

Supporting Information for

**Silver-Catalyzed Cyclization of 2-Pyridyl Alkynyl Carbinols
with Isocyanides: Divergent Synthesis of Indolizines and
Pyrroles**

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Contents

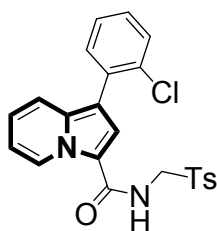
I. General information.....	S2
II. Synthesis and spectra data of compounds 3 , and 5	S2-S12
III. Crystallography.....	S14-S15
IV. NMR spectra copies.....	S16-S48

I. General information

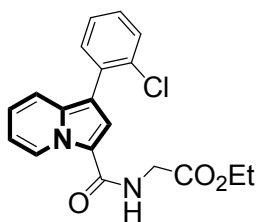
All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^1H -NMR and ^{13}C -NMR spectra were recorded at 25 °C on a Varian 500 MHz and 125 MHz, respectively, and TMS was used as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method.

II. Synthesis and spectra data of compounds 3 and 5

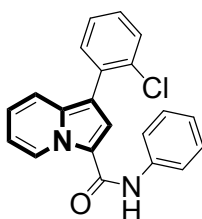
Typical synthetic procedure of 3 (with 3a as an example): A mixture of **1a** (0.122, 0.5 mmol) and isocyanide **2a** (0.293 g, 0.75 mmol) in 1,4-Dioxane (2.0 mL) stirred at 80 °C then add AgOAc (0.025g, 0.15 mmol), until the substrate **1a** was consumed as indicated by TLC about 10min. The resulting mixture was concentrated and the residue was taken up in DCM. The organic layer was washed with brine, dried over MgSO_4 and concentrated. Purification of the crude product by column chromatography (silica gel; petroleum ether: ethyl acetate:DCM = 10: 3: 1) afforded **3a** in 82% yield as a white solid.



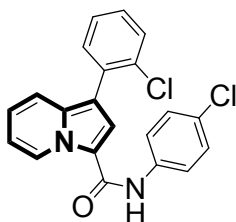
3a: White solid, m.p. 167-168 °C; ^1H -NMR (500 MHz, DMSO) δ 2.36 (s, 3H), 4.89 (d, J = 6.0 Hz, 2H), 6.91 (t, J = 6.5 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 7.38-7.44 (m, 5H), 7.51 (d, J = 7.0 Hz, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.76 (d, J = 7.5 Hz, 2H), 7.87 (s, 1H), 9.27 (t, J = 6.0 Hz, 1H), 9.33 (d, J = 7.0 Hz, 1H); ^{13}C -NMR (DMSO, 125 MHz) δ 21.6, 61.3, 112.1, 113.6, 115.6, 118.1, 119.8, 122.9, 127.3, 128.0, 129.1, 129.2, 130.2, 130.6, 132.6, 132.8, 133.4, 134.3, 135.6, 145.0, 160.8; **HRMS** (ESI) m/z calculated for $\text{C}_{23}\text{H}_{20}\text{ClN}_2\text{O}_3\text{S}[\text{M}+\text{H}]^+$: 439.0878, found: 439.0880



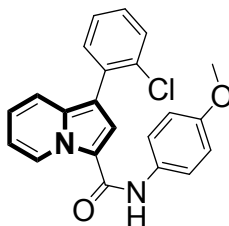
3b: White solid, m.p. 129-130 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 1.30 (t, *J* = 7.0 Hz, 3H), 4.22-4.27 (m, 4H), 6.55 (t, *J* = 5.0 Hz, 1H), 6.74-6.77 (m, 1H), 6.95-6.99 (m, 1H), 7.25-7.32 (m, 2H), 7.39-7.44 (m, 3H), 7.49-7.51 (m, 1H), 9.60-9.63 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 14.1, 41.2, 61.5, 112.3, 112.6, 115.5, 117.81, 117.82, 121.6, 126.7, 127.6, 128.0, 130.1, 132.0, 133.42, 133.43, 134.5, 161.7, 170.4; **HRMS** (ESI) *m/z* calculated for C₁₉H₁₇ClN₂NaO₃[M+Na]⁺ : 379.0820, found: 379.0830.



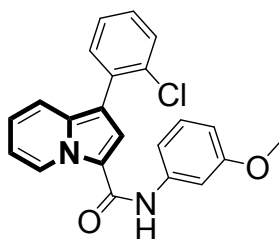
3c: White solid, m.p. 167-168 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 6.79 (t, *J* = 7.0 Hz, 1H), 7.01 (t, *J* = 7.0 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.24-7.35 (m, 4H), 7.42-7.47 (m, 3H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.73 (s, 1H), 9.66 (d, *J* = 7.5 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 112.5, 112.9, 115.9, 117.7, 117.9, 120.1, 122.0, 123.9, 126.8, 127.7, 128.2, 129.0, 130.1, 132.0, 133.2, 133.4, 134.9, 138.0, 159.8; **HRMS** (ESI) *m/z* calculated for C₂₁H₁₆ClN₂O₃[M+H]⁺ : 347.0946, found: 347.0956.



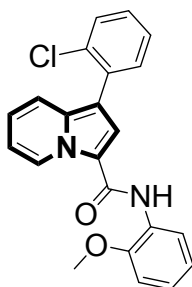
3d: Yellow solid, m.p. 175-176 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 6.85 (t, *J* = 6.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.28-7.37 (m, 4H), 7.42-7.50 (m, 3H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.68 (s, 1H), 9.67 (d, *J* = 7.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 112.7, 113.2, 115.6, 117.7, 118.0, 121.3, 122.3, 126.8, 127.8, 128.3, 128.8, 129.0, 130.2, 132.0, 133.1, 133.4, 135.2, 136.7, 159.6; **HRMS** (ESI) *m/z* calculated for C₂₁H₁₅Cl₂N₂O[M+H]⁺ : 381.0556, found: 381.0562.



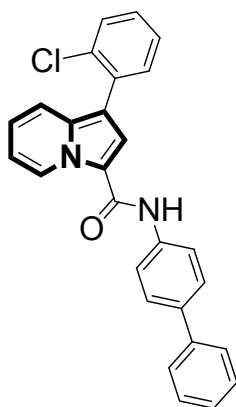
3e: Yellow solid, m.p. 160-161 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 3.78 (s, 3H), 6.76 (t, *J* = 6.5 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 2H), 6.96-7.00 (m, 1H), 7.24-7.32 (m, 2H), 7.40-7.44 (m, 2H), 7.45-7.51 (m, 4H), 7.74 (s, 1H), 9.65 (d, *J* = 7.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 55.4, 112.4, 112.8, 114.1, 116.0, 117.6, 117.9, 121.8, 122.3, 126.7, 127.7, 128.1, 130.1, 131.0, 132.0, 133.3, 133.4, 134.7, 156.2, 159.9; **HRMS** (ESI) *m/z* calculated for C₂₂H₁₈ClN₂O₂[M+H]⁺ : 377.1051, found: 377.1055.



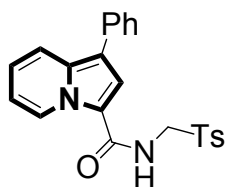
3f: White solid, m.p. 149-150 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 3.82 (s, 3H), 6.65-6.68 (m, 1H), 6.79-6.82 (m, 1H), 7.00-7.04 (m, 1H), 7.07-7.10 (m, 1H), 7.21-7.34 (m, 3H), 7.38 (t, *J* = 2.0 Hz, 1H), 7.42-7.47 (m, 3H), 7.51-7.53 (m, 1H), 7.72 (s, 1H), 9.67 (d, *J* = 7.5 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 55.3, 105.6, 109.9, 112.2, 112.6, 113.0, 116.0, 117.7, 117.9, 122.1, 126.8, 127.7, 128.2, 129.7, 130.1, 132.0, 133.2, 133.4, 135.0, 139.3, 159.7, 160.1; **HRMS** (ESI) *m/z* calculated for C₂₂H₁₈ClN₂O₂[M+H]⁺ : 377.1051, found: 377.1051



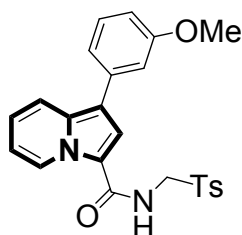
3g: White solid, m.p. 163-164 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 3.93 (s, 3H), 6.83 (t, *J* = 7.0 Hz, 1H), 6.91-7.06 (m, 4H), 7.30-7.36 (m, 2H), 7.44-7.49 (m, 3H), 7.54 (d, *J* = 7.5 Hz, 1H), 8.38 (s, 1H), 8.47-8.49 (m, 1H), 9.72 (d, *J* = 7.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 55.8, 109.9, 112.5, 112.9, 116.5, 117.7, 118.0, 119.4, 121.1, 121.8, 123.1, 126.8, 127.7, 128.0, 128.2, 130.1, 132.1, 133.4, 133.6, 134.8, 147.9, 159.5; **HRMS** (ESI) *m/z* calculated for C₂₂H₁₈ClN₂O₂[M+H]⁺ : 377.1051, found: 377.1060



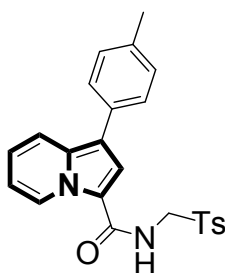
3h: White solid, m.p. 213-214 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 6.84 (t, *J* = 7.0 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 7.25-7.36 (m, 3H), 7.42-7.48 (m, 4H), 7.51 (s, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 4H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.75 (s, 1H), 9.70 (d, *J* = 7.5 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 112.6, 113.1, 115.9, 117.7, 118.0, 120.4, 122.2, 126.80, 126.82, 127.0, 127.7, 127.8, 128.2, 128.8, 130.2, 132.0, 133.2, 133.5, 135.1, 136.7, 137.4, 140.5, 159.7; **HRMS** (ESI) *m/z* calculated for C₂₇H₁₉ClN₂O[M+H]⁺: 423.9056, found: 423.9050.



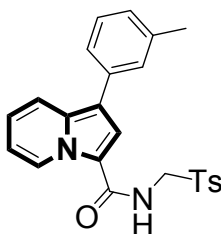
3i: White solid, m.p. 174-175 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.38 (s, 3H), 4.94 (d, *J* = 6.5 Hz, 2H), 6.72 (t, *J* = 7.0 Hz, 1H), 6.94-6.97 (m, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 3H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.83(d, *J* = 8.0 Hz, 2H), 9.27 (d, *J* = 7.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 21.7, 60.5, 113.0, 114.8, 116.2, 116.5, 117.7, 122.4, 126.4, 127.7, 127.8, 128.85, 128.89, 129.9, 134.1, 134.3, 134.7, 145.3, 160.0; **HRMS** (ESI) *m/z* calculated for C₂₃H₂₁N₂O₃S[M+H]⁺: 405.1267, found:405.1272.



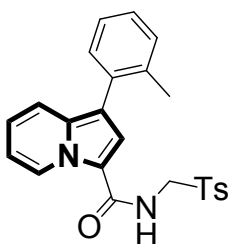
3j: White solid, m.p. 171-172 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.37 (s, 3H), 3.82-3.85 (m, 3H), 4.94 (d, *J* = 7.0 Hz, 2H), 6.69-6.73 (m, 1H), 6.83-6.85 (m, 1H), 6.99-7.10 (m, 4H), 7.22-7.26 (m, 2H), 7.29-7.35 (m, 1H), 7.44-7.47 (m, 1H), 7.76-7.79 (m, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 9.26 (d, *J* = 7.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 21.7, 55.2, 60.58, 111.9, 112.9, 113.3, 114.8, 116.0, 116.6, 117.7, 120.2, 122.4, 127.7, 128.8, 129.8, 129.9, 134.1, 134.3, 136.1, 145.2, 159.96, 160.02; **HRMS** (ESI) *m/z* calculated for C₂₄H₂₃N₂O₄S[M+H]⁺: 435.1373, found: 435.1367.



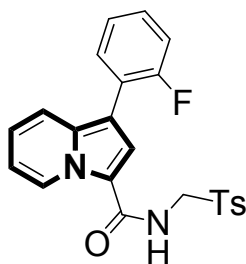
3k: White solid, m.p. 185-186 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.35 (s, 3H), 2.37 (s, 3H), 4.95 (d, *J* = 6.5 Hz, 2H), 6.67 (t, *J* = 7.0 Hz, 1H), 6.95-6.99 (m, 1H), 7.16-7.25 (m, 5H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.45 (s, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 9.25 (d, *J* = 7.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 21.1, 21.6, 60.7, 112.7, 114.7, 116.1, 116.6, 117.7, 122.0, 127.57, 127.59, 128.8, 129.5, 129.8, 131.7, 134.16, 134.2, 135.9, 145.1, 160.1; **HRMS** (ESI) *m/z* calculated for C₂₄H₂₃N₂O₃S[M+H]⁺: 419.1424, found: 419.1418



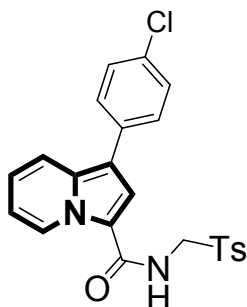
3l: White solid, m.p. 150-151 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.24 (s, 3H), 2.26 (s, 3H), 4.88 (d, *J* = 6.5 Hz, 2H), 6.58-6.62 (m, 1H), 6.88-6.92 (m, 1H), 6.98-7.00 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.15-7.21 (m, 4H), 7.41 (s, 1H), 7.65-7.67 (m, 1H), 7.73-7.75 (m, 2H), 9.17-9.18 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 21.4, 21.6, 60.6, 112.8, 114.7, 116.2, 116.8, 117.7, 122.1, 124.7, 127.0, 127.6, 128.5, 128.6, 128.8, 129.8, 134.1, 134.2, 134.6, 138.4, 145.1, 160.1; **HRMS** (ESI) *m/z* calculated for C₂₄H₂₃N₂O₃S[M+H]⁺: 419.1424, found: 419.1432.



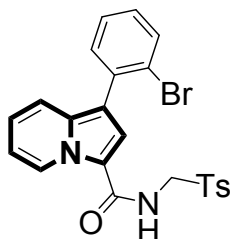
3m: White solid, m.p. 173-174 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.19 (s, 3H), 2.37 (s, 3H), 4.94 (d, *J* = 7.0 Hz, 2H), 6.70 (t, *J* = 7.0 Hz, 1H), 6.94 (t, *J* = 7.0 Hz, 1H), 7.06-7.10 (m, 1H), 7.20-7.33 (m, 8H), 7.80 (d, *J* = 8.0 Hz, 2H), 9.28 (d, *J* = 7.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 20.4, 21.6, 60.6, 112.7, 114.3, 115.4, 117.5, 117.88, 121.7, 125.7, 127.1, 127.4, 128.8, 129.8, 130.4, 130.7, 133.6, 134.2, 135.1, 136.7, 145.1, 160.1; **HRMS** (ESI) *m/z* calculated for C₂₄H₂₃N₂O₃S [M+H]⁺: 419.1424, found: 419.1430.



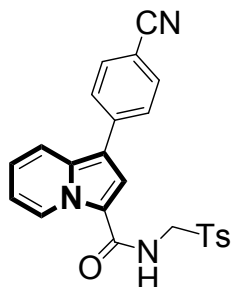
3n: White solid, m.p. 165-166 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.37 (s, 3H), 4.93 (d, *J* = 7.0 Hz, 2H), 6.73 (t, *J* = 6.5 Hz, 1H), 6.98-7.04 (d, *J* = 7.0 Hz, 2H), 7.15-7.20 (m, 2H), 7.24 (d, *J* = 9.0 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.43-7.48 (m, 2H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 9.27 (d, *J* = 7.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 21.6, 60.5, 109.3, 112.9, 115.0, 116.0 (d, *J* = 22.0 Hz), 118.0, 122.2 (d, *J* = 14.5 Hz), 124.3 (d, *J* = 3.5 Hz), 127.6, 128.1 (d, *J* = 8.0 Hz), 128.9, 129.9, 130.6 (d, *J* = 3.5 Hz), 134.1, 134.9, 145.2, 160.0, 160.6 (d, *J* = 247.0 Hz); **HRMS** (ESI) *m/z* calculated for C₂₃H₁₉FN₂NaO₃S[M+Na]⁺: 445.0993, found: 445.1005



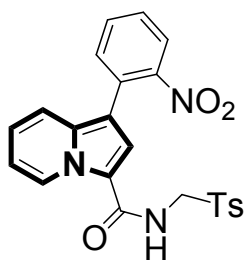
3o: White solid, m.p. 165-166 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.40 (s, 3H), 4.93 (d, *J* = 7.0 Hz, 2H), 6.73-6.76 (m, 1H), 6.89 (t, *J* = 7.0 Hz, 1H), 7.03-7.07 (m, 1H), 7.27-7.29 (m, 2H), 7.38-7.45 (m, 5H), 7.70-7.72 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 9.26-9.28 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 21.7, 60.61, 113.1, 114.8, 115.0, 116.6, 117.4, 122.7, 127.7, 128.8, 128.9, 129.9, 130.0, 132.0, 133.2, 134.1, 134.2, 145.3, 160.0; **HRMS** (ESI) *m/z* calculated for C₂₃H₂₀ClN₂O₃S[M+H]⁺: 439.0878, found: 439.0875.



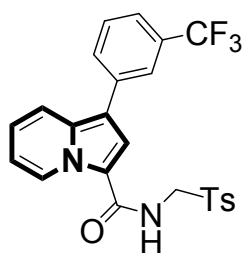
3p: White solid, m.p. 180-181 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.34 (s, 3H), 4.93 (d, *J* = 7.0 Hz, 2H), 6.73 (t, *J* = 7.0 Hz, 1H), 6.96-7.01 (m, 2H), 7.17-7.26 (m, 3H), 7.30-7.39 (m, 3H), 7.46 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 9.27 (d, *J* = 7.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 21.6, 60.5, 112.9, 114.4, 114.6, 118.0, 118.4, 122.2, 124.0, 127.3, 127.5, 128.5, 128.8, 129.8, 132.1, 133.4, 134.1, 135.0, 135.1, 145.1, 160.1; **HRMS** (ESI) *m/z* calculated for C₂₃H₂₀BrN₂O₃S[M+H]⁺: 483.0373, found: 483.0379.



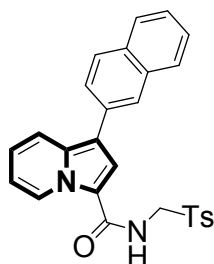
3q: White solid, m.p. 209-210 °C; **¹H-NMR** (500 MHz, DMSO) δ 2.36 (s, 3H), 4.90 (d, J = 6.5 Hz, 2H), 6.96 (t, J = 7.0 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.74-7.79 (m, 4H), 7.90 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 1H), 8.07 (s, 1H), 9.27-9.31 (m, 2H); **¹³C-NMR** (DMSO, 125 MHz) δ 21.7, 61.3, 108.4, 113.1, 114.3, 116.8, 118.1, 118.7, 119.8, 124.5, 127.8, 127.9, 129.2, 130.3, 133.6, 134.0, 135.5, 140.1, 145.3, 160.8; **HRMS** (ESI) m/z calculated for C₂₄H₂₀N₃O₃S [M+H]⁺: 430.1220, found: 430.1210.



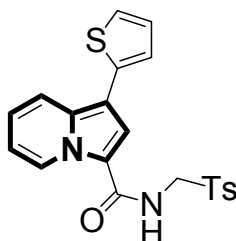
3r: White solid, m.p. 192-193 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.38 (s, 3H), 4.89 (d, J = 6.5 Hz, 2H), 6.73-6.77 (m, 1H), 7.01-7.04 (m, 1H), 7.08 (t, J = 7.0 Hz, 1H), 7.26-7.29 (m, 2H), 7.33-7.37 (m, 2H), 7.45-7.50 (m, 1H), 7.51-7.54 (m, 1H), 7.60-7.62 (m, 1H), 7.80-7.83 (m, 2H), 7.88-7.90 (m, 1H), 9.27-9.29 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 21.7, 60.4, 110.1, 113.2, 115.3, 116.8, 117.4, 123.1, 124.4, 127.77, 127.80, 128.7, 128.9, 129.9, 132.3, 132.7, 134.0, 134.9, 145.3, 149.7, 159.9; **HRMS** (ESI) m/z calculated for C₂₃H₂₀N₃O₅S [M+H]⁺: 450.1118, found: 450.1119



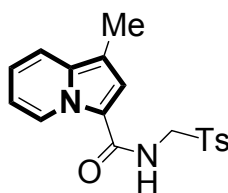
3s: White solid, m.p. 203-204 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.40 (s, 3H), 4.94 (d, J = 6.5 Hz, 2H), 6.76 (t, J = 6.5 Hz, 1H), 7.00-7.04 (m, 1H), 7.08 (d, J = 7.5 Hz, 1H), 7.28 (s, 2H), 7.49 (s, 1H), 7.51-7.55 (m, 2H), 7.69-7.74 (m, 2H), 7.78 (s, 1H), 7.83 (d, J = 8.0 Hz, 2H), 9.30 (d, J = 7.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 21.7, 60.6, 113.2, 114.5, 115.2, 116.7, 117.1, 122.8 (q, J = 3.5 Hz), 123.0, 124.2 (q, J = 3.5 Hz), 127.8, 128.8, 129.3, 129.9, 130.8, 131.2 (q, J = 33.5 Hz), 134.1, 134.3, 135.6, 145.3, 160.0; **HRMS** (ESI) m/z calculated for C₂₄H₂₀F₃N₂O₃S [M+H]⁺: 473.1141, found: 473.1143.



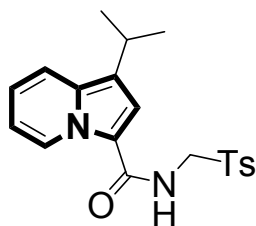
3t: White solid, m.p. 186-187 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.27 (s, 3H), 4.98 (d, *J* = 7.0 Hz, 2H), 6.67-6.71 (m, 1H), 6.99-7.03 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.0 Hz, 1H), 7.44-7.47 (m, 2H), 7.57-7.61 (m, 2H), 7.73-7.75 (m, 1H), 7.80-7.87 (m, 6H), 9.29 (d, *J* = 7.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 21.5, 60.7, 113.0, 115.0, 116.0, 117.0, 117.7, 122.5, 125.5, 125.8, 126.2, 126.4, 127.6, 127.7, 128.4, 128.8, 129.9, 132.0, 132.1, 133.7, 134.2, 134.4, 145.2, 160.1; **HRMS** (ESI) *m/z* calculated for C₂₇H₂₂N₂NaO₃S[M+Na]⁺: 477.1243, found: 477.1245



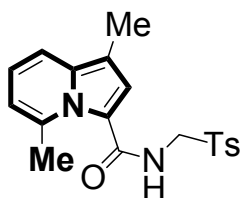
3u: Brown solid, m.p. 155-156 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.37 (s, 3H), 4.93 (d, *J* = 6.5 Hz, 2H), 6.68-6.72 (m, 1H), 7.02-7.07 (m, 2H), 7.13-7.17 (m, 2H), 7.21-7.23 (m, 1H), 7.24-7.27 (m, 2H), 7.48 (s, 1H), 7.81-7.84 (m, 3H), 9.23-9.25 (d, *J* = 7.5 Hz, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 21.6, 60.6, 109.4, 113.0, 114.8, 116.4, 117.8, 122.6, 123.06, 123.14, 127.56, 127.61, 128.8, 129.8, 133.9, 134.2, 136.7, 145.2, 159.9; **HRMS** (ESI) *m/z* calculated for C₂₁H₁₉N₂O₃S₂[M+H]⁺: 411.0832, found: 411.0839.



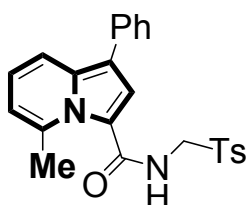
3v: White solid, m.p. 193-194 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.25 (s, 3H), 2.31 (s, 3H), 4.82 (d, *J* = 7.0 Hz, 2H), 6.55-6.60 (m, 2H), 6.84-6.88 (m, 1H), 7.01 (s, 1H), 7.18-7.20 (m, 2H), 7.29-7.33 (m, 1H), 7.72-7.74 (d, *J* = 8.0 Hz, 2H), 9.09-9.11 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 10.4, 21.66, 60.39, 110.1, 112.3, 113.2, 116.9, 117.6, 120.48, 127.3, 128.8, 129.8, 134.1, 135.7, 145.2, 159.8; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₈N₂SO [M+H]⁺: 343.4121, found: 343.4125.



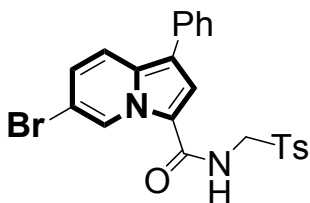
3w: White solid, m.p. 176-177 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 1.32 (d, *J* = 7.0 Hz, 6H), 2.39 (s, 3H), 3.18-3.22 (m, 1H), 4.89 (d, *J* = 6.5 Hz, 2H), 6.59 (t, *J* = 6.5 Hz, 1H), 6.65 (t, *J* = 7.0 Hz, 1H), 6.91-6.95 (m, 1H), 7.11 (s, 1H), 7.26-7.28 (m, 2H), 7.45 (d, *J* = 9.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 9.19 (d, *J* = 7.0 Hz, 1H); **¹³C-NMR** (CDCl₃, 100 MHz) δ 21.8, 23.9, 25.2, 60.6, 112.6, 113.5, 114.2, 117.2, 120.7, 122.7, 127.6, 129.1, 130.0, 134.4, 134.6, 145.3, 160.2; **HRMS** (ESI) *m/z* calculated for C₂₀H₂₃N₂O₃S[M+H]⁺: 371.1465, found: 371.1467



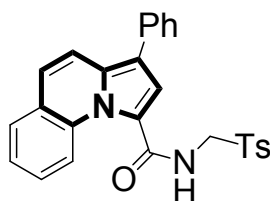
3x: White solid, m.p. 206-207 °C; **¹H-NMR** (500 MHz, DMSO) δ 2.13 (s, 3H), 2.29 (s, 3H), 2.39 (s, 3H), 4.85 (d, *J* = 7.0 Hz, 2H), 6.57 (d, *J* = 6.5 Hz, 1H), 6.89-6.93 (m, 1H), 7.08 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 3H), 7.89 (d, *J* = 8.0 Hz, 2H), 9.27 (t, *J* = 7.0 Hz, 1H); **¹³C-NMR** (DMSO, 125 MHz) δ 10.8, 21.6, 61.5, 79.5, 108.6, 113.5, 115.3, 117.6, 120.2, 121.9, 129.2, 130.3, 135.5, 135.9, 136.7, 145.0, 160.9; **HRMS** (ESI) *m/z* calculated for C₂₂H₁₈ClN₂O₂[M+H]⁺: 357.1273, found: 357.1267



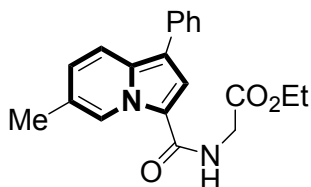
3y: White solid, m.p. 186-187 °C; **¹H-NMR** (500 MHz, DMSO) δ 2.19 (s, 3H), 2.39 (s, 3H), 4.93 (d, *J* = 6.0 Hz, 2H), 6.69 (d, *J* = 6.5 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.41-7.49 (m, 5H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 9.53 (t, *J* = 6.0 Hz, 1H); **¹³C-NMR** (DMSO, 125 MHz) δ 21.65, 21.69, 61.5, 114.46, 114.49, 115.6, 119.4, 120.5, 122.7, 126.5, 127.9, 129.3, 129.6, 130.3, 134.4, 135.49, 135.40, 137.3, 145.2, 161.1; **HRMS** (ESI) *m/z* calculated for C₂₂H₁₈ClN₂O₂[M+H]⁺: 419.1429, found: 419.1424



3z: White solid, m.p. 218-219 °C; ¹H-NMR (500 MHz, DMSO) δ 2.38 (s, 3H), 4.89 (d, *J* = 6.5 Hz, 2H), 7.20 (d, *J* = 9.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.0 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.94 (s, 1H), 9.36-9.39 (m, 1H); ¹³C-NMR (DMSO, 125 MHz) δ 21.6, 61.2, 107.8, 116.39, 116.42, 118.2, 119.2, 125.3, 126.8, 127.0, 127.7, 129.2, 129.6, 130.2, 131.4, 134.5, 135.4, 145.1, 160.6; **HRMS** (ESI) *m/z* calculated for C₂₂H₁₈ClN₂O₂[M+H]⁺: 483.0378, found: 483.0373



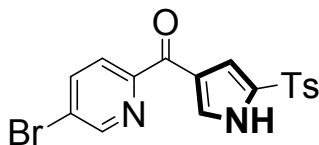
3aa: White solid, m.p. 193-194 °C; ¹H-NMR (500 MHz, DMSO) δ 2.40 (s, 3H), 5.02 (d, *J* = 6.0 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.40-7.45 (m, 3H), 7.48-7.52 (m, 4H), 7.58 (d, *J* = 7.5 Hz, 3H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 2H), 9.79 (t, *J* = 5.5 Hz, 1H); ¹³C-NMR (DMSO, 125 MHz) δ 21.8, 61.3, 117.3, 117.5, 119.3, 120.3, 122.8, 124.1, 125.0, 125.1, 127.0, 128.2, 128.24, 129.0, 129.3, 129.6, 130.4, 131.9, 133.1, 134.8, 135.4, 145.2, 162.3; **HRMS** (ESI) *m/z* calculated for C₂₂H₁₈ClN₂O₂[M+H]⁺: 455.1430, found: 455.1424



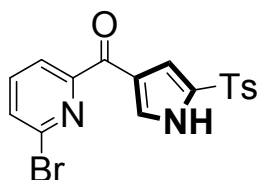
3ab: White solid, m.p. 185-186 °C; ¹H-NMR (500 MHz, DMSO) δ 1.22 (t, *J* = 7.0 Hz, 3H), 2.28 (s, 3H), 4.02 (d, *J* = 5.0 Hz, 2H), 4.12-4.15 (m, 2H), 6.98 (d, *J* = 9.0 Hz, 1H), 7.28 (t, *J* = 7.0 Hz, 1H), 7.47 (t, *J* = 7.0 Hz, 2H), 7.59 (d, *J* = 7.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.83 (s, 1H), 8.67 (s, 1H), 9.47 (s, 1H); ¹³C-NMR (DMSO, 125 MHz) δ 14.6, 18.5, 41.2, 60.9, 114.6, 116.2, 116.8, 117.4, 122.3, 124.9, 125.3, 126.3, 127.5, 129.4, 131.8, 135.4, 162.1, 170.7; **HRMS** (ESI) *m/z* calculated for C₂₀H₂₁N₂O₃[M+H]⁺: 337.1573, found: 337.1578.

Typical synthetic procedure of 5 (with 5a as an example): A mixture of **4a** (0.106, 0.5 mmol) and isocyanide **2a** (0.146 g, 0.75 mmol) in 1,4-Dioxane (2.0 mL) stirred at 80 °C then add AgCO₃ (0.014g, 0.05 mmol.), until the substrate **4a** was consumed as indicated by TLC about 10min. The resulting mixture was concentrated and the residue was taken up in DCM. The organic layer was washed with brine, dried over MgSO₄ and concentrated. Purification of the crude product by

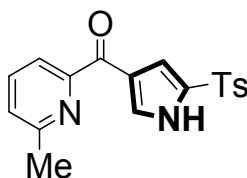
column chromatography (silica gel; petroleum ether: ethyl acetate= 10: 2) afforded **5a** in 87% yield as a white solid.



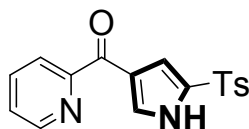
5a: White solid, m.p. 206-207 °C; **¹H-NMR** (500 MHz, DMSO) δ 2.41 (s, 3H), 7.31 (m, 2H), 7.63 (s, 1H), 7.85 (s, 2H), 8.01 (s, 2H), 8.30 (s, 1H), 8.74 (s, 1H), 9.99 (s, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 21.6, 117.3, 124.6, 124.7, 125.0, 127.1, 130.0, 130.2, 131.1, 138.3, 139.8, 144.6, 149.6, 152.9, 184.6; **HRMS** (ESI) m/z calculated for C₂₂H₁₈ClN₂O₂[M+H]⁺: 404.9911, found: 404.9903



5b: White solid, m.p. 214-215 °C; **¹H-NMR** (500 MHz, DMSO) δ 2.36 (s, 3H), 7.42 (t, *J* = 2.0 Hz, 2H), 7.44 (s, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.90-7.92 (m, 1H), 7.97 (t, *J* = 7.5 Hz, 1H), 8.00-8.02 (m, 1H), 8.13 (d, *J* = 1.5 Hz, 1H), 13.19 (s, 1H); **¹³C-NMR** (DMSO, 125 MHz) δ 21.6, 117.0, 123.2, 123.3, 127.4, 130.7, 131.1, 132.0, 132.7, 139.0, 140.6, 141.5, 144.9, 155.4, 183.9; **HRMS** (ESI) m/z calculated for C₂₂H₁₈ClN₂O₂[M+H]⁺: 404.9906, found: 404.9903

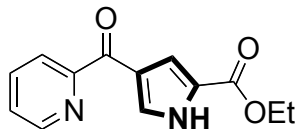


5c: White solid, m.p. 198-199 °C; **¹H-NMR** (500 MHz, DMSO) δ 2.37 (s, 3H), 2.58 (s, 3H), 7.42-7.45 (m, 3H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.86-7.91 (m, 3H), 8.25 (s, 1H), 13.09 (d, *J* = 7.5 Hz, 1H); **¹³C-NMR** (DMSO, 125 MHz) δ 21.6, 24.5, 117.2, 120.9, 123.9, 127.0, 127.4, 130.6, 130.7, 132.9, 138.3, 139.1, 144.8, 154.4, 157.9, 185.8; **HRMS** (ESI) m/z calculated for C₂₂H₁₈ClN₂O₂[M+H]⁺: 341.0962, found: 341.0954



5d: White solid, m.p. 161-162°C; **¹H-NMR** (500 MHz, CDCl₃) δ 2.41 (s, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.46-7.49 (m, 1H), 7.64 (d, *J* = 1.5 Hz, 1H), 7.84-7.89 (m, 3H), 8.10-8.12 (m, 1H), 8.33 (d, *J*

= 1.5 Hz, 1H), 8.68-8.69 (m, 1H), 9.75 (s, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 21.5, 117.4, 123.6, 124.8, 126.5, 127.1, 130.0, 131.3, 137.0, 138.4, 144.5, 148.4, 154.7, 185.8; **HRMS** (ESI) m/z calculated for C₁₇H₁₅N₂O₃S[M+H]⁺: 327.0798, found: 327.0801.



5e: Yellow solid, m.p. 121-122 °C; **¹H-NMR** (500 MHz, CDCl₃) δ 1.39 (t, *J* = 7.5 Hz, 3H), 4.36 (q, *J* = 7.0 Hz, 2H), 7.46-7.49 (m, 1H), 7.70-7.72 (M, 1H), 7.86-7.90 (m, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.30-8.31 (m, 1H), 8.71-8.73 (m, 2H), 9.65 (s, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 14.3, 60.9, 117.48, 123.70, 123.8, 124.5, 126.3, 131.0, 137.0, 148.4, 155.3, 161.3, 186.5; **HRMS** (ESI) m/z calculated for C₁₃H₁₃N₂O₃ [M+H]⁺: 245.0921, found: 245.0929.

III. Crystallography

Single-crystal X-ray diffraction data for the reported complex was recorded at a temperature of 293(2) K on a Oxford Diffraction Gemini R Ultra diffractometer, using a ω scan technique with Mo-K α radiation ($\lambda = 0.71073$ Å). The structure was solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.¹ Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of the ligands were refined as rigid groups. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1-2.

Ref: (a) G. M. Sheldrick, *SHELXS-97, Program for Solution of Crystal Structures*, University of Gottingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXL-97, Program for Refinement of Crystal Structures*, University of Gottingen, Germany, 1997.

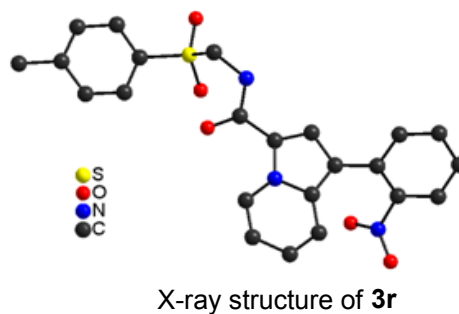
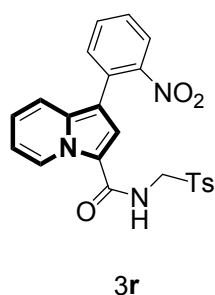
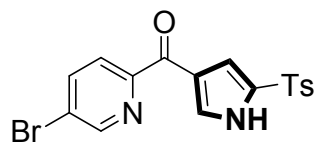


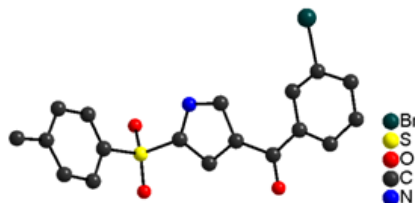
Table 1. Crystal data and structure refinement of 3r

Empirical formula	C ₂₃ H ₂₉ Cl N ₂ O ₃ S
Temperature	293(2)K
Wavelength	0.71073 Å
Unit cell dimensions	a=8.6842(6) Å b=10.9725(8) Å c=11.2956(8) Å alpha=100.9740(10) deg. beta=95.5290(10) deg. gamma=99.6870(10) deg.
Volume	1032.37(13) Å ³
Z	13
Calculated density	1.570 Mg/m ³
Absorption coefficient	0.751 mm ⁻¹
F(000)	494
Crystal size	? x ? x ? mm

Theta range for data collection	1.85 to 26.05 deg.
Reflections collected / unique	5599 / 3987 [R(int) = 0.0147]
Data / restraints / parameters	3987 / 0 / 129
Goodness-of-fit on F ²	2.124
Final R indices [I>2sigma(I)]	R1 = 0.0962, wR2 = 0.2771
R indices (all data)	R1 = 0.1095, wR2 = 0.3010



5a

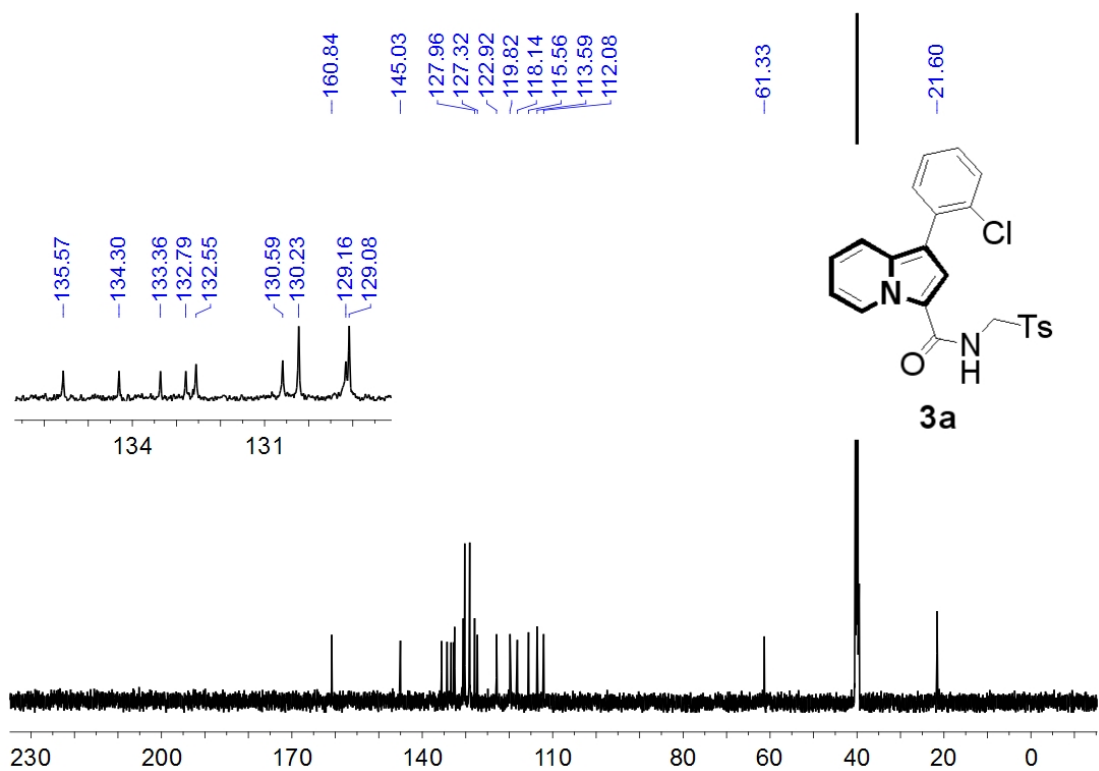
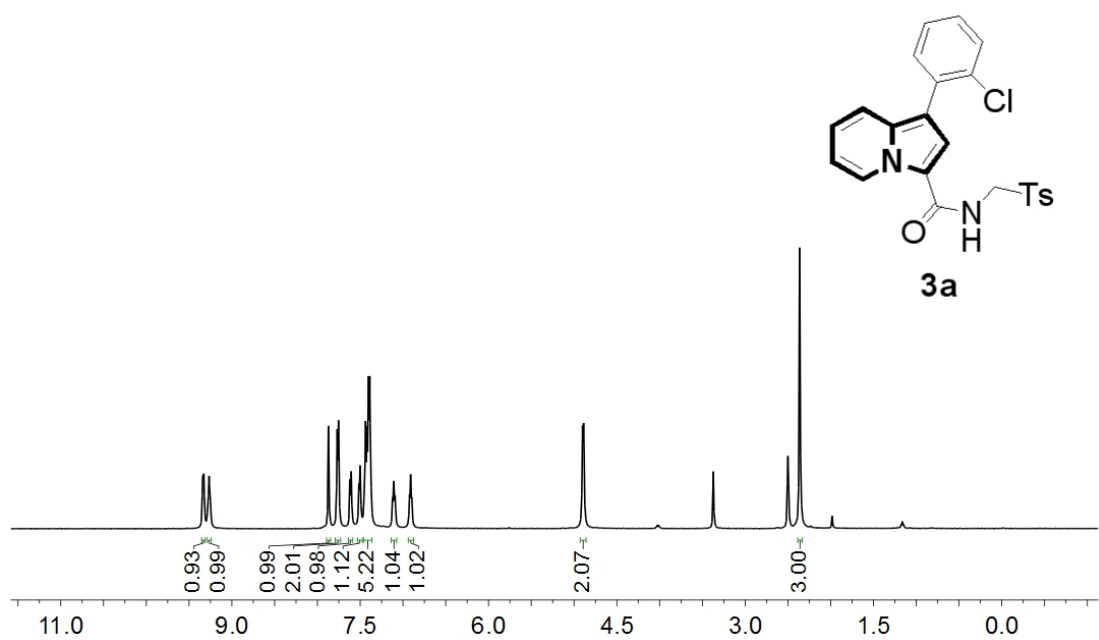


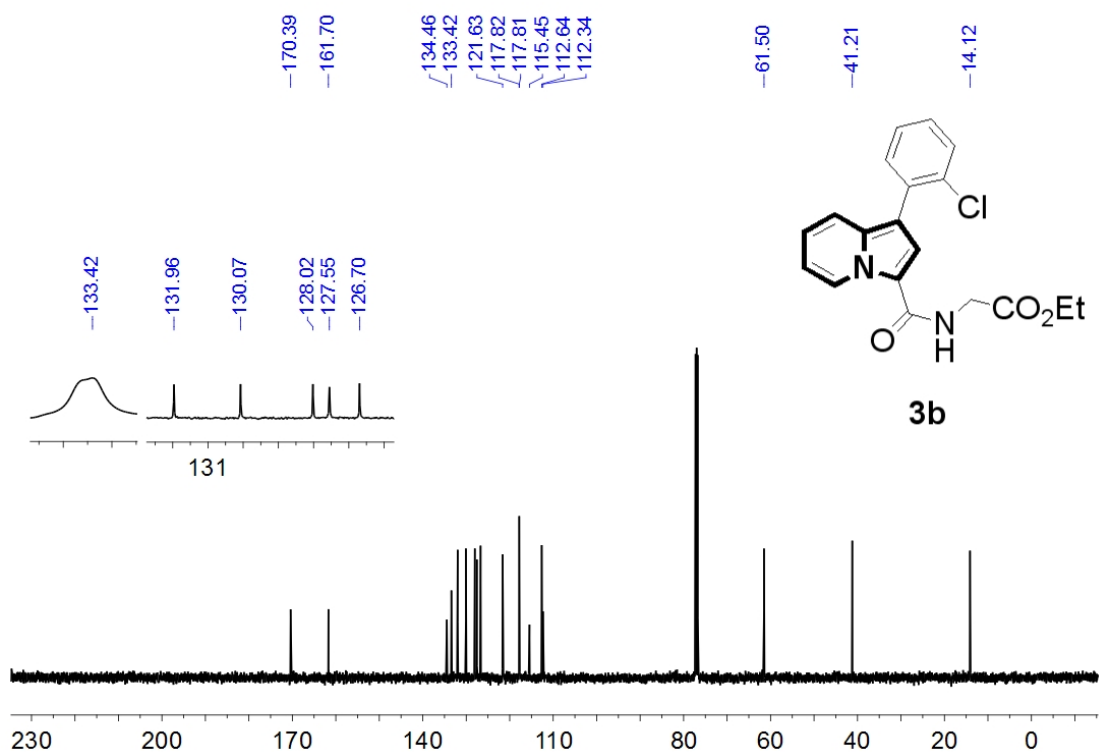
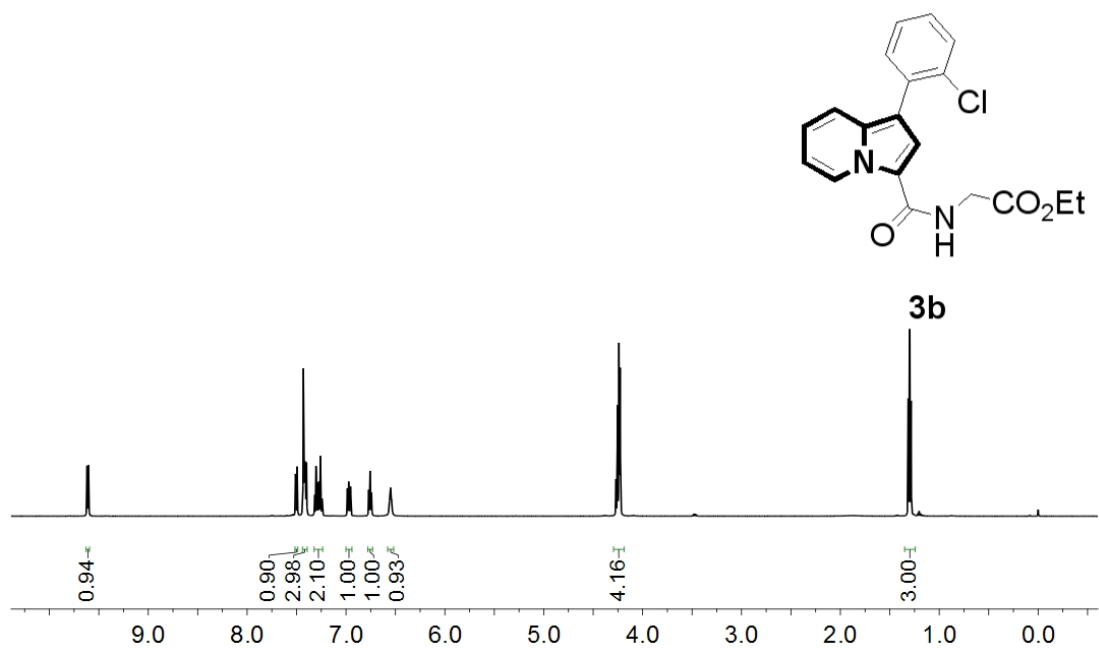
X-ray structure of **5a**

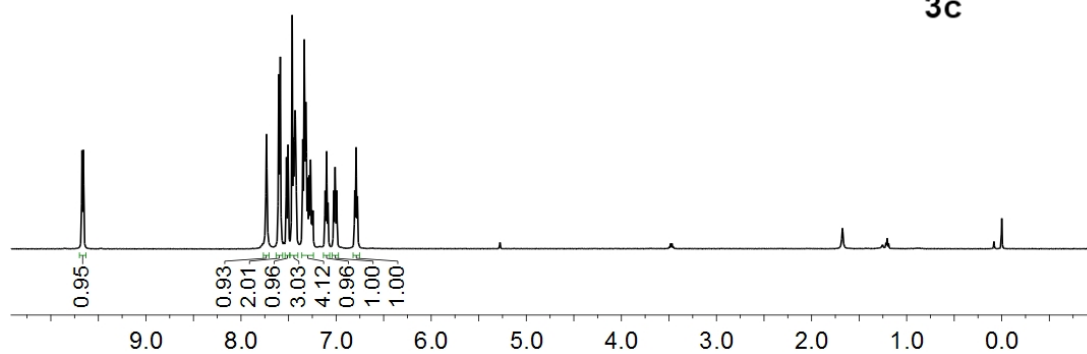
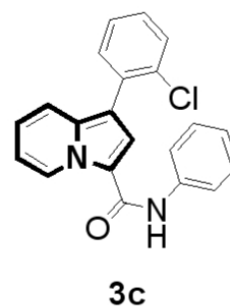
Table 2. Crystal data and structure refinement of 5a

Empirical formula	C ₁₇ H ₁₃ BrN ₂ O ₃ S
Temperature	293(2)K
Wavelength	0.71073 Å
Unit cell dimensions	a=7.1457(7) Å b=9.8623(11) Å c=11.5311(11) Å alpha=96.2120(10) deg. beta=94.4590(10) deg. gamma=97.0610(10) deg.
Volume	798.31(14) Å ³
Z	7
Calculated density	2.257 Mg/m ³
Absorption coefficient	9.291mm ⁻¹
F(000)	511
Crystal size	0.27 x 0.26 x 0.26mm
Theta range for data collection	2.10 to 25.07 deg.
Reflections collected / unique	4707 / 3906 [R(int) = 0.0161]
Data / restraints / parameters	3906 / 3 / 193
Goodness-of-fit on F ²	2.138
Final R indices [I>2sigma(I)]	R1 = 0.0921, wR2 = 0.2568
R indices (all data)	R1 = 0.1017, wR2 = 0.2716

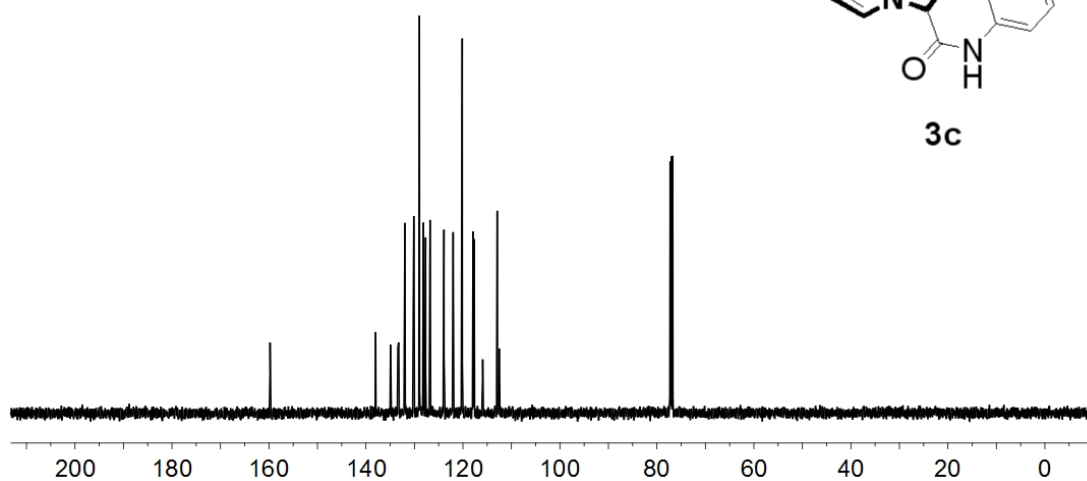
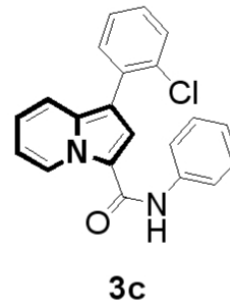
IV. NMR spectra copies

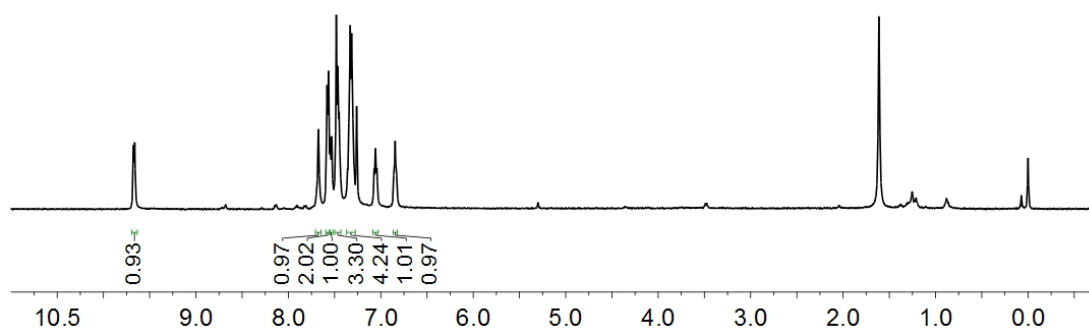
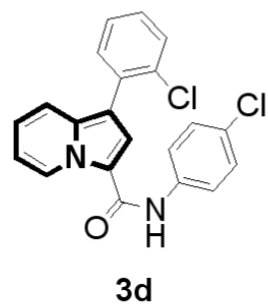






159.77
138.00
134.92
133.40
133.24
131.95
130.12
128.98
128.16
127.70
126.77
123.92
122.02
120.15
117.91
117.68
115.92
112.92
112.50





159.62
136.68
135.19
133.47
133.14
131.98
130.19
129.03
128.83
128.30
127.75
126.84
122.31
121.28
118.00
117.74
115.62
113.16
112.72

