

Supporting Information for

**Unprecedented single-electron-transfer reduction-based N→C
acyl migration reactions of imides enabled by redox-neutral
photocatalysis**

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1. General Information

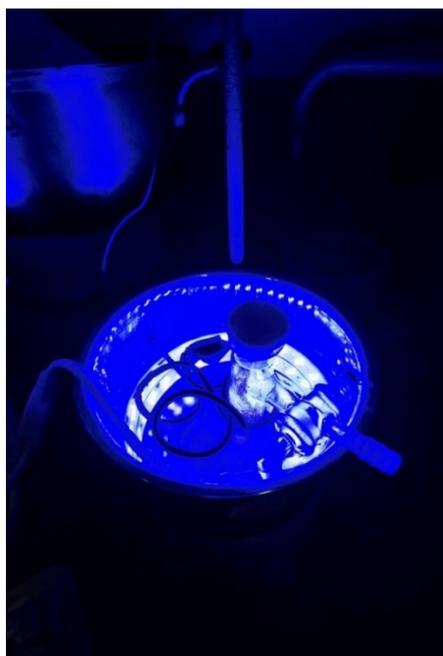
1.1 Solvents, Reagents, and Starting Materials

All reactions were carried out in glassware under inert (nitrogen) atmosphere unless otherwise noted. DMF and CH_2Cl_2 were dried from CaH. The dehydrated solvents DMSO, DMA and acetonitrile were purchased from Energy Chemical Chemicals. Photoredox catalysts and alkyl silicates were reported in our previous works.^[1] *N*-Vinylimides were prepared according to literature procedures.^[2] All other chemicals were purchased from local vendors and used as supplied unless otherwise stated.

1.2 Instruments

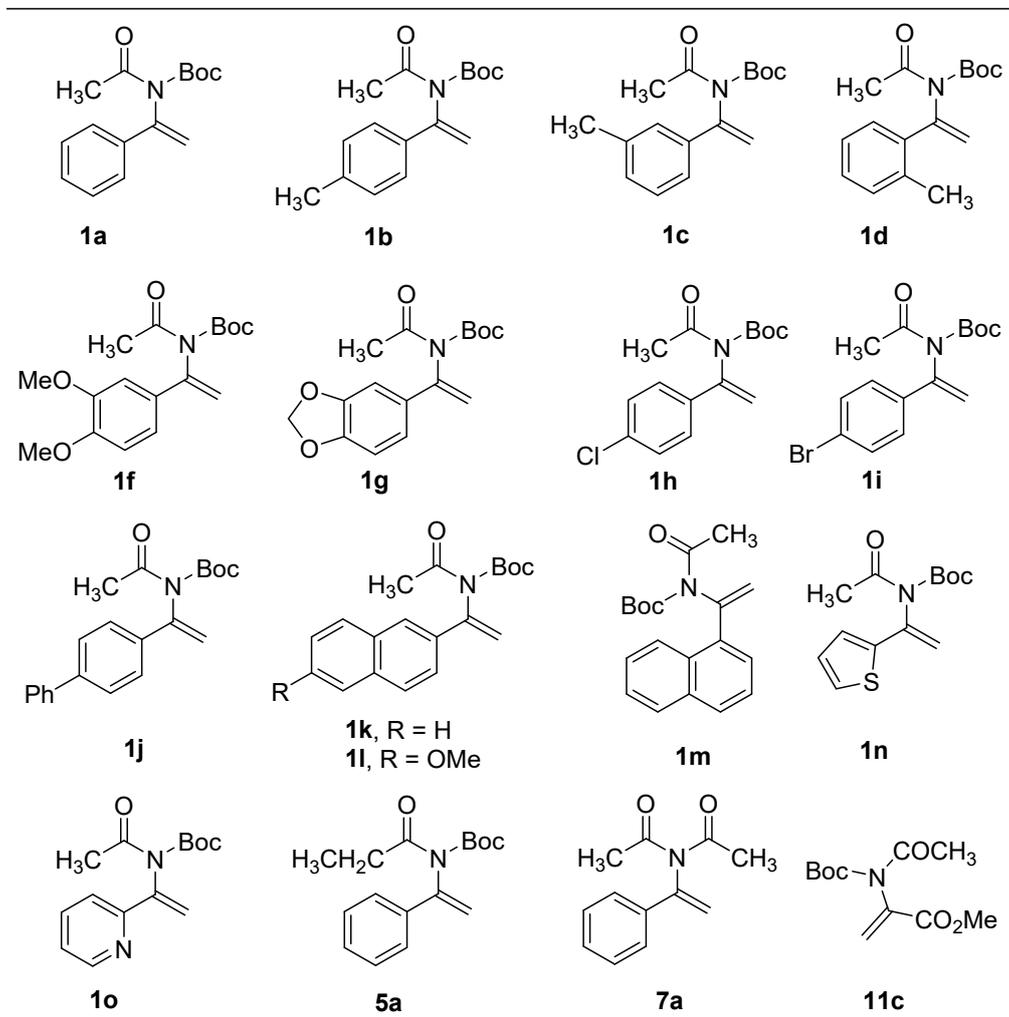
NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz). Chemical shifts were reported in ppm downfield from tetramethylsilane, and calibrated using residue undeuterated solvent (CHCl_3 at 7.26 ppm ^1H NMR, 77.0 ppm ^{13}C NMR). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were recorded on an ESI-Q-TOF spectrometer Agilent 6210 ESI/TOF. Single Crystal X-ray Diffraction (SC-XRD) recorded on a Bruker D8 Quest. TLC analyses were performed on precoated GF₂₅₄ silica gel plates and were visualized under UV254 nm light or by I_2 staining. Column chromatography was carried out using 300-400 mesh silica gel and eluted with petroleum/ethyl acetate unless otherwise noted.

1.3 Picture of a Typical Reaction Setup

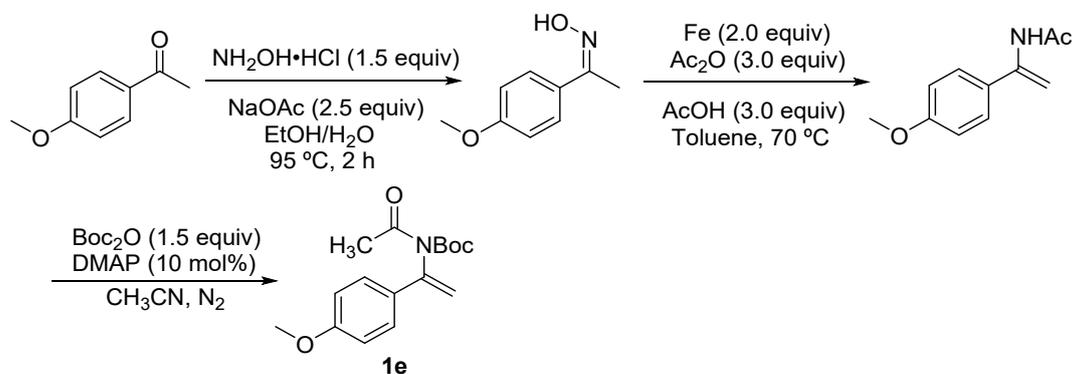


2. Preparation of *N*-vinylimides

2.1 Know substrates reported in our previous work^[3]



2.2 Synthesis of *N*-vinylimide **1e**

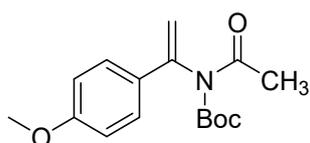


(a) A mixture of 4'-methoxyacetophenone (3.0 g, 20 mmol), $\text{NH}_2\text{OH}\cdot\text{HCl}$ (2.08 g, 30 mmol), and

NaOAc (4.1 g, 50 mmol) in EtOH (10 mL) and H₂O (30 mL) was placed into a 100 mL round-bottomed flask equipped with a condenser. Then the flask was heated to 95 °C and the reaction was monitored by TLC. Add water after cooling down to room temperature, then the mixture was extracted with ethyl acetate (3 × 10 mL). The organic layer was collected, dried over MgSO₄ and concentrated *in vacuo* to afford the ketoxime which was used without further purification for the next step.

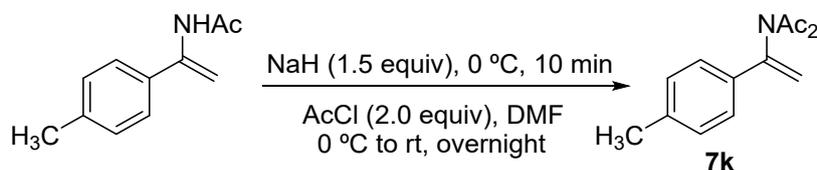
(b) To an oven-dried 50 mL two-neck round-bottom flask assembled with condenser was added the above ketoxime (1.65 g, 10 mmol). Anhydrous toluene (20 mL) was added followed by acetic anhydride (3.06 g, 30 mmol), acetic acid (1.8 g, 30 mmol) and iron powder (1.12 g, 20 mmol). The reaction flask was put into a 70 °C preheated oil bath and allowed to stir under nitrogen atmosphere. After the reaction completed and cooled to room temperature, ethyl acetate was added and the mixture was filtered through a short pad of celite. The solution thus was evaporated to get the crude enamide, which was directly purified by column chromatography.

(c) The above prepared enamide (955 mg, 5 mmol) and DMAP (61 mg, 0.5 mmol) were dissolved in CH₃CN (10 mL) in a dry two-necked round-bottom flask. Then Boc₂O (1.64 g, 7.5 mmol) was added dropwise at room temperature. The completion of the reaction was confirmed by checking TLC and the reaction was quenched by adding water (10 mL). The organic layer was extracted with ethyl acetate, dried, filtered, and evaporated under reduced pressure to give the crude product, which was purified by column chromatography over silica gel to give the pure product **1e**.



tert-Butyl acetyl(1-(4-methoxyphenyl)vinyl)carbamate (1e). Flash column chromatography to afford product as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.24 (m, 2H), 6.90-6.79 (m, 2H), 5.65 (s, 1H), 5.07 (s, 1H), 3.80 (s, 3H), 2.55 (s, 3H), 1.31 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 172.7, 159.8, 152.4, 143.4, 129.4, 126.5, 113.8, 112.0, 83.0, 55.2, 27.6, 26.1. HRMS (ESI) [M+Na]⁺: calculated for C₁₆H₂₁NO₄Na: 314.1368, found 314.1374.

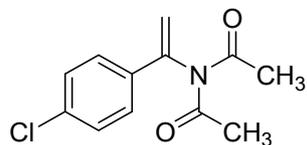
2.3 General procedure for the preparation of *N*-vinylimides **7k**, **7l**, and **9**



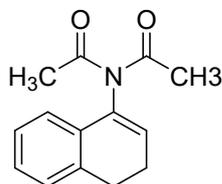
The enamide (5 mmol) was dissolved in dry DMF (10 mL) in a dry round-bottom flask. The solution was cooled to 0 °C and sodium hydride (60% dispersion in mineral oil) (300 mg, 7.5 mmol) was added in portions. The resulting suspension was stirred at the same temperature for 10 min. Then AcCl (785 mg, 10 mmol) was added dropwise and the final solution was continued to stir for overnight at room temperature. The completion of the reaction was confirmed by checking TLC and the excess of sodium hydride was quenched by adding water (10 mL) at 0 °C. The organic layer was extracted with ethyl acetate through stages of extraction with water. The organic layer was extracted with ethyl acetate, dried, filtered, and evaporated under reduced pressure to give the crude product, which was purified by column chromatography over silica gel to give the

the pure product **7**.

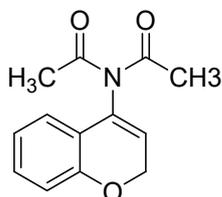
N-Acetyl-N-(1-(*p*-tolyl)vinyl)acetamide (7k). Flash column chromatography to afford product as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.29 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 1H), 5.96 (s, 0H), 5.24 (s, 1H), 2.39 (s, 6H), 2.34 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 172.7, 144.4, 139.1, 132.3, 129.6, 124.8, 114.6, 26.1, 21.0. HRMS (ESI) [M+H]⁺: calculated for C₁₃H₁₆NO₂: 218.1181, found 218.1180.



N-Acetyl-N-(1-(4-chlorophenyl)vinyl)acetamide (7l). Flash column chromatography to afford product as a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 7.41-7.29 (m, 4H), 6.00 (s, 1H), 5.33 (s, 0H), 2.40 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 172.6, 143.7, 135.1, 133.8, 129.2, 126.3, 116.2, 26.2. HRMS (ESI) [M+Na]⁺: calculated for C₁₂H₁₂NO₂ClNa: 260.0454, found 260.0450.

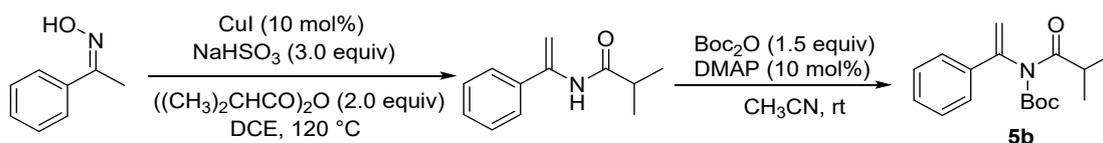


N-Acetyl-N-(3,4-dihydronaphthalen-1-yl)acetamide (9a). Flash column chromatography to afford product as a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 7.22-7.13 (m, 3H), 6.92-6.85 (m, 1H), 5.99 (t, *J* = 4.6 Hz, 1H), 2.91 (t, *J* = 8.2 Hz, 2H), 2.58-2.46 (m, 2H), 2.39 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 172.9, 136.5, 136.2, 131.3, 129.2, 128.3, 128.0, 127.0, 121.2, 27.1, 26.1, 22.9. HRMS (ESI) [M+Na]⁺: calculated for C₁₄H₁₅NO₂Na: 252.1000, found 252.1006.



N-Acetyl-N-(2H-chromen-4-yl)acetamide (9b). Flash column chromatography to afford product as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.23-7.10 (m, 1H), 6.93-6.76 (m, 3H), 5.75 (t, *J* = 3.8 Hz, 1H), 4.99 (d, *J* = 3.8 Hz, 2H), 2.41 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 172.4, 154.8, 134.2, 130.6, 122.2, 121.9, 121.8, 120.2, 116.5, 65.3, 26.0. HRMS (ESI) [M+Na]⁺: calculated for C₁₃H₁₃NO₃Na: 254.0793, found 254.0782.

2.4 Synthesis of *N*-vinylimide **5b**

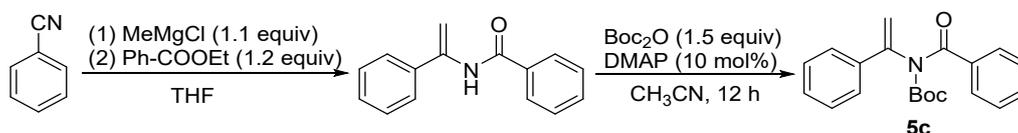


A mixture of acetophenone oxime (1.35 g, 10 mmol), isobutyric anhydride (3.16 g, 20 mmol), NaHSO₃ (3.12 g, 30 mmol) and CuI (0.19 g, 1 mmol) was stirred in 1,2-dichloroethane (100 mL) at 120 °C. After completion of the reaction (detected by TLC), the reaction mixture was cooled to room temperature, diluted with EtOAc, and washed with Na₂CO₃ and brine. The organic layers

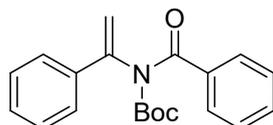
were dried over anhydrous Na_2SO_4 and evaporated *in vacuo*. The desired product was obtained after purification by flash chromatography on silica gel with hexane/ethyl acetate as the eluent. The procedure of *N*-Boc protection reaction for the preparation of **1e** was employed for the synthesis of **5b**.

***tert*-Butyl isobutyryl(1-phenylvinyl)carbamate (5b)**. Flash column chromatography to afford product as a pink oil. ^1H NMR (500 MHz, CDCl_3) δ 7.39-7.35 (m, 2H), 7.34-7.25 (m, 3H), 5.70 (s, 1H), 5.12 (s, 1H), 3.64 (hept, $J = 6.7$ Hz, 1H), 1.29 (s, 9H), 1.22 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 180.2, 152.3, 144.3, 137.1, 128.4, 128.3, 125.3, 113.1, 82.9, 34.7, 27.5, 19.6. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{Na}$: 312.1576, found 312.1577.

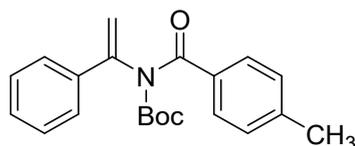
2.5 General procedure for the preparation of *N*-vinylimides **5c-5k**



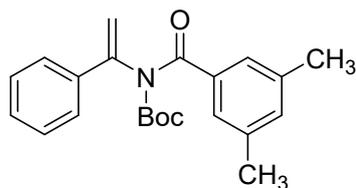
Benzonitrile (1.55 g, 15 mmol) and methyl magnesium chloride in THF (3.0 M, 5.5 mL, 16.5 mmol) were mixed, followed by heating to reflux for 30 min. After cooling to room temperature, the solution thus obtained was added to a solution of ethyl benzoate (2.7 g, 18 mmol) in THF (5.0 mL) at 0 °C. After 4 h, EtOAc (20 mL) and water (10 mL) were added. After vigorous stirring for 5 min, the mixture was filtered through celite pad. The solution were extracted with EtOAc (3 \times 20 mL), washed with brine, dried with anhydrous Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to give *N*-(1-phenylvinyl)benzamide. The procedure of *N*-Boc protection reaction for the preparation of **1e** was employed for the synthesis of **5c**.



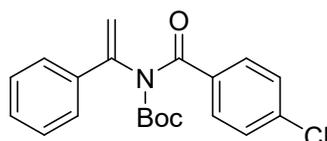
***tert*-Butyl benzoyl(1-phenylvinyl)carbamate (5c)**. Flash column chromatography to afford product as a yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, $J = 7.1$ Hz, 2H), 7.54 (d, $J = 7.7$ Hz, 2H), 7.49-7.43 (m, 1H), 7.42-7.36 (m, 2H), 7.35-7.30 (m, 2H), 7.30-7.25 (m, 1H), 5.68 (s, 1H), 5.24 (s, 1H), 1.14 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.2, 152.4, 144.8, 136.9, 136.0, 131.5, 128.3, 128.2, 128.0, 127.8, 125.4, 113.3, 82.9, 27.0. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{20}\text{H}_{21}\text{NO}_3\text{Na}$: 346.1419, found 346.1411.



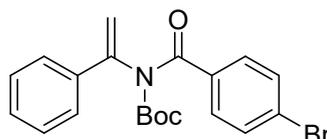
***tert*-Butyl (4-methylbenzoyl)(1-phenylvinyl)carbamate (5d)**. Flash column chromatography to afford product as a yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 7.67 (d, $J = 7.9$ Hz, 2H), 7.53 (d, $J = 7.4$ Hz, 2H), 7.37-7.24 (m, 3H), 7.20 (d, $J = 7.9$ Hz, 2H), 5.65 (s, 1H), 5.21 (s, 1H), 2.36 (s, 3H), 1.15 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.3, 152.6, 145.0, 142.3, 137.1, 133.1, 128.7, 128.3(1), 128.2(6), 128.2, 125.5, 113.0, 82.8, 27.1, 21.3. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{21}\text{H}_{23}\text{NO}_3\text{Na}$: 360.1576, found 360.1580.



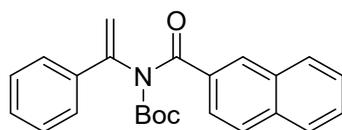
tert-Butyl (3,5-dimethylbenzoyl)(1-phenylvinyl)carbamate (5e). Flash column chromatography to afford product as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.56-7.51 (m, 2H), 7.39-7.29 (m, 5H), 7.16 (s, 1H), 5.71 (s, 1H), 5.26 (s, 1H), 2.35 (s, 6H), 1.15 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 173.0, 152.9, 145.1, 137.9, 137.2, 136.3, 133.5, 128.6, 128.5, 125.9, 125.8, 113.5, 83.1, 27.3, 21.2. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{22}\text{H}_{25}\text{NO}_3\text{Na}$: 374.1732, found 374.1739.



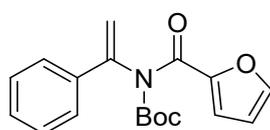
tert-Butyl (4-chlorobenzoyl)(1-phenylvinyl)carbamate (5f). Flash column chromatography to afford product as a pale yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 7.70 (d, $J = 8.5$ Hz, 2H), 7.53 (d, $J = 7.3$ Hz, 2H), 7.42 (d, $J = 8.5$ Hz, 2H), 7.39-7.29 (m, 3H), 5.71 (s, 1H), 5.24 (s, 1H), 1.19 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.4, 152.5, 144.8, 138.0, 137.0, 134.5, 129.5, 128.6, 128.5(0), 128.4(7), 125.6, 113.6, 83.5, 27.3. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{20}\text{H}_{20}\text{NO}_3\text{NaCl}$: 380.1029, found 380.1024.



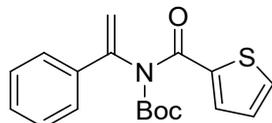
tert-Butyl (4-bromobenzoyl)(1-phenylvinyl)carbamate (5g). Flash column chromatography to afford product as a pale yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 7.59 (m, 4H), 7.55-7.47 (m, 2H), 7.41-7.29 (m, 3H), 5.71 (s, 1H), 5.23 (s, 1H), 1.18 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.7, 152.6, 144.9, 137.0, 135.0, 131.6, 129.7, 128.7, 128.6, 126.6, 125.7, 113.8, 83.7, 27.4. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{20}\text{H}_{20}\text{NO}_3\text{NaBr}$: 424.0524, found 424.0520.



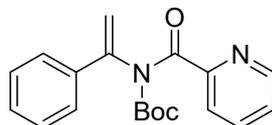
tert-Butyl (2-naphthoyl)(1-phenylvinyl)carbamate (5h). Flash column chromatography to afford product as a yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 8.34 (s, 1H), 7.94-7.84 (m, 4H), 7.66-7.61 (m, 2H), 7.59-7.52 (m, 2H), 7.43-7.38 (m, 2H), 7.37-7.32 (m, 1H), 5.76 (s, 1H), 5.35 (s, 1H), 1.15 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.5, 152.7, 145.0, 137.1, 134.7, 133.3, 132.3, 128.9, 128.8, 128.5, 128.4, 127.9, 127.8, 127.7, 126.7, 125.6, 124.4, 113.5, 83.2, 27.2. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{24}\text{H}_{23}\text{NO}_3\text{Na}$: 396.1576, found 396.1572.



tert-Butyl (furan-2-carbonyl)(1-phenylvinyl)carbamate (5i). Flash column chromatography to afford product as a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 7.59-7.49 (m, 3H), 7.40-7.29 (m, 3H), 7.20 (d, *J* = 3.5 Hz, 1H), 6.56-6.49 (m, 1H), 5.65 (s, 1H), 5.22 (s, 1H), 1.26 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 161.2, 152.1, 148.2, 145.1, 144.5, 137.0, 128.6, 128.5, 125.8, 118.1, 113.2, 112.2, 83.2, 27.4. HRMS (ESI) [M+Na]⁺: calculated for C₁₈H₁₉NO₄Na: 336.1212, found 336.1212.

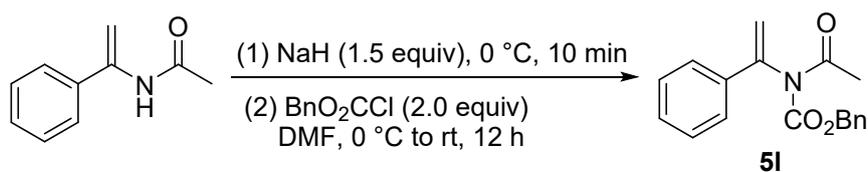


tert-Butyl (1-phenylvinyl)(thiophene-2-carbonyl)carbamate (5j). Flash column chromatography to afford product as a pale yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 7.68-7.65 (m, 1H), 7.60-7.53 (m, 3H), 7.40-7.30 (m, 3H), 7.08-7.03 (m, 1H), 5.63 (s, 1H), 5.23 (s, 1H), 1.25 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 165.4, 152.6, 145.2, 138.7, 137.2, 132.5, 132.4, 128.7, 128.6, 127.3, 125.9, 113.3, 83.3, 27.5. HRMS (ESI) [M+Na]⁺: calculated for C₁₈H₁₉NO₃NaS: 352.0983, found 352.0985.

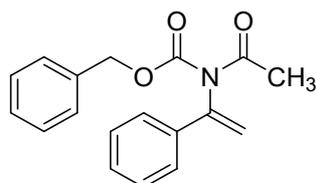


tert-Butyl (1-phenylvinyl)(picolinoyl)carbamate (5k). Flash column chromatography to afford product as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 8.64 (d, *J* = 4.7 Hz, 1H), 7.83 (d, *J* = 3.7 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.46-7.38 (m, 1H), 7.38-7.27 (m, 3H), 5.79 (s, 1H), 5.37 (s, 1H), 1.18 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 171.0, 153.4, 152.8, 148.3, 144.3, 136.9, 136.7, 128.6, 128.5, 125.7(8), 125.7(5), 123.5, 113.7, 83.2, 27.3. HRMS (ESI) [M+Na]⁺: calculated for C₁₉H₂₀N₂O₃Na: 347.1372, found 347.1374.

2.6 General procedure for the preparation of *N*-vinylimides **5l**, **11a**, and **11b**



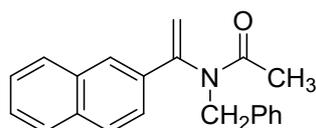
The *N*-(1-phenylvinyl)acetamide (322 mg, 2 mmol) was dissolved in 10 mL dry DMF in a dry two-necked round-bottom flask. The solution was cooled to 0 °C and sodium hydride (60% dispersion in mineral oil) (120 mg, 3 mmol) was added in portions. The resulting suspension was stirred at the same temperature for 10 min. Then benzyl chloroformate (738.5 mg, 4.3 mmol) was added dropwise and the resulting solution was continued to stir for overnight at room temperature. The completion of the reaction was confirmed by checking TLC and the excess of sodium hydride was quenched by adding water (10 mL) at 0 °C. The solution were extracted with EtOAc (3 × 10 mL), washed with brine, dried with anhydrous Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to give the pure product **5l**.



Benzyl acetyl(1-phenylvinyl)carbamate (5I). Flash column chromatography to afford product as a pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.48-7.30 (m, 5H), 7.30-7.22 (m, 3H), 7.13-7.01 (m, 2H), 5.89 (s, 1H), 5.25 (s, 1H), 5.15 (s, 2H), 2.64 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.3, 153.5, 142.9, 136.0, 134.9, 128.5(3), 128.5(1), 128.3, 128.1, 127.5, 125.0, 114.5, 68.3, 26.1. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{18}\text{H}_{17}\text{NO}_3\text{Na}$: 318.1106, found 318.1114.

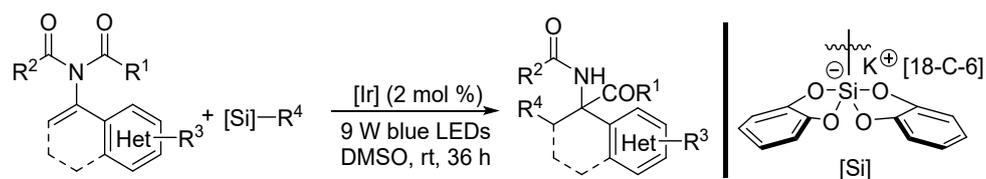


N-(1-([1,1'-Biphenyl]-4-yl)vinyl)-N-methylacetamide (11a). Flash column chromatography to afford product as a yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 7.68-7.56 (m, 4H), 7.53-7.42 (m, 4H), 7.42-7.33 (m, 1H), 5.75 (s, 1H), 5.26 (s, 1H), 3.13 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.0, 148.7, 142.0, 140.1, 134.3, 128.9, 127.7, 127.6, 127.0, 126.1, 112.3, 35.5, 21.8. This compound has been reported in the published literature.^[2a]



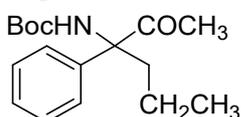
N-Benzyl-N-(1-(naphthalen-2-yl)vinyl)acetamide (11b). Flash column chromatography to afford product as a yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.92-7.80 (m, 3H), 7.77 (s, 1H), 7.61-7.46 (m, 3H), 7.38-7.18 (m, 5H), 5.77 (s, 1H), 5.00 (s, 1H), 4.77 (s, 2H), 2.15 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.9, 146.4, 137.6, 133.4, 133.2, 132.5, 129.0, 128.8, 128.4, 128.3, 127.6, 127.3, 126.8, 126.7, 124.9, 123.3, 115.0, 50.0, 22.0. This compound has been reported in the published literature.^[2b]

3. General procedure of photoredox-catalyzed acyl migration reactions and Giese-type reactions

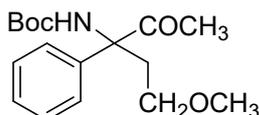


To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (4.5 mg, 0.004 mmol, 0.02 equiv), alkyl silicate (0.4 mmol, 2.0 equiv), *N*-vinylimide (0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with

nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 36 h (cooling with a fan). After the reaction was complete, the reaction solution was diluted with saturated Na₂CO₃ aqueous solution (10 mL), and was extracted with EtOAc (5 x 10 mL). The combined organic layer was washed with brine, dried over MgSO₄, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product.



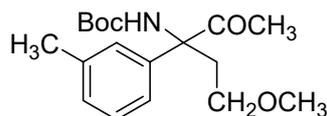
tert-Butyl (2-oxo-3-phenylhexan-3-yl)carbamate (3). Flash column chromatography to afford product as a pale yellow solid (54.1 mg, 93% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.38-7.30 (m, 4H), 7.28-7.22 (m, 1H), [6.35 (br, 0.75H), 6.28 (br, 0.25H)], [2.79 (m, 0.75H), 2.61-2.47 (m, 0.25)], 2.31-2.18 (m, 1H), 1.88 (s, 3H), [1.34 (s, 6.75H), 1.17-1.04 (s, 2.25H)], [1.34 (m, 1H), 0.97 (m, 1H)], 1.03-0.93 (m, 3H). ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 205.2, 153.5, 139.9, 128.7, 127.7, 126.1, 79.2, 69.4, 33.7, 28.3, 28.0, 23.5, 17.1, 14.3. HRMS (ESI) [M+Na]⁺: calculated for C₁₇H₂₅NO₃Na: 314.1732, found 314.1739. Single crystal of **3** was recrystallized from mixed solvents of ethanol and petroleum ether by slow evaporation at room temperature.



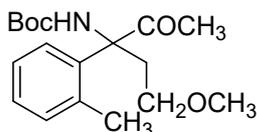
tert-Butyl (1-methoxy-4-oxo-3-phenylpentan-3-yl)carbamate (4a). Flash column chromatography to afford product as a white solid (59.6 mg, 97% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.44-7.30 (m, 4H), 7.30-7.21 (m, 1H), [6.61 (br, 0.75H), 6.50 (br, 0.25H)], 3.60-3.49 (m, 1H), 3.45-3.30 (m, 1H), 3.22 (s, 3H), [3.04-2.93 (m, 0.75H), 2.82-2.71 (m, 1.25H)], 1.93 (s, 3H), [1.35 (s, 6.75H), 1.07 (s, 2.25H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 204.3, 153.7, 140.0, 128.7, 127.7, 126.1, 79.2, 68.0, 67.6, 58.7, 32.3, 28.3, 27.9, 23.9. HRMS (ESI) [M+Na]⁺: calculated for C₁₇H₂₅NO₄Na: 330.1689, found 330.1689.



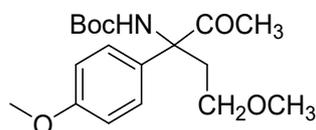
tert-Butyl (1-methoxy-4-oxo-3-(p-tolyl)pentan-3-yl)carbamate (4b). Flash column chromatography to afford product as a colorless oil (55.2 mg, 86% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.25-7.18 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), [6.57 (br, 0.80H), 6.46 (br, 0.20H)], 3.57-3.47 (m, 1H), 3.40-3.29 (m, 1H), 3.21 (s, 3H), [3.01-2.88 (m, 0.80H), 2.78-2.67 (m, 1.20H)], 2.30 (s, 3H), 1.92 (s, 3H), [1.35 (s, 7.20H), 1.08 (s, 1.80H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 204.4, 153.7, 137.3, 136.9, 129.5, 125.9, 79.1, 68.0, 67.3, 58.7, 32.3, 28.3, 27.9, 23.8, 20.9. HRMS (ESI) [M+Na]⁺: calculated for C₁₈H₂₇NO₄Na: 344.1838, found 344.1836.



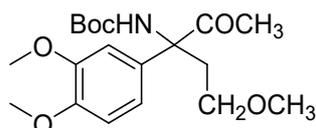
tert-Butyl (1-methoxy-4-oxo-3-(m-tolyl)pentan-3-yl)carbamate (4c). Flash column chromatography to afford product as a colorless oil (51.4 mg, 80% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.24-7.18 (m, 1H), 7.18-7.10 (m, 2H), 7.10-7.02 (m, 1H), [6.58 (br, 0.75H), 6.47 (br, 0.25H)], 3.58-3.47 (m, 1H), 3.41-3.30 (m, 1H), 3.21 (s, 3H), [3.00-2.90 (m, 0.75H), 2.79-2.67 (m, 1.25H)], 2.32 (s, 3H), 1.92 (s, 3H), [1.36 (s, 6.75H), 1.06 (s, 2.25H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 204.4, 153.7, 139.9, 138.2, 128.6, 128.5, 126.7, 123.2, 79.2, 68.0, 67.5, 58.7, 32.3, 28.3, 27.8, 23.8, 21.5. HRMS (ESI) [M+Na]⁺: calculated for C₁₈H₂₇NO₄Na: 344.1838, found 344.1831.



tert-Butyl (1-methoxy-4-oxo-3-(o-tolyl)pentan-3-yl)carbamate (4d). Flash column chromatography to afford product as a colorless oil (43.1 mg, 67% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.64-7.50 (m, 1H), 7.30-7.22 (m, 1H), 7.22-7.16 (m, 1H), 7.12-7.06 (m, 1H), [6.46 (br, 0.70H), 6.31 (br, 0.30H)], 3.57-3.47 (m, 1H), 3.41-3.27 (m, 1H), 3.22 (s, 3H), [3.16-3.07 (m, 0.70H), 2.82 (m, 0.30H)], 2.69-2.59 (m, 1H), 2.14 (s, 3H), 1.88 (s, 3H), [1.33 (s, 6.30H), 1.03 (s, 2.70H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 204.6, 152.9, 137.3, 136.4, 132.6, 127.9, 127.3, 126.5, 79.0, 67.6, 67.4, 58.6, 33.8, 28.3, 27.8, 24.4, 20.4. HRMS (ESI) [M+Na]⁺: calculated for C₁₈H₂₇NO₄Na: 344.1838, found 344.1835.

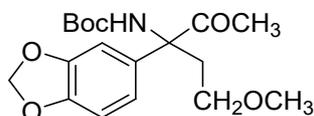


tert-Butyl (1-methoxy-3-(4-methoxyphenyl)-4-oxopentan-3-yl)carbamate (4e). Flash column chromatography to afford product as a yellow oil (49.2 mg, 73% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.30-7.21 (m, 2H), 6.89-6.81 (m, 2H), [6.57 (br, 0.75H), 6.45 (br, 0.25H)], 3.78 (s, 3H), 3.61-3.46 (m, 1H), 3.41-3.28 (m, 1H), 3.21 (s, 3H), [3.02-2.89 (m, 0.75H), 2.76-2.64 (m, 1.25H)], 1.92 (s, 3H), [1.35 (s, 6.75H), 1.10 (s, 2.25H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 204.5, 159.0, 153.7, 131.9, 127.3, 114.1, 79.1, 68.0, 67.0, 58.7, 55.1, 32.3, 28.3, 27.9, 23.8. HRMS (ESI) [M+Na]⁺: calculated for C₁₈H₂₇NO₅Na: 360.1787, found 360.1783.

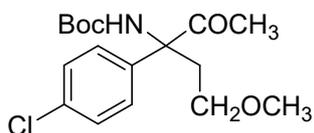


tert-Butyl (3-(3,4-dimethoxyphenyl)-1-methoxy-4-oxopentan-3-yl)carbamate (4f). Flash column chromatography to afford product as a yellow oil (48.5 mg, 66% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.01-6.90 (m, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 6.74 (d, *J* = 2.3 Hz, 1H), [6.57 (br, 0.75H), 6.45 (br, 0.25 H)], 3.84 (s, 3H), 3.81 (s, 3H), 3.56-3.47

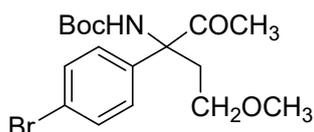
(m, 1H), 3.40-3.29 (m, 1H), 3.20 (s, 3H), [3.00-2.84 (m, 0.75H), 2.76-2.65 (m, 1.25H)], 1.93 (s, 3H), [1.35 (s, 6.75H), 1.10 (s, 2.25H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 204.4, 153.6, 149.1, 148.5, 132.5, 118.6, 111.1, 109.1, 79.2, 68.0, 67.2, 58.7, 55.8, 55.7, 32.4, 28.3, 27.9, 23.7. HRMS (ESI) [M+Na]⁺: calculated for C₁₉H₂₉NO₆Na: 390.1893, found 390.1884.



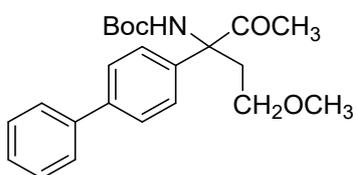
tert-Butyl (3-(benzo[d][1,3]dioxol-5-yl)-1-methoxy-4-oxopentan-3-yl)carbamate (4g). Flash column chromatography to afford product as a white solid (55.5 mg, 79% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 6.88-6.80 (m, 2H), 6.80-6.73 (m, 1H), [6.59 (br, 0.80H), 6.45 (br, 0.20H)], 6.00-5.90 (m, 2H), 3.59-3.46 (m, 1H), 3.41-3.28 (m, 1H), 3.21 (s, 3H), [2.97-2.86 (m, 0.80H), 2.74-2.59 (m, 1.20H)], 1.94 (s, 3H), [1.37 (s, 7.20H), 1.14 (s, 1.80H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 204.2, 153.6, 148.2, 147.1, 134.1, 119.7, 108.4, 106.7, 101.2, 79.3, 68.0, 67.1, 58.8, 32.4, 28.3, 28.0, 23.7. HRMS (ESI) [M+Na]⁺: calculated for C₁₈H₂₅NO₆Na: 374.1580, found 374.1588.



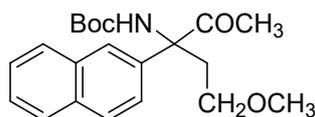
tert-Butyl (3-(4-chlorophenyl)-1-methoxy-4-oxopentan-3-yl)carbamate (4h). Flash column chromatography to afford product as a colorless oil (61.4 mg, 90% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.36-7.27 (m, 4H), [6.60 (br, 0.80H), 6.48 (br, 0.20H)], 3.57-3.49 (m, 1H), 3.40-3.30 (m, 1H), 3.20 (s, 3H), [2.93 (m, 0.80H), 2.77-2.64 (m, 1.20H)], 1.93 (s, 3H), [1.35 (s, 7.20H), 1.10 (s, 1.80H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 203.8, 153.6, 138.8, 133.7, 128.9, 127.6, 79.4, 67.8, 67.2, 58.8, 32.4, 28.3, 27.9, 23.9. HRMS (ESI) [M+Na]⁺: calculated for C₁₇H₂₄NO₄NaCl: 364.1292, found 364.1288.



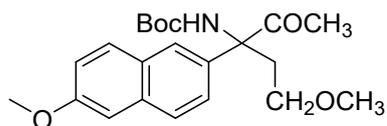
tert-Butyl (3-(4-bromophenyl)-1-methoxy-4-oxopentan-3-yl)carbamate (4i). Flash column chromatography to afford product as a colorless oil (65.5 mg, 85% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), [6.61 (br, 0.80H), 6.48 (br, 0.20H)], 3.57-3.49 (m, 1H), 3.40-3.31 (m, 1H), 3.21 (s, 3H), [2.98-2.88 (m, 0.80H), 2.75-2.66 (m, 1.20H)], 1.93 (s, 3H), [1.36 (s, 7.20H), 1.11 (s, 1.80H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 203.7, 153.6, 139.3, 131.9, 127.9, 122.0, 79.5, 67.8, 67.3, 58.8, 32.3, 28.3, 28.0, 23.9. HRMS (ESI) [M+Na]⁺: calculated for C₁₇H₂₄NO₄NaBr: 408.0786, found 408.0790.



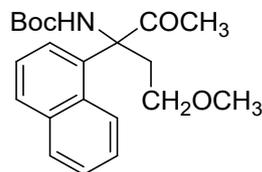
tert-Butyl (3-([1,1'-biphenyl]-4-yl)-1-methoxy-4-oxopentan-3-yl)carbamate (4j). Flash column chromatography to afford product as a white solid (62.8 mg, 82% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.63-7.55 (m, 4H), 7.47-7.38 (m, 4H), 7.38-7.30 (m, 1H), [6.66 (br, 0.75H), 6.54 (br, 0.25H)], 3.61-3.52 (m, 1H), 3.44-3.36 (m, 1H), 3.24 (s, 3H), [3.08-2.96 (m, 0.75H), 2.86-2.72 (m, 1.25H)], 1.99 (s, 3H), [1.38 (s, 6.75H), 1.10 (s, 2.25H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 204.2, 153.7, 140.4, 140.3, 139.0, 128.7, 127.4, 127.3, 127.0, 126.5, 79.3, 68.0, 67.5, 58.7, 32.4, 28.3, 27.9, 23.9. HRMS (ESI) [M+Na]⁺: calculated for C₂₃H₂₉NO₄Na: 406.1994, found 406.1987.



tert-Butyl (1-methoxy-3-(naphthalen-2-yl)-4-oxopentan-3-yl)carbamate (4k). Flash column chromatography to afford product as a white solid (60.0 mg, 84% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.98-7.86 (m, 1H), 7.86-7.78 (m, 3H), 7.56-7.44 (m, 2H), 7.44-7.34 (m, 1H), [6.74 (br, 0.75H), 6.63 (br, 0.25H)], 3.68-3.55 (m, 1H), 3.47-3.37 (m, 1H), 3.25 (s, 3H), [3.18-3.07 (m, 0.75H), 2.99-2.83 (m, 1.25H)], 1.95 (s, 3H), [1.36 (s, 6.75H), 0.98 (s, 2.25H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 204.4, 153.7, 137.4, 133.3, 132.7, 128.6, 128.3, 127.4, 126.2(5), 126.1(8), 125.5, 123.7, 79.3, 68.0, 67.7, 58.8, 32.3, 28.3, 27.8, 24.0. HRMS (ESI) [M+Na]⁺: calculated for C₂₁H₂₇NO₄Na: 380.1838, found 380.1840.

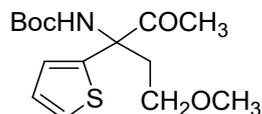


tert-Butyl (1-methoxy-3-(6-methoxynaphthalen-2-yl)-4-oxopentan-3-yl)carbamate (4l). Flash column chromatography to afford product as a white solid (58.8 mg, 76% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.86-7.76 (m, 1H), 7.76-7.66 (m, 2H), 7.39-7.31 (m, 1H), 7.20-7.07 (m, 2H), [6.68 (br, 0.75H), 6.57 (br, 0.25H)], 3.91 (s, 3H), 3.63-3.54 (m, 1H), 3.48-3.35 (m, 1H), 3.24 (s, 3H), [3.18-3.03 (m, 0.75H), 2.92-2.80 (m, 1.25H)], 1.94 (s, 3H), [1.35 (s, 6.75H), 0.99 (s, 2.25H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 204.5, 158.0, 153.7, 135.1, 133.9, 129.8, 128.8, 127.4, 125.3, 124.3, 119.1, 105.4, 79.2, 68.1, 67.6, 58.8, 55.3, 32.3, 28.3, 27.8, 23.9. HRMS (ESI) [M+Na]⁺: calculated for C₂₂H₂₉NO₅Na: 410.1943, found 410.1944.

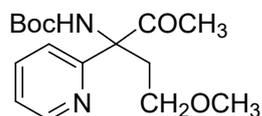


tert-Butyl (1-methoxy-3-(naphthalen-1-yl)-4-oxopentan-3-yl)carbamate (4m). Flash column chromatography to afford product as a yellow solid (55.7 mg, 78% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 8.00-7.73 (m, 4H), 7.57-7.36 (m, 3H), [6.74 (br, 0.66H), 6.59 (br, 0.34H)], 3.68-3.53 (m, 1H), 3.49-3.39 (m, 1H), 3.26 (s, 3H), [3.29 (m, 0.66), 2.94 (m, 0.34)], 2.74 (m, 1H), 1.82 (s, 3H), [1.19 (s, 6H), 0.79 (s, 3H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 206.3, 172.7, 153.0, 134.8, 134.4, 130.8, 129.3, 129.2, 126.2, 125.9, 125.3, 125.2, 124.0, 79.0, 67.6, 58.6, 34.3, 28.1, 27.6, 27.5, 24.6. HRMS (ESI)

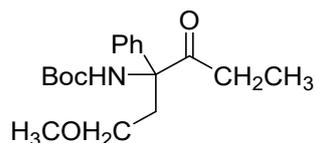
[M+Na]⁺: calculated for C₂₁H₂₇NO₄Na: 380.1838, found 380.1840. Single crystal of **4m** was recrystallized from mixed solvents of ethanol and petroleum ether by slow evaporation at room temperature.



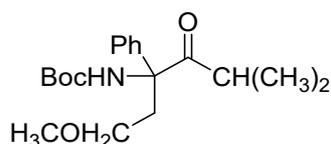
tert-Butyl (1-methoxy-4-oxo-3-(thiophen-2-yl)pentan-3-yl)carbamate (4n). Flash column chromatography to afford product as a pale yellow oil (51.4 mg, 82% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.27-7.21 (m, 1H), 7.05-6.93 (m, 2H), [6.63 (br, 0.80H), 6.51 (br, 0.20H)], 3.56-3.44 (m, 1H), 3.39-3.29 (m, 1H), 3.21 (s, 3H), [3.01-2.91 (m, 0.80H), 2.77-2.65 (m, 1.20H)], 2.07 (s, 3H), [1.39 (s, 7.20H), 1.19 (s, 1.80H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 203.0, 153.7, 145.3, 127.1, 125.4, 125.1, 79.5, 67.8, 66.1, 58.7, 34.4, 28.3, 28.0, 23.4. HRMS (ESI) [M+Na]⁺: calculated for C₁₅H₂₃NO₄NaS: 336.1245, found 336.1242.



tert-Butyl (1-methoxy-4-oxo-3-(pyridin-2-yl)pentan-3-yl)carbamate (4o). Flash column chromatography to afford product as a yellow solid (43.8 mg, 71% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 8.57 (d, *J* = 4.8 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.26-7.20 (m, 1H), [7.29 (br, 0.80H), 7.16-7.10 (br, 0.20H)], 3.34-3.24 (m, 1H), 3.24-3.16 (m, 1H), 3.12 (s, 3H), 2.95-2.83 (m, 1H), 2.73-2.59 (m, 1H), 1.96 (s, 3H), [1.45 (s, 7.20H), 1.31 (s, 1.80H)]. ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 205.4, 156.2, 154.3, 148.4, 137.1, 122.8, 120.9, 79.7, 69.3, 68.2, 58.4, 33.5, 28.4, 28.1, 24.1. HRMS (ESI) [M+Na]⁺: calculated for C₁₆H₂₄N₂O₄Na: 331.1634, found 331.1631.

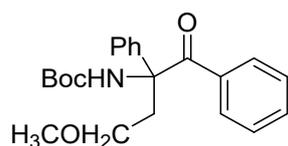


tert-Butyl (1-methoxy-4-oxo-3-phenylhexan-3-yl)carbamate (6a). Flash column chromatography to afford product as a colorless oil (57.8 mg, 90% yield). ¹H NMR (500 MHz, CDCl₃, observed as a mixture of rotamers) δ 7.37-7.28 (m, 4H), 7.28-7.20 (m, 1H), [6.65 (br, 0.70H), 6.57 (br, 0.30H)], 3.58-3.47 (m, 1H), 3.39-3.28 (m, 1H), 3.19 (s, 3H), [3.02-2.94 (m, 0.70H), 2.81-2.70 (m, 1.30H)], 2.50-2.36 (m, 1H), 2.08-1.94 (m, 1H), [1.34 (s, 6.30H), 1.05 (s, 2.70H)], 0.82 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃, observed as a mixture of rotamers) δ 207.4, 153.6, 140.2, 128.6, 127.5, 126.1, 79.1, 67.9, 67.3, 58.7, 32.4, 29.0, 28.3, 27.8, 8.4. HRMS (ESI) [M+Na]⁺: calculated for C₁₈H₂₇NO₄Na: 344.1838, found 344.1833.

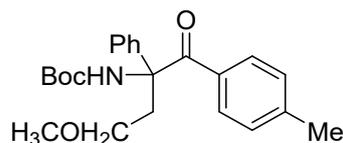


tert-Butyl (1-methoxy-5-methyl-4-oxo-3-phenylhexan-3-yl)carbamate (6b). Flash column

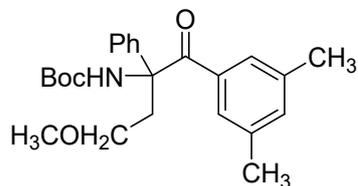
chromatography to afford product as a colorless oil (48.9 mg, 73% yield). ^1H NMR (500 MHz, CDCl_3 , observed as a mixture of rotamers) δ 7.40-7.33 (m, 2H), 7.33-7.29 (m, 2H), 7.27-7.21 (m, 1H), [6.61 (br, 0.70H), 6.51 (br, 0.30H)], 3.55-3.40 (m, 1H), 3.31-3.25 (m, 1H), 3.22 (s, 3H), [3.09-3.01 (m, 0.70H), 2.89-2.77 (m, 1.30H)], 2.77-2.67 (m, 1H), [1.35 (s, 6.30H), 1.05 (s, 2.70H)], 0.97 (d, $J = 6.7$ Hz, 3H), 0.42 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3 , observed as a mixture of rotamers) δ 211.4, 153.6, 139.5, 128.6, 127.7, 126.4, 79.1, 68.0, 67.7, 58.6, 34.1, 32.0, 28.3, 27.8, 21.7, 19.9. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{19}\text{H}_{29}\text{NO}_4\text{Na}$: 358.1994, found 358.1996.



tert-Butyl (4-methoxy-1-oxo-1,2-diphenylbutan-2-yl)carbamate (6c). Flash column chromatography to afford product as a white solid (51.7 mg, 70% yield). ^1H NMR (500 MHz, CDCl_3 , observed as a mixture of rotamers) δ 7.55-7.41 (m, 4H), 7.41-7.33 (m, 3H), 7.33-7.27 (m, 1H), 7.25-7.15 (m, 2H), 6.69 (br, 1H), 3.51-3.40 (m, 1H), 3.37-3.26 (m, 1H), [3.22-3.13 (m, 0.70H), 2.94 (m, 0.30H)], 3.11 (s, 3H), 2.82-2.70 (m, 1H), [1.30 (s, 6.30H), 1.13 (s, 2.70H)]. ^{13}C NMR (126 MHz, CDCl_3 , observed as a mixture of rotamers) δ 198.3, 153.6i, 139.6, 135.7, 131.7, 129.4, 128.8, 127.9, 127.8, 126.5, 79.3, 68.3, 67.0, 58.4, 33.6, 28.2. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{22}\text{H}_{27}\text{NO}_4\text{Na}$: 392.1838, found 392.1836.

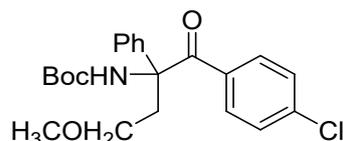


tert-Butyl (4-methoxy-1-oxo-2-phenyl-1-(p-tolyl)butan-2-yl)carbamate (6d). Flash column chromatography to afford product as a colorless oil (46.0 mg, 60% yield). ^1H NMR (500 MHz, CDCl_3 , observed as a mixture of rotamers) δ 7.49-7.38 (m, 4H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.31-7.25 (m, 1H), 7.01 (d, $J = 7.9$ Hz, 2H), 6.76 (br, 1H), 3.51-3.41 (m, 1H), 3.34-3.27 (m, 1H), [3.27-3.16 (m, .75H), 3.00 - 2.86 (m, 0.25H)], 3.11 (s, 3H), 2.83-2.69 (m, 1H), 2.27 (s, 3H), [1.31 (s, 6.75H), 1.15 (s, 2.25H)]. ^{13}C NMR (126 MHz, CDCl_3 , observed as a mixture of rotamers) δ 197.5, 153.5, 142.5, 140.1, 132.7, 129.6, 128.7, 128.6, 127.7, 126.6, 79.2, 68.3, 66.7, 58.4, 33.4, 28.2, 21.4. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{23}\text{H}_{29}\text{NO}_4\text{Na}$: 406.1994, found 406.1995.

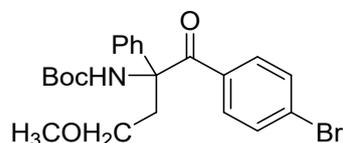


tert-Butyl (1-(3,5-dimethylphenyl)-4-methoxy-1-oxo-2-phenylbutan-2-yl)carbamate (6e). Flash column chromatography to afford product as a white solid (63.4 mg, 81% yield). ^1H NMR (500 MHz, CDCl_3 , observed as a mixture of rotamers) δ 7.48-7.42 (m, 2H), 7.39-7.33 (m, 2H), 7.32-7.27 (m, 1H), 7.07-7.01 (m, 2H), 6.99 (s, 1H), 6.75 (br, 1H), 3.50-3.41 (m, 1H), 3.36-3.26 (m, 1H), [3.26-3.18 (m, 0.80H), 3.05-2.88 (m, 0.20)] 3.13 (s, 3H), 2.81-2.70 (m, 1H), 2.17 (s, 6H), [1.37-1.27 (s, 7.20H), 1.21-1.06 (s, 1.80H)]. ^{13}C NMR (126 MHz, CDCl_3 , observed as a mixture of rotamers) δ 198.5, 153.5, 140.0, 137.3, 135.5, 133.4, 128.6, 127.8, 127.2, 126.7, 79.1, 68.3, 66.9,

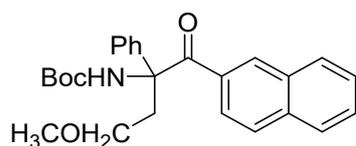
58.4, 33.3, 28.2, 21.1. HRMS (ESI) $[M+Na]^+$: calculated for $C_{24}H_{31}NO_4Na$: 420.2151, found 420.2156.



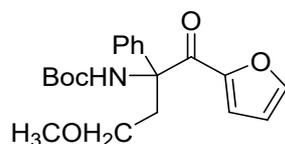
tert-Butyl (1-(4-chlorophenyl)-4-methoxy-1-oxo-2-phenylbutan-2-yl)carbamate (6f). Flash column chromatography to afford product as a colorless oil (57.2 mg, 71% yield). 1H NMR (500 MHz, $CDCl_3$, observed as a mixture of rotamers) δ 7.49-7.39 (m, 4H), 7.37 (t, $J = 7.6$ Hz, 2H), 7.33-7.28 (m, 1H), 7.18 (d, $J = 8.3$ Hz, 2H), 6.63 (br, 1H), 3.48-3.42 (m, 1H), 3.34-3.26 (m, 1H), 3.11 (s, 3H), [3.10-3.00 (m, 0.75H), 2.97-2.81 (m, 0.25)], 2.78-2.66 (m, 1H), [1.30 (s, 6.75H), 1.15 (s, 2.25H)]. ^{13}C NMR (126 MHz, $CDCl_3$, observed as a mixture of rotamers) δ 196.9, 153.8, 139.2, 137.9, 134.2, 130.8, 128.9, 128.1, 128.0, 126.4, 79.5, 68.3, 67.1, 58.4, 34.0, 28.2. HRMS (ESI) $[M+Na]^+$: calculated for $C_{22}H_{26}NO_4NaCl$: 426.1448, found 426.1450.



tert-Butyl (1-(4-bromophenyl)-4-methoxy-1-oxo-2-phenylbutan-2-yl)carbamate (6g). Flash column chromatography to afford product as a colorless oil (52.7 mg, 59% yield). 1H NMR (500 MHz, $CDCl_3$, observed as a mixture of rotamers) δ 7.47-7.42 (m, 3H), 7.40-7.33 (m, 3H), 7.33-7.27 (m, 1H), 7.25-7.17 (m, 2H), 6.69 (br, 1H), 3.52-3.37 (m, 1H), 3.36-3.27 (m, 1H), 3.24-3.13 (m, 1H), 3.11 (s, 3H), 2.81-2.70 (m, 1H), [1.30 (s, 6.30H), 1.14 (s, 2.70H)]. ^{13}C NMR (126 MHz, $CDCl_3$, observed as a mixture of rotamers) δ 198.3, 153.6, 139.6, 135.7, 131.7, 129.4, 128.8, 127.9, 127.8, 126.6, 79.3, 68.3, 67.0, 58.4, 33.6, 28.2. HRMS (ESI) $[M+Na]^+$: calculated for $C_{22}H_{26}NO_4NaBr$: 470.0943, found 470.0938.

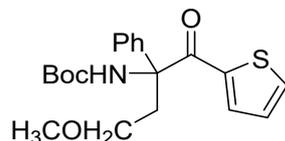


tert-Butyl (4-methoxy-1-(naphthalen-2-yl)-1-oxo-2-phenylbutan-2-yl)carbamate (6h). Flash column chromatography to afford product as a yellow solid (52.8 mg, 63% yield). 1H NMR (500 MHz, $CDCl_3$, observed as a mixture of rotamers) δ 7.92 (s, 1H), 7.81-7.72 (m, 1H), 7.72-7.60 (m, 3H), 7.57-7.47 (m, 3H), 7.47-7.37 (m, 3H), 7.37-7.30 (m, 1H), 6.82 (br, 1H), 3.52-3.44 (m, 1H), 3.42-3.32 (m, 1H), 3.31-3.16 (m, 1H), 3.11 (s, 3H), 2.92-2.82 (m, 1H), [1.38-1.27 (s, 7H), 1.22-1.10 (s, 2H)]. ^{13}C NMR (126 MHz, $CDCl_3$, observed as a mixture of rotamers) δ 198.0, 153.7, 140.0, 134.6, 132.9, 132.0, 130.7, 129.4, 128.8, 128.1, 127.9, 127.6, 127.4, 126.7, 126.4, 125.7, 79.3, 68.3, 67.1, 58.4, 33.7, 28.2. HRMS (ESI) $[M+Na]^+$: calculated for $C_{26}H_{29}NO_4Na$: 442.1994, found 442.1992.

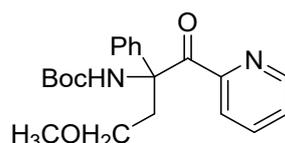


tert-Butyl (1-(furan-2-yl)-4-methoxy-1-oxo-2-phenylbutan-2-yl)carbamate (6i). Flash column

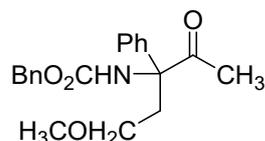
chromatography to afford product as a yellow oil (44.5 mg, 62% yield). ^1H NMR (500 MHz, CDCl_3 , observed as a mixture of rotamers) δ 7.52-7.40 (m, 2H), 7.38 (s, 1H), 7.35-7.27 (m, 2H), 7.25-7.17 (m, 1H), 6.80 (d, $J = 61.7$ Hz, 2H), 6.31 (br, 1H), 3.55-3.45 (m, 1H), 3.42-3.30 (m, 1H), 3.29-3.17 (m, 1H), 3.12 (s, 3H), 3.08-2.99 (m, 1H), [1.32 (s, 7H), 1.11 (s, 2H)]. ^{13}C NMR (126 MHz, CDCl_3 , observed as a mixture of rotamers) δ 185.7, 153.5, 150.1, 145.7, 140.0, 128.3, 127.5, 126.7, 119.2, 111.7, 79.2, 68.2, 66.0, 58.5, 33.1, 28.2. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{20}\text{H}_{25}\text{NO}_5\text{Na}$: 382.1630, found 382.1633.



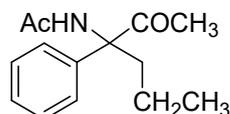
tert-Butyl (4-methoxy-1-oxo-2-phenyl-1-(thiophen-2-yl)butan-2-yl)carbamate (6j). Flash column chromatography to afford product as a yellow solid (48.8 mg, 65% yield). ^1H NMR (500 MHz, CDCl_3 , observed as a mixture of rotamers) δ 7.50-7.41 (m, 3H), 7.38-7.33 (m, 2H), 7.32-7.22 (m, 2H), 6.88 (s, 1H), [6.69 (m, 0.70H), 6.69 (m, 0.30H)], 3.53-3.42 (m, 1H), 3.40-3.25 (m, 1H), 3.22-3.15 (m, 1H), 3.14 (s, 3H), 2.90-2.75 (m, 1H), [1.33 (s, 6.30H), 1.12 (s, 2.70H)]. ^{13}C NMR (126 MHz, CDCl_3 , observed as a mixture of rotamers) δ 190.4, 153.6, 140.1, 139.9, 133.4, 132.9, 128.6, 127.9, 127.4, 126.9, 79.4, 68.3, 66.8, 58.5, 34.1, 28.2, 27.8. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{20}\text{H}_{25}\text{NO}_4\text{NaS}$: 398.1402, found 398.1406.



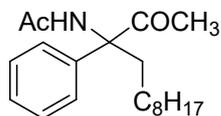
tert-Butyl (4-methoxy-1-oxo-2-phenyl-1-(pyridin-2-yl)butan-2-yl)carbamate (6k). Flash column chromatography to afford product as a yellow oil (30.4 mg, 41% yield). ^1H NMR (500 MHz, CDCl_3) δ 8.49-8.42 (m, 1H), 7.98 (d, $J = 7.9$ Hz, 1H), 7.76-7.69 (m, 1H), 7.56-7.49 (m, 2H), 7.33-7.25 (m, 3H), 7.23-7.16 (m, 1H), 7.08 (br, 1H), 3.97-3.84 (m, 1H), 3.62-3.47 (m, 2H), 3.10 (s, 3H), 3.09-3.01 (m, 1H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 196.0, 154.1, 152.7, 147.5, 140.8, 136.4, 127.8, 127.0, 126.9, 125.9, 124.2, 79.3, 68.7, 67.4, 58.3, 34.2, 28.1. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_4\text{Na}$: 393.1790, found 393.1783.



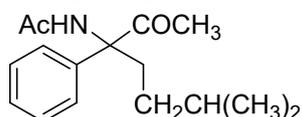
Benzyl (1-methoxy-4-oxo-3-phenylpentan-3-yl)carbamate (6l). Flash column chromatography to afford product as a yellow oil (53.2 mg, 78% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.41-7.26 (m, 10H), 6.94 (br, 1H), 5.00 (q, 2H), 3.60-3.47 (m, 1H), 3.40-3.30 (m, 1H), 3.20 (s, 3H), 3.11-3.01 (m, 1H), 2.86-2.71 (m, 1H), 1.94 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 204.0, 154.0, 139.7, 136.5, 128.9, 128.4, 128.0, 128.0, 127.9, 126.2, 67.8, 67.6, 66.3, 58.7, 32.1, 24.0. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{20}\text{H}_{23}\text{NO}_4\text{Na}$: 364.1525, found 364.1531.



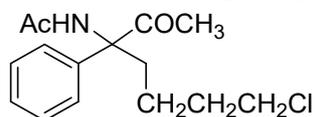
***N*-(2-Oxo-3-phenylhexan-3-yl)acetamide (8a)**. Flash column chromatography to afford product as a white solid (39.2 mg, 84% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.27-7.22 (m, 5H), 7.21-7.16 (m, 1H), 3.00-2.87 (m, 1H), 2.23-2.09 (m, 1H), 1.89 (s, 3H), 1.82 (s, 3H), 1.30-1.15 (m, 1H), 0.95-0.83 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 205.5, 168.2, 139.5, 128.8, 127.8, 126.1, 69.9, 32.9, 23.8, 23.4, 17.2, 14.2. HRMS (ESI) [M+Na]⁺: calculated for C₁₄H₁₉NO₂Na: 256.1313, found 256.1311.



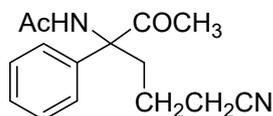
***N*-(2-Oxo-3-phenyl-dodecan-3-yl)acetamide (8b)**. Flash column chromatography to afford product as a white solid (43.8 mg, 69% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.32 (m, 4H), 7.30 (br, 1H), 7.29-7.25 (m, 1H), 3.10-2.97 (m, 1H), 2.32-2.21 (m, 1H), 1.98 (s, 3H), 1.91 (s, 3H), 1.37-1.22 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 205.6, 168.2, 139.5, 128.8, 127.8, 126.2, 69.9, 31.8, 30.7, 29.7, 29.5, 29.2, 23.8(9), 23.8(6), 23.4, 22.6, 14.1. HRMS (ESI) [M+H]⁺: calculated for C₂₀H₃₁NO₂: 340.2252, found 340.2256.



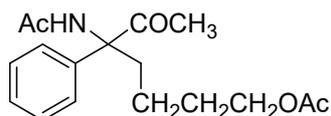
***N*-(6-Methyl-2-oxo-3-phenylheptan-3-yl)acetamide (8c)**. Flash column chromatography to afford product as a white solid (38.1 mg, 73% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.38-7.33 (m, 4H), 7.30 (br, 1H), 7.29-7.24 (m, 1H), 3.07-2.96 (m, 1H), 2.36-2.20 (m, 1H), 1.96 (s, 3H), 1.90 (s, 3H), 1.69-1.51 (m, 1H), 1.24-1.13 (m, 1H), 0.96-0.87 (m, 6H), 0.82-0.70 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 205.4, 168.1, 139.4, 128.7, 127.8, 126.1, 69.8, 32.7, 28.5, 28.0, 23.8, 23.3, 22.6, 22.4. HRMS (ESI) [M+H]⁺: calculated for C₁₆H₂₄NO₂: 262.1807, found 262.1806.



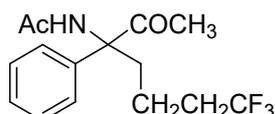
***N*-(7-Chloro-2-oxo-3-phenylheptan-3-yl)acetamide (8d)**. Flash column chromatography to afford product as a yellow solid (46.7 mg, 83% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.32 (m, 4H), 7.32-7.25 (m, 2H), 3.63-3.49 (m, 2H), 3.10-2.99 (m, 1H), 2.39-2.27 (m, 1H), 1.99 (s, 3H), 1.93 (s, 3H), 1.92-1.77 (m, 2H), 1.49-1.36 (m, 1H), 1.21-1.08 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 205.2, 168.4, 139.1, 128.9, 128.0, 126.0, 69.7, 44.5, 32.2, 29.8, 23.8, 23.3, 21.0. HRMS (ESI) [M+H]⁺: calculated for C₁₅H₂₁NO₂Cl: 282.1261, found 282.1252.



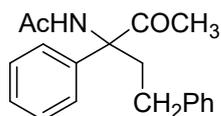
***N*-(6-Cyano-2-oxo-3-phenylhexan-3-yl)acetamide (8e)**. Flash column chromatography to afford product as a yellow oil (27.9 mg, 54% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.44-7.28 (m, 5H), 7.27 (br, 1H), 3.21-3.10 (m, 1H), 2.57-2.43 (m, 2H), 2.42-2.33 (m, 1H), 2.01 (s, 3H), 1.98 (s, 3H), 1.74-1.63 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 204.8, 168.6, 138.5, 129.1, 128.3, 125.9, 119.2, 69.4, 30.2, 23.8, 23.4, 20.5, 17.3. HRMS (ESI) [M+Na]⁺: calculated for C₁₅H₁₈N₂O₂Na: 281.1266, found 281.1263.



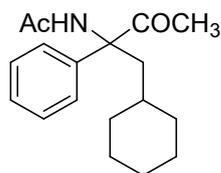
5-Acetamido-6-oxo-5-phenylheptyl acetate (8f). Flash column chromatography to afford product as a yellow solid (47.6 mg, 78% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.31 (m, 4H), 7.29 (br, 1H), 7.28-7.24 (m, 1H), 4.12-3.98 (m, 2H), 3.11-2.96 (m, 1H), 2.39-2.21 (m, 1H), 2.02 (s, 3H), 1.97 (s, 3H), 1.90 (s, 3H), 1.76-1.61 (m, 2H), 1.41-1.25 (m, 1H), 1.09-0.87 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 205.2, 171.0, 168.3, 139.1, 128.8, 127.9, 126.0, 69.7, 63.9, 30.4, 28.5, 23.8, 23.3, 20.9, 20.3. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{17}\text{H}_{24}\text{NO}_4$: 306.1705, found 306.1702.



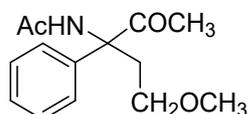
N-(7,7,7-Trifluoro-2-oxo-3-phenylheptan-3-yl)acetamide (8g). Flash column chromatography to afford product as a yellow solid (39.2 mg, 65% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.40-7.26 (m, 6H), 3.14-3.03 (m, 1H), 2.44-2.33 (m, 1H), 2.25-2.07 (m, 2H), 1.99 (s, 3H), 1.93 (s, 3H), 1.61-1.47 (m, 1H), 1.24-1.16 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 204.8, 168.6, 138.7, 129.0, 128.1, 127.9, 125.9, 125.7, 69.6, 33.6 (q, $J = 28.7$ Hz), 29.9, 23.5 (d, $J = 60.9$ Hz), 16.7 (q, $J = 3.0$ Hz). ^{19}F NMR (471 MHz, CDCl_3) δ -66.2. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{F}_3$: 302.1368, found 302.1363.



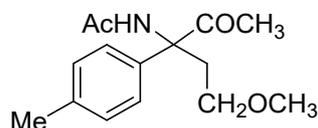
N-(4-Oxo-1,3-diphenylpentan-3-yl)acetamide (8h). Flash column chromatography to afford product as a yellow oil (39.6 mg, 67% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.41-7.26 (m, 8H), 7.24-7.15 (m, 3H), 3.48-3.37 (m, 1H), 2.73-2.54 (m, 2H), 2.34-2.22 (m, 1H), 1.98 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 205.2, 168.4, 140.9, 139.1, 128.9, 128.5, 128.4, 128.0, 126.2, 126.1, 69.8, 32.8, 30.4, 23.8, 23.4. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{19}\text{H}_{21}\text{NO}_2\text{Na}$: 318.1470, found 318.1469.



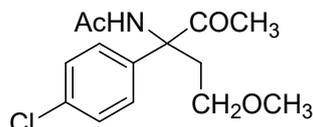
N-(1-Cyclohexyl-3-oxo-2-phenylbutan-2-yl)acetamide (8i). Flash column chromatography to afford product as a yellow solid (43.1 mg, 75% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.43 (br, 1H), 7.36-7.30 (m, 4H), 7.28-7.22 (m, 1H), 3.07-2.98 (m, 1H), 2.25-2.17 (m, 1H), 1.98 (s, 3H), 1.92 (s, 3H), 1.74-1.57 (m, 4H), 1.57-1.50 (m, 1H), 1.26-0.95 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 206.2, 168.2, 140.2, 128.8, 127.7, 126.0, 69.3, 38.2, 34.4, 33.9(2), 33.8(5), 26.2(9), 26.2(6), 26.1, 23.9(4), 23.8(5). HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{18}\text{H}_{26}\text{NO}_2$: 288.1964, found 288.1960.



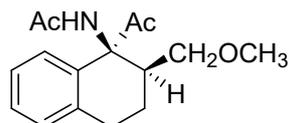
***N*-(1-Methoxy-4-oxo-3-phenylpentan-3-yl)acetamide (8j).** Flash column chromatography to afford product as a yellow oil (44.3 mg, 89% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.50 (br, 1H), 7.34 (m, 4H), 7.29-7.24 (m, 1H), 3.57-3.48 (m, 1H), 3.34-3.26 (m, 1H), 3.21 (s, 3H), 3.20-3.14 (m, 1H), 2.80-2.71 (m, 1H), 2.01 (s, 3H), 1.94 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 204.7, 168.5, 139.4, 128.8, 127.8, 126.1, 68.0(2), 68.0(1), 58.8, 31.7, 23.8(4), 23.8(2). HRMS (ESI) [M+Na]⁺: calculated for C₁₄H₁₉NO₃Na: 272.1263, found 272.1261.



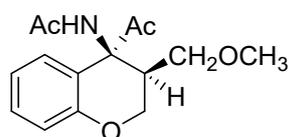
***N*-(1-Methoxy-4-oxo-3-(*p*-tolyl)pentan-3-yl)acetamide (8k).** Flash column chromatography to afford product as a pale yellow solid (42.6 mg, 81% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.48 (br, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 3.56-3.47 (m, 1H), 3.33-3.25 (m, 1H), 3.21 (s, 3H), 3.19-3.12 (m, 1H), 2.79-2.68 (m, 1H), 2.30 (s, 3H), 2.00 (s, 3H), 1.94 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 204.9, 168.5, 137.5, 136.4, 129.5, 125.9, 68.0, 67.8, 58.8, 31.7, 23.9, 23.8, 21.0. HRMS (ESI) [M+Na]⁺: calculated for C₁₅H₂₁NO₃Na: 286.1419, found 286.1417.



***N*-(3-(4-Chlorophenyl)-1-methoxy-4-oxopentan-3-yl)acetamide (8l).** Flash column chromatography to afford product as a yellow solid (54.3 mg, 96% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.51 (br, 1H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 3.57-3.48 (m, 1H), 3.32-3.24 (m, 1H), 3.21 (s, 3H), 3.17-3.08 (m, 1H), 2.77-2.67 (m, 1H), 2.01 (s, 3H), 1.94 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 204.3, 168.5, 138.1, 133.9, 129.0, 127.6, 67.8, 67.6, 58.8, 31.7, 23.9. HRMS (ESI) [M+H]⁺: calculated for C₁₄H₁₉NO₃Cl: 284.1053, found 284.1056.

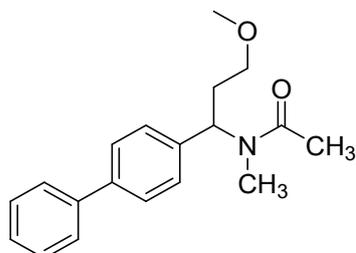


***N*-((1*S*^{*},2*S*^{*})-1-Acetyl-2-(methoxymethyl)-1,2,3,4-tetrahydronaphthalen-1-yl)acetamide ((+/-)-10a).** Flash column chromatography to afford product as a yellow oil (23.1 mg, 42% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.43 (br, 1H), 7.21-7.14 (m, 2H), 7.14-7.04 (m, 1H), 6.90 (d, *J* = 7.3 Hz, 1H), 3.35 (d, *J* = 7.0 Hz, 2H), 3.26 (s, 3H), 3.09-2.95 (m, 1H), 2.91-2.80 (m, 1H), 2.57-2.44 (m, 1H), 2.33-2.20 (m, 1H), 1.98 (s, 3H), 1.93 (s, 3H), 1.84-1.76 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 205.3, 168.9, 137.8, 133.7, 129.3, 127.7, 126.4(3), 126.3(5), 74.1, 67.5, 58.8, 41.9, 29.4, 24.9, 24.0, 22.1. HRMS (ESI) [M+Na]⁺: calculated for C₁₆H₂₁NO₃Na: 298.1419, found 298.1420.

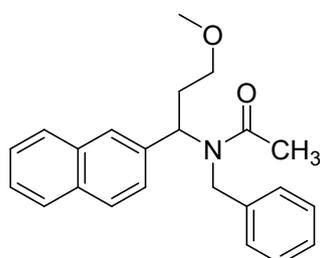


***N*-((3*S*^{*},4*S*^{*})-4-Acetyl-3-(methoxymethyl)chroman-4-yl)acetamide ((+/-)-10b).** Flash column

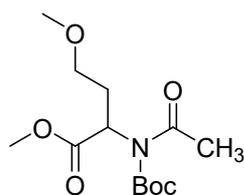
chromatography to afford product as a pale yellow solid (28.2 mg, 51% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.34 (br, 1H), 7.23-7.15 (m, 1H), 6.98-6.79 (m, 3H), 4.54 (t, $J = 10.2$ Hz, 1H), 4.28-4.19 (m, 1H), 3.41-3.29 (m, 2H), 3.28 (s, 3H), 2.96-2.86 (m, 1H), 2.00 (d, $J = 3.5$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 204.5, 169.5, 155.4, 129.8, 126.9, 121.2, 120.1, 117.6, 70.1, 65.1, 64.1, 59.0, 40.6, 24.6, 23.7. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{15}\text{H}_{19}\text{NO}_4\text{Na}$: 300.1212, found 300.1215. Single crystal of (+/-)-**10b** was recrystallized from mixed solvents of ethanol and petroleum ether by slow evaporation at room temperature.



***N*-(1-([1,1'-Biphenyl]-4-yl)-3-methoxypropyl)-*N*-methylacetamide (12a).** Flash column chromatography to afford product as a yellow oil (48.7 mg, 82% yield). ^1H NMR (500 MHz, CDCl_3 , observed as a mixture of rotamers) δ 7.62-7.52 (m, 4H), 7.49-7.39 (m, 2H), 7.39-7.28 (m, 3H), [6.09-6.01 (m, 0.5H), 5.26-5.20 (m, 0.5H)], 3.56 – 3.38 (m, 2H), [3.37 (s, 1.5H), 3.35 (s, 1.5H)], [2.71 (s, 1.5H), 2.68 (s, 1.5H)], [2.43-2.34 (m, 0.5H), 2.30-2.23 (m, 0.5H)], [2.32 (s, 1.5H), 2.14 (s, 1.5H)], [2.23-2.15 (m, 0.5H), 2.13-2.06 (m, 0.5H)]. ^{13}C NMR (126 MHz, CDCl_3 , observed as a mixture of rotamers) δ 171.5, 171.0, 140.5(0), 140.4(9), 140.3, 140.2, 138.6, 138.3, 128.8, 128.7, 128.0, 127.4, 127.3(4), 127.2(8), 127.2, 127.1, 126.9, 70.1, 68.3, 58.8, 58.6, 56.4, 51.9, 30.6, 30.4, 29.6, 27.6, 22.2, 21.4. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{19}\text{H}_{23}\text{NO}_2\text{Na}$: 320.1626, found 320.1629.

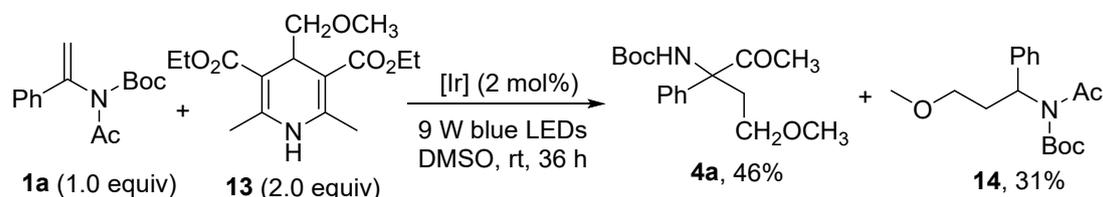


***N*-Benzyl-*N*-(3-methoxy-1-(naphthalen-2-yl)propyl)acetamide (12b).** Flash column chromatography to afford product as a yellow oil (54.2 mg, 79% yield). ^1H NMR (500 MHz, CDCl_3 , observed as a mixture of rotamers) δ [7.89-7.74 (m, 3.5H), 7.74-7.69 (m, 0.5H)], [7.56-7.44 (m, 2.5H), 7.39-7.30 (m, 0.5H)], 7.24-7.10 (m, 4H), 7.07-6.96 (m, 1H), [6.19-6.08 (m, 0.5H), 5.56-5.34 (m, 0.5H)], [5.05-4.85 (m, 0.5H), 3.97-3.74 (m, 0.5H)], [4.53-4.40 (m, 0.5H), 4.37-4.26 (m, 0.5H)], 3.52-3.35 (m, 1H), 3.29 (s, 3H), [3.29 (m, 0.5H), 3.27-3.17 (m, 0.5H)], 2.45 (s, 1H), [2.36-2.27 (m, 1.5H), 2.08 (s, 1.5H)]. ^{13}C NMR (126 MHz, CDCl_3 , observed as a mixture of rotamers) δ 172.0, 139.2, 137.8, 136.9, 136.8, 133.1, 132.8, 128.5, 128.3, 128.1, 128.0(0), 127.9(6), 127.6, 127.5, 127.1, 126.9(1), 126.8(5), 126.7, 126.4, 126.3, 126.1, 126.0, 125.9, 125.7, 70.0, 68.4, 58.6, 58.5, 58.0, 54.4, 48.6, 45.7, 31.6, 31.2, 22.8, 22.2. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calculated for $\text{C}_{23}\text{H}_{25}\text{NO}_2\text{Na}$: 370.1783, found 370.1790.



Methyl *N*-acetyl-*N*-(*tert*-butoxycarbonyl)-*O*-methylhomoserinate (12c). Flash column chromatography to afford product as a colorless oil (43.4 mg, 75% yield). ¹H NMR (500 MHz, CDCl₃) δ 5.43-5.31 (m, 1H), 3.66 (s, 3H), 3.42-3.36 (m, 1H), 3.36-3.28 (m, 1H), 3.24 (s, 3H), 2.48 (s, 3H), 2.44-2.32 (m, 1H), 2.10-1.95 (m, 1H), 1.46 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 172.7, 171.1, 152.1, 83.8, 69.5, 58.5, 53.2, 52.1, 30.1, 27.8, 26.4. HRMS (ESI) [M+Na]⁺: calculated for C₁₃H₂₃NO₆Na: 312.1423, found 312.1429.

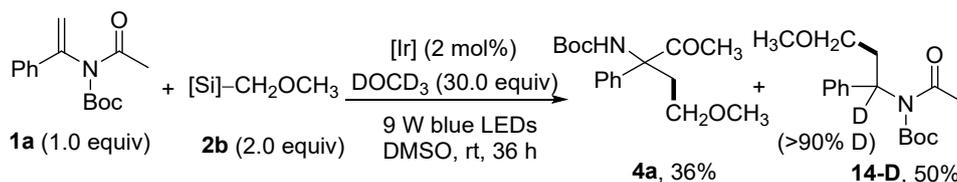
4. Reaction of *N*-vinylimide with 4-substituted Hantzsch ester



To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (4.5 mg, 0.004 mmol), DHP-CH₂OCH₃ **13** (118.9 mg, 0.4 mmol), and the *N*-vinylimide **1a** (52.2 mg, 0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 36 h (cooling with a fan). After the reaction was complete, the reaction solution was diluted with water (10 mL), and was extracted with EtOAc (5 x 10 mL). The organic layer was washed with brine, dried over MgSO₄, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the products **4a** (28.2 mg, 46% yield) and **14** (19.1 mg, 31% yield).

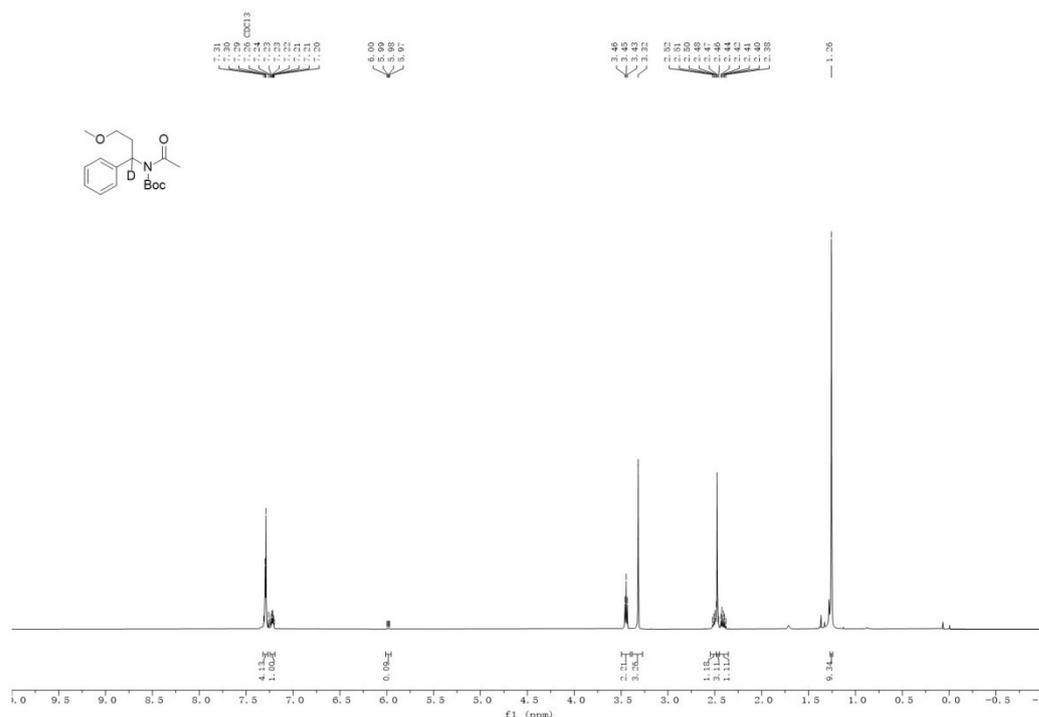
***tert*-Butyl acetyl(3-methoxy-1-phenylpropyl)carbamate (14).** Flash column chromatography to afford product as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.24 (m, 4H), 7.24-7.16 (m, 1H), 6.04-5.92 (m, 1H), 3.44 (t, *J* = 6.5 Hz, 2H), 3.31 (s, 3H), 2.55-2.48 (m, 1H), 2.47 (s, 3H), 2.44-2.37 (m, 1H), 1.25 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 173.5, 153.4, 140.7, 128.0, 126.8(5), 126.8(1), 83.1, 70.1, 58.6, 53.1, 31.0, 27.6, 26.5. HRMS (ESI) [M+Na]⁺: calculated for C₁₇H₂₅NO₄Na: 330.1681, found 330.1670.

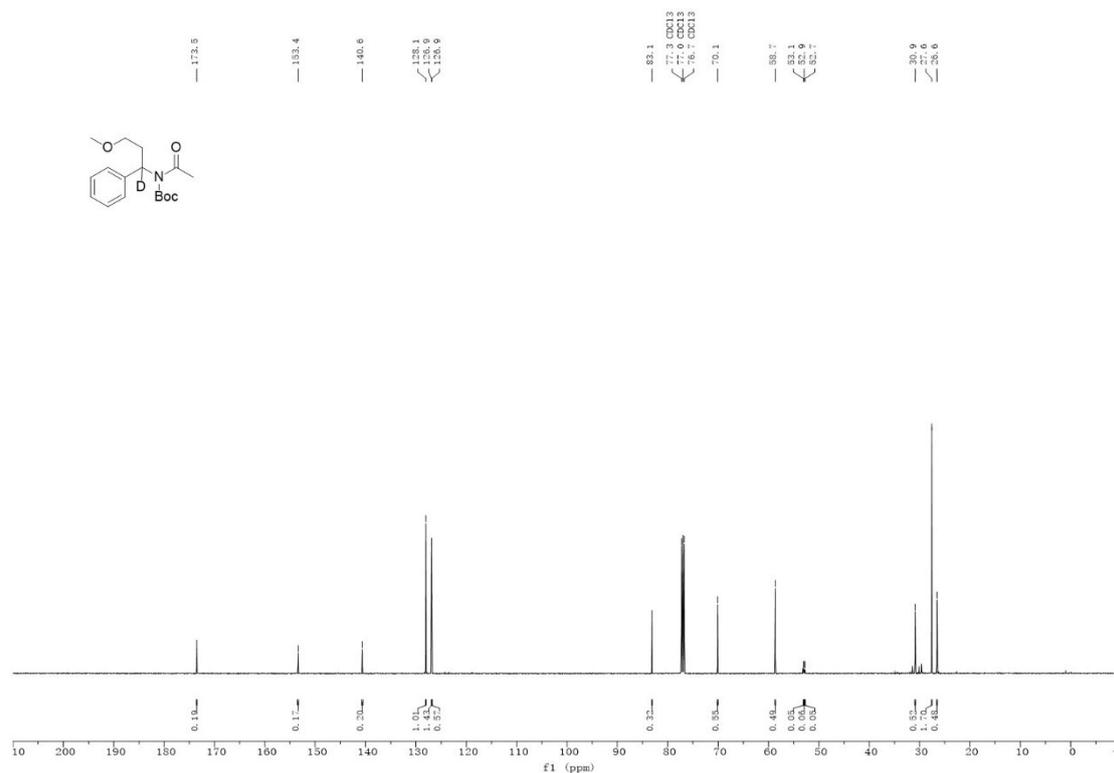
5. Deuteration experiments



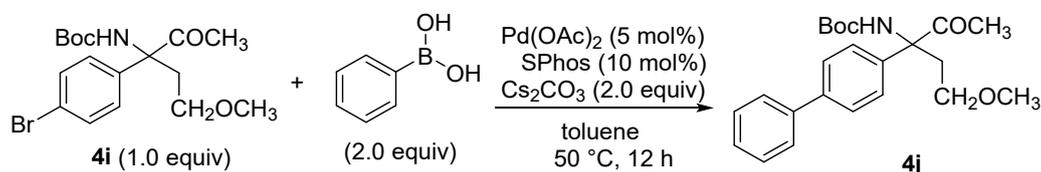
To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (4.5 mg, 0.004 mmol), potassium [18-crown-6] bis(catecholato)methoxymethylsilicate (237.2 mg, 0.4 mmol), *N*-vinylimide **1a** (52.2 mg, 0.2 mmol), DOCD₃ (6 mmol, 30.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 36 h (cooling with a fan). After the reaction was complete, the reaction solution was diluted with saturated Na₂CO₃ aqueous solution (10 mL), and was extracted with EtOAc (5 x 10 mL). The organic layer was washed with brine, dried over MgSO₄, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product (30.8 mg, 50% yield) as a colorless oil. The product **14-D** with more than 90% D-incorporation was determined by ¹H NMR.

tert-Butyl acetyl(3-methoxy-1-phenylpropyl-1-*d*)carbamate (14-D). Flash column chromatography to afford product as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.27 (m, 4H), 7.25-7.19 (m, 1H), 3.45 (t, *J* = 6.5 Hz, 2H), 3.32 (s, 3H), 2.55-2.48 (m, 1H), 2.47 (s, 3H), 2.45-2.36 (m, 1H), 1.26 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 173.5, 153.4, 140.6, 128.1, 126.9(2), 126.8(6), 83.1, 70.1, 58.7, 52.9 (t, *J* = 21.4 Hz), 30.9, 27.6, 26.6. HRMS (ESI) [M+Na]⁺: calculated for C₁₇H₂₄DNO₄Na: 331.1739, found 331.1735.



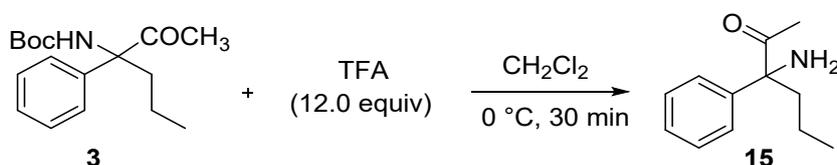


6. Procedure of Suzuki reaction



To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, compound **4i** (77 mg, 0.2 mmol), phenylboronic acid (48.8 mg, 0.4 mmol), Cs₂CO₃ (130 mg, 0.4 mmol), Pd(OAc)₂ (1.7 mg, 5 mol%), SPhos (8.2 mg, 10 mol%) were added. The tube was evacuated and filled with nitrogen for 3 times. Then toluene (2.0 mL) was introduced and the mixture was stirred at 50 °C for 12 h. After completion of the reaction, the mixture was cooled down to room temperature and diluted with EtOAc (15.0 mL). The catalyst and inorganic base were filtered off using a short pad of silica gel. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on a silica gel column using petroleum ether/EtOAc as the eluent to give the product **4j** (66.7 mg, 87% yield).

7. Procedure of *N*-Boc deprotection



To a solution of compound **3** (0.2 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C, was added trifluoroacetic acid (2.4 mmol) dropwise. After 30 min the reaction was transferred to a separation funnel containing CH_2Cl_2 and saturated Na_2CO_3 , extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were dried over Na_2SO_4 , then concentrated under reduced pressure to give the residue. The obtained residue was purified by column chromatography on neutral aluminum oxide to give the product **15** (34.4 mg, 90% yield).

3-Amino-3-phenylhexan-2-one (15). Flash column chromatography to afford product as a yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 7.47-7.30 (m, 4H), 7.30-7.14 (m, 1H), 2.08-2.02 (m, 2H), 2.00 (br, 2H), 1.96 (s, 3H), 1.36-1.22 (m, 1H), 1.22-1.09 (m, 1H), 0.95 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 209.6, 142.6, 128.7, 127.4, 125.8, 68.1, 39.7, 24.9, 16.9, 14.5. HRMS (ESI) $[\text{M}+\text{H}]^+$: calculated for $\text{C}_{12}\text{H}_{18}\text{NO}$: 192.1383, found 192.1382.

8. References

- [1] W. Luo, Y. Yang, Y. Fang, X. Zhang, X. Jin, G. Zhao, L. Zhang, Y. Li, W. Zhou, T. Xia, B. Chen, *Adv. Synth. Catal.* **2019**, *361*, 4215-4221.
- [2] a) W.-L. Yu, J. Chen, K. Gao, Z.-X. Liu, Y.-H. Zhang, *Org. Lett.* **2014**, *16*, 4870-4873; b) X.-H. Chang, Z.-L. Wang, M. Zhao, C. Yang, J.-J. Li, W.-W. Ma, Y.-H. Xu, *Org. Lett.* **2020**, *22*, 1326-1330.
- [3] L. Huai, L. Zhang, Z. Wang, H. Wu, Y. Fang, *Org. Chem. Front.* **2023**, *10*, 1245-1251.

9. X-ray crystal data for compounds **3**, **4m**, and (+/-)-**10b**

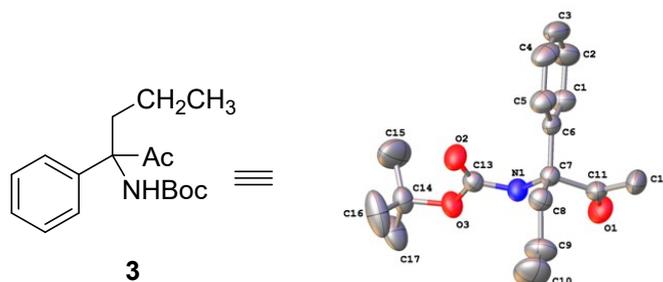


Table S1 Crystal data and structure refinement for 3

| | |
|---|---|
| Identification code | CCDC 2221827 (3) |
| Empirical formula | C ₁₇ H ₂₅ NO ₃ |
| Formula weight | 291.38 |
| Temperature/K | 265(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 6.1565(4) |
| b/Å | 9.7090(7) |
| c/Å | 15.2110(10) |
| α/° | 80.656(3) |
| β/° | 80.950(3) |
| γ/° | 81.145(3) |
| Volume/Å ³ | 878.26(10) |
| Z | 2 |
| ρ _{calc} /cm ³ | 1.102 |
| μ/mm ⁻¹ | 0.075 |
| F(000) | 316.0 |
| Crystal size/mm ³ | 0.25 × 0.18 × 0.12 |
| Radiation | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 6.464 to 50.284 |
| Index ranges | -7 ≤ h ≤ 7, -11 ≤ k ≤ 11, -18 ≤ l ≤ 18 |
| Reflections collected | 19479 |
| Independent reflections | 3111 [R _{int} = 0.0555, R _{sigma} = 0.0344] |
| Data/restraints/parameters | 3111/0/195 |
| Goodness-of-fit on F ² | 1.049 |
| Final R indexes [I ≥ 2σ (I)] | R ₁ = 0.0658, wR ₂ = 0.1751 |
| Final R indexes [all data] | R ₁ = 0.0814, wR ₂ = 0.1862 |
| Largest diff. peak/hole / e Å ⁻³ | 0.33/-0.22 |

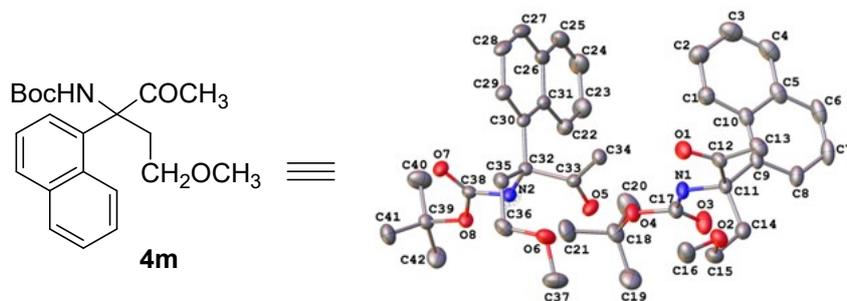


Table S2 Crystal data and structure refinement for 4m

| | |
|---|---|
| Identification code | CCDC 2222960 (4m) |
| Empirical formula | C ₂₁ H ₂₇ NO ₄ |
| Formula weight | 357.43 |
| Temperature/K | 265(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.695(5) |
| b/Å | 12.205(6) |
| c/Å | 16.604(8) |
| α/° | 102.948(14) |
| β/° | 104.306(13) |
| γ/° | 97.337(13) |
| Volume/Å ³ | 2007.8(16) |
| Z | 4 |
| ρ _{calc} /cm ³ | 1.182 |
| μ/mm ⁻¹ | 0.081 |
| F(000) | 768.0 |
| Crystal size/mm ³ | 0.35 × 0.27 × 0.18 |
| Radiation | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 4.776 to 50.054 |
| Index ranges | -12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19 |
| Reflections collected | 55126 |
| Independent reflections | 6987 [R _{int} = 0.0648, R _{sigma} = 0.0366] |
| Data/restraints/parameters | 6987/0/480 |
| Goodness-of-fit on F ² | 1.043 |
| Final R indexes [I >= 2σ (I)] | R ₁ = 0.0471, wR ₂ = 0.1100 |
| Final R indexes [all data] | R ₁ = 0.0729, wR ₂ = 0.1211 |
| Largest diff. peak/hole / e Å ⁻³ | 0.22/-0.17 |

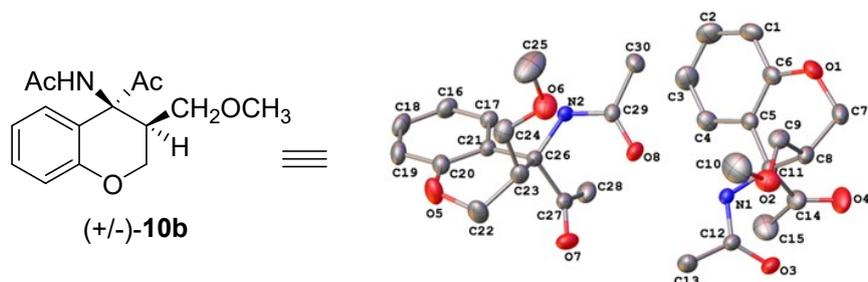
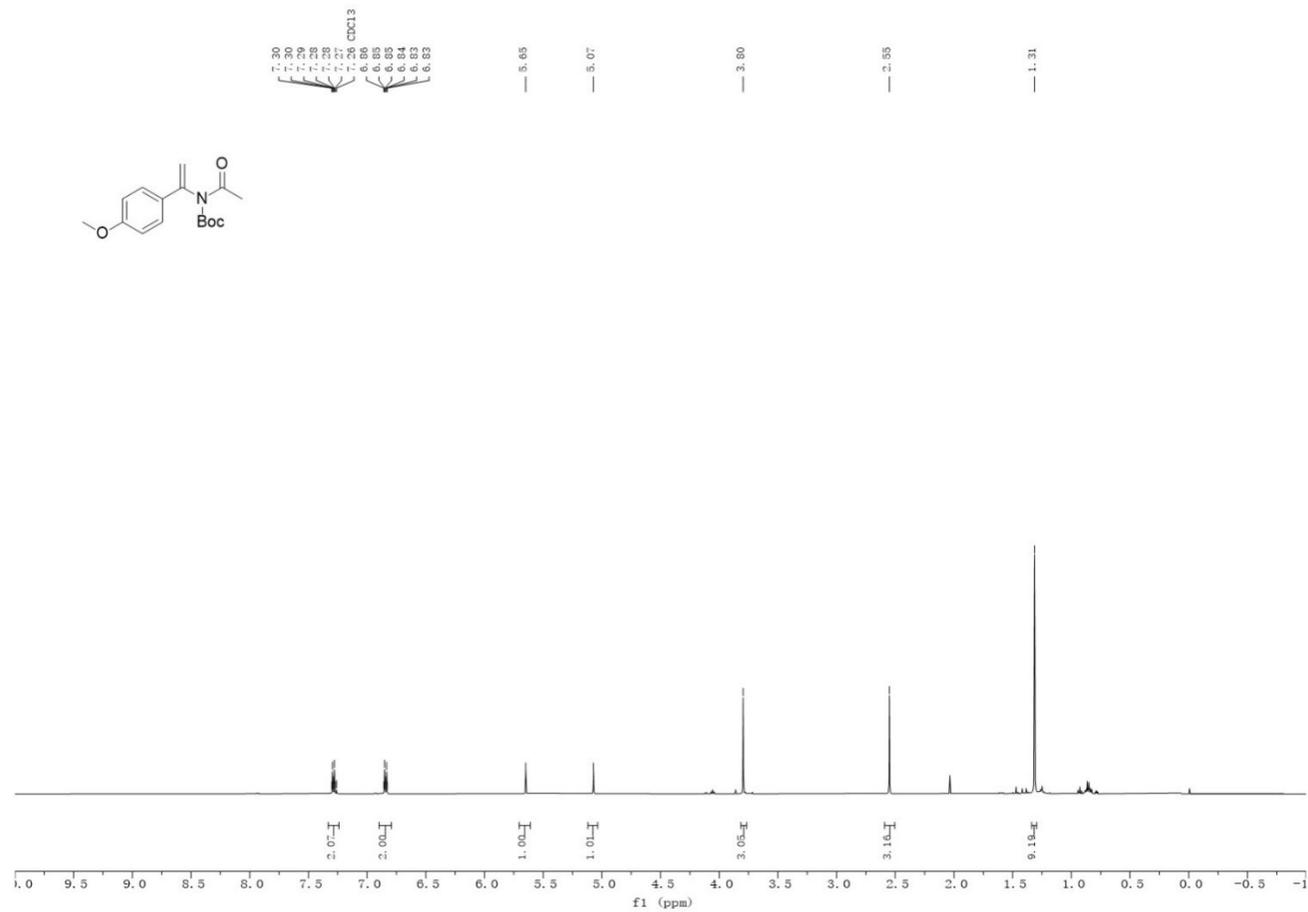
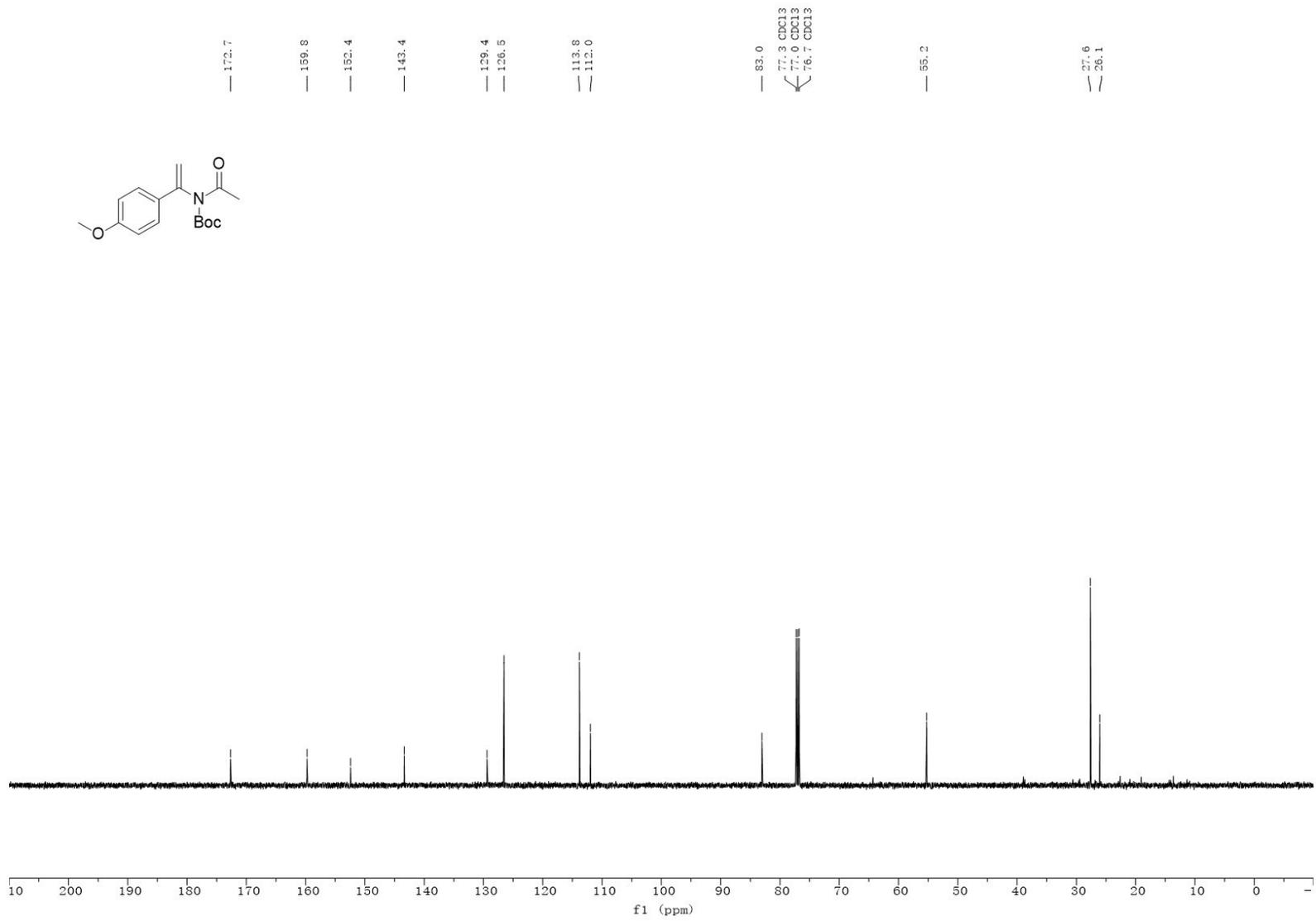


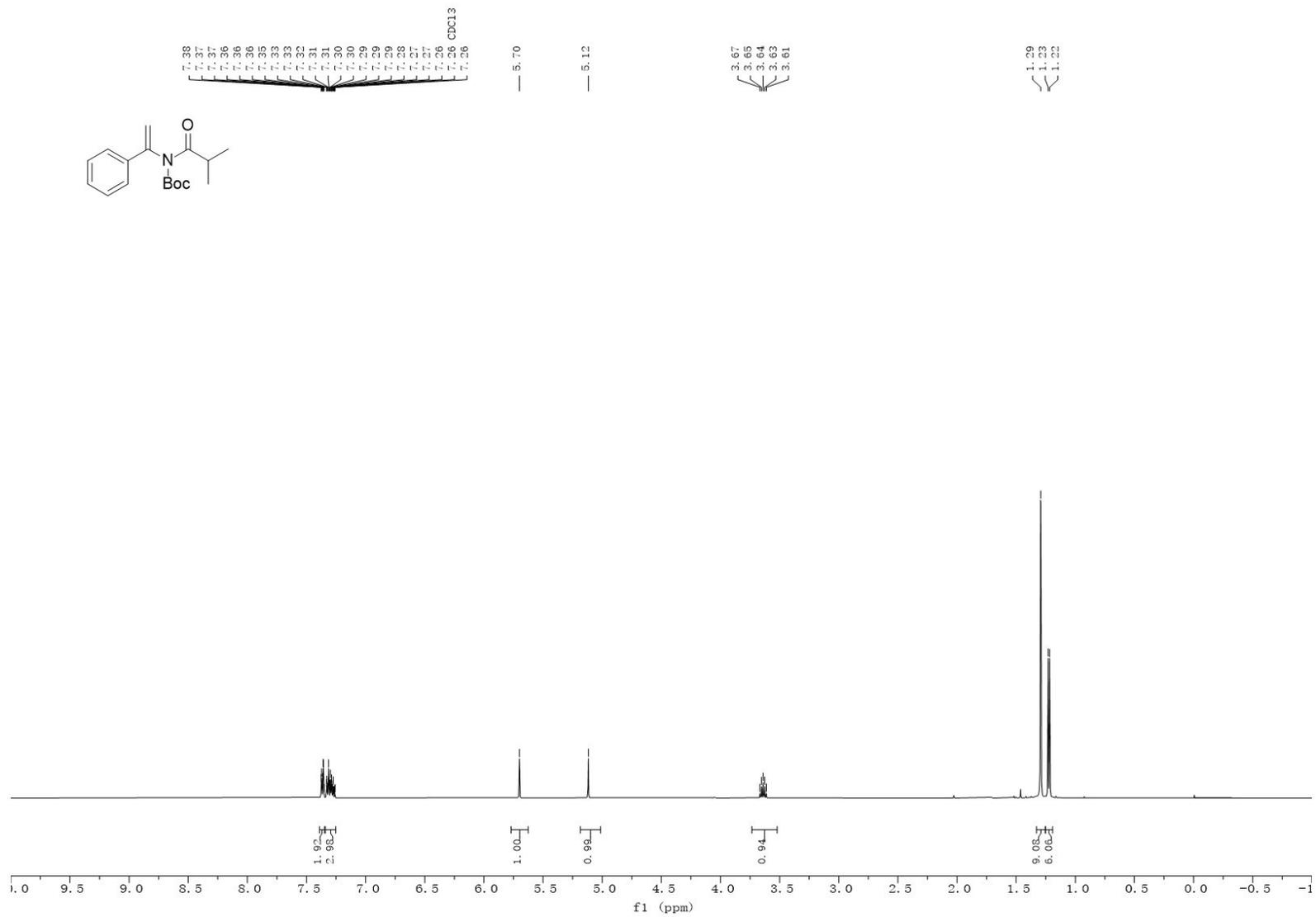
Table S3 Crystal data and structure refinement for (+/-)-10b

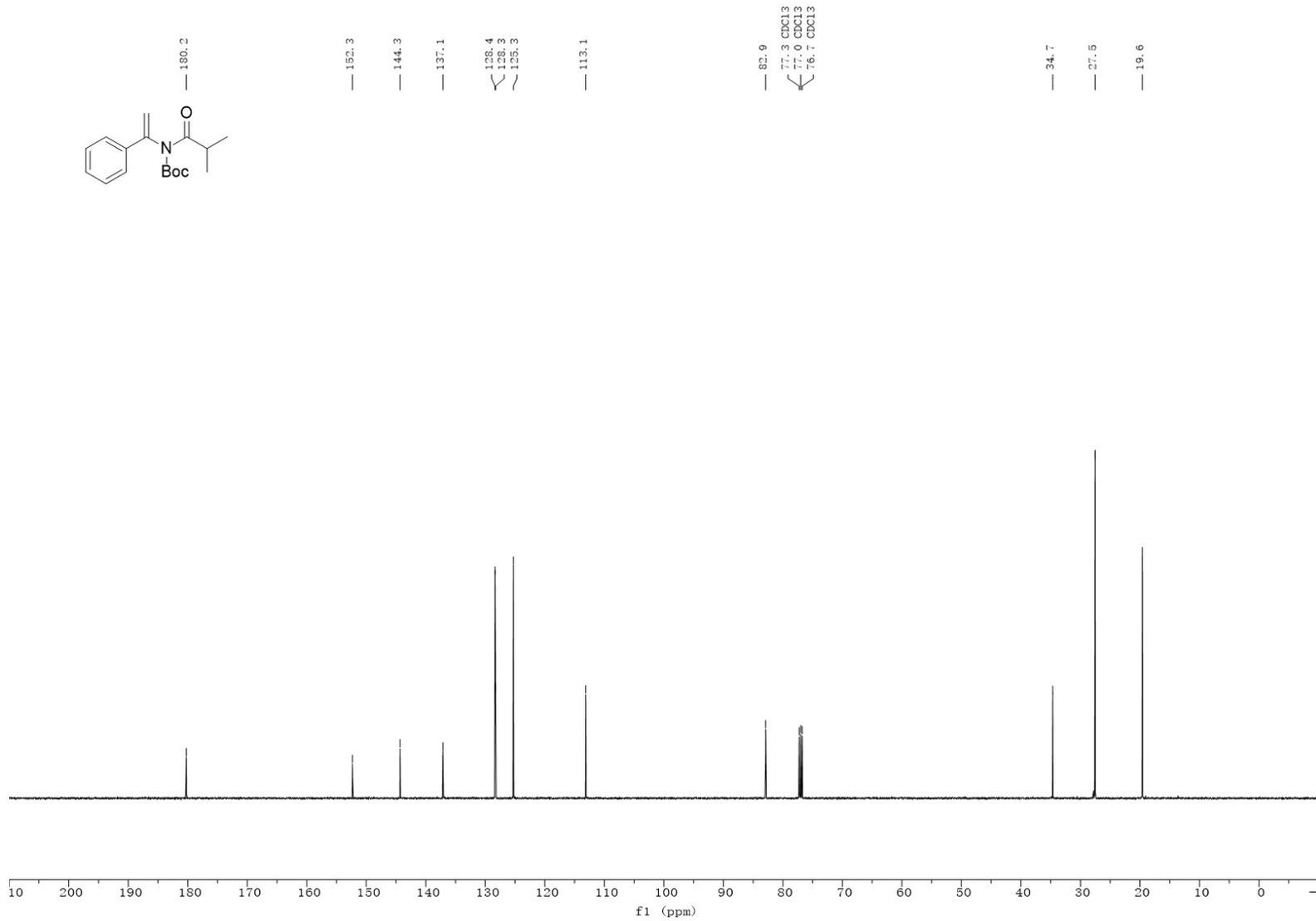
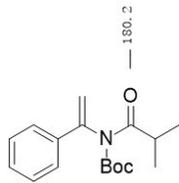
| | |
|---|---|
| Identification code | CCDC 2225643 ((+/-)-10b) |
| Empirical formula | C ₁₅ H ₁₉ NO ₄ |
| Formula weight | 277.31 |
| Temperature/K | 265(2) |
| Crystal system | monoclinic |
| Space group | P2 ₁ /c |
| a/Å | 9.3731(4) |
| b/Å | 29.9607(14) |
| c/Å | 10.5572(5) |
| α/° | 90 |
| β/° | 101.8490(10) |
| γ/° | 90 |
| Volume/Å ³ | 2901.5(2) |
| Z | 8 |
| ρ _{calc} /cm ³ | 1.270 |
| μ/mm ⁻¹ | 0.092 |
| F(000) | 1184.0 |
| Crystal size/mm ³ | 0.25 × 0.18 × 0.12 |
| Radiation | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 4.17 to 50.158 |
| Index ranges | -11 ≤ h ≤ 10, -35 ≤ k ≤ 35, -12 ≤ l ≤ 12 |
| Reflections collected | 64759 |
| Independent reflections | 5141 [R _{int} = 0.0643, R _{sigma} = 0.0283] |
| Data/restraints/parameters | 5141/0/368 |
| Goodness-of-fit on F ² | 1.068 |
| Final R indexes [I ≥ 2σ (I)] | R ₁ = 0.0480, wR ₂ = 0.1390 |
| Final R indexes [all data] | R ₁ = 0.0606, wR ₂ = 0.1482 |
| Largest diff. peak/hole / e Å ⁻³ | 0.29/-0.28 |

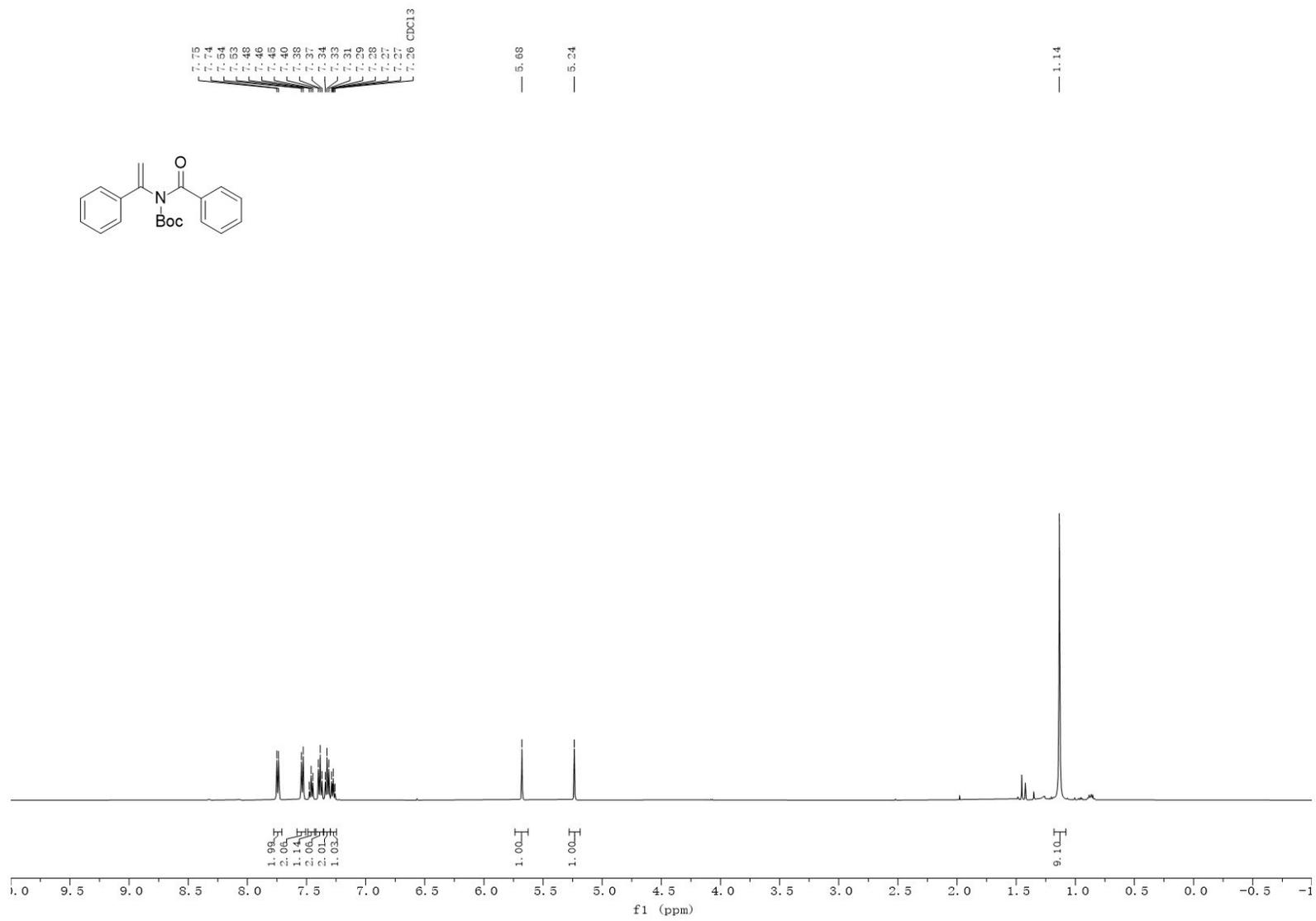
10. NMR Spectra of New Compounds

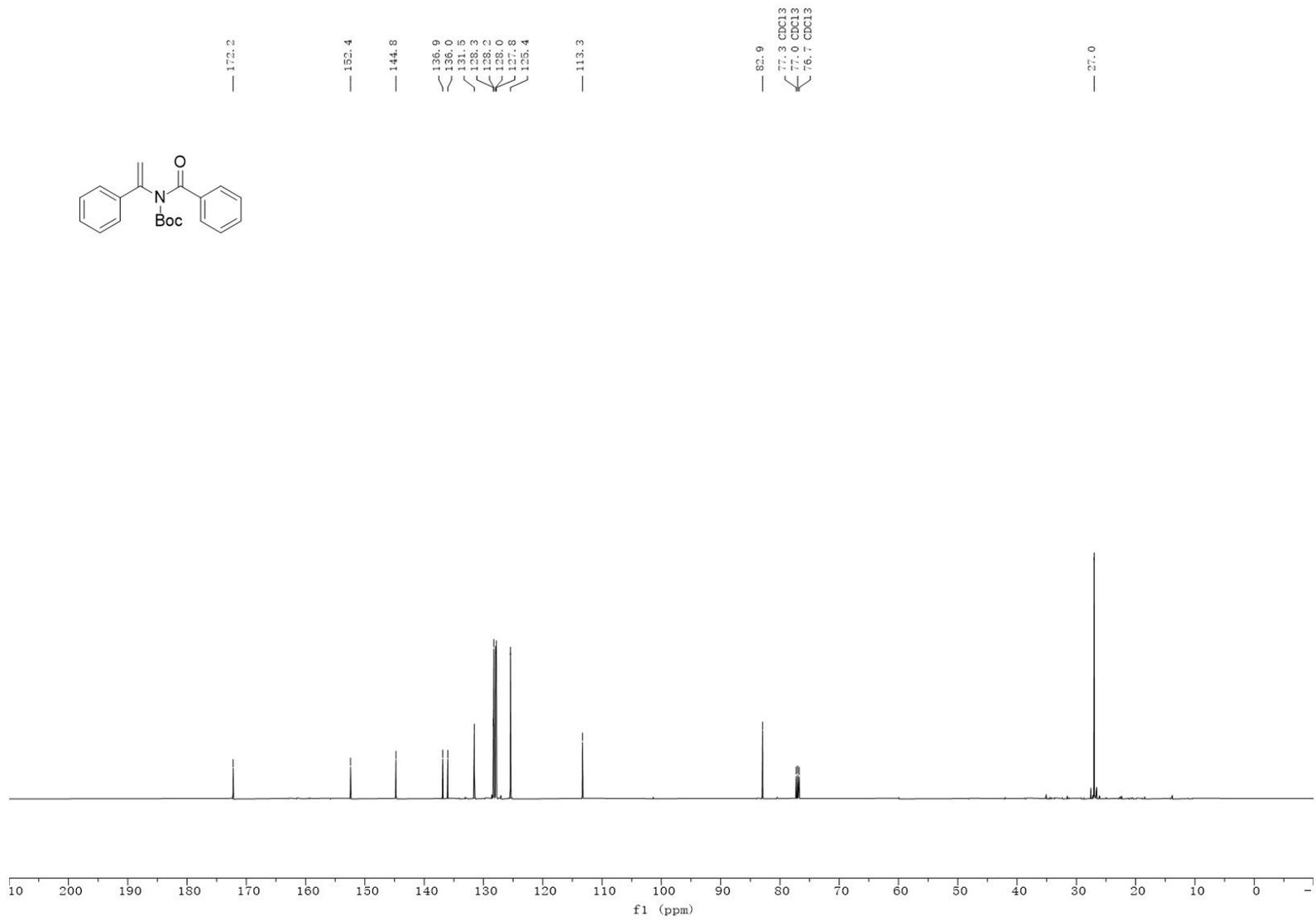




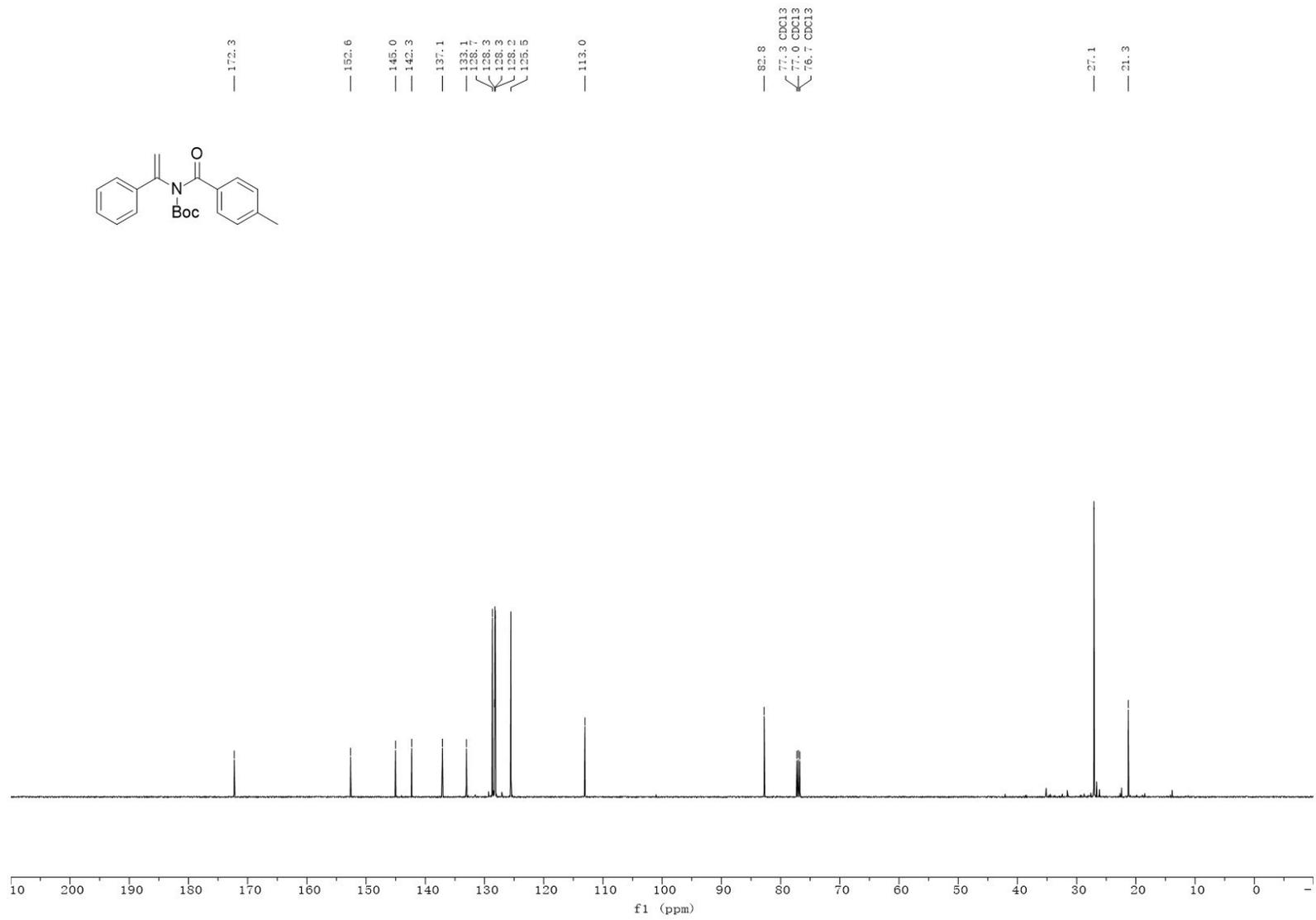


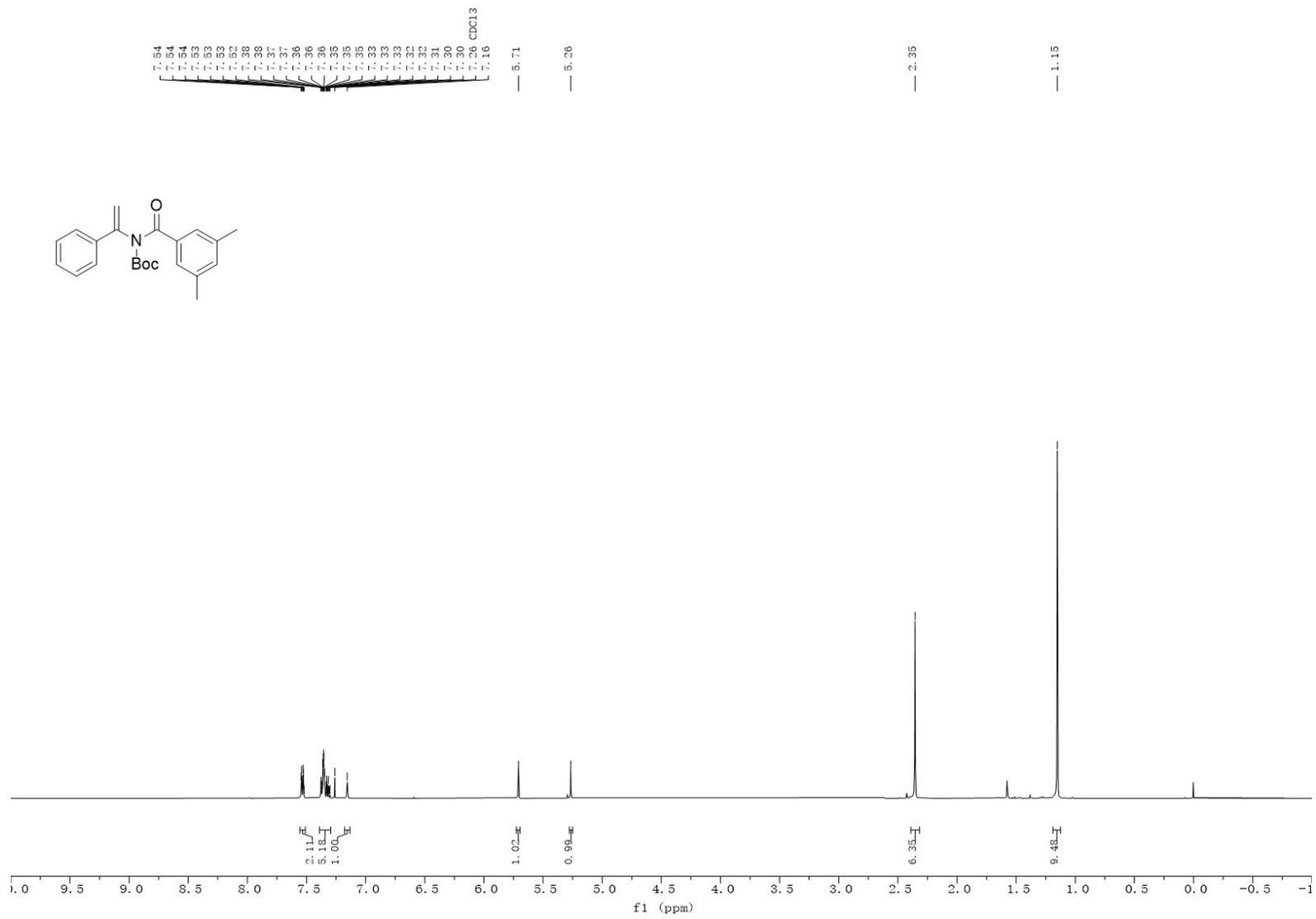


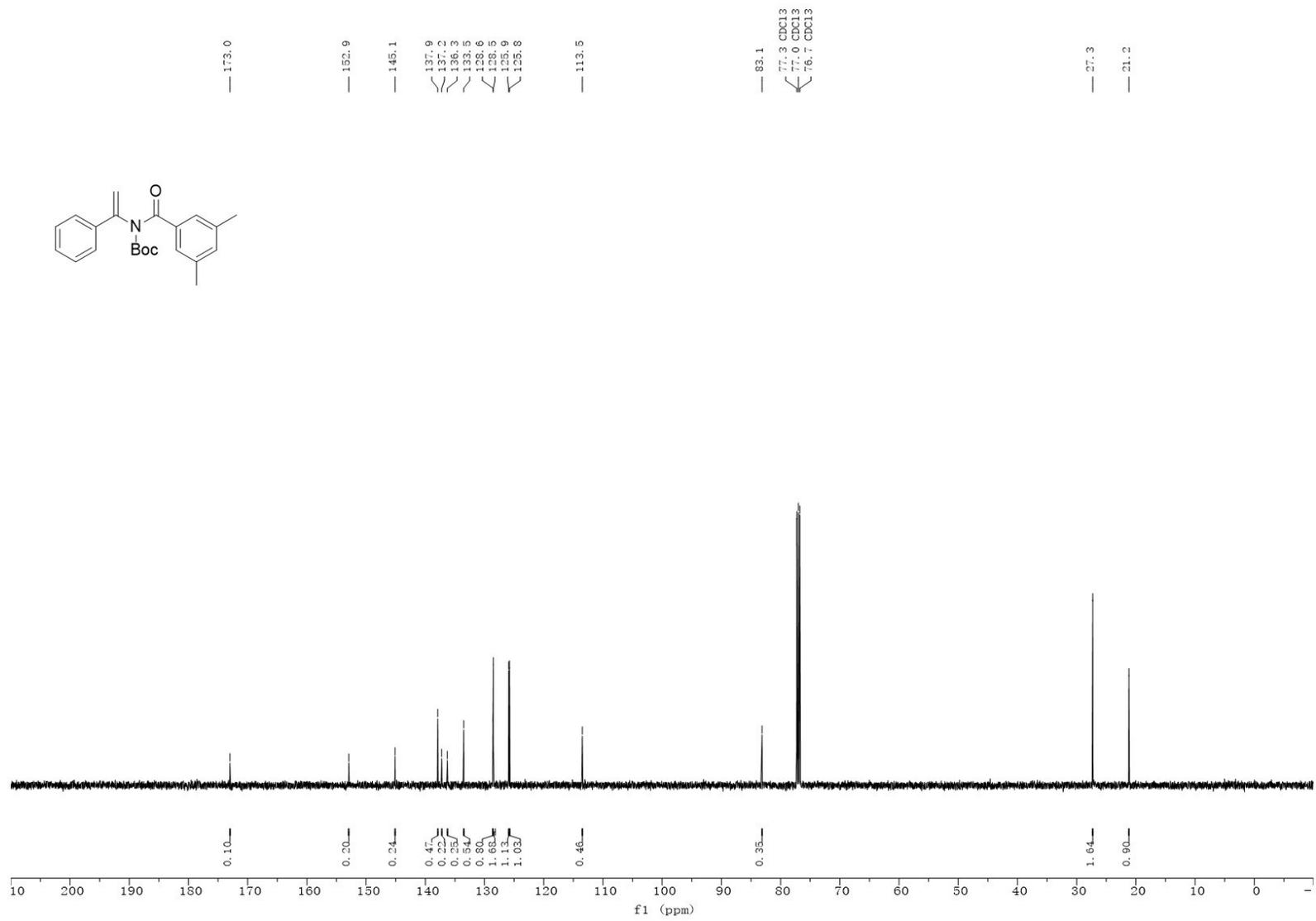


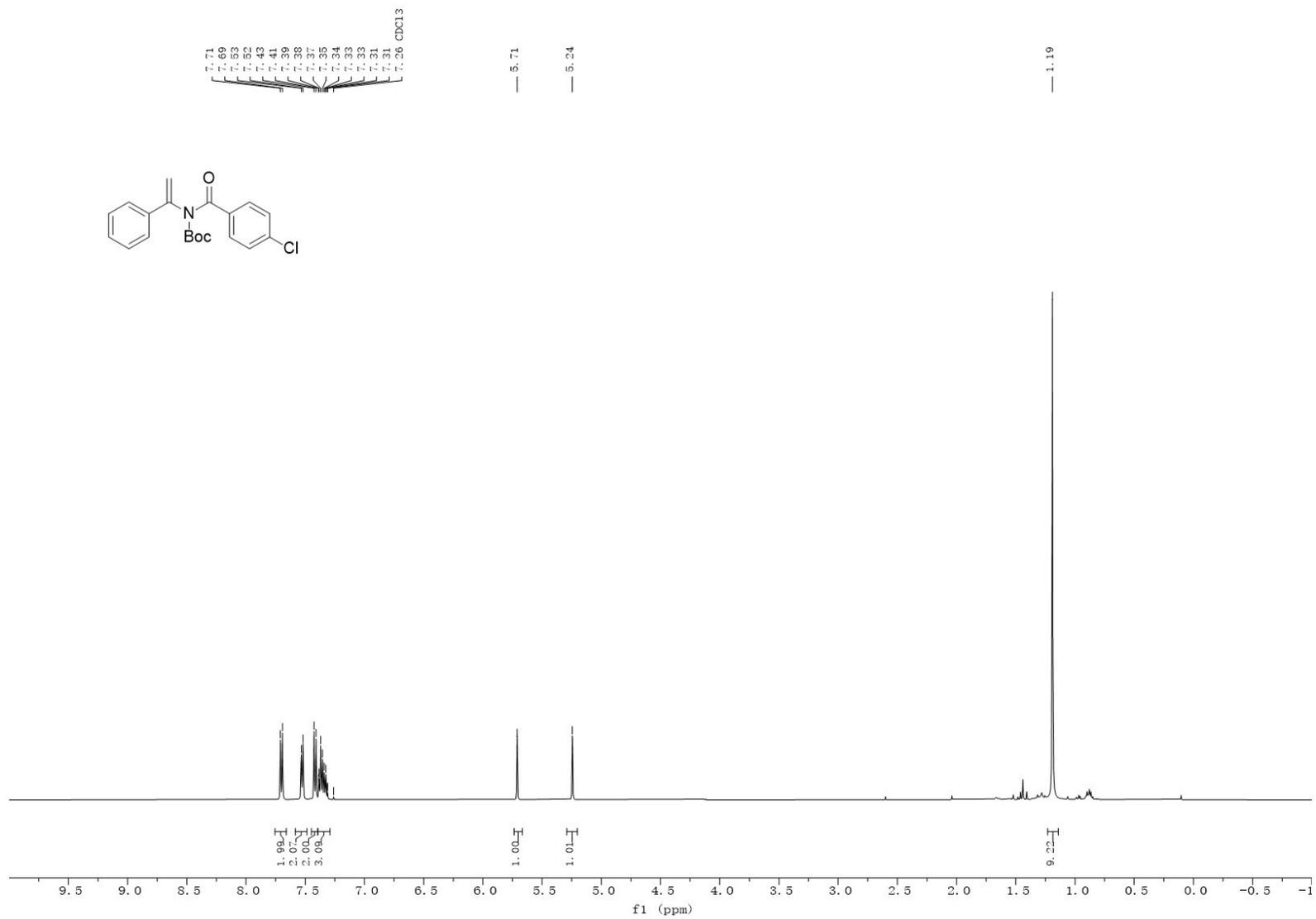


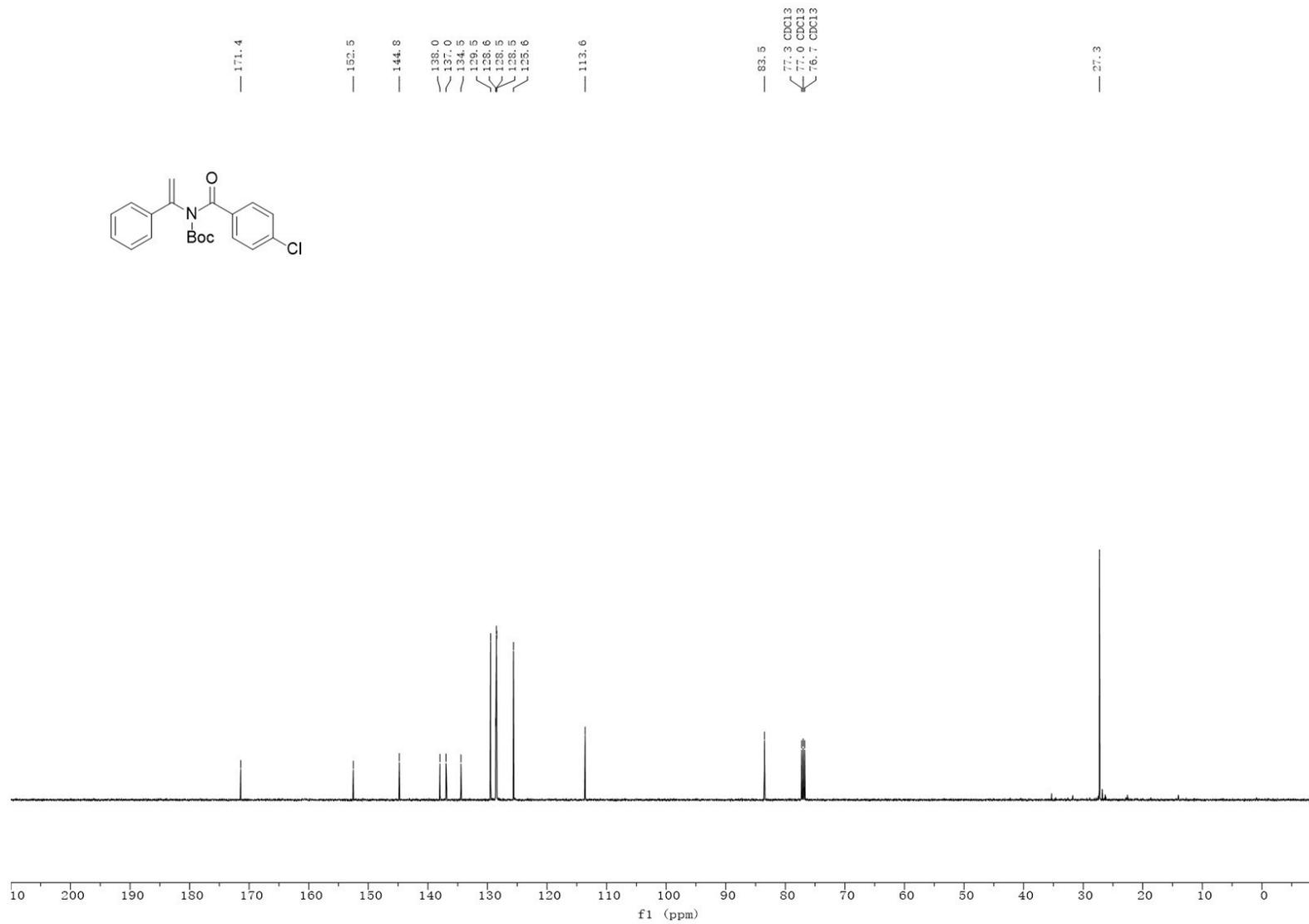


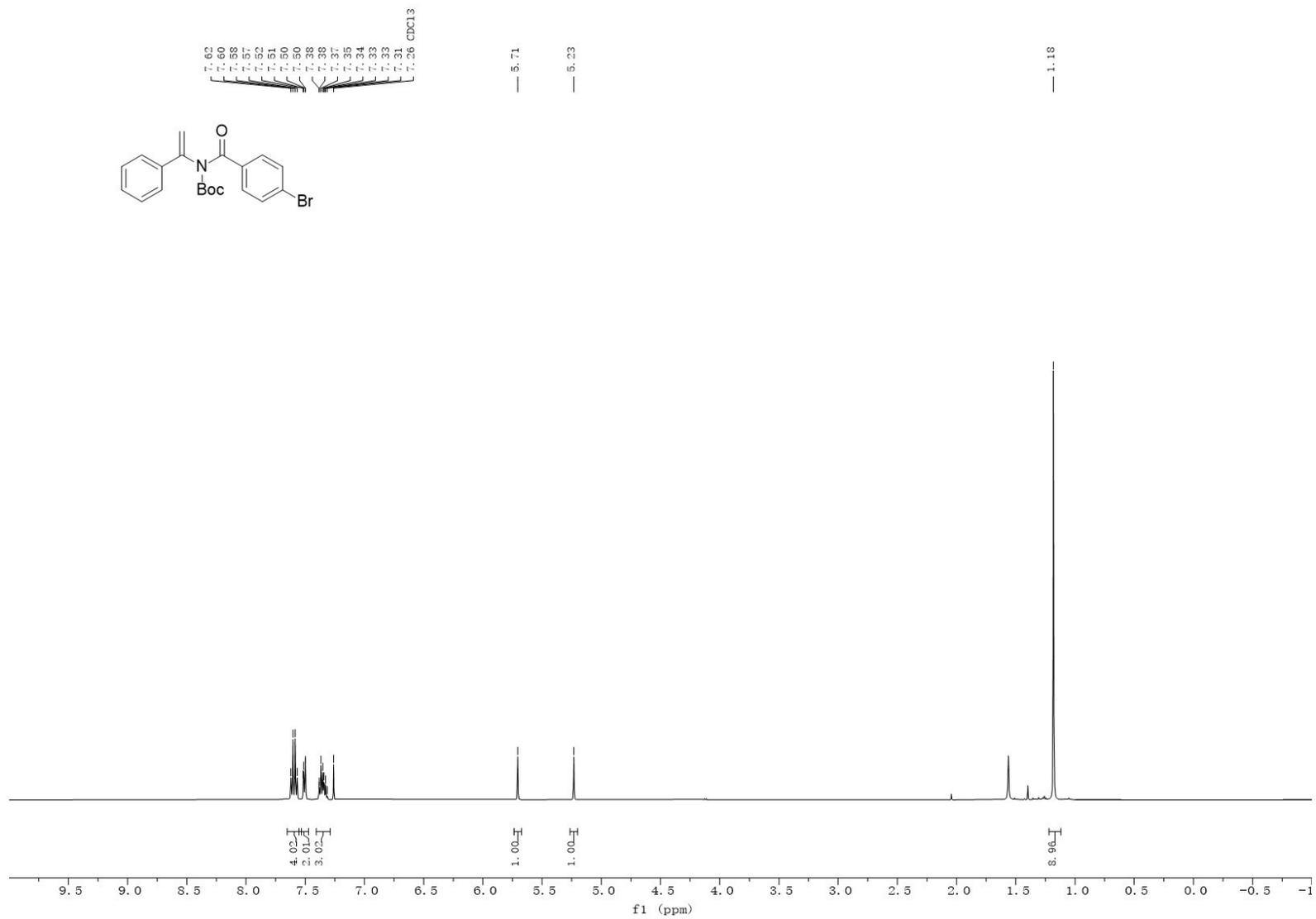


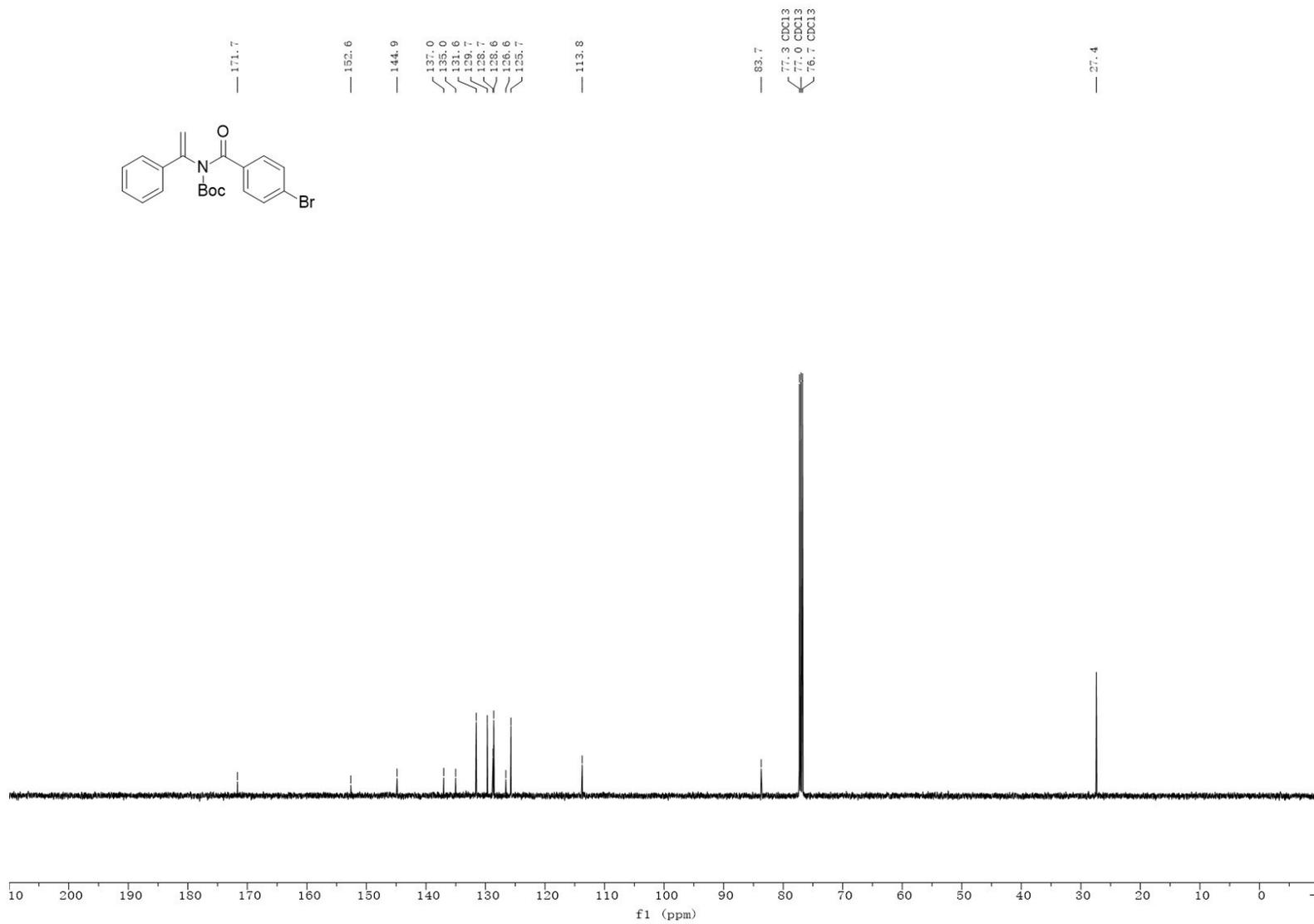
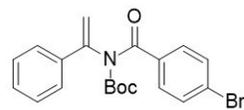


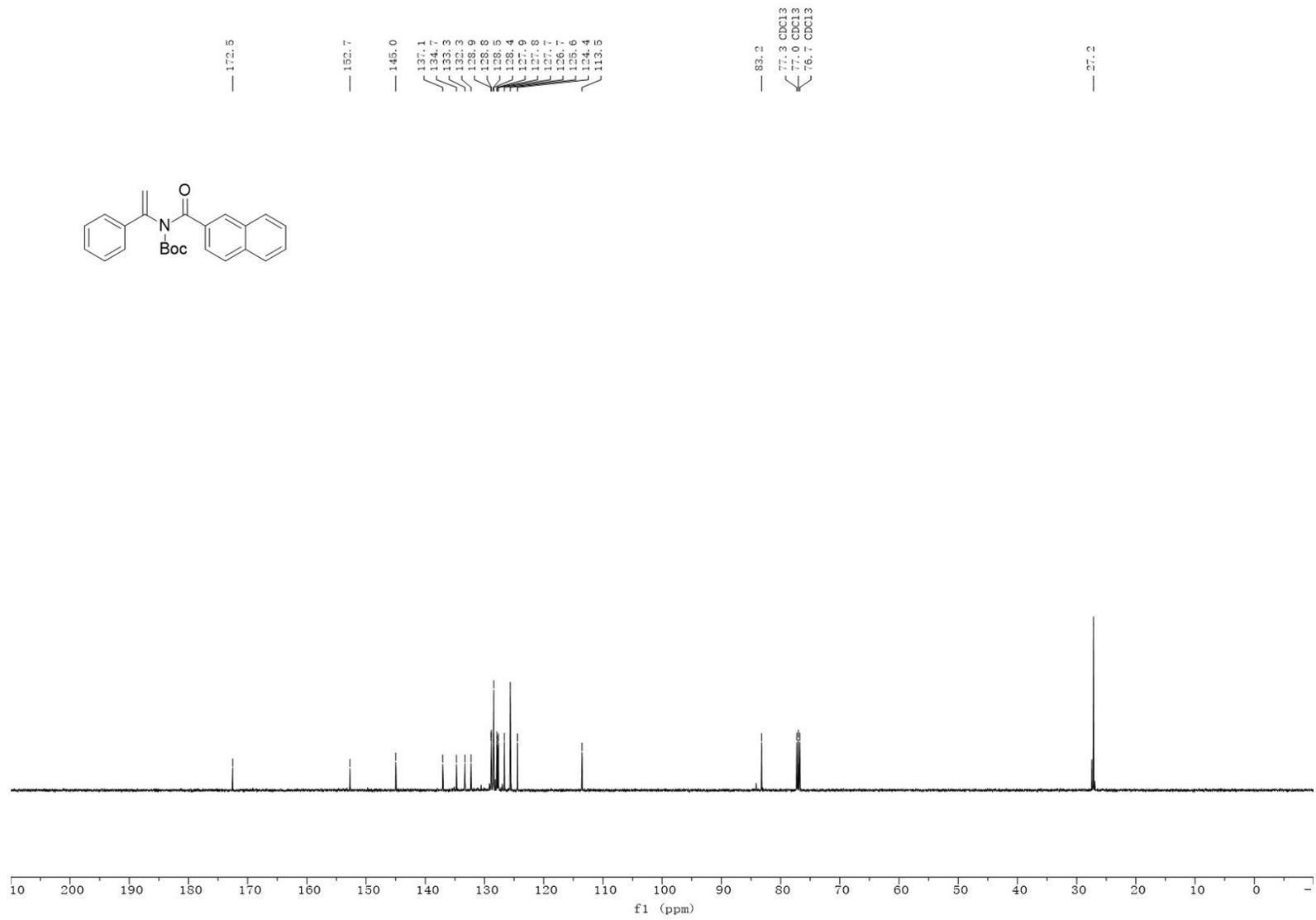


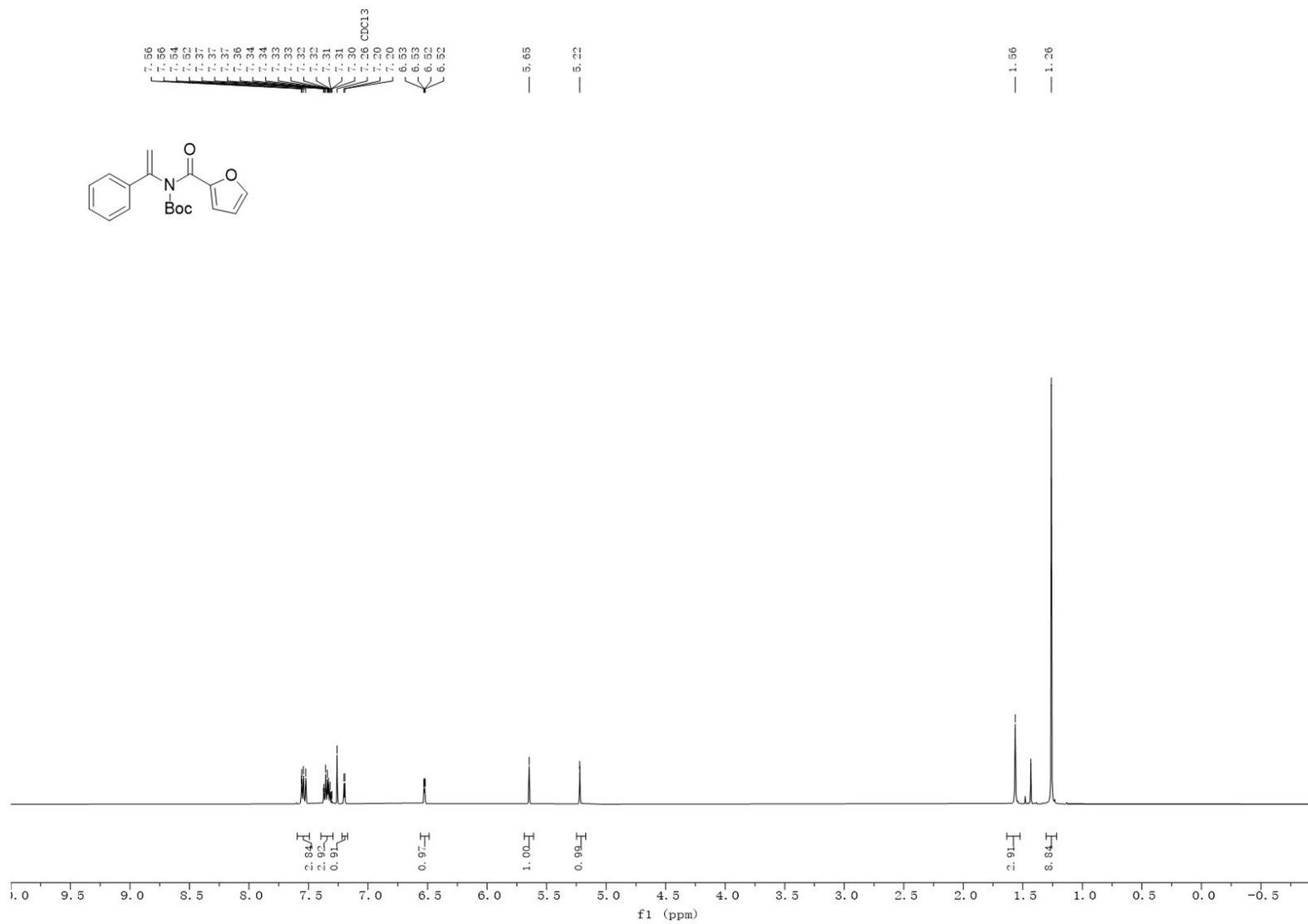


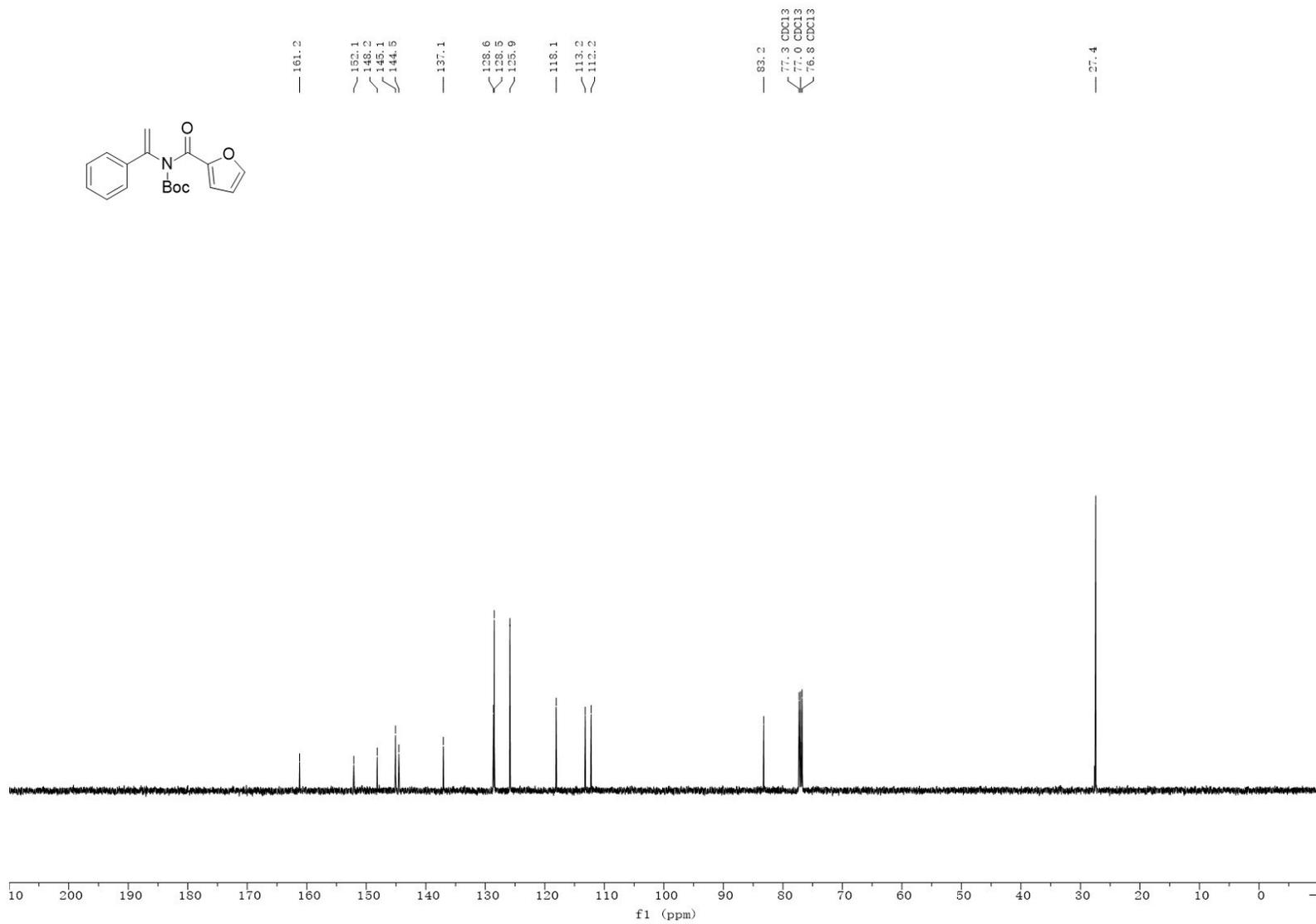
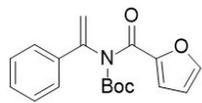


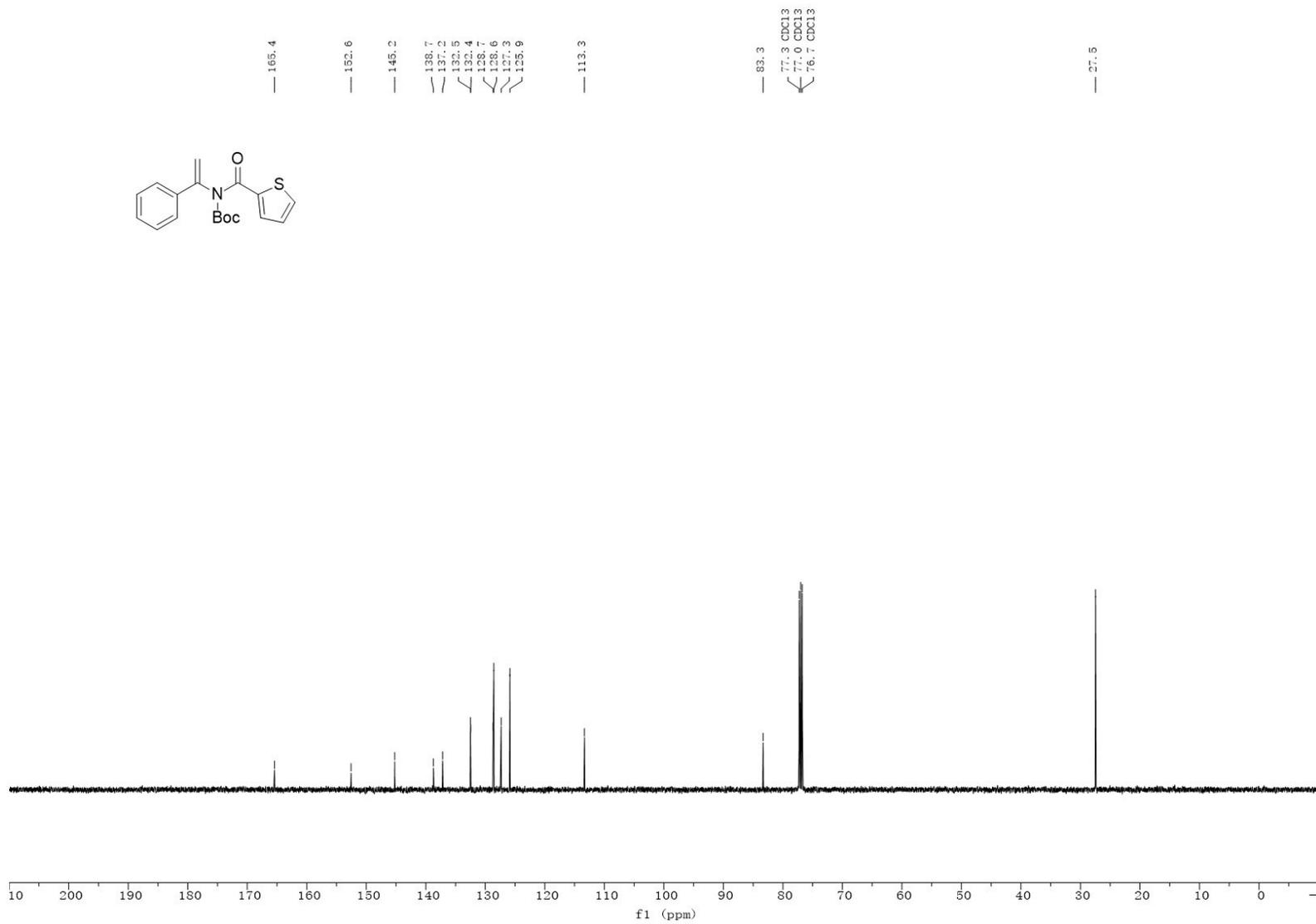
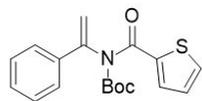


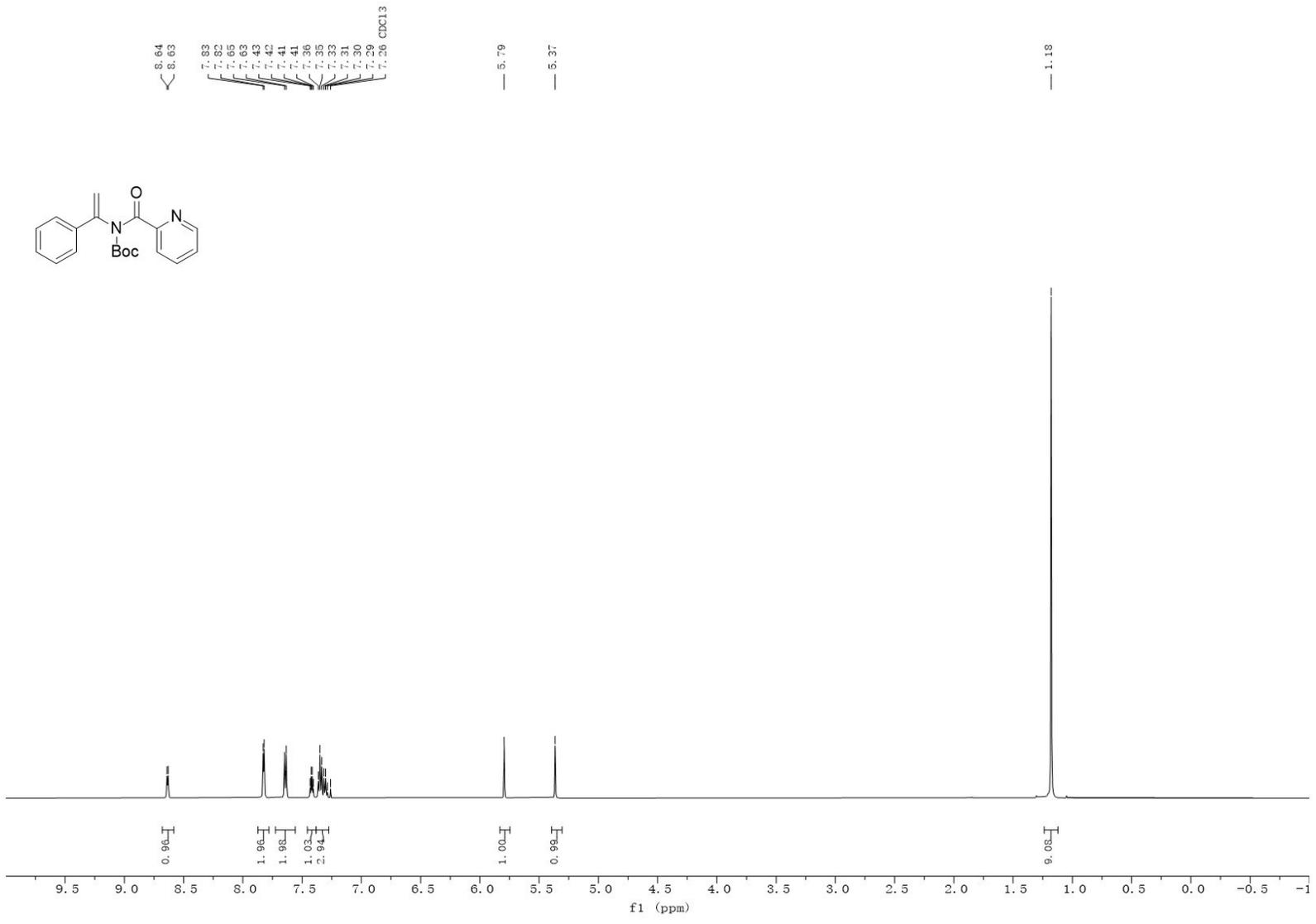


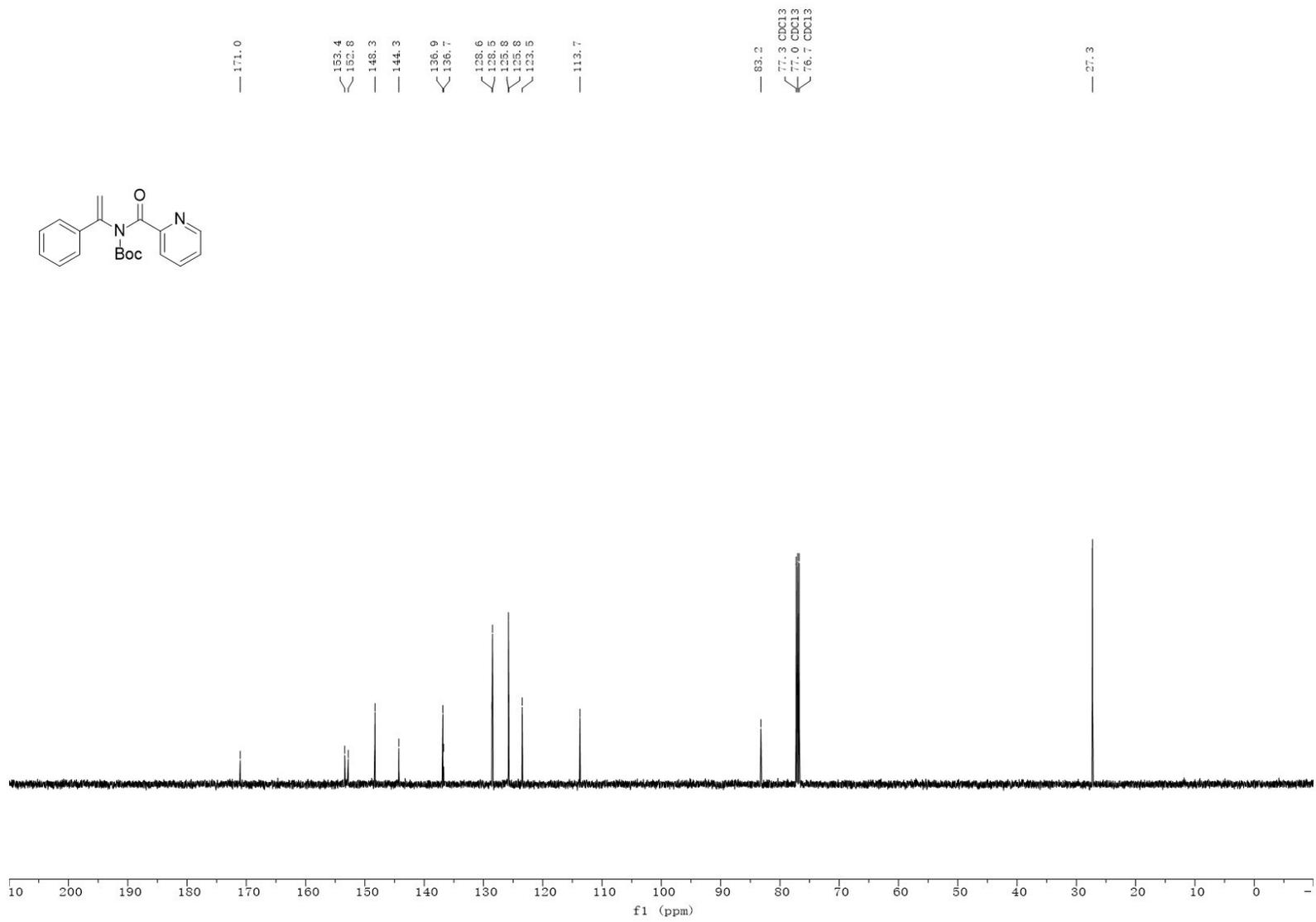


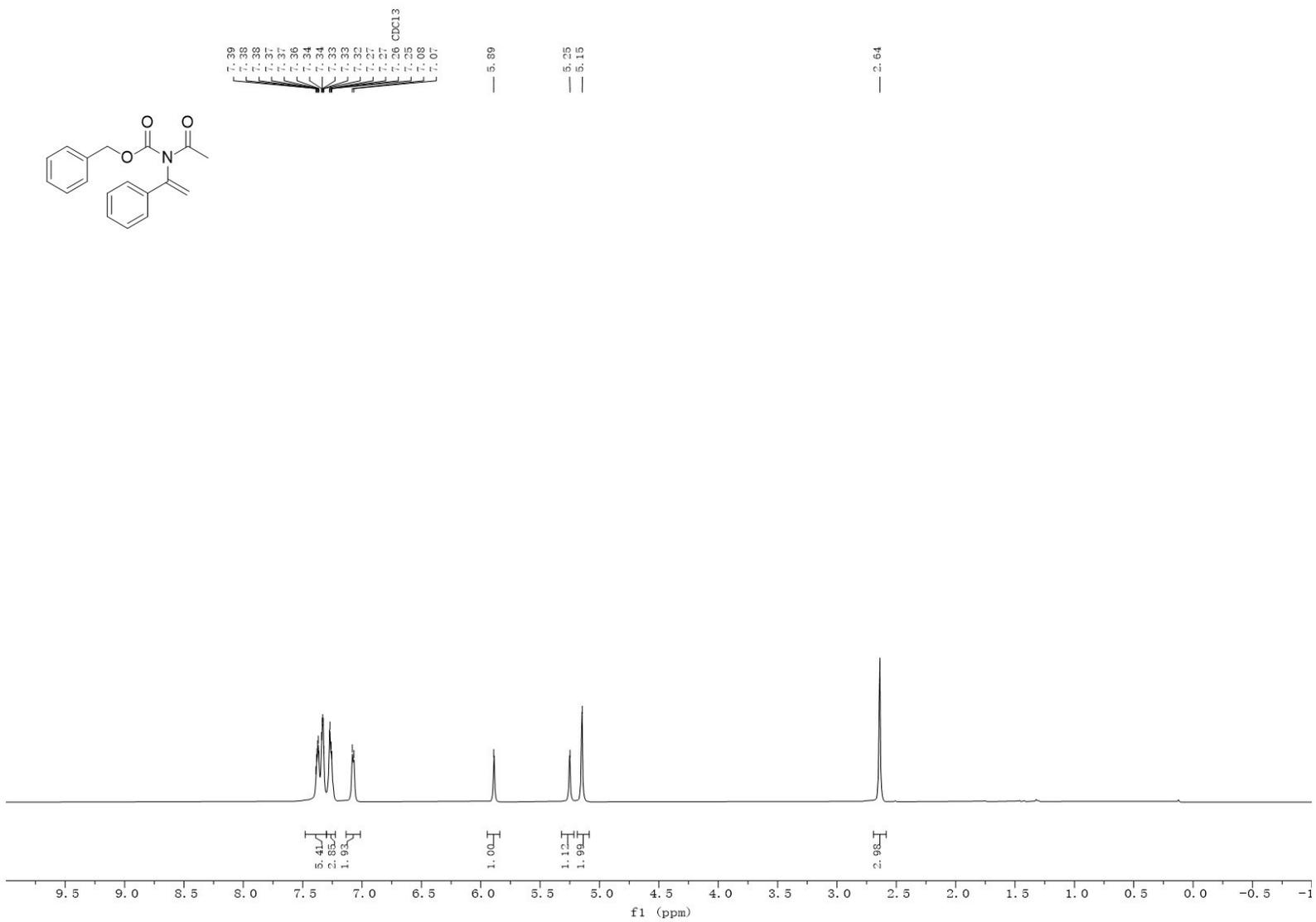


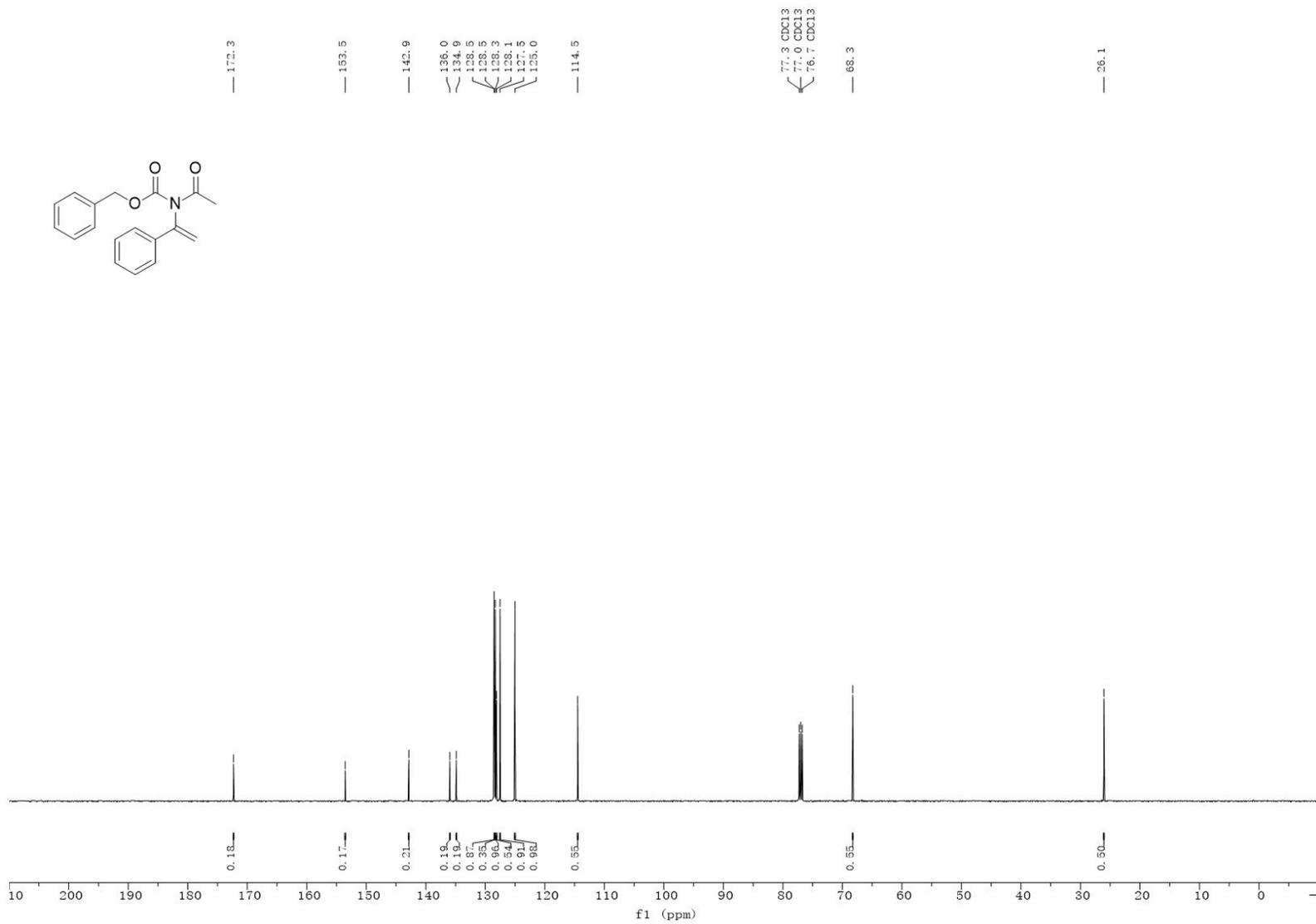


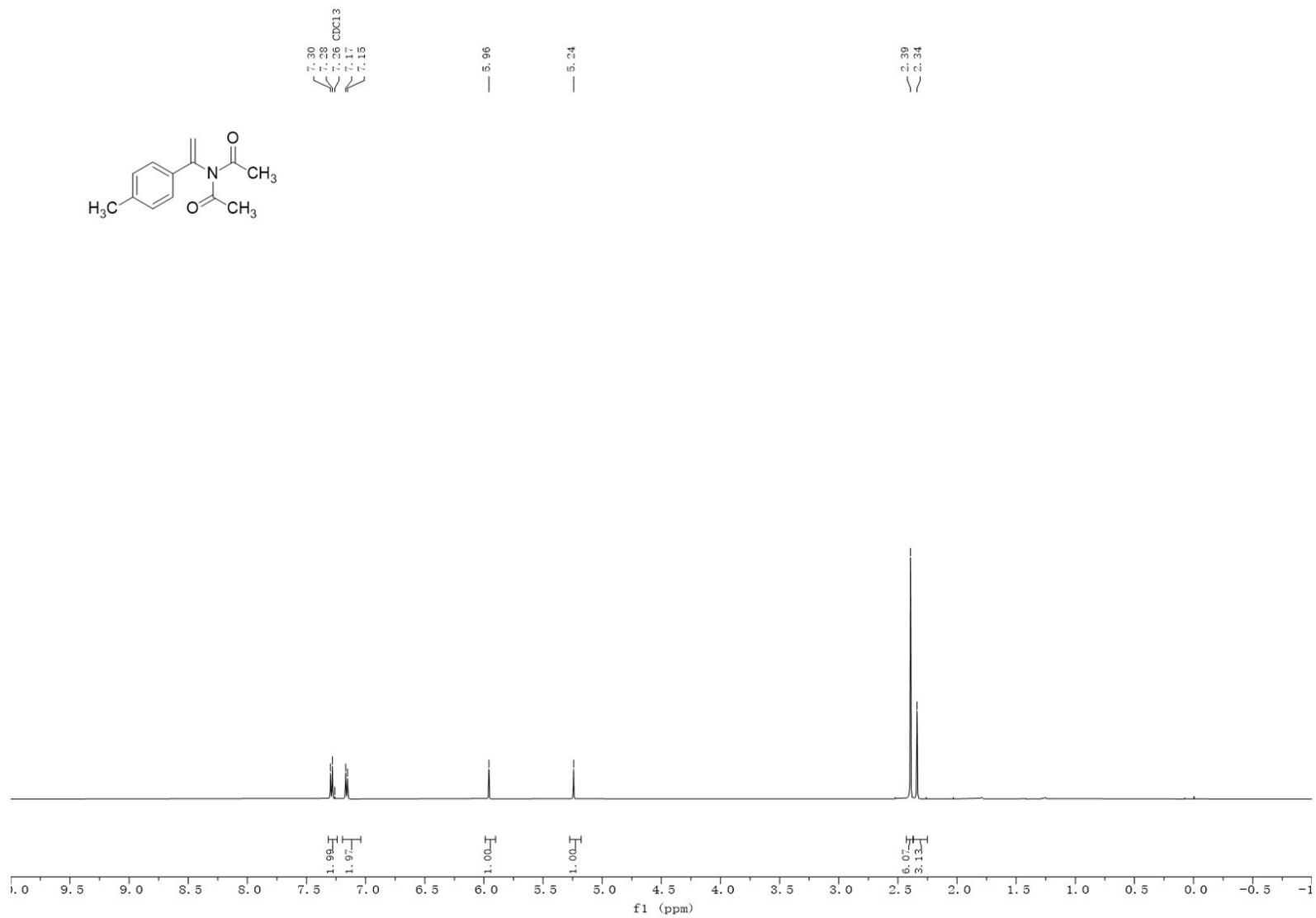
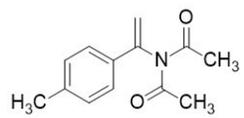


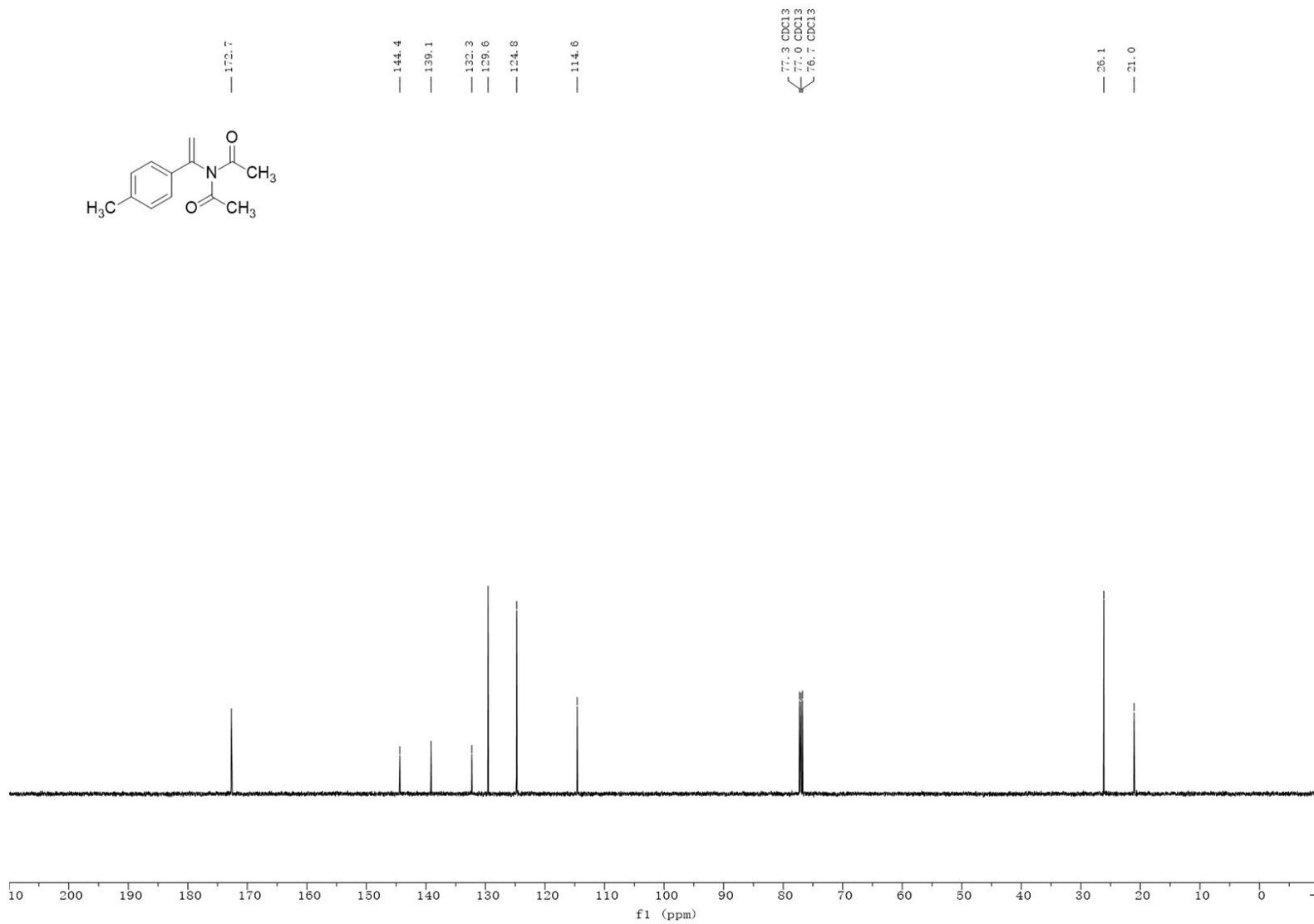
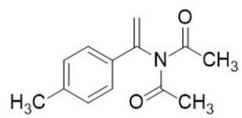


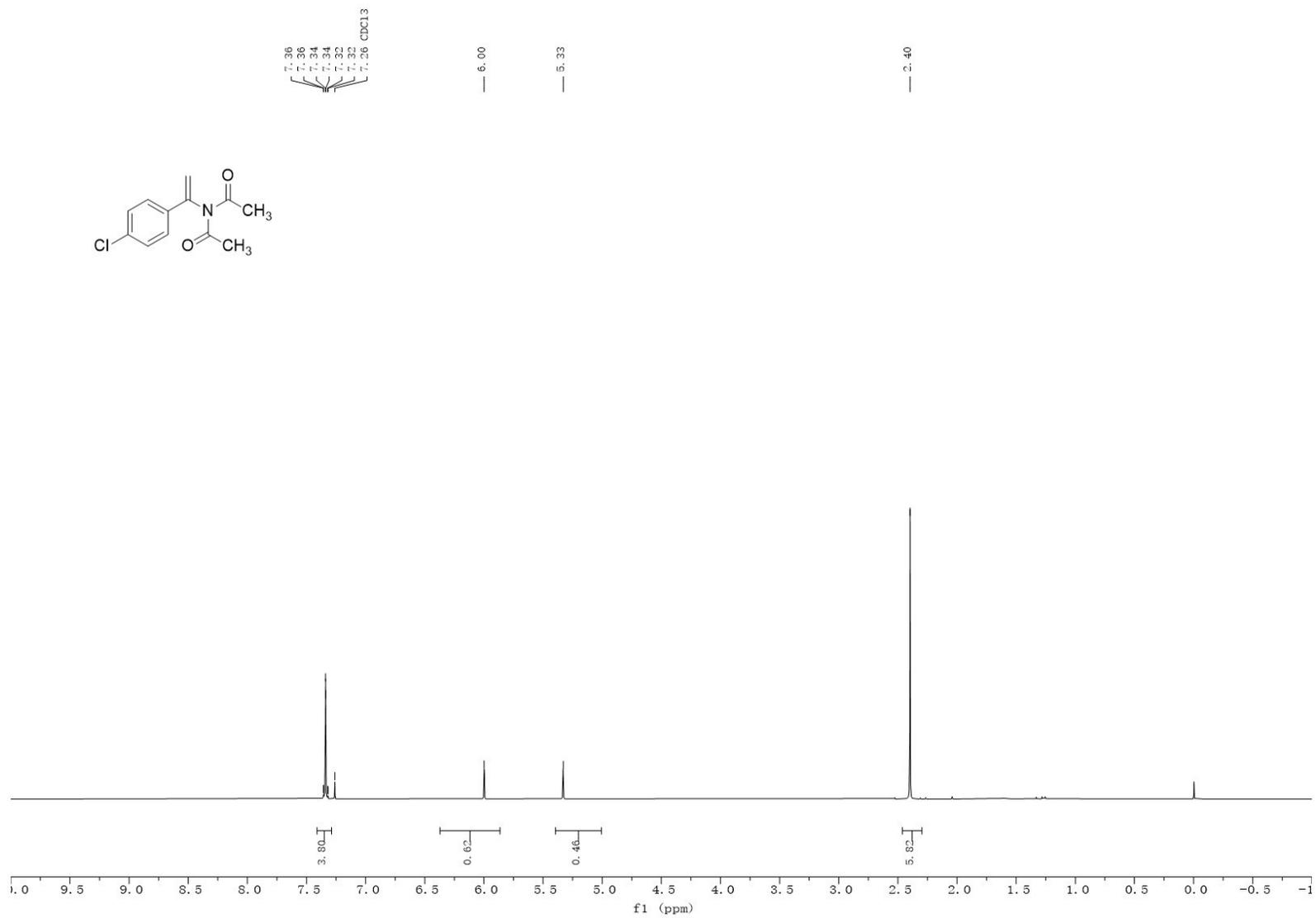


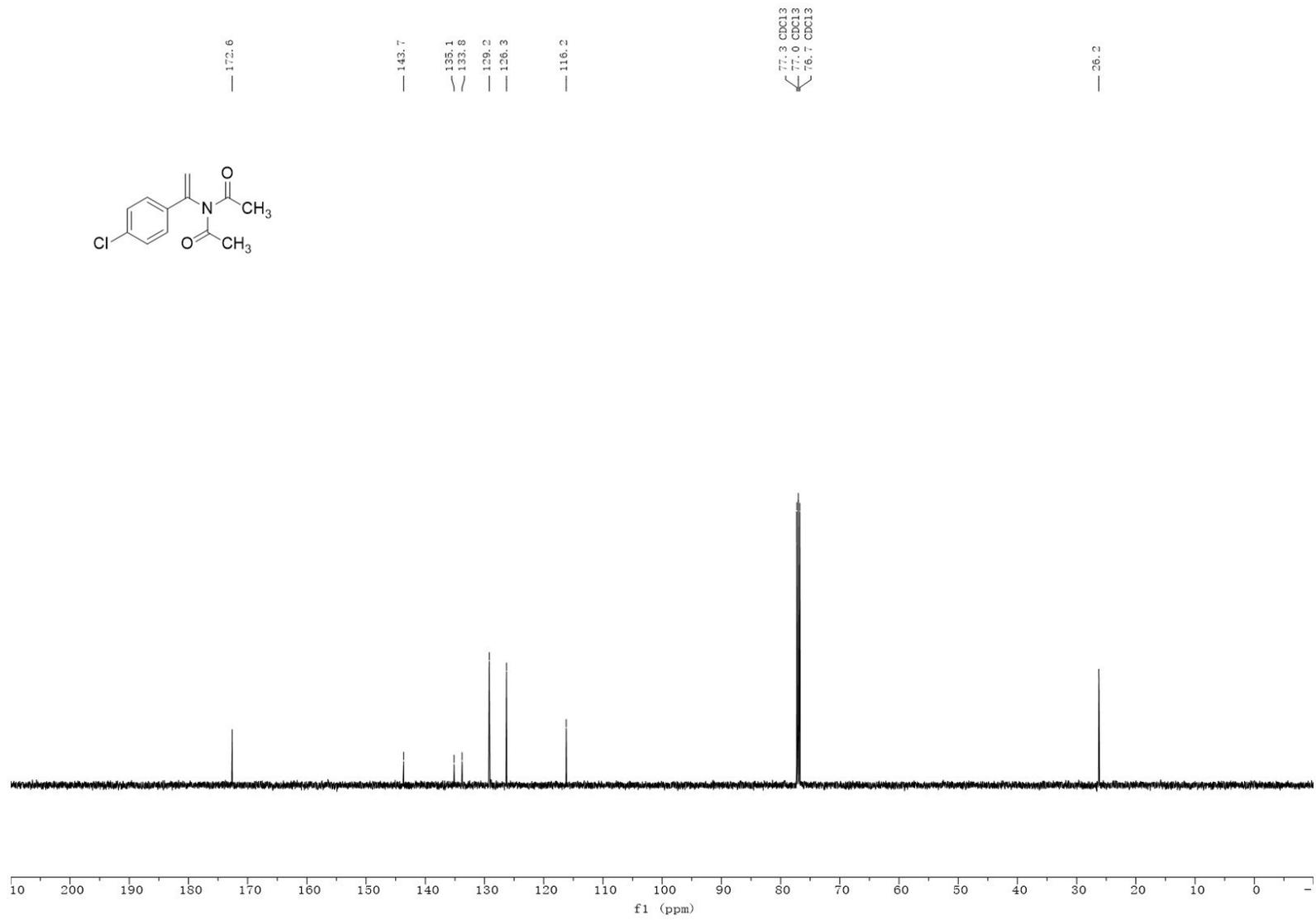


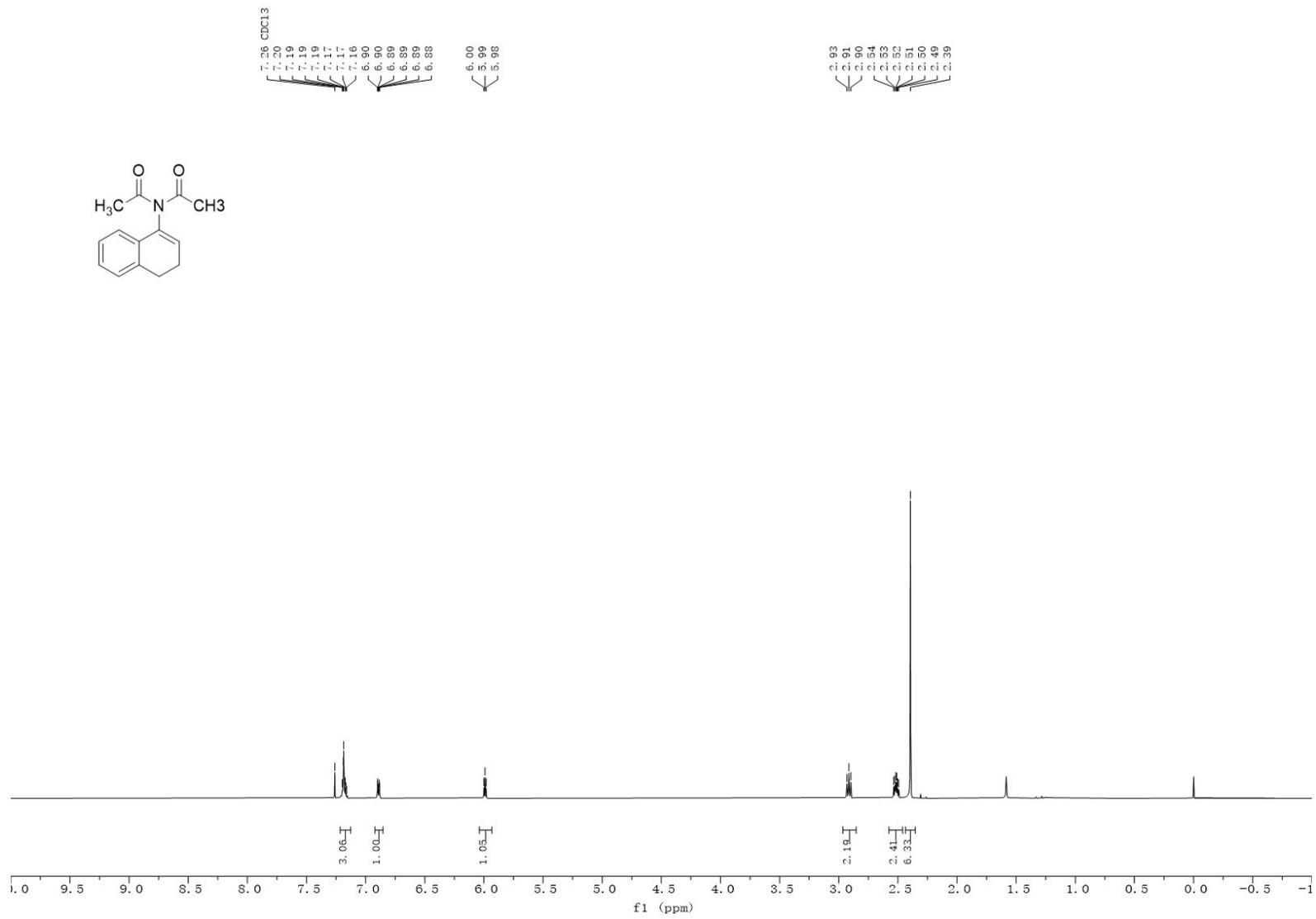


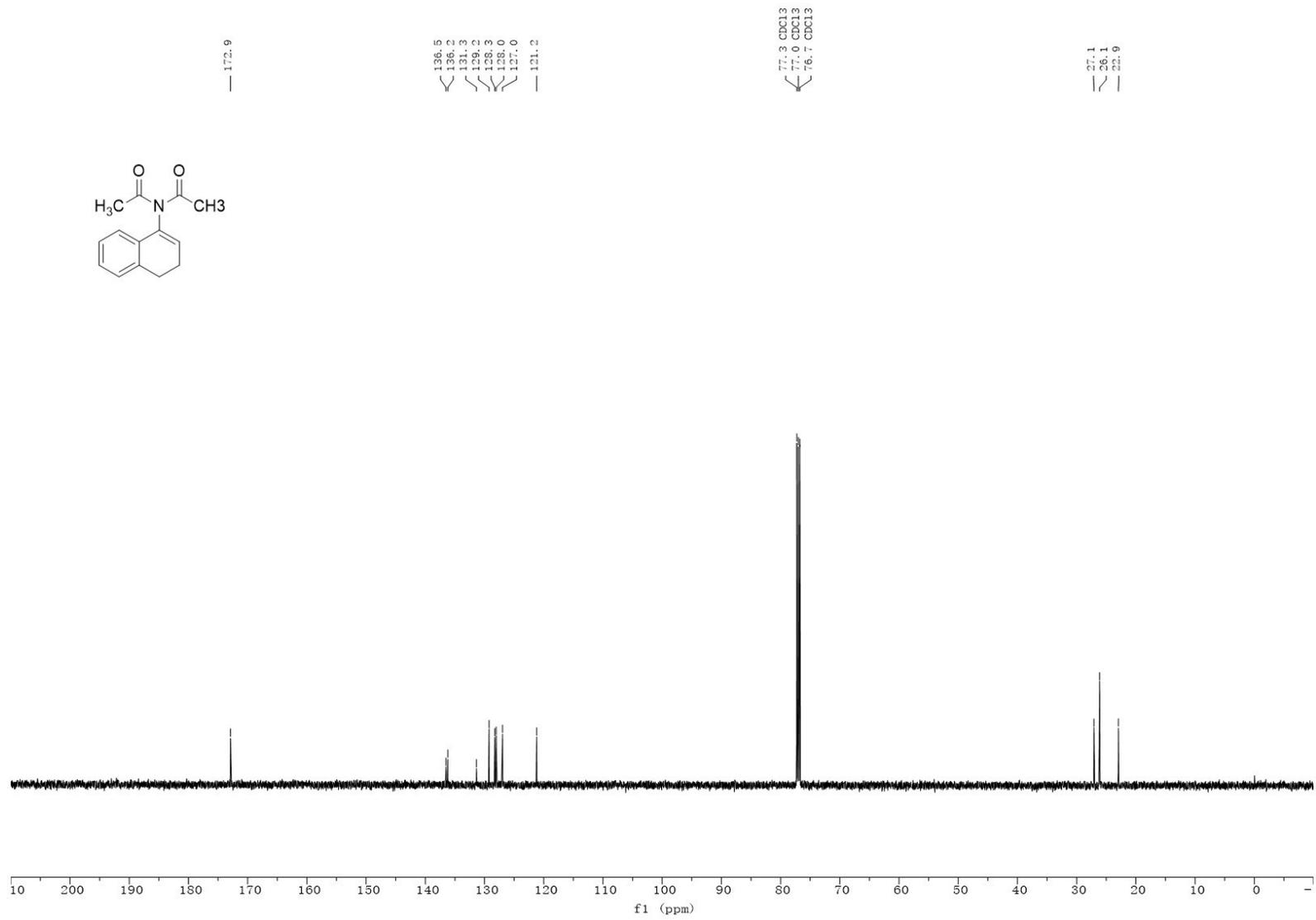


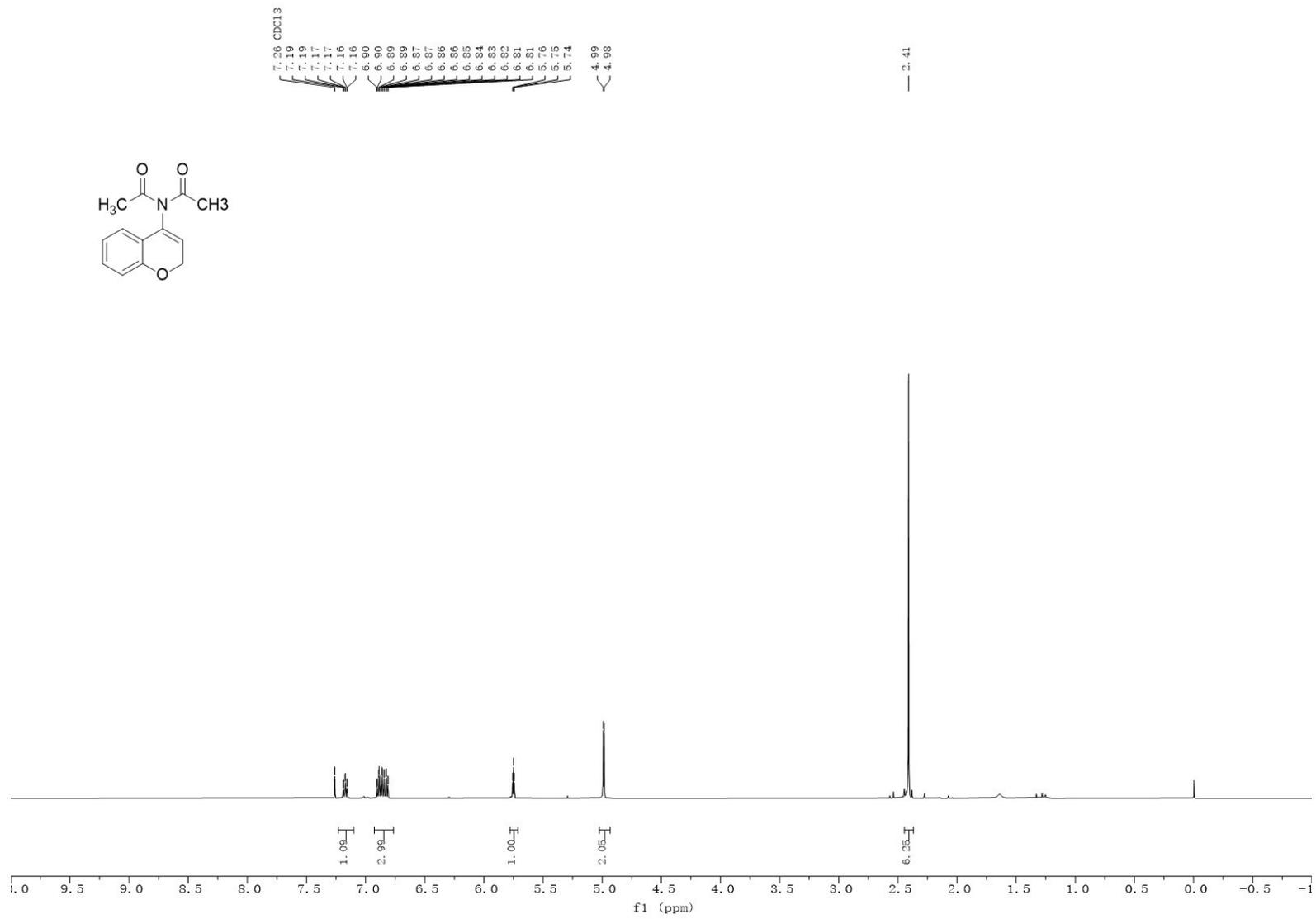


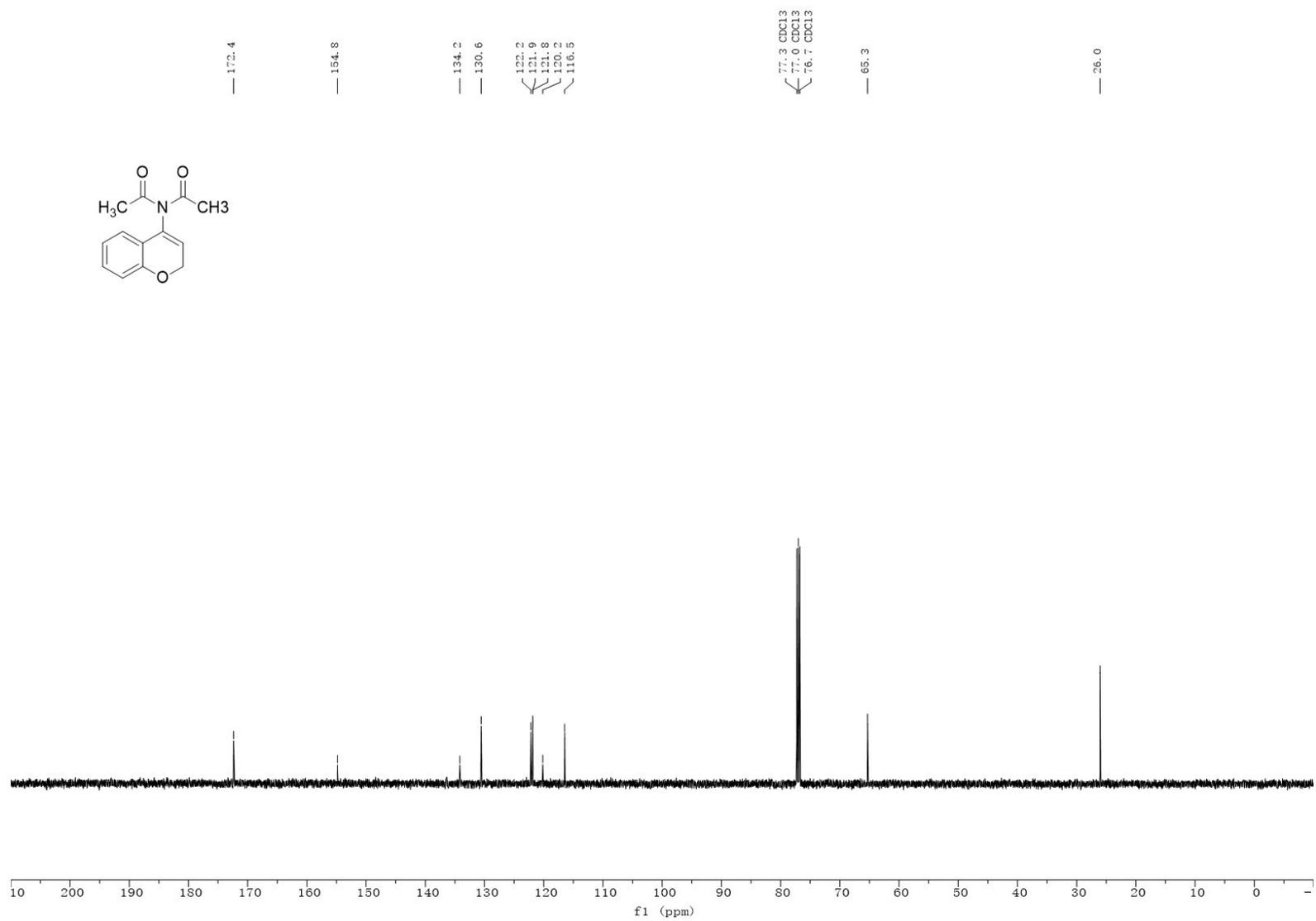


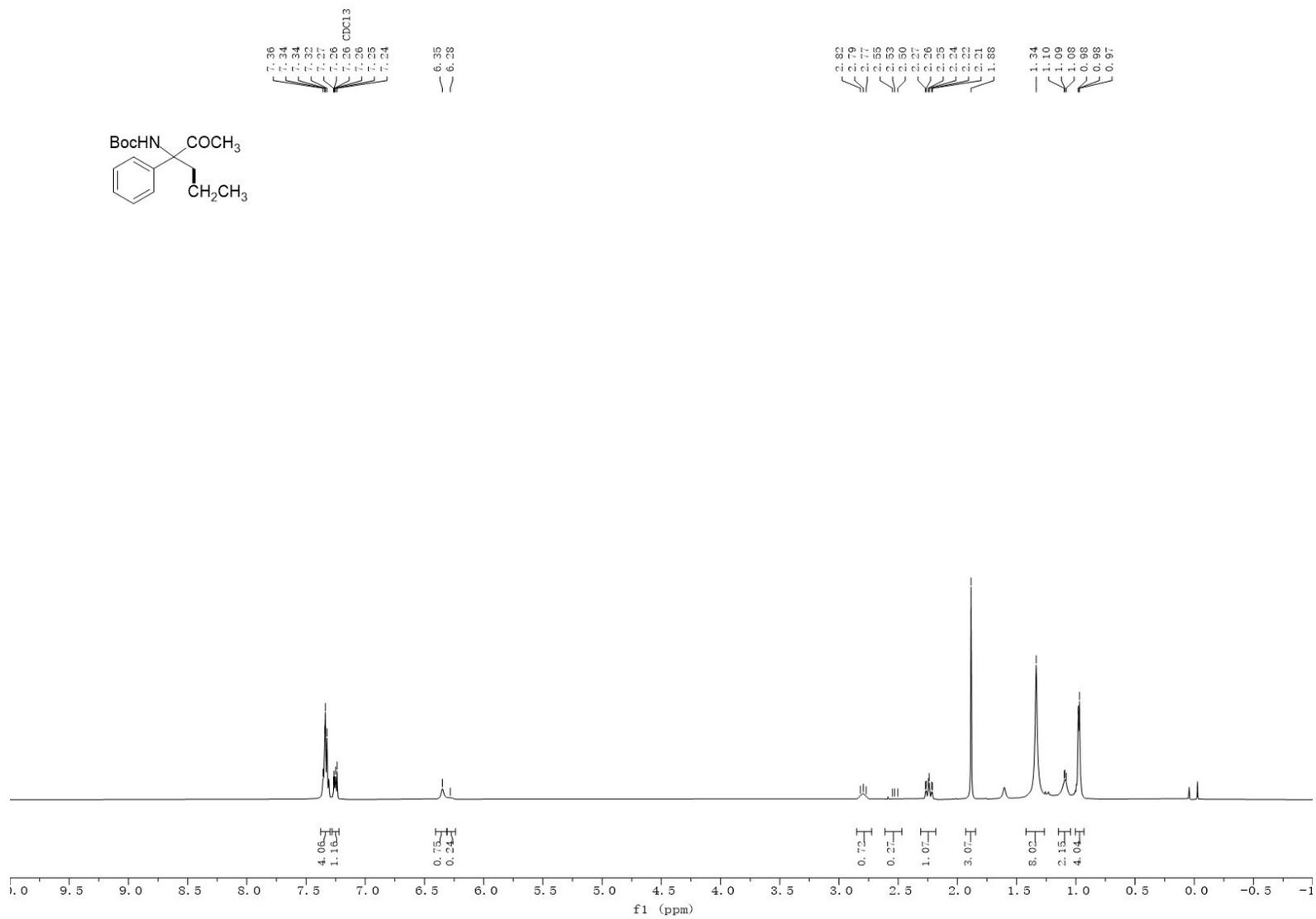


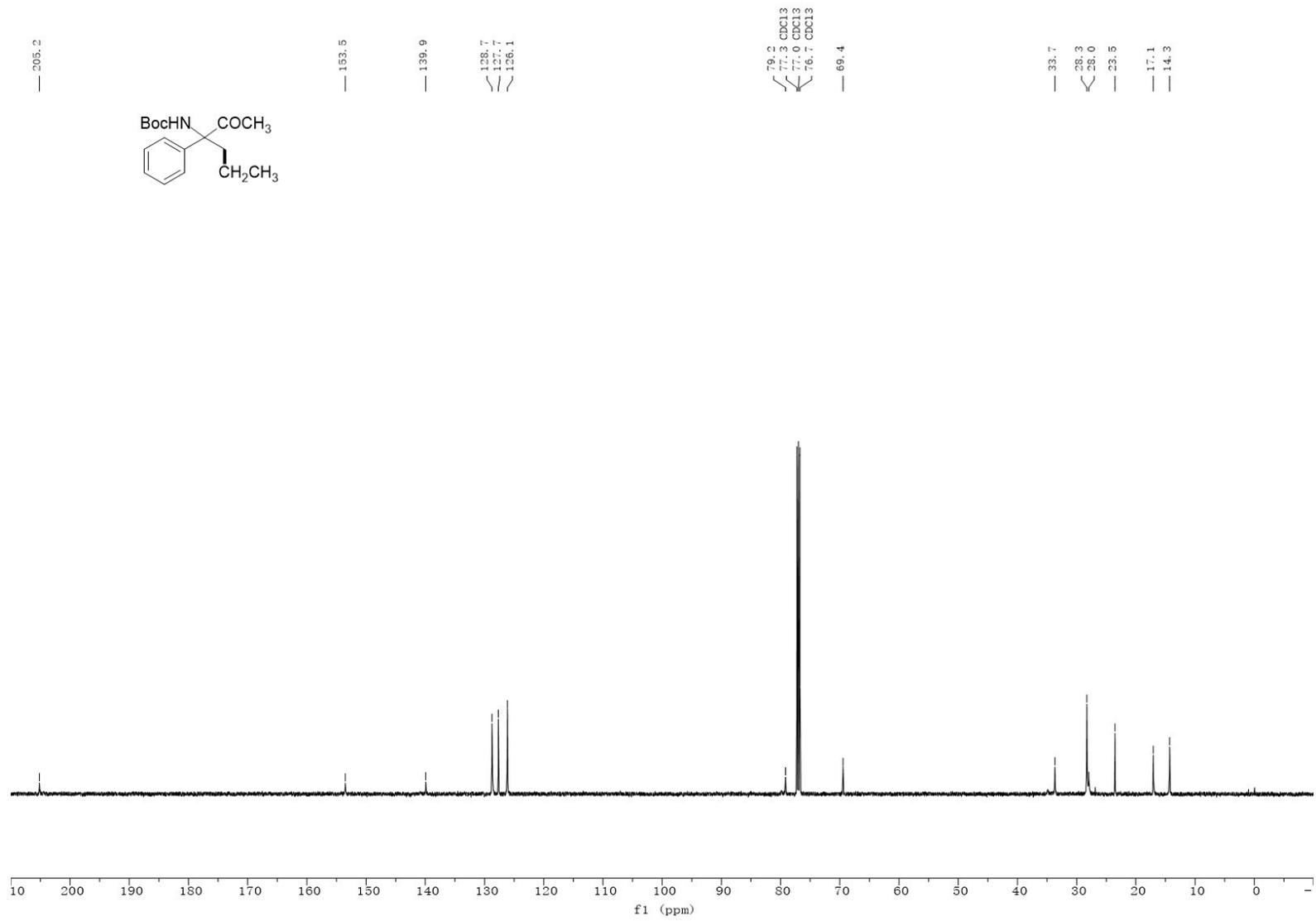


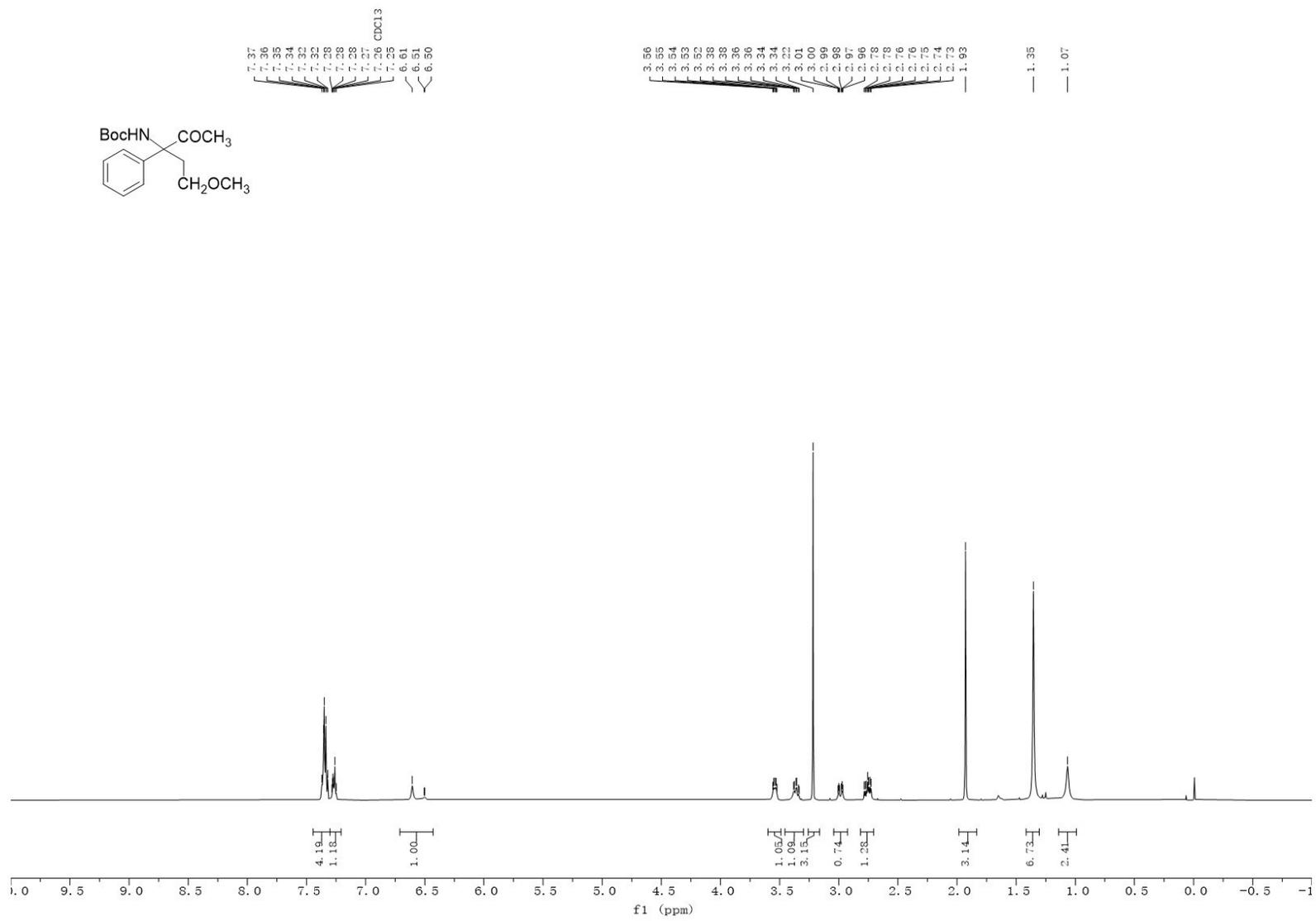


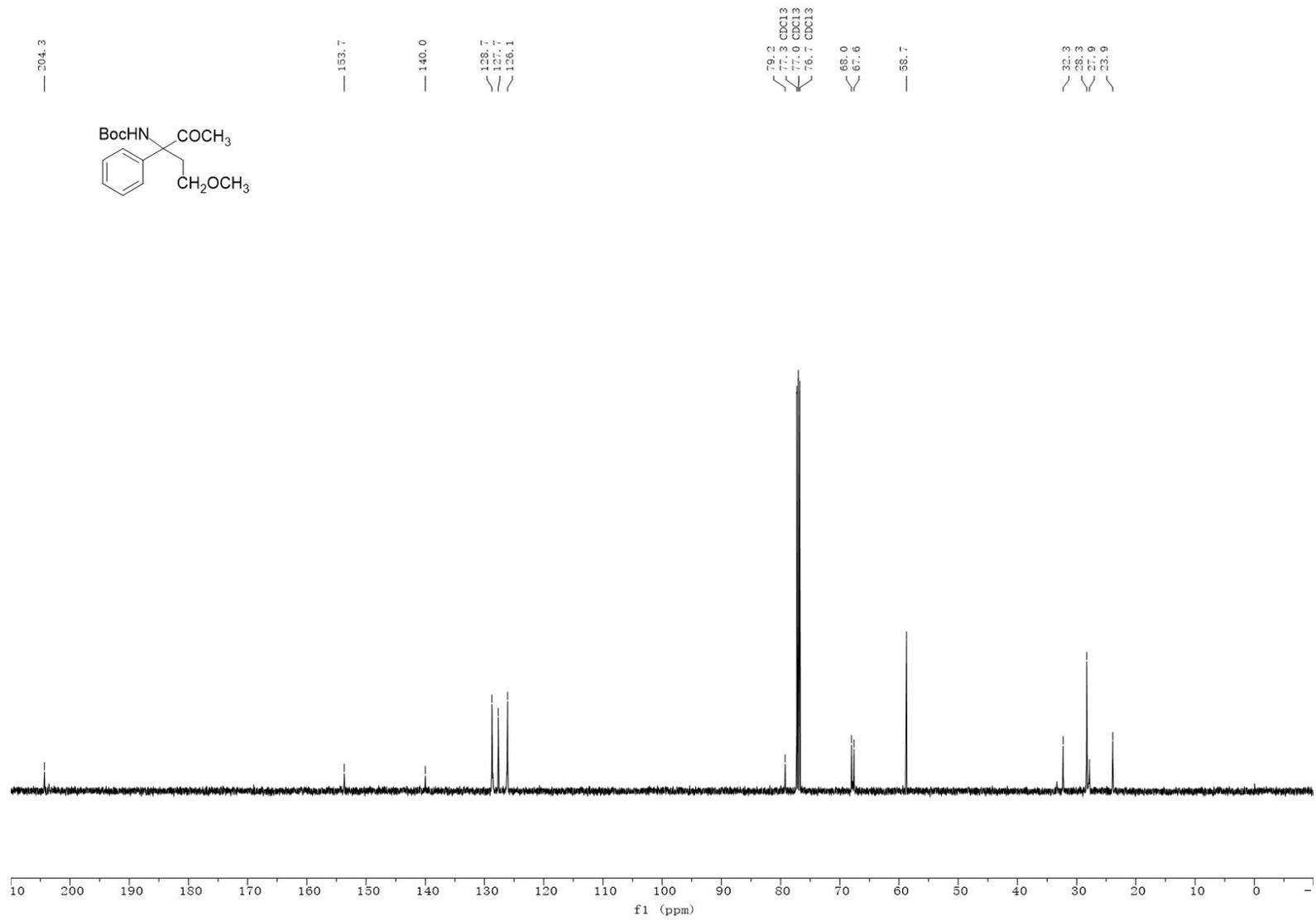


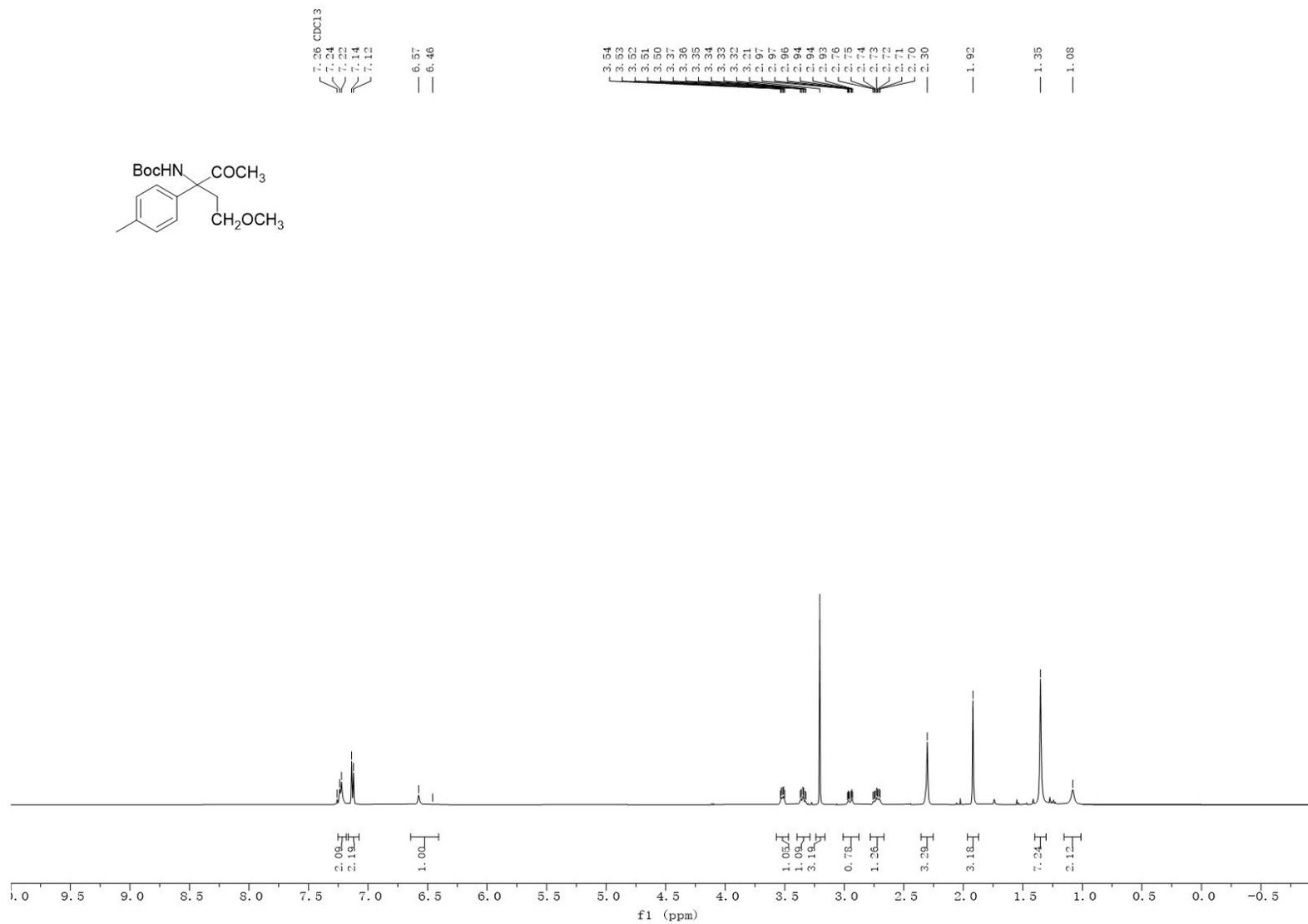


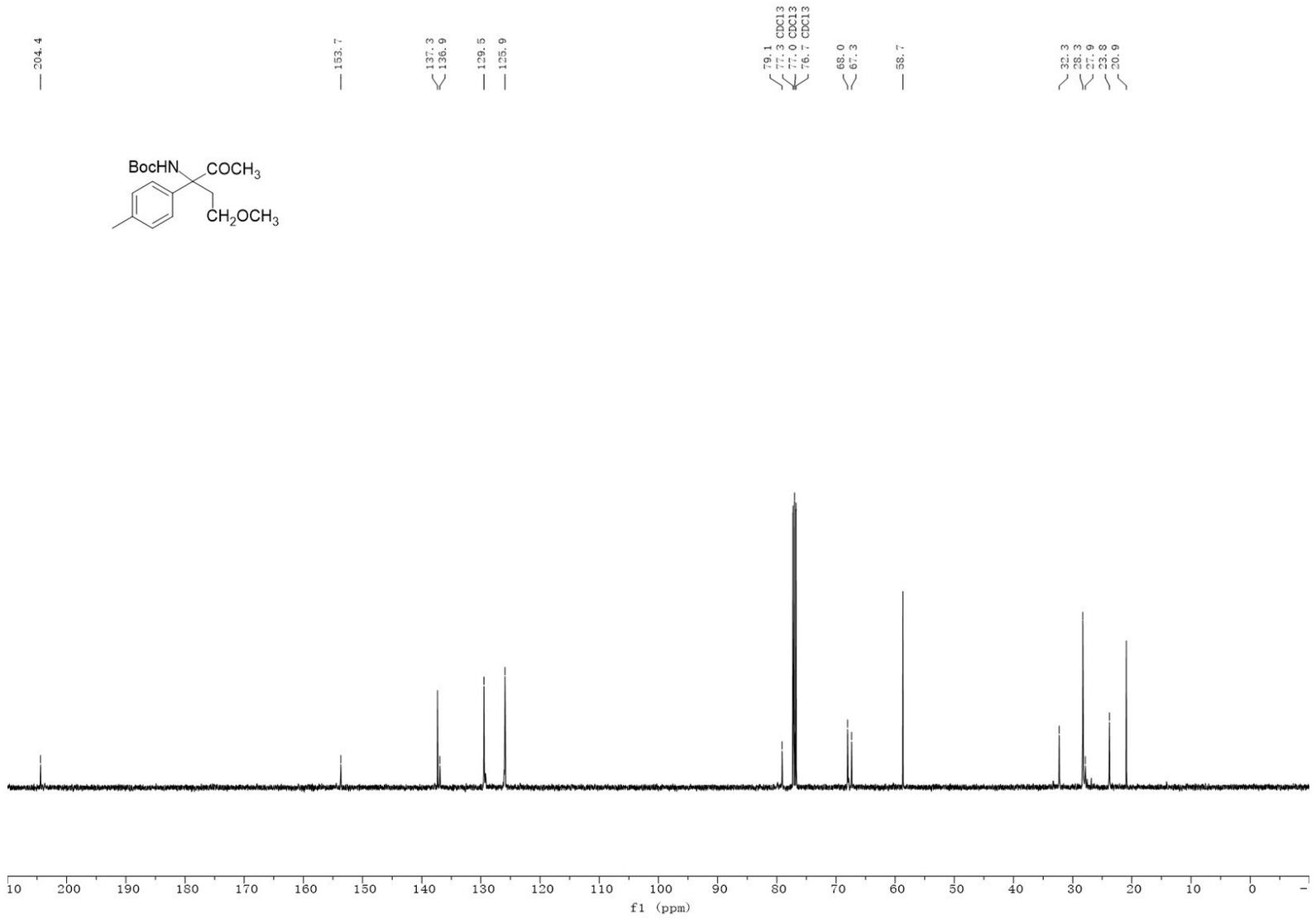


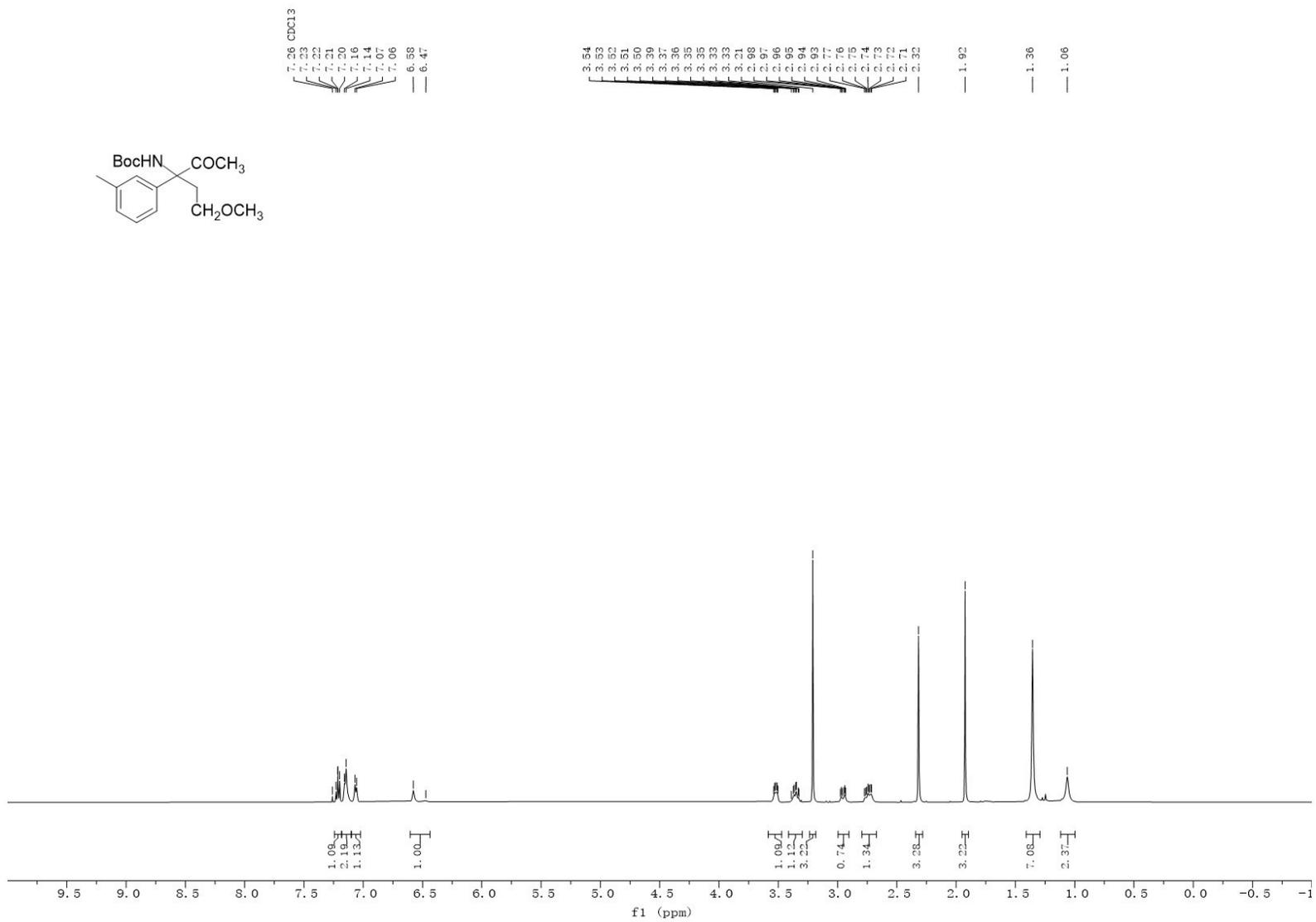


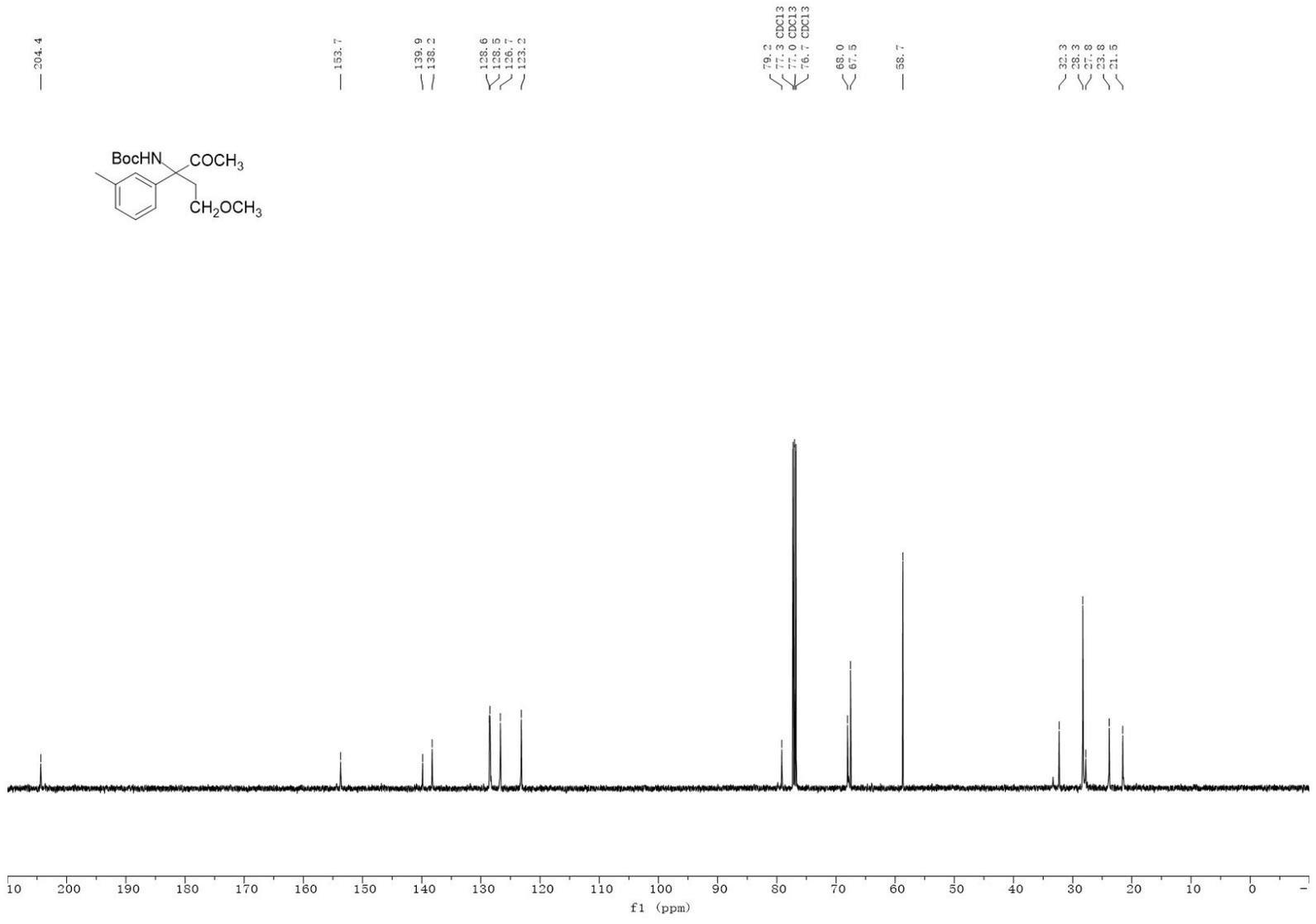


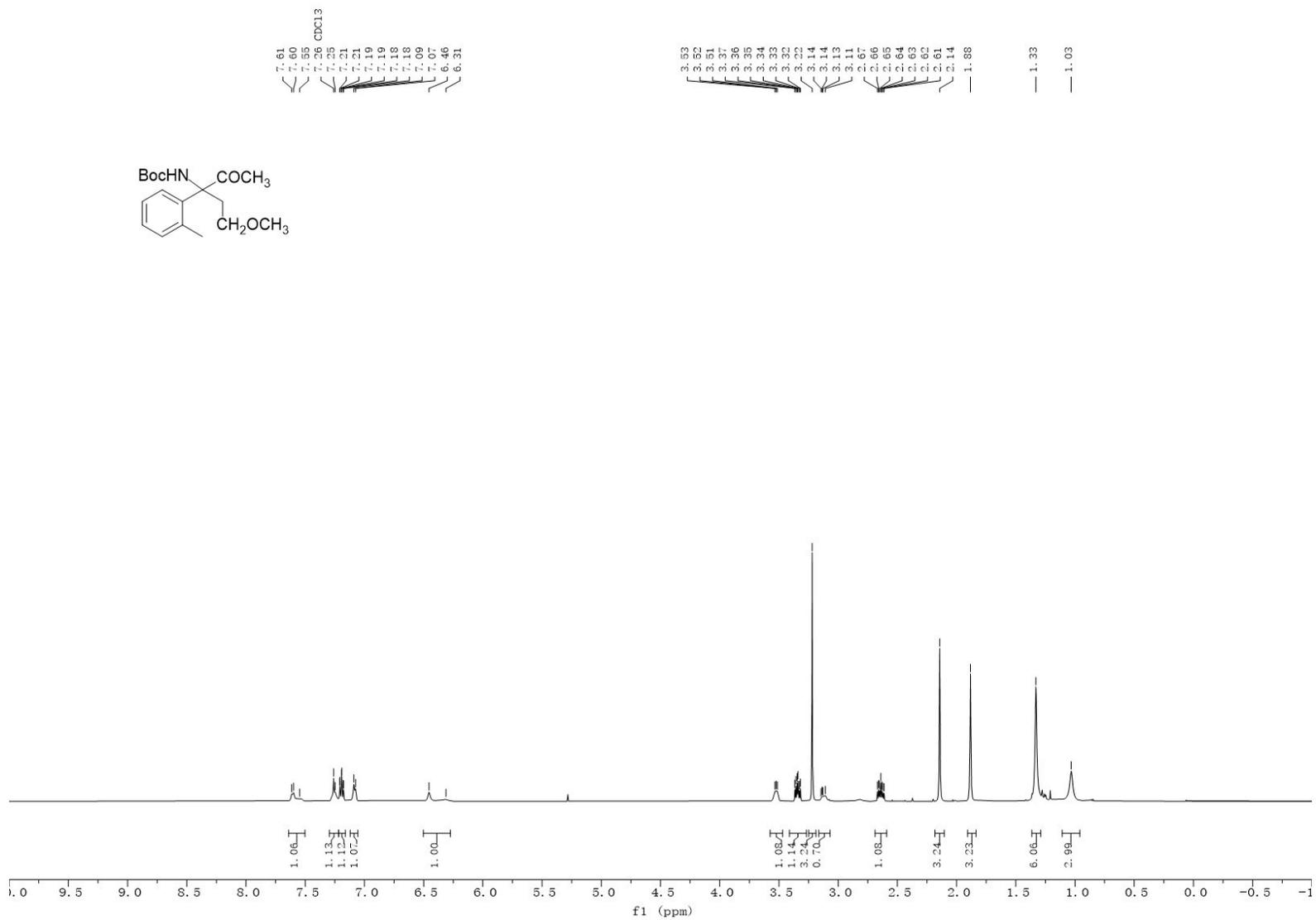
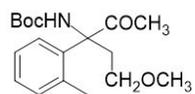


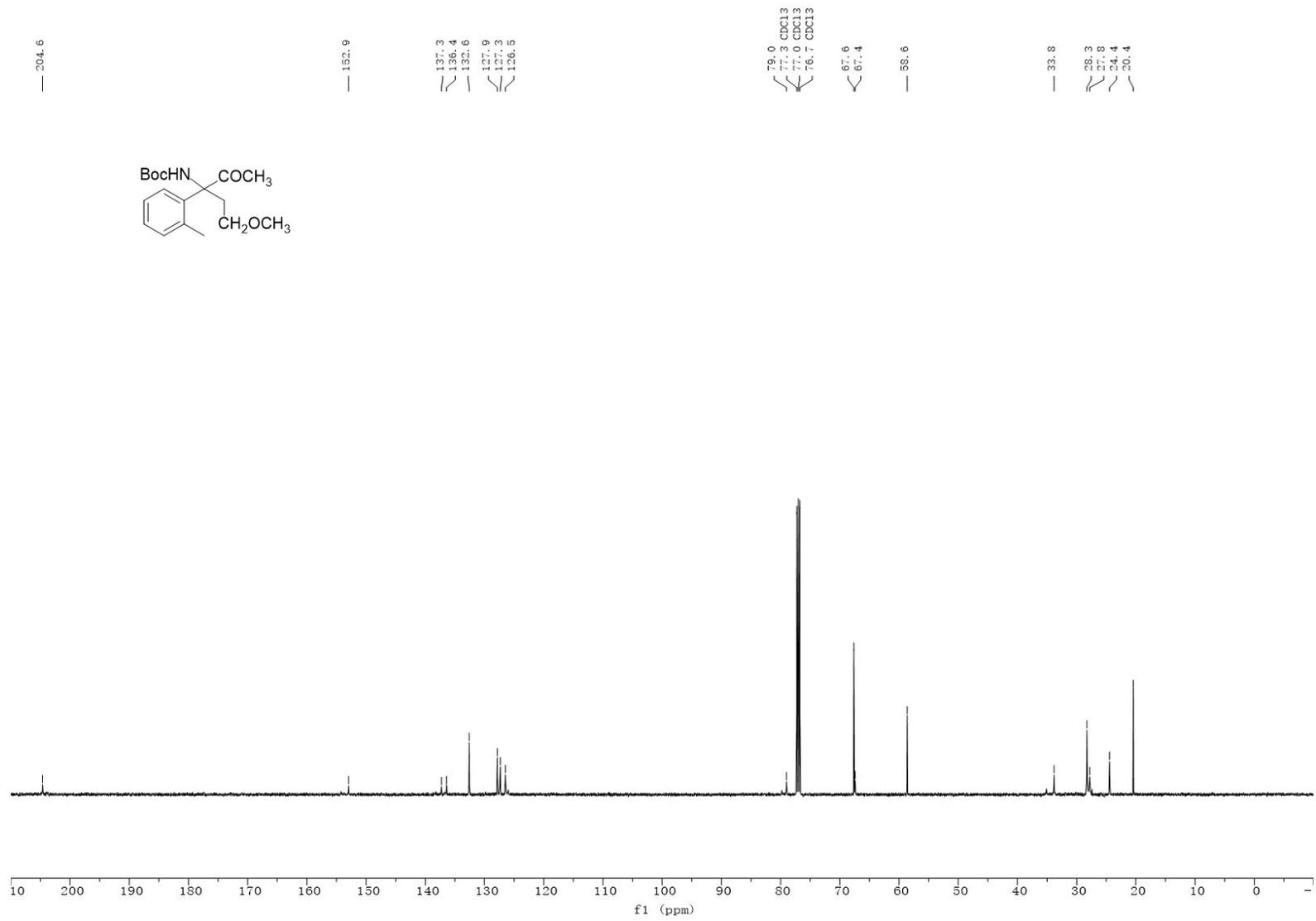


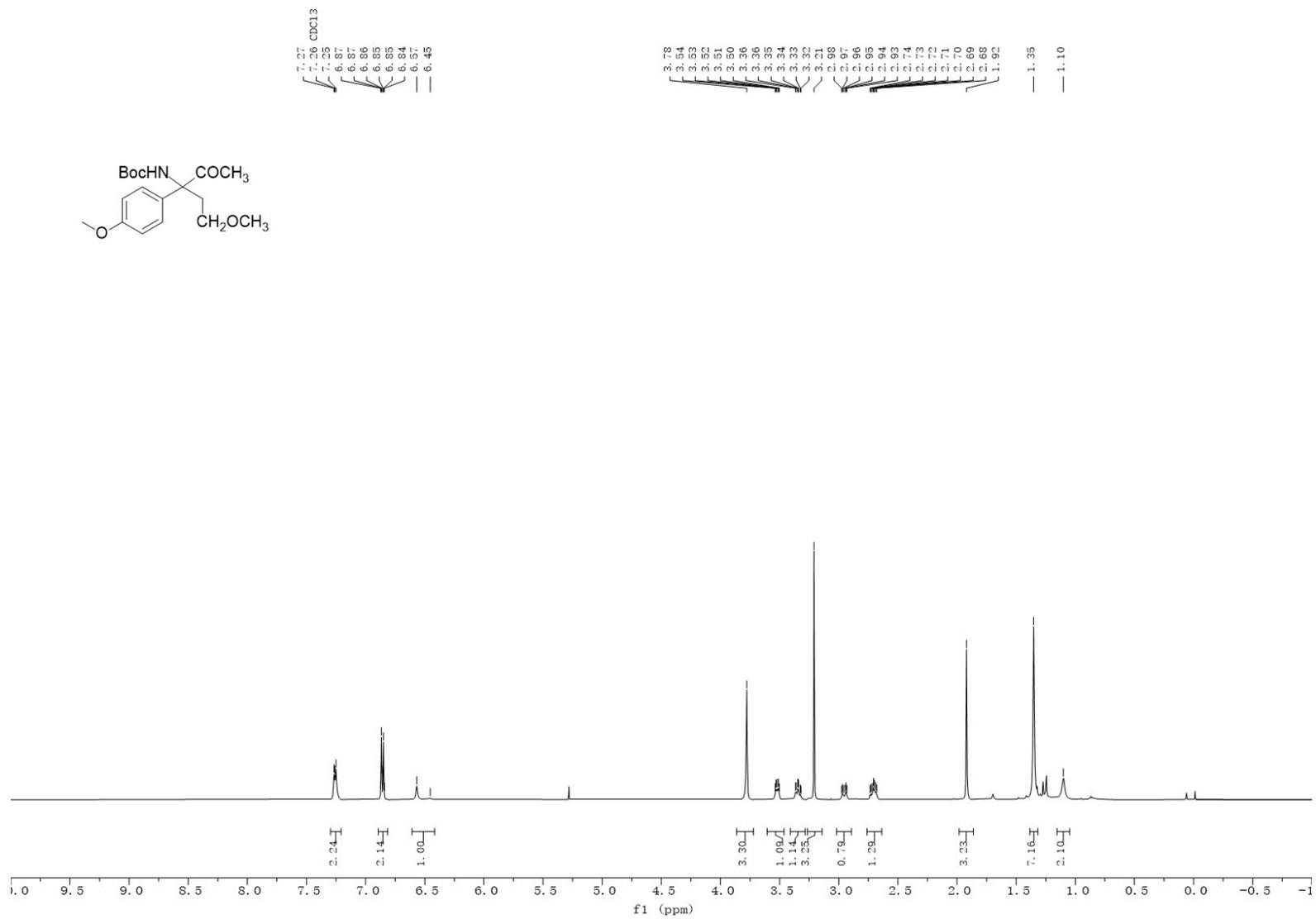
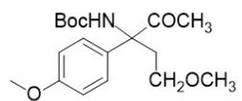


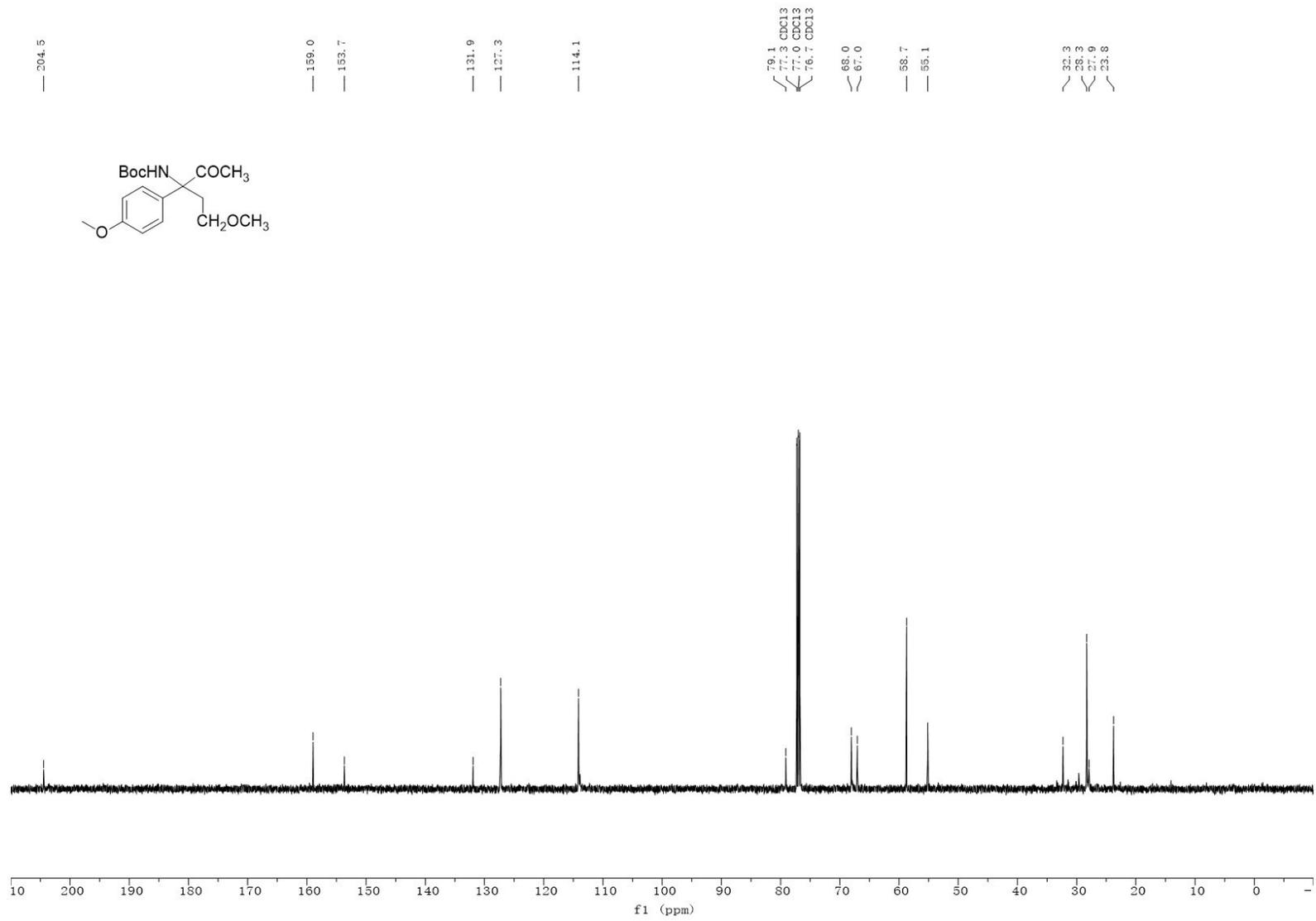


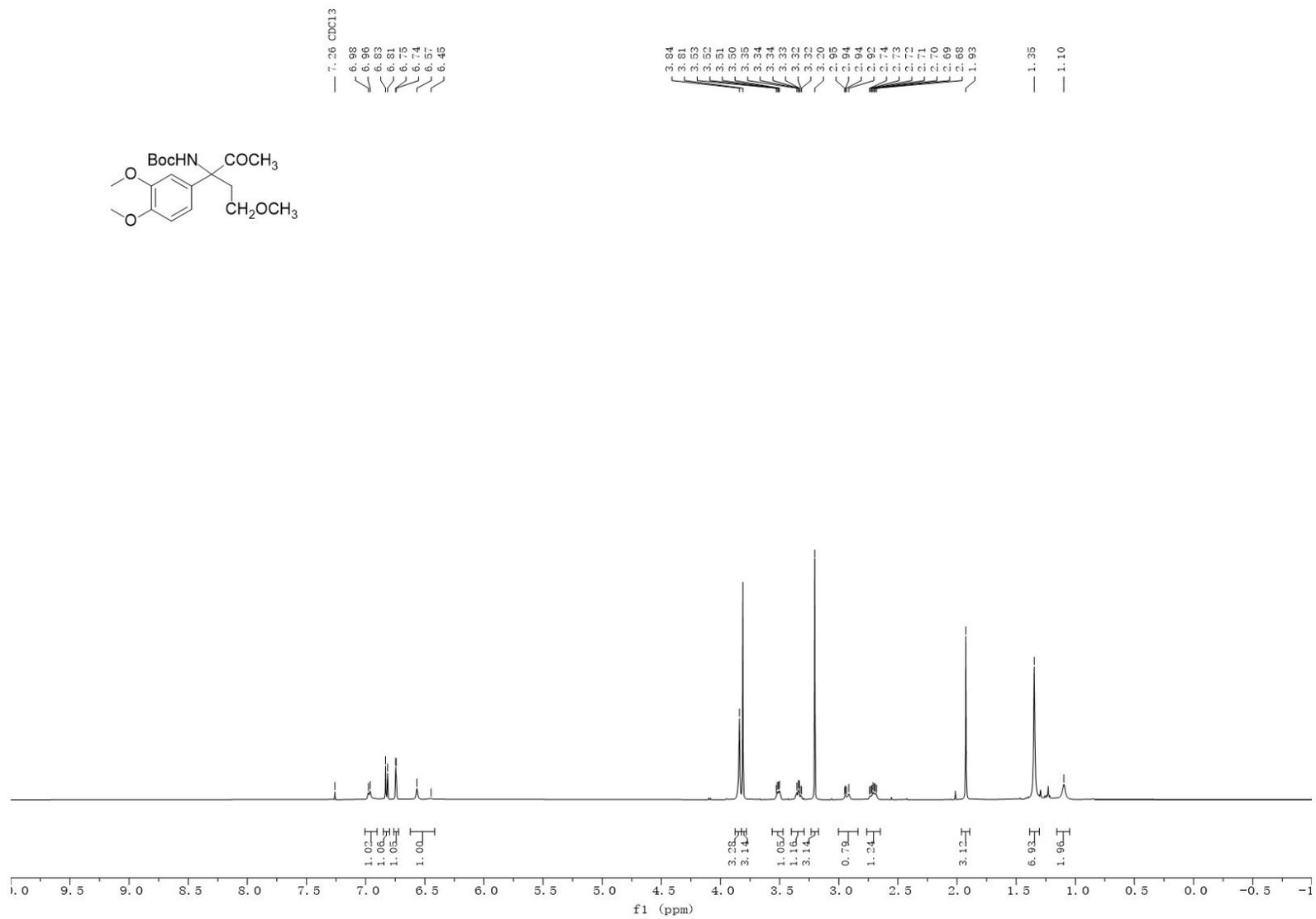


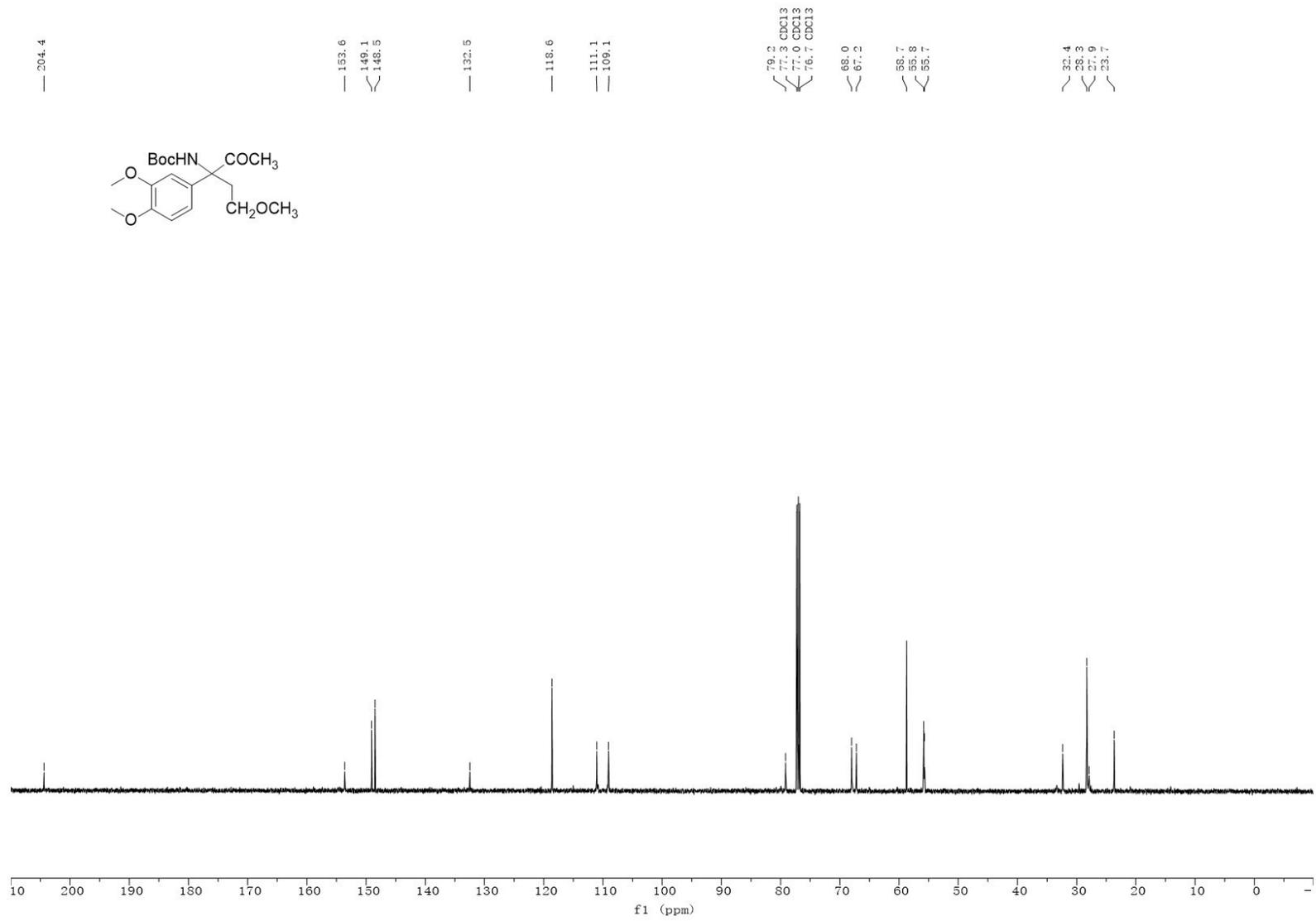


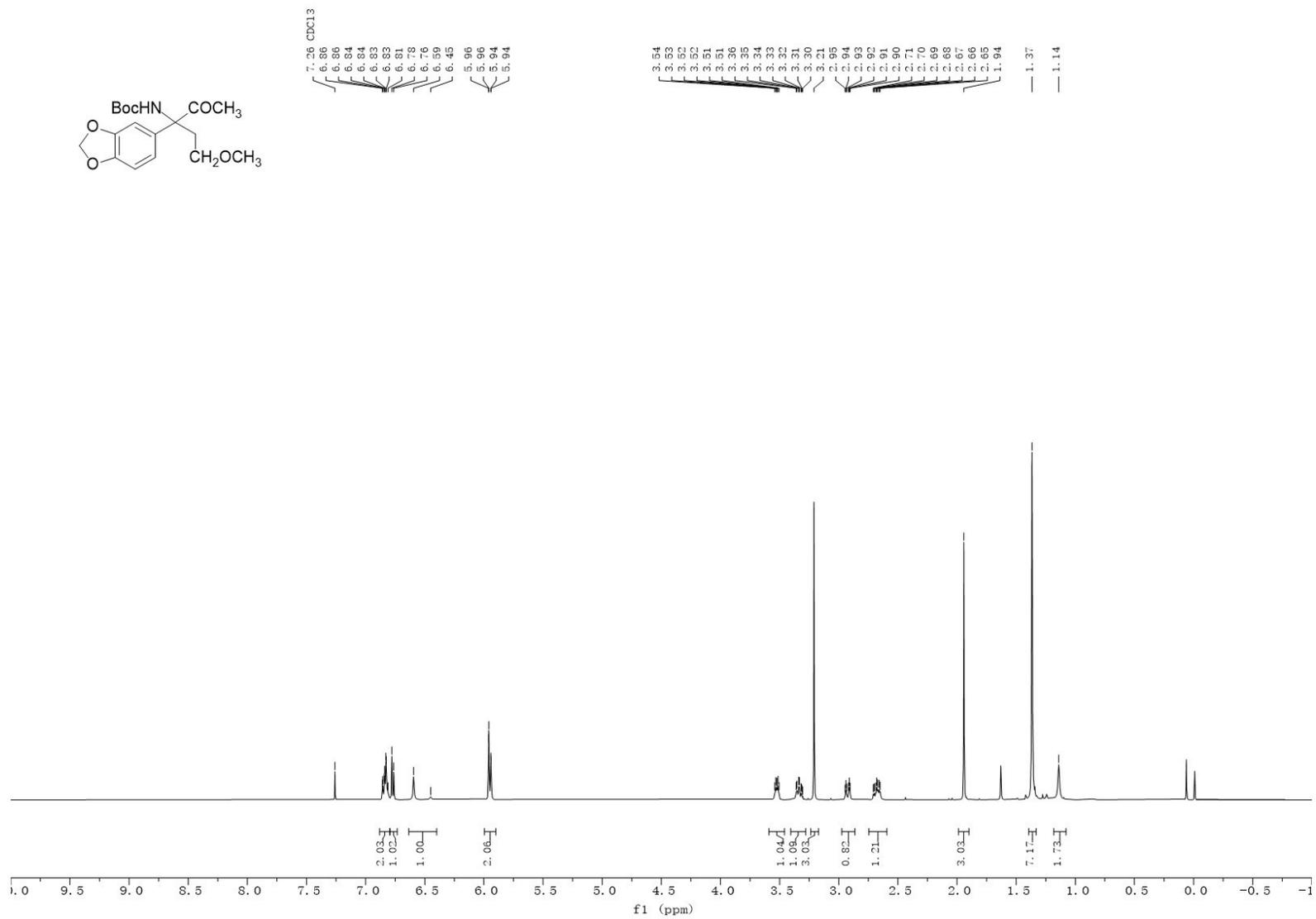
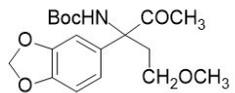


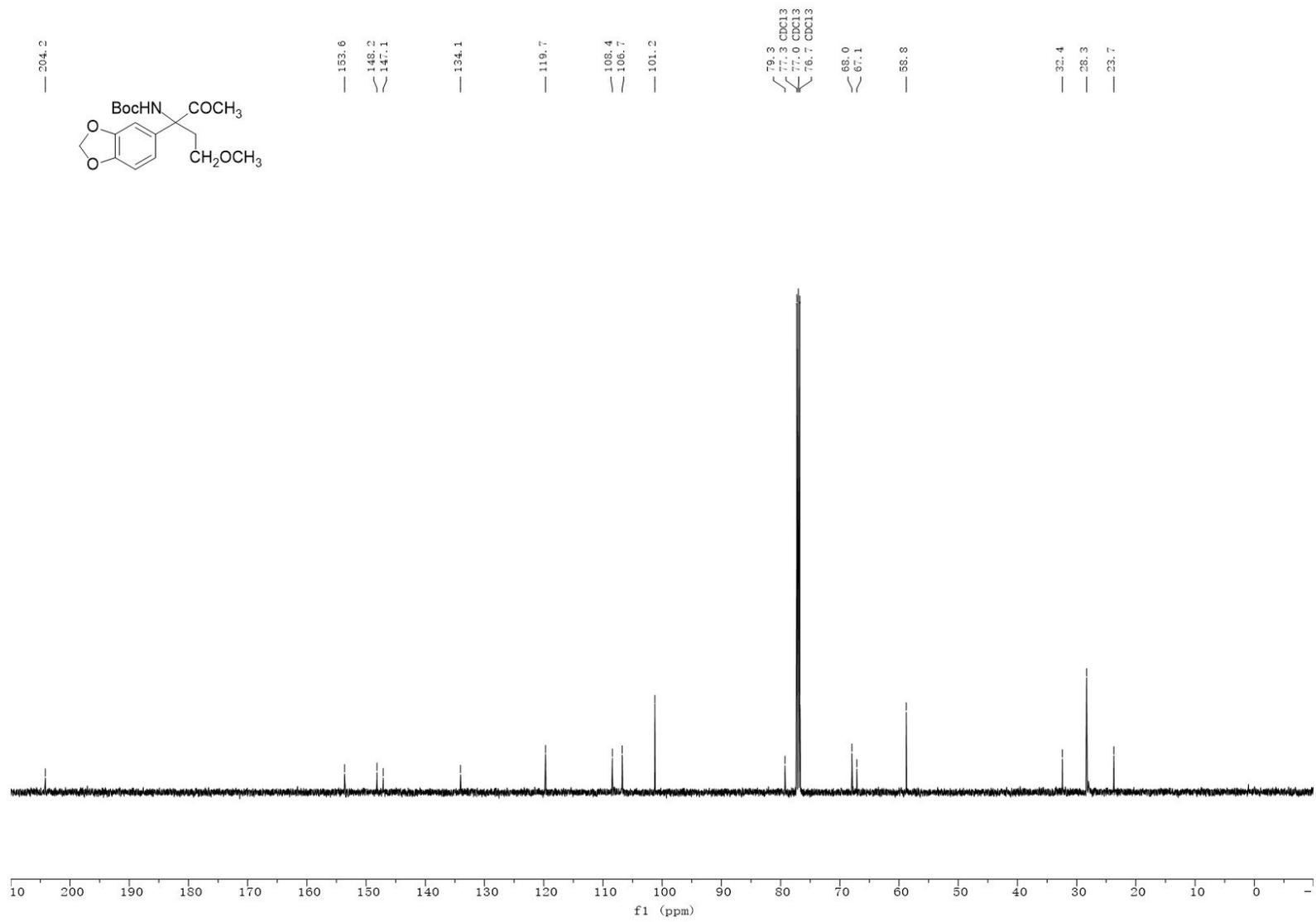


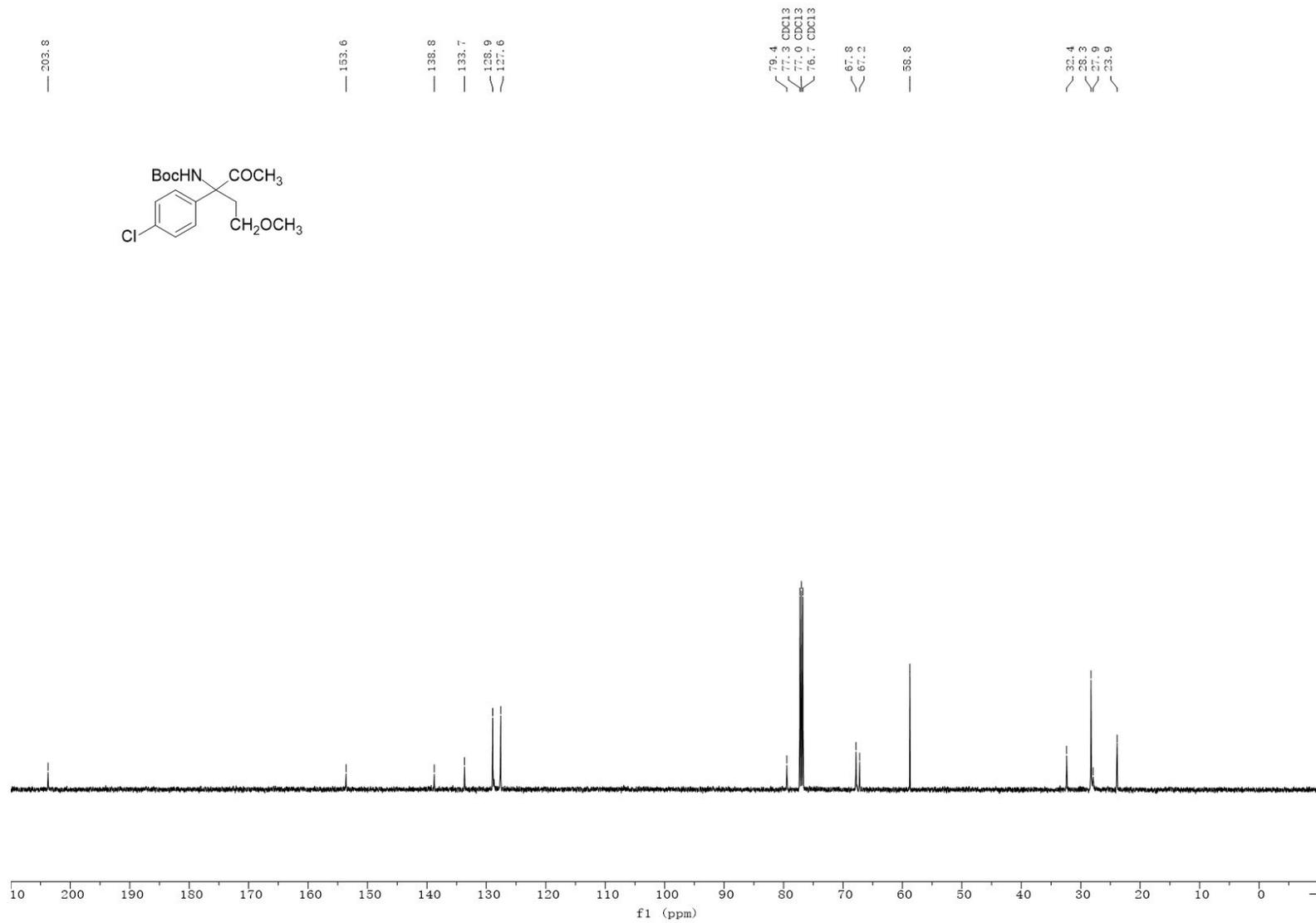


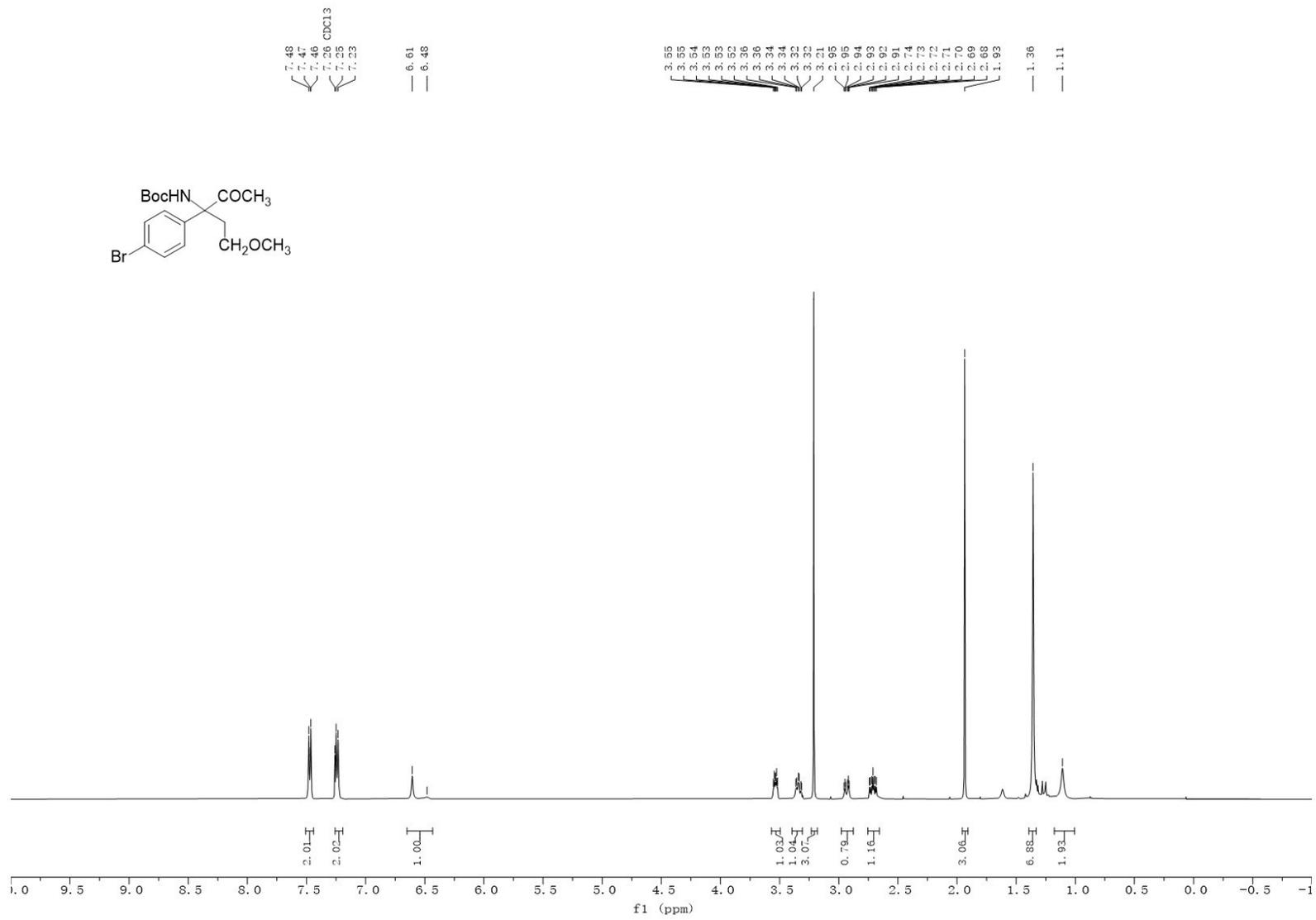


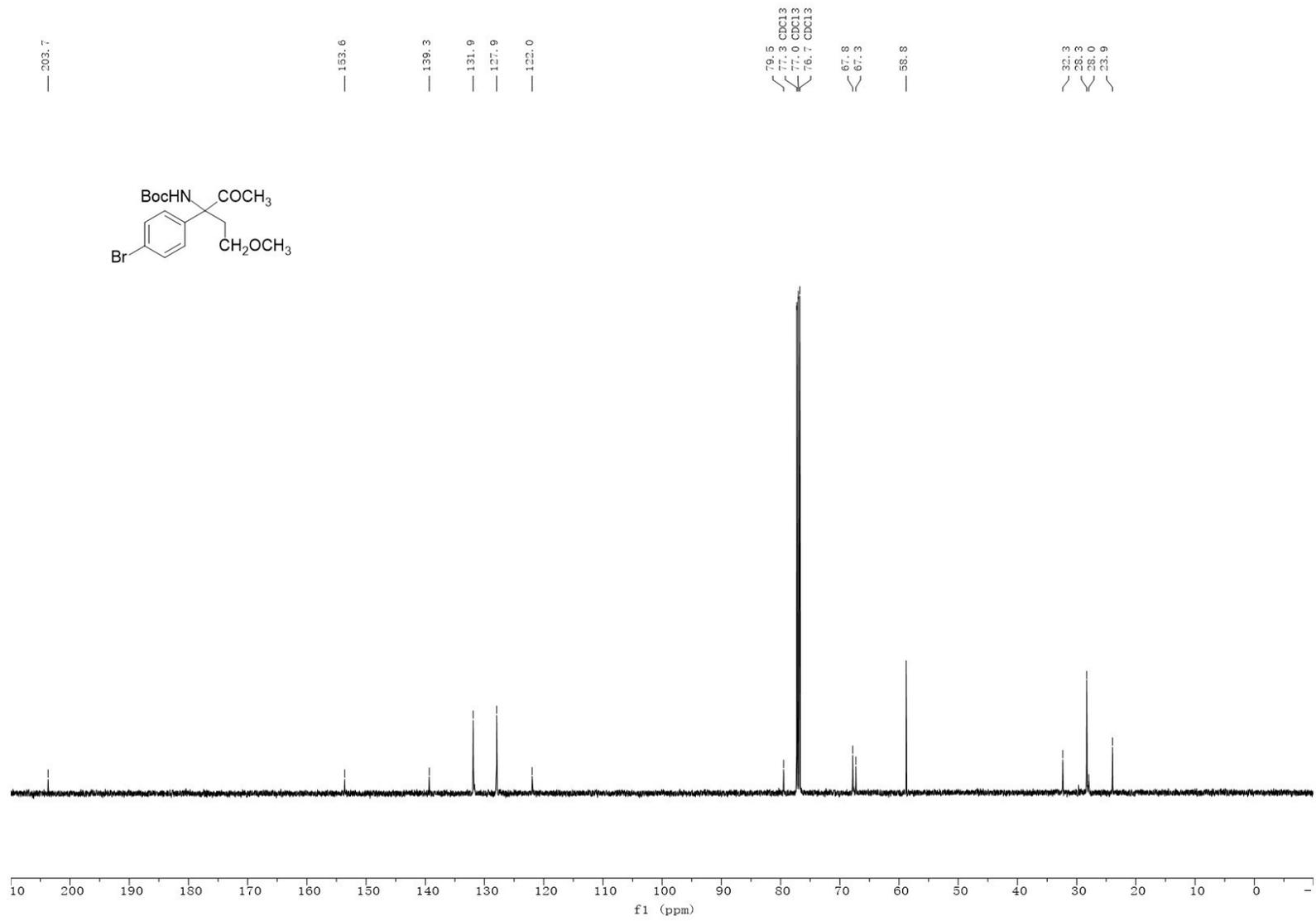


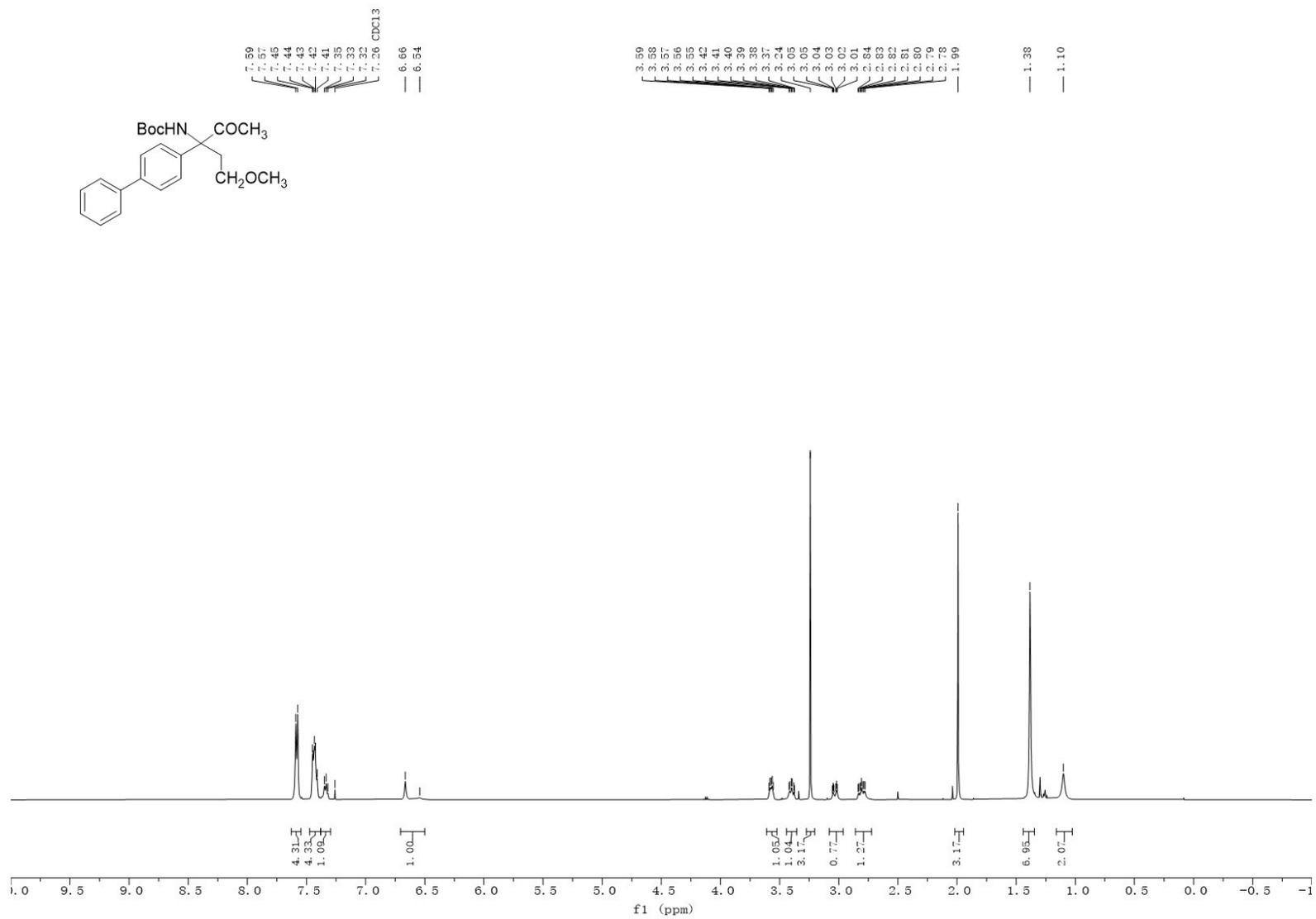
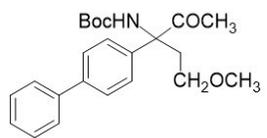


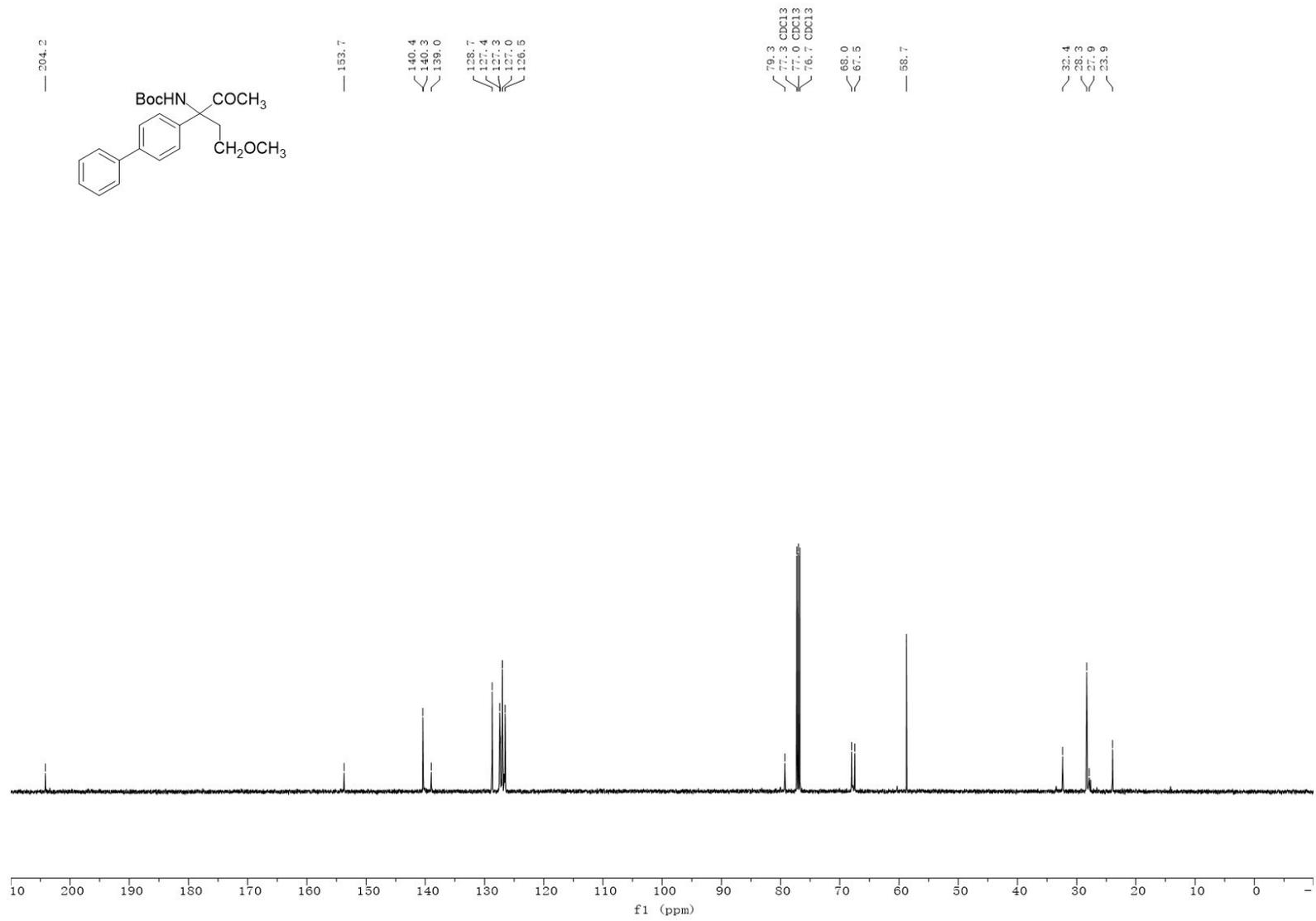


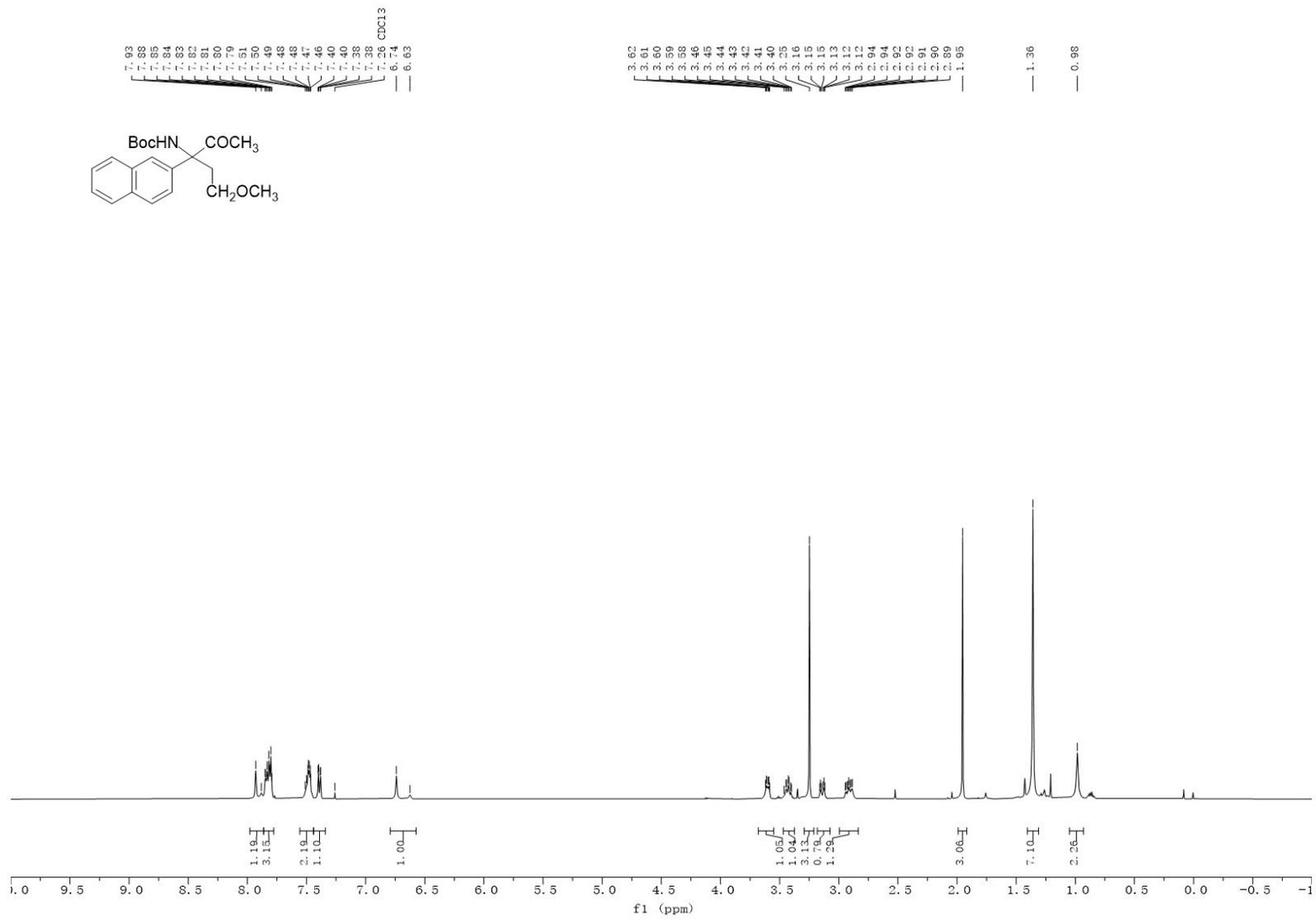


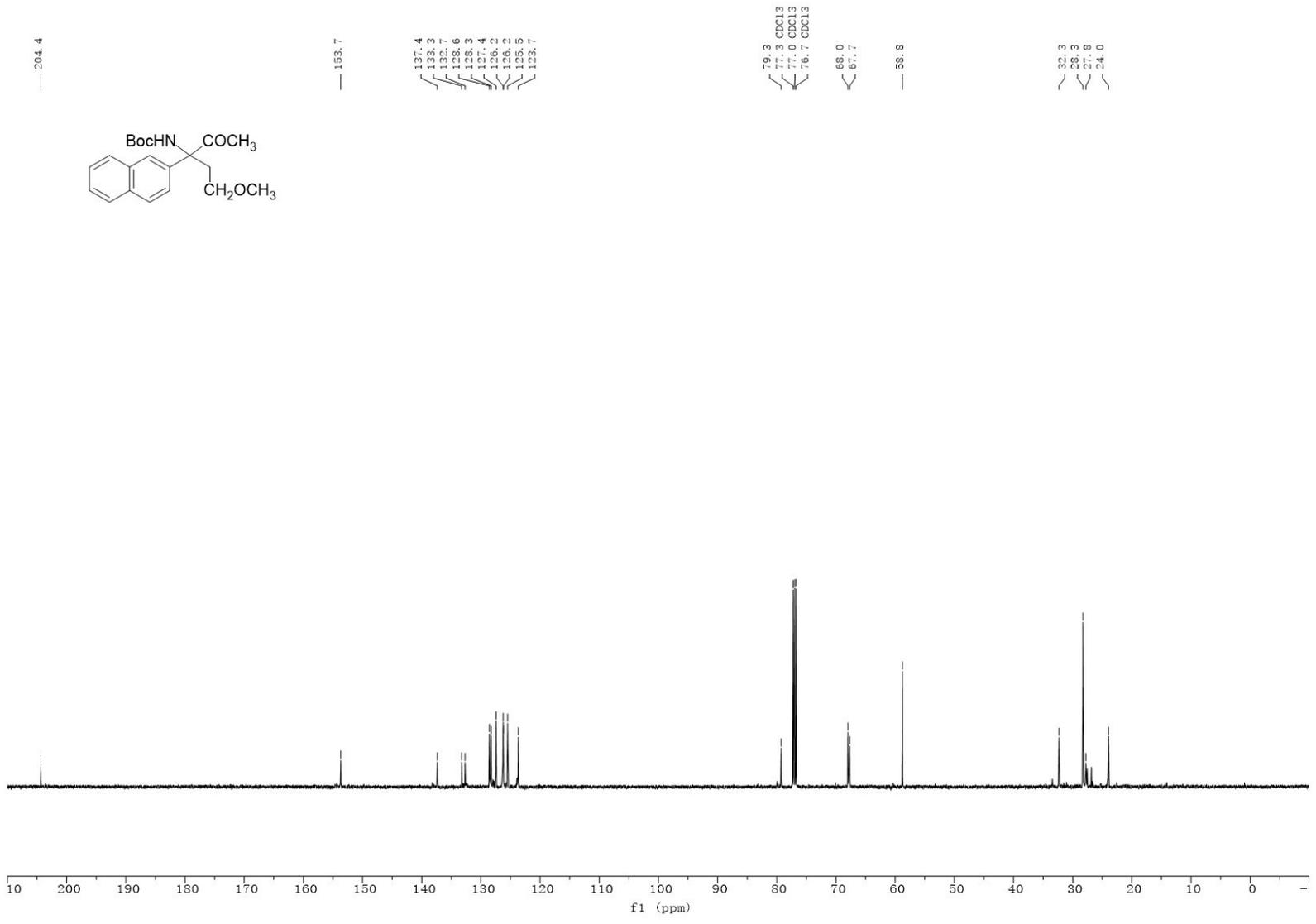


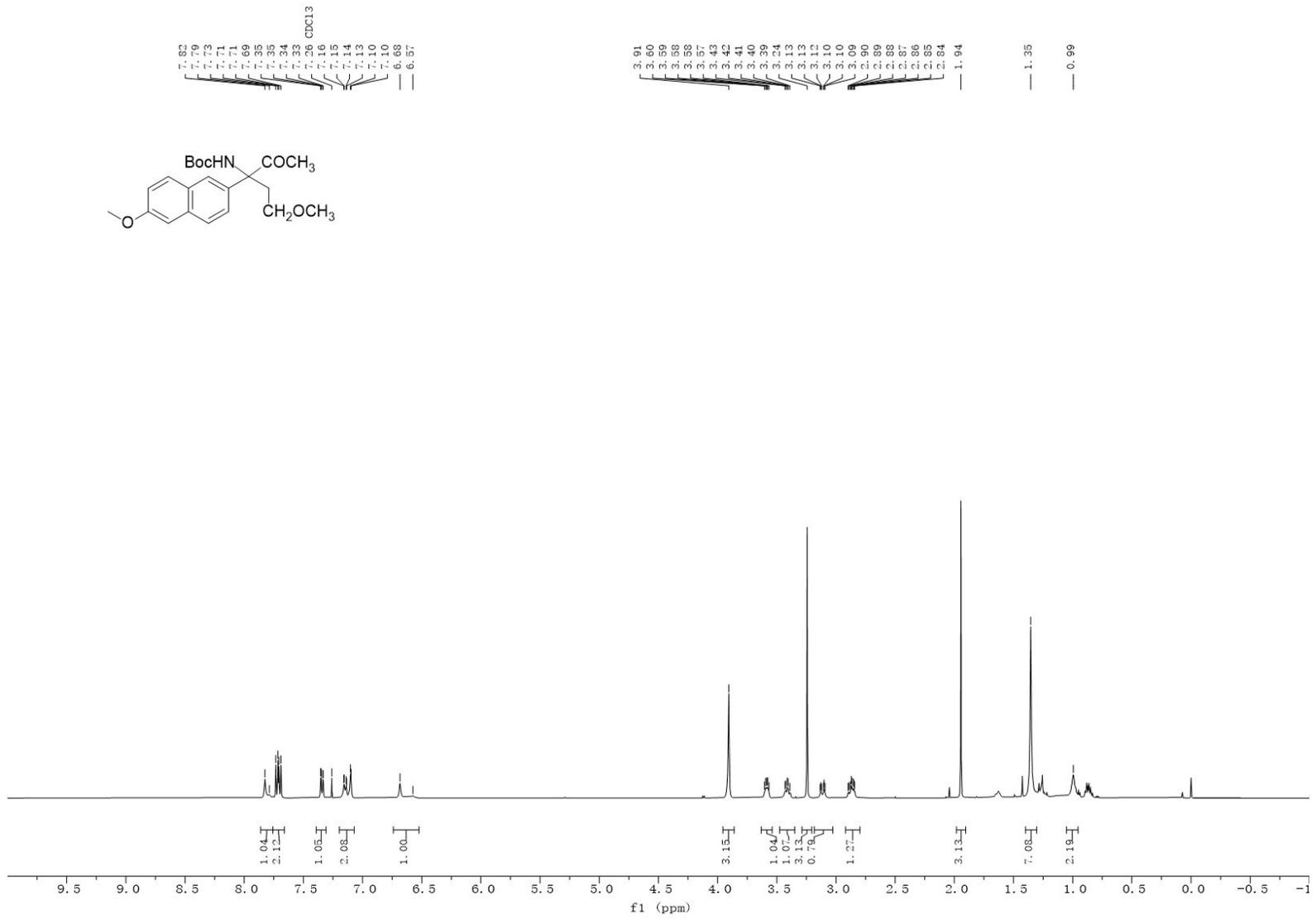


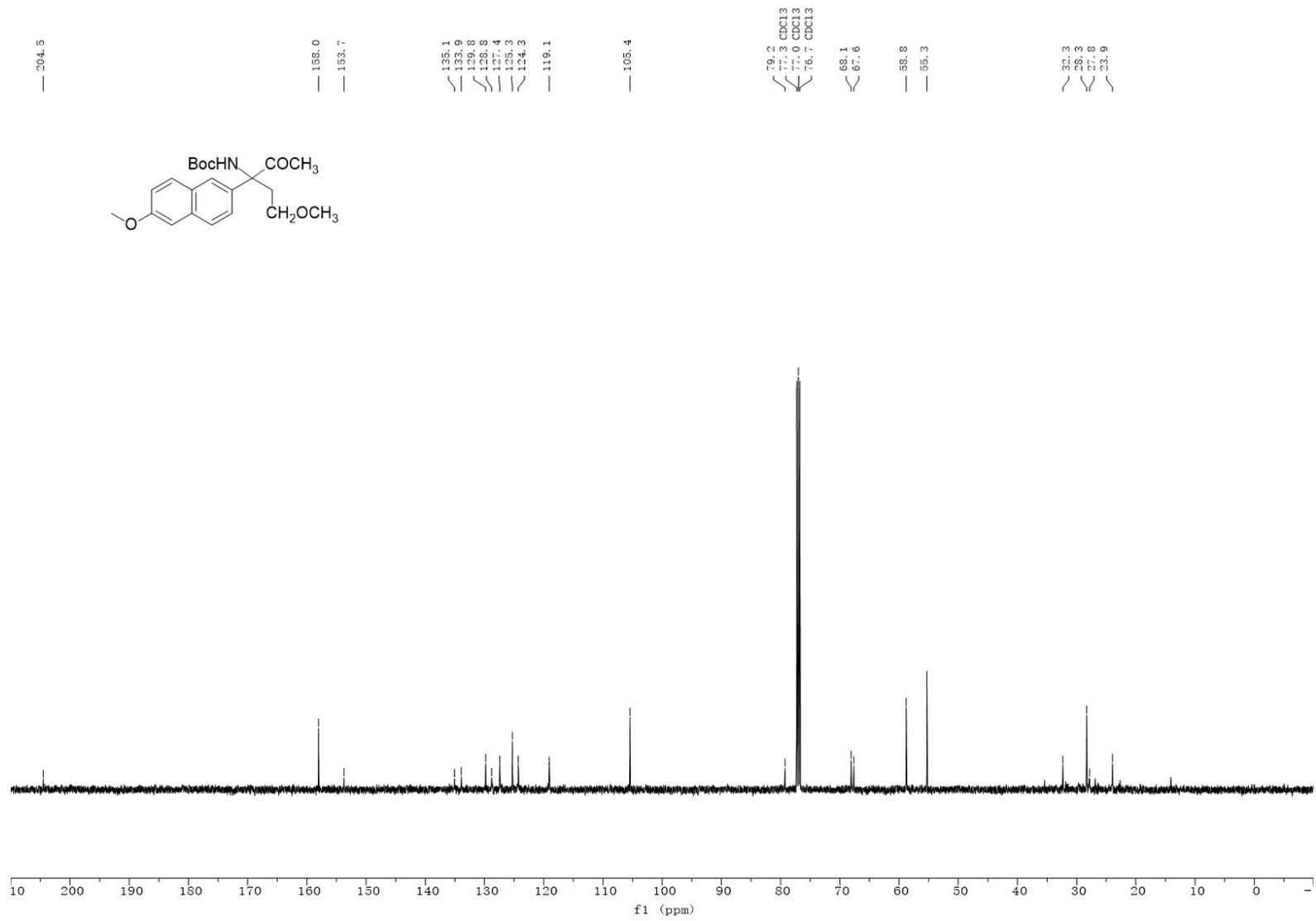


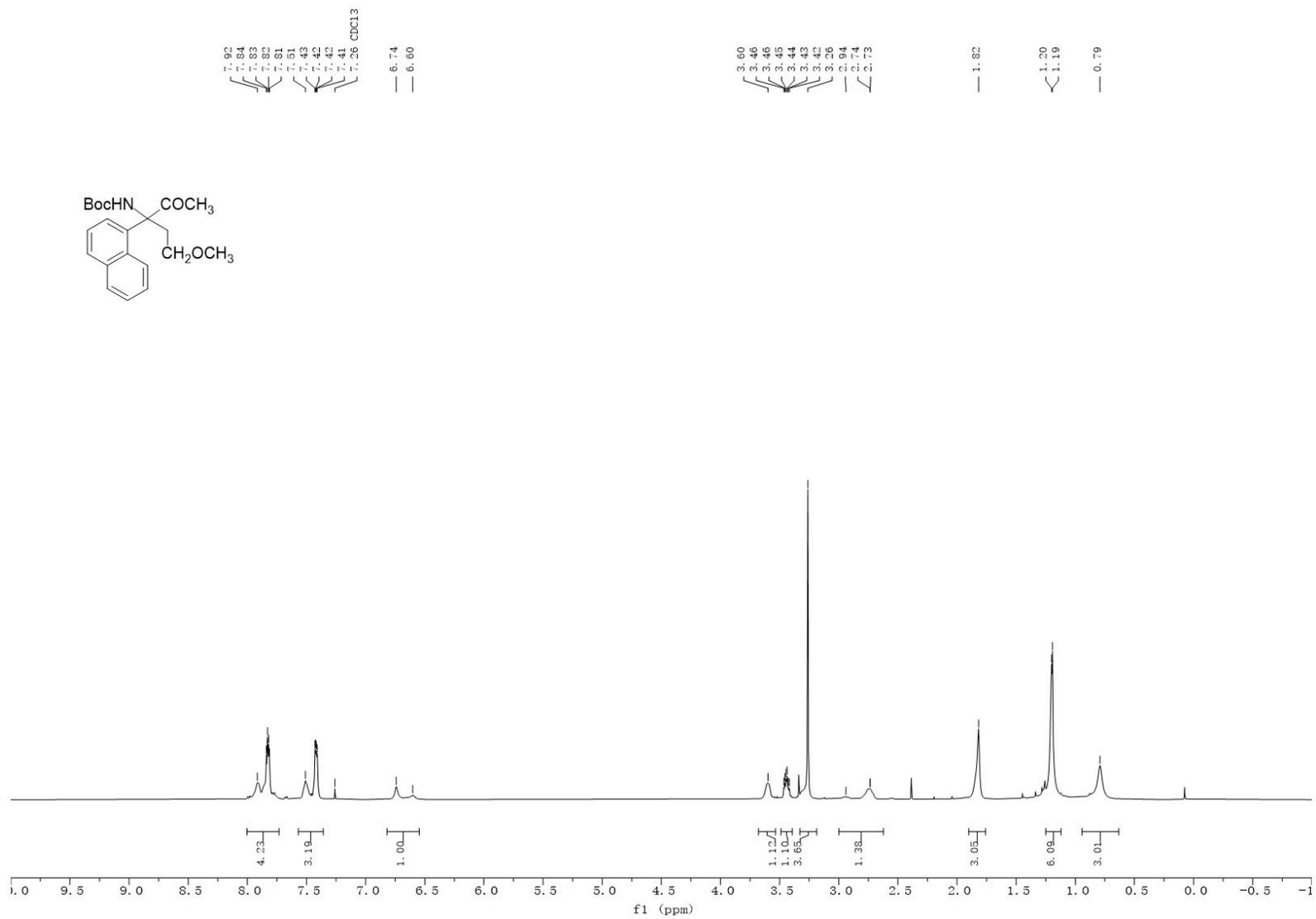
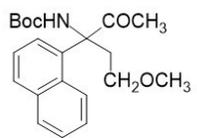


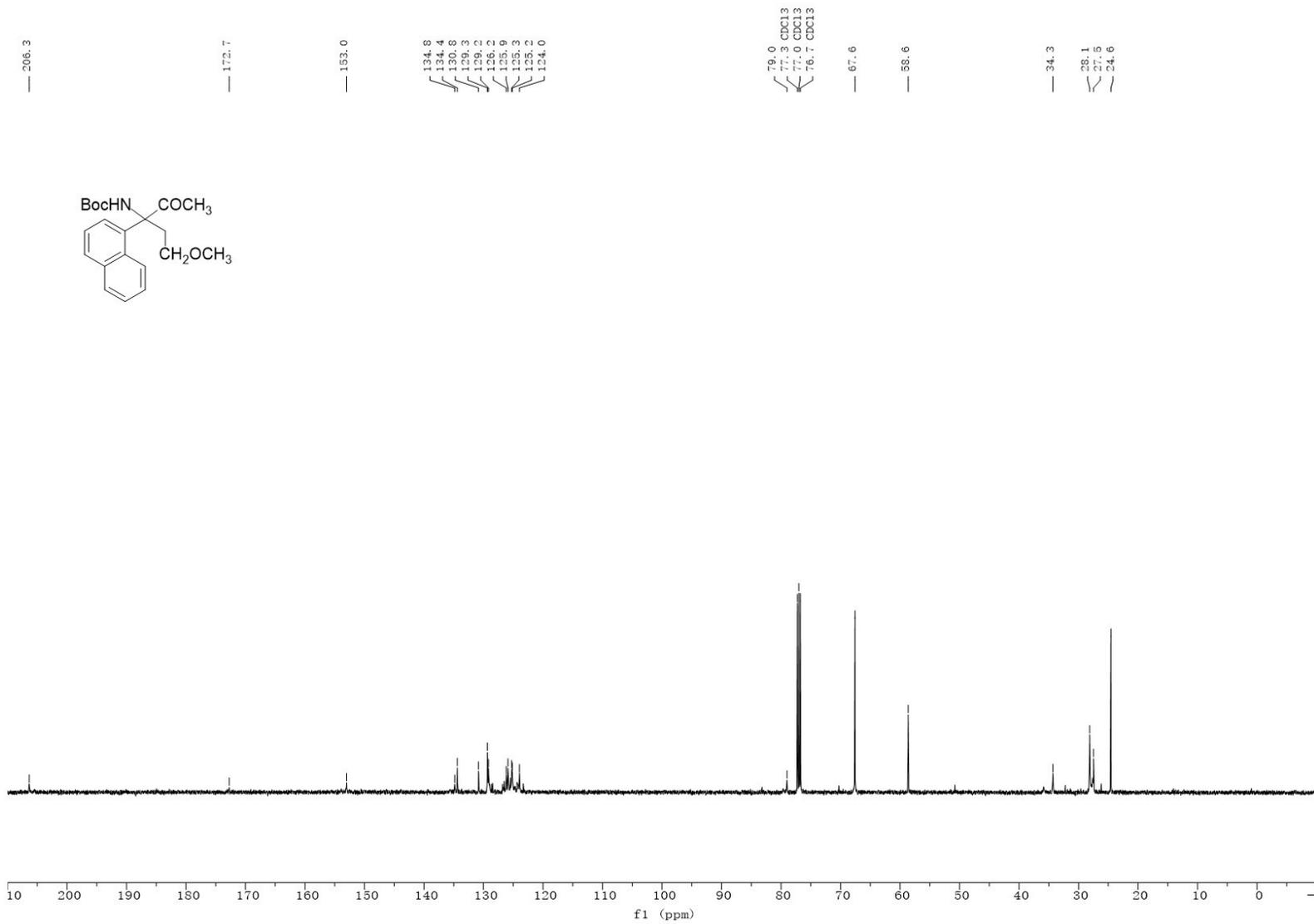


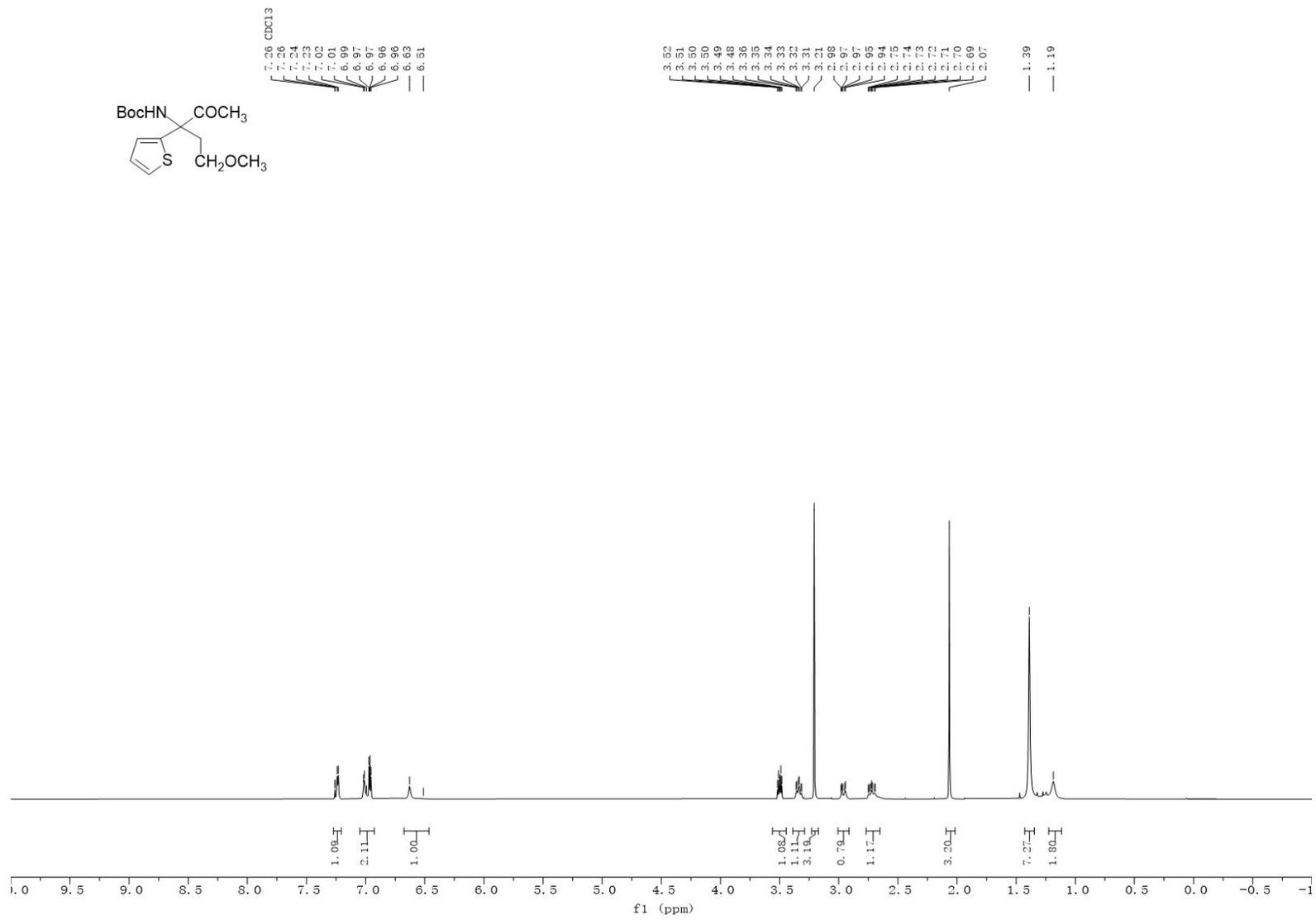


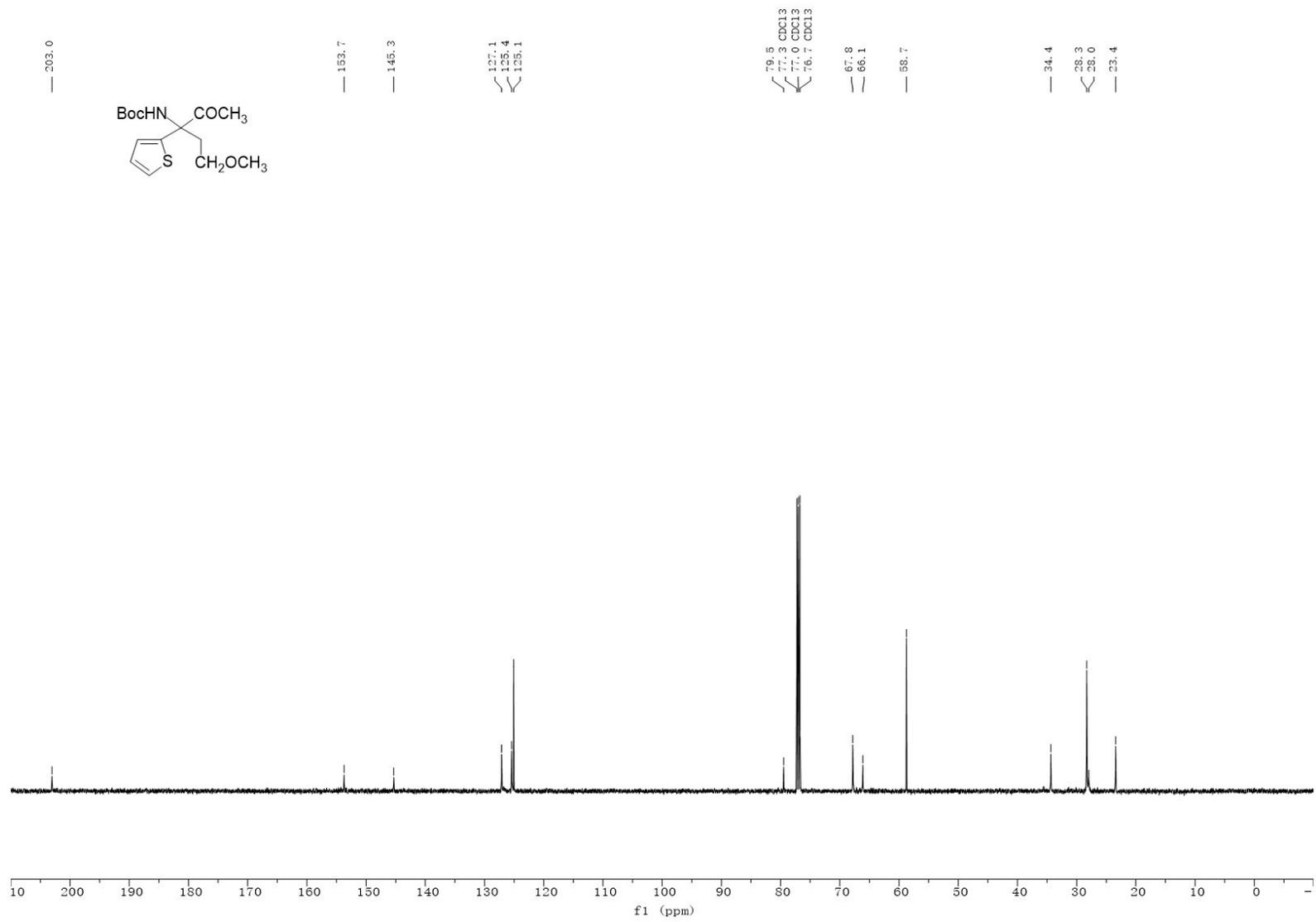


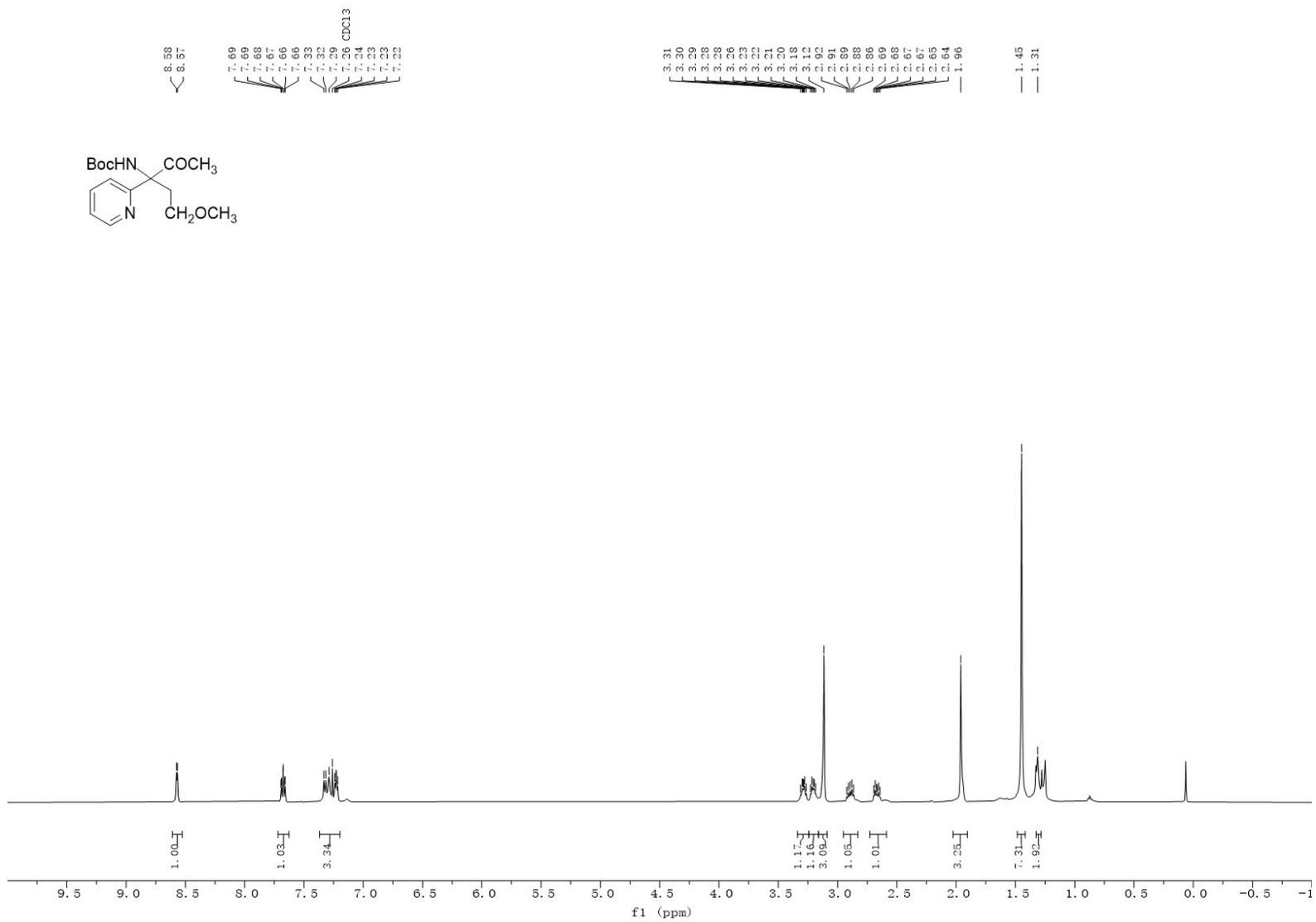
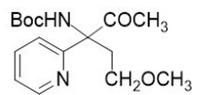


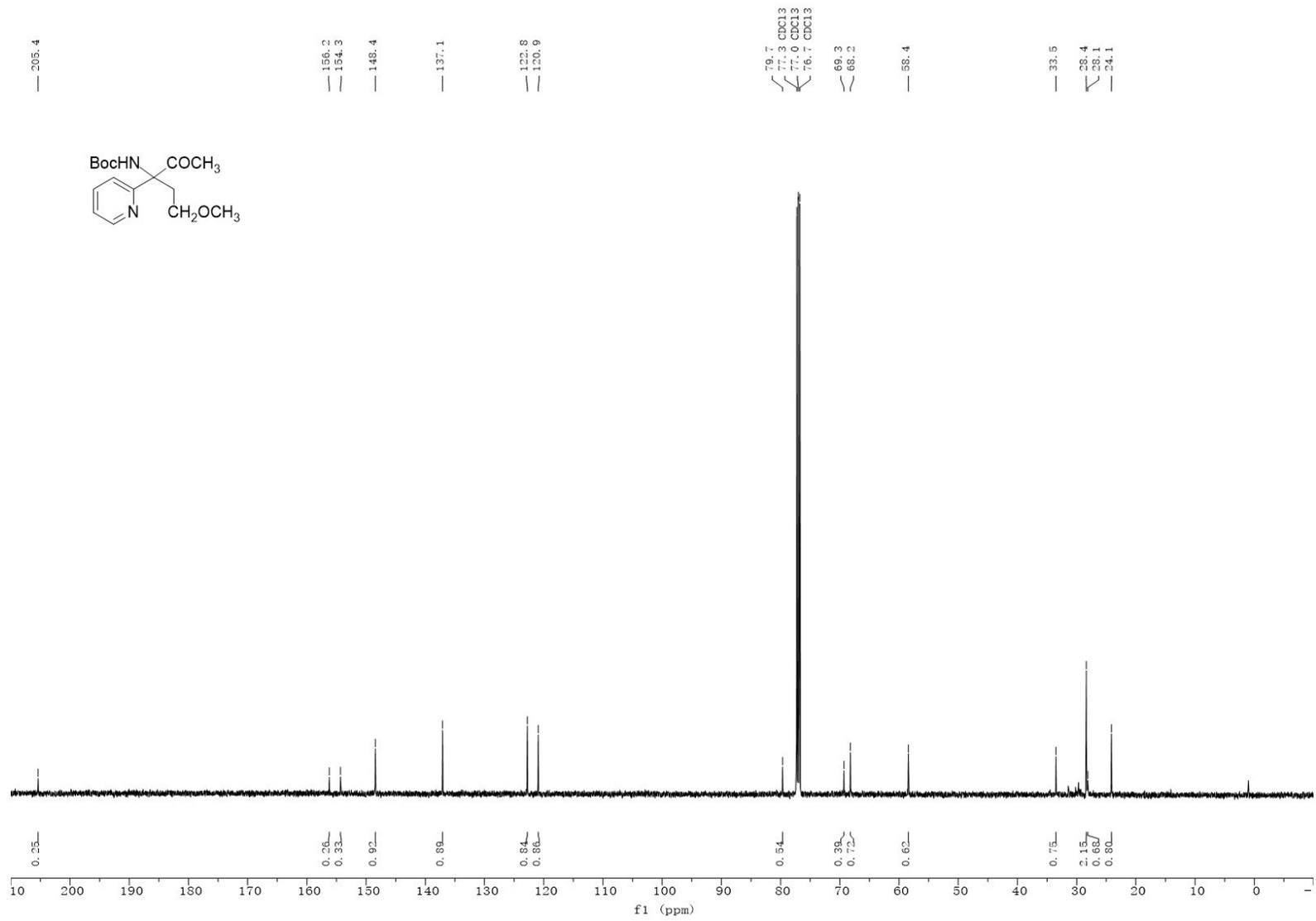


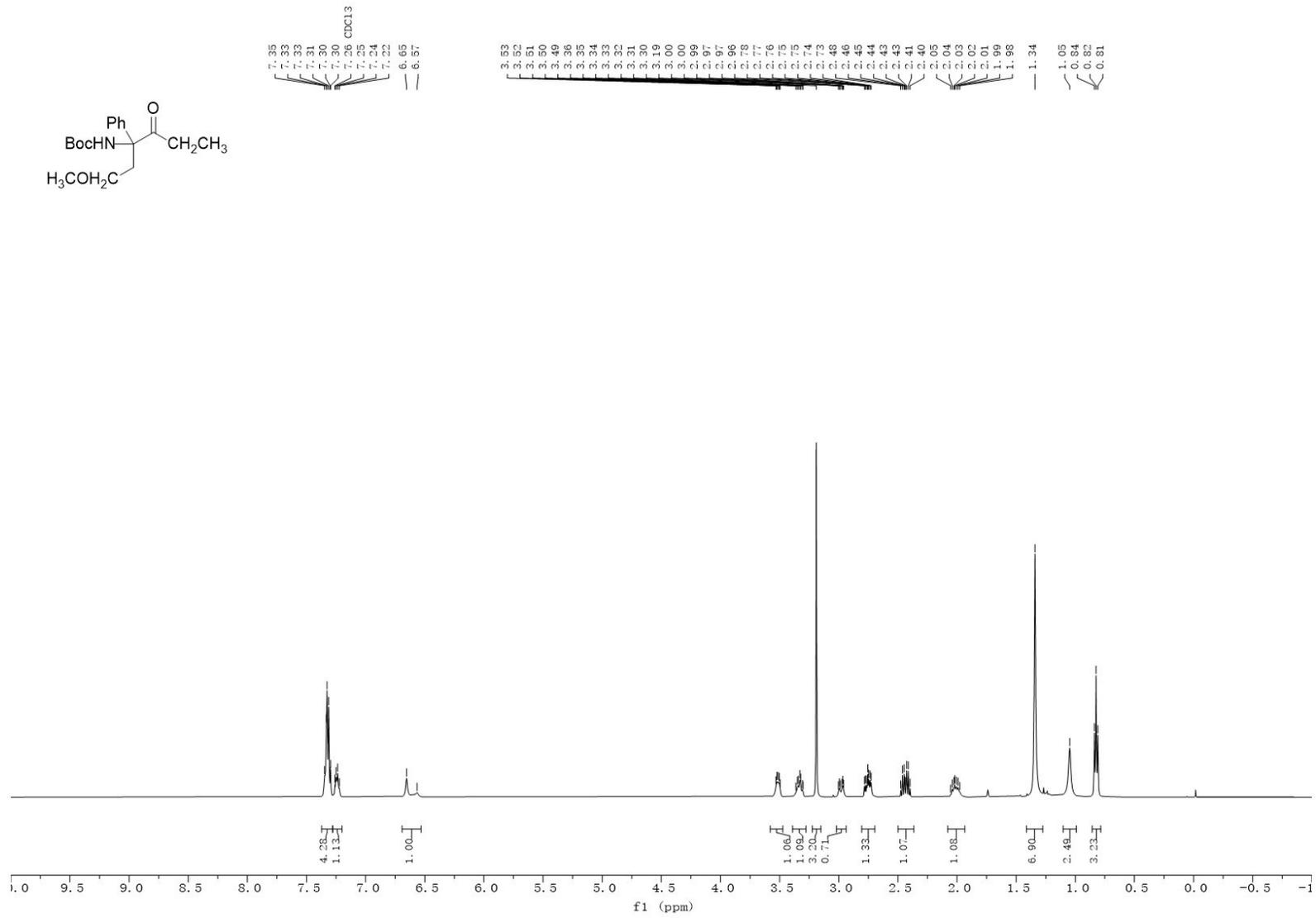
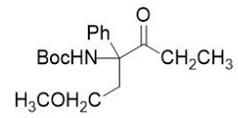


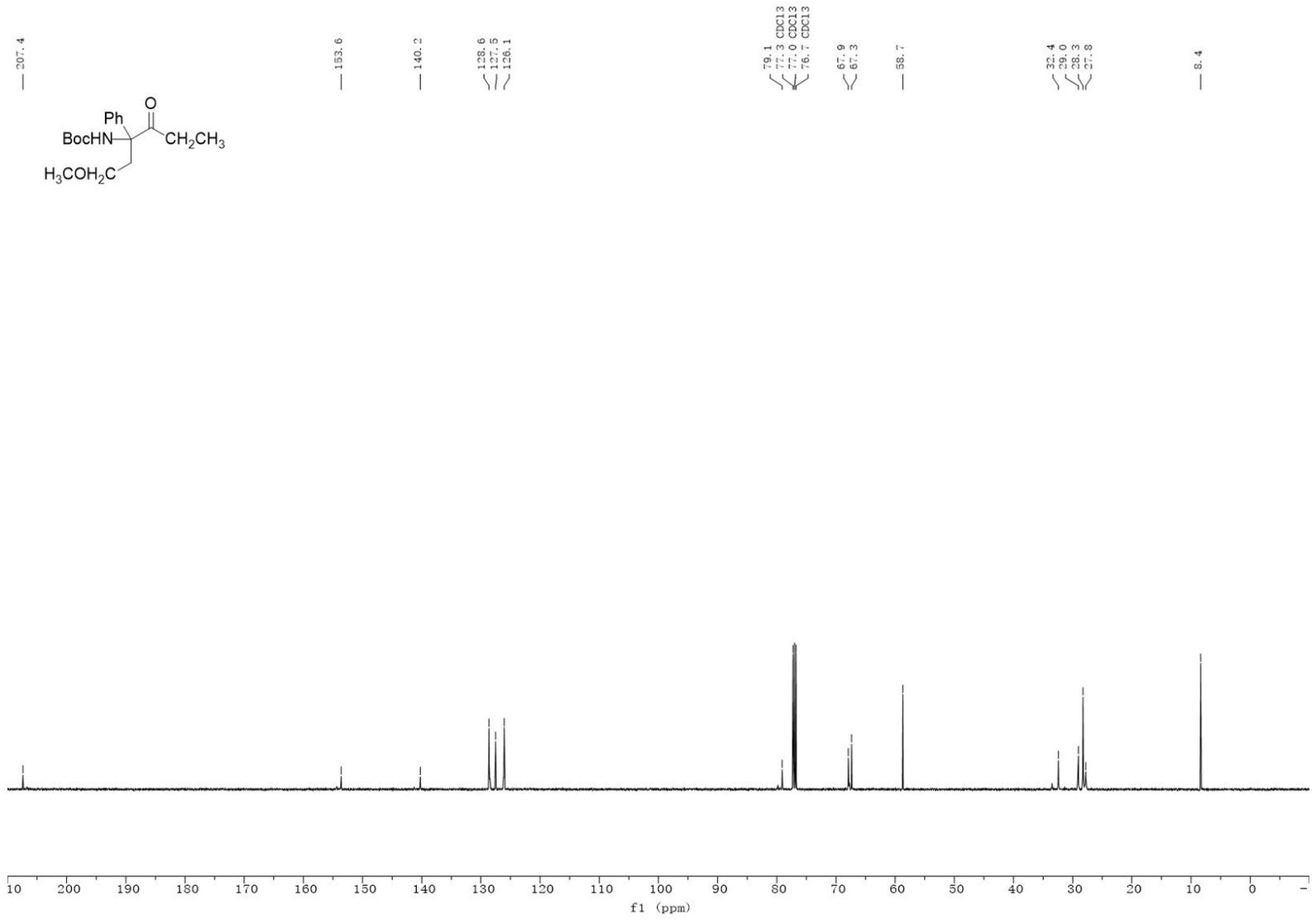


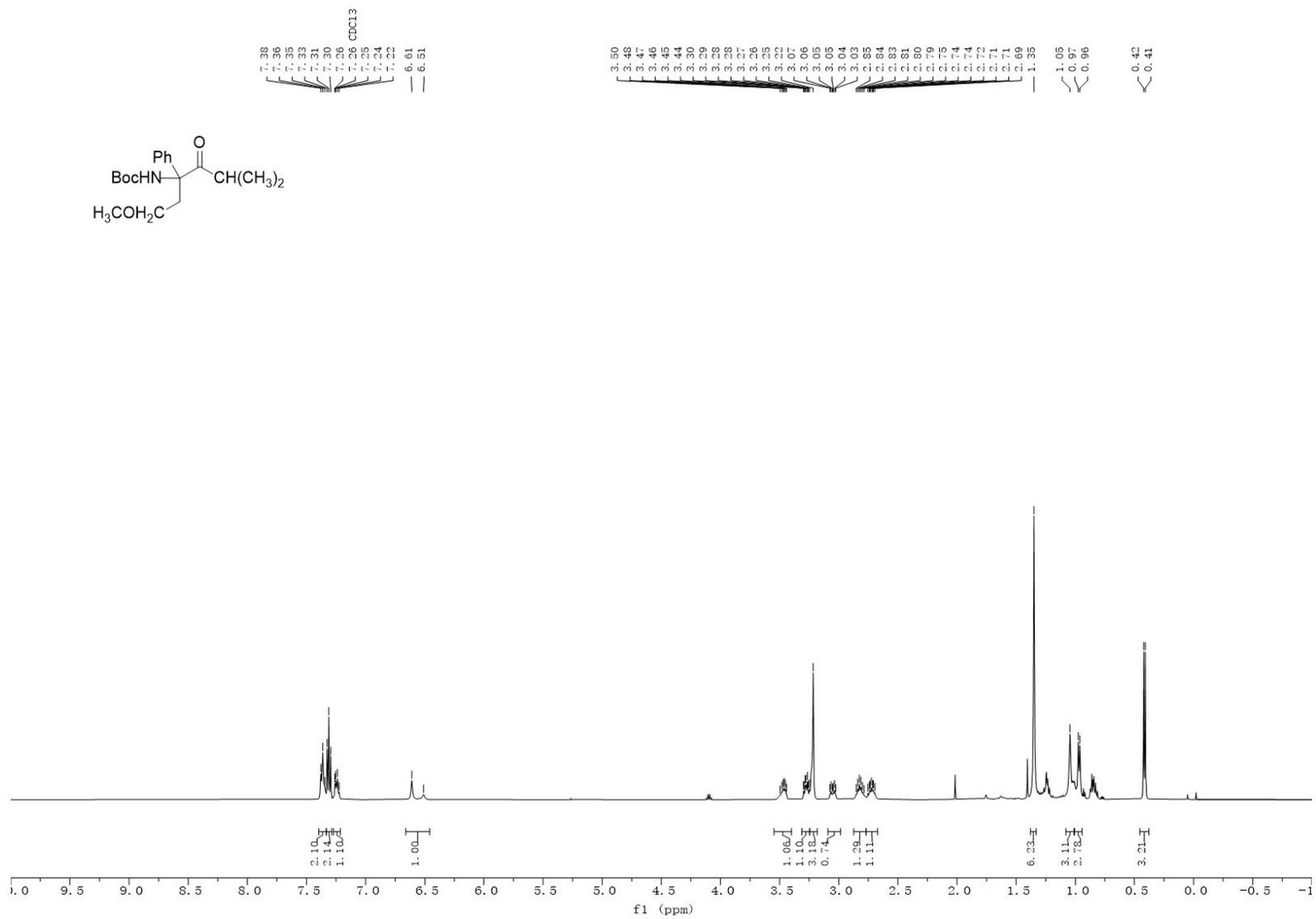
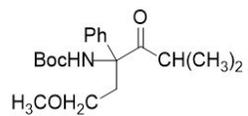


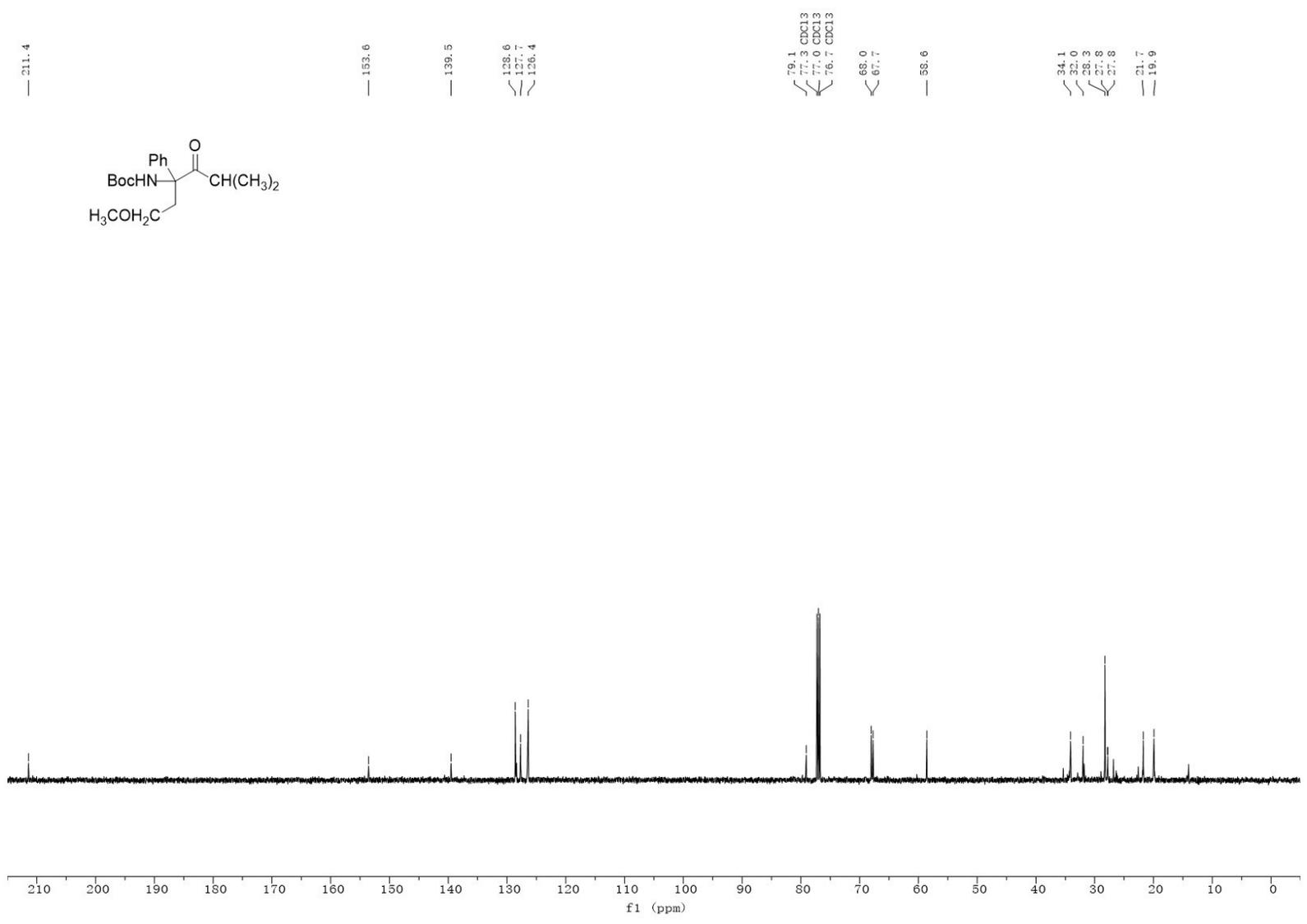


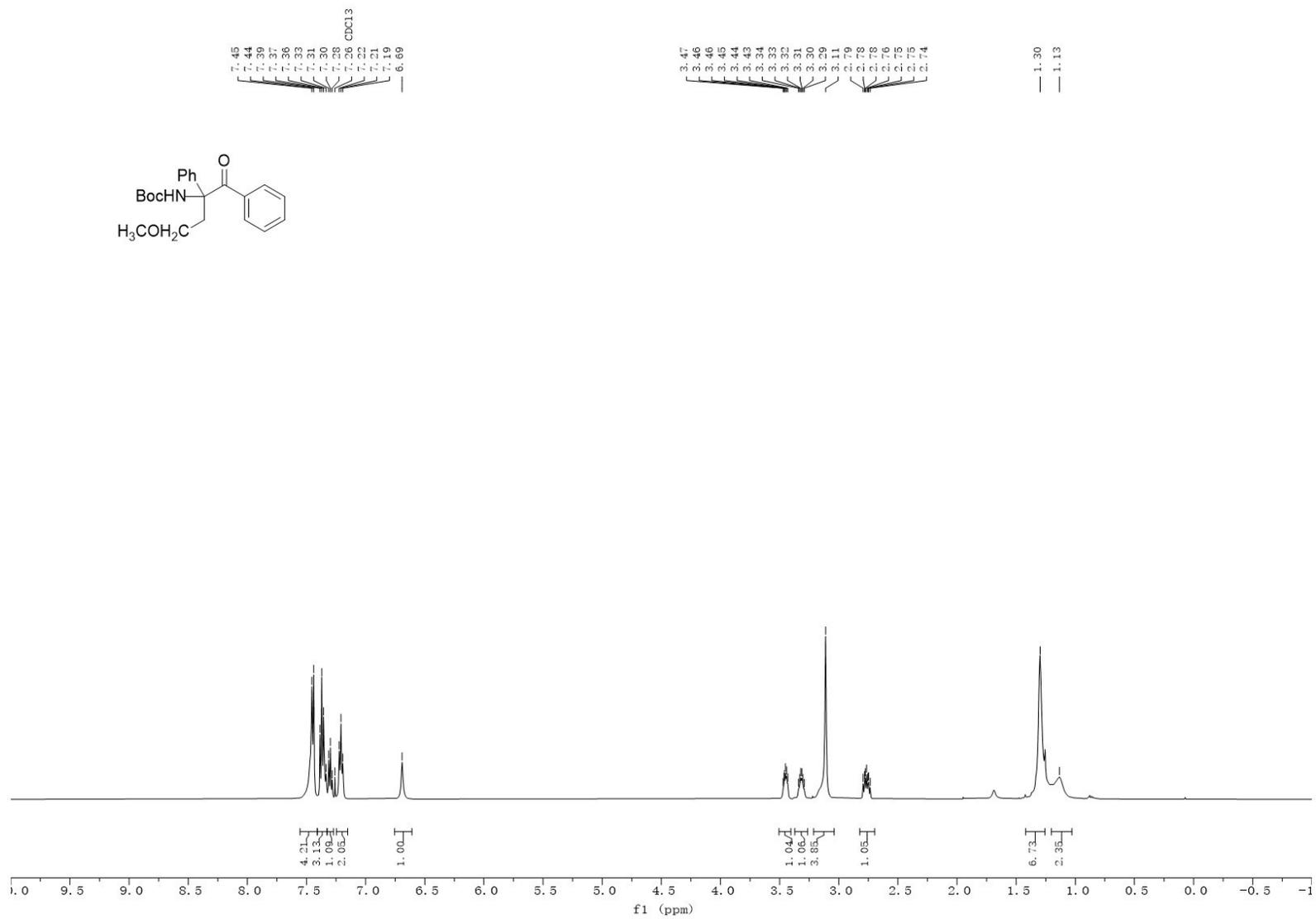
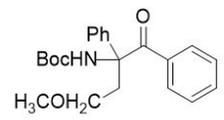


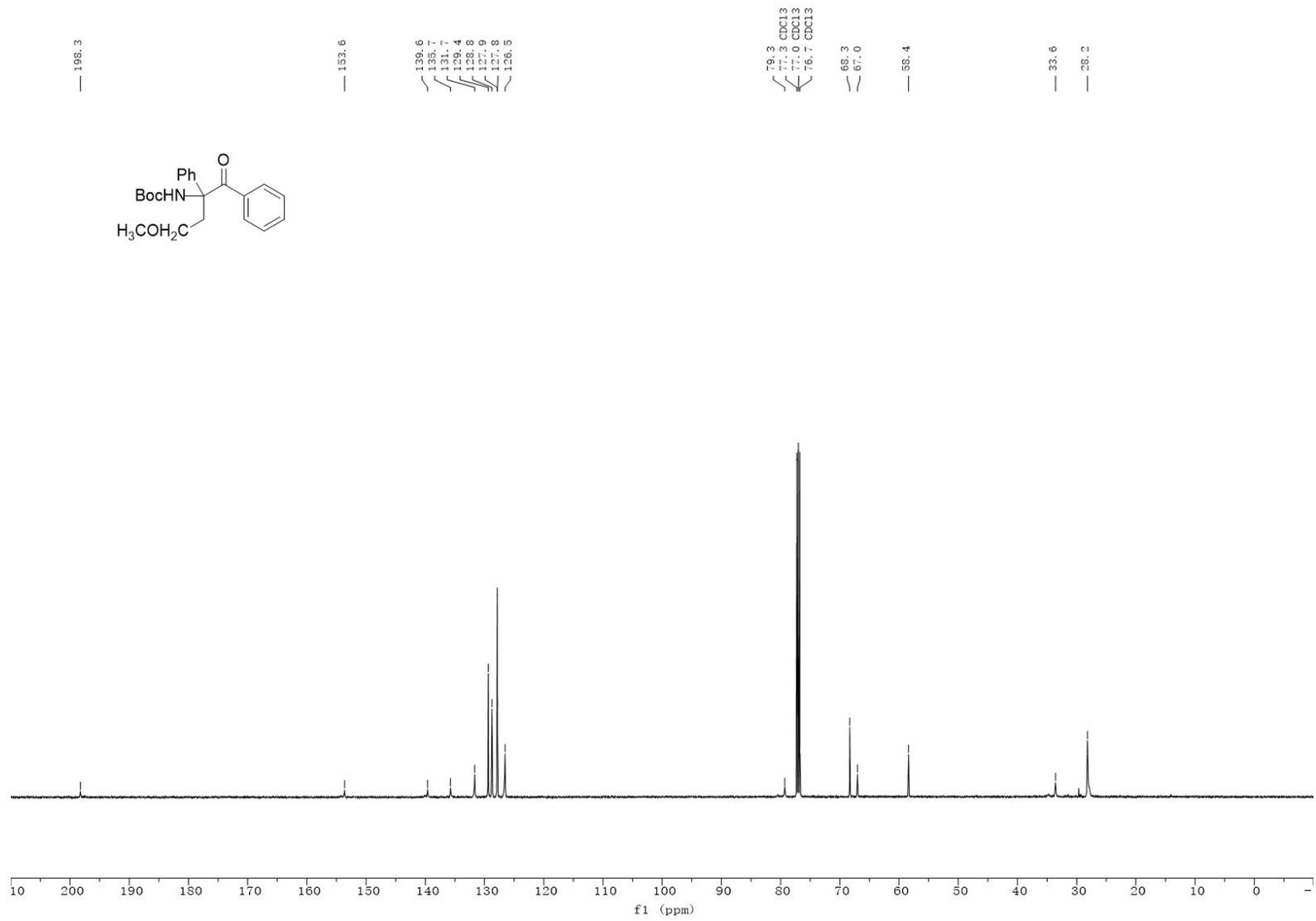


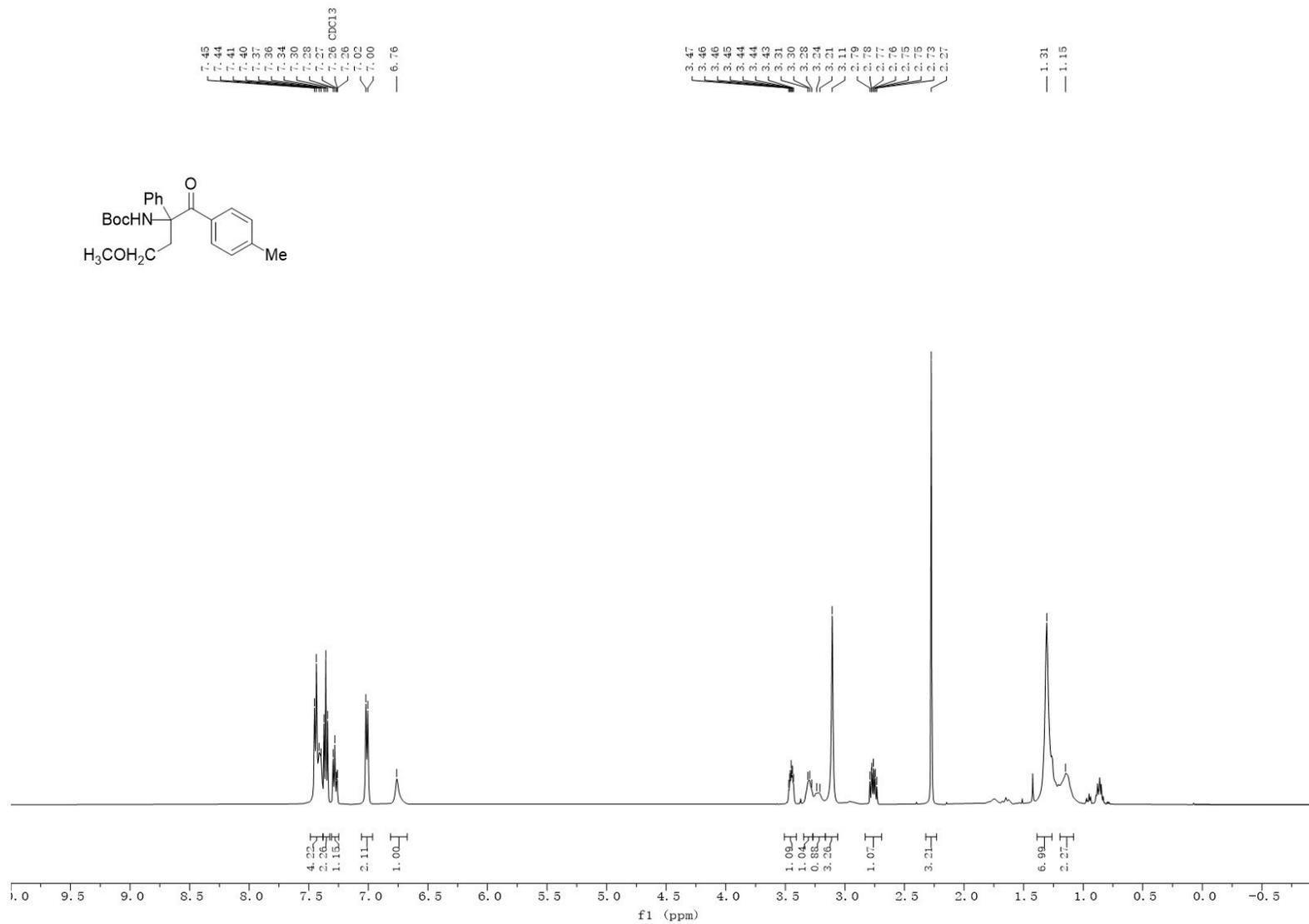
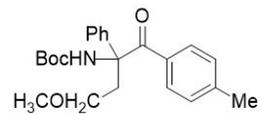


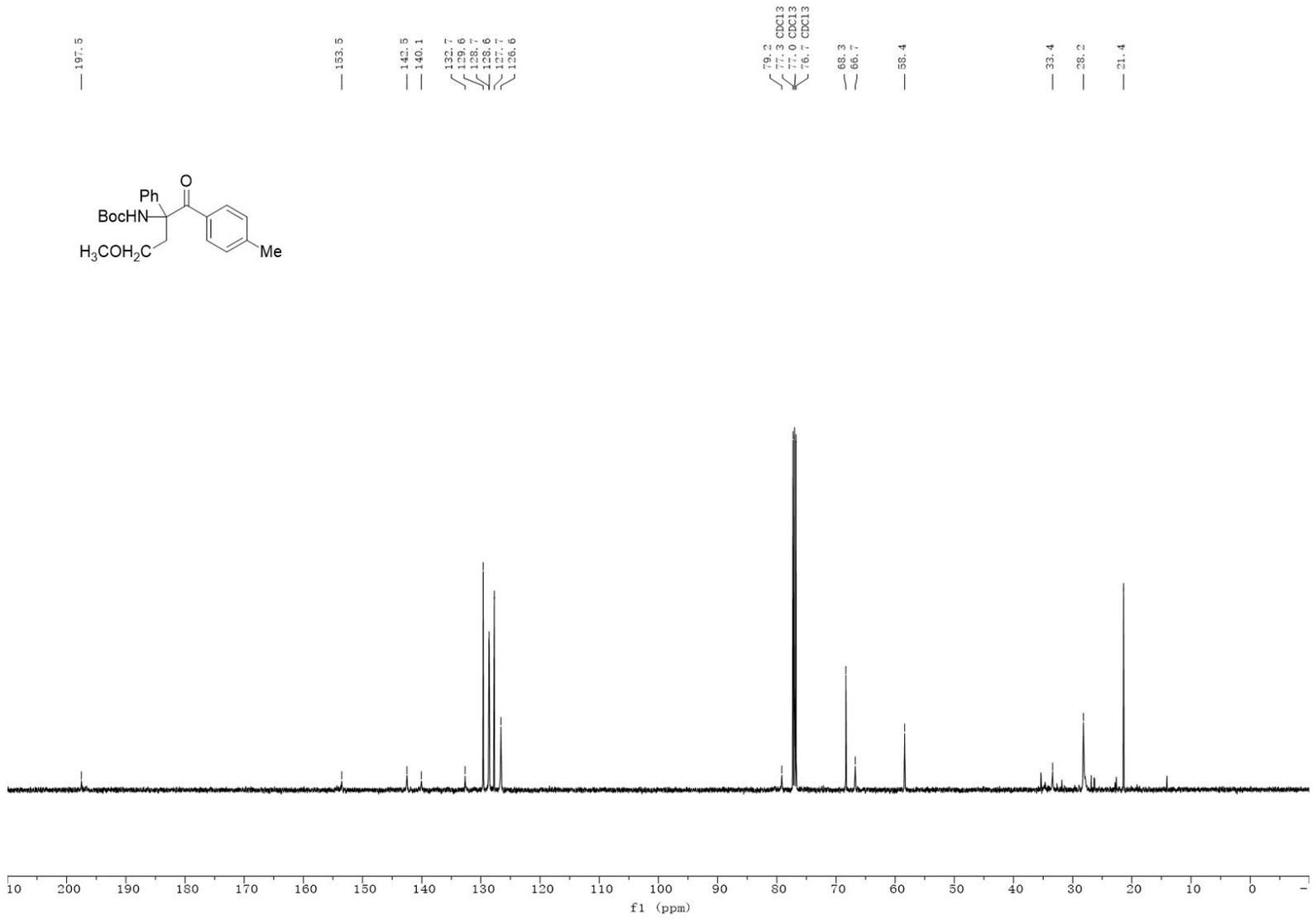


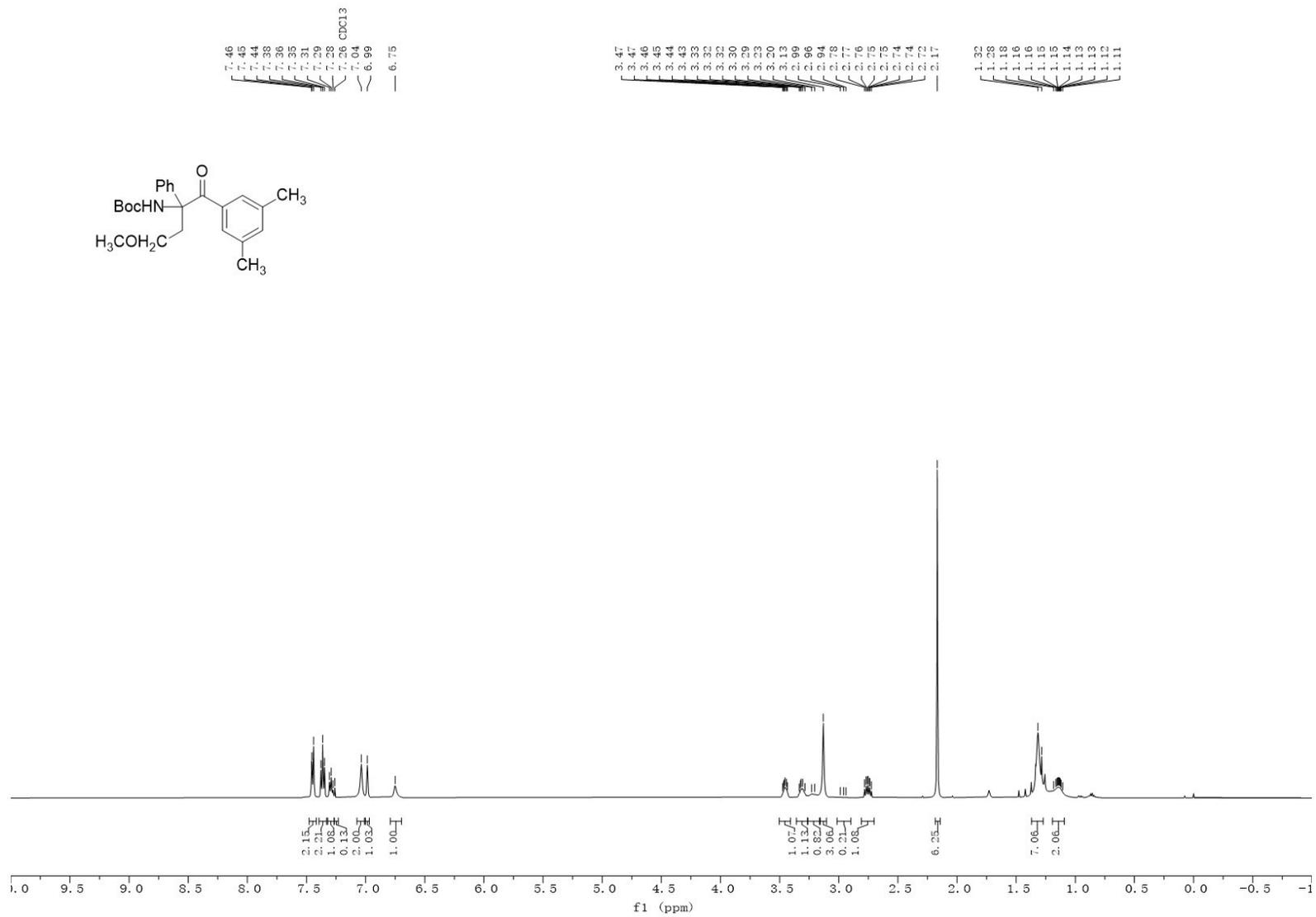




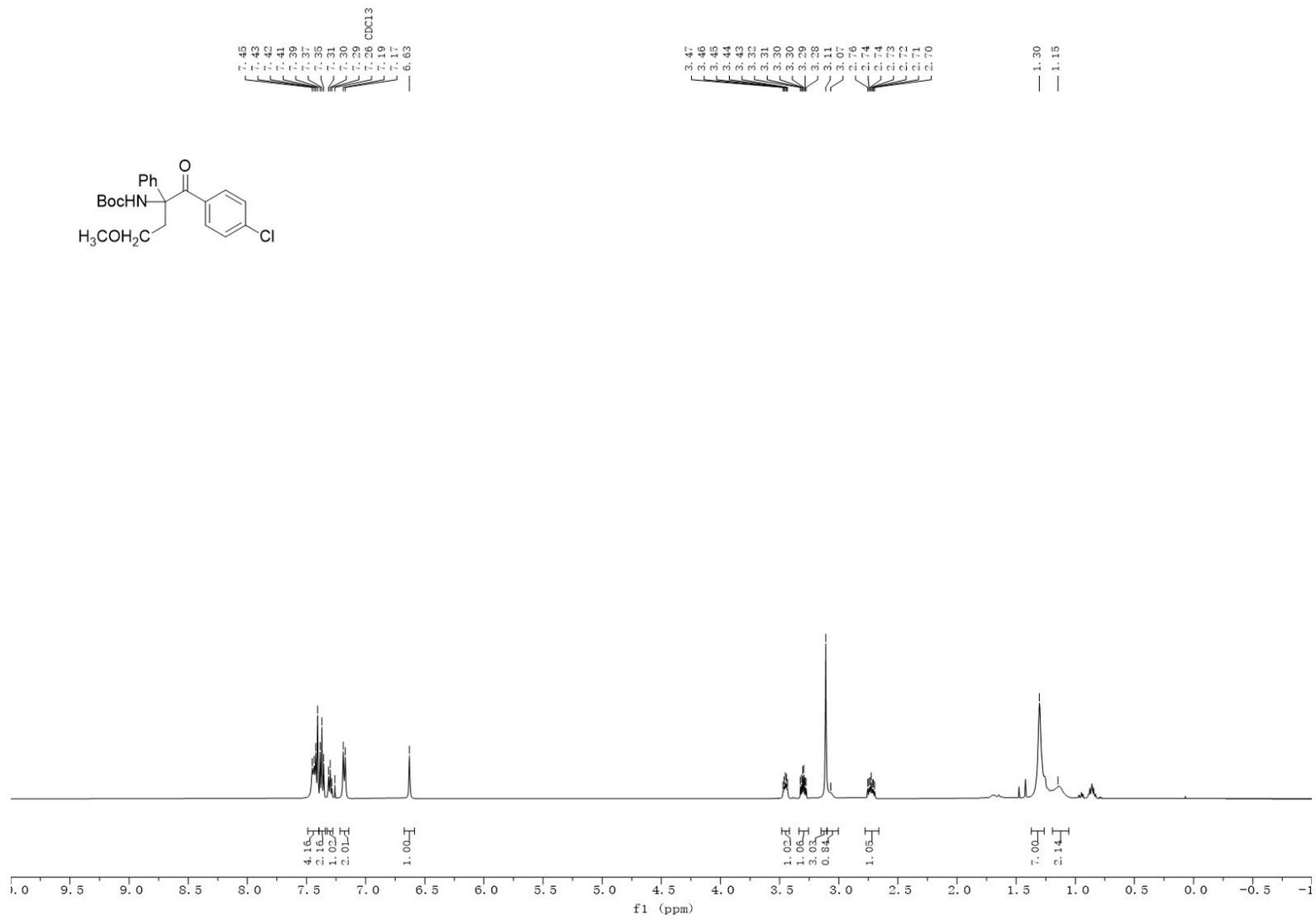


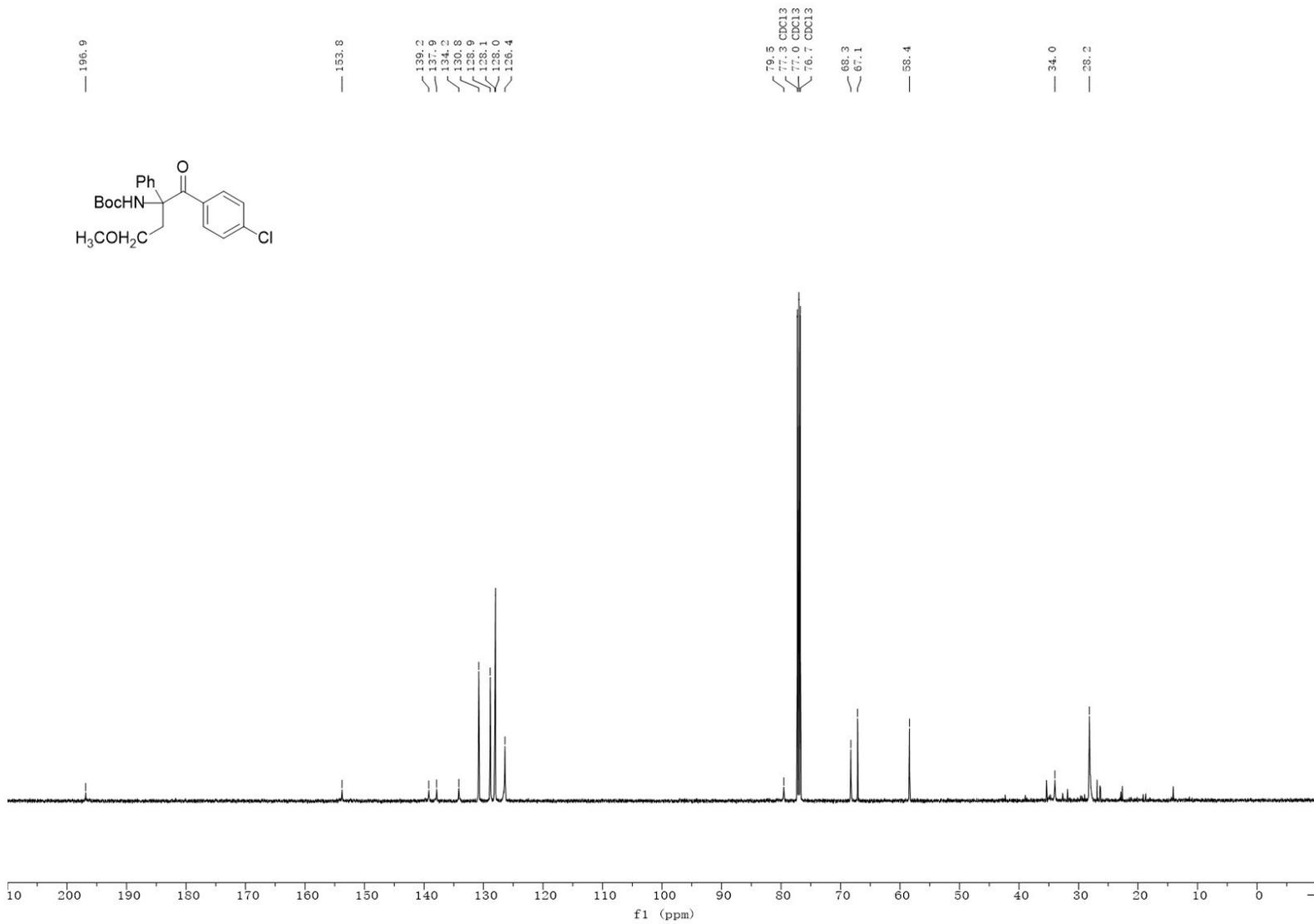


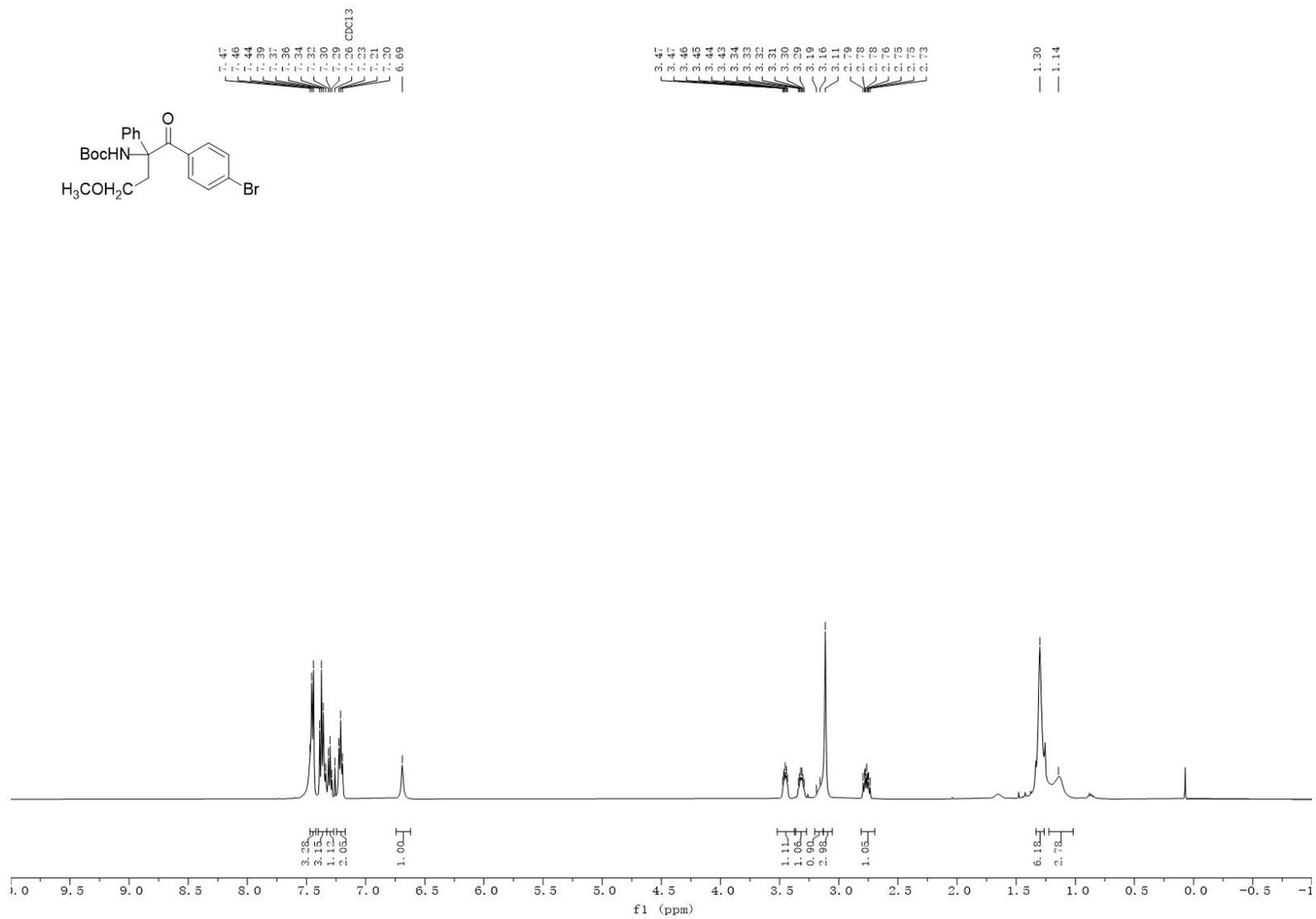
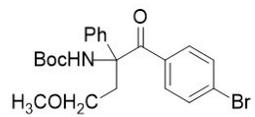


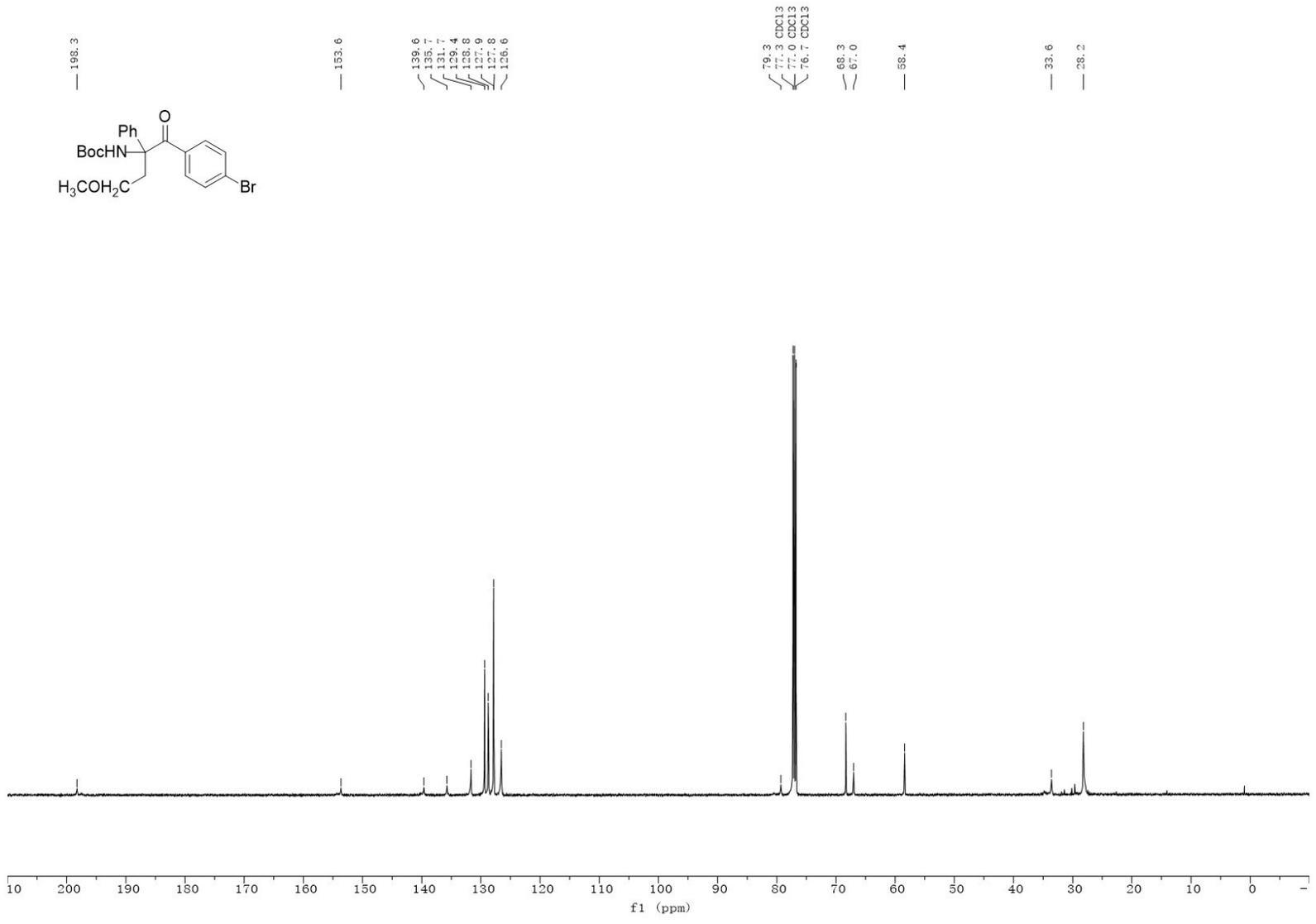


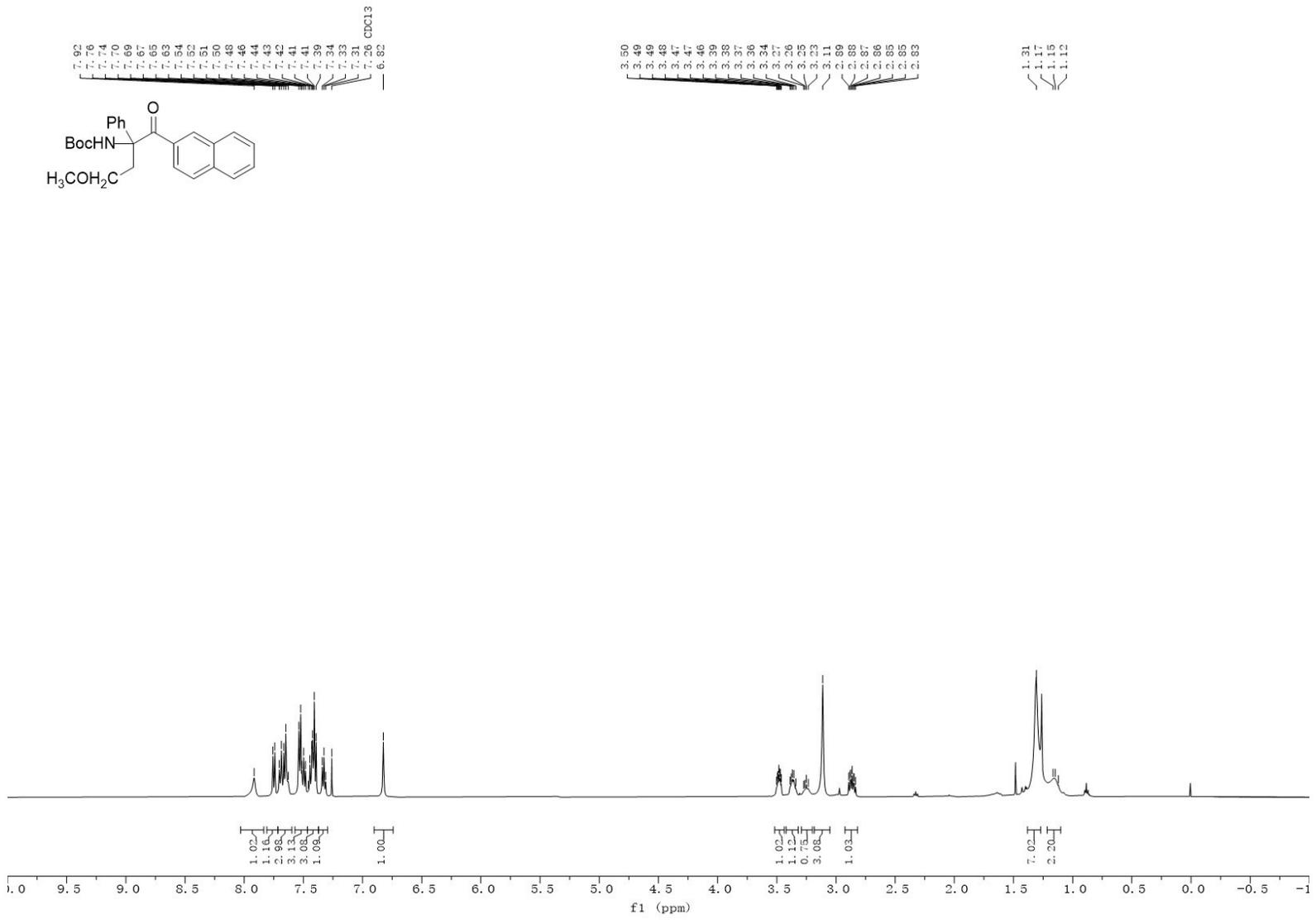


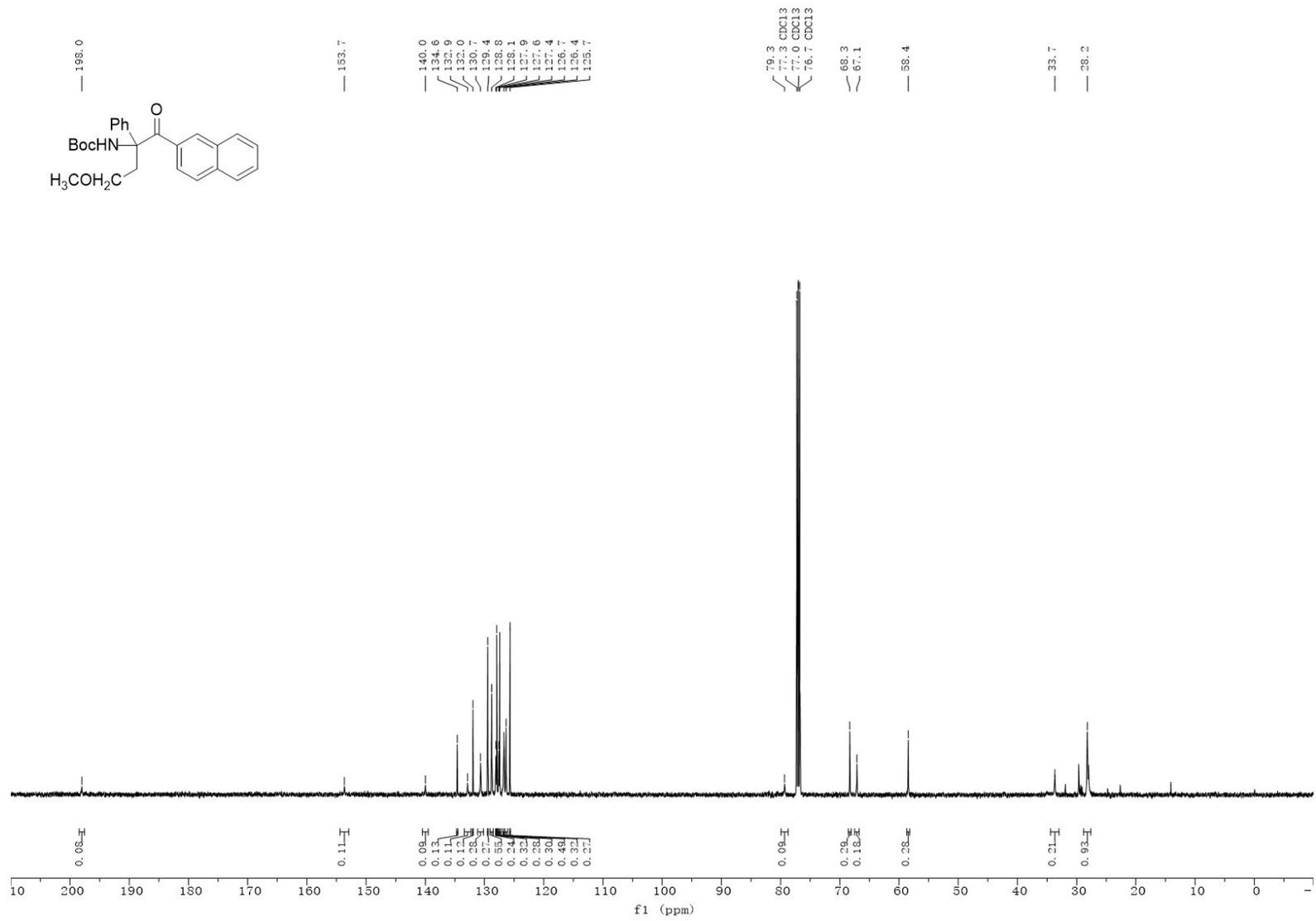


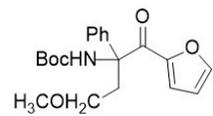








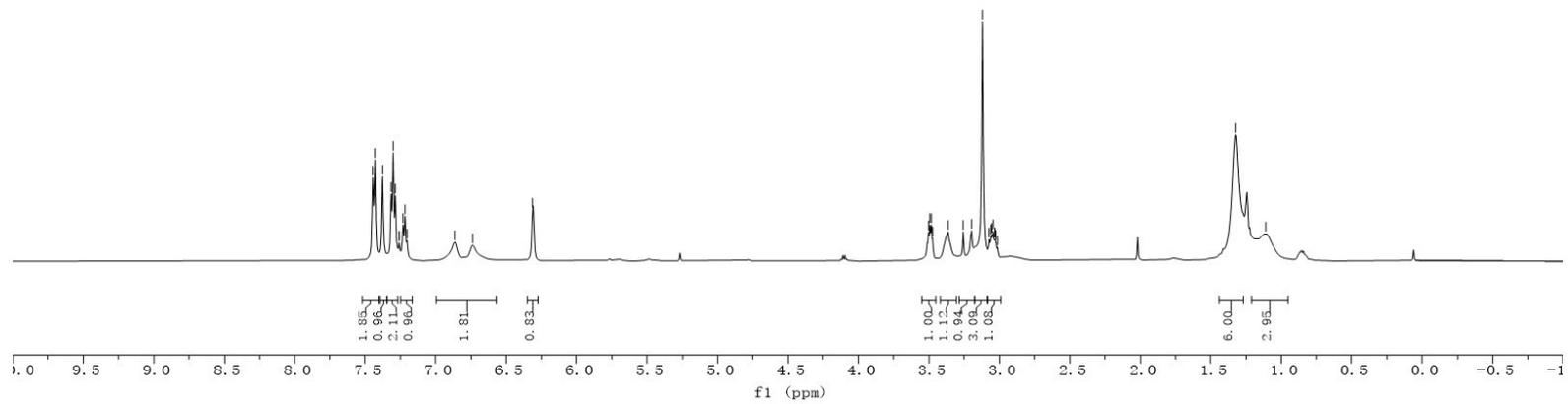


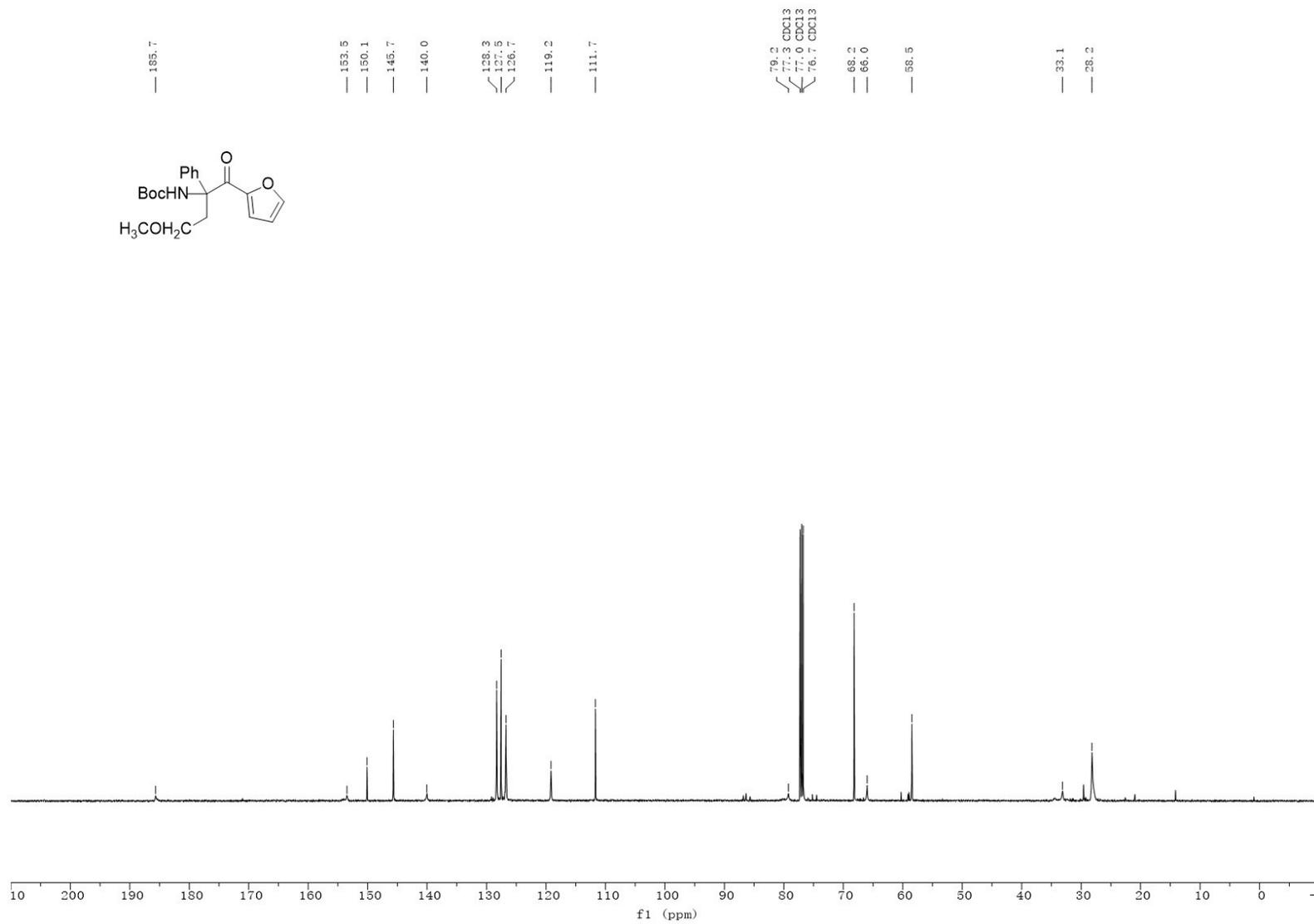
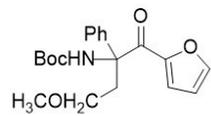


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6.31

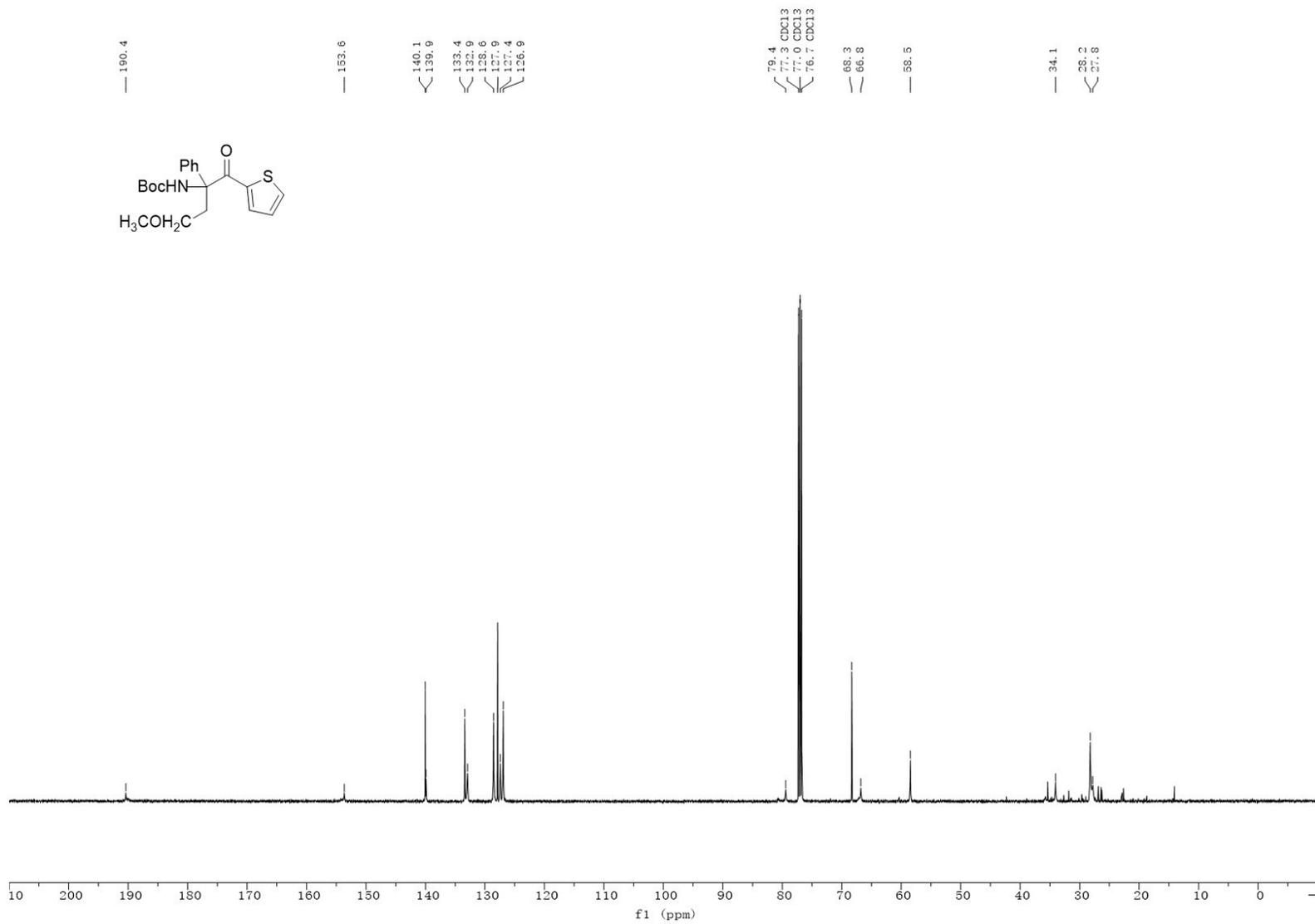
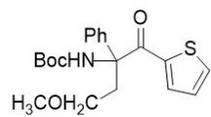
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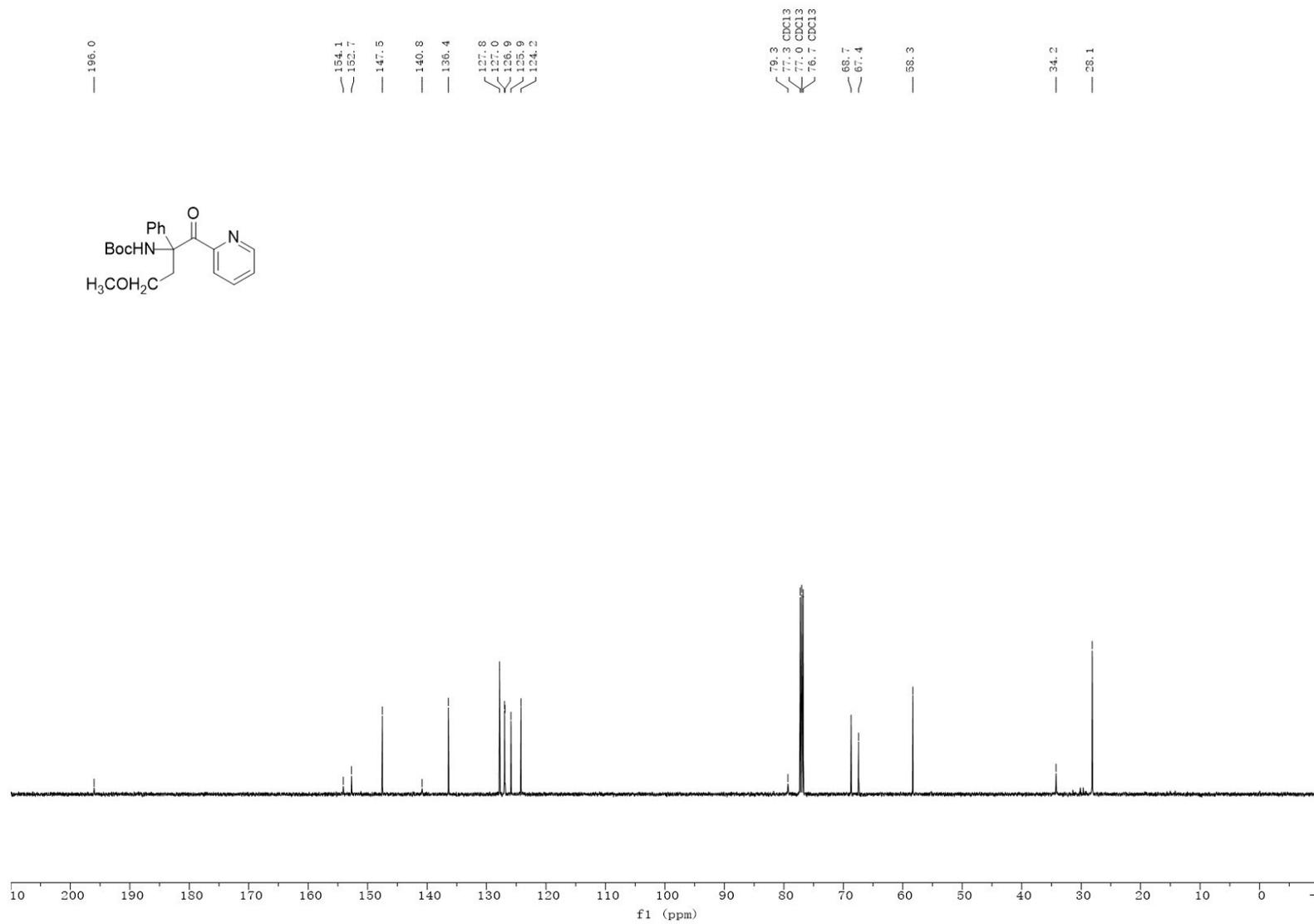
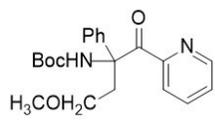
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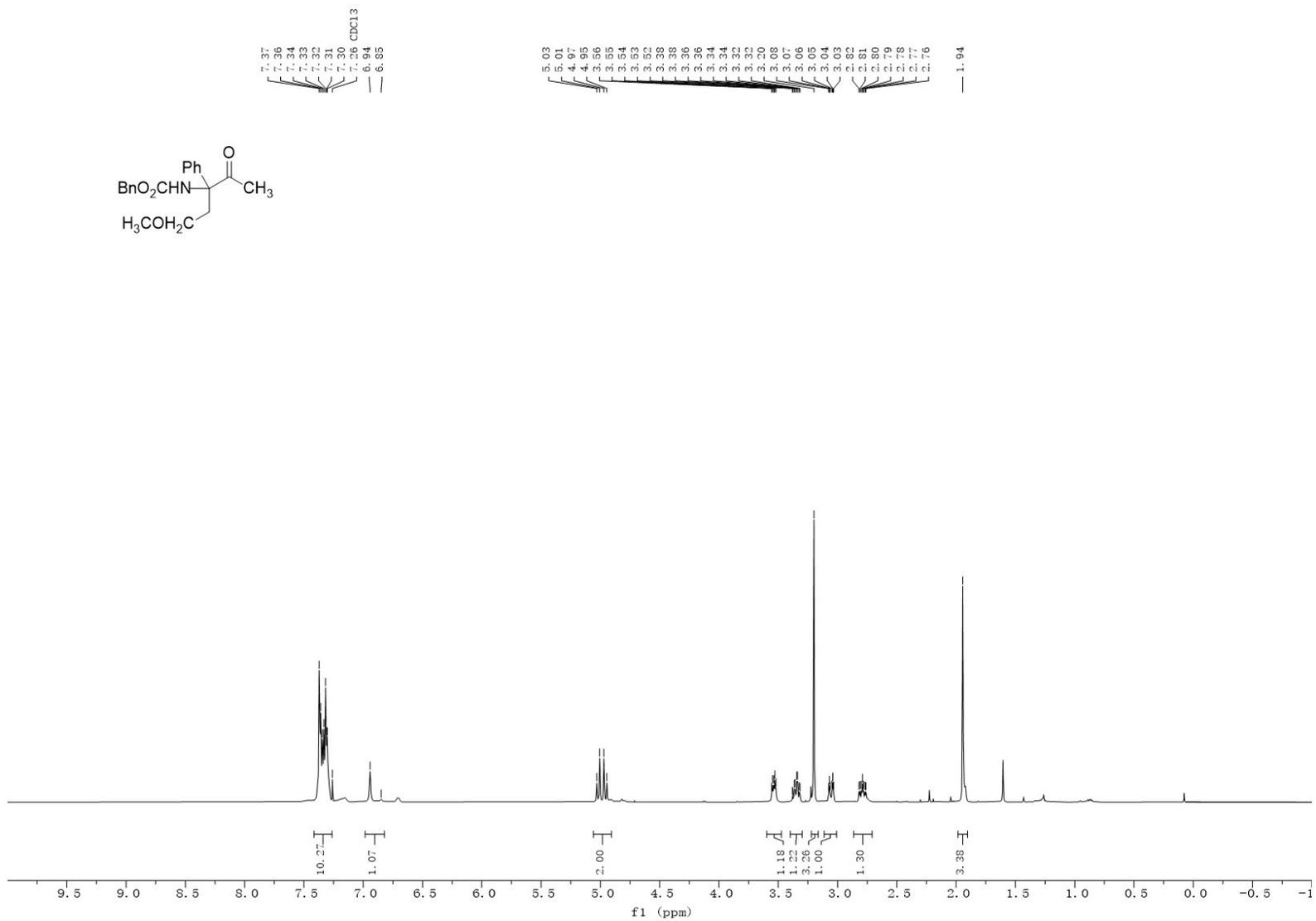
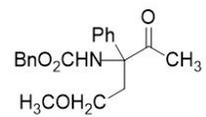


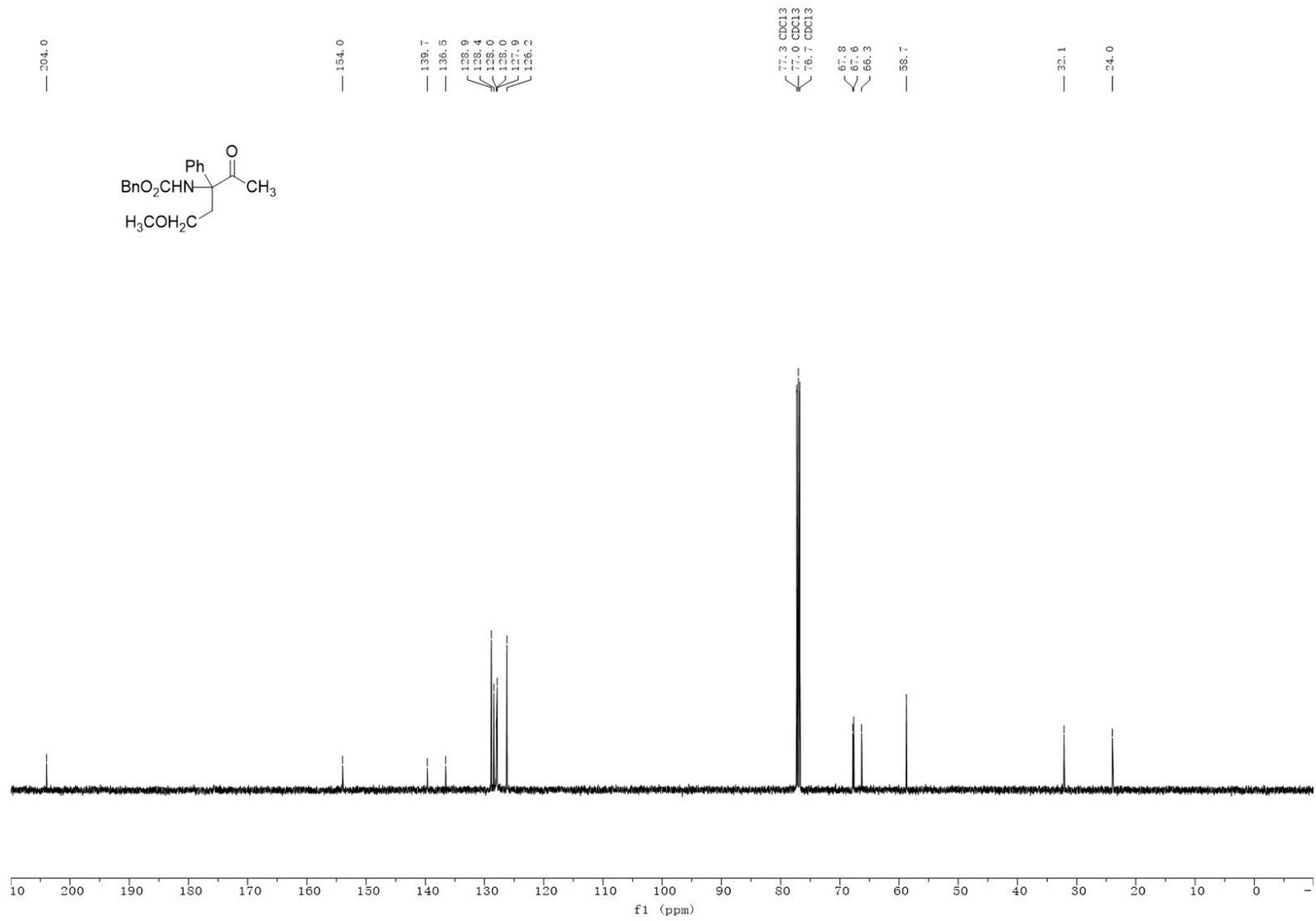


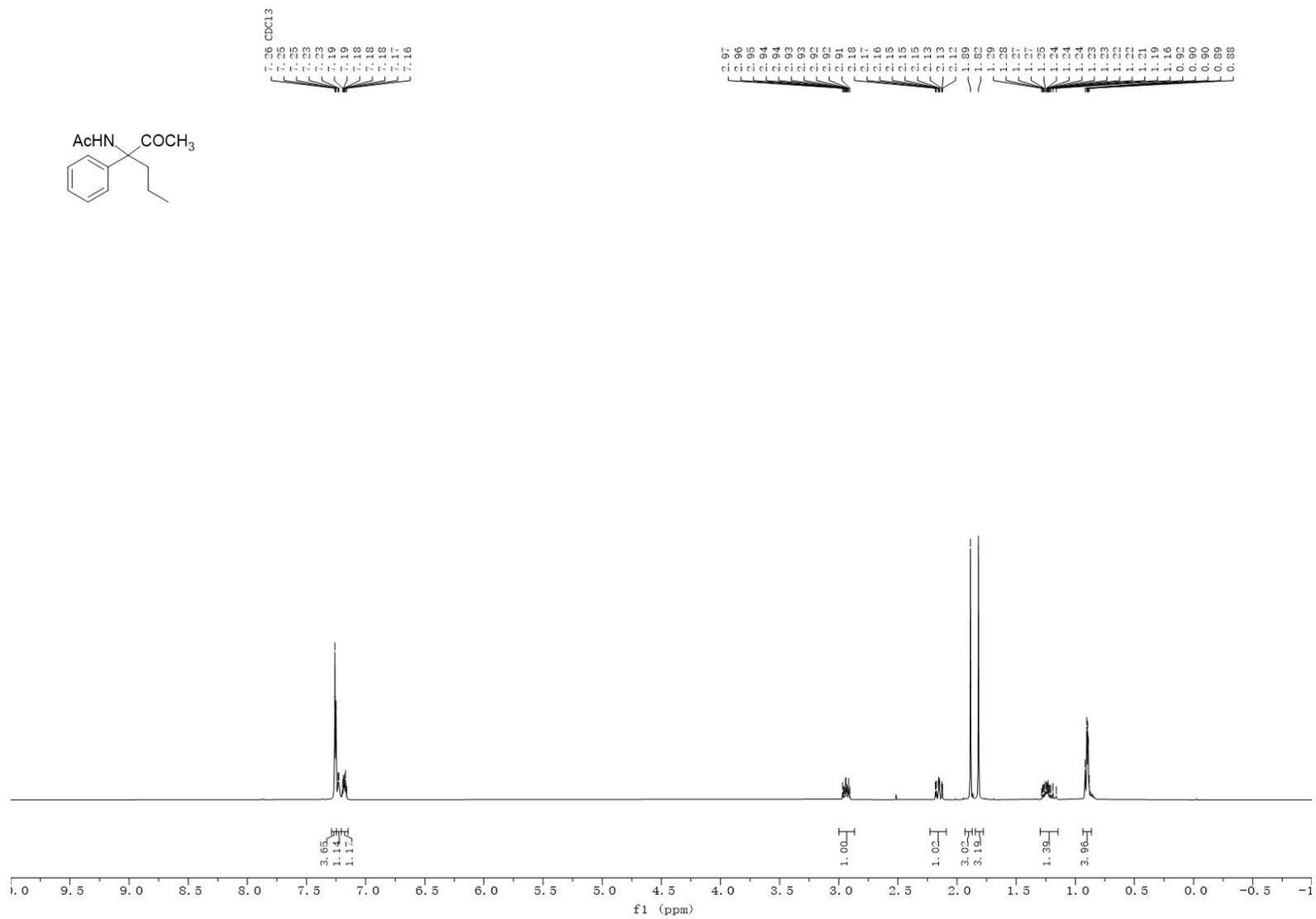
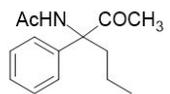
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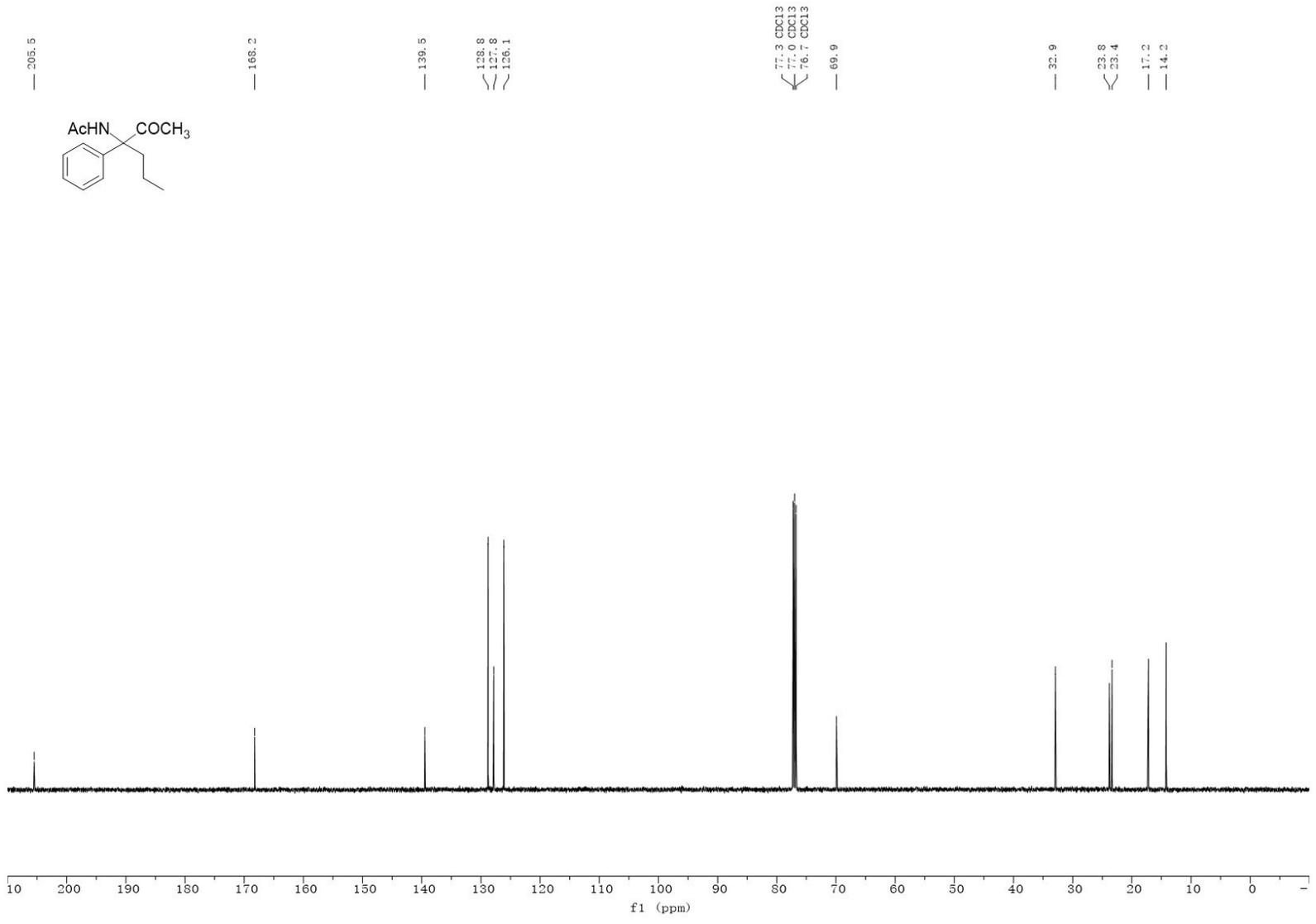


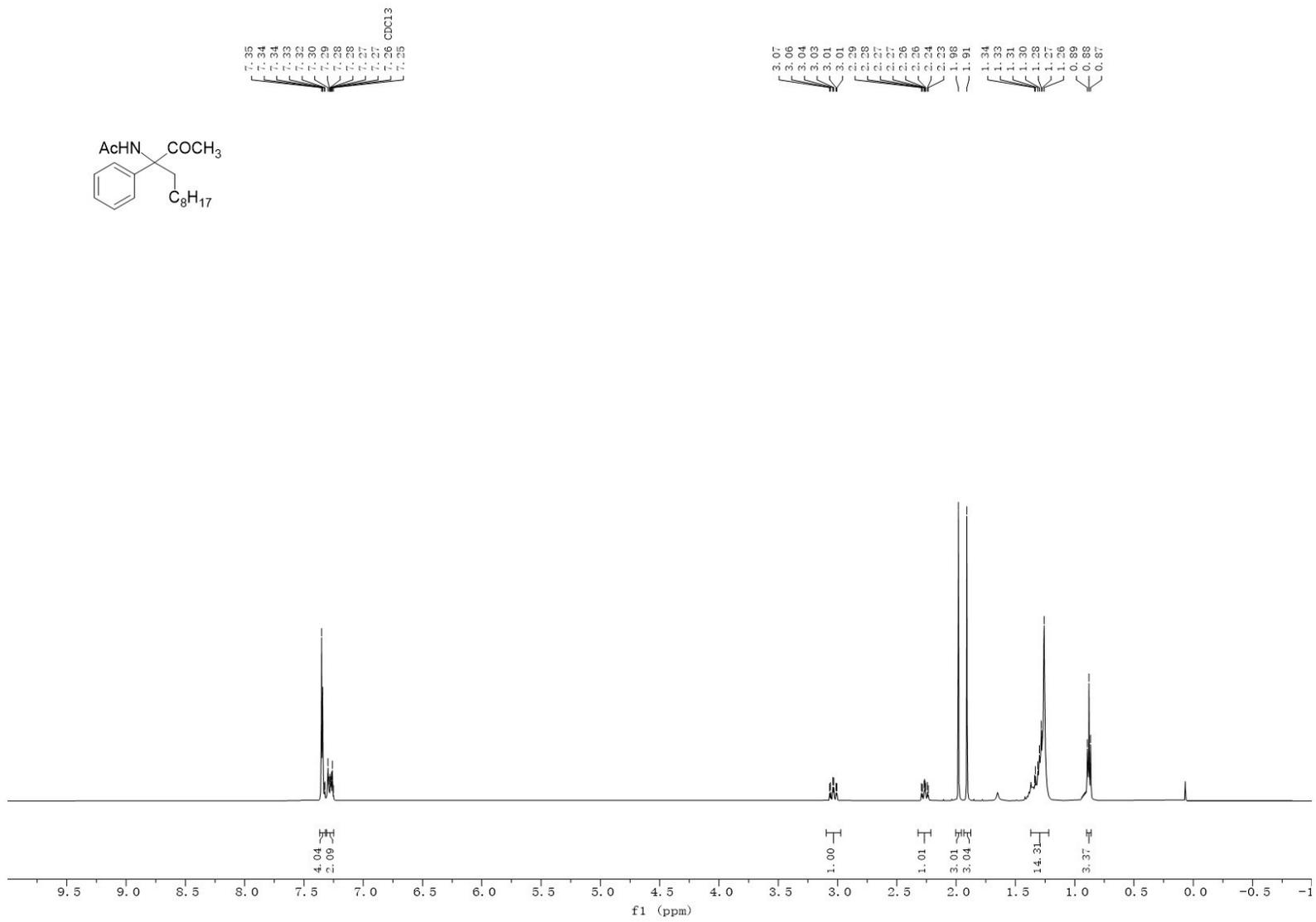


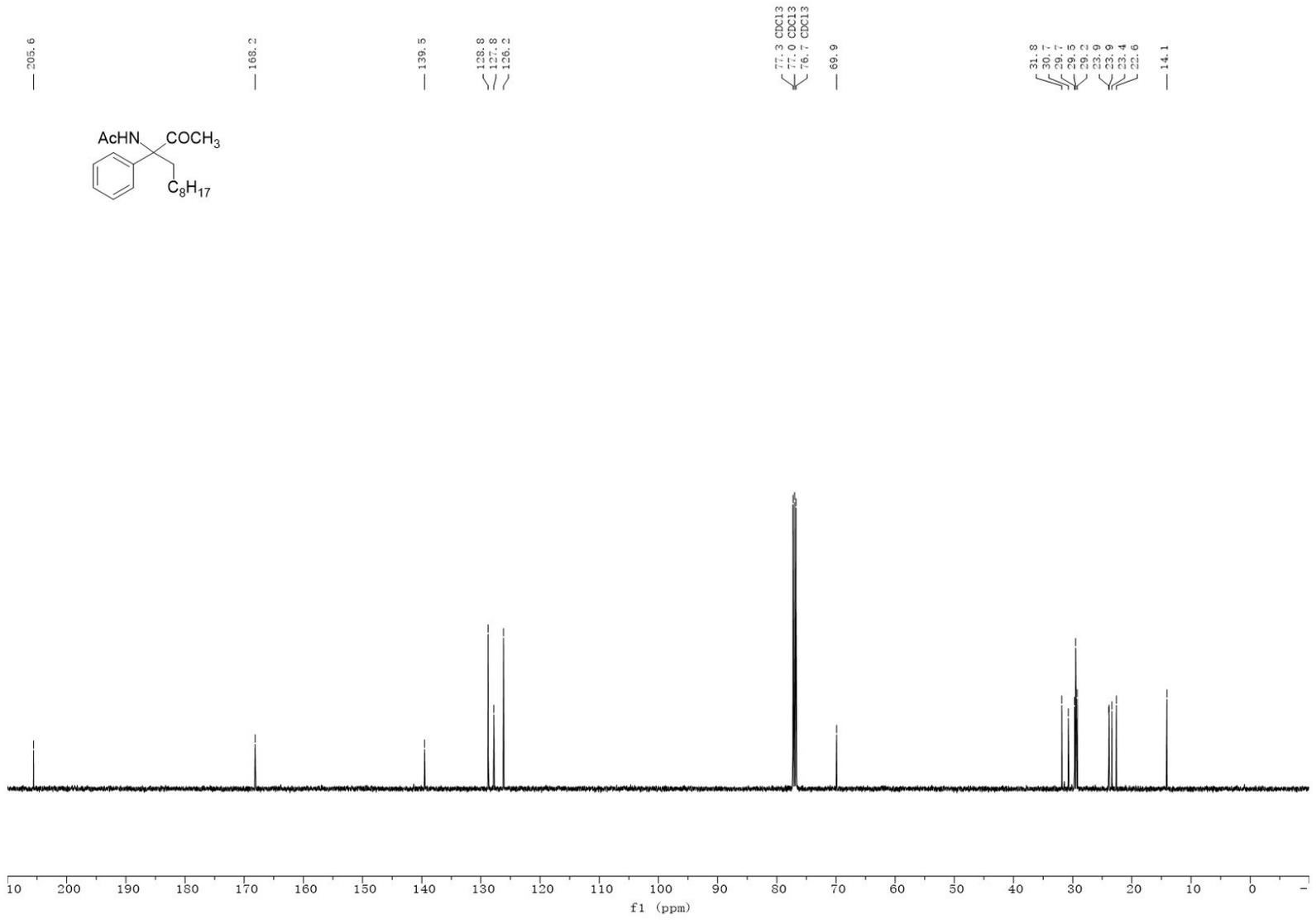


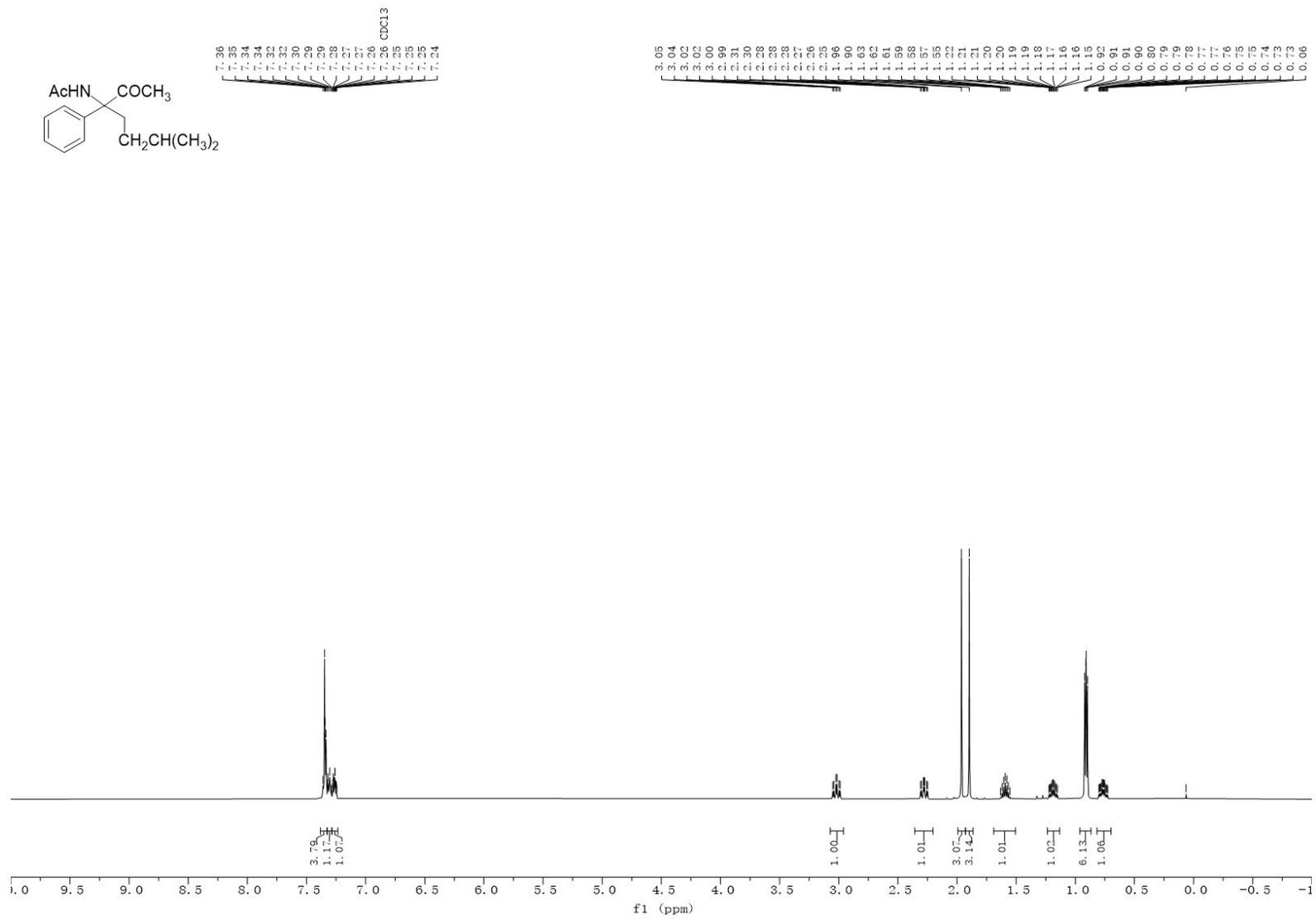


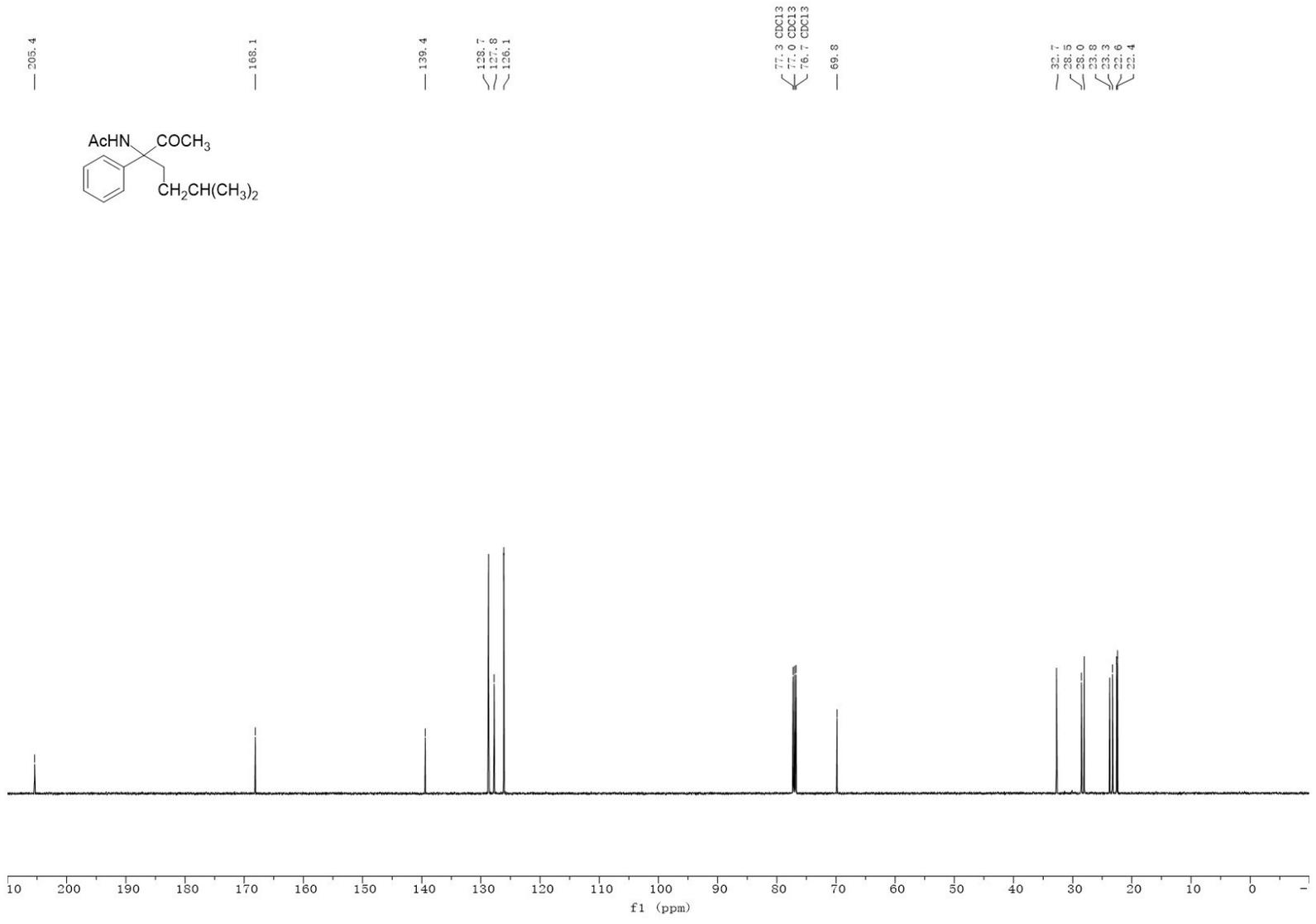


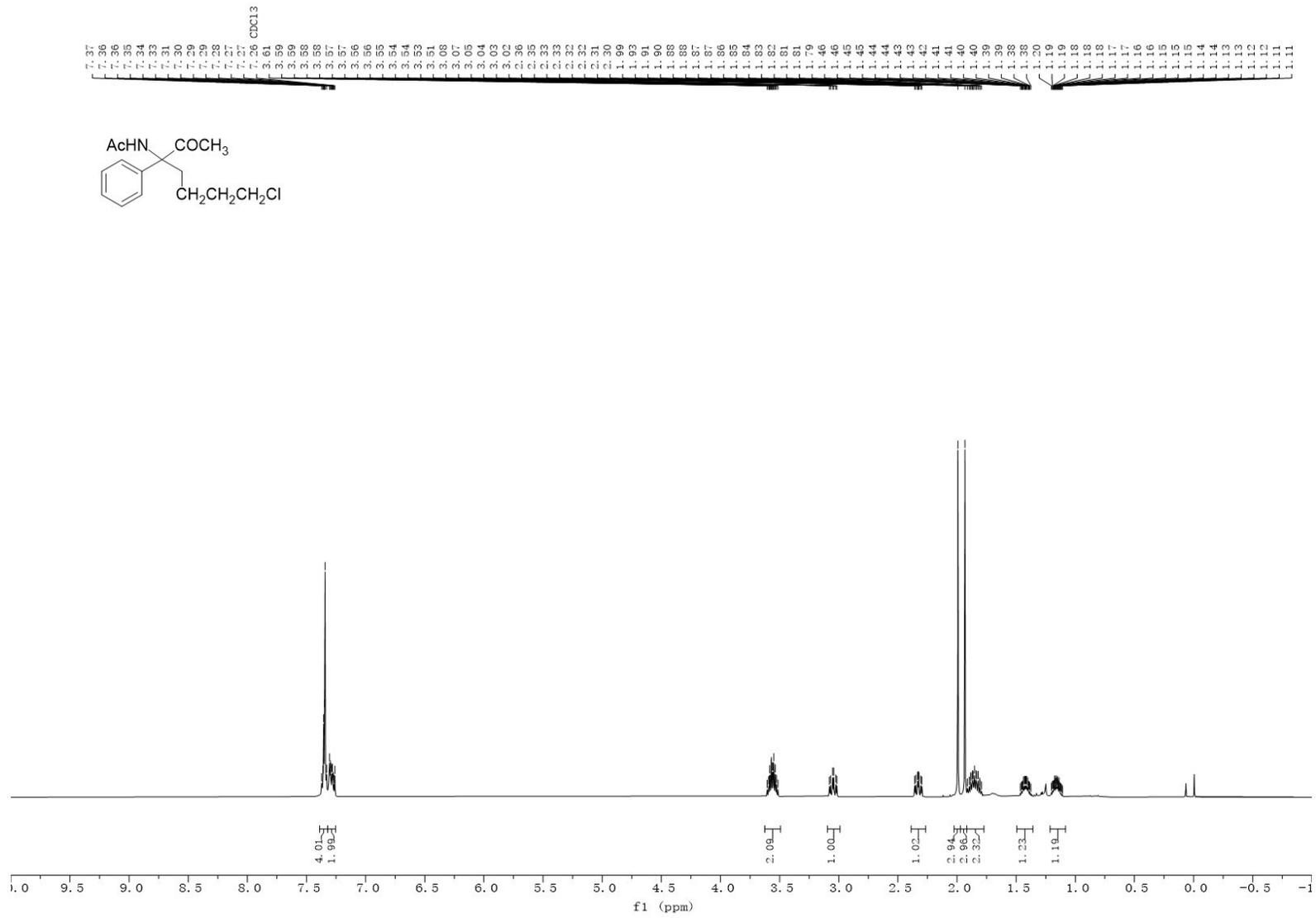


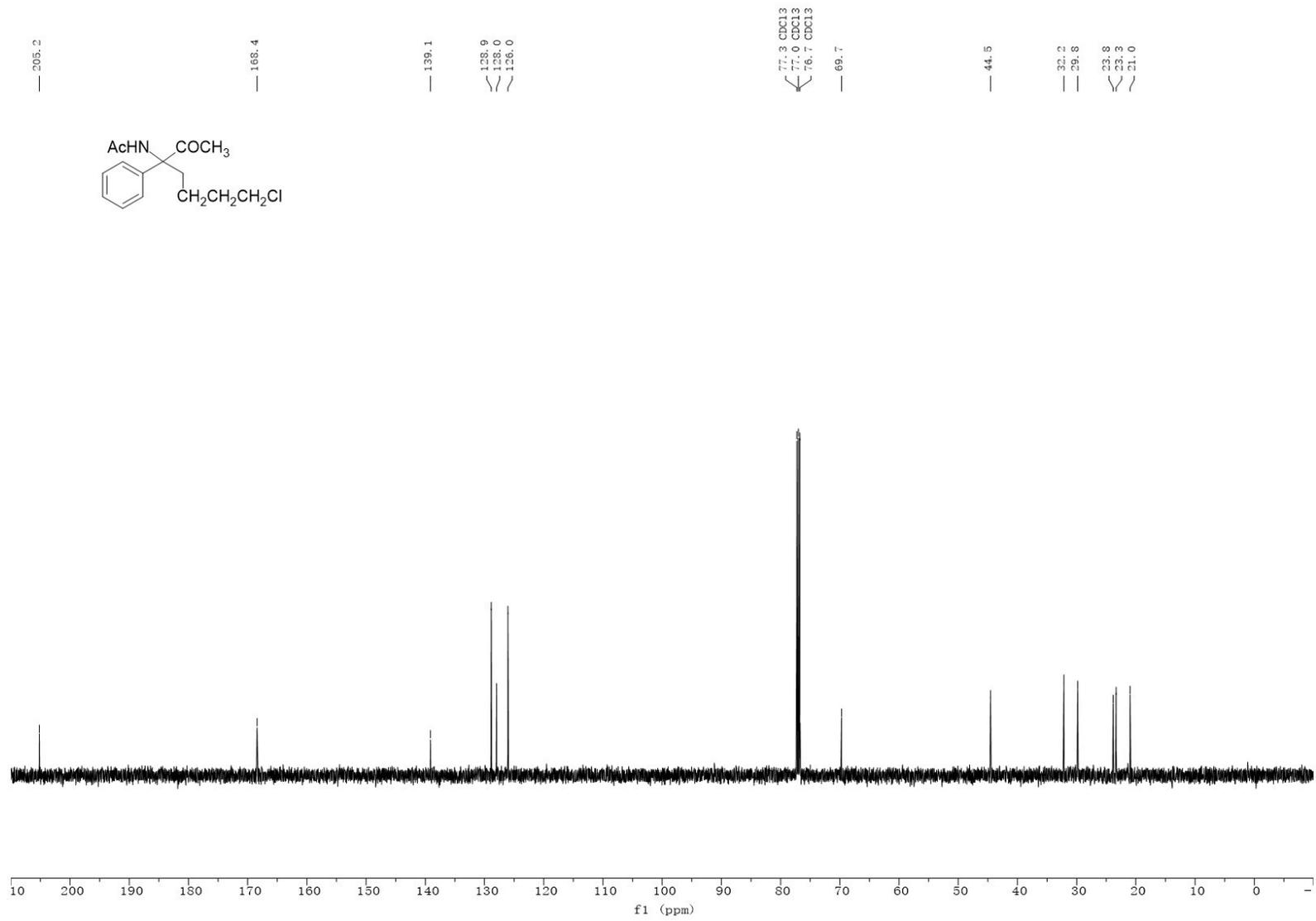


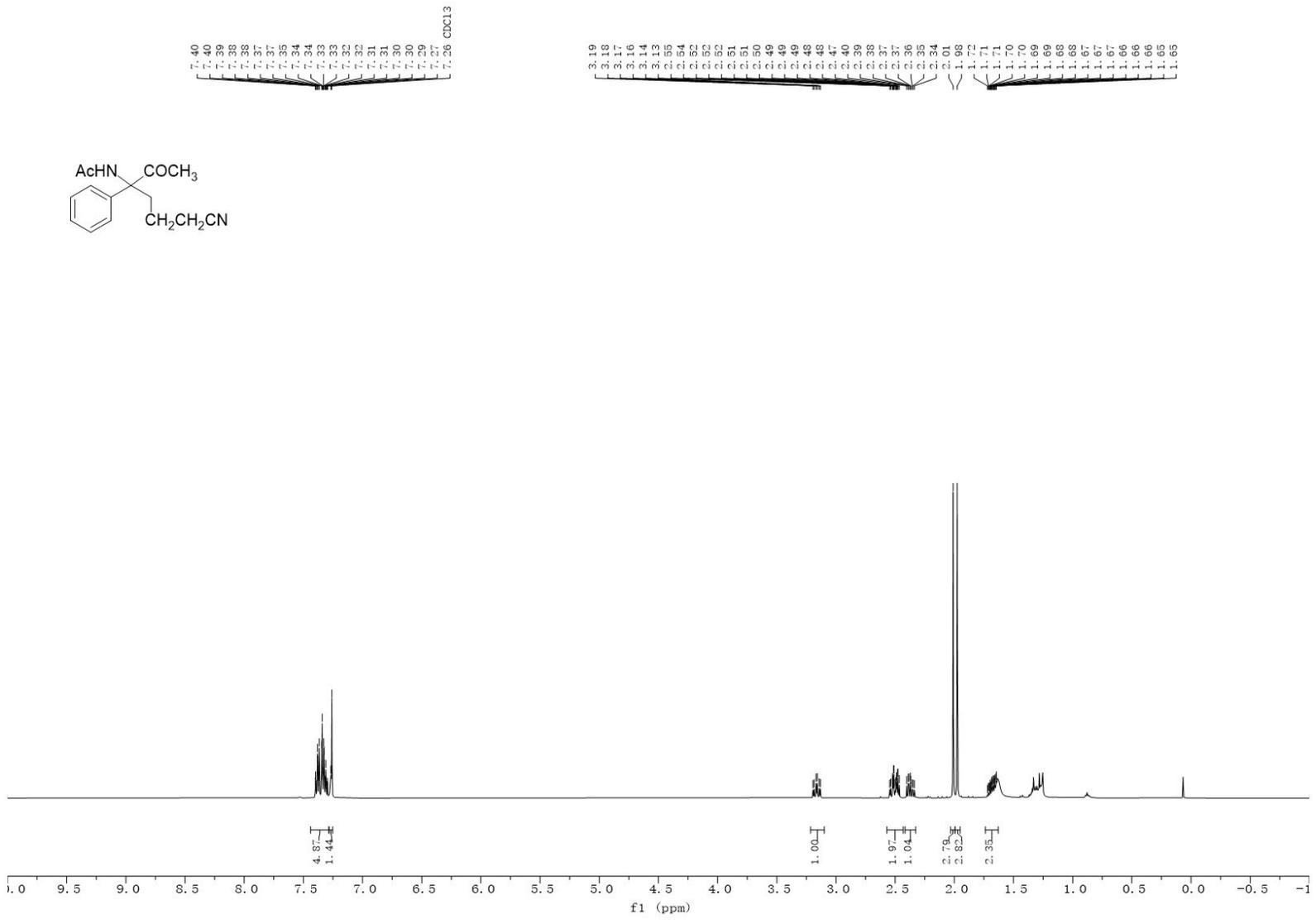


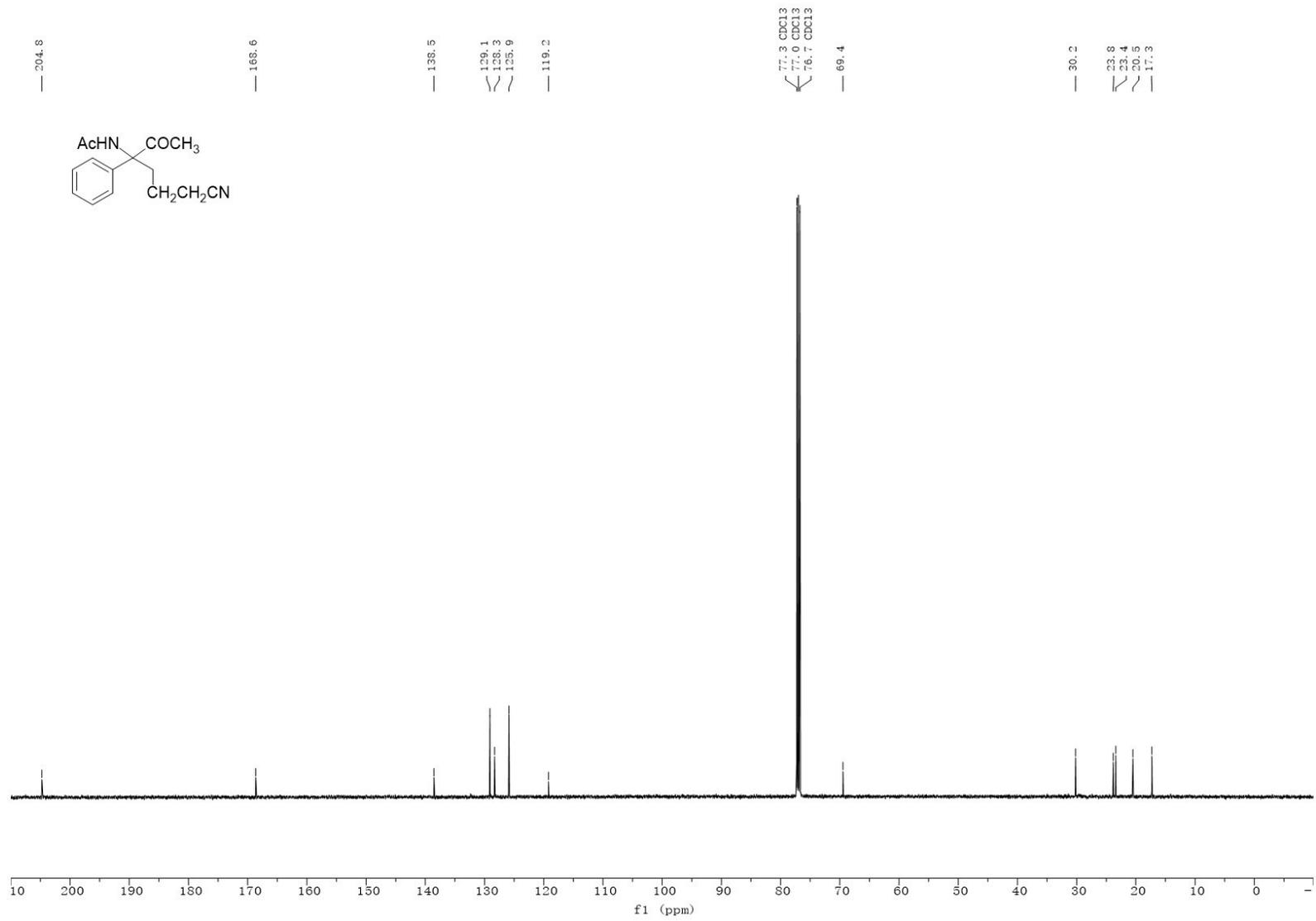


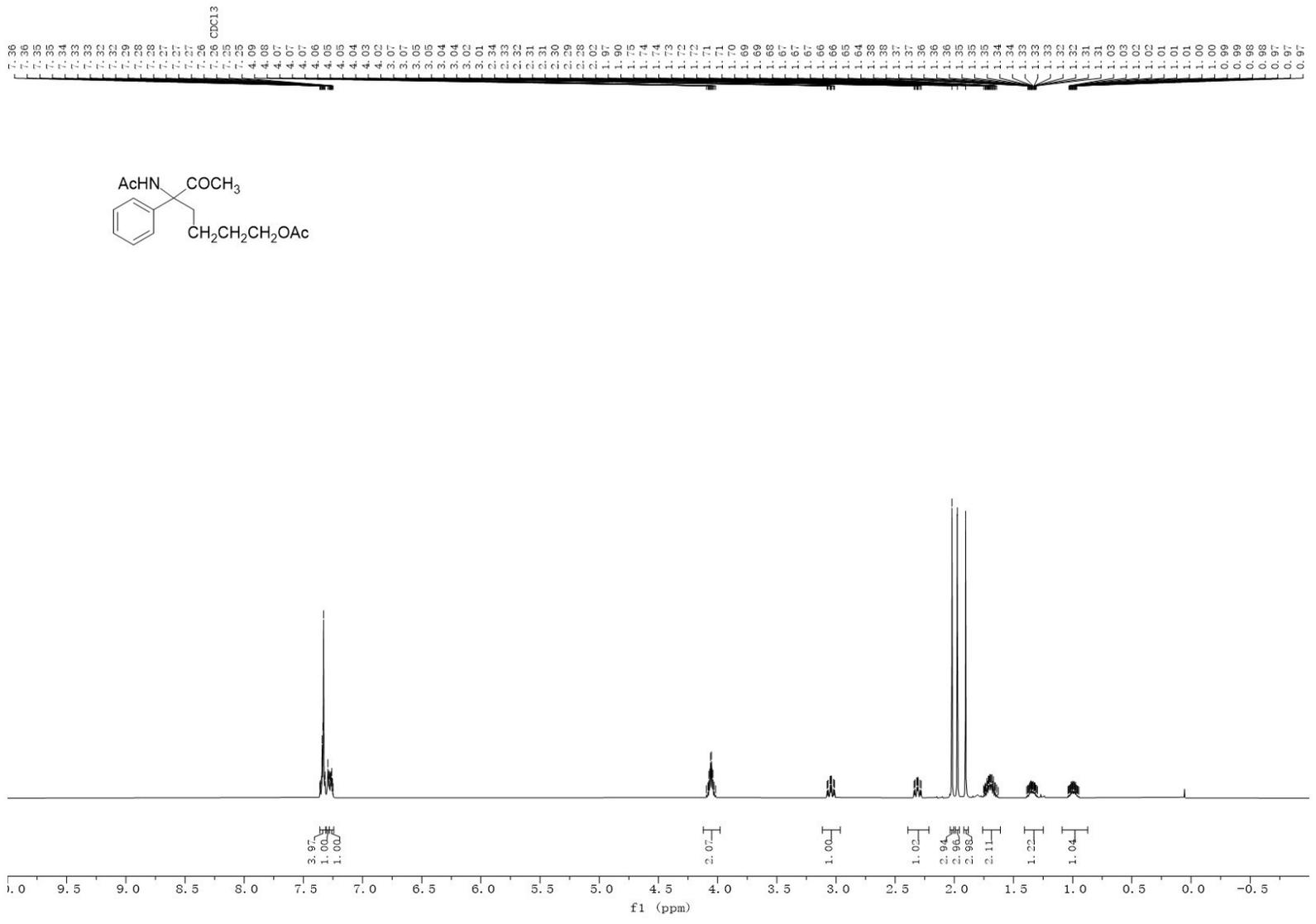


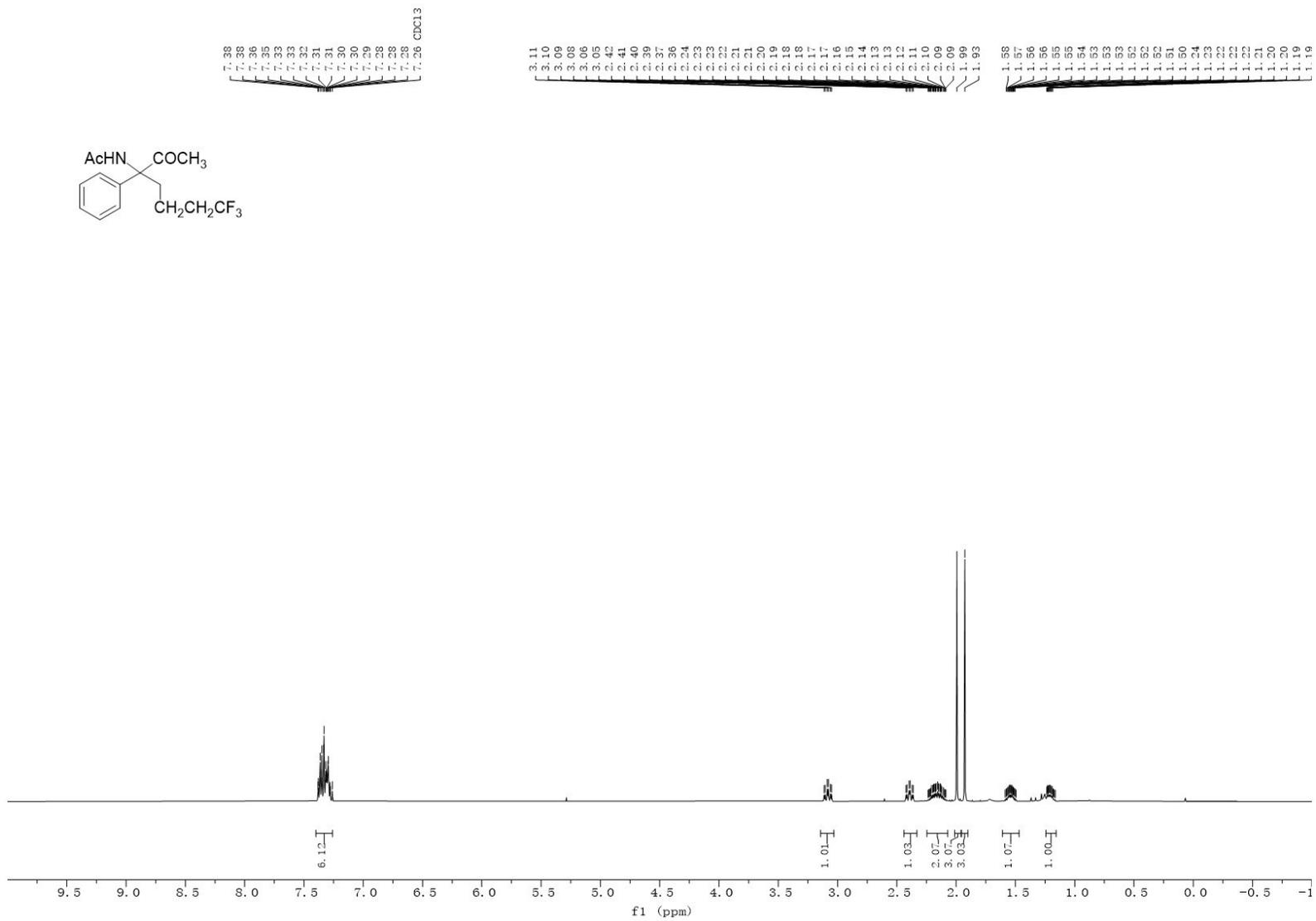
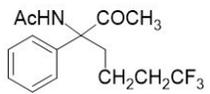


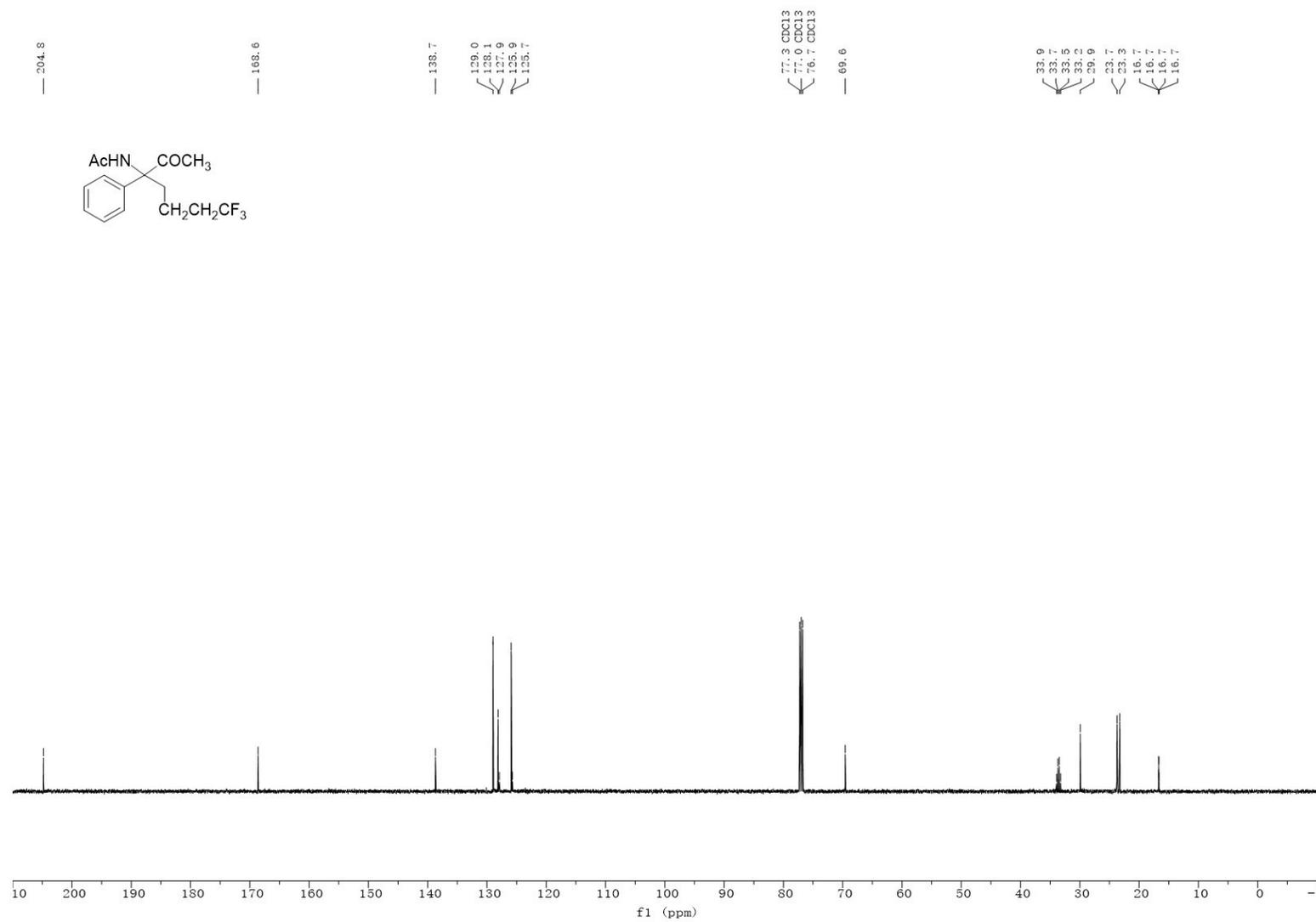


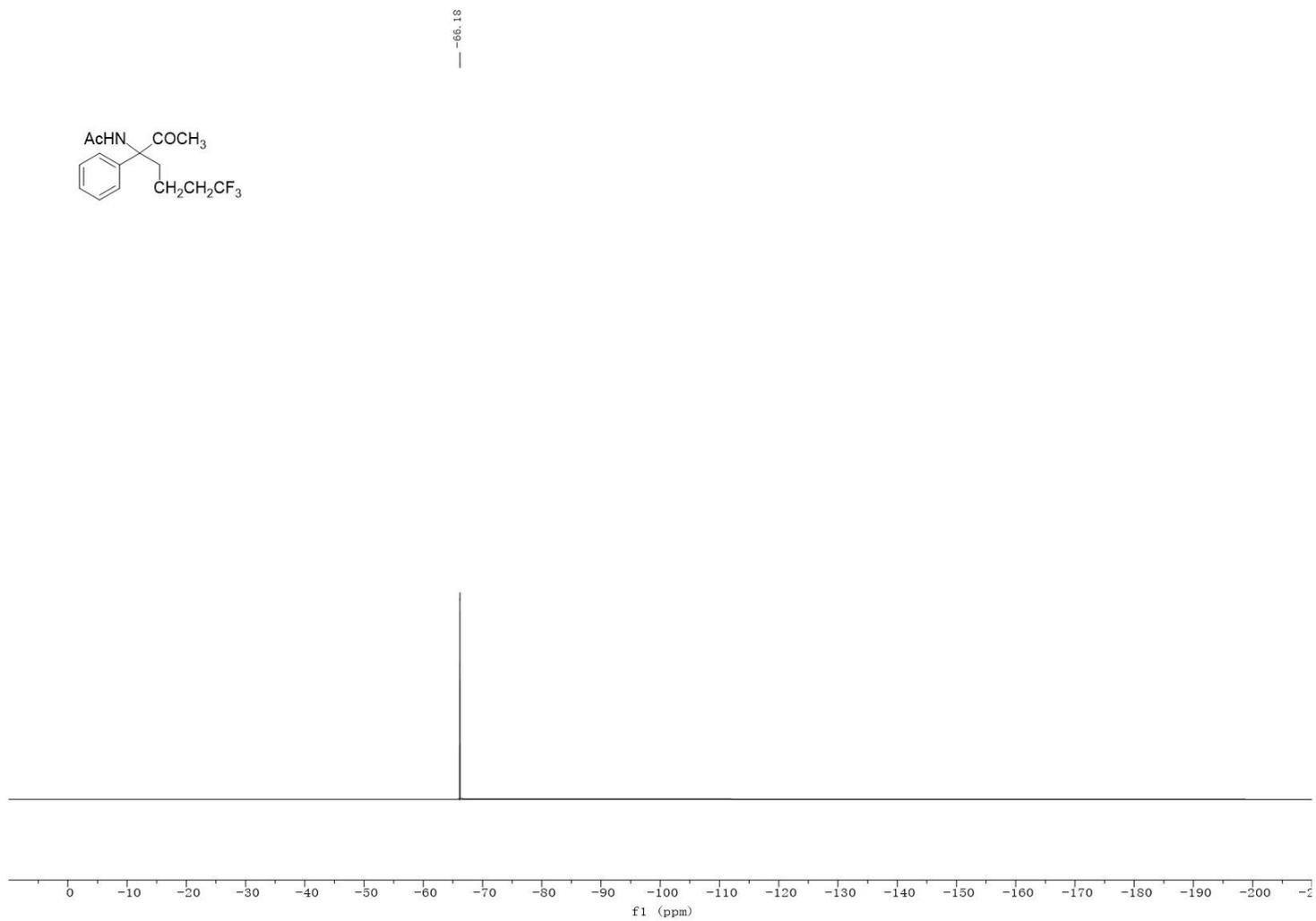
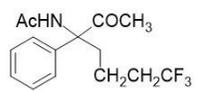


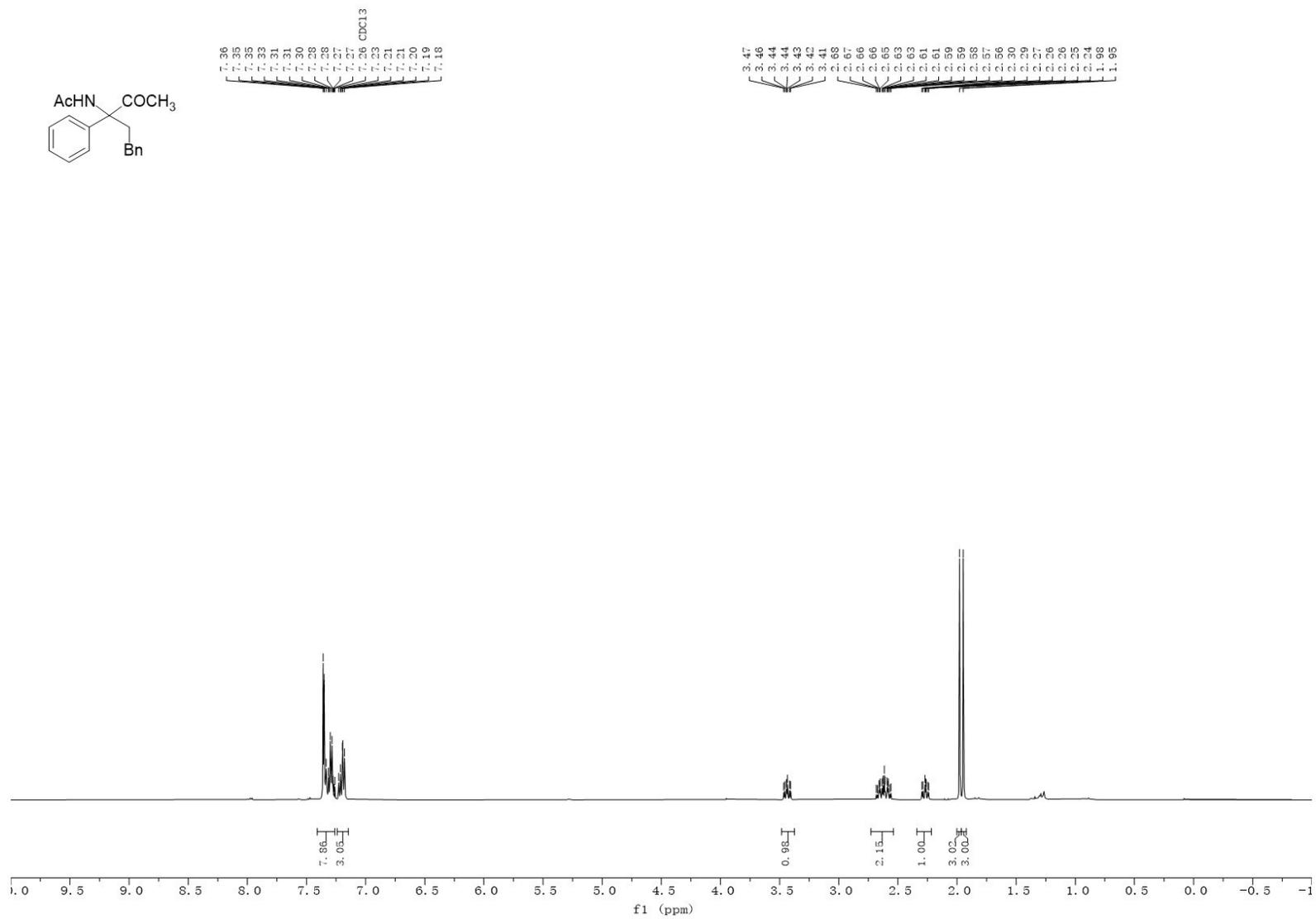
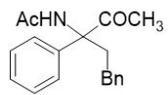


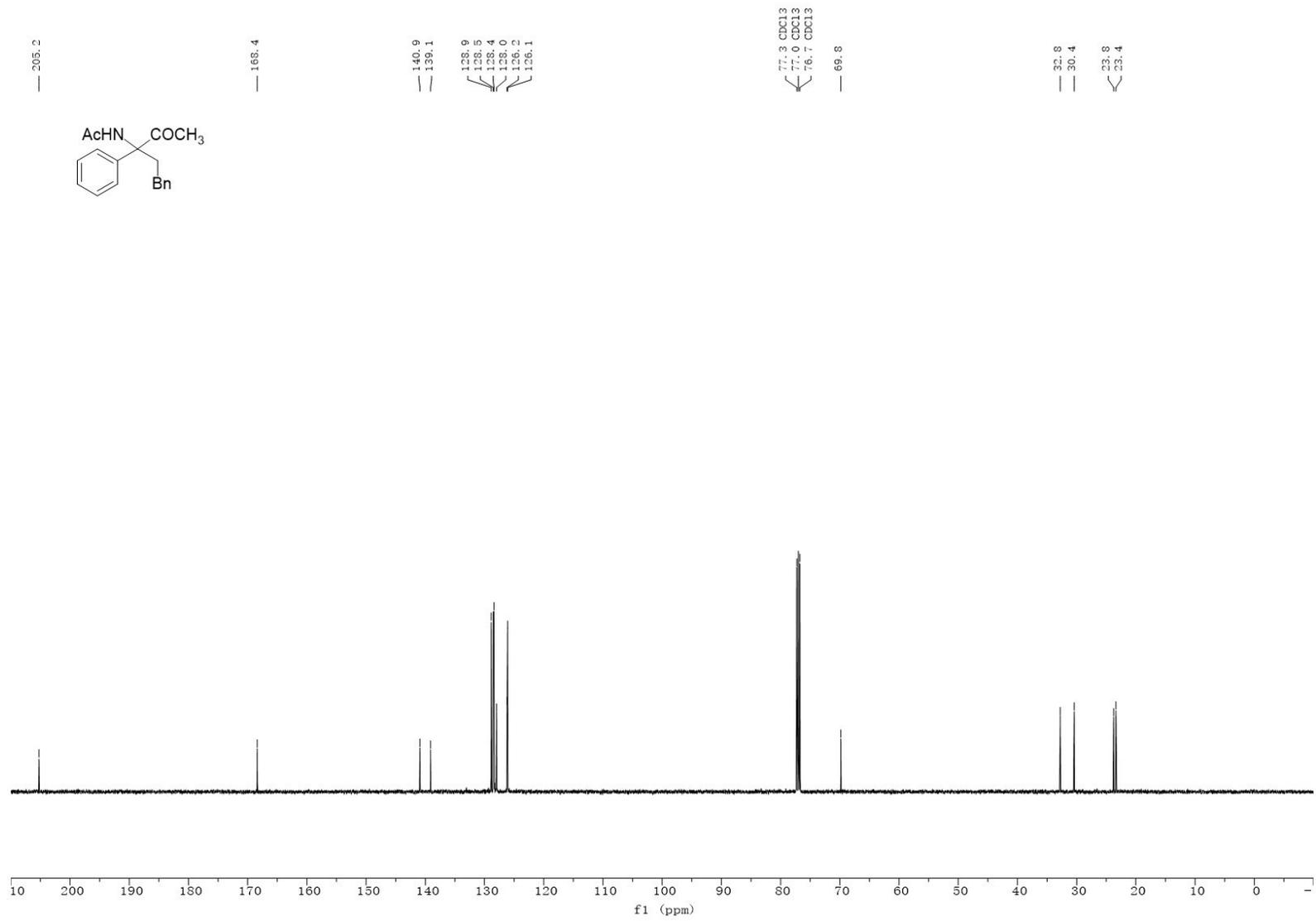


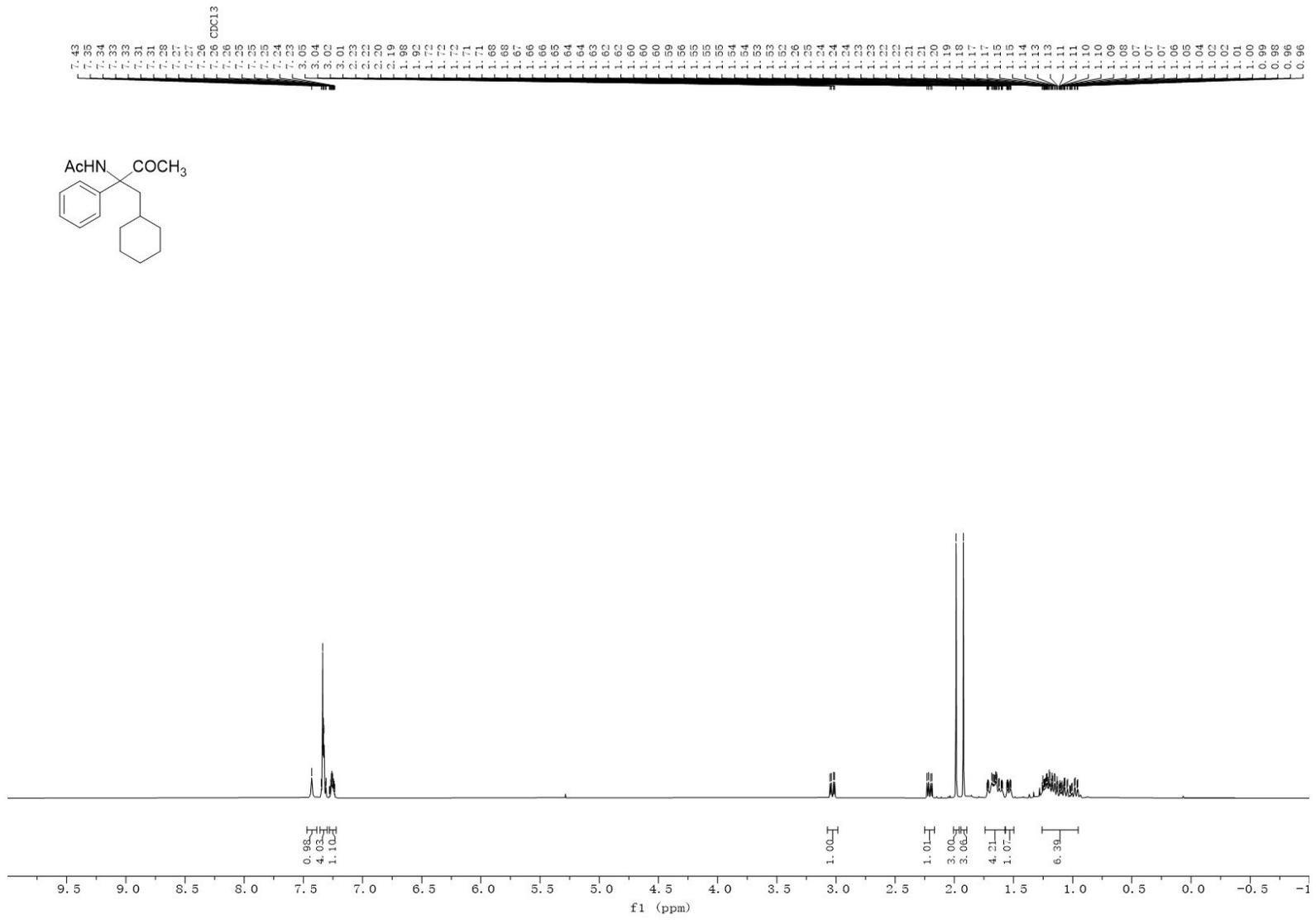


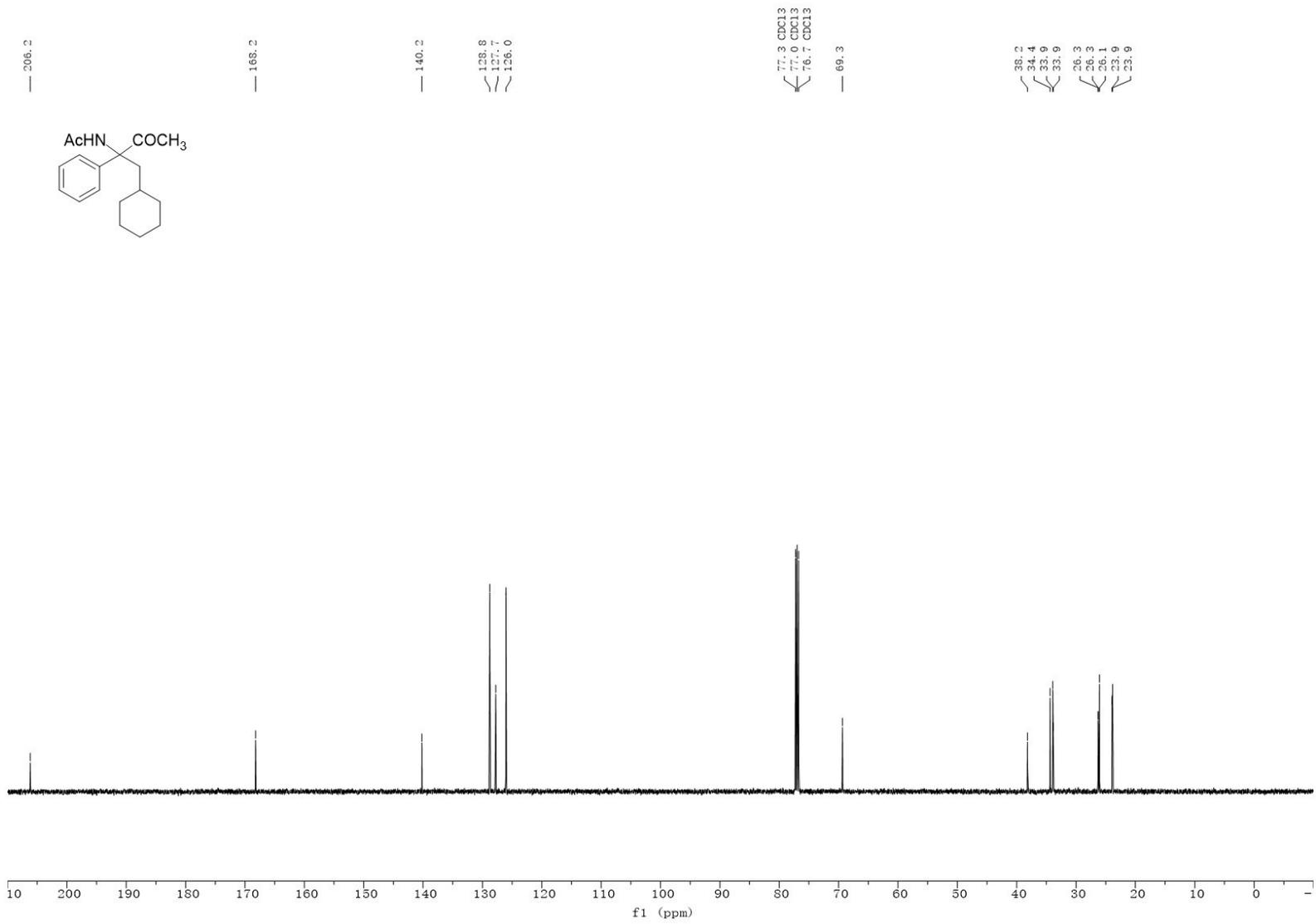




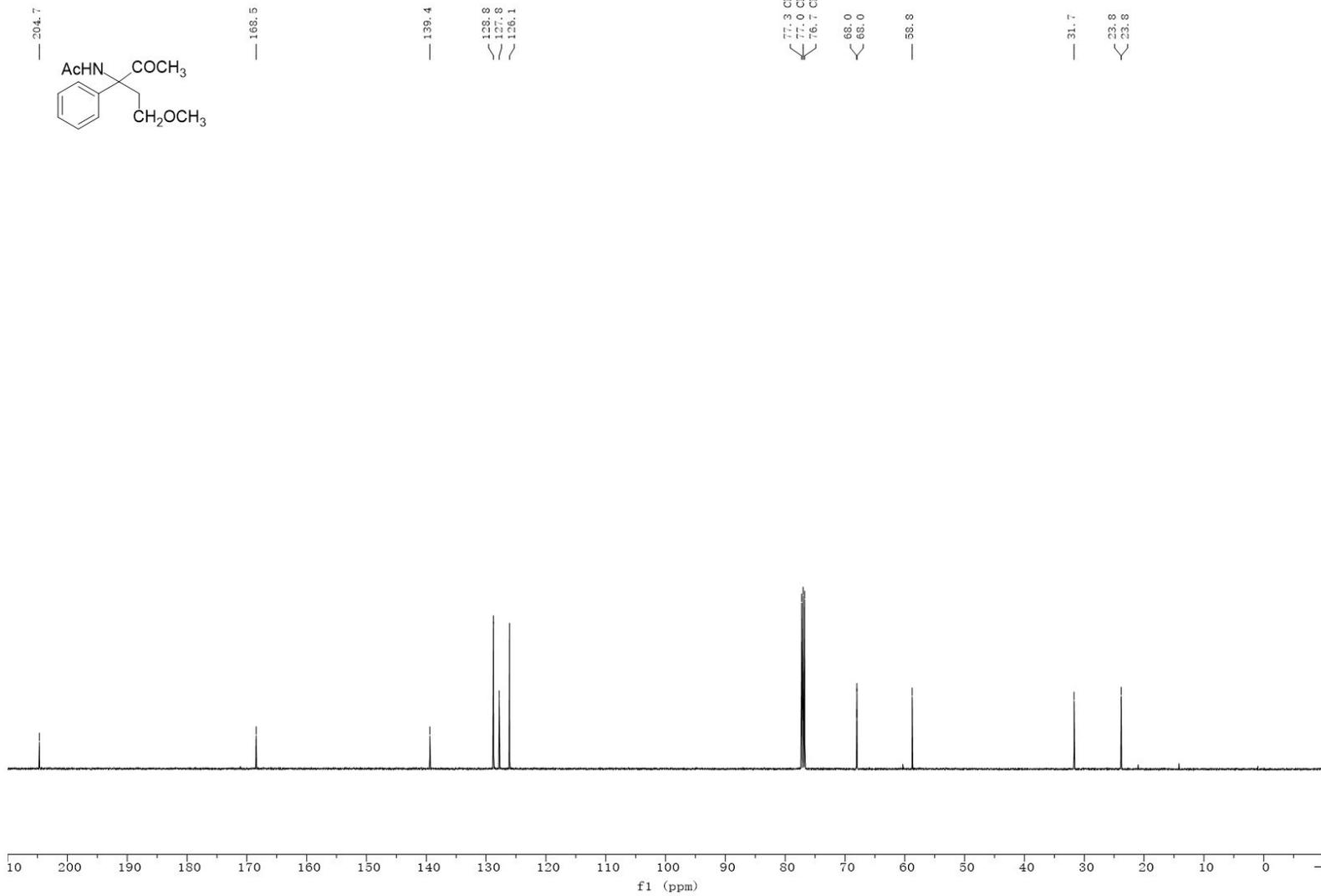


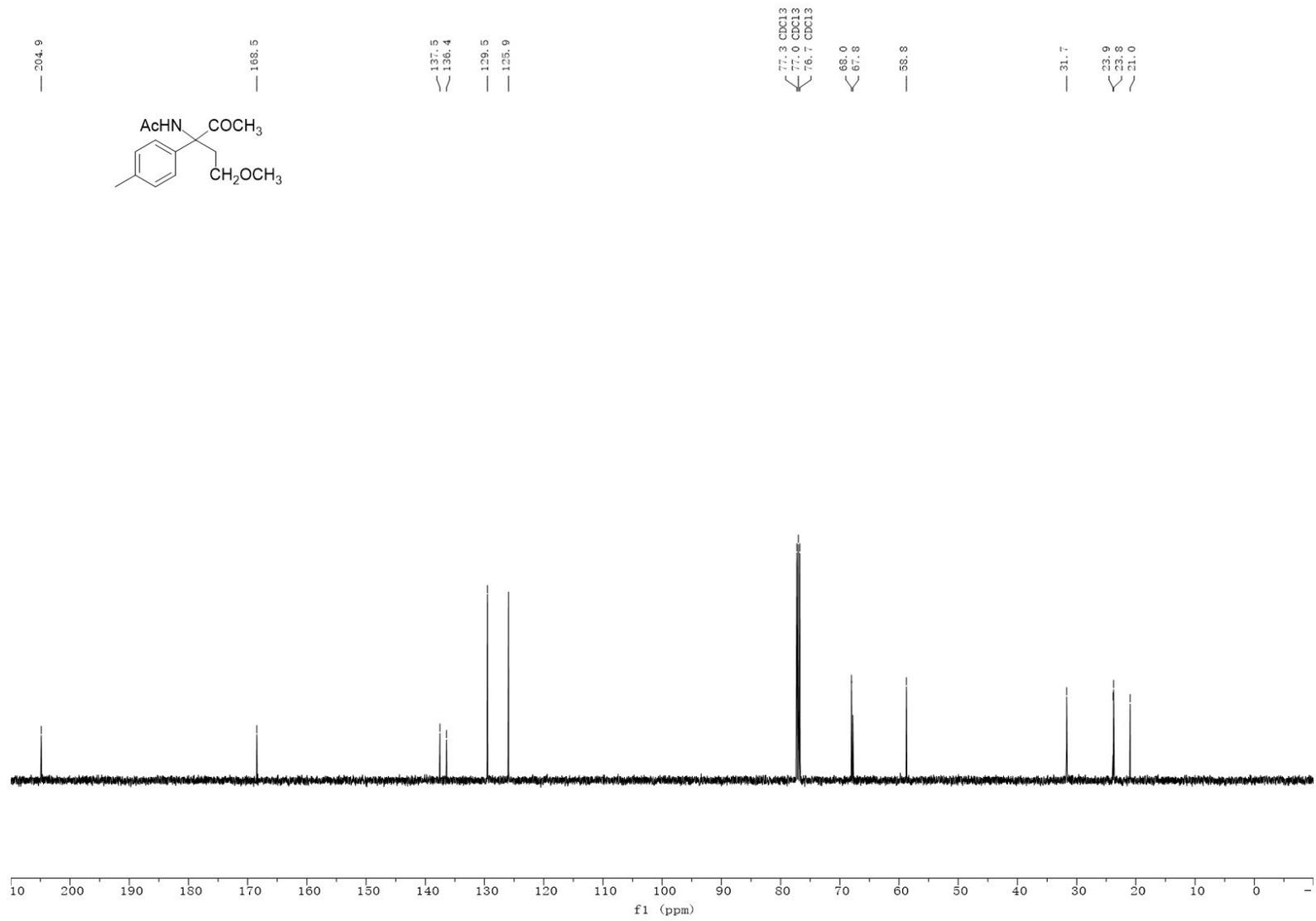


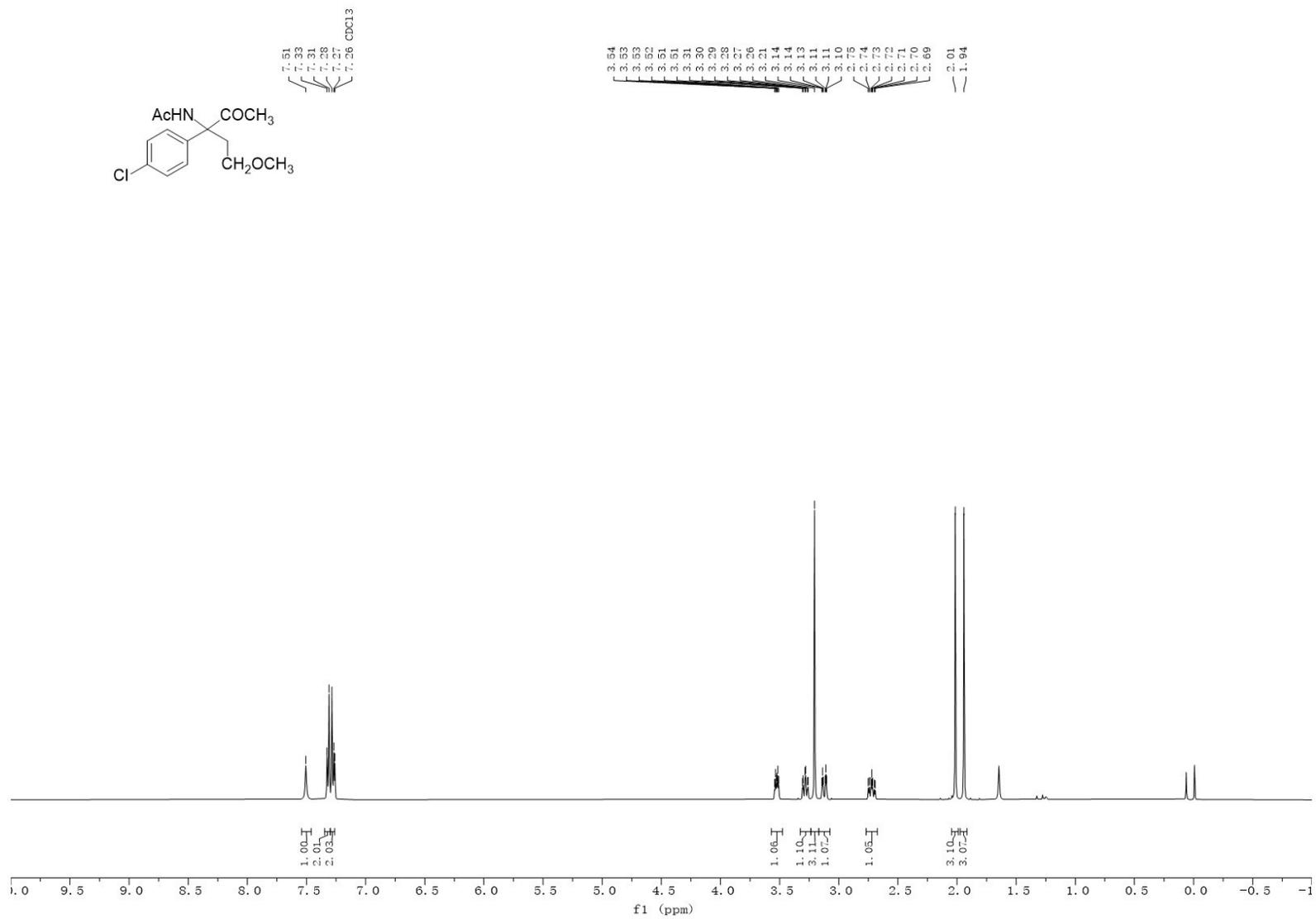


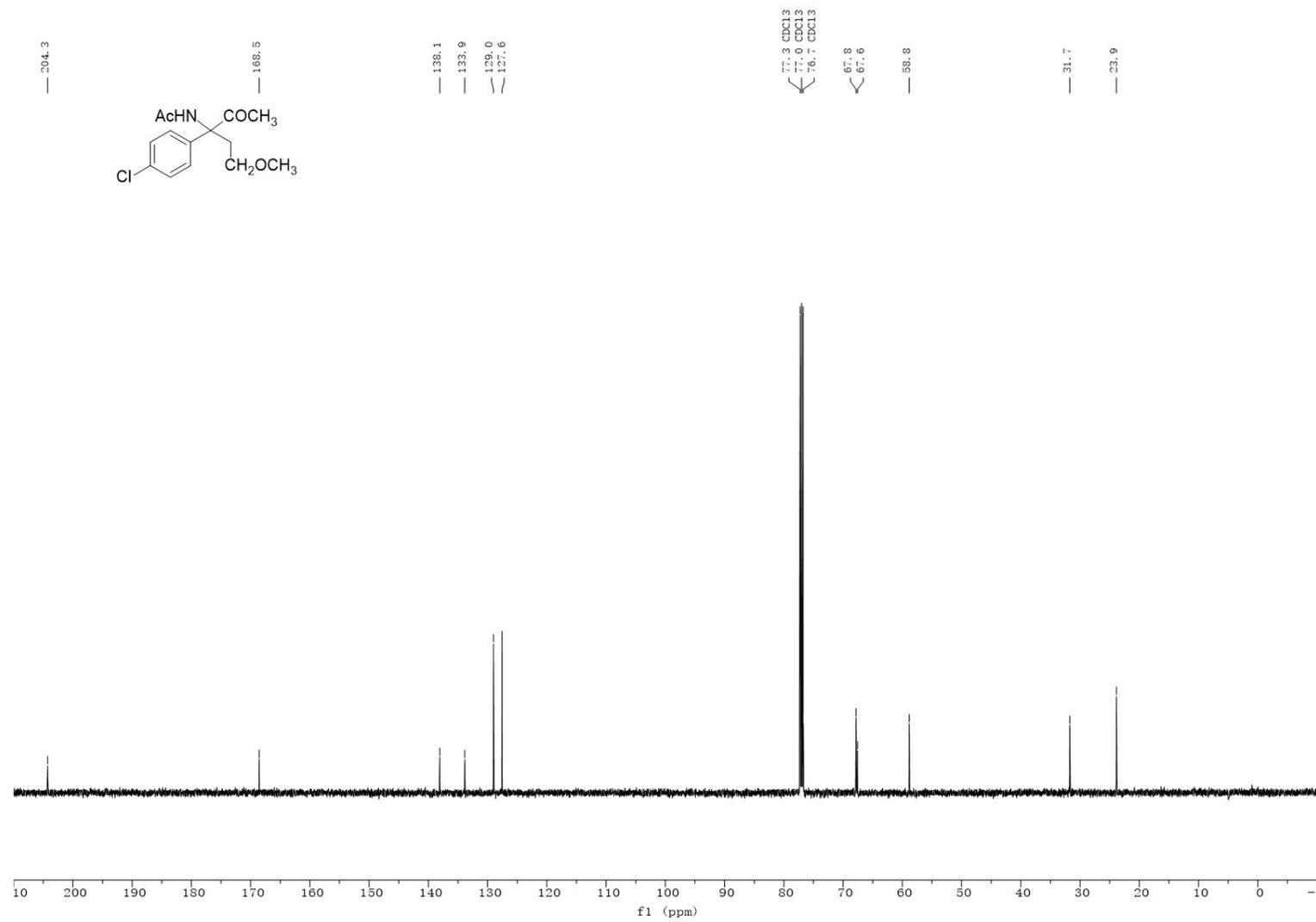


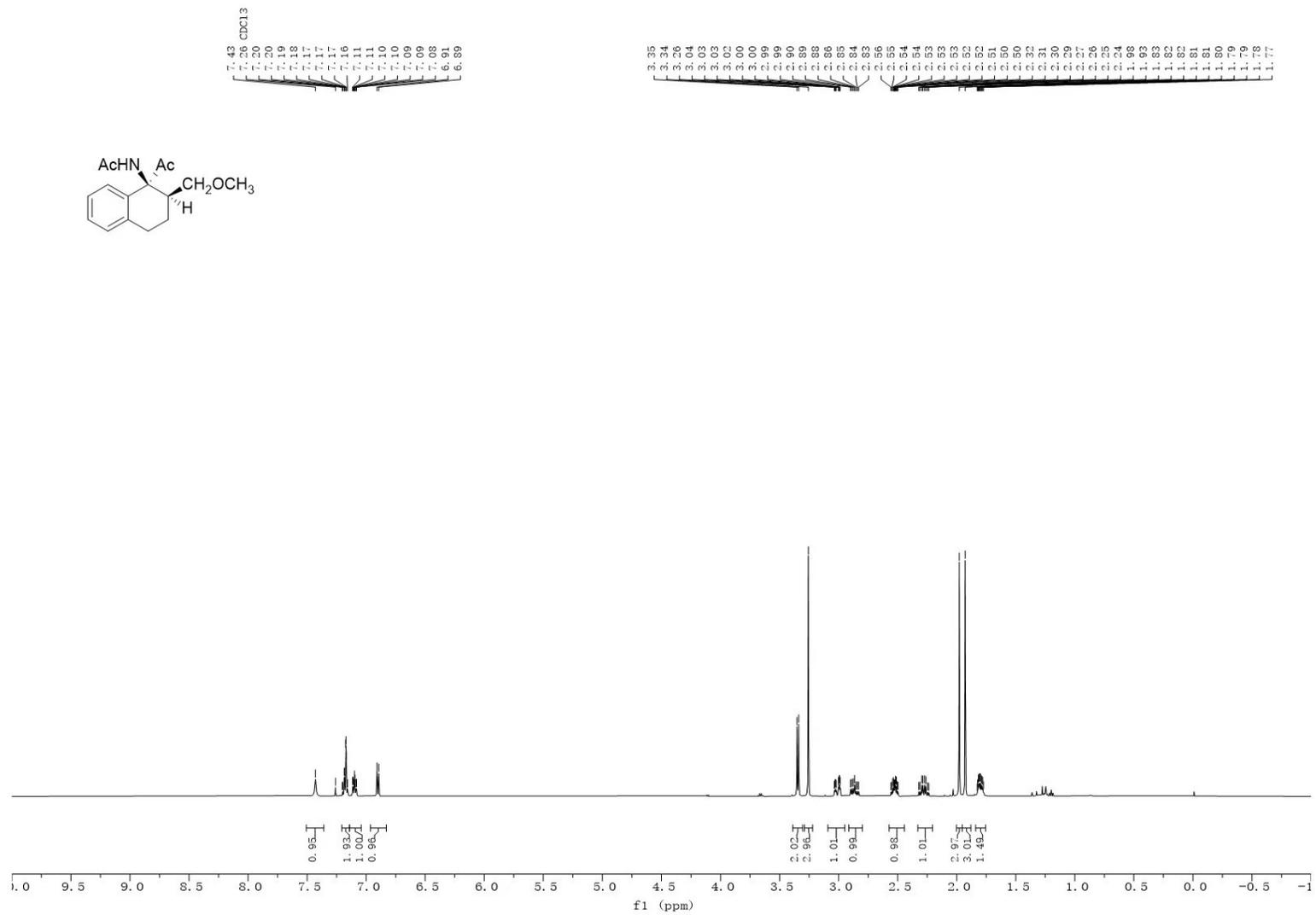
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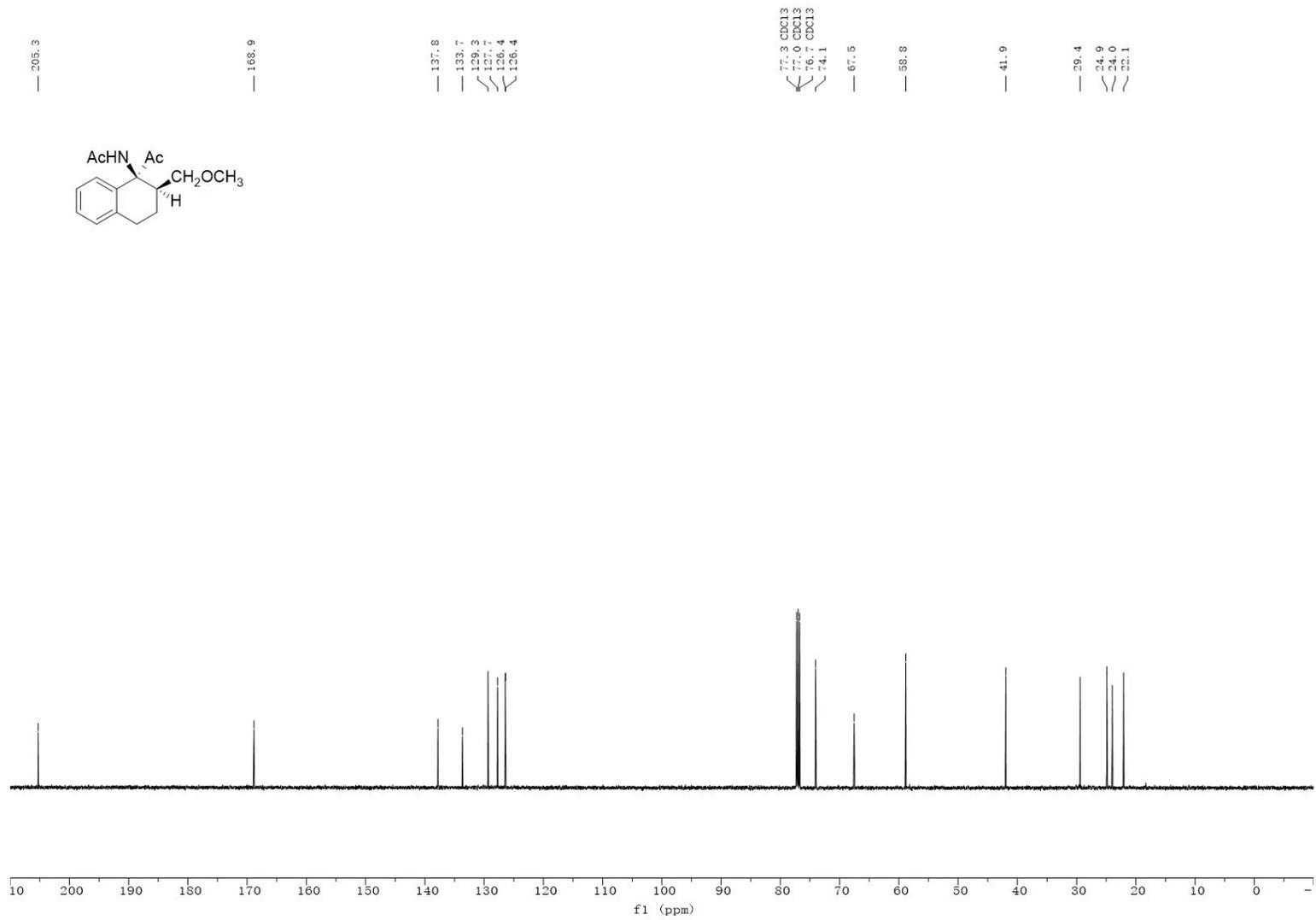


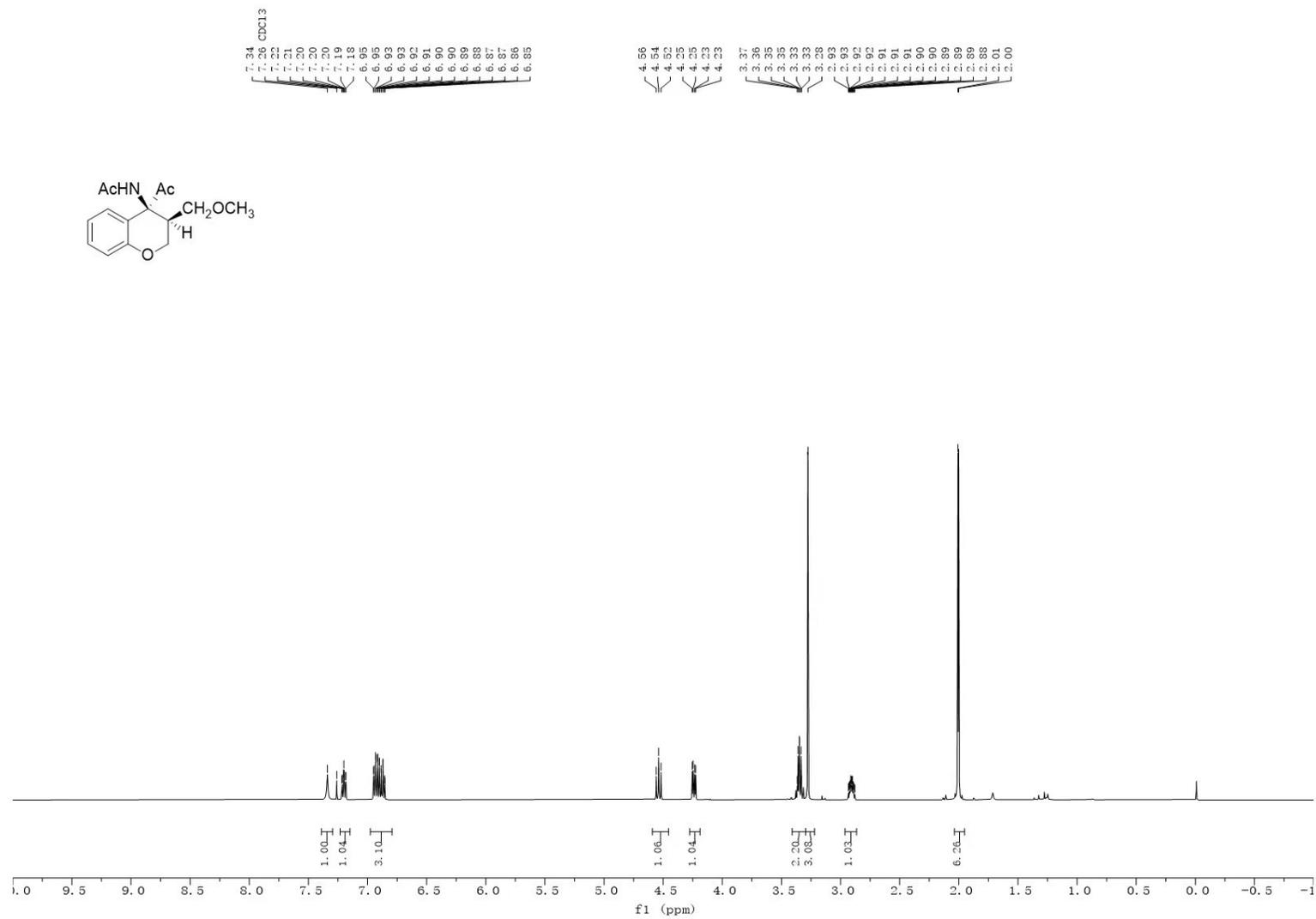


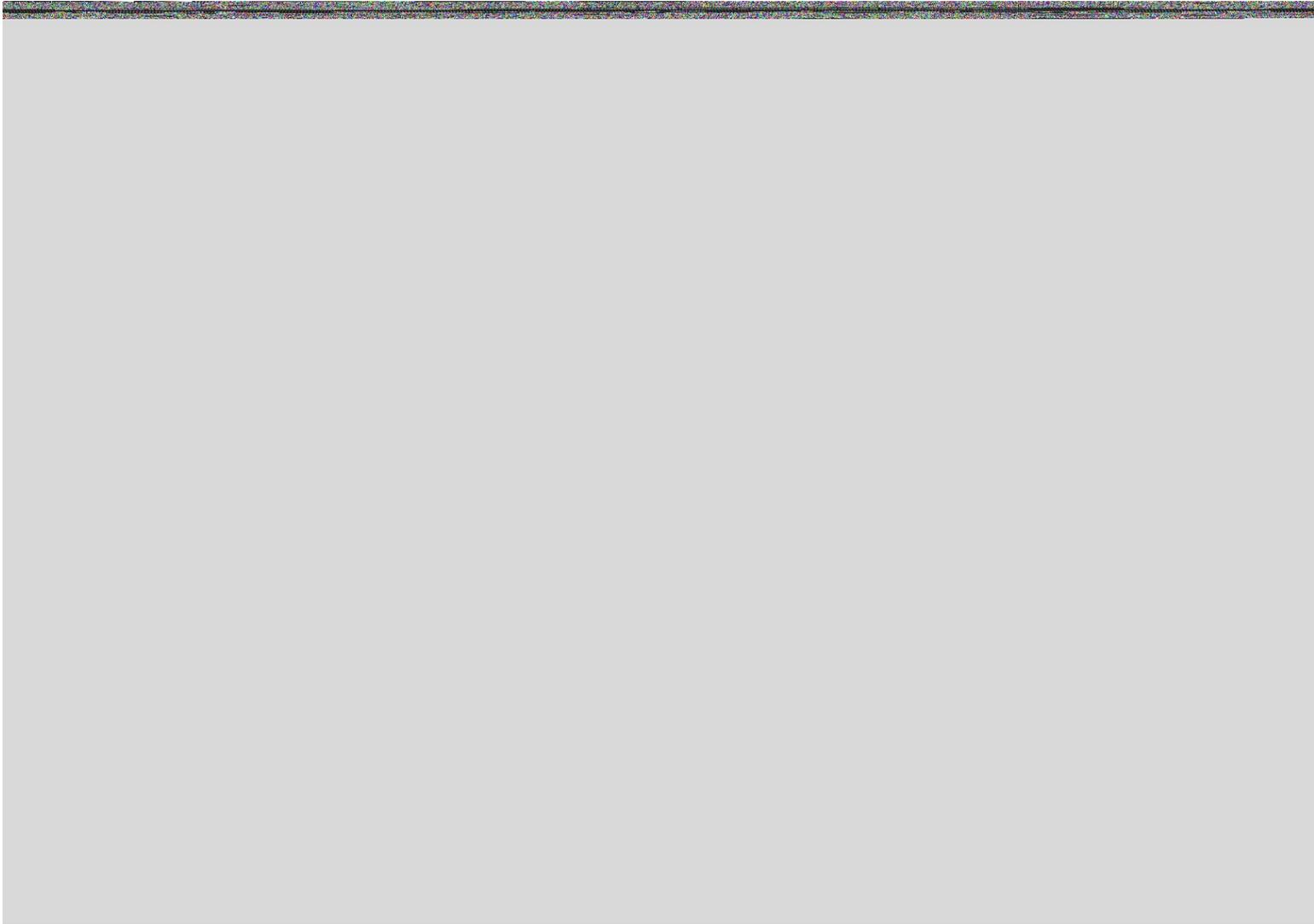


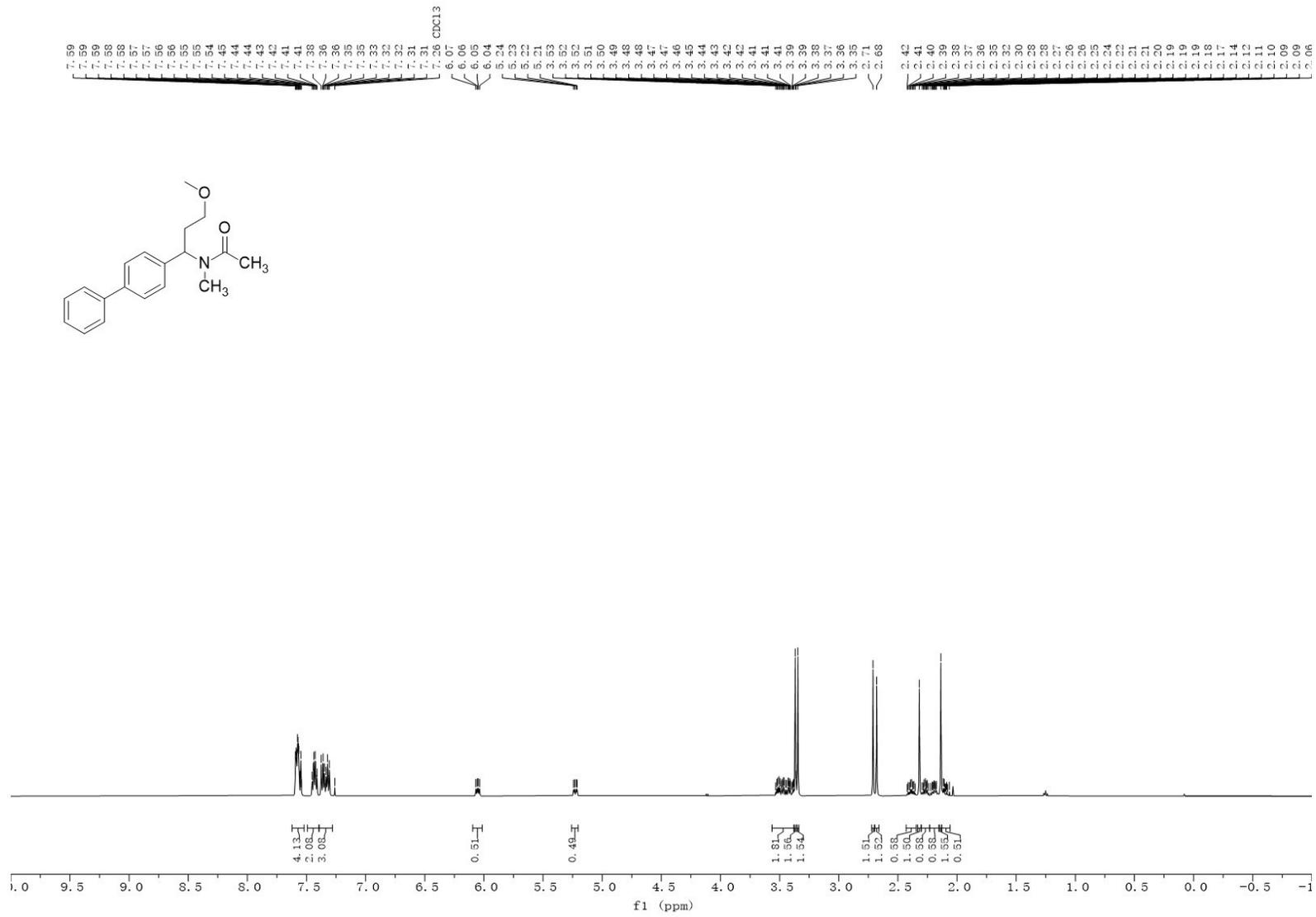


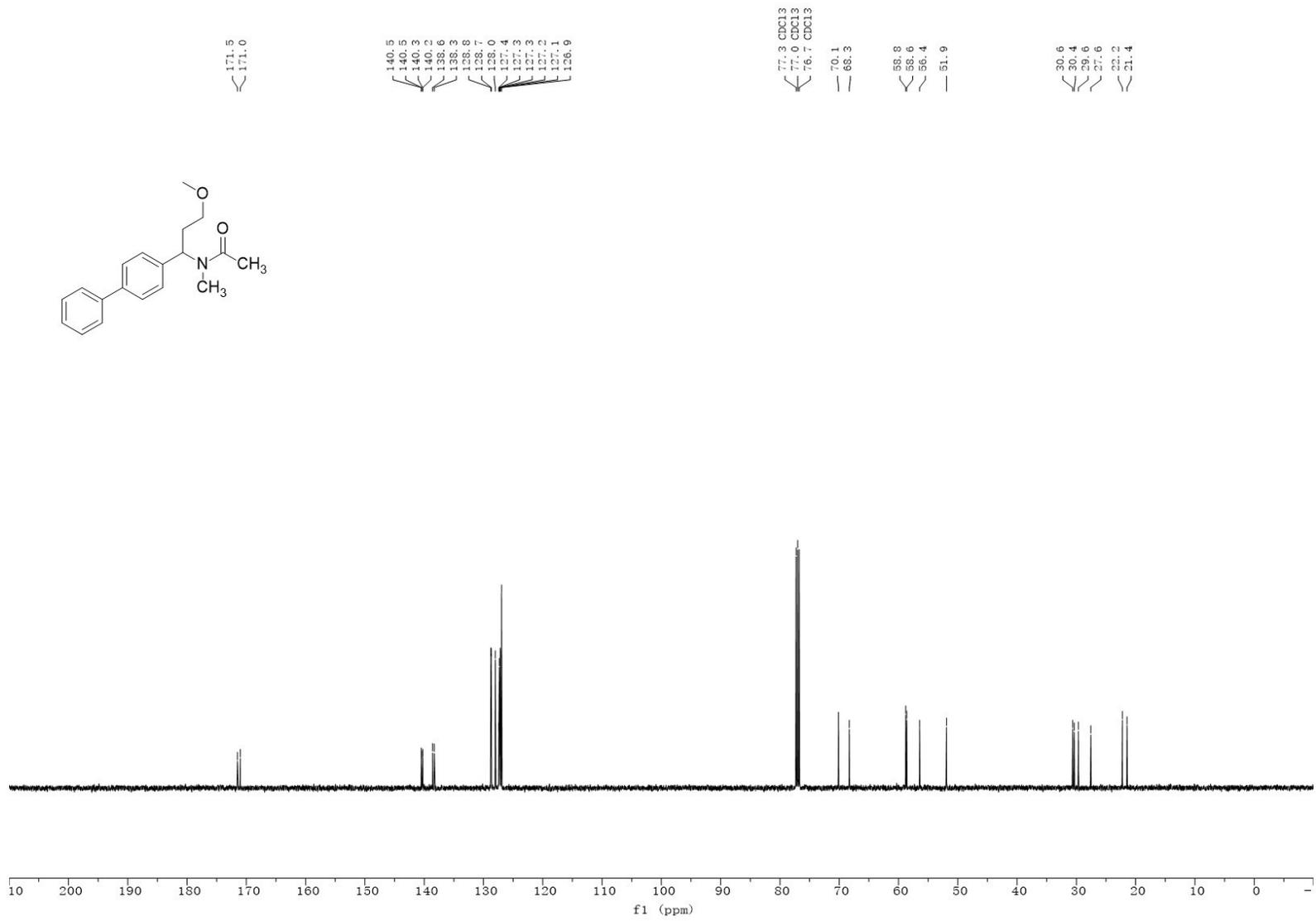


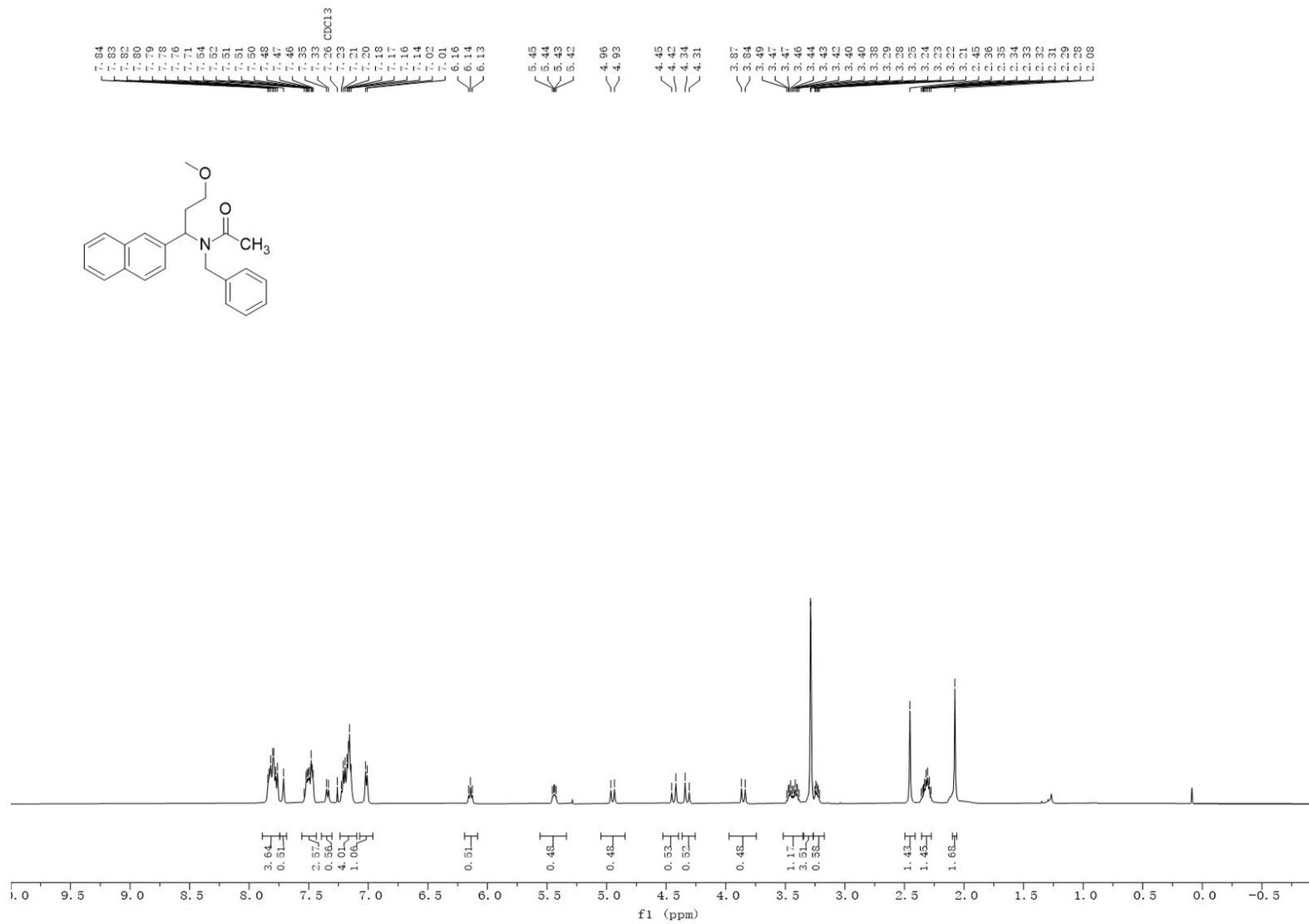


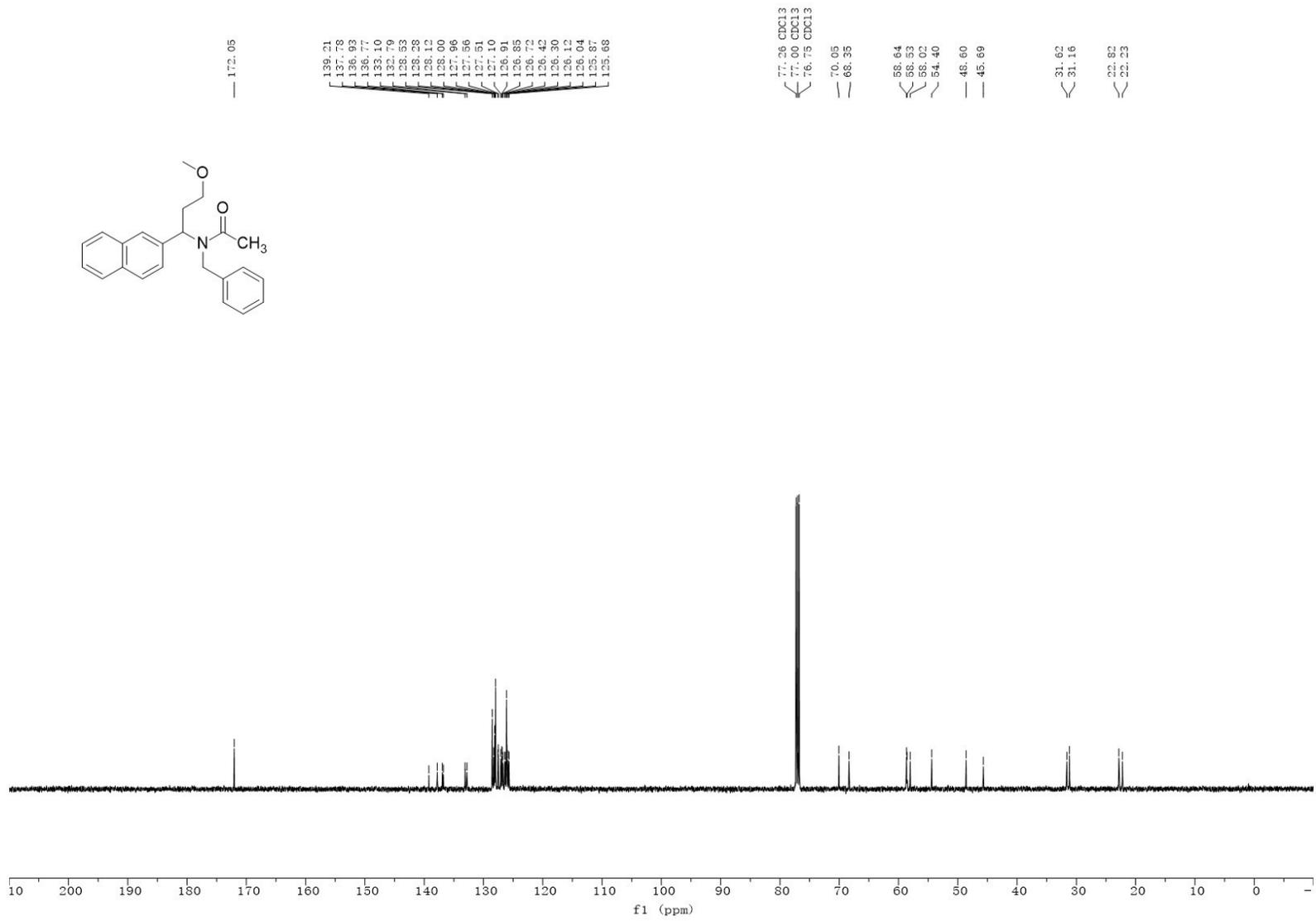


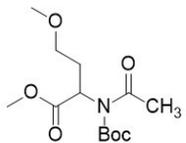




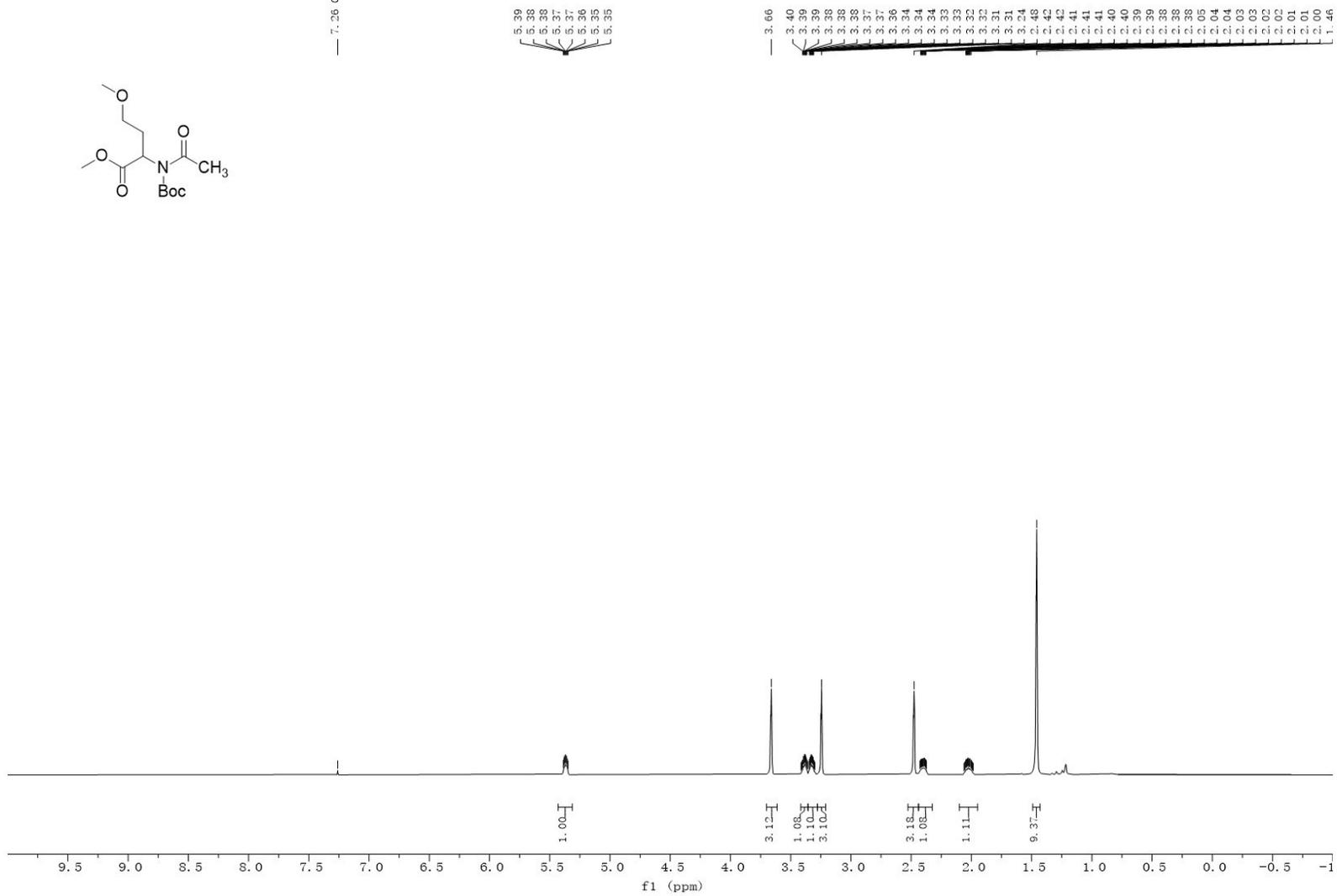




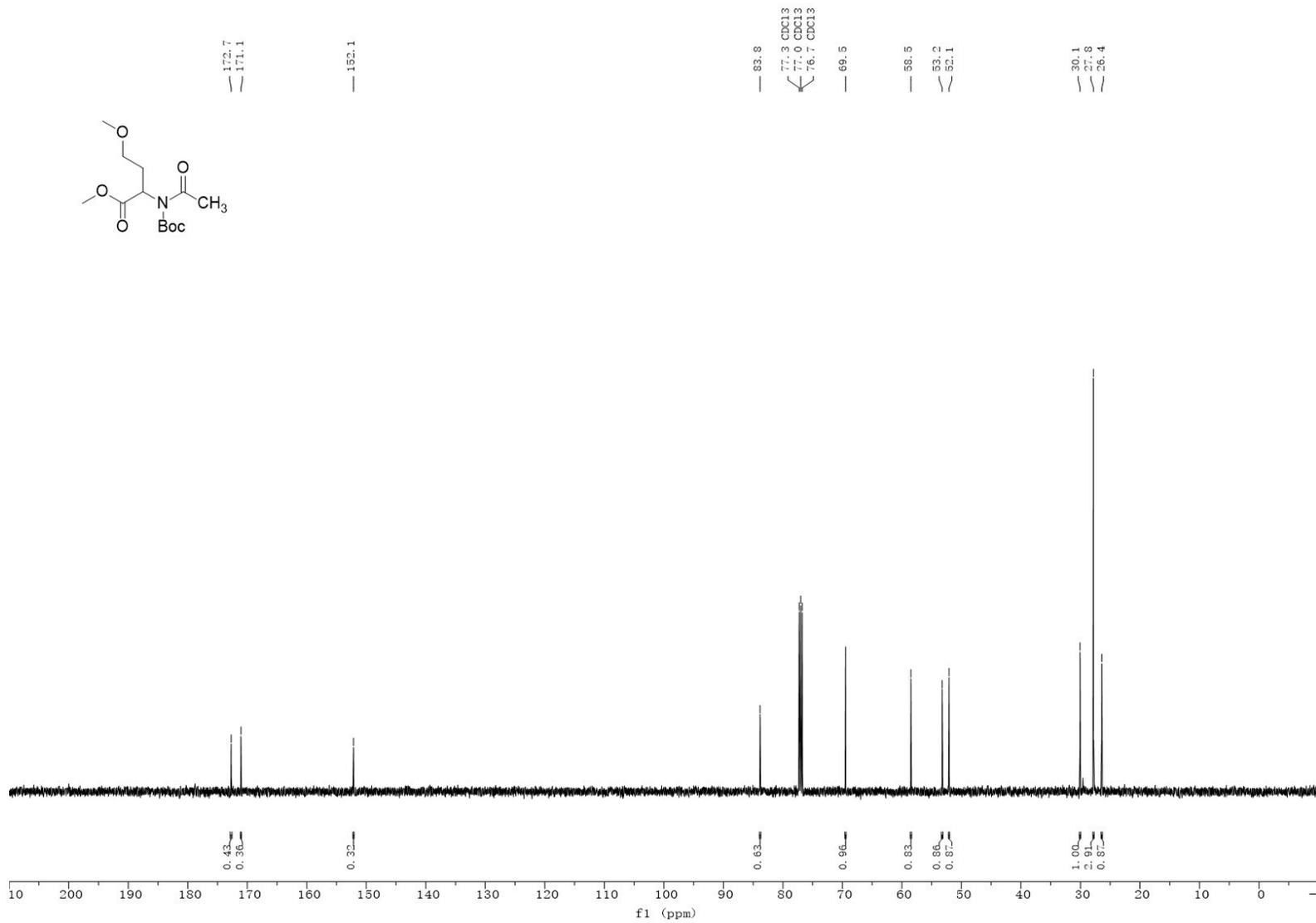
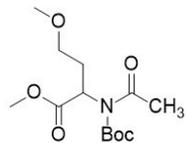


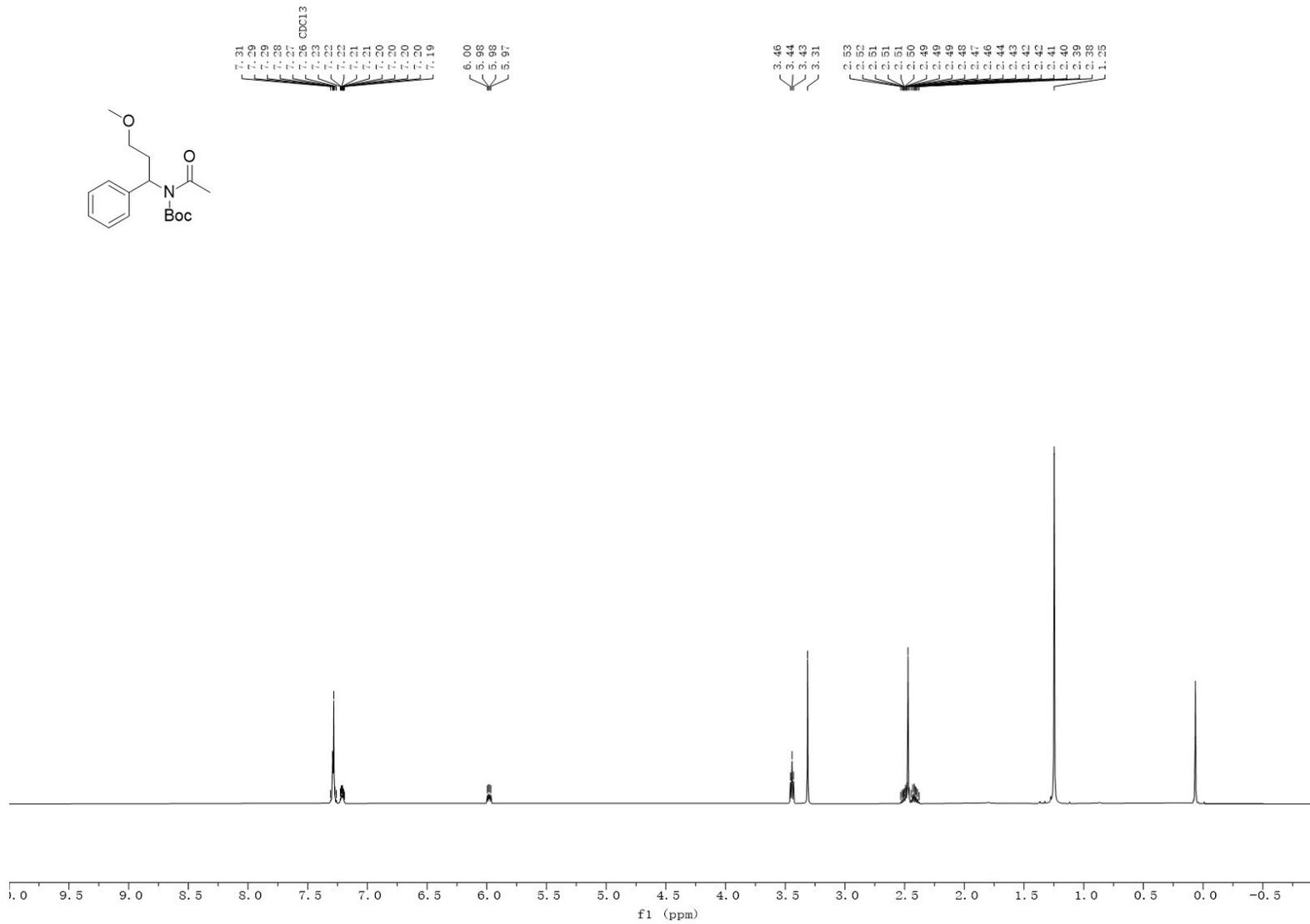
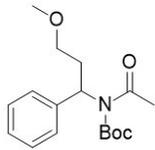


7.26 CDCl₃



S151





S153

