Supporting Information

Palladium-Catalyzed Carboxylative Coupling of Benzyl Chlorides with Allyltributylstannane: Remarkable Effect of Palladium Nanoparticles

Xiujuan Feng,* Anle Sun, Sheng Zhang, Xiaoqiang Yu, and Ming Bao*

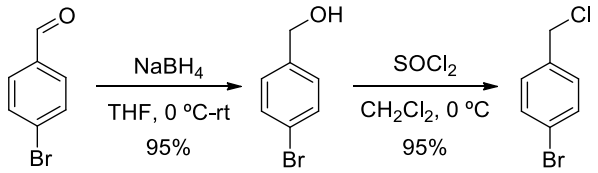
State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116023, China

Table of Contents

1. General Information

All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Solvents were purified by standard techniques without special instructions. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) or a Bruker Avance II-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C); $CDCl_3$ and TMS were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on either a Q-TOF mass spectrometry or a GC-TOF mass spectrometry. Transmission electron microscopy (TEM) was performed on a Tecnai G2 microscope operating at 120 kV. After the carboxylative coupling reaction of benzyl chloride with allyltributylstannane was performed for 12 h under optimized reaction conditions, the resultant mixture was used for TEM determination. TLC was carried out on SiO_2 (silica gel 60 F_{254}, Merck), and the spots were located with UV light, iodoplatinate reagent or 1% aqueous $KMnO_4$. Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 meth) or basic Al_2O_3 (Al_2O_3 90, 100-200 meth). Unless otherwise noted, carbon dioxide (99.999%) was used without further purification. The starting materials **1a–1c, 1e–1f, 1h, 1l–1m,** and allyltributylstannane are commercially available. The starting material **1n** appeared in the literature.[1]

2. Representative Procedure for Preparation of Starting Materials

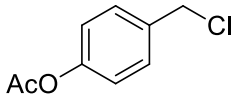


To a solution of 4-bromobenzaldehyde (2.78 g, 15 mmol) in THF (50 mL) at 0 °C, $NaBH_4$ (0.28 g, 7.5 mmol) was added slowly. After the resulting mixture was stirred overnight at room temperature, water (50 mL) was added slowly to quench the reaction. The product was extracted with ethyl ether (50 mL × 2), and the combined organic layers were washed with brine (50 mL × 2), dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 5:1) to afford (4-bromophenyl)methanol as a white solid (2.65 g, 95 % yield).

To a solution of (4-bromophenyl)methanol (1.87 g, 10 mmol) in CH_2Cl_2 (50 mL) at 0 °C, $SOCl_2$ (1.78 g, 15 mmol) was slowly added. The resulting mixture was stirred overnight at room temperature. The mixture was washed with water (50 mL× 2), and dried with Na_2SO_4. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 10:1) to afford 1-bromo-4-(chloromethyl)benzene (**1d**)[2] as a white solid (2.78 g, 95 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (s, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 1H).

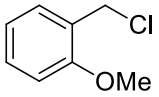
The following Starting Materials **1g** and **1i**–**1k** were prepared according to the above mentioned procedure.

4-(Chloromethyl)phenyl acetate (1g)[3]



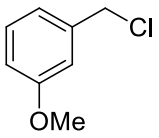
Brown oil (1.59 g, 85 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 4.64 (s, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H).

1-(Chloromethyl)-2-methoxybenzene (1i)[4]



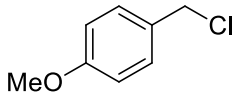
Colourless oil (2.00 g, 90 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 4.65 (s, 2H), 6.87–6.95 (m, 2H), 7.27–7.35 (m, 2H).

1-(Chloromethyl)-3-methoxybenzene (1j)[5]



Colourless oil (2.12 g, 95 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 4.54 (s, 2H), 6.83–6.86 (m, 1H), 6.92–6.96 (m, 2H), 7.25 (t, J = 8.0 Hz, 1H).

1-(Chloromethyl)-4-methoxybenzene (1k)[6]

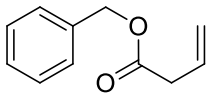


Colourless oil (2.08 g, 95 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 4.59 (s, 2H), 6.91 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.6 Hz, 2H).

3. Experimental Procedures and Characterization Data for All Products

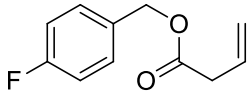
Representative Procedure for Obtaining Products 4a–4n: $Pd(acac)_2$ (7.6 mg, 0.025 mmol), TBAB (226.0 mg, 0.7 mmol), benzyl chloride (65.0 mg, 0.5 mmol), allyltributylstannane (199.0 mg, 0.6 mmol), and THF (5 mL) were placed in a 50 mL autoclave with a magnetic stir bar under a N_2 atmosphere. The autoclave was purged with CO_2 three times, filled with CO_2 to 2 MPa pressure, and heated to 70 ºC for 24 h. The autoclave was allowed to cool to room temperature and the remaining CO_2 was vented. The resultant mixture was evaporated in vacuo to give the crude product, which was then purified via silica gel chromatography (eluent: ethyl acetate/petroleum ether = 1:30) to afford benzyl but-3-enoate (**4a**) as a colorless oil (75.8 mg , 86 % yield).

Benzyl but-3-enoate (4a)[7]



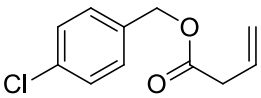
Colorless oil (75.8 mg, 86 % yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 3.12 (d, J = 6.8 Hz, 2H), 5.12 (s, 2H), 5.13–5.18 (m, 2H), 5.88–5.99 (m, 1H), 7.28–7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 66.5, 118.7, 128.2, 128.3, 128.6, 130.2, 135.9, 171.3.

4-Fluorobenzyl but-3-enoate (4b)



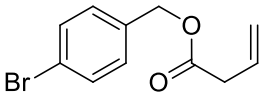
Yellowish oil (81.6 mg, 84 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.13 (d, J = 6.8 Hz, 2H), 5.09 (s, 2H), 5.14–5.19 (m, 2H), 5.88–5.98 (m, 1H), 7.02–7.07 (m, 2H), 7.31–7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 65.7, 115.5 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 118.7, 130.0, 130.3 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 131.7 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 162.7 (d, $^1J_{C\text{-}F}$ = 245.4 Hz), 171.3; IR (neat) 3082, 2959, 2897, 1739, 1643, 1606, 1513, 1451, 1169, 992, 924, 825 cm^{-1}; HRMS (ES) Calcd for $C_{11}H_{11}O_2NaF$: 217.0641 $[M+Na]^+$; Found: 217.0649.

4-Chlorobenzyl but-3-enoate (4c)



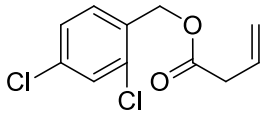
Yellowish oil (84.3 mg, 80 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.13 (d, J = 6.8 Hz, 2H), 5.08 (s, 2H), 5.14–5.18 (m, 2H), 5.87–5.98 (m, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.0, 65.6, 118.8, 128.7, 129.6, 130.0, 134.1, 134.4, 171.1. IR (neat) 3084, 2960, 1739, 1643, 1600, 1494, 1164, 992, 923, 806 cm^{-1}; HRMS (ES) Calcd for $C_{11}H_{11}O_2NaCl$: 233.0345 $[M+Na]^+$; Found: 233.0352.

4-Bromobenzyl but-3-enoate (4d)



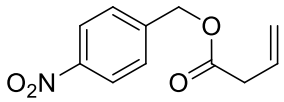
Yellowish oil (104.6 mg, 82 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.13 (d, J =7.0 Hz, 2H), 5.07 (s, 2H), 5.14–5.19 (m, 2H), 5.87–5.97 (m, 1H), 7.21 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.0, 65.6, 118.8, 122.3, 129.9, 130.0, 131.7, 134.9, 171.1; IR (neat) 3082, 2960, 2891, 1739, 1643, 1596, 1490, 1164, 991, 923, 802 cm^{-1}; HRMS (ES) Calcd for $C_{11}H_{11}O_2NaBr$: 276.9844 $[M+Na]^+$; Found: 276.9840.

2,4-Dichlorobenzyl but-3-enoate (4e)



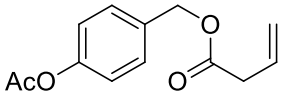
Colorless oil (98.0 mg, 80 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.17 (d, J = 7.2 Hz, 2H), 5.17–5.21 (m, 4H), 5.89–5.99 (m, 1H), 7.24 (dd, J = 8.3, 2.0 Hz, 1H), 7.34 (d, J = 8.3Hz, 1H), 7.39 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.9, 63.1, 118.9, 127.2, 129.4, 129.9, 130.6, 132.2, 134.4, 134.7, 170.9. IR (neat) 3084, 2959, 1743, 1643, 1591, 1564, 1477, 1164, 991, 923 856, 840 cm^{-1}; HRMS (ES) Calcd for $C_{11}H_{10}O_2NaCl_2$: 266.9956 $[M+Na]^+$; Found: 266.9951.

4-Nitrobenzyl but-3-enoate (4f)



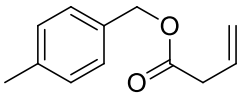
Yellowish oil (70.8 mg, 64 % yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 3.20 (d, J = 6.8 Hz, 2H), 5.19–5.27 (m, 4H), 5.90–6.00 (m, 1H), 7.53 (d, J = 8.7 Hz, 2H), 8.21 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.9, 64.8, 119.0, 123.7, 128.3, 129.7, 143.2, 147.6, 171.0; IR (neat) 3083, 2960, 2861, 1741, 1643, 1607, 1522, 1347, 1160, 992, 926, 859; HRMS (ES) Calcd for $C_{11}H_{11}NO_4Na$: 244.0586 $[M+Na]^+$; Found: 244.0582.

4-Acetoxybenzyl but-3-enoate (4g)



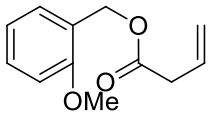
Yellowish oil (75.0 mg, 64 % yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.13 (d, J = 6.8 Hz, 2H), 5.11 (s, 2H), 5.14–5.19 (m, 2H), 5.88–5.98 (m, 1H), 7.08 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 39.0, 65.7, 118.7, 121.7, 129.5, 130.1, 133.5, 150.6, 162.6, 169.3, 171.2; IR (neat) 3082, 2958, 2897, 1763, 1738, 1643, 1609, 1509, 1163, 994, 911, 850 cm^{-1}; HRMS (ES) Calcd for $C_{13}H_{14}O_4Na$: 257.0790 $[M+Na]^+$; Found: 257.0801.

4-Methylbenzyl but-3-enoate (4h)



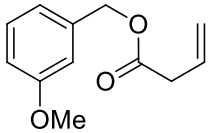
Yellowish oil (78.0 mg, 82 % yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 3.16 (d, J = 6.8 Hz, 2H), 5.13 (s, 2H), 5.18–5.23 (m, 2H), 5.93–6.03 (m, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 39.2, 66.4, 118.6, 128.4, 129.3, 130.3, 133.0, 138.1, 171.3; IR (neat) 3095, 3026, 2960, 2922, 1739, 1643, 1619, 1518, 1450, 1375, 1164, 990, 921, 805 cm^{-1}; HRMS (ES) Calcd for $C_{12}H_{14}O_2Na$: 213.0891 $[M+Na]^+$; Found: 213.0896.

2-Methoxybenzyl but-3-enoate (4i)



Yellowish oil (85.6 mg, 83 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.13 (d, J = 7.2 Hz, 2H), 3.81 (s, 3H), 5.14–5.22 (m, 4H), 5.90–6.00 (m, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.91–6.95 (m, 1H), 7.26–7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.2, 55.4, 61.9, 110.5, 118.5, 120.4, 124.2, 129.60, 129.64, 130.4, 157.5, 171.4; IR (neat) 3085, 2959, 2839, 1736, 1643, 1605, 1591, 1496, 1465, 1377, 1248, 1161, 993, 923, 755 cm^{-1}; HRMS (ES) Calcd for $C_{12}H_{14}O_3Na$: 229.0841 $[M+Na]^+$; Found: 229.0844.

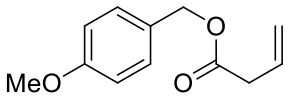
3-Methoxybenzyl but-3-enoate (4j)



Yellowish oil (83.5 mg, 81 % yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 3.14 (d, J = 6.8 Hz, 2H), 3.79 (s, 3H), 5.10 (s, 2H), 5.14–5.19 (m, 2H), 5.91–5.98 (m, 1H), 6.84–6.93 (m, 3H), 7.24–7.28 (m, 1H),; ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 55.2, 66.3, 113.6,

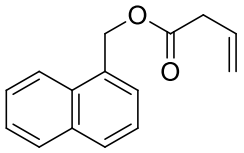
113.8, 118.7, 120.3, 129.6, 130.2, 137.4, 159.8, 171.2; IR (neat) 3082, 3008, 2957, 2837, 1739, 1643, 1604, 1588, 1492, 1458, 1375, 1168, 994, 924, 876 783 693cm^{-1}; HRMS (ES) Calcd for $C_{12}H_{14}O_3Na$: 229.0841 $[M+Na]^+$; Found: 229.0837.

4-Methoxybenzyl but-3-enoate (4k)



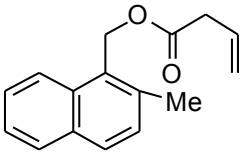
Colorless oil (79.4 mg, 77 % yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 3.10 (d, J = 6.8 Hz, 2H), 3.78 (s, 3H), 5.05 (s, 2H), 5.12–5.17 (m, 2H), 5.87–5.96 (m, 1H), 6.87 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 55.2, 66.3, 114.0, 118.6, 128.0, 130.1, 130.3, 159.7, 171.4; IR (neat) 3081, 3003, 2958, 2838, 1736, 1642, 1613, 1586, 1516, 1463, 1376, 1248, 1164, 993, 922, 822 cm^{-1}; HRMS (ES) Calcd for $C_{12}H_{14}O_3Na$: 229.0841 $[M+Na]^+$; Found: 229.0839.

Naphthalen-1-ylmethyl but-3-enoate (4l)[8]



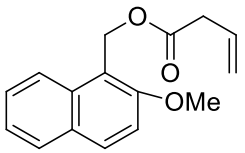
Yellowish oil (97.3 mg, 86 % yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 3.14 (d, J = 6.8 Hz, 2H), 5.14–5.18 (m, 2H), 5.58 (s, 2H), 5.89–5.97 (m, 1H), 7.42–7.57 (m, 4H), 7.83–7.88 (m, 2H), 7.99 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 64.8, 118.8, 123.6, 125.3, 126.0, 126.6, 127.5, 128.8, 129.4, 130.1, 131.4, 131.7, 133.8, 171.5.

(2-Methylnaphthalen-1-yl)methyl but-3-enoate (4m)



Yellowish oil (98.5 mg, 82 % yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (s, 3H), 3.17 (d, J = 6.8 Hz, 2H), 5.19–5.23 (m, 2H), 5.71 (s, 2H), 5.97–6.04 (m, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.48-7.52 (m, 1H), 7.58-7.62 (m, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 39.1, 60.4, 118.7, 123.6, 125.1, 126.8, 128.3, 128.6, 129.1, 129.3, 130.4, 132.5, 132.9, 136.3, 171.7; IR (neat) 3053, 2982, 2923, 1735, 1642, 1599, 1513, 1448, 1365, 1165, 977, 922, 812, 742 cm^{-1}; HRMS (ES) Calcd for $C_{16}H_{16}O_2Na$: 263.1048 $[M+Na]^+$; Found: 263.1053.

(2-Methoxynaphthalen-1-yl)methyl but-3-enoate (4n)

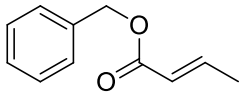


Yellowish oil (94.8 mg, 74 % yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (d, J = 6.8 Hz, 2H), 3.88 (s, 3H), 5.08–5.13 (m, 2H), 5.67 (s, 2H), 5.86–5.94 (m, 1H), 7.20 (d, J = 9.2 Hz, 1H), 7.30–7.34 (m, 1H), 7.45-7.50 (m, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 56.7, 57.6, 113.3, 116.1, 118.5, 123.1, 123.8, 127.3, 128.6, 129.1, 130.5, 131.2, 133.6, 156.2, 171.9; IR (neat) 3075, 3013, 2939, 2907, 2841, 1732, 1642, 1597, 1515, 1472, 1366, 1167, 977, 921, 810, 748 cm^{-1}; HRMS (ES) Calcd for $C_{16}H_{16}O_3Na$: 279.0997 $[M+Na]^+$; Found: 279.0992.

Representative Procedure for Obtaining Products 5a–f and 5h–n: The β,γ-unsaturated ester, benzyl but-3-enoate (**4a**, 52.9 mg, 0.3 mmol), was passed through a short basic alumina column (eluent: petroleum ether/ethyl acetate = 30:1). The solvents were removed under reduced pressure, and the isomer α,β-unsaturated ester (*E*)-Benzyl but-3-enoate (**5a**) was obtained as a yellowish oil (49.2 mg, 93 % yield).

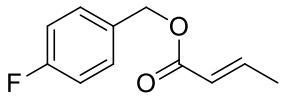
4-Acetoxybenzyl but-3-enoate (**4g**) could easily took place hydrolysis reaction under basic conditions to produce a mixture, and the corresponding α,β-unsaturated ester **5g** could not be separated.

(*E*)-Benzyl but-2-enoate (5a)[9]



Yellowish oil (49.2 mg, 93 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.89 (dd, J = 1.2, 6.8 Hz, 3H), 5.18 (s, 2H), 5.89–5.93 (m, 1H), 7.00–7.09 (m, 1H), 7.27–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 66.0, 122.5, 128.16, 128.18, 128.6, 136.2, 145.2, 166.3.

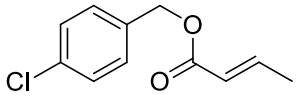
(*E*)-4-Fluorobenzyl but-2-enoate (5b)



Yellowish oil (54.8 mg, 93 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.87 (dd, J = 1.6, 6,8 Hz, 3H), 5.13 (s, 2H), 5.87–5.90 (m, 1H), 6.99–7.06 (m, 3H), 7.33–7.37 (m, 2H);

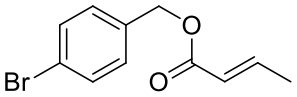
^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 65.2, 115.0 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 122.4, 130.1(d, $^3J_{C\text{-}F}$ = 8.2 Hz), 132.1 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 145.3, 162.6 (d, $^1J_{C\text{-}F}$ = 245.1 Hz), 166.2; IR (neat) 3053, 2924, 2854, 1721, 1659, 1607, 1513, 1445, 1157, 969, 825 cm^{-1}; HRMS (ES) Calcd for $C_{11}H_{11}O_2NaF$: 217.0641 $[M+Na]^+$; Found: 217.0649.

(*E*)-4-Chlorobenzyl but-2-enoate (5c)



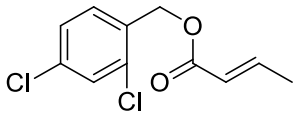
Colorless oil (58.8 mg, 92 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (dd, J =1.6, 6.8 Hz, 3H), 5.12 (s, 2H), 5.86–5.90 (m, 1H), 6.97–7.06 (m, 1H), 7.28–7.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 65.1, 122.3, 128.7, 129.5, 134.0, 134.7, 145.5, 166.1; IR (neat) 3054, 2947, 1721, 1658, 1600, 1493, 1444, 1172, 969, 807 cm^{-1}; HRMS (ES) Calcd for $C_{11}H_{11}O_2NaCl$: 233.0345 $[M+Na]^+$; Found: 233.0343.

(*E*)-4-Bromobenzyl but-2-enoate (5d)



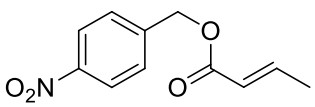
Yellowish oil (73.5 mg, 96 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (dd, J = 1.6, 6.8 Hz, 3H), 5.11 (s, 2H), 5.86–5.91 (m, 1H), 7.00–7.05 (m, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 65.1, 122.2, 122.3, 129.8, 131.7, 135.2, 145.6, 166.2; IR (neat) 3053, 2944, 2852, 1724, 1659, 1595, 1490, 1443, 1172, 968, 802 cm^{-1}; HRMS (ES) Calcd for $C_{11}H_{11}O_2NaBr$: 276.9844 $[M+Na]^+$; Found: 276.9840.

(*E*)-2,4-Dichlorobenzyl but-2-enoate (5e)



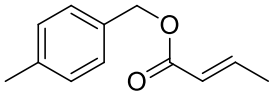
Colorless oil (69.1 mg, 94 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90 (dd, J = 1.6, 6.8 Hz, 3H), 5.23 (s, 2H), 5.88–5.94 (m, 1H), 7.01–7.08 (m, 1H), 7.24 (dd, J = 8.3, 2.1 Hz, 1H), 7.34 (d, J = 8.3Hz, 1H), 7.39 (d, J = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 62.6, 122.1, 127.2, 129.4, 130.5, 132.6, 134.3, 134.5, 145.9, 166.0; IR (neat) 3069, 2944, 2853, 1724, 1658, 1591, 1565, 1477, 1443, 1175, 968, 859, 838 cm^{-1}; HRMS (ES) Calcd for $C_{11}H_{10}O_2NaCl_2$: 266.9956 $[M+Na]^+$; Found: 266.9963.

(*E*)-4-Nitrobenzyl but-2-enoate (5f)[10]



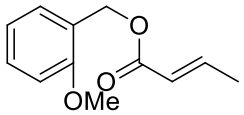
Colorless solid, mp 68–70 °C (63.2 mg, 95 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92 (dd, J = 1.6, 6.8 Hz, 2H), 5.27 (s, 2H), 5.91–5.95 (m, 1H), 7.03–7.12 (m, 1H), 7.53 (d, J = 8.4 Hz, 2H), 8.21 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 64.4, 121.9, 123.7, 128.2, 143.6, 146.2, 147.6, 165.8.

(*E*)-4-Methylbenzyl but-2-enoate (5h)



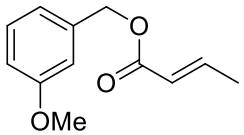
Colorless oil (55.4 mg, 97 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.87 (dd, J = 1.6, 6.8 Hz, 3H), 2.35 (s, 3H), 5.12 (s, 2H), 5.85–5.90 (m, 1H), 6.96–7.05 (m, 1H), 7.17 (d, J = 7.6 Hz, 2H), 7.26 (d, J = 8.0Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 21.2, 65.9, 122.6, 128.4, 129.2, 133.2, 138.0, 145.0, 166.4; IR (neat) 3032, 2950, 2921, 1721, 1659, 1519, 1444, 1376, 1175, 969, 806 cm^{-1}; HRMS (ES) Calcd for $C_{12}H_{14}O_2Na$: 213.0891 $[M+Na]^+$; Found: 213.0896.

(*E*)-2-Methoxybenzyl but-2-enoate (5i)



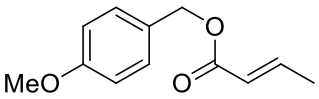
Colorless oil (59.4 mg, 96 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.87 (dd, J = 1.6, 7.2 Hz, 3H), 3.83 (s, 3H), 5.23 (s, 2H), 5.88–5.93 (m, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.92–6.96 (m, 1H), 6.97–7.05 (m, 1H), 7.27–7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 55.4, 61.4 110.4, 120.4, 122.7 124.5, 129.4, 129.5, 144.8, 157.5, 166.5; IR (neat) 3005, 2942, 2839, 1720, 1658, 1605, 1591, 1496, 1464, 1377, 1180, 969, 754 cm^{-1}; HRMS (ES) Calcd for $C_{12}H_{14}O_3Na$: 229.0841 $[M+Na]^+$; Found: 229.0844.

(*E*)-3-Methoxybenzyl but-2-enoate (5j)



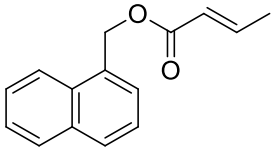
Yellowish oil (56.9 mg, 92 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (dd, J = 1.6, 6.8 Hz, 3H), 3.80 (s, 3H), 5.14 (s, 2H), 5.88–5.92 (m, 1H), 6.84–6.96 (m, 3H), 7.00–7.05 (m, 1H), 7.25–7.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 55.2, 65.8, 113.56, 113.62, 120.3, 122.5, 129.6, 137.7, 145.3, 159.7, 166.3; IR (neat) 3080, 3008, 2944, 2837, 1721, 1658, 1604, 1588, 1491, 1457, 1441, 1376, 1178, 969, 838, 784, 691 cm^{-1}; HRMS (ES) Calcd for $C_{12}H_{14}O_3Na$: 229.0841 $[M+Na]^+$; Found: 229.0837.

(*E*)-4-Methoxybenzyl but-2-enoate (5k)



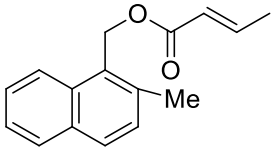
Yellowish oil (59.1 mg, 96 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.86 (dd, J = 1.6, 6.8 Hz, 3H), 3.79 (s, 3H), 5.10 (s, 2H), 5.84–5.88 (m, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.95–7.04 (m, 1H), 7.30 (d, J = 8.8Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 55.3, 65.8, 113.9, 122.6, 128.3, 130.1, 145.0, 159.6, 166.4; IR (neat) 3001, 2955, 2838, 1717, 1658, 1613, 1587, 1515, 1444, 1377, 1170, 970, 822 cm^{-1}; HRMS (ES) Calcd for $C_{12}H_{14}O_3Na$: 229.0841 $[M+Na]^+$; Found: 229.0839.

(*E*)-Naphthalen-1-ylmethyl but-2-enoate (5l)



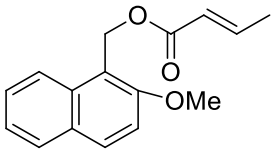
Colorless oil (65.9 mg, 97 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (dd, J = 1.6, 6.8 Hz, 3H), 5.61 (s, 2H), 5.85–5.90 (m, 1H), 6.96–7.05 (m, 1H), 7.40–7.55 (m, 4H), 7.81–7.86 (m, 2H), 8.01 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 64.4, 122.5, 123.7, 125.4, 126.0, 126.6, 127.5, 128.8, 129.3, 131.70, 131.72, 133.8, 145.4, 166.4; IR (neat) 3051, 2915, 2853, 1719, 1657, 1599, 1512, 1442, 1376, 1177, 969, 793, 777, 688 cm^{-1}; HRMS (ES) Calcd for $C_{15}H_{14}O_2Na$: 249.0891 $[M+Na]^+$; Found: 249.0889.

(*E*)-2-Methylnaphthalen-1-yl)methyl but-2-enoate (5m)



Yellowish oil (68.6 mg, 95 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (dd, J = 1.6, 7.2 Hz, 3H), 2.59 (s, 3H), 5.67 (s, 2H), 5.81–5.83 (m, 1H), 6.92–7.01 (m, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.41–7.44 (m, 1H), 7.49–7.53 (m, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 20.0, 59.8, 122.5, 123.6, 125.0, 126.7, 128.4, 128.5, 129.1, 129.2, 132.4, 132.8, 136.3, 145.2, 166.7; IR (neat) 3052, 2968, 2917, 1717, 1656, 1599, 1513, 1443, 1375, 1174, 969, 812, 742 cm^{-1}; HRMS (ES) Calcd for $C_{16}H_{16}O_2Na$: 263.1048 $[M+Na]^+$; Found: 263.1053.

(*E*)-2-Methoxynaphthalen-1-yl)methyl but-2-enoate (5n)



Yellowish solid, mp 76–78 °C (73.8 mg, 96 % yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (dd, J = 1.6, 7.2 Hz, 3H), 3.97 (s, 3H), 5.72 (s, 2H), 5.83-5.87 (m, 1H), 6.93–7.02 (m, 1H), 7.30 (d, J = 9.2 Hz, 1H), 7.35–7.38 (m, 1H), 7.49–7.53 (m, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 9.2 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 56.8, 57.0, 113.3, 116.3, 122.7, 123.2, 123.7, 127.2, 128.5, 129.0, 131.1, 133.6, 144.9, 156.1, 167.0; IR (neat) 3057, 2939, 2841, 1716, 1657, 1597, 1515, 1472, 1365, 1177, 970, 810, 748 cm^{-1}; HRMS (ES) Calcd for $C_{16}H_{16}O_3Na$: 279.0997 $[M+Na]^+$; Found: 279.0992.

4. References

(1) Zhang, S.; Wang, Y.; Feng, X.; Bao, M. *J. Am. Chem. Soc.* **2012**, *134*, 5492.

(2) Ding, R.; He, Y.; Wang, X.; Xu, J.; Chen, Y.; Feng, M.; Qi, C. *Molecules,* **2011**, *16*, 5665.

(3) Hulsman, N.; Medema, J. P.; Bos, C.; Jongejan, A.; Leurs, R.; Smit, M. J.; Esch, I. J. P. D.; Richel, D.; Wijtmans, M. *J. Med. Chem.* **2007**, *50*, 2424.

(4) Langlois, M.; Gaudy, F. *Synth. Commun.* **1992** , *22*, 1723.

(5) Collins, D. J.; Fallon, G. D.; Skene, C. E. *Aust. J. Chem.* **1992** , *45*, 71.

(6) Newman, S. G.; Bryan, C. S.; Perez, D.; Lautens, M. *Synthesis*, **2011**, *2*, 342.

(7) Pilarski, L. T.; Janson, P. G.; Szabó, K. J. *J. Org. Chem.* **2011**, *76*, 1503.

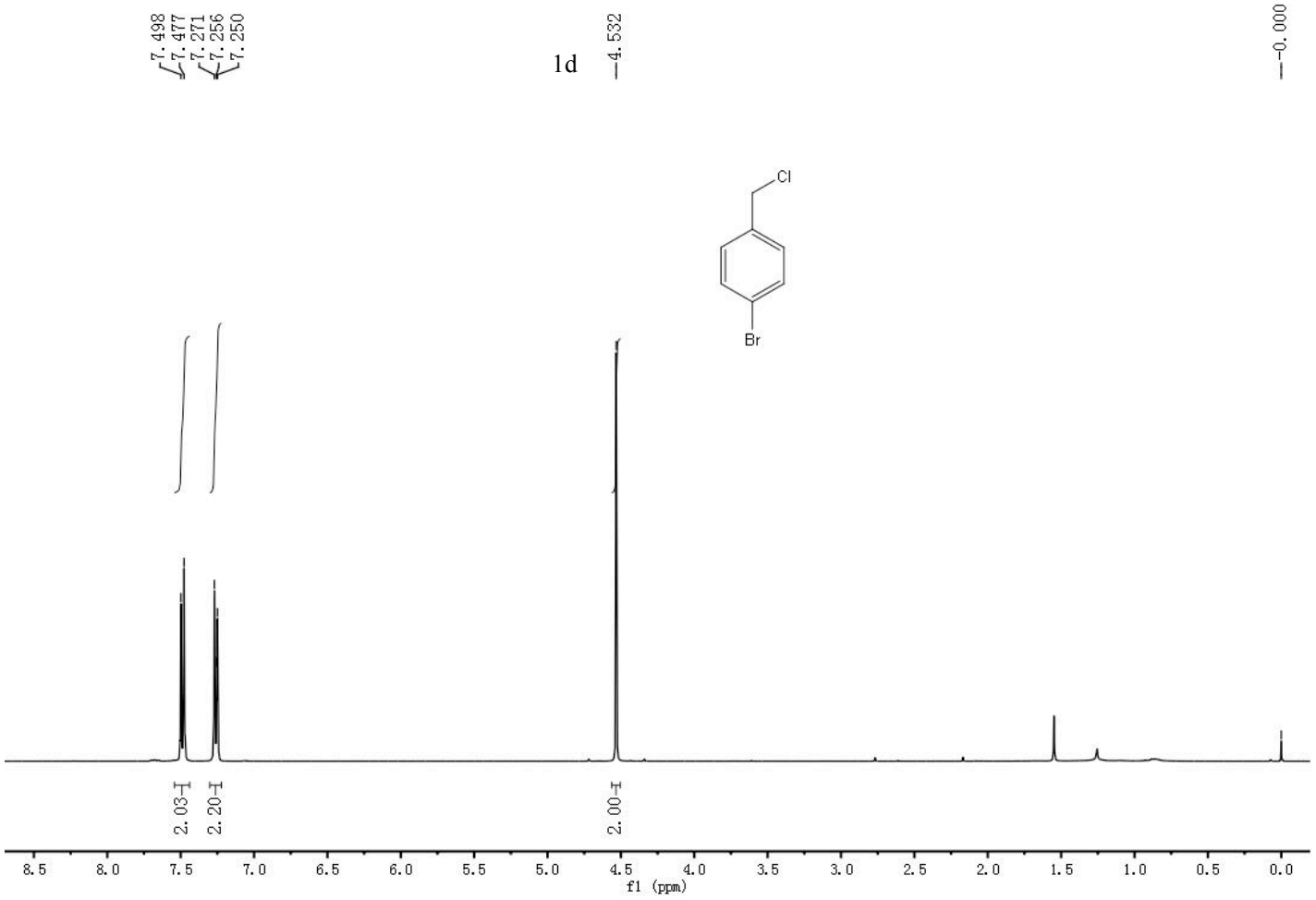
(8) Hilborn, J. W.; Pincock, J. A. *Can. J. Chem.*, **1992**, *70*, 992 .

(9) Lu, X.; Long, T. *J. Org. Chem*., **2010**, *75*, 249.

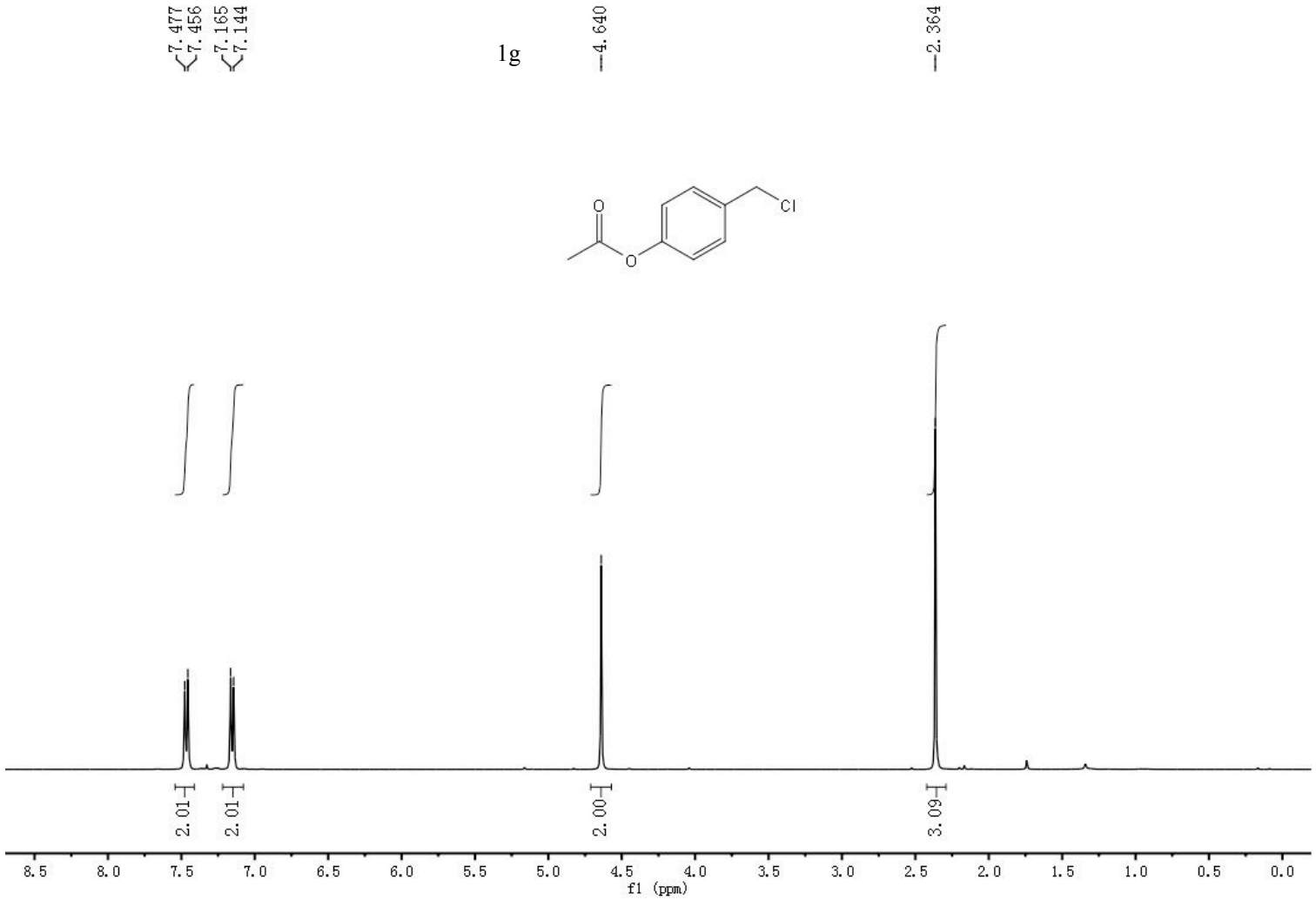
(10) Bateson, J. H.; Roberts, P. M.; Smale, T. C.; Southgate, R. *J. Chem. Soc., Perkin Trans. 1* **1990**, *6*, 1541.

5. Copies of ^{1}H and ^{13}C NMR Spectra of Starting Materials and Products

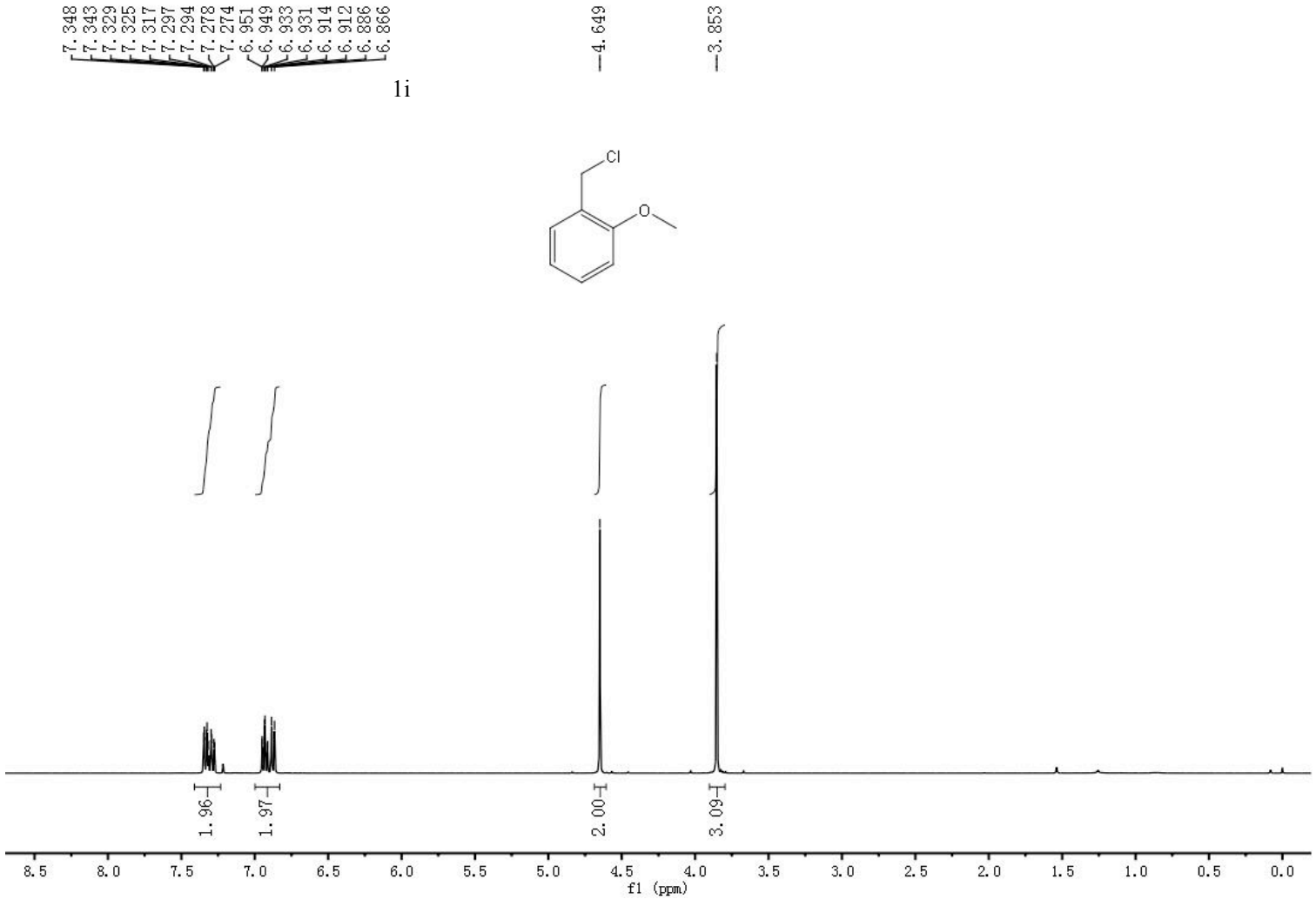
^{1}H NMR, 400 MHz, $CDCl_3$



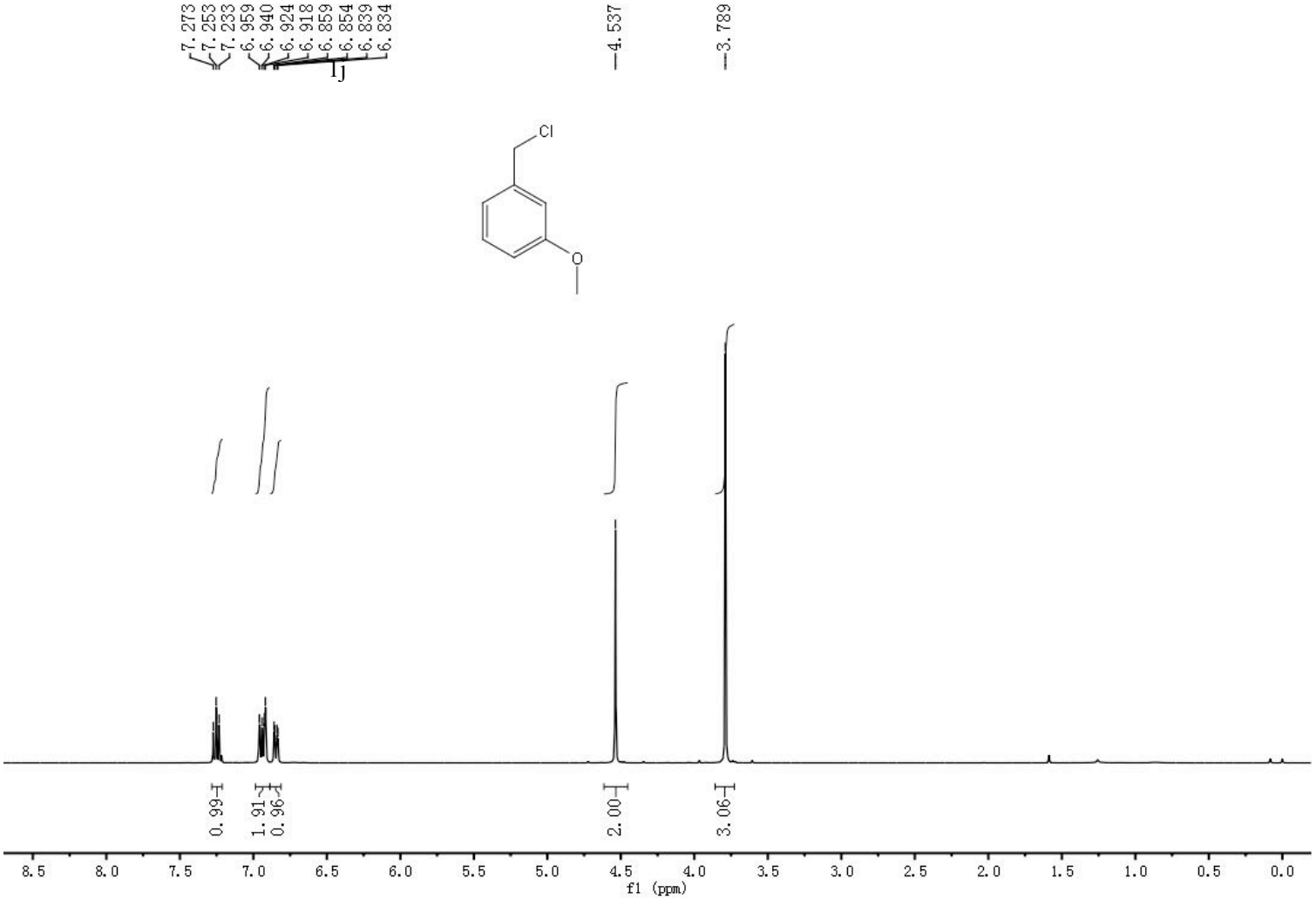
^{1}H NMR, 400 MHz, $CDCl_3$



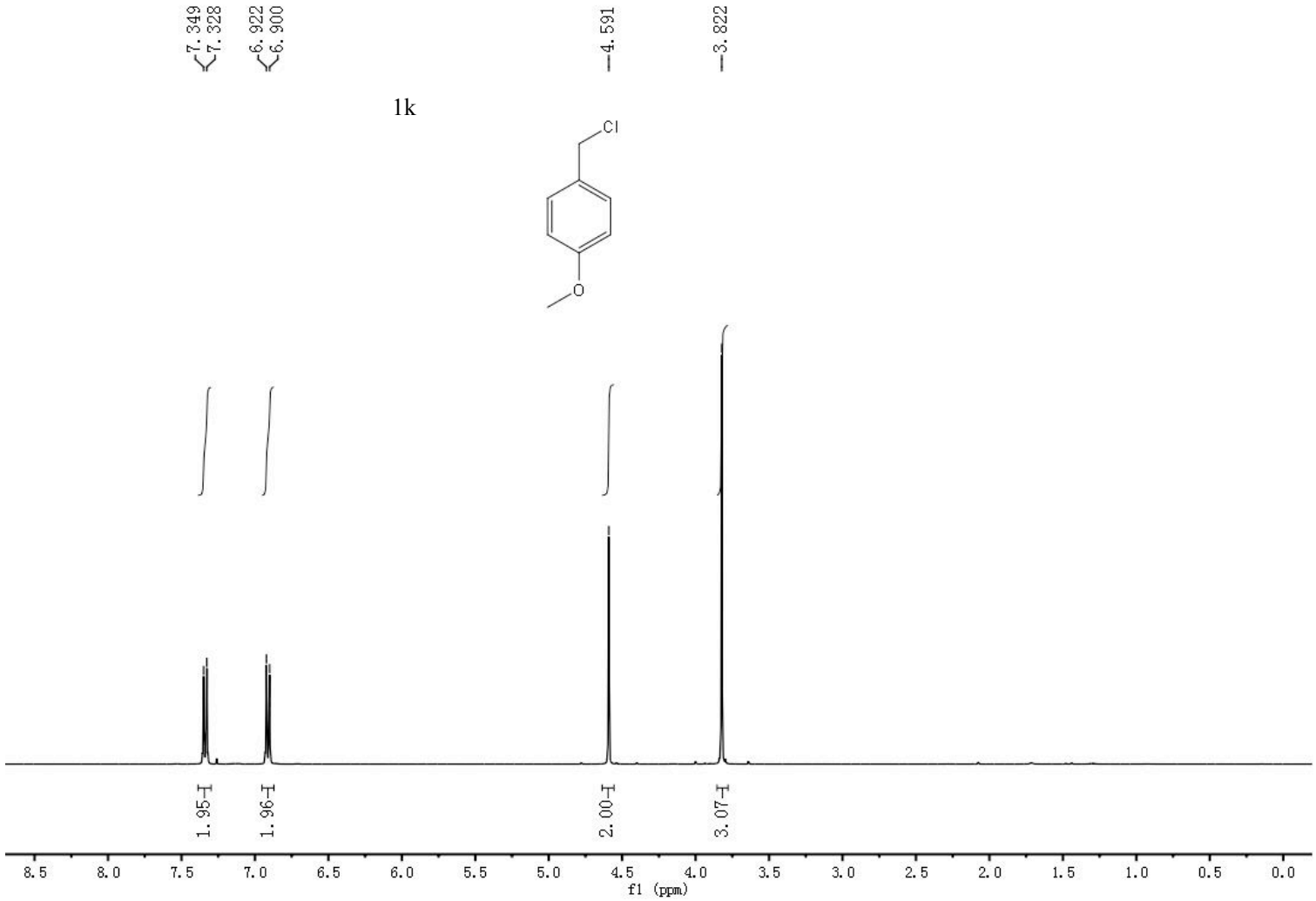
^{1}H NMR, 400 MHz, $CDCl_3$



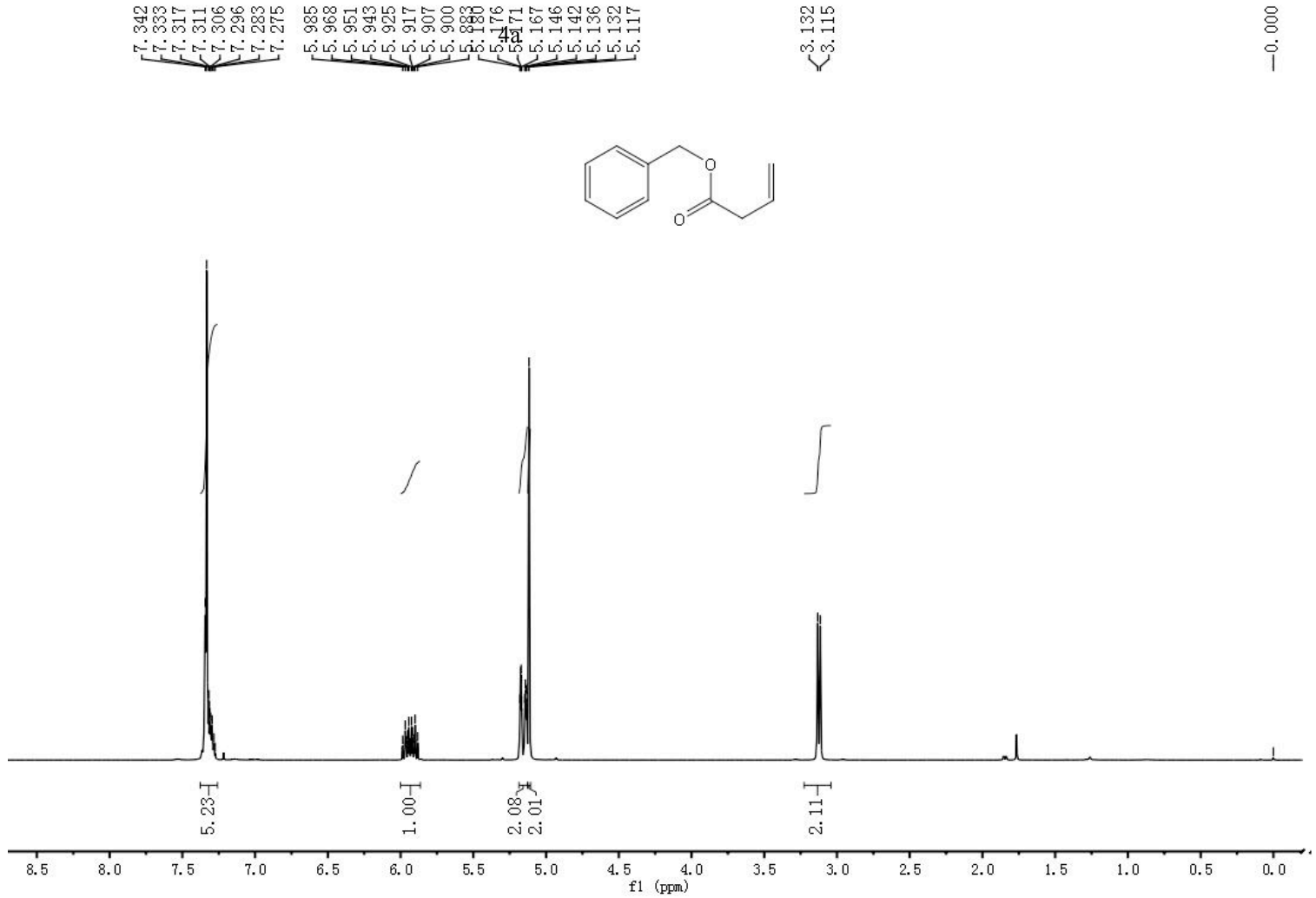
^{1}H NMR, 400 MHz, $CDCl_3$



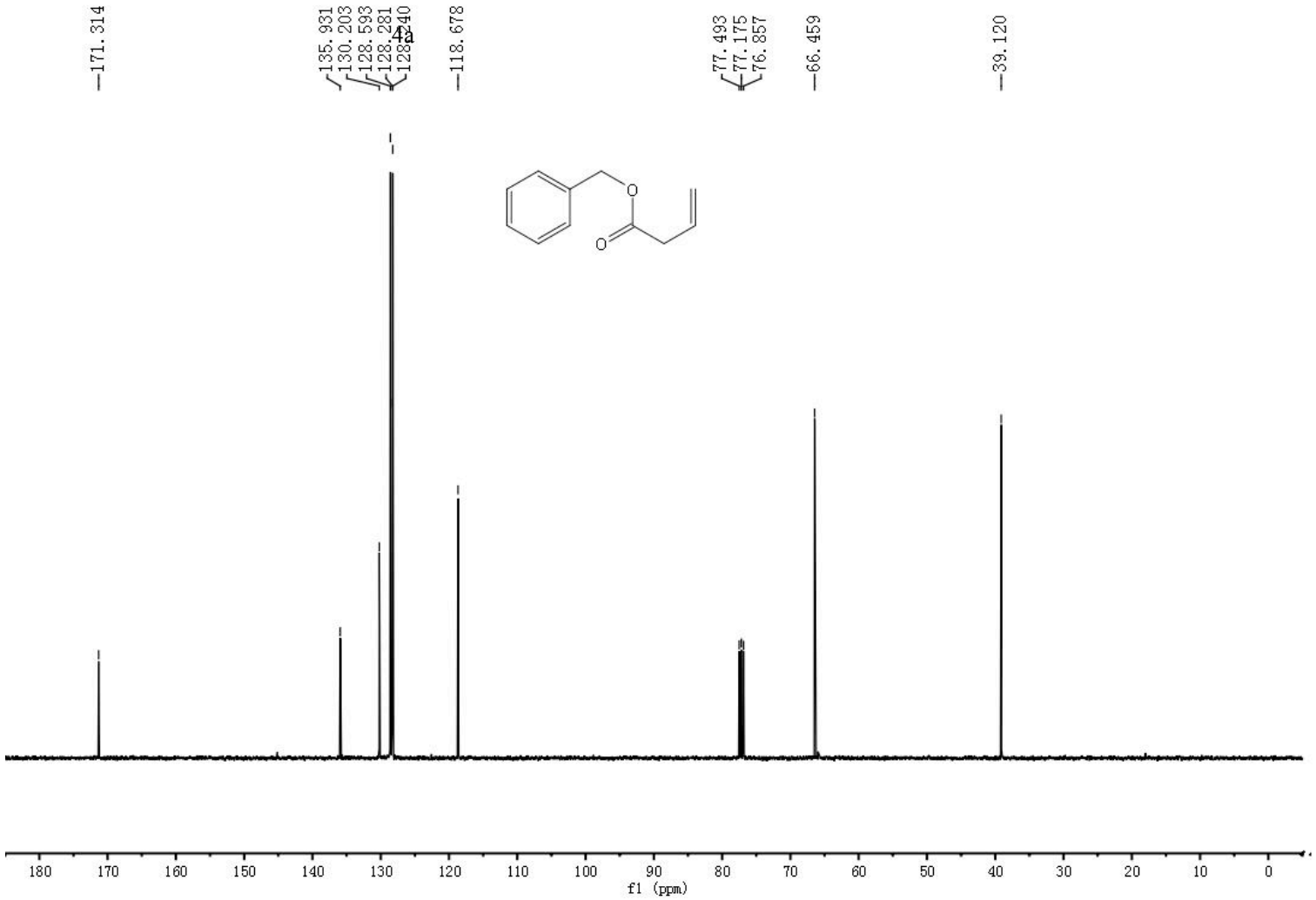
^{1}H NMR, 400 MHz, $CDCl_3$



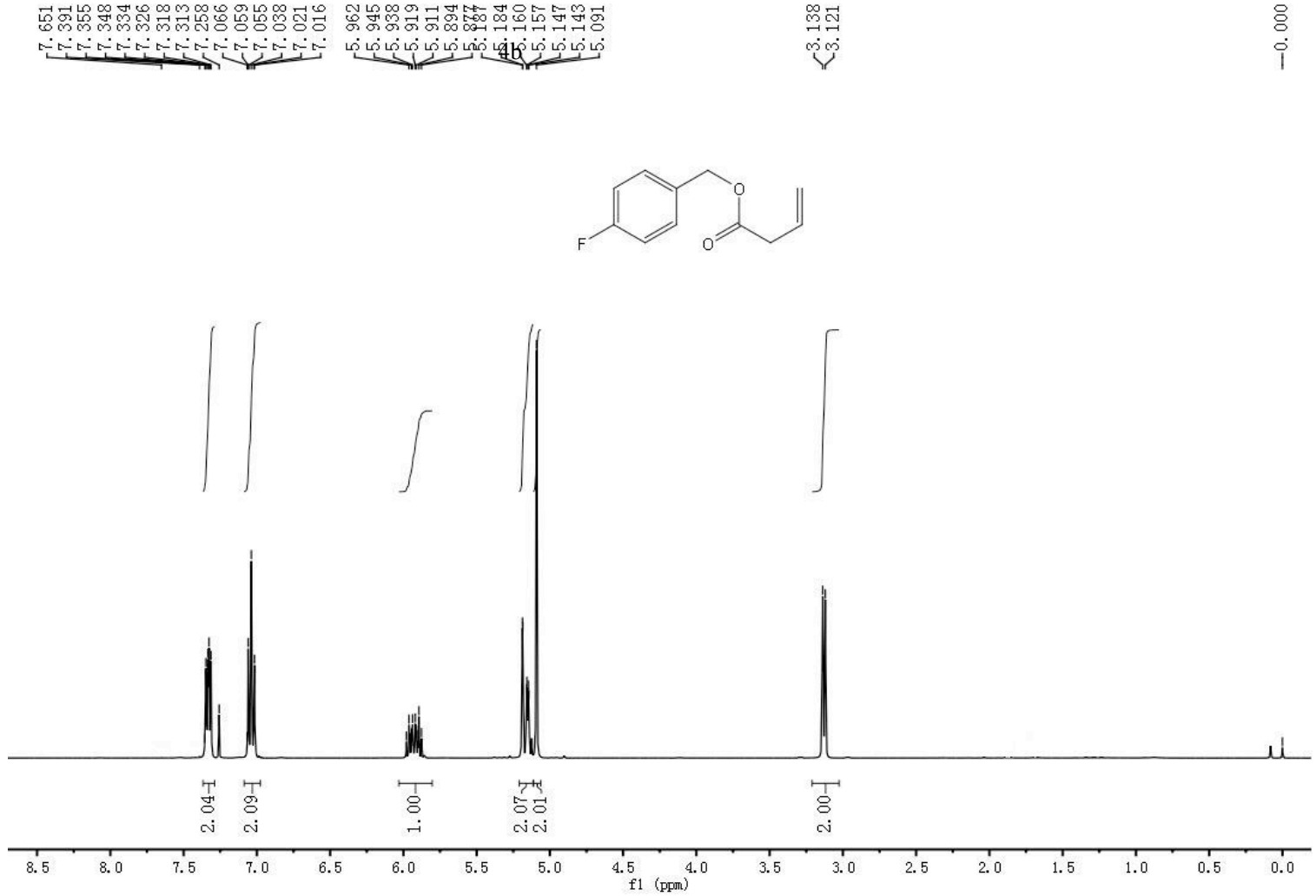
^{1}H NMR, 400 MHz, $CDCl_3$



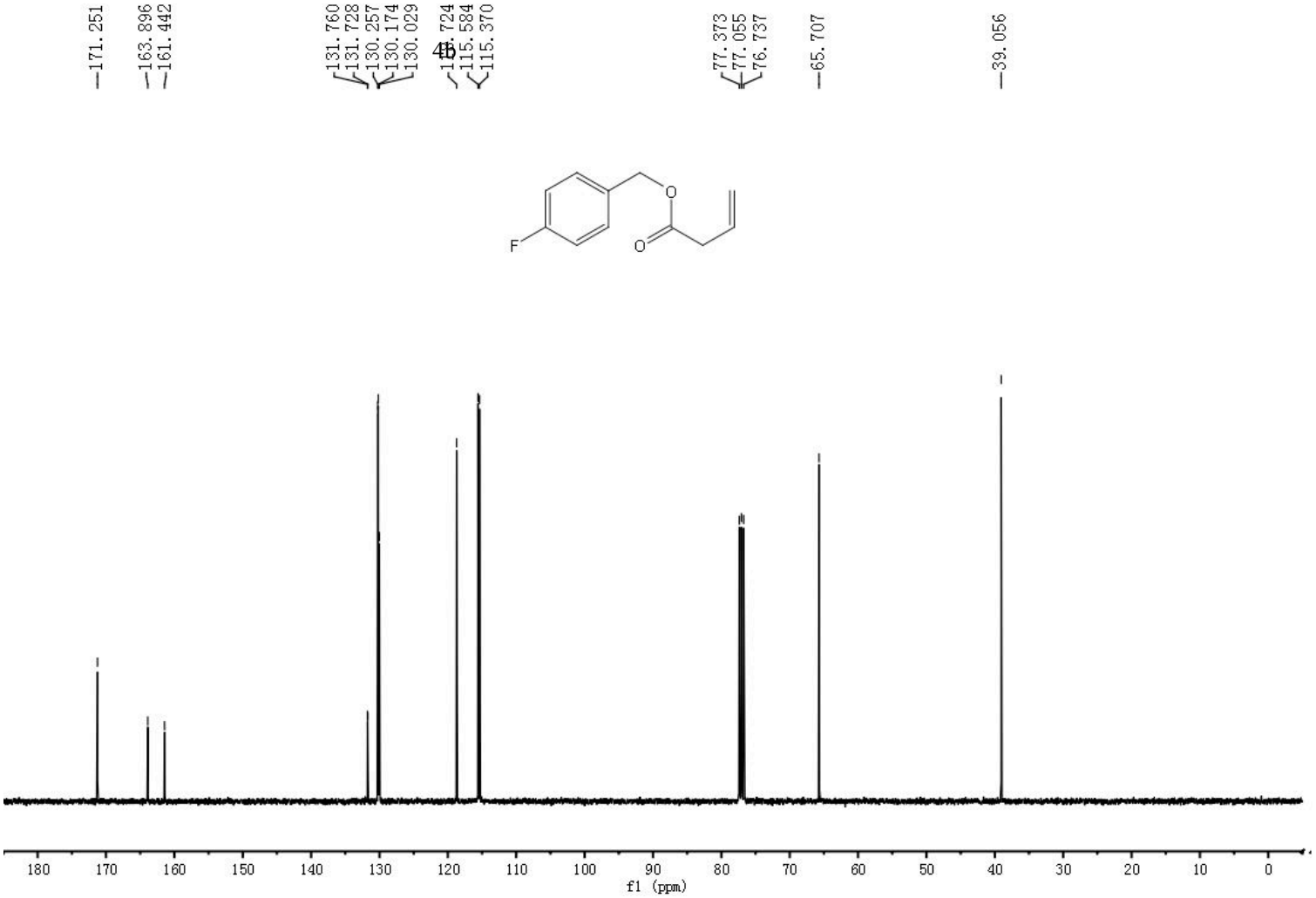
^{13}C NMR, 100 MHz, $CDCl_3$



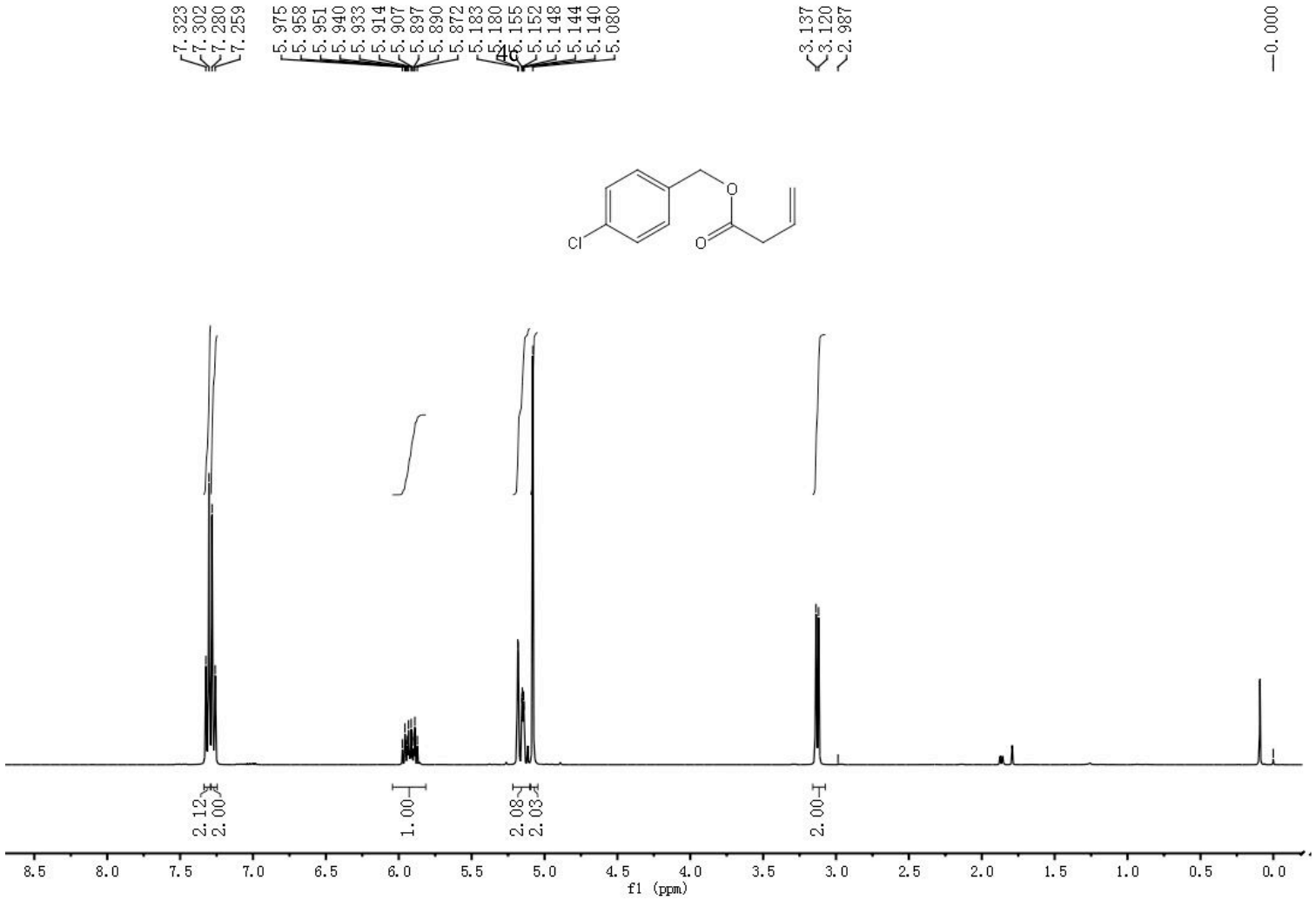
^{1}H NMR, 400 MHz, $CDCl_3$



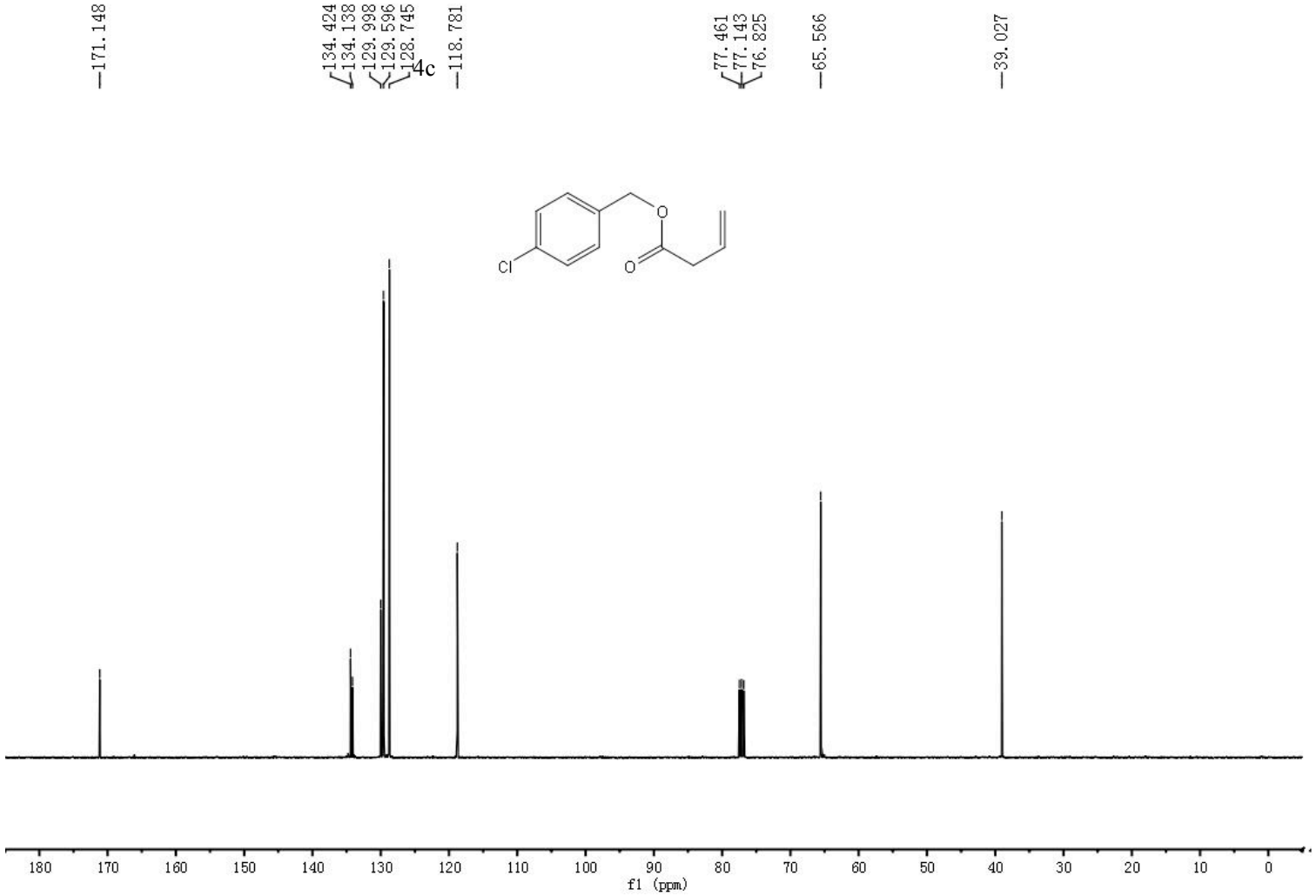
^{13}C NMR, 100 MHz, $CDCl_3$



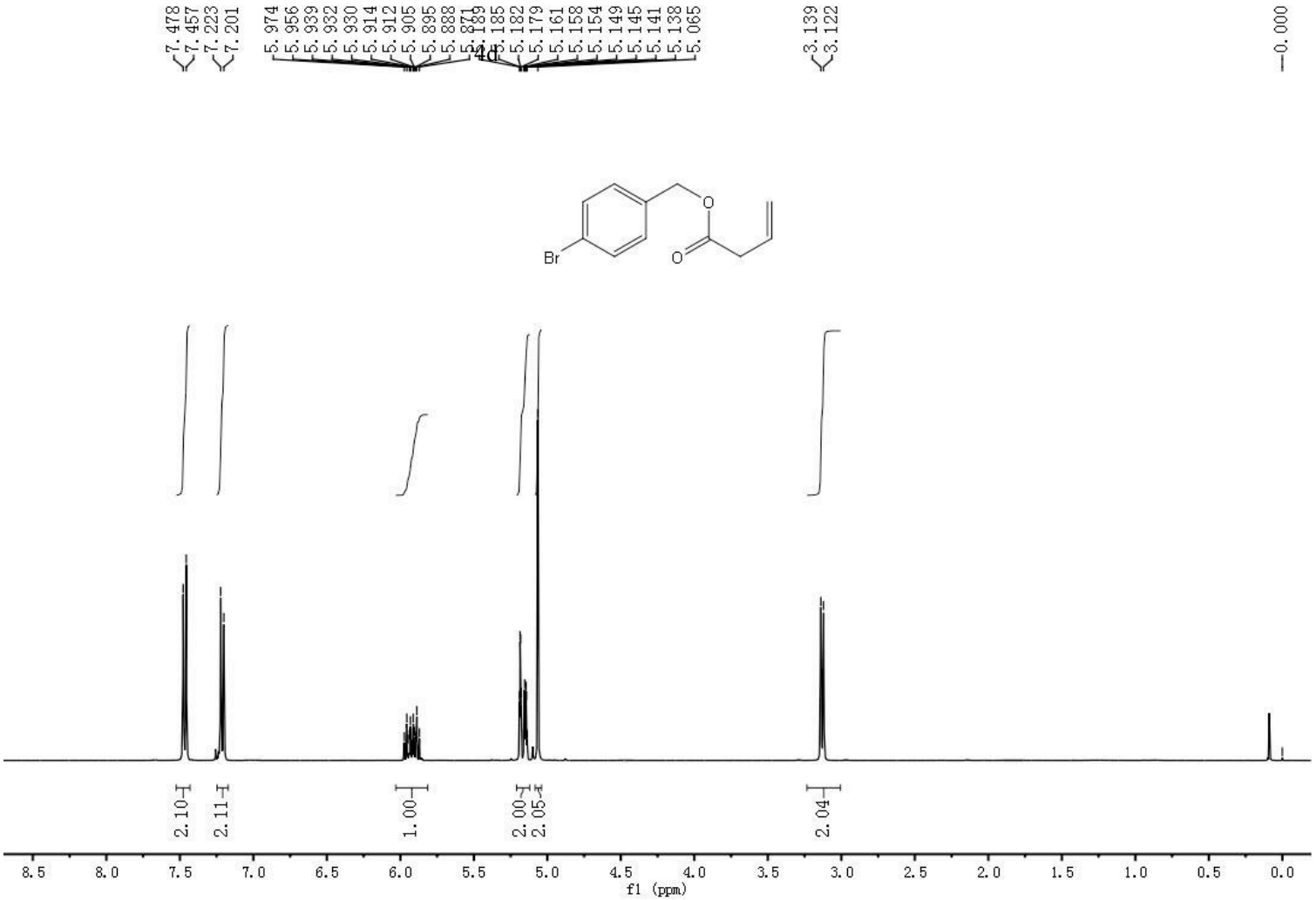
^{1}H NMR, 400 MHz, $CDCl_3$



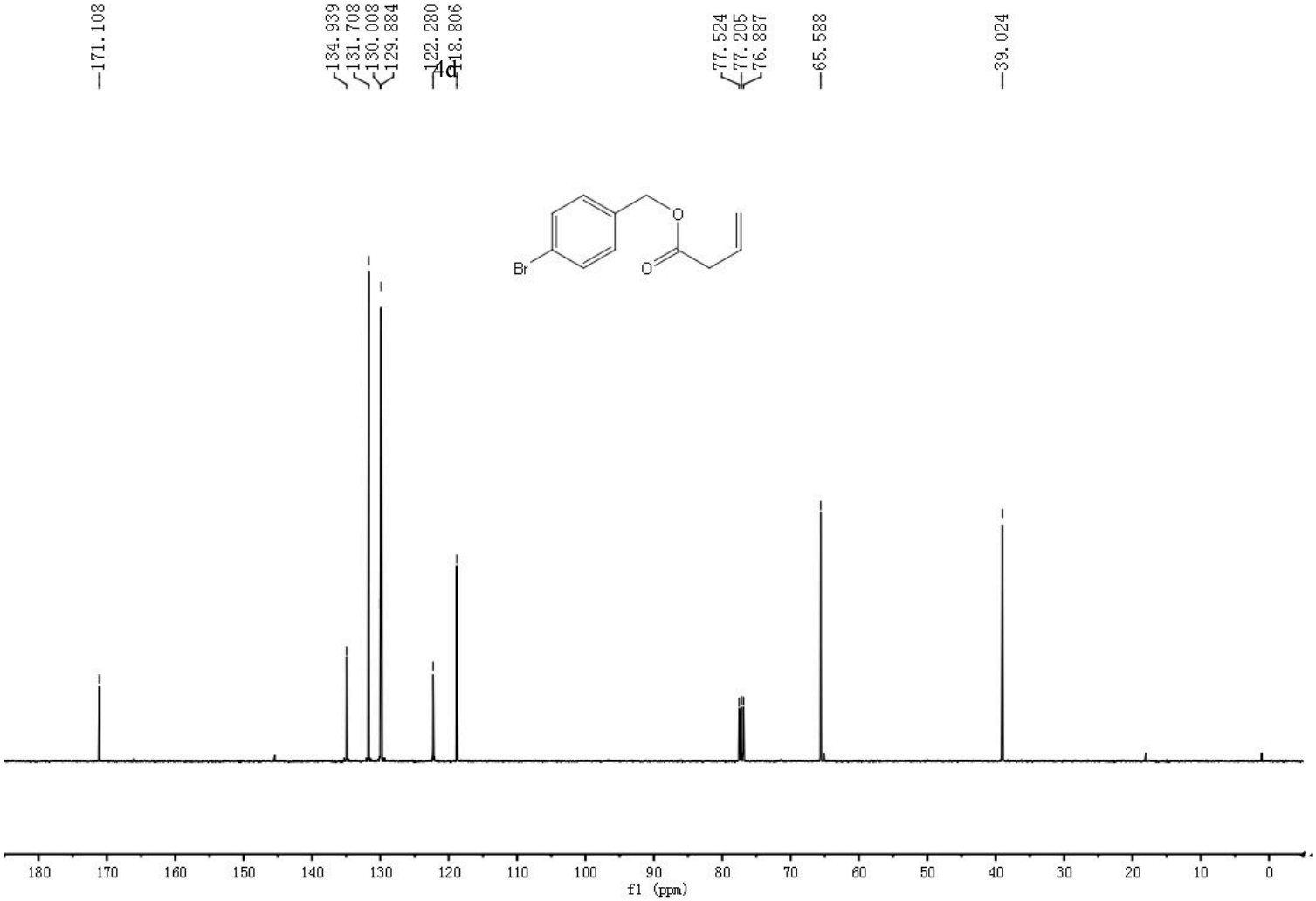
^{13}C NMR, 100 MHz, $CDCl_3$



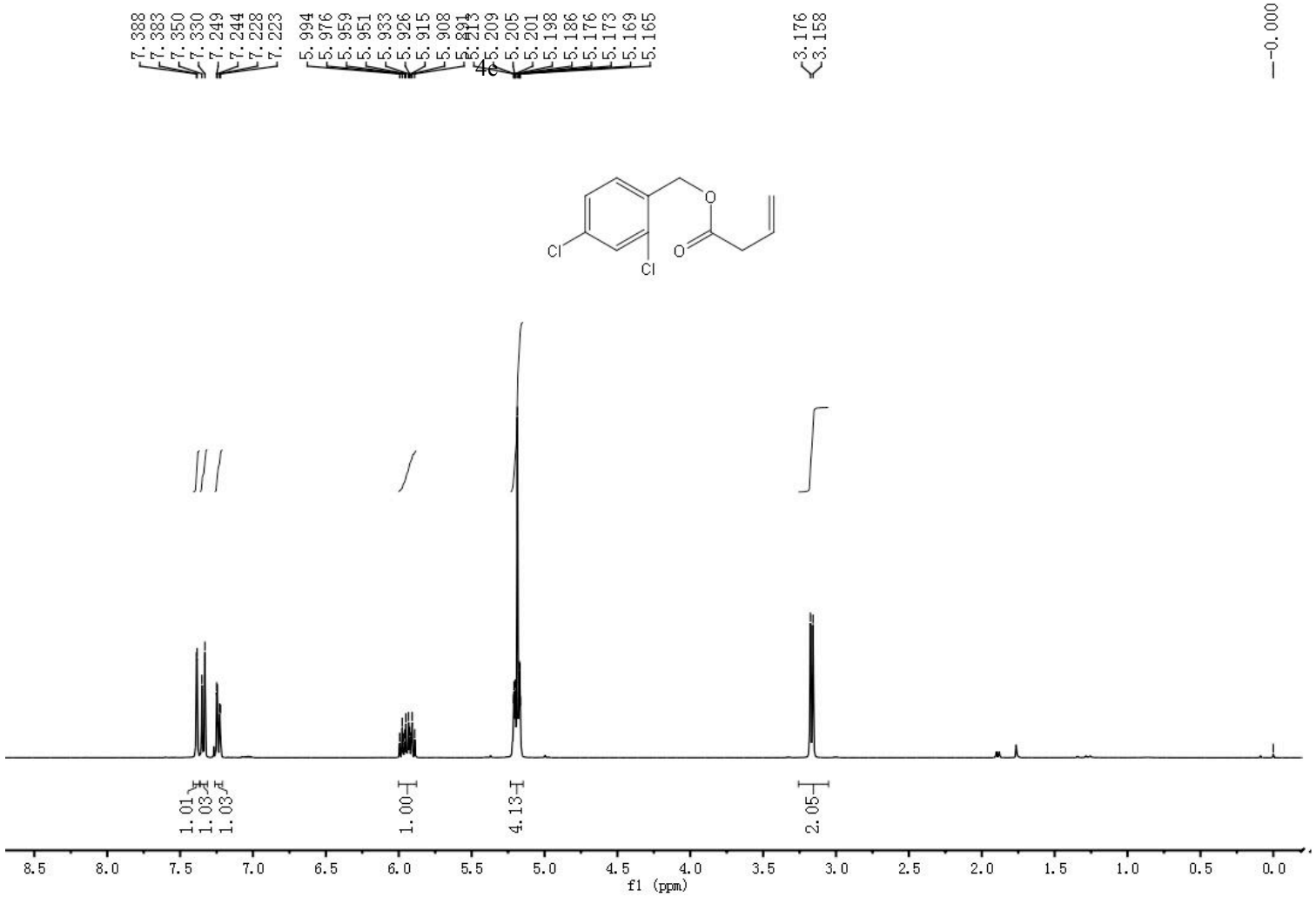
^{1}H NMR, 400 MHz, $CDCl_3$



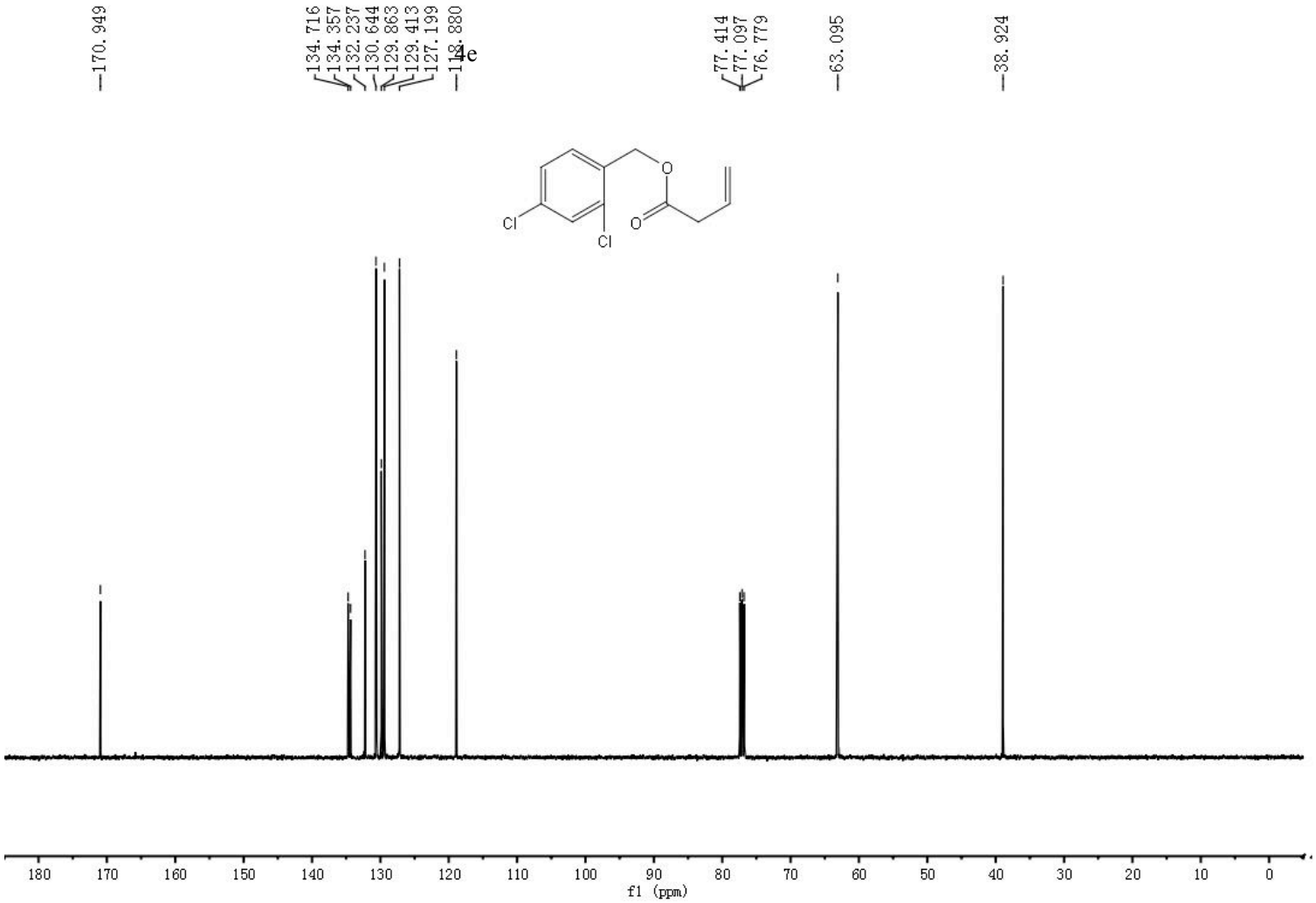
^{13}C NMR, 100 MHz, $CDCl_3$



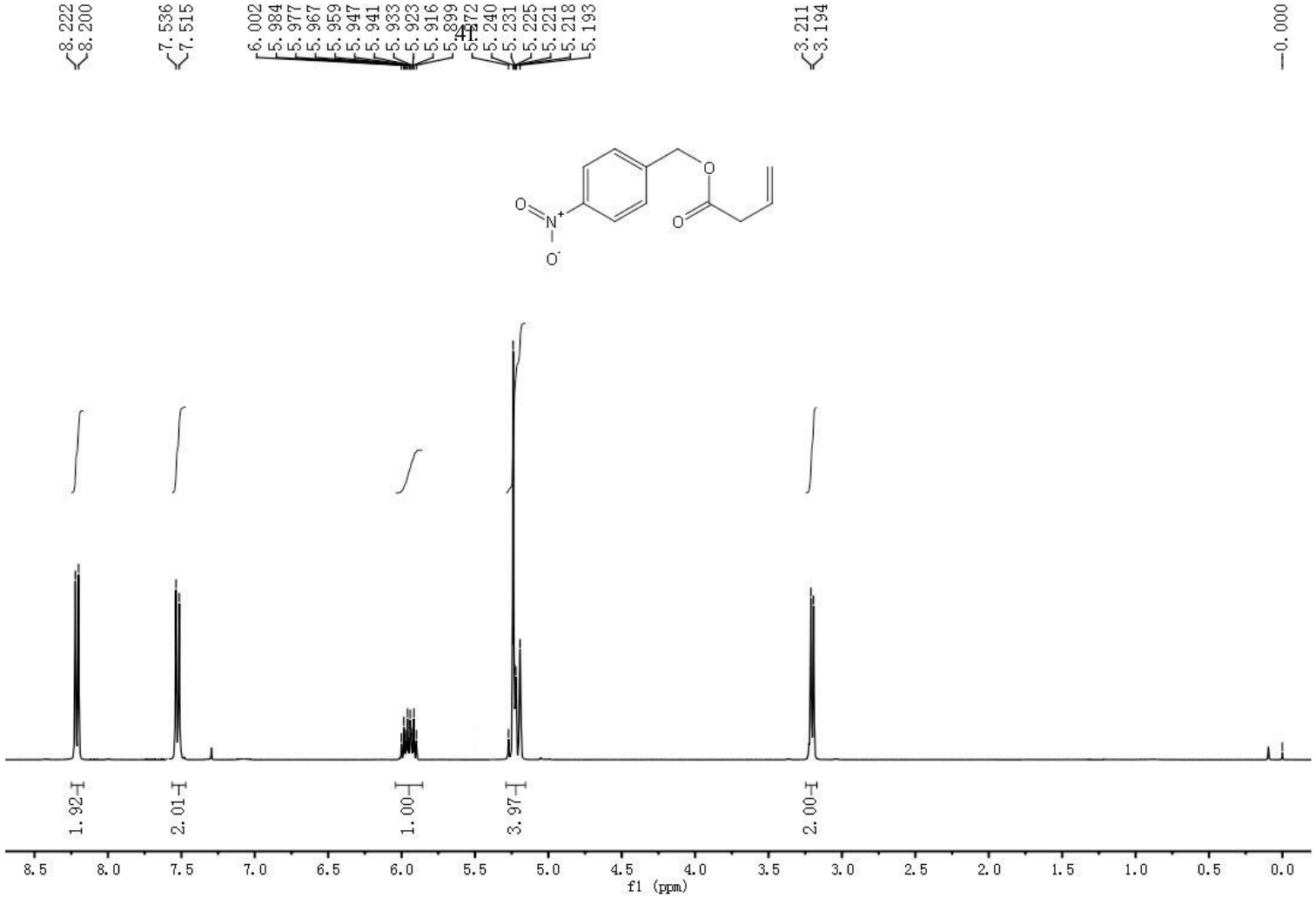
^{1}H NMR, 400 MHz, $CDCl_3$



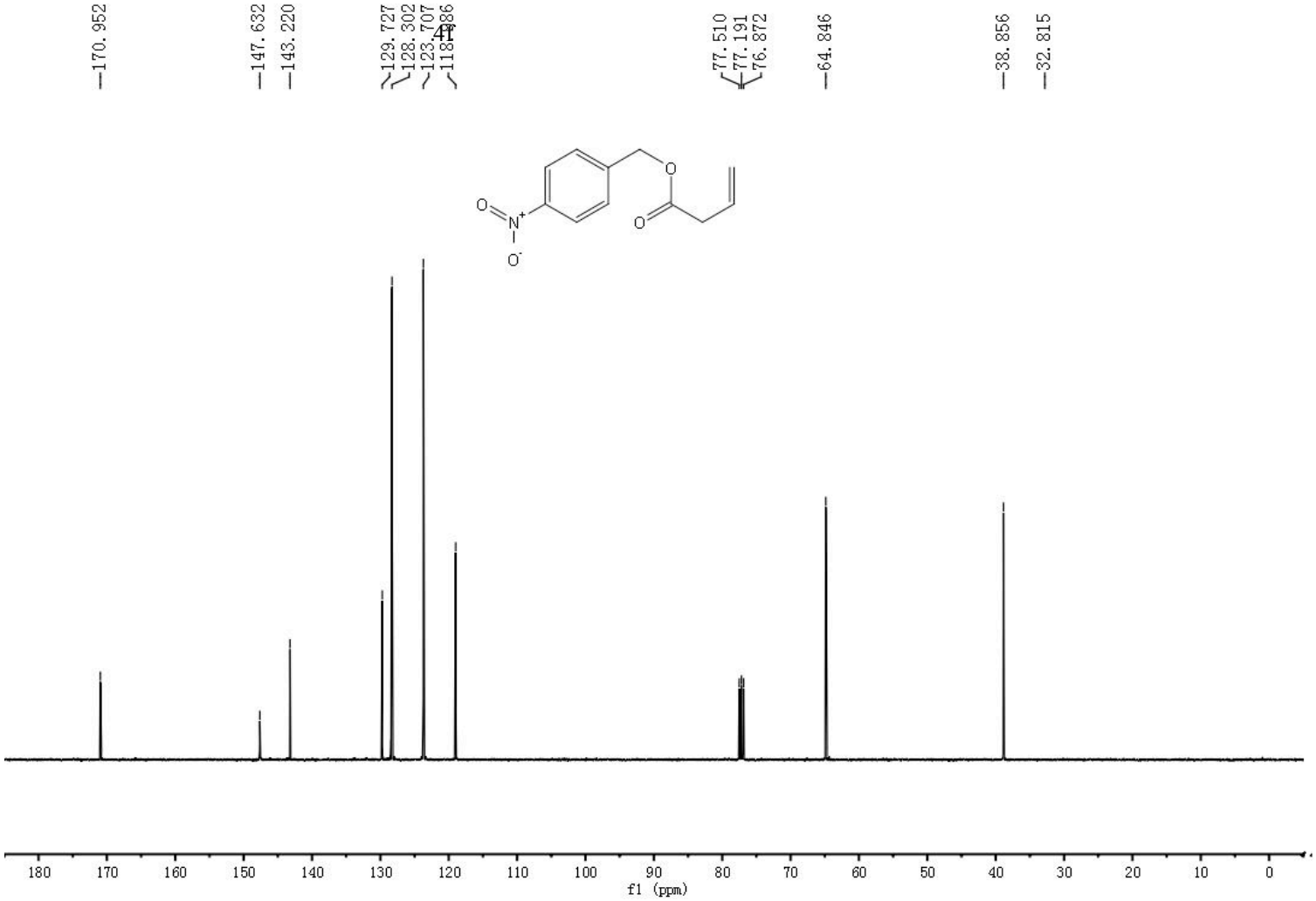
^{13}C NMR, 100 MHz, $CDCl_3$



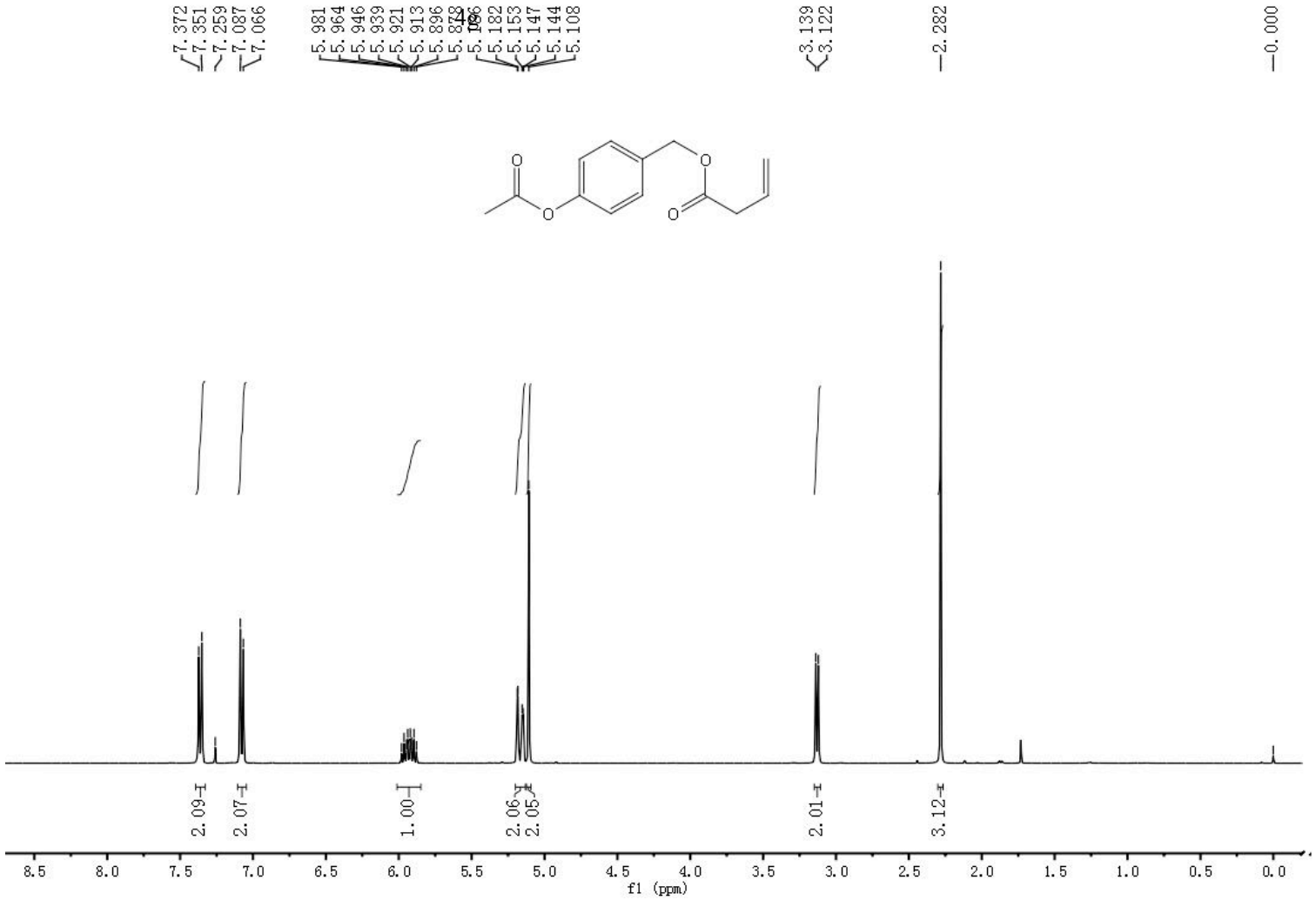
^{1}H NMR, 400 MHz, $CDCl_3$



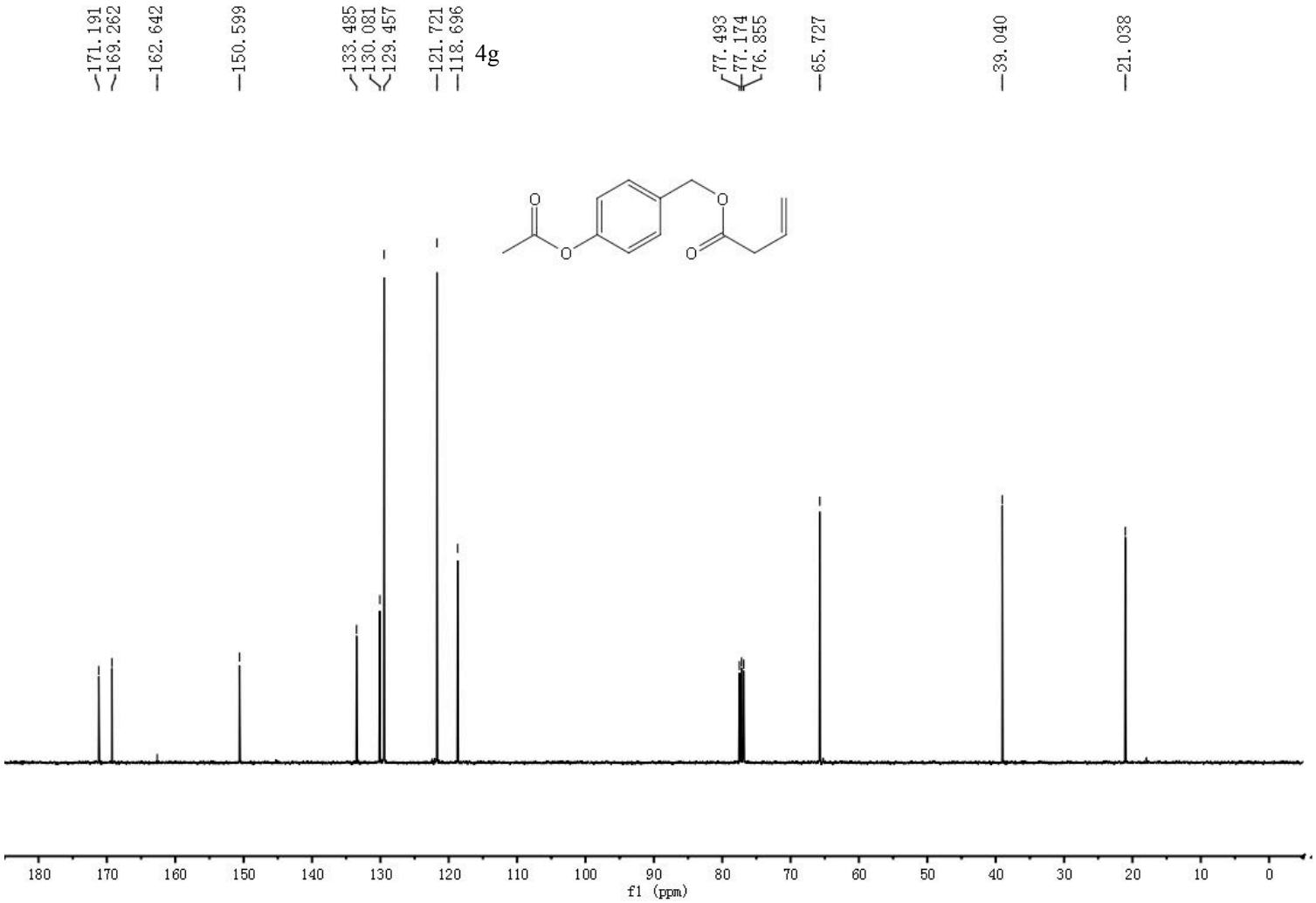
^{13}C NMR, 100 MHz, $CDCl_3$



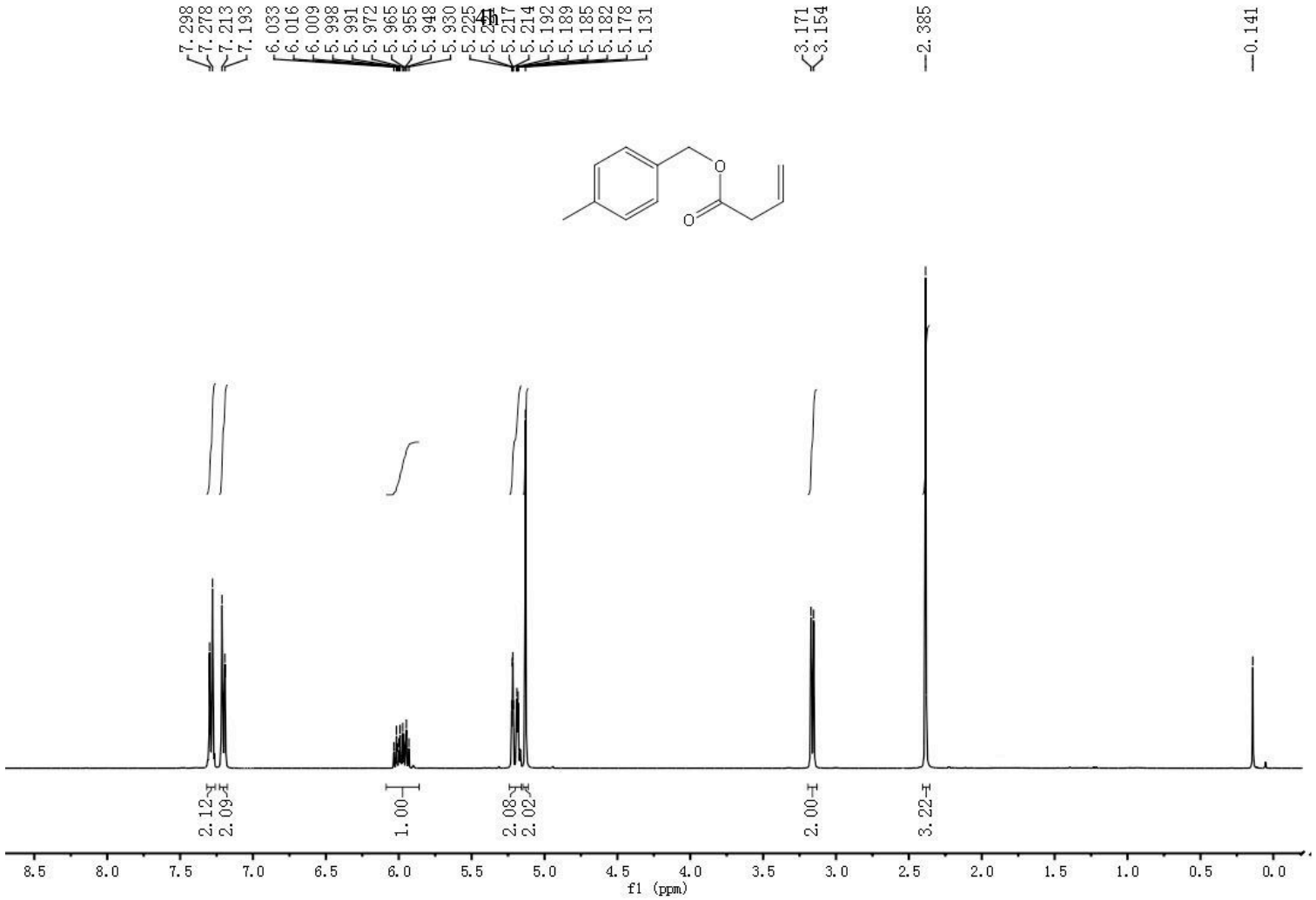
^{1}H NMR, 400 MHz, $CDCl_3$



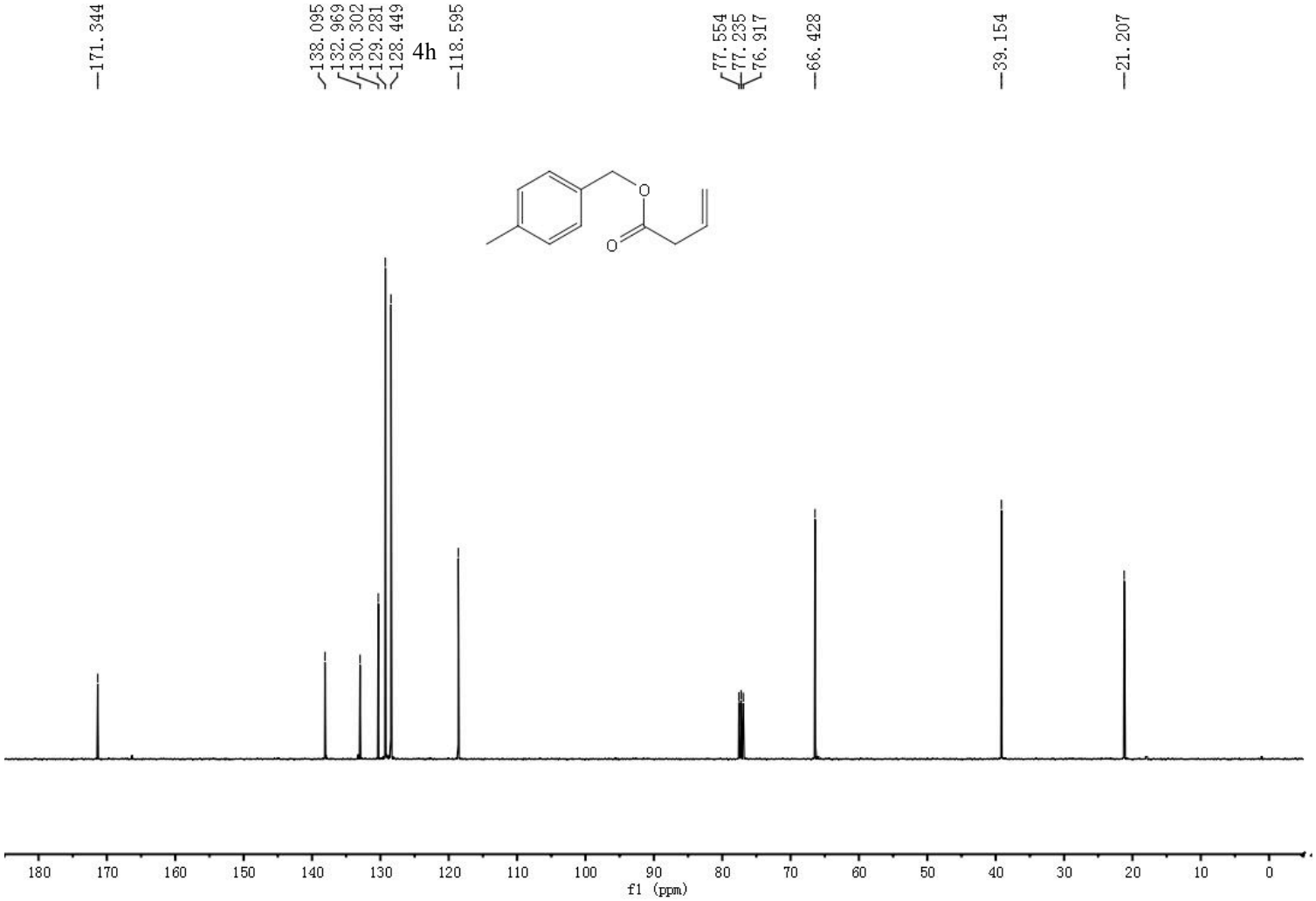
^{13}C NMR, 100 MHz, $CDCl_3$



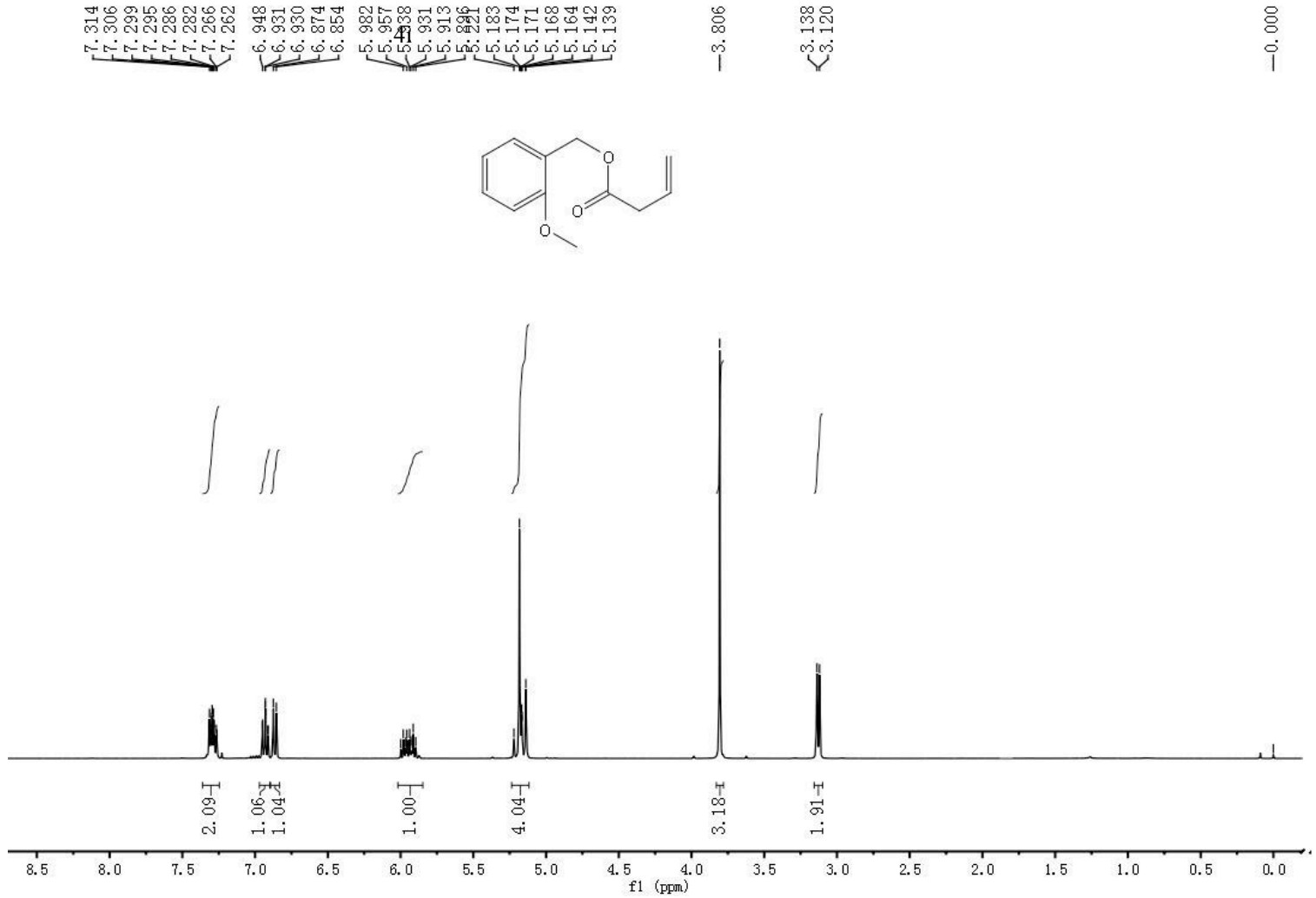
^{1}H NMR, 400 MHz, $CDCl_3$



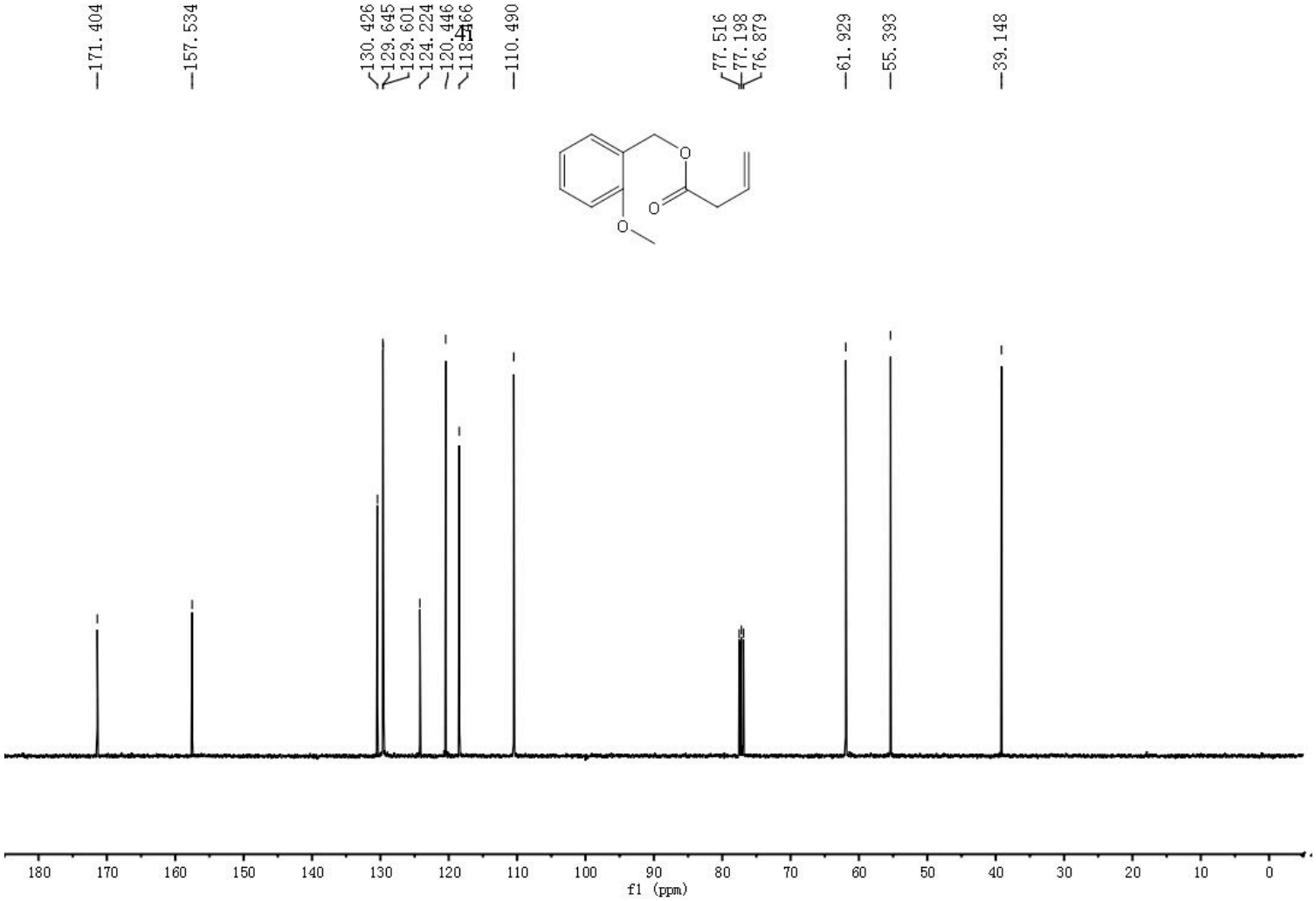
^{13}C NMR, 100 MHz, $CDCl_3$



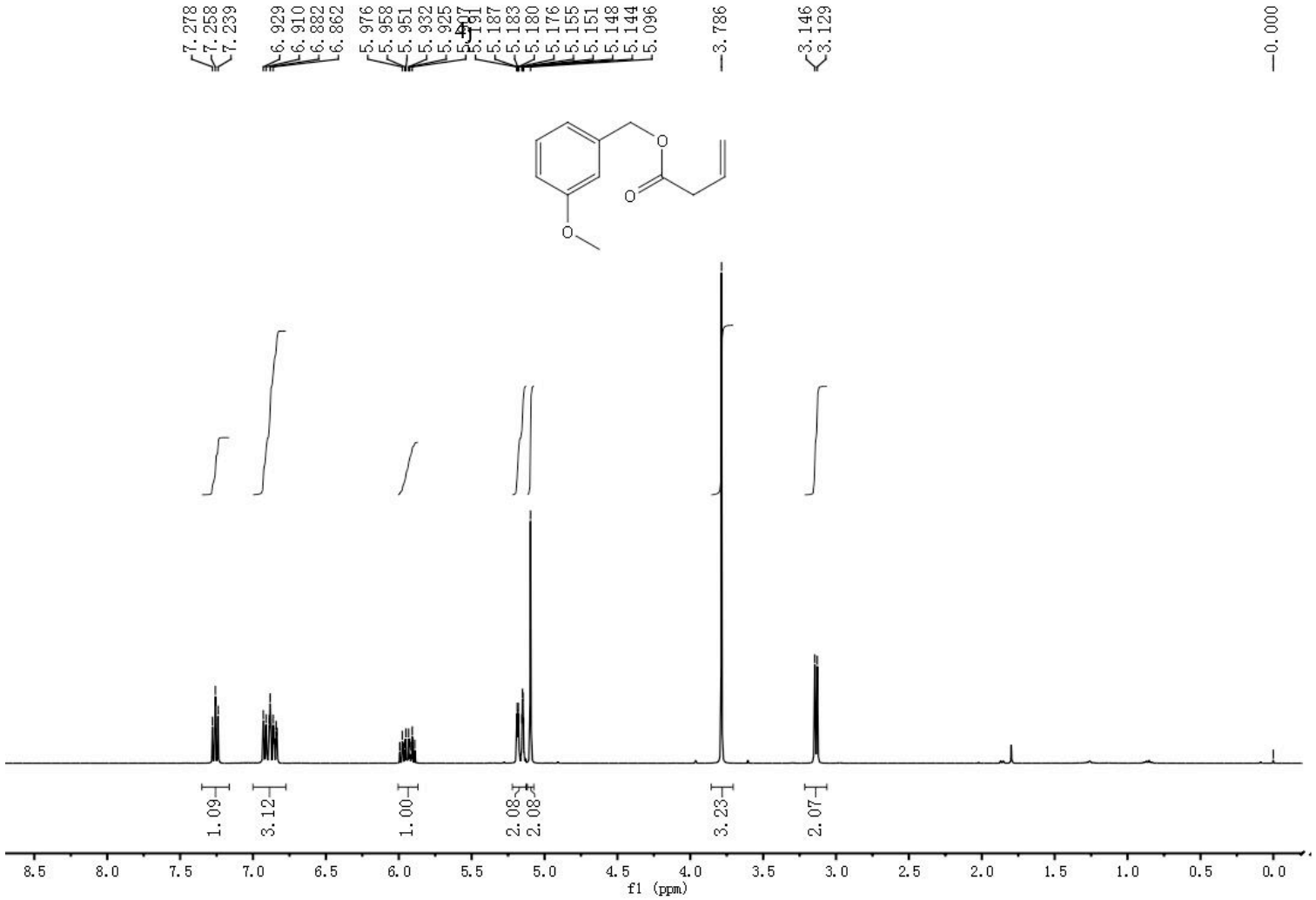
^{1}H NMR, 400 MHz, $CDCl_3$



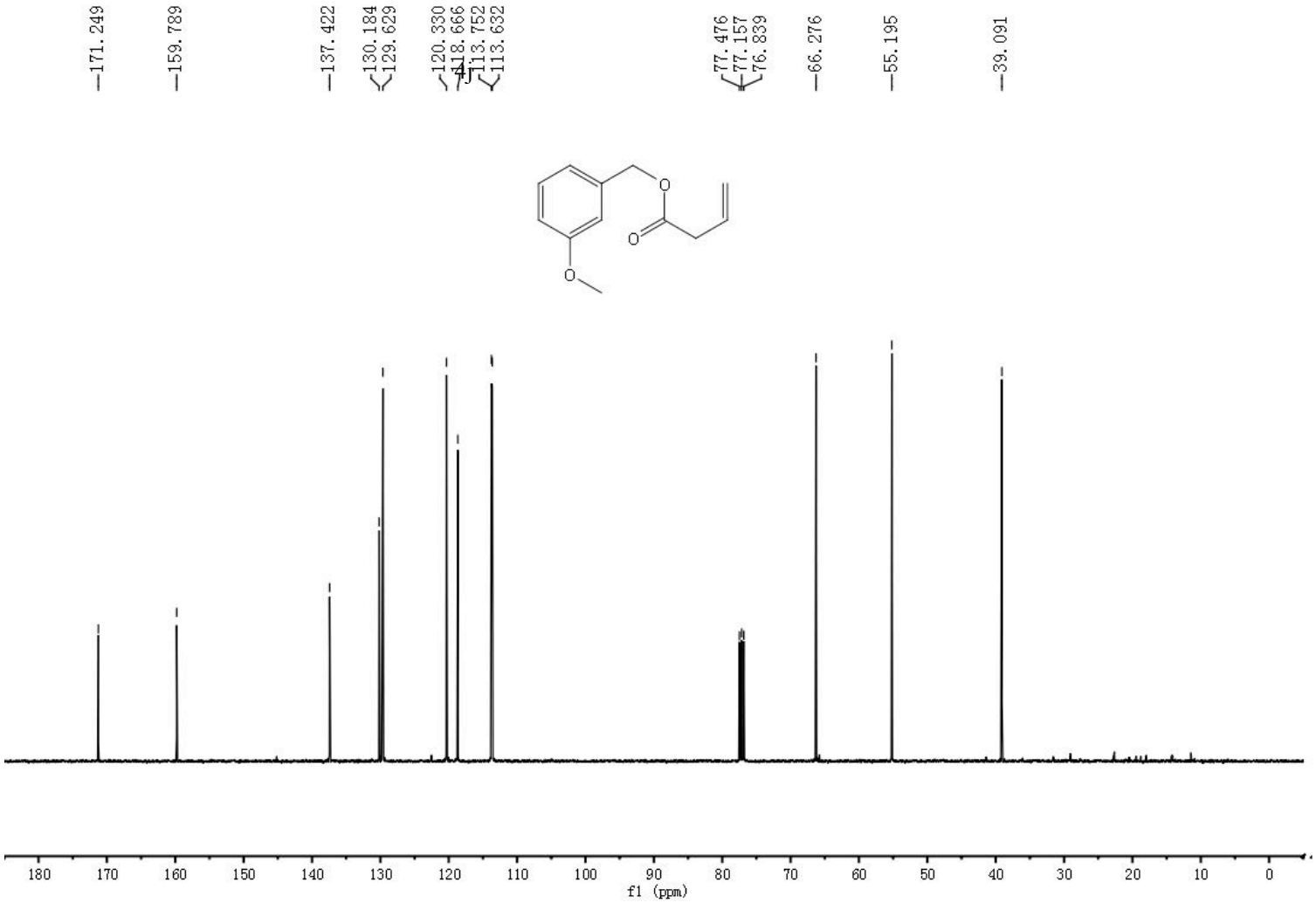
^{13}C NMR, 100 MHz, $CDCl_3$



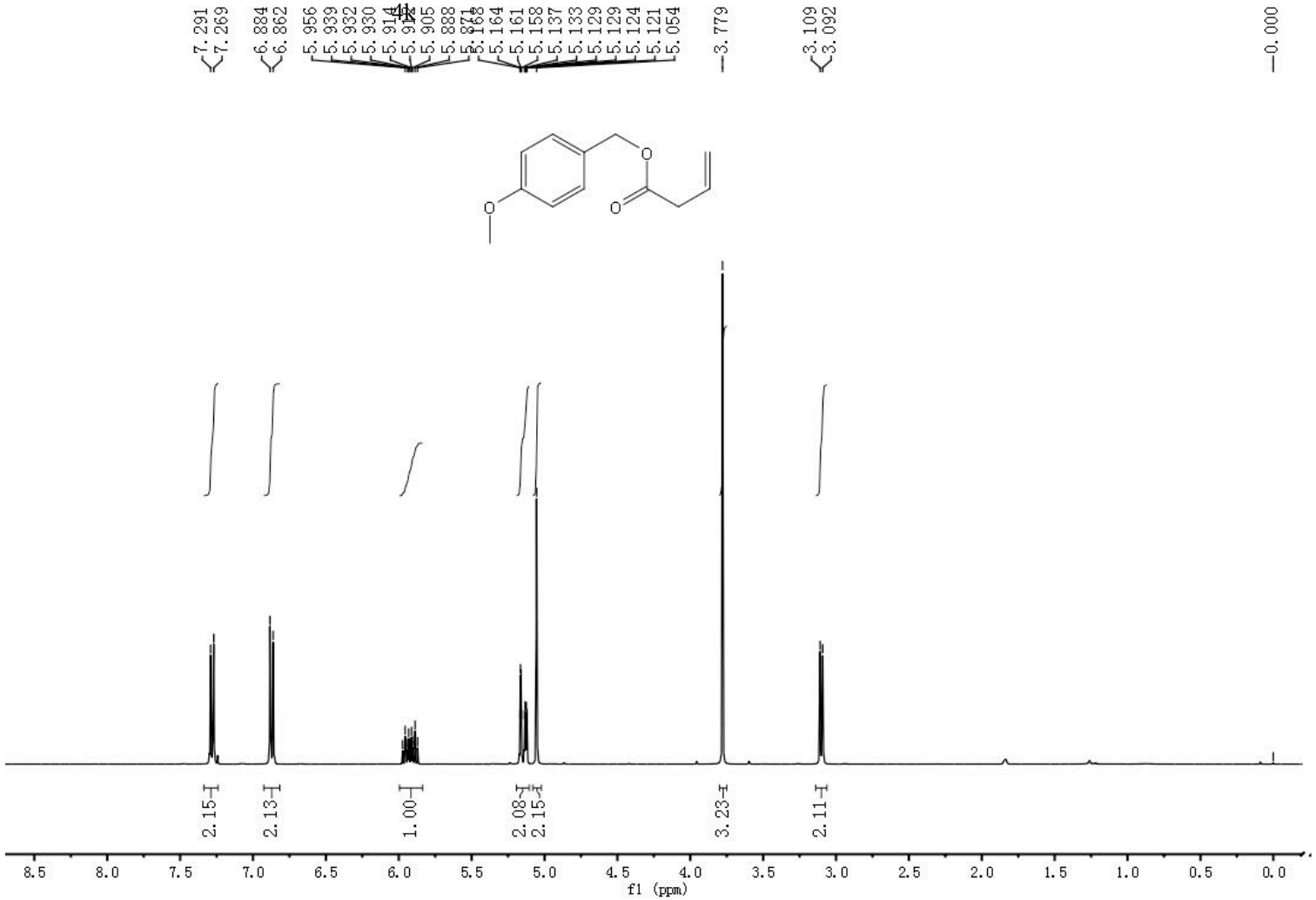
^{1}H NMR, 400 MHz, $CDCl_3$



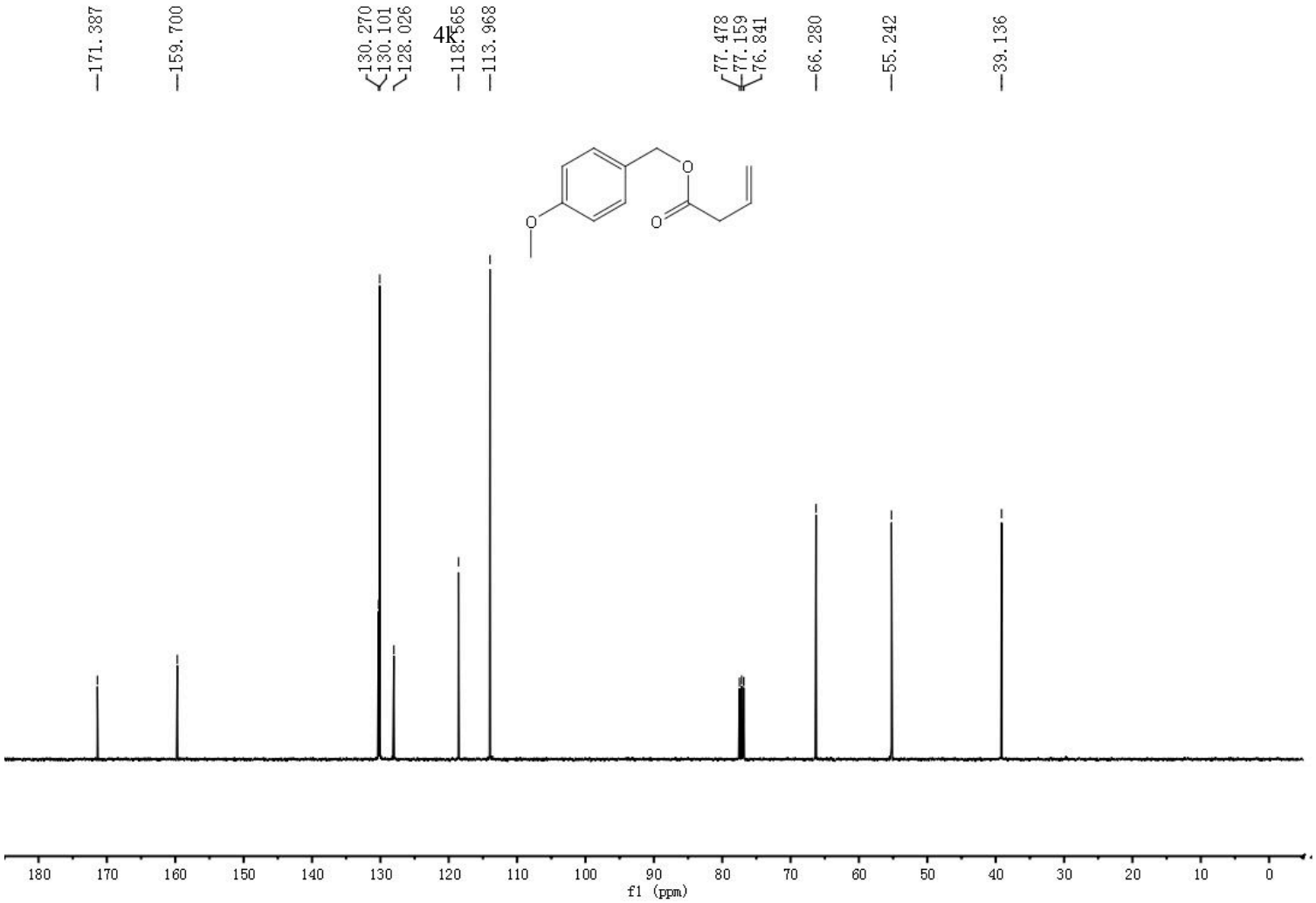
^{13}C NMR, 100 MHz, $CDCl_3$



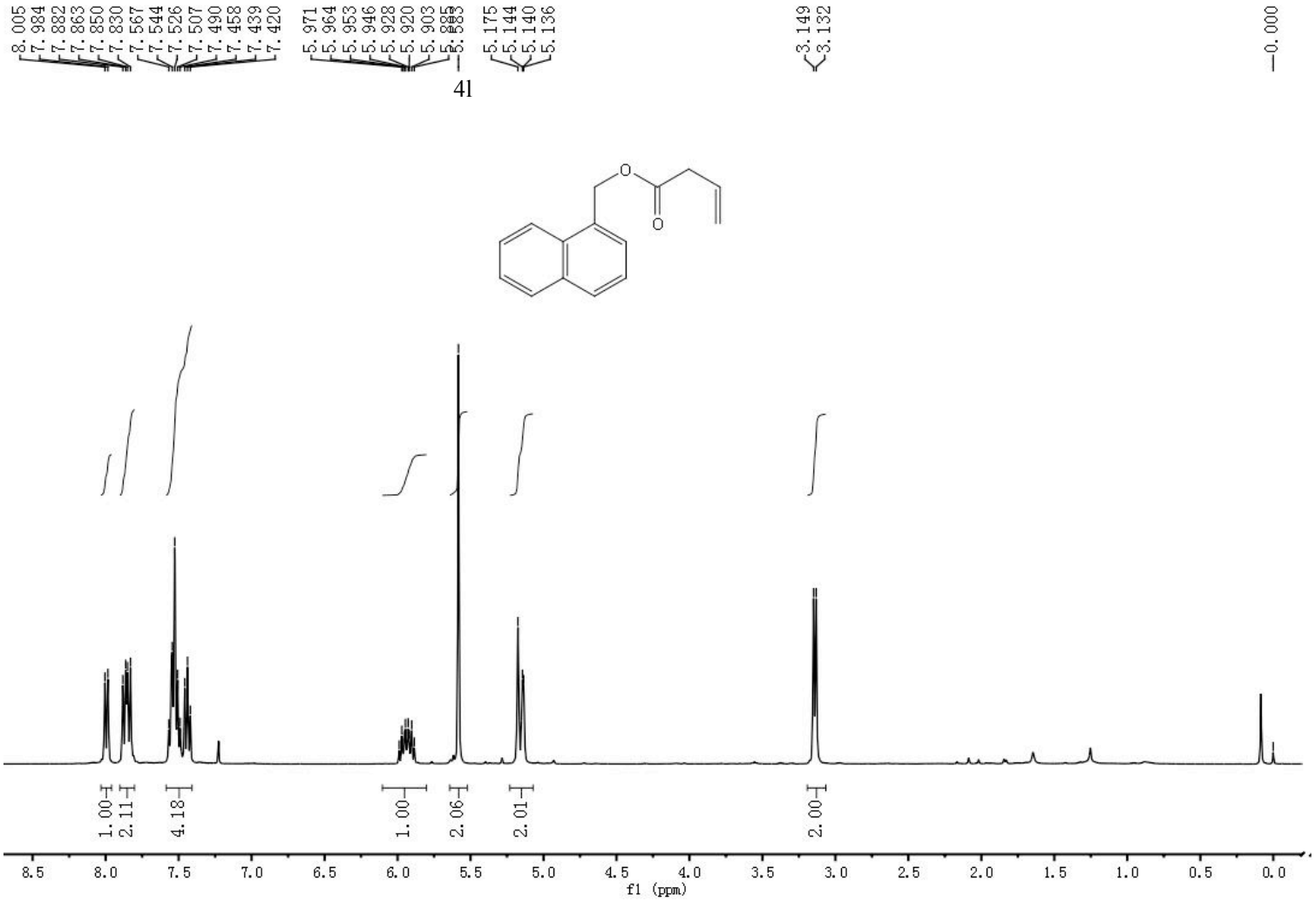
^{1}H NMR, 400 MHz, $CDCl_3$



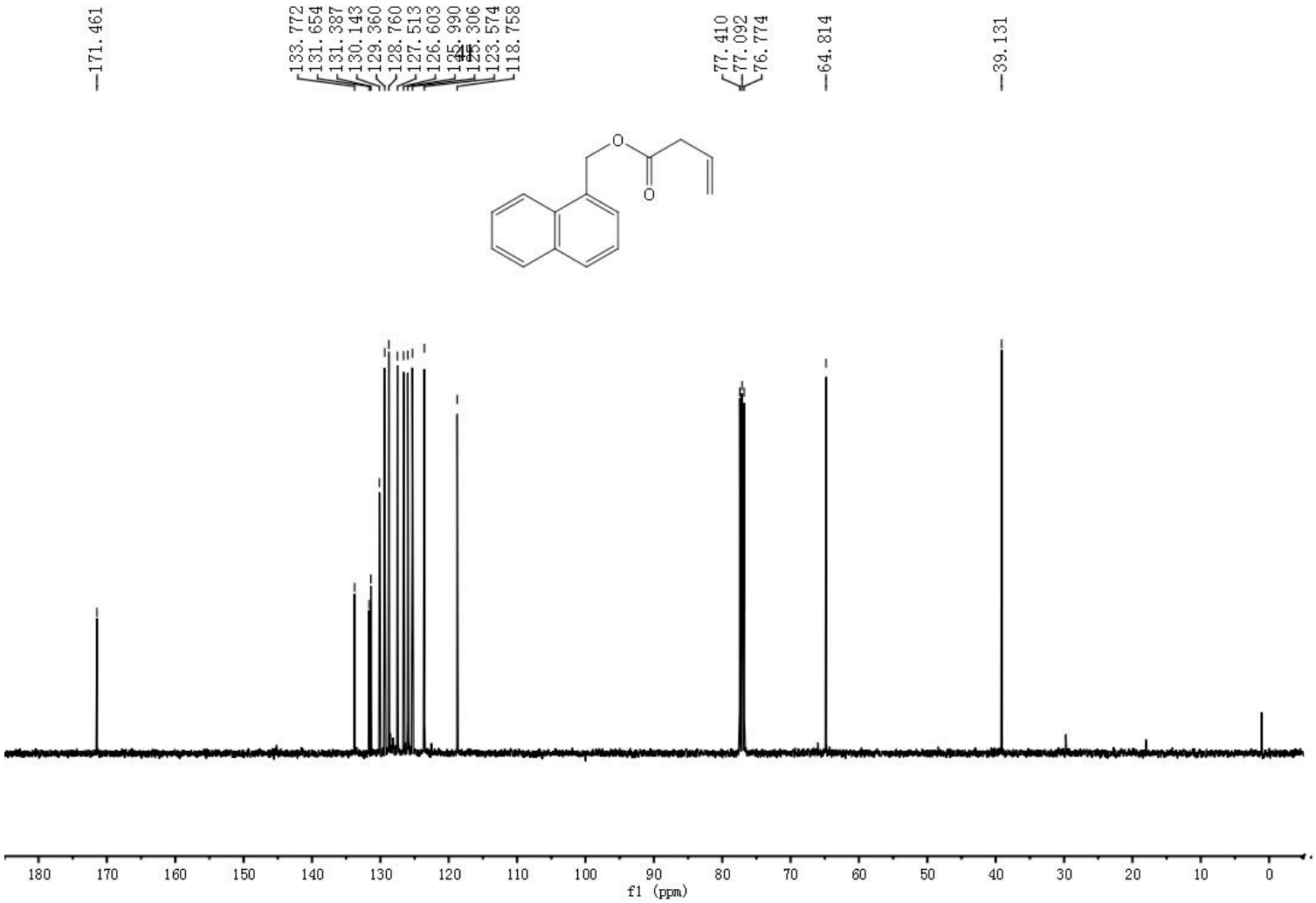
^{13}C NMR, 100 MHz, $CDCl_3$



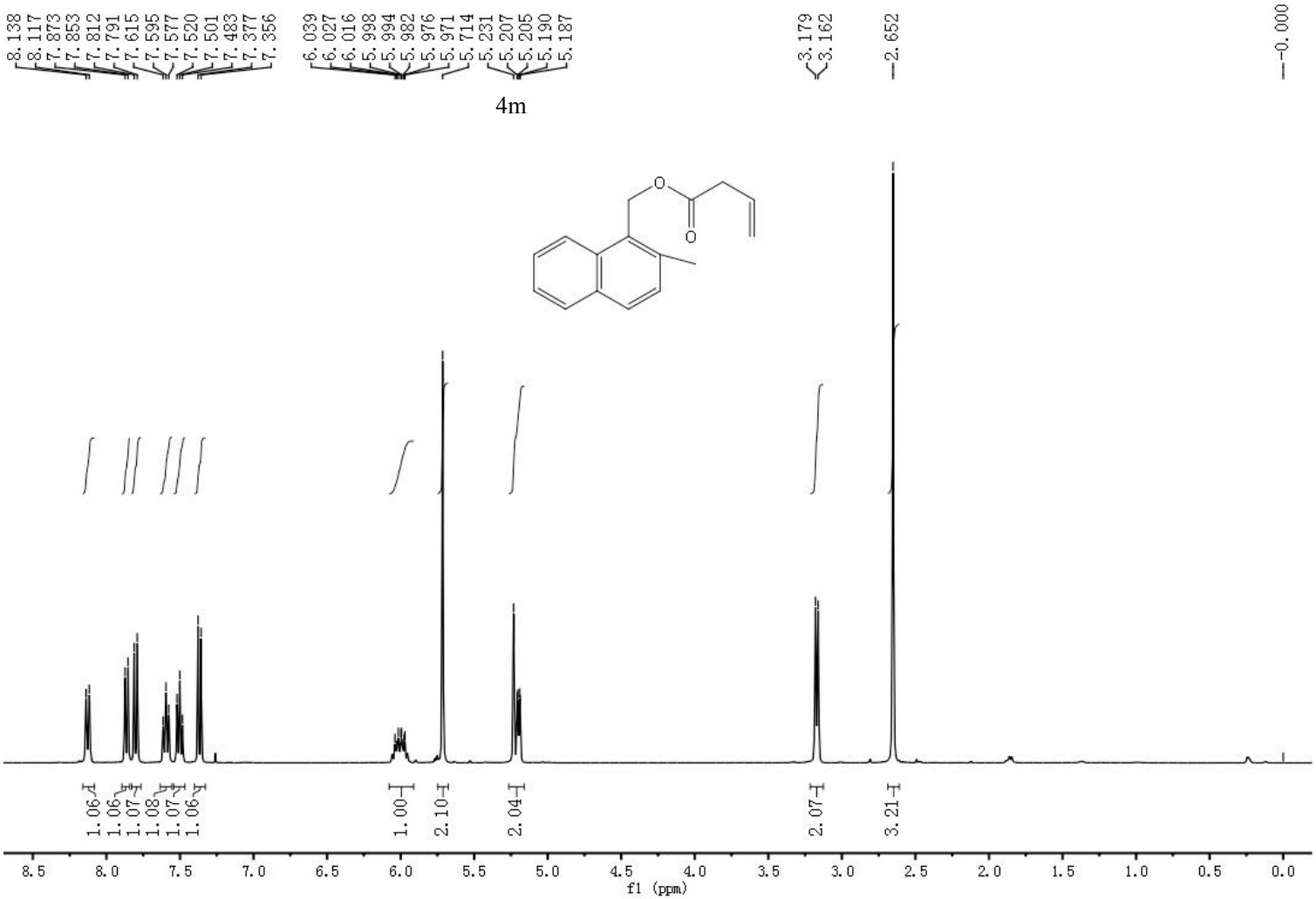
^{1}H NMR, 400 MHz, $CDCl_3$



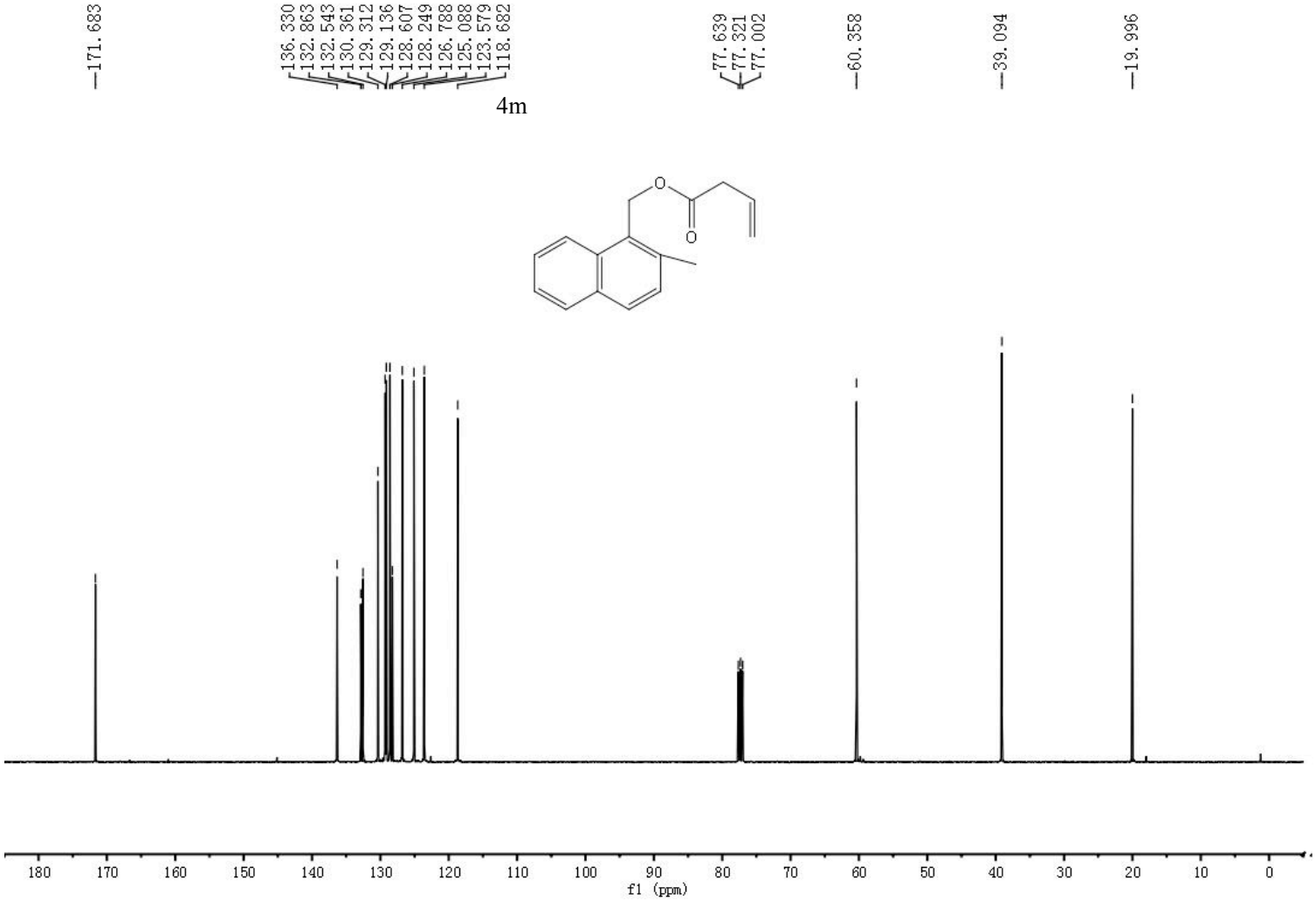
^{13}C NMR, 100 MHz, $CDCl_3$



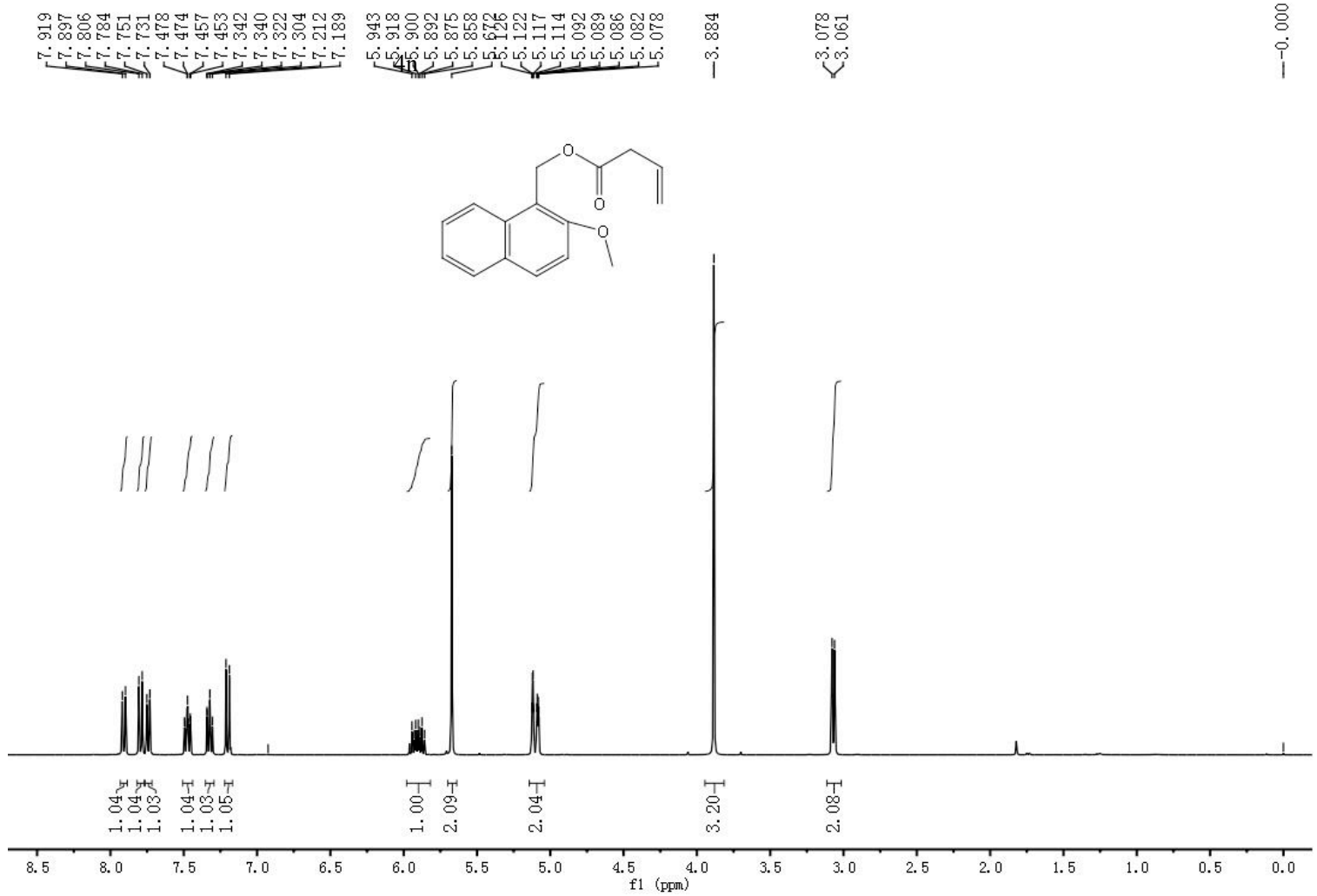
^{1}H NMR, 400 MHz, $CDCl_3$



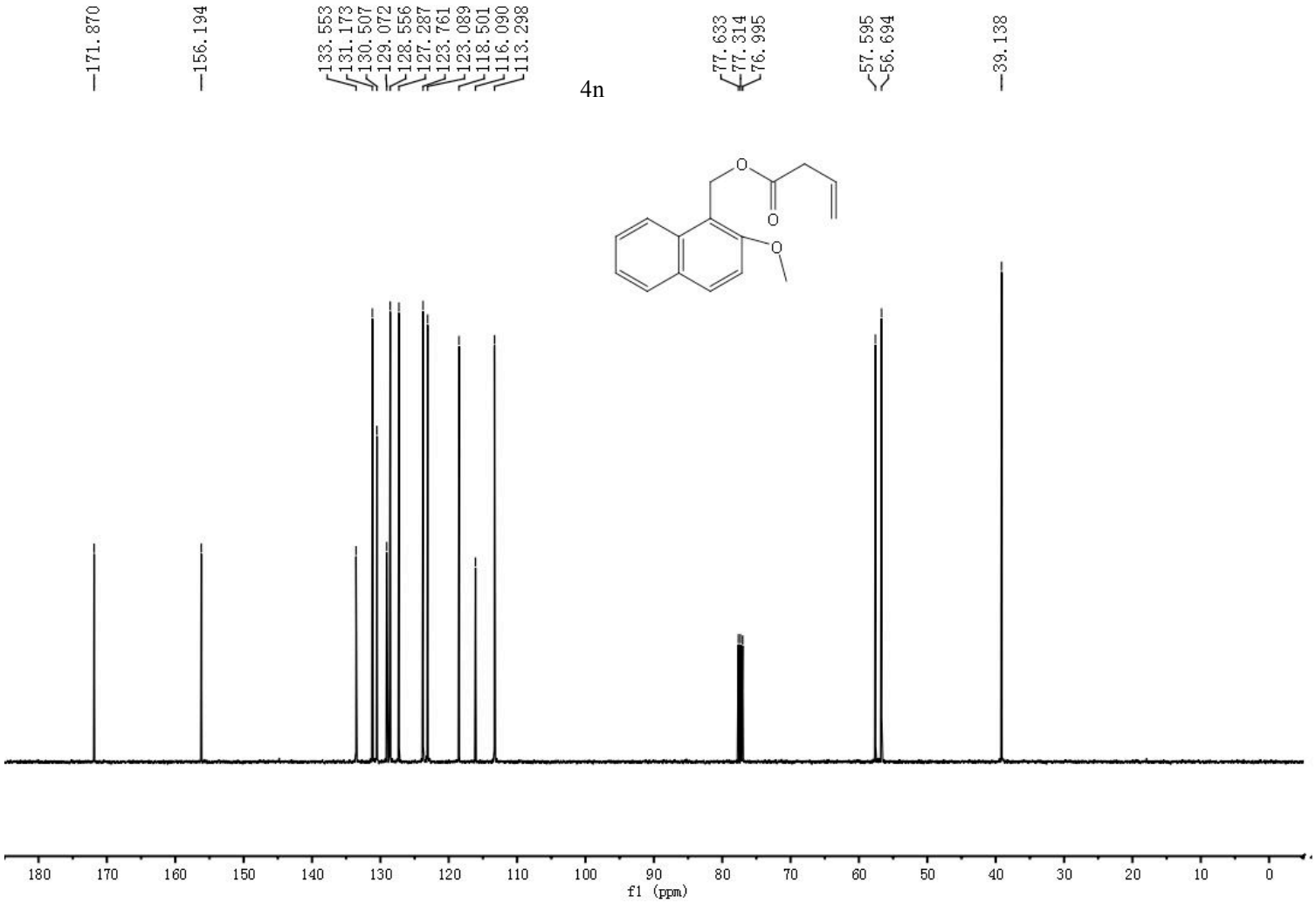
^{13}C NMR, 100 MHz, $CDCl_3$



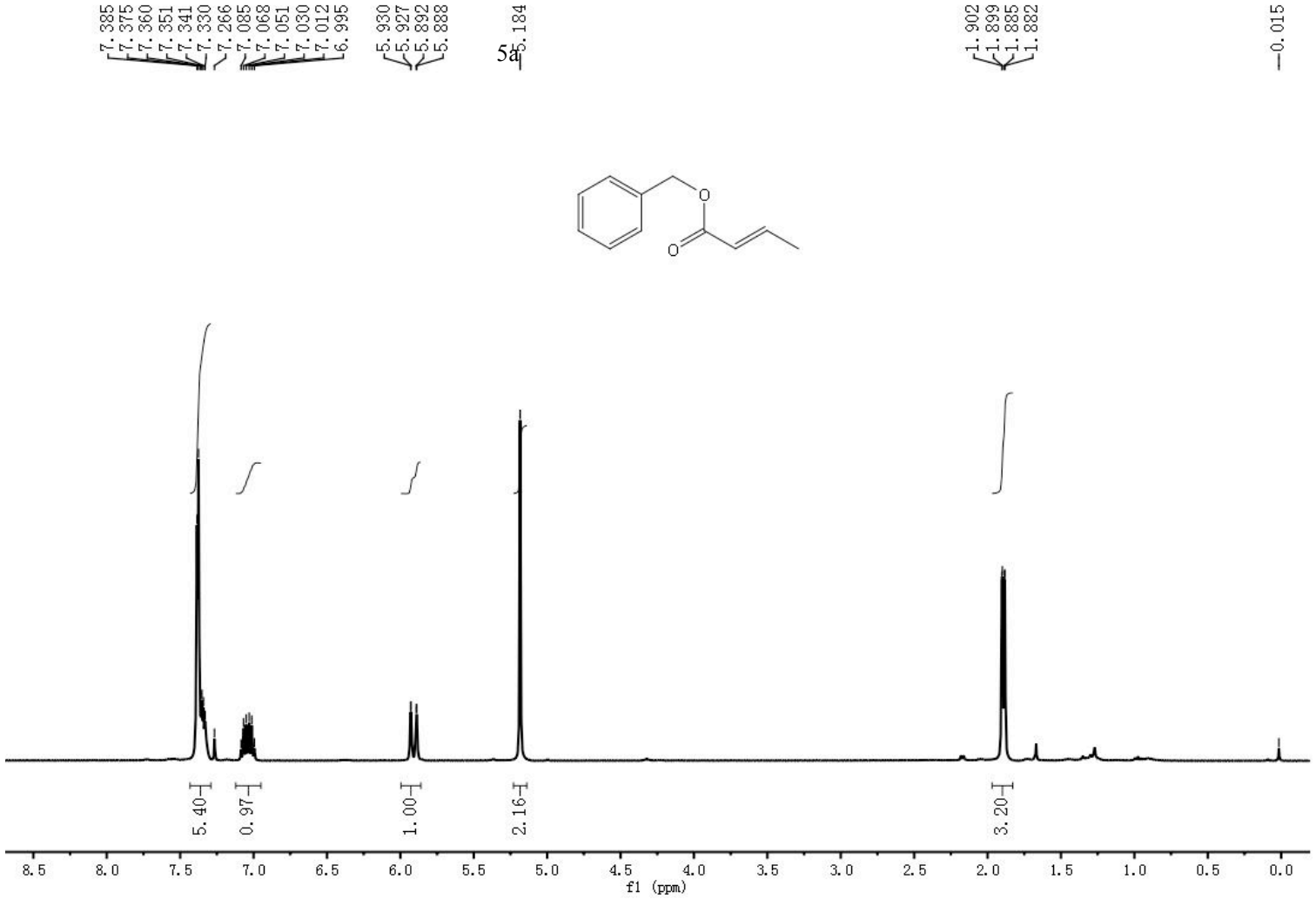
^{1}H NMR, 400 MHz, $CDCl_3$



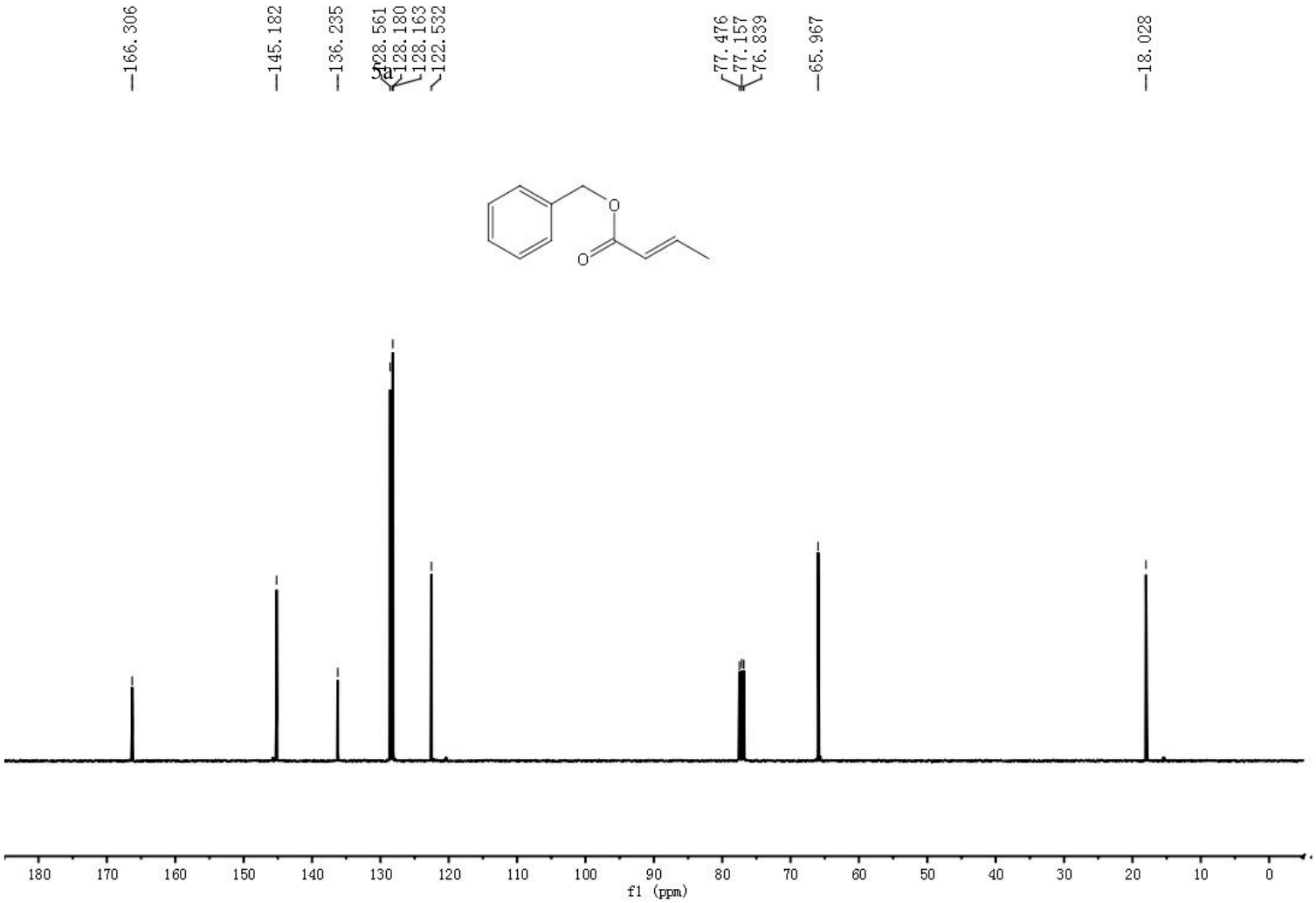
^{13}C NMR, 100 MHz, $CDCl_3$



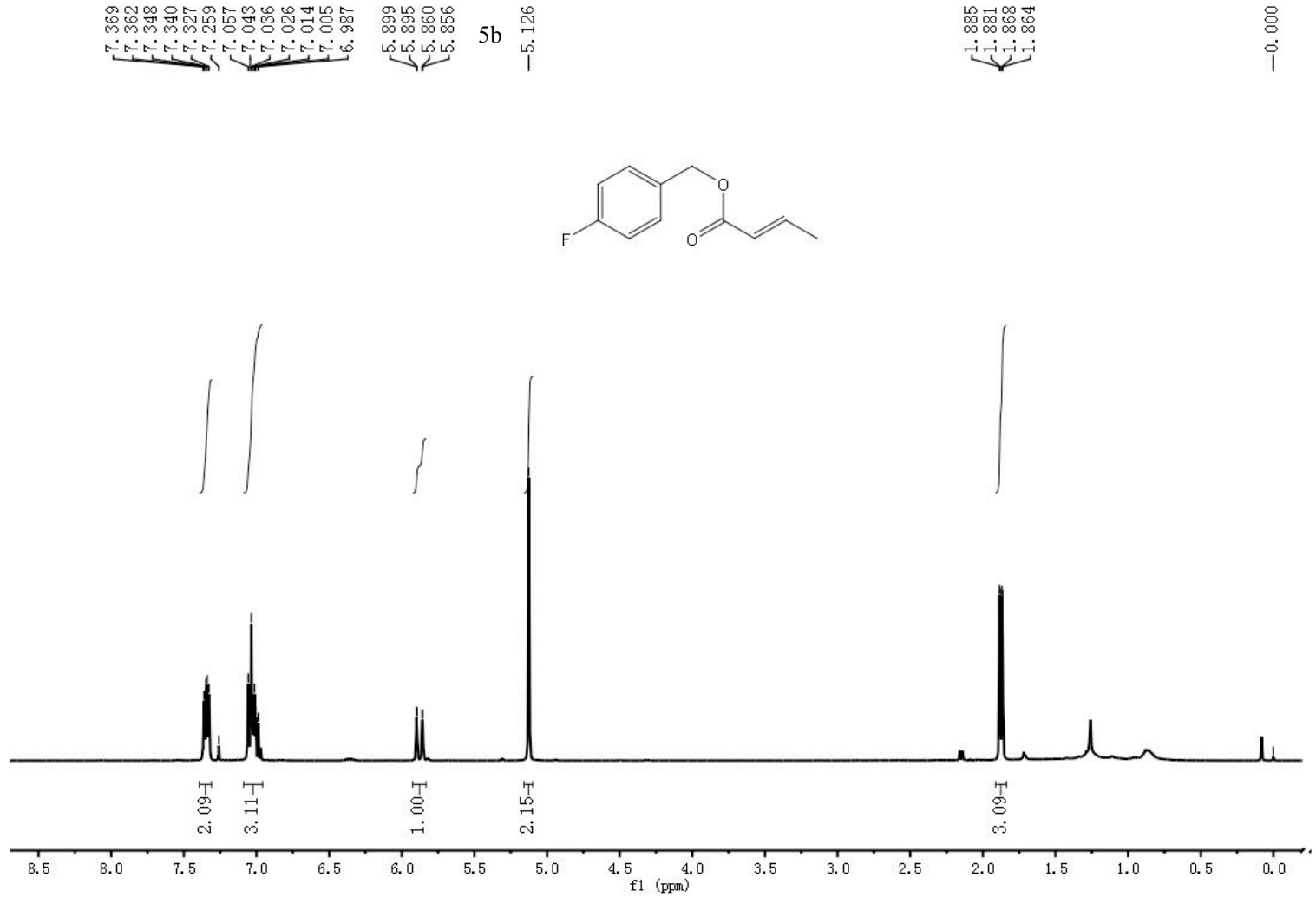
^{1}H NMR, 400 MHz, $CDCl_3$



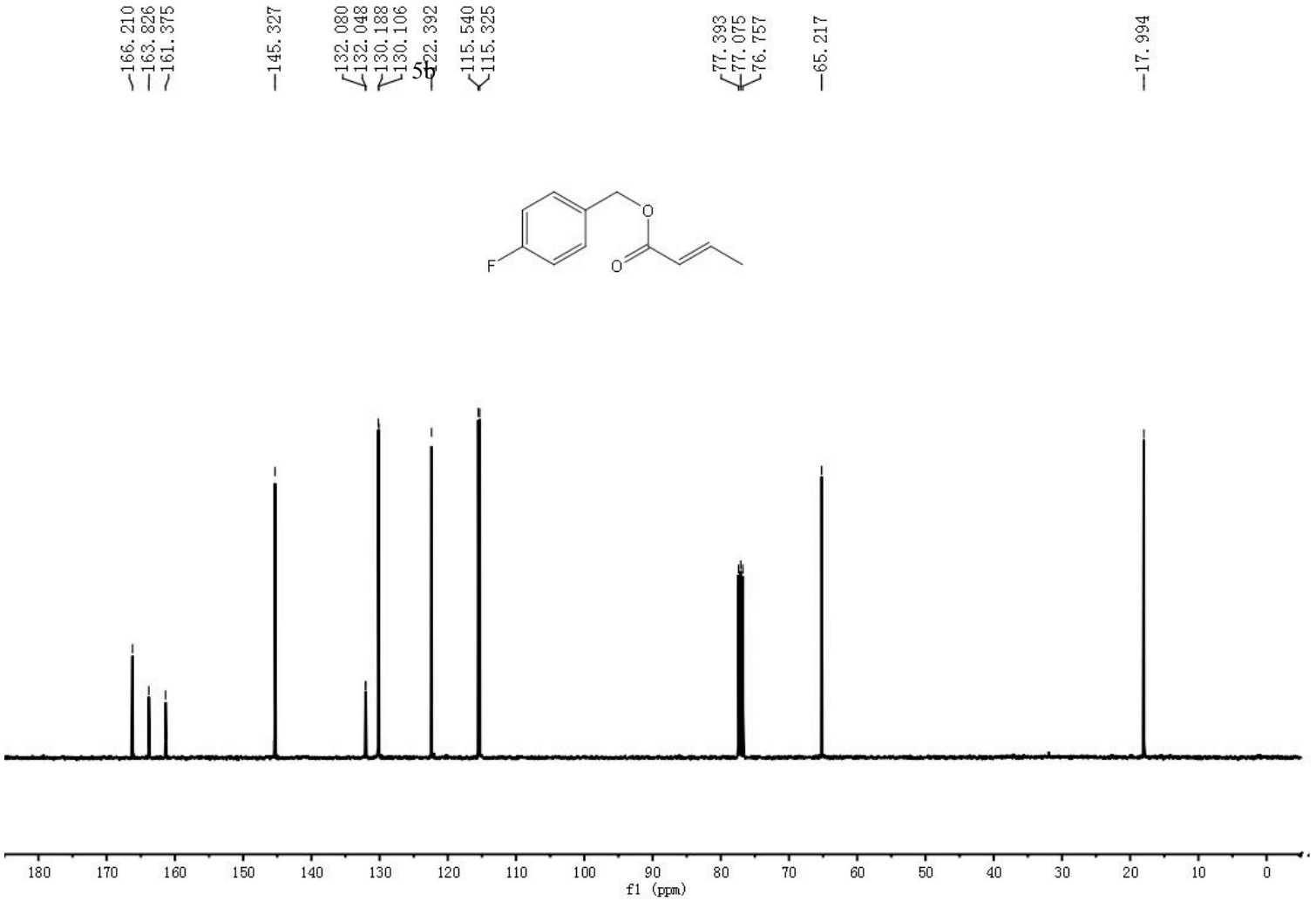
^{13}C NMR, 100 MHz, $CDCl_3$



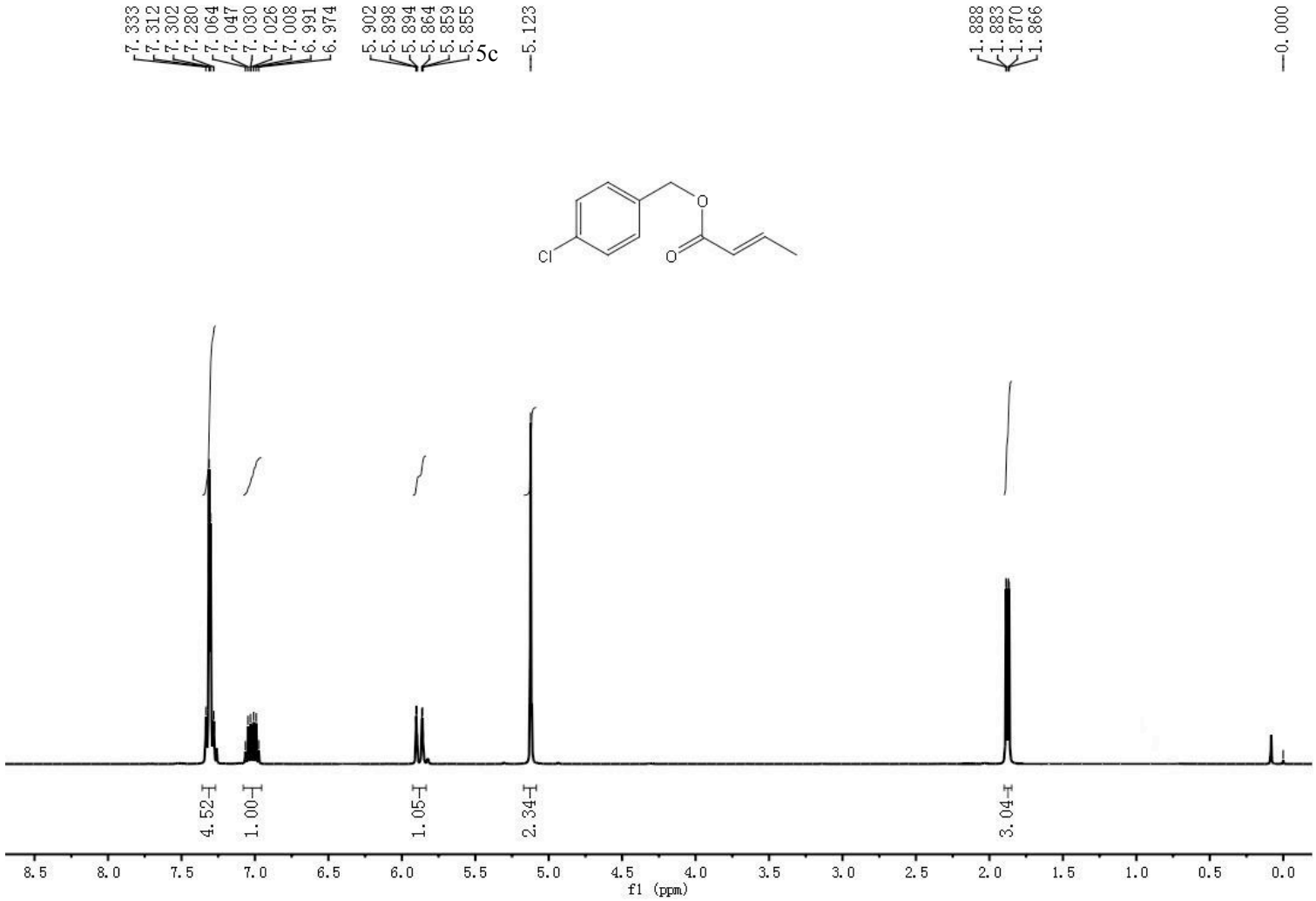
^{1}H NMR, 400 MHz, $CDCl_3$



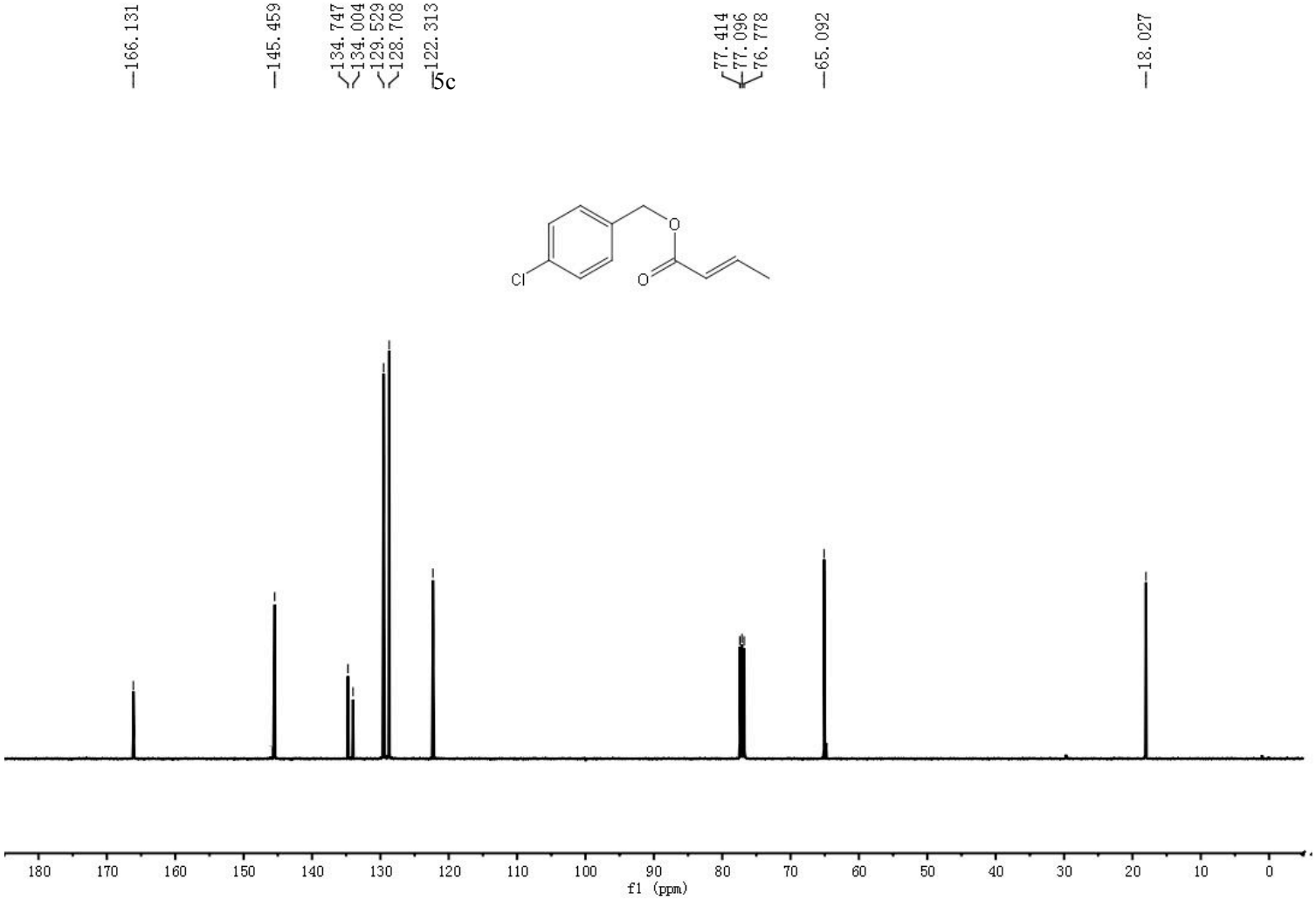
^{13}C NMR, 100 MHz, $CDCl_3$



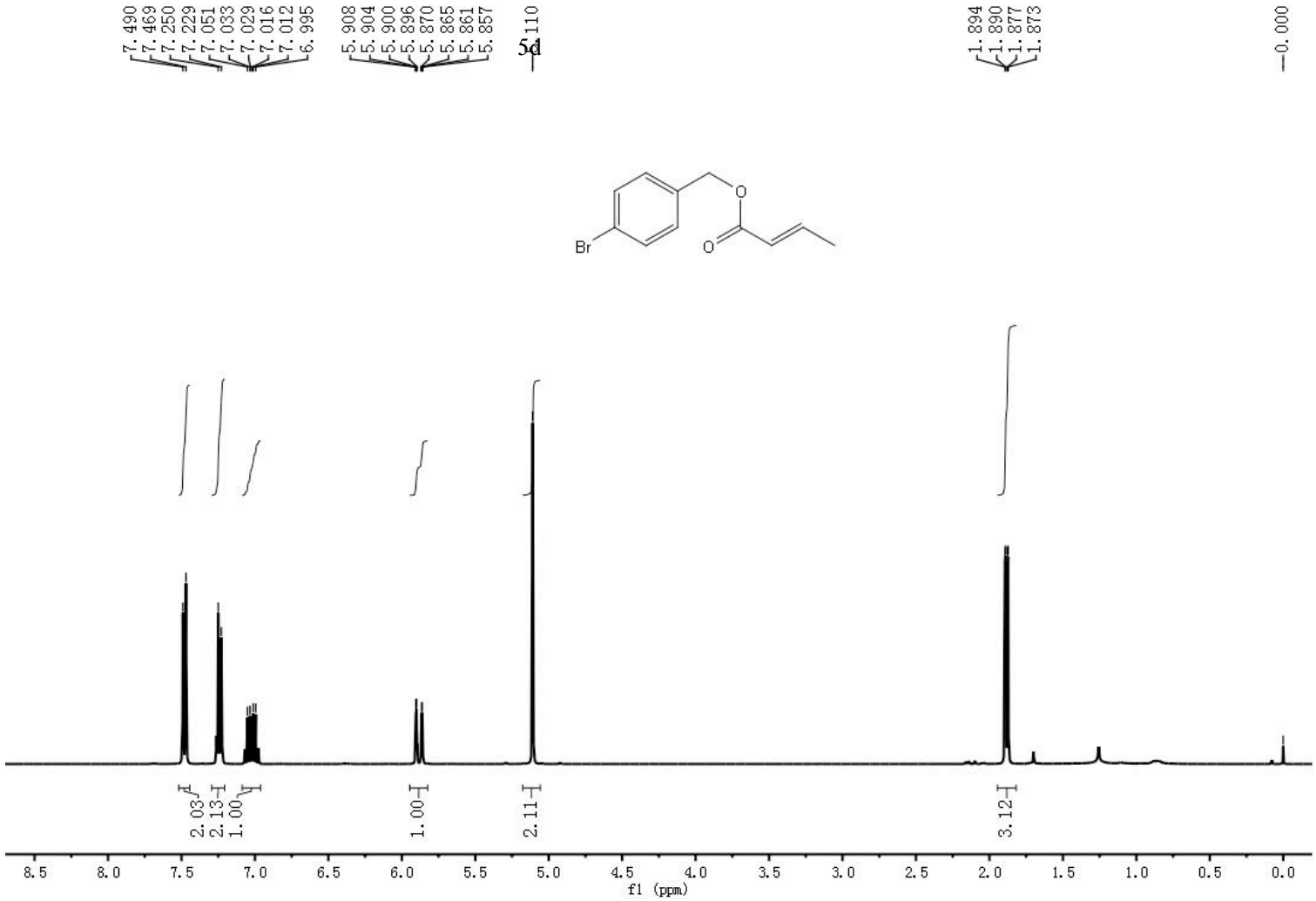
^{1}H NMR, 400 MHz, $CDCl_3$



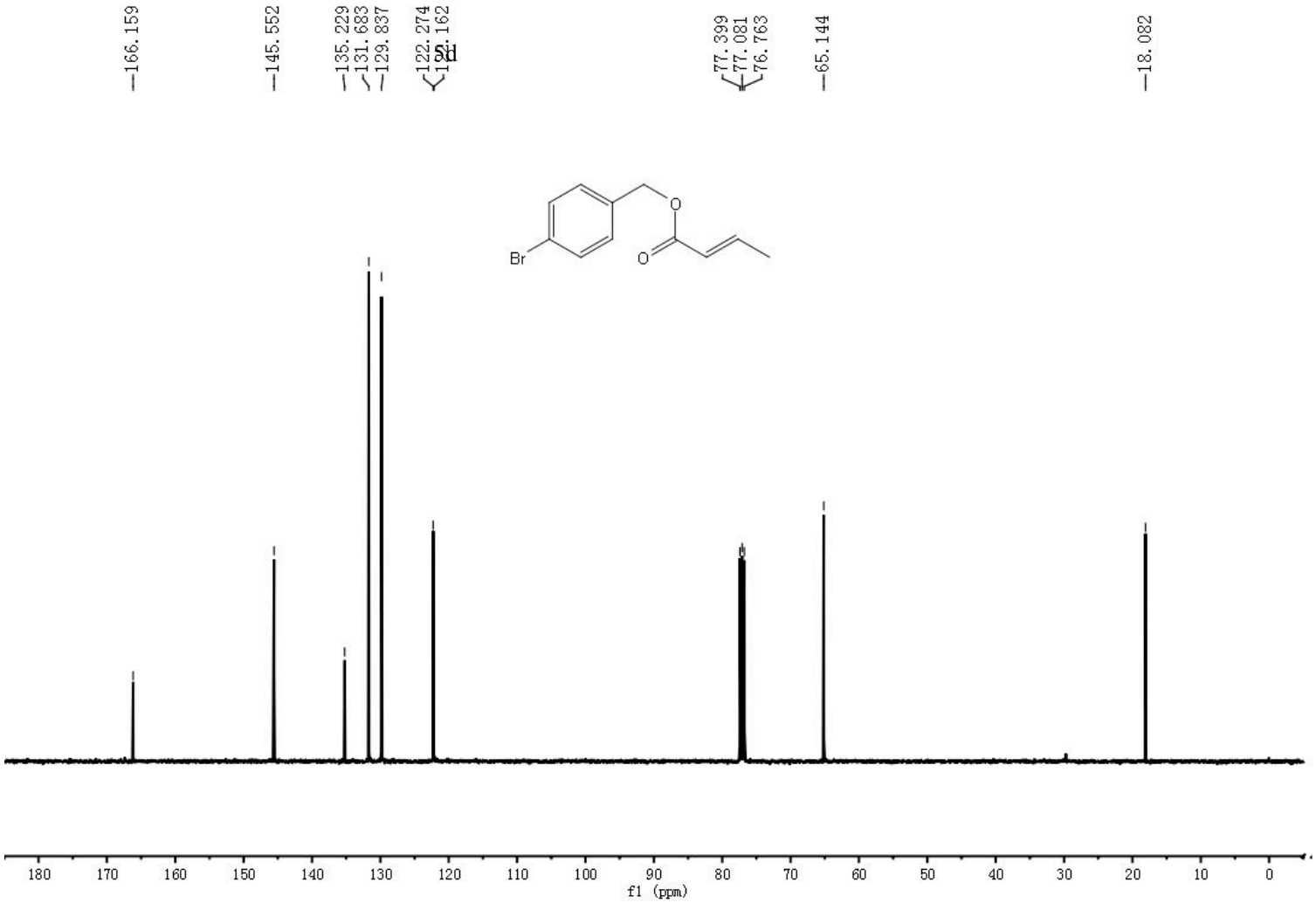
^{13}C NMR, 100 MHz, $CDCl_3$



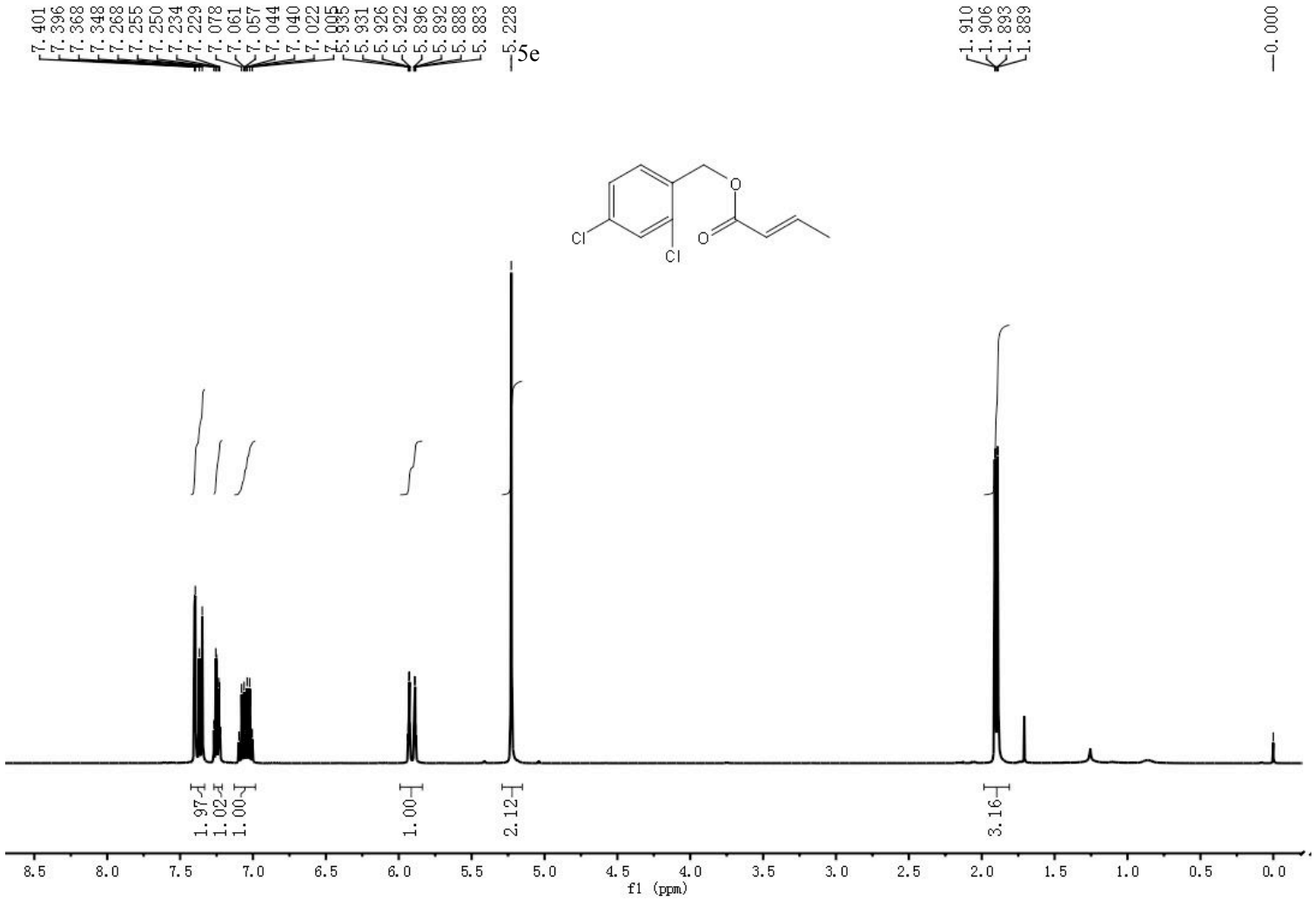
^{1}H NMR, 400 MHz, $CDCl_3$



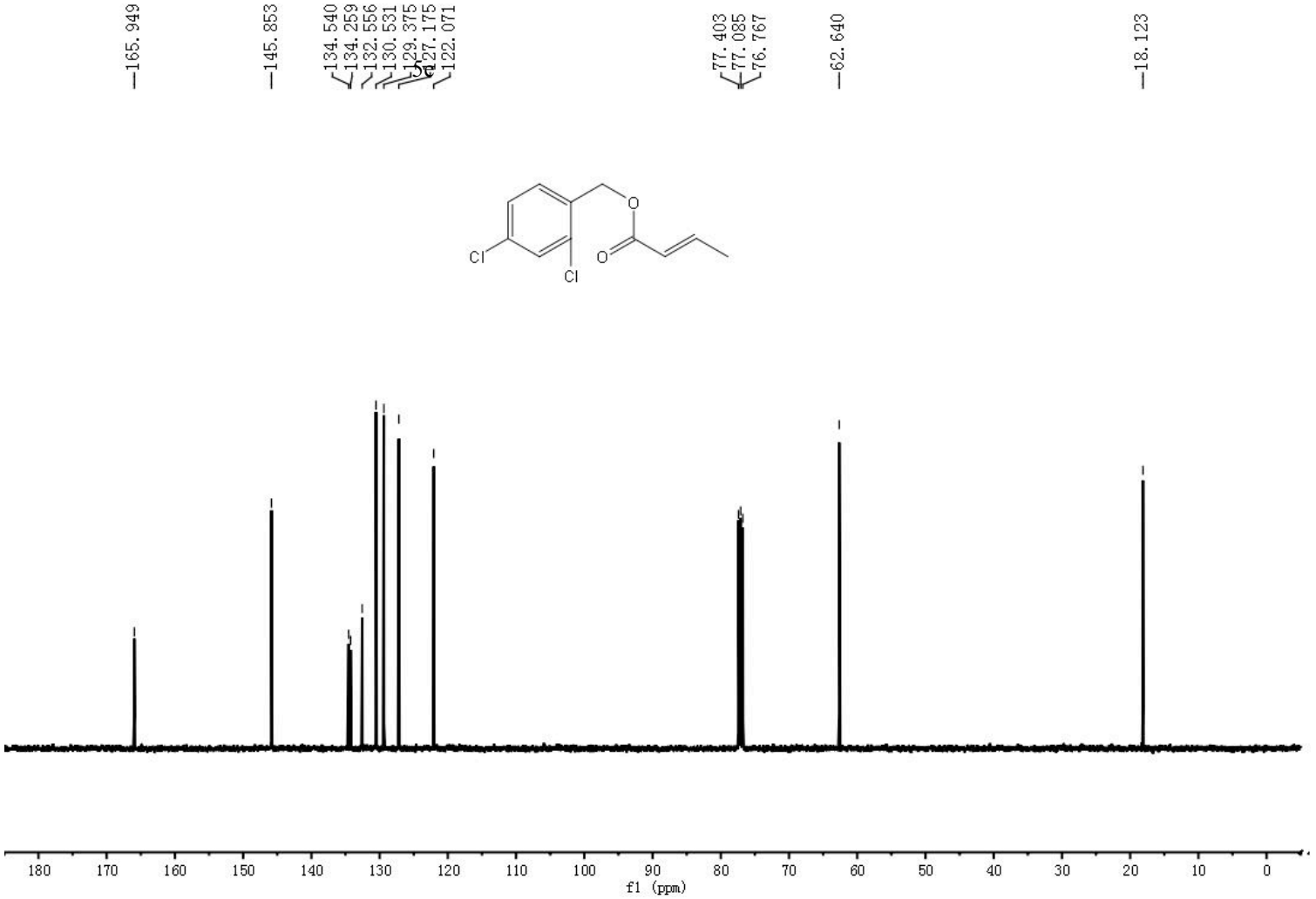
^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$

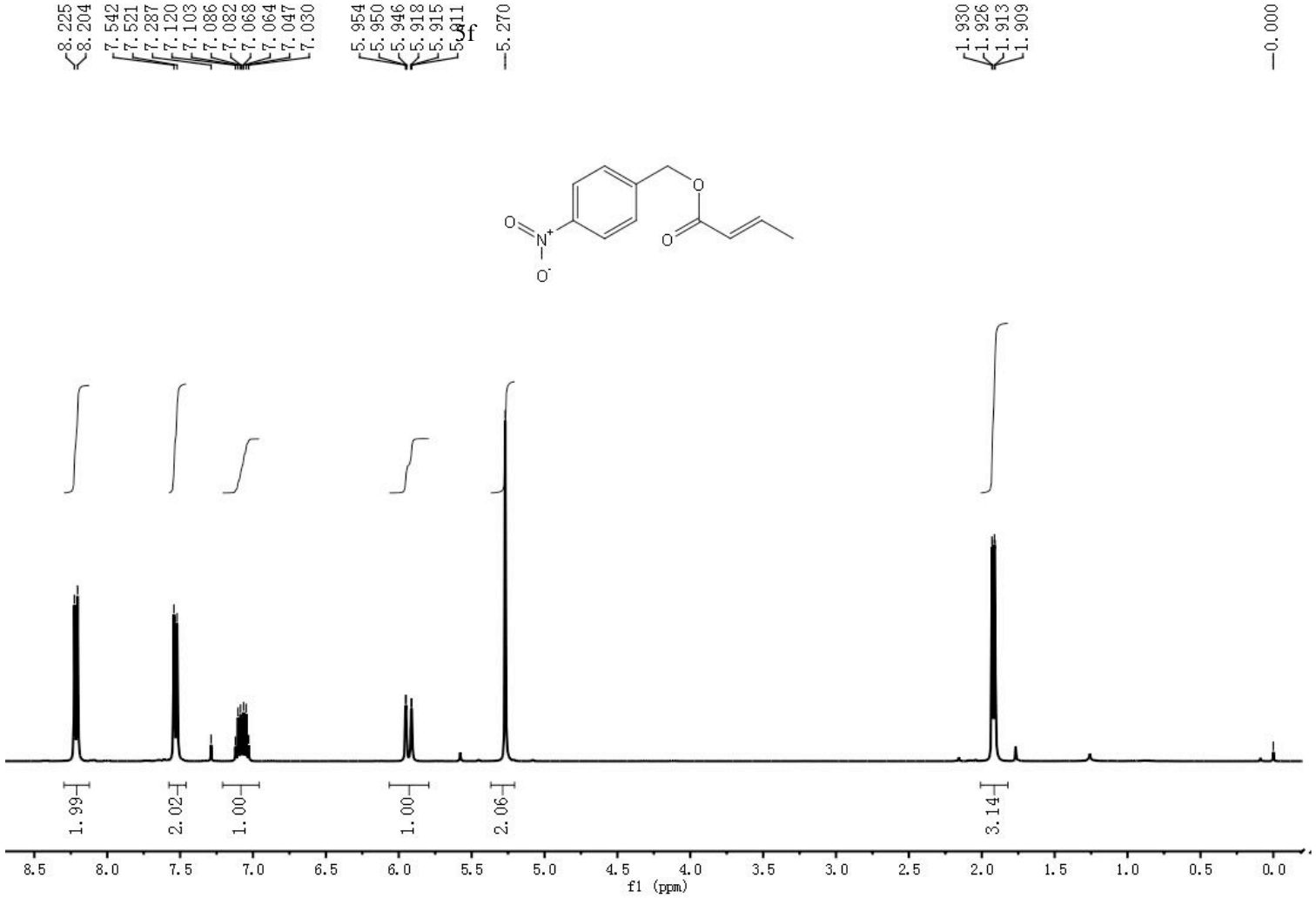


^{13}C NMR, 100 MHz, $CDCl_3$

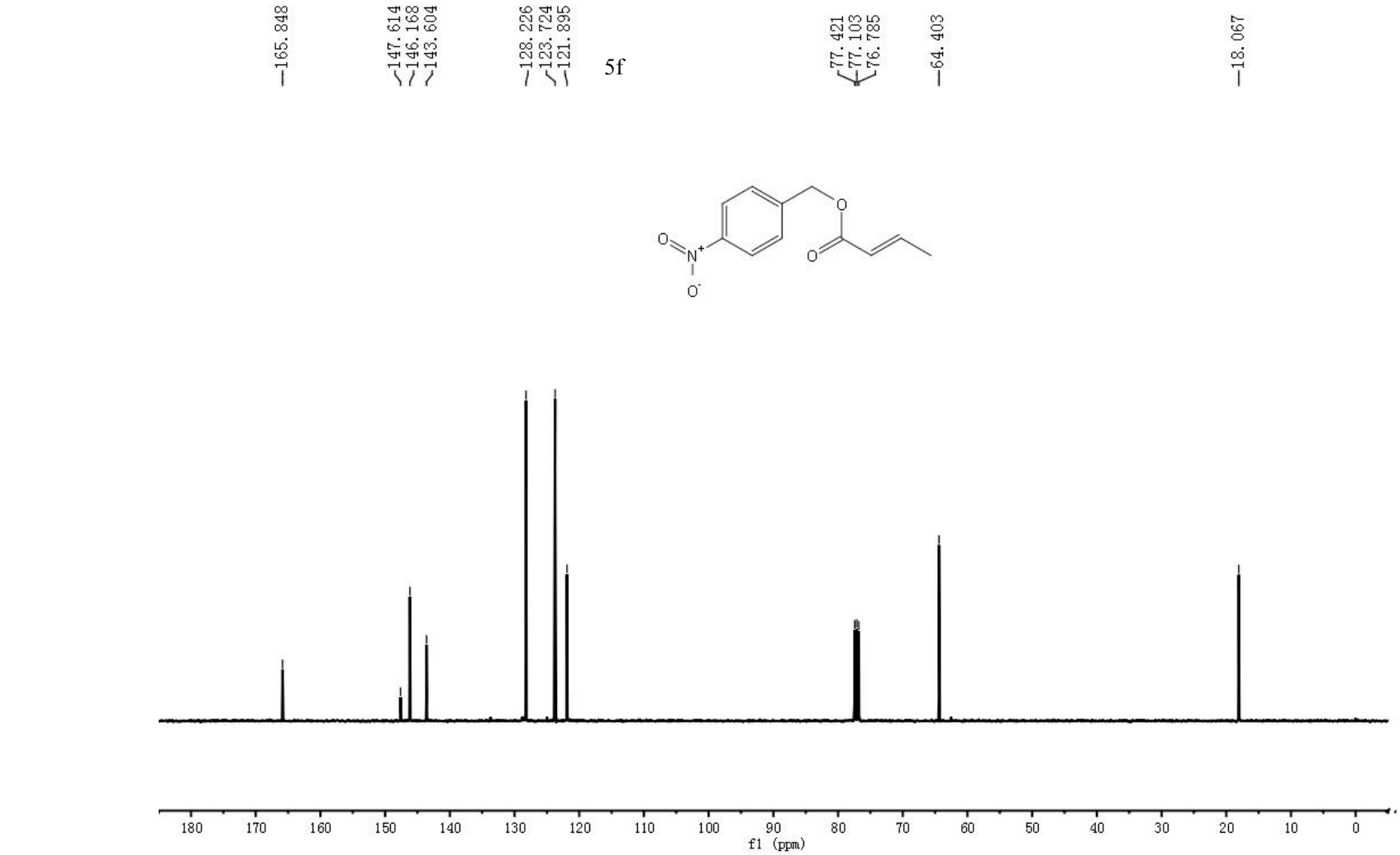


^{1}H NMR, 400 MHz, $CDCl_3$

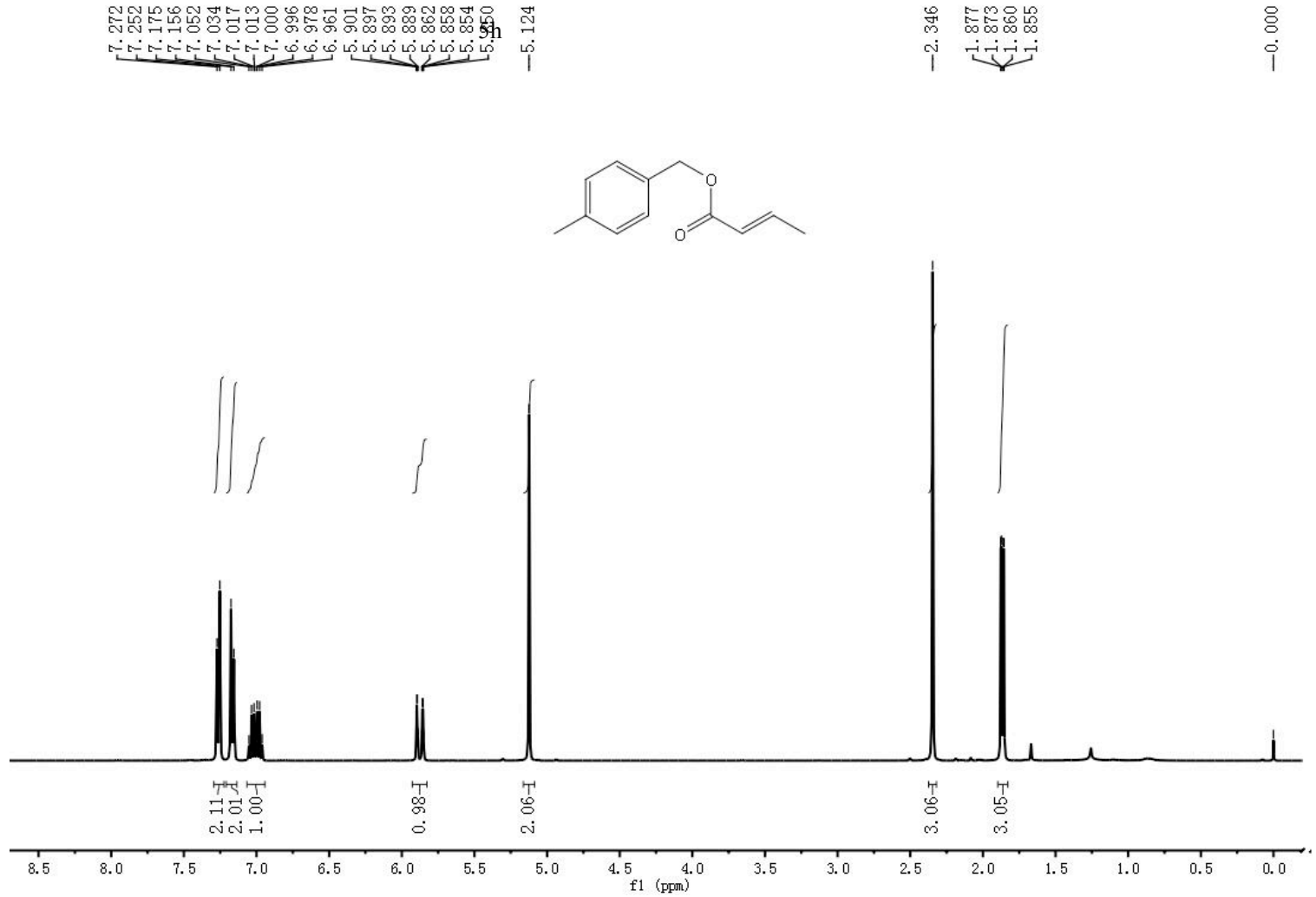
3f



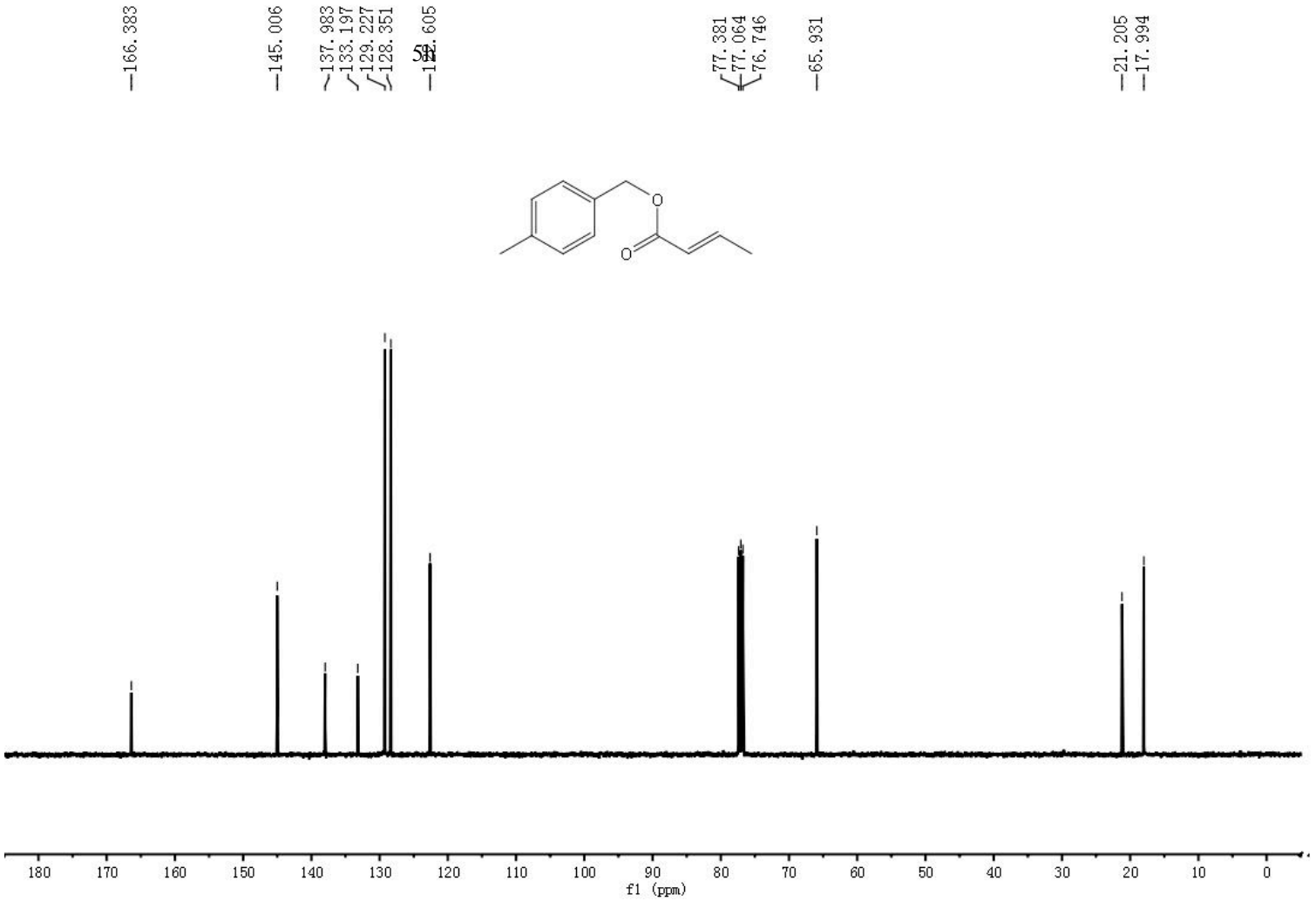
^{13}C NMR, 100 MHz, $CDCl_3$



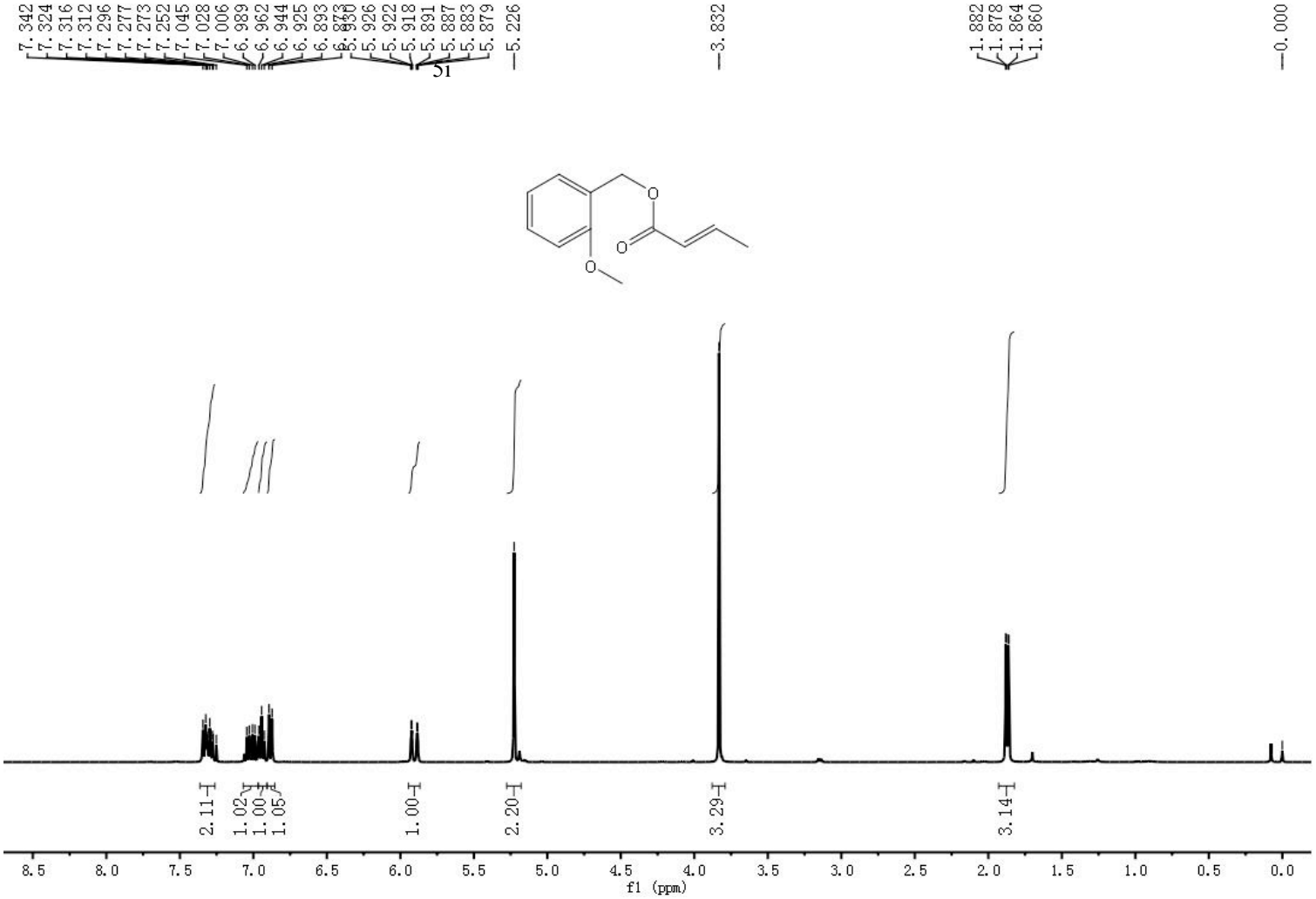
^{1}H NMR, 400 MHz, $CDCl_3$



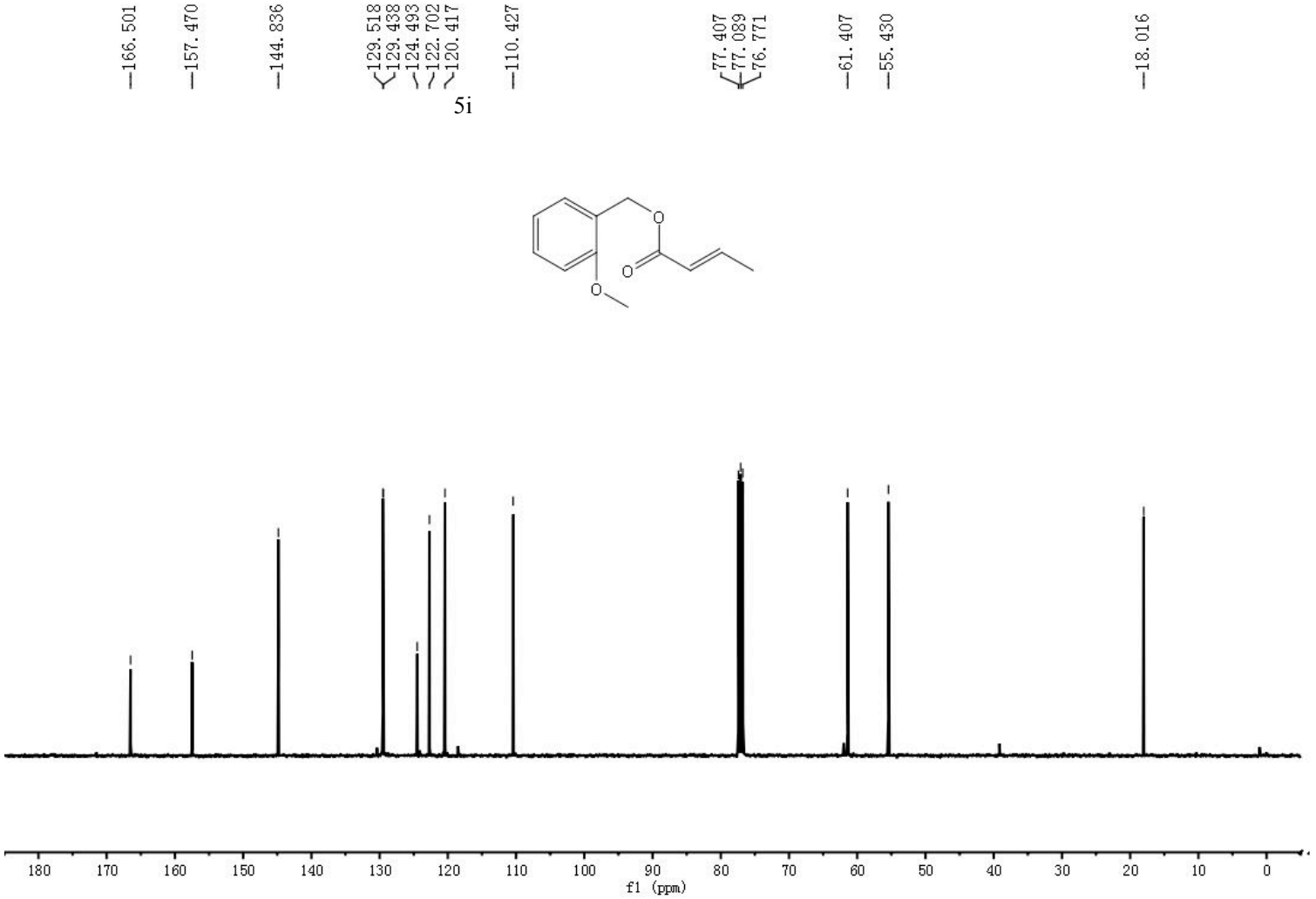
^{13}C NMR, 100 MHz, $CDCl_3$



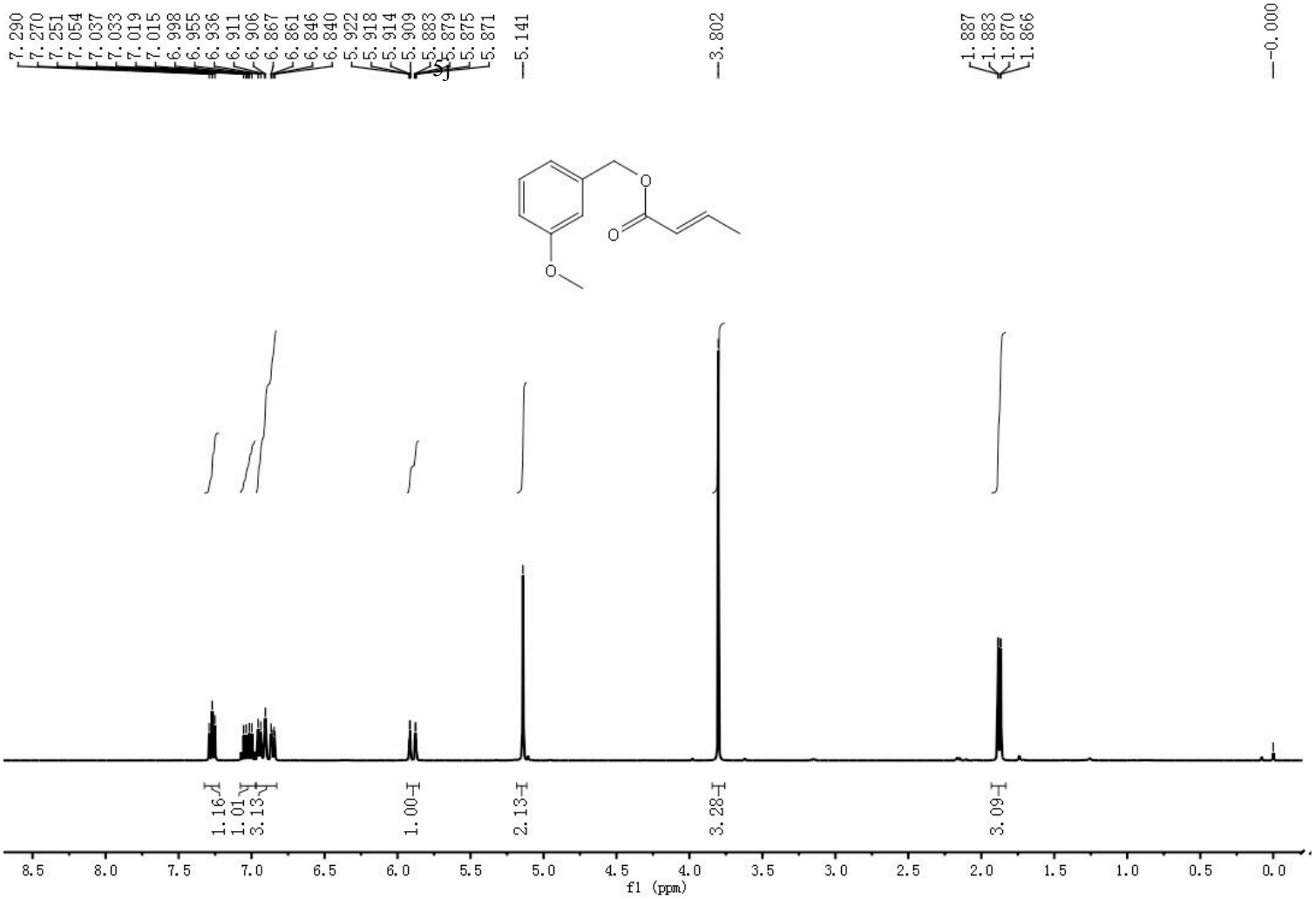
^{1}H NMR, 400 MHz, $CDCl_3$



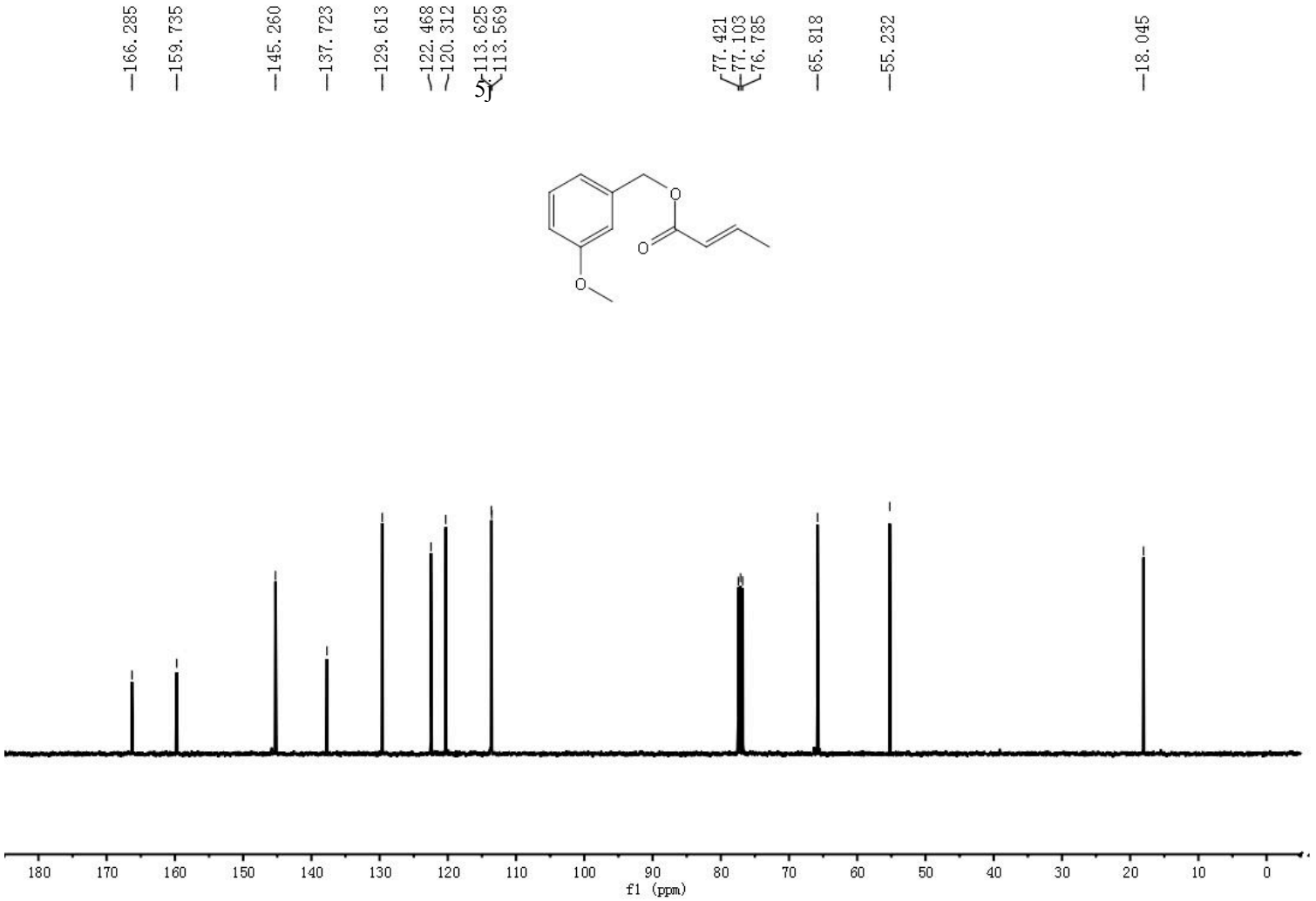
^{13}C NMR, 100 MHz, $CDCl_3$



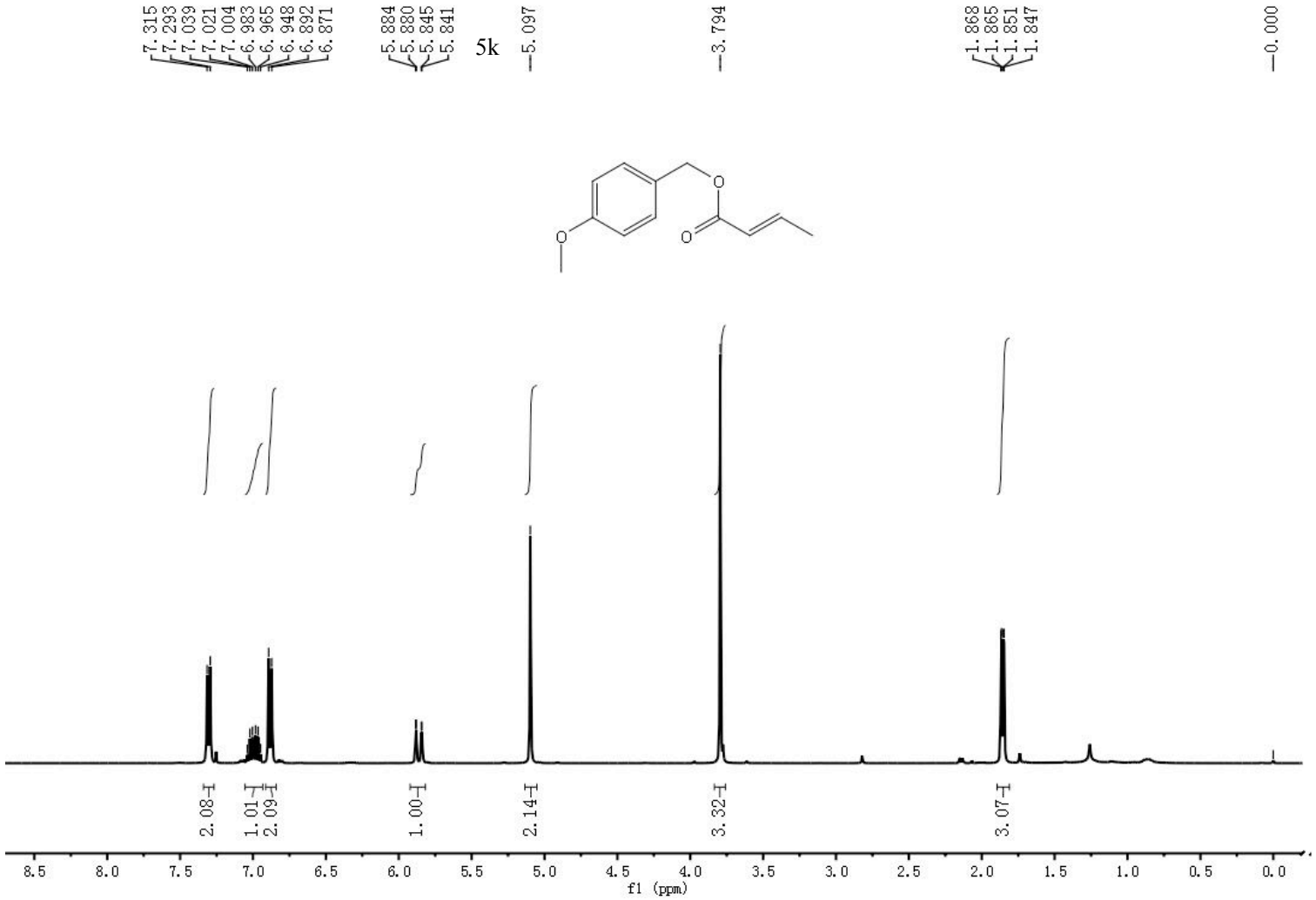
^{1}H NMR, 400 MHz, $CDCl_3$



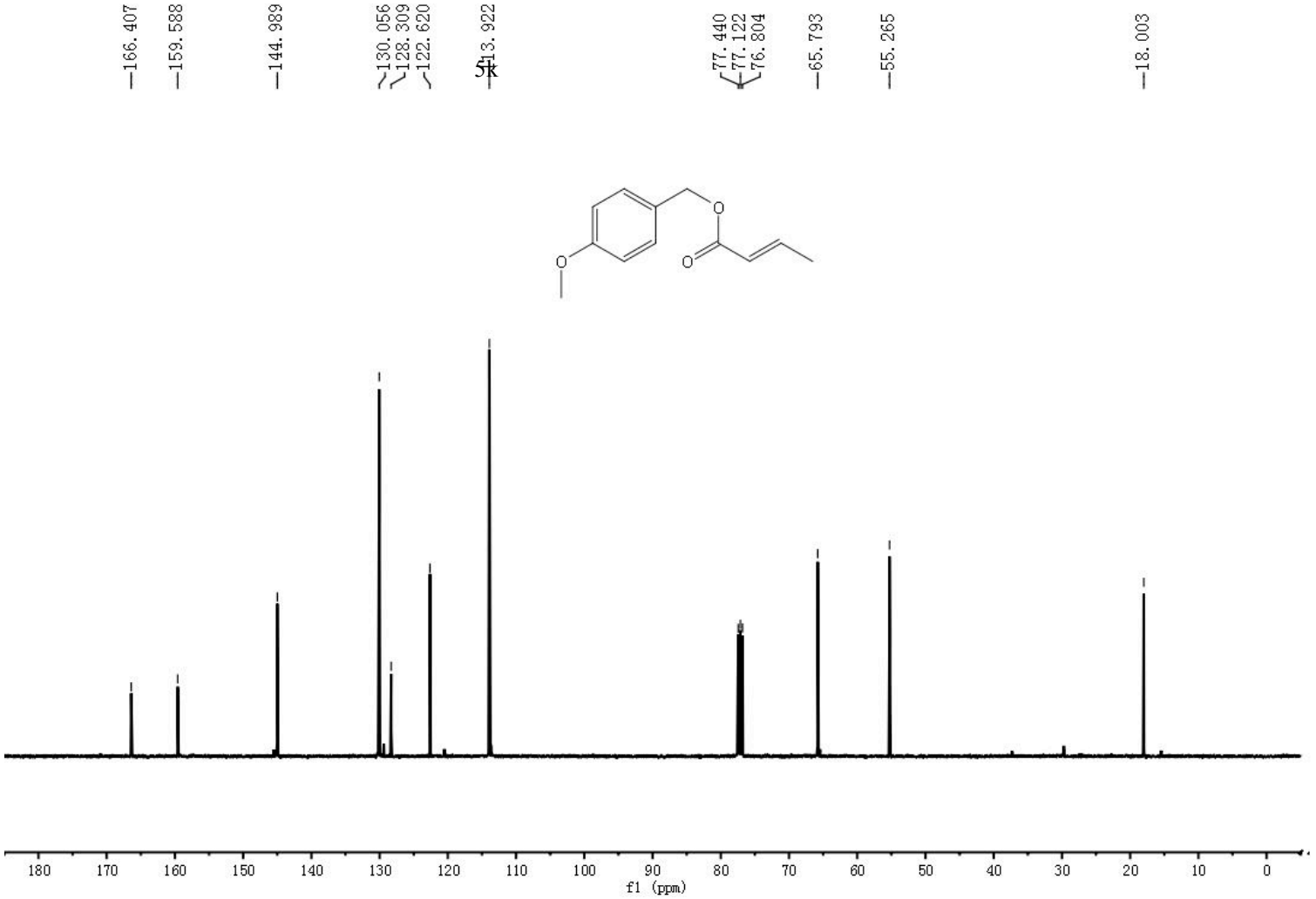
^{13}C NMR, 100 MHz, $CDCl_3$



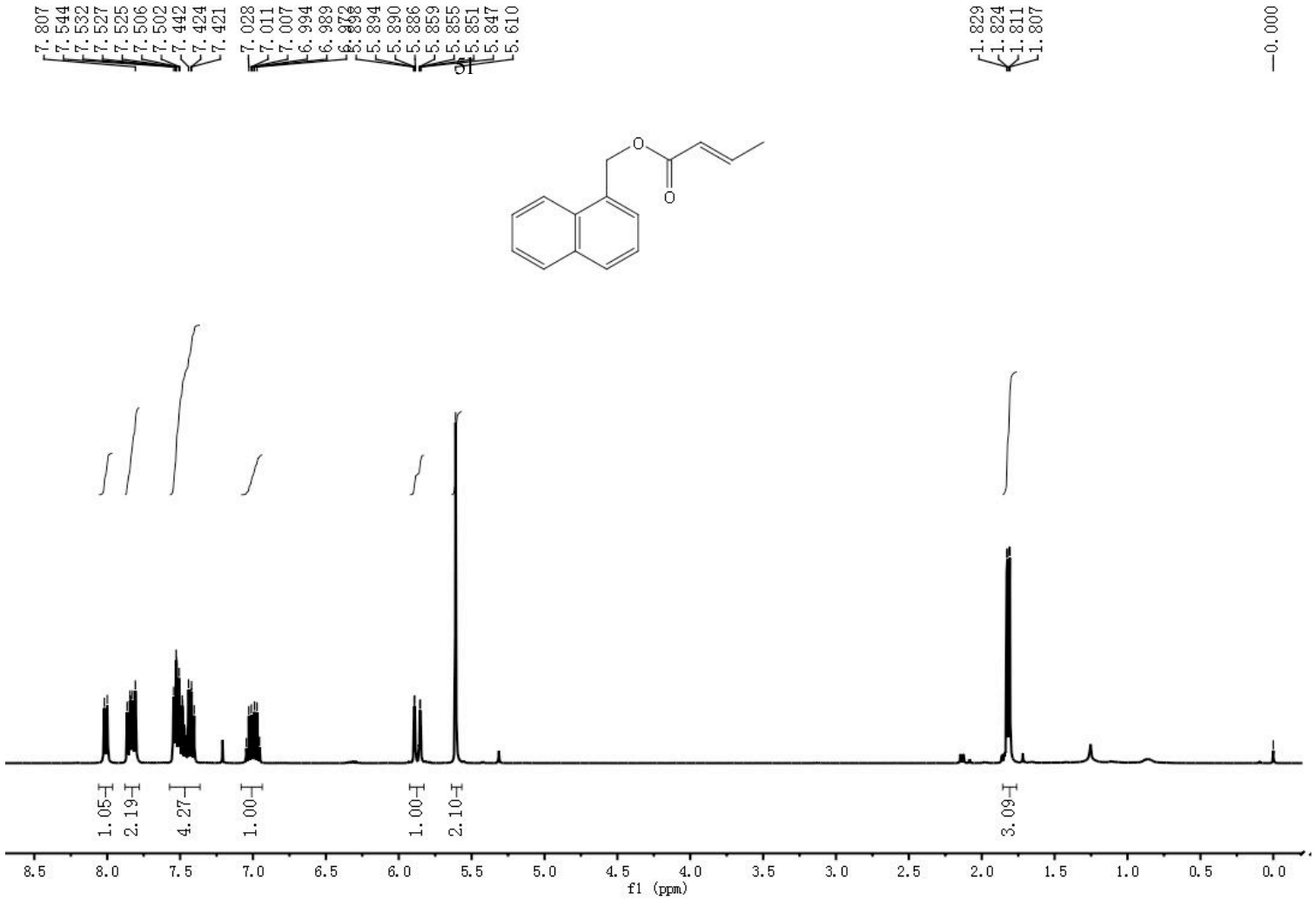
^{1}H NMR, 400 MHz, $CDCl_3$



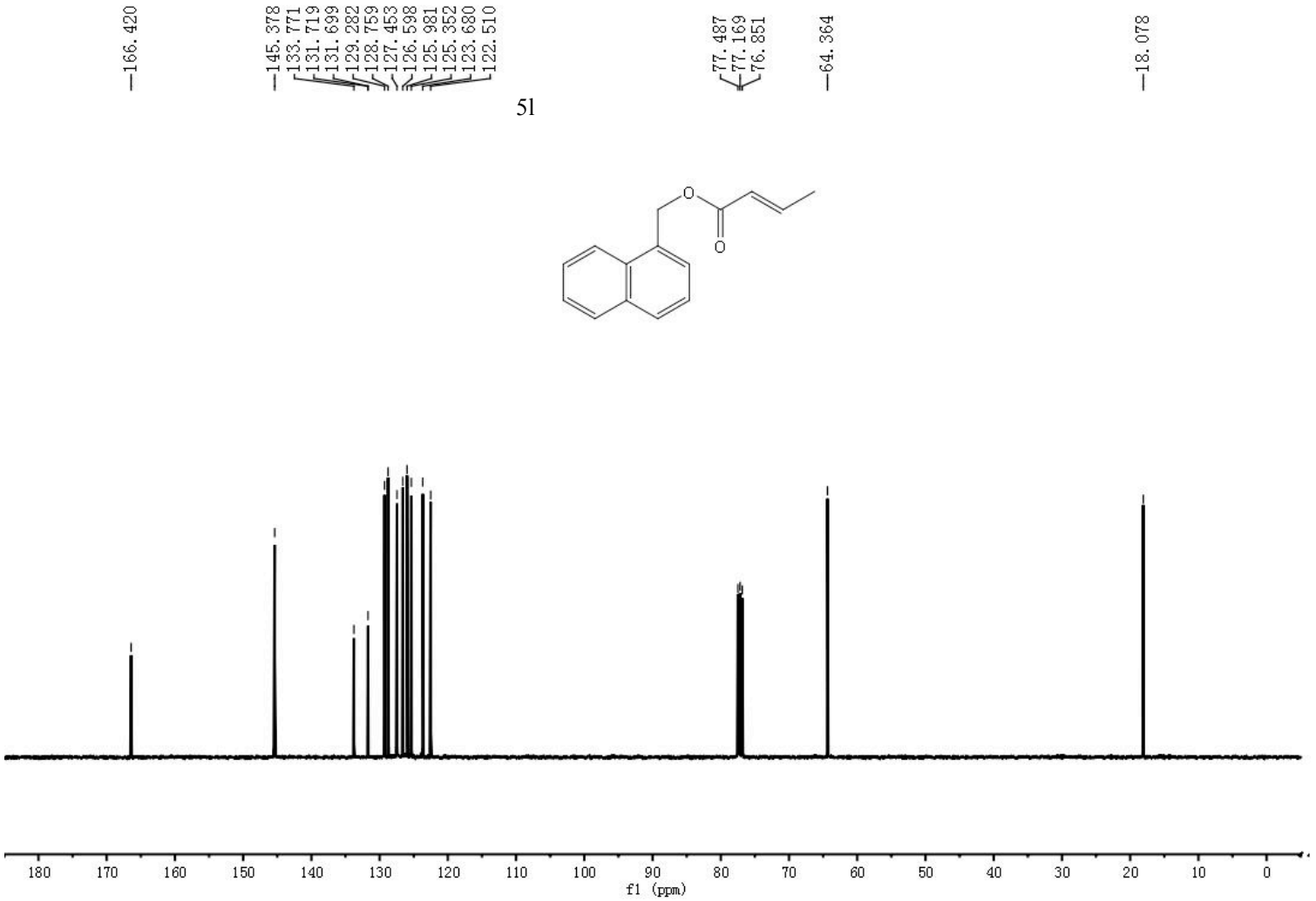
^{13}C NMR, 100 MHz, $CDCl_3$



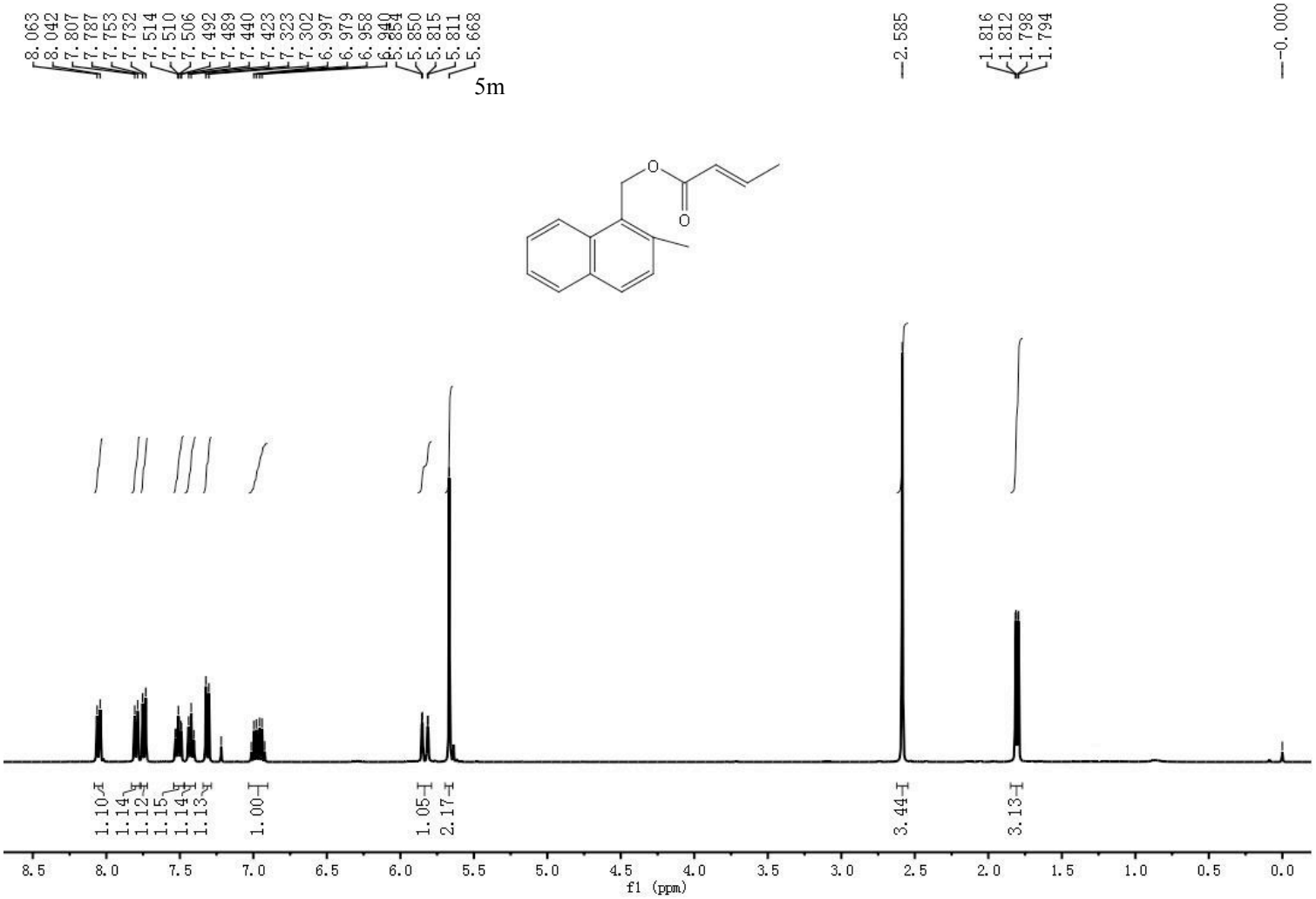
^{1}H NMR, 400 MHz, $CDCl_3$



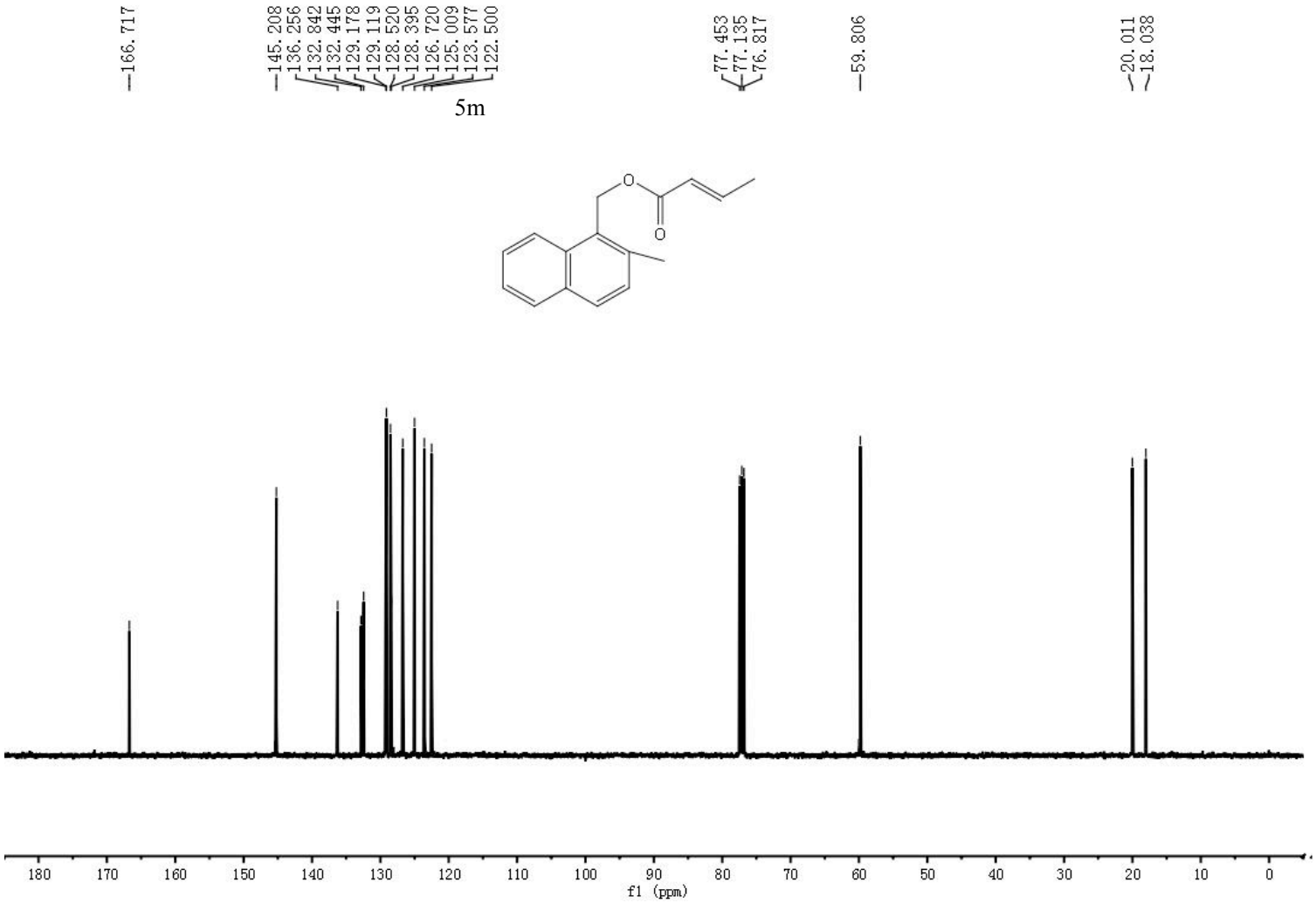
^{13}C NMR, 100 MHz, $CDCl_3$



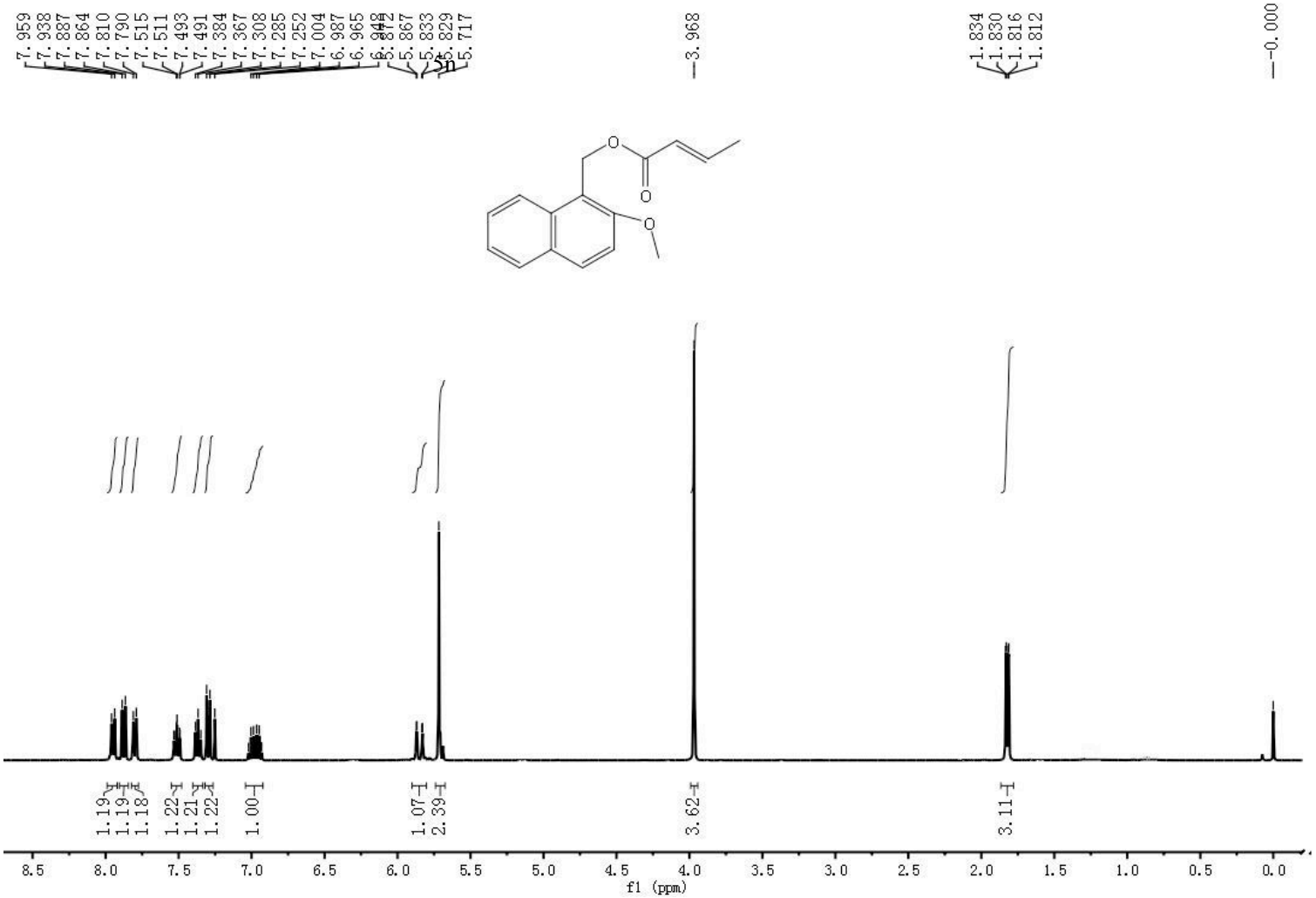
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$