Supporting Information for

Base-catalyzed controllable reaction of 3-ylideneoxindoles and O-Boc hydroxycarbamates for the synthesis of amidoacrylates and spiroaziridine oxindoles

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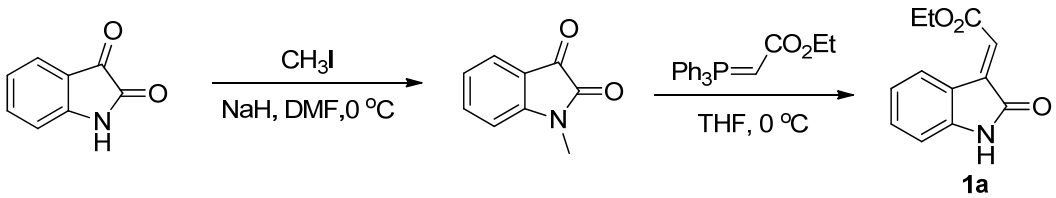
1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. 1H NMR spectra were recorded on 400 or 600 MHz spectrometers. Chemical shifts were reported on the delta (δ) scale in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded at 100 MHz with complete proton decoupling. Chemical shifts are reported in ppm relative to the central line of the triplet at 77.0 ppm for $CDCl_3$. Mass spectra were measured on a MS spectrometer (EI).

2. Preparation of substrates

2.1 General procedure for the preparation of 3-ylideneoxindoles



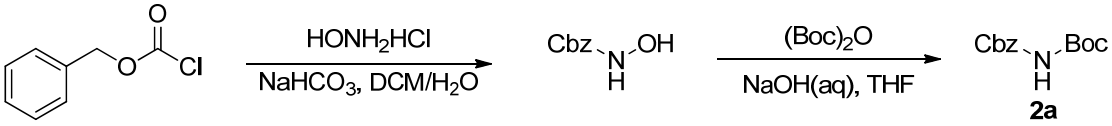
1a

Step 1: To a 250 mL 3-necked-round bottom flask equipped with a silicone oil bubbler was added commercially available isatin (7.7 g, 50 mmol) and anhydrous DMF (80 mL). And the mixture was cooled down to 0 °C. To this solution was added NaH (1.32 g, 55 mmol), then CH_3I was added 10 min later (without gas bubbling), and stirred at 0 °C for 15 min. Upon completion of the reaction (monitored by TLC), the mixture was diluted with saturated NH_4Cl solution and extracted with ethyl acetate, the ethyl acetate layer was washed with water and brine. The combined organic layer was then dried over $MgSO_4$, filtered, and concentrated to yield the crude N-methylindoline-2, 3-dione (7.6 g, 94% yield), which was used directly in the next step[1].

Step 2: To a stirred solution of ethyl 2-(triphenylphosphoranylidene) acetate (18.0 g, 51.7 mmol) in anhydrous THF (100 mL), the N-methylindoline-2, 3-dione (7.58 g, 47 mmol) was added at 0 °C. The mixture was stirred at the same temperature until the reaction was completed monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ ethyl acetate 5:1). Compound **1a** was obtained as a red solid (9.45 g, 87% yield)[2].

The other 3-ylideneoxindoles were prepared according to the above procedure.

2.2 General procedure for the preparation of O-Boc hydroxycarbamates



2a

Step 1: Sodium bicarbonate (21.0 g, 250 mmol) was added to a 500 mL round bottom flask and dissolved in H_2O (120 mL). Then, hydroxylamine hydrochloride (13.9 g, 200 mmol) was added into this solution. After this, the solution of benzyl chloroformate (8.8 g, 50 mmol) in CH_2Cl_2 (60 mL) was added to the mixture dropwisely and the mixture stirred at room temperature. Upon completion of the reaction (monitored by TLC), the system was acidized to pH 4-5 with 1M HCl solution. The aqueous layer was extracted with CH_2Cl_2. The combined organic layer was then dried over $MgSO_4$, filtered, and concentrated to yield the crude white solid benzyl hydroxycarbamate (8.3 g, 99% yield), which was used directly in the next step.

Step 2: benzyl hydroxycarbamate (8.3 g, 49.6 mmol) and ditertbutyl dicarbonate (10.8 g, 49.6 mmol) were dissolved into THF (60 mL) and the mixture stirred vigorously at RT. Then, aqueous NaOH solution (1M, 60 mL) was added to the mixture dropwise. Upon completion of the reaction, the crude product was diluted with ether and brine, the aqueous layer was extracted with ether, the combined organic layer was washed with brine and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel (petroleum ether/ ethyl acetate 10:1 to 5:1). Compound **2a** was obtained as a colorless oil (4.64 g, 35% yield)[3].

The other *N*-protected carbamates were prepared according to the above procedure.

References:

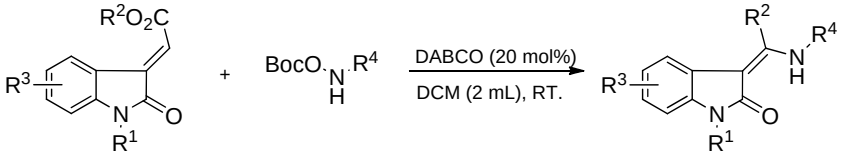
[1] B. M. Trost, Y. Zhang. *J. Am. Chem. Soc.*, **2007**, *129*, 14548.

[2] S.W. Duan, Y. Li, Y. Y. Liu, Y. Q. Zou, D. Q. Shi, and W. J. Xiao. *Chem. Commun.*, **2012**, *48*, 5160.

[3] S.-F. Lu, D.-M. Du, J.-X. Xu, *Org. Lett.*, **2006**, *8*, 2115.

3. Representative procedure for preparation of the products.

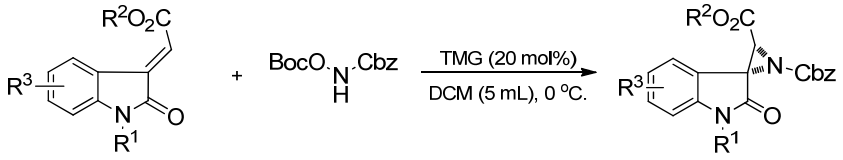
3.1 Representative procedure for preparation of the amidoacrylates 3.



1 **2** **4**

The compound **2** (xx mg, 0.24 mmol) and DABCO (4.5 mg, 0.04 mmol) were dissolved in CH_2Cl_2 (1 mL). Then, compound **1** (xx mg, 0.20 mmol) was added to the mixture. Upon the completion of the reaction (monitored by TLC), the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 8:1 to 5:1) to give the desired product **3** as a yellow or red solid.

3.2 Representative procedure for preparation of the spiroaziridine 4.

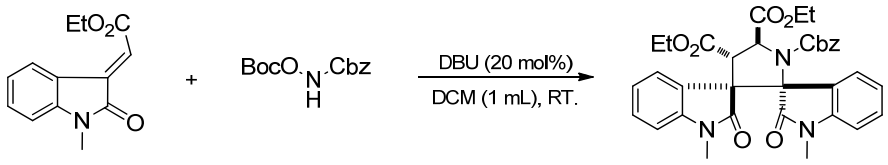


1 **2a** **4**

The compound **2** (xx mg, 0.36 mmol) and TMG (6.9 mg, 0.06 mmol) were dissolved in CH_2Cl_2 (5 mL). Then, compound **1** (0.30 mmol) was added to the mixture at 0 °C. Upon the completion of the

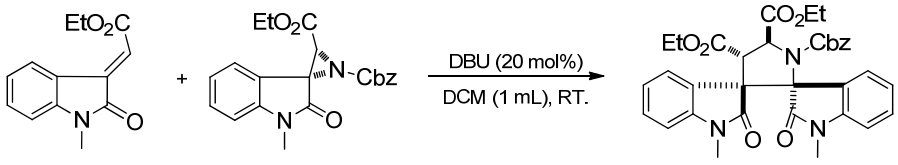
reaction (monitored by TLC), The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1 to 3:1) to give the desired product **4** as a white solid.

3.3 Representative procedure for preparation of the bispirooxindole 5.



1 **2a** **5**

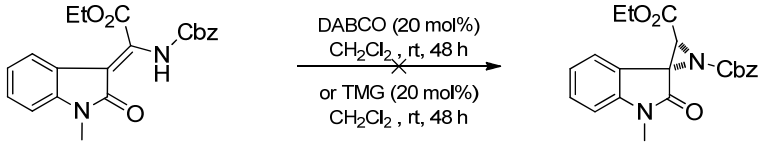
The compound **2** (91.3 mg, 0.24 mmol) and DBU (6.1 mg, 0.04 mmol) were dissolved in CH_2Cl_2 (1 mL). Then compound **1** (46.3 mg, 0.20 mmol) was added to the mixture and stirred at room temperature, Upon the completion of the reaction (monitored by TLC), The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 3:1 to 2:1), Compound **5** was obtained as a white solid (91.7 mg, 75% yield, 1.6:1 dr.) .



1 **4a** **5**

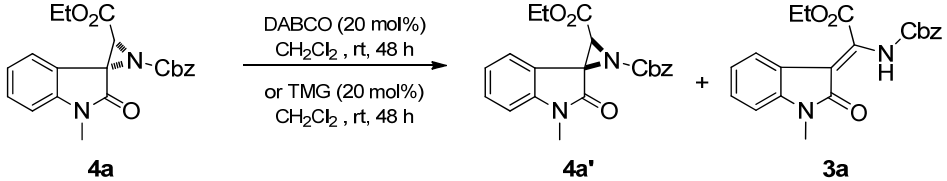
The compound **1** (46.3 mg, 0.20 mmol) and compound **4a** (91.3 mg, 0.24 mmol) were dissolved in CH_2Cl_2 (1 mL). Then DBU (6.1 mg, 0.04 mmol) was added to the mixture. Upon the completion of the reaction (monitored by TLC), The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 3:1 to 2:1), Compound **5** was obtained as a white solid (73.4 mg, 60% yield, 1.6:1 dr.) .

4. Control experiments.



3a **4a**

The compound **3a** (76.1 mg, 0.20 mmol) was dissolved in CH_2Cl_2 (1 mL). And either DABCO (4.5 mg, 0.04 mmol) or TMG (4.6 mg, 0.04 mmol) was added. The mixture were allowed to stirred at room temperature for 48 h, and no transformation was observed, and substrate **3a** was fully remained. This result proves the amidoacrylate is not the intermidate for the generation of spiroaziridine **4a**.

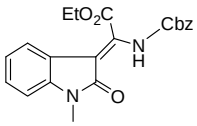


4a **4a'** **3a**

The compound **4a** (76.1 mg, 0.20 mmol) was dissolved in CH_2Cl_2 (1 mL). And DABCO (4.5 mg, 0.04 mmol) or TMG (4.6 mg, 0.04 mmol) was added. The mixture were allowed to stirred at room temperature for 48 h, however, no amidoacrylate **3a**; instead, the isomer **4a'** was isolated in 30% and 64% yield, respectively. This result rules out the possibility that the amidoacrylate product **3a** was formed through the spiroaziridine oxindole **4a**.

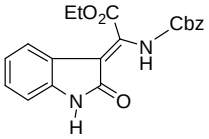
5. Spectral data of products

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(1-methyl-2-oxoindolin-3-ylidene)acetate (3a)



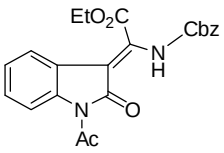
yellow solid; 99% yield in 24 h, mp 112-114 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.27 (s, 1H), 7.42 – 7.31 (m, 5H), 7.27 – 7.19 (m, 2H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 5.22 (s, 2H), 4.52 (s, 2H), 3.26 (d, *J* = 4.1 Hz, 3H), 1.42 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 162.4, 152.1, 140.6, 137.9, 134.8, 128.4, 128.2, 127.6, 122.1, 120.0, 119.6, 108.3, 104.1, 68.1, 62.6, 25.6, 13.7; HRMS (ESI): for $C_{21}H_{20}N_2O_5$ $[M]^+$: calcd 380.1372, found 380.1370.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(2-oxoindolin-3-ylidene)acetate (3b)



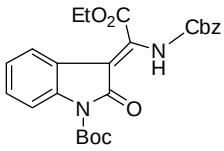
yellow solid; 98% yield in 24 h, mp 155-157 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.13 (d, *J* = 19.5 Hz, 1H), 8.43 (s, 1H), 7.39 (d, *J* = 6.1 Hz, 3H), 7.37 (d, *J* = 4.0 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.23 (s, 2H), 4.52 (s, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8, 162.5, 152.2, 138.6, 138.2, 134.8, 128.6, 128.5, 127.8, 122.3, 120.4, 120.4, 110.3, 104.5, 68.4, 62.9, 13.8; HRMS (ESI): for $C_{20}H_{18}N_2O_5$ $[M]^+$: calcd 366.1216, found 366.1215.

(Z)-ethyl 2-(1-acetyl-2-oxoindolin-3-ylidene)-2-(((benzyloxy)carbonyl)amino)acetate (3c)



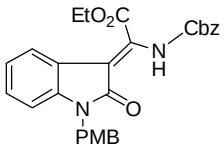
yellow solid; 95% yield in 24 h, mp 104-107 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.01 (s, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 7.40 (s, 4H), 7.36 (d, *J* = 2.4 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 5.24 (s, 2H), 4.54 (d, *J* = 6.3 Hz, 2H), 2.71 (d, *J* = 1.8 Hz, 3H), 1.42 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 169.7, 162.0, 151.8, 139.8, 137.0, 134.4, 128.8, 128.6, 128.2, 124.9, 120.4, 119.3, 116.5, 102.9, 68.74, 63.1, 26.9, 13.7; HRMS (ESI): for $C_{22}H_{20}N_2O_6$ $[M]^+$: calcd 408.1321, found 408.1321.

(Z)-tert-butyl 3-(1-(((benzyloxy)carbonyl)amino)-2-ethoxy-2-oxoethylidene)-2-oxoindoline-1-carboxylate (3d)



yellow solid; 94% yield in 24 h, mp 99-102 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.17 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.33 (m, 5H), 7.30 – 7.25 (m, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 5.22 (s, 2H), 4.53 (d, *J* = 5.7 Hz, 2H), 1.65 (s, 9H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.0, 162.2, 151.9, 148.7, 139.4, 136.8, 134.6, 128.6, 128.5, 128.3, 127.9, 124.2, 120.0, 119.5, 114.9, 103.0, 84.6, 68.5, 63.0, 28.0, 13.7; HRMS (ESI): for $C_{25}H_{26}N_2O_7$ $[M]^+$: calcd 466.1740, found 466.1741.

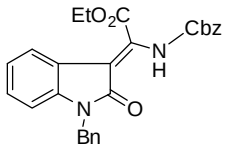
(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(1-(4-methoxybenzyl)-2-oxoindolin-3-ylidene)acetate(3e)



yellow solid; 98% yield in 24 h, mp 97-100 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ =11.31 (s, 1H), 7.41 – 7.31 (m, 5H), 7.21 (dd, *J* = 17.7, 8.1 Hz, 3H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.80 (dd, *J* = 11.8, 8.4 Hz, 3H), 5.26 – 5.17 (m, 2H), 4.90 (d, *J* = 17.3 Hz, 2H), 4.53 (s, 2H), 3.78 – 3.68 (m, 3H), 1.41 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR

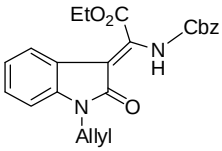
(100 MHz, $CDCl_3$): δ = 168.8, 162.5, 159.0, 152.2, 140.0, 138.3, 134.8, 128.6, 128.4, 127.7, 127.6, 122.3, 120.2, 120.0, 114.1, 109.2, 104.0, 68.3, 62.8, 55.2, 42.8, 13.8; HRMS (ESI): for $C_{28}H_{26}N_2O_6$ $[M]^+$: calcd 486.1791, found 486.1787.

(Z)-ethyl 2-(1-benzyl-2-oxoindolin-3-ylidene)-2-(((benzyloxy)carbonyl)amino)acetate (3f)



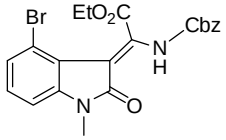
yellow solid; 98% yield in 24 h, mp 118-121 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ=11.31 (s, 1H), 7.43 – 7.30 (m, 5H), 7.30 – 7.19 (m, 6H), 7.12 (t, J = 7.6 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.76 (d, J = 7.9 Hz, 1H), 5.21 (s, 2H), 4.94 (s, 2H), 4.53 (s, 2H), 1.41 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =168.7, 162.4, 152.1, 139.8, 138.3, 135.5, 134.7, 128.7, 128.5, 128.3, 127.6, 127.6, 127.0, 122.3, 120.2, 119.9, 109.2, 103.9, 68.2, 62.8, 43.2, 13.7; HRMS (ESI): for $C_{27}H_{24}N_2O_5$ $[M]^+$: calcd 456.1685, found 456.1681.

(Z)-ethyl 2-(1-allyl-2-oxoindolin-3-ylidene)-2-(((benzyloxy)carbonyl)amino)acetate (3g)



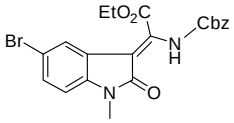
yellow solid; 99% yield in 24 h, mp 80-83 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ=11.27 (s, 1H), 7.38 – 7.32 (m, 5H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.20 (td, *J* = 7.8, 0.8 Hz, 1H), 7.00 (dd, *J* = 17.2, 9.5 Hz, 1H), 6.87 – 6.81 (m, 1H), 5.86 – 5.75 (m, 1H), 5.20 (d, *J* = 4.7 Hz, 2H), 5.20 – 5.14 (m, 2H), 4.52 (s, 2H), 4.42 – 4.33 (m, 2H), 1.41 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 168.5, 162.5, 152.2, 139.9, 138.3, 134.8, 131.0, 128.5, 128.3, 127.7, 122.3, 120.2, 119.9, 117.5, 109.1, 104.0, 68.2, 62.8, 41.9, 13.8; HRMS (ESI): for $C_{23}H_{22}N_2O_5$ $[M]^+$: calcd 406.1529, found 406.1526.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(4-bromo-1-methyl-2-oxoindolin-3-ylidene)acetate (3h)



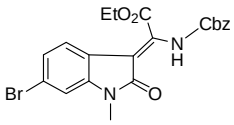
yellow solid; 98% yield in 24 h, mp 118-120 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ= 11.96 (s, 1H), 7.43 – 7.32 (m, 5H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.09 (s, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.21 (s, 2H), 4.46 (d, *J* = 7.2 Hz, 2H), 3.28 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.9, 162.5, 152.2, 142.5, 140.8, 134.8, 128.5, 128.4, 128.2, 127.9, 120.6, 116.1, 107.0, 105.2, 68.1, 62.8, 26.0, 13.5; HRMS (ESI): for $C_{21}H_{19}BrN_2O_5$ $[M]^+$: calcd 458.0477, found 458.0475.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(5-bromo-1-methyl-2-oxoindolin-3-ylidene)acetate (3i)



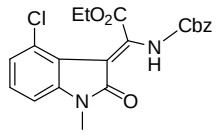
yellow solid; 98% yield in 24 h, mp 121-124 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ=11.23 (s, 1H), 7.41 – 7.30 (m, 6H), 7.29 (s, 1H), 6.70 (d, J = 8.3 Hz, 1H), 5.22 (s, 2H), 4.54 (s, 2H), 3.22 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 162.1, 152.1, 139.6, 139.3, 134.7, 130.2, 128.7, 128.6, 128.4, 123.2, 121.7, 115.1, 109.6, 103.1, 68.4, 63.1, 25.9, 13.8; HRMS (ESI): for $C_{21}H_{19}BrN_2O_5$ $[M]^+$: calcd 458.0477, found 458.0461.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(6-bromo-1-methyl-2-oxoindolin-3-ylidene)acetate (3j)



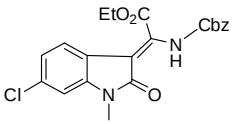
yellow solid; 99% yield in 24 h, mp 130-132 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ=11.18 (s, 1H), 7.45 – 7.30 (m, 5H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 7.02 (s, 1H), 5.22 (s, 2H), 4.51 (s, 2H), 3.26 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 168.4, 162.3, 152.0, 141.7, 138.6, 134.7, 128.5, 128.4, 128.3, 128.2, 125.0, 121.1, 118.7, 111.7, 103.3, 68.3, 62.9, 25.8, 13.7; HRMS (ESI): for $C_{21}H_{19}BrN_2O_5$ $[M]^+$: calcd 458.0477, found 458.0477.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(4-chloro-1-methyl-2-oxoindolin-3-ylidene)acetate (3k)



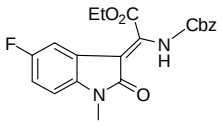
yellow solid; 99% yield in 24 h, mp 129-131°C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 12.15 (s, 1H), 7.43 – 7.32 (m, 5H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 5.21 (s, 2H), 4.44 (d, *J* = 7.2 Hz, 2H), 3.29 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 162.6, 152.1, 142.1, 141.6, 134.8, 128.5, 128.4, 128.3, 128.2, 127.8, 124.5, 118.5, 106.6, 103.5, 68.1, 62.5, 26.1, 13.6; HRMS (ESI): for $C_{21}H_{19}ClN_2O_5$ $[M]^+$: calcd 414.0982, found 414.0967.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)acetate (3l)



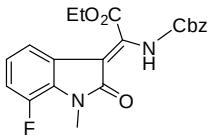
yellow solid; 98% yield in 24 h, mp 152-155 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ= 11.16 (s, 1H), 7.45 – 7.31 (m, 5H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.98 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.86 (d, *J* = 1.6 Hz, 1H), 5.22 (s, 2H), 4.51 (s, 2H), 3.25 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 168.7, 162.3, 152.1, 141.7, 138.5, 134.7, 133.4, 128.6, 128.4, 122.2, 121.0, 118.3, 108.9, 103.4, 68.4, 62.9, 25.9, 13.8; HRMS (ESI): for $C_{21}H_{19}ClN_2O_5$ $[M]^+$: calcd 414.0982, found 414.0974.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(5-fluoro-1-methyl-2-oxoindolin-3-ylidene)acetate (3m)



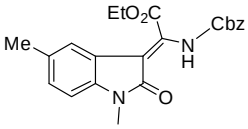
yellow solid; 98% yield in 24 h, mp 123-125 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ =11.29 (s, 1H), 7.38 (d, *J* = 8.5 Hz, 5H), 6.96 (d, *J* = 7.4 Hz, 2H), 6.82 – 6.73 (m, 1H), 5.23 (s, 2H), 4.53 (s, 2H), 3.26 (s, 3H), 1.42 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 162.1, 160.0, 157.6, 152.0, 139.1, 136.8, 134.7, 128.5, 128.3, 120.9, 114.0, 113.8, 108.6, 108.6, 108.0, 107.7, 103.8, 68.3, 62.9, 25.8, 13.7; HRMS (ESI): for $C_{21}H_{19}FN_2O_5$ $[M]^+$: calcd 398.1278, found 398.1266.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(7-fluoro-1-methyl-2-oxoindolin-3-ylidene)acetate (3n)



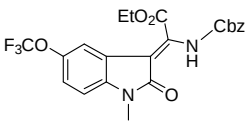
yellow solid; 98% yield in 24 h, mp 131-134 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.32 (s, 1H), 7.44 – 7.31 (m, 5H), 6.96 (ddd, *J* = 13.0, 12.4, 6.2 Hz, 3H), 5.23 (s, 2H), 4.52 (s, 2H), 3.49 (d, *J* = 2.4 Hz, 3H), 1.41 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 162.2, 152.0, 149.1, 146.7, 139.2, 134.6, 128.5, 128.39, 128.3, 127.3, 127.2, 122.7, 122.6, 115.9, 115.2, 115.0, 103.4, 68.3, 62.9, 28.2, 13.7; HRMS (ESI): for $C_{21}H_{19}FN_2O_5$ $[M]^+$: calcd 398.1278, found 398.1271.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(1,5-dimethyl-2-oxoindolin-3-ylidene)acetate(3o)



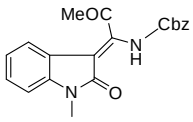
yellow solid; 98% yield in 24 h, mp 98-101 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.28 (s, 1H), 7.38 (d, *J* = 3.8 Hz, 3H), 7.36 (t, *J* = 3.6 Hz, 2H), 7.16 – 6.92 (m, 2H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.22 (d, *J* = 3.1 Hz, 2H), 4.53 (d, *J* = 6.4 Hz, 2H), 3.25 (s, 3H), 2.32 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 162.6, 152.3, 138.7, 137.7, 134.9, 131.6, 128.5, 128.3, 128.2, 120.9, 119.8, 108.0, 104.4, 68.2, 62.7, 25.8, 21.3, 13.8; HRMS (ESI): for $C_{22}H_{22}N_2O_5$ $[M]^+$: calcd 394.1529, found 394.1512.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(1-methyl-2-oxo-5-(trifluoromethoxy)indolin-3-ylidene)acetate (3p)



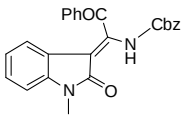
yellow solid; 98% yield in 24 h, mp 77-80 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 11.23 (s, 1H), 7.46 – 7.33 (m, 5H), 7.17 – 7.06 (m, 2H), 6.85 (d, *J* = 8.5 Hz, 1H), 5.23 (s, 2H), 4.51 (s, 2H), 3.29 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 162.1, 152.1, 144. 4, 139.7, 139.2, 134.7, 128.6, 128.4, 121.8, 121.0, 120.7, 119.2, 113.9, 108.6, 103.3, 68.5, 63.1, 26.0, 13.7. HRMS (ESI): for $C_{22}H_{19}F_3N_2O_6$ $[M]^+$: calcd 464.1195, found 464.1189.

(Z)-benzyl (1-(1-methyl-2-oxoindolin-3-ylidene)-2-oxopropyl)carbamate (3q)



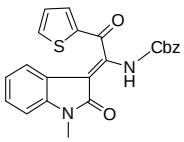
yellow solid; 98% yield in 24 h, mp 139-141 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.39 (s, 1H), 7.37 (d, *J* = 8.9 Hz, 5H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.22 (s, 2H), 3.29 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.8, 186.2, 168.9, 152.8, 145.8, 140.7, 134.7, 128.6, 128.6, 128.4, 127.6, 122.4, 120.3, 119.6, 108.3, 102.1, 68.4, 30.0, 25.7; HRMS (ESI-TOF) for $C_{20}H_{18}N_2NaO_4$ $[M+Na]^+$: calcd 373.1159, found 373.1161.

(Z)-benzyl (1-(1-methyl-2-oxoindolin-3-ylidene)-2-oxo-2-phenylethyl)carbamate (3r)



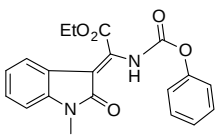
red solid; 98% yield in 24 h, mp 165-167 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.65 (s, 1H), 8.05 (s, 2H), 7.62 (s, 1H), 7.50 (s, 2H), 7.33 – 7.25 (m, 5H), 7.15 (s, 1H), 6.89 – 6.75 (m, 3H), 5.10 (d, *J* = 12.5 Hz, 2H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.7, 168.7, 152.3, 144.5, 140.6, 134.9, 134.7, 134.3, 129.12, 128.7, 128.5, 128.3, 127.4, 122.2, 121.0, 119.8, 108.2, 104.3, 68.3, 25.8; HRMS (ESI-TOF) for $C_{25}H_{20}N_2NaO_4$ $[M+Na]^+$: calcd 435.1315, found 435.1304.

(Z)-benzyl (1-(1-methyl-2-oxoindolin-3-ylidene)-2-oxo-2-(thiophen-2-yl)ethyl)carbamate (3s)



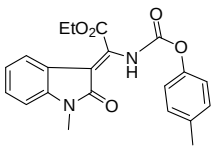
yellow solid; 99% yield in 24 h, mp 146-148 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.56 (s, 1H), 7.78 (d, *J* = 4.7 Hz, 1H), 7.70 (d, *J* = 3.5 Hz, 1H), 7.33 (d, *J* = 3.3 Hz, 5H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.12 – 7.08 (m, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.85 (t, J = 7.3 Hz, 2H), 5.14 (s, 2H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.2, 181.5, 168.7, 152.1, 143.6, 142.0, 140.7, 135.8, 134.5, 128.6, 128.5, 128.3, 127.5, 122.3, 121.1, 119.7, 108.2, 104.5, 68.3, 25.8; HRMS (ESI-TOF) for $C_{23}H_{18}N_2NaO_4S$ $[M+Na]^+$: calcd 441.0879, found 441.0879.

(Z)-ethyl 2-((benzoyloxy)amino)-2-(1-methyl-2-oxoindolin-3-ylidene)acetate (3t)



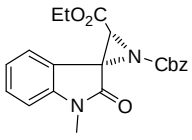
yellow solid; 99% yield in 24 h. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.54 (s, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.29 – 7.23 (m, 4H), 7.23 – 7.19 (m, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.51 (q, *J* = 7.2 Hz, 2H), 3.31 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 162.2, 150.8, 150.0, 140.9, 137.5, 129.4, 128.0, 126.1, 122.4, 121.2, 120.3, 119.6, 108.4, 105.1, 62.9, 25.8, 13.8; HRMS (ESI-TOF) for $C_{20}H_{18}N_2NaO_5$ $[M+Na]^+$: calcd 389.1108, found 389.1105.

(Z)-ethyl 2-(1-methyl-2-oxoindolin-3-ylidene)-2-(((4-methylbenzoyl)oxy)amino)acetate (3u)



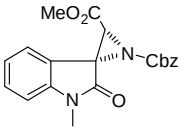
yellow solid; 99% yield in 24 h. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 11.51 (s, 1H), 7.29 – 7.25 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 7.04 (s, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.50 (q, *J* = 7.2 Hz, 2H), 3.31 (s, 3H), 2.34 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.8, 162.3, 151.0, 147.9, 141.0, 137. 7, 135.8, 129.9, 128.0, 122.4, 120.9, 120.4, 119.7, 108.4, 105.0, 62.9, 25.8, 20.8, 13.8; HRMS (ESI-TOF) for $C_{21}H_{20}N_2NaO_5$ $[M+Na]^+$: calcd 403.1264, found 403.1257.

1-benzyl 3-ethyl 1'-methyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4a)



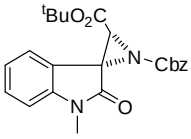
white solid; 82% yield in 2.5 h, >95:5 d.r. mp 120-122 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.38 – 7.24 (m, 5H), 7.16 (dd, *J* = 7.7 Hz, 1.6, 2H), 6.92 – 6.83 (m, 2H), 6.55 (d, *J* = 7.4 Hz, 1H), 5.18 – 5.03 (m, 2H), 4.32 (dd, *J* = 7.2 Hz, 4.6, 2H), 3.88 (s, 1H), 3.24 (s, 4H), 1.34 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 164.1, 158.3, 144.8, 134.51, 130.4, 128.7, 128.5, 128.3, 122.5, 120.7, 119.8, 109.0, 69.0, 62.1, 48.7, 46.8, 26.6, 14.0; HRMS (ESI-TOF) for $C_{21}H_{20}N_2NaO_5$ $[M+Na]^+$: calcd 402.1264, found 402.1259.

1-benzyl 3-methyl 1'-methyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4b)



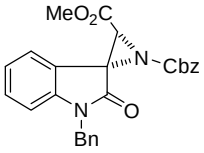
white solid; 75% yield in 2 h, >95:5 d.r. mp 130-132°C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 – 7.21 (m, 4H), 7.17 (s, 2H), 6.87 (t, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 7.3 Hz, 1H), 5.10 (dd, *J* = 28.5, 11.7 Hz, 2H), 3.91 (s, 1H), 3.84 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 164.6, 158.2, 144.8, 134.5, 130.4, 128.7, 128.5, 128.4, 122.6, 120.7, 119.7, 109.1, 69.1, 52.8, 48.7, 46.7, 26.6; HRMS (ESI-TOF) for $C_{20}H_{18}N_2NaO_5$ $[M+Na]^+$: calcd 389.1108, found 389.1104.

1-benzyl 3-tert-butyl 1'-methyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4c)



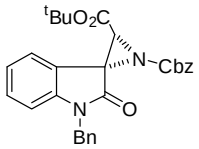
white solid; 74% yield in 2 h, >95:5 d.r. mp 139-142 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.28 (dt, *J* = 12.8, 6.8Hz, 5H), 7.20 – 7.11 (m, 2H), 6.92 – 6.82 (m, 2H), 6.54 (d, *J* =7.4 Hz, 1H), 5.08 (dd, *J* = 28.4, 12.0 Hz, 2H), 3.80 (s, 1H), 3.23 (d, *J* = 8.3 Hz, 3H), 1.54 – 1.49 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.0, 162.9, 158.5, 157.8, 144.9, 134.7, 130.2, 128.6, 128.4, 128.3, 122.4, 120.7, 120.3, 108.9, 83.2, 68.9, 48.7, 47.5, 27.9, 26.6; HRMS (ESI-TOF) for $C_{23}H_{24}N_2NaO_5$ $[M+Na]^+$: calcd 431.1577, found 431.1559.

1-benzyl 3-methyl 1'-benzyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4d)



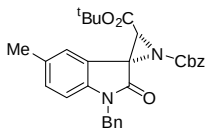
white solid; 84% yield in 2 h, >95:5 d.r. mp 112-114 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.31 – 7.22 (m, 9H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 5.10 (dd, *J* = 43.7, 12.0 Hz, 2H), 4.94 (d, *J* = 10.5 Hz, 2H), 3.97 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 164.6, 158.2, 144.0, 134.8, 134.5, 130.4, 128.8, 128.5, 128.5, 128.4, 127.7, 127.1, 122.7, 120.8, 119.9, 110.2, 69.1, 52.9, 48.8, 46.9, 44.2; HRMS (ESI-TOF) for $C_{26}H_{22}N_2NaO_5$ $[M+Na]^+$: calcd 465.1421, found 465.1421.

1-benzyl 3-tert-butyl 1'-benzyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4e)



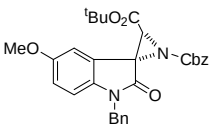
white solid; 95% yield in 2 h, >95:5 d.r. mp 108-110 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.31 – 7.21 (m, 10H), 7.12 (d, *J* = 7.4 Hz, 2H), 6.83 (s, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 6.57 (d, *J* = 7.5Hz, 1H), 5.11 (dd, *J* = 44.0, 12.2 Hz, 2H), 4.95 (dd, *J* = 105.6, 15.9 Hz, 2H), 3.86 (s, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 162.7, 158.5, 144.0, 135.1, 134.7, 130.1, 128.7, 128.5, 128.4, 128.3, 127.6, 127.0, 122.6, 120.8, 120.4, 110.0, 83.3, 68.9, 48.7, 47.8, 44.0, 27.9, 27.5; HRMS (ESI-TOF) for $C_{29}H_{28}N_2NaO_5$ $[M+Na]^+$: calcd 507.1890, found 507.1866.

1-benzyl 3-tert-butyl 1'-benzyl-5'-methyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4f)



white solid; 96% yield in 2 h, >95:5 d.r. mp 122-124 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 5.2 Hz, 9H), 7.13 (d, *J* = 6.8 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.40 (s, 1H), 5.13 (dd, *J* = 30.6, 12.1 Hz, 2H), 4.94 (dd, *J*=73.8, 15.8 Hz, 2H), 3.82 (s, 1H), 2.11 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 162.7, 158.4, 141.6, 135.2, 134.8, 132.3, 130.5, 128.7, 128.4, 128.3, 127.6, 127.0, 121.5, 120.4, 109. 8, 83.2, 68.8, 48.8, 47.8, 44.0, 27.9, 20.9; HRMS (ESI-TOF) for $C_{30}H_{30}N_2NaO_5$ $[M+Na]^+$: calcd 521.2047, found 521.2036.

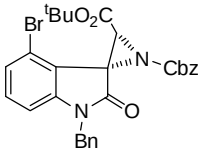
1-benzyl 3-tert-butyl 1'-benzyl-5'-methoxy-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4g)



white solid; 98% yield in 6 h, >95:5 d.r. mp 136-138 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.27 – 7.24 (m, 6H), 7.23 (s, 2H), 7.13 (s, 1H), 7.11 (s, 1H), 6.72 (dd, *J* = 8.6, 2.4,

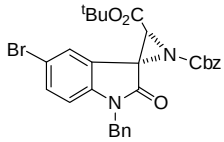
1H), 6.64 (d, *J* = 8.6 Hz, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 5.13 (dd, *J* = 28.7, 12.1 Hz, 2H), 4.93 (dd, *J* = 65.6, 15.8 Hz, 2H), 3.84 (s, 1H), 3.57 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.0, 162.7, 158.4, 137.2, 135.2, 134.7, 128.7, 128.4, 128.3, 128.1, 127.6, 127.0, 121.6, 114.8, 110.6, 107.9, 83.3, 68.8, 55.6, 48.9, 47.8, 44.1, 27.9; HRMS (ESI-TOF) for $C_{30}H_{30}N_2NaO_6$ $[M+Na]^+$: calcd 537.1996, found 537.1983.

1-benzyl 3-tert-butyl 1'-benzyl-4'-bromo-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4h)



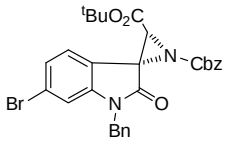
white solid; 93% yield in 15 min, >95:5 d.r. mp 159-161 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.26 (dd, *J* =12.2, 5.8 Hz, 10H), 7.08 (d, *J* = 5.9 Hz, 2H), 6.71 (dd, *J* = 6.0, 2.5 Hz, 1H), 5.17 (s, 2H), 5.05 (d, *J* = 15.9 Hz, 1H), 4.86 (s, 1H), 4.83 (d, *J* = 16.0 Hz, 1H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.0, 163.2, 156.9, 146.4, 134.8, 134.6, 131.2, 128.8, 128.4, 128.3, 128.3, 127.8, 127.2, 126.9, 118.2, 118.1, 109.2, 83.4, 69.0, 48.9, 44.2, 43.1, 28.0; HRMS (ESI-TOF) for $C_{29}H_{27}BrN_2NaO_5$ $[M+Na]^+$: calcd 585.0996, found 585.0992.

1-benzyl 3-tert-butyl 1'-benzyl-5'-bromo-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4i)



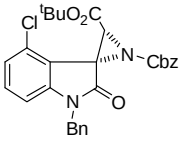
white solid; 92% yield in 15 min, >95:5 d.r. mp 123-126 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32 – 7.24 (m, 8H), 7.21 (d, *J* = 10.1 Hz, 4H), 6.77 (s, 1H), 6.60 (d, *J* = 8.3 Hz, 1H), 5.15 (dd, *J* = 44.1, 12.1 Hz, 2H), 4.93 (dd, *J* = 81.3, 15.8 Hz, 2H), 3.84 (s, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7, 162.3, 158.0, 142.9, 134.6, 134.5, 133.0, 128.8, 128.7, 128.6, 128.4, 127.8, 126.9, 124.1, 122.5, 115.2, 111.4, 83.5, 69.2, 48.0, 44.1, 27.9; HRMS (ESI-TOF) for $C_{29}H_{27}BrN_2NaO_5$ $[M+Na]^+$: calcd 585.0996, found 585.0990.

1-benzyl 3-tert-butyl 1'-benzyl-6'-bromo-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4j)



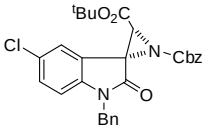
white solid; 90% yield in 15 min, >95:5 d.r. mp 72-74 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32 – 7.24 (m, 8H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.88 (d, *J* = 6.5 Hz, 2H), 6.31 (d, *J* = 8.4 Hz, 1H), 5.12 (s, 2H), 5.01 (d, *J* = 15.8 Hz, 1H), 4.83 (d, *J* = 15.9 Hz, 1H), 3.82 (s, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 162.4, 158.2, 145.2, 134.7, 134.6, 128.9, 128.7, 128.6, 128.4, 127.9, 127.0, 125.4, 123.9, 122.0, 119.3, 113.3, 83.5, 69.0, 48.2, 47.8, 44.2, 27.9; HRMS (ESI-TOF) for $C_{29}H_{27}BrN_2NaO_5$ $[M+Na]^+$: calcd 585.0996, found 585.0993.

1-benzyl 3-tert-butyl 1'-benzyl-4'-chloro-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4k)



white solid; 99% yield in 15 min, >95:5 d.r. mp 149-152 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.28 (s, 3H), 7.23 (d, *J* = 6.7 Hz, 5H), 7.18 – 7.12 (m, 2H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 5.16 (s, 2H), 5.06 (d, *J* = 15.9 Hz, 1H), 4.83 (d, *J* = 15.9 Hz, 1H), 4.71 (s, 1H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.0, 163.1, 157.3, 146.1, 134.8, 134.6, 131.0, 130.0, 128.8, 128.4, 128.3, 127.8, 127.0, 124.0, 116.6, 108.7, 83.4, 69.0, 48.5, 44.2, 43.4, 28.0; HRMS (ESI-TOF) for $C_{29}H_{27}ClN_2NaO_5$ $[M+Na]^+$: calcd 541.1501, found 541.1509.

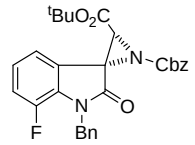
1-benzyl 3-tert-butyl 1'-benzyl-5'-chloro-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4l)



white solid; 90% yield in 15 min, >95:5 d.r. mp 128-131 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.26 (s, 6H), 7.19 (dd, *J* = 16.0, 9.9 Hz, 5H), 6.65 (d, *J* = 8.4 Hz, 1H), 6.60 (s, 1H), 5.15 (dd, *J* = 38.5, 12.0 Hz, 2H), 4.93 (dd, *J* = 79.2, 15.9 Hz, 2H), 3.83 (s, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 162.3, 158.0, 142.4, 134.6, 134.5, 130.1, 128.8, 128.61, 128.5, 128.4, 128.2, 127.8, 127.0, 122.2, 121.4, 111.0, 83.6, 69.2, 48.0, 44.2, 27.9;

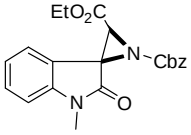
HRMS (ESI-TOF) for $C_{29}H_{27}ClN_2NaO_5$ [M+Na]+: calcd 541.1501, found 541.1500.

1-benzyl 3-tert-butyl 1'-benzyl-7'-fluoro-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4m)



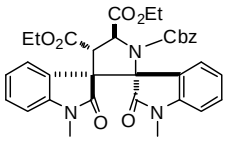
white solid; 90% yield in 15 min, >95:5 d.r. mp 92-95°C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.31 – 7.19 (m, 10H), 7.15 (d, *J* = 6.7 Hz, 2H), 7.00 – 6.92 (m, 1H), 6.75 (d, *J* = 4.2 Hz, 1H), 6.31 (s, 1H), 5.19 – 5.11 (m, 2H), 5.05 (dd, *J* = 20.6, 13.7 Hz, 2H), 3.82 (s, 1H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.2, 174.2, 168.0, 162.3, 158.1, 148.9, 146.4, 136.3, 134.6, 130.6, 128.6, 128.5, 128.4, 127.6, 127.2, 123.3, 118.4, 118.2, 116.7, 83.4, 69.0, 48.4, 48.2, 45.7, 27.9; HRMS (ESI-TOF) for $C_{29}H_{27}FN_2NaO_5$ $[M+Na]^+$: calcd 525.1796, found 525.1784.

1-benzyl 3-ethyl 1'-methyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4a')



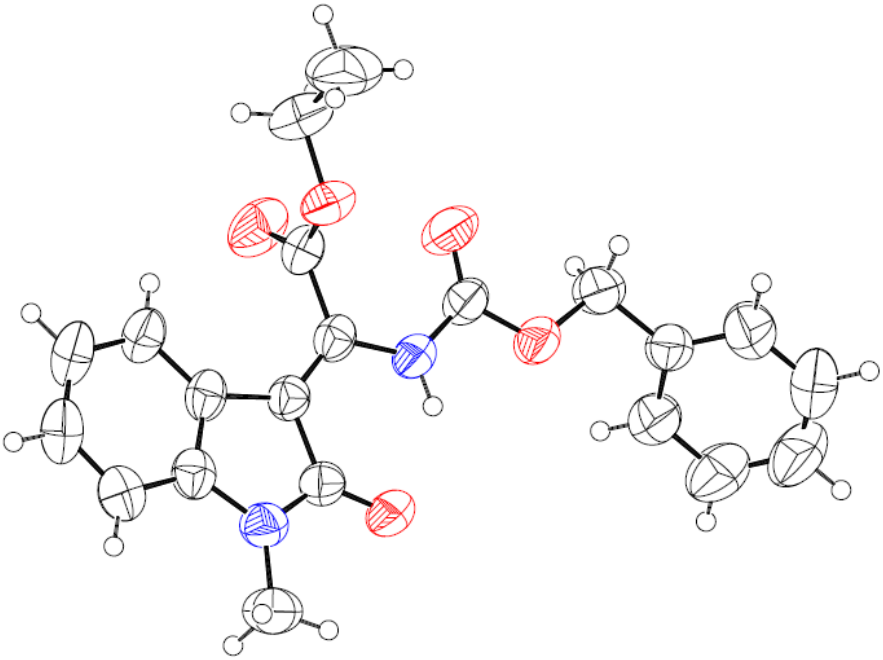
white solid; >95:5 d.r. mp 120-122 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41-7.33 (m, 7H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 5.18 (dd, *J* = 38.1, 12.0 Hz, 2H), 4.22 (dt, *J* = 17.8, 10.8 Hz, 2H), 3.90 (s, 1H), 3.26 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =168.1, 164.3, 157.9, 144.6, 134.5, 130.0, 128.2, 128.0, 128.0, 123.8, 122.6, 120.1, 108.6, 68.8, 61.9, 48.8, 47.8, 26.6, 14.0; HRMS (ESI-TOF) for $C_{21}H_{20}N_2NaO_5$ $[M+Na]^+$: calcd 402.1264, found 402.1259.

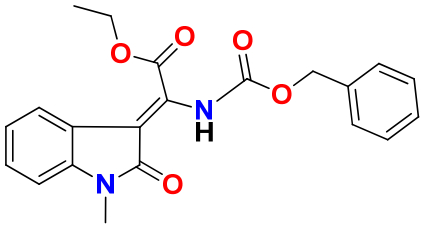
1-benzyl 3-tert-butyl 1'-benzyl-5'-bromo-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (5)



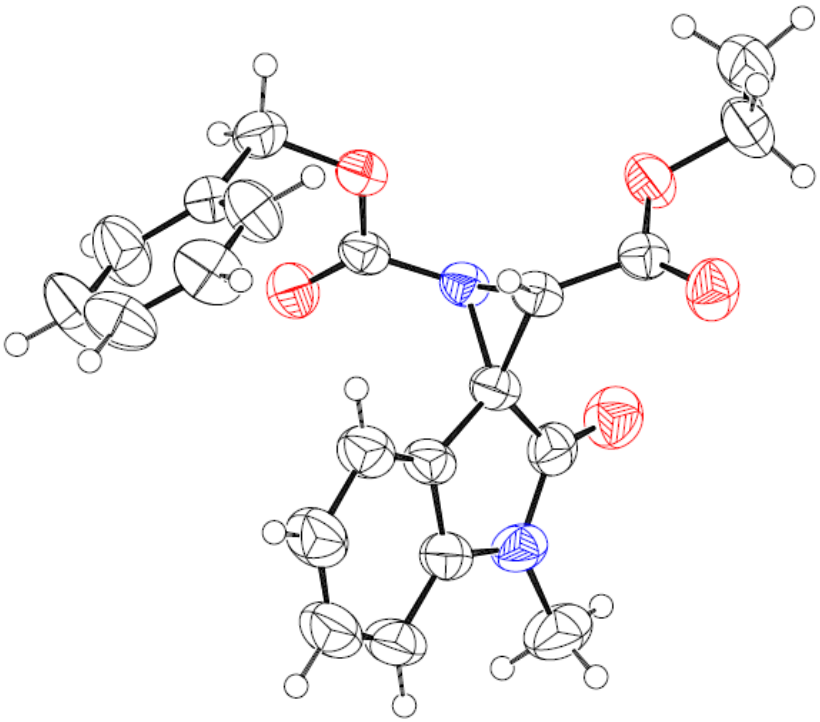
white solid; 75% yield, 1.6:1 d.r. mp 156-159 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 6.9 Hz, 1H), 7.95 (d, *J* = 7.1 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.30 (s, 4H), 7.16 (dd, *J* = 15.1, 7.3 Hz, 5H), 7.09 (t, *J* = 7.5 Hz, 2H), 6.77 – 6.66 (m, 4H), 6.43 (d, *J* = 7.1 Hz, 1H), 5.39 (d, *J* = 9.2 Hz, 2H), 5.05 (dd, *J* = 39.4, 12.0 Hz, 1H), 4.79 (dd, *J* = 30.2, 11.5 Hz, 2H), 4.38 (dd, *J* = 15.0, 7.2 Hz, 2H), 4.29 (dd, *J* = 17.7, 9.0 Hz, 2H), 4.06 (s, 1H), 3.91 (s, 1H), 3.84 (s, 2H), 3.79 (d, *J* = 7.6 Hz, 2H), 3.48 (d, *J* = 6.5 Hz, 1H), 2.98 (d, *J* = 9.6 Hz, 7H), 2.30 (s, 3H), 1.62 (d, *J* = 6.9 Hz, 3H), 1.38 (t, *J* = 6.4 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 1H), 1.10 (s, 2H), 0.81 (d, *J* = 6.1 Hz, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.4, 171.1, 170.8, 170.5, 166.1, 152.2, 151.7, 142.6, 141.9, 136.9, 134.9, 134.1, 129.8, 129.1, 127.9, 127.6, 127.2, 126.7, 126.2, 125.2, 122.9, 121.5, 121.1, 107.5, 72.0, 71.3, 67.5, 61.4, 60.8, 60.2, 59.4, 53.5, 52.7, 26.1, 25.5, 13.6, 13.4, 13.0; HRMS (ESI-TOF) for $C_{34}H_{34}N_3O_8$ $[M+H]^+$: calcd 612.2268, found 612.2337.

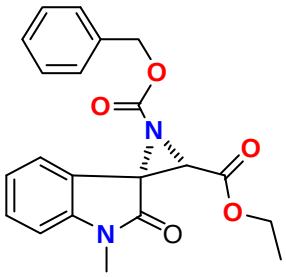
6. X-Ray single crystal diffraction structures of 3a, 4a, 4a'and 5.



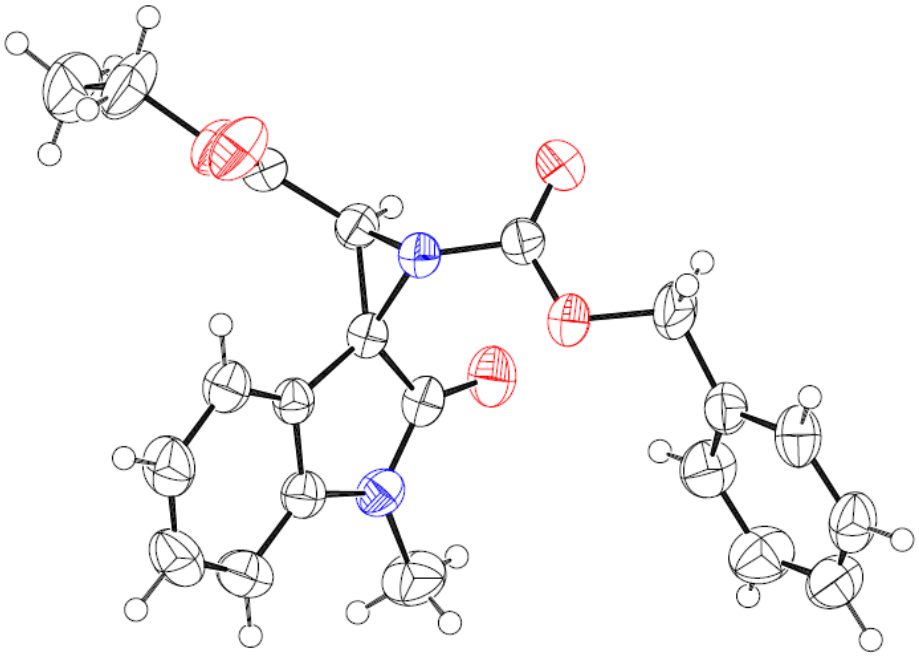


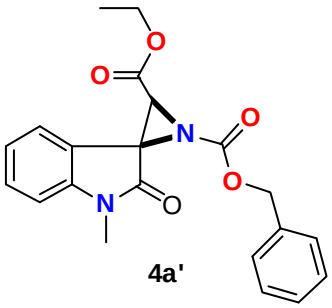
3a



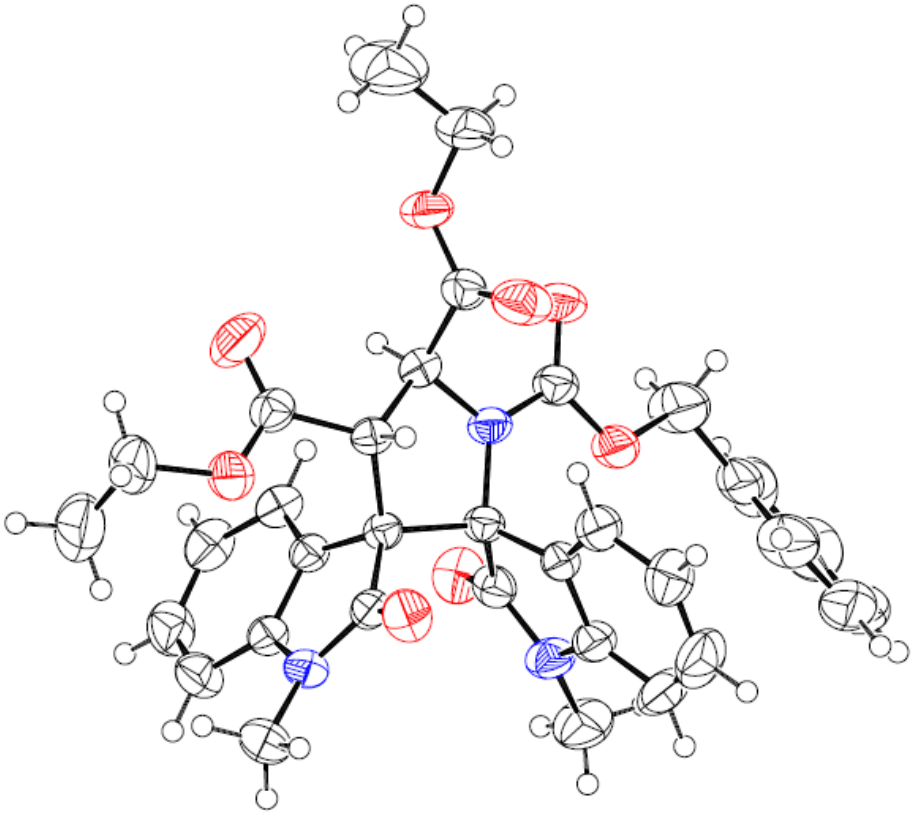


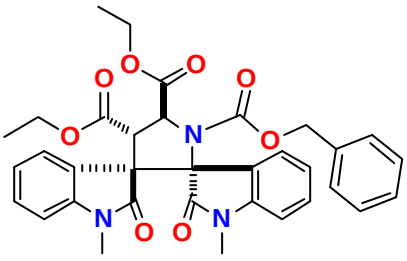
4a





4a'

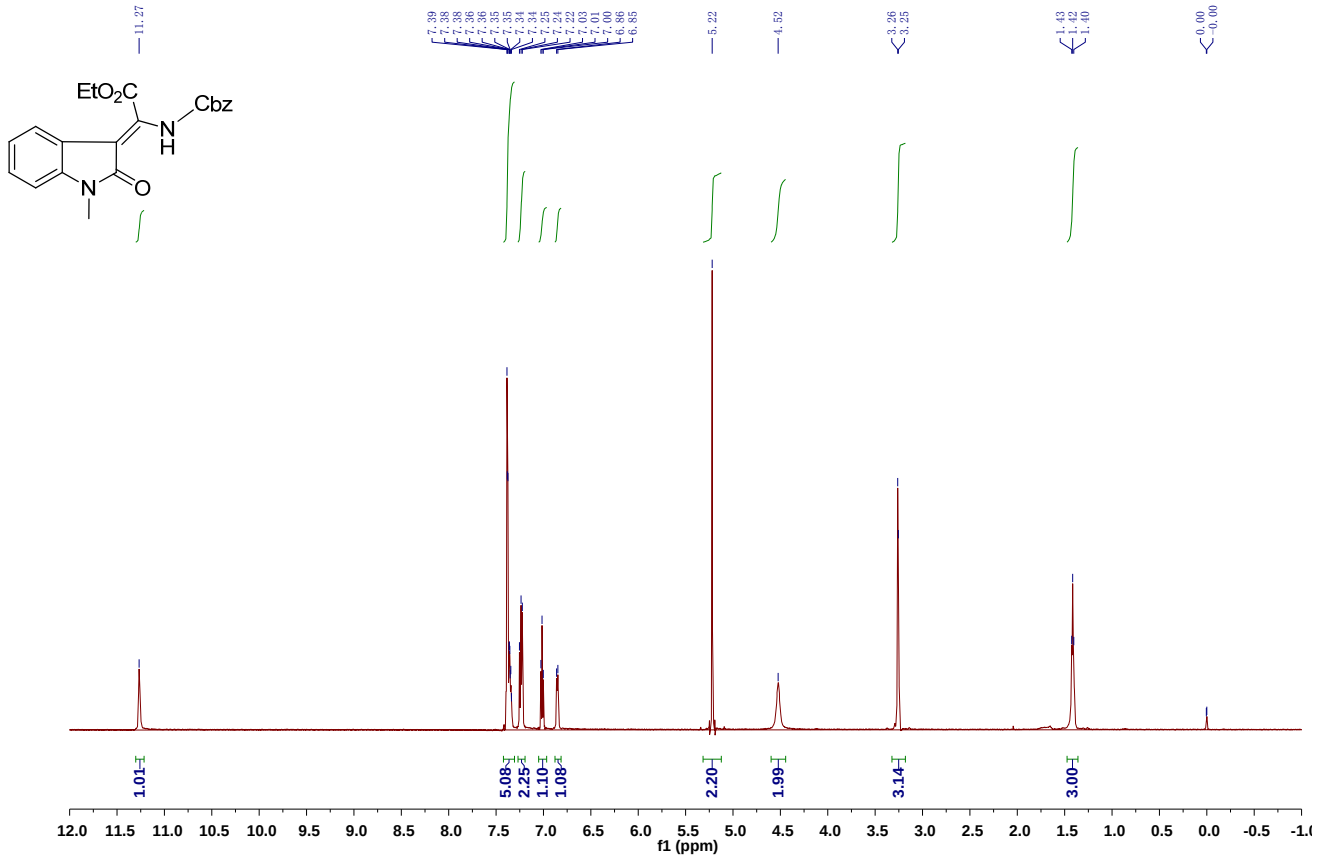


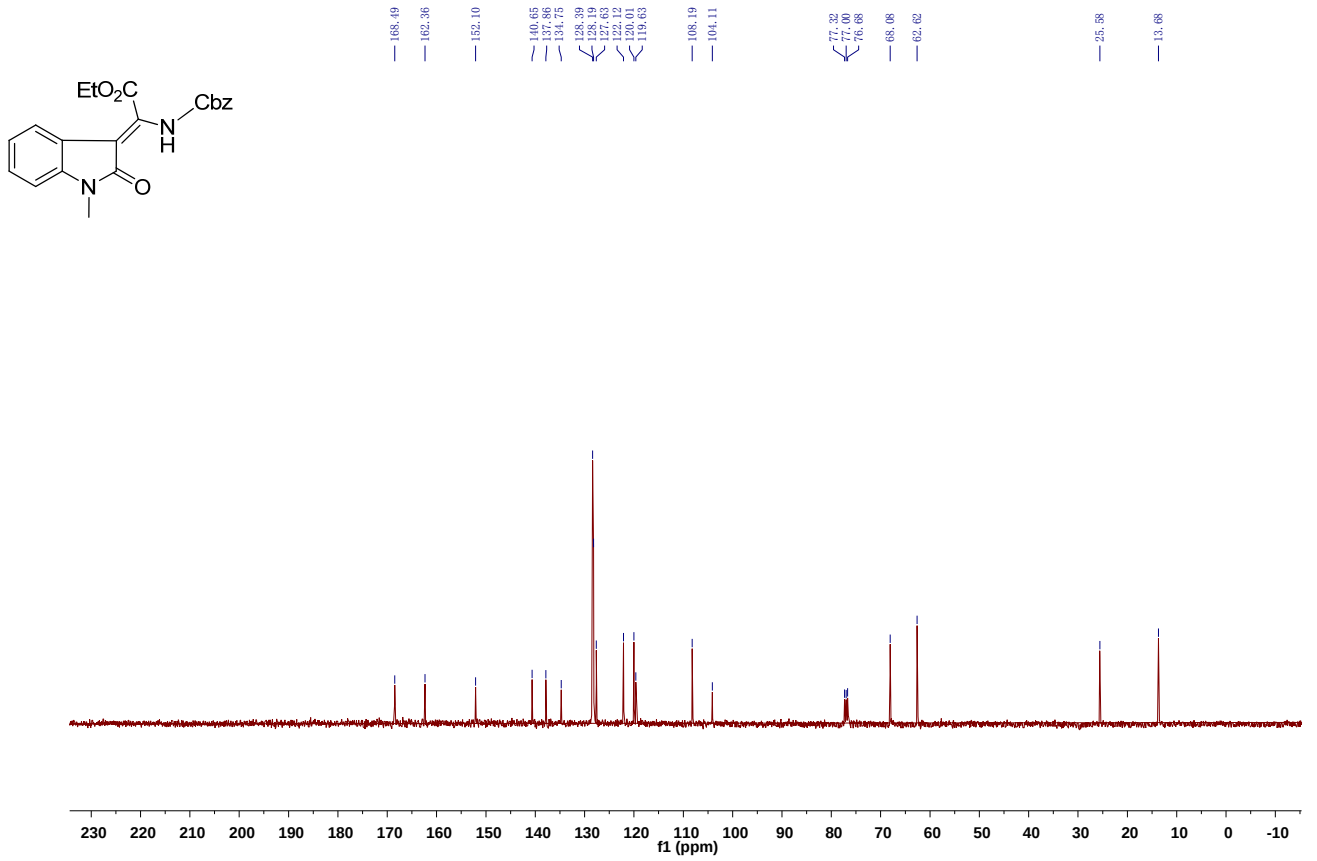


5

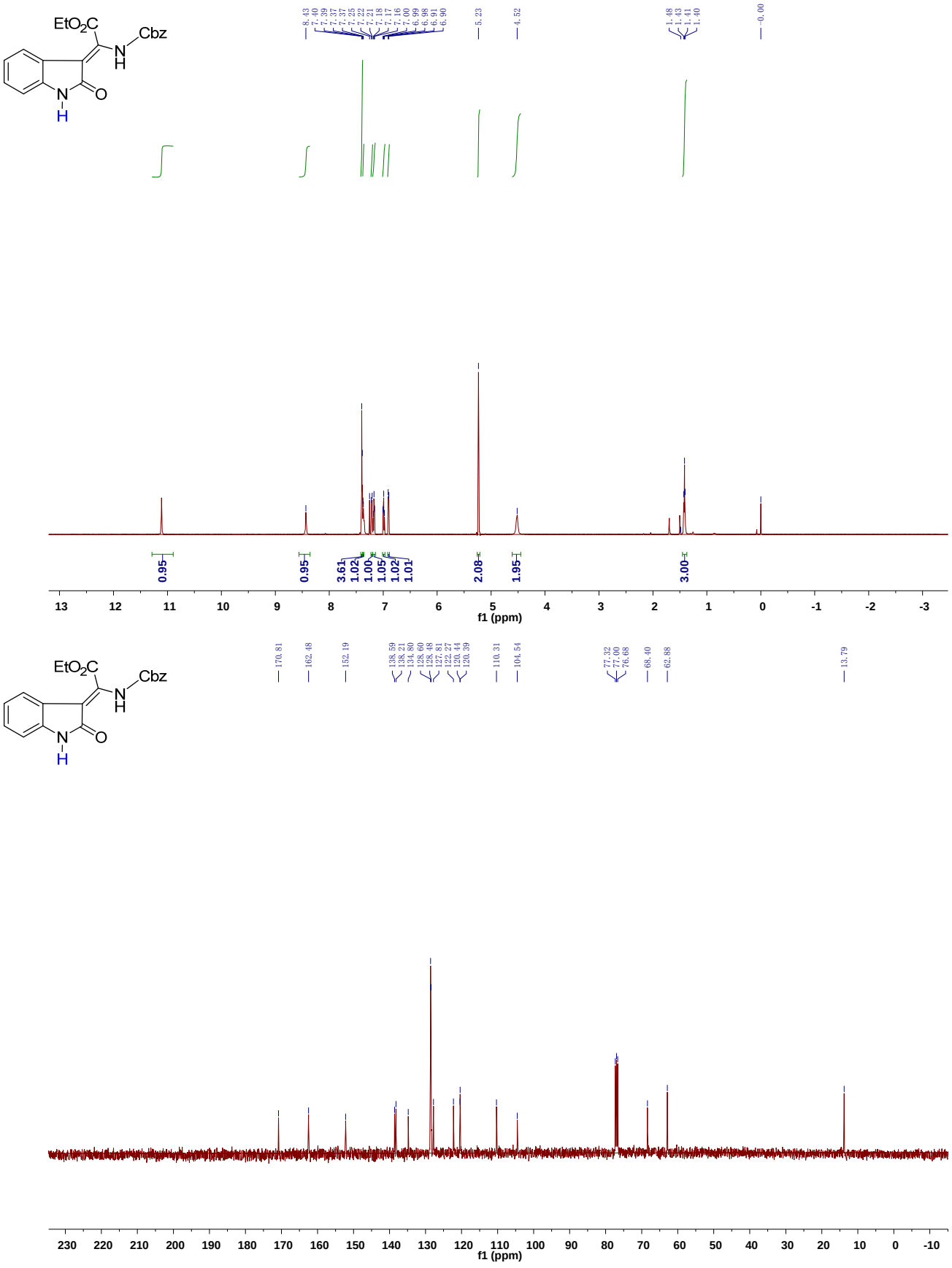
7. Copies of ^{1}H NMR and ^{13}C NMR spectra

^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 3a

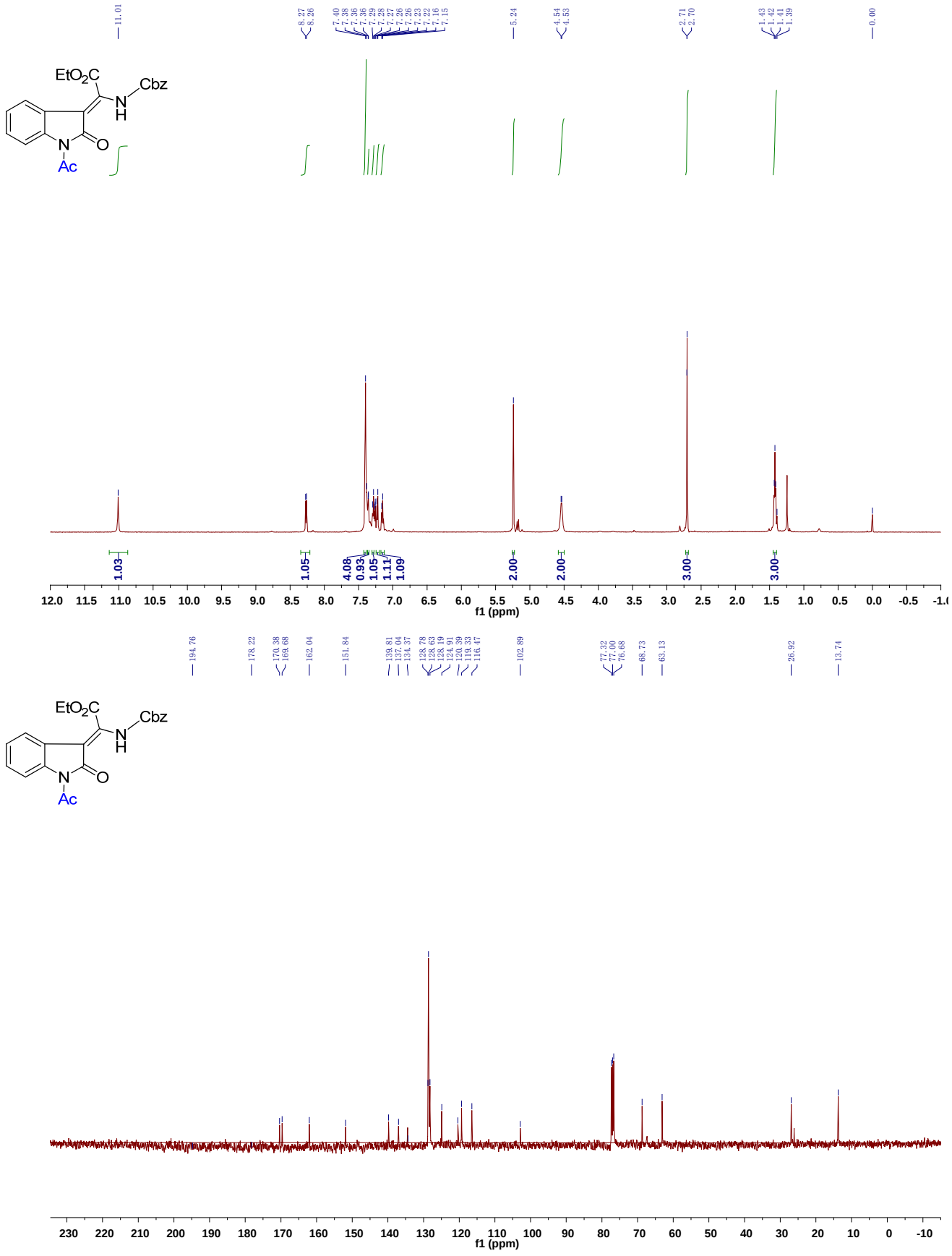




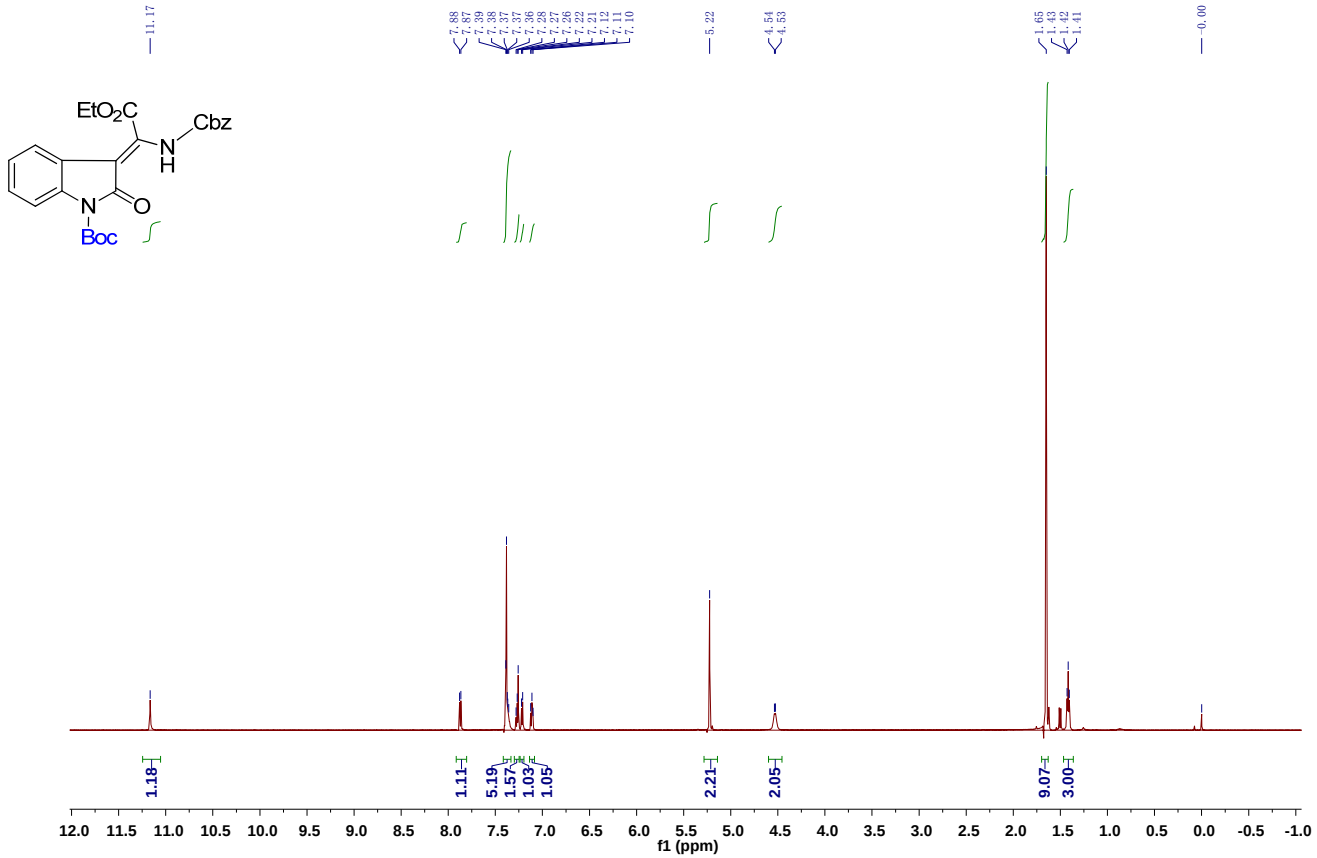
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3b

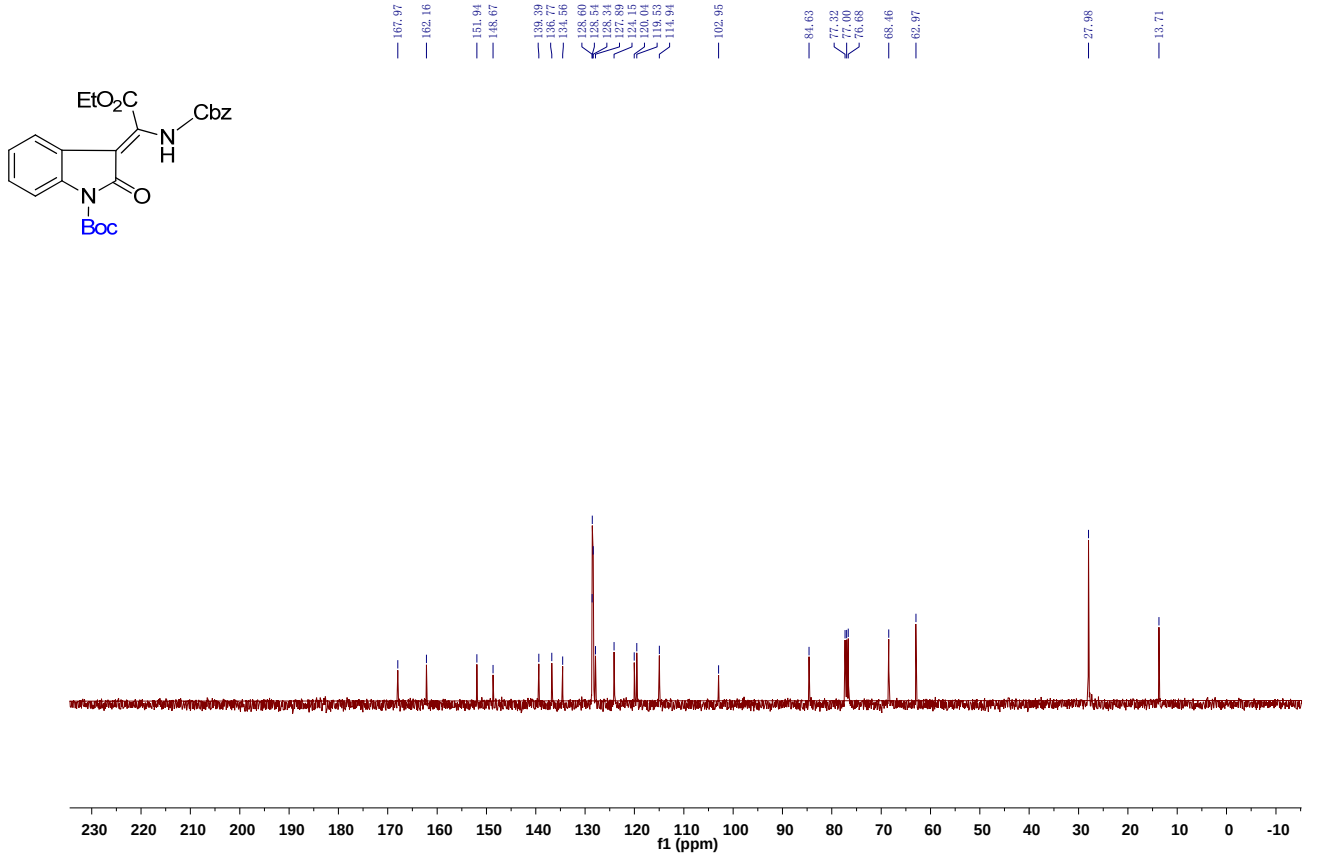


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3c

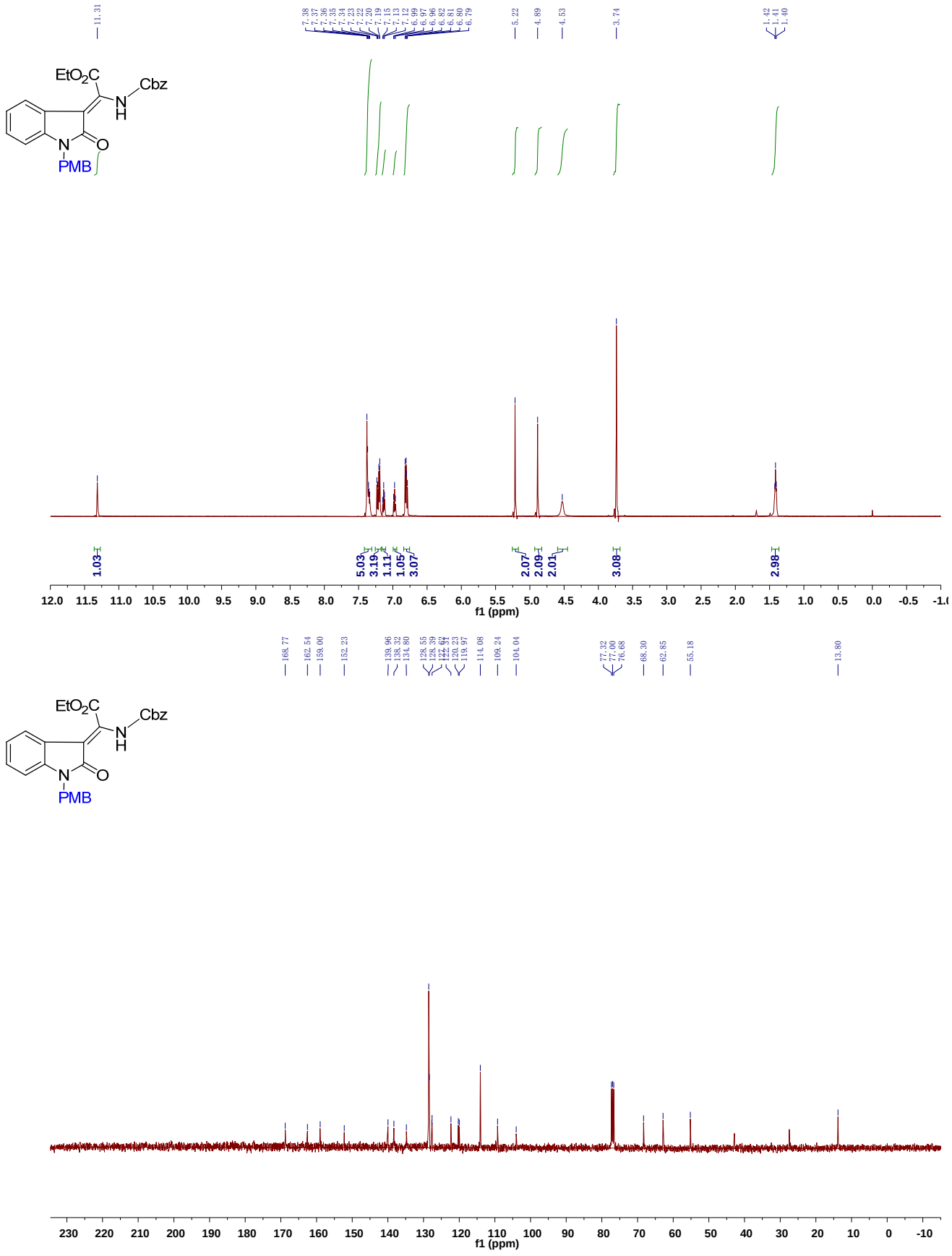


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3d

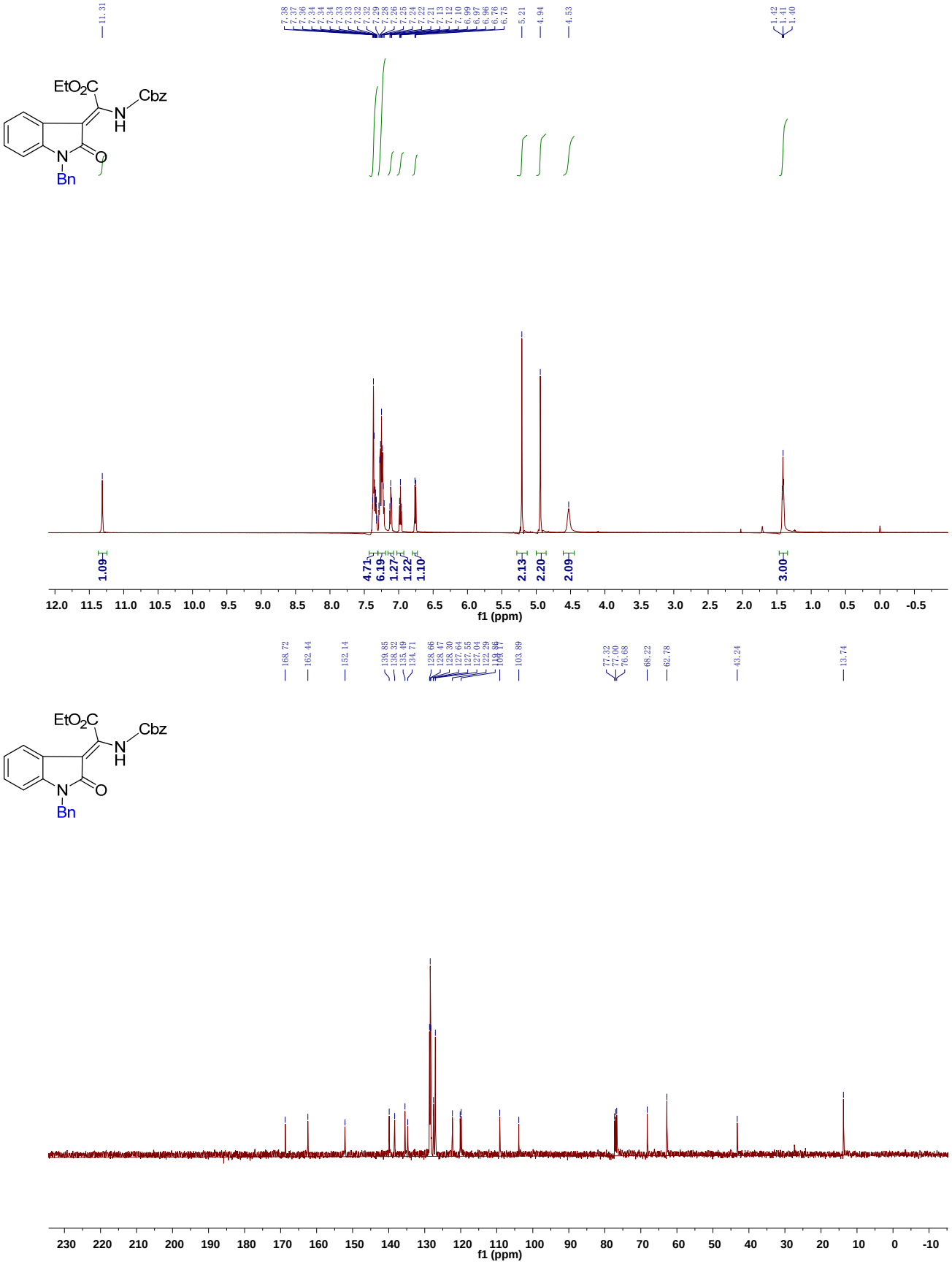




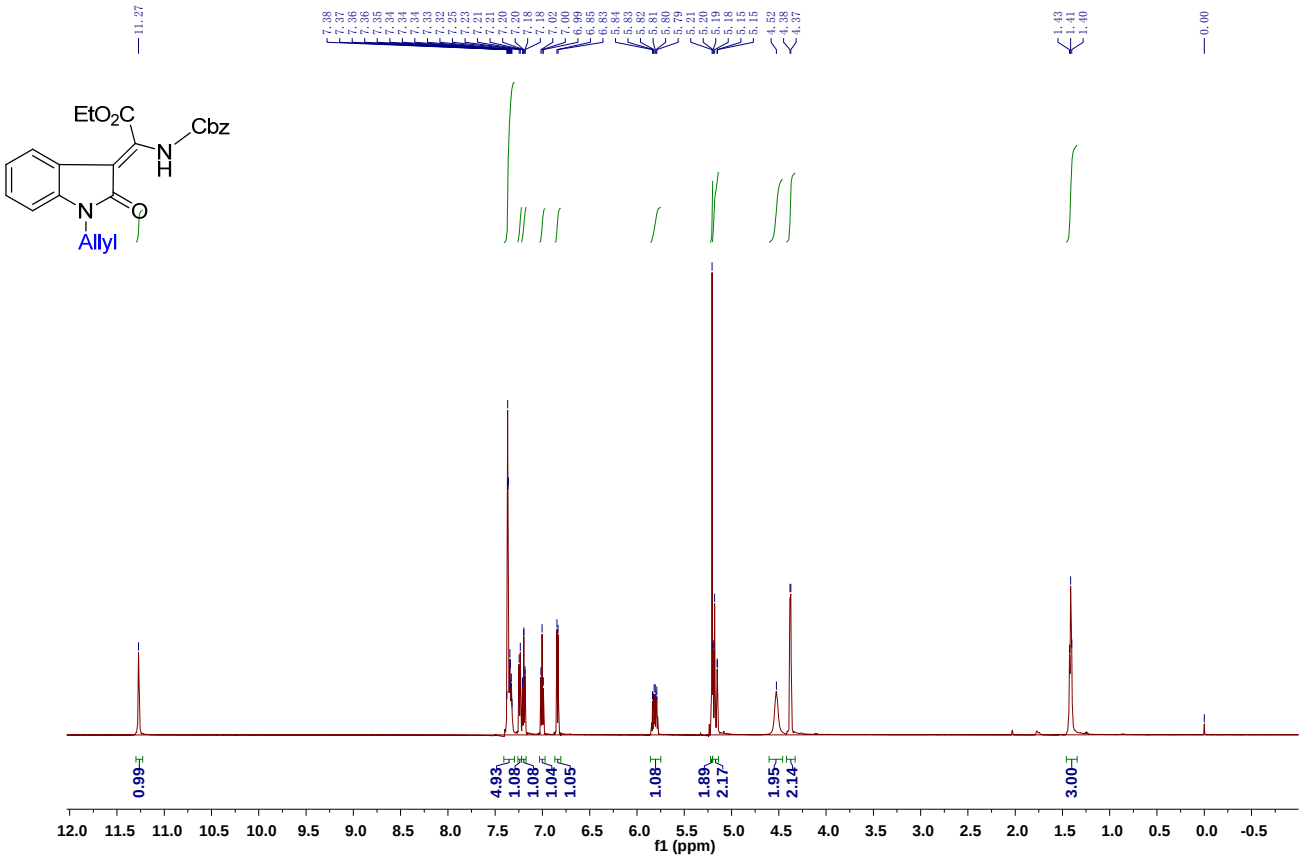
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3e

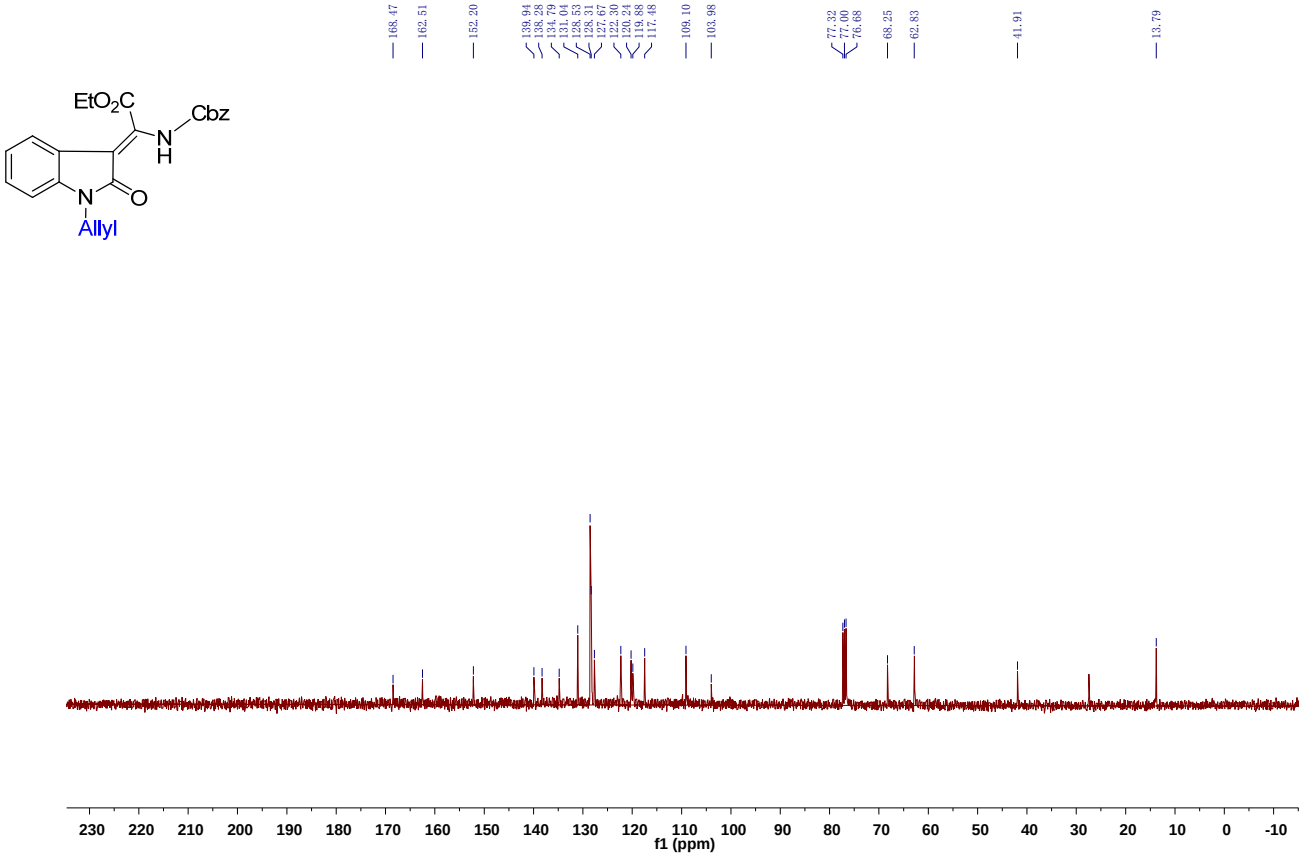


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3f

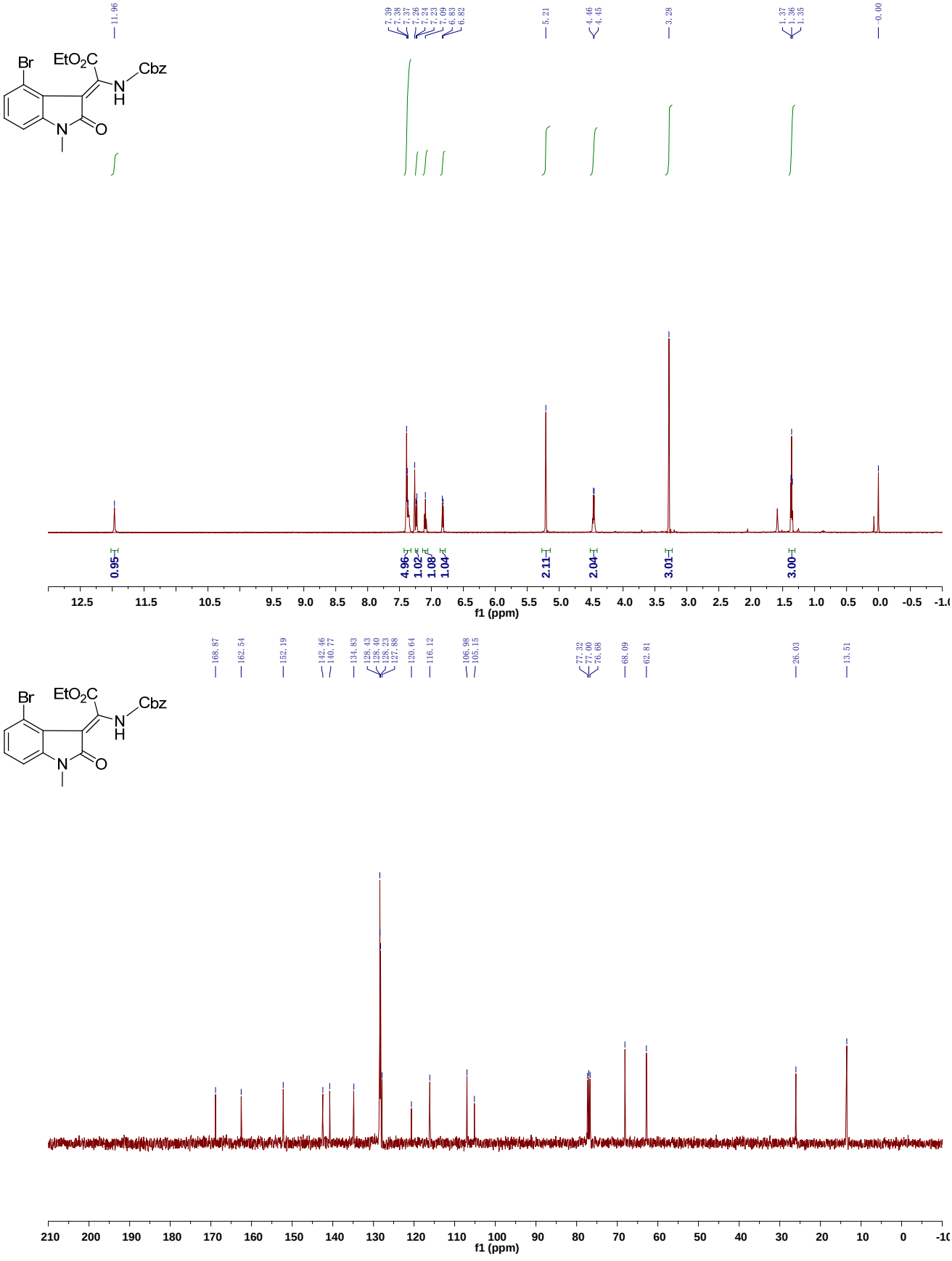


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3g

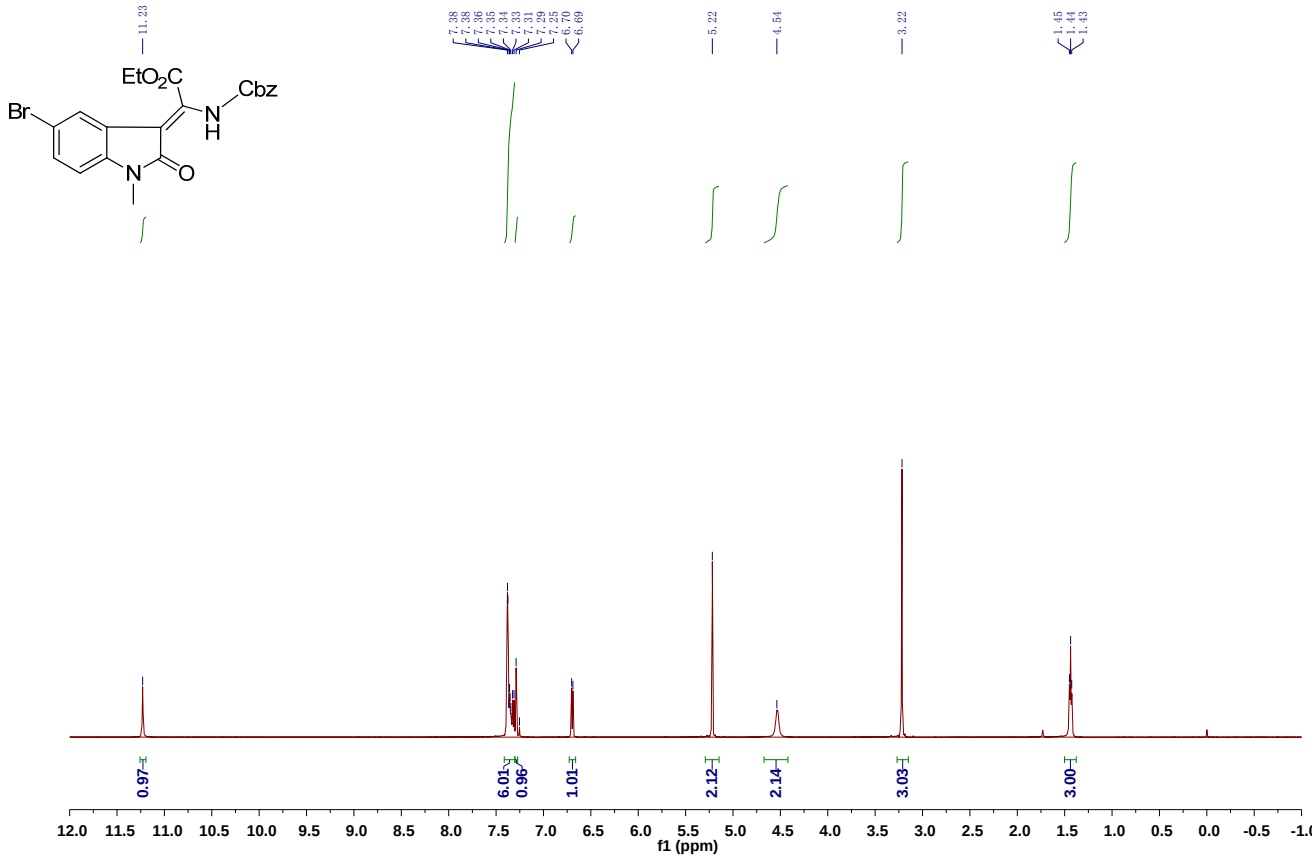


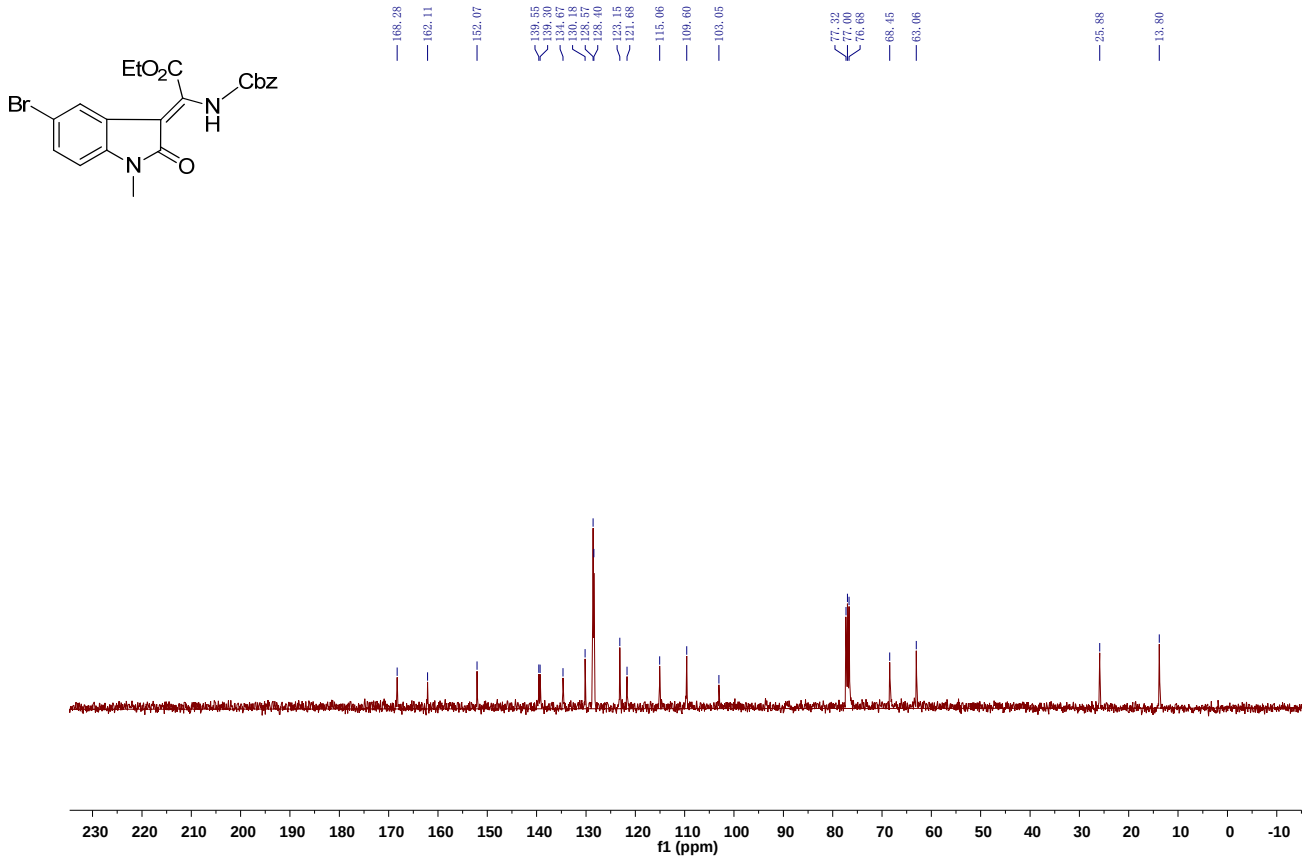


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3h

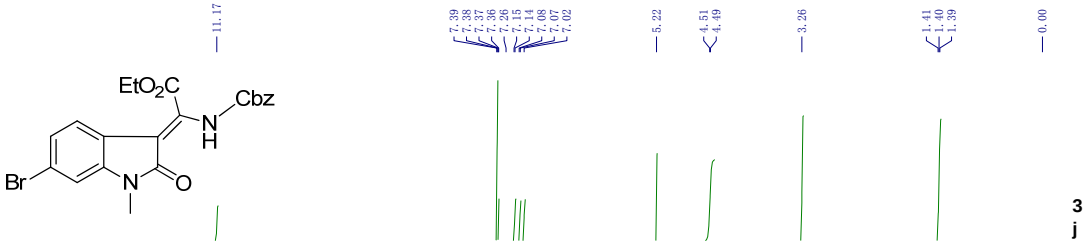


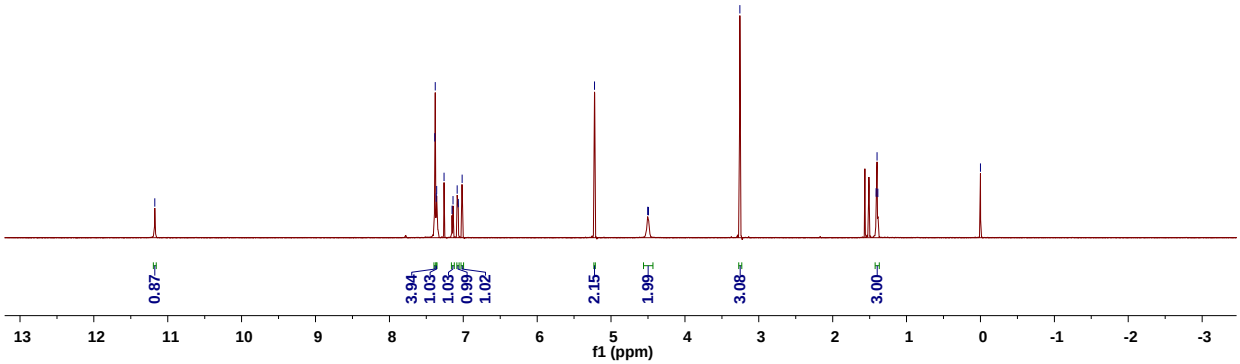
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3i

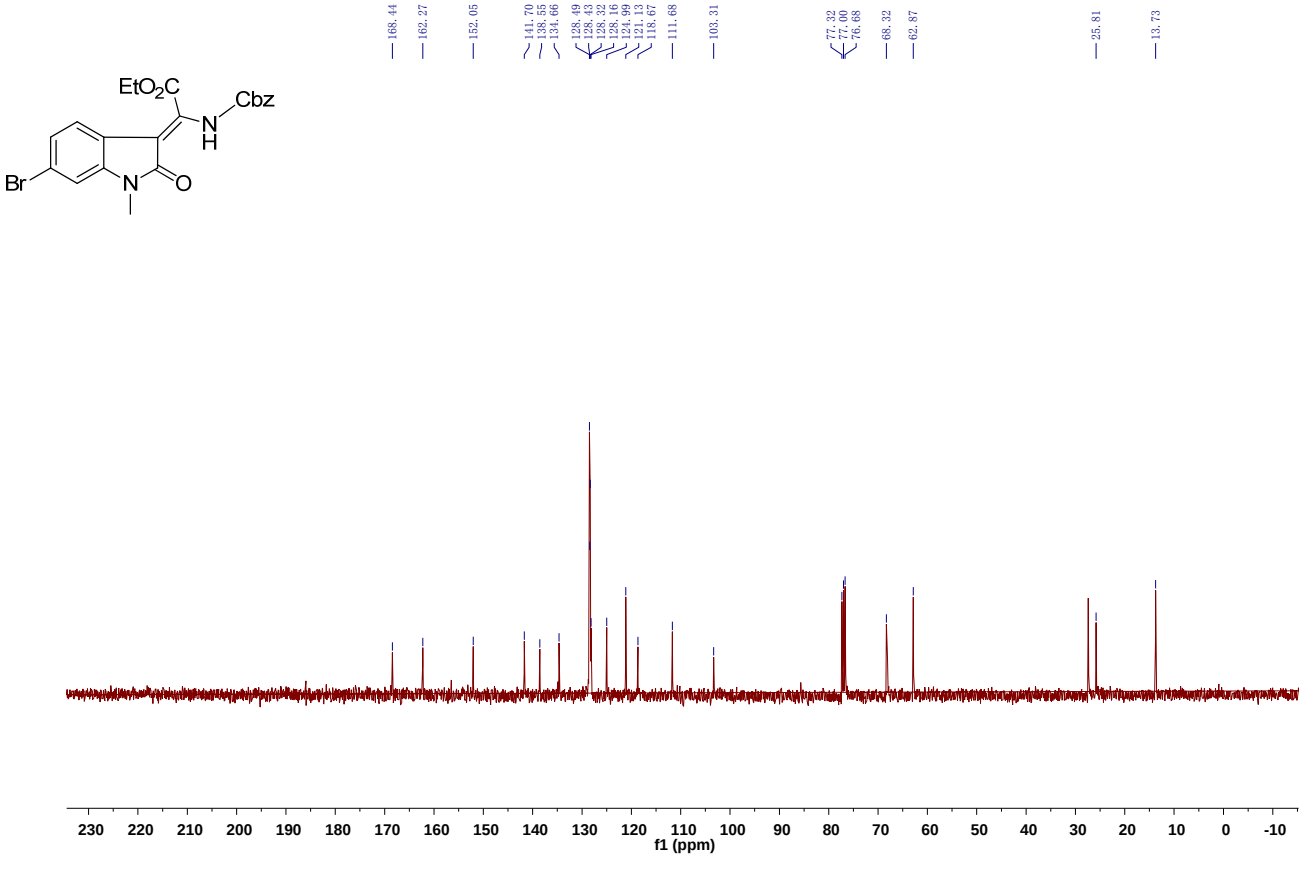




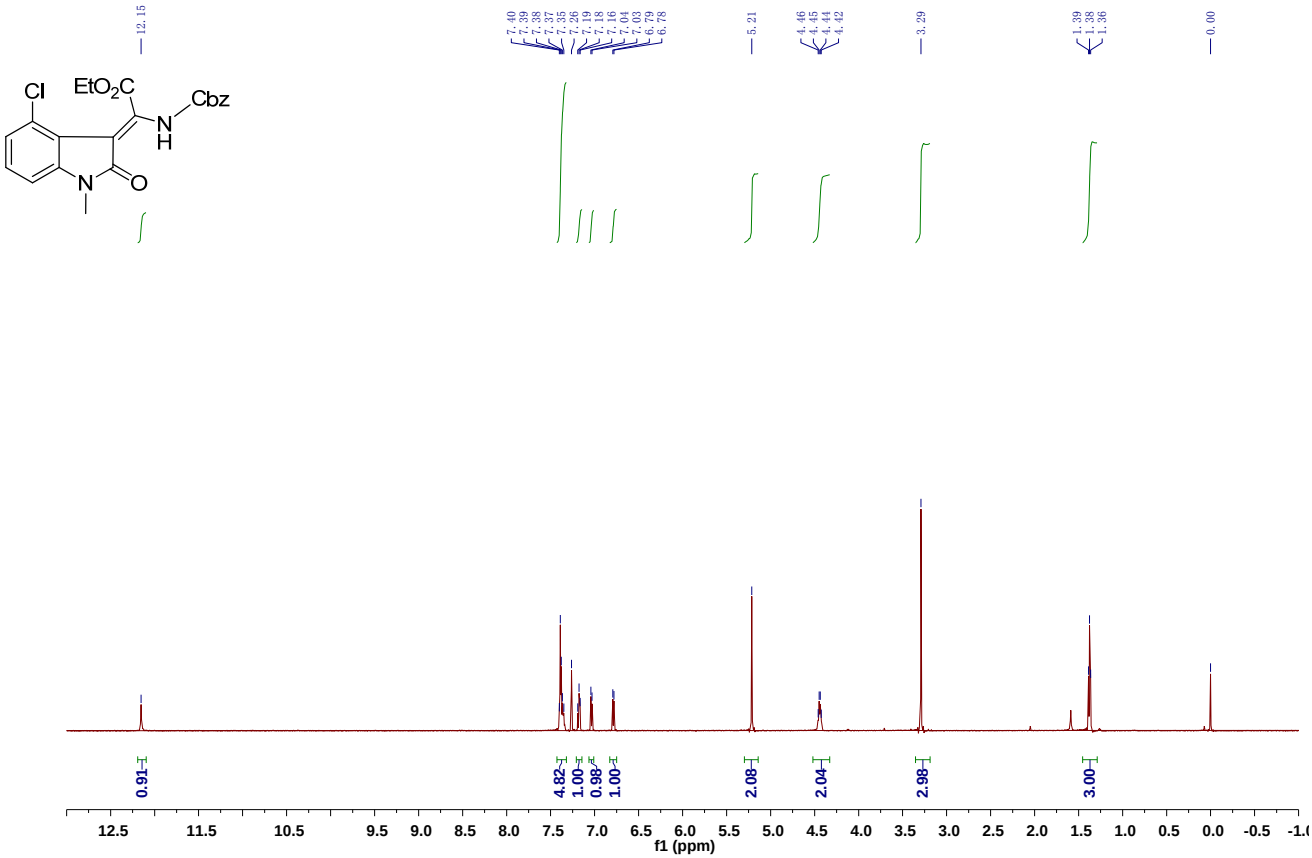
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3j

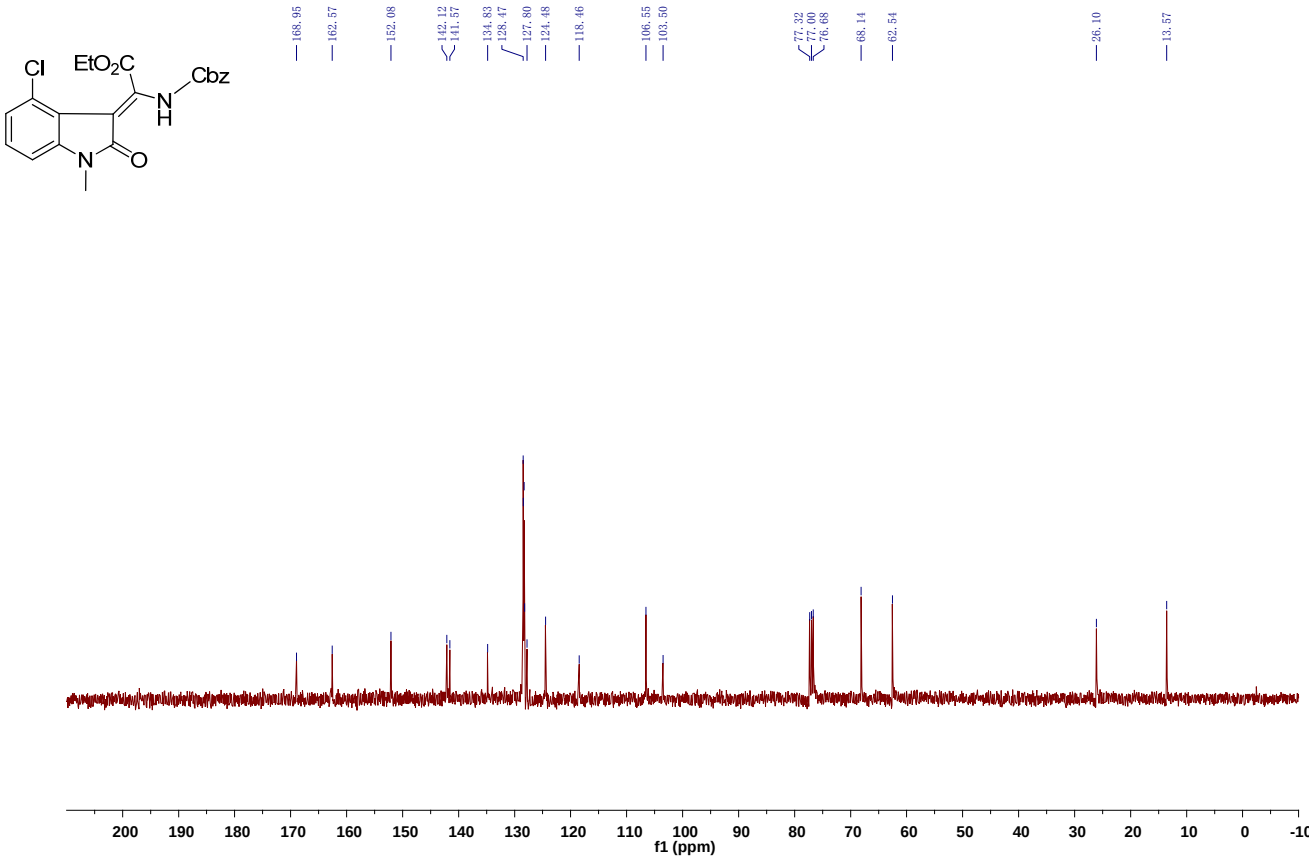




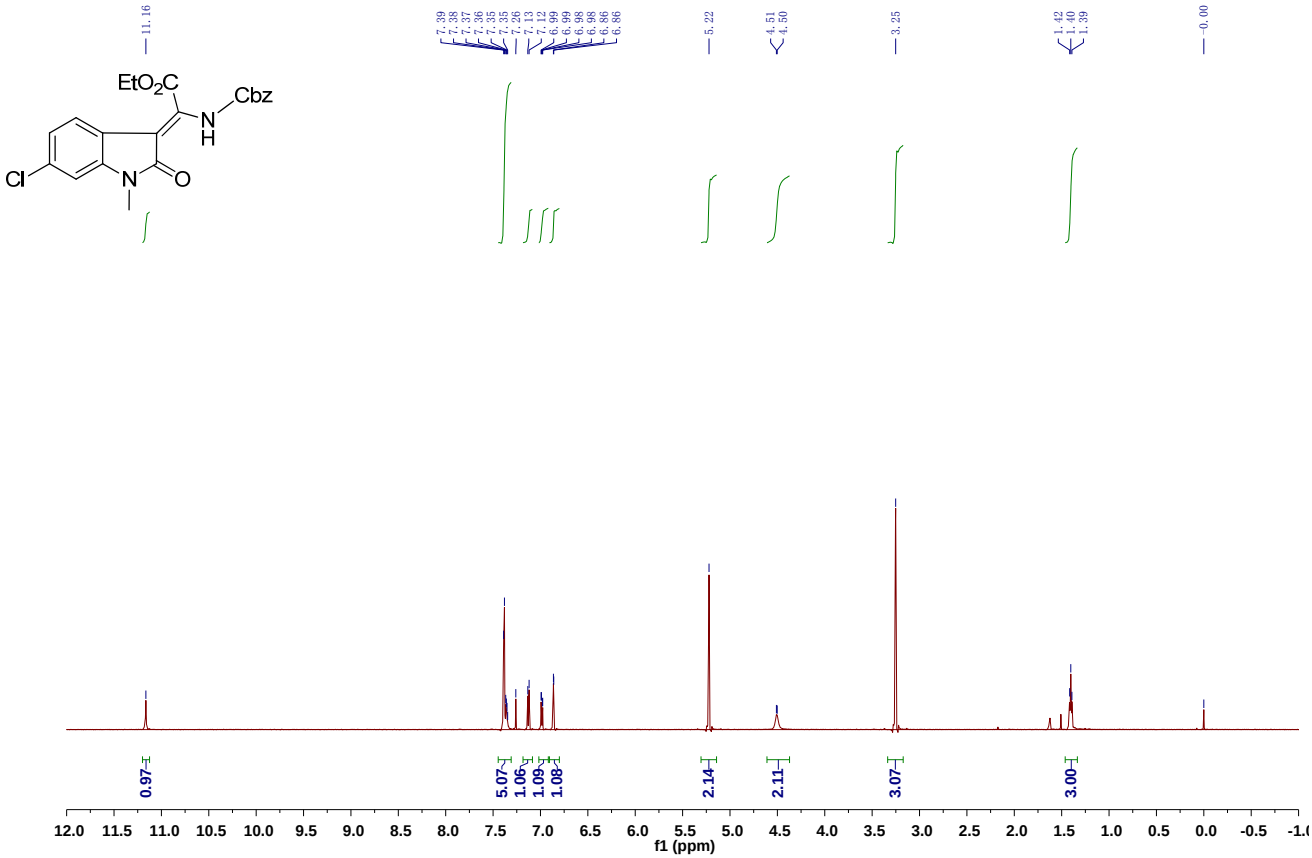


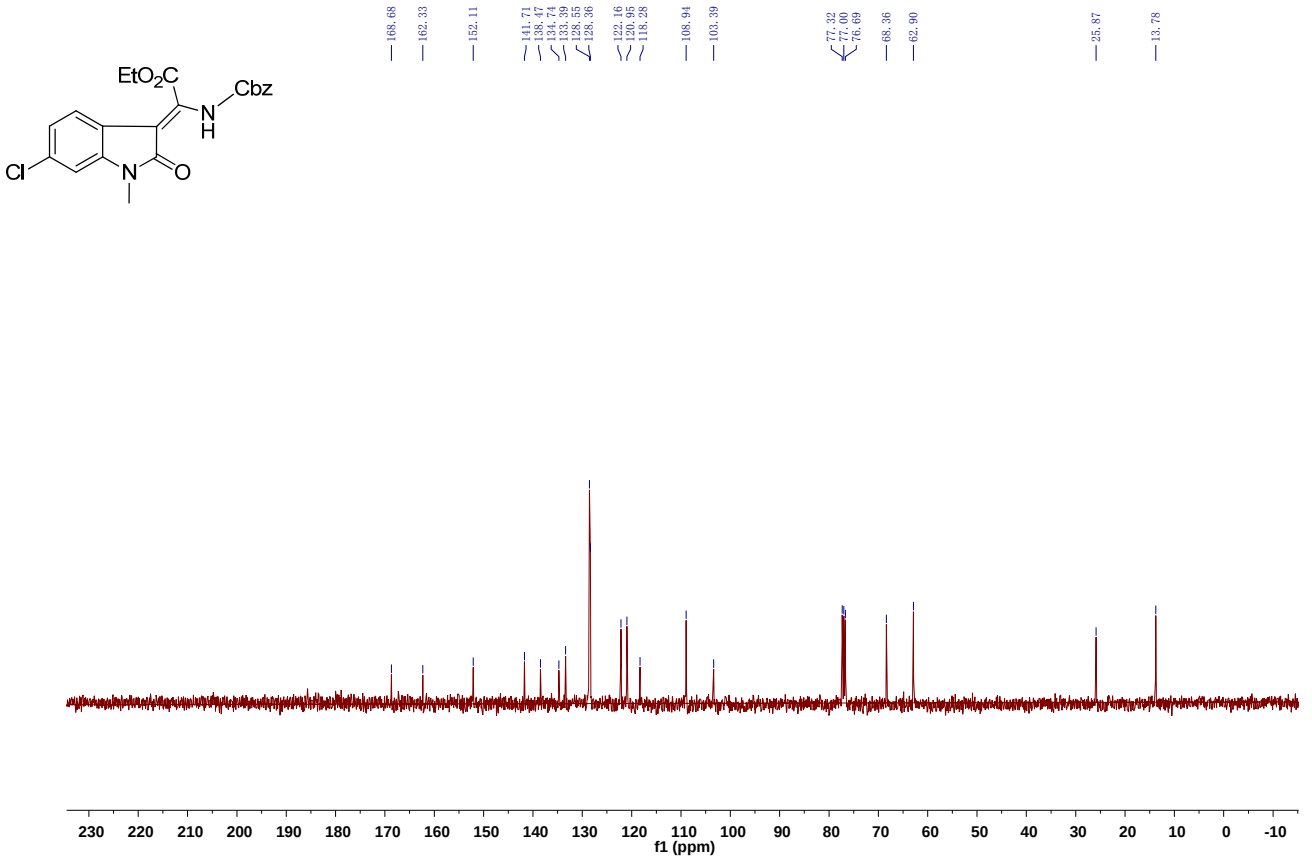
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3k



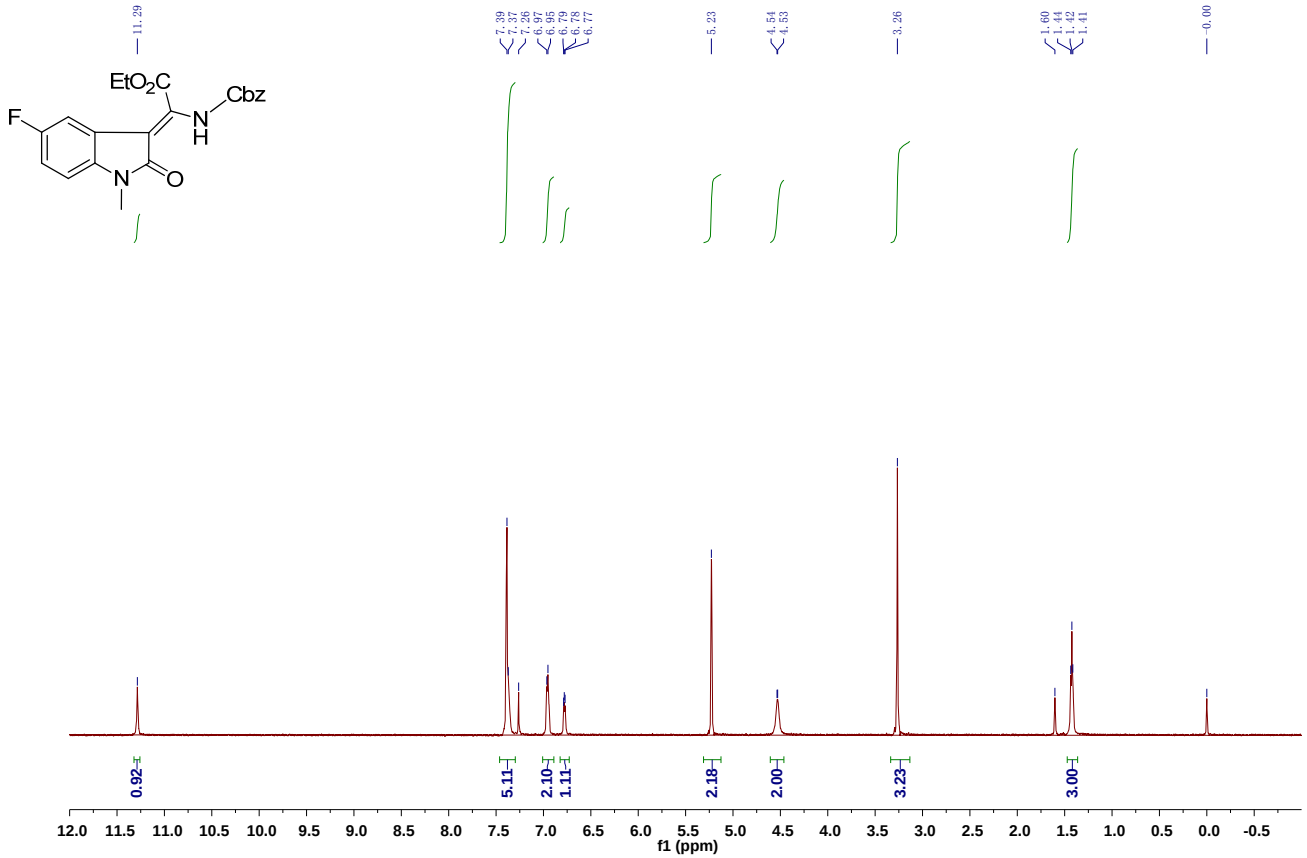


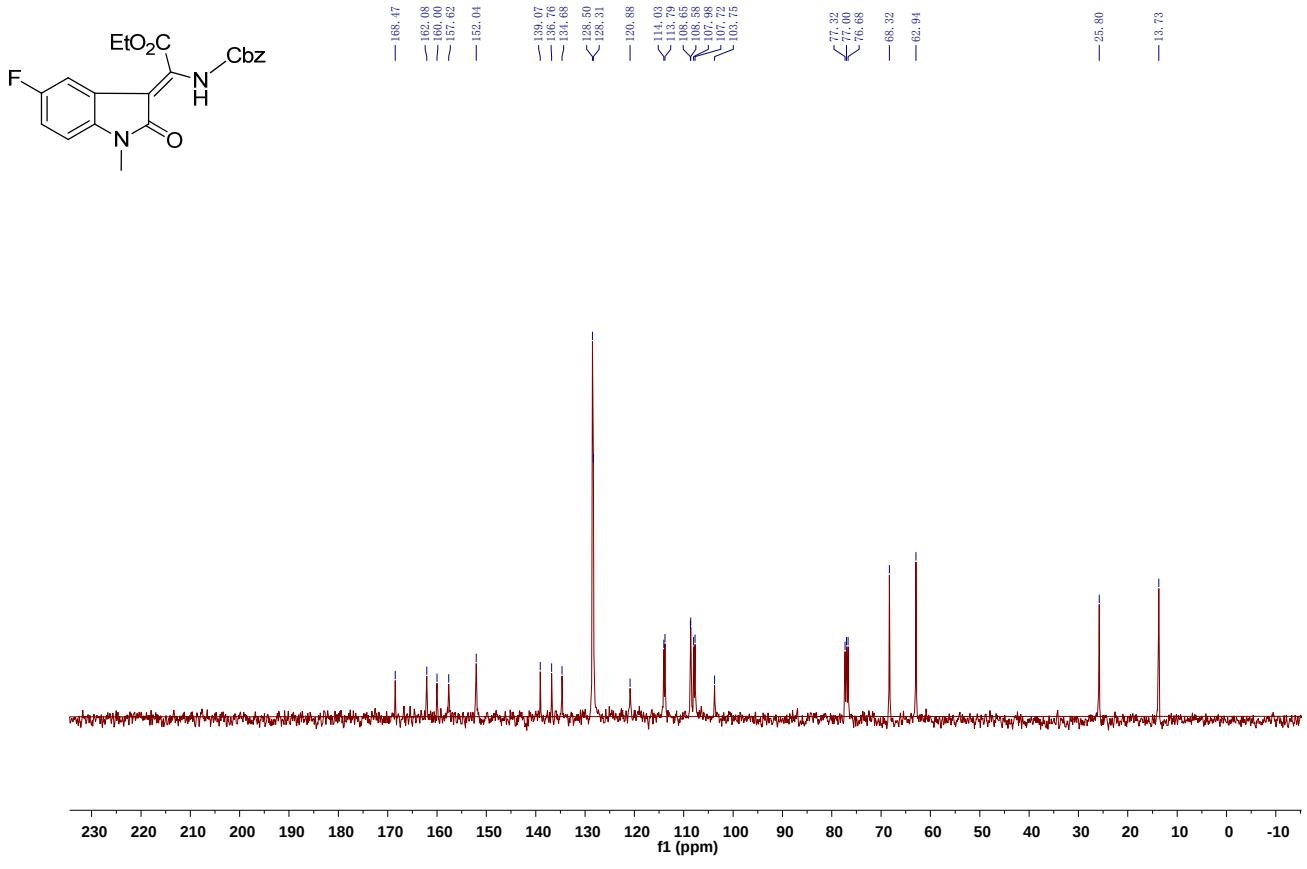
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3l



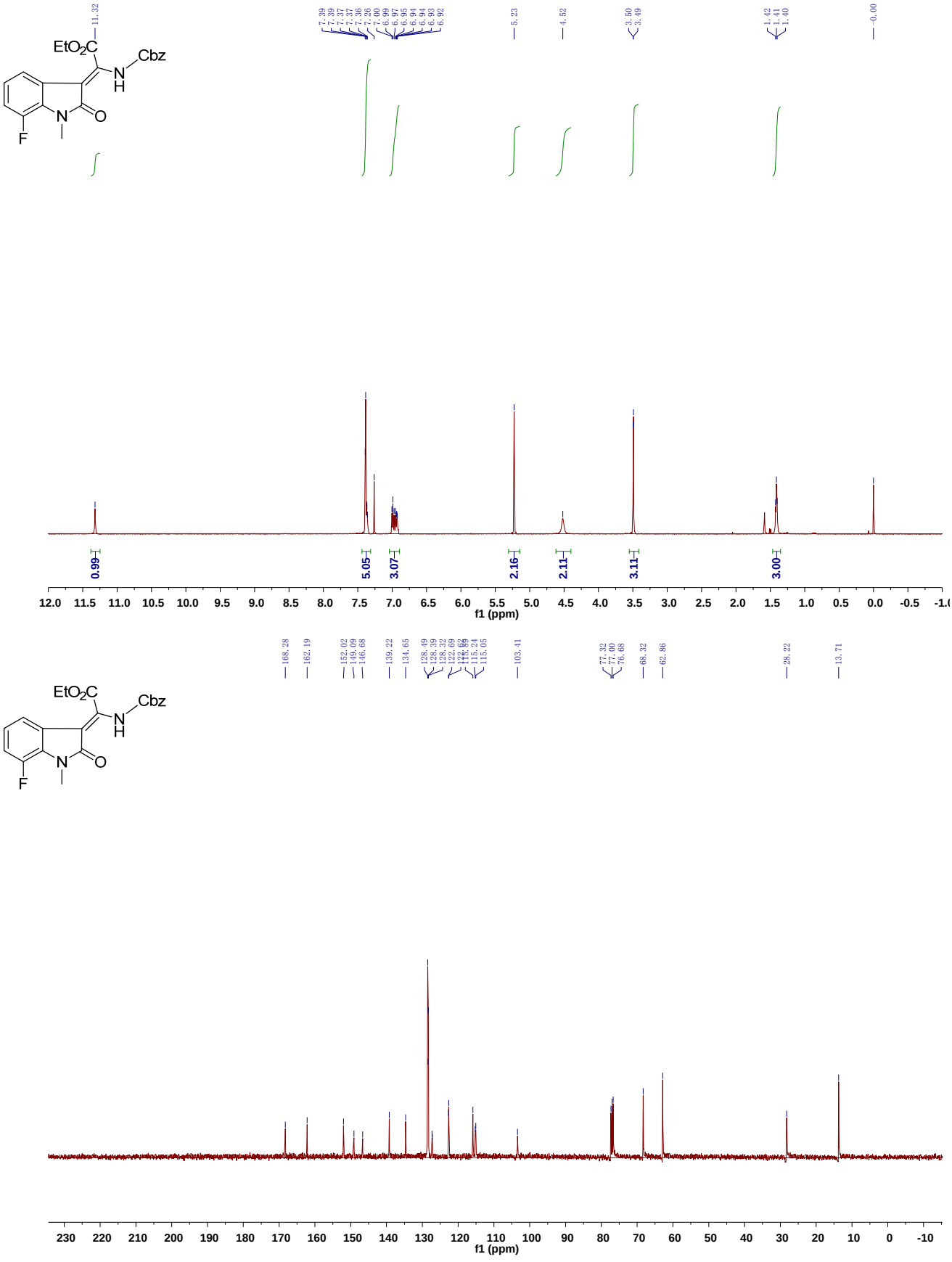


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3m

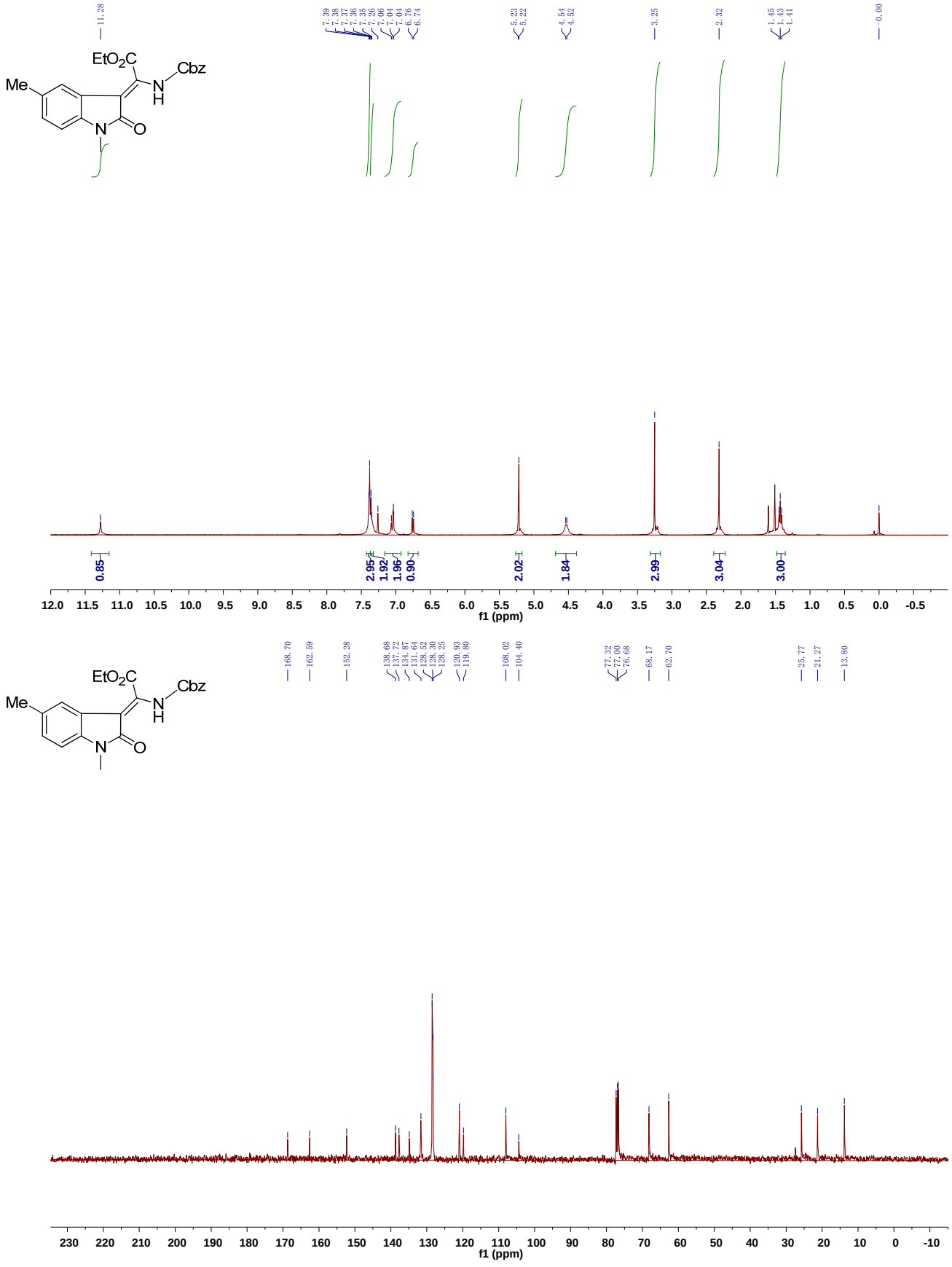




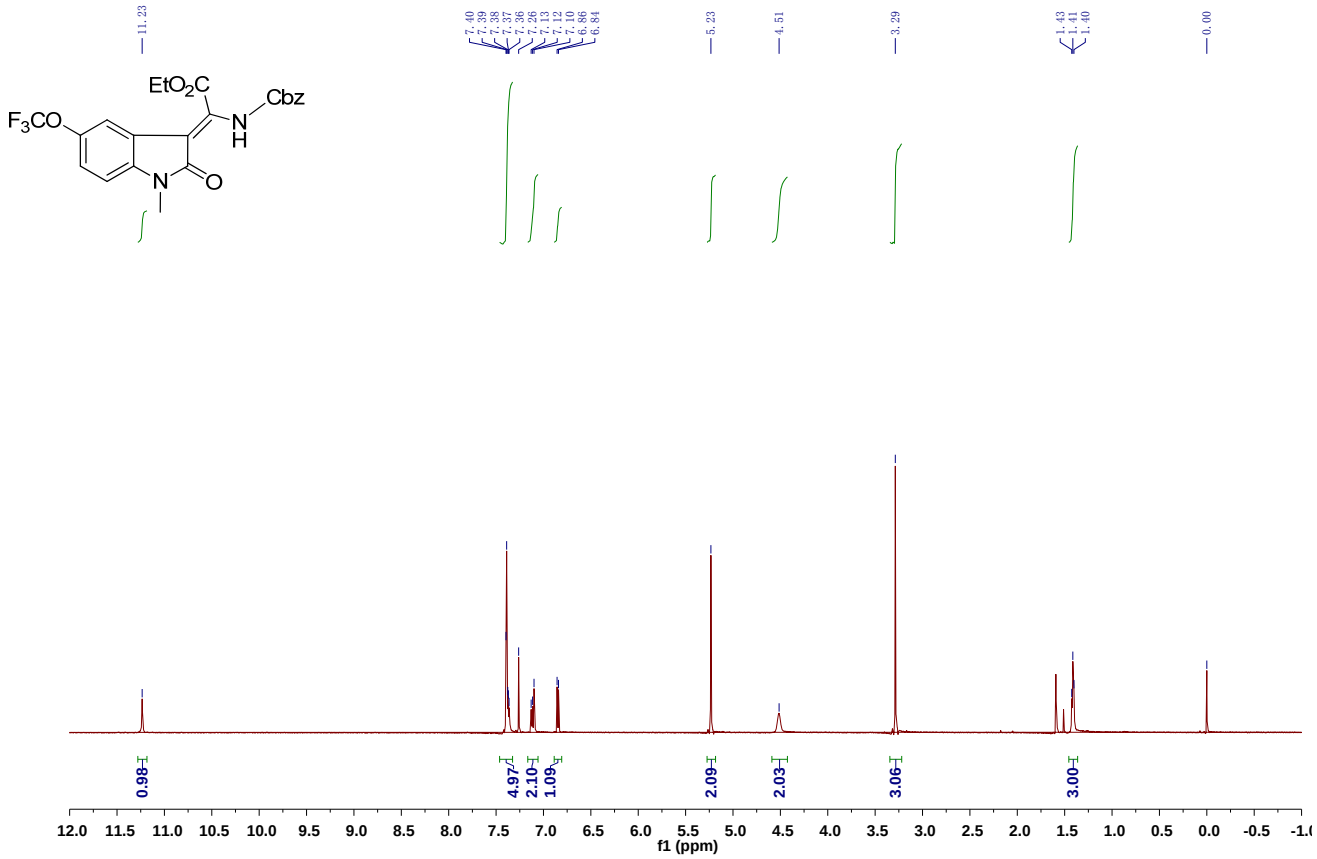
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3n

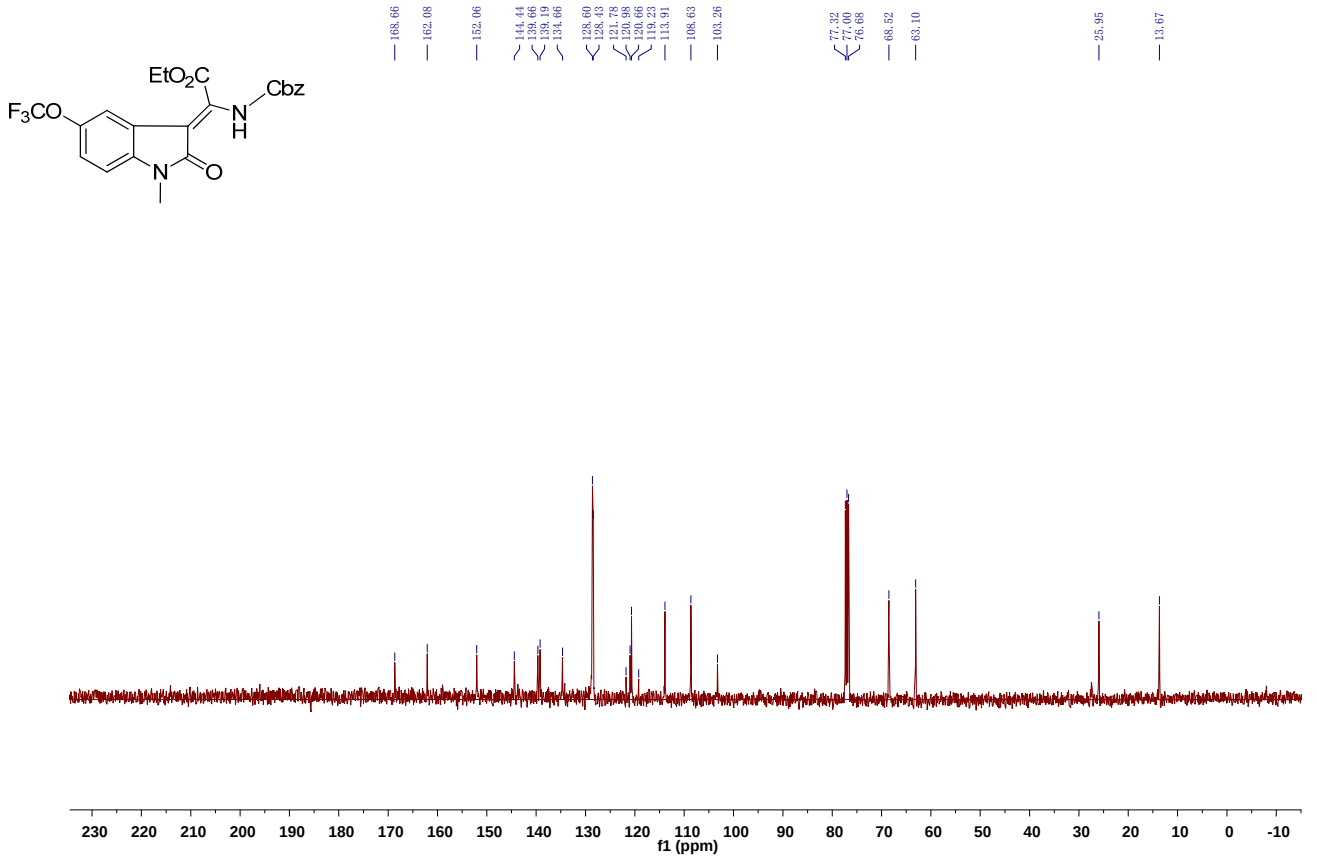


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3o

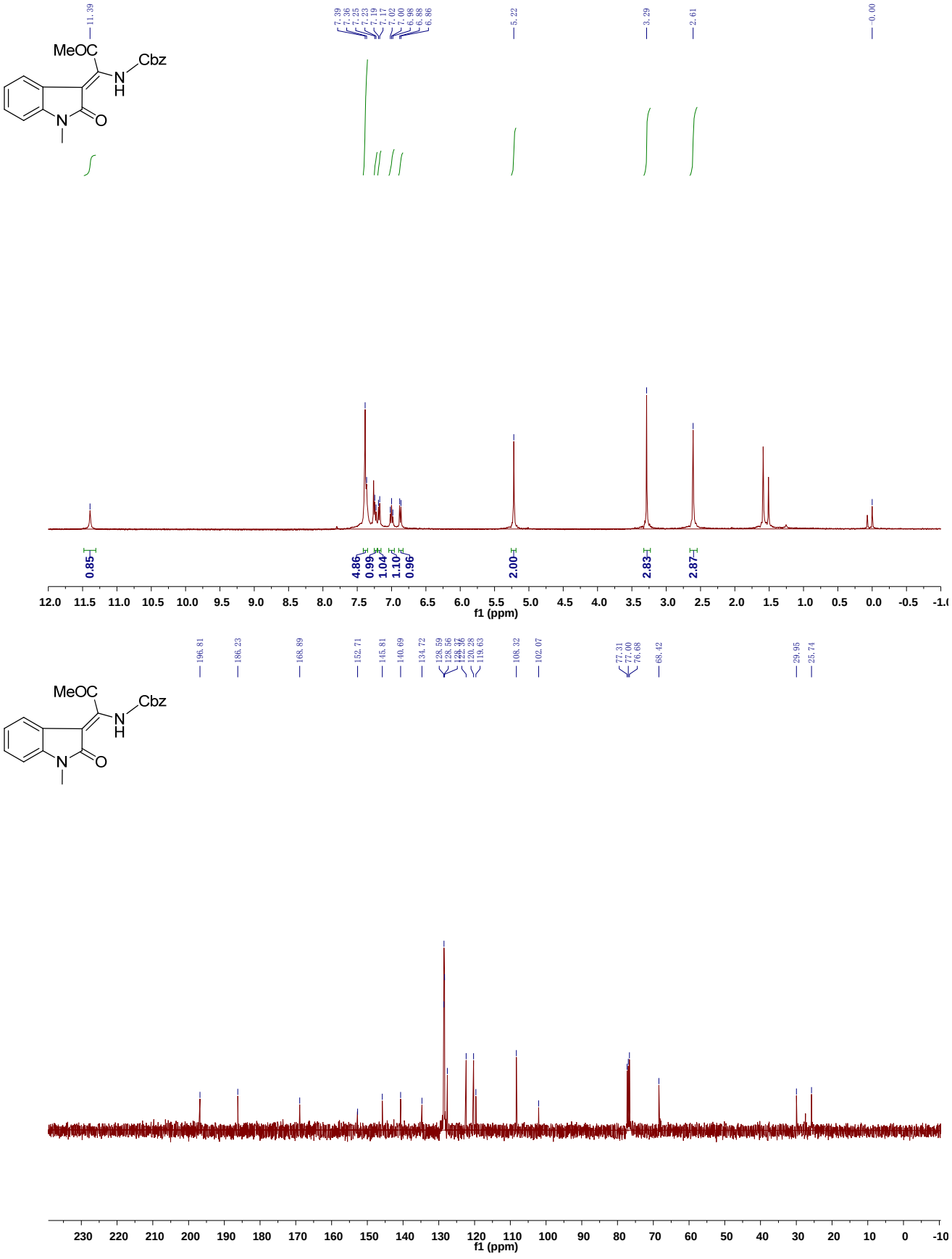


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3p

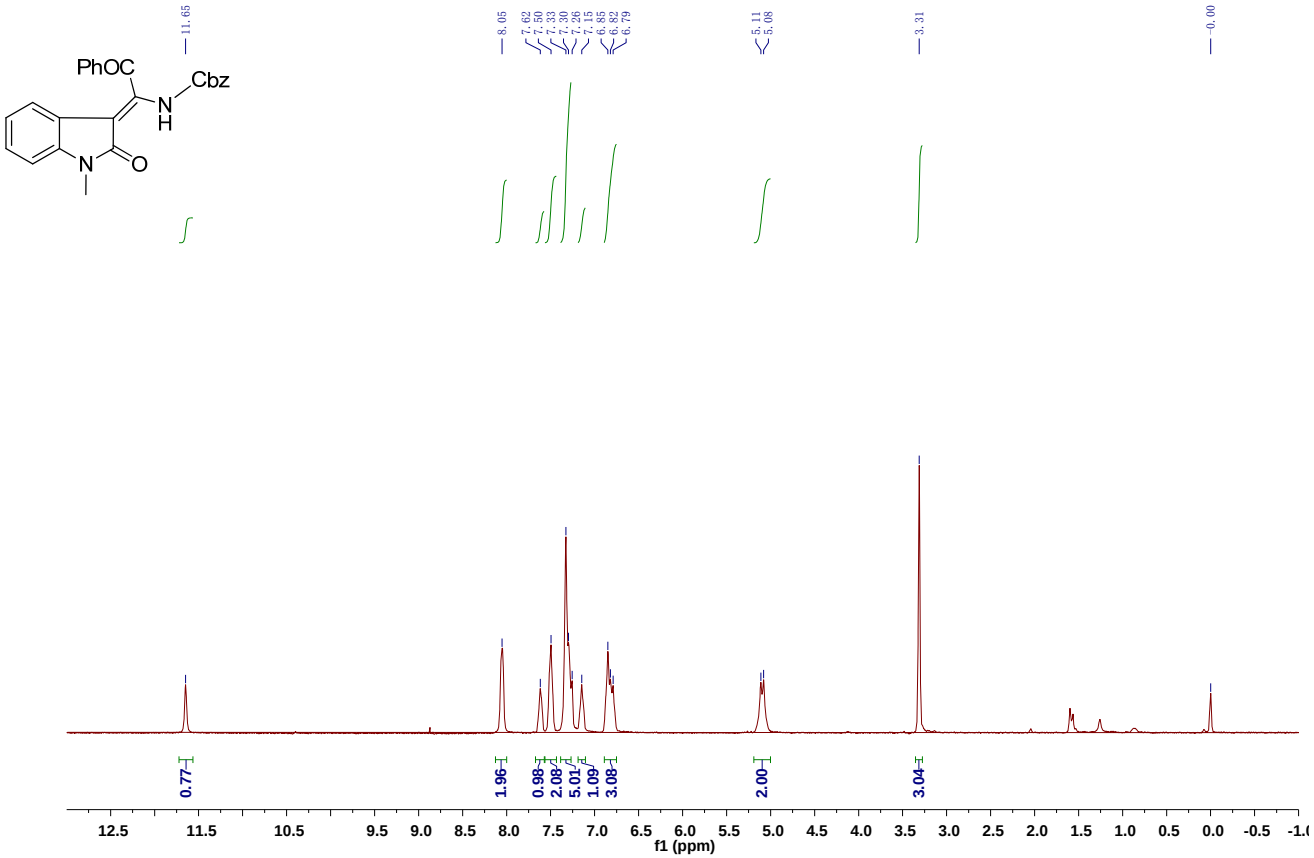


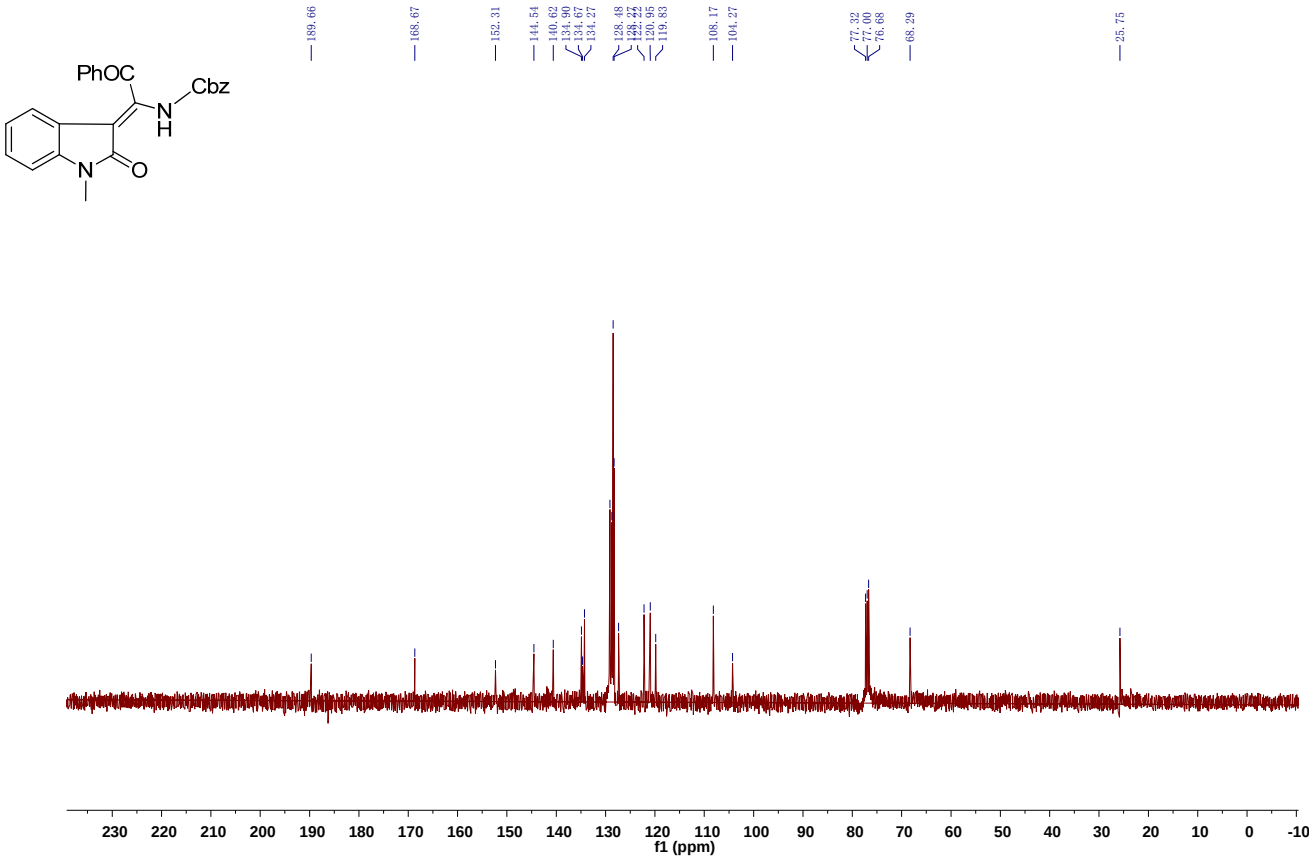


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3q

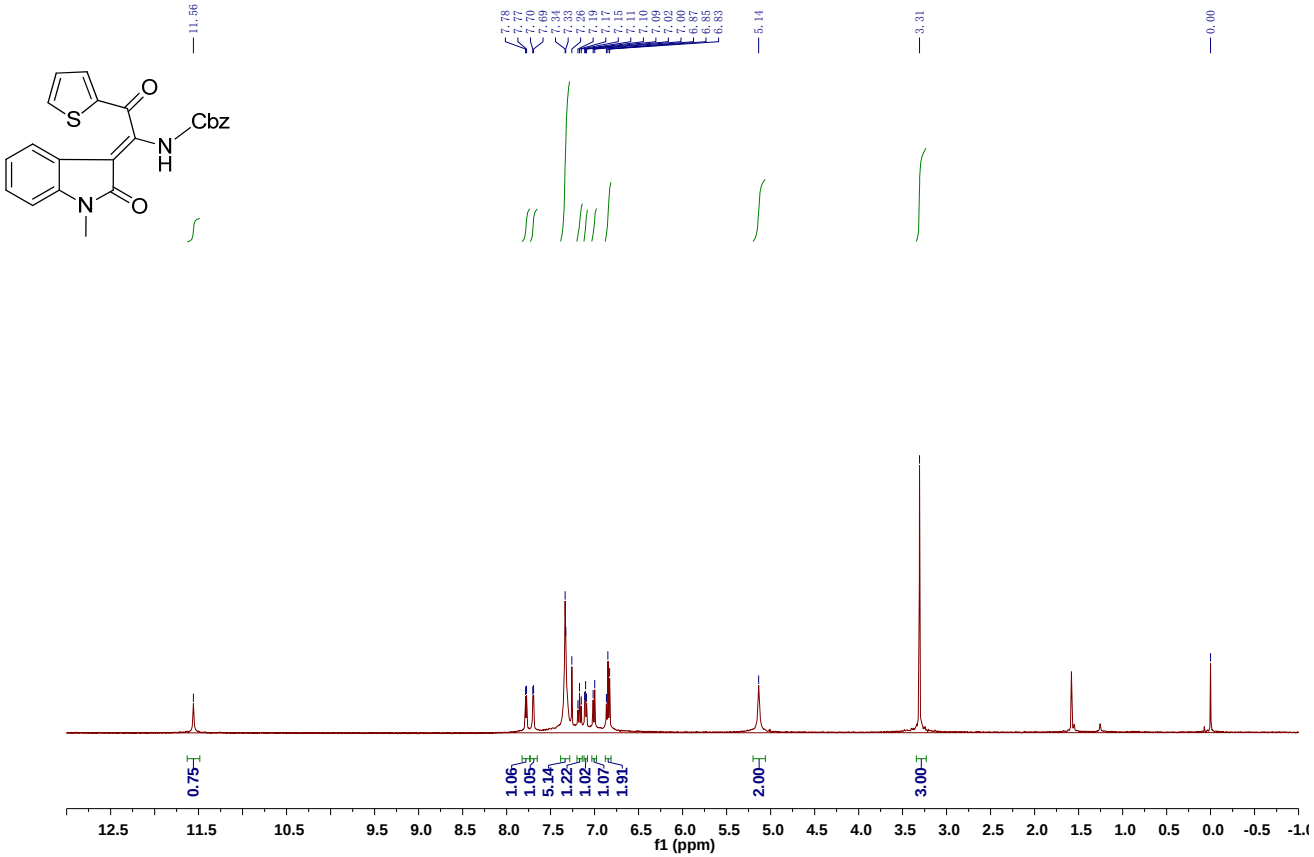


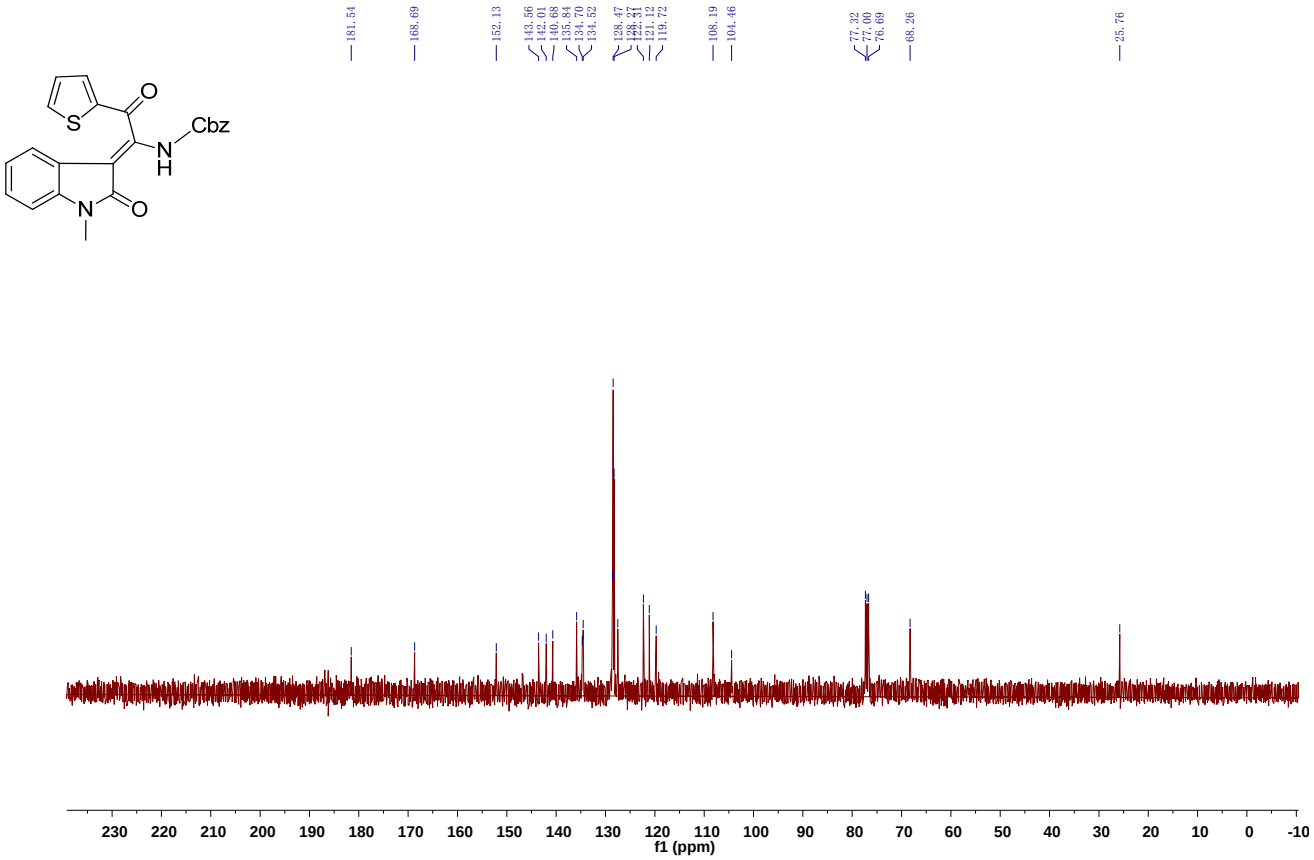
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3r



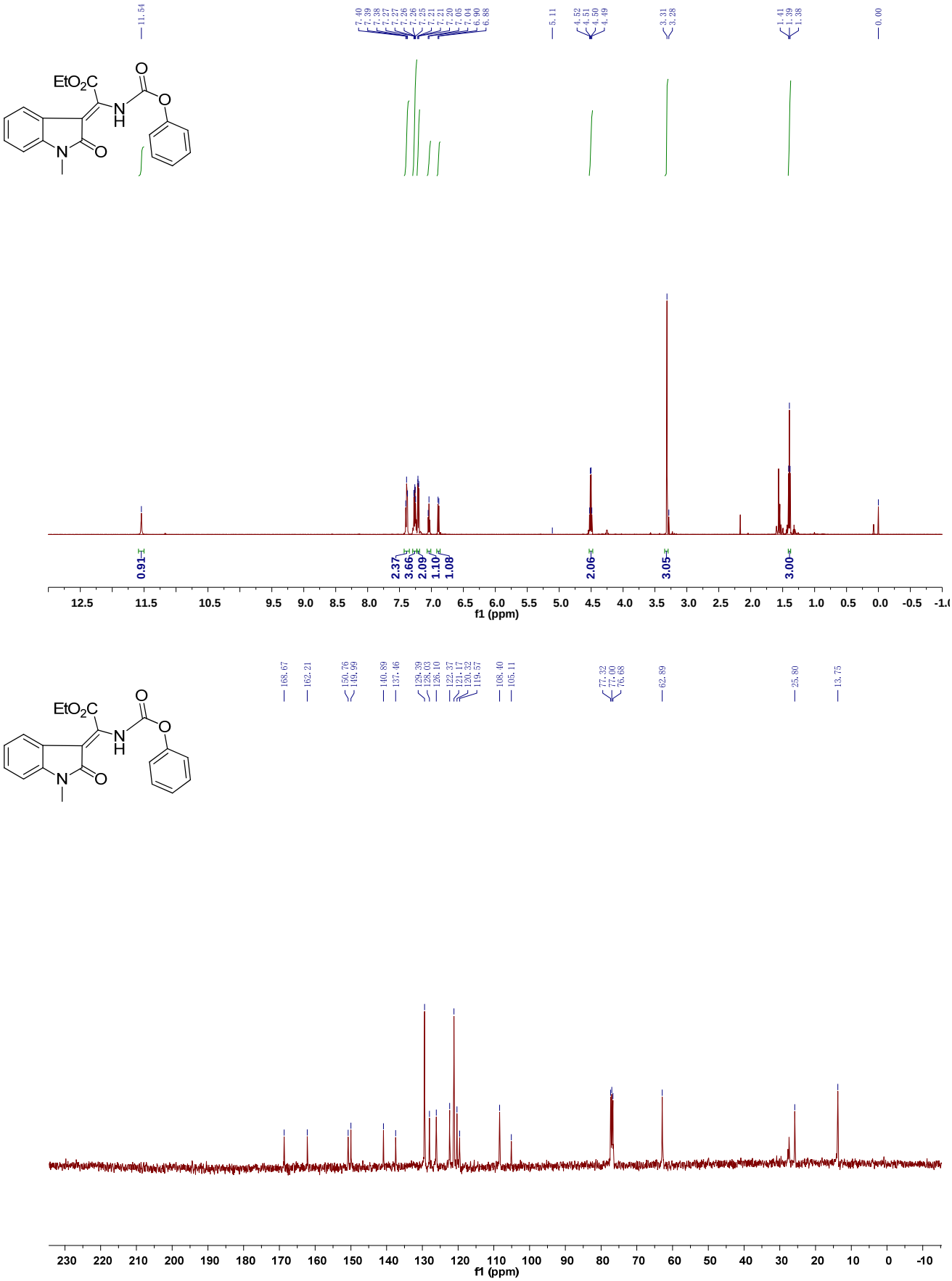


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3s

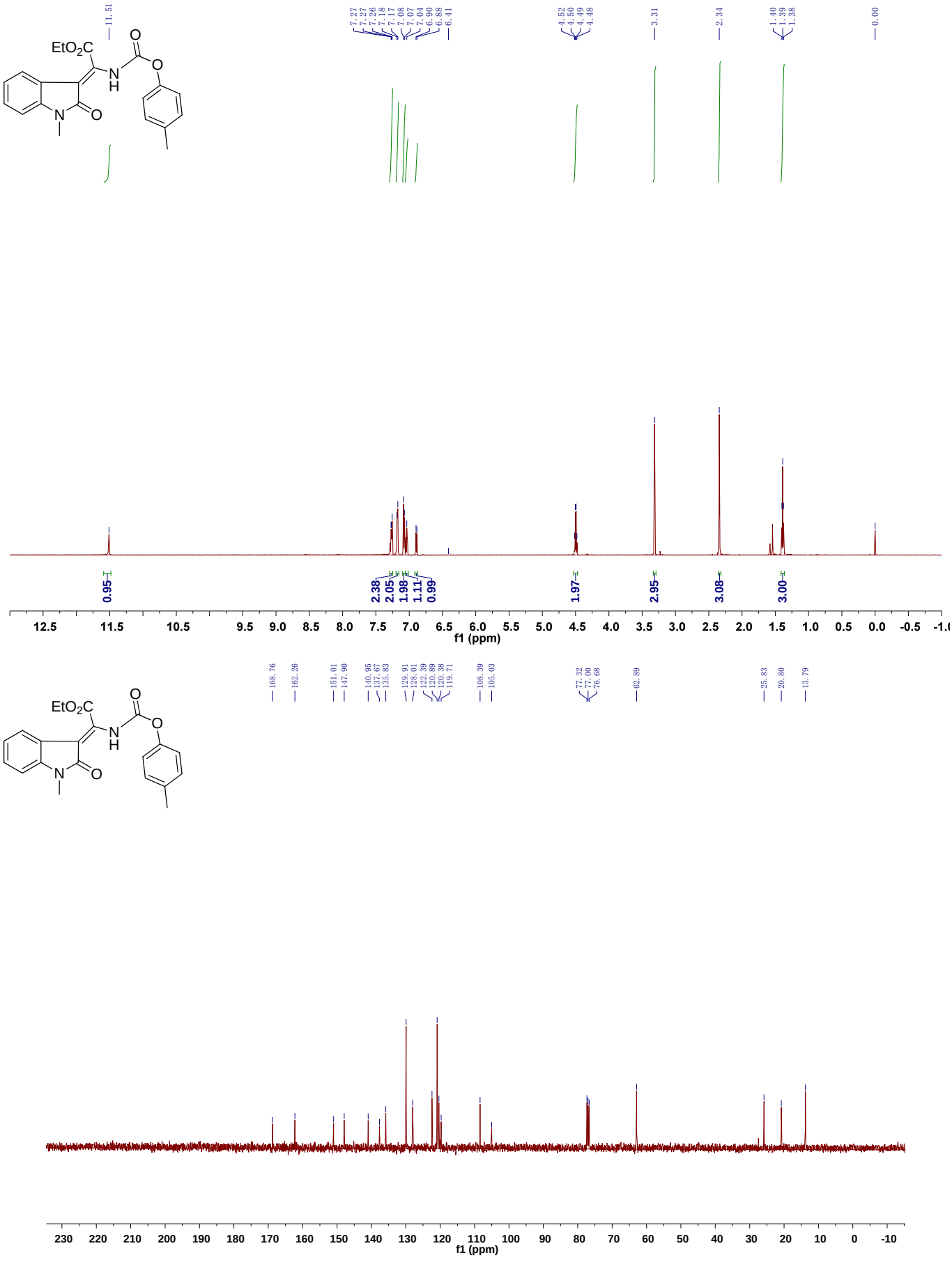




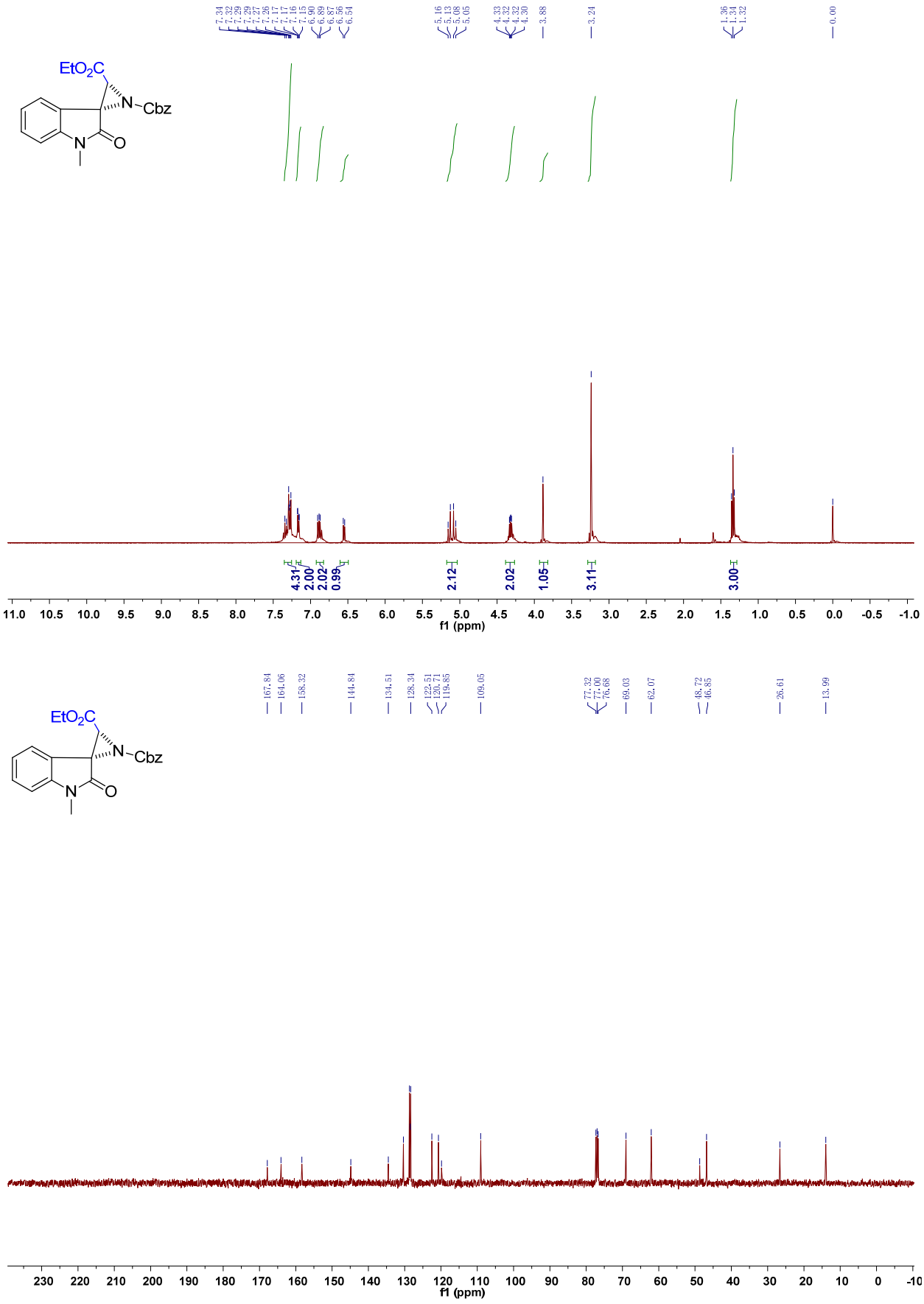
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3t



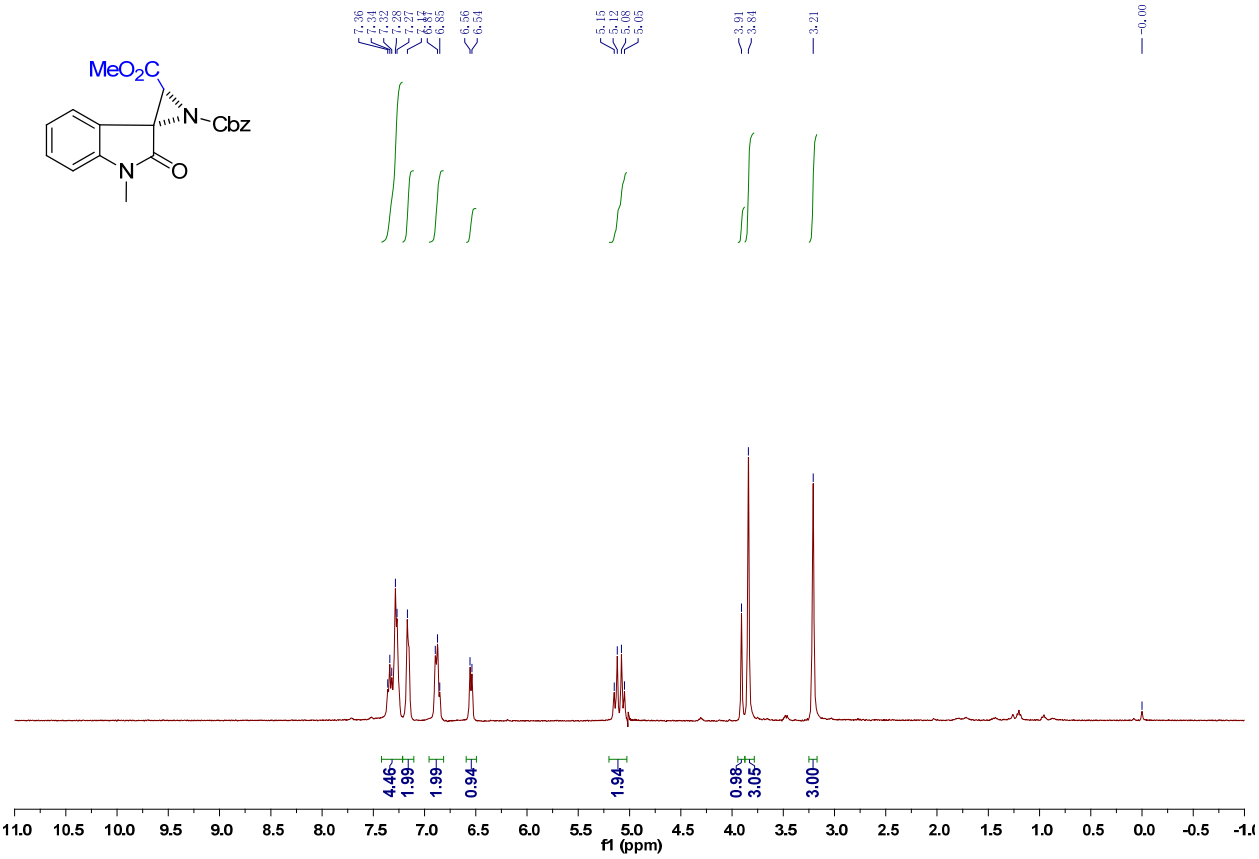
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3u

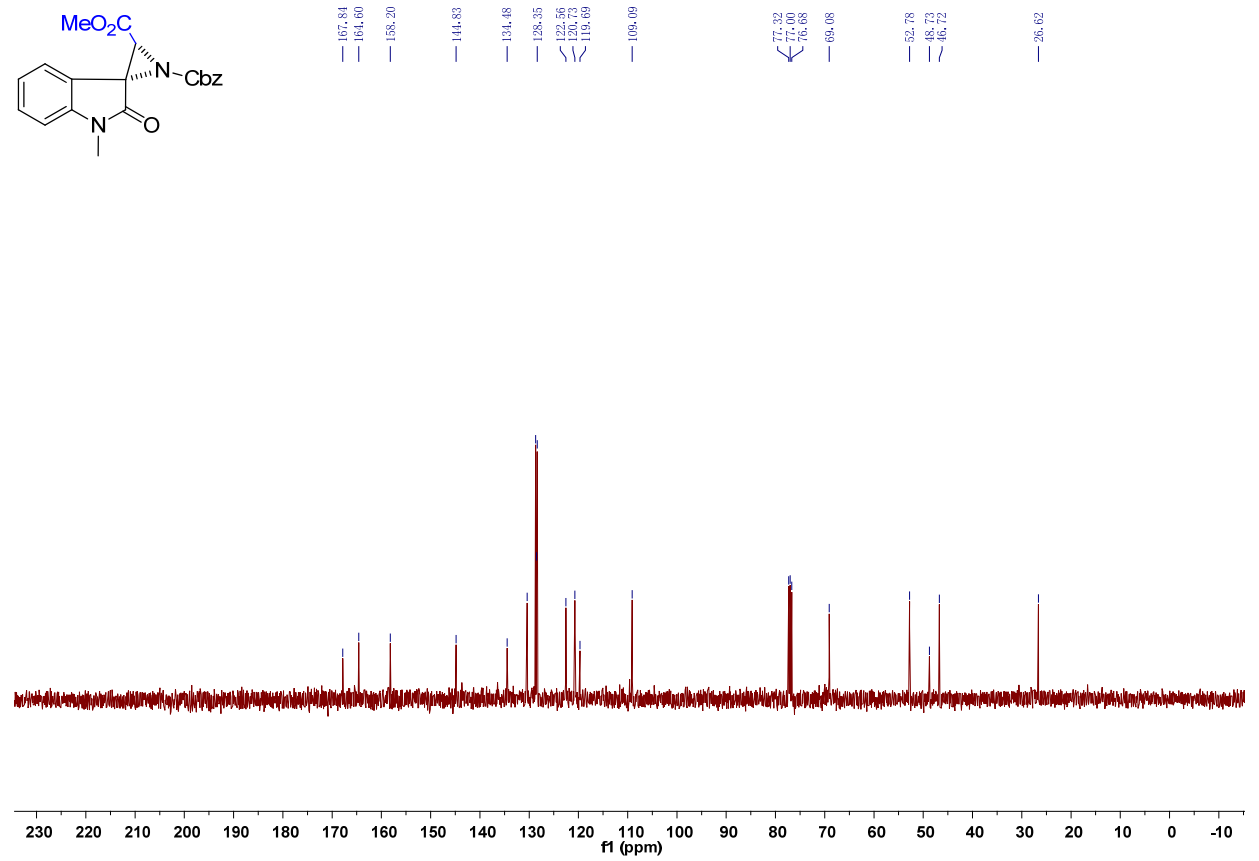


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4a

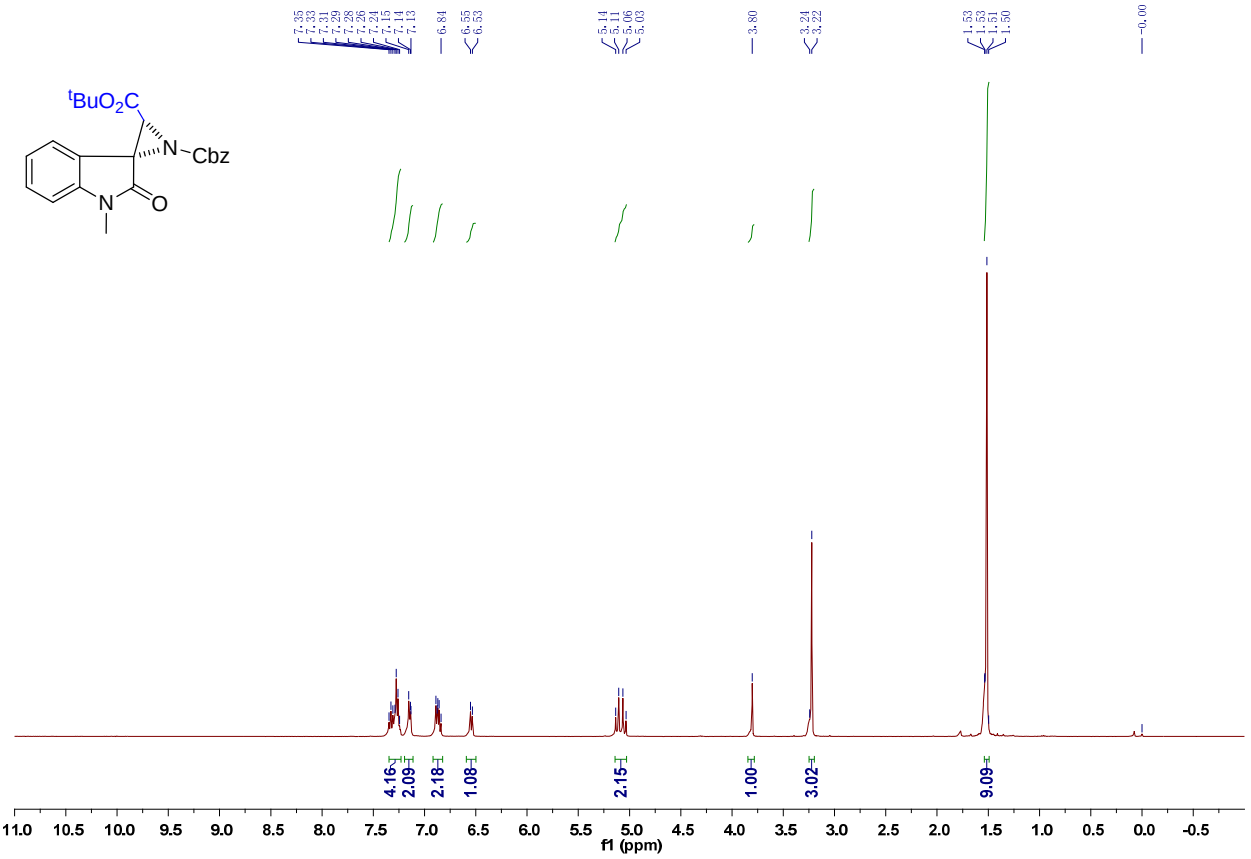


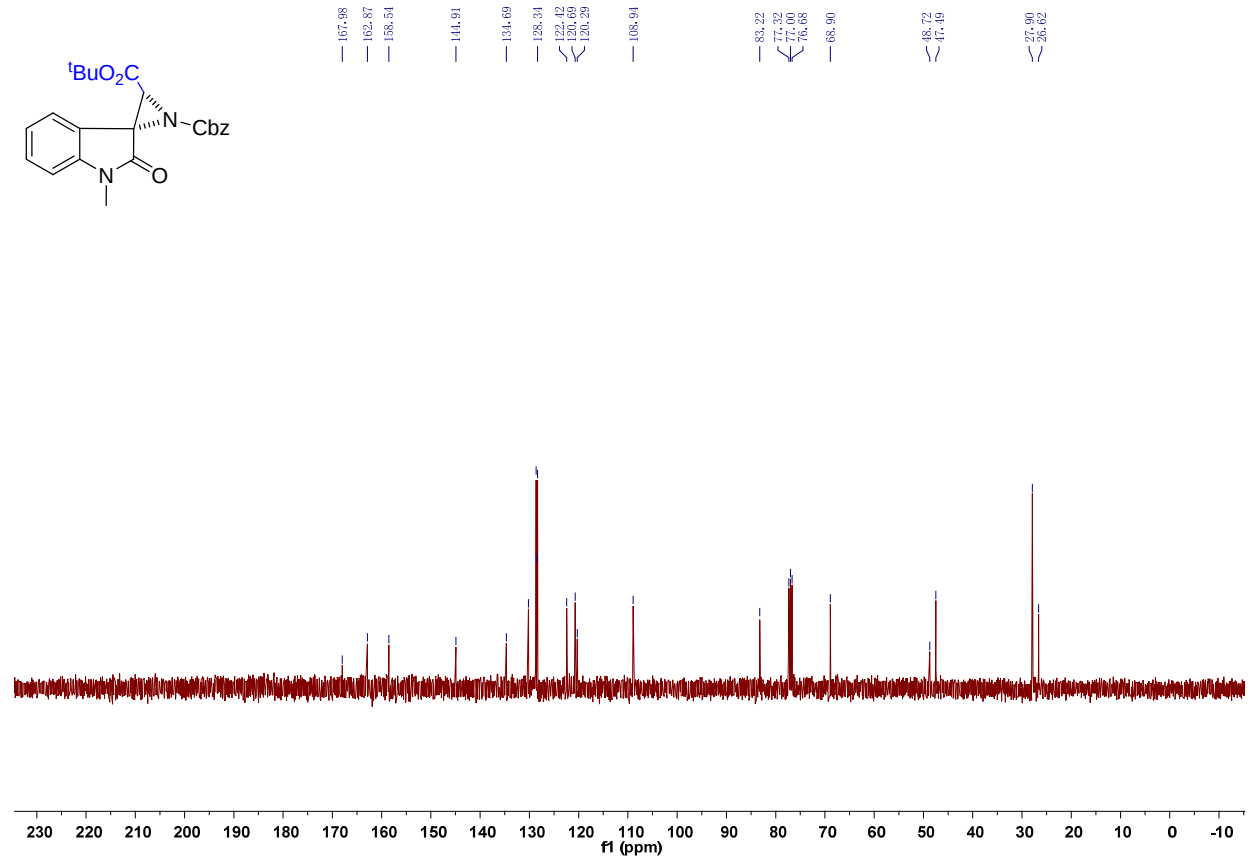
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4b



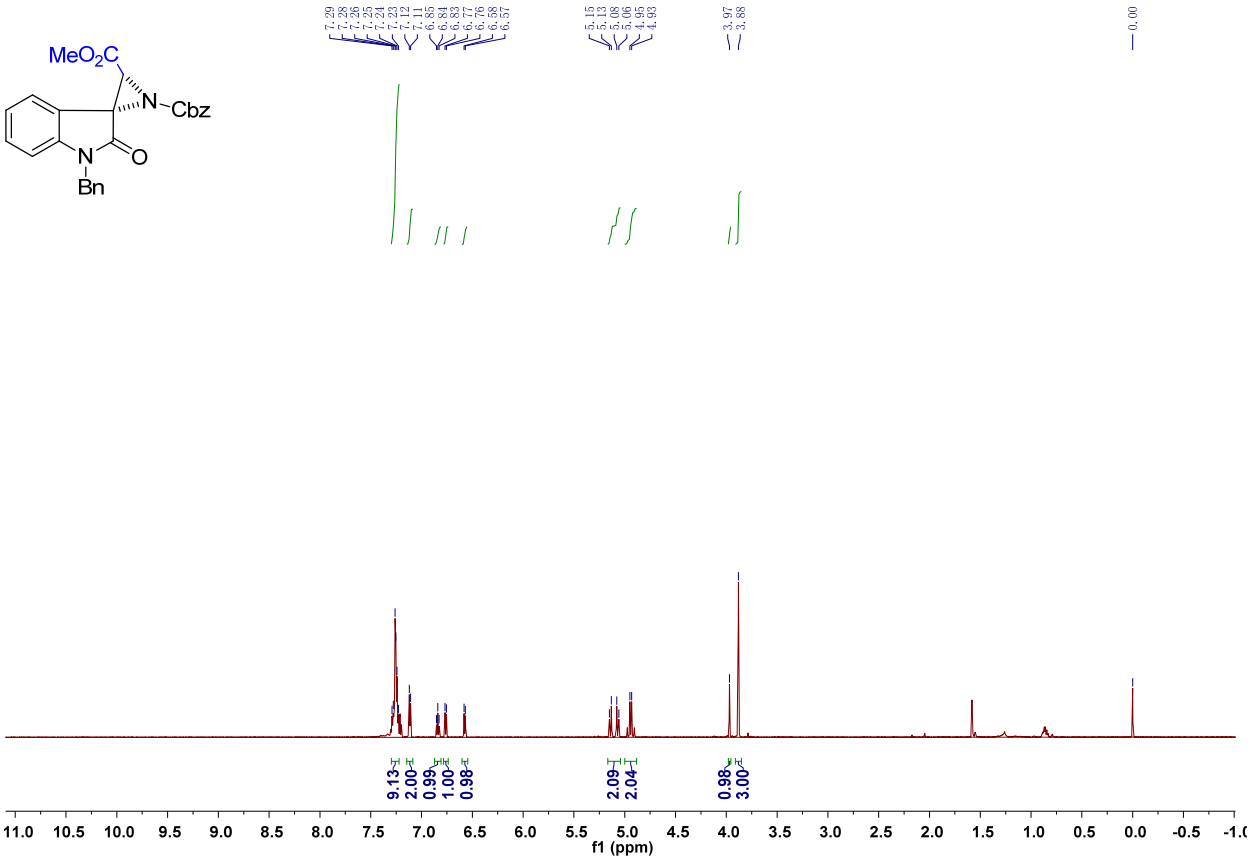


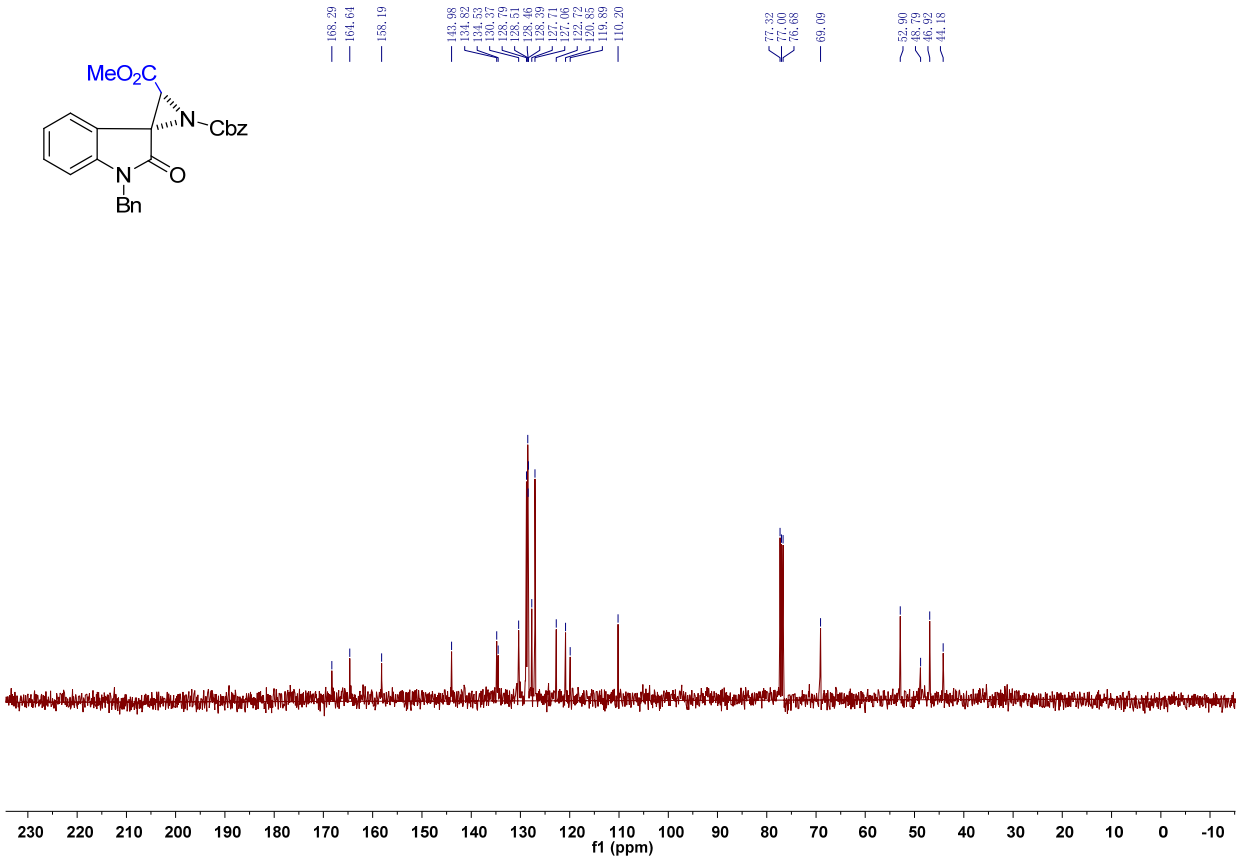
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4c



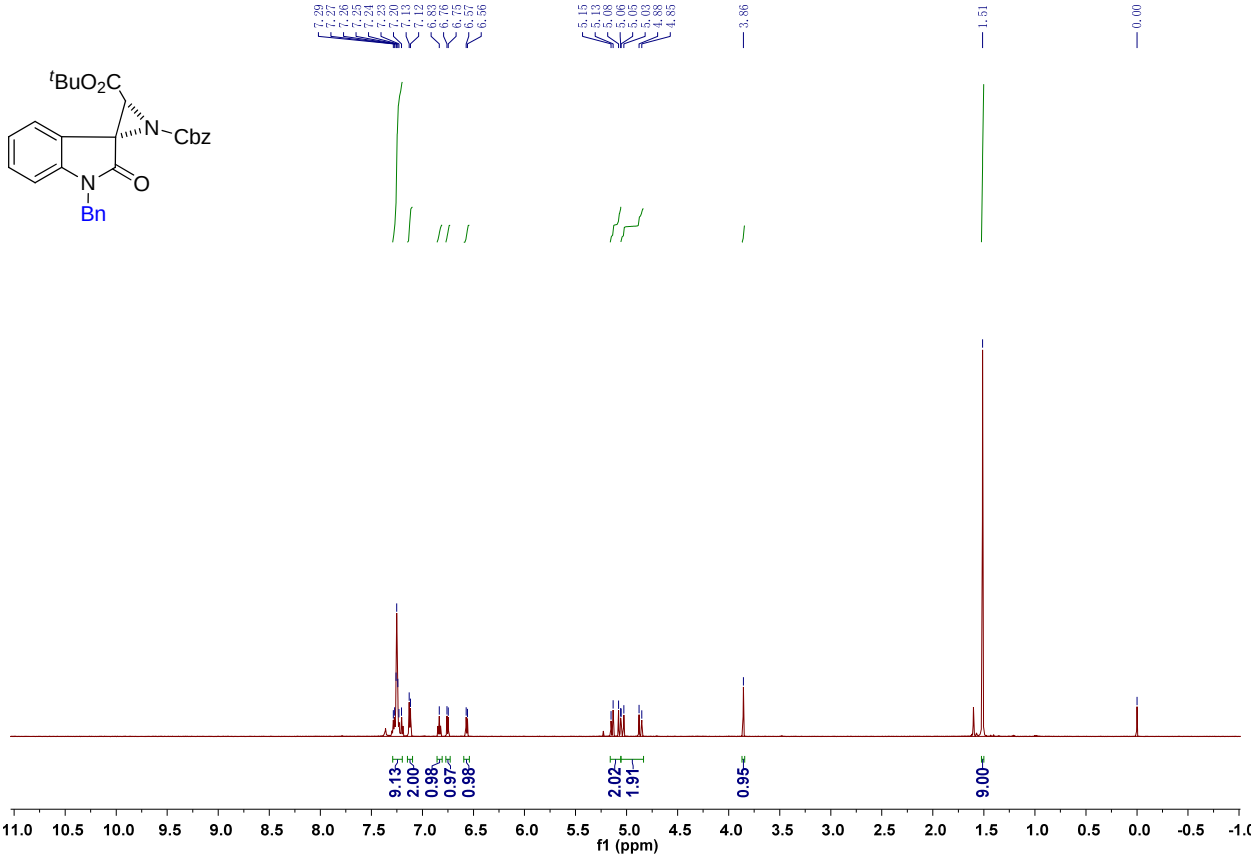


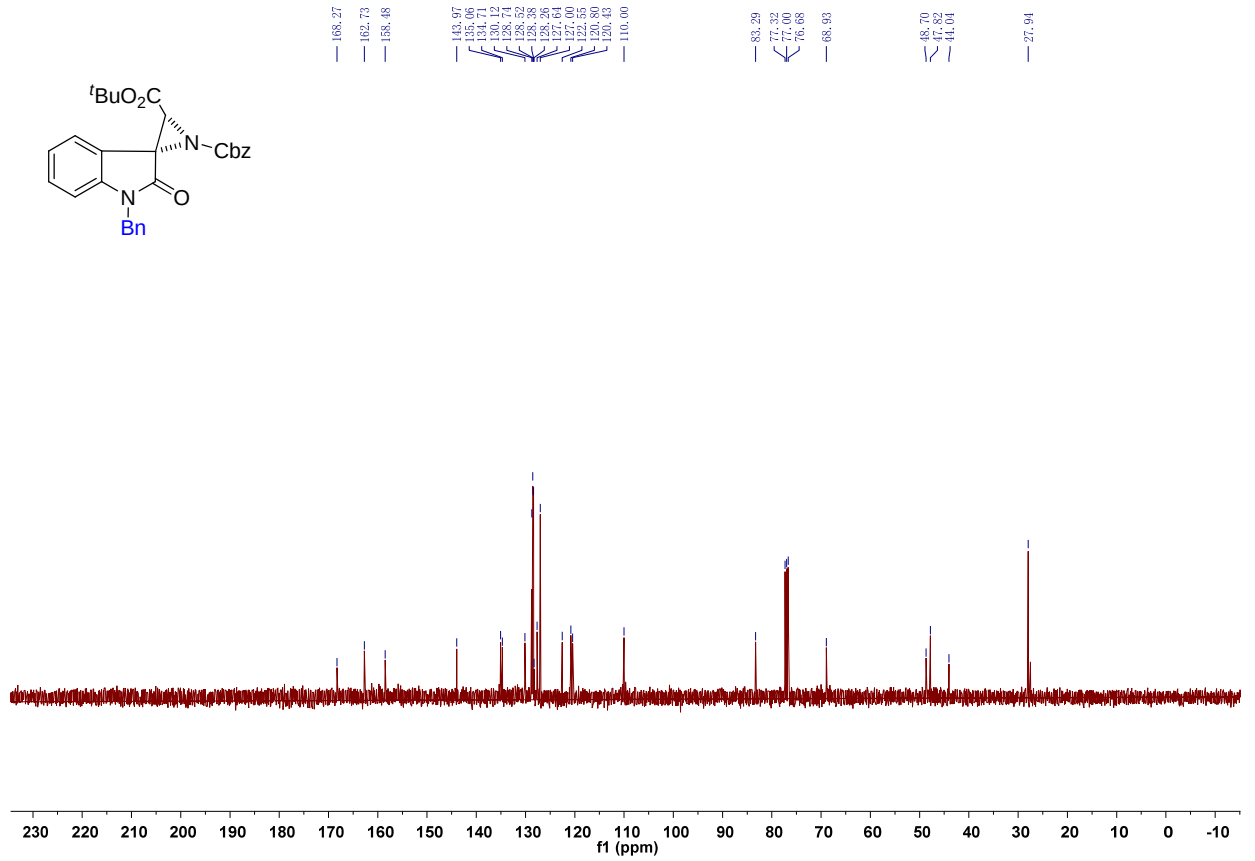
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4d



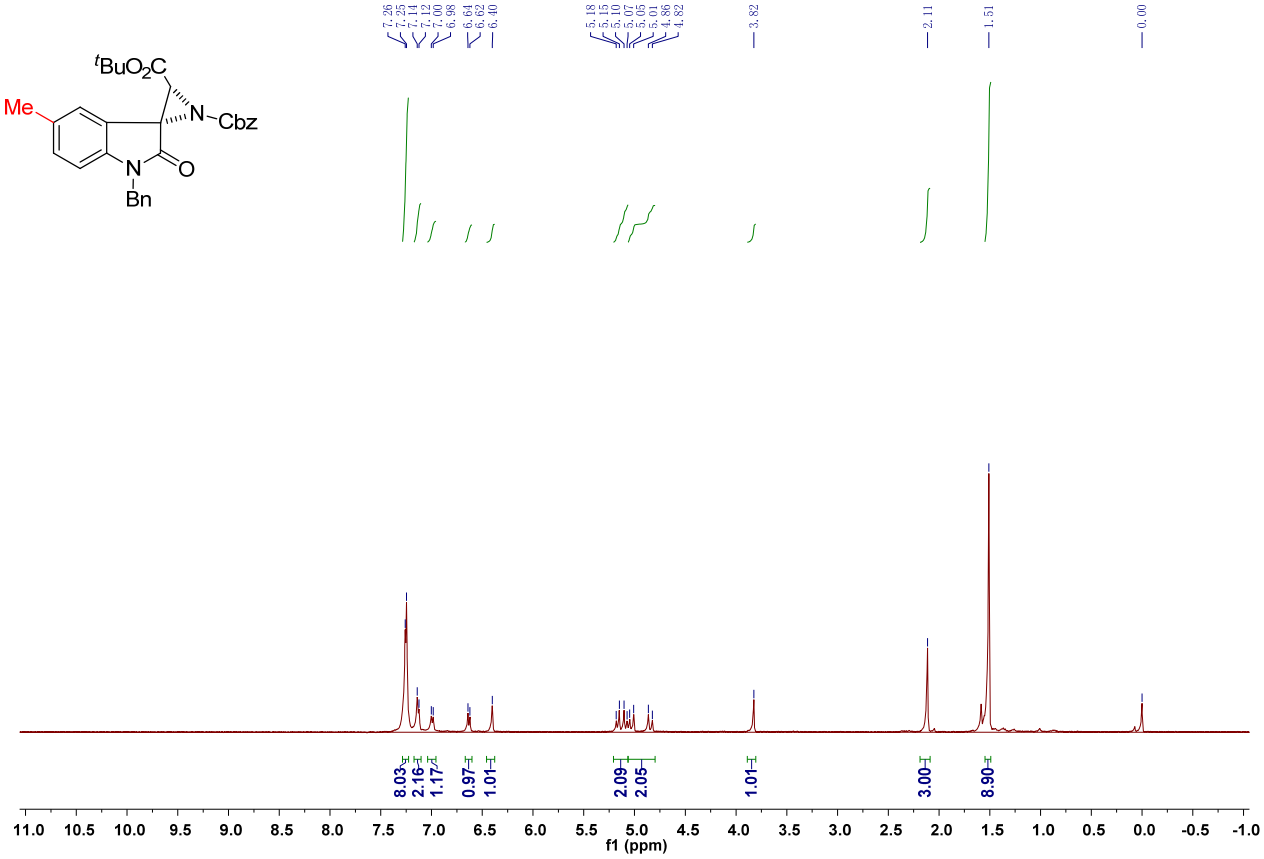


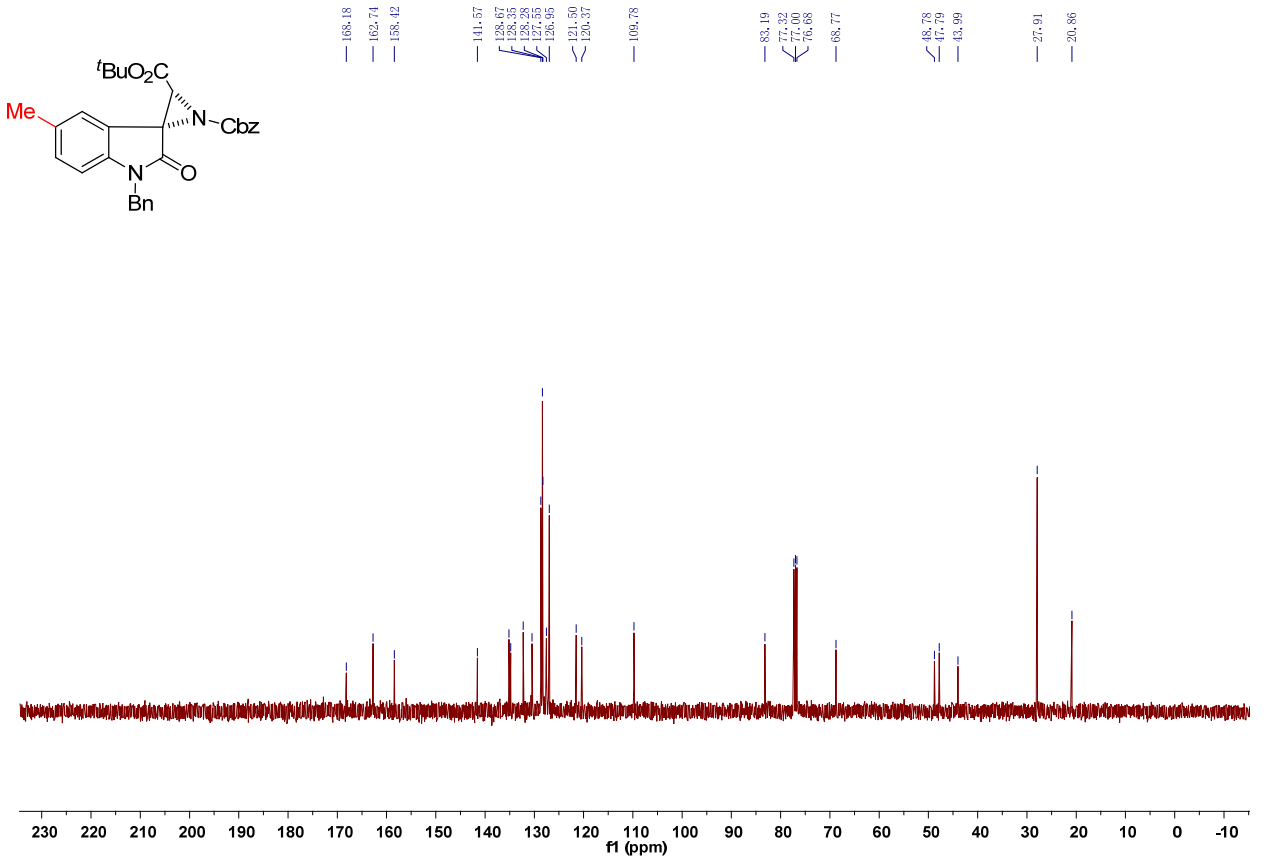
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4e



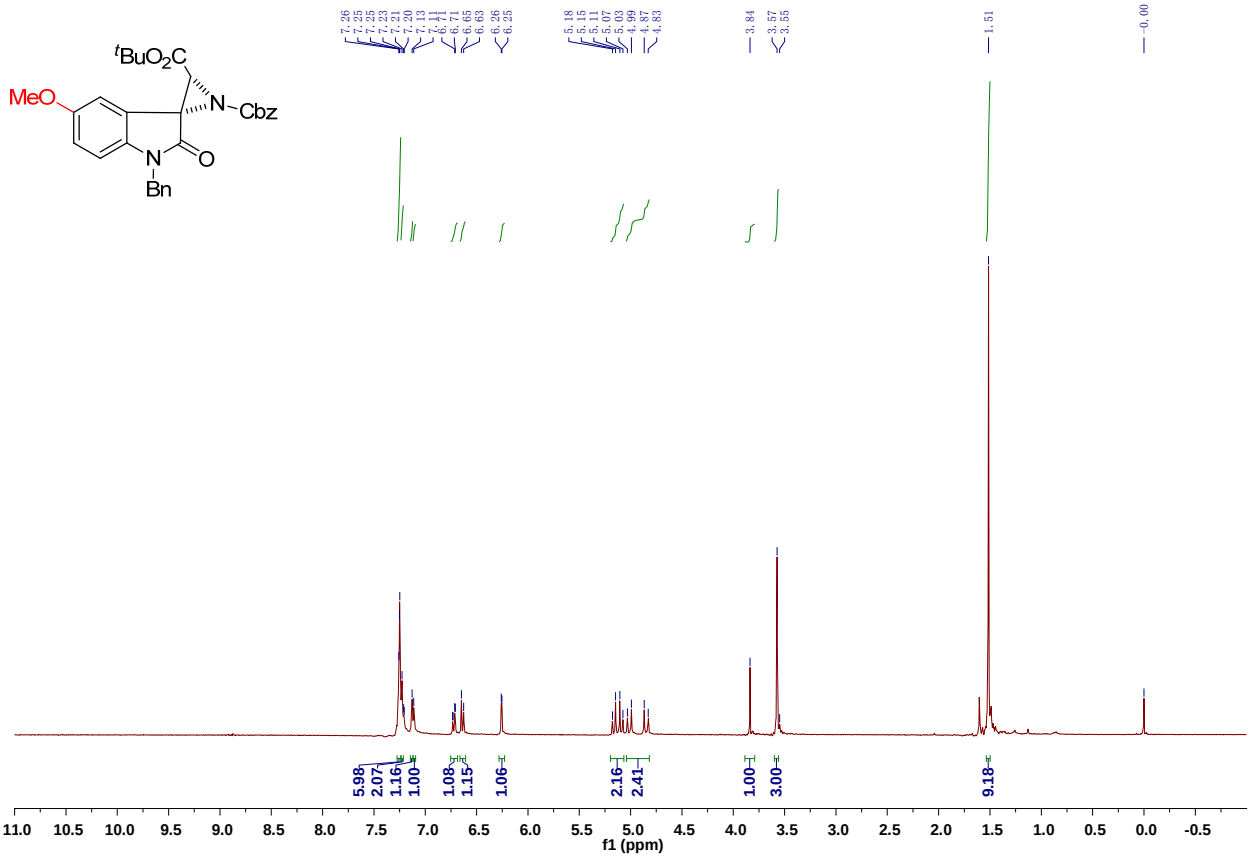


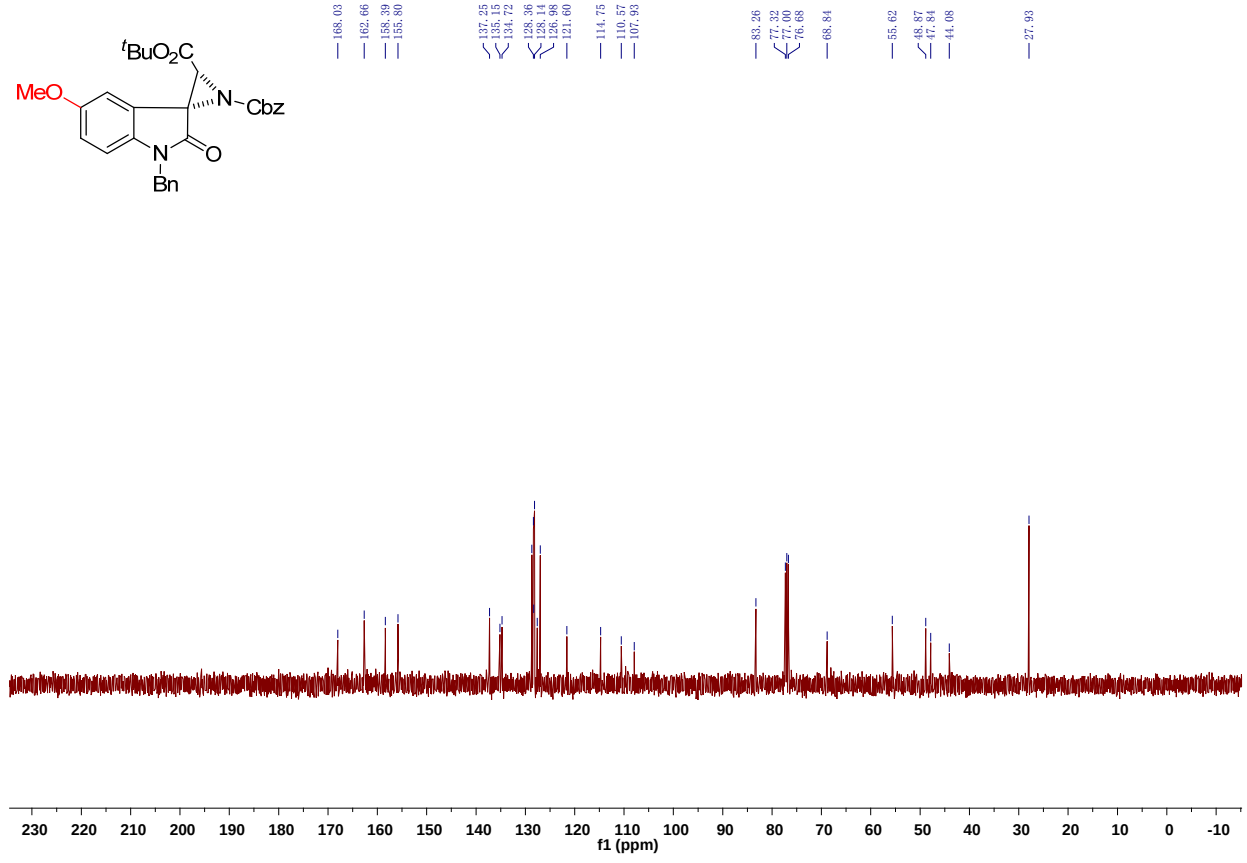
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4f



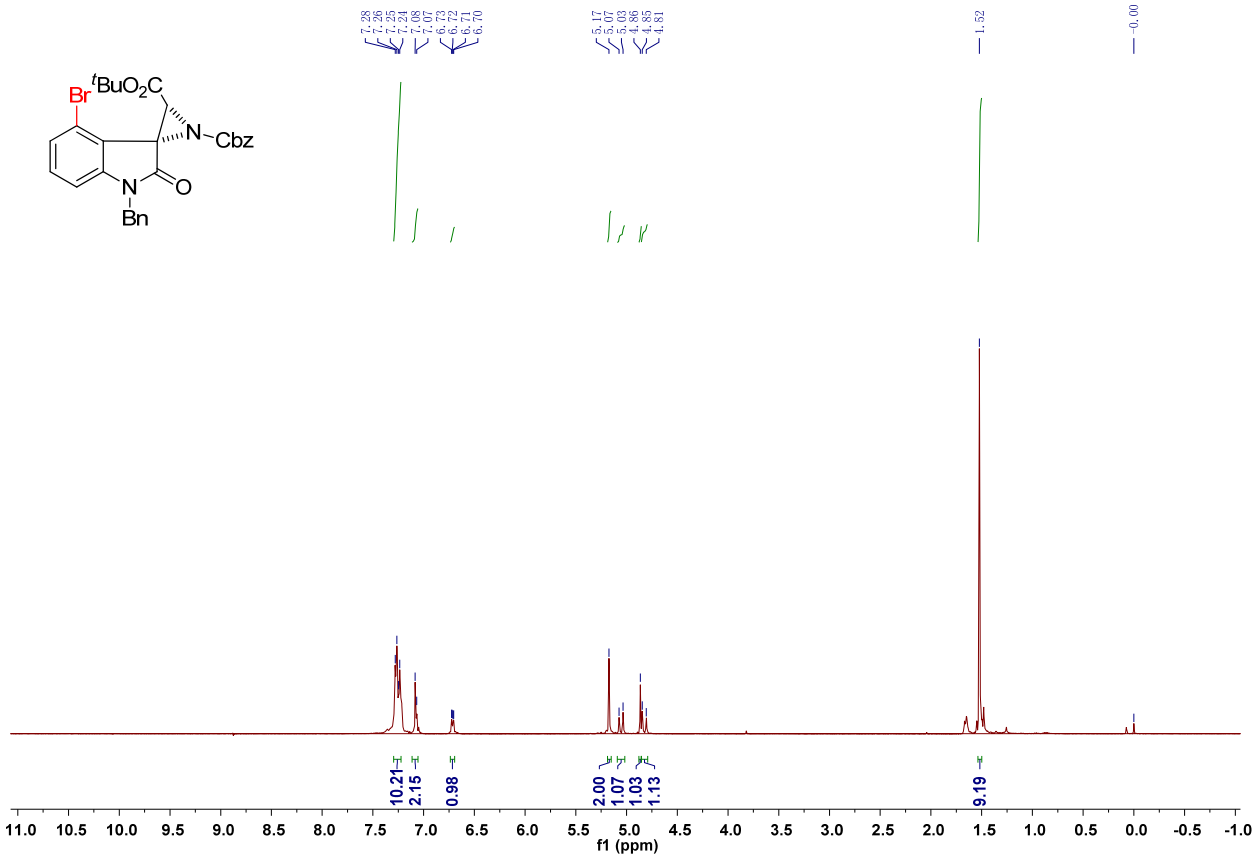


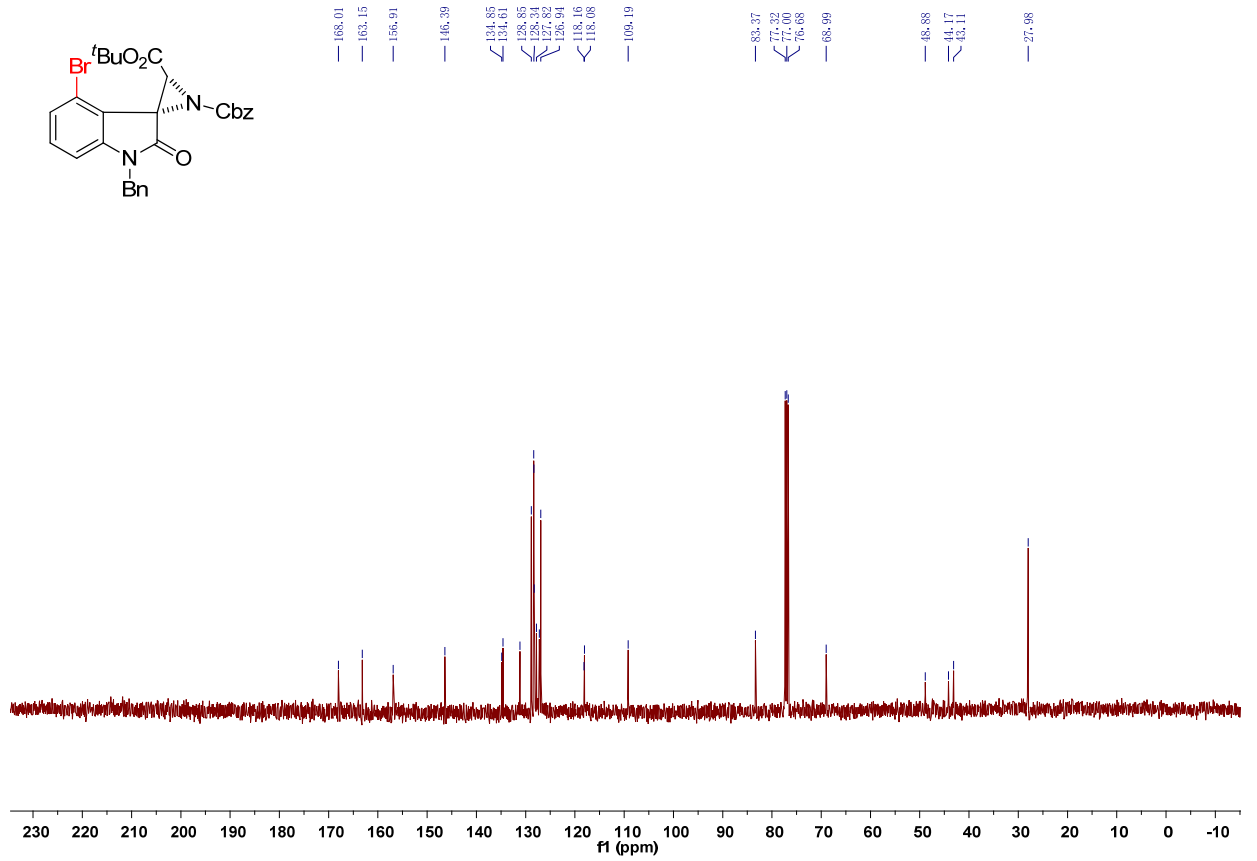
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4g



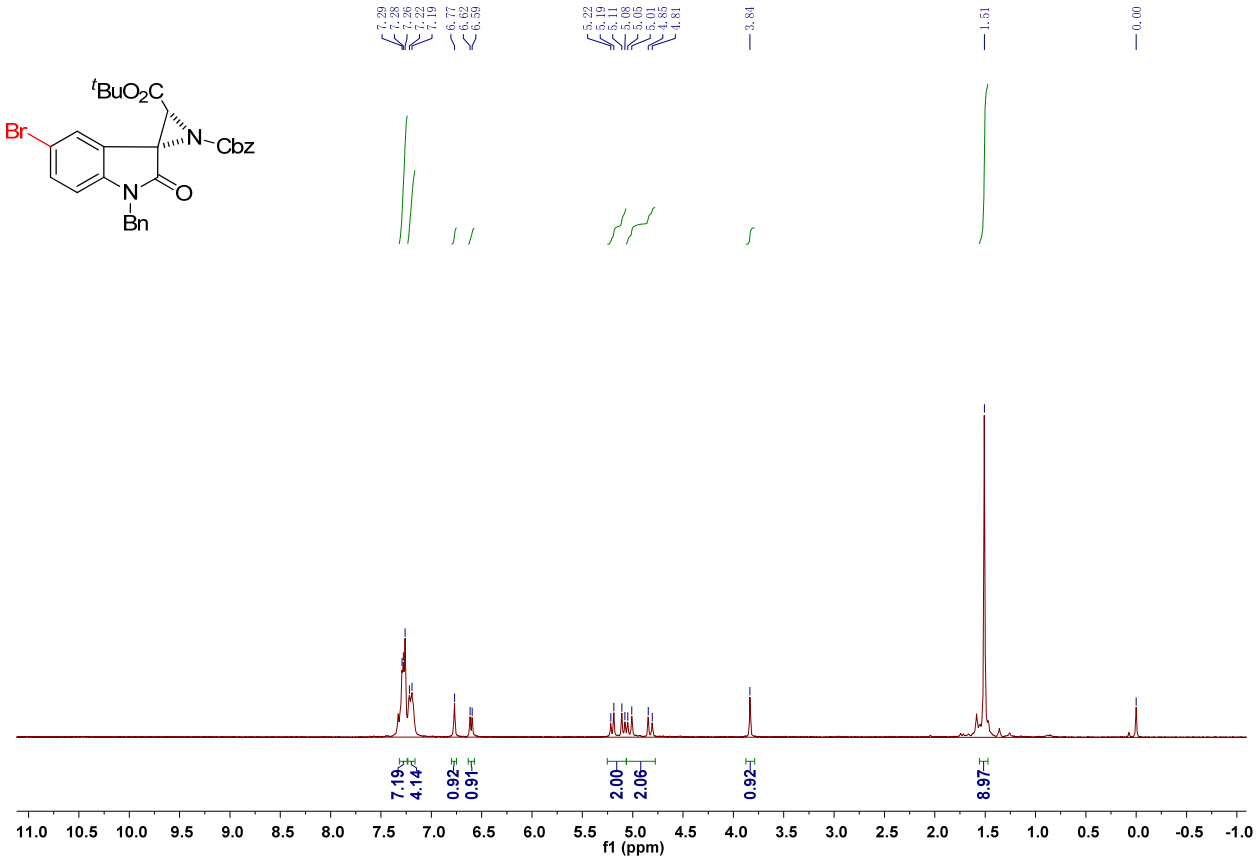


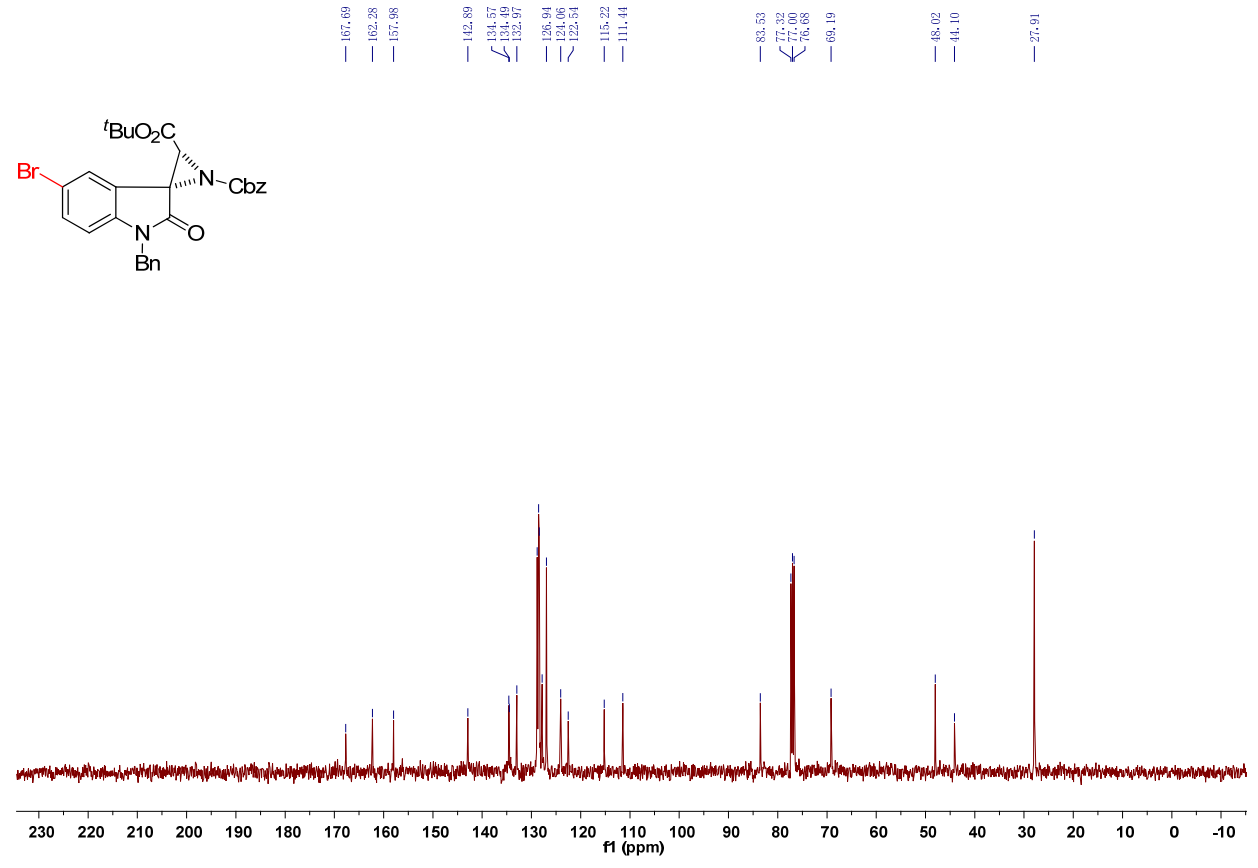
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4h



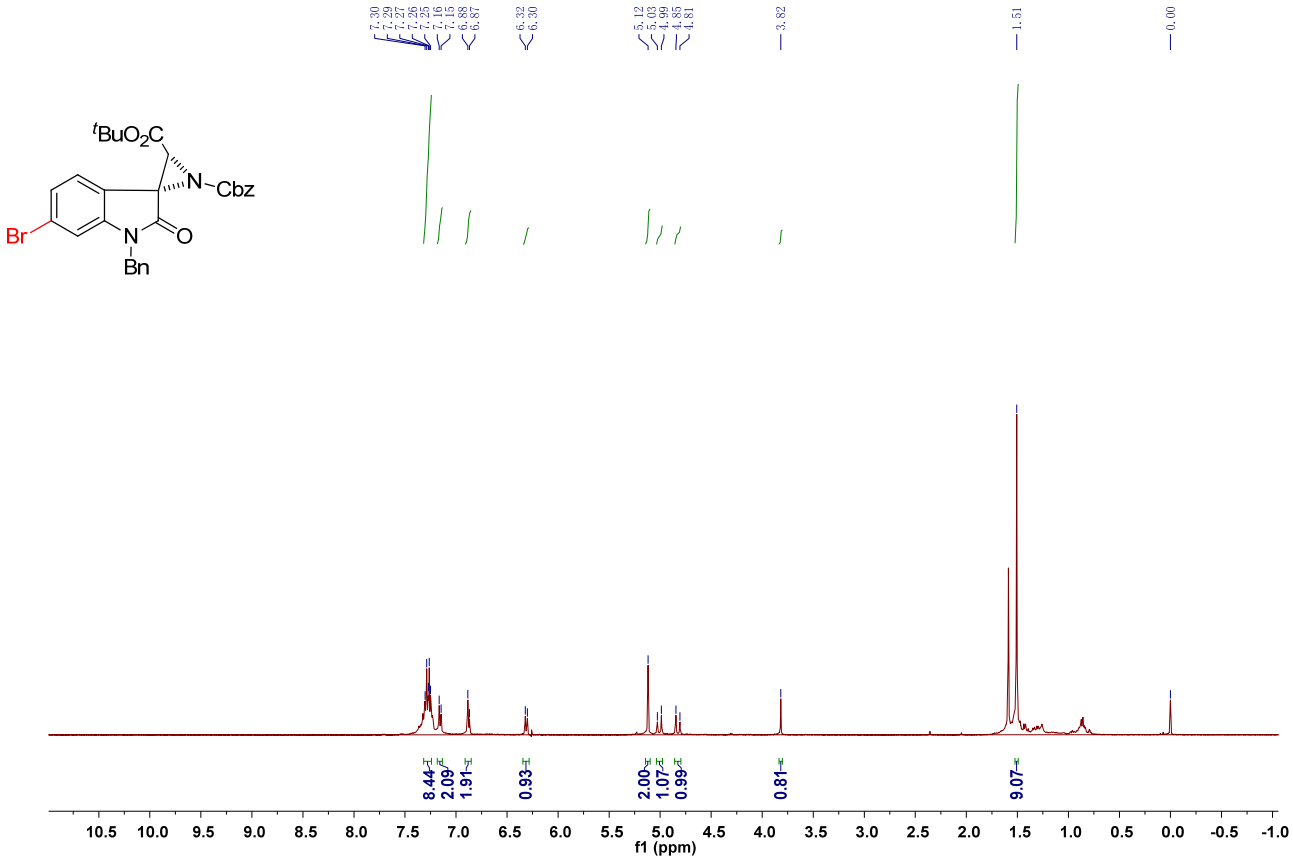


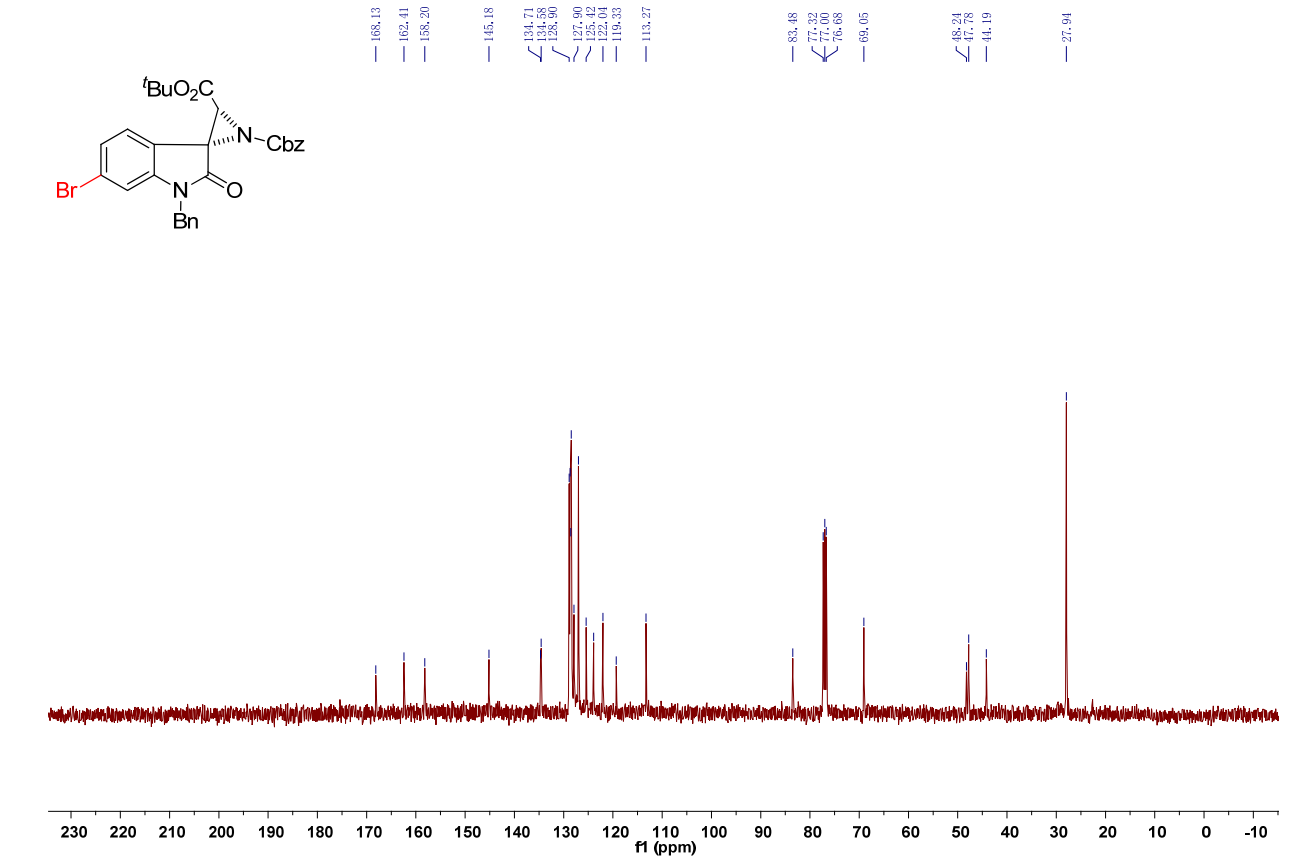
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4i



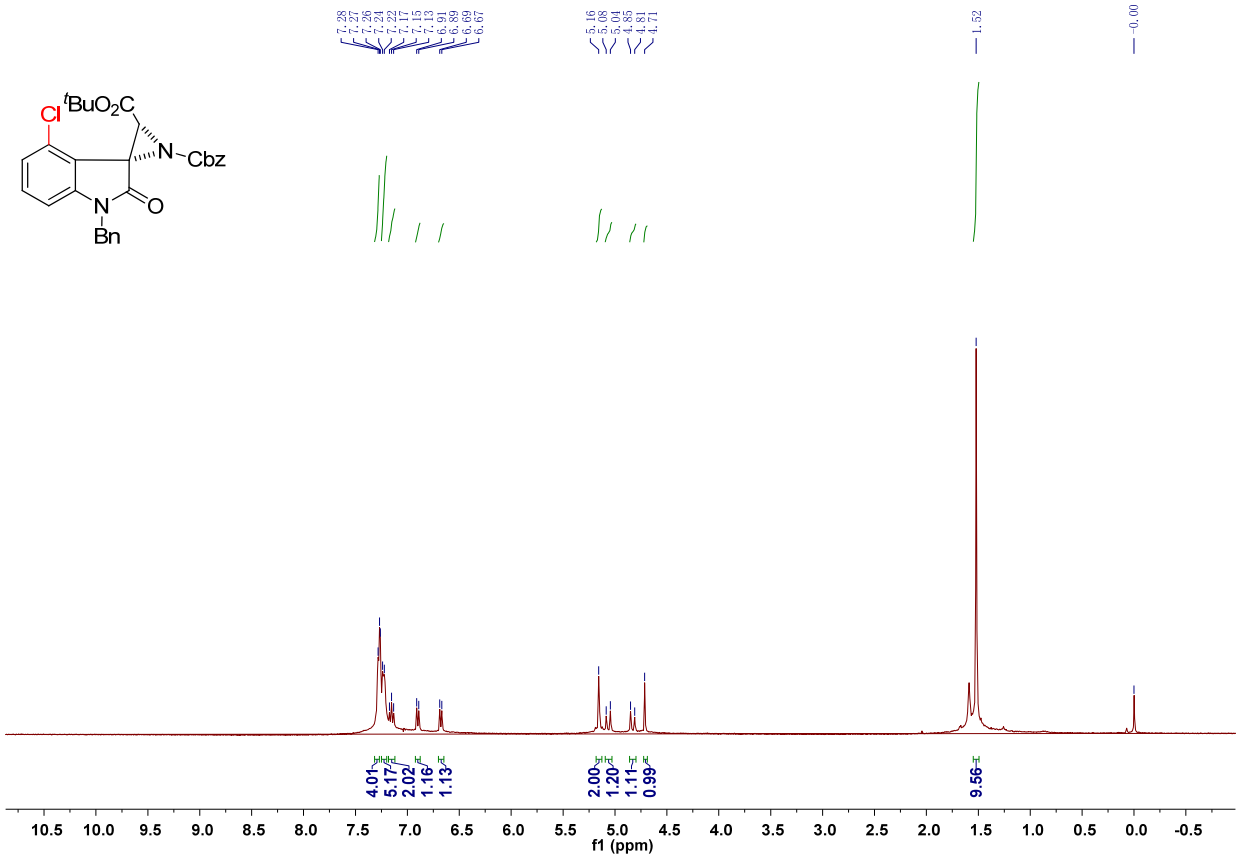


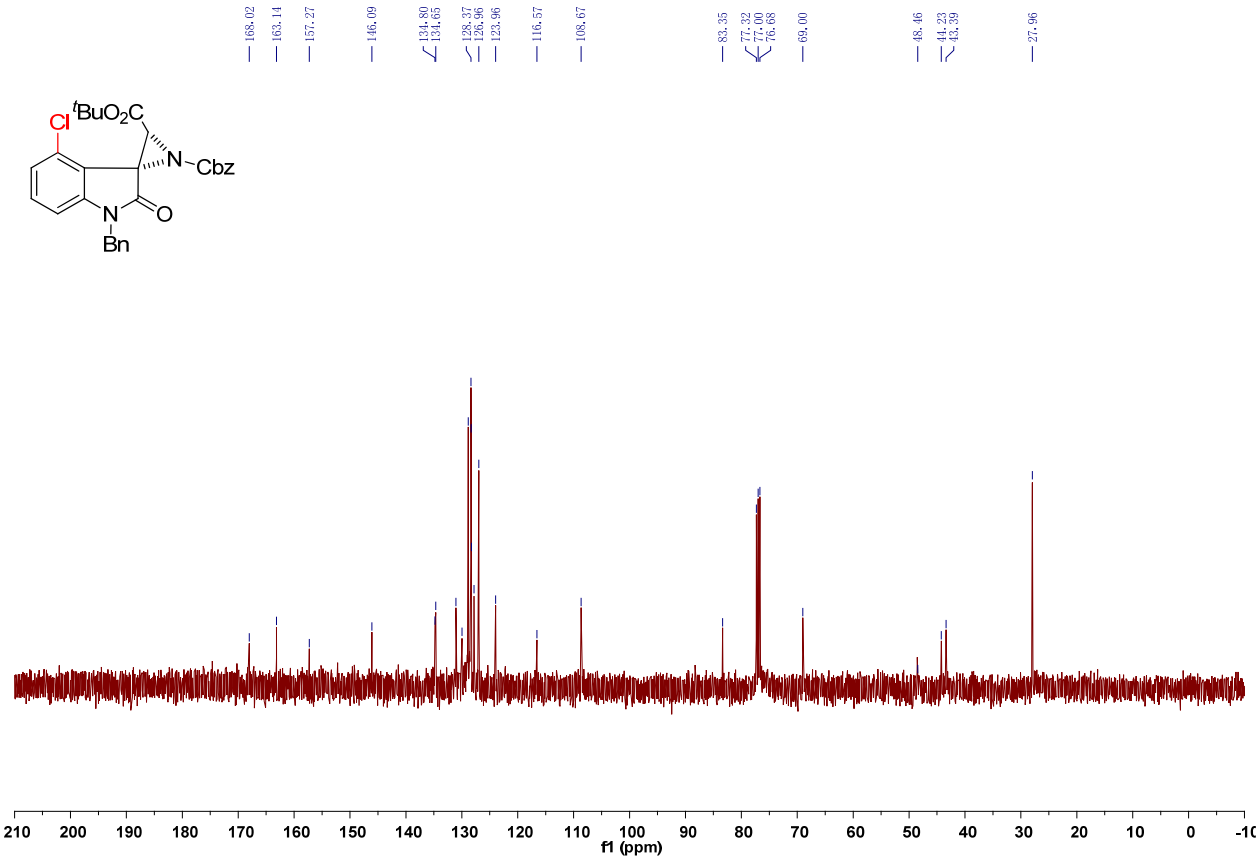
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4j



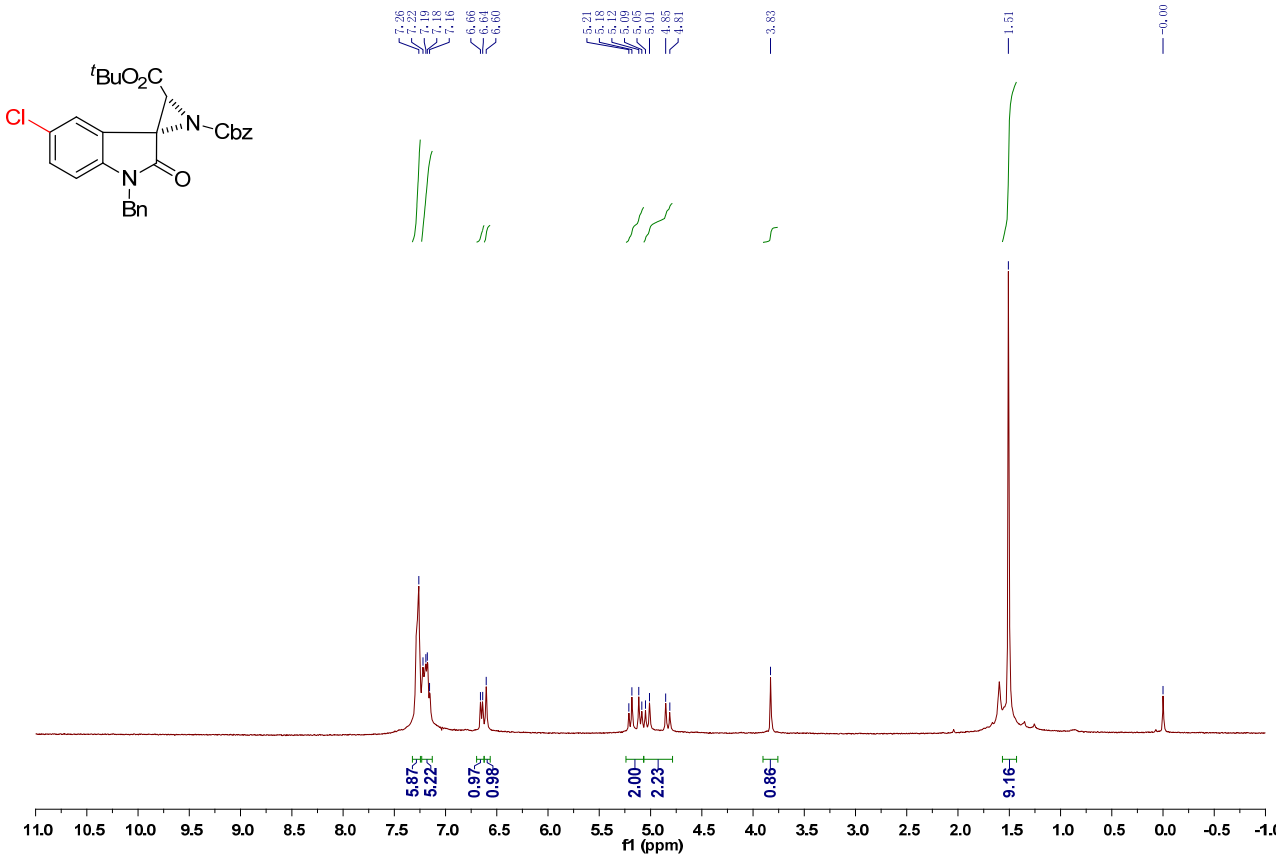


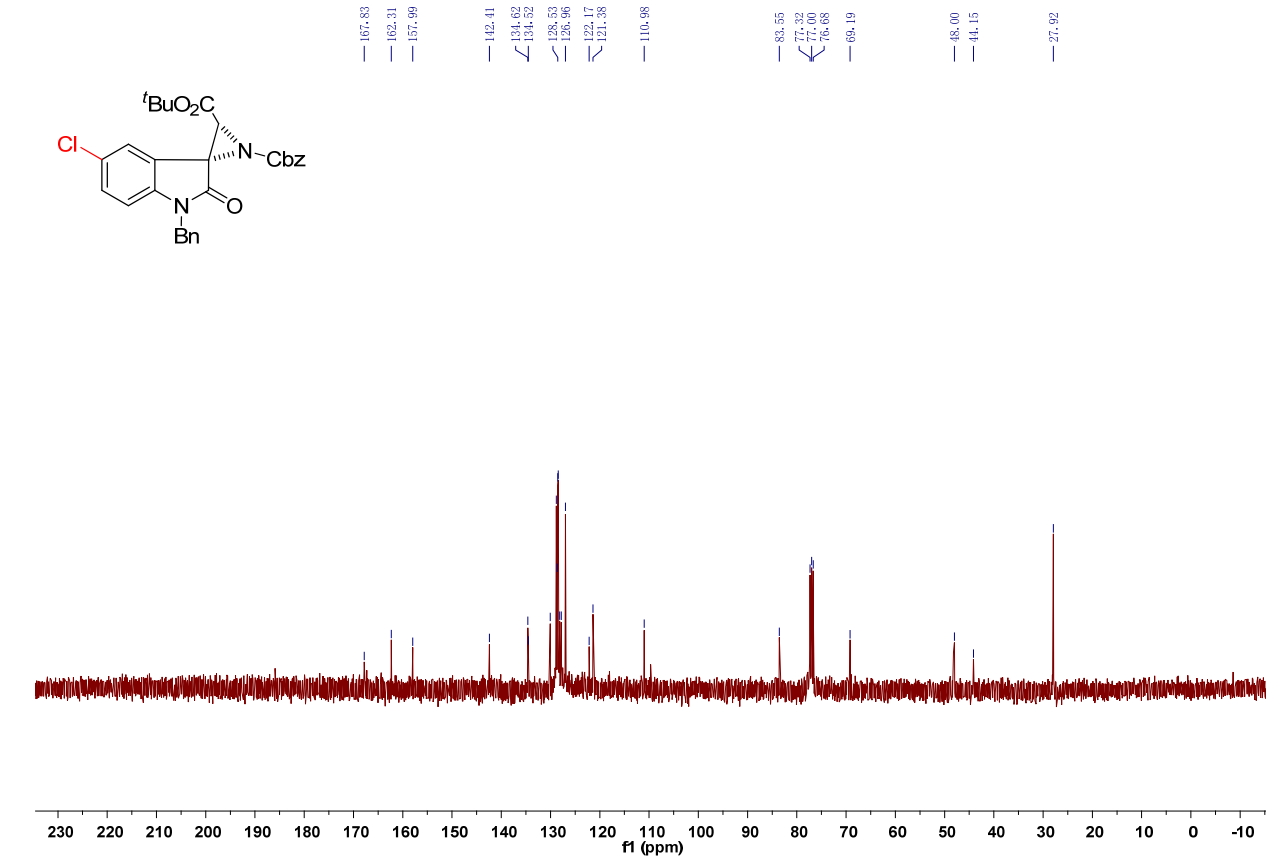
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4k



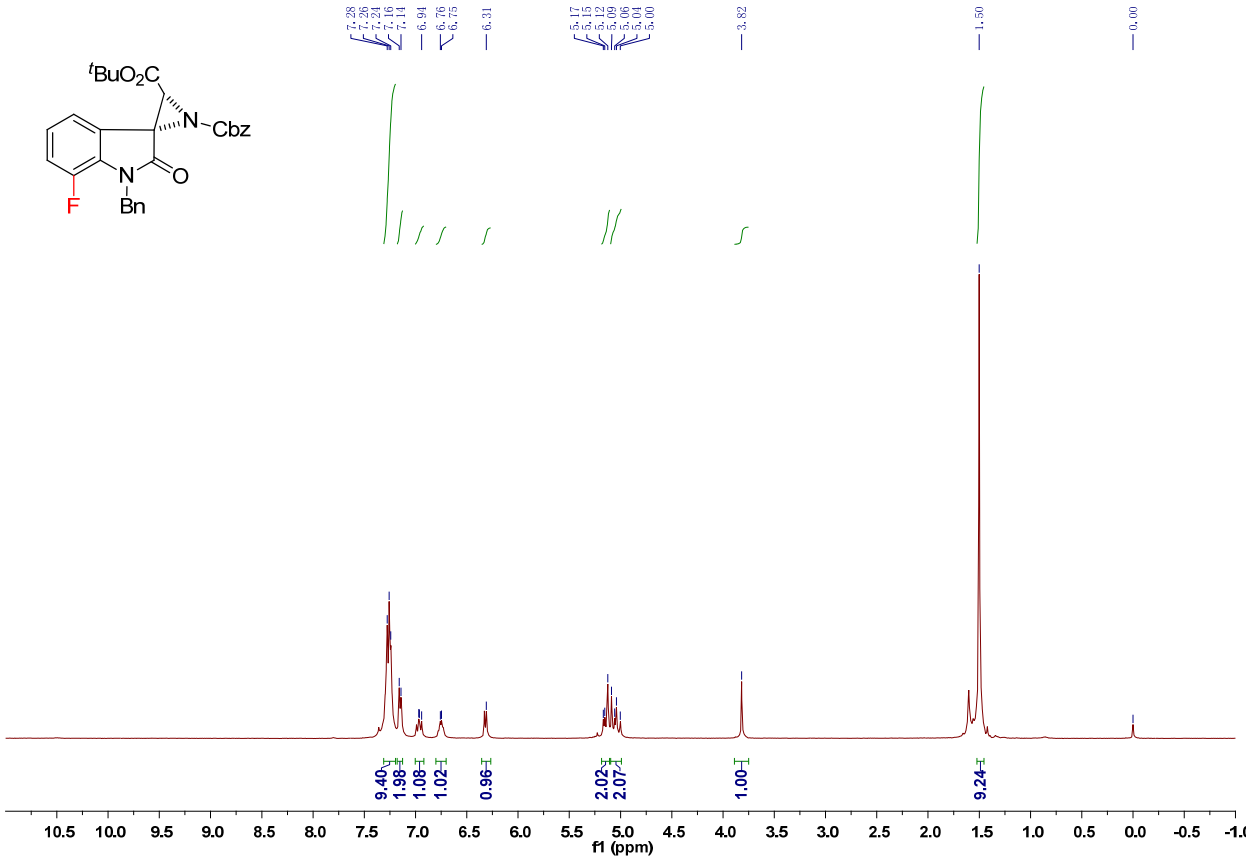


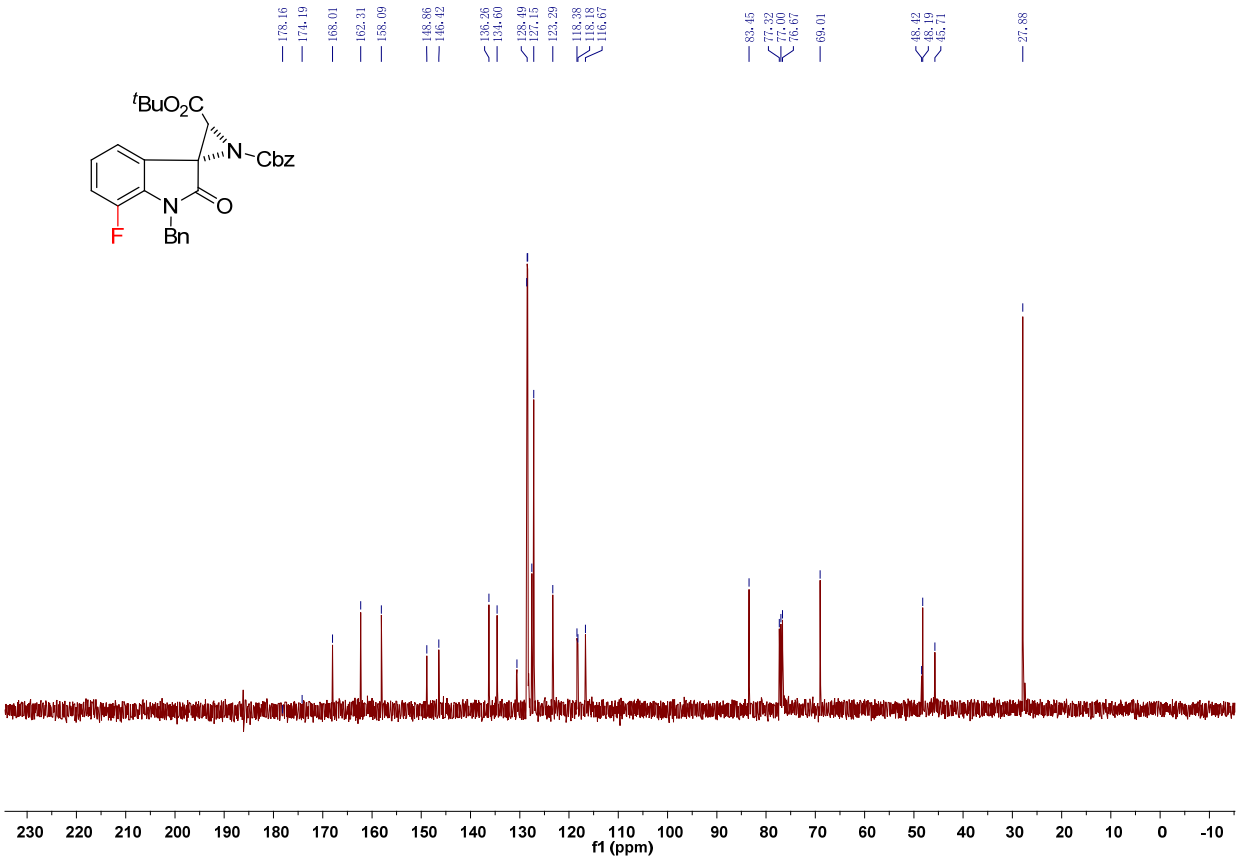
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4l



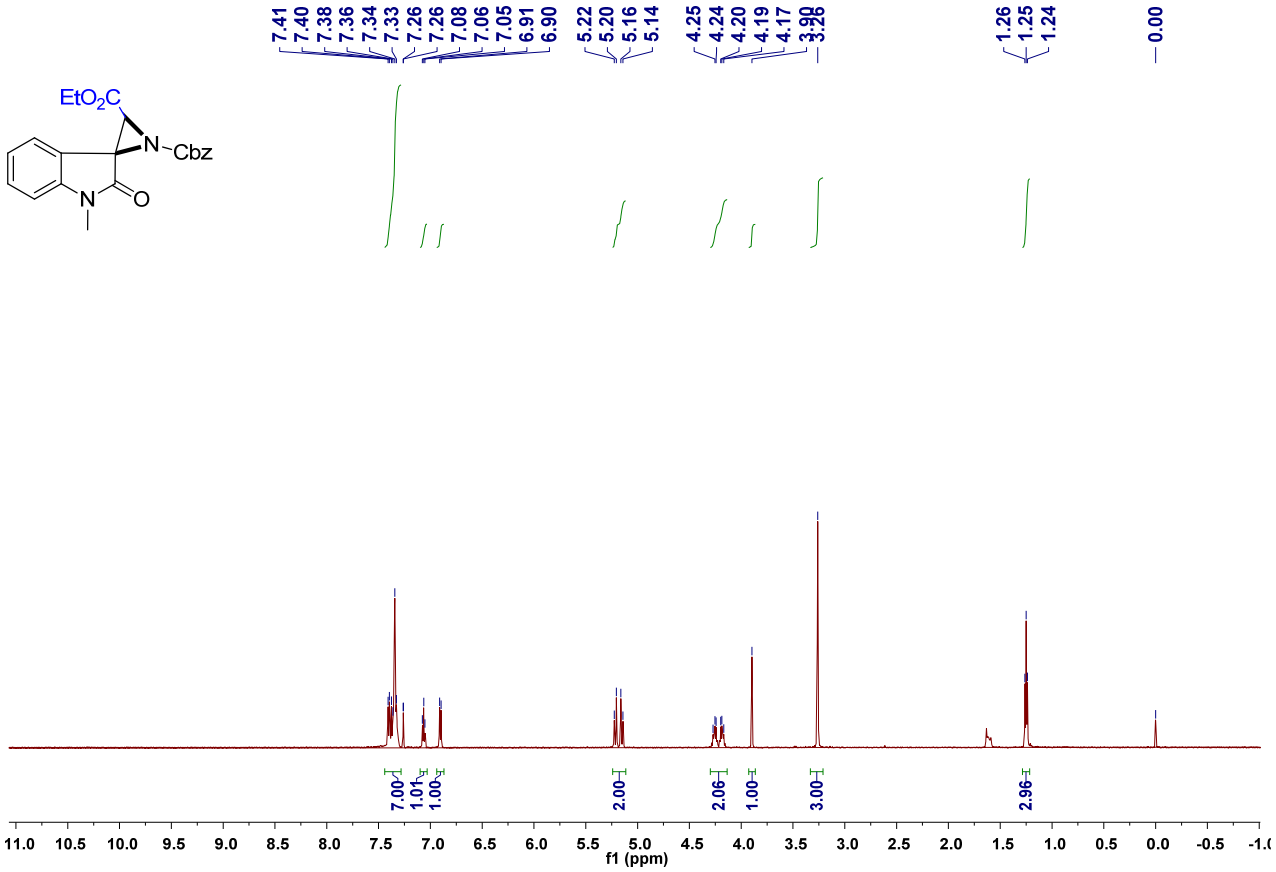


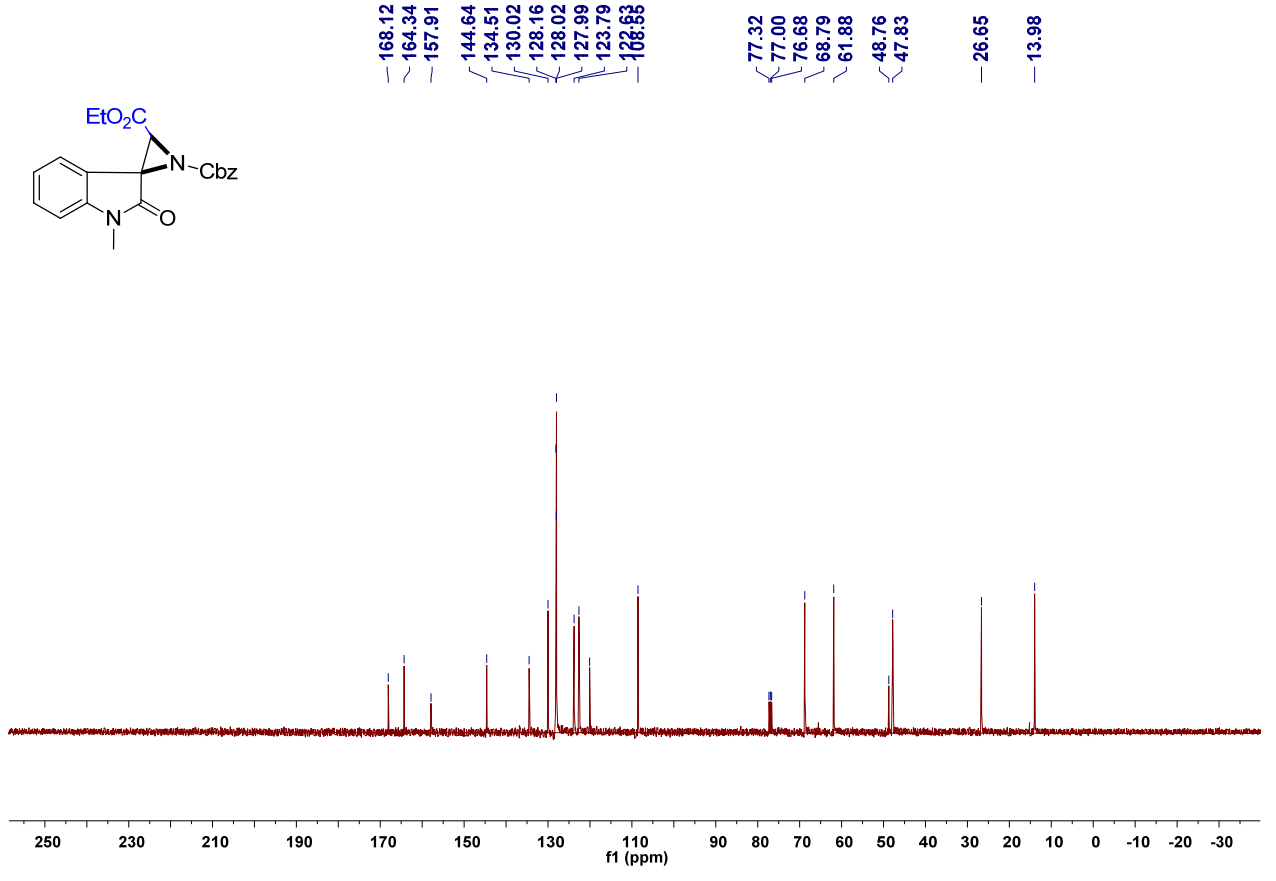
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4m





^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 4a'





^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 5 (d.r. = 1.6:1)