

Supporting Information

Recyclable gold(I)-catalyzed heterocyclization of ynamides with benzyl or indolyl azides towards 2-aminoindoles or 3- amino- β -carboline

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1. Experimental Section

1.1. General Information

Mesoporous SBA-15 and other starting materials were provided by different commercial suppliers and employed without further purification before use. Ynamides **1** and benzyl or indolyl azides **2** or **4** were prepared according to a literature method.¹ The triethoxysilyl-functionalized NHC-AuCl complex, (1,3-bis(2,6-diisopropyl-4-(3-(triethoxysilyl)propyl)phenyl)-2,3-dihydro-1*H*-imidazol-2-yl)gold(I) chloride [(EtO)₃Si-IPrAuCl] was prepared following a described route.² MeCN and dichloroethane (DCE) were dried over CaH₂ and distilled prior to use. THF and toluene were dried over sodium and distilled before use. Products were purified by silica gel column chromatography with a mixture of petroleum ether and EtOAc as eluent. ¹H and ¹³C NMR spectra were recorded at 400 or 100 MHz with CDCl₃ as the solvent and TMS as an internal standard. Chemical shifts are given as δ values relative to TMS. HRMS spectra were recorded on a Q-ToF spectrometer with micromass MS software using electrospray ionization (ESI). Melting points are uncorrected. Gold contents of the heterogenized gold(I) catalysts were measured by ICP-AES analysis. X-ray diffraction (XRD) measurements were carried out at room temperature using a Bruker D8 Advance X-ray powder diffractometer. Energy dispersive spectroscopy (EDS) was performed by using JEOL JSM-7600F scan electron microscope. Nitrogen adsorption/desorption isotherms were measured at 77 K by using a Bel Japan Inc. Belsorp-HP instrument. Samples were degassed for 6 h at 423 K before gas adsorption measurements. X-ray photoelectron spectroscopic (XPS) measurements were conducted on a Kratos Axis Ultra Imaging X-ray photoelectron spectrometer equipped with a Mg anode and a multichannel detector.

1.2. Synthesis of the IPr-SBA-15-AuNTf₂ Complex

(1,3-Bis(2,6-diisopropyl-4-(3-(triethoxysilyl)propyl)phenyl)-2,3-dihydro-1*H*-imidazol-2-yl)gold(I) chloride [(EtO)₃Si-IPrAuCl] (515 mg, 0.5 mmol) was added to a suspension of mesoporous SBA-15 (1.0 g) in dry toluene (90 mL) under an atmos-

phere of argon. The resultant mixture was stirred at 110 °C in an oil bath for 48 h. After cooling to room temperature, the product was collected by filtration, washed with dry toluene (35 mL), and dried at 110 °C under vacuum for 6 h. The resultant powdery solid was subsequently silylated with (Me₃Si)₂NH (4.0 mL) in dry toluene (80 mL) at ambient temperature for 24 h, and then filtered, washed with acetone (2 × 35 mL), and dried at 90 °C under vacuo for 2 h to give 1.392 g of the SBA-15-anchored sterically demanding NHC-gold(I) chloride complex (IPr-SBA-15-AuCl) with gold content of 0.38 mmol g⁻¹ by ICP-AES analysis. Finally, IPr-SBA-15-AuCl (1.046 g) was treated with AgNTf₂ (157 mg, 0.4 mmol) in dry CH₂Cl₂ (50 mL) at ambient temperature for 1 h under Ar. The product was collected by filtration, followed by washing with 25 wt% NH₃·H₂O (2 × 35 mL), distilled water (35 mL), and acetone (2 × 35 mL) and dried at 80 °C in vacuo to give 1.029 g of the IPr-SBA-15-AuNTf₂ complex with gold content of 0.37 mmol g⁻¹.

Similarly, IPr-SBA-15-AuOTf, IPr-SBA-15-AuSbF₆, IPr-SBA-15-AuBF₄, and IPr-SBA-15-AuPF₆ were also prepared by using IPr-SBA-15-AuCl (1.046 g) and various silver salts (0.4 mmol) as the starting materials. Their Au contents were determined to be 0.37 mmol g⁻¹, 0.36 mmol g⁻¹, 0.35 mmol g⁻¹, and 0.36 mmol g⁻¹, respectively, based on ICP-AES analysis.

1.3. General procedure for the heterogeneous gold(I)-catalyzed heterocyclization of ynamides with benzyl azides

To a solution of ynamide **1** (0.2 mmol) and benzyl azide **2** (0.4 mmol) in dry DCE (4.0 mL) were added IPr-SBA-15-AuNTf₂ (28 mg, 0.01 mmol) and 4 Å MS (40 mg). The reaction mixture was stirred at room temperature or 80 °C in an oil bath for 4-10 h (monitored by TLC). The gold(I) catalyst was separated by centrifugation, washed with ethanol (2 × 3 mL), and dried at 100 °C under vacuum for 2 h and reused in the next run. The resulting reaction solution was concentrated in vacuo and the residue was then purified by silica gel column chromatography (petroleum ether/ethyl acetate) to yield the desired product **3**.

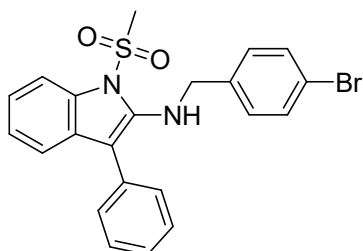
1.4. A gram-scale synthesis of compound 3q.

To a solution of ynamide **1h** (3.0 mmol, 1.051 g) and benzyl azide **2d** (6.0 mmol, 1.272 g) in dry DCE (45 mL) were added IPr-SBA-15-AuNTf₂ (415 mg, 0.15 mmol) and 4 Å MS (0.5 g). The reaction mixture was stirred at room temperature for 12 h. The gold(I) catalyst was separated by centrifugation, washed with ethanol (2 × 30 mL), and dried at 100 °C under vacuum for 2 h and reused in the next run. The resulting reaction solution was concentrated in vacuo and the residue was then purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20 : 1) to afford the desired product **3q** (1.394 g, 87% yield) as a white solid.

1.5. General procedure for the heterogeneous gold(I)-catalyzed heterocyclization of ynamides with indolyl azides

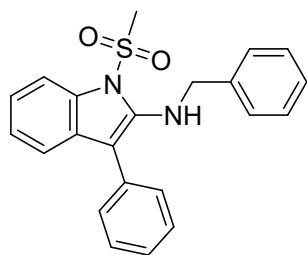
To a solution of ynamide **1** (0.2 mmol), indolyl azide **4** (0.3 mmol) and AgOAc (0.22 mmol) in dry DCE (4.0 mL) were added IPr-SBA-15-AuNTf₂ (28 mg, 0.01 mmol) and 4 Å MS (40 mg) at room temperature. The reaction mixture was stirred at 60 °C in an oil bath for 40 h (monitored by TLC). After being cooled to room temperature, the gold(I) catalyst was separated by centrifugation, washed with ethanol (2 × 3 mL), and dried at 100 °C in vacuo for 2 h and reused in the next run. The resulting reaction solution was concentrated in vacuo and the residue was then purified by silica gel column chromatography (petroleum ether/ethyl acetate) to give the desired product **5**.

2. ¹H and ¹³C NMR data of compounds **3a-x** and **5a-s**.

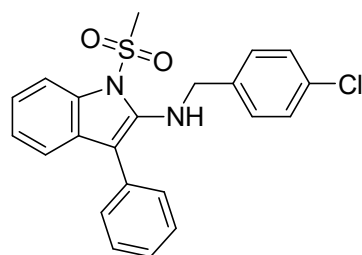


N-(4-Bromobenzyl)-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine (**3a**).¹ White solid (69.2 mg, 76%). Mp: 65-67 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.49-7.42 (m, 4H), 7.38-7.32 (m, 3H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.21-7.12 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 5.80 (brs, 1H), 4.02 (d, *J* = 6.0 Hz, 2H), 2.81 (s, 3H).

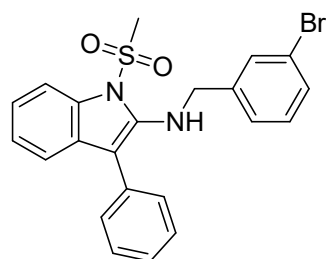
^{13}C NMR (100 MHz, CDCl_3): δ 140.3, 138.3, 133.4, 132.5, 131.9, 131.7, 130.2, 129.6, 128.7, 127.2, 124.6, 122.4, 121.4, 117.4, 114.0, 102.8, 49.5, 39.6.



***N*-Benzyl-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine (3b).**¹ Pale yellow oil (48.2 mg, 64%). ^1H NMR (400 MHz, CDCl_3): δ 7.85 (d, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.37-7.30 (m, 2H), 7.24-7.16 (m, 4H), 7.12 (t, $J = 7.6$ Hz, 1H), 7.08 (d, $J = 6.4$ Hz, 2H), 5.82 (brs, 1H), 4.04 (s, 2H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.7, 139.5, 133.7, 132.6, 132.0, 130.2, 128.7, 128.1, 127.6, 127.1, 124.5, 122.2, 117.3, 114.1, 102.6, 50.3, 39.5.

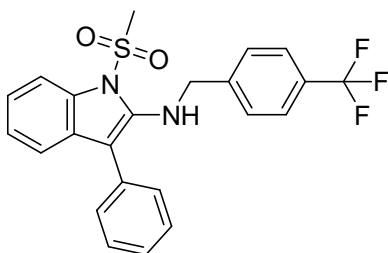


***N*-(4-Chlorobenzyl)-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine (3c).**¹ White solid (46.1 mg, 56%). Mp: 63-65 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.85 (d, $J = 7.6$ Hz, 1H), 7.48-7.42 (m, 4H), 7.37-7.31 (m, 1H), 7.30-7.26 (m, 1H), 7.21-7.12 (m, 4H), 6.98 (d, $J = 8.4$ Hz, 2H), 5.78 (brs, 1H), 4.03 (d, $J = 6.0$ Hz, 2H), 2.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.3, 137.8, 133.5, 133.4, 132.6, 132.0, 130.2, 129.3, 128.8, 128.7, 127.2, 124.6, 122.4, 117.4, 114.1, 102.9, 49.6, 39.6.



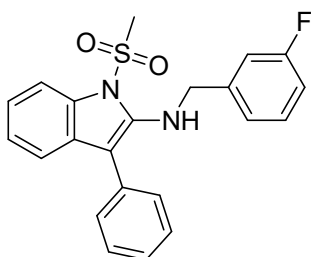
***N*-(3-Bromobenzyl)-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine (3d).**¹ White solid (81.9 mg, 90%). Mp: 75-77 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.85 (d, $J = 8.4$

Hz, 1H), 7.46-7.42 (m, 4H), 7.38-7.24 (m, 3H), 7.20-7.10 (m, 3H), 7.07 (t, $J = 7.8$ Hz, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 5.85 (t, $J = 6.4$ Hz, 1H), 4.05 (d, $J = 6.4$ Hz, 2H), 2.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.6, 140.2, 133.4, 132.5, 132.1, 131.0, 130.6, 130.3, 130.2, 128.7, 127.3, 126.4, 124.6, 122.6, 122.4, 117.5, 114.0, 102.8, 49.5, 39.6.



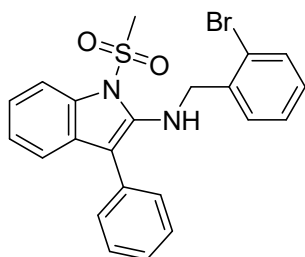
***N*-(4-Trifluoromethylbenzyl)-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine**

(3e). Pale yellow oil (69.3 mg, 78%). ^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, $J = 7.6$ Hz, 1H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.44-7.40 (m, 4H), 7.36-7.31 (m, 1H), 7.27-7.24 (m, 1H), 7.21-7.12 (m, 4H), 5.84 (brs, 1H), 4.15 (d, $J = 5.2$ Hz, 2H), 2.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 143.2, 140.1, 133.3, 132.6, 131.9, 130.9, 130.1 (q, $J = 32.4$ Hz), 128.7, 128.0, 127.3, 125.5 (q, $J = 3.7$ Hz), 124.6, 124.2 (q, $J = 270.1$ Hz), 122.5, 117.5, 114.0, 103.1, 49.7, 39.6. HRMS calcd for $\text{C}_{23}\text{H}_{19}\text{F}_3\text{N}_2\text{NaO}_2\text{S}^+$ [$\text{M} + \text{Na}$] $^+$: 467.1012, found 467.1019.

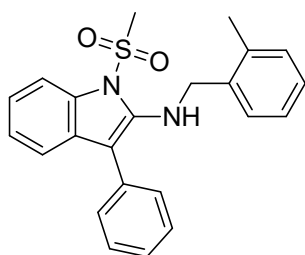


***N*-(3-Fluorobenzyl)-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine (3f).** Pale yellow oil (59.2 mg, 75%). ^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, $J = 7.6$ Hz, 1H), 7.49-7.41 (m, 4H), 7.37-7.31 (m, 1H), 7.27-7.24 (m, 1H), 7.21-7.10 (m, 3H), 6.91-6.83 (m, 2H), 6.74 (d, $J = 9.6$ Hz, 1H), 5.82 (brs, 1H), 4.07 (d, $J = 5.6$ Hz, 2H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 162.9 (d, $J = 245.1$ Hz), 141.9 (d, $J = 6.8$ Hz), 140.3, 133.4, 132.6, 132.0, 130.3, 130.2 (d, $J = 8.2$ Hz), 128.7, 127.3, 124.5, 123.4 (d, $J = 2.7$ Hz), 122.4, 117.4, 114.8 (d, $J = 21.3$ Hz), 114.4 (d, $J = 21.0$ Hz), 114.0, 102.8,

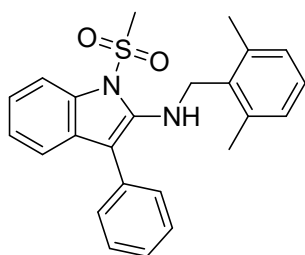
49.7, 39.6. HRMS calcd for $C_{22}H_{19}FN_2NaO_2S^+$ $[M + Na]^+$: 417.1043, found 417.1038.



***N*-(2-Bromobenzyl)-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine (3g).**¹ White solid (73.8 mg, 81%). Mp: 65-67 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.48-7.40 (m, 5H), 7.36-7.31 (m, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.21-7.11 (m, 3H), 7.10-7.04 (m, 2H), 5.84 (brs, 1H), 4.17 (d, *J* = 5.6 Hz, 2H), 2.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 140.3, 138.3, 133.5, 133.0, 132.6, 132.0, 130.3, 129.9, 129.3, 128.7, 127.7, 127.2, 124.4, 124.2, 122.3, 117.4, 114.0, 102.8, 50.6, 39.7.

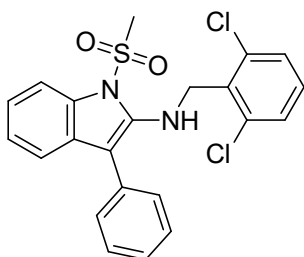


***N*-(2-Methylbenzyl)-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine (3h).** Pale yellow oil (55.4 mg, 71%). ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.53-7.50 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35-7.27 (m, 2H), 7.22-7.16 (m, 1H), 7.15-7.12 (m, 1H), 7.11-7.08 (m, 2H), 7.07-7.03 (m, 2H), 5.68 (brs, 1H), 4.03 (s, 2H), 2.71 (s, 3H), 2.16 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 140.8, 137.3, 136.4, 133.8, 132.5, 132.2, 130.6, 130.3, 128.6, 128.3, 127.8, 127.1, 126.2, 124.5, 122.1, 117.3, 114.0, 102.3, 48.4, 39.5, 18.8. HRMS calcd for $C_{23}H_{22}N_2NaO_2S^+$ $[M + Na]^+$: 413.1294, found 413.1297.



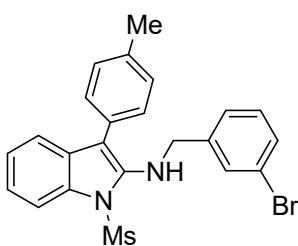
***N*-(2,6-Dimethylbenzyl)-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine (3i).**

Pale yellow oil (55.1 mg, 68%). ^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, $J = 7.6$ Hz, 1H), 7.58-7.55 (m, 2H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.36-7.28 (m, 2H), 7.19 (t, $J = 7.4$ Hz, 1H), 7.15-7.10 (m, 1H), 7.05-7.01 (m, 1H), 6.95 (d, $J = 7.2$ Hz, 2H), 5.30 (brs, 1H), 4.01 (s, 2H), 2.83 (s, 3H), 2.24 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.5, 137.2, 135.6, 133.9, 132.4, 132.1, 130.5, 128.6, 128.5, 127.9, 127.1, 124.4, 122.1, 117.3, 113.9, 101.9, 46.0, 39.5, 19.7. HRMS calcd for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{NaO}_2\text{S}^+$ [$\text{M} + \text{Na}$] $^+$: 427.1451, found 427.1459.

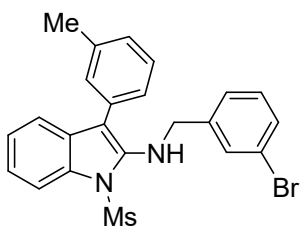


***N*-(2,6-Dichlorobenzyl)-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine (3j).**

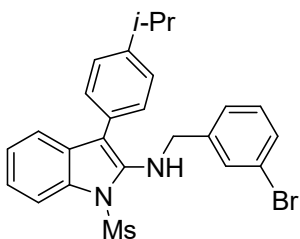
Pale yellow oil (62.3 mg, 70%). ^1H NMR (400 MHz, CDCl_3): δ 7.90 (d, $J = 7.6$ Hz, 1H), 7.52-7.49 (m, 2H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.33 (t, $J = 6.8$ Hz, 2H), 7.25-7.08 (m, 5H), 5.36 (t, $J = 4.8$ Hz, 1H), 4.33 (d, $J = 5.6$ Hz, 2H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.5, 136.1, 134.8, 133.4, 132.7, 131.7, 130.3, 129.7, 128.6, 128.5, 127.1, 124.3, 122.5, 117.6, 114.1, 103.7, 47.1, 39.7. HRMS calcd for $\text{C}_{22}\text{H}_{18}\text{Cl}_2\text{N}_2\text{NaO}_2\text{S}^+$ [$\text{M} + \text{Na}$] $^+$: 467.0358, found 467.0352.



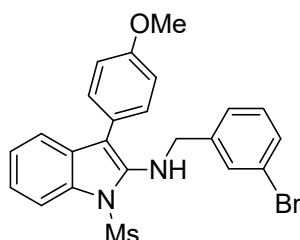
***N*-(3-Bromobenzyl)-1-(methylsulfonyl)-3-*p*-tolyl-1*H*-indol-2-amine(3k).**¹ White solid (72.3 mg, 77%). Mp: 76-78 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 1H), 7.26-7.23 (m, 3H), 7.18-7.09 (m, 3H), 7.07 (t, $J = 7.8$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 1H), 5.80 (t, $J = 5.8$ Hz, 1H), 4.05 (d, $J = 6.4$ Hz, 2H), 2.83 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.7, 140.0, 137.0, 132.5, 132.2, 131.0, 130.5, 130.2, 130.1, 129.4, 126.3, 124.5, 122.6, 122.2, 117.5, 114.0, 102.8, 49.4, 39.5, 21.4.



***N*-(3-Bromobenzyl)-1-(methylsulfonyl)-3-*m*-tolyl-1*H*-indol-2-amine(3l).**¹ White solid (73.2 mg, 78%). Mp: 78-80 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.25-7.21 (m, 3H), 7.19-7.10 (m, 4H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 5.85 (t, *J* = 6.0 Hz, 1H), 4.06 (d, *J* = 6.4 Hz, 2H), 2.85 (s, 3H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 141.7, 140.1, 138.3, 133.1, 132.5, 132.1, 131.0, 130.5, 130.1, 128.5, 128.1, 127.4, 126.3, 124.5, 122.6, 122.3, 117.5, 114.0, 102.8, 49.4, 39.5, 21.6.

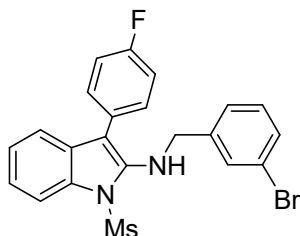


***N*-(3-Bromobenzyl)-3-(4-isopropylphenyl)-1-(methylsulfonyl)-1*H*-indol-2-amine (3m).**¹ Pale yellow oil (83.5 mg, 84%). ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.36-7.26 (m, 6H), 7.19-7.11 (m, 3H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.82 (t, *J* = 6.6 Hz, 1H), 4.06 (d, *J* = 6.4 Hz, 2H), 3.01-2.94 (m, 1H), 2.84 (s, 3H), 1.32 (d, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 147.9, 141.8, 140.0, 132.5, 132.2, 131.0, 130.5, 130.4, 130.2, 130.1, 126.6, 126.3, 124.5, 122.6, 122.2, 117.6, 114.0, 102.9, 49.4, 39.5, 34.0, 24.2.



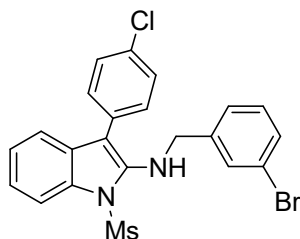
***N*-(3-Bromobenzyl)-3-(4-methoxyphenyl)-1-(methylsulfonyl)-1*H*-indol-2-amine (3n).**¹ White solid (67.1 mg, 69%). Mp: 78-80 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.36-7.32 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.24-7.20 (m, 1H), 7.19-7.11 (m, 3H), 7.09 (t, *J* = 7.8 Hz, 1H), 7.02-6.96 (m, 3H), 5.81 (brs, 1H), 4.06 (d,

$J = 5.6$ Hz, 2H), 3.87 (s, 3H), 2.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 158.9, 141.8, 140.0, 132.5, 132.4, 131.5, 131.0, 130.6, 130.2, 126.3, 125.3, 124.5, 122.6, 122.3, 117.4, 114.2, 114.0, 102.5, 55.5, 49.4, 39.6.



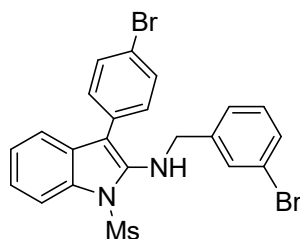
***N*-(3-Bromobenzyl)-3-(4-fluorophenyl)-1-(methylsulfonyl)-1*H*-indol-2-amine**

(3o).¹ White solid (75.7 mg, 80%). Mp: 76-78 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, $J = 8.0$ Hz, 1H), 7.41-7.35 (m, 2H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.21-7.10 (m, 6H), 7.08 (t, $J = 7.8$ Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 1H), 5.89 (t, $J = 5.6$ Hz, 1H), 4.04 (d, $J = 6.0$ Hz, 2H), 2.87 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 162.0 (d, $J = 245.3$ Hz), 141.5, 140.2, 132.4, 132.0 (d, $J = 7.8$ Hz), 131.9, 130.8, 130.7, 130.2, 129.2 (d, $J = 3.3$ Hz), 126.2, 124.6, 122.7, 122.4, 117.2, 115.6 (d, $J = 21.3$ Hz), 114.0, 101.5, 49.4, 39.7.



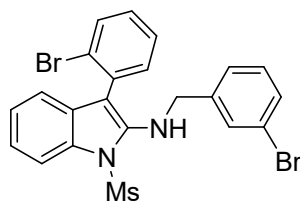
***N*-(3-Bromobenzyl)-3-(4-chlorophenyl)-1-(methylsulfonyl)-1*H*-indol-2-amine**

(3p).¹ Pale yellow oil (81.3 mg, 83%). ^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, $J = 7.6$ Hz, 1H), 7.43-7.35 (m, 4H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.22-7.11 (m, 4H), 7.08 (t, $J = 7.8$ Hz, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 5.93 (t, $J = 6.4$ Hz, 1H), 4.04 (d, $J = 6.4$ Hz, 2H), 2.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.3, 140.3, 133.0, 132.3, 131.8, 131.6, 131.5, 130.8, 130.7, 130.2, 128.8, 126.2, 124.6, 122.7, 122.5, 117.1, 113.9, 101.2, 49.4, 39.7.



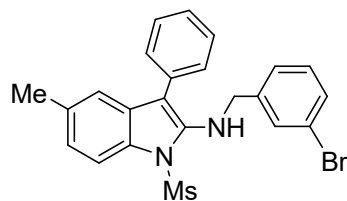
***N*-(3-Bromobenzyl)-3-(4-bromophenyl)-1-(methylsulfonyl)-1*H*-indol-2-amine**

(3q).¹ White solid (94.1 mg, 88%). Mp: 78-80 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.31-7.28 (m, 3H), 7.22-7.09 (m, 4H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 5.93 (t, *J* = 6.6 Hz, 1H), 4.03 (d, *J* = 6.4 Hz, 2H), 2.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 141.3, 140.2, 132.3, 131.8, 131.7, 131.4, 130.8, 130.6, 130.2, 126.2, 124.6, 122.6, 122.4, 121.1, 117.1, 113.9, 101.1, 49.4, 39.7.



***N*-(3-Bromobenzyl)-3-(2-bromophenyl)-1-(methylsulfonyl)-1*H*-indol-2-amine**

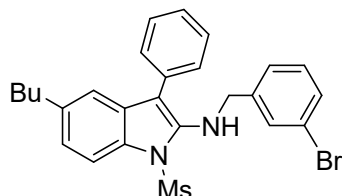
(3r).¹ White solid (84.4 mg, 79%). Mp: 78-80 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.31-7.18 (m, 4H), 7.15-7.03 (m, 4H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.03 (t, *J* = 6.0 Hz, 1H), 4.10-3.93 (m, 2H), 2.98 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 141.3, 140.3, 134.2, 133.5, 132.7, 132.3, 132.1, 130.5, 130.3, 130.1, 129.4, 127.2, 126.8, 125.7, 124.6, 122.6, 121.9, 117.3, 114.0, 100.4, 48.5, 39.3.



***N*-(3-Bromobenzyl)-5-methyl-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine**

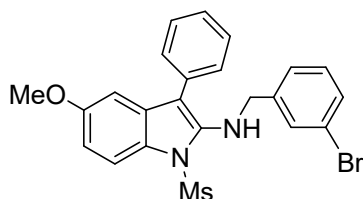
(3s).¹ Pale yellow oil (81.6 mg, 87%). ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.48-7.41 (m, 4H), 7.38-7.32 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.13 (s, 1H), 7.09-7.04 (m, 2H), 6.95 (t, *J* = 7.6 Hz, 2H), 5.83 (brs, 1H), 4.03 (d, *J* = 6.4 Hz, 2H), 2.81 (s, 3H), 2.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 141.7, 140.4, 134.3, 133.5,

132.3, 131.0, 130.7, 130.6, 130.3, 130.1, 128.7, 127.2, 126.4, 123.4, 122.6, 117.6, 113.9, 102.7, 49.5, 39.3, 21.4.



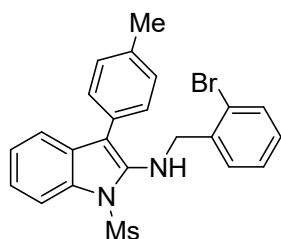
***N*-(3-Bromobenzyl)-5-*n*-butyl-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine**

(3t).¹ Pale yellow oil (86.9 mg, 85%). ¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, J = 8.4 Hz, 1H), 7.47-7.43 (m, 4H), 7.38-7.33 (m, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.13 (s, 1H), 7.09-7.04 (m, 2H), 6.96 (d, J = 8.4 Hz, 2H), 5.81 (brs, 1H), 4.03 (d, J = 2.8 Hz, 2H), 2.83 (s, 3H), 2.59 (t, J = 7.8 Hz, 2H), 1.58-1.52 (m, 2H), 1.35-1.28 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 141.7, 140.3, 139.5, 133.5, 132.1, 131.0, 130.8, 130.6, 130.3, 130.2, 128.7, 127.2, 126.4, 122.9, 122.6, 117.0, 113.8, 102.9, 49.5, 39.4, 35.8, 34.3, 22.6, 14.1.



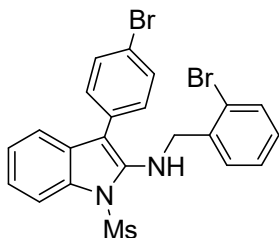
***N*-(3-Bromobenzyl)-5-methoxy-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine**

(3u).¹ Pale yellow oil (80.5 mg, 83%). ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, J = 8.8 Hz, 1H), 7.47-7.39 (m, 4H), 7.38-7.32 (m, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.13 (s, 1H), 7.07 (t, J = 7.8 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.74-6.69 (m, 2H), 5.83 (t, J = 6.4 Hz, 1H), 4.04 (d, J = 6.4 Hz, 2H), 3.75 (s, 3H), 2.79 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 157.7, 141.6, 141.4, 133.4, 133.3, 131.0, 130.6, 130.3, 130.2, 128.7, 127.3, 126.9, 126.3, 122.6, 115.0, 109.6, 102.9, 101.5, 55.8, 49.4, 39.0.



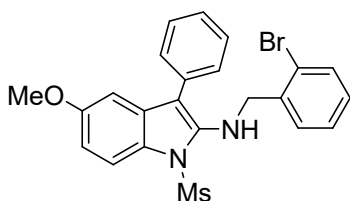
***N*-(2-Bromobenzyl)-1-(methylsulfonyl)-3-*p*-tolyl-1*H*-indol-2-amine (3v).** White solid (67.6 mg, 72%). Mp: 66-68 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, J = 8.0

Hz, 1H), 7.48-7.45 (m, 1H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.26-7.22 (m, 3H), 7.19-7.03 (m, 5H), 5.80 (t, $J = 6.2$ Hz, 1H), 4.17 (d, $J = 6.4$ Hz, 2H), 2.80 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.1, 138.4, 136.9, 133.0, 132.6, 132.1, 130.3, 130.1, 130.0, 129.4, 129.2, 127.6, 124.4, 124.2, 122.2, 117.4, 114.0, 102.8, 50.5, 39.6, 21.4. HRMS calcd for $\text{C}_{23}\text{H}_{21}\text{BrN}_2\text{NaO}_2\text{S}^+ [\text{M} + \text{Na}]^+$: 491.0399, found 491.0402.



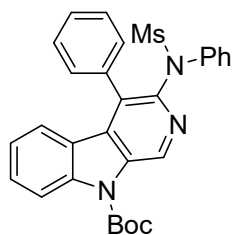
***N*-(2-Bromobenzyl)-3-(4-bromophenyl)-1-(methylsulfonyl)-1*H*-indol-2-amine**

(3w). White solid (88.6 mg, 83%). Mp: 78-80 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 7.6$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.23-7.13 (m, 4H), 7.12-7.05 (m, 2H), 5.89 (t, $J = 6.0$ Hz, 1H), 4.16 (d, $J = 6.4$ Hz, 2H), 2.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.4, 138.0, 133.1, 132.5, 132.4, 131.9, 131.8, 131.5, 129.7, 129.4, 127.7, 124.5, 124.1, 122.4, 121.1, 117.1, 114.0, 101.3, 50.7, 39.8. HRMS calcd for $\text{C}_{22}\text{H}_{18}\text{Br}_2\text{N}_2\text{NaO}_2\text{S}^+ [\text{M} + \text{Na}]^+$: 554.9348, found 554.9345.

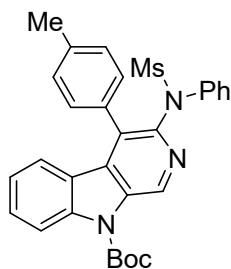


***N*-(2-Bromobenzyl)-5-methoxy-1-(methylsulfonyl)-3-phenyl-1*H*-indol-2-amine**

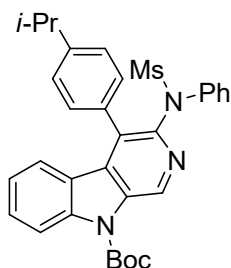
(3x).¹ Pale yellow oil (75.7 mg, 78%). ^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, $J = 8.8$ Hz, 1H), 7.48-7.41 (m, 5H), 7.36-7.31 (m, 1H), 7.18-7.14 (m, 1H), 7.10-7.05 (m, 2H), 6.75 (d, $J = 2.4$ Hz, 1H), 6.70 (dd, $J = 9.0, 2.6$ Hz, 1H), 5.82 (brs, 1H), 4.16 (d, $J = 4.0$ Hz, 2H), 3.76 (s, 3H), 2.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 157.6, 141.1, 138.3, 133.5, 133.4, 133.0, 130.2, 129.9, 129.3, 128.8, 127.7, 127.3, 126.9, 124.2, 115.1, 109.5, 103.0, 101.4, 55.8, 50.6, 39.1. HRMS calcd for $\text{C}_{23}\text{H}_{21}\text{BrN}_2\text{NaO}_3\text{S}^+ [\text{M} + \text{Na}]^+$: 507.0348, found 507.0357.



tert-Butyl 4-phenyl-3-(N-phenylmethylsulfonamido)-9H-pyrido[3,4-b]indole-9-carboxylate (5a).¹ White solid (99.6 mg, 97%). Mp: 203-205 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.52 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.50-7.40 (m, 4H), 7.22-7.17 (m, 2H), 7.14-7.09 (m, 3H), 7.05-6.98 (m, 3H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.39 (s, 3H), 1.81 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 150.4, 146.8, 140.5, 140.1, 135.9, 134.6, 133.3, 130.1, 129.8, 129.7, 128.7, 128.6, 128.3, 128.1, 127.2, 123.8, 123.4, 123.3, 116.4, 85.3, 40.1, 28.5.

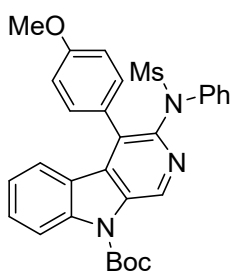


tert-Butyl 3-(N-phenylmethylsulfonamido)-4-p-tolyl-9H-pyrido[3,4-b]indole-9-carboxylate (5b).¹ White solid (93.9 mg, 89%). Mp: 210-212 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.50 (s, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.15-7.02 (m, 8H), 6.93 (d, *J* = 8.0 Hz, 1H), 3.38 (s, 3H), 2.47 (s, 3H), 1.81 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 150.5, 147.0, 140.6, 140.1, 138.1, 135.8, 134.6, 133.5, 131.6, 130.3, 129.7, 129.6, 129.4, 128.7, 128.1, 127.1, 124.0, 123.5, 123.4, 116.4, 85.3, 40.1, 28.6, 21.6.

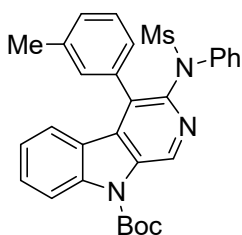


tert-Butyl 4-(4-isopropylphenyl)-3-(N-phenylmethylsulfonamido)-9H-pyrido[3,4-b]indole-9-carboxylate (5c). White solid (102.2 mg, 92%). Mp: 210-212 °C. ¹H

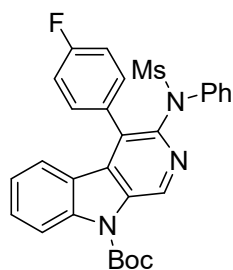
NMR (400 MHz, CDCl₃): δ 9.49 (s, 1H), 8.36 (d, J = 8.8 Hz, 1H), 7.50-7.46 (m, 1H), 7.26 (d, J = 7.2 Hz, 1H), 7.14-7.02 (m, 7H), 6.97 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 7.2 Hz, 2H), 3.42 (s, 3H), 3.05-2.98 (m, 1H), 1.81 (s, 9H), 1.36 (d, J = 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 150.4, 149.2, 147.2, 140.4, 140.0, 135.6, 134.5, 133.3, 131.8, 129.9, 129.7, 129.6, 128.5, 128.2, 127.1, 126.7, 123.9, 123.5, 123.4, 116.3, 85.2, 40.2, 34.2, 28.5, 24.3. HRMS calcd for C₃₂H₃₃N₃NaO₄S⁺ [M + Na]⁺: 578.2084, found 578.2086.



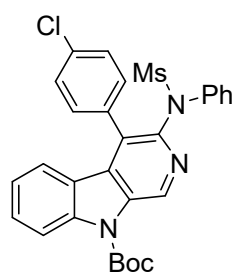
tert-Butyl 4-(4-methoxyphenyl)-3-(N-phenylmethylsulfonamido)-9H-pyrido[3,4-*b*]indole-9-carboxylate (5d).¹ White solid (77.2 mg, 71%). Mp: 210-212 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.50 (s, 1H), 8.37 (d, J = 8.4 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.18-7.10 (m, 5H), 7.09-7.02 (m, 3H), 7.01-6.94 (m, 3H), 3.92 (s, 3H), 3.40 (s, 3H), 1.81 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 159.7, 150.4, 147.1, 140.5, 140.0, 135.7, 134.6, 133.6, 130.9, 129.9, 129.7, 128.7, 128.1, 127.2, 126.8, 123.9, 123.5, 123.4, 116.3, 114.2, 85.3, 55.5, 40.0, 28.5.



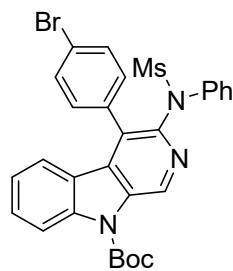
tert-Butyl 3-(N-phenylmethylsulfonamido)-4-*m*-tolyl-9H-pyrido[3,4-*b*]indole-9-carboxylate (5e).¹ White solid (86.5 mg, 82%). Mp: 203-205 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.51 (s, 1H), 8.36 (d, J = 8.4 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.33-7.27 (m, 2H), 7.14-7.11 (m, 3H), 7.06-6.95 (m, 4H), 6.89 (d, J = 8.0 Hz, 2H), 3.39 (s, 3H), 2.31 (s, 3H), 1.81 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 150.4, 146.8, 140.5, 140.0, 138.3, 135.7, 134.5, 134.4, 133.3, 130.2, 130.1, 129.7, 129.0, 128.6, 128.5, 128.2, 127.1, 126.6, 123.8, 123.5, 123.4, 116.3, 85.3, 40.1, 28.5, 21.5.



tert-Butyl 4-(4-fluorophenyl)-3-(N-phenylmethylsulfonamido)-9H-pyrido[3,4-b]indole-9-carboxylate (5f).¹ White solid (99.8 mg, 94%). Mp: 203-205 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.54 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.19-7.11 (m, 7H), 7.09-7.00 (m, 3H), 6.88 (d, *J* = 8.0 Hz, 1H), 3.40 (s, 3H), 1.81 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 162.9 (d, *J* = 246.1 Hz), 150.3, 146.9, 140.3, 140.0, 136.1, 134.5, 133.3, 131.6 (d, *J* = 8.1 Hz), 130.5 (d, *J* = 3.3 Hz), 129.9, 128.9, 128.8, 127.9, 127.3, 123.6, 123.5, 123.2, 116.5, 115.9 (d, *J* = 21.3 Hz), 85.4, 40.0, 28.5.

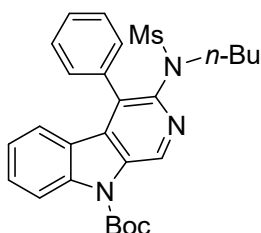


tert-Butyl 4-(4-chlorophenyl)-3-(N-phenylmethylsulfonamido)-9H-pyrido[3,4-b]indole-9-carboxylate (5g).¹ White solid (104.1 mg, 95%). Mp: 205-207 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.53 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.22-7.01 (m, 8H), 6.90 (d, *J* = 7.6 Hz, 1H), 3.39 (s, 3H), 1.81 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 150.3, 146.7, 140.3, 140.1, 136.3, 134.6, 134.5, 133.1, 131.2, 130.0, 129.1, 128.9, 128.8, 127.9, 127.3, 123.6, 123.5, 123.2, 116.5, 85.5, 40.0, 28.5.

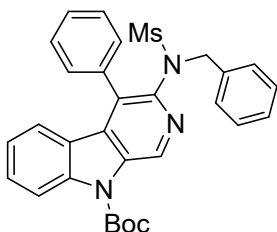


tert-Butyl 4-(4-bromophenyl)-3-(N-phenylmethylsulfonamido)-9H-pyrido[3,4-

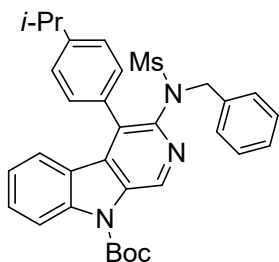
b]indole-9-carboxylate (5h).¹ White solid (110.2 mg, 93%). Mp: 212-214 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.53 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.18-7.13 (m, 3H), 7.12-7.05 (m, 3H), 7.04-6.99 (m, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.39 (s, 3H), 1.81 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 150.4, 146.7, 140.4, 140.1, 136.3, 134.6, 133.7, 133.1, 132.0, 131.6, 130.0, 128.9, 128.8, 127.9, 127.3, 123.6, 123.5, 123.2, 122.8, 116.5, 85.5, 40.1, 28.5.



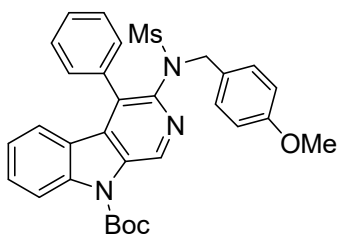
tert-Butyl 3-(*N*-butylmethylsulfonamido)-4-phenyl-9*H*-pyrido[3,4-*b*]indole-9-carboxylate (5i).¹ White solid (66.1 mg, 67%). Mp: 193-195 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.47 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.61-7.46 (m, 6H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.47 (t, *J* = 7.6 Hz, 2H), 3.15 (s, 3H), 1.80 (s, 9H), 1.29-1.23 (m, 2H), 1.11-1.03 (m, 2H), 0.75 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 150.4, 145.1, 140.1, 136.4, 135.0, 134.6, 133.2, 131.6, 130.3, 129.7, 128.7, 128.6, 123.9, 123.5, 123.4, 116.4, 85.3, 51.1, 38.9, 30.3, 28.5, 20.1, 13.8.



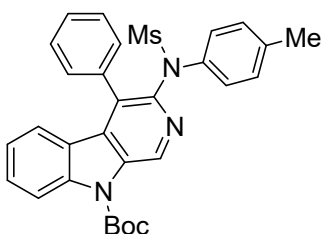
tert-Butyl 3-(*N*-benzylmethylsulfonamido)-4-phenyl-9*H*-pyrido[3,4-*b*]indole-9-carboxylate (5j).¹ White solid (81.2 mg, 77%). Mp: 199-201 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.51 (s, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.49-7.40 (m, 2H), 7.38-7.32 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 2H), 7.01-6.92 (m, 5H), 6.63 (d, *J* = 8.0 Hz, 1H), 4.67 (s, 2H), 3.11 (s, 3H), 1.81 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 150.4, 144.9, 140.0, 136.3, 135.3, 134.6, 134.5, 133.2, 131.8, 130.1, 129.9, 129.6, 128.5, 128.4, 128.1, 127.8, 123.9, 123.5, 123.4, 116.3, 85.3, 55.1, 39.1, 28.5.



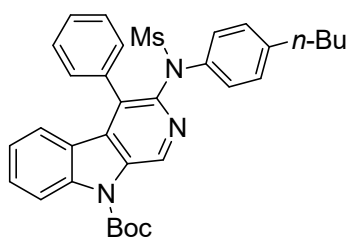
tert-Butyl 3-(N-benzylmethylsulfonamido)-4-(4-isopropylphenyl)-9H-pyrido[3,4-b]indole-9-carboxylate (5k). White solid (84.3 mg, 74%). Mp: 206-208 °C. ^1H NMR (400 MHz, CDCl_3): δ 9.48 (s, 1H), 8.33 (d, $J = 8.4$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.23-7.16 (m, 4H), 7.11 (t, $J = 7.4$ Hz, 2H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.95-6.91 (m, 3H), 6.70 (d, $J = 8.0$ Hz, 1H), 4.64 (s, 2H), 3.10 (s, 3H), 3.04-2.97 (m, 1H), 1.80 (s, 9H), 1.35 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.4, 148.8, 145.2, 140.0, 136.1, 135.4, 134.6, 133.3, 131.8, 131.7, 129.9, 129.8, 129.5, 128.4, 127.8, 126.4, 124.0, 123.6, 123.3, 116.2, 85.3, 55.1, 39.4, 34.1, 28.5, 24.2. HRMS calcd for $\text{C}_{33}\text{H}_{35}\text{N}_3\text{NaO}_4\text{S}^+ [\text{M} + \text{Na}]^+$: 592.2240, found 592.2235.



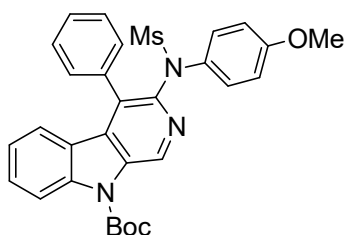
tert-Butyl 3-(N-(4-methoxybenzyl)methylsulfonamido)-4-phenyl-9H-pyrido[3,4-b]indole-9-carboxylate (5l). White solid (80.3 mg, 72%). Mp: 200-202 °C. ^1H NMR (400 MHz, CDCl_3): δ 9.50 (s, 1H), 8.34 (d, $J = 8.4$ Hz, 1H), 7.49-7.33 (m, 6H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.85 (d, $J = 8.4$ Hz, 2H), 6.67-6.63 (m, 3H), 4.61 (s, 2H), 3.74 (s, 3H), 3.09 (s, 3H), 1.81 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.4, 150.4, 145.0, 140.0, 136.3, 134.7, 134.6, 133.2, 131.9, 131.2, 130.1, 129.6, 128.3, 128.1, 127.4, 123.9, 123.5, 123.4, 116.3, 113.9, 85.4, 55.4, 54.6, 39.1, 28.6. HRMS calcd for $\text{C}_{31}\text{H}_{31}\text{N}_3\text{NaO}_5\text{S}^+ [\text{M} + \text{Na}]^+$: 580.1877, found 580.1879.



***tert*-Butyl 4-phenyl-3-(*N*-*p*-tolylmethylsulfonamido)-9*H*-pyrido[3,4-*b*]indole-9-carboxylate (5m).**¹ White solid (99.1 mg, 94%). Mp: 198-200 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.51 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.50-7.41 (m, 4H), 7.25-7.20 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.94-6.86 (m, 5H), 3.37 (s, 3H), 2.25 (s, 3H), 1.81 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 150.4, 146.8, 140.0, 137.7, 137.2, 135.9, 134.6, 134.5, 133.2, 130.0, 129.7, 129.6, 129.3, 128.7, 128.3, 128.1, 123.8, 123.4, 123.3, 116.3, 85.3, 39.8, 28.5, 21.1.

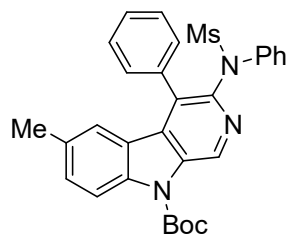


***tert*-Butyl 3-(*N*-(4-butylphenyl)methylsulfonamido)-4-phenyl-9*H*-pyrido[3,4-*b*]indole-9-carboxylate (5n).** Pale yellow oil (104.7 mg, 92%). ¹H NMR (400 MHz, CDCl₃): δ 9.50 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.50-7.41 (m, 4H), 7.21-7.17 (m, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.93-6.85 (m, 5H), 3.40 (s, 3H), 2.50 (t, *J* = 7.6 Hz, 2H), 1.81 (s, 9H), 1.54-1.47 (m, 2H), 1.29-1.23 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 150.4, 147.0, 142.1, 140.0, 137.9, 135.8, 134.7, 134.5, 133.3, 129.9, 129.8, 129.7, 128.7, 128.6, 128.3, 128.0, 123.8, 123.4, 116.3, 85.3, 40.0, 35.2, 33.5, 28.5, 22.3, 14.0. HRMS calcd for C₃₃H₃₅N₃NaO₄S⁺ [M + Na]⁺: 592.2240, found 592.2249.

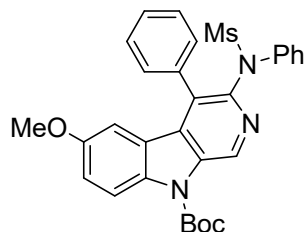


***tert*-Butyl 3-(*N*-(4-methoxyphenyl)methylsulfonamido)-4-phenyl-9*H*-pyrido[3,4-*b*]indole-9-carboxylate (5o).**¹ White solid (101.1 mg, 93%). Mp: 200-202 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.49 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.51-7.43 (m, 4H), 7.25-7.21 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.92-6.85 (m, 3H), 6.64 (d, *J* = 9.2 Hz, 2H), 3.72 (s, 3H), 3.38 (s, 3H), 1.81 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 158.8, 150.4, 147.0, 140.0, 135.9, 134.7, 134.5, 133.3, 133.0, 129.9, 129.8, 129.7, 129.6,

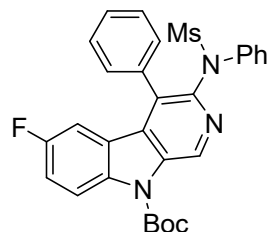
128.8, 128.4, 123.8, 123.4, 116.3, 113.9, 85.3, 55.5, 39.8, 28.5.



tert-Butyl 6-methyl-4-phenyl-3-(N-phenylmethylsulfonamido)-9H-pyrido[3,4-b]indole-9-carboxylate (5p).¹ White solid (96.1 mg, 91%). Mp: 201-203 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.49 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.49-7.40 (m, 3H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.20-7.17 (m, 2H), 7.14-7.10 (m, 3H), 7.00-6.97 (m, 2H), 6.60 (s, 1H), 3.40 (s, 3H), 2.17 (s, 3H), 1.80 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 150.4, 146.8, 140.6, 138.2, 135.9, 134.8, 134.7, 133.3, 133.0, 131.0, 130.1, 129.8, 128.7, 128.6, 128.3, 128.1, 127.1, 124.0, 123.4, 116.0, 85.1, 40.1, 28.5, 21.3.

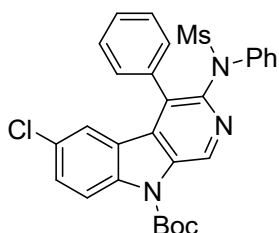


tert-Butyl 6-methoxy-4-phenyl-3-(N-phenylmethylsulfonamido)-9H-pyrido[3,4-b]indole-9-carboxylate (5q).¹ White solid (103.2 mg, 95%). Mp: 212-214 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.49 (s, 1H), 8.24 (d, *J* = 9.2 Hz, 1H), 7.47-7.41 (m, 3H), 7.22-7.18 (m, 2H), 7.15-7.11 (m, 3H), 7.07 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.03-6.99 (m, 2H), 6.25 (d, *J* = 2.4 Hz, 1H), 3.44 (s, 3H), 3.41 (s, 3H), 1.80 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 155.8, 150.4, 146.4, 140.6, 136.0, 135.0, 134.6, 134.5, 133.1, 130.0, 129.9, 128.7, 128.6, 128.3, 128.1, 127.2, 124.5, 118.6, 117.2, 105.6, 85.1, 55.2, 40.1, 28.5.



tert-Butyl 6-fluoro-4-phenyl-3-(N-phenylmethylsulfonamido)-9H-pyrido[3,4-b]indole-9-carboxylate (5r).¹ White solid (93.5 mg, 88%). Mp: 207-209 °C. ¹H NMR

(400 MHz, CDCl₃): δ 9.51 (s, 1H), 8.35 (dd, $J = 9.2, 4.4$ Hz, 1H), 7.51-7.41 (m, 3H), 7.24-7.10 (m, 6H), 7.01-6.98 (m, 2H), 6.50 (dd, $J = 8.8, 2.4$ Hz, 1H), 3.39 (s, 3H), 1.81 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 158.8 (d, $J = 240.0$ Hz), 150.2, 146.7, 140.3, 136.3, 136.1, 135.0, 133.9, 132.5 (d, $J = 3.8$ Hz), 130.2, 129.5, 128.9, 128.7 (d, $J = 7.8$ Hz), 128.1, 127.3, 124.7 (d, $J = 9.9$ Hz), 117.5, 117.4 (d, $J = 25.8$ Hz), 109.2 (d, $J = 25.1$ Hz), 85.6, 40.0, 28.5.

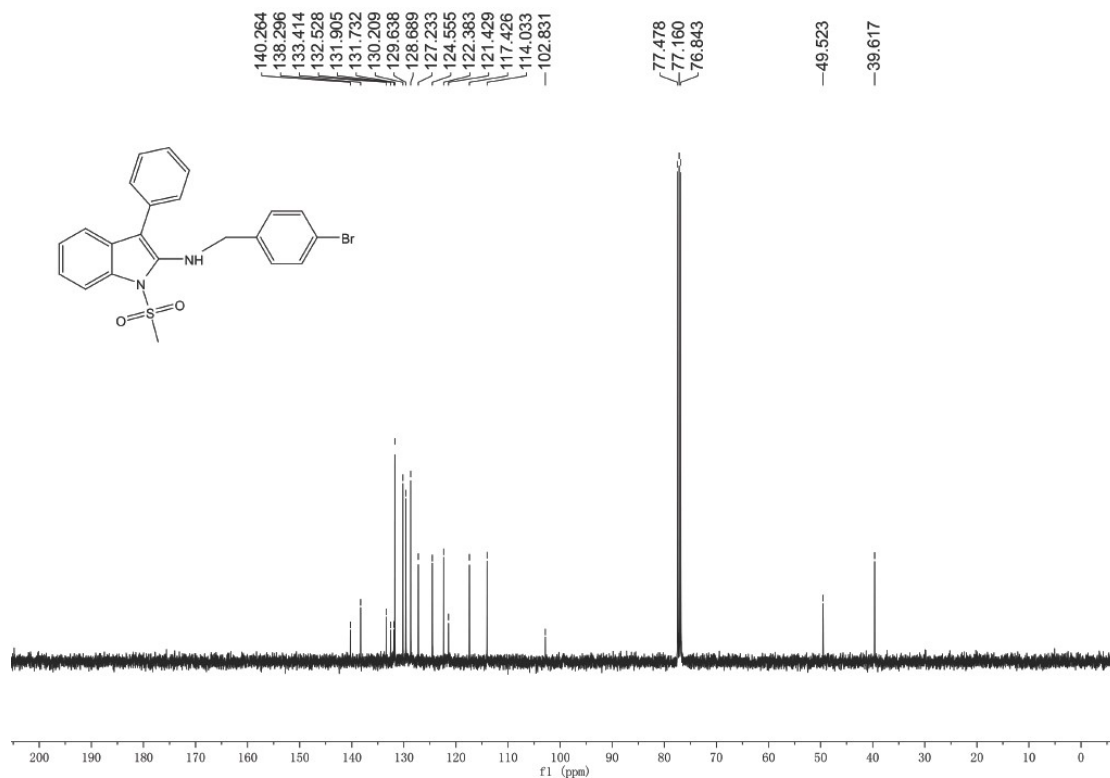
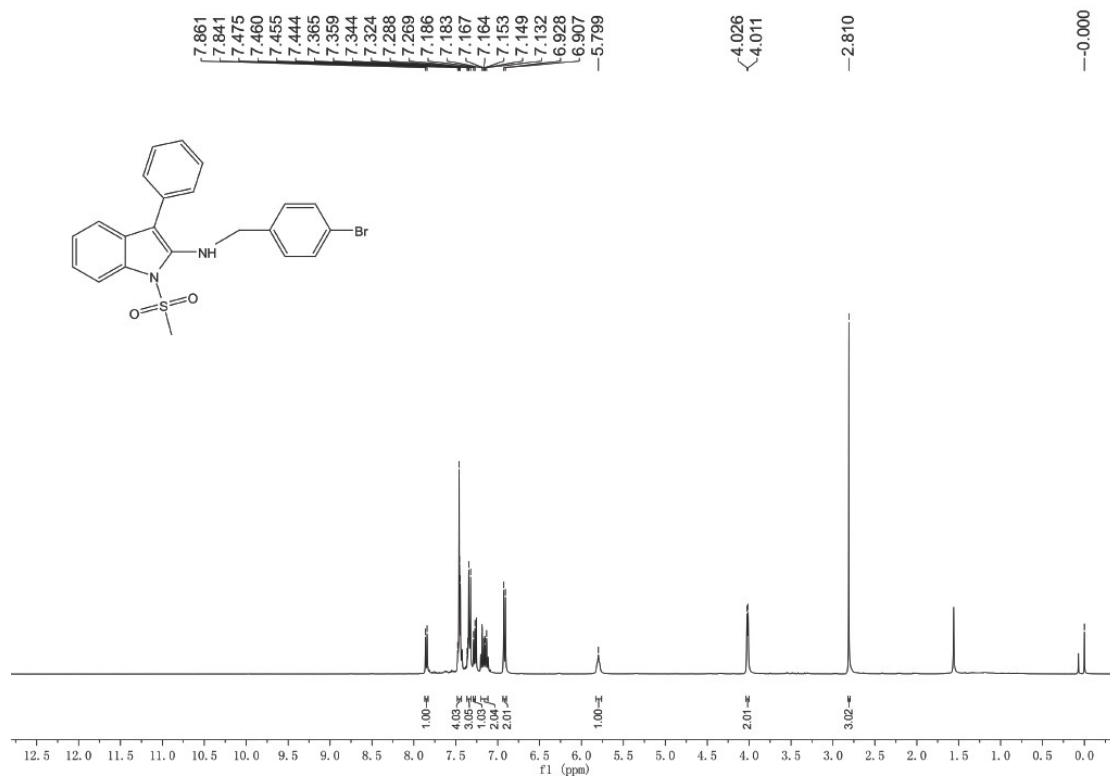


tert-Butyl 6-chloro-4-phenyl-3-(N-phenylmethylsulfonamido)-9H-pyrido[3,4-b]indole-9-carboxylate (5s).¹ White solid (92.1 mg, 84%). Mp: 200-202 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.50 (s, 1H), 8.31 (d, $J = 8.8$ Hz, 1H), 7.50-7.42 (m, 4H), 7.18-7.11 (m, 5H), 6.99-6.96 (m, 2H), 6.78 (d, $J = 2.0$ Hz, 1H), 3.39 (s, 3H), 1.81 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 150.1, 146.9, 140.3, 138.4, 136.1, 134.8, 133.9, 132.2, 130.2, 129.9, 129.5, 129.0, 128.9, 128.7, 128.6, 128.1, 127.3, 125.0, 123.0, 117.5, 85.8, 40.1, 28.5.

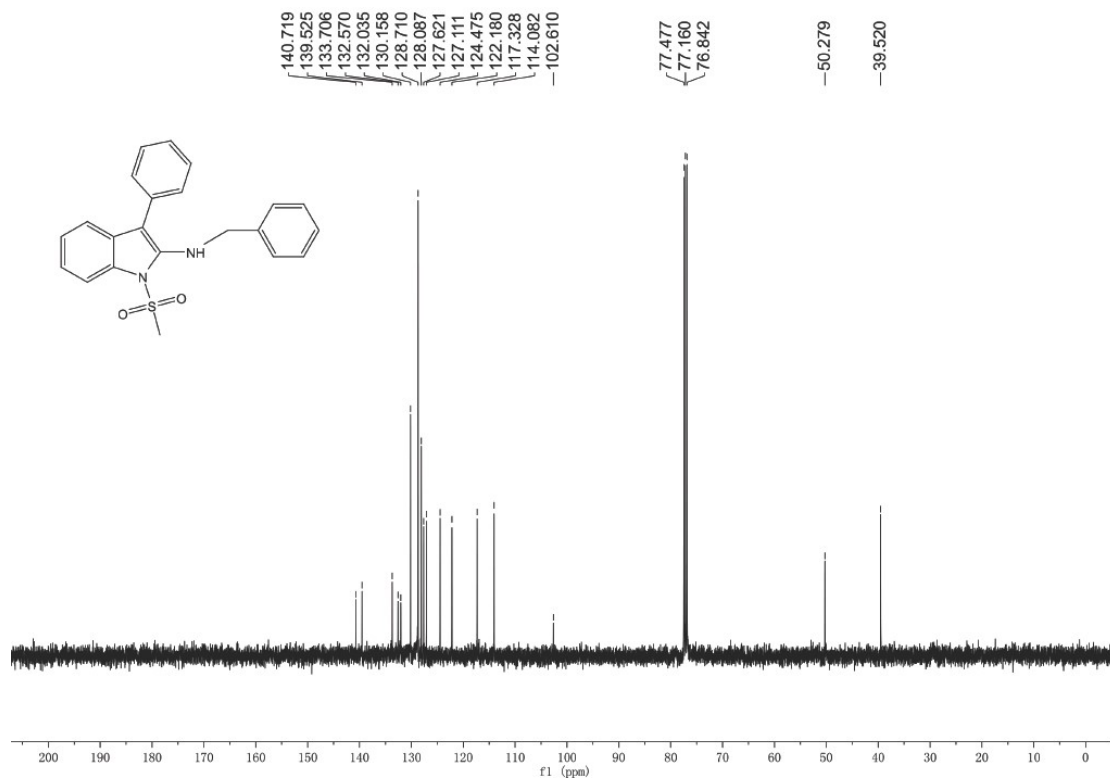
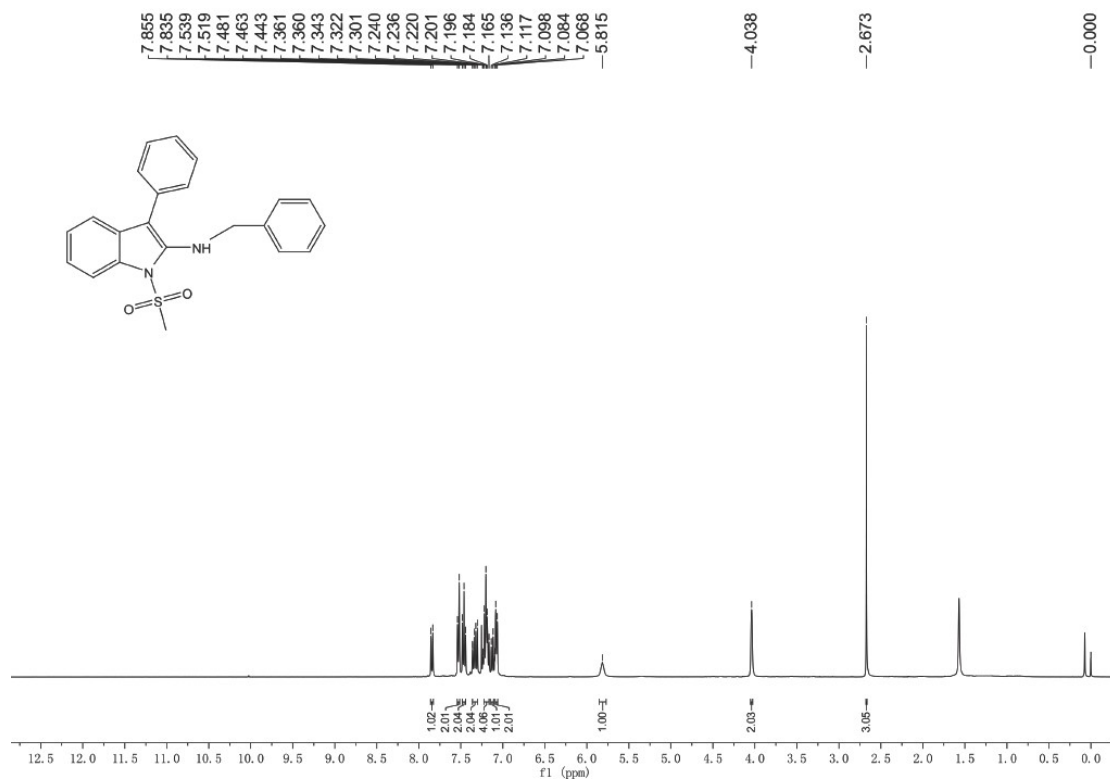
3. References

- 1 C. Shu, Y.-H. Wang, B. Zhou, X.-L. Li, Y.-F. Ping, X. Lu and L.-W. Ye, *J. Am. Chem. Soc.*, 2015, **137**, 9567-9570.
- 2 J. T. Sarmiento, S. Suarez-Pantiga, A. Olmos, T. Varea and G. Asensio, *ACS Catal.*, 2017, **7**, 7146-7155.

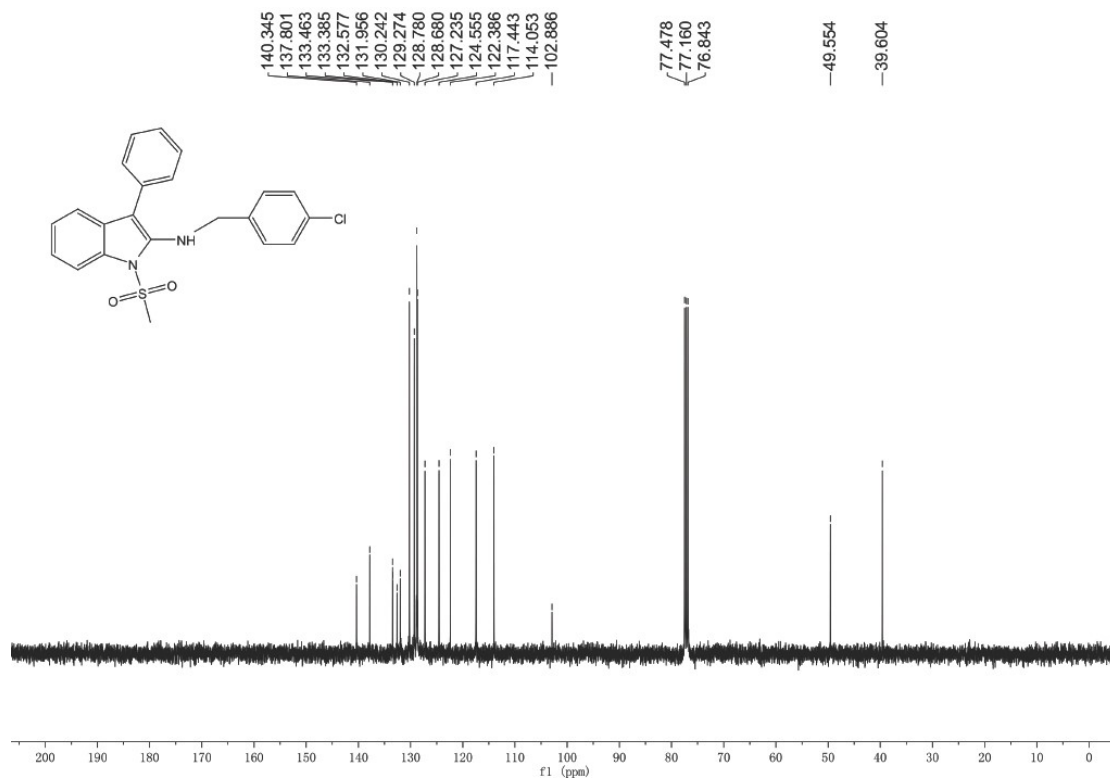
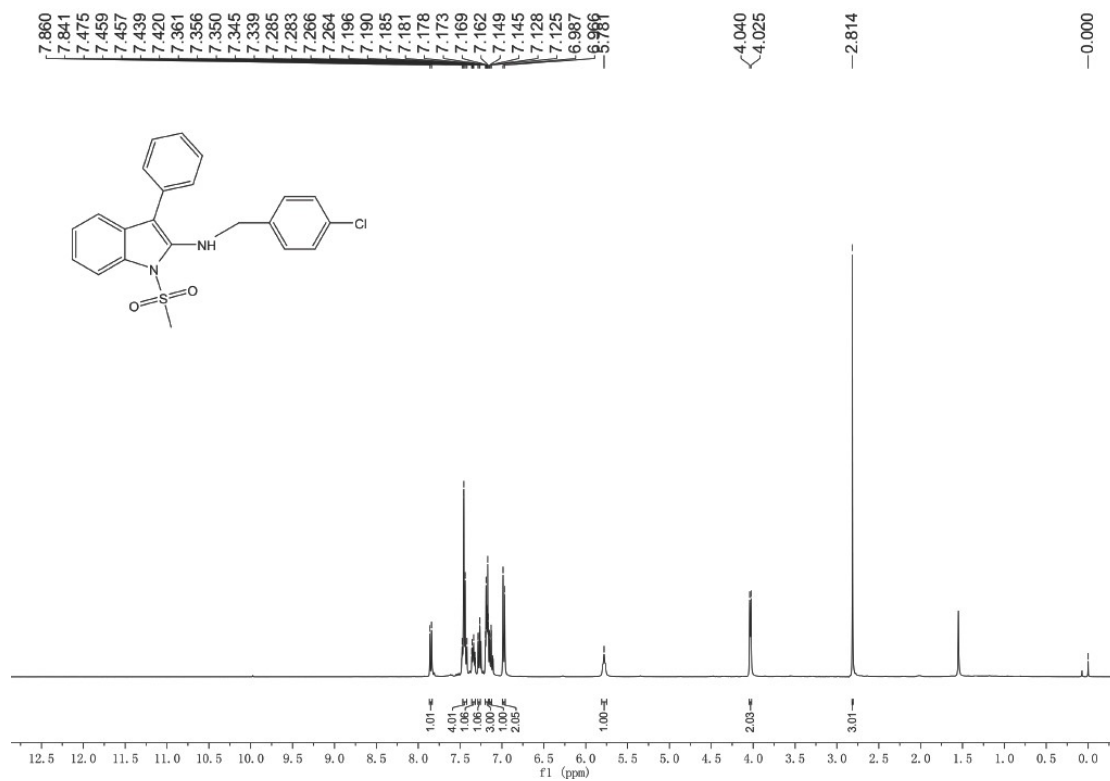
4. Copies of ^1H NMR and ^{13}C NMR spectra of compounds 3a-x and 5a-s.



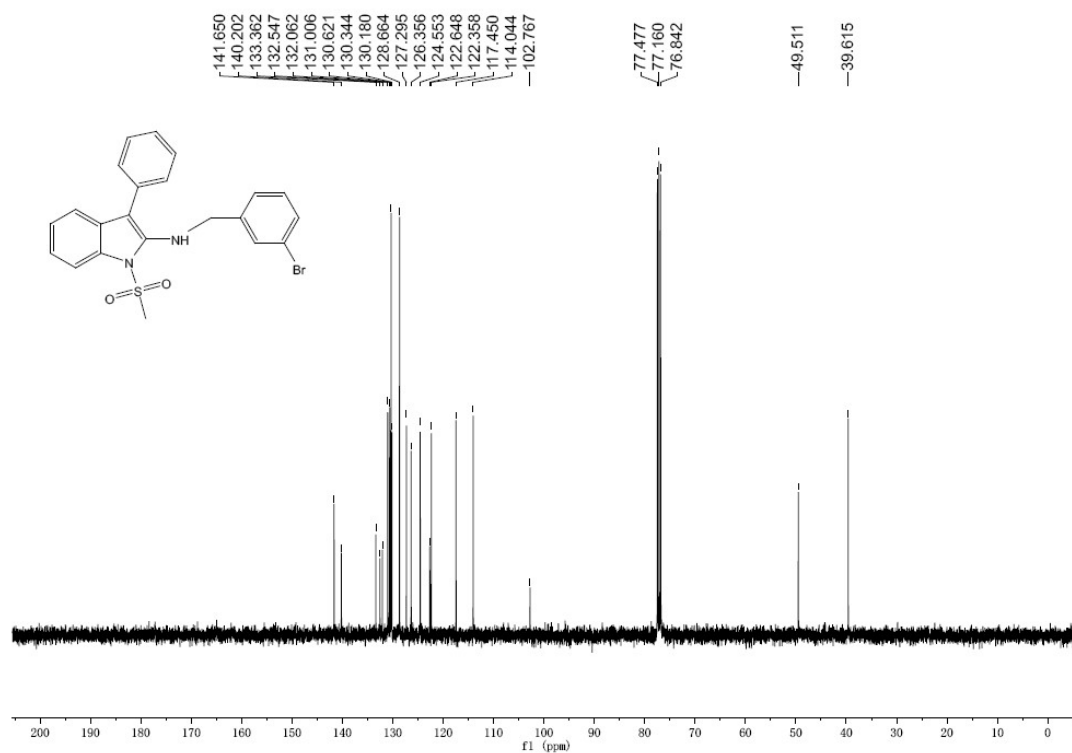
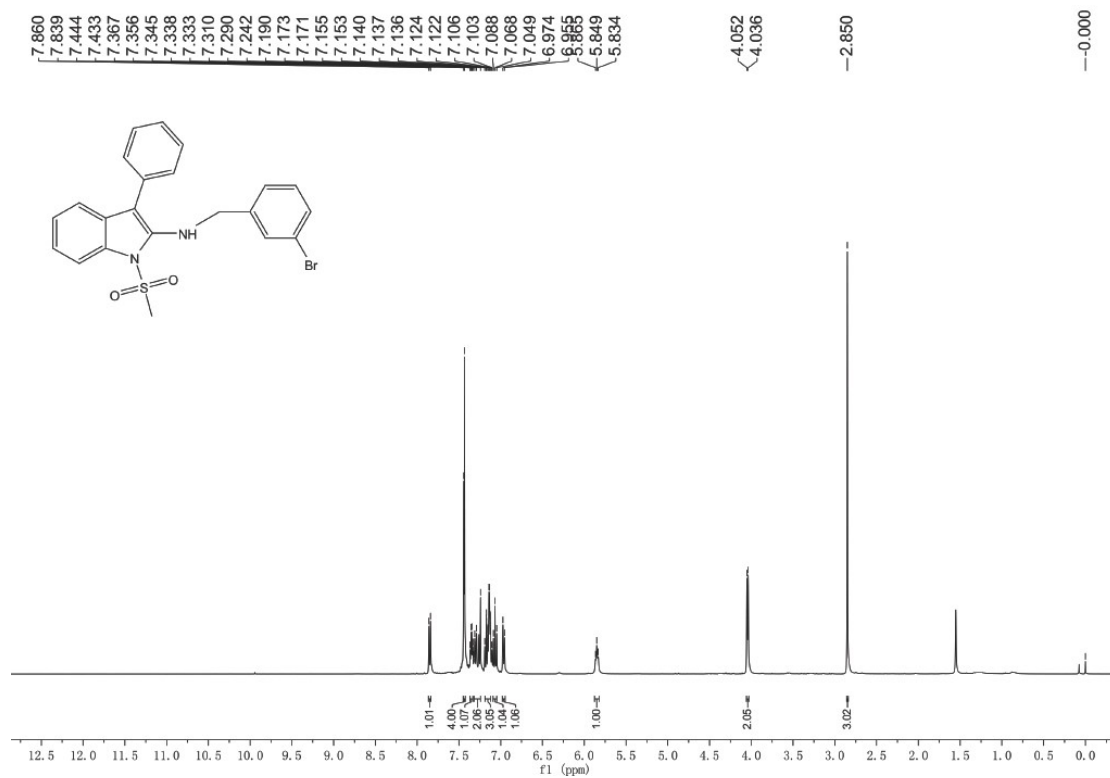
¹H NMR and ¹³C NMR spectra of compound **3a**



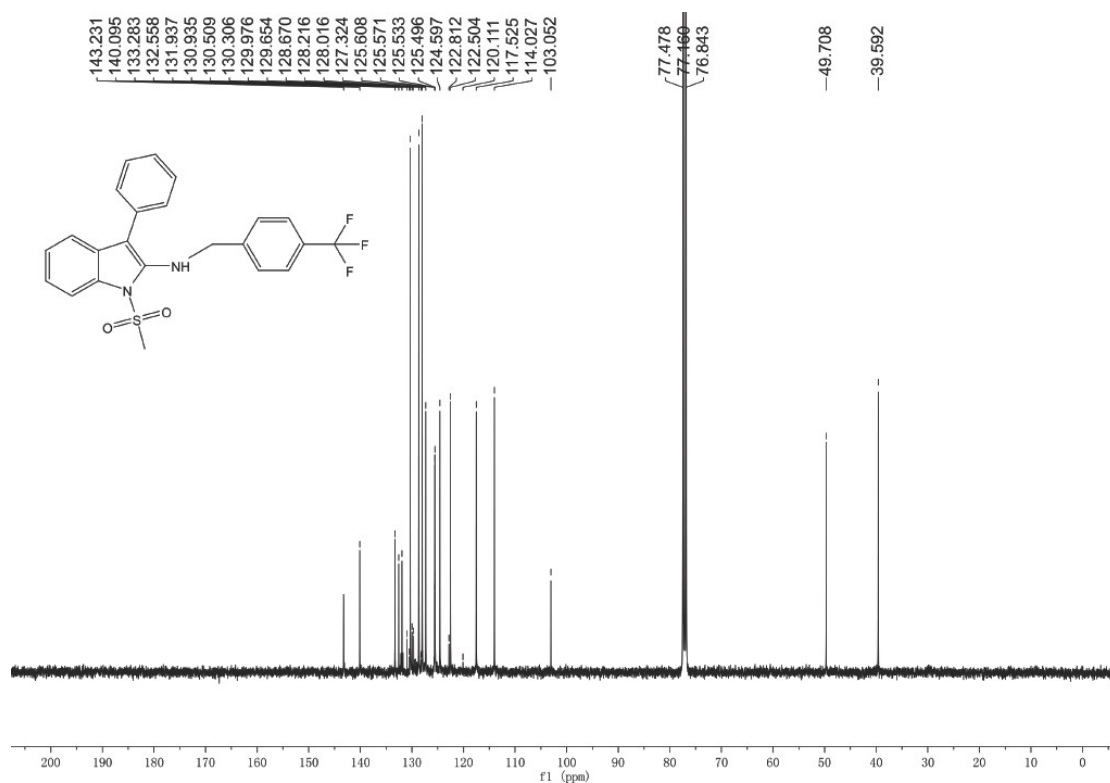
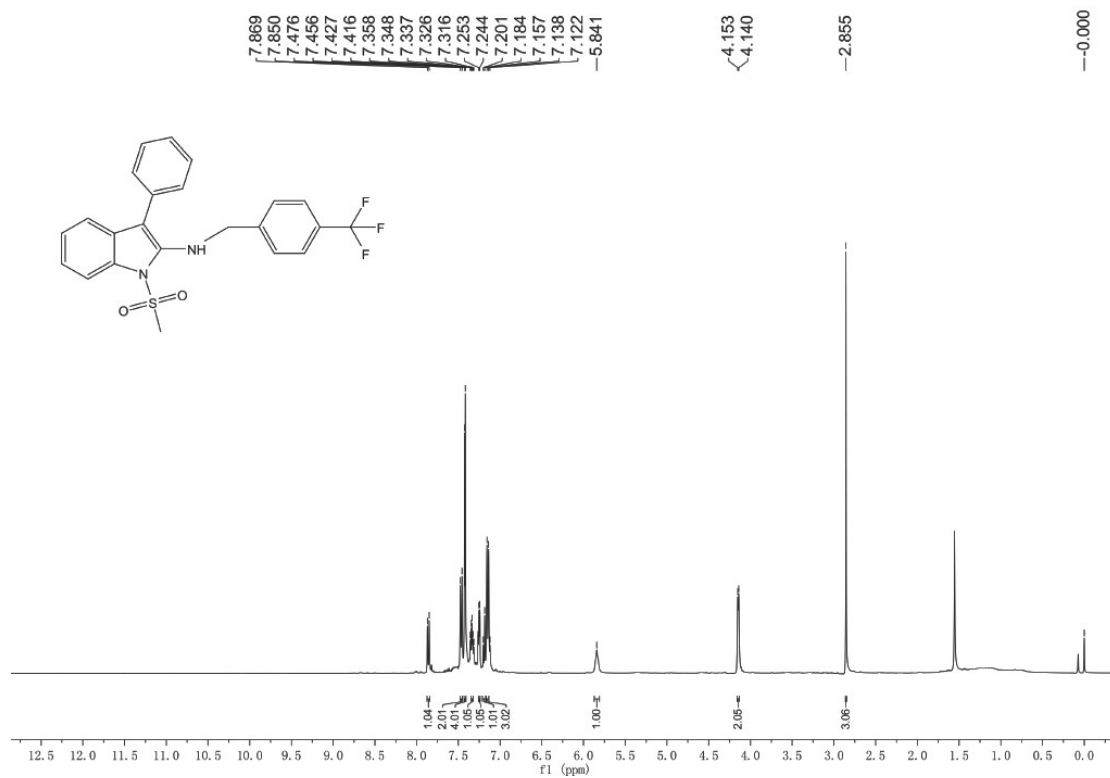
¹H NMR and ¹³C NMR spectra of compound **3b**



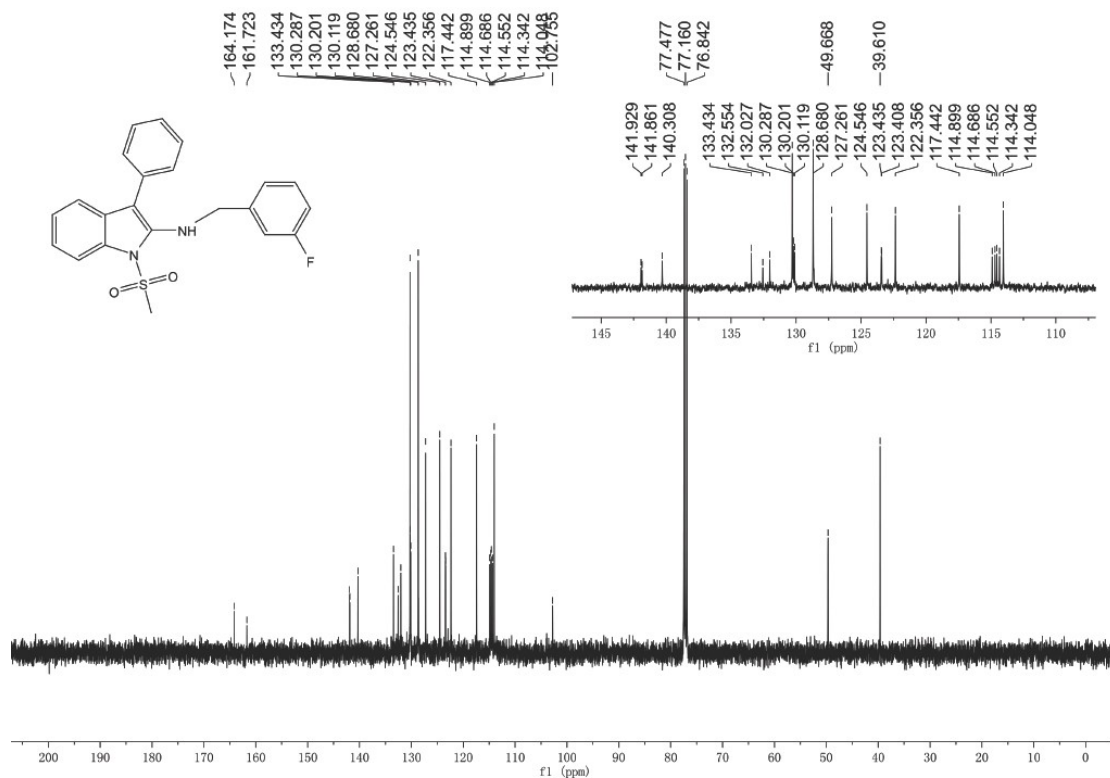
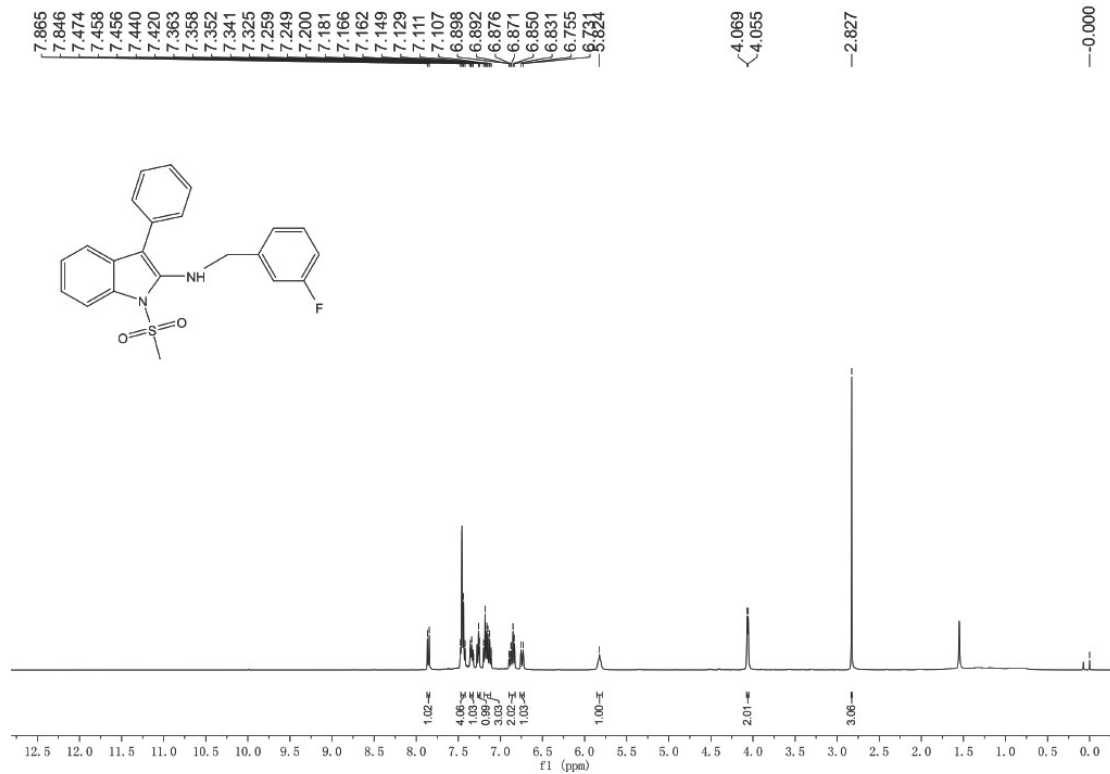
¹H NMR and ¹³C NMR spectra of compound 3c



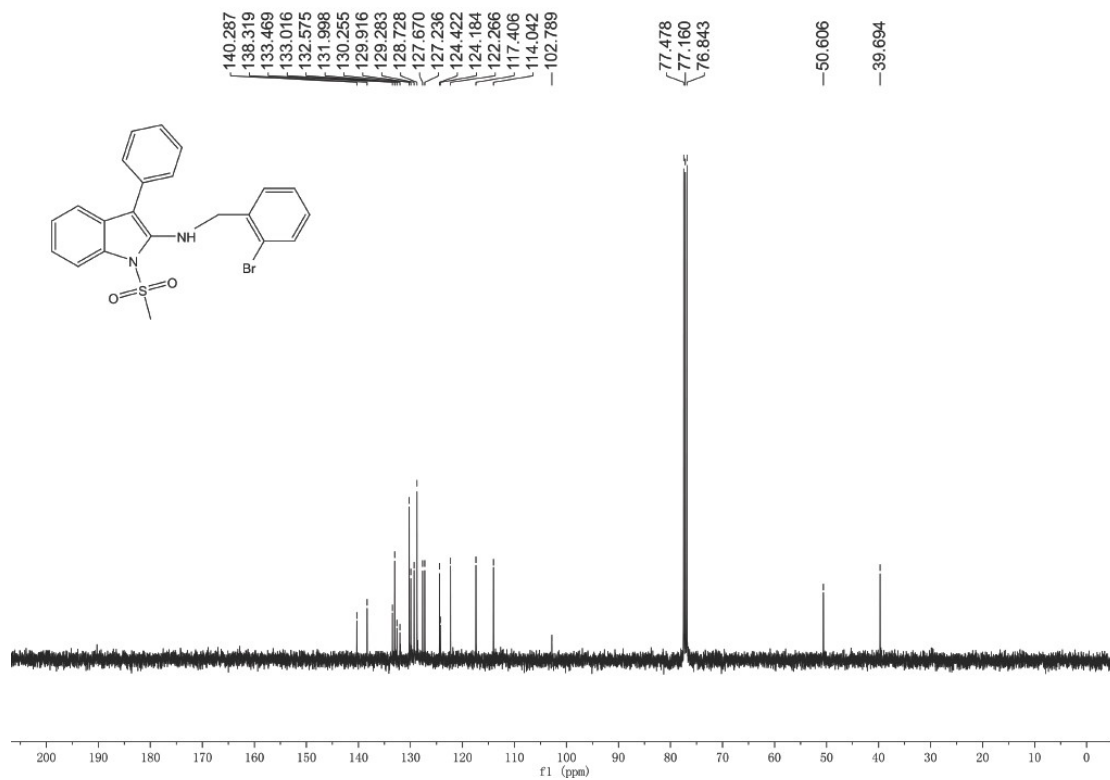
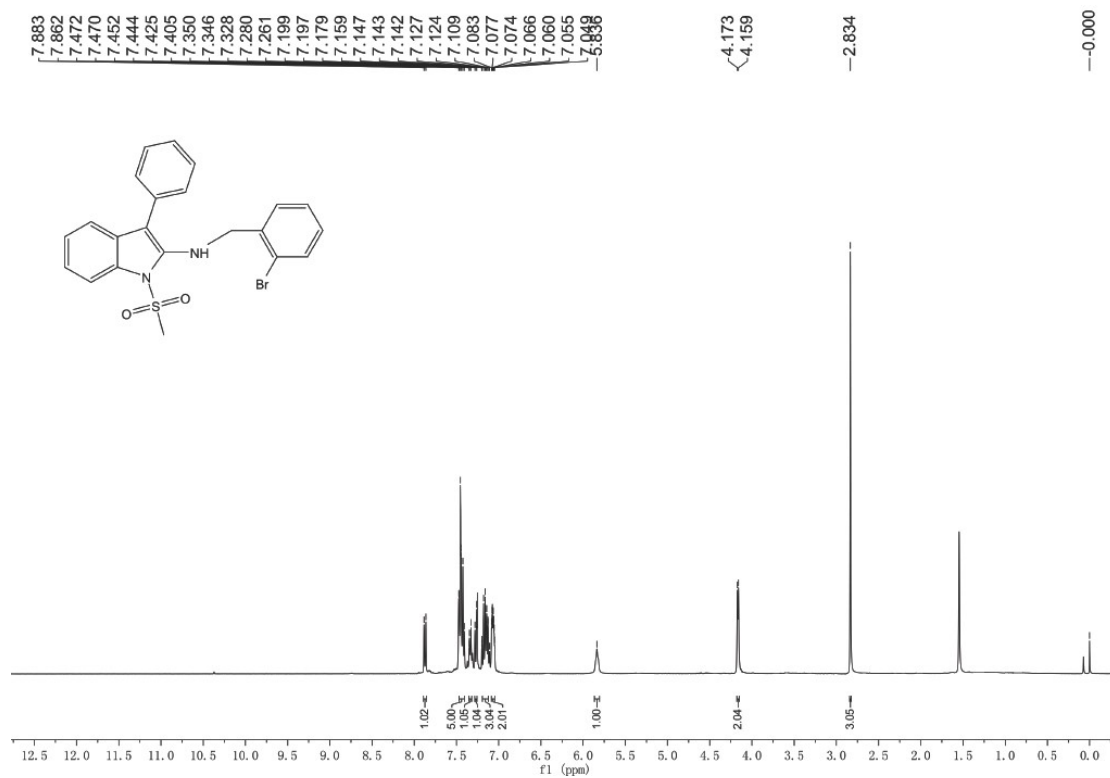
¹H NMR and ¹³C NMR spectra of compound **3d**



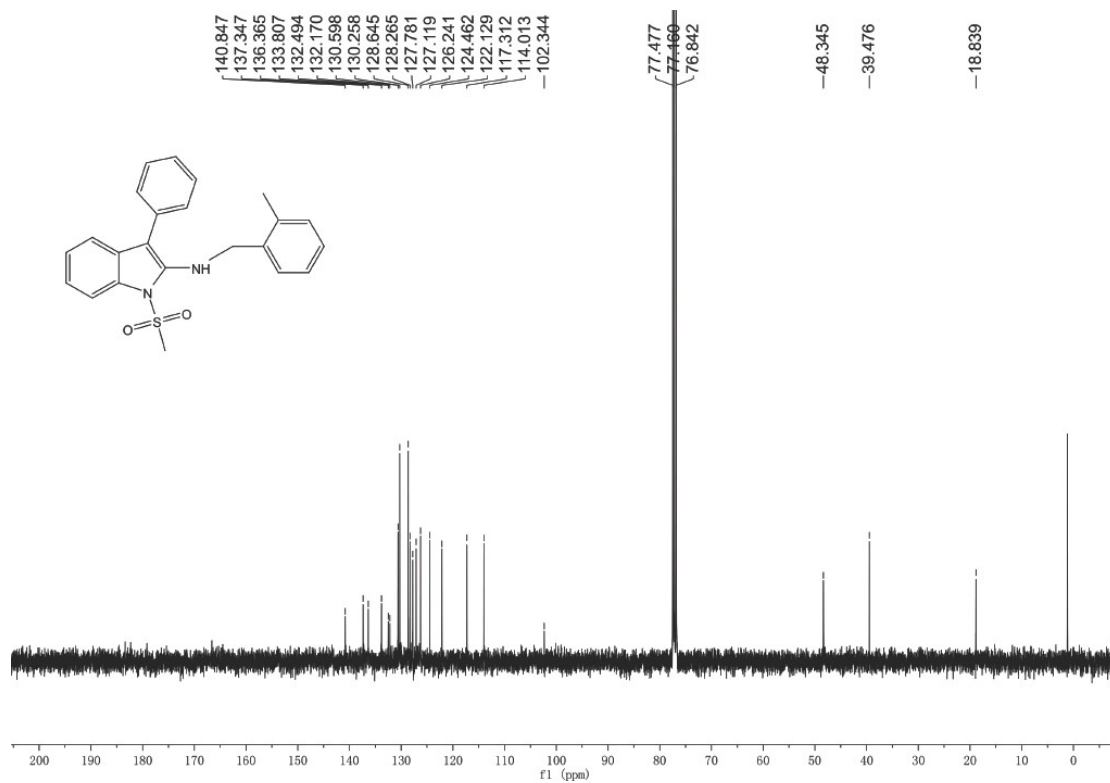
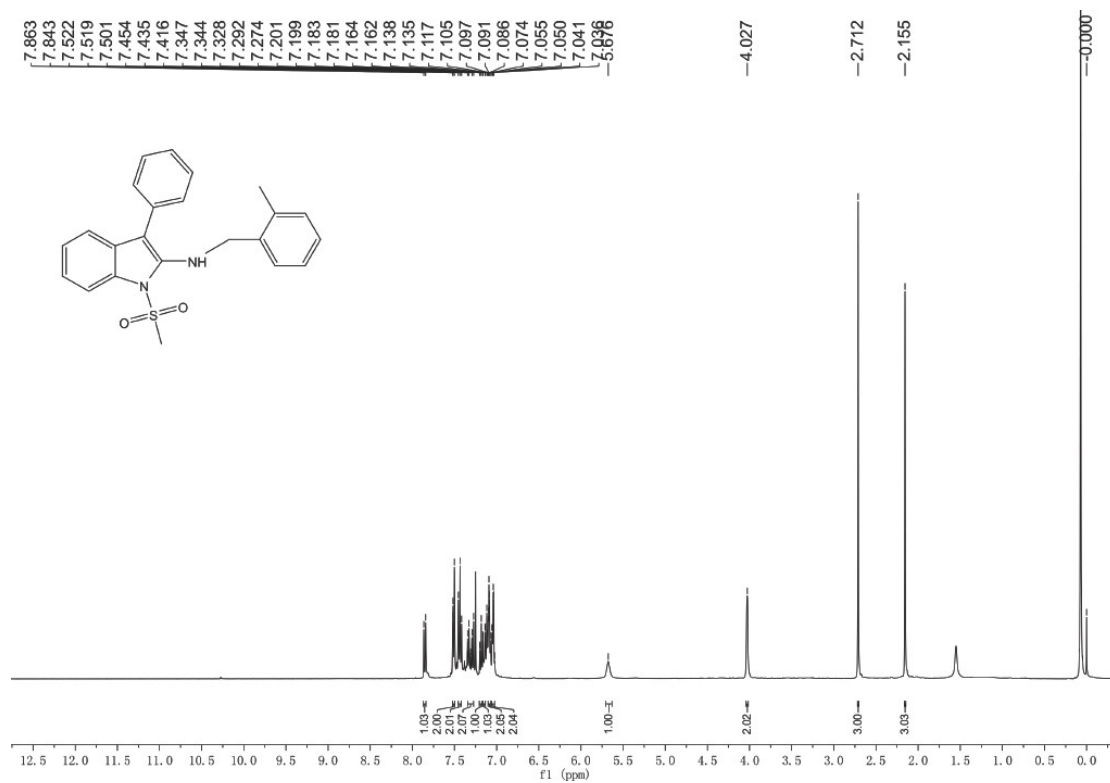
¹H NMR and ¹³C NMR spectra of compound 3e



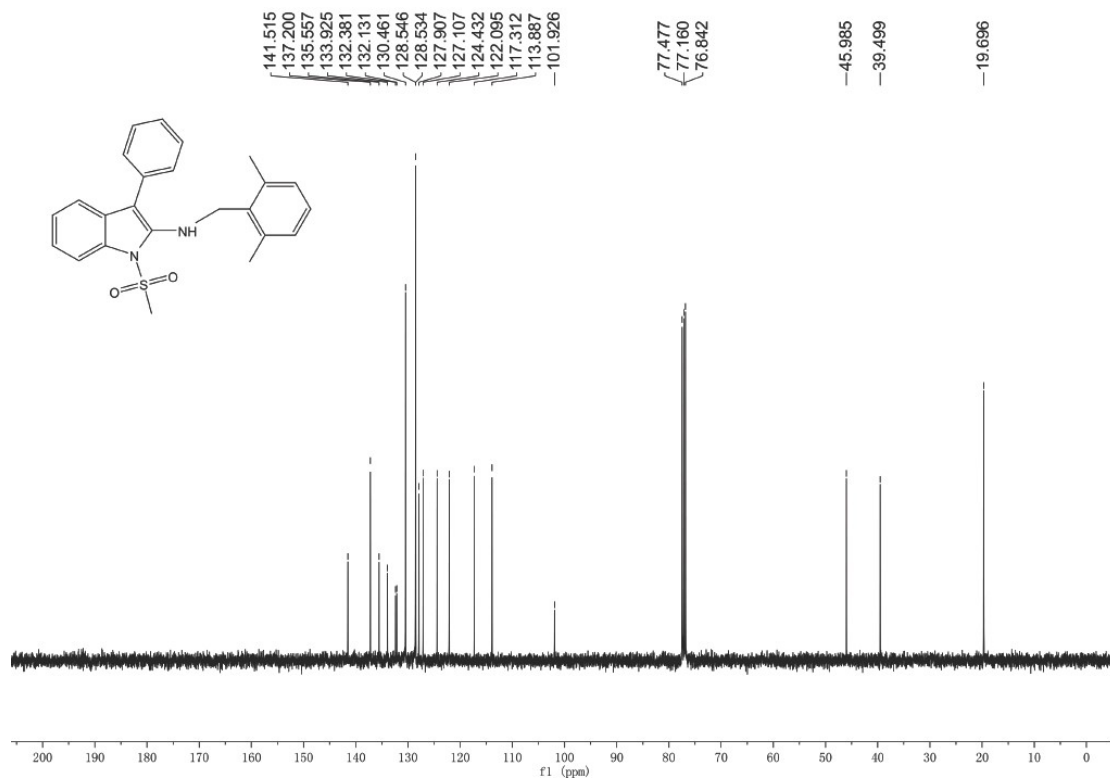
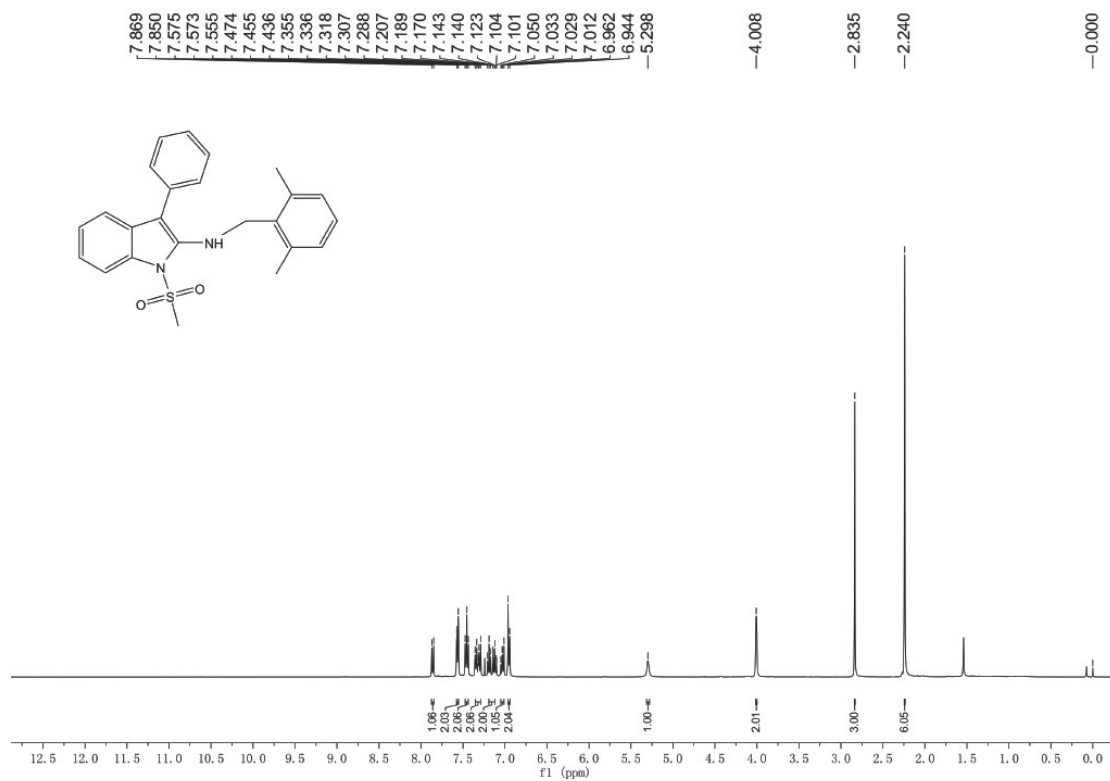
¹H NMR and ¹³C NMR spectra of compound **3f**



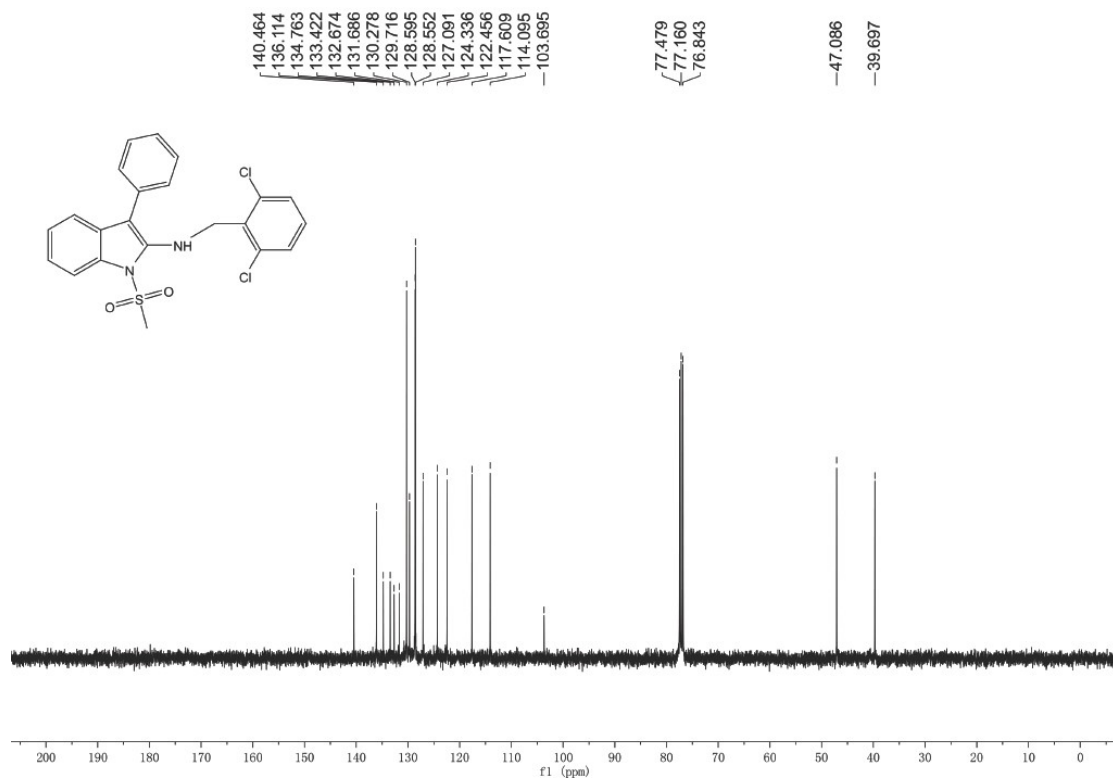
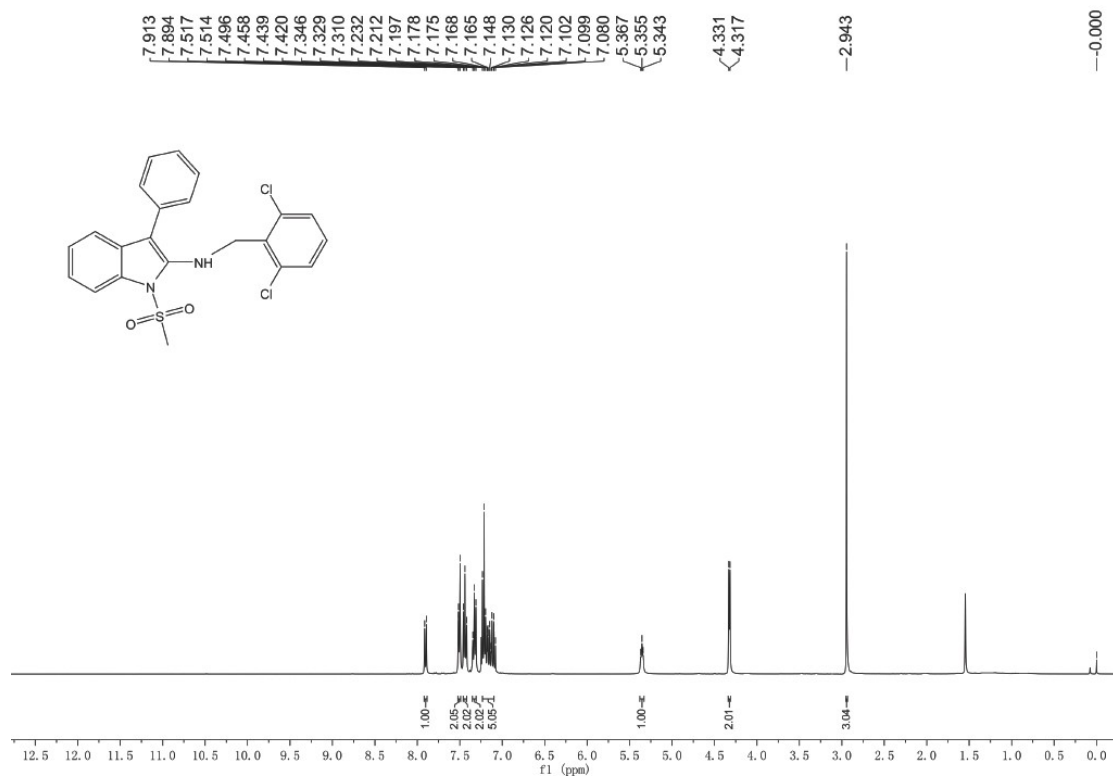
¹H NMR and ¹³C NMR spectra of compound **3g**



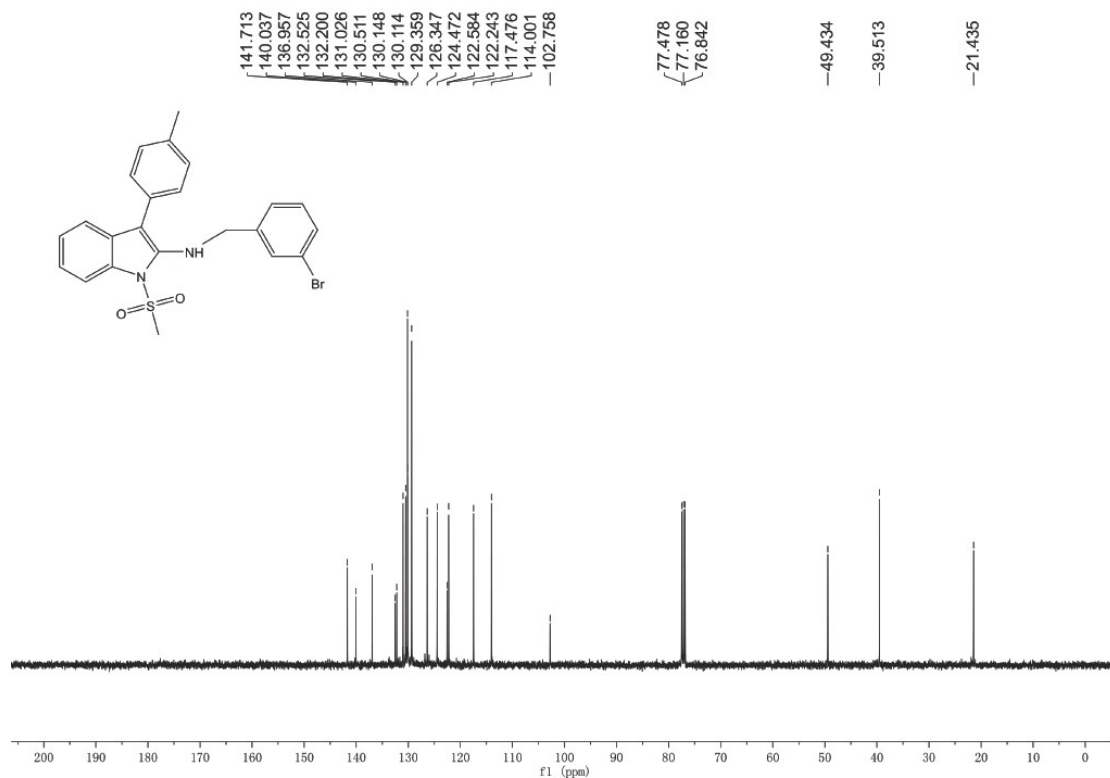
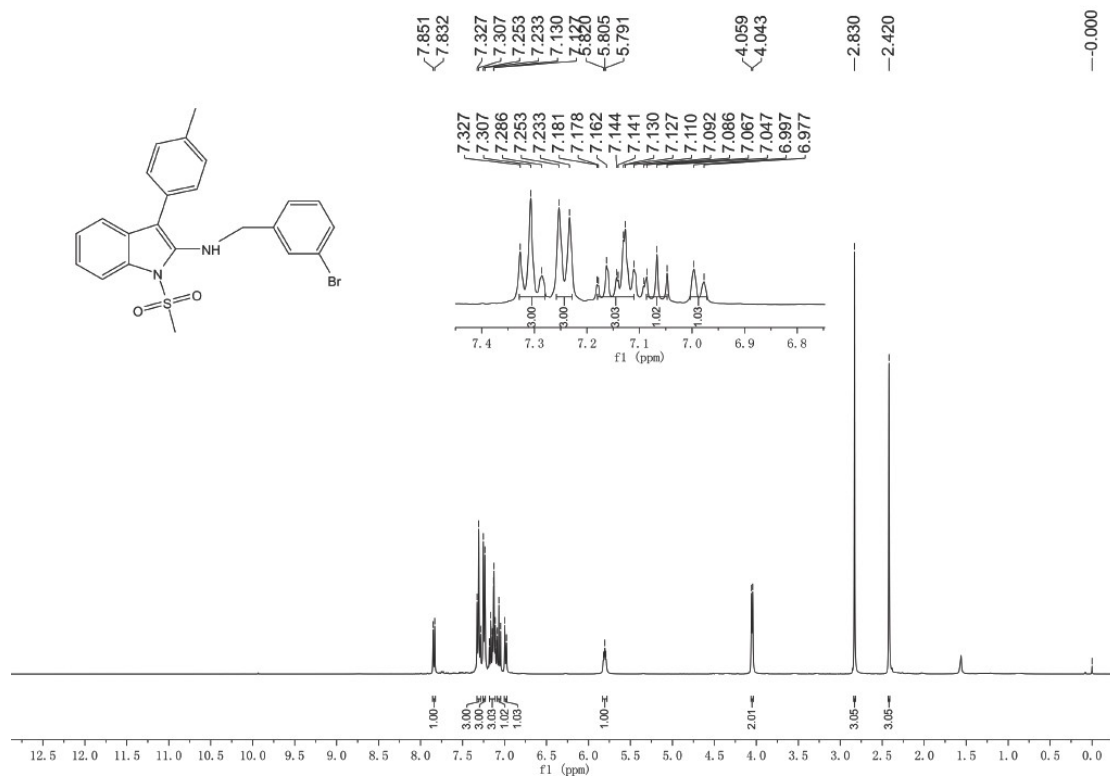
¹H NMR and ¹³C NMR spectra of compound 3h



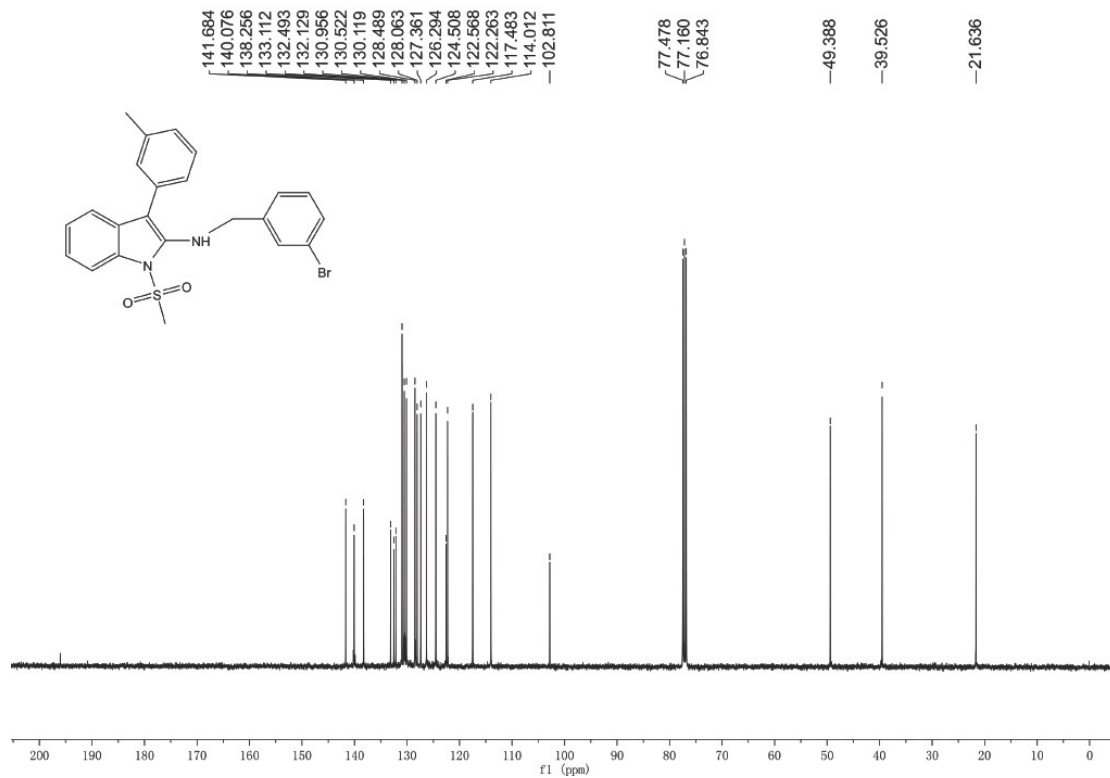
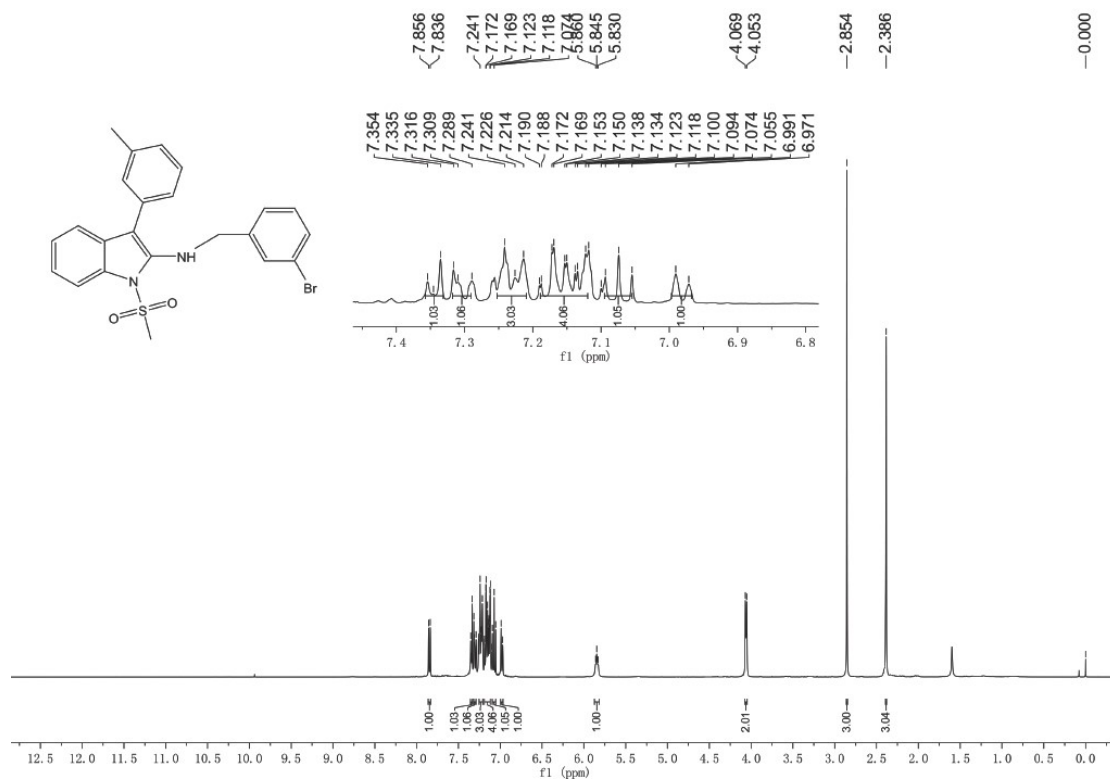
¹H NMR and ¹³C NMR spectra of compound **3i**



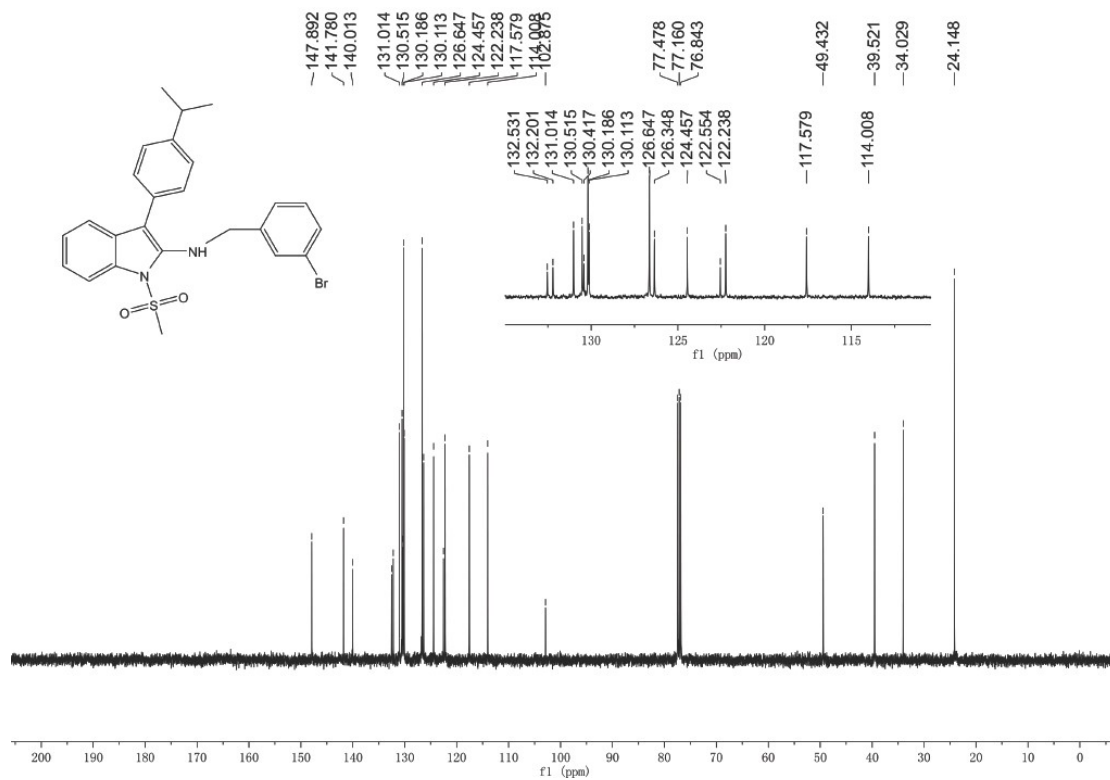
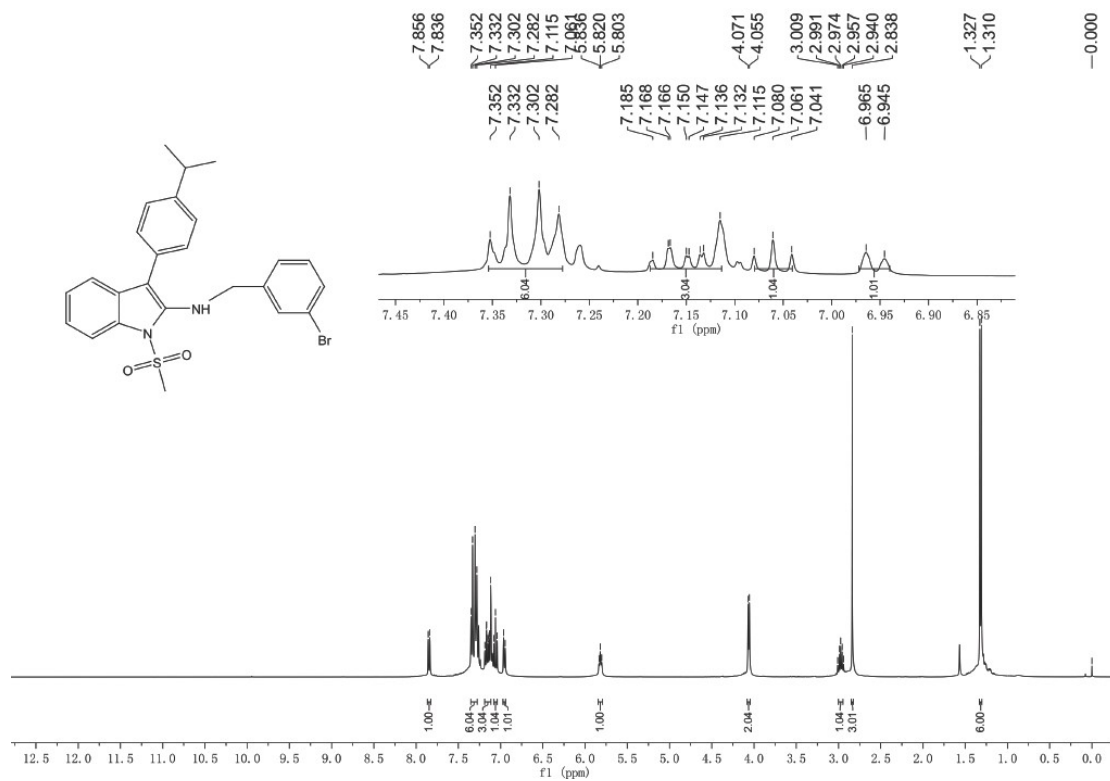
¹H NMR and ¹³C NMR spectra of compound 3j



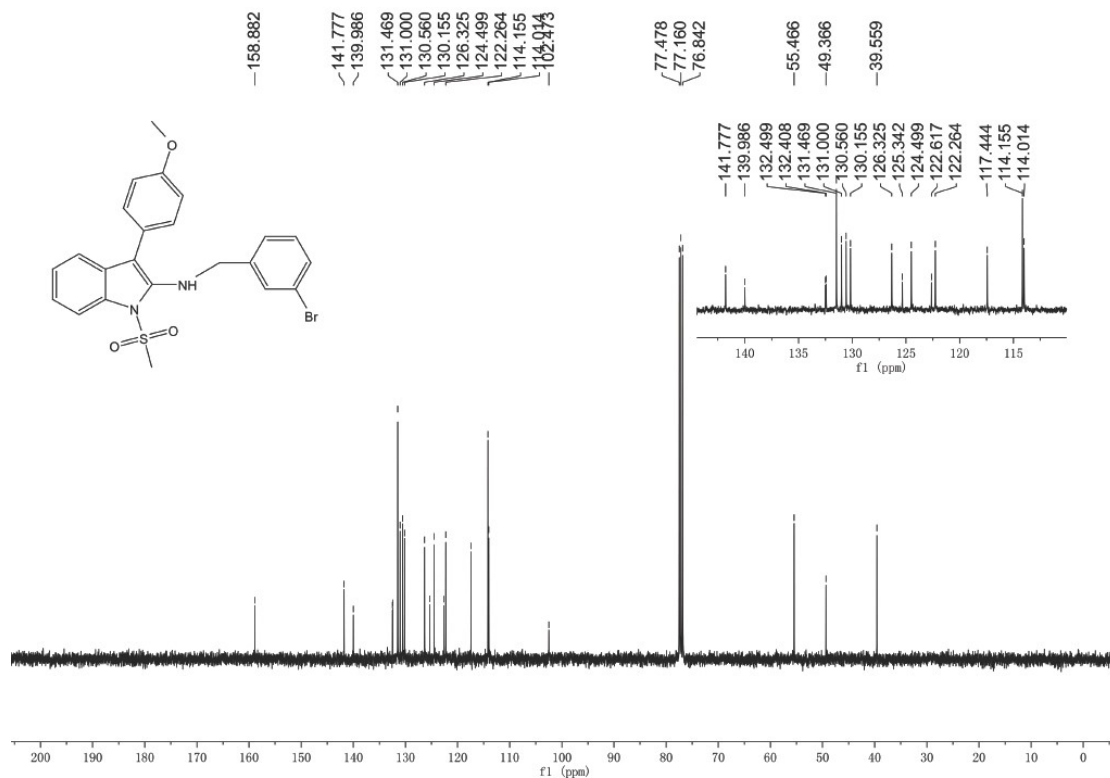
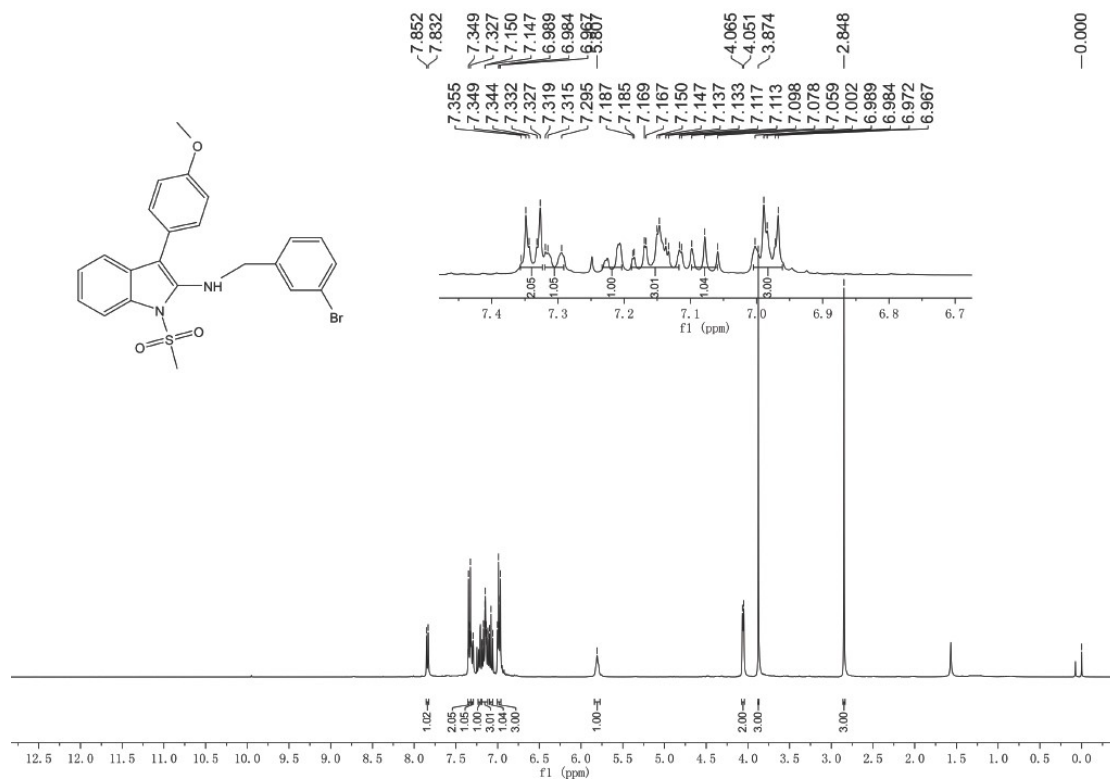
¹H NMR and ¹³C NMR spectra of compound 3k



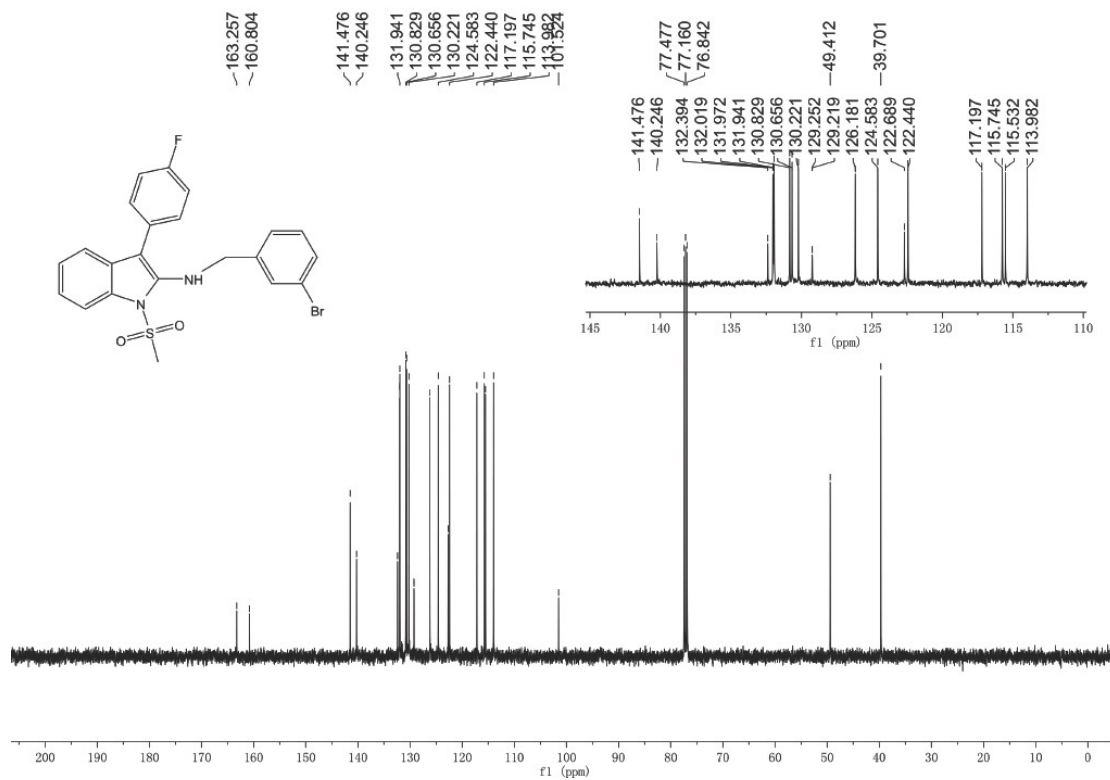
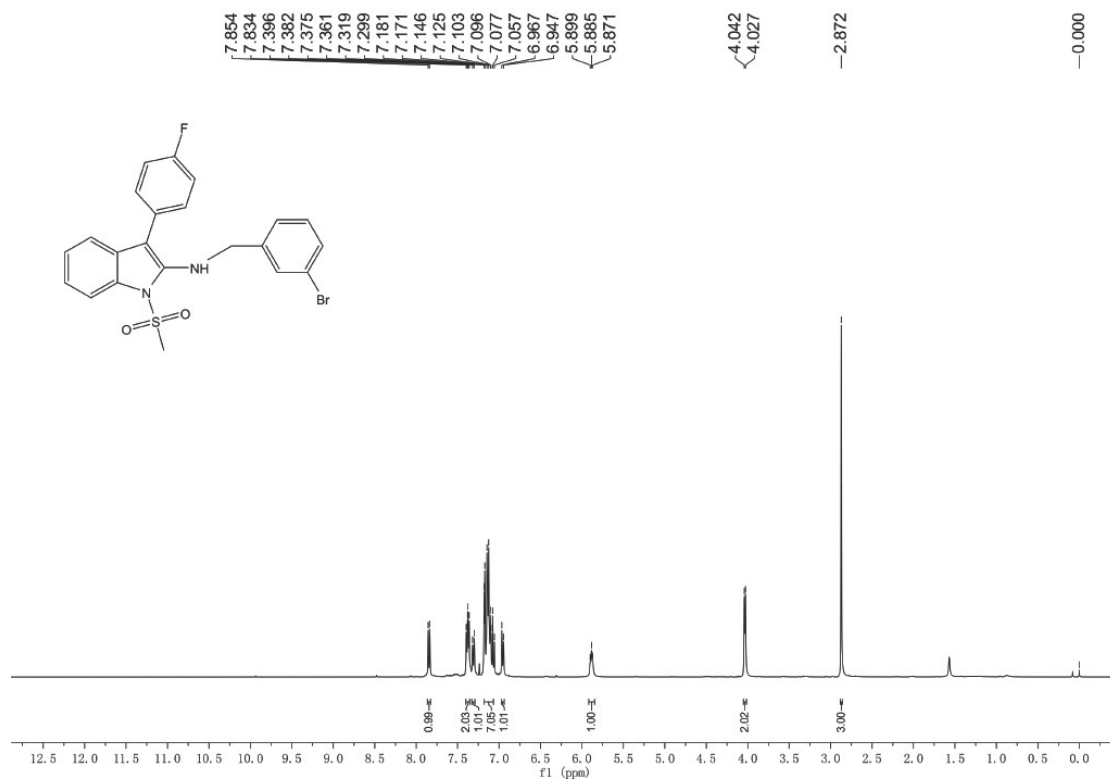
¹H NMR and ¹³C NMR spectra of compound 31



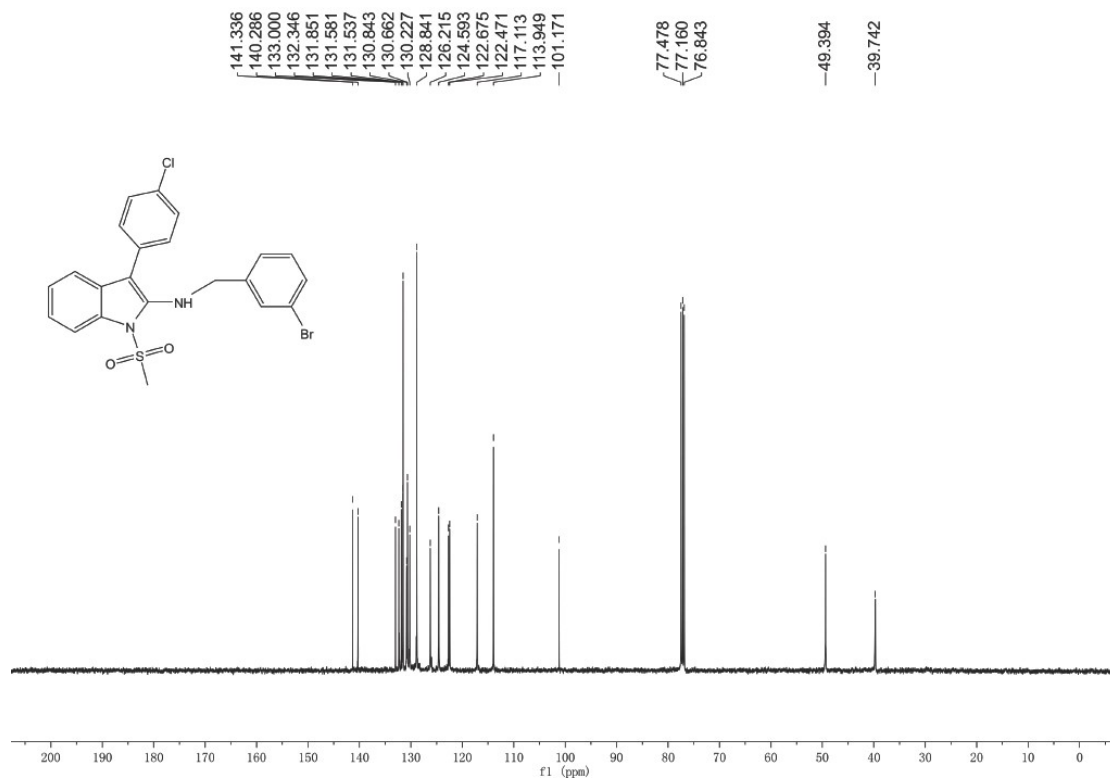
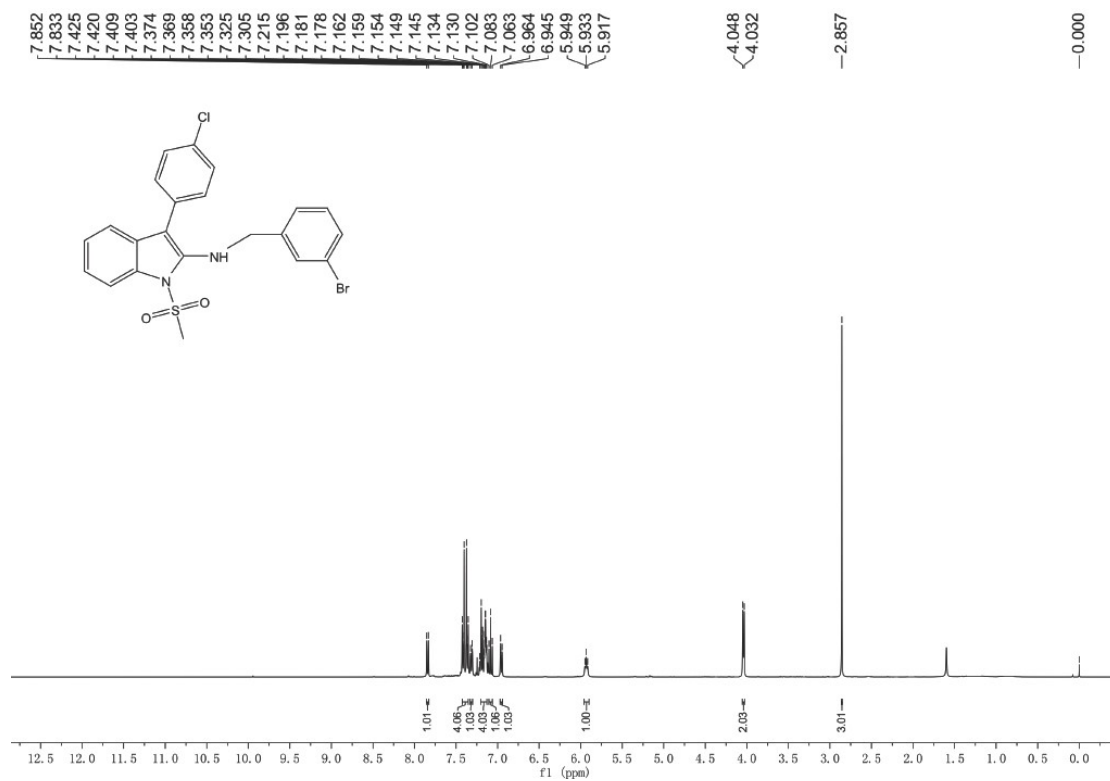
¹H NMR and ¹³C NMR spectra of compound 3m



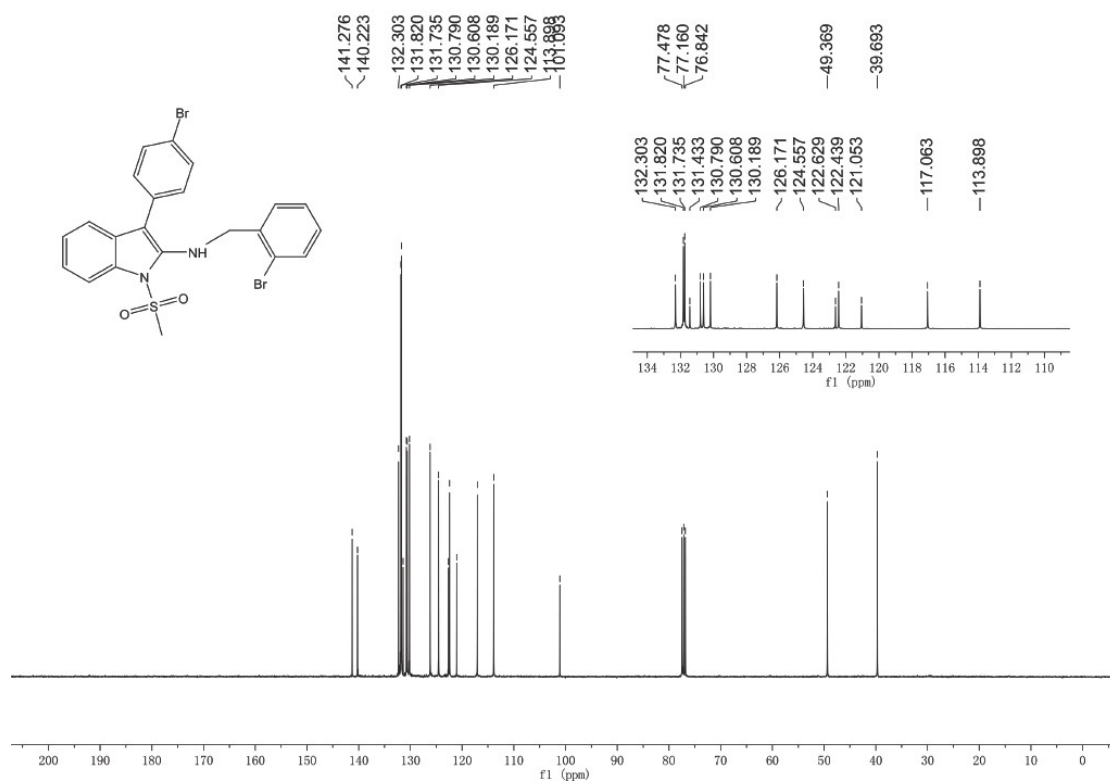
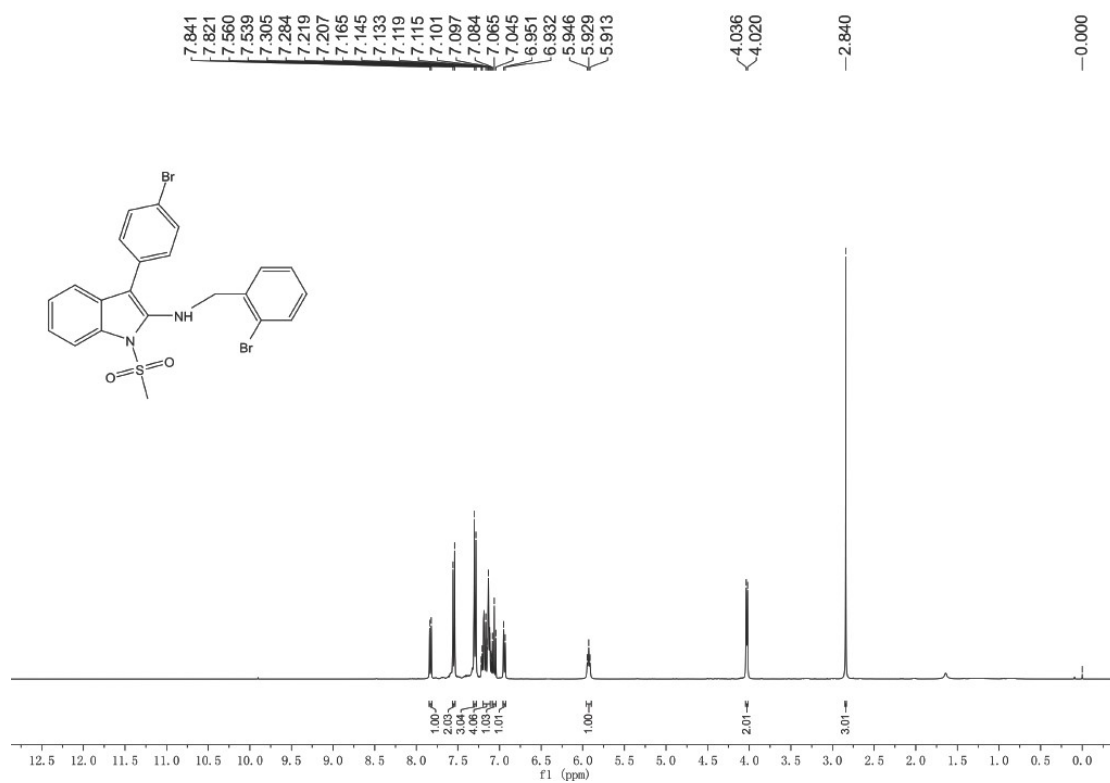
¹H NMR and ¹³C NMR spectra of compound 3n



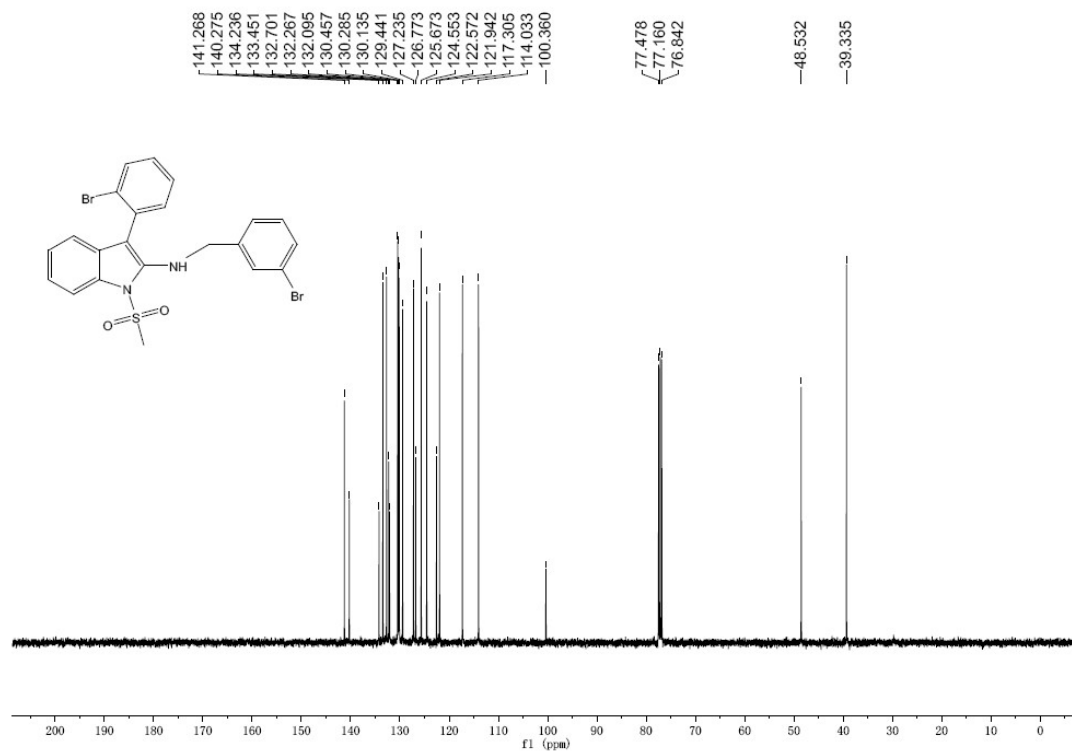
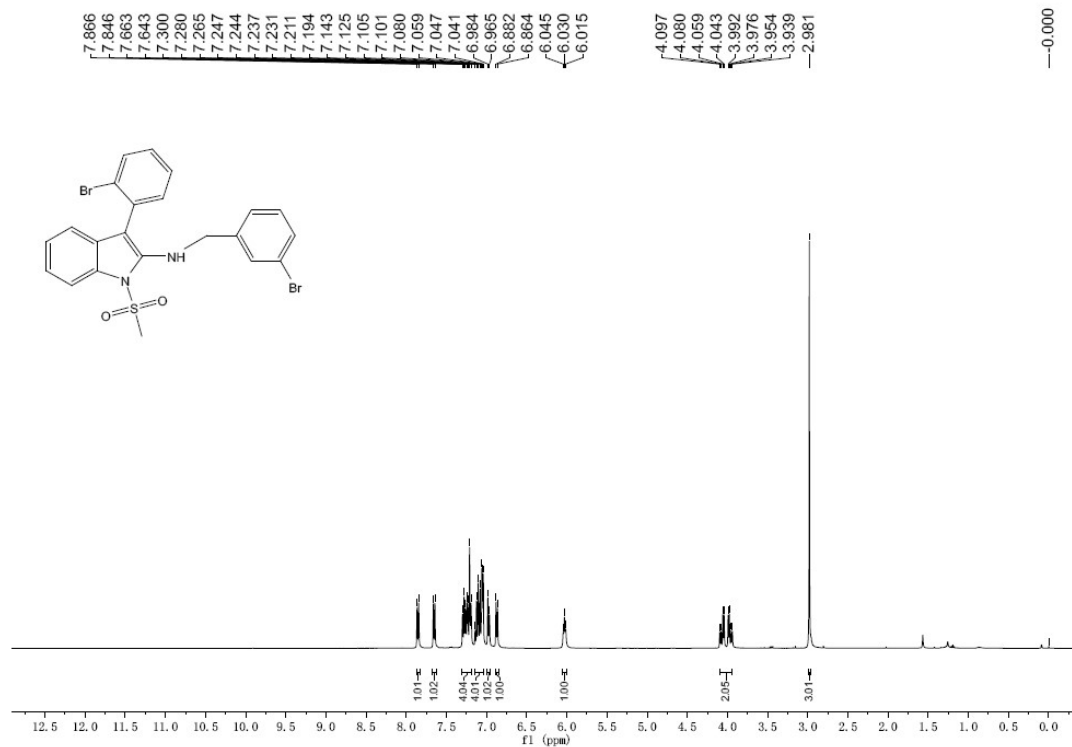
¹H NMR and ¹³C NMR spectra of compound 30



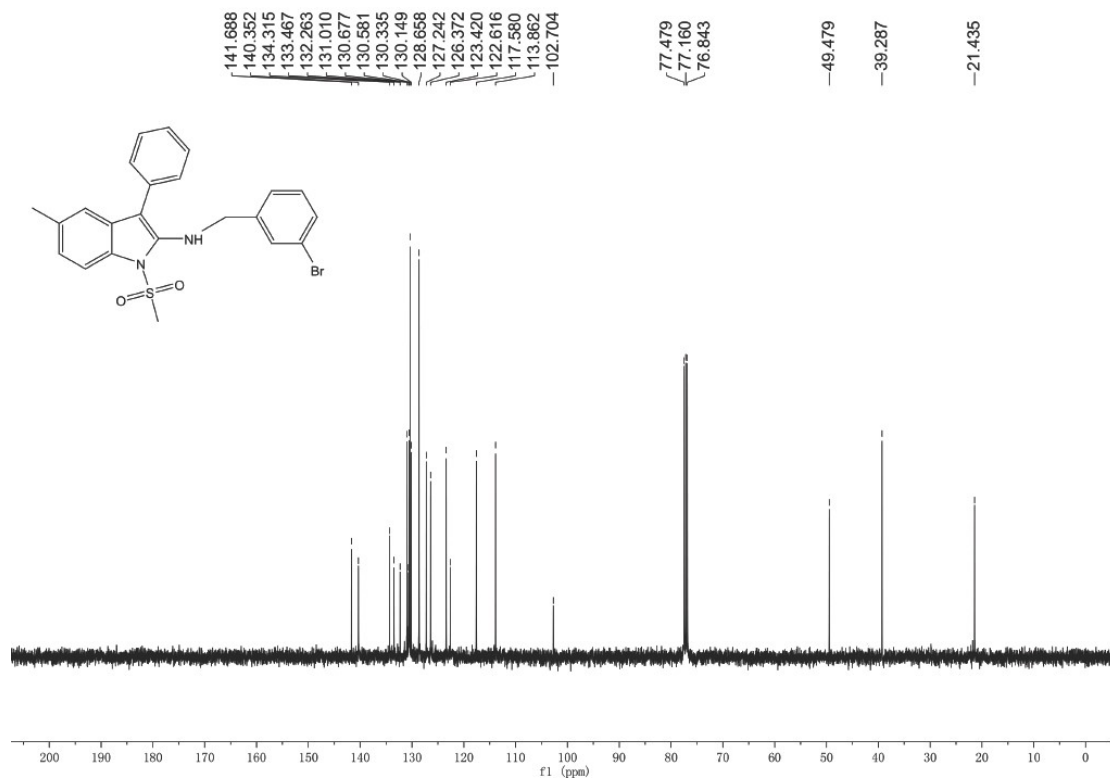
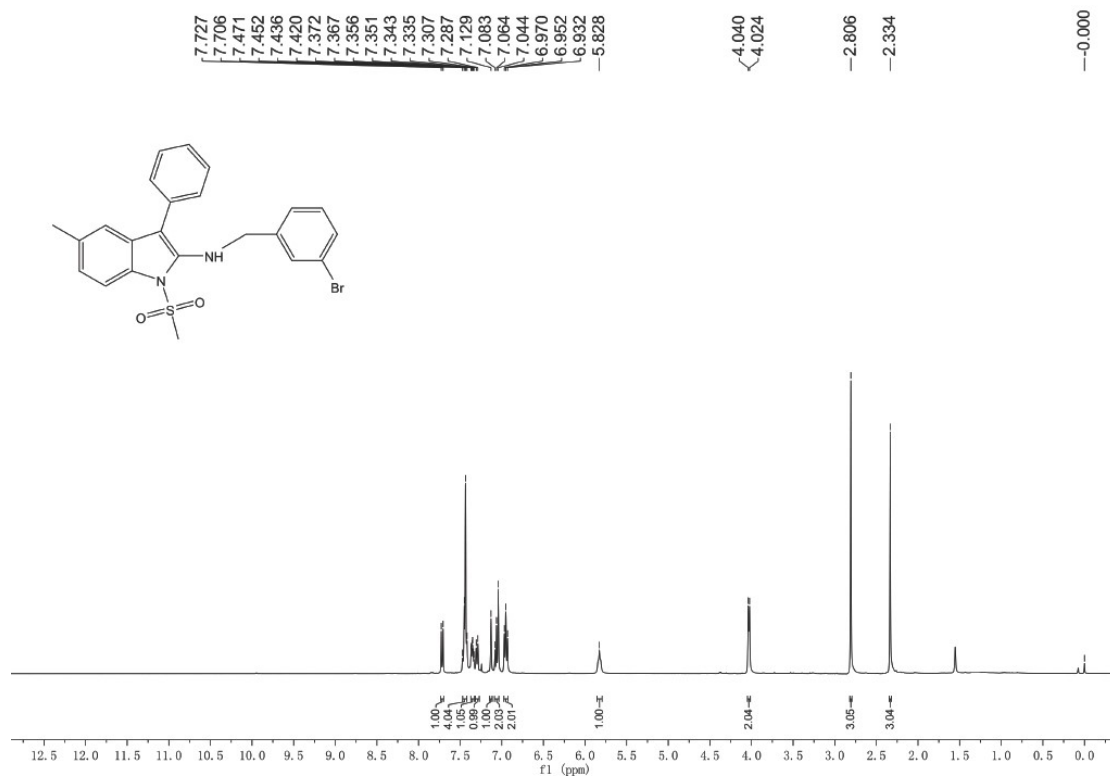
¹H NMR and ¹³C NMR spectra of compound **3p**



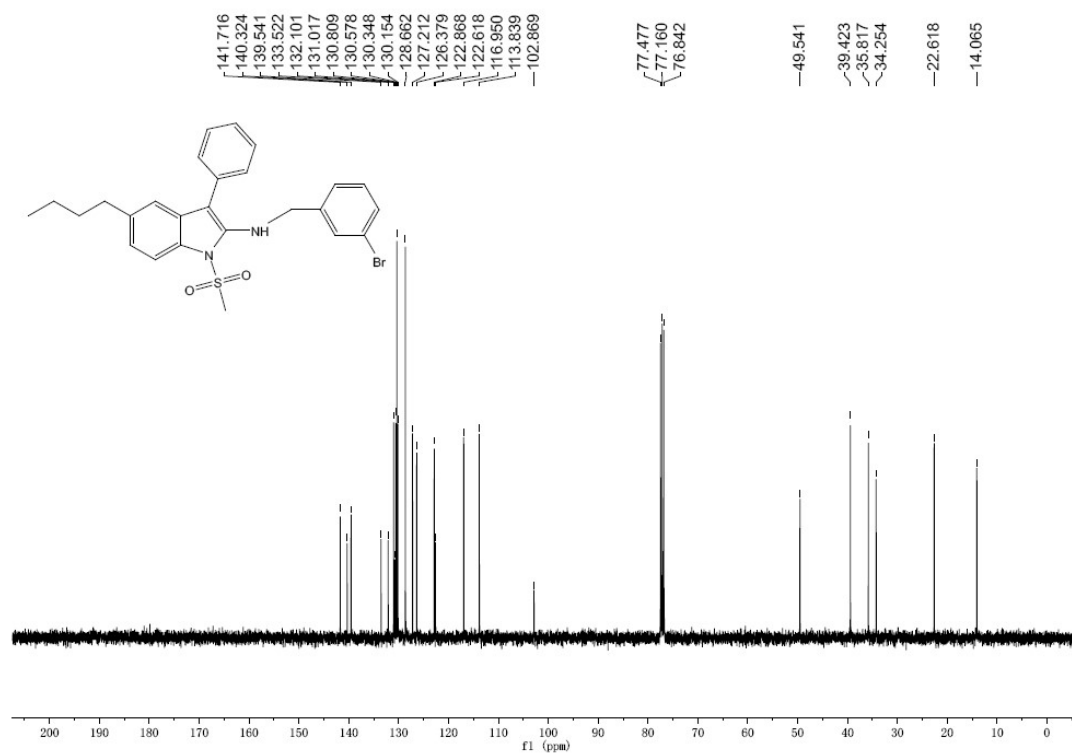
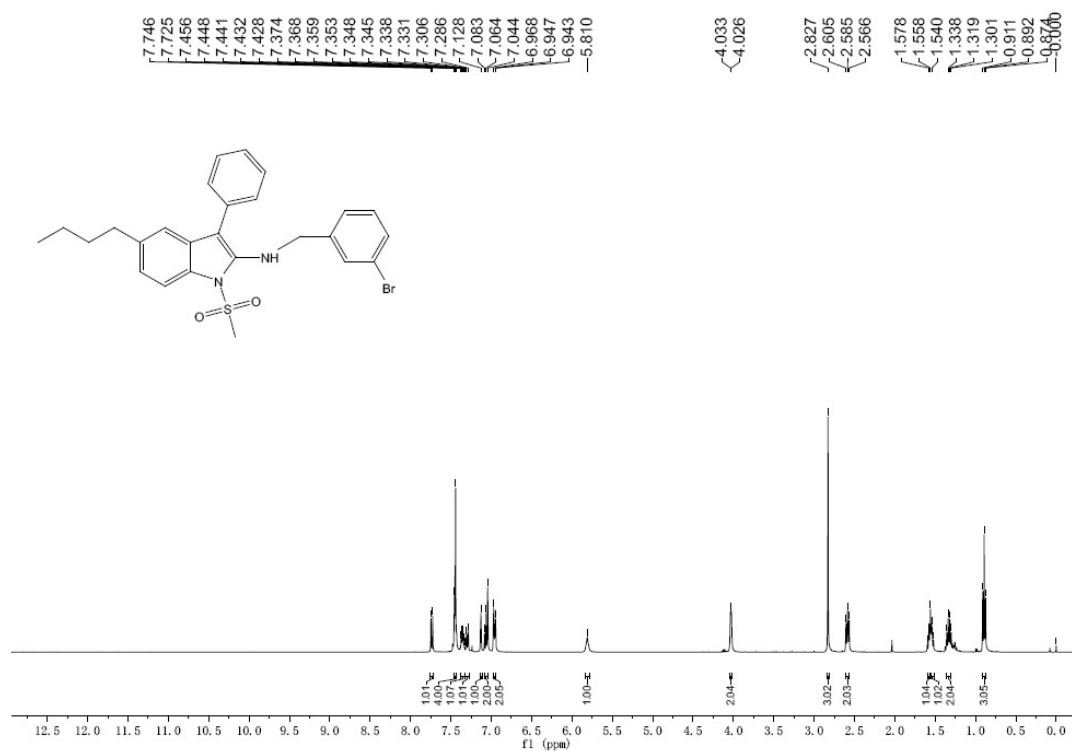
¹H NMR and ¹³C NMR spectra of compound 3q



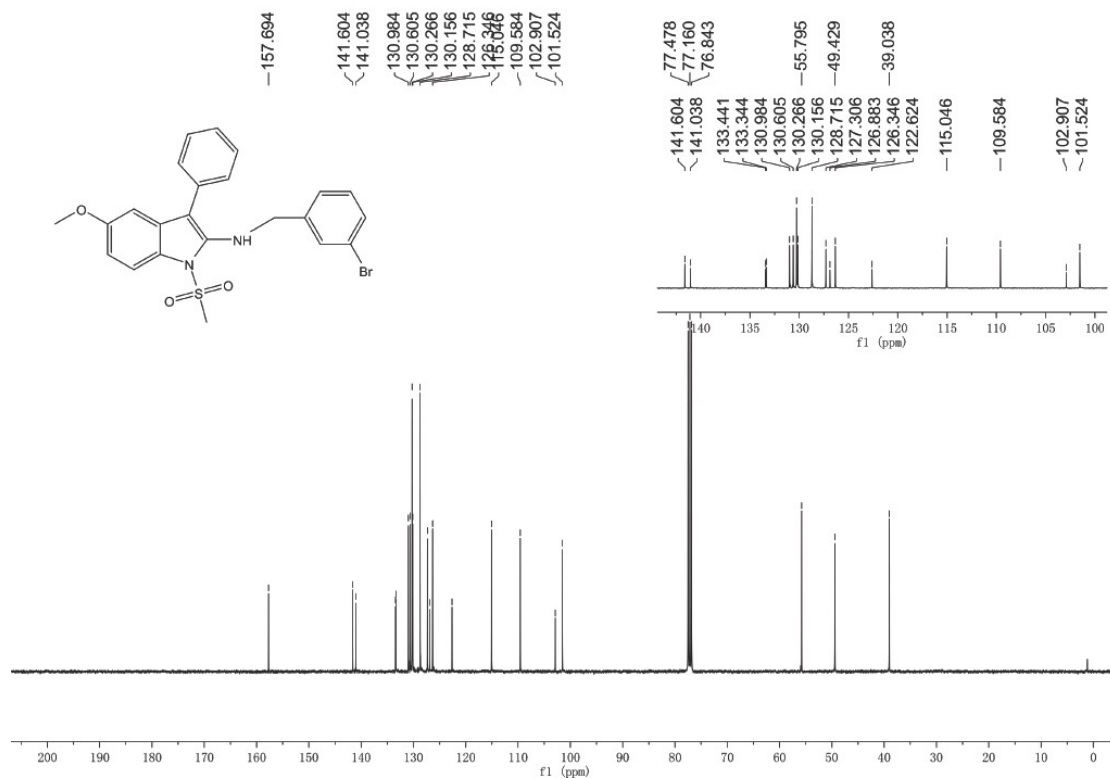
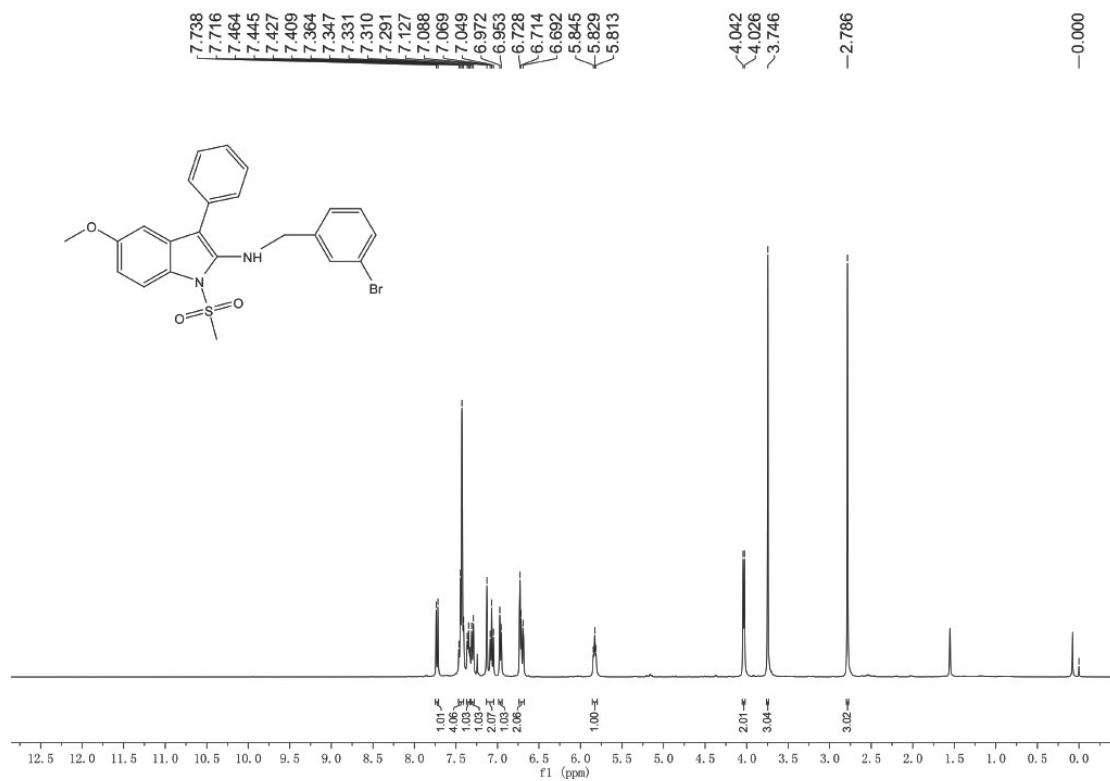
¹H NMR and ¹³C NMR spectra of compound **3r**



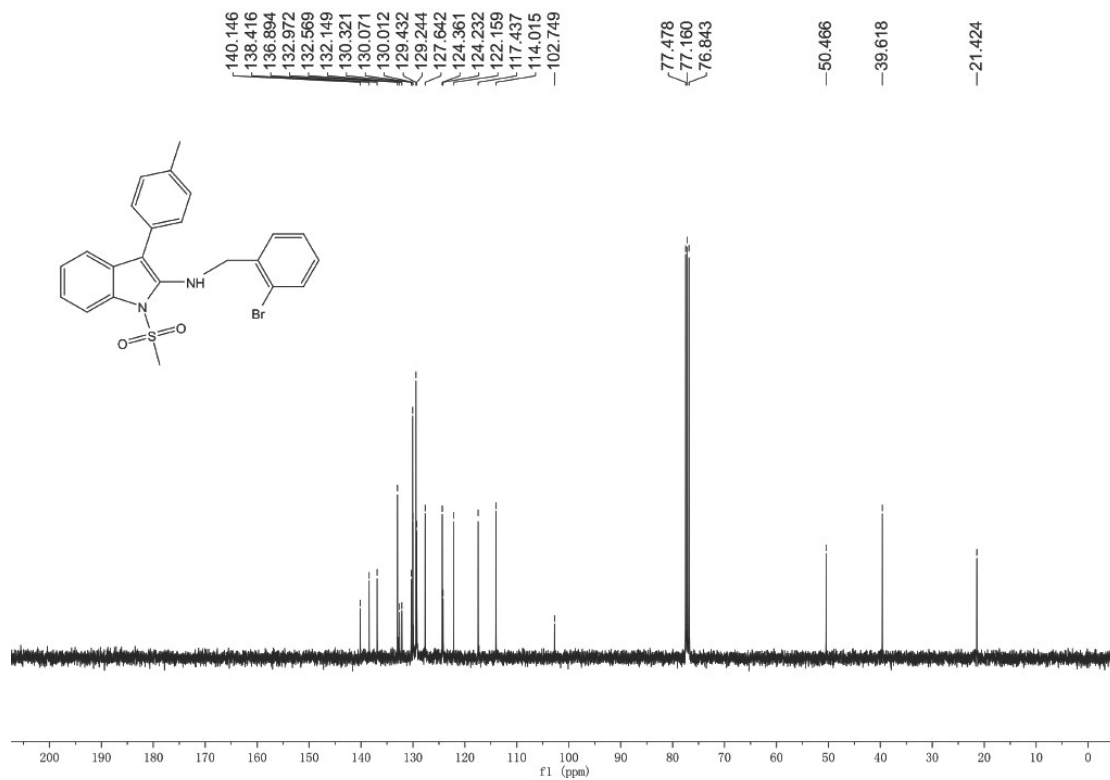
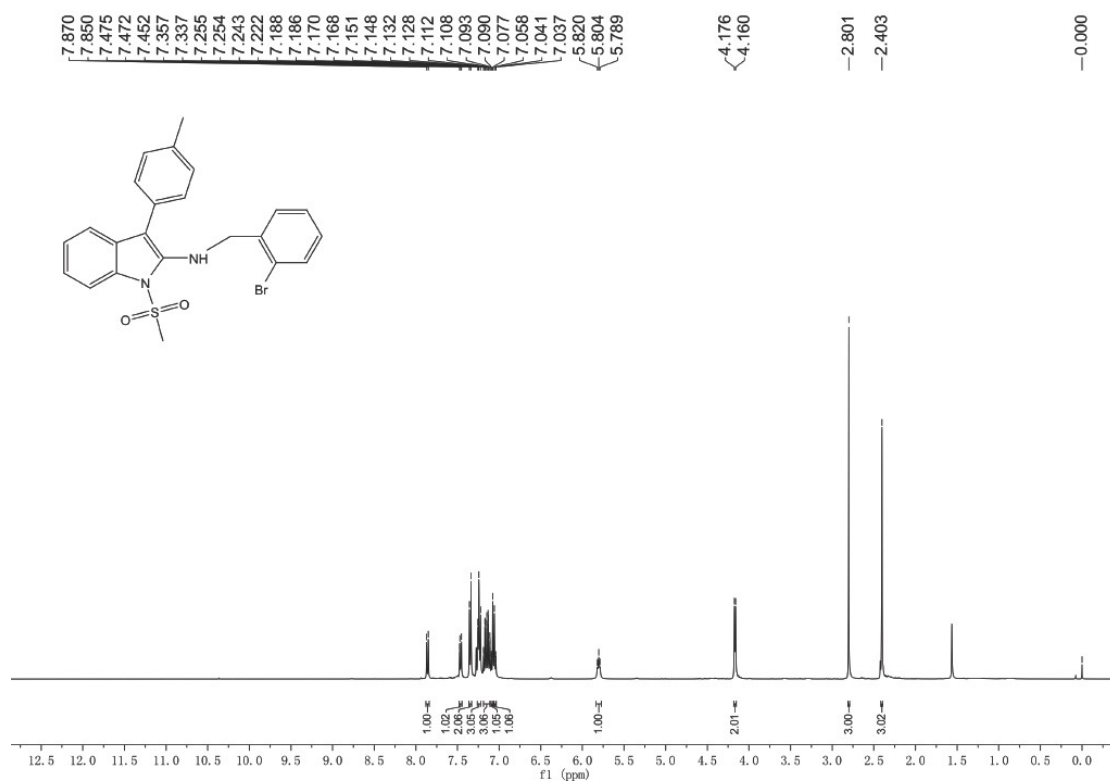
¹H NMR and ¹³C NMR spectra of compound **3s**



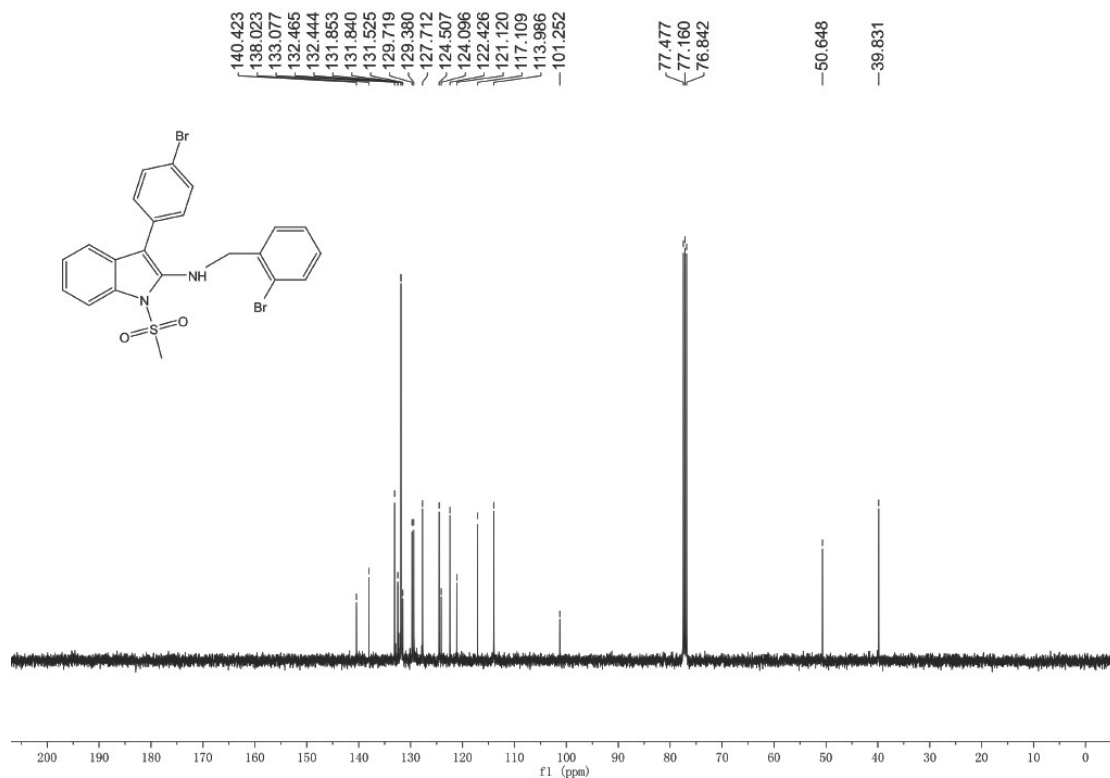
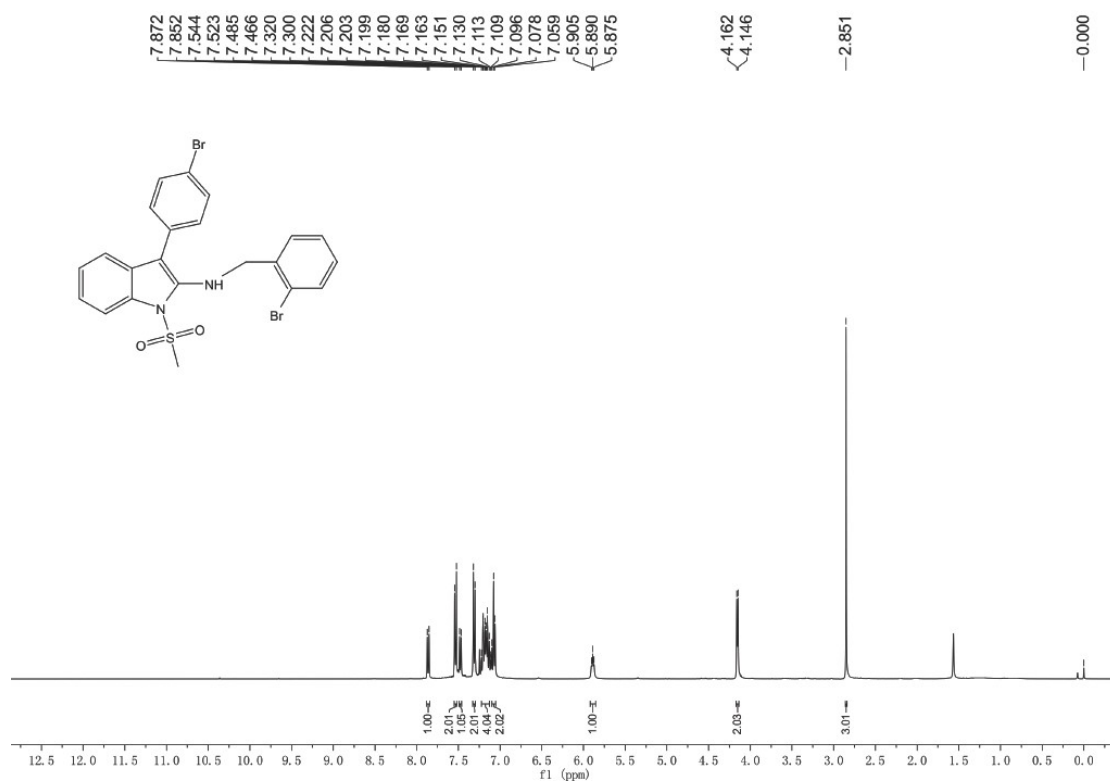
¹H NMR and ¹³C NMR spectra of compound 3t



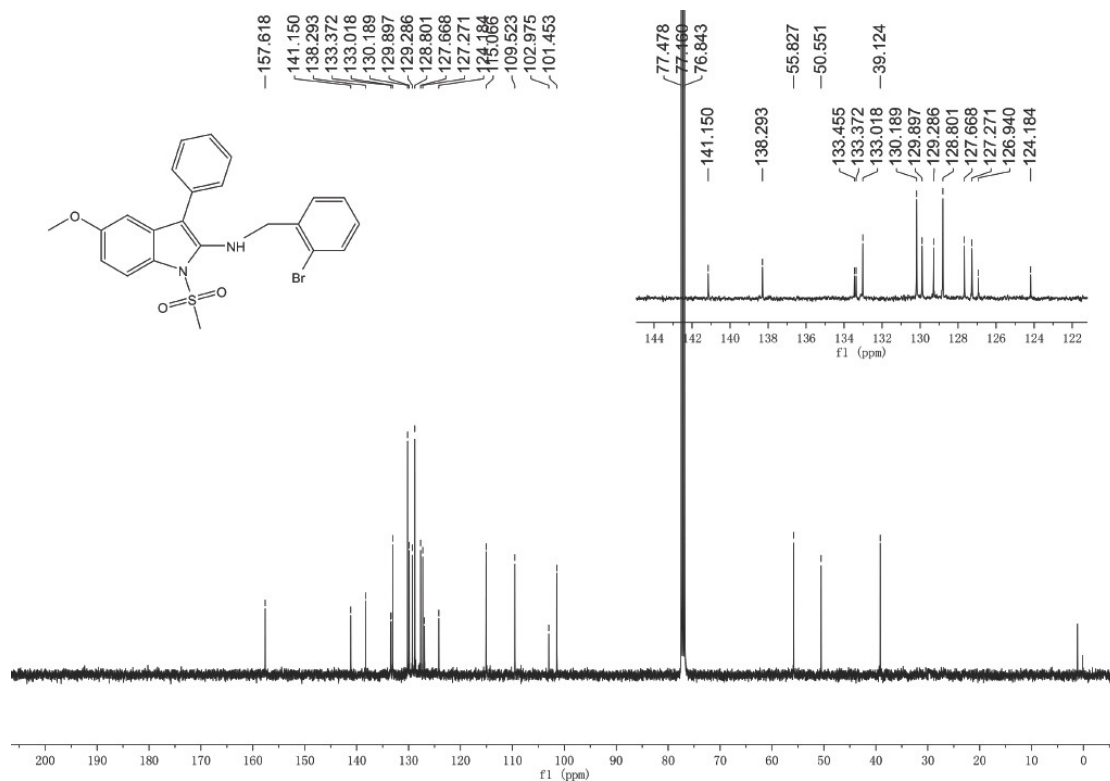
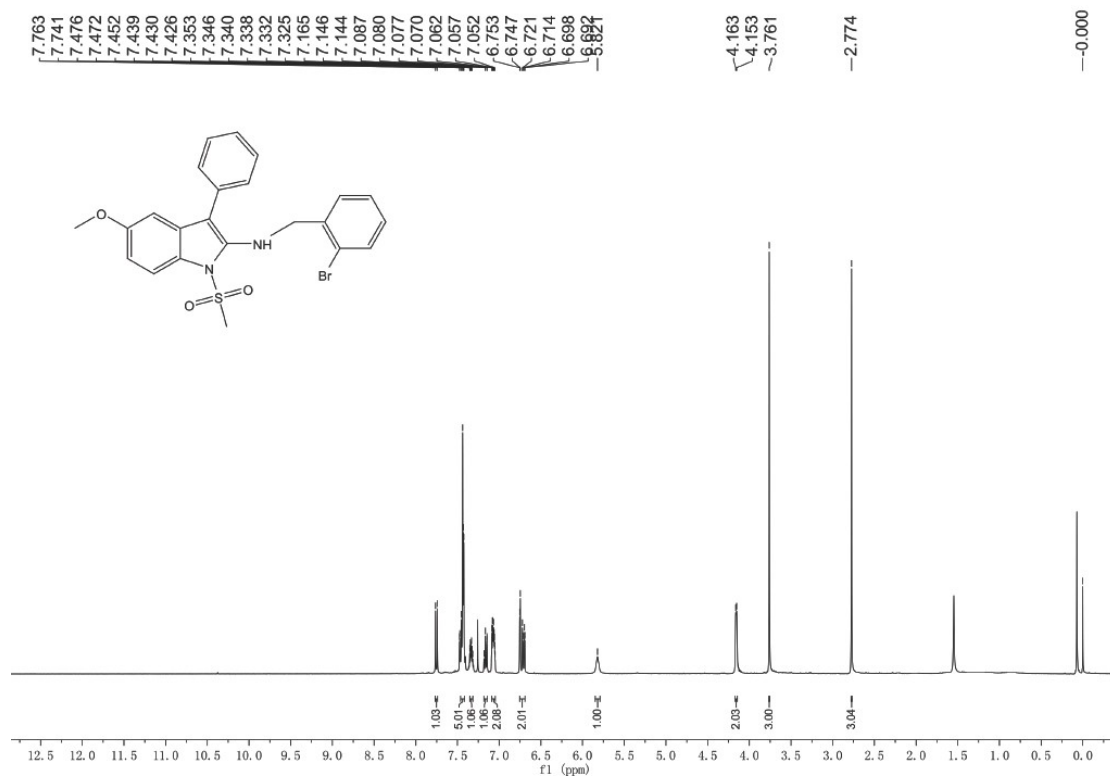
¹H NMR and ¹³C NMR spectra of compound **3u**



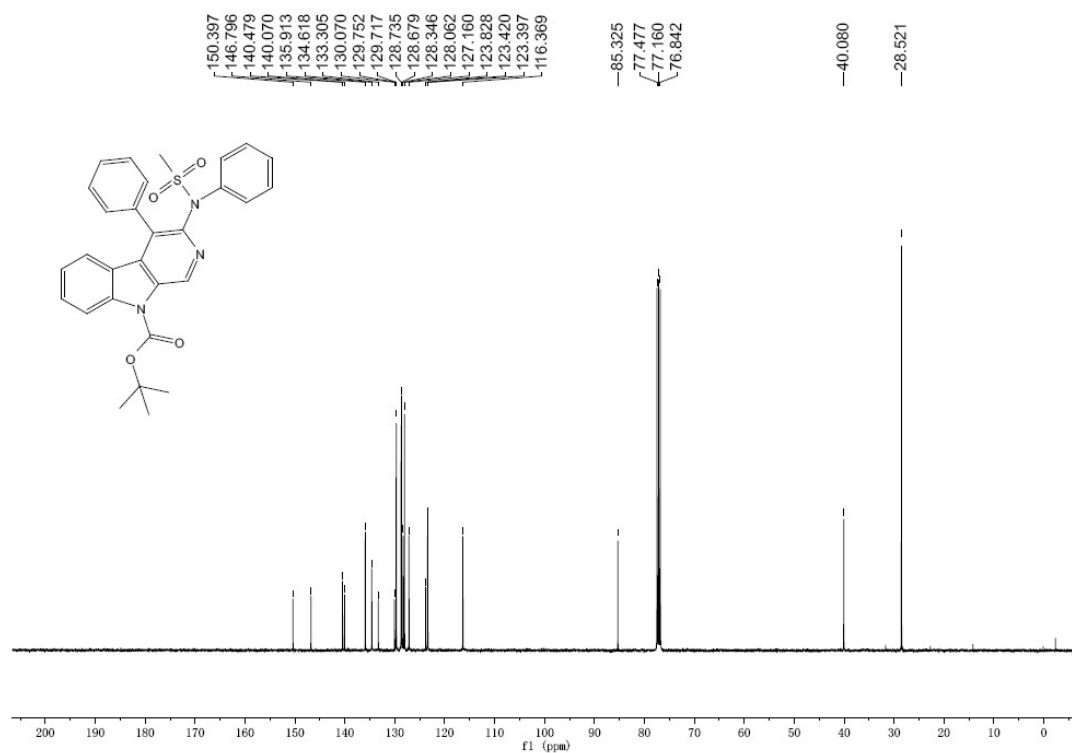
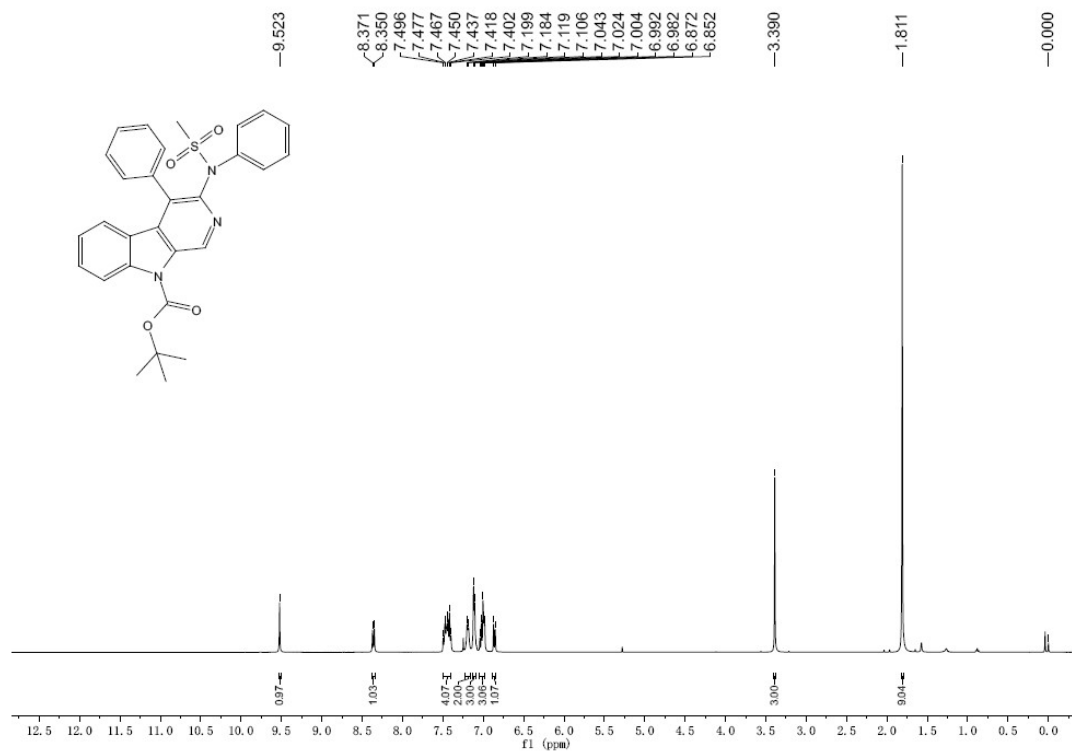
^1H NMR and ^{13}C NMR spectra of compound **3v**



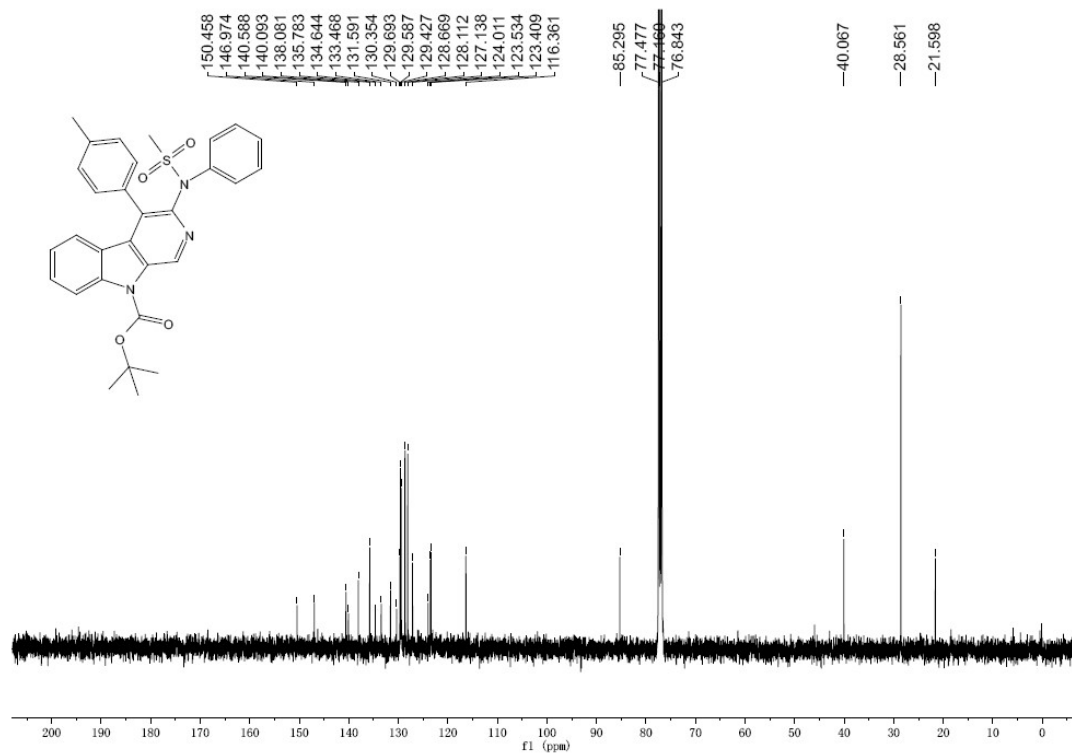
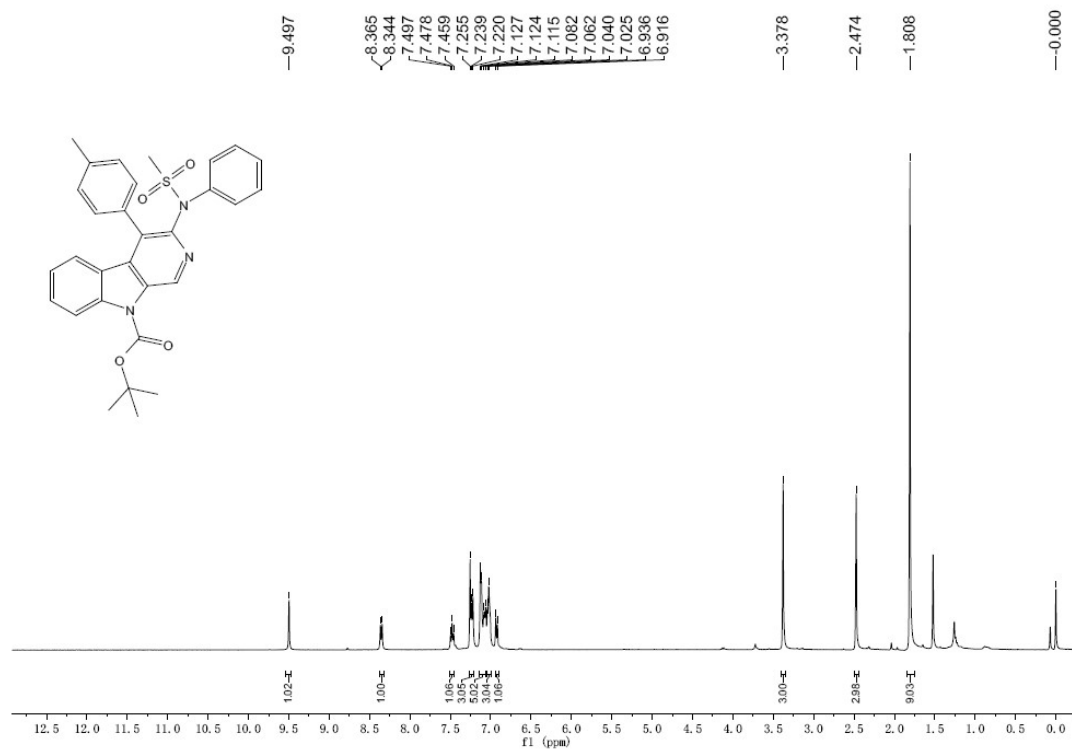
¹H NMR and ¹³C NMR spectra of compound **3w**



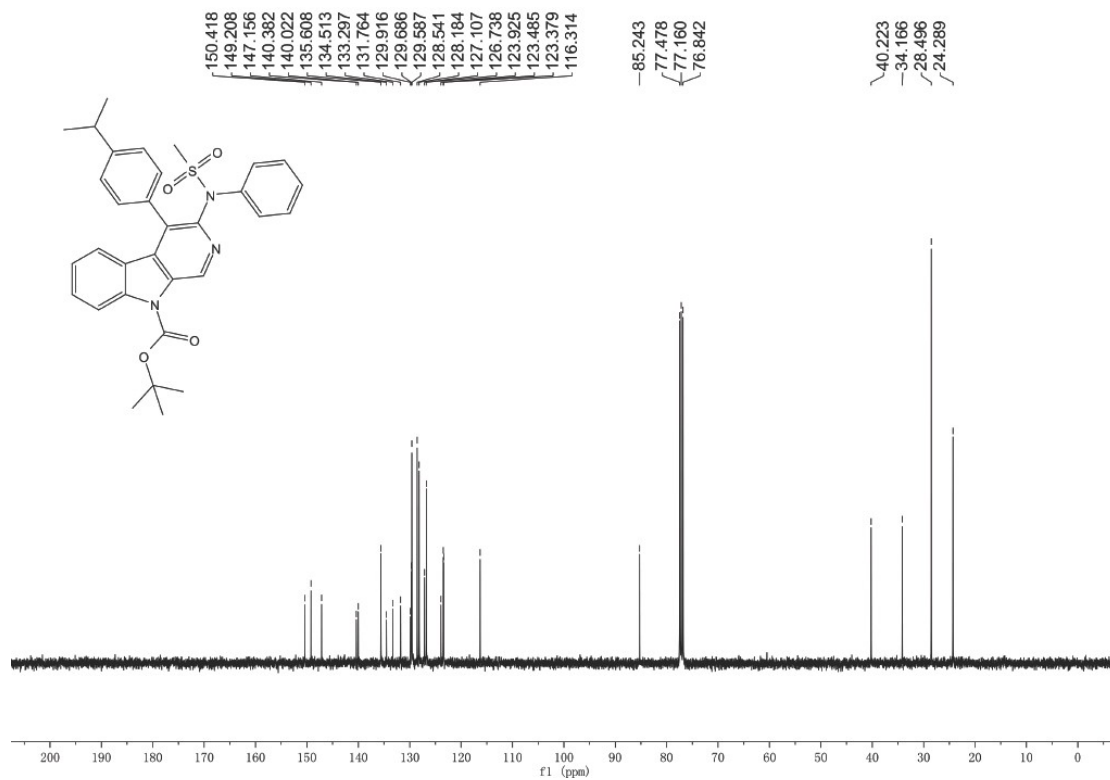
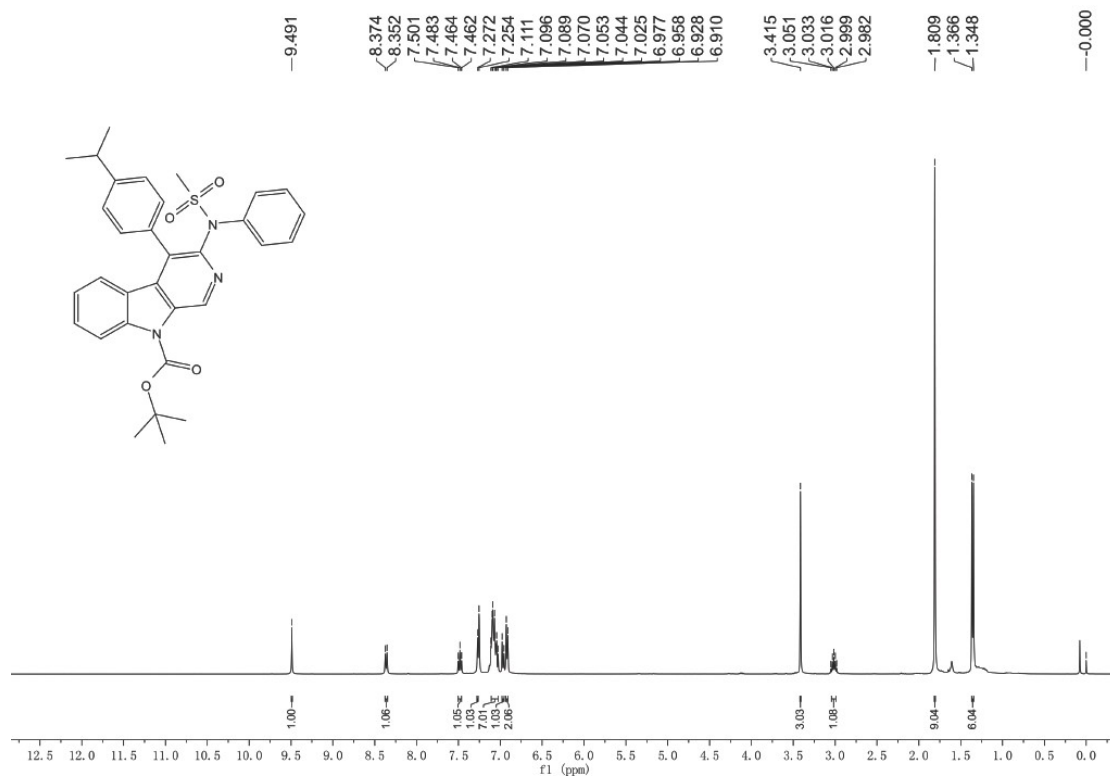
¹H NMR and ¹³C NMR spectra of compound 3x



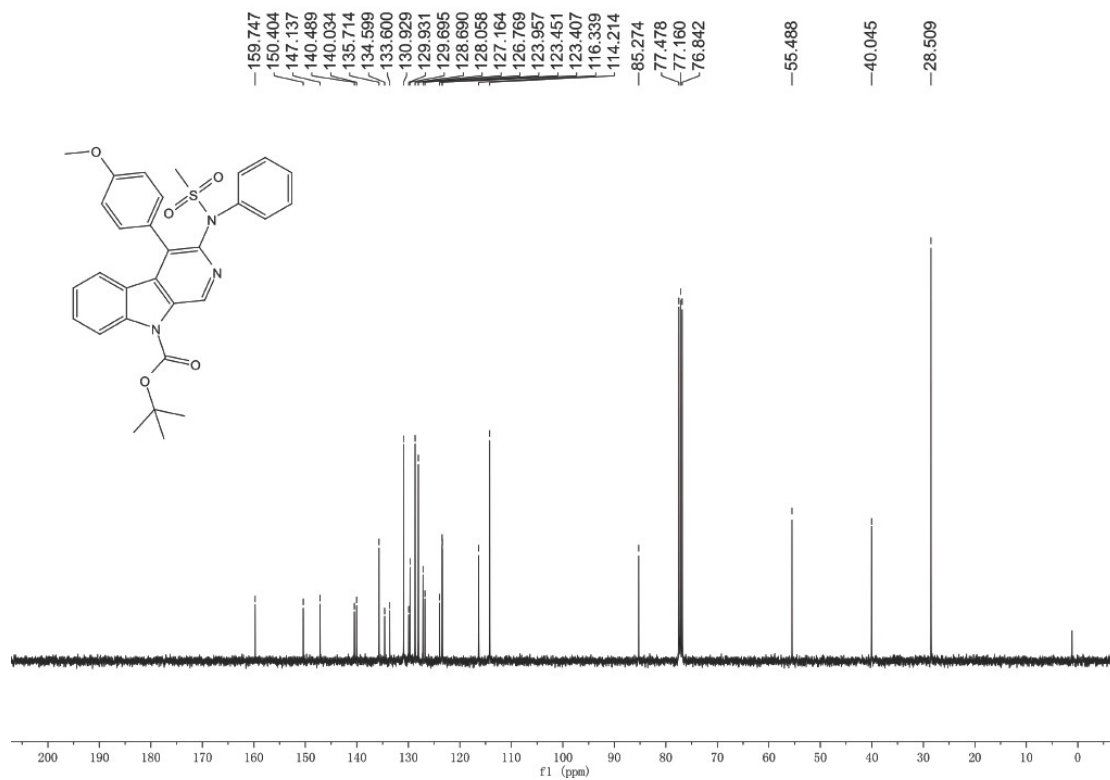
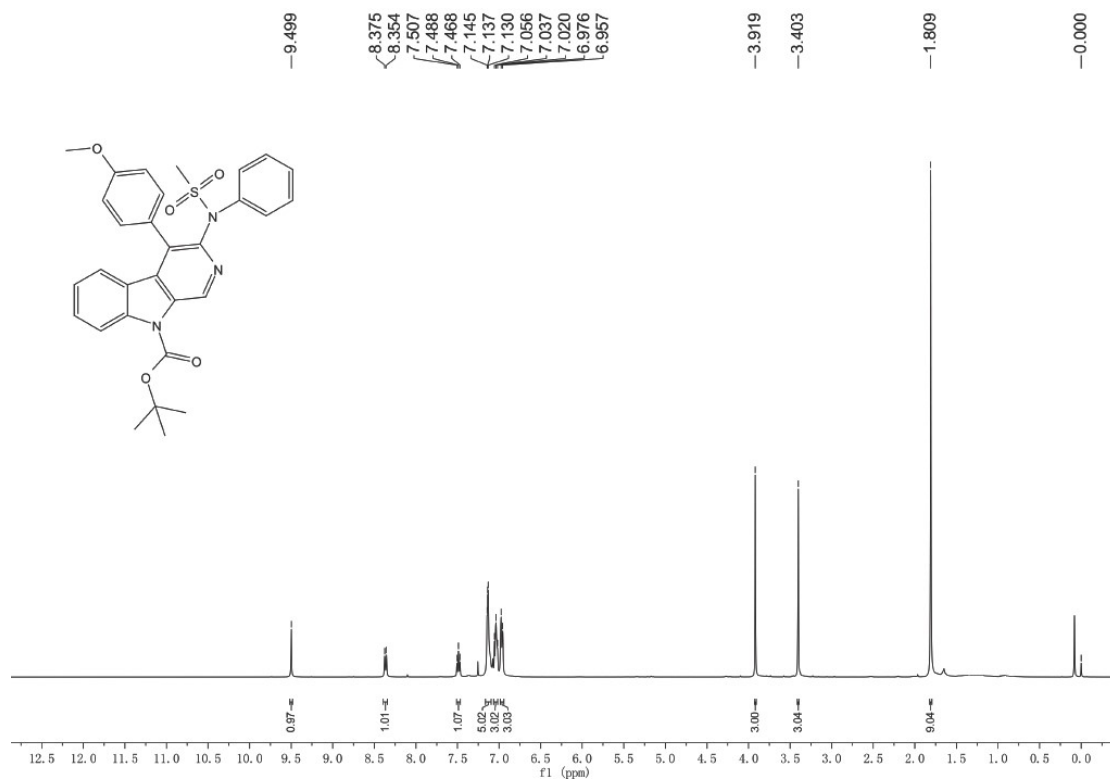
¹H NMR and ¹³C NMR spectra of compound 5a



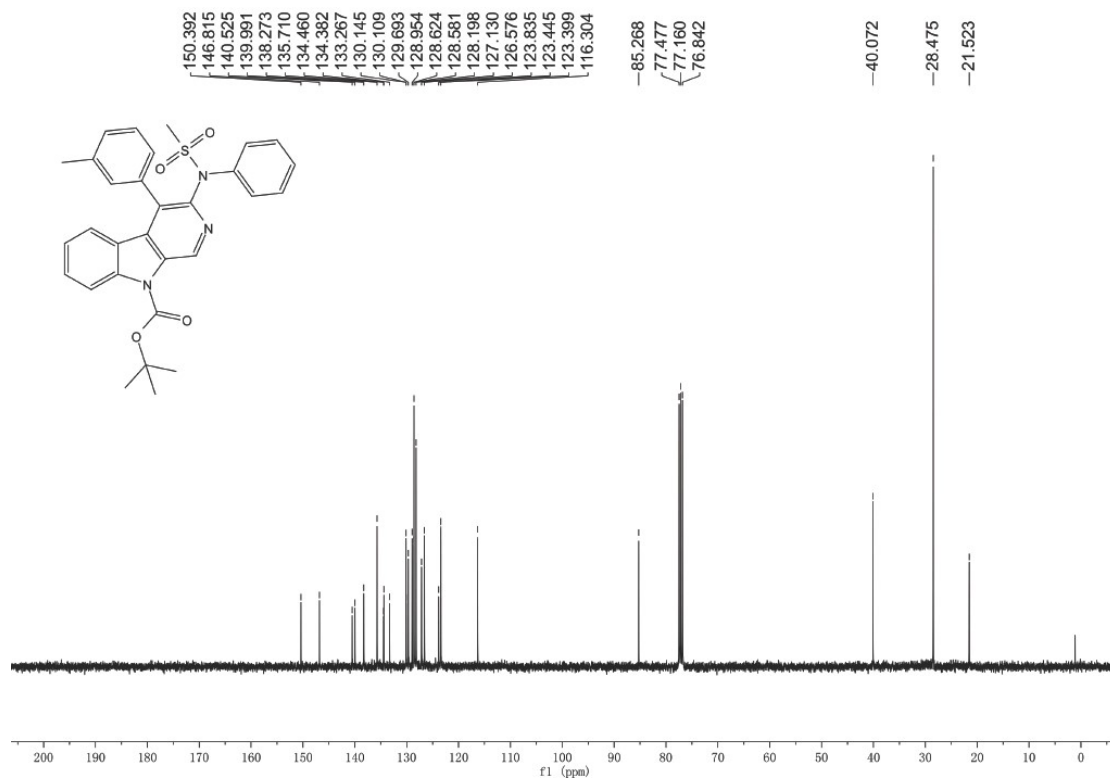
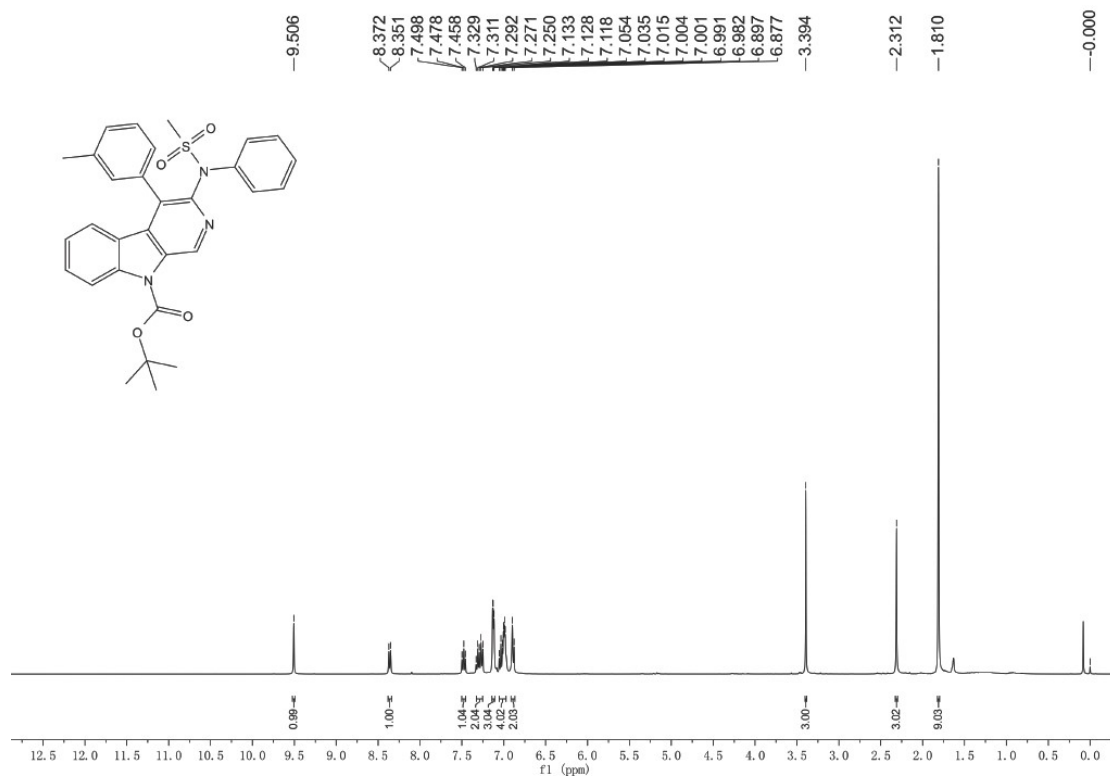
¹H NMR and ¹³C NMR spectra of compound **5b**



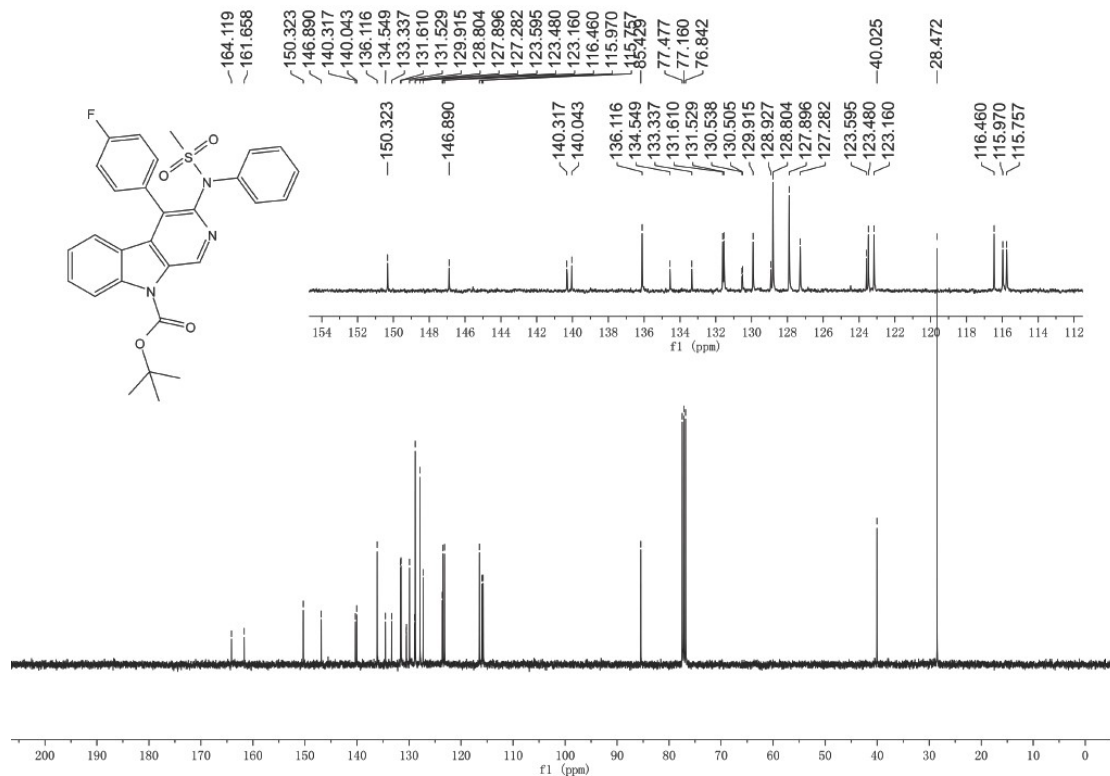
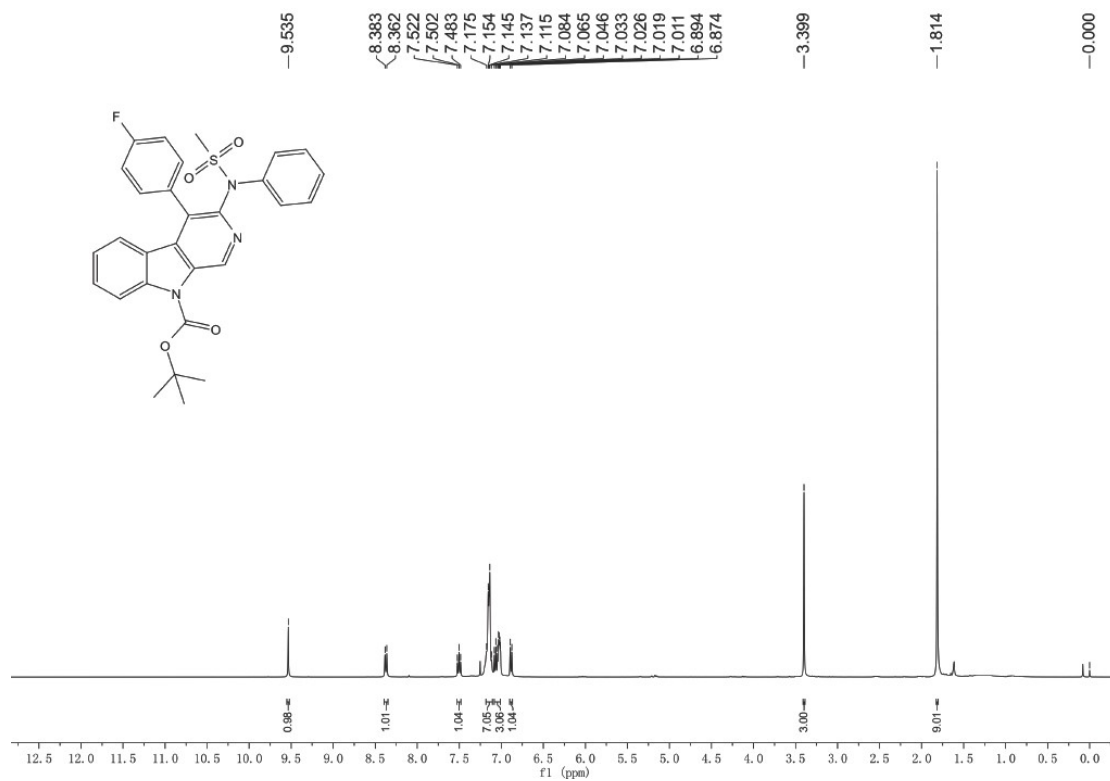
¹H NMR and ¹³C NMR spectra of compound 5c



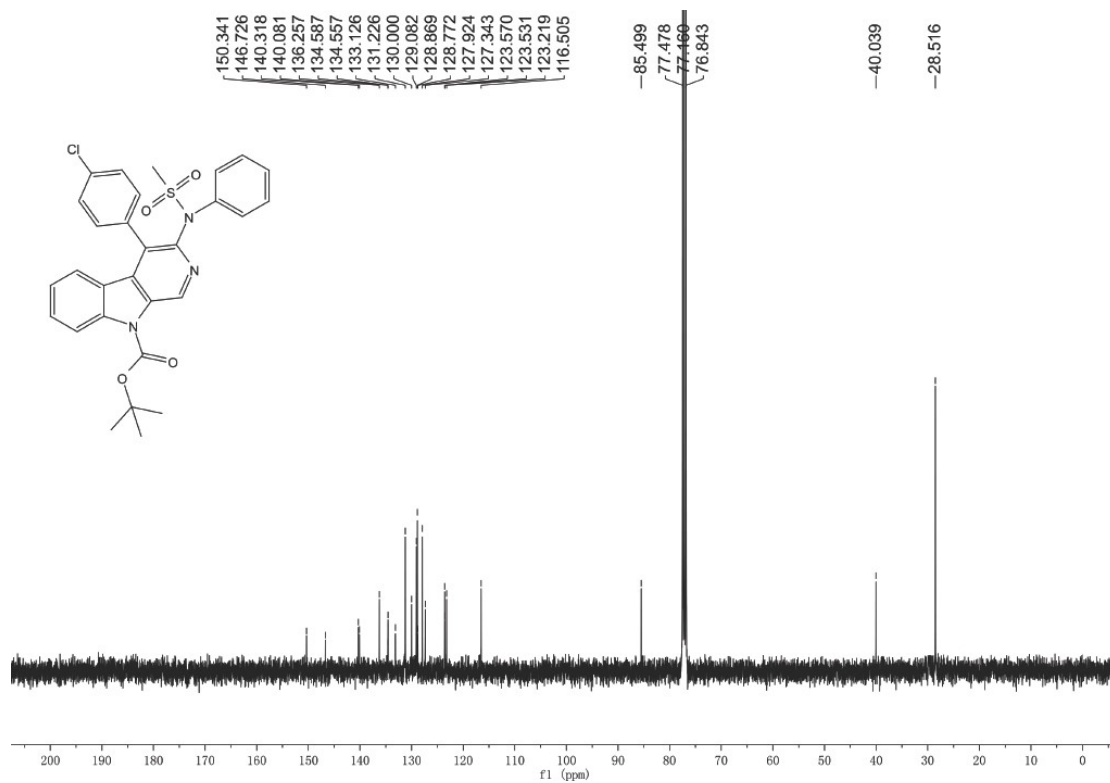
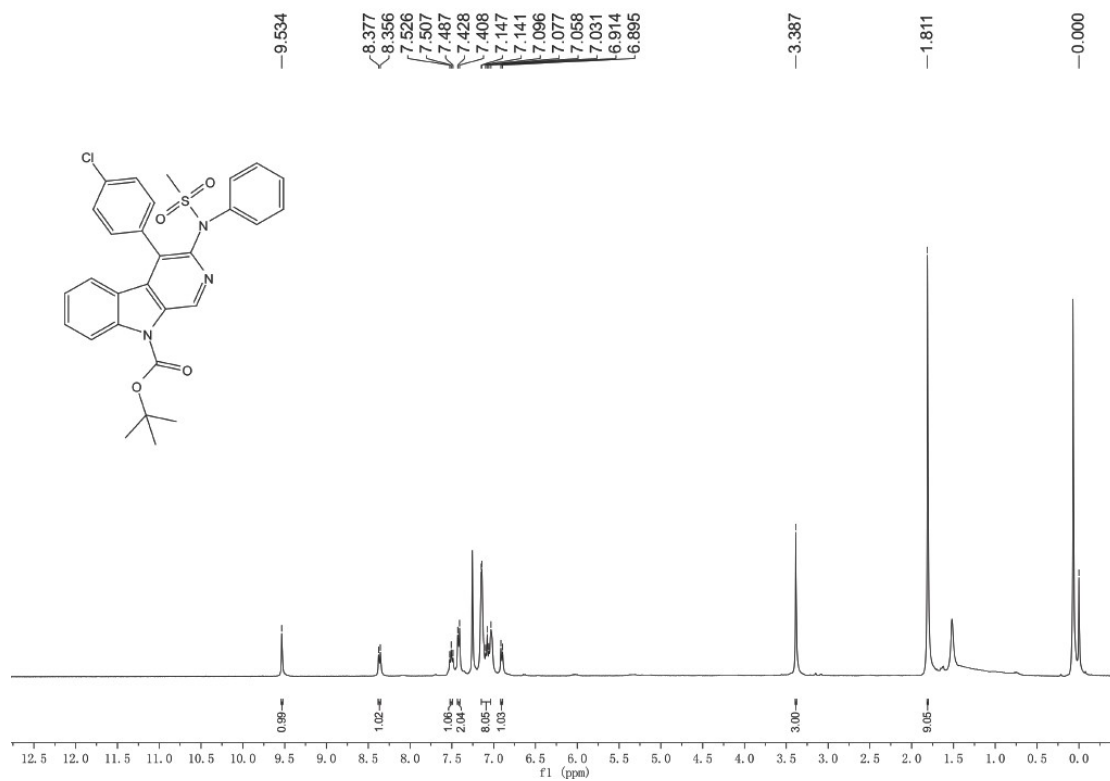
¹H NMR and ¹³C NMR spectra of compound **5d**



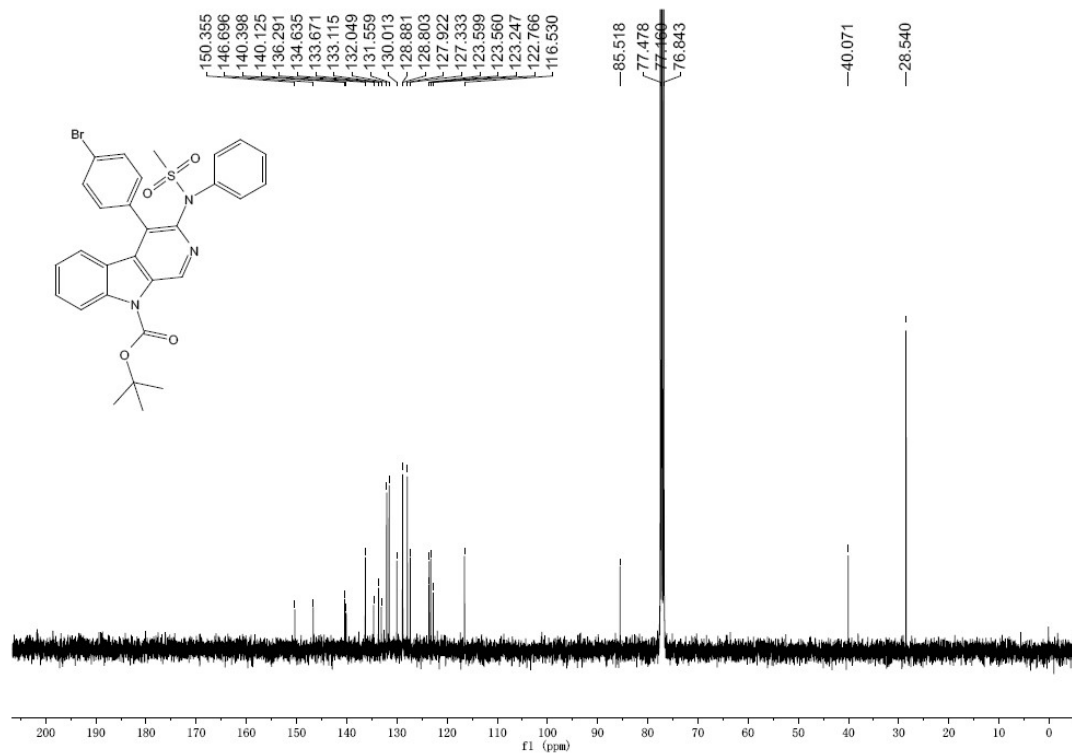
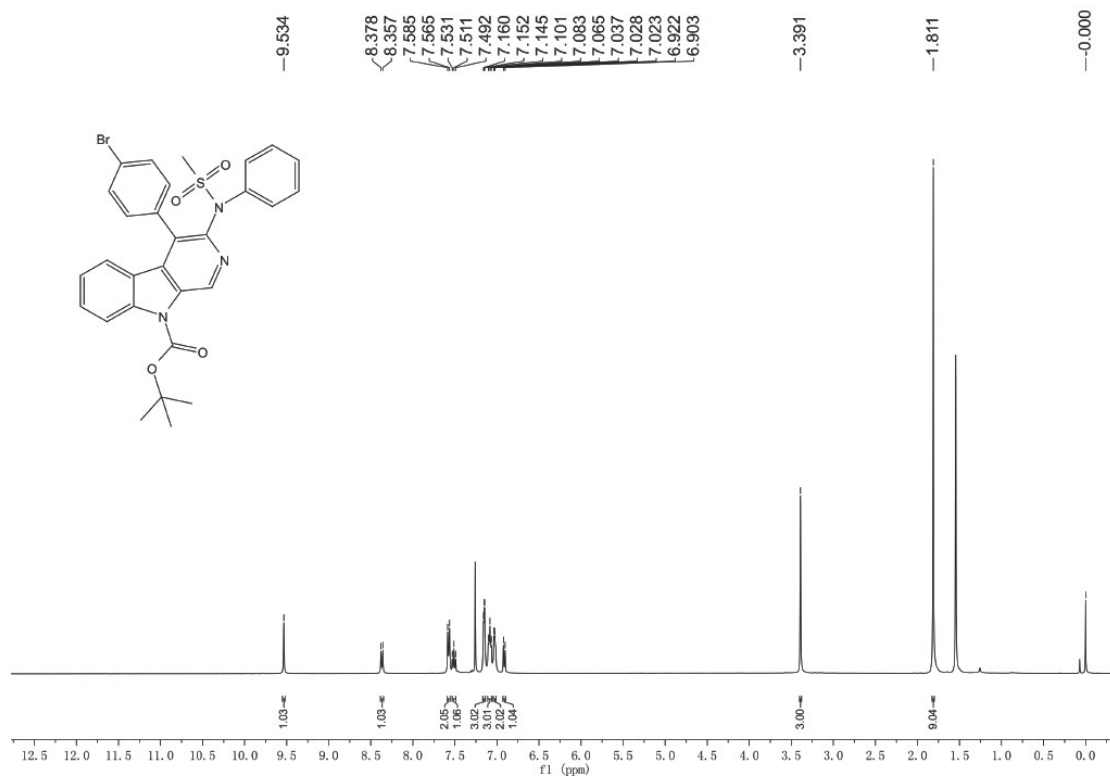
¹H NMR and ¹³C NMR spectra of compound 5e



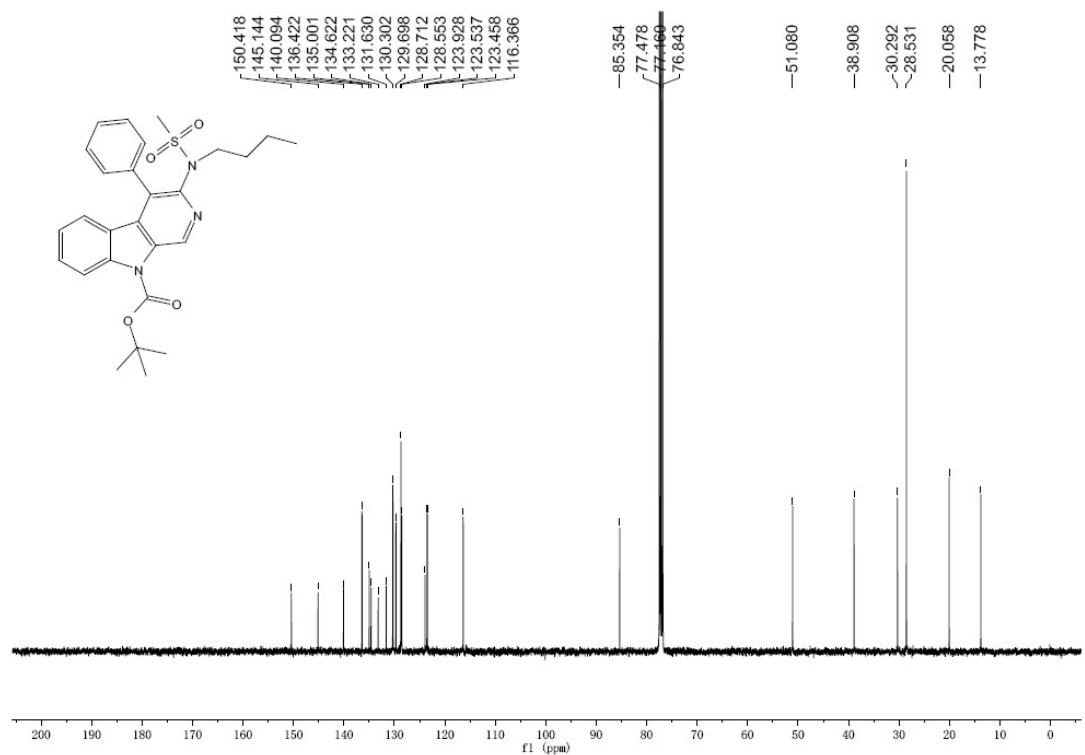
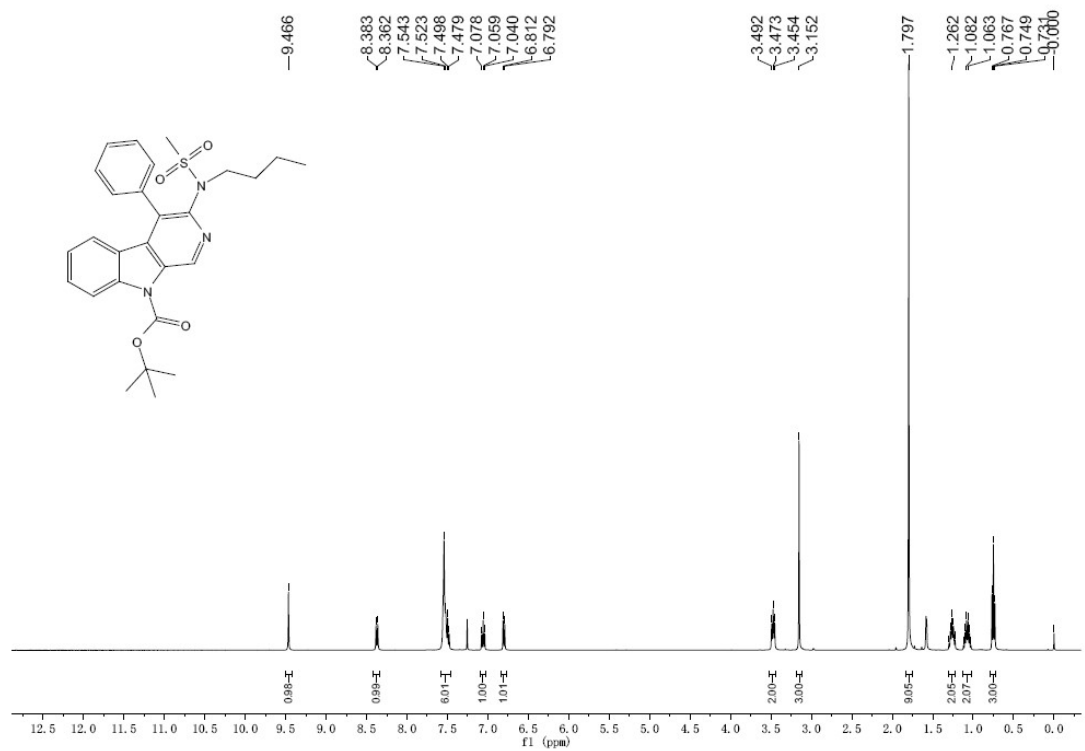
¹H NMR and ¹³C NMR spectra of compound 5f



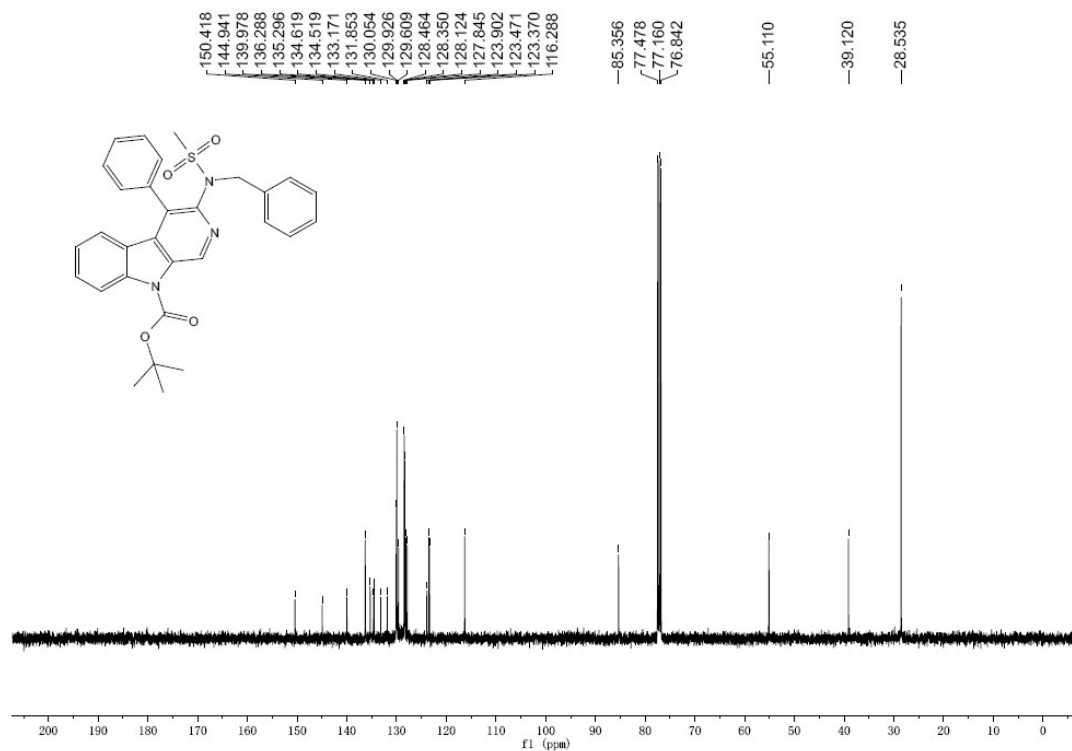
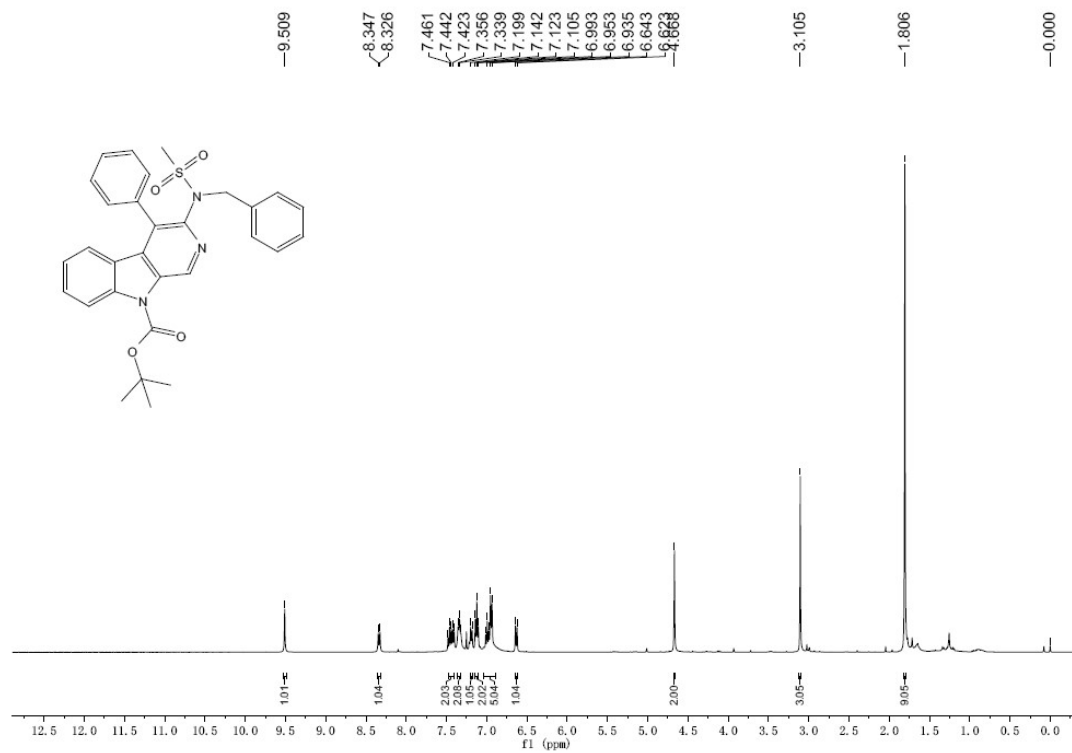
¹H NMR and ¹³C NMR spectra of compound **5g**



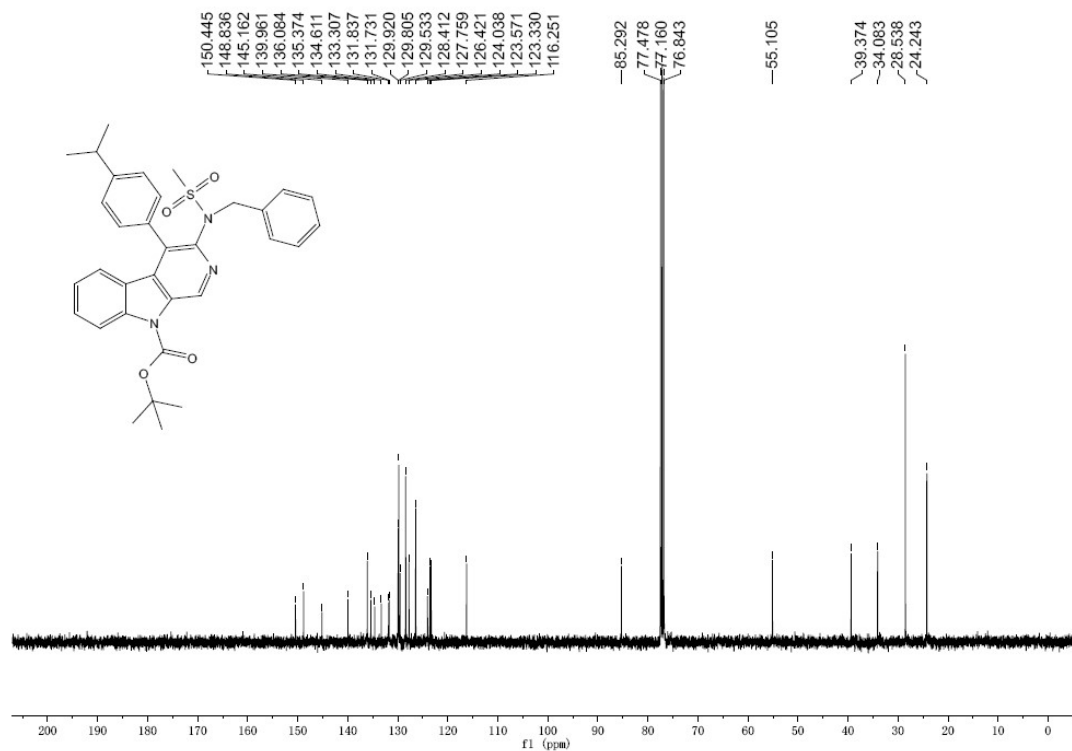
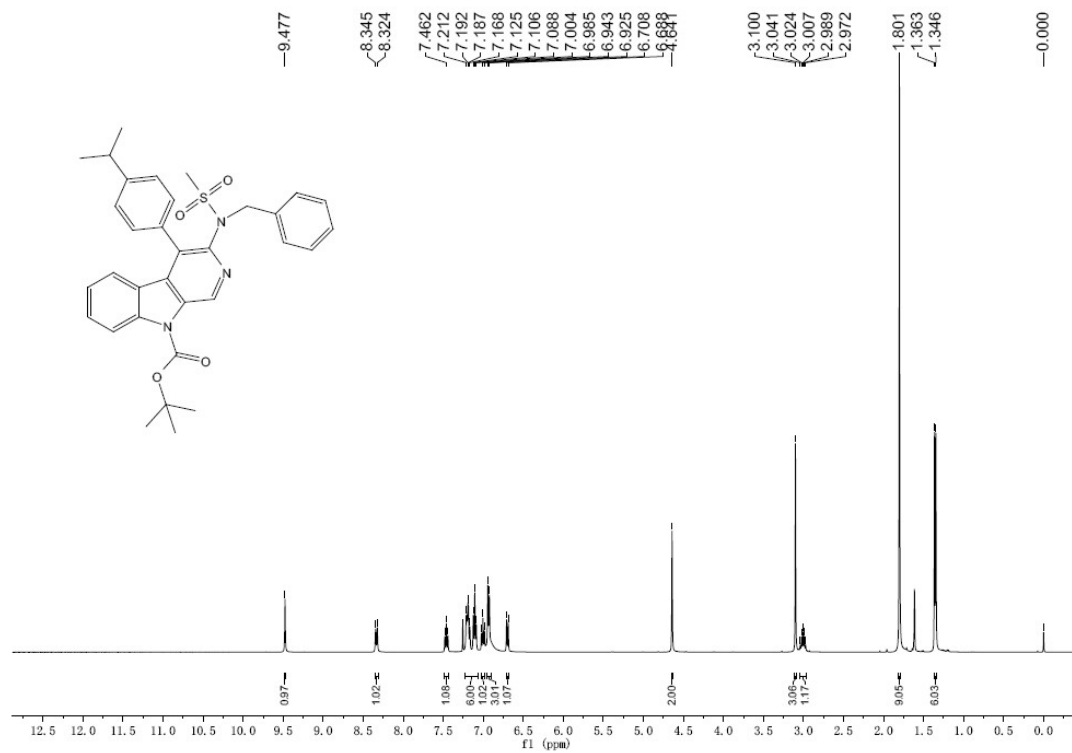
¹H NMR and ¹³C NMR spectra of compound **5h**



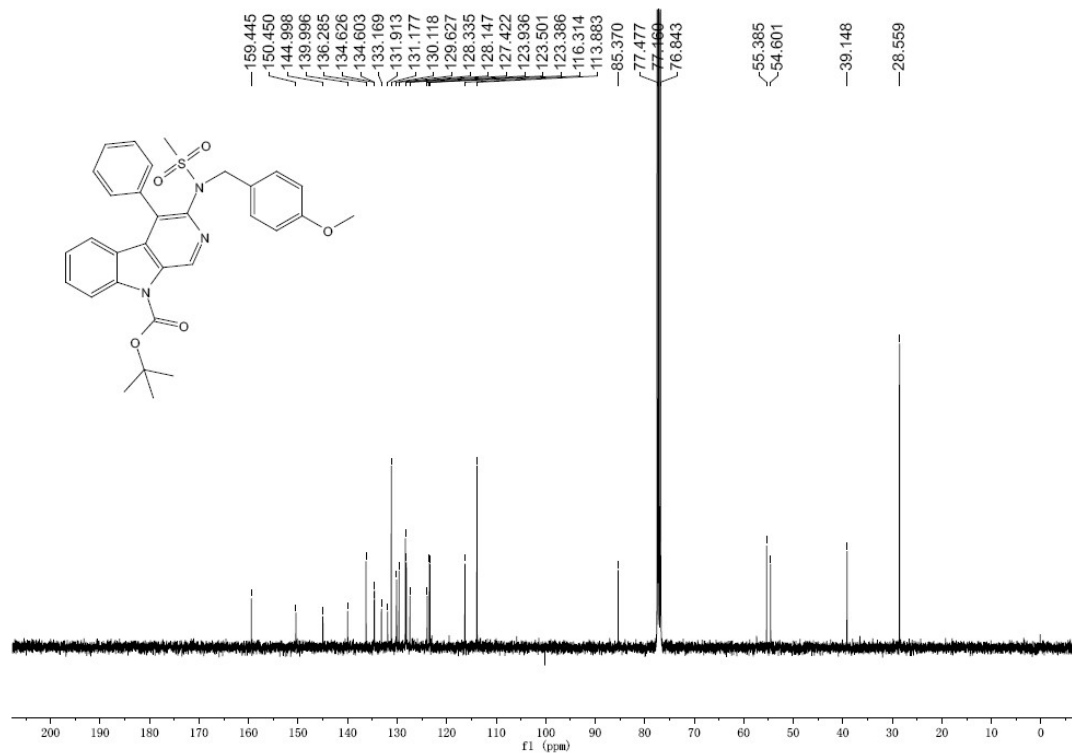
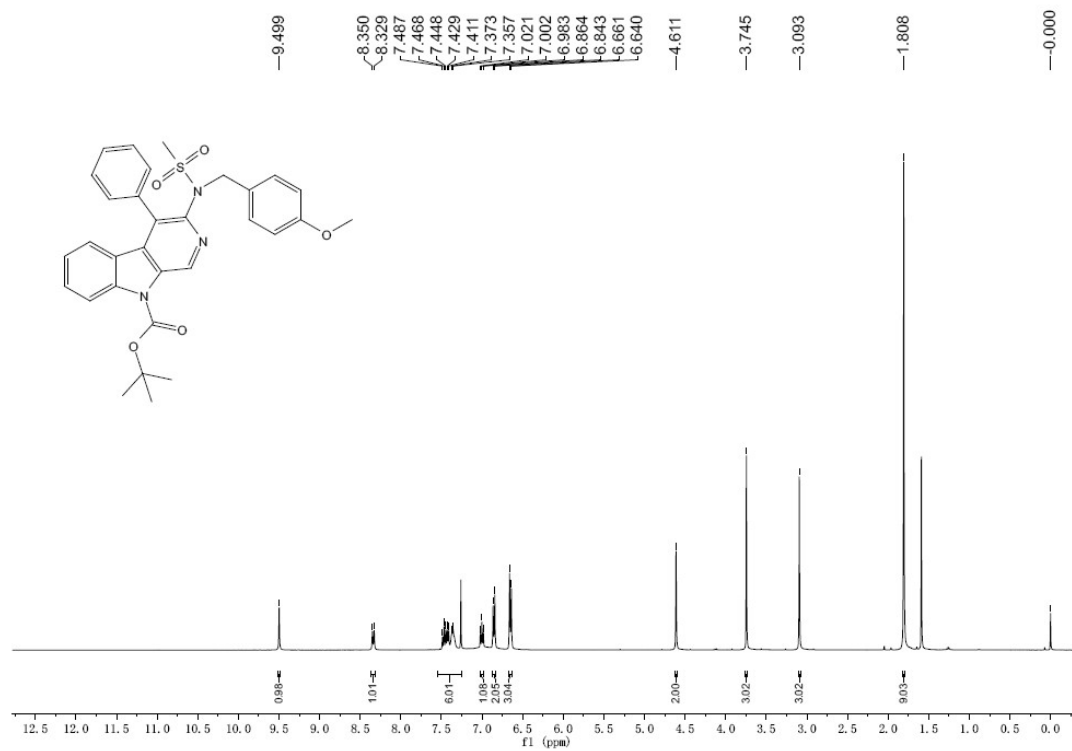
^1H NMR and ^{13}C NMR spectra of compound **5i**



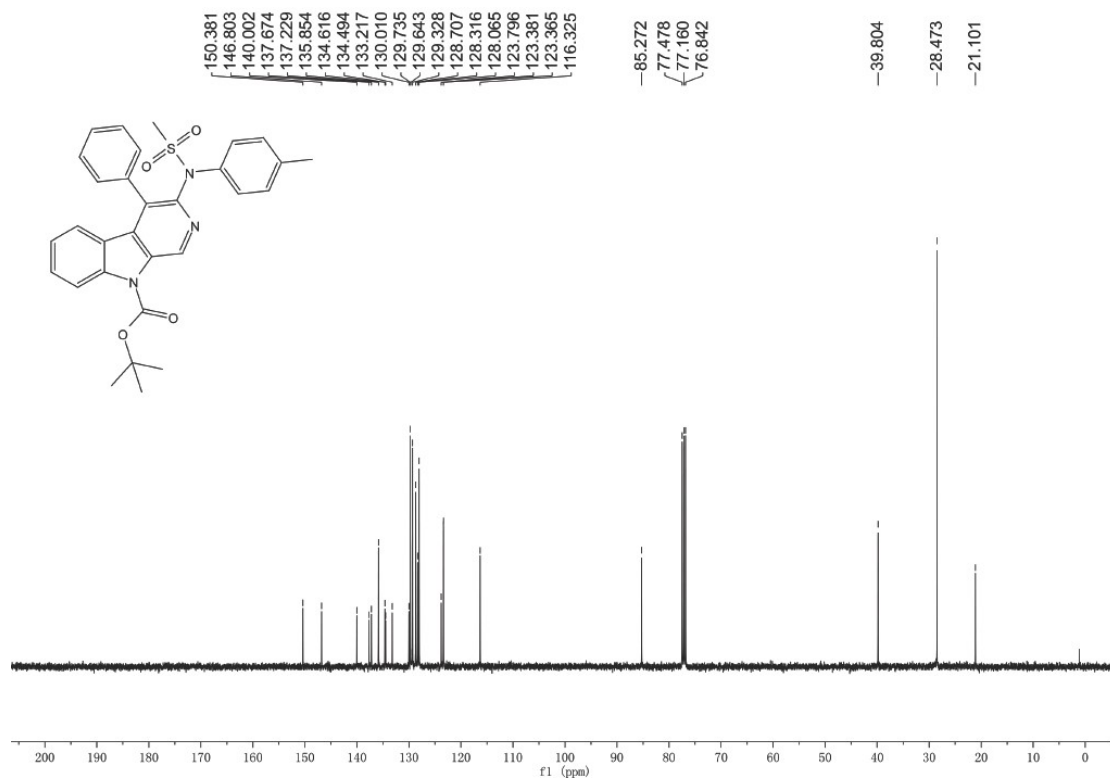
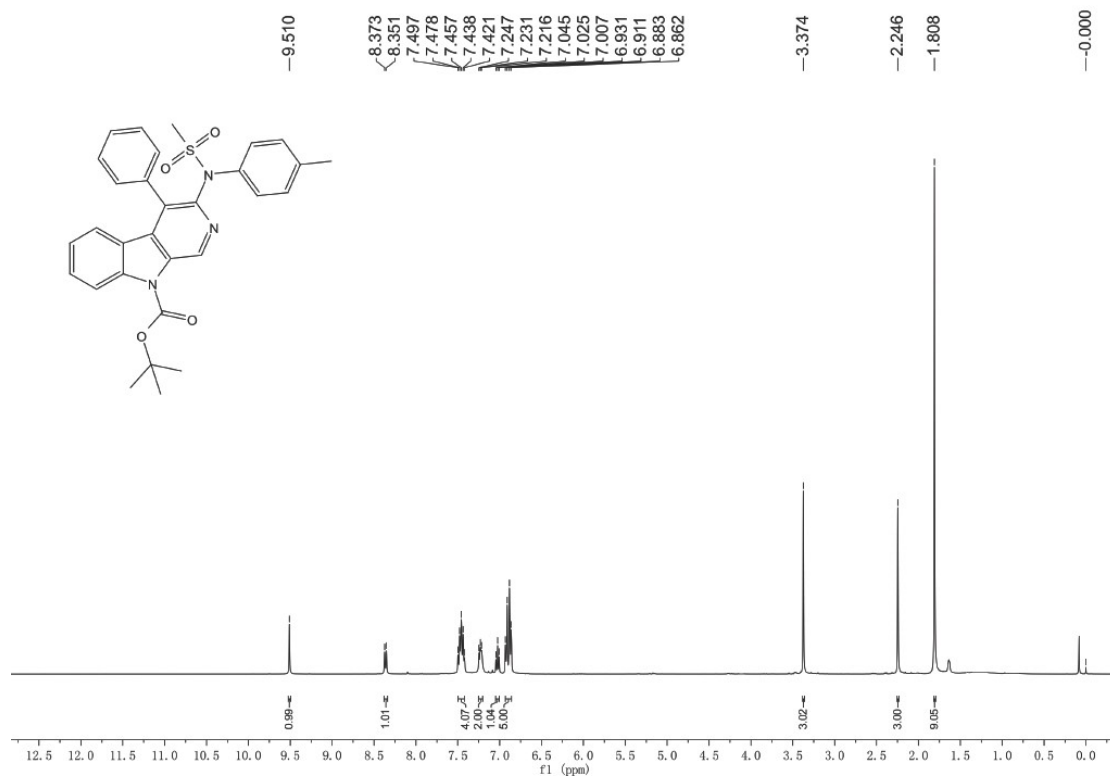
¹H NMR and ¹³C NMR spectra of compound 5j



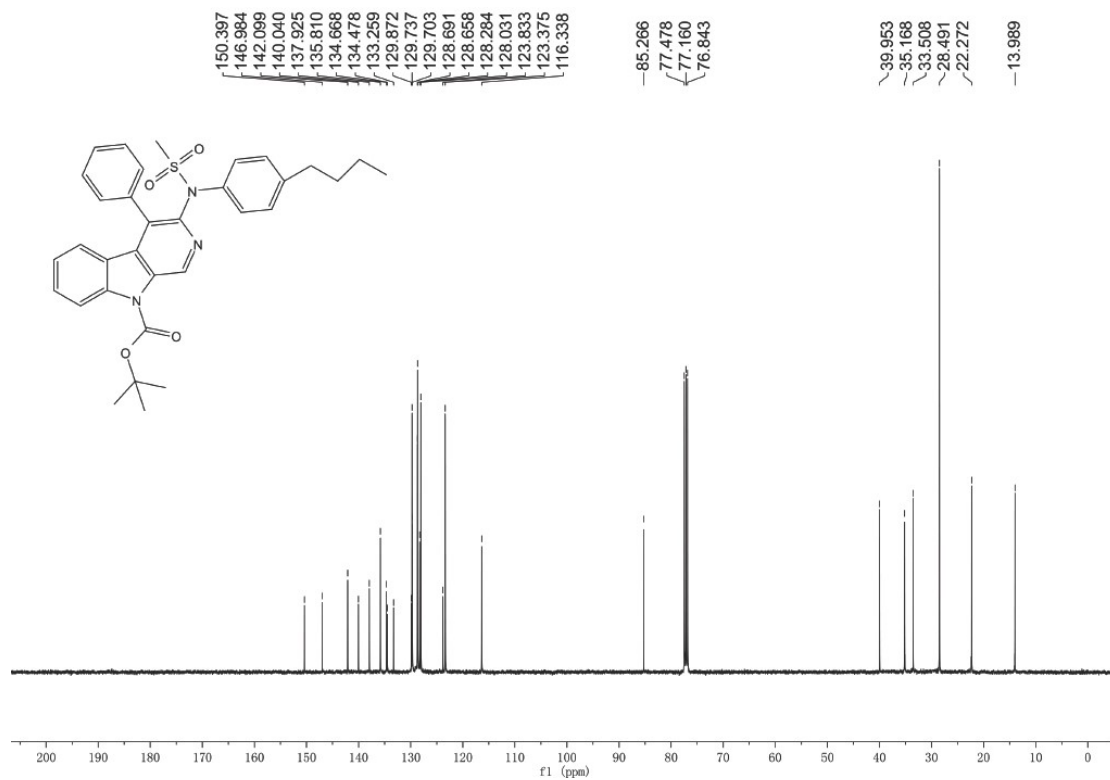
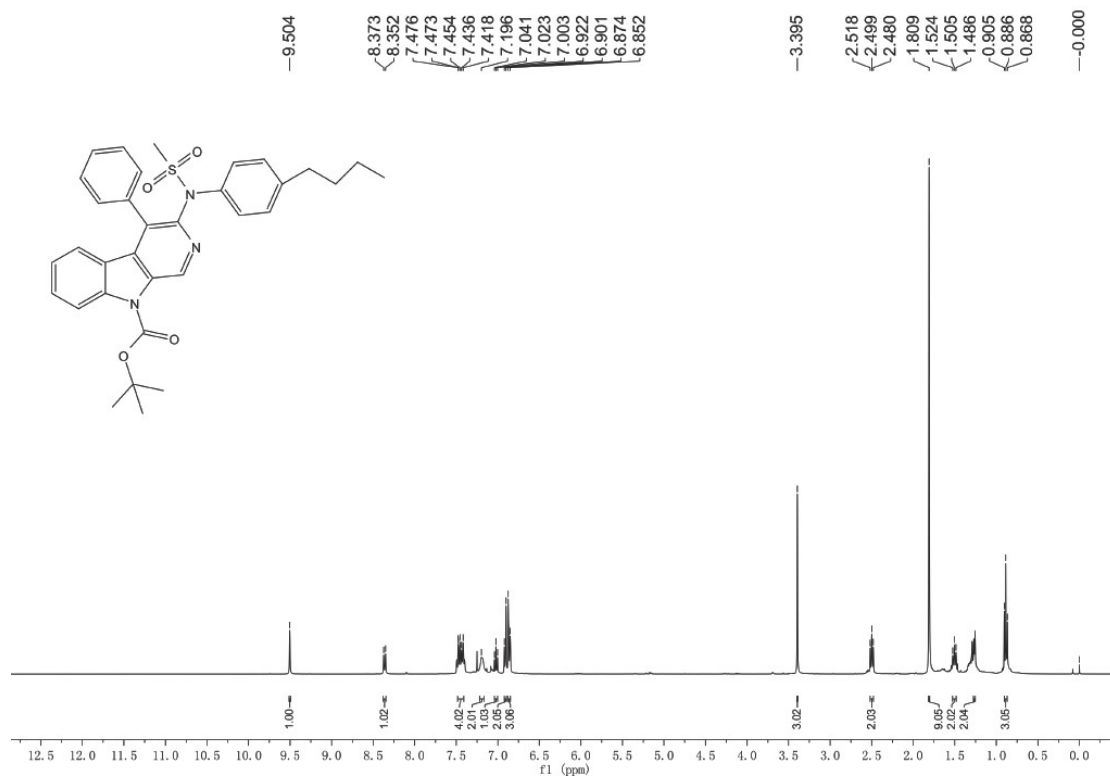
^1H NMR and ^{13}C NMR spectra of compound 5k



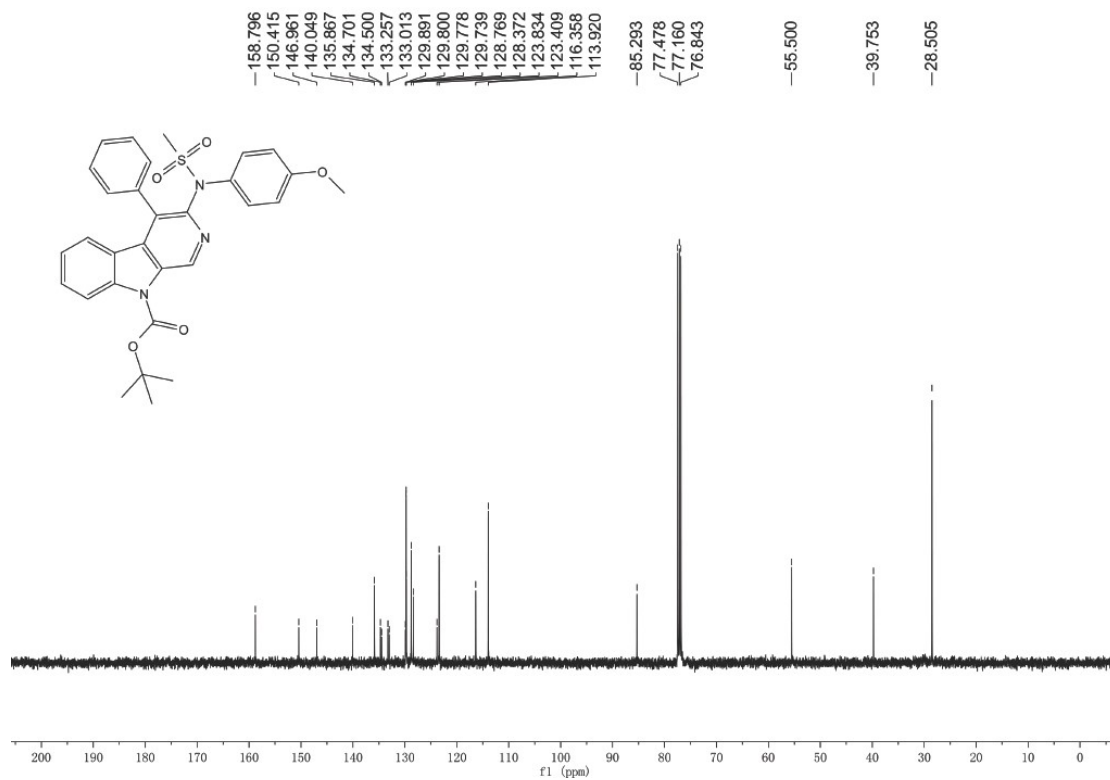
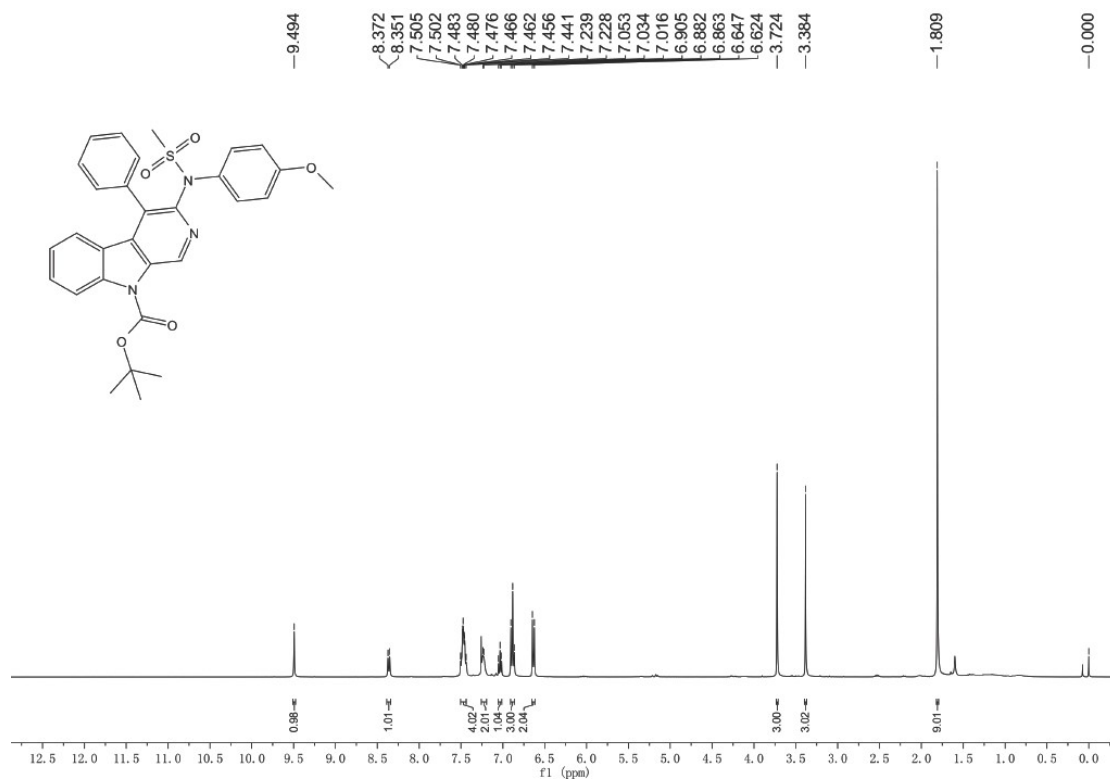
¹H NMR and ¹³C NMR spectra of compound 51



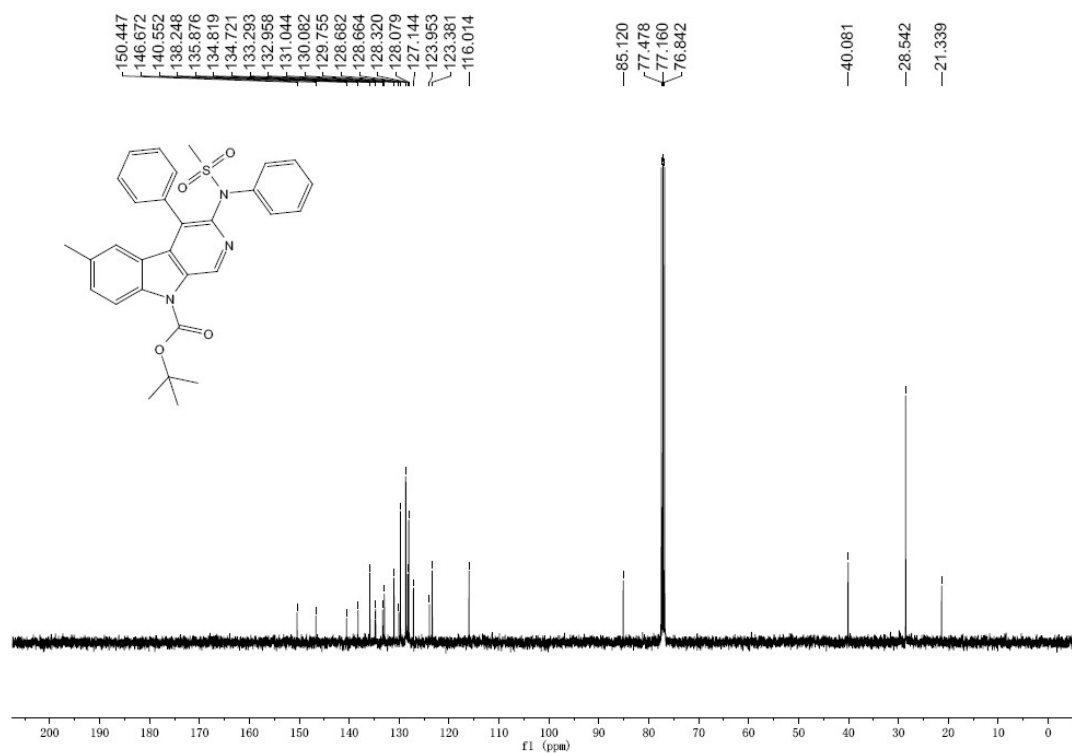
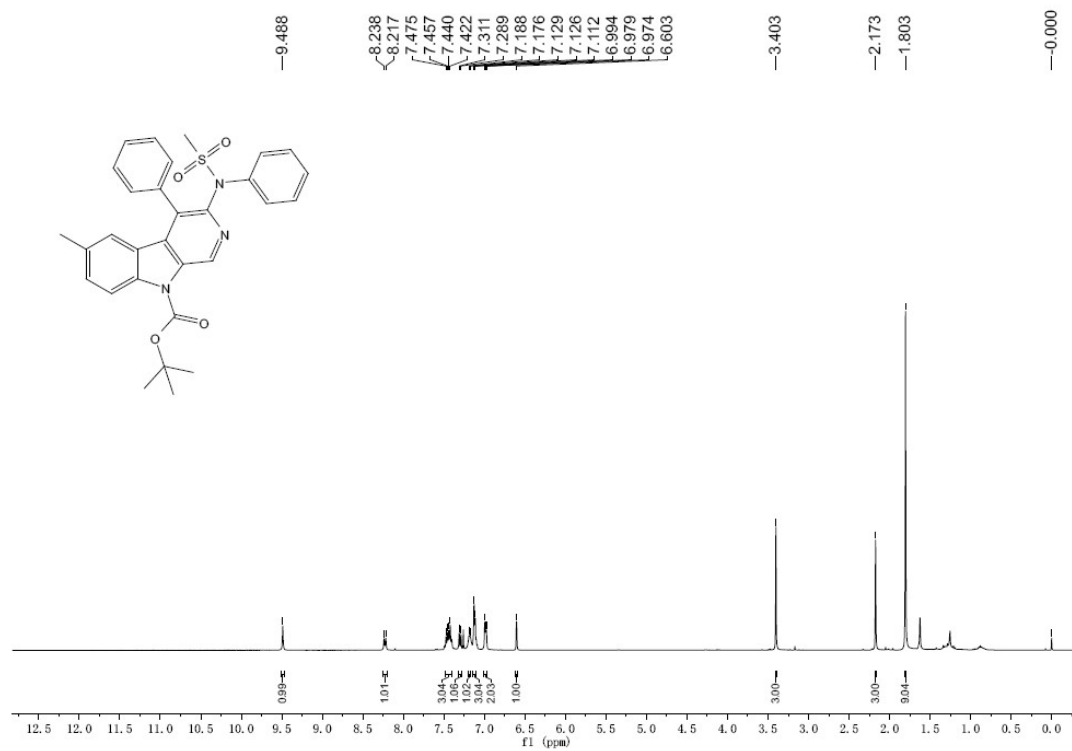
¹H NMR and ¹³C NMR spectra of compound **5m**



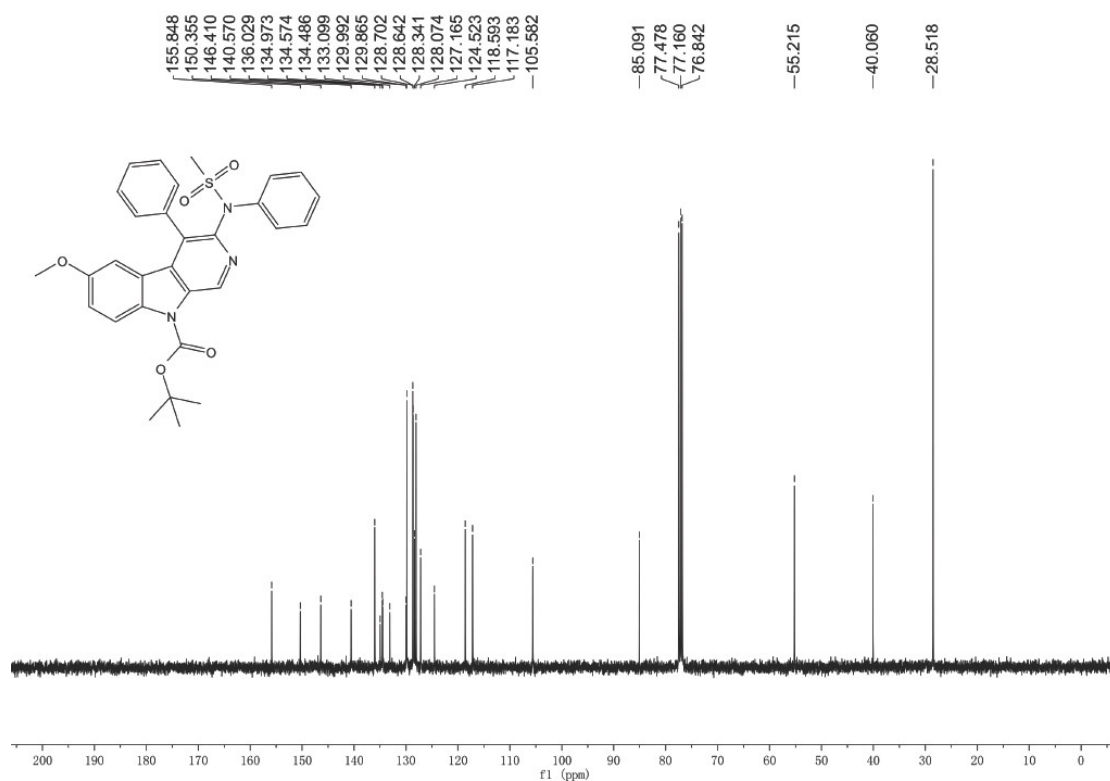
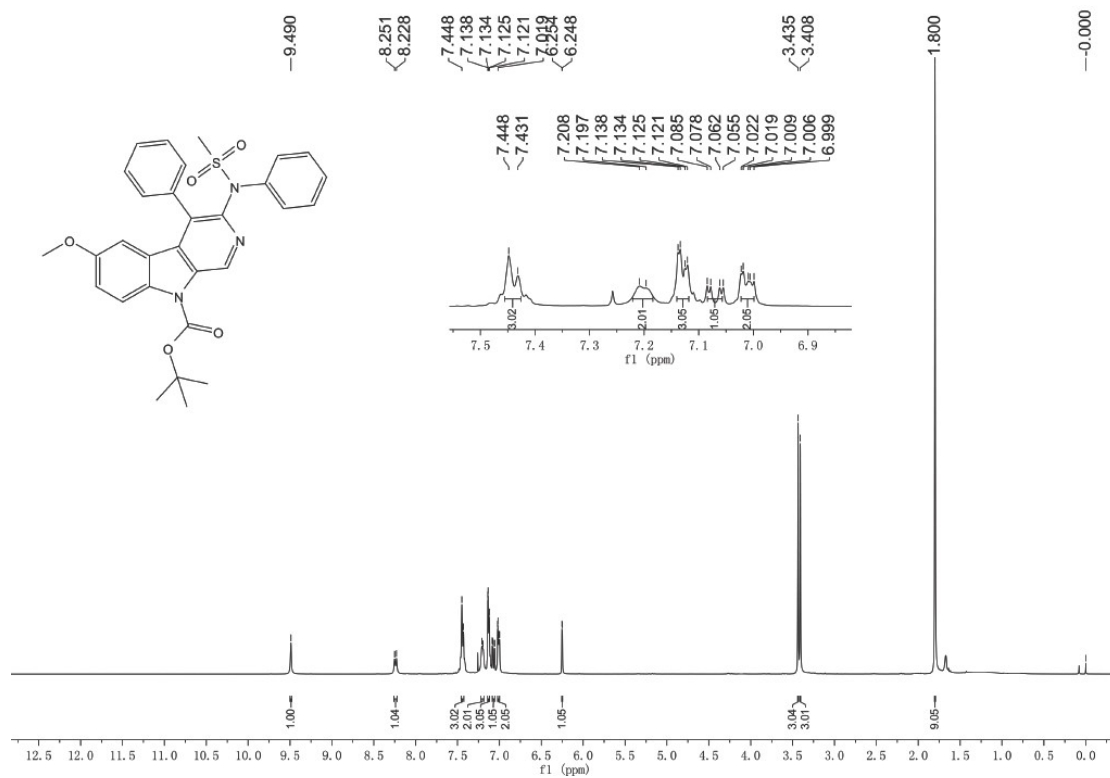
^1H NMR and ^{13}C NMR spectra of compound **5n**



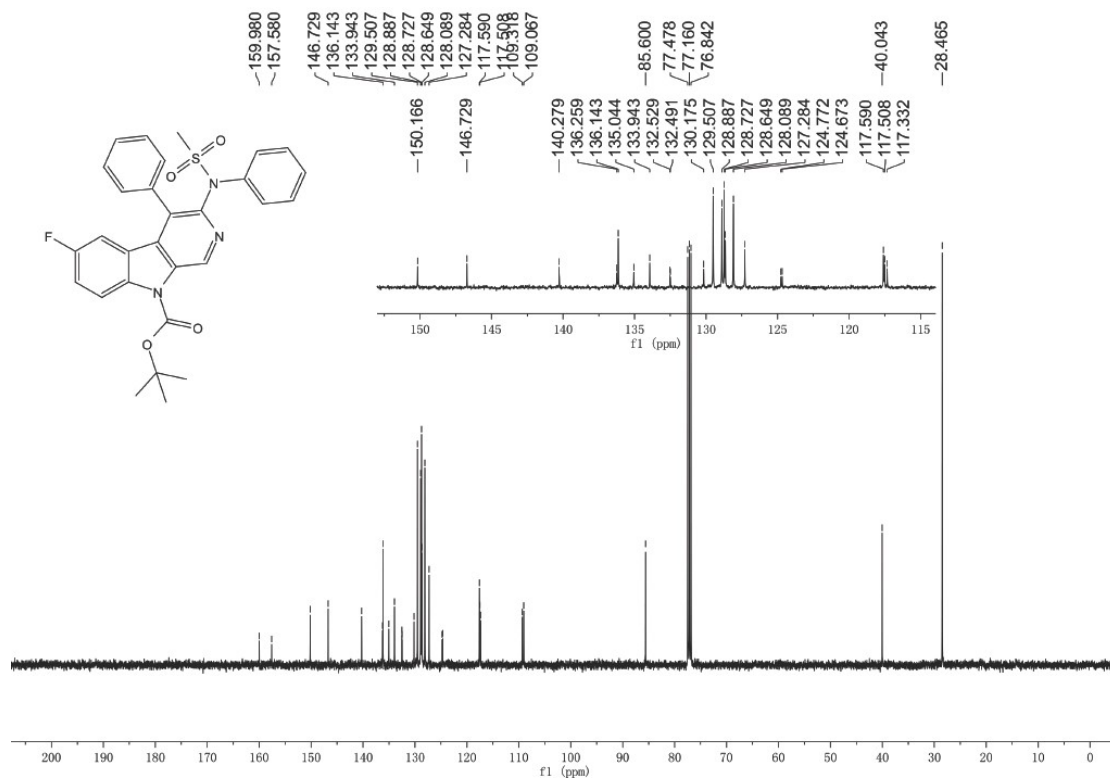
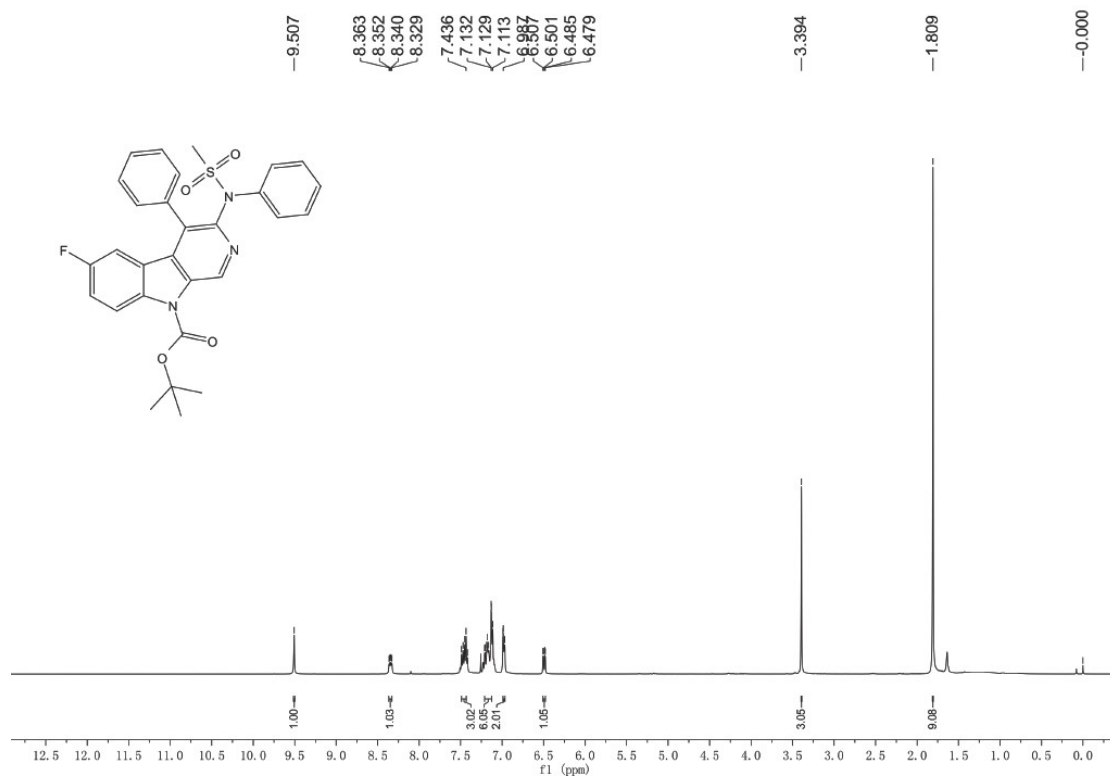
¹H NMR and ¹³C NMR spectra of compound **5o**



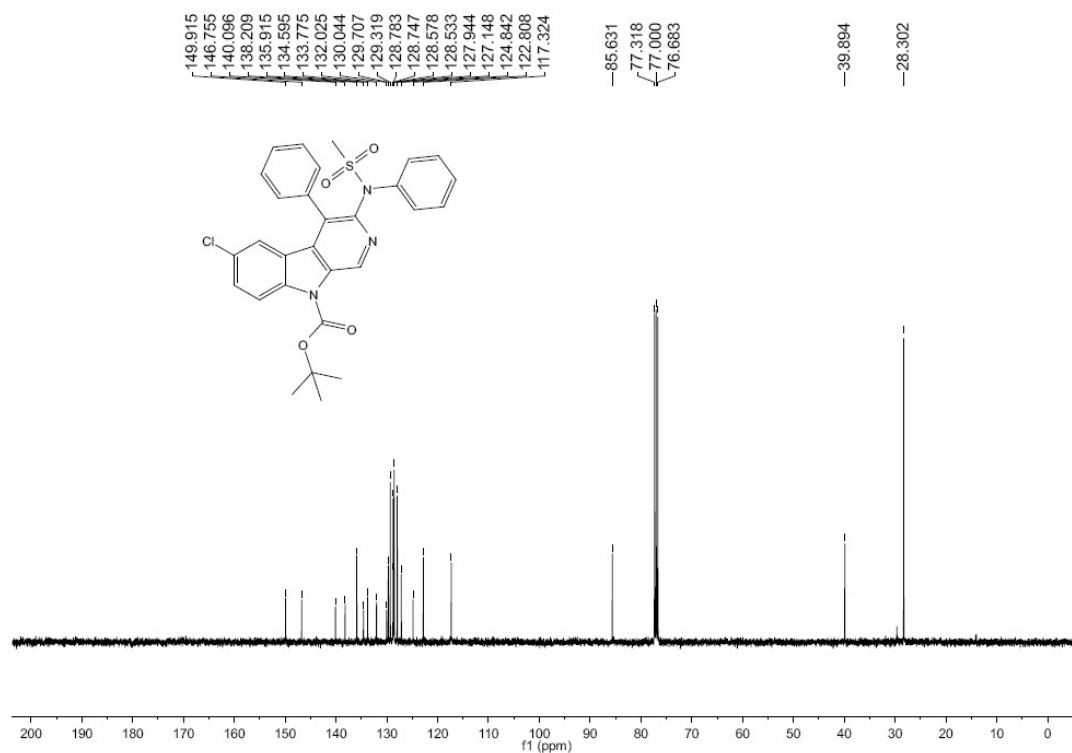
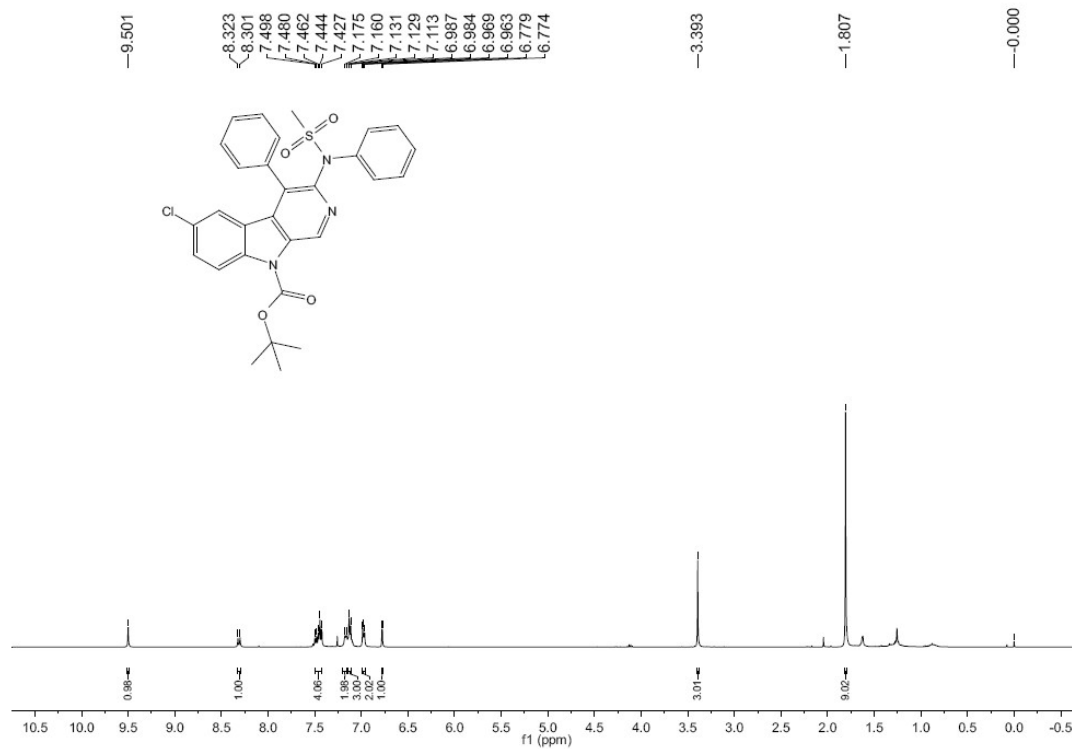
¹H NMR and ¹³C NMR spectra of compound 5p



¹H NMR and ¹³C NMR spectra of compound **5q**



^1H NMR and ^{13}C NMR spectra of compound **5r**



¹H NMR and ¹³C NMR spectra of compound **5s**