Supporting information for

“Visible-light photoredox catalysis: direct synthesis of fused β-carbolines through oxidation/[3+2] cycloaddition/oxidative aromatization reaction cascade in batch and flow microreactors”

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Materials and methods

All the reagents, chemicals, solvents were purchased from commercial suppliers and used without further any purification. The 11 W white light LED bulb commonly used for domestic lighting was used for our study. The syringe pumps, visible light transparent capillaries (PFA capillaries, id = 500µm), and fittings were obtained from commercial suppliers. The reactions were monitored using thin layer chromatography (TLC) visualised under UV irradiation and iodine. All the new compounds were characterized by their 1H, 13C NMR, IR, MS/HRMS spectra obtained from the central instrumental facility of the institute.

Synthetic procedures

General experimental procedures for the synthesis of N-alkylated of tetrahydro-β-carbolines 1a-f: In a 25 mL round bottom flask, tryptoline (86 mg, 0.5 mmol), α-halo carbonyls (0.5 mmol), Et₃N (50 mg, 0.5 mmol) and CH₂Cl₂ (5 mL) was taken and the reaction mixture was stirred at ambient temperature for 2 h. Next the reaction mixture was diluted with CH₂Cl₂ (15 mL) and washed with water. The organic layer was dried over anhydrous Na₂SO₄ and evaporated to yield a crude product which was purified by silica-gel column chromatography using ethyl acetate/hexane in increasing polarity to yield compounds 1a-f.

General experimental procedures for the visible light photoredox catalyzed coupling of N-alkylated of tetrahydro-β-carbolines 1a-f with dipolarophiles 2a-g under batch conditions: In a 25 mL round bottom flask, tetrahydro-β-carbolines 1a-f (0.1 mmol), dipolarophiles 2a-g (0.1 mmol), [Ru(bpy)₃Cl₂]·6H₂O (0.5 mol%) and MeCN (5 mL) was taken. The reaction vessel was kept at a distance of 10 cm (approx.) from a visible light source (11W white LED bulb) and the reaction mixture was stirred in open air condition until the reaction was complete (TLC). Next the reaction mixture was concentrated to give a crude product which was purified
by silica-gel column chromatography using ethyl acetate/hexane in increasing polarity to yield compounds 3a-n.

**General experimental procedures for the visible light photoredox catalyzed coupling of N-alkylated of tetrahydro-β-carbolines 1a with dipolarophiles 2a in flow microreactors:**

A solution of tetrahydro-β-carboline 1a (0.2 mmol) and dipolarophile 2a (0.2 mmol) in MeCN (5 mL) was kept in one syringe and the solutions of photocatalyst [Ru(bpy)₃Cl₂]·6H₂O (0.001 mmol in 5 mL MeCN) and t-BuOOH (2 mmol in 2 mL MeCN) were taken in two separate syringes. All the three solutions were pumped via two syringe pumps and mixed on an X-junction and flown through the capillary microreactor wrapped over a visible light source (11W white LED bulb). Under stable conditions, exactly 6 mL of the reaction mixture was collected, concentrated to yield a crude product which was purified by silica-gel column chromatography using ethyl acetate/hexane in increasing polarity to yield compounds 3a.

**Characterization data for the synthesized compounds:**

**Methyl 2-(1,3,4,9-tetrahydro-2H-pyrido[3,4-b]indol-2-yl)acetate 1a:**

From 0.5 mmol of tryptoline, 97 mg (80%) of 1a was obtained as a pale yellow solid. Mp. 140-143 °C (Lit.¹ 141-144 °C). Spectral data was found in accordance with literature.¹

**Ethyl 2-(1,3,4,9-tetrahydro-2H-pyrido[3,4-b]indol-2-yl)acetate 1b:**

From 1.0 mmol of tryptoline, 198 mg (77%) of 1b was obtained as a pale yellow solid. Mp. 140-142 °C. Rf = 0.74 (EtOAc/Hexane = 1:1). IR (KBr, cm⁻¹): 3066, 2899, 1735, 1451, 1414, 1297. ¹H NMR (500 MHz, CDCl₃) δ 7.94 (s, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 7.9 Hz, 1H), 7.17 – 7.02 (m, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.92 (s, 2H), 3.50 (s, 2H), 3.05 (t, J = 5.8 Hz, 2H), 2.84 (t, J = 5.7 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.81, 136.13, 131.40, 127.19, 121.32, 119.28, 117.94, 110.93, 107.81, 60.77, 58.05, 50.69, 49.58, 21.01, 14.34. HRMS calcd. for C₂₅H₂₇N₂O₂ (M+H): 259.14465; found: 259.14375.

**Benzyl 2-(1,3,4,9-tetrahydro-2H-pyrido[3,4-b]indol-2-yl)acetate 1c:**
From 1.0 mmol of tryptoline, 250 mg (78%) of 1c was obtained as a pale yellow solid. Mp. 168-170 °C. Rf = 0.75 (EtOAc/Hexane = 1:1). IR (KBr, cm\(^{-1}\)): 3061, 2898, 1736, 1451, 1346, 1297. \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.72 (s, 1H), 7.46 (d, \(J = 7.7\) Hz, 1H), 7.40 – 7.30 (m, 5H), 7.28 (dd, \(J = 7.9, 2.7\) Hz, 1H), 7.12 (dd, \(J = 11.0, 4.0\) Hz, 1H), 7.08 (td, \(J = 7.5, 1.1\) Hz, 1H), 5.20 (s, 2H), 3.88 (s, 2H), 3.55 (s, 2H), 3.03 (t, \(J = 5.7\) Hz, 2H), 2.83 (t, \(J = 5.7\) Hz, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ 170.58, 136.01, 135.66, 131.13, 128.66, 128.45, 127.20, 121.44, 119.38, 117.99, 110.75, 108.07, 66.50, 58.00, 50.73, 49.65, 20.93. HRMS calcd for C\(_{20}\)H\(_{21}\)N\(_2\)O\(_2\) (M+H): 321.16030; found: 321.16007.

4-Nitrobenzyl 2-(1,3,4,9-tetrahydro-2\(H\)-pyrido[3,4-\(b\)]indol-2-yl)acetate 1d:

From 0.5 mmol of tryptoline, 135 mg (74%) of 1d was obtained as a yellow solid; Mp. 200-202 °C; Rf = 0.77 (EtOAc/Hexane = 1:1); IR (KBr, cm\(^{-1}\)): 2848, 1736, 1519, 1347, 1165. \(^1\)H NMR (300 MHz, CDCl\(_3\)+DMSO) δ 10.35 (s, 1H), 8.22 (d, \(J = 8.6\) Hz, 2H), 7.61 (d, \(J = 8.6\) Hz, 2H), 7.37 (d, \(J = 7.5\) Hz, 1H), 7.28 (d, \(J = 7.8\) Hz, 1H), 7.05-6.93 (m, 2H), 5.50 (s, 2H), 3.87 (s, 2H), 3.61 (s, 2H), 3.00 (t, \(J = 5.5\) Hz, 2H), 2.80 (t, \(J = 5.5\) Hz, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)+DMSO-d6) δ 175.08, 152.31, 148.69, 141.08, 137.23, 133.58, 131.84, 128.58, 125.45, 123.38, 122.40, 115.97, 111.29, 69.45, 62.87, 55.47, 54.51, 26.26. HRMS calcd for C\(_{20}\)H\(_{20}\)N\(_3\)O\(_4\) (M+H): 366.14538; found: 366.14384.

1-Phenyl-2-(1,3,4,9-tetrahydro-2\(H\)-pyrido[3,4-\(b\)]indol-2-yl)ethan-1-one 1e:

From 0.5 mmol of tryptoline, 109 mg (75%) of 1e was obtained as a yellow solid. Mp. 75-77 °C (Lit.\(^2\) 78 °C). Spectral data was found in accordance with literature.\(^2\)

1-(4-chlorophenyl)-2-(1,3,4,9-tetrahydro-2\(H\)-pyrido[3,4-\(b\)]indol-2-yl)ethan-1-one 1f:
From 0.5 mmol of tryptoline, 125 mg (77%) of 1f was obtained as a light brown solid. Mp. 168-170\(^\circ\)C; R\(_f\) = 0.40 (EtOAc/Hexane = 1:1). IR (KBr, cm\(^{-1}\)): 3056, 2851, 1692, 1586, 1450, 1204. \(^1\)H NMR (300 MHz, CDCl\(_3\)+DMSO) \(\delta\) 10.55 (s, 1H), 8.05 (d, \(J = 7.6\) Hz, 2H), 7.51 (dd, \(J = 8.5, 1.8\) Hz, 2H), 7.35 (d, \(J = 7.5\) Hz, 1H), 7.26 (d, \(J = 7.7\) Hz, 1H), 7.03-6.91 (m, 2H), 4.09 (s, 2H), 3.81 (s, 2H), 2.96 (t, \(J = 5.6\) Hz, 3H), 2.76 (t, \(J = 5.1\) Hz, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)+DMSO) \(\delta\) 194.18, 136.79, 134.19, 132.53, 130.24, 129.26, 128.23, 126.85, 126.70, 124.95, 118.61, 116.53, 115.53, 109.10, 104.46, 61.51, 49.08, 48.21, 19.18. HRMS calcd. for C\(_{19}\)H\(_{18}\)ClN\(_2\)O (M+H): 325.11077; found: 325.11002.

Methyl 1,4-dioxo-1,7,8,13-tetrahydro-4\(H\)-benzo[1,2]indolizino[8,7-\(b\)]indole-5-carboxylate 3a:

Following the batch synthesis, on 0.1 mmol scale reaction, 24 mg (69%) of 3a was obtained as a blue solid. Mp. 190-192\(^\circ\)C. R\(_f\) = 0.79 (EtOAc/Hexane = 2:3). IR (KBr, cm\(^{-1}\)): 3194, 2924, 2853, 1729, 1637, 1517, 1466, 1282, 1259. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 11.03 (s, 1H), 7.60 (d, \(J = 8.0\) Hz, 1H), 7.34-7.30 (m, 1H), 7.18 (t, \(J = 7.5\) Hz, 1H), 6.81 (d, \(J = 10.3\) Hz, 1H), 4.58 (t, \(J = 7.4\) Hz, 2H), 4.04 (s, 3H), 3.31 (t, \(J = 7.4\) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 182.17, 180.23, 161.11, 140.68, 138.74, 136.69, 136.55, 131.77, 125.94, 125.54, 124.70, 121.22, 120.60, 119.18, 114.44, 112.46, 111.49, 52.93, 44.59, 20.54. HRMS calcd. for C\(_{20}\)H\(_{15}\)N\(_2\)O\(_4\) (M+H): 347.10318; found: 347.10208.

Methyl 9,14-dioxo-5,9,14,15-tetrahydro-6\(H\)-naphtho[2',3':1,2]indolizino[8,7-\(b\)]indole-8-carboxylate 3b:

Following the batch synthesis, on 0.1 mmol scale reaction, 27 mg (68%) of 3b was obtained as a brown solid. Mp. 196-198\(^\circ\)C. R\(_f\) = 0.74 (EtOAc/Hexane = 2:3). IR (KBr, cm\(^{-1}\)): 3299, 2924, 2853, 1729, 1637, 1517, 1466, 1282, 1259. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 11.32 (s, 1H), 8.34–8.29 (m, 1H), 8.27–8.22 (m, 1H), 7.79–7.70 (m, 2H), 7.60 (d, \(J = 8.0\) Hz, 1H), 7.53 (d, \(J = 8.3\) Hz, 1H), 7.34-7.30 (m, 1H), 7.18 (t, \(J = 7.5\) Hz, 1H), 6.81 (d, \(J = 10.3\) Hz, 1H), 6.76 (d, \(J = 10.3\) Hz, 1H), 4.58 (t, \(J = 7.4\) Hz, 2H), 4.04 (s, 3H), 3.31 (t, \(J = 7.4\) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 180.53, 178.20, 161.11, 140.68, 138.74, 136.69, 136.55, 131.77, 125.94, 125.54, 124.70, 121.22, 120.60, 119.18, 114.44, 112.46, 111.49, 52.93, 44.59, 20.54. HRMS calcd. for C\(_{24}\)H\(_{17}\)N\(_2\)O\(_4\) (M+H): 397.11883; found: 397.11756.
Ethyl 1,4-dioxo-1,7,8,13-tetrahydro-4H-benzo[1,2]indolizino[8,7-b]indole-5-carboxylate 3c:

Following the batch synthesis, on 0.1 mmol scale reaction, 25 mg (69%) of 3c was obtained as a brown solid. Mp. 210-212 °C. Rf = 0.70 (EtOAc/Hexane = 2:3). IR (KBr, cm⁻¹): 3448, 2921, 1707, 1654, 1648, 1578, 1476, 1419, 1281. ¹H NMR (500 MHz, CDCl₃) δ 11.03 (s, 1H), 7.59 (dd, J = 8.0, 0.8 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.32 (ddd, J = 8.2, 7.0, 1.1 Hz, 1H), 7.18 (ddd, J = 7.9, 7.1, 0.9 Hz, 1H), 6.80 (d, J = 10.3 Hz, 1H), 6.75 (d, J = 10.3 Hz, 1H), 4.57 (t, J = 7.4 Hz, 2H), 4.51 (q, J = 7.1 Hz, 2H), 3.31 (t, J = 7.4 Hz, 2H), 1.49 (t, J = 7.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 179.77, 178.51, 160.61, 145.03, 139.17, 136.79, 132.14, 126.23, 125.42, 124.53, 124.15, 120.56, 120.45, 119.02, 114.17, 112.63, 111.40, 62.32, 44.50, 20.44, 14.00. HRMS calcd for C₂₁H₁₇N₂O₄ (M+H): 361.11883; found: 361.11702.

Ethyl 3-(4-(tert-butyl)phenyl)-1,4-dioxo-1,7,8,13-tetrahydro-4H-benzo[1,2]indolizino[8,7-b]indole-5-carboxylate 3d:

Following the batch synthesis, on 0.1 mmol scale reaction, 14 mg (28%) of 3d was obtained as a brown solid. Mp. 210-212 °C. Rf = 0.84 (EtOAc/Hexane = 2:3). IR (KBr, cm⁻¹): 3452, 2924, 1711, 1658, 1641, 1599, 1485, 1263. ¹H NMR (500 MHz, CDCl₃) δ 11.05 (s, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.55 – 7.45 (m, 5H), 7.31 (t, J = 7.3 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 6.91 (s, 1H), 4.56-4.49 (m, 4H), 3.32 (t, J = 7.4 Hz, 2H), 1.48 (t, J = 7.2 Hz, 3H), 1.36 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 182.25, 179.66, 161.00, 153.03, 150.14, 136.72, 135.61, 131.26, 130.75, 129.28, 129.11, 127.27, 125.66, 125.39, 124.94, 124.53, 121.68, 120.53, 119.11, 114.81, 112.47, 111.05, 62.44, 44.54, 34.82, 31.24, 20.64, 14.04. HRMS calcd. for C₃₁H₂₉N₂O₄ (M+H): 493.21273; found: 493.21180.

Ethyl 2-(4-(tert-butyl)phenyl)-1,4-dioxo-1,7,8,13-tetrahydro-4H-benzo[1,2]indolizino[8,7-b]indole-5-carboxylate 3d’:

Following the batch synthesis, on 0.1 mmol scale reaction, 15 mg (30%) of 3d’ was obtained as a brown solid. Mp. 213-214 °C. Rf = 0.82 (EtOAc/Hexane = 2:3). IR (KBr, cm⁻¹): 3439, 2924, 1709,
1654, 1642, 1618, 1577, 1236. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 11.18 (s, 1H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.52 (s, 4H), 7.47 (d, $J = 8.3$ Hz, 1H), 7.33 – 7.27 (m, 1H), 7.20 – 7.15 (m, 1H), 6.83 (s, 1H), 4.59 (t, $J = 7.4$ Hz, 2H), 4.53 (q, $J = 7.1$ Hz, 2H), 3.32 (t, $J = 7.4$ Hz, 2H), 1.51 (t, $J = 7.2$ Hz, 3H), 1.38 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 181.83, 180.34, 160.83, 152.96, 148.34, 137.67, 136.64, 132.31, 131.01, 129.11, 125.94, 125.57, 125.47, 124.61, 121.70, 120.53, 119.14, 115.14, 112.42, 111.54, 62.37, 44.62, 34.84, 31.26, 20.59, 14.01.

HRMS calcd. for C$_{31}$H$_{29}$N$_2$O$_4$ (M+H): 493.21273; found: 493.21152.

**Ethyl 2-methyl-1,3-dioxo-1,2,3,6,7,12-hexahydropyrrolo[3',4':1,2]indolizino[8,7-b]indole-4-carboxylate 3e:**

Following the batch synthesis, on 0.1 mmol scale reaction, 22 mg (61%) of 3e was obtained as a yellow solid. Mp. 196-198 °C. Rf = 0.72 (EtOAc/Hexane = 2:3). IR (KBr, cm$^{-1}$): 3411, 2923, 1753, 1693, 1643, 1425, 1270. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.02 (s, 1H), 7.59 (d, $J = 7.8$ Hz, 1H), 7.48 (d, $J = 8.2$ Hz, 1H), 7.38 – 7.28 (m, 1H), 7.19 (t, $J = 7.5$ Hz, 1H), 4.84 (t, $J = 7.4$ Hz, 2H), 4.44 (q, $J = 7.1$ Hz, 2H), 3.29 (t, $J = 7.4$ Hz, 2H), 3.14 (s, 3H), 1.49 (t, $J = 7.1$ Hz, 3H), 1.27 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 164.54, 162.70, 159.52, 137.52, 126.36, 125.57, 124.66, 124.46, 124.22, 120.73, 119.52, 119.29, 114.28, 112.01, 110.91, 61.55, 44.59, 24.19, 20.78, 14.18. HRMS calcd. for C$_{20}$H$_{18}$N$_3$O$_4$ (M+H): 364.12973; found: 364.12882.

**Ethyl 2-ethyl-1,3-dioxo-1,2,3,6,7,12-hexahydropyrrolo[3',4':1,2]indolizino[8,7-b]indole-4-carboxylate 3f:**

Following the batch synthesis, on 0.1 mmol scale reaction, 25 mg (66%) of 3f was obtained as a yellow solid. Mp. 202-204 °C. Rf = 0.75 (EtOAc/Hexane = 2:3). IR (KBr, cm$^{-1}$): 3420, 1759, 1698, 1651, 1273. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.01 (s, 1H), 7.58 (d, $J = 7.9$ Hz, 1H), 7.48 (d, $J = 8.2$ Hz, 1H), 7.38 – 7.24 (m, 1H), 7.20 – 7.07 (m, 1H), 4.83 (t, $J = 7.4$ Hz, 2H), 4.44 (q, $J = 7.1$ Hz, 2H), 3.69 (q, $J = 7.2$ Hz, 2H), 3.28 (t, $J = 7.4$ Hz, 2H), 1.49 (t, $J = 7.1$ Hz, 3H), 1.27 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 164.44, 162.53, 159.59, 137.47, 126.41, 125.56, 124.43, 124.30, 120.70, 119.45, 119.32, 114.37, 112.00, 110.89, 61.60, 44.63, 33.10, 20.84, 14.21, 14.10. HRMS calcd. for C$_{21}$H$_{20}$N$_3$O$_4$ (M+H): 378.14538; found: 378.14434.

**Benzyl 1,4-dioxo-1,7,8,13-tetrahydro-4H-benzo[1,2]indolizino[8,7-b]indole-5-carboxylate 3g:**
Following the batch synthesis, on 0.1 mmol scale reaction, 30 mg (71%) of 3g was obtained as a blue solid. Mp. 207-208 °C. Rf = 0.70 (EtOAc/Hexane = 2:3). IR (KBr, cm⁻¹): 3322, 2852, 1730, 1638, 1464, 1284. ¹H NMR (500 MHz, CDCl₃) δ 11.03 (s, 1H), 7.59-7.56 (m, 3H), 7.52 (d, J = 8.3 Hz, 1H), 7.42 (t, J = 7.3 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 6.81 (d, J = 10.3 Hz, 1H), 6.77 (d, J = 10.3 Hz, 1H), 5.47 (s, 2H), 4.55 (t, J = 7.4 Hz, 2H), 3.29 (t, J = 7.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 182.13, 180.06, 160.55, 140.57, 138.62, 136.61, 134.84, 131.72, 128.77, 128.64, 125.47, 124.63, 121.24, 120.53, 119.12, 116.12, 114.40, 112.41, 111.44, 68.22, 44.55, 20.48. HRMS calcd. for C₂₉H₁₉N₄O₄ (M+H): 423.13448; found: 423.13350.

Benzyl 9,14-dioxo-5,9,14,15-tetrahydro-6H-naphtho[2',3':1,2]indolizino[8,7-b]indole-8-carboxylate 3h:

Following the batch synthesis, on 0.1 mmol scale reaction, 29 mg (61%) of 3h was obtained as a light red solid. Mp. 210-212 °C. Rf = 0.75 (EtOAc/Hexane = 2:3). IR (KBr, cm⁻¹): 3449, 1706, 1666, 1594, 1584, 1479, 1270. ¹H NMR (500 MHz, CDCl₃) δ 11.32 (s, 1H), 8.32-8.27 (m, 2H), 7.82 - 7.71 (m, 2H), 7.59 (d, J = 7.7 Hz, 3H), 7.55 (d, J = 8.2 Hz, 1H), 7.43 (t, J = 7.3 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 5.53 (s, 2H), 4.52 (t, J = 7.4 Hz, 2H), 3.30 (t, J = 7.4 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 180.55, 178.54, 160.94, 136.59, 135.67, 135.04, 134.63, 133.49, 133.18, 132.00, 128.71, 128.66, 128.58, 127.35, 126.69, 126.50, 125.57, 124.94, 124.40, 122.59, 115.59, 112.42, 110.91, 68.26, 44.69, 20.46. HRMS calcd for C₂₉H₂₁N₄O₄ (M+H): 473.15013; found: 473.14868.

Benzyl 2-methyl-1,3-dioxo-1,2,3,6,7,12-hexahydropyrrrolo[3',4':1,2]indolizino[8,7-b]indole-4-carboxylate 3i:

Following the batch synthesis, on 0.1 mmol scale reaction, 27 mg (64%) of 3i was obtained as a yellow solid. Mp. 202-204 °C. Rf = 0.80 (EtOAc/Hexane = 2:3). IR (KBr, cm⁻¹): 3408, 2923, 1752, 1691, 1497, 1428, 1383, 1348, 1326, 1268. ¹H NMR (500 MHz, CDCl₃) δ 9.00 (s, 1H), 7.60 (d, J = 7.4 Hz, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 5.44 (s, 2H), 4.82 (t, J = 7.4 Hz, 2H),
3.27 (t, J = 7.4 Hz, 2H), 3.13 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 164.57, 162.65, 159.32, 137.50, 135.44, 128.56, 128.30, 128.23, 126.60, 125.54, 124.93, 124.50, 124.18, 120.74, 119.34, 119.06, 114.44, 112.03, 111.02, 66.98, 44.70, 24.31, 20.80. HRMS calcd. for C$_{25}$H$_{20}$N$_3$O$_4$ (M+H): 426.1453; found: 426.14451.

Benzyl 2-benzyl-1,3-dioxo-1,2,3,6,7,12-hexahydropyrrolo[3’,4’:1,2]indolizino[8,7-b]indole-4-carboxylate 3j:

Following the batch synthesis, on 0.1 mmol scale reaction, 31 mg (62%) of 3j was obtained as a yellow solid. Mp. 208-210 °C. R$_f$ = 0.79 (EtOAc/Hexane = 2:3). IR (KBr, cm$^{-1}$): 3404, 2923, 2853, 1743, 1704, 1647, 1268, 1175. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.00 (s, 1H), 7.73 – 7.52 (m, 3H), 7.51 – 7.23 (m, 10H), 7.16 (t, J = 7.3 Hz, 1H), 5.45 (s, 2H), 4.88 – 4.70 (m, 4H), 3.25 (t, J = 7.4 Hz, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 164.36, 162.14, 159.31, 137.55, 136.96, 135.55, 128.62, 128.57, 128.36, 128.28, 128.25, 127.61, 126.82, 125.54, 124.82, 124.55, 124.16, 120.75, 119.35, 119.28, 114.28, 111.99, 111.07, 66.98, 44.77, 41.90, 20.82. HRMS calcd. for C$_{31}$H$_{24}$N$_3$O$_4$ (M+H): 502.17668; found: 502.17579.

4-Nitrobenzyl 1,4-dioxo-1,7,8,13-tetrahydro-4H-benzo[1,2]indolizino[8,7-b]indole-5-carboxylate 3k:

Following the batch synthesis, on 0.1 mmol scale reaction, 32 mg (68%) of 3k was obtained as a brown solid. Mp. 212-214 °C. R$_f$ = 0.71 (EtOAc/Hexane = 2:3). IR (KBr, cm$^{-1}$): 3444, 2920, 1712, 1650, 1597, 1482, 1463, 1454, 1265. $^1$H NMR (400 MHz, CDCl$_3$) δ 11.05 (s, 1H), 8.29 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.34 (dd, J = 11.2, 4.1 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 6.84 (d, J = 10.3 Hz, 1H), 6.79 (d, J = 10.3 Hz, 1H), 5.54 (s, 2H), 4.61 (t, J = 7.4 Hz, 3H), 3.32 (t, J = 7.4 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 182.17, 180.27, 160.50, 142.14, 140.74, 138.83, 136.77, 132.40, 128.96, 125.49, 124.86, 124.82, 124.56, 123.88, 121.86, 120.68, 119.24, 116.18, 114.66, 112.50, 111.76, 66.60, 44.72, 20.60. HRMS calcd. for C$_{31}$H$_{18}$N$_3$O$_6$ (M+H): 468.11956; found: 468.11850.

8-Benzoyl-5,15-dihydro-6H-naphtho[2’,3’:1,2]indolizino[8,7-b]indole-9,14-dione 3l:
Following the batch synthesis, on 0.1 mmol scale reaction, 30 mg (68%) of 3I was obtained as a red solid. Mp. 280-282 °C. Rf = 0.60 (EtOAc/Hexane = 3:7). IR (KBr, cm⁻¹): 3317, 2920, 1664, 1596, 1584, 1566, 1480, 1449, 1420, 1397, 1270. ¹H NMR (400 MHz, CDCl₃) δ 11.29 (s, 1H), 8.35 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 8.03 (d, J = 7.6 Hz, 2H), 7.76-7.68 (m, 3H), 7.59 (t, J = 7.7 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.5 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 4.38 (t, J = 7.4 Hz, 2H), 3.32 (t, J = 7.4 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 188.78, 180.66, 178.85, 137.18, 136.75, 135.33, 135.11, 134.31, 133.47, 133.38, 133.35, 132.16, 129.63, 128.86, 127.31, 126.89, 125.73, 125.12, 124.48, 122.29, 120.52, 119.12, 115.03, 112.46, 110.95, 44.49, 20.64. HRMS calcd. for C₂₉H₁₉N₂O₃ (M+H): 443.13957; found: 443.13887.

8-(4-Chlorobenzoyl)-5,15-dihydro-6H-naphtho[2',3':1,2]indolizino[8,7-b]indole-9,14-dione 3m:

Following the batch synthesis, on 0.1 mmol scale reaction, 32 mg (67%) of 3m was obtained as a red solid. Mp. 298-300 °C. Rf = 0.68 (EtOAc/Hexane = 2:3). IR (KBr, cm⁻¹): 3422, 2923, 1657, 1587, 1482, 1267. ¹H NMR (500 MHz, CDCl₃) δ 11.27 (s, 1H), 8.33 (d, J = 7.0 Hz, 1H), 8.08 (d, J = 6.9 Hz, 1H), 7.97 (d, J = 8.6 Hz, 2H), 7.76 (t, J = 6.9 Hz, 1H), 7.70 (dd, J = 10.7, 4.2 Hz, 1H), 7.58 (dd, J = 10.9, 8.3 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.19 (t, J = 7.4 Hz, 1H), 4.38 (t, J = 7.4 Hz, 2H), 3.31 (t, J = 7.4 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 187.45, 180.56, 178.94, 140.80, 136.74, 135.65, 135.16, 135.00, 133.53, 132.60, 132.50, 130.93, 129.21, 127.29, 126.91, 125.66, 124.95, 124.57, 122.56, 120.54, 119.16, 112.47, 111.11, 44.51, 20.61 HRMS calcd. for C₂₉H₁₉ClN₂O₃ (M+H): 477.10060; found: 477.10001.

1,2-diethyl 3-methyl 5,6,11,11b-tetrahydro-1H-indolizin[8,7-b]indole-1,2,3-tricarboxylate 3n:

Following the batch synthesis, on 0.1 mmol scale reaction, 27 mg (65%) of 3n was obtained as a white solid. Mp. 170-172 °C. Rf = 0.55 (EtOAc/Hexane = 2:3). IR (KBr, cm⁻¹): 3301, 2987, 1744, 1647, 1571, 1560, 1491, 1339, 1244. ¹H NMR (500 MHz, CDCl₃) δ 8.06 (bs, 1H, H11), 7.45(dd, Jₙₙ.,
$J_{H3} = 8.0$ Hz, $J_{H4-H2} = 1.0$ Hz, 1H, H4), 7.29(td, $J_{H1-H2} = 8.0$ Hz, $J_{H1-H3} = 1.0$ Hz, 1H, H1), 7.16(td, $J_{H1-H2} = 8.0$ Hz, $J_{H3-H2} = 8.0$, 1H, H2), 7.09(td, $J_{H1-H2} = 8.0$ Hz, $J_{H3-H2} = 8.0$ Hz, 1H, H3), 5.55(dt, $J_{H10-H9} = 12.5$ Hz, $J_{H9-H5} = 2.0$, J$H9-H6 = 2.0$ Hz, 1H, H9), 4.37 (d, $J_{H10-H9} = 12.5$ Hz, 1H, H10), 4.10(m, 2H, -OCH$_2$), 3.98(s, 3H, OMe), 3.81(m, 2H, -OCH$_2$), 3.65(ddd, $J_{H7-H8} = 13.8$ Hz, $J_{H7-H6} = 5.3$, $J_{H7-H5} = 1.0$ Hz, 1H, H7), 3.24(ddd, $J_{H7-H8} = 13.8$, $J_{H5-H8} = 11.8$, $J_{H6-H8} = 4.0$ Hz, 1H, H8), 2.95(m, 1H, H6), 2.77(m, 1H, H5), 1.19(t, $J = 7.1$ Hz, 3H, -OCH$_2$-CMe), 0.78(t, $J = 7.1$ Hz, 3H, -OCH$_2$-CMe) (All proton resonances were assigned using 2D-DQFCOSY, NOESY and HSQC experiments). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 170.58, 163.97, 163.23, 152.96, 136.29, 128.39, 126.36, 122.51, 119.76, 118.25, 110.95, 110.57, 100.26, 61.20, 60.69, 59.61, 53.10, 51.42, 43.49, 21.75, 14.33, 13.60.

Following the batch synthesis, on 0.1 mmol scale reaction, 33 mg (80%) of 3o was obtained as a white solid. Mp. 160-162 6C. R$_f$ = 0.56 (EtOAc/Hexane = 1:3). IR (KBr, cm$^{-1}$): 3342, 2980, 1740, 1682, 1529, 1474, 1438, 1418, 1382. $^1$H NMR (500 MHz, CDCl$_3$) δ 11.03 (s, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.46 (d, $J = 8.2$ Hz, 1H), 7.31 – 7.21 (m, 1H), 7.20 – 7.04 (m, 1H), 4.76 (t, $J = 7.5$ Hz, 2H), 4.41-4.33 (m, 4H), 3.21 (t, $J = 7.5$ Hz, 2H), 1.41-4.36 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.96, 164.48, 160.25, 136.55, 134.26, 126.61, 125.35, 125.03, 123.81, 120.17, 120.04, 118.96, 112.19, 110.83, 107.72, 61.57, 61.22, 51.93, 44.41, 20.48, 14.29, 14.08. HRMS calcd. for C$_{22}$H$_{24}$N$_2$NaO$_6$ (M+Na): 435.15321; found: 435.15266.

References:

$^1$H NMR Spectrum of 3a:
$^{13}$C NMR Spectrum of 3a:
$^1$H NMR Spectrum of 3b:
$^{13}$C NMR Spectrum of 3b:
$^1$H NMR Spectrum of 3c:
$^{13}$C NMR Spectrum of 3c:
$^1$H NMR Spectrum of 3d:
$^{13}$C NMR Spectrum of 3d:
$^1$H NMR Spectrum of 3d$: 

![NMR Spectrum Image]

- Note: The image shows a typical NMR spectrum with peaks at various chemical shifts.
$^{13}$C NMR Spectrum of 3d':
\(^{1}H\) NMR Spectrum of 3e:
$^{13}$C NMR Spectrum of 3e:
$^1$H NMR Spectrum of 3f:
$^{13}$C NMR Spectrum of 3f:
$^1$H NMR Spectrum of 3g:
$^{13}$C NMR Spectrum of 3g:
$^1$H NMR Spectrum of 3h:
$^{13}$C NMR Spectrum of 3h:
$^1$H NMR Spectrum of 3i:
$^{13}$C NMR Spectrum of 3i:
$^1$H NMR Spectrum of 3j:
$^{13}$C NMR Spectrum of 3j:
$^1$H NMR Spectrum of 3k:
$^{13}$C NMR Spectrum of 3k:
$^1$H NMR Spectrum of 3I:
$^{13}$C NMR Spectrum of 3i:
$^1$H NMR Spectrum of 3m:
$^{13}$C NMR Spectrum of 3m:
^H NMR Spectrum of 3n:
DQFCOSY Spectrum of 3n:
NOESY Spectrum of 3n:
HSQC Spectrum of 3n:
$^3$H NMR Spectrum of 3o:
$^{13}$C NMR Spectrum of 3o: