Supporting Information

A Green Aspect for Multicomponent Synthesis of Spiro[4*H*-indeno[1,2-*b*]pyridine-4,3'-[3*H*]indoles]

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A. General Information:

IR spectra were recorded on a Perkin–Elmer FT-IR 783 spectrophotometer. NMR spectra were recorded on a Bruker AC-300 MHz spectrometer in DMSO-*d*₆ using tetramethylsilane as internal standard. Mass spectra were recorded on a Shimadzu QP2010 GCMS. High resolution mass spectra (HRMS) were performed on Thermo Scientific Q – Exactive, Accela 1250 pump, instrument. Elemental analysis was done by using the EURO EA3000 vector model. UV–visible spectra and Fluorescence spectra were recorded on a Shimadzu Spectrophotometer and on Jasco (FP-750) Spectrofluorometer in respective solvents. The concentration of each sample was maintained in the range of $\sim 10^{-5}$ M for absorption and fluorescence study.

B. Typical Procedure:

Isatin (1 mmol), 1,3-indanedione (1 mmol), ethyl acetoacetate (1 mmol) and NH_4OAc (1 mmol) were placed in 25 mL round-bottom flask in **ethanol : Water (9:1)** (5 mL). The resulting mixture was stirred at room temperature for the time mentioned in Table 2, till the completion of reaction monitored by TLC. After completion of the reaction, the mixture was filtered and washed with little quantity of ethanol furnished pure spiro[4*H*-indeno-[1,2-*b*]pyridine-4,3'-[3*H*]indoles]. The structure of the product was confirmed by IR, ^1H and ^{13}C NMR, GCMS, HRMS and elemental analysis.

C. Spectral data of Synthesized Compound:

Entry A, Table 2: Ethyl 5'-Methyl-1,1',2',5-tetrahydro-2-methyl-2',5-dioxospiro[4*H*-indeno[1,2-*b*]pyridine-4,3'-[3*H*]indole]-3-carboxylate

Red powder; M.P. 274-276 $^{\circ}\text{C}$; **IR** (KBr) (Fig. 1) : 3347, 1677, 1509, 1300 cm^{-1} ; **^1H -NMR** (300 MHz, DMSO-d_6) (Fig. 2) : δ (ppm): 10.32 (s, 1H, -NH, D_2O exchangeable), 10.13 (s, 1H, -NH, D_2O exchangeable), 7.62-7.64 (d, 1H, $J = 7.2$ Hz), 7.43-7.48 (dd, 1H, $J = 7.8, 7.2$ Hz), 7.31-7.36 (dd, 1H, $J = 7.2, 7.5$ Hz), 7.17-7.19 (d, 1H, $J = 6.9$ Hz), 6.89-6.91 (d, 1H, $J = 7.8$ Hz), 6.78 (s, 1H), 6.63-6.66 (d, 1H, $J = 7.8$ Hz), 3.72-3.79 (m, 2H, $-\text{OCH}_2$), 2.43 (s, 3H), 2.15 (s, 3H), 0.83-0.88 (t, 3H); **^{13}C NMR** (75 MHz, DMSO-d_6) (Fig. 3) : δ (ppm): 189.67, 179.97, 166.14, 153.93, 146.92, 140.40, 137.11, 135.95, 133.48, 132.36, 130.90, 130.32, 128.44, 124.38, 120.98,

119.92, 59.93, 49.96, 21.04, 19.53, 13.54; **MS (EI)** (Fig. 4) : 400 (M⁺), 372, 327, 299 m/z.; **HRMS** (Fig. 5) : mass calculated for [C₂₄H₂₀N₂O₃]: 401.1496 [M + H]⁺; Obs. Mass: 401.1495 [M + H]⁺ Ana. Calc. for C₂₄H₂₀N₂O₄ (400) : C(71.99%), H(5.03%), N(7.00%), O(15.98%); found : C(71.84%), H(5.33%), N(7.16%), O(15.67%).

Entry B, Table 2: Ethyl 5'-methoxy-1,1',2',5-tetrahydro-2-methyl-2',5-dioxospiro[4H-indeno[1,2-b]pyridine-4,3'-[3H]indole]-3-carboxylate

Red powder; M.P. 257-259 °C; **IR** (KBr) (Fig. 6) : 3734, 3596, 3343, 1672, 1515 cm⁻¹; **¹H-NMR** (300 MHz, DMSO-d₆) (Fig. 7) : δ (ppm): 10.23 (s, 1H, -NH, D₂O exchangeable), 10.05 (s, 1H, -NH, D₂O exchangeable), 7.57-7.60 (d, 1H, *J* = 7.2 Hz), 7.28-7.37 (d, 2H, *J* = 6.0 Hz), 7.13-7.15 (d, 1H, *J* = 6.6 Hz), 6.61-6.68 (m, 2H), 6.54 (s, 1H), 3.75- 3.78 (m, 2H, -OCH₂), 3.62 (s, 3H, -OCH₃), 2.41 (s, 3H), 0.84-0.89 (t, 3H); **¹³C NMR** (75 MHz, DMSO-d₆) (Fig. 8) : δ (ppm): 189.60, 180.13, 166.01, 155.24, 154.04, 146.96, 138.23, 136.26, 136.05, 133.60, 131.89, 130.44, 120.72, 119.76, 112.36, 110.98, 109.22, 107.04, 105.57, 59.78, 55.71, 50.56, 19.52, 13.51; **MS (EI)** (Fig. 9) : 416 (M⁺), 388, 343, 315, 300, 272 m/z; **HRMS** (Fig. 10) : mass calculated for [C₂₄H₂₀N₂O₅]: 417.1445 [M + H]⁺; Obs. Mass: 417.1443 [M + H]⁺ Ana. Calc. for C₂₄H₂₀N₂O₅ (416) : C(69.22%), H(4.84%), N(6.73%), O(19.21%); found : C(69.01%), H(4.74%), N(6.84%), O(15.41%).

Entry D, Table 2: Ethyl 5'-Chloro-1,1',2',5-tetrahydro-2-methyl-2',5-dioxospiro[4H-indeno[1,2-b]pyridine-4,3'-[3H]indole]-3-carboxylate

Red powder; M.P. 265-267 °C; **IR** (KBr) (Fig. 11) : 3467, 3328, 3071, 2978, 1702, 1643, 1516 cm^{-1} ; **¹H-NMR** (300 MHz, DMSO- d_6) (Fig. 12) : δ (ppm): 10.44 (s, 1H, -NH, D_2O exchangeable), 10.42 (s, 1H, -NH, D_2O exchangeable), 7.64-7.67 (d, 1H, $J = 7.2$ Hz), 7.45-7.50 (dd, 1H, $J = 7.5, 7.2$ Hz), 7.33-7.38 (dd, 1H, $J = 7.2, 7.8$ Hz), 7.14-7.21 (m, 2H), 7.03-7.04 (d, 1H, $J = 2.1$ Hz), 6.76-6.78 (d, 1H, $J = 8.1$ Hz), 3.76-3.82 (m, 2H, $-\text{OCH}_2$), 2.45 (s, 3H), 0.84-0.89 (t, 3H); **¹³C NMR** (75 MHz, DMSO- d_6) (Fig. 13) : δ (ppm): 189.68, 179.79, 165.96, 154.26, 147.87, 141.84, 138.97, 135.83, 133.39, 132.45, 131.05, 128.08, 125.57, 123.83, 121.12, 120.14, 110.46, 106.45, 104.89, 60.08, 50.24, 19.60, 13.58; **MS (EI)** (Fig. 14) : 420 (M^+), 392, 363, 347, 319, 284, 134 m/z ; Ana. Calc. for $\text{C}_{23}\text{H}_{17}\text{ClN}_2\text{O}_4$ (420) : C(65.64%), H(4.07%), Cl(8.42), N(6.66%), O(15.21%); found : C(65.50%), H(4.15%), Cl(8.44), N(6.34%), O(15.57%).

Entry E, Table 2: Ethyl 5'7'-Dimethyl-1,1',2',5-tetrahydro-2-methyl-2',5-dioxospiro[4H-indeno[1,2-b]pyridine-4,3'-[3H]indole]-3-carboxylate

Red powder; M.P. 271-273 °C; **IR** (KBr) (Fig. 15) : 3406, 3187, 3038, 1673, 1599, 1497 cm⁻¹; **¹H-NMR** (300 MHz, DMSO-d₆) (Fig. 16) : δ (ppm): 10.35 (s, 1H, -NH, D₂O exchangeable), 10.20 (s, 1H, -NH, D₂O exchangeable), 7.61-7.63 (d, 1H, *J* = 6.9 Hz), 7.43-7.48 (dd, 1H, *J* = 7.5, 7.2 Hz), 7.31-7.36 (dd, 1H, *J* = 7.2, 7.8 Hz), 7.16-7.18 (d, 1H, *J* = 6.9 Hz), 6.73 (s, 1H), 6.59 (s, 1H), 3.71-3.77 (m, 2H, -OCH₂), 2.42 (s, 3H), 2.17 (s, 3H), 2.11 (s, 3H), 0.83- 0.85 (t, 3H); **¹³C NMR** (75 MHz, DMSO-d₆) (Fig. 17) : δ (ppm): 180.55, 166.22, 154.06, 146.80, 138.83, 136.75, 135.88, 133.46, 130.94, 130.36, 121.77, 120.99, 119.88, 117.84, 107.30, 60.00, 50.17, 20.94, 19.42, 16.70, 13.34; **MS (EI)** (Fig. 18) : 414 (M⁺), 386, 358, 341, 313 m/z; **HRMS** (Fig. 19) : mass calculated for [C₂₅H₂₂N₂O₄]: 415.1652 [M + H]⁺ and 437.1472 [M + Na]⁺ ; Obs. Mass: 415.1651 [M + H]⁺ and 437.1471[M + Na]⁺ Ana. Calc. for C₂₅H₂₂N₂O₄ (414) : C(72.45%), H(5.35%), N(6.76%), O(15.44%); found : C(72.40%), H(5. 04%), N(6.85%), O(15.71%).

Entry F, Table 2: Ethyl 5'-Iodo-1,1',2',5-tetrahydro-2-methyl-2',5-dioxospiro[4H-indeno[1,2-b]pyridine-4,3'-[3H]indole]-3-carboxylate

Red powder; M.P. 258-260 °C; **IR** (KBr) (Fig. 20) : 3426, 3322, 1700, 1674, 1648, 1515 cm⁻¹; **¹H-NMR** (300 MHz, DMSO-d₆) (Fig. 21) : δ (ppm): 10.35 (s, 1H, -NH, D₂O exchangeable), 10.31 (s, 1H, -NH, D₂O exchangeable), 7.56 (s, 1H), 7.36-7.38 (d, 2H, *J* = 6.9 Hz), 7.26 (s, 1H), 7.13-7.16 (d, 2H, *J* = 8.4 Hz), 6.60- 6.63 (d, 1H, *J* = 8.1 Hz), 3.76 - 3.80 (m, 2H, -OCH₂), 2.43 (s, 3H), 0.86 - 0.90 (t, 3H); **¹³C NMR** (75 MHz, DMSO-d₆) (Fig. 22) : δ (ppm): 189.97, 179.81, 166.07, 154.45, 147.98, 142.51, 139.53, 136.89, 135.60, 133.26, 132.53, 131.79, 131.17, 121.23,

120.12, 111.89, 106.23, 104.85, 84.16, 60.29, 49.98, 19.47, 13.48; **MS (EI)** (Fig. 23) : 512 (M⁺), 484, 456, 439, 411 m/z. **HRMS** (Fig. 24) : mass calculated for [C₂₃H₁₇N₂O₄I]: 513.0306 [M + H]⁺ and 535.0125 [M + Na]⁺; Obs. Mass: 513.0314 [M + H]⁺ and 535.0134 [M + Na]⁺; Ana. Calc. for C₂₃H₁₇IN₂O₄ (512) : C(53.92%), H(3.34%), I(24.77), N(5.47%), O(12.49%); found : C(54.24%), H(3.45%), I(24.60), N(5.36%), O(12.35%).

Entry G, Table 2: Ethyl 1,1',2',5-Tetrahydro-2-Methyl-2',5-dioxospiro[4H-indeno[1,2-b]pyridine-4,3'-[3H]indole]-3-carboxylate

Red powder; M.P. Observed = >300 °C (Lit = >300 °C)¹⁸; **IR** (KBr) (Fig.25) : 3333, 3165, 3053, 2980, 1679, 1514 cm⁻¹; **¹H-NMR** (300 MHz, DMSO-d₆) (Fig. 26) : δ (ppm): 10.22 (s, 1H, -NH, D₂O exchangeable), 10.20 (s, 1H, -NH, D₂O exchangeable), 7.56-7.58 (d, 1H, *J* = 6.9 Hz), 7.32-7.37 (dd, 1H, *J* = 7.5, 6.9 Hz), 7.22-7.27 (dd, 1H, *J* = 6.9, 7.8 Hz), 7.11-7.14 (d, 1H, *J* = 6.6 Hz), 7.03-7.08 (dd, 1H, *J* = 7.8, 7.5 Hz), 6.92-6.94 (d, 1H, *J* = 7.2 Hz), 6.74-6.81 (m, 2H), 3.69-3.79 (m, 2H, -OCH₂), 2.41 (s, 3H), 0.81-0.86 (t, 3H); **¹³C NMR** (75 MHz, DMSO-d₆) (Fig. 27) : δ (ppm): 189.64, 179.97, 166.09, 153.98, 146.99, 142.87, 137.00, 135.95, 133.47, 132.37, 130.90, 128.21, 123.76, 121.61, 120.97, 119.96, 109.02, 107.11, 105.62, 59.90, 49.92, 19.54, 13.54; **MS (EI)** (Fig. 28) : 386 (M⁺), 358, 313, 285, 256 m/z; **HRMS** (Fig. 29): mass calculated for [C₂₃H₁₈N₂O₄]: 409.1159 [M + Na]⁺; Obs. Mass: 409.1161 [M + Na]⁺ Ana. Calc. for C₂₃H₁₈N₂O₄ (386) : C (71.49 %), H(4.70 %), N(7.25 %), O(16.56 %); found : C(71.44 %), H(4.65 %), N(7.28 %), O(16.63 %).

Entry I, Table 2: Ethyl 5'-Flouro-1,1',2',5-tetrahydro-2-methyl-2',5-dioxospiro[4H-indeno[1,2-b]pyridine-4,3'-[3H]indole]-3-carboxylate

Red powder; M.P. 269-272 °C; **IR** (KBr) (Fig. 30) : 3435, 3326, 1696, 1514, 1258 cm⁻¹; **¹H-NMR** (300 MHz, DMSO-d₆) (Fig. 31) : δ (ppm): 10.44 (s, 1H, -NH, D₂O exchangeable), 10.32 (s, 1H, -NH, D₂O exchangeable), 7.64-7.66 (d, 1H, *J* = 7.2 Hz), 7.45-7.50 (dd, 1H, *J* = 7.5, 7.2 Hz), 7.33-7.38 (dd, 1H, *J* = 7.2, 7.5 Hz), 7.18-7.20 (d, 1H, *J* = 6.9 Hz), 6.88-6.95 (m, 2H), 6.71-6.75 (m, 1H), 3.75-3.79 (m, 2H, OCH₂), 2.28 (s, 3H), 0.82-0.87 (t, 3H); **¹³C NMR** (75 MHz, DMSO-d₆) : δ (ppm): Due to insufficient solubility we are unable to scan its ¹³C NMR; **MS (EI)** (Fig. 32) : 404 (M⁺), 376, 348, 331, 303 m/z; **HRMS** (Fig. 33) : mass calculated for [C₂₃H₁₇N₂O₄F]: 405.1245 [M + H]⁺; Obs. Mass: 405.1244 [M + H]⁺. Ana. Calc. for C₂₃H₁₇FN₂O₄ (404) : C(68.31%), H(4.24%), F(4.70), N(6.93%), O(15.83%); found : C(68.18%), H(4.35%), F(4.54), N(7.23%), O(15.70%).

Entry A, Table 2:

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Entry B, Table 2:

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Entry D, Table 2:

Fig. 11

Fig 12

Fig. 13

Fig. 14

Entry E, Table 2:

Fig. 15

Fig. 16

Fig. 17

Fig. 18

Fig. 19

Entry F, Table 2:

Fig. 20

Fig. 21

Fig. 22

Fig. 23

Fig. 24

Entry G, Table 2:

Fig. 25

Fig. 26

Fig. 27

Fig. 28

Fig. 29

Entry I, Table 2:

Fig. 30

Fig. 31

Fig. 32

Fig. 33