

Flow Chemistry-Assisted Visible Light-Induced Radical Addition of β -Amino Iodides with Enones en Route to Efficient Construction of *cis*-2,6-Piperidines

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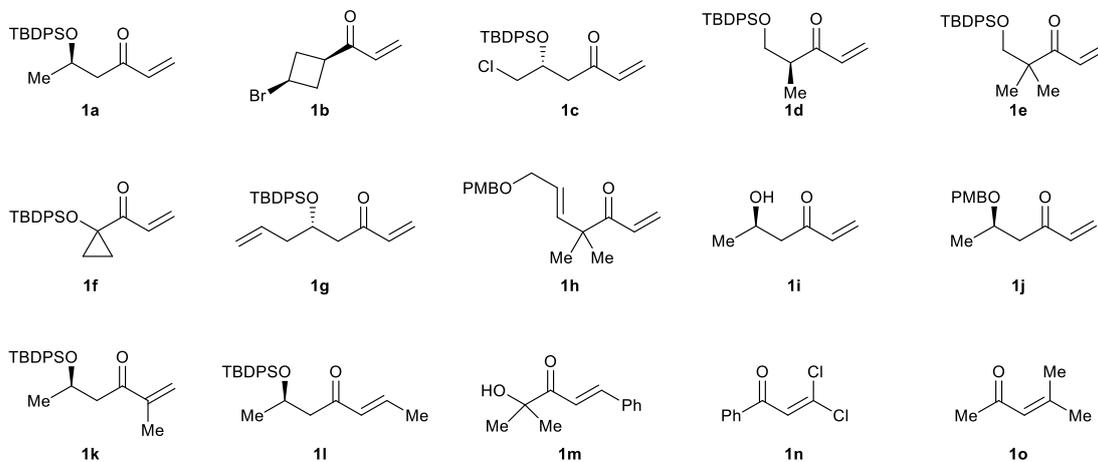
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1. General Information

General Information: All commercially available reagents were used without further purification. Reagents were purchased as commercial products from suppliers such as J&K, Aldrich, Acros, Alfa Aesar, TCI, or Energy Chemicals. Solvents used in reactions were distilled over appropriate drying agents prior to use. Solvents for extraction and purification were also distilled before use. Reactions requiring inert atmosphere and moisture control were carried out under a nitrogen atmosphere using oven-dried glassware. Thin-layer chromatography (TLC) was performed using TLC silica gel 60 F254. Compounds were visualized under ultraviolet light ($\lambda = 254$ nm) or by staining with KMnO_4 solution followed by heating. Products were purified by flash chromatography on silica gel (200 - 300 mesh). Nuclear magnetic resonance (NMR) spectra were recorded under the following conditions: ^1H NMR spectra were recorded at 400 MHz (Varian) and 600 MHz (Agilent), and ^{13}C NMR spectra were recorded at 101 MHz (Varian) and 150 MHz (Agilent), using CDCl_3 as the solvent (unless otherwise specified), with tetramethylsilane (TMS) or residual solvent as the internal standard. Infrared (IR) spectra were obtained using a PerkinElmer Spectrum Two FTIR spectrometer. High-resolution mass spectrometry (HRMS) analyses were performed on a Waters Q-TOF. Enantiomeric excess was determined by high-performance liquid chromatography (HPLC, Agilent Technologies: 1260 Infinity II) on a chiral column.

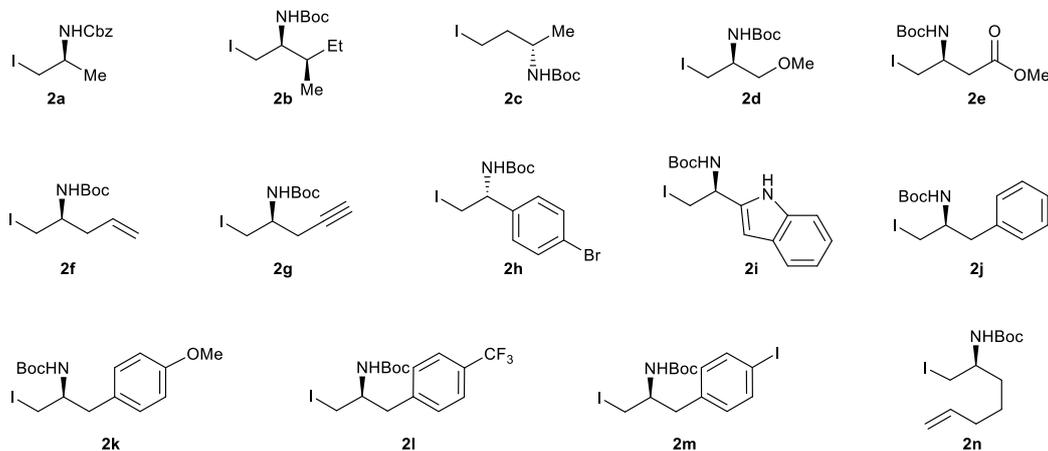
2. Preparation of Enones and β -Amino Iodides.

preparation of enones

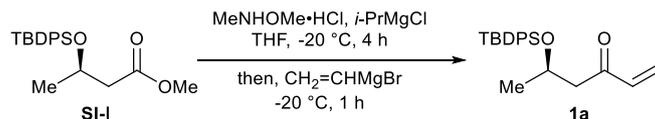


- 1a, 1b, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1k, 1l were synthesized via **General Procedure A** ($^1\text{H}/^{13}\text{C}$ NMR, HRMS, IR were characterized).
- 1o was commercially available.
- 1h,^[1] 1m^[2], 1n^[3] were known compounds (^1H NMR was characterized and in accordance with the reported data).

preparation of β -amino iodides

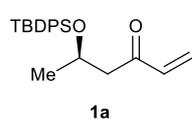


- 2a-2n were synthesized via **General Procedure B** ($^1\text{H}/^{13}\text{C}$ NMR, HRMS, IR were characterized in subsequent sections).



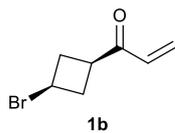
General Procedure A: A solution of methyl (*R*)-3-((*tert*-butyldiphenylsilyl)oxy)butanoate **SI-I** (1.78 g, 5.0 mmol) and *N*, *O*-dimethylhydroxylamine hydrochloride (975.4 mg, 10.0 mmol) in anhydrous THF (15.0 mL) was placed in a flame-dried reaction vessel. Under an argon atmosphere, a solution of isopropylmagnesium chloride (2.0 M in THF, 10.5 mL, 21.0 mmol) was added dropwise via a syringe at -20 °C. The reaction mixture was stirred at -20 °C for 3 h, after which a solution of vinylmagnesium bromide (1.0 M in THF, 10.0 mL, 10.0 mmol) was added dropwise via a syringe over 30 min at the same temperature. The mixture was stirred for an additional 1 h, then quenched by pouring into 1.0 M aqueous HCl at 0 °C. The resulting mixture was extracted with ethyl acetate (3 × 30.0 mL), and the combined organic layers were washed with saturated aqueous NaCl (20.0 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel to afford enone **1a** (1.41 g, 80% yield).

(*R*)-5-((*tert*-butyldiphenylsilyl)oxy)hex-1-en-3-one (1a)



- Yellow oil liquid.
- $R_f = 0.4$ (ethyl acetate/petroleum ether = 5%).
- ¹H NMR (400 MHz, CDCl₃) δ 7.70-7.60 (m, 4H), 7.43-7.37 (m, 6H), 6.26 (dd, $J_1 = 18.0$ Hz, $J_2 = 10.8$ Hz, 1H), 6.06 (dd, $J_1 = 18.0$ Hz, $J_2 = 1.2$ Hz, 1H), 5.75 (dd, $J_1 = 10.8$ Hz, $J_2 = 1.2$ Hz, 1H), 4.41-4.33 (m, 1H), 2.86 (dd, $J_1 = 14.8$ Hz, $J_2 = 6.0$ Hz, 1H), 2.60 (dd, $J_1 = 15.2$ Hz, $J_2 = 6.8$ Hz, 1H), 1.12 (d, $J = 6.0$ Hz, 3H), 1.03 (s, 9H).
- ¹³C NMR (101 MHz, CDCl₃) δ 199.1, 137.0, 135.8, 135.8, 134.3, 133.8, 129.6, 129.5, 128.3, 127.5, 127.4, 66.7, 49.2, 26.9, 23.7, 19.1.
- IR (neat) cm⁻¹ 2931, 2857, 1681, 1472, 1427, 1376, 1111, 996, 822, 771, 739, 702.
- HRMS (ESI-TOF, *m/z*) calcd for C₂₂H₂₈O₂Si (M+Na)⁺ 375.1792, found 375.1768.
- $[\alpha]_D^{25.2} = -6.5$ ($c = 2.0$ in CHCl₃).

1-((1*S*,3*S*)-3-bromocyclobutyl)prop-2-en-1-one (1b)

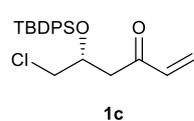


According to the general procedure A, solution of methyl (1*S*, 3*S*)-3-bromocyclobutane-1-carboxylate (959.9 mg, 5.0 mmol), *N*, *O*-dimethylhydroxylamine hydrochloride (975.4 mg, 10.0 mmol), isopropylmagnesium chloride (2.0 M in THF, 10.5 mL, 21.0 mmol) and vinylmagnesium bromide (1.0 M in THF, 10.0 mL, 10.0 mmol) in anhydrous THF (15.0 mL) afforded **1b** (676.7 mg, 72%).

- Yellow oil liquid.

- $R_f = 0.6$ (ethyl acetate/petroleum ether = 5%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.30 (dd, $J_1 = 18.0$ Hz, $J_2 = 10.4$ Hz, 1H), 6.17 (dd, $J_1 = 18.0$ Hz, $J_2 = 1.2$ Hz, 1H), 5.88 (dd, $J_1 = 10.4$ Hz, $J_2 = 1.2$ Hz, 1H), 4.54-4.48 (m, 1H), 3.87-3.79 (m, 1H), 2.95-2.89 (m, 2H), 2.69-2.63 (m, 2H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 200.0, 134.8, 129.3, 40.6, 39.7, 36.7.
- IR (neat) cm^{-1} 1021, 418.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_7\text{H}_9\text{BrO}$ ($\text{M}+\text{H}$) $^+$ 188.9873, found 188.9875.
- $[\alpha]_{\text{D}}^{25.1} = 1.38$ ($c = 2.75$ in CHCl_3).

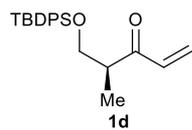
(R)-5-((tert-butylidiphenylsilyl)oxy)-6-chlorohex-1-en-3-one (1c)



According to the general procedure A, solution of methyl (*R*)-3-((*tert*-butylidiphenylsilyl)oxy)-4-chlorobutanoate (1.95 g, 5.0 mmol), *N*, *O*-dimethylhydroxylamine hydrochloride (975.4 mg, 10.0 mmol) isopropylmagnesium chloride (2.0 M in THF, 10.5 mL, 21.0 mmol) and vinylmagnesium bromide (1.0 M in THF, 10.0 mL, 10.0 mmol) in anhydrous THF (15.0 mL), afforded **1c** (1.35 g, 70%).

- Yellow oil liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 5%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.71-7.65 (m, 4H), 7.45-7.38 (m, 6H), 6.24 (dd, $J_1 = 17.6$ Hz, $J_2 = 10.4$ Hz, 1H), 6.11 (dd, $J_1 = 17.6$ Hz, $J_2 = 0.8$ Hz, 1H), 5.80 (dd, $J_1 = 10.4$ Hz, $J_2 = 0.8$ Hz, 1H), 4.49-4.43 (m, 1H), 3.49 (d, $J = 4.0$ Hz, 2H), 2.98 (dd, $J_1 = 16.4$ Hz, $J_2 = 6.4$ Hz, 1H), 2.87 (dd, $J_1 = 16.4$ Hz, $J_2 = 5.6$ Hz, 1H), 1.05 (s, 9H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 198.1, 136.7, 135.8, 135.7, 133.42, 133.12, 129.93, 129.91, 128.80, 127.71, 69.01, 48.71, 43.69, 26.83, 19.29.
- IR (neat) cm^{-1} 2932, 2857, 1681, 1615, 1427, 1111, 1081, 963, 870, 822, 740, 702, 612, 506, 487, 429, 402.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{22}\text{H}_{27}\text{ClO}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 409.1392, found 409.1391.
- $[\alpha]_{\text{D}}^{23.9} = 14.19$ ($c = 2.10$ in CHCl_3).

(R)-5-((tert-butylidiphenylsilyl)oxy)-4-methylpent-1-en-3-one (1d)

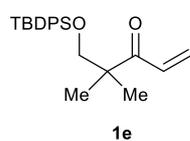


According to the general procedure A, solution of methyl (*R*)-3-((*tert*-butylidiphenylsilyl)oxy)-2-methylpropanoate (1.78 g, 5.0 mmol), *N*, *O*-dimethylhydroxylamine hydrochloride (975.4 mg, 10.0 mmol) isopropylmagnesium chloride (2.0 M in THF, 10.5 mL, 21.0 mmol) and vinylmagnesium bromide (1.0 M in THF, 10.0 mL, 10.0 mmol) in anhydrous THF (15.0 mL), afforded **1d** (1.14 g, 65%).

- Yellow oil liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 5%).

- ^1H NMR (400 MHz, CDCl_3) δ 7.66-7.62 (m, 4H), 7.45-7.36 (m, 6H), 6.45 (dd, $J_1 = 17.6$ Hz, $J_2 = 10.4$ Hz, 1H), 6.23 (dd, $J_1 = 17.6$ Hz, $J_2 = 1.2$ Hz, 1H), 5.77 (dd, $J_1 = 10.4$ Hz, $J_2 = 1.2$ Hz, 1H), 3.87 (dd, $J_1 = 9.6$ Hz, $J_2 = 7.2$ Hz, 1H), 3.67 (dd, $J_1 = 10.0$ Hz, $J_2 = 5.6$ Hz, 1H), 3.16-3.08 (m, 1H), 1.08 (d, $J = 7.2$ Hz, 3H), 1.02 (s, 9H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 202.9, 135.8, 135.6, 135.5, 133.4, 133.3, 129.6, 128.0, 127.6, 66.0, 45.6, 26.7, 19.1, 13.2.
- IR (neat) cm^{-1} 2932, 1678, 1472, 1427, 1111, 823, 739, 702, 614, 504, 402.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{22}\text{H}_{28}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 375.1792, found 375.1794.
- $[\alpha]_{\text{D}}^{24.9} = 24.69$ ($c = 1.45$ in CHCl_3).

5-((tert-butyldiphenylsilyl)oxy)-4,4-dimethylpent-1-en-3-one (1e)

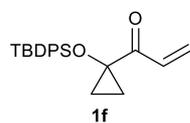


According to the general procedure A, solution of methyl 3-((tert-butyldiphenylsilyl)oxy)-2,2-dimethylpropanoate (1.85 g, 5.0 mmol), N, O - dimethylhydroxylamine hydrochloride (975.4 mg, 10.0 mmol)

isopropylmagnesium chloride (2.0 M in THF, 10.5 mL, 21.0 mmol) and vinylmagnesium bromide (1.0 M in THF, 10.0 mL, 10.0 mmol) in anhydrous THF (15.0 mL), afforded **1e** (1.28 g, 70%).

- Yellow oil liquid.
- $R_f = 0.6$ (ethyl acetate/petroleum ether = 10%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.65-7.62 (m, 4H), 7.44-7.38 (m, 6H), 6.80 (dd, $J_1 = 16.8$ Hz, $J_2 = 10.4$ Hz, 1H), 6.35 (dd, $J_1 = 17.2$ Hz, $J_2 = 2.0$ Hz, 1H), 5.62 (dd, $J_1 = 10.4$ Hz, $J_2 = 2.0$ Hz, 1H), 3.68 (s, 2H), 1.17 (s, 6H), 1.03 (s, 9H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 203.0, 135.6, 133.2, 131.4, 129.6, 127.8, 127.6, 70.1, 48.7, 26.7, 21.1, 19.2.
- IR (neat) cm^{-1} 2961, 1697, 1428, 1111, 824, 701, 504.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{23}\text{H}_{30}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 389.1892, found 389.1894.

1-(1-((tert-butyldiphenylsilyl)oxy)cyclopropyl)prop-2-en-1-one (1f)



According to the general procedure A, solution of methyl 1-((tert-butyldiphenylsilyl)oxy)cyclopropane-1-carboxylate (1.77 g, 5.0 mmol), N, O - dimethylhydroxylamine hydrochloride (975.4 mg, 10.0 mmol)

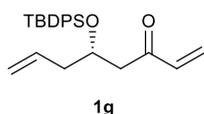
isopropylmagnesium chloride (2.0 M in THF, 10.5 mL, 21.0 mmol) and vinylmagnesium bromide (1.0 M in THF, 10.0 mL, 10.0 mmol) in anhydrous THF (15.0 mL), afforded **1f** (1.05 g, 60%).

- Yellow oil liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 5%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.65-7.63 (m, 4H), 7.42-7.34 (m, 6H), 7.11 (dd, $J_1 = 17.2$ Hz, $J_2 = 10.4$ Hz, 1H), 6.23 (dd, $J_1 = 17.2$ Hz, $J_2 = 2.4$ Hz, 1H), 5.61 (dd, $J_1 = 10.4$ Hz, $J_2 = 2.0$ Hz,

1H), 1.22-1.18 (m, 2H), 1.12-1.08 (m, 11H).

- ¹³C NMR (101 MHz, CDCl₃) δ 200.2, 135.5, 133.5, 130.5, 129.8, 128.1, 127.6, 64.4, 26.9, 26.7, 19.4, 19.1.
- IR (neat) cm⁻¹ 2158, 1074, 702, 500, 404.
- HRMS (ESI-TOF, m/z) calcd for C₂₂H₂₆O₂Si (M+Na)⁺ 373.1592, found 373.1593.

(S)-5-((tert-butyldiphenylsilyl)oxy)octa-1,7-dien-3-one (1g)

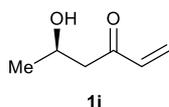


According to the general procedure A, solution of methyl (S)-3-((tert-butyldiphenylsilyl)oxy)hex-5-enoate (1.91 g, 5.0 mmol), N, O - dimethylhydroxylamine hydrochloride (975.4 mg, 10.0 mmol)

isopropylmagnesium chloride (2.0 M in THF, 10.5 mL, 21.0 mmol) and vinylmagnesium bromide (1.0 M in THF, 10.0 mL, 10.0 mmol) in anhydrous THF (15.0 mL), afforded **1g** (1.32 g, 70%).

- Yellow oil liquid.
- R_f = 0.6 (ethyl acetate/petroleum ether = 5%).
- ¹H NMR (400 MHz, CDCl₃) δ 7.70-7.65 (m, 4H), 7.42-7.35 (m, 6H), 6.20 (dd, J₁ = 18.0 Hz, J₂ = 10.8 Hz, 1H), 6.02 (dd, J₁ = 17.6 Hz, J₂ = 1.2 Hz, 1H), 5.79-5.68 (m, 2H), 5.02-4.91 (m, 2H), 4.38-4.32 (m, 1H), 2.74 (dd, J₁ = 15.6 Hz, J₂ = 6.0 Hz, 1H), 2.68 (dd, J₁ = 15.6 Hz, J₂ = 6.4 Hz, 1H), 2.29-2.14 (m, 2H), 1.03 (s, 9H).
- ¹³C NMR (101 MHz, CDCl₃) δ 199.1, 137.0, 135.9, 135.8, 134.0, 134.0, 133.7, 129.6, 129.6, 128.2, 127.5, 127.5, 117.8, 69.6, 45.9, 41.4, 26.9, 19.3.
- IR (neat) cm⁻¹ 2931, 1681, 1427, 1111, 822, 739, 702, 611, 508, 459, 428, 403.
- HRMS (ESI-TOF, m/z) calcd for C₂₄H₃₀O₂Si (M+Na)⁺ 410.1892, found 410.1895.
- [α]_D^{23.5} = -23.52 (c = 0.85 in CHCl₃).

(R)-5-hydroxyhex-1-en-3-one (1i)



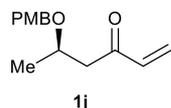
Solution of methyl (R)-3-hydroxybutanoate (590.30 mg, 5.0 mmol), N, O - dimethylhydroxylamine hydrochloride (975.4 mg, 10.0 mmol), isopropylmagnesium chloride (2.0 M in THF, 12.5 mL, 25 mmol) and

vinylmagnesium bromide (1.0 M in THF, 10.0 mL, 10.0 mmol) in anhydrous THF (15.0 mL), afforded **1i** (511.2 mg, 71%).

- Yellow oil liquid.
- R_f = 0.5 (ethyl acetate/petroleum ether = 40%).
- ¹H NMR (400 MHz, CDCl₃) δ 6.30 (dd, J₁ = 17.6 Hz, J₂ = 10.4 Hz, 1H), 6.20 (dd, J₁ = 17.6 Hz, J₂ = 1.2 Hz, 1H), 5.85 (dd, J₁ = 10.0 Hz, J₂ = 1.2 Hz, 1H), 4.26-4.19 (m, 1H), 3.28 (s, 1H), 2.73 (dd, J₁ = 17.2 Hz, J₂ = 3.2 Hz, 1H), 2.65 (dd, J₁ = 17.2 Hz, J₂ = 8.4 Hz, 1H), 1.72 (d, J = 6.4 Hz, 3H).

- ^{13}C NMR (101 MHz, CDCl_3) δ 160.0, 131.8, 119.2, 69.3, 51.6, 39.2.
- IR (neat) cm^{-1} 1219, 772, 430, 402.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_6\text{H}_{10}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$ 137.0592, found 137.0591.
- $[\alpha]_{\text{D}}^{24.6} = -49.33$ ($c = 0.30$ in CHCl_3).

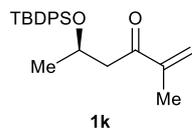
(R)-5-((4-methoxybenzyl)oxy)hex-1-en-3-one (1j)



According to the general procedure A, solution of methyl (*R*)-3-((4-methoxybenzyl)oxy)butanoate (1.19 g, 5.0 mmol), N, O - dimethylhydroxylamine hydrochloride (975.4 mg, 10.0 mmol) isopropylmagnesium chloride (2.0 M in THF, 10.5 mL, 21.0 mmol) and vinylmagnesium bromide (1.0 M in THF, 10.0 mL, 10.0 mmol) in anhydrous THF (15.0 mL), afforded **1j** (760.50 mg, 65%).

- Yellow oil liquid.
- $R_f = 0.3$ (ethyl acetate/petroleum ether = 10%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.21 (d, $J = 8.4$ Hz, 2H), 6.86-6.84 (d, $J = 8.8$ Hz, 2H), 6.36 (dd, $J_1 = 17.6$ Hz, $J_2 = 10.4$ Hz, 1H), 6.21 (dd, $J_1 = 17.6$ Hz, $J_2 = 1.2$ Hz, 1H), 5.83 (dd, $J_1 = 10.4$ Hz, $J_2 = 1.2$ Hz, 1H), 4.44 (d, $J = 10.8$ Hz, 1H), 4.40 (d, $J = 11.2$ Hz, 1H), 4.10-4.03 (m, 1H), 3.79 (s, 3H), 2.98 (dd, $J_1 = 16.0$ Hz, $J_2 = 6.8$ Hz, 1H), 2.61 (dd, $J_1 = 15.6$ Hz, $J_2 = 5.6$ Hz, 1H), 1.24 (d, $J = 6.4$ Hz, 3H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 199.2, 159.1, 137.0, 130.6, 129.2, 128.5, 113.7, 71.4, 70.6, 55.2, 46.7, 20.1.
- IR (neat) cm^{-1} 2970, 1681, 1613, 1513, 1401, 1374, 1302, 1247, 1173, 10344, 986, 822, 479.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3$ ($\text{M}+\text{Na}$) $^+$ 257.1192, found 257.1188.
- $[\alpha]_{\text{D}}^{24.6} = -7.57$ ($c = 1.91$ in CHCl_3).

(R)-5-((tert-butylidiphenylsilyl)oxy)-2-methylhex-1-en-3-one (1k)



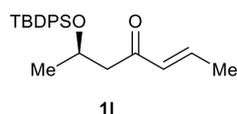
According to the general procedure A, solution of methyl (*R*)-3-((*tert*-butylidiphenylsilyl)oxy)butanoate (1.78 g, 5.0 mmol), N, O - dimethylhydroxylamine hydrochloride (975.4 mg, 10.0 mmol) isopropylmagnesium chloride (2.0 M in THF, 10.5 mL, 21.0 mmol) and vinylmagnesium bromide (1.0 M in THF, 10.0 mL, 10.0 mmol) in anhydrous THF (15.0 mL), afforded **1k** (1.09 g, 60%).

- Yellow oil liquid.
- $R_f = 0.6$ (ethyl acetate/petroleum ether = 10%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.70-7.66 (m, 4H), 7.42-7.35 (m, 6H), 5.77 (s, 1H), 5.70 (s, 1H), 4.42-4.34 (m, 1H), 3.01 (dd, $J_1 = 15.2$ Hz, $J_2 = 6.4$ Hz, 1H), 2.63 (dd, $J_1 = 15.2$ Hz, $J_2 = 6.8$ Hz, 1H), 1.80 (s, 3H), 1.10 (d, $J = 6.4$ Hz, 3H), 1.02 (s, 9H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 200.3, 144.9, 135.8, 134.4, 133.9, 129.6, 129.5, 127.5, 127.4,

125.3, 67.2, 47.2, 26.9, 23.8, 19.1, 17.4.

- IR (neat) cm^{-1} 2008, 1676, 1427, 1111, 702, 611, 496, 422.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{23}\text{H}_{30}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$)⁺ 389.1892, found 389.1895.
- $[\alpha]_{\text{D}}^{24.4} = -6.50$ ($c = 1.60$ in CHCl_3).

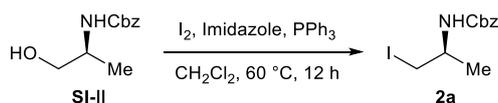
(R,E)-6-((tert-butylidiphenylsilyl)oxy)hept-2-en-4-one (11)



According to the general procedure A, solution of methyl (R)-3-((tert-butylidiphenylsilyl)oxy)butanoate (1.78 g, 5.0 mmol), N, O - dimethylhydroxylamine hydrochloride (975.4 mg, 10.0 mmol)

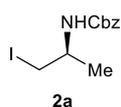
isopropylmagnesium chloride (2.0 M in THF, 10.5 mL, 21.0 mmol) and vinylmagnesium bromide (1.0 M in THF, 10.0 mL, 10.0 mmol) in anhydrous THF (15.0 mL), afforded **11** (732.0 mg, 40%).

- Yellow oil liquid.
- $R_f = 0.6$ (ethyl acetate/petroleum ether = 10%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.69-7.67 (m, 4H), 7.45-7.36 (m, 6H), 6.68-6.58 (m, 1H), 6.00 (dd, $J_1 = 15.6$ Hz, $J_2 = 1.6$ Hz, 1H), 4.37-4.30 (m, 1H), 2.81 (dd, $J_1 = 14.8$ Hz, $J_2 = 6.0$ Hz, 1H), 2.52 (dd, $J_1 = 14.8$ Hz, $J_2 = 6.8$ Hz, 1H), 1.82 (dd, $J_1 = 6.8$ Hz, $J_2 = 1.6$ Hz, 3H), 1.11 (d, $J = 6.0$ Hz, 3H), 1.03 (s, 9H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 198.7, 143.0, 135.8, 135.8, 134.3, 133.8, 132.6, 129.6, 129.5, 127.5, 127.4, 66.9, 49.7, 26.8, 23.6, 19.1, 18.2.
- IR (neat) cm^{-1} 1668, 1111, 702, 509, 428, 408.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{23}\text{H}_{30}\text{O}_2\text{Si}$ ($\text{M}+\text{Na}$)⁺ 389.1892, found 389.1895.
- $[\alpha]_{\text{D}}^{24.0} = -3.42$ ($c = 0.72$ in CHCl_3).



General Procedure B: A solution of PPh_3 (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol), and I_2 (989.9 mg, 3.9 mmol) in dry CH_2Cl_2 (35.0 mL) was placed in a flame-dried reaction vessel. Under an argon atmosphere, amino alcohol **SI-II** (3.0 mmol) was added at room temperature. The reaction mixture was heated to 60 °C and stirred for 12 h, then quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (20.0 mL) at room temperature, followed by extraction with ethyl acetate (3×50.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel to afford compound **2a** (765.6 mg, 80% yield)..

benzyl (S)-(1-iodopropan-2-yl)carbamate (2a)



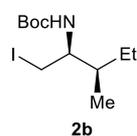
■ White solid.

■ M.p. = 76.2-79.8 °C.

■ $R_f = 0.4$ (ethyl acetate/petroleum ether = 40%).

- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37-7.32 (m, 5H), 5.14-5.06 (m, 2H), 4.90 (s, 1H), 3.64-3.57 (m, 1H), 3.43 (dd, $J_1 = 10.4$ Hz, $J_2 = 4.4$ Hz, 1H), 3.30 (dd, $J_1 = 10.0$ Hz, $J_2 = 3.6$ Hz, 1H), 1.22 (d, $J = 6.8$ Hz, 3H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.2, 136.2, 128.5, 128.2, 128.1, 66.8, 46.3, 21.2, 15.6.
- IR (neat) cm^{-1} 1694, 1530, 1219, 772, 412.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{11}\text{H}_{14}\text{INO}_2$ ($\text{M}+\text{Na}$) $^+$ 341.9992, found 341.9982.
- $[\alpha]_{\text{D}}^{24.9} = 15.69$ ($c = 0.65$ in CHCl_3).

tert-butyl ((2S,3R)-1-iodo-3-methylpentan-2-yl)carbamate (2b)

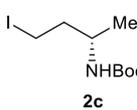


According to the general procedure B, *tert*-butyl ((2*S*, 3*R*)-1-hydroxy-3-methylpentan-2-yl)carbamate (651.0 mg, 3.0 mmol, 1.0 equiv.), PPh_3 (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol) and I_2 (989.8 mg, 3.9 mmol) in dry CH_2Cl_2

(35.0 mL) at 60 °C for 12 h afforded **2b** (882.9 mg, 90%).

- White solid.
- M.p. = 74.6-77.2 °C.
- $R_f = 0.4$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.56 (d, $J = 8.0$ Hz, 1H), 3.45 (dd, $J_1 = 10.4$ Hz, $J_2 = 4.0$ Hz, 1H), 3.31 (dd, $J_1 = 10.4$ Hz, $J_2 = 4.4$ Hz, 1H), 3.18-3.11 (m, 1H), 1.58-1.49 (m, 2H), 1.45 (s, 9H), 1.20-1.14 (m, 1H), 0.92-0.87 (m, 6H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.3, 79.5, 54.1, 38.7, 28.3, 24.7, 15.2, 14.0, 11.2.
- IR (neat) cm^{-1} 1671, 1162, 528, 447, 412.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{11}\text{H}_{22}\text{INO}_2$ ($\text{M}+\text{Na}$) $^+$ 350.0587, found 350.0582.
- $[\alpha]_{\text{D}}^{23.0} = -19.42$ ($c = 0.35$ in CHCl_3).

tert-butyl (S)-(4-iodobutan-2-yl)carbamate (2c)



According to the general procedure B, *tert*-butyl (*S*)-(4-hydroxybutan-2-yl)carbamate (567.0 mg, 3.0 mmol, 1.0 equiv.), PPh_3 (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol) and I_2 (989.8 mg, 3.9 mmol) in dry CH_2Cl_2 (35.0

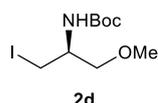
mL) at 60 °C for 12 h afforded **2c** (744.5 mg, 83%).

- White solid.
- M.p. = 58.9-61.3 °C.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 25%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.35 (s, 1H), 3.76-3.65 (m, 1H), 3.16 (t, $J = 7.6$ Hz, 2H), 2.02-

1.94 (m, 2H), 1.43 (s, 9H), 1.14 (d, $J = 6.8$ Hz, 3H).

- ^{13}C NMR (101 MHz, CDCl_3) δ 155.3, 79.3, 47.6, 41.6, 28.4, 20.8, 1.3.
- IR (neat) cm^{-1} 1219, 772, 413.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_9\text{H}_{18}\text{INO}_2$ ($\text{M}+\text{Na}$) $^+$ 322.0274, found 322.0273.
- $[\alpha]_{\text{D}}^{24.8} = 4.0$ ($c = 0.40$ in CHCl_3).

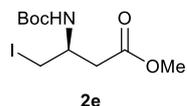
tert-butyl (S)-(1-iodo-3-methoxypropan-2-yl)carbamate (2d)



According to the general procedure B, *tert*-butyl (*R*)-(1-hydroxy-3-methoxypropan-2-yl)carbamate (615.0 mg, 3.0 mmol, 1.0 equiv.), PPh_3 (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol) and I_2 (989.8 mg, 3.9 mmol) in dry CH_2Cl_2 (35.0 mL) at 60 °C for 12 h afforded **2d** (803.3 mg, 85%).

- Yellow oil liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 50%).
- ^1H NMR (400 MHz, CDCl_3) δ 4.93 (s, 1H), 3.74-3.66 (m, 1H), 3.60 (dd, $J_1 = 9.2$ Hz, $J_2 = 4.0$ Hz, 1H), 3.39-3.30 (m, 6H), 1.44 (s, 9H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 153.9, 79.9, 72.8, 59.1, 50.2, 28.3, 8.2.
- IR (neat) cm^{-1} 1164, 495, 424, 412.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_9\text{H}_{18}\text{INO}_3$ ($\text{M}+\text{Na}$) $^+$ 338.0223, found 338.0219.
- $[\alpha]_{\text{D}}^{24.5} = 12.66$ ($c = 0.31$ in CHCl_3).

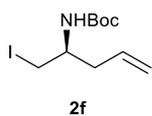
methyl (S)-3-((tert-butoxycarbonyl)amino)-4-iodobutanoate (2e)



According to the general procedure B, methyl (*S*)-3-((*tert*-butoxycarbonyl)amino)-4-hydroxybutanoate (699.0 mg, 3.0 mmol, 1.0 equiv.), PPh_3 (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol) and I_2 (989.8 mg, 3.9 mmol) in dry CH_2Cl_2 (35.0 mL) at 60 °C for 12 h afforded **2e** (905.5 mg, 88%).

- White solid.
- M.p. = 60.9-63.7 °C.
- $R_f = 0.4$ (ethyl acetate/petroleum ether = 50%).
- ^1H NMR (400 MHz, CDCl_3) δ 5.08 (d, $J = 8.0$ Hz, 1H), 3.94-3.86 (m, 1H), 3.69 (s, 3H), 3.45-3.37 (m, 2H), 2.74 (dd, $J_1 = 16.4$ Hz, $J_2 = 5.6$ Hz, 1H), 2.62 (dd, $J_1 = 16.4$ Hz, $J_2 = 6.0$ Hz, 1H), 1.43 (s, 9H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 171.1, 154.7, 80.0, 51.9, 47.6, 38.4, 28.3, 11.1.
- IR (neat) cm^{-1} 2977, 1715, 1517, 1366, 1248, 1163, 434, 406.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{10}\text{H}_{18}\text{INO}_4$ ($\text{M}+\text{Na}$) $^+$ 366.0173, found 366.0171.
- $[\alpha]_{\text{D}}^{23.9} = 6.52$ ($c = 0.95$ in CHCl_3).

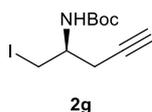
tert-butyl (S)-(1-iodopent-4-en-2-yl)carbamate (2f)



According to the general procedure B, *tert*-butyl (*S*)-(1-iodopent-4-en-2-yl)carbamate (603.0 mg, 3.0 mmol, 1.0 equiv.), PPh₃ (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol) and I₂ (989.8 mg, 3.9 mmol) in dry CH₂Cl₂ (35.0 mL) at 60 °C for 12 h afforded **2f** (765.1 mg, 82%).

- Yellow oil liquid.
- $R_f = 0.6$ (ethyl acetate/petroleum ether = 25%).
- ¹H NMR (400 MHz, CDCl₃) δ 5.77-5.67 (m, 1H), 5.21-5.12 (m, 2H), 4.62 (s, 1H), 3.45-3.41 (m, 2H), 3.33-3.30 (m, 1H), 2.34-2.26 (m, 2H), 1.44 (s, 9H).
- ¹³C NMR (150 MHz, CDCl₃) δ 154.9, 133.1, 118.7, 79.7, 49.3, 39.1, 28.3, 13.7.
- IR (neat) cm⁻¹ 2201, 2016, 1260, 1015, 801, 623, 555, 496, 447.
- HRMS (MALDI, m/z) calcd for C₁₀H₁₈INO₂ (M+Na)⁺ 334.0274, found 334.0276.
- $[\alpha]_D^{25.2} = 3.11$ ($c = 4.5$ in CHCl₃).

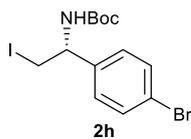
tert-butyl (*S*)-(1-iodopent-4-yn-2-yl)carbamate (2g)



According to the general procedure B, *tert*-butyl (*S*)-(1-iodopent-4-yn-2-yl)carbamate (597.0 mg, 3.0 mmol, 1.0 equiv.), PPh₃ (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol) and I₂ (989.8 mg, 3.9 mmol) in dry CH₂Cl₂ (35.0 mL) at 60 °C for 12 h afforded **2g** (750.8 mg, 81%).

- White solid.
- M.p. = 47.8-52.6 °C.
- $R_f = 0.4$ (ethyl acetate/petroleum ether = 50%).
- ¹H NMR (400 MHz, CDCl₃) δ 4.82 (s, 1H), 3.75-3.67 (m, 1H), 3.47 (dd, $J_1 = 10.0$ Hz, $J_2 = 4.4$ Hz, 1H), 3.38 (dd, $J_1 = 10.0$ Hz, $J_2 = 6.4$ Hz, 1H), 2.68-2.62 (m, 1H), 2.49-2.42 (m, 1H), 2.07 (t, $J = 2.8$ Hz, 1H), 1.44 (s, 9H).
- ¹³C NMR (101 MHz, CDCl₃) δ 154.6, 80.1, 79.0, 71.5, 49.1, 28.3, 24.3, 10.2.
- IR (neat) cm⁻¹ 557, 447, 423, 412.
- HRMS (ESI-TOF, m/z) calcd for C₁₀H₁₆INO₂ (M+Na)⁺ 332.0118, found 332.0123.
- $[\alpha]_D^{23.5} = 25.77$ ($c = 0.45$ in CHCl₃).

tert-butyl (*R*)-(1-(4-bromophenyl)-2-iodoethyl)carbamate (2h)

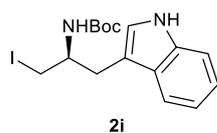


According to the general procedure B, *tert*-butyl (*R*)-(1-(4-bromophenyl)-2-iodoethyl)carbamate (945.0 mg, 3.0 mmol, 1.0 equiv.), PPh₃ (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol) and I₂ (989.8 mg, 3.9 mmol) in dry CH₂Cl₂ (35.0 mL) at 60 °C for 12 h afforded **2h** (1.03 g, 81%).

- White solid.
- M.p. = 132.8-134.2 °C.

- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50-7.47 (m, 2H), 7.17-7.15 (m, 2H), 5.03 (s, 1H), 4.73 (s, 1H), 3.53-3.40 (m, 2H), 1.44 (s, 9H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.7, 139.3, 131.8, 127.9, 121.9, 80.4, 54.2, 28.3, 11.7.
- IR (neat) cm^{-1} 1683, 1165, 463.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{13}\text{H}_{17}\text{BrINO}_2$ ($\text{M}+\text{Na}$) $^+$ 447.9379, found 447.9384.
- $[\alpha]_{\text{D}}^{24.5} = -32.80$ ($c = 0.50$ in CHCl_3).

tert-butyl (S)-(1-(1H-indol-3-yl)-3-iodopropan-2-yl)carbamate (2i)

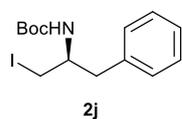


According to the general procedure B, *tert*-butyl (*S*)-(1-hydroxy-3-(1H-indol-3-yl)propan-2-yl)carbamate (870.48 mg, 3.0 mmol, 1.0 equiv.), PPh_3 (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol) and I_2 (989.8 mg, 3.9 mmol)

in dry CH_2Cl_2 (35.0 mL) at 60 °C for 12 h afforded **2i** (1.07 g, 93%).

- White solid.
- M.p. = 132.0-134.2 °C.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 50%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.14 (s, 1H), 7.71 (d, $J = 8.0$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.23-7.12 (m, 3H), 4.76 (s, 1H), 3.79-3.70 (m, 1H), 3.40 (dd, $J_1 = 9.6$ Hz, $J_2 = 6.0$ Hz, 1H), 3.20 (dd, $J_1 = 10.0$ Hz, $J_2 = 3.6$ Hz, 1H), 3.09 (dd, $J_1 = 14.4$ Hz, $J_2 = 4.8$ Hz, 1H), 2.93 (dd, $J_1 = 14.4$ Hz, $J_2 = 8.0$ Hz, 1H), 1.46 (s, 9H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.0, 136.2, 127.3, 122.8, 122.2, 119.7, 119.0, 111.2, 111.1, 49.9, 30.5, 28.4, 14.5.
- IR (neat) cm^{-1} 1691, 1164, 742, 407.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{16}\text{H}_{21}\text{IN}_2\text{O}_2$ ($\text{M}+\text{Na}$) $^+$ 423.0540, found 423.0543.
- $[\alpha]_{\text{D}}^{24.0} = 22.66$ ($c = 0.30$ in CHCl_3).

tert-butyl (S)-(1-iodo-3-phenylpropan-2-yl)carbamate (2j)



According to the general procedure B, *tert*-butyl (*S*)-(1-hydroxy-3-(4-methoxyphenyl)propan-2-yl)carbamate (753.45 mg, 3.0 mmol, 1.0 equiv.), PPh_3 (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol) and I_2 (989.8 mg, 3.9

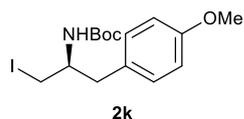
mmol) in dry CH_2Cl_2 (35.0 mL) at 60 °C for 12 h afforded (996.3 mg, 92%).

- White solid.
- M.p. = 117.9-121.4 °C.
- $R_f = 0.4$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.26-7.22 (m, 2H), 7.19-7.16 (m, 3H), 4.62 (d, $J = 8.0$ Hz, 1H), 3.57-3.49 (m, 1H), 3.33 (dd, $J_1 = 10.8$ Hz, $J_2 = 4.4$ Hz, 1H), 3.10 (dd, $J_1 = 10.4$ Hz, $J_2 = 4.0$

Hz, 1H), 2.84 (dd, $J_1 = 13.2$ Hz, $J_2 = 5.2$ Hz, 1H), 2.71 (dd, $J_1 = 14.0$ Hz, $J_2 = 8.4$ Hz, 1H), 1.37 (s, 9H).

- ^{13}C NMR (101 MHz, CDCl_3) δ 154.8, 137.0, 129.0, 128.7, 126.8, 79.8, 50.9, 40.6, 28.3, 14.0.
- IR (neat) cm^{-1} 1685, 1169, 450, 422.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{14}\text{H}_{20}\text{INO}_2$ ($\text{M}+\text{Na}$) $^+$ 384.0431, found 384.0428.
- $[\alpha]_{\text{D}}^{23.5} = 16.02$ ($c = 0.75$ in CHCl_3).

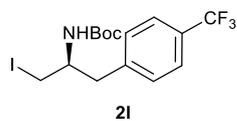
tert-butyl (S)-(1-iodo-3-(4-methoxyphenyl)propan-2-yl)carbamate (2k)



According to the general procedure B, *tert*-butyl (*S*)-(1-hydroxy-3-(4-methoxyphenyl)propan-2-yl) carbamate (843.4 mg, 3.0 mmol, 1.0 equiv.), PPh_3 (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol) and I_2 (989.8 mg, 3.9 mmol) in dry CH_2Cl_2 (35.0 mL) at 60 °C for 12 h afforded **2k** (1.03 g, 88%).

- White solid.
- M.p. = 84.5-87.9 °C.
- $R_f = 0.4$ (ethyl acetate/petroleum ether = 50%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.19-7.16 (m, 2H), 6.86-6.83 (m, 2H), 4.67 (d, $J = 8.4$ Hz, 1H), 3.79 (s, 3H), 3.58-3.50 (m, 1H), 3.39 (dd, $J_1 = 10.0$ Hz, $J_2 = 4.0$ Hz, 1H), 3.15 (dd, $J_1 = 10.0$ Hz, $J_2 = 3.6$ Hz, 1H), 2.85 (dd, $J_1 = 13.6$ Hz, $J_2 = 5.6$ Hz, 1H), 2.70 (dd, $J_1 = 13.6$ Hz, $J_2 = 8.4$ Hz, 1H), 1.43 (s, 9H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 158.5, 154.8, 130.2, 128.9, 114.1, 79.8, 55.2, 51.1, 39.6, 28.3, 14.1.
- IR (neat) cm^{-1} 1512, 1248, 772, 449, 412.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{15}\text{H}_{22}\text{INO}_3$ ($\text{M}+\text{Na}$) $^+$ 414.0536, found 414.0531.
- $[\alpha]_{\text{D}}^{24.1} = 18.28$ ($c = 0.35$ in CHCl_3).

tert-butyl (S)-(1-iodo-3-(4-(trifluoromethyl)phenyl)propan-2-yl)carbamate (2l)



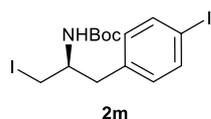
According to the general procedure B, *tert*-butyl (*S*)-(1-hydroxy-3-(4-(trifluoromethyl)phenyl)propan-2-yl)carbamate (957.4 mg, 3.0 mmol, 1.0 equiv.), PPh_3 (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol) and I_2 (989.8 mg, 3.9 mmol) in dry CH_2Cl_2 (35.0 mL) at 60 °C for 12 h afforded **2l** (1.09 g, 85%).

- White solid.
- M.p. = 131.0-134.5 °C.
- $R_f = 0.4$ (ethyl acetate/petroleum ether = 50%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.49 (m, 2H), 7.46-7.42 (m, 2H), 4.69 (d, $J = 8.4$ Hz, 1H), 3.67-3.60 (s, 1H), 3.40 (dd, $J_1 = 10.4$ Hz, $J_2 = 4.4$ Hz, 1H), 3.16 (dd, $J_1 = 10.4$ Hz, $J_2 = 4.0$ Hz, 1H), 2.95 (dd, $J_1 = 13.6$ Hz, $J_2 = 6.4$ Hz, 1H), 2.87 (dd, $J_1 = 13.6$ Hz, $J_2 = 7.6$ Hz, 1H), 1.41 (s,

9H).

- ^{13}C NMR (101 MHz, CDCl_3) δ 154.7, 138.1, 132.6, 131.0, 130.8, 129.1, 125.9, 123.7, 80.0, 50.8, 40.6, 28.2, 13.4.
- IR (neat) cm^{-1} 2158, 1682, 1526, 1163, 1126, 469, 447, 411.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{15}\text{H}_{19}\text{F}_3\text{INO}_2$ ($\text{M}+\text{Na}$) $^+$ 452.0305, found 452.0310.
- $[\alpha]_{\text{D}}^{24.1} = 9.33$ ($c = 0.30$ in CHCl_3).

tert-butyl (S)-(1-iodo-3-(4-iodophenyl)propan-2-yl)carbamate (2m)

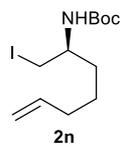


According to the general procedure B, *tert*-butyl (*S*)-(1-hydroxy-3-(4-iodophenyl)propan-2-yl)carbamate (1.13 g, 3.0 mmol, 1.0 equiv.), PPh_3 (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol) and I_2 (989.8 mg, 3.9 mmol)

in dry CH_2Cl_2 (35.0 mL) at 60 °C for 12 h afforded **2m** (1.28 g, 88%).

- White solid.
- M.p. = 73.7-75.8 °C.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 40%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 4.65 (d, $J = 8.4$ Hz, 1H), 3.60-3.51 (m, 1H), 3.37 (dd, $J_1 = 10.0$ Hz, $J_2 = 4.0$ Hz, 1H), 3.15 (dd, $J_1 = 10.4$ Hz, $J_2 = 4.0$ Hz, 1H), 2.84 (dd, $J_1 = 14.0$ Hz, $J_2 = 6.0$ Hz, 1H), 2.72 (dd, $J_1 = 13.6$ Hz, $J_2 = 8.0$ Hz, 1H), 1.43 (s, 9H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 154.8, 137.7, 136.7, 131.2, 92.2, 80.0, 50.7, 42.2, 29.1, 13.6.
- IR (neat) cm^{-1} 3357, 1686, 1531, 1006, 643, 414.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{14}\text{H}_{19}\text{I}_2\text{NO}_2$ ($\text{M}+\text{Na}$) $^+$ 509.9397, found 509.9399.
- $[\alpha]_{\text{D}}^{23.7} = 17.66$ ($c = 0.61$ in CHCl_3).

tert-butyl (S)-(1-iodohept-6-en-2-yl)carbamate (2n)



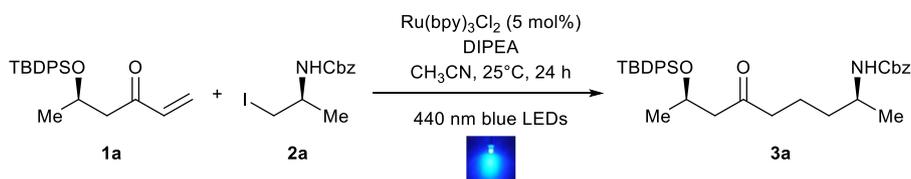
According to the general procedure B, *tert*-butyl (*S*)-(1-hydroxyhept-6-en-2-yl)carbamate (687.5 mg, 3.0 mmol, 1.0 equiv.), PPh_3 (996.7 mg, 3.8 mmol), imidazole (510.6 mg, 7.5 mmol) and I_2 (989.8 mg, 3.9 mmol) in dry CH_2Cl_2 (35.0 mL) at 60 °C

for 12 h afforded **2n** (864.6 mg, 85%).

- Yellow oil liquid.
- $R_f = 0.4$ (ethyl acetate/petroleum ether = 40%).
- ^1H NMR (400 MHz, CDCl_3) δ 5.71-5.81 (m, 1H), 4.94-5.02 (m, 2H), 4.57 (d, $J = 8.4$ Hz, 1H), 3.26-3.44 (m, 3H), 2.03-2.09 (m, 2H), 1.38-1.54 (m, 13H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 155.0, 138.0, 115.0, 79.6, 49.5, 34.5, 33.2, 28.3, 24.9, 15.1.
- IR (neat) cm^{-1} 2036, 1688, 1513, 1167, 636, 417.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{11}\text{H}_{22}\text{INO}_2$ ($\text{M}+\text{Na}$) $^+$ 362.0587, found 362.0585.

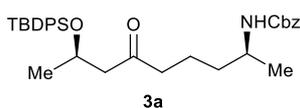
- $[\alpha]_D^{24.9} = -12.4$ ($c = 1.0$ in CHCl_3).

3. Synthesis of 1, 5-Amino Ketones 3



General Procedure C (In flask): A solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (3.2 mg, 5 mol%), (*R*)-5-((*tert*-butyldiphenylsilyl)oxy)hex-1-en-3-one (52.8 mg, 0.15 mmol), benzyl (*S*)-(1-iodopropan-2-yl)carbamate (31.9 mg, 0.1 mmol), and DIPEA (52.0 μL , 0.3 mmol) in 1 mL of acetonitrile were irradiated with 440 nm blue LEDs at room temperature for 24 h. The mixture was concentrated under reduced pressure and purified by flash column chromatography to afford **3a** (43.7 mg, 80% yield).

benzyl ((2*S*,8*R*)-8-((*tert*-butyldiphenylsilyl)oxy)-6-oxononan-2-yl)carbamate (3a)

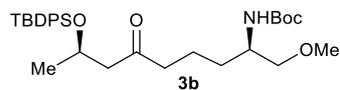


Flow-chemistry conditions: A solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (640.5 mg, 1.0 mmol) was dissolved in a mixed solvent consisting of 25.0 mL of acetonitrile and 15.0 mL of water, a solution of (*R*)-5-((*tert*-butyldiphenylsilyl)oxy)hex-1-en-3-one **1a** (10.56 g, 30.0 mmol) in 40 mL of acetonitrile, a solution of benzyl (*S*)-(1-iodopropan-2-yl)carbamate **2a** (6.38 g, 20.0 mmol) in 40 mL of acetonitrile, and a solution of DIPEA (10.45 mL, 60.0 mmol) in 40 mL of acetonitrile were each loaded into a 50 mL syringe. The mixture was pumped at a rate of 10 mL/h into a flow reactor, which was irradiated with a blue LED light ($h\nu = 440$ nm) at a distance of 1.0 cm at room temperature. The products were collected and the acetonitrile was removed under reduced pressure. The crude products were purified by silica gel flash column chromatography to afford **3a** (9.27 g, 85% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.67 (d, $J = 7.2$ Hz, 4H), 7.31-7.45 (m, 11H), 5.05-5.12 (m, 2H), 4.60 (d, $J = 8.8$ Hz, 1H), 4.28-4.36 (m, 1H), 3.65-3.72 (m, 1H), 2.61 (dd, $J_1 = 14.8$ Hz, $J_2 = 6.0$ Hz, 1H), 2.26-2.44 (m, 3H), 1.47-1.56 (m, 2H), 1.32-1.38 (m, 2H), 1.07-1.13 (m, 6H), 1.03 (s, 9H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 208.9, 155.7, 136.6, 135.7, 134.2, 133.7, 129.6, 129.5, 128.4, 128.0, 127.5, 127.4, 66.4, 66.4, 52.3, 46.8, 43.3, 36.2, 26.8, 23.6, 21.0, 19.5, 19.1.
- IR (neat) cm^{-1} 2931, 1711, 1528, 1454, 1427, 1375, 1111, 822, 739, 702.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{33}\text{H}_{43}\text{NO}_4\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 568.2853, found 568.2850.

- $[\alpha]_D^{24.5} = 3.24$ ($c = 0.05$ in CHCl_3).

tert-butyl ((2R,8R)-8-((tert-butyldiphenylsilyloxy)-1-methoxy-6-oxononan-2-yl)carbamate (3b)

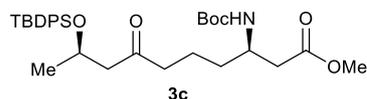


According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-((*tert*-butyldiphenylsilyloxy)hex-1-en-3-one (105.6 mg, 0.3mmol), *tert*-butyl (*S*)-(1-iodo-3-methoxypropan-2-

yl)carbamate (63.1 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3b** (92.1 mg, 85% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 30%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65-7.67 (m, 4H), 7.35-7.44 (m, 6H), 4.69 (d, $J = 9.2$ Hz, 1H) 4.28-4.34 (m, 1H), 3.62-3.68 (m, 1H), 3.30-3.35 (m, 5H), 2.62 (dd, $J_1 = 15.2$ Hz, $J_2 = 6.0$ Hz, 1H), 2.26-2.45 (m, 3H), 1.35-1.55 (m, 13H), 1.07 (d, $J = 6.0$ Hz, 3H), 1.02 (s, 9H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 209.1, 155.5, 135.7, 134.2, 133.7, 129.6, 129.5, 127.5, 127.4, 79.1, 74.2, 66.5, 59.0, 52.2, 49.8, 43.5, 31.3, 28.3, 23.6, 19.7, 19.1.
- IR (neat) cm^{-1} 2930, 2858, 1712, 1502, 1427, 1365, 1172, 1111, 822, 741, 703.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{31}\text{H}_{47}\text{NO}_5\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 564.3116, found 564.3109.
- $[\alpha]_D^{24.5} = 6.34$ ($c = 9.0$ in CHCl_3).

methyl (3R,9R)-3-((tert-butoxycarbonyl)amino)-9-((tert-butyldiphenylsilyloxy)-7-oxodecanoate (3c)



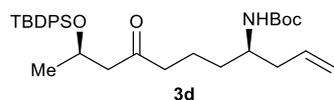
According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-((*tert*-butyldiphenylsilyloxy)hex-1-en-3-one (105.6 mg, 0.3mmol), methyl (*S*)-3-((*tert*-

butoxycarbonyl)amino)-4-iodobutanoate (68.6 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3c** (91.1 mg, 80% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 30%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 (d, $J = 7.2$ Hz, 4H), 7.35-7.42 (m, 6H), 4.92 (d, $J = 9.2$ Hz, 1H), 4.28-4.32 (m, 1H), 3.84-3.89 (m, 1H), 3.66 (s, 3H), 2.61 (dd, $J_1 = 15.2$ Hz, $J_2 = 6.0$ Hz, 1H), 2.27-2.53 (m, 5H), 1.42-1.58 (m, 13H), 1.07 (d, $J = 6.0$ Hz, 3H), 1.01 (s, 9H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 208.8, 171.9, 155.2, 135.7, 134.2, 133.7, 129.6, 129.5, 127.5, 127.4, 79.2, 66.4, 52.2, 51.6, 47.2, 43.2, 38.9, 33.6, 28.3, 26.9, 23.6, 19.7, 19.1.
- IR (neat) cm^{-1} 2931, 2857, 1712, 1505, 1428, 1365, 1246, 1169, 1111, 822, 741, 703.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{32}\text{H}_{47}\text{NO}_6\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 592.3065, found 592.3060.

- $[\alpha]_D^{24.5} = 14.6$ ($c = 0.21$ in CHCl_3).

tert-butyl ((4R,10R)-10-((tert-butyldiphenylsilyl)oxy)-8-oxoundec-1-en-4-yl)carbamate (3d)

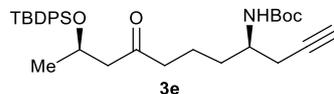


According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-((*tert*-butyldiphenylsilyl)oxy)hex-1-en-3-one (105.6 mg, 0.3mmol), *tert*-butyl (*S*)-(1-iodopent-4-en-2-yl)carbamate

(62.2 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3d** (79.5 mg, 74% yield).

- Colorless oily liquid.
- $R_f = 0.6$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 (d, $J = 7.2$ Hz, 4H), 7.35-7.42 (m, 6H), 5.69-5.79 (m, 1H), 5.03-5.08 (m, 2H), 4.29-4.34 (m, 2H), 3.56-3.59 (m, 1H), 2.61 (dd, $J_1 = 15.2$ Hz, $J_2 = 6.0$ Hz, 1H), 2.11-2.44 (m, 5H), 1.35-1.58 (m, 13H), 1.07 (d, $J = 6.0$ Hz, 3H), 1.02 (s, 9H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 209.1, 155.5, 135.8, 134.3, 134.2, 133.8, 129.6, 129.5, 127.6, 127.5, 117.7, 79.0, 66.5, 52.3, 49.7, 43.4, 39.4, 33.8, 28.4, 26.9, 23.7, 19.6, 19.1.
- IR (neat) cm^{-1} 1712, 1110, 702, 403.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{32}\text{H}_{47}\text{NO}_4\text{Si}$ ($\text{M}+\text{H}$) $^+$ 538.3373, found 538.3377.
- $[\alpha]_D^{24.5} = 17.4$ ($c = 3.0$ in CHCl_3).

tert-butyl ((4R,10R)-10-((tert-butyldiphenylsilyl)oxy)-8-oxoundec-1-yn-4-yl)carbamate (3e)

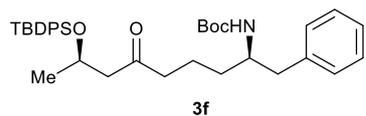


According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-((*tert*-butyldiphenylsilyl)oxy)hex-1-en-3-one (105.6 mg, 0.3mmol), *tert*-butyl (*S*)-(1-iodopent-4-yn-2-yl)carbamate

(61.8 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3e** (86.7 mg, 81% yield).

- Colorless oily liquid.
- $R_f = 0.6$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 (d, $J = 7.2$ Hz, 4H), 7.35-7.44 (m, 6H), 4.62 (d, $J = 8.8$ Hz, 1H), 4.27-4.35 (m, 1H), 3.65-3.71 (m, 1H), 2.61 (dd, $J_1 = 15.2$ Hz, $J_2 = 6.0$ Hz, 1H), 2.27-2.46 (m, 5H), 1.97-1.99 (m, 1H), 1.44-1.57 (m, 13H), 1.08 (d, $J = 6.0$ Hz, 3H), 1.02 (s, 9H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 208.9, 155.2, 135.7, 134.2, 133.7, 129.6, 129.5, 127.6, 127.4, 80.2, 79.3, 70.7, 66.5, 52.2, 48.3, 43.3, 32.9, 28.3, 26.9, 24.5, 23.7, 19.6, 19.1.
- IR (neat) cm^{-1} 3312, 2931, 2857, 1712, 1503, 1427, 1365, 1247, 822, 741, 703.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{32}\text{H}_{45}\text{NO}_4\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 558.3010, found 558.3001.
- $[\alpha]_D^{24.5} = 20.3$ ($c = 0.26$ in CHCl_3).

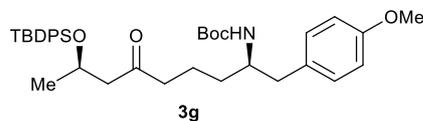
tert-butyl ((2R,8R)-8-((tert-butyldiphenylsilyl)oxy)-6-oxo-1-phenylnonan-2-yl)carbamate (3f)



According to the General Procedure C, Ru(bpy)₃Cl₂ (6.4 mg, 5 mol%), (R)-5-((*tert*-butyldiphenylsilyl)oxy)hex-1-en-3-one (105.6 mg, 0.3 mmol), *tert*-butyl (*S*)-(1-iodo-3-phenylpropan-2-yl)carbamate (72.2 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3f** (93.9 mg, 80% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, $J = 4.8$ Hz, 4H), 7.13-7.43 (m, 11H), 4.27-4.35 (m, 2H), 3.77 (s, 1H), 2.55-2.80 (m, 3H), 2.21-2.42 (m, 3H), 1.33-1.61 (m, 13H), 1.07 (d, $J = 4.0$ Hz, 3H), 1.02 (s, 9H).
- ¹³C NMR (101 MHz, CDCl₃) δ 209.0, 155.4, 138.0, 135.7, 134.2, 133.7, 129.6, 129.5, 129.4, 129.3, 128.2, 127.5, 127.4, 126.2, 79.0, 66.4, 52.3, 51.2, 43.3, 41.2, 33.2, 28.3, 26.8, 23.6, 19.6, 19.1.
- IR (neat) cm⁻¹ 2931, 2857, 1710, 1496, 1454, 1427, 1365, 1170, 1111, 1037, 997, 822, 701.
- HRMS (ESI-TOF, m/z) calcd for C₃₆H₄₉NO₄Si (M+Na)⁺ 610.3323, found 610.3317.
- $[\alpha]_D^{24.5} = 4.82$ ($c = 7.0$ in CHCl₃).

***tert*-butyl ((2*R*,8*R*)-8-((*tert*-butyldiphenylsilyl)oxy)-1-(4-methoxyphenyl)-6-oxononan-2-yl)carbamate (3g)**

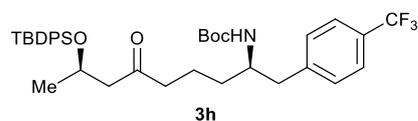


According to the General Procedure C, Ru(bpy)₃Cl₂ (6.4 mg, 5 mol%), (R)-5-((*tert*-butyldiphenylsilyl)oxy)hex-1-en-3-one (105.6 mg, 0.3 mmol), *tert*-butyl (*S*)-(1-iodo-3-(4-methoxyphenyl)propan-2-yl)carbamate (78.2 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3g** (118.5 mg, 96% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 30%).
- ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, $J = 7.2$ Hz, 4H), 7.36-7.43 (m, 6H), 7.07 (d, $J = 5.2$ Hz, 2H), 6.83 (d, $J = 5.2$ Hz, 2H), 4.29-4.33 (m, 2H), 3.72-3.78 (m, 4H), 2.58-2.73 (m, 3H), 2.22-2.42 (m, 3H), 1.36-1.60 (m, 13H), 1.07 (d, $J = 6.0$ Hz, 3H), 1.02 (s, 9H).
- ¹³C NMR (101 MHz, CDCl₃) δ 209.1, 158.0, 155.4, 135.7, 134.2, 133.7, 130.3, 130.0, 129.6, 129.5, 127.5, 127.4, 113.6, 78.9, 66.4, 55.1, 52.3, 51.3, 43.4, 40.2, 33.1, 28.3, 26.8, 23.6, 19.6, 19.1.
- IR (neat) cm⁻¹ 2931, 2857, 1710, 1612, 1454, 1427, 1365, 1247, 1111, 1037, 997, 822, 741, 703.
- HRMS (ESI-TOF, m/z) calcd for C₃₇H₅₁NO₅Si (M+Na)⁺ 640.3429, found 640.3425.

- $[\alpha]_D^{24.5} = 9.89$ ($c = 0.28$ in CHCl_3).

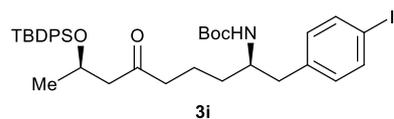
tert-butyl ((2R,8R)-8-((tert-butyldiphenylsilyloxy)-6-oxo-1-(4-(trifluoromethyl)phenyl)nonan-2-yl)carbamate (3h)



According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-((*tert*-butyldiphenylsilyloxy)hex-1-en-3-one (105.6 mg, 0.3mmol), *tert*-butyl (*S*)-(1-iodo-3-(4-(trifluoromethyl)phenyl)propan-2-yl)carbamate (85.8 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3h** (119.3 mg, 91% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 (d, $J = 7.2$ Hz, 4H), 7.35-7.48 (m, 10H), 4.29-4.34 (m, 2H), 3.75-3.79 (m, 1H), 2.80 (d, $J = 4.8$ Hz, 2H), 2.60 (dd, $J_1 = 10.0$ Hz, $J_2 = 4.0$ Hz, 1H), 2.23-2.42 (m, 3H), 1.33-1.63 (m, 13H), 1.07 (d, $J = 4.0$ Hz, 3H), 1.02 (s, 9H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 208.9, 155.3, 139.1, 135.7, 134.2, 133.7, 132.7, 129.6, 129.5, 128.7, 127.5, 127.4, 126.1, 123.1, 123.1, 79.2, 66.5, 52.3, 51.2, 43.2, 41.1, 33.3, 28.2, 26.8, 23.6, 19.6, 19.1.
- IR (neat) cm^{-1} 2932, 1709, 1505, 1450, 1428, 1366, 1124, 1074, 822, 740, 702, 611.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{37}\text{H}_{48}\text{F}_3\text{NO}_4\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 678.3197, found 678.3193.
- $[\alpha]_D^{24.5} = 8.03$ ($c = 0.22$ in CHCl_3).

tert-butyl ((2R,8R)-8-((tert-butyldiphenylsilyloxy)-1-(4-iodophenyl)-6-oxononan-2-yl)carbamate (3i)

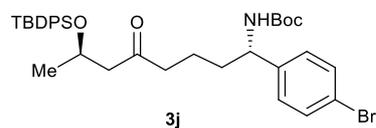


According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-((*tert*-butyldiphenylsilyloxy)hex-1-en-3-one (105.6 mg, 0.3mmol), *tert*-butyl (*S*)-(1-iodo-3-(4-iodophenyl)propan-2-yl)carbamate (97.4 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3i** (122.7 mg, 86% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 (d, $J = 6.4$ Hz, 4H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.34-7.44 (m, 6H), 6.91 (d, $J = 8.0$ Hz, 2H), 4.26-4.33 (m, 2H), 3.72 (s, 1H), 2.57-2.73 (m, 3H), 2.20-2.42 (m, 3H), 1.32-1.61 (m, 13H), 1.07 (d, $J = 6.0$ Hz, 3H), 1.02 (s, 9H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 209.0, 155.4, 137.8, 137.3, 135.8, 134.2, 133.7, 131.5, 129.7, 129.6, 127.6, 127.5, 91.6, 79.2, 66.5, 52.3, 51.2, 43.3, 40.8, 33.2, 28.3, 26.9, 23.7, 19.6, 19.1.

- IR (neat) cm^{-1} 2930, 2856, 1709, 1485, 1427, 1365, 1248, 1169, 1111, 822, 740, 705.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{36}\text{H}_{48}\text{INO}_4\text{Si}$ ($\text{M}+\text{Na}$)⁺ 736.2289, found 736.2288.
- $[\alpha]_{\text{D}}^{24.5} = 8.22$ ($c = 0.18$ in CHCl_3).

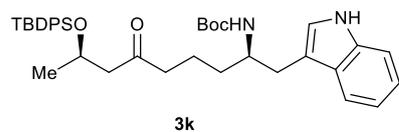
tert-butyl ((1S,7R)-1-(4-bromophenyl)-7-((tert-butyldiphenylsilyl)oxy)-5-oxooctyl)carbamate (3j)



According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-((*tert*-butyldiphenylsilyl)oxy)hex-1-en-3-one (105.6 mg, 0.3mmol), *tert*-butyl (*R*)-(1-(4-bromophenyl)-2-iodoethyl)carbamate (85.0 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3j** (106.8 mg, 82% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 7.2$ Hz, 4H), 7.10-7.67 (m, 10H), 4.87 (d, $J = 7.6$ Hz, 1H), 4.51 (s, 1H), 4.28-4.32 (m, 1H), 3.65-3.71 (m, 1H), 2.59 (dd, $J_1 = 15.2$ Hz, $J_2 = 6.0$ Hz, 1H), 2.31-2.42 (m, 3H), 1.41-1.60 (m, 13H), 1.07 (d, $J = 6.0$ Hz, 3H), 1.01 (s, 9H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 208.7, 155.2, 141.9, 135.7, 134.2, 133.8, 131.1, 129.7, 129.6, 127.9, 127.6, 127.5, 120.9, 79.6, 66.5, 54.6, 52.6, 43.3, 36.3, 28.8, 27.4, 23.1, 20.1, 19.1.
- IR (neat) cm^{-1} 2930, 1702, 1488, 1427, 1365, 1512, 1247, 1275, 1169, 1111, 822, 740, 702.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{35}\text{H}_{46}\text{BrNO}_4\text{Si}$ ($\text{M}+\text{Na}$)⁺ 674.2271, found 674.2266.
- $[\alpha]_{\text{D}}^{24.5} = -9.5$ ($c = 0.10$ in CHCl_3).

tert-butyl ((2R,8R)-8-((tert-butyldiphenylsilyl)oxy)-1-(1H-indol-3-yl)-6-oxononan-2-yl)carbamate (3k)



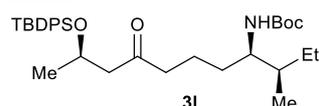
According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-((*tert*-butyldiphenylsilyl)oxy)hex-1-en-3-one (105.6 mg, 0.3mmol), *tert*-butyl (*S*)-(1-(1H-indol-3-yl)-3-iodopropan-2-yl)carbamate (80.0 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3k** (102.7 mg, 82% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 2.4$ Hz, 1H), 7.66 (d, $J = 7.2$ Hz, 4H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.34-7.43 (m, 6H), 7.19 (m, 2H), 6.99 (s, 1H), 4.44 (d, $J = 8.8$ Hz, 1H), 4.29-4.33 (m, 1H), 3.89 (s, 1H), 2.87-2.93 (m, 2H), 2.59 (dd, $J_1 = 15.2$ Hz, $J_2 = 6.0$ Hz, 1H), 2.19-2.42 (m, 3H), 1.36-1.61 (m, 13H), 1.07 (d, $J = 6.0$ Hz, 3H), 1.03 (s, 9H).

- ^{13}C NMR (101 MHz, CDCl_3) δ 209.2, 155.6, 136.1, 135.7, 134.2, 133.8, 129.7, 129.5, 127.9, 127.6, 127.4, 122.6, 121.8, 119.3, 119.0, 111.9, 111.0, 78.9, 66.4, 52.3, 50.7, 43.3, 33.5, 30.5, 28.3, 26.8, 23.6, 19.8, 19.1.
- IR (neat) cm^{-1} 2930, 1692, 1365, 1219, 1111, 772, 702.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{38}\text{H}_{50}\text{N}_2\text{O}_4\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 649.3432, found 649.3431.
- $[\alpha]_{\text{D}}^{24.5} = 3.72$ ($c = 3.0$ in CHCl_3).

tert-butyl ((3R,4R,10R)-10-((tert-butyldiphenylsilyl)oxy)-3-methyl-8-oxoundecan-4-yl)carbamate

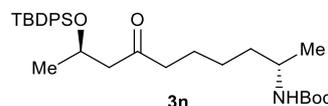
e (3l)



According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-((*tert*-butyldiphenylsilyl)oxy)hex-1-en-3-one (105.6 mg, 0.3 mmol), *tert*-butyl ((2*S*,3*R*)-1-iodo-3-methylpentan-2-yl)carbamate (65.4 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3l** (84.1 mg, 76% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 7.2$ Hz, 4H), 7.35-7.44 (m, 6H), 4.28-4.34 (m, 2H), 3.41-3.48 (m, 1H), 2.62 (dd, $J_1 = 15.2$ Hz, $J_2 = 6.0$ Hz, 1H), 2.36-2.45 (m, 2H), 2.23-2.31 (m, 1H), 1.56-1.65 (m, 2H), 1.33-1.49 (m, 13H), 1.14-1.22 (m, 1H), 1.07 (d, $J = 8.0$ Hz, 3H), 1.02 (s, 9H), 0.89 (t, $J = 8.0$ Hz, 3H), 0.83 (d, $J = 8.0$ Hz, 3H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 209.2, 155.8, 135.7, 134.3, 133.8, 129.6, 129.5, 127.5, 127.4, 78.8, 66.5, 54.2, 52.3, 43.5, 38.7, 30.7, 28.4, 26.9, 25.0, 23.6, 19.9, 19.1, 15.0, 11.7.
- IR (neat) cm^{-1} 2963, 2931, 2858, 1711, 1504, 1460, 1427, 1171, 1111, 822, 740, 702.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{33}\text{H}_{51}\text{NO}_4\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 576.3479, found 576.3476.
- $[\alpha]_{\text{D}}^{24.5} = 0.86$ ($c = 0.90$ in CHCl_3).

tert-butyl ((2S,9R)-9-((tert-butyldiphenylsilyl)oxy)-7-oxodecan-2-yl)carbamate (3n)



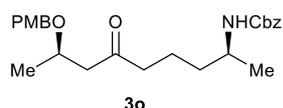
According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-((*tert*-butyldiphenylsilyl)oxy)hex-1-en-3-one (105.6 mg, 0.3 mmol), *tert*-butyl (*S*)-(4-iodobutan-2-yl)carbamate (59.8 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3n** (87.2 mg, 83% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 7.2$ Hz, 4H), 7.35-7.42 (m, 6H), 4.29-4.33 (m, 2H), 3.58-3.64 (m, 1H), 2.61 (dd, $J_1 = 15.2$ Hz, $J_2 = 6.0$ Hz, 1H), 2.42 (dd, $J_1 = 15.2$ Hz, $J_2 = 6.0$

Hz, 1H), 2.28-2.33 (m, 2H), 1.43-1.50 (m, 11H), 1.21-1.37 (m, 5H), 1.07-1.09 (m, 6H), 1.02 (s, 9H).

- ^{13}C NMR (101 MHz, CDCl_3) δ 209.2, 155.3, 135.7, 134.2, 133.7, 129.6, 129.5, 127.5, 127.4, 78.8, 66.5, 52.2, 43.7, 37.1, 28.3, 26.8, 25.5, 23.6, 23.2, 21.2, 19.1.
- IR (neat) cm^{-1} 2931, 2857, 1709, 1505, 1427, 1365, 1245, 1170, 1111, 822, 742, 702.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{31}\text{H}_{47}\text{NO}_4\text{Si}$ ($\text{M}+\text{Na}$) $^+$ 548.3166 found 548.3163.
- $[\alpha]_{\text{D}}^{24.5} = 4.48$ ($c = 7.0$ in CHCl_3).

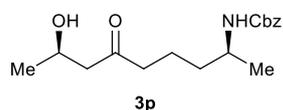
benzyl ((2S,8R)-8-((4-methoxybenzyl)oxy)-6-oxononan-2-yl)carbamate (3o)



According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-((4-methoxybenzyl)oxy)hex-1-en-3-one (70.3 mg, 0.3 mmol), benzyl (*S*)-(1-iodopropan-2-yl)carbamate (63.8 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3o** (64.1 mg, 75% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 30%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.37 (m, 5H), 7.21 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 5.04-5.11 (m, 2H), 4.59 (d, $J = 9.2$ Hz, 1H), 4.47 (d, $J = 10.8$ Hz, 1H), 4.35 (d, $J = 11.2$ Hz, 1H), 3.95-4.04 (m, 1H), 3.77 (s, 3H), 3.65-3.72 (m, 1H), 2.73 (dd, $J_1 = 15.6$ Hz, $J_2 = 7.6$ Hz, 1H), 2.37-2.44 (m, 3H), 1.50-1.64 (m, 2H), 1.35-1.41 (m, 2H), 1.20 (d, $J = 6.4$ Hz, 3H), 1.11 (d, $J = 6.4$ Hz, 3H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 209.3, 159.1, 155.8, 136.6, 130.6, 129.3, 128.6, 128.5, 128.0, 113.7, 71.4, 70.5, 66.5, 55.2, 49.9, 46.8, 43.4, 36.3, 21.1, 19.8, 19.7.
- IR (neat) cm^{-1} 3331, 2967, 2036, 1710, 1612, 1513, 1454, 1247, 1173, 1034, 822, 698.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{25}\text{H}_{33}\text{NO}_5$ ($\text{M}+\text{Na}$) $^+$ 450.2251, found 450.2245.
- $[\alpha]_{\text{D}}^{24.5} = -12.5$ ($c = 0.13$ in CHCl_3).

benzyl ((2S,8R)-8-hydroxy-6-oxononan-2-yl)carbamate (3p)



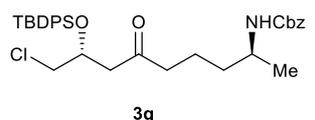
According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-hydroxyhex-1-en-3-one (34.3 mg, 0.3 mmol), benzyl (*S*)-(1-iodopropan-2-yl)carbamate (63.8 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3p** (43.6 mg, 71% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.37 (m, 5H), 5.07 (s, 2H), 4.61 (d, $J = 8.8$ Hz, 1H), 4.16-

4.24 (m, 1H), 3.67-3.74 (m, 1H), 3.01 (s, 1H), 2.36-2.59 (m, 4H), 1.38-1.67 (m, 4H), 1.12-1.18 (m, 6H).

- ^{13}C NMR (101 MHz, CDCl_3) δ 211.8, 155.8, 136.6, 128.5, 128.1, 128.0, 66.5, 63.9, 50.5, 46.7, 42.8, 36.3, 22.4, 21.1, 19.7.
- IR (neat) cm^{-1} 3333, 2917, 1698, 1534, 1251, 1089, 697, 466.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_4$ ($\text{M}+\text{Na}$) $^+$ 330.1676, found 330.1674.
- $[\alpha]_{\text{D}}^{24.5} = -11.6$ ($c = 6.0$ in CHCl_3).

benzyl ((2S,8R)-8-((tert-butylidiphenylsilyl)oxy)-9-chloro-6-oxononan-2-yl)carbamate (3q)

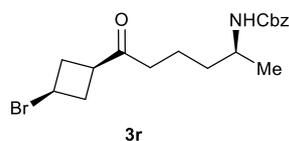


According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-((*tert*-butylidiphenylsilyl)oxy)-6-chlorohex-1-en-3-one (115.9 mg, 0.3 mmol), benzyl (*S*)-(1-iodopropan-2-yl)carbamate (63.8 mg,

0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3q** (95.0 mg, 82% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.63-7.70 (m, 4H), 7.28-7.47 (m, 11H), 5.05-5.12 (m, 2H), 4.37-4.58 (m, 2H), 3.64-3.71 (m, 1H), 3.47 (d, $J = 4.4$ Hz, 2H), 2.62-2.81 (m, 2H), 2.30-2.33 (m, 2H), 1.44-1.56 (m, 2H), 1.31-1.37 (m, 2H), 1.12 (d, $J = 6.8$ Hz, 3H), 1.04 (s, 9H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 208.0, 155.7, 136.5, 135.7, 133.3, 133.1, 129.9, 129.9, 128.4, 128.0, 127.7, 127.7, 127.7, 68.7, 66.4, 48.5, 46.9, 46.8, 43.1, 36.2, 26.8, 21.0, 19.6, 19.2.
- IR (neat) cm^{-1} 2932, 1712, 1529, 1427, 1245, 1111, 822, 740, 701.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{33}\text{H}_{42}\text{ClNO}_4\text{Si}$ ($\text{M}+\text{H}$) $^+$ 580.2673, found 580.2677.
- $[\alpha]_{\text{D}}^{24.5} = 8.44$ ($c = 7.0$ in CHCl_3).

benzyl ((S)-6-((1S,3R)-3-bromocyclobutyl)-6-oxohexan-2-yl)carbamate (3r)



According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), 1-((1*S*, 3*S*)-3-bromocyclobutyl)prop-2-en-1-one (56.4 mg, 0.3 mmol), benzyl (*S*)-(1-iodopropan-2-yl)carbamate (63.8 mg, 0.2 mmol), and

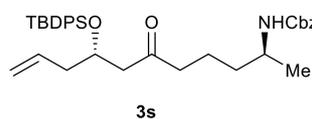
DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3r** (56.4 mg, 74% yield).

- Yellow oil liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.37 (m, 5H), 5.07 (s, 2H), 4.46-4.60 (m, 2H), 3.47-3.74 (m, 2H), 2.80-2.86 (m, 2H), 2.55-2.62 (m, 2H), 2.32-2.47 (m, 2H), 1.52-1.64 (m, 2H), 1.37-1.43 (m, 2H), 1.12-1.14 (d, $J = 6.4$ Hz, 3H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 210.2, 155.8, 136.6, 128.5, 128.1, 128.0, 66.5, 46.7, 42.4, 40.7,

40.3, 36.6, 36.4, 21.1, 19.7.

- IR (neat) cm^{-1} 2937, 1704, 1525, 1453, 1219, 1068, 772, 697.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{18}\text{H}_{24}\text{BrNO}_3$ ($\text{M}+\text{Na}$)⁺ 404.0832, found 404.0840.
- $[\alpha]_{\text{D}}^{24.5} = 5.35$ ($c = 0.10$ in CHCl_3).

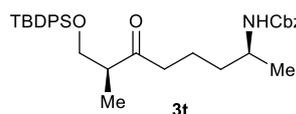
benzyl ((2S,8S)-8-((tert-butyldiphenylsilyl)oxy)-6-oxoundec-10-en-2-yl)carbamate (3s)



According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*S*)-5-((*tert*-butyldiphenylsilyl)oxy)octa-1,7-dien-3-one (113.5 mg, 0.3mmol), benzyl (*S*)-(1-iodopropan-2-yl)carbamate (63.8 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3s** (82.3 mg, 72% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65-7.69 (m, 4H), 7.30-7.44 (m, 11H), 5.64-5.75 (m, 1H), 4.89-5.12 (m, 4H), 4.56 (d, $J = 8.4$ Hz, 1H), 4.26-4.32 (m, 1H), 3.63-3.70 (m, 1H), 2.50 (d, $J = 6.4$ Hz, 2H), 2.13-2.32 (m, 4H), 1.29-1.52 (m, 4H), 1.11 (d, $J = 6.8$ Hz, 3H), 1.03 (s, 9H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 208.8, 155.7, 136.6, 135.8, 135.8, 134.0, 133.9, 133.8, 129.6, 129.6, 128.4, 128.0, 127.6, 127.5, 127.5, 117.7, 69.3, 66.4, 49.0, 46.8, 43.3, 41.5, 36.2, 26.9, 21.0, 19.5, 19.2.
- IR (neat) cm^{-1} 2932, 1711, 1526, 1427, 1219, 1111, 772, 702, 611.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{35}\text{H}_{45}\text{NO}_4\text{Si}$ ($\text{M}+\text{Na}$)⁺ 594.3010, found 594.3005.
- $[\alpha]_{\text{D}}^{24.5} = 6.80$ ($c = 5.0$ in CHCl_3).

benzyl ((2S,7R)-8-((tert-butyldiphenylsilyl)oxy)-7-methyl-6-oxooctan-2-yl)carbamate (3t)

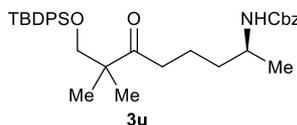


According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R*)-5-((*tert*-butyldiphenylsilyl)oxy)-4-methylpent-1-en-3-one (105.6 mg, 0.3mmol), benzyl (*S*)-(1-iodopropan-2-yl)carbamate (63.8 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3t** (92.7 mg, 85% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62-7.65 (m, 4H), 7.29-7.45 (m, 11H), 5.05-5.12 (m, 2H), 4.61-4.63 (d, $J = 8.4$ Hz, 1H), 3.62-3.83 (m, 3H), 2.77-2.81 (m, 1H), 2.45-2.60 (m, 2H), 1.54-1.68 (m, 2H), 1.38-1.44 (m, 2H), 1.14 (d, $J = 6.8$ Hz, 3H), 0.99-1.03 (m, 12H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 213.1, 155.8, 136.7, 135.6, 135.5, 133.3, 133.2, 129.7, 128.5, 128.1, 128.0, 127.7, 66.5, 66.2, 48.5, 47.0, 42.0, 36.4, 26.8, 21.1, 19.6, 19.2, 13.0.

- IR (neat) cm^{-1} 3336, 2931, 1710, 1528, 1454, 1428, 1245, 1111, 823, 740, 702.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{33}\text{H}_{43}\text{NO}_4\text{Si}$ ($\text{M}+\text{H}$)⁺ 546.3073, found 546.3076.
- $[\alpha]_{\text{D}}^{24.5} = 17.9$ ($c = 0.41$ in CHCl_3).

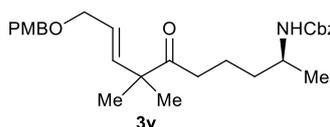
benzyl (S)-8-((tert-butylidiphenylsilyl)oxy)-7,7-dimethyl-6-oxooctan-2-yl)carbamate (3u)



According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), 5-((*tert*-butyldiphenylsilyl)oxy)-4,4-dimethylpent-1-en-3-one (109.8 mg, 0.3 mmol), benzyl (*S*)-(1-iodopropan-2-yl)carbamate (63.8 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3u** (102.9 mg, 92% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 8.0$ Hz, 4H), 7.29-7.45 (m, 11H), 5.05-5.12 (m, 2H), 4.64 (d, $J = 8.4$ Hz, 1H), 3.61-3.75 (m, 3H), 2.49-2.55 (m, 2H), 1.53-1.67 (m, 2H), 1.37-1.42 (m, 2H), 1.11-1.14 (m, 9H), 1.04 (s, 9H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 214.3, 155.7, 136.6, 135.6, 133.1, 129.7, 128.4, 128.0, 127.9, 127.6, 70.7, 66.4, 49.5, 46.9, 37.3, 36.3, 26.7, 21.6, 21.0, 19.6, 19.2.
- IR (neat) cm^{-1} 2931, 1705, 1528, 1472, 1427, 1246, 1111, 823, 740, 701.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{34}\text{H}_{45}\text{NO}_4\text{Si}$ ($\text{M}+\text{Na}$)⁺ 560.3173, found 560.3170.
- $[\alpha]_{\text{D}}^{24.5} = 3.50$ ($c = 6.0$ in CHCl_3).

benzyl (S,E)-(10-((4-methoxybenzyl)oxy)-7,7-dimethyl-6-oxodec-8-en-2-yl)carbamate (3v)



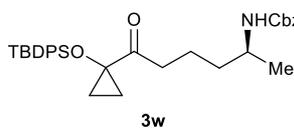
According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*E*)-7-((4-methoxybenzyl)oxy)-4,4-dimethylhepta-1,5-dien-3-one (82.3 mg, 0.3 mmol), benzyl (*S*)-(1-iodopropan-2-yl)carbamate (63.8 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3v** (75.7 mg, 81% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 40%).
- ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.35 (m, 7H), 6.87 (d, $J = 8.8$ Hz, 2H), 5.62-5.79 (m, 2H), 5.06-5.10 (m, 2H), 4.62 (d, $J = 8.4$ Hz, 1H), 4.43 (s, 2H), 3.99 (d, $J = 5.6$ Hz, 2H), 3.79 (s, 3H), 3.64-3.71 (m, 1H), 2.43-2.48 (m, 2H), 1.33-1.60 (m, 4H), 1.21 (s, 6H), 1.11 (d, $J = 6.4$ Hz, 1H).
- ^{13}C NMR (101 MHz, CDCl_3) δ 212.7, 159.2, 155.7, 137.3, 136.6, 130.2, 129.4, 128.5, 128.1, 128.0, 126.4, 113.8, 71.9, 70.3, 66.4, 55.2, 49.9, 46.9, 36.9, 36.3, 23.9, 21.1, 20.1.
- IR (neat) cm^{-1} 3329, 2966, 1706, 1612, 1513, 1454, 1362, 1301, 1247, 1173, 979, 820, 736.

■ HRMS (ESI-TOF, m/z) calcd for C₂₈H₃₇NO₅ (M+H)⁺ 468.2773, found 468.2777.

■ [α]_D^{24.5} = 9.03 (c = 0.15 in CHCl₃).

benzyl (S)-6-(1-((tert-butyldiphenylsilyl)oxy)cyclopropyl)-6-oxohexan-2-yl)carbamate (3w)



According to the General Procedure C, Ru(bpy)₃Cl₂ (6.4 mg, 5 mol%), 1-(1-((tert-butyldiphenylsilyl)oxy)cyclopropyl)prop-2-en-1-one (105.1 mg, 0.3mmol), benzyl (S)-(1-iodopropan-2-yl)carbamate (63.8

mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3w** (90.2 mg, 83% yield).

■ Colorless oily liquid.

■ R_f = 0.5 (ethyl acetate/petroleum ether = 20%).

■ ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 8.0 Hz, 4H), 7.29-7.45 (m, 11H), 5.05-5.12 (m, 2H), 4.57 (d, J = 8.4 Hz, 1H), 3.61-3.68 (m, 1H), 2.58-2.61 (m, 2H), 1.43-1.52 (m, 2H), 1.23-1.29 (m, 3H), 1.06-1.16 (m, 15H).

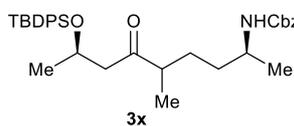
■ ¹³C NMR (101 MHz, CDCl₃) δ 211.2, 155.6, 136.6, 135.5, 133.6, 133.6, 129.9, 128.4, 128.0, 128.0, 127.6, 66.4, 64.4, 47.0, 38.2, 36.2, 26.8, 21.0, 19.7, 19.2, 19.1, 19.0.

■ IR (neat) cm⁻¹ 3337, 2932, 2857, 1702, 1528, 1453, 1427, 1265, 1110, 1061, 822, 740.

■ HRMS (ESI-TOF, m/z) calcd for C₃₃H₄₁NO₄Si (M+H)⁺ 544.2873, found 544.2870.

■ [α]_D^{24.5} = 6.40 (c = 5.0 in CHCl₃).

benzyl ((2S,8R)-8-((tert-butyldiphenylsilyl)oxy)-5-methyl-6-oxononan-2-yl)carbamate (3x)



According to the General Procedure C, Ru(bpy)₃Cl₂ (6.4 mg, 5 mol%), (R)-5-((tert-butyldiphenylsilyl)oxy)-2-methylhex-1-en-3-one (109.9 mg, 0.3mmol), benzyl (S)-(1-iodopropan-2-yl)carbamate (63.8 mg,

0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3x** (98.5 mg, 88% yield).

■ Colorless oily liquid.

■ R_f = 0.5 (ethyl acetate/petroleum ether = 20%).

■ ¹H NMR (400 MHz, CDCl₃) δ 7.66-7.70 (m, 4H), 7.28-7.44 (m, 11H), 5.05-5.12 (m, 2H), 4.50-4.55 (m, 1H), 4.31-4.37 (m, 1H), 3.61-3.68 (m, 1H), 2.60-2.72 (m, 1H), 2.33-2.52 (m, 2H), 1.21-1.63 (m, 4H), 1.07-1.12 (m, 6H), 1.03 (d, J = 2.0 Hz, 9H), 0.96-0.99 (m, 3H).

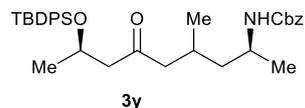
■ ¹³C NMR (101 MHz, CDCl₃) δ 212.2, 155.7, 136.6, 136.5, 135.8, 135.7, 134.4, 134.3, 133.9, 133.8, 129.6, 129.6, 129.5, 129.5, 128.4, 128.1, 128.0, 127.6, 127.5, 127.5, 127.4, 127.4, 66.4, 66.1, 66.0, 50.7, 50.7, 47.0, 46.5, 46.4, 34.4, 28.6, 28.5, 26.9, 23.7, 23.6, 21.1, 19.1, 16.1, 15.9.

■ IR (neat) cm⁻¹ 2965, 2857, 1707, 1530, 1455, 1427, 1241, 1110, 822, 737, 702.

■ HRMS (ESI-TOF, m/z) calcd for C₃₄H₄₅NO₄Si (M+H)⁺ 560.3173, found 560.3171.

- $[\alpha]_D^{24.5} = -1.23$ ($c = 3.0$ in CHCl_3).

benzyl ((2*S*,8*R*)-8-((*tert*-butyldiphenylsilyl)oxy)-4-methyl-6-oxononan-2-yl)carbamate (3y)

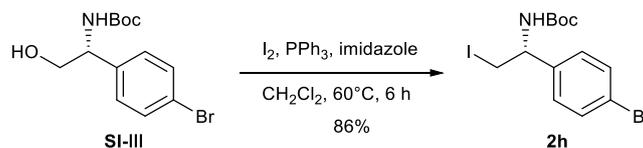


According to the General Procedure C, $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (6.4 mg, 5 mol%), (*R, E*)-6-((*tert*-butyldiphenylsilyl)oxy)hept-2-en-4-one (109.9 mg, 0.3 mmol), benzyl (*S*)-(1-iodopropan-2-yl)carbamate (63.8 mg, 0.2 mmol), and DIPEA (0.1 mL, 0.6 mmol) in acetonitrile (2.0 mL) with irradiation using 440 nm blue LEDs at room temperature for 24 h afforded **3y** (95.1 mg, 85% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66-7.69 (m, 4H), 7.29-7.44 (m, 11H), 5.03-5.15 (m, 2H), 4.54-4.79 (m, 1H), 4.27-4.35 (m, 1H), 3.70-3.77 (m, 1H), 2.34-2.62 (m, 1H), 2.23 (d, $J = 6.8$ Hz, 1H), 1.94-2.04 (m, 1H), 1.23-1.33 (m, 2H), 1.07-1.13 (m, 6H), 1.03 (d, $J = 1.6$ Hz, 9H), 0.84-0.88 (m, 3H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 208.9, 208.7, 155.9, 155.6, 136.7, 136.6, 135.8, 134.3, 134.2, 133.9, 133.8, 129.7, 129.7, 129.6, 129.6, 128.5, 128.5, 128.0, 128.0, 128.0, 127.6, 127.6, 127.5, 66.5, 66.4, 66.3, 66.3, 52.9, 51.1, 50.8, 45.1, 44.9, 44.1, 43.9, 26.9, 25.8, 25.3, 23.7, 22.2, 21.0, 19.8, 19.7, 19.2.
- IR (neat) cm^{-1} 2930, 1706, 1524, 1427, 1238, 1110, 821, 701, 609, 457.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{34}\text{H}_{45}\text{NO}_4\text{Si}$ ($\text{M}+\text{H}$) $^+$ 560.3173, found 560.3176.
- $[\alpha]_D^{24.5} = -3.80$ ($c = 4.0$ in CHCl_3).

4. Synthesis of H_3 Antagonist **8a**

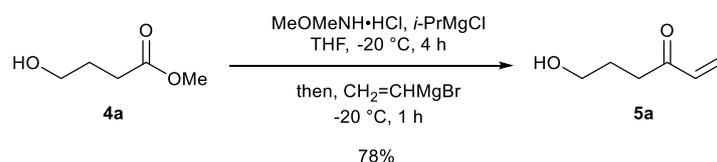
Synthesis of **2h**



A solution of I_2 (5.21 g, 20.5 mmol) and PPh_3 (4.99 g, 18.9 mmol) in CH_2Cl_2 (80.0 mL) was placed in a flame-dried 250 mL round-bottom flask and stirred at room temperature for 5 min, after which imidazole (2.69 g, 39.5 mmol) was added. The mixture was stirred for an additional 15 min, followed by the addition of **SI-III** (5.0 g, 15.8 mmol). The reaction was heated to reflux at 60 °C for 6 h and then cooled to room temperature. The mixture was slowly quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$, followed by extraction with CH_2Cl_2 (4 \times 50.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate =

25:1) to afford compound **2h** (5.8 g, 86% yield).

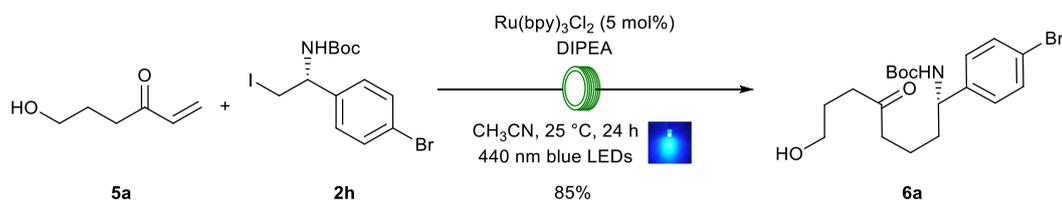
Synthesis of 5a



A solution of compound **4a** (7.67 g, 65.0 mmol) and *N*, *O*-dimethylhydroxylamine hydrochloride (12.68 g, 130.0 mmol) in THF (150.0 mL) was placed in a flame-dried 1 L round-bottom. Under an argon atmosphere, isopropylmagnesium chloride (164.0 mL, 325.0 mmol, 2.0 M in THF) was added dropwise at $-20\text{ }^\circ\text{C}$. The reaction mixture was stirred for 4 h, after which vinylmagnesium bromide (130.0 mL, 130.0 mmol, 1.0 M in THF) was slowly added to the system. The reaction was continued to stir for 1 h, then quenched with ice-cold 1.0 M aqueous HCl (200.0 mL), followed by extraction with CH_2Cl_2 (3 \times 100.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford compound **5a** (5.78 g, 78% yield).

- Yellow oil liquid.
- $R_f = 0.4$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.35 (dd, $J_1 = 17.6\text{ Hz}$, $J_2 = 10.4\text{ Hz}$, 1H), 6.23 (dd, $J_1 = 18.0\text{ Hz}$, $J_2 = 1.6\text{ Hz}$, 1H), 5.83 (dd, $J_1 = 10.4\text{ Hz}$, $J_2 = 1.2\text{ Hz}$, 1H), 3.65 (t, $J = 6.0\text{ Hz}$, 2H), 2.72 (t, $J = 6.8\text{ Hz}$, 2H), 1.90-1.83 (m, 2H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 201.1, 136.4, 128.4, 62.0, 36.2, 26.5.
- IR (neat) cm^{-1} 1711, 1111, 425.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_6\text{H}_{10}\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 115.0773, found 115.0768.

Synthesis of 6a

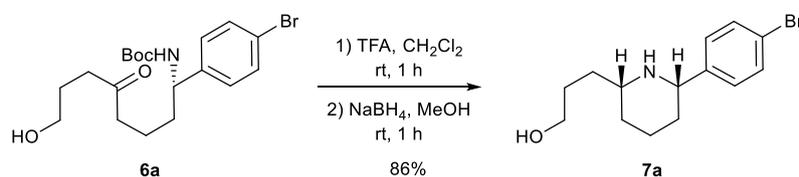


Flow-chemistry conditions: A solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (480.0 mg, 0.75 mmol) was dissolved in a mixed solvent consisting of 25.0 mL of acetonitrile and 15.0 mL of water, a solution of **5a** (2.56 g, 22.5 mmol) in 40.0 mL of acetonitrile, a solution of **2h** (6.41 g, 15.0 mmol) in 40.0 mL of acetonitrile, and a solution of DIPEA (7.8 mL, 45.0 mmol) in 40.0 mL of acetonitrile were each

loaded into a 50 mL syringe. The mixture was pumped at a rate of 10.0 mL/h into a flow reactor, which was irradiated with a blue LED light ($h\nu = 440$ nm) at a distance of 1.0 cm at room temperature. The products were collected and the acetonitrile was removed under reduced pressure. The crude products were purified by silica gel flash column chromatography to afford **6a** (5.26 g, 85%). After multiple cycles of continuous flow chemistry, 10.0 g of **6a** was finally prepared.

- White solid.
- M.p. = 64.5-69.1 °C.
- $R_f = 0.6$ (methanol/dichloromethane = 10%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 5.03 (s, 1H), 4.52 (s, 1H), 3.58 (t, $J = 6.4$ Hz, 2H), 2.50-2.30 (m, 4H), 1.78 (t, $J = 6.4$ Hz, 2H), 1.67-1.47 (m, 4H), 1.37 (s, 9H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 211.1, 155.3, 141.9, 131.6, 128.0, 120.9, 79.6, 62.0, 54.1, 42.0, 39.4, 35.9, 35.8, 28.3, 26.4, 20.2.
- IR (neat) cm^{-1} 3347, 2930, 1691, 1522, 1488, 1453, 1408, 1390, 1365, 1284, 1248, 1167, 1071, 1010, 870, 823, 530.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{19}\text{H}_{28}\text{BrNO}_4$ ($\text{M}+\text{Na}$) $^+$ 436.1092, found 436.1096.
- $[\alpha]_{\text{D}}^{24.5} = -18.64$ ($c = 2.5$ in CHCl_3).

Synthesis of 7a

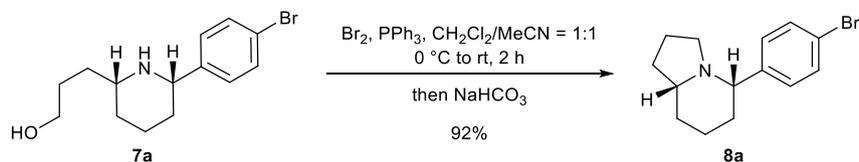


A solution of compound **6a** (949.0 mg, 2.3 mmol) and trifluoroacetic acid (5.1 mL, 69.0 mmol) in CH_2Cl_2 (25.0 mL) was added to a flame-dried 50 mL flask and stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous NaHCO_3 (15.0 mL), followed by extraction with CH_2Cl_2 (3×20.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure.

A solution of the resulting crude product in dry methanol (15.0 mL) was prepared under an argon atmosphere, and NaBH_4 (348.0 mg, 9.2 mmol) was added. The reaction was stirred at room temperature for 1 h, then quenched with saturated aqueous NaHCO_3 (10.0 mL) and extracted with ethyl acetate (3×20.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (dichloromethane/methanol = 100:1) to afford compound **7a** (587.0 mg, 86% yield, $\text{dr} > 20:1$).

- White solid.
- M.p. = 64.6-70.4 °C.
- R_f = 0.4 (methanol/dichloromethane = 10%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 3.68 (dd, J_1 = 11.2 Hz, J_2 = 2.8 Hz, 1H), 3.52 (t, J = 5.6 Hz, 2H), 3.40 (s, 1H), 2.84-2.78 (m, 1H), 1.98-1.25 (m, 10H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.2, 131.6, 128.6, 121.3, 62.6, 61.3, 57.3, 34.9, 33.0, 30.4, 29.0, 24.7.
- IR (neat) cm^{-1} 3295, 2929, 2850, 1488, 1440, 1326, 1072, 1009, 822, 668, 523, 424.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{14}\text{H}_{20}\text{BrNO}$ ($\text{M}+\text{H}$) $^+$ 298.0773, found 298.0772.
- $[\alpha]_{\text{D}}^{24.5}$ = -19.60 (c = 0.5 in CHCl_3).

Synthesis of H_3 Antagonist **8a**



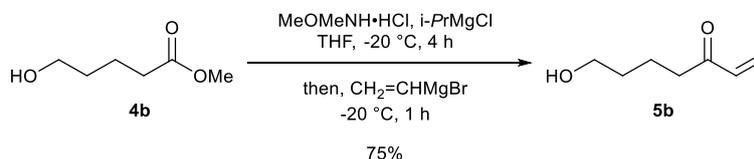
A solution of bromine (12.9 μL , 0.25 mmol) in CH_2Cl_2 (4.2 mL) was added to a flame-dried 25 mL round-bottom flask, followed by the addition of triphenylphosphine (PPh_3 , 137.7 mg, 0.53 mmol). The mixture was stirred at room temperature for 15 min, after which a solution of compound **7a** (74.3 mg, 0.25 mmol) in CH_3CN (4.2 mL) was introduced. The reaction was stirred for an additional 2 h, then quenched with saturated aqueous NaHCO_3 (14.0 mL), followed by extraction with ethyl acetate (3×10.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (dichloromethane/methanol = 100:1) to afford compound **8a** (64.1 mg, 92% yield).

- Off-white foam.
- R_f = 0.6 (methanol/dichloromethane = 10%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 2.91 (dd, J_1 = 10.4 Hz, J_2 = 2.8 Hz, 1H), 2.71 (t, J = 8.8 Hz, 1H), 2.00-1.93 (m, 1H), 1.87-1.75 (m, 4H), 1.70-1.64 (m, 2H), 1.59-1.40 (m, 4H), 1.35-1.26 (m, 1H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.8, 131.3, 129.1, 120.3, 69.0, 65.0, 52.5, 35.4, 30.7, 30.4, 25.0, 20.2.
- IR (neat) cm^{-1} 2931, 1487, 1010, 808, 536, 418.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_{14}\text{H}_{18}\text{BrN}$ ($\text{M}+\text{H}$) $^+$ 280.0673, found 280.0677.

- $[\alpha]_D^{24.5} = -65.20$ ($c = 0.5$ in CHCl_3).

5. Synthesis of H_3 Antagonist **8b**

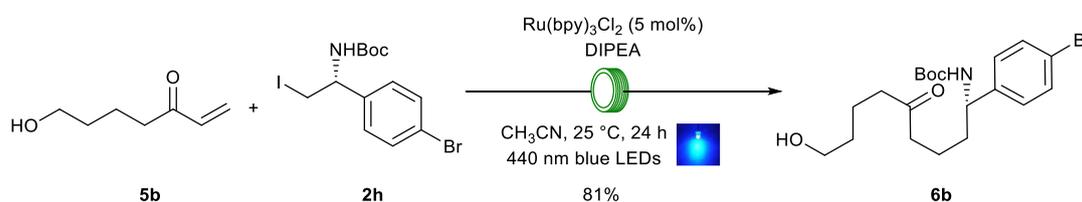
Synthesis of **5b**



According to the synthetic method of compound **5a**, compound **4b** (8.58 g, 65.0 mmol) was converted to compound **5b** (6.24 g, 75% yield).

- Yellow oil liquid.
- $R_f = 0.4$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.34 (dd, $J_1 = 17.6$ Hz, $J_2 = 10.4$ Hz, 1H), 6.20 (d, $J = 17.6$ Hz, 1H), 5.81 (d, $J = 9.2$ Hz, 1H), 3.61 (t, $J = 6.4$ Hz, 2H), 2.62 (t, $J = 7.2$ Hz, 2H), 2.01 (s, 1H), 1.73-1.66 (m, 2H), 1.60-1.53 (m, 2H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 201.0, 136.4, 128.2, 62.2, 39.1, 32.0, 19.8.
- IR (neat) cm^{-1} 3412, 2929, 1677, 1614, 1404, 1060, 987, 432.
- HRMS (ESI-TOF, m/z) calcd for $\text{C}_7\text{H}_{12}\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 129.0873, found 129.0869.

Synthesis of **6b**



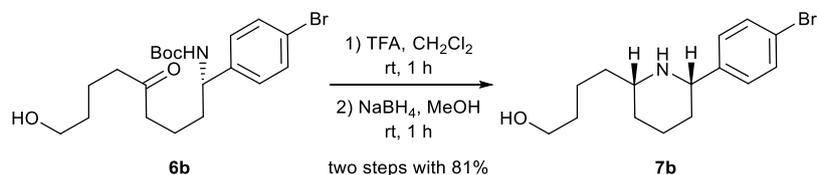
According to the synthetic method of compound **6a**, compound **5b** (4.89 g, 37.1 mmol) and compound **2h** (10.50 g, 24.7 mmol) were converted to compound **6b** (8.54 g, 81% yield).

- White solid.
- M.p. = 69.1-71.4 $^\circ\text{C}$.
- $R_f = 0.5$ (methanol/dichloromethane = 10%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 4.96-4.93 (m, 1H), 4.54 (s, 1H), 3.61 (t, $J = 6.4$ Hz, 2H), 2.43-2.38 (m, 4H), 1.70-1.58 (m, 4H), 1.55-1.48 (m, 4H), 1.40 (s, 9H).
- $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 210.9, 155.3, 141.9, 132.2, 131.6, 128.0, 120.9, 62.1, 42.3, 41.8, 35.9, 32.0, 28.3, 20.1, 19.8.
- IR (neat) cm^{-1} 3347, 2933, 1695, 1518, 1487, 1453, 1390, 1365, 1247, 1167, 1072, 1045, 1010,

823, 528, 407.

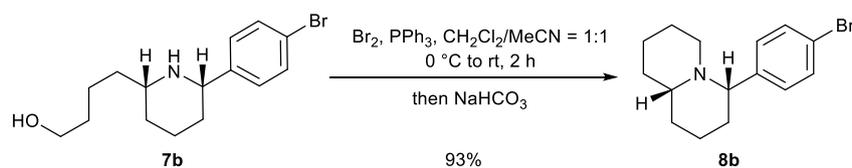
- HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{30}BrNO_4$ ($M+Na$)⁺ 450.1292, found 450.1291.
- $[\alpha]_D^{24.5} = -15.46$ ($c = 1.5$ in $CHCl_3$).

Synthesis of H_3 Antagonist **8b**



According to the synthetic method of compound **7a**, compound **6b** (1.06 g, 2.5 mmol) was converted to compound **7b** (629.7 mg, 81% yield with two steps).

- Off-white foam.
- $R_f = 0.4$ (methanol/dichloromethane = 10%).
- 1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, $J = 8.4$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 3.63-3.58 (m, 3H), 2.68-2.63 (m, 1H), 1.90-1.80 (m, 3H), 1.76-1.67 (m, 2H), 1.58-1.53 (m, 2H), 1.48-1.37 (m, 5H).
- ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 131.3, 128.5, 120.6, 62.5, 61.7, 57.5, 36.8, 34.6, 32.7, 31.8, 25.1, 22.0.
- IR (neat) cm^{-1} 2917, 1010, 426, 410.
- HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{22}BrNO$ ($M+H$)⁺ 312.0973, found 312.0972.
- $[\alpha]_D^{24.5} = -9.00$ ($c = 0.4$ in $CHCl_3$).



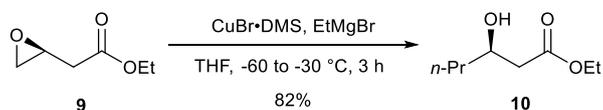
According to the synthetic method of compound **8a**, compound **7b** (77.7 mg, 0.25 mmol) was converted to compound **8b** (68.1 mg, 93% yield).

- Off-white foam.
- $R_f = 0.6$ (methanol/dichloromethane = 10%).
- 1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, $J = 8.8$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 2.86 (dd, $J_1 = 10.8$ Hz, $J_2 = 2.8$ Hz, 1H), 2.62-2.59 (m, 1H), 1.93-1.86 (m, 2H), 1.72-1.53 (m, 6H), 1.46-1.25 (m, 6H).
- ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 131.3, 129.2, 120.1, 69.7, 63.2, 53.6, 36.6, 33.9, 33.6, 26.1, 24.9, 24.6.
- IR (neat) cm^{-1} 2929, 2854, 2781, 1486, 1443, 1383, 1127, 1089, 1069, 1010, 821, 537, 415.
- HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{20}BrN$ ($M+H$)⁺ 294.0873, found 294.0869.

- $[\alpha]_D^{24.5} = -62.08$ ($c = 0.5$ in CHCl_3).

6. Synthesis of (-)-6-*epi*-Porantheridine

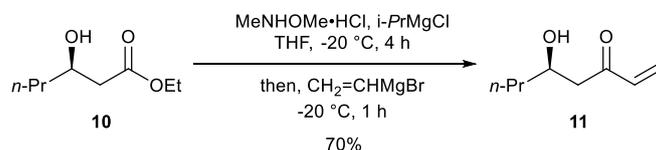
Synthesis of 10



A solution of compound **9** (12.0 g, 92.2 mmol) and $\text{CuBr}\cdot\text{DMS}$ (20.84 g, 101.4 mmol) in THF (400.0 mL) was placed in a flame-dried 1 L round-bottom flask. Ethylmagnesium bromide (202.0 mL, 202.0 mmol, 1 M in THF) was added dropwise at -60 °C. The reaction mixture was warmed to -30 °C and stirred for 3 h, then slowly quenched with saturated aqueous NH_4Cl , followed by extraction with ethyl acetate (4×80.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford compound **10** (12.11 g, 82% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 20%).
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.15 (q, $J = 7.2$ Hz, 2H), 4.03-3.96 (m, 1H), 2.48 (dd, $J = 16.4, 3.2$ Hz, 1H), 2.39 (dd, $J = 16.4, 8.8$ Hz, 1H), 1.54-1.42 (m, 2H), 1.42-1.32 (m, 2H), 1.26 (t, $J = 6.8$ Hz, 3H), 0.91 (t, $J = 6.8$ Hz, 3H).
- $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 173.1, 67.7, 60.6, 41.3, 38.6, 18.6, 14.1, 13.9.
- IR (neat) cm^{-1} 1219, 772, 434.
- HRMS (MALDI, m/z) calcd for $\text{C}_8\text{H}_{16}\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 161.1172, found 161.1175.
- $[\alpha]_D^{24.1} = -20.77$ ($c = 1.3$ in CHCl_3).

Synthesis of 11

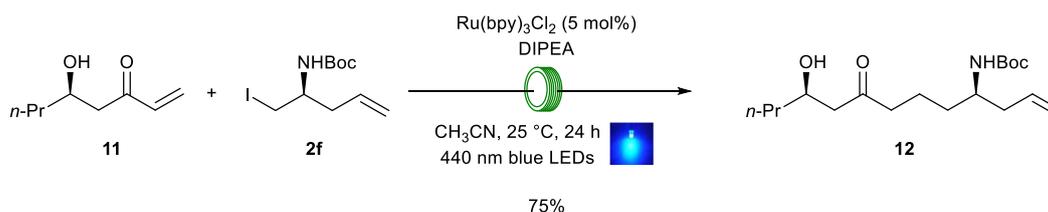


A solution of compound **10** (10.0 g, 62.5 mmol) and *N, O*-dimethylhydroxylamine hydrochloride (12.19 g, 125.0 mmol) in THF (400.0 mL) was placed in a flame-dried 1 L round-bottom flask. Under an argon atmosphere, isopropylmagnesium chloride (156.5 mL, 312.5 mmol, 2.0 M in THF) was added dropwise at -20 °C. The reaction mixture was stirred at this temperature for 4 h, after which vinylmagnesium bromide (125.0 mL, 125.0 mmol, 1.0 M in THF) was slowly added to the system. The reaction was continued to stir for 1 h, then quenched with ice-cold 1.0 M aqueous HCl (200.0 mL), followed by extraction with CH_2Cl_2 (3×100.0 mL). The combined

organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford compound **11** (6.2 g, 70% yield).

- Colorless oily liquid.
- R_f = 0.5 (ethyl acetate/petroleum ether = 50%).
- ¹H NMR (400 MHz, CDCl₃) δ 6.34 (dd, *J* = 17.6, 10.4 Hz, 1H), 6.22 (d, *J* = 17.6 Hz, 1H), 5.87 (d, *J* = 10.4 Hz, 1H), 4.12-4.05 (m, 1H), 3.10 (s, 1H), 2.80 (dd, *J* = 17.2, 2.8 Hz, 1H), 2.64 (dd, *J* = 17.6, 9.2 Hz, 1H), 1.54-1.45 (m, 2H), 1.42-1.34 (m, 2H), 0.91 (t, *J* = 6.8 Hz, 3H).
- ¹³C NMR (150 MHz, CDCl₃) δ 200.8, 136.3, 129.1, 67.3, 45.7, 38.6, 18.6, 13.9.
- IR (neat) cm⁻¹ 2959, 1675, 1403, 1219, 772, 436.
- HRMS (MALDI, *m/z*) calcd for C₈H₁₄O₂ (M+Na)⁺ 165.0886, found 165.0889.
- [α]_D^{24.2} = -45.6 (*c* = 1.0 in CHCl₃).

Synthesis of 12

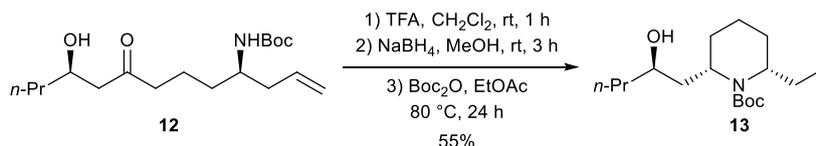


A solution of Ru(bpy)₃Cl₂ (480.0 mg, 0.75 mmol) was dissolved in a mixed solvent consisting of 25.0 mL of acetonitrile and 15.0 mL of water, a solution of **11** (3.2 g, 22.5 mmol) in 40.0 mL of acetonitrile, a solution of **2f** (4.67 g, 15.0 mmol) in 40.0 mL of acetonitrile, and a solution of DIPEA (7.8 mL, 45.0 mmol) in 40 mL of acetonitrile were each loaded into a 50 mL syringe. The mixture was pumped at a rate of 10.0 mL/h into a flow reactor, which was irradiated with a blue LED light (*hν* = 440 nm) at a distance of 1.0 cm at room temperature. The products were collected and the acetonitrile was removed under reduced pressure. The crude products were purified by silica gel flash column chromatography to afford **12** (3.68 g, 75%). After multiple cycles of continuous flow chemistry, 20 g of **12** was finally prepared.

- White solid.
- M.p. = 69.1 - 71.4 °C.
- R_f = 0.5 (ethyl acetate/petroleum ether = 20%).
- ¹H NMR (400 MHz, CDCl₃) 5.81-5.70 (m, 1H), 5.08-5.06 (m, 2H), 4.35-4.33 (m, 1H), 4.06-4.00 (m, 1H), 3.62 (s, 1H), 3.00 (s, 1H), 2.61-2.37 (m, 4H), 2.27-2.07 (m, 2H), 1.70-1.55 (m, 4H), 1.53-1.30 (m, 13H), 0.92 (m, 3H).

- ^{13}C NMR (150 MHz, CDCl_3) δ 212.0, 155.6, 134.2, 117.8, 79.1, 67.4, 49.5, 49.1, 42.9, 39.5, 38.6, 33.9, 28.4, 19.7, 18.6, 13.9.
- IR (neat) cm^{-1} 2959, 1675, 1403, 1219, 772, 426.
- HRMS (MALDI, m/z) calcd for $\text{C}_{18}\text{H}_{33}\text{NO}_4$ ($\text{M}+\text{Na}$) $^+$ 350.2302, found 350.2309.
- $[\alpha]_{\text{D}}^{24.8} = -3.33$ ($c = 0.3$ in CHCl_3).

Synthesis of 13



A solution of compound **12** (981.7 mg, 3.0 mmol) in CH_2Cl_2 (20.0 mL) was added to a flame-dried 50 mL round-bottom flask, and trifluoroacetic acid (8.8 mL) was then added dropwise at 0 °C. The mixture was warmed to room temperature and stirred continuously for 1 h. The reaction was slowly quenched with saturated aqueous NaHCO_3 , followed by extraction with CH_2Cl_2 (3×10.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuo. The resulting crude product was used directly in the subsequent step without further purification.

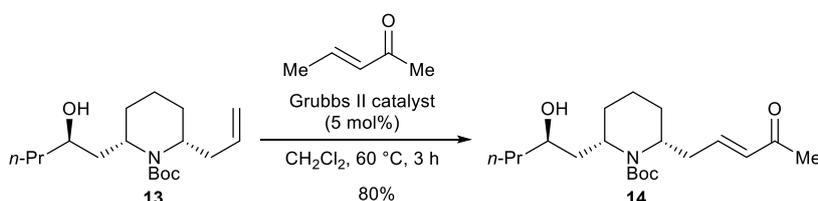
A solution of the crude product from the preceding step in methanol (20 mL) was transferred to a flame-dried 50 mL round-bottom flask, and sodium borohydride (NaBH_4 , 405.0 mg, 10.7 mmol) was then added portionwise. The mixture was stirred at 0 °C for 5 min, after which the reaction was allowed to warm to room temperature and proceed for 2 h. The reaction was slowly quenched with sat. aq. NH_4Cl , followed by extraction with dichloromethane (CH_2Cl_2 , 3×10.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuo. The resulting crude product was used directly in the subsequent step without further purification.

A solution of the crude product from the preceding step in ethyl acetate (20.0 mL) was transferred to a flame-dried 50 mL round-bottom flask, followed by the dropwise addition of Boc_2O . The reaction mixture was heated to 90 °C and stirred for 24 h. After cooling, the mixture was concentrated directly under reduced pressure, and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to afford compound **13** (513.6 mg, 55% yield over three steps).

- Colorless oily liquid.
- $R_f = 0.4$ (ethyl acetate/petroleum ether = 50%)

- ^1H NMR (400 MHz, CDCl_3) δ 5.79-5.68 (m, 1H), 5.07-5.01 (m, 2H), 4.18 (s, 1H), 4.10 (s, 1H), 3.55-3.50 (m, 1H), 2.28-2.23 (m, 2H), 1.83-1.76 (m, 1H), 1.71-1.35 (m, 20H), 0.71 (t, $J = 6.0$ Hz, 3H).
- ^{13}C NMR (150 MHz, CDCl_3) δ 155.8, 136.2, 116.9, 79.9, 69.9, 50.2, 47.6, 44.3, 40.1, 39.0, 29.7, 28.4, 26.6, 18.9, 14.1, 13.7
- IR (neat) cm^{-1} 3398, 2953, 1660, 1366, 1184, 1112, 1066, 938, 850, 562.
- HRMS (MALDI, m/z) calcd for $\text{C}_{18}\text{H}_{33}\text{NO}_3$ ($\text{M}+\text{Na}$) $^+$ 334.2353, found 334.2356.
- $[\alpha]_{\text{D}}^{25} = -14.8$ ($c = 0.5$ in CHCl_3).

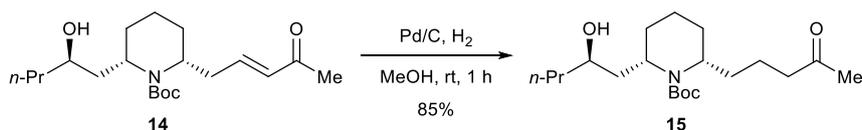
Synthesis of 14



A solution of compound **13** (500.0 mg, 1.6 mmol) in CH_2Cl_2 (50.0 mL) was transferred to a flame-dried 100 mL three-necked flask. *trans*-3-Penten-2-one was subsequently added, and the resulting mixture was heated to reflux at 55 °C. After stirring at reflux for 5 min, a solution of Grubbs II catalyst (5 mol%) in CH_2Cl_2 (10.0 mL) was added dropwise via a syringe pump over 1 h. The reaction was allowed to proceed for an additional 2 h. Upon completion, the mixture was concentrated directly under reduced pressure, and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 8:1) to afford compound **14** (452 mg, 80% yield).

- Colorless oily liquid.
- $R_f = 0.5$ (ethyl acetate/petroleum ether = 30%).
- ^1H NMR (400 MHz, CDCl_3) δ 6.73 (dq, $J = 16.0, 6.4$ Hz, 1H), 6.07 (d, $J = 15.6$ Hz, 1H), 4.25-4.23 (m, 2H), 3.56-3.50 (m, 1H), 2.50-2.36 (m, 2H), 2.23 (s, 3H), 1.81-1.33 (m, 25H), 0.92 (t, $J = 6.0$ Hz, 3H).
- ^{13}C NMR (150 MHz, CDCl_3) δ 198.4, 155.5, 145.2, 132.9, 80.3, 77.2, 69.7, 49.5, 47.5, 43.9, 40.1, 37.8, 28.4, 27.4, 26.9, 18.9, 14.1, 13.7.
- IR (neat) cm^{-1} 3398, 2953, 1660, 1366, 1184, 1112, 1066, 938, 850, 562.
- HRMS (MALDI, m/z) calcd for $\text{C}_{20}\text{H}_{35}\text{NO}_4$ ($\text{M}+\text{H}$) $^+$ 354.2639, found 354.2636.
- $[\alpha]_{\text{D}}^{26.9} = -39.6$ ($c = 0.5$ in CHCl_3).

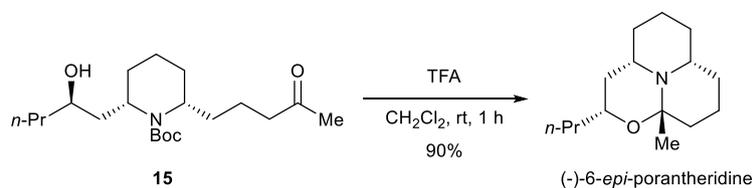
Synthesis of 15



A solution of compound **14** (400.0 mg, 1.13 mmol) in MeOH (40.0 mL) was placed in a flame-dried 100 mL round-bottom flask, followed by the addition of 10% Pd/C (5 mol%). The reaction was stirred under a hydrogen atmosphere (balloon, 1 atm) at room temperature. After 1 h, the reaction mixture was filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure, and the resulting crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 5:1) to afford compound **15** (341.9 mg, 85% yield).

- Colorless oily liquid.
- $R_f = 0.4$ (ethyl acetate/petroleum ether = 50%)
- $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.20 (m, 1H), 4.04 (s, 1H), 3.54-3.47 (m, 1H), 2.47-2.44 (m, 2H), 2.12 (s, 3H), 1.76-1.31 (m, 25H), 0.90 (t, $J = 6.8$ Hz, 3H).
- $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 208.6, 155.9, 79.8, 77.2, 69.9, 50.2, 47.7, 44.3, 43.3, 39.9, 33.9, 29.9, 28.4, 27.4, 21.3, 18.9, 14.1, 13.9
- IR (neat) cm^{-1} 1219, 772, 562.
- HRMS (MALDI, m/z) calcd for $\text{C}_{20}\text{H}_{37}\text{NO}_4$ ($\text{M}+\text{Na}$) $^+$ 378.2615, found 378.2610.
- $[\alpha]_D^{25} = -35.0$ ($c = 0.5$ in CHCl_3).

Synthesis of (-)-6-*epi*-porantheridine



A solution of compound **15** (100.0 mg, 0.28 mmol) in CH_2Cl_2 (20.0 mL) was transferred to a flame-dried 50 mL round-bottom flask. Trifluoroacetic acid (0.22 mL, 2.8 mmol) was then added dropwise via a syringe. After stirring at 0 °C for 10 min, the reaction mixture was allowed to warm to room temperature and stirred for an additional 1 h. The reaction was slowly quenched with saturated aqueous NaHCO_3 , followed by extraction with CH_2Cl_2 (3×10.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuo. The resulting crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 5:1) to afford (-)-6-*epi*-porantheridine (60.1 mg, 90% yield).

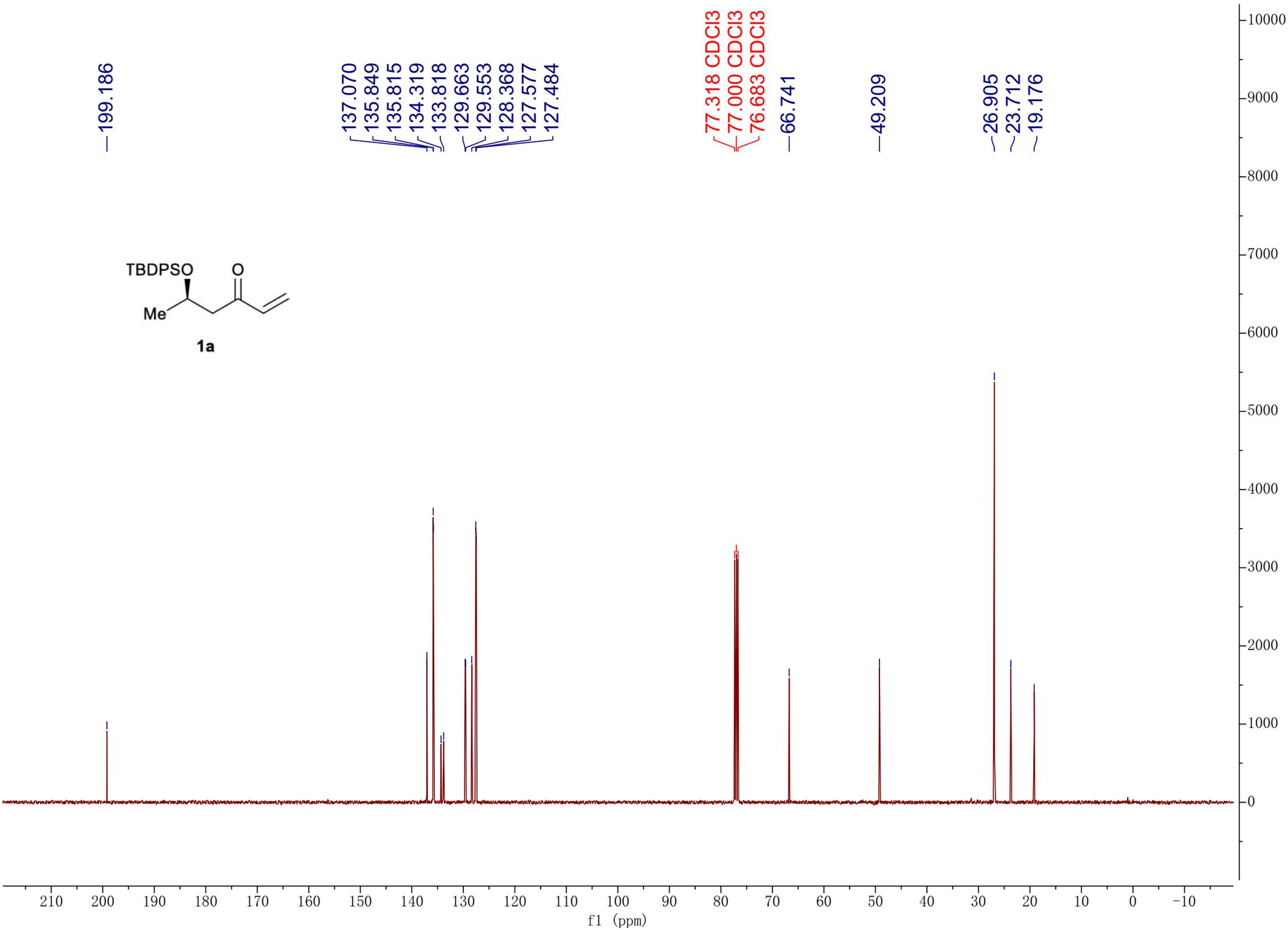
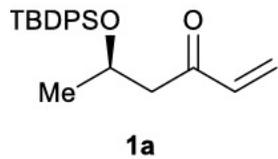
- Colorless oily liquid.
- $R_f = 0.4$ (ethyl acetate/petroleum ether = 50%)

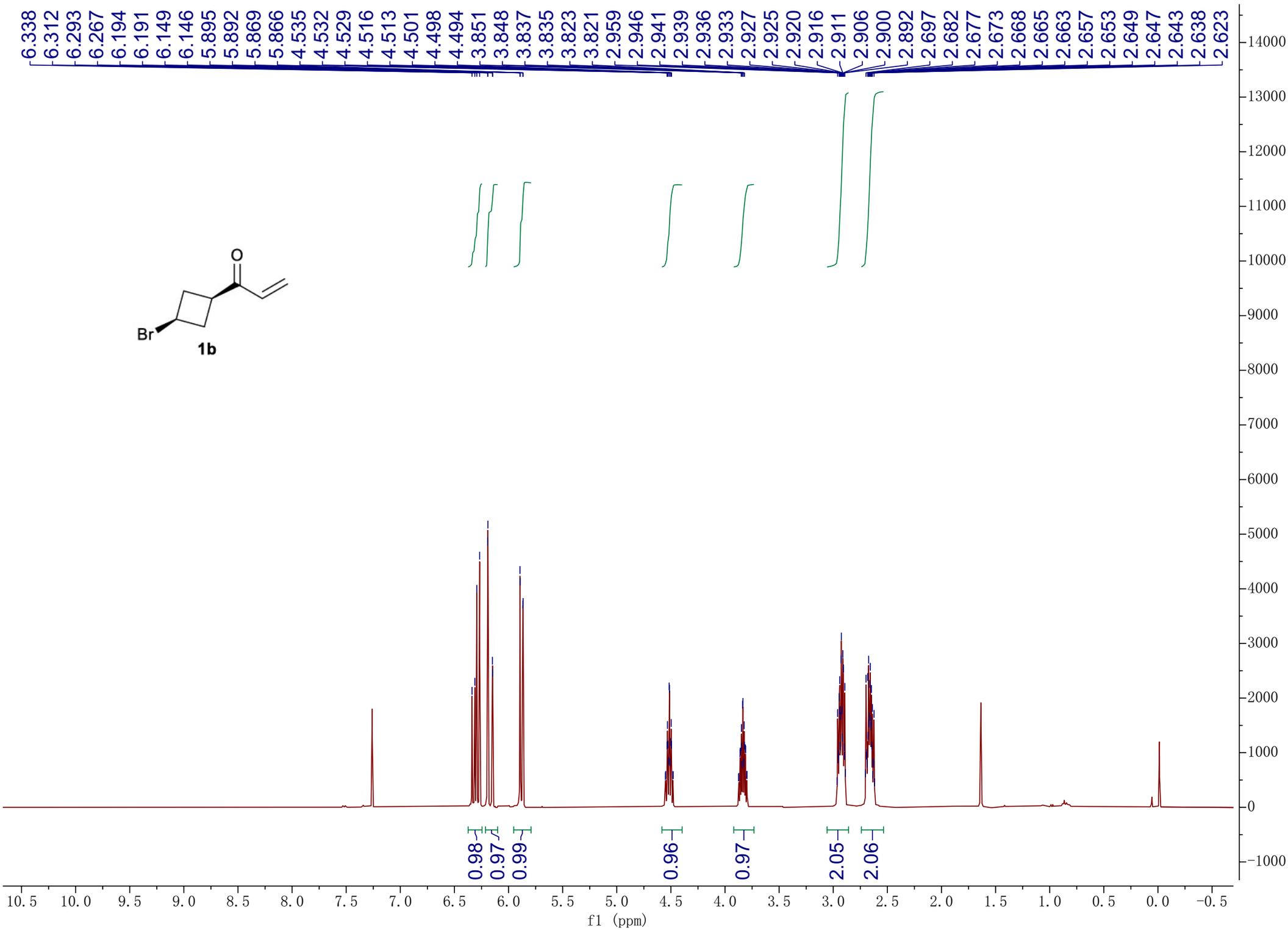
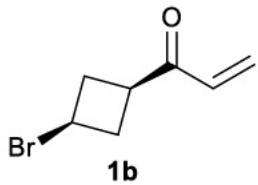
- ¹H NMR (400 MHz, CDCl₃) δ 3.80-3.73 (m, 1H), 2.49-2.43 (m, 1H), 2.16-2.06 (m, 1H), 1.69-1.17 (m, 21H), 0.91-0.83 (m, 3H).
- ¹³C NMR (150 MHz, CDCl₃) δ 86.4, 67.7, 55.2, 51.8, 39.6, 39.2, 38.6, 34.4, 34.2, 33.8, 23.5, 20.8, 18.4, 14.1, 11.5.
- IR (neat) cm⁻¹ 2922, 2851, 1644, 1219, 772.
- HRMS (MALDI, m/z) calcd for C₁₅H₂₇NO (M+Na)⁺ 260.1985, found 260.1986.
- [α]_D²⁵ = 6.0 (c = 0.1 in CHCl₃).

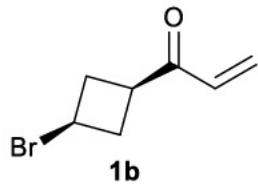
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8. ^1H and ^{13}C NMR Spectral Copies







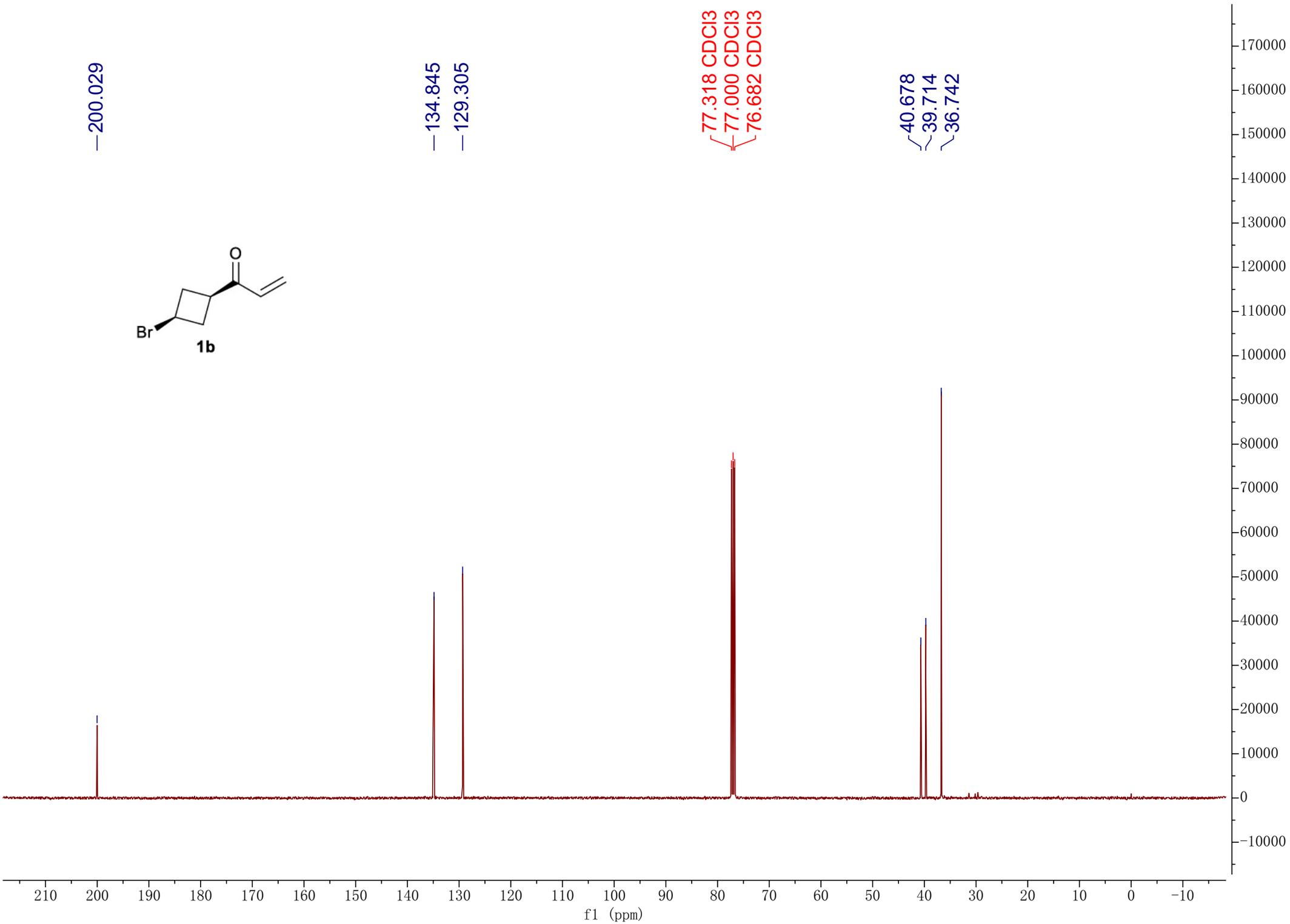
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—129.305

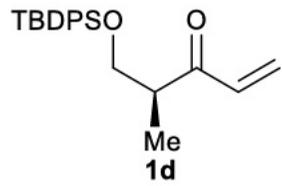
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76.682 CDCI3

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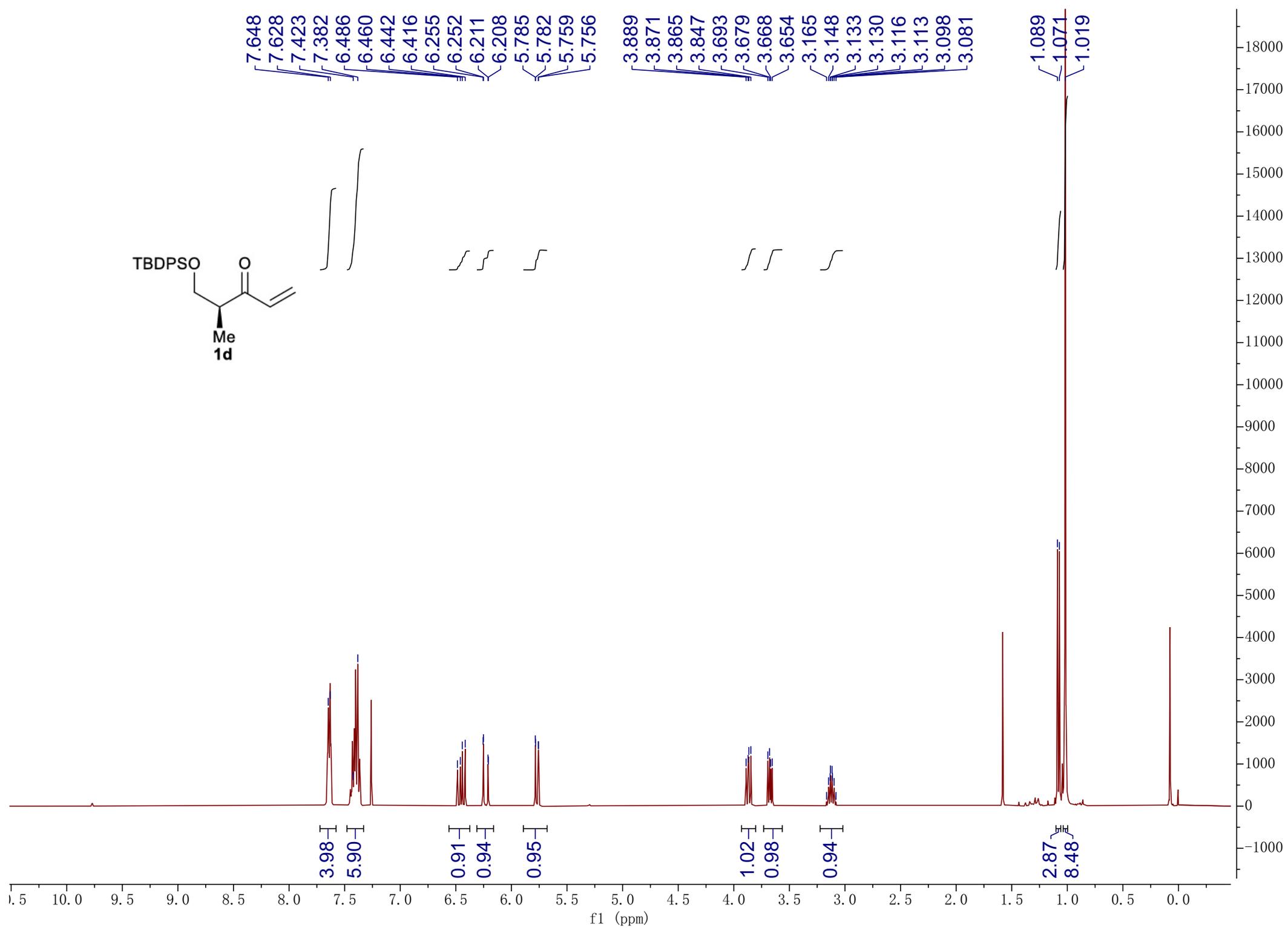


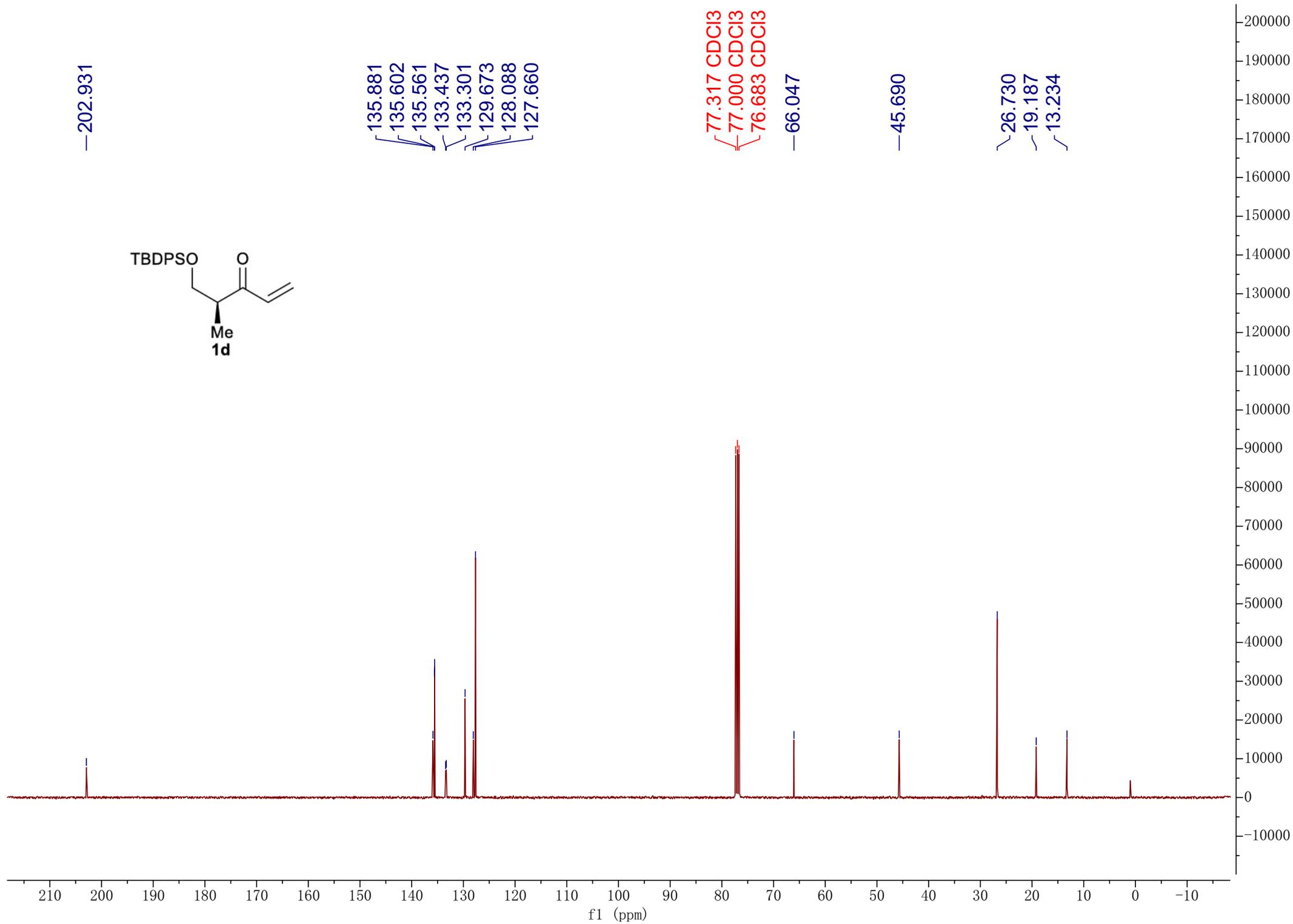
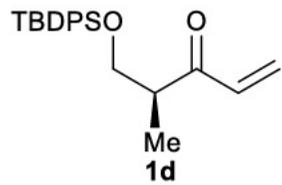
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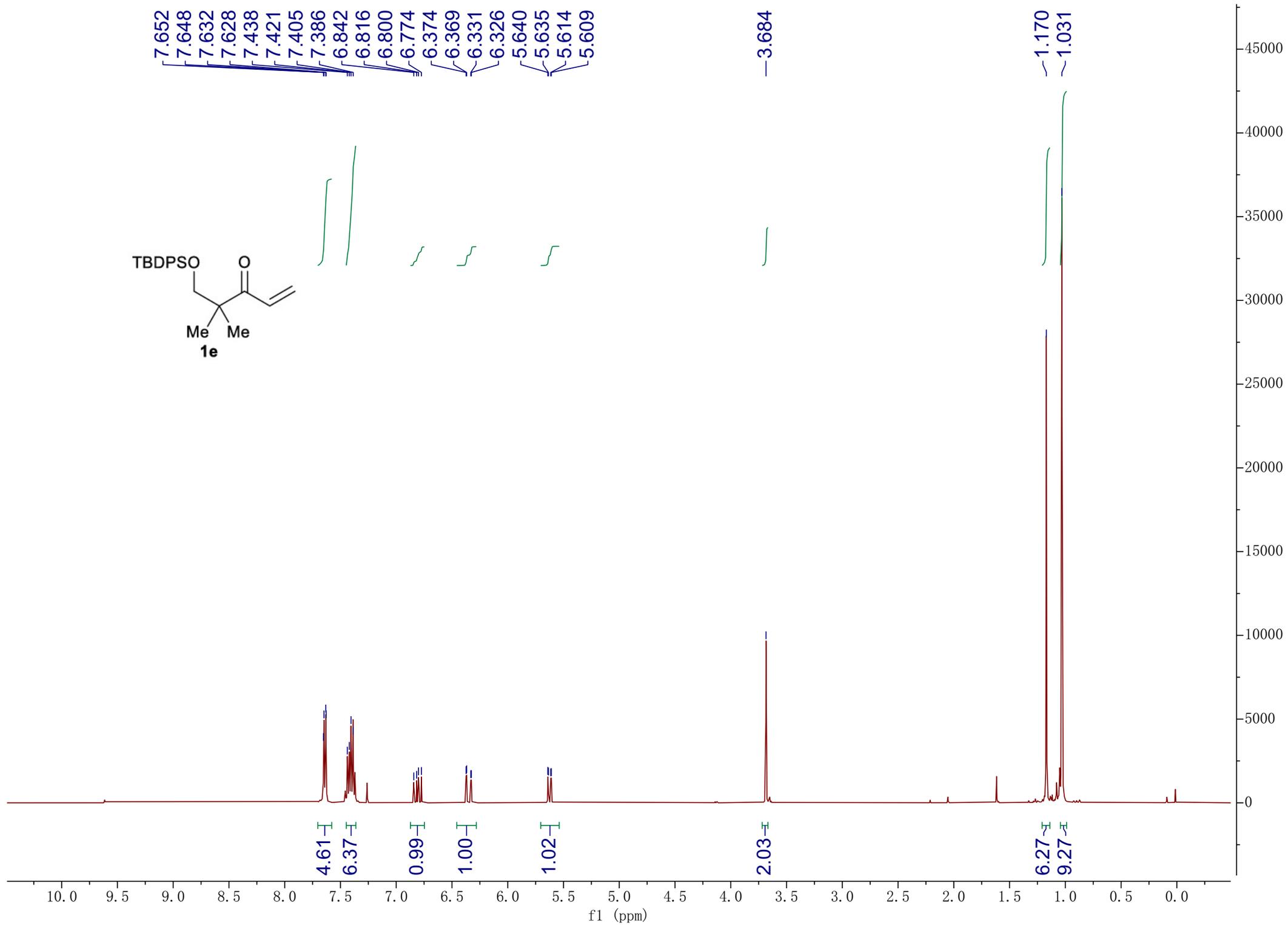
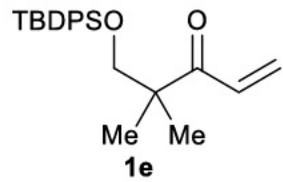
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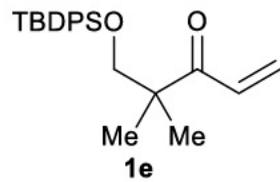


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 6.416
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 6.211
 6.208
 5.785
 5.782
 5.759
 5.756
 3.889
 3.871
 3.865
 3.847
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 3.113
 3.098
 3.081









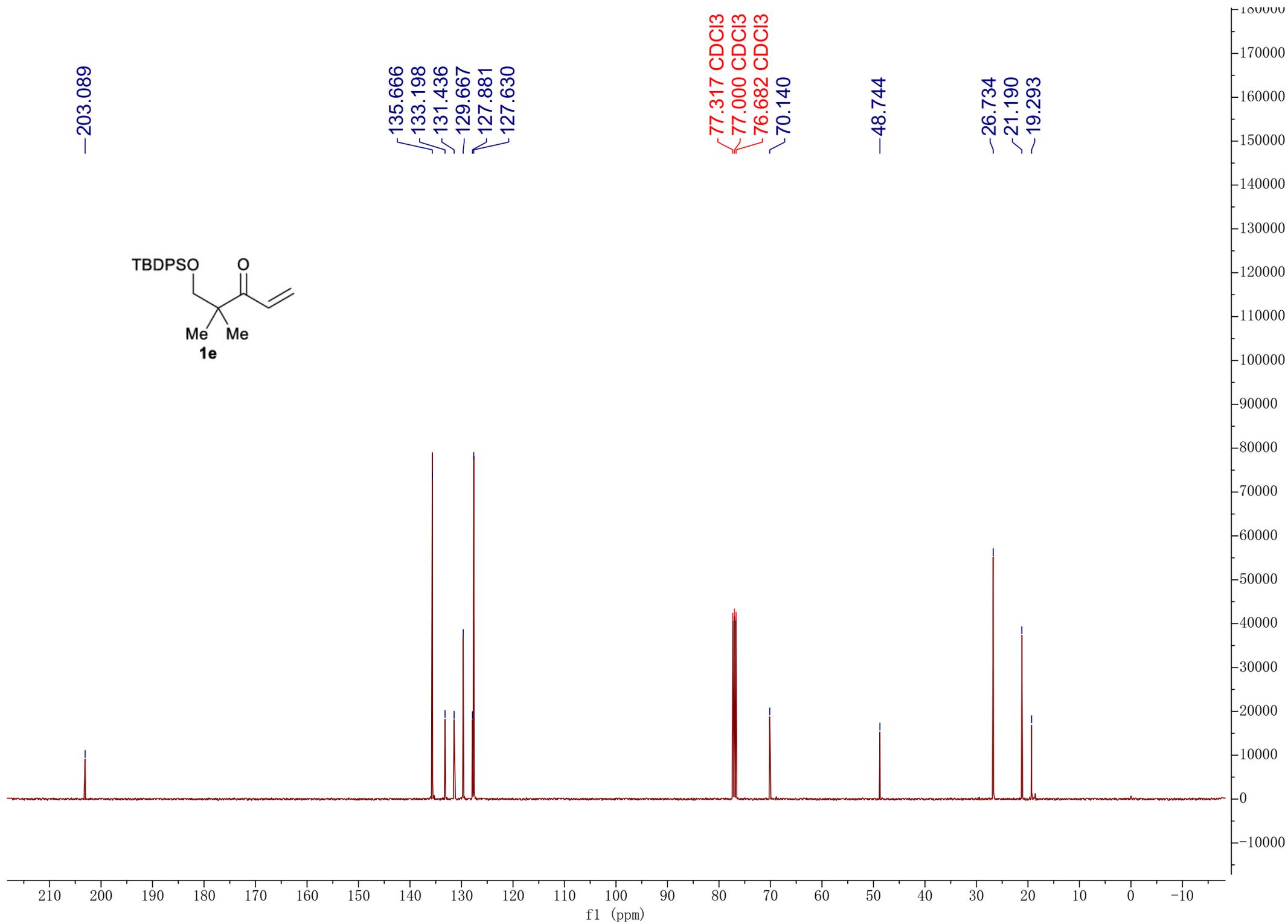
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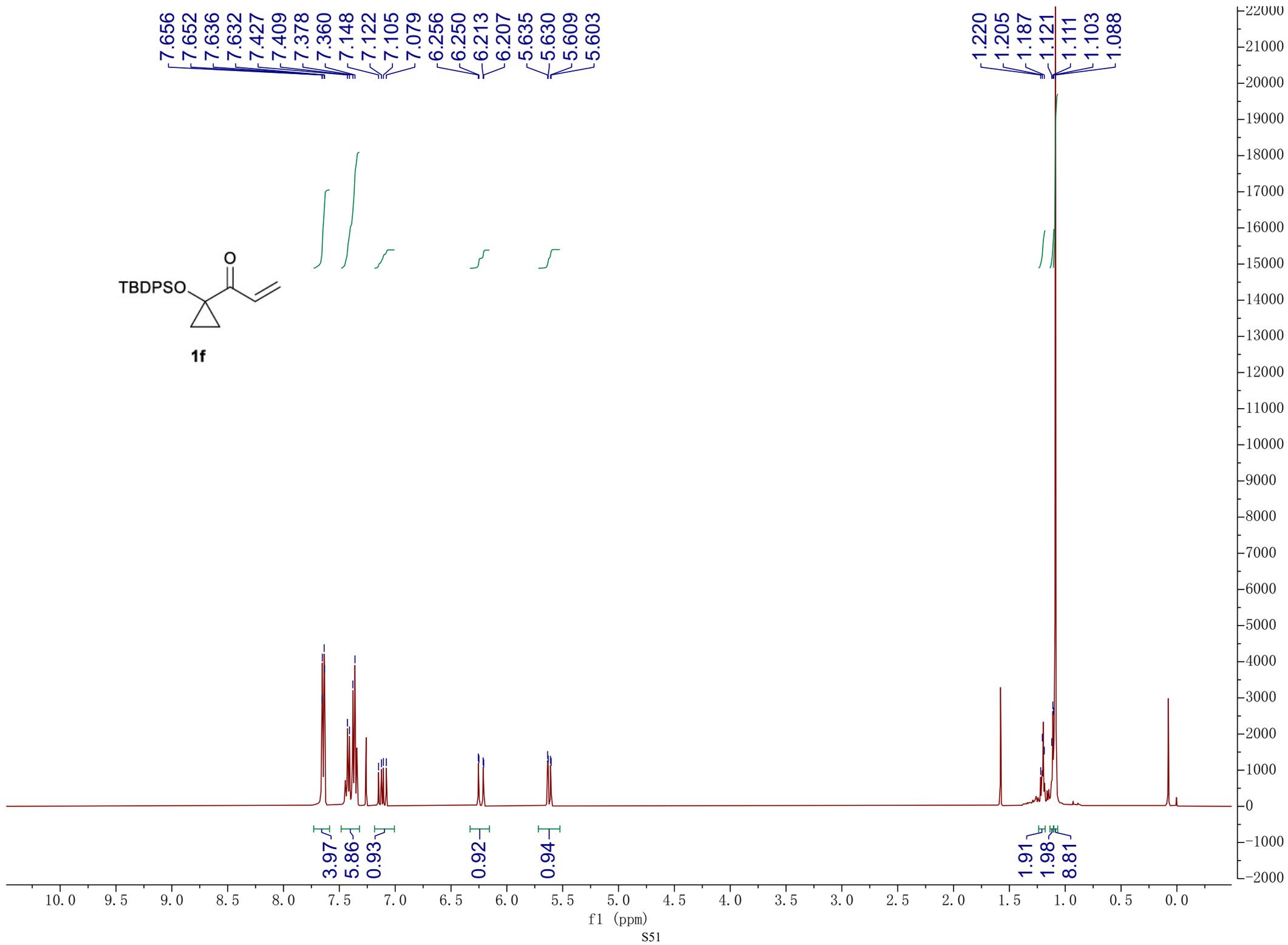
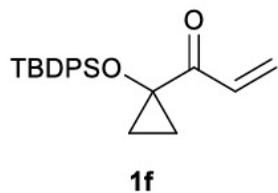
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127.630

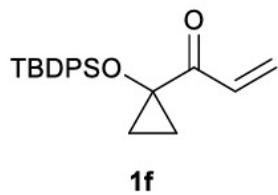
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70.140

— 48.744

26.734
21.190
19.293







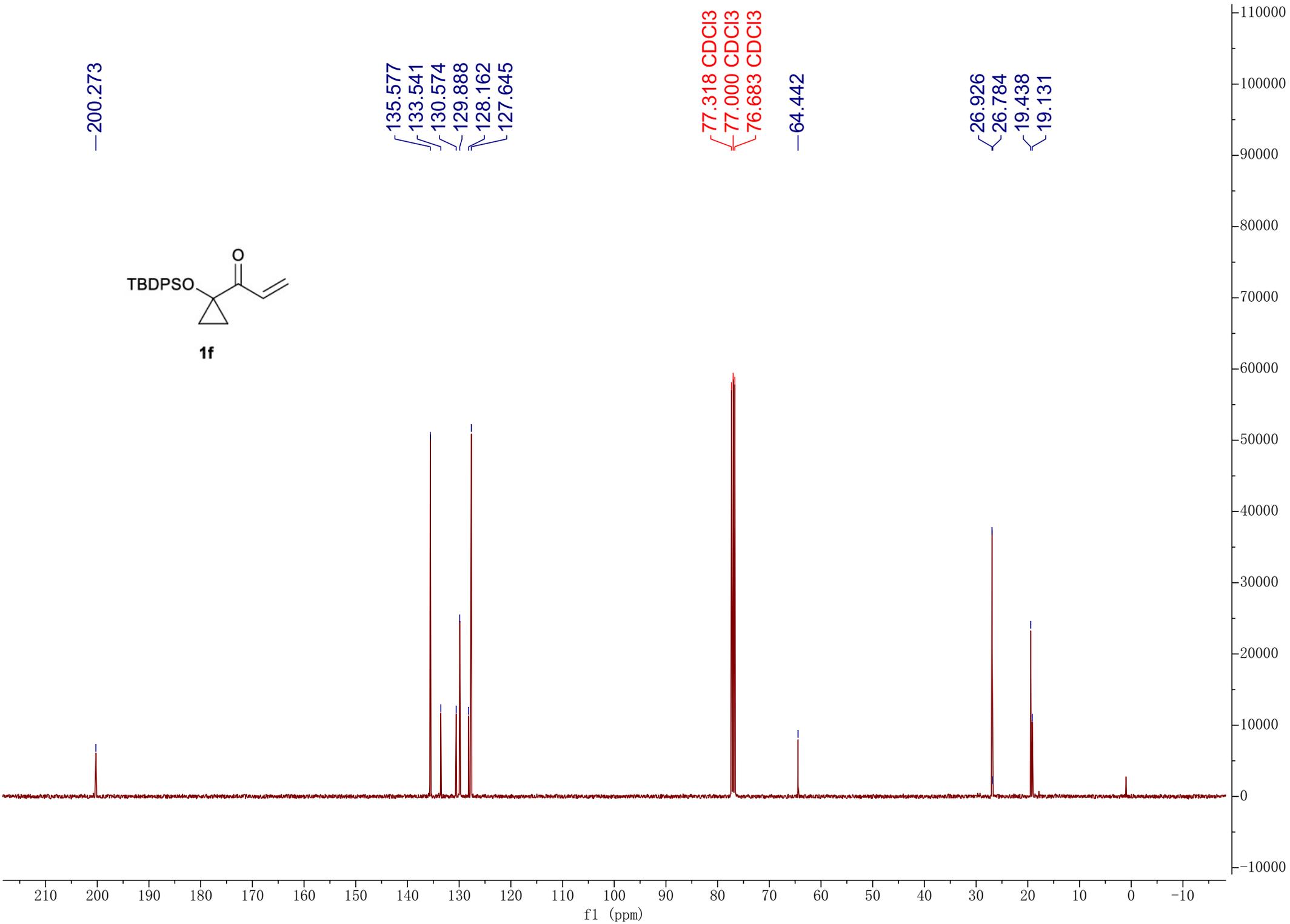
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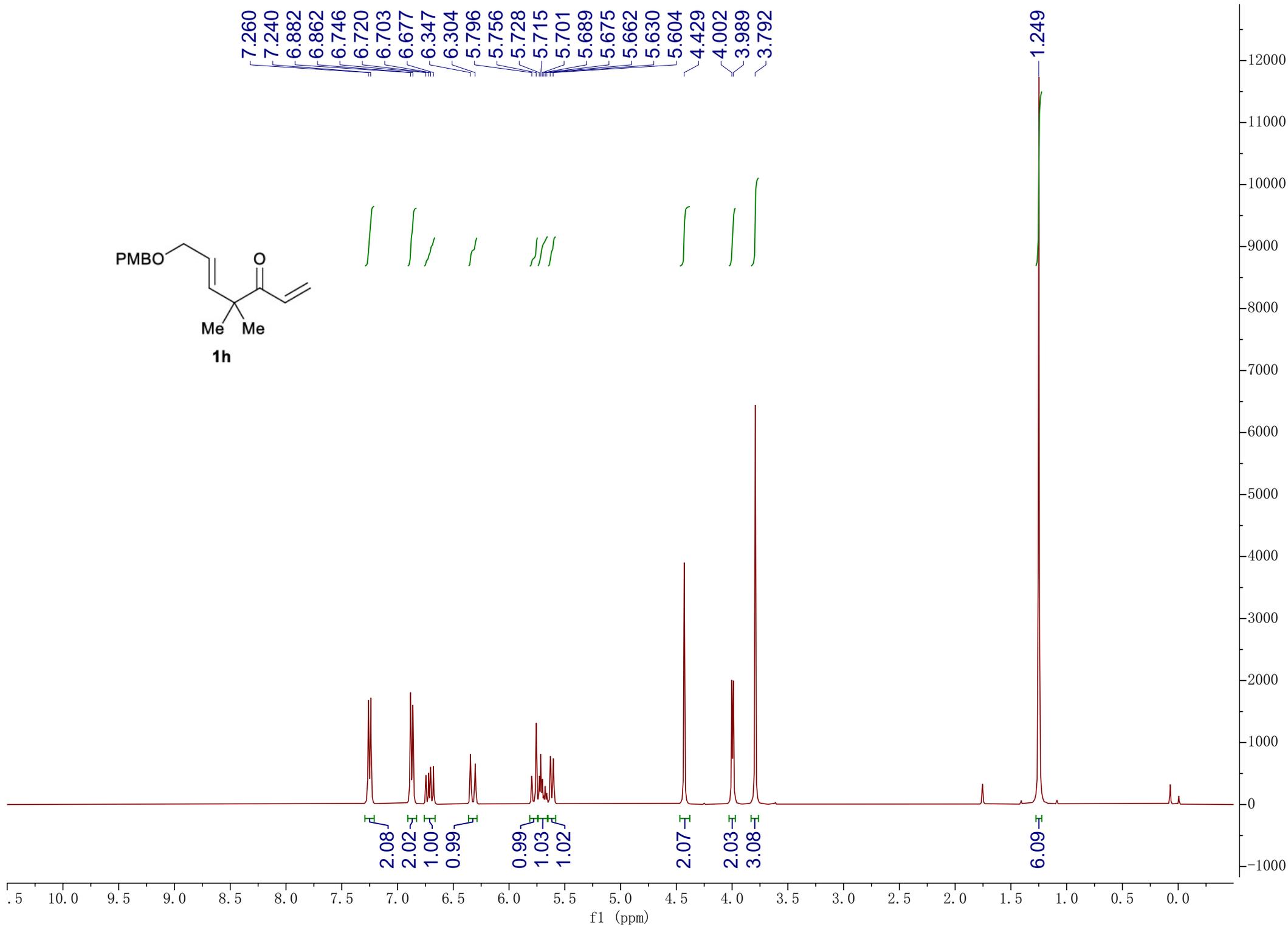
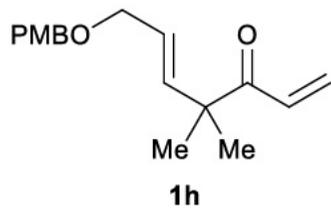
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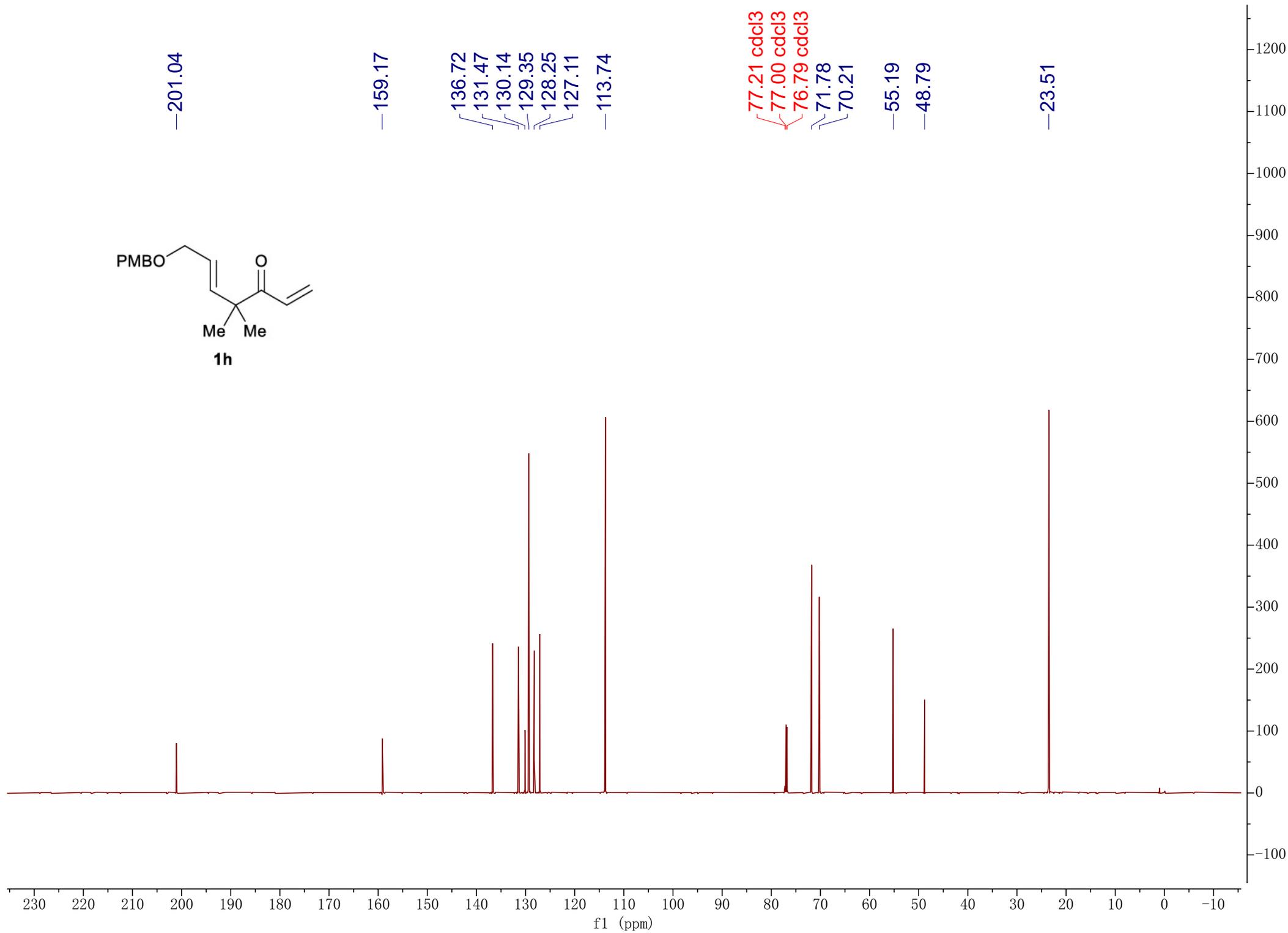
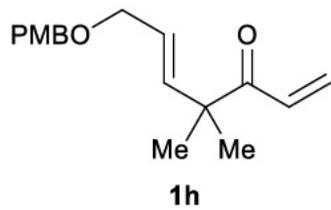
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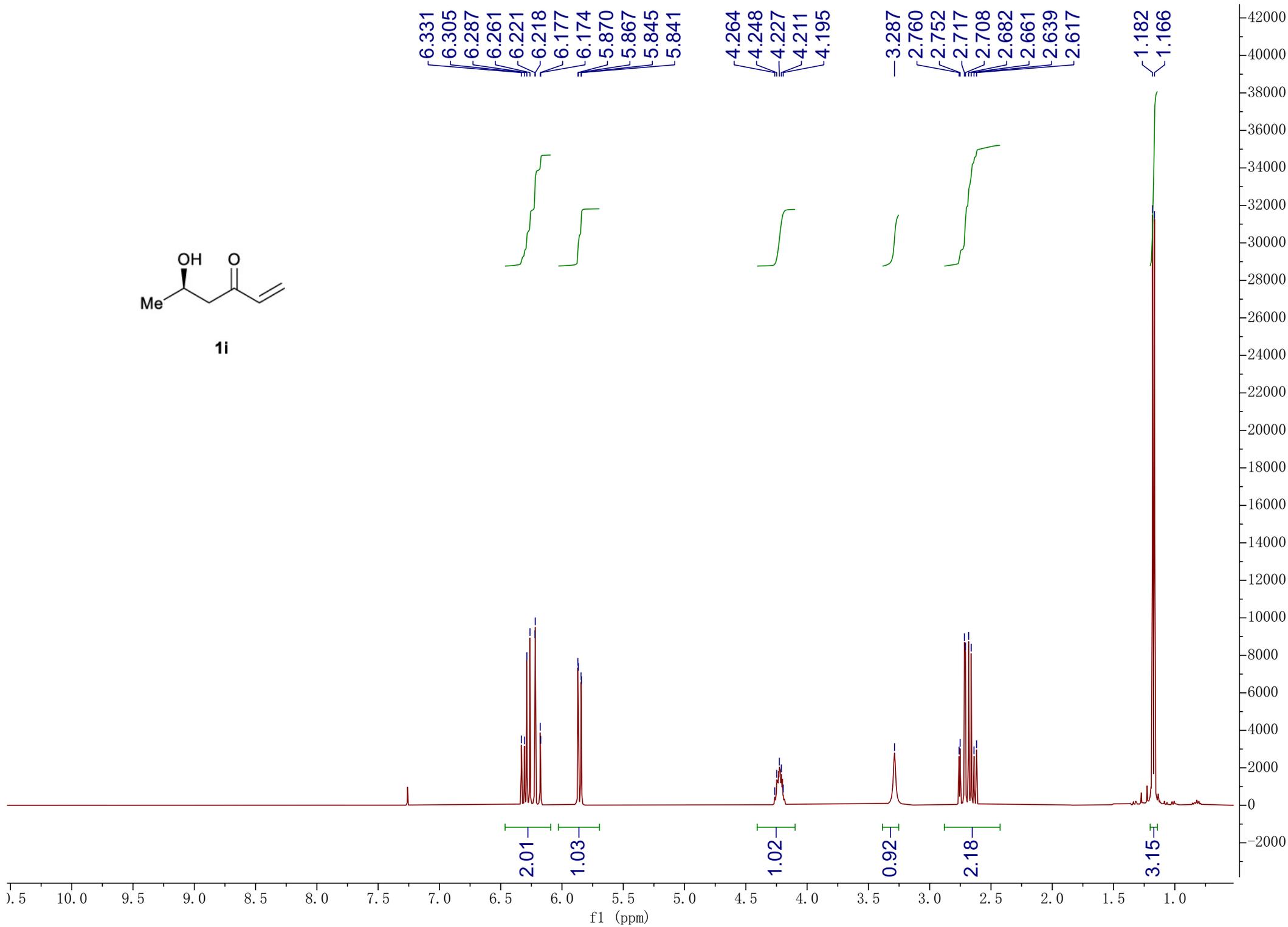
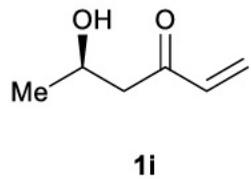
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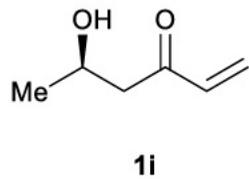
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19.438
19.131











—201.240

—136.639

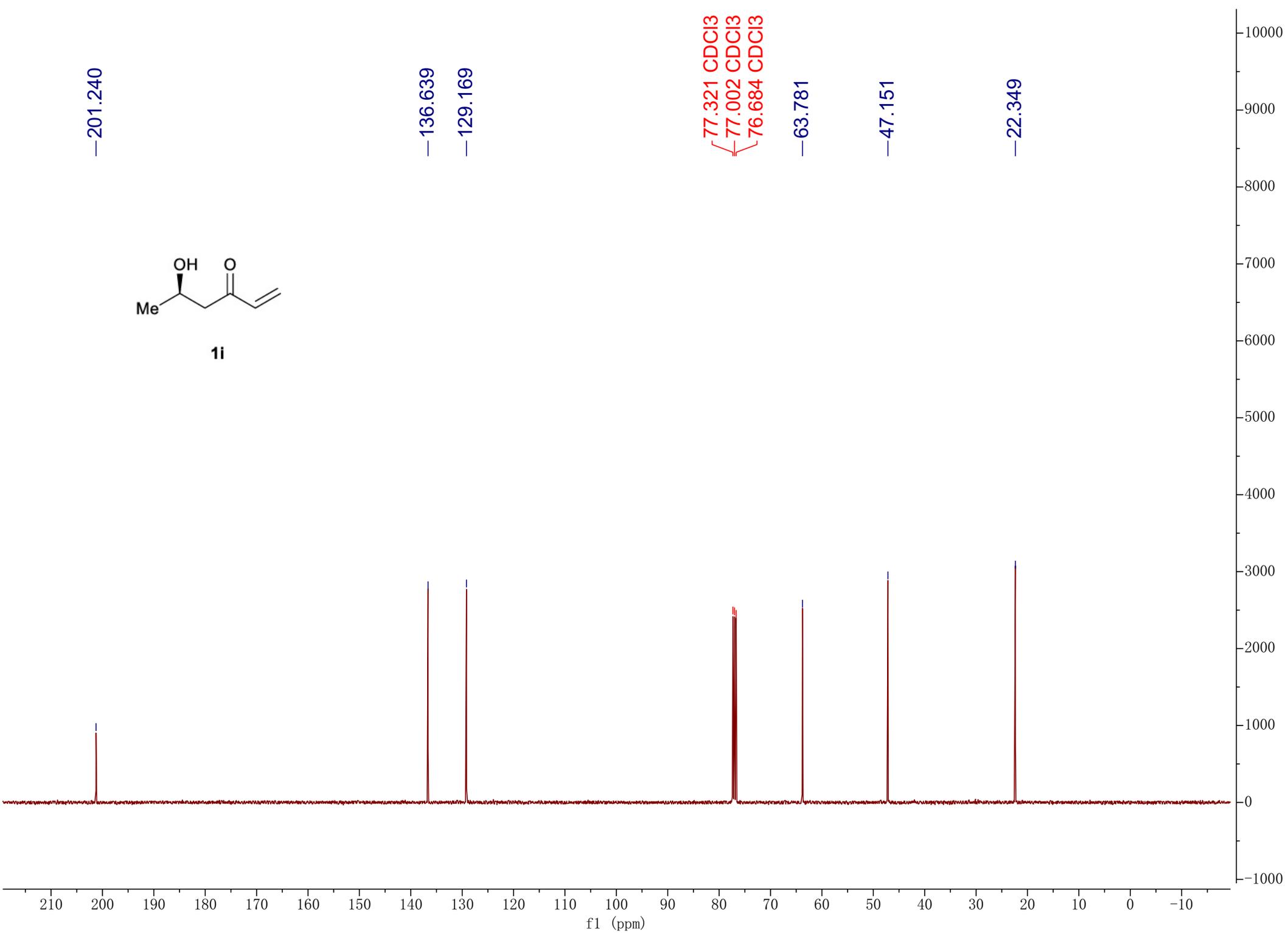
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—63.781

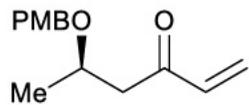
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—22.349

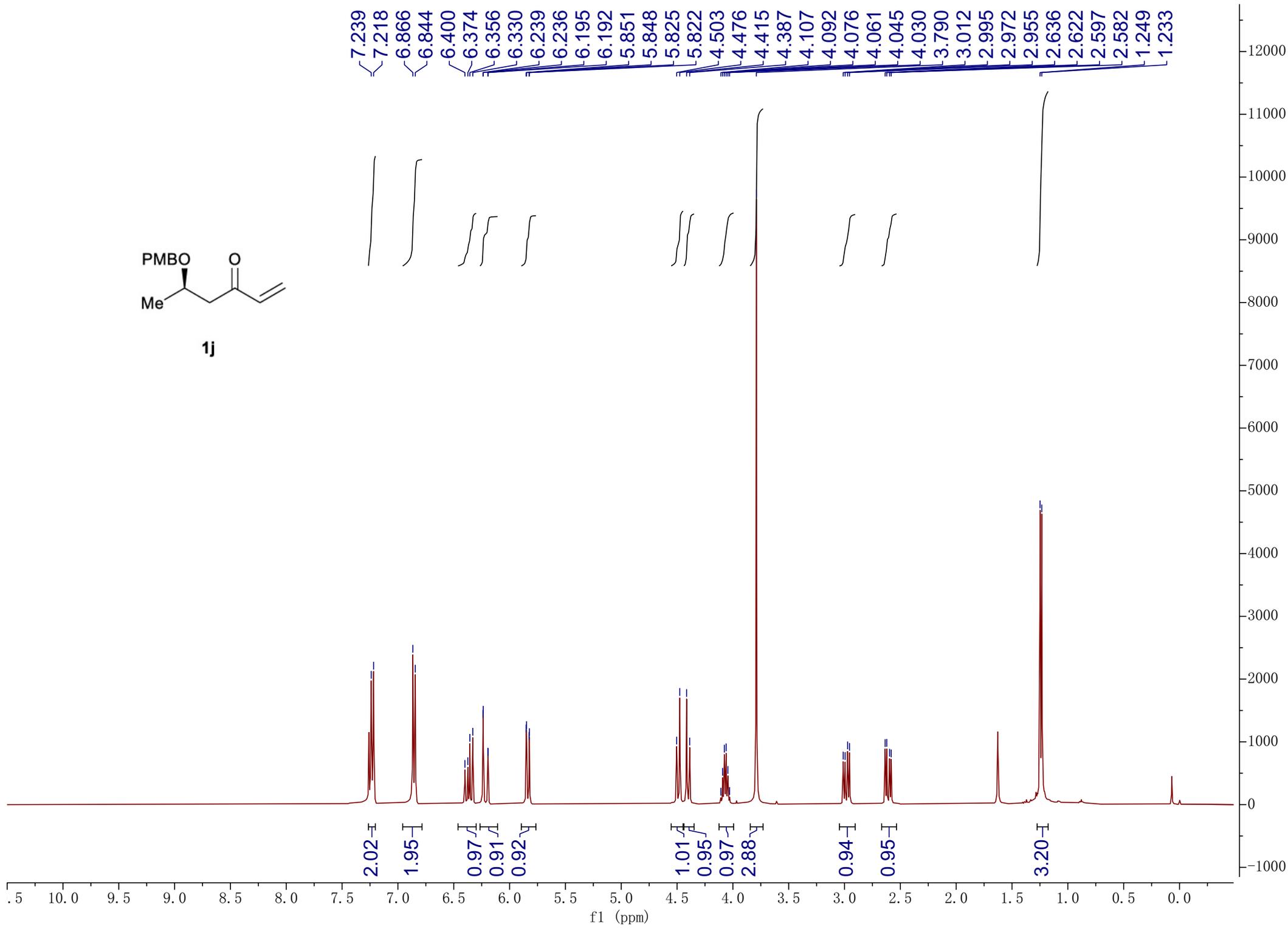


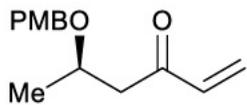
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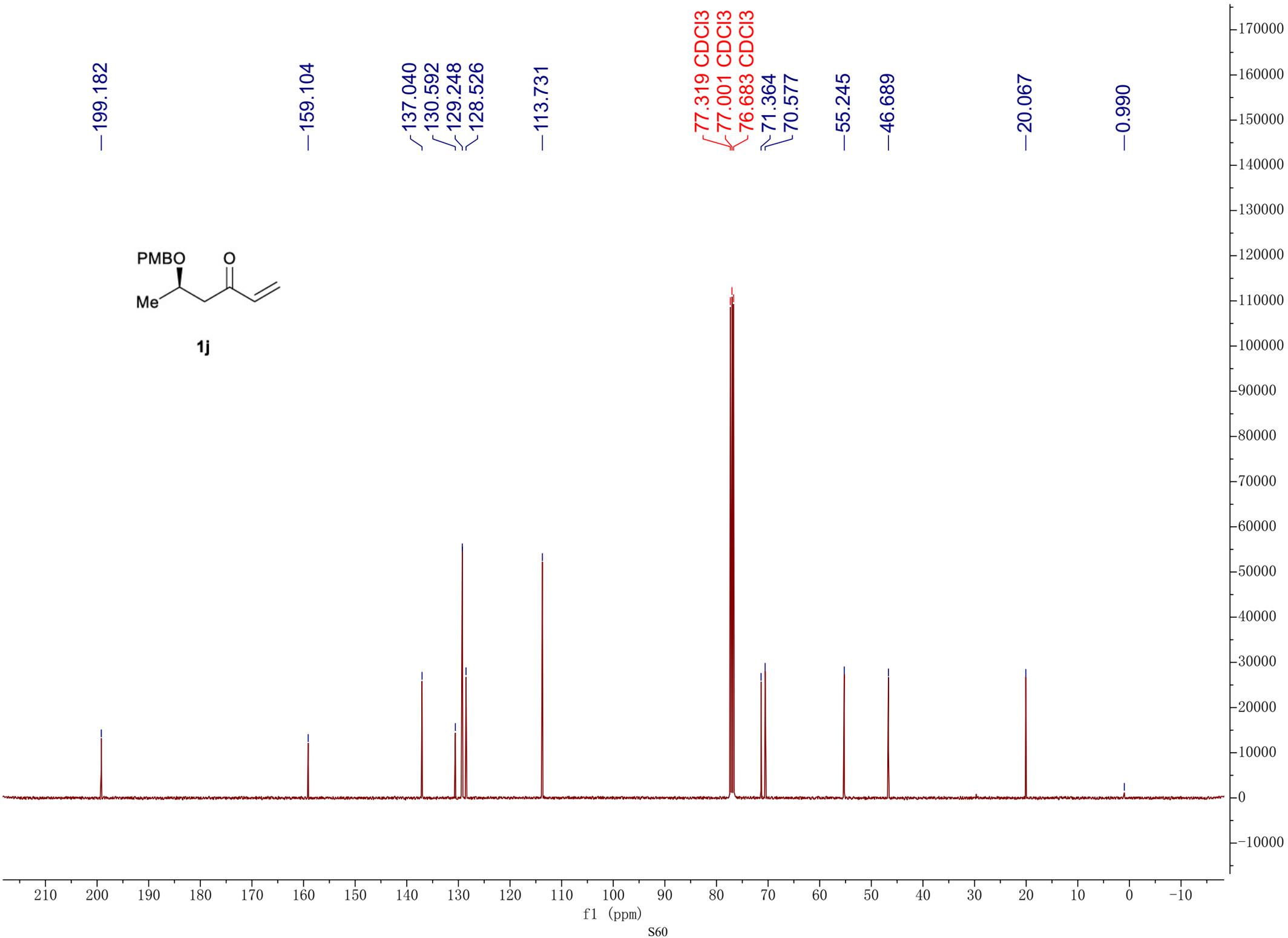


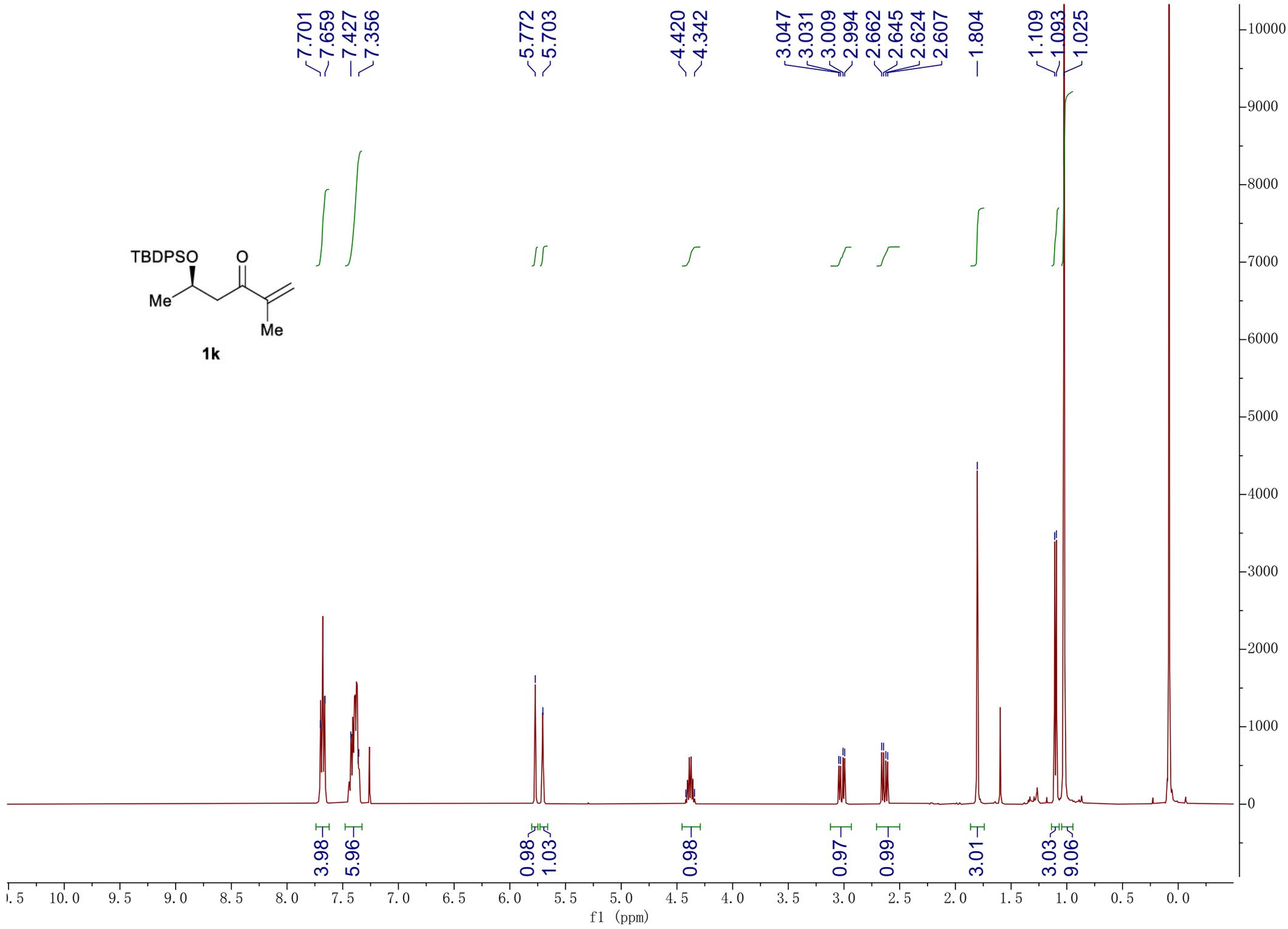
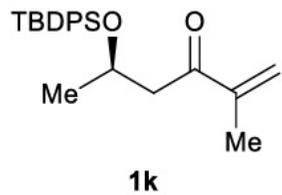
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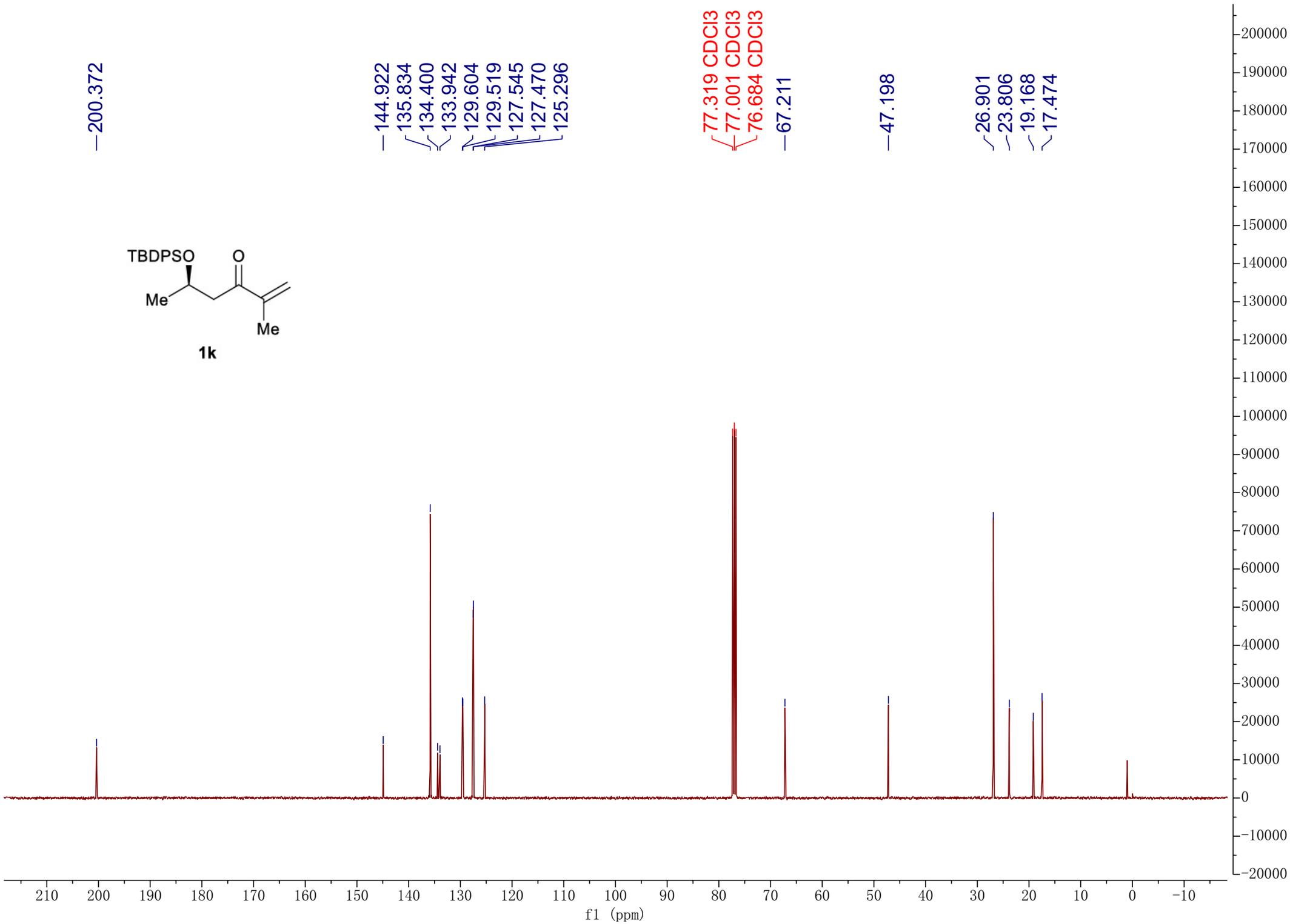
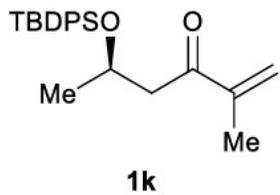


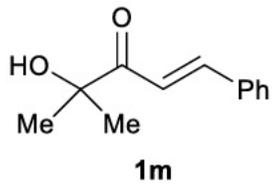


1j









7.872
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7.609
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7.596
7.589
7.432
7.424
7.419
7.411
7.407
7.396
7.062
7.022

3.999

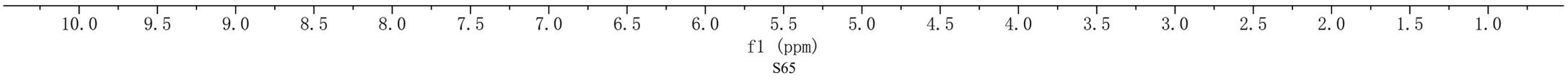
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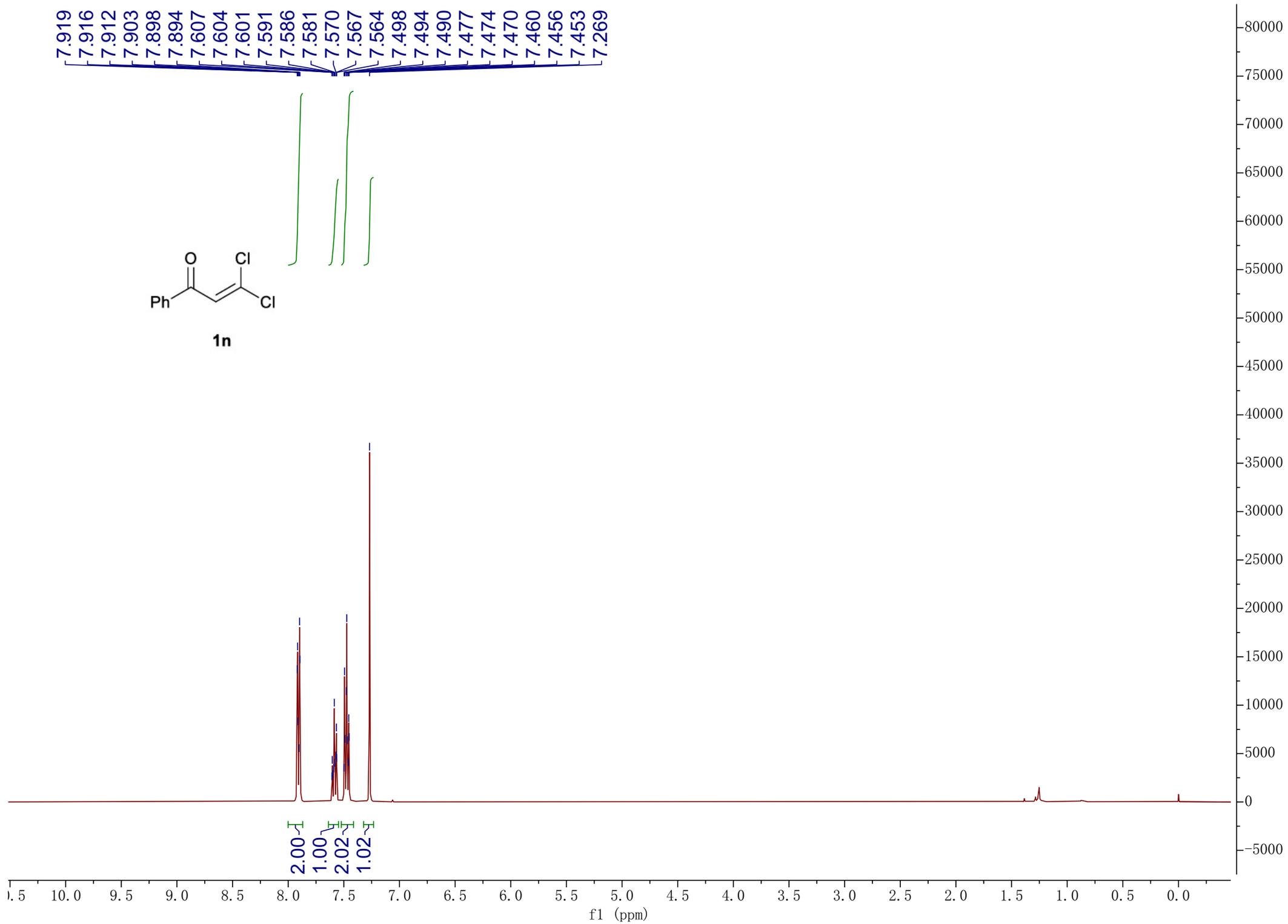
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3.04
1.06

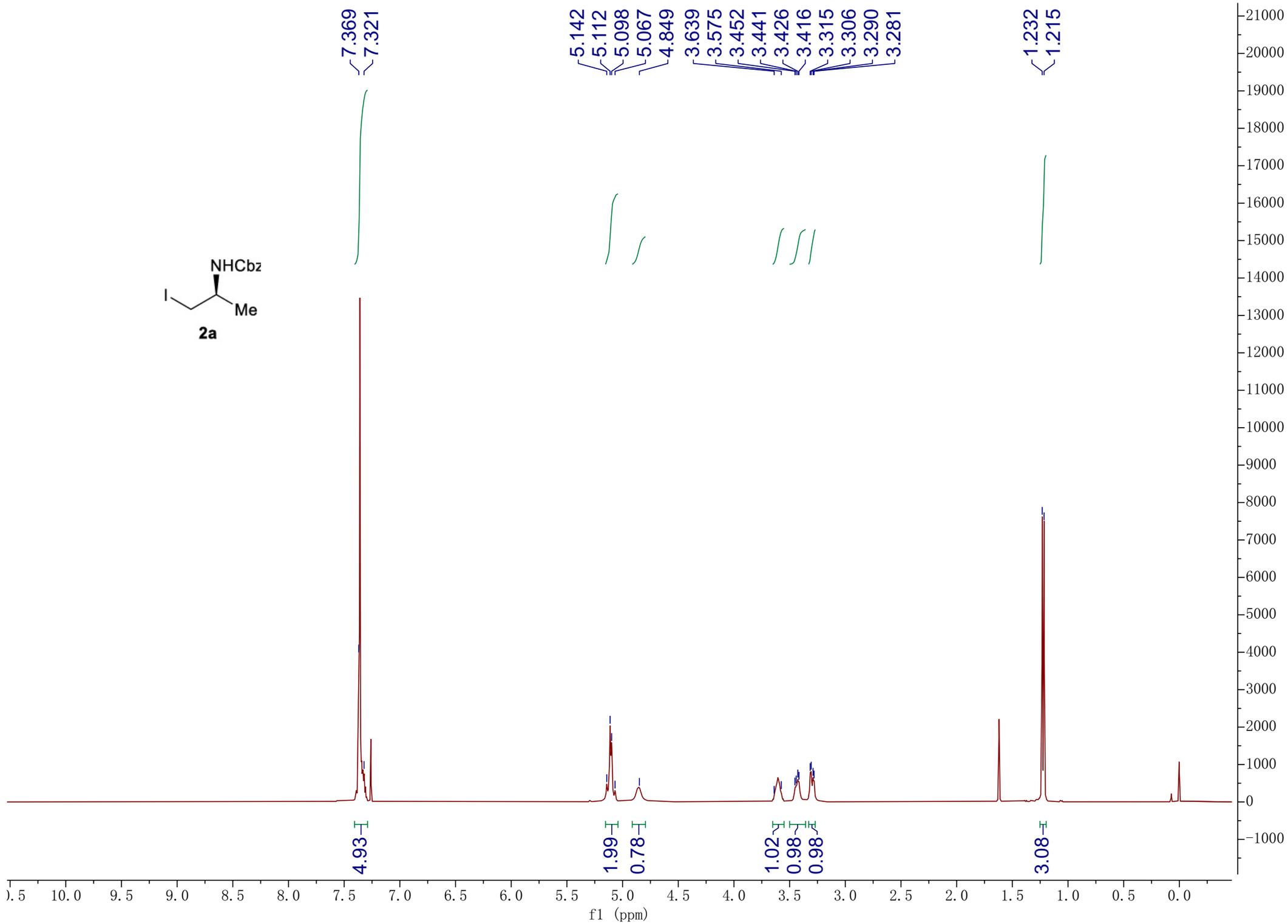
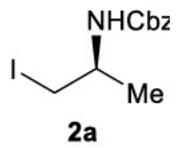
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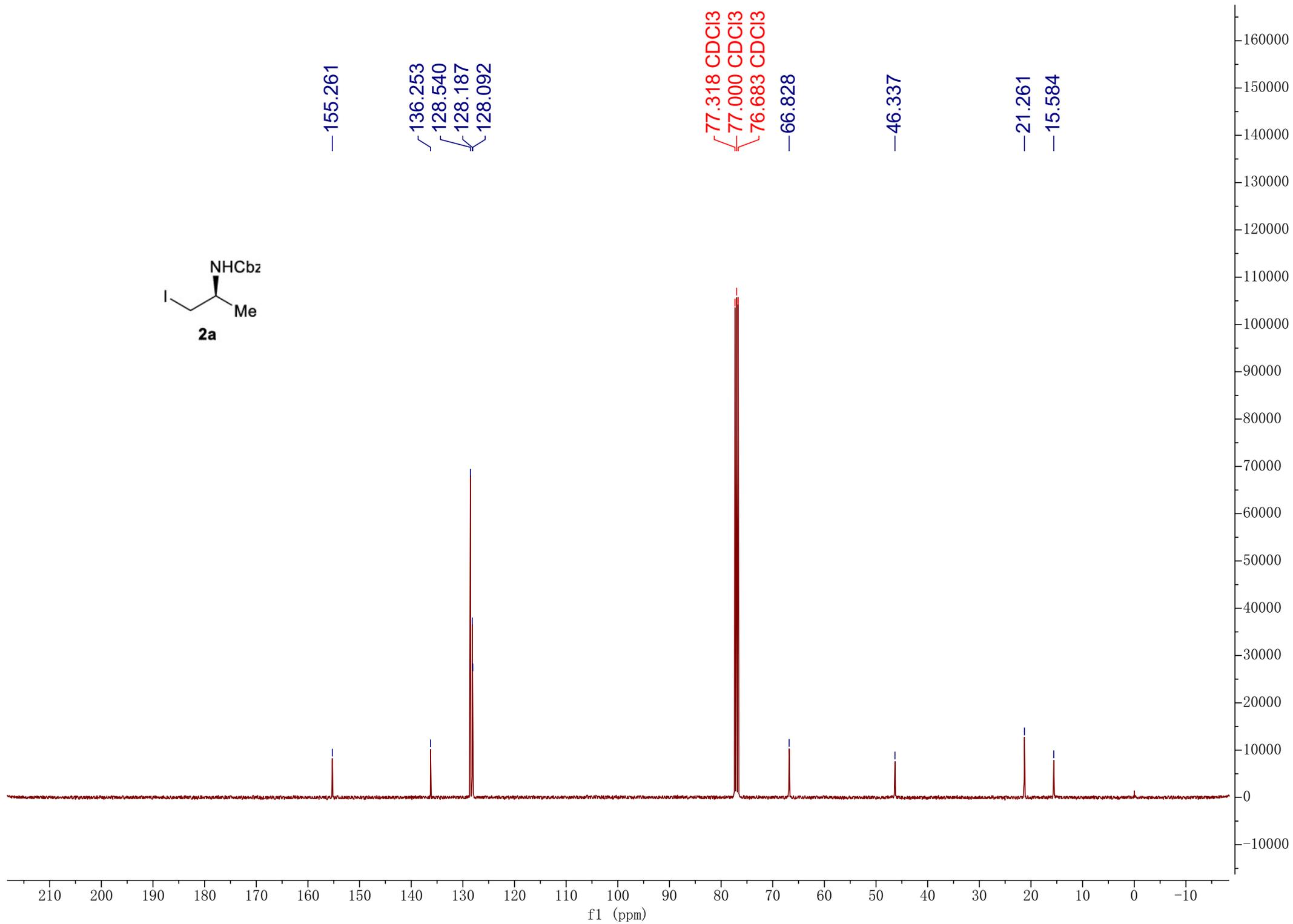
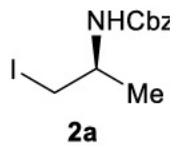
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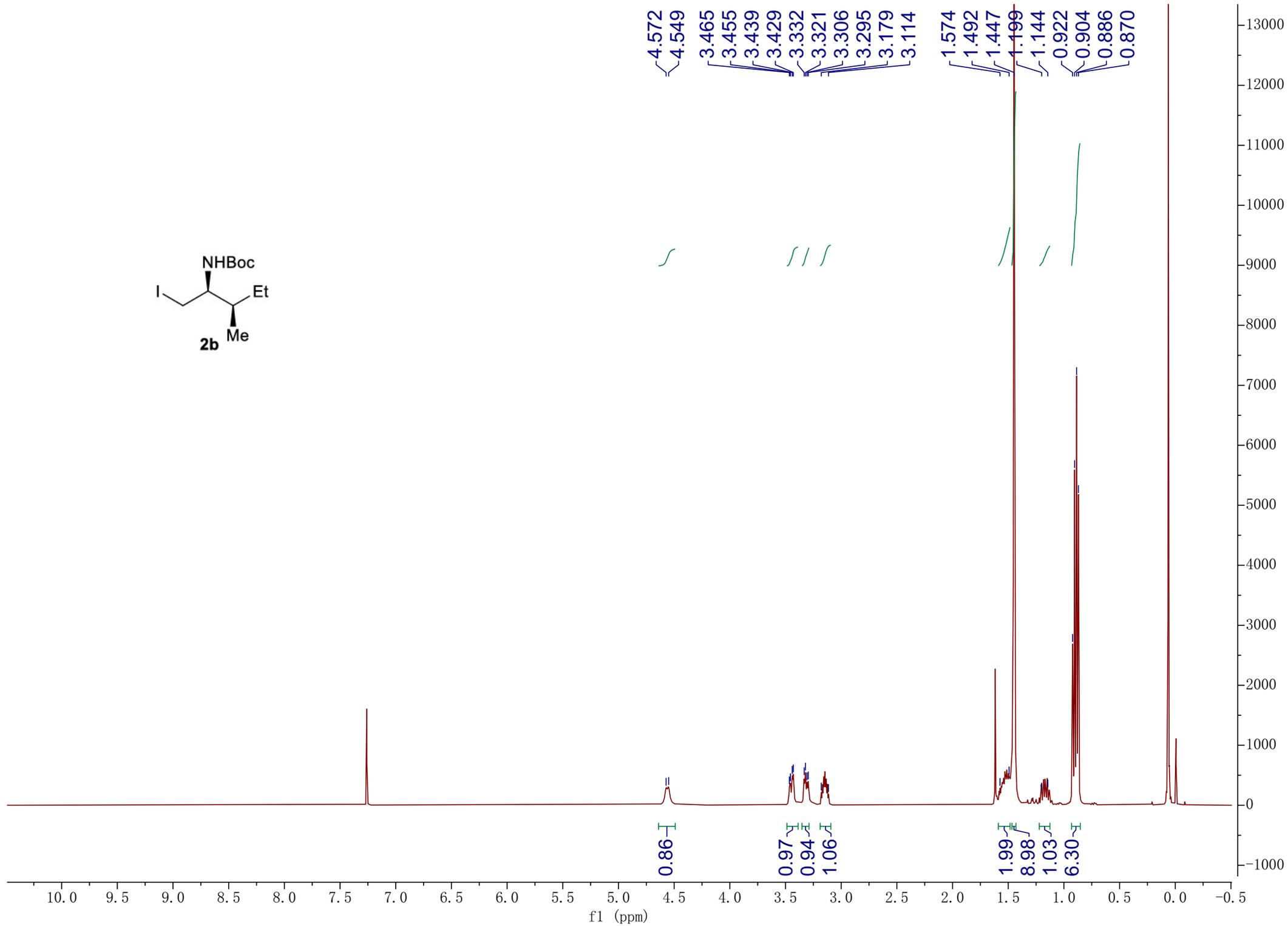
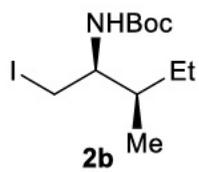


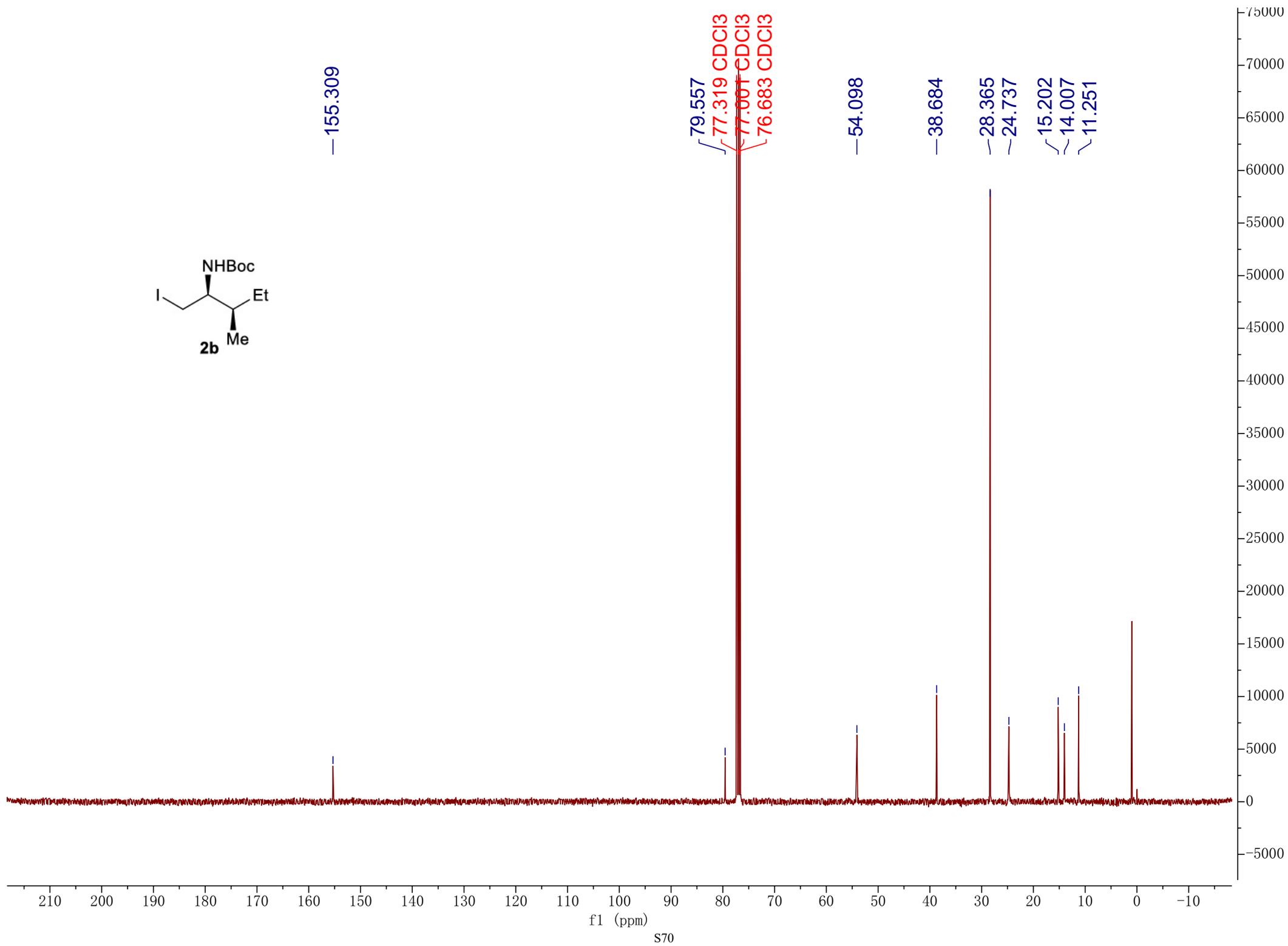
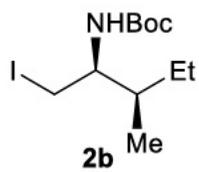
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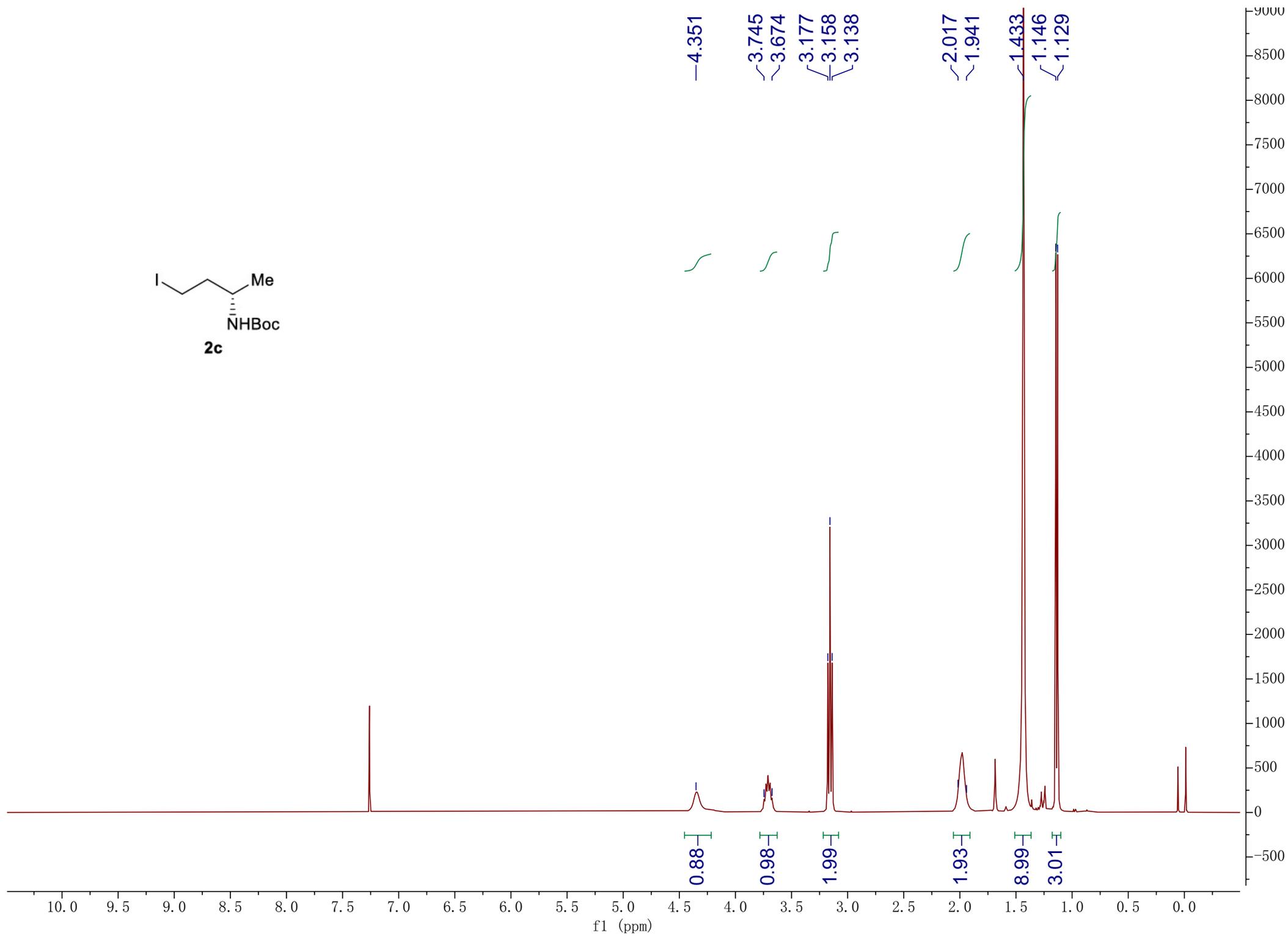
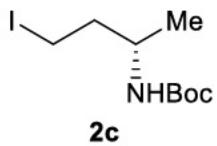


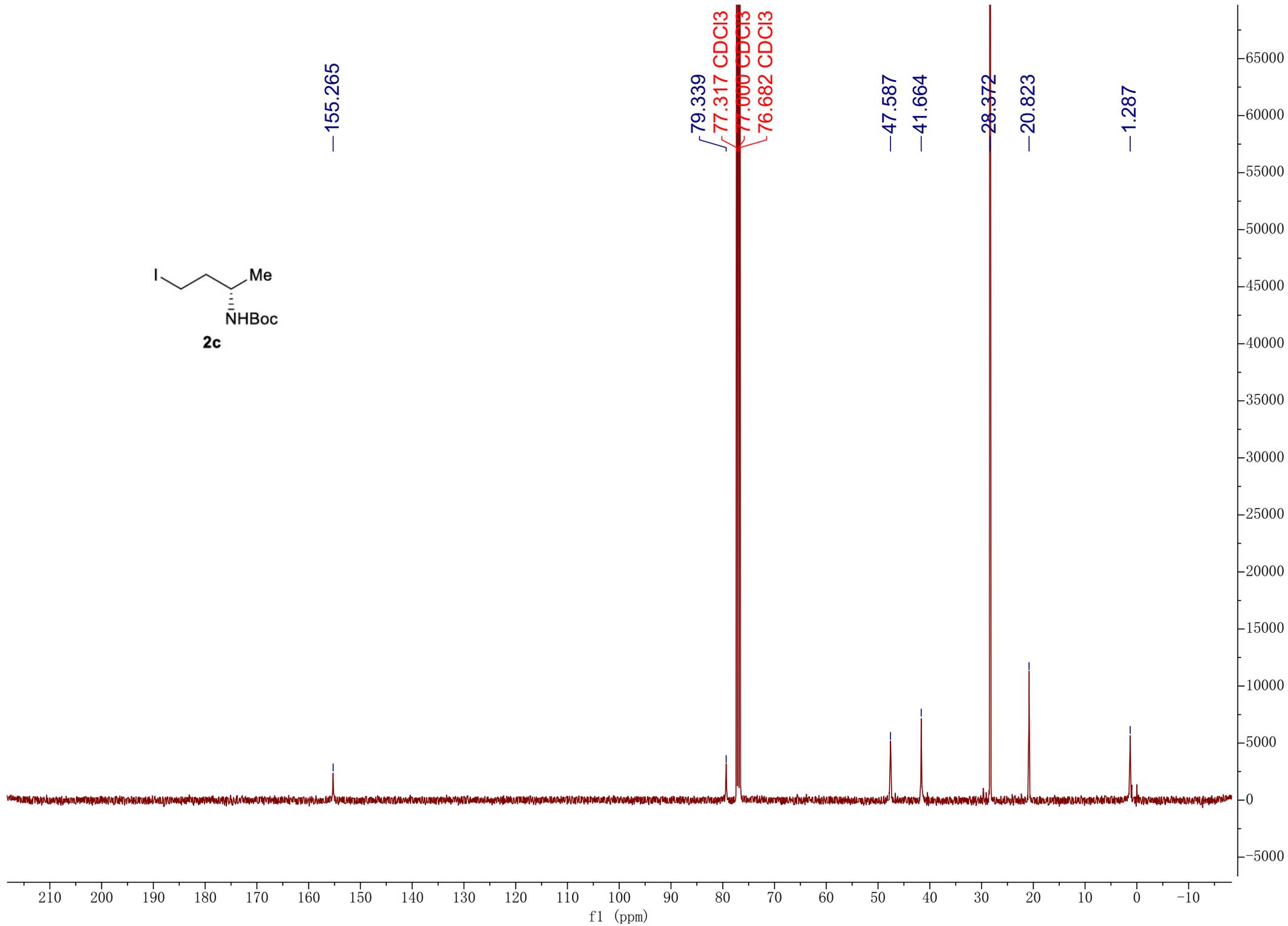
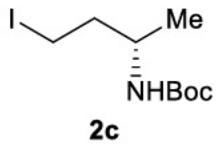


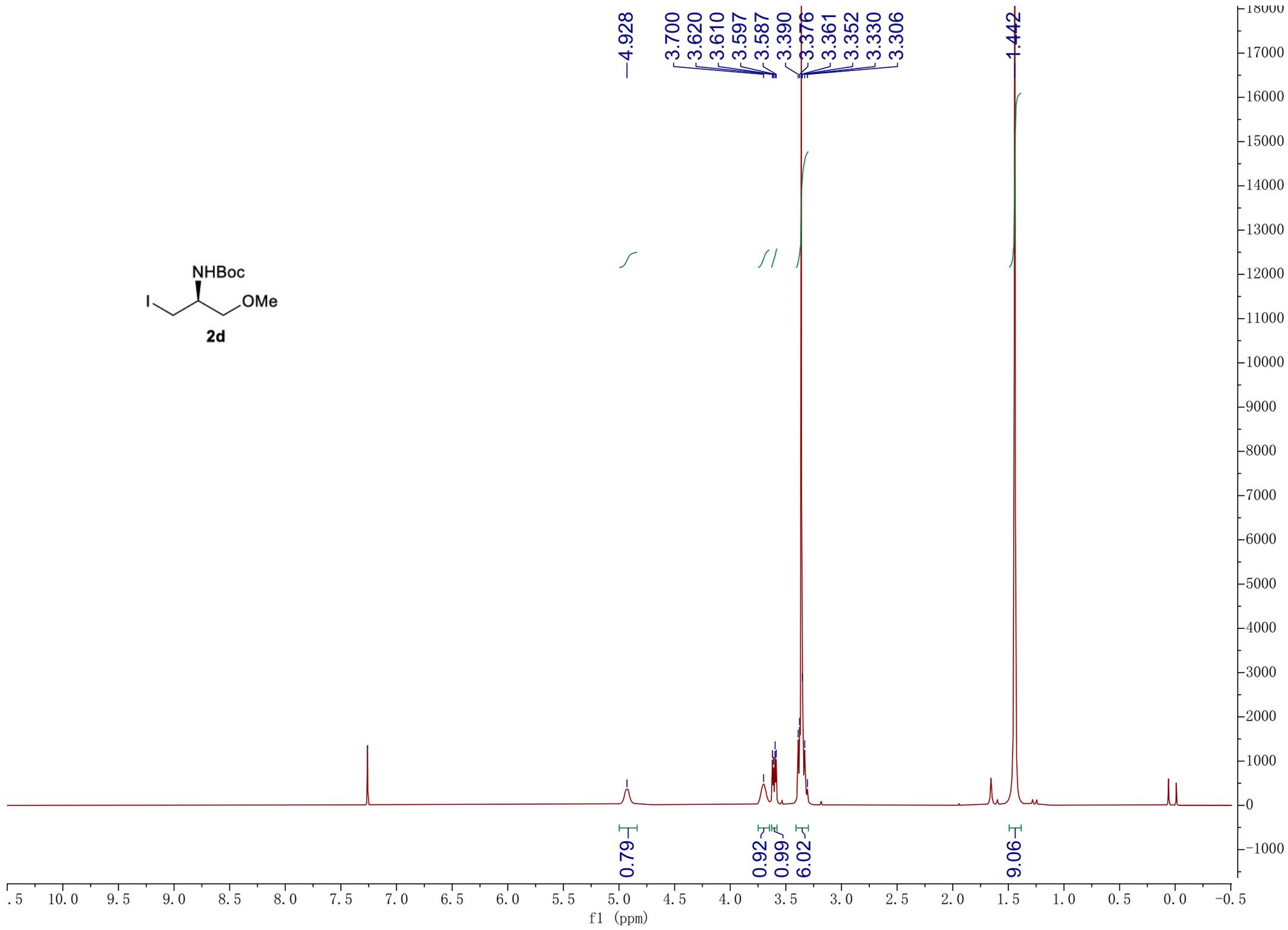
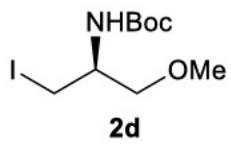


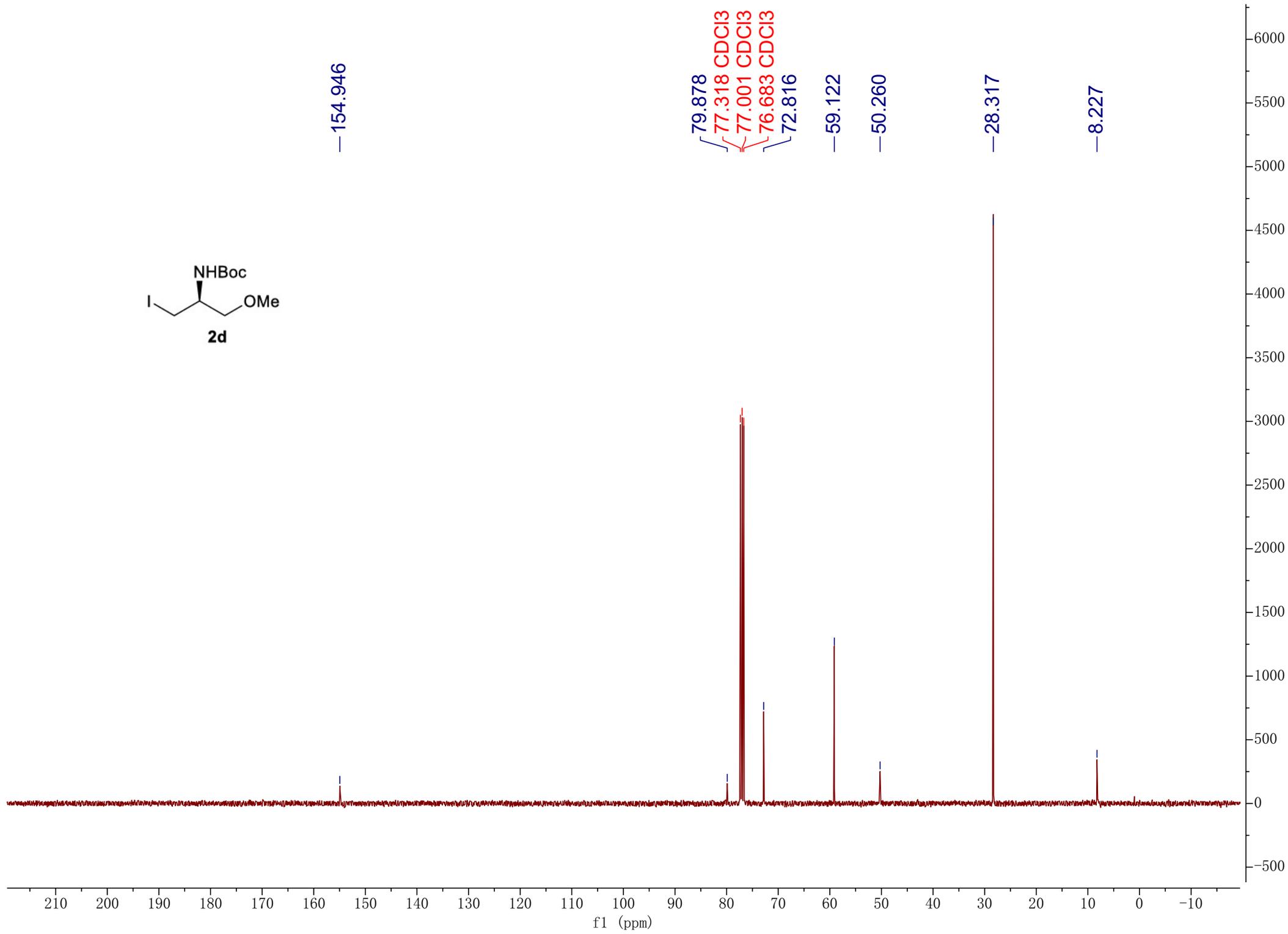
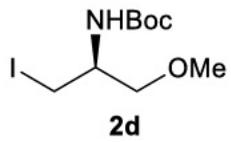


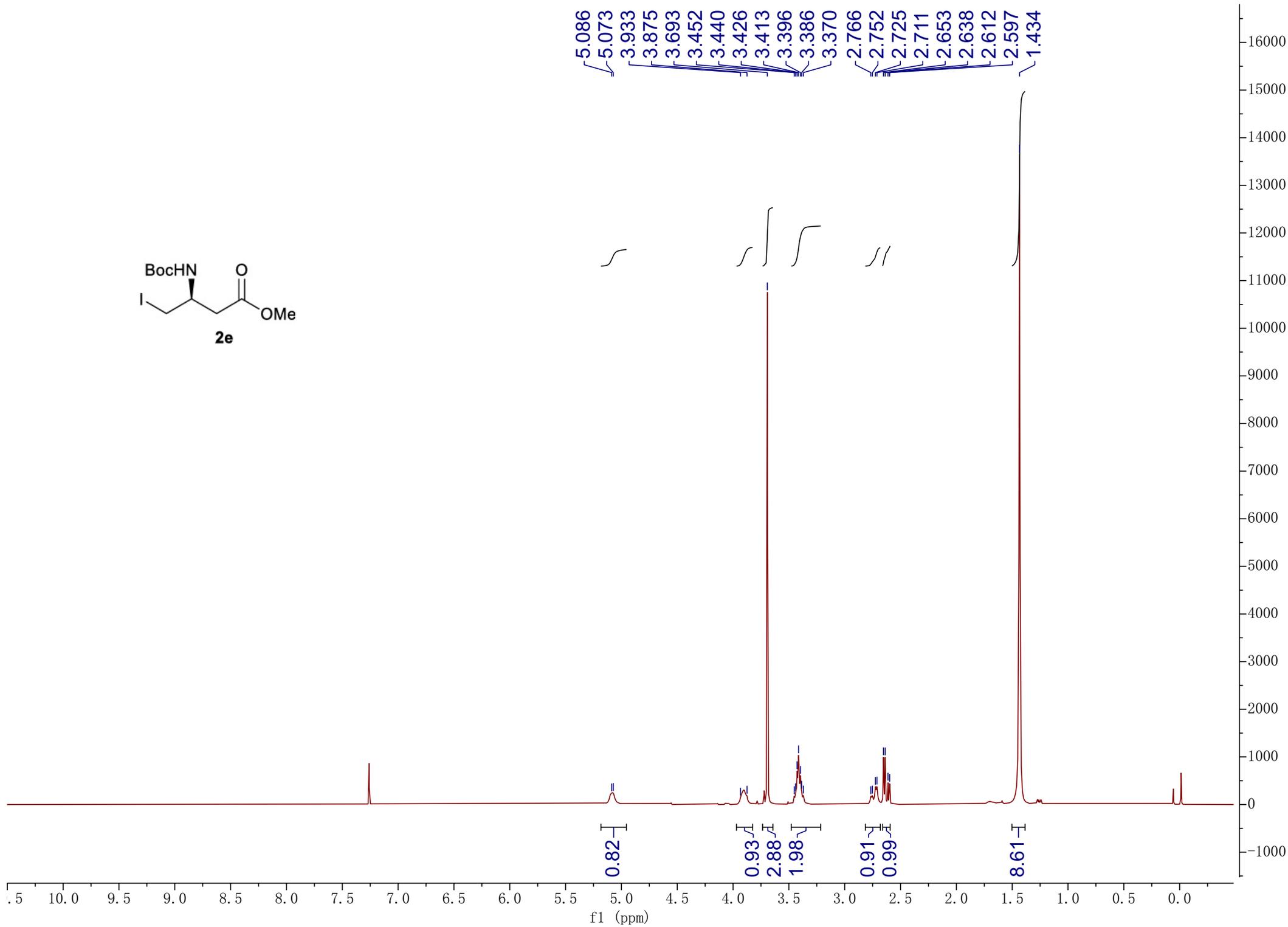
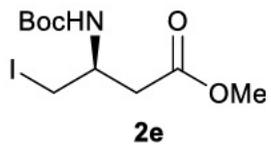


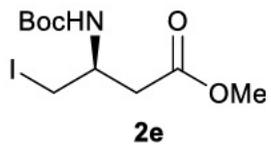












—171.152

—154.675

80.008
77.318 CDCI3
77.000 CDCI3
76.683 CDCI3

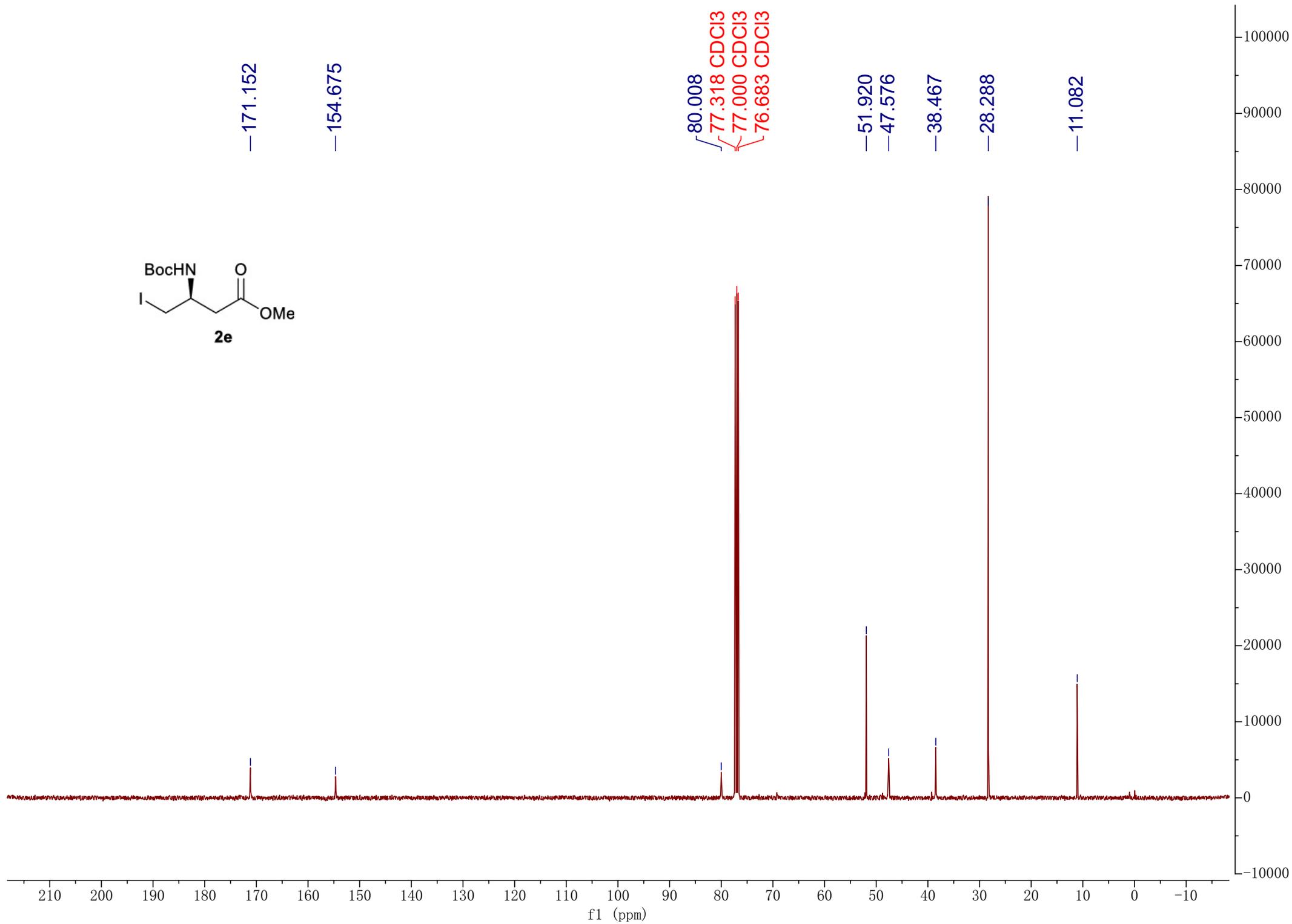
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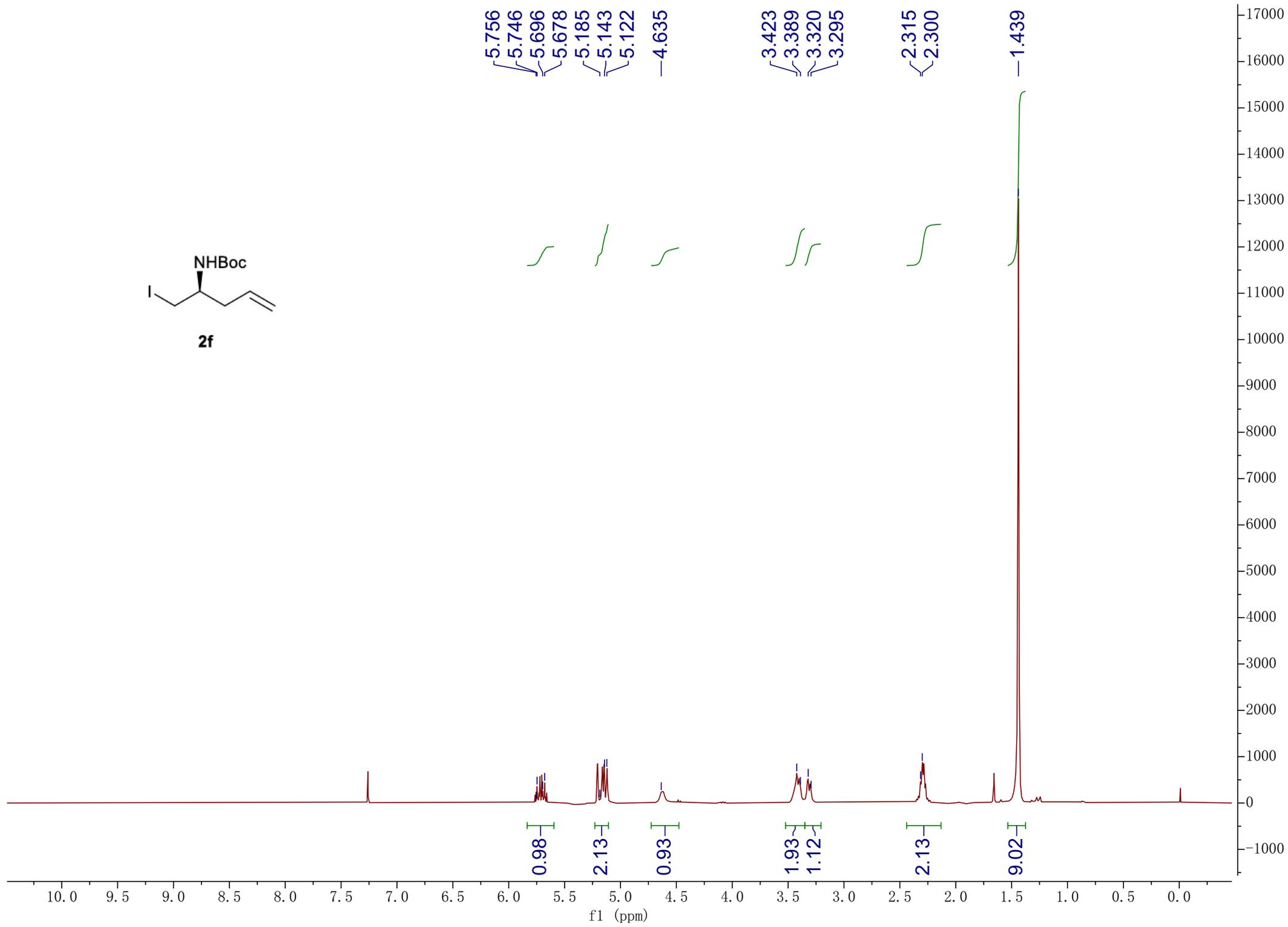
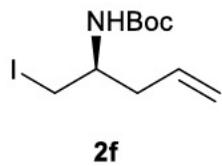
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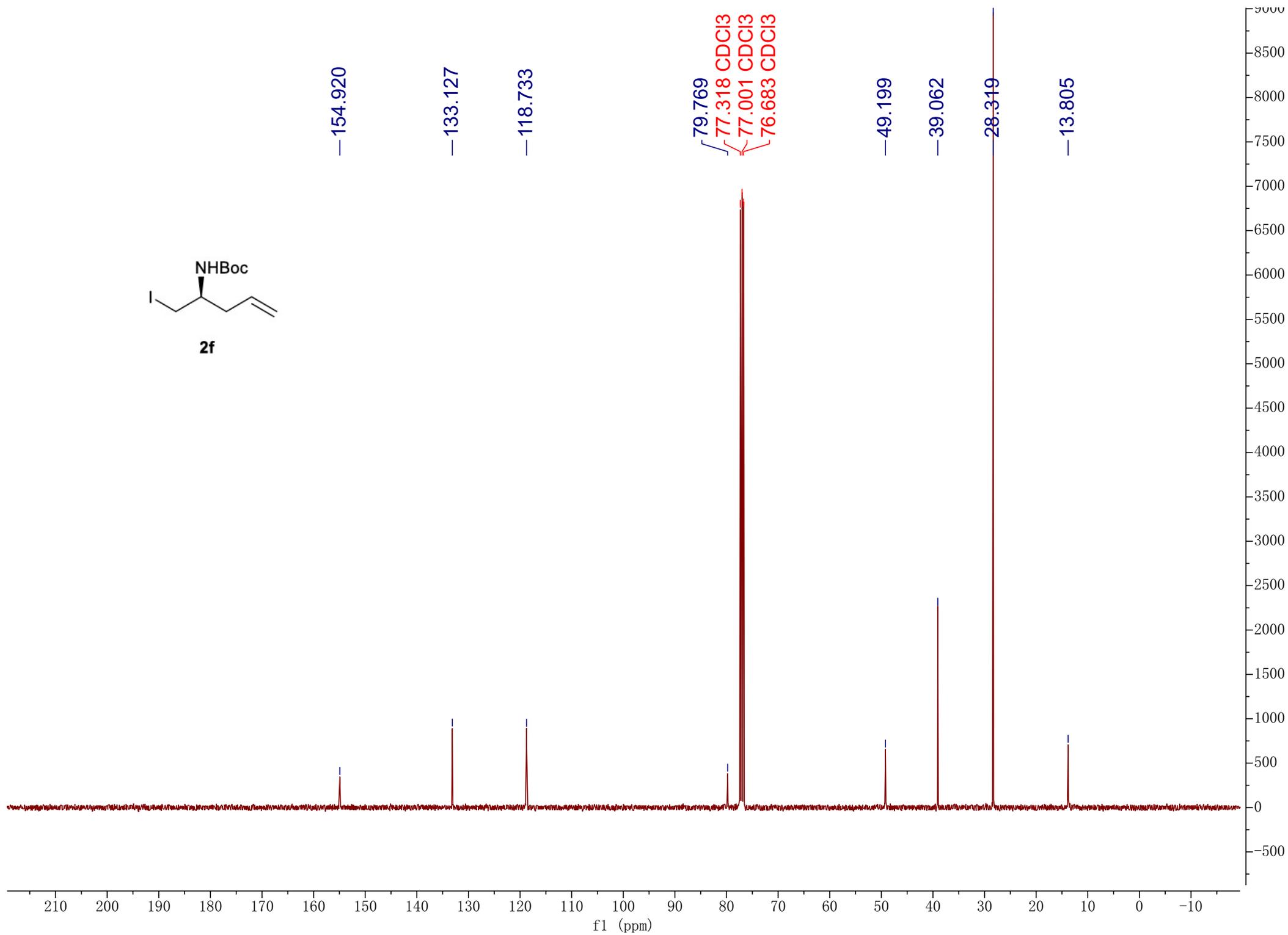
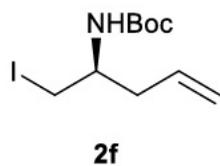
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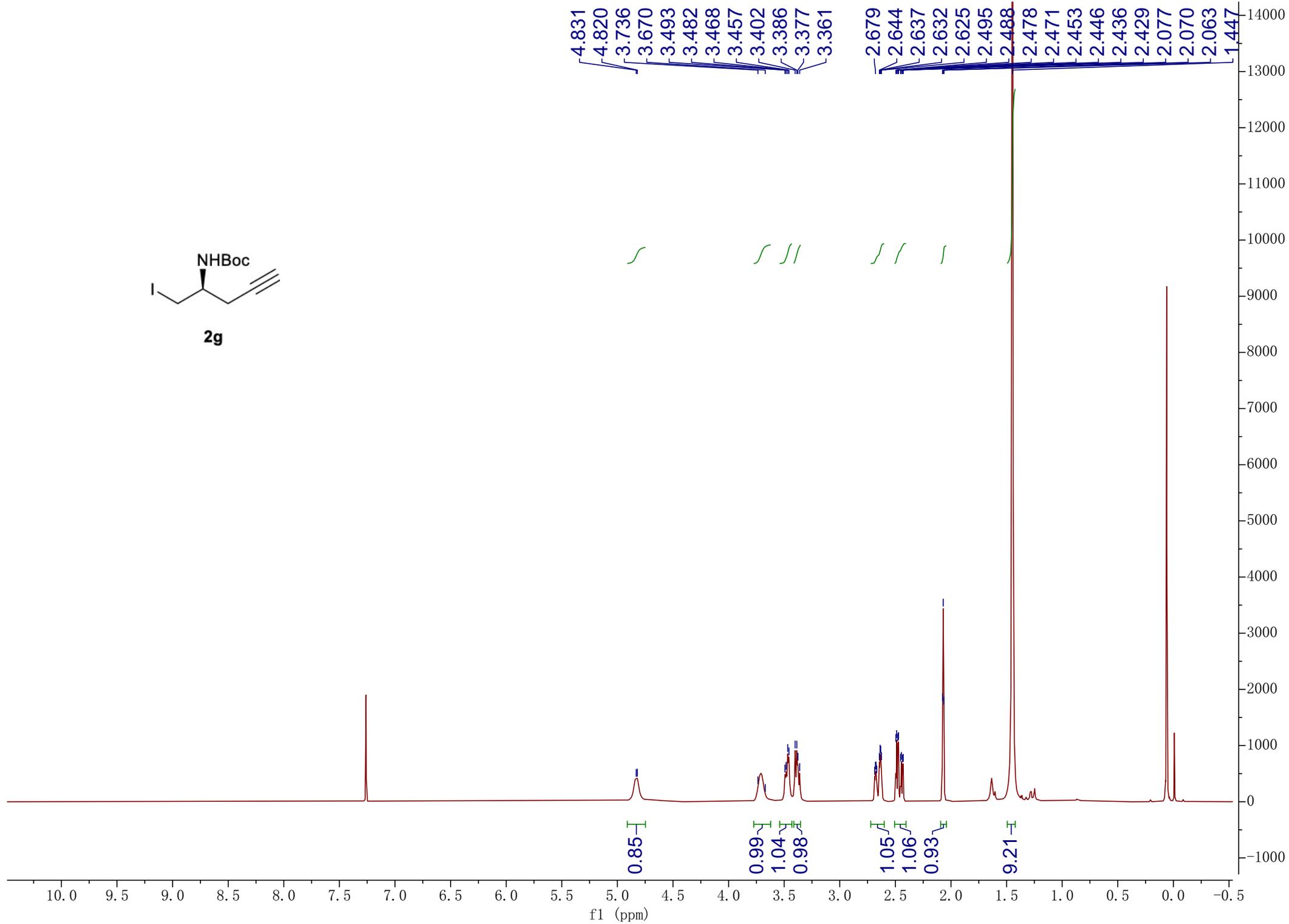
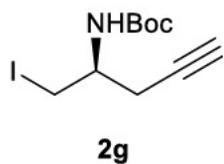
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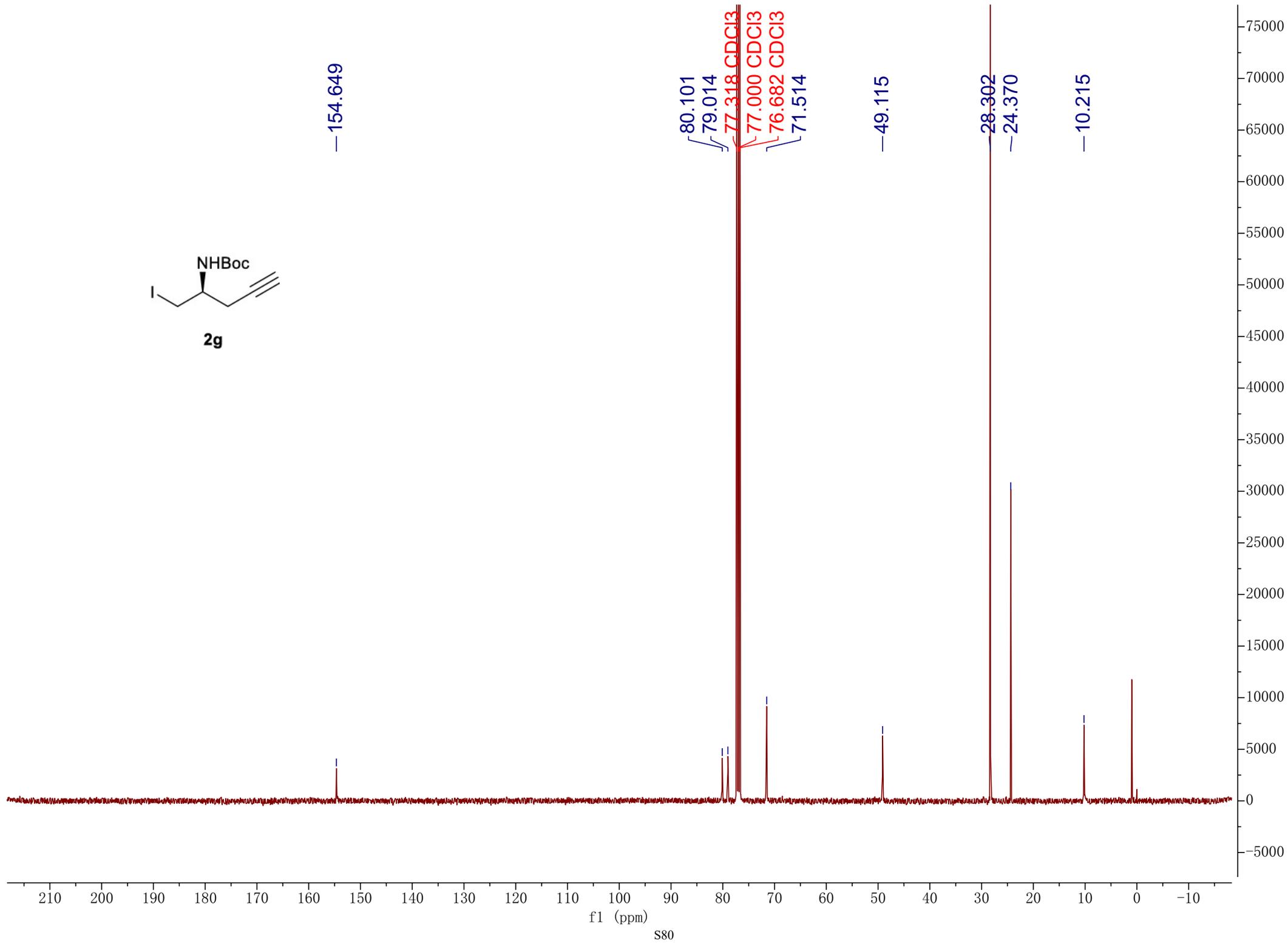
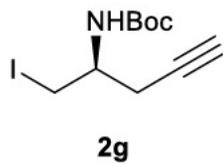
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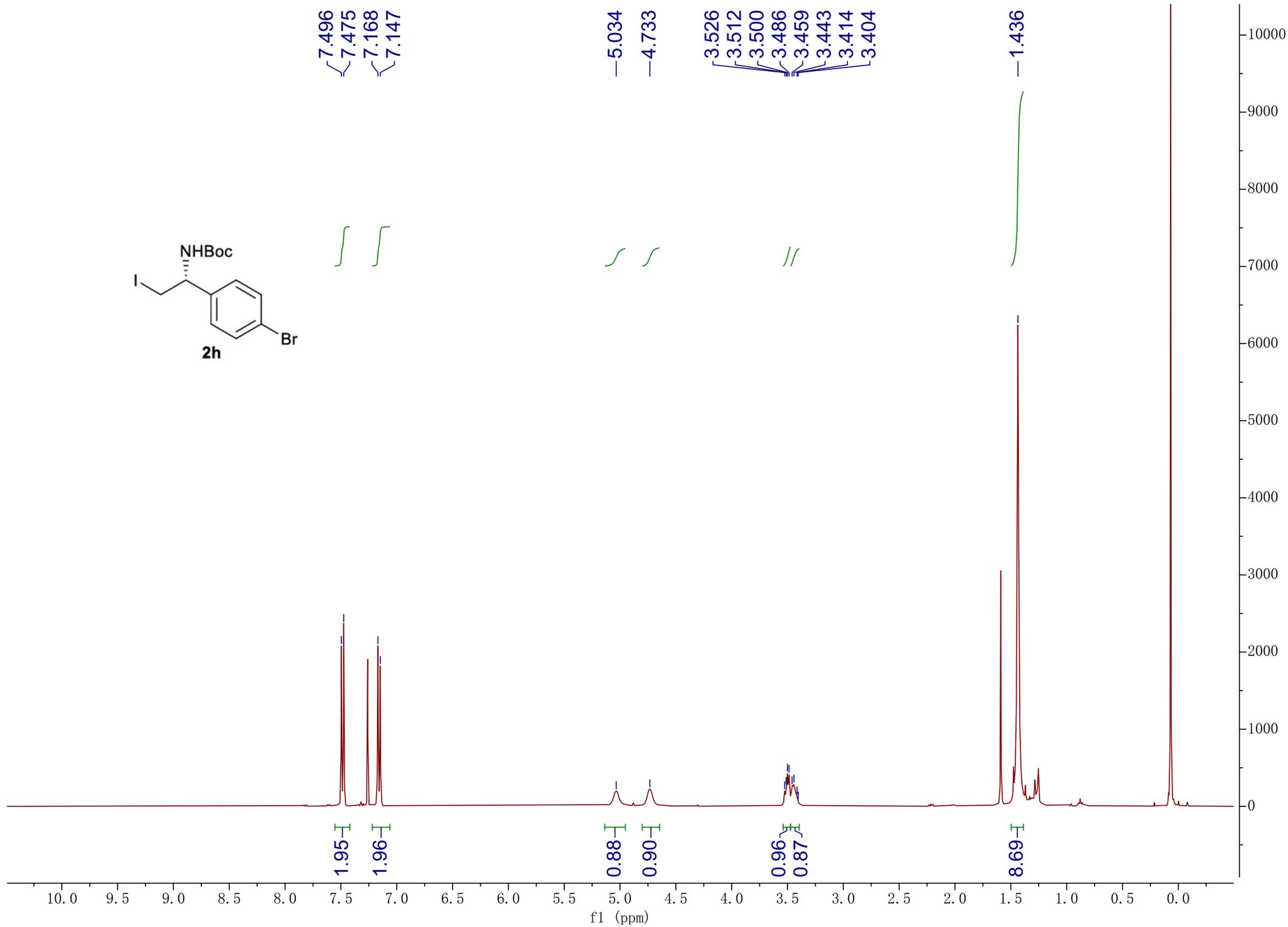
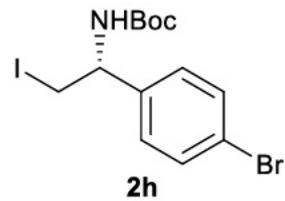


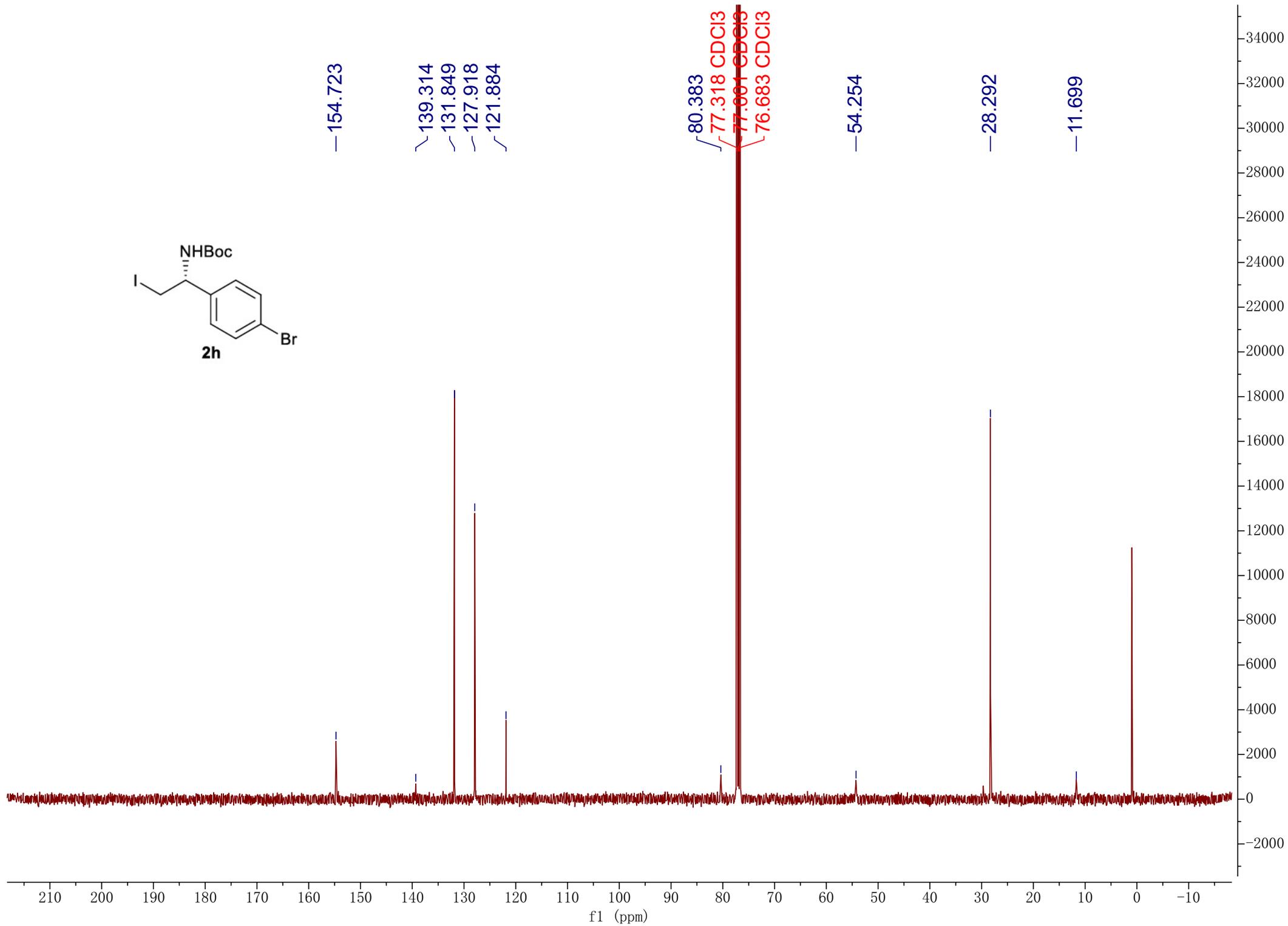
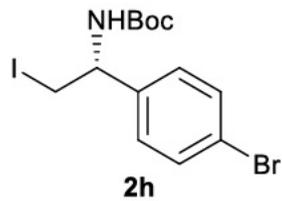


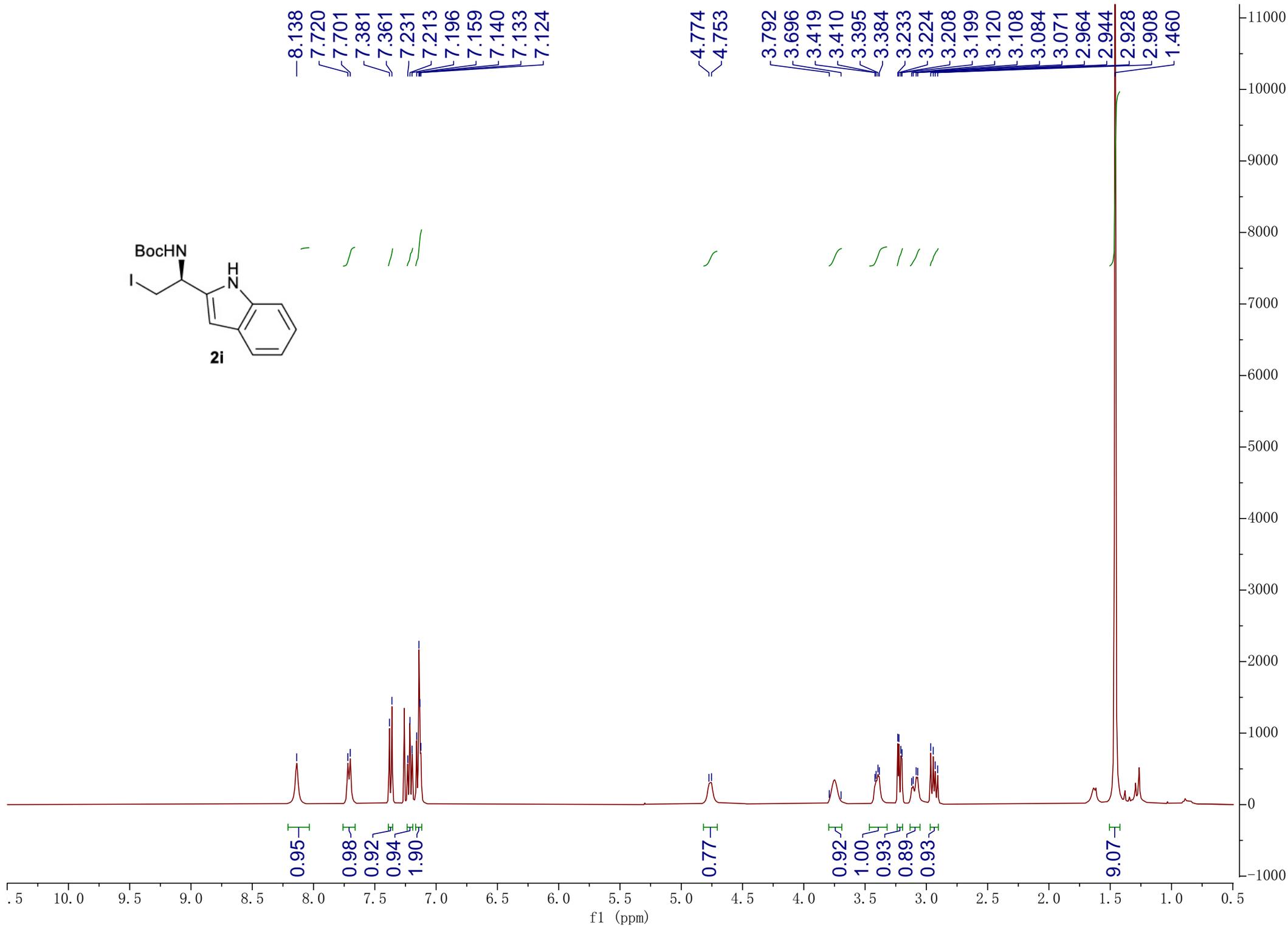
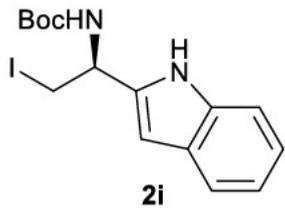


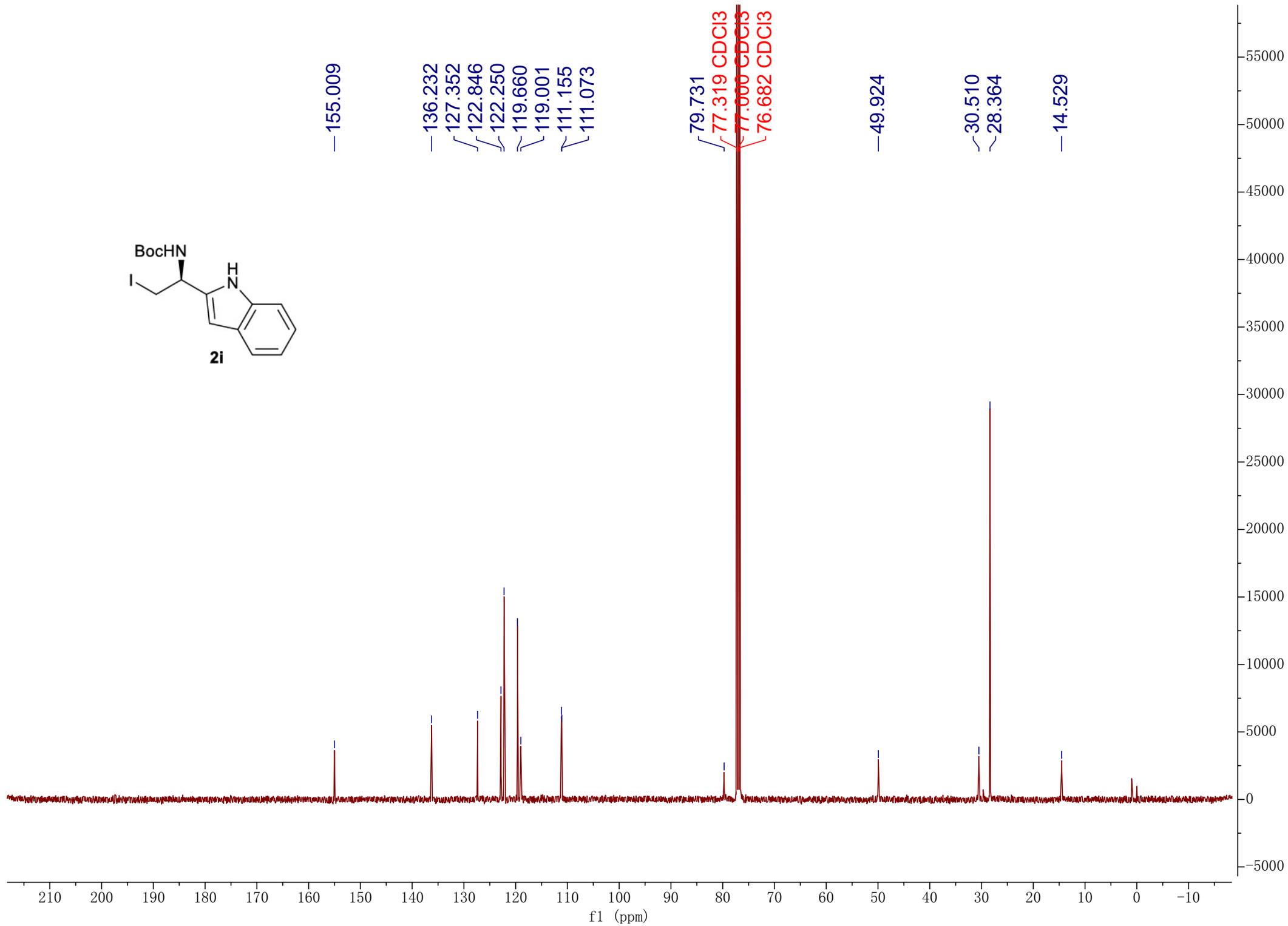
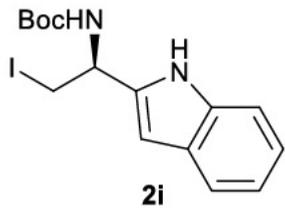


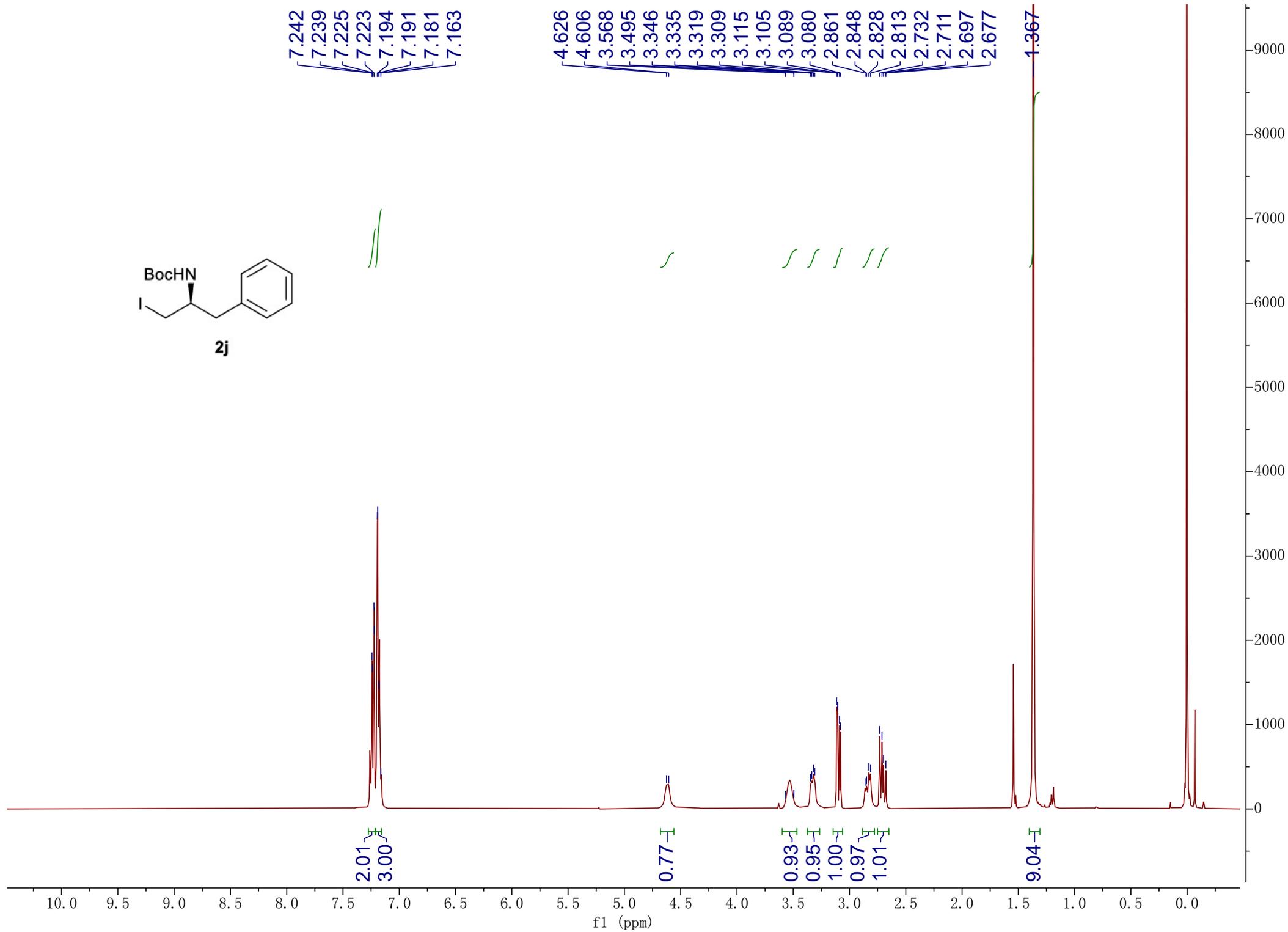
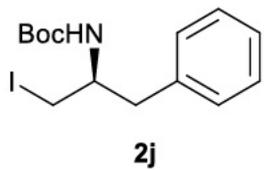


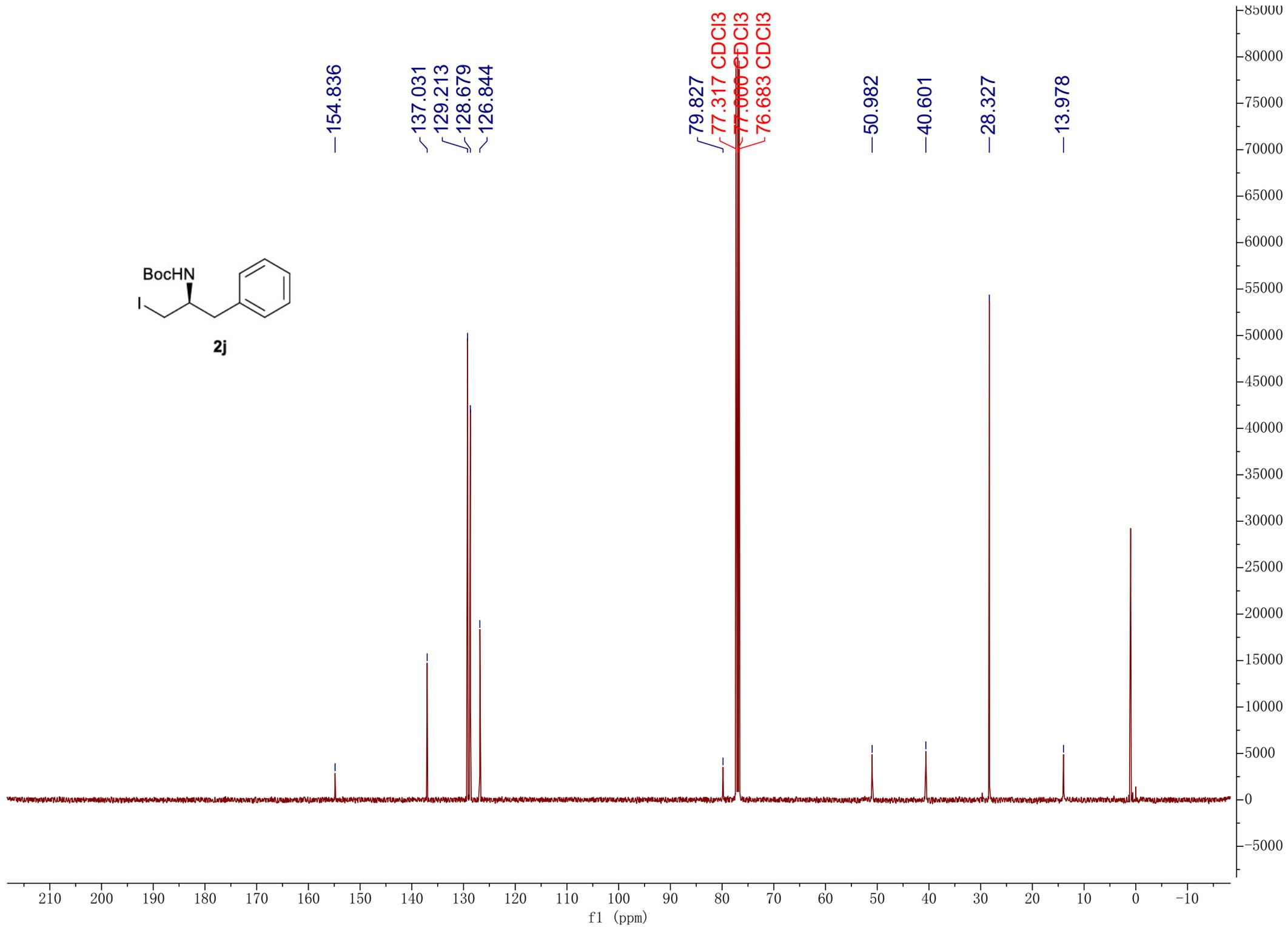
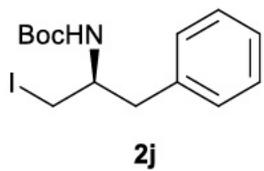


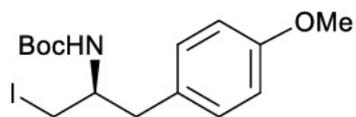




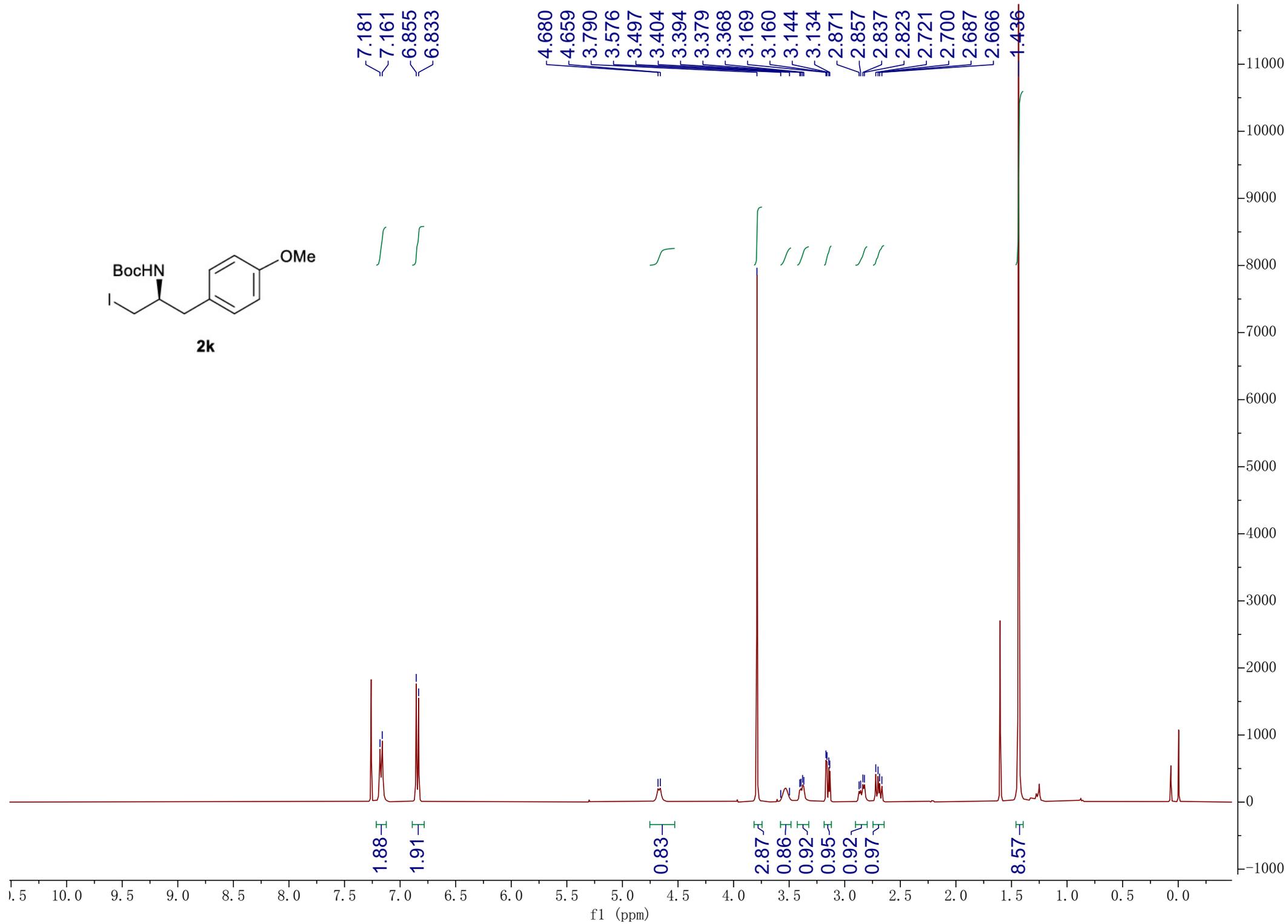


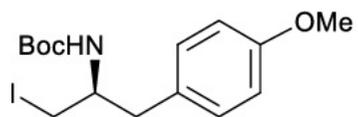




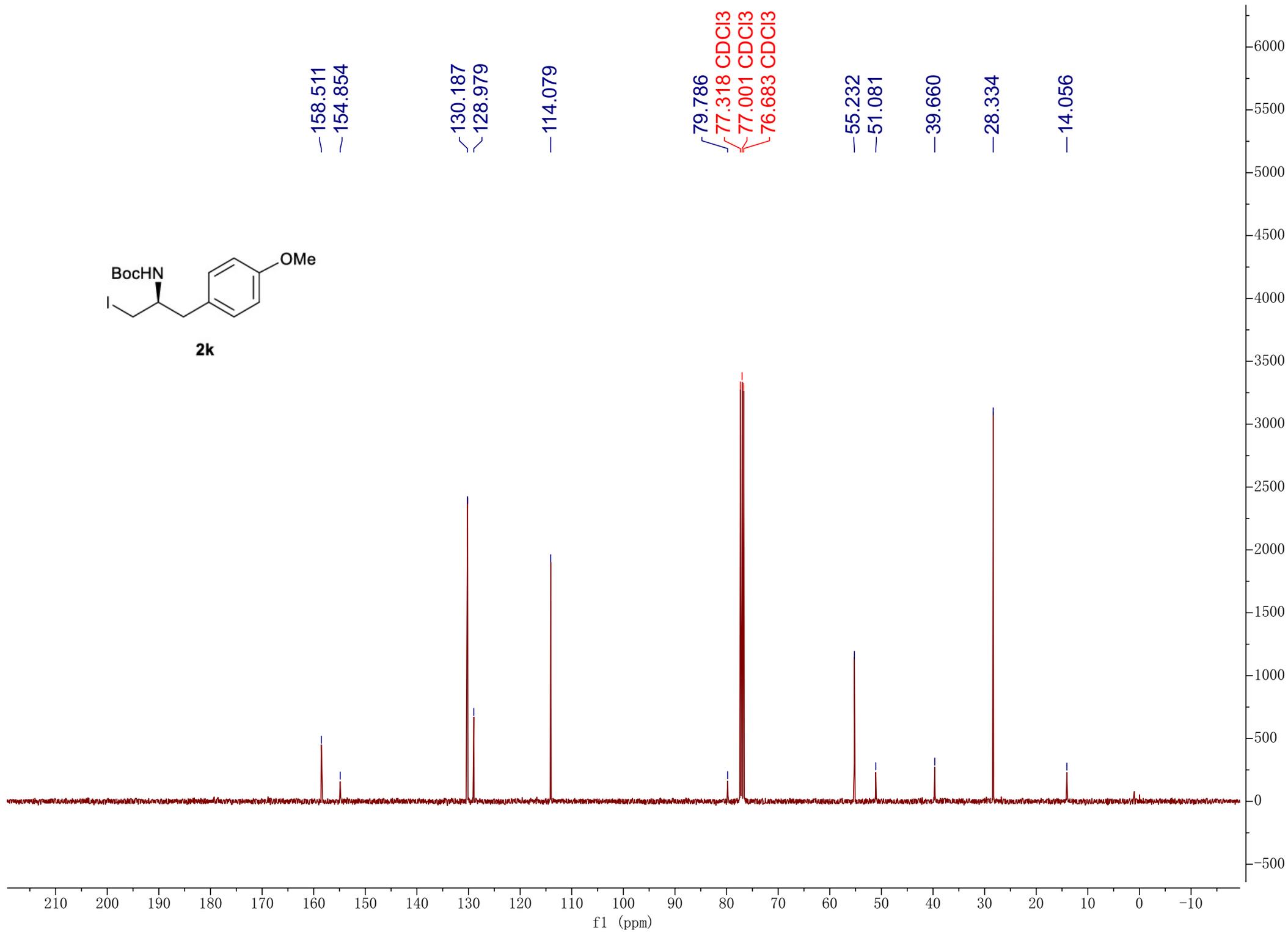


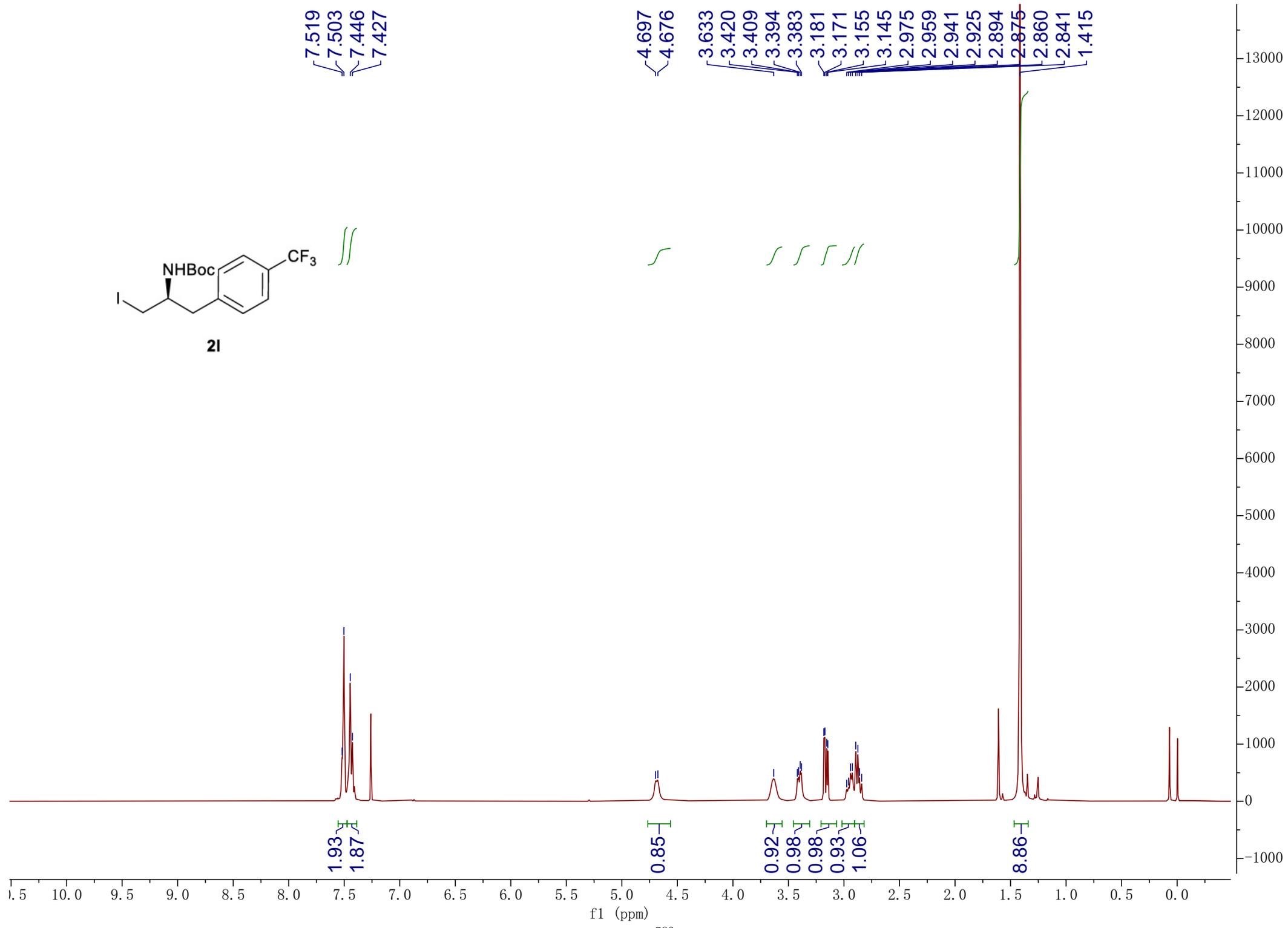
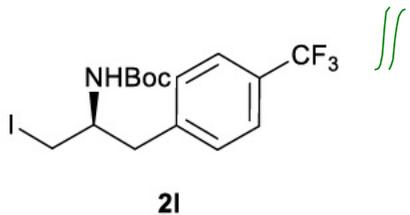
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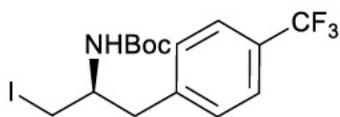




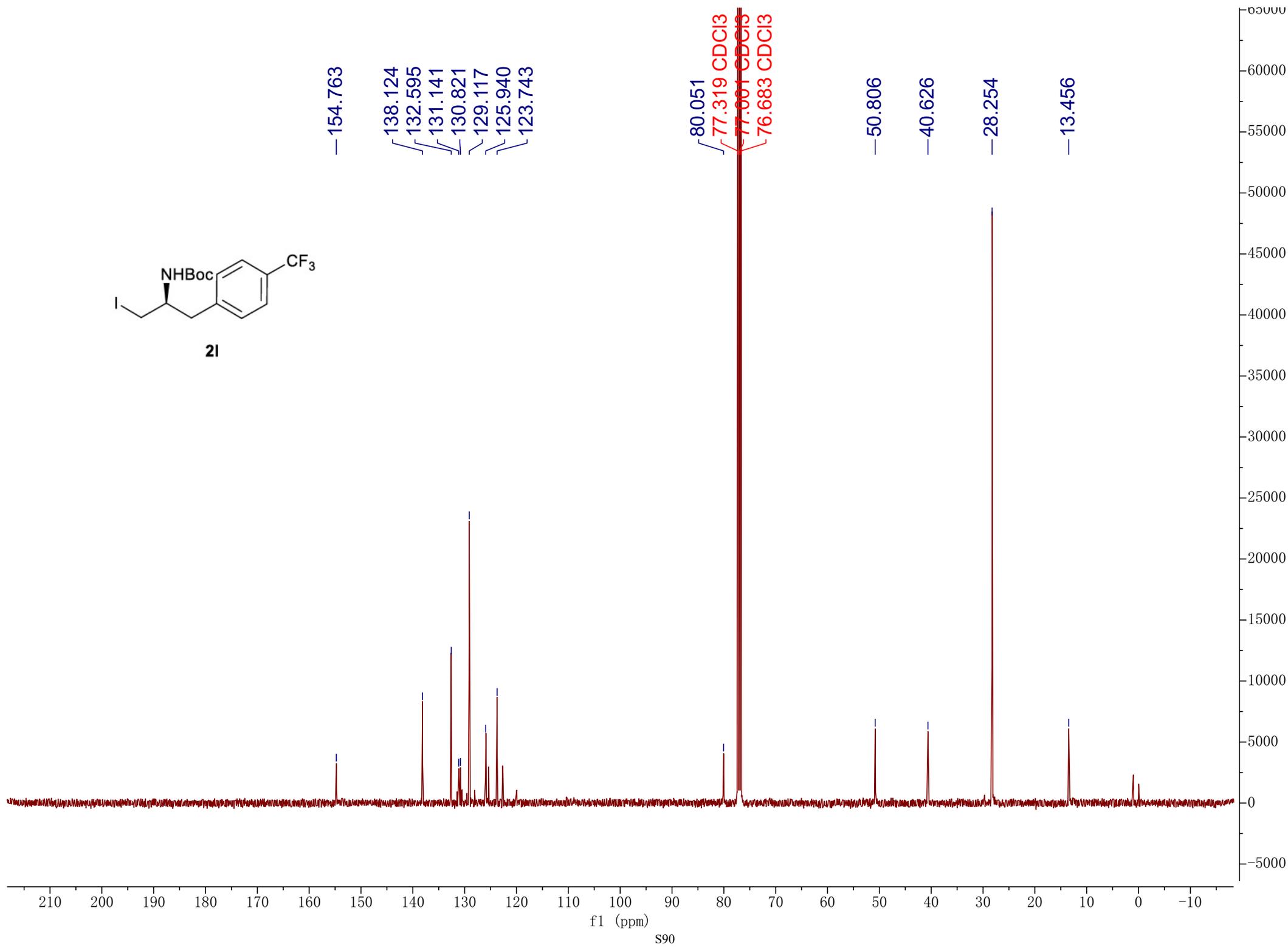
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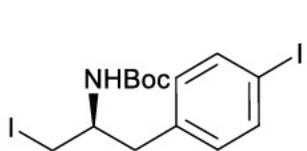




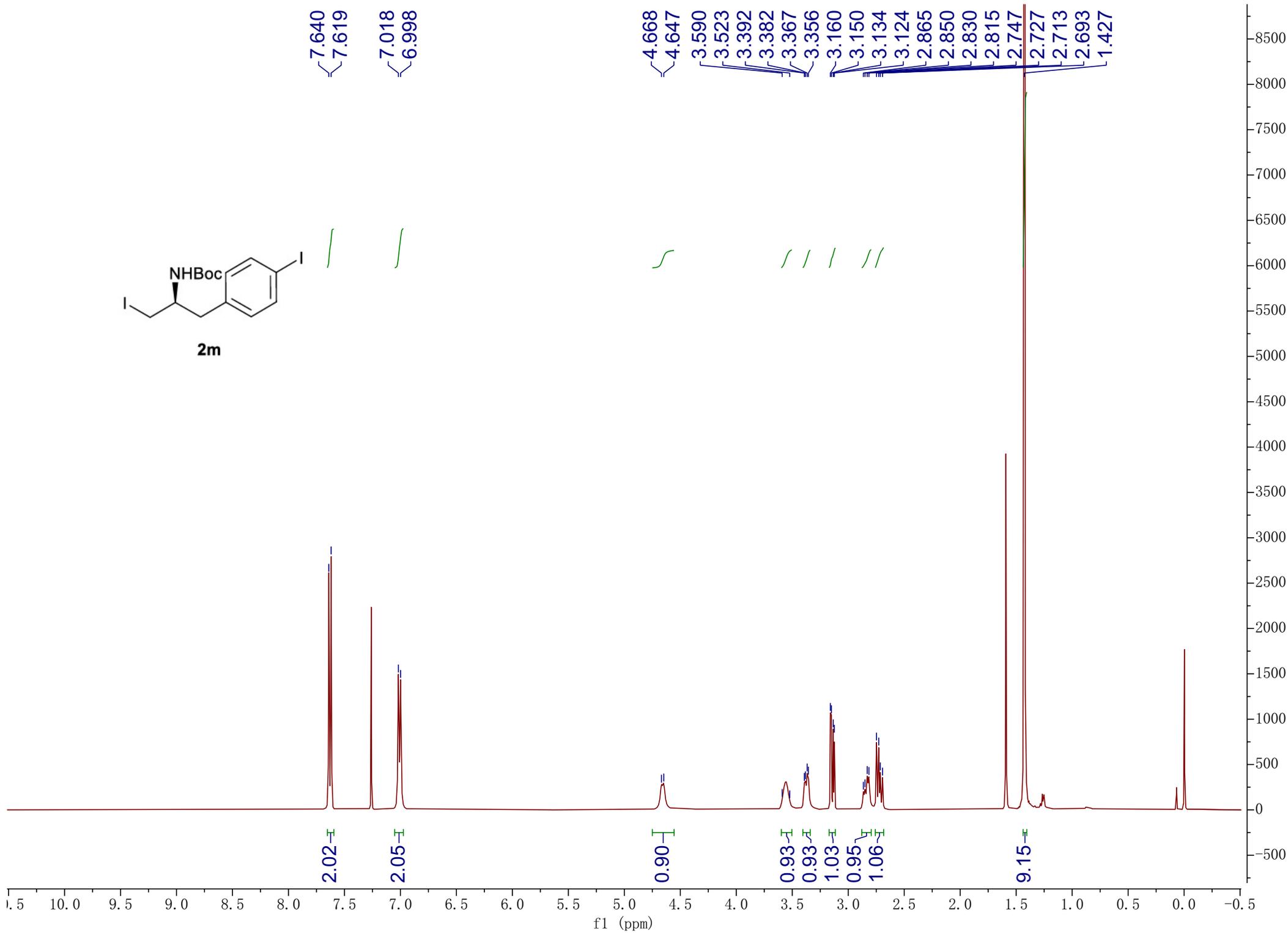


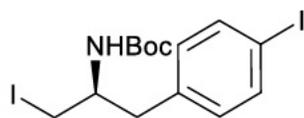
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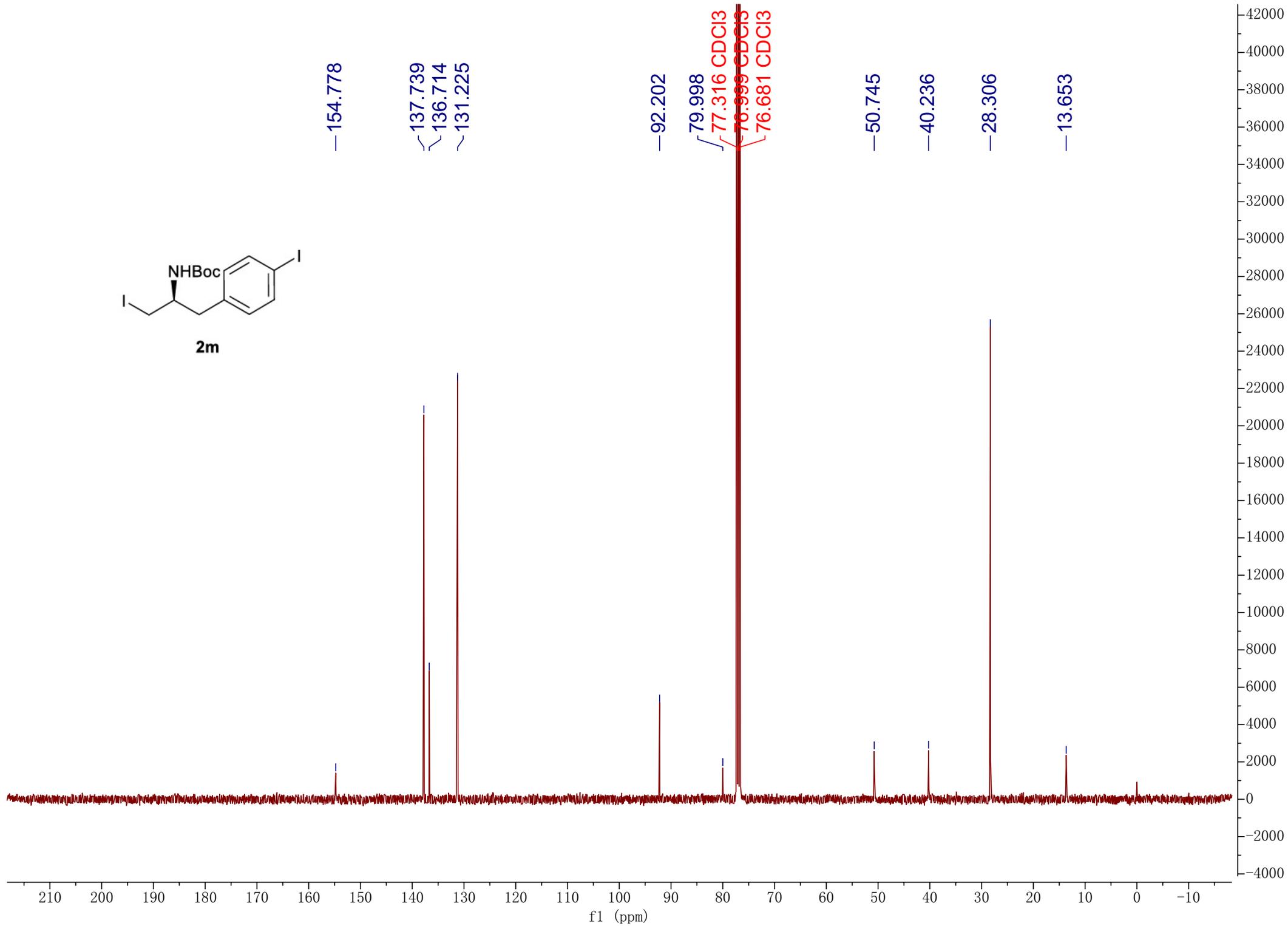


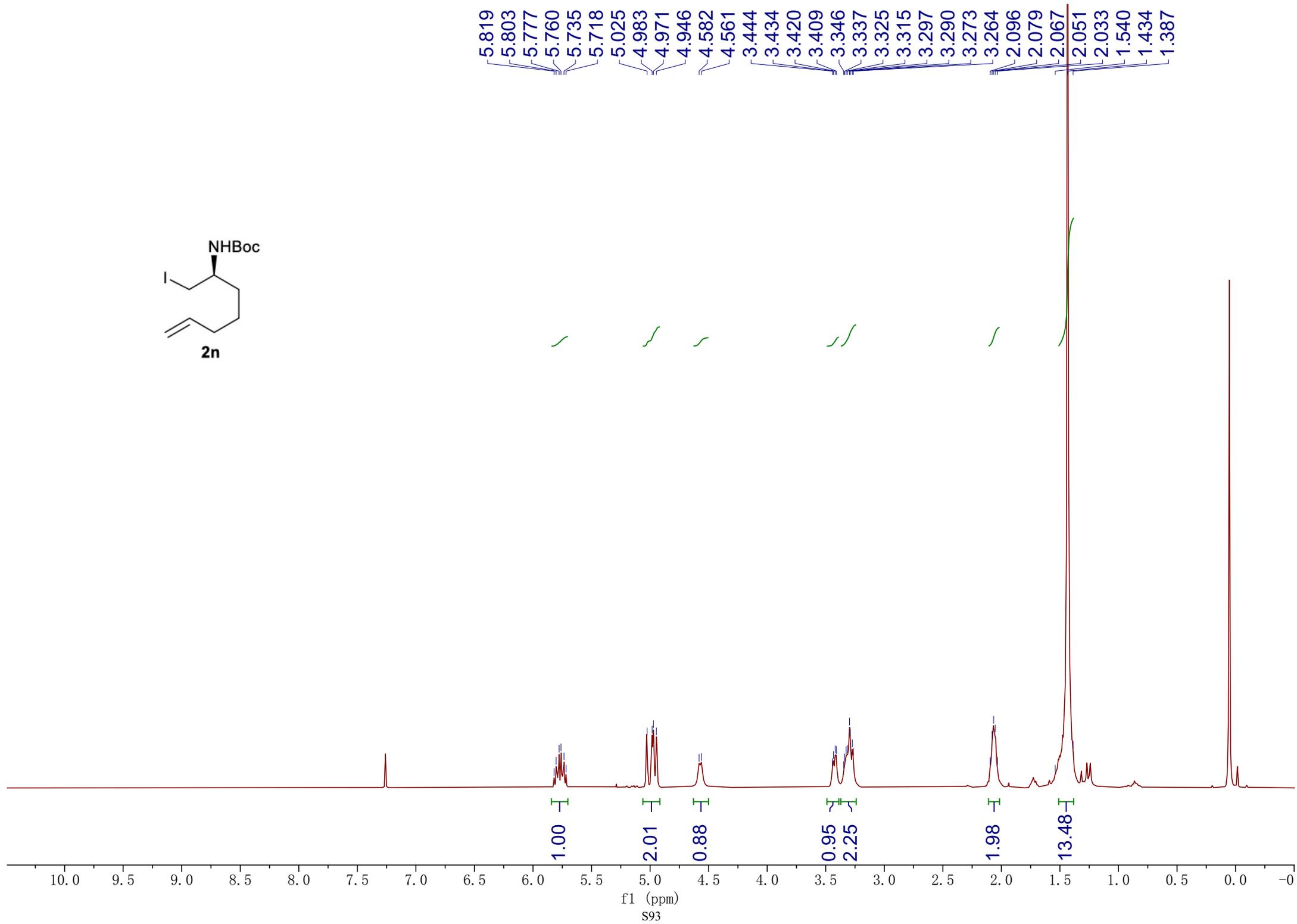
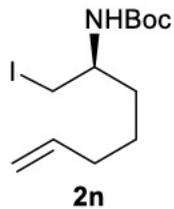
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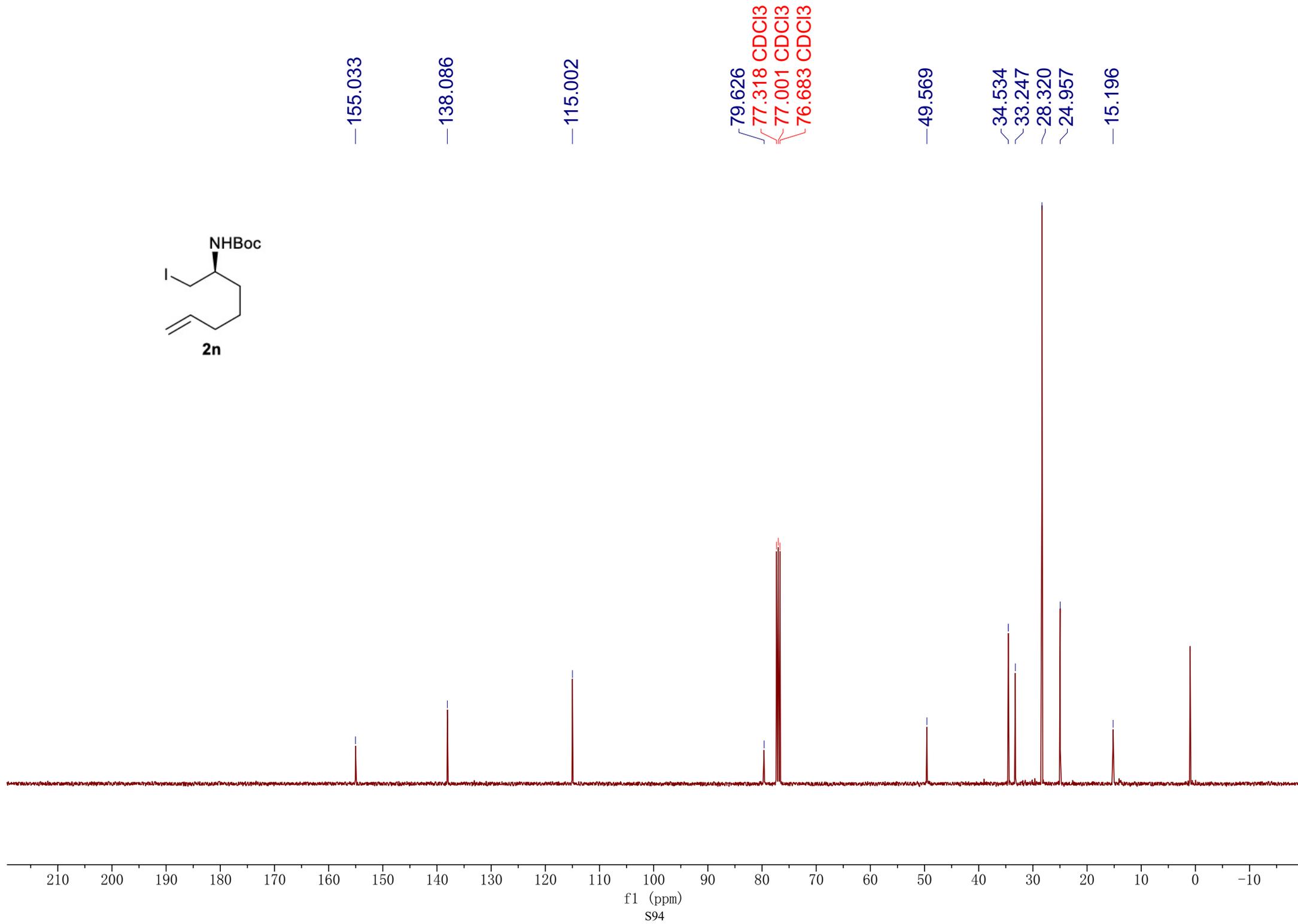
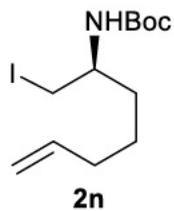


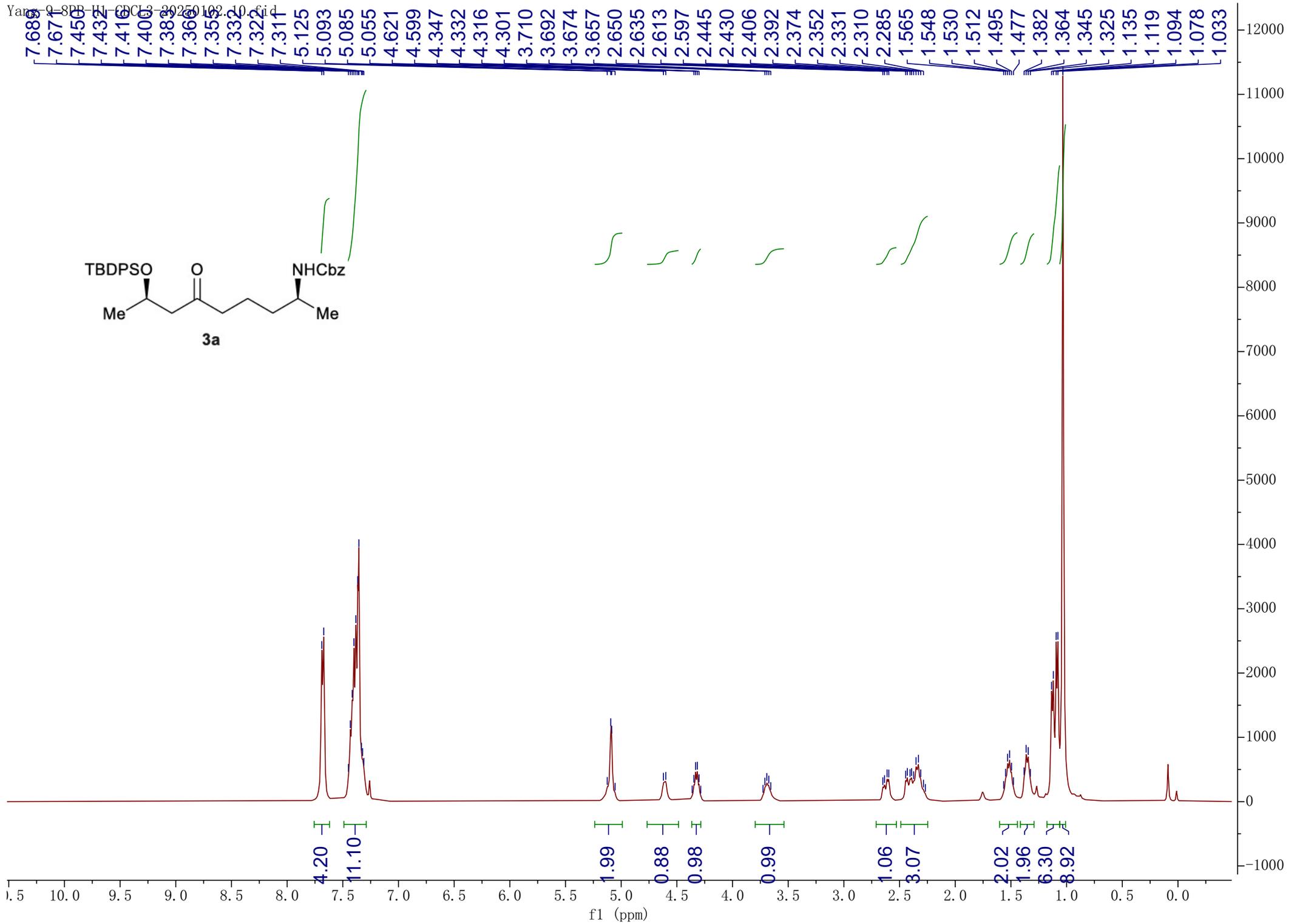


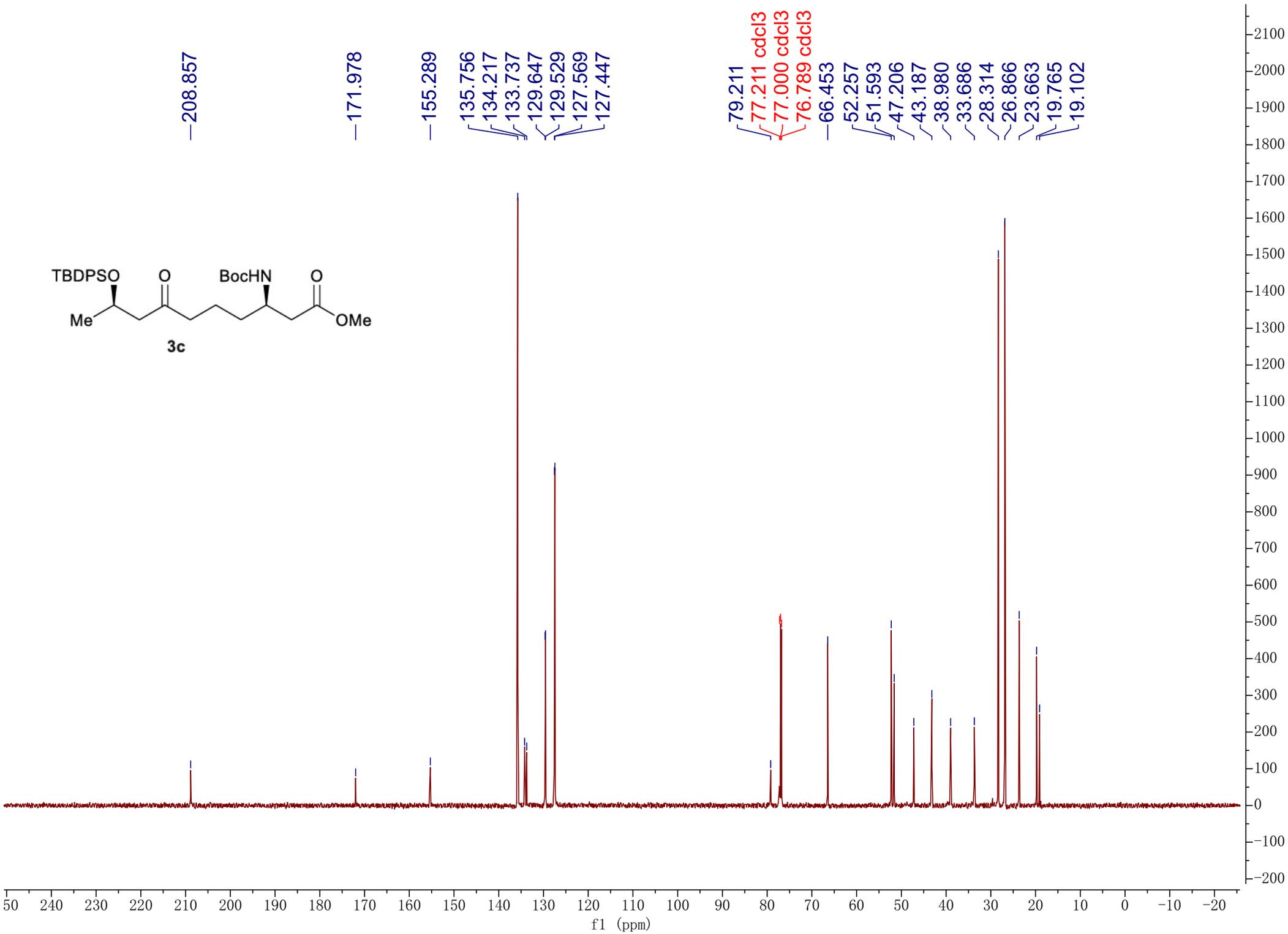
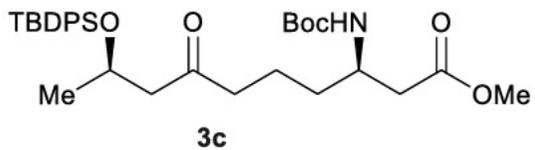
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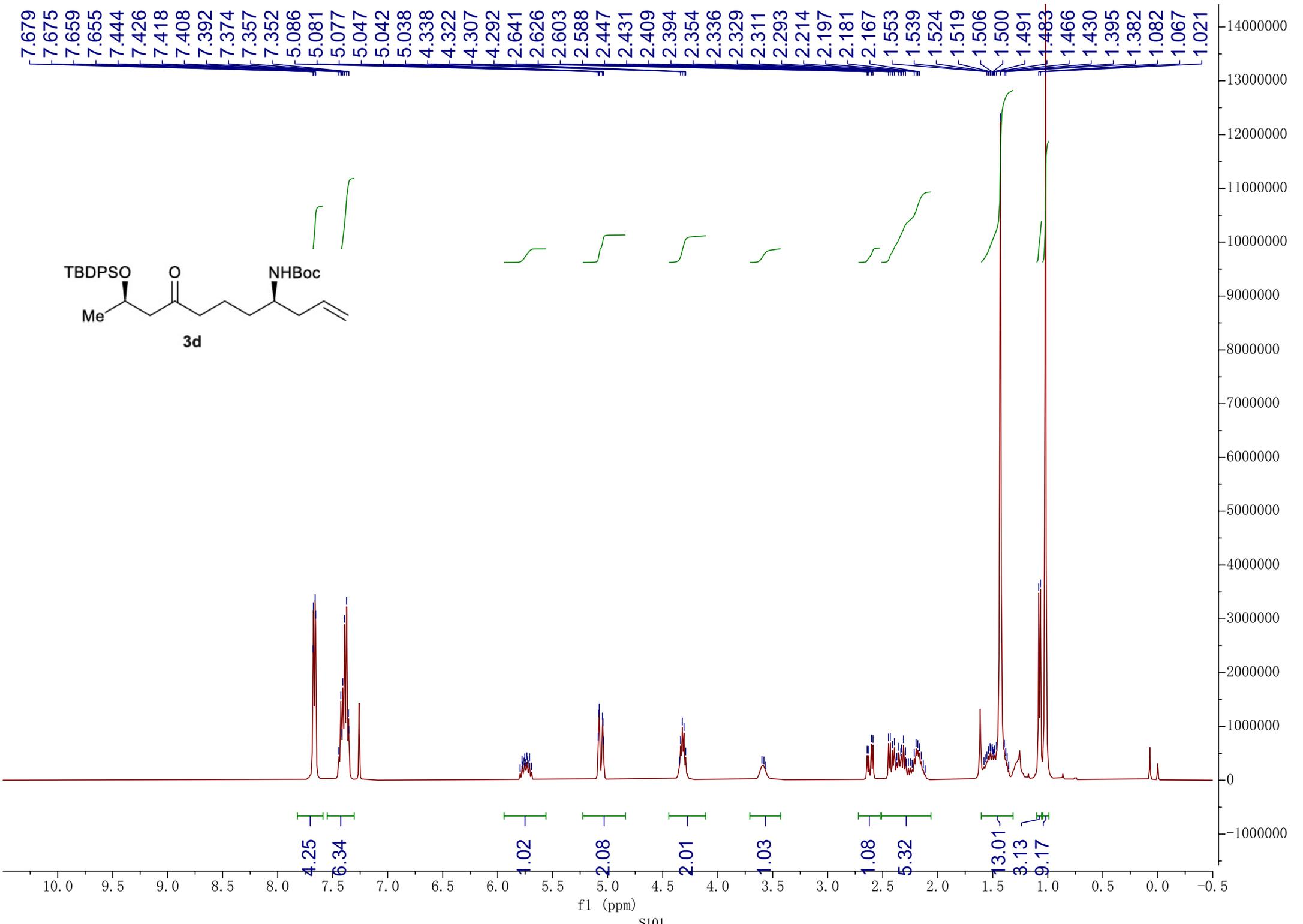


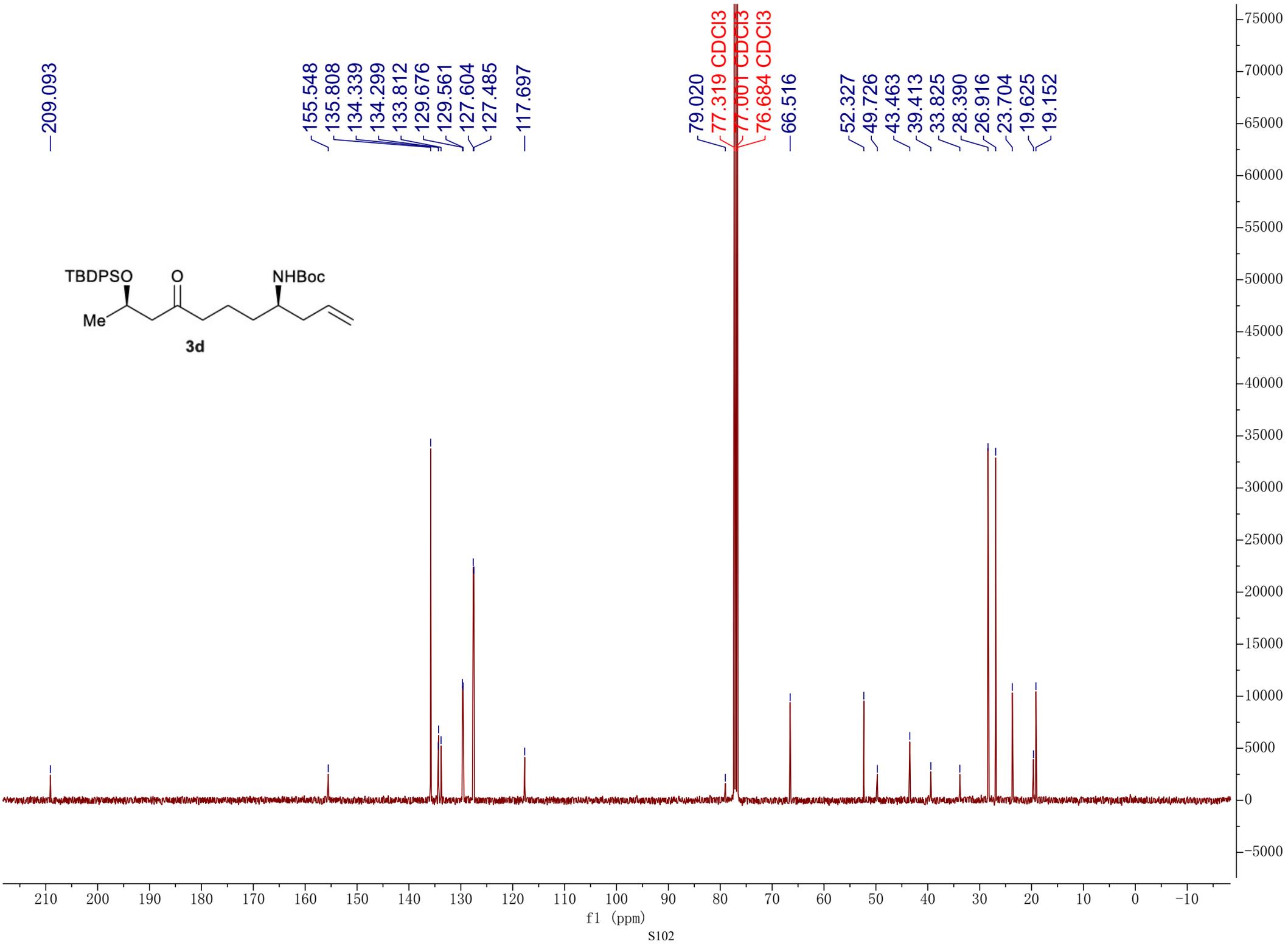
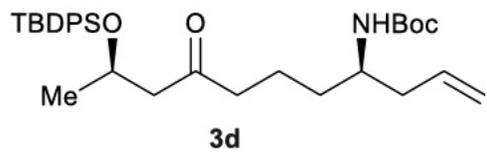


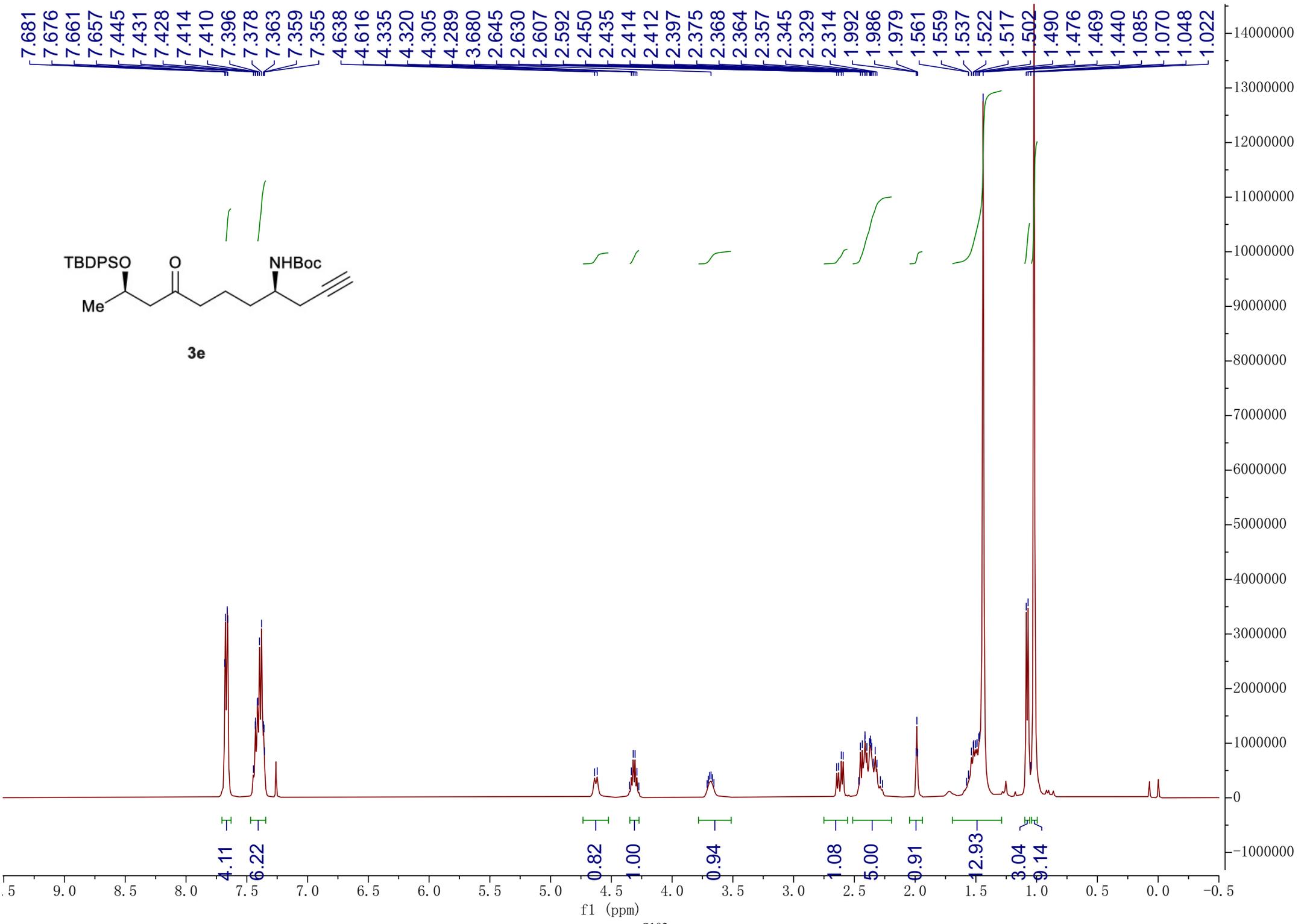


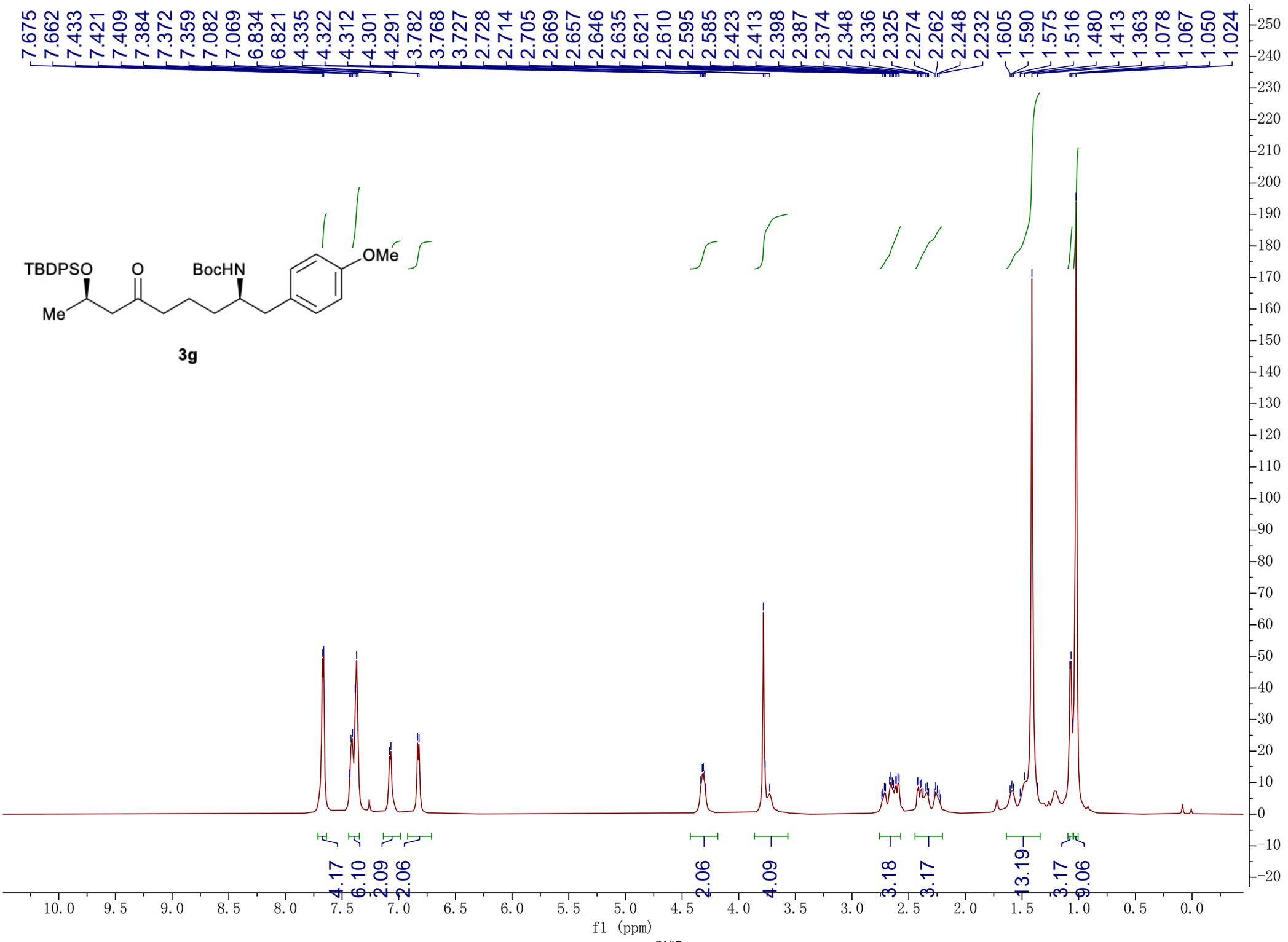


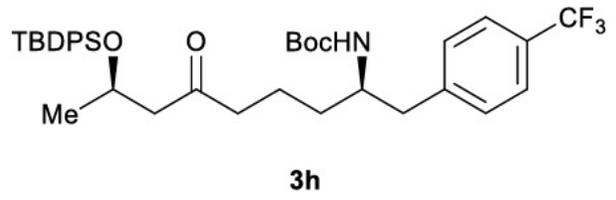










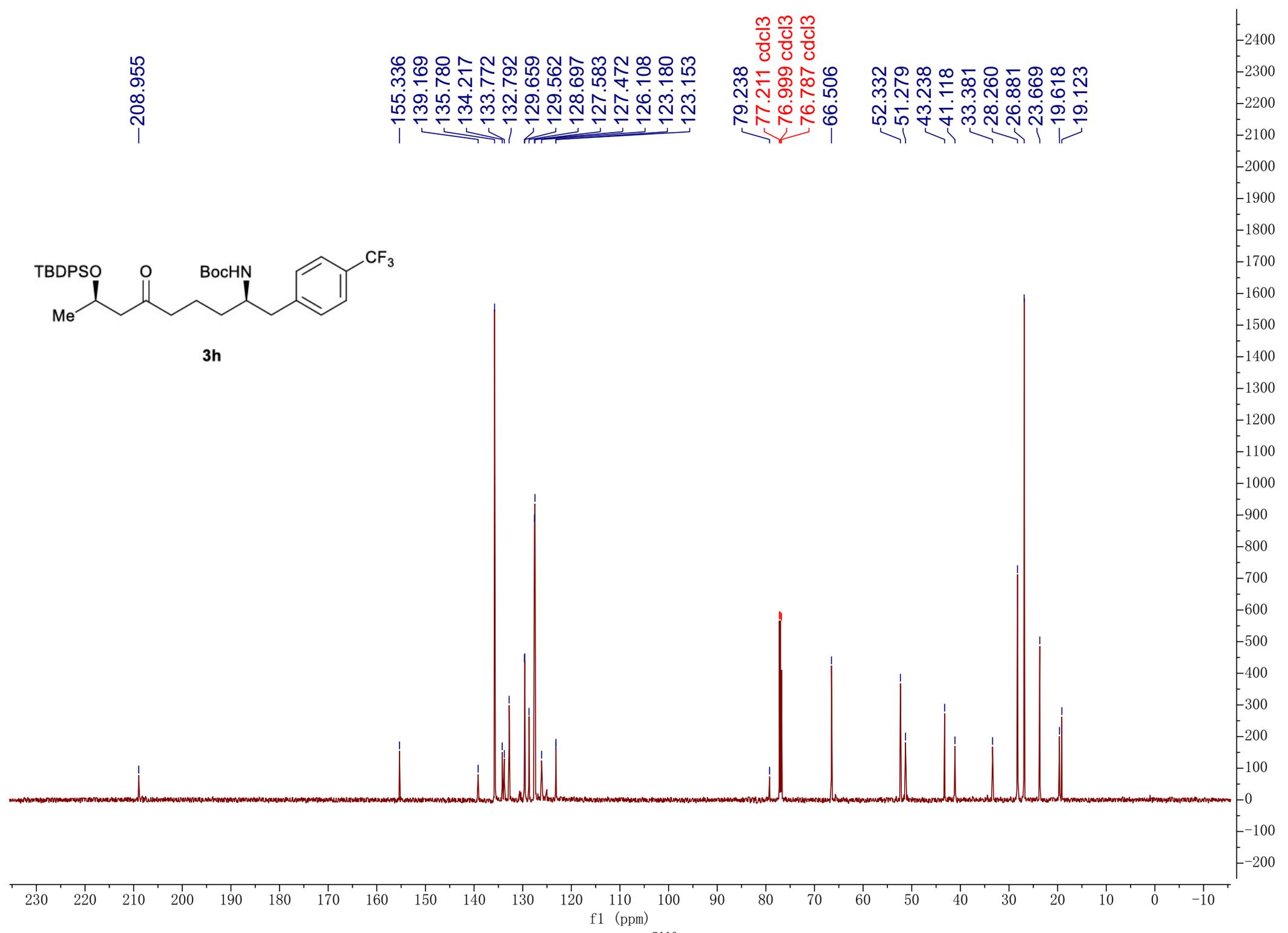


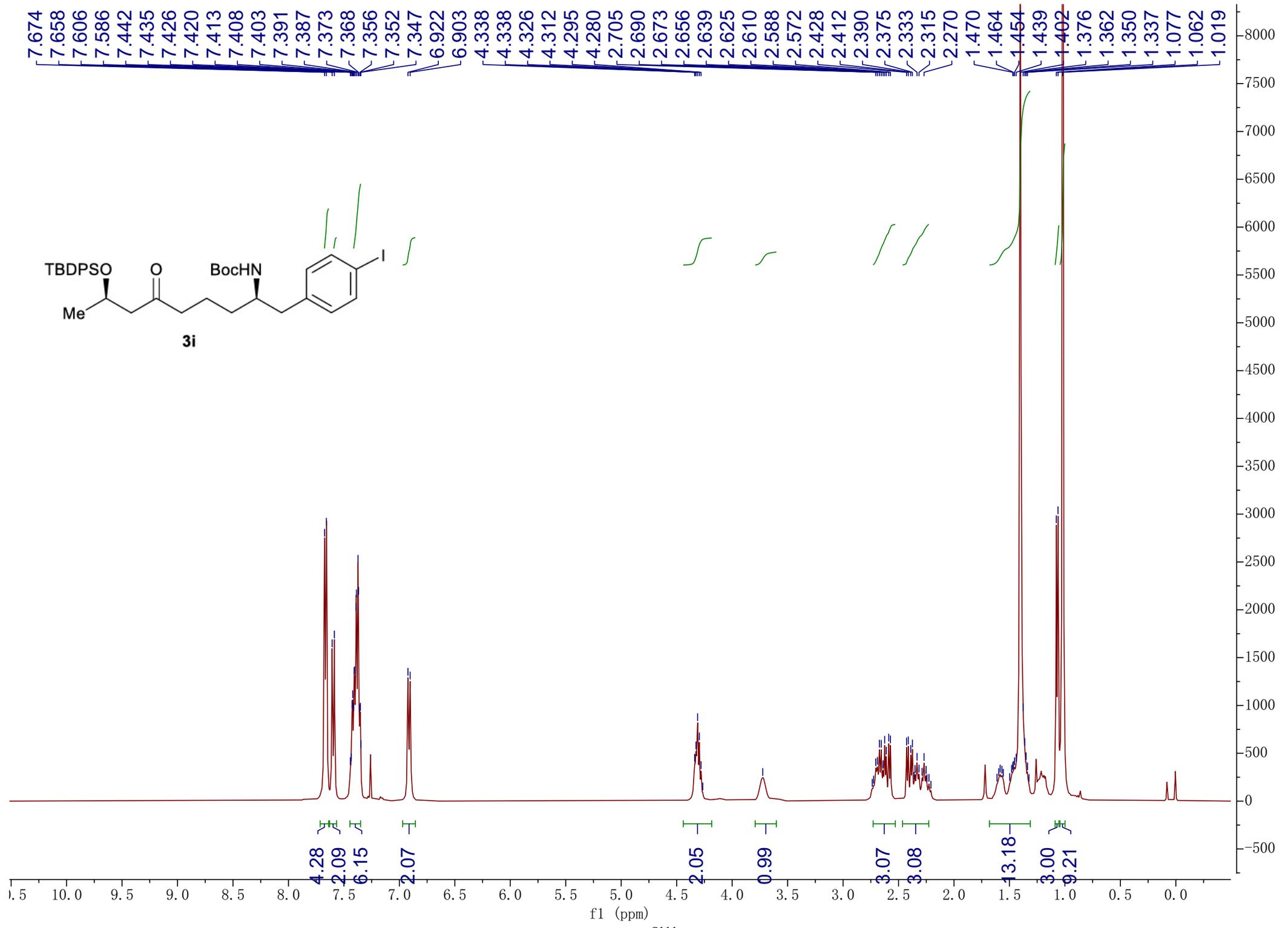
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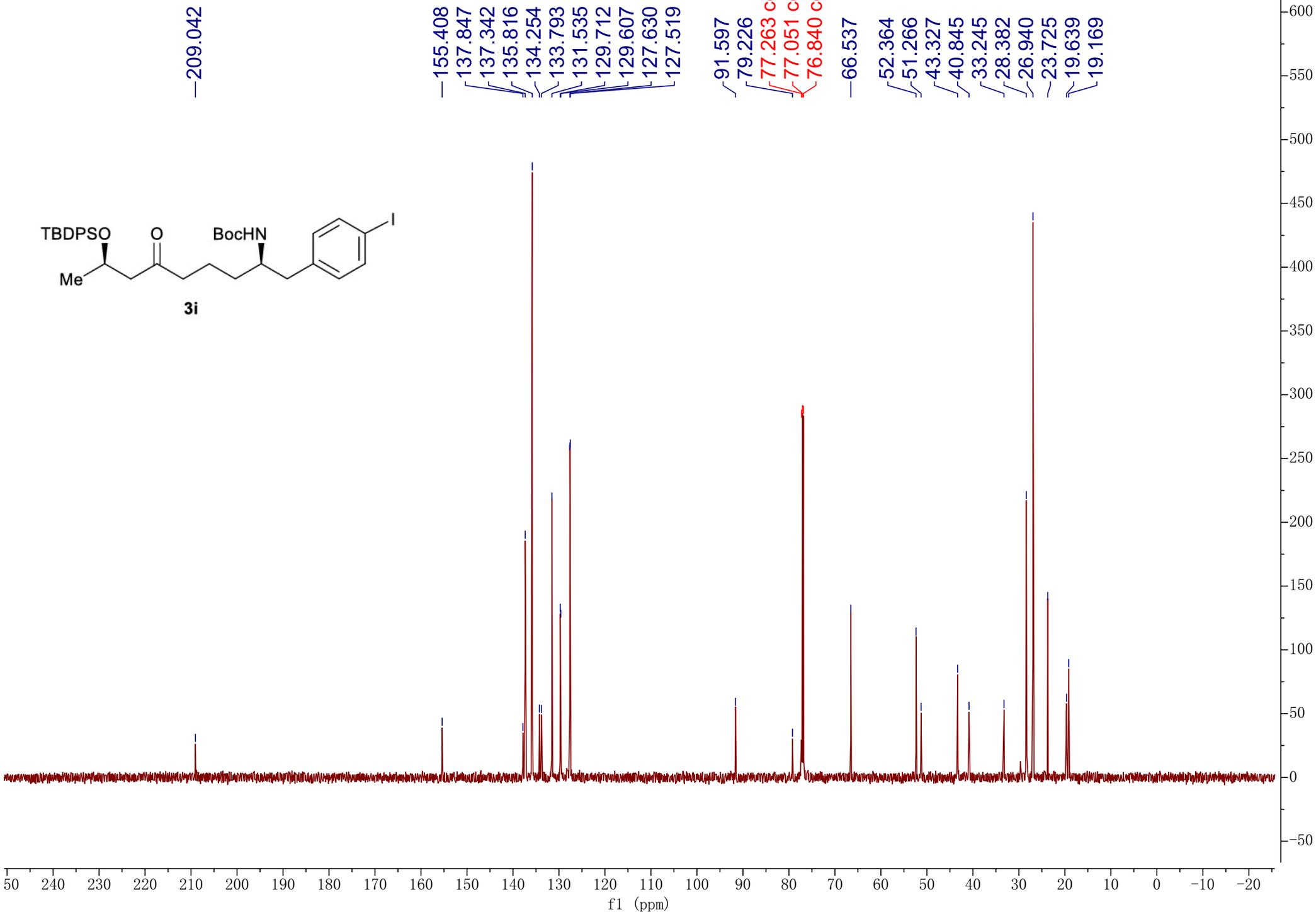
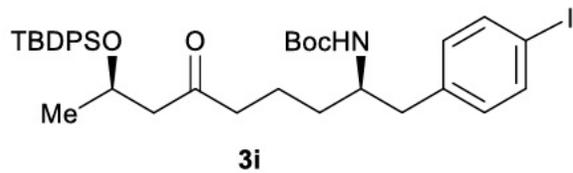
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 — 139.169
 — 135.780
 — 134.217
 — 133.772
 — 132.792
 — 129.659
 — 129.562
 — 128.697
 — 127.583
 — 127.472
 — 126.108
 — 123.180
 — 123.153

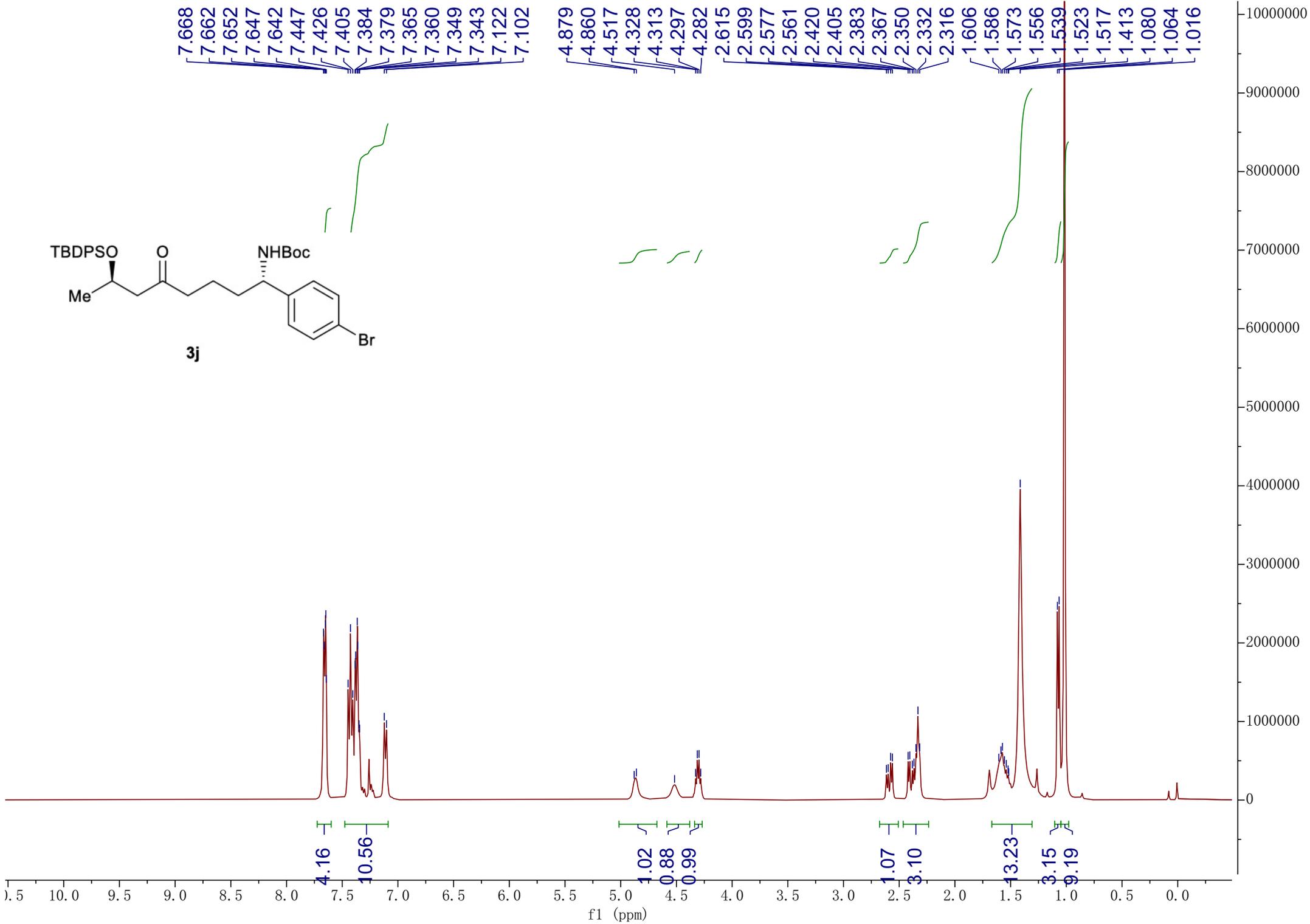
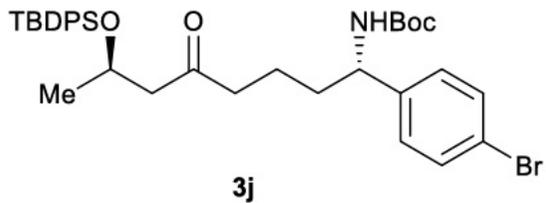
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 76.999 cdcl3
 76.787 cdcl3
 — 66.506

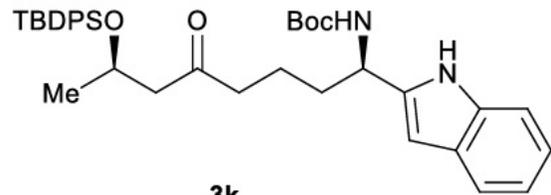
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 41.118
 33.381
 28.260
 26.881
 23.669
 19.618
 19.123









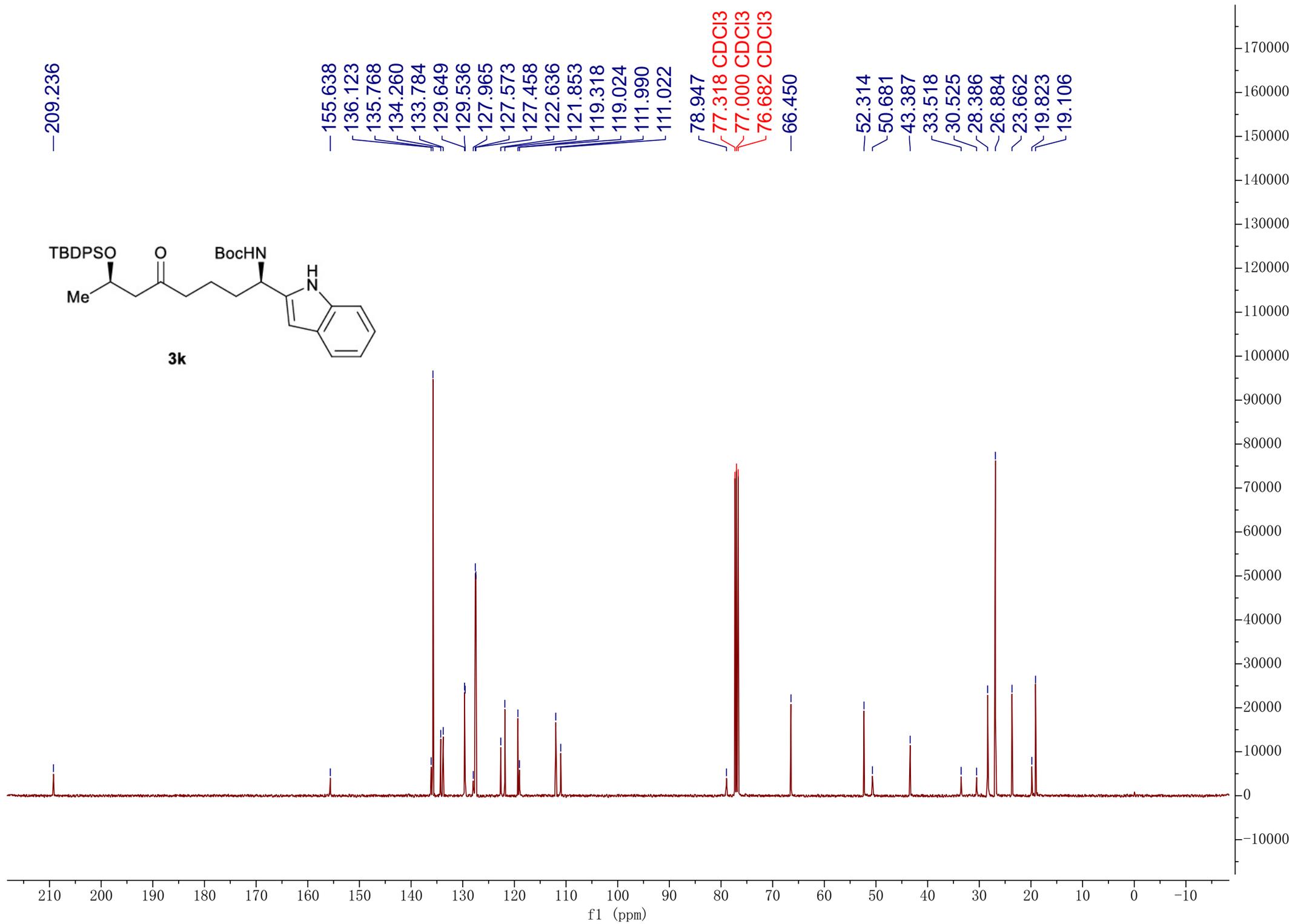


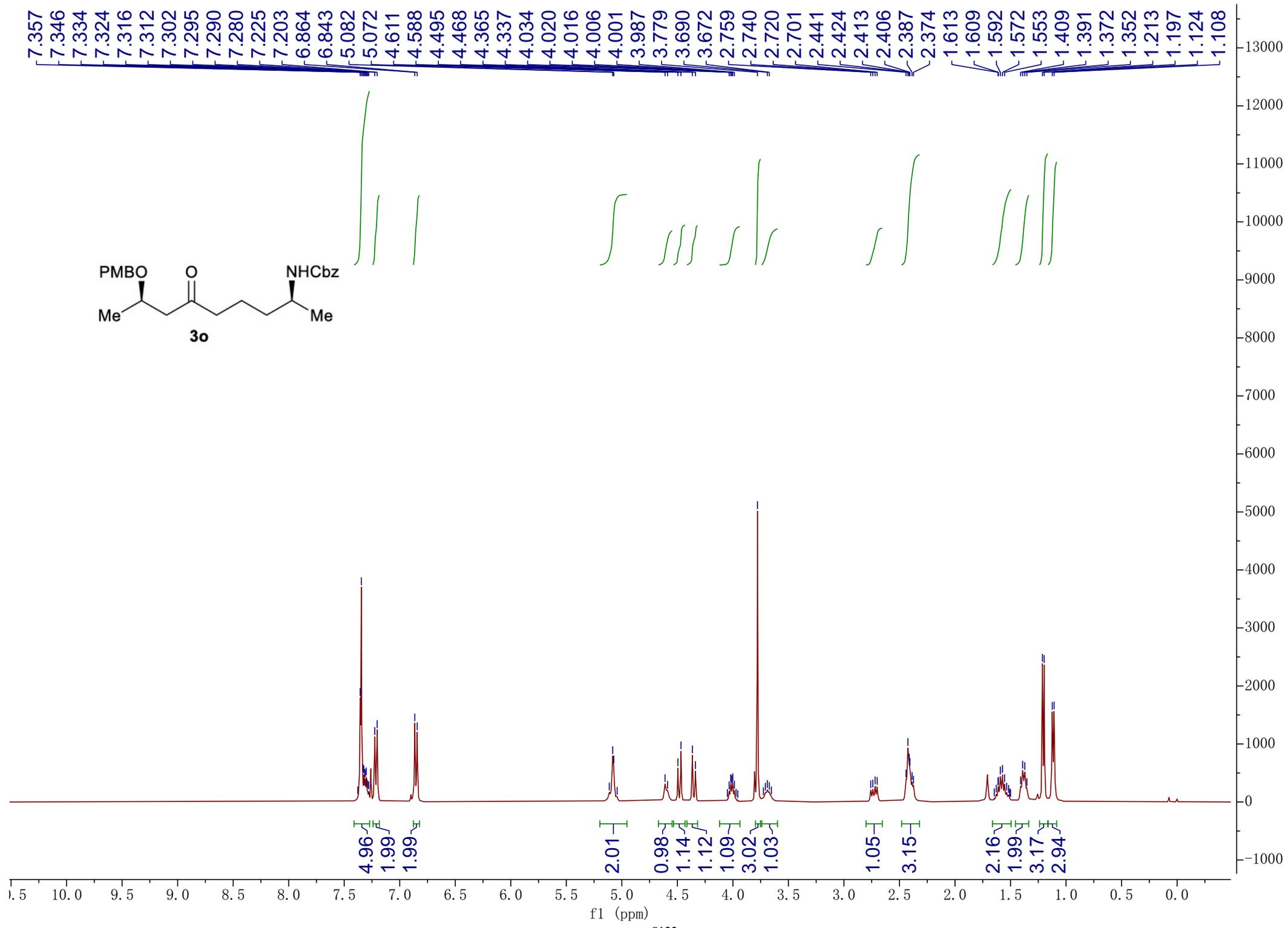
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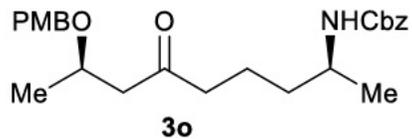
— 155.638
 — 136.123
 — 135.768
 — 134.260
 — 133.784
 — 129.649
 — 129.536
 — 127.965
 — 127.573
 — 127.458
 — 122.636
 — 121.853
 — 119.318
 — 119.024
 — 111.990
 — 111.022

— 78.947
 — 77.318 CDCl₃
 — 77.000 CDCl₃
 — 76.682 CDCl₃
 — 66.450

— 52.314
 — 50.681
 — 43.387
 — 33.518
 — 30.525
 — 28.386
 — 26.884
 — 23.662
 — 19.823
 — 19.106







— 209.238

— 159.096
— 155.744

136.600
130.569
129.247
128.586
128.468
128.016

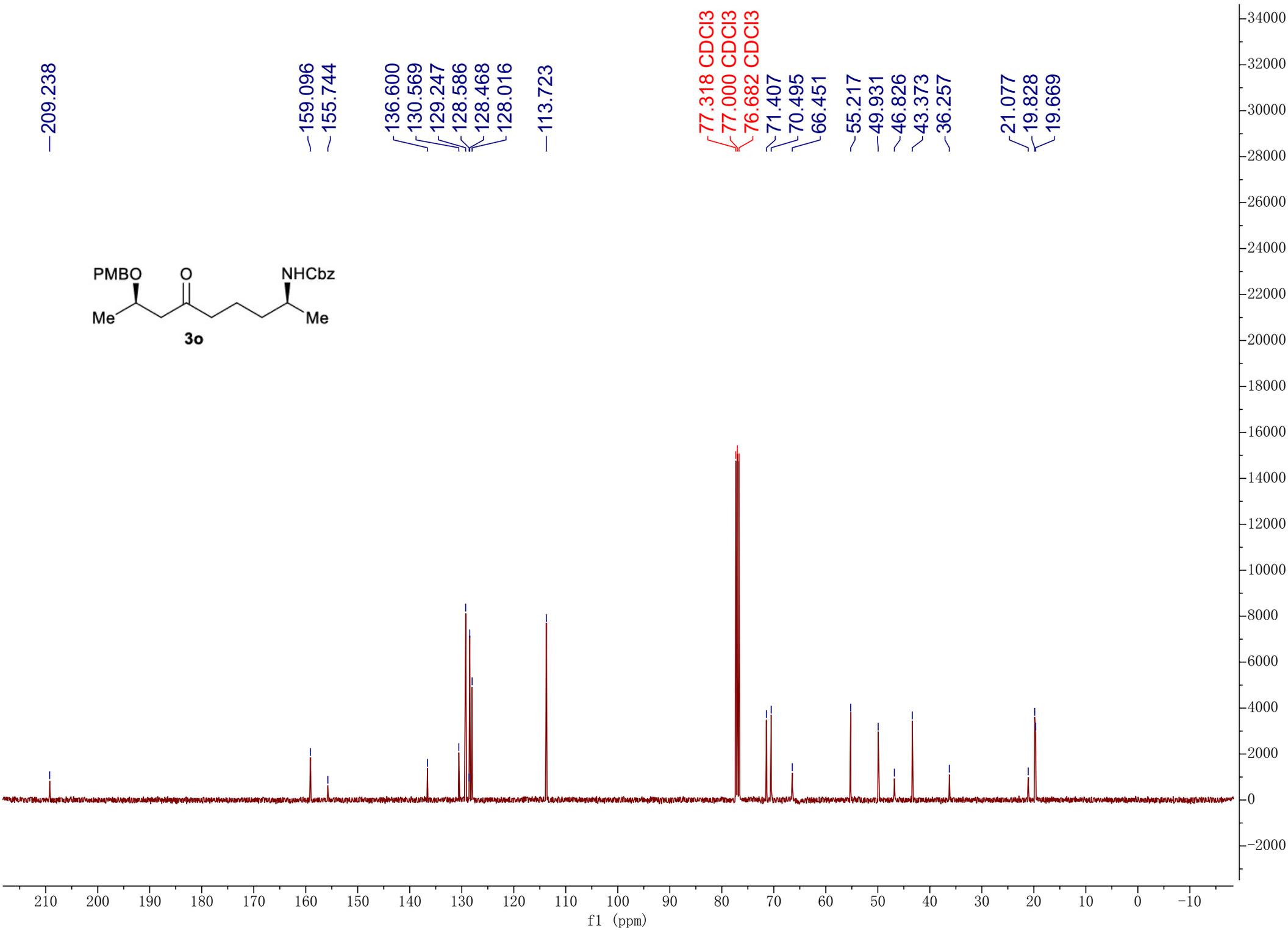
— 113.723

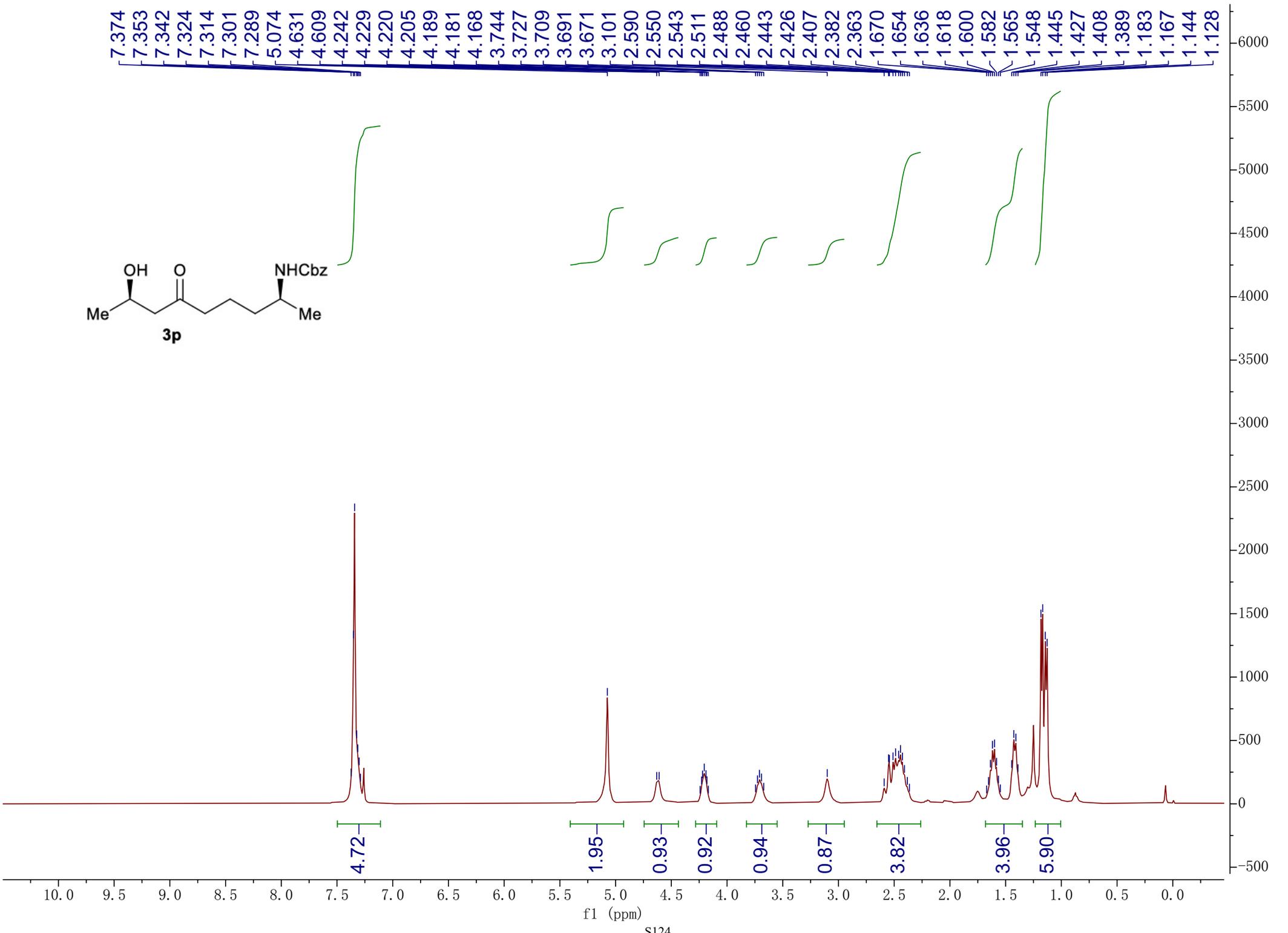
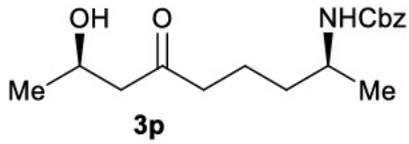
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21.077
19.828
19.669





-211.747

-155.790

136.547

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128.030

77.318 CDC13

77.000 CDC13

76.682 CDC13

66.505

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50.519

46.664

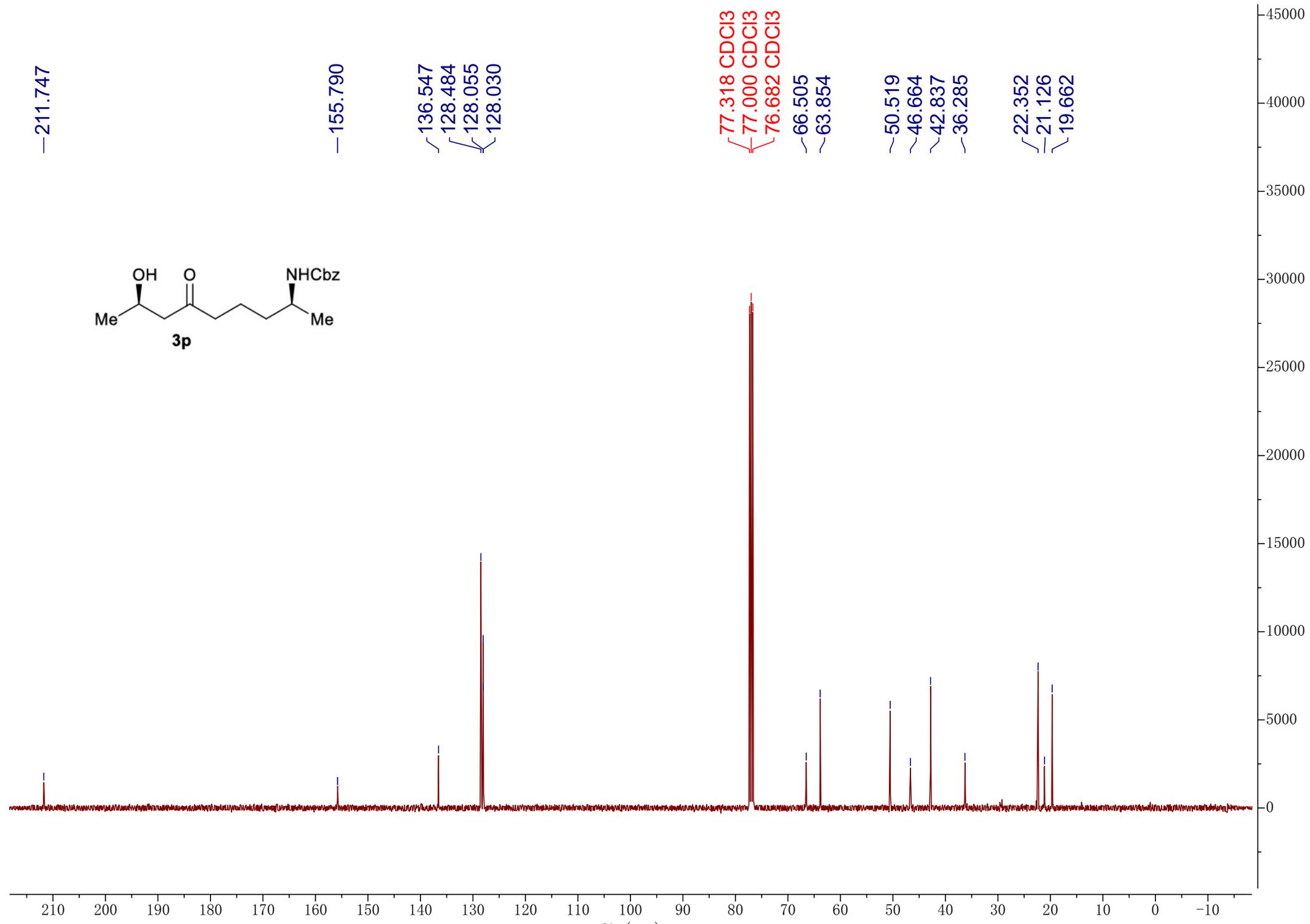
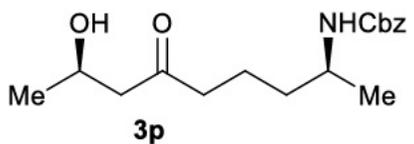
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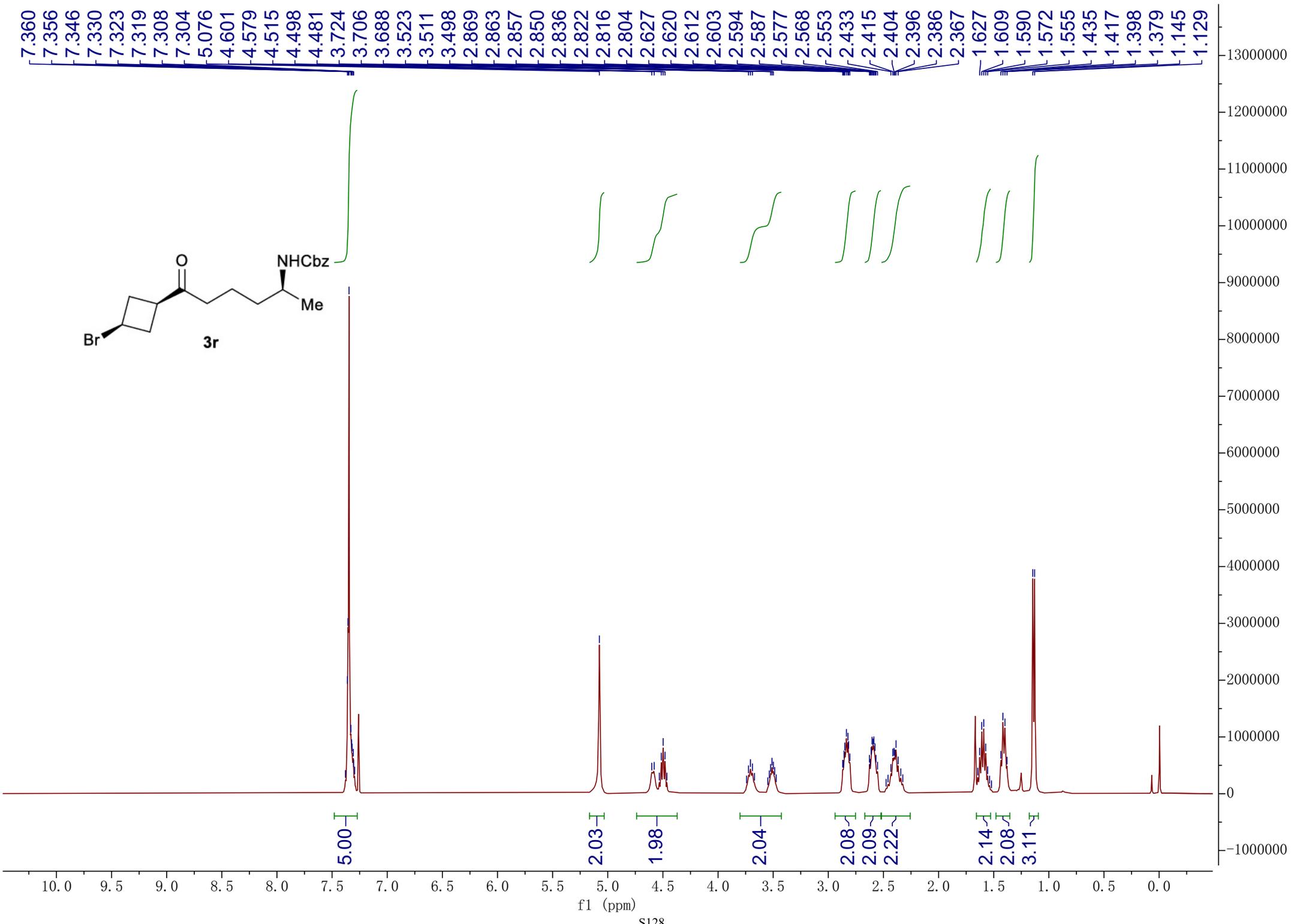
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22.352

21.126

19.662





—210.185

—155.756

136.559

128.493

128.067

128.034

77.318 CDCl3

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76.683 CDCl3

—66.503

46.671

42.368

40.681

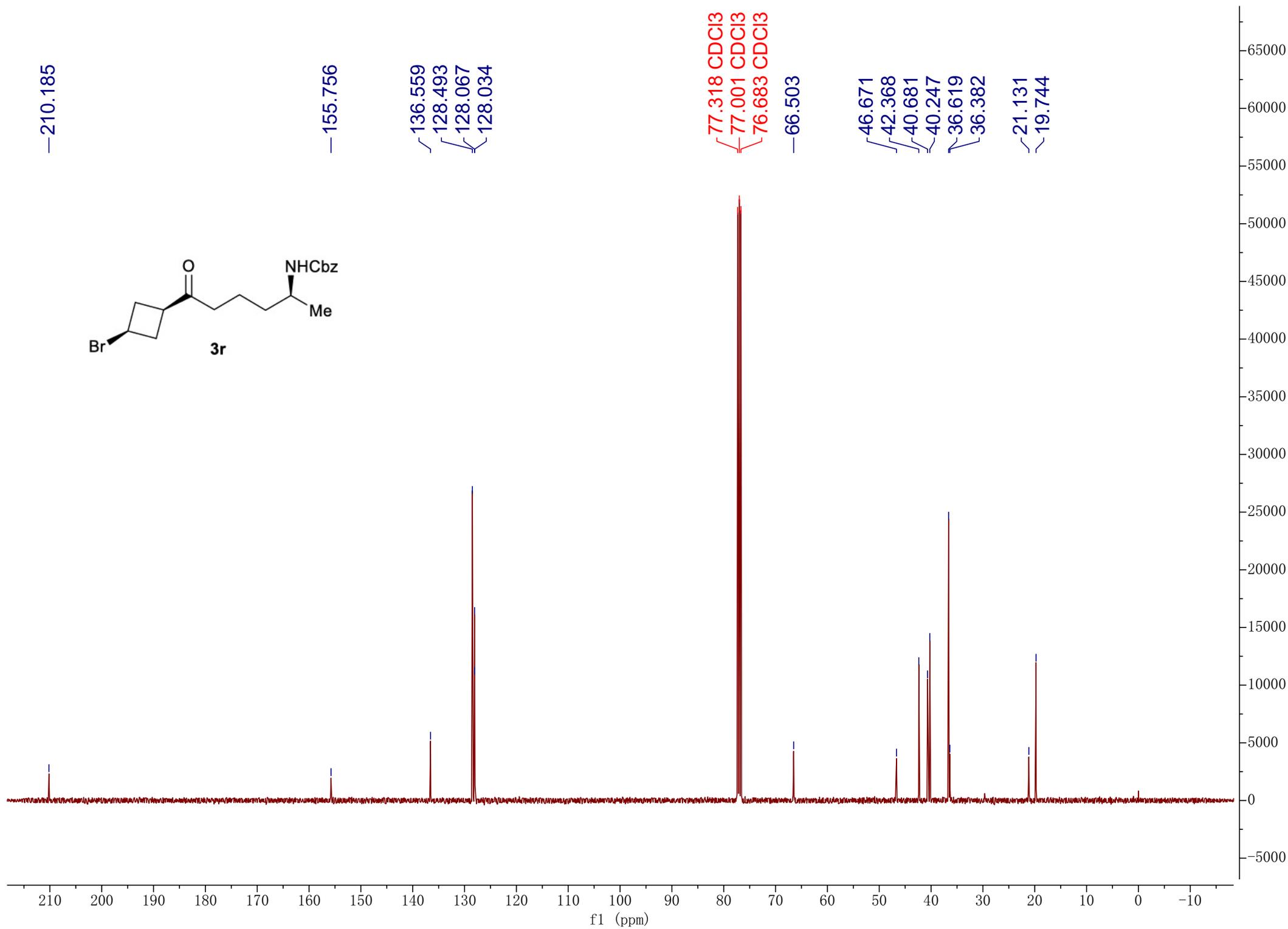
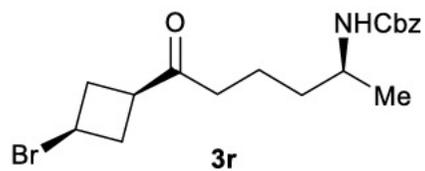
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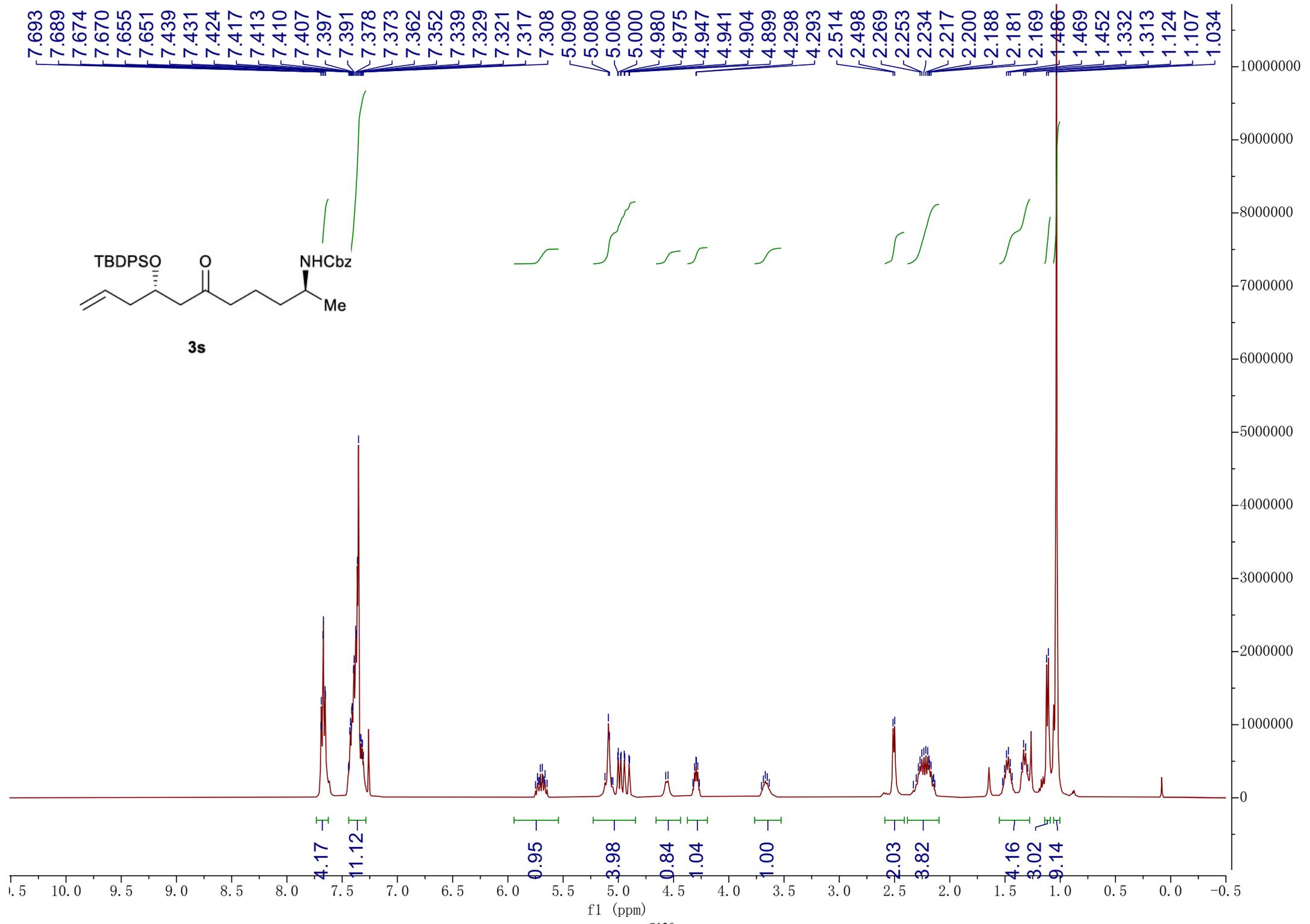
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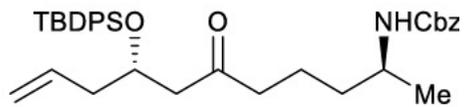
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21.131

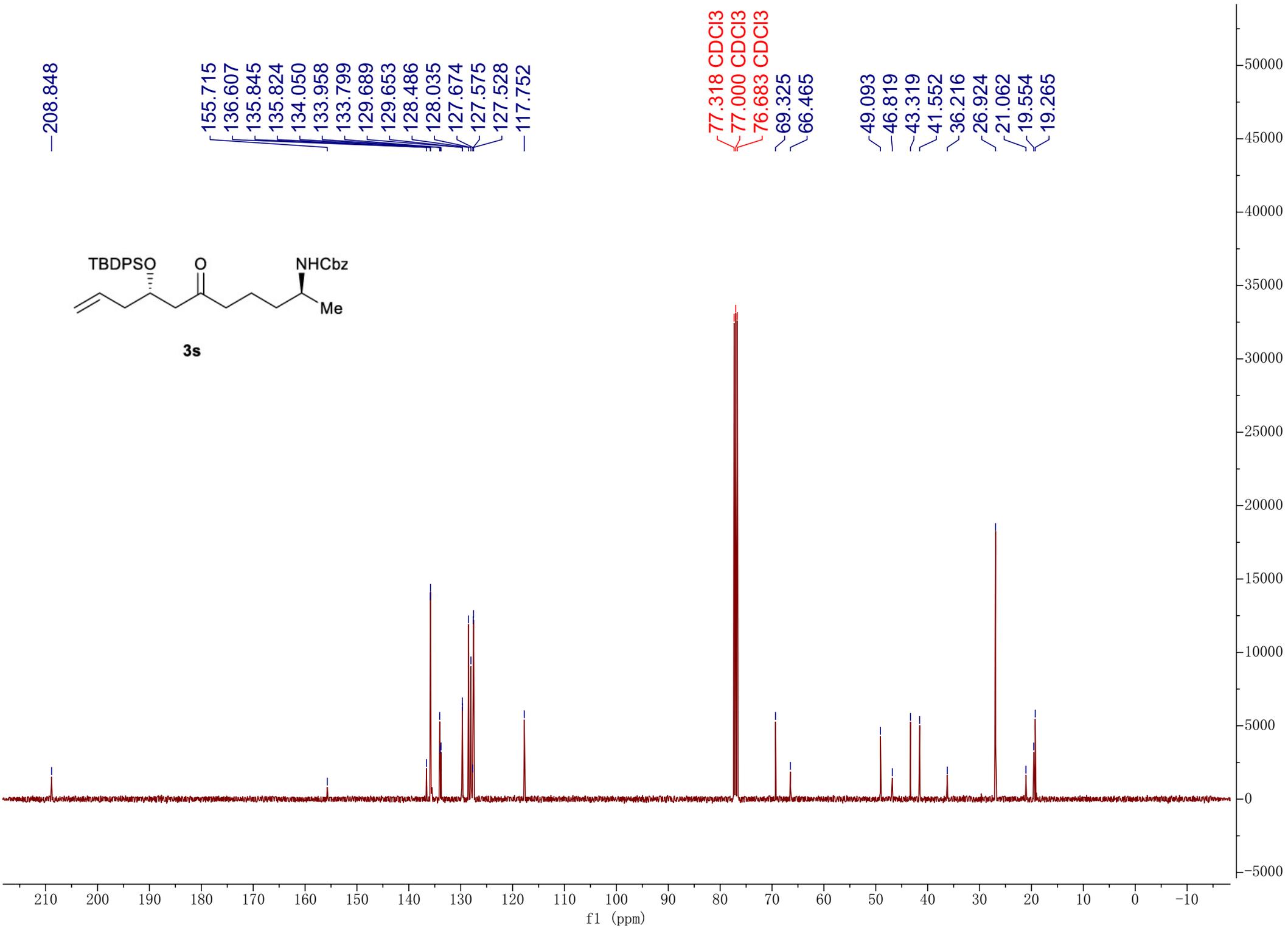
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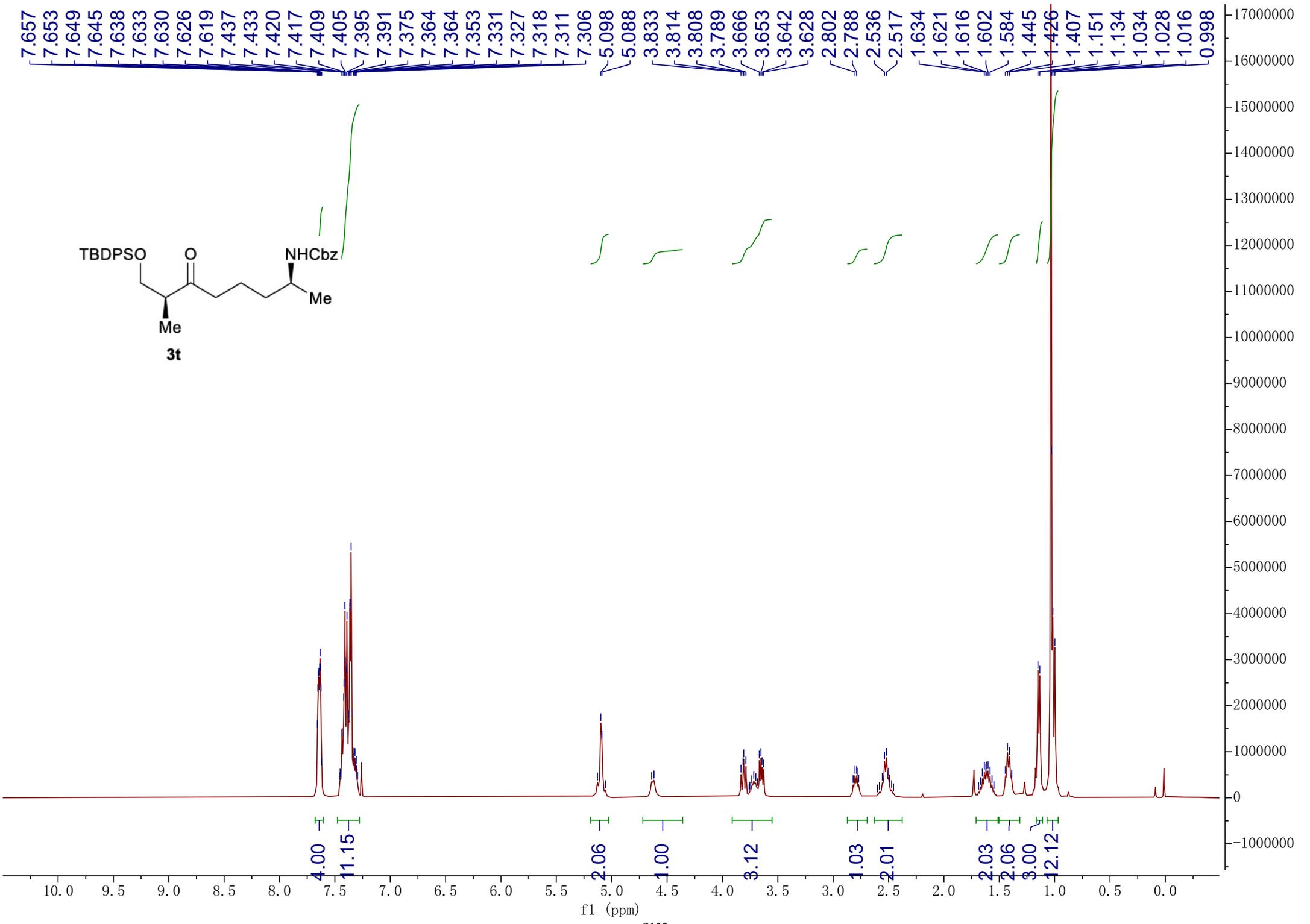




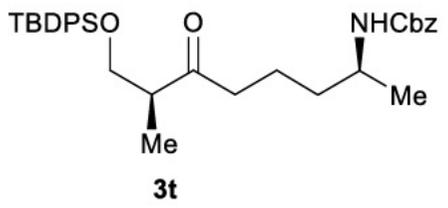


3s





—213.190

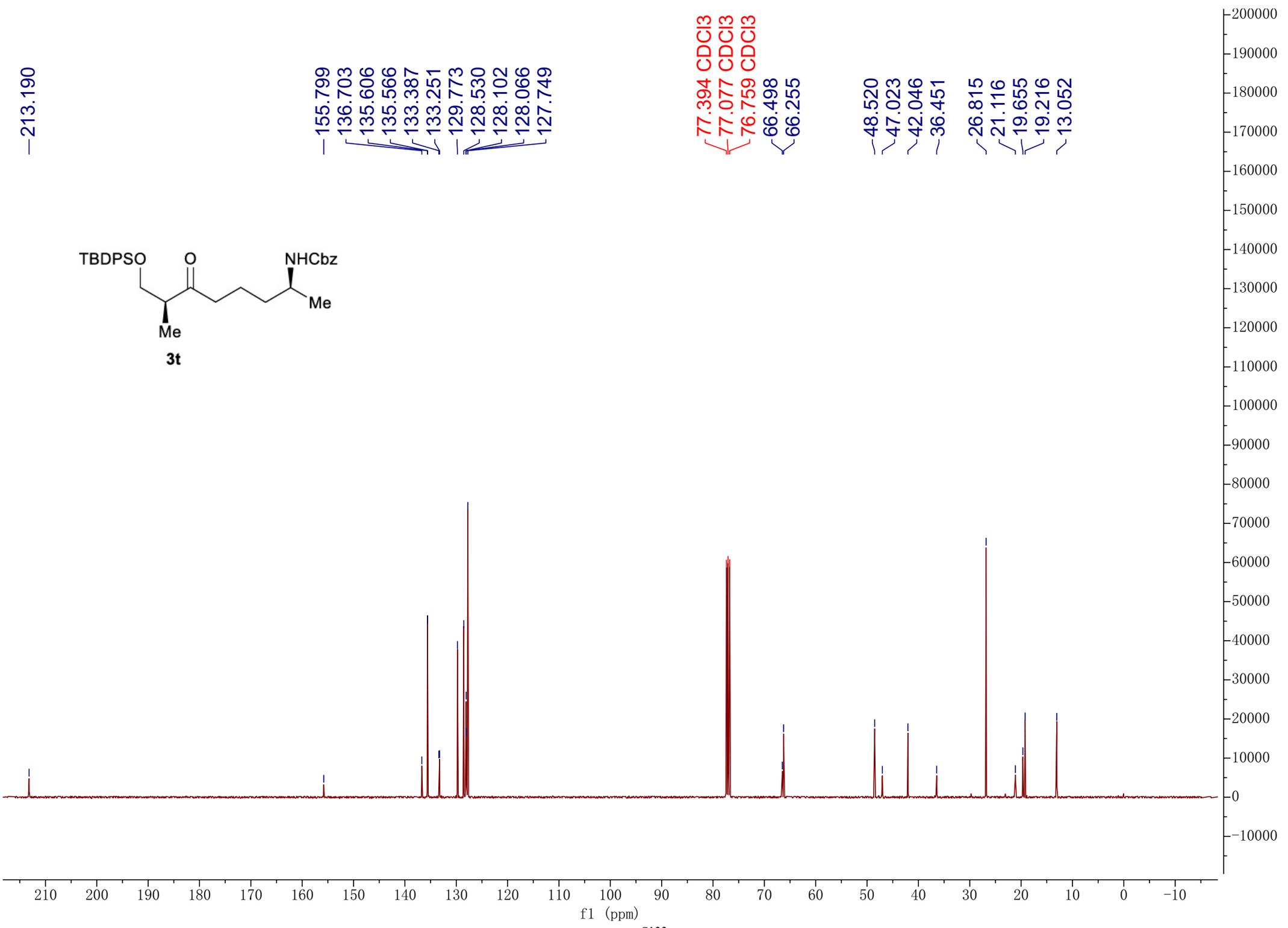


—155.799
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135.566
133.387
133.251
—129.773
128.530
128.102
128.066
127.749

77.394 CDCI3
77.077 CDCI3
76.759 CDCI3
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66.255

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36.451

26.815
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19.216
13.052



—214.314

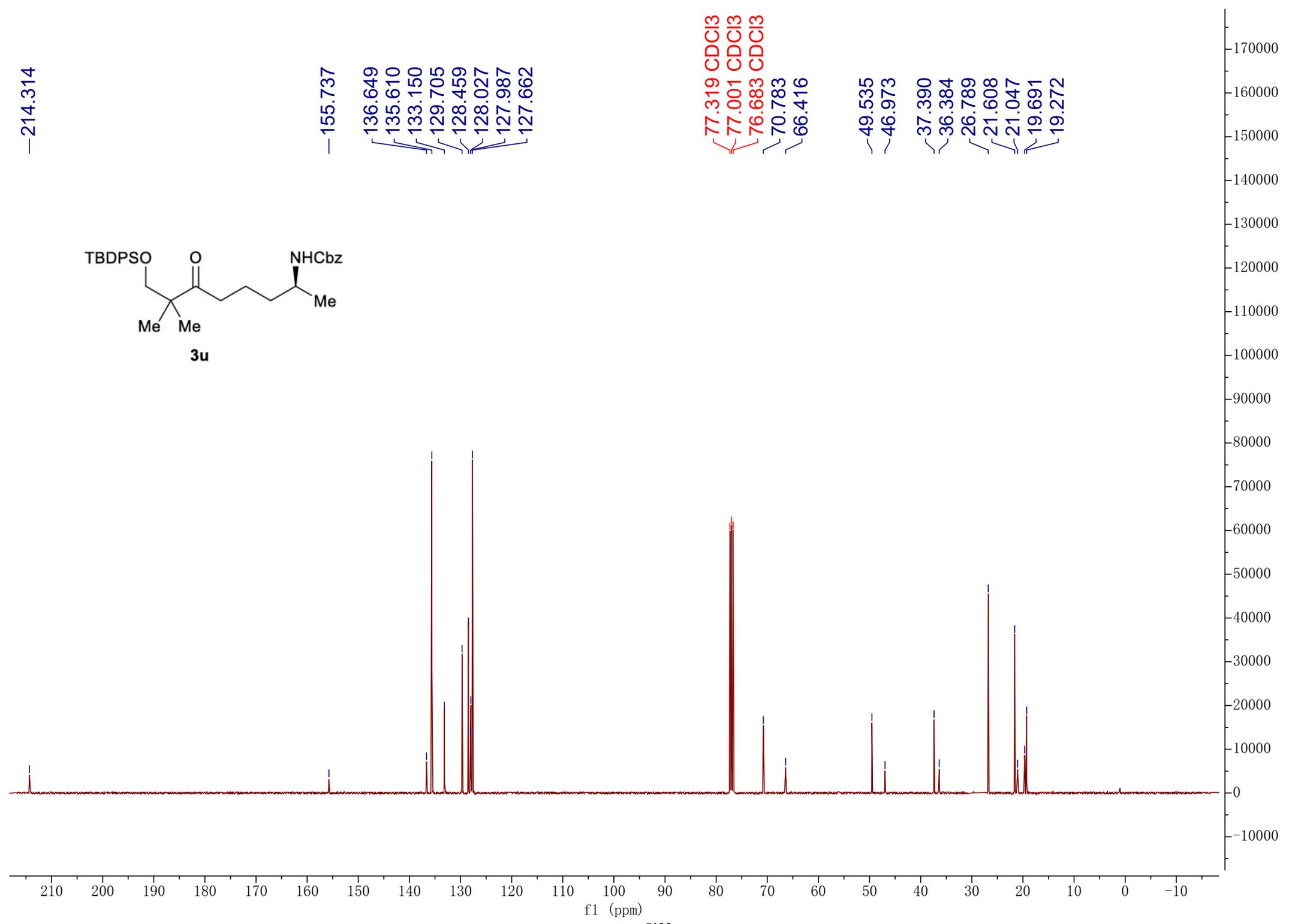
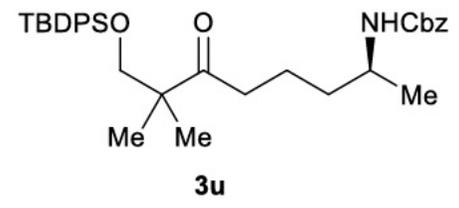
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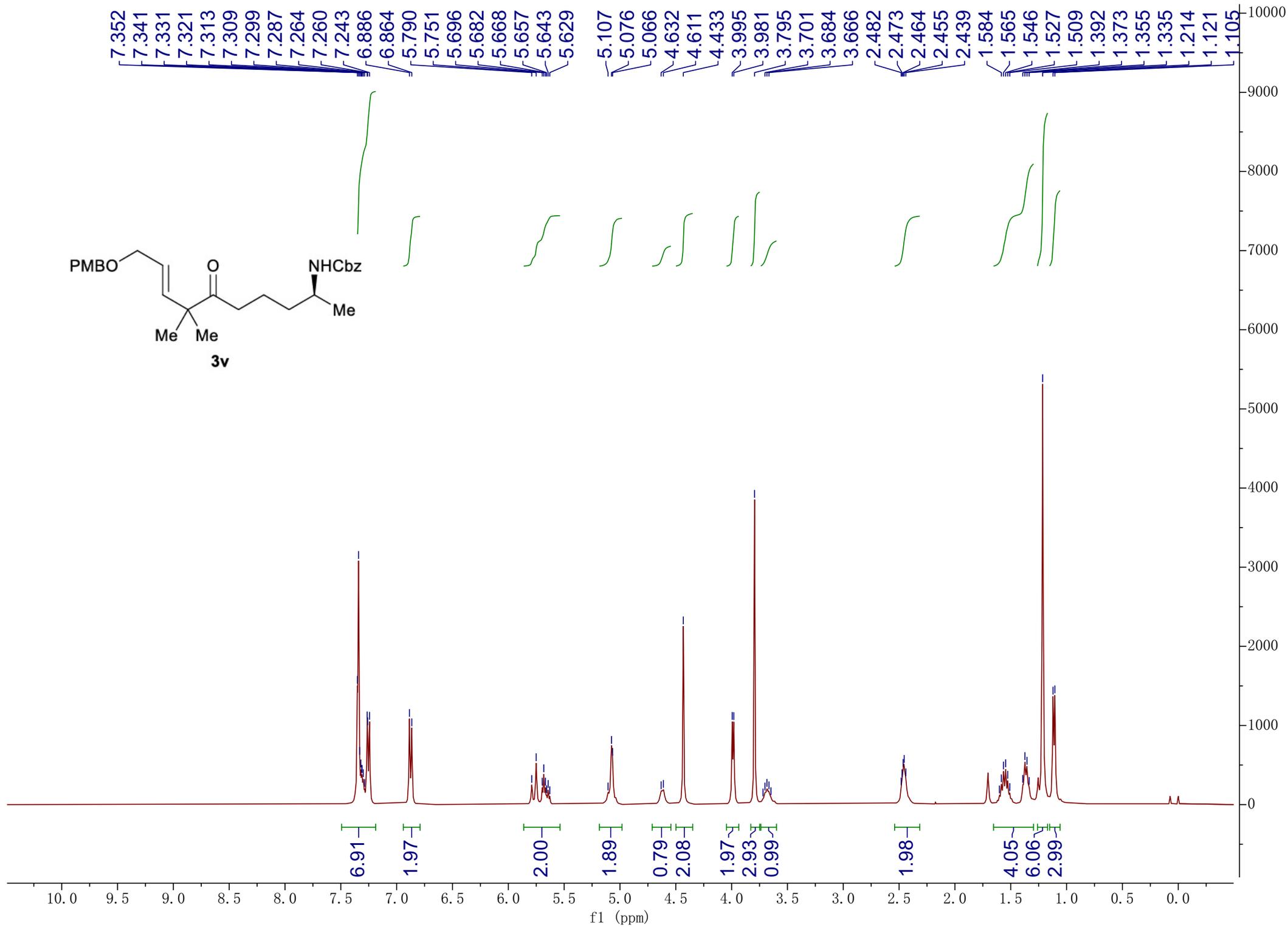
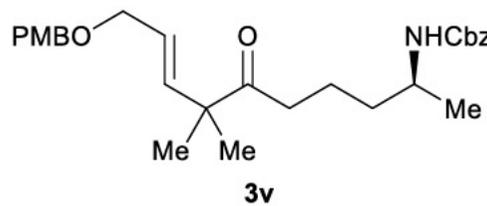
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76.683 CDCI3
70.783
66.416

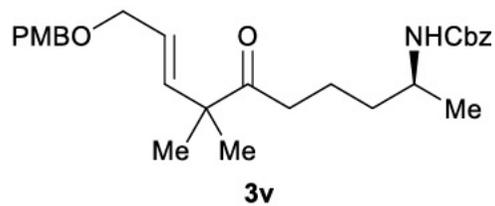
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21.608
21.047
19.691
19.272





-212.689



-159.197
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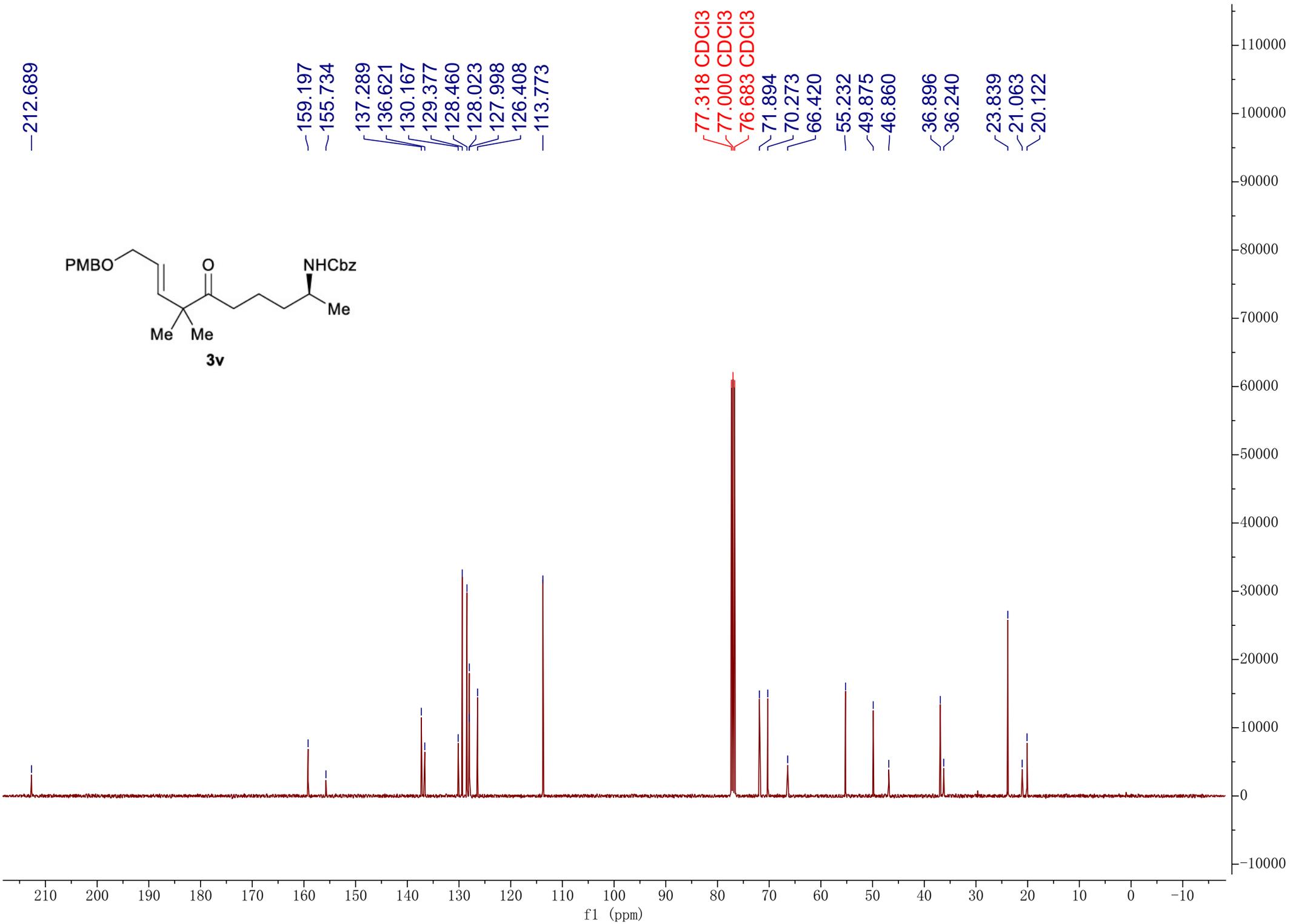
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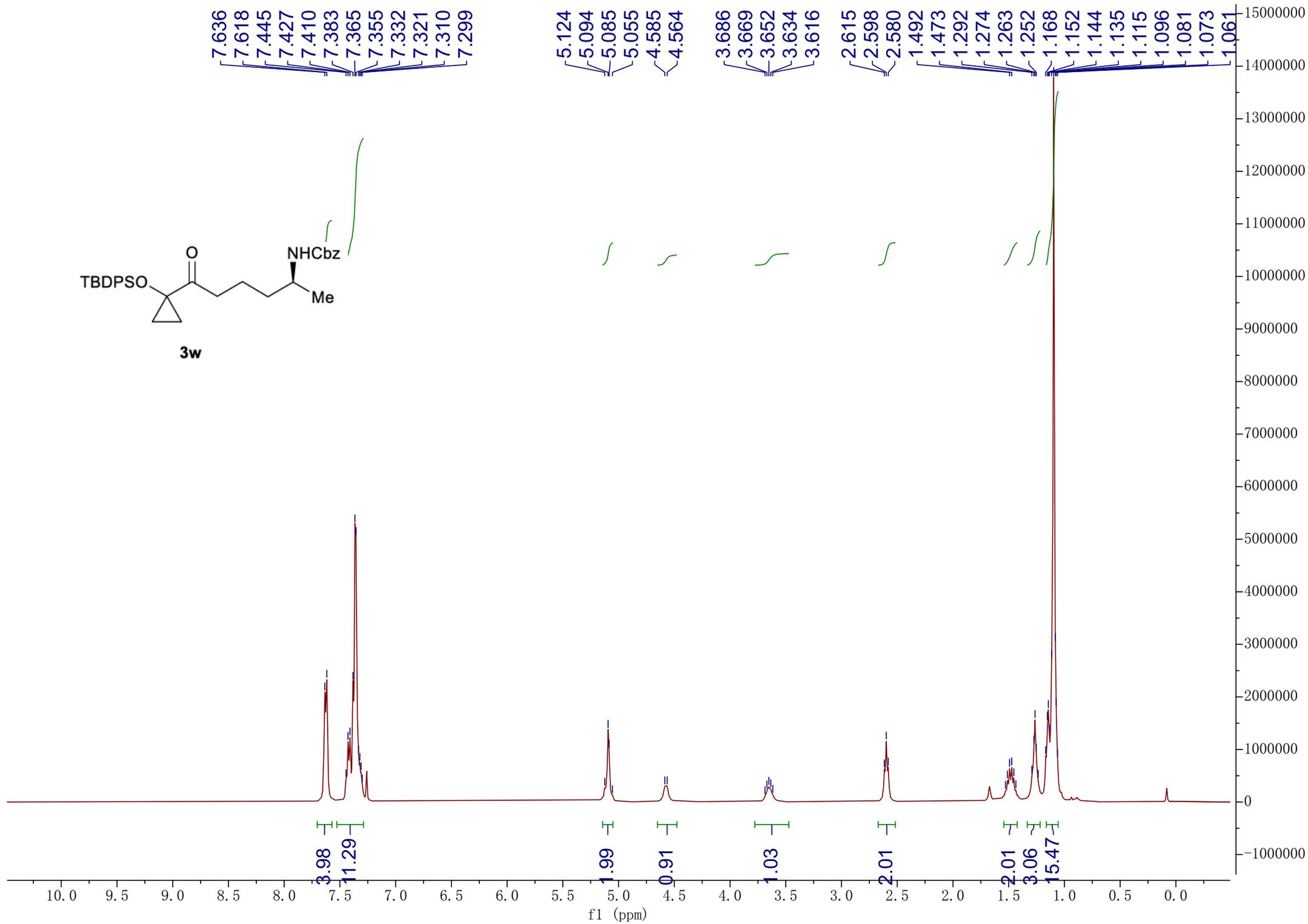
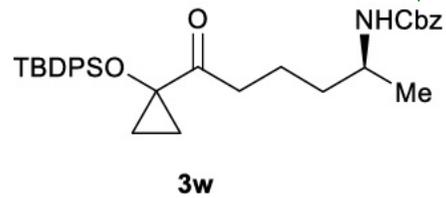
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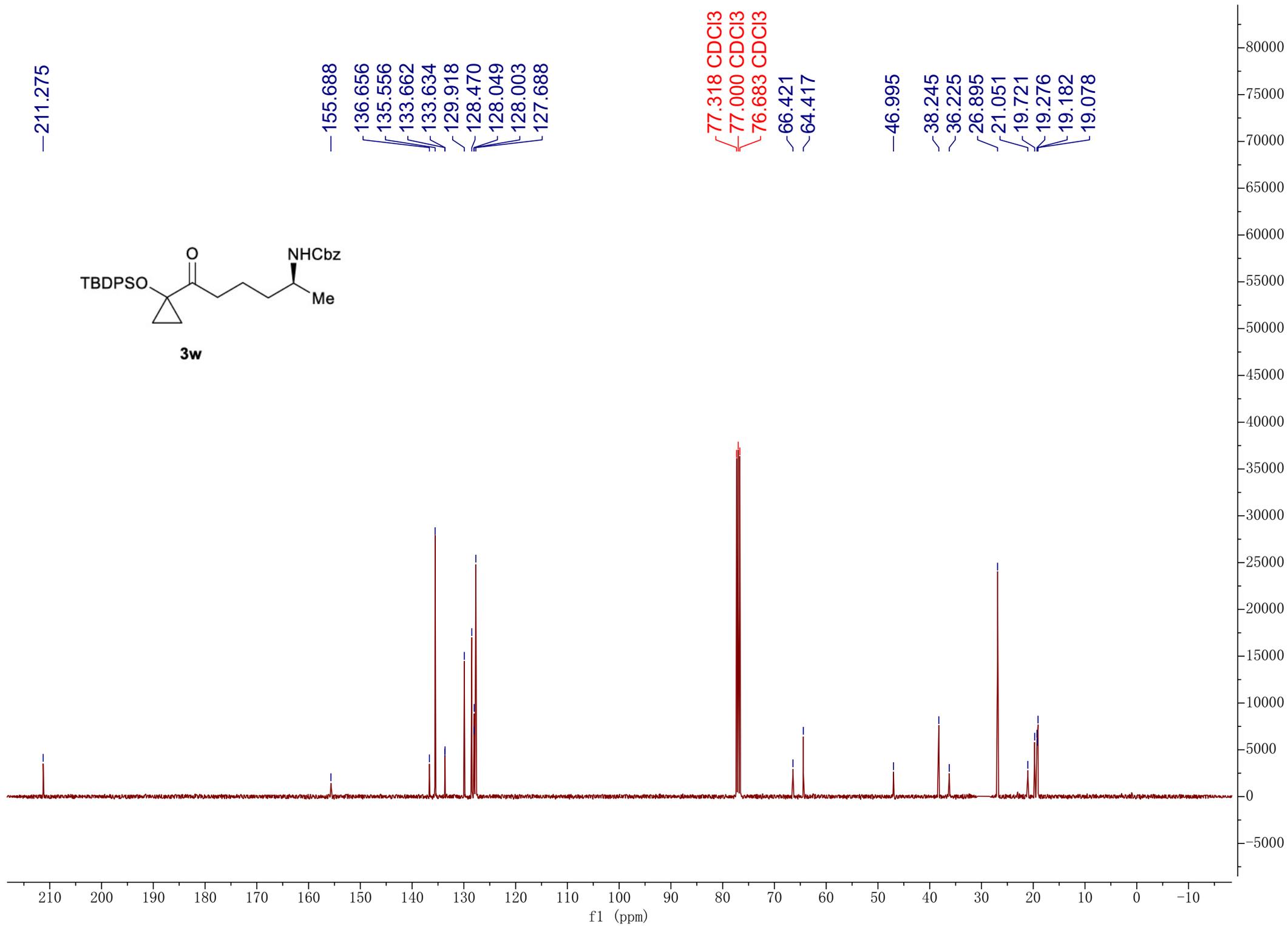
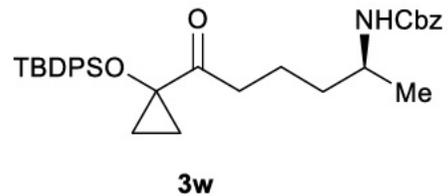
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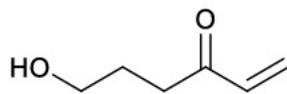
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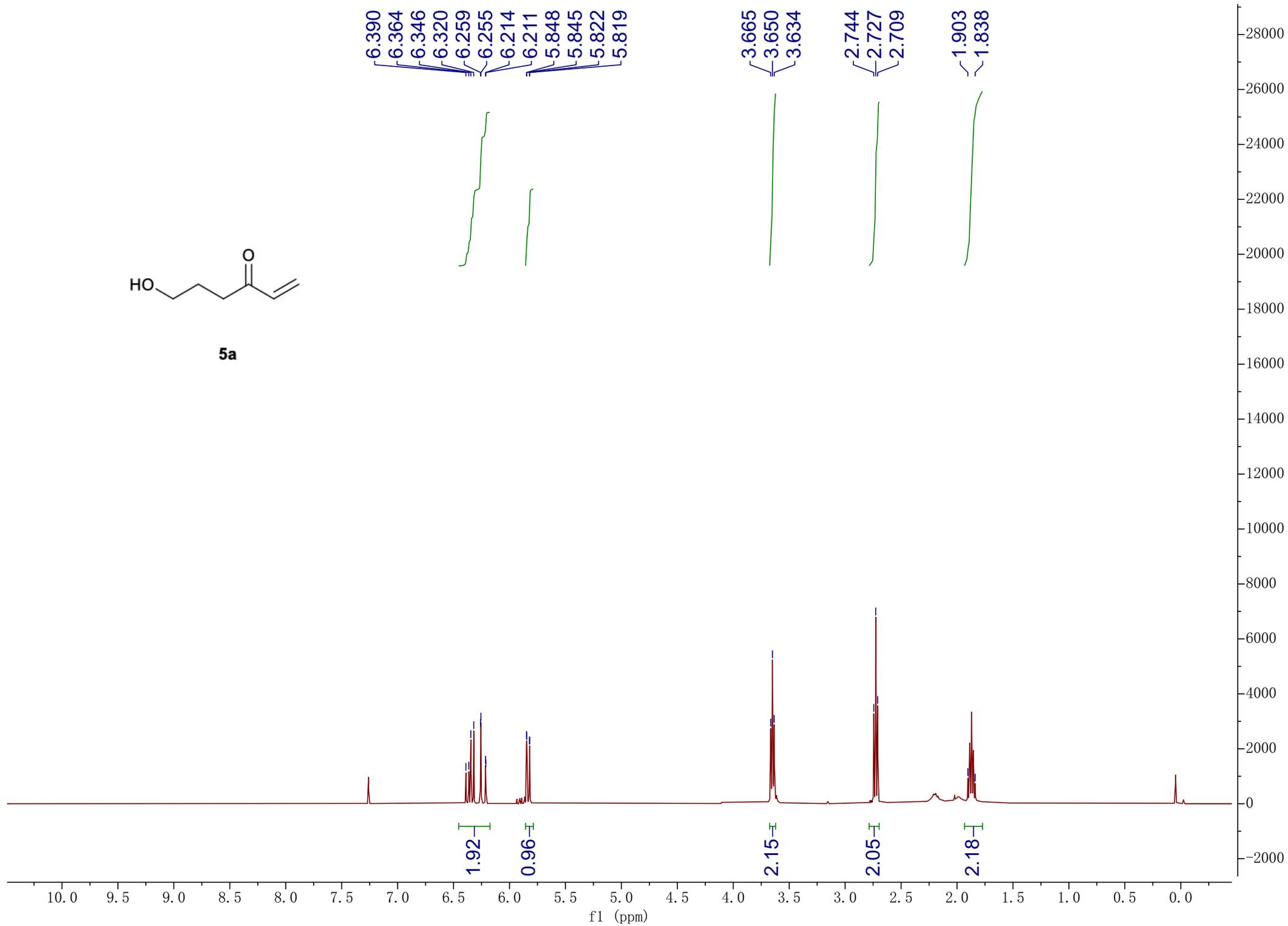


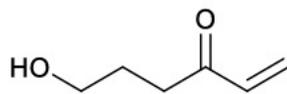






5a





5a

—201.106

—136.396

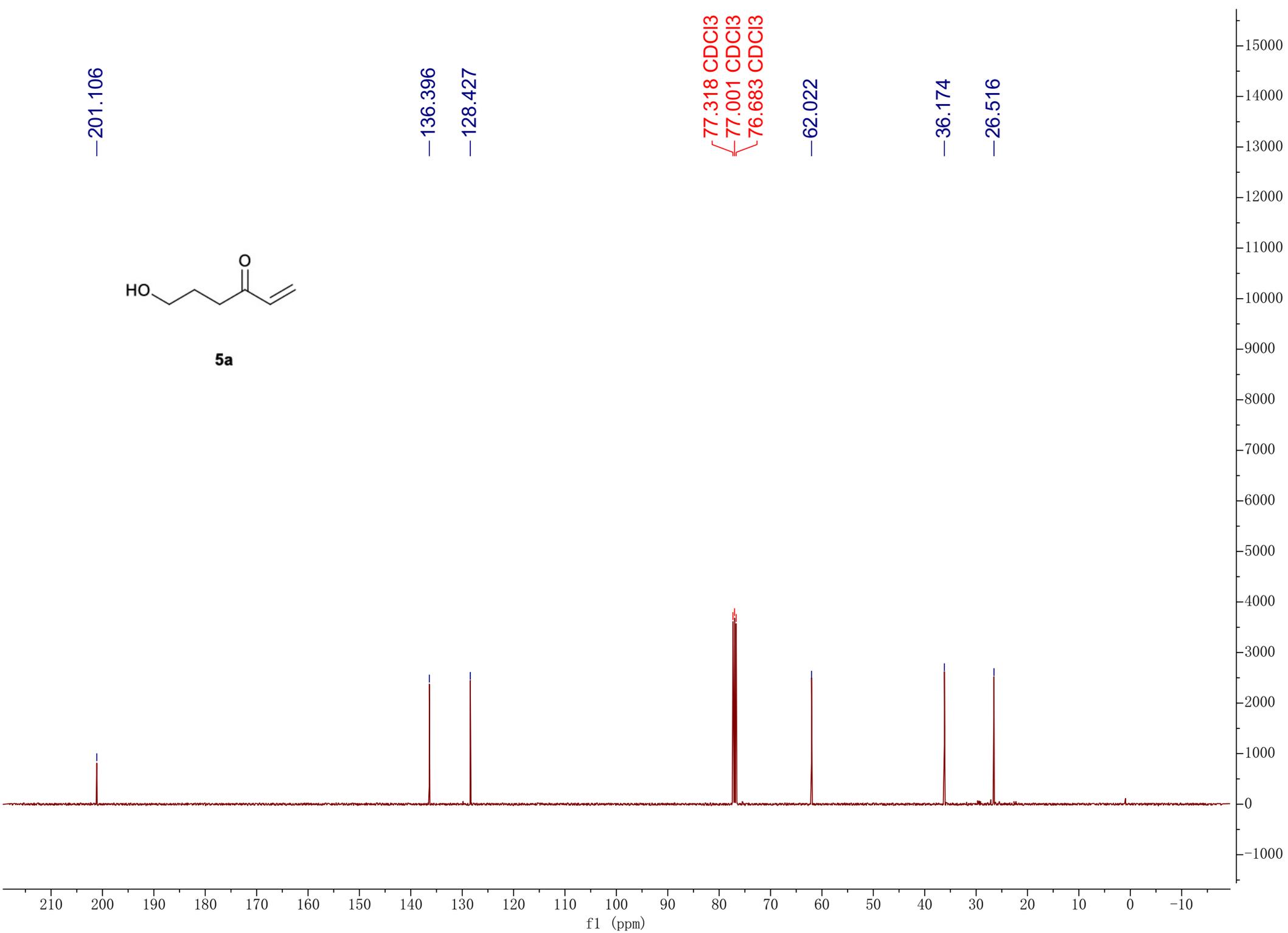
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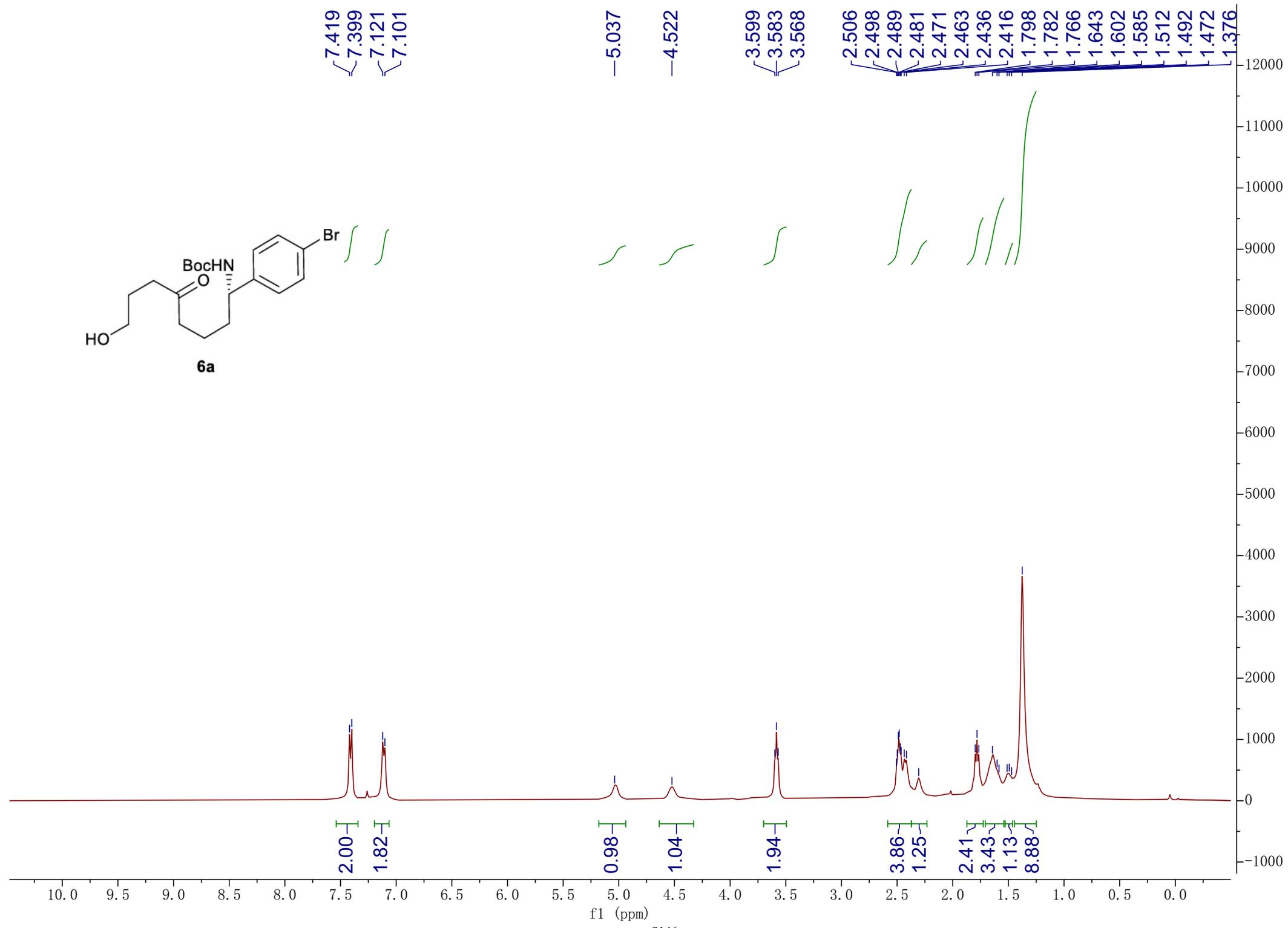
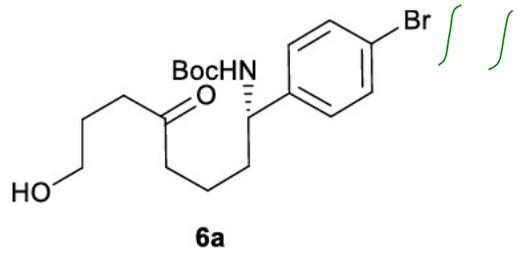
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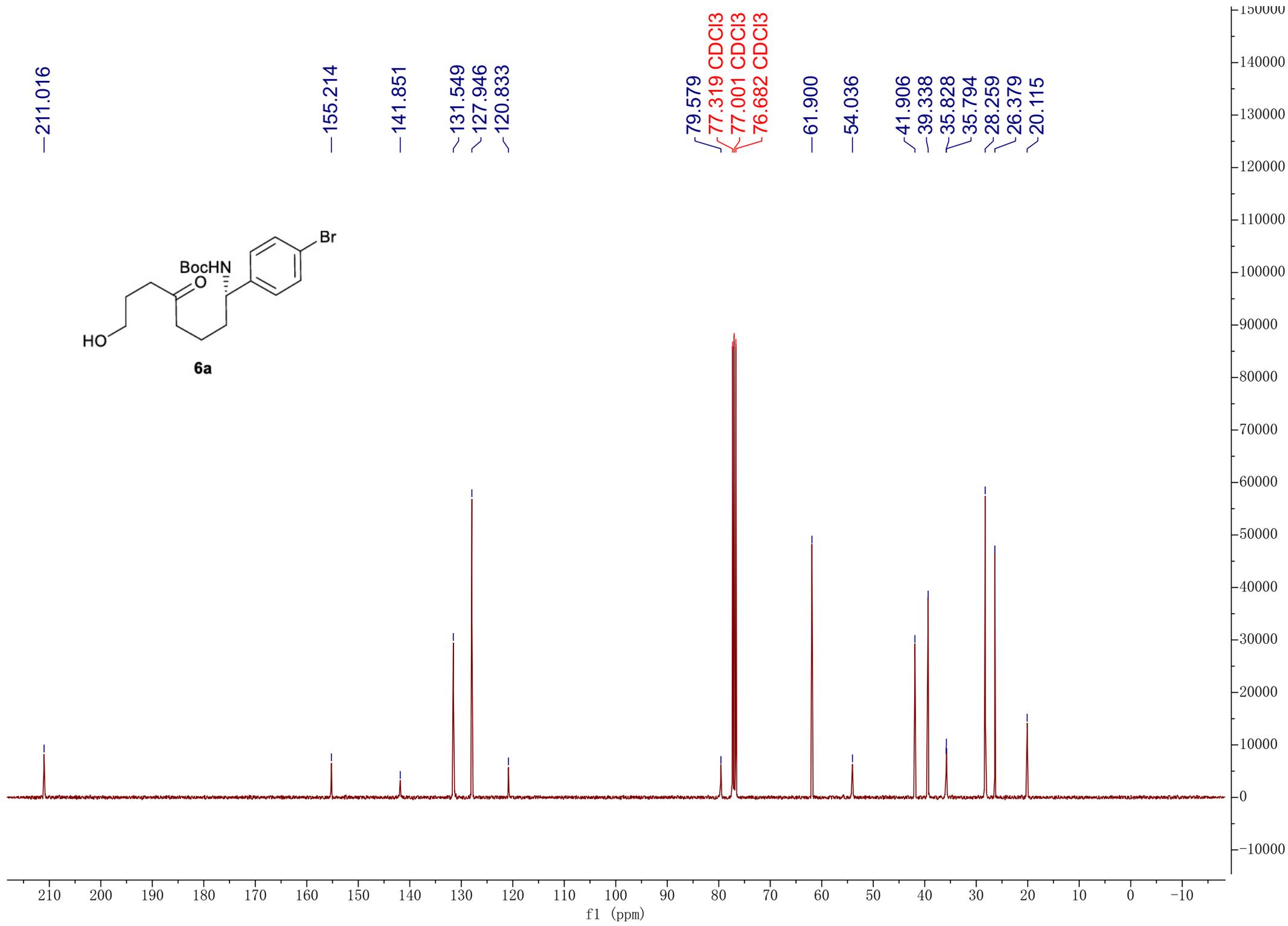
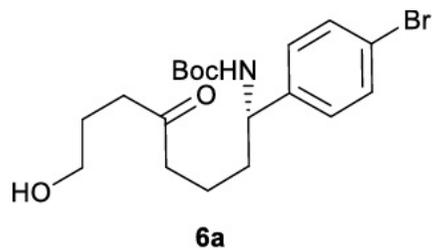
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—36.174

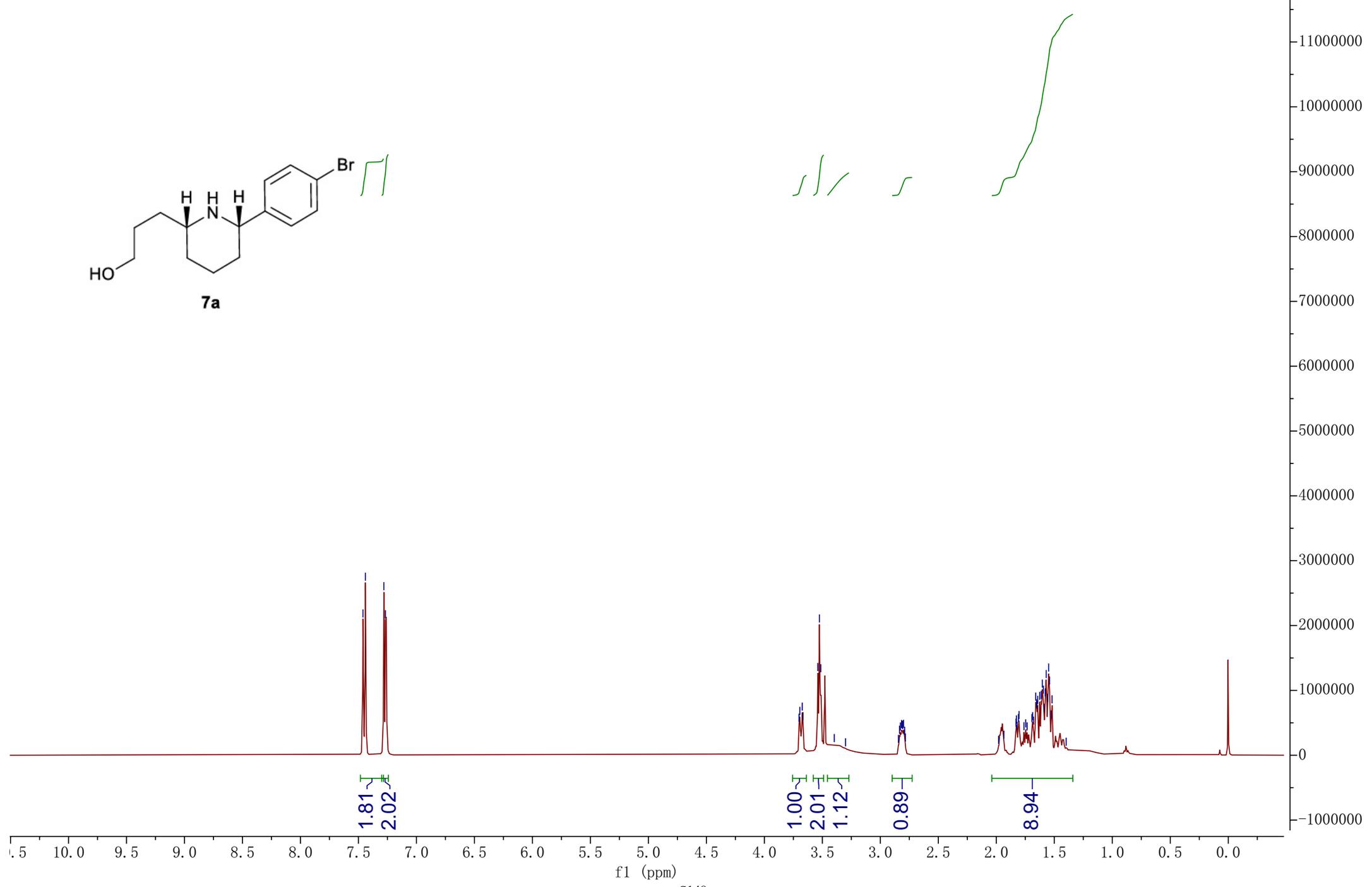
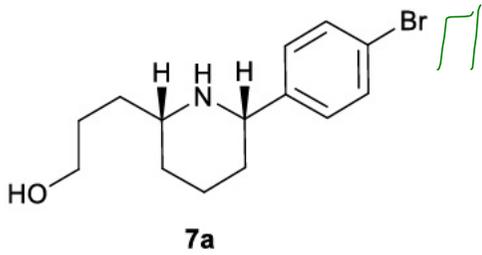
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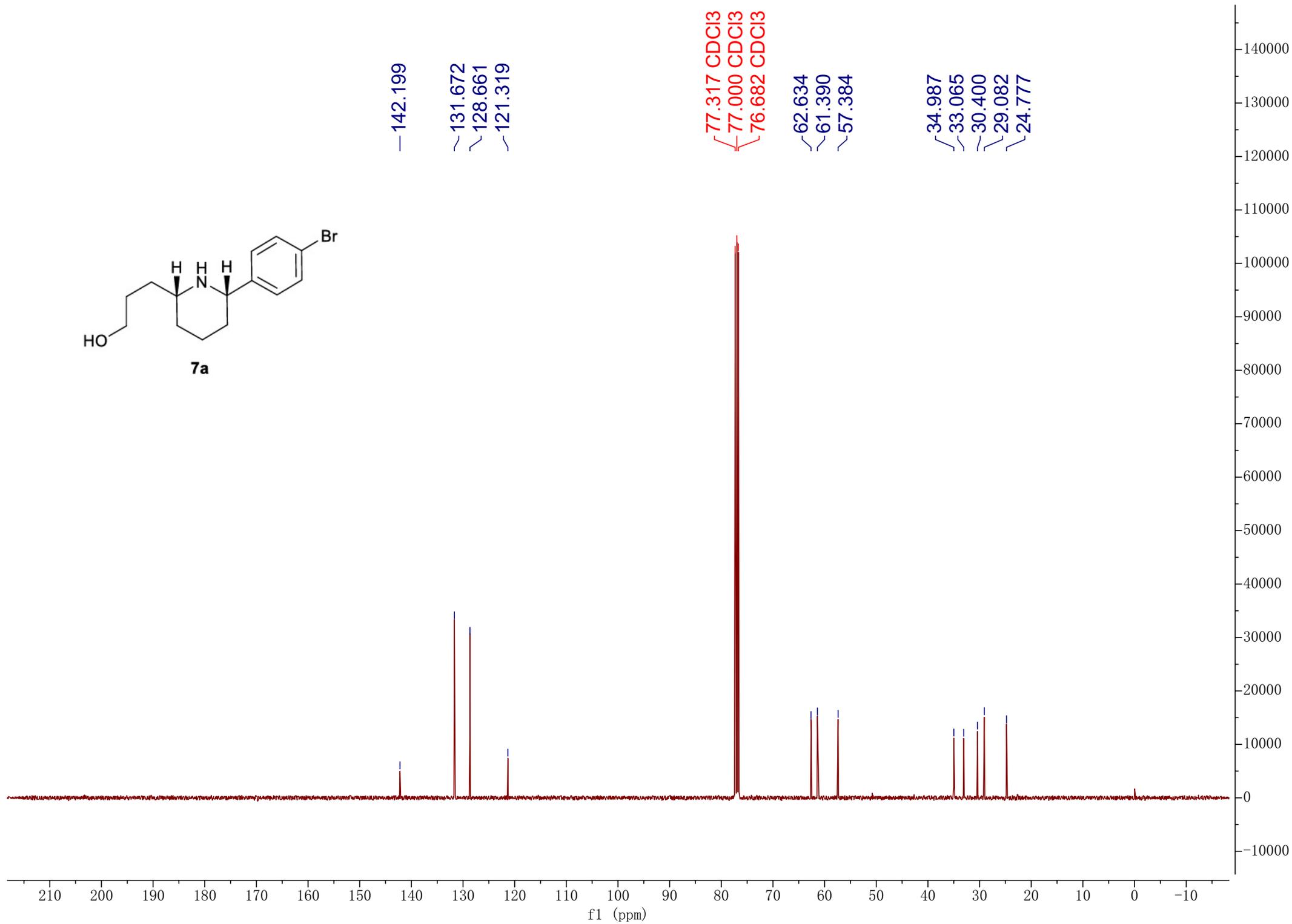
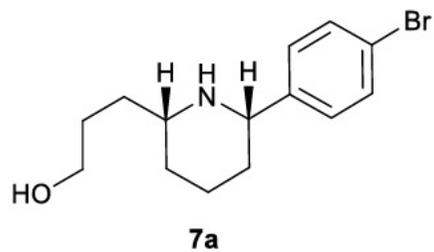


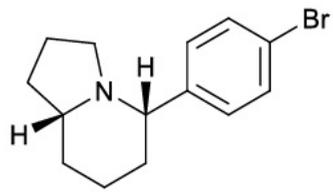




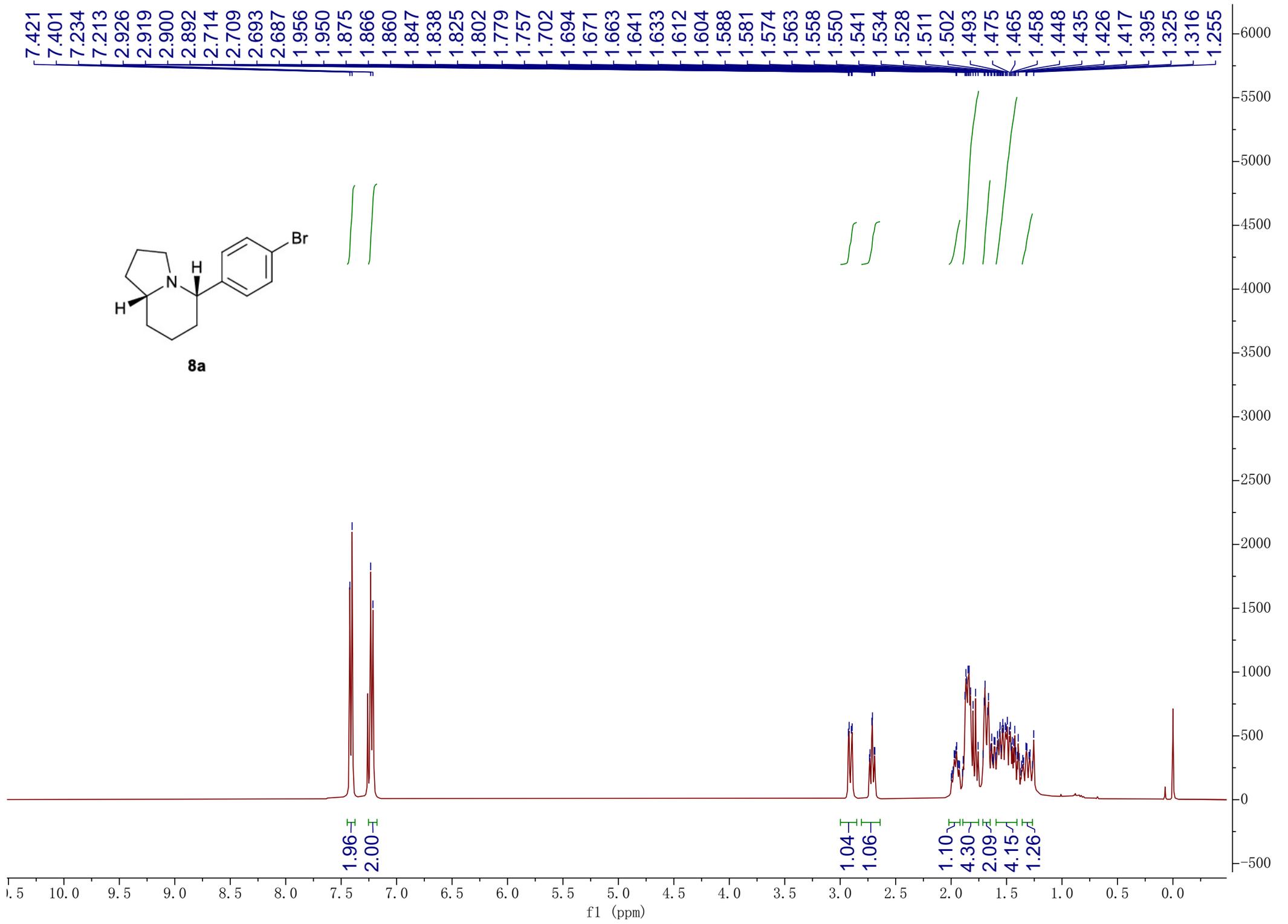
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2.835
2.827
2.817
2.810
2.807
2.800
2.790
2.784
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1.934
1.831
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1.820
1.810
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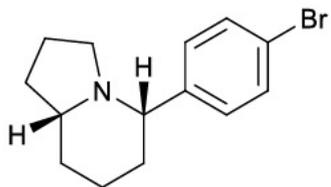




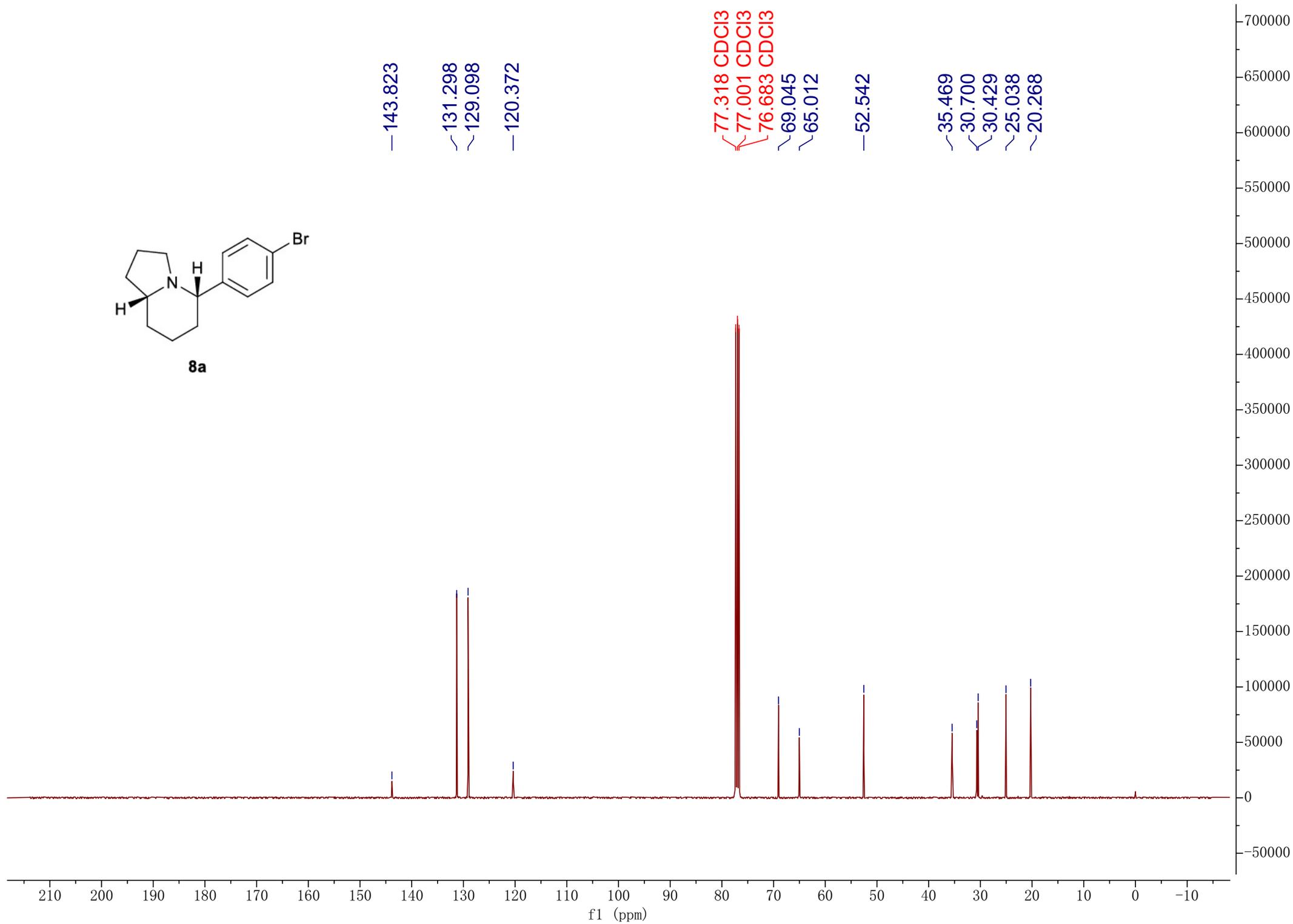


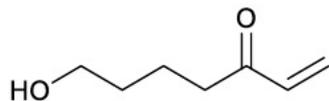
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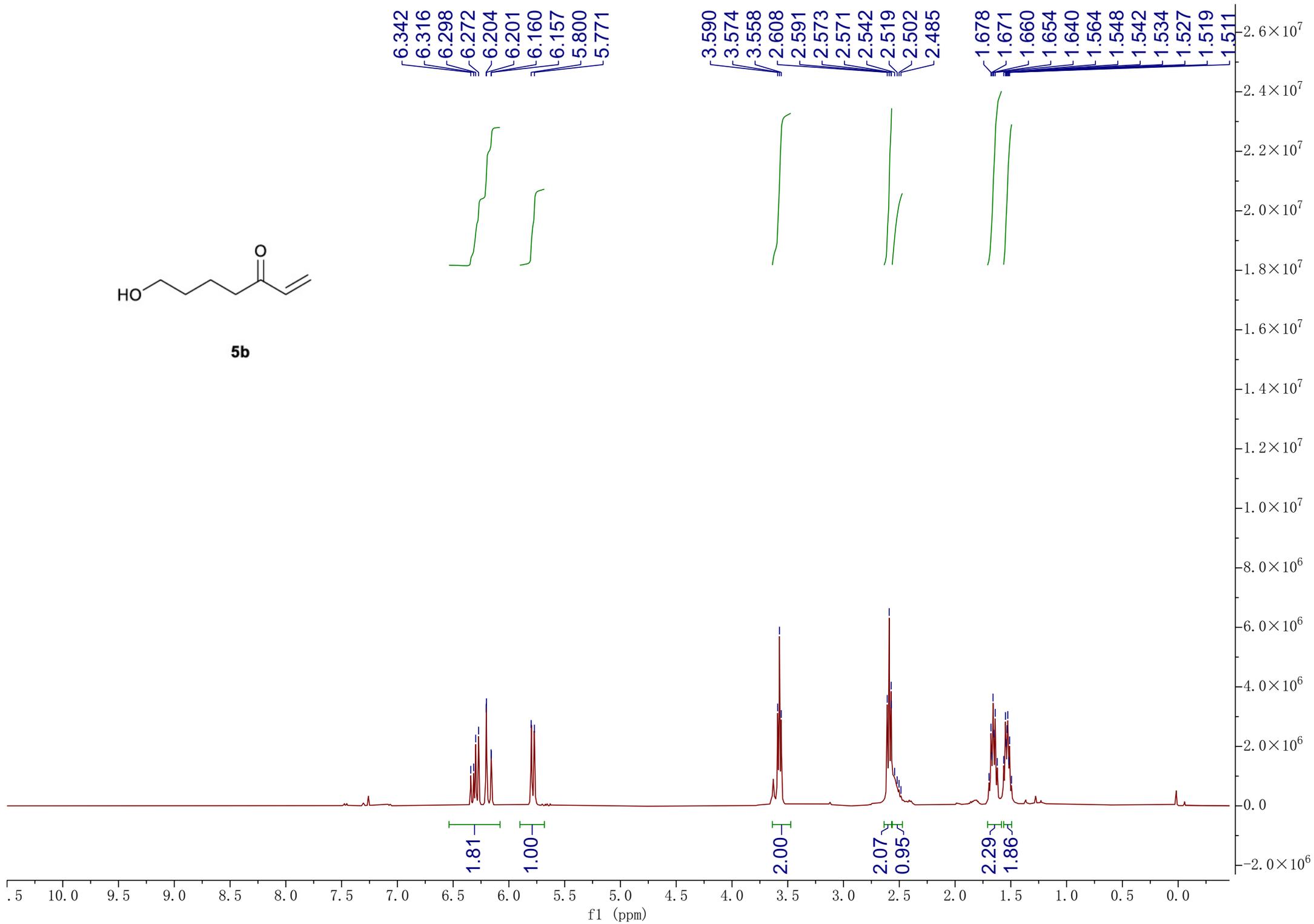


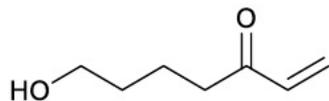
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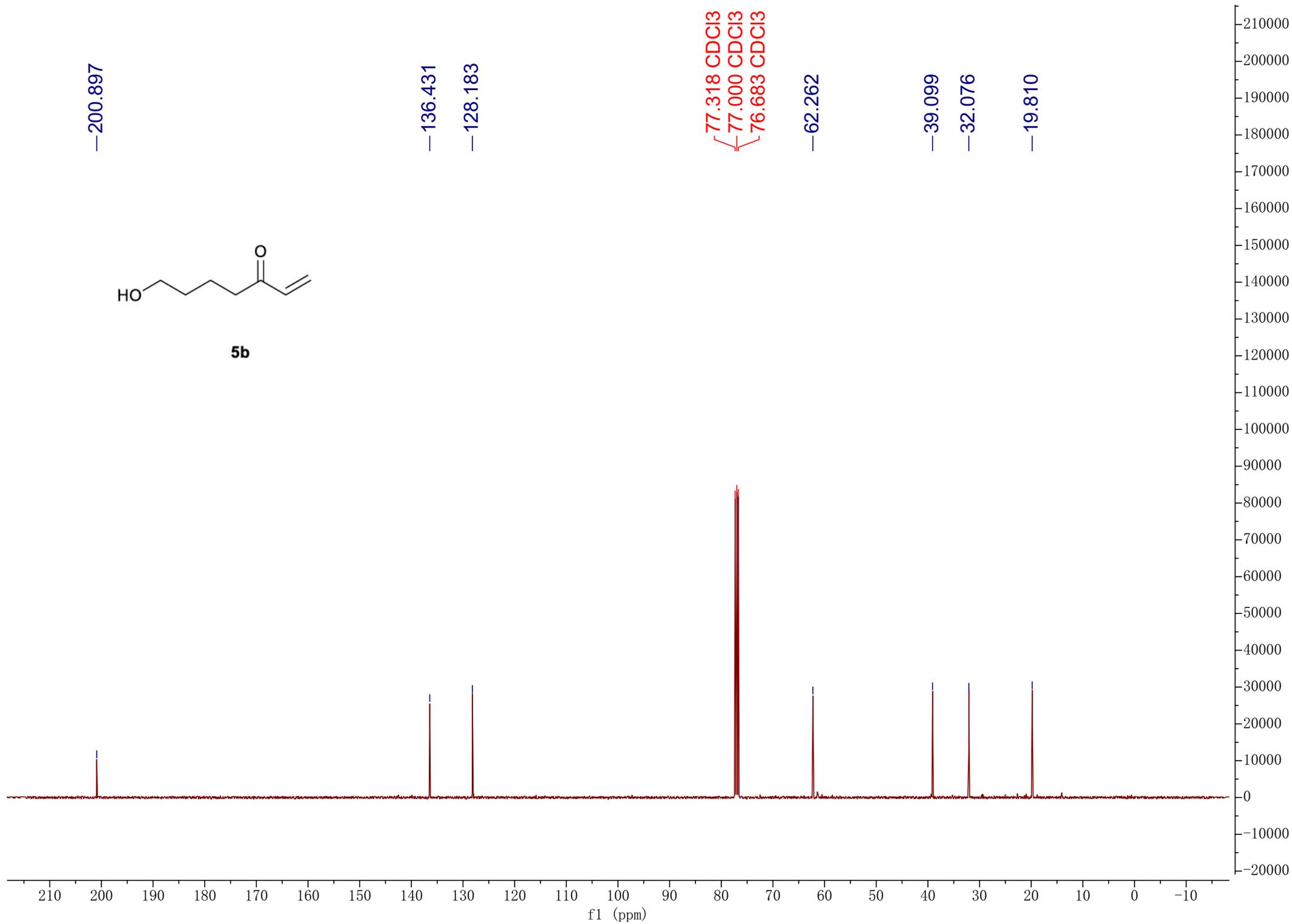


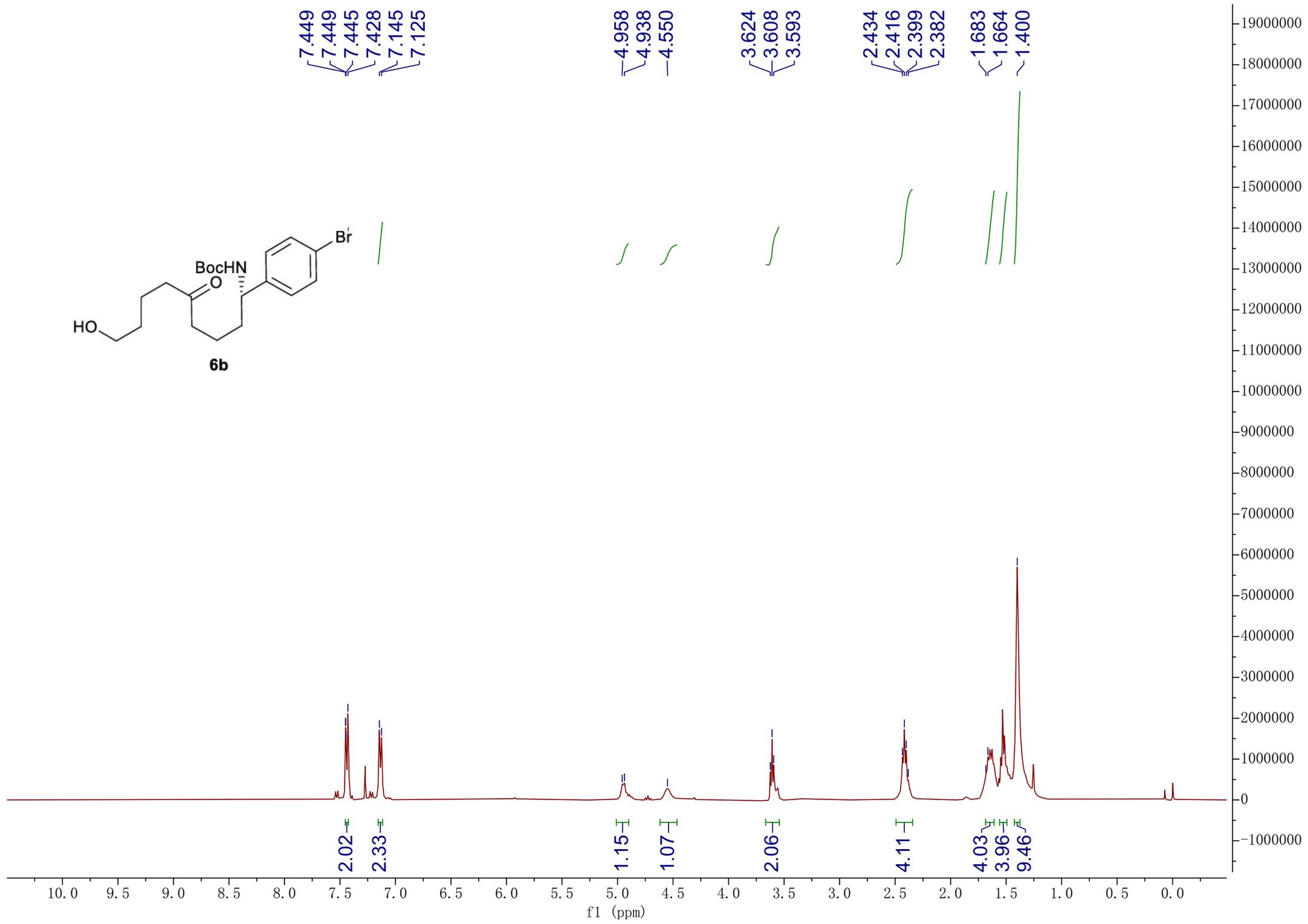
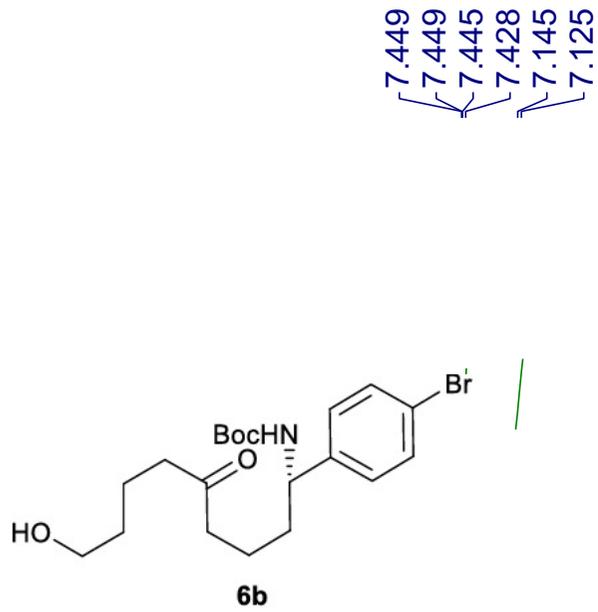
5b





5b





-210.797

-155.202

-141.864

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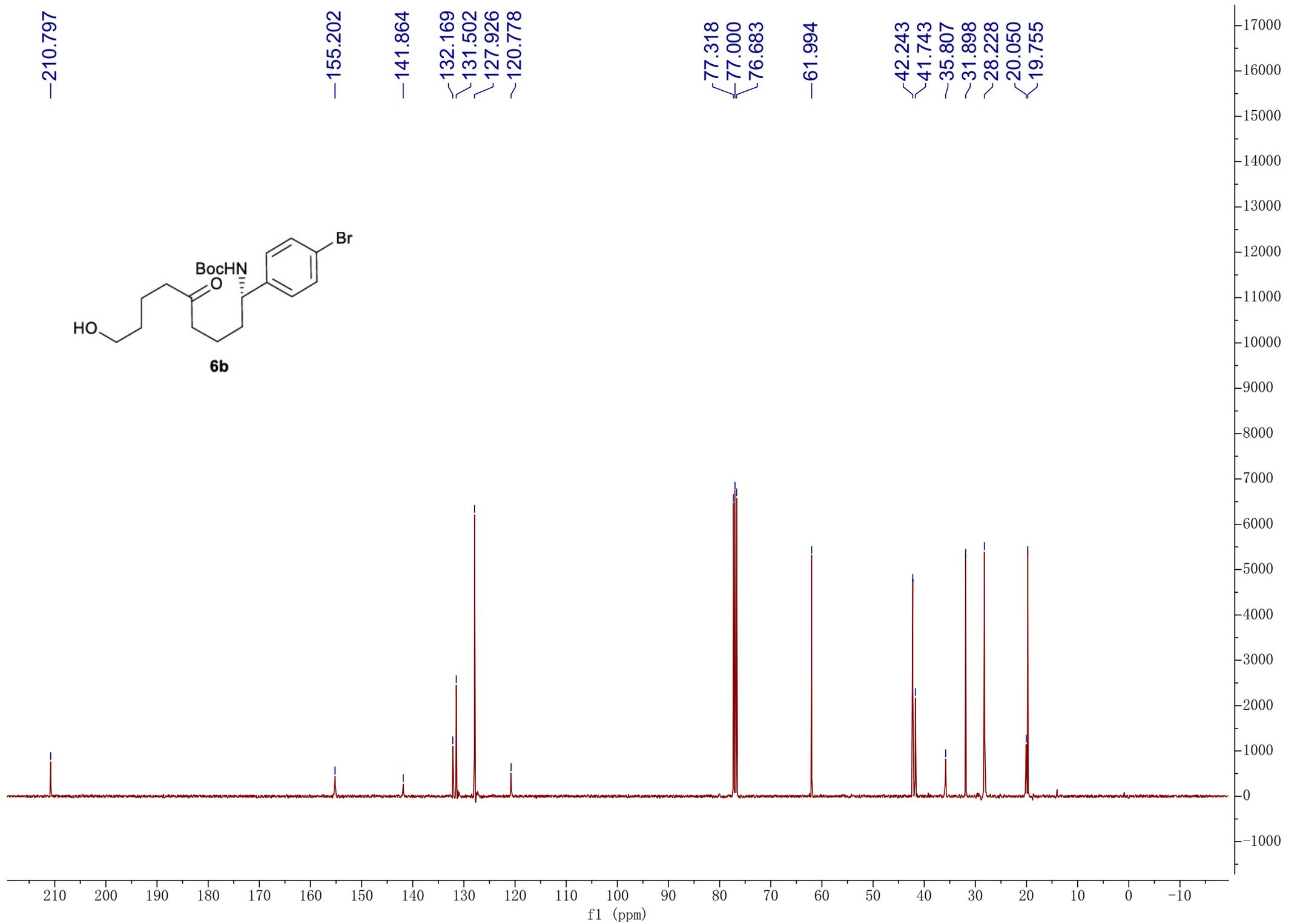
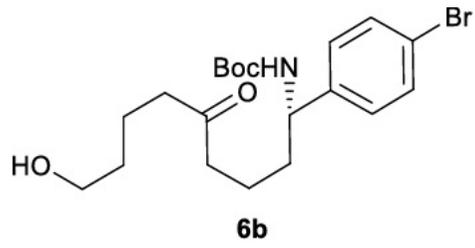
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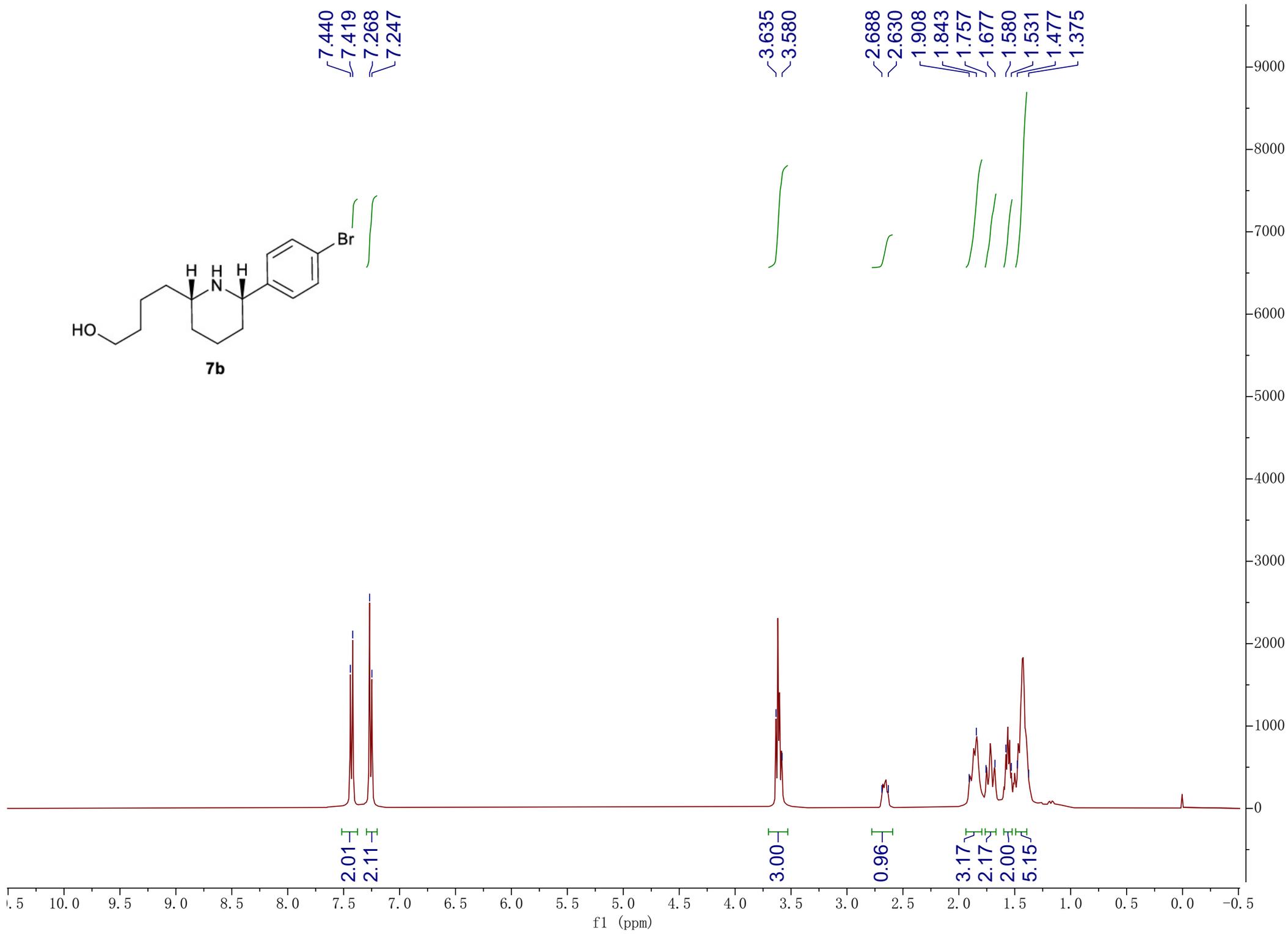
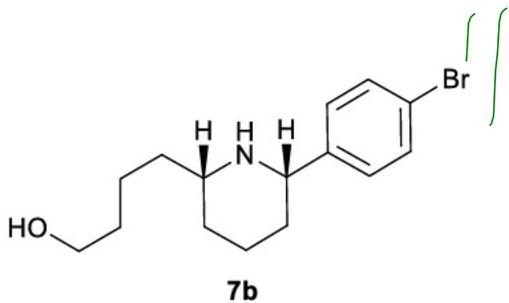
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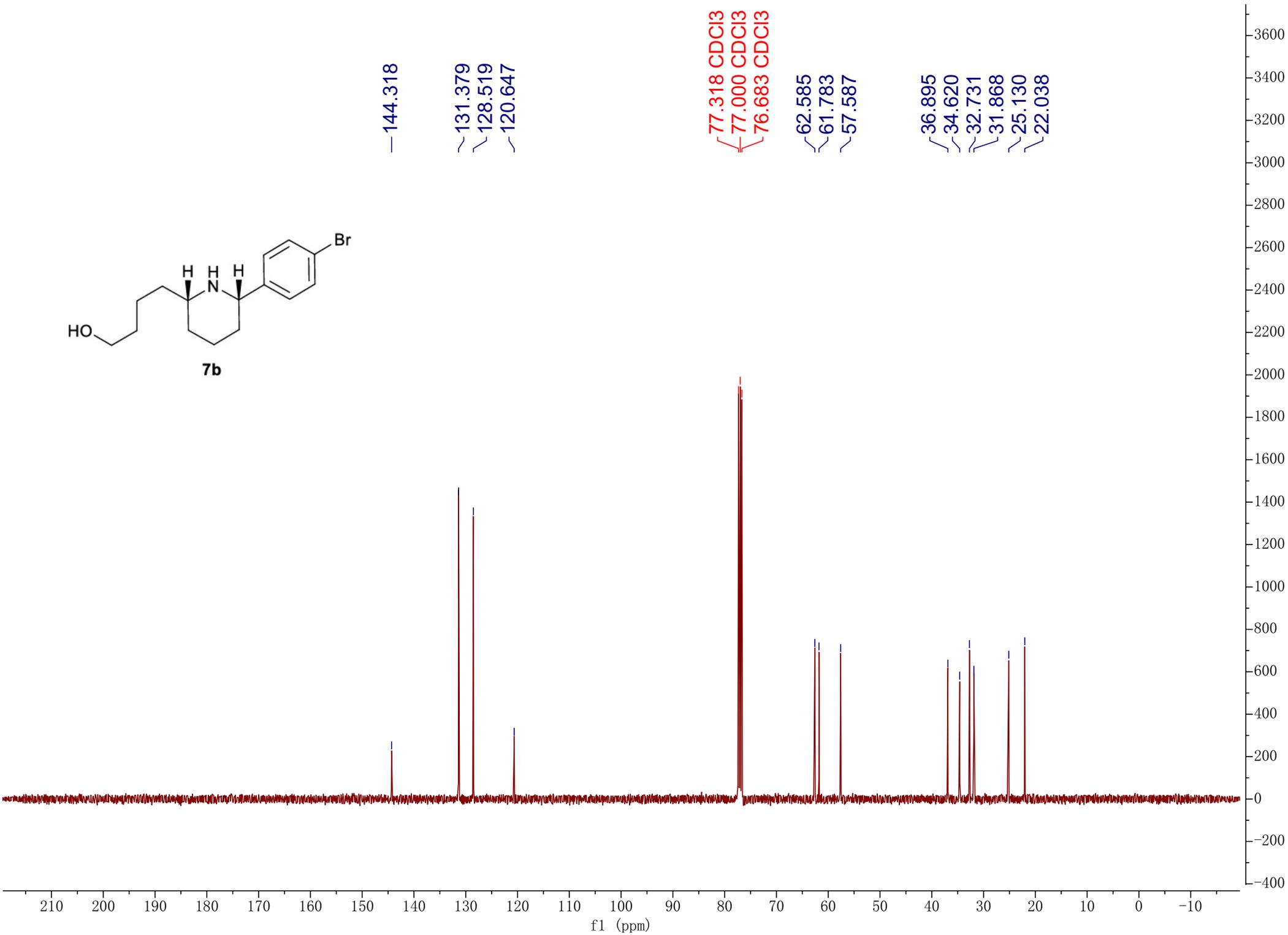
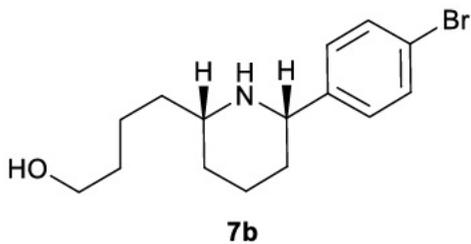
28.228

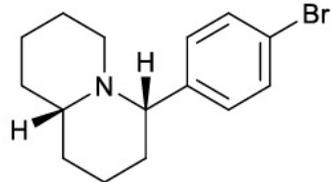
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19.755

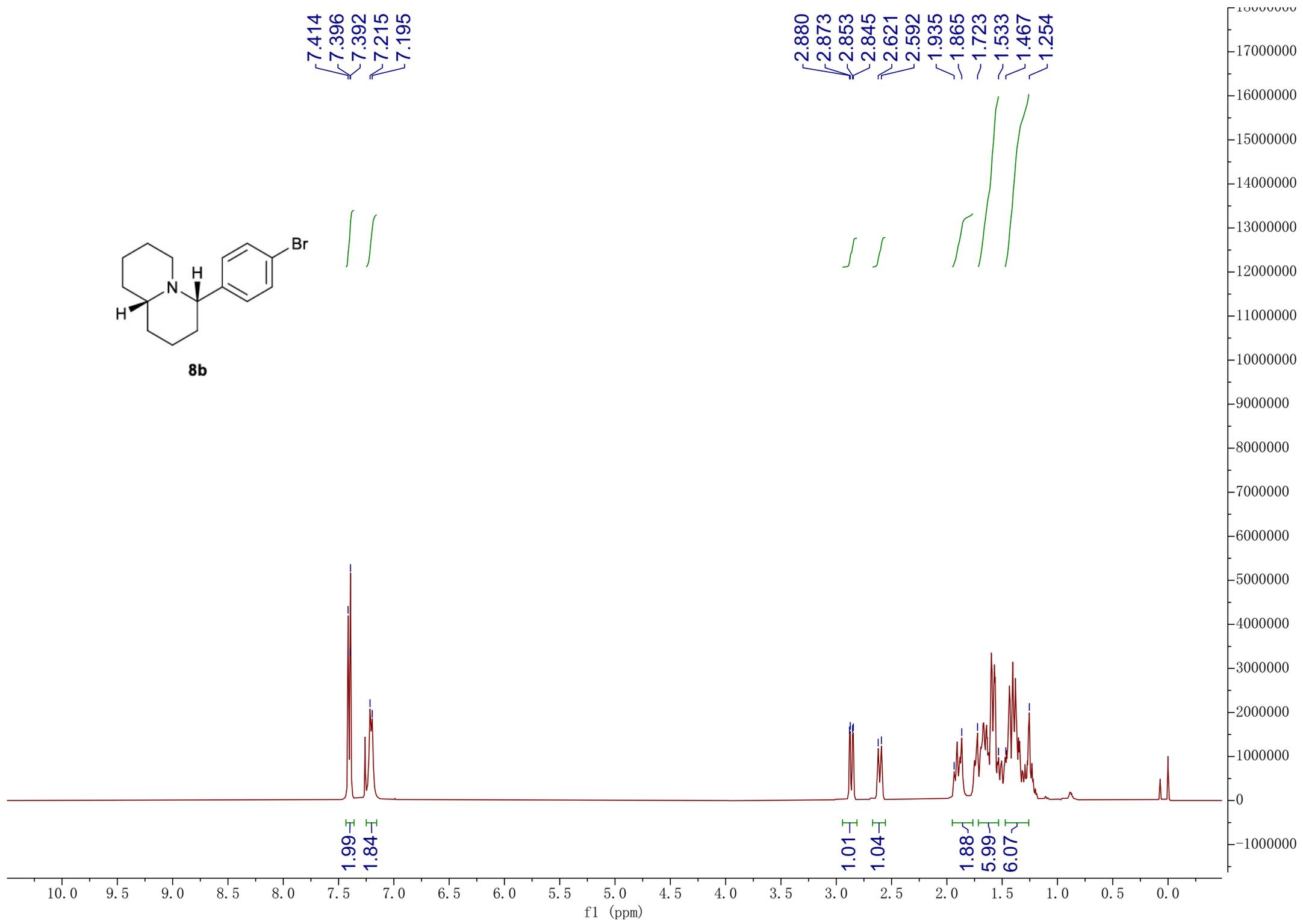


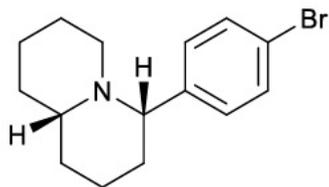




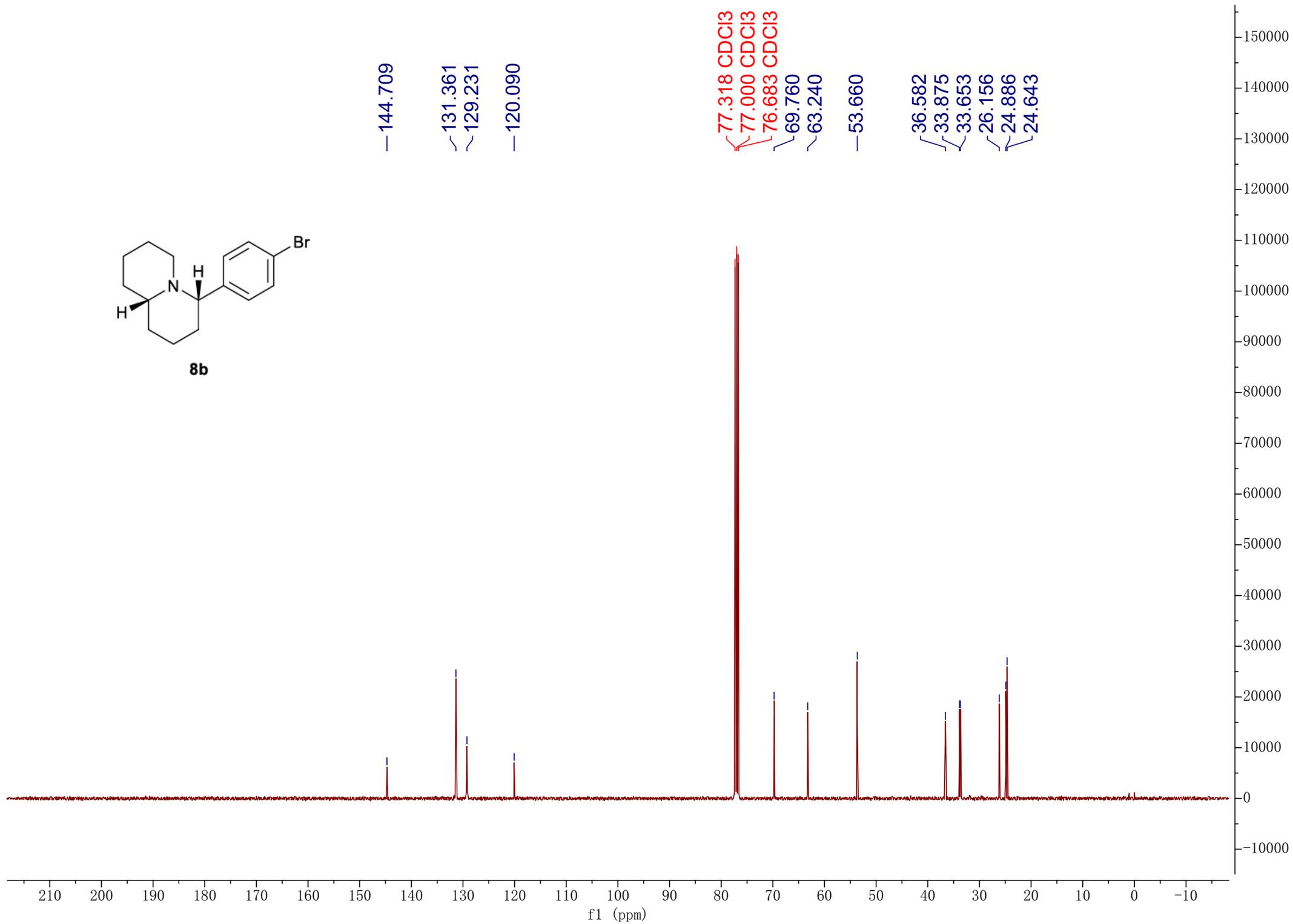


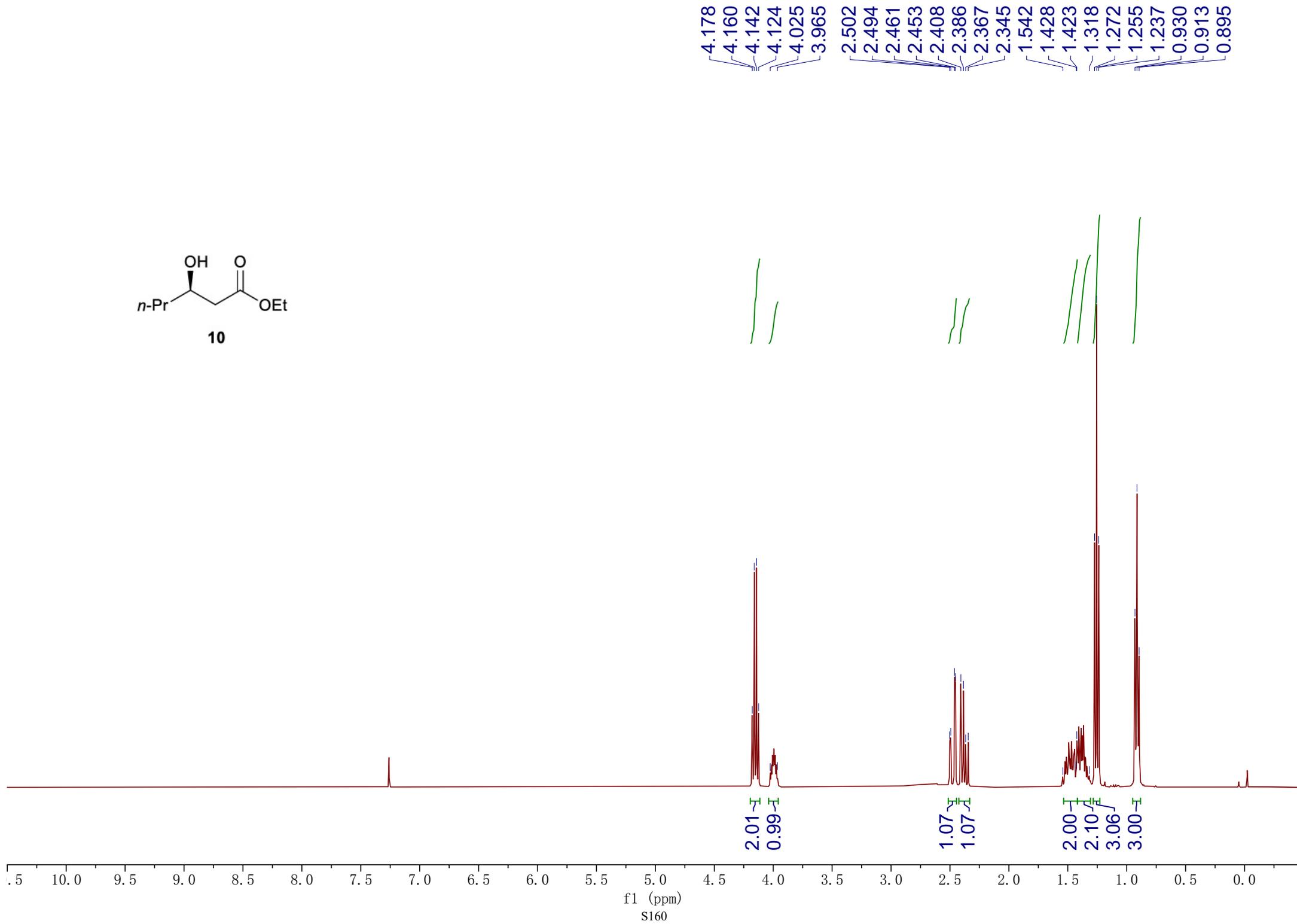
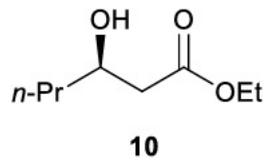
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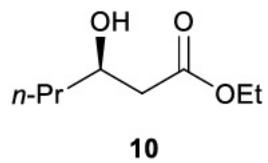




8b







—173.074

77.317 CDCl₃
76.999 CDCl₃
76.681 CDCl₃

—67.691

—60.603

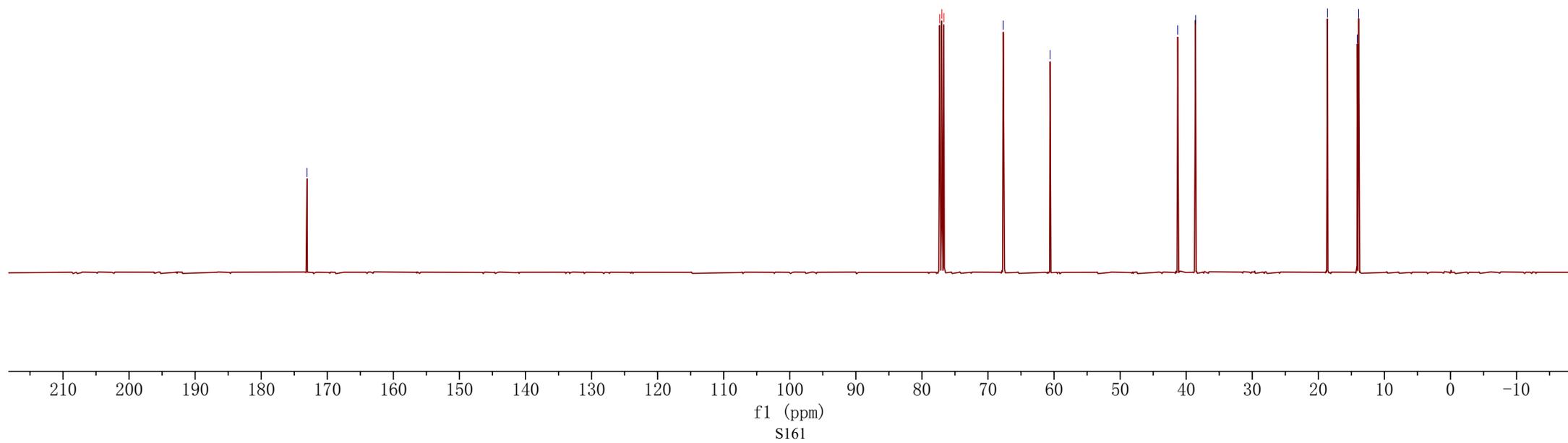
~41.288

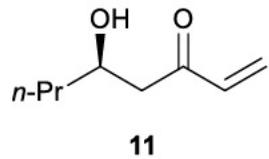
~38.589

~18.618

~14.115

~13.898



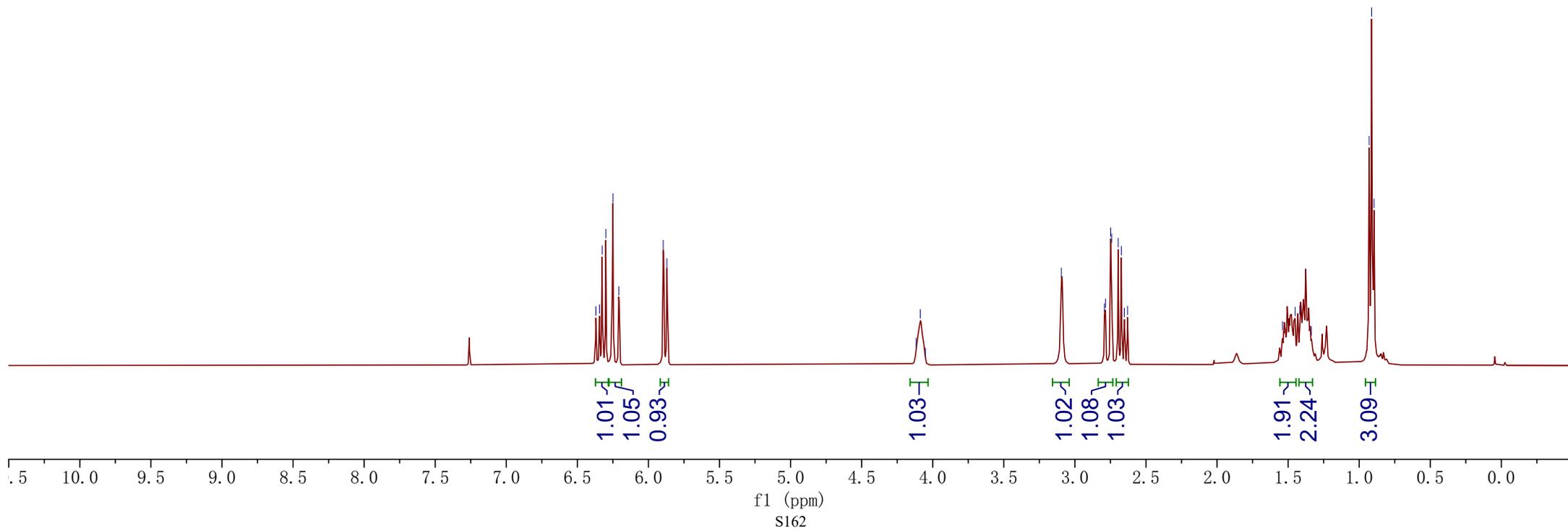
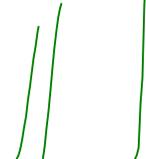


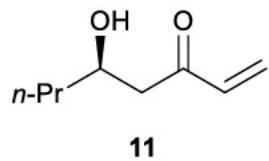
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6.344
6.326
6.300
6.250
6.209
5.896
5.870

4.116
4.087
4.051

3.095
2.792
2.785
2.749
2.741
2.696
2.673
2.652
2.630

1.539
1.451
1.418
1.336
0.930
0.913
0.895





—200.777

—136.288

—129.101

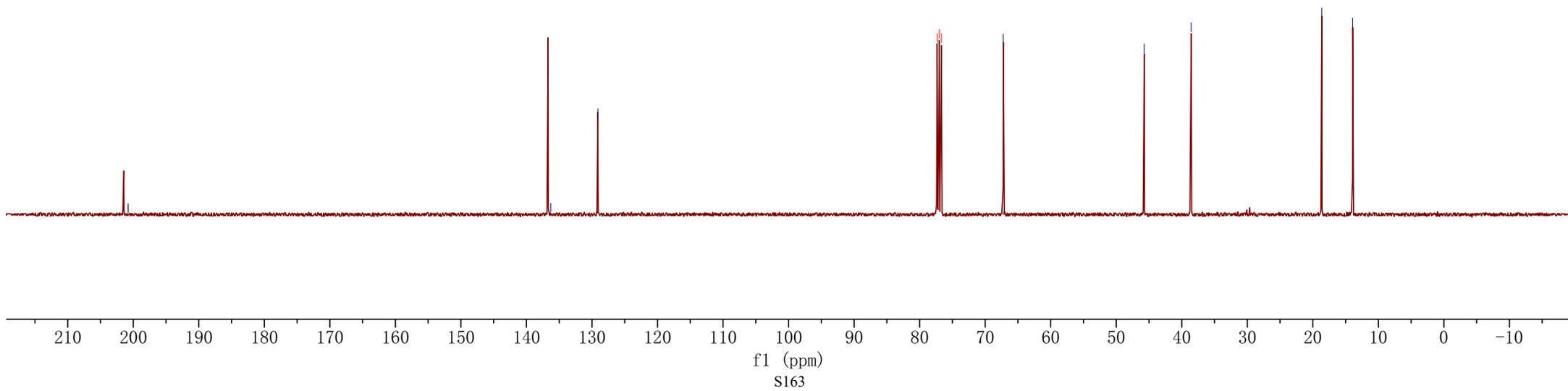
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77.000 CDCI3
76.683 CDCI3
—67.238

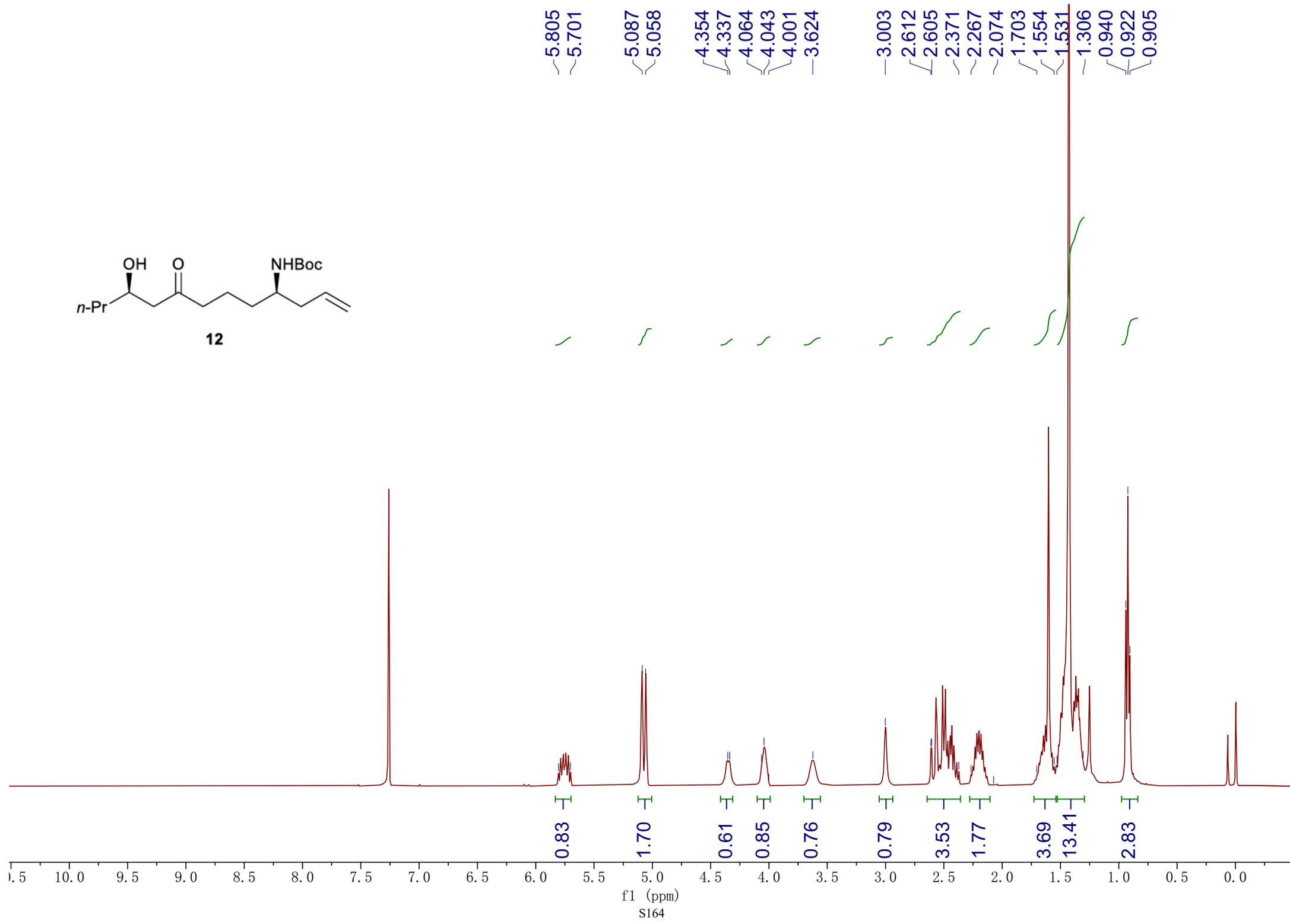
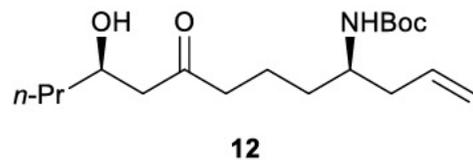
—45.725

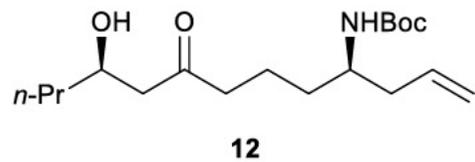
—38.559

—18.633

—13.922







— 212.052

— 155.627

— 134.230

— 117.836

79.144

77.317 CDCl₃

77.000 CDCl₃

76.682 CDCl₃

67.400

49.520

49.087

42.967

39.496

38.611

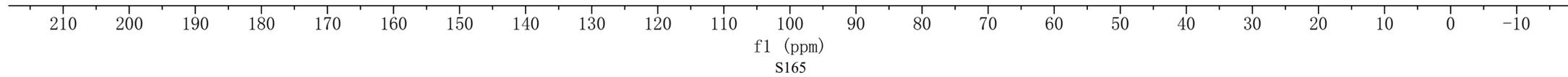
33.907

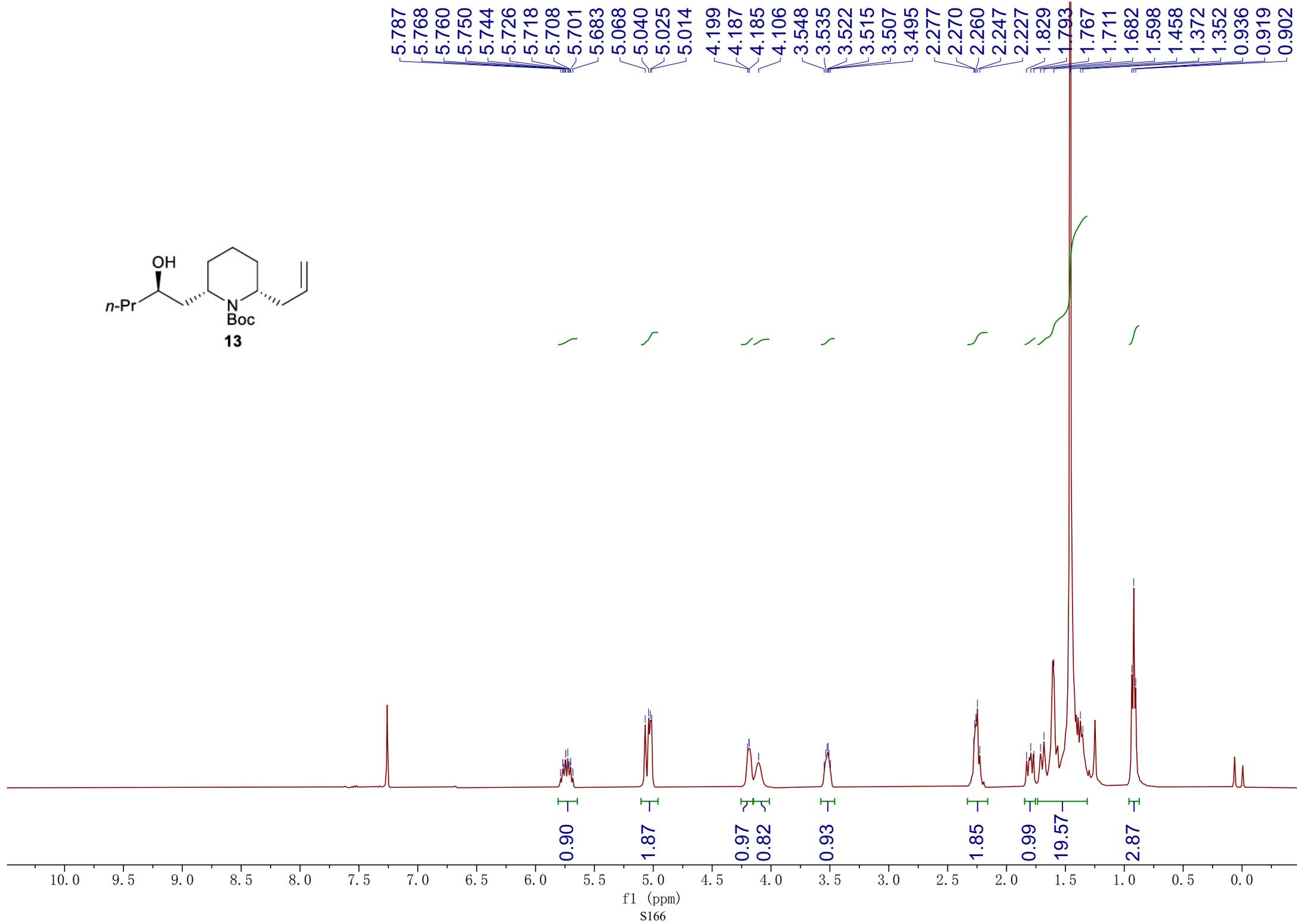
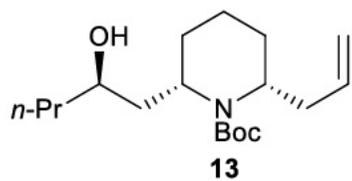
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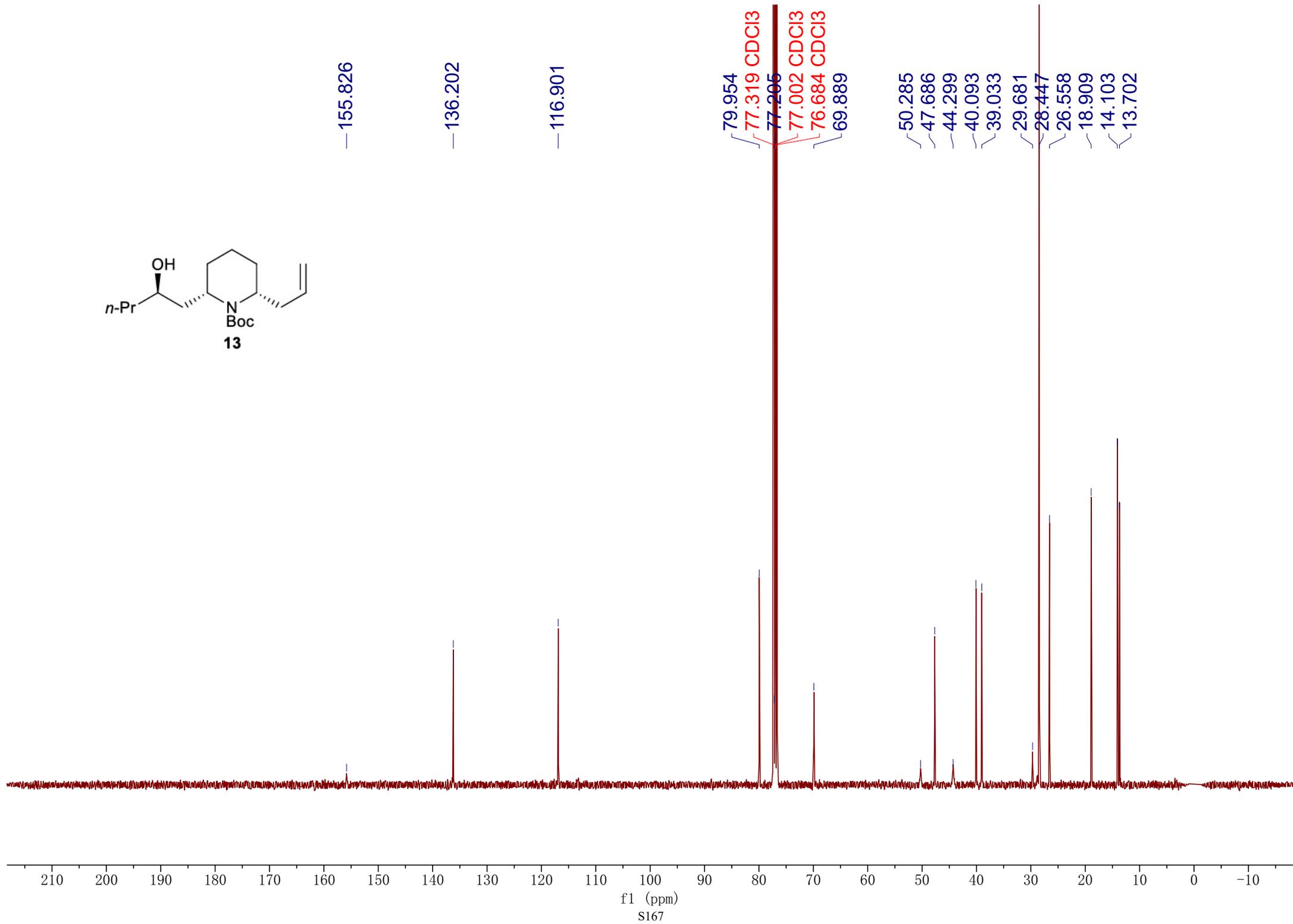
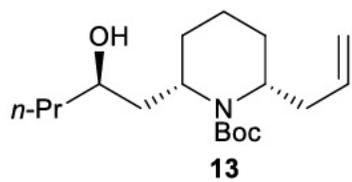
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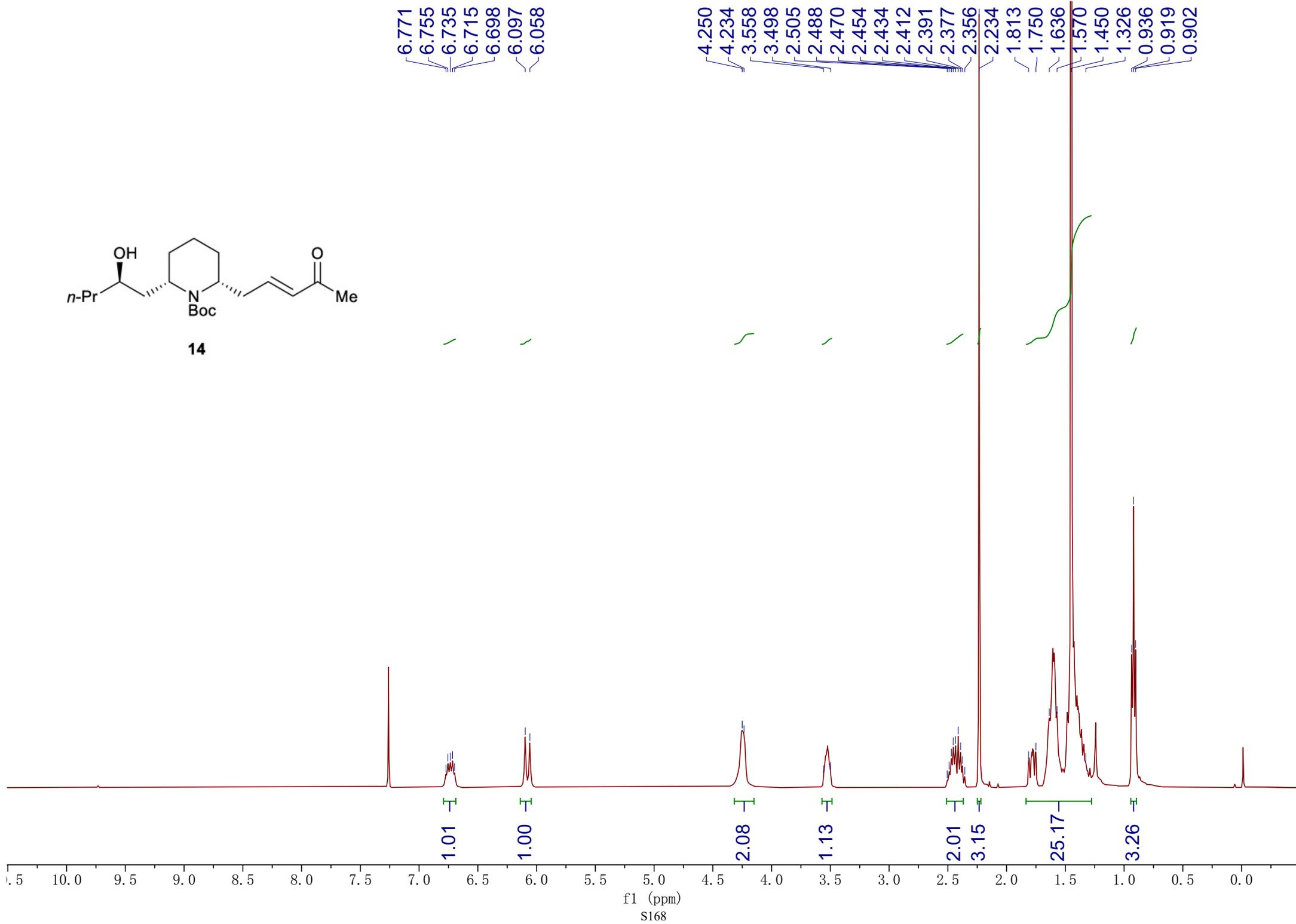
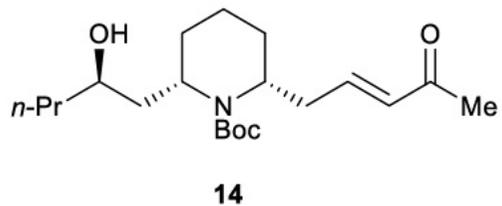
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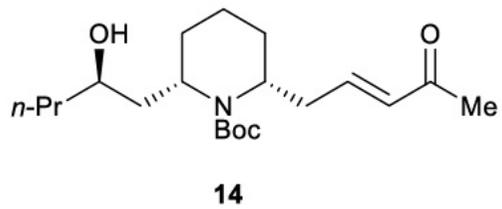
13.962











— 198.391

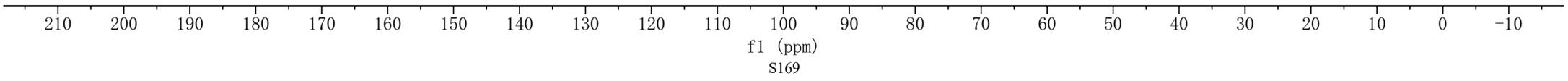
— 155.480

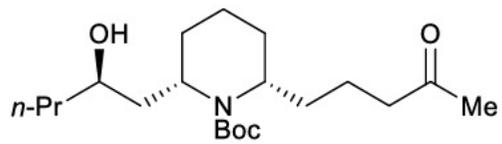
— 145.208

— 132.919

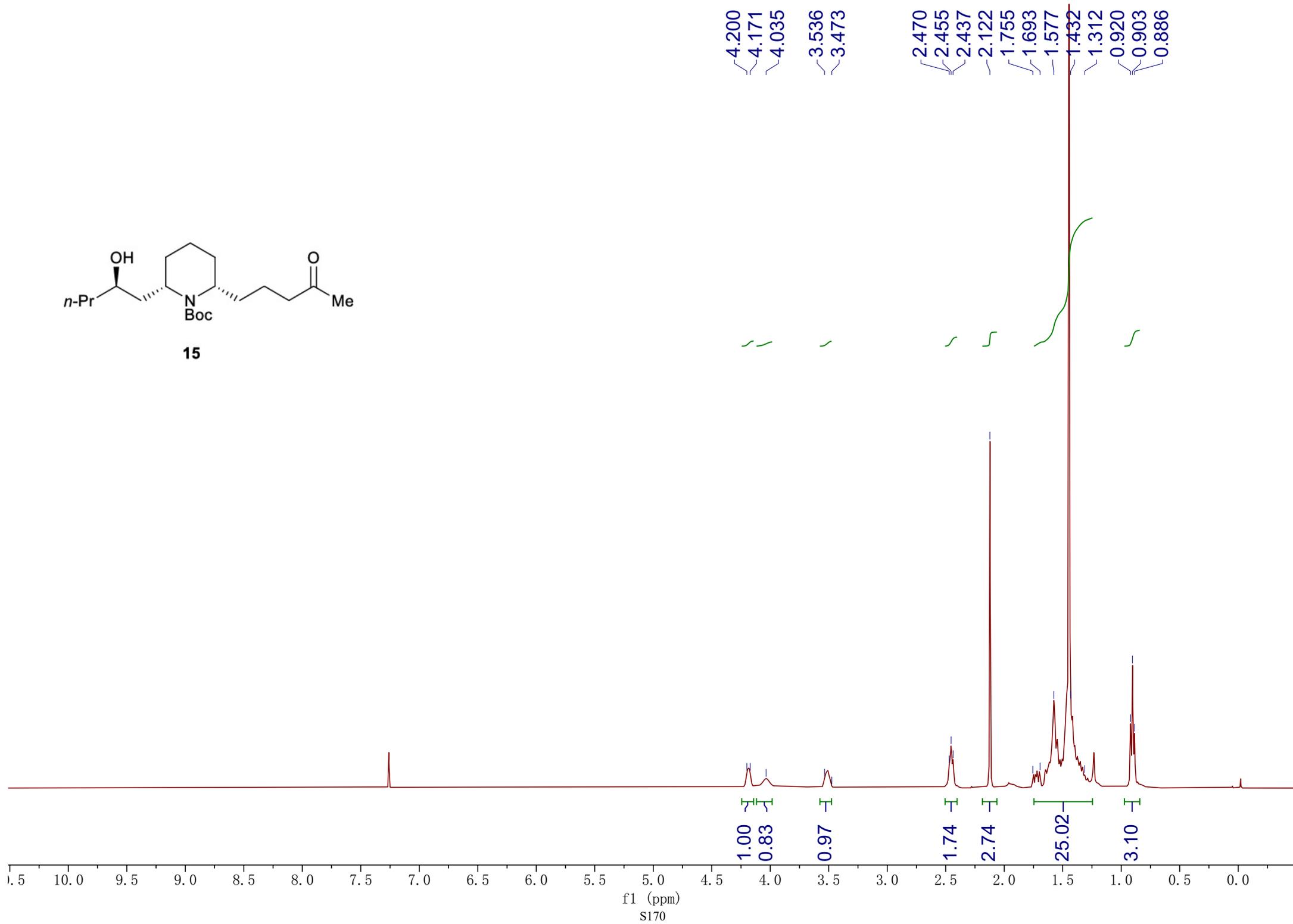
80.278
77.318 CDCl₃
77.202
77.000 CDCl₃
76.683 CDCl₃
69.684

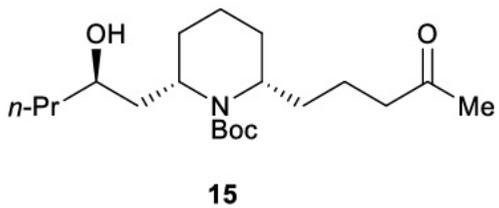
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43.887
40.099
37.855
28.421
27.422
26.938
18.879
14.052
13.736





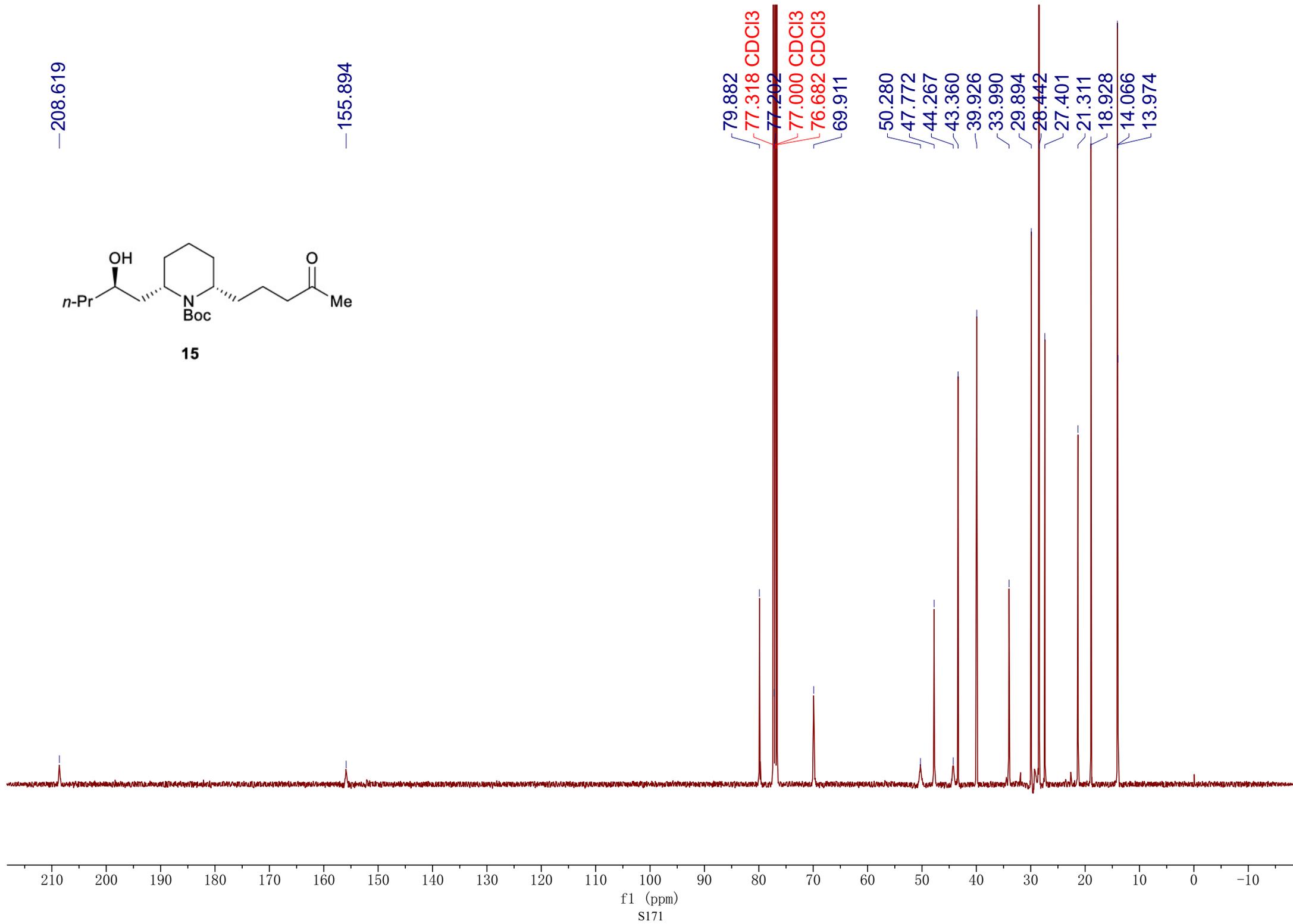
15

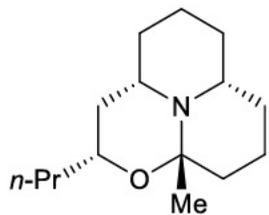




—208.619

—155.894





(-)-6-*epi*-porantheridine

3.802
3.732
2.492
2.425
2.163
2.066
1.685
1.168
0.910
0.839

