

Supplementary Material

Efficient Solvent-Free Synthesis of Indolizines Using CuBr Catalyst from Pyridine, Acetophenone, and Electron-Deficient Alkenes

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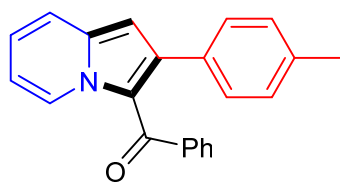
1. General remark

^1H NMR spectra were recorded at 400 MHz or 500 MHz in CDCl_3 , ^{13}C NMR spectra were recorded on 101 MHz or 126 MHz in CDCl_3 , with using TMS as internal standard. The chemical shifts (δ) were measured in ppm and with the solvents as references (For CDCl_3 , ^1H : $\delta = 7.26$ ppm, ^{13}C : $\delta = 77.0$ ppm). All compounds were further characterized by HRMS; copies of their ^1H NMR and ^{13}C NMR spectra are provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined on a microscopic apparatus without correction. Unless otherwise noted, commercially reagents and were used without further purification.

2. General procedure for the synthesis of phenyl(2-(p-tolyl)indolizin-3-yl)methanone **4a** and (1-nitro-2-(p-tolyl)indolizin-3-yl)(phenyl)methanone **4a'**

1a (0.8 mmol), **2a** (0.4 mmol), **3a** (0.2 mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (1.0 equiv) and CuBr (0.3 equiv), were heated at 130 °C for 5 h in a sealed tube. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature. The product **4a** and **4a'** was purified by column chromatography on silica gel (petroleum ether/EtOAc = 6:1).

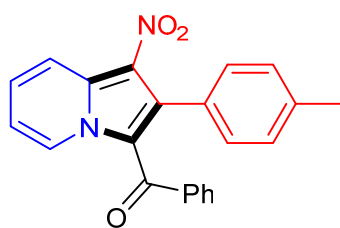
3. Compounds Characterization Data



4a

phenyl(2-(p-tolyl)indolizin-3-yl)methanone (4a) Yellow solid; mp 109-110 °C

^1H NMR (500 MHz, CDCl_3) δ 9.79 (d, $J = 7.1$ Hz, 1H), 7.53 (d, $J = 8.8$ Hz, 1H), 7.41 (dd, $J = 8.1, 1.1$ Hz, 2H), 7.15 (dd, $J = 10.9, 4.8$ Hz, 2H), 7.01 (t, $J = 7.7$ Hz, 2H), 6.96 (d, $J = 8.0$ Hz, 2H), 6.88 (td, $J = 7.0, 1.3$ Hz, 1H), 6.81 (d, $J = 7.9$ Hz, 2H), 6.56 (s, 1H), 2.20 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 186.77, 140.15, 139.80, 137.57, 136.23, 132.88, 130.38, 129.90, 129.56, 128.21, 128.14, 127.29, 124.03, 120.01, 118.25, 113.34, 103.99, 20.97. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{NO}$ ($M + \text{H}$) $^+$ 312.1388; found: 312.1385.

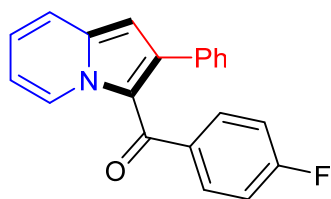


H

4a'

(1-nitro-2-(p-tolyl)indolizin-3-yl)(phenyl)methanone (4a') Yellow solid; mp 138-140 °C

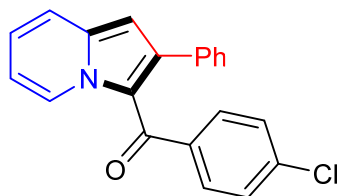
^1H NMR (500 MHz, CDCl_3) δ 9.53 – 9.40 (m, 1H), 8.65 (dt, $J = 9.1, 1.1$ Hz, 1H), 7.64 (ddd, $J = 9.0, 6.9, 1.0$ Hz, 1H), 7.38 (dd, $J = 8.2, 1.2$ Hz, 2H), 7.24 – 7.20 (m, 1H), 7.17 (td, $J = 7.0, 1.4$ Hz, 1H), 7.09 – 7.00 (m, 4H), 6.84 (d, $J = 7.8$ Hz, 2H), 2.18 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 188.49, 138.23, 137.99, 134.62, 134.16, 131.58, 130.94, 130.19, 129.21, 128.10, 128.06, 127.70, 127.62, 121.39, 119.34, 116.30, 21.09. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{17}\text{N}_2\text{O}_3$ ($M + \text{H}$) $^+$ 357.1239; found: 357.1236.



4b

(4-fluorophenyl)(2-phenylindolizin-3-yl)methanone (4b) Yellow solid; mp 106-109 °C

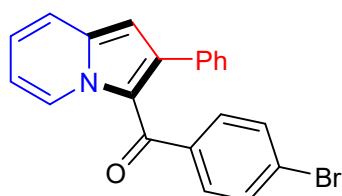
^1H NMR (500 MHz, CDCl_3) δ 9.76 (d, J = 7.2 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.42 (dd, J = 8.7, 5.5 Hz, 2H), 7.18 (ddd, J = 8.7, 6.8, 0.9 Hz, 1H), 7.10 – 7.03 (m, 5H), 6.90 (td, J = 7.1, 1.2 Hz, 1H), 6.68 (t, J = 8.7 Hz, 2H), 6.59 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 185.14, 165.10, 163.10, 139.65, 137.66, 136.36, 136.34, 135.76, 131.87, 131.80, 131.12, 130.08, 128.11, 127.66, 127.55, 126.78, 124.26, 119.84, 118.37, 114.42, 114.24, 113.59, 104.18, ^{19}F NMR (471 MHz, CDCl_3) δ -109.12. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{FNO}$ ($\text{M} + \text{H}$) $^+$ 316.1138; found: 316.1135.



4c

(4-chlorophenyl)(2-phenylindolizin-3-yl)methanone (4c) Yellow solid; mp 110-113 °C

^1H NMR (500 MHz, CDCl_3) δ 9.80 (d, J = 7.0 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.19 (dd, J = 11.2, 4.3 Hz, 1H), 7.09 – 7.02 (m, 5H), 6.98 – 6.94 (m, 2H), 6.91 (td, J = 7.1, 1.2 Hz, 1H), 6.59 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 185.16, 139.89, 138.59, 137.83, 136.65, 135.70, 130.87, 130.10, 128.23, 127.72, 127.54, 126.82, 124.52, 118.40, 113.75, 104.36. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{ClNO}$ ($\text{M} + \text{H}$) $^+$ 332.0842; found: 332.0840.

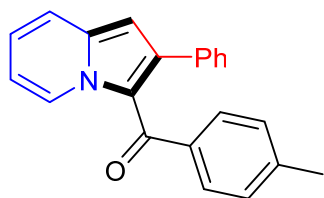


4d

(4-bromophenyl)(2-phenylindolizin-3-yl)methanone (4d) Yellow solid; mp 109-110 °C

^1H NMR (500 MHz, CDCl_3) δ 9.73 (d, J = 6.9 Hz, 1H), 7.48 (d, J = 8.8 Hz, 1H), 7.17 (d, J = 8.4 Hz,

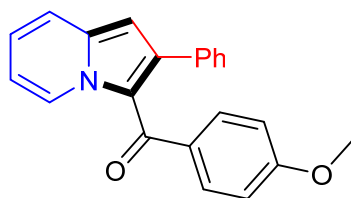
2H), 7.14 – 7.09 (m, 1H), 7.03 (dd, $J = 12.4, 6.7$ Hz, 3H), 6.97 (d, $J = 4.3$ Hz, 4H), 6.83 (td, $J = 7.0, 1.1$ Hz, 1H), 6.51 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 184.20, 138.91, 137.99, 136.82, 134.64, 129.97, 129.46, 129.06, 127.22, 126.69, 125.76, 124.13, 123.53, 118.81, 117.36, 112.74, 103.36. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{BrNO}$ ($\text{M} + \text{H}$) $^+$ 376.0337; found: 376.0339.



4e

(2-phenylindolizin-3-yl)(p-tolyl)methanone (4e) Yellow solid; mp 110-111 °C

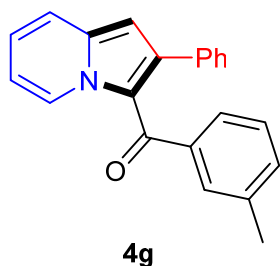
^1H NMR (400 MHz, CDCl_3) δ 9.73 (d, $J = 7.2$ Hz, 1H), 7.53 (d, $J = 8.8$ Hz, 1H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.16 – 7.11 (m, 1H), 7.05 (ddd, $J = 6.8, 5.6, 1.8$ Hz, 5H), 6.89 – 6.78 (m, 3H), 6.58 (s, 1H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 186.72, 141.08, 139.36, 137.33, 136.01, 130.08, 129.76, 128.01, 127.53, 126.34, 123.78, 120.14, 118.34, 113.30, 103.83, 21.33. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{NO}$ ($\text{M} + \text{H}$) $^+$ 312.1388; found: 312.1386.



4f

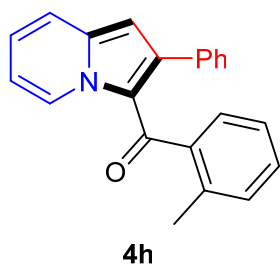
(4-methoxyphenyl)(2-phenylindolizin-3-yl)methanone (4f) Yellow solid; mp 119-120 °C

^1H NMR (500 MHz, CDCl_3) δ 9.65 (d, $J = 7.2$ Hz, 1H), 7.53 (d, $J = 8.8$ Hz, 1H), 7.43 (d, $J = 8.8$ Hz, 2H), 7.15 – 7.10 (m, 3H), 7.08 – 7.03 (m, 3H), 6.85 (td, $J = 7.0, 1.3$ Hz, 1H), 6.59 (s, 1H), 6.54 – 6.50 (m, 2H), 3.70 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 185.87, 161.83, 138.90, 137.21, 136.05, 132.61, 131.81, 130.12, 127.88, 127.67, 126.53, 123.54, 120.06, 118.38, 113.17, 112.74, 103.58, 55.28 (s). HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{NO}_2$ ($\text{M} + \text{H}$) $^+$ 328.1338; found: 328.1336.



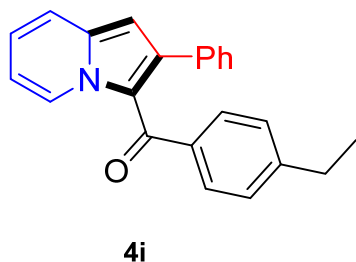
(2-phenylindolizin-3-yl)(m-tolyl)methanone (4g) Yellow solid; mp 87-88 °C

^1H NMR (400 MHz, CDCl_3) δ 9.80 (d, $J = 7.2$ Hz, 4H), 7.54 (d, $J = 8.8$ Hz, 4H), 7.29 (dd, $J = 6.1, 2.5$ Hz, 4H), 7.16 (dd, $J = 10.5, 4.9$ Hz, 8H), 7.08 (dt, $J = 6.2, 3.7$ Hz, 10H), 7.04 – 6.99 (m, 12H), 6.94 (dd, $J = 5.2, 4.4$ Hz, 9H), 6.88 (td, $J = 7.0, 1.3$ Hz, 4H), 6.58 (s, 4H), 2.06 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 186.91 (s), 139.83 (d, $J = 16.7$ Hz), 137.48, 136.86, 136.18, 131.33, 130.90, 130.68, 129.89, 128.18, 127.46, 127.32, 126.57, 124.06, 120.14, 118.34, 113.48, 104.09, 20.90. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{NO}$ ($\text{M} + \text{H}$) $^+$ 312.1388; found: 312.1391



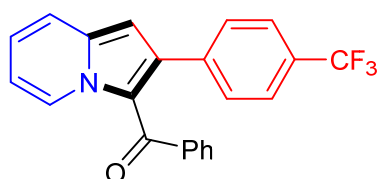
(2-phenylindolizin-3-yl)(o-tolyl)methanone (4h) Yellow solid; mp 97-98 °C

^1H NMR (500 MHz, CDCl_3) δ 10.09 (d, $J = 7.1$ Hz, 1H), 7.55 (d, $J = 8.8$ Hz, 1H), 7.25 – 7.20 (m, 1H), 7.04 – 6.93 (m, 8H), 6.87 (d, $J = 7.6$ Hz, 1H), 6.72 (t, $J = 7.4$ Hz, 1H), 6.52 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 187.63, 140.79, 140.56, 137.81, 135.86, 135.71, 130.03, 129.50, 129.16, 128.86, 127.16, 126.48, 124.76, 124.69, 120.74, 118.25, 113.89, 105.04, 19.68. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{NO}$ ($\text{M} + \text{H}$) $^+$ 312.1388; found: 312.1389



(4-ethylphenyl)(2-phenylindolizin-3-yl)methanone (4i) Yellow solid; mp 86-88 °C

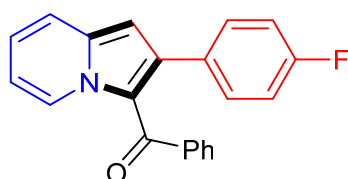
^1H NMR (500 MHz, CDCl_3) δ 9.77 (dd, $J = 7.2, 0.6$ Hz, 1H), 7.53 (d, $J = 8.9$ Hz, 1H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.14 (ddd, $J = 8.7, 6.7, 0.9$ Hz, 1H), 7.08 – 7.04 (m, 2H), 7.02 – 6.95 (m, 3H), 6.87 (td, $J = 7.1, 1.3$ Hz, 1H), 6.81 (d, $J = 8.1$ Hz, 2H), 6.58 (s, 1H), 2.47 (q, $J = 7.6$ Hz, 2H), 1.09 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 186.76, 147.37, 139.57, 137.55, 136.05, 130.07, 129.81, 128.12, 127.50, 126.87, 126.44, 123.89, 120.19, 118.35, 113.37, 103.93, 28.83, 15.53. HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{20}\text{NO}$ ($M + \text{H}$) $^+$ 326.1545; found: 326.1546



4j

phenyl(2-(4-(trifluoromethyl)phenyl)indolizin-3-yl)methanone (4j) Yellow solid; mp 62–63 °C

^1H NMR (500 MHz, CDCl_3) δ 9.83 (dd, $J = 7.2, 0.6$ Hz, 1H), 7.58 (d, $J = 8.8$ Hz, 1H), 7.36 (dd, $J = 8.2, 1.2$ Hz, 2H), 7.26 – 7.19 (m, 3H), 7.15 (ddd, $J = 5.6, 4.5, 2.2$ Hz, 3H), 7.00 (t, $J = 7.8$ Hz, 2H), 6.94 (td, $J = 7.0, 1.3$ Hz, 1H), 6.60 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 186.51, 139.93, 139.76, 138.11, 137.62, 130.85, 130.20, 129.42, 128.24, 127.50, 124.54, (124.361, 124.33, 124.30, 124.27 (q, $J = 3.9$ Hz), 120.12, 118.51, 114.05, 104.22, ^{19}F NMR (471 MHz, CDCl_3) δ -62.77 (s). HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{15}\text{F}_3\text{NO}$ ($M + \text{H}$) $^+$ 366.1106; found: 366.1104

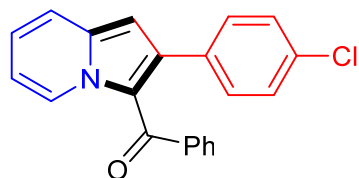


4k

(2-(4-fluorophenyl)indolizin-3-yl)(phenyl)methanone (4k) Yellow solid; mp 72–74 °C

^1H NMR (400 MHz, CDCl_3) δ 9.73 (dd, $J = 7.2, 0.7$ Hz, 1H), 7.47 (d, $J = 8.8$ Hz, 1H), 7.35 – 7.29 (m, 2H), 7.14 – 7.08 (m, 2H), 6.99 – 6.93 (m, 4H), 6.83 (td, $J = 7.0, 1.4$ Hz, 1H), 6.65 – 6.59 (m, 2H), 6.47 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 186.61, 162.95, 160.50, 140.04, 138.59, 137.58, 131.46, 130.76,

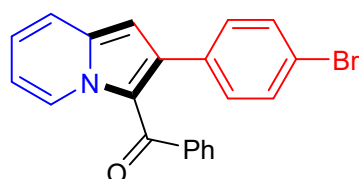
129.54, 128.19, 127.46, 124.34, 118.33, 114.60, 114.39, 113.67, 104.11, ^{19}F NMR (376 MHz, CDCl_3) δ -115.75 (s). HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{FNO}$ ($\text{M} + \text{H}$) $^+$ 316.1138; found: 316.1134.



4l

(2-(4-chlorophenyl)indolizin-3-yl)(phenyl)methanone (4l) Yellow solid; mp 175-176 °C

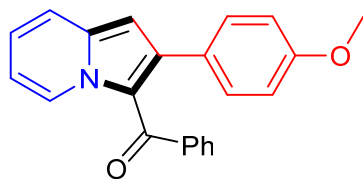
^1H NMR (500 MHz, CDCl_3) δ 9.80 (d, J = 7.1 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.39 (d, J = 7.1 Hz, 2H), 7.20 (dt, J = 15.9, 7.7 Hz, 2H), 7.07 – 6.97 (m, 6H), 6.94 – 6.87 (m, 1H), 6.55 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 186.57, 140.02, 138.33, 137.58, 134.48, 132.71, 131.16, 130.79, 129.53, 128.18, 127.68, 127.52, 124.34, 120.00, 118.38, 113.75, 104.05, HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{ClNO}$ ($\text{M} + \text{H}$) $^+$ 332.0842; found: 332.0840.



4m

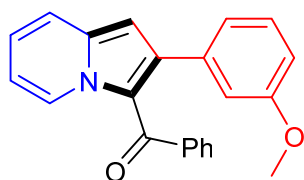
(2-(4-bromophenyl)indolizin-3-yl)(phenyl)methanone (4m) Yellow solid; mp 149-150 °C

^1H NMR (400 MHz, CDCl_3) δ 9.80 (d, J = 7.2 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.44 – 7.33 (m, 2H), 7.23 – 7.16 (m, 2H), 7.15 – 7.08 (m, 2H), 7.05 (t, J = 7.7 Hz, 2H), 6.94 – 6.89 (m, 3H), 6.55 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 186.56, 139.99, 138.33, 137.59, 134.94, 131.48, 130.80, 130.63, 129.53, 128.19, 127.55, 124.38, 120.91, 118.40, 113.79, 104.01. HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{BrNO}$ ($\text{M} + \text{H}$) $^+$ 376.0337; found: 376.0334.



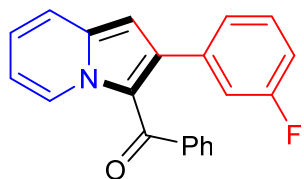
4n

(2-(4-methoxyphenyl)indolizin-3-yl)(phenyl)methanone (4n) Yellow solid; mp 139-140 °C
¹H NMR (400 MHz, CDCl₃) δ 10.06 (d, *J* = 7.1 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.45 – 7.38 (m, 2H), 7.31 – 7.24 (m, 4H), 7.13 (td, *J* = 7.0, 1.3 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 3H), 3.95 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 186.75, 158.44, 140.14, 139.51, 137.64, 132.31, 131.14, 130.57, 129.60, 129.30, 128.36, 128.18, 127.39, 124.14, 120.01, 118.22, 113.34, 113.18, 103.89, 55.25. HRMS (ESI): *m/z* calcd for C₂₂H₁₈NO₂ (*M* + H)⁺ 328.1338; found: 328.1339.



4o

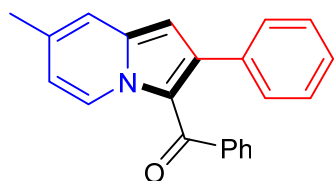
(2-(3-methoxyphenyl)indolizin-3-yl)(phenyl)methanone (4o) Yellow solid; mp 135-138 °C
¹H NMR (500 MHz, CDCl₃) δ 9.81 (d, *J* = 7.1 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.16 (dt, *J* = 8.4, 3.9 Hz, 2H), 7.04 (t, *J* = 7.7 Hz, 2H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.88 (tt, *J* = 9.6, 4.8 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.61 – 6.53 (m, 3H), 3.59 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 186.68, 158.73, 140.28, 139.63, 137.57, 137.29, 130.74, 129.49, 128.68, 128.19, 127.40, 124.26, 122.57, 120.01, 118.40, 115.37, 113.64, 113.04, 104.24, 55.08. HRMS (ESI): *m/z* calcd for C₂₂H₁₈NO₂ (*M* + H)⁺ 328.1338; found: 328.1341



4p

(2-(3-fluorophenyl)indolizin-3-yl)(phenyl)methanone (4p) Yellow solid; mp 124-126 °C

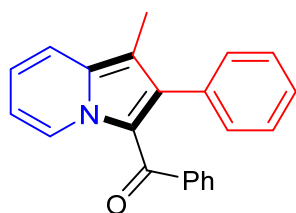
^1H NMR (500 MHz, CDCl_3) δ 9.80 (d, $J = 7.2$ Hz, 1H), 7.55 (d, $J = 8.8$ Hz, 1H), 7.42 (d, $J = 7.2$ Hz, 2H), 7.19 (t, $J = 7.5$ Hz, 2H), 7.05 (t, $J = 7.6$ Hz, 2H), 6.93 (ddd, $J = 21.7, 10.5, 4.4$ Hz, 2H), 6.85 – 6.77 (m, 2H), 6.71 (td, $J = 8.4, 2.2$ Hz, 1H), 6.57 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 186.61, 163.03, 161.08, 140.14, 138.26, 138.25, 138.22, 137.50, 130.85, 129.43, 129.43, 129.02, 128.16, 127.48, 125.93, 124.35, 119.98, 118.46, 116.87, 116.69, 113.85, 113.53, 113.36, 104.14. ^{19}F NMR (376 MHz, CDCl_3) δ -114.56 (s). HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{15}\text{FNO}$ ($\text{M} + \text{H}$) $^+$ 316.1138; found: 316.1137.



4q

(7-methyl-2-phenylindolizin-3-yl)(phenyl)methanone (4q) Yellow solid; mp 106-108 °C

^1H NMR (500 MHz, CDCl_3) δ 9.75 (d, $J = 7.2$ Hz, 1H), 7.39 (d, $J = 7.2$ Hz, 2H), 7.31 (s, 1H), 7.12 (t, $J = 7.4$ Hz, 1H), 7.06 (dd, $J = 6.5, 2.9$ Hz, 2H), 6.99 (dd, $J = 8.7, 4.8$ Hz, 5H), 6.75 (dd, $J = 7.2, 1.5$ Hz, 1H), 6.45 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 186.21 (s), 140.35, 140.29, 138.19, 136.12, 135.33, 130.37, 130.04, 129.53, 127.82, 127.47, 127.27, 126.50, 119.65, 116.86, 116.15, 103.28, 21.26. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{NO}$ ($\text{M} + \text{H}$) $^+$ 312.1388; found: 312.1384

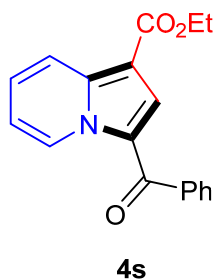


4r

(1-methyl-2-phenylindolizin-3-yl)(phenyl)methanone (4r) Yellow solid; mp 132-134 °C

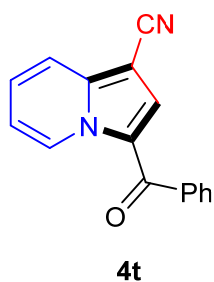
^1H NMR (500 MHz, CDCl_3) δ 9.87 (d, $J = 7.1$ Hz, 1H), 7.52 (d, $J = 8.8$ Hz, 1H), 7.32 (d, $J = 7.0$ Hz, 2H), 7.17 (ddd, $J = 8.7, 6.8, 0.8$ Hz, 1H), 7.08 (t, $J = 7.4$ Hz, 1H), 7.04 – 6.92 (m, 7H), 6.88 (td, $J = 7.0, 1.3$ Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 186.30, 140.42, 137.79, 136.58, 134.93, 131.00, 130.07, 129.22, 128.29, 127.36, 127.20, 126.42, 123.59, 120.27, 116.79, 113.62, 110.72, 9.20.

HRMS (ESI): m/z calcd for $C_{22}H_{18}NO$ ($M + H$)⁺ 312.1388; found: 312.1391



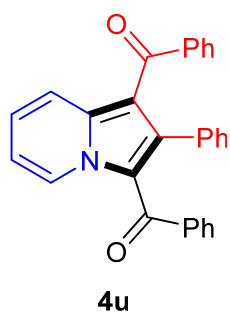
ethyl 3-benzoylindolizine-1-carboxylate (4s) Yellow solid; mp 75-76 °C

¹H NMR (500 MHz, CDCl₃) δ 9.97 (d, J = 7.0 Hz, 1H), 8.40 (d, J = 8.9 Hz, 1H), 7.82 (dd, J = 6.3, 2.0 Hz, 3H), 7.60 – 7.55 (m, 1H), 7.52 (t, J = 7.4 Hz, 2H), 7.45 (ddd, J = 8.8, 6.9, 1.0 Hz, 1H), 7.09 (td, J = 7.0, 1.2 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 185.59, 164.08, 139.93, 139.90, 131.47, 129.02, 128.97, 128.40, 127.69, 122.54, 119.52, 115.29, 106.31, 60.11, 14.55. HRMS (ESI): m/z calcd for $C_{18}H_{16}NO_3$ ($M + H$)⁺ 294.1130; found: 294.1132



3-benzoylindolizine-1-carbonitrile (4t) Yellow solid; mp 113-114 °C

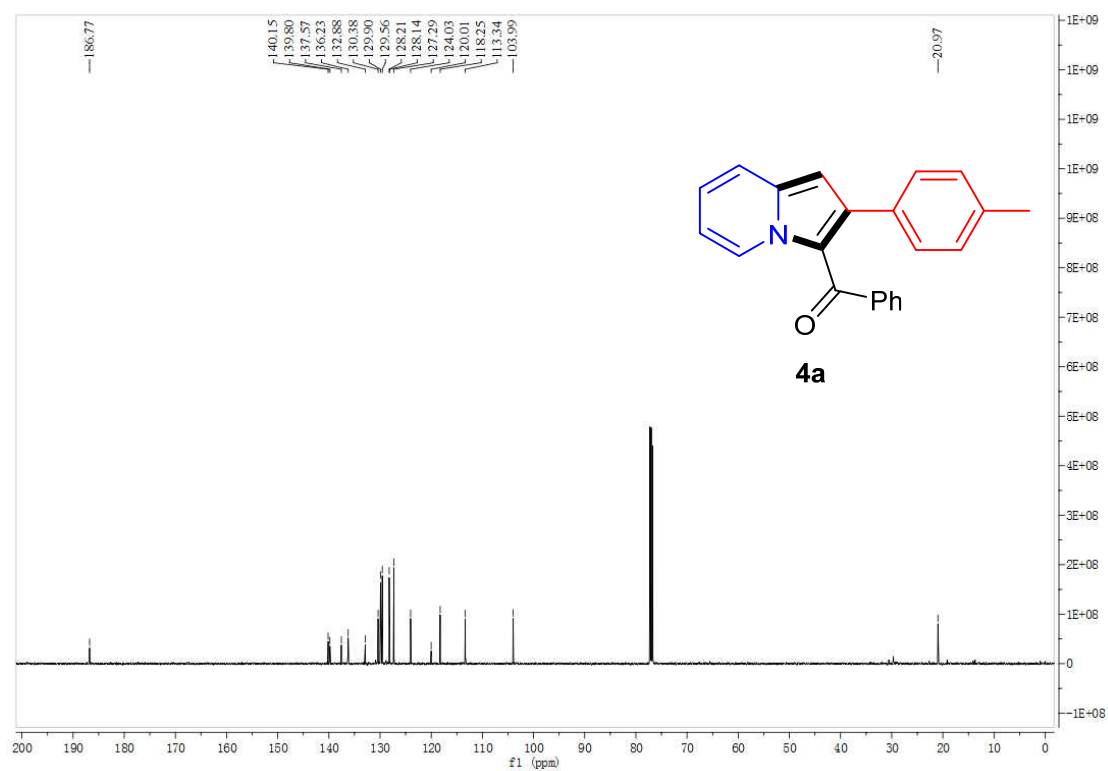
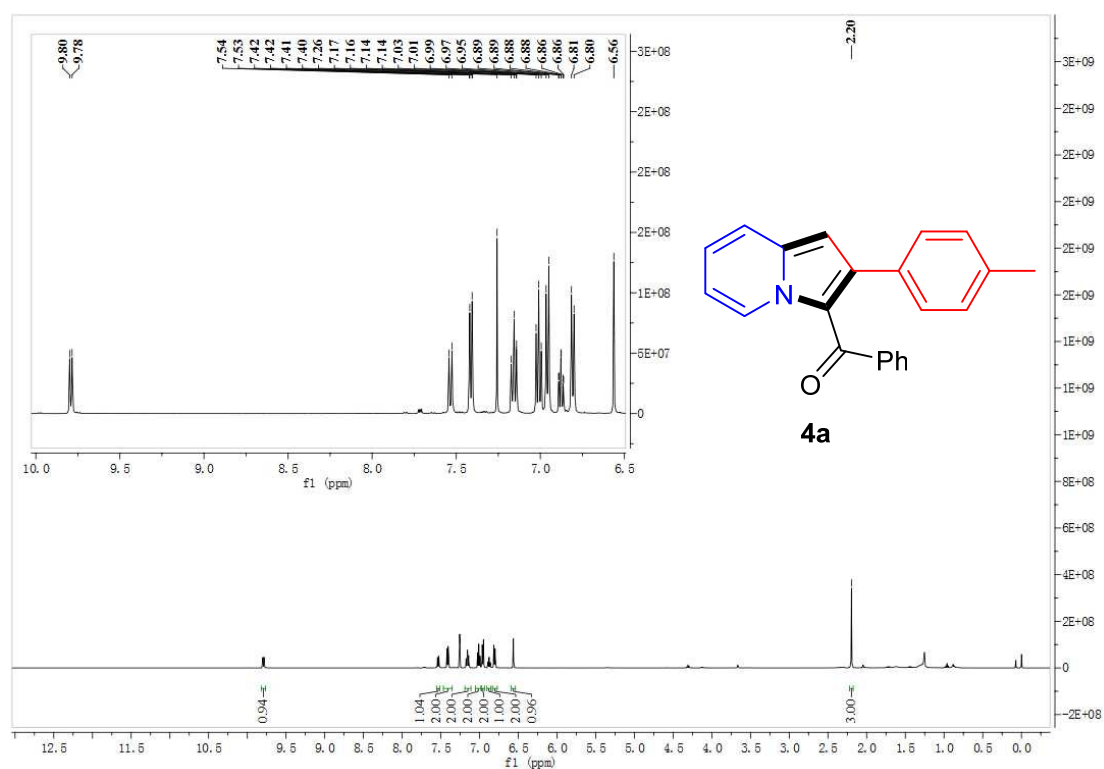
¹H NMR (500 MHz, CDCl₃) δ 9.87 (d, J = 7.1 Hz, 1H), 7.73 (dd, J = 19.6, 8.2 Hz, 3H), 7.57 – 7.49 (m, 2H), 7.48 – 7.38 (m, 3H), 7.07 (t, J = 7.0 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 185.16, 141.25, 139.22, 132.00, 129.52, 129.27, 128.92, 128.87, 128.56, 127.88, 127.76, 122.93, 117.52, 115.89, 115.13, 84.85. HRMS (ESI): m/z calcd for $C_{16}H_{11}N_2O$ ($M + H$)⁺ 247.0871; found: 247.0874.

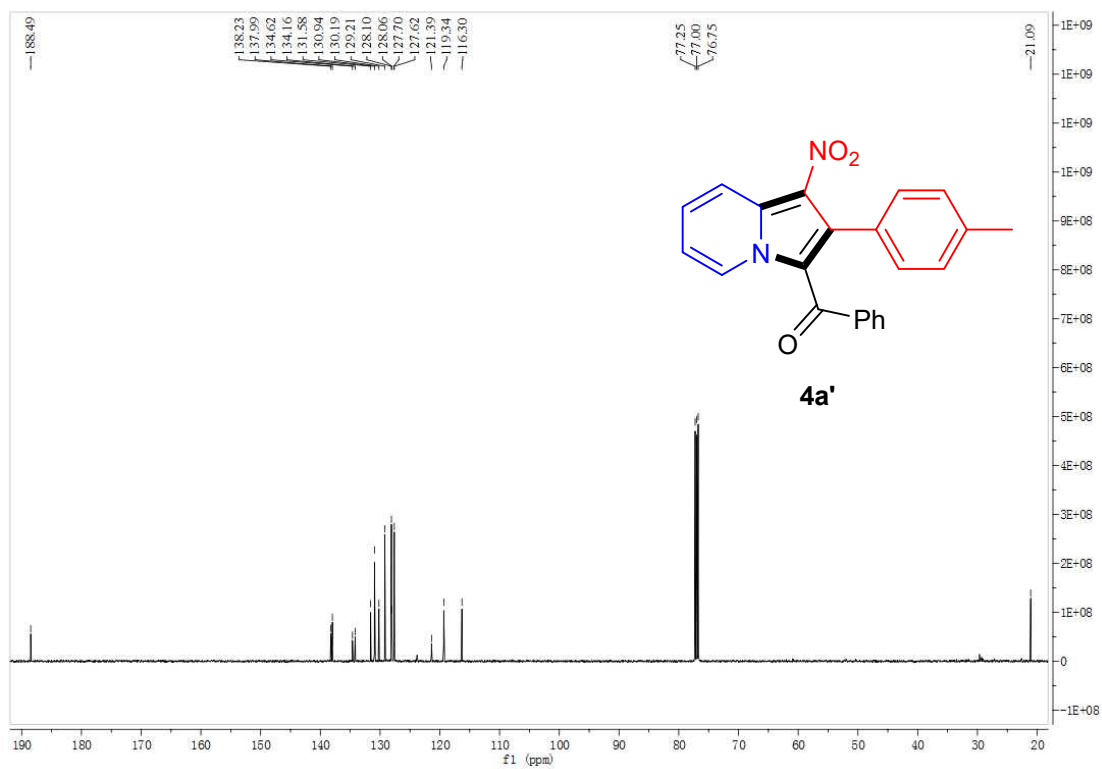
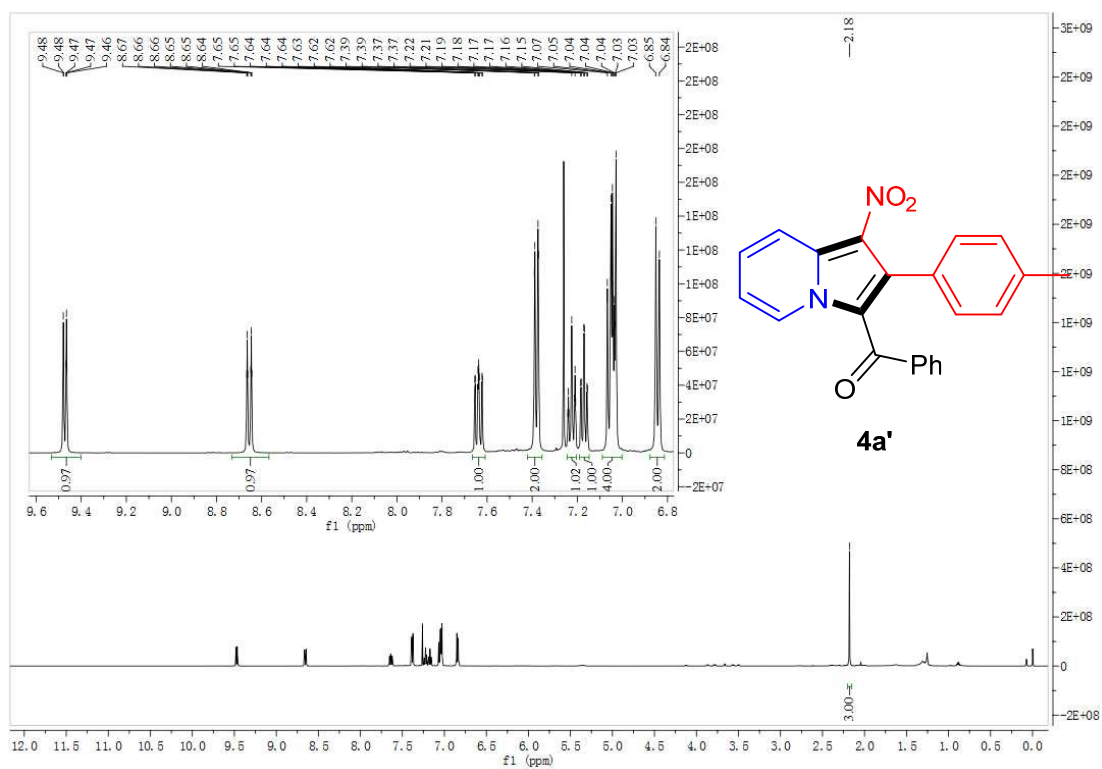


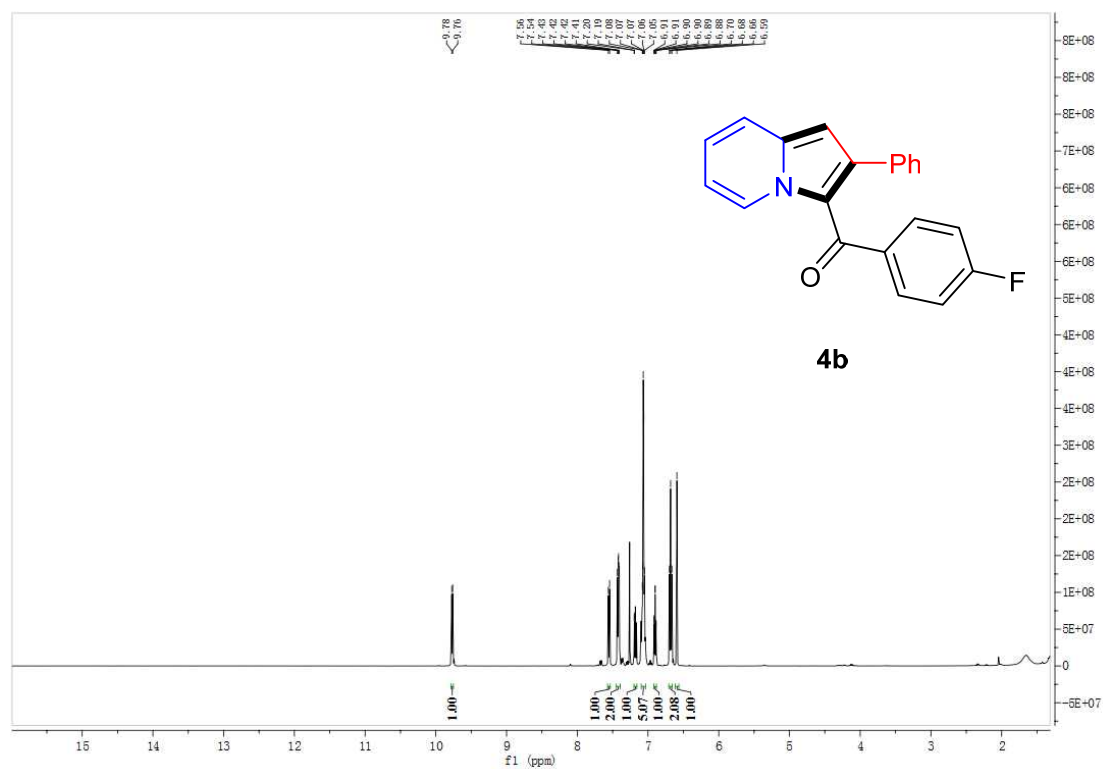
(2-phenylindolizine-1,3-diyl)bis(phenylmethanone): Yellow solid; mp 184-186 °C.

^1H NMR (500 MHz, CDCl_3) δ 9.68 (d, $J = 7.1$ Hz, 1H), 8.19 (d, $J = 8.9$ Hz, 1H), 7.48 – 7.31 (m, 5H), 7.17 (t, $J = 7.4$ Hz, 1H), 7.13 – 7.05 (m, 2H), 7.03 (t, $J = 7.7$ Hz, 2H), 6.96 (t, $J = 7.7$ Hz, 2H), 6.87 – 6.81 (m, 2H), 6.75 – 6.66 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 192.92 (s), 188.44 (s), 139.14, 133.32, 131.64, 131.46, 131.23, 129.43, 129.41, 127.75, 127.53, 127.44, 127.24, 127.06, 126.91, 121.13, 119.20, 115.30, 114.08. HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{20}\text{NO}_2$ ($\text{M} + \text{H}$) $^+$ 402.1489; found: 402.1483

4. ^1H and ^{13}C NMR spectra of the products







¹⁹F NMR (471 MHz, CDCl₃) δ -109.12 (s).

