Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Palladium-Catalyzed Carbonylative Synthesis of Indole-3-Carboxamides from 2-Ethynylanilines and Nitroarenes

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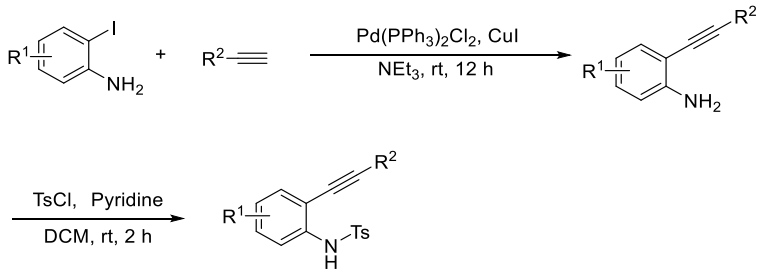
1. General experimental information

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. All commercially available reagents were used without further purification. All of the solvents were treated according to known methods. Column chromatography was performed on silica gel (200-400 mesh). ^{1}H NMR (400 MHz) chemical shifts were reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. ^{13}C NMR (100 MHz) chemical shifts were reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz) and integration. HRMS measurements were obtained on a TOF analyzer.

2. General procedure for the synthesis of *N*-Ts-2-ethynylanilines (1a-n)

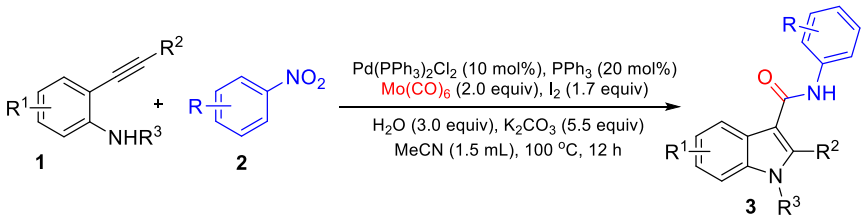
The *N*-Ts-2-ethynylanilines were prepared according to a general procedure reported by Knochel[1].



To a solution of corresponding 2-iodoanilines (2.19 g, 10 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (140 mg, 2 mol %), and CuI (38 mg, 2 mol %) in NEt_3 (40 mL) was added terminal alkynes (1.12 g, 11 mmol, 1.1 equiv). The resulting mixture was stirred at room temperature for 12 h. The mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) to afford 2-ethynylanilines.

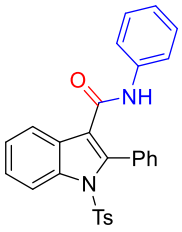
To a solution of 2-ethynylanilines (0.772 g, 4 mmol, 1.0 equiv), TsCl (1 g, 5.2 mmol, 1.3 equiv), and pyridine (500 μL) in DCM (8 mL). The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with ice-cold water and extracted with DCM. The combined organic layer was washed with 2N HCl solution, dried and evaporated to give crude residue. The residue was purified by flash chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) to afford *N*-Ts-2-ethynylanilines.

3. General procedure for the synthesis of indole-3-carboxamides (3aa-am, 3ba-na)

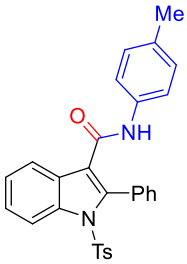


N-Ts-2-ethynylanilines **1** (0.2 mmol, 1.0 equiv), I_2 (86.3 mg, 0.34 mmol, 1.7 equiv) and K_2CO_3 (82.9 mg, 0.6 mmol, 3.0 equiv) were added to an oven-dried tube (15.0 mL) which was then placed under vacuum and refilled with nitrogen three times. CH_3CN (1.0 mL) was added into the tube via syringe and the tube was sealed and stirred at 50 °C for 2.5 h. Then nitroarenes **2** (0.30 mmol, 1.5 equiv), $Mo(CO)_6$ (105.6 mg, 0.4 mmol, 2.0 equiv), $Pd(PPh_3)_2Cl_2$ (14.0 mg, 10 mol %), PPh_3 (15.6 mg, 20 mol %), H_2O (10.8 mg, 0.6 mmol, 3.0 equiv) and CH_3CN (0.5 mL) were added into the tube via syringe. The tube was sealed and stirred at 100 °C for 12 h. Upon the reaction was completed, the resulting mixture was purified by silica gel column using chromatography (petroleum ether / ethyl acetate = 5:1) to obtain products **3**.

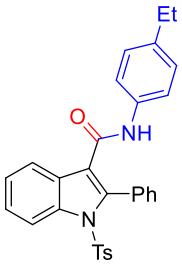
4. Characterization data of products 3aa-am and 3ba-na



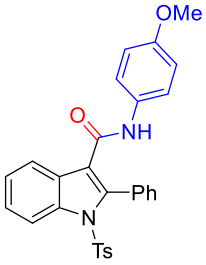
***N*,2-diphenyl-1-tosyl-1*H*-indole-3-carboxamide (3aa)[2].** The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 68.1 mg, 73% yield, mp 158 – 159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.4 Hz, 1H), 8.32 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.5 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.41 (t, J = 7.7 Hz, 1H), 7.37 (d, J = 8.2 Hz, 2H). 7.19 (t, J = 7.8 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.08 – 6.98 (m, 3H), 6.76 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 145.6, 139.3, 137.6, 136.5, 135.5, 131.7, 130.6, 130.0, 129.8, 128.9, 128.7, 128.4, 127.0, 126.0, 124.9, 124.2, 122.3, 119.5, 118.2, 115.2, 21.7.



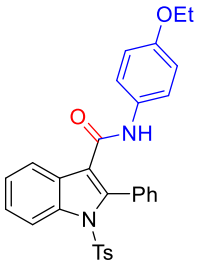
2-phenyl-*N*-(*p*-tolyl)-1-tosyl-1*H*-indole-3-carboxamide (3ab). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 73.9 mg, 77% yield, mp 255 – 256 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 7.8 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.49 – 7.43 (m, 3H), 7.42 – 7.38 (m, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 8.1 Hz, 2H), 6.66 (s, 1H), 2.34 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 145.5, 139.1, 136.5, 135.5, 135.0, 133.8, 131.6, 130.5, 130.1, 129.7, 129.4, 128.6, 128.4, 127.0, 126.0, 124.9, 122.3, 119.5, 118.3, 115.2, 21.6, 20.8; HRMS (ESI-TOF) Calcd. For $C_{29}H_{25}N_2O_3S^+$ $[M+H]^+$: 481.1580; found: 481.1586.



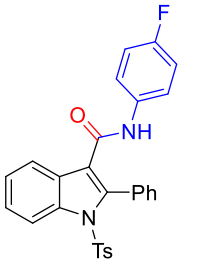
***N*-(4-ethylphenyl)-2-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3ac).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 64.2 mg, 65% yield, mp 199 – 201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.48 – 7.45 (m, 3H), 7.41 (d, J = 6.7 Hz, 1H), 7.37 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 7.03 (d, J = 8.3 Hz, 2H), 6.95 (d, J = 8.2 Hz, 2H), 6.70 (s, 1H), 2.55 (q, J = 7.6 Hz, 2H), 2.34 (s, 3H), 1.17 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 145.5, 140.3, 139.1, 136.5, 135.5, 135.2, 131.7, 130.5, 130.1, 129.7, 128.6, 128.4, 128.2, 127.0, 126.0, 124.9, 122.3, 119.6, 118.3, 115.2, 28.3, 21.7, 15.7; HRMS (ESI-TOF) Calcd. for $C_{30}H_{27}N_2O_3S^+$ $[M+H]^+$: 495.1737; found: 495.1742.



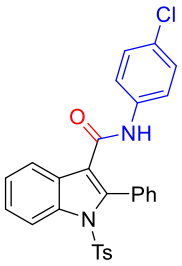
***N*-(4-methoxyphenyl)-2-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3ad)[2].** The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 67.5 mg, 68% yield, mp 209 – 212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.7 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.4 Hz, 2H), 7.49 – 7.43 (m, 3H), 7.34 – 7.41 (m, 3H), 7.12 (d, J = 8.3 Hz, 2H), 6.95 (d, J = 9.0 Hz, 2H), 6.73 (d, J = 9.0 Hz, 2H), 6.63 (s, 1H), 3.73 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 156.4, 145.5, 139.1, 136.5, 135.5, 131.7, 130.7, 130.4, 130.1, 129.7, 128.6, 128.4, 127.0, 126.0, 124.9, 122.2, 121.2, 118.4, 115.2, 114.1, 55.5, 21.6.



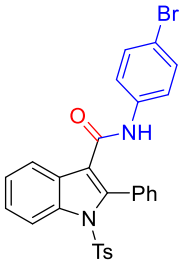
***N*-(4-ethoxyphenyl)-2-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3ae).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 67.3 mg, 66% yield, mp 155 – 156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 7.9 Hz, 1H), 7.61 (t, J = 7.3 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.48 – 7.43 (m, 3H), 7.40 (d, J = 7.4 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 6.72 (d, J = 8.9 Hz, 2H), 6.65 (s, 1H), 3.94 (q, J = 6.9 Hz, 2H), 2.33 (s, 3H), 1.36 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 155.7, 145.5, 139.1, 136.6, 135.5, 131.7, 130.6, 130.4, 130.1, 129.7, 128.6, 128.5, 127.0, 126.0, 124.9, 122.2, 121.2, 118.4, 115.2, 114.7, 63.7, 21.7, 14.9; HRMS (ESI-TOF) Calcd. for $C_{30}H_{27}N_2O_4S^+$ $[M+H]^+$: 511.1686; found: 511.1691.



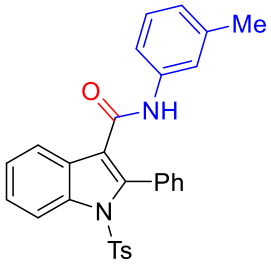
***N*-(4-fluorophenyl)-2-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3af).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 79.4 mg, 82% yield, mp 152 – 154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 7.9 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.49 – 7.43 (m, 3H), 7.42 – 7.34 (m, 3H), 7.12 (d, J = 8.0 Hz, 2H), 7.03 – 6.95 (m, 2H), 6.87 (t, J = 8.5 Hz, 2H), 6.72 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 159.2 (d, J = 243.5 Hz, 1C), 145.6, 139.3, 136.5, 135.5, 133.6 (d, J = 2.9 Hz, 1C), 131.7, 130.5, 130.0, 129.8, 128.7, 128.3, 127.0, 126.1, 124.9, 122.2, 121.2 (d, J = 7.9 Hz, 1C), 118.0, 115.5 (d, J = 22.4 Hz, 1C), 115.2, 21.7; HRMS (ESI-TOF) Calcd. for $C_{28}H_{22}FN_2O_3S^+$ $[M+H]^+$: 485.1330; found: 485.1328.



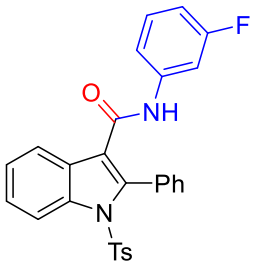
***N*-(4-chlorophenyl)-2-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3ag).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 59.1 mg, 59% yield, mp 197 – 199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.3 Hz, 1H), 8.29 (d, J = 7.3 Hz, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.41 (t, J = 7.0 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.15 – 7.10 (m, 4H), 6.96 (d, J = 8.8 Hz, 2H), 6.70 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 145.6, 139.4, 136.5, 136.2, 135.5, 131.7, 130.6, 130.0, 129.9, 129.1, 128.9, 128.7, 128.2, 127.0, 126.1, 125.0, 122.2, 120.6, 117.9, 115.2, 21.7; HRMS (ESI-TOF) Calcd. for $C_{28}H_{22}ClN_2O_3S^+$ $[M+H]^+$: 501.1034; found: 501.1033.



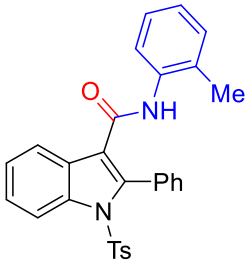
***N*-(4-bromophenyl)-2-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3ah).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 63.1 mg, 58% yield, mp 188 – 191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 8.29 (d, J = 7.0 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.42 – 7.33 (m, 3H), 7.28 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.70 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 145.6, 139.4, 136.7, 136.5, 135.5, 131.8, 131.7, 130.6, 130.0, 129.8, 128.7, 128.2, 127.0, 126.1, 125.0, 122.2, 120.9, 117.8, 116.6, 115.2, 21.7; HRMS (ESI-TOF) Calcd. for $C_{28}H_{22}BrN_2O_3S^+$ $[M+H]^+$: 545.0529; found: 545.0523.



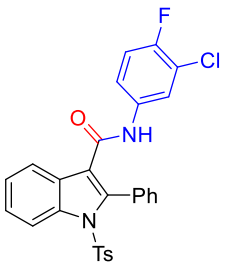
2-phenyl-*N*-(*m*-tolyl)-1-tosyl-1*H*-indole-3-carboxamide (3ai). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 64.3 mg, 67% yield, mp 159 – 161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.3 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.5 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.42 (d, J = 7.3 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 7.06 (t, J = 7.8 Hz, 1H), 7.01 (s, 1H), 6.83 (d, J = 7.5 Hz, 1H), 6.74 – 6.67 (m, 2H), 2.34 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 145.5, 139.2, 138.8, 137.5, 136.5, 135.5, 131.7, 130.5, 130.1, 129.8, 128.7, 128.4, 127.0, 126.0, 125.0, 124.9, 122.3, 120.2, 118.3, 116.5, 115.2, 21.7, 21.5; HRMS (ESI-TOF) Calcd. for $C_{29}H_{25}N_2O_3S^+$ $[M+H]^+$: 481.1580; found: 481.1586.



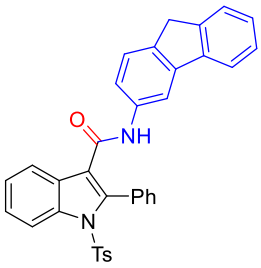
***N*-(3-fluorophenyl)-2-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3aj).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 54.2 mg, 56% yield, mp 155 – 157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.49 – 7.41 (m, 4H), 7.37 (d, J = 8.3 Hz, 2H), 7.14 – 7.07 (m, 4H), 6.77 (s, 1H), 6.70 (td, J = 8.3, 2.5 Hz, 1H), 6.50 (d, J = 8.0 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, J = 244.7 Hz, 1C), 161.7, 145.6, 139.4, 139.0 (d, J = 10.9 Hz, 1C), 136.5, 135.5, 131.6, 130.7, 129.92, 129.91 (d, J = 9.4 Hz, 1C), 129.8, 128.7, 128.2, 127.0, 126.1, 125.0, 122.2, 117.7,115.2, 114.6 (d, J = 2.9 Hz, 1C), 110.8 (d, J = 21.2 Hz, 1C), 106.9 (d, J = 26.5 Hz, 1C), 21.7; HRMS (ESI-TOF) Calcd. For $C_{28}H_{22}FN_2O_3S^+$ $[M+H]^+$: 485.1330; found: 485.1329.



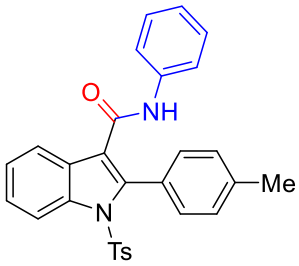
2-phenyl-*N*-(*o*-tolyl)-1-tosyl-1*H*-indole-3-carboxamide (3ak). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 43.2 mg, 45% yield, mp 123 – 125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 7.9 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.52 – 7.44 (m, 5H), 7.40 (t, J = 7.0 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.19 – 7.13 (m, 1H), 7.11 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 5.8 Hz, 1H), 6.99 (d, J = 7.2 Hz, 1H), 6.71 (s, 1H), 2.34 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 145.5, 139.0, 136.7, 135.6, 135.4, 131.8, 130.5, 130.3, 129.9, 129.7, 128.6, 128.2, 126.9, 126.7, 126.0, 125.0, 124.8, 122.2, 122.1, 118.6, 115.4, 21.7, 17.0; HRMS (ESI-TOF) Calcd. for $C_{29}H_{25}N_2O_3S^+$ $[M+H]^+$: 481.1580; found: 481.1586.



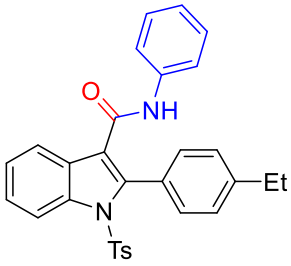
***N*-(3-chloro-4-fluorophenyl)-2-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3al).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 73.6 mg, 71% yield, mp 166 – 168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 7.9 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.49 – 7.41 (m, 4H), 7.36 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 4.7 Hz, 1H), 7.13 (d, J = 8.1 Hz, 2H), 6.92 (t, J = 8.8 Hz, 1H), 6.68 – 6.65 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 154.6 (d, J = 246.0 Hz, 1C), 145.7, 139.4, 136.4, 135.5, 134.2 (d, J = 3.4 Hz, 1C), 131.6, 130.7, 130.0, 129.8, 128.8, 128.1, 127.0, 126.2, 125.0, 122.1, 121.6, 121.0 (d, J = 18.5 Hz, 1C), 118.9 (d, J = 6.9 Hz), 117.6, 116.5 (d, J = 22.0 Hz, 1C), 115.2, 21.7; HRMS (ESI-TOF) Calcd. for $C_{28}H_{21}ClFN_2O_3S^+$ $[M+H]^+$: 519.0940; found: 519.0949.



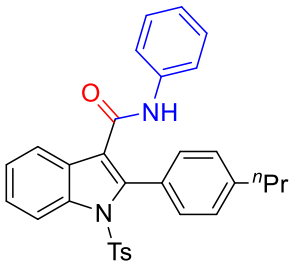
***N*-(9*H*-fluoren-3-yl)-2-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3am).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 70.9 mg, 64% yield, mp 173 – 176; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.3 Hz, 1H), 8.35 (d, J = 7.8 Hz, 1H), 7.72 – 7.60 (m, 1H), 7.61 – 7.51 (m, 3H), 7.49 (d, J = 7.4 Hz, 4H), 7.44 (d, J = 7.3 Hz, 1H), 7.38 (d, J = 8.3 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.13 (d, J = 8.2 Hz, 2H), 6.85 (s, 1H), 6.67 (d, J = 7.5 Hz, 1H), 3.81 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 145.6, 144.3, 143.2, 141.3, 139.2, 138.0, 136.6, 136.4, 135.5, 131.7, 130.5, 130.1, 129.8, 128.7, 128.4, 127.0, 126.8, 126.3, 126.0, 125.0, 124.9, 122.3, 120.0, 119.5, 118.3, 118.1, 116.4, 115.2, 37.1, 21.7; HRMS (ESI-TOF) Calcd. for $C_{35}H_{27}N_2O_3S^+$ $[M+H]^+$: 555.1737; found: 555.1738.



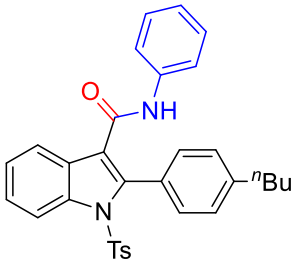
***N*-phenyl-2-(*p*-tolyl)-1-tosyl-1*H*-indole-3-carboxamide (3ba).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 49.0 mg, 51% yield, mp 151 – 152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.3 Hz, 1H), 8.32 (d, J = 7.7 Hz, 1H), 7.46 (td, 1H), 7.42 – 7.38 (m, 2H), 7.38 – 7.36 (m, 5H), 7.20 (t, J = 7.9 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.06 – 7.00 (m, 3H), 6.81 (s, 1H), 2.52 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 145.5, 140.8, 139.6, 137.7, 136.5, 135.5, 131.5, 129.7, 129.4, 128.9, 128.5, 127.0, 126.9, 125.9, 124.9, 124.1, 122.2, 119.5, 118.0, 115.2, 21.7; HRMS (ESI-TOF) Calcd. for $C_{29}H_{25}N_2O_3S^+$ $[M+H]^+$: 481.1580; found: 481.1589.



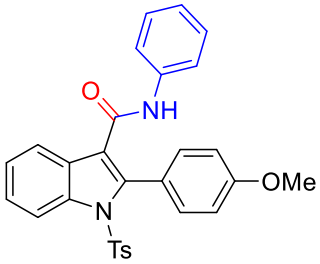
2-(4-ethylphenyl)-*N*-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3ca). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 55.4 mg, 56% yield, mp 130 – 132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.37 (m, 5H), 7.18 (m, J = 7.8, 5.7 Hz, 2H), 7.12 (d, J = 6.8 Hz, 2H), 7.02 – 6.98 (m, 3H), 6.76 (s, 1H), 2.85 – 2.78 (m, 2H), 2.34 (s, 3H), 1.36 (td, J = 7.6, 2.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 147.1, 145.5, 139.6, 137.7, 136.5, 135.6, 131.7, 129.7, 128.8, 128.4, 128.3, 127.2, 127.0, 125.9, 124.9, 124.0, 122.3, 119.4, 118.0, 115.2, 29.0, 21.7, 15.7; HRMS (ESI-TOF) Calcd. for $C_{30}H_{27}N_2O_3S^+$ $[M+H]^+$: 495.1737; found: 495.1738.



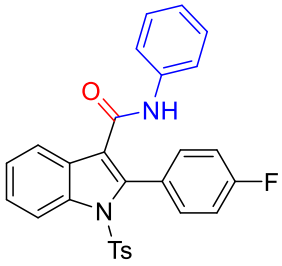
***N*-phenyl-2-(4-propylphenyl)-1-tosyl-1*H*-indole-3-carboxamide (3da).** The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 51.8 mg, 51% yield, mp 135 – 137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.8 Hz, 1H), 8.34 (d, J = 7.7 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.43 – 7.40 (m, 1H), 7.39 – 7.34 (m, 6H), 7.21 – 7.15 (m, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.05 – 6.98 (m, 3H), 6.80 (s, 1H), 2.76 (td, J = 8.4, 7.7, 2.6 Hz, 2H), 2.35 (s, 3H), 1.80 – 1.74 (m, 2H), 1.04 (td, J = 7.4, 2.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 145.6, 145.5, 139.6, 137.7, 136.5, 135.6, 131.6, 129.7, 128.8, 128.4, 127.1, 127.0, 125.9, 124.8, 124.0, 122.3, 119.3, 117.9, 115.2, 38.0, 24.6, 21.6, 13.9; HRMS (ESI-TOF) Calcd. for $C_{31}H_{29}N_2O_3S^+$ $[M+H]^+$: 509.1893; found: 509.1897.



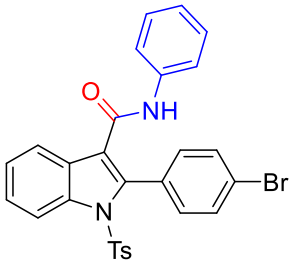
2-(4-butylphenyl)-*N*-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3ea). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 52.3 mg, 50% yield, mp 177 – 179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.5 Hz, 1H), 8.34 (d, J = 7.6 Hz, 1H), 7.46 (td, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.38 – 7.35 (m, 6H), 7.18 (t, J = 7.9 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 7.05 – 6.98 (m, 3H), 6.79 (s, 1H), 2.78 (t, J = 7.7 Hz, 2H), 2.34 (s, 3H), 1.72 (p, J = 7.5 Hz, 2H), 1.44 (h, J = 7.4 Hz, 2H), 1.00 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 145.8, 145.5, 139.6, 137.7, 136.5, 135.6, 131.6, 129.7, 128.8, 128.4, 127.1, 127.0, 125.9, 124.8, 124.0, 122.3, 119.4, 117.9, 115.2, 35.7, 33.7, 22.4, 21.7, 14.1; HRMS (ESI-TOF) Calcd. for $C_{32}H_{31}N_2O_3S^+$ $[M+H]^+$: 523.2050; found: 523.2052.



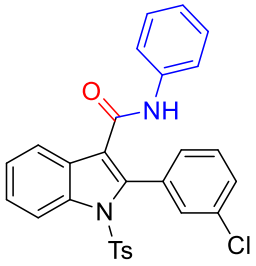
2-(4-methoxyphenyl)-*N*-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3fa). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); Yellow solid, 52.6 mg, 53% yield, mp 203 – 204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 7.8 Hz, 1H), 7.45 (t, J = 7.1 Hz, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.38 – 7.33 (m, 4H), 7.21 (t, J = 7.8 Hz, 2H), 7.14 – 7.08 (m, 4H), 7.05 (d, J = 8.8 Hz, 2H), 7.01 (t, J = 7.3 Hz, 1H), 6.88 (s, 1H), 3.93 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 161.3, 145.5, 139.5, 137.7, 136.6, 135.6, 133.2, 129.7, 128.9, 128.4, 126.9, 125.9, 124.9, 124.2, 122.2, 121.5, 119.6, 118.0, 115.3, 114.1, 55.6, 21.7; HRMS (ESI-TOF) Calcd. for $C_{29}H_{25}N_2O_4S^+$ $[M+H]^+$: 497.1530; found: 497.1532.



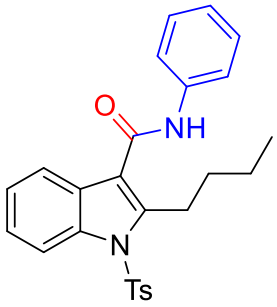
2-(4-fluorophenyl)-*N*-phenylbenzofuran-3-carboxamide (3ga). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 48.4 mg, 50% yield, mp 155 – 156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 7.9 Hz, 1H), 7.51 – 7.37 (m, 4H), 7.32 (d, J = 7.3 Hz, 2H), 7.26 – 7.20 (m, 4H), 7.13 – 7.10 (m, 4H), 7.04 (t, J = 7.4 Hz, 1H), 6.75 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9 (d, J = 252.5 Hz), 161.6, 145.7, 138.1, 137.4, 136.7, 135.4, 133.7 (d, J = 8.5 Hz, 1C), 129.8, 129.0, 128.2, 126.9, 126.2, 125.8 (d, J = 3.7 Hz, 1C), 125.0, 124.5, 122.0, 119.5, 118.8, 115.8 (d, J = 21.9 Hz, 1C), 115.4, 21.7; HRMS (ESI-TOF) Calcd. for $C_{28}H_{22}FN_2O_3S^+$ $[M+H]^+$: 485.1330; found: 485.1335.



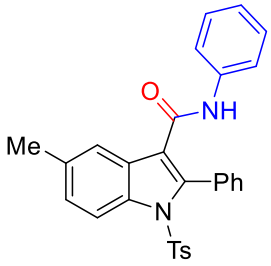
2-(4-bromophenyl)-*N*-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3ha). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 47.9 mg, 44% yield, mp 161 – 164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 7.9 Hz, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 7.1 Hz, 1H), 7.40 (t, J = 7.1 Hz, 1H), 7.34 (d, J = 8.1 Hz, 4H), 7.26 – 7.19 (m, 2H), 7.16 – 7.09 (m, 4H), 7.06 (t, J = 7.3 Hz, 1H), 6.73 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 145.7, 138.0, 137.4, 136.7, 135.2, 133.1, 131.7, 129.8, 129.1, 128.8, 128.2, 126.9, 126.3, 125.1, 125.0, 124.5, 121.9, 119.6, 119.0, 115.5, 21.7; HRMS (ESI-TOF) Calcd. for $C_{28}H_{22}BrN_2O_3S^+$ $[M+H]^+$: 545.0529; found: 545.0523.



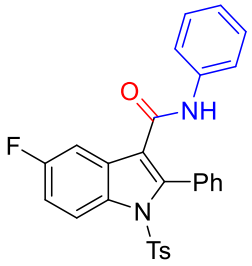
2-(3-chlorophenyl)-*N*-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3ia). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 68.0 mg, 68% yield, mp 150 – 153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 7.9 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.51 (s, 1H), 7.50 – 7.38 (m, 5H), 7.22 (t, J = 7.7 Hz, 2H), 7.19 – 7.12 (m, 4H), 7.04 (t, J = 7.3 Hz, 1H), 6.93 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 145.7, 137.6, 136.2, 136.0, 135.5, 133.3, 131.9, 130.0, 129.8, 129.7, 129.0, 127.9, 127.2, 126.9, 126.2, 124.7, 124.4, 122.1, 119.7, 118.6, 114.8, 21.7; HRMS (ESI-TOF) Calcd. For $C_{28}H_{22}ClN_2O_3S^+$ $[M+H]^+$: 501.1034; found: 501.1035.



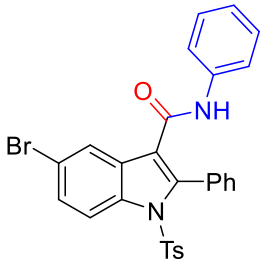
2-butyl-*N*-phenyl-1-tosyl-1*H*-indole-3-carboxamide (3ja). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 38.4 mg, 43% yield, mp 139 – 141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 7.3 Hz, 1H), 7.71 – 7.65 (m, 3H), 7.59 (d, J = 8.0 Hz, 2H), 7.55 (s, 1H), 7.40 – 7.29 (m, 4H), 7.22 (d, J = 8.2 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 3.32 (t, 2H), 2.36 (s, 3H), 1.84 – 1.73 (m, 2H), 1.46 (h, J = 7.4 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 145.6, 145.4, 137.8, 136.1, 136.0, 130.1, 129.3, 127.0, 126.5, 124.9, 124.7, 124.4, 120.0, 119.0, 116.6, 115.5, 33.6, 26.9, 22.9, 21.6, 13.8; HRMS (ESI-TOF) Calcd. For $C_{26}H_{27}N_2O_3S^+$ $[M+H]^+$: 447.1737; found: 447.1734.



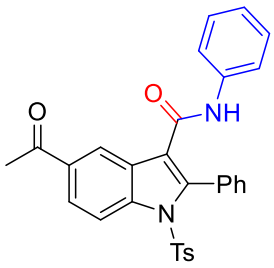
5-methyl-*N*,2-diphenyl-1-tosyl-1*H*-indole-3-carboxamide (3ka). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 42.3 mg, 44% yield; mp 140 – 142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.6 Hz, 1H), 8.10 (s, 1H), 7.67 – 7.59 (m, 1H), 7.55 (t, J = 6.7 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.35 (dd, J = 8.5, 2.1 Hz, 2H), 7.32 – 7.24 (m, 1H), 7.19 (t, J = 7.0 Hz, 2H), 7.12 (d, J = 7.2 Hz, 2H), 7.03 – 6.99 (m, 3H), 6.72 (s, 1H), 2.49 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 145.4, 139.3, 137.6, 135.5, 134.8, 131.7, 130.5, 130.1, 129.7, 128.9, 128.6, 127.4, 126.9, 124.2, 122.0, 119.5, 118.0, 114.9, 21.7, 21.4; HRMS (ESI-TOF) Calcd. for $C_{29}H_{25}N_2O_3S^+$ $[M+H]^+$: 481.1580; found: 481.1579.



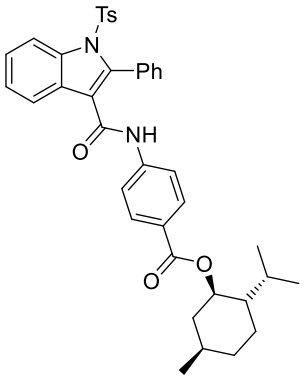
5-fluoro-*N*,2-diphenyl-1-tosyl-1*H*-indole-3-carboxamide (3la). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 48.4 mg, 50% yield; mp 145 – 146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, J = 9.2, 4.5 Hz, 1H), 8.03 (dd, J = 9.2, 2.7 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.44 (d, J = 7.2 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.18 – 7.09 (m, 3H), 7.04 – 6.98 (m, 3H), 6.70 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 160.5 (d, J = 241.8 Hz, 1C), 145.8, 140.6, 137.4, 135.3, 132.8, 131.6, 130.8, 129.8, 129.7, 129.6, 129.4, 128.9, 128.8, 127.0, 124.3, 119.4, 117.7, 116.4 (d, J = 9.0 Hz, 1C), 115.4, 114.1 (d, J = 25.3 Hz, 1C), 108.1 (d, J = 25.6 Hz, 1C), 21.7; HRMS (ESI-TOF) Calcd. for $C_{28}H_{22}FN_2O_3S^+$ $[M+H]^+$: 485.1330; found: 485.1333.



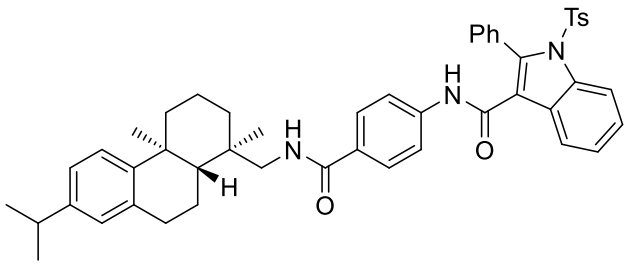
5-bromo-*N*,2-diphenyl-1-tosyl-1*H*-indole-3-carboxamide (3ma). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); White solid, 57.7 mg, 53% yield, mp 173 – 175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.25 (d, J = 9.0 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.58 – 7.54 (m, 3H), 7.43 (d, J = 7.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 7.19 (t, J = 7.8 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 7.04 – 6.98 (m, 3H), 6.69 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 145.9, 140.2, 137.4, 135.3, 135.2, 131.7, 130.8, 130.0, 129.9, 129.5, 129.0, 128.9, 128.8, 127.0, 125.1, 124.3, 119.5, 118.6, 117.2, 116.6, 21.7. HRMS (ESI-TOF) Calcd. for $C_{28}H_{22}BrN_2O_3S^+$ $[M+H]^+$: 545.0529; found: 545.0523.



5-acetyl-*N*,2-diphenyl-1-tosyl-1H-indole-3-carboxamide (3na). The product was purified by column chromatography (petroleum ether / ethyl acetate = 3:1); White solid, 53.9 mg, 53% yield, mp 199 – 201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.44 (d, J = 8.9 Hz, 1H), 8.12 (dd, J = 8.9, 1.9 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.6 Hz, 2H), 7.45 (d, J = 7.0 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.20 (t, J = 7.9 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 7.05 – 7.01 (m, 3H), 6.76 (s, 1H), 2.71 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 161.3, 146.0, 140.4, 138.9, 137.3, 135.3, 134.1, 131.6, 130.9, 129.9, 129.4, 129.0, 128.8, 128.1, 127.0, 125.6, 124.4, 124.0, 119.6, 118.0, 115.2, 26.9, 21.7. HRMS (ESI-TOF) Calcd. for $C_{30}H_{25}N_2O_4S^+$ $[M+H]^+$: 509.1530; found: 509.1534.

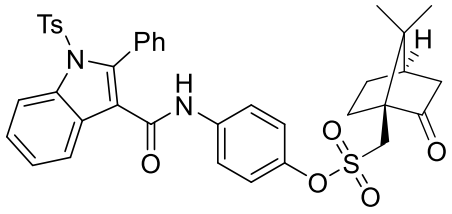


Compound (6). The product was purified by column chromatography (petroleum ether / ethyl acetate = 5:1); Yellow solid, 55.8 mg, 43% yield, mp 160– 163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.3 Hz, 1H), 8.32 (d, J = 7.9 Hz, 1H), 7.87 (d, J = 8.6 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.5 Hz, 2H), 7.50 – 7.40 (m, 4H), 7.37 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H), 6.87 (s, 1H), 4.87 (td, J = 10.9, 4.4 Hz, 1H), 2.34 (s, 3H), 2.08 (d, J = 12.0 Hz, 1H), 1.94 – 1.87 (m, 1H), 1.71 (d, J = 11.6 Hz, 2H), 1.56 – 1.48 (m, 2H), 1.16 – 1.01 (m, 2H), 0.90 (t, J = 7.0 Hz, 7H), 0.76 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 161.8, 145.7, 141.5, 139.6, 136.5, 135.5, 131.7, 130.7, 129.9, 129.8, 128.8, 128.2, 127.0, 126.2, 125.0, 122.3, 118.4, 117.7, 115.2, 74.7, 47.3, 41.1, 34.4, 31.5, 26.6, 23.7, 22.1, 21.7, 20.8, 16.6.



Compound (8). The product was purified by column chromatography (petroleum ether / ethyl acetate = 2:1); White solid, 62.2 mg, 40% yield, mp 165 – 167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.4 Hz, 4H), 7.48 – 7.45 (m, 2H), 7.43 – 7.38 (m, 2H), 7.38 – 7.37 (m, 1H), 7.35 (s, 1H), 7.17 (d, J = 8.2 Hz, 1H), 7.12 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.2 Hz, 1H), 6.88 (s, 1H), 6.86 (s, 1H), 6.08 (t, J = 6.2 Hz, 1H), 3.37 (dd, J = 13.6, 6.3 Hz, 1H), 3.27 (dd, J = 13.7, 6.5 Hz, 1H), 2.91 (dd, J = 17.0, 6.2 Hz, 1H), 2.86 – 2.75 (m, 2H), 2.34 (s, 3H), 2.29 (d, J = 13.2 Hz, 1H), 1.96 – 1.92 (m, 1H), 1.79 – 1.68 (m, 3H), 1.47 (t, J = 11.1 Hz, 2H), 1.41 – 1.32 (m, 2H), 1.23 (d, J =

4.5 Hz, 6H), 1.22 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 161.8, 147.1, 145.7, 145.6, 140.4, 139.6, 136.5, 135.5, 134.8, 131.7, 130.7, 130.1, 129.9, 129.8, 128.8, 128.2, 127.8, 127.02, 126.96, 126.1, 125.0, 124.3, 123.9, 122.2, 118.8, 117.8, 115.2, 50.3, 45.9, 38.4, 37.8, 37.6, 36.5, 33.5, 30.5, 25.5, 24.0, 21.7, 19.1, 18.8, 18.7.



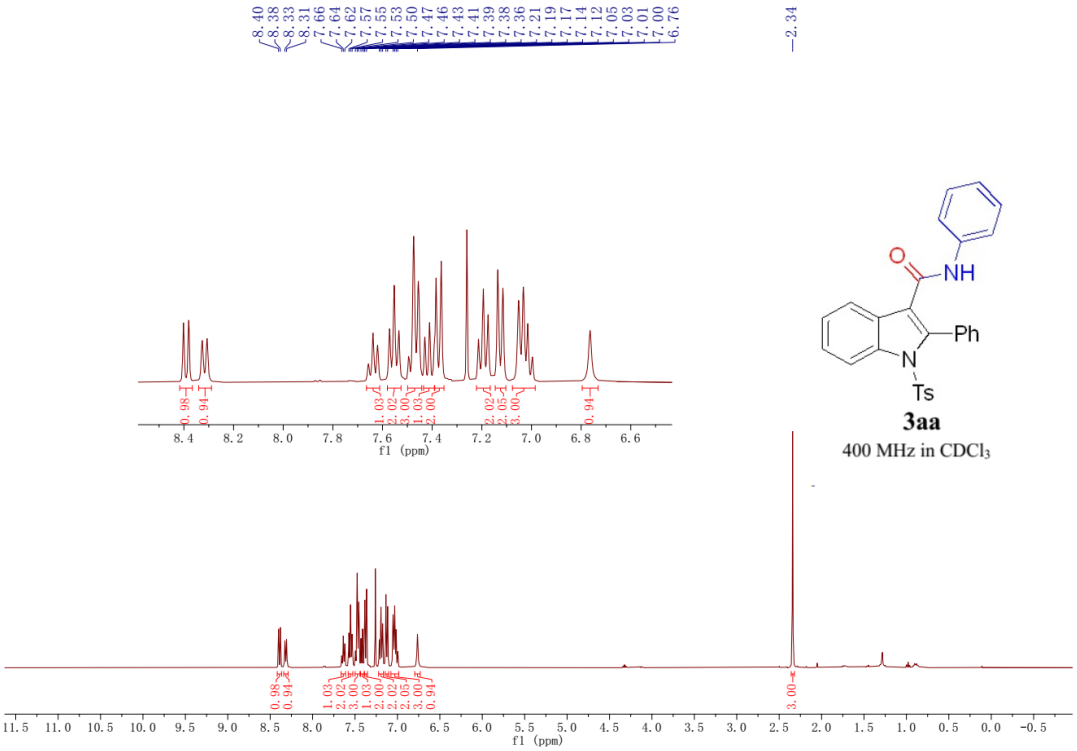
Compound (11). The product was purified by column chromatography (petroleum ether / ethyl acetate = 2:1); White solid, 47.3 mg, 34% yield, mp 185 – 187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.3 Hz, 1H), 8.30 (d, J = 7.9 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.44 – 7.38 (m, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 9.1 Hz, 4H), 7.05 (d, J = 9.1 Hz, 2H), 6.78 (s, 1H), 3.74 (d, J = 15.0 Hz, 1H), 3.13 (d, J = 15.0 Hz, 1H), 2.55 – 2.46 (m, 1H), 2.40 (dt, J = 18.5, 4.1 Hz, 1H), 2.34 (s, 3H), 2.12 (t, J = 4.5 Hz, 1H), 2.10 – 2.01 (m, 1H), 1.95 (d, J = 18.5 Hz, 1H), 1.72 – 1.65 (m, 1H), 1.48 – 1.39 (m, 1H), 1.13 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.1, 161.7, 145.6, 145.0, 139.4, 136.5, 136.5, 135.5, 131.6, 130.7, 129.9, 129.8, 128.8, 128.2, 127.0, 126.1, 125.0, 122.6, 122.2, 120.6, 117.7, 115.2, 58.2, 48.0, 47.5, 42.9, 42.5, 26.9, 25.2, 21.7, 20.0, 19.7.

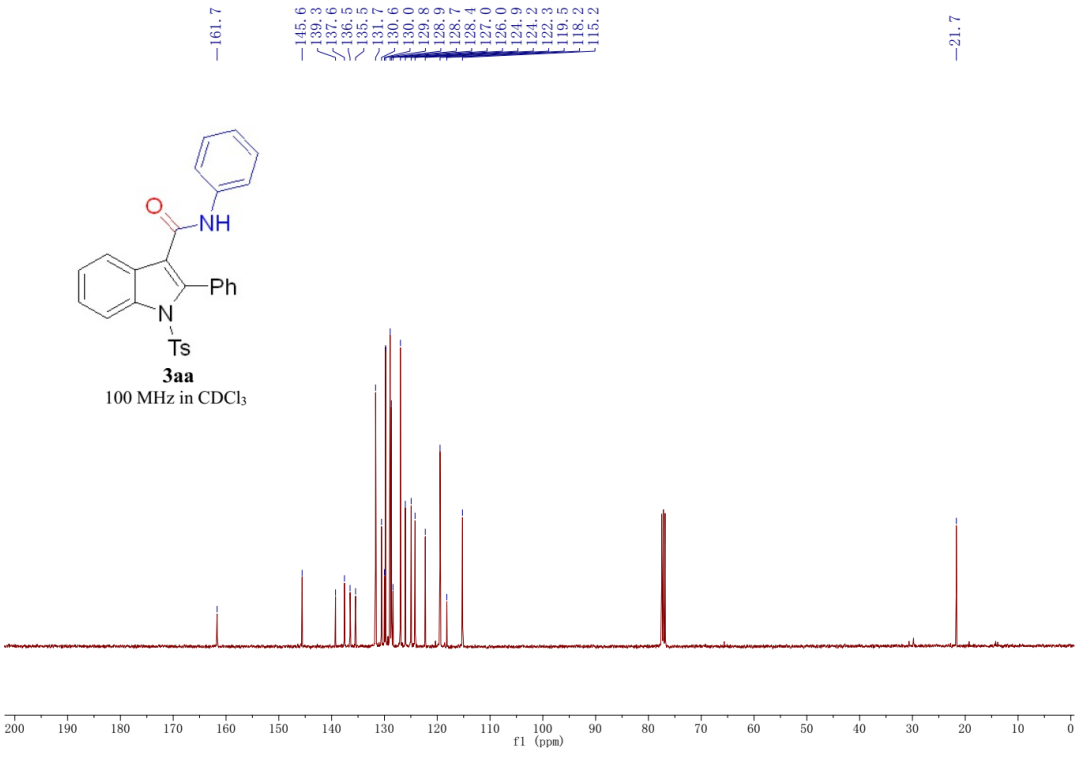
5. References

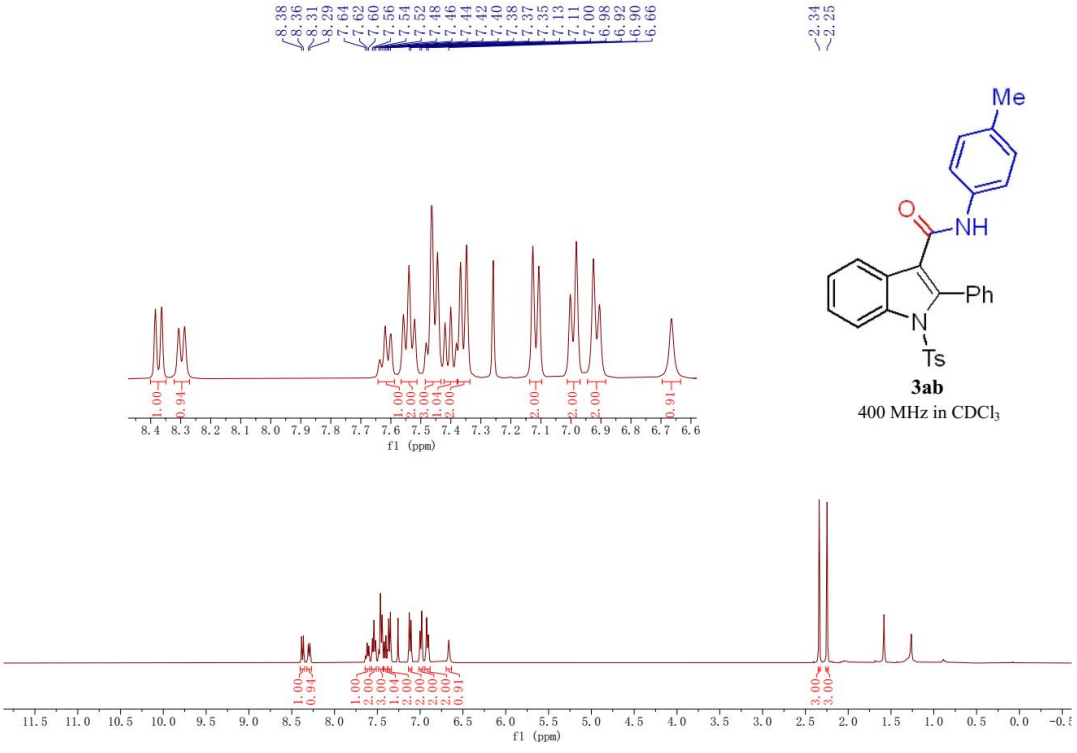
[1] C. Koradin, W. Dohle, A. L. Rodriguez, B. Schmid and P. Knochel, Synthesis of polyfunctional indoles and related heterocycles mediated by cesium and potassium bases, *Tetrahedron Lett.*, 2004, **45**, 539−541.

[2] A. Mizukami, Y. Ise, T. Kimachi, and K. Inamoto, Rhodium-catalyzed cyclization of 2-ethynylanilines in the presence of isocyanates: approach toward indole-3-carboxamides, *Org. Lett.*, 2016, **18**, 748−751.

6. ^{1}H, ^{13}C spectra of compounds 3aa–am, 3ba–na, 6, 8, and 11







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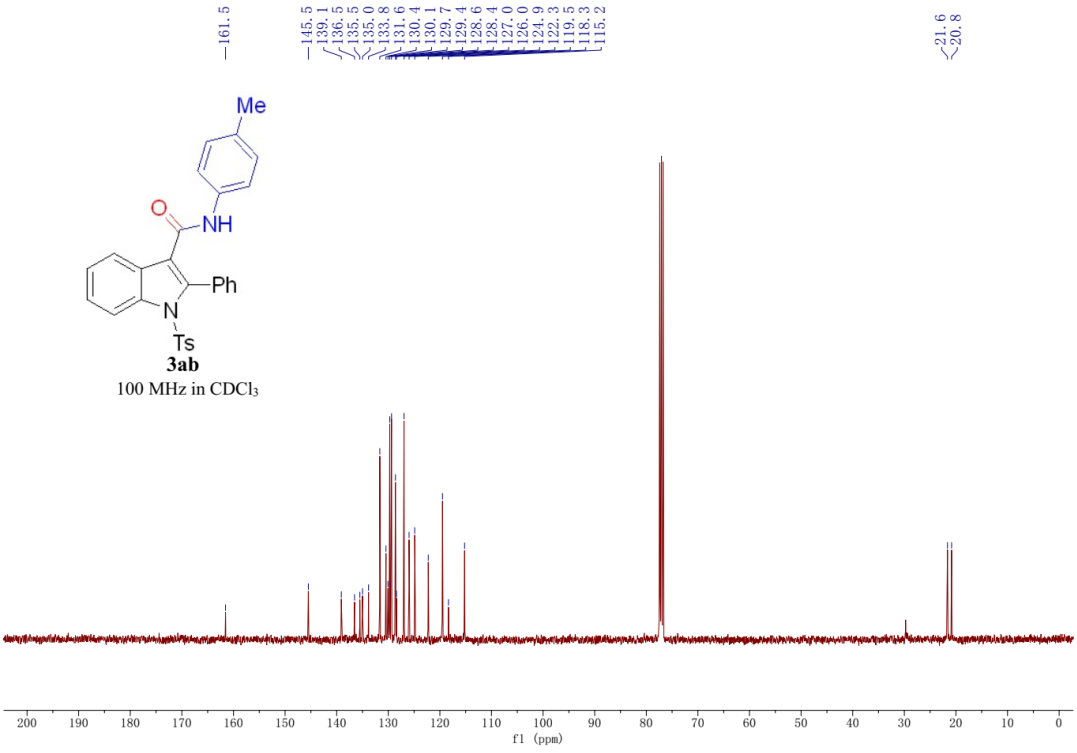

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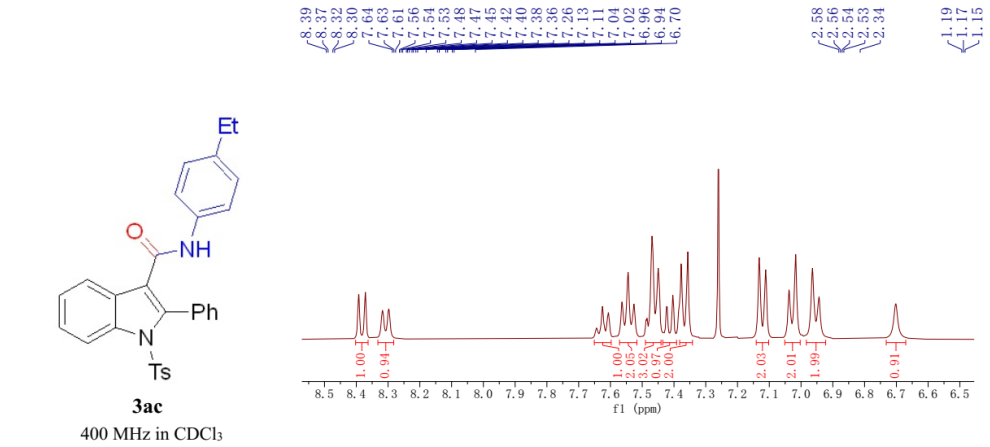

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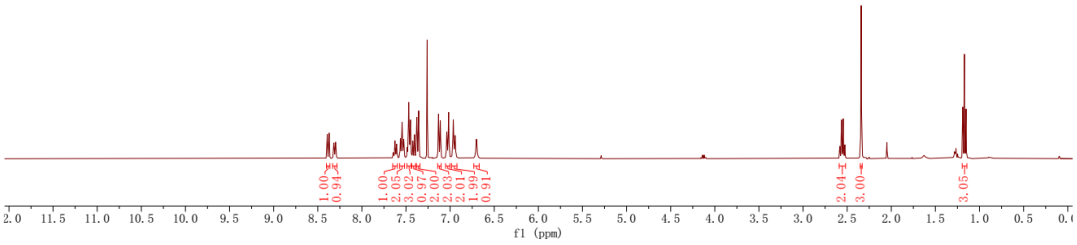

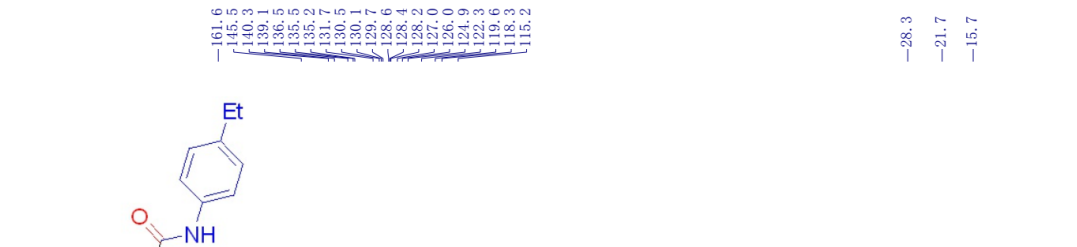

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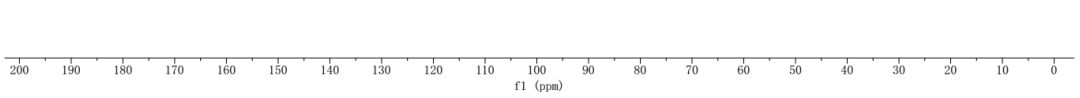

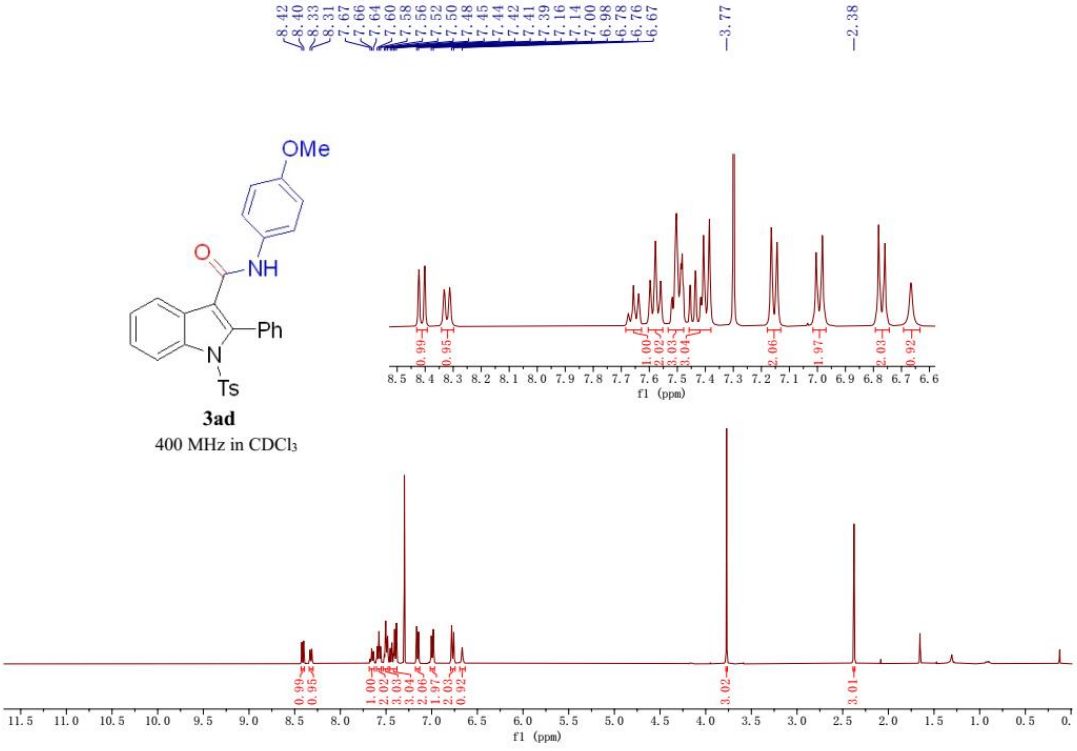
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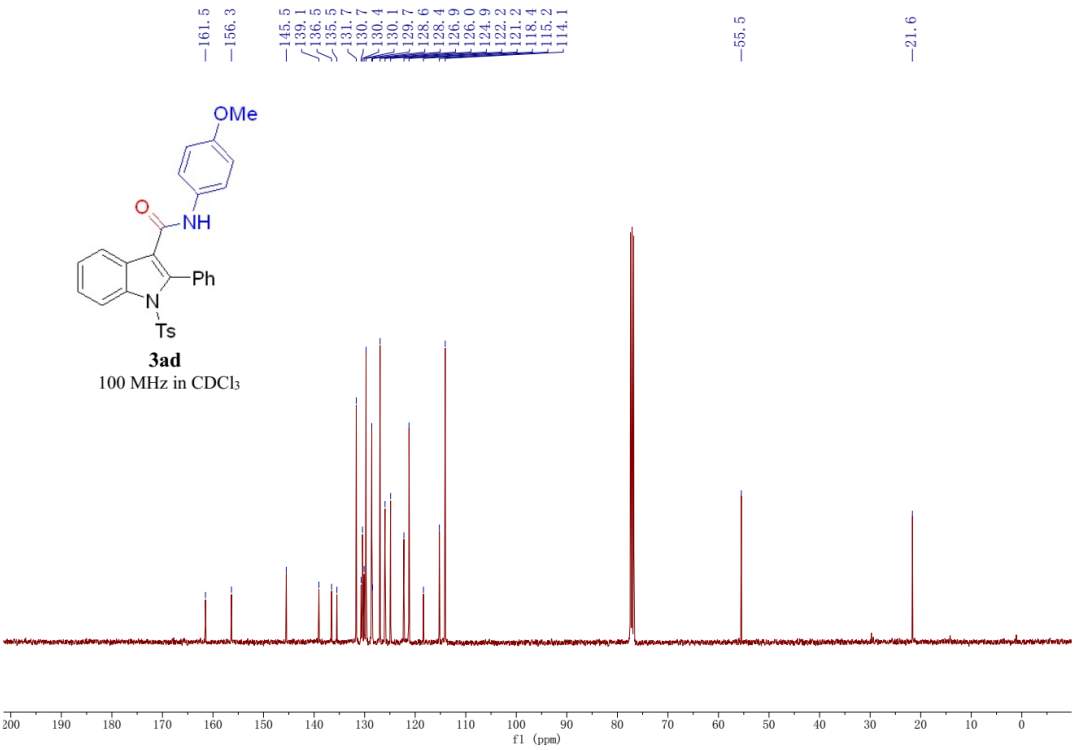
Ph
N
Ts
3ad
400 MHz in CDCl3
f1 (ppm)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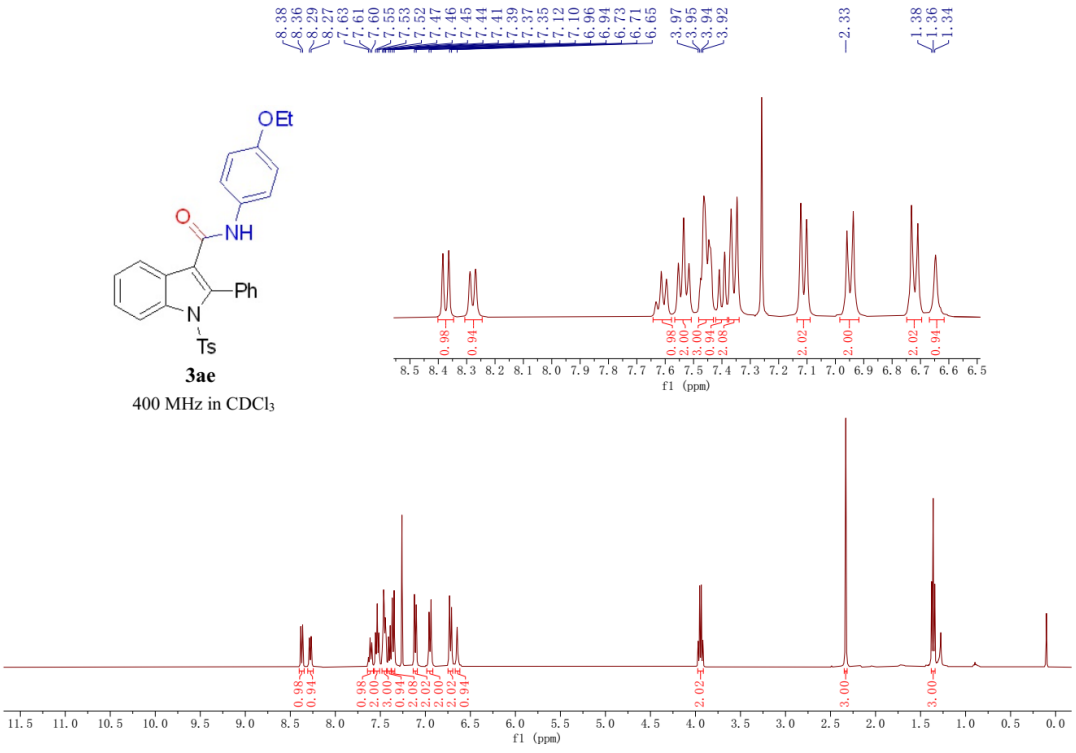
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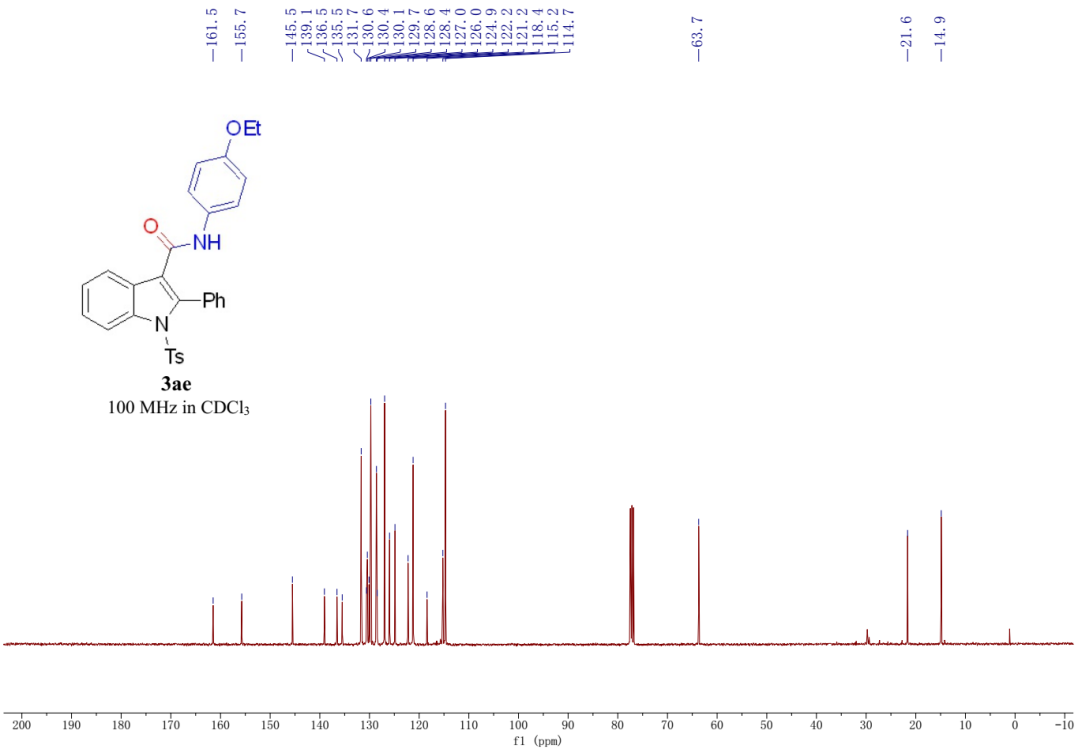
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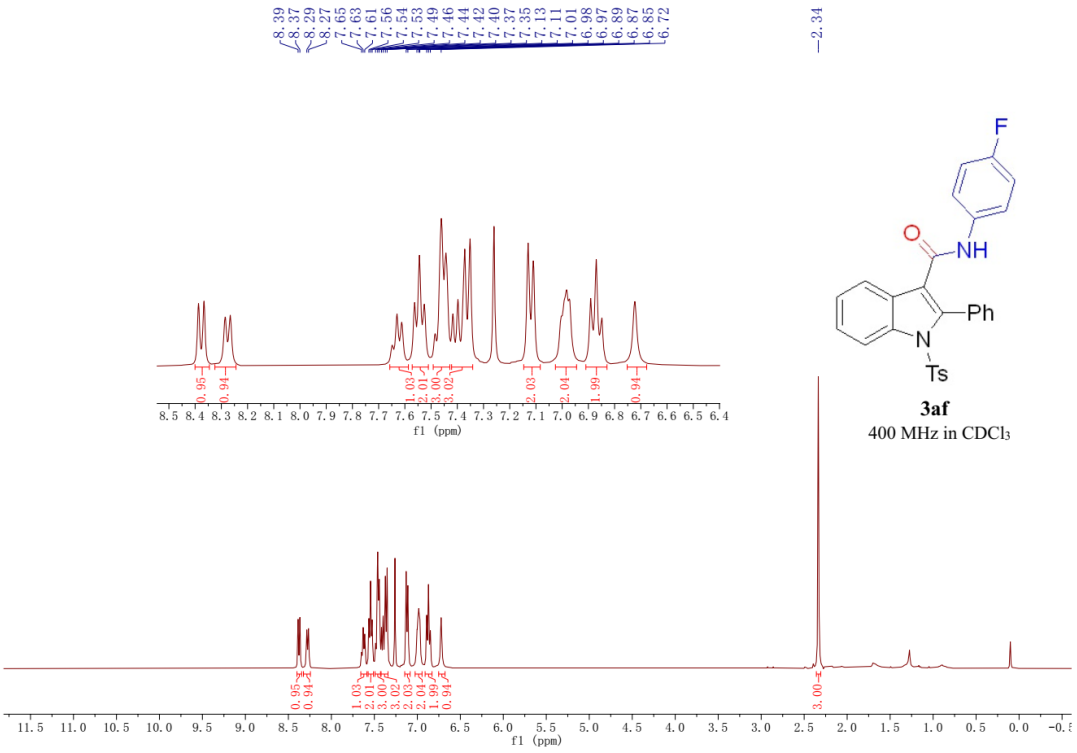
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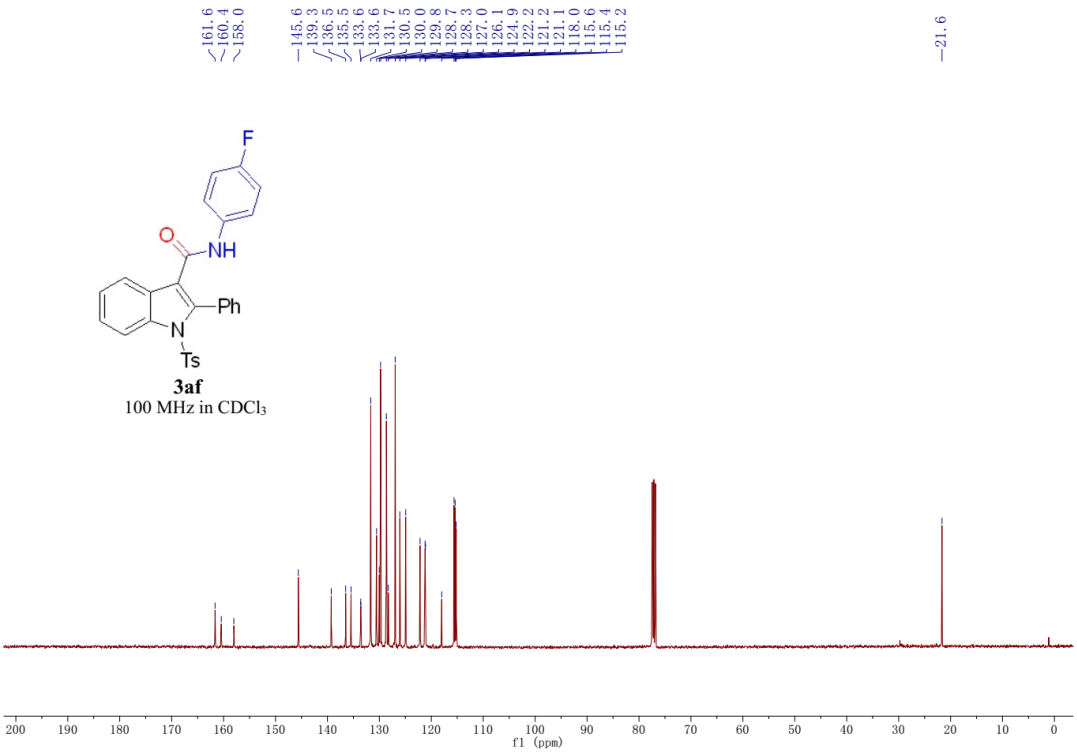
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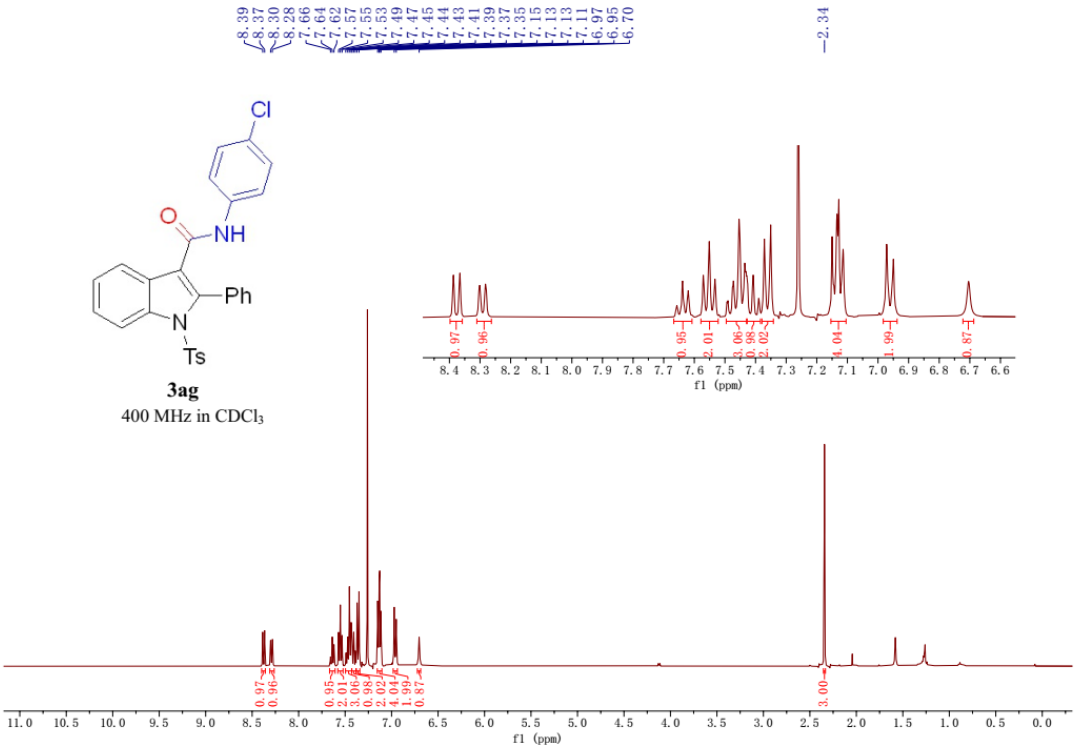
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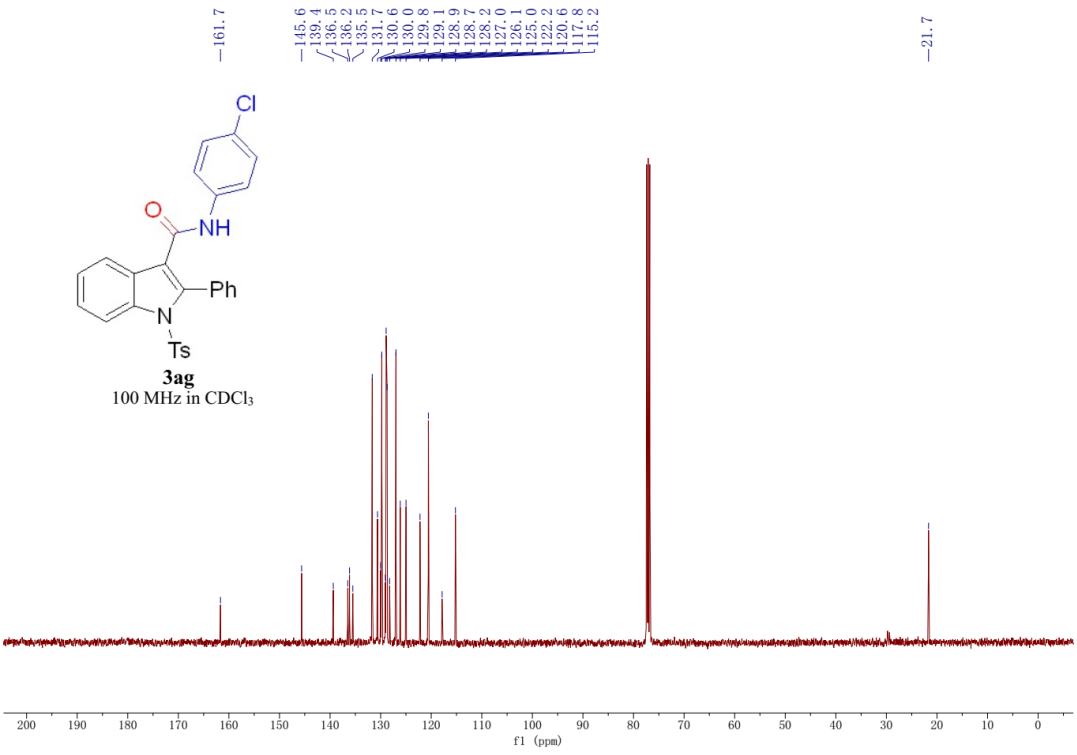
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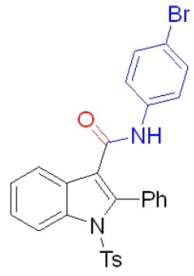

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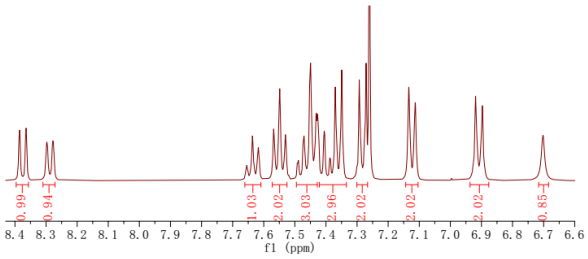

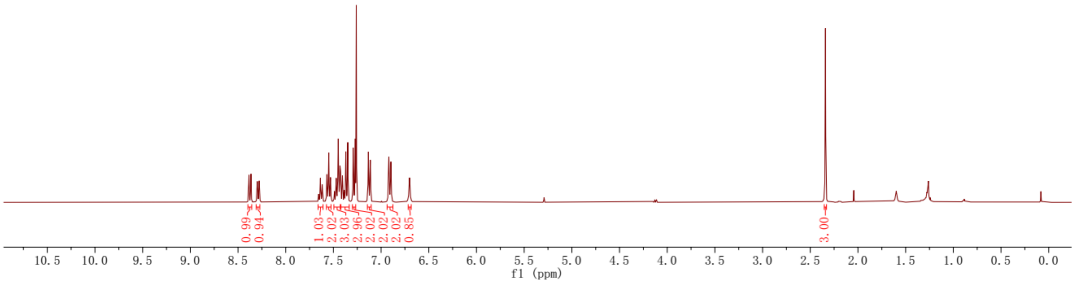

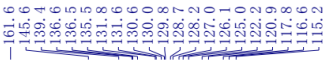

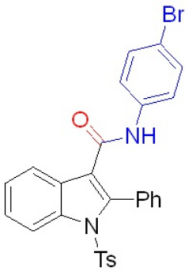

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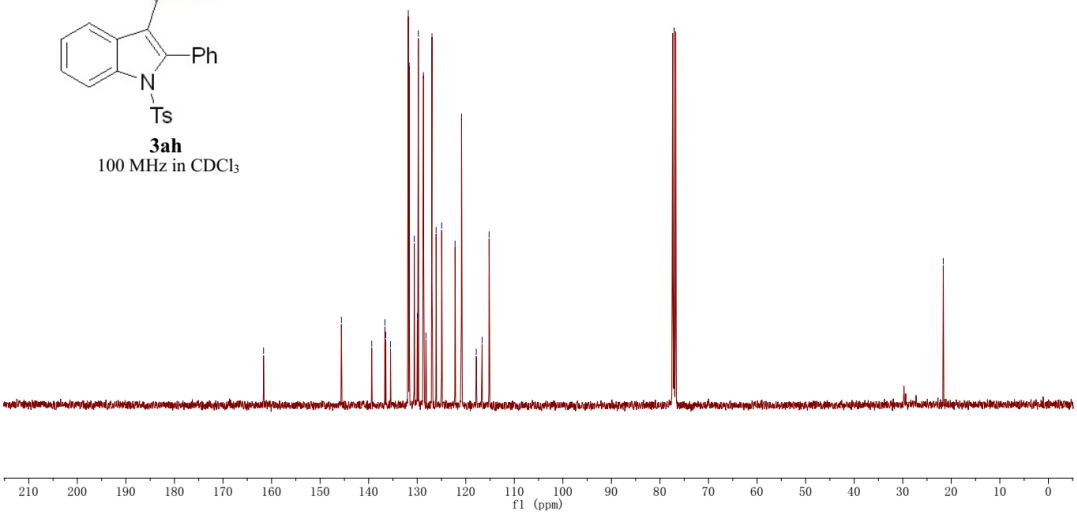

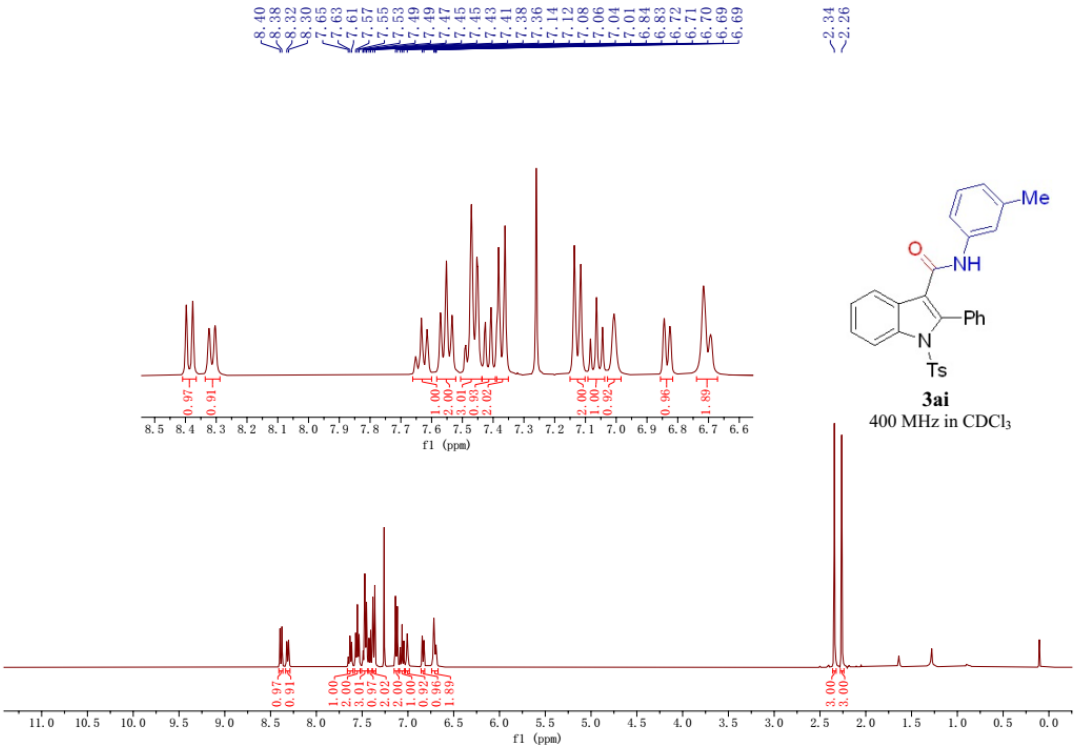

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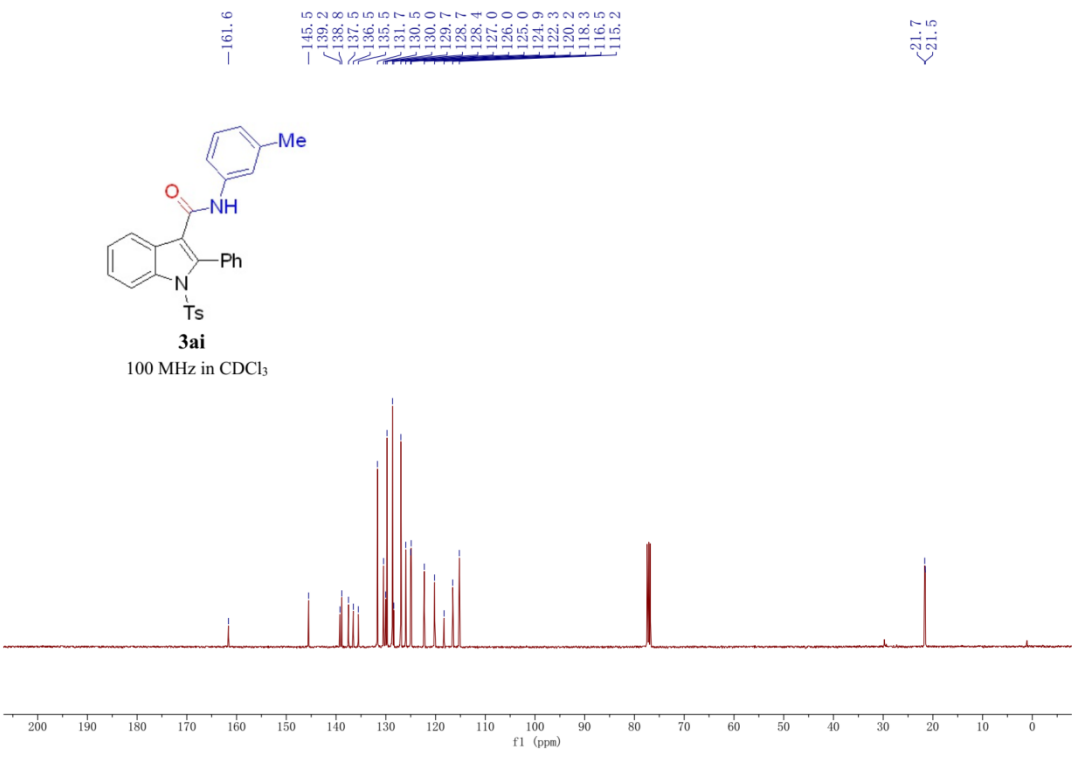

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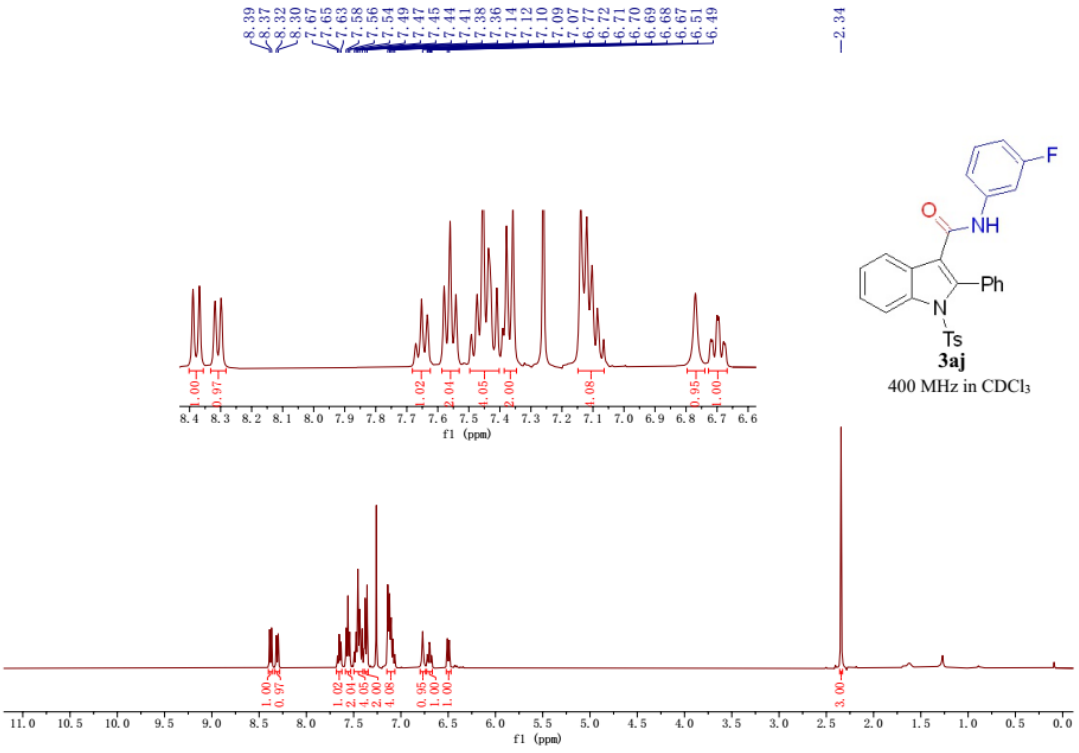
100 MHz in $CDCl_3$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Ts
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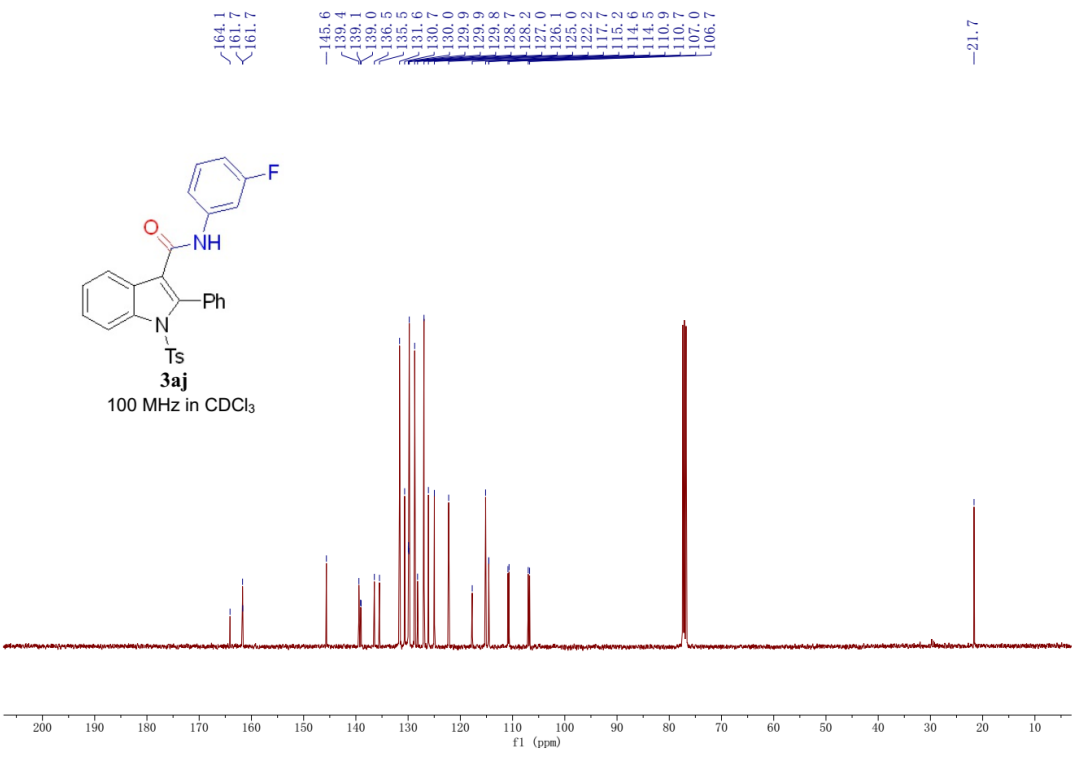
f1 (ppm)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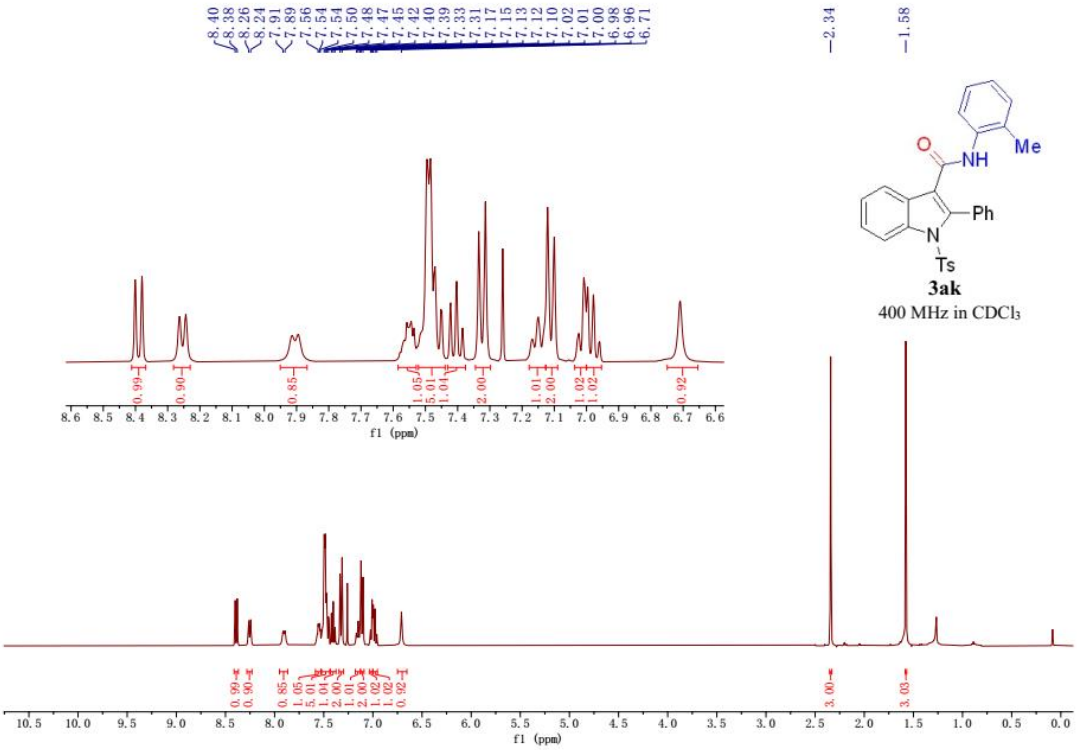
f1 (ppm)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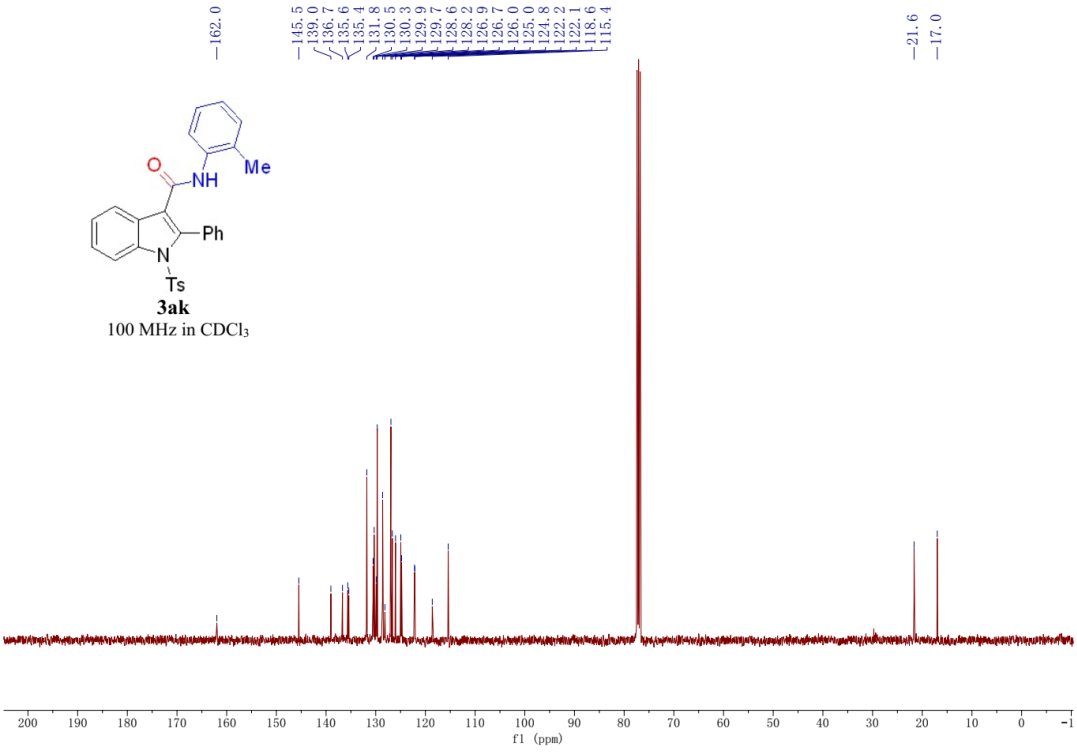
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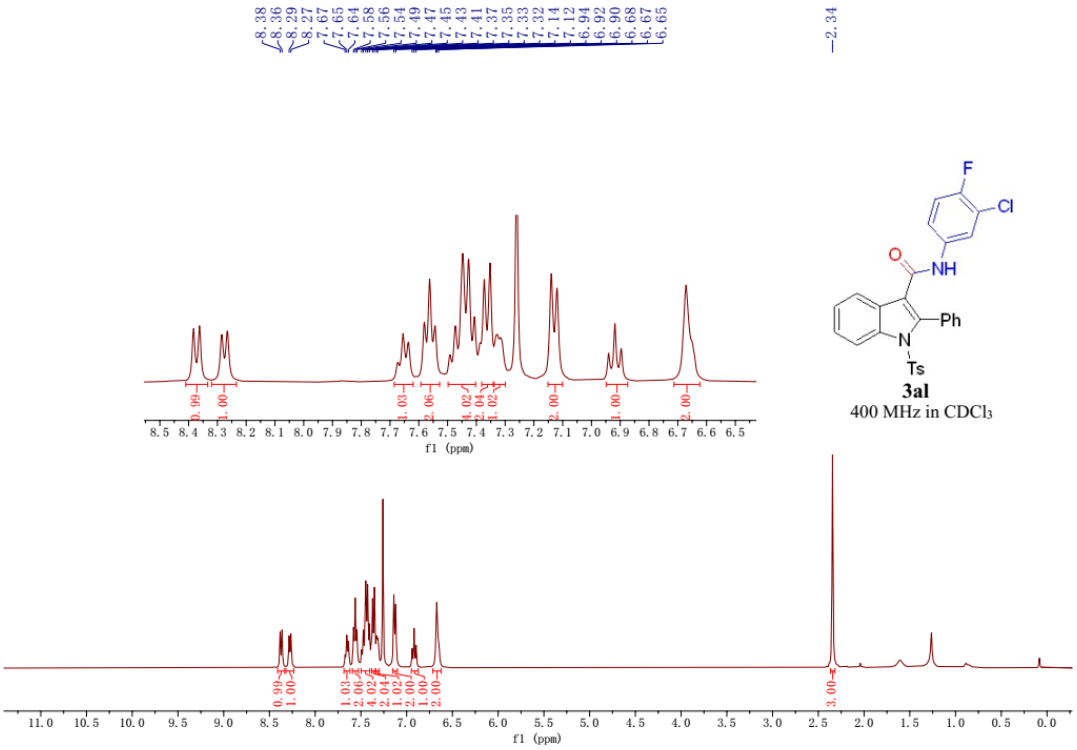
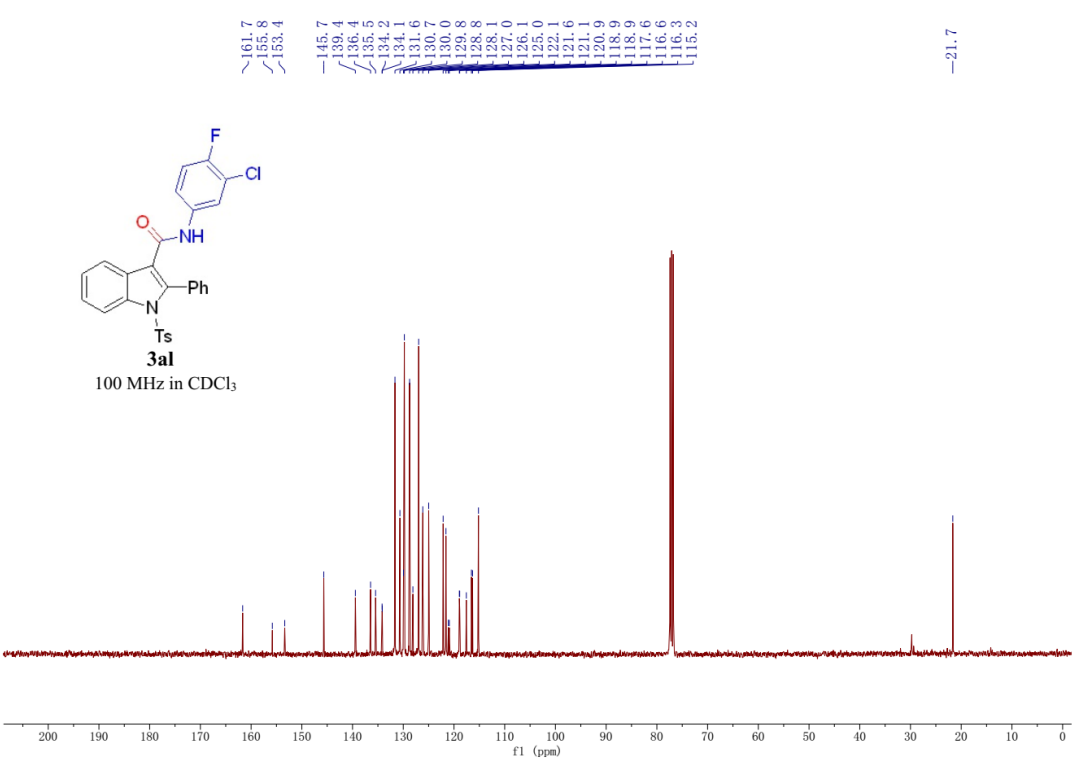
129.9
129.7
128.6
128.2
126.9
126.7
126.0
125.0
124.8
122.2
122.1
118.6
115.4
21.6
17.0
O
NH
Me
Ph
N
Ts
3ak
100 MHz in CDCl3
f1 (ppm)



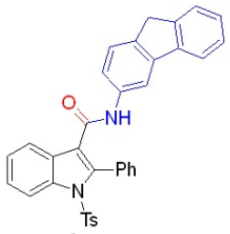
3al

400 MHz in $CDCl_3$



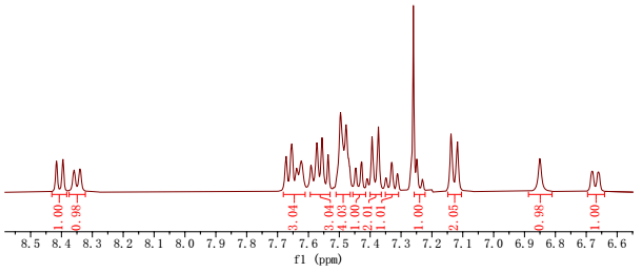
3al

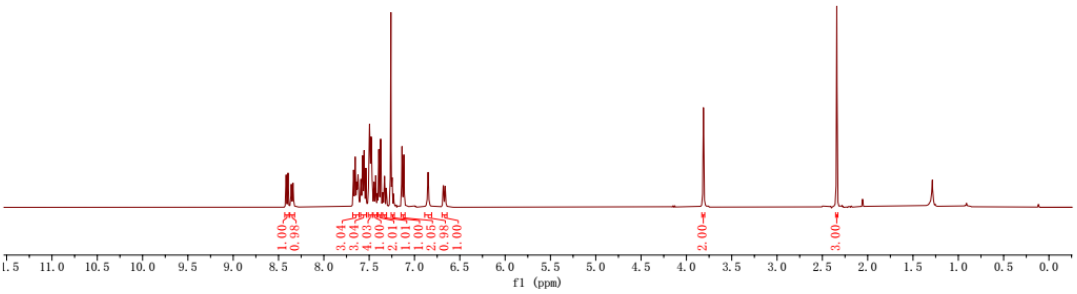
100 MHz in $CDCl_3$

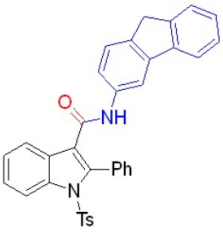


3am

400 MHz in $CDCl_3$

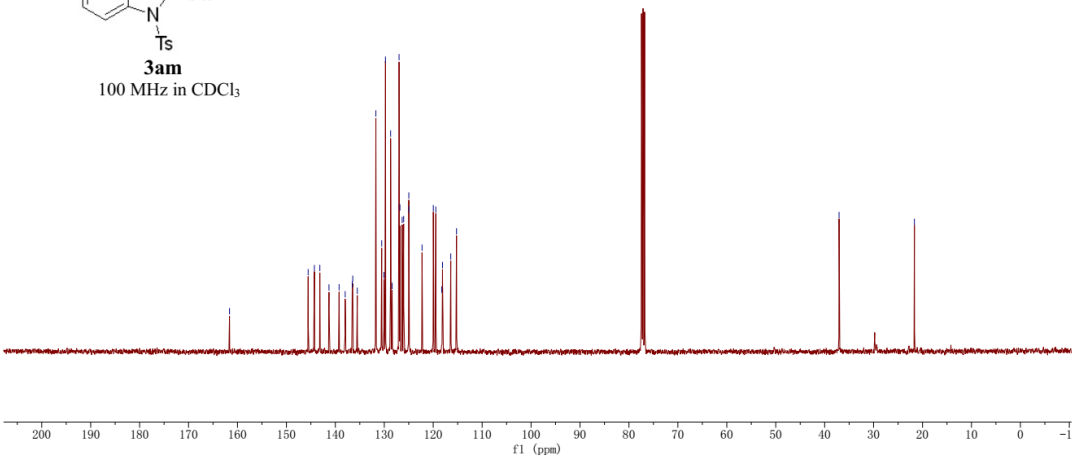


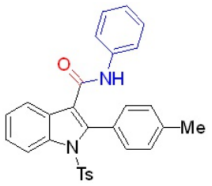




3am

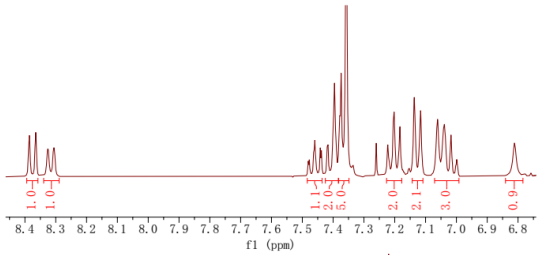
100 MHz in $CDCl_3$

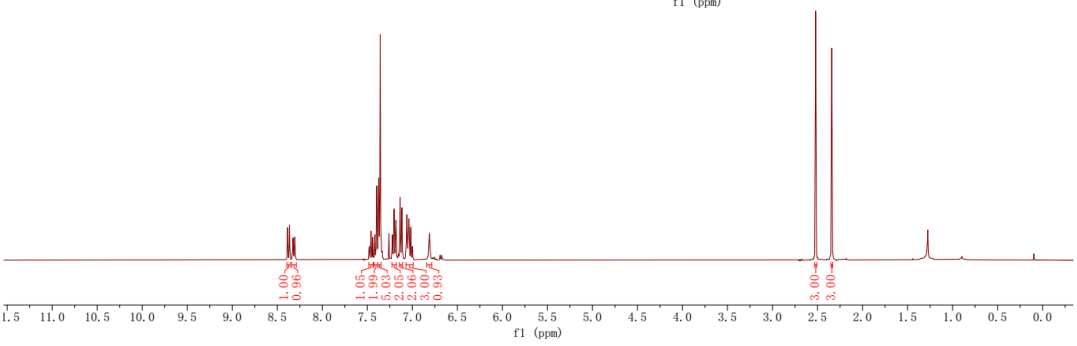


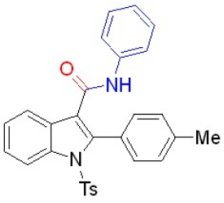


3ba

400 MHz in $CDCl_3$

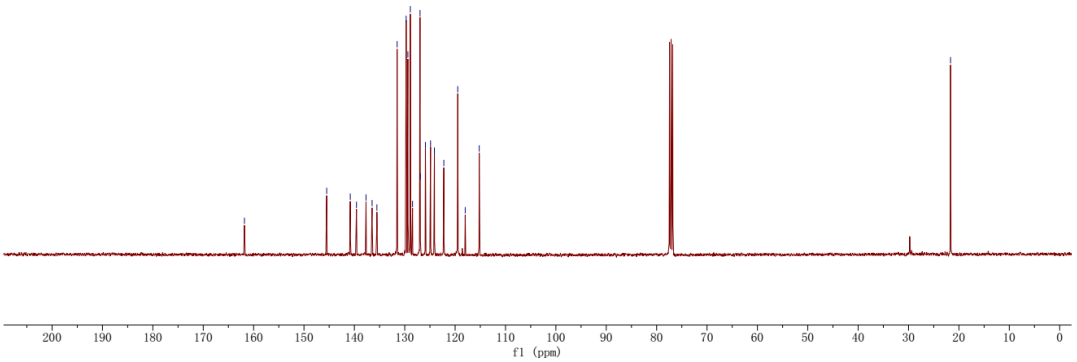


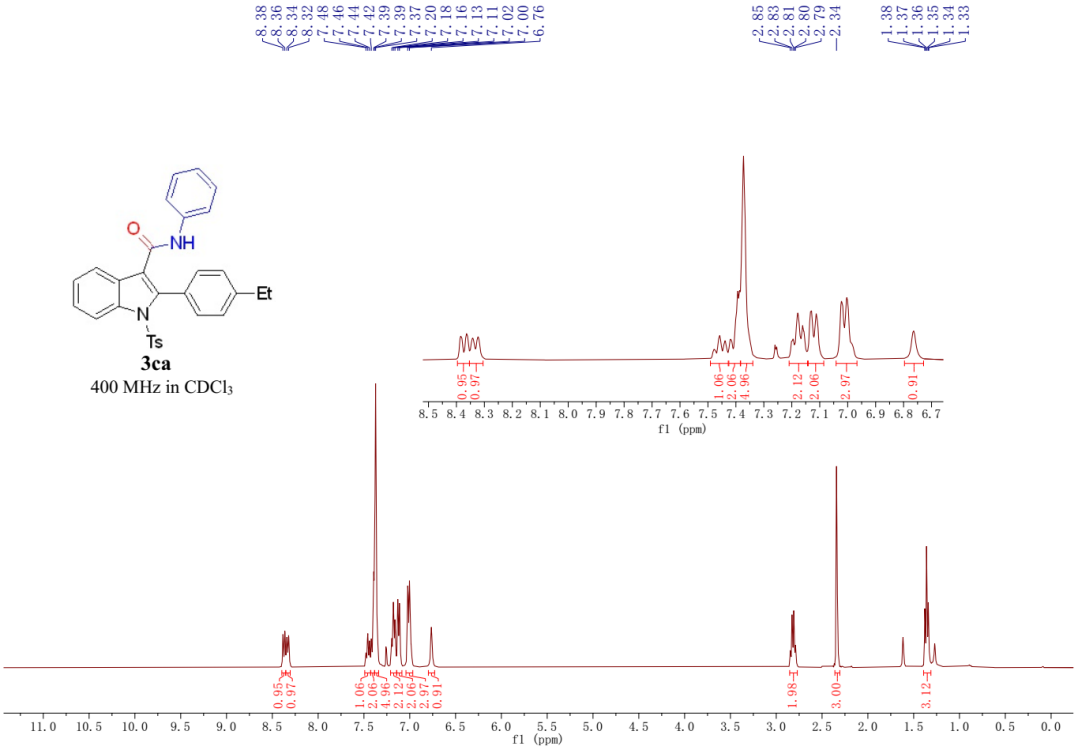


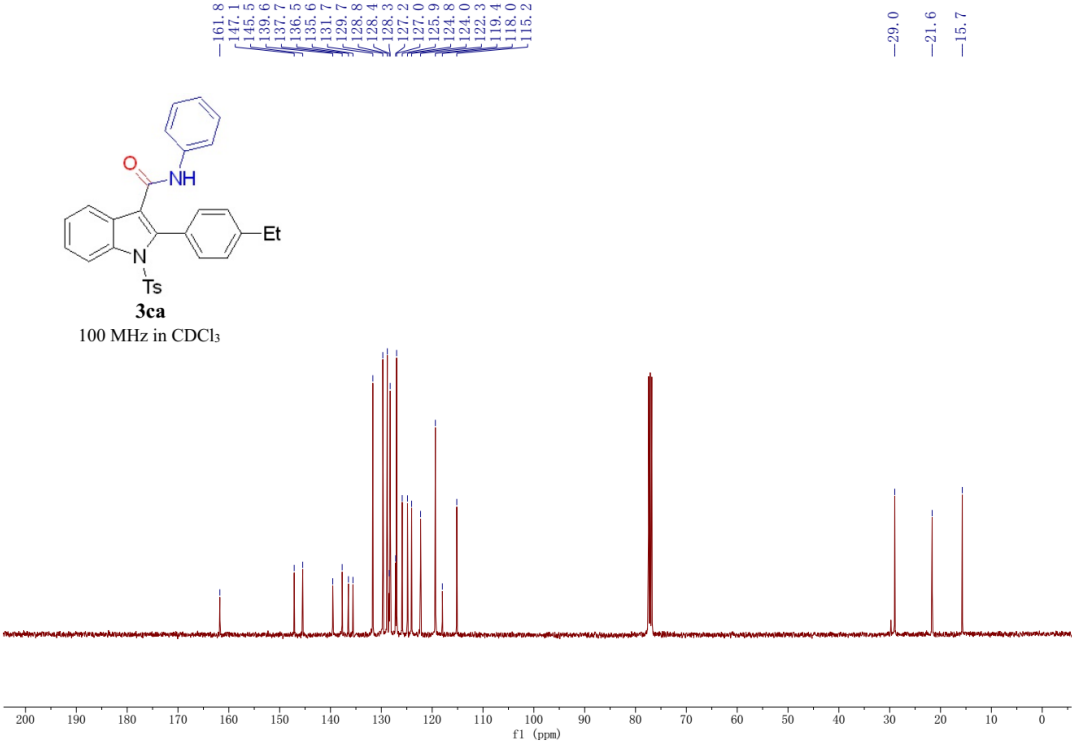


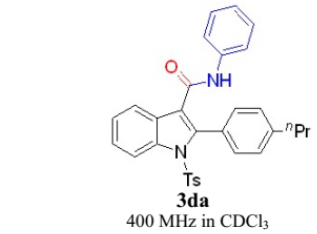
3ba

100 MHz in $CDCl_3$



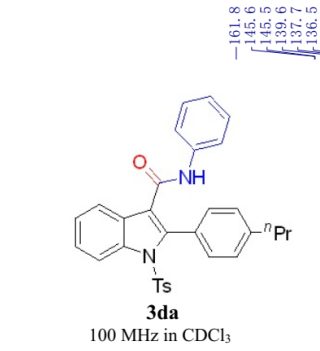

8.38
8.36
8.34
8.32
7.48
7.46
7.44
7.42
7.39
7.39
7.37
7.20
7.18
7.16
7.13
7.11
7.02
7.00
6.76
2.85
2.83
2.81
2.80
2.79
2.34
1.38
1.37
1.36
1.35
1.34
1.33
O
NH
Et
N
Ts
3ca
400 MHz in CDCl3
0.95
0.97
1.06
2.06
4.96
2.12
2.06
2.97
0.91
1.98
3.00
3.12
f1 (ppm)


161.8
147.1
145.5
139.6
137.7
136.5
135.6
131.7
129.7
128.8
128.4
128.3
127.2
127.0
125.9
124.8
124.0
122.3
119.4
118.0
115.2
29.0
21.6
15.7
O
NH
Et
N
Ts
3ca
100 MHz in CDCl3
f1 (ppm)



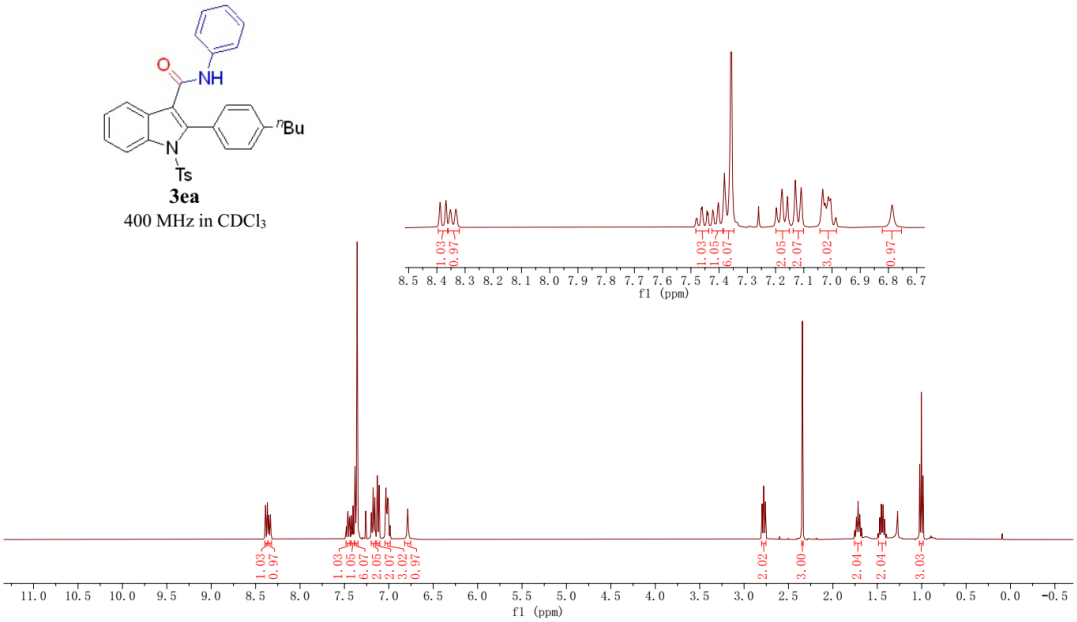
3da

400 MHz in $CDCl_3$



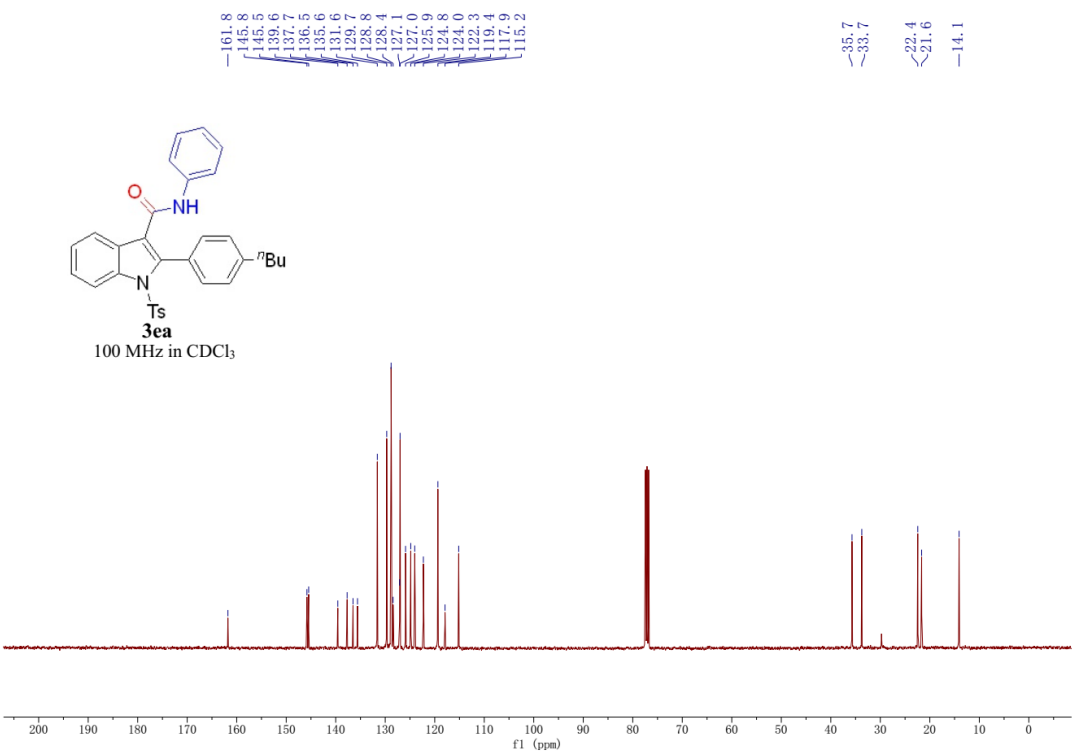
3da

100 MHz in $CDCl_3$



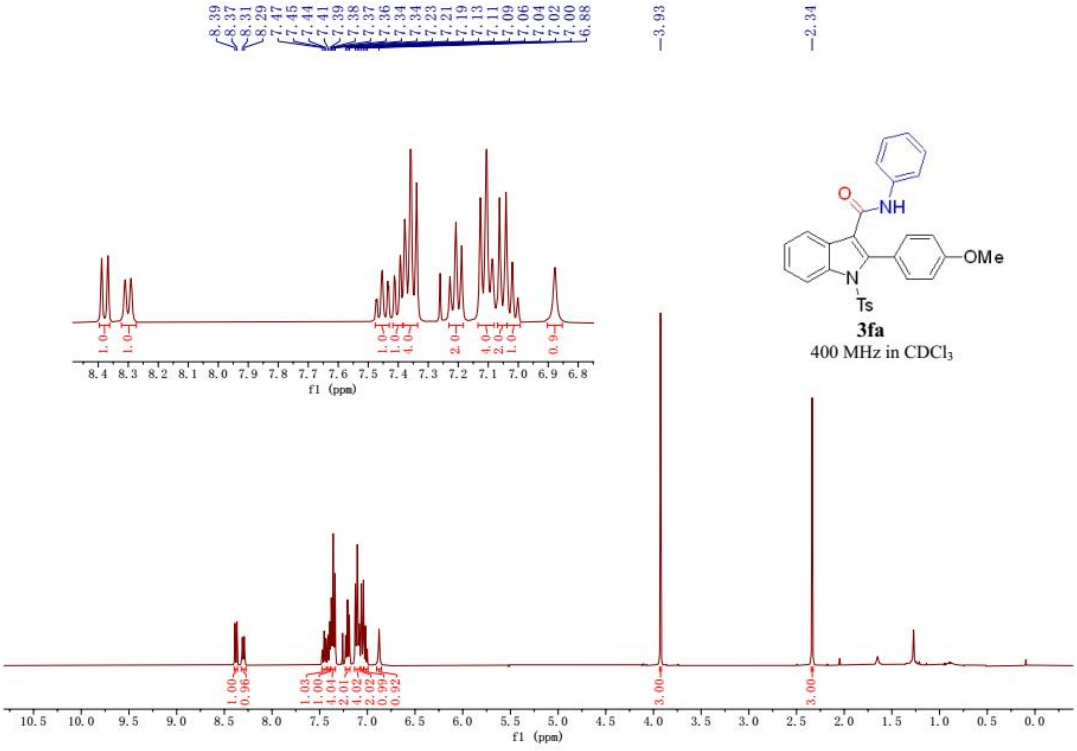
3ea

400 MHz in $CDCl_3$



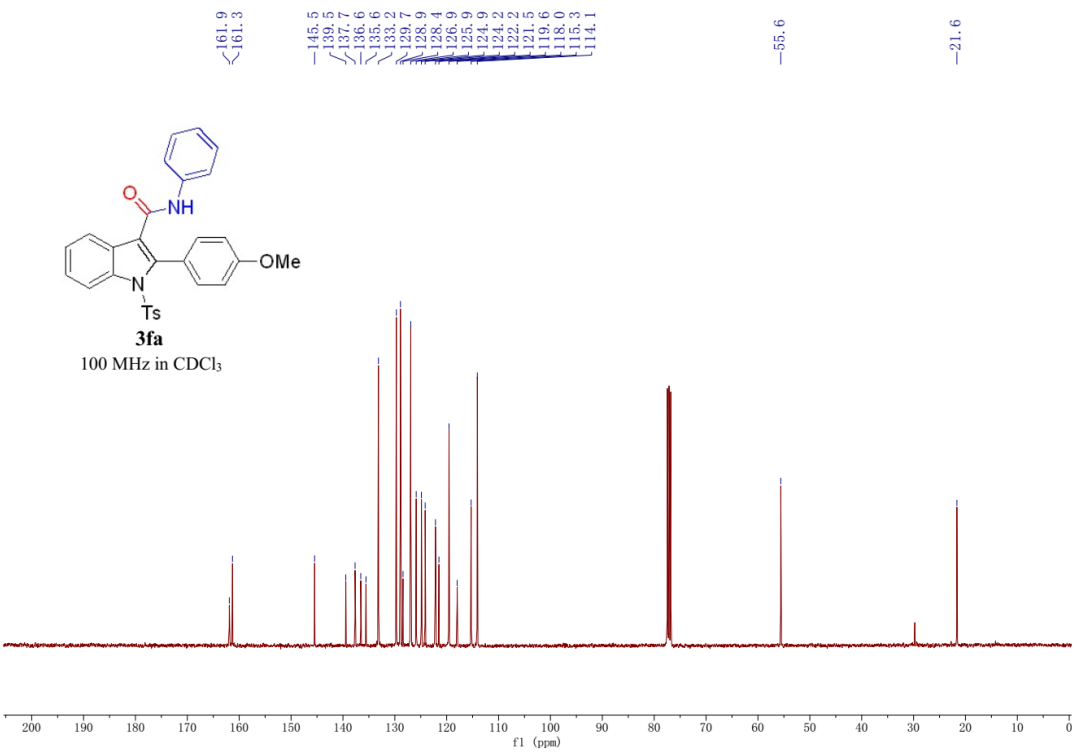
3ea

100 MHz in $CDCl_3$



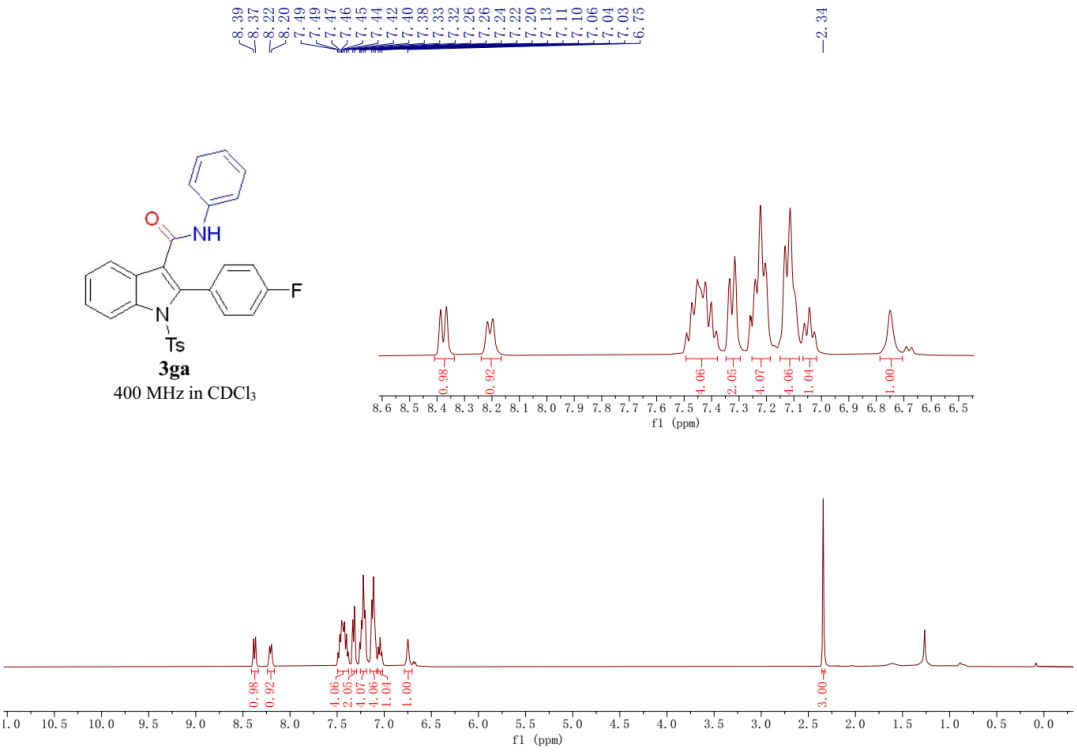
3fa

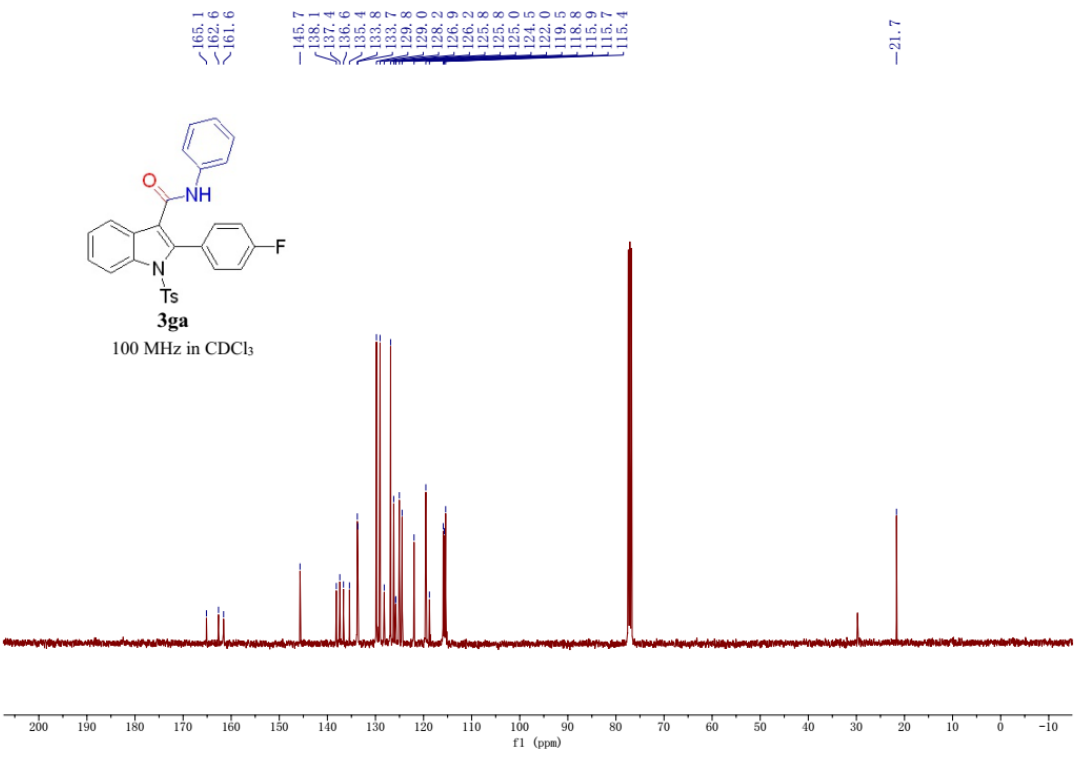
400 MHz in $CDCl_3$

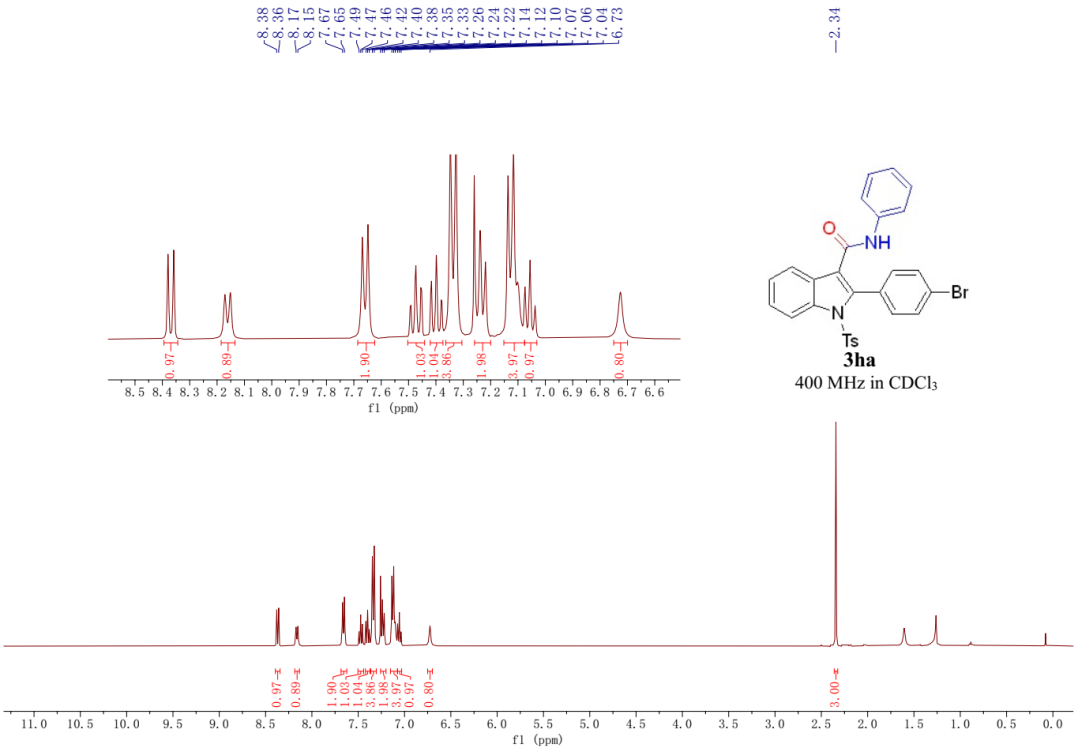


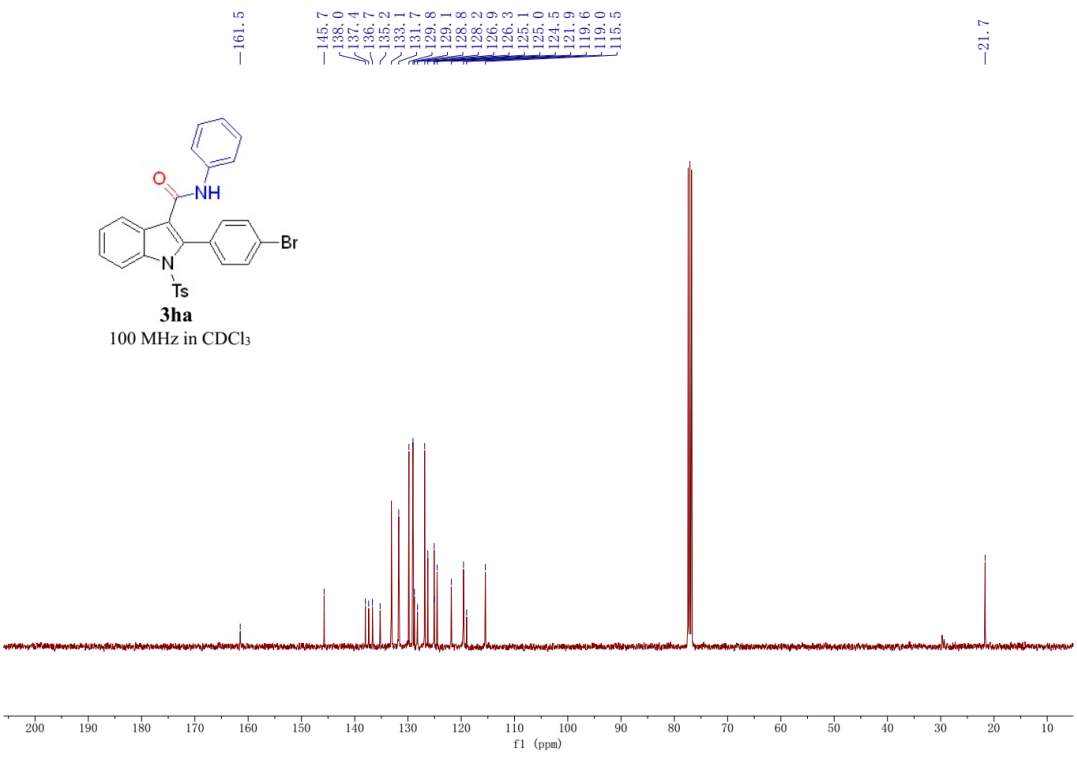
3fa

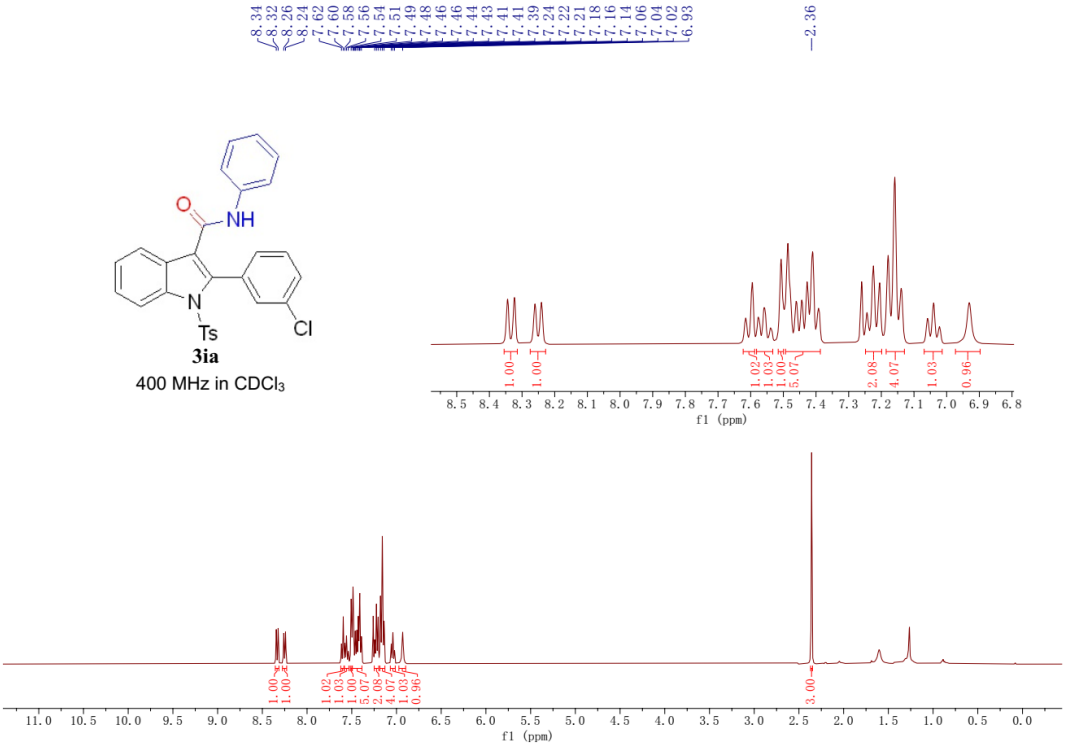
100 MHz in $CDCl_3$

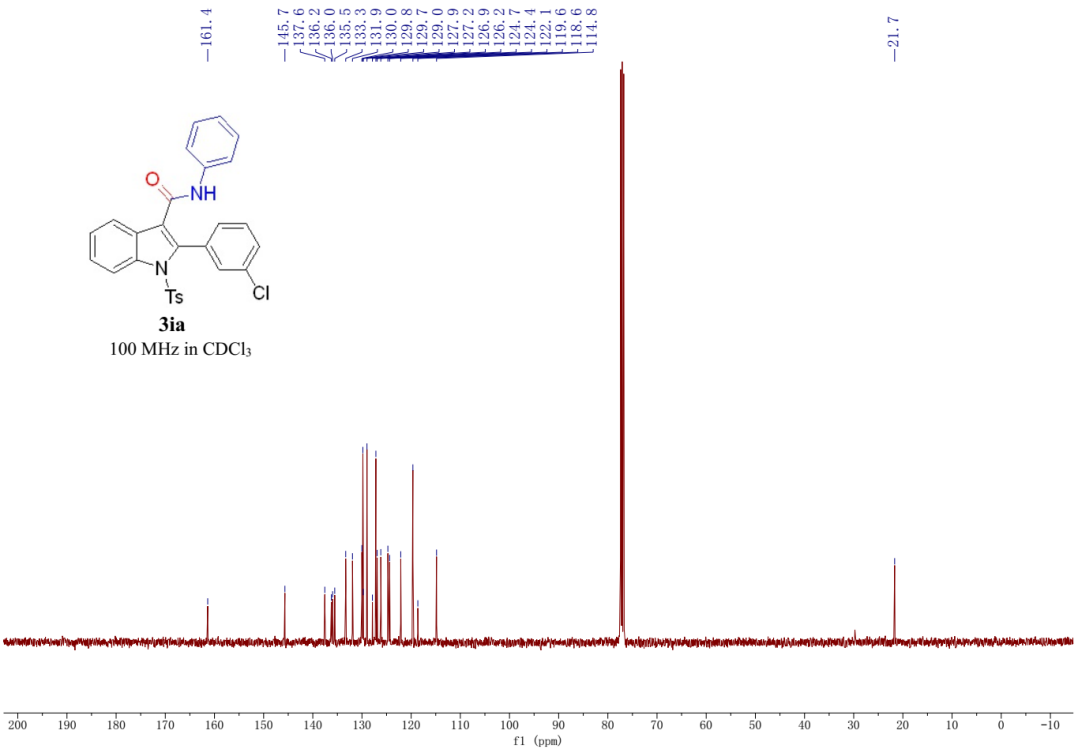

8.39
8.37
8.22
8.20
7.49
7.49
7.47
7.46
7.45
7.44
7.42
7.40
7.38
7.33
7.32
7.26
7.26
7.24
7.22
7.20
7.13
7.11
7.10
7.06
7.04
7.03
6.75
2.34
NH
O
F
N
Ts
3ga
400 MHz in CDCl3
0.98
0.92
4.06
2.05
4.07
4.06
1.04
1.00
f1 (ppm)
0.98
0.92
4.06
2.05
4.07
4.06
1.04
1.00
3.00
f1 (ppm)

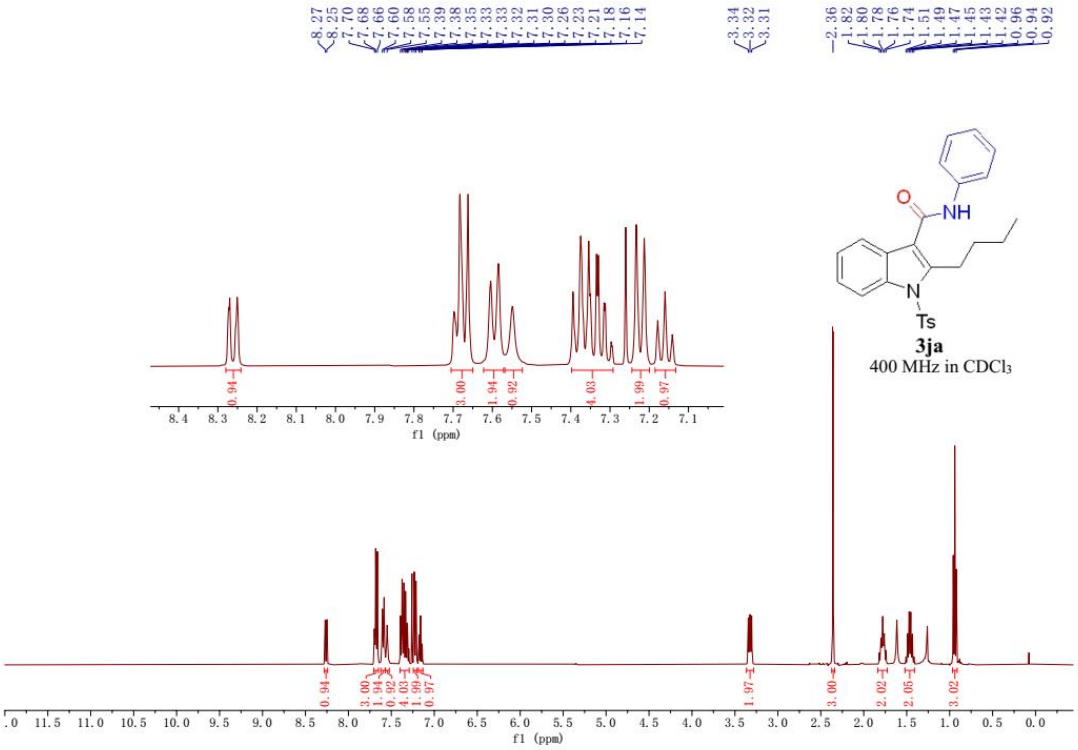

165.1
162.6
161.6
145.7
138.1
137.4
136.6
135.4
133.8
133.7
129.8
129.0
128.2
126.9
126.2
125.8
125.8
125.0
124.5
122.0
119.5
118.8
115.9
115.7
115.4
21.7
NH
O
F
N
Ts
3ga
100 MHz in CDCl3
f1 (ppm)

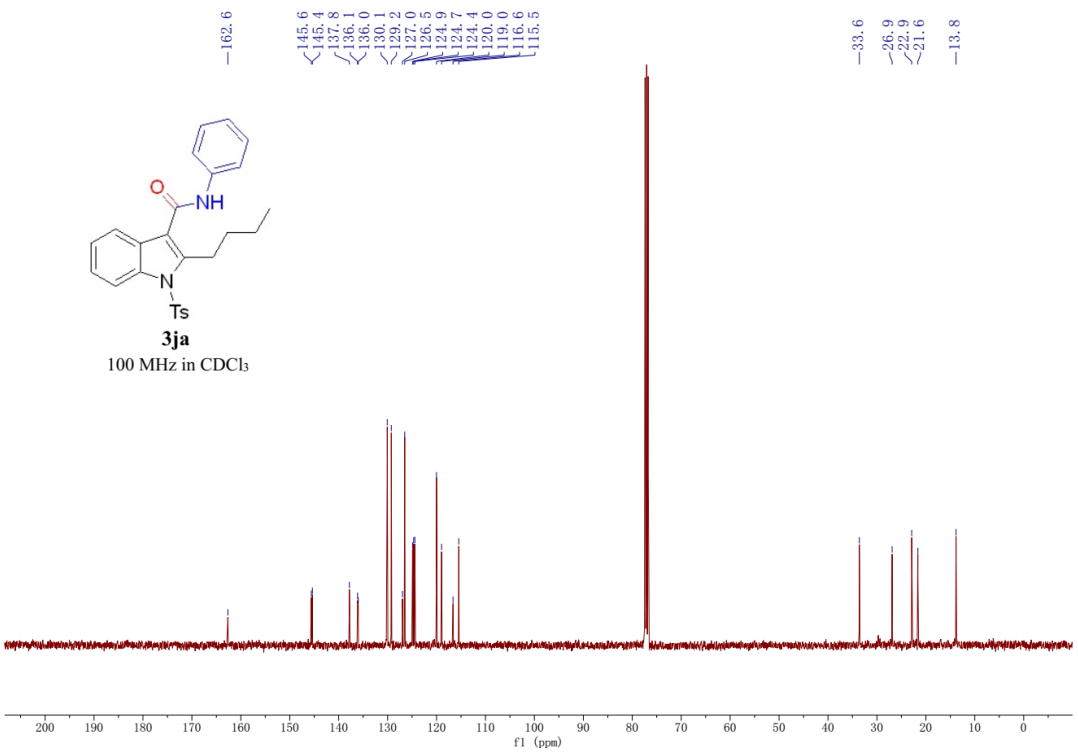

8.38
8.36
8.17
8.15
7.67
7.65
7.49
7.47
7.46
7.42
7.40
7.38
7.35
7.33
7.26
7.24
7.22
7.14
7.12
7.10
7.07
7.06
7.04
6.73
2.34
0.97
0.89
1.90
1.03
1.04
3.86
1.98
3.97
0.97
0.80
f1 (ppm)
O
NH
Br
N
Ts
3ha
400 MHz in CDCl3
3.00
f1 (ppm)

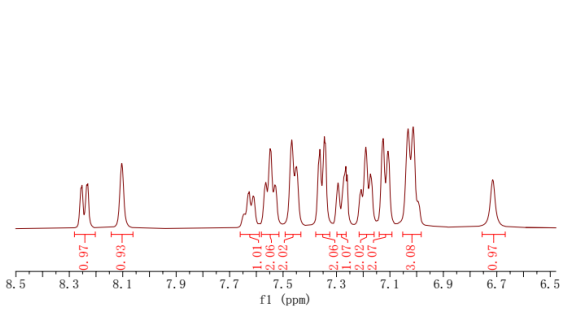

161.5
145.7
138.0
137.4
136.7
135.2
133.1
131.7
129.8
129.1
128.8
128.2
126.9
126.3
125.1
125.0
124.5
121.9
119.6
119.0
115.5
21.7
O
NH
Br
N
Ts
3ha
100 MHz in CDCl3
f1 (ppm)

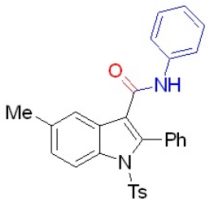

8.34
8.32
8.26
8.24
7.62
7.60
7.58
7.56
7.54
7.51
7.49
7.48
7.46
7.46
7.44
7.43
7.41
7.41
7.39
7.24
7.22
7.21
7.18
7.16
7.14
7.06
7.04
7.02
6.93
2.36
O
NH
N
Ts
Cl
3ia
400 MHz in CDCl3
1.00
1.00
1.02
1.03
1.00
5.07
2.08
4.07
1.03
0.96
f1 (ppm)
3.00
f1 (ppm)


161.4
145.7
137.6
136.2
136.0
135.5
133.3
131.9
130.0
129.8
129.7
129.0
127.9
127.2
126.9
126.2
124.7
124.4
122.1
119.6
118.6
114.8
21.7
O
NH
N
Ts
Cl
3ia
100 MHz in CDCl3
f1 (ppm)


3ja
400 MHz in CDCl3
f1 (ppm)

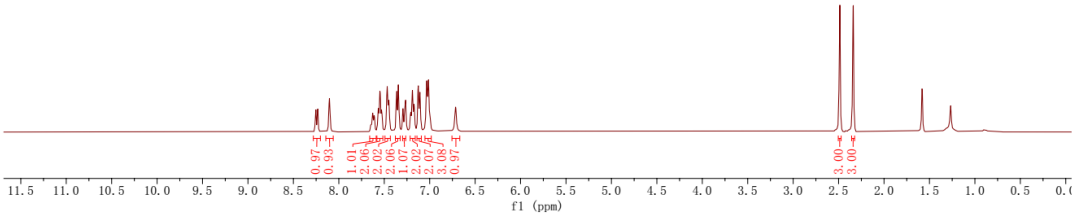

3ja
100 MHz in CDCl3
f1 (ppm)

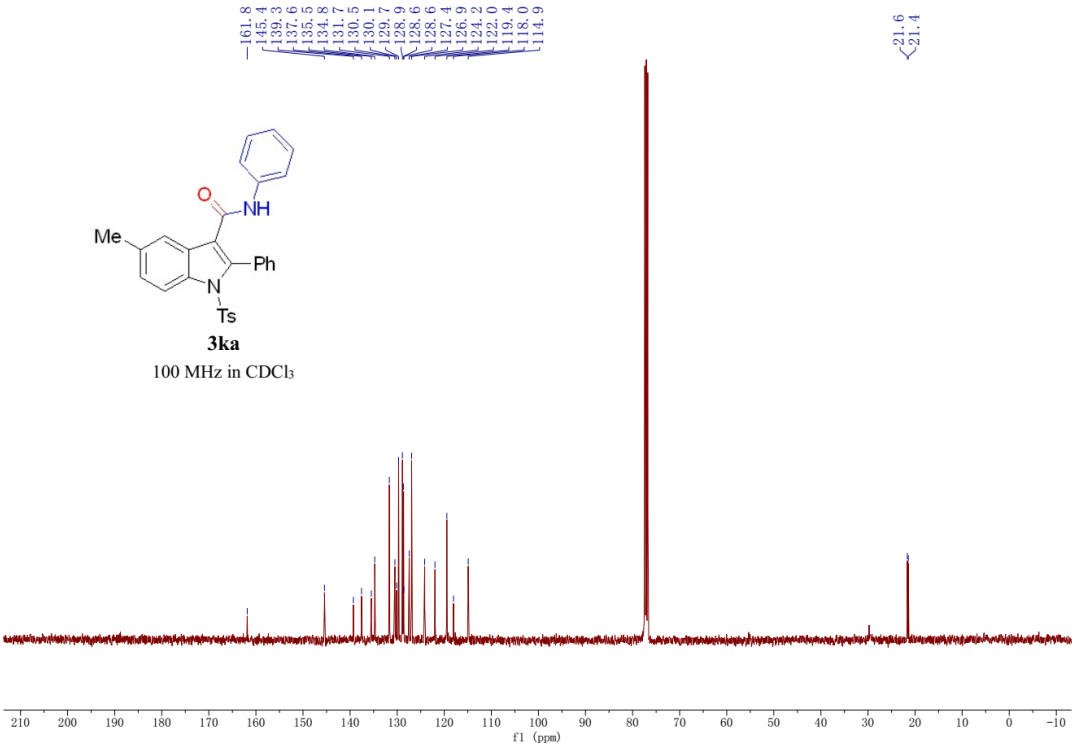




3ka

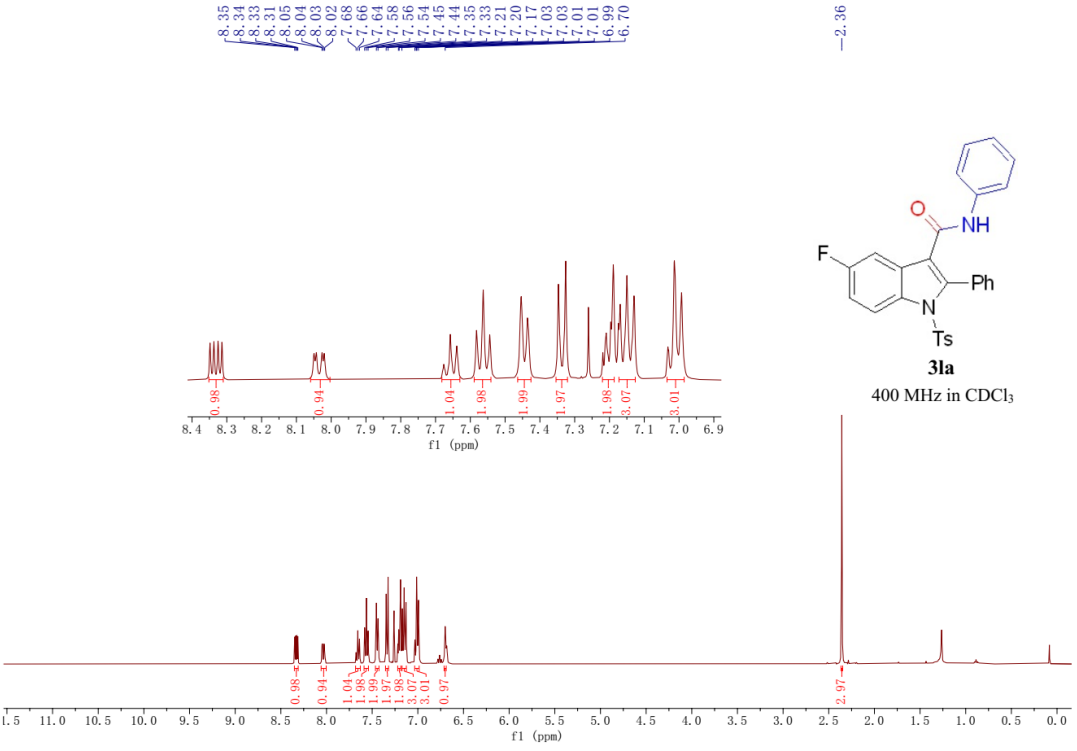
400 MHz in $CDCl_3$





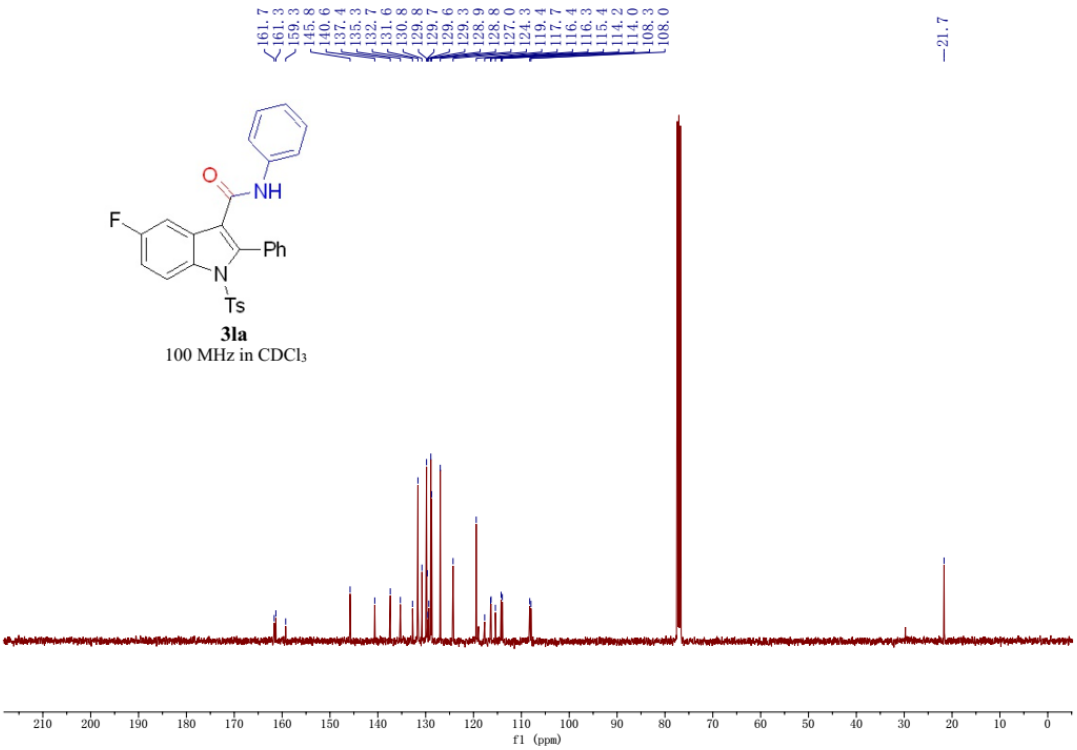
3ka

100 MHz in $CDCl_3$



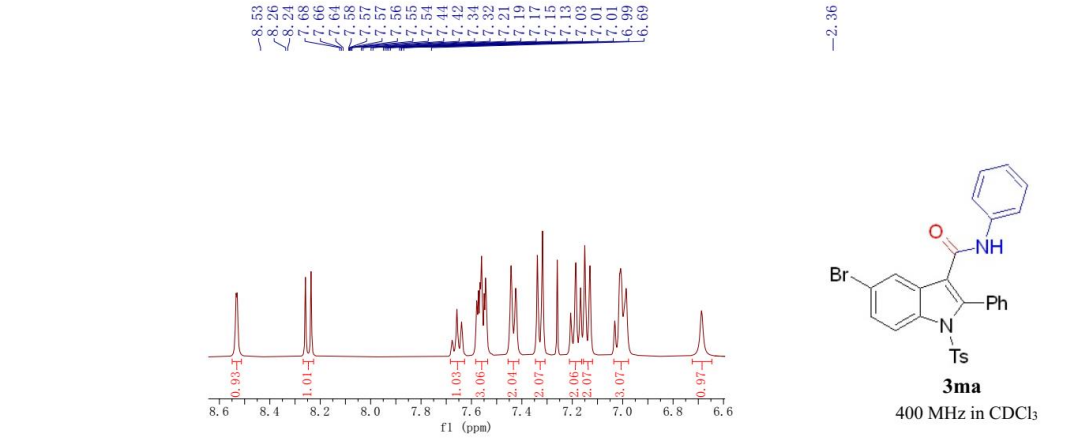
3la

400 MHz in $CDCl_3$

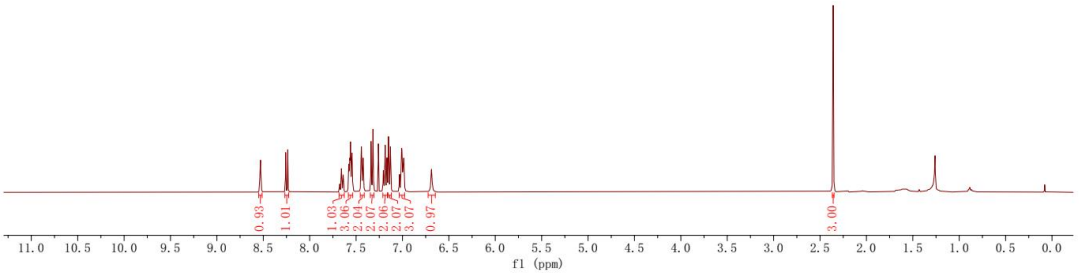


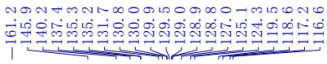
3la

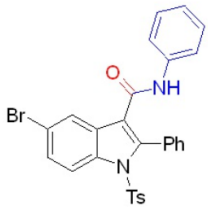
100 MHz in $CDCl_3$



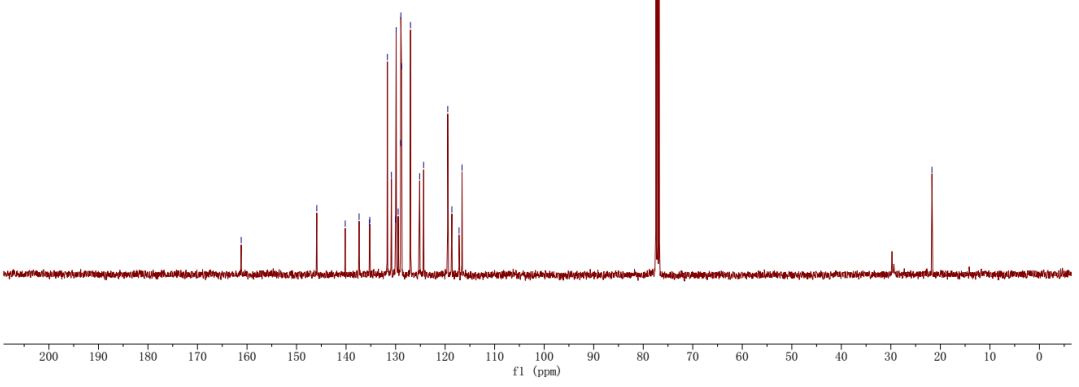
3ma
400 MHz in $CDCl_3$

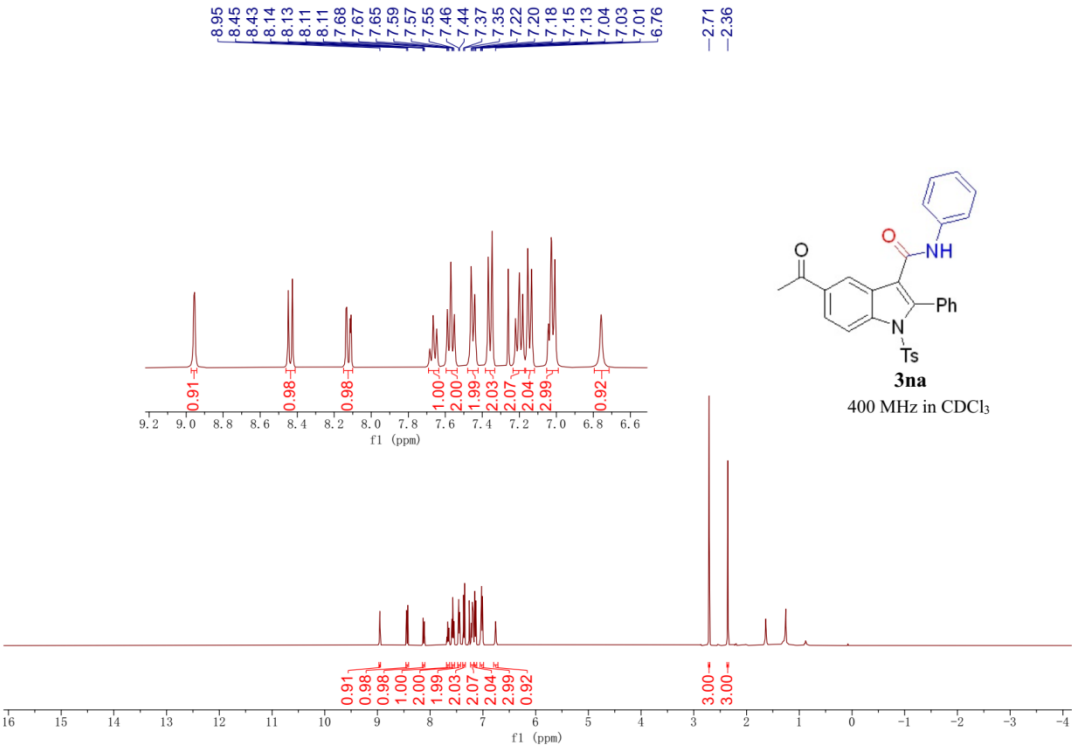


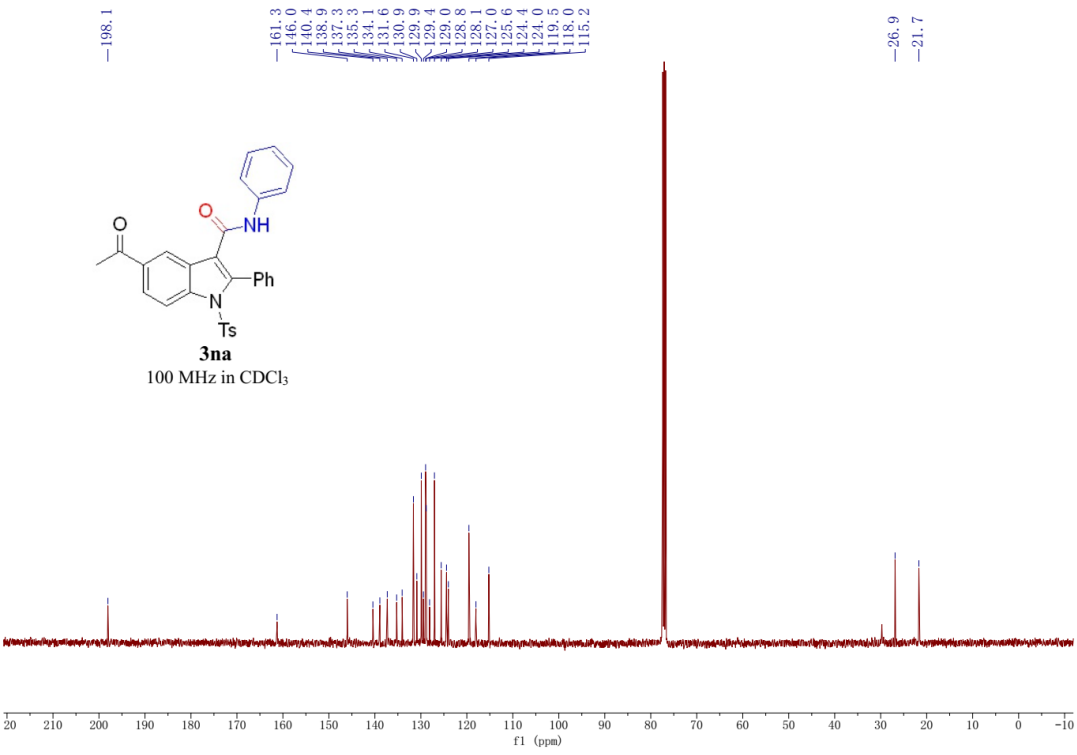


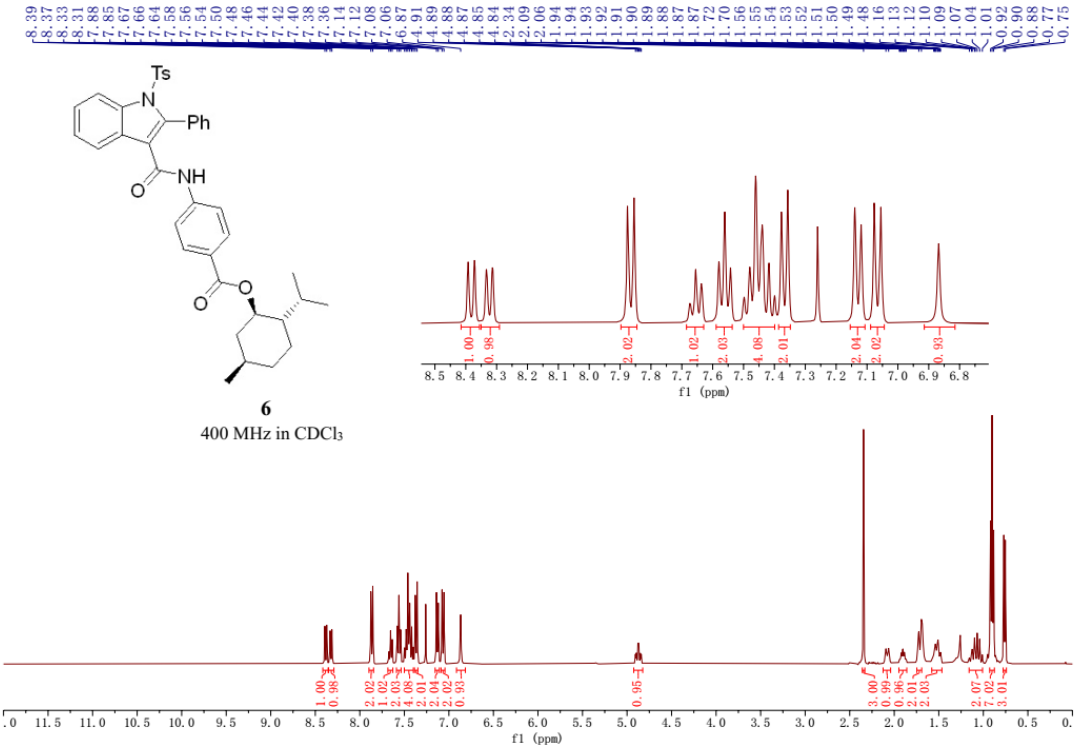


3ma
100 MHz in $CDCl_3$



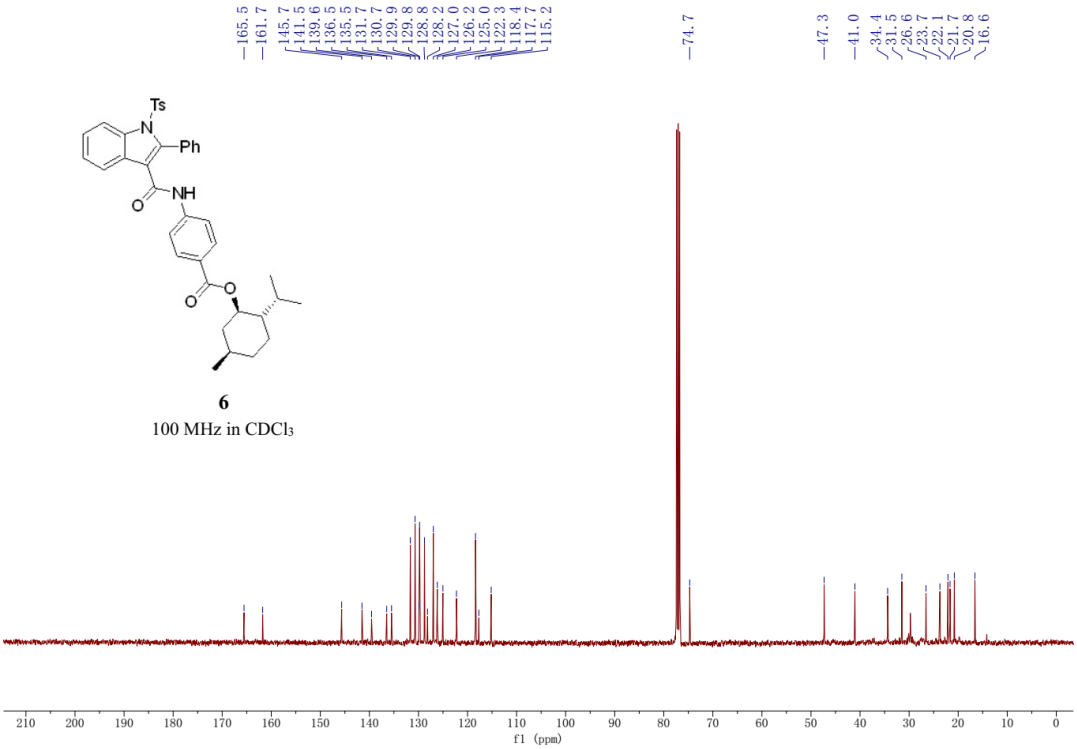

8.95
8.45
8.43
8.14
8.13
8.11
8.11
7.68
7.67
7.65
7.59
7.57
7.55
7.46
7.44
7.37
7.35
7.22
7.20
7.18
7.15
7.13
7.04
7.03
7.01
6.76
2.71
2.36
0.91
0.98
0.98
1.00
2.00
1.99
2.03
2.07
2.04
2.99
0.92
f1 (ppm)
O
NH
Ph
N
Ts
3na
400 MHz in CDCl3
0.91
0.98
0.98
1.00
2.00
1.99
2.03
2.07
2.04
2.99
0.92
3.00
3.00
f1 (ppm)


198.1
161.3
146.0
140.4
138.9
137.3
135.3
134.1
131.6
130.9
129.9
129.4
129.0
128.8
128.1
127.0
125.6
124.4
124.0
119.5
118.0
115.2
26.9
21.7
O
NH
Ph
N
Ts
3na
100 MHz in CDCl3
f1 (ppm)



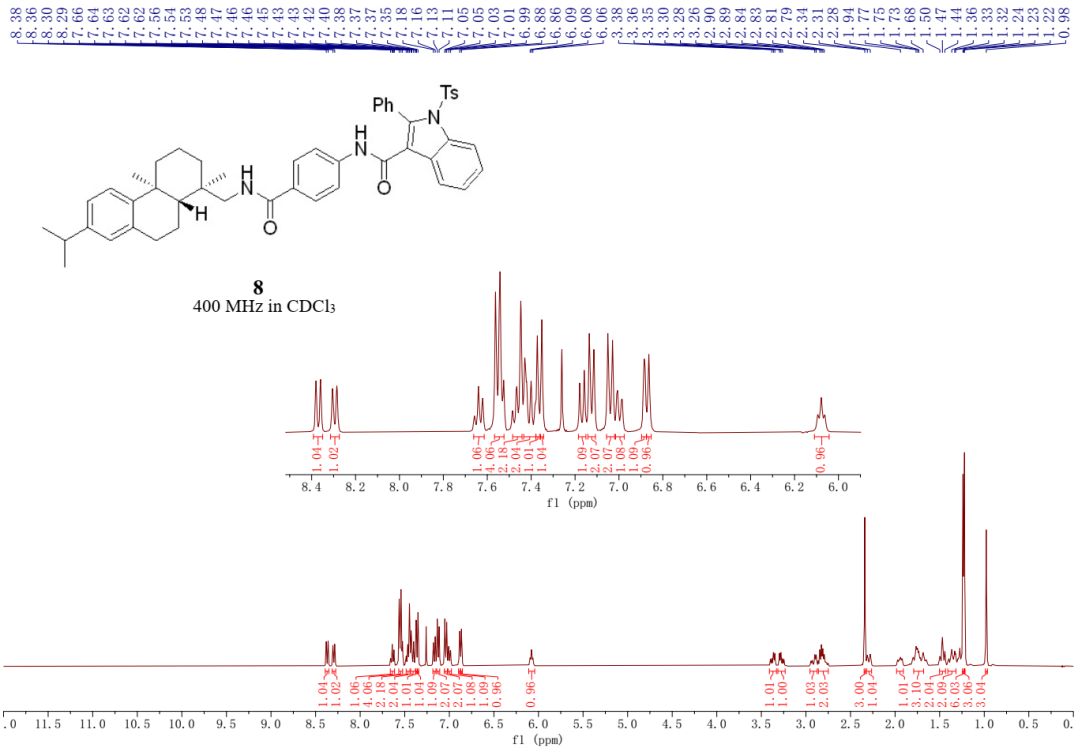
6

400 MHz in $CDCl_3$



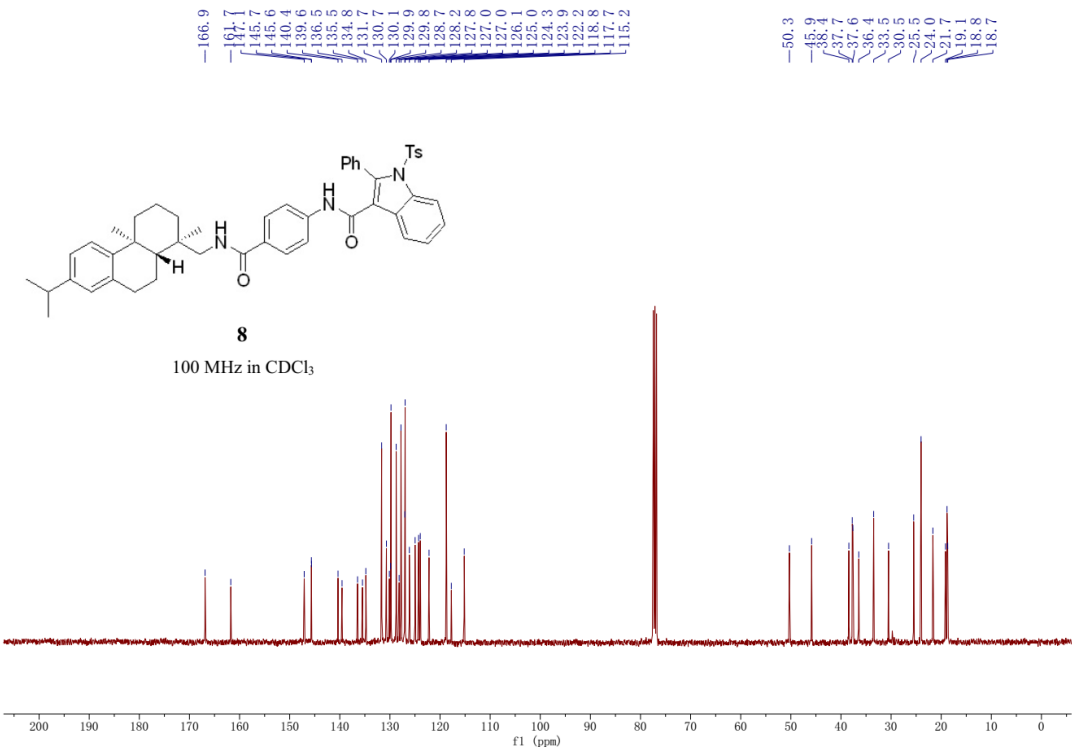
6

100 MHz in $CDCl_3$



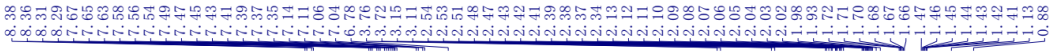
8

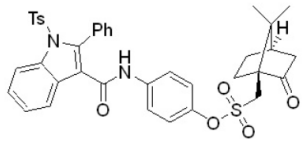
400 MHz in $CDCl_3$



8

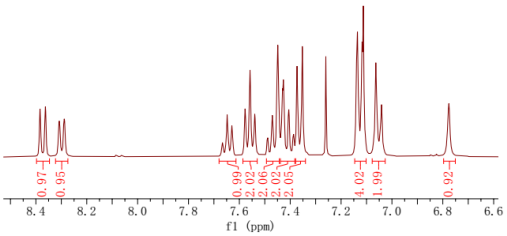
100 MHz in $CDCl_3$

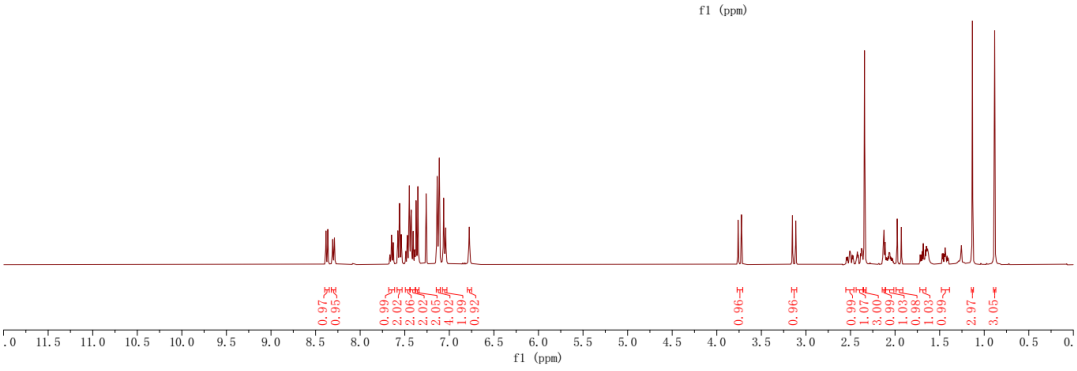


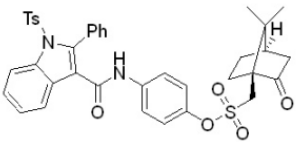


11

400 MHz in $CDCl_3$







11

100 MHz in $CDCl_3$