

Supporting Information

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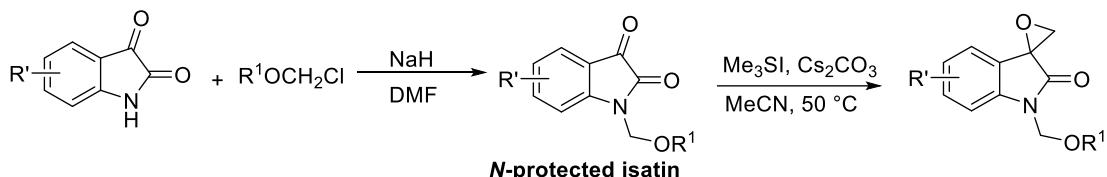
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1. General Details

All air and moisture sensitive manipulations were carried out with standard Schlenk techniques nitrogen atmosphere. Column chromatography was performed using 200-300 mesh silica gels. Acetone, Dichloromethane (CH_2Cl_2) and Acetonitrile (MeCN) were dried and distilled from calcium hydride. Methyl *tert*-butyl ether (MTBE), Ether (Et_2O), Tetrahydrofuran (THF), 1,4-Dioxane and Toluene were dried and distilled from metal sodium and benzophenone. The dry Ethanol was purchased from Energy Chemical Inc. The NMR spectra were recorded on a Varian MERCURY plus-400 (400 MHz), Bruker AscendTM 400 (400 MHz), and Bruker AscendTM 500 (500 MHz) spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvents. Mass spectrometry analysis was carried out using an electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer and Fourier Transform Ion Cyclotron Mass Spectrometry at the Instrumental Analysis Center of Shanghai Jiao Tong University. Melting points were measured with SGW X-4 micro melting point apparatus. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm. Chiral analyses were performed on a Shimadzu LC-2010 HPLC system and using Daicel Chiralcel columns with *n*-hexane/*i*-propyl alcohol as an elute. Chiralpak AD-H, OD-H, OJ-H and IE were purchased from Daicel Chiral Technologies (China) Co., Ltd.

2. Preparation of Starting Materials and Chiral BOX Ligands

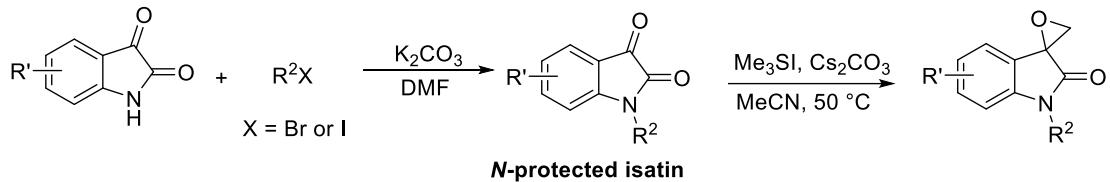
2.1 General Procedure for Preparation of Spiro-Epoxyoxindole



Method A: Non-commercial available R¹OCH₂Cl reagents were prepared according to the literature procedure.¹ A solution of alcohol (R¹OH) (1.0 equiv) and paraformaldehyde (1.0 equiv) in TMSCl was stirred for 3-5 h at room temperature and then concentrated to the crude product (R¹OCH₂Cl), which was used in the subsequent step without further purification.

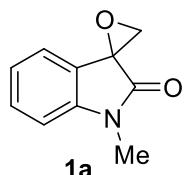
To a solution of isatin (1.0 equiv.) in dry DMF (0.50 M) was added sodium hydride (60% wt, 1.2 equiv) at 0 °C under nitrogen atmosphere. After stirring for 10-20 min at room temperature, alcohol chloromethyl ether (R¹OCH₂Cl) (1.2 equiv) was added dropwise to the above mixture. After warming to room temperature, the reaction mixture was stirred overnight. The reaction was then quenched by water and extracted with EtOAc. The organic layer was separated and washed with water, then the organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated in vacuum. The crude product *N*-protected isatin was used in the subsequent step without further purification.²

Trimethylsulphonium iodide (2.0 equiv.), cesium carbonate (2.0 equiv) and acetonitrile (0.50 M) were added to a flame-dried flask. The resulting mixture was stirred at 50 °C for 1 h under nitrogen atmosphere. A solution of *N*-protected isatin (1.0 equiv) in acetonitrile was added slowly. The suspension was stirred overnight at 50 °C. After completion of reaction (monitored by TLC), the mixture was filtered through a celite bed. The filtrate was evaporated to dryness and the residue was purified by flash chromatography on silica gel, eluting with petroleum ether/ethyl acetate 10:1 (v/v), to afford the pure product.³

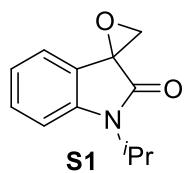


Method B: To a solution of isatin (1.0 equiv) in DMF (0.50 M) was added potassium carbonate (2.0 equiv) and R^2X ($X = Br$ or I), the reaction mixture was stirred overnight at room temperature. The reaction was then quenched by water and extracted with CH_2Cl_2 . The organic layer was separated and washed with water, then the organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuum. The crude product *N*-protected isatin was used in the subsequent step without further purification.⁴

The epoxidation followed the procedure shown in **Method A**.

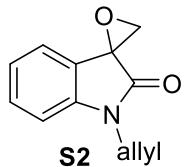


1-Methylspiro[indoline-3,2'-oxiran]-2-one (1a). The product was prepared following the general procedure **Method B** and obtained (starting from 30 mmol of the corresponding isatin; 4.1 g, 78% yield) as a pale pink solid. $M_p = 81\sim82$ °C; 1H NMR (500 MHz, $CDCl_3$) δ 7.39 (td, $J = 7.5, 1.5$ Hz, 1H), 7.13 – 7.06 (m, 2H), 6.92 (d, $J = 8.0$ Hz, 1H), 3.58 (d, $J = 7.0$ Hz, 1H), 3.44 (d, $J = 6.5$ Hz, 1H), 3.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 145.1, 130.4, 122.9, 122.7, 122.1, 108.9, 56.4, 54.1, 26.7; HRMS (ESI) calcd for $C_{10}H_9NNaO_2$ ($M+Na$)⁺ 198.0525, found 198.0524.

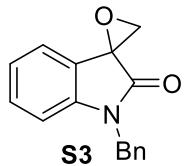


1-Isopropylspiro[indoline-3,2'-oxiran]-2-one (S1). The product was prepared following general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.3 g, 64% yield) as a yellow solid. $M_p = 42\sim44$ °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.35 (td, $J = 8.0, 1.6$ Hz, 1H), 7.13 – 7.03 (m, 3H), 4.66 (hept, $J = 6.8$ Hz, 1H), 3.57 (d, $J = 6.8$ Hz, 1H), 3.41 (d, $J = 6.8$ Hz, 1H), 1.51 (d, $J = 6.8$ Hz,

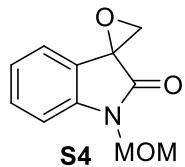
6H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.3, 143.8, 130.2, 123.2, 122.33, 122.31, 110.5, 56.2, 54.4, 44.5, 19.5, 19.3; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 226.0838, found 226.0832.



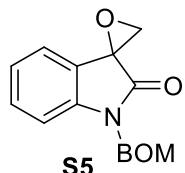
1-Allylspiro[indoline-3,2'-oxiran]-2-one (S2). The product was prepared following the general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.0 g, 50% yield) as a white solid. Mp = 65~67 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.35 (td, J = 7.6, 1.6 Hz, 1H), 7.13 – 7.06 (m, 2H), 6.93 (d, J = 7.6 Hz, 1H), 5.91 – 5.81 (m, 1H), 5.32 – 5.23 (m, 2H), 4.47 – 4.34 (m, 2H), 3.61 (d, J = 6.8 Hz, 1H), 3.45 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 144.3, 131.0, 130.3, 122.9, 122.7, 122.2, 118.1, 109.8, 56.3, 54.2, 42.9; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{11}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 224.0682, found 224.0680.



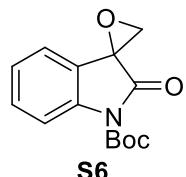
1-Benzylspiro[indoline-3,2'-oxiran]-2-one (S3). The product was prepared following the general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.4 g, 56% yield) as a yellow solid. Mp = 97~98 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.32 (m, 4H), 7.30 – 7.24 (m, 2H), 7.12 (dd, J = 7.6, 1.6 Hz, 1H), 7.04 (td, J = 7.6, 0.8 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 5.00 (d, J = 15.6 Hz, 1H), 4.93 (d, J = 15.6 Hz, 1H), 3.65 (d, J = 6.8 Hz, 1H), 3.47 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 144.3, 135.3, 130.3, 128.9, 127.8, 127.4, 122.9, 122.7, 122.2, 109.9, 56.4, 54.3, 44.3; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{13}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 274.0838, found 274.0833.



1-(Methoxymethyl)spiro[indoline-3,2'-oxiran]-2-one (S4). The product was prepared following the general procedure **Method A** and obtained (starting from 10 mmol of the corresponding isatin; 0.88 g, 43% yield) as a pale pink solid. Mp = 78~80 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.36 (m, 1H), 7.15 – 7.10 (m, 3H), 5.20 (d, *J* = 10.8 Hz, 1H), 5.15 (d, *J* = 11.2 Hz, 1H), 3.62 (d, *J* = 6.4 Hz, 1H), 3.47 (d, *J* = 6.8 Hz, 1H), 3.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.5, 143.4, 130.6, 123.5, 122.3, 122.2, 110.4, 71.7, 56.5, 56.4, 54.5; HRMS (ESI) calcd for C₁₁H₁₁NNaO₃ (M+Na)⁺ 228.0631, found 228.0626.



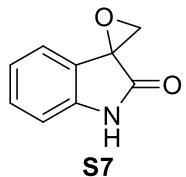
1-(Benzyl)spiro[indoline-3,2'-oxiran]-2-one (S5). The product was prepared following the general procedure **Method A** and obtained (starting from 50 mmol of the corresponding isatin; 9.0 g, 64% yield) as a pale yellow solid. Mp = 106~108 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.36 (m, 1H), 7.33 – 7.26 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.14 – 7.10 (m, 2H), 5.32 (d, *J* = 11.0 Hz, 1H), 5.28 (d, *J* = 11.5 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 3.57 (d, *J* = 6.5 Hz, 1H), 3.42 (d, *J* = 7.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 172.3, 143.4, 137.1, 130.5, 128.4, 127.90, 127.87, 123.4, 122.19, 122.17, 110.5, 71.1, 70.0, 56.4, 54.5; HRMS (ESI) calcd for C₁₇H₁₅NNaO₃ (M+Na)⁺ 304.0944, found 304.0939.



To a solution of **S7** (322 mg, 2.0 mmol, 1.0 equiv) and 4-dimethylaminopyridine (244 mg, 2.0 mmol, 1.0 equiv) in CH₂Cl₂ (2.0 mL) was added triethylamine (202 mg, 2.0 mmol, 2.0 equiv) and di-*tert*-butyl dicarbonate (872 mg, 4.0 mmol, 2.0 equiv) at

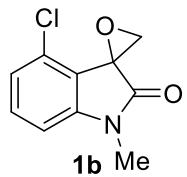
room temperature. After stirring overnight, the solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel, eluting with petroleum ether/ethyl acetate 3:1 (v/v), to afford **S6** as a yellow solid.³

tert-Butyl 2-oxospiro[indoline-3,2'-oxirane]-1-carboxylate (S6). 418 mg, 80% yield, yellow solid. Mp = 57~59 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.42 (td, *J* = 8.0, 1.2 Hz, 1H), 7.20 (td, *J* = 7.6, 1.2 Hz, 1H), 7.12 (dd, *J* = 7.6, 1.6 Hz, 1H), 3.61 (d, *J* = 6.8 Hz, 1H), 3.43 (d, *J* = 6.8 Hz, 1H), 1.65 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 148.9, 141.4, 130.7, 124.8, 121.9, 121.8, 115.7, 84.9, 56.2, 55.5, 28.1; HRMS (ESI) calcd for C₁₄H₁₅NNaO₄ (M+Na)⁺ 284.0893, found 284.0896.

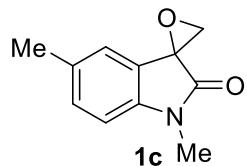


This substrate was prepared according to literature reported procedure. To a solution of trimethylsulphonium iodide (6.1 g, 30 mmol, 2.0 equiv) in dry DMF (40 mL), sodium hydride (60% wt, 5.8 g, 144 mmol, 7.2 equiv) was added at room temperature. The resulting mixture was stirred for 1 h under nitrogen atmosphere. Then the reaction mixture was stirred at -20 °C. To this solution isatin (3.0 g, 20 mmol, 1.0 equiv) in dry DMF (10 mL) was added dropwise over 20 min. The suspension was stirred overnight at -20 °C. After that, the mixture was poured into the ice water slowly, then extracted with EtOAc, washed with brine solution and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel, eluting with petroleum ether/ethyl acetate 3:1 (v/v), to afford the pure product as a yellow solid.³

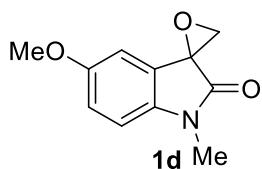
Spiro[indoline-3,2'-oxiran]-2-one (S7). 2.0 g, 62% yield, yellow solid. Mp = 168~170 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.62 (s, 1H), 7.33 (td, *J* = 7.6, 1.6 Hz, 1H), 7.14 – 7.04 (m, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 3.59 (d, *J* = 6.4 Hz, 1H), 3.45 (d, *J* = 6.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 142.1, 130.5, 123.00, 122.96, 122.5, 110.9, 56.6, 54.3; HRMS (ESI) calcd for C₉H₇NNaO₂ (M+Na)⁺ 184.0369, found 184.0360.



4-Chloro-1-methylspiro[indoline-3,2'-oxiran]-2-one (1b). The product was prepared following general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.8 g, 86% yield) as a white solid. Mp = 124~125 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (t, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.83 (dd, *J* = 8.0, 0.8 Hz, 1H), 4.06 (d, *J* = 7.2 Hz, 1H), 3.49 (d, *J* = 7.2 Hz, 1H), 3.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 146.8, 131.3, 130.6, 124.1, 118.8, 107.4, 56.8, 50.5, 26.9; HRMS (ESI) calcd for C₁₀H₈ClNNaO₂ (M+Na)⁺ 232.0136, found 232.0143.

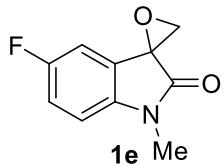


1,5-Dimethylspiro[indoline-3,2'-oxiran]-2-one (1c). The product was prepared following general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.3 g, 69% yield) as a white solid. Mp = 104~105 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.18 (ddd, *J* = 8.0, 2.0, 0.8 Hz, 1H), 6.95 – 6.92 (m, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.58 (d, *J* = 6.8 Hz, 1H), 3.42 (d, *J* = 6.8 Hz, 1H), 3.26 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.7, 142.7, 132.6, 130.6, 122.8, 122.6, 108.6, 56.5, 54.1, 26.7, 21.0; HRMS (ESI) calcd for C₁₁H₁₁NNaO₂ (M+Na)⁺ 212.0682, found 212.0688.

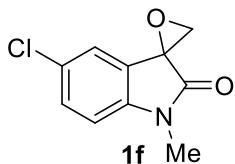


5-Methoxy-1-methylspiro[indoline-3,2'-oxiran]-2-one (1d). The product was prepared following general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.4 g, 68% yield) as an orange solid. Mp = 122~124 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.91 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.72 (d, *J* = 2.8 Hz, 1H), 3.79 (s, 3H), 3.58 (d, *J* = 6.4 Hz, 1H), 3.41 (d, *J* = 6.8 Hz,

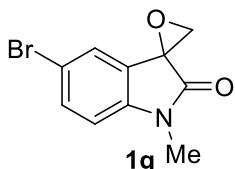
1H), 3.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 156.3, 138.4, 123.9, 115.1, 109.4, 109.0, 56.7, 55.9, 54.2, 26.8; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{11}\text{NNaO}_3$ ($\text{M}+\text{Na}$) $^+$ 228.0631, found 228.0635.



5-Fluoro-1-methylspiro[indoline-3,2'-oxiran]-2-one (1e). The product was prepared following general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.2 g, 62% yield) as a white solid. Mp = 153~155 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.09 (td, J = 8.8, 2.8 Hz, 1H), 6.89 – 6.83 (m, 2H), 3.60 (d, J = 6.8 Hz, 1H), 3.42 (d, J = 6.8 Hz, 1H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 159.3 (d, J = 240.8 Hz), 141.0 (d, J = 2.1 Hz), 124.4 (d, J = 8.5 Hz), 116.7 (d, J = 23.6 Hz), 110.4 (d, J = 25.3 Hz), 109.5 (d, J = 7.9 Hz), 56.4 (d, J = 2.1 Hz), 54.3, 26.8; ^{19}F NMR (470 MHz, CDCl_3) δ -119.76; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_8\text{FNNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 216.0431, found 216.0438.

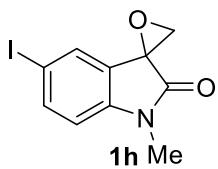


5-Chloro-1-methylspiro[indoline-3,2'-oxiran]-2-one (1f). The product was prepared following general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.2 g, 57% yield) as a pale yellow solid. Mp = 157~158 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.36 (dd, J = 8.4, 2.0 Hz, 1H), 7.09 (d, J = 2.0 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 3.59 (d, J = 6.8 Hz, 1H), 3.43 (d, J = 6.4 Hz, 1H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.3, 143.6, 130.3, 128.5, 124.5, 122.6, 109.8, 56.2, 54.3, 26.8; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_8\text{ClNNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 232.0136, found 232.0140.

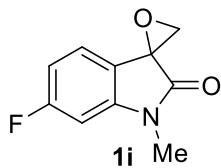


5-Bromo-1-methylspiro[indoline-3,2'-oxiran]-2-one (1g). The product was prepared

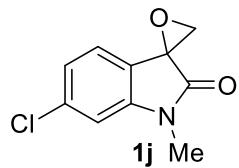
following general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.5 g, 59% yield) as a pale yellow solid. Mp = 158~159 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.51 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 3.59 (d, *J* = 6.8 Hz, 1H), 3.43 (d, *J* = 6.8 Hz, 1H), 3.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.2, 144.0, 133.2, 125.4, 124.8, 115.6, 110.3, 56.1, 54.3, 26.8; HRMS (ESI) calcd for C₁₀H₉BrNO₂ (M+H)⁺ 253.9811, found 253.9815.



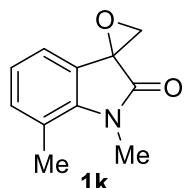
5-Iodo-1-methylspiro[indoline-3,2'-oxiran]-2-one (1h). The product was prepared following general procedure **Method B** and obtained (starting from 8.0 mmol of the corresponding isatin; 1.5 g, 62% yield) as a pale yellow solid. Mp = 152~153 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.70 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.39 (d, *J* = 2.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 3.58 (d, *J* = 6.8 Hz, 1H), 3.43 (d, *J* = 6.4 Hz, 1H), 3.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.0, 144.7, 139.1, 130.9, 125.1, 110.8, 85.2, 55.9, 54.3, 26.8; HRMS (ESI) calcd for C₁₀H₉INO₂ (M+H)⁺ 301.9672, found 301.9678.



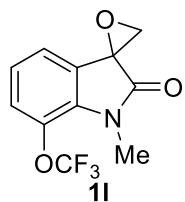
6-Fluoro-1-methylspiro[indoline-3,2'-oxiran]-2-one (1i). The product was prepared following general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.3 g, 67% yield) as a pink solid. Mp = 92~93 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.06 (dd, *J* = 8.5, 5.0 Hz, 1H), 6.79 – 6.74 (m, 1H), 6.68 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.58 (d, *J* = 6.5 Hz, 1H), 3.43 (d, *J* = 6.5 Hz, 1H), 3.27 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.1, 164.5 (d, *J* = 246.8 Hz), 146.8 (d, *J* = 11.6 Hz), 123.5 (d, *J* = 10.0 Hz), 117.9 (d, *J* = 3.0 Hz), 109.2 (d, *J* = 22.9 Hz), 98.0 (d, *J* = 27.5 Hz), 56.1, 54.0, 26.8; ¹⁹F NMR (470 MHz, CDCl₃) δ -108.26; HRMS (ESI) calcd for C₁₀H₈FNNaO₂ (M+Na)⁺ 216.0431, found 216.0435.



6-Chloro-1-methylspiro[indoline-3,2'-oxiran]-2-one (1j). The product was prepared following general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.2 g, 57% yield) as a yellow solid. Mp = 142~144 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.06 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 3.59 (d, *J* = 6.5 Hz, 1H), 3.44 (d, *J* = 6.5 Hz, 1H), 3.27 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.7, 146.2, 136.3, 123.1, 122.8, 121.0, 109.7, 56.1, 54.2, 26.8; HRMS (ESI) calcd for C₁₀H₈ClNNaO₂ (M+Na)⁺ 232.0136, found 232.0141.

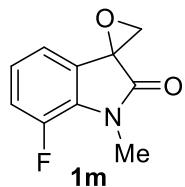


1,7-Dimethylspiro[indoline-3,2'-oxiran]-2-one (1k). The product was prepared following general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.2 g, 63% yield) as a pale yellow solid. Mp = 105~106 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.10 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.93 (dd, *J* = 7.5, 1.5 Hz, 1H), 3.57 (d, *J* = 6.5 Hz, 1H), 3.55 (s, 3H), 3.39 (d, *J* = 6.5 Hz, 1H), 2.59 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.6, 142.8, 134.2, 123.4, 122.9, 120.7, 119.9, 56.0, 54.6, 30.1, 19.0; HRMS (ESI) calcd for C₁₁H₁₁NNaO₂ (M+Na)⁺ 212.0682, found 212.0690.

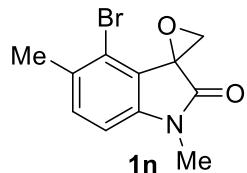


1-Methyl-7-(trifluoromethoxy)spiro[indoline-3,2'-oxiran]-2-one (1l). The product was prepared following general procedure **Method B** and obtained (starting from 4.3 mmol of the corresponding isatin; 0.55 g, 49% yield) as a white solid. Mp = 78~79 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.27 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.01 (dd, *J* = 2.5, 1.0 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 3.62 (d, *J* = 6.5 Hz, 1H), 3.46 (d, *J* = 7.0 Hz, 1H), 3.30

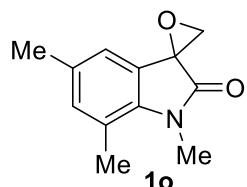
(s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.5, 144.9 (q, $J = 1.9$ Hz), 143.6, 124.3, 123.6, 120.5 (q, $J = 255.5$ Hz), 116.2, 109.4, 56.2, 54.4, 26.9; ^{19}F NMR (470 MHz, CDCl_3) δ -58.42; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_9\text{F}_3\text{NO}_3$ ($\text{M}+\text{H}$) $^+$ 260.0529, found 260.0527.



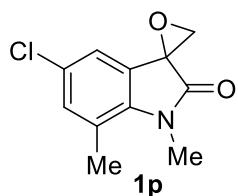
7-Fluoro-1-methylspiro[indoline-3,2'-oxiran]-2-one (1m). The product was prepared following general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.5 g, 78% yield) as a yellow solid. Mp = 103~104 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.13 – 7.09 (m, 1H), 7.04 – 6.99 (m, 1H), 6.90 (dd, $J = 7.5, 1.5$ Hz, 1H), 3.59 (d, $J = 6.5$ Hz, 1H), 3.49 (d, $J = 2.5$ Hz, 3H), 3.43 (d, $J = 6.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.5, 148.0 (d, $J = 243.4$ Hz), 131.5 (d, $J = 9.0$ Hz), 125.7 (d, $J = 3.6$ Hz), 123.6 (d, $J = 6.2$ Hz), 118.5 (d, $J = 19.2$ Hz), 117.9 (d, $J = 3.5$ Hz), 56.3 (d, $J = 3.8$ Hz), 54.6, 29.3 (d, $J = 5.5$ Hz); ^{19}F NMR (470 MHz, CDCl_3) δ -136.84; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_8\text{FNNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 216.0431, found 216.0438.



4-Bromo-1,5-dimethylspiro[indoline-3,2'-oxiran]-2-one (1n). The product was prepared following general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.8 g, 67% yield) as a white solid. Mp = 146~148 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.25 (dd, $J = 8.0, 0.5$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 4.22 (d, $J = 7.0$ Hz, 1H), 3.43 (d, $J = 7.0$ Hz, 1H), 3.25 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.2, 144.8, 132.9, 131.7, 120.8, 120.6, 107.6, 57.6, 50.0, 26.7, 22.0; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{10}\text{BrNNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 289.9787, found 289.9791.



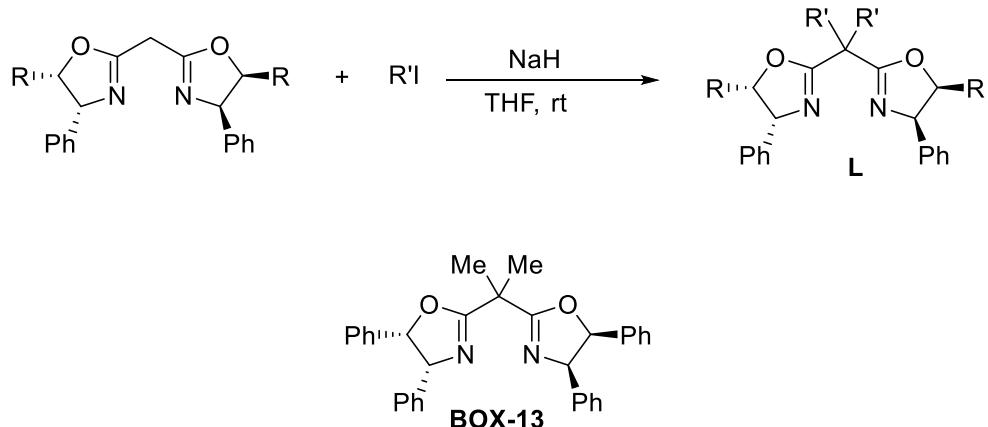
1,5,7-Trimethylspiro[indoline-3,2'-oxiran]-2-one (1o). The product was prepared following general procedure **Method B** and obtained (starting from 10 mmol of the corresponding isatin; 1.5 g, 74% yield) as an orange solid. Mp = 134~136 °C; ¹H NMR (500 MHz, CDCl₃) δ 6.91 (s, 1H), 6.74 (s, 1H), 3.56 (dd, *J* = 6.5, 1.5 Hz, 1H), 3.52 (d, *J* = 1.5 Hz, 3H), 3.37 (dd, *J* = 6.5, 1.5 Hz, 1H), 2.54 (s, 3H), 2.27 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.6, 140.3, 134.6, 132.5, 123.4, 120.5, 120.4, 56.1, 54.6, 30.0, 20.7, 18.8; HRMS (ESI) calcd for C₁₂H₁₃NNaO₂ (M+Na)⁺ 226.0838, found 226.0840.



5-Chloro-1,7-dimethylspiro[indoline-3,2'-oxiran]-2-one (1p). The product was prepared following general procedure **Method B** and obtained (starting from 5.1 mmol of the corresponding isatin; 0.66 g, 58% yield) as yellow solid. Mp = 149~150 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.10 – 7.09 (m, 1H), 6.90 (d, *J* = 1.5 Hz, 1H), 3.58 (d, *J* = 6.5 Hz, 1H), 3.53 (s, 3H), 3.38 (d, *J* = 6.5 Hz, 1H), 2.57 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.2, 141.3, 133.6, 128.1, 125.1, 122.3, 120.2, 55.8, 54.7, 30.1, 18.8; HRMS (ESI) calcd for C₁₁H₁₁ClNO₂ (M+H)⁺ 224.0473, found 224.0477.

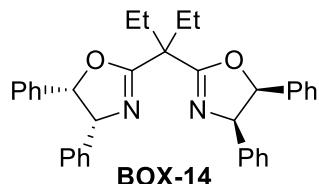
2.2 Preparation of Chiral BOX Ligands

BOX-13, BOX-14, BOX-16, SL20 were synthesized according to the literatures.⁵



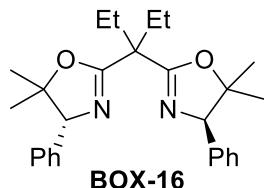
(4*R*,4'*R*,5*S*,5'*S*)-2,2'-(Propane-2,2-diyil)bis(4,5-diphenyl-4,5-dihydrooxazole)

(BOX-13). 210 mg, 86% yield, white solid, Mp = 160~161 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.04 – 6.94 (m, 20H) 5.96 (d, *J* = 10.0 Hz, 2H), 5.59 (d, *J* = 10.0 Hz, 2H), 1.92 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 170.4, 137.5, 136.2, 127.9, 127.62, 127.61, 127.4, 126.9, 126.6, 86.3, 73.8, 39.6, 24.8; HRMS (ESI) calcd for C₃₃H₃₁N₂O₂ (M+H)⁺ 487.2380, found 487.2380.



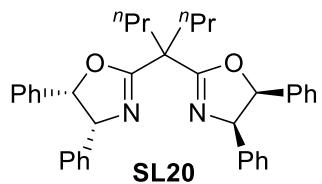
(4*R*,4'*R*,5*S*,5'*S*)-2,2'-(Pentane-3,3-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole)

(BOX-14). 200 mg, 78% yield, white solid, Mp = 91~93 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.05 – 6.90 (m, 20H), 5.95 (d, *J* = 10.0 Hz, 2H), 5.59 (d, *J* = 10.0 Hz, 2H), 2.50 – 2.41 (m, 2H), 2.35 – 2.27 (m, 2H), 1.14 (t, *J* = 7.5 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 169.0, 137.5, 136.1, 127.9, 127.6, 127.4, 126.9, 126.7, 86.0, 73.7, 47.6, 25.9, 8.8; HRMS (ESI) calcd for C₃₅H₃₅N₂O₂ (M+H)⁺ 515.2693, found 515.2695.



(4*R*,4'i*R*)-2,2'-(Pentane-3,3-diyl)bis(5,5-dimethyl-4-phenyl-4,5-dihydrooxazole)

(BOX-16). 120 mg, 57% yield, white solid, Mp = 115~116 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.31 – 7.22 (m, 10H), 4.89 (s, 2H), 2.28 – 2.19 (m, 2H), 2.15 – 2.07 (m, 2H), 1.58 (s, 6H), 0.97 (t, *J* = 7.5 Hz, 6H), 0.84 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 167.8, 139.1, 128.0, 127.4, 127.3, 86.9, 78.2, 46.7, 29.4, 24.3, 23.9, 8.2; HRMS (ESI) calcd for C₂₇H₃₅N₂O₂ (M+H)⁺ 419.2693, found 419.2695.



(4R,4'R,S,5'S)-2,2'-(Heptane-4,4-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole)

(SL20). 180 mg, 66% yield, white solid, Mp = 179~180 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.05 – 6.90 (m, 20H), 5.94 (d, J = 10.0 Hz, 2H), 5.58 (d, J = 10.0 Hz, 2H), 2.43 – 2.37 (m, 2H), 2.28 – 2.21 (m, 2H), 1.60 – 1.49 (m, 4H), 1.07 (t, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.2, 137.4, 136.0, 127.9, 127.6, 127.4, 126.9, 126.7, 86.1, 73.7, 46.9, 35.4, 17.7, 14.5; HRMS (ESI) calcd for $\text{C}_{37}\text{H}_{39}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 543.3006, found 543.3008.

3. Asymmetric Ring Opening Reaction of Spiro-Epoxyoxindoles with Allylboron

3.1 Optimizations of Cobalt-Catalyzed Asymmetric Ring Opening Reaction of Spiro-Epoxyoxindoles with Allylboron

Table S1. Optimization of Solvent and Cobalt Salt^[a]

1a

$+ \text{CH}_2=\text{CH}-\text{BF}_3\text{K}$

$\xrightarrow[\text{Solvent, } 70^\circ\text{C, 24 h}]{\text{Co salt (10 mol\%)} \\ \text{BOX-1 (12 mol\%)}}$

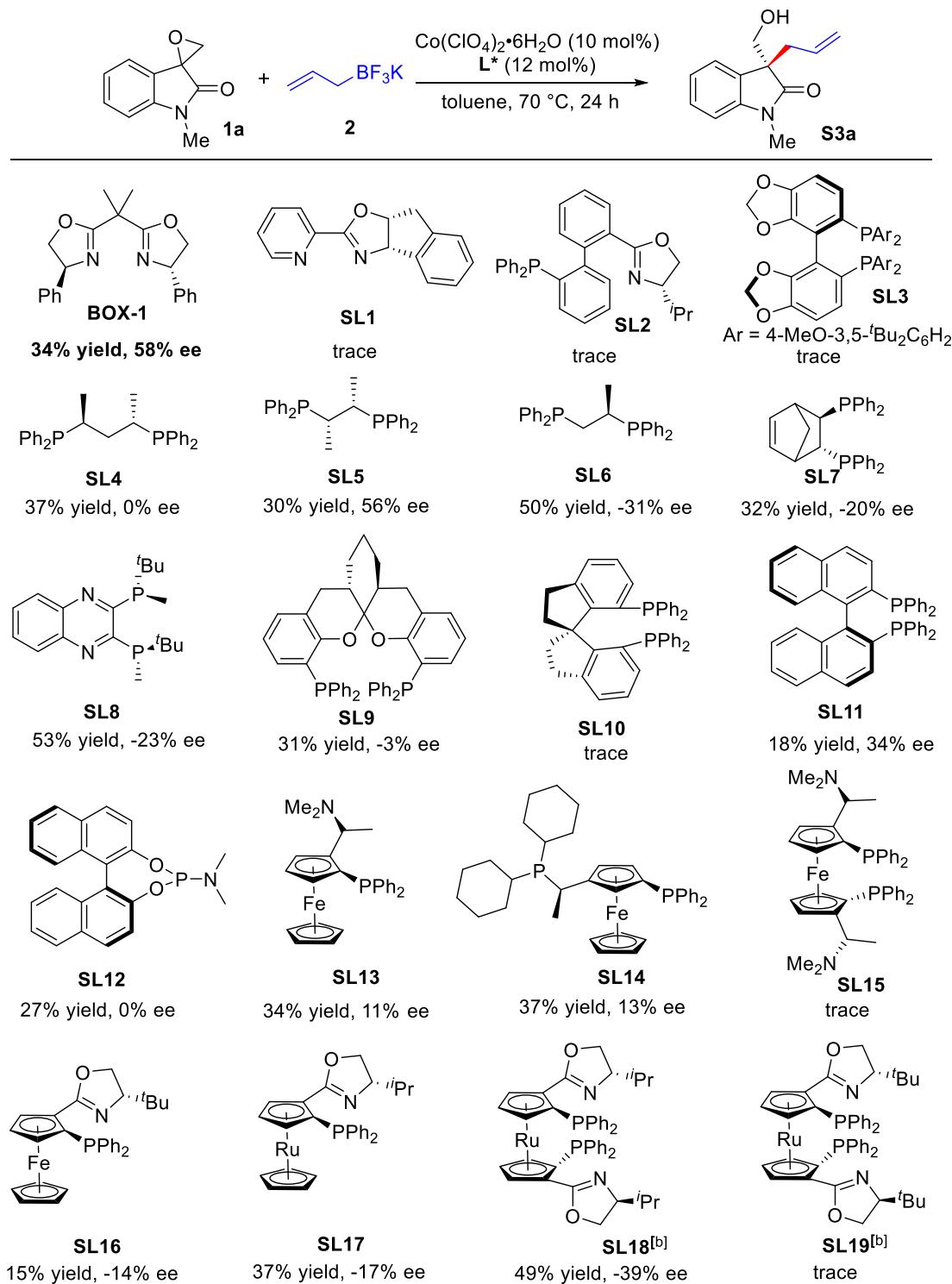
S3a

BOX-1

Entry	Co salt	Solvent	Yield [%] ^[b]	ee [%] ^[c]
1	Co(OTf) ₂ ·2MeCN	MTBE	23	53
2	Co(OTf) ₂ ·2MeCN	Et ₂ O	34	43
3	Co(OTf) ₂ ·2MeCN	THF	37	40
4	Co(OTf) ₂ ·2MeCN	Dioxane	30	40
5	Co(OTf) ₂ ·2MeCN	DCM	29	25
6	Co(OTf) ₂ ·2MeCN	toluene	34	54
7	Co(OTf) ₂ ·2MeCN	MeCN	25	43
8	Co(OTf) ₂ ·2MeCN	MeOH	ND	--
9	Co(ClO₄)₂·6H₂O	toluene	34	58
10	Co(BF ₄) ₂ ·6H ₂ O	toluene	27	50
11	CoI ₂	toluene	trace	--

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2** (0.20 mmol, 2.0 equiv), Solvent (1.5 mL), Co salt (10 mol%), **BOX-1** (12 mol%). [b] Isolated yields. [c] Enantioselectivity was determined by HPLC using a chiral column.

Scheme S1. Optimization of Chiral Ligands^[a]



[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2** (0.20 mmol, 2.0 equiv), toluene (1.5 mL), $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mol%), L^* (12 mol%). Isolated yields. Enantioselectivity was determined by HPLC using a chiral column. [b] L^* (6 mol%).

Table S2. Optimization of Additive^[a]

Entry	Additive	Yield [%] ^[b]	ee [%] ^[c]
1	TMSOTf	trace	--
2	TFAA	trace	--
3	Ac ₂ O	trace	--
4 ^[d]	Boc ₂ O	46	57
5 ^[d,e]	Boc ₂ O	60	56
6^[d,e,f]	Boc₂O	79	59
7 ^[d,e,g]	Boc ₂ O	80	59

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2** (0.20 mmol, 2.0 equiv), toluene (1.5 mL), Co(ClO₄)₂·6H₂O (10 mol%), **BOX-1** (12 mol%), Additive (0.20 mmol 2.0 equiv) [b] Isolated yields. [c] Enantioselectivity was determined by HPLC using a chiral column. [d] R = Boc. [e] 72 h. [f] Boc₂O (5.0 equiv). [g] Boc₂O (10.0 equiv).

Table S3. Optimization of Solvent and Temperatures^[a]

Entry	Solvent	Yield [%] ^[b]	ee [%] ^[c]
1	MTBE	89	59
2	Et ₂ O	92	59
3	ETBT	94	39
4	THF	81	32
5	DCM	83	27
6	toluene	83	73
7	Hexane	92	54
8	Acetone	12	47
9	DMF	trace	--
10	DMSO	trace	--
11	Benzene	64	71
12	<i>o</i> -xylene	84	71
13	<i>p</i> -xylene	64	61
14	Chlorobenzene	90	55
15 ^[d]	toluene	74	60
16 ^[e]	toluene	46	65

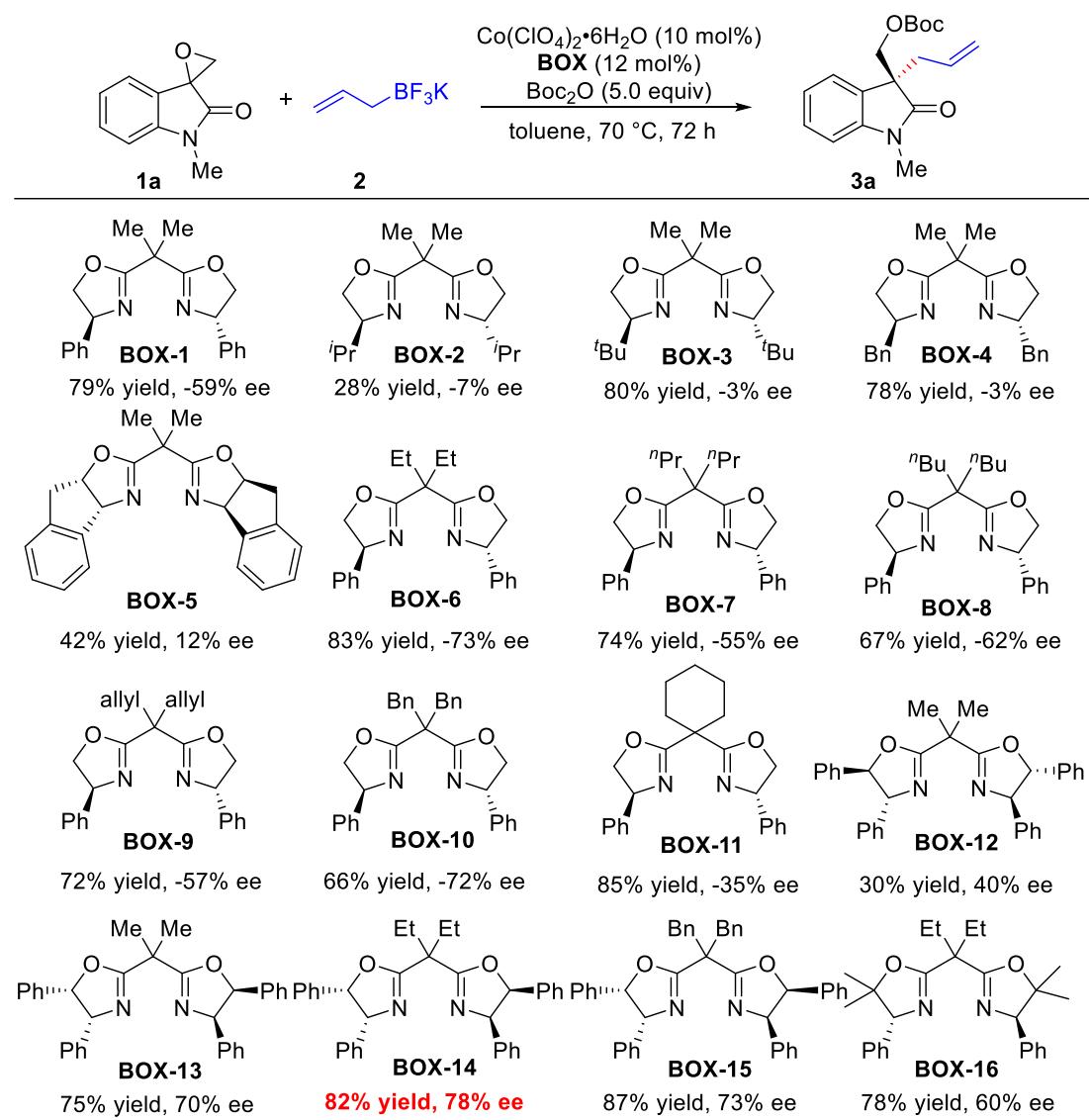
[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2** (0.20 mmol, 2.0 equiv), Solvent (1.5 mL), Co(ClO₄)₂·6H₂O (10 mol%), **BOX-6** (12 mol%), Boc₂O (0.50 mmol, 5.0 equiv). [b] Isolated yields. [c] Enantioselectivity was determined by HPLC using a chiral column. [d] 100 °C. [e] 40 °C.

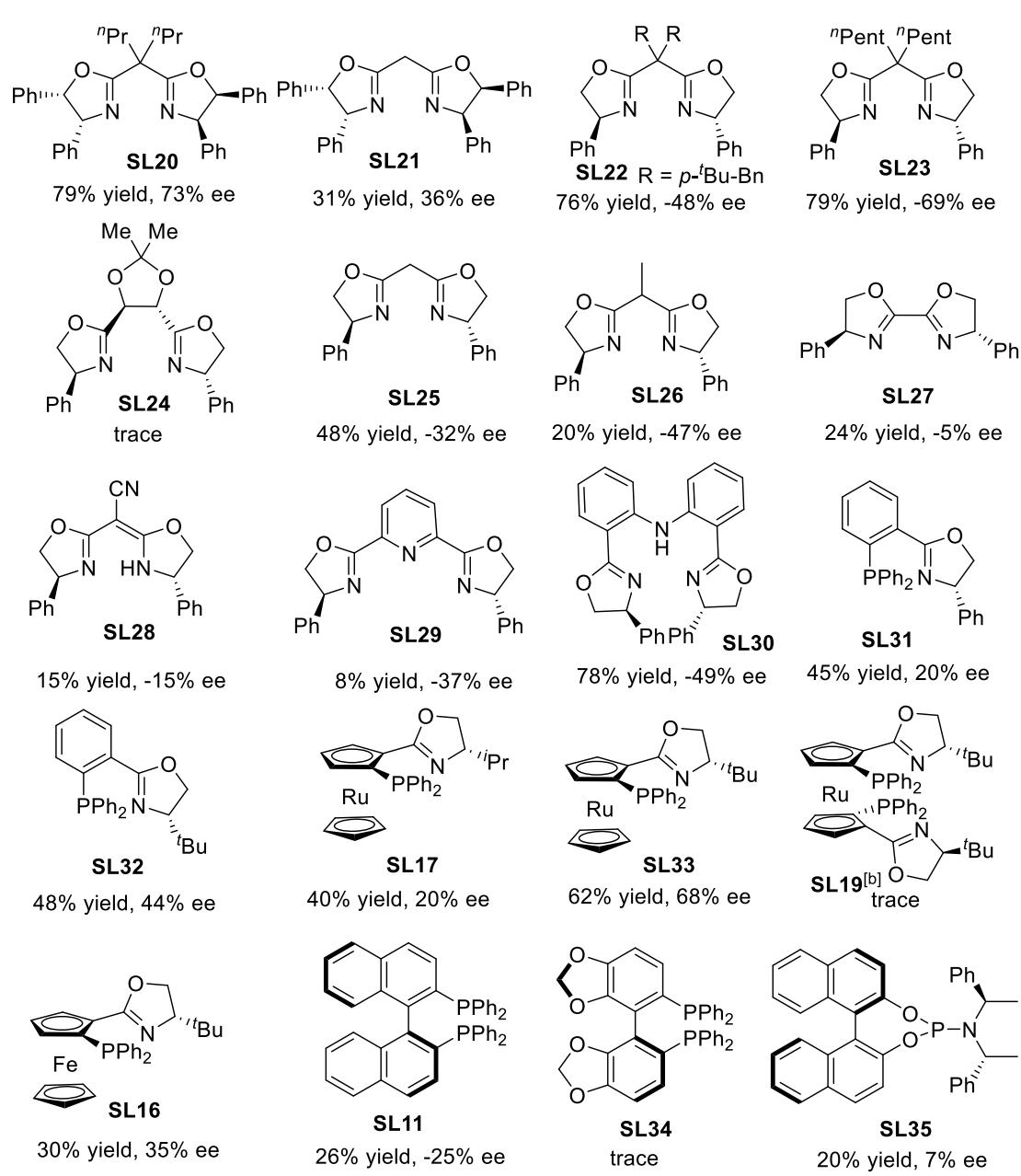
Table S4. Optimization of Metal Salt^[a]

Entry	Metal salt	Yield [%] ^[b]	ee [%] ^[c]
1	Co(OTf) ₂ ·2MeCN	44	64
2	Co(ClO₄)₂·6H₂O	83	73
3	Co(BF ₄) ₂ ·6H ₂ O	73	66
4	Co(acac) ₂	ND	--
5	Co(OAc) ₂	ND	--
6	CoBr ₂	60	20
7	Ni(ClO ₄) ₂ ·6H ₂ O	ND	--
8	Cu(ClO ₄) ₂ ·6H ₂ O	ND	--
9	Ni(OTf) ₂	ND	--
10	Sc(OTf) ₃	ND	--
11	Yb(OTf) ₃	ND	--

[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2** (0.20 mmol, 2.0 equiv), toluene (1.5 mL), Metal salt (10 mol%), **BOX-6** (12 mol%), Boc₂O (0.50 mmol 5.0 equiv) [b] Isolated yields. [c] Enantioselectivity was determined by HPLC using a chiral column.

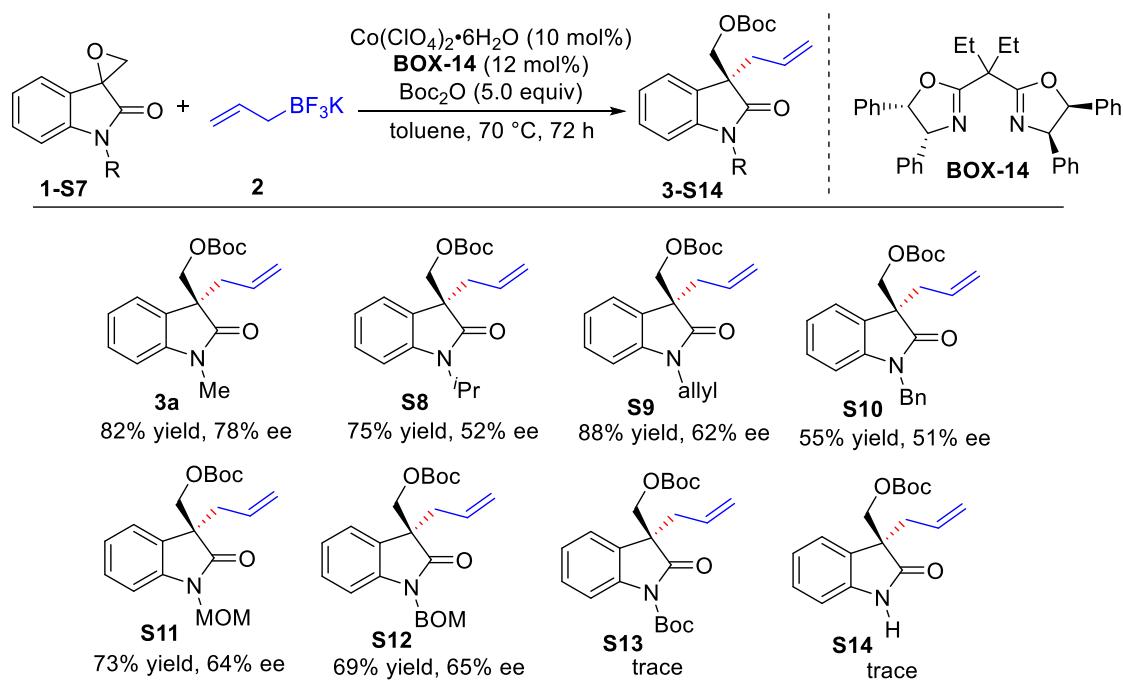
Scheme S2. Optimization of Chiral Ligands^[a]





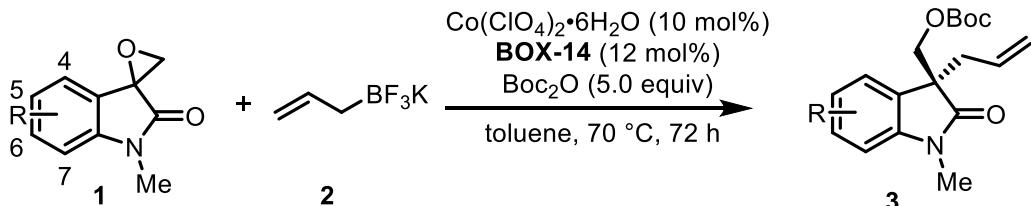
[a] Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2** (0.20 mmol, 2.0 equiv), toluene (1.5 mL), Co(ClO₄)₂·6H₂O (10 mol%), **L*** (12 mol%), Boc₂O (0.50 mmol, 5.0 equiv). Isolated yields. Enantioselectivity was determined by HPLC using a chiral column. [b] **L*** (6 mol%).

Scheme S3. Optimization of R Group^[a]

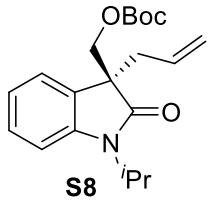


[a] Reaction conditions: **1-S7** (0.20 mmol, 1.0 equiv), **2** (0.40 mmol, 2.0 equiv), toluene (3.0 mL), $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mol%), **BOX-14** (12 mol%), Boc_2O (1.0 mmol, 5.0 equiv). Isolated yields. Enantioselectivity was determined by HPLC using a chiral column.

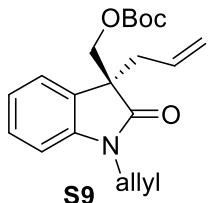
3.2 General Procedure for the Enantioselective Catalysis



To a dried Schlenk tube were added $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (7.4 mg, 0.020 mmol) and ligand **BOX-14** (12.4 mg, 0.024 mmol) under N_2 ; 3.0 mL of toluene was subsequently added using a syringe. The resulting mixture was stirred at room temperature for 30 min, after which the Spiro-Epoxyxidoles **1** (0.20 mmol) and Potassium Allyltrifluoroborate **2** (0.40 mmol) were added. The mixture was stirred at 70 °C for 72 hours, then it was cooled to room temperature, and the solvent was removed by rotary evaporation. The residue was purified by preparative TLC on silica gel (normal ratio: petroleum ether/ethyl acetate = 6/1) to give the product **3**. The ee was determined by chiral HPLC.

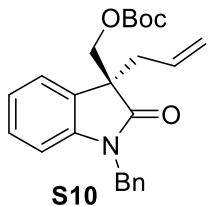


(S)-(3-Allyl-1-isopropyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (S8). 51.8 mg, 75% yield, colorless gummy oil; ^1H NMR (500 MHz, CDCl_3) δ 7.30 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.24 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.03 (td, $J = 7.5, 1.0$ Hz, 1H), 6.99 (d, $J = 7.5$ Hz, 1H), 5.39 – 5.31 (m, 1H), 5.03 – 4.99 (m, 1H), 4.92 – 4.89 (m, 1H), 4.62 (hept, $J = 7.0$ Hz, 1H), 4.43 (d, $J = 10.5$ Hz, 1H), 4.24 (d, $J = 11.0$ Hz, 1H), 2.63 – 2.55 (m, 2H), 1.46 (t, $J = 7.0$ Hz, 6H), 1.34 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.4, 153.1, 142.8, 131.2, 129.4, 128.1, 124.2, 121.8, 119.2, 109.7, 82.0, 69.4, 52.2, 43.9, 38.0, 27.6, 19.5, 19.3; HPLC [Daicel Chiraldapak AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.8 mL/min. $t_{R1} = 8.2$ min (major), $t_{R2} = 11.8$ min (minor)]; ee = 52%, $[\alpha]^{25}_{\text{D}} = -16.0$ ($c = 0.15$, CHCl_3); HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{28}\text{NO}_4$ ($\text{M}+\text{H}$) $^+$ 346.2013, found 346.2014.

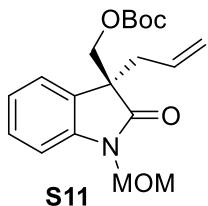


(S)-*tert*-Butyl ((1,3-diallyl-2-oxoindolin-3-yl)methyl) carbonate (S9). 60.4 mg, 88% yield, colorless gummy oil; ^1H NMR (500 MHz, CDCl_3) δ 7.30 (dd, $J = 7.5, 1.0$ Hz, 1H), 7.25 (td, $J = 8.0, 1.0$ Hz, 1H), 7.05 (td, $J = 7.5, 1.0$ Hz, 1H), 6.80 (d, $J = 7.5$ Hz, 1H), 5.84 – 5.77 (m, 1H), 5.46 – 5.38 (m, 1H), 5.23 – 5.19 (m, 1H), 5.18 – 5.15 (m, 1H), 5.06 – 5.02 (m, 1H), 4.96 – 4.93 (m, 1H), 4.51 (d, $J = 10.5$ Hz, 1H), 4.41 – 4.36 (m, 1H), 4.34 – 4.29 (m, 1H), 4.28 (d, $J = 10.5$ Hz, 1H), 2.65 – 2.57 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.6, 153.0, 143.2, 131.1, 131.0, 128.8, 128.3, 124.0, 122.3, 119.5, 117.1, 109.0, 82.1, 69.1, 52.7, 42.1, 37.9, 27.6; HPLC [Daicel Chiraldapak AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.8 mL/min. $t_{R1} = 10.3$ min (major), $t_{R2} = 14.6$ min (minor)]; ee = 62%, $[\alpha]^{25}_{\text{D}} = -16.0$ ($c = 0.15$, CHCl_3); $[\alpha]^{25}_{\text{D}} =$

-19.0 (c = 0.20, CHCl₃); HRMS (ESI) calcd for C₂₀H₂₆NO₄ (M+H)⁺ 344.1856, found 344.1857.

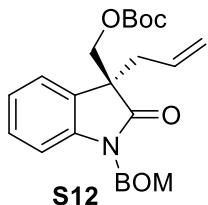


(S)-(3-Allyl-1-benzyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (S10). 43.3 mg, 55% yield, pale gummy ointment; ¹H NMR (500 MHz, CDCl₃) δ 7.31 – 7.21 (m, 6H), 7.14 (td, *J* = 8.0, 1.5 Hz, 1H), 7.02 (td, *J* = 7.5, 1.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.45 (ddt, *J* = 17.0, 10.0, 7.0 Hz, 1H), 5.07 (dd, *J* = 17.0, 2.0 Hz, 1H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.98 – 4.95 (m, 1H), 4.83 (d, *J* = 16.0 Hz, 1H), 4.56 (d, *J* = 10.5 Hz, 1H), 4.34 (d, *J* = 10.5 Hz, 1H), 2.69 – 2.61 (m, 2H), 1.34 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 177.0, 153.1, 143.2, 135.5, 131.2, 128.8, 128.7, 128.4, 127.4, 127.1, 124.0, 122.4, 119.6, 109.2, 82.2, 69.3, 52.7, 43.7, 38.0, 27.6; HPLC [Daicel Chiralpak AD-H, hexane/i-PrOH = 90/10, 254 nm, 0.8 mL/min. t_{R1} = 10.8 min (major), t_{R2} = 17.2 min (minor)]; ee = 51%, [α]²⁵_D = -10.0 (c = 1.00, CHCl₃); HRMS (ESI) calcd for C₂₄H₂₈NO₄ (M+H)⁺ 394.2013, found 394.2014.

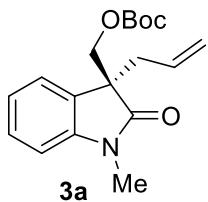


(S)-(3-Allyl-1-(methoxymethyl)-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (S11). 50.7 mg, 73% yield, colorless ointment; ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.27 (m, 2H), 7.10 (td, *J* = 8.0, 1.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 5.46 – 5.37 (m, 1H), 5.17 (d, *J* = 11.0 Hz, 1H), 5.11 (d, *J* = 11.0 Hz, 1H), 5.05 (dd, *J* = 17.0, 2.0 Hz, 1H), 4.97 – 4.94 (m, 1H), 4.52 (d, *J* = 10.5 Hz, 1H), 4.28 (d, *J* = 10.5 Hz, 1H), 3.30 (s, 3H), 2.66 – 2.57 (m, 2H), 1.31 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 177.5, 152.9, 142.3, 131.0, 128.6, 128.3, 124.0, 122.9, 119.7, 109.6, 82.2, 71.2, 69.1, 56.0, 53.2,

38.0, 27.6; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.8 mL/min. t_{R1} = 7.0 min (major), t_{R2} = 40.1 min (minor)]; ee = 64%, $[\alpha]^{25}_D$ = -39.9 (c = 0.10, CHCl₃); HRMS (ESI) calcd for C₁₉H₂₆NO₅ (M+H)⁺ 348.1805, found 348.1806.

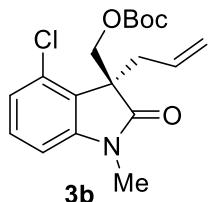


(S)-(3-Allyl-1-((benzyloxy)methyl)-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (S12). 58.4 mg, 69% yield, yellow ointment; ¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.26 (m, 7H), 7.14 – 7.09 (m, 2H), 5.47 – 5.38 (m, 1H), 5.30 (d, *J* = 11.5 Hz, 1H), 5.21 (d, *J* = 11.0 Hz, 1H), 5.07 (dd, *J* = 17.0, 2.0 Hz, 1H), 4.97 – 4.94 (m, 1H), 4.53 (d, *J* = 10.5 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.46 (d, *J* = 11.5 Hz, 1H), 4.30 (d, *J* = 10.5 Hz, 1H), 2.66 – 2.56 (m, 2H), 1.27 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 177.5, 153.0, 142.3, 137.3, 131.0, 128.6, 128.3, 128.2, 127.8, 127.1, 123.9, 123.0, 119.7, 109.8, 82.3, 70.1, 69.3, 69.1, 53.1, 38.0, 27.5; HPLC [Daicel Chiralpak OD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.8 mL/min. t_{R1} = 9.7 min (major), t_{R2} = 55.0 min (minor)]; ee = 65%, $[\alpha]^{25}_D$ = -21.3 (c = 0.21, CHCl₃); HRMS (ESI) calcd for C₂₅H₃₀NO₅ (M+H)⁺ 424.2118, found 424.2121.

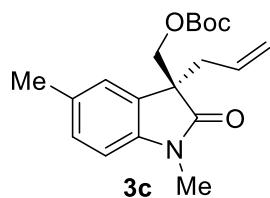


(S)-(3-Allyl-1-methyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (3a). 52.0 mg, 82% yield, colorless gummy oil; ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.26 (m, 2H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 6.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.40 (ddt, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.02 (dd, *J* = 16.8, 1.6 Hz, 1H), 4.95 – 4.92 (m, 1H), 4.48 (d, *J* = 10.4 Hz, 1H), 4.25 (d, *J* = 10.4 Hz, 1H), 3.21 (s, 3H), 2.66 – 2.54 (m, 2H), 1.35 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 176.7, 153.1, 144.0, 131.2, 128.9, 128.4, 124.0, 122.4,

119.4, 108.0, 82.2, 69.0, 52.5, 38.1, 27.6, 26.2; HPLC [Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. t_{R1} = 8.1 min (major), t_{R2} = 11.0 min (minor)]; ee = 78%, $[\alpha]^{25}_D$ = -22.6 (c = 0.31, CHCl₃); HRMS (ESI) calcd for C₁₈H₂₄NO₄ (M+H)⁺ 318.1700, found 318.1702.

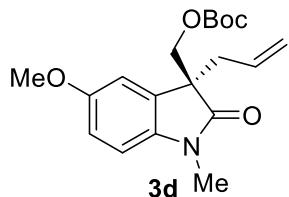


(S)-(3-Allyl-4-chloro-1-methyl-2-oxoindolin-3-yl)methyl tert-butyl carbonate (3b). 52.1 mg, 74% yield, white solid, Mp = 65~67 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.23 (t, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.73 (dd, *J* = 7.6, 0.8 Hz, 1H), 5.25 (ddt, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.07 – 5.00 (m, 1H), 4.87 – 4.83 (m, 1H), 4.84 (d, *J* = 10.4 Hz, 1H), 4.37 (d, *J* = 10.4 Hz, 1H), 3.20 (s, 3H), 2.94 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.61 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.32 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 176.4, 152.8, 146.2, 131.0, 130.5, 129.7, 124.8, 123.5, 119.3, 106.5, 82.2, 67.2, 54.6, 34.9, 27.6, 26.5; HPLC [Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. t_{R1} = 8.1 min (major), t_{R2} = 14.7 min (minor)]; ee = 57%, $[\alpha]^{25}_D$ = -11.0 (c = 0.50, CHCl₃); HRMS (ESI) calcd for C₁₈H₂₃ClNO₄ (M+H)⁺ 352.1310, found 352.1311.

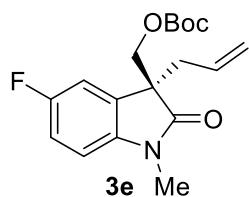


(S)-(3-Allyl-1,5-dimethyl-2-oxoindolin-3-yl)methyl tert-butyl carbonate (3c). 53.7 mg, 81% yield, colorless gummy oil; ¹H NMR (400 MHz, CDCl₃) δ 7.11 – 7.07 (m, 2H), 6.72 (d, *J* = 7.6 Hz, 1H), 5.40 (ddt, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.03 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.93 (dd, *J* = 10.0, 1.6 Hz, 1H), 4.46 (d, *J* = 10.4 Hz, 1H), 4.26 (d, *J* = 10.4 Hz, 1H), 3.18 (s, 3H), 2.63 – 2.53 (m, 2H), 2.34 (s, 3H), 1.35 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 176.7, 153.1, 141.6, 131.8, 131.3, 128.9, 128.6, 124.8, 119.3,

107.7, 82.2, 69.0, 52.6, 38.1, 27.6, 26.3, 21.2; HPLC [Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. t_{R1} = 7.2 min (major), t_{R2} = 9.8 min (minor)]; ee = 72%, $[\alpha]^{25}_D$ = -12.0 (c = 0.19, CHCl₃); HRMS (ESI) calcd for C₁₉H₂₅NNaO₄ (M+Na)⁺ 354.1676, found 354.1677.

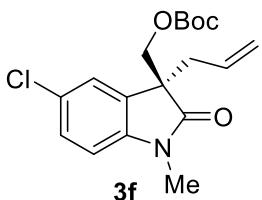


(S)-(3-Allyl-5-methoxy-1-methyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (3d). 59.1 mg, 85% yield, colorless gummy oil; ¹H NMR (500 MHz, CDCl₃) δ 6.92 (d, *J* = 2.5 Hz, 1H), 6.81 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 5.41 (ddt, *J* = 17.5, 10.0, 7.5 Hz, 1H), 5.03 (dd, *J* = 17.0, 2.0 Hz, 1H), 4.95 – 4.93 (m, 1H), 4.44 (d, *J* = 10.5 Hz, 1H), 4.25 (d, *J* = 11.0 Hz, 1H), 3.80 (s, 3H), 3.18 (s, 3H), 2.63 – 2.54 (m, 2H), 1.36 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 176.4, 155.9, 153.1, 137.5, 131.2, 130.3, 119.4, 112.6, 111.6, 108.3, 82.3, 69.0, 55.8, 52.9, 38.2, 27.6, 26.3; [Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. t_{R1} = 10.8 min (major), t_{R2} = 14.9 min (minor)]; ee = 72%, $[\alpha]^{25}_D$ = -8.99 (c = 0.12, CHCl₃); HRMS (ESI) calcd for C₁₉H₂₆NO₅ (M+H)⁺ 348.1805 found 348.1807.

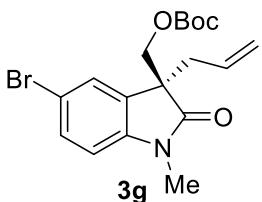


(S)-(3-Allyl-5-fluoro-1-methyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (3e). 48.3 mg, 72% yield, colorless gummy oil; ¹H NMR (500 MHz, CDCl₃) δ 7.06 (dd, *J* = 7.5, 2.5 Hz, 1H), 6.99 (td, *J* = 8.5, 2.5 Hz, 1H), 6.75 (dd, *J* = 8.5, 4.0 Hz, 1H), 5.39 (ddt, *J* = 17.0, 10.0, 7.0 Hz, 1H), 5.03 (dd, *J* = 17.5, 2.0 Hz, 1H), 4.97 – 4.94 (m, 1H), 4.45 (d, *J* = 10.5 Hz, 1H), 4.25 (d, *J* = 10.5 Hz, 1H), 3.20 (s, 3H), 2.64 – 2.55 (m, 2H), 1.37 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 176.4, 159.2 (d, *J* = 239.1 Hz), 153.0, 139.9 (d, *J* = 2.1 Hz), 130.8, 130.6 (d, *J* = 8.4 Hz), 119.8, 114.6 (d, *J* = 23.2 Hz),

112.3 (d, $J = 24.9$ Hz), 108.4 (d, $J = 8.2$ Hz), 82.5, 68.7, 53.1 (d, $J = 2.0$ Hz), 38.1, 27.6, 26.4; ^{19}F NMR (470 MHz, CDCl_3) δ -120.80; [Daicel Chiraldak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. $t_{\text{R}1} = 9.0$ min (major), $t_{\text{R}2} = 12.3$ min (minor)]; ee = 67%, $[\alpha]^{25}_{\text{D}} = -15.7$ ($c = 0.14$, CHCl_3); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{22}\text{FNNaO}_4$ ($\text{M}+\text{Na}$) $^+$ 358.1425, found 358.1427.

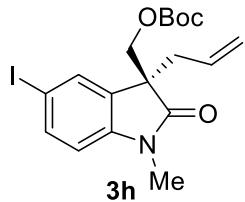


(S)-(3-Allyl-5-chloro-1-methyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (3f). 49.2 mg, 70% yield, white ointment; ^1H NMR (500 MHz, CDCl_3) δ 7.28 – 7.26 (m, 2H), 6.76 (d, $J = 9.0$ Hz, 1H), 5.39 (ddt, $J = 17.5, 10.0, 7.5$ Hz, 1H), 5.04 (dd, $J = 17.0, 1.5$ Hz, 1H), 4.97 – 4.95 (m, 1H), 4.45 (d, $J = 11.0$ Hz, 1H), 4.26 (d, $J = 10.5$ Hz, 1H), 3.19 (s, 3H), 2.63 – 2.55 (m, 2H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.3, 153.0, 142.6, 130.7, 128.4, 127.8, 124.5, 119.9, 109.0, 82.5, 68.6, 52.9, 38.1, 27.6, 26.4; [Daicel Chiraldak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. $t_{\text{R}1} = 8.9$ min (major), $t_{\text{R}2} = 11.1$ min (minor)]; ee = 60%, $[\alpha]^{25}_{\text{D}} = -5.06$ ($c = 0.75$, CHCl_3); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{23}\text{ClNO}_4$ ($\text{M}+\text{H}$) $^+$ 352.1310, found 352.1311.



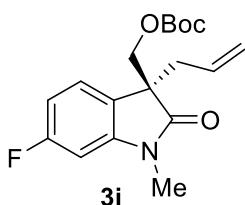
(S)-(3-Allyl-5-bromo-1-methyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (3g). 50.7 mg, 64% yield, pale yellow ointment; ^1H NMR (500 MHz, CDCl_3) δ 7.43 – 7.39 (m, 2H), 6.71 (d, $J = 8.0$ Hz, 1H), 5.39 (ddt, $J = 17.0, 10.0, 7.0$ Hz, 1H), 5.04 (dd, $J = 17.0, 2.0$ Hz, 1H), 4.98 – 4.95 (m, 1H), 4.45 (d, $J = 11.0$ Hz, 1H), 4.26 (d, $J = 10.5$ Hz, 1H), 3.19 (s, 3H), 2.63 – 2.52 (m, 2H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.2, 153.0, 143.1, 131.3, 131.0, 130.6, 127.2, 119.9, 115.1, 109.5, 82.6, 68.6, 52.9,

38.1, 27.6, 26.4; [Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. t_{R1} = 9.2 min (major), t_{R2} = 11.4 min (minor)]; ee = 68%, $[\alpha]^{25}_D$ = -2.84 (c = 0.38, CHCl₃); HRMS (ESI) calcd for C₁₈H₂₃BrNO₄ (M+H)⁺ 396.0805, found 396.0805.



(S)-(3-Allyl-5-iodo-1-methyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (3h).

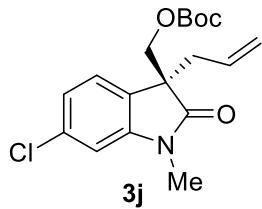
58.5 mg, 66% yield, pale yellow ointment; ¹H NMR (500 MHz, CDCl₃) δ 7.61 (dd, J = 8.0, 1.5 Hz, 1H), 7.56 (d, J = 2.0 Hz, 1H), 6.62 (d, J = 8.5 Hz, 1H), 5.38 (ddt, J = 17.5, 10.0, 7.5 Hz, 1H), 5.04 (dd, J = 17.0, 2.0 Hz, 1H), 4.97 – 4.95 (m, 1H), 4.43 (d, J = 11.0 Hz, 1H), 4.26 (d, J = 11.0 Hz, 1H), 3.18 (s, 3H), 2.61 – 2.52 (m, 2H), 1.38 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 176.0, 153.0, 143.8, 137.3, 132.7, 131.4, 130.6, 119.9, 110.1, 84.9, 82.6, 68.6, 52.7, 38.1, 27.7, 26.3; [Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. t_{R1} = 9.4 min (major), t_{R2} = 12.4 min (minor)]; ee = 73%, $[\alpha]^{25}_D$ = -1.20 (c = 0.50, CHCl₃); HRMS (ESI) calcd for C₁₈H₂₃INO₄ (M+H)⁺ 444.0666, found 444.0667.



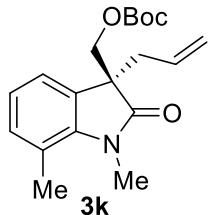
(S)-(3-Allyl-6-fluoro-1-methyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (3i).

50.3 mg, 75% yield, colorless gummy oil; ¹H NMR (500 MHz, CDCl₃) δ 7.22 (dd, J = 8.5, 5.5 Hz, 1H), 6.77 – 6.71 (m, 1H), 6.58 (dd, J = 8.5, 2.0 Hz, 1H), 5.38 (ddt, J = 17.0, 9.5, 7.5 Hz, 1H), 5.02 (dd, J = 17.5, 2.0 Hz, 1H), 4.96 – 4.93 (m, 1H), 4.47 (d, J = 10.5 Hz, 1H), 4.23 (d, J = 11.0 Hz, 1H), 3.19 (s, 3H), 2.62 – 2.53 (m, 2H), 1.36 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 177.1, 163.3 (d, J = 243.6 Hz), 153.0, 145.5 (d, J

δ = 11.4 Hz), 130.9, 125.1 (d, J = 9.8 Hz), 124.1 (d, J = 3.0 Hz), 119.7, 108.4 (d, J = 22.1 Hz), 96.9 (d, J = 27.5 Hz), 82.4, 68.8, 52.3, 38.1, 27.6, 26.4; ^{19}F NMR (470 MHz, CDCl_3) δ -111.92; [Daicel Chiraldak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. $t_{\text{R}1}$ = 8.3 min (major), $t_{\text{R}2}$ = 12.4 min (minor)]; ee = 77%, $[\alpha]^{25}_{\text{D}} = -17.5$ (c = 0.50, CHCl_3); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{23}\text{FNO}_4$ ($\text{M}+\text{H}$) $^+$ 336.1606, found 336.1606.

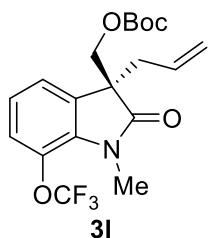


(S)-(3-Allyl-6-chloro-1-methyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (3j). 49.9 mg, 71% yield, colorless gummy oil; ^1H NMR (500 MHz, CDCl_3) δ 7.20 (d, J = 8.0 Hz, 1H), 7.04 (dd, J = 8.0, 2.0 Hz, 1H), 6.83 (d, J = 1.5 Hz, 1H), 5.38 (ddt, J = 17.0, 10.0, 7.0 Hz, 1H), 5.02 (dd, J = 17.0, 1.5 Hz, 1H), 4.96 – 4.94 (m, 1H), 4.46 (d, J = 10.5 Hz, 1H), 4.23 (d, J = 10.5 Hz, 1H), 3.19 (s, 3H), 2.62 – 2.53 (m, 2H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.7, 153.0, 145.2, 134.3, 130.7, 127.2, 125.0, 122.2, 119.8, 108.8, 82.4, 68.7, 52.4, 38.0, 27.6, 26.4; [Daicel Chiraldak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. $t_{\text{R}1}$ = 8.4 min (major), $t_{\text{R}2}$ = 11.5 min (minor)]; ee = 67%, $[\alpha]^{25}_{\text{D}} = -17.0$ (c = 0.50, CHCl_3); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{23}\text{ClNO}_4$ ($\text{M}+\text{H}$) $^+$ 352.1310, found 352.1311.

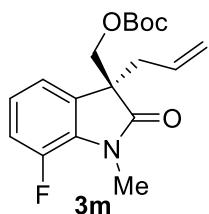


(S)-(3-Allyl-1,7-dimethyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (3k). 57.0 mg, 86% yield, colorless gummy oil; ^1H NMR (500 MHz, CDCl_3) δ 7.11 (d, J = 7.0 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 5.39 (ddt, J = 17.5, 10.0, 7.5 Hz, 1H), 5.02 (dd, J = 17.0, 1.5 Hz, 1H), 4.95 – 4.92 (m, 1H), 4.42 (d, J = 11.0 Hz,

1H), 4.24 (d, $J = 10.5$ Hz, 1H), 3.48 (s, 3H), 2.58 (d, $J = 7.0$ Hz, 2H), 2.57 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 177.4, 153.1, 141.7, 132.2, 131.3, 129.5, 122.3, 121.8, 119.6, 119.3, 82.2, 69.3, 51.8, 38.4, 29.6, 27.6, 19.1; [Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. $t_{\text{R}1} = 7.8$ min (major), $t_{\text{R}2} = 11.3$ min (minor)]; ee = 73%, $[\alpha]^{25}_{\text{D}} = -22.2$ ($c = 0.50$, CHCl_3); HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{26}\text{NO}_4$ ($\text{M}+\text{H})^+$ 332.1856, found 332.1857.

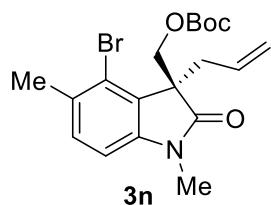


(S)-(3-Allyl-1-methyl-2-oxo-7-(trifluoromethoxy)indolin-3-yl)methyl *tert*-butyl carbonate (3l). 52.2 mg, 65% yield, white ointment; ^1H NMR (500 MHz, CDCl_3) δ 7.20 – 7.16 (m, 2H), 6.82 (d, $J = 8.5$ Hz, 1H), 5.43 – 5.34 (m, 1H), 5.02 (d, $J = 17.0$ Hz, 1H), 4.96 (d, $J = 10.0$ Hz, 1H), 4.48 (d, $J = 11.0$ Hz, 1H), 4.26 (d, $J = 11.0$ Hz, 1H), 3.21 (s, 3H), 2.65 – 2.55 (m, 2H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.5, 152.9, 144.6 (q, $J = 2.1$ Hz), 142.6, 130.5, 130.4, 121.6, 120.6 (q, $J = 255.2$ Hz), 120.0, 118.3, 108.4, 82.6, 68.5, 53.0, 38.1, 27.5, 26.4; ^{19}F NMR (470 MHz, CDCl_3) δ -58.40; [Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.8 mL/min. $t_{\text{R}1} = 8.7$ min (major), $t_{\text{R}2} = 9.9$ min (minor)]; ee = 63%, $[\alpha]^{25}_{\text{D}} = -13.0$ ($c = 0.50$, CHCl_3); HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{23}\text{F}_3\text{NO}_5$ ($\text{M}+\text{H})^+$ 402.1523, found 402.1523.

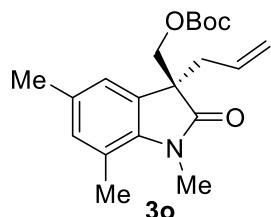


(S)-(3-Allyl-7-fluoro-1-methyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (3m). 49.6 mg, 74% yield, pale yellow ointment; ^1H NMR (500 MHz, CDCl_3) δ 7.07 (dd, $J = 7.0, 2.0$ Hz, 1H), 7.04 – 6.96 (m, 2H), 5.38 (ddt, $J = 17.5, 10.0, 7.5$ Hz, 1H), 5.02

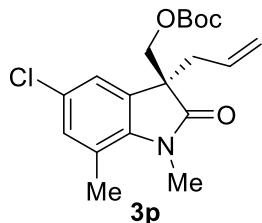
(dd, $J = 17.0, 1.5$ Hz, 1H), 4.97 – 4.95 (m, 1H), 4.46 (d, $J = 10.5$ Hz, 1H), 4.26 (d, $J = 11.0$ Hz, 1H), 3.42 (d, $J = 3.0$ Hz, 3H), 2.58 (d, $J = 7.5$ Hz, 2H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.4, 153.0, 147.7 (d, $J = 241.9$ Hz), 131.8 (d, $J = 3.1$ Hz), 130.7, 130.6 (d, $J = 8.1$ Hz), 122.9 (d, $J = 6.2$ Hz), 119.8 (d, $J = 3.2$ Hz), 119.7, 116.4 (d, $J = 19.1$ Hz), 82.4, 68.9, 53.0 (d, $J = 1.9$ Hz), 38.3, 28.7 (d, $J = 5.6$ Hz), 27.6; ^{19}F NMR (470 MHz, CDCl_3) δ -136.64; [Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. $t_{\text{R}1} = 6.7$ min (major), $t_{\text{R}2} = 9.7$ min (minor)]; ee = 66%, $[\alpha]^{25}_{\text{D}} = -15.6$ ($c = 0.50$, CHCl_3); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{23}\text{FNO}_4$ ($\text{M}+\text{H}$) $^+$ 336.1606, found 336.1606.



(S)-(3-Allyl-4-bromo-1,5-dimethyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (3n). 57.4 mg, 70% yield, white solid, Mp = 75~77 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.17 (d, $J = 7.5$ Hz, 1H), 6.68 (d, $J = 7.5$ Hz, 1H), 5.23 (ddt, $J = 17.0, 10.0, 7.0$ Hz, 1H), 5.04 (dd, $J = 17.0, 2.0$ Hz, 1H), 4.97 (d, $J = 10.5$ Hz, 1H), 4.84 (dd, $J = 10.0, 2.0$ Hz, 1H), 4.33 (d, $J = 10.5$ Hz, 1H), 3.18 (s, 3H), 3.08 (dd, $J = 13.5, 7.0$ Hz, 1H), 2.55 (dd, $J = 13.5, 7.5$ Hz, 1H), 2.38 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.4, 152.8, 144.2, 132.0, 130.7, 130.3, 126.7, 122.0, 119.1, 106.8, 82.2, 67.0, 55.7, 34.6, 27.6, 26.4, 22.4; [Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. $t_{\text{R}1} = 8.4$ min (major), $t_{\text{R}2} = 14.7$ min (minor)]; ee = 63%, $[\alpha]^{25}_{\text{D}} = -14.4$ ($c = 0.50$, CHCl_3); HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{25}\text{BrNO}_4$ ($\text{M}+\text{H}$) $^+$ 410.0961, found 410.0962.



(S)-(3-Allyl-1,5,7-trimethyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (3o). 62.2 mg, 90% yield, pale yellow ointment; ^1H NMR (500 MHz, CDCl_3) δ 6.92 (s, 1H), 6.81 (s, 1H), 5.39 (ddt, $J = 17.0, 10.0, 7.5$ Hz, 1H), 5.02 (d, $J = 17.0$ Hz, 1H), 4.94 (d, $J = 10.0$ Hz, 1H), 4.40 (d, $J = 11.0$ Hz, 1H), 4.24 (d, $J = 10.5$ Hz, 1H), 3.45 (s, 3H), 2.56 (d, $J = 7.0$ Hz, 2H), 2.52 (s, 3H), 2.28 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 177.4, 153.1, 139.3, 132.6, 131.6, 131.4, 129.6, 122.4, 119.2, 119.1, 82.2, 69.3, 51.9, 38.4, 29.6, 27.6, 20.8, 18.9; [Daicel Chiraldak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. $t_{\text{R}1} = 6.9$ min (major), $t_{\text{R}2} = 9.9$ min (minor)]; ee = 68%, $[\alpha]^{25}_{\text{D}} = -15.7$ ($c = 0.50$, CHCl_3); HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{28}\text{NO}_4$ ($\text{M}+\text{H}$) $^+$ 346.2013, found 346.2014.

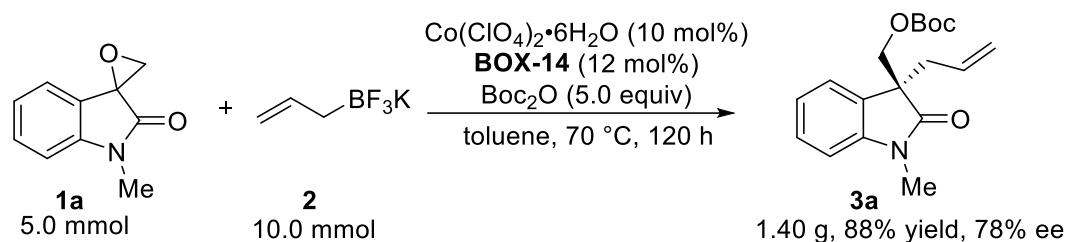


(S)-(3-Allyl-5-chloro-1,7-dimethyl-2-oxoindolin-3-yl)methyl *tert*-butyl carbonate (3p). 49.7 mg, 68% yield, pale yellow ointment; ^1H NMR (500 MHz, CDCl_3) δ 7.09 (d, $J = 2.0$ Hz, 1H), 7.02 – 7.00 (m, 1H), 5.37 (ddt, $J = 17.5, 10.0, 7.5$ Hz, 1H), 5.03 (dd, $J = 17.5, 2.0$ Hz, 1H), 4.97 – 4.95 (m, 1H), 4.38 (d, $J = 11.0$ Hz, 1H), 4.25 (d, $J = 11.0$ Hz, 1H), 3.46 (s, 3H), 2.56 (d, $J = 7.0$ Hz, 2H), 2.54 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 177.0, 153.0, 140.4, 131.7, 131.3, 130.8, 127.4, 122.0, 121.1, 119.7, 82.5, 68.9, 52.2, 38.4, 29.6, 27.6, 18.9; [Daicel Chiraldak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. $t_{\text{R}1} = 8.0$ min (major), $t_{\text{R}2} = 11.0$ min (minor)]; ee = 77%, $[\alpha]^{25}_{\text{D}} = -12.5$ ($c = 0.40$, CHCl_3); HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{25}\text{ClNO}_4$ ($\text{M}+\text{H}$) $^+$ 366.1467, found 366.1467.

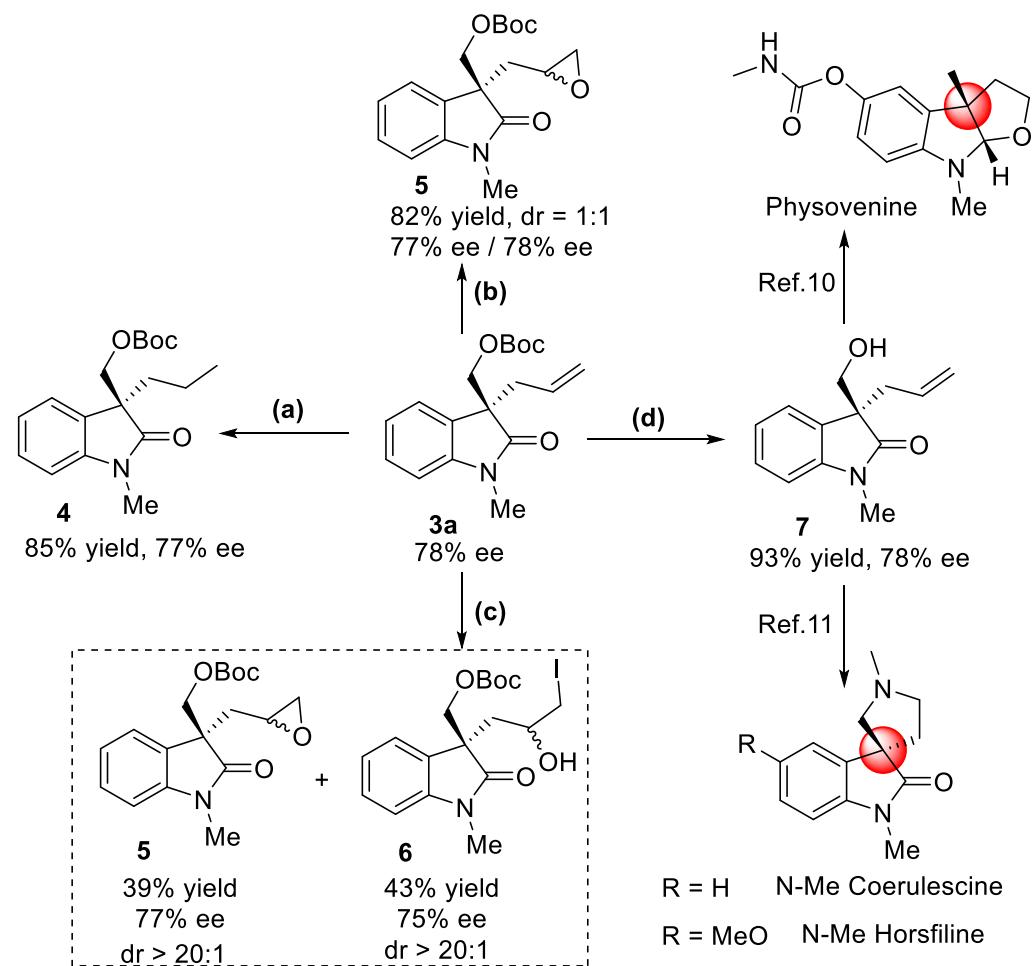
4. Transformations

To confirm the scalability of the present protocol, the scaleup reaction of spiro-epoxyoxindole **1a** with potassium allyltrifluoroborate **2** was carried out, and product **3a** was readily isolated in 88% yield and 78% ee (Scheme S4).

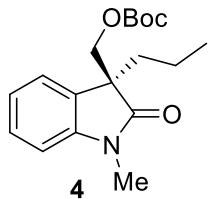
Scheme S4. Scale-Up Reaction of **1a** with **2**



Scheme S5. Transformations of **3a**

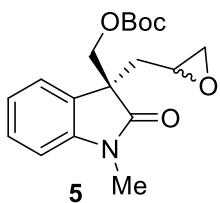


(a) To a solution of **3a** (31.7 mg, 0.10 mmol, 1.0 equiv) in MeOH (3.0 mL), 10% Pd/C (20.0 mg) was added in one portion under nitrogen atmosphere. Then the vial was charged with 1 atm. of H₂ three times (balloon) and the reaction mixture was stirred at room temperature overnight. Then the reaction mixture was filtered through a plug of silica gel. The solvent was removed under vacuum and the residue was purified by preparative TLC on silica gel (petroleum ether/ethyl acetate = 5/1) to give the product **4** as a colorless gummy oil (27.1 mg, 85% yield).⁶



(S)-tert-Butyl ((1-methyl-2-oxo-3-propylindolin-3-yl)methyl) carbonate (4). Colorless gummy oil; ¹H NMR (500 MHz, CDCl₃) δ 7.29 (td, *J* = 7.5, 1.5 Hz, 1H), 7.25 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.44 (d, *J* = 11.0 Hz, 1H), 4.22 (d, *J* = 10.5 Hz, 1H), 3.22 (s, 3H), 1.91 – 1.77 (m, 2H), 1.34 (s, 9H), 1.08 – 0.98 (m, 1H), 0.91 – 0.82 (m, 1H), 0.78 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 177.4, 153.1, 144.2, 129.5, 128.3, 123.6, 122.4, 108.0, 82.1, 69.6, 53.0, 35.9, 27.6, 26.2, 17.1, 14.1; [Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. t_{R1} = 7.4 min (major), t_{R2} = 14.5 min (minor)]; ee = 77%, [α]²⁵_D = -7.56 (c = 0.28, CHCl₃); HRMS (ESI) calcd for C₁₈H₂₆NO₄ (M+H)⁺ 320.1856, found 320.1858.

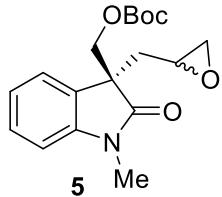
(b) To a solution of **3a** (31.7 mg, 0.10 mmol, 1.0 equiv) in CH₂Cl₂ (2.0 mL) was added *m*-CPBA (75%, 46.0 mg, 0.20 mmol, 2.0 equiv.) at 0 °C. The reaction mixture was then stirred at room temperature overnight. Then treated with saturated aqueous Na₂SO₃. The phases were separated and removed under vacuum and the residue was purified by preparative TLC on silica gel (petroleum ether/ethyl acetate = 4/1) to give the product **5** (27.4 mg, 82% yield) as a pale yellow ointment.⁷



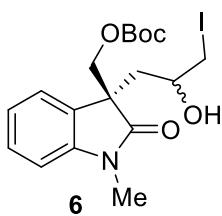
tert-Butyl (((3*S*)-1-methyl-3-(oxiran-2-ylmethyl)-2-oxoindolin-3-yl)methyl) carbonate (5). Diastereomers can be separated by preparative TLC on silica gel. ^1H NMR analysis of the crude mixture showed a dr of 1:1. First diastereoisomers (**5-1**): pale yellow ointment; ^1H NMR (500 MHz, CDCl_3) δ 7.36 (dd, $J = 7.0, 1.0$ Hz, 1H), 7.33 (td, $J = 7.5, 1.0$ Hz, 1H), 7.10 (td, $J = 7.5, 1.0$ Hz, 1H), 6.88 (d, $J = 8.0$ Hz, 1H), 4.50 (d, $J = 10.5$ Hz, 1H), 4.22 (d, $J = 11.0$ Hz, 1H), 3.25 (s, 3H), 2.64 – 2.60 (m, 1H), 2.58 – 2.56 (m, 1H), 2.44 (dd, $J = 5.0, 2.5$ Hz, 1H), 2.22 (dd, $J = 14.0, 5.5$ Hz, 1H), 2.01 (dd, $J = 14.0, 6.0$ Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.6, 153.0, 143.7, 128.8, 128.6, 124.3, 122.7, 108.3, 82.4, 69.0, 51.4, 48.0, 46.5, 36.6, 27.6, 26.4; [Daicel Chiraldak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. $t_{R1} = 14.0$ min (major), $t_{R2} = 17.7$ min (minor)]; ee = 77%, $[\alpha]^{25}_{\text{D}} = -12.0$ ($c = 0.20$, CHCl_3); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_5$ ($\text{M}+\text{H}$) $^+$ 334.1649, found 334.1650. Second diastereoisomers (**5-2**): pale yellow ointment; ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.30 (m, 2H), 7.08 (td, $J = 7.5, 1.0$ Hz, 1H), 6.88 (dd, $J = 8.0, 1.0$ Hz, 1H), 4.48 (d, $J = 11.0$ Hz, 1H), 4.26 (d, $J = 10.5$ Hz, 1H), 3.26 (s, 3H), 2.71 – 2.67 (m, 1H), 2.52 (dd, $J = 5.0, 4.0$ Hz, 1H), 2.31 (dd, $J = 5.0, 2.5$ Hz, 1H), 2.17 (dd, $J = 14.0, 4.5$ Hz, 1H), 2.07 (dd, $J = 14.0, 7.5$ Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.6, 153.0, 144.0, 128.8, 128.7, 124.1, 122.5, 108.4, 82.4, 69.0, 51.1, 48.0, 46.8, 36.9, 27.6, 26.5; [Daicel Chiraldak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. $t_{R1} = 15.6$ min (major), $t_{R2} = 33.1$ min (minor)]; ee = 78%, $[\alpha]^{25}_{\text{D}} = -20.5$ ($c = 0.15$, CHCl_3); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_5$ ($\text{M}+\text{H}$) $^+$ 334.1649, found 334.1651.

(c) To a solution of **3a** (63.4 mg, 0.20 mmol, 1.0 equiv) and NaHCO_3 (50.4 mg, 0.60 mmol, 3.0 equiv) in MeCN (4.0 mL) was added I_2 (153 mg, 0.60 mmol, 3.0 equiv) portionwise. The mixture was stirred at room temperature for 13 hours. Then treated with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$. The phases were separated and removed under

vacuum and the residue was purified by preparative TLC on silica gel (petroleum ether/ethyl acetate = 4/1) to give the product **5** (26.0 mg, 39% yield) a pale yellow ointment and **6** (39.7 mg, 43% yield) as a white ointment.⁸



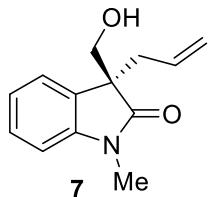
tert-Butyl (((3S)-1-methyl-3-(oxiran-2-ylmethyl)-2-oxoindolin-3-yl)methyl) carbonate (5). Pale yellow ointment, ¹H NMR analysis of the crude mixture showed a dr of >20:1. ¹H NMR (500 MHz, CDCl₃) δ 7.36 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.33 (td, *J* = 7.5, 1.0 Hz, 1H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.50 (d, *J* = 11.0 Hz, 1H), 4.22 (d, *J* = 11.0 Hz, 1H), 3.25 (s, 3H), 2.64 – 2.60 (m, 1H), 2.58 – 2.56 (m, 1H), 2.44 (dd, *J* = 5.0, 2.5 Hz, 1H), 2.22 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.01 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.36 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 176.6, 153.0, 143.7, 128.8, 128.7, 124.3, 122.7, 108.3, 82.4, 69.0, 51.4, 48.0, 46.5, 36.6, 27.6, 26.4; [Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. t_{R1} = 14.0 min (major), t_{R2} = 17.7 min (minor)]; ee = 77%, [α]²⁵_D = -11.2 (c = 0.25, CHCl₃); HRMS (ESI) calcd for C₁₈H₂₄NO₅ (M+H)⁺ 334.1649, found 334.1649.



tert-Butyl (((3S)-3-(2-hydroxy-3-iodopropyl)-1-methyl-2-oxoindolin-3-yl)methyl) carbonate (6). White ointment; ¹H NMR analysis of the crude mixture showed a dr of >20:1. ¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.31 (m, 2H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 6.88 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.57 (d, *J* = 10.5 Hz, 1H), 4.25 (d, *J* = 11.0 Hz, 1H), 3.81 – 3.74 (m, 1H), 3.50 (d, *J* = 3.5 Hz, 1H), 3.27 (dd, *J* = 10.5, 4.5 Hz, 1H), 3.25 (s, 3H), 3.19 (dd, *J* = 10.0, 5.0 Hz, 1H), 2.23 (dd, *J* = 15.0, 2.5 Hz, 1H), 1.99 (dd, *J* = 14.5, 9.5 Hz, 1H), 1.37 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 177.9, 152.9,

143.2, 129.8, 128.9, 124.1, 123.1, 108.6, 82.6, 68.6, 67.5, 51.2, 40.0, 27.6, 26.6, 14.8; [Daicel Chiraldak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. $t_{R1} = 25.1$ min (major), $t_{R2} = 48.2$ min (minor)]; ee = 75%, $[\alpha]^{25}_D = -17.5$ ($c = 0.40$, CHCl₃); HRMS (ESI) calcd for C₁₈H₂₅INO₅ (M+H)⁺ 462.0772, found 462.0774.

(d) **3a** (570 mg, 1.80 mmol) was dissolved in 36.0 mL of 6 M HCl in MeOH. The mixture was stirred overnight at room temperature. The reaction was quenched with saturated NaHCO₃ aqueous solution, and the mixture was extracted with EtOAc and dried over anhydrous Na₂SO₄. After filtration, the residue was purified by flash chromatography on silica gel, eluting with petroleum ether/ethyl acetate 2:1 (v/v), to afford the product **7** as a white ointment (362 mg, 93% yield).⁹



(S)-3-Allyl-3-(hydroxymethyl)-1-methylindolin-2-one (7). White ointment; ¹H NMR (500 MHz, CDCl₃) δ 7.31 (td, $J = 7.5, 1.0$ Hz, 1H), 7.23 (dd, $J = 7.5, 1.0$ Hz, 1H), 7.09 (td, $J = 7.5, 1.0$ Hz, 1H), 6.87 (d, $J = 8.0$ Hz, 1H), 5.45 (ddt, $J = 17.5, 10.0, 8.0$ Hz, 1H), 5.03 (dd, $J = 17.0, 1.5$ Hz, 1H), 4.96 – 4.92 (m, 1H), 3.90 (dd, $J = 11.0, 9.5$ Hz, 1H), 3.76 (dd, $J = 11.0, 3.0$ Hz, 1H), 3.21 (s, 3H), 2.71 – 2.60 (m, 2H), 2.45 – 2.39 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 178.9, 144.1, 131.8, 129.5, 128.4, 123.3, 122.6, 119.1, 108.2, 66.4, 54.1, 37.3, 26.2; [Daicel Chiraldak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min. $t_{R1} = 11.7$ min (minor), $t_{R2} = 12.8$ min (major)]; ee = 78%, $[\alpha]^{25}_D = -3.14$ ($c = 0.70$, CHCl₃); HRMS (ESI) calcd for C₁₃H₁₆NO₂ (M+H)⁺ 218.1176, found 218.1175.

5. References

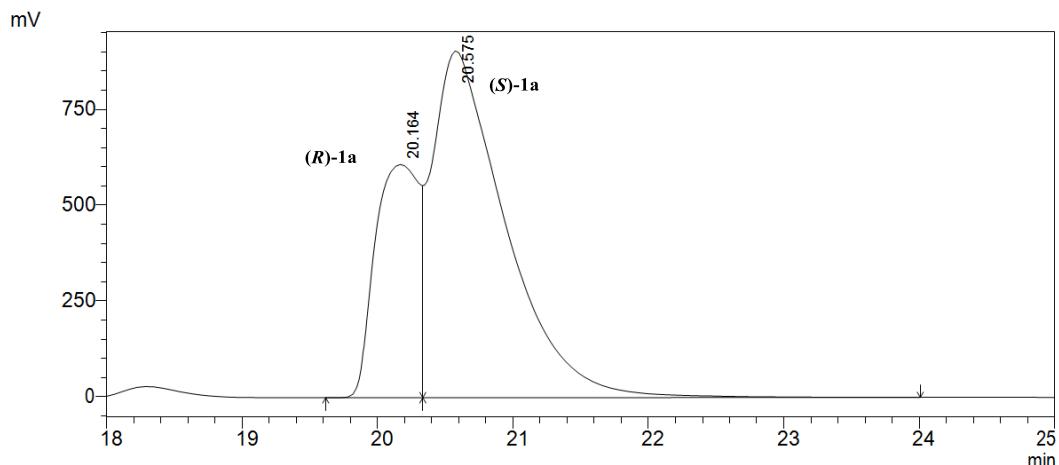
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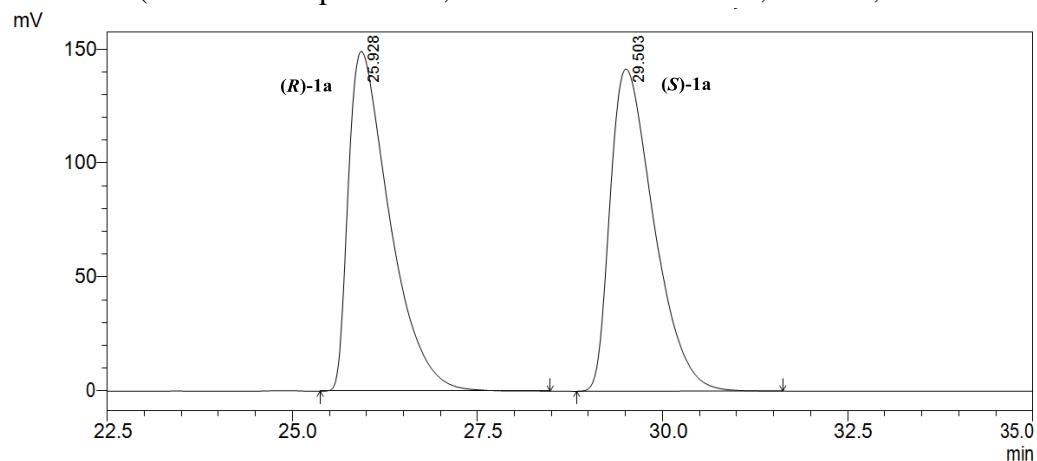
6. X-Ray Crystal Structure Data

The two enantionmers of **1a** were separated by preparative chiral HPLC (Preparative Daicel Chiralpak OD-H, hexane/*i*-PrOH = 92/8, 254 nm, 8.0 mL/min. $t_{R1} = 37.1$ min (*R*), $t_{R2} = 42.2$ min (*S*)). The first (t_{R1}) enantiomer was used in the stereochemical course experiment shown in Scheme 3b. Colorless crystal of **enantiopure 1a** suitable for X-ray crystallographic analysis were obtained by recrystallization from ethyl acetate/petroleum ether. The ORTEP drawing of (*R*)-**1a** is shown in Figure S1. The crystal structure has been deposited at the Cambridge Crystallographic Centre (deposition number: CCDC 1965672). The two enantionmers of **1a** could not be separated well by the Daicel Chiralpak OD-H column, but could be separated well by the Daicel Chiralpak OJ-H column.

1a HPLC (Daicel Chiralpak OD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.8 mL/min.)



1a HPLC (Daicel Chiralpak OJ-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min.)



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.928	5791739	149254	49.966	51.340
2	29.503	5799733	141464	50.034	48.660
Total		11591472	290719	100.000	100.000

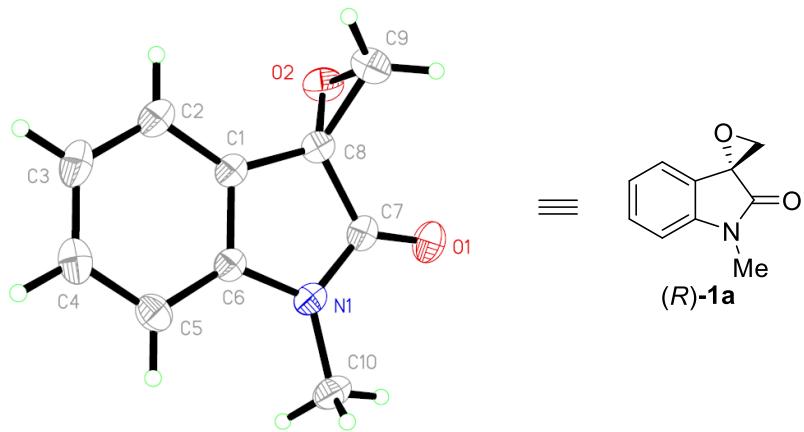


Figure S1 (R)-1a

Table S5. Crystal data and structure refinement for a_a.

Identification code	a_a
Empirical formula	C10 H9 N O2
Formula weight	175.18
Temperature	296(2) K
Wavelength	1.54178 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 4.5388(9) Å alpha = 90 deg. b = 13.550(3) Å beta = 90 deg. c = 14.103(3) Å gamma = 90 deg.
Volume	867.4(3) Å^3
Z, Calculated density	4, 1.341 Mg/m^3
Absorption coefficient	0.777 mm^-1
F(000)	368
Crystal size	0.200 x 0.180 x 0.160 mm
Theta range for data collection	4.525 to 68.206 deg.
Limiting indices	-5<=h<=5, -16<=k<=16, -14<=l<=16
Reflections collected / unique	8405 / 1578 [R(int) = 0.0490]
Completeness to theta = 67.679	99.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1578 / 0 / 119
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0892
R indices (all data)	R1 = 0.0399, wR2 = 0.0911
Absolute structure parameter	0.03(9)
Extinction coefficient	n/a
Largest diff. peak and hole	0.094 and -0.098 e.Å^-3

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) a_a

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No syntax errors found. [CIF dictionary](#) [Interpreting this report](#)

Datablock: a_a

Bond precision: C-C = 0.0031 Å Wavelength=1.54178

Cell: a=4.5388 (9) b=13.550 (3) c=14.103 (3)
alpha=90 beta=90 gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	867.4 (3)	867.4 (3)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C10 H9 N O2	C10 H9 N O2
Sum formula	C10 H9 N O2	C10 H9 N O2
Mr	175.18	175.18
Dx, g cm-3	1.342	1.341
Z	4	4
Mu (mm-1)	0.777	0.777
F000	368.0	368.0
F000'	369.18	
h,k,lmax	5,16,16	5,16,16
Nref	1594 [968]	1578
Tmin, Tmax	0.856, 0.883	0.636, 0.753
Tmin'	0.856	

Correction method= # Reported T Limits: Tmin=0.636 Tmax=0.753
AbsCorr = ?

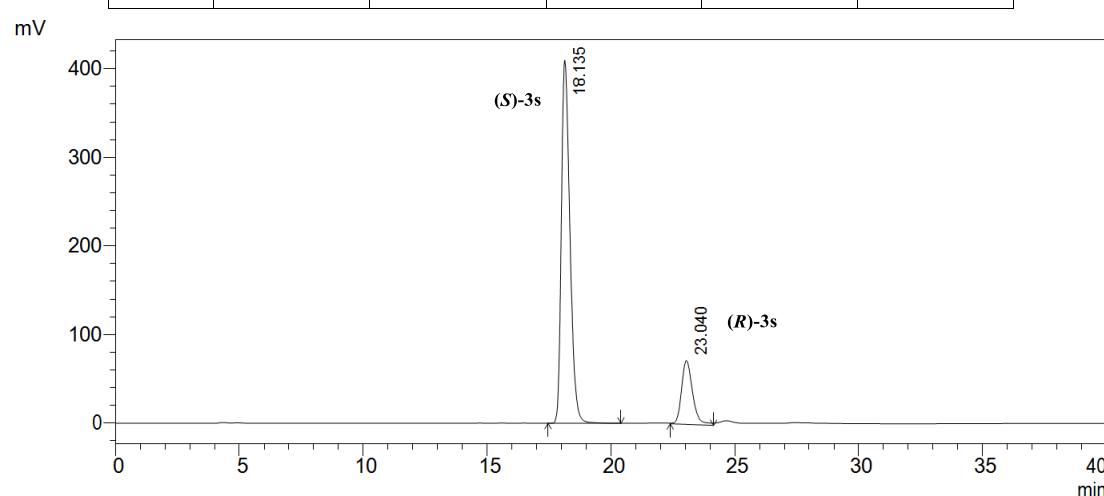
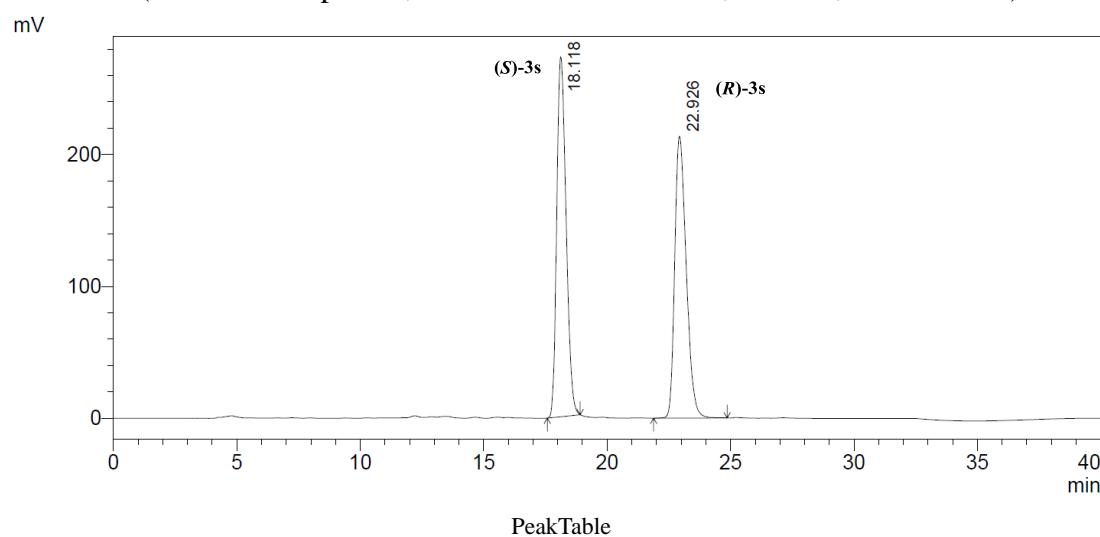
Data completeness= 1.63/0.99 Theta(max) = 68.206

R(reflections) = 0.0307(1396) wR2(reflections) = 0.0911(1578)

S = 1.039 Npar= 119

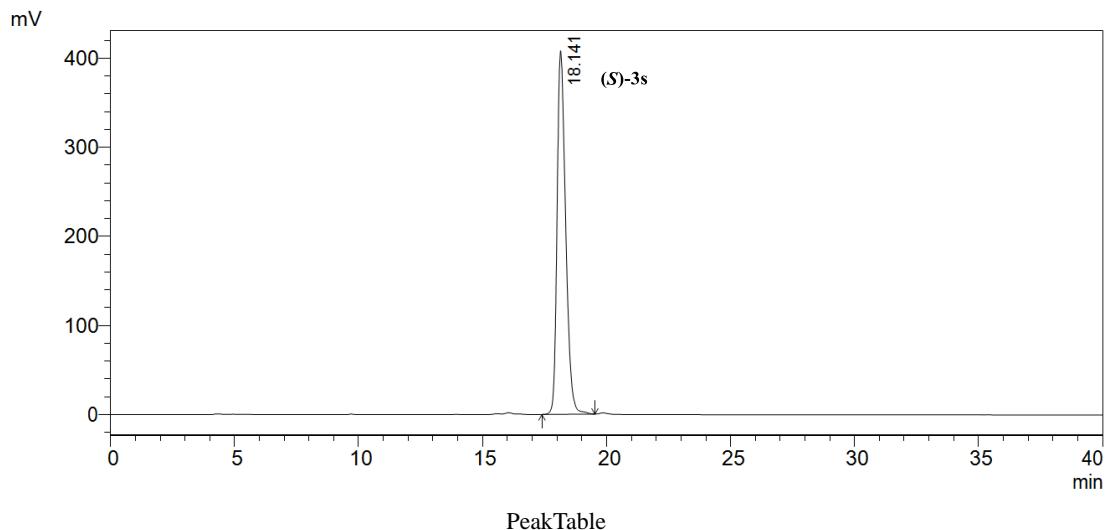
The two enantiomers of **3n** were separated by preparative chiral HPLC (Preparative Daicel Chiralpak IE, hexane/*i*-PrOH = 92/8, 254 nm, 8.0 mL/min. t_{R1} = 32.5 min (major), t_{R2} = 42.7 min (minor)). Colorless crystal of major enantiopure **3n** suitable for X-ray crystallographic analysis were obtained by recrystallization from *n*-hexane. The ORTEP drawing of (*S*)-**3n** is shown in Figure S2. The crystal structure has been deposited at the Cambridge Crystallographic Centre (deposition number: CCDC 1956332).

3n HPLC (Daicel Chiralpak IE, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min.)



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.135	9857243	409689	81.519	85.026
2	23.040	2234760	72151	18.481	14.974
Total		12092003	481840	100.000	100.000



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
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Total		9843571	407740	100.000	100.000

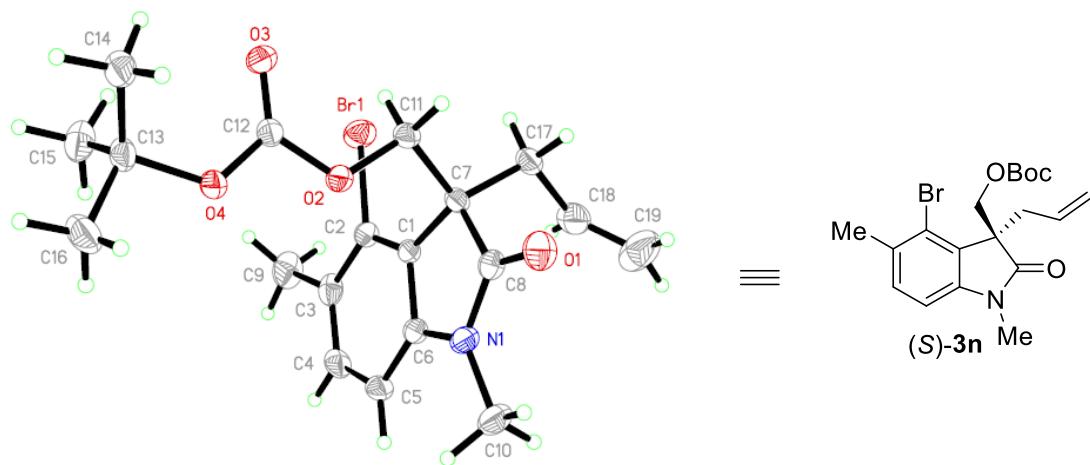


Figure S2 (S)-3s

Table S6. Crystal data and structure refinement for t_a.

Identification code	t_a
Empirical formula	C19 H24 Br N O4
Formula weight	410.30
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 9.4837(7) Å alpha = 90 deg. b = 21.349(2) Å beta = 95.070(7) deg. c = 9.5572(10) Å gamma = 90 deg.
Volume	1927.5(3) Å^3
Z, Calculated density	4, 1.414 Mg/m^3
Absorption coefficient	3.095 mm^-1
F(000)	848
Crystal size	0.200 x 0.200 x 0.200 mm
Theta range for data collection	4.645 to 68.181 deg.
Limiting indices	-11<=h<=11, -25<=k<=25, -11<=l<=11
Reflections collected / unique	18309 / 6958 [R(int) = 0.0226]
Completeness to theta = 67.679	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6958 / 1 / 461
Goodness-of-fit on F^2	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0208, wR2 = 0.0530
R indices (all data)	R1 = 0.0212, wR2 = 0.0534
Absolute structure parameter	0.017(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.292 and -0.280 e.Å^-3

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) t_a

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No syntax errors found. [CIF dictionary](#) [Interpreting this report](#)

Datablock: t_a

Bond precision: C-C = 0.0039 Å Wavelength=1.54178

Cell: a=9.4837 (7) b=21.349 (2) c=9.5572 (10)
alpha=90 beta=95.070 (7) gamma=90
Temperature: 173 K

	Calculated	Reported
Volume	1927.5 (3)	1927.5 (3)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C19 H24 Br N O4	?
Sum formula	C19 H24 Br N O4	C19 H24 Br N O4
Mr	410.29	410.30
Dx, g cm-3	1.414	1.414
Z	4	4
Mu (mm-1)	3.095	3.095
F000	848.0	848.0
F000'	847.48	
h,k,lmax	11,25,11	11,25,11
Nref	7065 [3636]	6958
Tmin, Tmax	0.565, 0.538	0.541, 0.753
Tmin'	0.513	

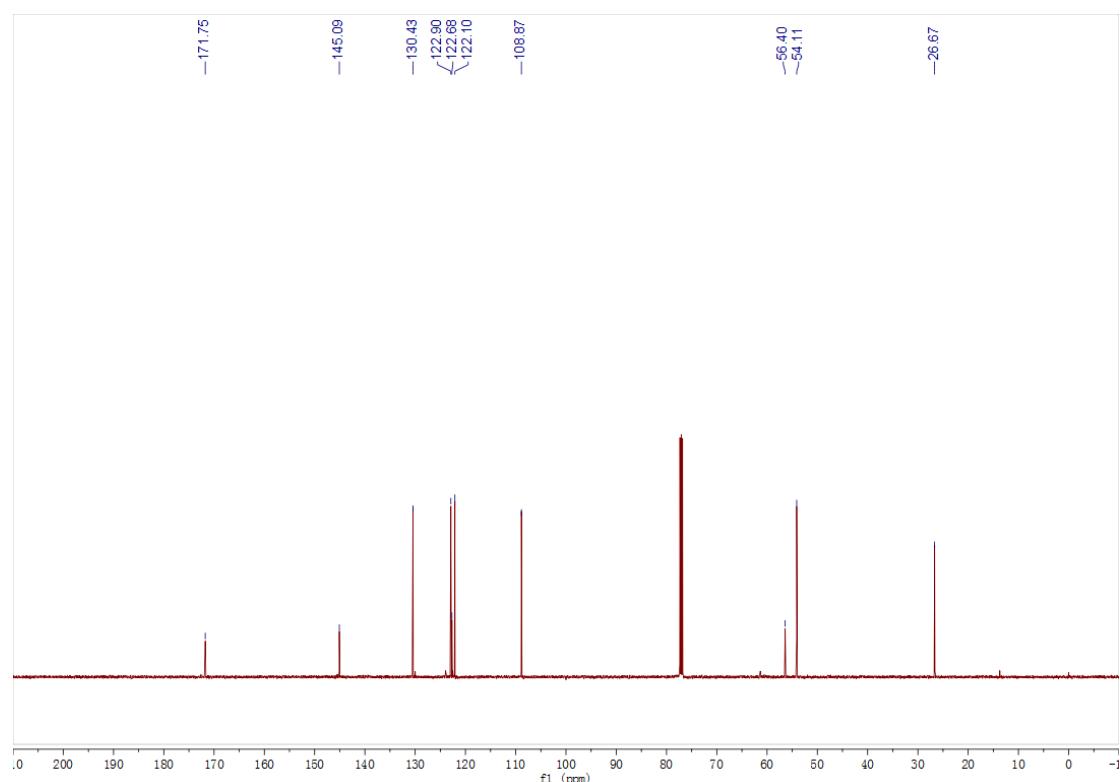
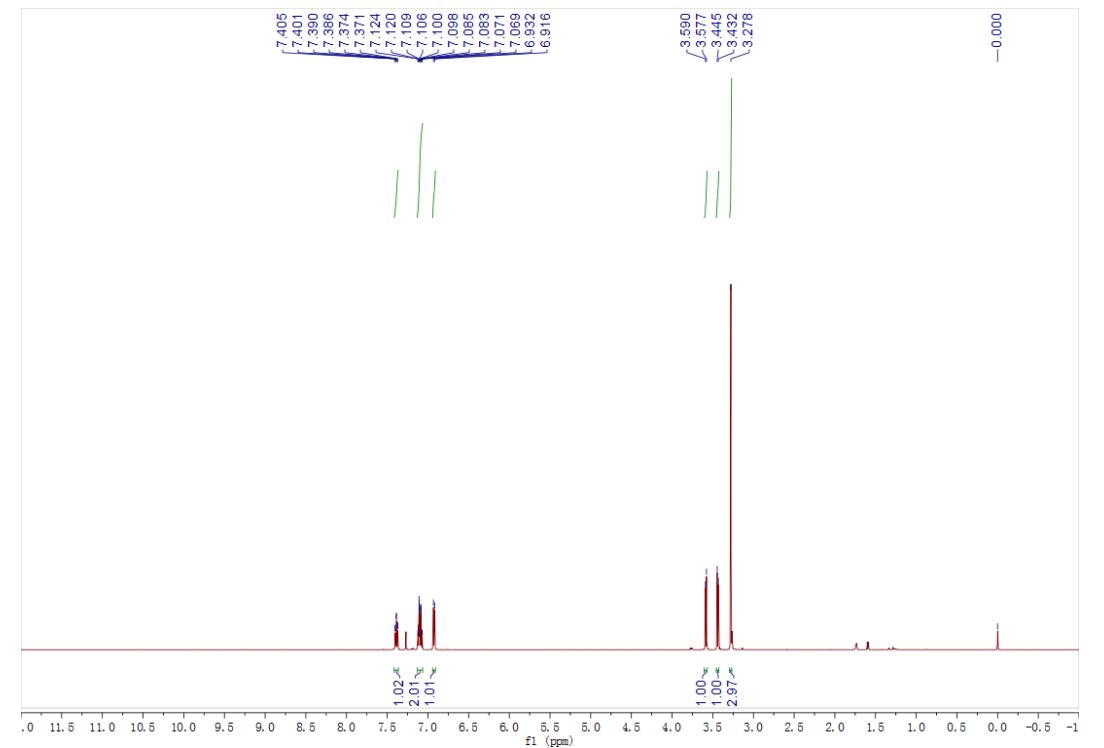
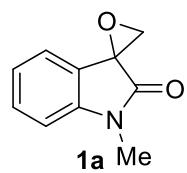
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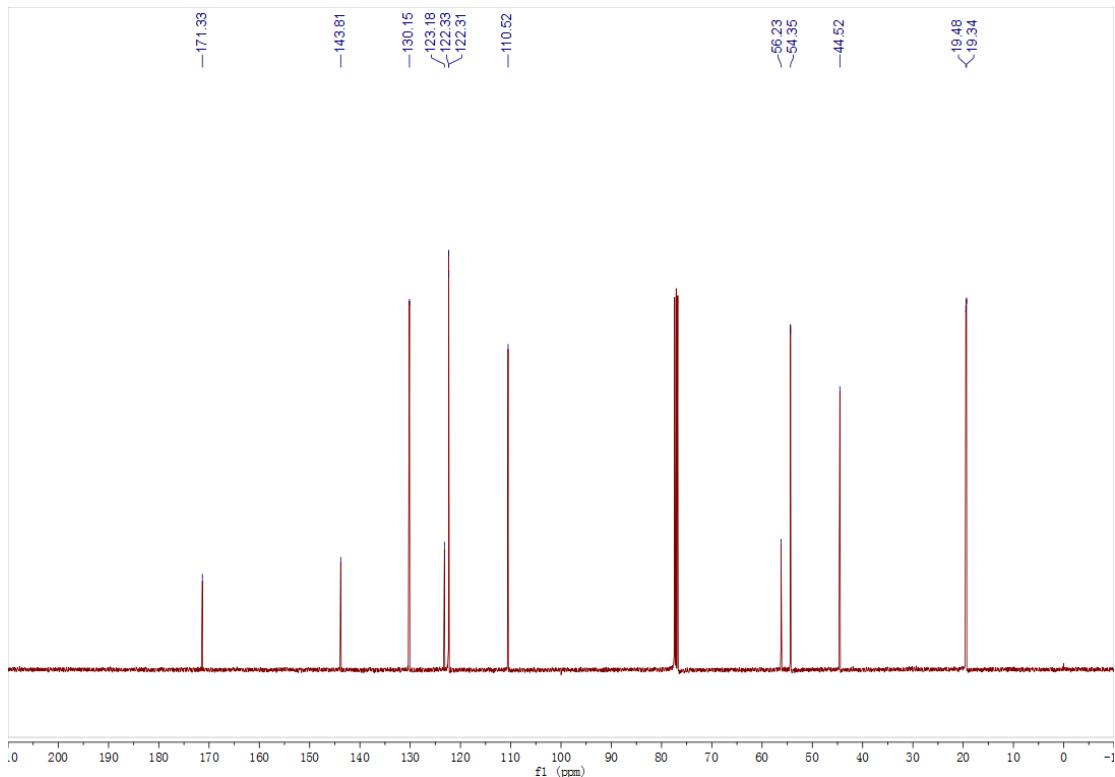
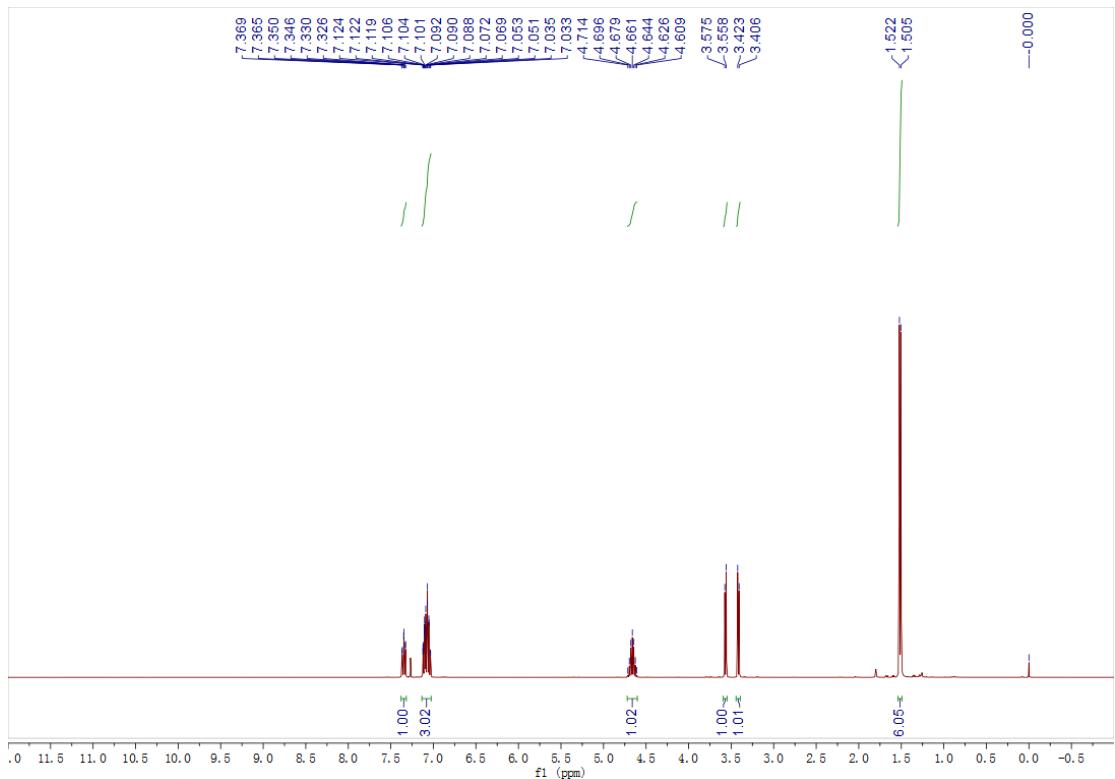
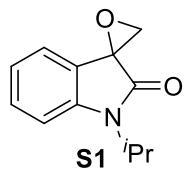
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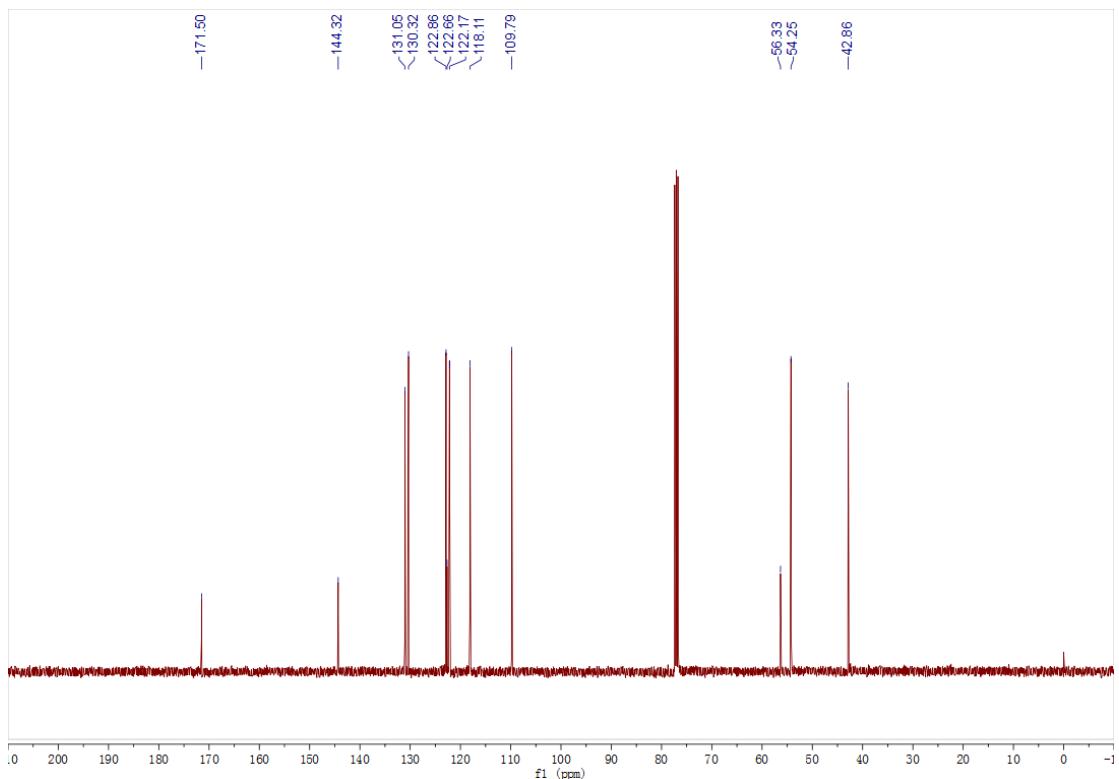
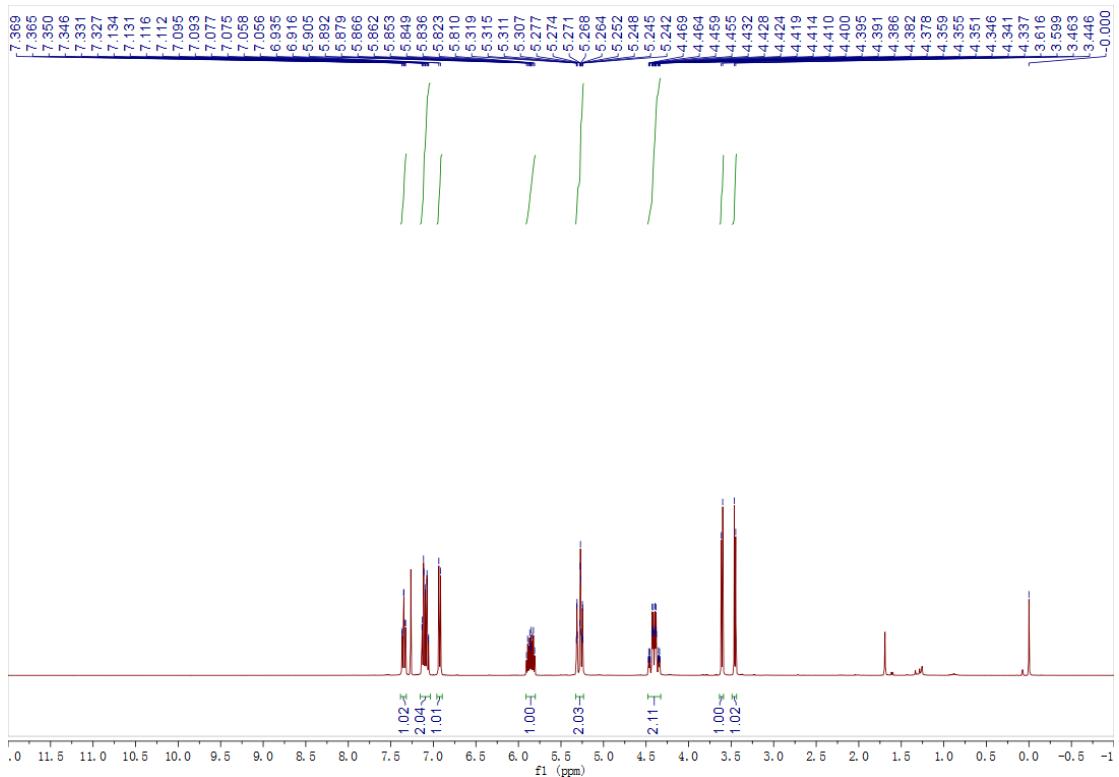
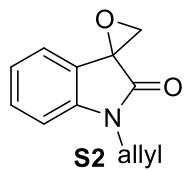
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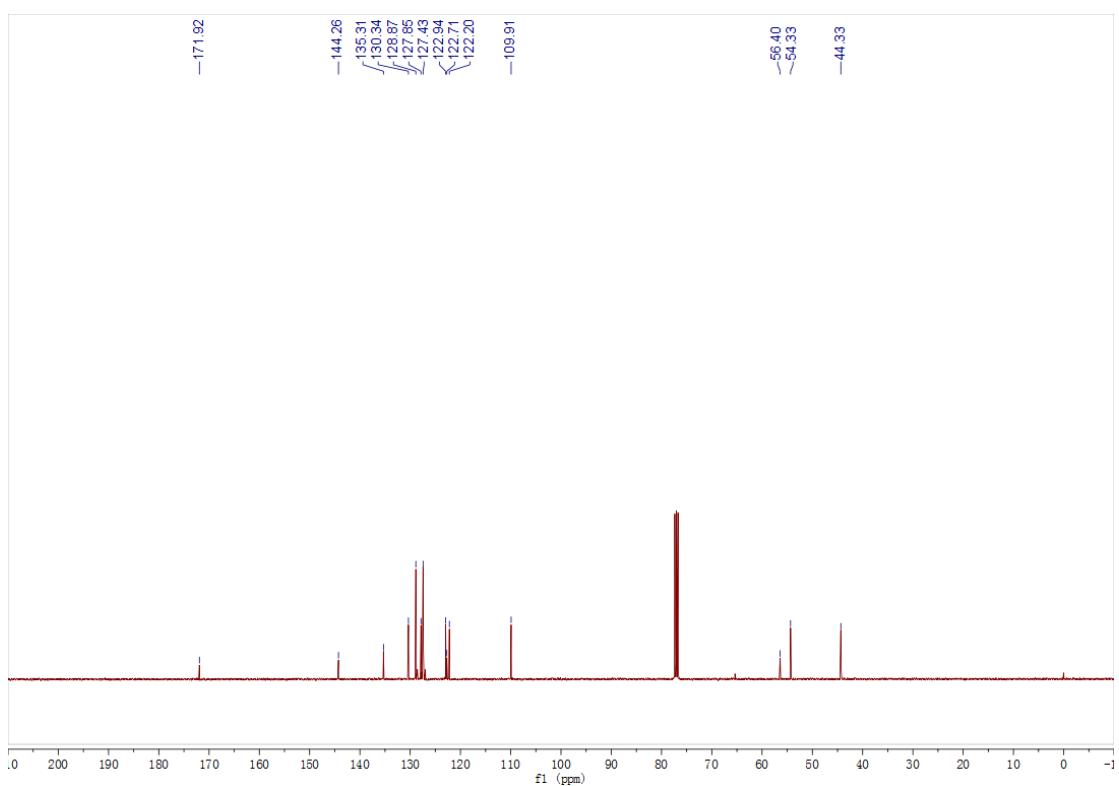
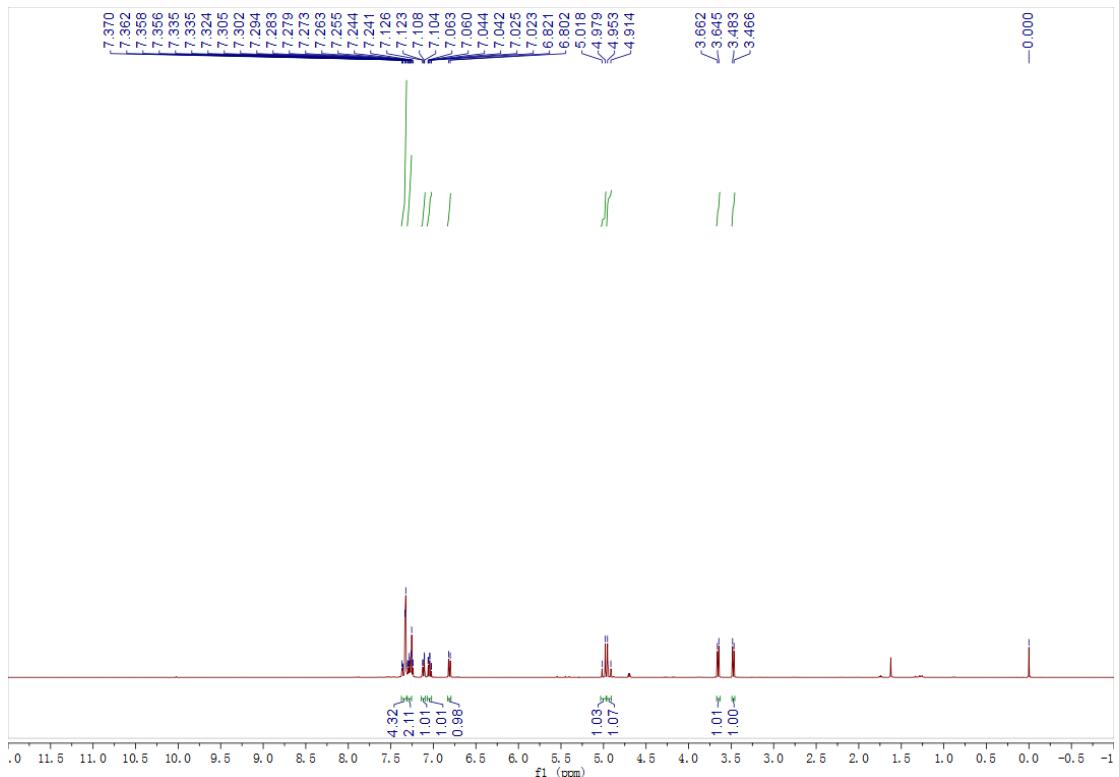
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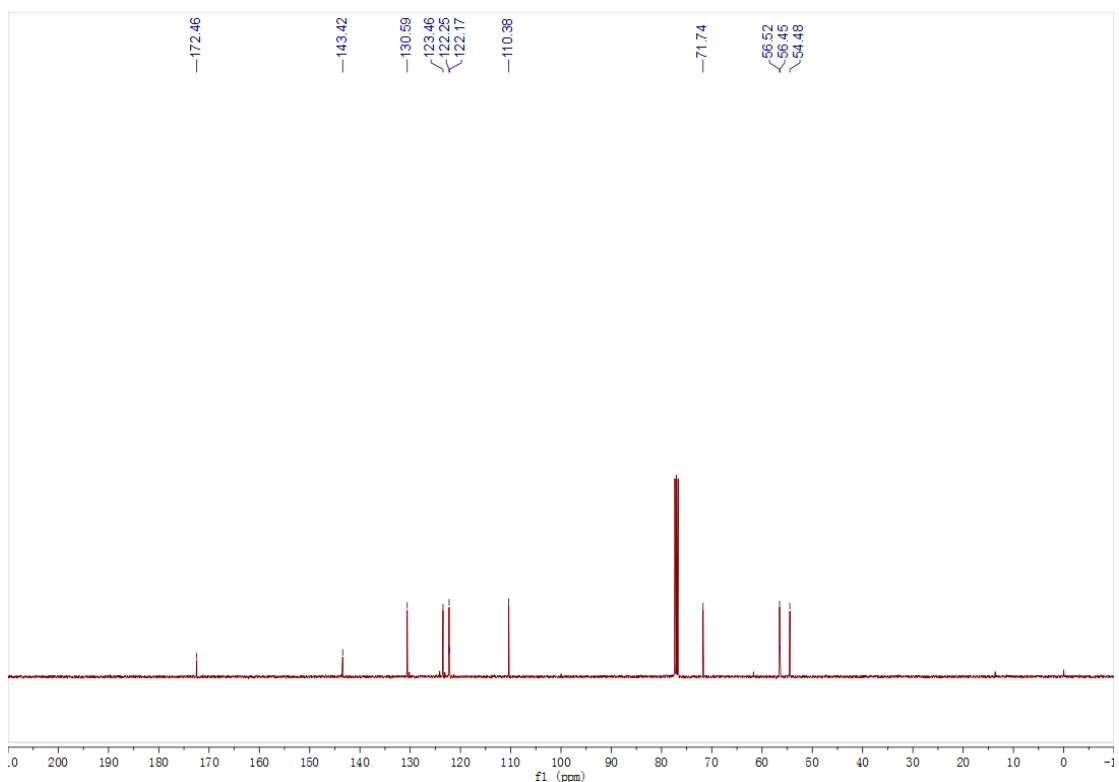
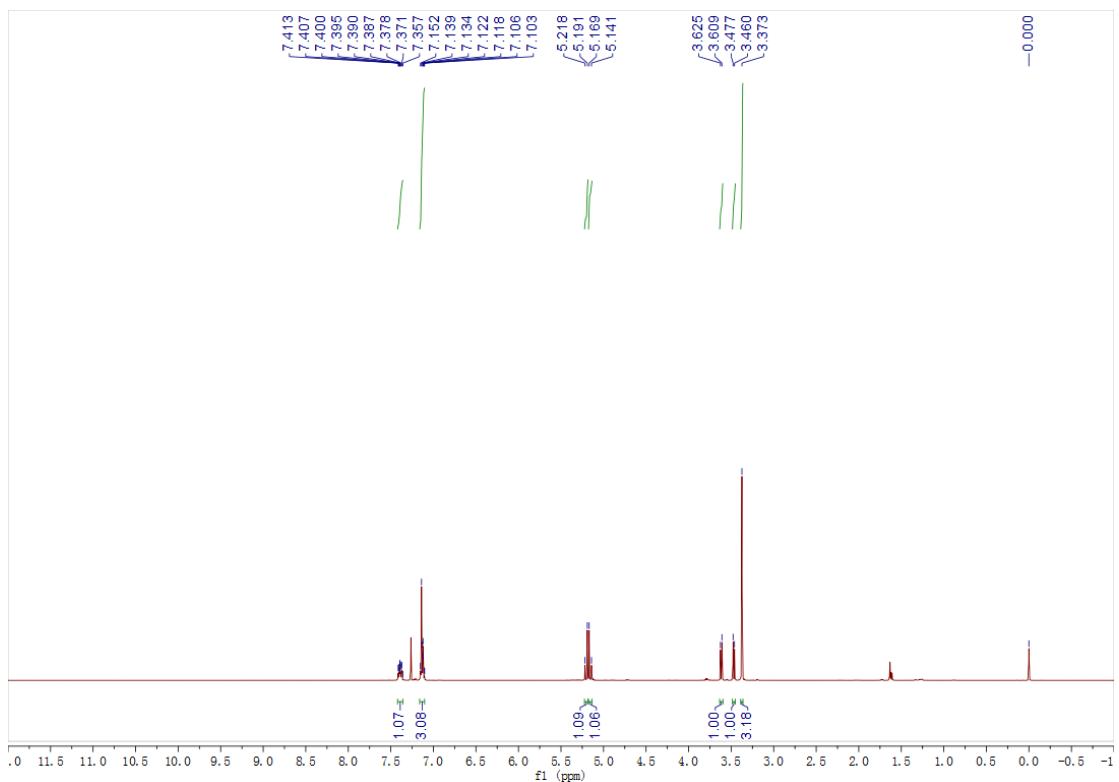
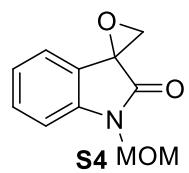
7. Spectra of New Products and HPLC Charts

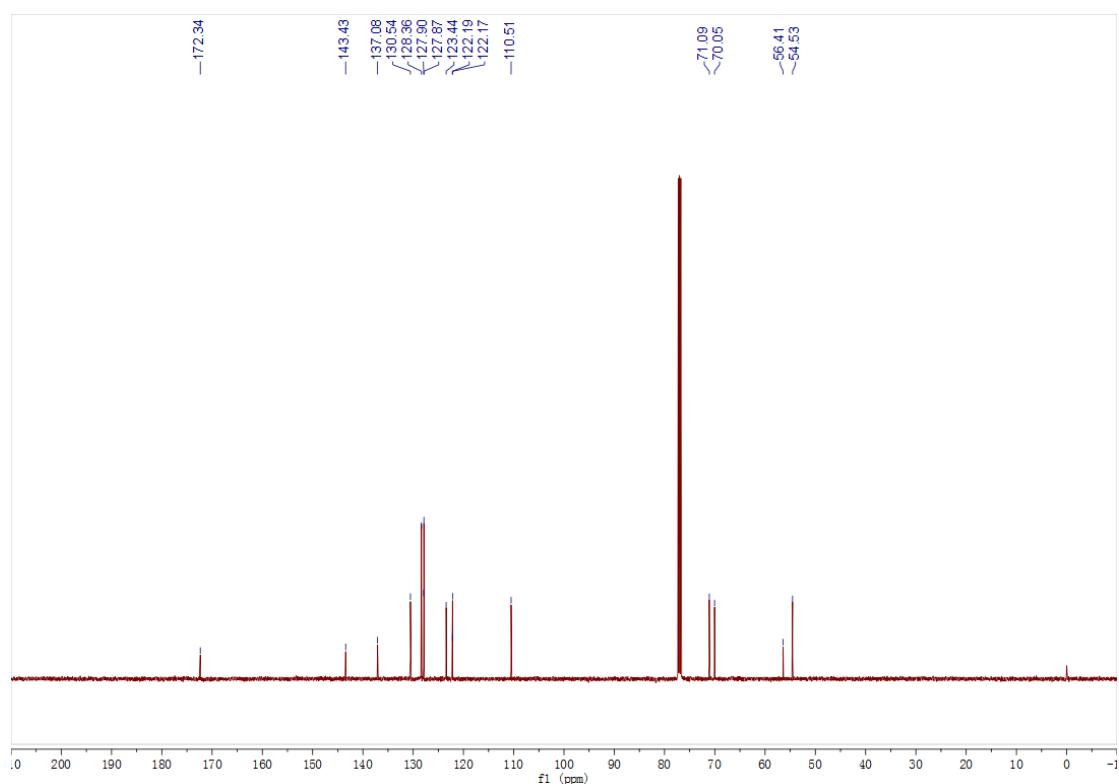
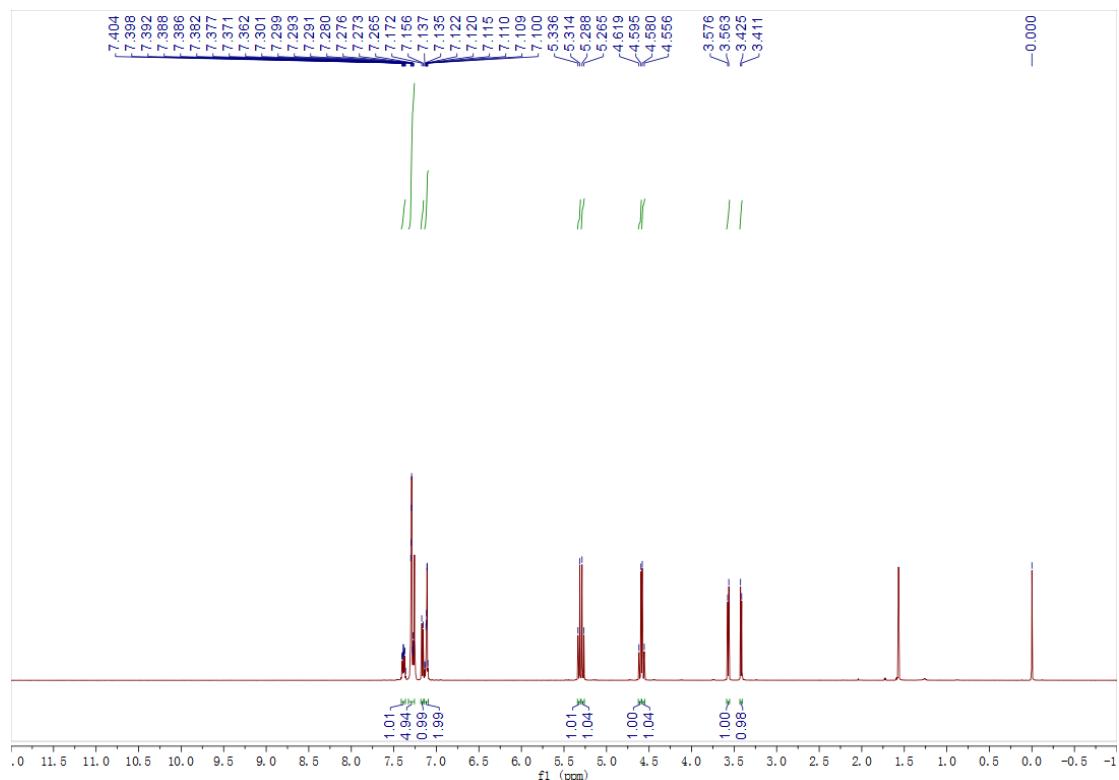
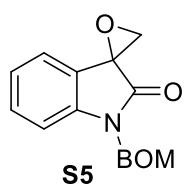


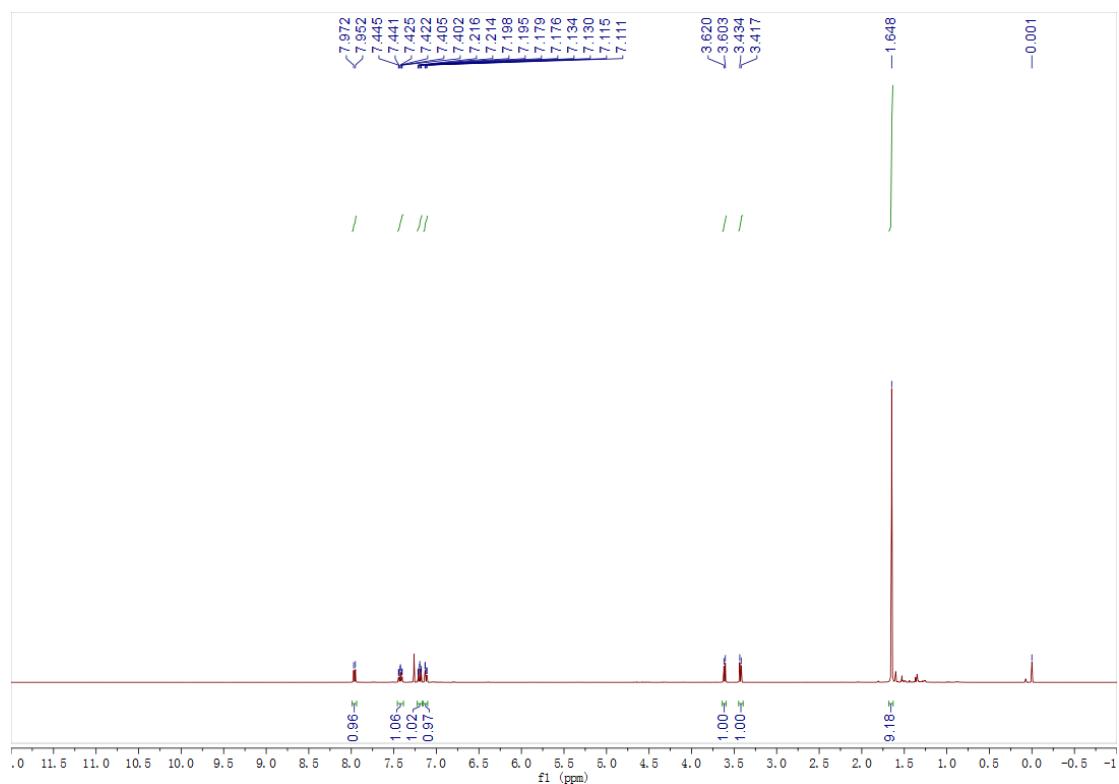
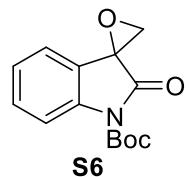


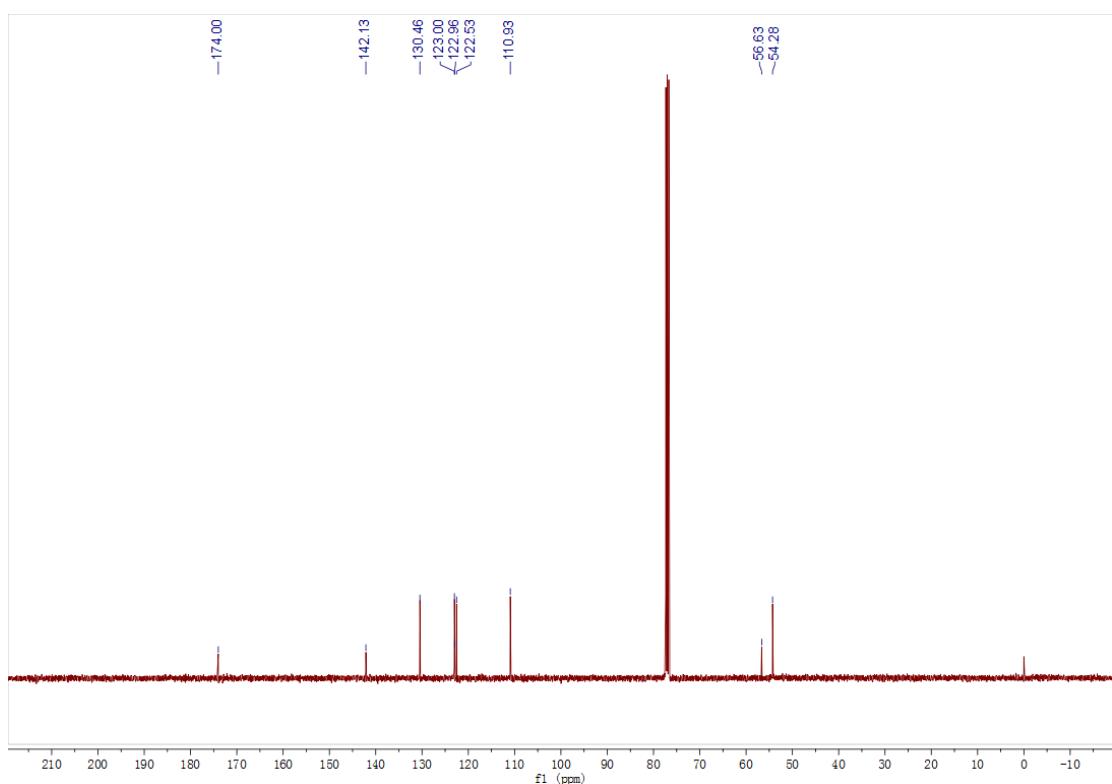
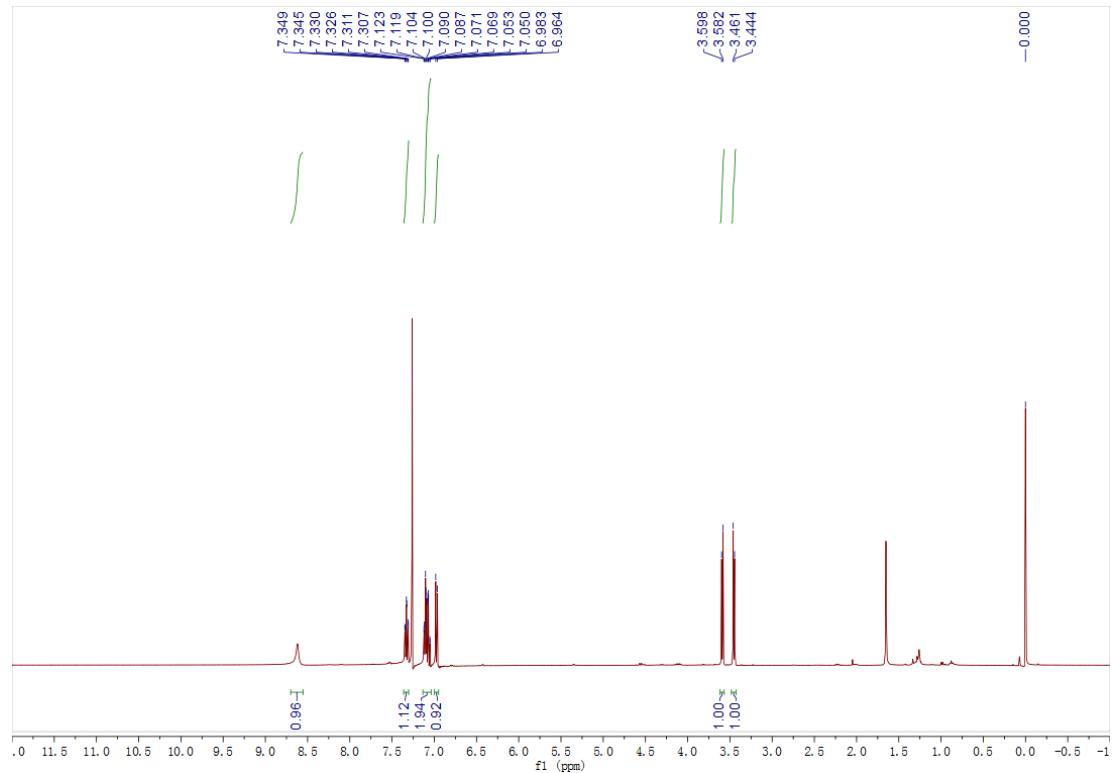
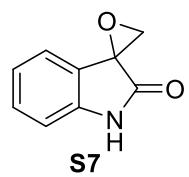


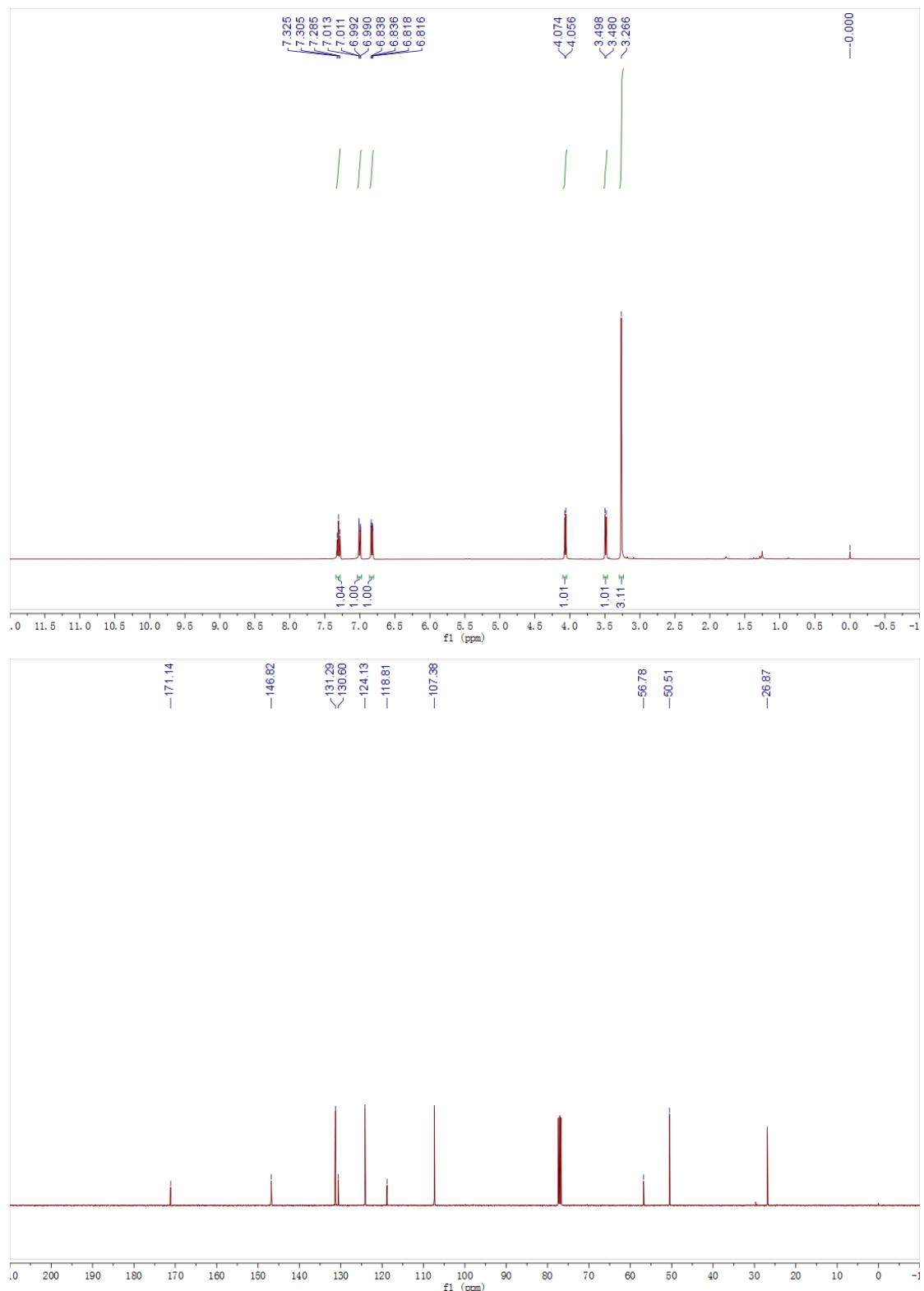
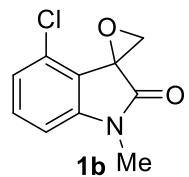


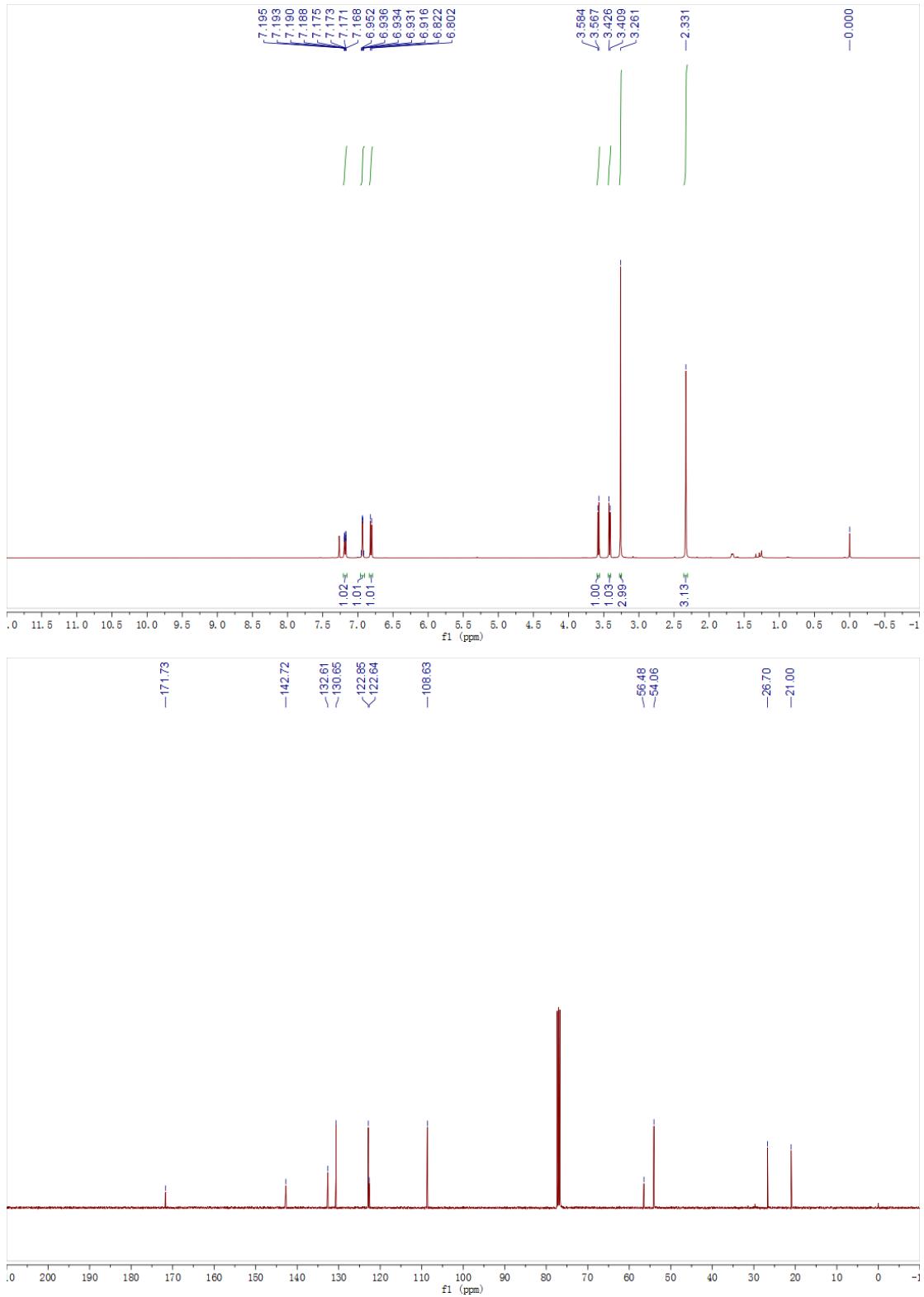
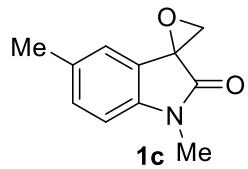


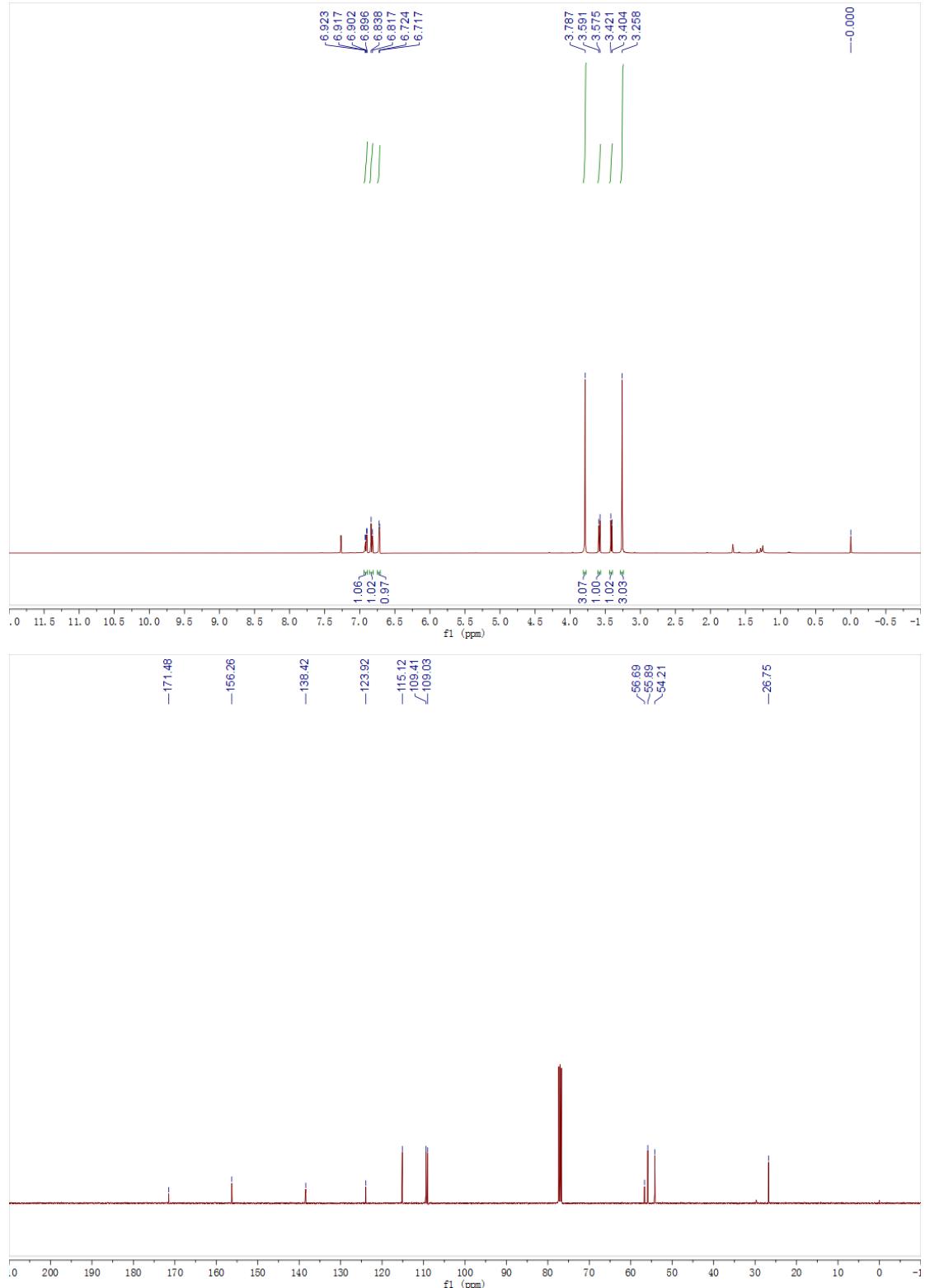
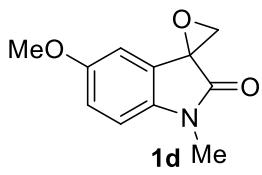


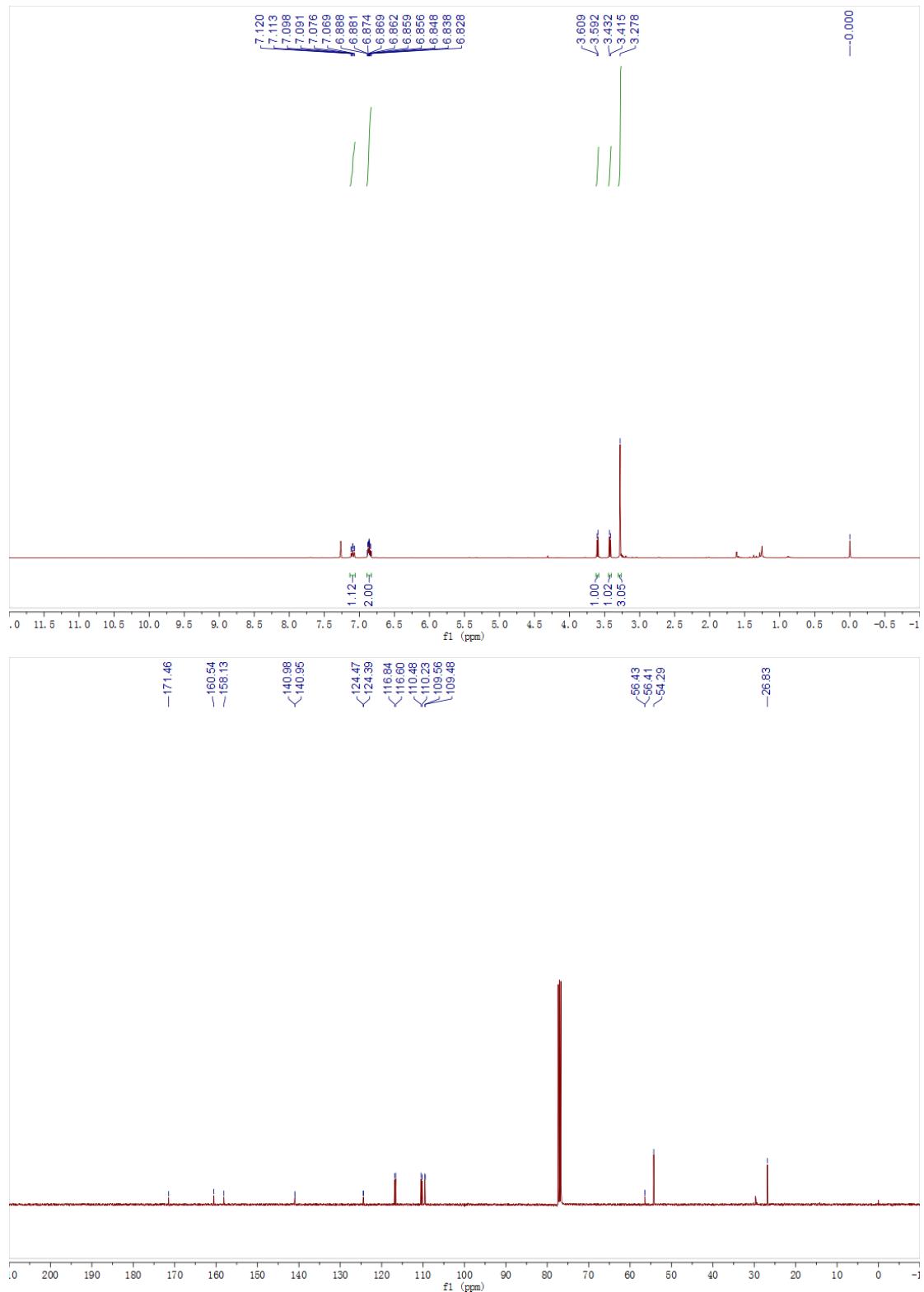
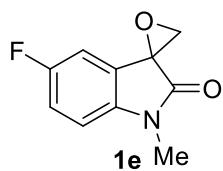


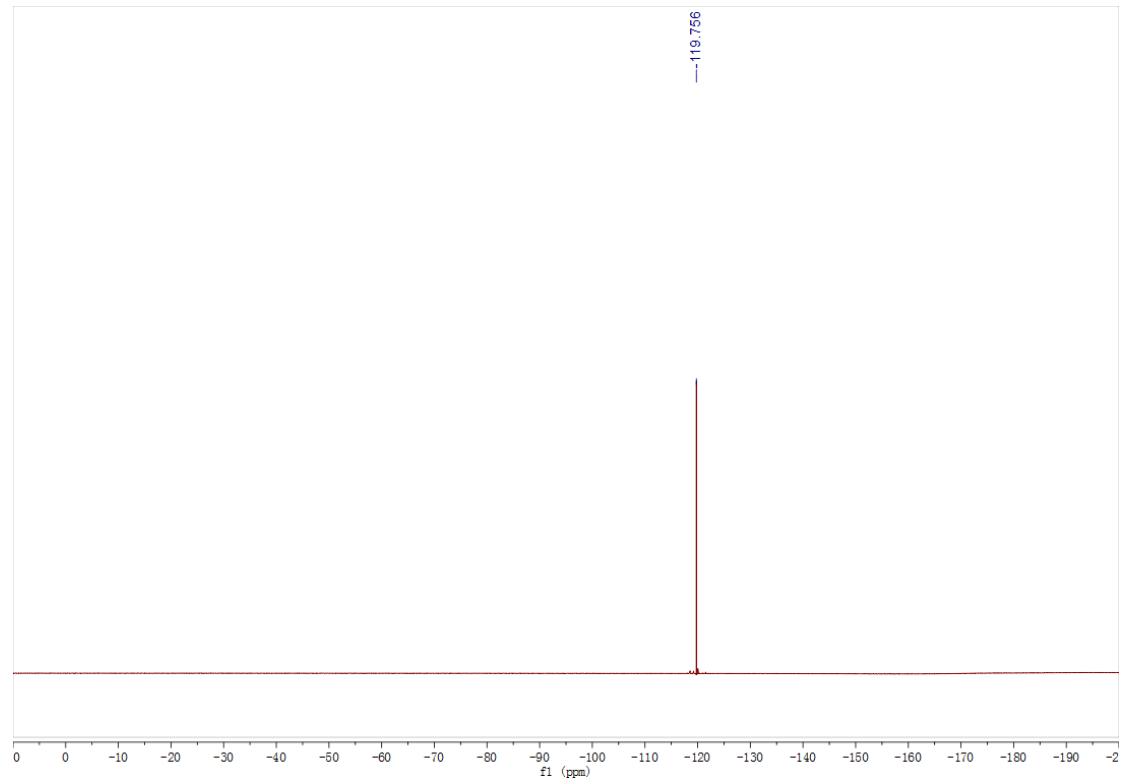


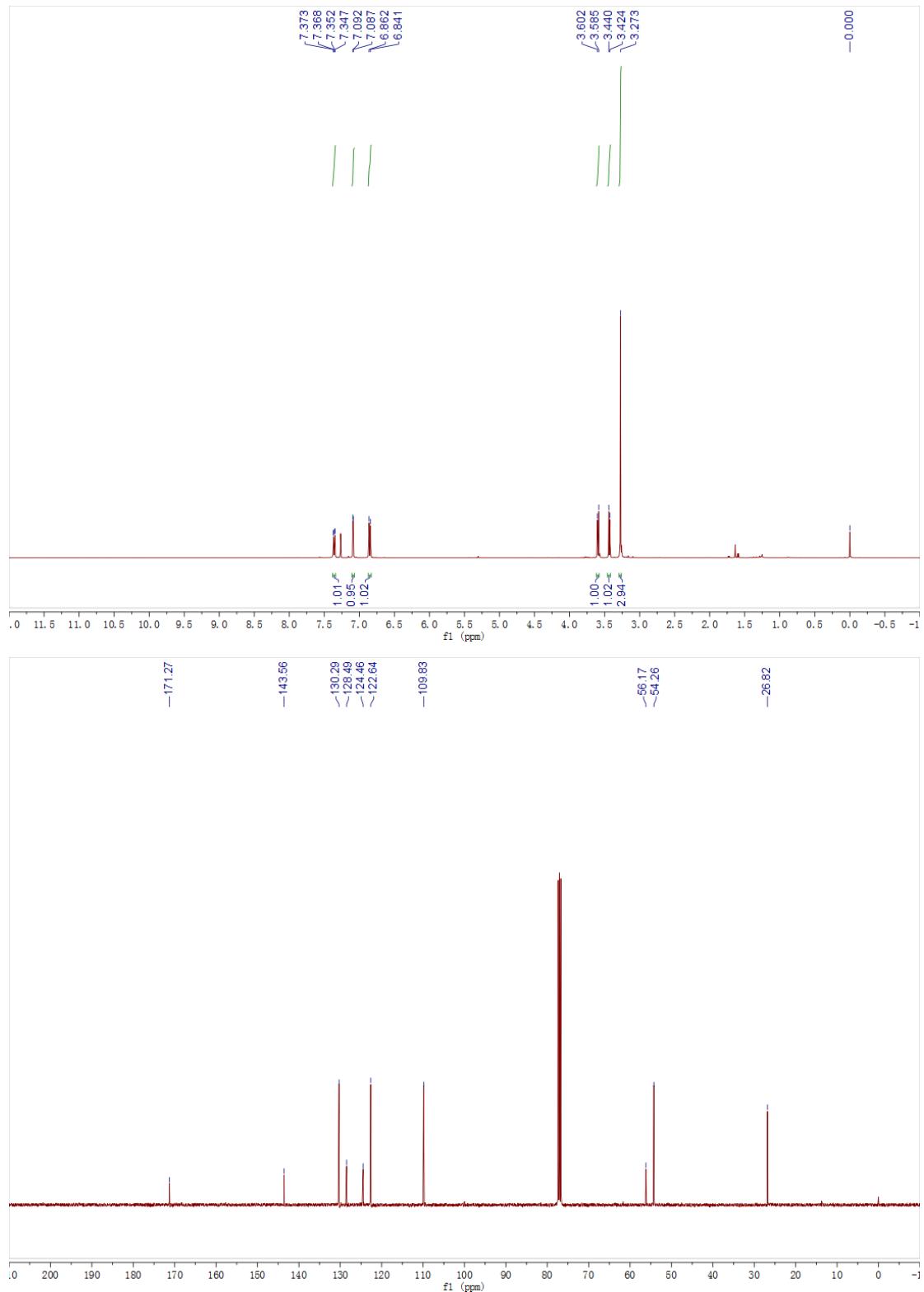
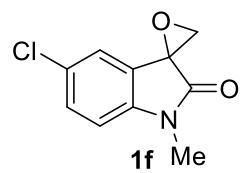


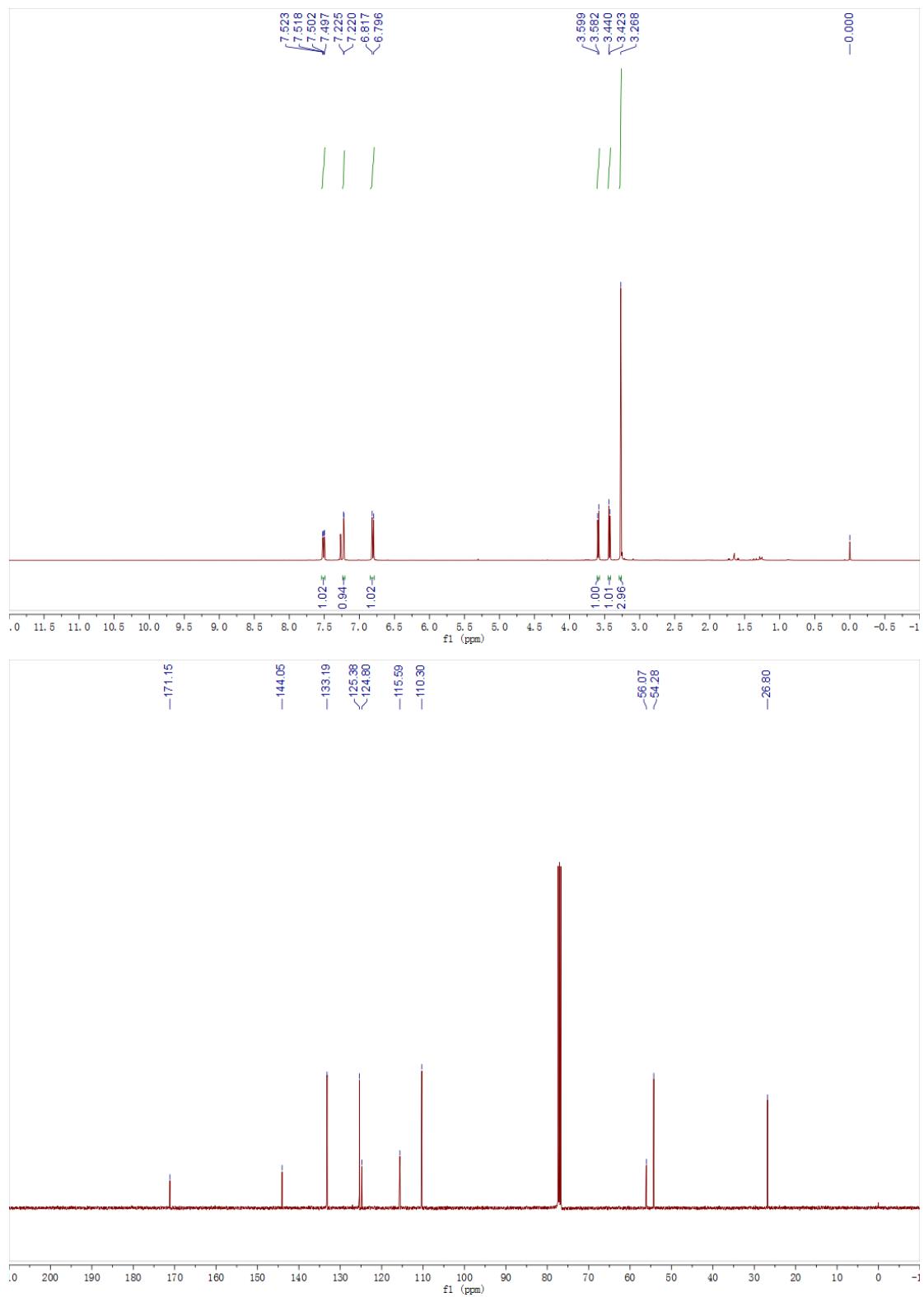
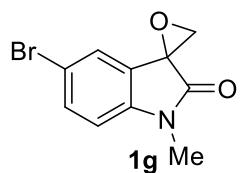


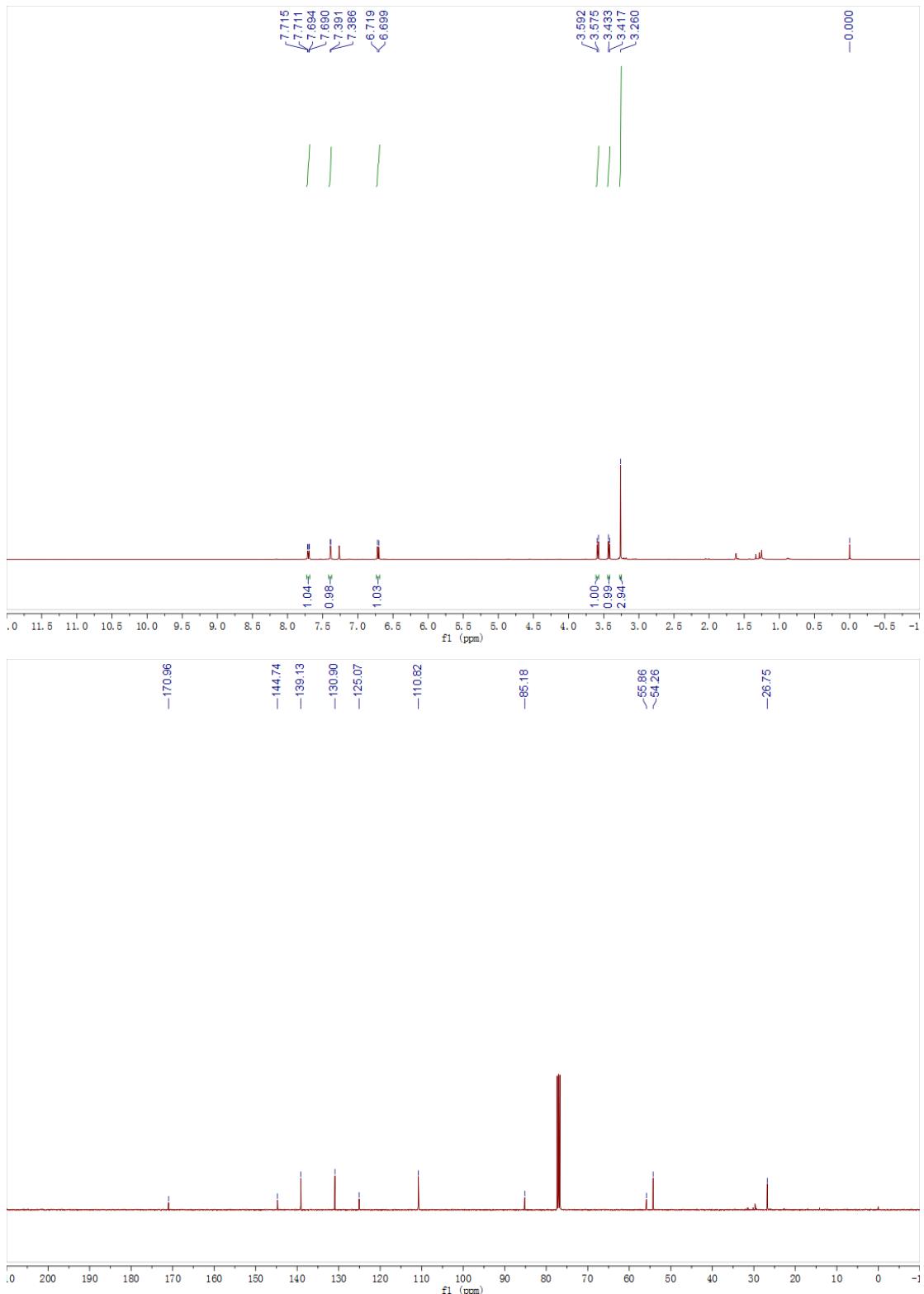
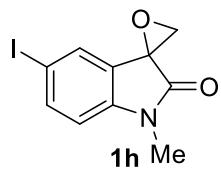


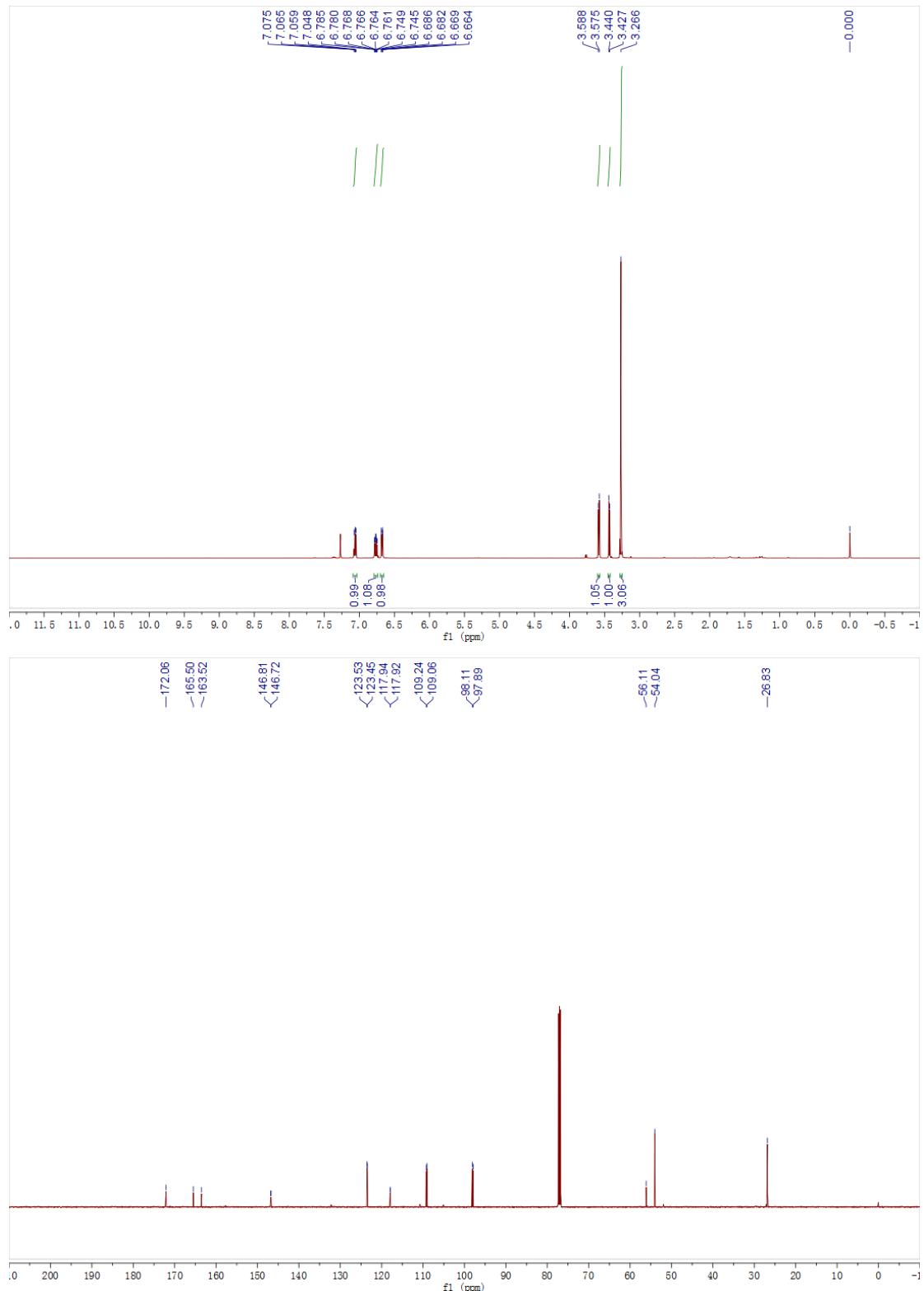
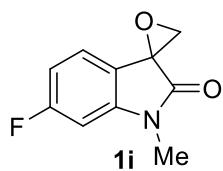


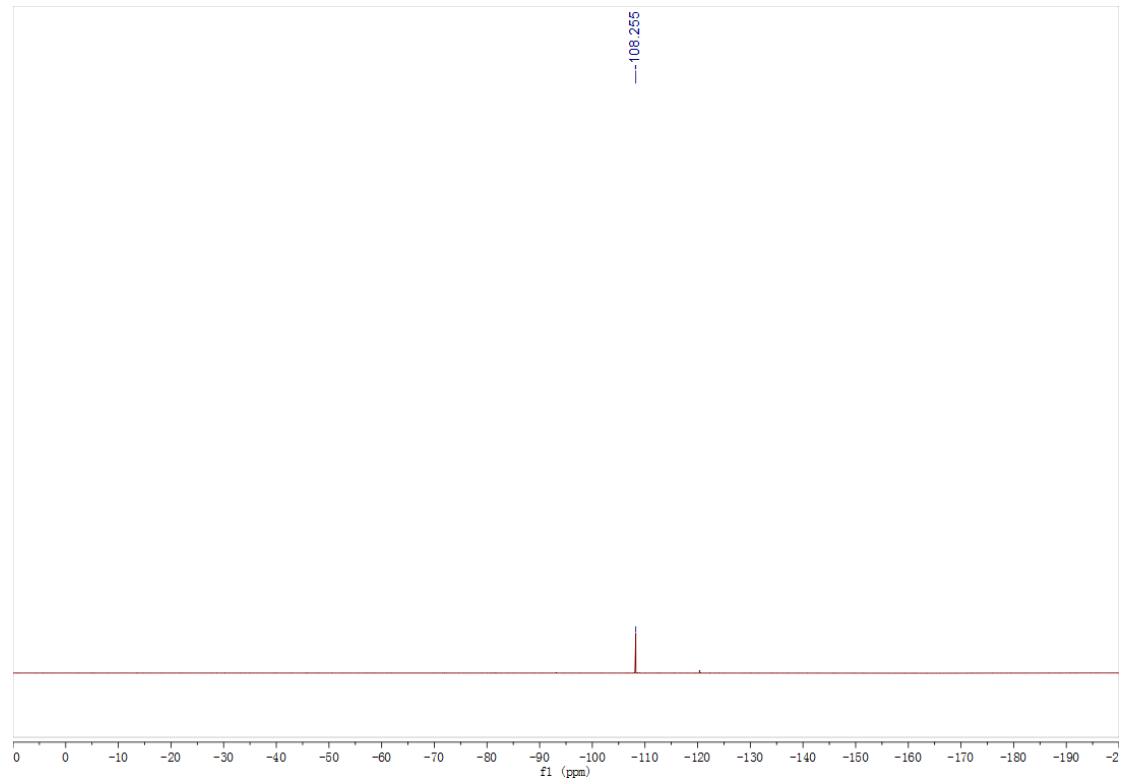


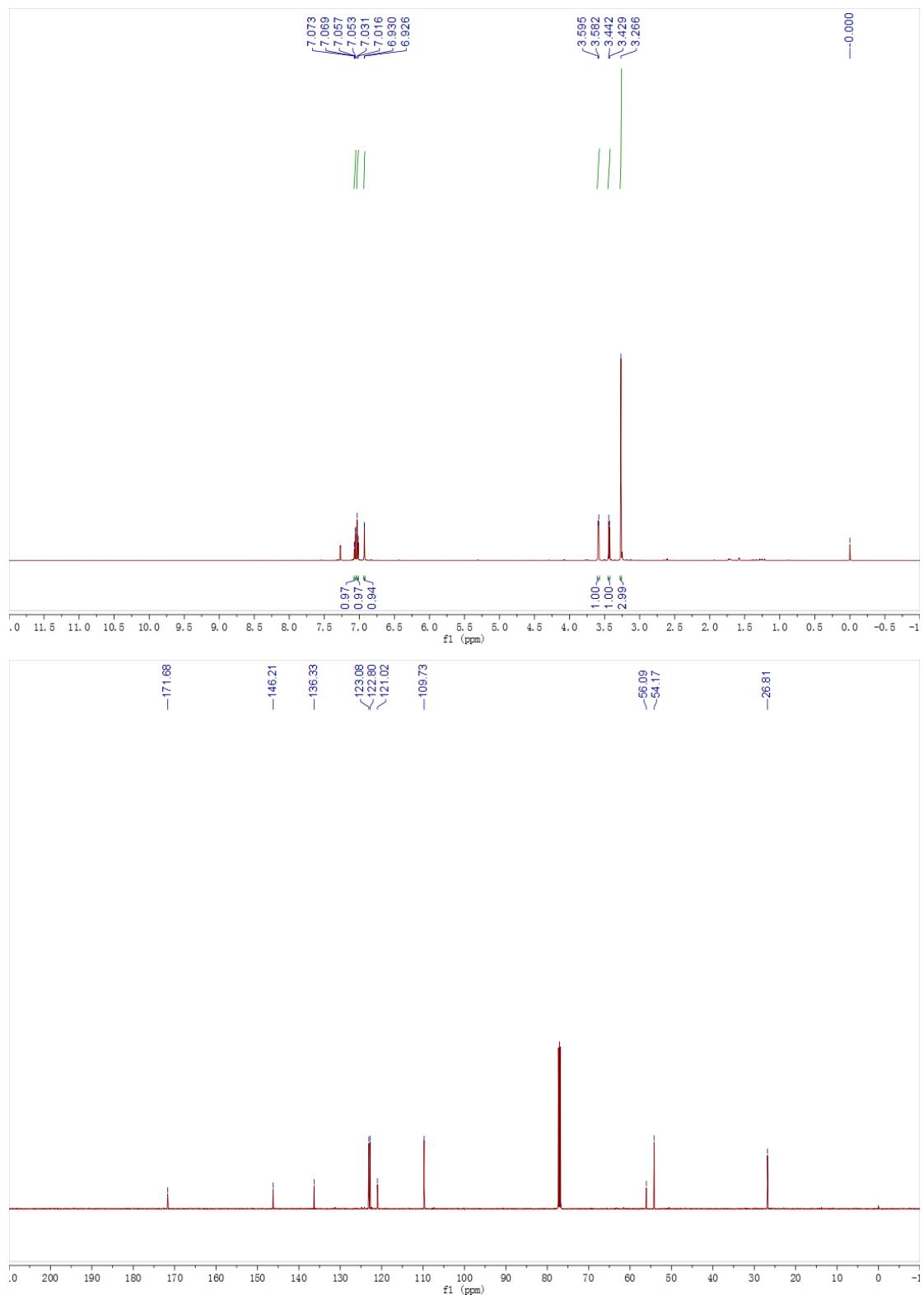
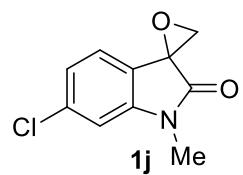


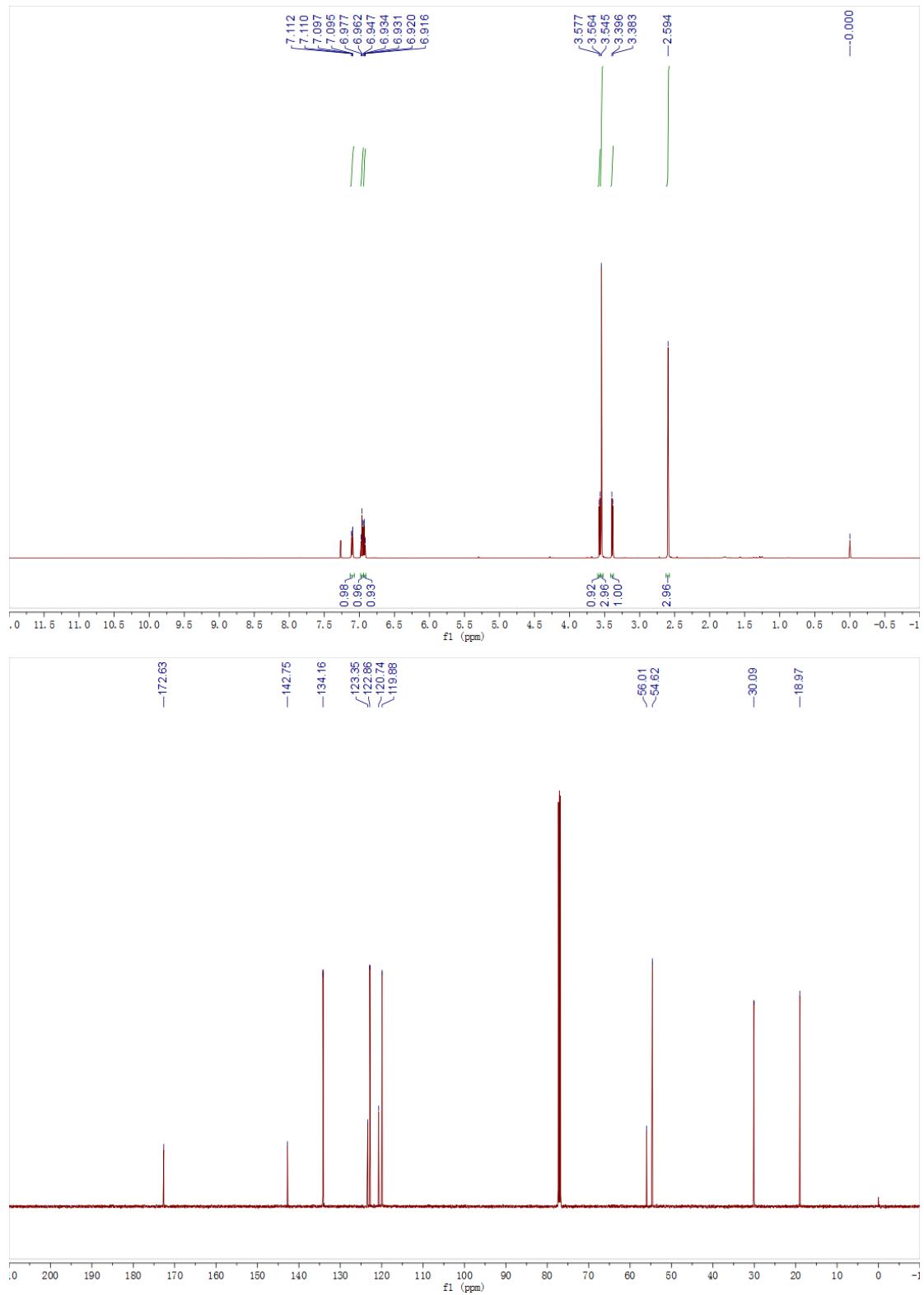
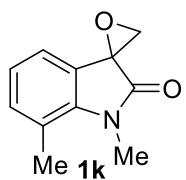


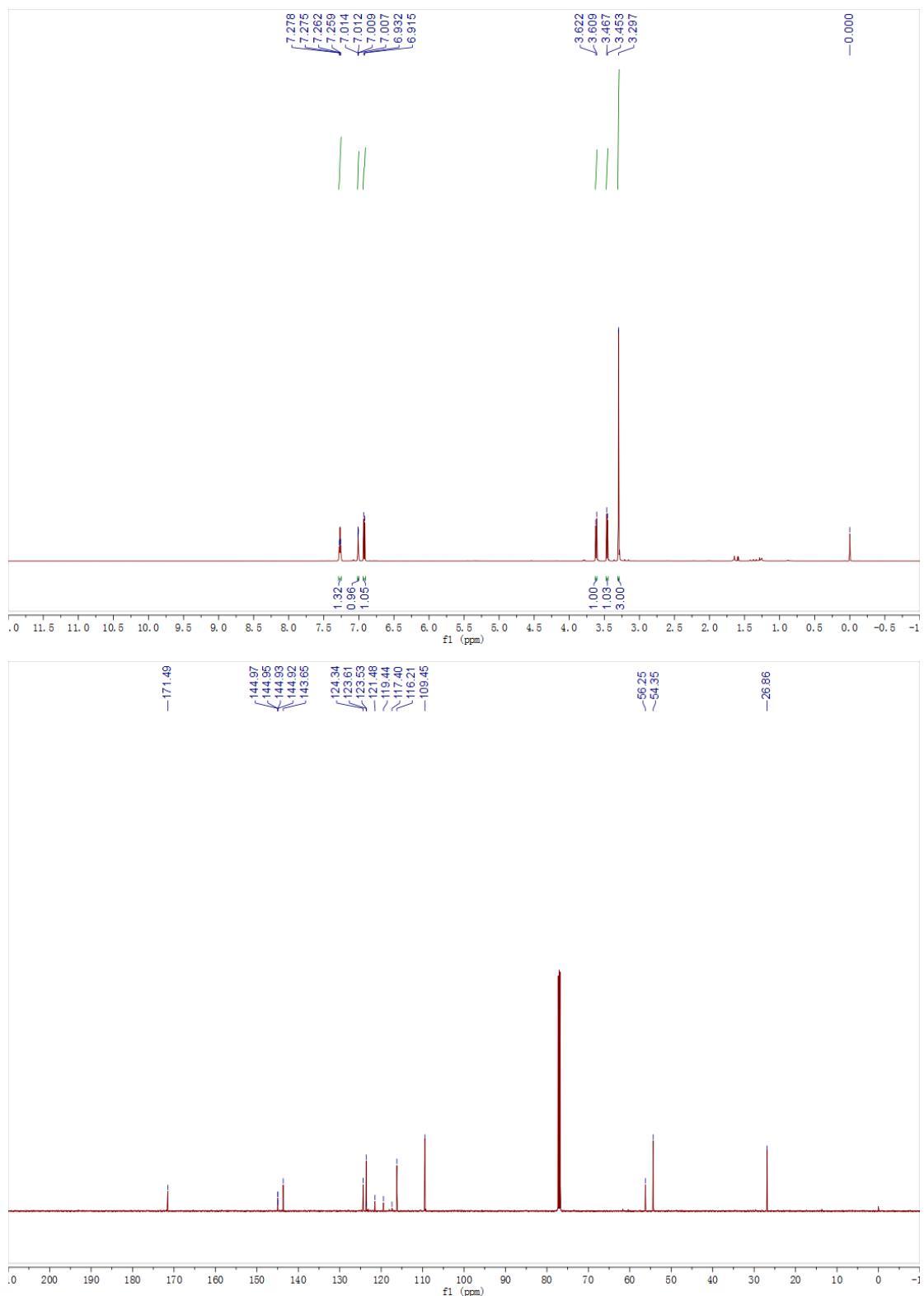
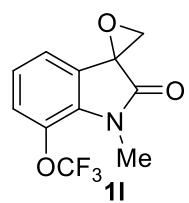


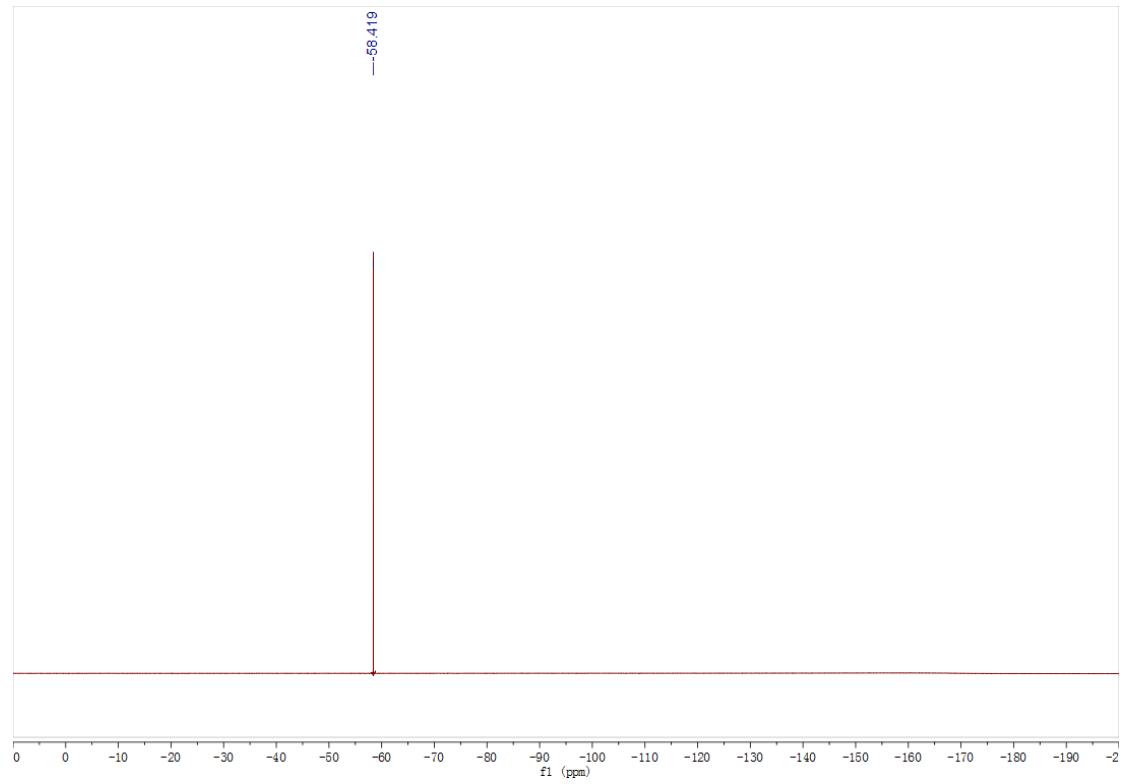


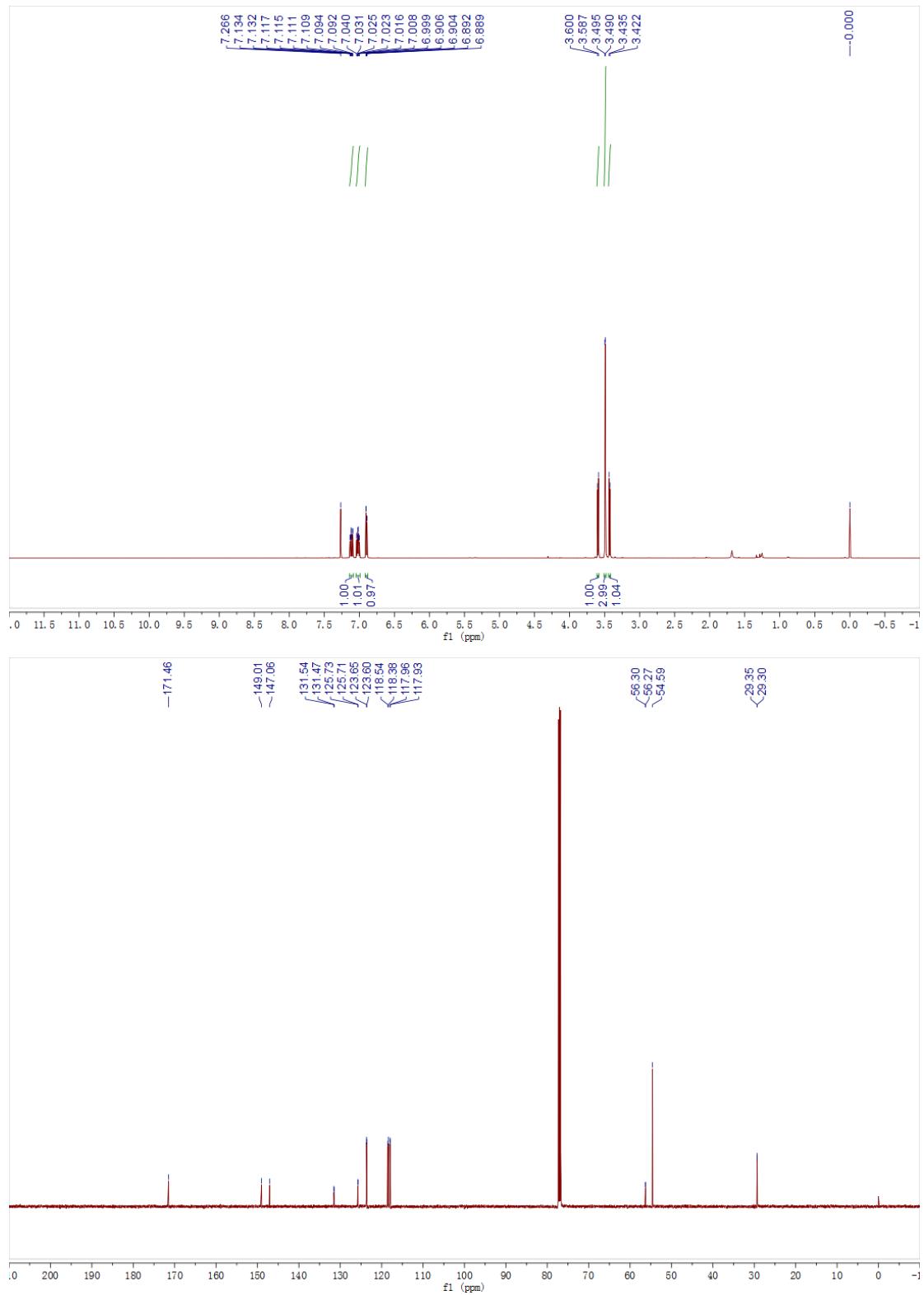
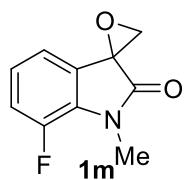


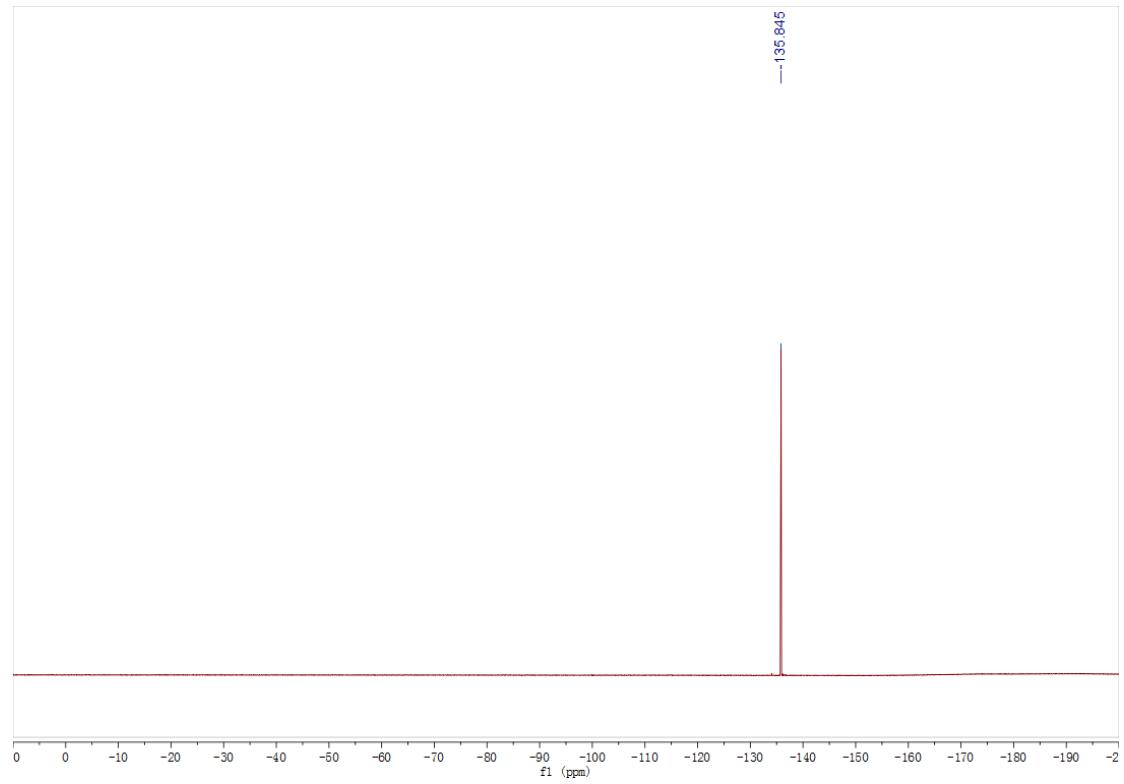


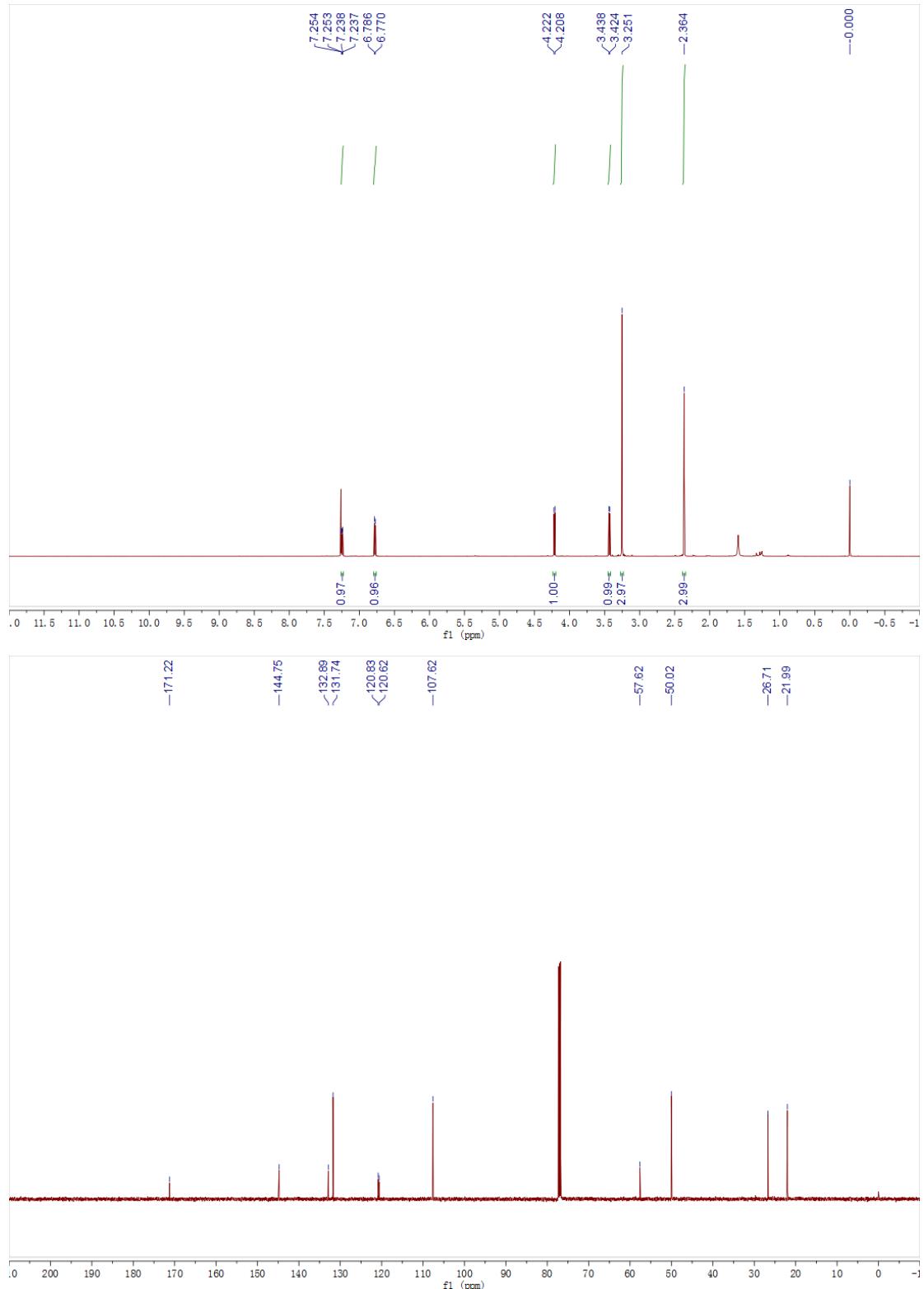
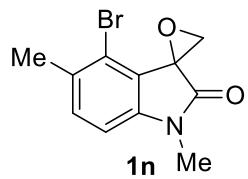


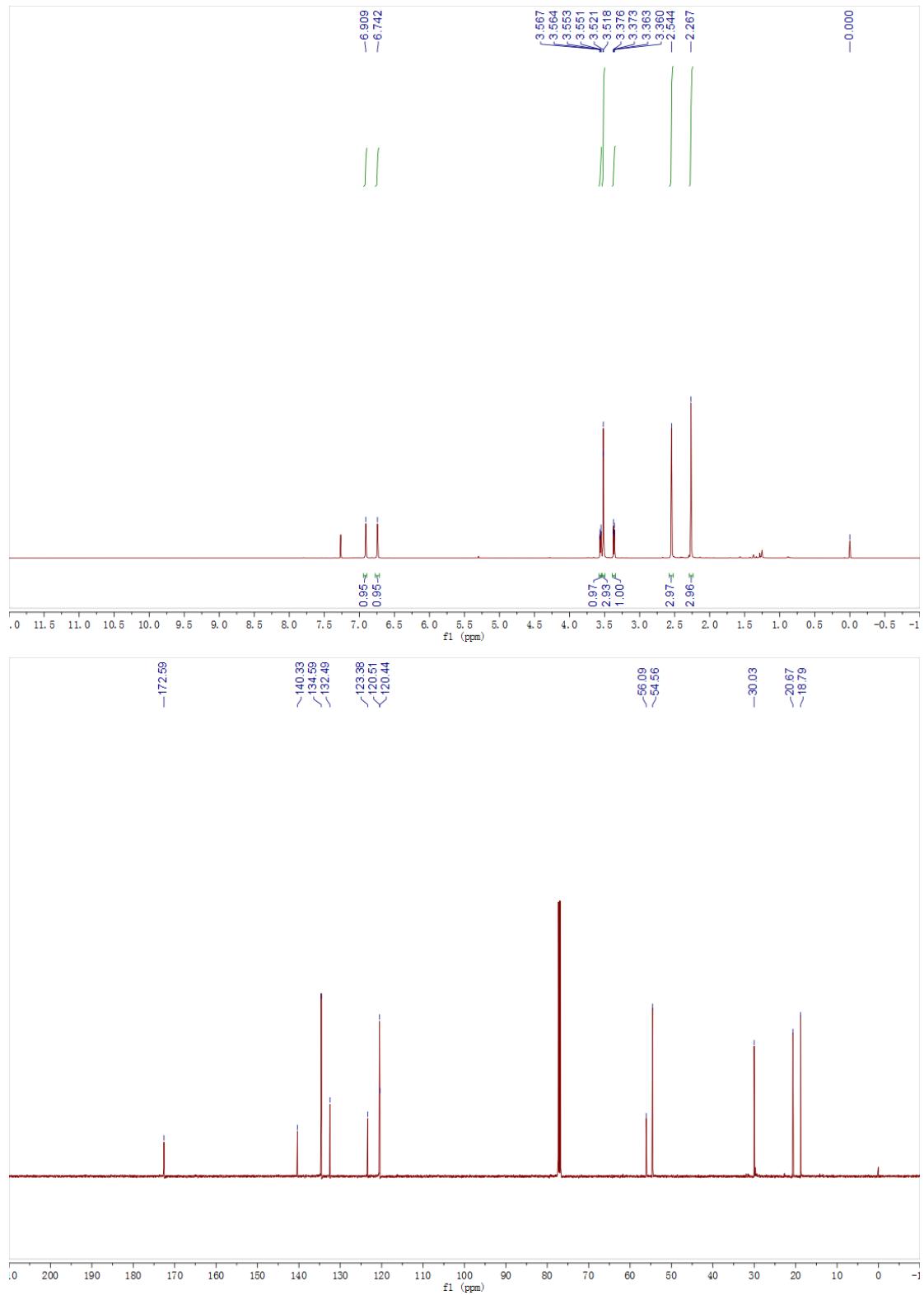
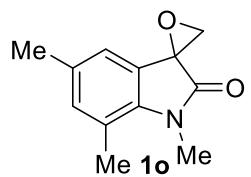


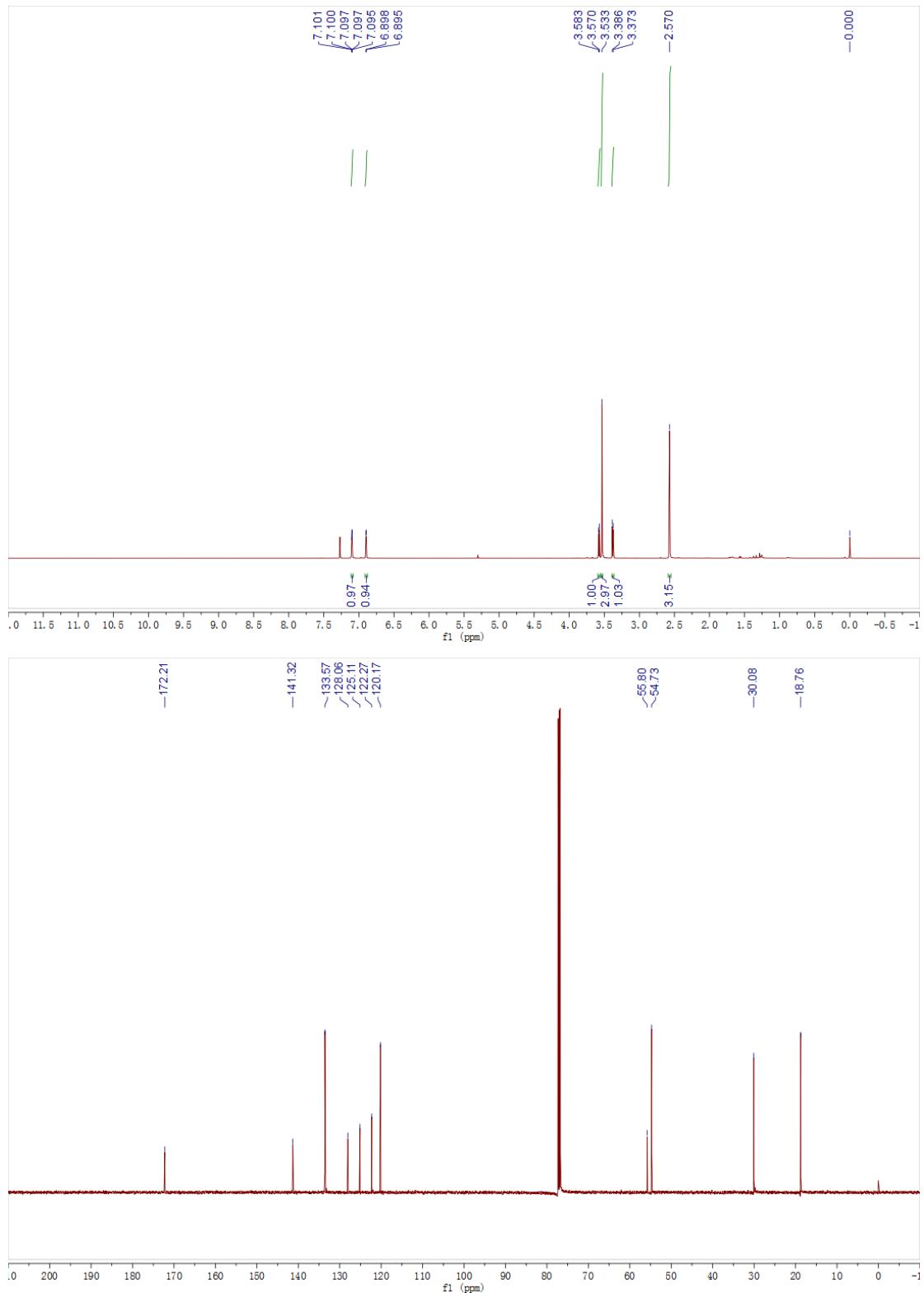
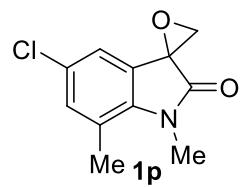


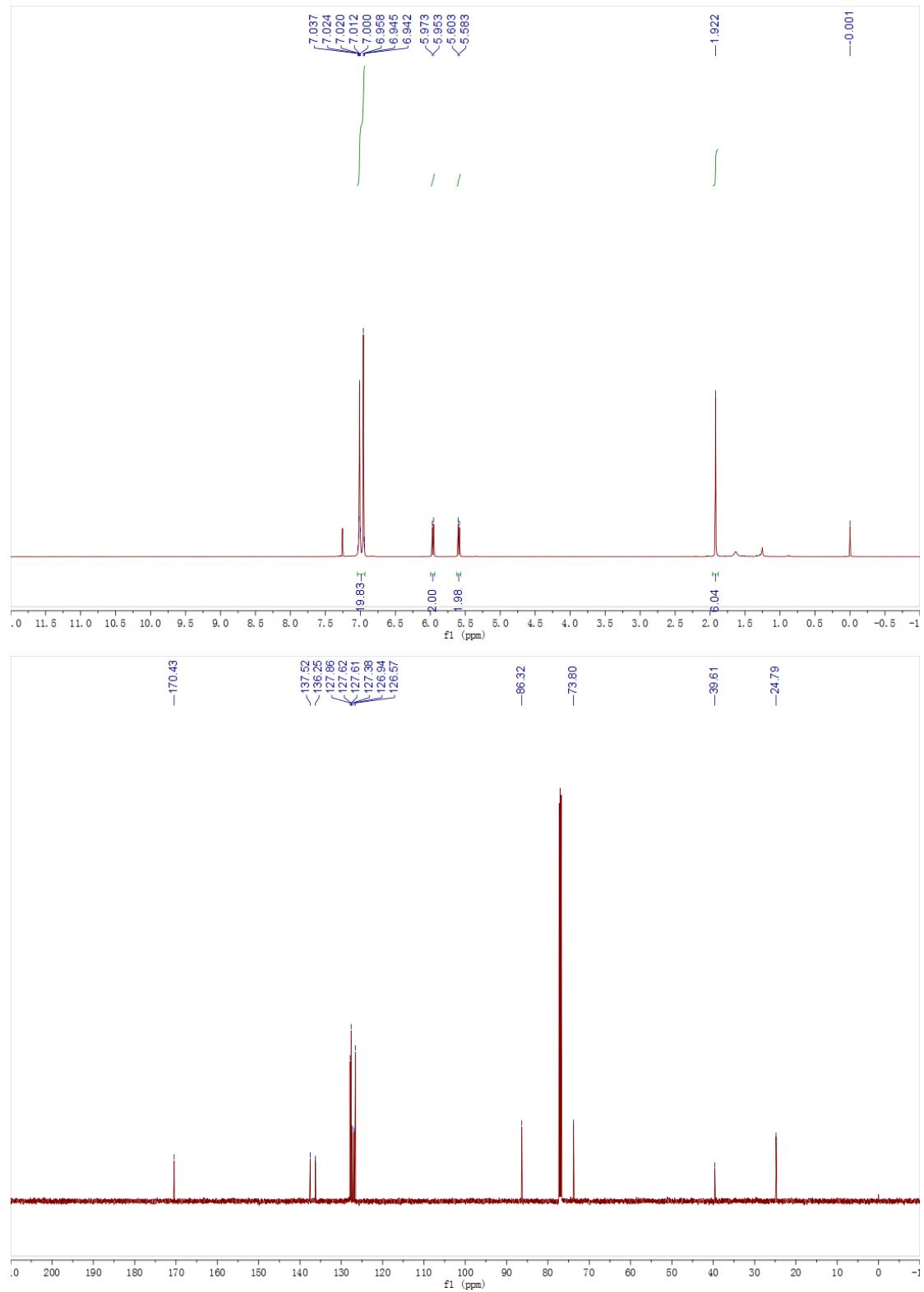
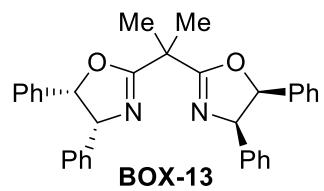


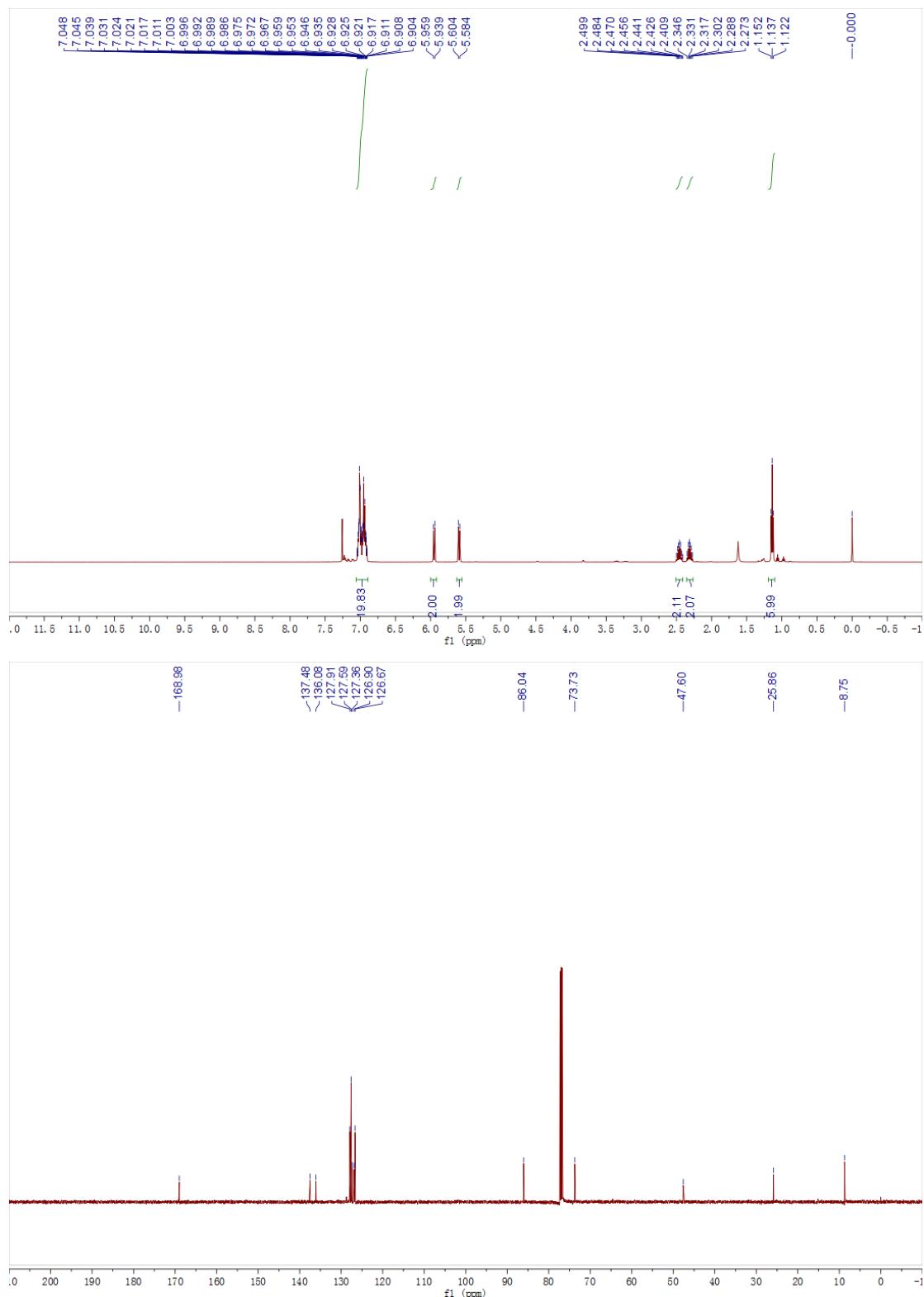
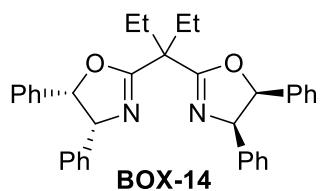


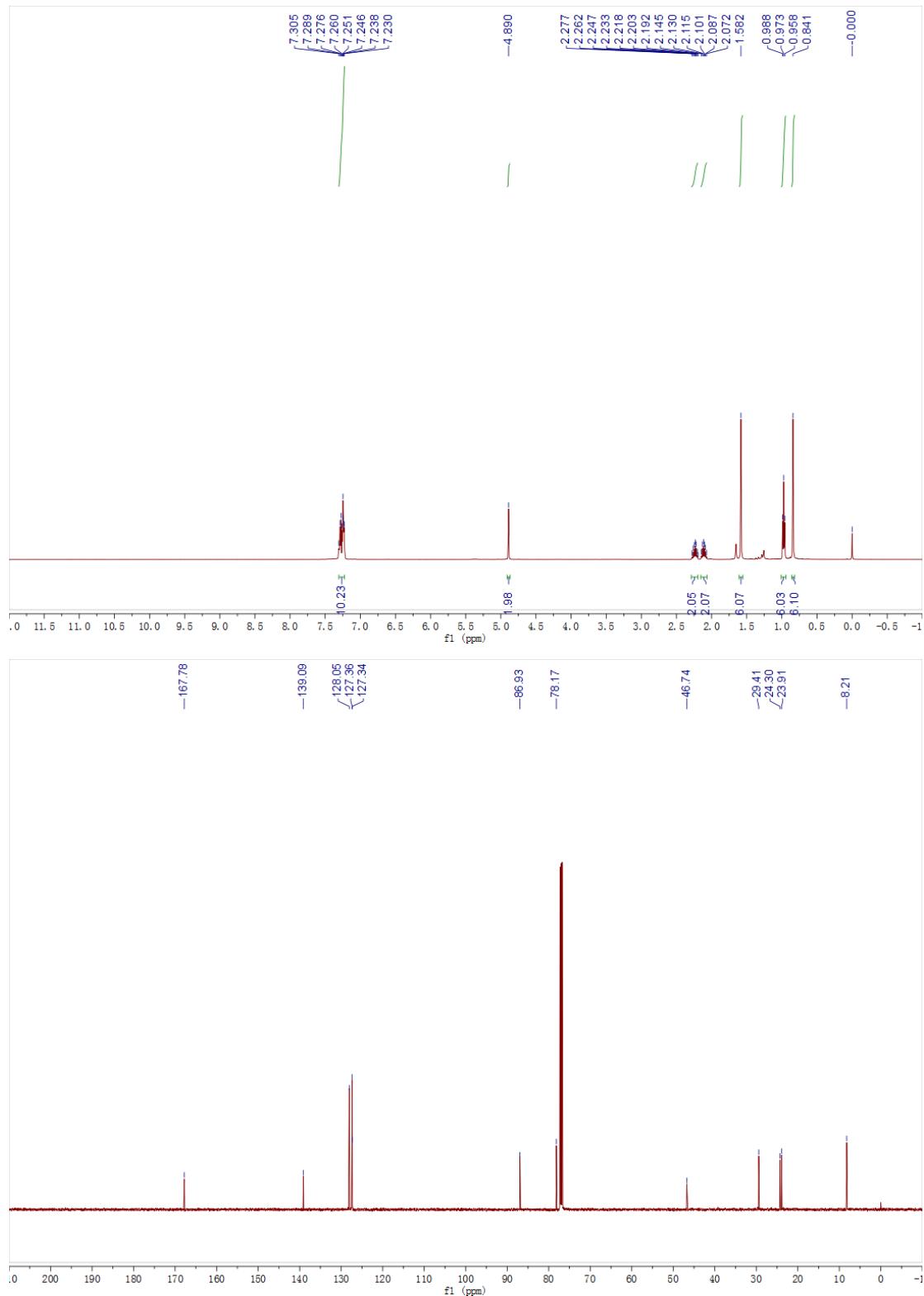
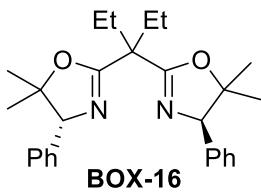


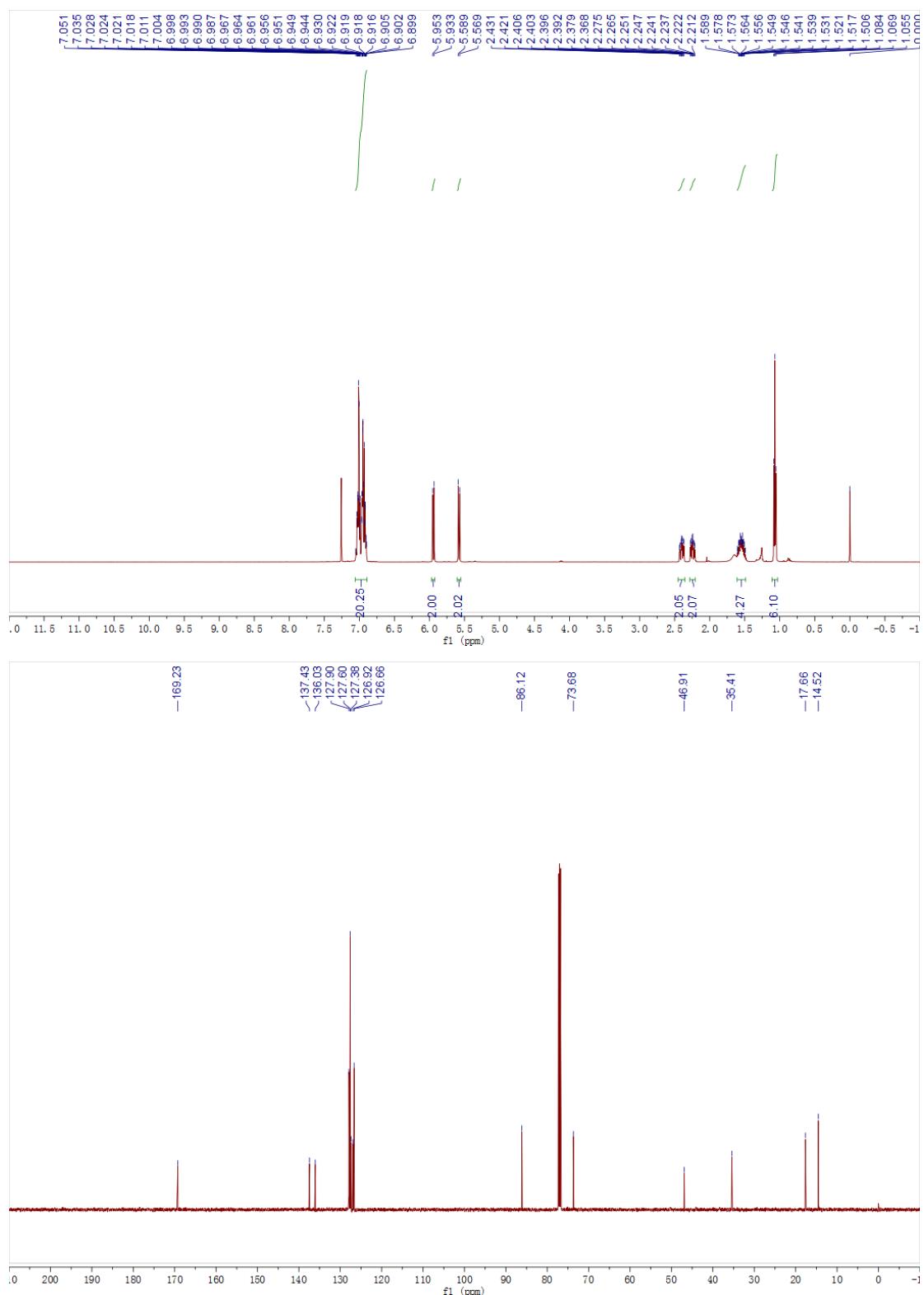
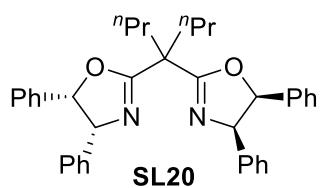


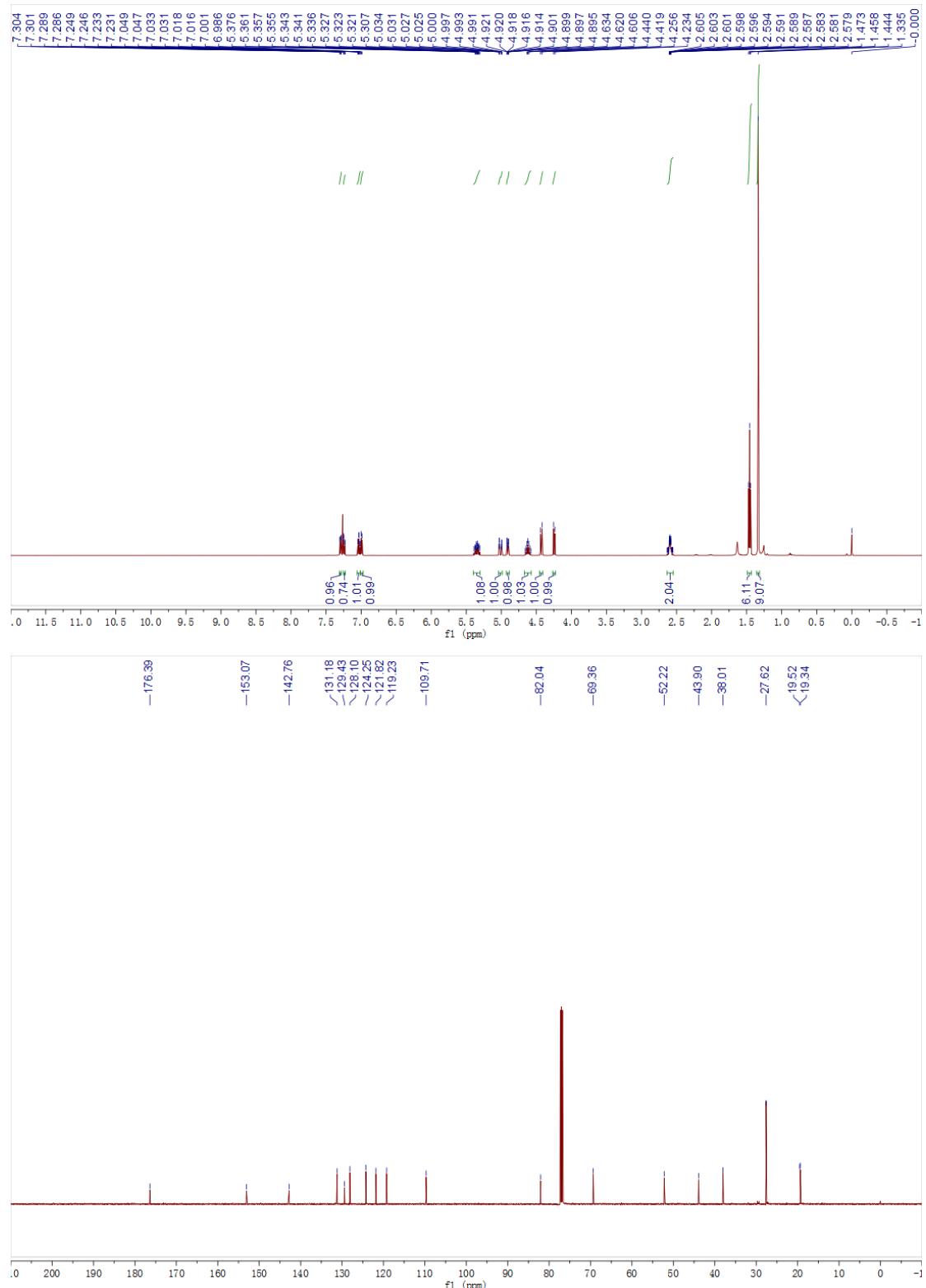
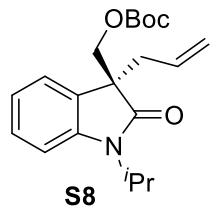


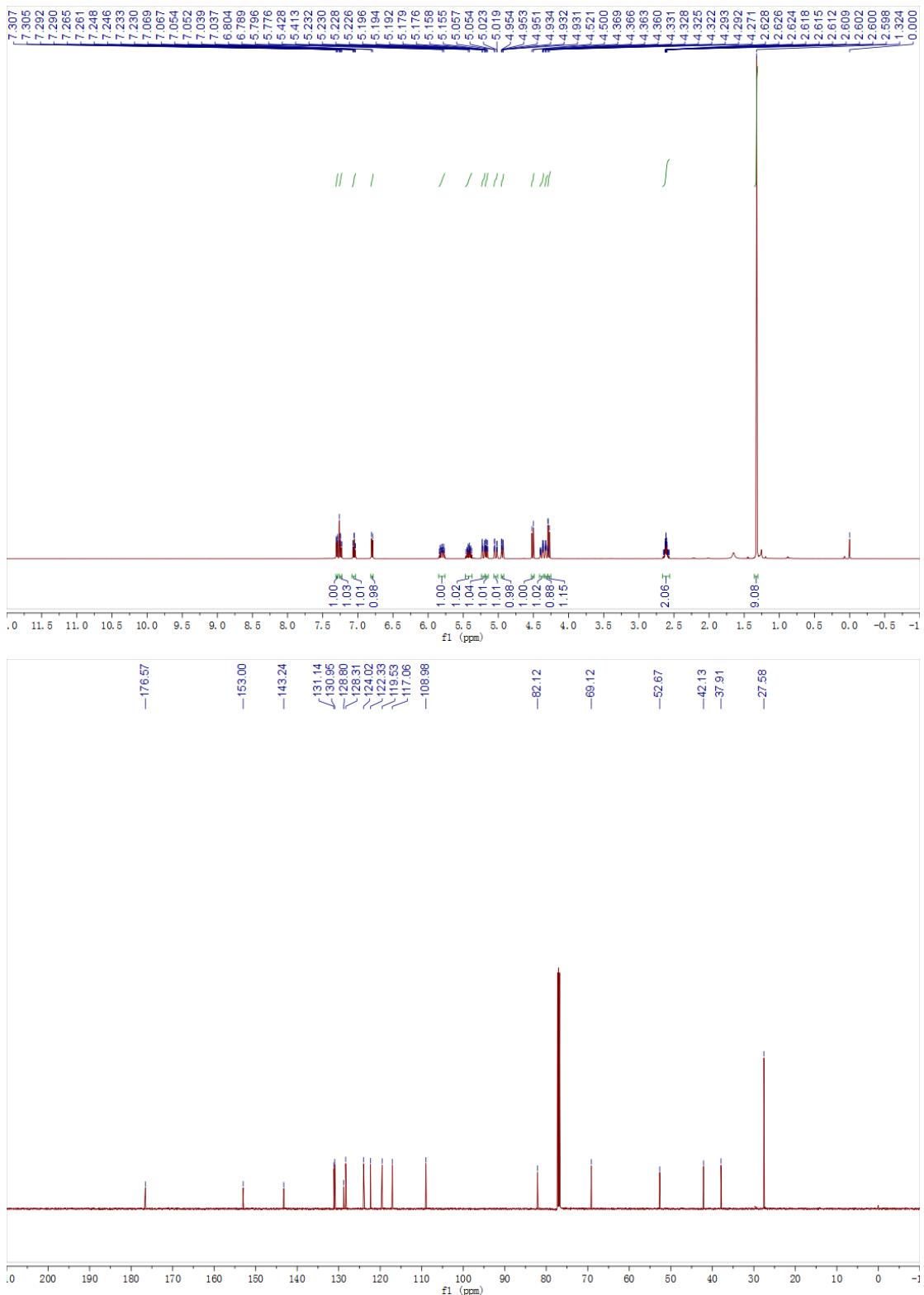
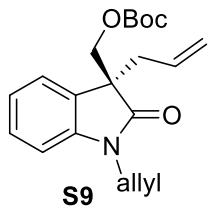


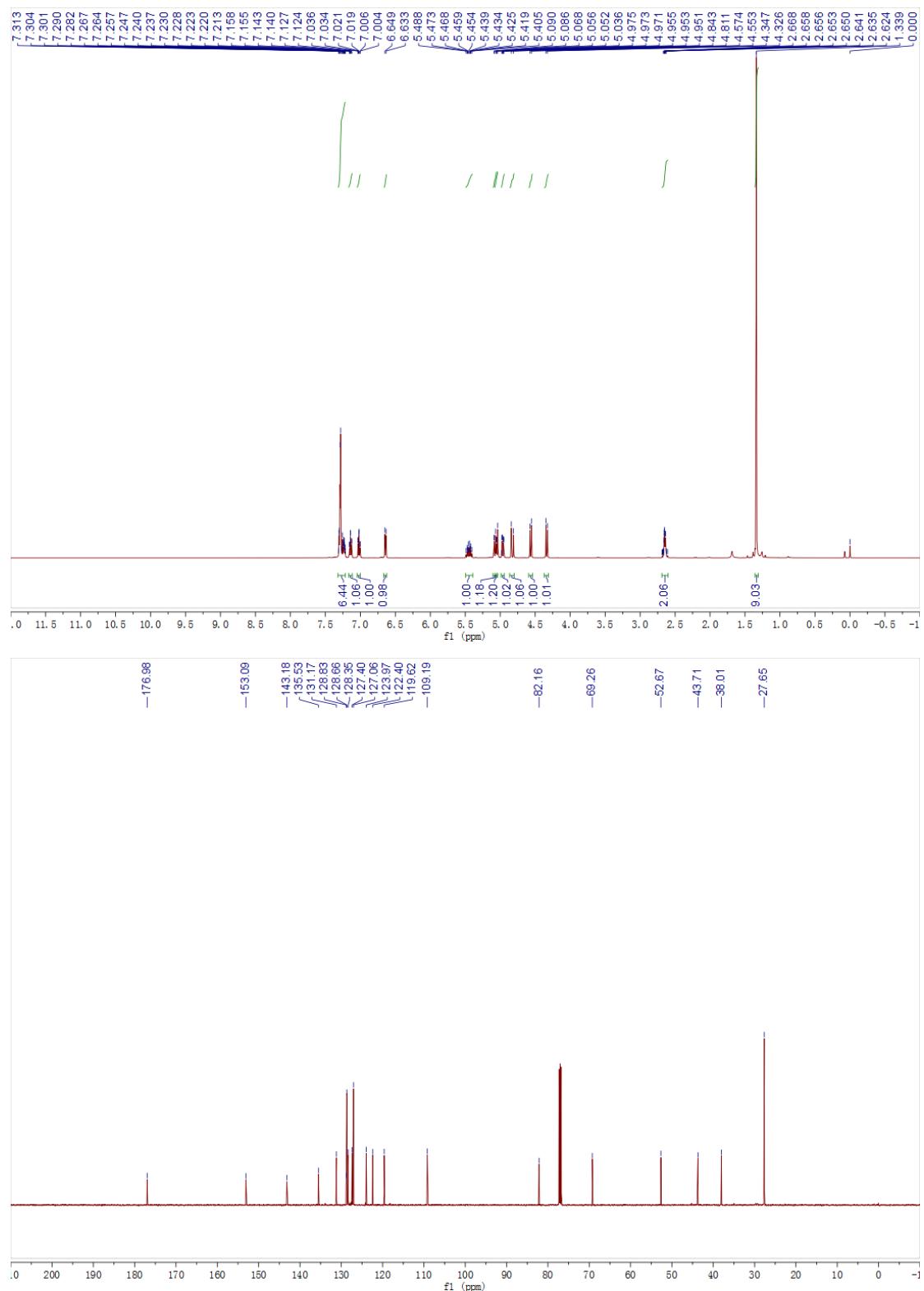
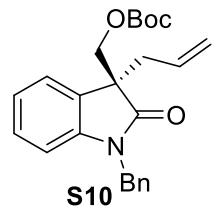


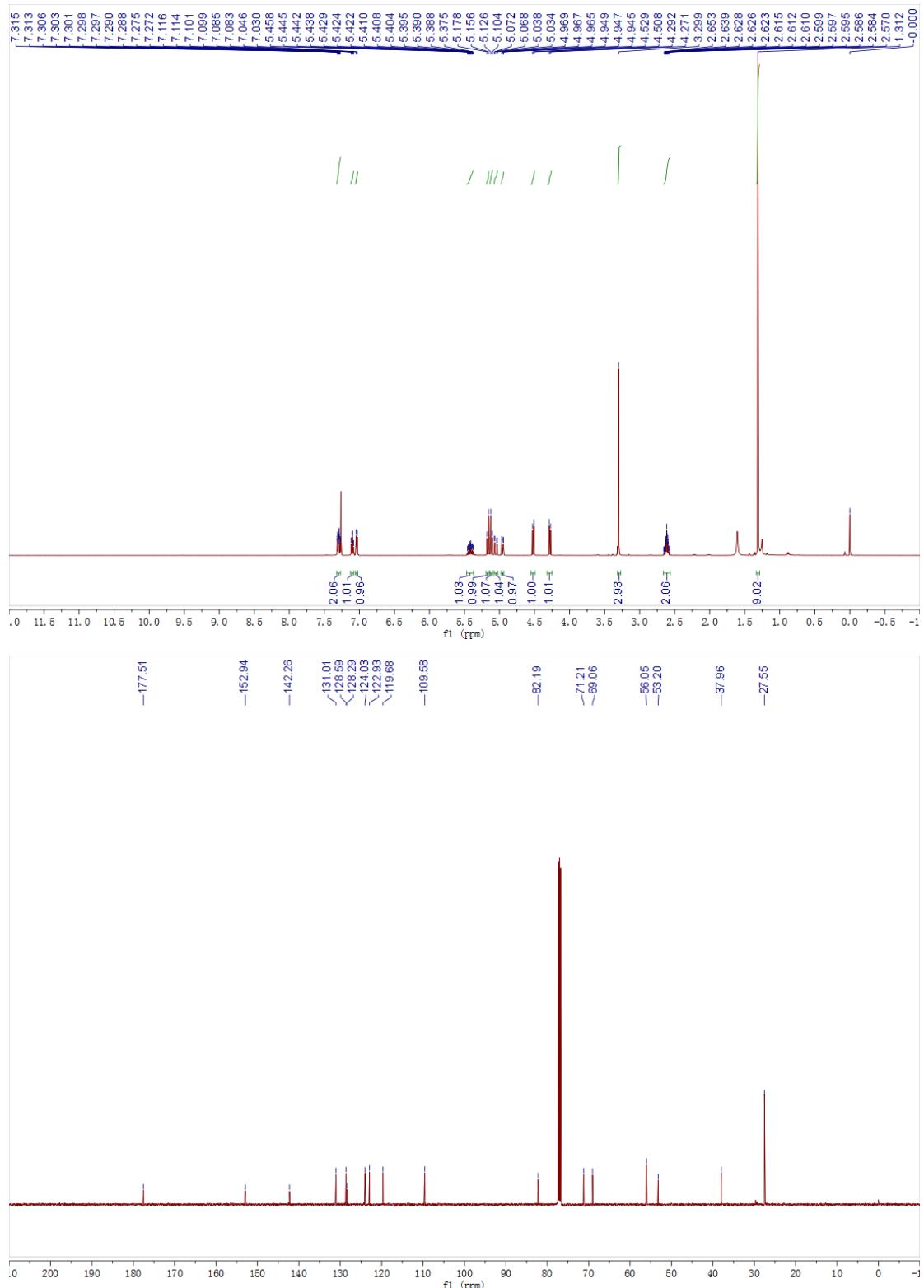
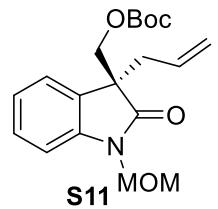


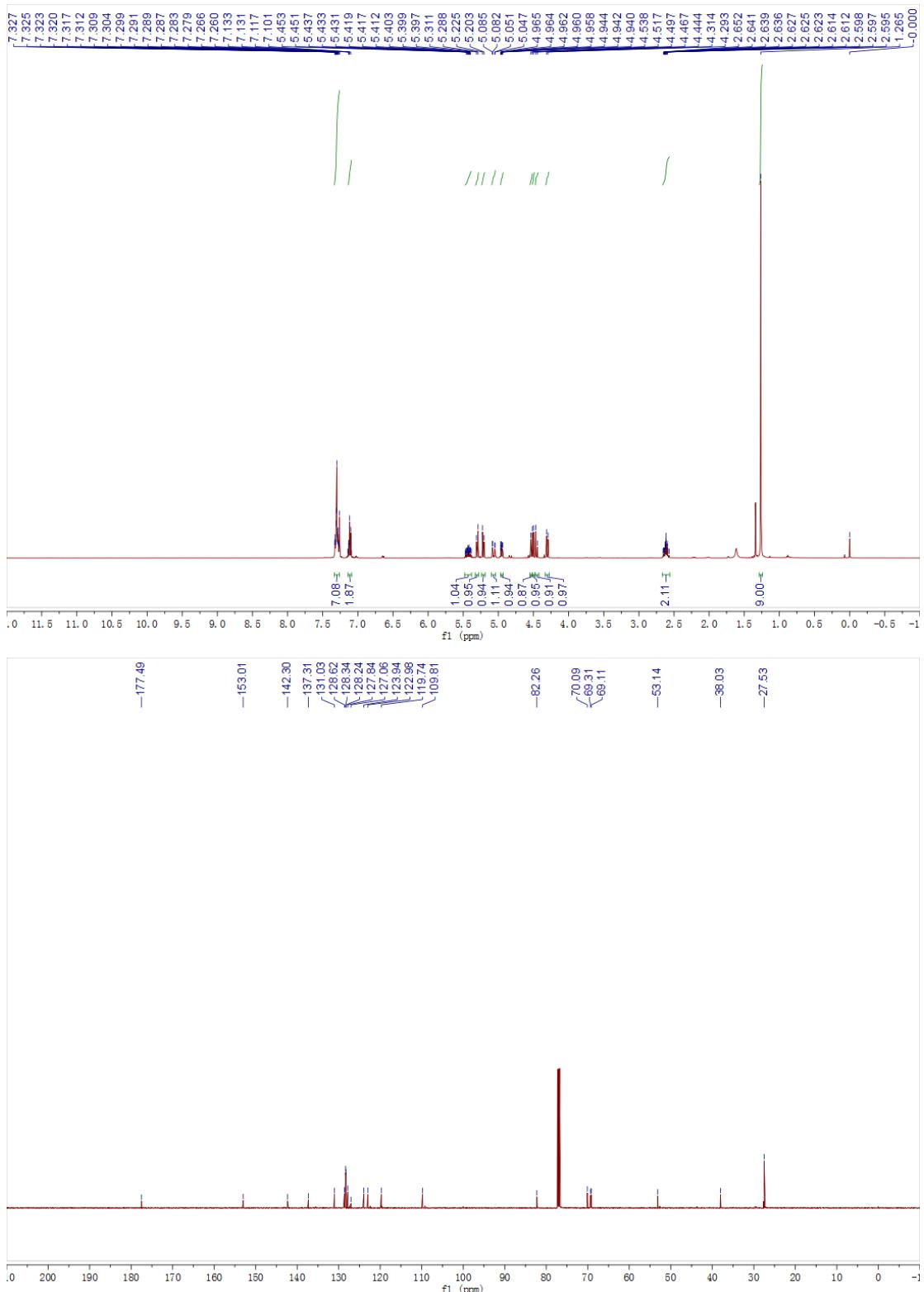
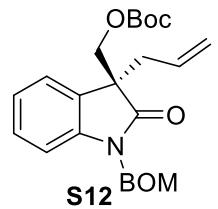


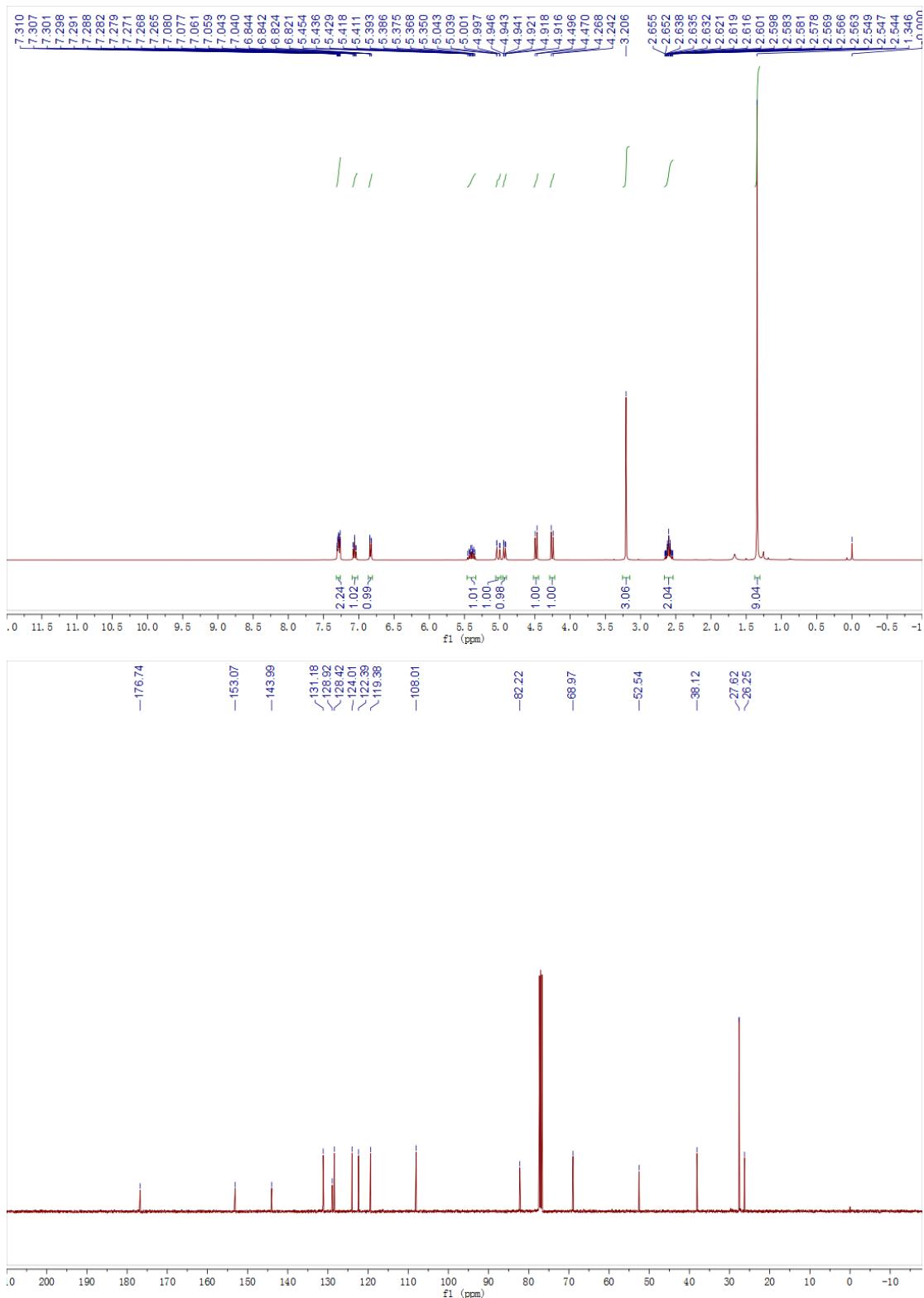
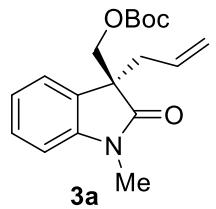


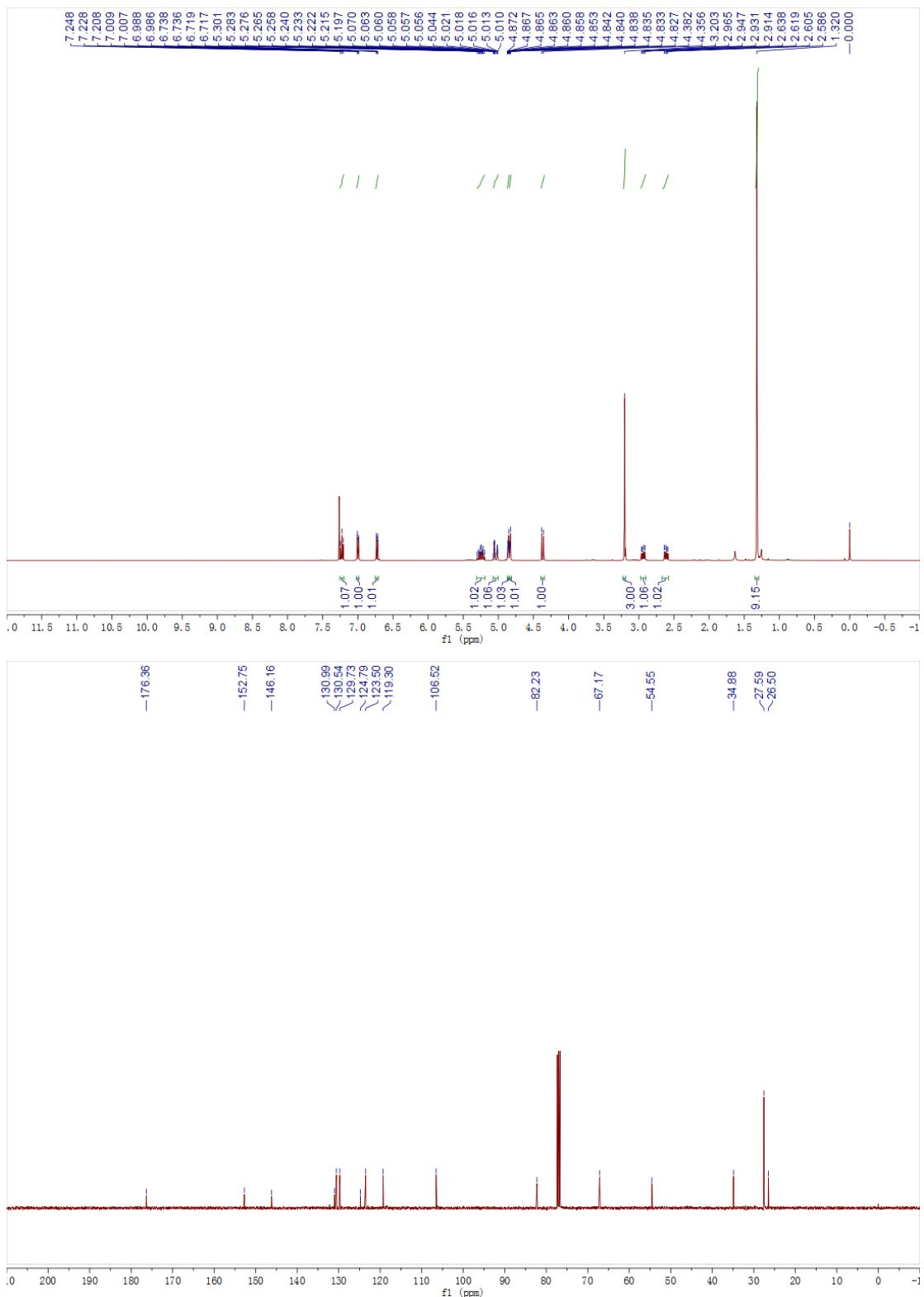
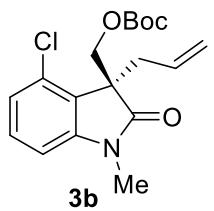


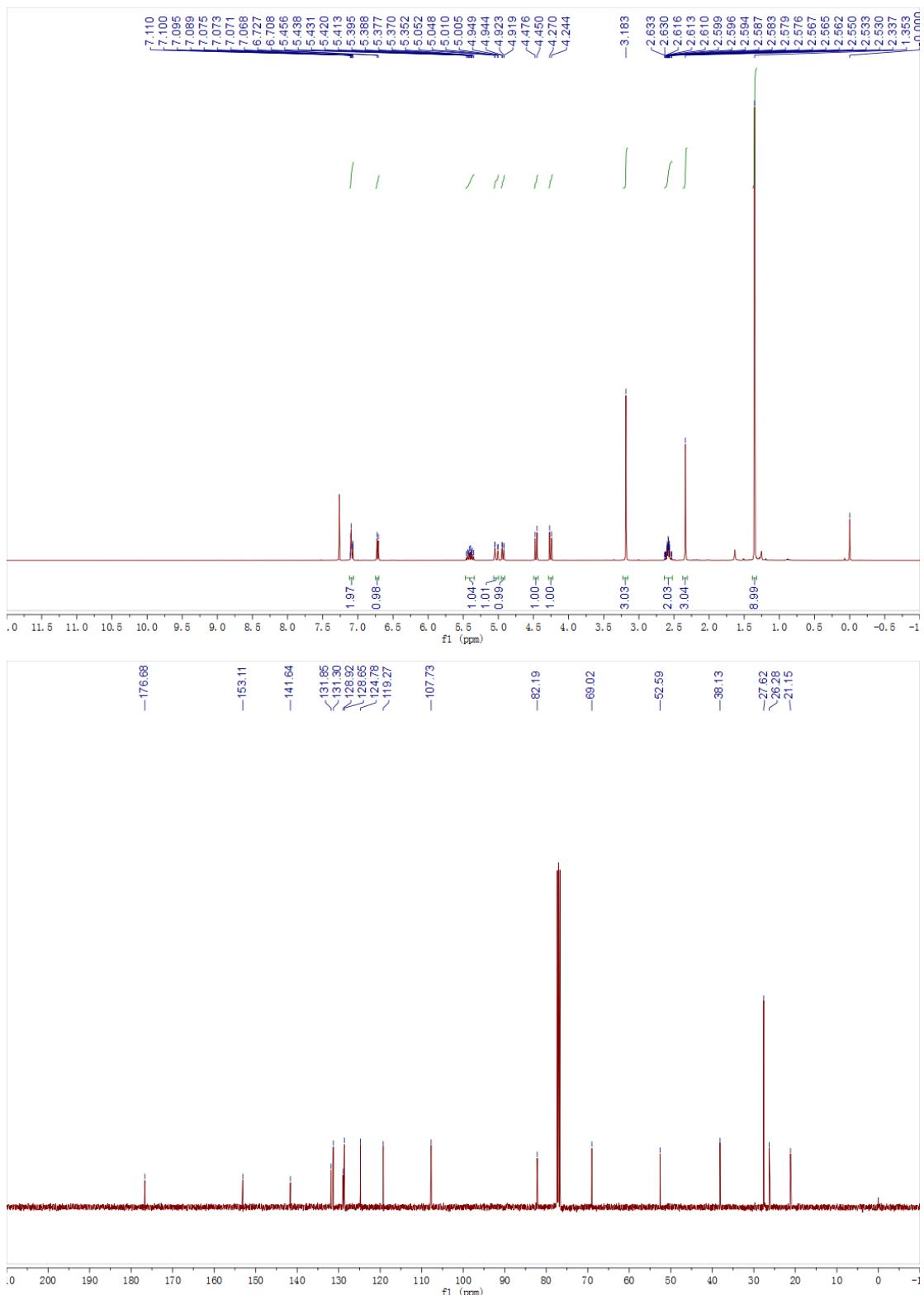
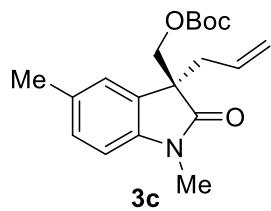


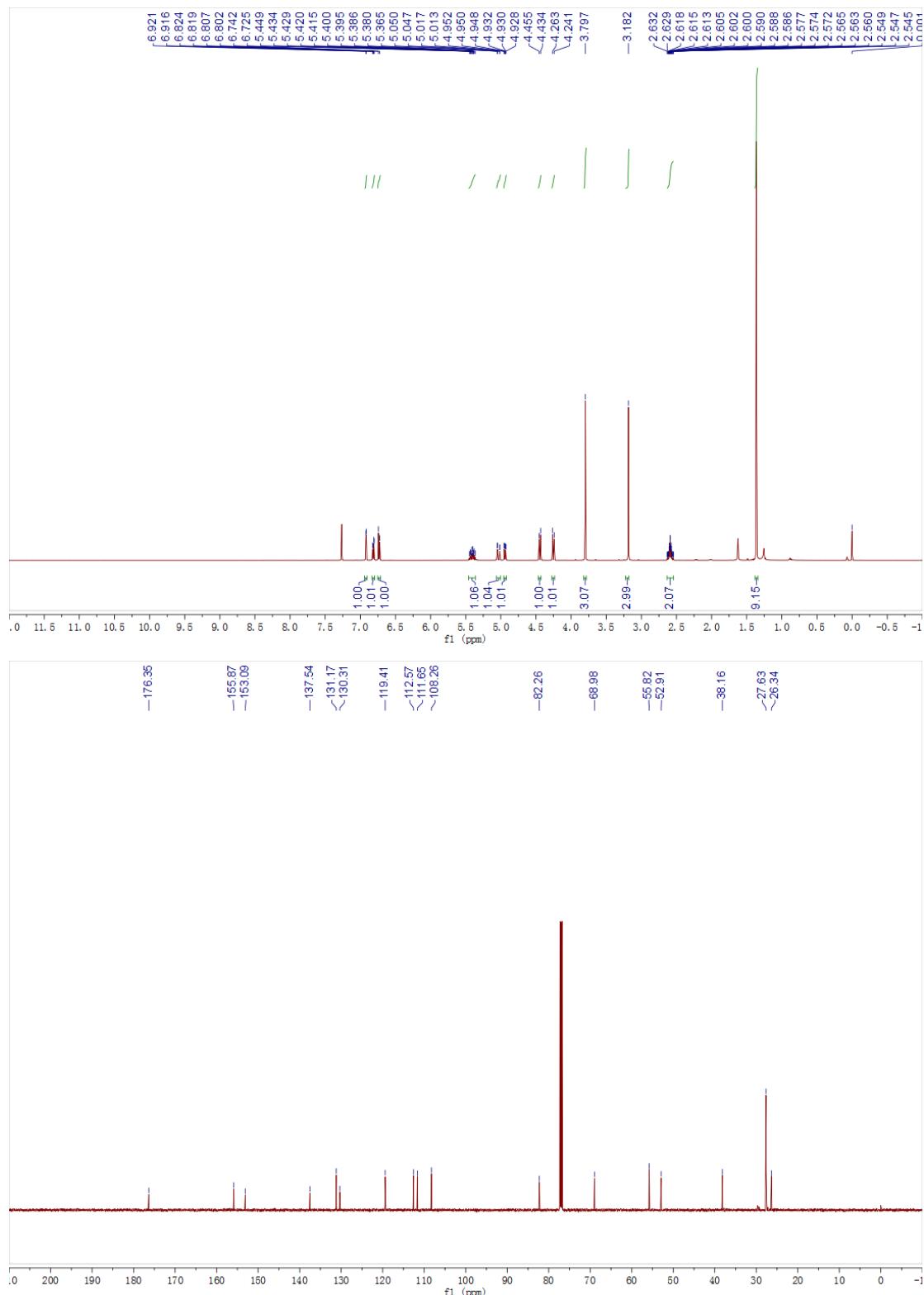
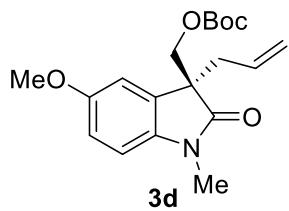


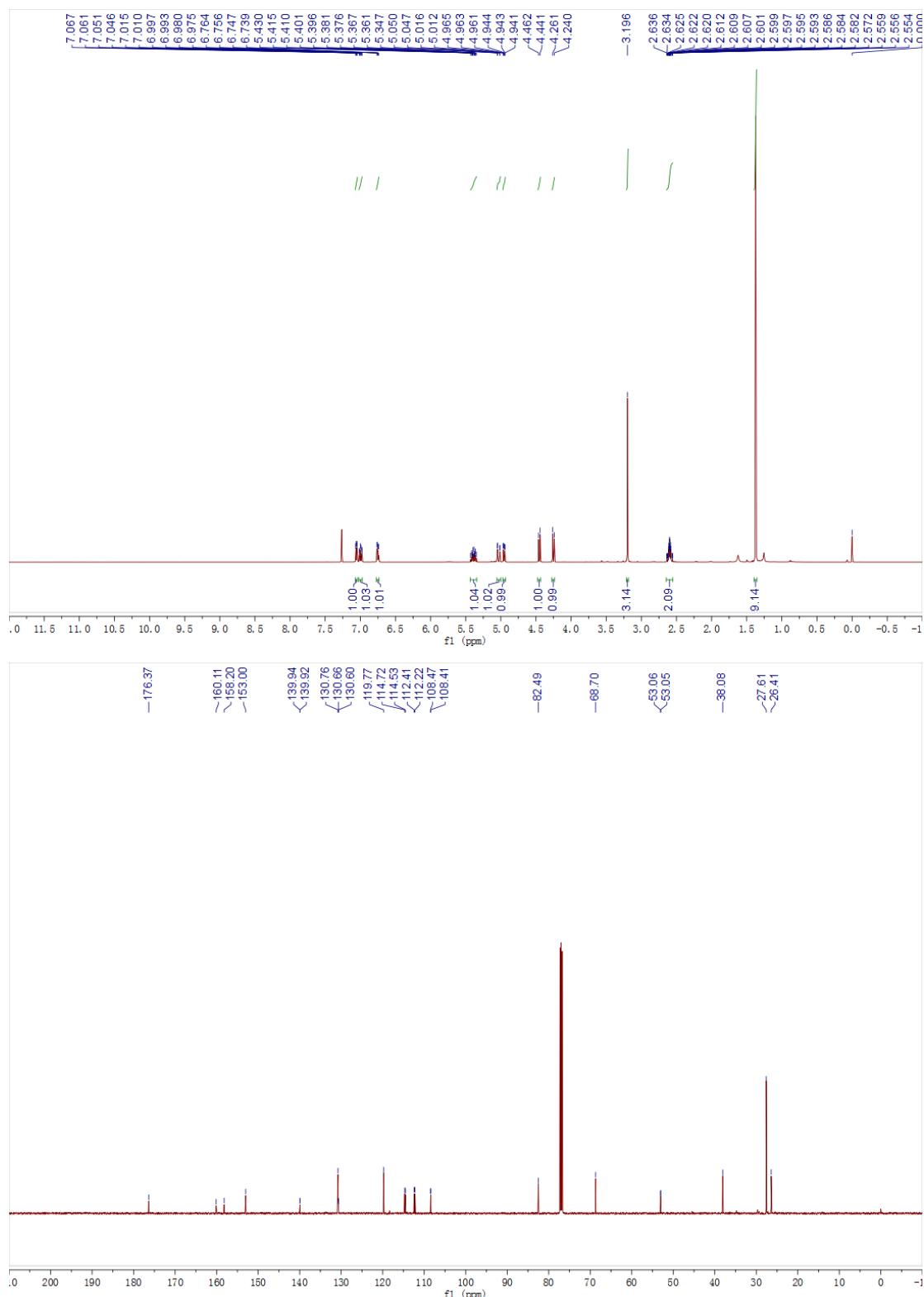
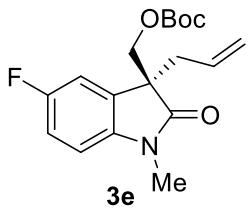


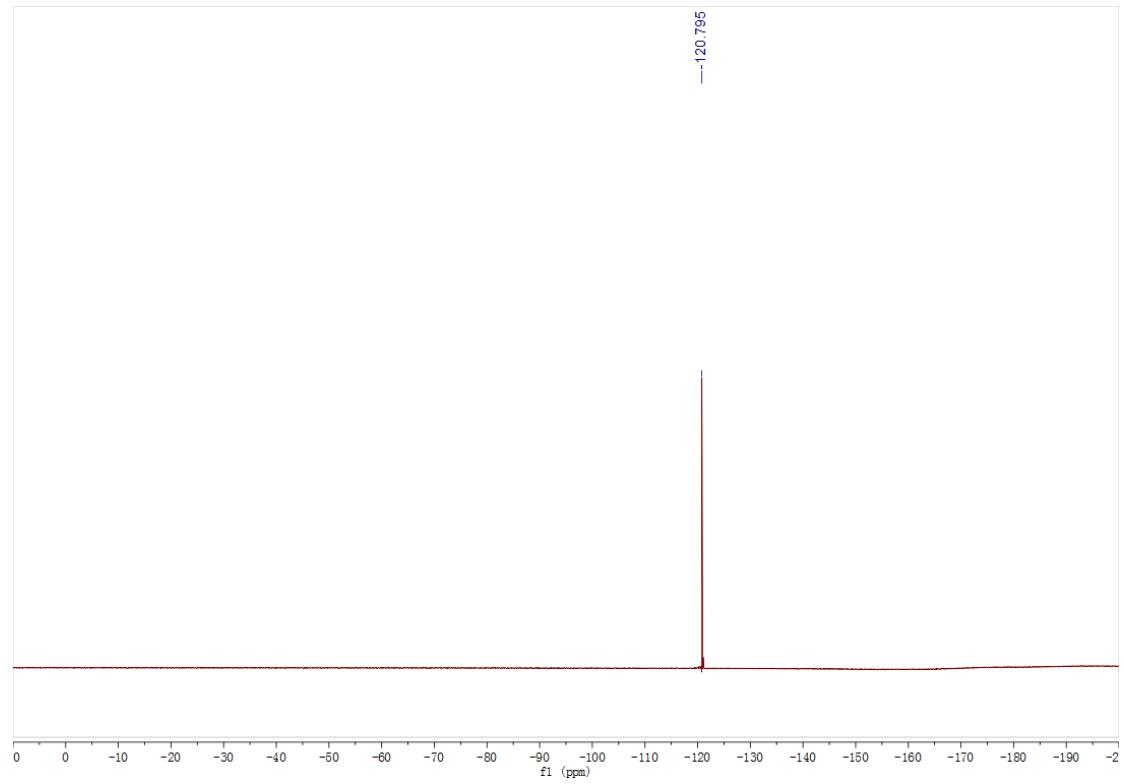


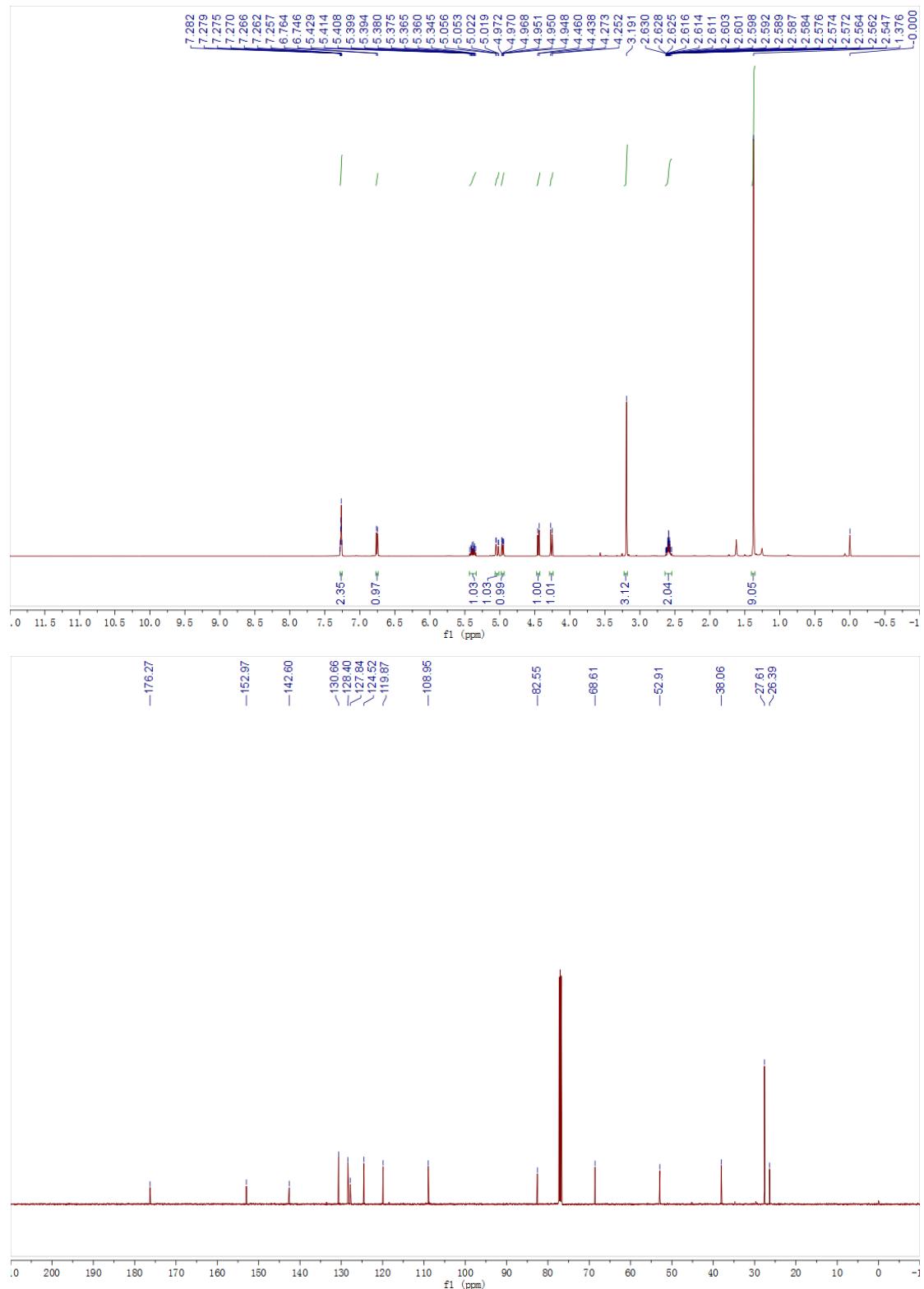
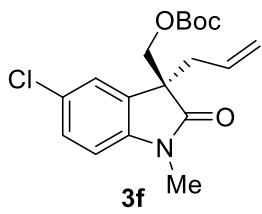


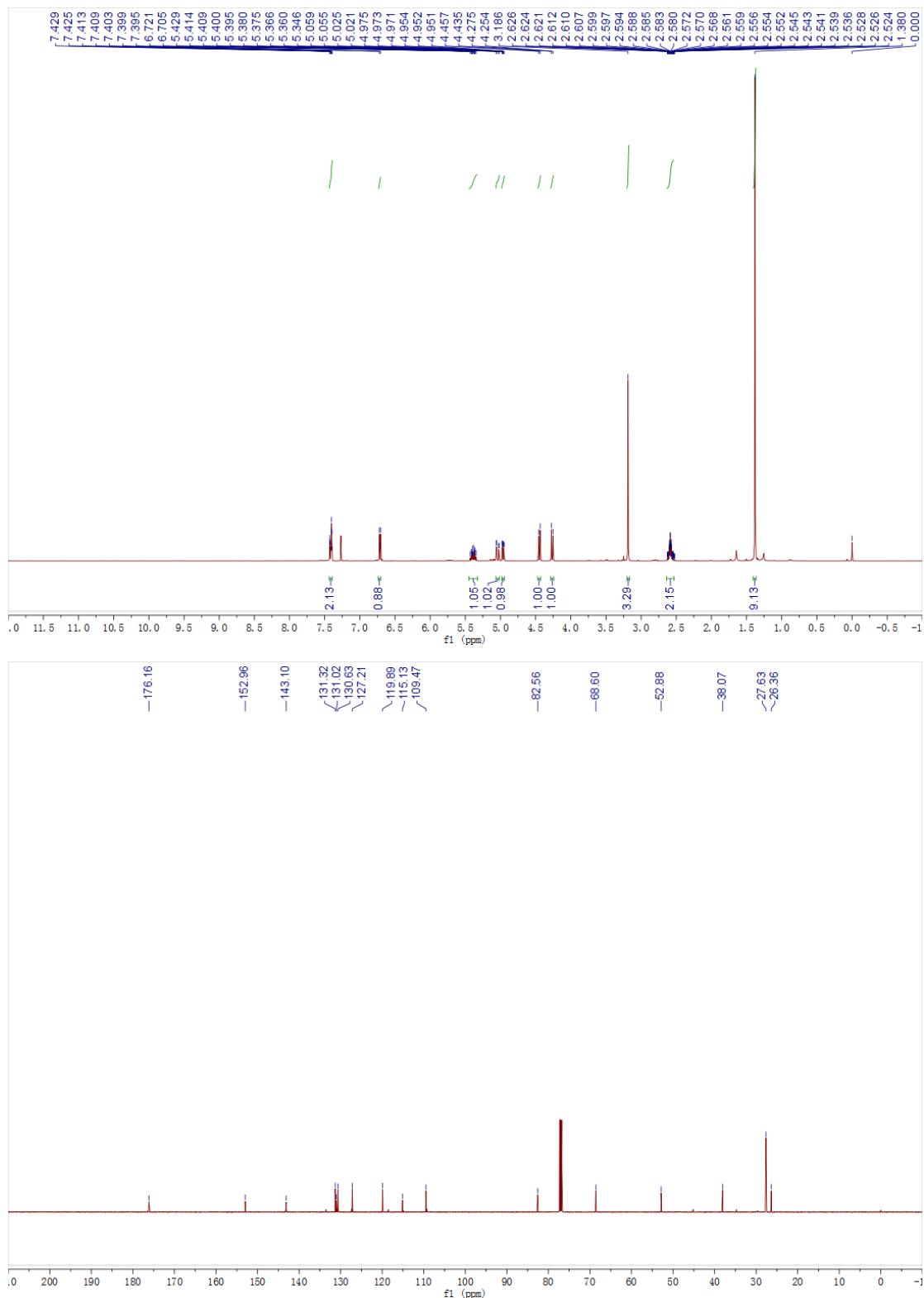
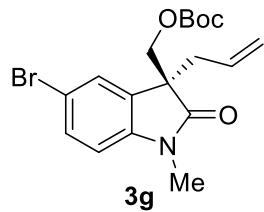


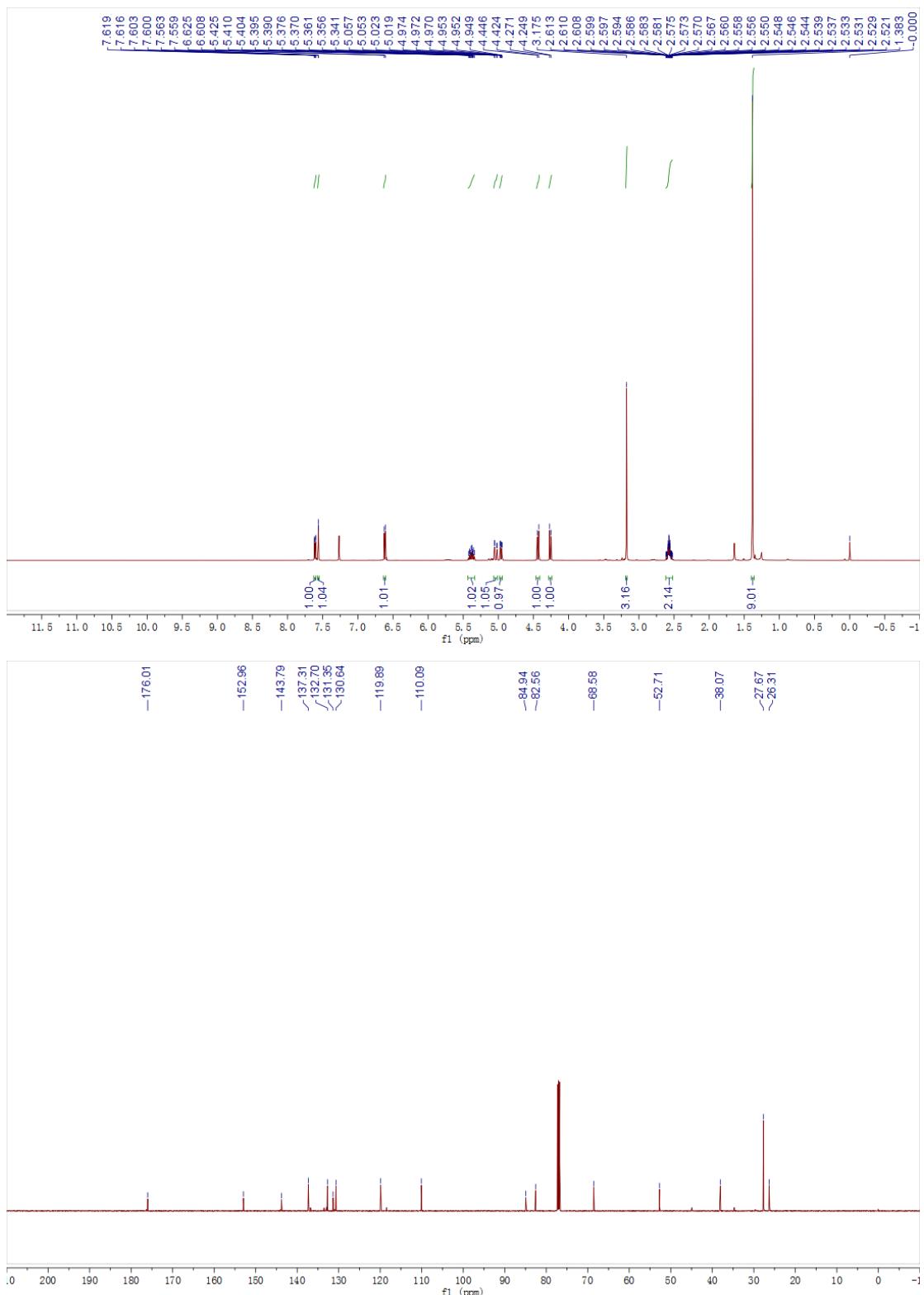
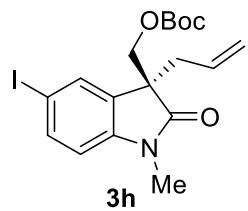


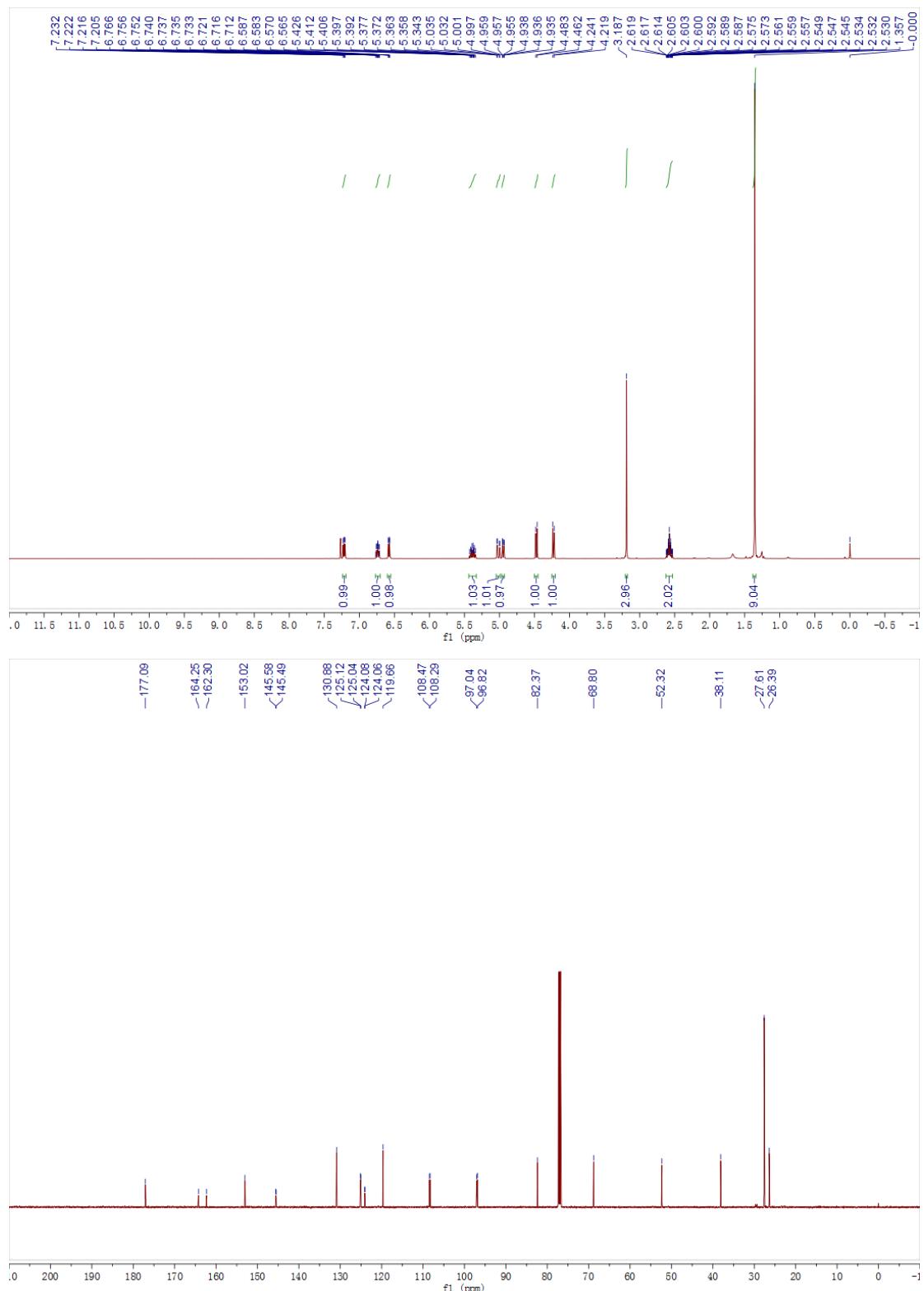
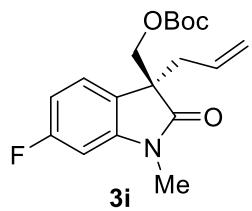


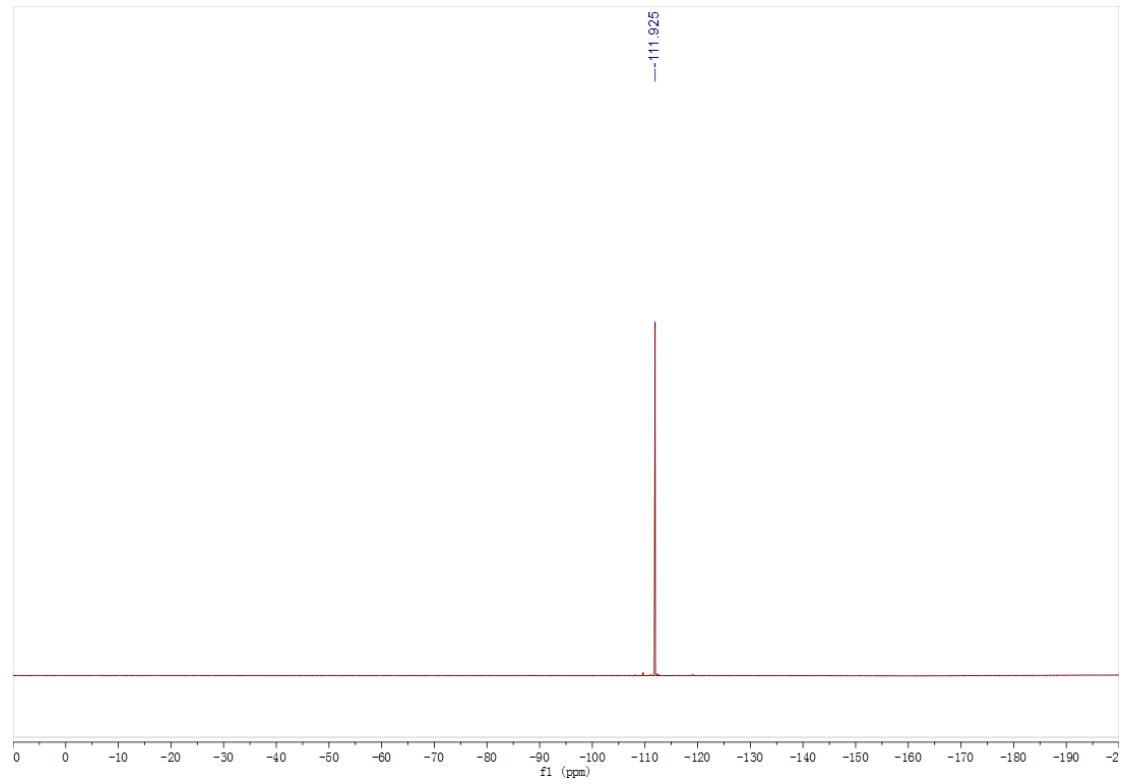


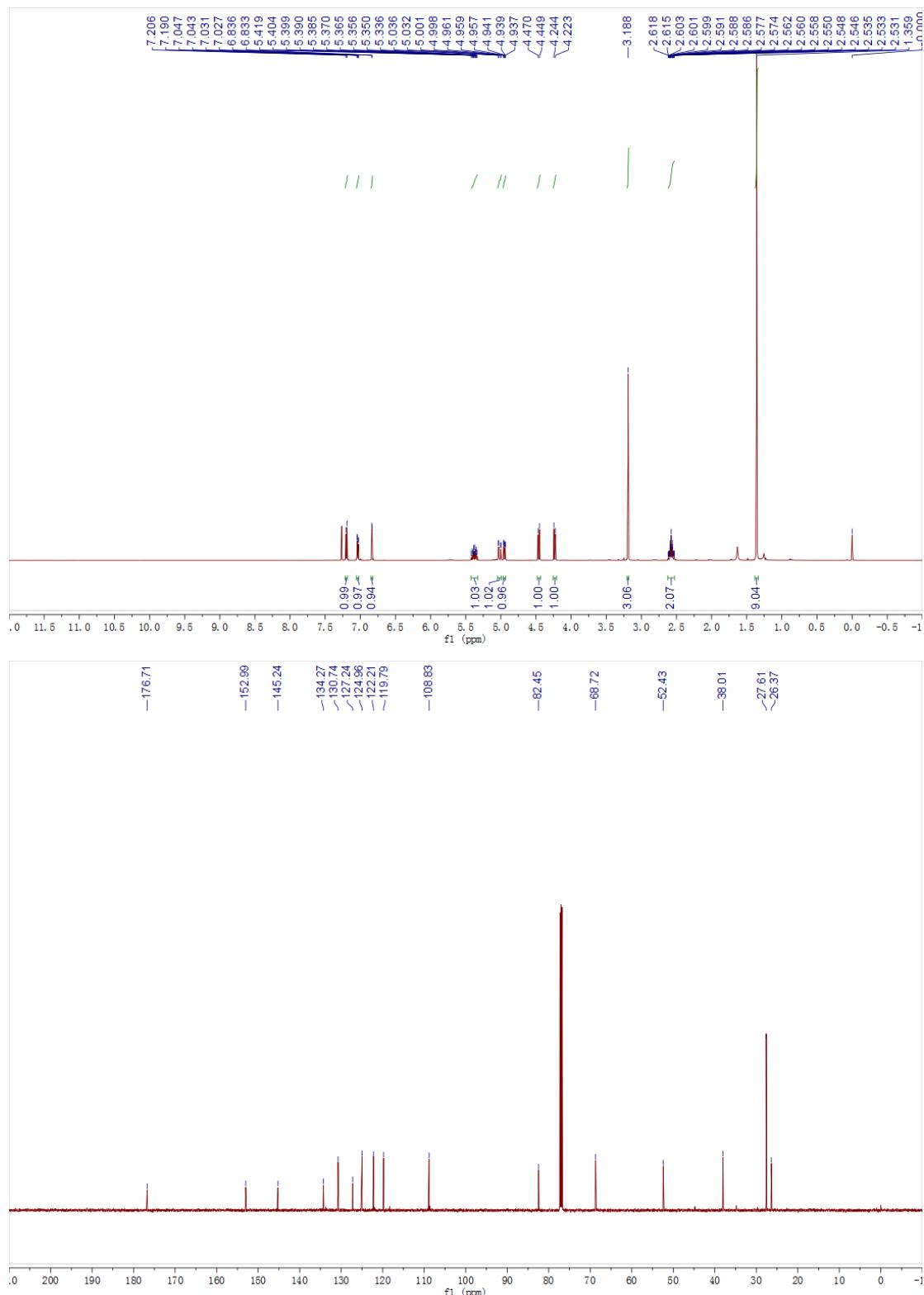
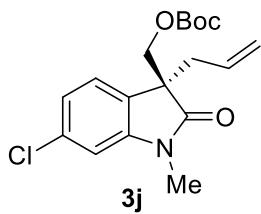


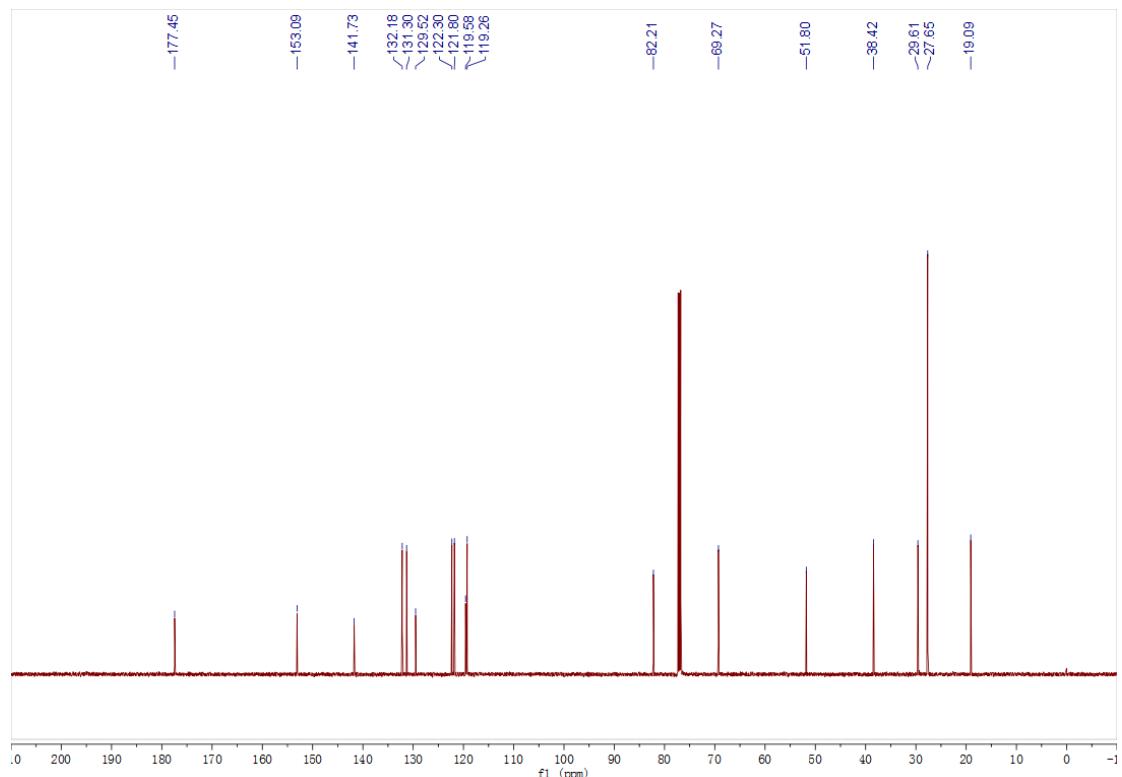
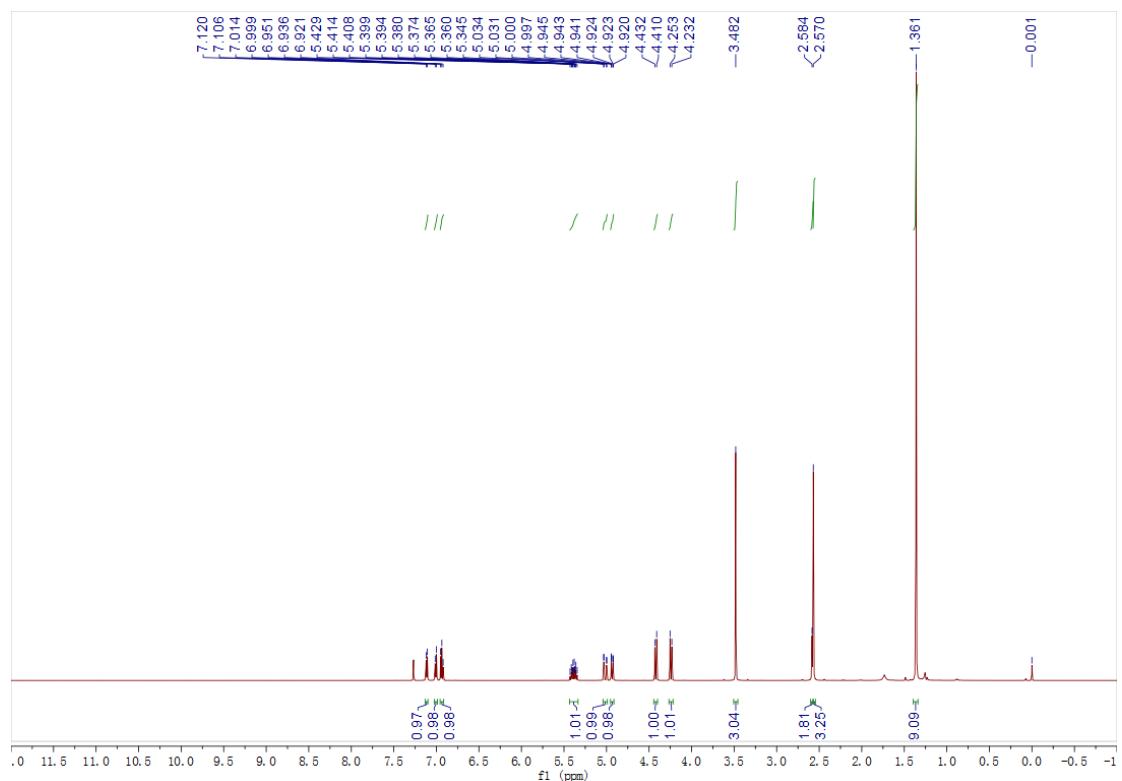
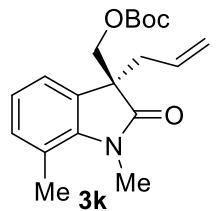


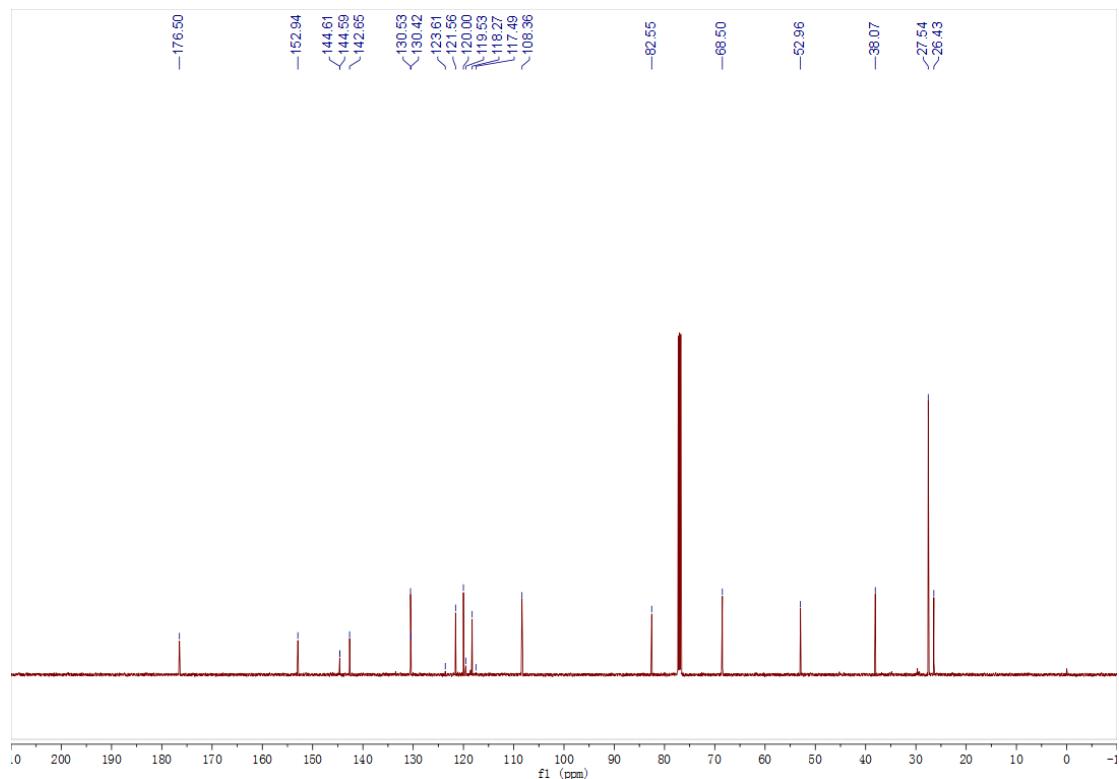
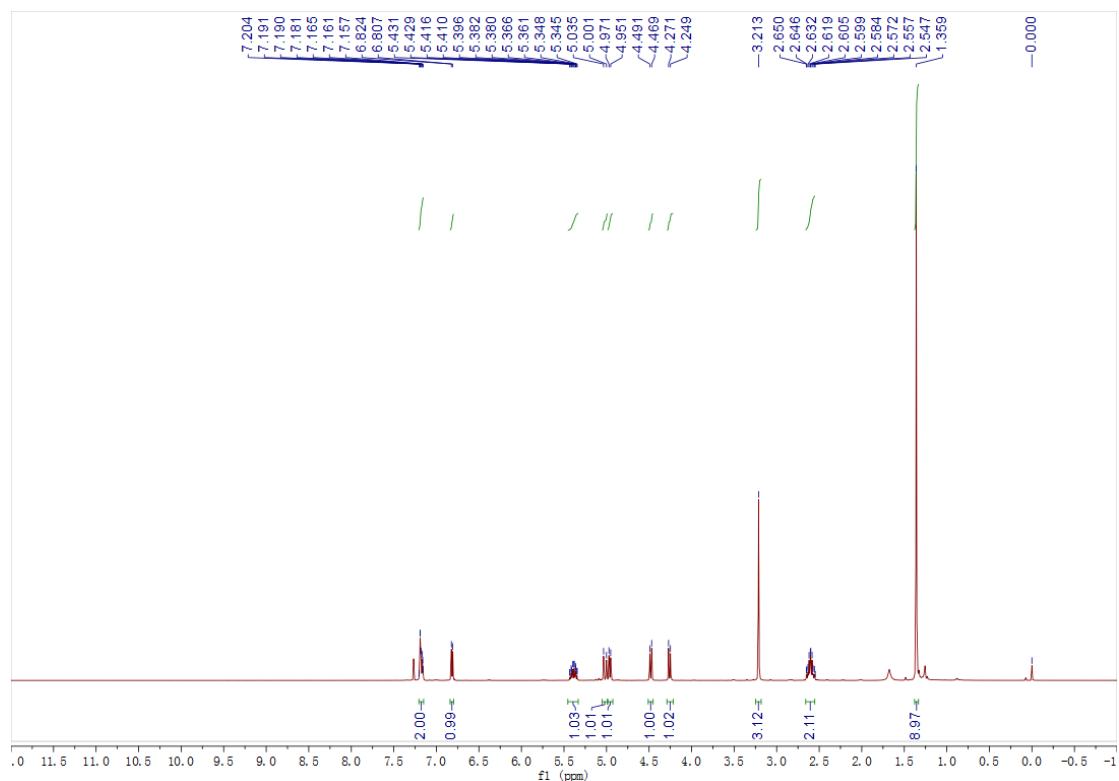
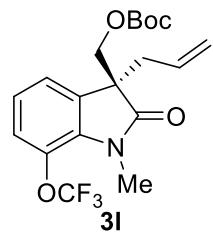


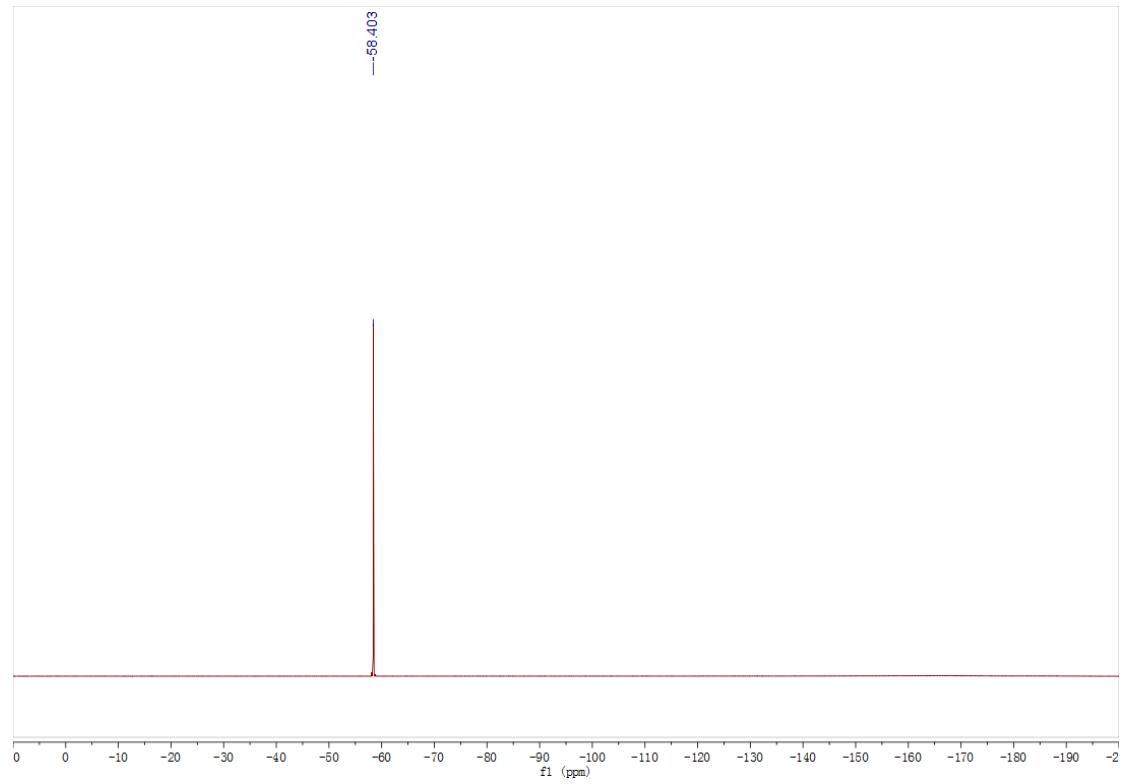




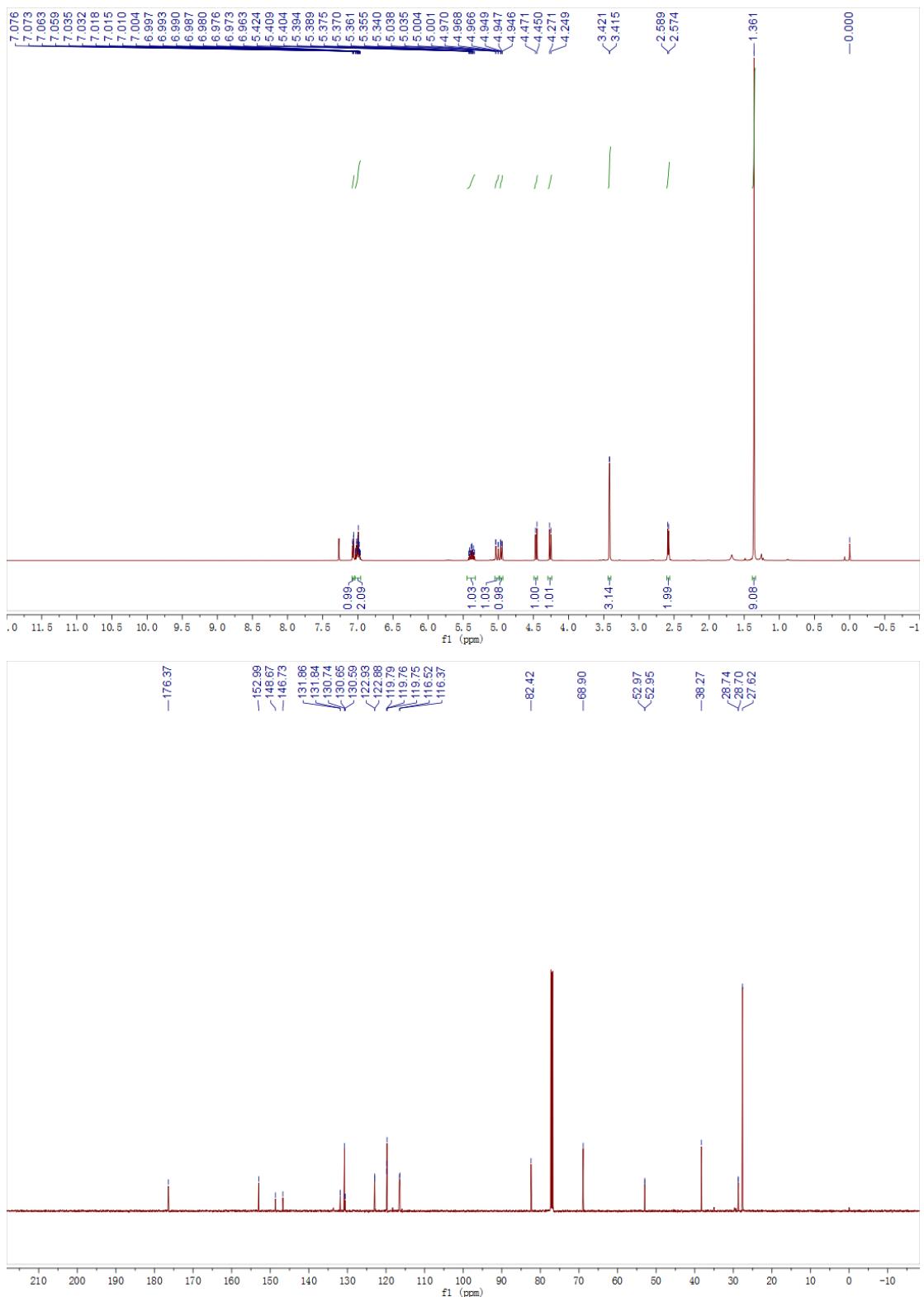
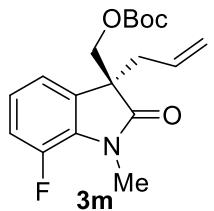


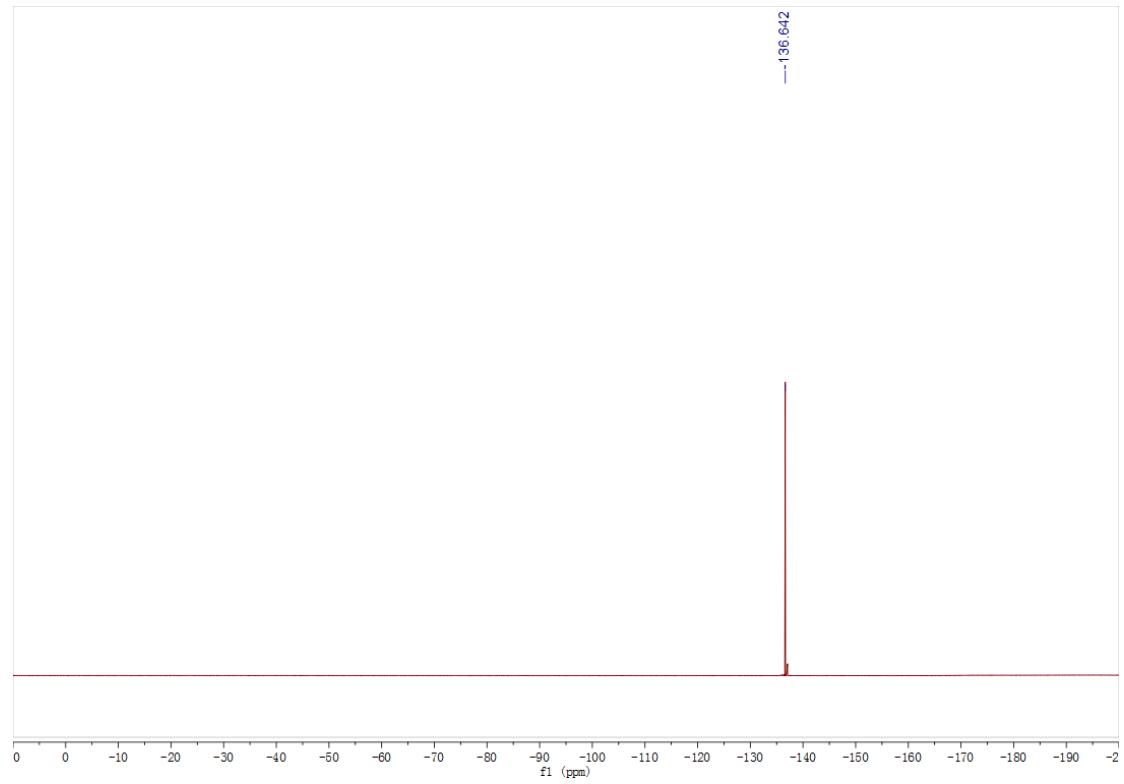


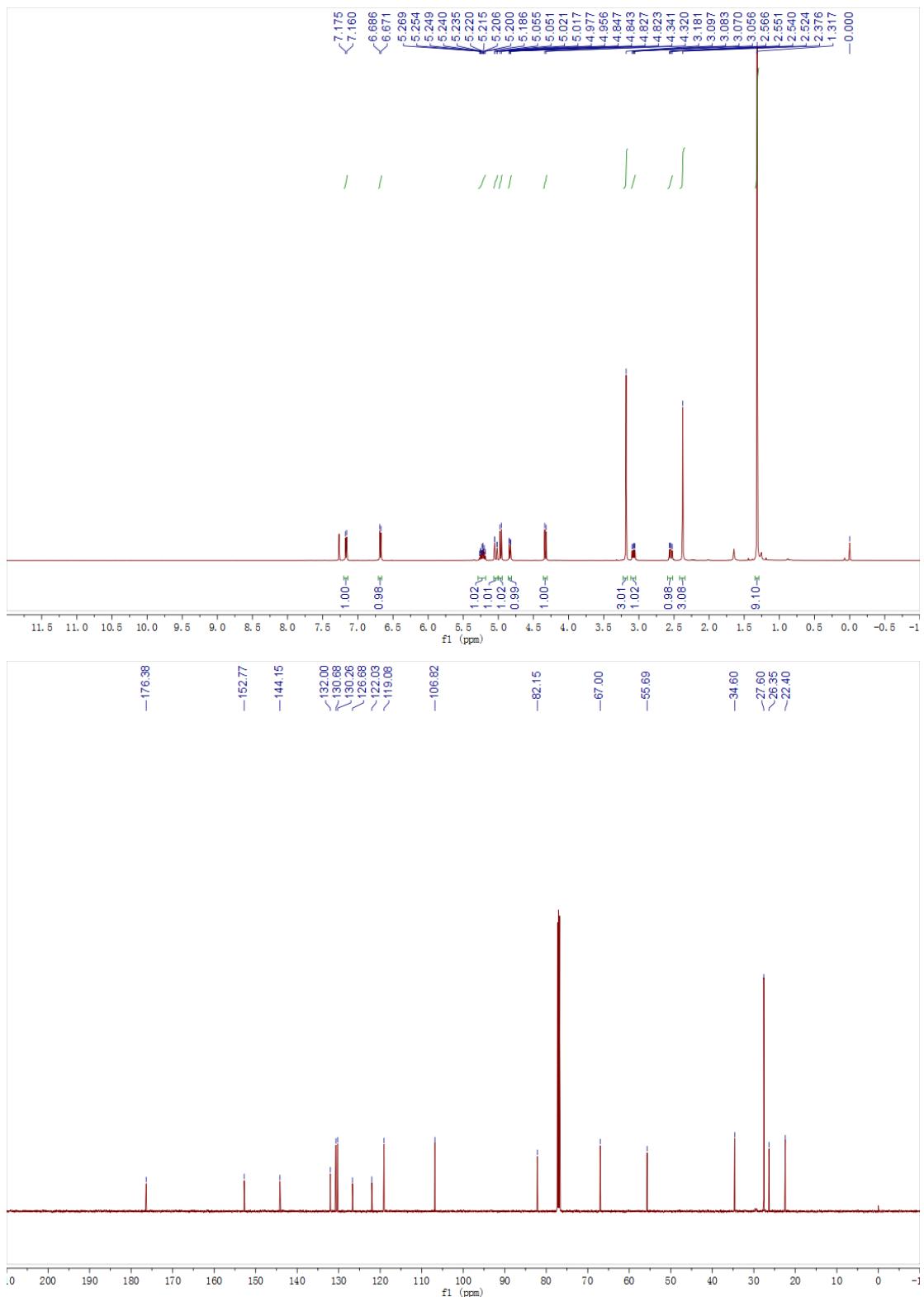
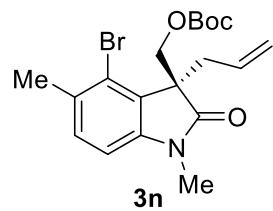


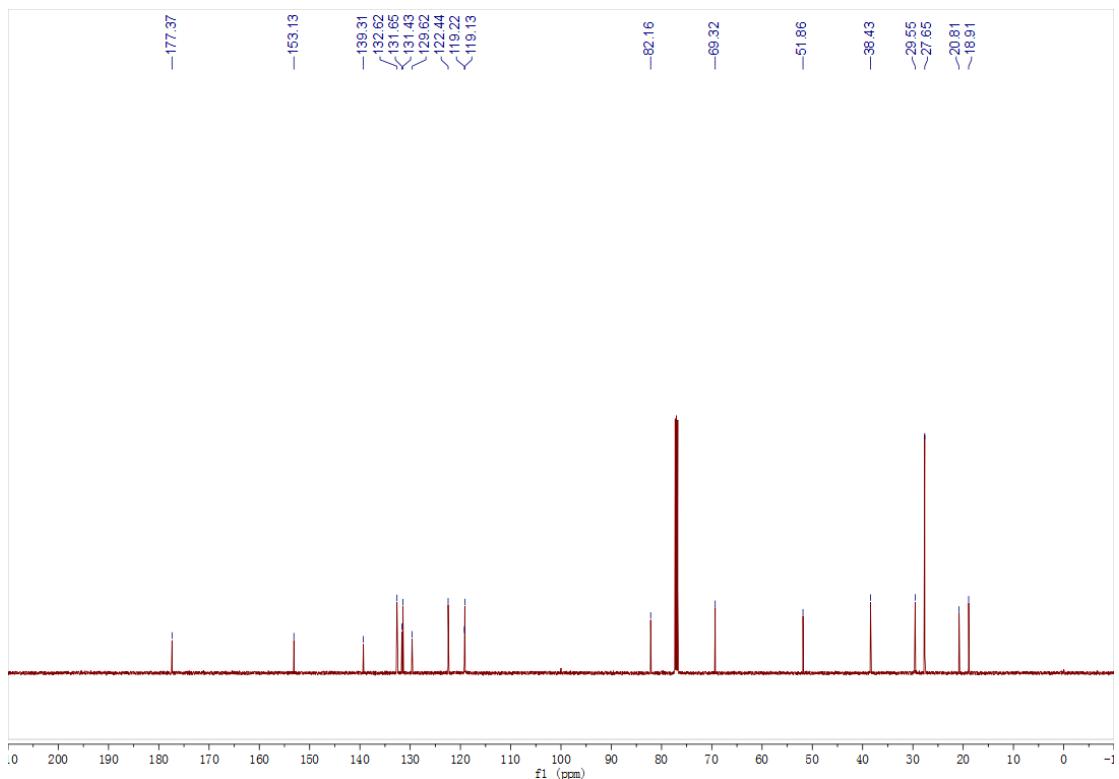
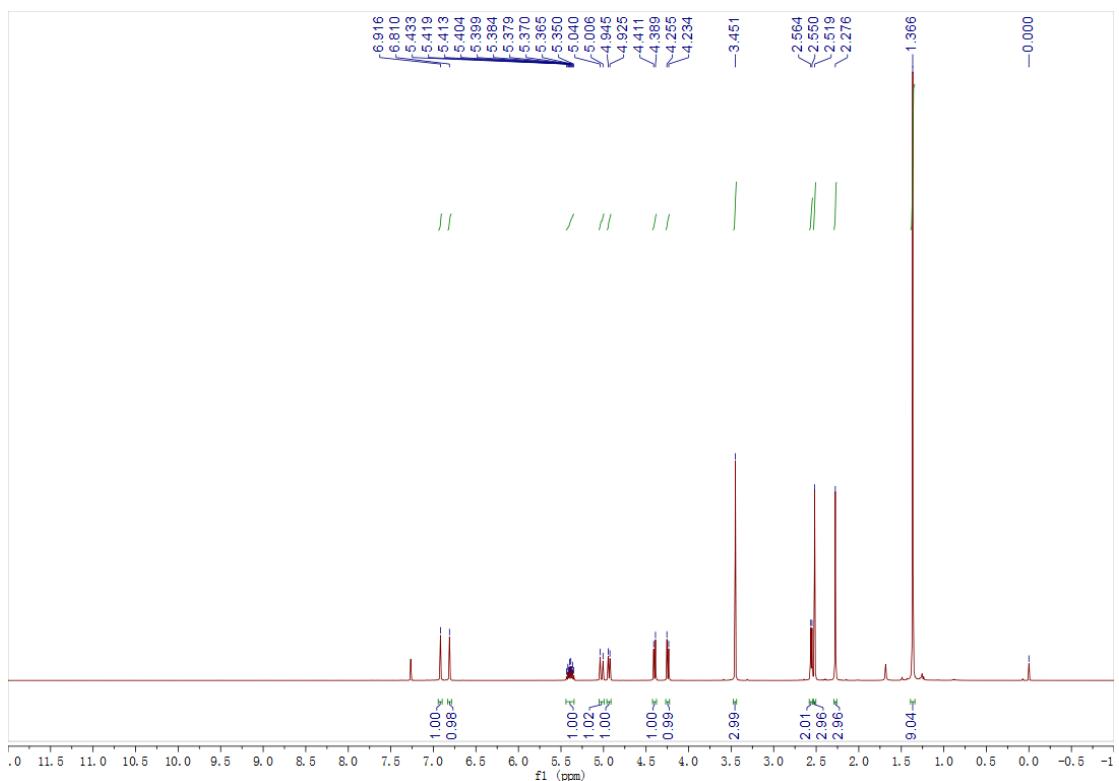
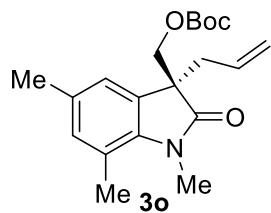


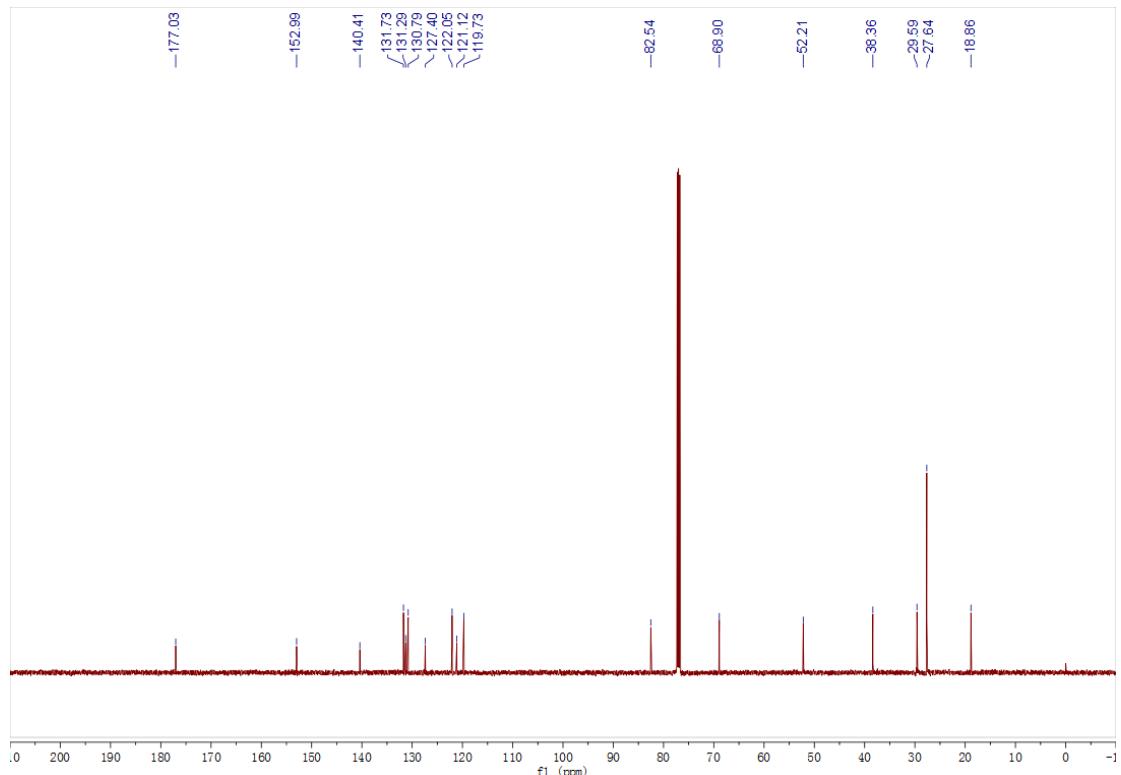
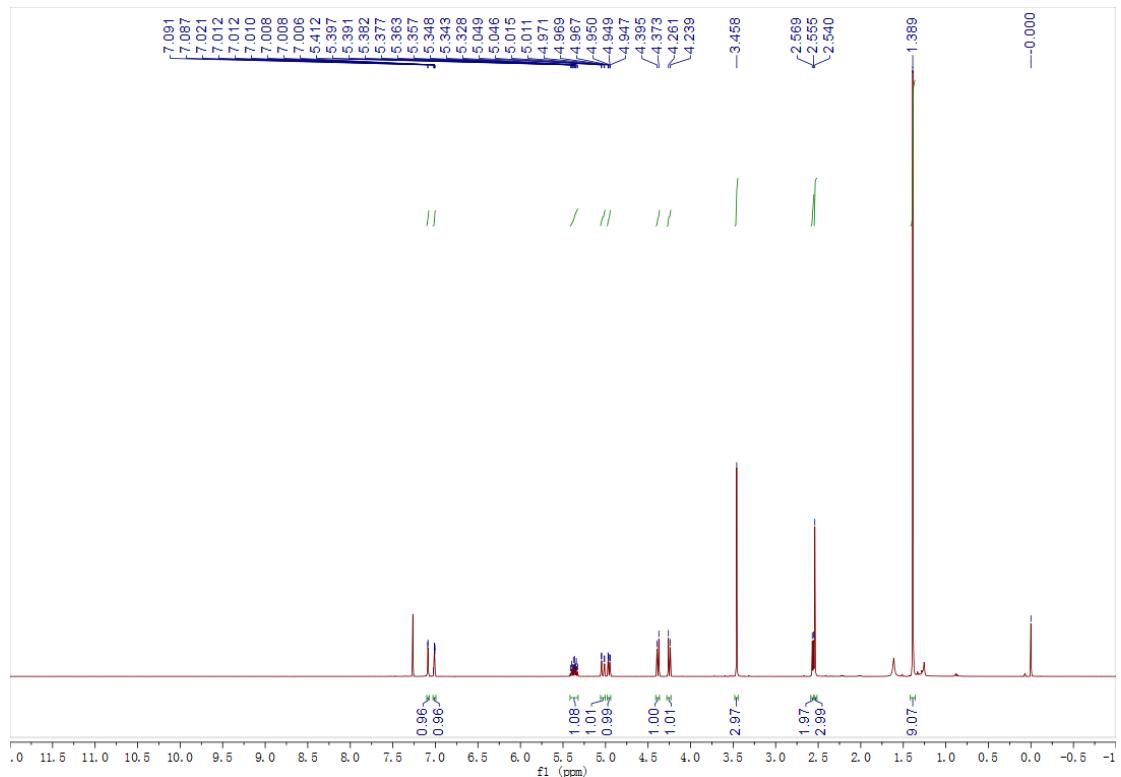
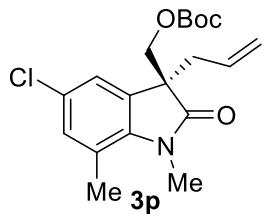
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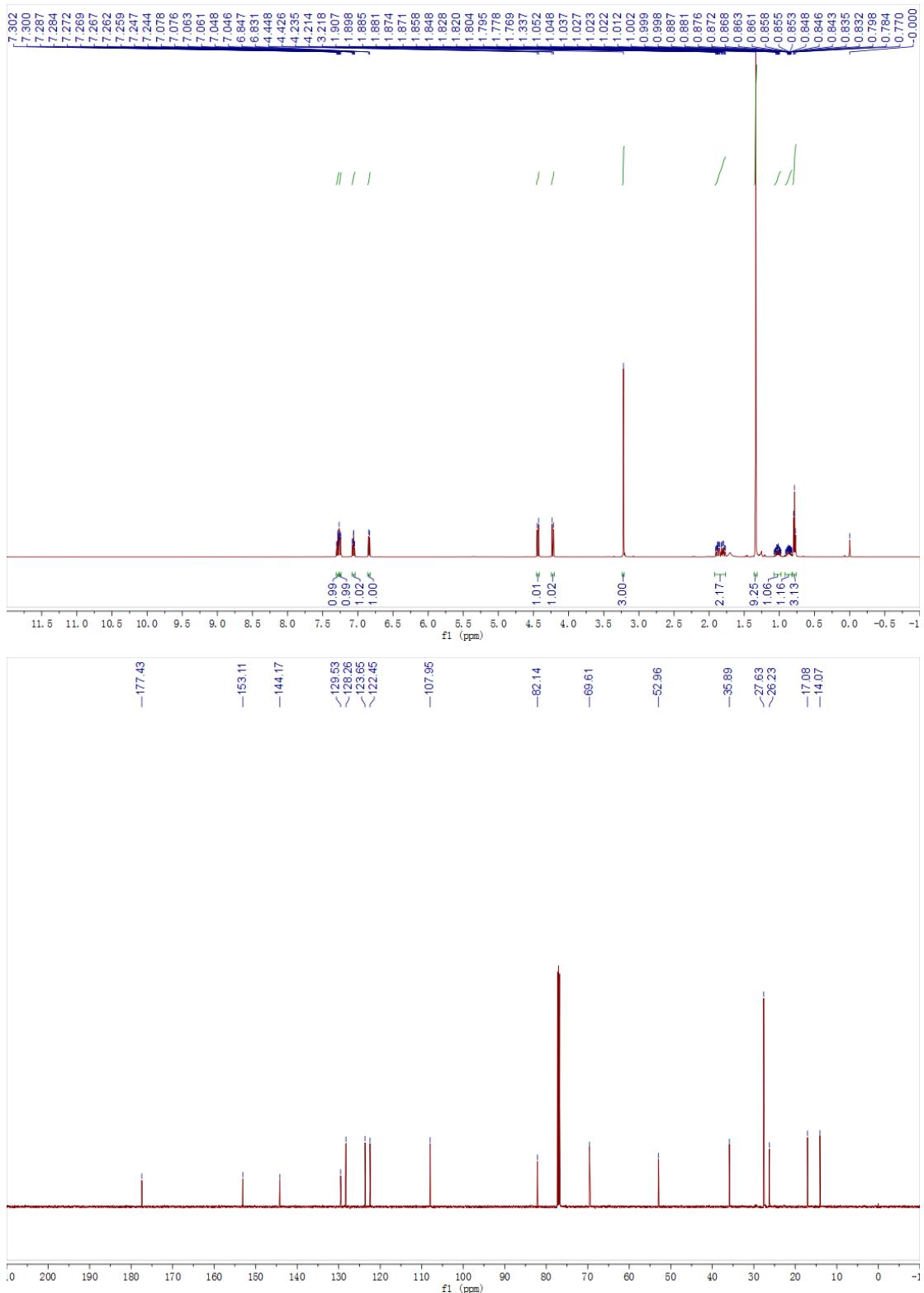
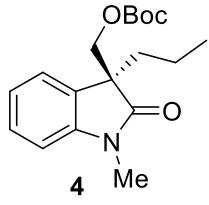


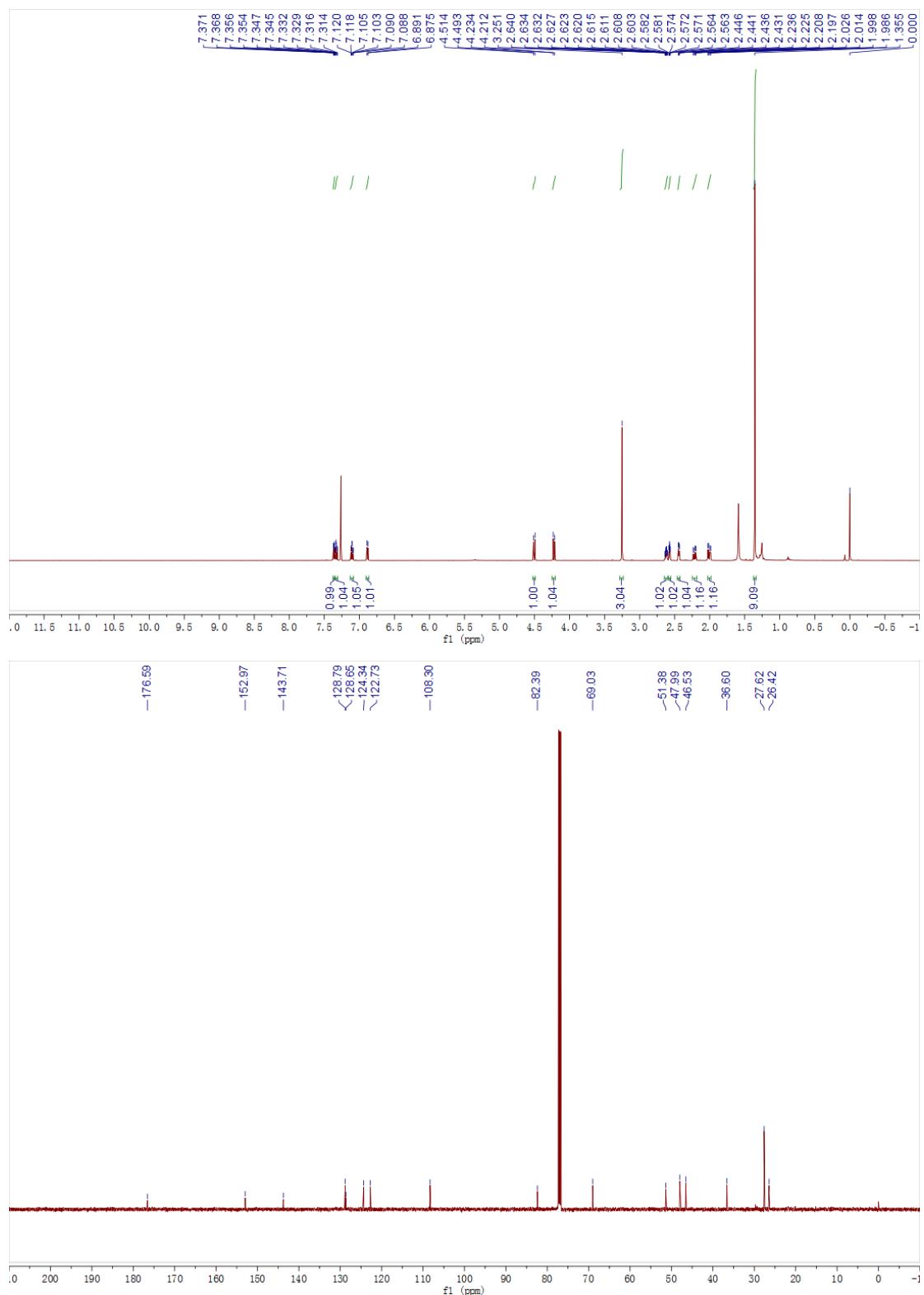
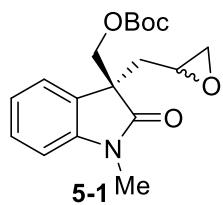


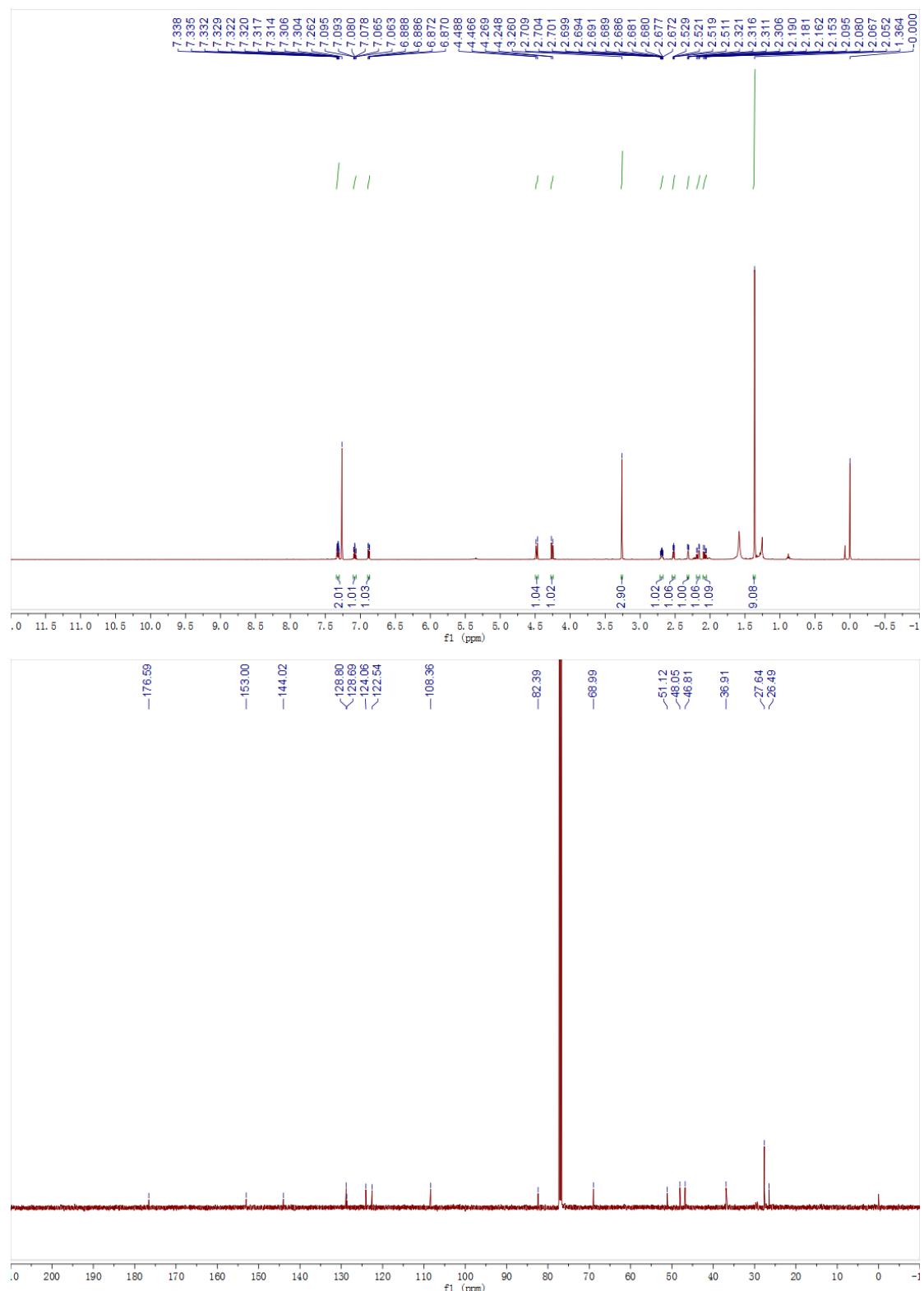
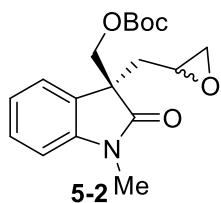


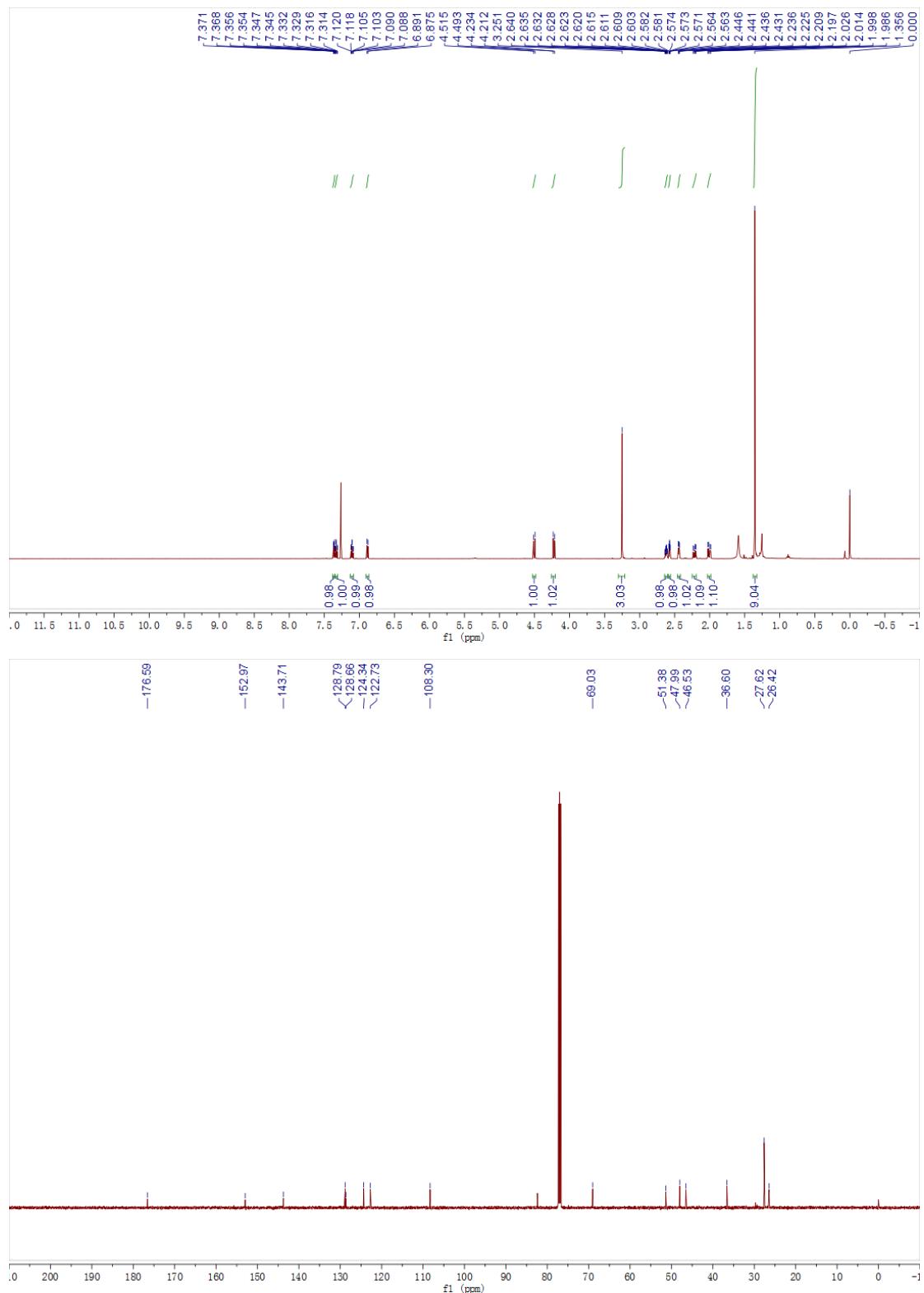
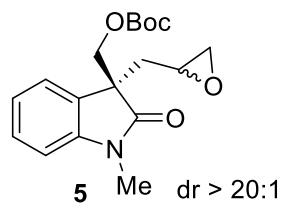


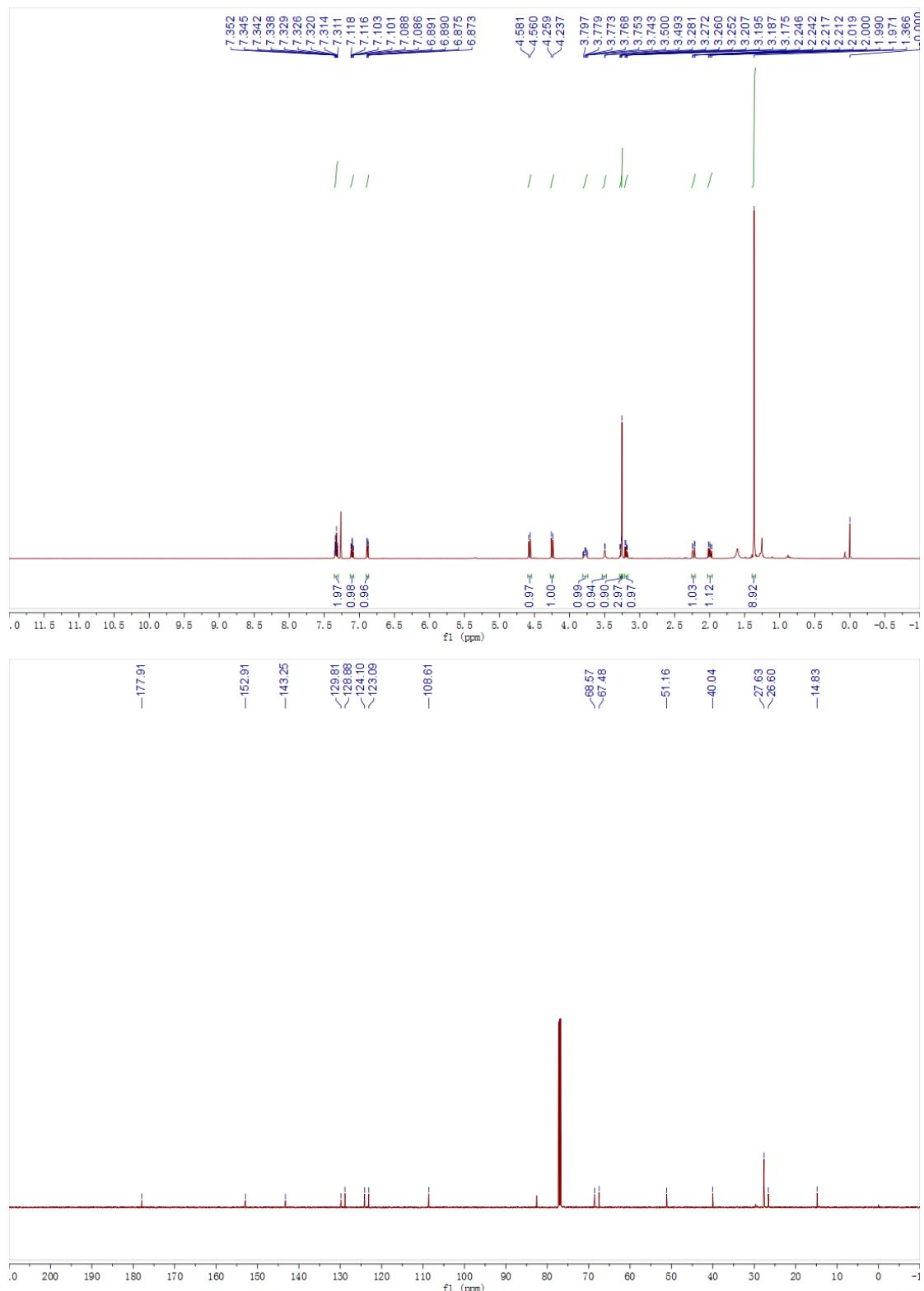
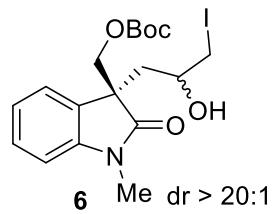


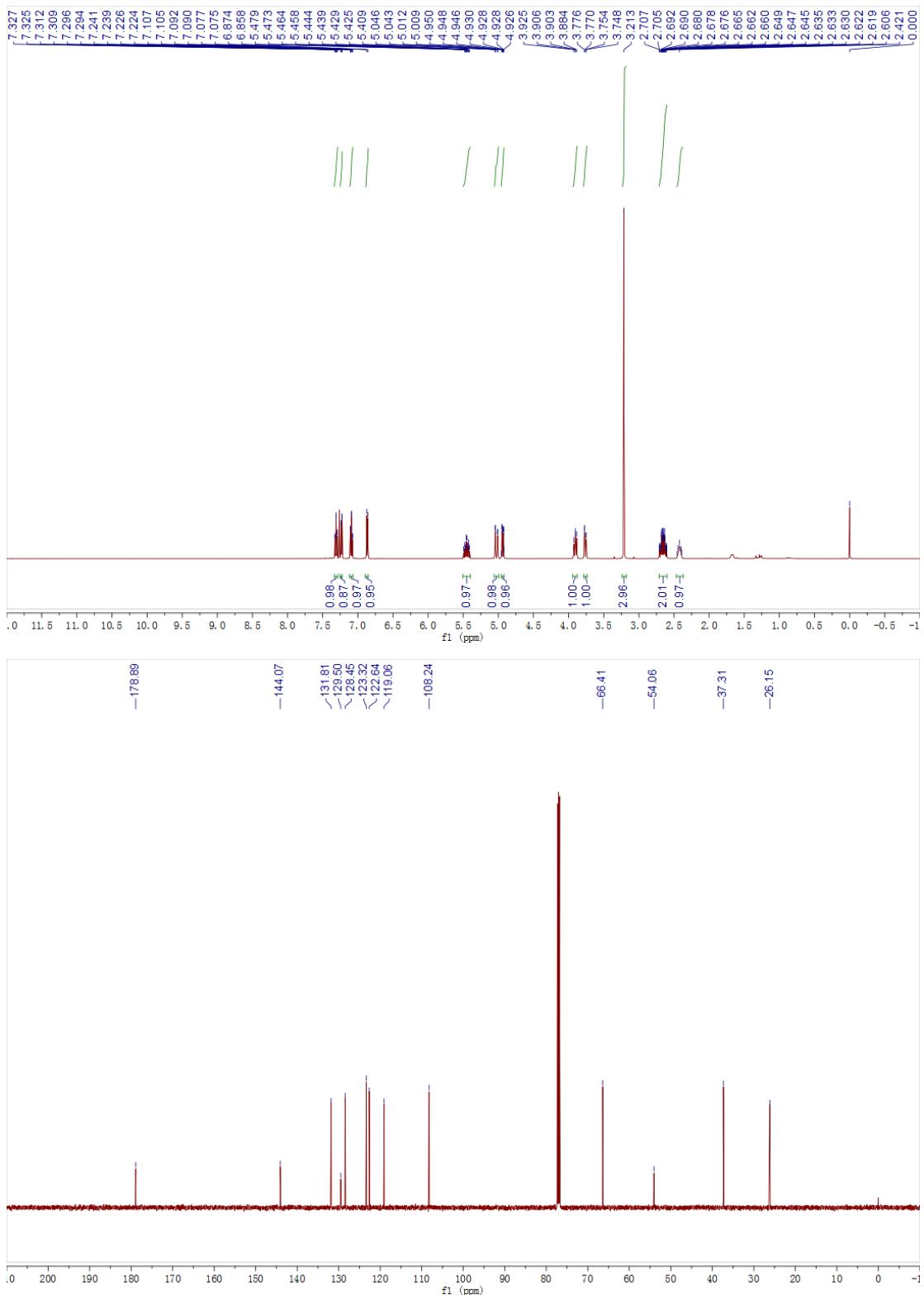
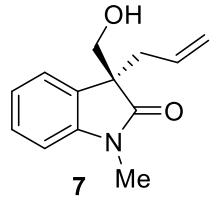


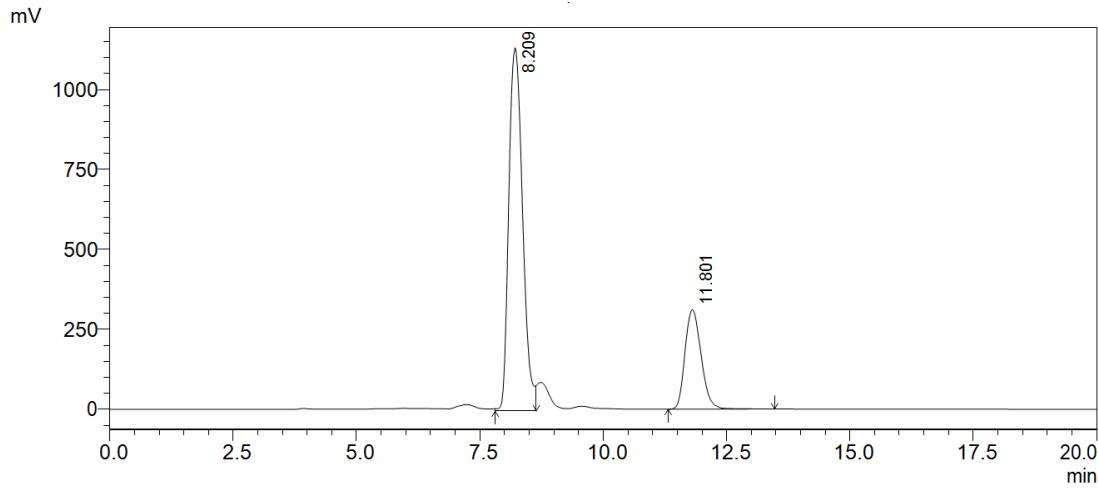
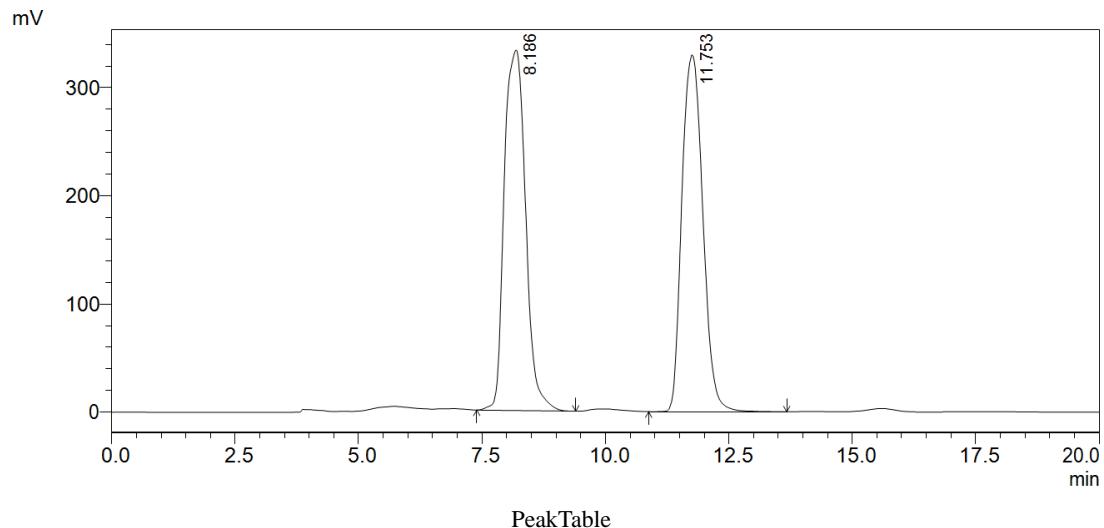
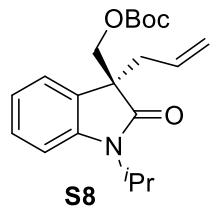


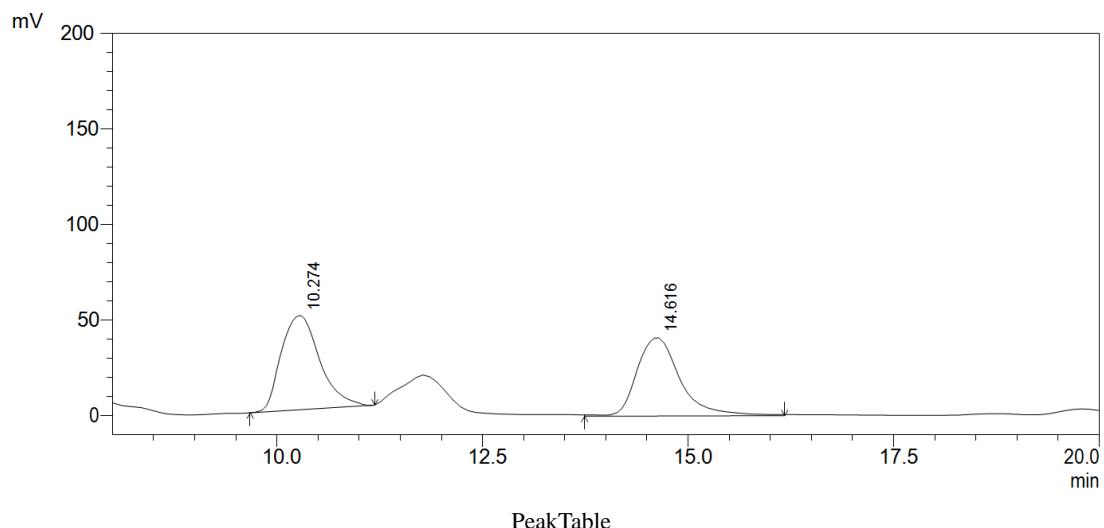
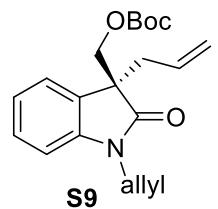




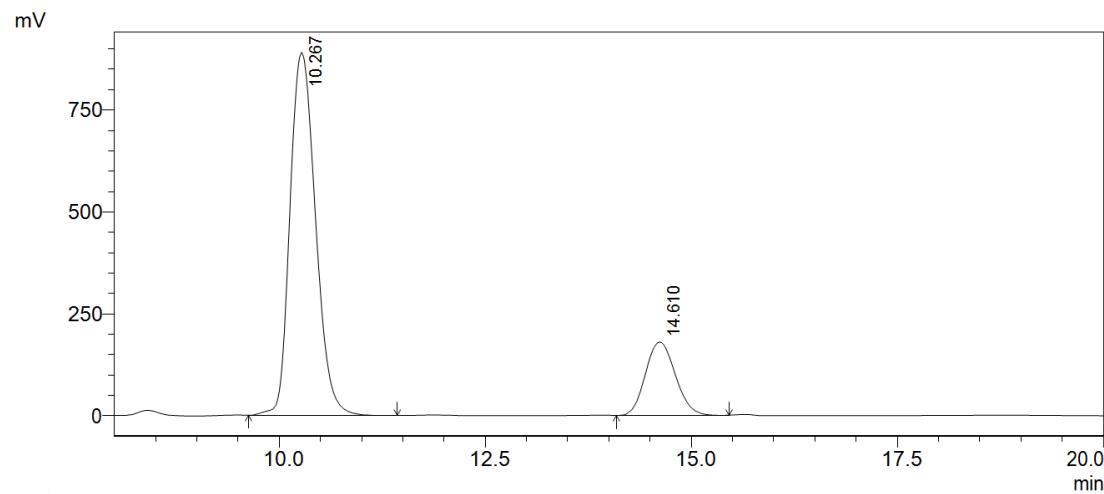






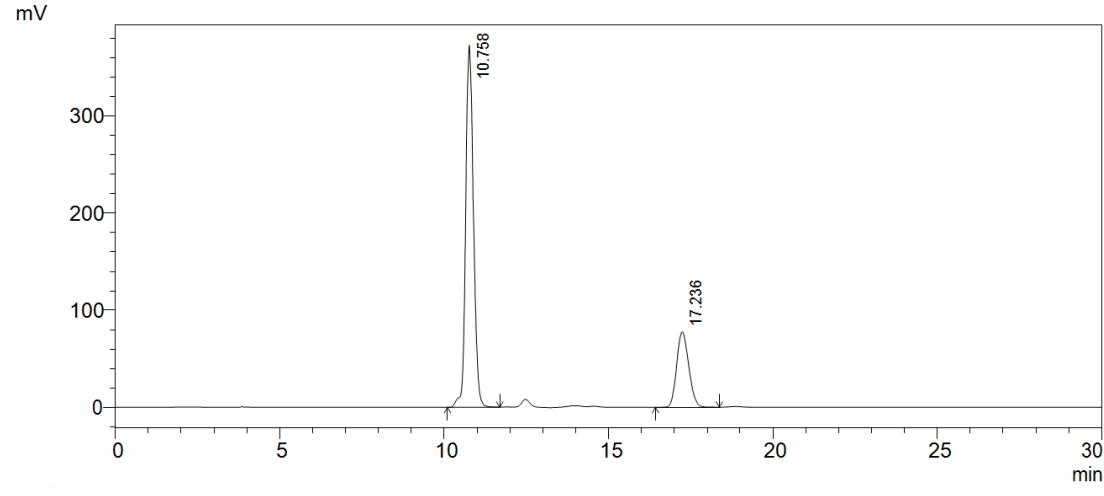
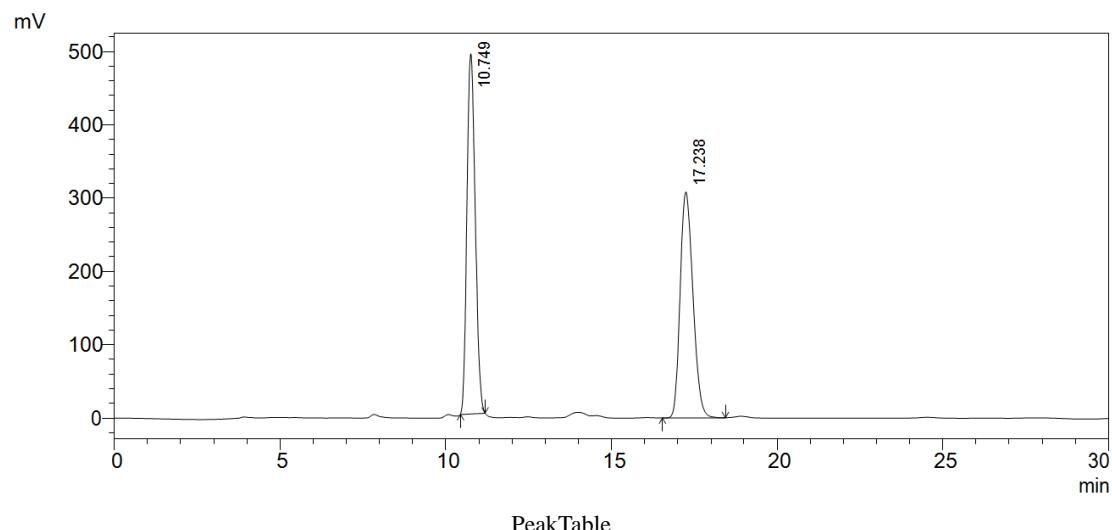
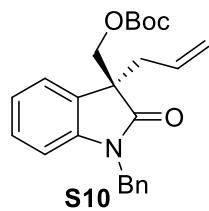


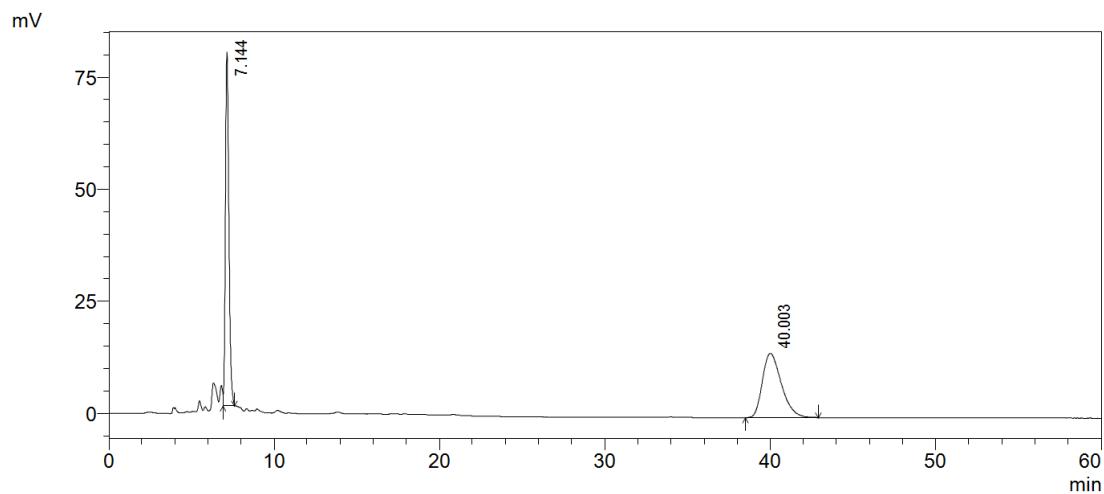
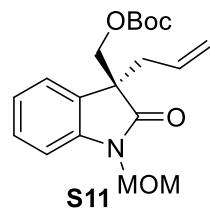
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.274	1605314	49409	51.761	54.590
2	14.616	1496098	41100	48.239	45.410
Total		3101413	90509	100.000	100.000



PeakTable

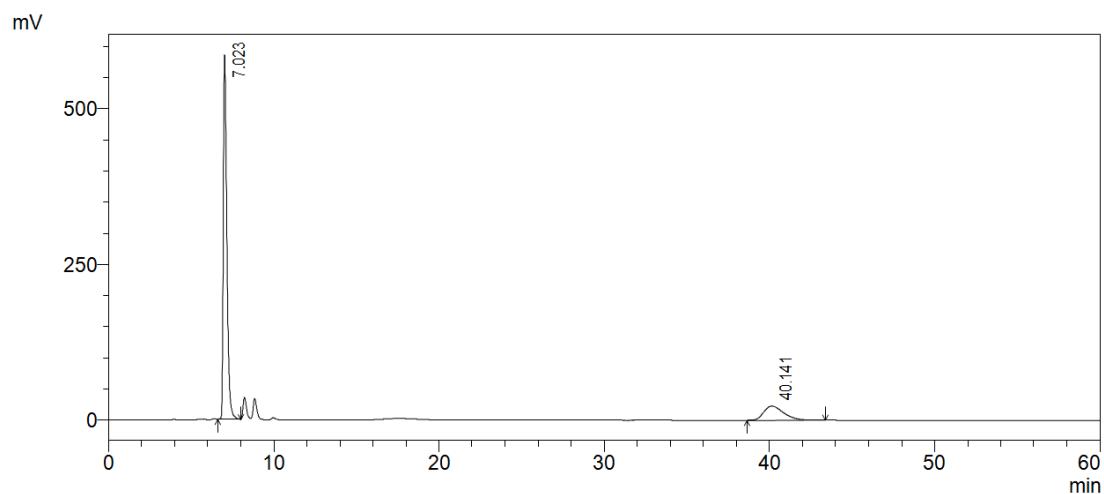
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.267	19190773	890459	80.888	83.159
2	14.610	4534215	180337	19.112	16.841
Total		23724989	1070797	100.000	100.000





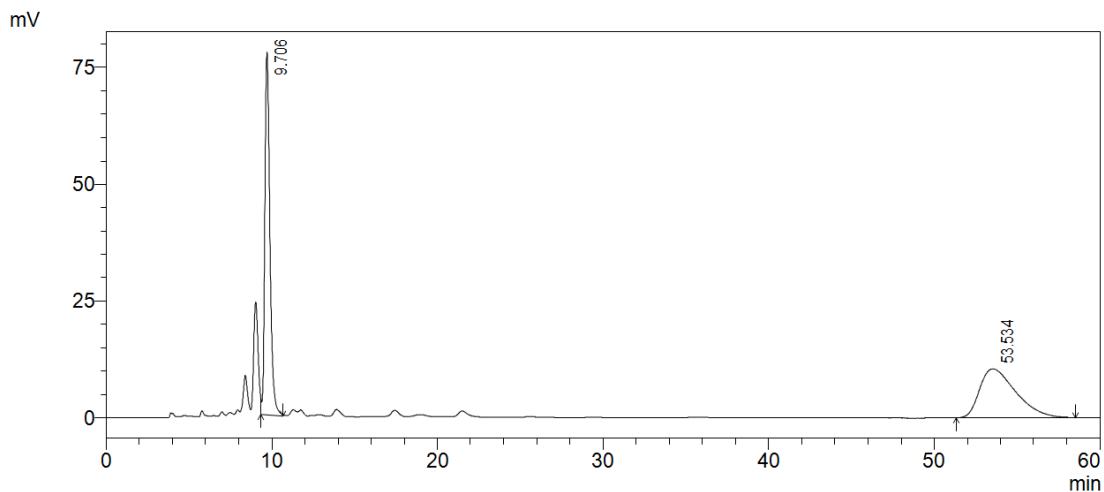
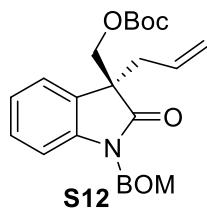
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.144	1145313	78905	49.939	84.603
2	40.003	1148099	14360	50.061	15.397
Total		2293412	93264	100.000	100.000



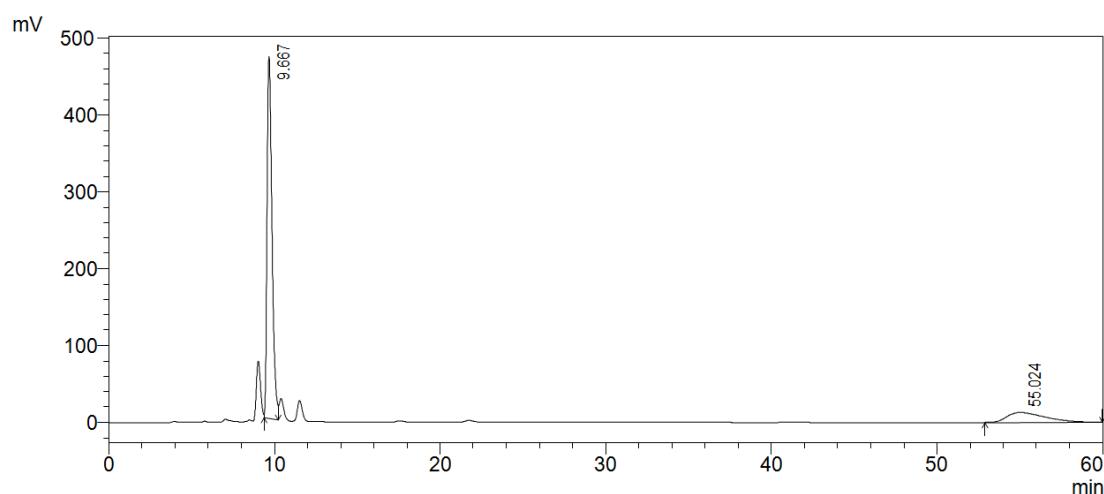
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.023	8763570	585279	82.054	96.251
2	40.141	1916646	22796	17.946	3.749
Total		10680217	608075	100.000	100.000



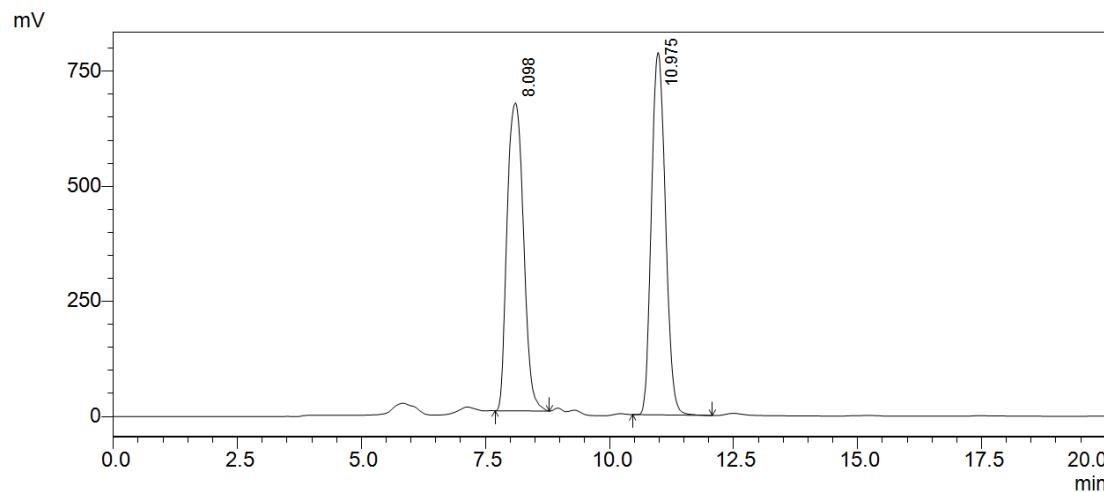
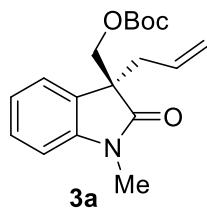
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.706	1646604	77586	50.854	88.098
2	53.534	1591301	10482	49.146	11.902
Total		3237905	88068	100.000	100.000



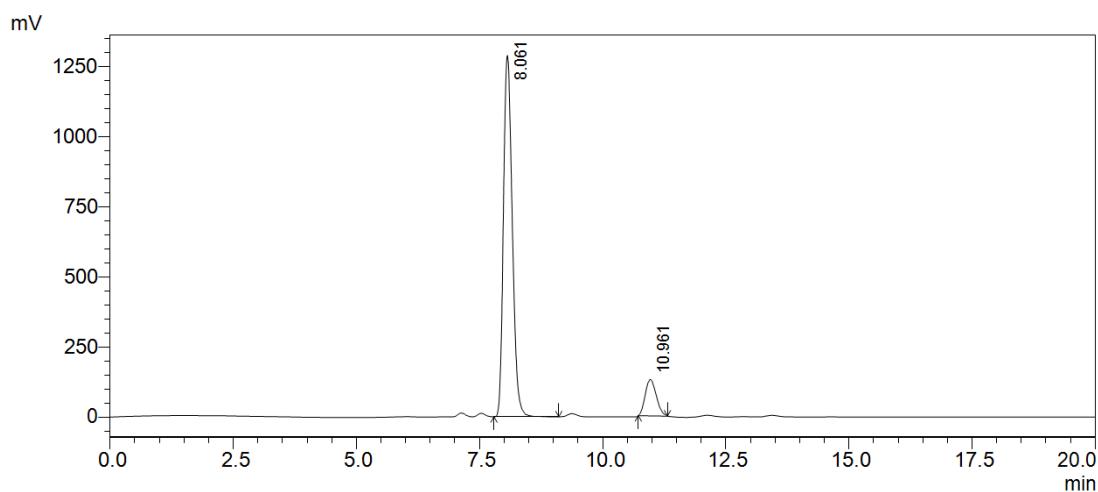
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.667	9731670	470862	82.616	97.351
2	55.024	2047786	12811	17.384	2.649
Total		11779456	483673	100.000	100.000



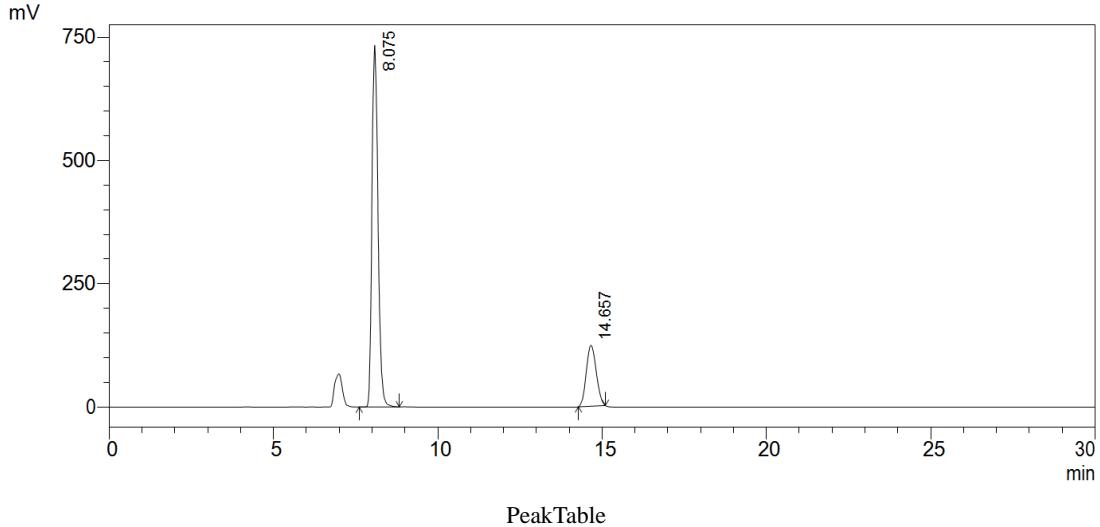
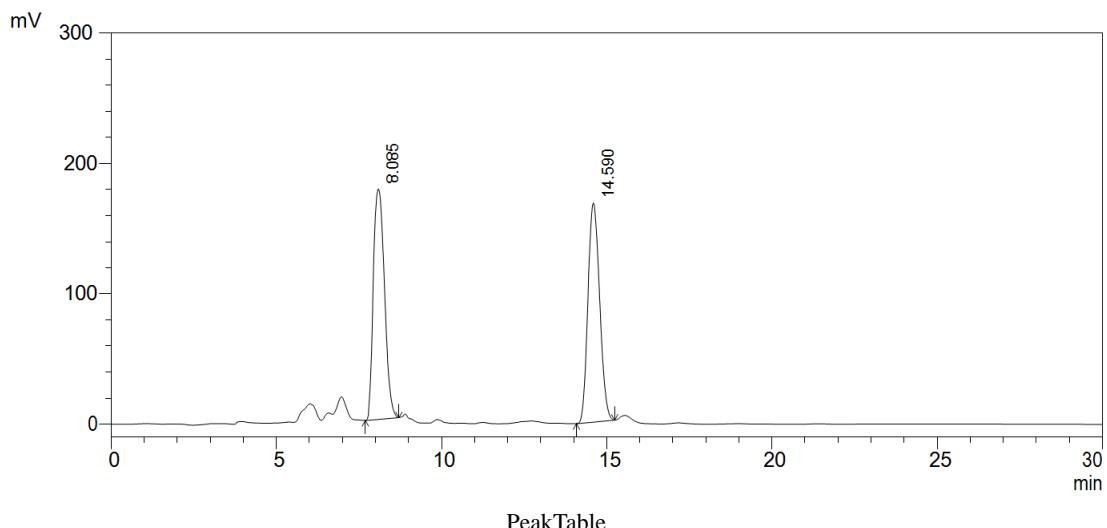
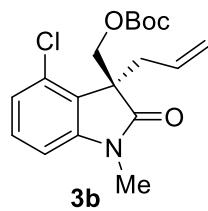
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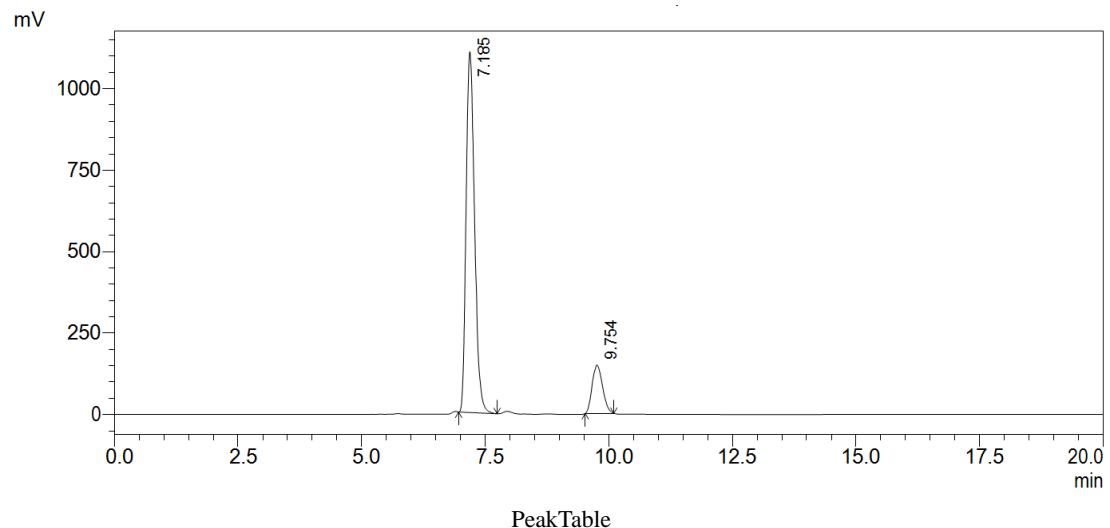
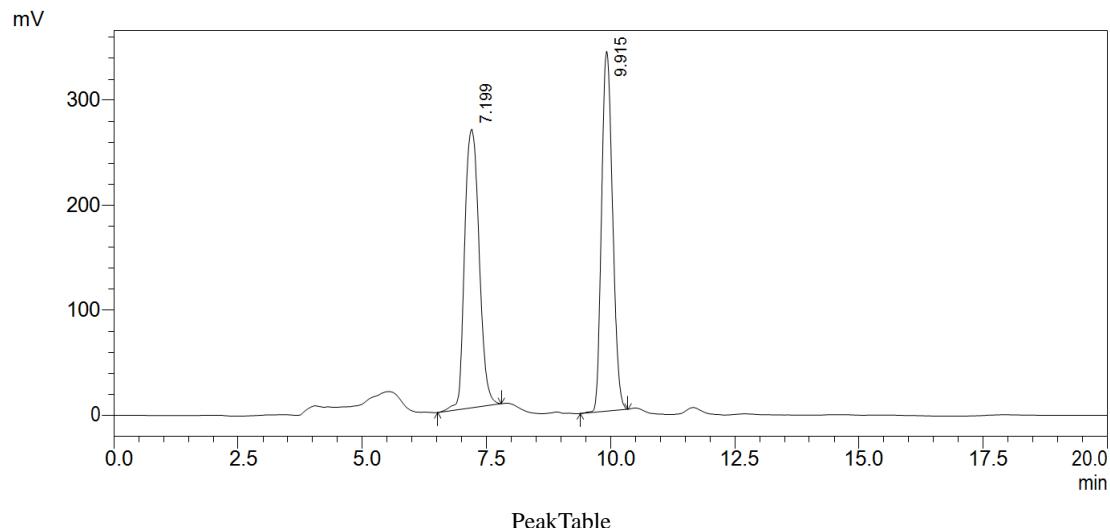
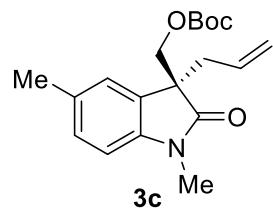
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.098	15407239	669526	49.817	45.957
2	10.975	15520428	787336	50.183	54.043
Total		30927667	1456862	100.000	100.000

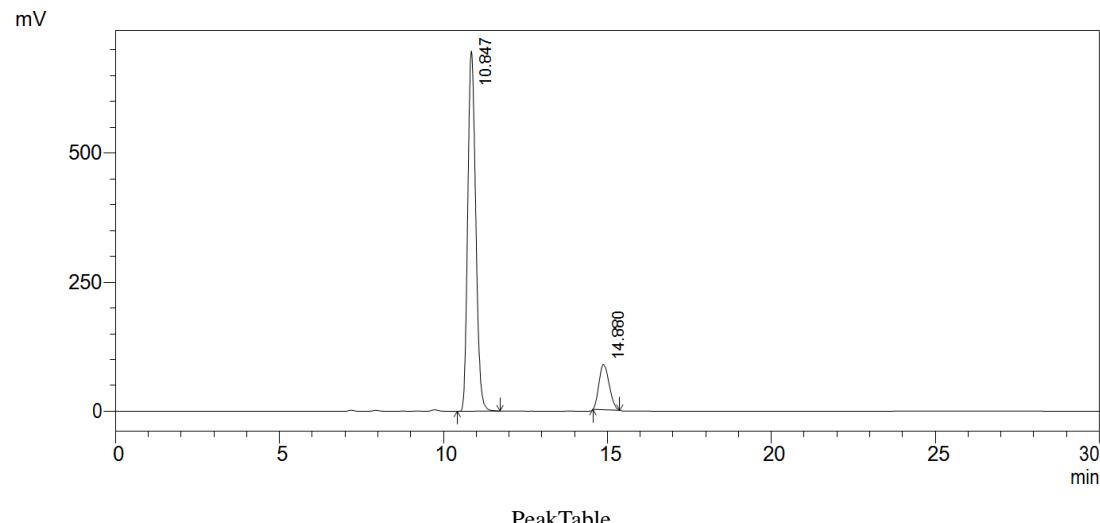
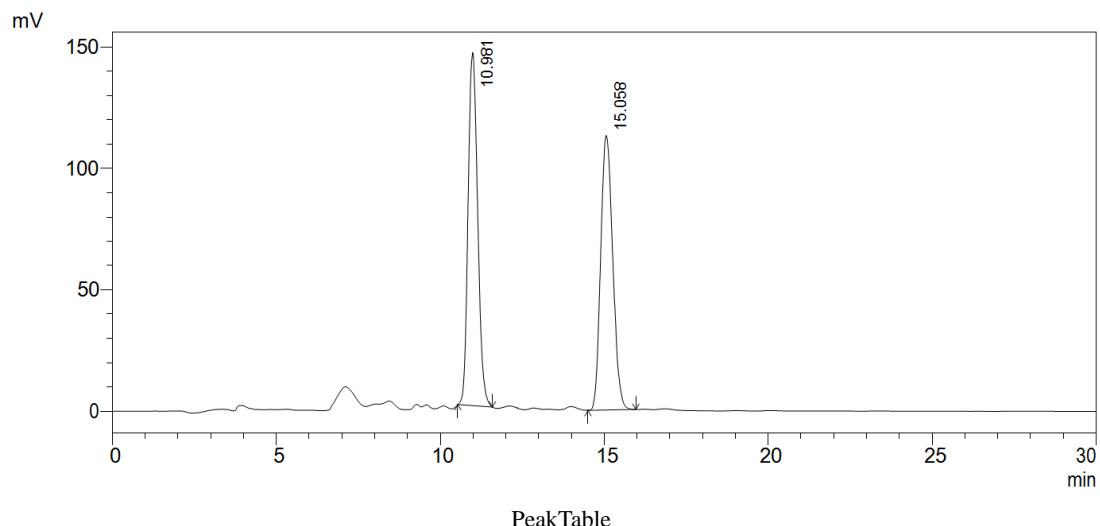
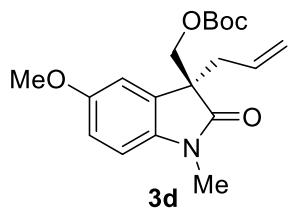


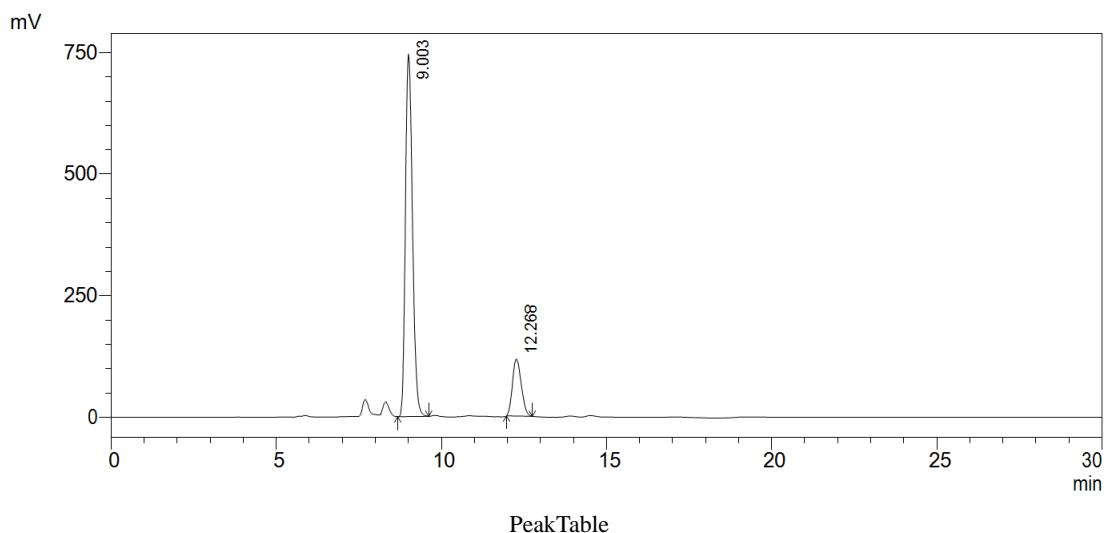
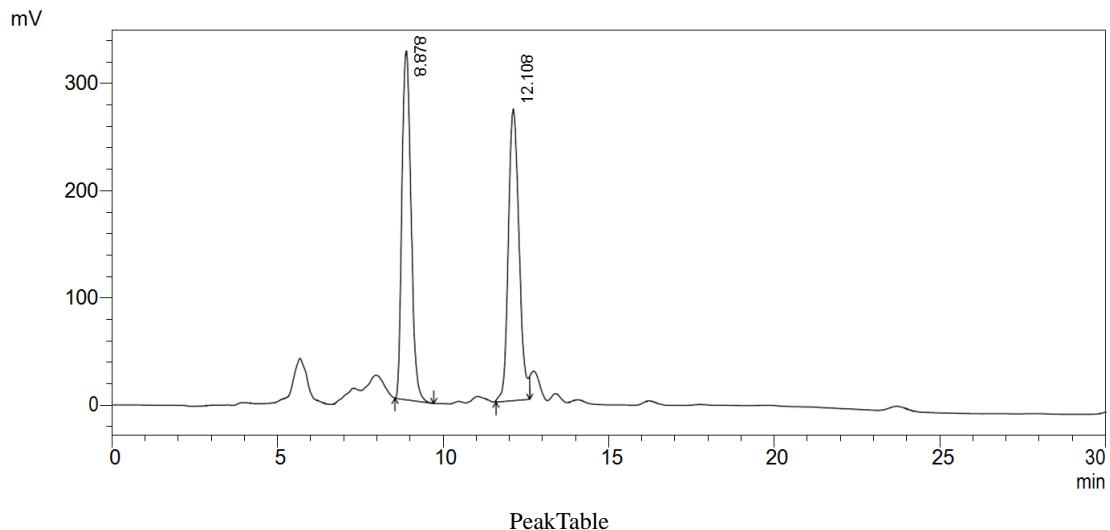
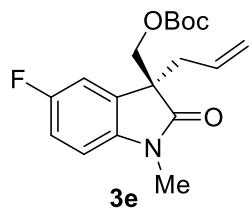
PeakTable

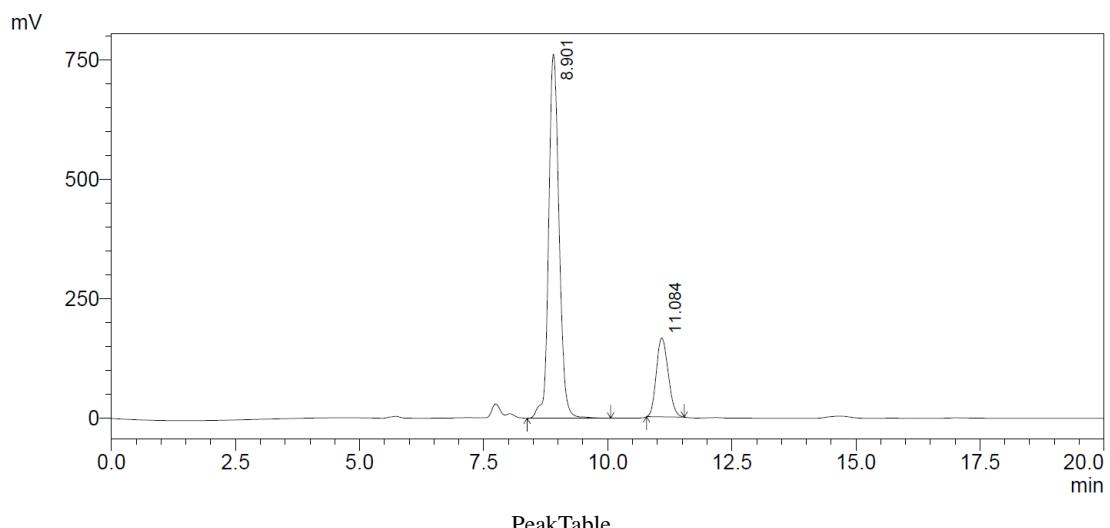
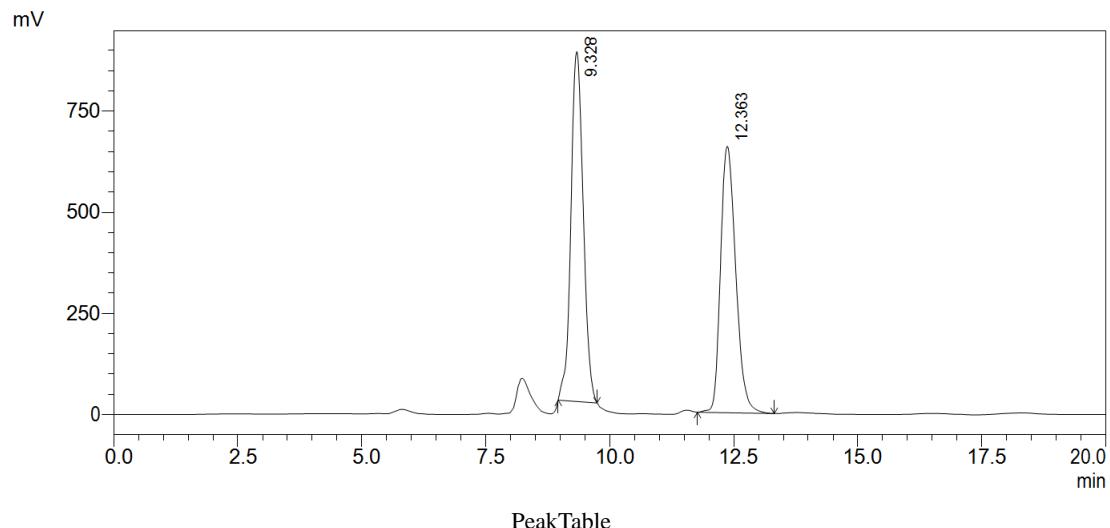
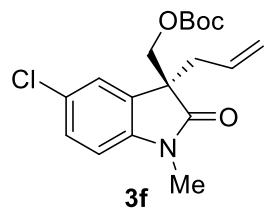
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.061	16110840	1290913	88.832	90.834
2	10.961	2025383	130261	11.168	9.166
Total		18136223	1421174	100.000	100.000

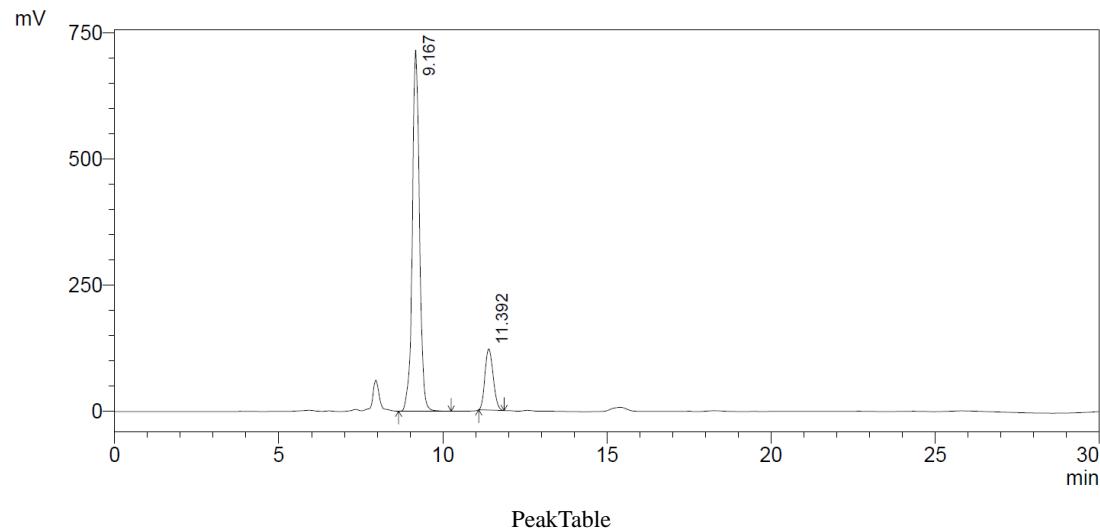
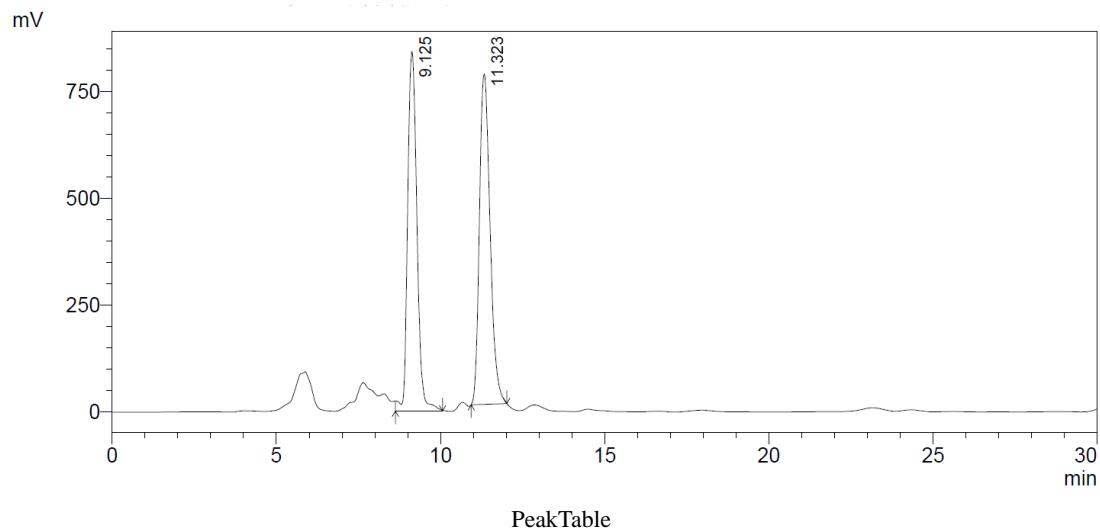
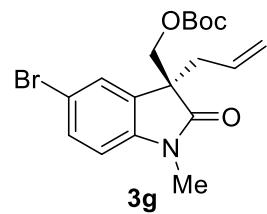


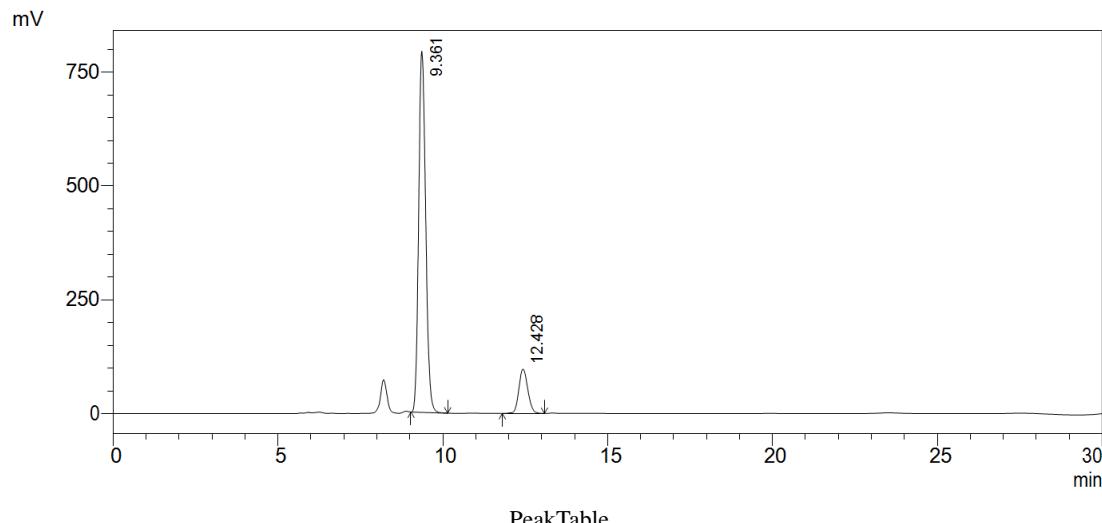
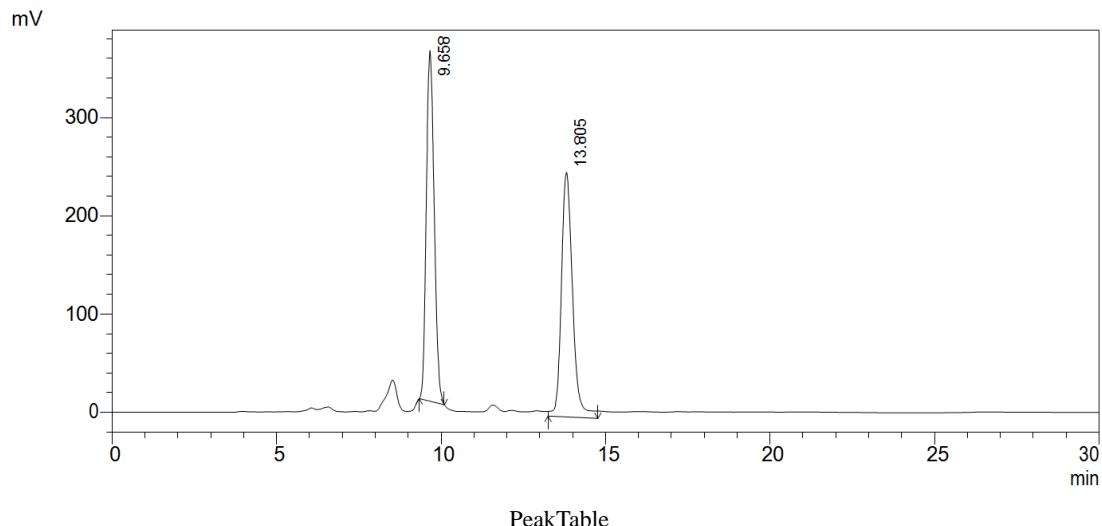
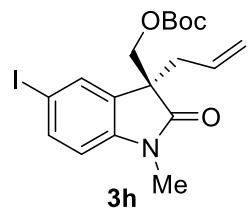


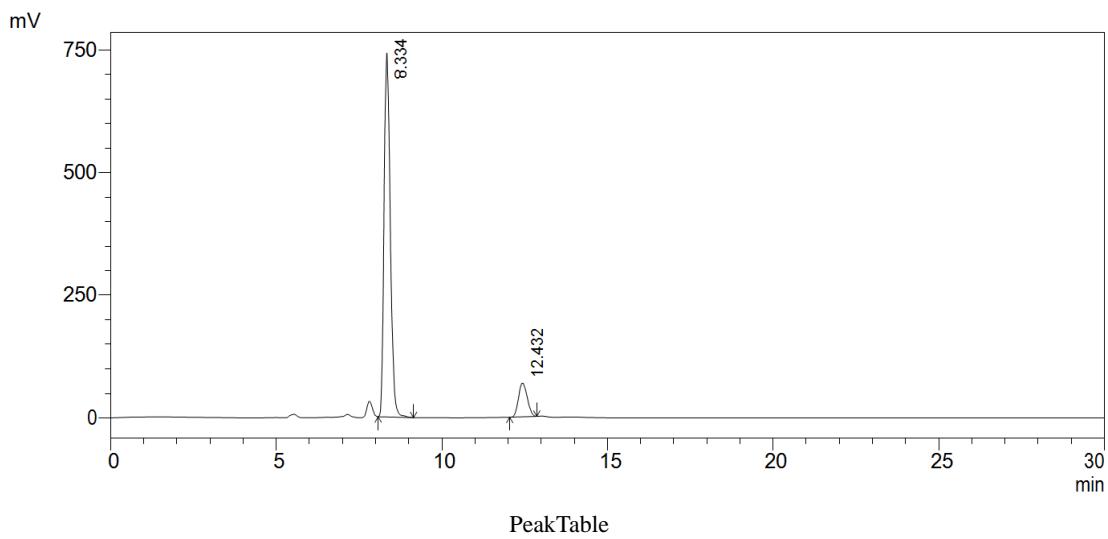
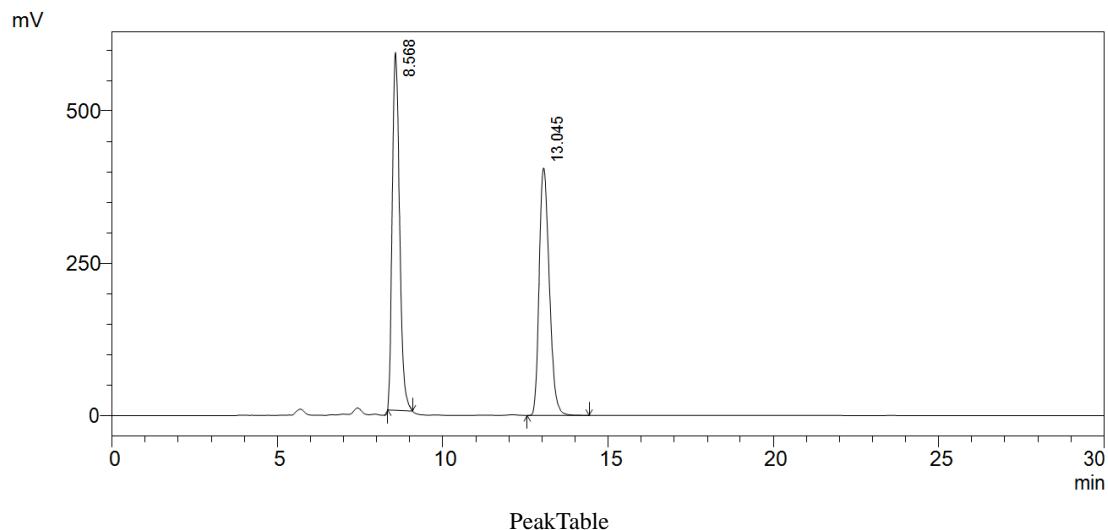
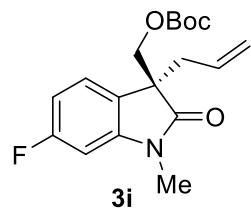


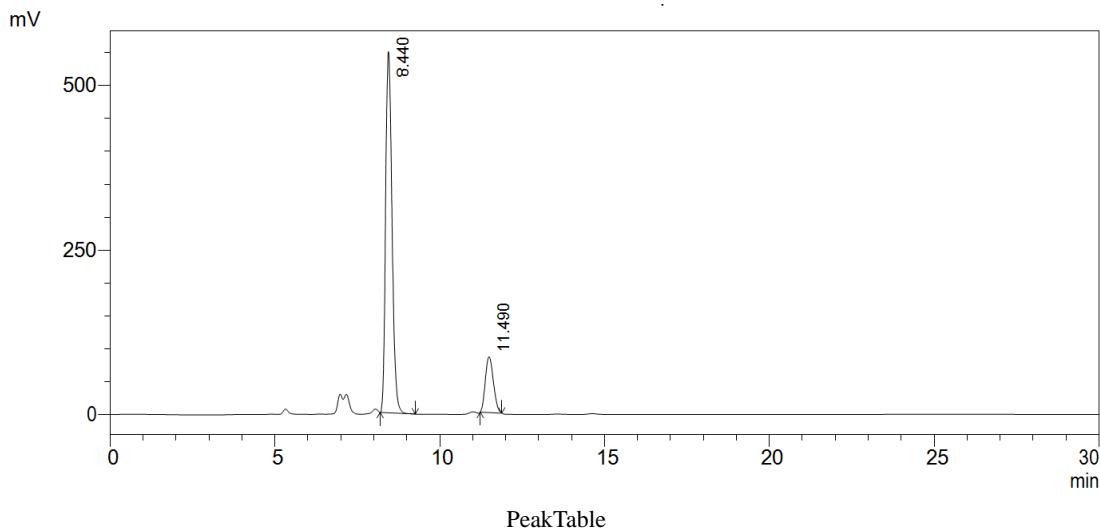
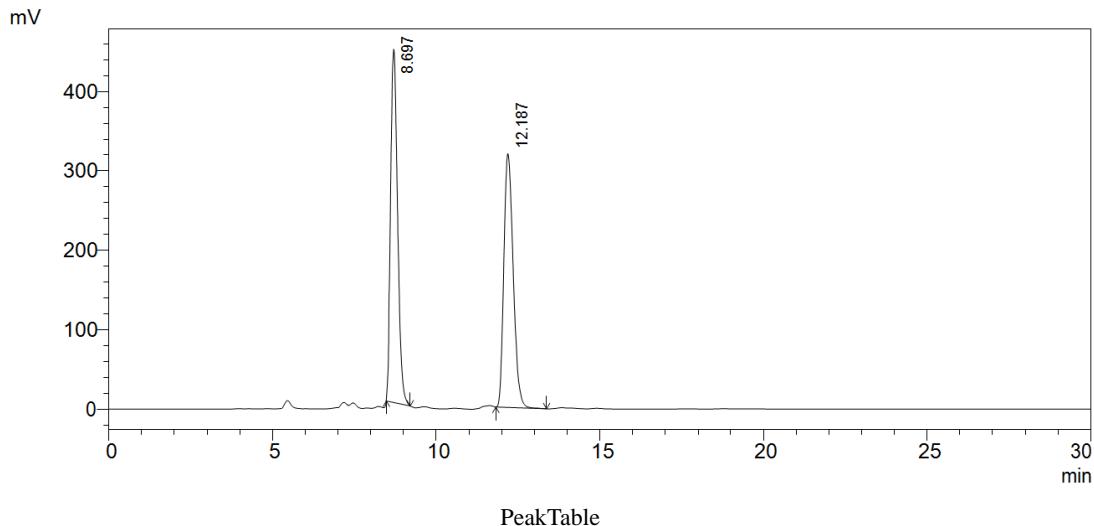
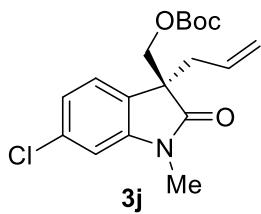


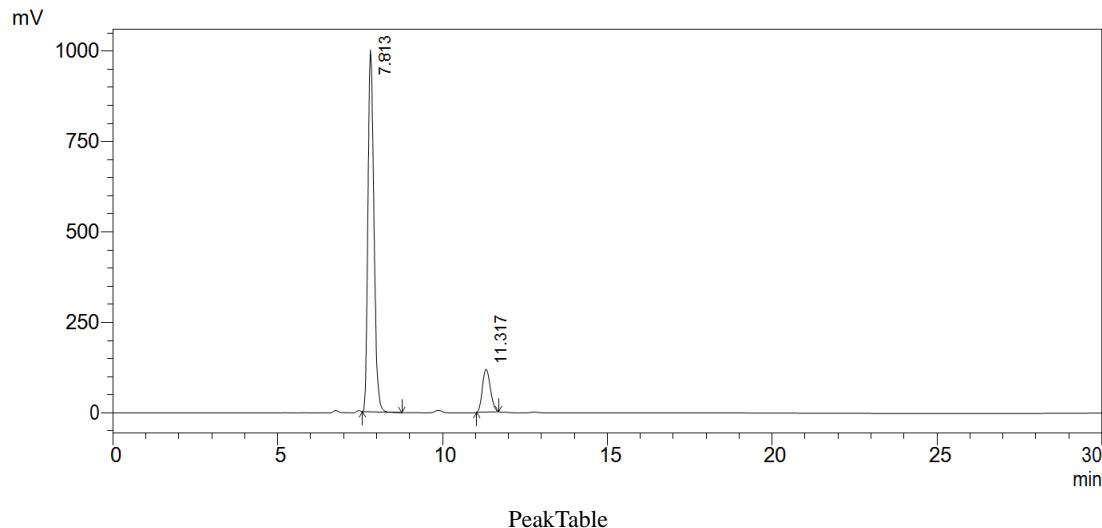
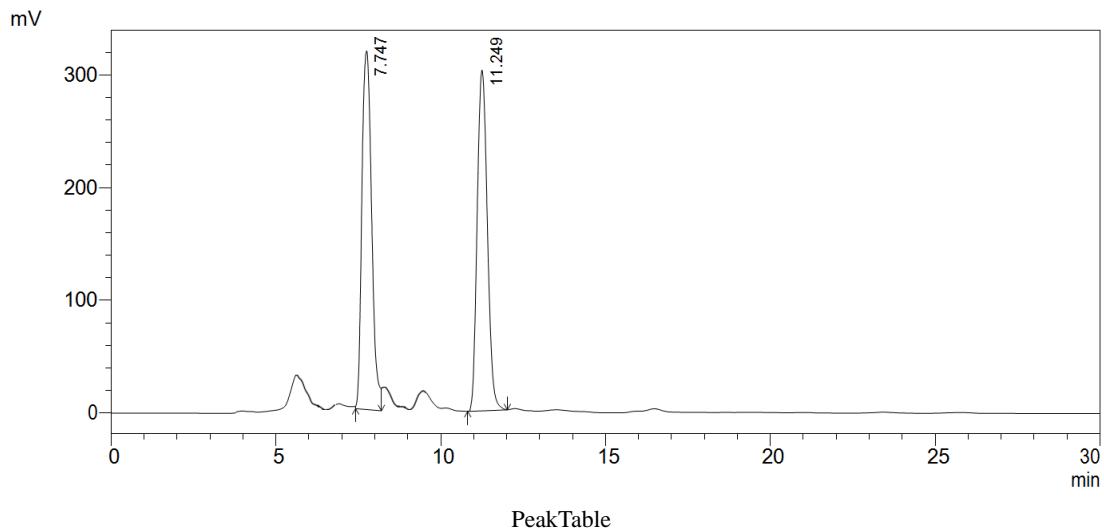
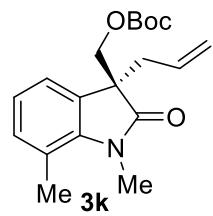


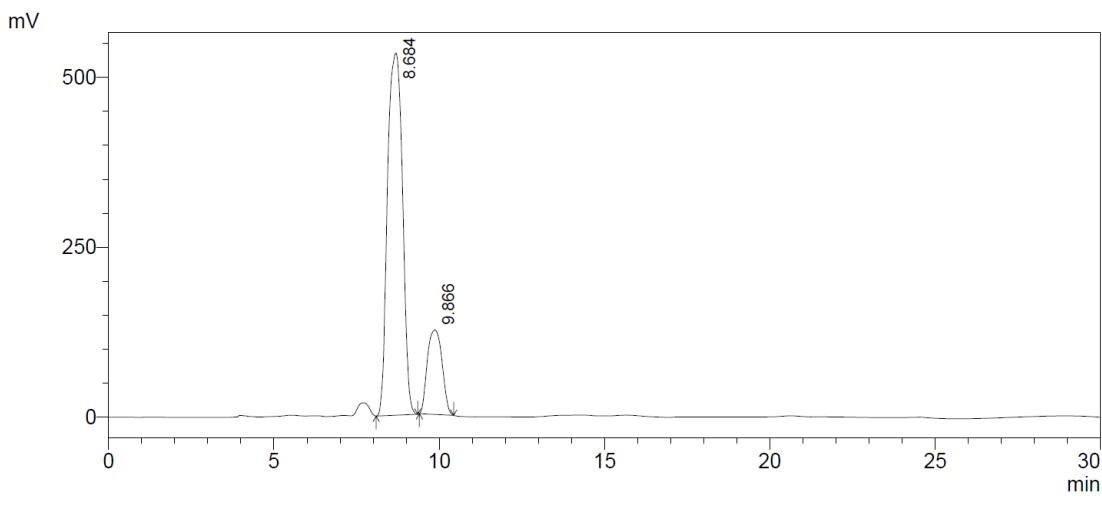
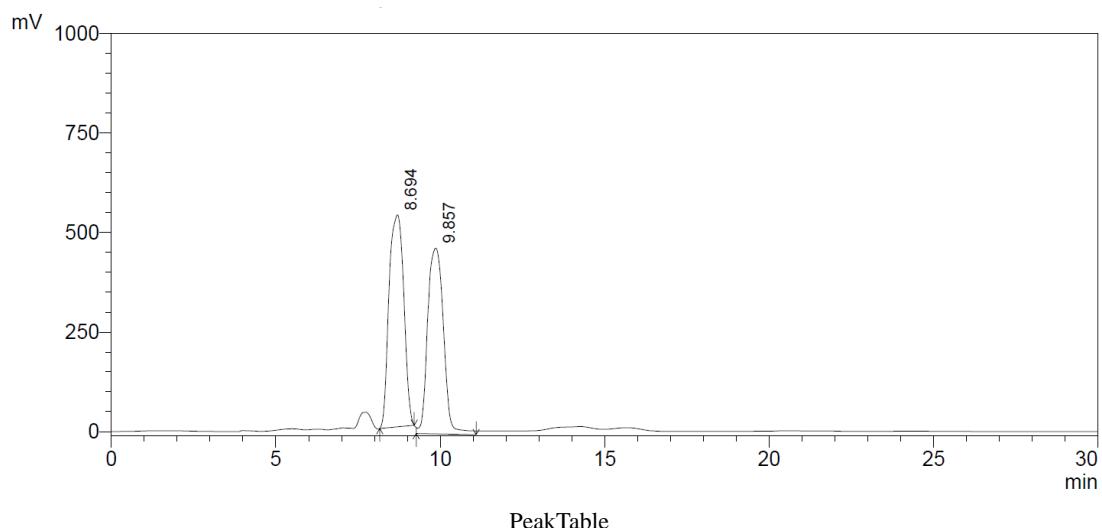
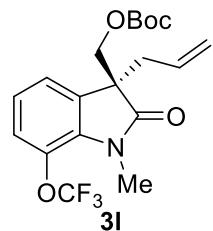


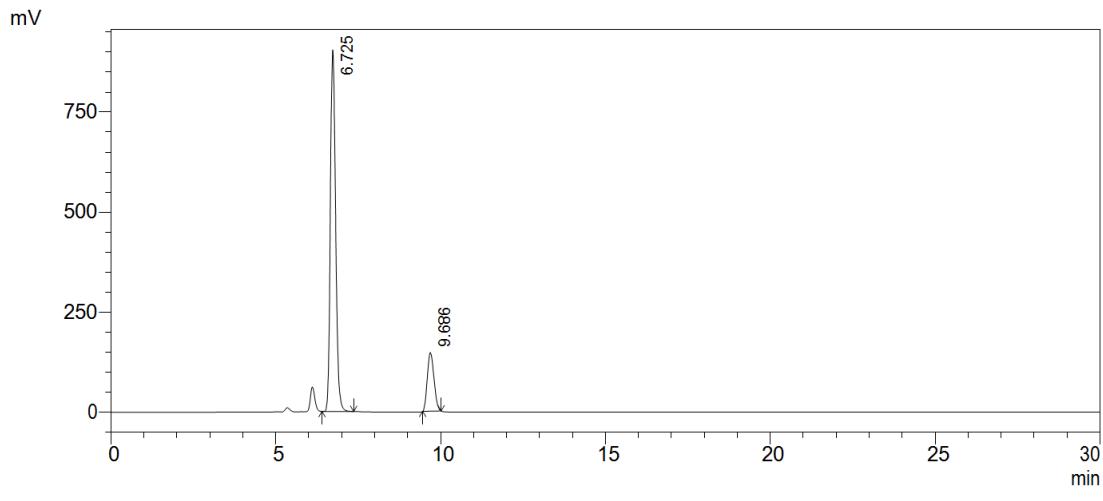
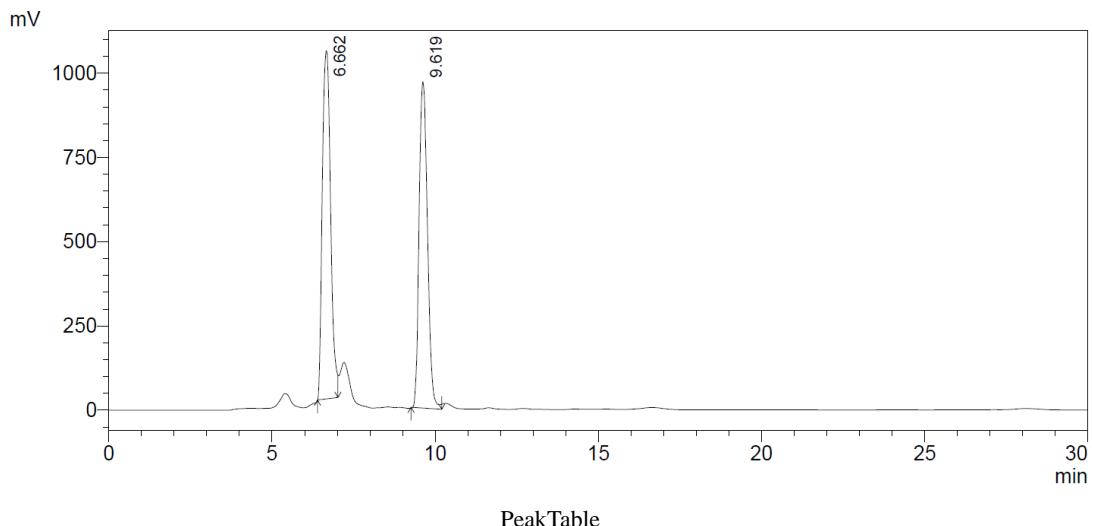
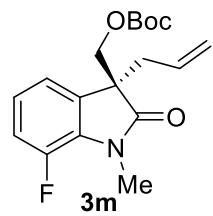


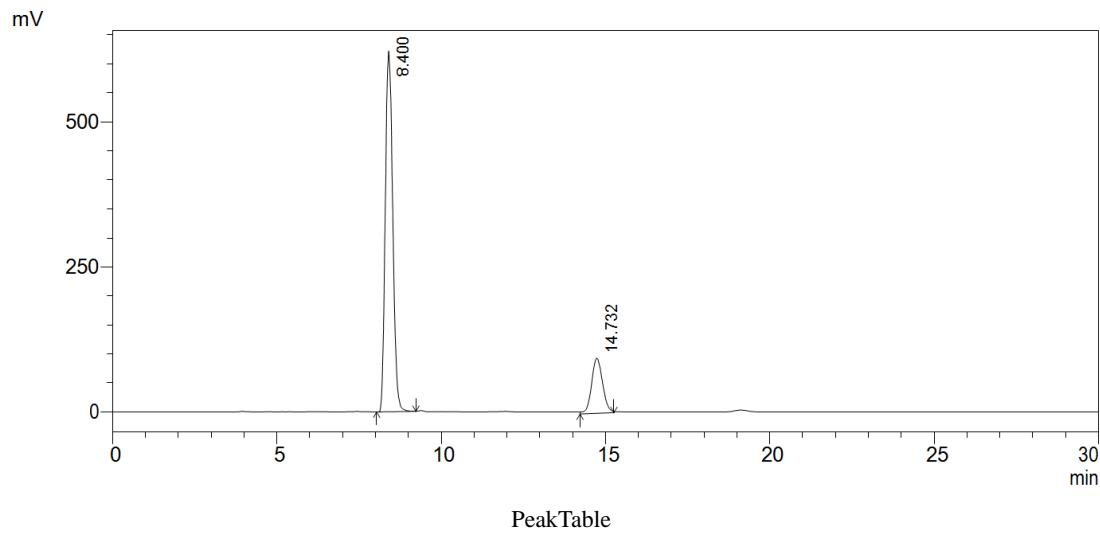
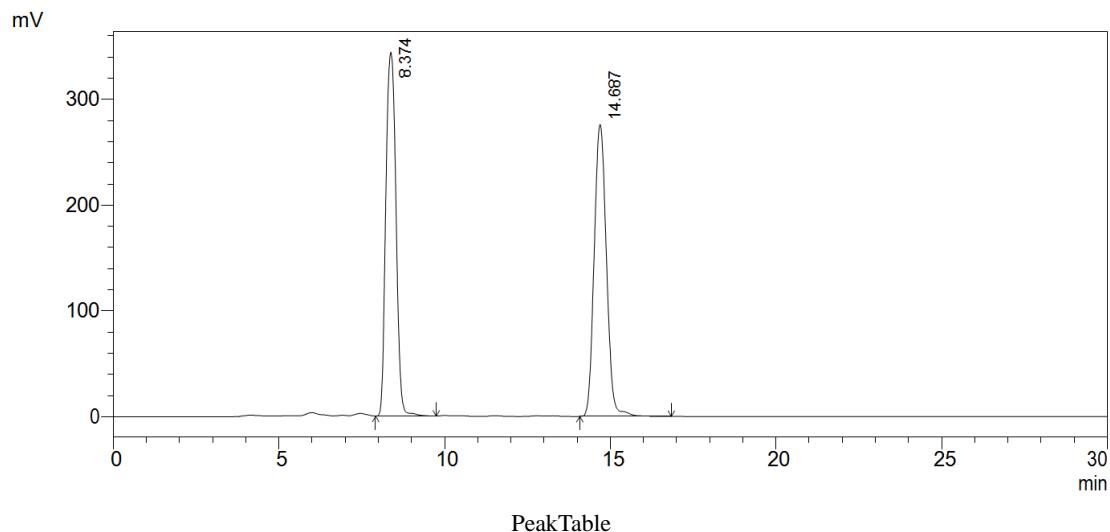
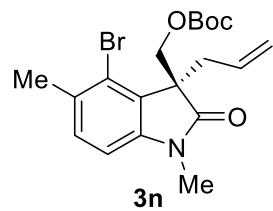


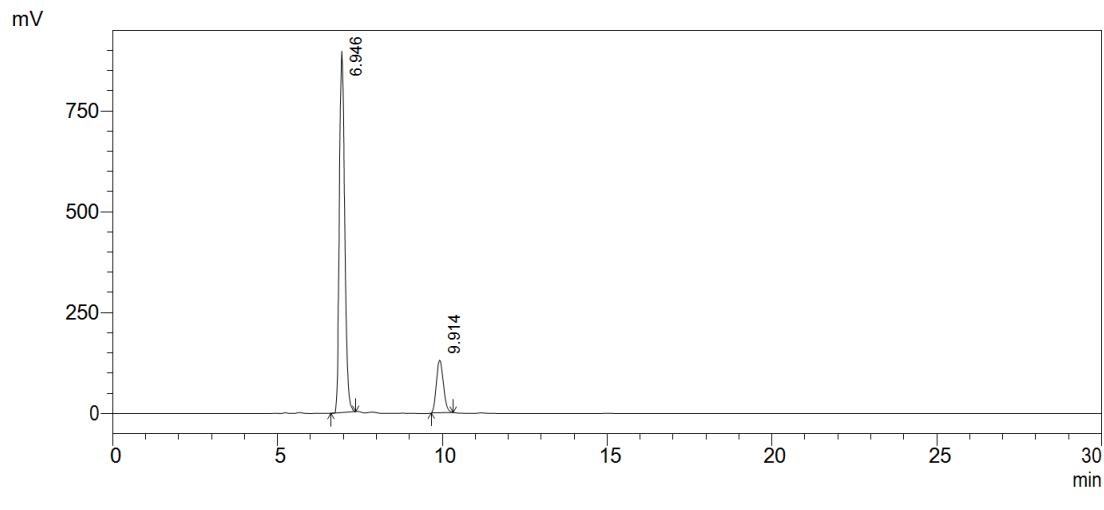
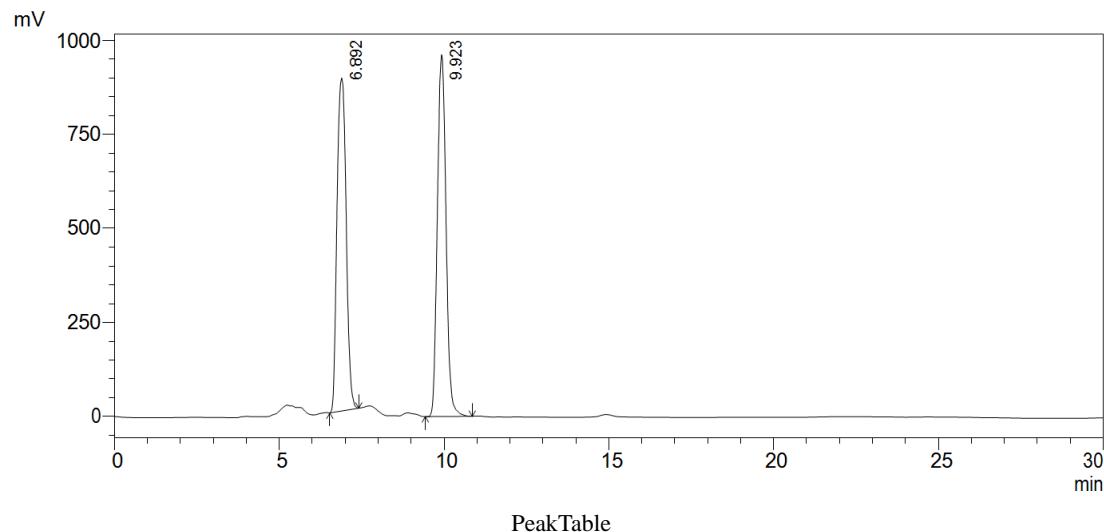
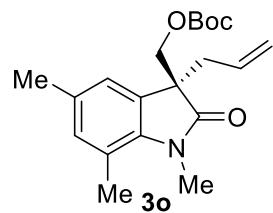


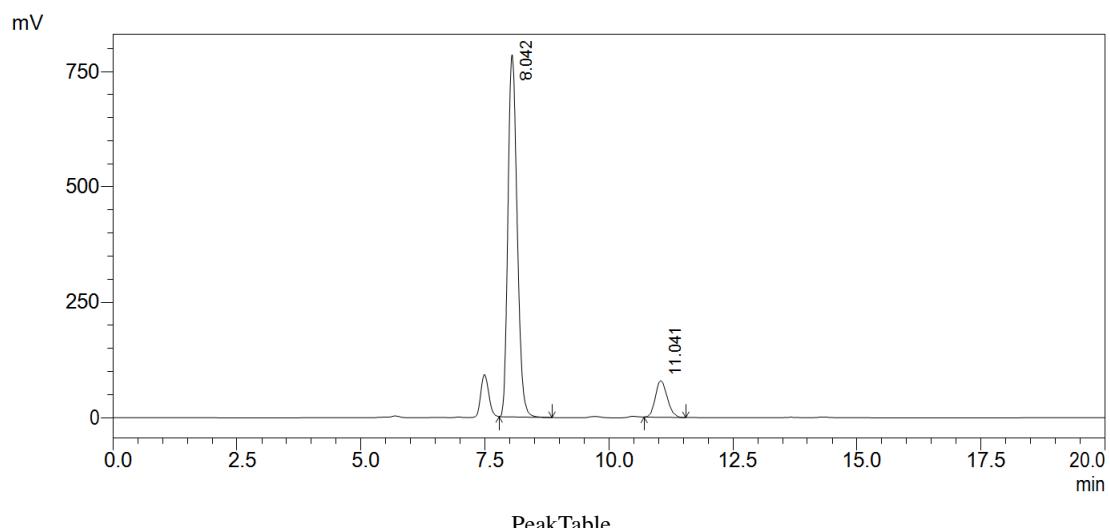
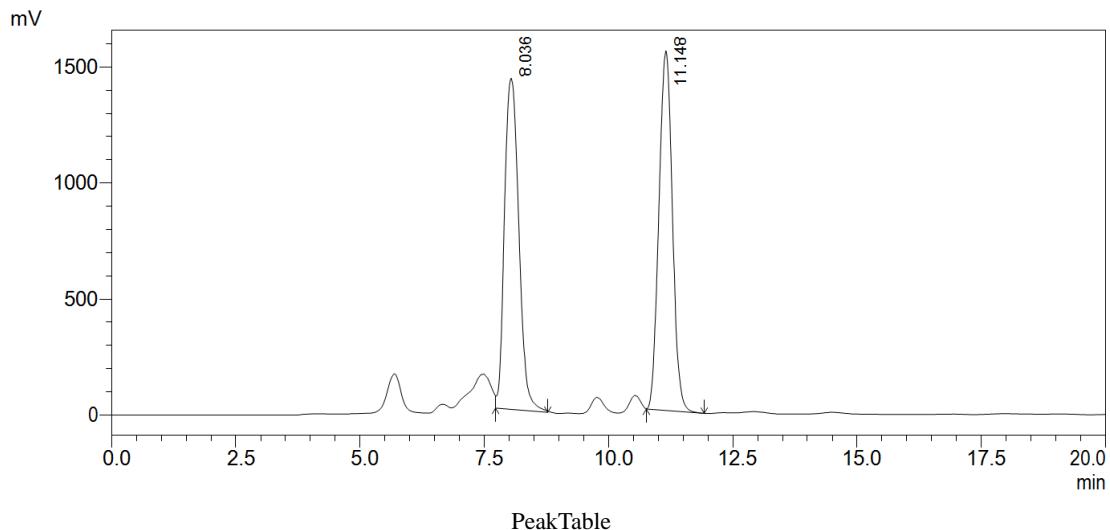
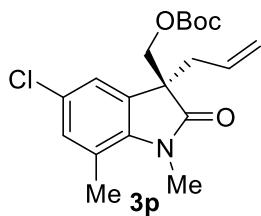


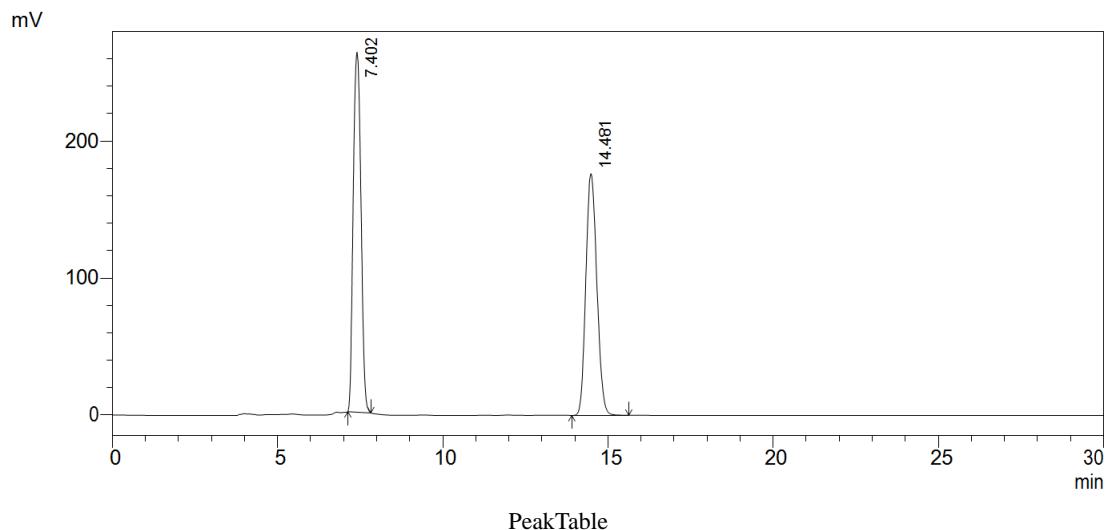
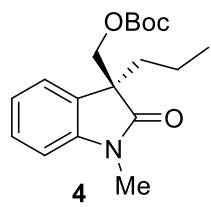




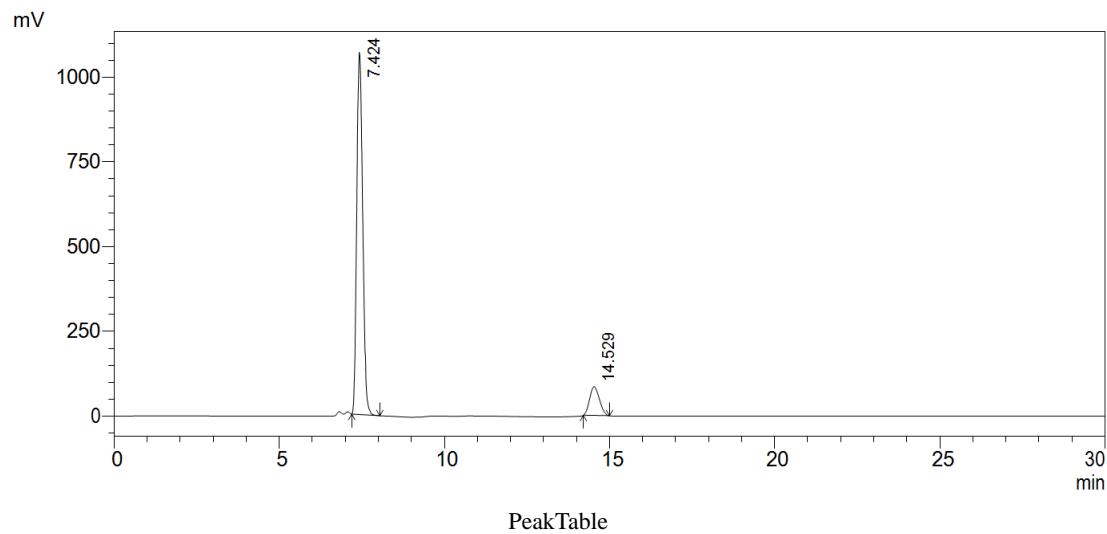




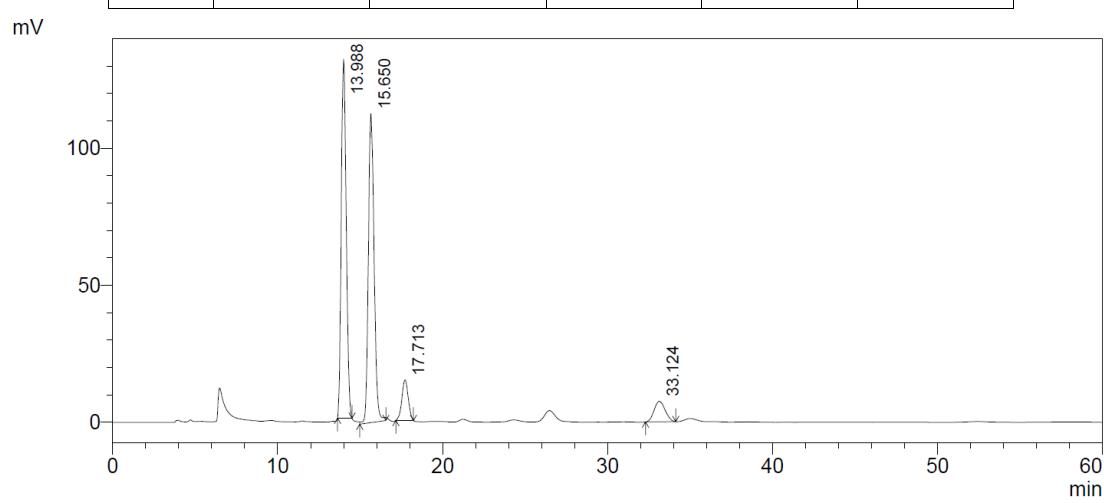
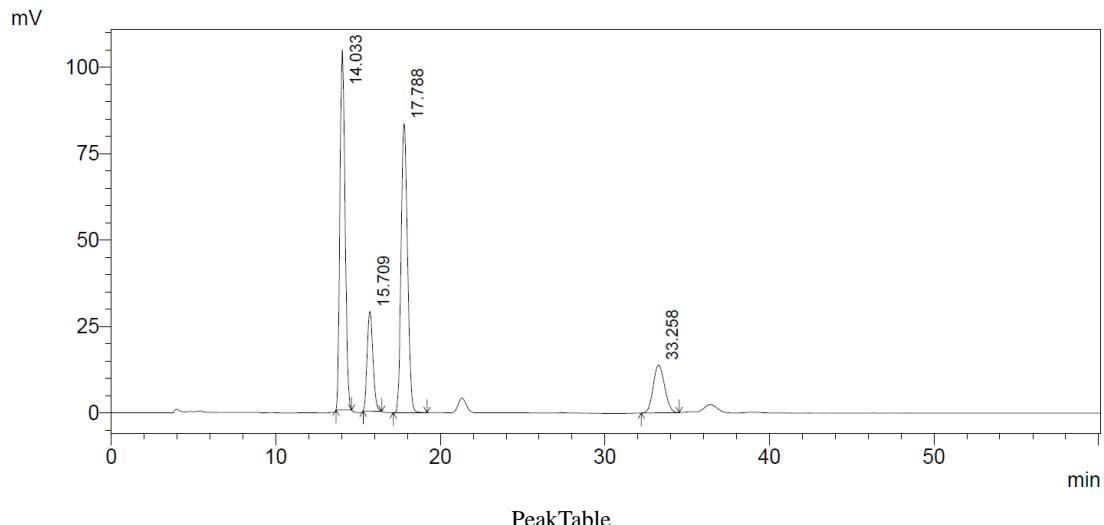
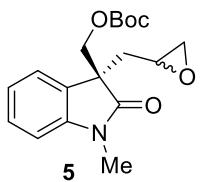




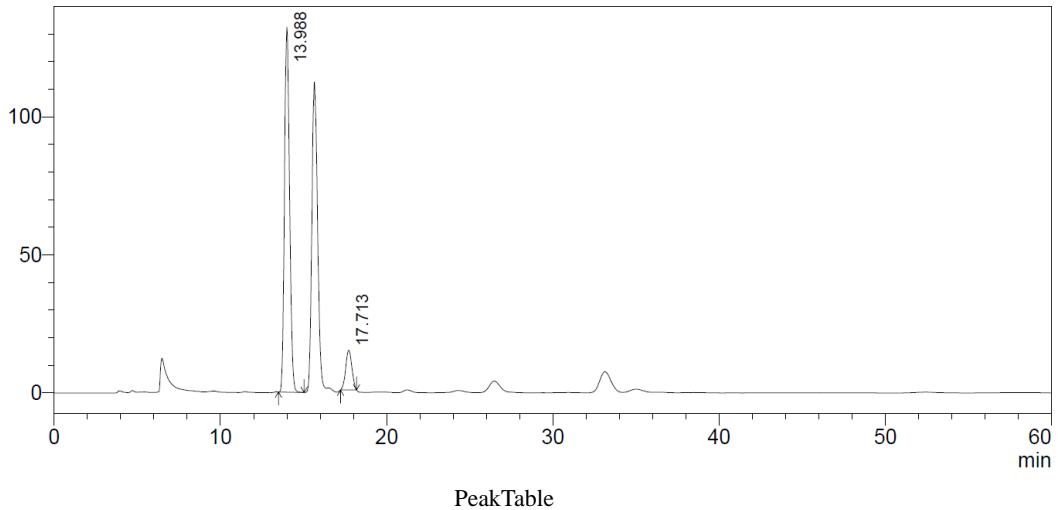
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.402	4256790	262743	51.075	59.838
2	14.481	4077674	176351	48.925	40.162
Total		8334464	439093	100.000	100.000



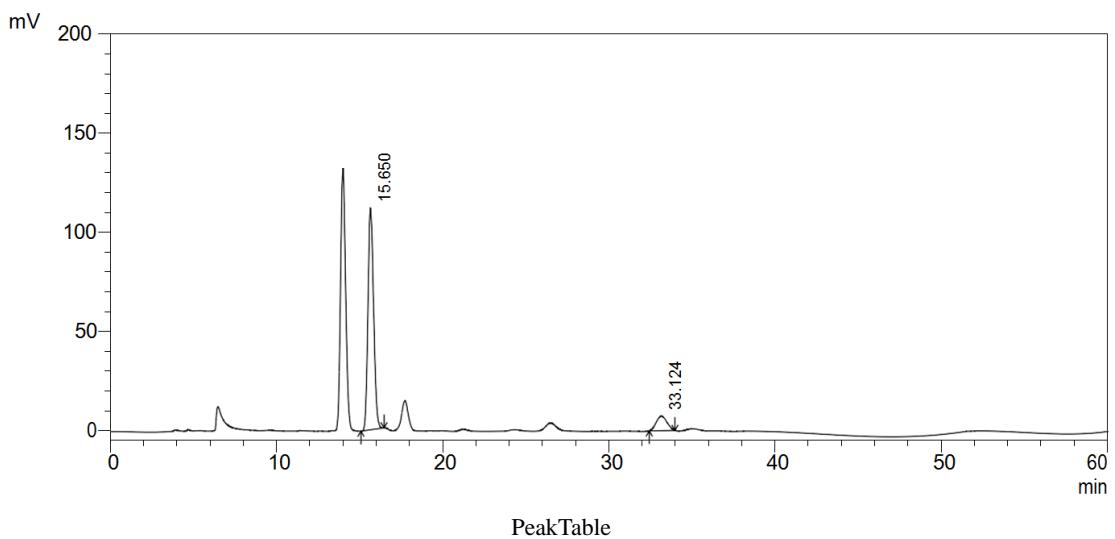
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.424	13389030	1069135	88.495	92.672
2	14.529	1740736	84544	11.505	7.328
Total		15129766	1153679	100.000	100.000

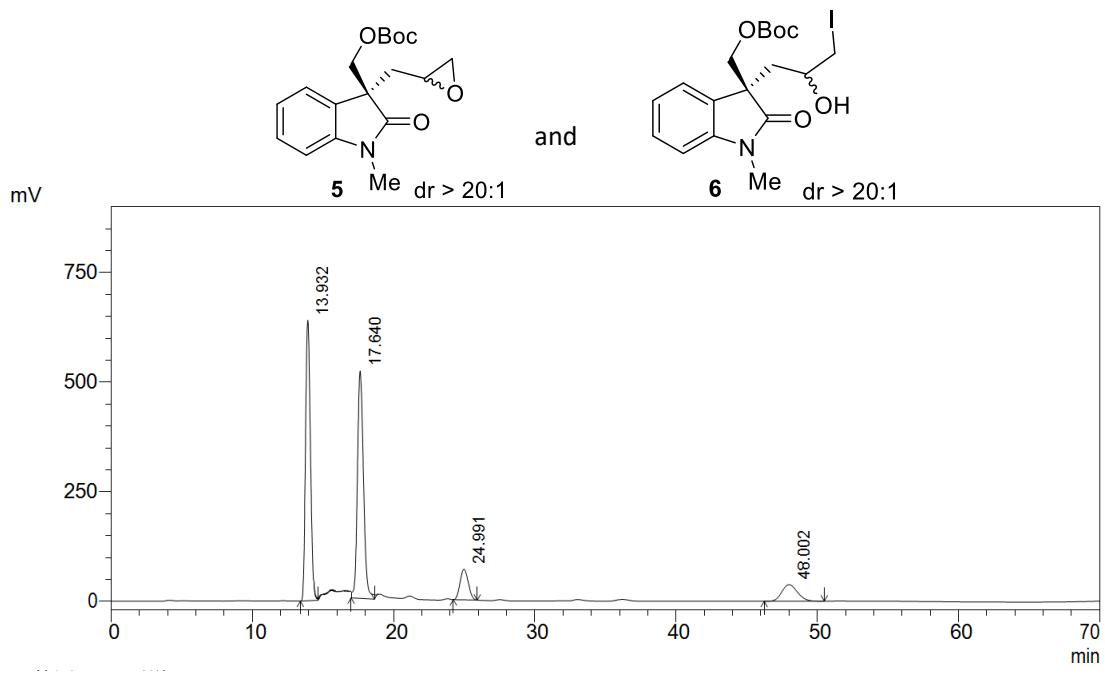


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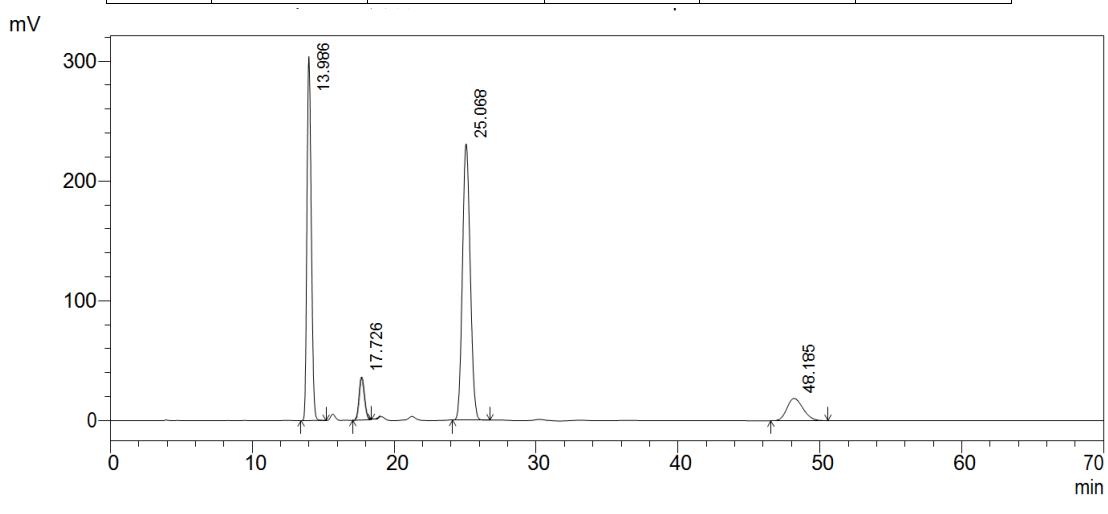


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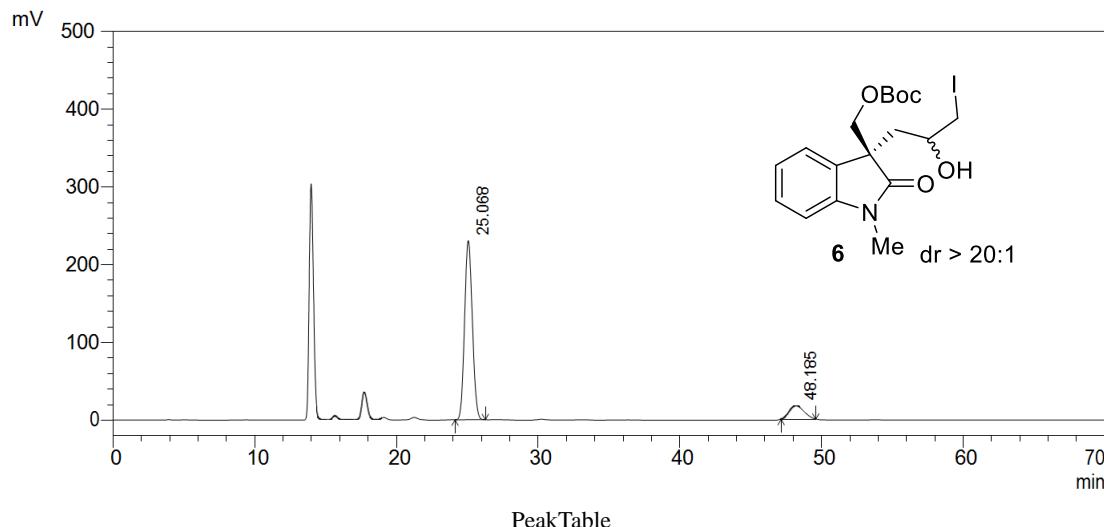




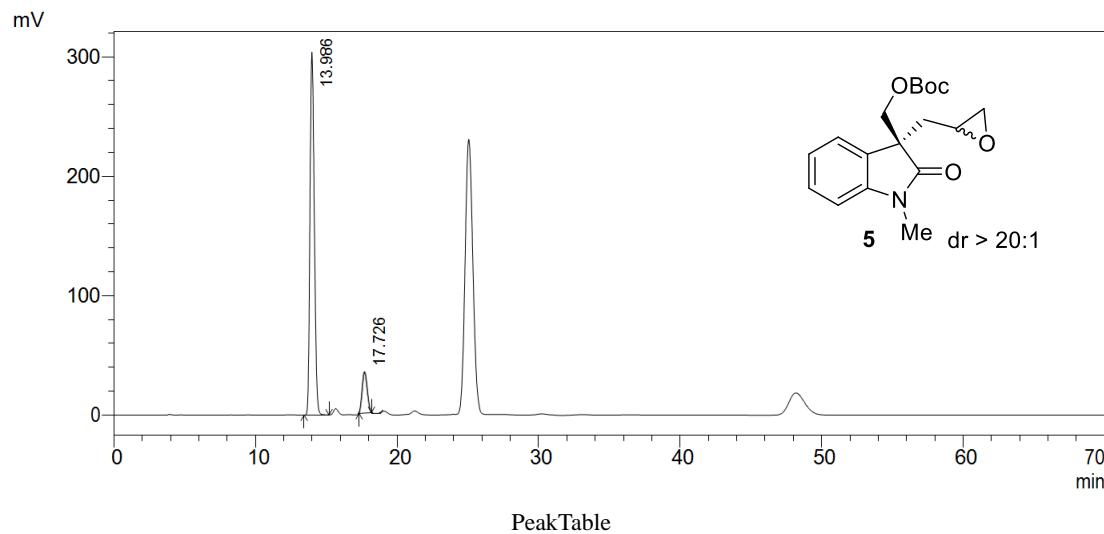
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.932	15299904	640298	41.843	50.526
2	17.640	15510325	519065	42.418	40.960
3	24.991	2830202	70026	7.740	5.526
4	48.002	2924809	37868	7.999	2.988
Total		36565242	1267256	100.000	100.000



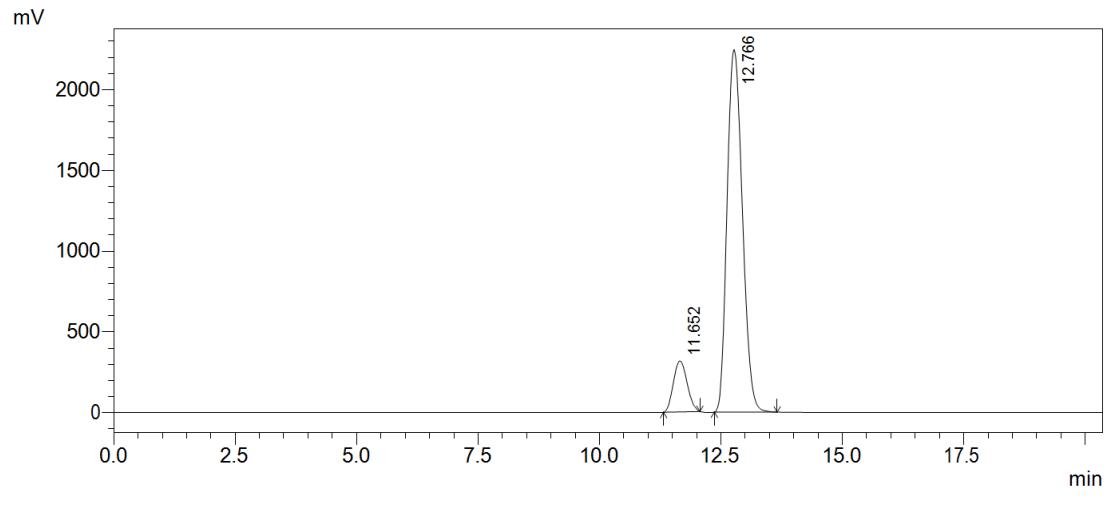
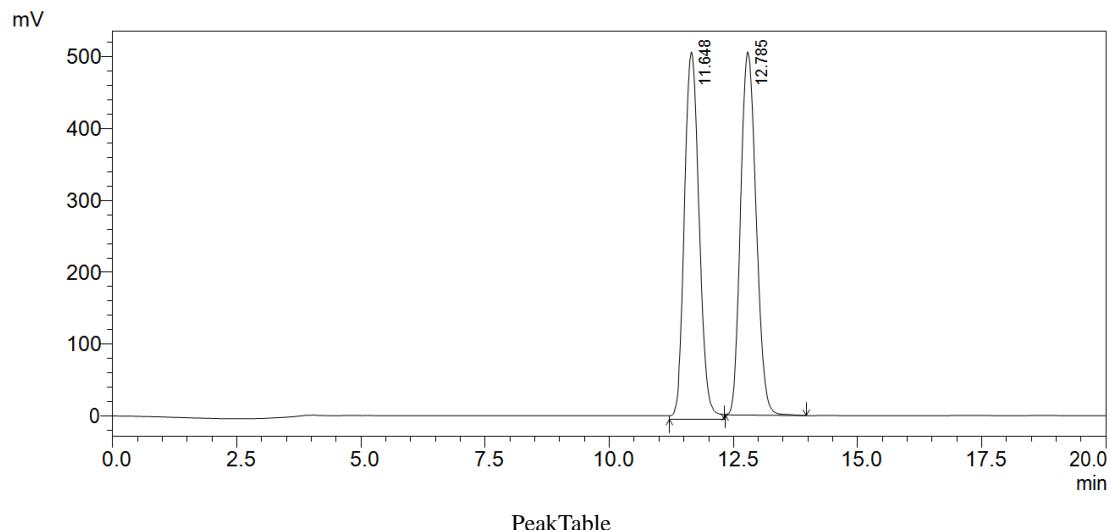
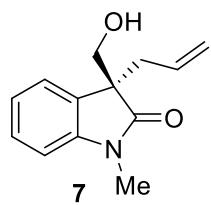
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.986	6444545	303928	36.604	51.628
2	17.726	922736	35753	5.241	6.073
3	25.068	8765055	230380	49.785	39.135
4	48.185	1473557	18623	8.370	3.163
Total		17605894	588684	100.000	100.000

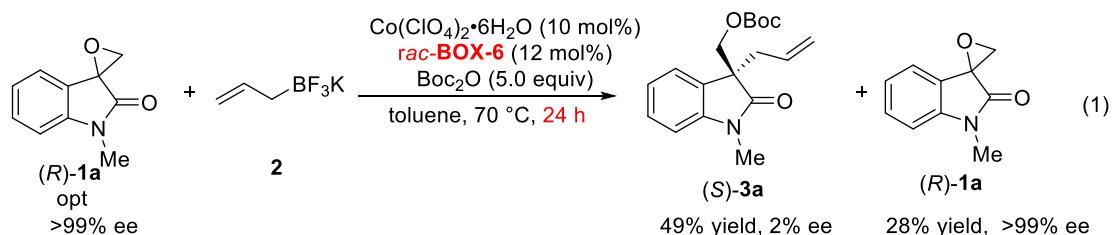


Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.068	8754642	230320	87.463	92.996
2	48.185	1254932	17346	12.537	7.004
Total		10009575	247666	100.000	100.000

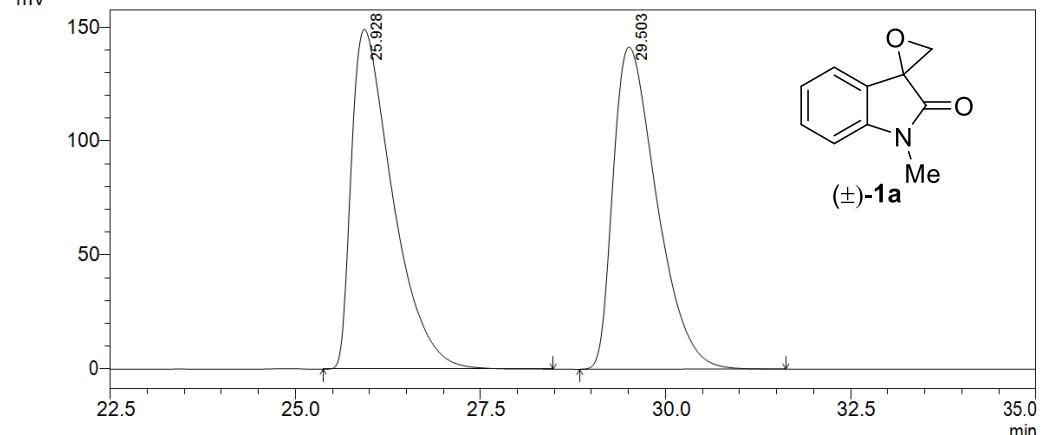


Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.986	6444545	303928	88.397	89.820
2	17.726	845884	34448	11.603	10.180
Total		7290430	338376	100.000	100.000





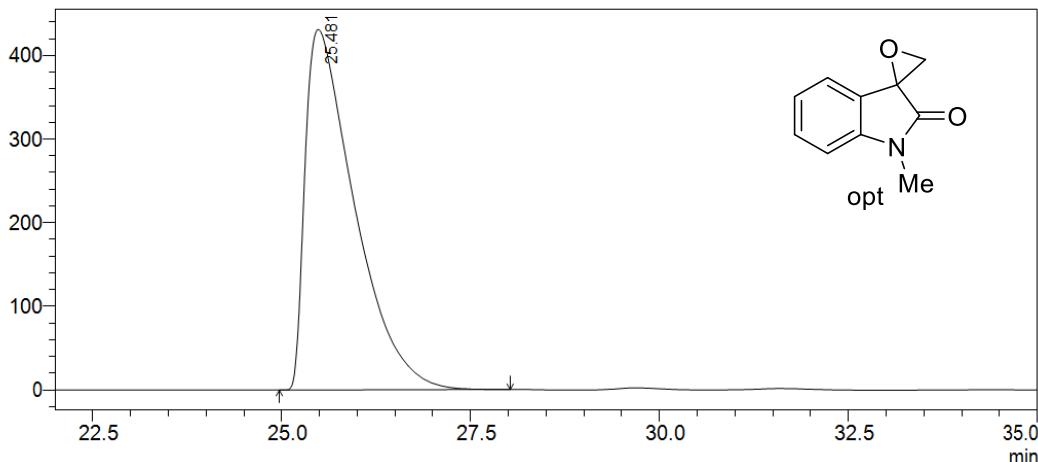
1a HPLC (Daicel Chiralpak OJ-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min.)



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.928	5791739	149254	49.966	51.340
2	29.503	5799733	141464	50.034	48.660
Total		11591472	290719	100.000	100.000

mV



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.481	19589413	431225	100.000	100.000
Total		19589413	431225	100.000	100.000

3a HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 90/10, 254 nm, 0.8 mL/min.)

