Supporting information

An efficient green approach for the synthesis of spiro[indoline-3,4'-pyrazolo[3,4-*b*]quinoline]diones using [NMP]H₂PO₄, their solvatochromic and pH studies.

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General Procedure for the Synthesis of compound (4a-4k)

A mixture of isatin (**1**) (1.0 mmol), 5-amino-3-methyl-1-phenylpyrazole (**2**) (1.0 mmol), 1,3-dicarbonyl compounds (**3**) (1.0 mmol), and [NMP]H₂PO₄ (20 mol%) in H₂O:EtOH (4:1 v/v) was placed in a 100 ml round-bottomed flask which was stirred at 80°C on a pre-heated oil bath for an appropriate time as shown in Table 2. After completion of the reaction as confirmed by TLC (ethyl acetate: petroleum ether, 40:60 v/v), the reaction mixture was cooled to room temperature. The precipitated product was filtered at pump, washed with water : ethanol (1:1) and dried. It was recrystallized from ethanol to afford the pure products (**4a-4k**) in excellent yield. All the products were characterized using ¹H NMR, ¹³C NMR, IR and Mass spectra.

Spectral data

3',7',7'-Trimethyl-1'-phenyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-*b*]quinoline]-2,5'(1'*H*)-dione (4a)^[26]

Color- White, Yield- 92%, M.p.- 242-244°C

IR ($\nu_{\max}$, cm^{-1}) (KBr): 3284, 3163, 2958, 1709, 1617, 1532, 1468, 1364, 1124, 748, 684; ^1H NMR (400 MHz, DMSO d_6): δ : 9.66 (s, 1H, N-H), 7.55-7.38 (m, 5H, Ar-H), 7.11-7.03 (m, 1H, Ar-H), 6.85-6.75 (m, 3H, Ar-H), 2.68-2.48 (m, 2H, CH_2), 2.19-1.96 (m, 2H, CH_2), 1.55 (s, 3H, $-\text{CH}_3$), 1.01 (s, 3H, $-\text{CH}_3$), 0.92 (s, 3H, $-\text{CH}_3$); ^{13}C NMR (100 MHz, DMSO d_6): δ : 193.3, 179.6, 153.0, 145.0, 141.7, 137.8, 136.9, 136.6, 129.4, 127.2, 127.1, 123.4, 123.1, 121.4, 108.5, 107.9, 101.5, 50.4, 48.7, 48.5, 40.9, 32.1, 28.1, 26.9, 11.3.

3',7'-Dimethyl-1'-phenyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-*b*]quinoline]-2,5'(1'*H*)-dione (4b)^[27]

Color- White, Yield- 88%, M.p.- > 300°C

IR ($\nu_{\max}$, cm^{-1}) (KBr): 3152, 2927, 1707, 1618, 1533, 1123, 760; ^1H NMR (400 MHz, DMSO d_6): δ : 9.67 (s, 1H, N-H), 7.55-7.48 (m, 4H, Ar-H), 7.42-7.38 (m, 1H, Ar-H), 7.10-7.06 (m, 1H, Ar-H), 6.83-6.77 (m, 3H, Ar-H), 2.78-2.68 (m, 2H, CH_2), 2.49-2.31 (m, 2H, CH_2), 1.95-1.84 (m, 1H, CH), 1.54 (s, 3H, $-\text{CH}_3$), 0.99-0.97 (d, 3H, $-\text{CH}_3$); ^{13}C NMR (100 MHz, DMSO d_6): δ : 193.3, 179.6, 153.8, 144.9, 141.7, 141.6, 137.8, 136.9, 136.5, 129.4, 127.1, 123.4, 123.1, 121.3, 108.6, 108.4, 101.6, 48.7, 48.4, 44.8, 35.1, 30.1, 28.2, 28.1, 11.3.

3'-Methyl-1'-phenyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-*b*]quinoline]-2,5'(1'*H*)-dione (4c)^[26]

Color- White, Yield- 89%, M.p.- > 300°C

IR ($\nu_{\max}$, cm^{-1}) (KBr): 3229, 3149, 2948, 1698, 1618, 1529, 1467, 1358, 1118, 749, 680; ^1H NMR (400 MHz, DMSO d_6): δ : 9.72 (s, 1H, N-H), 7.55-7.38 (m, 5H, Ar-H), 7.10-7.07 (m, 1H, Ar-H), 6.86-6.77 (m, 3H, Ar-H), 2.72-2.49 (m, 2H, CH_2), 2.21-2.08 (m, 2H, CH_2), 1.90-1.78 (m, 2H, CH_2), 1.53 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO d_6): δ : 193.5, 179.6,

154.9, 144.9, 141.7, 137.8, 137.0, 136.5, 129.4, 127.2, 123.4, 123.2, 121.3, 109.2, 108.4, 101.5, 48.8, 36.9, 27.6, 21.0, 11.3;.

3-Methyl-1-phenyl-6,7-dihydro-1*H*-spiro[cyclopenta[*e*]pyrazolo[3,4-*b*]pyridine-4,3'-indoline]-2',5(8*H*)-dione (4d)^[26]

Color- White, Yield- 87%, M.p.- > 300°C

IR ($\nu_{\max}$, cm^{-1}) (KBr): 3228, 3088, 2928, 1718, 1611, 1525, 1472, 1348, 1112, 754, 686; ^1H NMR (400 MHz, DMSO d_6): δ : 10.47 (s, 1H, N-H), 7.58-7.41 (m, 5H, Ar-H), 7.17-7.13 (m, 1H, Ar-H), 6.92-6.83 (m, 3H, Ar-H), 2.73-2.68 (m, 2H, CH₂), 2.26-2.25 (m, 2H, CH₂), 1.51 (s, 3H, CH₃); ^{13}C NMR (100 MHz, DMSO d_6): δ : 199.3, 178.2, 167.3, 145.3, 141.6, 138.5, 137.6, 134.9, 129.5, 127.8, 127.3, 124.2, 123.4, 121.7, 113.2, 108.9, 101.7, 47.2, 33.4, 24.5, 11.2.

3',6',8'-Trimethyl-1'-phenylspiro[indoline-3,4'-pyrazolo[3,4-*b*]pyrido[2,3-*d*]pyrimidine]-2,5',7'(1'*H*, 6'*H*, 8'*H*, 9'*H*)trione (4e)

Color- White, Yield- 88%, M.p.- 300°C

IR ($\nu_{\max}$, cm^{-1}) (KBr): 3214, 1708, 1615, 1550, 1209, 1117, 757, 680; ^1H NMR (400 MHz, DMSO d_6): δ : 9.53 (s, 1H, N-H), 7.68-7.66 (m, 2H, Ar-H), 7.55-7.51 (m, 2H, Ar-H), 7.37-7.34 (m, 1H, Ar-H), 7.15-7.12 (m, 1H, Ar-H), 6.89-6.83 (m, 3H, Ar-H), (NMe) 1.57 (s, 3H, CH₃) ^{13}C NMR (100 MHz, DMSO d_6): δ : 178.6, 159.9, 150.5, 144.6, 142.0, 138.4, 135.6, 129.4, 127.7, 126.6, 123.3, 121.7, 121.6, 108.8, 101.7, 48.5, 48.4, 30.5, 30.0, 28.9, 27.5, 17.1, 11.2; MS (ESI) m/z [$\text{M}^+ + \text{H}$] calculated for C₂₄H₂₁N₆O₃ 441.16 found 441.25.

5-Bromo-3',7',7'-trimethyl-1'-phenyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-*b*]quinoline]-2,5'(1'*H*)-dione (4f)^[27]

Color- White, Yield- 90%, M.p.- 301-303°C

IR ($\nu_{\max}$, cm^{-1}) (KBr): 3351, 2960, 2864, 1727, 1617, 1528, 1472, 1375, 1119, 762, 693; ^1H

NMR (400 MHz, DMSO d_6): δ : 9.71 (s, 1H, N-H), 7.47-7.40 (m, 4H, Ar-H), 7.35-7.31 (m, 1H, Ar-H), 7.21-7.19 (m, 1H, Ar-H), 6.91-6.90 (m, 1H, Ar-H), 6.72-6.69 (m, 1H, Ar-H), 2.53-2.41 (m, 2H, CH_2), 2.02-1.93 (m, 2H, CH_2), 1.50 (s, 3H, $-\text{CH}_3$), 0.92 (s, 3H, $-\text{CH}_3$), 0.91 (s, 3H, $-\text{CH}_3$); ^{13}C NMR (100 MHz, DMSO d_6): δ : 193.5, 179.2, 153.5, 144.8, 141.1, 139.3, 137.7, 136.8, 130.0, 129.4, 127.3, 125.9, 123.6, 113.1, 110.5, 107.3, 100.8, 50.3, 48.9, 40.8, 32.2, 27.85, 27.3, 11.4.

5-Bromo-3'-methyl-1'-phenyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-b]quinoline]-2,5'(1'H)-dione (4g)^[28]

Color- White, Yield- 90%, M.p.- 359-361°C

IR ($\nu_{\max}$, cm^{-1}) (KBr): 3217, 3129, 2953, 1714, 1606, 1526, 1465, 1362, 1115, 768, 694; ^1H

NMR (400 MHz, DMSO d_6): δ : 9.8 (s, 1H, N-H), 7.55-7.38 (m, 5H, Ar-H), 7.28-7.26 (m, 1H, Ar-H), 7.01-7.00 (m, 1H, Ar-H), 6.77-6.75 (m, 1H, Ar-H), 2.74-2.59 (m, 2H, CH_2), 2.18-2.14 (m, 2H, CH_2), 1.88-1.84 (m, 2H, CH_2), 1.57 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO d_6): δ : 193.7, 179.2, 155.4, 144.8, 141.1, 139.3, 137.7, 136.6, 130.0, 129.4, 127.3, 125.9, 123.7, 113.0, 110.4, 108.6, 100.8, 49.0, 36.8, 27.5, 20.9, 11.3.

3',7',7'-Trimethyl-5-nitro-1'-phenyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-b]quinoline]-2,5'(1'H)-dione (4h)^[28]

Color- Yellow, Yield- 90%, M.p.- 288-290°C

IR ($\nu_{\max}$, cm^{-1}) (KBr): 3233, 3155, 2961, 1718, 1615, 1534, 1467, 1337, 1127, 773, 694; ^1H

NMR (400 MHz, DMSO d_6): δ : 9.76 (s, 1H, N-H), 8.00-7.98 (m, 1H, Ar-H), 7.58-7.57 (m, 1H, Ar-H), 7.41-7.40 (m, 4H, Ar-H), 7.31-7.27 (m, 1H, Ar-H), 6.91-6.89 (m, 1H, Ar-H),

2.53-2.36 (m, 2H, CH₂), 1.98-1.89 (m, 2H, CH₂), 1.45 (s, 3H, CH₃), 0.87 (s, 3H, -CH₃), 0.86 (s, 3H, -CH₃); ¹³C NMR (100 MHz, DMSO *d*₆): δ: 193.6, 180.0, 153.9, 148.3, 144.6, 142.2, 137.7, 137.6, 136.9, 129.3, 127.4, 125.0, 123.7, 118.3, 108.7, 106.9, 100.1, 50.1, 48.7, 40.7, 32.1, 27.6, 27.3, 11.4.

3',7'-Dimethyl-5-nitro-1'-phenyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-*b*]quinoline]-2,5'(1'*H*)-dione (4i)

Color- Yellow, Yield- 87%, M.p.- 327-329°C

IR (ν_{max}, cm⁻¹) (KBr): 3229, 3149, 2946, 1726, 1612, 1533, 1472, 1335, 1127, 754, 690; ¹H NMR (400 MHz, DMSO *d*₆): δ: 9.94 (s, 1H, N-H), 8.13-8.10 (m, 1H, Ar-H), 7.74-7.70 (m, 1H, Ar-H), 7.54-7.40 (m, 5H, Ar-H), 7.03-7.01 (m, 1H, Ar-H), 2.80-2.34 (m, 2H, CH₂), 2.23-2.07 (m, 2H, CH₂), 2.01-1.94 (m, 1H, CH), 1.57 (s, 3H, CH₃), 0.99-0.98 (m, 3H, CH₃) ¹³C NMR (100 MHz, DMSO *d*₆): δ: 193.7, 180.2, 148.3, 144.6, 142.2, 137.8, 137.6, 129.4, 127.5, 125.1, 123.8, 118.7, 118.5, 108.7, 107.9, 107.6, 100.2, 100.1, 48.8, 44.6, 35.2, 28.3, 28.1, 20.3, 11.4; MS (ESI) *m/z* [M⁺ + H] calculated for C₂₅H₂₂N₅O₄ 456.16 found 456.31.

3'-Methyl-5-nitro-1'-phenyl-6',7',8',9'-tetrahydrospiro[indoline-3,4'-pyrazolo[3,4-*b*]quinoline]-2,5'(1'*H*)-dione (4j)

Color- Yellow, Yield- 89%, M.p.- 305-307°C

IR (ν_{max}, cm⁻¹) (KBr): 3147, 3048, 2928, 1727, 1611, 1525, 1472, 1333, 1124, 752, 691; ¹H NMR (400 MHz, DMSO *d*₆): δ: 9.93 (s, 1H, N-H), 8.10-8.07 (m, 1H, Ar-H), 7.71-7.70 (m, 1H, Ar-H), 7.53-7.48 (m, 4H, Ar-H), 7.41-7.36 (m, 1H, Ar-H), 7.0-6.98 (m, 1H, Ar-H), 2.75-2.59 (m, 2H, CH₂), 2.20-2.04 (m, 2H, CH₂), 1.94-1.80 (m, 2H, CH₂), 1.53 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO *d*₆): δ: 193.9, 180.2, 156.0, 148.3, 144.6, 142.2, 137.8, 137.6, 136.8,

129.4, 127.5, 125.1, 123.8, 118.6, 108.7, 108.2, 100.1, 48.9, 36.7, 27.6, 20.9, 11.4; MS (ESI) m/z [$M^+ + H$] calculated for $C_{24}H_{20}N_5O_4$ 442.15 found 442.24.

3-Methyl-5'-nitro-1-phenyl-6,7-dihydro-1*H*-spiro[cyclopenta[*e*]pyrazolo[3,4-*b*]pyridine-4,3'-indoline]-2',5(8*H*)-dione (4k)

Color- Yellow, Yield- 92%, M.p.- 339-341°C

IR ($\nu_{\max}$, cm^{-1}) (KBr): 3197, 3150, 2928, 1727, 1616, 1539, 1474, 1333, 1108, 759, 697; ^1H NMR (400 MHz, DMSO d_6): δ : 10.7 (s, 1H, N-H), 8.18-8.16 (m, 1H, Ar-H), 7.816-7.810 (m, 1H, Ar-H), 7.57-7.56 (m, 4H, Ar-H), 7.47-7.42 (m, 1H, Ar-H), 7.09-7.07 (m, 1H, Ar-H), 2.82-2.70 (m, 2H, CH_2), 2.30-2.27 (m, 2H, CH_2), 1.55 (m, 3H, CH_3) ^{13}C NMR (100 MHz, DMSO d_6): δ : 199.5, 178.8, 167.9, 148.1, 145.1, 142.5, 138.9, 137.5, 135.7, 129.5, 127.6, 125.5, 123.7, 119.7, 112.0, 109.2, 100.3, 47.2, 33.3, 30.6, 24.7, 11.3; MS (ESI) m/z [$M^+ + H$] calculated for $C_{23}H_{18}N_5O_4$ 428.13 found 428.22.