

Enantioselective domino reaction of CO₂, amine and allyl chloride under iridium catalysis: formation of allyl carbamates

Min Zhang, Xiaoming Zhao,* Shengcai Zheng

*Department of Chemistry, State Key Laboratory of Pollution Control and Resource Reuse,
Tongji University 1239 Siping Road, Shanghai 200092, P. R. China
E-mail: xmzhao08@mail.tongji.edu.cn*

General	1
Synthesis of allyl chloride 2k	2
General procedure for enantioselective domino reaction of allyl chloride 2 , CO ₂ 1 , and amine 3	2
Synthesis of 5a and 6	5
Synthesis of compound 7k	9
Controlling experiment	10
NMR spectra of the compounds 2k , 4 , 5 , 6 and 7k	12
HPLC chromatograms of the chiral compounds	69

General: All manipulations were carried out under the argon atmosphere using standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

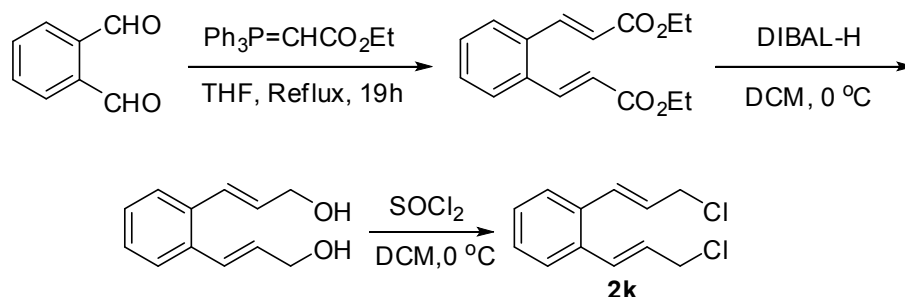
All reagents were obtained from commercial sources and used without further purification. ¹H NMR spectra were obtained at 400 MHz and recorded relative to tetramethylsilane signal (0 ppm) or residual protio-solvent. ¹³C NMR spectra were obtained at 100 MHz and chemical shifts were recorded relative to the solvent resonance (CDCl₃, 77.0 ppm). Data for ¹H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ¹³C NMR are reported in terms of chemical shift (δ, ppm).

The phosphoramidite ligands^[1], ligand L6^[2] and substituted allyl chlorides^[3] were prepared according to the known procedures.

Synthesis of the allylic chloride (**2k**)

An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with (2*E*,2'*E*)-3,3'-(1,2-phenylene)diprop-2-en-1-ol^[4] (5.26 mmol), 1*H*-benzo[*d*]-[1,2,3]tirazole (12.63 mmol, 2.4 equiv) and dichloromethane (10.0 mL) under argon atmosphere. The solution was cooled to 0 °C and thionyl chloride (12.63 mmol, 2.4 equiv) was added dropwise. The reaction mixture was stirred at 0 °C for 2 h, and then warmed to room temperature for 1 h. The reaction mixture was filtered and washed with 2 % NaOH aqueous solution and brine, respectively. The organic layer was dried over anhydrous

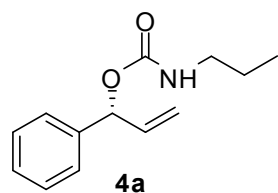
sodium sulfate, filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatography (hexane/ethyl acetate/ triethylamine) to provide 1,2-bis((*E*)-3-chloroprop-1-enyl)benzene (830 mg, 70 % yield).



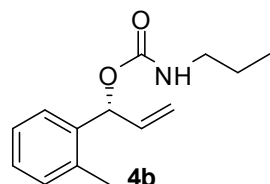
1,2-Bis((*E*)-3-chloroprop-1-enyl)benzene 2k: White solid, m.p. 81.2–81.7 °C, 70 % yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.44-7.42 (m, 2H), 7.28-7.25 (m, 2H), 6.92 (d, *J* = 15.6 Hz, 2H), 6.19 (dt, *J* = 15.2, 7.2 Hz, 2H), 4.26 ppm (dd, *J* = 16.8, 1.2 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ = 134.5, 131.5, 128.3, 127.8, 126.9, 45.2 ppm. IR (KBr): ν_{max} (cm⁻¹) = 3058, 1617, 1248, 964, 749, 670, 614. Anal. calcd for C₁₂H₁₂Cl₂: C, 63.46; H, 5.32; Cl, 31.22. Found: C, 63.50; H, 5.31; Cl, 31.19.

General procedure for domino reaction of allyl chloride (**2**), CO₂ (**1**) and amine (**3**) in the presence of iridium complex:

[Ir(COD)Cl]₂ (0.008 mmol, 4 mol %), phosphoramidite ligand L1, [*O,O'*-(*S*)-(1,1'-dinaphthyl-2,2'-diyl)-*N,N'*-di-(*S,S*)-[phenylethylphosphoramidite] (0.016 mmol, 8 mol %) were dissolved in THF (0.5 mL) and propylamine (0.3 mL) in a dry Schlenk tube filled with argon. The reaction mixture was heated at 50 °C for 30 min, and then the volatile solvents were removed under vacuum to give a yellow solid. After that, DABCO (0.4 mmol, 200 mol %), amine **3** (0.20 mmol, 100 mol %), and toluene (2.0 mL) were added, the solution was bubbled CO₂ **1** (1 atm) for 10 minutes, then allyl chloride **2** (0.24 mmol, 120 mol %) was added. The reaction was stirring at 15 °C and kept bubbling CO₂ **1** (1 atm). After the completion of the reaction monitoring by TLC, the crude reaction mixture was filtrated with celite and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to give the desired products **4**.

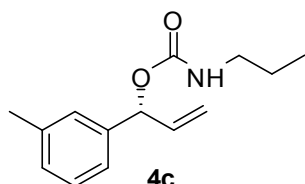


(*R*)-1-Phenylallyl propylcarbamate (4a): Colorless oil, 51 % yield, b/l = 90/10, 94 % *ee*. The *ee* of the product was determined by chiral HPLC. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 6.019 (major), 7.008 (minor) min]. [α]_D²⁰ = +16.6° (c 0.4, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 7.38 (d, *J* = 4.4 Hz, 4H), 7.33-7.28 (m, 1H), 6.18 (d, *J* = 5.6 Hz, 1H), 6.02 (ddd, *J* = 16.8, 10.4, 6.0 Hz, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.23 (dt, *J* = 10.4, 1.2 Hz, 1H), 4.79 (br, 1H), 3.18-3.12 (m, 2H), 1.51 (sext, *J* = 7.2 Hz, 2H), 0.91 ppm (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 155.6, 139.4, 136.8, 128.5, 128.0, 127.0, 116.5, 76.5, 42.8, 23.2, 11.2 ppm. IR(KBr): ν_{max} (cm⁻¹) = 3476, 2964, 2918, 2843, 1696 (C=O), 1523, 1262, 1263, 698. HRMS (ESI+) calcd for C₁₃H₁₇NNaO₂ [M+Na]⁺: 242.1151, Found: 242.1134.

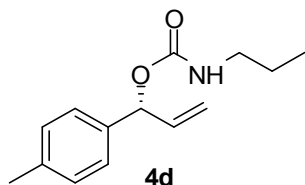


(*R*)-1-*p*-Tolylallyl propylcarbamate (4b): Colorless oil, 74 % yield, b/l = 92/8, 84 % *ee*. The *ee* of the product was determined by chiral HPLC. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 95/5; flow rate = 1.0 mL/min; detection

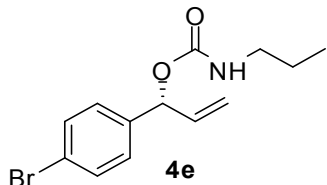
wavelength = 214 nm; t_R = 7.574 (major), 8.978 (minor) min]. $[\alpha]_D^{20}$ = +5.0° (c 0.4, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 7.35-7.33 (m, 1H), 7.21-7.19 (m, 2H), 7.18-7.14 (m, 1H), 6.36 (d, J = 5.2 Hz, 1H), 6.01 (ddd, J = 16.4, 10.8, 5.6 Hz, 1H), 5.22 (d, J = 10.4 Hz, 1H), 5.21 (d, J = 17.2 Hz, 1H), 4.80 (br, 1H), 3.18-3.13 (m, 2H), 2.38 (s, 3H), 1.51 (sext, J = 7.2 Hz, 2H), 0.90 ppm (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 155.7, 137.5, 136.3, 135.8, 130.5, 127.8, 126.7, 126.1, 116.4, 76.6, 42.8, 23.2, 19.2, 11.2 ppm. IR(KBr): ν_{\max} (cm⁻¹) = 3445, 2969, 2922, 2871, 1696 (C=O), 1649, 1556, 1509, 1453, 1267, 1141, 1038, 982, 926, 731. HRMS (ESI+) calcd for C₁₄H₁₉NNaO₂ [M+Na]⁺: 256.1308, Found: 256.1309.



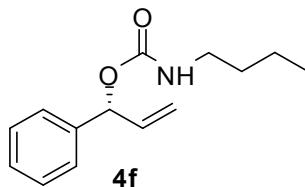
(R)-1-*m*-Tolylallyl propylcarbamate (4c): Colorless oil, 72 % yield, b/l = 96/4, 85 % *ee*. The *ee* of the product was determined by chiral HPLC. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 5.331 (major), 6.319 (minor) min]. $[\alpha]_D^{20}$ = +20.5° (c 0.6, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 7.23 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.2 Hz, 1H), 6.14 (d, J = 5.6 Hz, 1H), 6.01 (ddd, J = 16.8, 10.4, 6.0 Hz, 1H), 5.30 (d, J = 17.2 Hz, 1H), 5.22 (d, J = 10.4, Hz, 1H), 4.78 (br, 1H), 3.19-3.11 (m, 2H), 2.35 (s, 3H), 1.51 (sext, J = 7.2 Hz, 2H), 0.91 ppm (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 155.7, 139.3, 138.1, 136.9, 128.7, 128.4, 127.7, 124.1, 116.3, 76.7, 42.8, 23.2, 21.4, 11.2 ppm. IR(KBr): ν_{\max} (cm⁻¹) = 3412, 2960, 2922, 2862, 1696 (C=O), 1523, 1453, 1267, 1234, 1132, 1034, 983, 922, 763, 694. HRMS (ESI+) calcd for C₁₄H₁₉NNaO₂ [M+Na]⁺: 256.1308, Found: 256.1325.



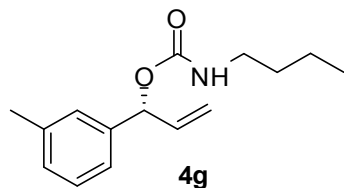
(R)-1-*p*-Tolylallyl propylcarbamate (4d): Colorless oil, 48 % yield, b/l = 95/5, 90 % *ee*. The *ee* of the product was determined by chiral HPLC. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 4.824 (minor), 5.299 (major) min]. $[\alpha]_D^{20}$ = +18.0° (c 0.5, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 7.25 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.14 (d, J = 5.6 Hz, 1H), 6.01 (ddd, J = 16.4, 10.4, 5.6 Hz, 1H), 5.28 (d, J = 17.2 Hz, 1H), 5.22 (d, J = 10.4, Hz, 1H), 4.77 (br, 1H), 3.16-3.09 (m, 2H), 2.34 (s, 3H), 1.51 (sext, J = 7.2 Hz, 2H), 0.90 ppm (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 155.7, 137.8, 136.9, 136.5, 129.2, 127.1, 116.2, 76.3, 42.8, 23.2, 21.1, 11.2 ppm. IR(KBr): ν_{\max} (cm⁻¹) = 3477, 2964, 2922, 2848, 1715 (C=O), 1514, 1258, 1225, 1132, 1038, 982, 927, 815, 745. HRMS (ESI+) calcd for C₁₄H₁₉NNaO₂ [M+Na]⁺: 256.1308, Found: 256.1309.



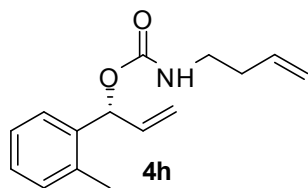
(R)-1-(4-Bromophenyl)allyl propylcarbamate (4e): Colorless oil, 44 % yield, b/l = 94/6, 59 % *ee*. The *ee* of the product was determined by chiral HPLC. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 0.6 mL/min; detection wavelength = 214 nm; t_R = 9.894 (major), 10.346 (minor) min]. $[\alpha]_D^{20}$ = +6.6° (c 0.6, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 7.48 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.12 (d, J = 5.6 Hz, 1H), 5.97 (ddd, J = 16.8, 10.4, 7.0 Hz, 1H), 5.28 (d, J = 17.2 Hz, 1H), 5.25 (d, J = 10.8, Hz, 1H), 4.79 (br, 1H), 3.18-3.09 (m, 2H), 1.51 (sext, J = 7.2 Hz, 2H), 0.91 ppm (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 155.4, 138.5, 136.3, 131.6, 128.8, 122.0, 117.0, 75.8, 42.8, 23.1, 11.2 ppm. IR(KBr): ν_{\max} (cm⁻¹) = 3449, 3048, 2927, 2848, 1720 (C=O), 1505, 1258, 1226, 1137, 983, 937, 820, 741. HRMS (ESI+) calcd for C₁₃H₁₆BrNNaO₂ [M+Na]⁺: 320.0257, Found: 320.0266.



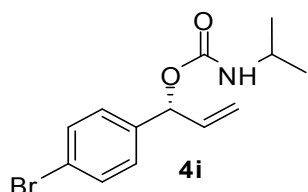
(R)-1-Phenylallyl butylcarbamate (4f): Colorless oil, 52 % yield, b/l = 92/8, 94 % *ee*. The *ee* of the product was determined by chiral HPLC. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 5.598 (major), 6.609 (minor) min]. $[\alpha]_D^{20}$ = +26.8° (c 0.5, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 7.35 (d, J = 4.4 Hz, 4H), 7.32-7.27 (m 1H), 6.17 (d, J = 5.6 Hz, 1H), 6.02 (ddd, J = 16.8, 10.4, 6.0 Hz, 1H), 5.29 (d, J = 17.2 Hz, 1H), 5.24 (dd, J = 10.4, 0.8, Hz, 1H), 4.77 (br, 1H), 3.21-3.15 (m, 2H), 1.51-1.44 (m, 2H), 1.38-1.29 (m, 2H), 0.91 ppm (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 155.6, 139.4, 136.8, 128.5, 128.0, 127.0, 116.5, 76.4, 40.8, 32.0, 19.9, 13.7 ppm. IR(KBr): ν_{max} (cm⁻¹) = 3486, 2964, 2932, 2848, 1701 (C=O), 1510, 1449, 1244, 1128, 1021, 927, 736, 690. HRMS (ESI+) calcd for C₁₄H₁₉NNaO₂ [M+Na]⁺: 256.1308, Found: 256.1311.



(R)-1-*m*-Tolylallyl butylcarbamate (4g): Colorless oil, 47 % yield, b/l = 95/5, 83 % *ee*. The *ee* of the product was determined by chiral HPLC. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 5.068 (major), 6.146 (minor) min]. $[\alpha]_D^{20}$ = +22.5° (c 0.4, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 7.23 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.6 Hz, 1H), 6.14 (d, J = 5.6 Hz, 1H), 6.01 (ddd, J = 16.4, 10.0, 5.6 Hz, 1H), 5.29 (d, J = 16.8 Hz, 1H), 5.22 (d, J = 10.4, Hz, 1H), 4.76 (br, 1H), 3.21-3.15 (m, 2H), 2.35 (s, 3H), 1.51-1.44 (m, 2H), 1.37-1.29 (m, 2H), 0.91 ppm (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 155.7, 139.4, 136.2, 137.0, 128.8, 128.4, 127.8, 124.1, 116.3, 76.5, 40.8, 32.0, 21.4, 19.9, 13.7 ppm. IR(KBr): ν_{max} (cm⁻¹) = 3449, 3048, 2972, 2932, 2843, 1715 (C=O), 1505, 1263, 1240, 1132, 1025, 983, 932, 732. HRMS (ESI+) calcd for C₁₅H₂₁NNaO₂ [M+Na]⁺: 270.1465, Found: 270.1459.

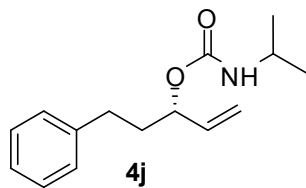


(R)-1-*m*-Tolylallyl butylcarbamate (4h): Colorless oil, 50 % yield, b/l = 93/7, 93 % *ee*. The *ee* of the product was determined by chiral HPLC. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 5.962 (major), 6.522 (minor) min]. $[\alpha]_D^{20}$ = +3.2° (c 0.5, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 7.34-7.32 (m, 1H), 7.21-7.17 (m, 2H), 7.16-7.13 (m, 1H), 6.36 (d, J = 4.4 Hz, 1H), 6.00 (ddd, J = 15.6, 10.8, 5.6 Hz, 1H), 5.79-5.68 (m, 1H), 5.22 (d, J = 10.4 Hz, 1H), 5.21 (d, J = 18.0 Hz, 1H), 5.08 (d, J = 18.0 Hz, 1H), 5.09 (d, J = 8.8.0 Hz, 1H), 4.83 (br, 1H), 3.28-3.25 (m, 2H), 2.38 (s, 3H), 2.27-2.22 ppm (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 155.6, 137.4, 136.2, 135.7, 135.0, 130.5, 127.9, 126.7, 126.1, 117.3, 116.5, 73.6, 40.0, 34.1, 19.2 ppm. IR(KBr): ν_{max} (cm⁻¹) = 3426, 3081, 2848, 1705 (C=O), 1649, 1509, 1458, 1248, 1127, 1029, 996, 912, 749. HRMS (ESI+) calcd for C₁₅H₁₉NNaO₂ [M+Na]⁺: 268.1308, Found: 268.1297.



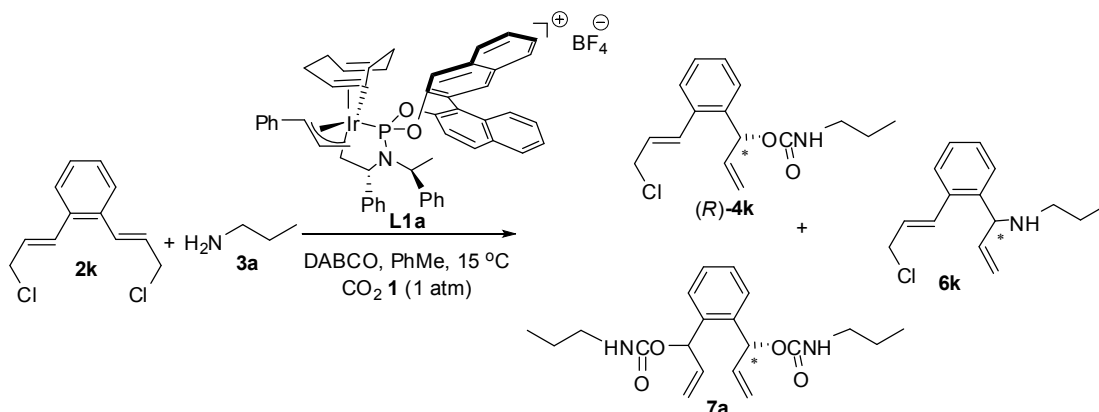
(R)-1-(4-Bromophenyl)allyl isopropylcarbamate (4i): White solid. m.p. 83.7–85.5 °C. 35 % yield, b/l = 88/12, 68 % *ee*. The *ee* of the product was determined by chiral HPLC. [Daicel CHIRALPAK AD (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 6.432 (major), 8.636 (minor) min]. $[\alpha]_D^{20}$ = +9.2° (c 1.1, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 7.48 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.11 (d, J = 4.8 Hz, 1H), 5.96 (ddd, J = 16.8, 10.0, 5.6 Hz, 1H), 5.28 (d, J = 16.8 Hz, 1H), 5.24 (d, J = 10.4 Hz, 1H), 4.61 (br, 1H), 3.85-3.77 (m, 1H), 1.17 (d, J = 6.4 Hz, 3H), 1.14 ppm (d, J = 6.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 154.5, 138.5, 136.4,

131.6, 128.8, 121.9, 116.9, 75.6, 43.2, 23.0 ppm. IR(KBr): ν_{\max} (cm⁻¹) = 3477, 3421, 2960, 2913, 1701 (C=O), 1645, 1617, 1514, 1244, 1071, 936, 619. HRMS (ESI+) calcd for C₁₃H₁₆BrNNaO₂[M+Na]⁺: 320.0257, Found: 320.0255.

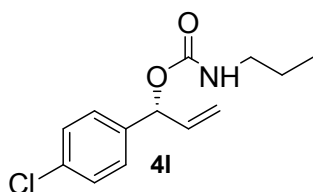


(S)-5-Phenylpent-1-en-3-yl isopropylcarbamate (4j): Colorless oil, 41 % yield, b/l = 99/1, 38 % *ee*. The *ee* of the product was determined by chiral HPLC. [Daicel CHIRALPAK IC (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 6.106 (major), 6.958 (minor) min]. $[\alpha]_D^{20}$ = +3.5° (c 0.4, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ = 7.35-7.27 (m, 2H), 7.19-7.17 (m, 3H), 5.82 (ddd, J = 16.8, 10.4, 7.2 Hz, 1H), 5.27 (d, J = 17.2 Hz, 1H), 5.18 (d, J = 10.4 Hz, 2H), 4.50 (br, 1H), 3.84-3.79 (m, 1H), 2.7-2.6 (m, 2H), 2.04-1.86 (m, 2H), 1.17 (d, J = 2.4 Hz, 3H), 1.15 ppm (d, J = 2.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 155.1, 141.6, 137.0, 128.4, 128.3, 125.9, 116.3, 74.4, 43.0, 36.2, 31.4, 23.0 ppm. IR(KBr): ν_{\max} (cm⁻¹) = 3414, 3054, 2983, 2929, 2858, 1716 (C=O), 1645, 1509, 1456, 1267, 1227, 1074, 992, 931, 735. HRMS (ESI+) calcd for C₁₅H₂₁NNaO₂[M+Na]⁺: 270.1465, Found: 270.1461.

(R,E)-1-(2-(3-Chloroprop-1-enyl)phenyl)allyl propylcarbamate (4k):

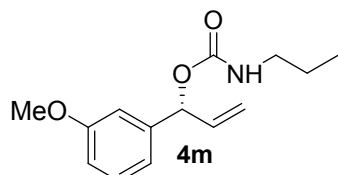


light yellow semisolid, 60 % yield, b/l = 95/5, 96 % *ee*. The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 6.840 (major), 10.871 (minor) min]. $[\alpha]_D^{20}$ = +11.4° (c 0.3, CHCl₃). When the same reaction with **2k** was performed using the ligand (*R,R,Ra*)-L1, (*S*)-**4k** was obtained in 56% yield with b/l 99/1 and 99% *ee*, which is determined by a chiral HPLC [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 6.840 (major), 10.871 (minor) min]. ¹H NMR (400 MHz, CDCl₃) δ = 7.47-7.45 (m, 1H), 7.38-7.36 (m, 1H), 7.30-7.28 (m, 2H), 7.06 (d, J = 15.6 Hz, 1H), 6.40 (d, J = 4.4 Hz, 1H), 6.17 (dt, J = 14.8, 7.2 Hz, 1H), 6.02 (ddd, J = 16.0, 10.4, 4.8 Hz, 1H), 5.23 (d, J = 10.8 Hz, 1H), 5.20 (dd, J = 16.8, 1.6 Hz, 1H), 4.79 (br, 1H), 4.25 (d, J = 7.2 Hz, 2H), 3.18-3.10 (m, 2H), 1.54-1.48 (m, 2H), 0.90 ppm (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 155.5, 136.8, 136.3, 134.9, 131.6, 128.3, 128.2, 127.6, 127.5, 126.9, 116.8, 73.6, 45.3, 42.8, 23.2, 11.2 ppm. IR(KBr): ν_{\max} (cm⁻¹) = 3473, 3412, 2964, 2913, 2843, 1710 (C=O), 1645, 1645, 1617, 1509, 1252, 745, 614, 474. HRMS (ESI+) calcd for C₁₆H₂₀ClNNaO₂[M+Na]⁺: 316.1075, Found: 316.1068.



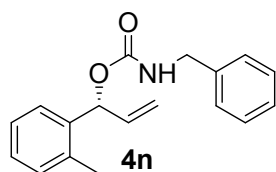
(R)-1-(4-chlorophenyl)allyl propylcarbamate (4l): Colorless oil, 46% yield, b/l = 90/10, 63% *ee*. The *ee* of the product was determined by HPLC. [Daicel CHIRALCEL OD-H (0.46 cm

x 25 cm); hexane/2-propanol = 90/10; flow rate = 0.7 mL/min; detection wavelength = 214 nm; t_R = 13.246 (minor), 13.997 (major) min]. $[\alpha]_D^{20} = +8.6^\circ$ (c 0.4, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.33-7.26 (m, 4H), 6.13 (d, J = 5.2 Hz, 1H), 5.97 (ddd, J = 16.4, 10.4, 5.6 Hz, 1H), 5.28 (d, J = 17.6 Hz, 1H), 5.24 (d, J = 10.8 Hz, 1H), 4.82 (br, 1H), 3.17-3.12 (m, 2H), 1.51 (sext, J = 7.2 Hz, 2H), 0.91 (t, J = 7.2 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 155.4, 138.0, 136.4, 133.8, 128.6, 128.4, 116.9, 75.7, 42.8, 23.1, 11.2. IR(KBr): ν_{max} (cm^{-1}) = 3454, 3053, 2960, 2932, 2843, 1719, 1509, 1262, 1220, 1085, 978, 931, 819, 731. HRMS (ESI+) calcd for $\text{C}_{13}\text{H}_{16}\text{ClNNaO}_2$ $[\text{M}+\text{Na}]^+$: 276.0762, Found: 276.0762.



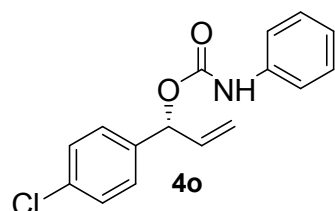
(R)-1-(3-methoxyphenyl)allyl propylcarbamate (4m):

Colorless oil, 51% yield, b/l = 95/5, 87% *ee*. The *ee* of the product was determined by HPLC. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 7.490 (minor), 10.733 (major) min]. $[\alpha]_D^{20} = +10.1^\circ$ (c 0.5, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.27 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 7.2 Hz, 1H), 6.89 (s, 1H), 6.84 (dd, J = 8.0, 2.4 Hz, 1H), 6.14 (d, J = 5.6 Hz, 1H), 6.00 (ddd, J = 16.4, 10.4, 5.6 Hz, 1H), 5.30 (d, J = 16.8 Hz, 1H), 5.23 (d, J = 10.4 Hz, 1H), 4.82 (br, 1H), 3.80 (s, 1H), 3.19-3.10 (m, 2H), 1.51 (sext, J = 7.2 Hz, 2H), 0.91 (t, J = 7.2 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 159.7, 155.6, 141.0, 136.7, 129.5, 119.3, 116.5, 113.4, 112.6, 76.4, 55.2, 42.8, 23.1, 11.2. IR(KBr): ν_{max} (cm^{-1}) = 3347, 2974, 2932, 1705, 1603, 1528, 1500, 1267, 1132, 982, 782, 712. HRMS (ESI+) calcd for $\text{C}_{14}\text{H}_{19}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$: 272.1257, Found: 272.1254.



(R)-1-o-tolylallyl benzylcarbamate (4n):

Colorless oil, 60% yield, b/l = 94/6, 92% *ee*. The *ee* of the product was determined by HPLC. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 90/10; flow rate = 1.0 mL/min; detection wavelength = 214 nm; t_R = 7.806 (minor), 8.675 (major) min]. $[\alpha]_D^{20} = +5.0^\circ$ (c 1.0, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.34-7.30 (m, 3H), 7.27-7.25 (m, 3H), 7.21-7.16 (m, 3H), 6.45 (d, J = 5.6 Hz, 1H), 6.01 (ddd, J = 16.4, 10.0, 5.6 Hz, 1H), 5.3 (d, J = 10.8 Hz, 1H), 5.2 (d, J = 16.4 Hz, 1H), 5.1 (br, 1H), 4.41-4.35 (m, 2H), 2.39 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ = 155.6, 138.3, 137.3, 136.3, 136.1, 135.5, 130.5, 128.6, 127.9, 127.5, 126.7, 126.1, 116.6, 74.0, 45.1, 19.2. IR(KBr): ν_{max} (cm^{-1}) = 3407, 3053, 3025, 2960, 2918, 1696, 1519, 1248, 1127, 1029, 978, 922, 754. HRMS (ESI+) calcd for $\text{C}_{14}\text{H}_{19}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$: 301.1308, Found: 301.1317.



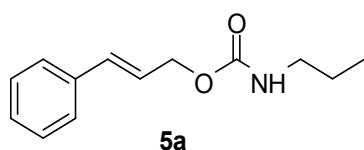
(R)-1-(4-chlorophenyl)allyl phenylcarbamate (4o):

Aniline **3f** was used in this reaction under the optimized reaction conditions, but failed to give the corresponding allyl carbamate **4o**.

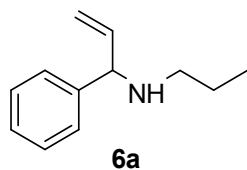
Synthesis of Cinnamyl propylcarbamate 5a^[5]:

An oven-dried 25 mL round bottom flask was sequentially charged with a stir bar, the allyl alcohol (0.5 mmol) and CH_2Cl_2 (3 mL). To the mixture was added propyl isocyanate (2.5 mmol) dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and stir overnight. Then diluted with H_2O , the aqueous layer was

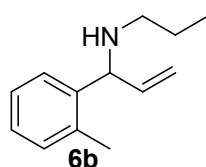
extracted with CH₂Cl₂ twice and the combined organic layers were dried over Na₂SO₄, filtered, and concentrated in vacuo. Purification by flash chromatography provided the cinnamyl propylcarbamate **5a** (82 mg, 75 % yield).



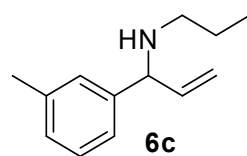
5a: White solid, m.p. 47.1–48.0 °C, 75 % yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.39 (d, *J* = 7.2 Hz, 2H), 7.30 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.27–7.23 (m, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.29 (dt, *J* = 15.6, 6.4 Hz, 1H), 4.72 (d, *J* = 6.0 Hz, 3H), 3.19–3.14 (m, 2H), 1.53 (sext, *J* = 7.2 Hz, 2H), 0.93 ppm (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 156.3, 136.4, 133.5, 128.5, 127.9, 126.6, 124.1, 65.2, 42.8, 23.2, 11.2 ppm.



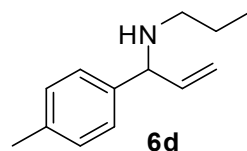
1-Phenyl-N-propylprop-2-en-1-amine (6a)^[6]: Colorless oil, 13 % yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.34–7.30(m, 4H), 7.26–7.22 (m, 1H), 5.93 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.20 (d, *J* = 16.8 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 4.17 (d, *J* = 7.2 Hz, 1H), 2.59–2.53 (m, 1H), 2.49–2.42 (m, 1H), 1.51 (sext, *J* = 7.2 Hz, 2H), 1.40 (br, 1H), 0.90 ppm (t, *J* = 7.2 Hz, 3H).



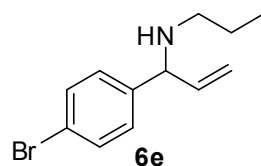
N-Propyl-1-o-tolylprop-2-en-1-amine (6b): Colorless oil, 11 % yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.43 (d, *J* = 7.6 Hz, 1H), 7.23–7.19 (m, 1H), 7.15–7.13 (m, 2H), 5.87 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.15 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 10.4 Hz, 1H), 4.40 (d, *J* = 7.2 Hz, 1H), 2.60–2.54 (m, 1H), 2.50–2.44 (m, 1H), 2.35 (s, 3H), 1.59 (br, 1H), 1.55–1.49(m, 2H), 0.91 ppm (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 140.7, 140.2, 135.7, 130.4, 126.7, 126.3, 126.2, 114.9, 61.8, 49.7, 23.3, 19.3, 11.8 ppm. IR(KBr): ν_{max} (cm⁻¹) = 3412, 3086, 2955, 2918, 2848, 1635, 1621, 1458, 1267, 1118, 908, 759. HRMS (ESI+) calcd for C₁₃H₂₀N [M+H]⁺: 190.1590, Found: 190.1586.



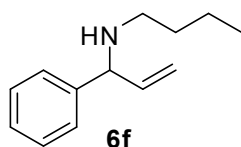
N-Propyl-1-m-tolylprop-2-en-1-amine (6c): Colorless oil, 17 % yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.22 (dd, *J* = 7.2, 7.6 Hz, 2H), 7.15–7.12 (m, 2H), 7.06 (d, *J* = 7.2 Hz, 1H), 5.93 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.08 (d, *J* = 10.4 Hz, 1H), 4.14 (d, *J* = 6.8 Hz, 1H), 2.59–2.53 (m, 1H), 2.49–2.43 (m, 1H), 2.34 (s, 3H), 1.56–1.47 (m, 3H), 0.90 ppm (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 143.0, 141.2, 138.1, 128.4, 127.9, 124.3, 114.7, 114.0, 66.2, 49.5, 23.2, 21.4, 11.8 ppm. IR(KBr): ν_{max} (cm⁻¹) = 3403, 3226, 2918, 2843, 1640, 1621, 1463, 628. HRMS (ESI+) calcd for C₁₃H₂₀N [M+H]⁺: 190.1590, Found: 190.1588.



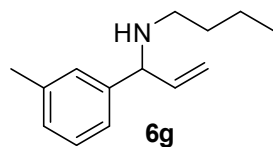
N-Propyl-1-p-tolylprop-2-en-1-amine (6d): Colorless oil, 15 % yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.22 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 5.92 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.18 (d, *J* = 17.2 Hz, 1H), 5.07 (d, *J* = 10.4 Hz, 1H), 4.14 (d, *J* = 7.6 Hz, 1H), 2.58–2.52 (m, 1H), 2.49–2.42 (m, 1H), 2.33 (s, 3H), 1.56–1.44 (m, 3H), 0.89 ppm (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 141.3, 140.0, 136.7, 129.2, 127.1, 114.6, 65.9, 49.5, 23.2, 21.1, 11.8 ppm. IR(KBr): ν_{max} (cm⁻¹) = 3440, 2922, 2843, 1635, 1463, 1374, 1188, 959, 824, 600. HRMS (ESI+) calcd for C₁₃H₂₀N [M+H]⁺: 190.1590, Found: 190.1585.



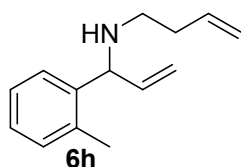
1-(4-Bromophenyl)-*N*-propylprop-2-en-1-amine (6e): Colorless oil, 11 % yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.45 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.87 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 4.15 (d, *J* = 7.2 Hz, 1H), 2.57-2.51 (m, 1H), 2.46-2.39 (m, 1H), 1.82 (br, 1H), 1.50 (sext, *J* = 6.8 Hz, 2H), 0.90 ppm (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 142.0, 140.6, 131.5, 129.0, 120.8, 115.3, 65.5, 49.4, 23.2, 11.7 ppm. IR(KBr): ν_{max} (cm⁻¹) = 3650, 3076, 2955, 2918, 2857, 1654, 1463, 1383, 1006, 922, 824, 749, 521. MS (EI+, *m/z*, rel. intensity) 116 (100), 253 (M⁺). HRMS (EI+) calcd for C₁₂H₁₆NBr (M⁺): 253.0466, Found: 253.0463.



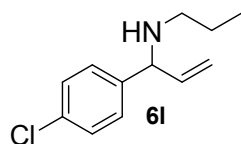
***N*-(1-Phenylallyl)butan-1-amine (6f)**^[7]: Colorless oil, 16 % yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.34-7.32 (m, 4H), 7.27-7.22 (m, 1H), 5.93 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.20 (dd, *J* = 16.8, 1.2 Hz, 1H), 5.09 (dd, *J* = 10.0, 1.2 Hz, 1H), 4.17 (d, *J* = 7.2 Hz, 1H), 2.62-2.56 (m, 1H), 2.52-2.45 (m, 1H), 1.52-1.42 (m, 2H), 1.37-1.29 (m, 3H), 0.89 ppm (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 143.1, 141.3, 128.5, 127.2, 127.1, 114.7, 66.3, 47.4, 32.3, 20.5, 14.0 ppm. IR(KBr): ν_{max} (cm⁻¹) = 3477, 2950, 2922, 2853, 1645, 1459, 1114, 918, 704, 615.



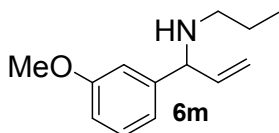
***N*-(1-*m*-Tolylallyl)butan-1-amine (6g)**: Colorless oil, 10 % yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.22 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.15-7.11 (m, 2H), 7.06 (d, *J* = 7.2 Hz, 1H), 5.92 (ddd, *J* = 17.2, 10.4, 7.2 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.08 (d, *J* = 10.0 Hz, 1H), 4.13 (d, *J* = 6.8 Hz, 1H), 2.62-2.56 (m, 1H), 2.52-2.46 (m, 1H), 2.34 (s, 3H), 1.52-1.44 (m, 2H), 1.37-1.29 (m, 3H), 0.89 ppm (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 143.1, 141.3, 138.1, 128.4, 127.9, 127.8, 124.3, 114.7, 66.3, 47.4, 32.3, 21.4, 20.5, 14.0 ppm. IR(KBr): ν_{max} (cm⁻¹) = 3463, 3025, 2960, 2927, 2848, 1641, 1454, 1123, 918, 733, 616. HRMS (ESI+) calcd for C₁₄H₂₂N [M+H]⁺: 204.1747, Found: 204.1747.



***N*-(1-*o*-Tolylallyl)but-3-en-1-amine (6h)**: Colorless oil, 10 % yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.41 (d, *J* = 7.6 Hz, 2H), 7.23-7.19 (m, 1H), 7.15-7.13 (m, 1H), 5.90 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.82-5.72 (m, 1H), 5.15 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 10.4 Hz, 1H), 5.08 (d, *J* = 17.2 Hz, 1H), 5.03 (d, *J* = 10.0 Hz, 1H), 4.21 (d, *J* = 6.8 Hz, 1H), 2.71-2.65 (m, 1H), 2.61-2.55 (m, 1H), 2.34 (s, 3H), 2.29-2.24 ppm (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 140.6, 140.1, 136.5, 135.3, 130.4, 126.7, 126.3, 126.2, 116.3, 115.0, 61.7, 46.6, 34.3, 19.3 ppm. IR(KBr): ν_{max} (cm⁻¹) = 3408, 3076, 2922, 2848, 1645, 1607, 1458, 926, 745, 614. HRMS (ESI+) calcd for C₁₄H₂₀N [M+H]⁺: 202.1590, Found: 202.1589.

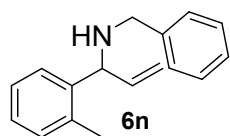


1-(4-chlorophenyl)-*N*-propylprop-2-en-1-amine (6l): Colorless oil, 9% yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.29-7.26 (m, 4H), 5.87 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 4.15 (d, *J* = 7.2 Hz, 1H), 2.57-2.50 (m, 1H), 2.46-2.39 (m, 1H), 1.53-1.47 (m, 3H), 0.90 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 141.6, 140.9, 132.7, 128.6, 128.5, 115.1, 65.5, 49.5, 23.2, 11.8. IR(KBr): ν_{max} (cm⁻¹) = 3431, 3086, 2964, 2927, 2871, 1486, 1388, 1094, 1020, 1006, 917, 829, 516. HRMS (EI+) calcd for C₁₂H₁₆NCl [M]⁺: 209.0971, Found: 209.0965.



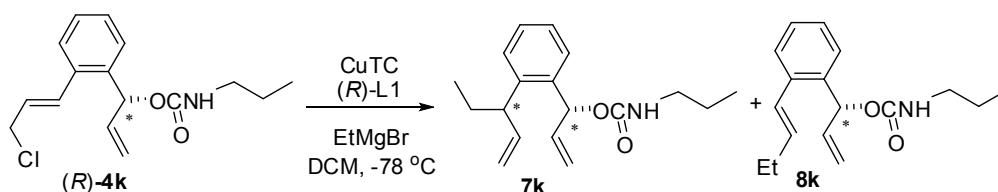
1-(3-methoxyphenyl)-*N*-propylprop-2-en-1-amine (6m): Colorless oil, 11% yield. ¹H NMR (400 MHz, CDCl₃) δ = 7.24 (dd, *J* = 8.0, 7.6 Hz, 1H), 6.93-6.91 (m, 2H), 6.79 (dd, *J* = 8.0, 1.2

Hz, 1H), 5.92 (ddd, $J = 17.2, 10.4, 7.6$ Hz, 1H), 5.20 (d, $J = 16.8$ Hz, 1H), 5.08 (d, $J = 10.0$ Hz, 1H), 4.15 (d, $J = 7.2$ Hz, 1H), 3.81 (s, 1H), 2.59-2.52 (m, 1H), 2.49-2.43 (m, 1H), 1.54-1.46 (m, 3H), 0.90 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 159.8, 144.9, 141.1, 129.4, 119.6, 114.8, 112.7, 112.5, 66.2, 55.2, 49.5, 23.3, 11.8$. IR(KBr): ν_{max} (cm^{-1}) = 3319, 2960, 2927, 2876, 2829, 1603, 1467, 1383, 1262, 1052, 922, 782, 703. HRMS (EI+) calcd for $\text{C}_{13}\text{H}_{18}\text{NO}$ $[\text{M}-\text{H}]^+$: 204.1388, Found: 204.1391.



***N*-benzyl-1-*o*-tolylprop-2-en-1-amine (6n)**: Colorless oil, 12% yield. ^1H NMR (400 MHz, CDCl_3) $\delta = 7.51$ (d, $J = 6.0$ Hz, 1H), 7.33-7.29 (m, 4H), 7.27-7.21 (m, 2H), 7.17-7.12 (m, 2H), 5.90 (ddd, $J = 13.6, 8.0, 5.6$ Hz, 1H), 5.18 (d, $J = 14.8$ Hz, 1H), 5.12 (d, $J = 8.4$ Hz, 1H), 4.44 (d, $J = 6.0$ Hz, 1H), 3.73 (d, $J = 6.0$ Hz, 2H), 2.26 (s, 3H), 1.60 (br, 1H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 140.5, 140.4, 140.0, 135.9, 130.4, 128.4, 128.2, 126.9, 126.8, 126.4, 126.3, 115.2, 60.8, 51.4, 19.2$. IR(KBr): ν_{max} (cm^{-1}) = 3412, 3225, 1612, 1556, 922, 609. HRMS (ESI+) calcd for $\text{C}_{13}\text{H}_{18}\text{NO}$ $[\text{M}+\text{Na}]^+$: 260.1410, Found: 204.1417.

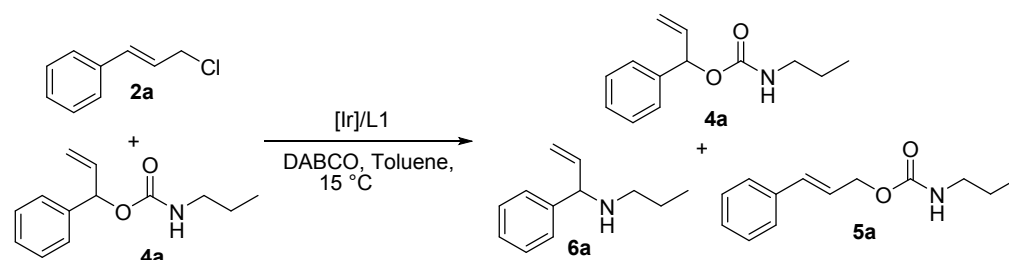
Synthesis of the branched allylic compound **7k**^[8]:



CuTC (0.0075 mmol, 7.5 mol %), phosphoramidite ligand *anti*-L1 [*O,O'*-(*R*)-(1,1'-dinaphthyl-2,2'-diyl)-*N,N'*-di-(*R,R*)-[phenylethylphosphoramidite)] (0.0083 mmol, 8.3 mol %) were dissolved in DCM (0.5 mL) in a dry Schlenk tube filled with argon. The mixture was stirred at room temperature for 10 min. The allyl chloride **4k** (0.1 mmol in 0.5 mL DCM) was added dropwise and the reaction mixture was stirred at room temperature for an additional 5 min before cooling the reaction mixture to -78 °C using an ethyl acetate/dry ice cold bath. The Grignard reagent (3 M in diethyl ether, 1.2 equiv) was added manually over a 20 min period. Once the addition was completed, the reaction mixture was left at -78 °C for an additional 4h. The reaction was quenched by addition of aqueous hydrochloric acid (1 M, 3 mL). Diethyl ether (5 mL) was added and the aqueous phase was separated and extracted with diethyl ether (3×5 mL). The combined organic fractions were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatography (hexane/ethyl acetate) to give an inseparable mixture of the branched product **7k** and linear product **8k**. (*R*)-1-(2-((*S*)-Pent-1-en-3-yl)phenyl)allyl propylcarbamate (**7k**): light yellow oil, 51 % yield, b/l = 84/16, 98 % *ee*, *dr* 3.1:1. The *ee* of **7k** was determined by HPLC. [Daicel CHIRALCEL OD-H (0.46 cm x 25 cm); hexane/2-propanol = 98/2; flow rate = 0.5 mL/min; detection wavelength = 214 nm; $t_{\text{R}} = 15.401$ (major), 16.847 (minor) min]. $[\alpha]_{\text{D}}^{20} = +33.9^\circ$ (c 0.3, CHCl_3). ^1H NMR (400 MHz, CDCl_3) $\delta = 7.36$ (d, $J = 7.2$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.26-7.19 (m, 2H), 6.52 (d, $J = 4.0$ Hz, 1H), 6.03 (ddd, $J = 17.2, 10.8, 4.8$ Hz, 1H), 5.92 (ddd, $J = 17.2, 10.4, 7.2$, Hz, 1H), 5.22 (d, $J = 10.8$, Hz, 1H), 5.19 (d, $J = 17.2$ Hz, 1H), 5.15 (d, $J = 10.0$ Hz, 1H), 4.97 (d, $J = 16.8$ Hz, 1H), 4.77 (br, 1H), 3.62-3.56 (m, 1H), 3.17-3.12 (m, 2H), 1.80-1.72 (m, 2H), 1.56-1.47(m, 2H), 0.93-0.86 ppm (m, 6H); **8k** : ^1H NMR $\delta = 7.43$ (d, $J = 6.8$ Hz, 1H), 6.73 (d, $J = 15.6$ Hz, 1H), 6.46 (d, $J = 5.2$ Hz, 1H), 6.11-6.09 (m, 1H), 2.23-2.18 ppm (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) $\delta = 155.6, 142.3, 142.0, 137.0, 136.9, 136.6, 128.2, 128.0, 127.6, 127.1, 126.5, 126.1, 116.0, 114.5, 72.9, 45.7, 42.8, 35.3, 28.5, 23.2, 22.5, 13.7, 12.1, 11.2$ ppm. IR(KBr): ν_{max} (cm^{-1}) = 3412, 3072, 2960, 2922, 2871,

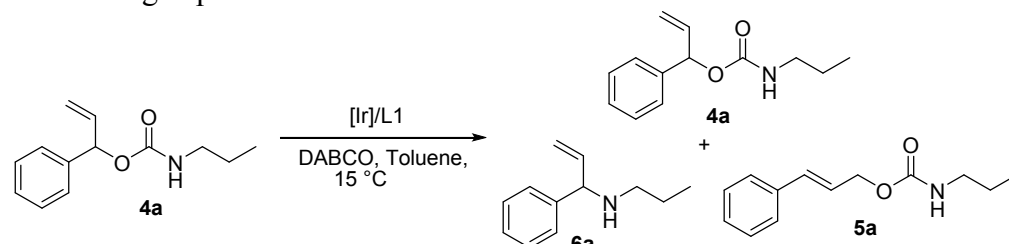
1701 (C=O), 1631, 1509, 1262, 1230, 1141, 1038, 982, 917, 754, 619. HRMS (ESI+) calcd for C₁₈H₂₅NNaO₂ [M+Na]⁺: 310.1778, Found: 310.1780.

Controlling experiment 1:



[Ir(COD)Cl]₂ (0.008 mmol, 4 mol %), phosphoramidite ligand L1 (0.016 mmol, 8 mol %) were dissolved in THF (0.5 mL) and propylamine (0.3 mL) in a dry Schlenk tube filled with argon. The reaction mixture was heated at 50 °C for 30 min, and then the volatile solvents were removed under vacuum to give a yellow solid. After that, allylic carbonate **2a** (0.04 mmol), **4a** (0.2 mmol), DABCO (0.4 mmol), and toluene (2.0 mL) were added. The reaction was stirring at 15 °C in 2 h. Then the reaction mixture was filtrated with celite and the solvents were removed under reduced pressure. The organic layer was evaporated to give the crude products. ¹H NMR analysis of the crude products showed that **4a/6a** is in a ratio of 15/1.

Controlling experiment 2:



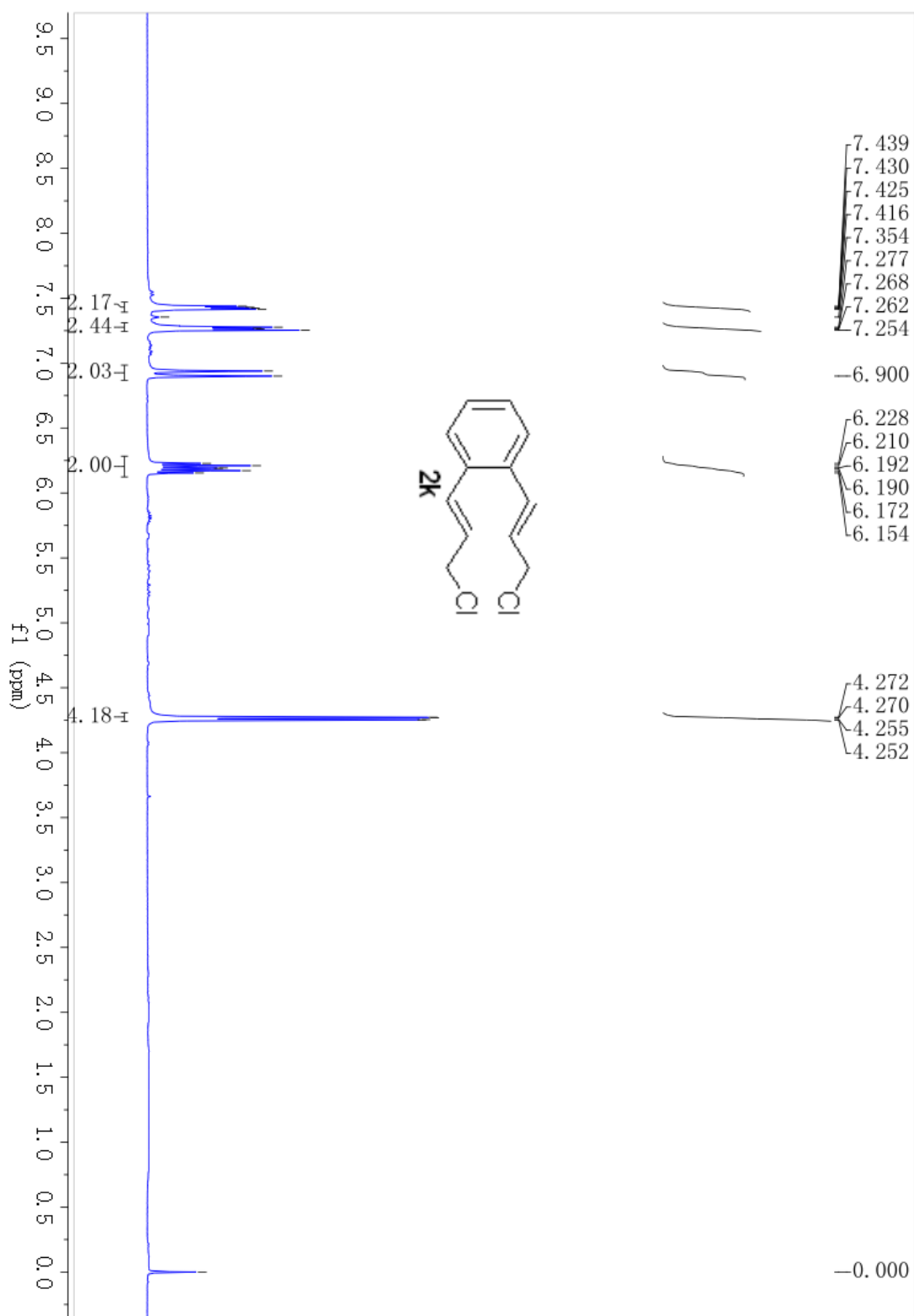
[Ir(COD)Cl]₂ (0.008 mmol, 4 mol %), phosphoramidite ligand L1 (0.016 mmol, 8 mol %) were dissolved in THF (0.5 mL) and propylamine (0.3 mL) in a dry Schlenk tube filled with argon. The reaction mixture was heated at 50 °C for 30 min, and then the volatile solvents were removed under vacuum to give a yellow solid. After that, **4a** (0.2 mmol), DABCO (0.4 mmol), and toluene (2.0 mL) were added. The reaction was stirring at 15 °C in 2 h. Then the reaction mixture was filtrated with celite and the solvents were removed under reduced pressure. The organic layer was evaporated to give the crude products. ¹H NMR analysis of the crude products showed that **4a/6a** is in a ratio of 5/1.

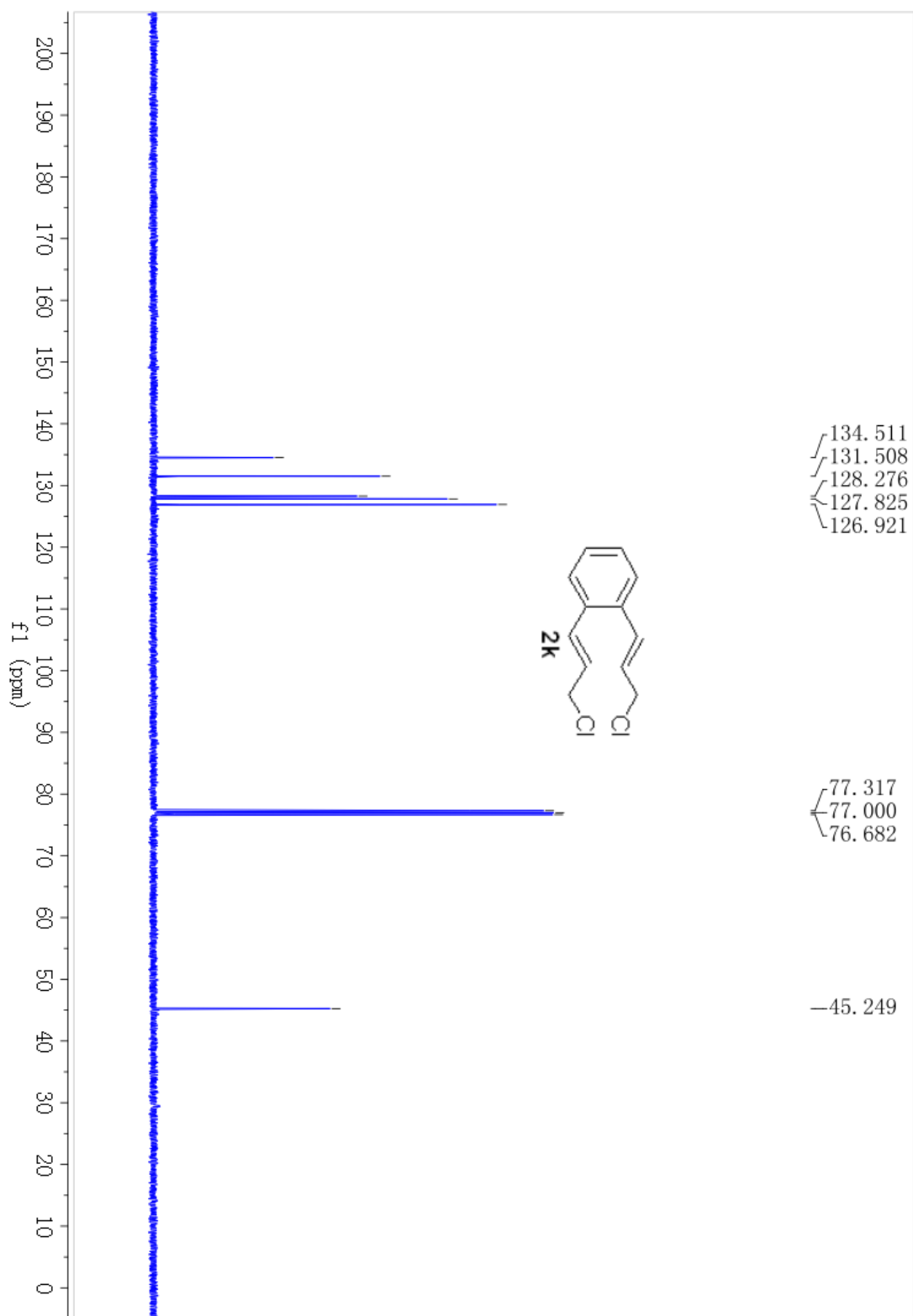
References:

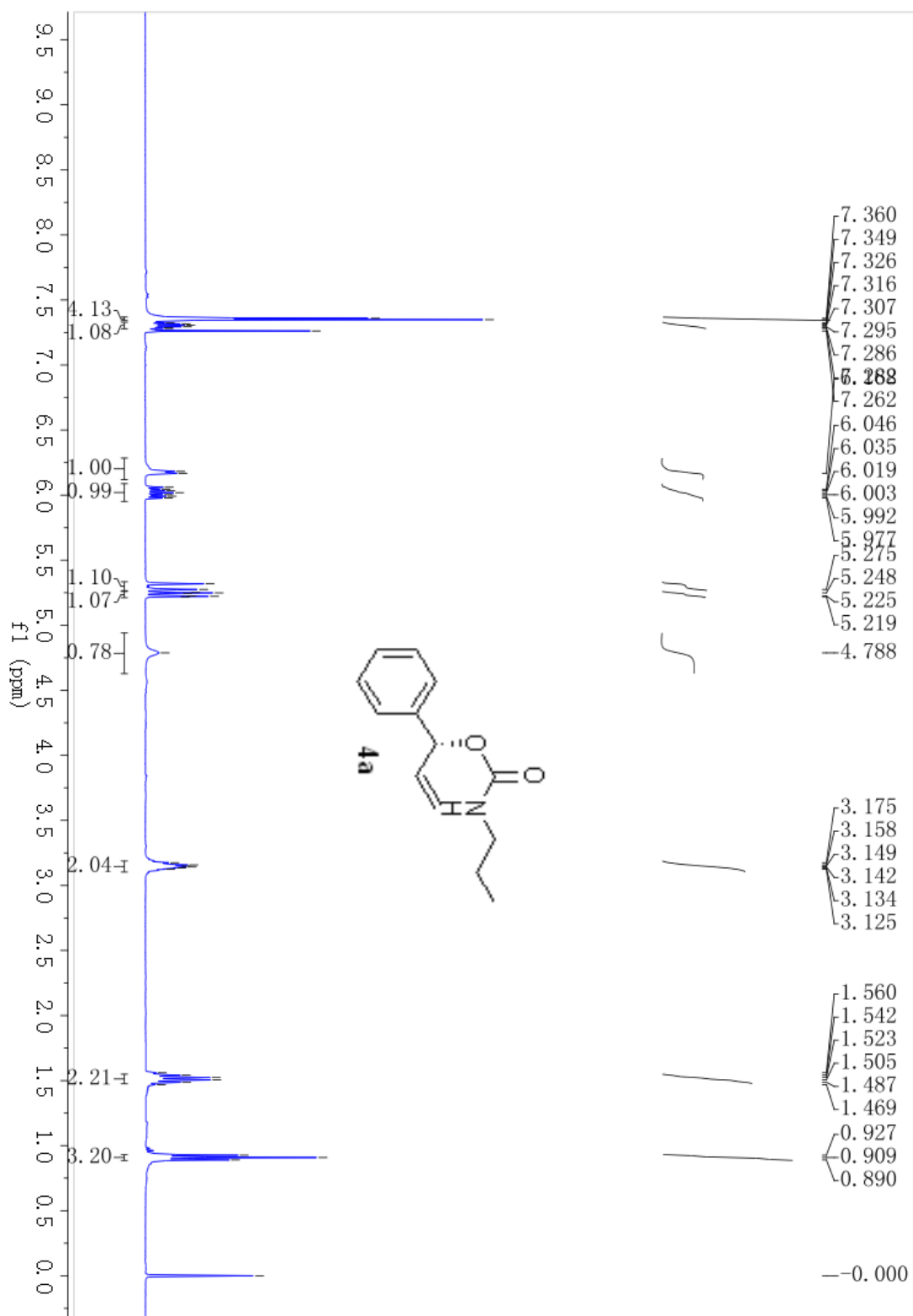
- [1] a) A. Alexakis, S. Rosset, J. Allamand, S. March, F. Guillen, C. Benhaim, *Synlett* **2001**, 9, 1375; b) R. Naasz, L. A. Arnold, A. J. Minnaard, B. L. Feringa, *Angew. Chem. Int. Ed.* **2001**, 40, 927; c) K. Tissot-Croset, D. Polet, A. Alexakis, *Synthesis* **2004**, 15, 2586.
- [2] M. Yan, L. W. Yang, K. Y. Wong, A. S. C. Chan, *Chem. Commun.* **1999**, 11.
- [3] L. Brozek, A. M. J. Ardolino, J. P. Morken, *J. Am. Chem. Soc.*, **2011**, 133, 16778.
- [4] N. Darby, T. M. Cresp, F. Sondheimer, *J. Org. Chem.* **1997**, 42, 1960.
- [5] L. W. Fancher, *Ger. Offen.* DE 1916971 A 1969 1106, 1969.
- [6] D. Marković, J. F. Hartwig, *J. Am. Chem. Soc.* **2007**, 129, 11680.

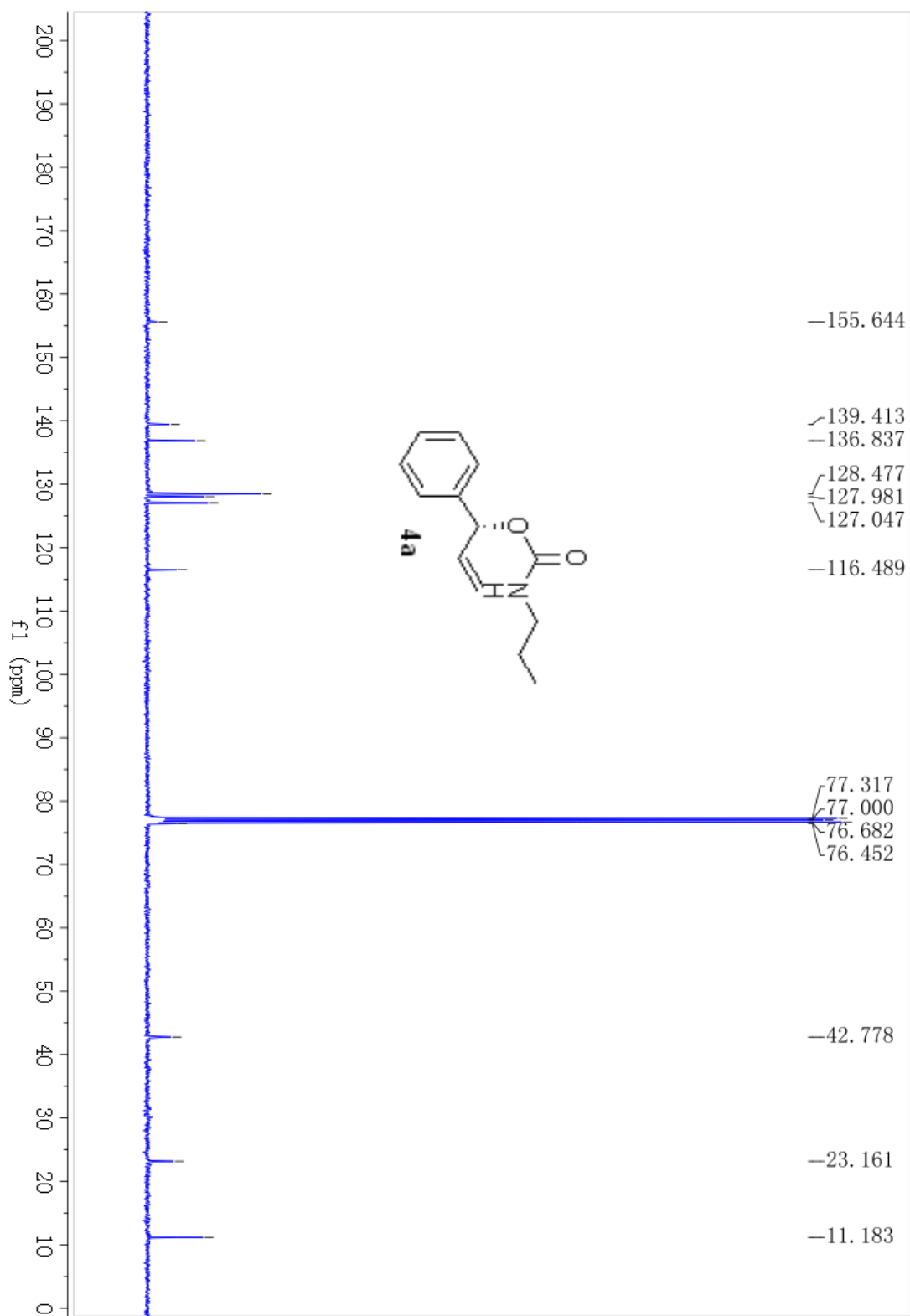
- [7] R. Takeuchi, N. Ue, K. Tanabe, K. Yamashita, N. Shiga, *J. Am. Chem. Soc.* **2001**, *123*, 9525.
- [8] H. Li, A. Alexakis, *Angew. Chem. Int. Ed.* **2012**, *51*, 1055.

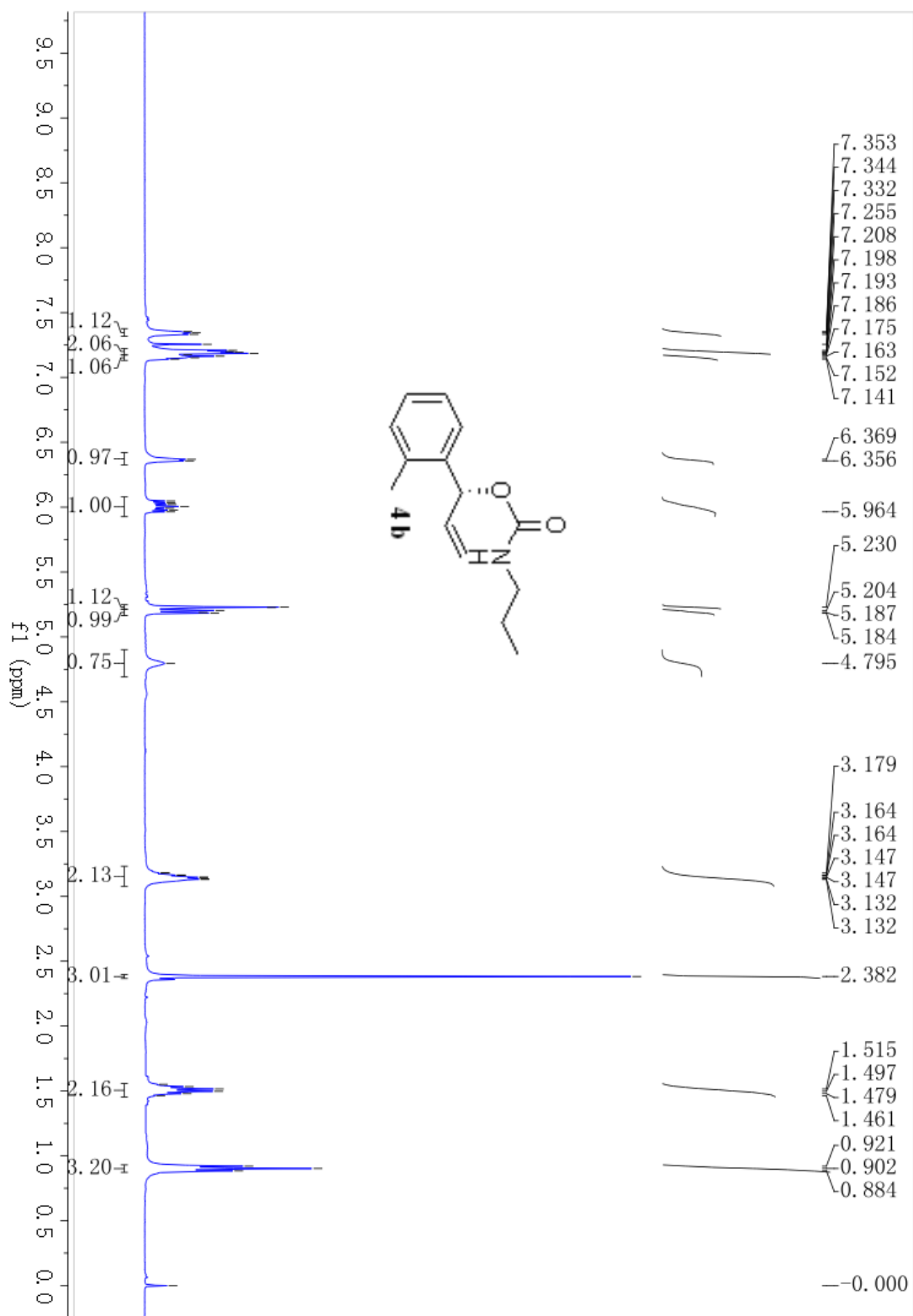
NMR Spectra of the compounds 2k, 4, 5, 6 and 7k

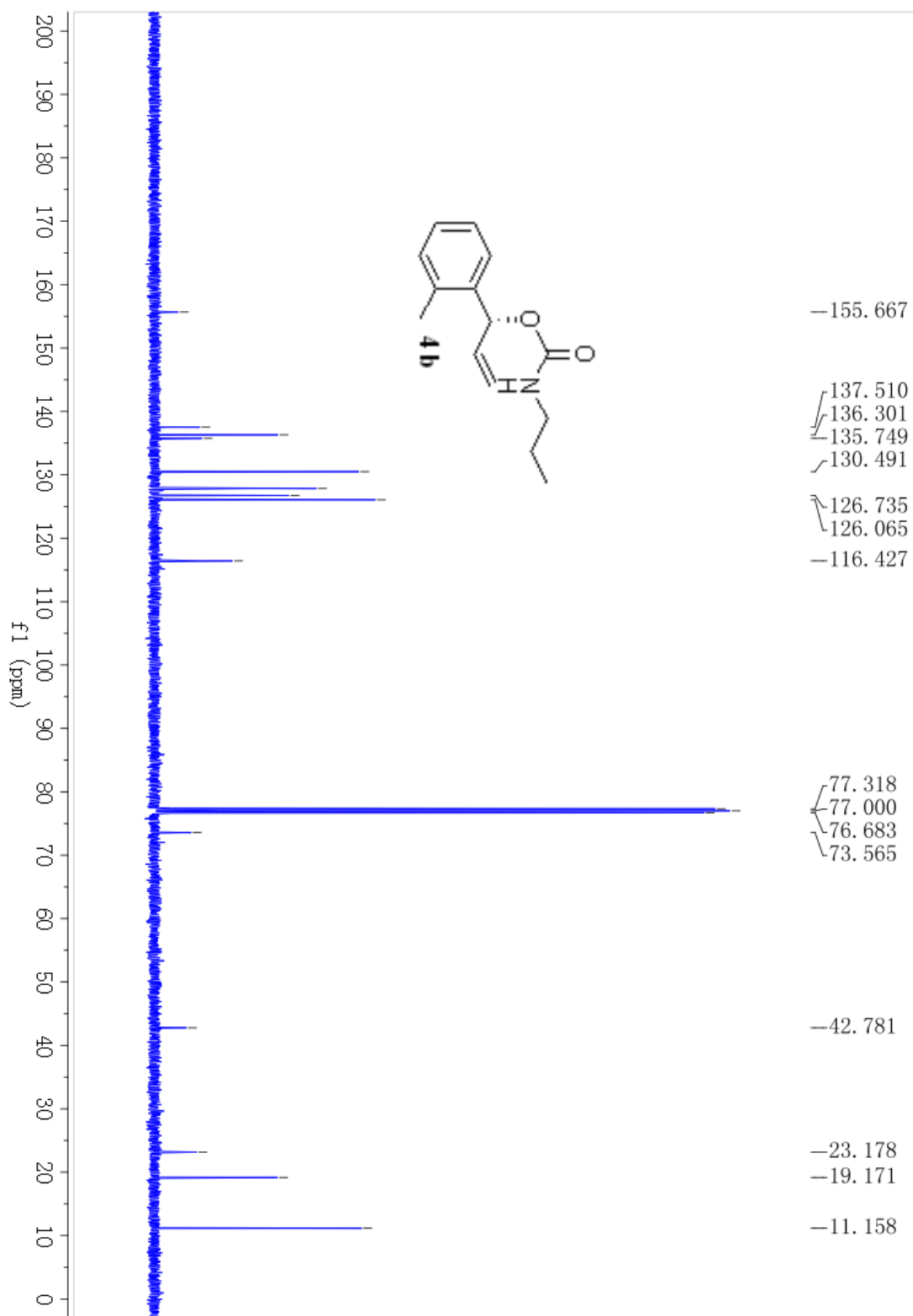


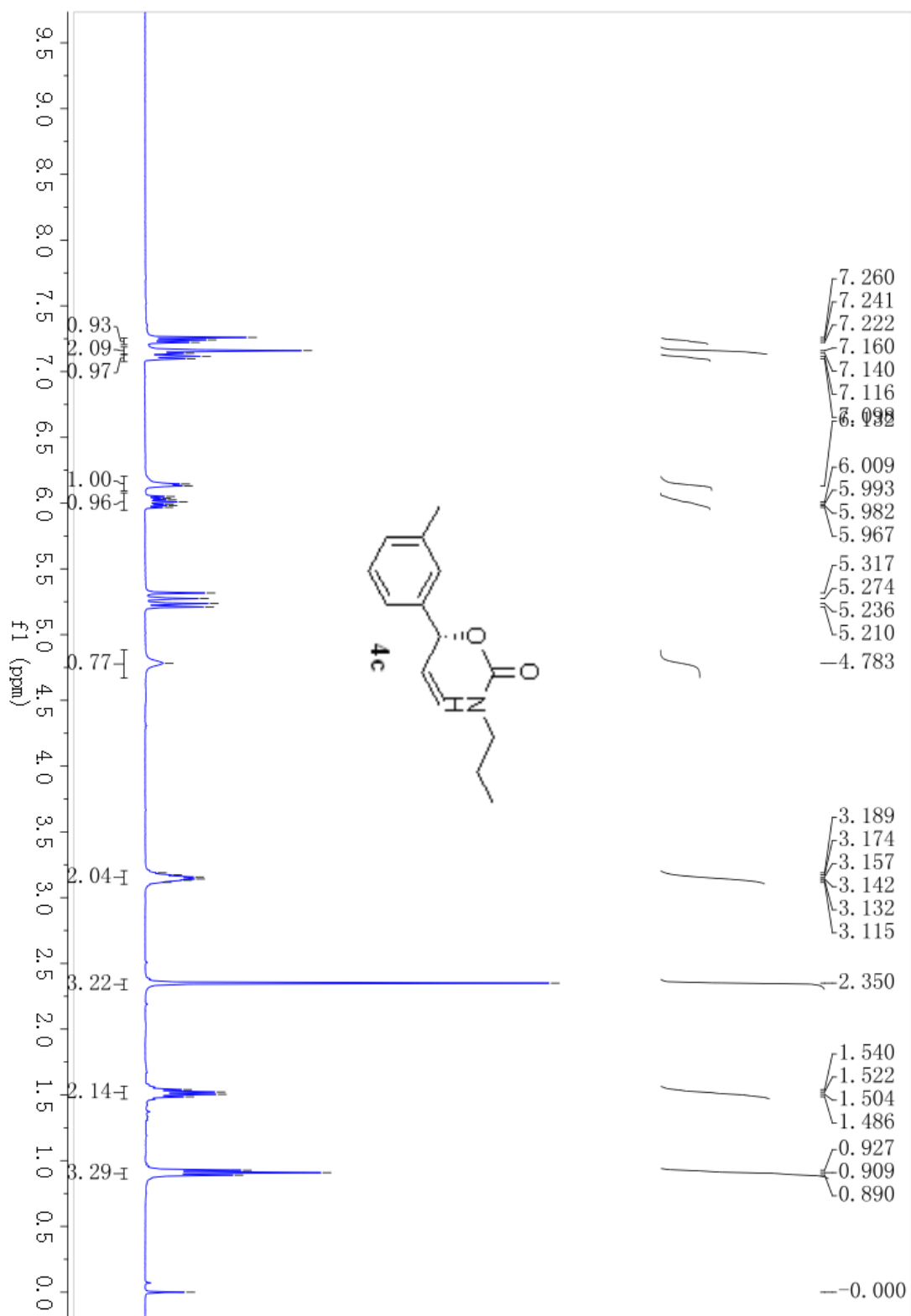


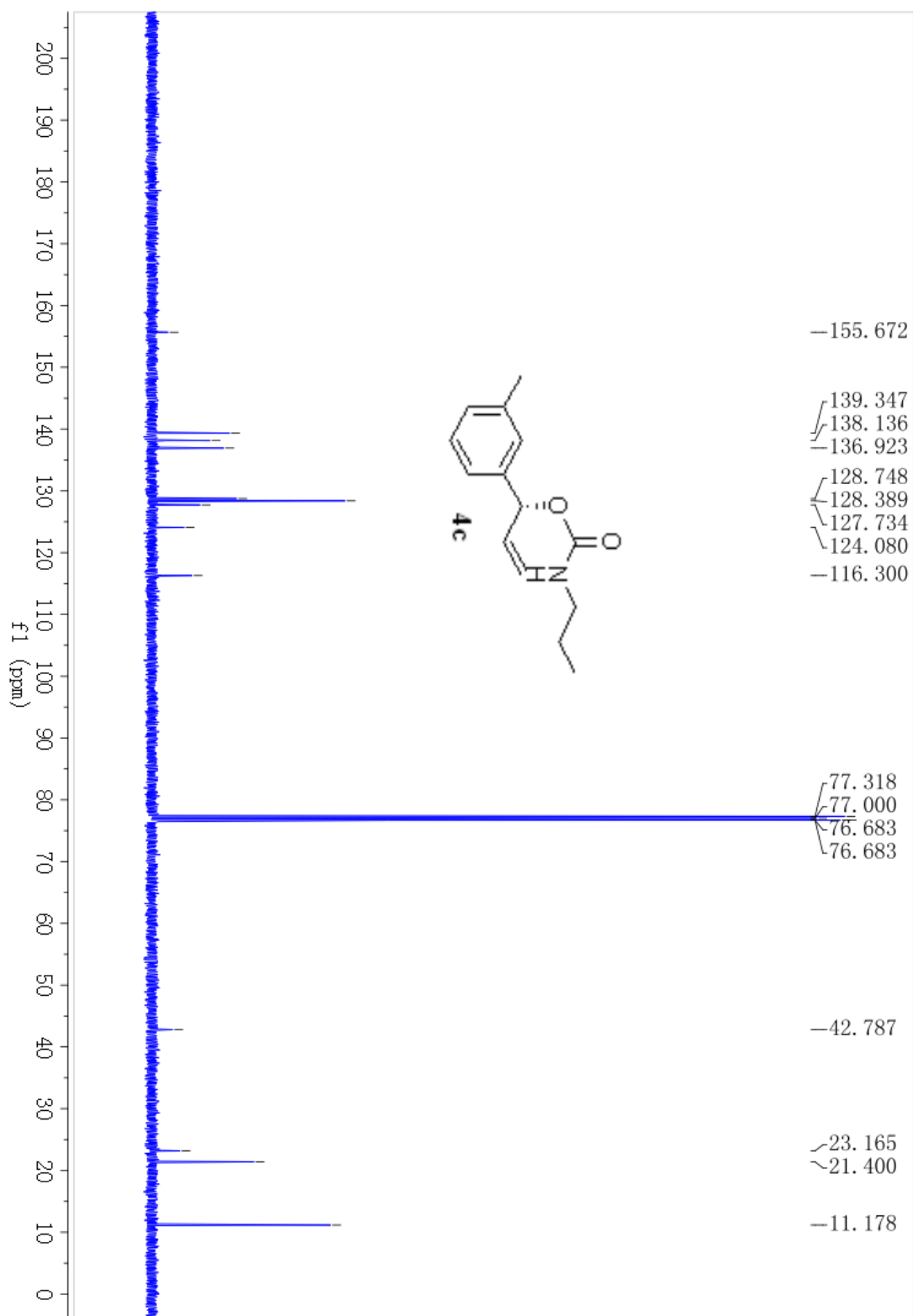


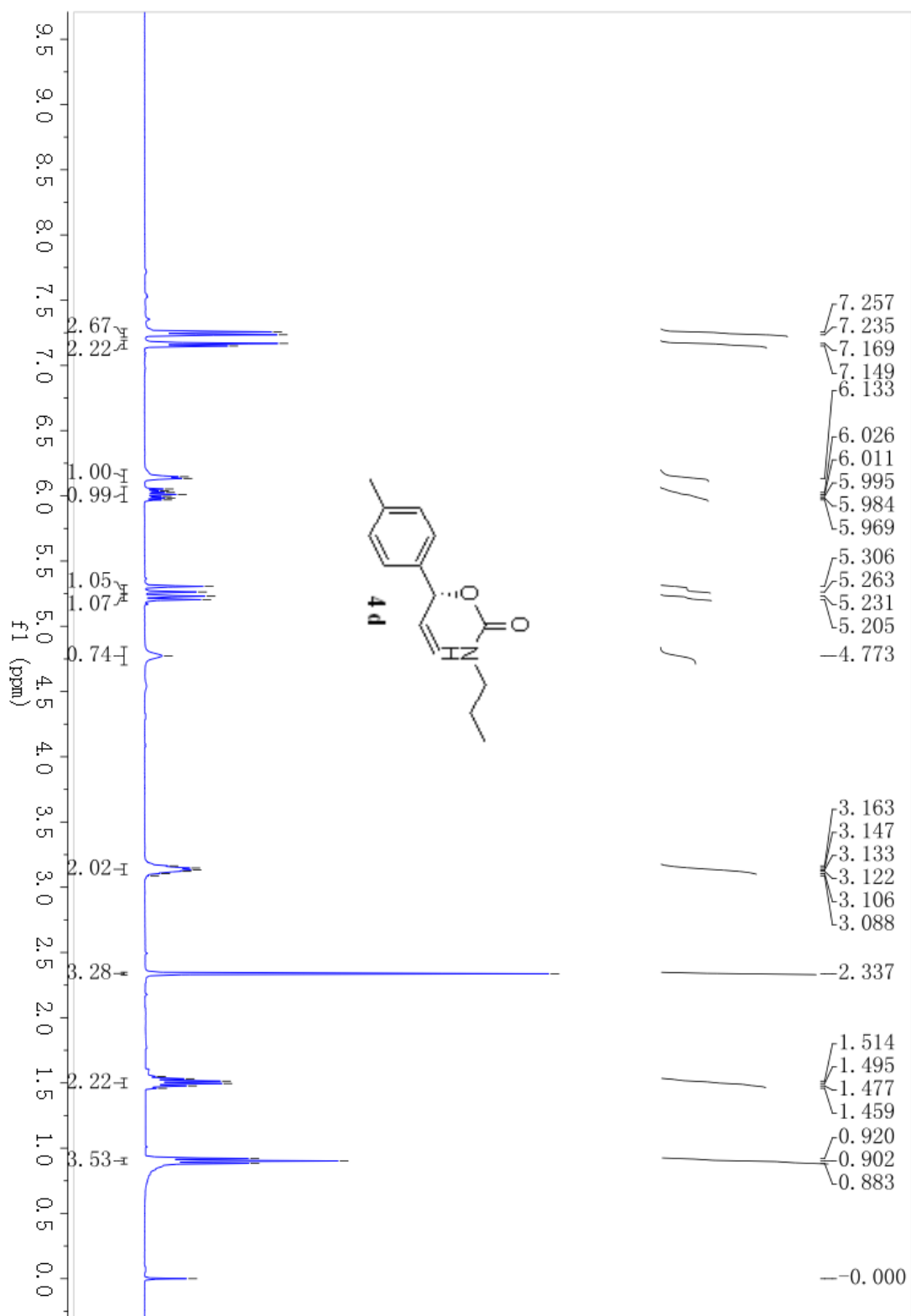


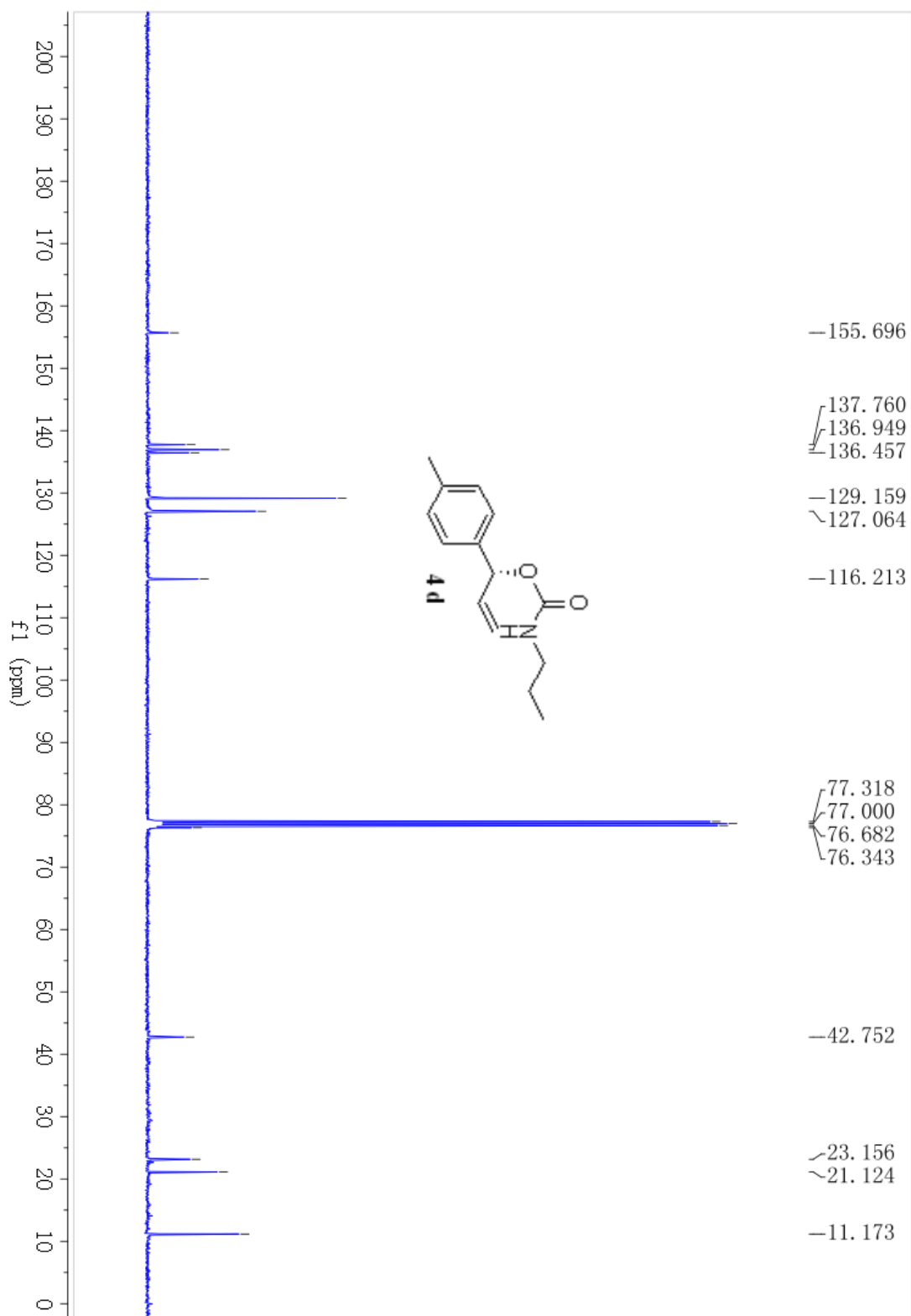


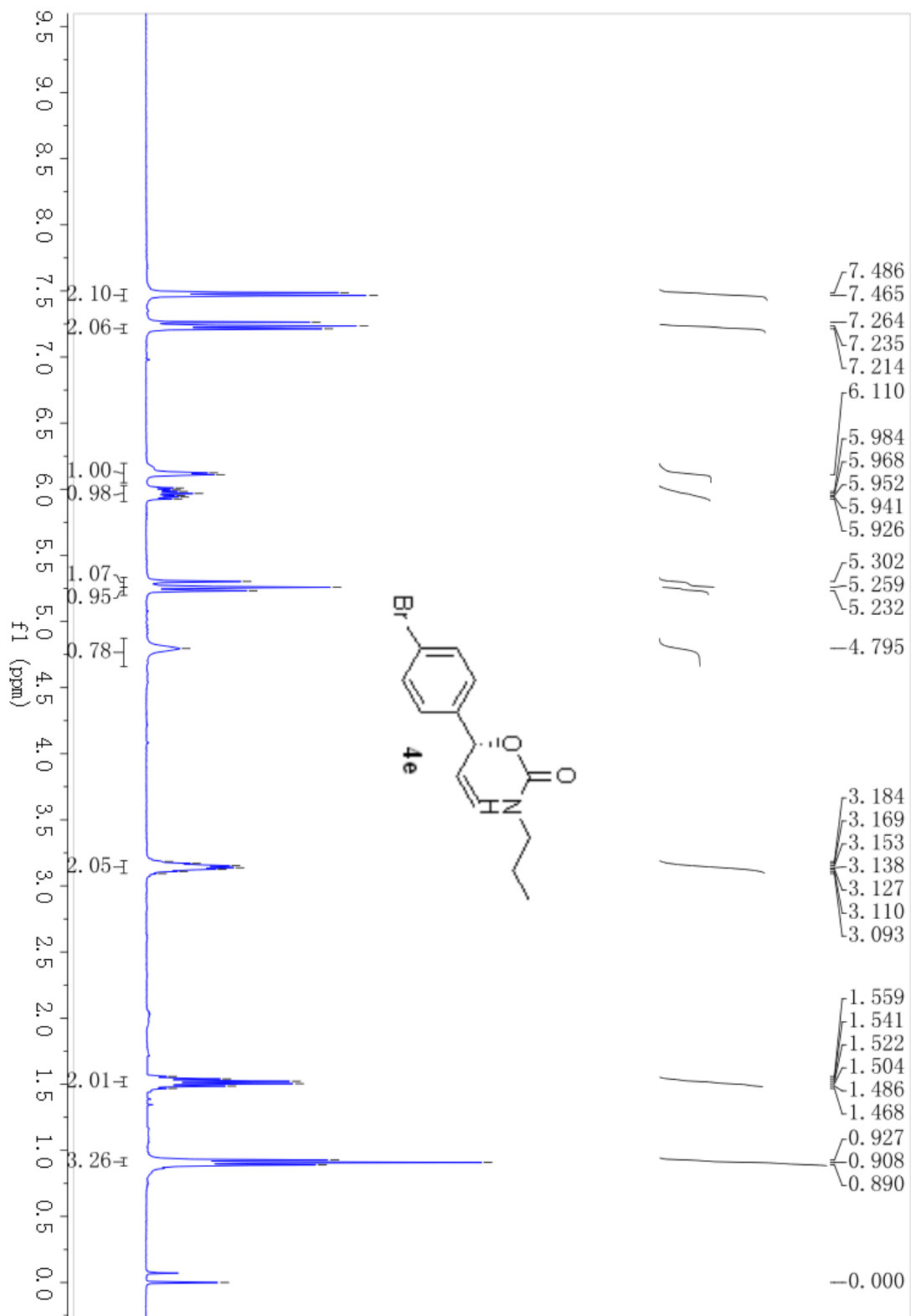


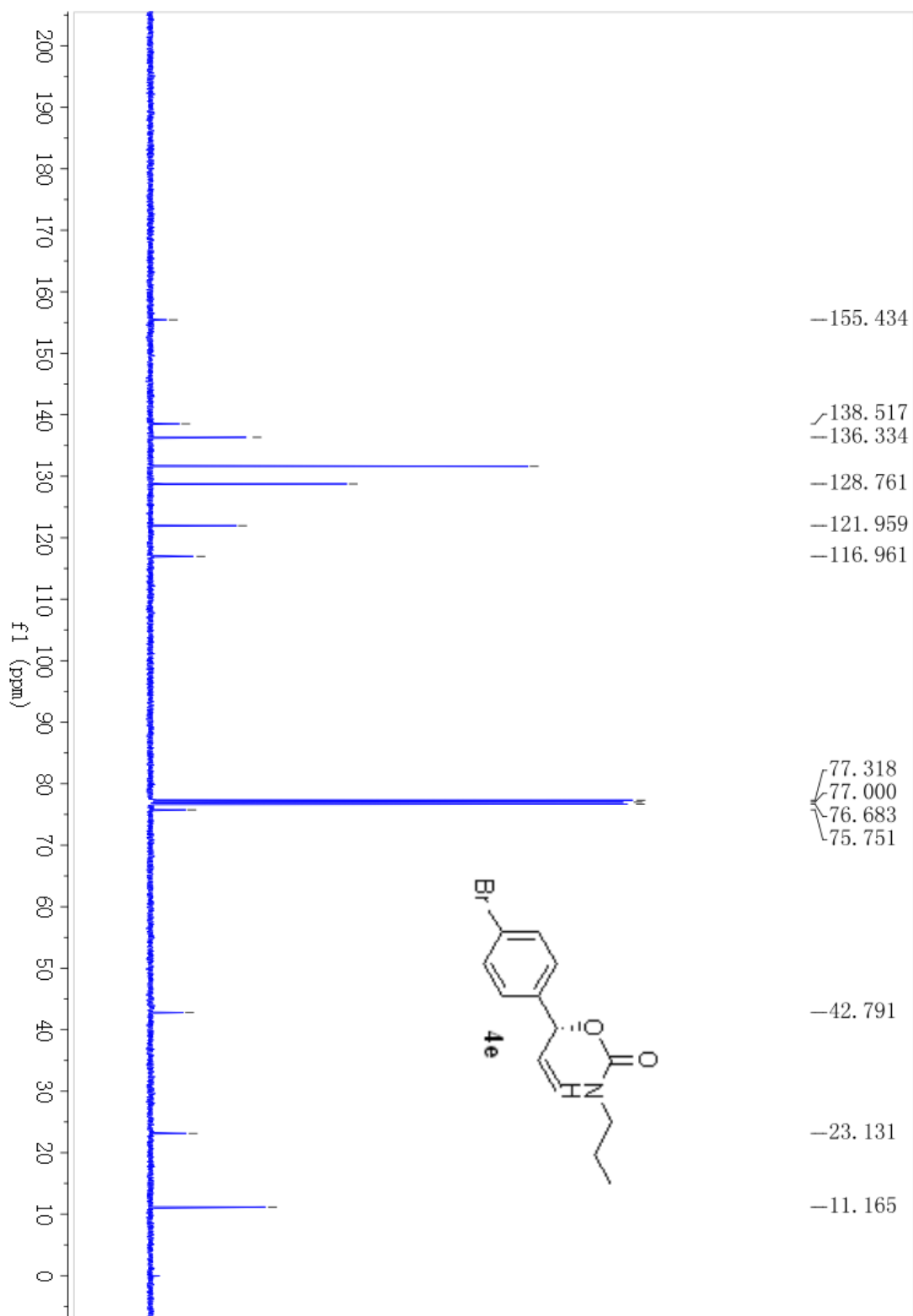


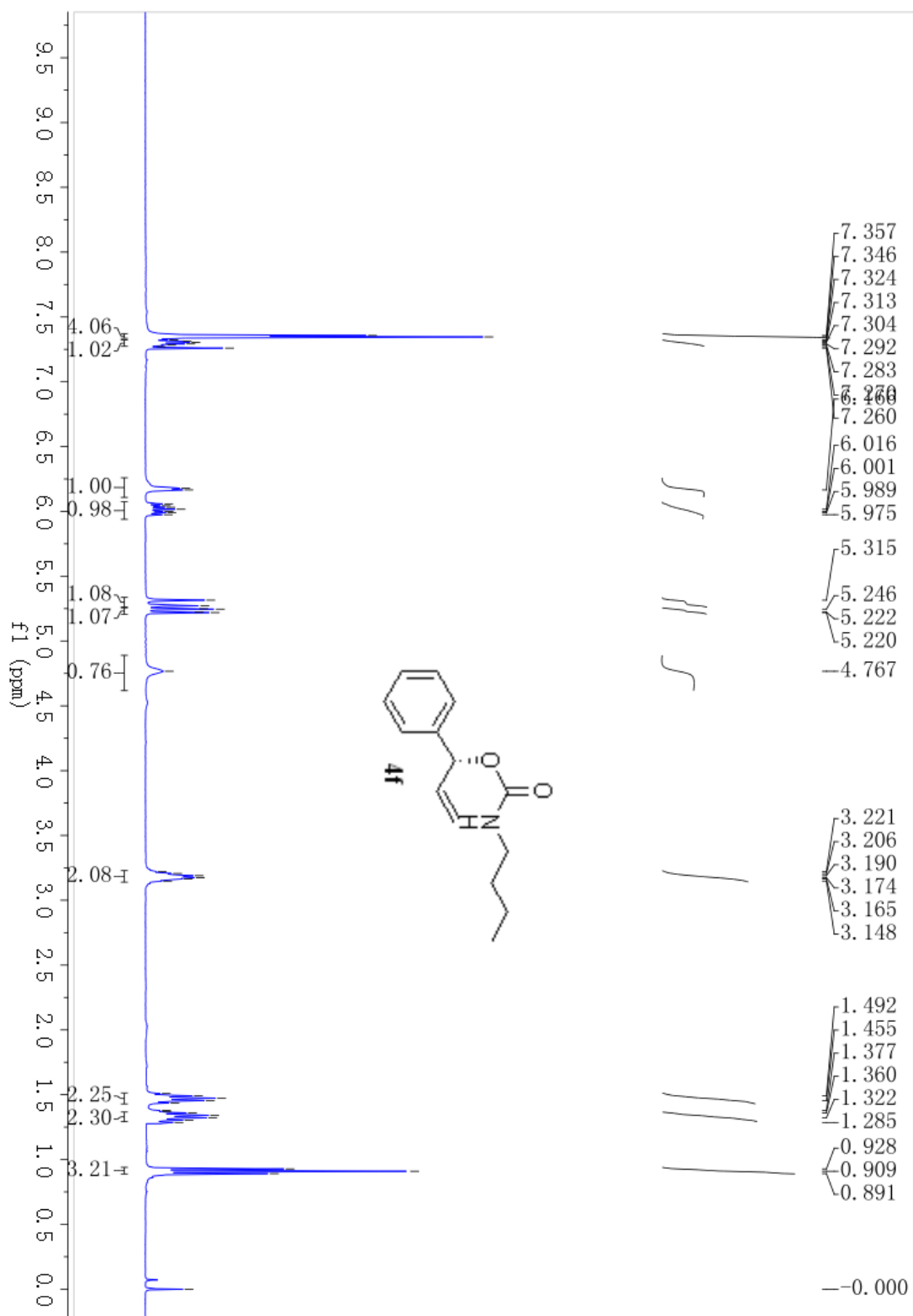


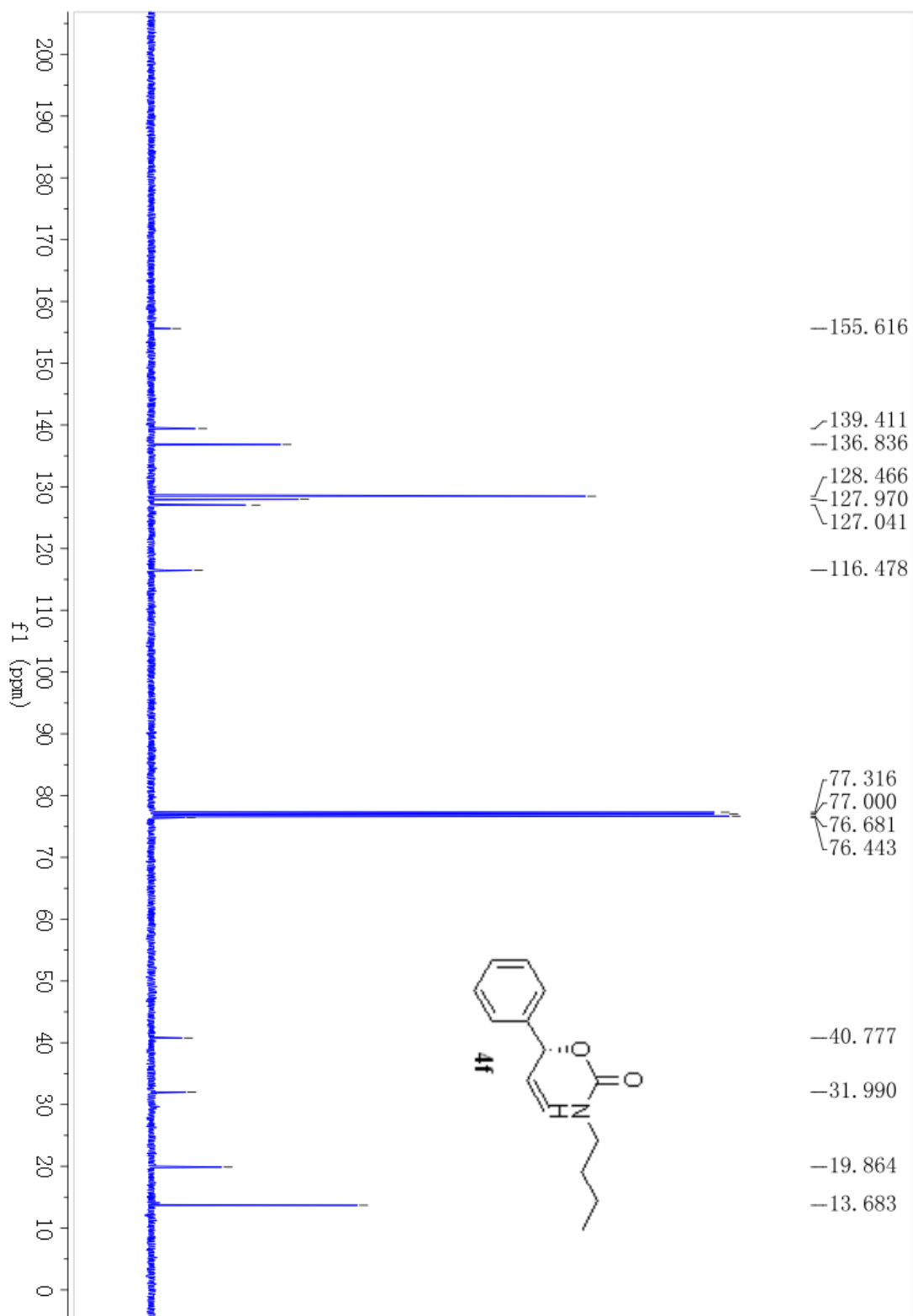


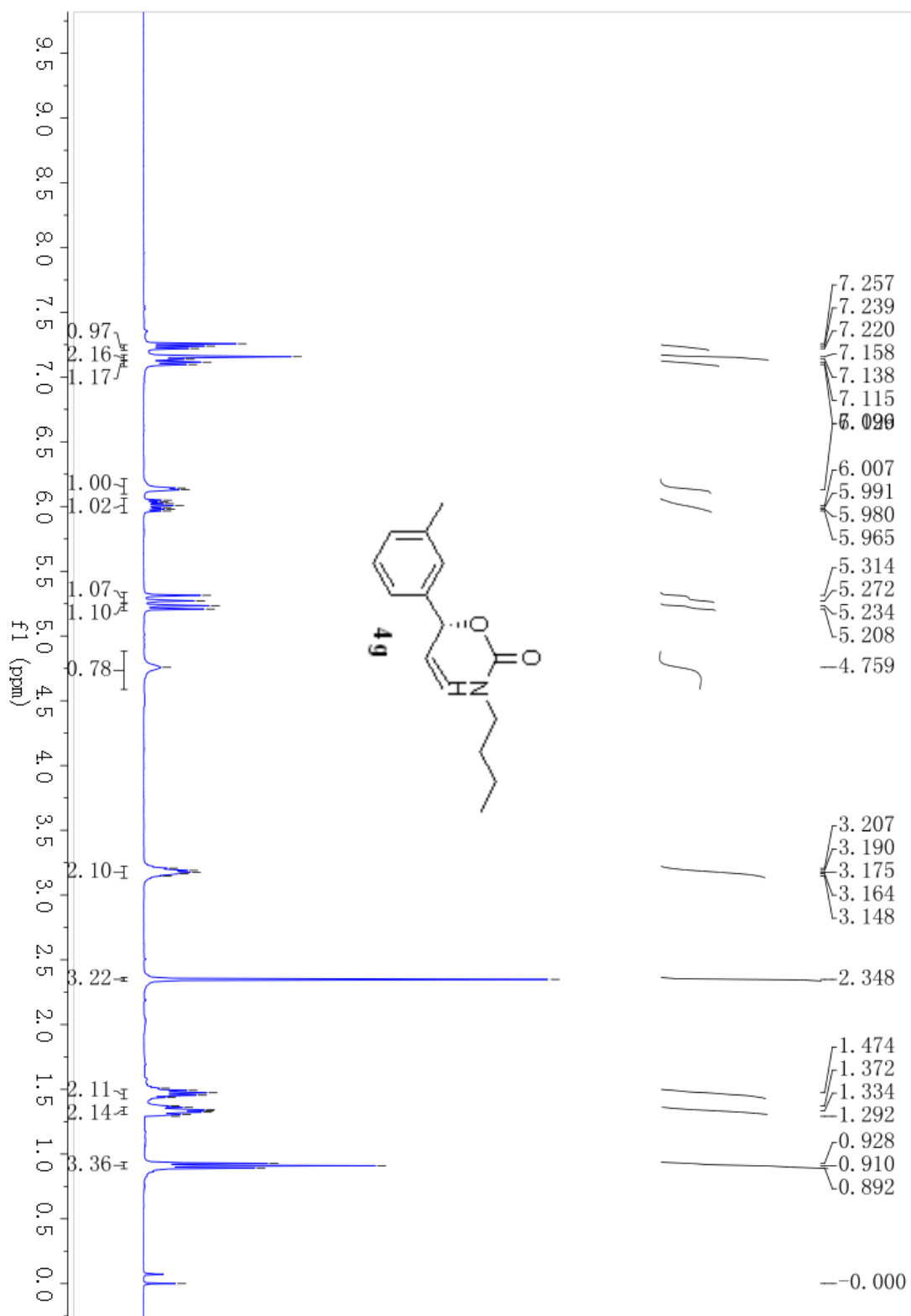


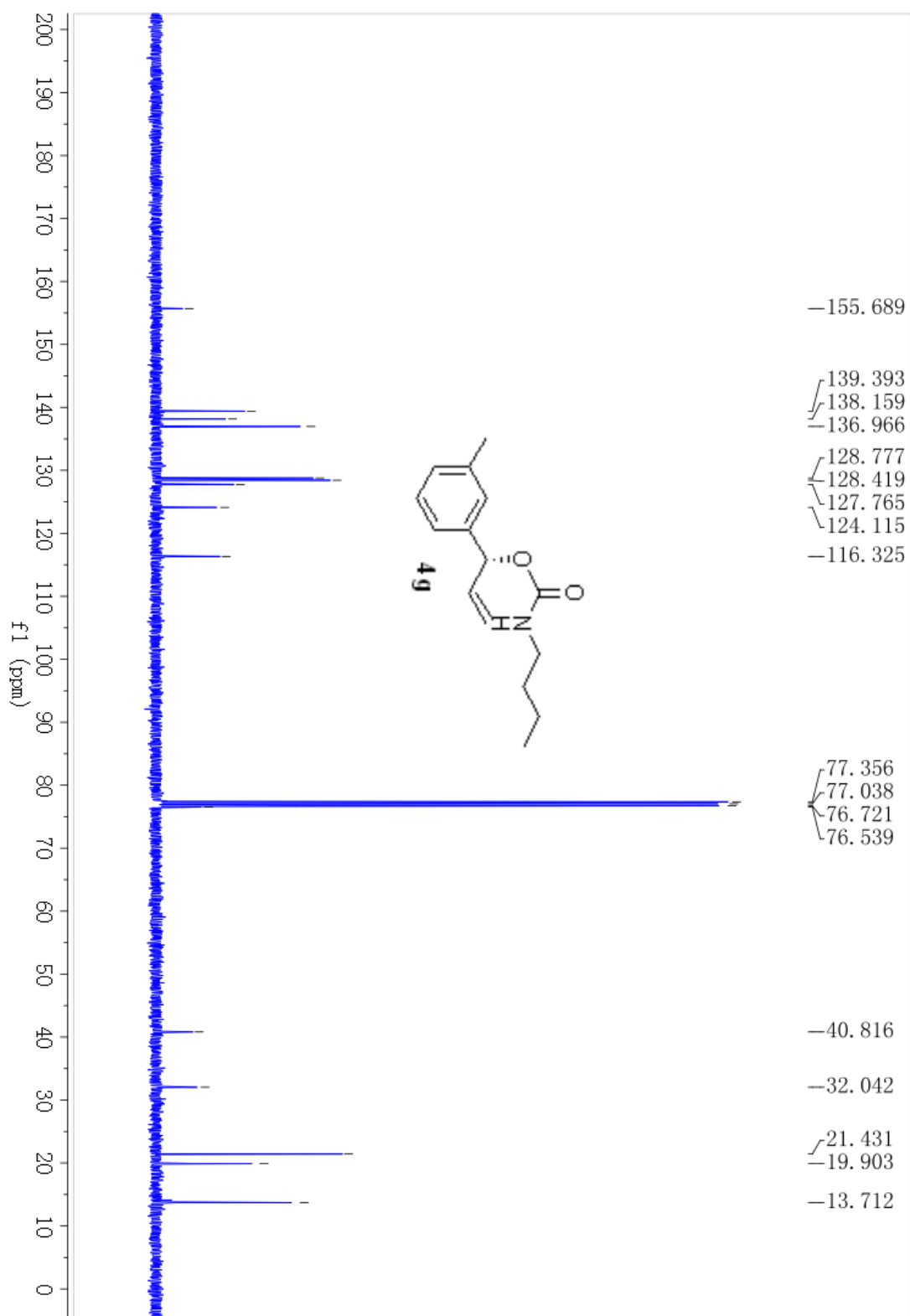


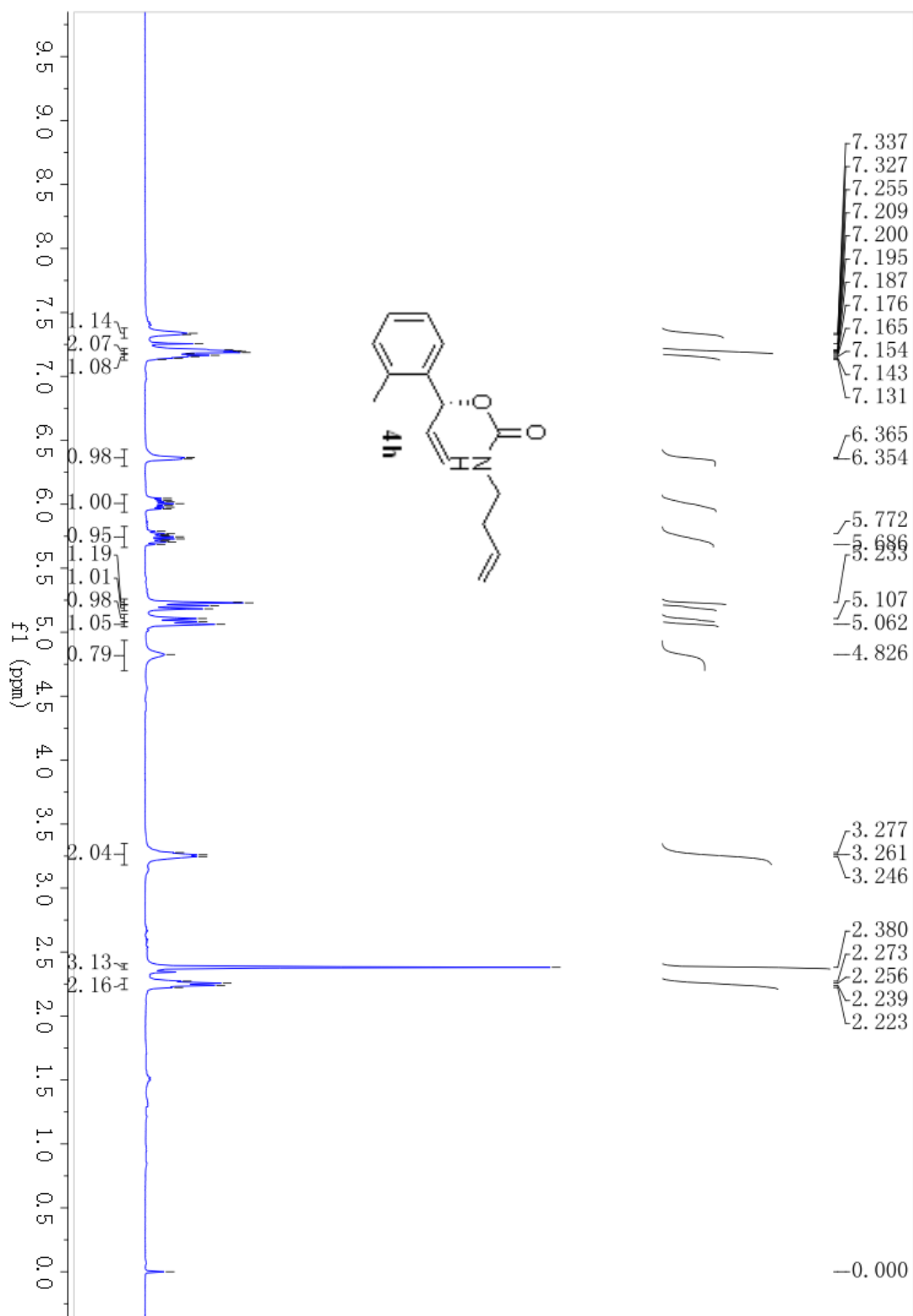


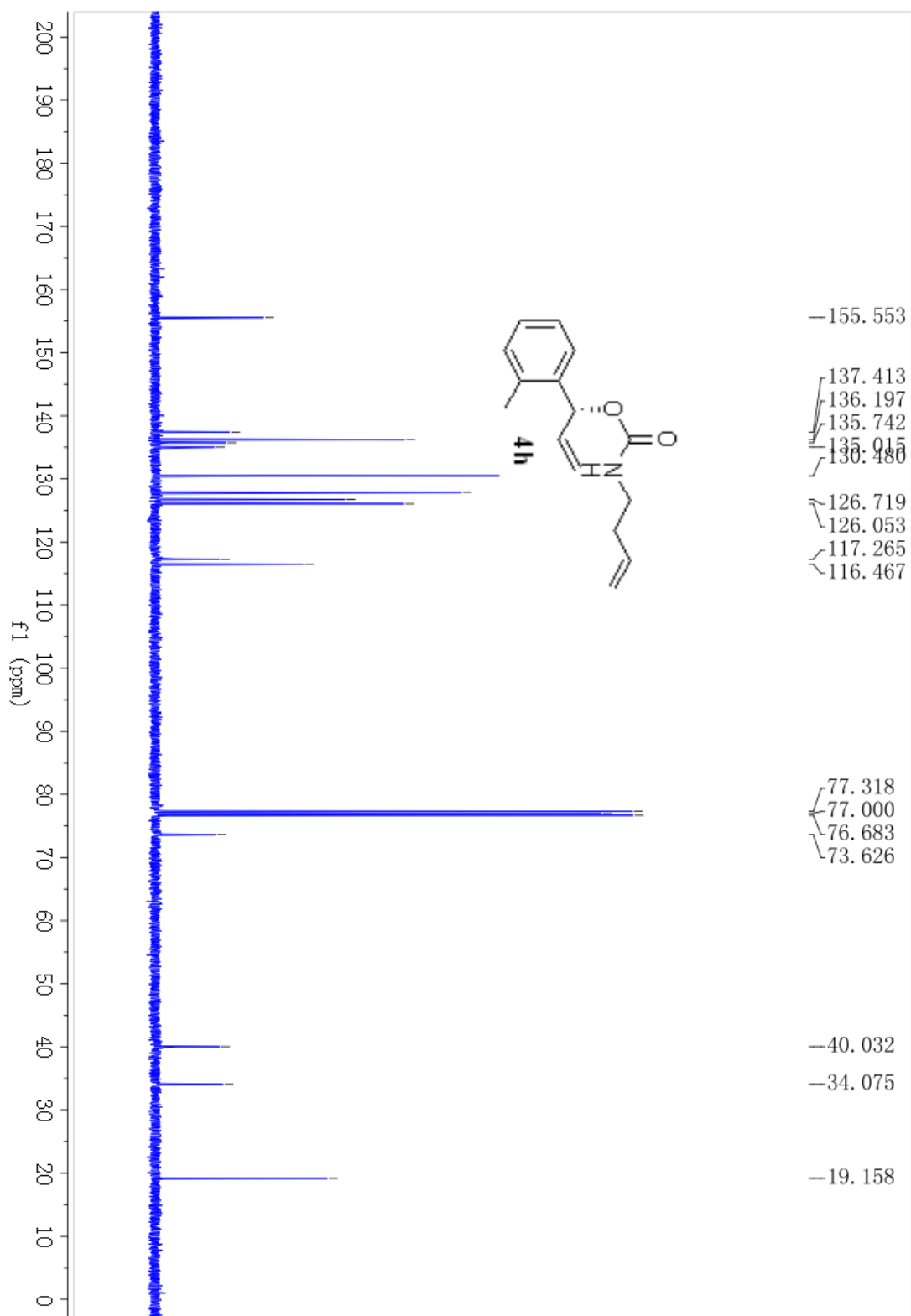


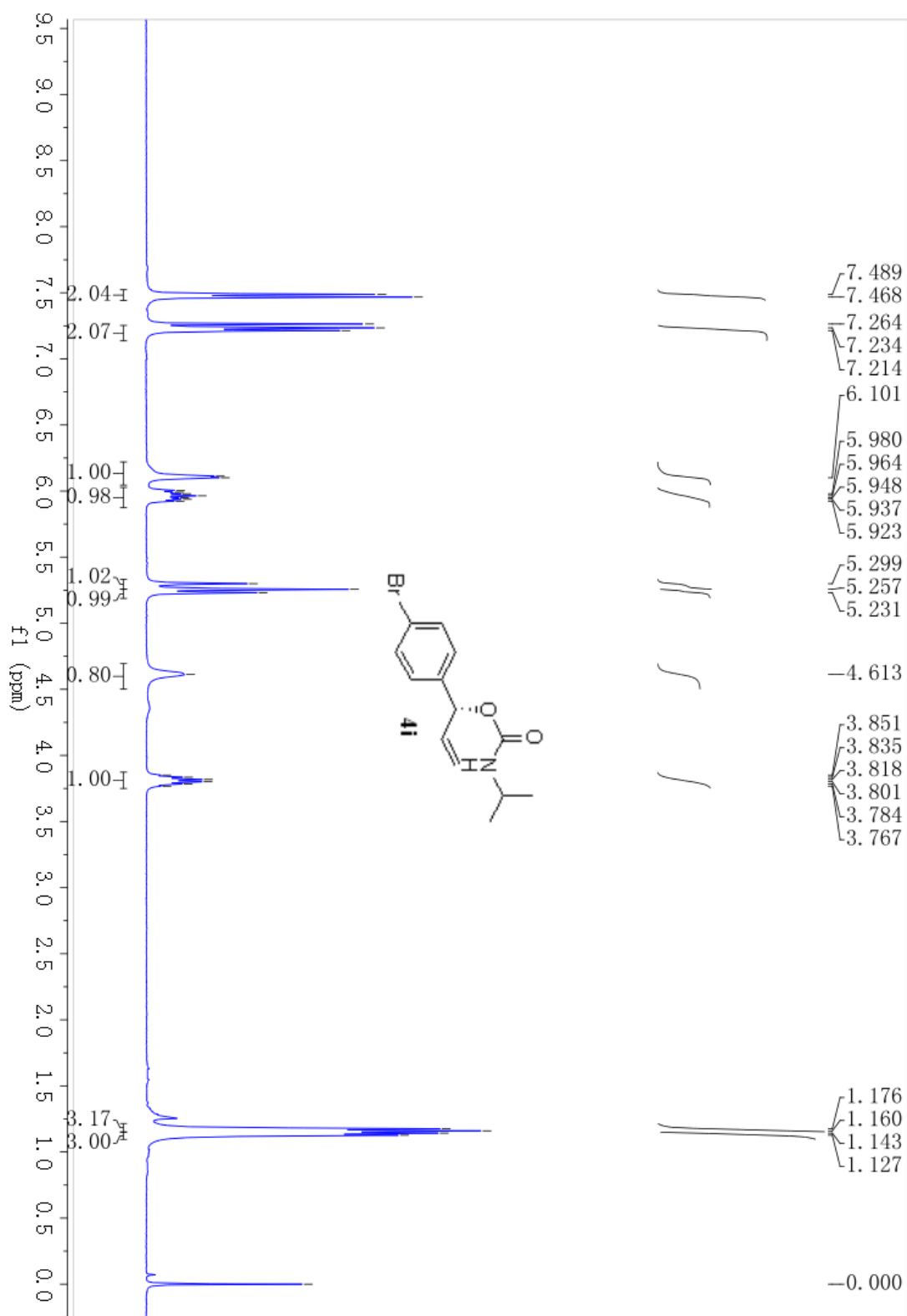


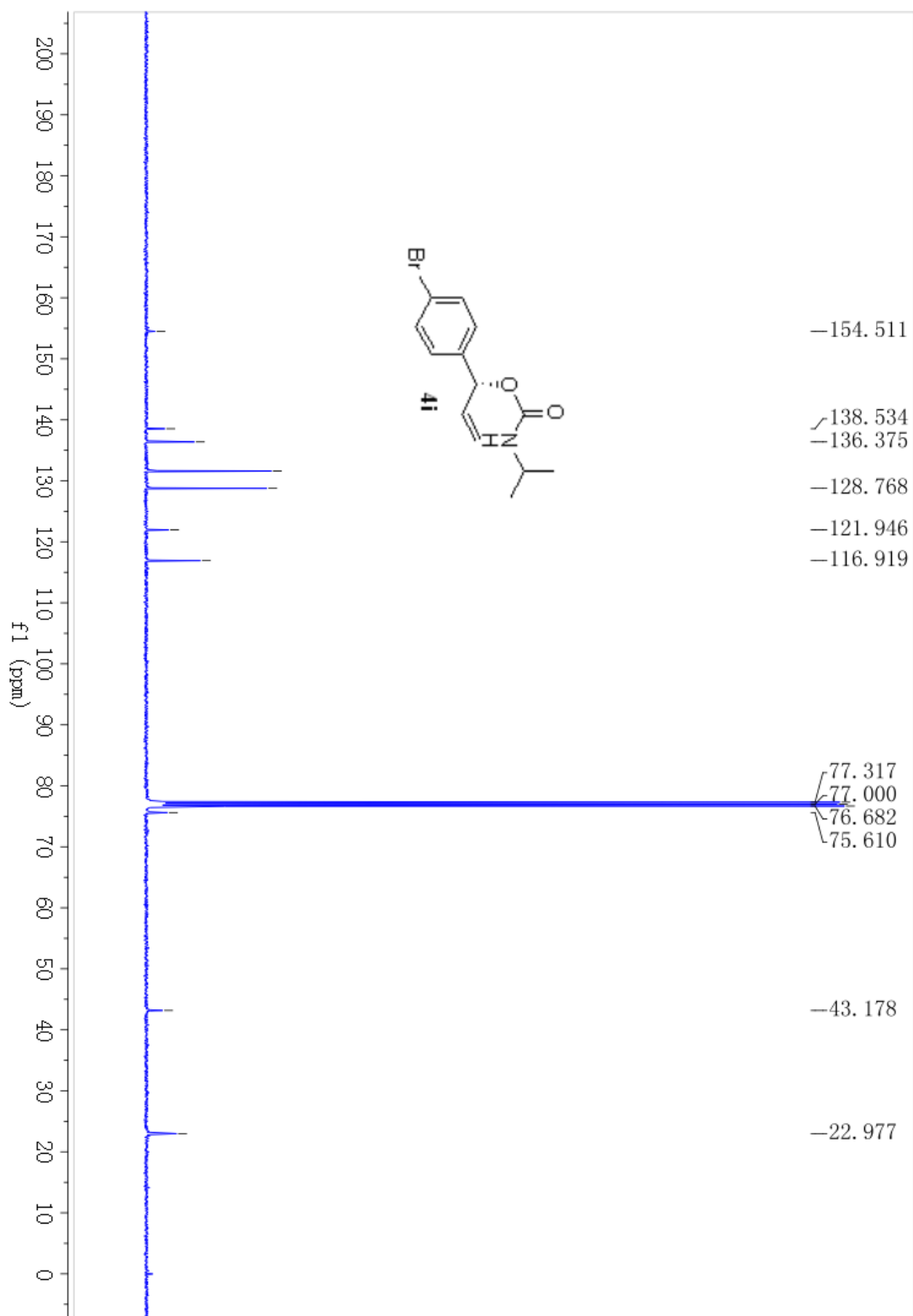


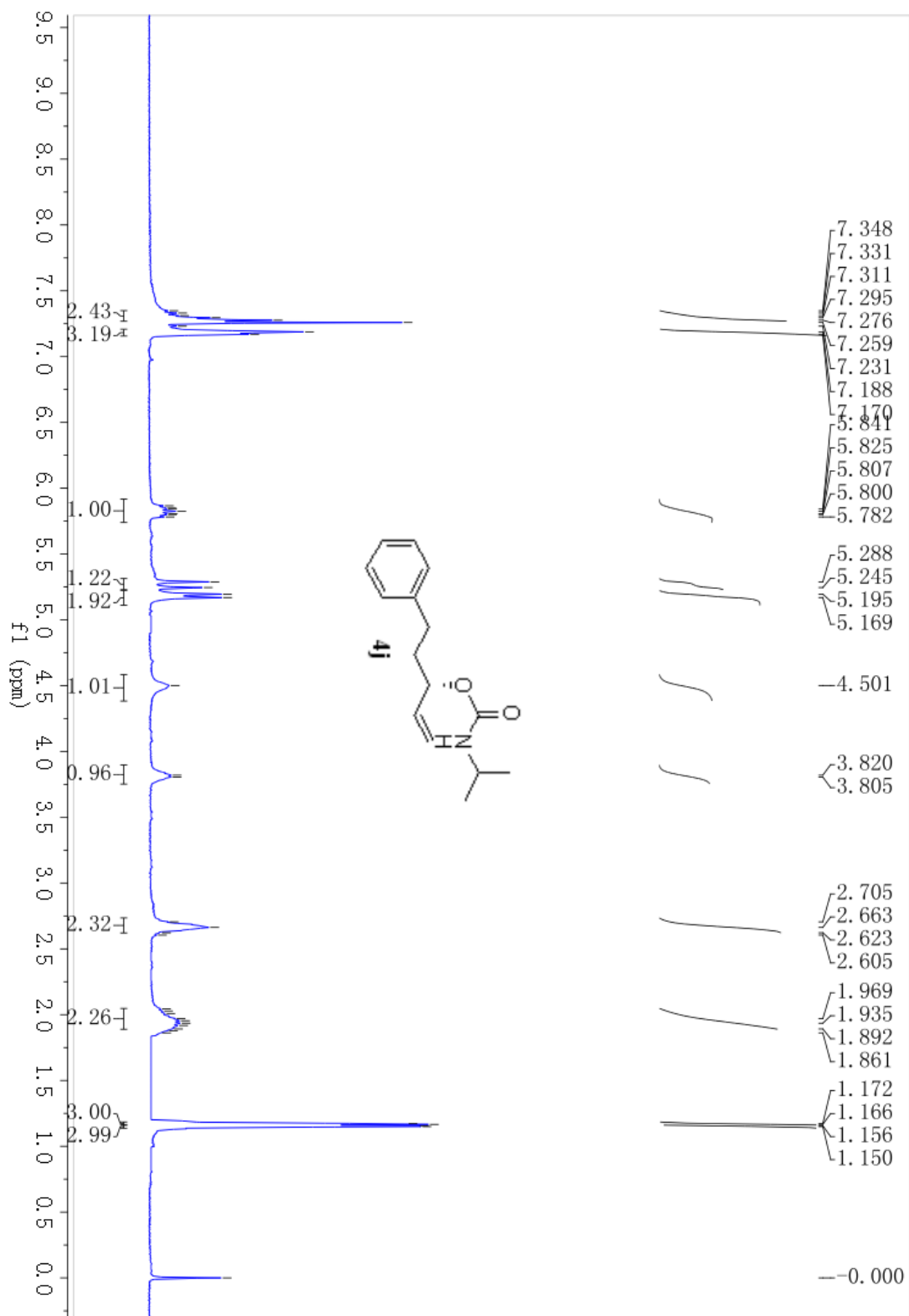


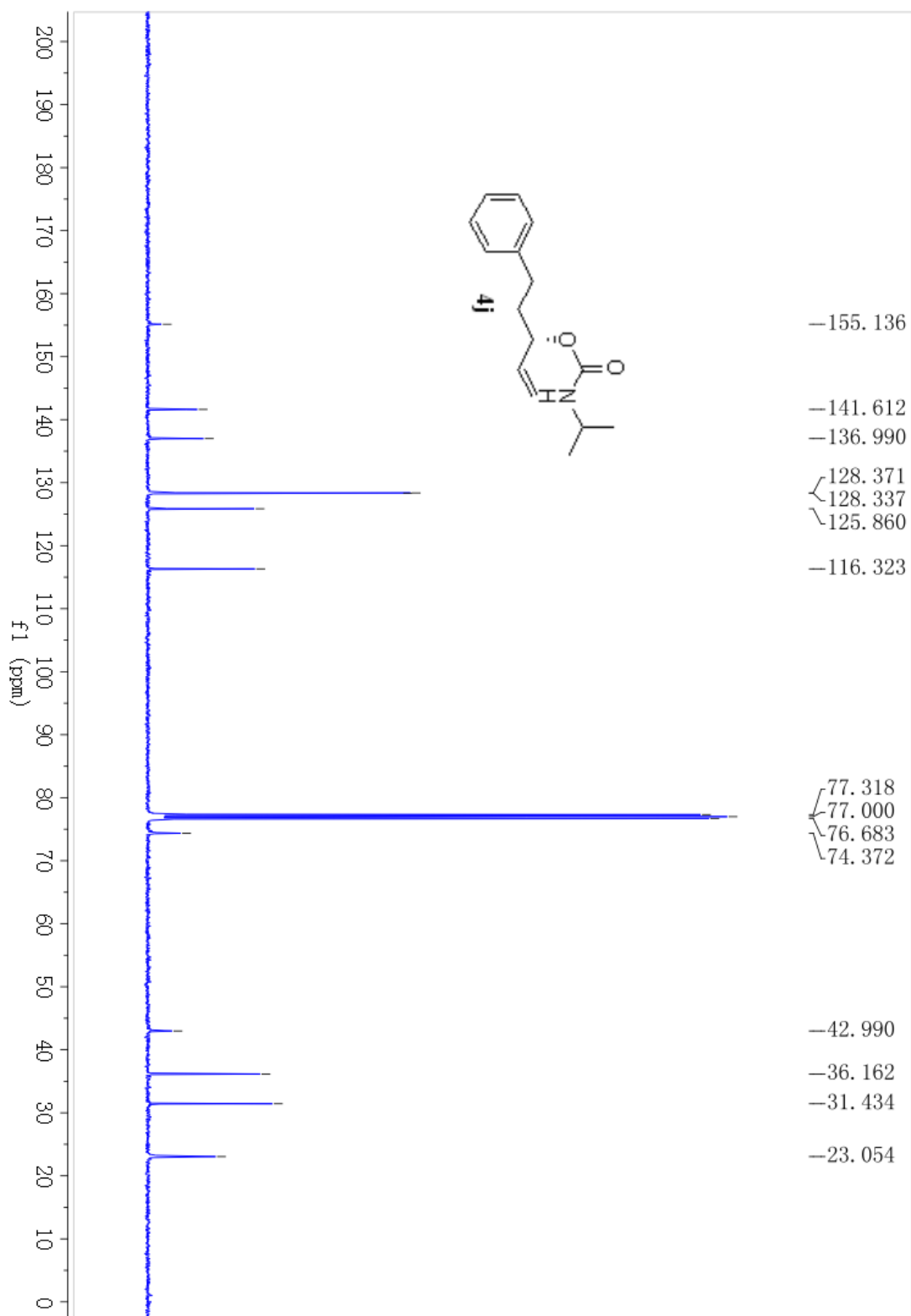


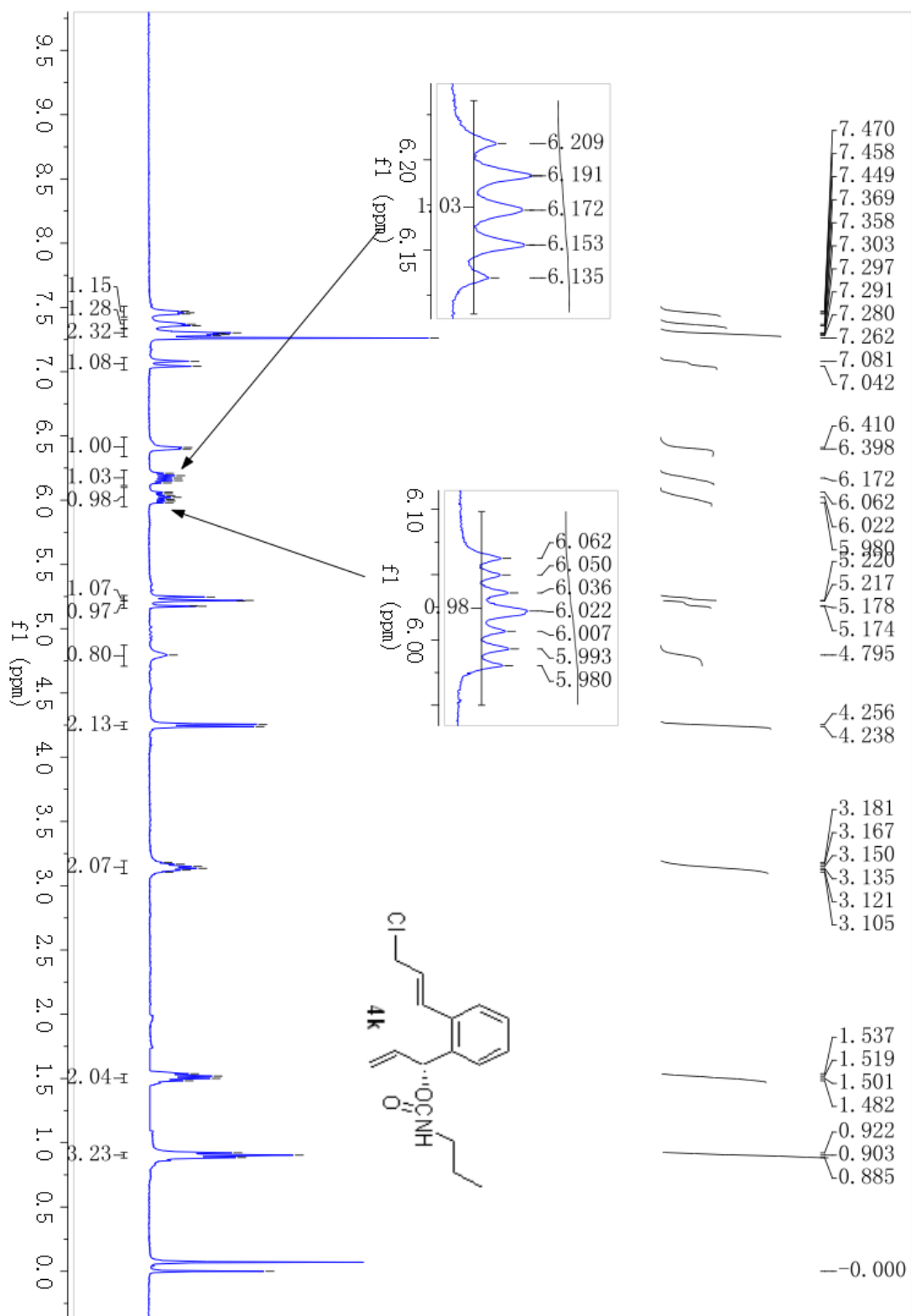


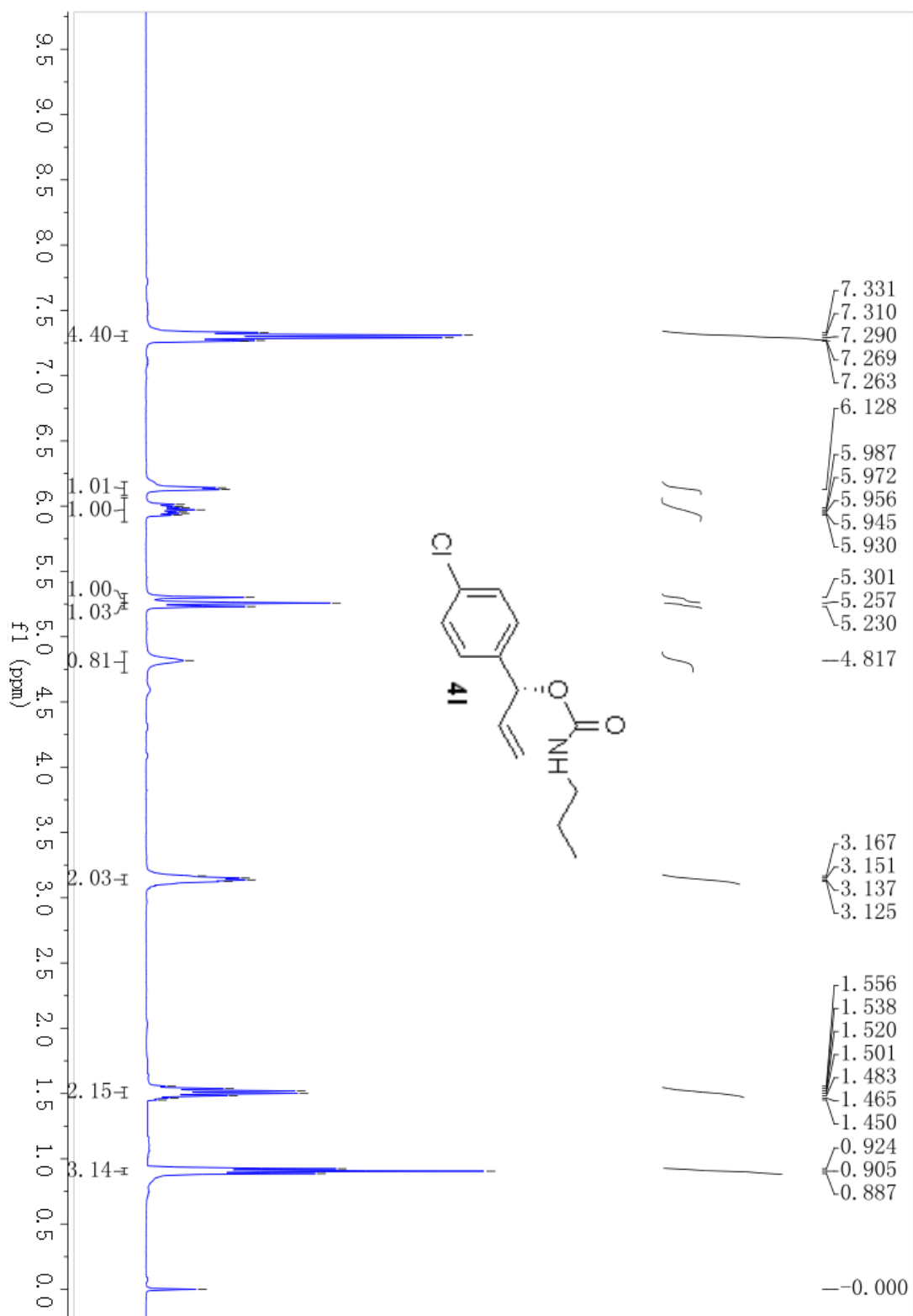


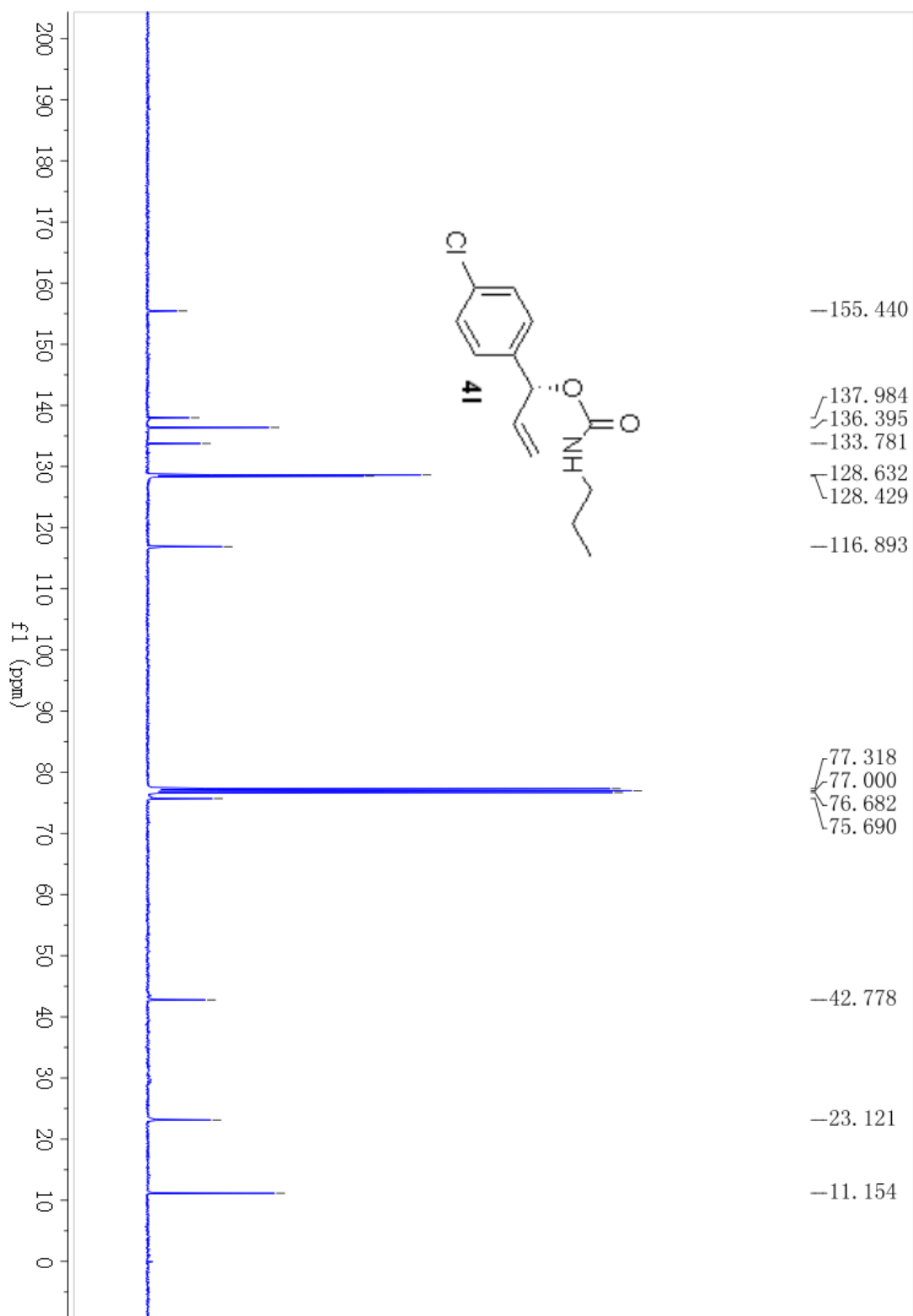


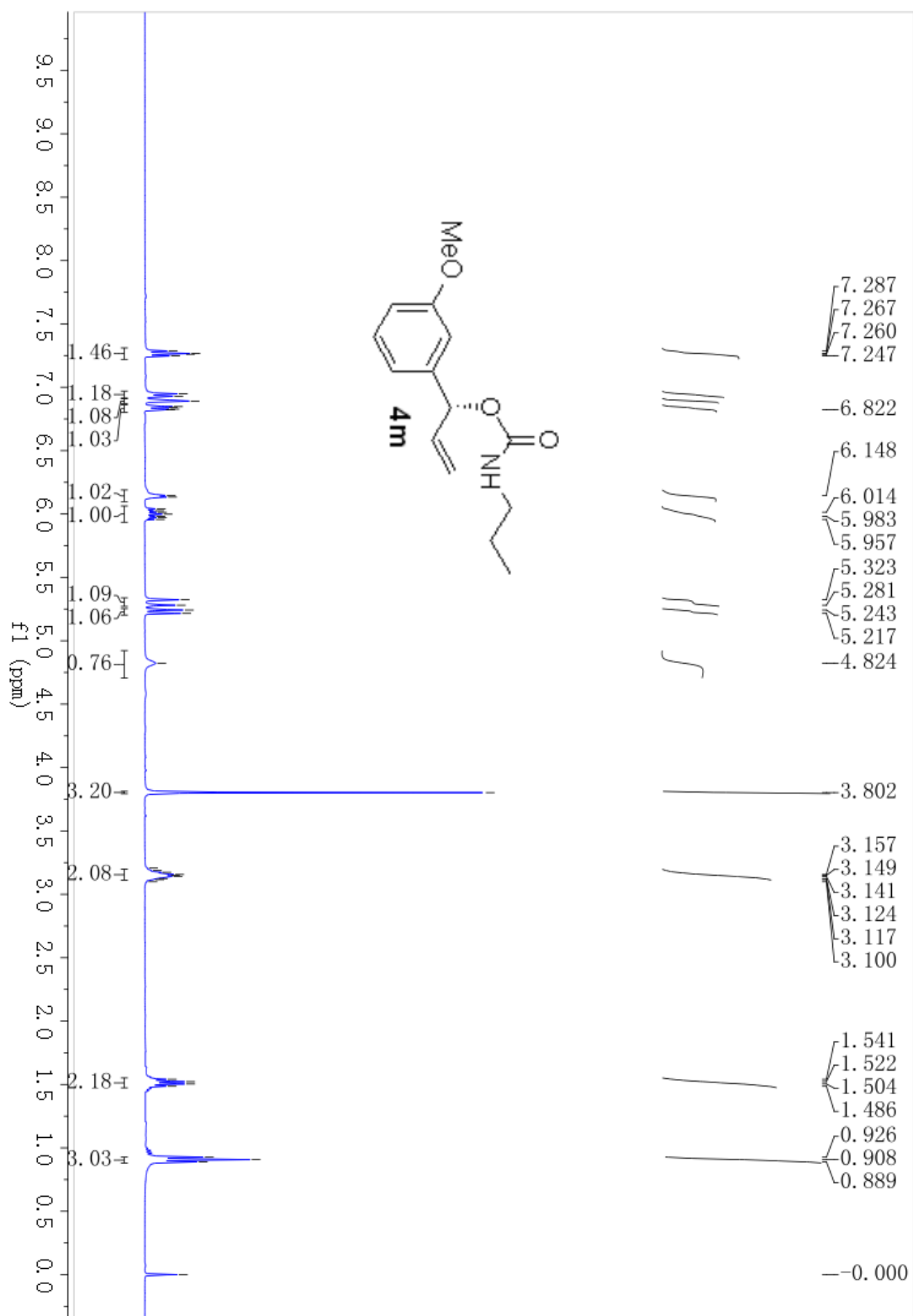


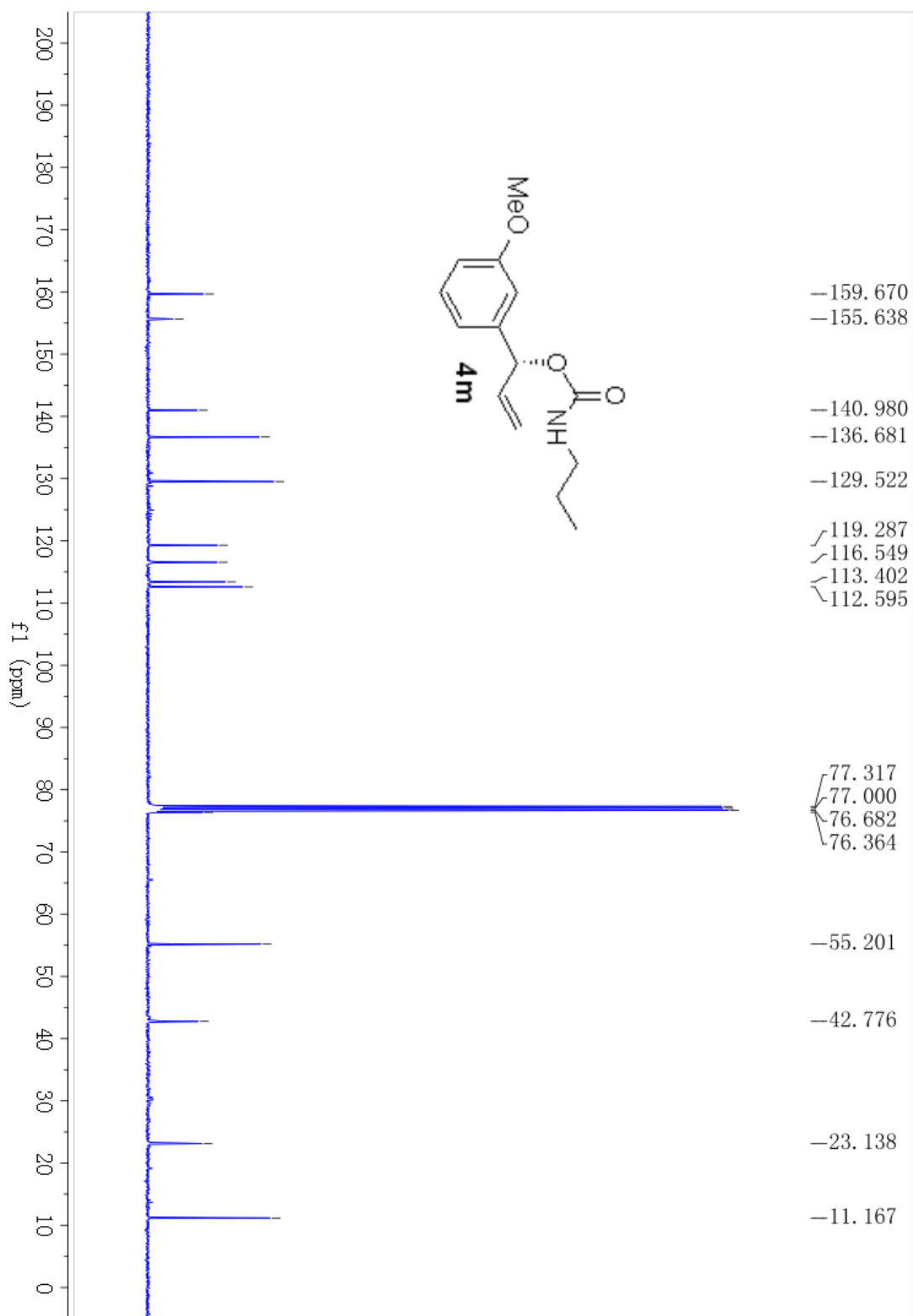


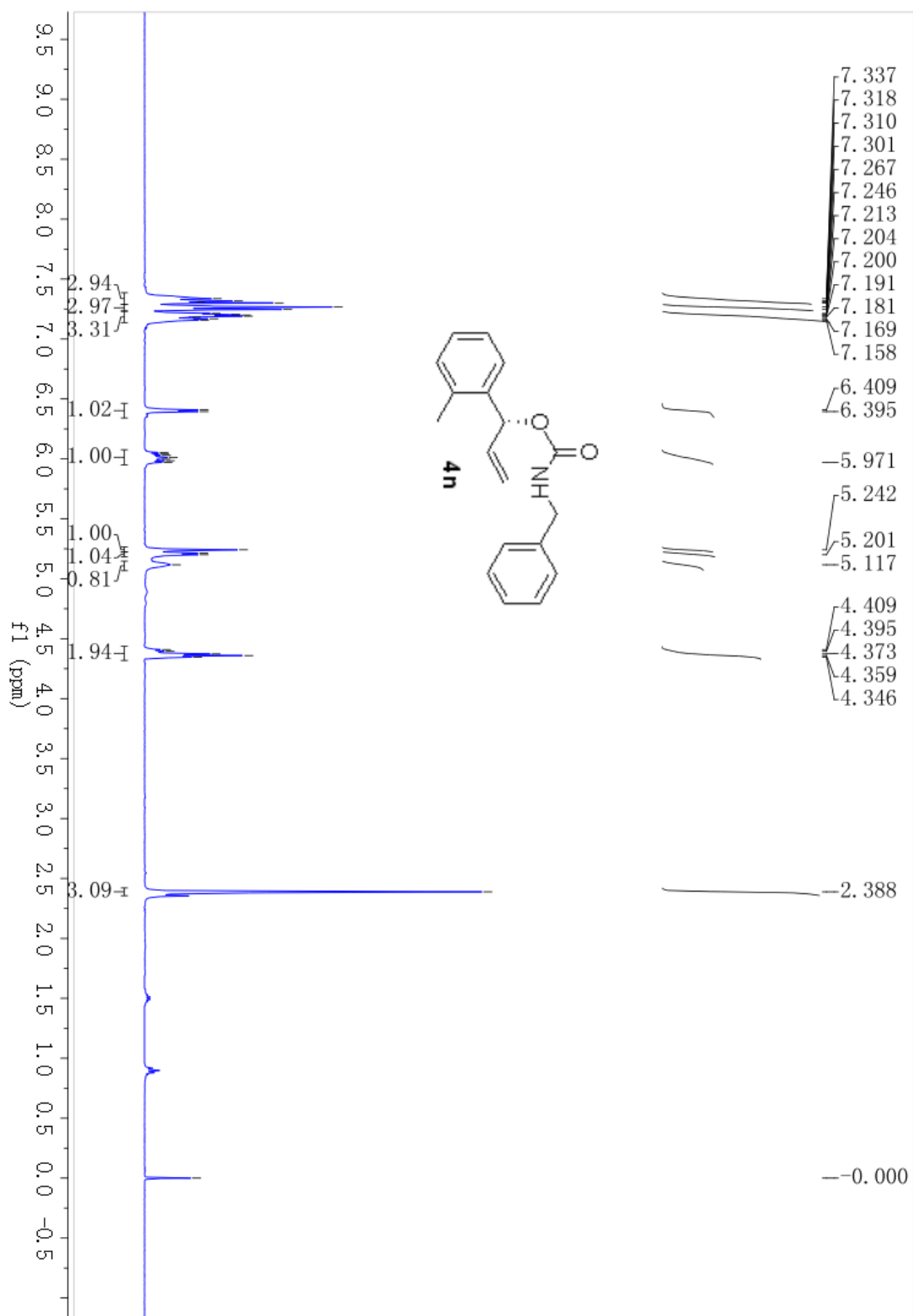


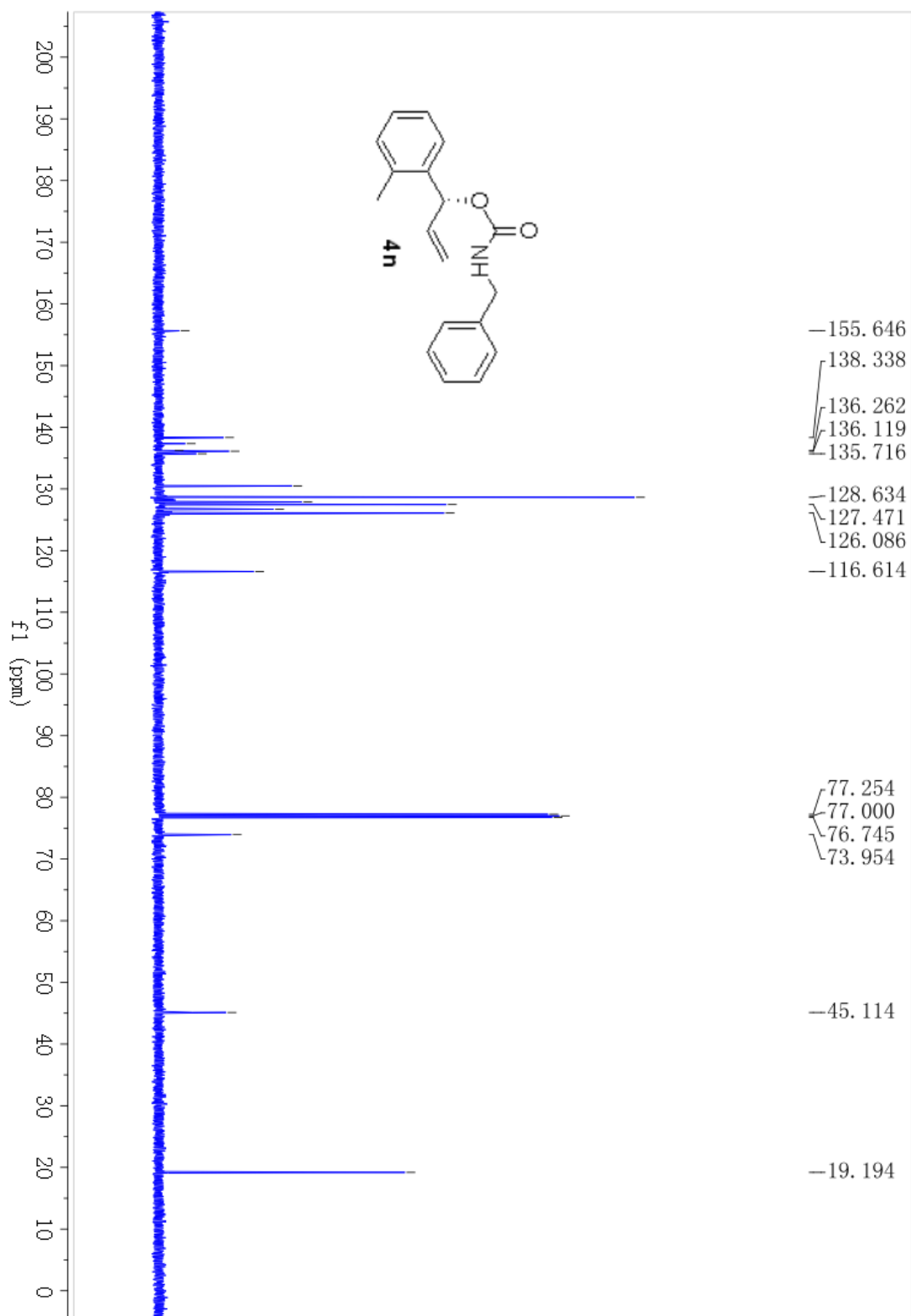


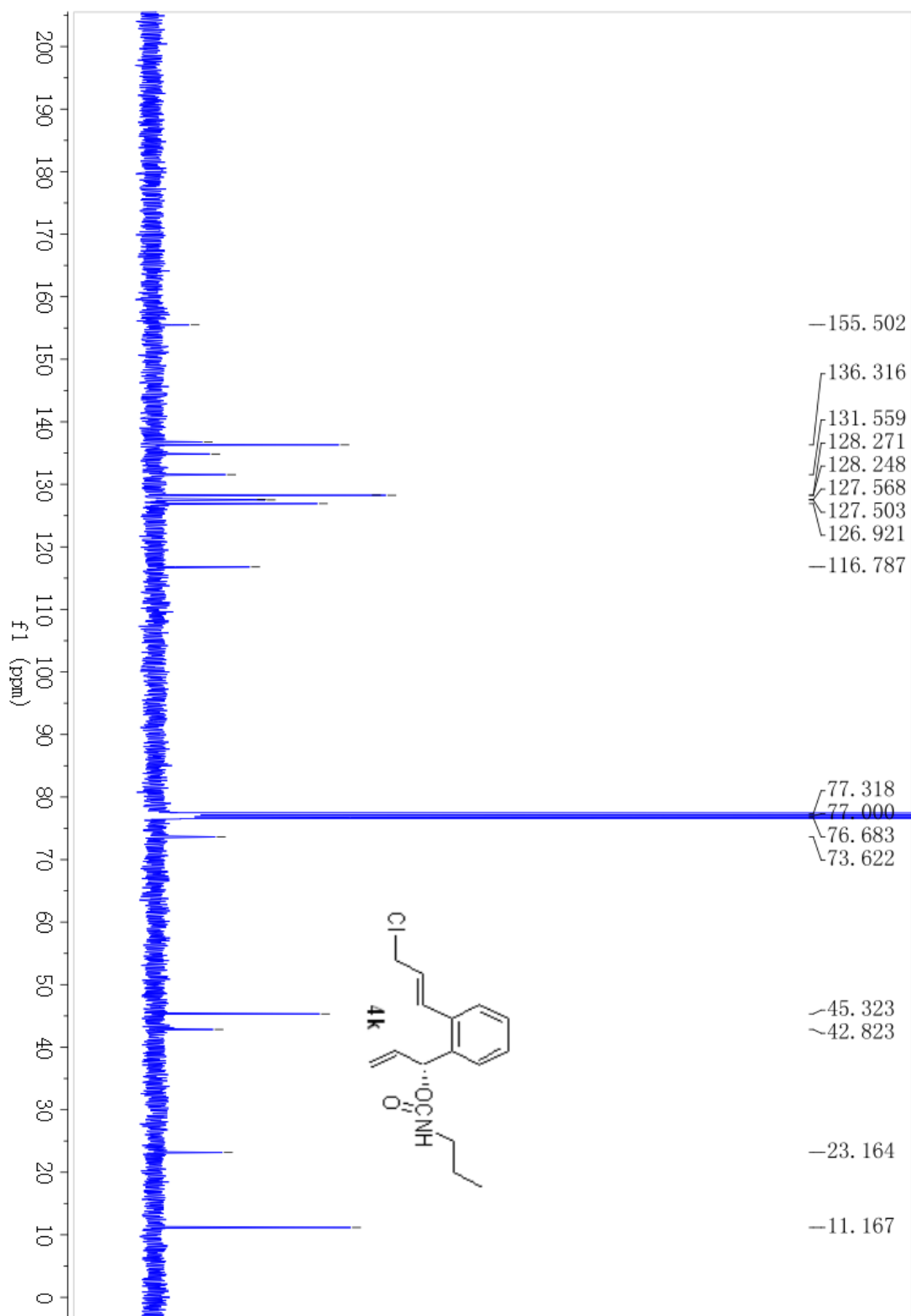


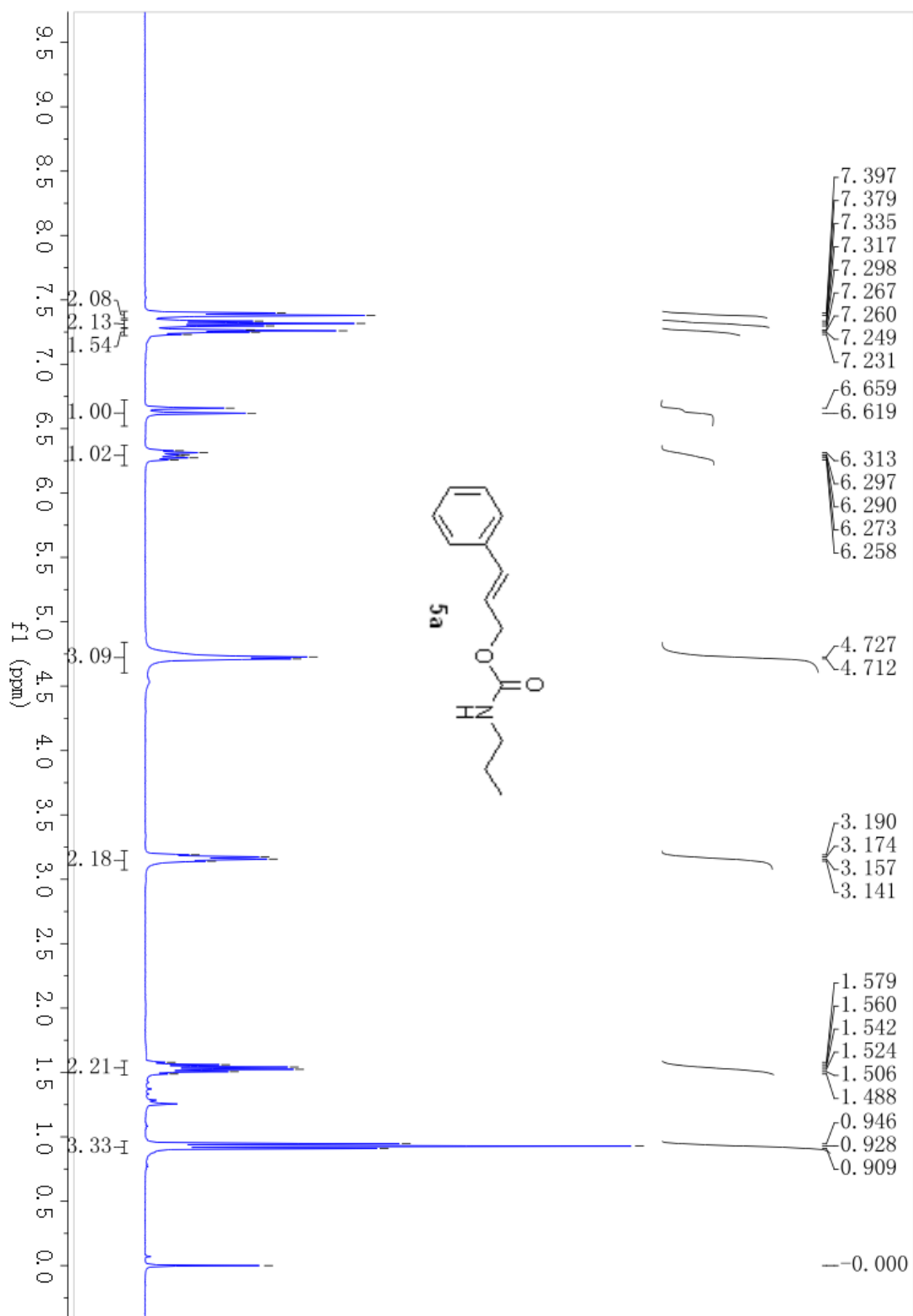


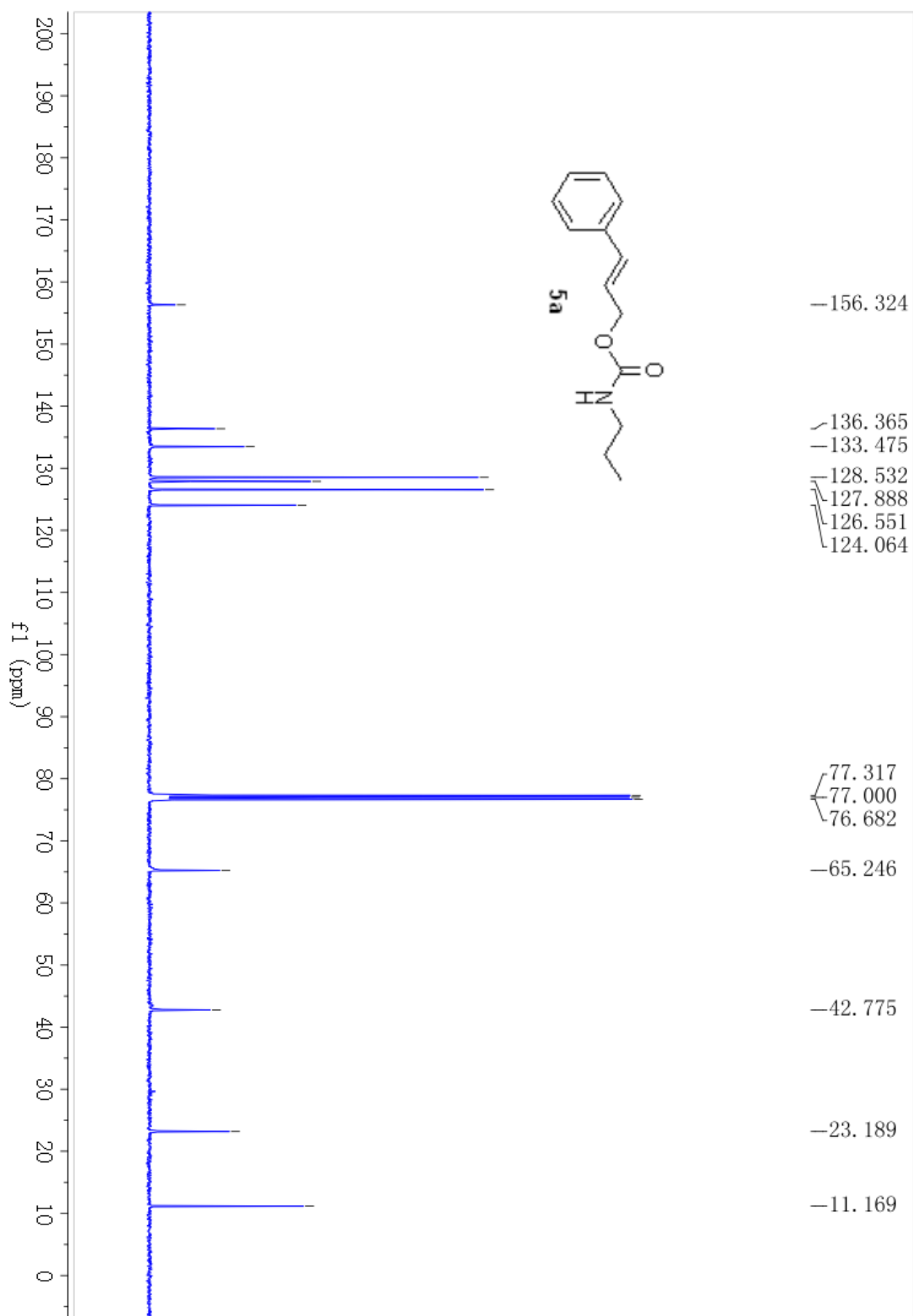


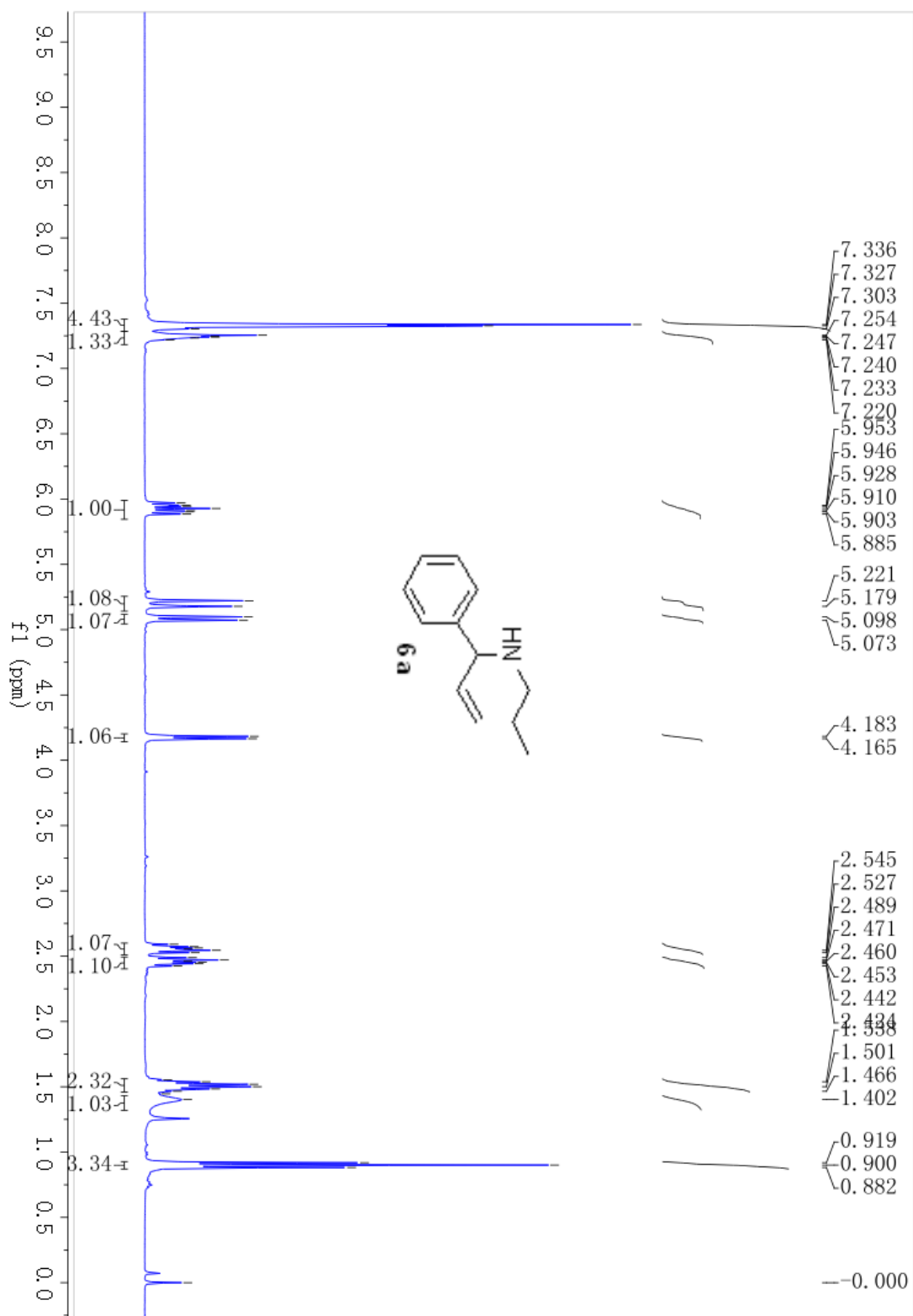


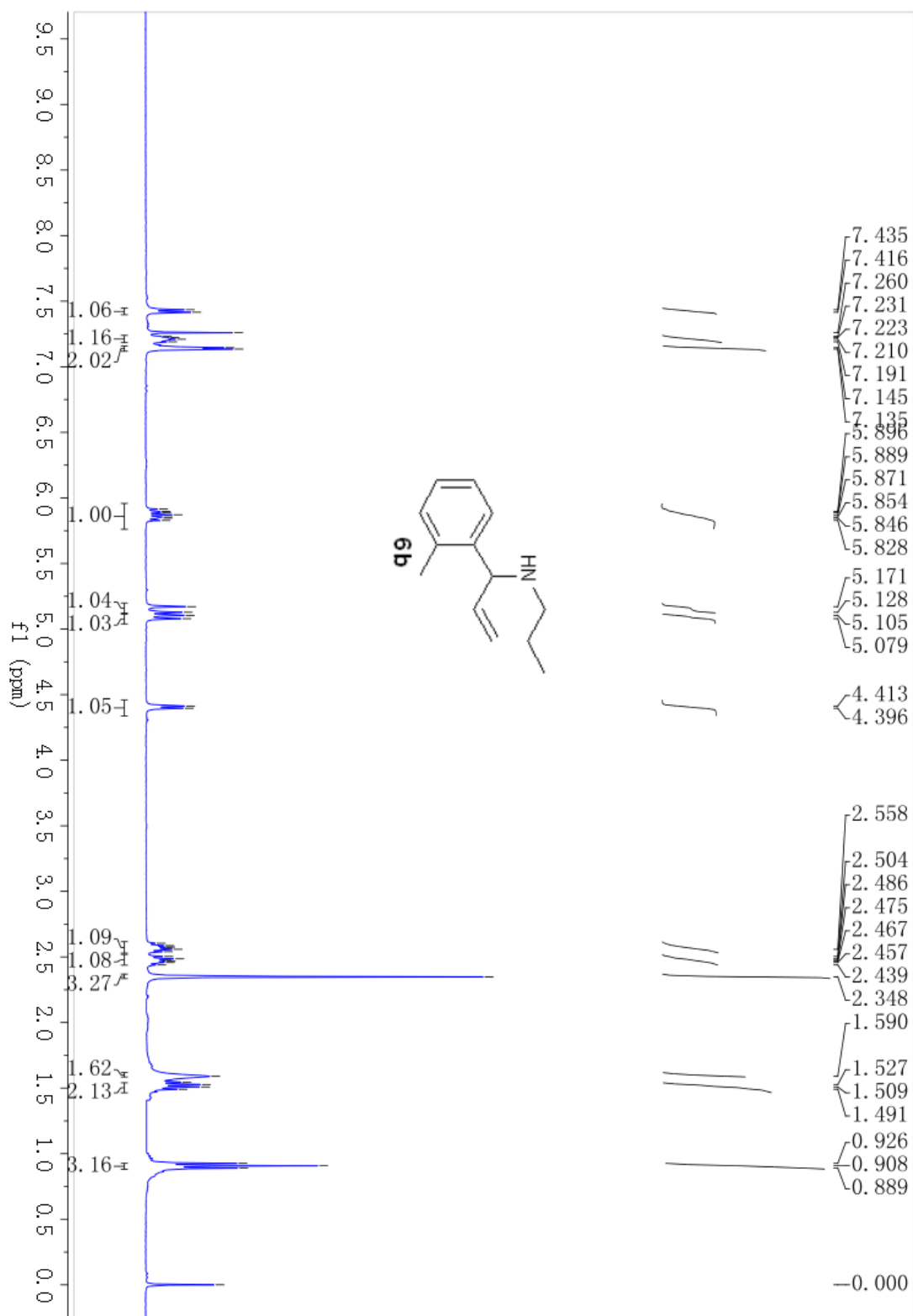


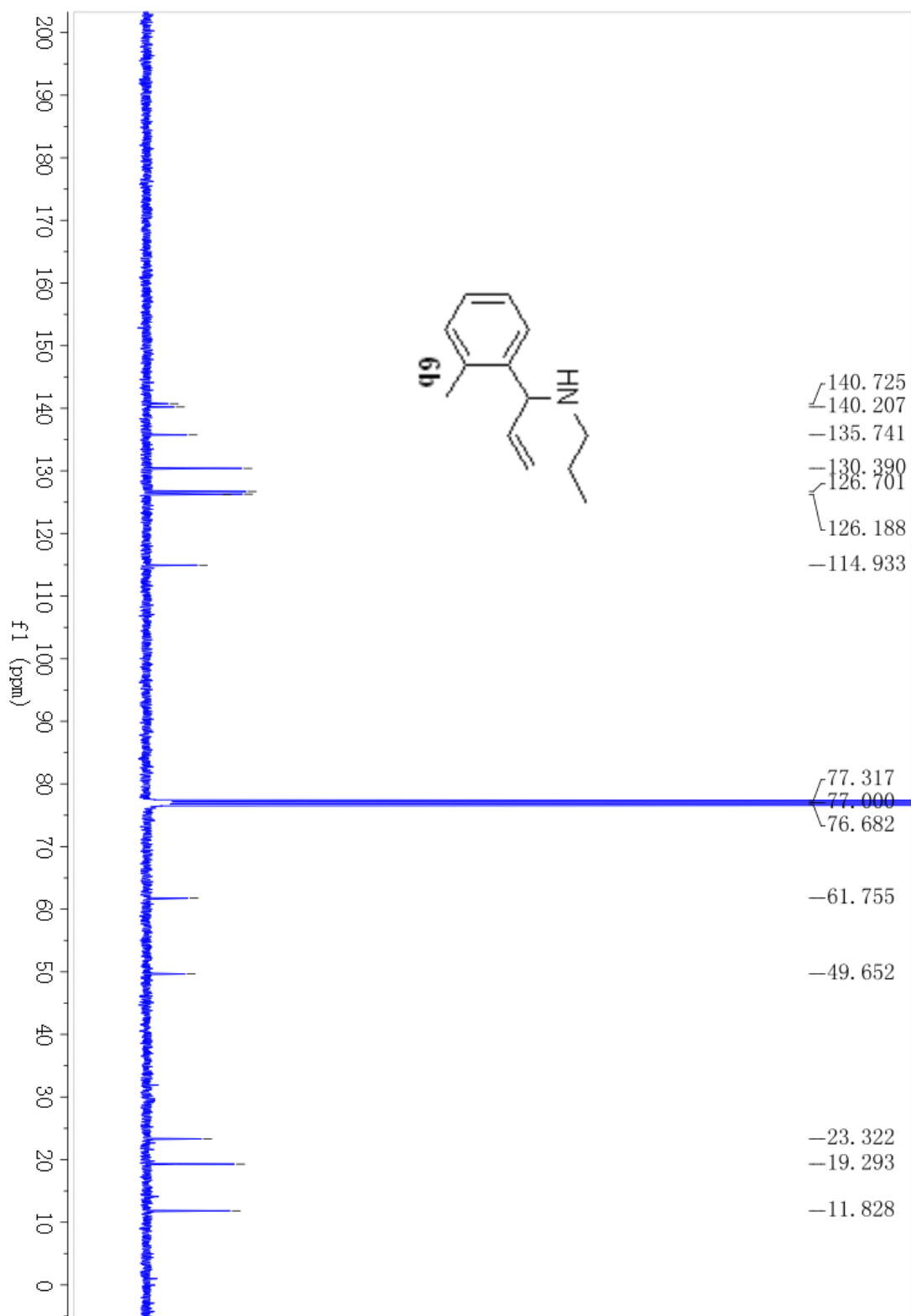


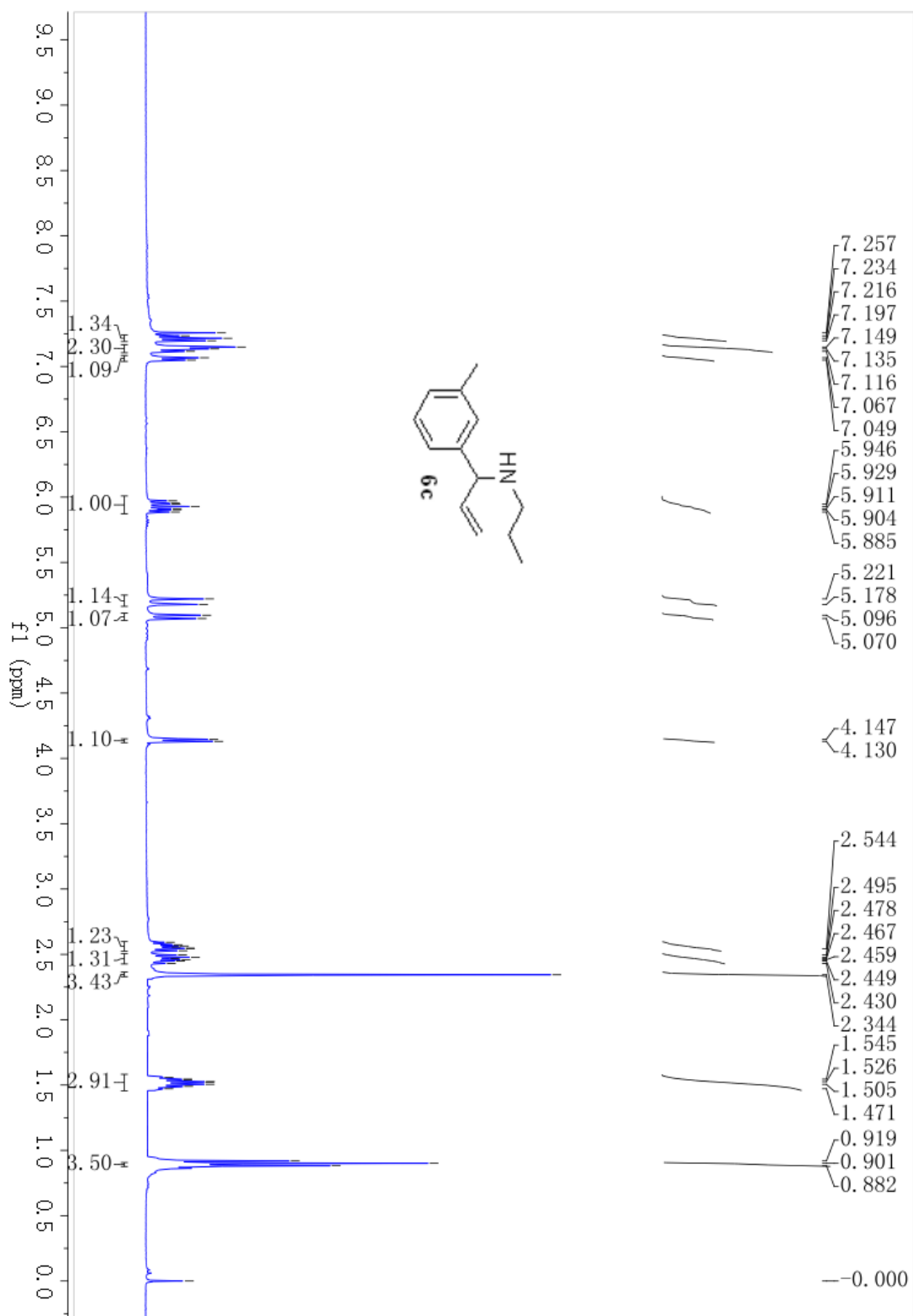


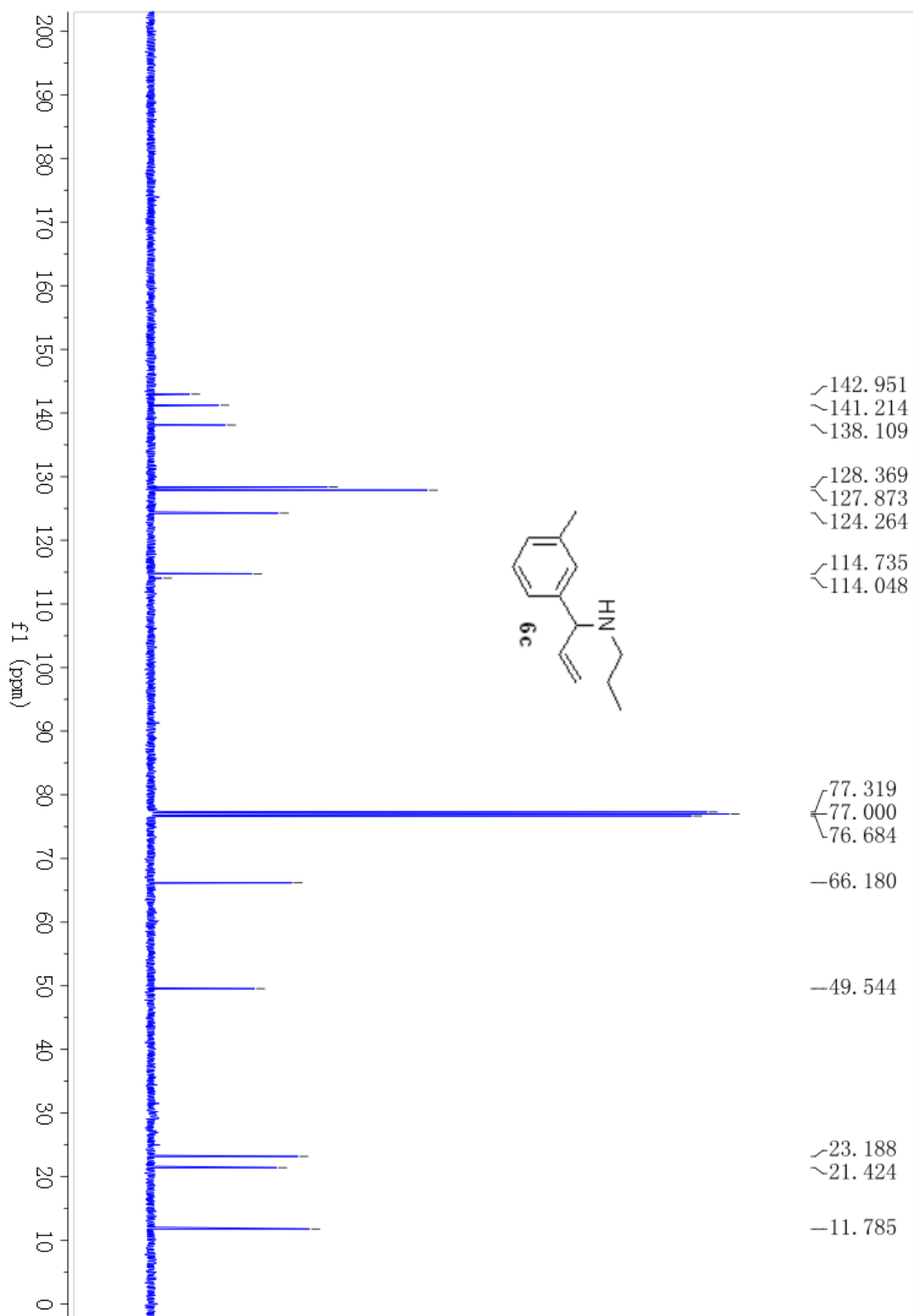


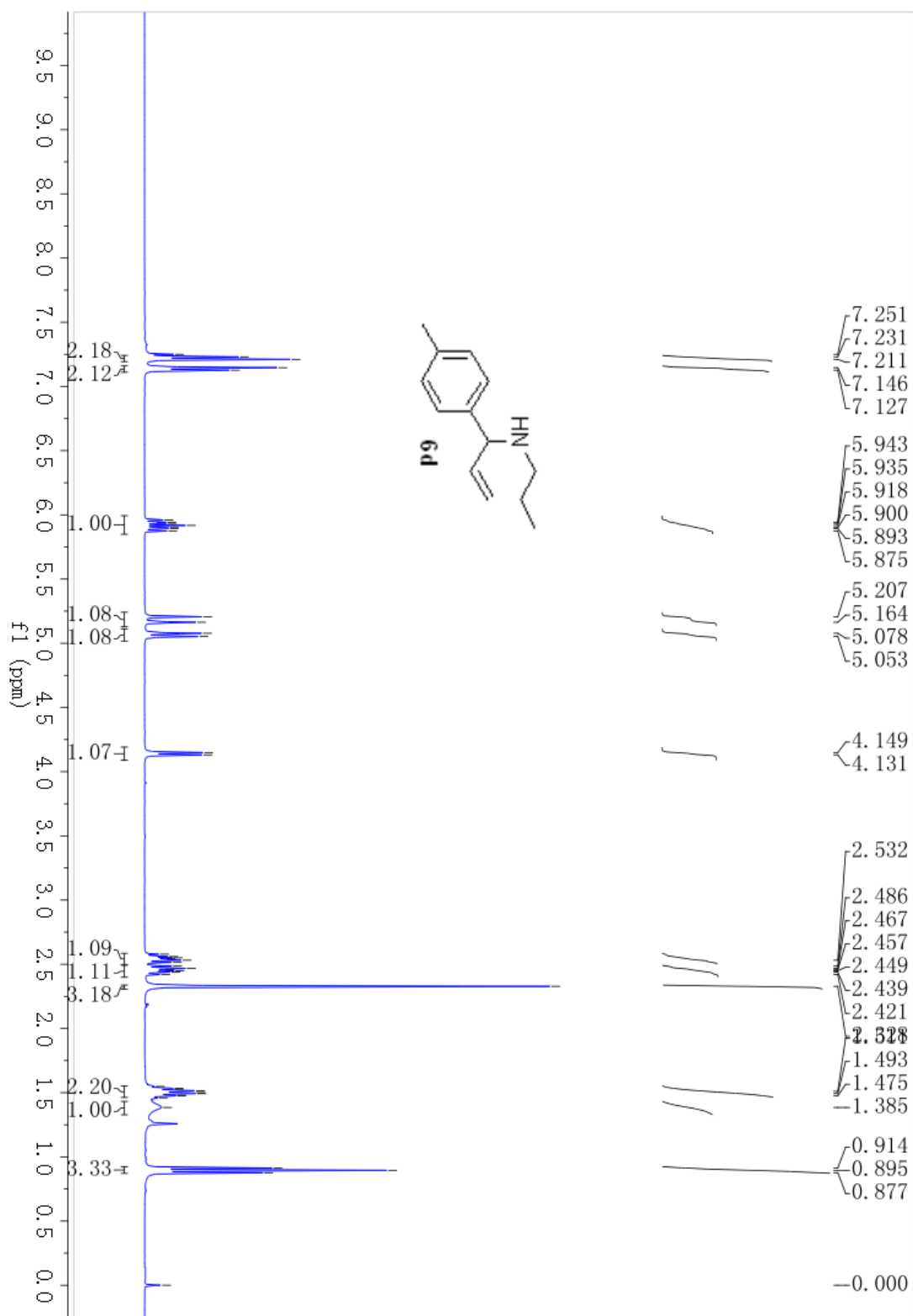


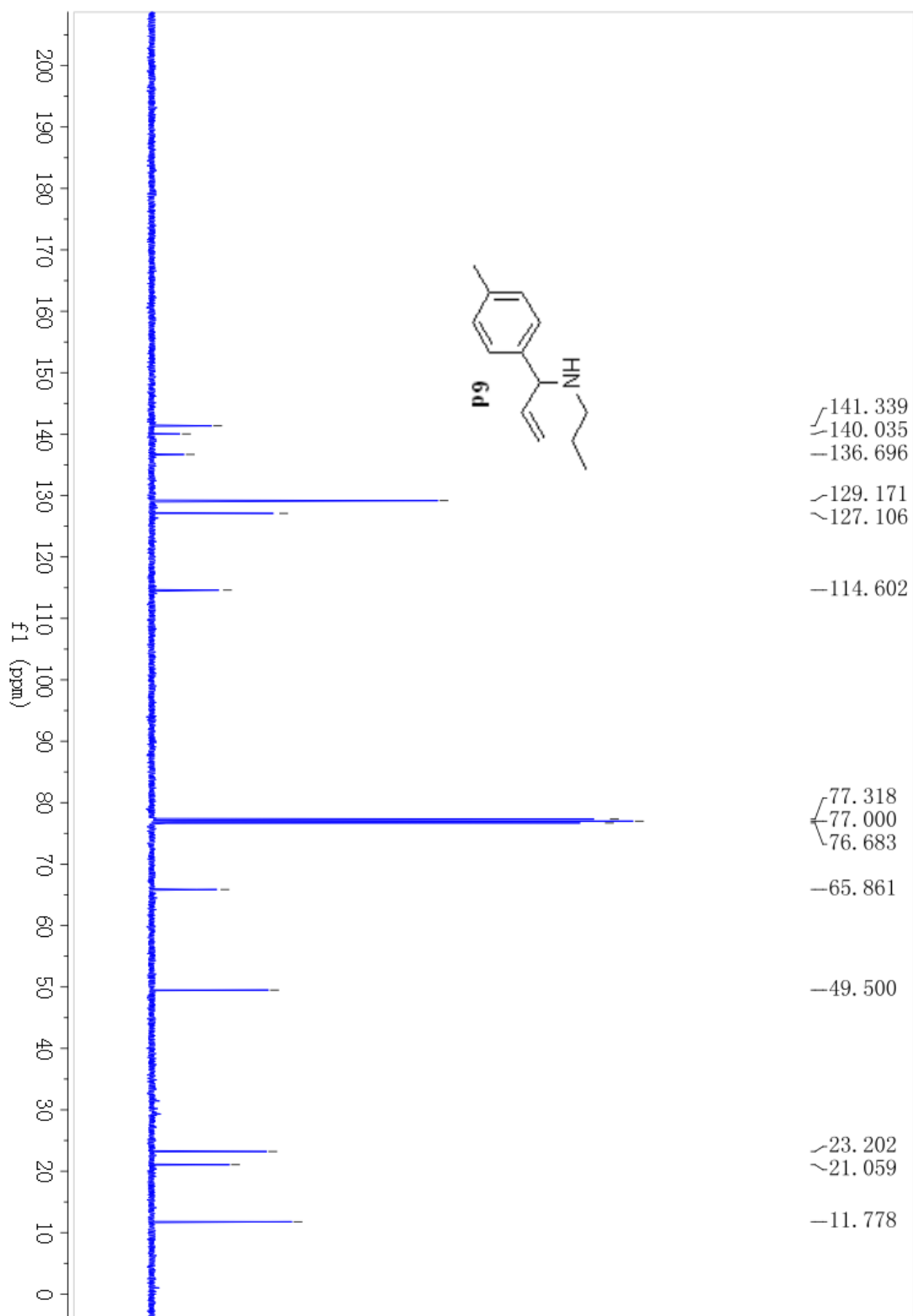


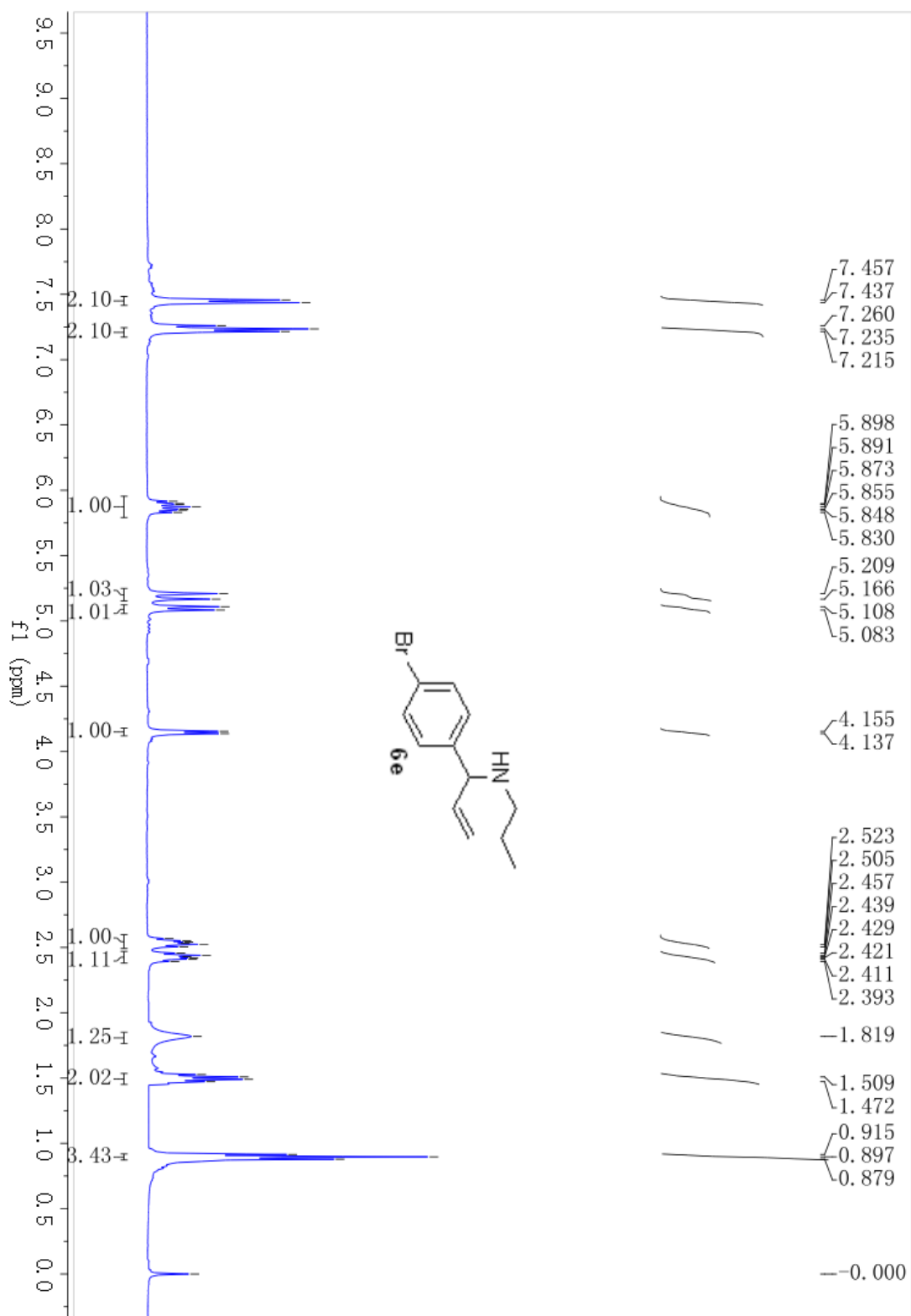


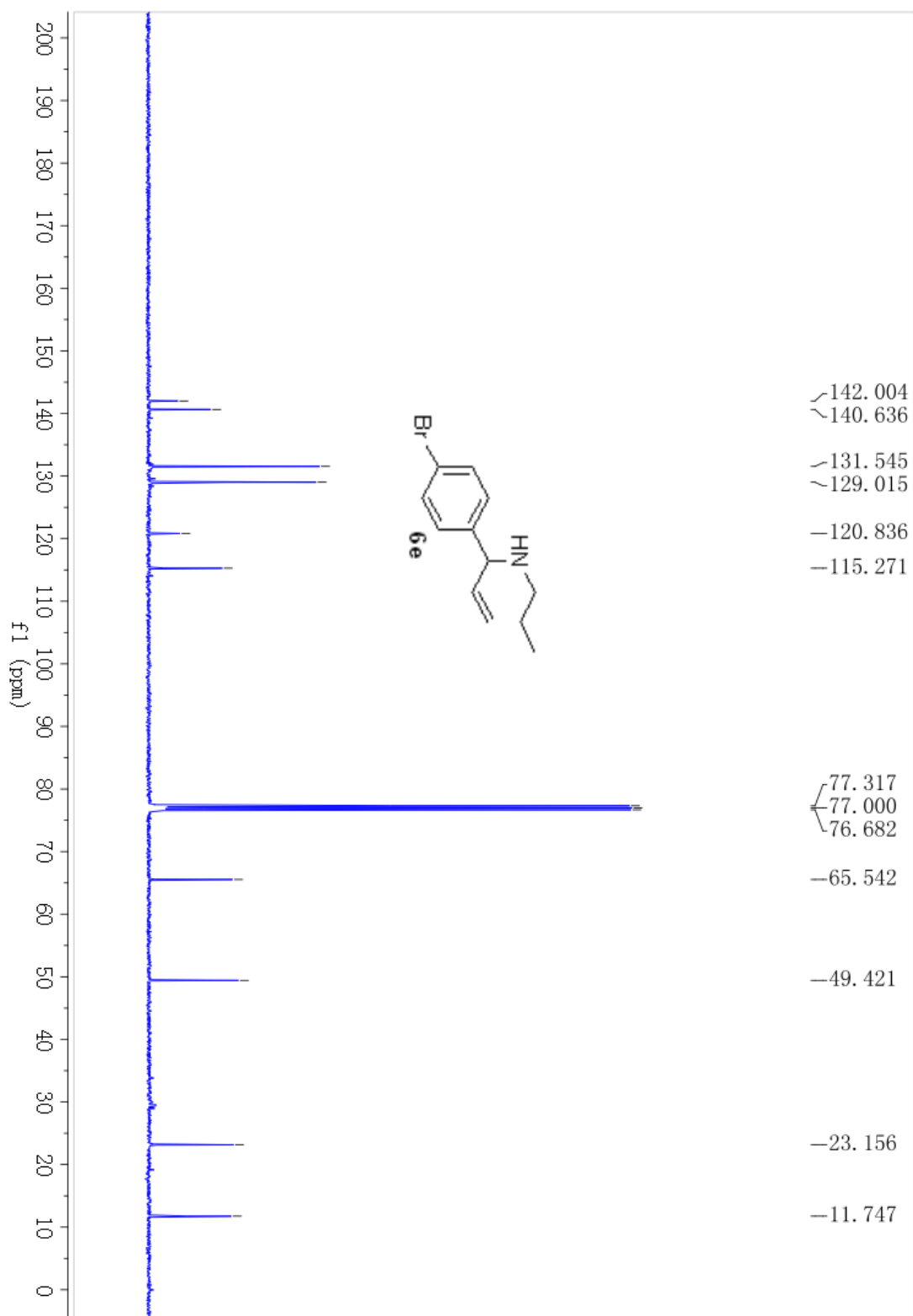


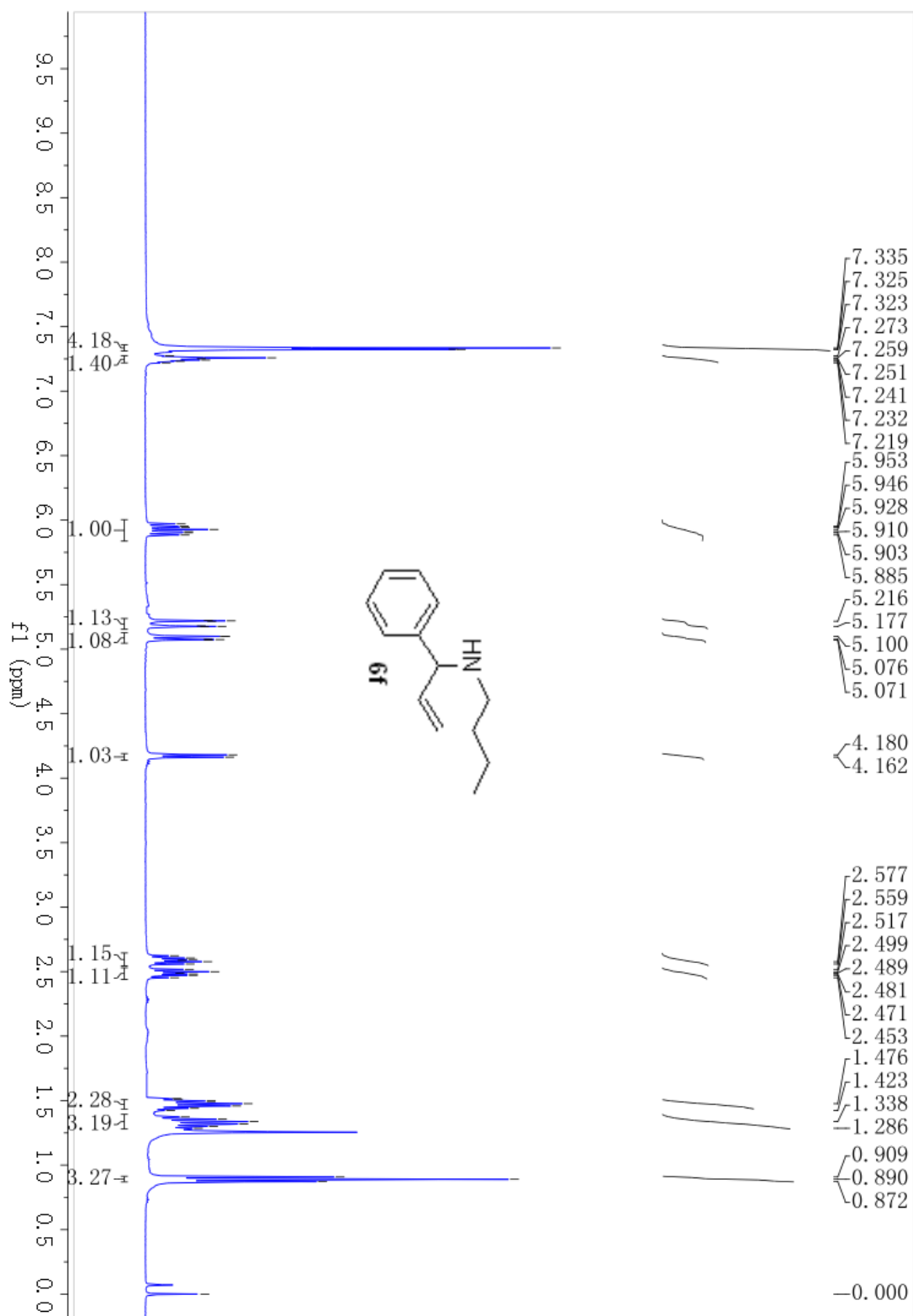


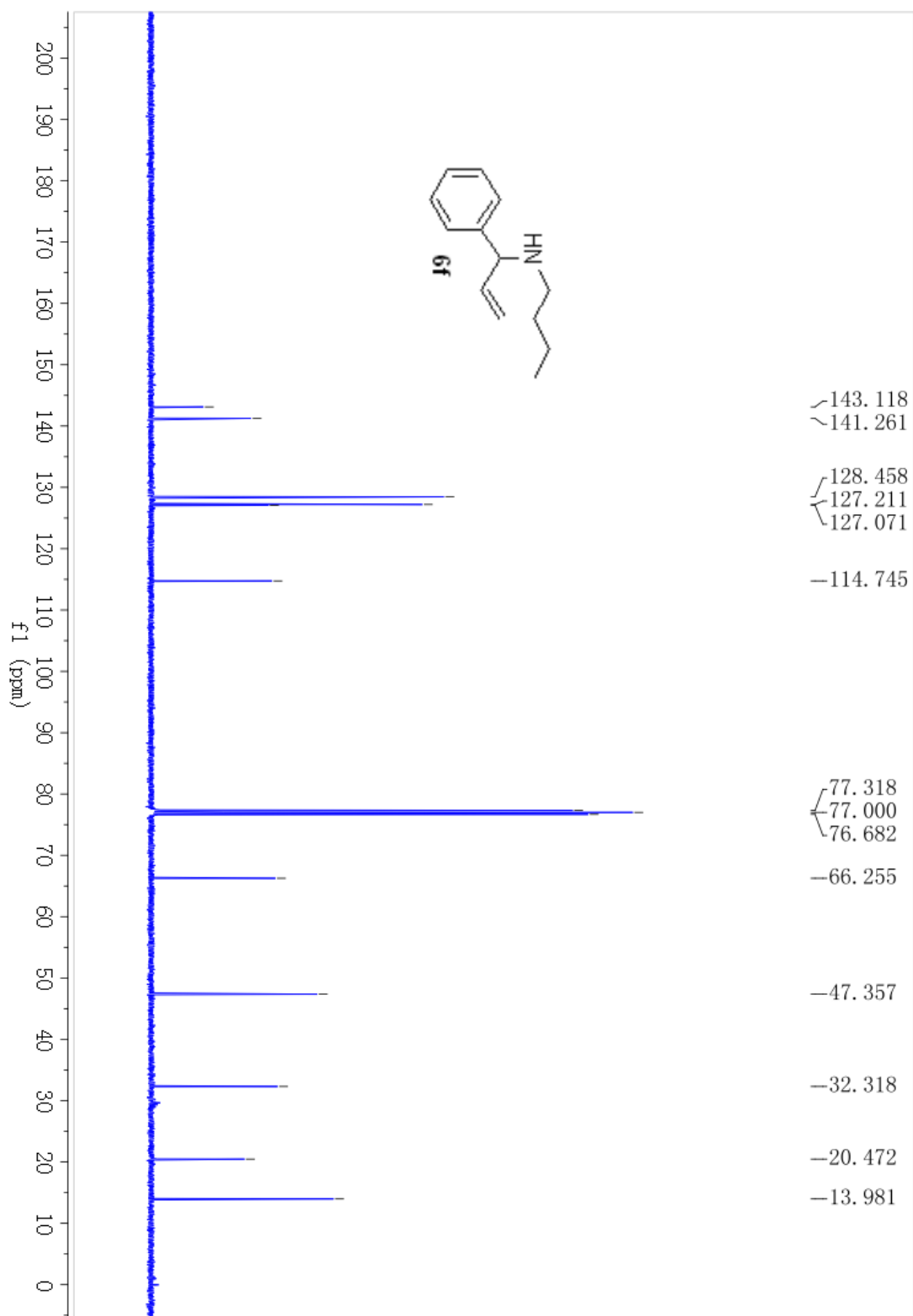


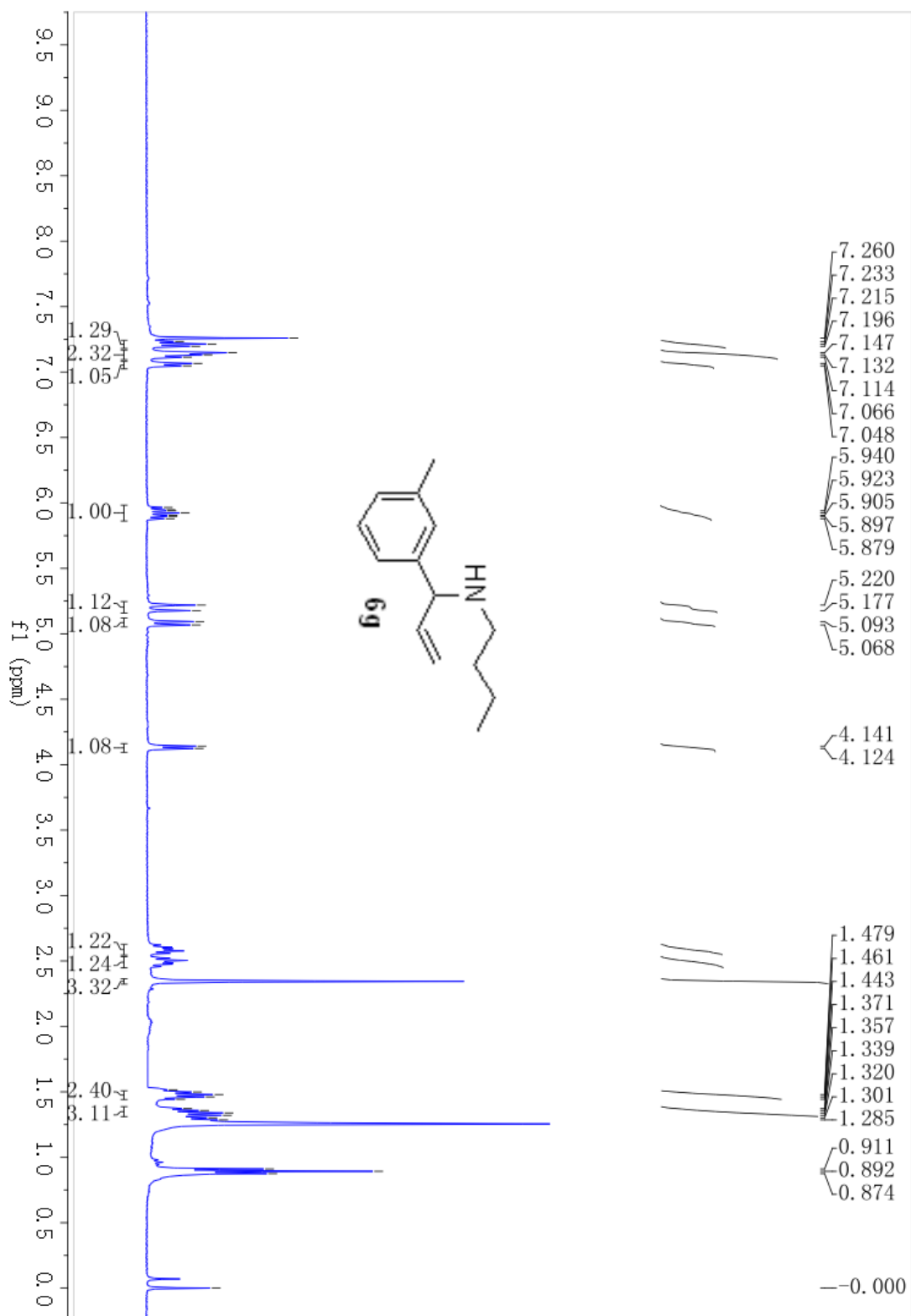


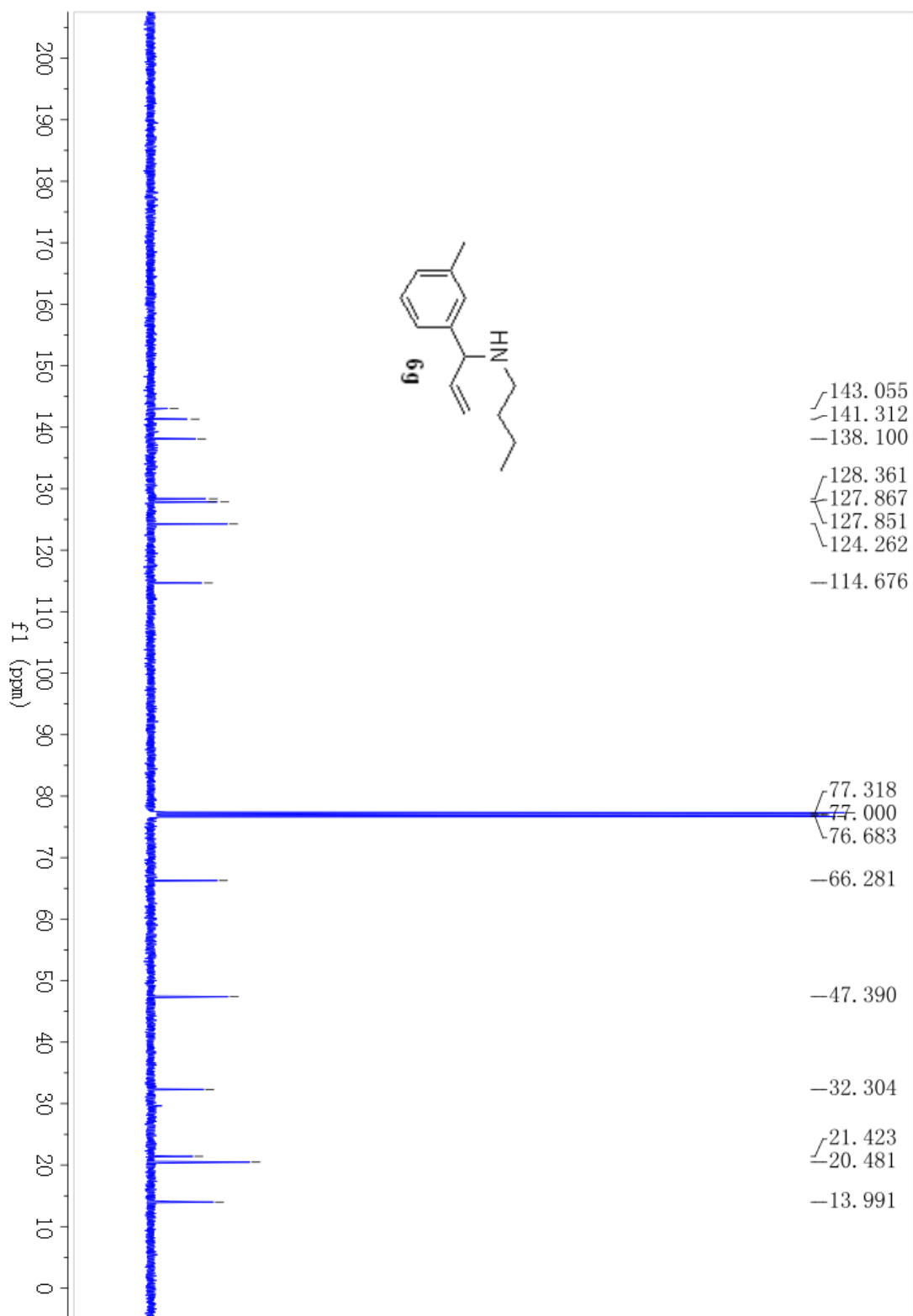


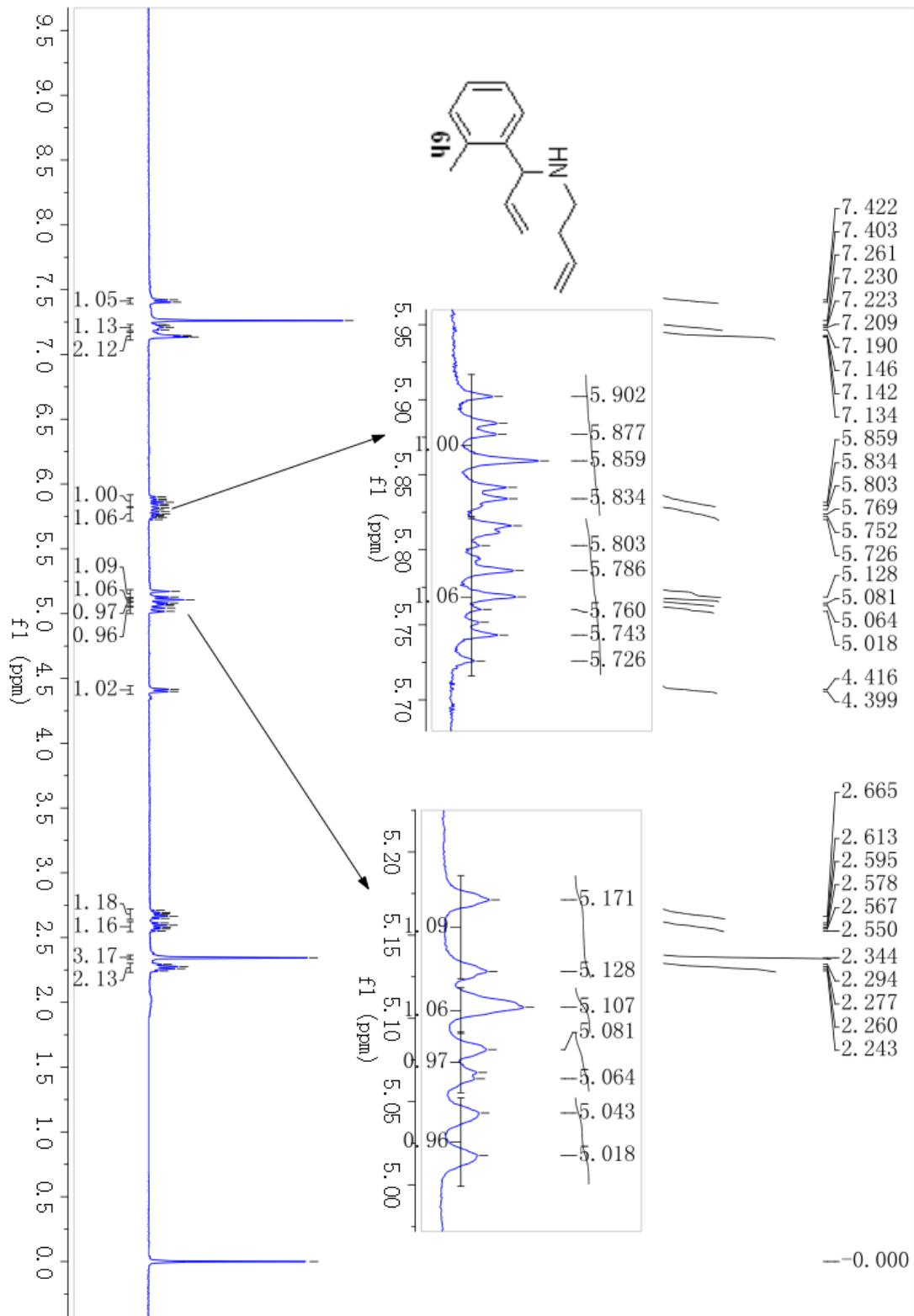


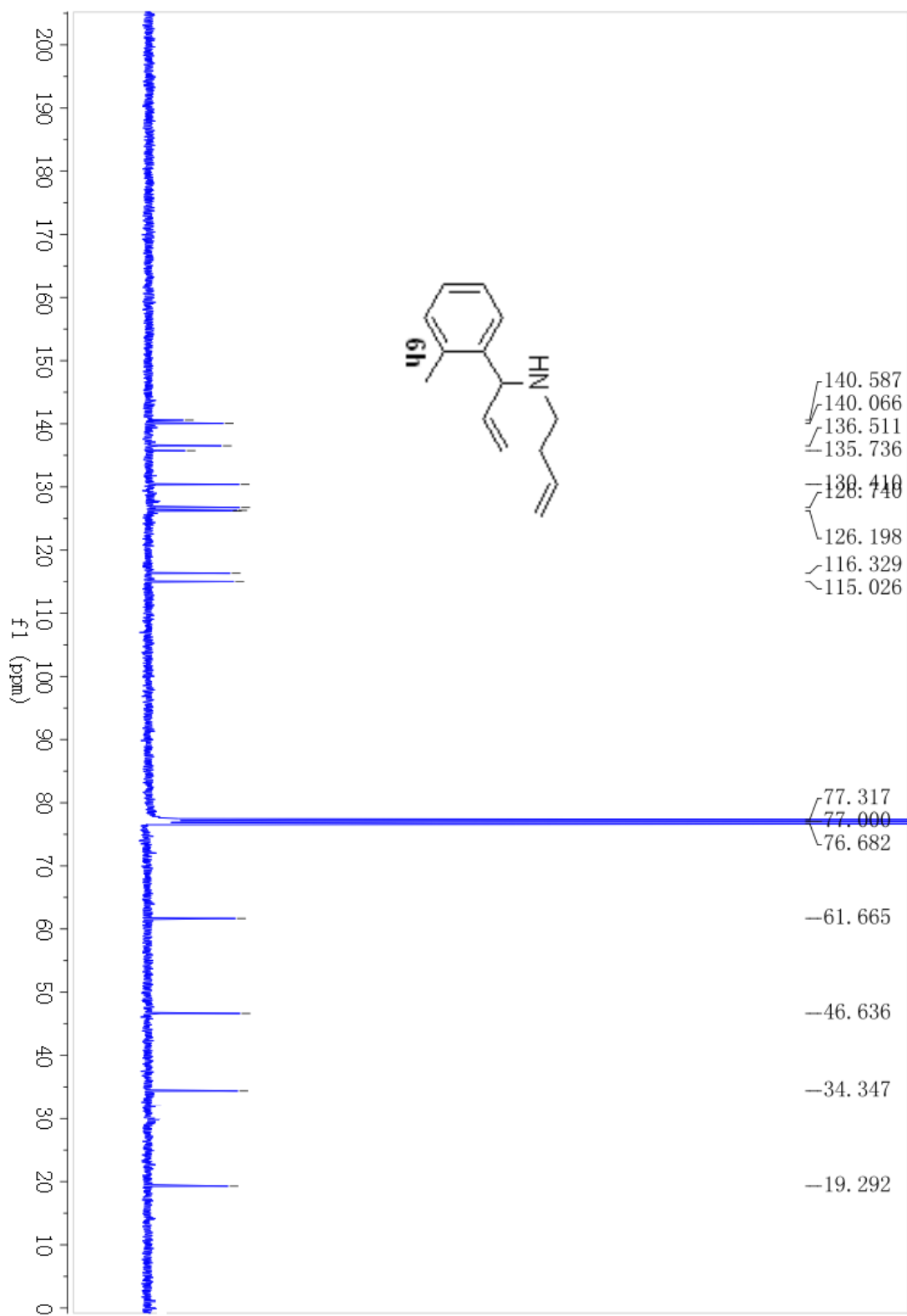


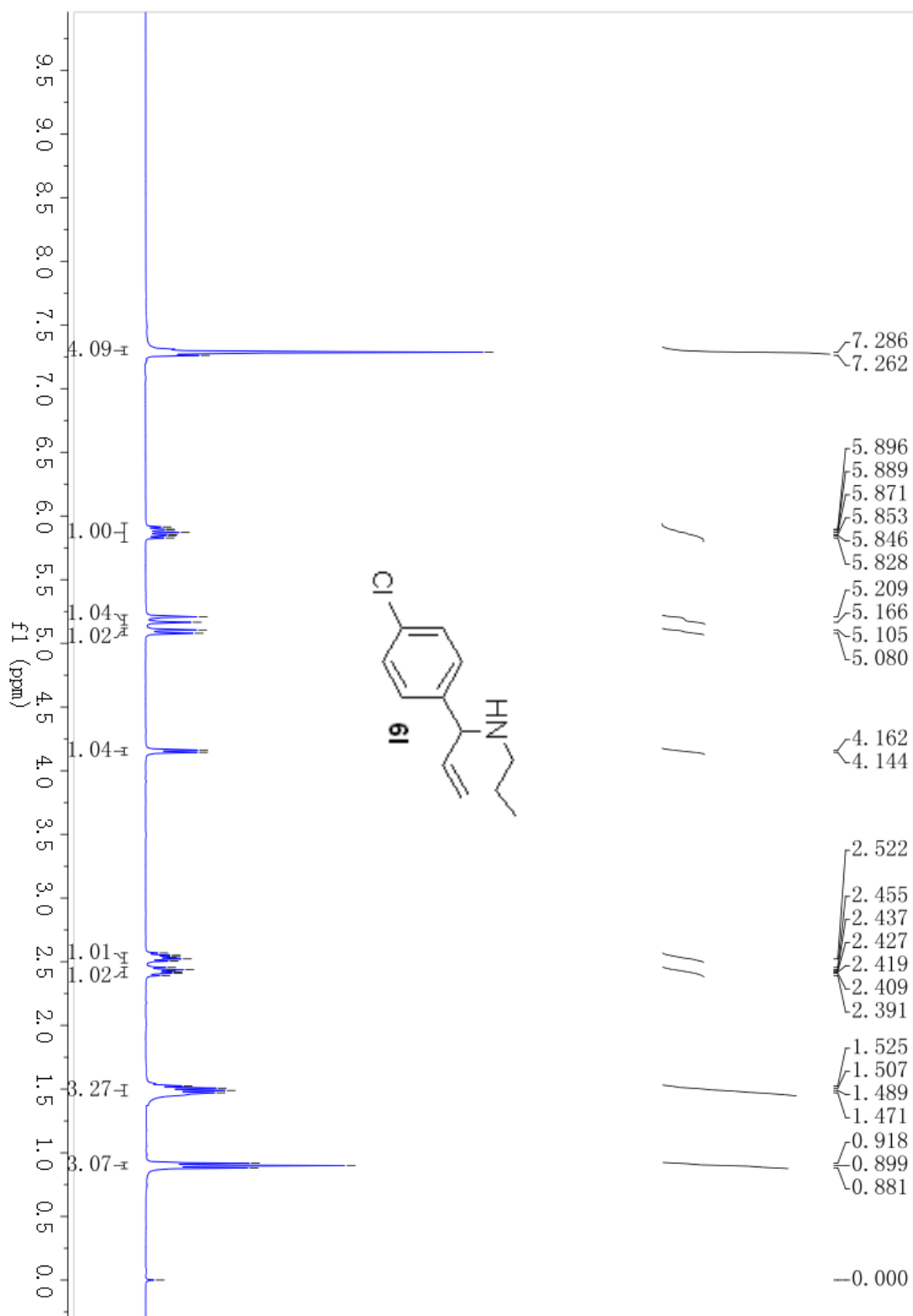


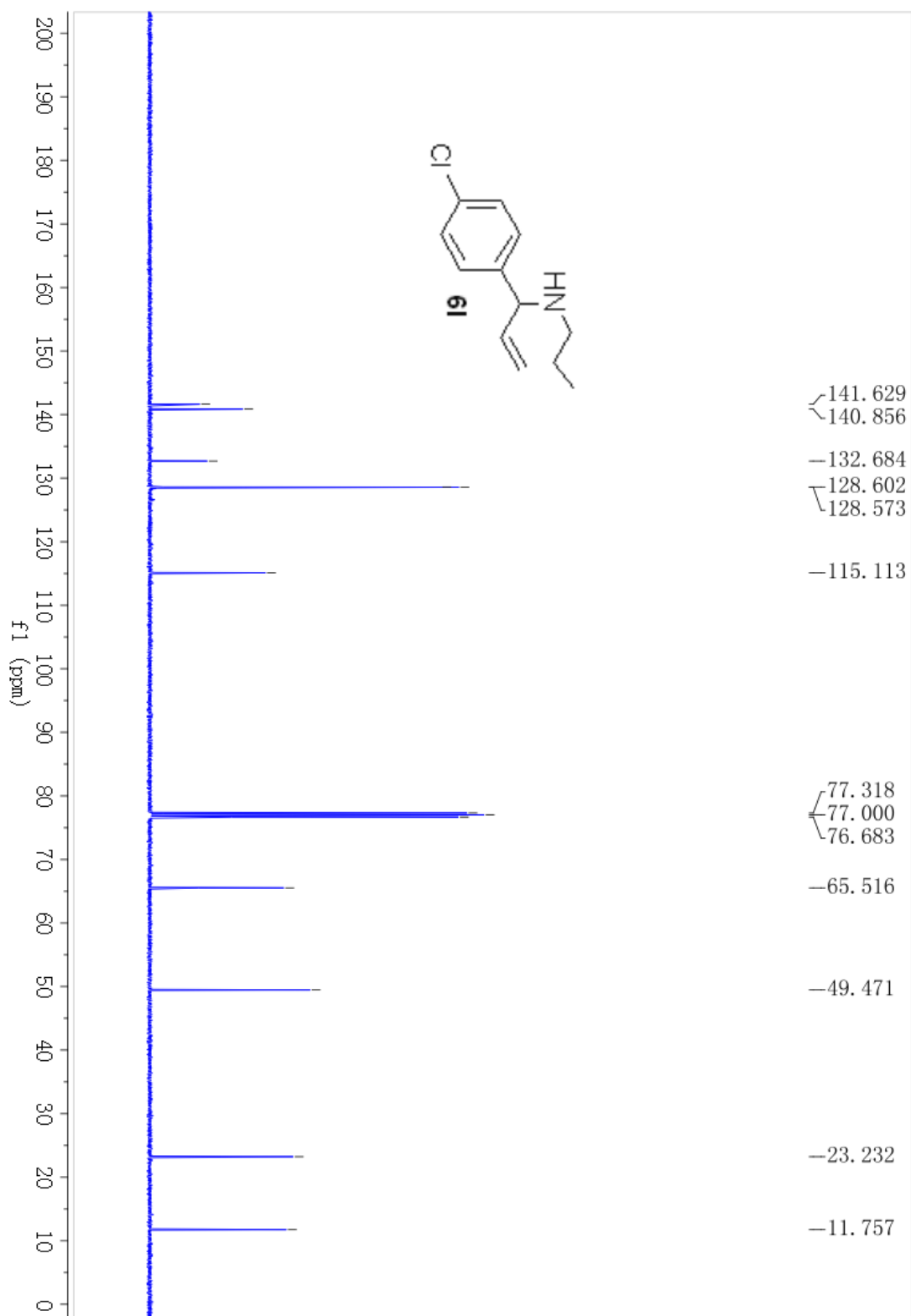


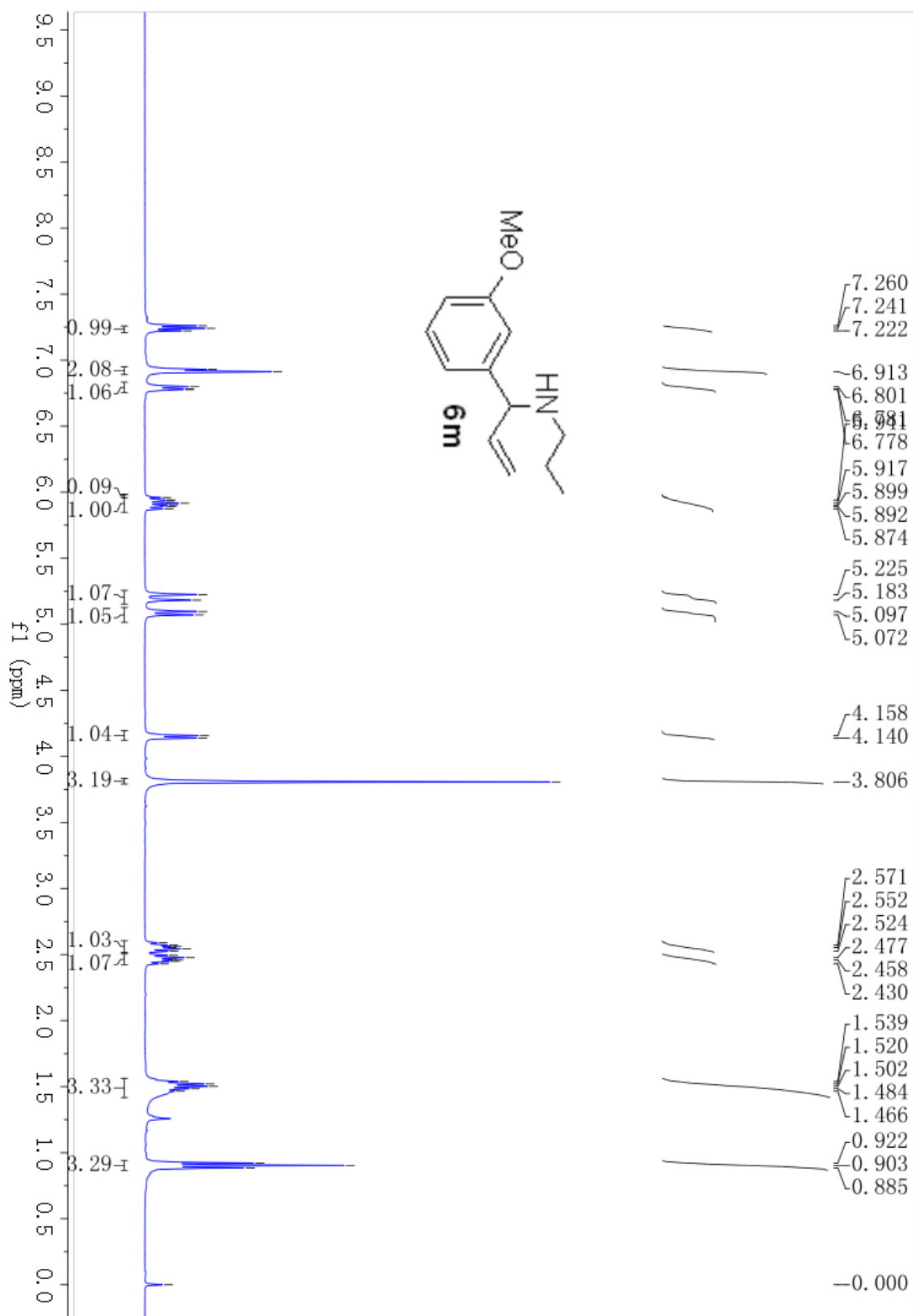


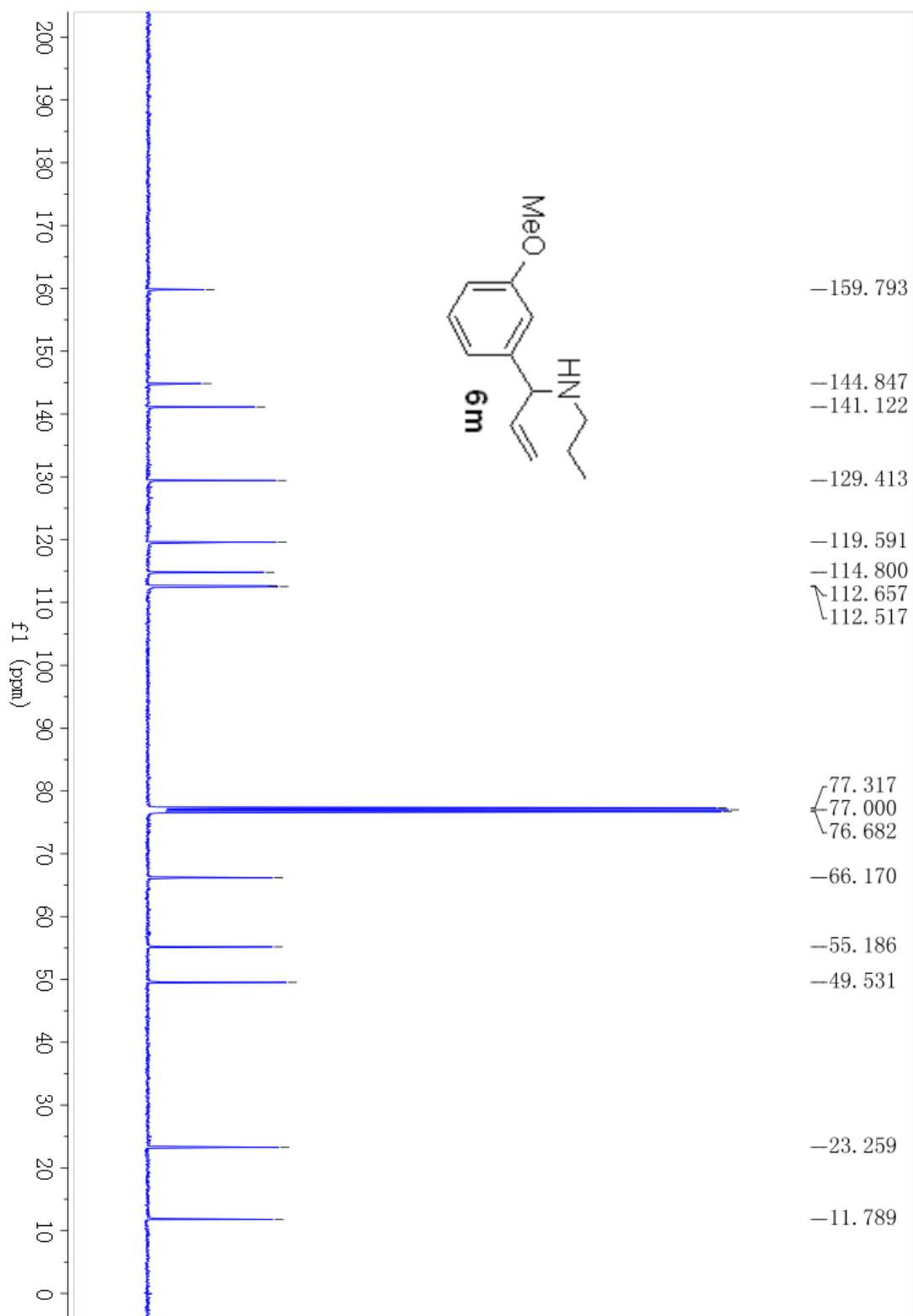


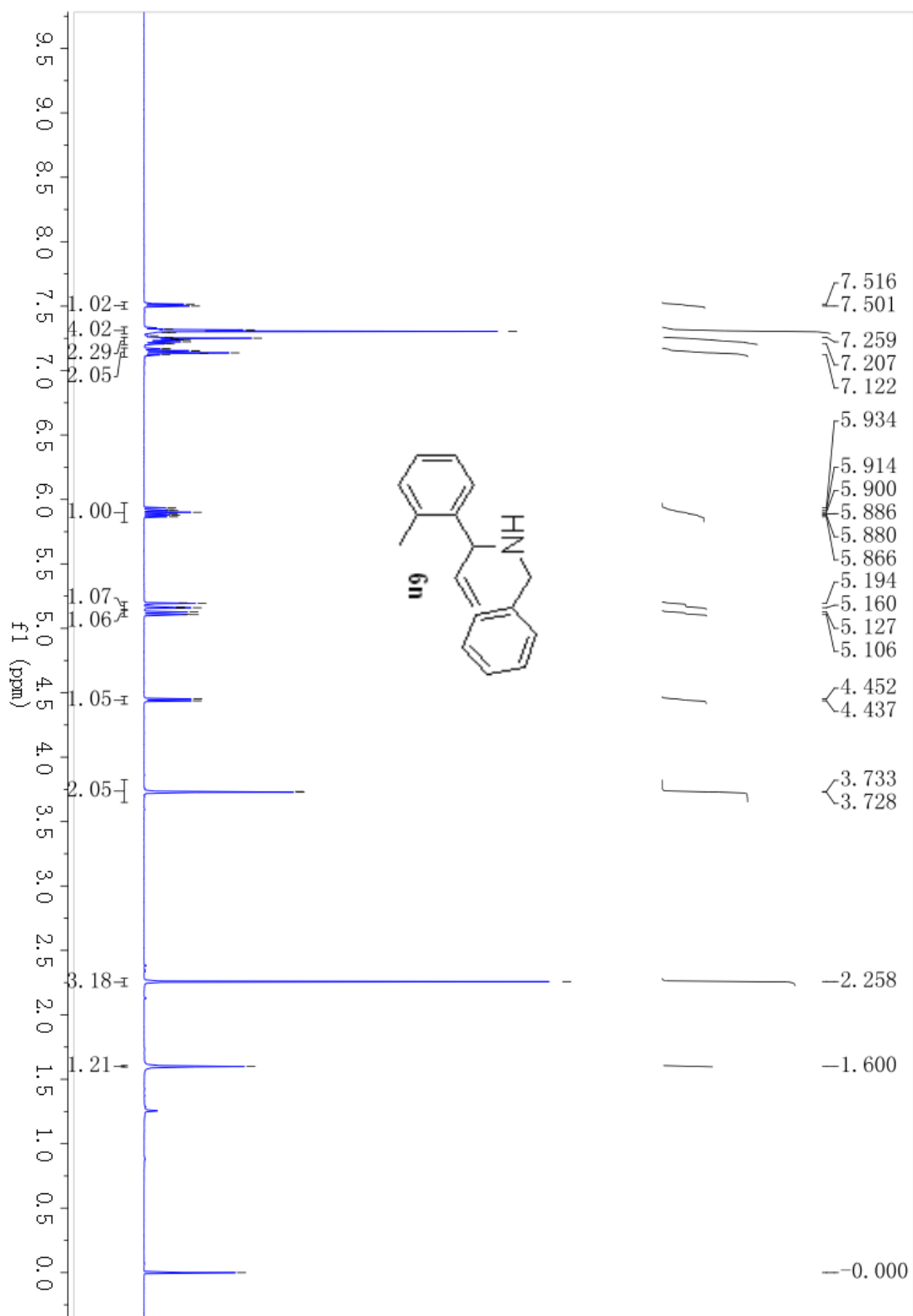


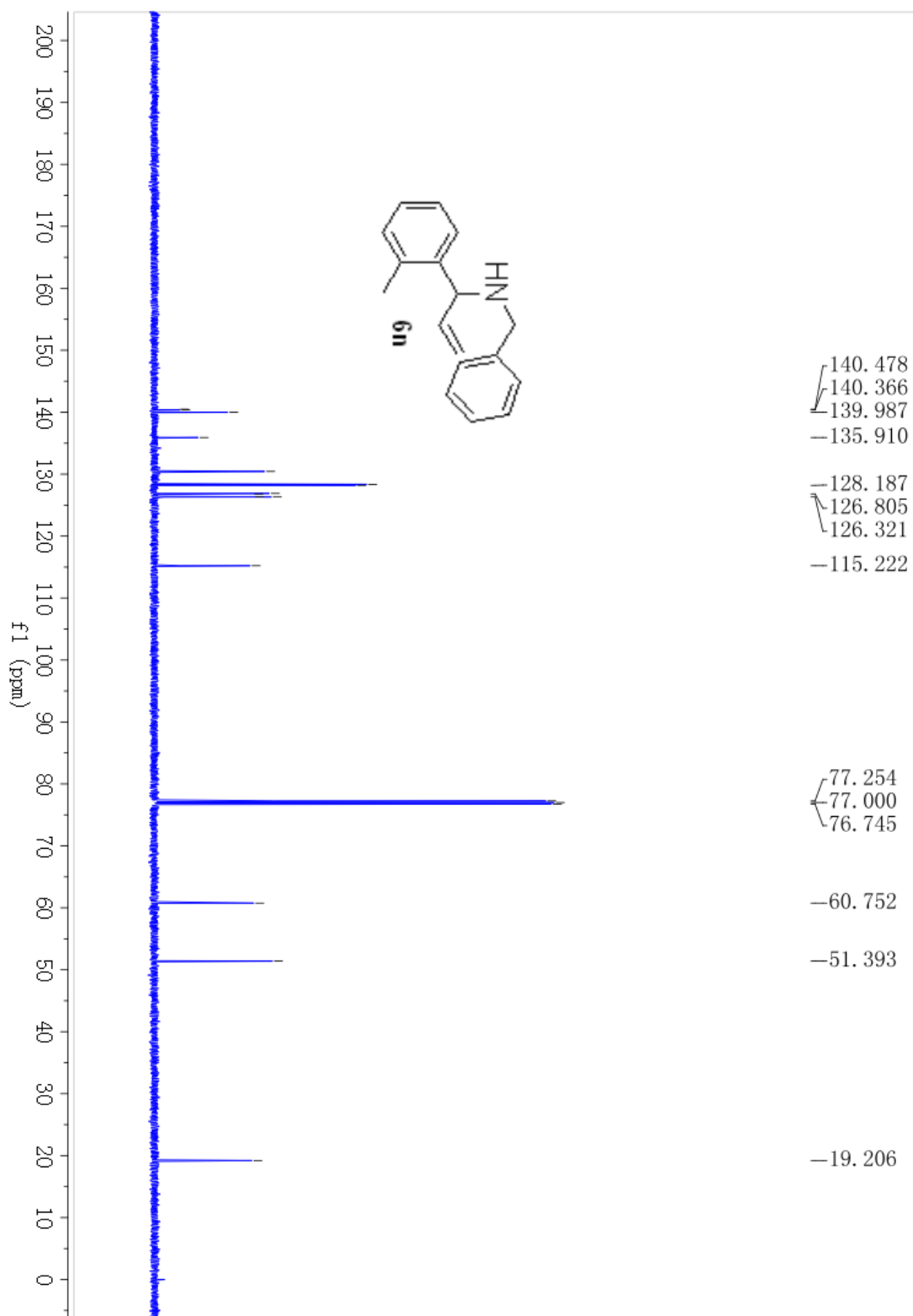


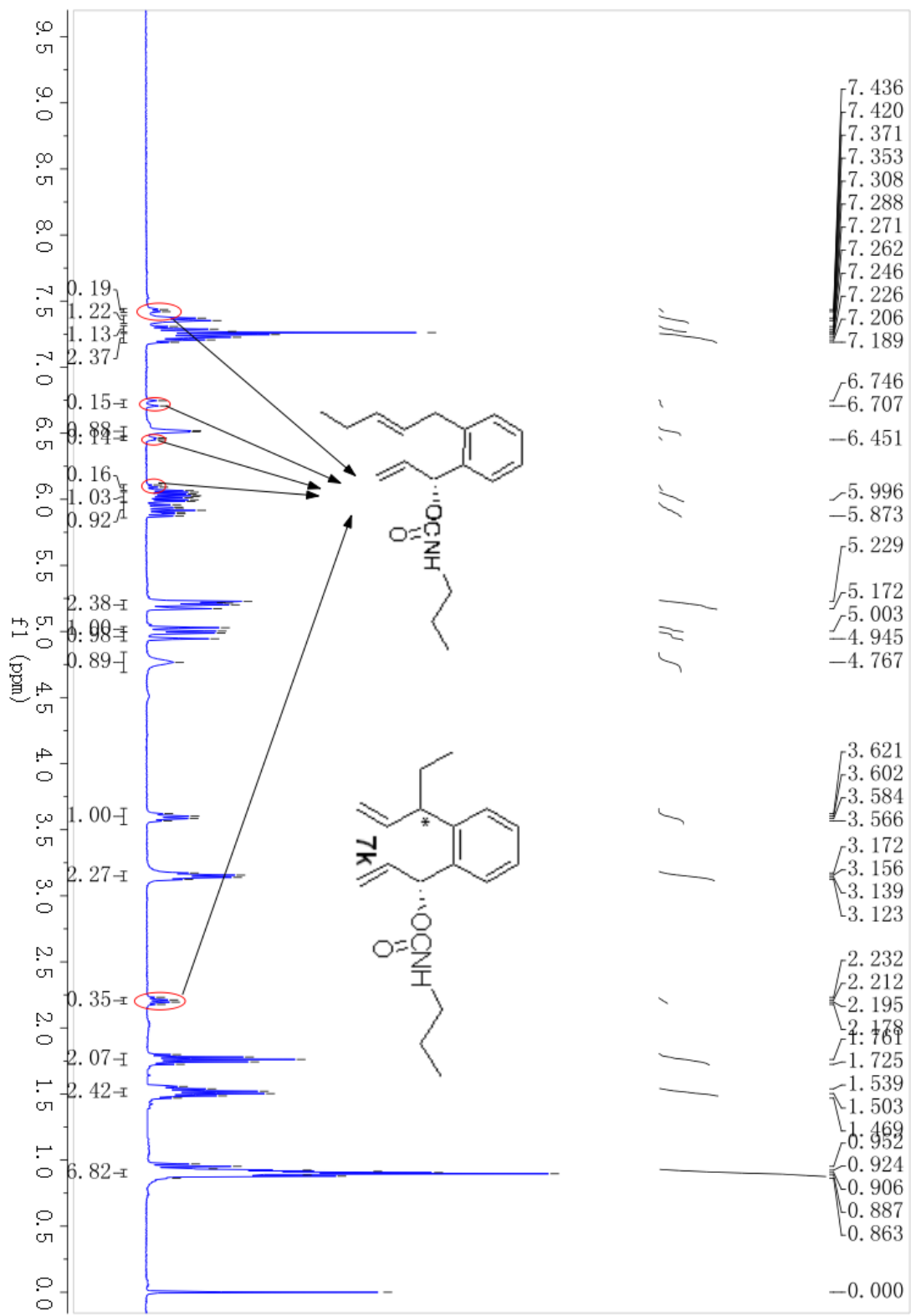


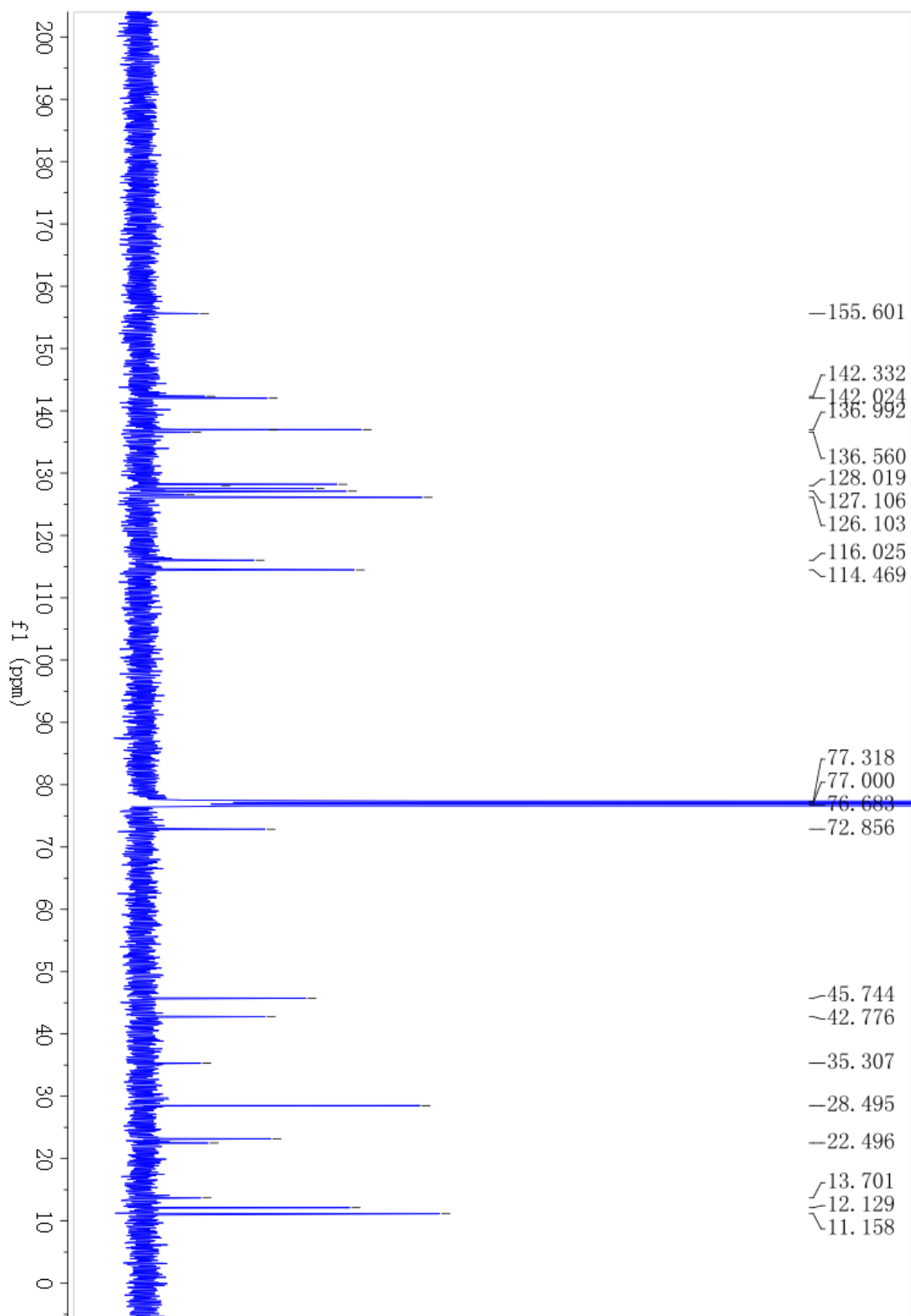




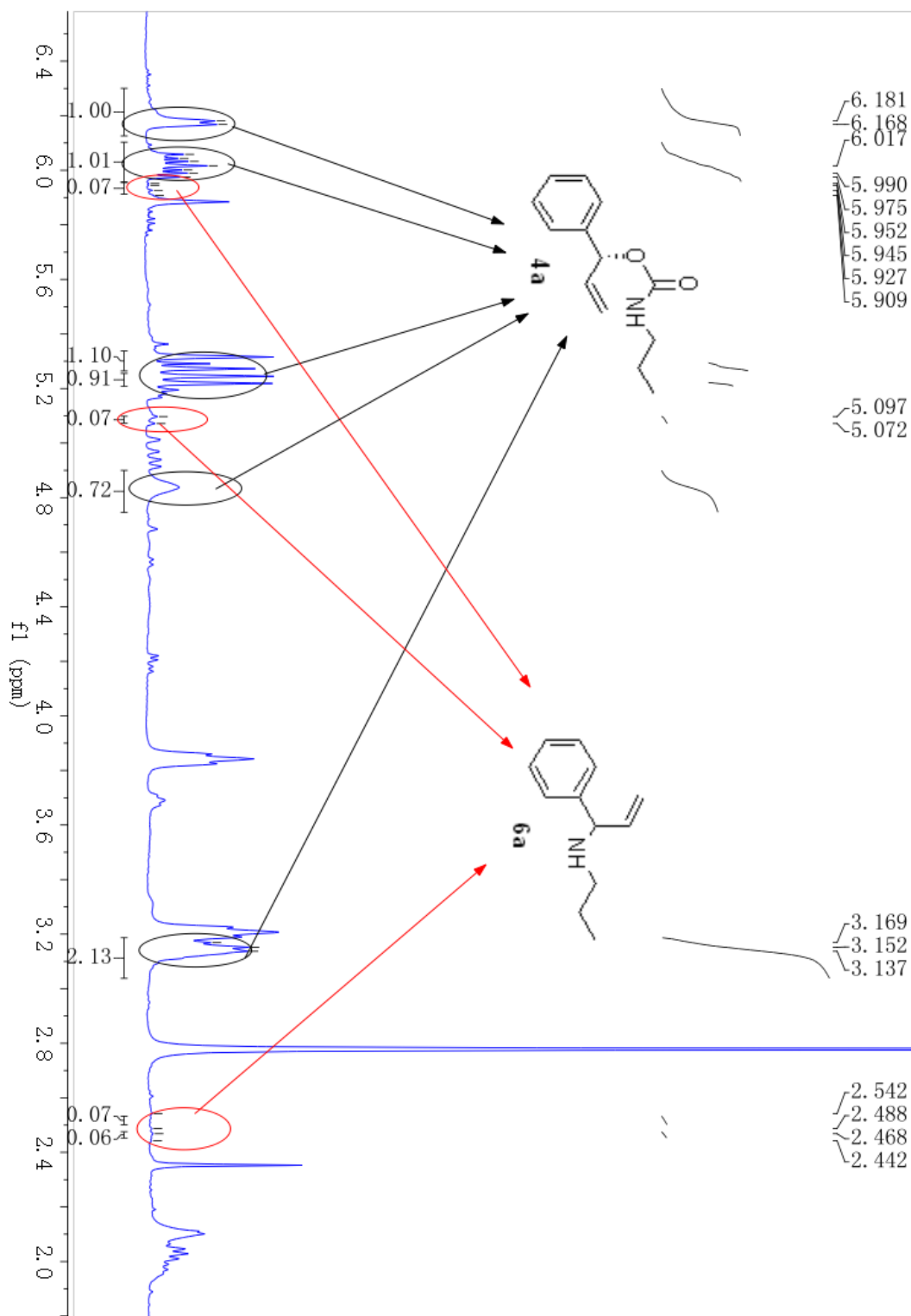




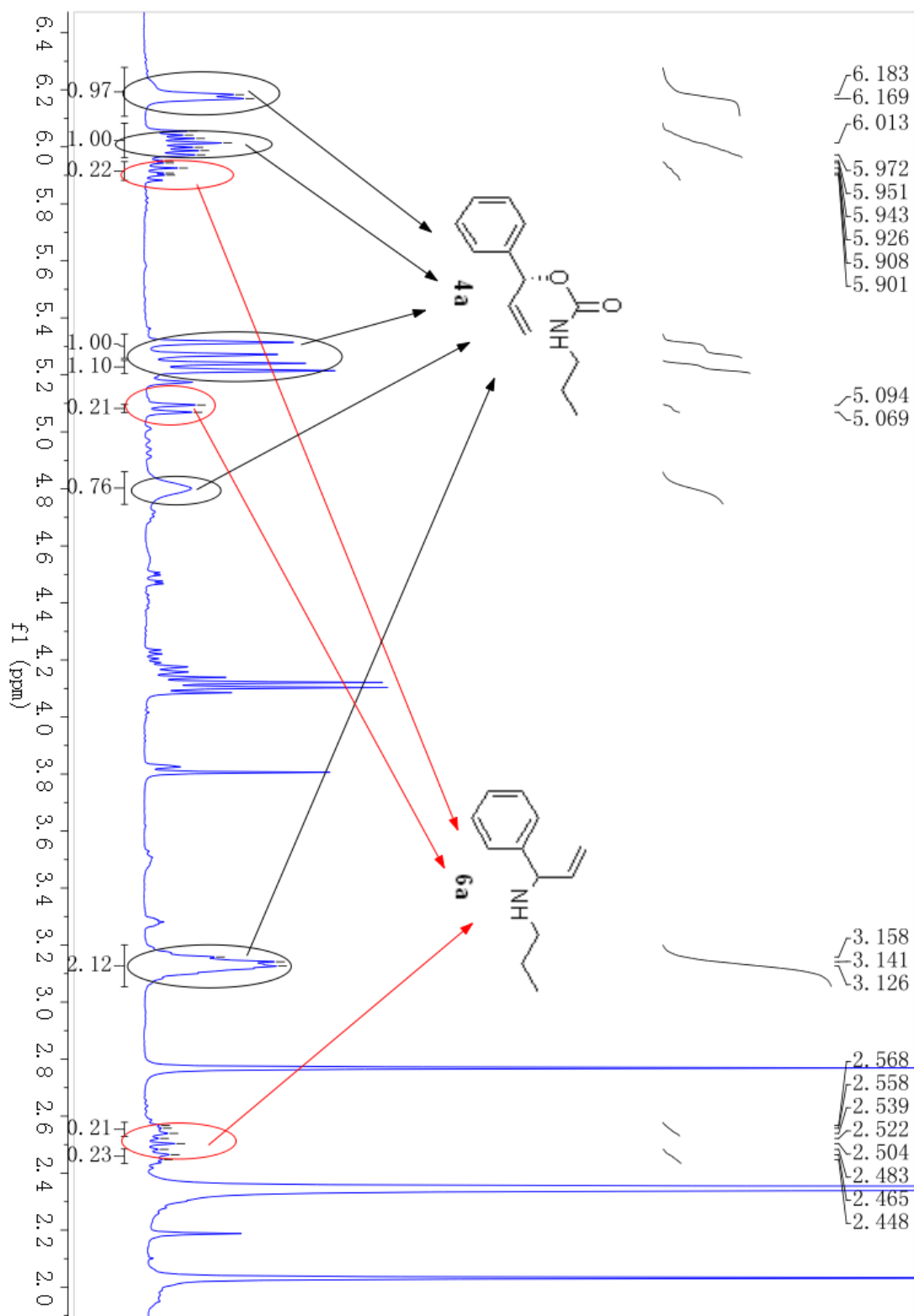




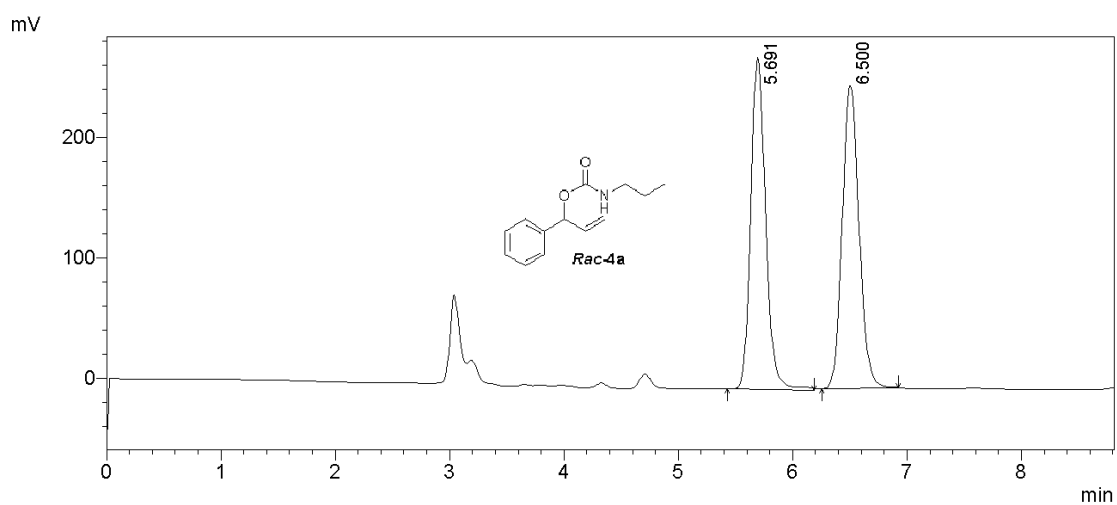
^1H NMR spectrum for the controlling experiment 1:



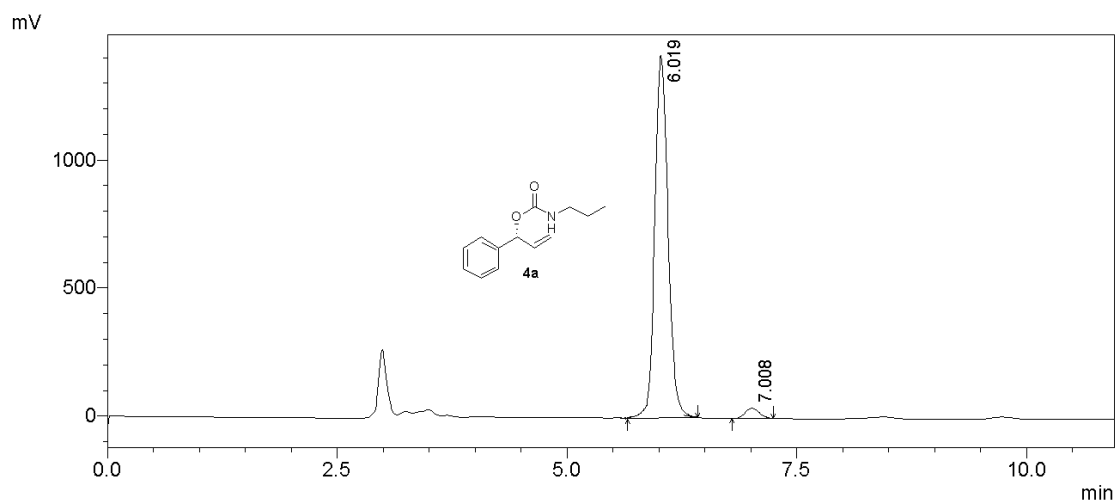
^1H NMR spectrum for the controlling experiment 2:



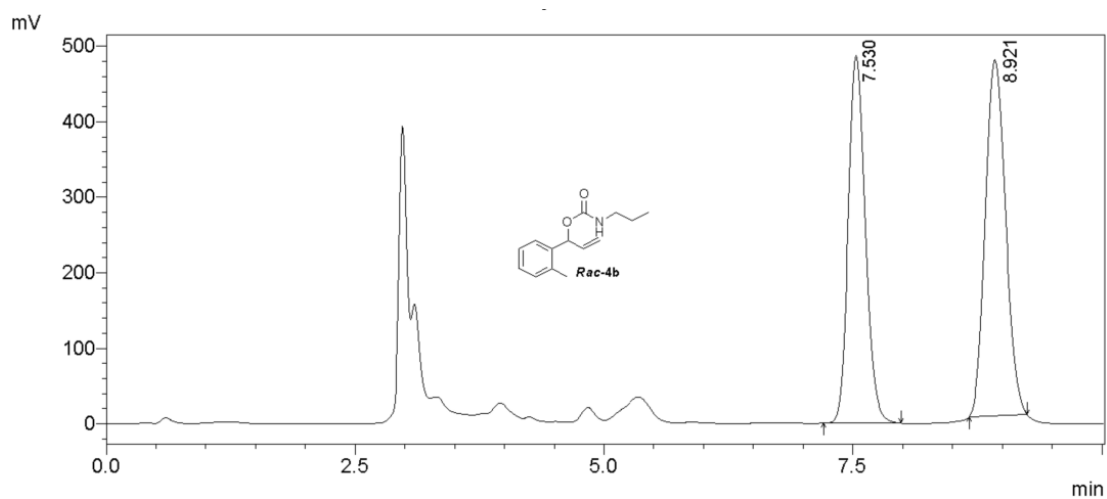
HPLC Chromatograms of the Chiral Compounds



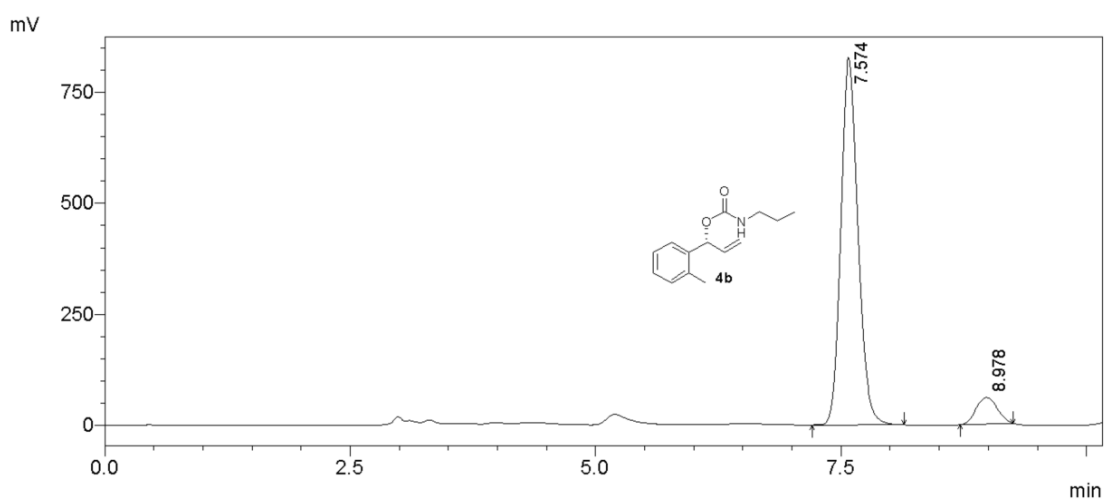
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	5.691	2508378	275573	49.454	52.314
2	6.500	2563792	251190	50.546	47.686



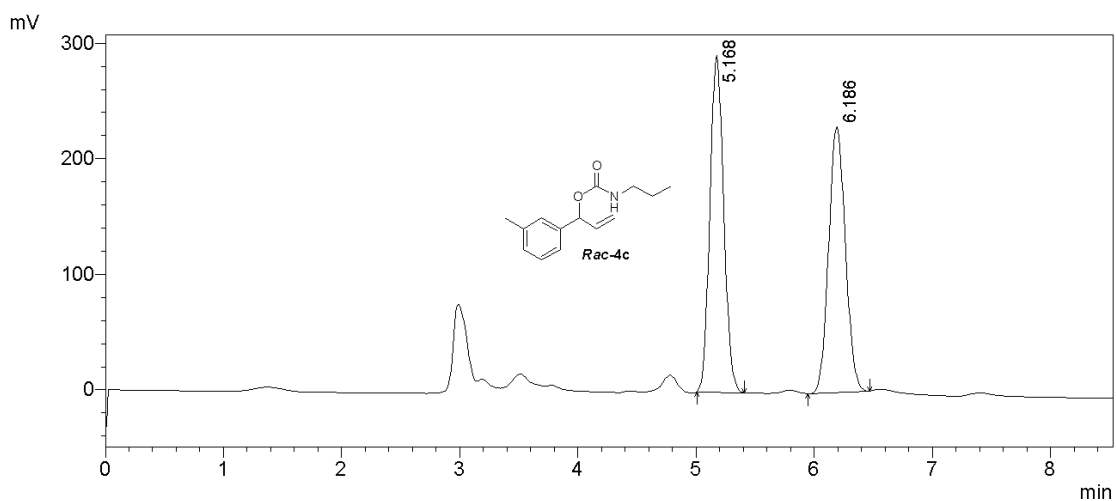
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	6.019	13478314	1390420	96.892	97.220
2	7.008	432301	39754	3.108	2.780



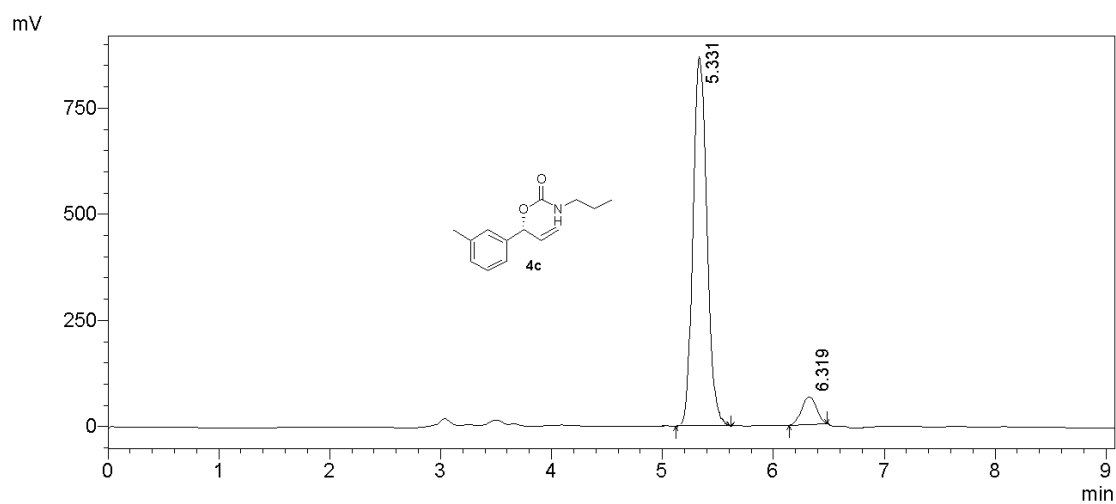
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	7.530	5785818	486727	46.528	50.805
2	8.921	6649432	471310	53.472	49.195



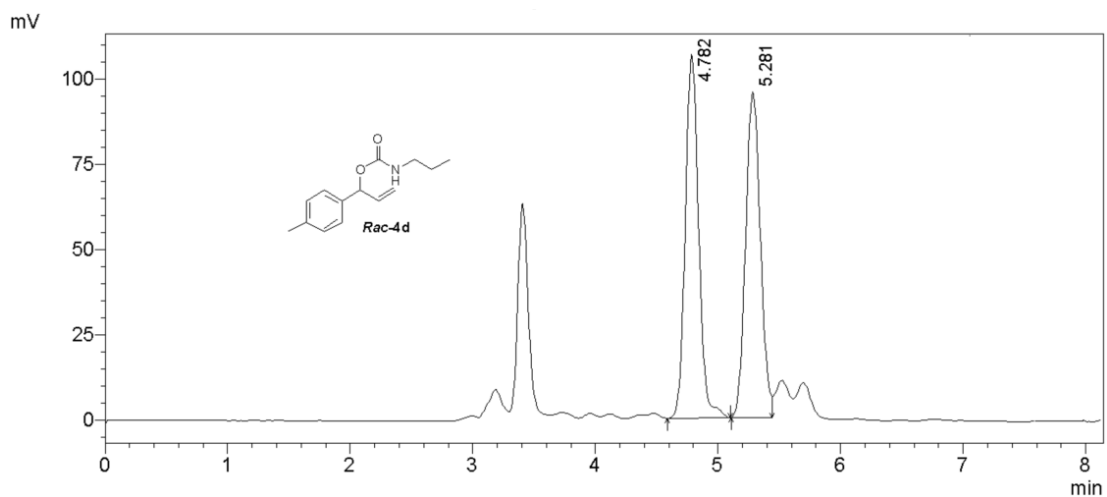
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	7.574	1005691	826759	91.827	93.288
2	8.978	895004	59484	8.173	6.712



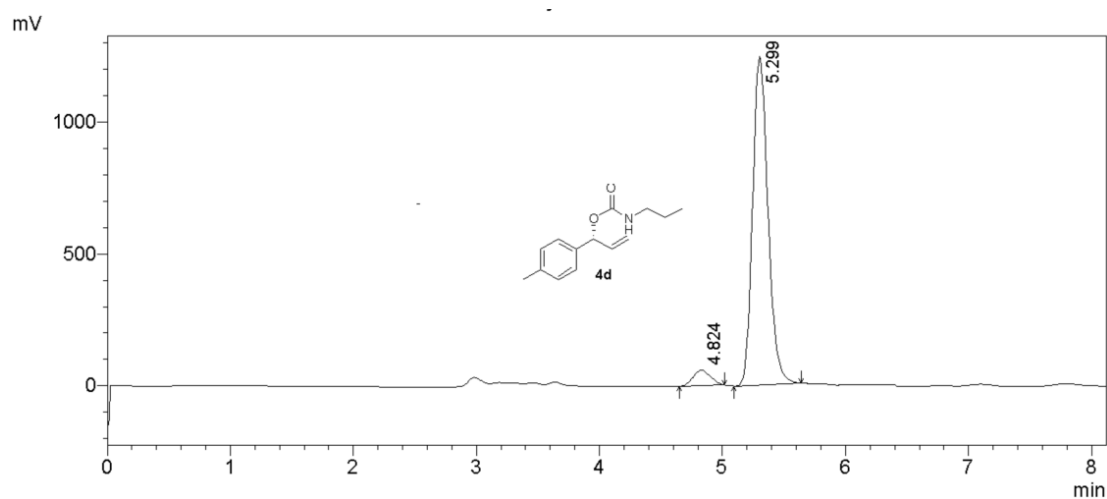
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	5.168	2357983	290964	50.994	55.898
2	6.186	2266036	229561	49.006	44.102



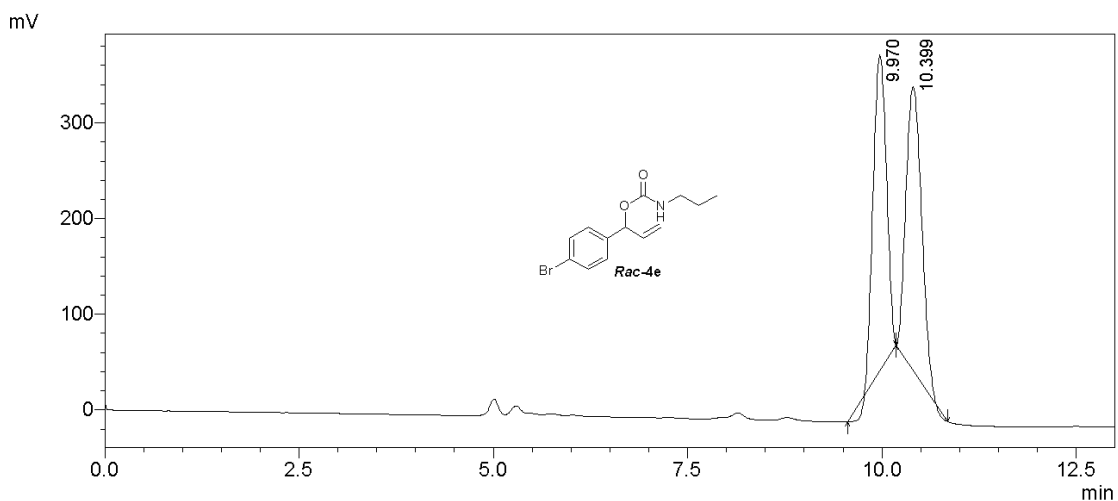
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	5.331	7267803	855617	92.286	92.938
2	6.319	607528	65010	7.714	7.062



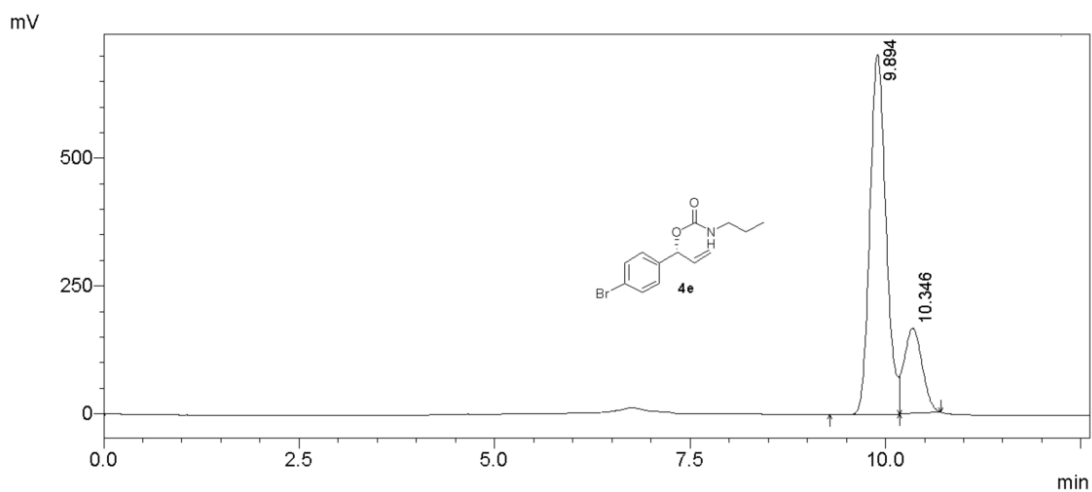
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	4.782	808182	106559	50.221	52.713
2	5.281	801085	95592	49.779	47.287



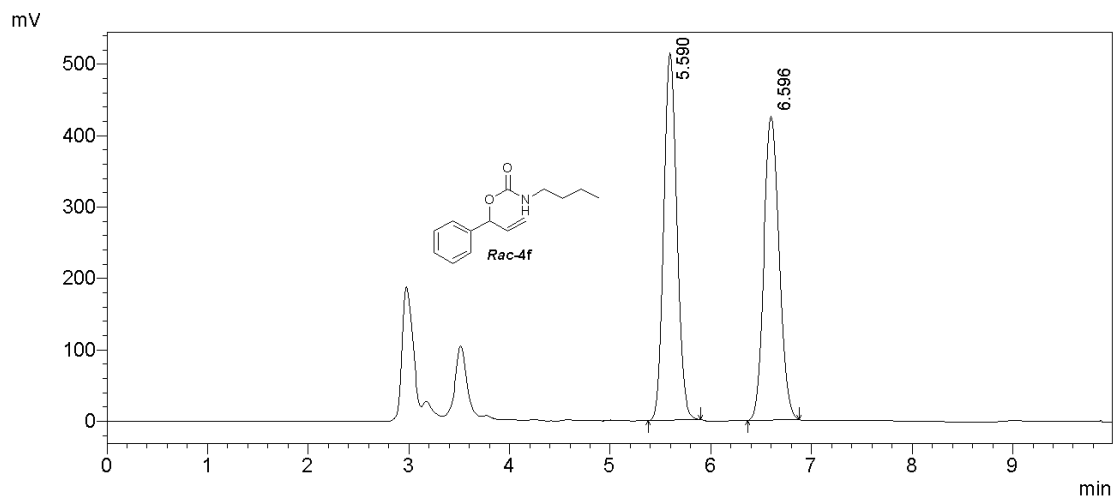
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	4.824	577432	58379	5.058	4.481
2	5.299	10839596	1244296	94.942	95.519



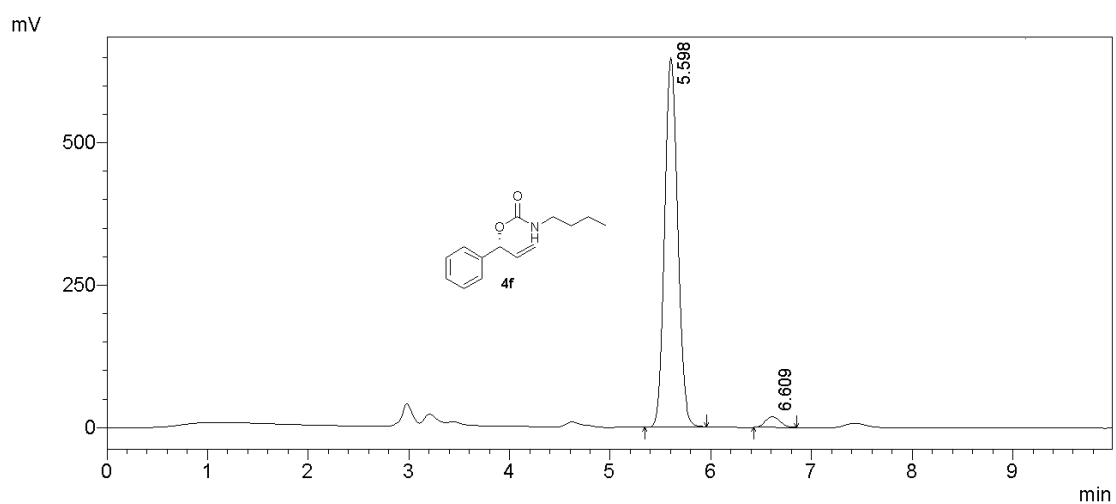
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	9.970	3991933	330557	48.310	52.724
2	10.399	4153549	296403	51.690	47.276



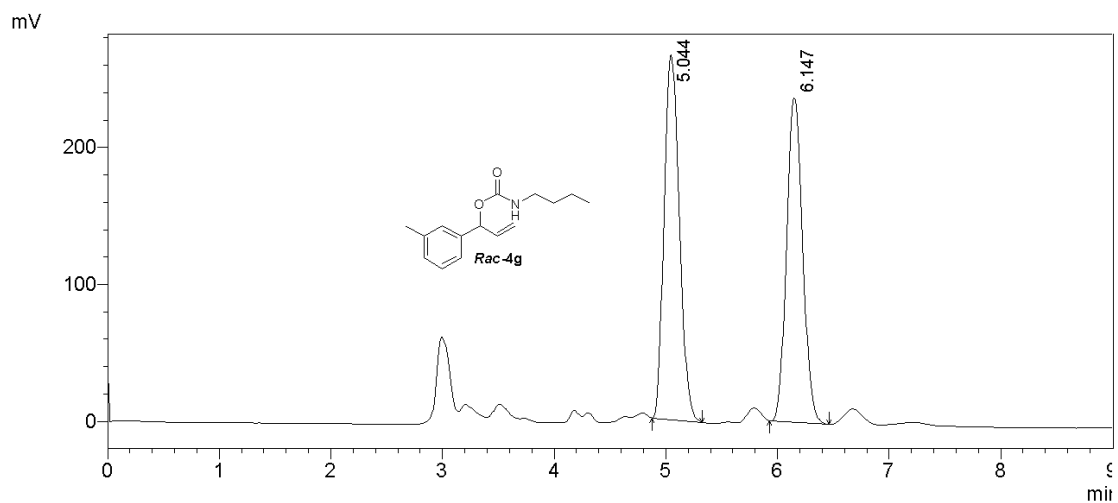
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	9.894	10124812	704348	79.407	80.926
2	10.346	2625759	166017	20.593	19.074



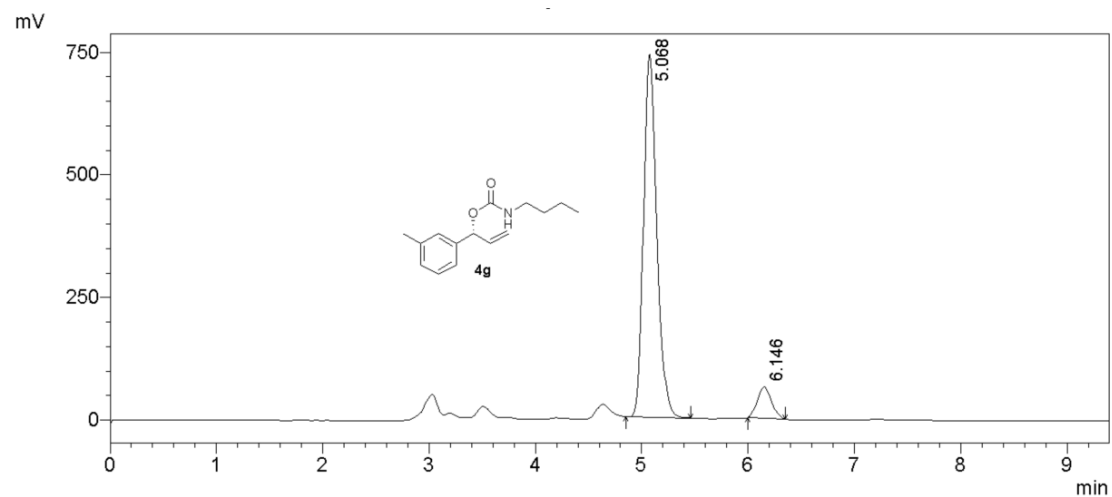
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	5.590	4586158	514145	50.425	54.703
2	6.596	4508853	425748	49.575	45.297



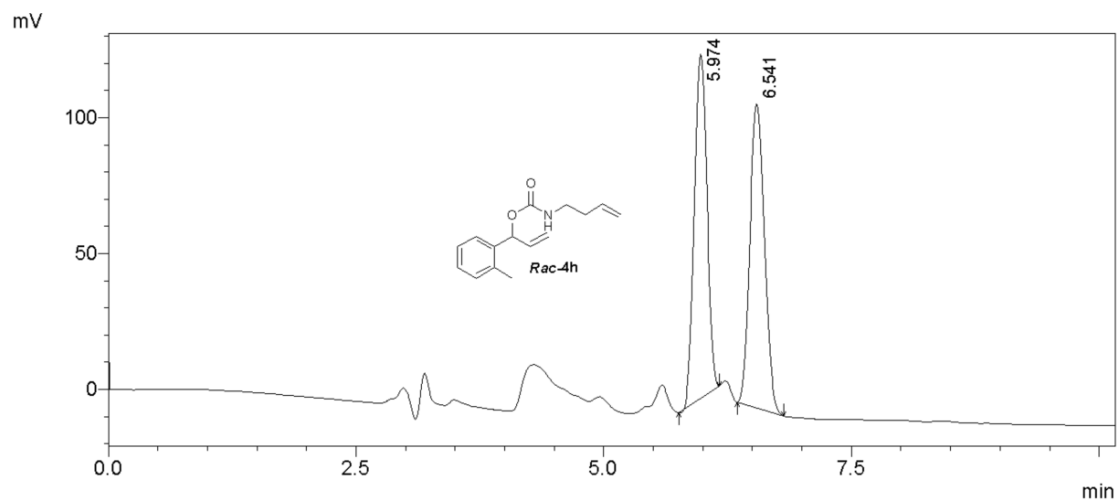
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	5.598	5767939	647633	96.768	97.169
2	6.609	192642	18871	3.232	2.831



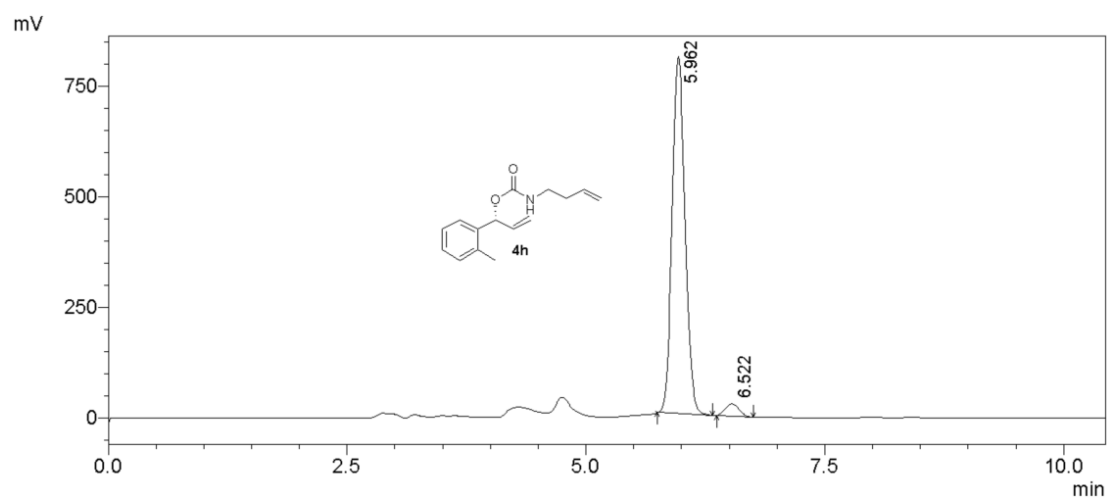
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	5.044	2534034	266060	51.623	52.911
2	6.147	2374671	236782	48.377	47.089



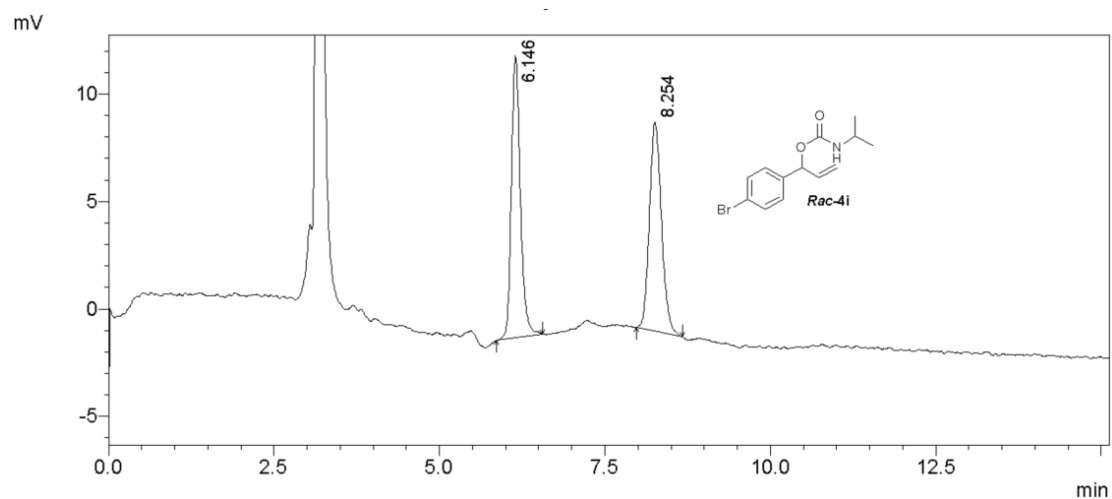
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	5.068	6431588	739037	91.520	92.068
2	6.146	595904	63674	8.480	7.932



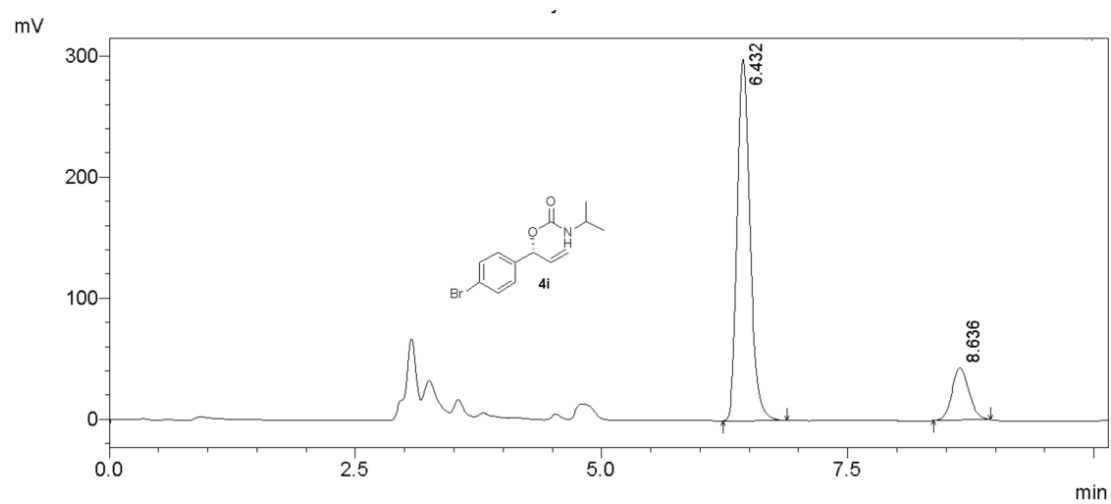
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	5.974	1120307	126652	49.375	53.095
2	6.541	1148660	111885	50.625	46.905



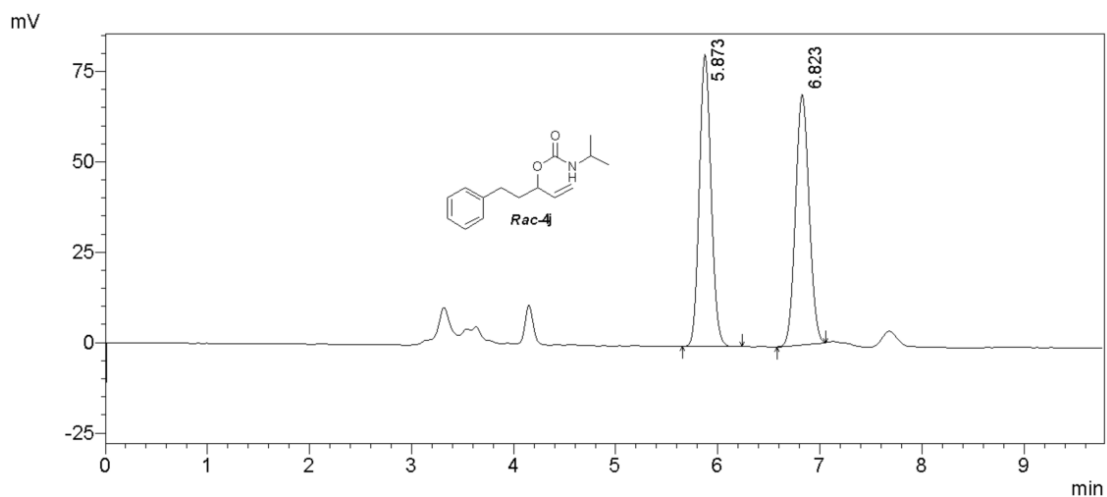
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	5.962	7592272	806749	96.440	96.627
2	6.522	280243	28162	3.560	3.373



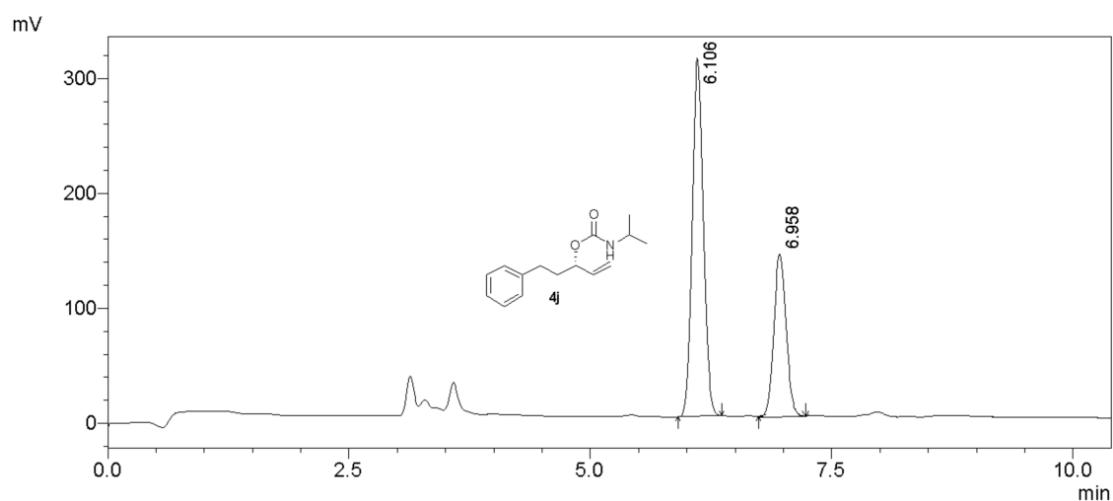
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	6.146	119560	12990	49.526	57.319
2	8.254	121848	9673	50.474	42.681



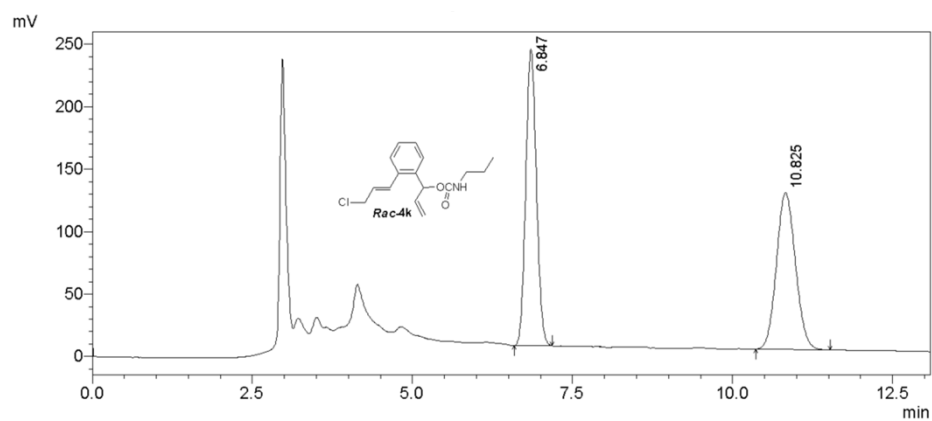
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	6.432	2686867	298599	83.789	57.3374
2	8.636	519839	43295	16.211	12.663



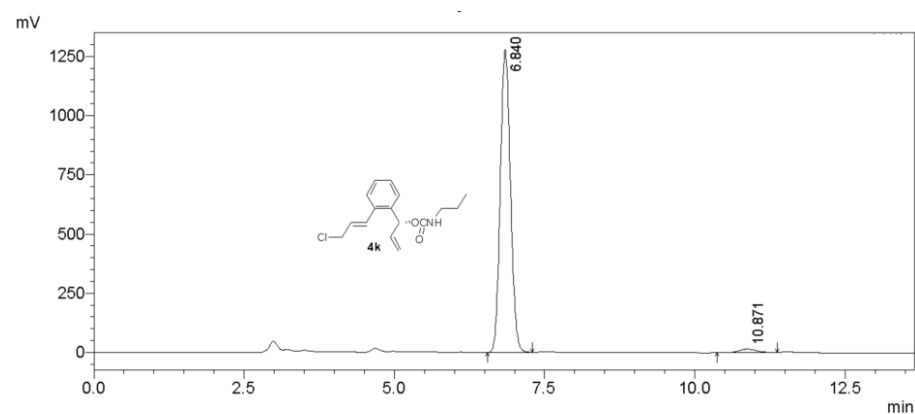
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	5.873	647615	80702	50.329	53.859
2	6.823	639151	69138	49.671	46.141



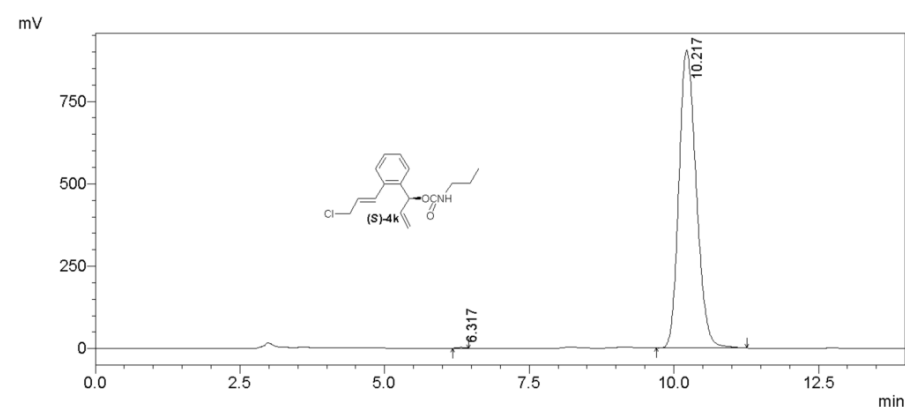
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	6.106	2508992	311928	68.819	89.616
2	6.958	1136808	136140	31.181	30.384



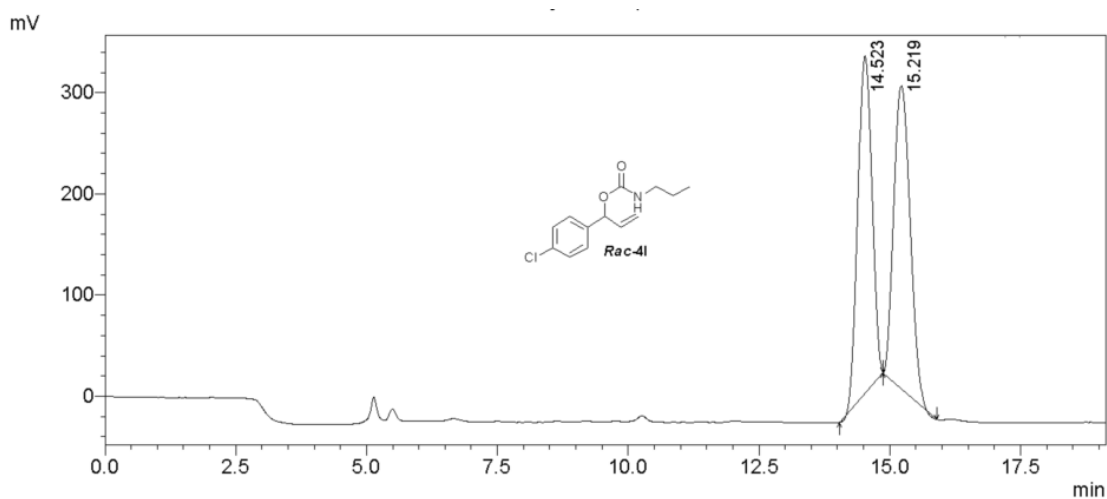
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	6.847	2730040	237337	51.341	65.452
2	10.825	2587396	125274	48.659	34.548



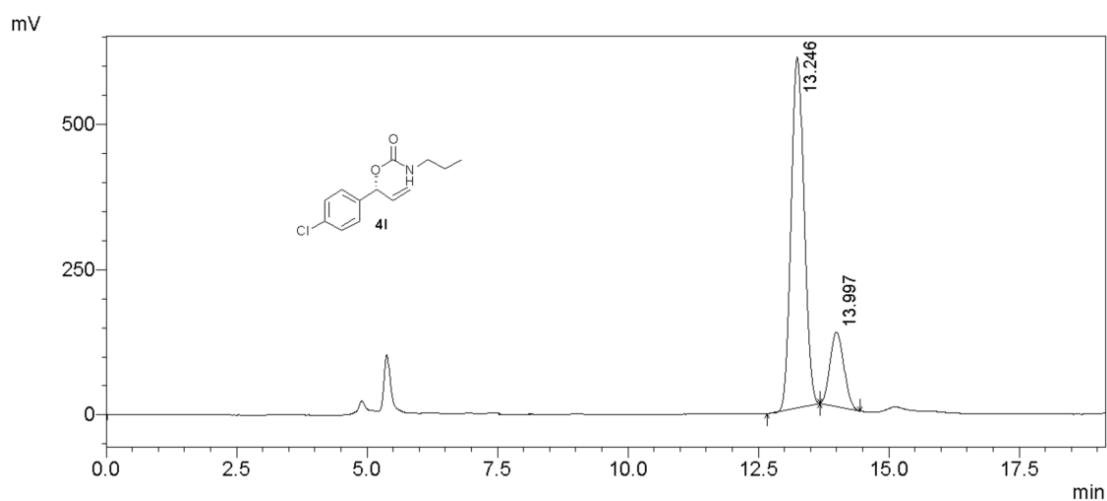
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	6.840	14965253	1277382	98.220	98.906
2	10.871	271153	14124	1.780	1.094



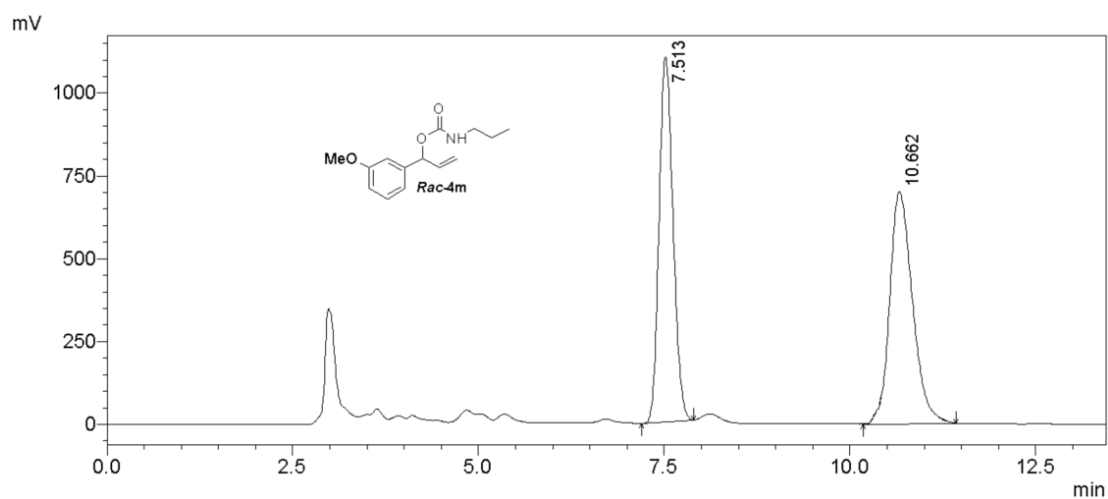
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	6.317	20004	2272	0.106	0.251
2	10.217	18861850	903590	99.894	99.749



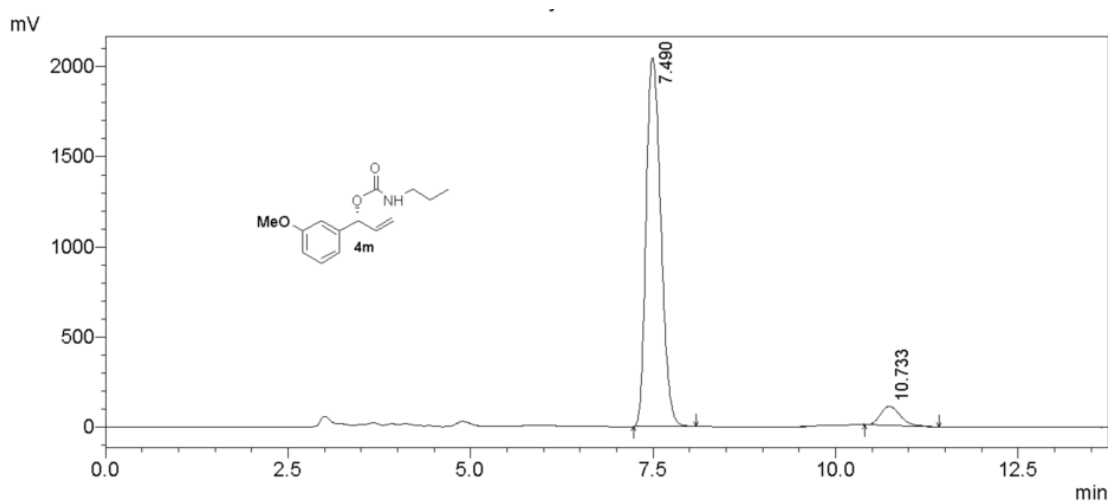
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	14.523	6303820	333080	49.245	52.698
2	15.219	6497208	298971	50.755	47.302



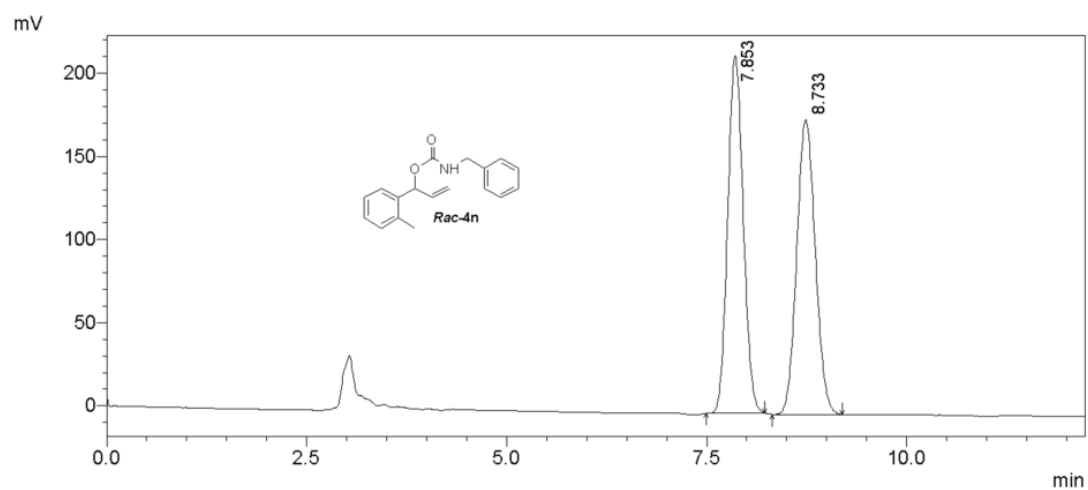
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	13.246	10440940	603587	81.448	82.462
2	13.997	2378257	128375	18.552	17.538



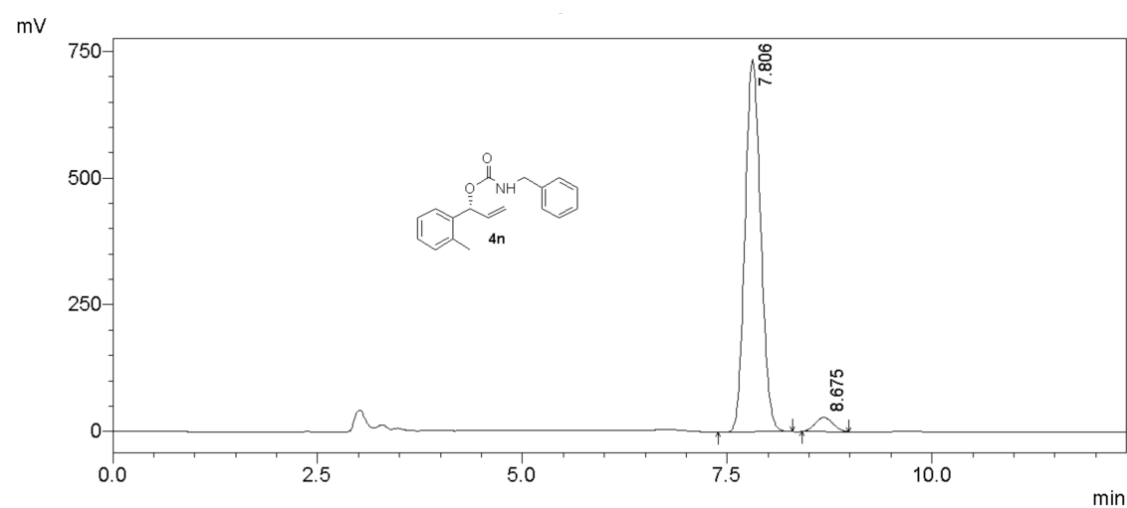
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	7.513	14414957	1103109	52.886	62.723
2	10.662	12841764	655595	47.114	37.277



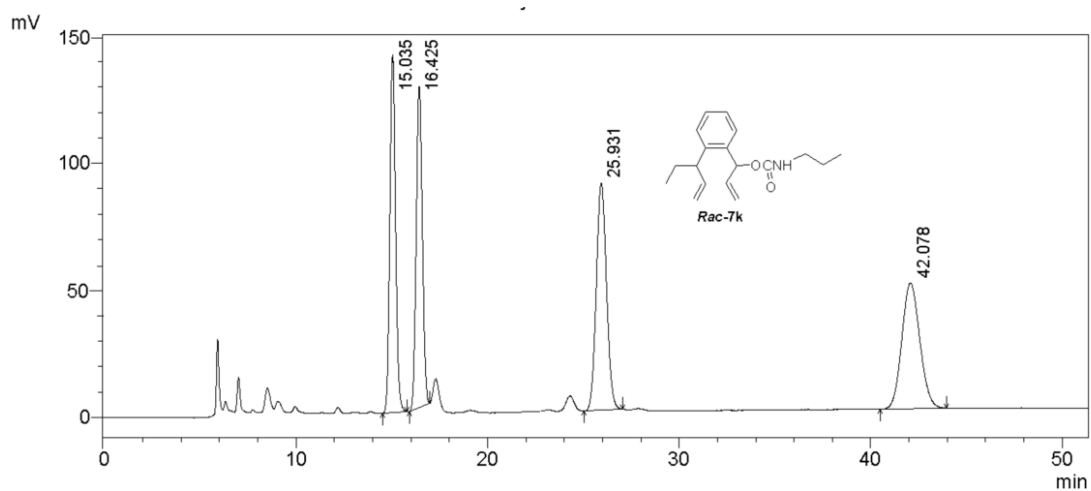
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	7.490	28608906	2047175	93.590	95.126
2	10.733	1959298	104888	6.410	4.874



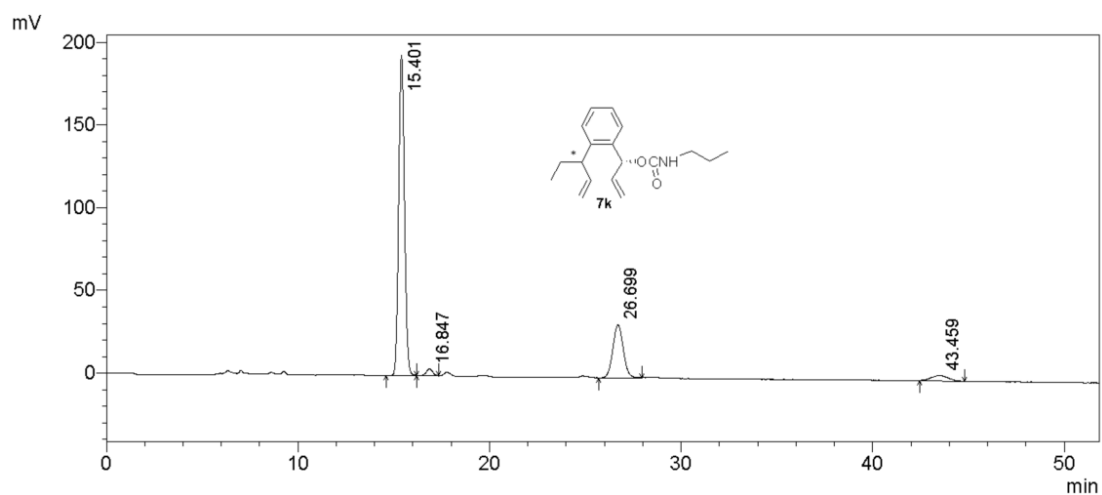
Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	7.853	2903371	214775	50.413	54.802
2	8.733	2855827	177134	49.587	45.198



Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	7.806	9790799	734623	95.881	96.353
2	8.675	420586	27810	4.119	3.647



Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	15.035	2939683	140579	23.878	34.631
2	16.425	2817323	126422	22.884	31.144
3	25.931	3319413	89371	26.963	22.017
4	42.078	3234683	49556	26.275	12.208



Peak #	R. Time	Area	Height	Area (%)	Height (%)
1	15.401	4076996	193306	73.089	83.059
2	16.847	99820	4234	1.789	1.819
3	26.699	1201611	31985	21.541	23.743
4	43.459	199729	3208	3.581	1.379