

Supporting Information

Electrochemical-mediated fixation of CO₂: three-component synthesis of carbamate compounds from CO₂, amines and N- alkenylsulfonamides

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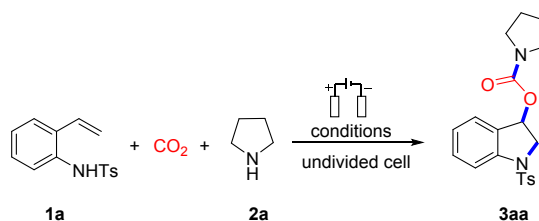
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1. General Methods

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. Column chromatography on silica gel (300-400 mesh) was carried out using technical grade 60-90 °C petroleum ether and analytical grade EtOAc (without further purification). ^1H and ^{13}C spectra were recorded on a 400 MHz, 500 MHz or 600MHz spectrometer. Chemical shifts were reported in ppm. ^1H NMR spectra were referenced to CDCl_3 (7.26 ppm) or DMSO (2.5 ppm), and ^{13}C -NMR spectra were referenced to CDCl_3 (77.0 ppm) or DMSO (39.5 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. The HRMS spectrum was measured by micromass QTOF2 Quadrupole/Time of Flight Tandem mass spectrometer with electron spray ionization. Cyclic voltammograms were recorded on a CHI 660E potentiostat.

2. Supplementary experiments

Table S1 Screening of Reaction electrode^a



Entry	electrode	Yield (%) ^b
1	Pt (+) / Pt (-)	77
2	C (+) / Pt (-)	42
3	Pt (+) / C (-)	39
4	Pt (+) / Ni (-)	61
5	Pt (+) / Cu (-)	8
6	Pt (+) / Al (-)	trace
7	Pt (+) / Ag (-)	trace

^aReaction conditions: **1a** (0.3 mmol), **2a** (1.2 mmol), CO₂ (atmospheric pressure), NH₄I as electrolyte (0.3 mmol), CH₃CN as solvent (3 mL), electrolysis at a constant current of 25 mA for 3 h in an undivided cell at -10 °C.

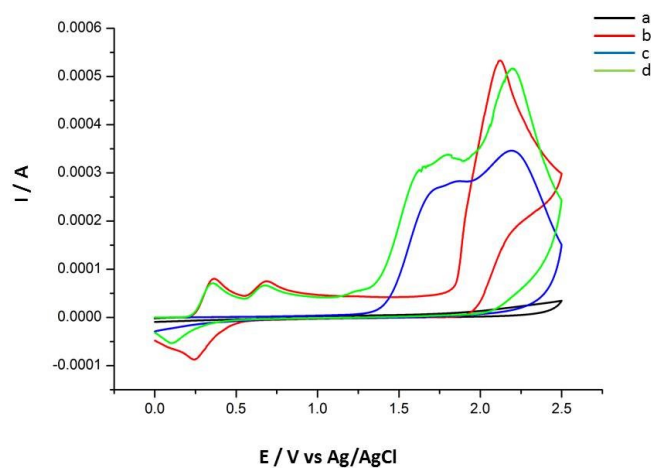


Fig. S1 Cyclic voltammograms. a) background, b) NH₄I (3mmol/L), c) **1a** (8 mmol/L), and d) NH₄I (3 mmol/L) and **1a** (8 mmol/L).

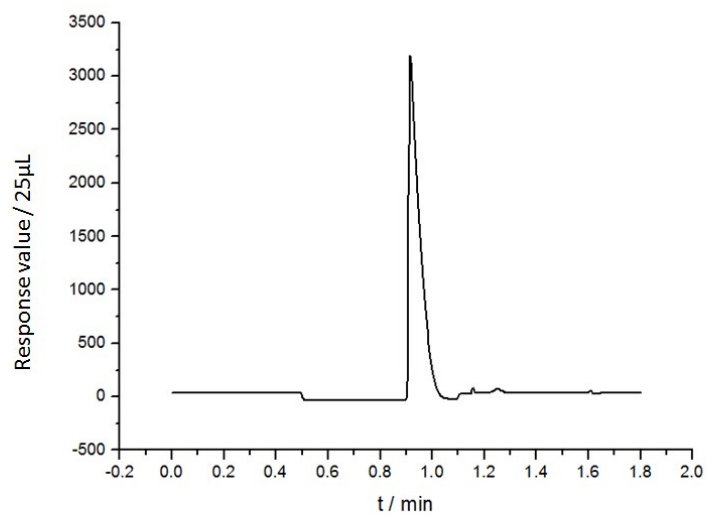


Fig. S2 GC spectrum of pure hydrogen

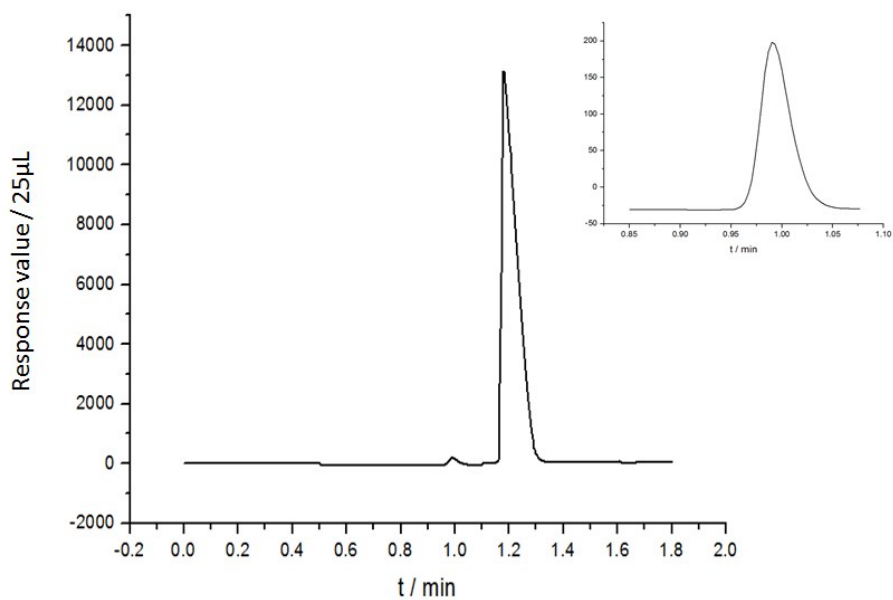


Fig. S3 Gas spectrum of reaction bottle (Reaction time: 60 minutes)

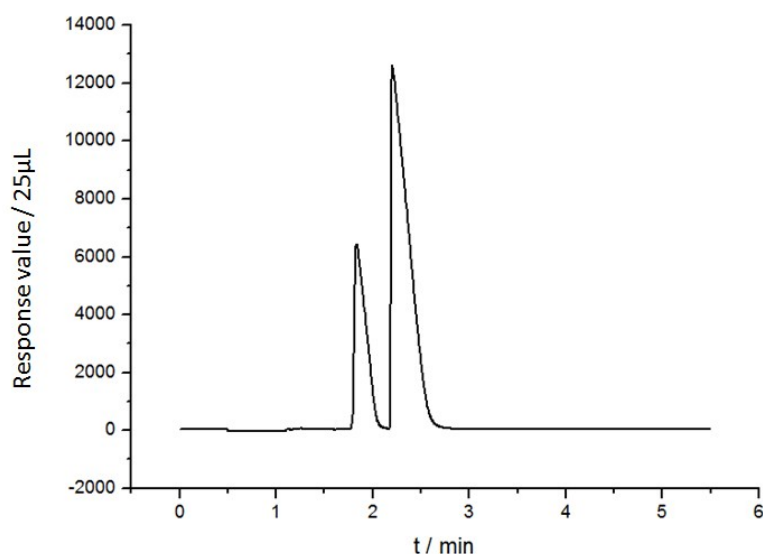
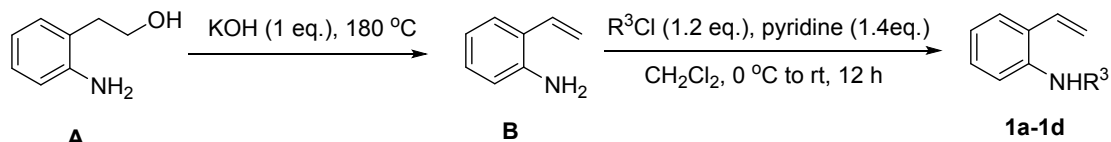


Fig. S4 GC spectrum of air

3. Synthesis of Substrates and Characterization

(1) N-(2-vinylphenyl)-sulfonamides (**1a-1d**)



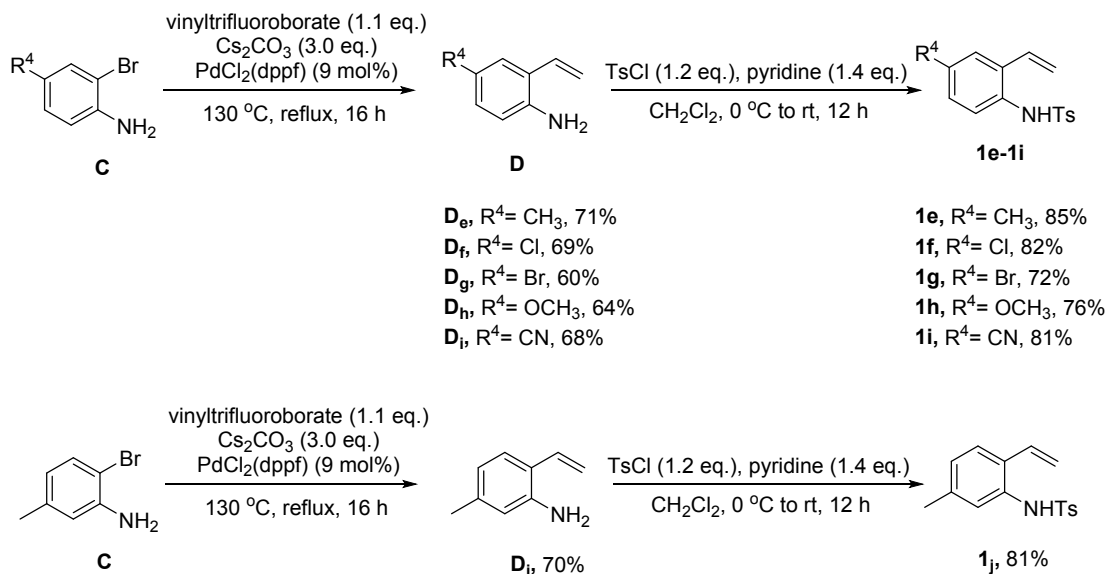
1a, R³ = SO₂C₆H₄CH₃, 81%
1b, R³ = SO₂Ph, 83%
1c, R³ = SO₂C₆H₄OCH₃, 81%
1d, R³ = SO₂C₆H₄Cl, 84%

Scheme S1 Synthesis of N-(2-vinylphenyl)-sulfonamides (**1a-1d**)

A dry round bottom flask charged with 2-(2-aminophenyl)ethan-1-ol (4.571 g, 20 mmol) and KOH (1.122 g, 20 mmol) was stirred at 180 °C for 4 h, the mixture was then cooled to room temperature, and H₂O (20 mL) was added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate, then the combined organic phase was washed with brine, dried over Na₂SO₄, filtered, and concentrated by rotary evaporation. The mixture was purified by column chromatography on silica gel (PE/EA = 10/1) to afford the corresponding product 2-vinylaniline **B** as a yellow oil. (1.380 g, 58 %).

To a solution of 2-vinylaniline (**B**) (1.119 g, 10 mmol) in CH₂Cl₂ (40 mL) were added pyridine (1.105 g, 14 mmol) and RCl (12 mmol) at 0 °C. After being stirred at 25 °C for 12h, the reaction mixture was poured into water and the product was extracted with CH₂Cl₂ (30 mL x 3), dried over Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude mixture was purified by column chromatography on silica gel (PE/EA = 10/1) to afford the corresponding product **1a-1d** as a white solid.

(2) N-(2-vinylphenyl)-sulfonamides (**1e-1j**)

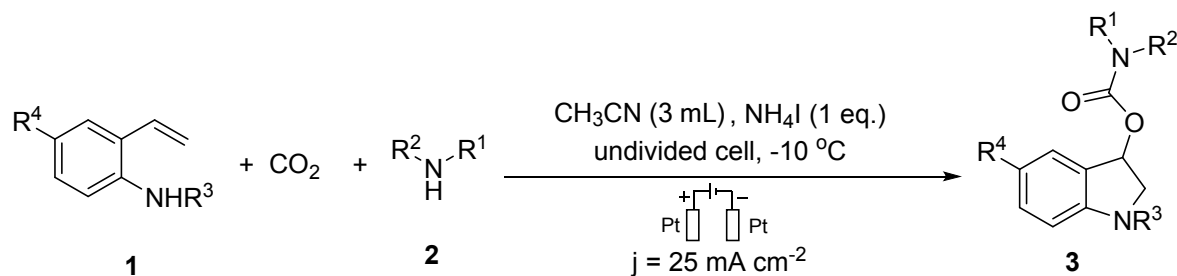


Scheme S2 Synthesis of N-(2-vinylphenyl)-sulfonamides (**1e-1j**)

To a suspension of potassium vinyltrifluoroborate (0.736 g, 5.5 mmol), Cs₂CO₃ (4.875 g, 15 mmol), PdCl₂(dppf) (0.363 g, 0.45 mmol) and the corresponding 2-bromoaniline (5 mmol) in THF (50 mL) was added water (5.0 mL). The reaction mixture was heated to 130 °C under reflux for 16 h, then cooled to room temperature and diluted with water (30 mL) followed by extraction with ether (30 mL x 3). The ethereal solution was washed with brine (50 mL), and then dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (PE/EA = 10/1) to give the desired products **D** as a yellow oil.

To a solution of products **D** (2 mmol) in CH₂Cl₂ (20 mL) were added pyridine (0.221 g, 2.8 mmol) and TsCl (0.457 g, 2.4 mmol) at 0 °C. After being stirred at 25 °C for 12 h, the reaction mixture was poured into water and the product was extracted with CH₂Cl₂ (20 mL x 3), dried over Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude mixture was purified by column chromatography on silica gel (PE/EA = 10/1) to afford the corresponding product **1e-1j** as a white solid.

4. General procedure for the preparation of products 3

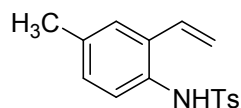


Scheme S3 Synthesis of products **3**

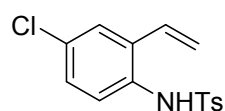
A 10 mL three-necked round-bottomed flask was charged with the **1** derivatives (0.3 mmol) and NH_4I (0.3 mmol). The cell was equipped with platinum electrodes ($1.0 \times 1.0 \text{ cm}^2$) as both the anode and cathode. The three-necked flask is pumped and ventilated three times so that the inside is filled with CO_2 . Then inject amine **2** (1.2 mmol), CH_3CN (3 mL) into the three-necked flask. Continuously inject CO_2 into the bottle at room temperature. After half an hour, place the reaction flask in cold hydrazine at -10°C and electrolyzed at a constant current of 25 mA for corresponding time. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel to afford the desired product **3**.

5. Characterization Data for the Substrates Products

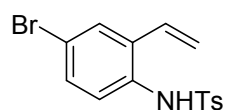
5.1 Characterization data for the products



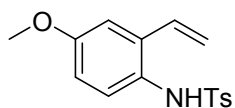
4-methyl-N-(4-methyl-2-vinylphenyl)benzenesulfonamide (**1e**). White solid (0.487 g, 85%). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.59 (d, $J = 8.0$ Hz, 2H), 7.22-7.18 (m, 3H), 7.14 (d, $J = 8.1$ Hz, 1H), 7.00 (d, $J = 7.9$ Hz, 1H), 6.58-6.51 (m, 2H), 5.49 (d, $J = 17.4$ Hz, 1H), 5.20 (d, $J = 11.1$ Hz, 1H), 2.34 (d, $J = 35.3$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.68, 136.50, 136.37, 133.11, 131.56, 130.39, 129.52, 129.25, 127.20, 127.10, 125.69, 117.45, 21.50, 20.96.



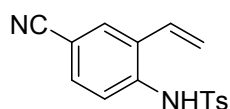
N-(4-chloro-2-vinylphenyl)-4-methylbenzenesulfonamide (**1f**). White solid (0.503 g, 82%). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.60 (d, $J = 8.3$ Hz, 2H), 7.33 (d, $J = 2.4$ Hz, 1H), 7.24-7.21 (m, 3H), 7.16-7.13 (m, 1H), 6.92 (s, 1H), 6.57-6.50 (m, 1H), 5.52 – 5.48 (m, 1H), 5.27-5.24 (m, 1H), 2.38 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 144.05, 135.93, 134.69, 132.21, 131.57, 130.36, 129.65, 128.35, 127.13, 126.74, 126.51, 118.97, 21.49.



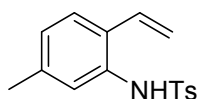
N-(4-bromo-2-vinylphenyl)-4-methylbenzenesulfonamide (**1g**). White solid (0.504 g, 72%). $^1\text{H NMR}$ (600 MHz, Chloroform-*d*) δ 7.60 (d, $J = 8.2$ Hz, 2H), 7.47 (d, $J = 2.2$ Hz, 1H), 7.31-7.29 (m, 1H), 7.22 (d, $J = 8.1$ Hz, 1H), 7.19 (d, $J = 8.6$ Hz, 0H), 6.76 (s, 1H), 6.51-6.46 (m, 1H), 5.50 (d, $J = 17.3$ Hz, 1H), 5.28 (d, $J = 11.1$ Hz, 1H), 2.39 (s, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 144.12, 135.94, 134.72, 132.15, 131.37, 130.25, 129.71, 129.62, 127.14, 126.63, 120.03, 119.33, 21.54.



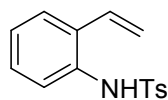
N-(4-methoxy-2-vinylphenyl)-4-methylbenzenesulfonamide (**1h**). White solid (0.460 g, 76%). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.92 (d, *J* = 2.9 Hz, 1H), 6.72-6.69 (m, 2H), 6.63-6.58 (m, 1H), 5.49 (d, *J* = 17.4 Hz, 1H), 5.16 (d, *J* = 11.2 Hz, 1H), 3.77 (s, 3H), 2.37 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 158.39, 143.57, 136.19, 135.91, 131.57, 129.43, 128.74, 127.20, 125.67, 116.99, 113.91, 110.88, 21.44.



N-(4-cyano-2-vinylphenyl)-4-methylbenzenesulfonamide (**1i**). Red solid (0.482 g, 81%). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.54-7.51 (m, 2H), 7.46 (d, *J* = 10.1 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.05 (s, 1H), 6.53-6.48 (m, 1H), 5.56 (d, *J* = 17.3 Hz, 1H), 5.46 (d, *J* = 11.0 Hz, 1H), 2.38 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 144.72, 137.59, 135.75, 132.14, 131.46, 131.15, 129.96, 129.63, 127.11, 121.68, 121.63, 118.29, 108.66, 21.58.

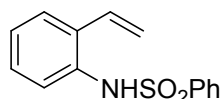


4-methyl-N-(5-methyl-2-vinylphenyl)benzenesulfonamide (**1j**). White solid (0.464 g, 81%). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.26-7.16 (m, 4H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.45-6.40 (m, 2H), 5.44 (d, *J* = 18.3 Hz, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 2.38 (s, 3H), 2.29 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 143.81, 138.77, 136.35, 132.85, 131.19, 129.69, 129.56, 127.33, 127.16, 126.61, 125.44, 117.40, 21.54, 21.16.

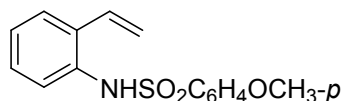


4-methyl-N-(2-vinylphenyl)benzenesulfonamide (**1a**). White solid (2.211 g, 81%). ¹H

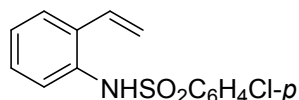
NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, $J = 8.3$ Hz, 2H), 7.37-7.35(m, 1H), 7.32 - 7.28 (m, 1H), 7.21-7.13 (m, 4H), 6.81 (s, 1H), 6.64 - 6.56 (m, 1H), 5.51 (d, $J = 17.4$ Hz, 1H), 5.24 (d, $J = 11.0$ Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 143.90, 136.37, 133.16, 132.94, 131.53, 129.66, 128.58, 127.26, 126.85, 126.55, 125.11, 118.07, 21.59.



N-(2-vinylphenyl)benzenesulfonamide (**1b**). White solid (2.150 g, 83%). **^1H NMR** (400 MHz, Chloroform-*d*) δ 7.75-7.72 (m, 2H), 7.55-7.51 (m, 1H), 7.43-7.39 (m, 2H), 7.38-7.36 (m, 1H), 7.31-7.29 (m, 1H), 7.22-7.14 (m, 2H), 6.89 (s, 1H), 6.61-6.54 (m, 1H), 5.51-5.47 (m, 1H), 5.23-5.20 (m, 1H). **^{13}C NMR** (101 MHz, CDCl_3) δ 139.12, 133.07, 132.93, 132.83, 131.25, 128.94, 128.48, 127.09, 126.67, 125.39, 117.92,.

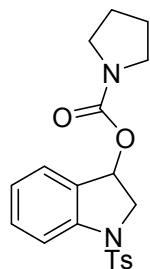


4-methoxy-N-(2-vinylphenyl)benzenesulfonamide (**1c**). White solid (2.349g, 83%). **^1H NMR** (600 MHz, Chloroform-*d*) δ 7.65 (d, $J = 8.9$ Hz, 1H), 7.37-7.36 (m, 1H), 7.28 (d, $J = 7.9$ Hz, 1H), 7.20-7.17 (m, 1H), 7.16-7.13 (m, 1H), 6.89-6.85 (m, 3H), 6.66-6.61 (m, 1H), 5.51 (d, $J = 17.4$ Hz, 1H), 5.23 (d, $J = 11.0$ Hz, 1H), 3.80 (s, 3H). **^{13}C NMR** (151 MHz, CDCl_3) δ 163.02, 133.08, 132.93, 131.40, 130.70, 129.27, 128.41, 126.63, 126.44, 125.18, 117.74, 114.03, 55.49.

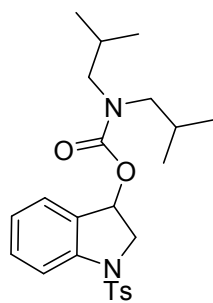


4-chloro-N-(2-vinylphenyl)benzenesulfonamide (**1d**). White solid (2.473 g, 84%). **^1H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (d, $J = 8.7$ Hz, 2H), 7.39 (d, $J = 8.6$ Hz, 3H), 7.30-7.28 (m, 1H), 7.24-7.17 (m, 2H), 6.83 (s, 1H), 6.61-6.54 (m, 1H), 5.54-5.49 (m, 1H), 5.26-5.23 (m, 1H). **^{13}C NMR** (101 MHz, CDCl_3) δ 139.50, 137.64, 133.20, 132.48, 131.14, 129.25, 128.62, 127.00, 126.85, 125.53, 118.20.

5.2 Characterization data for the products

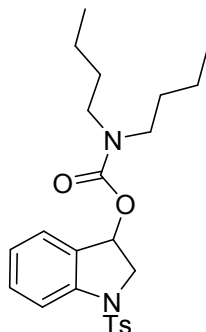


1-tosylindolin-3-yl pyrrolidine-1-carboxylate (**3aa**). White solid (0.089 g, 77%). mp: 107-109°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.74 (d, $J = 8.2$ Hz, 1H), 7.68 (d, $J = 8.3$ Hz, 2H), 7.40 – 7.34 (m, 2H), 7.21 (d, $J = 8.1$ Hz, 2H), 7.07-7.03 (m, 1H), 5.93-5.90 (m, 1H), 4.01 (d, $J = 5.2$ Hz, 2H), 3.37-3.33 (m, 2H), 2.97-2.94 (m, 2H), 2.35 (s, 3H), 1.82-1.76 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.04, 144.07, 142.76, 133.88, 130.62, 129.69, 129.62, 127.33, 126.90, 123.93, 115.00, 71.59, 56.13, 46.12, 45.62, 25.57, 24.85, 21.47. **HRMS** (m/z) [ESI]: calculated for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_4\text{SNa}^+ [\text{M}+\text{Na}]^+$: 409.1300, found 409.1195.

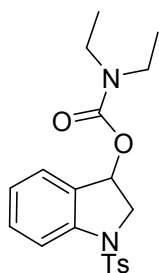


1-tosylindolin-3-yl diisobutylcarbamate (**3ab**). White solid (0.092 g, 69%). mp: 135-137°C. Petroleum ether/ethyl acetate = 20/1 (v/v) as eluent for column chromatography. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.74 (d, $J = 8.2$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 2H), 7.37-7.31 (m, 2H), 7.21 (d, $J = 8.1$ Hz, 2H), 7.06-7.02 (m, 1H), 5.94-5.92 (m, 1H), 4.06-4.01 (m, 1H), 3.94-3.90 (m, 1H), 3.16-3.10 (m, 1H), 2.98-2.93 (m, 1H), 2.80-2.69 (m, 2H), 2.35 (s, 3H), 1.96-1.89 (m, 1H), 1.74-1.67 (m, 1H), 0.87 (d, $J = 6.6$ Hz, 6H), 0.73-0.65 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.94, 144.12, 142.70, 133.75, 130.56, 129.68, 129.38, 127.25, 126.66, 123.87, 114.87,

71.77, 56.01, 54.75, 54.04, 27.18, 26.81, 21.50, 19.96, 19.78. **HRMS** (m/z) [ESI]: calculated for C₂₄H₃₂N₂O₄SNa⁺ [M+Na]⁺: 467.2083, found 467.1984.

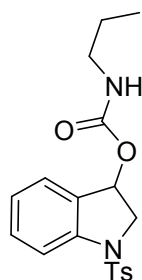


1-tosylindolin-3-yl dibutylcarbamate (**3ac**). White solid (0.061 g, 47%). mp: 129-131°C. Petroleum ether/ethyl acetate = 20/1(v/v) as eluent for column chromatography. **¹H NMR** (600 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.37-7.33 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.06-7.03 (m, 1H), 5.93-5.91 (m, 1H), 4.03-3.95 (m, 2H), 3.26-3.21 (m, 1H), 3.15-3.11 (m, 1H), 2.91-2.88 (m, 1H), 2.36 (s, 3H), 1.50-1.47 (m, 2H), 1.10-1.06 (m, 2H), 0.94-0.92 (m, 3H), 0.77-0.75 (m, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 155.43, 144.15, 142.70, 133.74, 130.59, 129.67, 129.47, 127.30, 126.68, 123.86, 114.85, 77.21, 77.00, 76.79, 71.80, 56.04, 47.10, 46.17, 30.53, 30.10, 21.54, 20.01, 19.68, 13.87, 13.72. **HRMS** (m/z) [ESI]: calculated for C₂₄H₃₂N₂O₄SNa⁺ [M+Na]⁺: 467.2083, found 467.1982.

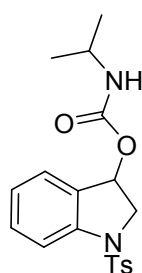


1-tosylindolin-3-yl diethylcarbamate (**3ad**). Yellow oil (0.084 g, 72%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.43-7.34 (m, 4H), 7.12-7.08 (m, 1H), 5.86-5.84 (m, 1H), 4.16-4.11 (m, 1H), 3.89-3.85 (m, 1H), 3.33-3.13 (m, 2H), 2.78 (d, *J* = 6.7 Hz, 2H), 2.32 (s, 3H), 1.03-1.00 (m, 3H), 0.79-

0.76 (m, 3H). ^{13}C NMR (101 MHz, DMSO) δ 154.15, 144.46, 142.11, 133.10, 130.73, 129.96, 129.90, 127.06, 126.94, 124.20, 114.56, 71.24, 55.76, 41.26, 40.47, 20.97, 13.80, 13.35. HRMS (m/z) [ESI]: calculated for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4\text{SNa}^+$ [M+Na] $^+$: 411.1457, found 411.1352.

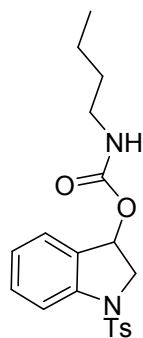


1-tosylindolin-3-yl propylcarbamate (**3ae**). White solid (0.084 g, 75%). mp: 109-111°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, J = 8.2 Hz, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.39-7.34 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.08-7.04 (m, 1H), 5.88-5.86 (m, 1H), 4.39 (s, 1H), 4.01-3.92 (m, 2H), 3.12-3.06 (m, 2H), 2.36 (s, 3H), 1.52-1.43 (m, 2H), 0.91-0.87 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.42, 144.04, 142.83, 133.78, 130.76, 129.58, 129.46, 127.48, 126.69, 124.12, 115.35, 71.51, 56.05, 42.68, 23.08, 21.50, 11.15. HRMS (m/z) [ESI]: calculated for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_4\text{SNa}^+$ [M+Na] $^+$: 397.1300, found 397.1188.

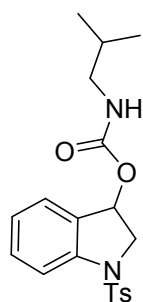


1-tosylindolin-3-yl isopropylcarbamate (**3af**). White solid (0.058 g, 52%). mp: 113-115°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.73 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 7.9 Hz, 2H), 7.38-7.35 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.07-7.05 (m, 1H), 5.85 (d, J = 5.7 Hz, 1H), 4.21 (d, J = 6.9 Hz, 1H), 3.99-3.94 (m, 2H), 3.78-3.73 (m, 1H), 2.36 (s, 3H), 1.14-1.09 (m, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 154.47, 143.97,

142.82, 133.72, 130.74, 129.59, 129.51, 127.47, 126.67, 124.16, 115.43, 71.33, 56.08, 43.04, 22.86, 21.53. **HRMS** (m/z) [ESI]: calculated for C₁₉H₂₂N₂O₄SNa⁺ [M+Na]⁺: 397.1300, found 397.1184.

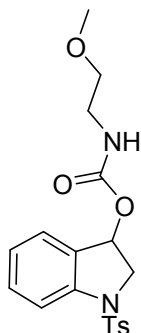


1-tosylindolin-3-yl butylcarbamate (**3ag**). White solid (0.078 g, 67%). mp:121-123°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.38-7.34 (m, 2H), 7.08-7.04 (m, 1H), 5.87-5.85 (m, 1H), 4.38 (s, 1H), 4.00-3.91 (m, 2H), 3.15-3.09 (m, 2H), 2.36 (s, 3H), 1.45-1.41 (m, 2H), 1.33-1.28 (m, 2H), 0.93-0.89 (m, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 155.39, 144.04, 142.80, 133.73, 130.75, 129.57, 129.44, 127.46, 126.68, 124.11, 115.32, 71.48, 56.04, 40.66, 31.87, 21.49, 19.80, 13.66. **HRMS** (m/z) [ESI]: calculated for C₂₀H₂₄N₂O₄SNa⁺ [M+Na]⁺: 411.1457, found 411.1347.

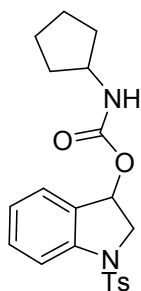


1-tosylindolin-3-yl isobutylcarbamate (**3ah**). White solid (0.055 g, 47%). mp: 135-137°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.39-7.34 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.08-7.04 (m, 1H), 5.88-5.86 (m, 1H), 4.45-4.43 (m, 1H), 4.01-3.92 (m, 2H), 2.97-2.93 (m, 2H), 2.36 (s,

3H), 1.73-1.66 (m, 1H), 0.88–0.86 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.53, 144.05, 142.81, 133.75, 130.76, 129.45, 127.47, 126.68, 124.12, 115.33, 71.51, 56.04, 48.36, 28.69, 21.50, 19.83. **HRMS** (m/z) [ESI]: calculated for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4\text{SNa}^+$ [M+Na] $^+$: 411.1457, found 411.13473.

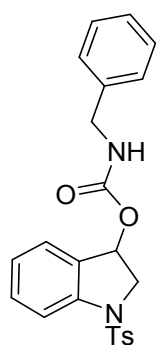


1-tosylindolin-3-yl (2-methoxyethyl)carbamate (**3ai**). Yellow oil (0.070 g, 65%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, $J = 7.8$ Hz, 1H), 7.63 (d, $J = 6.7$ Hz, 2H), 7.37-7.33 (m, 2H), 7.21 (d, $J = 6.7$ Hz, 2H), 7.07-7.03 (m, 1H), 5.85-5.84 (m, 1H), 4.75 (s, 1H), 4.00-3.93 (m, 2H), 3.40-3.30 (m, 7H), 2.36-2.35 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.38, 144.15, 142.82, 133.64, 130.75, 129.53, 129.43, 127.42, 126.68, 124.16, 115.52, 71.62, 71.11, 58.70, 56.04, 40.69, 21.42. **HRMS** (m/z) [ESI]: calculated for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_5\text{SNa}^+$ [M+Na] $^+$: 413.1249, found 413.1138.

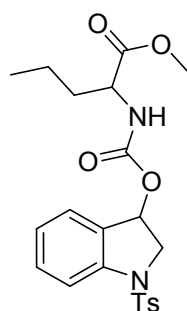


1-tosylindolin-3-yl cyclopentylcarbamate (**3aj**). White solid (0.068 g, 57%). mp: 157-159°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.74 (d, $J = 8.1$ Hz, 1H), 7.66 (d, $J = 8.1$ Hz, 2H), 7.38-7.35 (m, 2H), 7.22 (d, $J = 8.1$ Hz, 2H), 7.08-7.05 (m, 1H), 5.86 (d, $J = 5.5$ Hz, 1H), 4.31 (d, $J = 6.8$ Hz, 1H), 4.00-3.93 (m, 2H), 2.37 (s, 3H),

1.95-1.91 (m, 2H), 1.63-1.59 (m, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 154.83, 144.01, 142.84, 133.74, 130.77, 129.59, 129.47, 127.49, 126.68, 124.15, 115.41, 71.40, 56.11, 52.66, 33.11, 23.43, 21.55. HRMS (m/z) [ESI]: calculated for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_4\text{SNa}^+$ [M+Na] $^+$: 423.1457, found 423.1341.

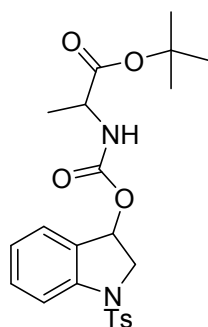


1-tosylindolin-3-yl benzylcarbamate (**3ak**). White solid (0.061 g, 49%). mp:161-163°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, $J = 8.3$ Hz, 1H), 7.62 (d, $J = 8.2$ Hz, 2H), 7.40-7.29 (m, 5H), 7.23 (d, $J = 7.0$ Hz, 2H), 7.14-7.06 (m, 3H), 5.90-5.88 (m, 1H), 4.60 (s, 1H), 4.36-4.24 (m, 2H), 4.02-3.98 (m, 2H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.32, 144.02, 142.88, 137.92, 133.76, 130.85, 129.53, 129.46, 128.73, 127.70, 127.53, 127.45, 126.73, 124.26, 115.66, 71.85, 56.06, 45.05, 21.33. HRMS (m/z) [ESI]: calculated for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_4\text{SNa}^+$ [M+Na] $^+$: 445.1300, found 445.1188.

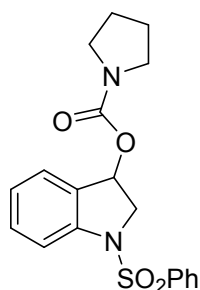


methyl 2-((((1-tosylindolin-3-yl)oxy)carbonyl)amino)pentanoate (**3al**). Yellow oil (0.044 g, 33%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, $J = 8.2$ Hz, 1H), 7.66-7.64 (m, 2H), 7.39-7.34 (m, 2H), 7.24-7.22 (m, 2H), 7.08-7.06 (m, 1H), 5.86 (d,

$J = 4.3$ Hz, 1H), 4.88-4.80 (m, 1H), 4.30 (d, $J = 7.9$ Hz, 1H), 4.01-3.98 (m, 2H), 3.74 (d, $J = 25.8$ Hz, 2H), 2.37 (d, $J = 2.2$ Hz, 3H), 1.78-1.74 (m, 2H), 1.36-1.33 (m, 2H), 0.91-0.86 (m, 3H). **^{13}C NMR** (151 MHz, CDCl_3) δ 172.76, 154.86, 144.18, 142.90, 133.70, 130.89, 129.58, 127.52, 126.71, 124.26, 115.75, 115.56, 71.96, 56.05, 53.51, 52.36, 34.78, 21.52, 18.45, 13.63. **HRMS** (m/z) [ESI]: calculated for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_6\text{SNa}^+ [\text{M}+\text{Na}]^+$: 469.1512, found 469.1405.

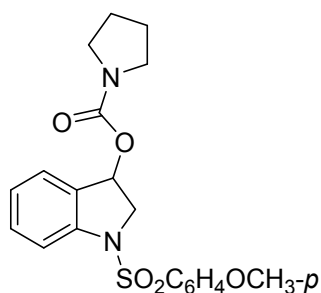


tert-butyl (((1-tosylindolin-3-yl)oxy)carbonyl)alaninate (**3ak**). Yellow oil (0.042 g, 31%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. **^1H NMR** (600 MHz, Chloroform-*d*) δ 7.74 (d, $J = 8.1$ Hz, 1H), 7.64-7.62 (m, 2H), 7.38-7.34 (m, 2H), 7.23-7.21 (m, 2H), 7.08-7.05 (m, 1H), 5.86-5.82 (m, 1H), 4.95-4.91 (m, 1H), 4.17-4.14 (m, 1H), 3.99-3.98 (m, 2H), 2.37 (s, 3H), 1.44 (d, $J = 4.6$ Hz, 9H), 1.36-1.34 (m, 3H). **^{13}C NMR** (151 MHz, CDCl_3) δ 171.79, 154.49, 144.24, 142.87, 133.65, 130.81, 129.59, 129.37, 127.43, 126.73, 124.27, 115.70, 82.09, 71.73, 56.04, 49.97, 49.30, 27.92, 21.48, 19.28. **HRMS** (m/z) [ESI]: calculated for $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_6\text{SNa}^+ [\text{M}+\text{Na}]^+$: 483.1668, found 483.1559.

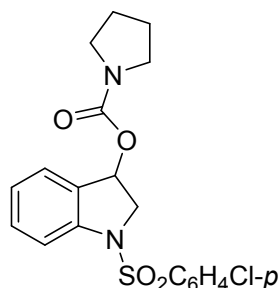


1-(phenylsulfonyl)indolin-3-yl pyrrolidine-1-carboxylate (**3ba**). White solid (0.084 g, 75%). mp:117-119°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. **^1H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (d, $J = 7.3$ Hz,

1H), 7.75 (d, $J = 8.2$ Hz, 1H), 7.56-7.52 (m, 1H), 7.45-7.35 (m, 4H), 7.08-7.04 (m, 1H), 5.93-5.90 (m, 1H), 4.04-4.03 (m, 2H), 3.36-3.33 (m, 2H), 2.97-2.94 (m, 2H), 1.82-1.77 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 154.03, 142.65, 136.90, 133.16, 130.68, 129.66, 129.03, 127.29, 126.96, 124.04, 114.95, 71.58, 56.19, 46.16, 45.66, 25.52, 24.85. **HRMS** (m/z) [ESI]: calculated for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 395.1144, found 395.1035.

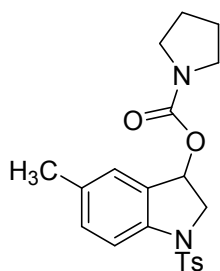


1-((4-methoxyphenyl)sulfonyl)indolin-3-yl pyrrolidine-1-carboxylate (**3ca**). White solid (0.081 g, 67%). mp:137-139°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. ^1H NMR (400 MHz, Chloroform- d) δ 7.75-7.72 (m, 3H), 7.40-7.34 (m, 2H), 7.07-7.03 (m, 1H), 6.88 (d, $J = 8.8$ Hz, 2H), 5.92-5.90 (m, 1H), 4.00 (d, $J = 4.6$ Hz, 2H), 3.80 (s, 3H), 3.36-3.33 (m, 2H), 2.99-2.96 (m, 2H), 1.82-1.76 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.35, 154.05, 142.86, 130.61, 129.71, 129.45, 128.43, 126.90, 123.90, 115.03, 114.15, 71.65, 56.10, 55.51, 46.14, 45.67, 25.52, 24.85. **HRMS** (m/z) [ESI]: calculated for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_5\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 425.1249, found 425.1140.

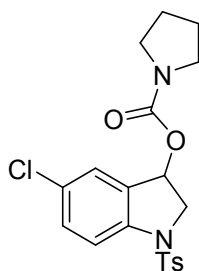


1-((4-chlorophenyl)sulfonyl)indolin-3-yl pyrrolidine-1-carboxylate (**3da**). White solid (0.090 g, 73%). mp:131-133°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. ^1H NMR (400 MHz, Chloroform- d) δ 7.73 (t, $J =$

8.1 Hz, 2H), 7.45-7.34 (m, 3H), 7.09 (td, $J = 7.5, 0.8$ Hz, 1H), 5.89 (dd, $J = 6.8, 2.1$ Hz, 1H), 3.34 (t, $J = 6.1$ Hz, 2H), 2.89 (dt, $J = 9.1, 5.0$ Hz, 2H), 1.86-1.75 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 153.90, 142.39, 139.82, 135.33, 130.77, 129.87, 129.30, 128.66, 127.05, 124.46, 115.28, 71.53, 56.22, 46.17, 45.66, 25.58, 24.84. HRMS (m/z) [ESI]: calculated for $\text{C}_{19}\text{H}_{19}\text{ClN}_2\text{O}_4\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 429.0754, found 429.0634.

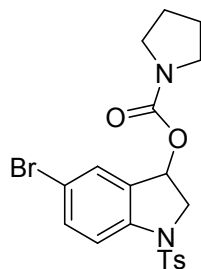


5-methyl-1-tosylindolin-3-yl pyrrolidine-1-carboxylate (**3ea**). White solid (0.090 g, 75%). mp:152-153°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.67-7.61 (m, 3H), 7.21-7.15 (m, 4H), 5.88-5.86 (m, 1H), 3.39-3.38 (m, 2H), 3.36-3.33 (m, 2H), 2.96-2.93 (m, 2H), 2.32 (d, $J = 32.7$ Hz, 6H), 1.82-1.77 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 154.08, 143.94, 140.43, 133.81, 133.75, 131.33, 129.83, 129.59, 127.23, 114.93, 71.69, 56.26, 46.12, 45.63, 25.58, 24.86, 21.49, 20.85. HRMS (m/z) [ESI]: calculated for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_4\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 423.1457, found 423.1368.

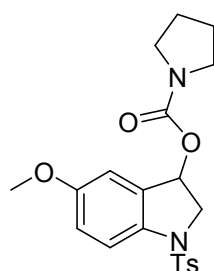


5-chloro-1-tosylindolin-3-yl pyrrolidine-1-carboxylate (**3fa**). White solid (0.066 g, 53%). mp:126-128°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.68-7.65 (m, 3H), 7.37 (d, $J = 1.8$ Hz, 1H), 7.32-7.31 (m, 1H), 7.23 (d, $J = 8.1$ Hz, 2H), 5.87-5.86 (m, 1H), 4.02-4.00 (m, 2H), 3.36-3.34 (m, 2H), 2.96-2.94 (m, 2H), 2.37 (s, 3H), 1.83-1.78

(m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 153.74, 144.37, 141.39, 133.51, 131.53, 130.68, 129.75, 129.11, 127.32, 127.04, 116.13, 70.98, 56.26, 46.18, 45.67, 25.58, 24.84, 21.51. **HRMS** (m/z) [ESI]: calculated for $\text{C}_{20}\text{H}_{21}\text{ClN}_2\text{O}_4\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 443.0911, found 443.0798.

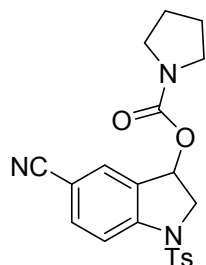


5-bromo-1-tosylindolin-3-yl pyrrolidine-1-carboxylate (**3ga**). White solid (0.050 g, 36%). mp:133-135°C. Petroleum ether/ethyl acetate = 20/1-5/1 (v/v) as eluent for column chromatography. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.7 Hz, 1H), 7.52 (d, J = 1.8 Hz, 1H), 7.47-7.45 (m, 1H), 7.24 (d, J = 8.1 Hz, 2H), 5.88-5.87 (m, 1H), 4.01-3.99 (m, 2H), 3.36-3.34 (m, 2H), 2.97-2.95 (m, 2H), 2.37 (s, 3H), 1.83-1.78 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 153.73, 144.40, 141.91, 133.55, 133.50, 131.89, 129.96, 129.77, 127.31, 116.53, 116.48, 70.90, 56.20, 46.19, 45.68, 25.58, 24.84, 21.52. **HRMS** (m/z) [ESI]: calculated for $\text{C}_{20}\text{H}_{21}\text{BrN}_2\text{O}_4\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: 487.0405, found 489.0274.

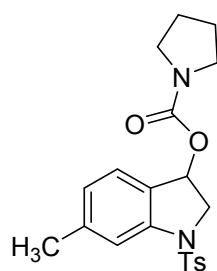


5-methoxy-1-tosylindolin-3-yl pyrrolidine-1-carboxylate (**3ha**). White solid (0.028 g, 23%). mp:116-118°C. Petroleum ether/ethyl acetate = 20/1-5/1 (v/v) as eluent for column chromatography. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.67 (d, J = 9.6 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 6.92-6.91 (m, 2H), 5.85-5.84 (m, 1H), 4.05-4.01 (m, 1H), 3.97-3.95 (m, 1H), 3.76 (s, 3H), 3.36-3.32 (m, 2H), 2.91-2.89 (m, 2H), 2.35 (s, 4H), 1.82-1.77 (m, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 156.72,

153.97, 143.89, 136.18, 133.61, 131.30, 129.56, 127.45, 116.74, 116.53, 111.40, 71.81, 56.40, 55.68, 46.13, 45.61, 25.59, 24.86, 21.49. **HRMS** (m/z) [ESI]: calculated for C₂₁H₂₄N₂O₅SNa⁺ [M+Na]⁺: 439.1406, found 439.1293.



5-cyano-1-tosylindolin-3-yl pyrrolidine-1-carboxylate (**3ia**). White solid (0.039 g, 32%). mp: 119-120°C. Petroleum ether/ethyl acetate = 10/1-8/1 (v/v) as eluent for column chromatography. ¹H NMR (600 MHz, Chloroform-d) δ 7.77 (d, J = 8.5 Hz, 1H), 7.69-7.67 (m, 3H), 7.62-7.61 (m, 1H), 7.24 (d, J = 4.1 Hz, 2H), 5.93-5.91 (m, 1H), 4.04-4.03 (m, 2H), 3.35-3.33 (m, 2H), 3.02-2.97 (m, 2H), 2.36 (s, 3H), 1.82-1.78 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 153.55, 146.28, 144.96, 135.06, 133.50, 131.29, 130.65, 129.97, 127.15, 118.54, 114.79, 106.87, 70.31, 56.14, 46.25, 45.73, 25.56, 24.81, 21.55. **HRMS** (m/z) [ESI]: calculated for C₂₁H₂₁N₃O₄SNa⁺ [M+Na]⁺: 434.1100, found 434.1105.

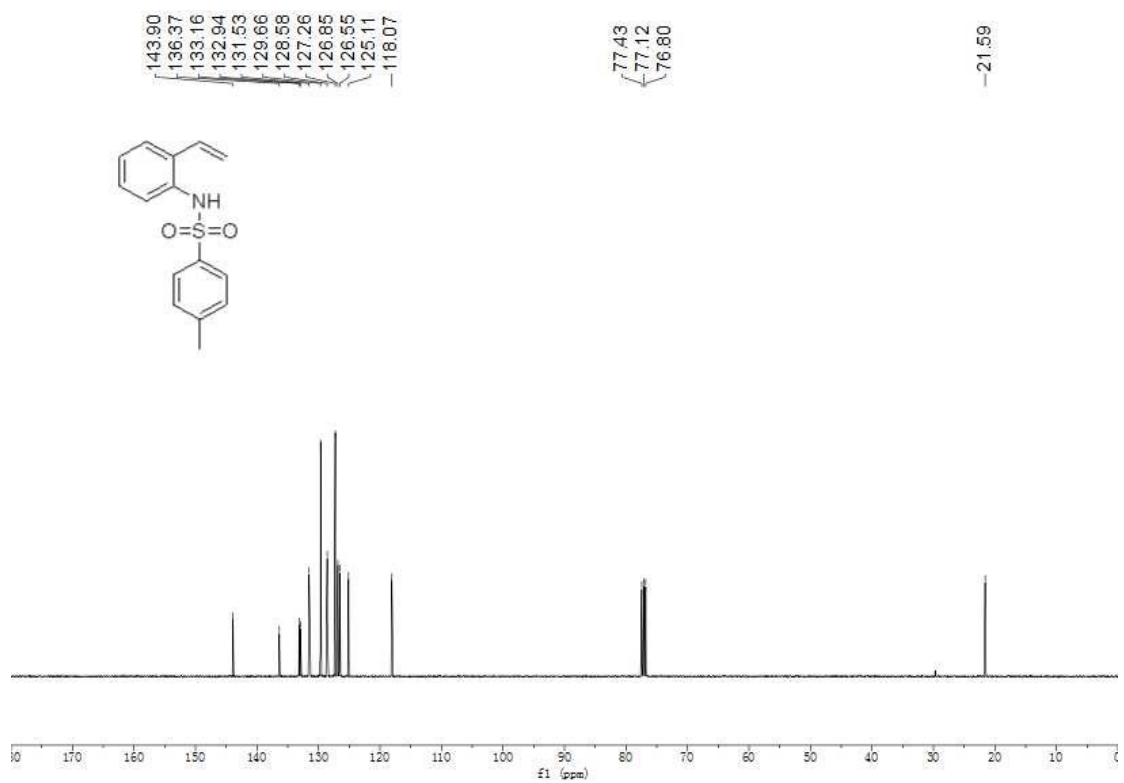
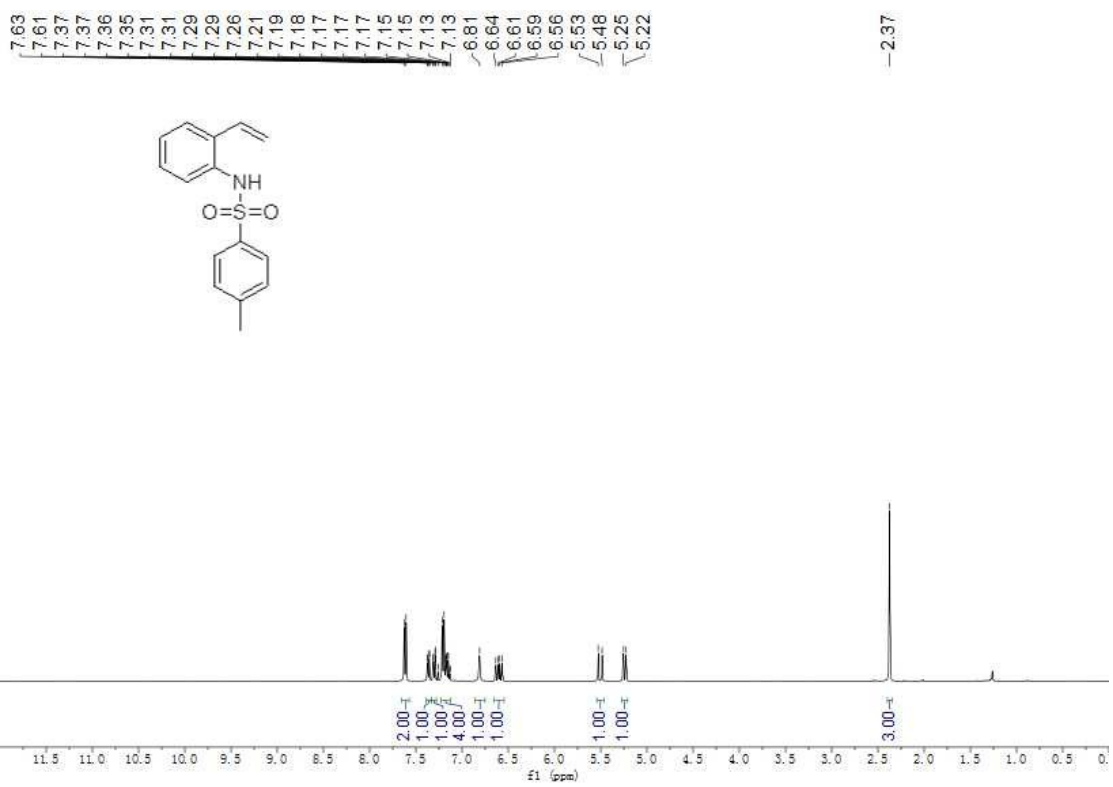


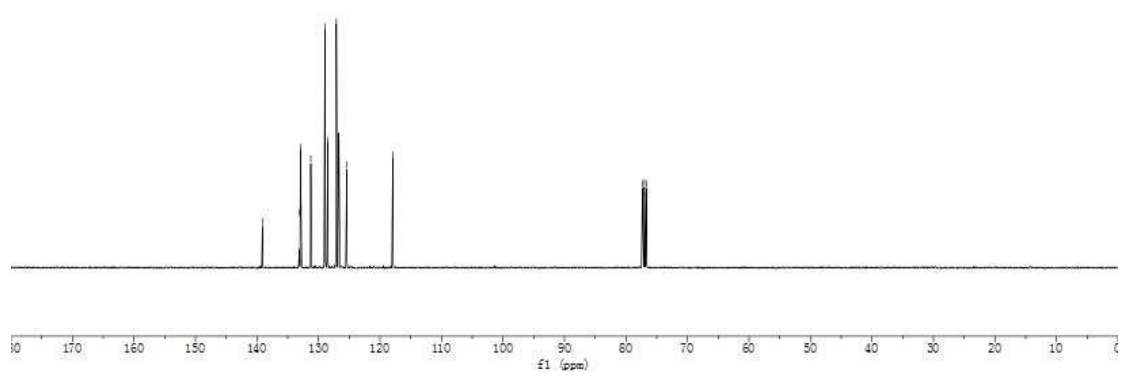
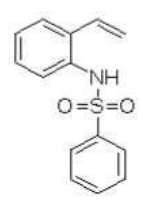
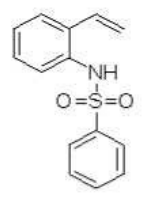
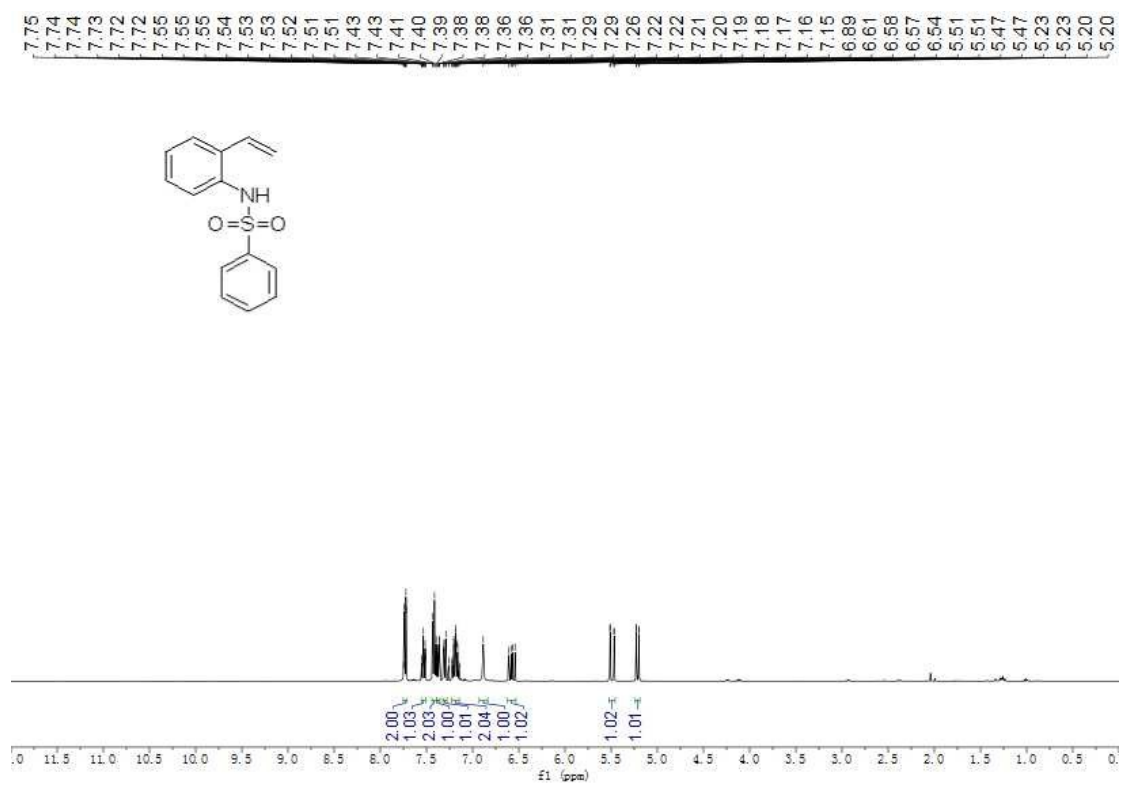
6-methyl-1-tosylindolin-3-yl pyrrolidine-1-carboxylate (**3ja**). White solid (0.080 g, 67%). mp: 123-125°C. Petroleum ether/ethyl acetate = 10/1-8/1 (v/v) as eluent for column chromatography. ¹H NMR (600 MHz, Chloroform-d) δ 7.67 (d, J = 8.2 Hz, 2H), 7.56 (s, 1H), 7.25 (d, J = 6.6 Hz, 2H), 7.21 (d, J = 8.1 Hz, 1H), 6.86 (d, J = 7.7 Hz, 1H), 5.86-5.85 (m, 1H), 3.98 (d, J = 4.6 Hz, 2H), 3.34-3.31 (m, 2H), 2.93-2.91 (m, 2H), 2.39 (s, 3H), 2.34 (s, 3H), 1.80-1.74 (m, 3H). ¹³C NMR (151 MHz, CDCl₃) δ

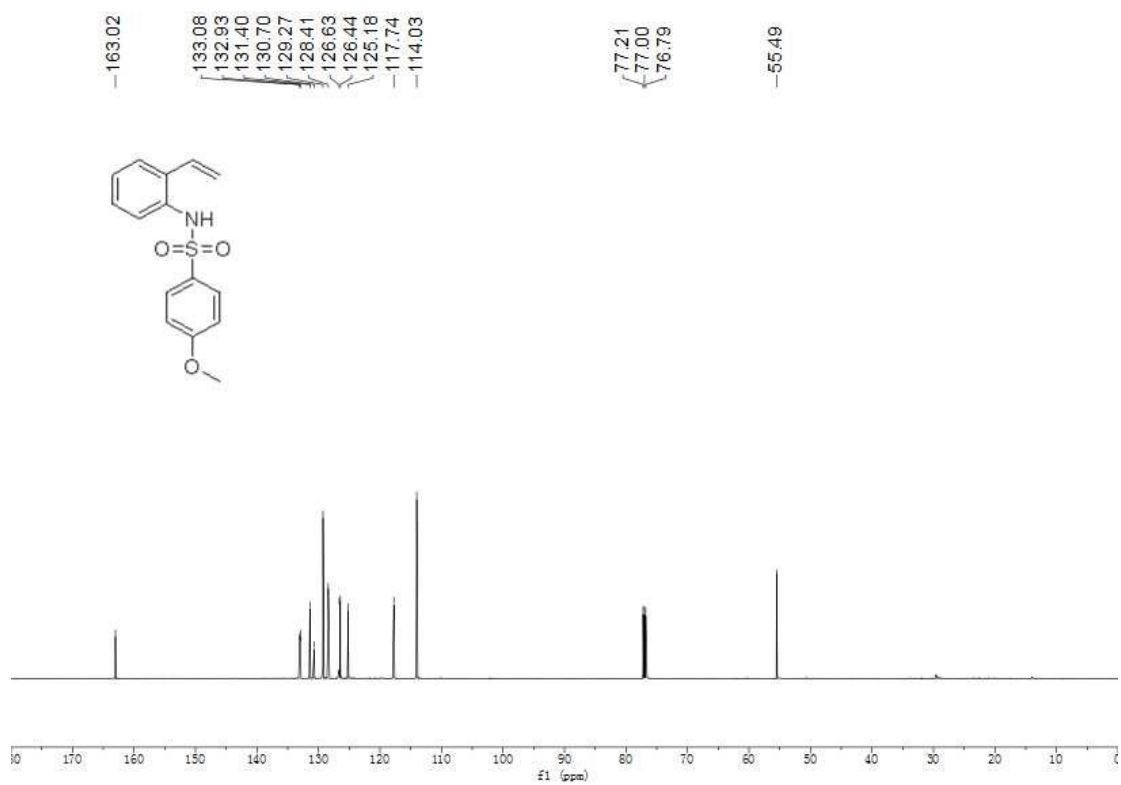
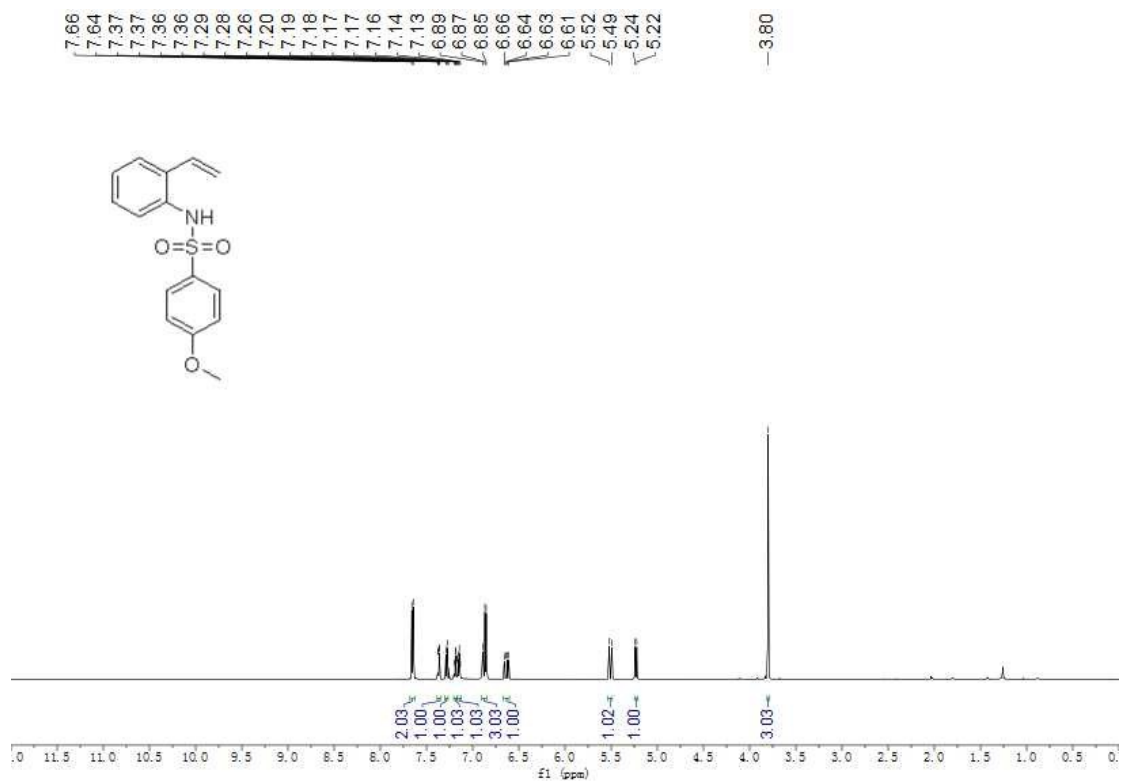
154.11, 144.00, 142.95, 141.12, 133.96, 129.62, 127.29, 126.89, 126.53, 124.89,
115.46, 71.47, 56.44, 46.08, 45.59, 25.57, 24.85, 21.91, 21.49. **HRMS** (m/z) [ESI]:
calculated for $C_{21}H_{24}N_2O_4SNa^+$ [M+Na]⁺: 423.1457, found 423.1364.

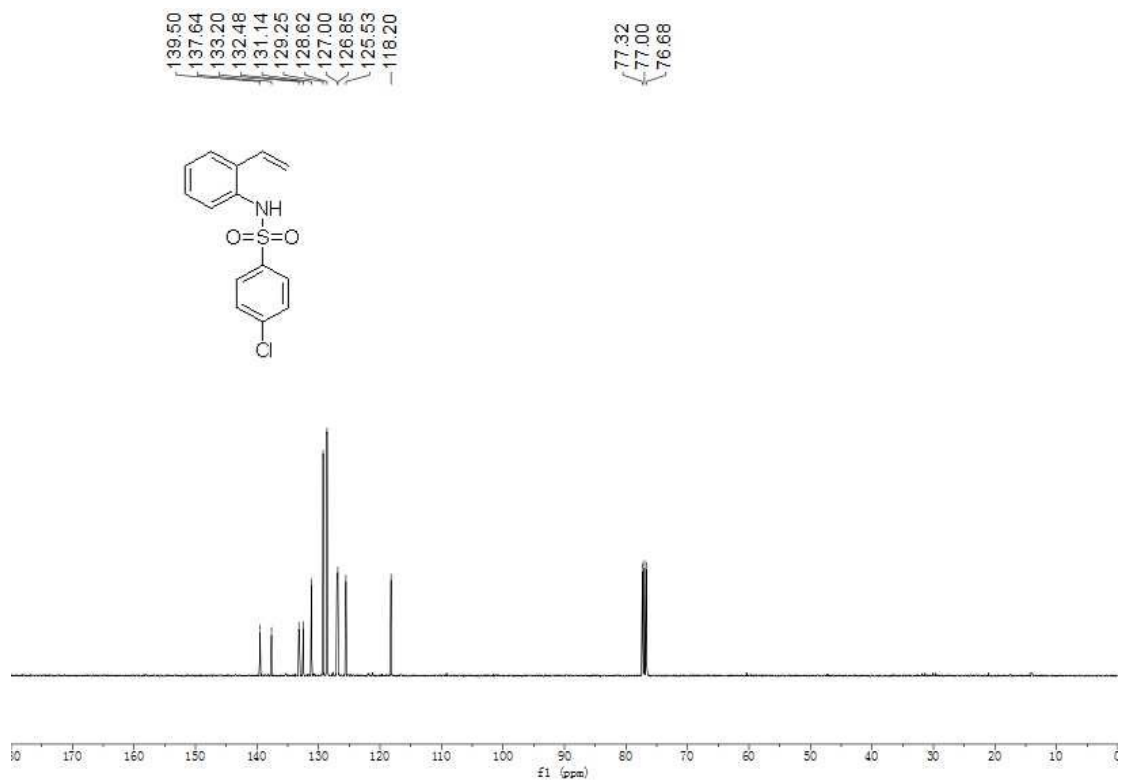
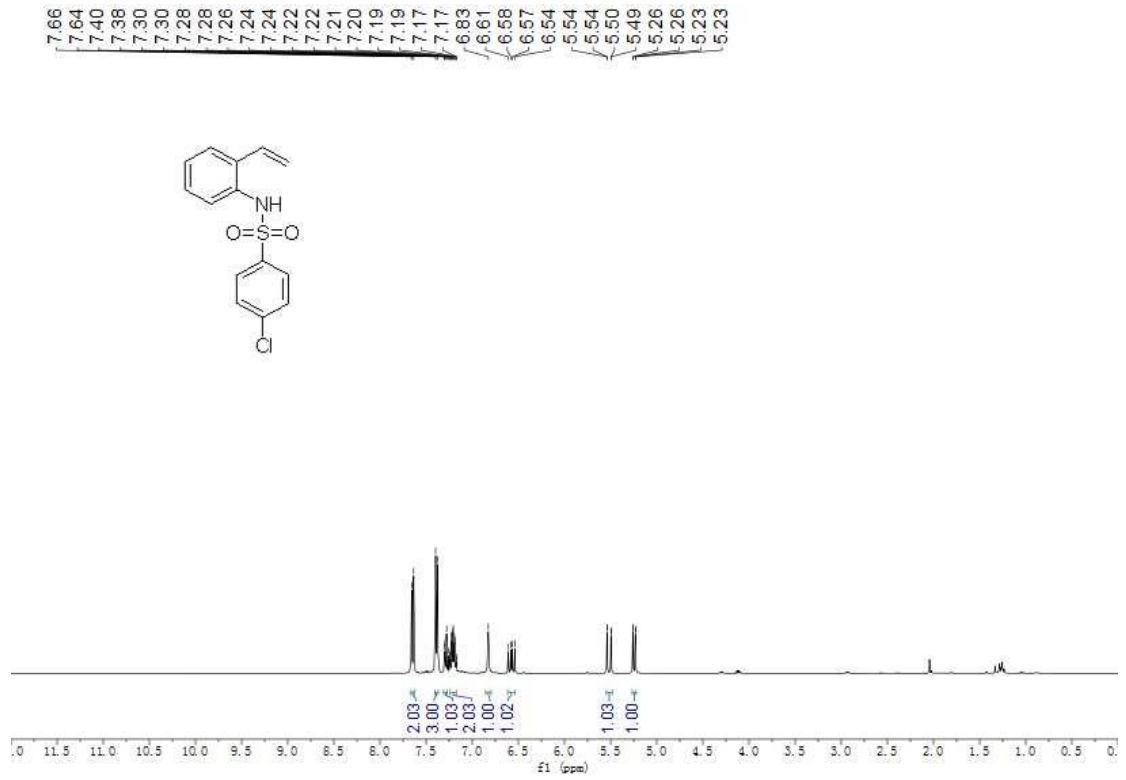
6. NMR Data

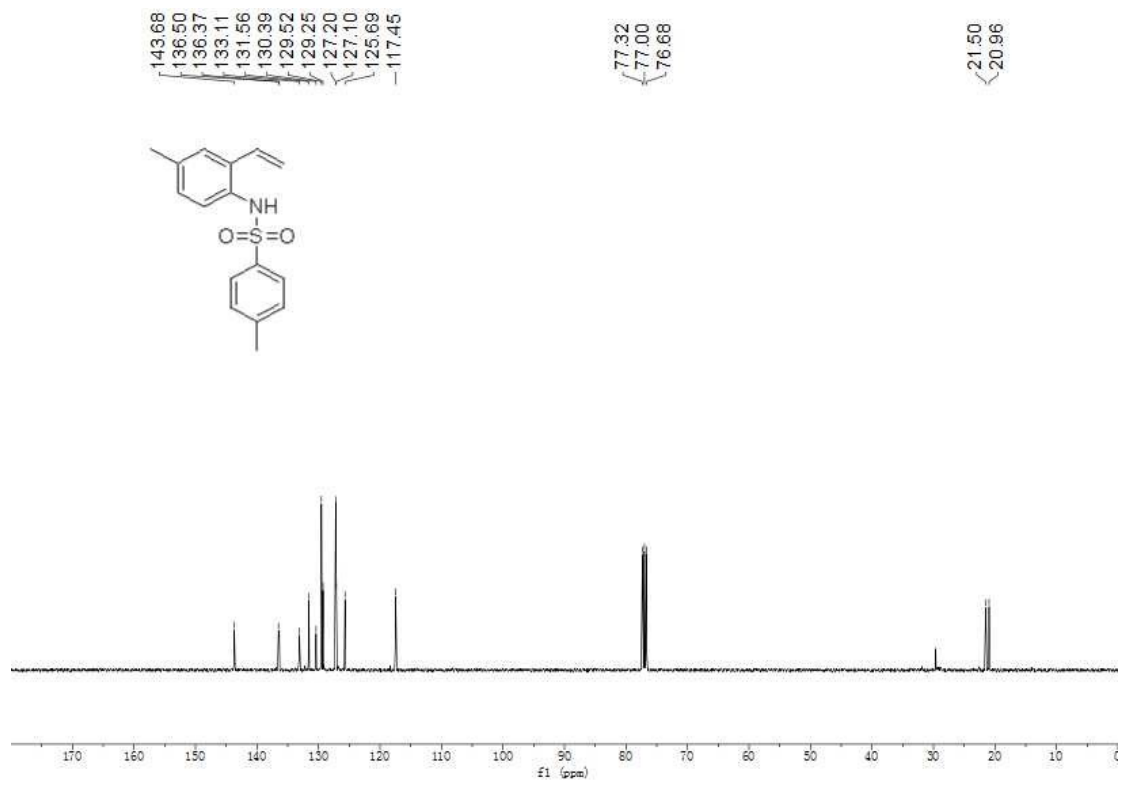
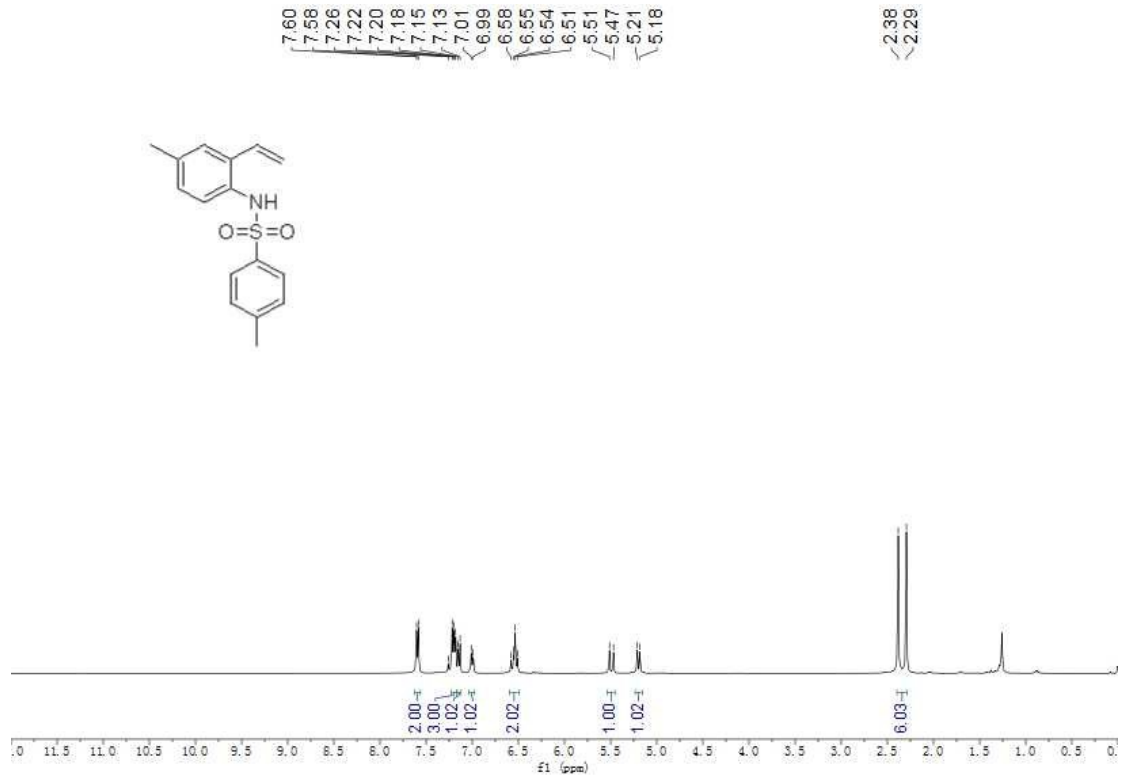
NMR Spectra of Substrates

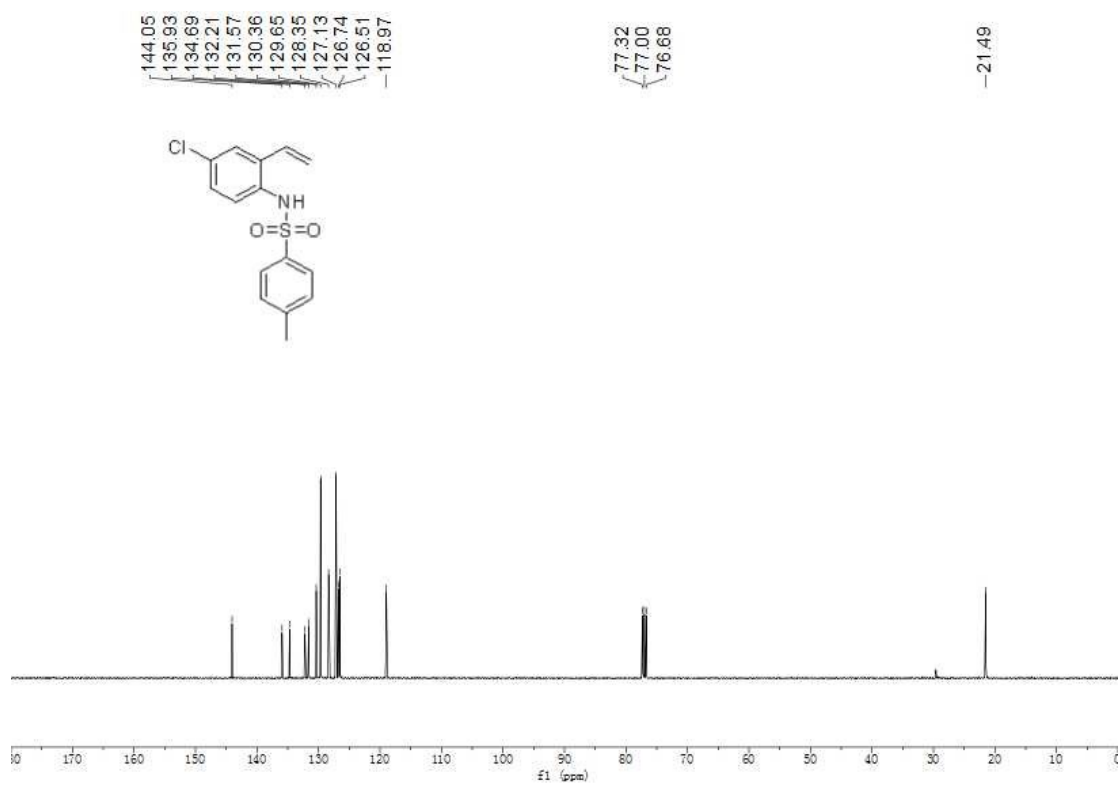
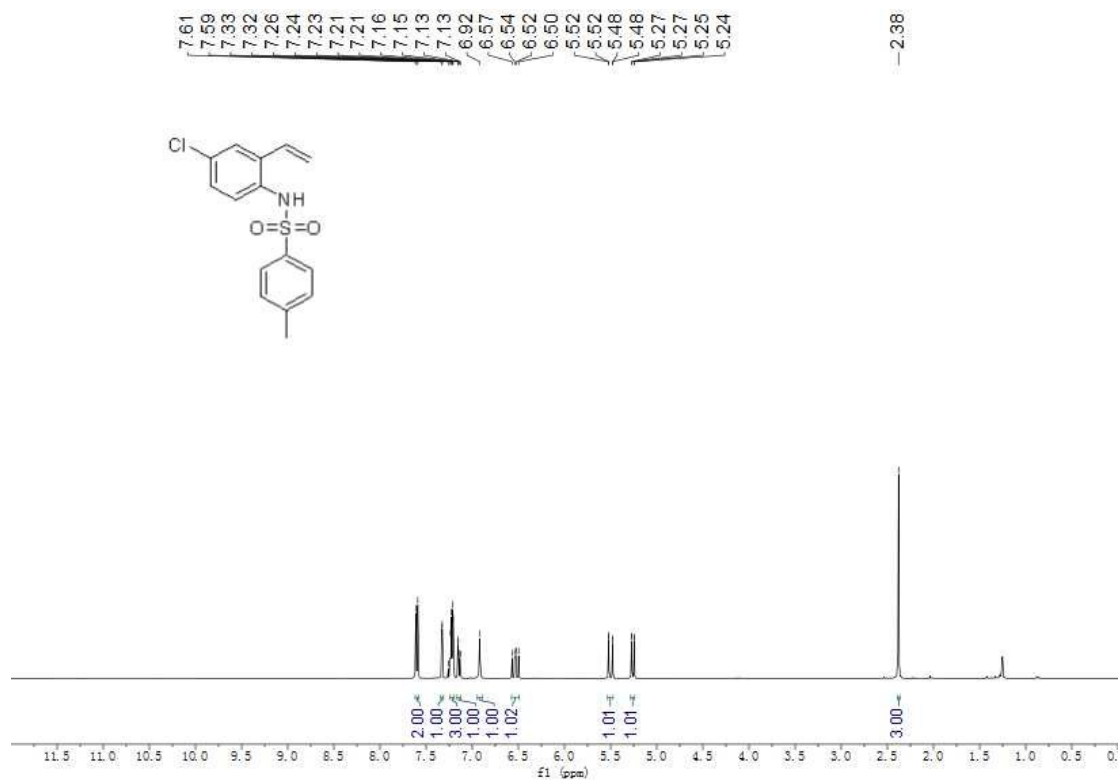


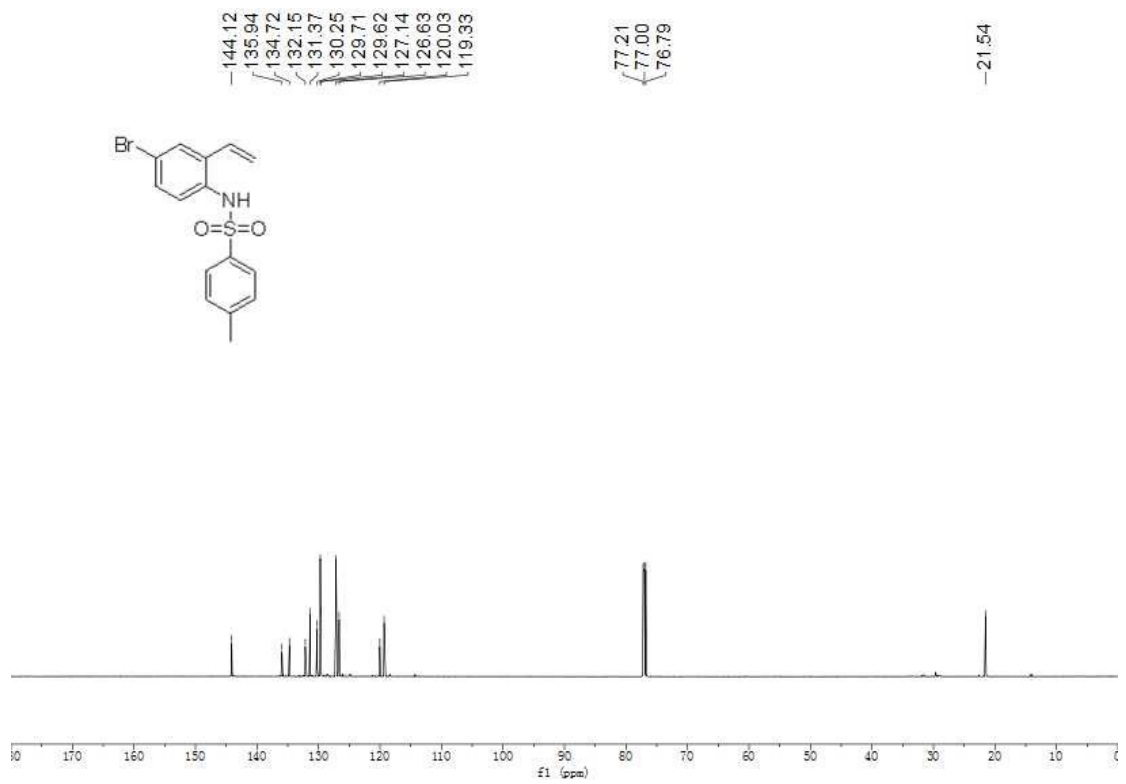
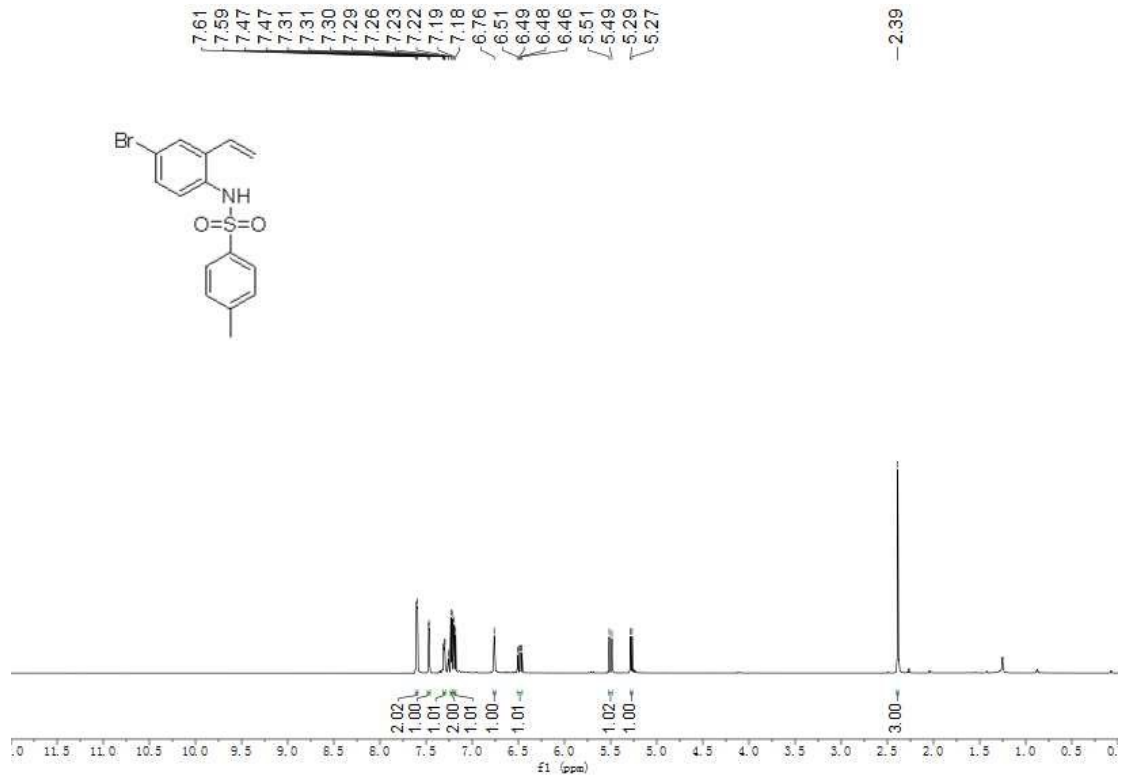


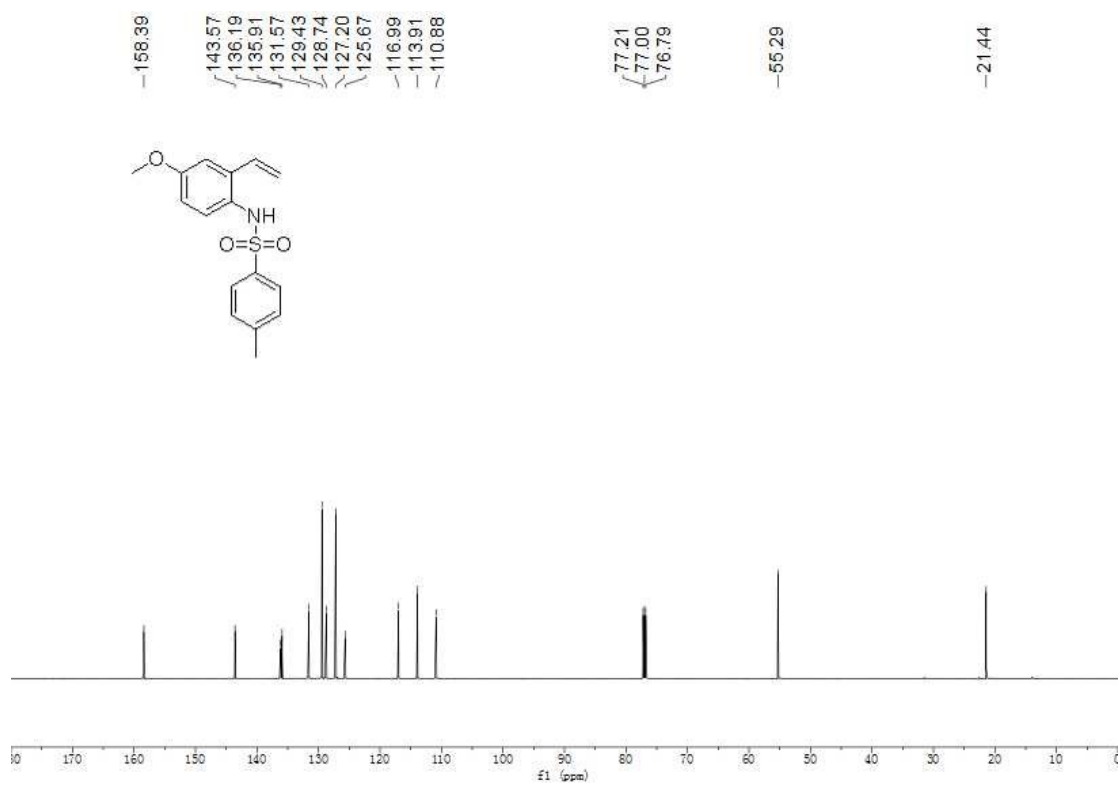
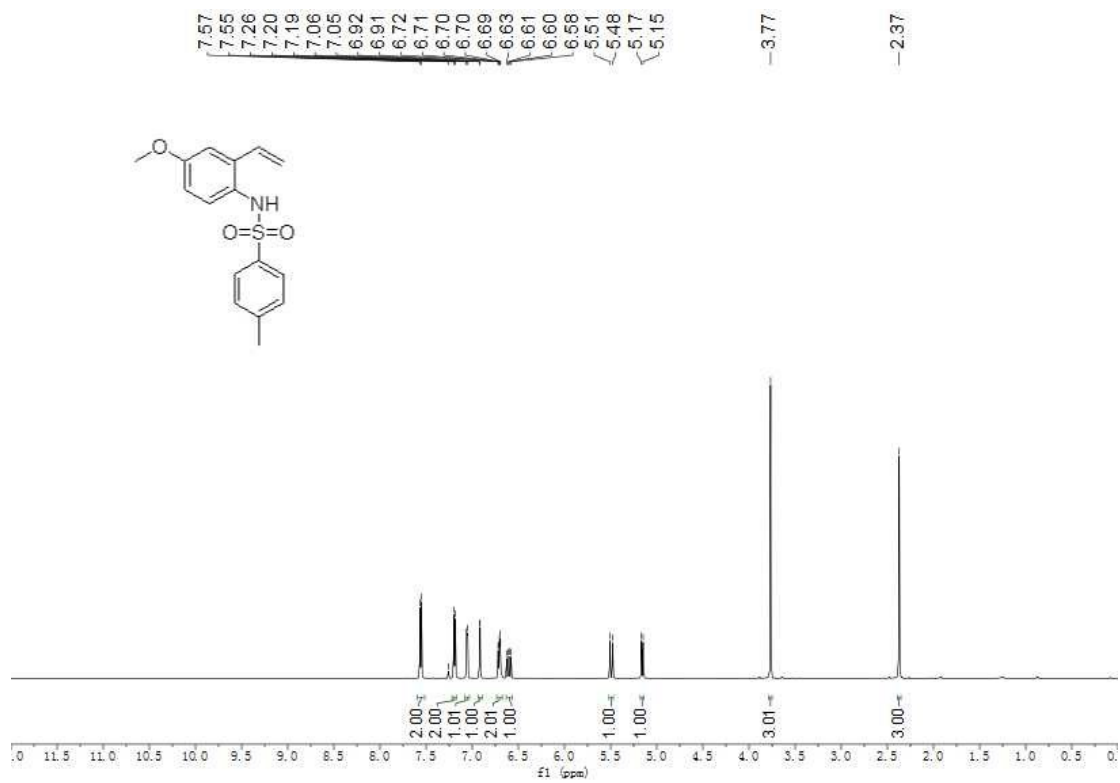




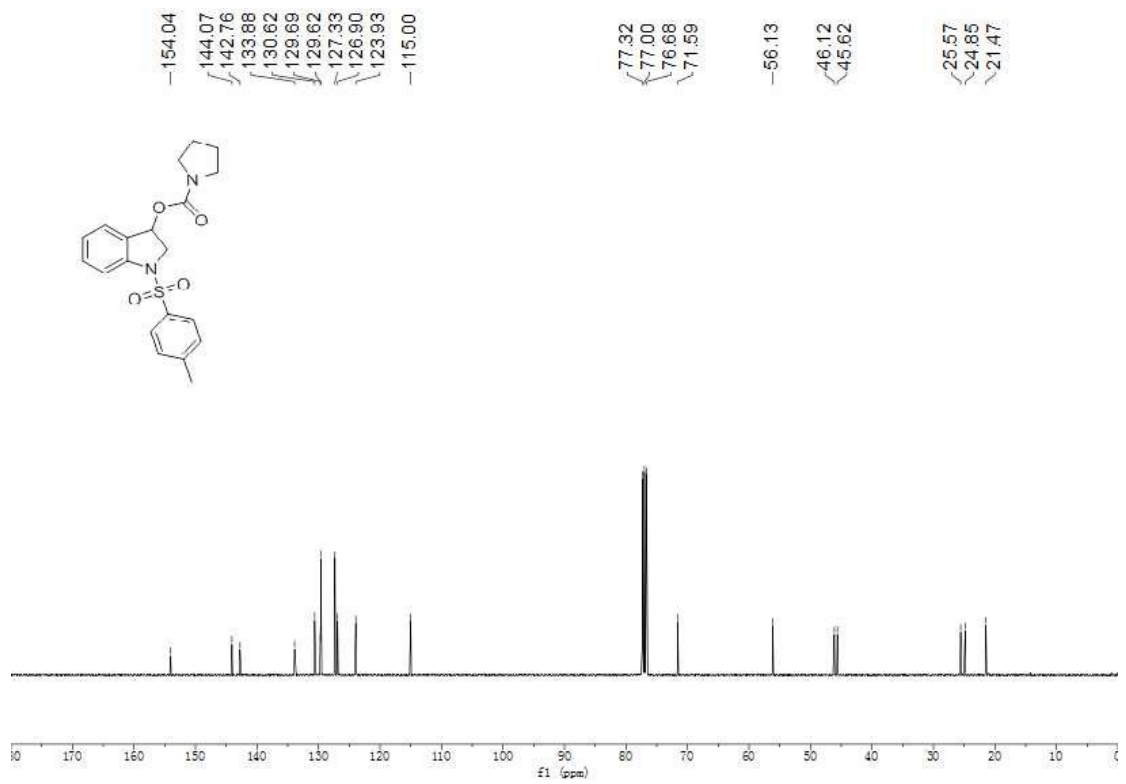
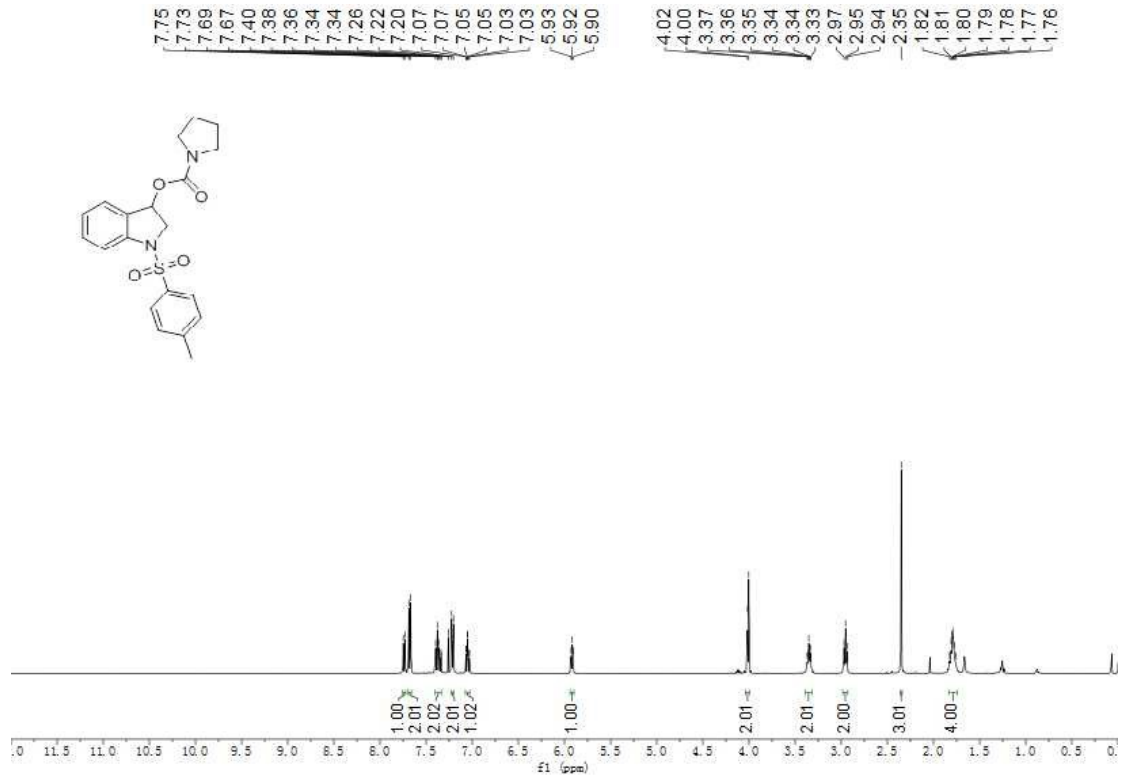


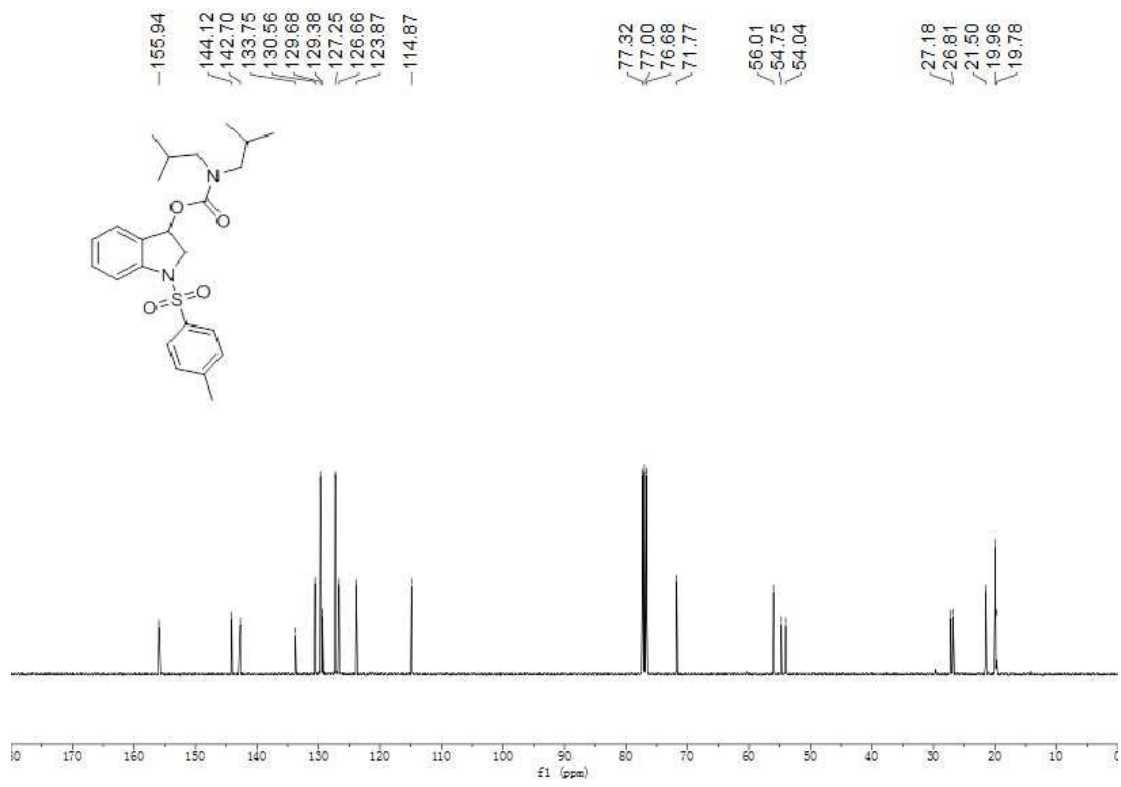
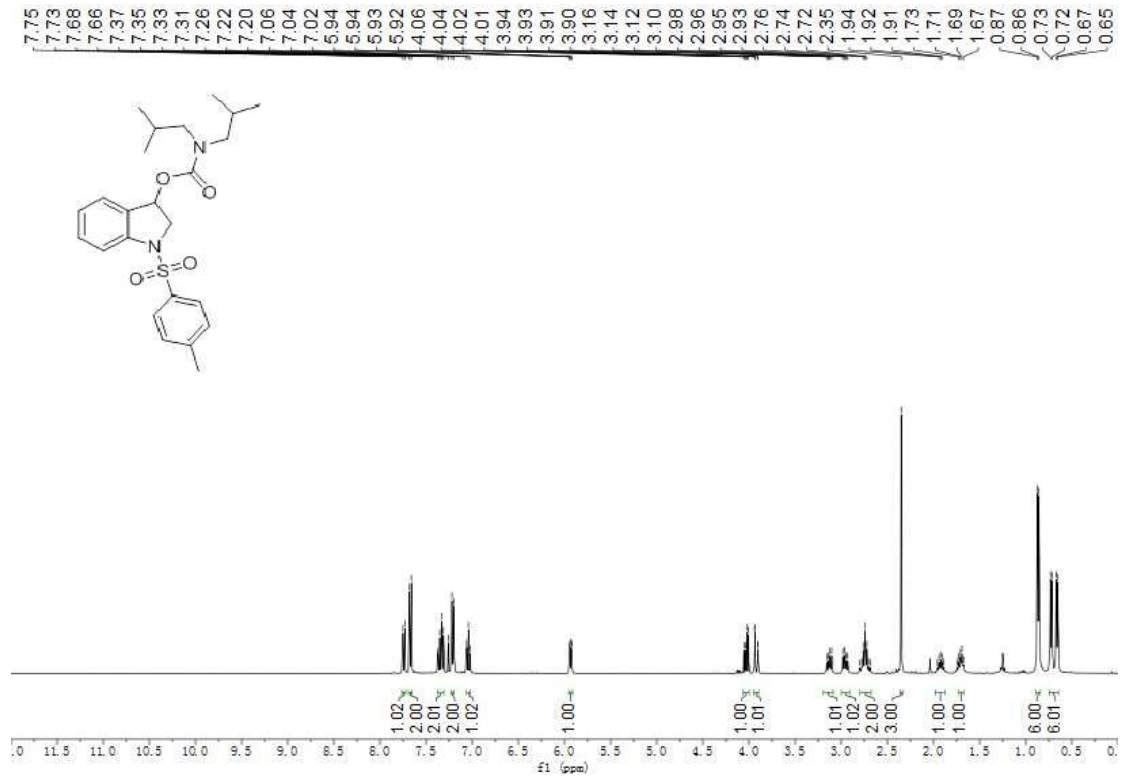


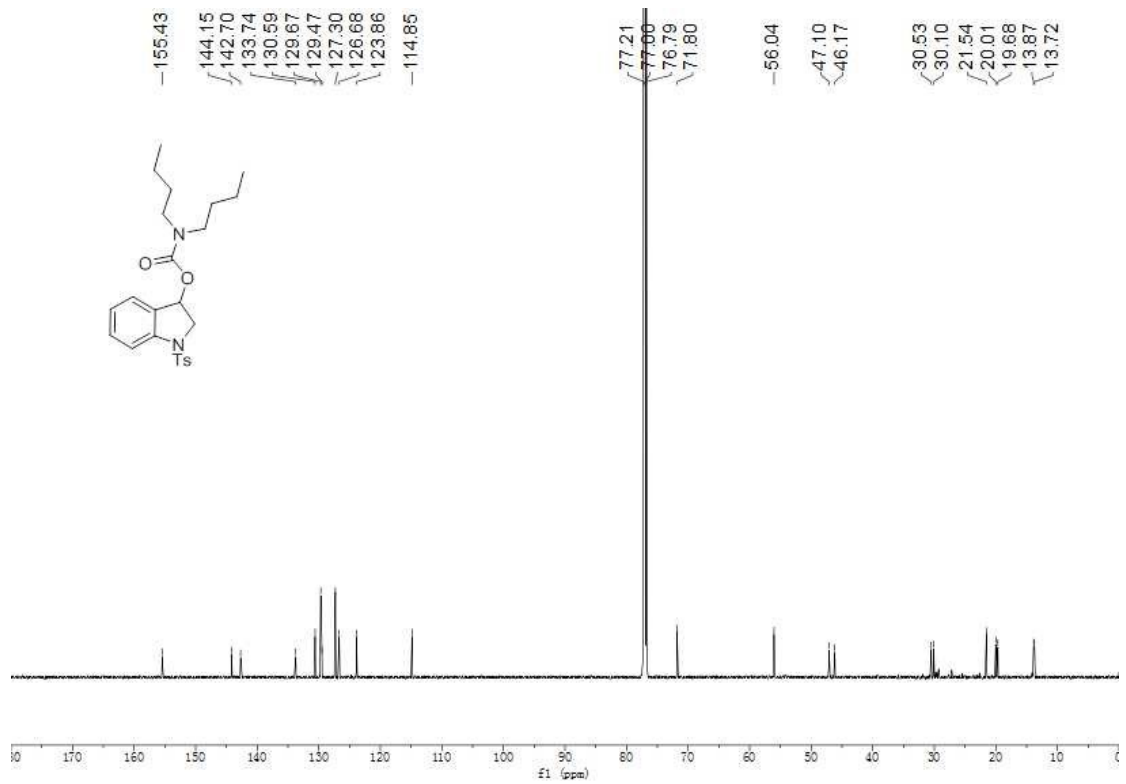
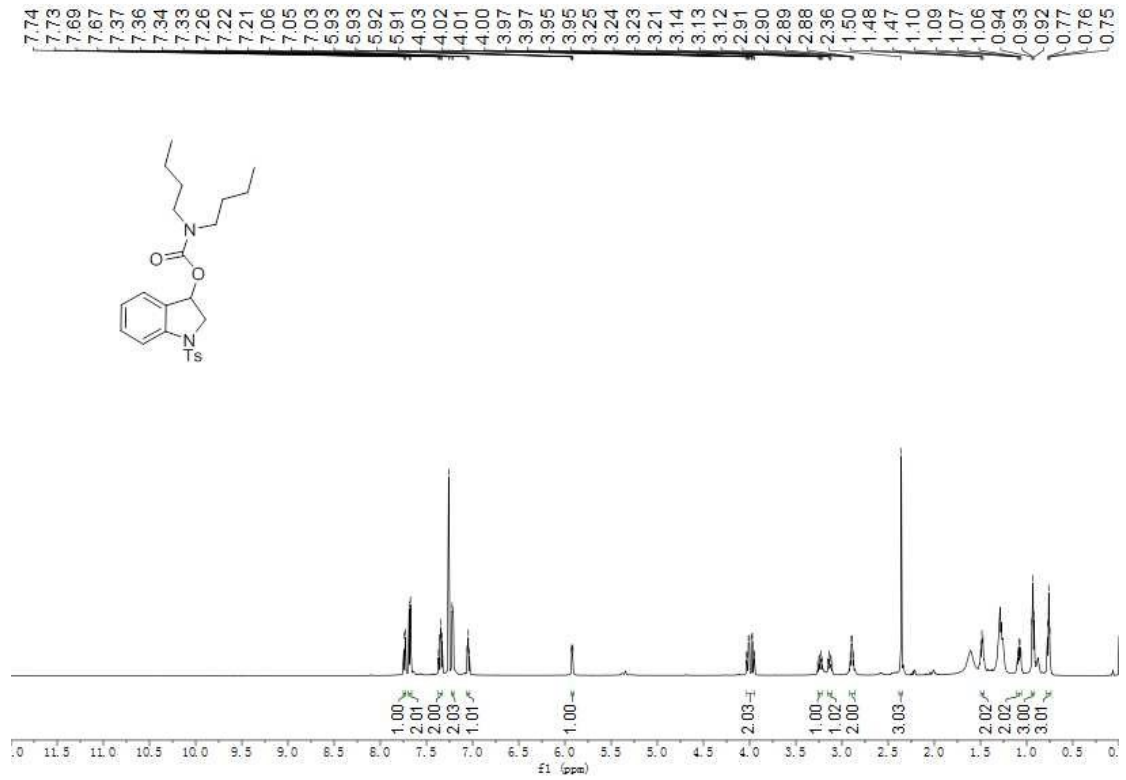


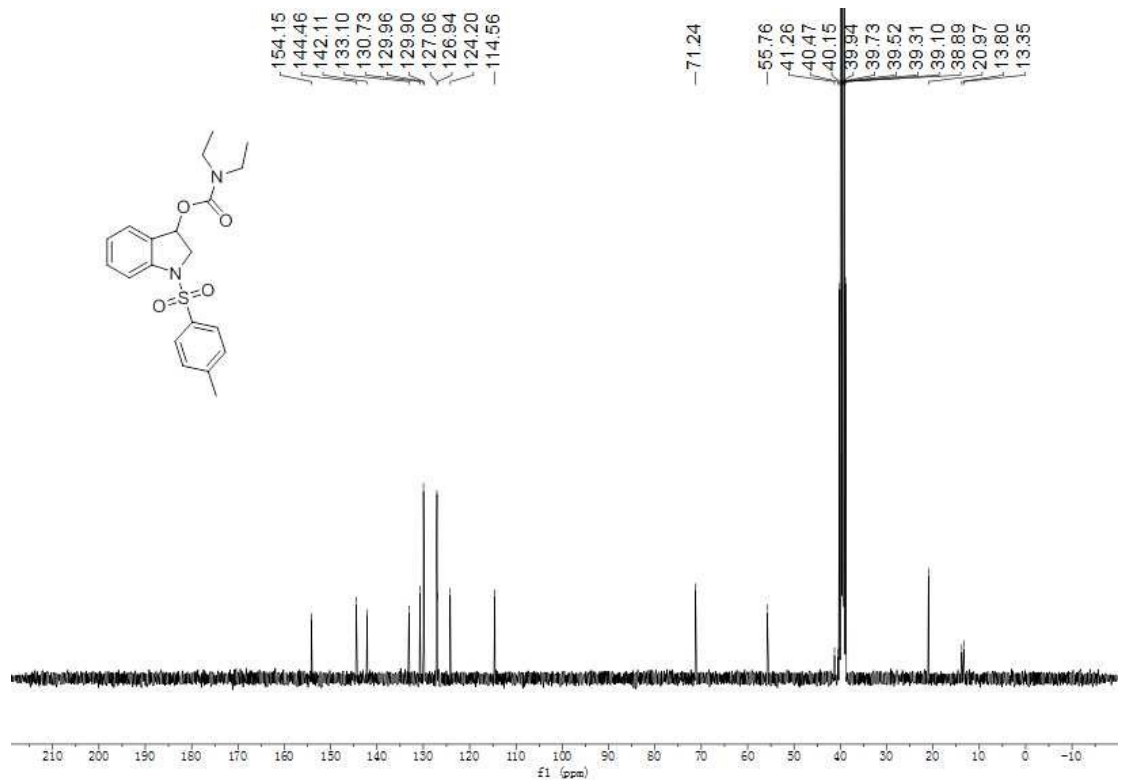
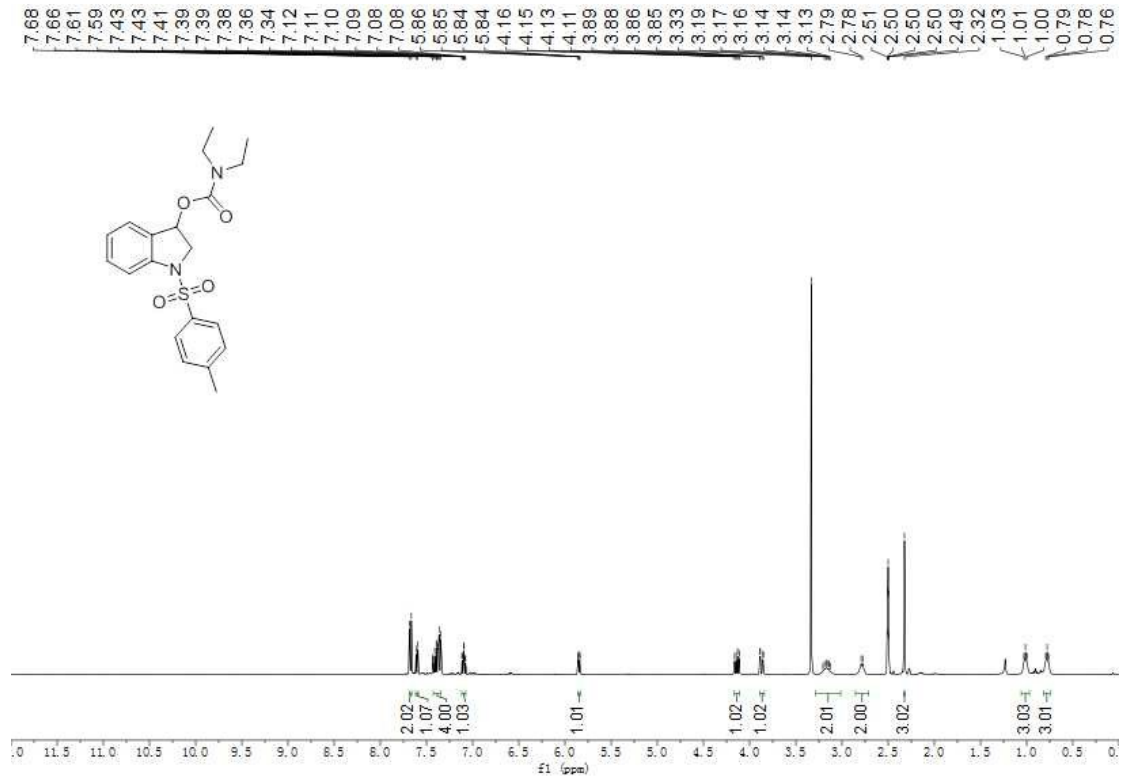


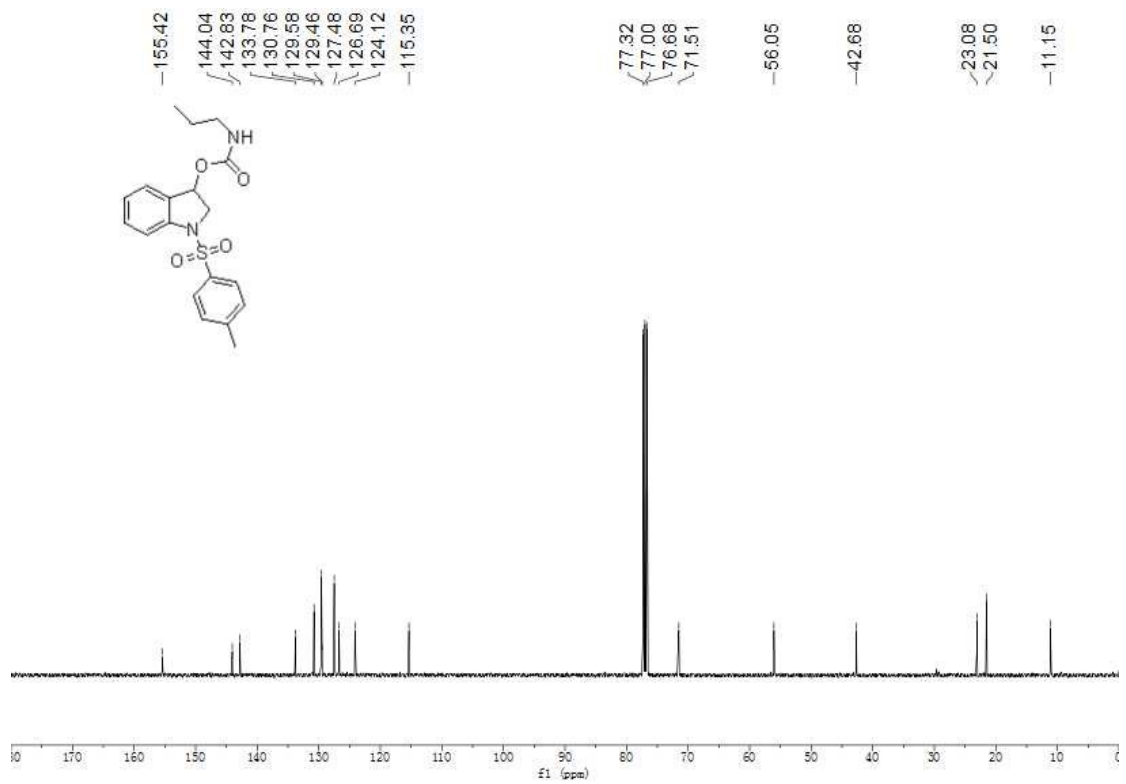
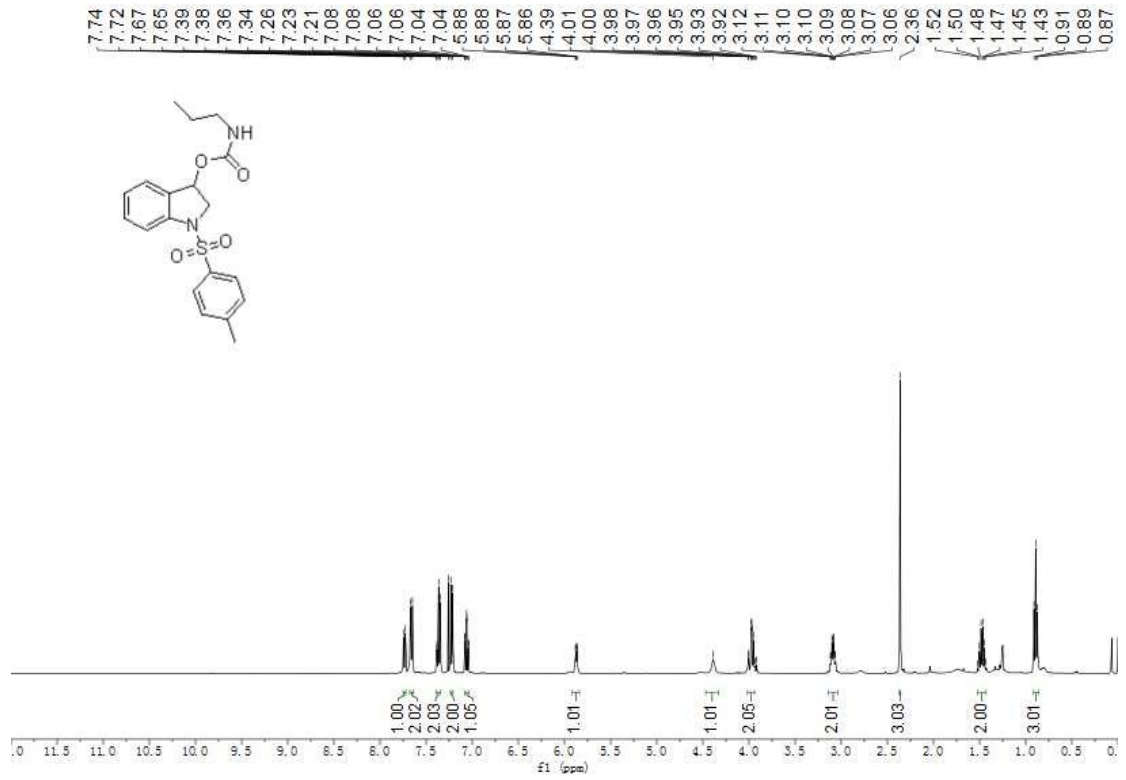
NMR spectra for the products

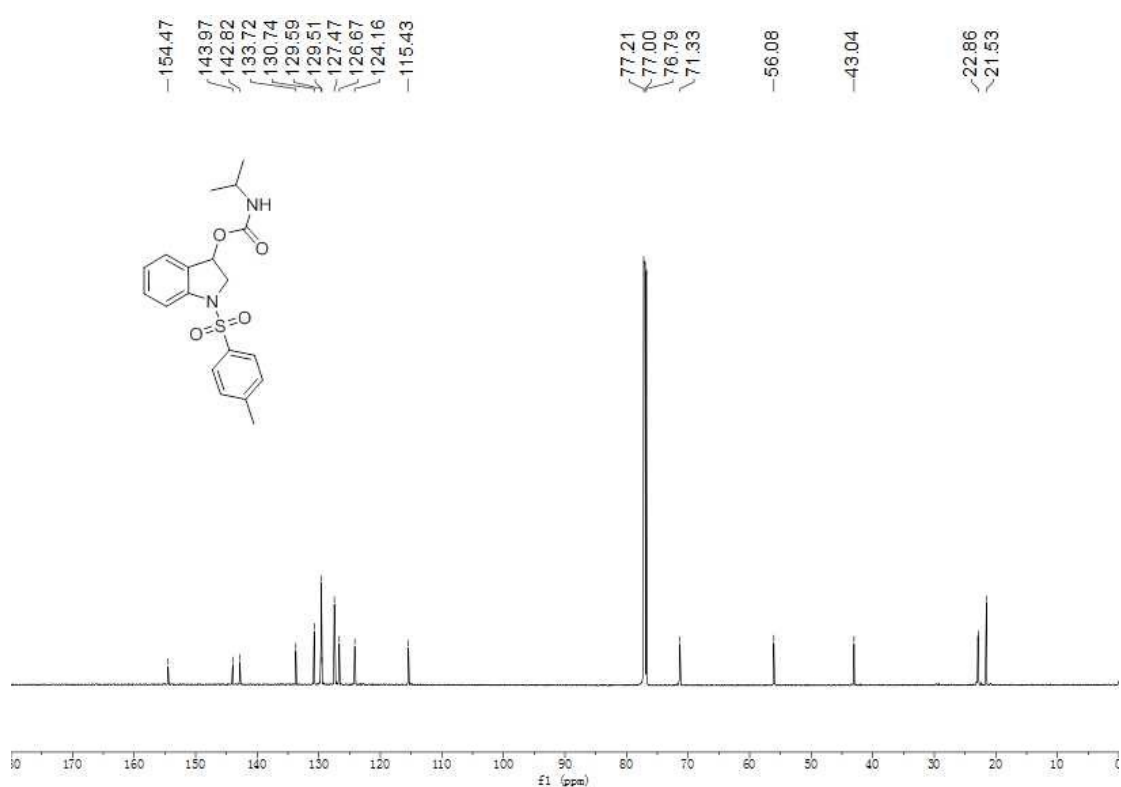
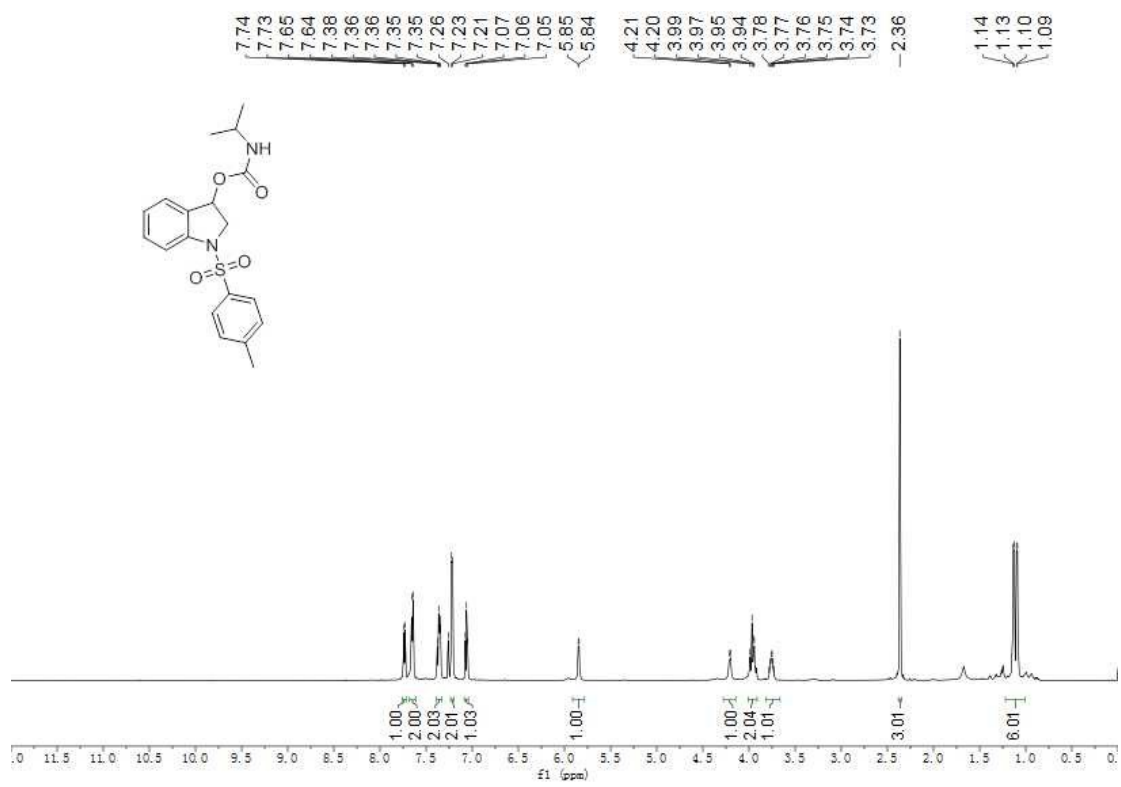


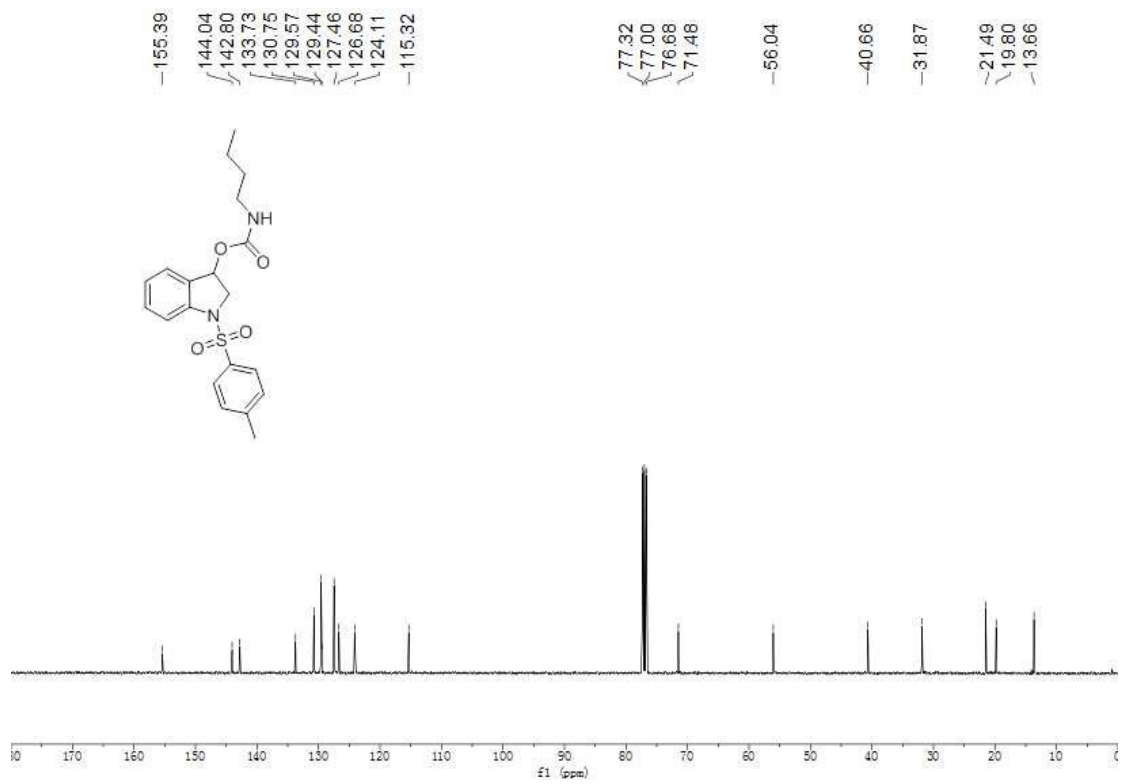
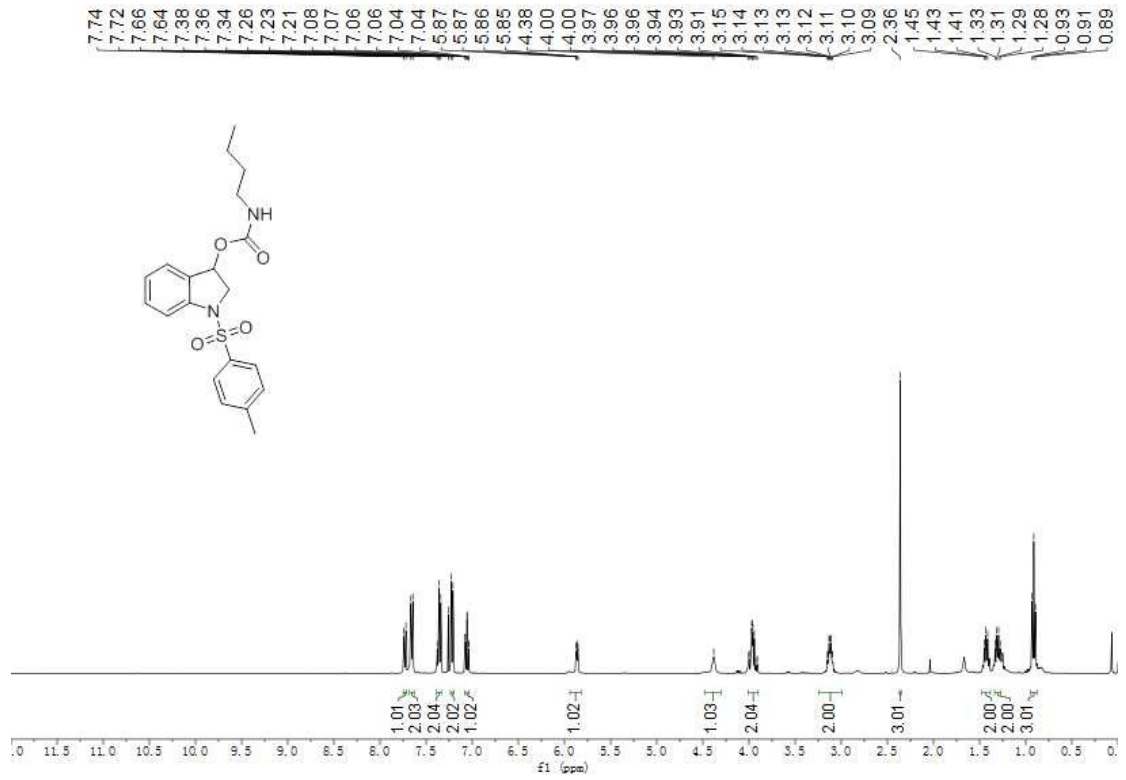


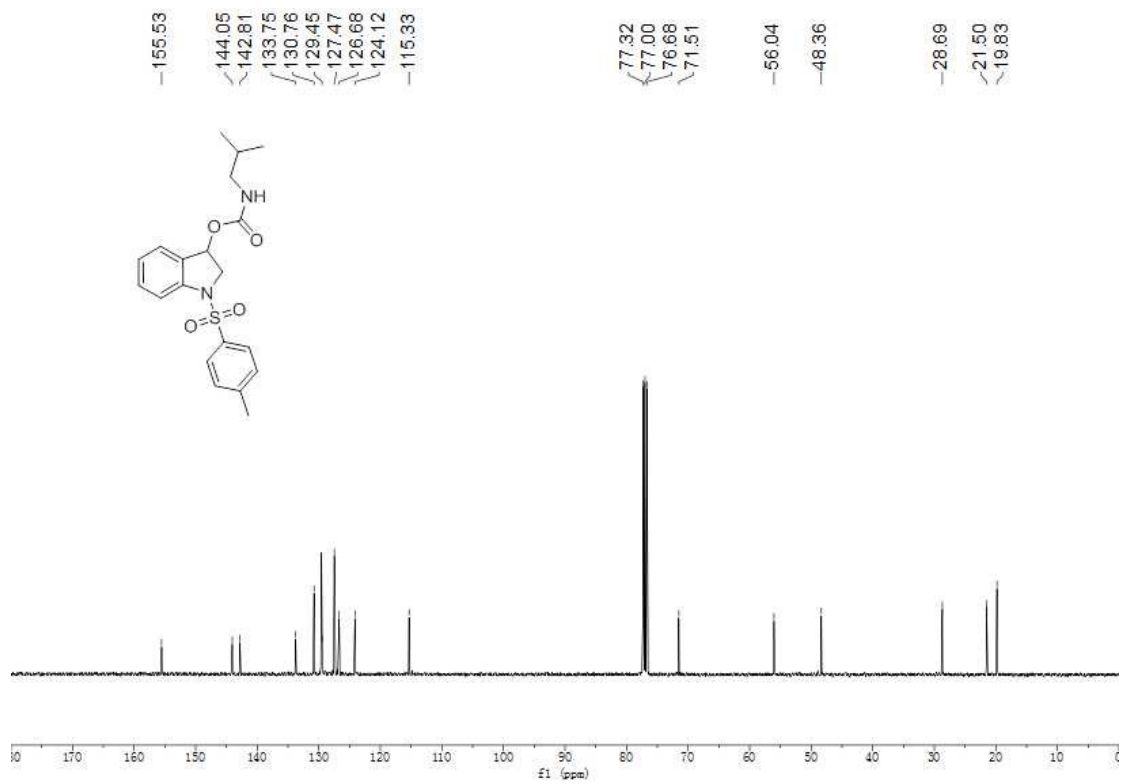
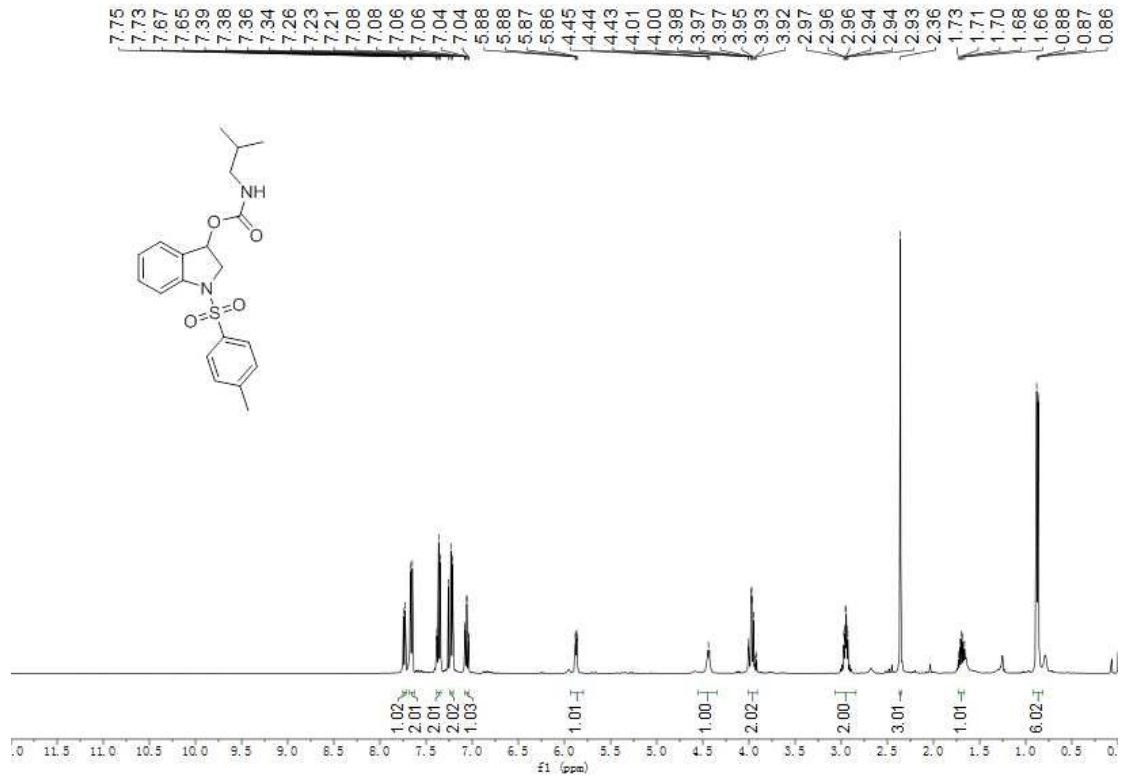


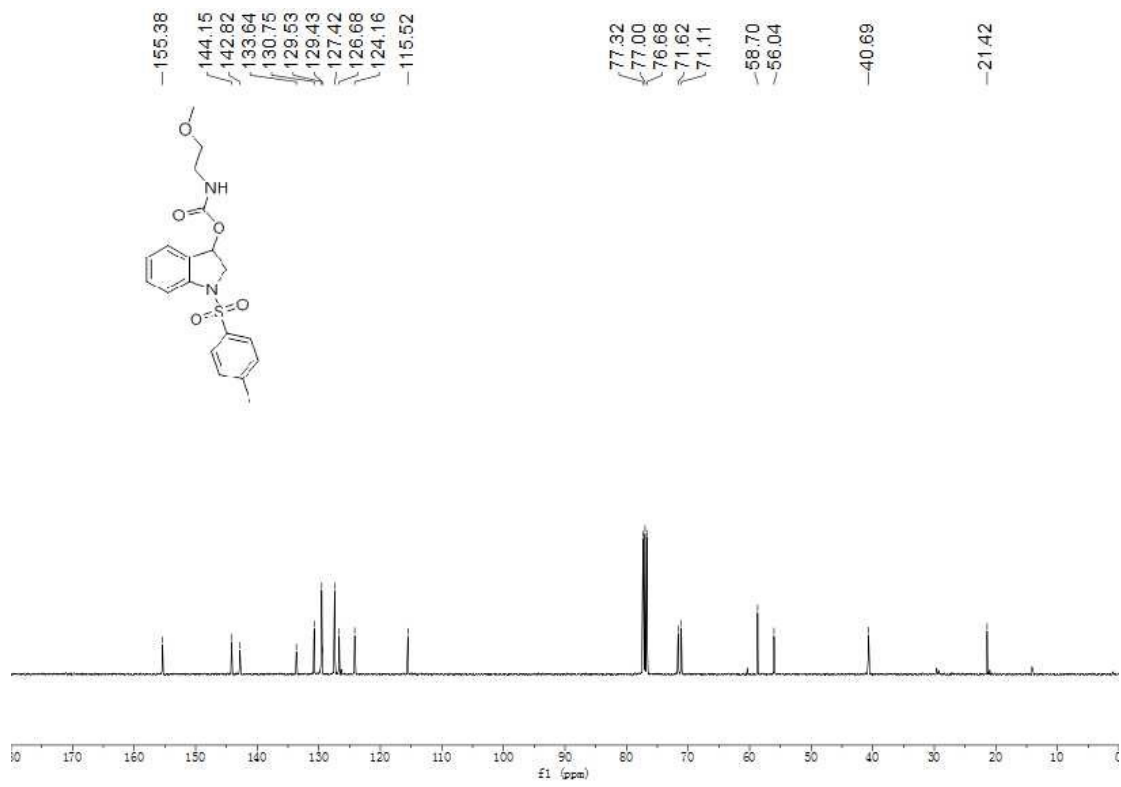
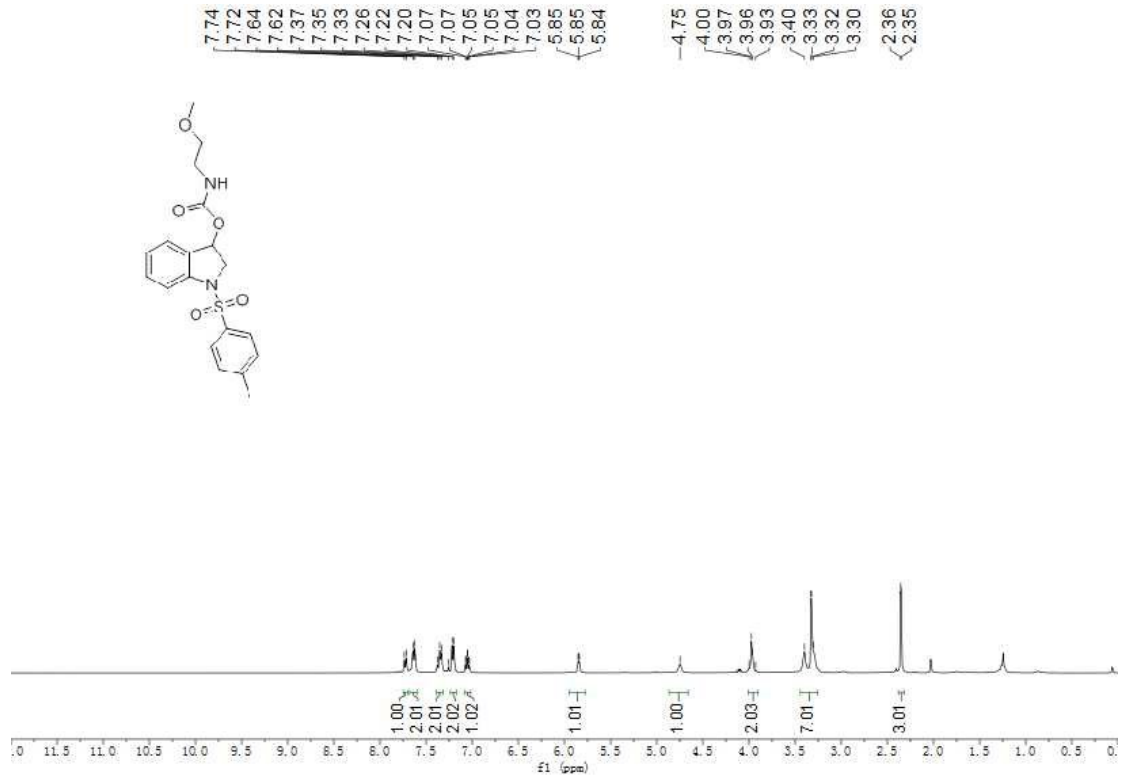


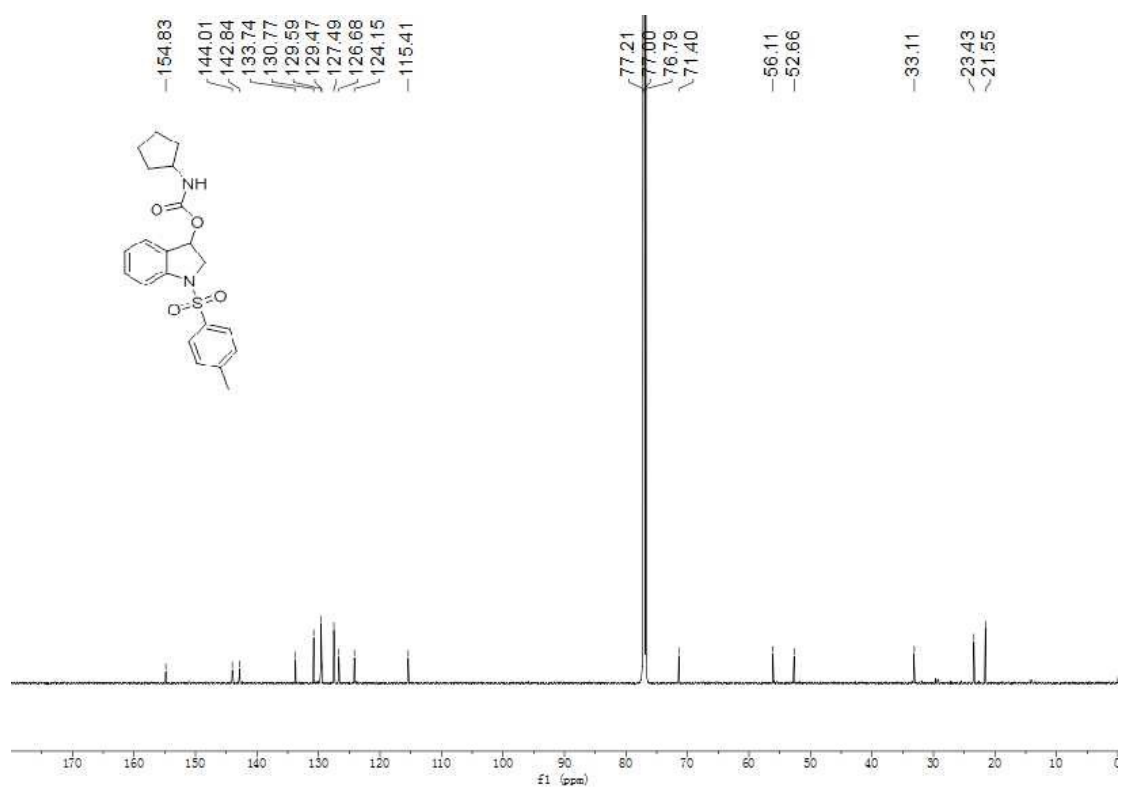
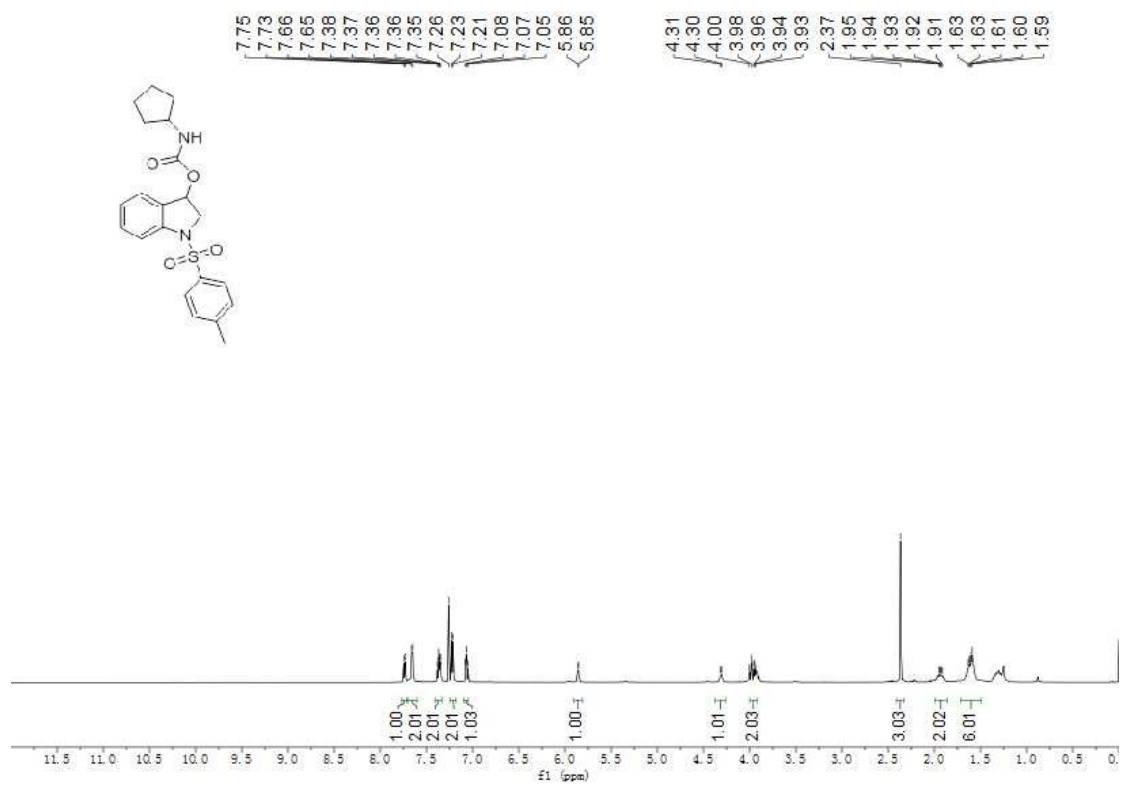


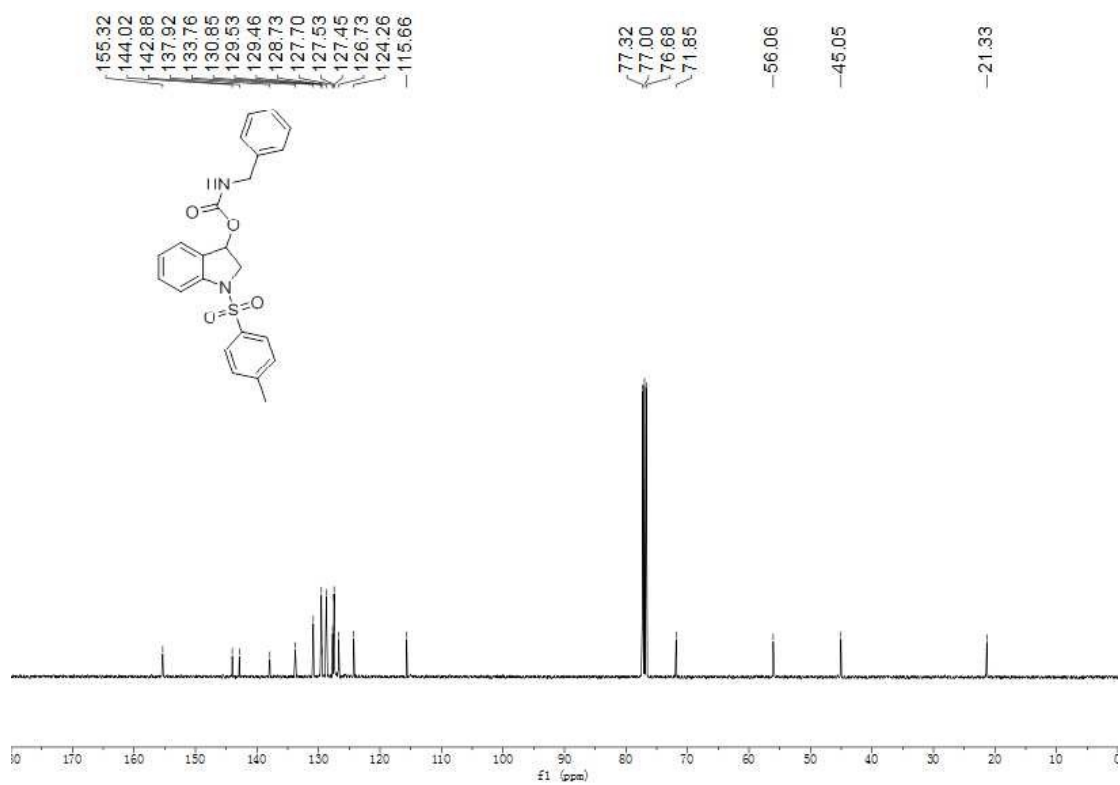
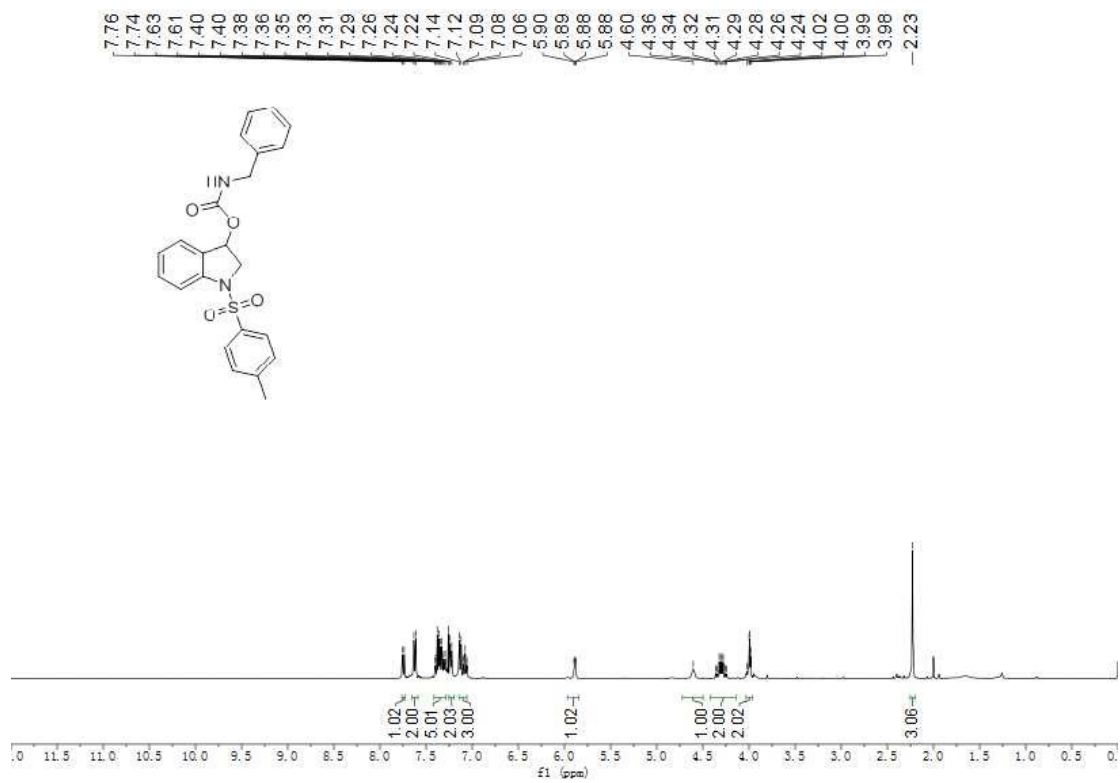


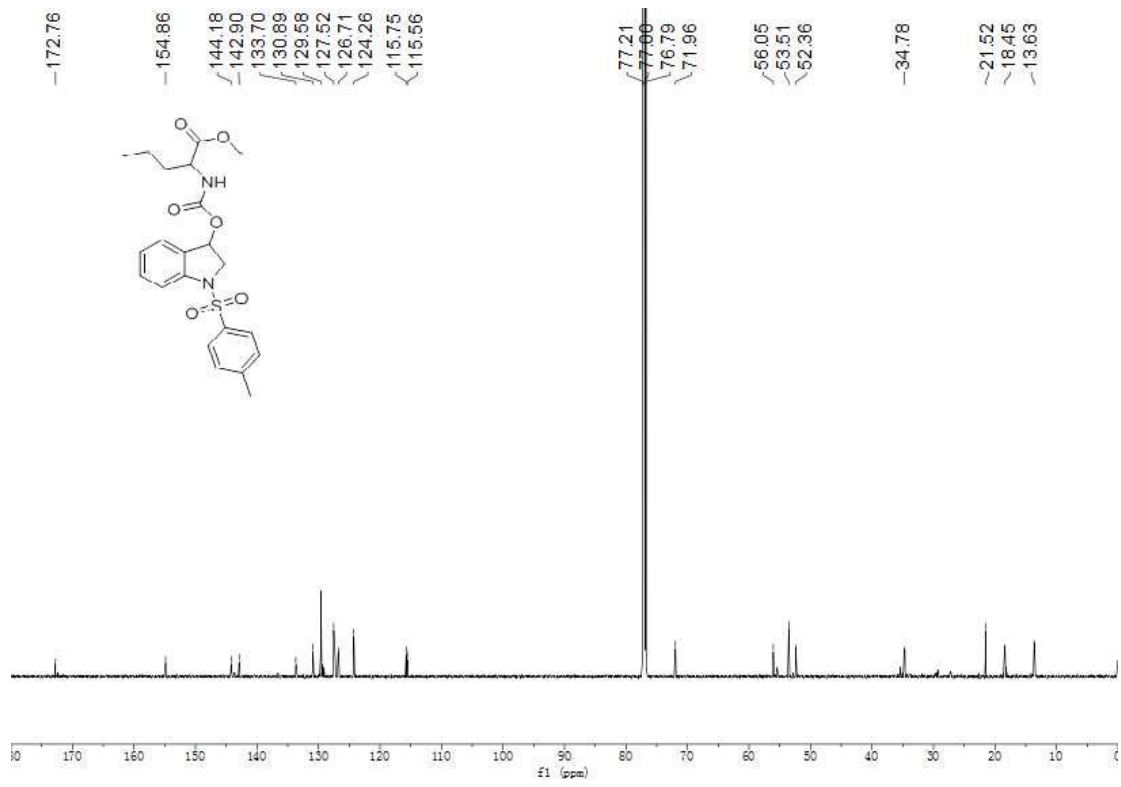
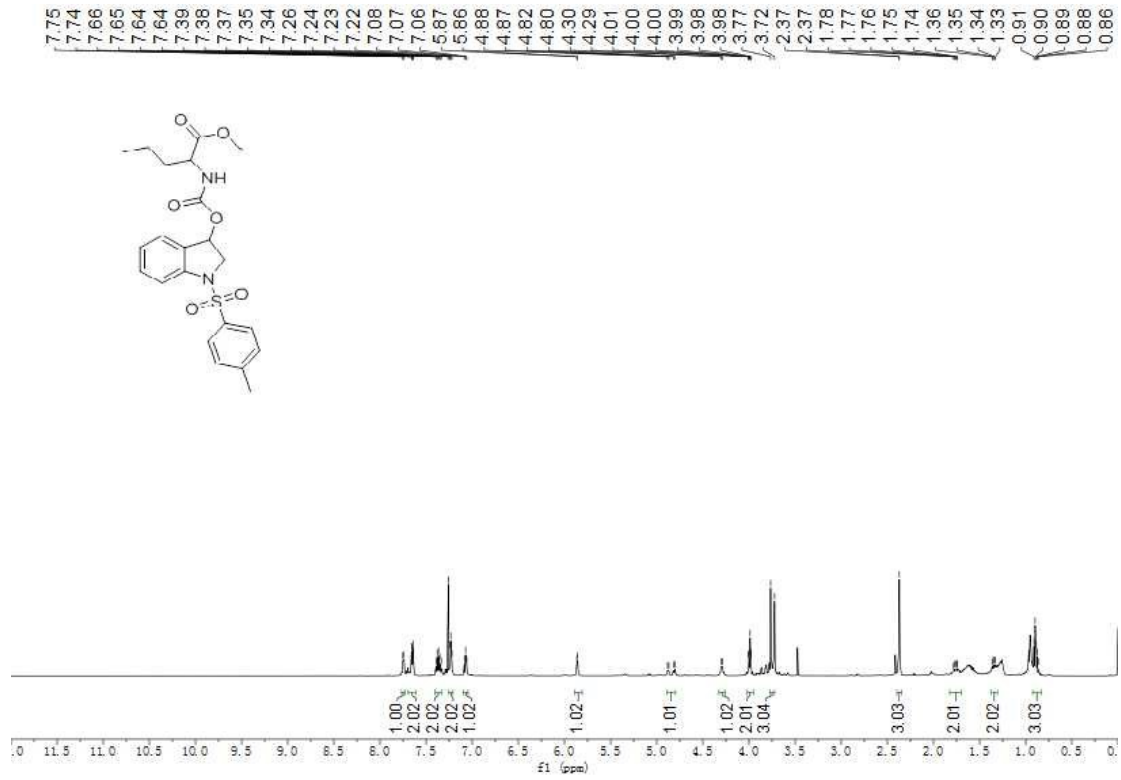


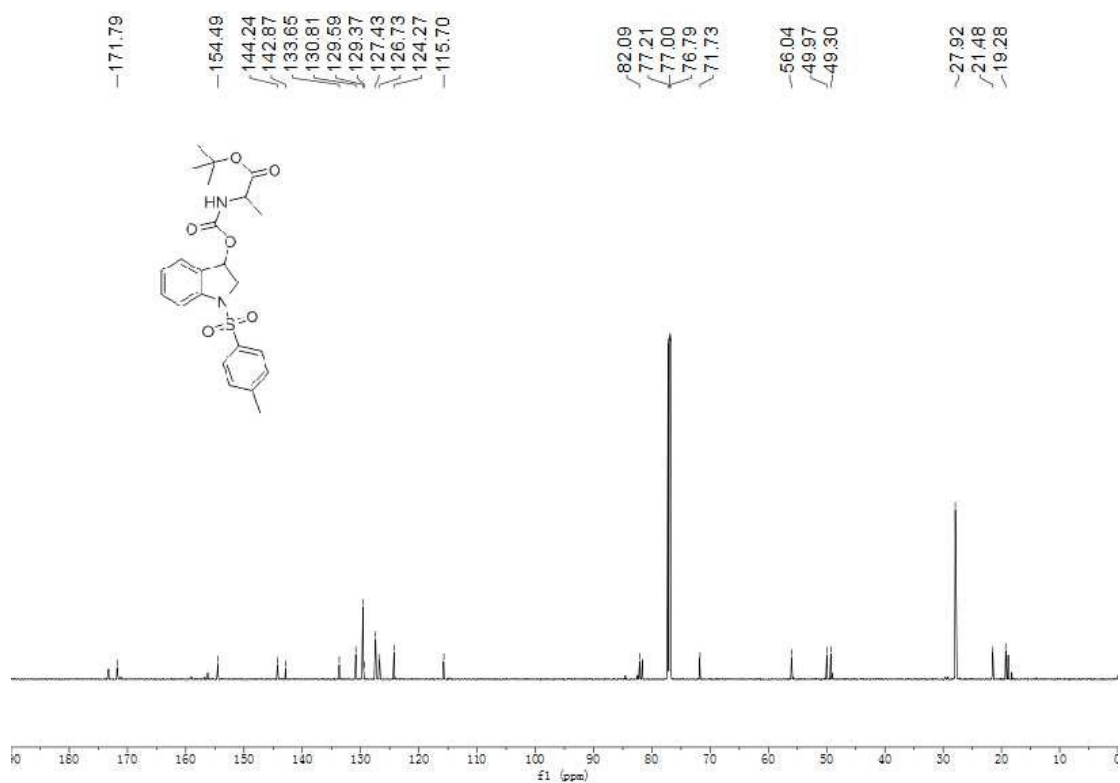
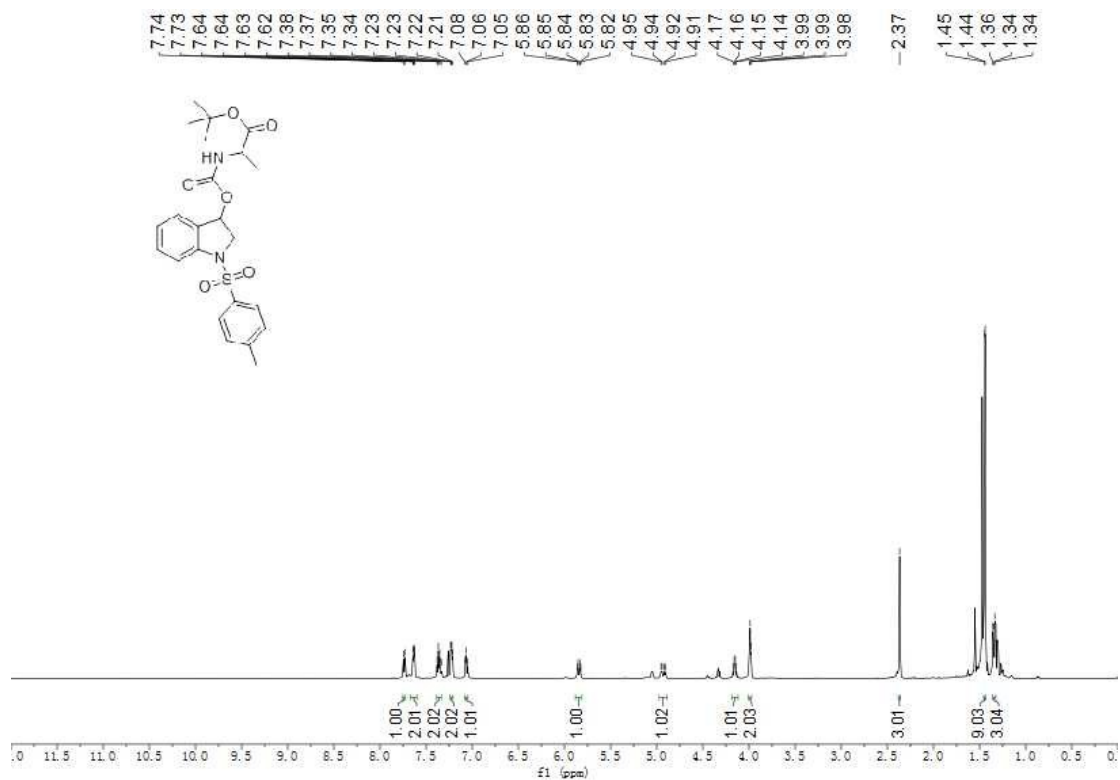


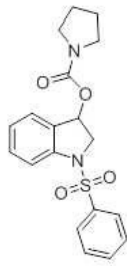






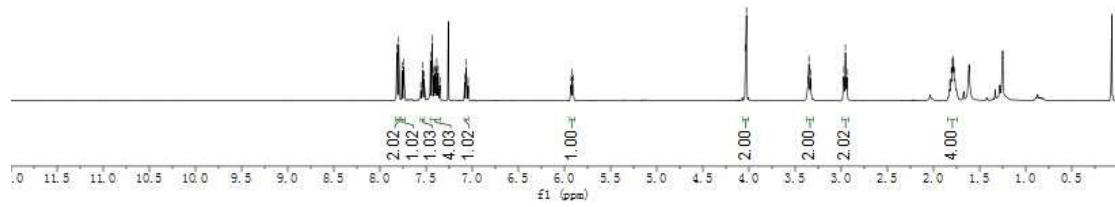






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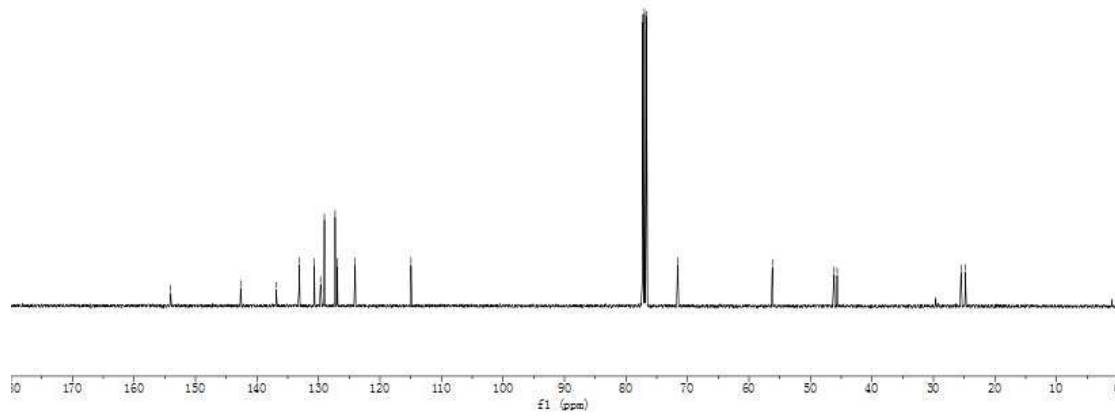
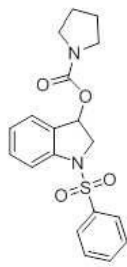
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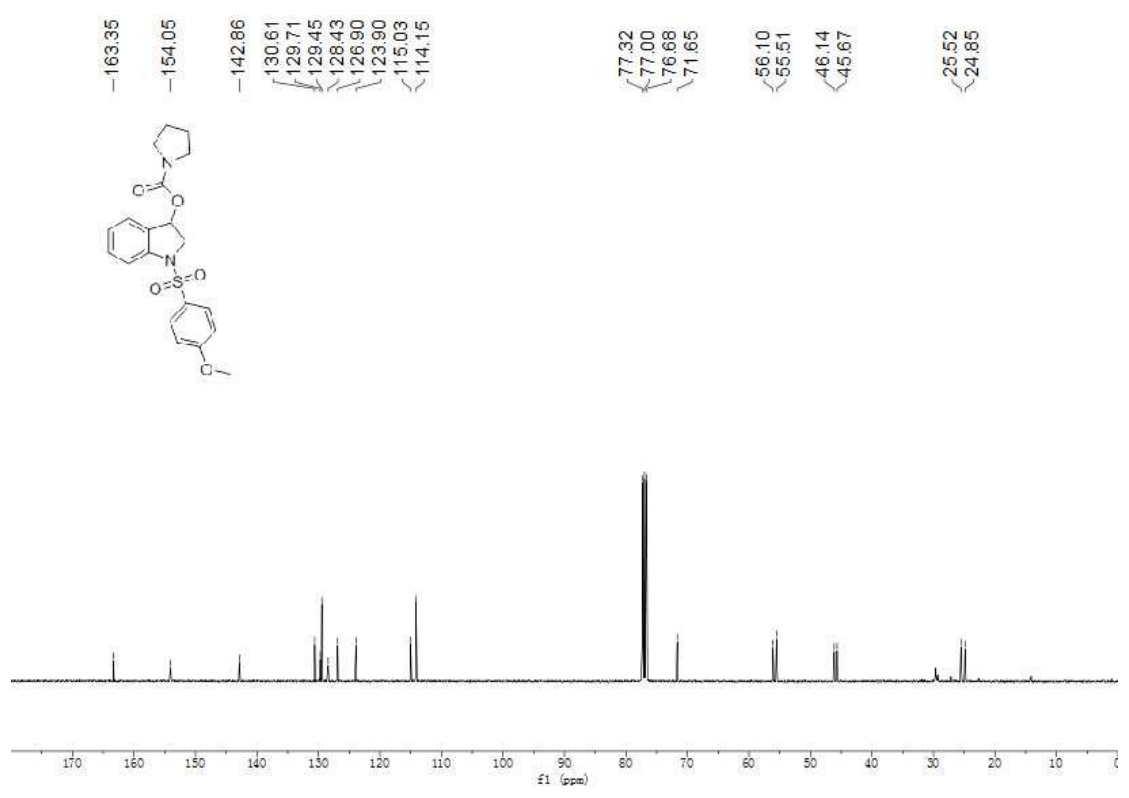
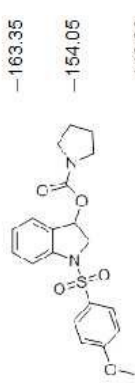
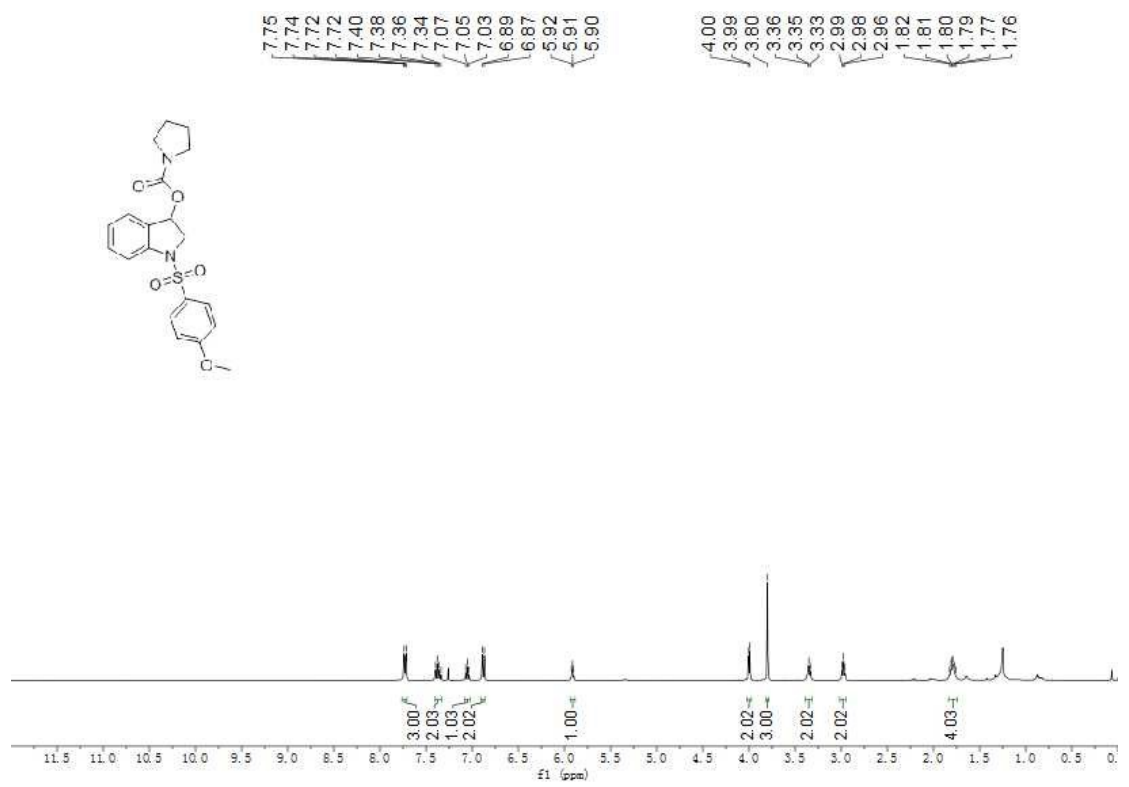
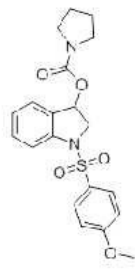
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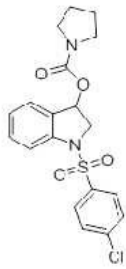
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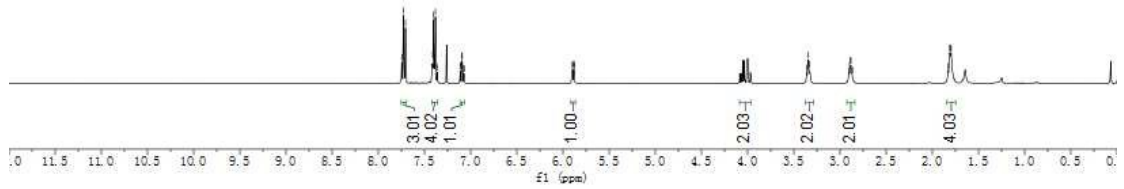
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