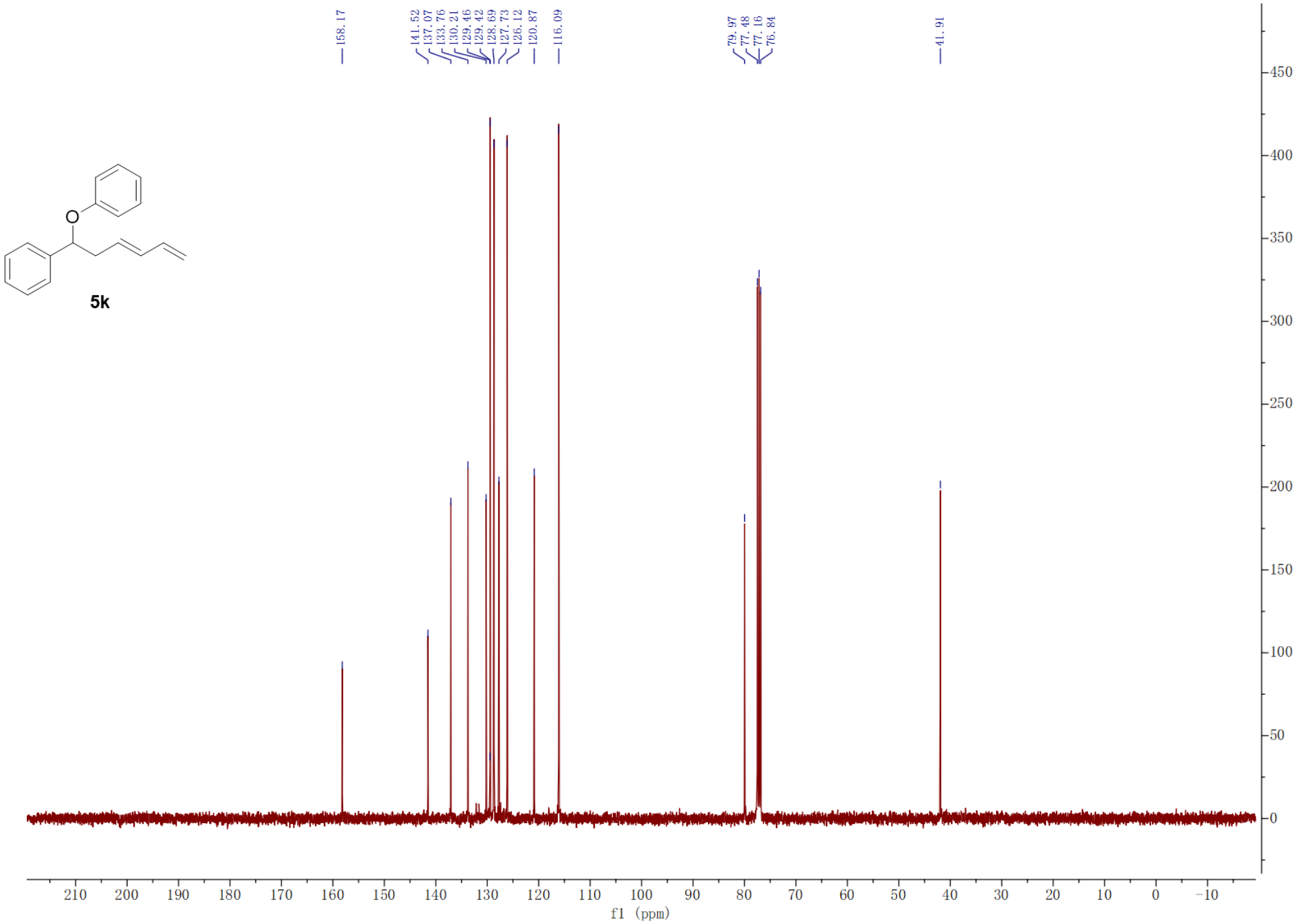
7.26
7.25
7.23
7.19
7.17
7.15
6.88
6.86
6.85
6.83
6.34
6.32
6.30
6.29
6.27
6.25
6.15
6.13
6.12
6.09
5.78
5.76
5.74
5.72
5.71
5.14
5.13
5.11
5.09
5.01
4.98
2.82
2.80
2.78
2.77
2.75
2.64
2.62
2.60
2.58
2.57
1.54
-0.00
O
5k
4.02
1.21
2.00
3.00
0.99
0.99
0.98
2.00
1.00
1.00
1.00
f1 (ppm)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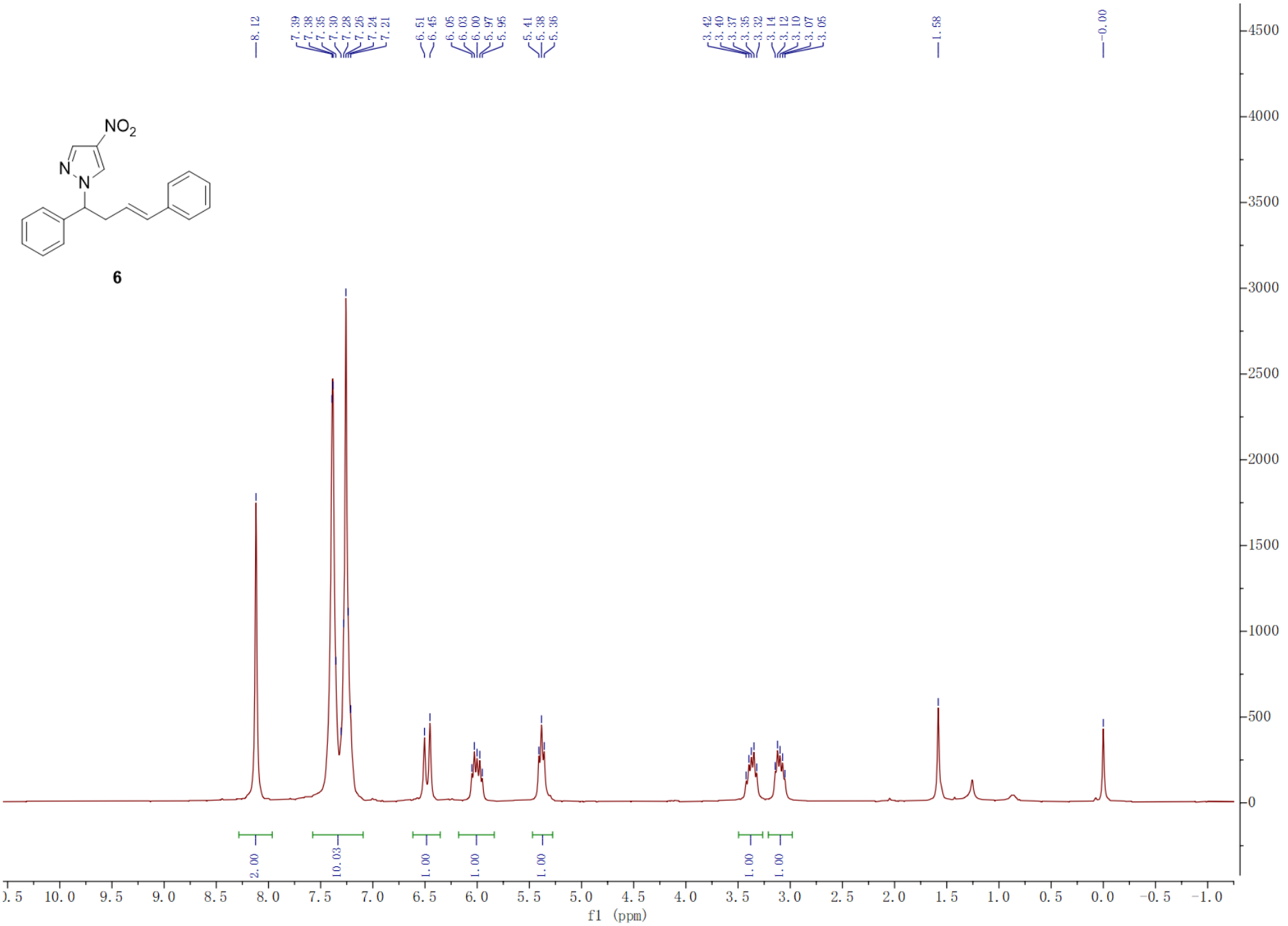
129.46
129.42
128.69
127.73
126.12
120.87
116.09
79.97
77.48
77.16
76.84
41.91
O
5k
450
400
350
300
250
200
150
100
50
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.24
7.21
6.51
6.45
6.05
6.03
6.00
5.97
5.95
5.41
5.38
5.36
3.42
3.40
3.37
3.35
3.32
3.14
3.12
3.10
3.07
3.05
1.58
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N
6
2.00
10.03
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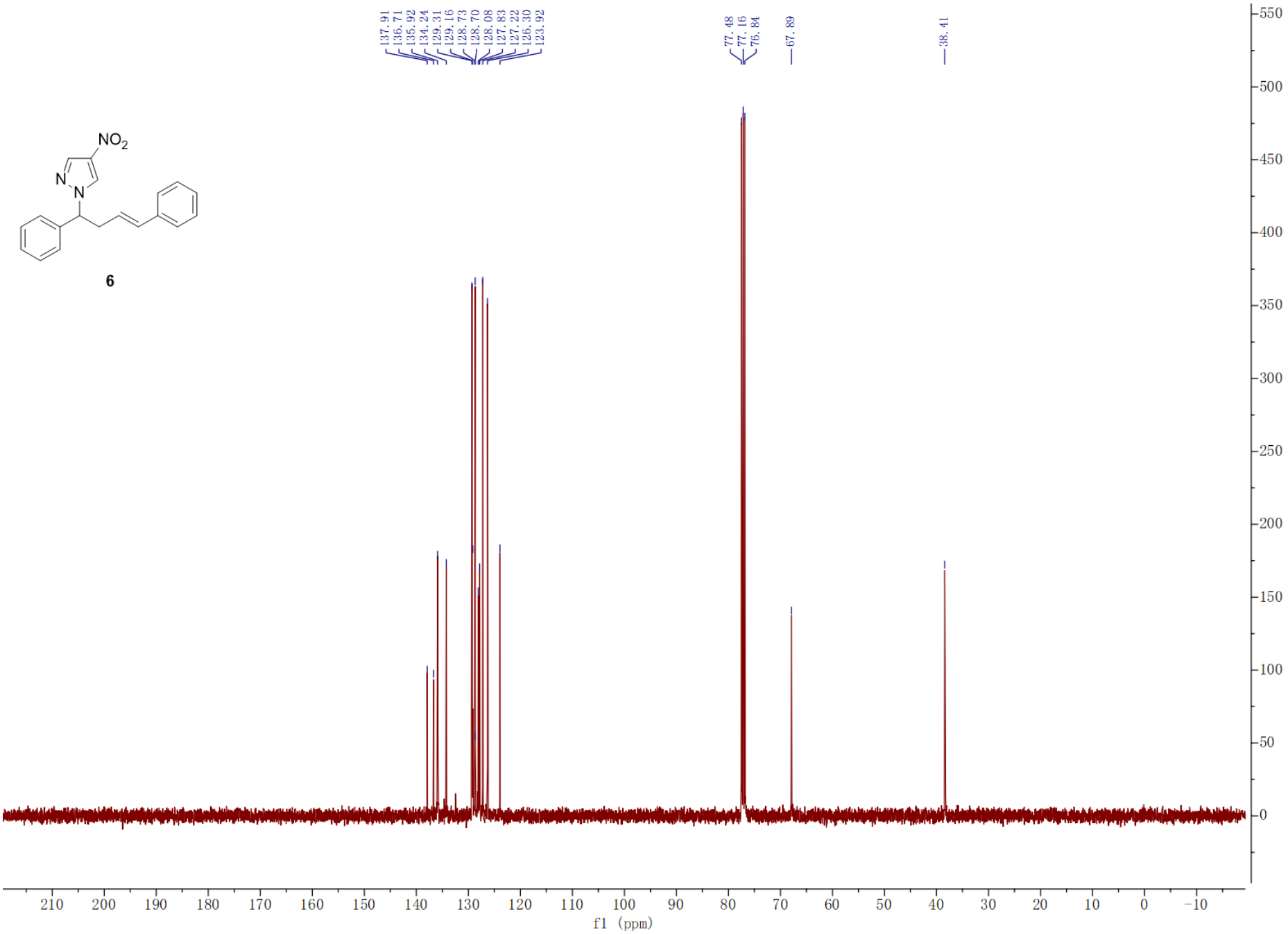
1.00
1.00
1.00
1.00
f1 (ppm)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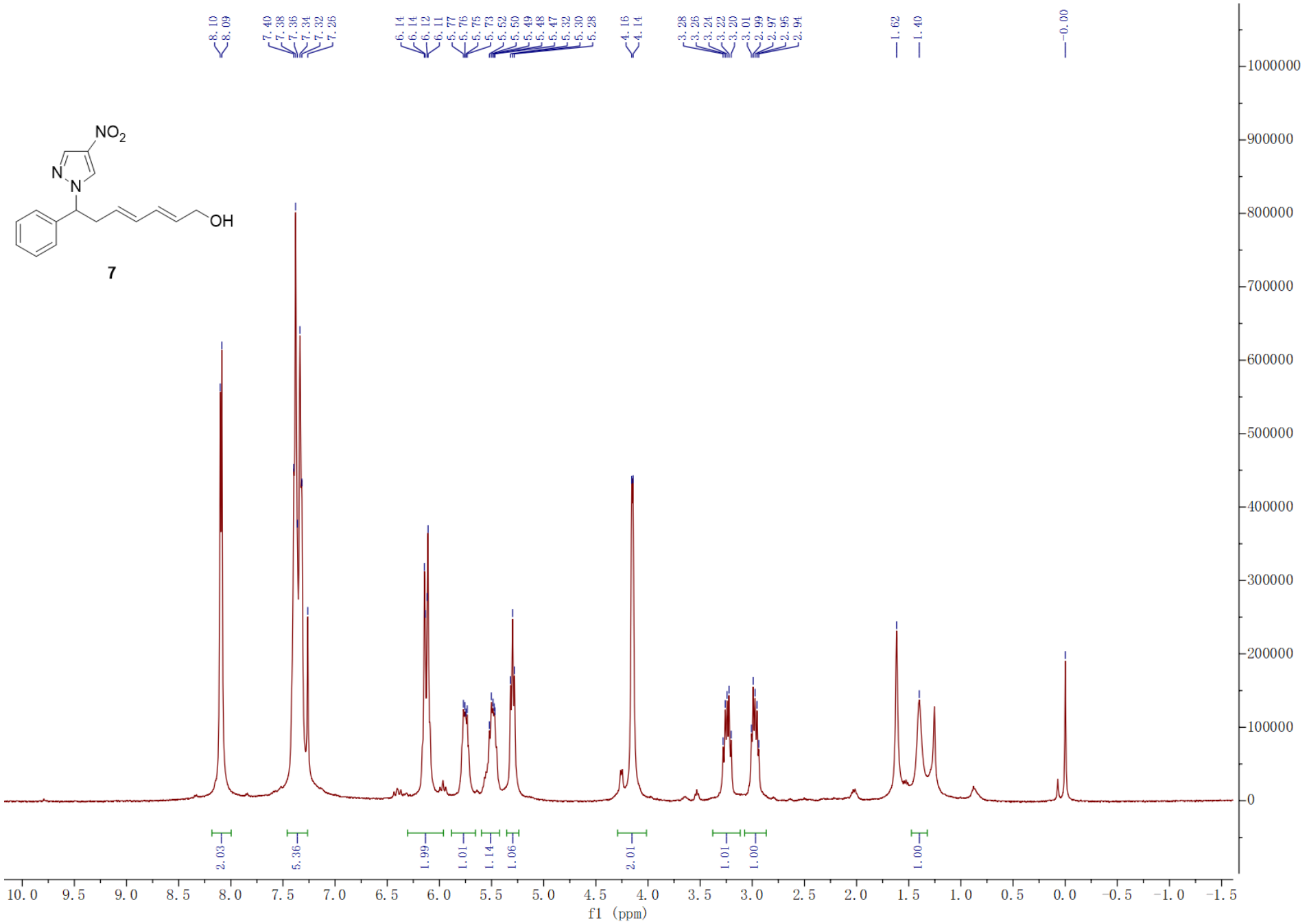
128.70
128.08
127.83
127.22
126.30
123.92
77.48
77.16
76.84
67.89
38.41
NO2
N
N
6
550
500
450
400
350
300
250
200
150
100
50
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.34
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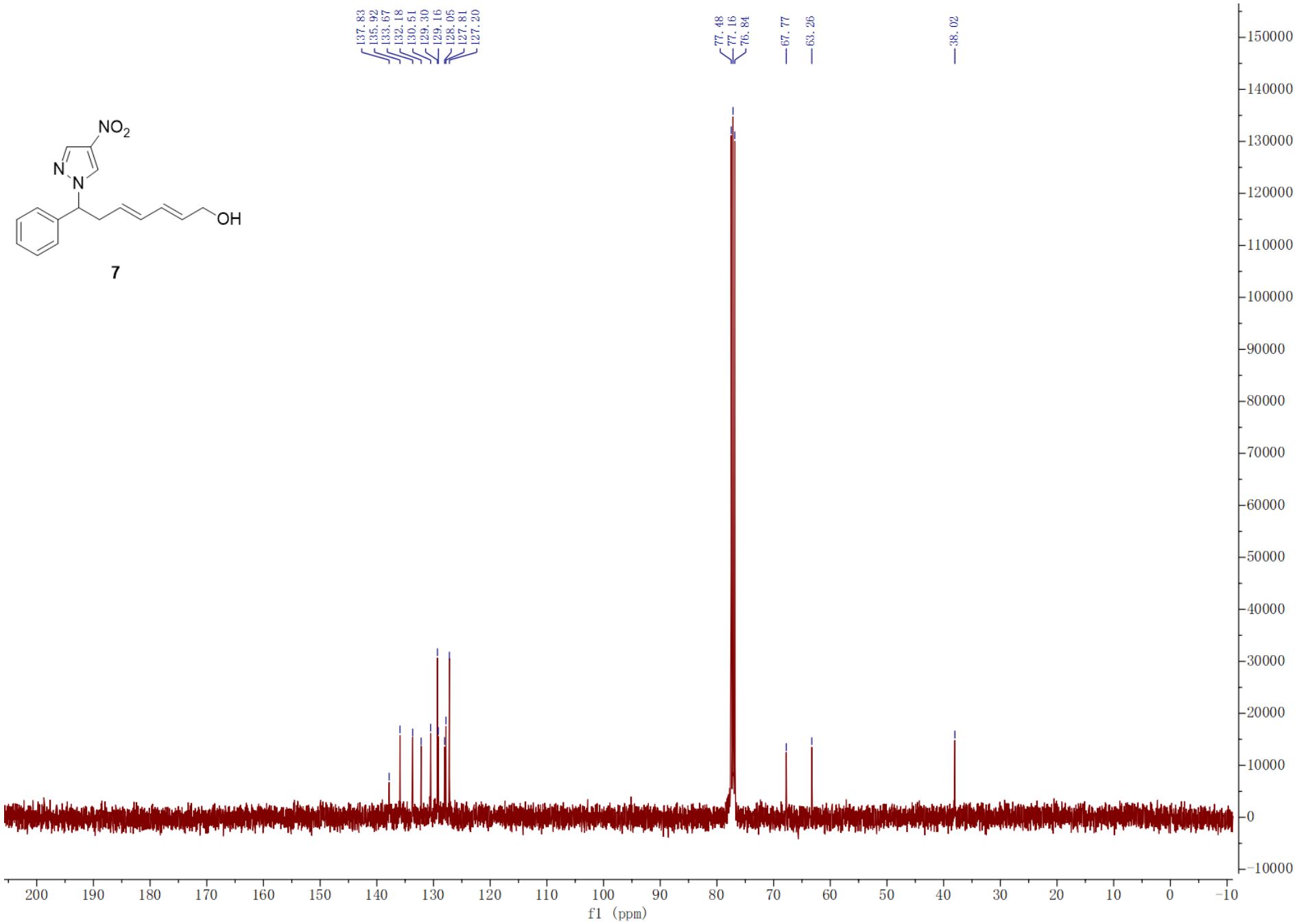
7.26
6.14
6.14
6.12
6.11
5.77
5.76
5.75
5.73
5.52
5.50
5.49
5.48
5.47
5.32
5.30
5.28
4.16
4.14
3.28
3.26
3.24
3.22
3.20
3.01
2.99
2.97
2.95
2.94
1.62
1.40
0.00
NO2
N
N
OH
7
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
2.03
5.36
1.99
1.01
1.14
1.06
2.01
1.01
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)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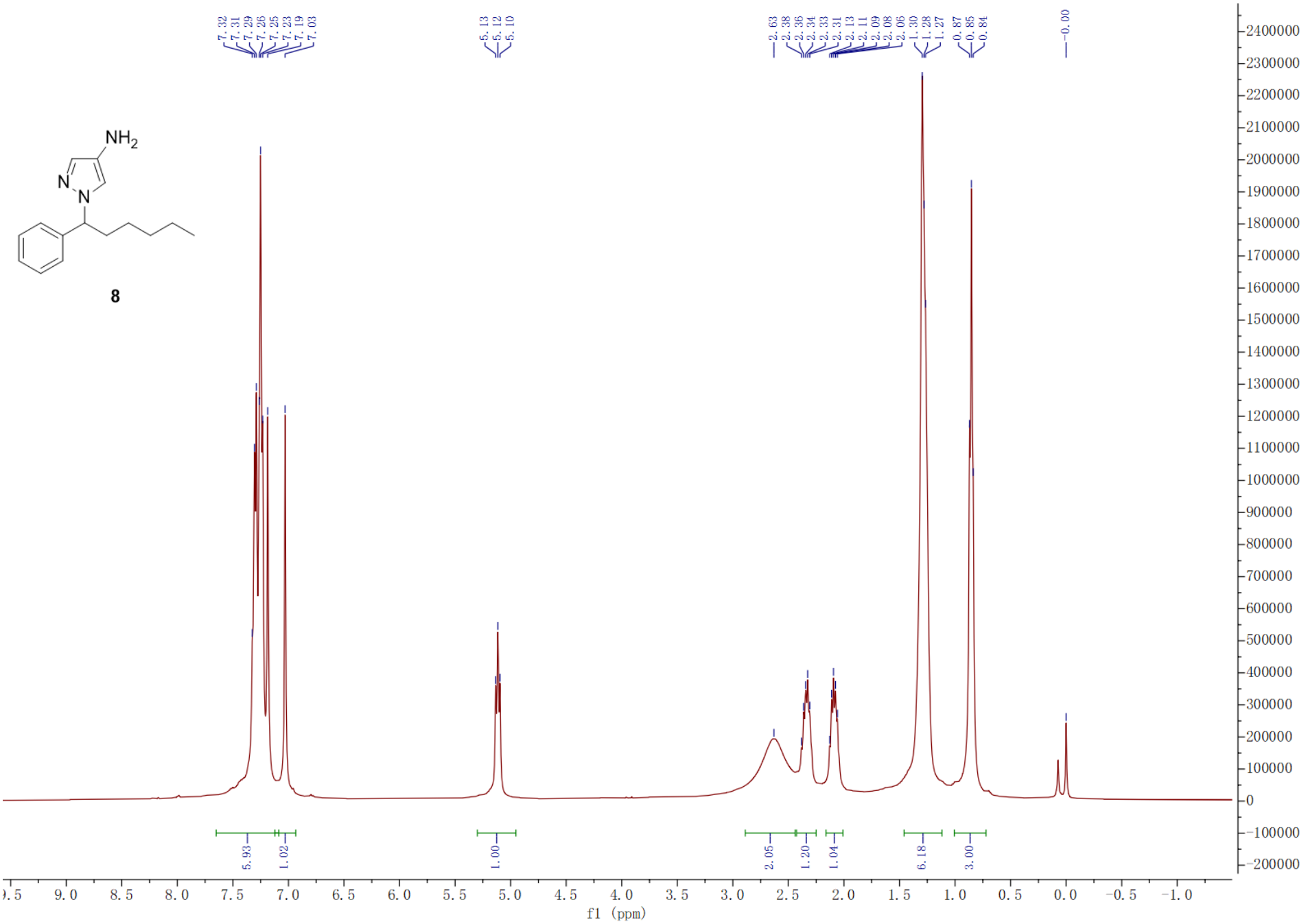
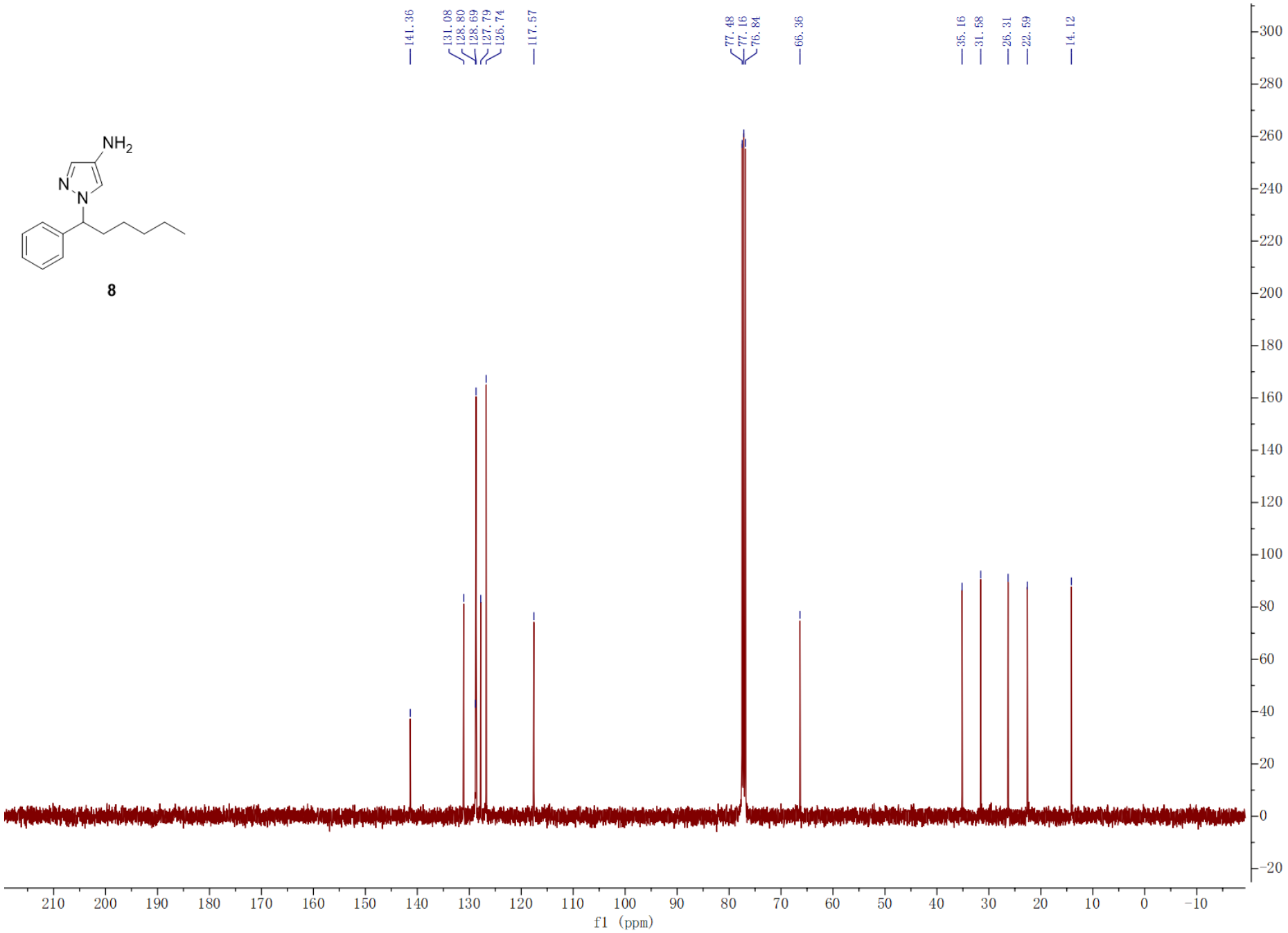
129.16
128.05
127.81
127.20
77.48
77.16
76.84
67.77
63.26
38.02
NO2
N
N
OH
7
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.32
7.31
7.29
7.26
7.25
7.23
7.19
7.03
5.13
5.12
5.10
2.63
2.38
2.36
2.34
2.33
2.31
2.13
2.11
2.09
2.08
2.06
1.30
1.28
1.27
0.87
0.85
0.84
-0.00
NH2
N
N
8
5.93
1.02
1.00
2.05
1.20
1.04
6.18
3.00
f1 (ppm)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127.79
126.74
117.57
77.48
77.16
76.84
66.36
35.16
31.58
26.31
22.59
14.12
NH2
N
N
8
f1 (ppm)