

Supporting Information

An elimination/Heck coupling/allylation cascade reaction: synthesis of 2,3-dihydrobenzofurans from allenate adducts

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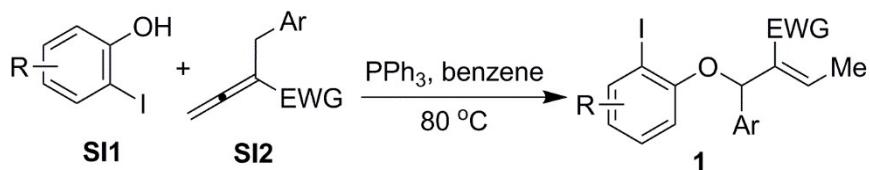
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General Information

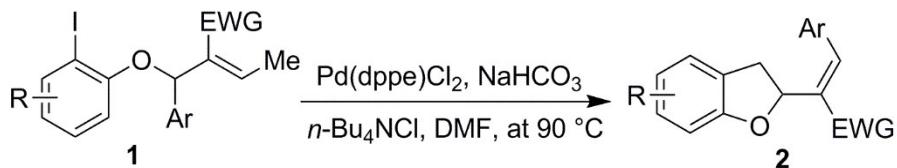
All reactions were performed under a N₂ atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Toluene and benzene were freshly distilled from CaH₂. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching under UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Thermo Nicolet 6700 instrument. ¹H and ¹³C NMR spectra were recorded in CDCl₃ using a Bruker Avance 400 MHz NMR spectrometer (referenced internally to Me₄Si). Chemical shifts (δ , ppm) are reported relative to tetramethylsilane (TMS) with the resonance of the nondeuterated solvent or TMS as the internal standard. ¹H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ¹³C NMR spectra are reported in terms of chemical shift. Accurate mass measurements were performed using a Varian instrument with the TOF EI-MS technique. Melting points were determined using a X-4 digital micro melting point apparatus. X-ray crystallographic data were collected using a Bruker Smart Apex CCD apparatus. All Allenes were provided by Prof. Hongchao Guo (synthesized in the National Key Technologies R&D Program of China, 2015BAK45B01, CAU).

General procedure for the synthesis of substrates **1:**



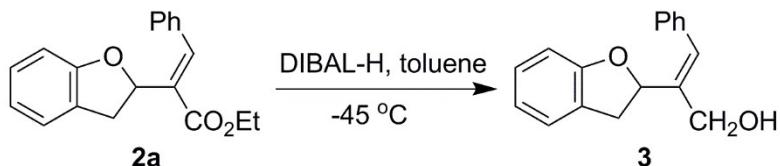
An over-dried Schlenk tube was charged with the appropriate 2-iodophenol (**SI1**) (1.0 mmol), triphenylphosphine (0.2 mmol) under N₂. Distilled benzene (2 mL) was added via syringe. The mixture was stirred at 80 °C. Finally, the corresponding allene (**SI2**) (1.2 mmol) was weighed in a syringe, mixed with distilled benzene (1 mL) and added dropwise to the reaction mixture over 3 h. The reaction was left to proceed until the 2-iodophenol was consumed, typically 12 h (TLC, 40:1 Petroleum ether/EtOAc). The crude reaction mixture was concentrated and loaded onto a silica gel column and separated chromatographically (Petroleum ether /EtOAc, 40:1) to give the desired substrate (**1**).

General procedure for the synthesis of 2,3-dihydrobenzofuran products **2 from substrates **1**:**



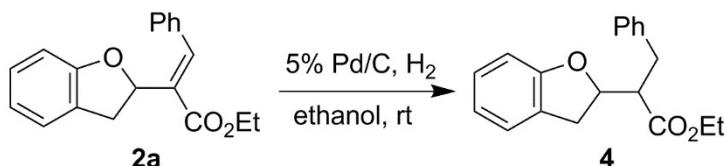
An over-dried Schlenk tube was charged with **1** (0.5 mmol), Pd(dppe)Cl₂ (0.025 mmol), *n*-Bu₄NCl (0.5 mmol), NaHCO₃ (1.0 mmol) and dry DMF (5 mL) under N₂. The mixture was stirred at 90 °C for 8 h and monitored by TLC. Finally, EtOAc (5 mL) and H₂O (5 mL) were added, and the solution was partitioned. The aqueous layer was washed with EtOAc, and EtOAc extracts were washed sequentially with water and saturated NaCl solution. The combined extracts were dried (Na₂SO₄), and the crude reaction mixture was concentrated and loaded onto a silica gel column and separated chromatographically (Petroleum ether /EtOAc, 20:1) to give the desired product (**2**).

Procedure of 1,2-reduction of product 2a:



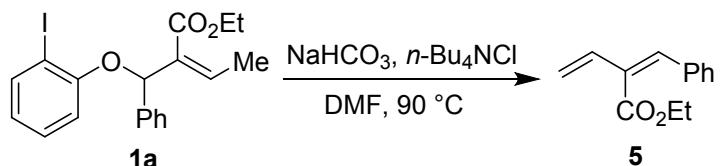
An over-dried Schlenk tube was charged with **6a** (1 mmol) and dry toluene(4 mL) under N₂. The solution was cooled to -45 °C in a dry alcohol bath. Finally, The 1 mL (1.5 mmol) of a 1.5 M solution of DIBAL-H in toluene was added dropwise to the reaction mixture over 0.5 h, and the solution was stirred at -45 °C for 2 h, until reduction was complete (monitored by TLC). Excess hydride was destroyed by the addition of 1 mL of a 1 M HCl solution, and the solution was partitioned. The aqueous layer was washed with EtOAc, and EtOAc extracts were washed sequentially with water and saturated NaCl solution. The combined extracts were dried (Na₂SO₄), and the crude reaction mixture was concentrated and loaded onto a silica gel column and separated chromatographically (Petroleum ether /EtOAc, 3:1) to give the desired product (**3**) in 90% yield.

Procedure of 1,4-reduction of product 2a:



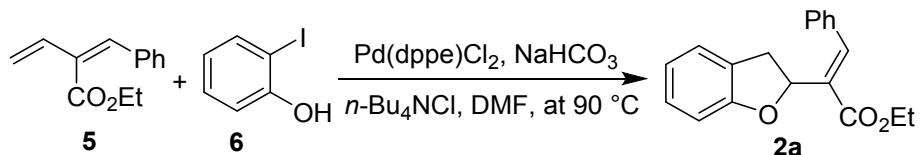
A round-bottom flask was charged with **2a** (0.5 mmol), 5% Pd/C (14.7 mg) and ethanol (50 mL) under H₂. Hydrogen gas was supplied to the reaction mixture from a balloon connected via a syringe through the septum. After stirring for 48 h at room temperature the catalyst was removed from the reaction mixture by filtration (monitored by TLC). The crude reaction mixture was concentrated and loaded onto a silica gel column and separated chromatographically (Petroleum ether /EtOAc, 20:1) to give the desired product (**4**) in 75% yield.

Procedure for transformation of 1a to 5:



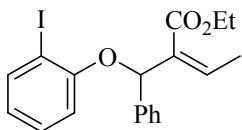
An over-dried Schlenk tube was charged with **1a** (0.5 mmol), *n*-Bu₄NCl (0.5 mmol), NaHCO₃ (1.0 mmol) and dry DMF (5 mL) under N₂. The mixture was stirred at 90 °C for 6 h and monitored by TLC. Finally, EtOAc (5 mL) and H₂O (5 mL) were added, and the solution was partitioned. The aqueous layer was washed with EtOAc, and EtOAc extracts were washed sequentially with water and saturated NaCl solution. The combined extracts were dried (Na₂SO₄), and the crude reaction mixture was concentrated and loaded onto a silica gel column and separated chromatographically (Petroleum ether /EtOAc, 20:1) to give the compound (**5**) in 82%.

Procedure for transformation of 5 and 6 to 2a:

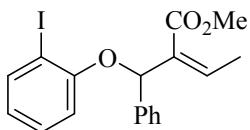


An over-dried Schlenk tube was charged with **5** (0.5 mmol), **6** (0.5 mmol), Pd(dppe)Cl₂ (0.025 mmol), *n*-Bu₄NCl (0.5 mmol), NaHCO₃ (1.0 mmol) and dry DMF (5 mL) under N₂. The mixture was stirred at 90 °C for 8 h and monitored by TLC. Finally, EtOAc (5 mL) and H₂O (5 mL) were added, and the solution was partitioned. The aqueous layer was washed with EtOAc, and EtOAc extracts were washed sequentially with water and saturated NaCl solution. The combined extracts were dried (Na₂SO₄), and the crude reaction mixture was concentrated and loaded onto a silica gel column and separated chromatographically (Petroleum ether /EtOAc, 20:1) to give the desired product (**2a**) in 92% yield.

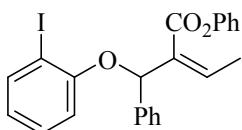
Characterization Data:



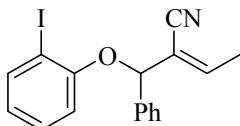
Compound 1a: 98% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 1.23 (t, J = 7.2 Hz, 3H), 2.02 (dd, J = 7.2, 1.2 Hz, 3H), 4.22 (q, J = 7.2 Hz, 2H), 6.19 (s, 1H), 6.40 (q, J = 7.2 Hz, 1H), 6.63 (t, J = 7.2 Hz, 1H), 6.75 (d, J = 7.6 Hz, 1H), 7.14 (t, J = 6.8 Hz, 1H), 7.22 - 7.35 (m, 3H), 7.46 (d, J = 7.2 Hz, 2H), 7.73 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.2, 15.7, 60.6, 79.6, 87.1, 113.8, 122.7, 127.2, 128.0, 128.5, 129.3, 133.0, 138.8, 139.2, 139.4, 156.2, 166.5 ppm; HRMS (TOF EI): m/z calcd for $\text{C}_{19}\text{H}_{19}\text{IO}_3^+$ (M^+) 422.0373, Found 422.0378. The stereochemistry was confirmed by NOESY (δ 6.40 and 6.19).



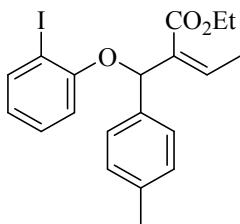
Compound 1b: 92% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 2.03 (d, J = 7.2 Hz, 3H), 3.77 (s, 3H), 6.18 (s, 1H), 6.43 (q, J = 7.2 Hz, 1H), 6.66 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 7.2 Hz, 1H), 7.17 (t, J = 8.4 Hz, 1H), 7.29 (d, J = 7.2 Hz, 1H), 7.35 (t, J = 7.2 Hz, 2H), 7.46 (d, J = 7.2 Hz, 2H), 7.75 (d, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 15.7, 51.6, 79.4, 87.0, 113.7, 122.7, 127.0, 128.0, 128.5, 129.2, 132.6, 139.0, 139.1, 139.4, 156.1, 166.9; HRMS (TOF EI): m/z calcd for $\text{C}_{18}\text{H}_{17}\text{IO}_3^+$ (M^+) 408.0217, Found 408.0223.



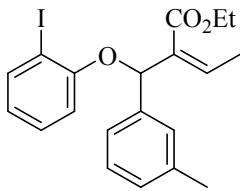
Compound 1c: 90% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 2.16 (d, J = 7.2 Hz, 3H), 6.32 (s, 1H), 6.66 (m, 2H), 6.80 (d, J = 7.2 Hz, 1H), 7.03 (d, J = 7.6 Hz, 2H), 7.15 - 7.23 (m, 2H), 7.29 - 7.40 (m, 5H), 7.52 (d, J = 7.2 Hz, 2H), 7.77 (dd, J = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 16.0, 79.4, 87.1, 113.7, 121.7, 122.8, 125.9, 127.3, 128.2, 128.6, 129.3, 129.4, 132.2, 138.7, 139.5, 141.5, 150.3, 155.9, 164.7; HRMS (TOF EI): m/z calcd for $\text{C}_{23}\text{H}_{19}\text{IO}_3^+$ (M^+) 470.0373, Found 470.0369.



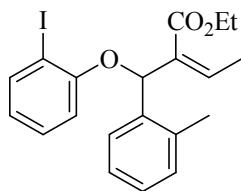
Compound 1d: 89% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 2.05 (t, J = 7.2 Hz, 3H), 5.74 (s, 1H), 6.67 - 6.79 (m, 3H), 7.17 (t, J = 7.2 Hz, 1H), 7.32 - 7.41 (m, 3H), 7.49 (d, J = 6.8 Hz, 2H), 7.78 (dd, J = 8.0, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 18.1, 32.9, 89.7, 97.1, 119.4, 120.8, 126.8, 127.1, 128.7, 128.8, 129.8, 137.8, 139.9, 153.7, 163.7; HRMS (TOF EI): m/z calcd for $\text{C}_{17}\text{H}_{14}\text{INO}^+(\text{M}^+)$ 375.0115, Found 375.0124.



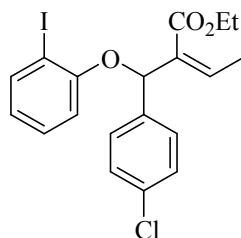
Compound 1e: 97% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 1.24 (t, J = 7.2 Hz, 3H), 2.02 (d, J = 7.2 Hz, 3H), 2.32 (s, 3H), 4.22 (q, J = 7.2 Hz, 2H), 6.15 (s, 1H), 6.38 (q, J = 7.2 Hz, 1H), 6.64 (t, J = 7.6 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 7.14 - 7.18 (m, 3H), 7.34 (d, J = 7.6 Hz, 2H), 7.73 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.2, 15.7, 21.2, 60.6, 87.1, 113.7, 122.6, 127.1, 129.2, 129.3, 133.1, 136.0, 137.7, 138.5, 139.4, 156.2, 166.5; HRMS (TOF EI): m/z calcd for $\text{C}_{20}\text{H}_{21}\text{IO}_3^+(\text{M}^+)$ 436.0530, Found 436.0539.



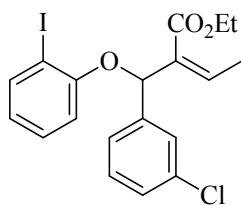
Compound 1f: 94% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 1.24 (t, J = 7.2 Hz, 3H), 2.03 (d, J = 7.2 Hz, 3H), 2.34 (s, 3H), 4.23 (q, J = 7.2 Hz, 2H), 6.15 (s, 1H), 6.36 (q, J = 7.2 Hz, 1H), 6.64 (t, J = 7.6 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 7.07 - 7.27 (m, 5H), 7.73 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.3, 15.7, 21.6, 60.6, 79.7, 87.1, 113.8, 122.7, 124.3, 127.8, 128.4, 128.8, 129.3, 133.1, 138.2, 138.8, 139.0, 139.4, 156.3, 166.5; HRMS (TOF EI): m/z calcd for $\text{C}_{20}\text{H}_{21}\text{IO}_3^+(\text{M}^+)$ 436.0530, Found 436.0538.



Compound 1g: 98% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 1.19 (t, J = 7.2 Hz, 3H), 2.01 (d, J = 7.2 Hz, 3H), 2.34 (s, 3H), 4.17 - 4.28 (m, 2H), 5.92 (q, J = 7.2 Hz, 1H), 6.28 (s, 1H), 6.59 - 6.68 (m, 2H), 7.12 - 7.23 (m, 4H), 7.44 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.2, 15.6, 19.3, 60.7, 78.2, 86.9, 113.4, 122.6, 126.4, 127.5, 128.1, 129.3, 130.6, 131.9, 135.8, 136.1, 139.1, 139.4, 156.8, 166.8; HRMS (TOF EI): m/z calcd for $\text{C}_{20}\text{H}_{21}\text{IO}_3^+$ (M^+) 436.0530, Found 436.0531.

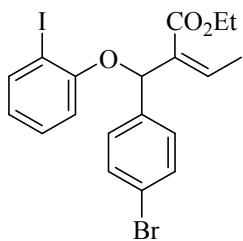


Compound 1h: 93% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 1.24 (t, J = 7.2 Hz, 3H), 2.04 (d, J = 7.2 Hz, 3H), 4.22 (q, J = 7.2 Hz, 2H), 6.16 (s, 1H), 6.46 (q, J = 7.2 Hz, 1H), 6.66 (t, J = 7.6 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 7.17 (t, J = 8.4 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.2, 15.7, 60.7, 78.9, 87.1, 113.8, 123.0, 128.6, 128.7, 129.3, 132.5, 133.8, 137.8, 139.2, 139.5, 155.9, 166.3; HRMS (TOF EI): m/z calcd for $\text{C}_{19}\text{H}_{18}\text{ClIO}_3^+$ (M^+) 455.9984, Found 455.9988.

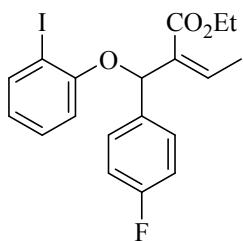


Compound 1i: 92% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 1.26 (t, J = 7.2 Hz, 3H), 2.06 (d, J = 7.2 Hz, 3H), 4.21 - 4.27 (m, 2H), 6.15 (s, 1H), 6.47 (q, J = 7.2 Hz, 1H), 6.66 - 6.75 (m, 2H), 7.17 - 7.21 (m, 1H), 7.24 - 7.29 (m, 2H), 7.34 - 7.37 (m, 1H), 7.48 (s, 1H), 7.75 (dd, J = 6.4, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.2, 15.7, 60.7, 78.8, 87.1, 113.8, 123.0, 125.2, 127.3, 128.2, 129.3, 129.8, 132.3, 134.4,

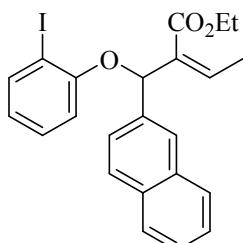
139.5, 139.6, 141.5, 155.9, 166.2; HRMS (TOF EI): m/z calcd for $C_{19}H_{18}ClO_3^+$ (M^+) 455.9984, Found 455.9984.



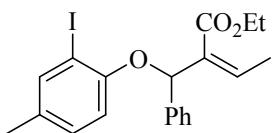
Compound 1j: 92% yield; Colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ : 1.25 (t, J = 7.2 Hz, 3H), 2.05 (d, J = 7.2 Hz, 3H), 4.23 (q, J = 7.2 Hz, 2H), 6.14 (s, 1H), 6.45 (q, J = 7.2 Hz, 1H), 6.66 - 6.74 (m, 2H), 7.18 (t, J = 7.2 Hz, 1H), 7.35 (d, J = 7.2 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 14.2, 15.8, 60.8, 78.8, 87.1, 113.7, 122.0, 123.0, 128.9, 129.3, 131.7, 132.3, 138.3, 139.3, 139.5, 155.8, 166.3; HRMS (TOF EI): m/z calcd for $C_{19}H_{18}BrIO_3^+$ (M^+) 499.9479, Found 499.9485.



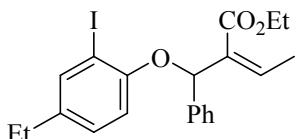
Compound 1k: 91% yield; Colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ : 1.25 (t, J = 6.8 Hz, 3H), 2.05 (d, J = 7.2 Hz, 3H), 4.23 (q, J = 7.2 Hz, 2H), 6.16 (s, 1H), 6.44 (q, J = 7.2 Hz, 1H), 6.67 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 7.03 (t, J = 8.0 Hz, 2H), 7.18 (t, J = 8.4 Hz, 1H), 7.42 - 7.46 (m, 2H), 7.75 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 14.2, 15.7, 60.7, 78.9, 87.1, 113.7, 115.4 (d, J = 21.4 Hz), 122.9, 128.9 (d, J = 8.2 Hz), 129.3, 132.6, 135.0 (d, J = 3.2 Hz), 138.8, 139.5, 155.9, 162.4 (d, J = 245.0 Hz), 166.3; HRMS (TOF EI): m/z calcd for $C_{19}H_{18}FIO_3^+$ (M^+) 440.0279, Found 440.0287.



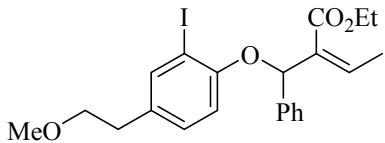
Compound 1l: 90% yield; Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ : 1.22 (t, J = 7.2 Hz, 3H), 2.03 (d, J = 7.2 Hz, 3H), 4.22 (q, J = 7.2 Hz, 2H), 6.35 (s, 1H), 6.43 (q, J = 7.2 Hz, 1H), 6.62 (t, J = 7.6 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H), 7.45 (d, J = 4.0 Hz, 2H), 7.56 (d, J = 8.4 Hz, 1H), 7.72 - 7.83 (m, 4H), 7.93 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.3, 15.8, 60.7, 79.9, 87.2, 113.9, 122.8, 124.9, 126.3, 126.5, 127.8, 128.2, 128.5, 129.3, 132.9, 133.0, 133.1, 133.2, 136.5, 139.3, 139.5, 156.3, 166.5; HRMS (TOF EI): m/z calcd for $\text{C}_{23}\text{H}_{21}\text{IO}_3^+$ (M^+) 472.0530, Found 472.0534.



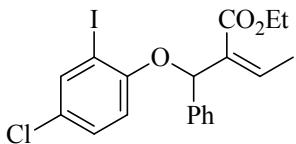
Compound 1m: 96% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 1.25 (t, J = 7.2 Hz, 3H), 2.03 (d, J = 7.6 Hz, 3H), 2.20 (s, 3H), 4.22 (q, J = 7.2 Hz, 2H), 6.14 (s, 1H), 6.41 (q, J = 7.2 Hz, 1H), 6.63 (d, J = 8.4 Hz, 1H), 6.95 (dd, J = 8.4, 1.6 Hz, 1H), 7.27 (d, J = 7.2 Hz, 1H), 7.34 (t, J = 6.8 Hz, 2H), 7.45 (d, J = 7.2 Hz, 2H), 7.57 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.2, 15.7, 20.0, 60.6, 79.5, 86.9, 113.4, 127.2, 127.9, 128.5, 129.7, 132.2, 133.0, 138.7, 139.3, 139.7, 154.1, 166.5; HRMS (TOF EI): m/z calcd for $\text{C}_{20}\text{H}_{21}\text{IO}_3^+$ (M^+) 436.0530, Found 436.0536.



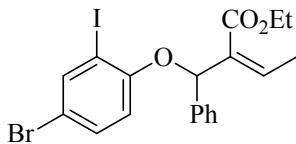
Compound 1n: 95% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 1.15 (t, J = 7.6 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 2.03 (d, J = 7.2 Hz, 3H), 2.50 (q, J = 7.6 Hz, 2H), 4.22 (q, J = 7.2 Hz, 2H), 6.41 (s, 1H), 6.40 (q, J = 7.2 Hz, 1H), 6.66 (d, J = 8.4 Hz, 1H), 6.98 (dd, J = 2.0, 8.4 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.34 (t, J = 7.2 Hz, 2H), 7.46 (d, J = 7.2 Hz, 2H), 7.58 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.2, 15.6, 15.7, 27.5, 60.6, 79.5, 87.0, 113.5, 127.2, 127.9, 128.5, 128.6, 133.0, 138.63, 138.67, 138.7, 139.3, 154.3, 166.5; HRMS (TOF EI): m/z calcd for $\text{C}_{21}\text{H}_{23}\text{IO}_3^+$ (M^+) 450.0686, Found 450.0694.



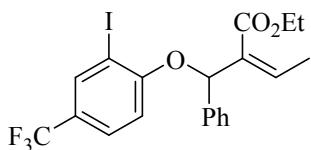
Compound 1o: 93% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 1.24 (t, J = 7.2 Hz, 3H), 2.02 (d, J = 7.2 Hz, 3H), 2.74 (t, J = 7.0 Hz, 2H), 3.32 (s, 3H), 3.51 (t, J = 7.0 Hz, 2H), 4.23 (q, J = 7.2 Hz, 2H), 6.14 (s, 1H), 6.38 (q, J = 7.2 Hz, 1H), 6.66 (t, J = 8.4 Hz, 1H), 7.01 (dd, J = 8.4, 1.6 Hz, 1H), 7.28 (t, J = 7.2 Hz, 1H), 7.34 (t, J = 6.8 Hz, 2H), 7.45 (d, J = 7.2 Hz, 2H), 7.61 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.2, 15.7, 34.7, 58.7, 60.6, 73.4, 79.5, 87.0, 113.4, 127.1, 127.9, 128.5, 129.6, 133.0, 133.4, 138.8, 139.2, 139.5, 154.7, 166.5; HRMS (TOF EI): m/z calcd for $\text{C}_{22}\text{H}_{25}\text{IO}_4^+$ (M^+) 480.0792, Found 480.0800.



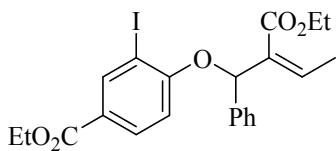
Compound 1p: 90% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 1.25 (t, J = 7.6 Hz, 3H), 2.03 (d, J = 7.2 Hz, 3H), 4.23 (q, J = 7.2 Hz, 2H), 6.14 (s, 1H), 6.35 (q, J = 7.2 Hz, 1H), 6.66 (d, J = 8.8 Hz, 1H), 7.13 (dd, J = 8.8, 2.8 Hz, 1H), 7.29 (d, J = 7.2 Hz, 1H), 7.35 (d, J = 7.2 Hz, 2H), 7.43 (d, J = 6.8 Hz, 2H), 7.71 (d, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.3, 15.7, 60.7, 80.0, 87.2, 114.2, 126.6, 127.1, 128.2, 128.6, 129.0, 132.7, 138.5, 138.6, 139.1, 155.1, 166.4; HRMS (TOF EI): m/z calcd for $\text{C}_{19}\text{H}_{18}\text{ClIO}_3^+$ (M^+) 455.9984, Found 455.9984.



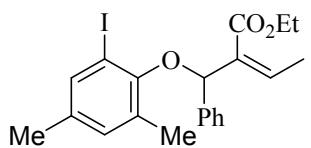
Compound 1q: 89% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 1.25 (t, J = 6.8 Hz, 3H), 2.03 (d, J = 7.2 Hz, 3H), 4.23 (q, J = 6.8 Hz, 2H), 6.14 (s, 1H), 6.34 (q, J = 7.2 Hz, 1H), 6.62 (d, J = 8.8 Hz, 1H), 7.27 - 7.37 (m, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.43 (d, J = 6.8 Hz, 2H), 7.85 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.2, 15.7, 60.7, 79.9, 87.8, 113.7, 114.7, 127.1, 128.2, 128.6, 132.0, 132.6, 138.5, 139.2, 141.1, 155.5, 166.4; HRMS (TOF EI): m/z calcd for $\text{C}_{19}\text{H}_{18}\text{BrIO}_3^+$ (M^+) 499.9479, Found 499.9491.



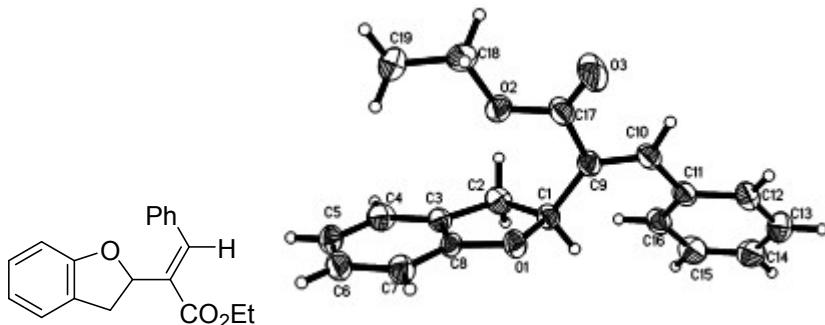
Compound 1r: 86% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.26 (t, $J = 7.2$ Hz, 3H), 2.04 (d, $J = 7.2$ Hz, 3H), 4.24 (q, $J = 7.2$ Hz, 2H), 6.24 (s, 1H), 6.33 (q, $J = 7.2$ Hz, 1H), 6.80 (d, $J = 8.8$ Hz, 1H), 7.31 (d, $J = 6.8$ Hz, 1H), 7.37 (d, $J = 7.2$ Hz, 2H), 7.44 (d, $J = 6.8$ Hz, 3H), 7.37 (d, $J = 1.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.2, 15.7, 60.8, 80.1, 86.6, 113.0, 115.8, 123.2 (q, $J = 270.6$ Hz), 124.7 (q, $J = 32.7$ Hz), 126.8 (q, $J = 4.0$ Hz), 128.2, 128.7, 132.5, 136.5 (q, $J = 4.1$ Hz), 138.2, 139.4, 158.7, 166.3; HRMS (TOF EI): m/z calcd for $\text{C}_{20}\text{H}_{18}\text{F}_3\text{IO}_3^+ (\text{M}^+)$ 490.0247, Found 490.0258.



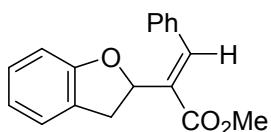
Compound 1s: 82% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 1.32 - 1.39 (m, 6H), 1.93 (d, $J = 7.6$ Hz, 3H), 4.27 - 4.37 (m, 4H), 6.69 (s, 1H), 6.89 (d, $J = 8.4$ Hz, 1H), 7.16 (q, $J = 7.6$ Hz, 1H), 7.30 (t, $J = 7.2$ Hz, 1H), 7.38 (t, $J = 7.2$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 2H), 7.96 (dd, $J = 8.4, 2.0$ Hz, 1H), 8.48 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 14.3, 14.4, 15.5, 61.0, 61.3, 75.8, 85.6, 112.0, 124.8, 125.9, 127.5, 128.4, 131.5, 131.6, 139.1, 141.1, 144.8, 159.4, 165.0, 166.8; HRMS (TOF EI): m/z calcd for $\text{C}_{22}\text{H}_{23}\text{IO}_5^+ (\text{M}^+)$ 494.0585, Found 494.0584.



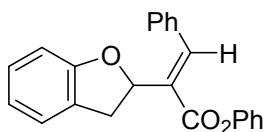
Compound 1t: 85% yield; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 0.95 (t, $J = 7.2$ Hz, 3H), 1.67 (s, 3H), 2.09 - 2.12 (m, 6H), 3.88 - 3.94 (m, 2H), 5.75 (s, 1H), 6.72 - 6.74 (m, 2H), 7.17-7.18 (m, 5H), 7.36 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 13.9, 15.6, 17.3, 20.1, 60.0, 83.6, 92.0, 127.9, 128.0, 128.3, 132.0, 132.1, 132.9, 135.1, 137.9, 139.3, 139.8, 153.6, 166.0; HRMS (TOF EI): m/z calcd for $\text{C}_{21}\text{H}_{23}\text{INaO}_3^+ ([\text{M}+\text{Na}]^+)$ 473.0584, Found 473.0584.



(E)-ethyl -2-(2,3-dihydrobenzofuran-2-yl)-3-phenylacrylate (2a): 88% yield; White solid; M.p.: 75-76 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.90 (s, 1H), 7.41-7.35 (m, 5H), 7.15 (d, J = 7.4 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.83 (t, J = 7.6 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 5.81 (dd, J = 10.4, 8.8 Hz, 1H), 4.17-4.09 (m, 2H), 3.52 (dd, J = 15.2, 8.8 Hz, 1H), 3.42 (dd, J = 15.2, 10.4 Hz, 1H), 0.97 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 159.8, 142.5, 134.4, 131.9, 129.2, 129.0, 128.6, 127.8, 127.3, 124.4, 120.2, 109.0, 77.6, 60.8, 35.9, 13.6; IR (neat): 3019, 1215, 758, 669 cm^{-1} ; HRMS (TOF EI): m/z calcd for $\text{C}_{19}\text{H}_{18}\text{O}_3^+$ (M^+) 294.1250, Found 294.1254.

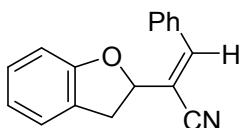


(E)-methyl-2-(2,3-dihydrobenzofuran-2-yl)-3-phenylacrylate (2b): 86% yield; White solid; M.p.: 91-92 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (s, 1H), 7.43-7.35 (m, 5H), 7.16 (dd, J = 6.8, 0.4 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.84 (td, J = 7.6, 0.4 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 5.79 (dd, J = 10.0, 9.0 Hz, 1H), 3.71 (s, 3H), 3.56 (dd, J = 15.2, 9.0 Hz, 1H), 3.38 (dd, J = 15.2, 10.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.6, 159.6, 143.0, 134.3, 131.2, 129.2, 129.1, 128.6, 127.8, 127.2, 124.5, 120.3, 109.1, 77.8, 51.9, 35.7; IR (neat): 3019, 1717, 1215, 758, 669 cm^{-1} ; HRMS (TOF EI): m/z calcd for $\text{C}_{18}\text{H}_{16}\text{O}_3^+$ (M^+) 280.1094, Found 280.1098.

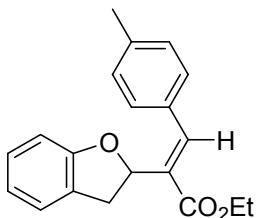


(E)-phenyl-2-(2,3-dihydrobenzofuran-2-yl)-3-phenylacrylate (2c): 70% yield; White solid; M.p.: 149-150 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.11 (s, 1H), 7.46-7.40

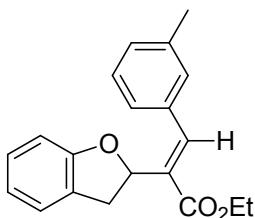
(m, 5H), 7.34-7.30 (m, 2H), 7.21-7.15 (m, 2H), 7.09 (t, $J = 8.0$ Hz, 1H), 7.01-6.99 (m, 2H), 6.84-6.76 (m, 2H), 5.90 (dd, $J = 10.4, 8.8$ Hz, 1H), 3.69 (dd, $J = 15.2, 8.8$ Hz, 1H), 3.49 (dd, $J = 15.2, 10.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.7, 159.6, 150.6, 144.2, 134.1, 131.1, 129.4, 129.3, 129.3, 128.7, 127.9, 127.1, 125.7, 124.6, 121.4, 120.4, 109.1, 77.6, 35.8; IR (neat): 3019, 1215, 756, 669 cm^{-1} ; HRMS (TOF EI): m/z calcd for $\text{C}_{23}\text{H}_{18}\text{O}_3^+$ (M^+) 342.1250, Found 342.1259.



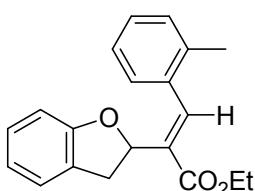
(Z)-2-(2,3-dihydrobenzofuran-2-yl)-3-phenylacrylonitrile (2d): 76% yield; White solid; M.p.: 93-94 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.79-7.77 (m, 2H), 7.43-7.42 (m, 3H), 7.28 (s, 1H), 7.20-7.15 (m, 2H), 6.93-6.87 (m, 2H), 5.41 (t, $J = 9.2$ Hz, 1H), 3.56 (dd, $J = 15.4, 9.2$ Hz, 1H), 3.38 (dd, $J = 15.4, 9.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 144.2, 132.7, 130.9, 129.2, 129.0, 128.5, 125.3, 125.0, 121.5, 116.6, 111.3, 109.6, 82.5, 35.7; IR (neat): 3019, 1478, 1215, 758, 690, 669 cm^{-1} ; HRMS (TOF EI): m/z calcd for $\text{C}_{17}\text{H}_{13}\text{NO}^+$ (M^+) 247.0992, Found 247.1001.



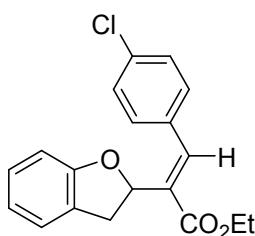
(E)-ethyl-2-(2,3-dihydrobenzofuran-2-yl)-3-(p-tolyl)acrylate (2e): 82% yield; White solid; M.p.: 77-78 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.86 (s, 1H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 7.2$ Hz, 1H), 7.09 (t, $J = 7.6$ Hz, 1H), 6.82 (t, $J = 7.2$ Hz, 1H), 6.73 (d, $J = 7.6$ Hz, 1H), 5.84 (dd, $J = 10.4, 8.4$ Hz, 1H), 4.16-4.08 (m, 2H), 3.51 (dd, $J = 15.2, 8.4$ Hz, 1H), 3.40 (dd, $J = 15.2, 10.4$ Hz, 1H), 2.37 (s, 3H), 0.97 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.6, 159.8, 142.7, 139.3, 131.5, 131.1, 129.3, 129.2, 127.8, 127.4, 124.4, 120.2, 109.0, 77.6, 60.7, 35.9, 21.3, 13.6; IR (neat): 3019, 1705, 1481, 1215, 758, 669 cm^{-1} ; HRMS (TOF EI): m/z calcd for $\text{C}_{20}\text{H}_{20}\text{O}_3^+$ (M^+) 308.1407, Found 308.1415.



(E)-ethyl-2-(2,3-dihydrobenzofuran-2-yl)-3-(m-tolyl)acrylate (2f): 79% yield; White solid; M.p.: 85-86 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.19-7.15 (m, 4H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.83 (td, *J* = 7.2, 0.8 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 5.83 (dd, *J* = 10.4, 8.4 Hz, 1H), 4.16-4.10 (m, 2H), 3.51 (dd, *J* = 15.2, 8.4 Hz, 1H), 3.42 (dd, *J* = 15.2, 10.4 Hz, 1H), 2.36 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.5, 159.8, 142.8, 138.2, 134.4, 131.6, 129.9, 129.8, 128.4, 127.8, 127.4, 126.3, 124.4, 120.2, 109.0, 77.6, 60.8, 35.9, 21.4, 13.56; IR (neat): 3019, 1215, 758, 669 cm⁻¹; HRMS (TOF EI): m/z calcd for C₂₀H₂₀O₃⁺ (M⁺): 308.1407, Found 308.1408.

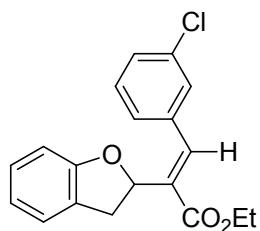


(E)-ethyl-2-(2,3-dihydrobenzofuran-2-yl)-3-(o-tolyl)acrylate (2g): 75% yield; White solid; M.p.: 86-87 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (s, 1H), 7.29-7.06 (m, 6H), 6.81 (td, *J* = 7.6, 0.8 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 5.64 (dd, *J* = 10.4, 8.4 Hz, 1H), 4.19-4.08 (m, 2H), 3.50 (dd, *J* = 15.2, 8.4 Hz, 1H), 3.37 (dd, *J* = 15.2, 10.4 Hz, 1H), 2.35 (s, 3H), 0.96 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 159.8, 142.3, 137.0, 133.8, 132.2, 130.2, 129.0, 128.9, 127.8, 127.4, 125.8, 124.4, 120.2, 109.0, 77.8, 60.8, 35.9, 20.1, 13.5; IR (neat): 3019, 2399, 1701, 1470, 760 cm⁻¹; HRMS (TOF EI): m/z calcd for C₂₀H₂₀O₃⁺ (M⁺): 308.1407, Found 308.1413.

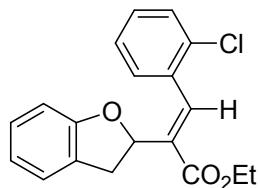


(E)-ethyl-3-(4-chlorophenyl)-2-(2,3-dihydrobenzofuran-2-yl)acrylate (2h): 76% yield; White solid; M.p.: 88-89 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.82 (s, 1H), 7.37

(d, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 7.16-7.08 (m, 2H), 6.84 (t, $J = 7.2$ Hz, 1H), 6.72 (d, $J = 8.0$ Hz, 1H), 5.74 (t, $J = 9.6$ Hz, 1H), 4.16-4.11 (m, 2H), 3.49 (dd, $J = 15.2, 9.6$ Hz, 1H), 3.41 (dd, $J = 15.2, 9.6$ Hz, 1H), 0.99 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 159.7, 141.1, 135.1, 132.9, 132.5, 130.5, 128.8, 127.9, 127.1, 124.4, 120.4, 109.1, 77.4, 60.9, 35.9, 13.6; IR (neat): 3019, 1717, 1481, 1215, 1015, 758 cm^{-1} ; HRMS (TOF EI): m/z calcd for $\text{C}_{19}\text{H}_{17}\text{ClO}_3^+$ (M^+) 328.0861, Found 328.0869.

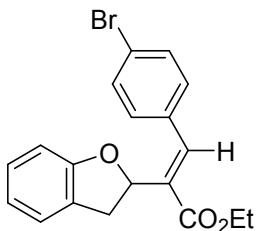


(E)-ethyl-3-(3-chlorophenyl)-2-(2,3-dihydrobenzofuran-2-yl)acrylate (2i): 81% yield; White solid; M.p.: 91-92 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (s, 1H), 7.33-7.32 (m, 3H), 7.24-7.21 (m, 1H), 7.15 (d, $J = 7.6$ Hz, 1H), 7.09 (t, $J = 8.0$ Hz, 1H), 6.83 (t, $J = 7.2$ Hz, 1H), 6.72 (d, $J = 8.0$ Hz, 1H), 5.73 (dd, $J = 10.4, 8.4$ Hz, 1H), 4.18-4.10 (m, 2H), 3.50 (dd, $J = 15.2, 8.4$ Hz, 1H), 3.42 (dd, $J = 15.2, 10.4$ Hz, 1H), 0.99 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 159.7, 140.6, 136.2, 134.6, 133.3, 129.8, 129.1, 129.0, 127.9, 127.2, 127.1, 124.5, 120.4, 109.1, 77.4, 61.0, 36.0, 13.6; IR (neat): 3019, 1215, 758, 669 cm^{-1} ; HRMS (TOF EI): m/z calcd for $\text{C}_{19}\text{H}_{17}\text{ClO}_3^+$ (M^+) 328.0861, Found 328.0870.

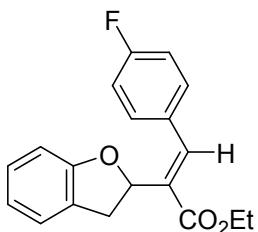


(E)-ethyl-3-(2-chlorophenyl)-2-(2,3-dihydrobenzofuran-2-yl)acrylate (2j): 85% yield; White solid; M.p.: 76-77 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.94 (s, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.32-7.24 (m, 3H), 7.13 (d, $J = 7.2$ Hz, 1H), 7.07 (t, $J = 8.0$ Hz, 1H), 6.82 (t, $J = 7.2$ Hz, 1H), 6.69 (d, $J = 8.0$ Hz, 1H), 5.62 (dd, $J = 10.4, 8.4$ Hz, 1H), 4.19-4.13 (m, 2H), 3.49 (dd, $J = 15.2, 8.4$ Hz, 1H), 3.34 (dd, $J = 15.2, 10.4$ Hz, 1H), 1.02 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.8, 159.7, 139.8, 134.1,

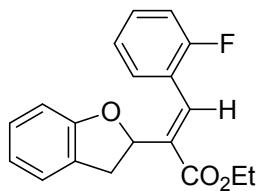
133.3, 133.2, 130.4, 130.1, 129.7, 127.8, 127.2, 126.6, 124.4, 120.3, 109.0, 77.9, 61.0, 35.8, 13.6; IR (neat): 3019, 1215, 756, 669 cm⁻¹; HRMS (TOF EI): m/z calcd for C₁₉H₁₇ClO₃⁺(M⁺) 328.0861, Found 328.0866.



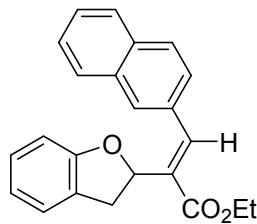
(E)-ethyl-3-(4-bromophenyl)-2-(2,3-dihydrobenzofuran-2-yl)acrylate (2k): 70% yield; White solid. M.p.: 90-91 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 7.2 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.84 (td, J = 7.6, 0.8 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 5.74 (dd, J = 8.4 Hz, 1H), 4.16-4.10 (m, 2H), 3.49 (dd, J = 15.2, 8.4 Hz, 1H), 3.41 (dd, J = 15.2, 10.4 Hz, 1H), 0.98 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 159.6, 141.2, 133.3, 132.5, 131.8, 130.8, 127.9, 127.1, 124.5, 123.4, 120.4, 109.1, 77.4, 61.0, 35.9, 13.6; IR (neat): 3019, 1715, 1636, 1481, 1215, 1011, 758 cm⁻¹; HRMS (TOF EI): m/z calcd for C₁₉H₁₇BrO₃⁺(M⁺) 372.0356, Found 372.0359.



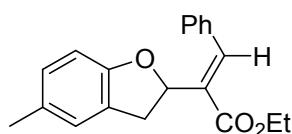
(E)-ethyl-2-(2,3-dihydrobenzofuran-2-yl)-3-(4-fluorophenyl)acrylate (2l): 73% yield; White solid; M.p.: 76-77 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (s, 1H), 7.37-7.33 (m, 2H), 7.15 (d, J = 7.6 Hz, 1H), 7.11-7.07 (m, 3H), 6.84 (t, J = 7.2 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 5.77 (dd, J = 10.4, 8.4 Hz, 1H), 4.16-4.10 (m, 2H), 3.50 (dd, J = 15.2, 8.4 Hz, 1H), 3.41 (dd, J = 15.2, 10.4 Hz, 1H), 0.98 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 163.0 (d, J = 248.9 Hz), 159.7, 141.4, 131.8, 131.3 (d, J = 8.2 Hz), 130.5 (d, J = 3.6 Hz), 127.9, 127.2, 124.5, 120.3, 115.7 (d, J = 22.4 Hz), 109.1, 77.4, 60.9, 35.8, 13.6; IR (neat): 3019, 2357, 1506, 1215, 758, 669 cm⁻¹; HRMS (TOF EI): m/z calcd for C₁₉H₁₇FO₃⁺(M⁺) 312.1156, Found 312.1161.



(E)-ethyl-2-(2,3-dihydrobenzofuran-2-yl)-3-(2-fluorophenyl)acrylate (2m): 85% yield; White solid; M.p.: 67-68 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.86 (s, 1H), 7.38-7.31 (m, 2H), 7.19-7.07 (m, 4H), 6.83 (td, *J*=7.2, 0.8 Hz, 1H), 6.71 (d, *J*=7.6 Hz, 1H), 5.68 (t, *J*=9.4 Hz, 1H), 4.18-4.12 (m, 2H), 3.52 (dd, *J*=15.2, 9.4 Hz, 1H), 3.44 (dd, *J*=15.2, 9.4 Hz, 1H), 1.00 (t, *J*=7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.8, 160.2 (d, *J*=248.5 Hz), 159.7, 135.6 (d, *J*=2.9 Hz), 133.73, 131.0 (d, *J*=8.7 Hz), 130.7 (d, *J*=3.9 Hz), 127.8, 127.3, 124.4, 124.1 (d, *J*=3.0 Hz), 122.4 (d, *J*=14.5 Hz), 120.3, 115.8 (d, *J*=21.5 Hz), 109.0, 78.0, 61.0, 35.6, 13.6; IR (neat): 3019, 1717, 1481, 1215, 758 cm⁻¹; HRMS (TOF EI): m/z calcd for C₁₉H₁₇FO₃⁺ (M⁺): 312.1156, Found 312.1162.

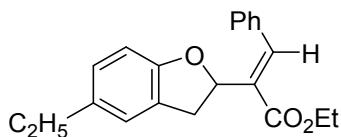


(E)-ethyl-2-(2,3-dihydrobenzofuran-2-yl)-3-(naphthalen-2-yl)acrylate (2n): 80% yield; White solid; M.p.: 124-125 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (s, 1H), 7.88-7.84 (m, 4H), 7.54-7.46 (m, 3H), 7.17 (d, *J*=6.8 Hz, 1H), 7.10 (t, *J*=7.6 Hz, 1H), 6.84 (td, *J*=7.6, 0.8 Hz, 1H), 6.75 (d, *J*=8.0 Hz, 1H), 5.93 (dd, *J*=10.4, 8.4 Hz, 1H), 4.20-4.14 (m, 2H), 3.56 (dd, *J*=15.2, 8.4 Hz, 1H), 3.47 (dd, *J*=15.2, 10.4 Hz, 1H), 1.00 (t, *J*=7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.5, 159.8, 142.7, 133.2, 132.9, 131.9, 131.8, 129.1, 128.4, 128.2, 127.8, 127.7, 127.3, 127.0, 126.7, 126.5, 124.4, 120.2, 109.1, 77.7, 60.9, 35.9, 13.6; IR (neat): 3019, 1215, 756, 669 cm⁻¹; HRMS (EI): m/z calcd for C₂₃H₂₀O₃⁺ (M⁺) 344.1407, Found 344.1409.

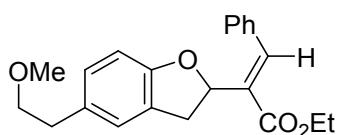


(E)-ethyl-2-(5-methyl-2,3-dihydrobenzofuran-2-yl)-3-phenylacrylate (2o): 75%
S18

yield; White solid; M.p.: 101-102 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 1H), 7.42-7.34 (m, 5H), 6.96 (s, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.61 (d, J = 8.0 Hz, 1H), 5.78 (dd, J = 10.4, 8.8 Hz, 1H), 4.20-4.09 (m, 2H), 3.49 (dd, J = 15.2, 8.8 Hz, 1H), 3.36 (dd, J = 15.2, 10.4 Hz, 1H), 2.27 (s, 3H), 1.02 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 157.7, 142.3, 134.5, 132.0, 129.4, 129.2, 128.9, 128.5, 128.1, 127.3, 125.0, 108.5, 77.7, 60.8, 36.0, 20.8, 13.7; IR (neat): 3019, 1709, 1493, 1263, 758 cm^{-1} ; HRMS (TOF EI): m/z calcd for $\text{C}_{20}\text{H}_{20}\text{O}_3^+$ (M^+) 308.1407, Found 308.1408.

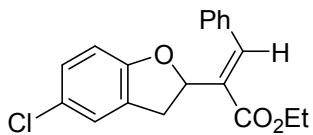


(E)-ethyl-2-(5-ethyl-2,3-dihydrobenzofuran-2-yl)-3-phenylacrylate (2p): 74% yield; White solid; M.p.: 38-39 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.88 (s, 1H), 7.43-7.35 (m, 5H), 6.99 (s, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 5.79 (dd, J = 10.4, 8.4 Hz, 1H), 4.18-4.10 (m, 2H), 3.50 (dd, J = 15.2, 8.4 Hz, 1H), 3.38 (dd, J = 15.2, 10.4 Hz, 1H), 2.57 (q, J = 7.6 Hz, 2H), 1.19 (t, J = 7.6 Hz, 3H), 0.99 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 157.8, 142.4, 136.2, 134.4, 131.9, 129.2, 129.0, 128.5, 127.3, 127.0, 123.9, 108.6, 77.6, 60.8, 36.0, 28.4, 16.3, 13.6; IR (neat): 3053, 2986, 2305, 1711, 1491, 1206, 895, 739 cm^{-1} ; HRMS (TOF EI): m/z calcd for $\text{C}_{21}\text{H}_{22}\text{O}_3^+$ (M^+) 322.1563, Found 322.1566.

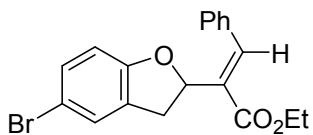


(E)-ethyl-2-(5-(2-methoxyethyl)-2,3-dihydrobenzofuran-2-yl)-3-phenylacrylate (2q): 78% yield; White solid; M.p.: 62-63 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.43-7.35 (m, 5H), 7.02 (s, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 5.80 (dd, J = 10.4, 8.8 Hz, 1H), 4.18-4.10 (m, 2H), 3.56-3.47 (m, 3H), 3.38 (dd, J = 15.2, 10.4 Hz, 1H), 3.35 (s, 3H), 2.81 (t, J = 7.2 Hz, 2H), 0.98 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 158.4, 142.5, 134.4, 131.8, 130.6, 129.2, 129.0, 128.6, 128.2, 127.5, 124.9, 108.7, 77.7, 74.3, 60.8, 58.6, 35.9, 35.7, 13.6; IR (neat): 3019, 1215, 758, 669 cm^{-1} ; HRMS (TOF EI): m/z calcd for $\text{C}_{22}\text{H}_{24}\text{O}_4^+$ (M^+) 352.1669,

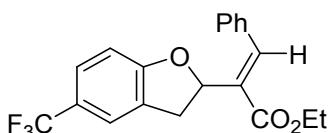
Found 352.1671.



(E)-ethyl-2-(5-chloro-2,3-dihydrobenzofuran-2-yl)-3-phenylacrylate (2r): 75% yield; White solid; M.p.: 111-112 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.44-7.33 (m, 5H), 7.11 (t, *J* = 0.8 Hz, 1H), 7.06 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 5.83 (dd, *J* = 10.4, 8.4 Hz, 1H), 4.18-4.12 (m, 2H), 3.50 (dd, *J* = 15.2, 8.4 Hz, 1H), 3.40 (dd, *J* = 15.2, 10.4 Hz, 1H), 1.03 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 158.6, 143.0, 134.2, 131.3, 129.4, 129.2, 129.1, 128.6, 127.7, 124.8, 124.6, 109.8, 78.3, 60.9, 35.8, 13.7; IR (neat): 3019, 1215, 758, 669 cm⁻¹; HRMS (TOF EI): m/z calcd for C₁₉H₁₇ClO₃⁺ (M⁺) 328.0861, Found 328.0864.

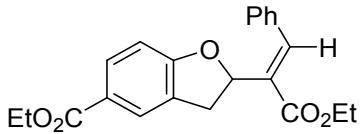


(E)-ethyl-2-(5-bromo-2,3-dihydrobenzofuran-2-yl)-3-phenylacrylate (2s): 71% yield; White solid; M.p.: 109-110 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.42-7.33 (m, 5H), 7.25 (s, 1H), 7.19 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 5.83 (dd, *J* = 10.4, 8.4 Hz, 1H), 4.18-4.11 (m, 2H), 3.51 (dd, *J* = 15.2, 8.4 Hz, 1H), 3.40 (dd, *J* = 15.2, 10.4 Hz, 1H), 1.03 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 159.1, 143.0, 134.2, 131.3, 130.6, 130.0, 129.2, 129.1, 128.6, 127.4, 111.9, 110.5, 78.2, 60.9, 35.7, 13.7; IR (neat): 3019, 1707, 1477, 1215, 756 cm⁻¹; HRMS (TOF EI): m/z calcd for C₁₉H₁₇BrO₃⁺ (M⁺): 372.0356, Found 372.0361.

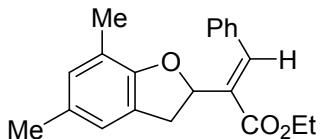


(E)-ethyl-3-phenyl-2-(5-(trifluoromethyl)-2,3-dihydrobenzofuran-2-yl)acrylate (2t): 70% yield; White solid; M.p.: 91-92 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.45-7.25 (m, 7H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.90 (dd, *J* = 10.4, 8.4 Hz, 1H), 4.20-4.08 (m, 2H), 3.54 (dd, *J* = 15.6, 8.4 Hz, 1H), 3.46 (dd, *J* = 15.6, 8.4 Hz, 1H), 0.99 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 162.5, 143.4, 134.2, 131.1, 129.2,

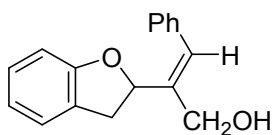
129.1, 128.7, 128.4, 125.9 (q, $J = 3.8$ Hz), 125.0 (q, $J = 300.0$ Hz), 123.0 (q, $J = 32.0$ Hz), 121.8 (q, $J = 3.5$ Hz), 108.9, 78.6, 61.0, 35.4, 13.6; IR (neat): 3019, 2359, 1717, 1327, 1163, 758 cm⁻¹; HRMS (TOF EI): m/z calcd for C₂₀H₁₇F₃O₃⁺ (M⁺): 362.1124, Found 362.1129.



(E)-ethyl-2-(3-ethoxy-3-oxo-1-phenylprop-1-en-2-yl)-2,3-dihydrobenzofuran-5-carboxylate (2u): 70% yield; White solid; M.p.: 82-83 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.89-7.87 (m, 2H), 7.45-7.31 (m, 5H), 6.74 (d, $J = 8.8$ Hz, 1H), 5.91 (dd, $J = 10.4, 8.4$ Hz, 1H), 4.34 (q, $J = 7.2$ Hz, 2H), 4.17-4.08 (m, 2H), 3.55-3.42 (m, 2H), 1.38 (t, $J = 7.2$ Hz, 3H), 0.97 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.6, 166.1, 163.9, 143.2, 134.2, 131.2, 131.0, 129.2, 128.7, 128.0, 126.2, 122.8, 108.6, 78.8, 60.9, 60.6, 35.2, 14.4, 13.6; IR (neat): 3019, 1705, 1275, 1215, 758 cm⁻¹; HRMS (TOF EI): m/z calcd for C₂₂H₂₂O₅⁺ (M⁺) 366.1462, Found 366.1465.

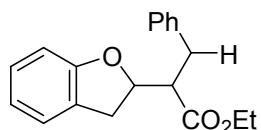


(E)-ethyl-3-phenyl-2-(5-(trifluoromethyl)-2,3-dihydrobenzofuran-2-yl)acrylate (2v): 72% yield; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (s, 1H), 7.39-7.35 (m, 5H), 6.80 (s, 1H), 6.71 (s, 1H), 5.77 (dd, $J = 10.4, 9.2$ Hz, 1H), 4.21-4.08 (m, 2H), 3.51 (dd, $J = 15.2, 8.8$ Hz, 1H), 3.40 (dd, $J = 15.2, 10.4$ Hz, 1H), 2.24 (s, 3H), 2.09 (s, 3H), 1.01 (t, $J = 7.0$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.6, 156.1, 141.8, 134.6, 132.4, 129.5, 129.3, 129.2, 128.9, 128.5, 126.4, 122.3, 118.5, 77.4, 60.7, 36.5, 20.8, 15.3, 13.7; IR (neat): 3018, 2922, 1716, 1483, 1254, 698 cm⁻¹; HRMS (TOF EI): m/z calcd for C₂₁H₂₂NaO₃⁺ ([M+Na]⁺) 345.1461, Found 345.1442.

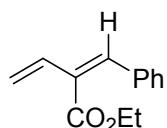


(Z)-2-(2,3-dihydrobenzofuran-2-yl)-3-phenylprop-2-en-1-ol (3): 90% yield; White solid; M.p.: 81-82 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.34 (m, 2H), 7.30-7.22 (m, 5H), 5.91 (dd, $J = 10.4, 8.4$ Hz, 1H), 4.34 (q, $J = 7.2$ Hz, 2H), 4.17-4.08 (m, 2H), 3.55-3.42 (m, 2H), 1.38 (t, $J = 7.2$ Hz, 3H), 0.97 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.6, 166.1, 163.9, 143.2, 134.2, 131.2, 131.0, 129.2, 128.7, 128.0, 126.2, 122.8, 108.6, 78.8, 60.9, 60.6, 35.2, 14.4, 13.6; IR (neat): 3019, 1705, 1275, 1215, 758 cm⁻¹; HRMS (TOF EI): m/z calcd for C₂₂H₂₂O₅⁺ (M⁺) 366.1462, Found 366.1465.

3H), 7.16 (d, J = 7.6 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.88-6.84 (m, 2H), 6.78 (d, J = 8.0 Hz, 1H), 5.75 (t, J = 9.6 Hz, 1H), 4.45 (d, J = 13.2 Hz, 1H), 4.29 (d, J = 13.2 Hz, 1H), 3.39 (dd, J = 15.6, 9.6 Hz, 1H), 3.30 (dd, J = 15.6, 9.6 Hz, 1H), 2.14 (br, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.3, 139.6, 136.1, 130.4, 128.7, 128.4, 128.2, 127.4, 126.6, 124.8, 120.9, 109.4, 80.7, 63.2, 35.8; IR (neat): 3053, 2986, 1479, 1265, 895, 739, 704 cm^{-1} ; HRMS (TOF EI): m/z calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2^+$ (M^+): 252.1145, Found 252.1147.

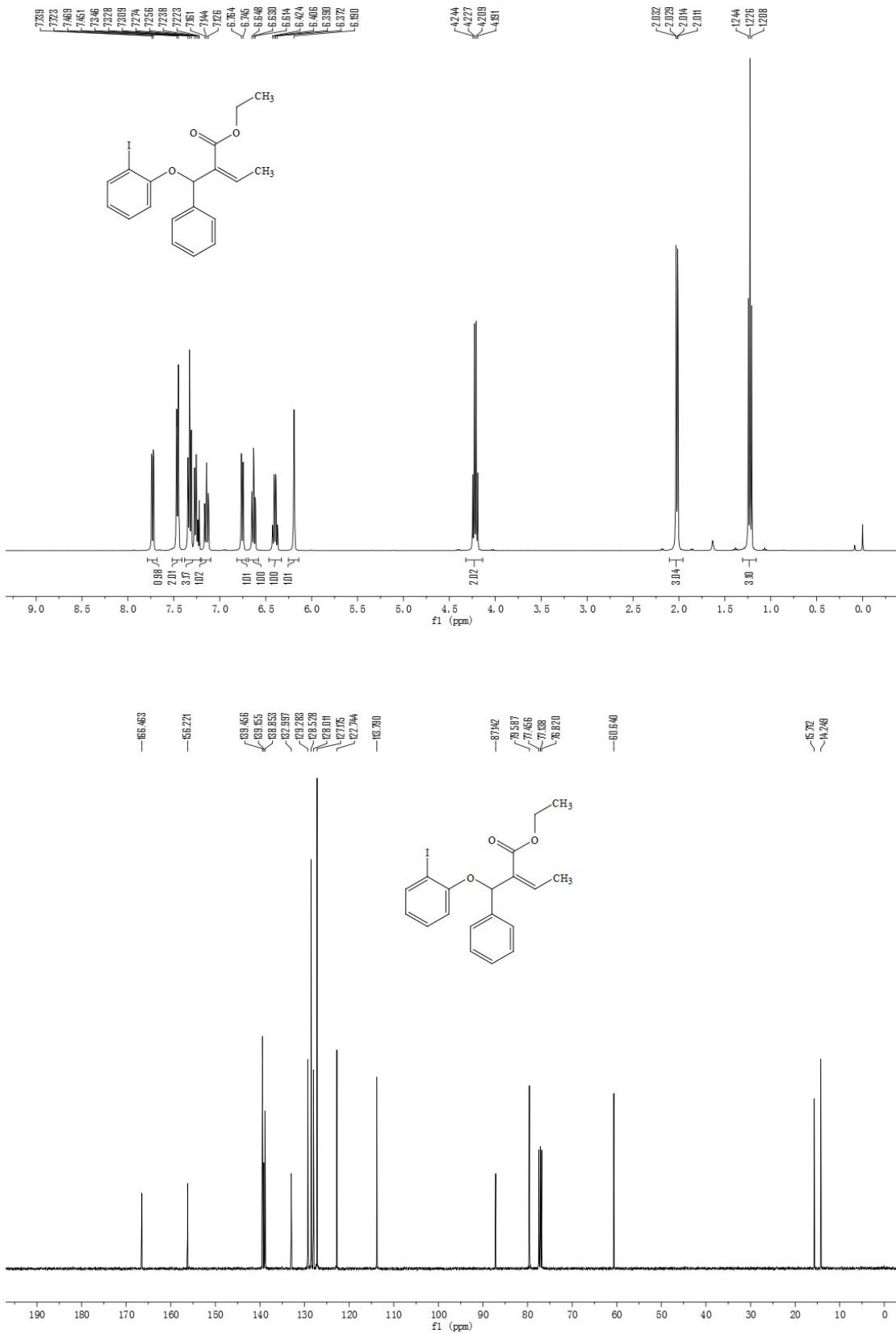


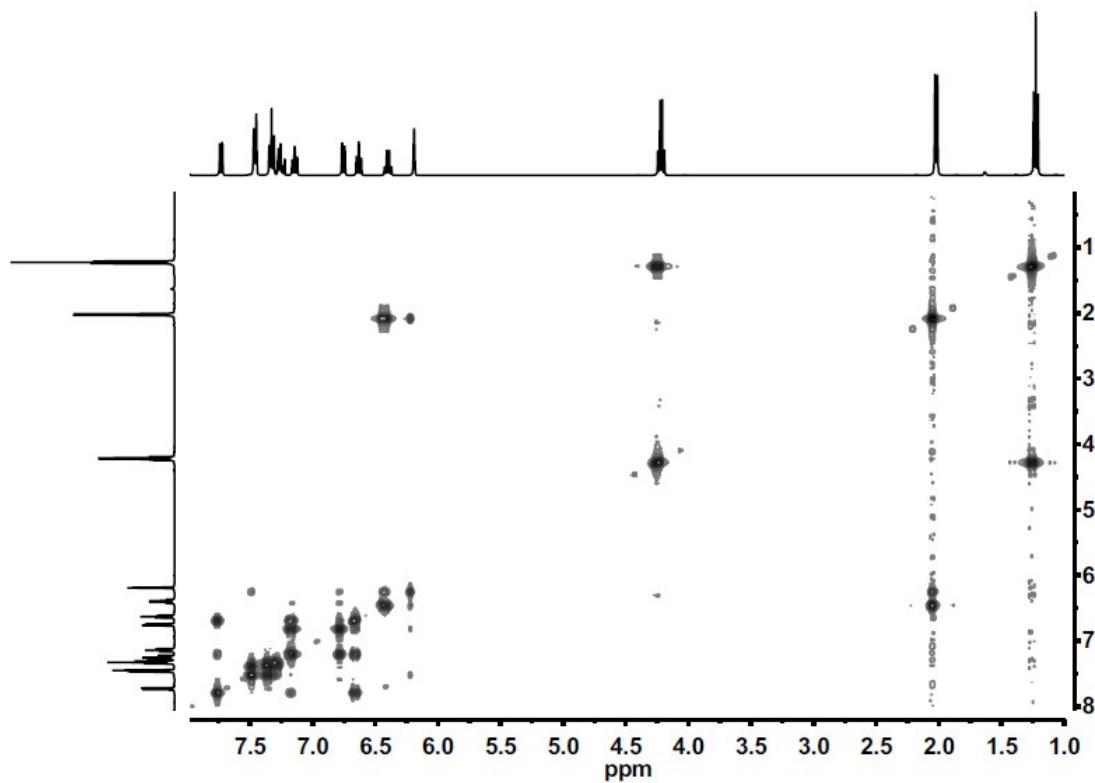
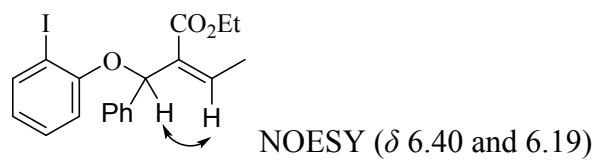
Ethyl-2-(2,3-dihydrobenzofuran-2-yl)-3-phenylpropanoate (4): 75% yield; Colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.25 (m, 2H), 7.20-7.18 (m, 3H), 7.15 (d, J = 7.6 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.83 (t, J = 7.2 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 5.02-4.96 (m, 1H), 4.02 (q, J = 7.2 Hz, 2H), 3.30 (dd, J = 15.6, 9.2 Hz, 1H), 3.11 (dd, J = 15.6, 7.2 Hz, 1H), 3.01-2.90 (m, 3H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.6, 159.3, 138.3, 129.0, 128.5, 128.2, 126.6, 126.1, 124.8, 120.6, 109.6, 82.7, 60.6, 53.1, 34.3, 33.5, 14.0; IR (neat): 3052, 2934, 1732, 1599, 1157, 858, 565 cm^{-1} ; HRMS (TOF EI): m/z calcd for $\text{C}_{19}\text{H}_{20}\text{O}_3^+$ (M^+): 296.1407, Found 296.1413.



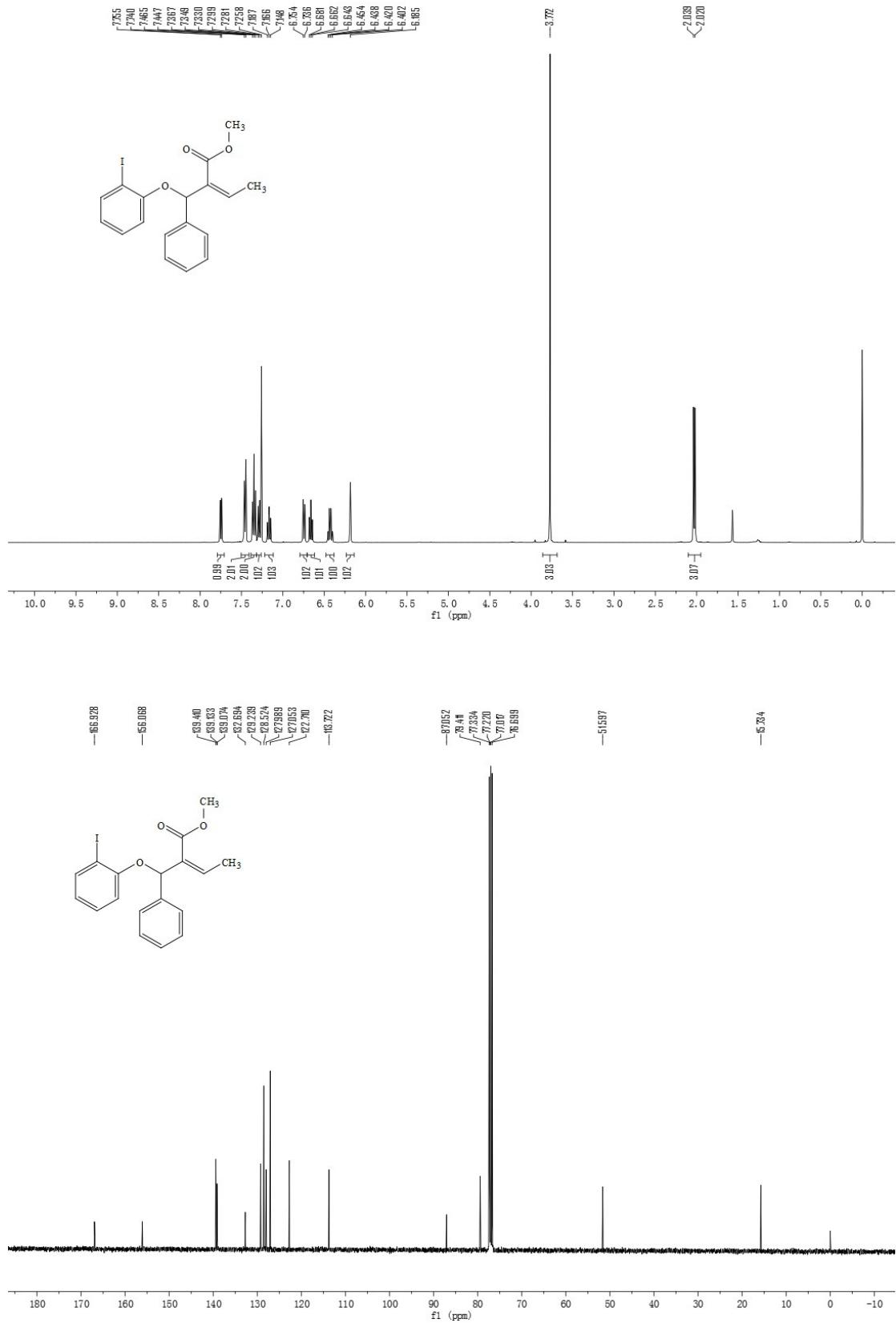
(Z)-ethyl 2-benzylidenebut-3-enoate (5): 82% yield; Colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (s, 1H), 7.43-7.32 (m, 5H), 6.64 (ddd, J = 18.0, 11.6, 0.8 Hz, 1H), 5.86 (dd, J = 18.0, 1.6 Hz, 1H), 5.44 (dt, J = 11.6, 1.2 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 139.1, 135.3, 130.4, 130.0, 129.7, 128.7, 128.3, 120.9, 61.0, 14.3; HRMS (TOF EI): m/z calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2^+$ (M^+): 202.0988, Found 202.0992. *Z* stereochemistry was confirmed by NOESY (δ 7.54 and 6.64).

1a

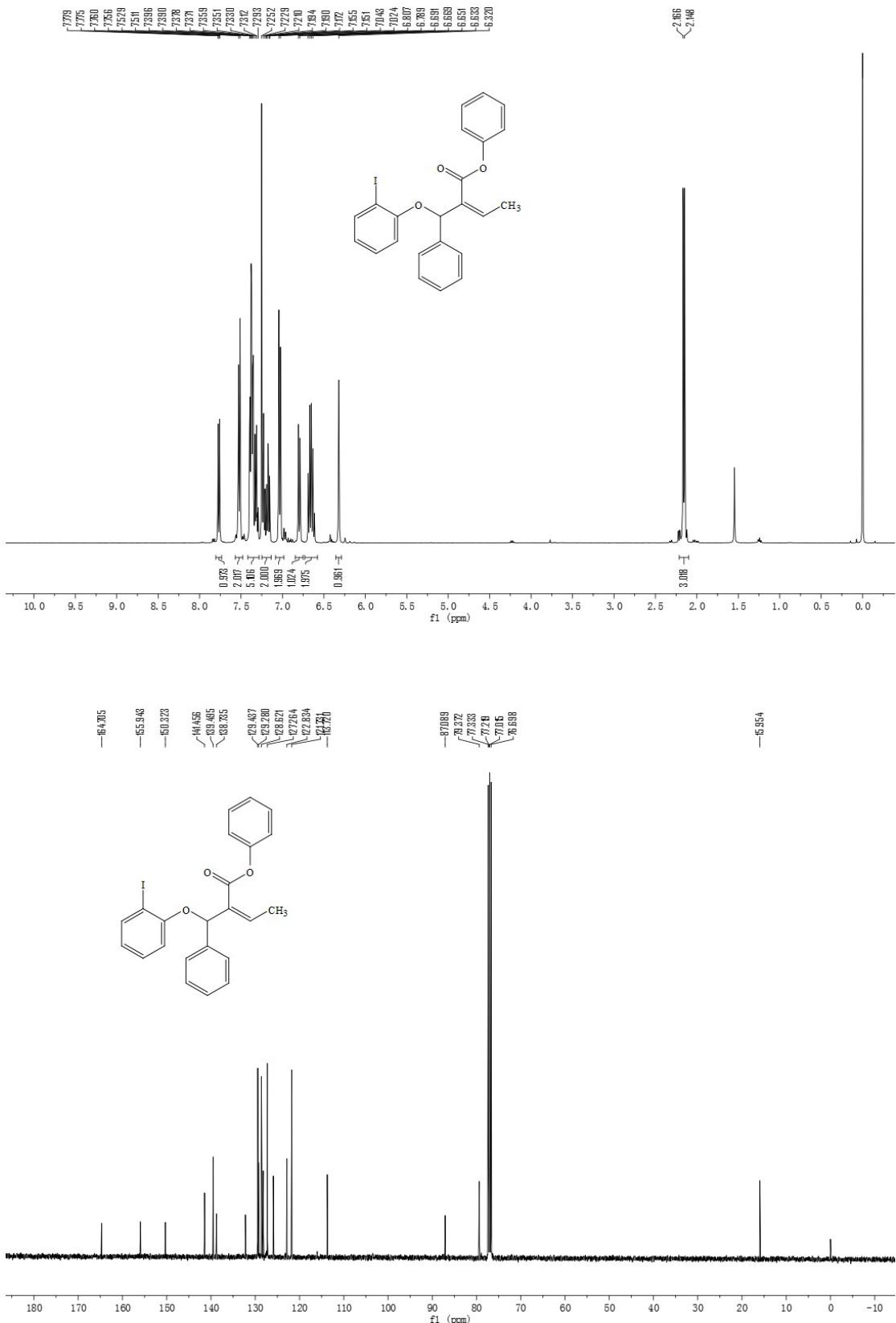


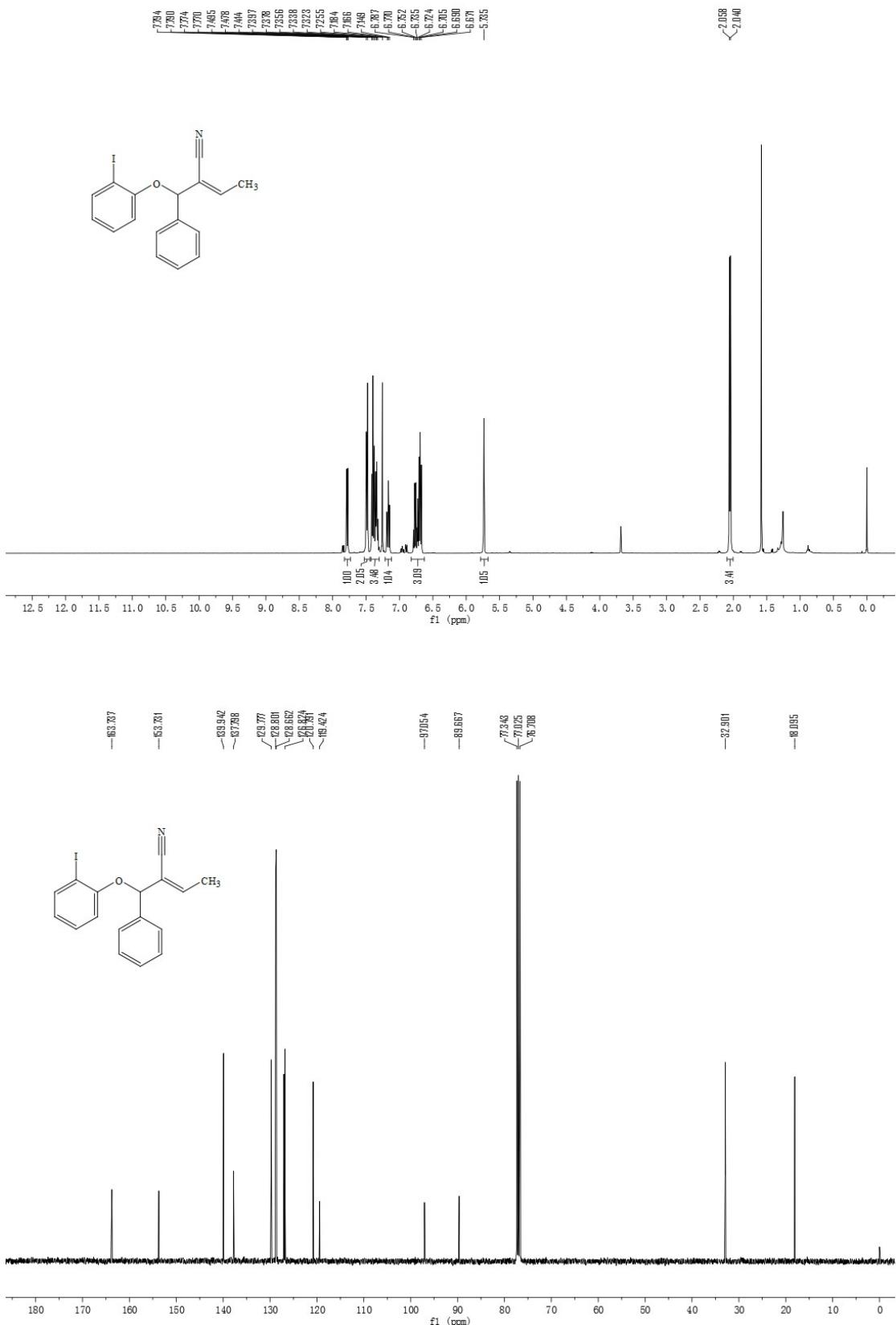


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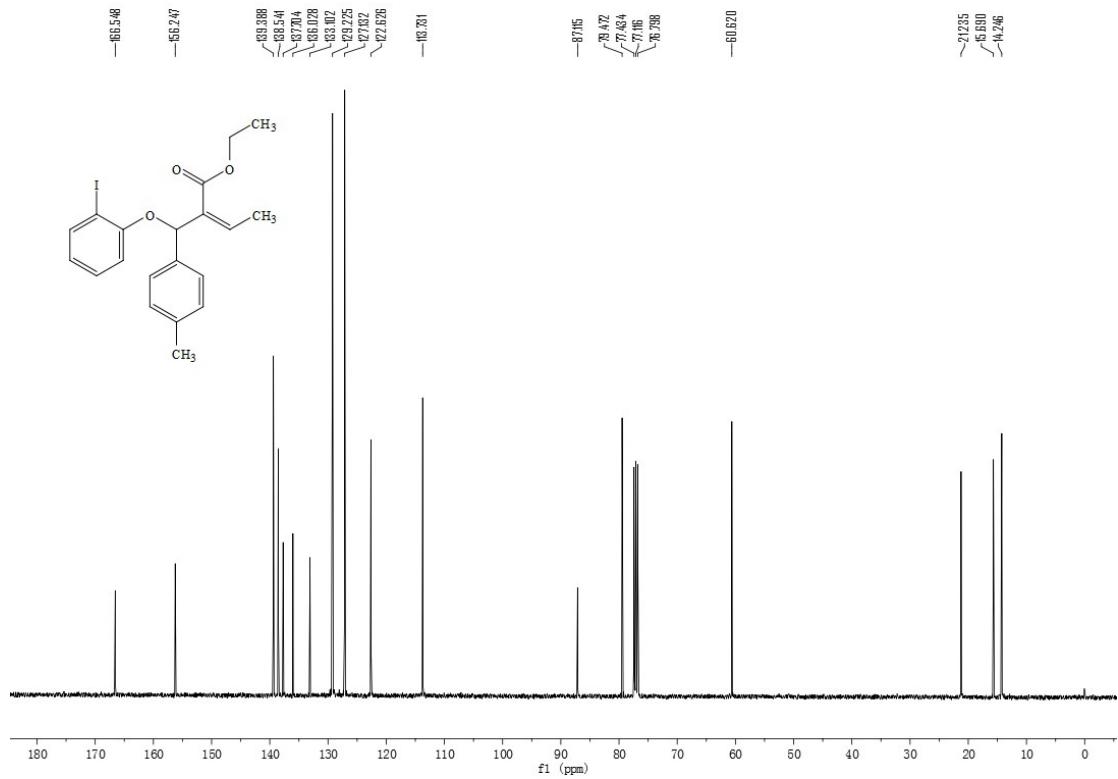
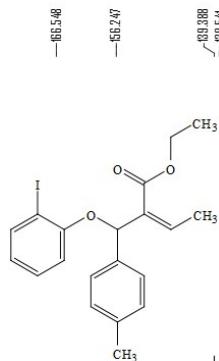
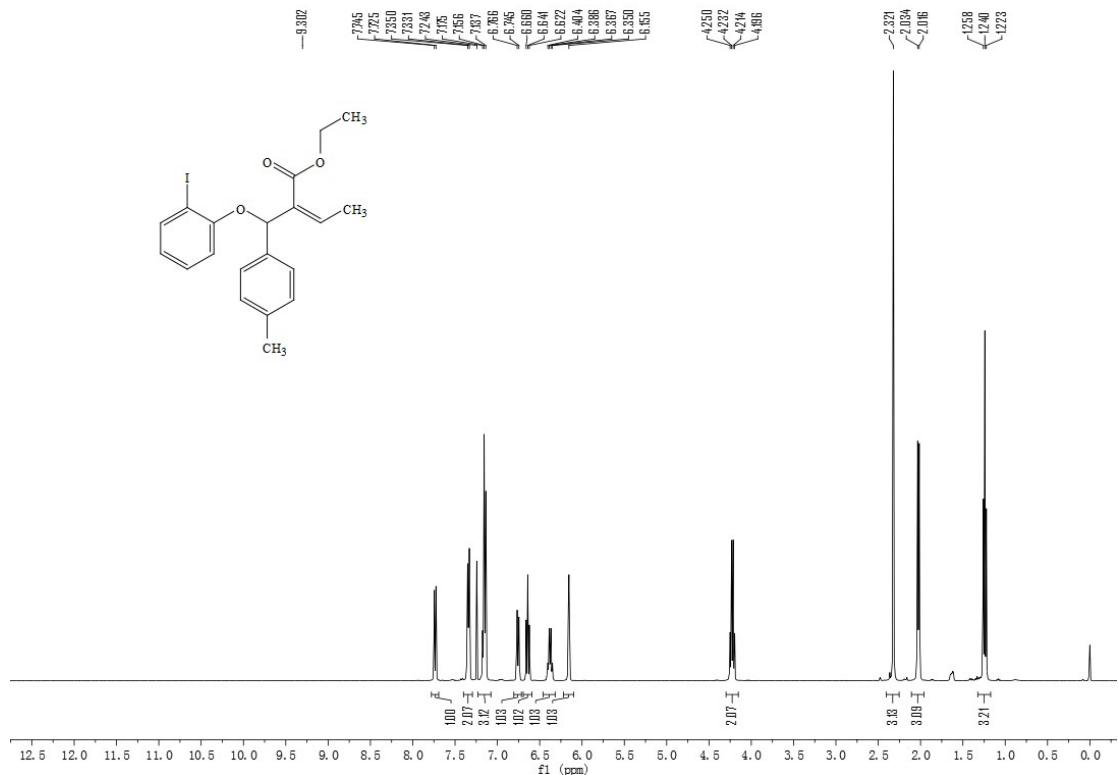
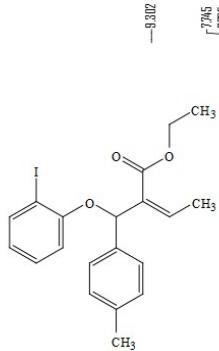


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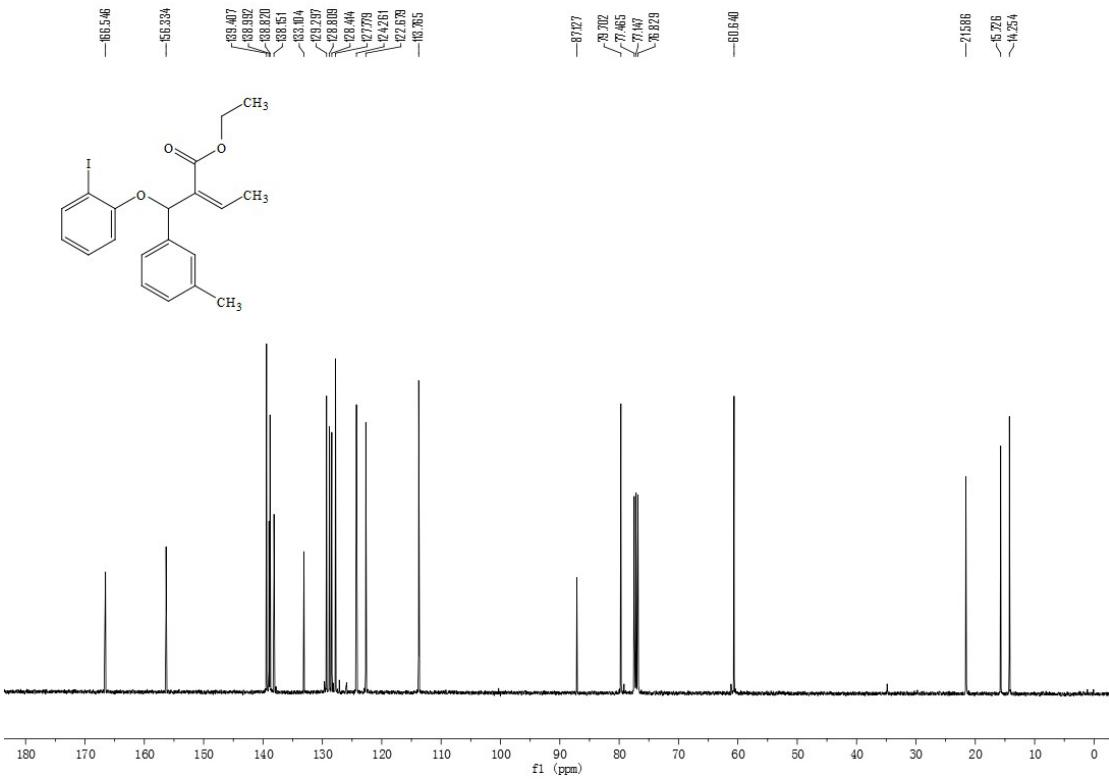
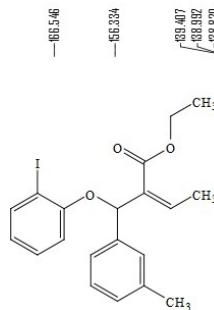
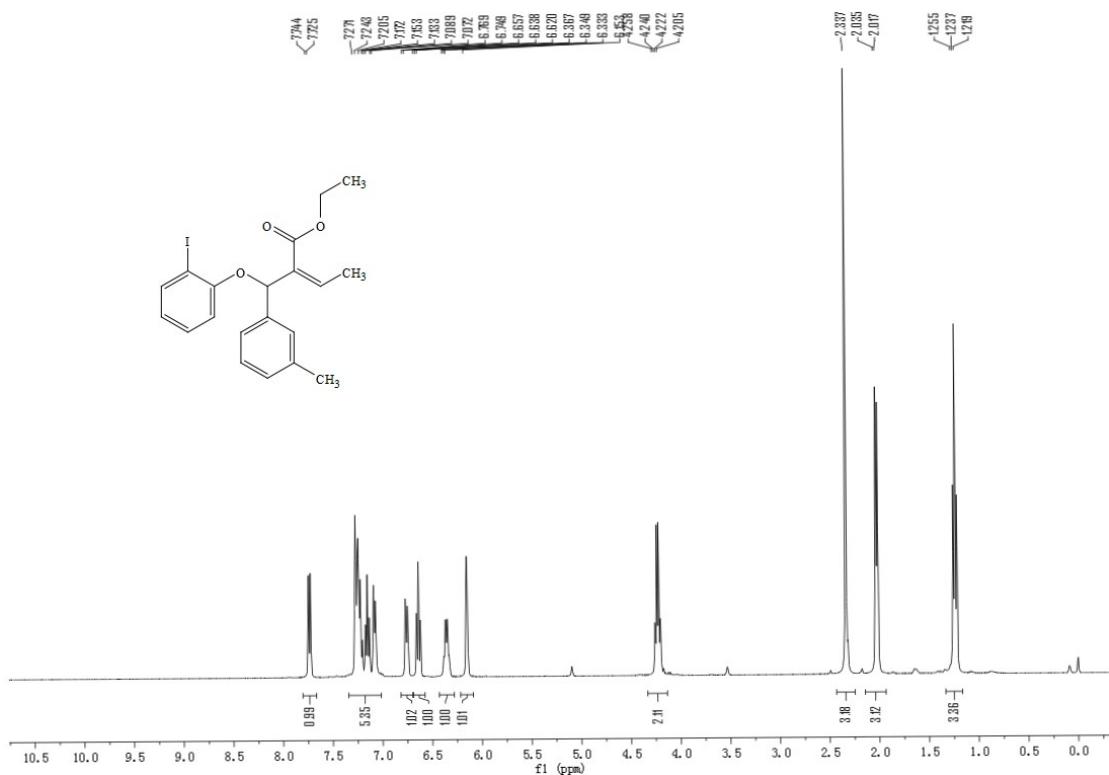
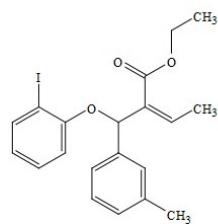


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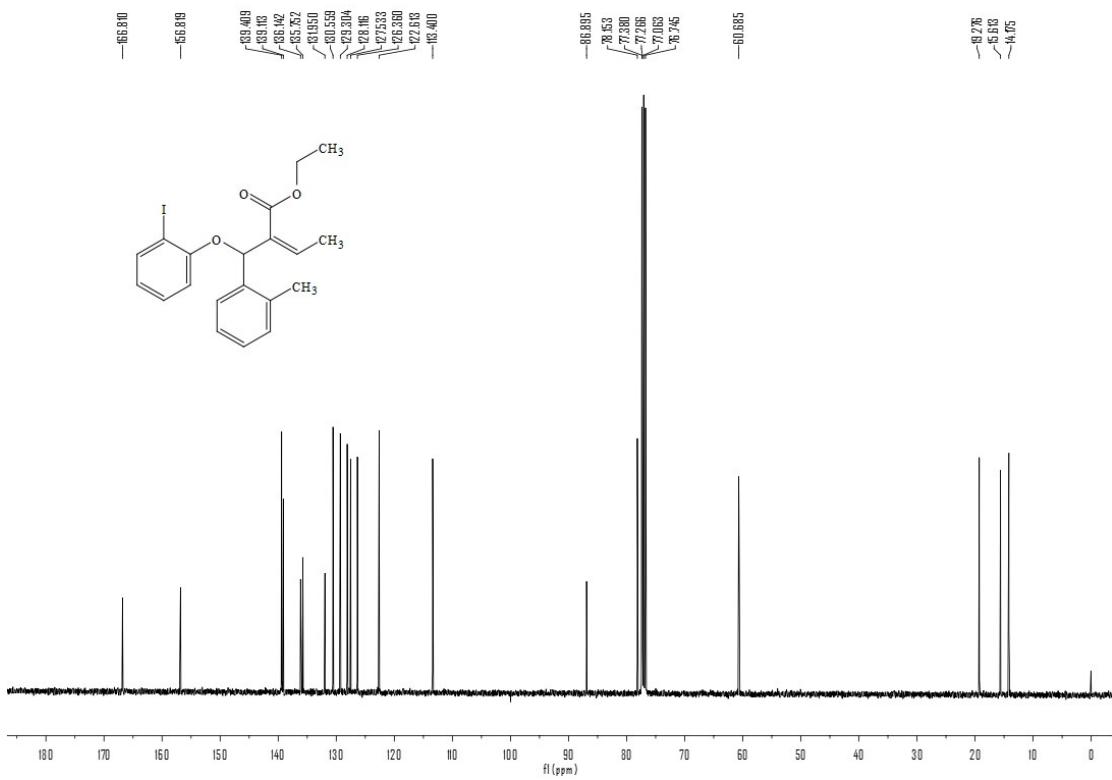
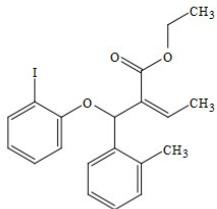
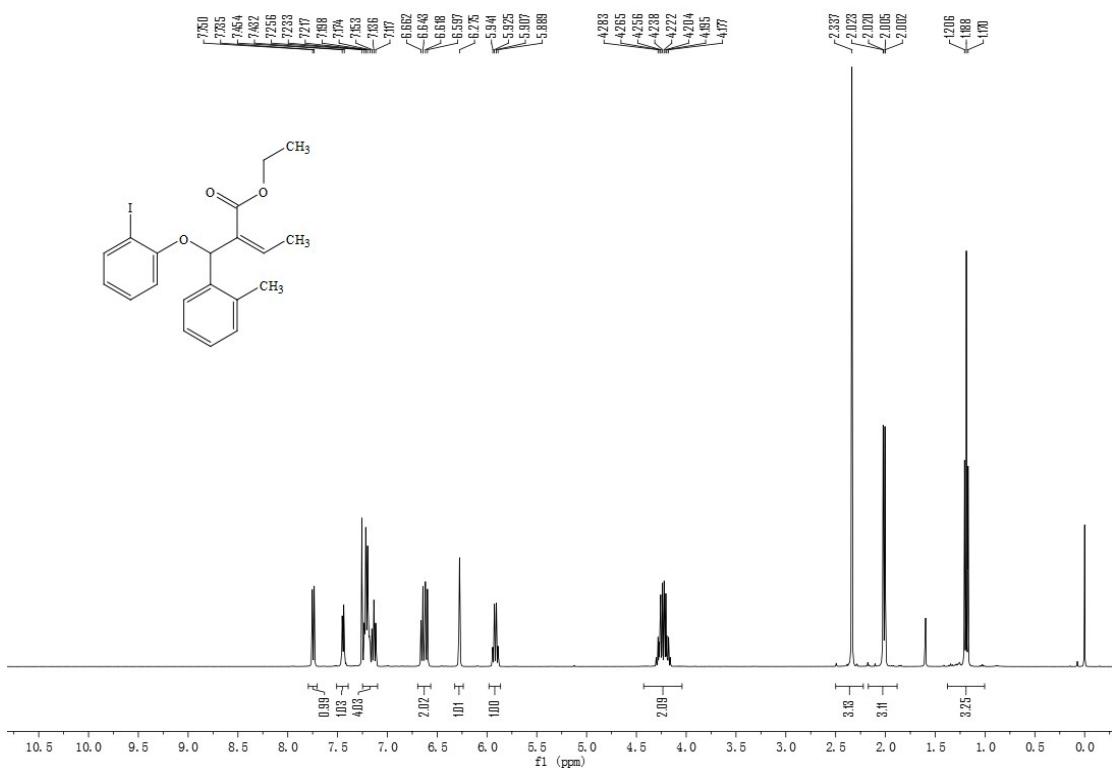
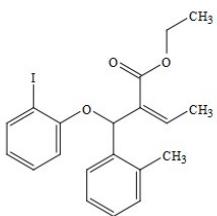
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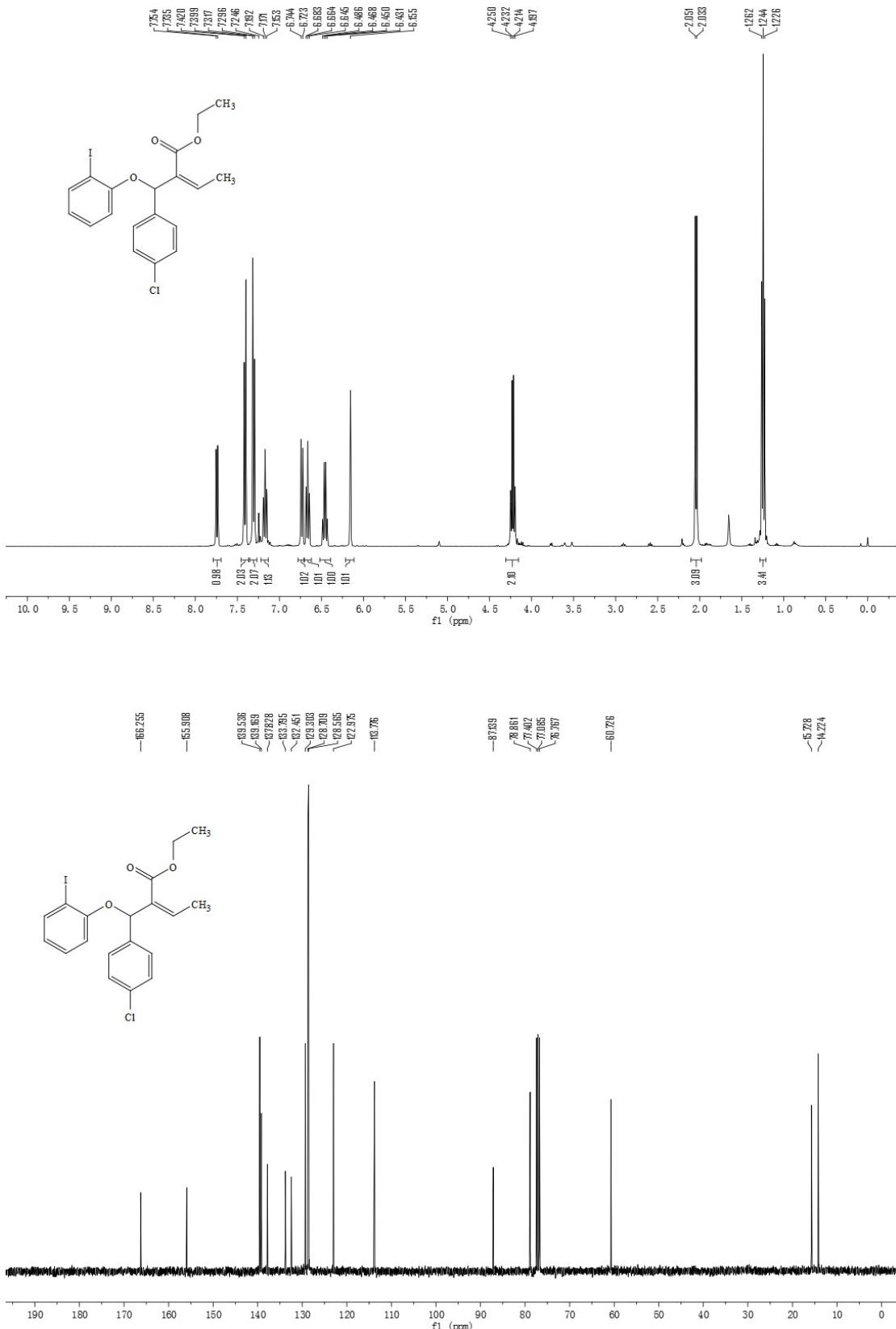
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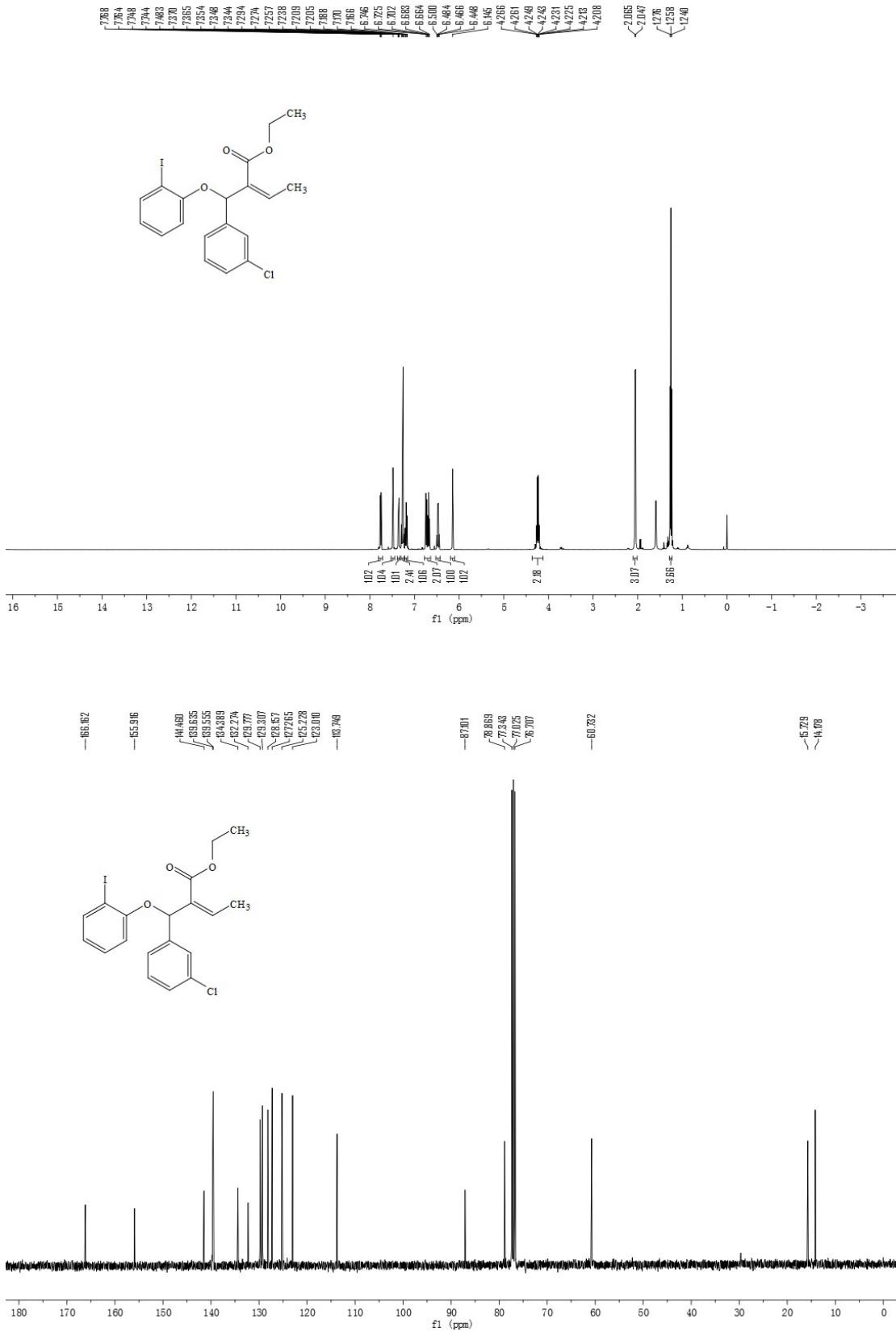
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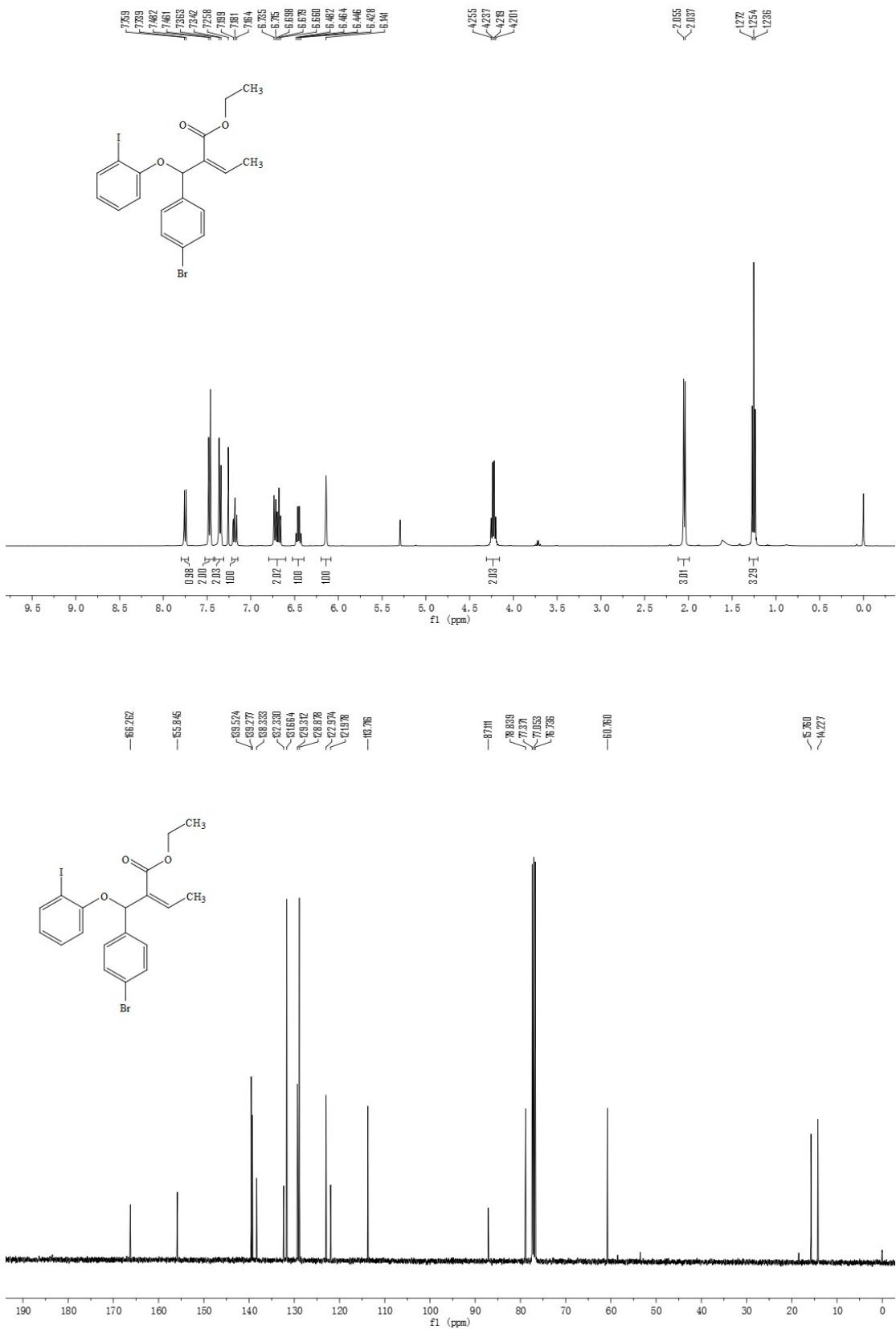
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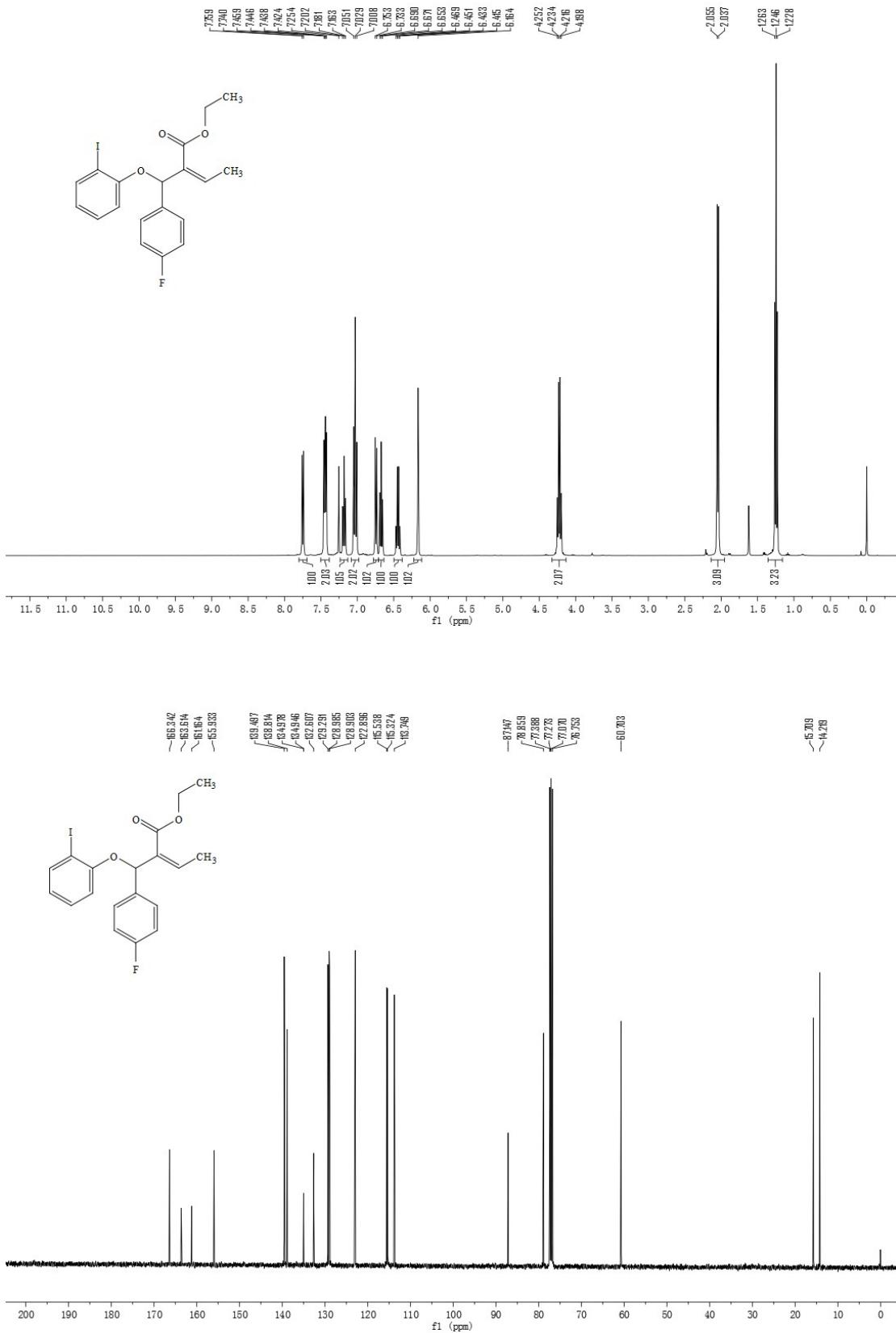
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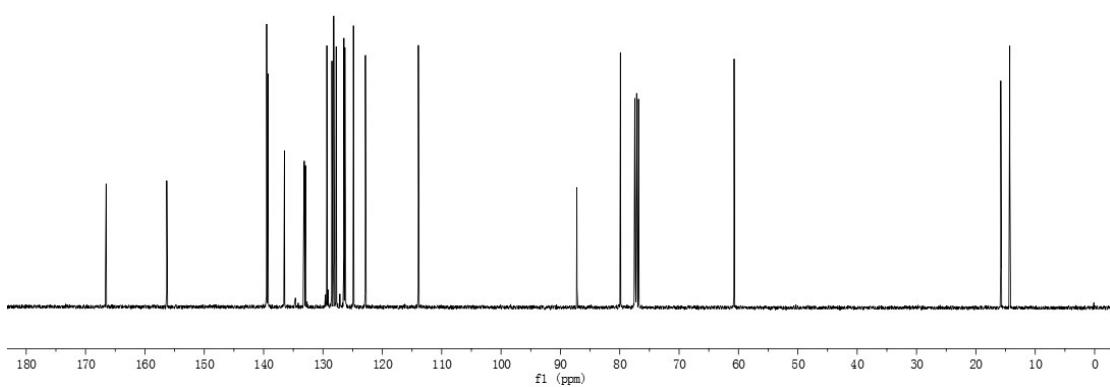
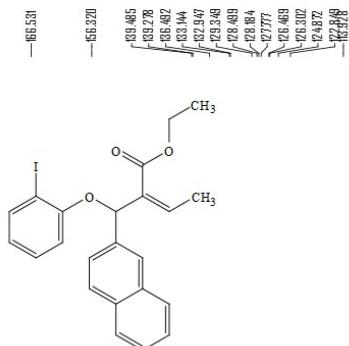
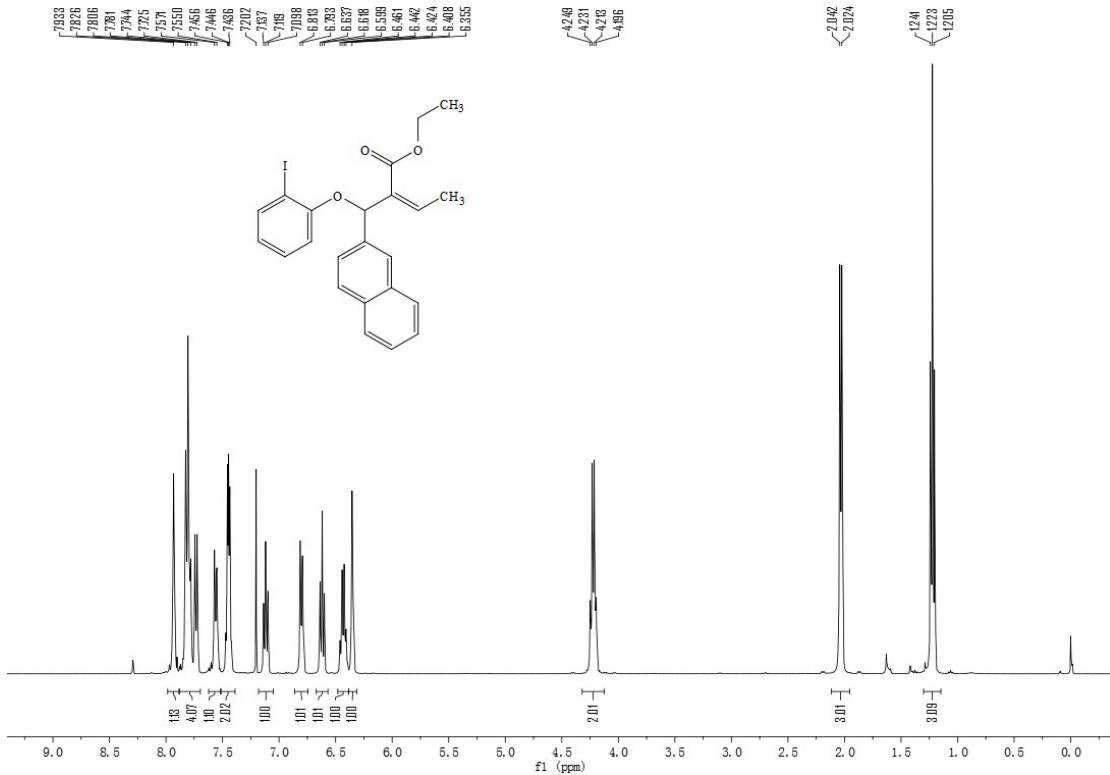
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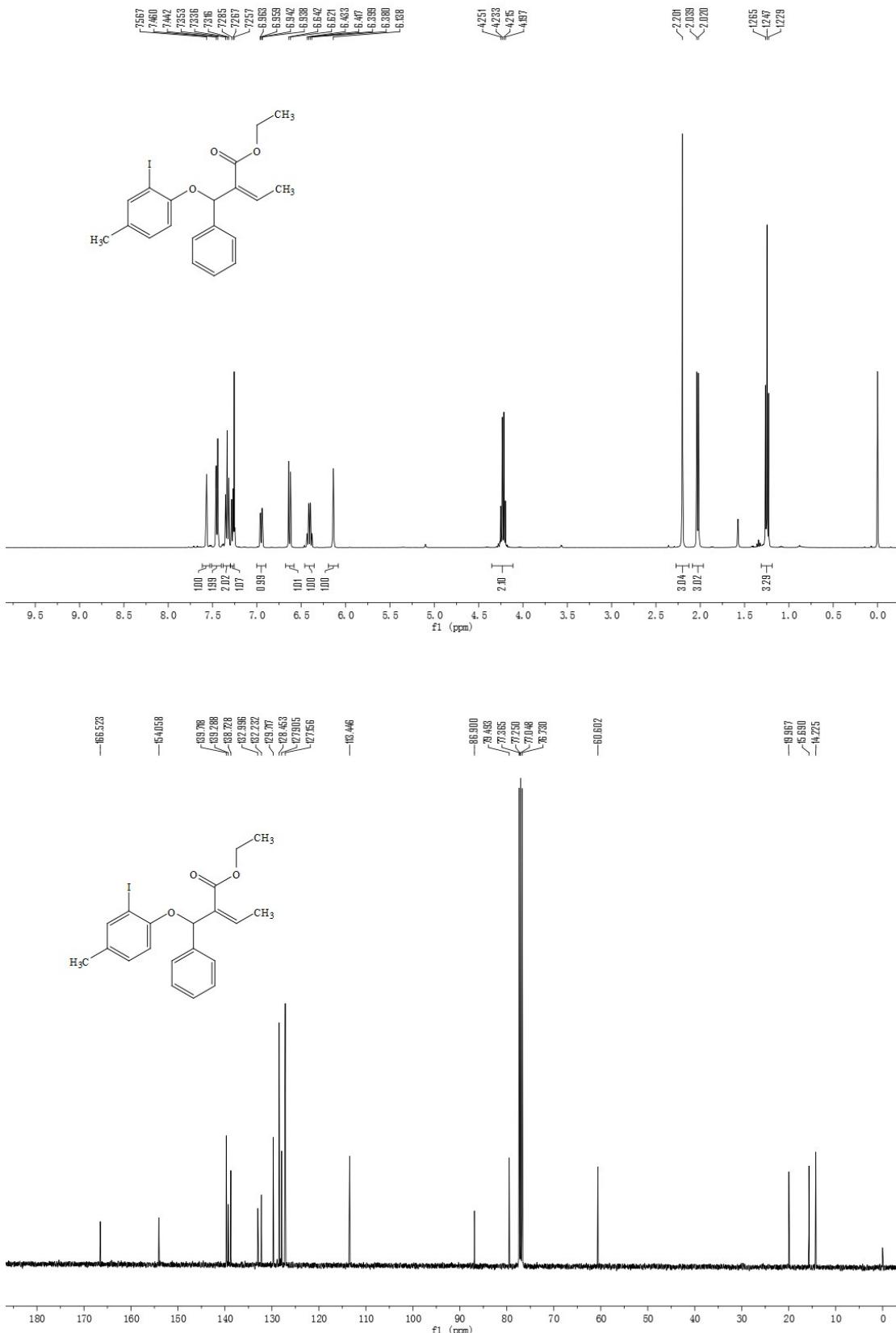


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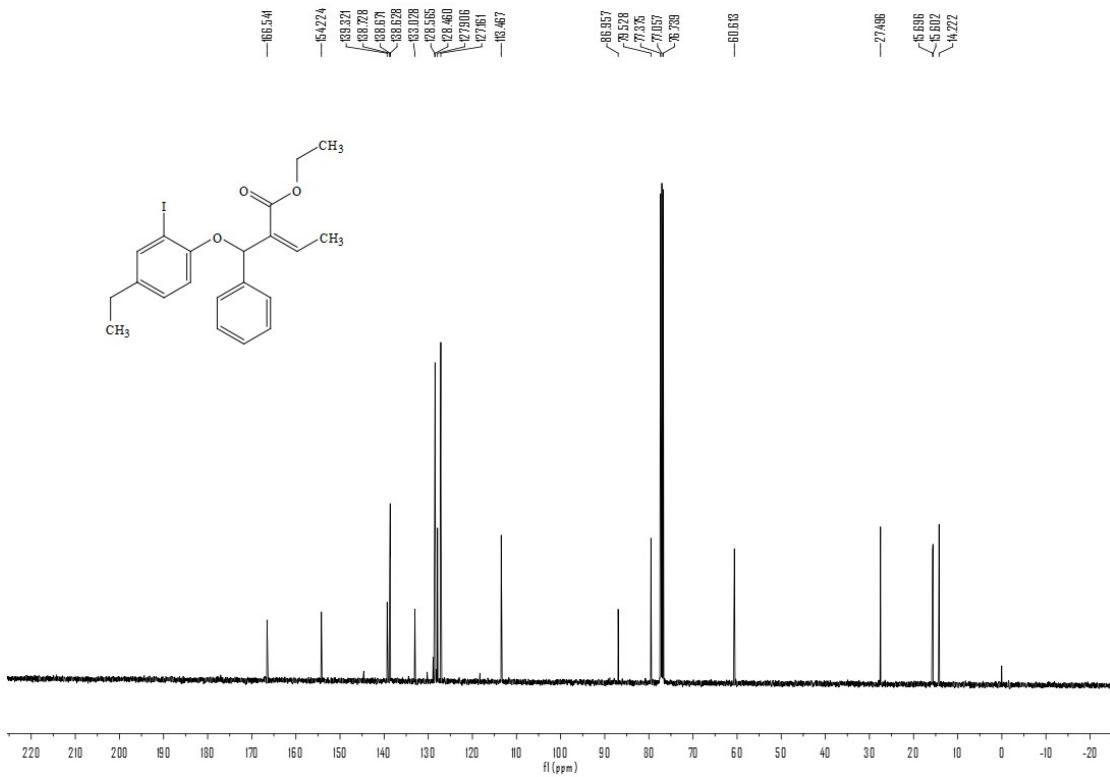
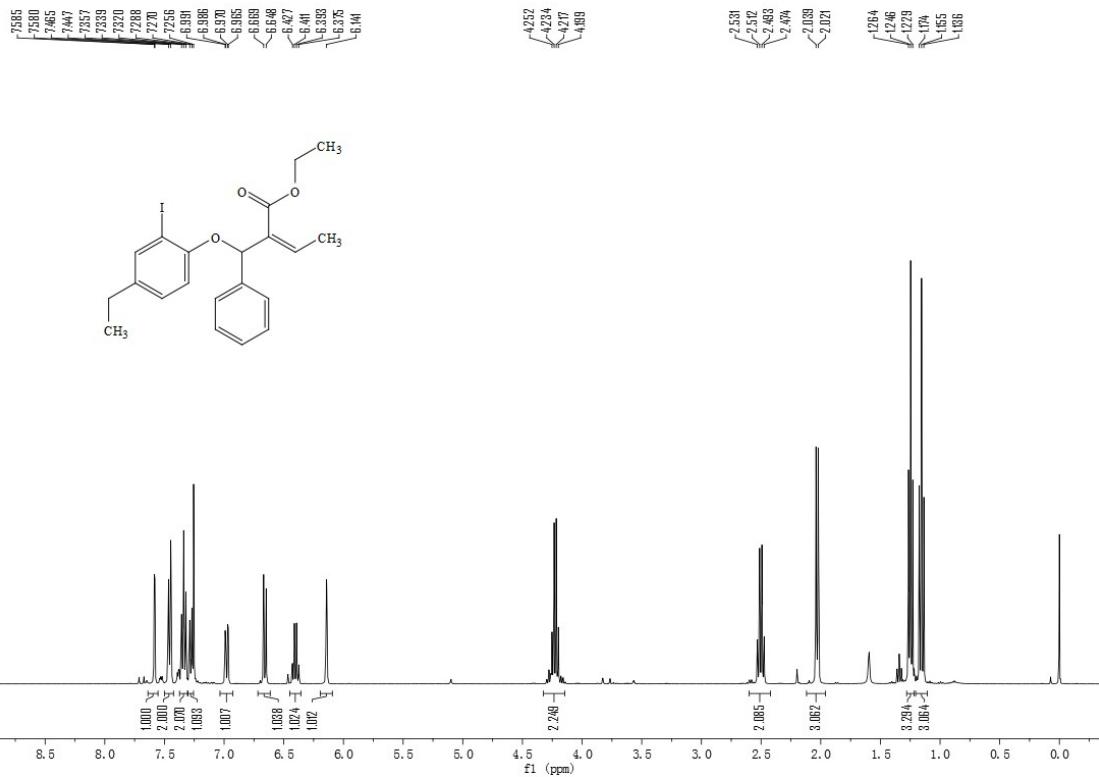


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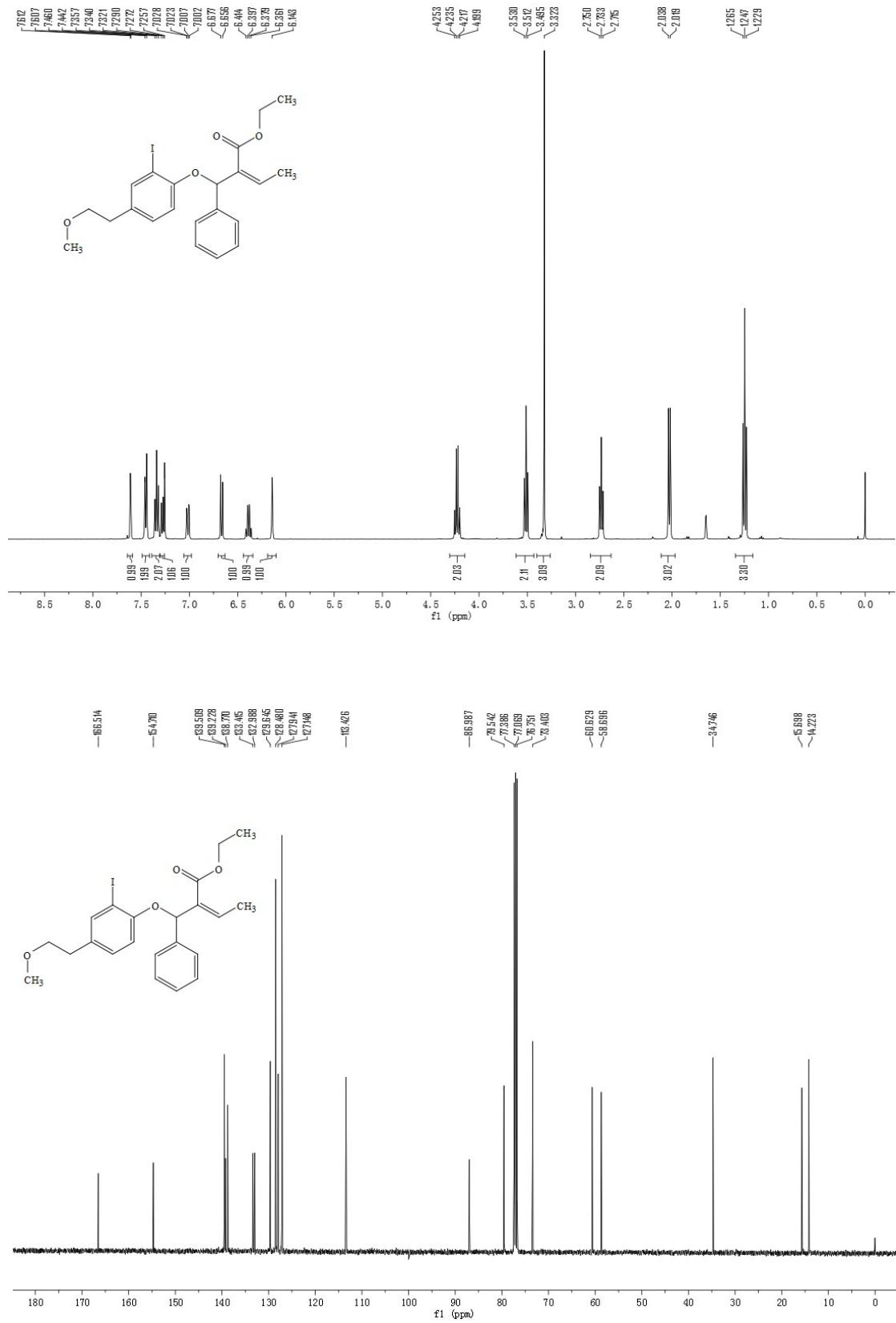


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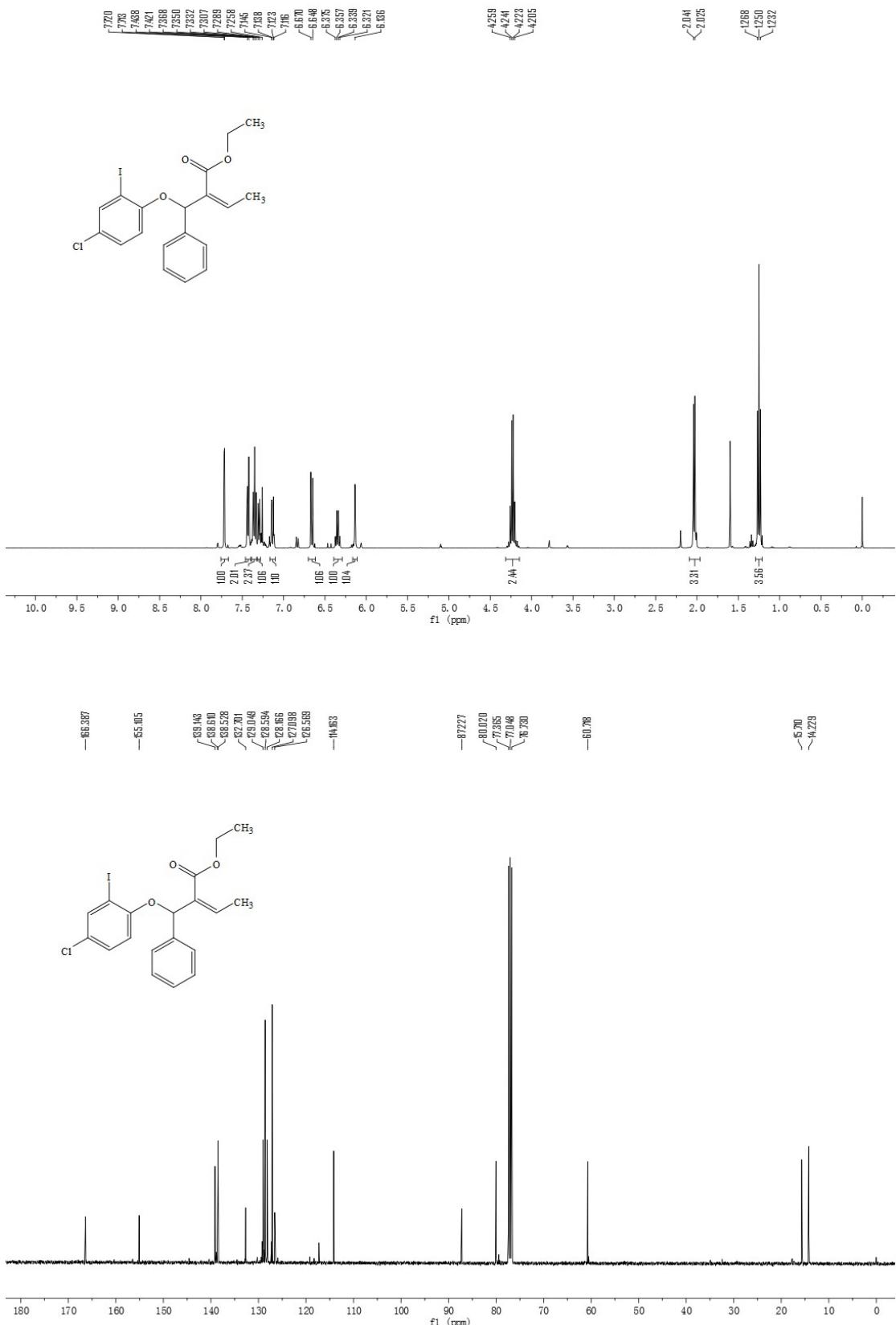
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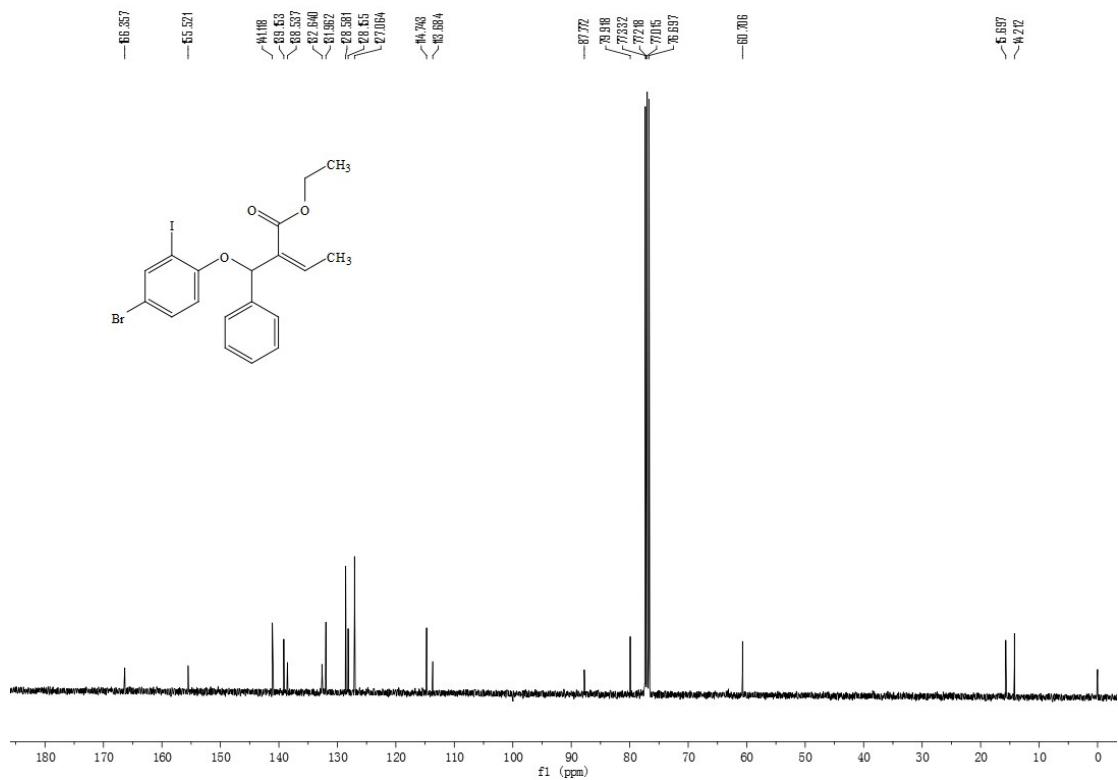
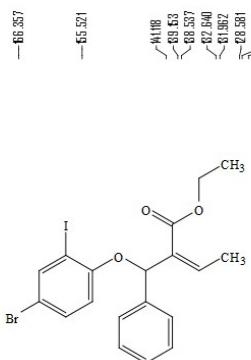
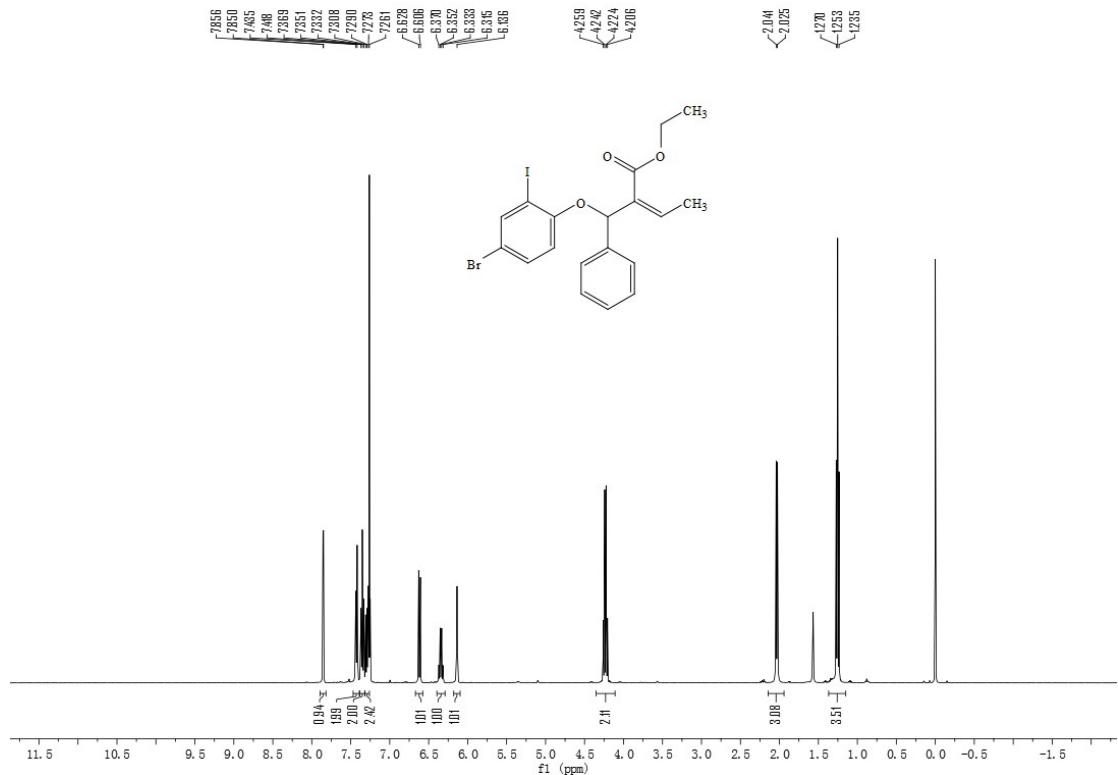
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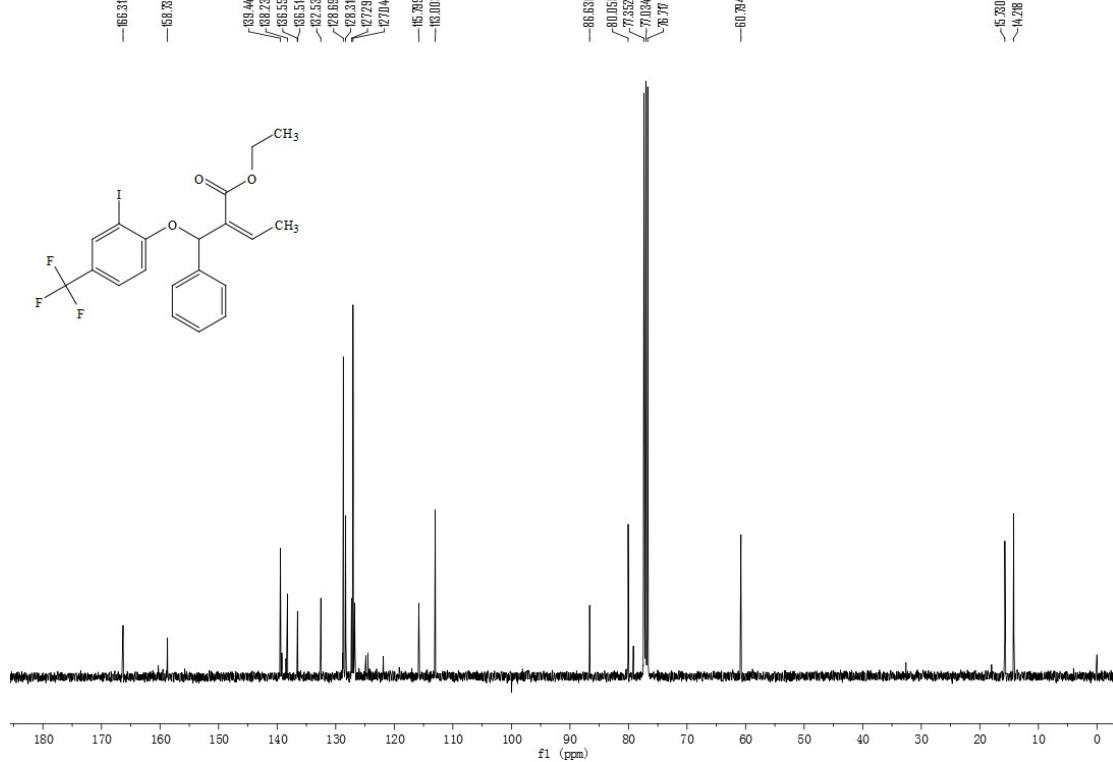
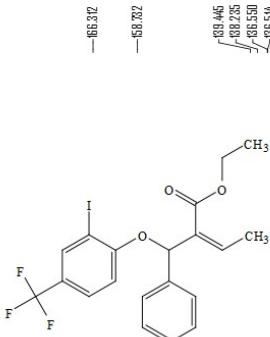
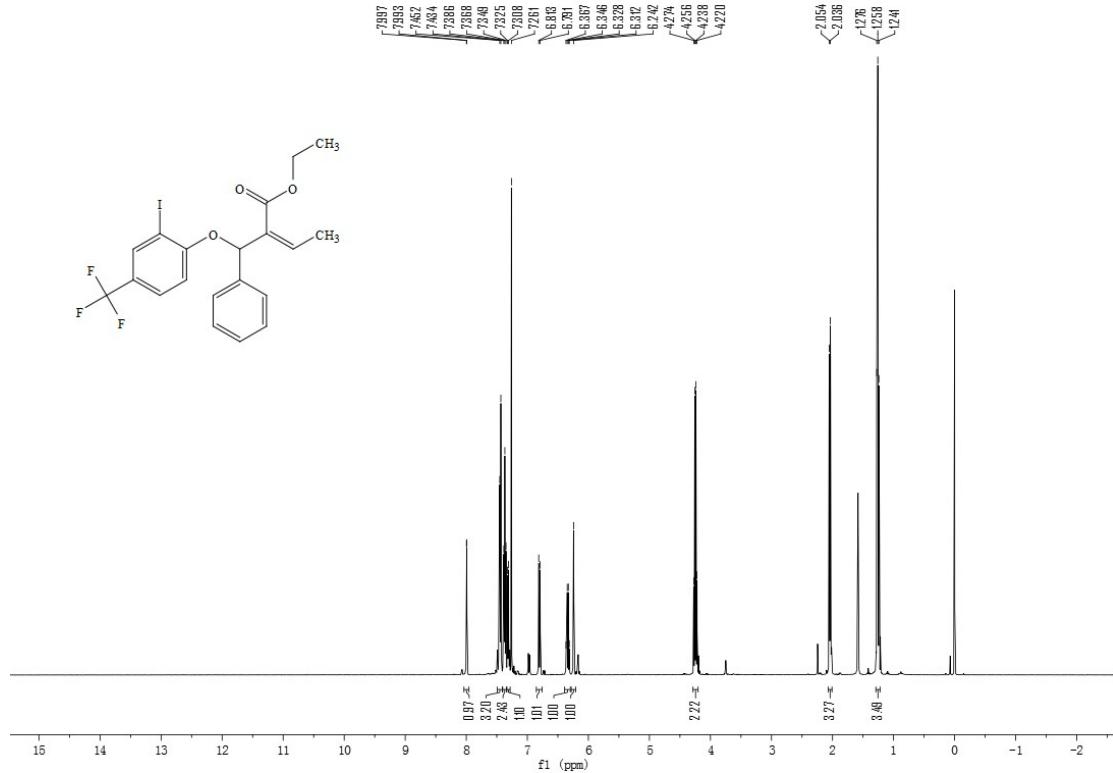
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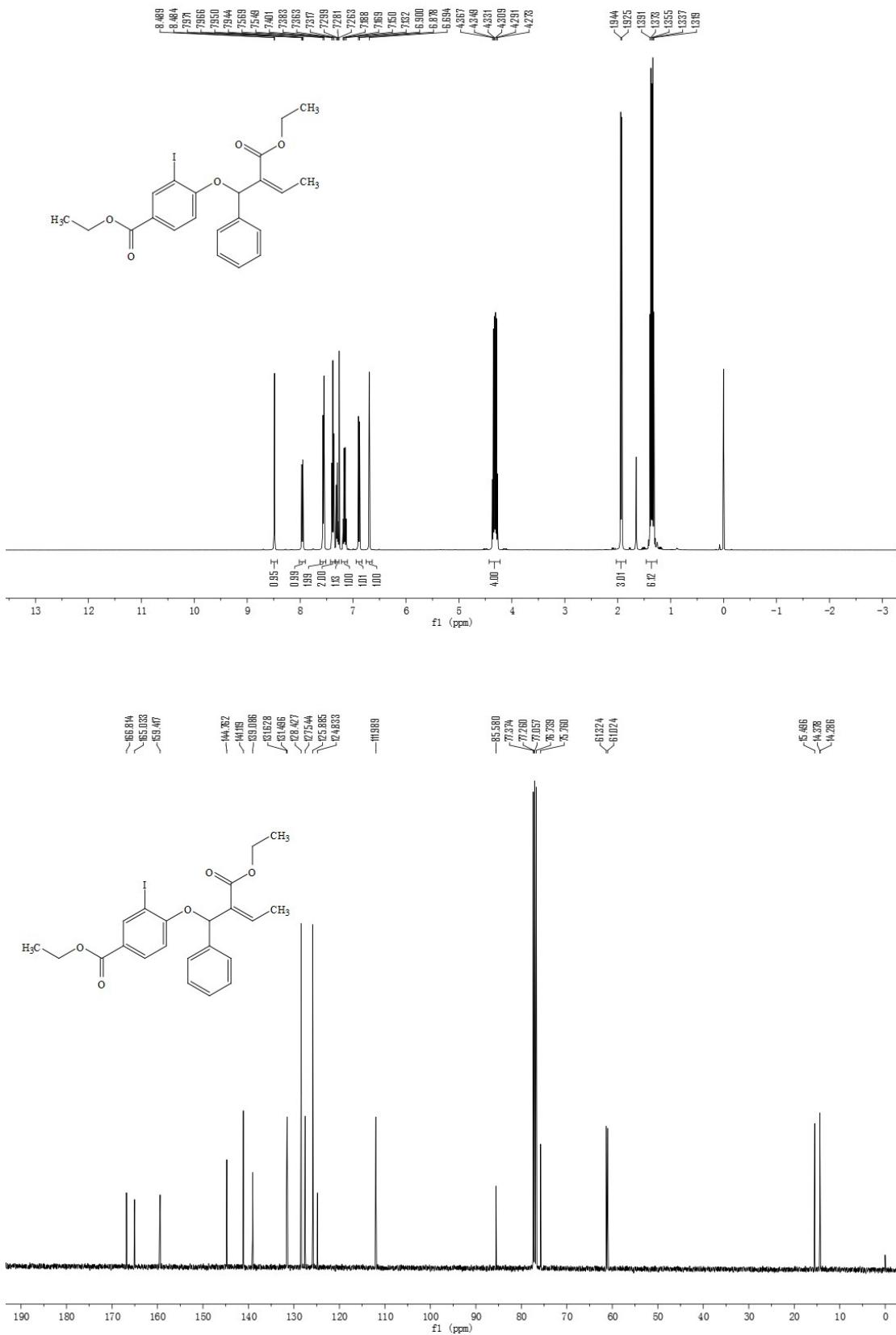


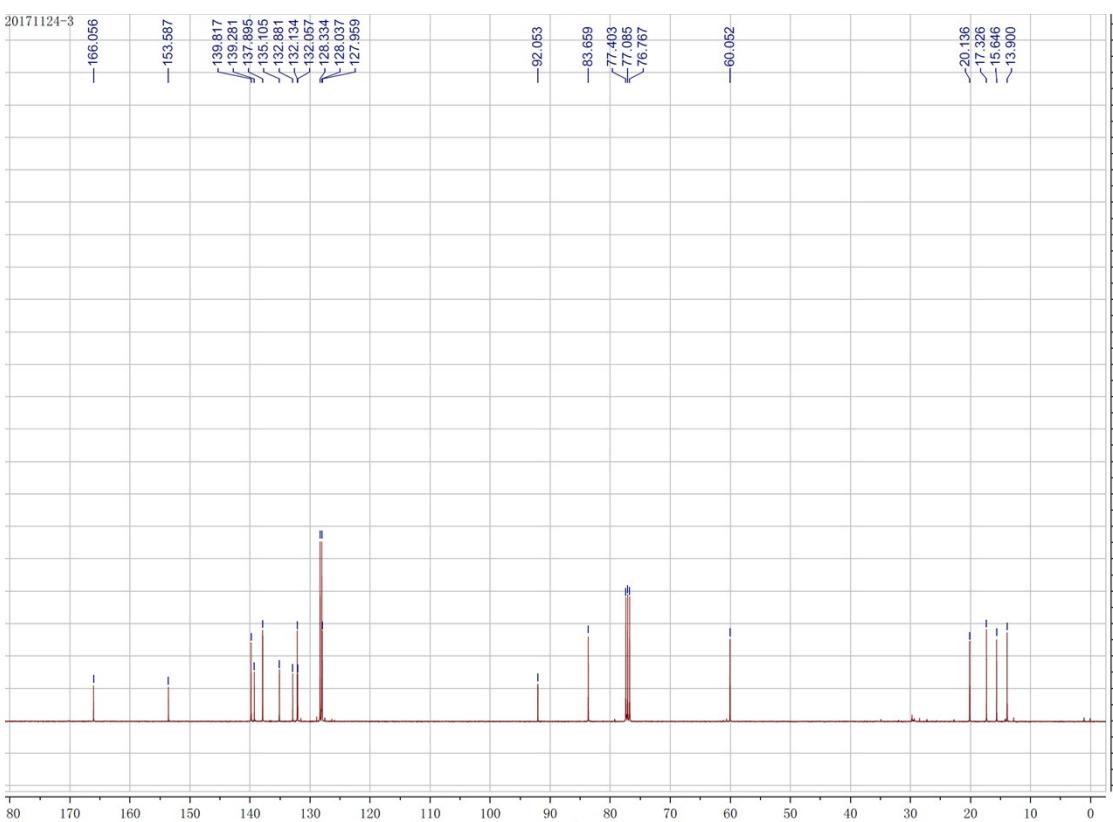
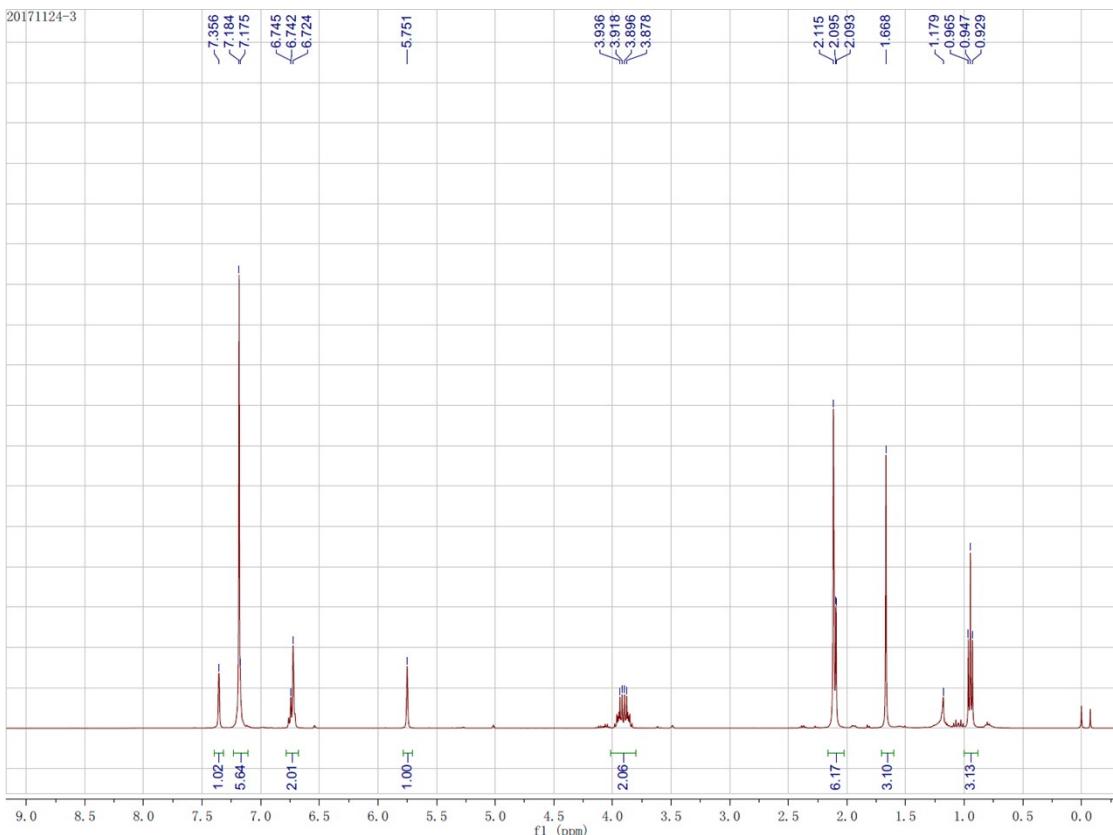
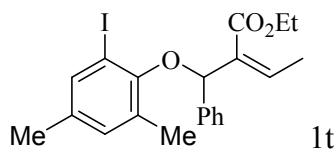
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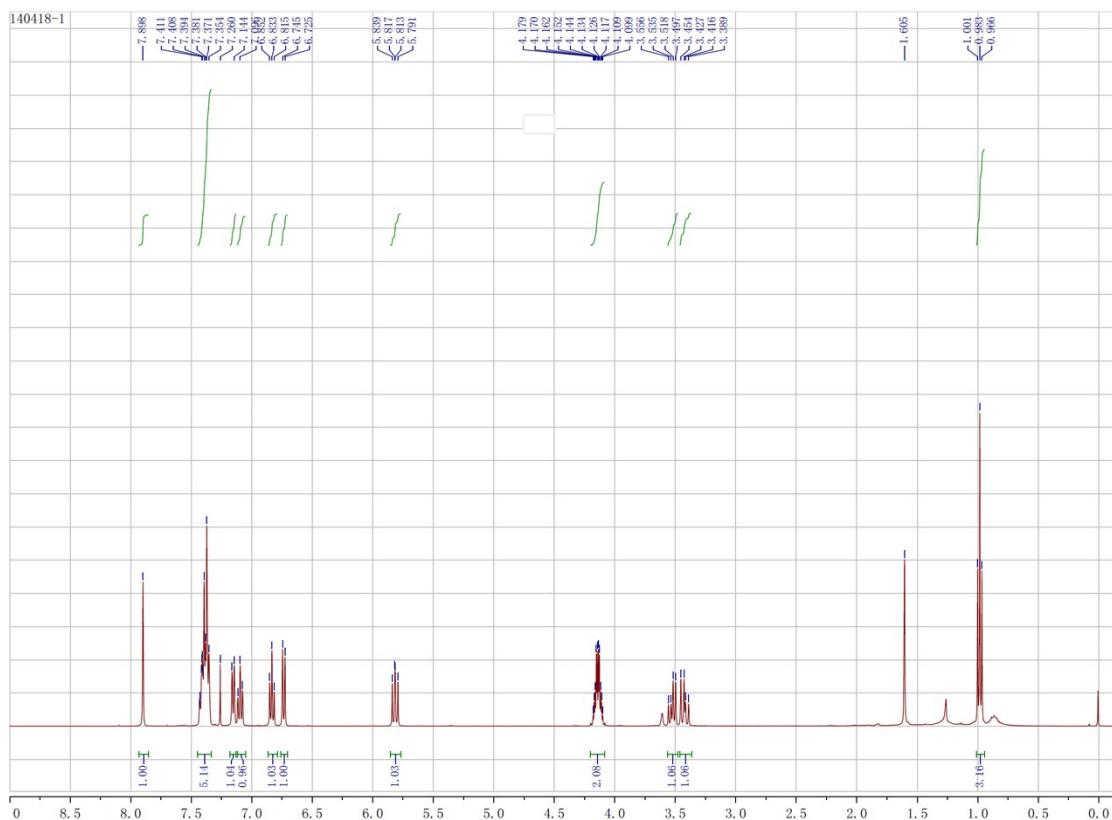
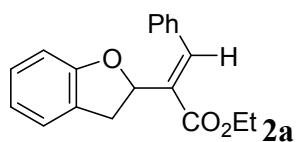


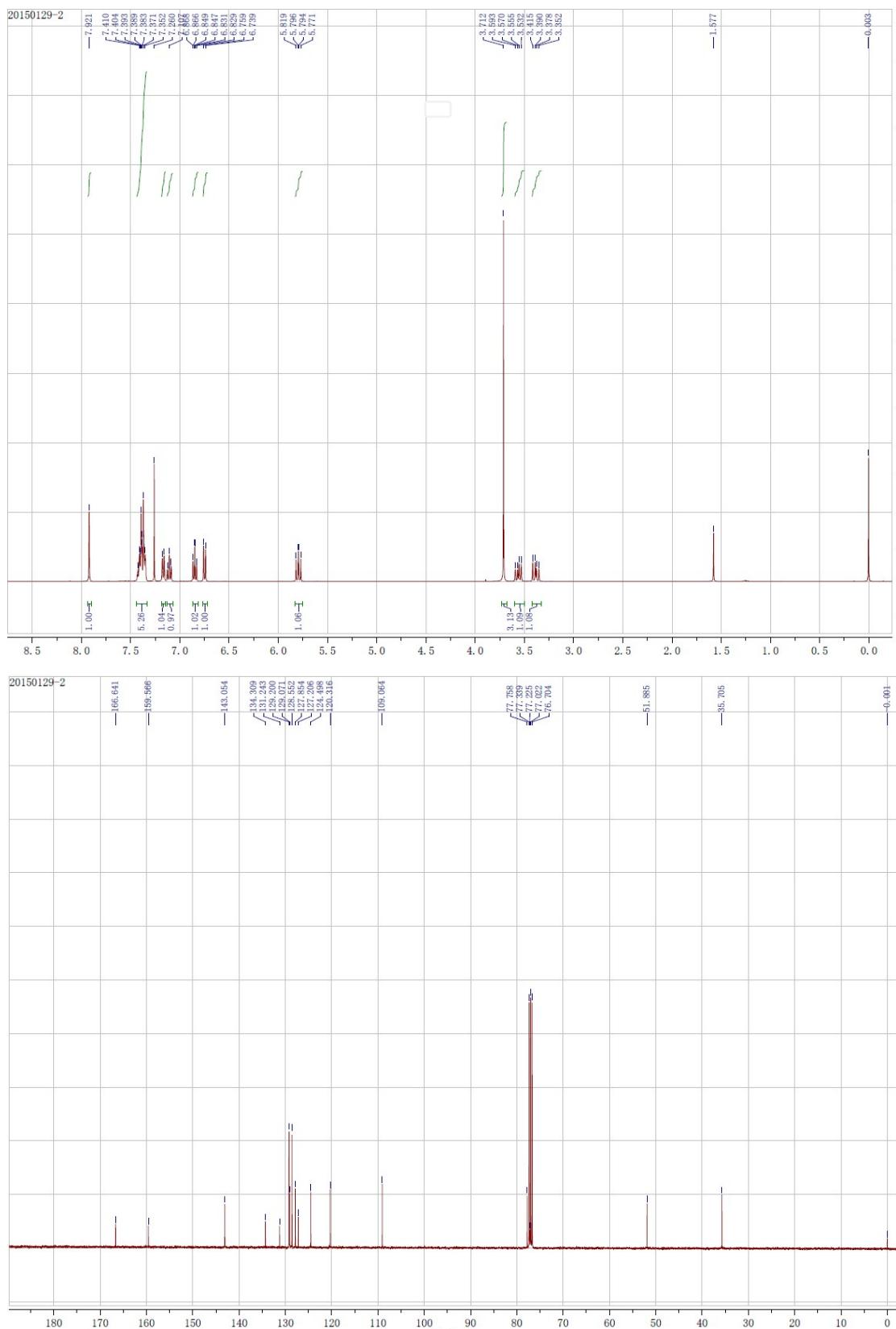
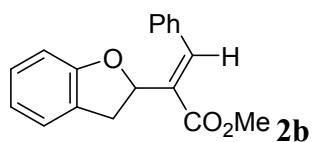
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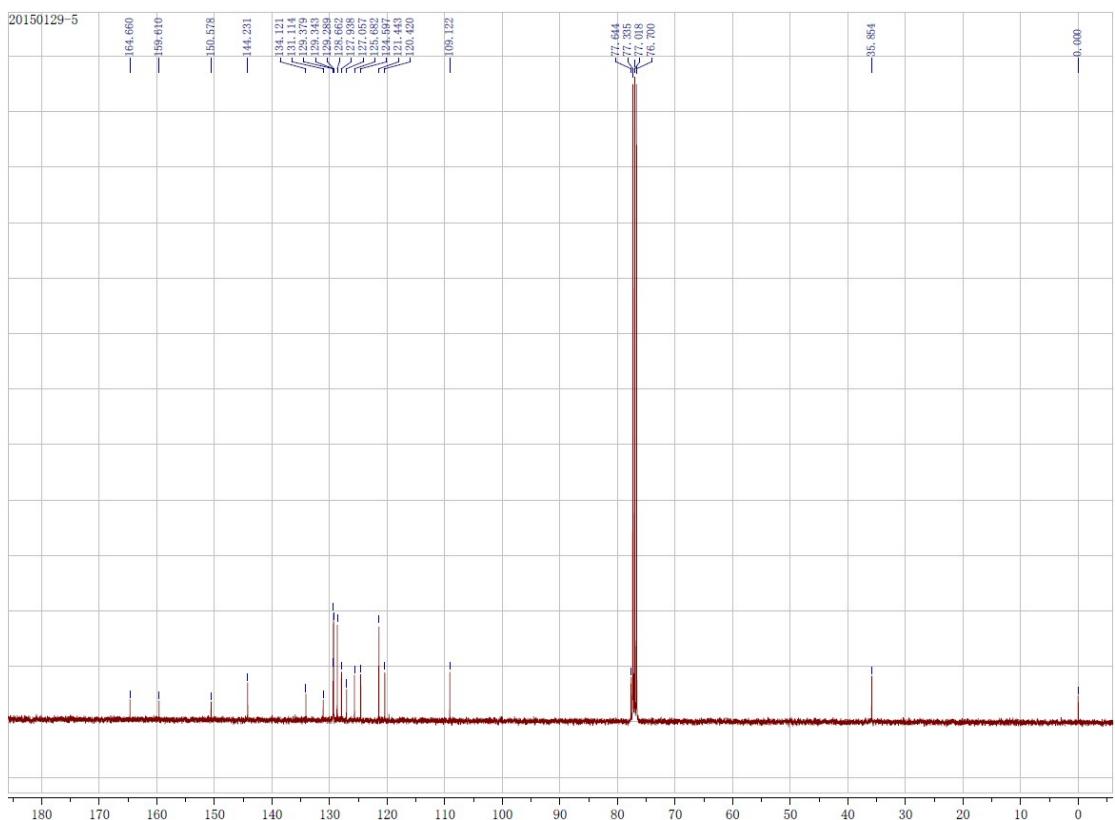
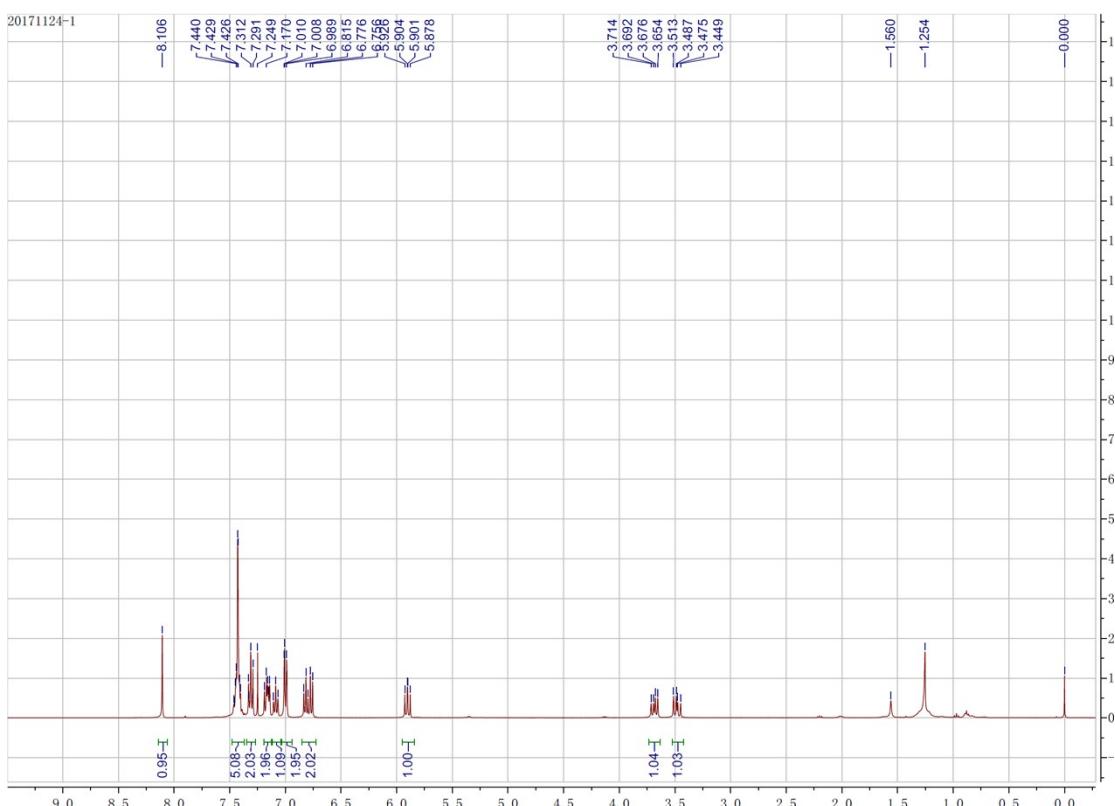
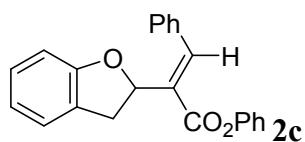


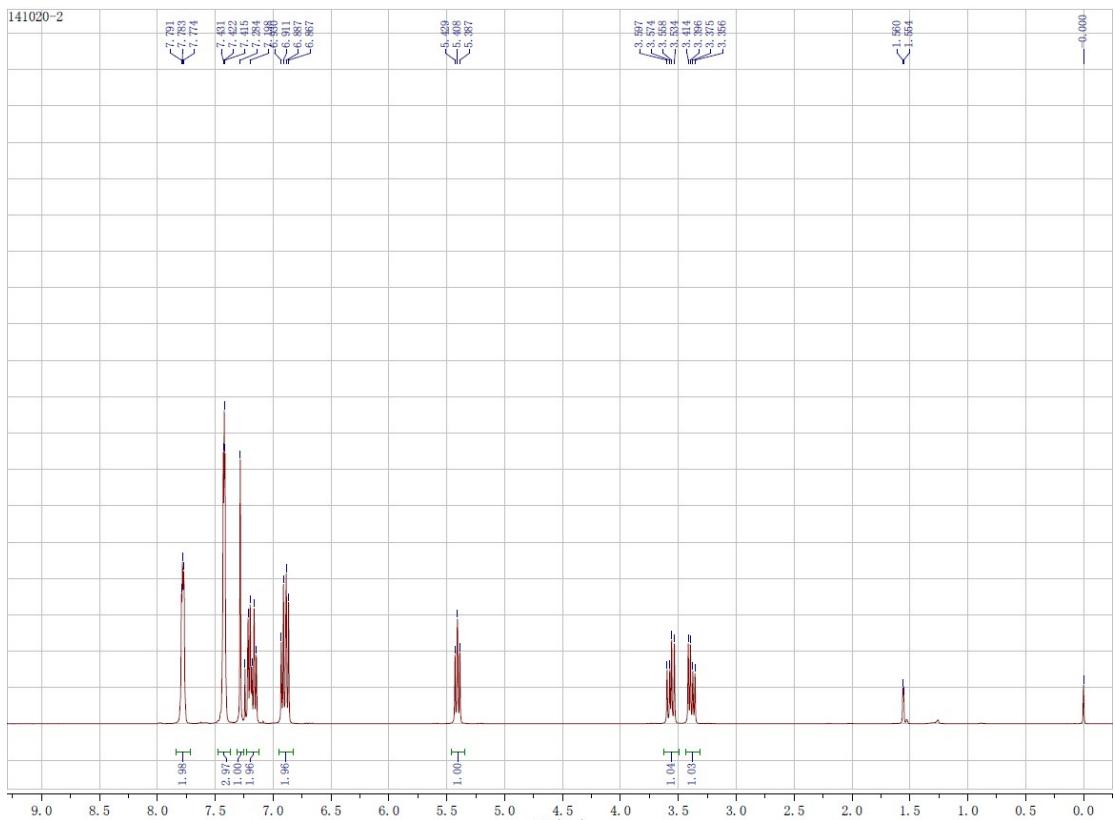
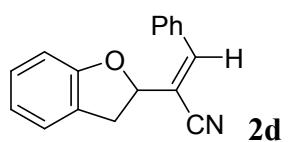
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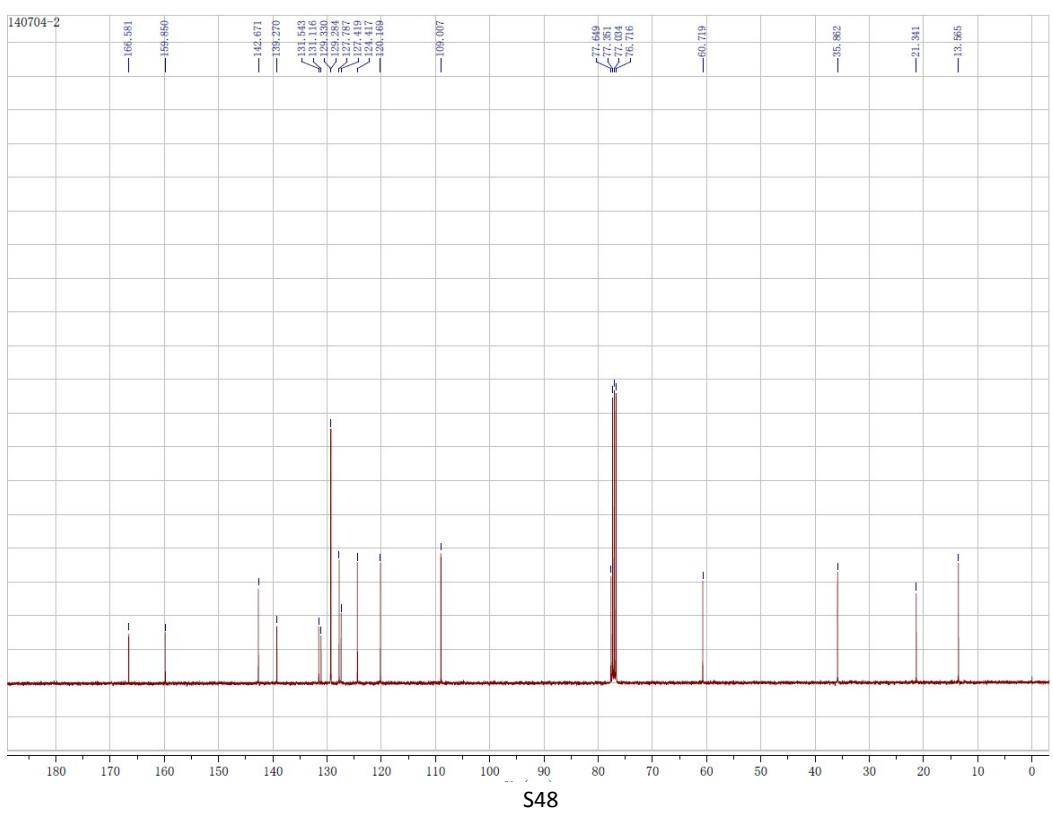
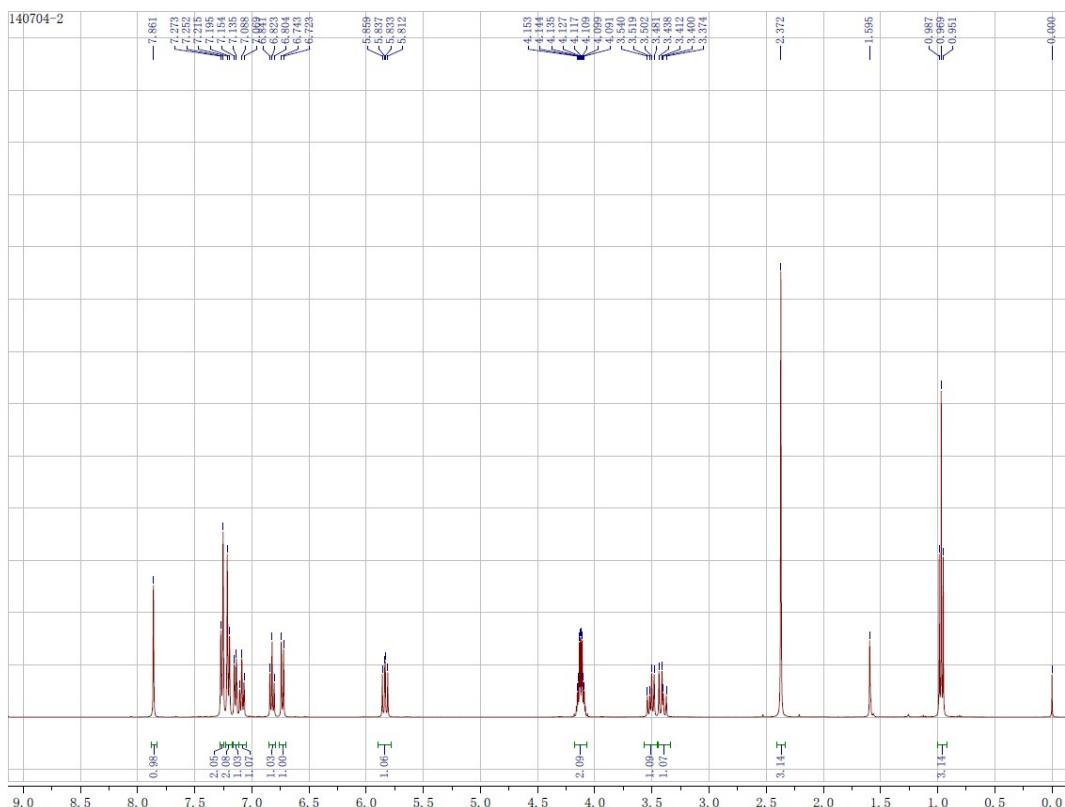
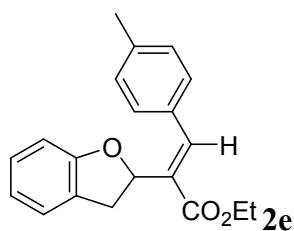


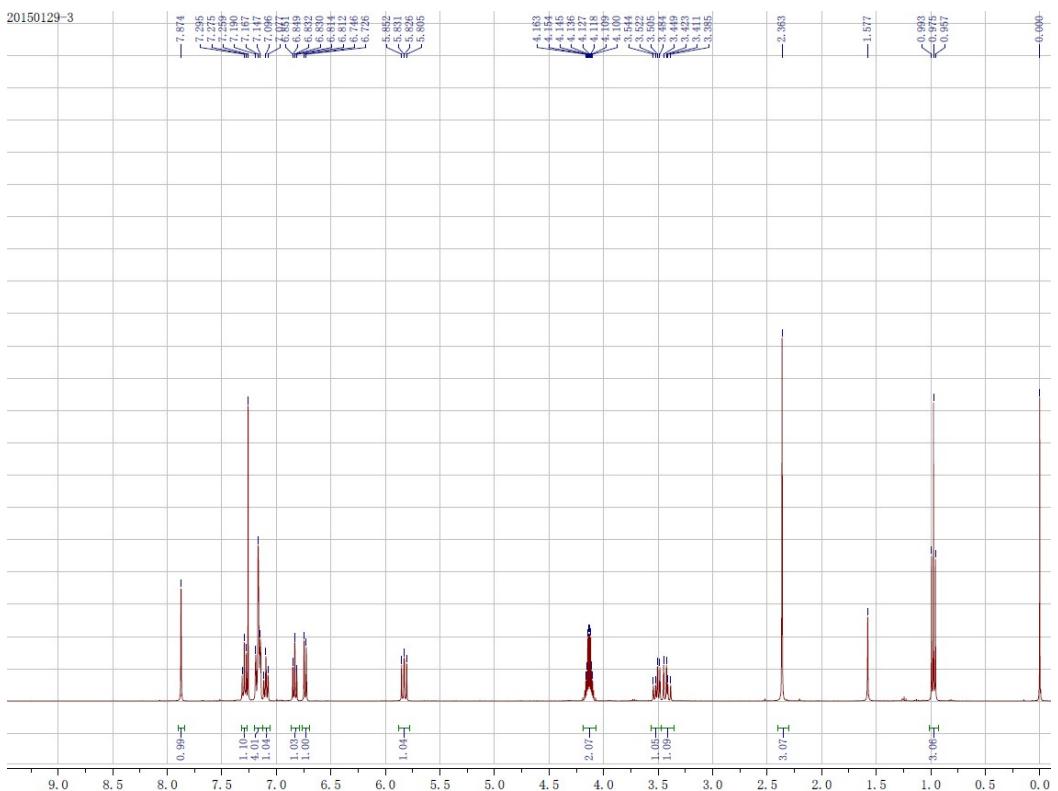
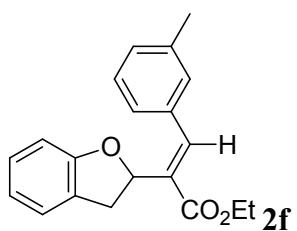


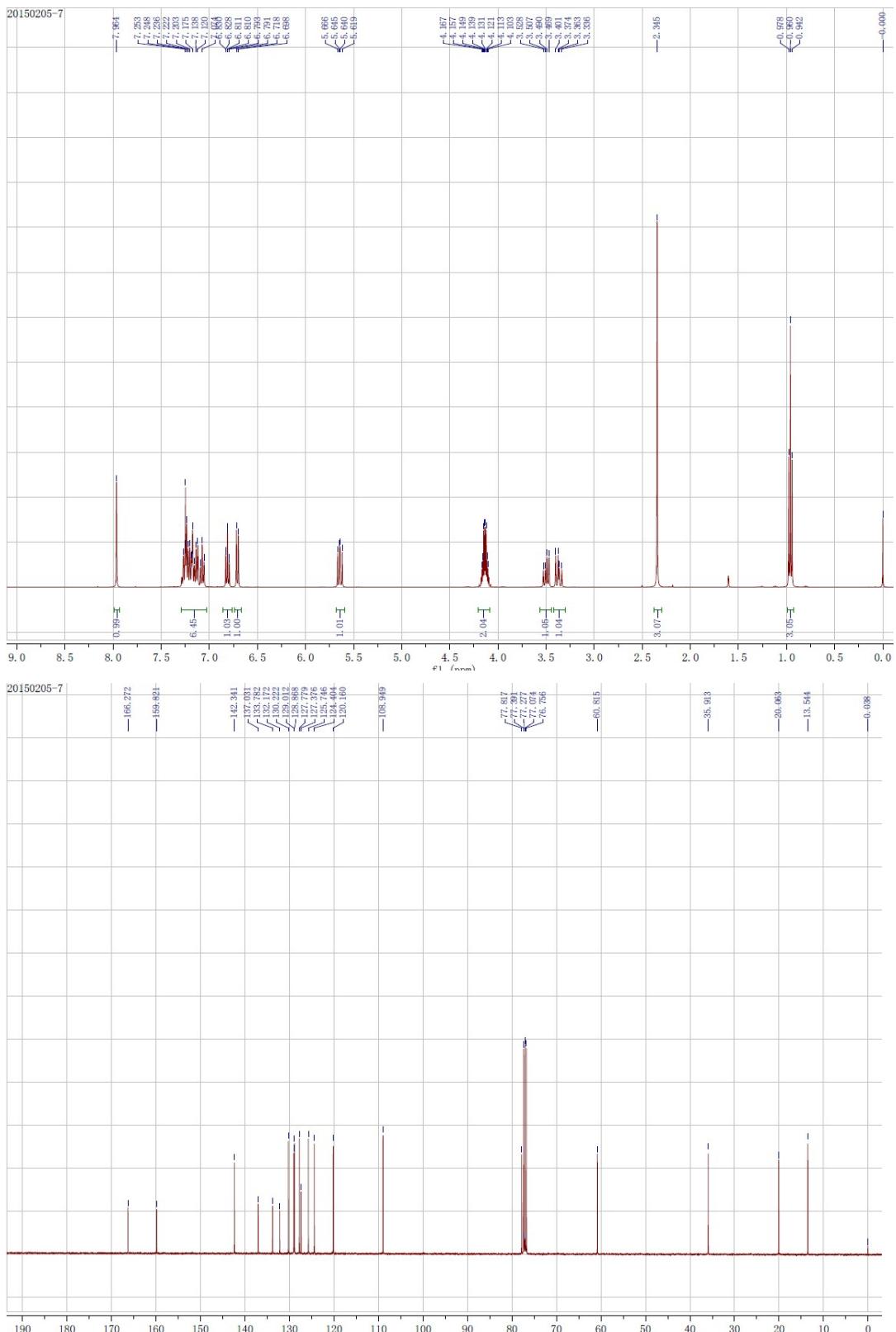
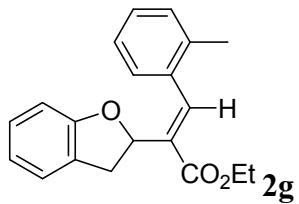


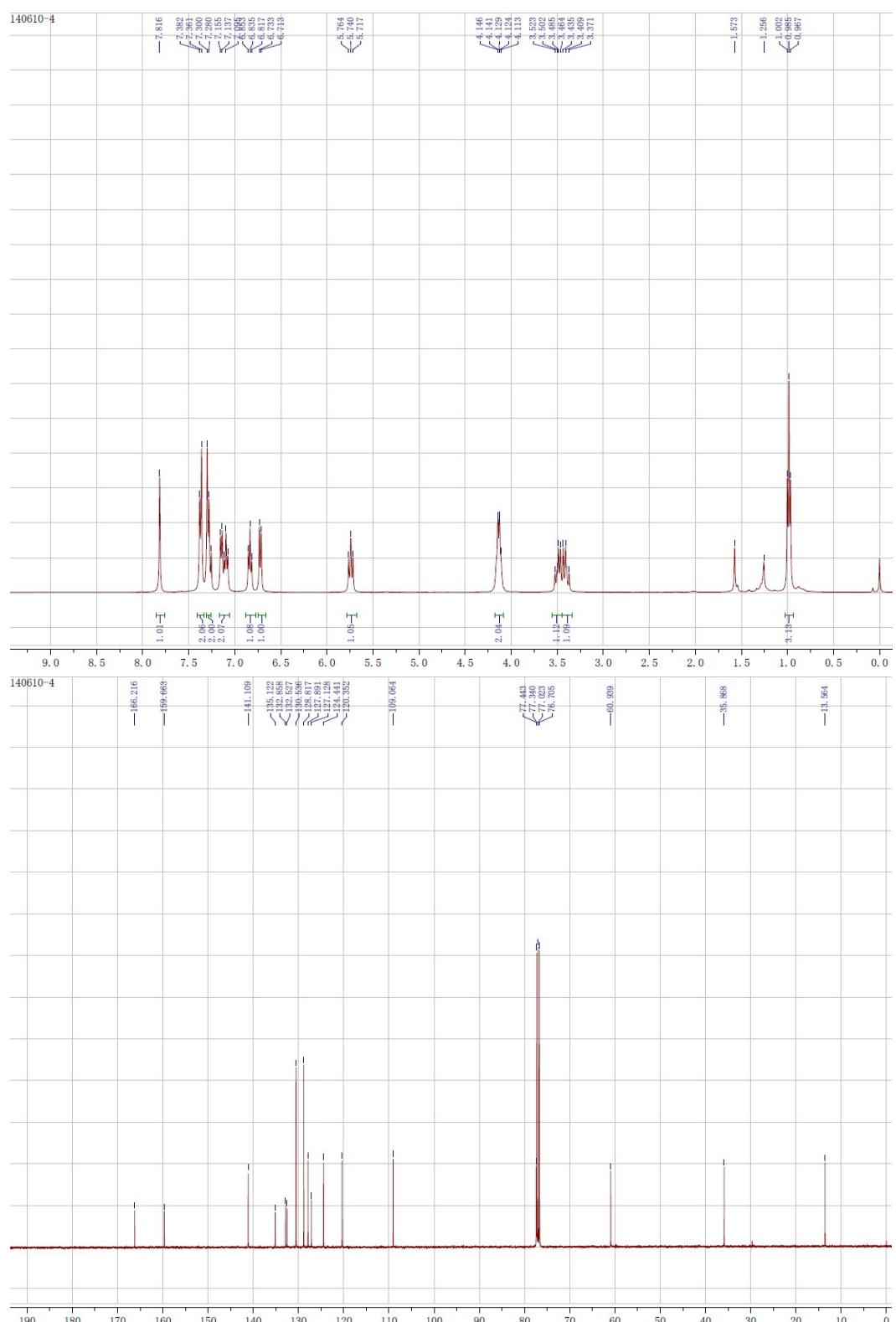
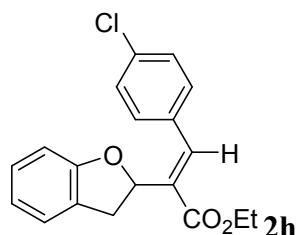


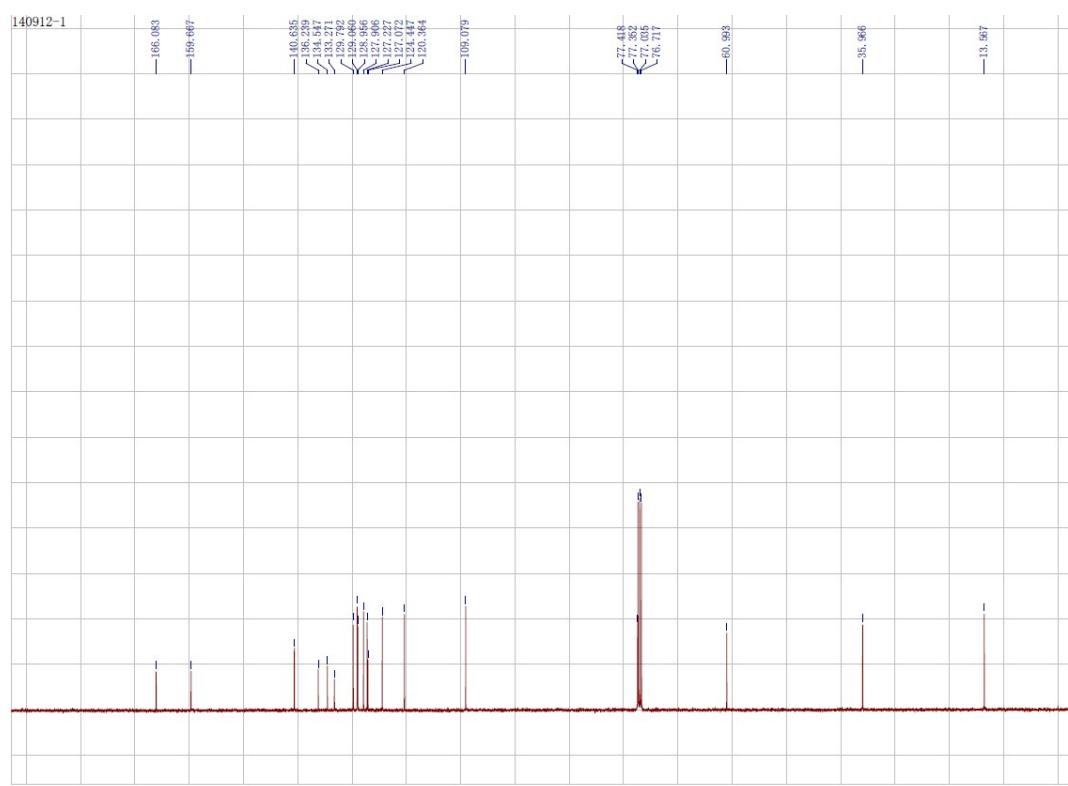
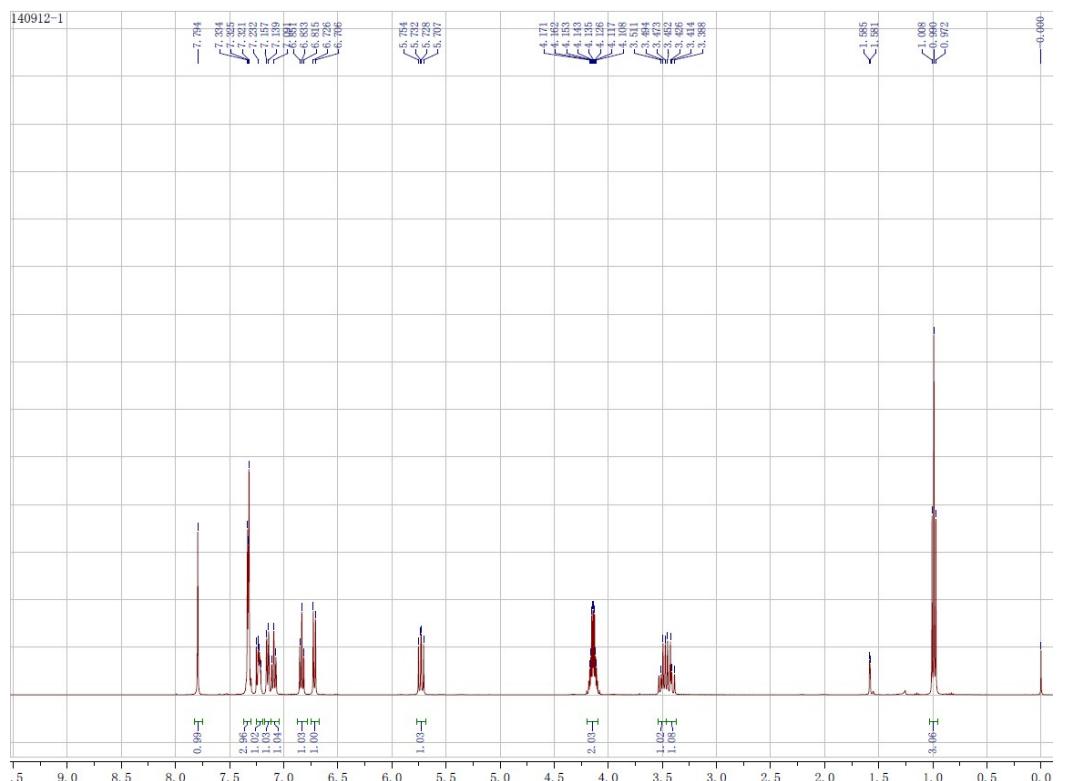
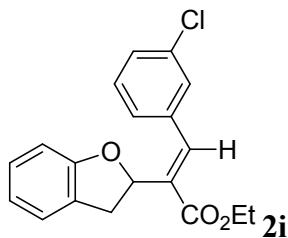


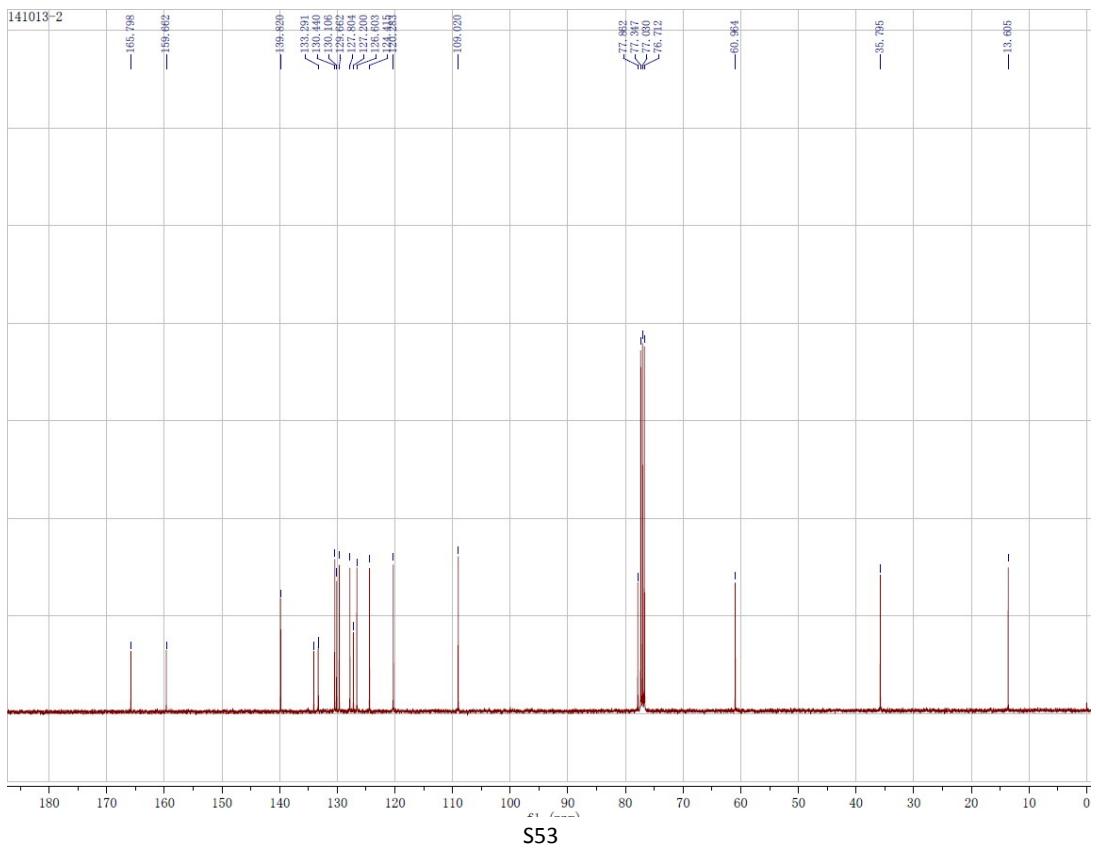
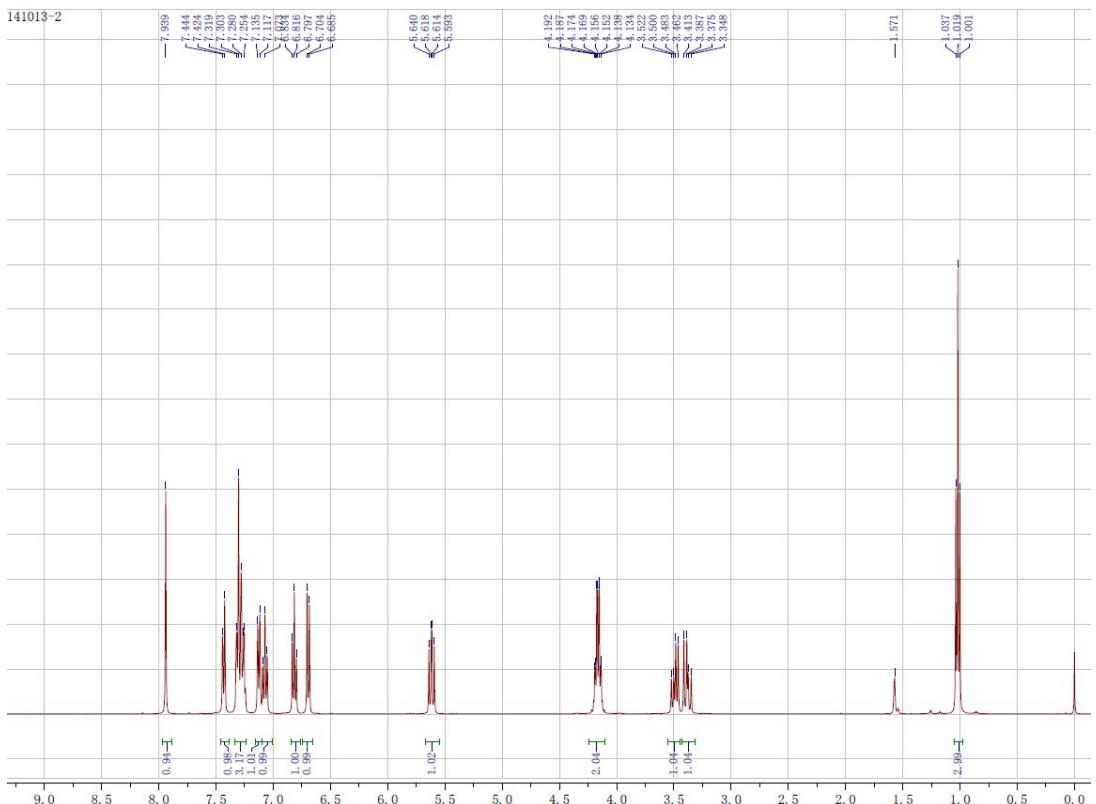
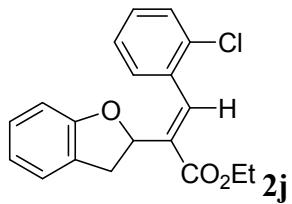


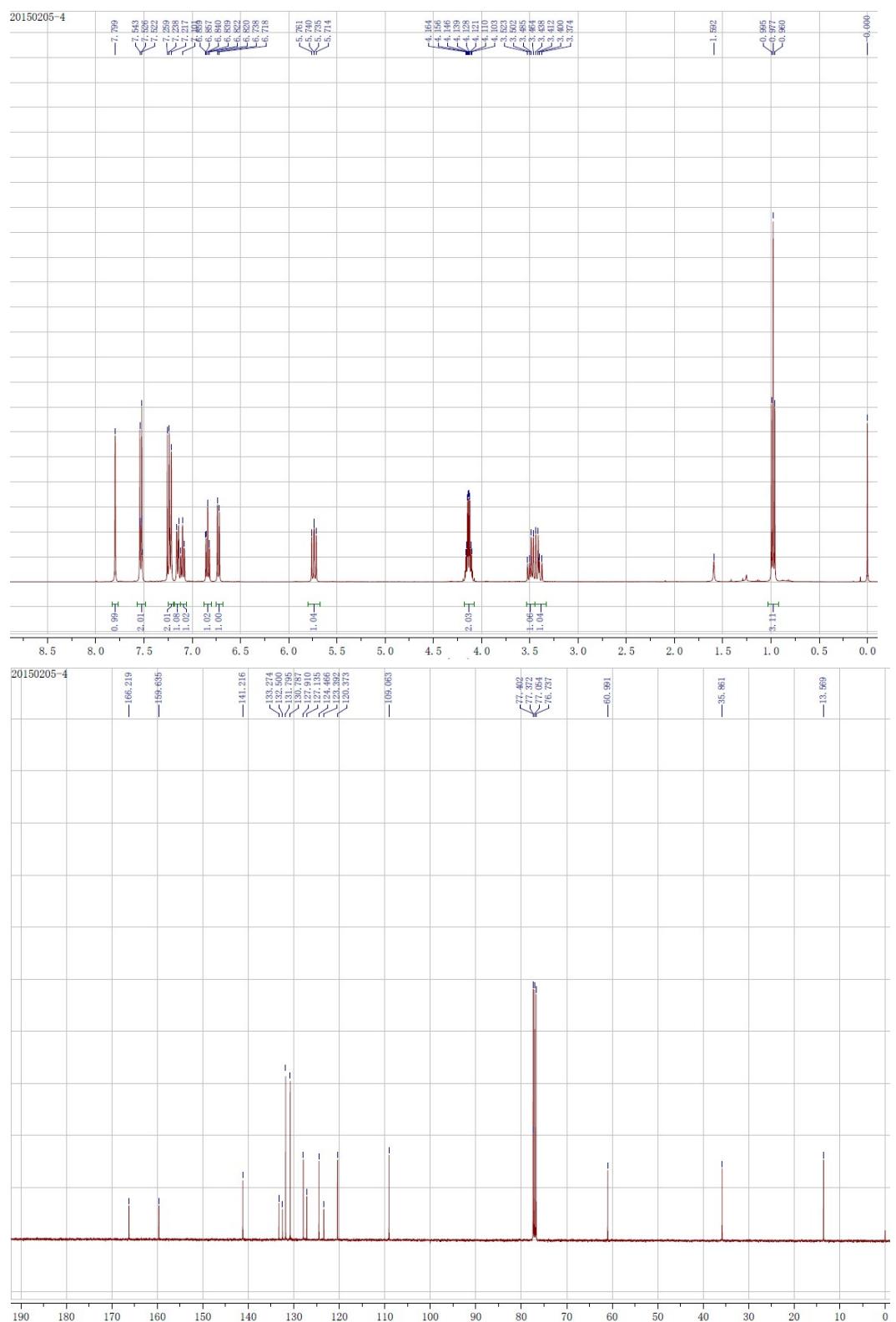
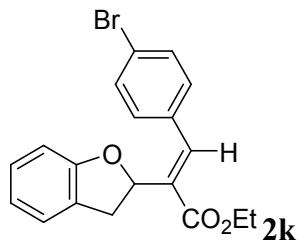


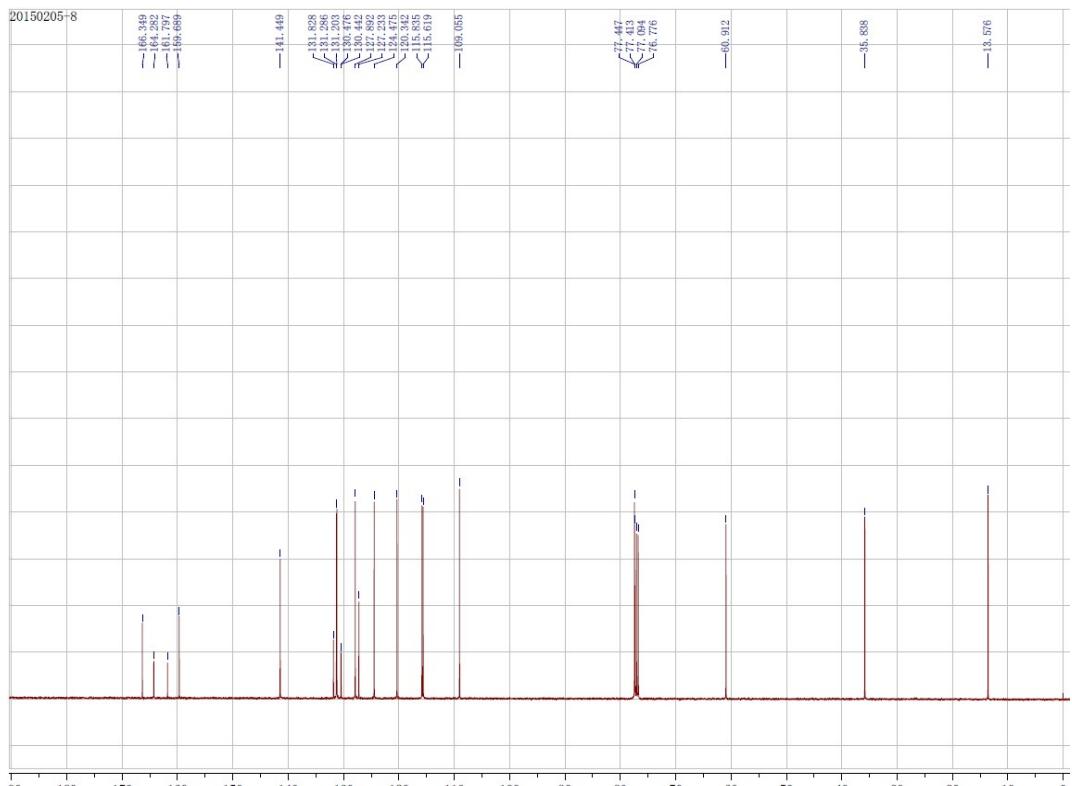
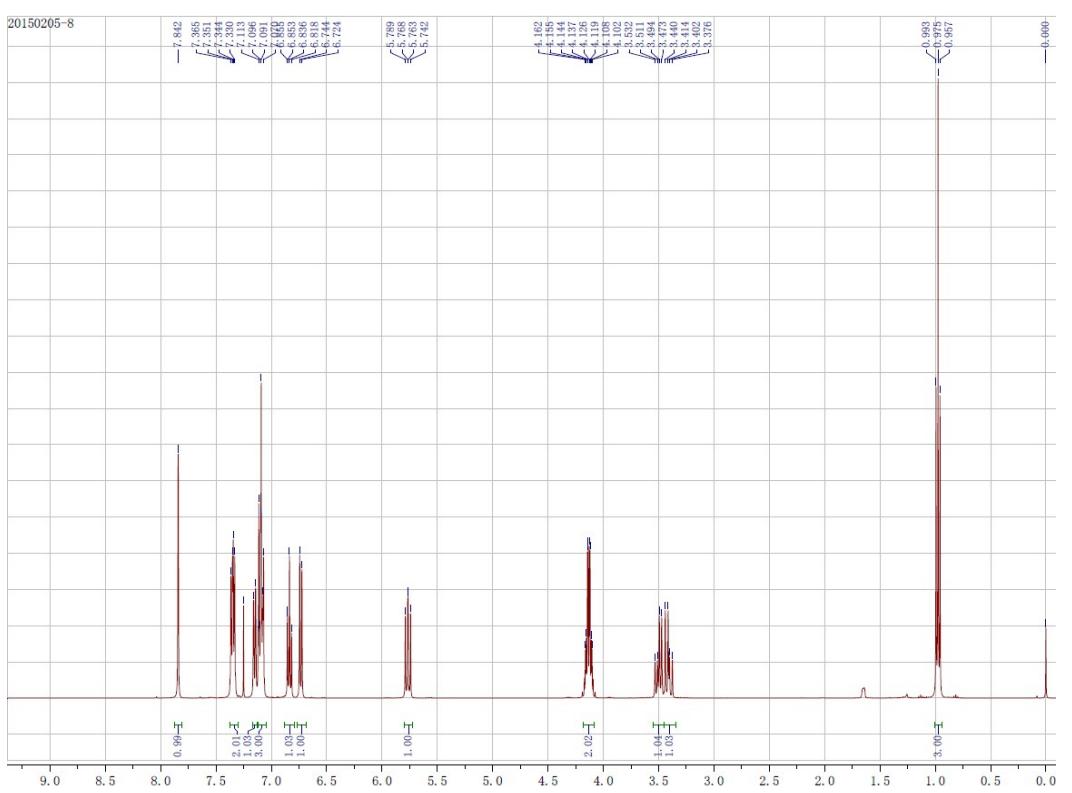
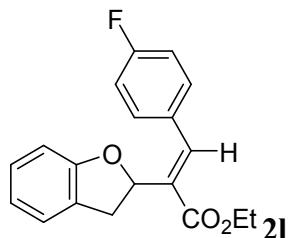


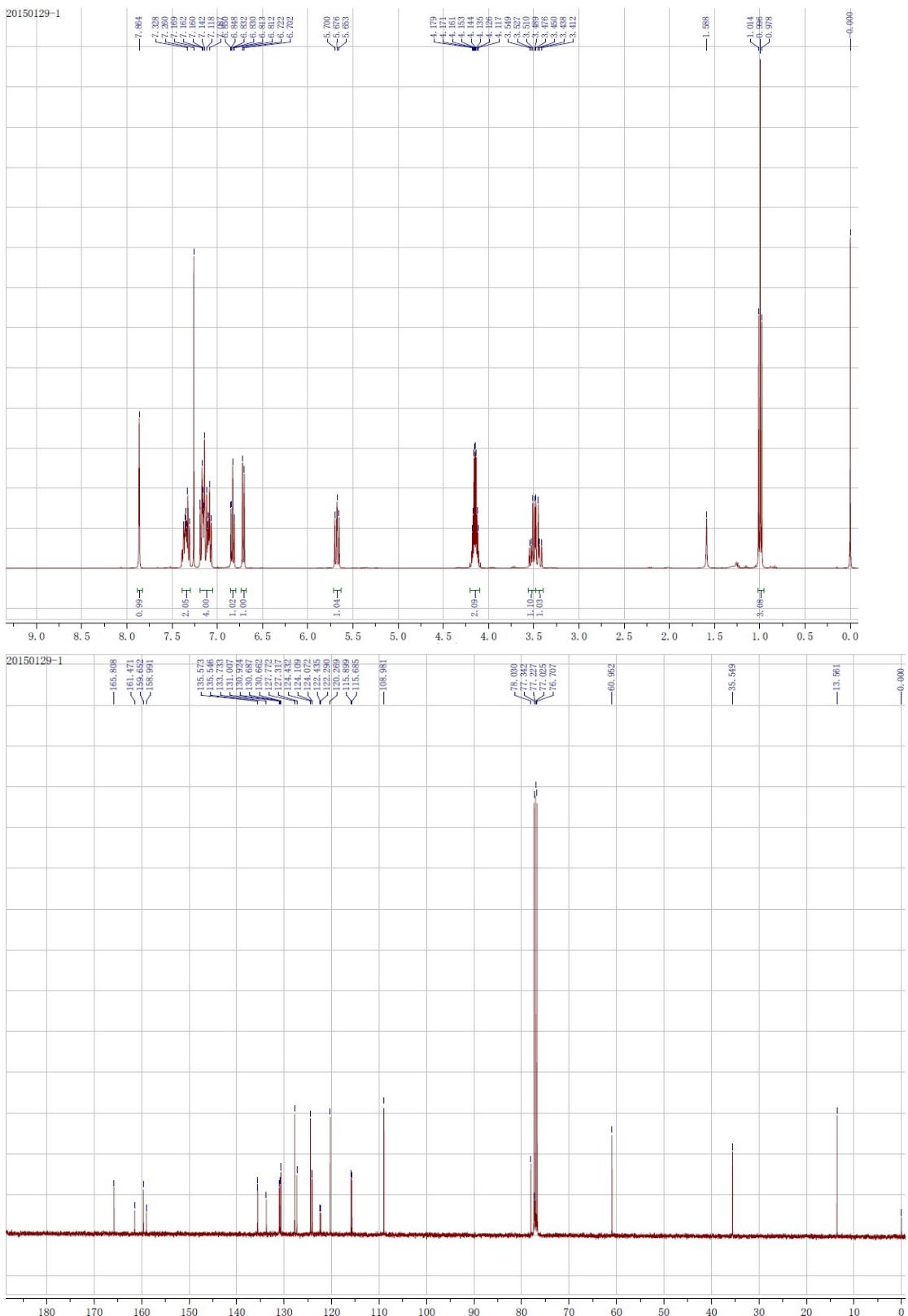
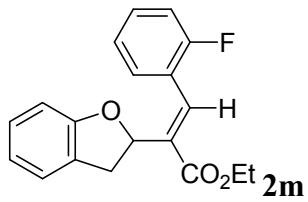


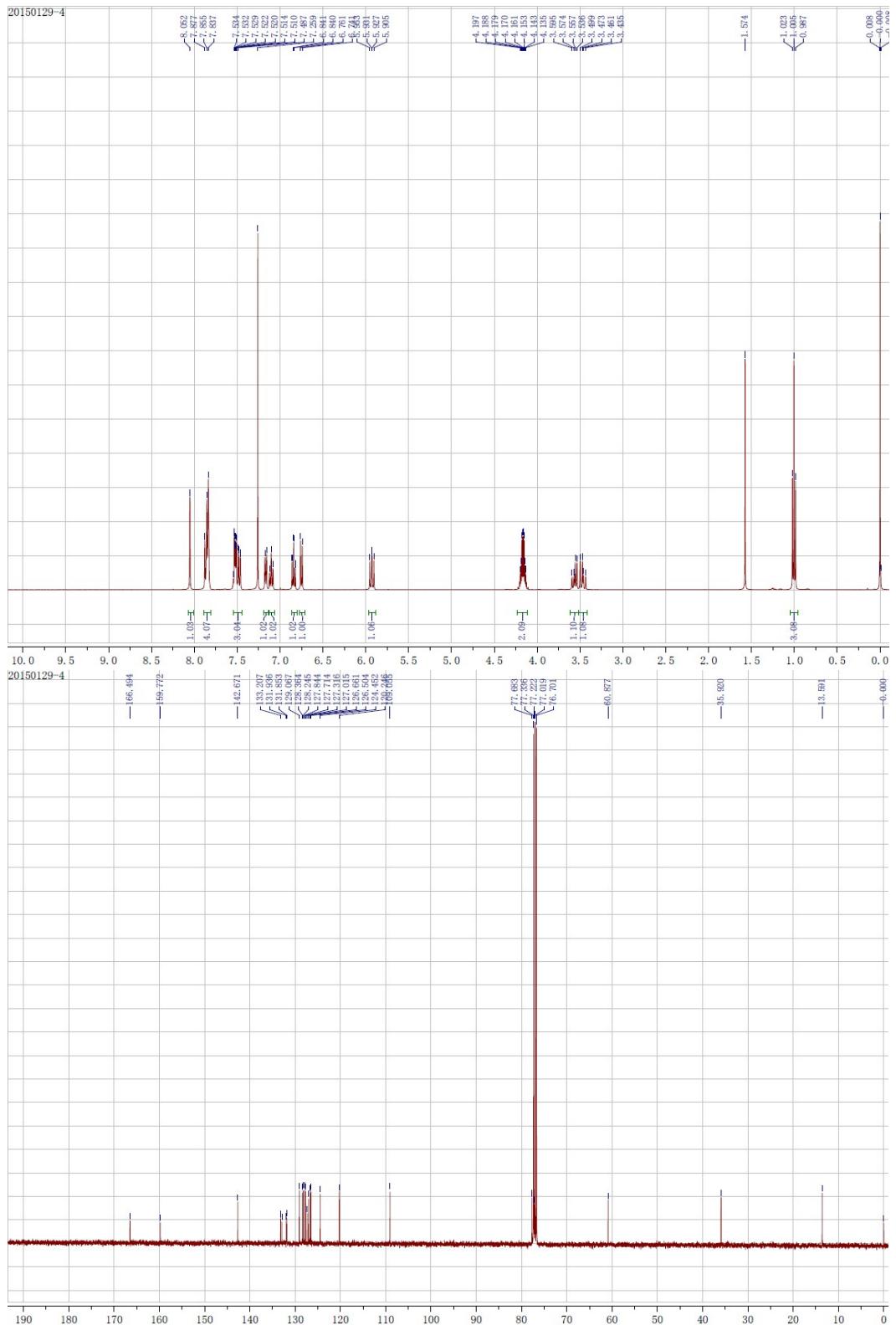
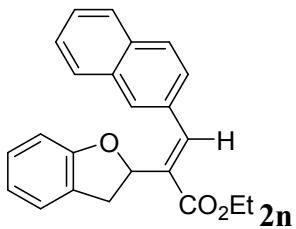


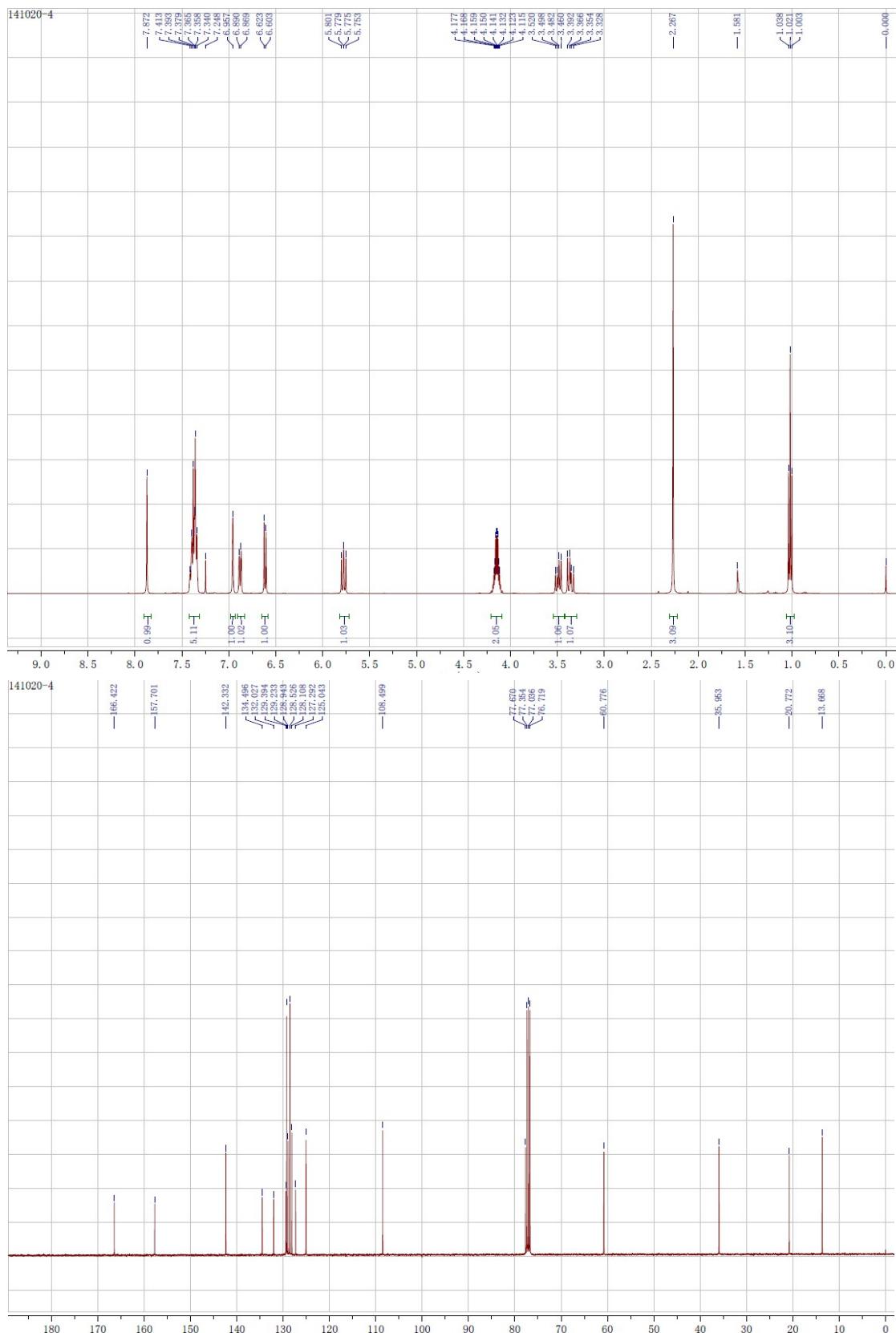
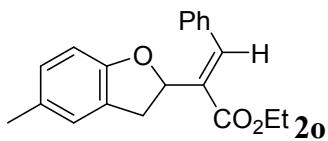


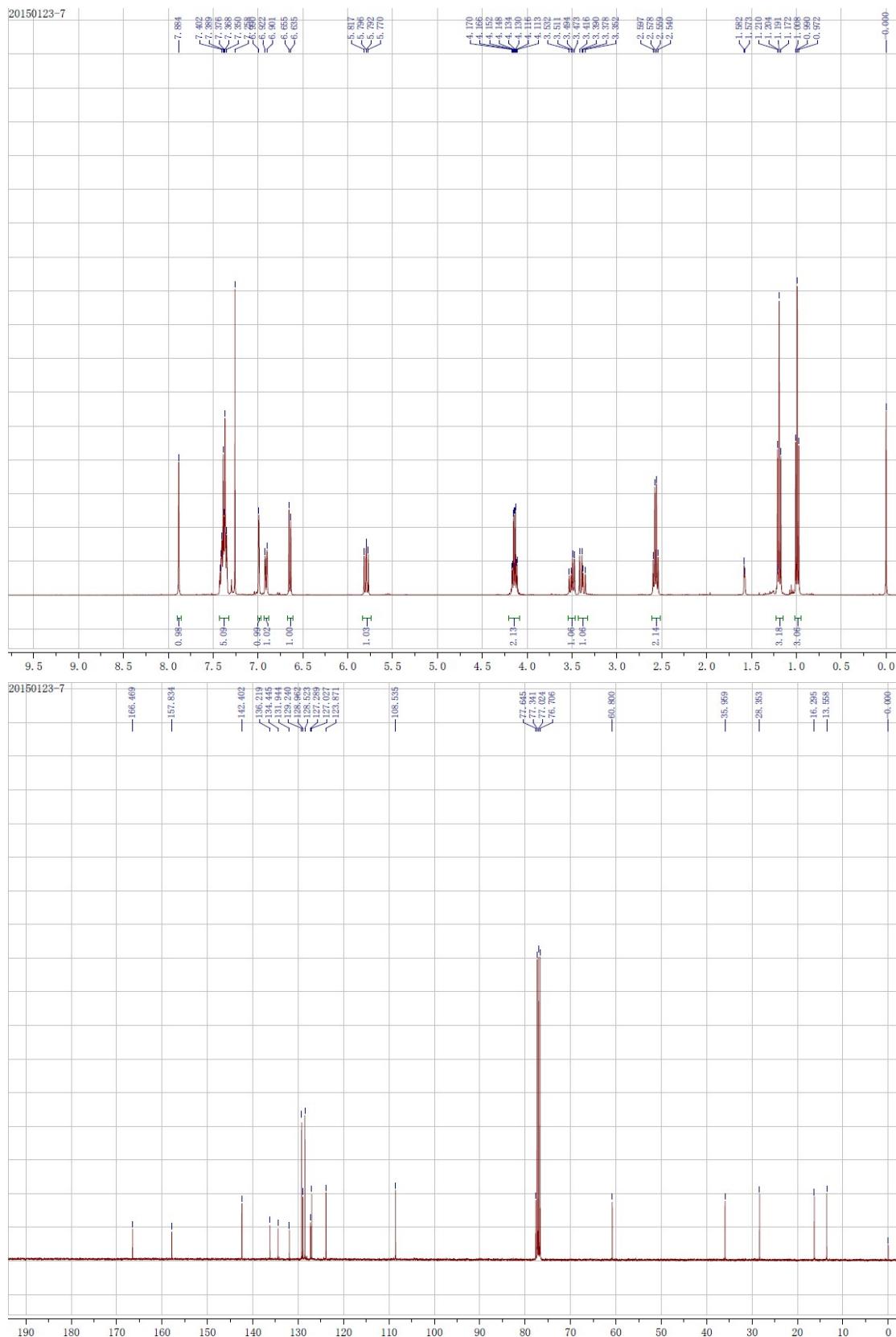
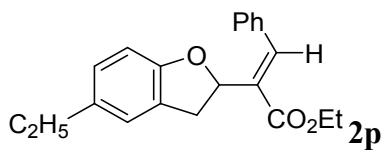


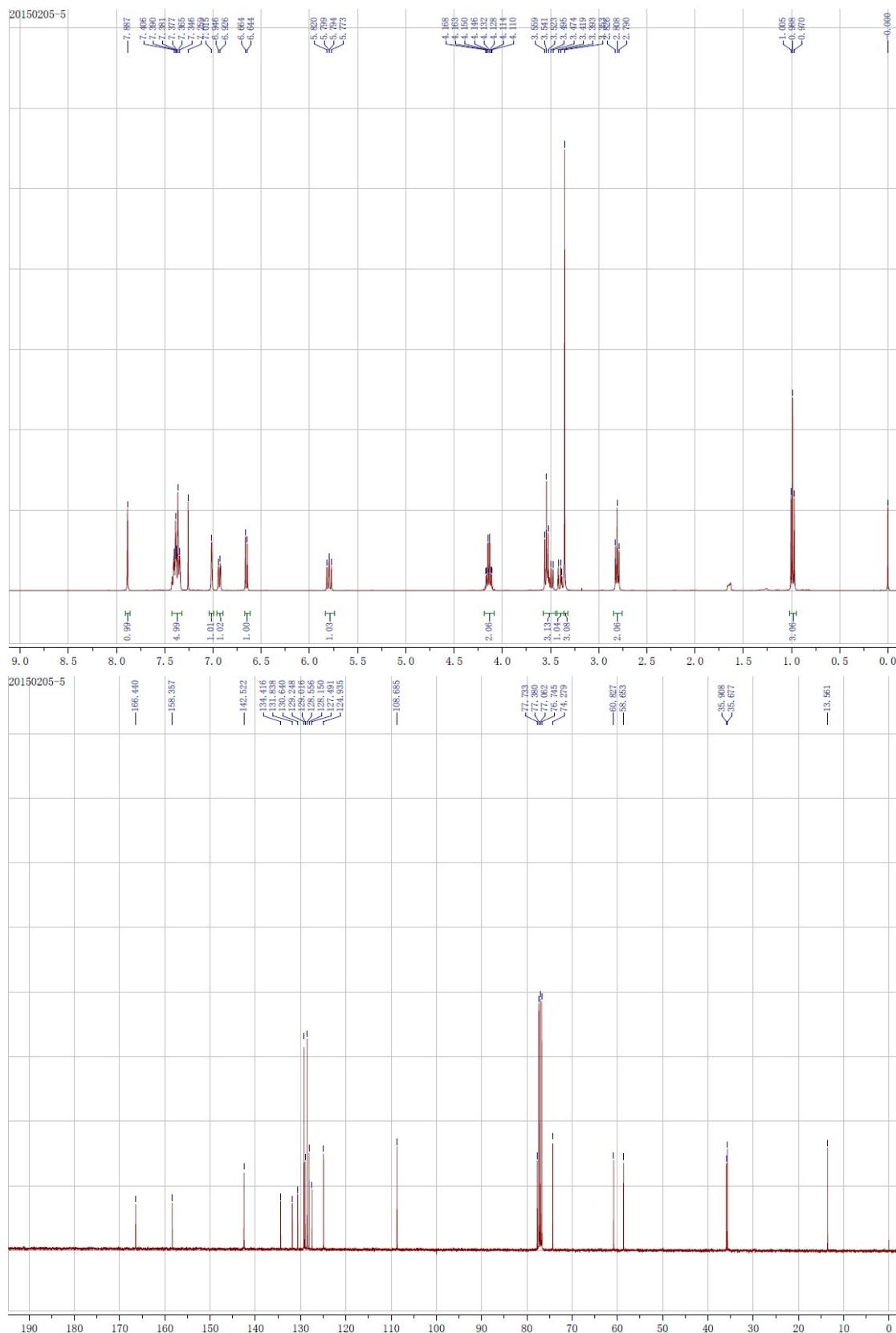
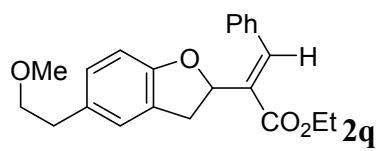


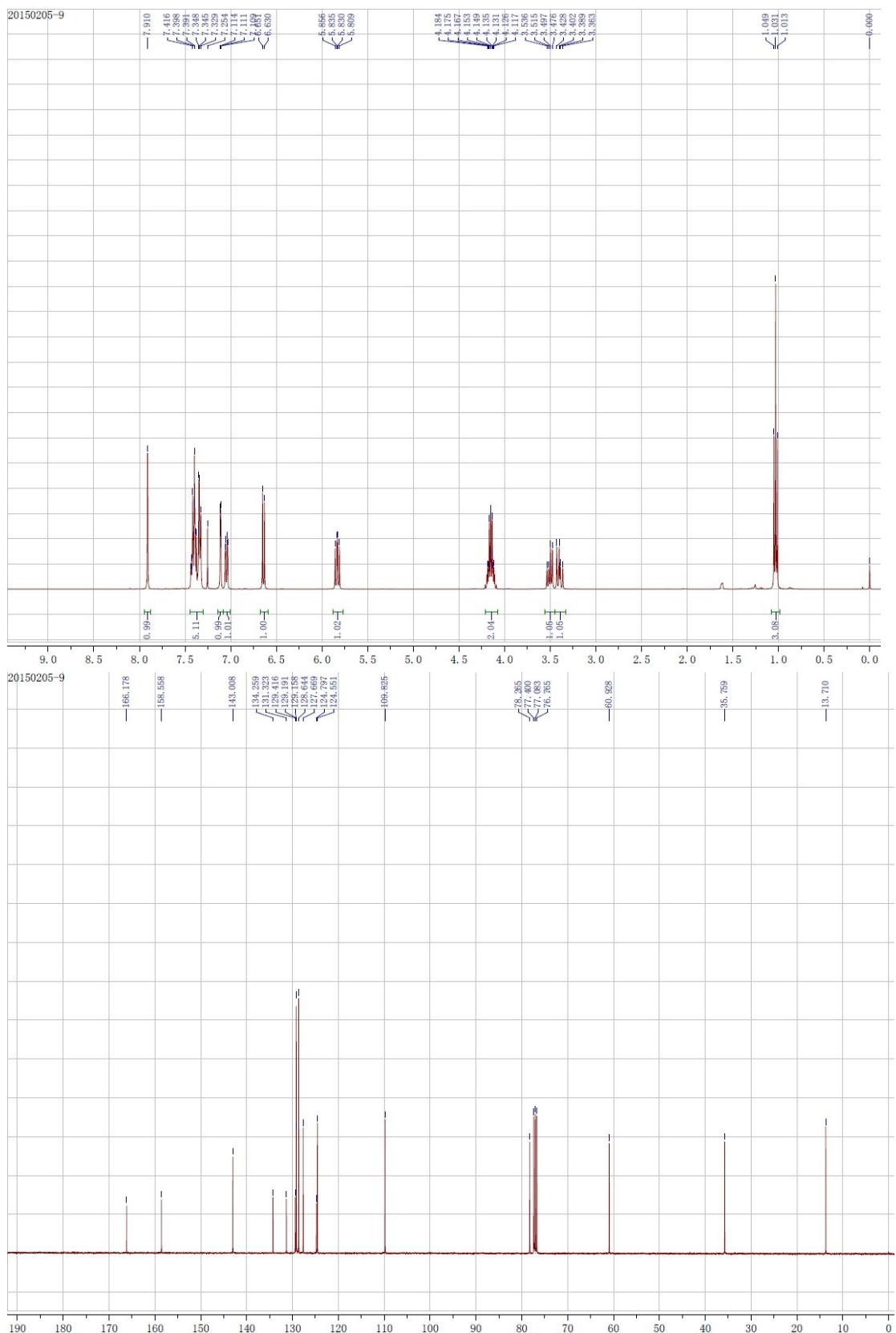
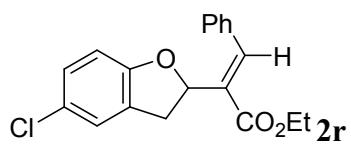


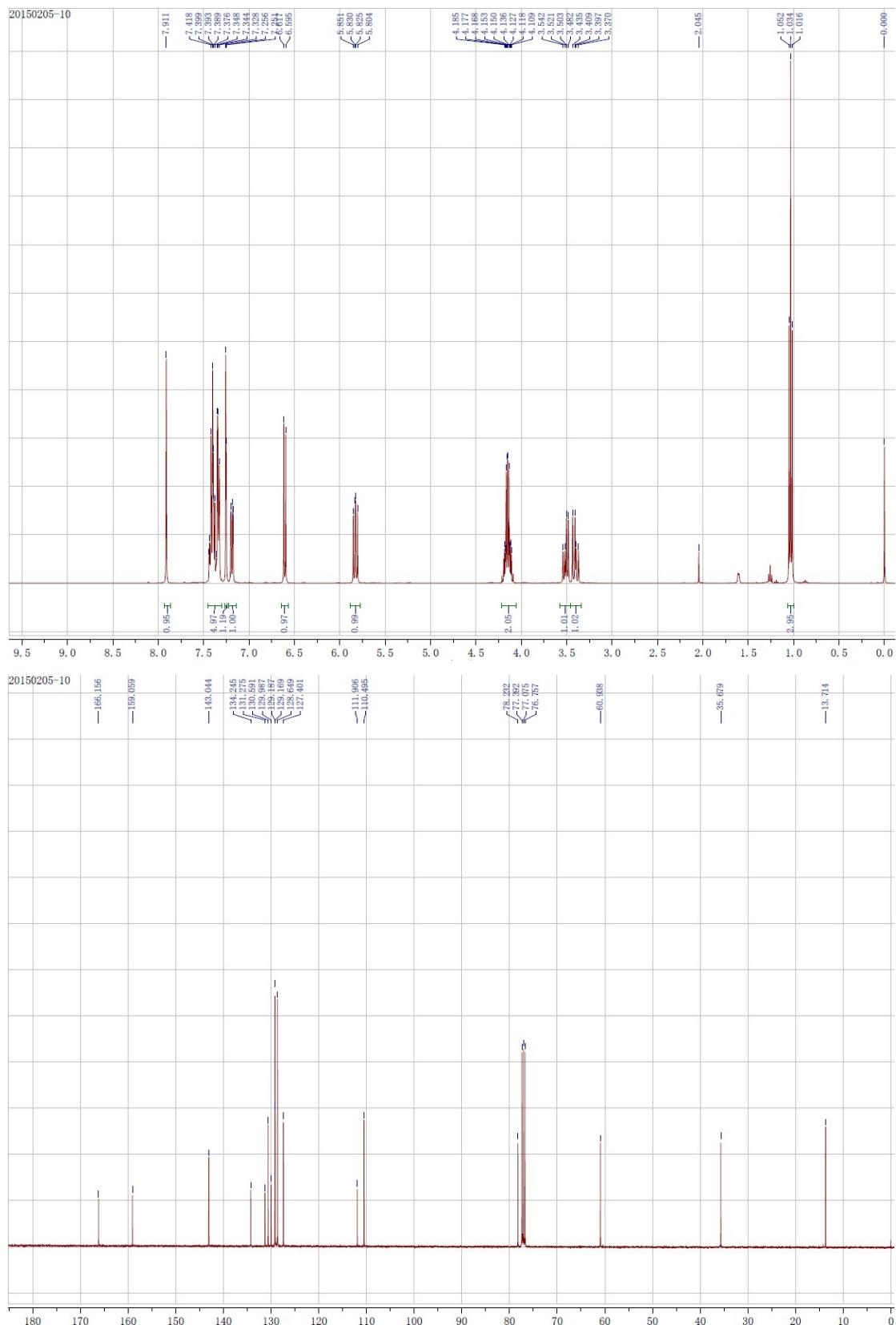
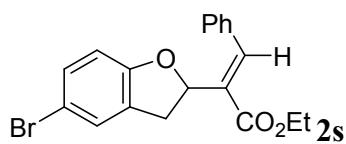


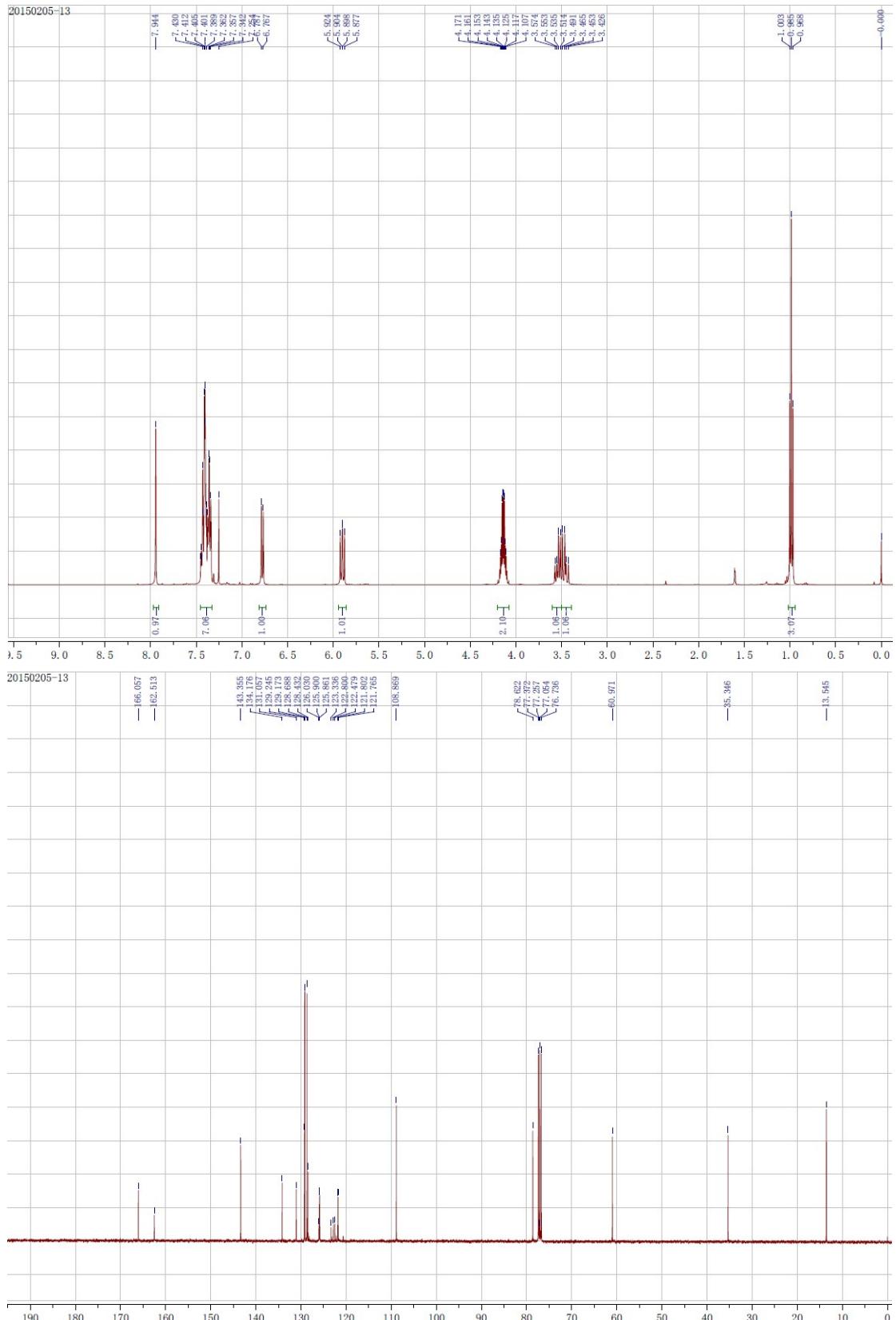
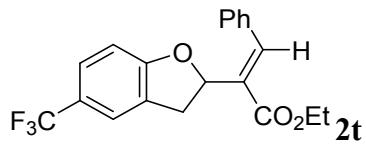


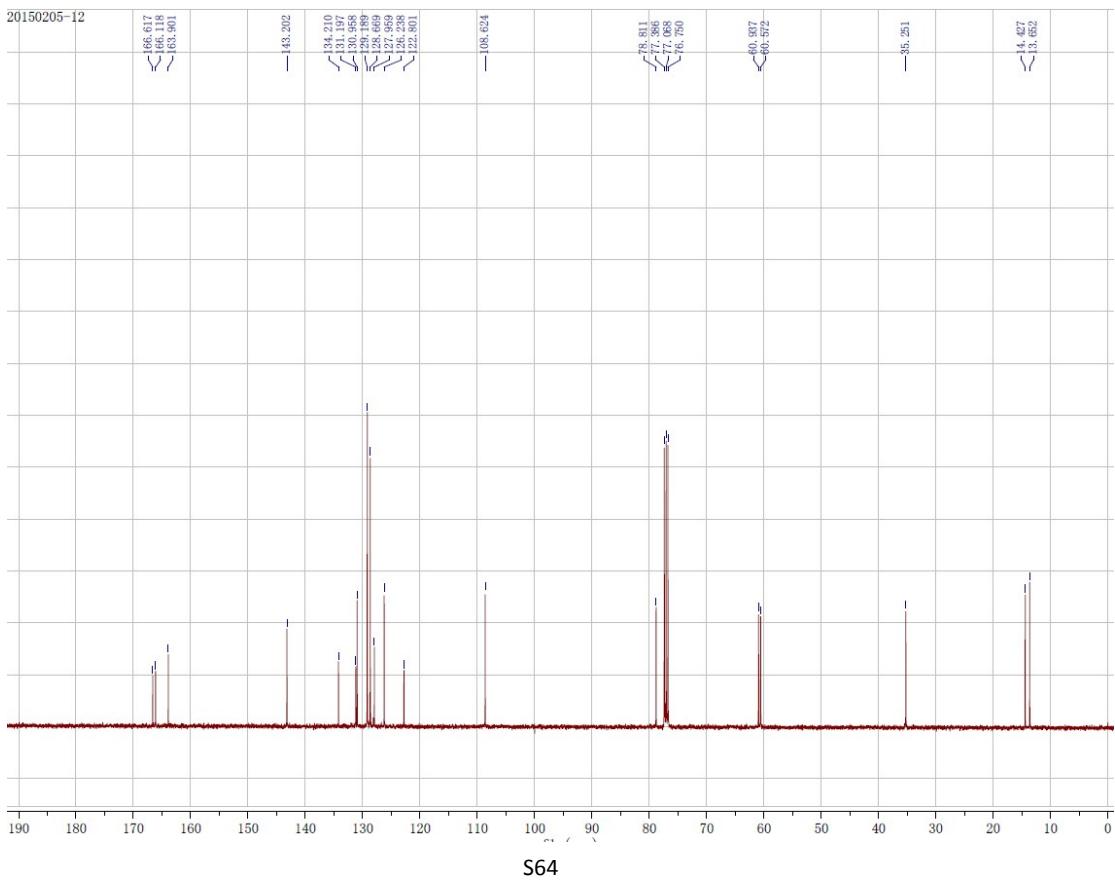
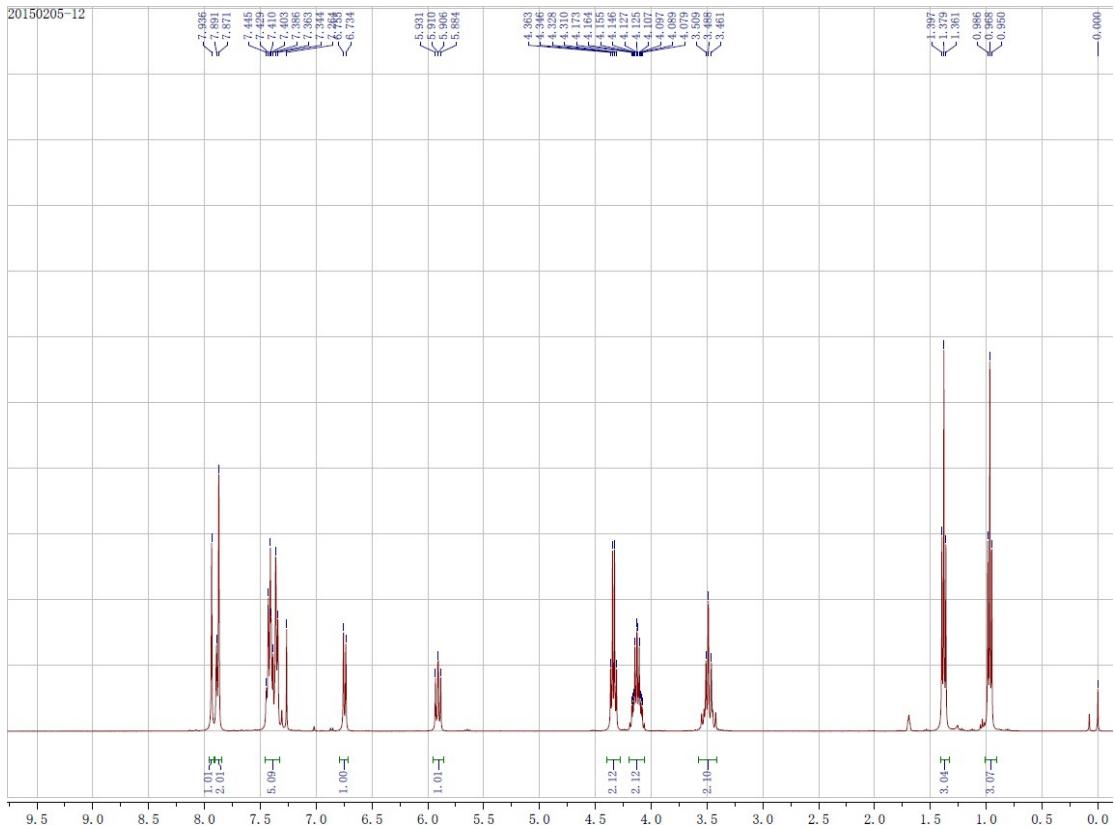
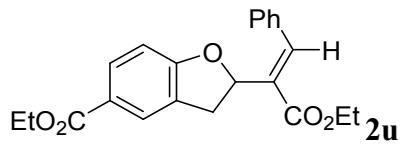


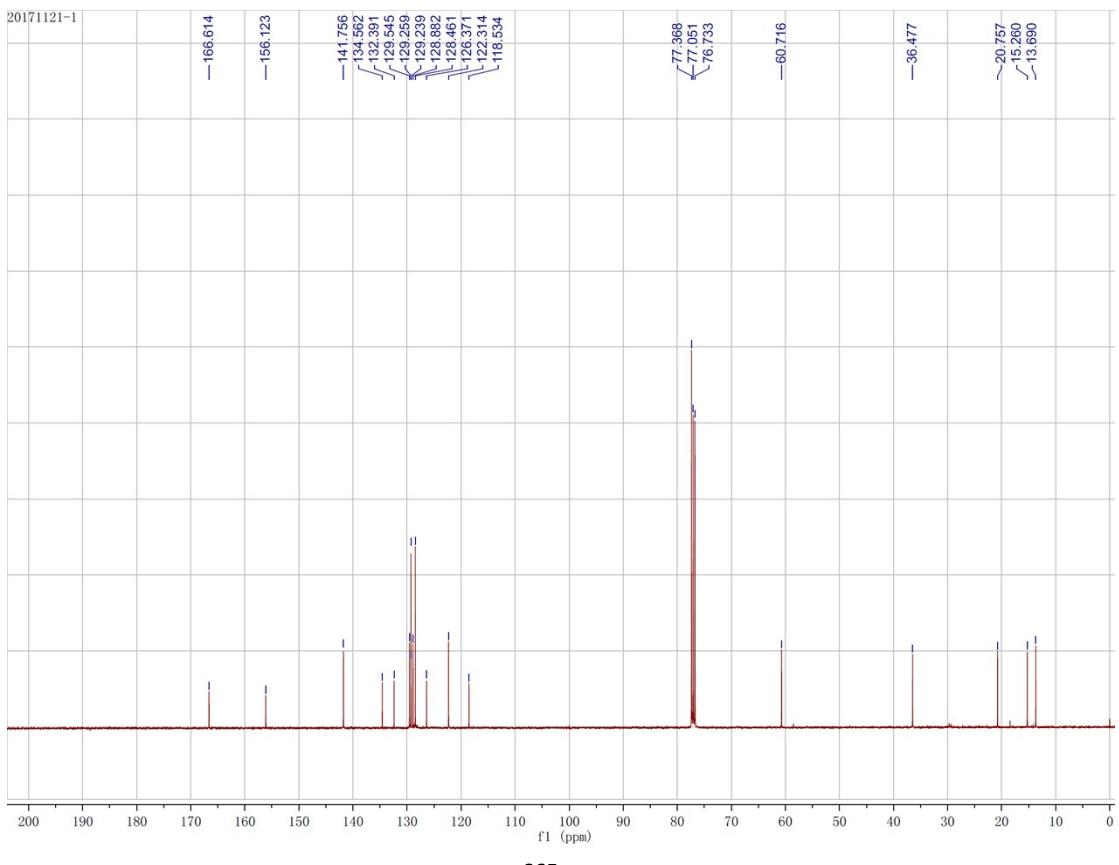
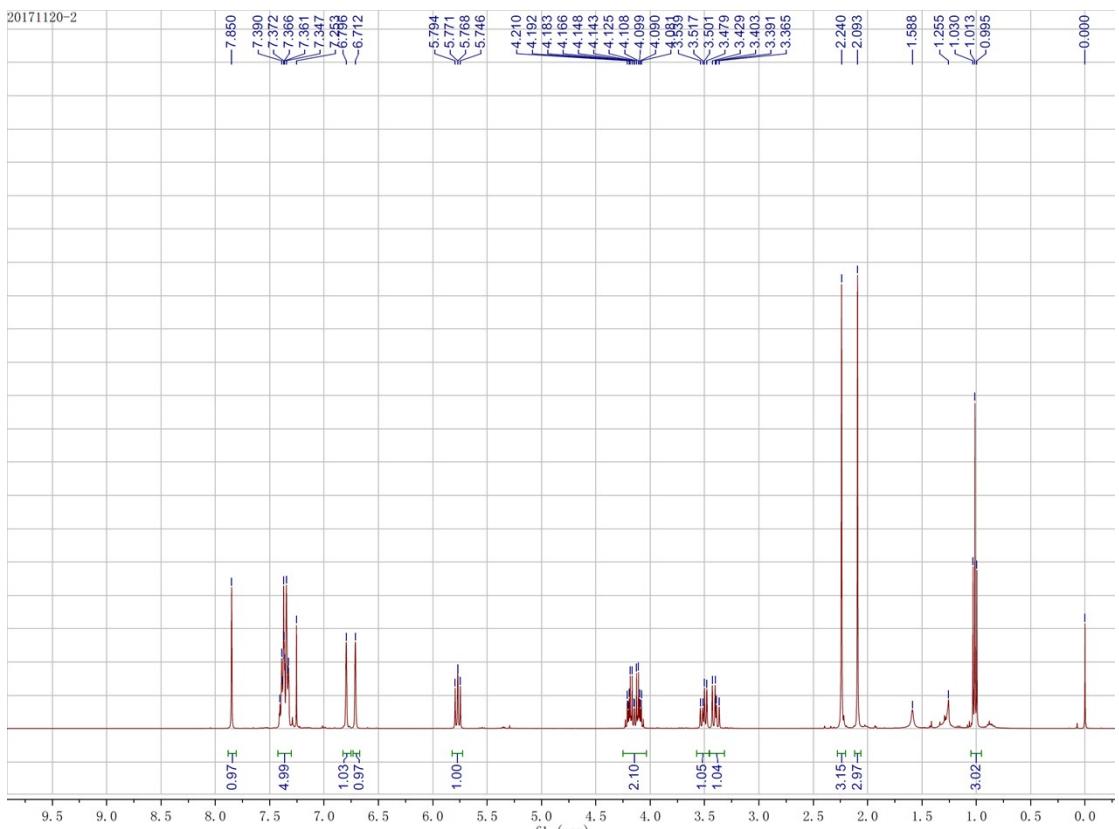
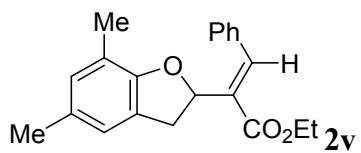


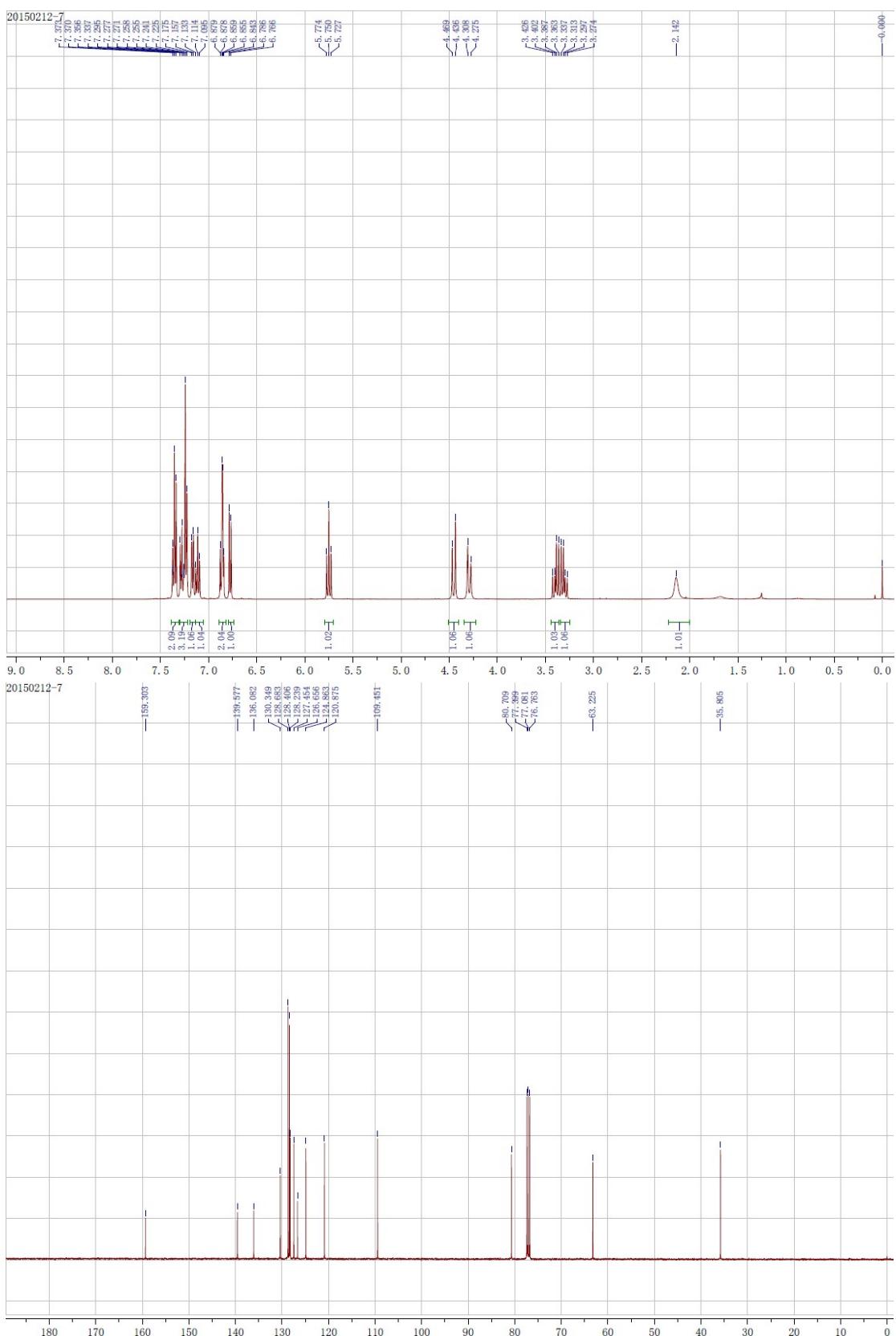
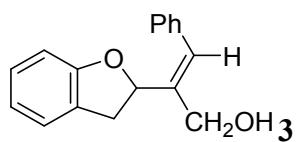


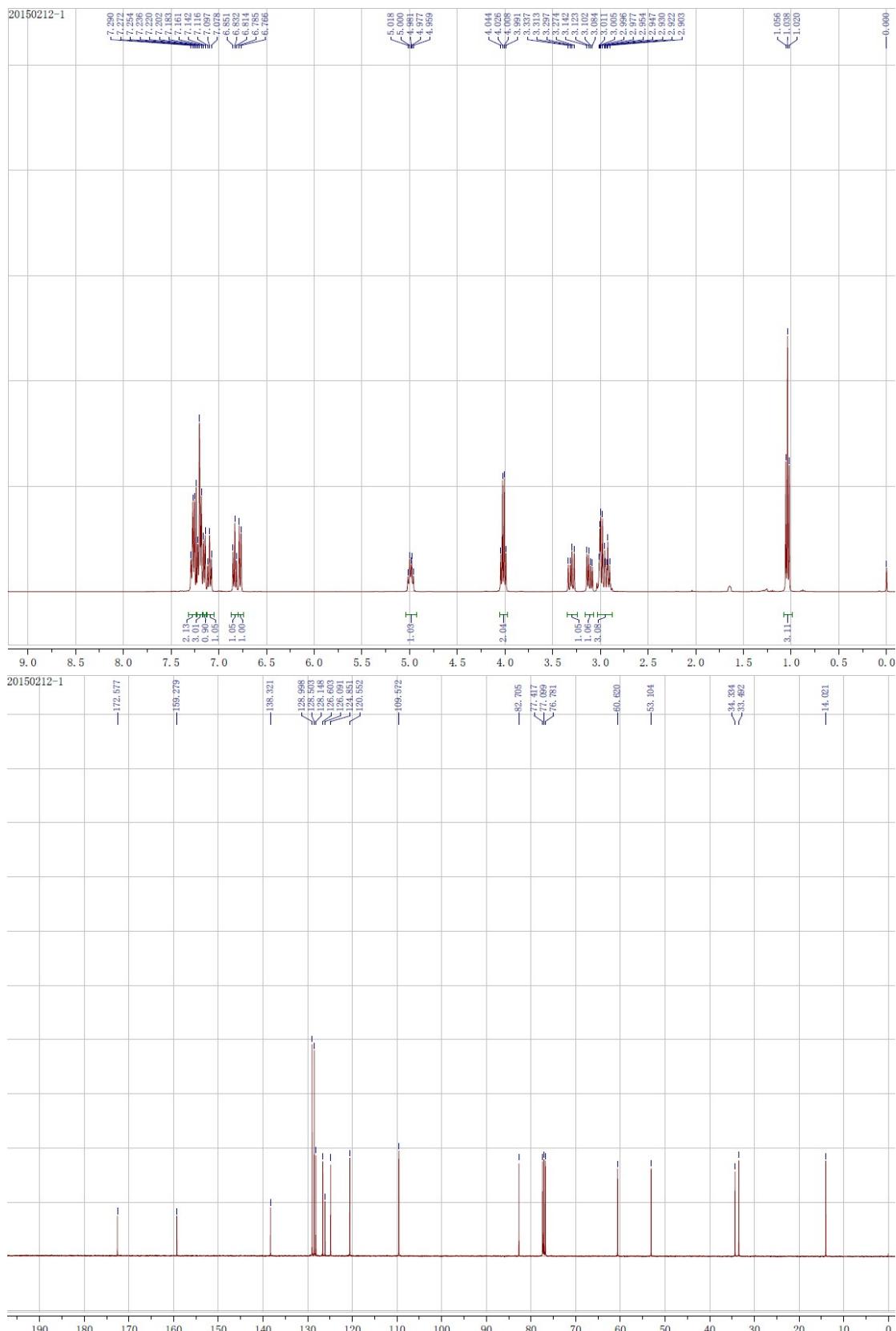
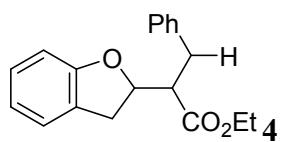


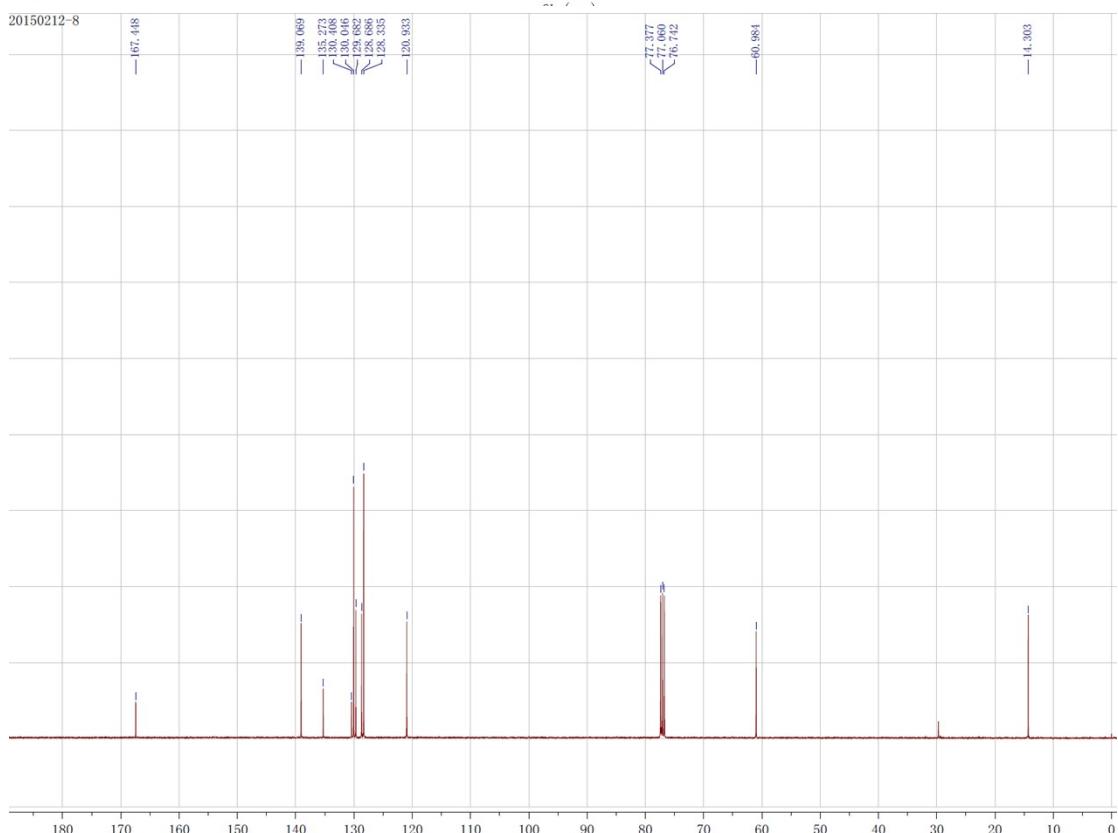
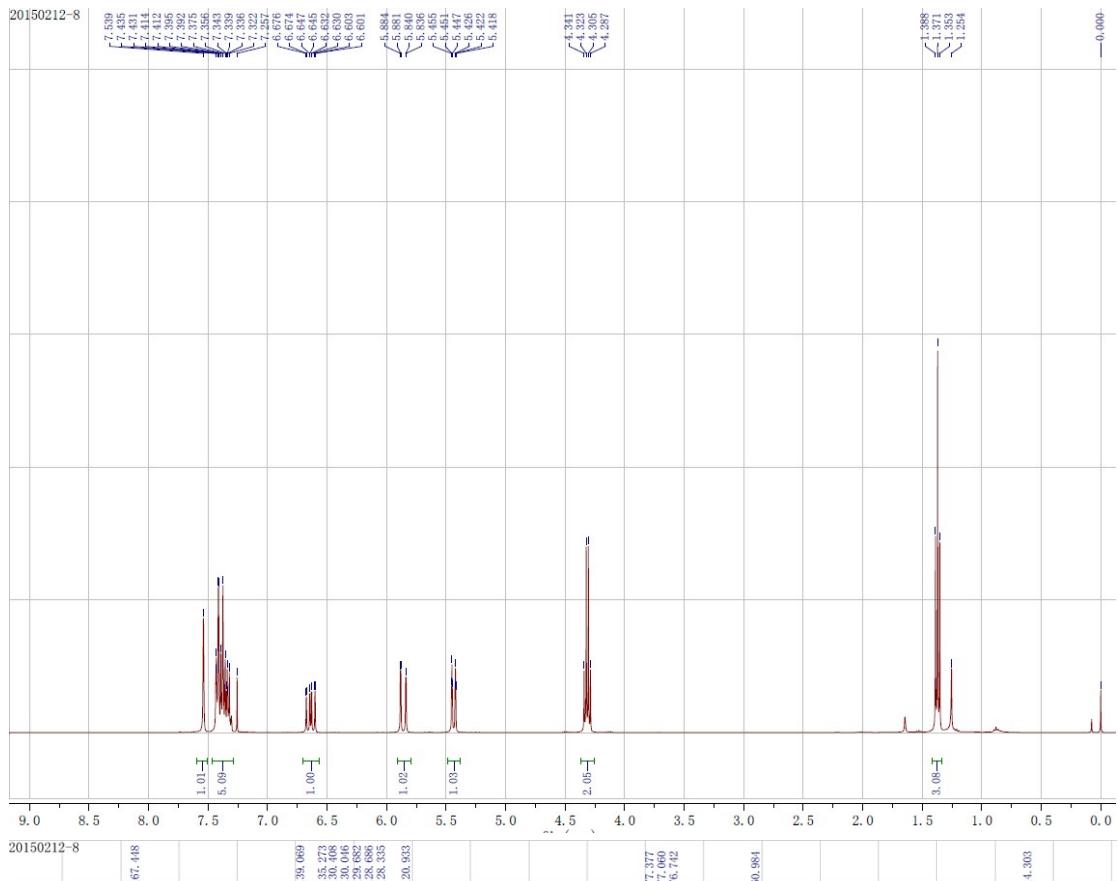
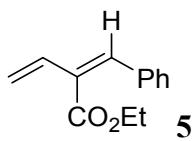


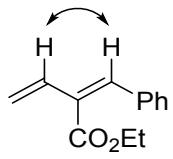




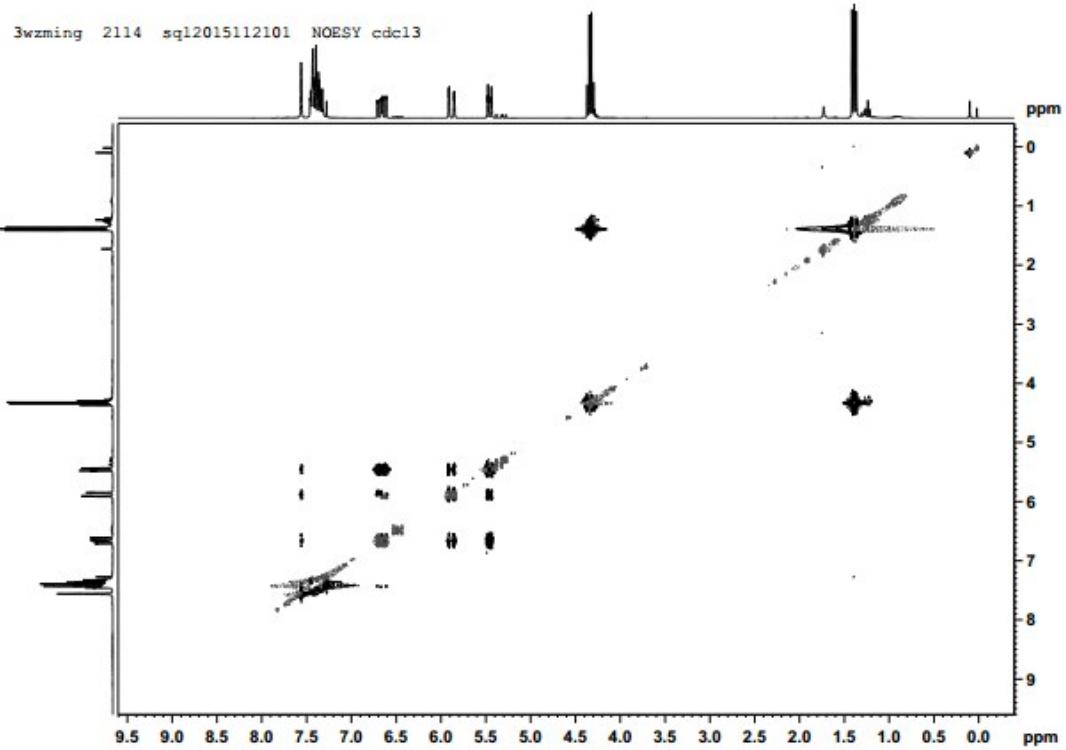








NOESY (δ 7.54 and 6.64)



2a : 2o = 0.8 : 1

