Efficient synthesis of spiro[diindenopyridine-indoline]triones catalysed by PEGOSO₃H-H₂O and [NMP]H₂PO₄

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Procedure for synthesis of compounds 4a–4n using PEG-OSO₃H in water under conventional heating conditions.

A mixture of indan-1,3-dione (2.0 mmol), substituted isatin (1.0 mmol), aromatic amine (1.0 mmol), PEG-OSO₃H (30 mol%, 1.8 g) and water (10 mL) was placed in a 50 mL round-bottomed flask. The mixture was heated in an oil bath maintained at 80°C for appropriate time as mentioned in Table 2. After completion of reaction as monitored by TLC using ethyl acetate: petroleum ether (30:70, v/v) as eluent, the reaction mixture was allowed to cool to room temperature. The precipitate formed was collected by filtration at pump, washed with water, followed by cold ethanol and dried to yield pure 5-aryl-5*H*-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-2',10,12-triones (**4a–4n**) in high yields.

Procedure for preparation of compounds 4a–4n using PEG-OSO₃H as catalyst in water under ultrasonic irradiation.

A mixture of indan-1,3-dione (0.96 mmol), substituted isatin (0.48 mmol), aromatic amine (0.48), PEG-OSO₃H (30 mol%, 0.84 g) and water (5 mL) was placed in a 50 mL round-bottomed flask. The mixture was sonicated at 40°C for appropriate time as mentioned in Table 2. After completion of reaction as monitored by TLC as above, the reaction mixture was allowed to cool to room temperature. The precipitate formed was collected by filtration

at pump, washed first with water, then with cold ethanol and dried to yield pure products **4a-4n** in high yields.

Procedure for preparation of compounds 4a–4n using [NMP]H₂PO₄ as catalyst under conventional heating conditions.

A mixture of indan-1,3-dione (0.96 mmol), substituted isatin (0.48 mmol), aromatic amine (0.48 mmol) and [NMP]H₂PO₄ (30 mol%) was placed in a 50 mL round-bottomed flask. The mixture was heated in an oil bath maintained at 80°C for appropriate time as mentioned in Table 3. After completion of reaction as monitored by TLC using ethyl acetate: petroleum ether (30:70, v/v) as eluent, the reaction mixture was worked up as above to yield pure 5-aryl-5*H*-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-2',10,12-triones (**4a-4n**) in high yields.

Procedure for preparation of compounds 4a–4n using [NMP]H₂PO₄ as catalyst under ultrasonic irradiation.

A mixture of indan-1,3-dione (0.96 mmol), substituted isatin (0.48 mmol), aromatic amine (0.48 mmol) and [NMP]H₂PO₄ (30 mol%) was placed in a 50 mL round-bottomed flask. The mixture was sonicated at 40°C for appropriate time as mentioned in Table 3. After completion of reaction, the products **4a-4n** were collected after filtration at pump, washing with water, followed by cold ethanol and drying. Pure 5-aryl-5*H*-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-2',10,12-triones (**4a-4n**) were obtained in high yields.

Spectral data

5-(4-Methoxyphenyl)-5*H*-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-2',10,12-trione (4a**)**¹⁴ mp >300 °C (ethanol); ¹H NMR (400 MHz, DMSO, *d*₆) δ_H: 10.62 (1H, s, NH), 8.04-8.01 (1H, m, Ar-H), 7.83-7.80 (1H, m, Ar-H), 7.38-7.36 (1H, m, Ar-H), 7.30-7.23 (6H, m, Ar-H), 7.19-7.14 (3H, m, Ar-H), 6.89-6.84 (2H, m, Ar-H), 5.61 (2H, d, ³*J*_{HH} = 7.2 Hz, ArH), 3.95 (3H, s, OCH₃); ¹³C NMR (100 MHz, DMSO, *d*₆) δ_C: 189.7, 177.7, 161.0, 156.3,

142.1, 136.2, 134.4, 132.5, 132.4, 131.1, 130.9, 130.3, 128.6, 124.5, 121.6, 121.5, 115.3, 115.2, 113.4, 111.4, 109.1, 55.8.

5-(4-Methylphenyl)-5*H*-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-2',10,12-trione (4b) ¹⁴ mp >300 °C (ethanol); ¹H NMR (400 MHz, CDCl₃) δ_H: 7.60 (2H, m, H-Ar), 7.47-7.45 (2H, m, H-Ar), 7.30-7.28 (2H, m, H-Ar), 7.22-7.10 (4H, m, H-Ar), 6.94-6.91 (4H, m, H-Ar), 5.55 (2H, d, ³J_{HH} = 7.2 Hz, ArH), 2.61 (3H, s, CH₃); ¹³C NMR (100 MHz, DMSO, *d*₆) δ_C: 189.6, 177.6, 156.0, 142.1, 141.6, 136.2, 135.3, 134.4, 132.5, 132.4, 130.8, 130.7, 130.3, 129.7, 128.6, 124.5, 121.6, 121.5, 111.4, 109.1, 30.7.

5-(4-Nitrophenyl)-5*H*-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-2',10,12-trione (4c) ¹⁴ mp >300 °C (ethanol); ¹H NMR (400 MHz, DMSO, *d*₆) δ_H: 10.66 (1H, s, NH), 8.60-6.87 (14H, m, ArH), 5.55 (2H, d, ³J_{HH} = 7.2 Hz, ArH).

5-(4-Bromophenyl)-5*H*-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-2',10,12-trione (4d) ¹⁴ mp >300 °C (ethanol); ¹H NMR (400 MHz, DMSO, *d*₆) δ_H: 10.65 (1H, s, NH), 8.13-8.15 (1H, m, Ar-H), 8.00-7.93 (3H, m, Ar-H), 7.38-7.36 (1H, m, Ar-H), 7.27-7.22 (4H, m, Ar-H), 7.18-7.13 (3H, m, Ar-H), 6.87-6.82 (2H, m, Ar-H), 5.54 (2H, d, ³J_{HH} = 7.2 Hz, ArH).

5-Phenyl-5*H*-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-2',10,12-trione (4e) ¹⁴ mp >300 °C (ethanol); ¹H NMR (400 MHz, DMSO, *d*₆) δ_H: 10.65 (1H, s, NH), 8.13-8.11 (1H, m, Ar-H), 7.92-7.84 (2H, m, Ar-H), 7.78-7.74 (2H, m, Ar-H), 7.37-7.35 (1H, m, Ar-H), 7.23-7.22 (4H, m, Ar-H), 7.17-7.13 (1H, m, Ar-H), 7.01-7.06 (2H, m, Ar-H), 6.88-6.82 (2H, m, Ar-H), 5.43 (2H, d, ³J_{HH} = 7.2 Hz, ArH). ¹³C NMR (100 MHz, DMSO, *d*₆) δ_C: 189.6, 177.6, 155.8, 142.0, 138.0, 135.8, 134.5, 132.6, 131.8, 130.4, 128.6, 124.2, 121.4, 111.4, 109.1, 45.6.

5-(4-Methoxyphenyl)-5'-nitro-5*H*-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-2',10,12-trione (4f) ¹⁴ mp >300 °C (ethanol); ¹H NMR (400 MHz, DMSO, *d*₆) δ_H: 11.3 (1H,

s, NH), 8.40 (2H, m, Ar-H), 8.18-8.10 (2H, m, Ar-H), 7.81-7.78 (1H, m, Ar-H), 7.30-7.06 (8H, m, Ar-H) 5.59 (2H, d, $^3J_{\text{HH}} = 7.6$ Hz, ArH), 3.93 (3H, s, OCH₃); ^{13}C NMR (100 MHz, DMSO, d_6) δ_{C} : 189.7, 178.4, 161.1, 157.2, 148.8, 142.6, 136.2, 135.0, 132.7, 132.3, 131.3, 130.8, 130.6, 130.2, 126.2, 121.9, 121.6, 120.5, 115.3, 115.1, 110.1, 109.3, 55.8.

5'-Nitro-5-(4-nitrophenyl)-5H-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-

2',10,12-trione (4g) 14 mp >300 °C (ethanol); ^1H NMR (400 MHz, DMSO, d_6) δ_{H} : 11.43 (1H, s, NH), 7.09-8.67 (13H, m, ArH), 5.58 (2H, d, $^3J_{\text{HH}} = 7.5$ Hz, ArH); ^{13}C NMR (100 MHz, DMSO, d_6) δ_{C} : 189.7, 178.4, 156.6, 149.7, 149.2, 143.4, 143.0, 136.2, 135.3, 133.4 132.4, 131.0, 126.7, 126.0, 122.4, 122.1, 121.1, 110.8, 109.7.

5'-Nitro-5-(4-methylphenyl)-5H-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-

2',10,12-trione (4h) 14 mp >300 °C (ethanol); ^1H NMR (400 MHz, DMSO, d_6) δ_{H} : 11.38 (1H, s, NH), 8.41-8.40 (1H, m, ArH), 8.18-8.15 (1H, m, ArH), 8.10-8.08 (1H, m, ArH), 7.78-7.75 (1H, m, ArH), 7.59-7.23 (4H, m, ArH), 7.14-7.06 (3H, m, ArH), 5.52 (2H, d, $^3J_{\text{HH}} = 7.6$ Hz, ArH), 2.54 (3H, s, CH₃); ^{13}C NMR (100 MHz, DMSO, d_6) δ_{C} : 189.7, 178.4, 156.8, 148.8, 142.6, 141.6, 136.1, 135.2, 135.0, 132.6, 132.3, 130.7, 130.6, 129.9, 129.3, 126.2, 121.8, 121.6, 120.5, 110.1, 109.2, 30.7.

5-(4-Bromophenyl)-5'-nitro-5H-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-

2',10,12-trione (4i) 14 mp >300 °C (ethanol); ^1H NMR (400 MHz, DMSO, d_6) δ_{H} : 11.42 (1H, s, NH), 8.46-7.09 (13H, m, ArH), 5.57 (2H, d, $^3J_{\text{HH}} = 6.0$ Hz, ArH).

5'-Nitro-5-phenyl-5H-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-2',10,12-

trione (4j) 14 mp >300 °C (ethanol); ^1H NMR (400 MHz, DMSO, d_6) δ_{H} : 11.41 (1H, s, NH), 8.45-7.10(14H, m, ArH), 5.48 (2H, d, $^3J_{\text{HH}} = 7.2$ Hz, ArH).

5'-Bromo-5-(4-methylphenyl)-5H-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-

2',10,12-trione (4k) 14 mp>300°C (ethanol); ^1H NMR (400 MHz, DMSO, d_6) δ_{H} : 10.7 (1H, s, NH), 8.04-8.01 (1H, m, ArH), 7.74-7.29 (1H, m, ArH), 7.63-7.51(3H, m, ArH), 7.33-

7.31(1H, m, ArH), 7.23-7.21(4H, m ArH), 7.11-7.07(2H, m, ArH), 6.82-6.70(1H, m, ArH) 5.49-5.47(2H, d, $^3J_{\text{HH}} = 8$, ArH), 2.52(3H, s, CH₃); ^{13}C NMR (100 MHz, DMSO, d_6) δ_{C} : 189.7, 177.5, 156.5, 141.6, 136.6, 136.2, 135.3, 132.5, 132.4, 131.4, 130.7, 130.5, 129.9, 129.4, 127.4, 121.6, 113.6, 111.1, 110.7, 46.0, 21.2.

5'-Bromo-5-phenyl-5H-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-2',10,12-trione (4l) ¹⁴ mp>300°C (ethanol); ^1H NMR (400 MHz, DMSO, d_6) δ_{H} : 10.7 (1H, s, NH), 8.20-8.18 (1H, m, ArH), 7.89-7.67 (5H, m, ArH), 7.34-7.32(1H, m, ArH), 7.24-7.23(4H, m, ArH), 7.11-7.08(2H, m ArH), 6.81-6.79(1H, m, ArH) 5.42-5.40(2H, d, $^3J_{\text{HH}} = 7.2$, ArH); ^{13}C NMR (100 MHz, DMSO, d_6) δ_{C} : 189.6, 177.3, 156.2, 141.5, 137.8, 136.5, 136.1, 132.5, 132.3, 131.7, 131.3, 130.5, 130.3, 127.3, 121.6, 121.5, 113.5, 111.0, 110.7, 45.9.

5'-Bromo-5-(4-nitrophenyl)-5H-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-2',10,12-trione (4m) ¹⁴ mp>300°C (ethanol); ^1H NMR (400 MHz, DMSO, d_6) δ_{H} : 10.7 (1H, s, NH), 8.61-8.54 (3H, m, ArH), 8.27-8.14 (1H, m, ArH), 7.71(1H, m, ArH), 7.35-7.24(5H, m ArH), 7.12-7.08(2H, m, ArH) 6.82-6.70(1H, m, ArH), 5.53-5.51(2H, d, $^3J_{\text{HH}} = 7.2$, ArH).

5'-Bromo-5-(4-methoxyphenyl)-5H-spiro[diindeno[1,2-*b*:2',1'-*e*]pyridine-11,3'-indoline]-2',10,12-trione (4n) ¹⁴ mp>300°C (ethanol); ^1H NMR (400 MHz, DMSO, d_6) δ_{H} : 10.7 (1H, s, NH), 8.08-8.06 (1H, m, ArH), 7.78-7.65(1H, m, ArH), 7.33-7.13(10H, m ArH), 6.81-6.79(1H, m, ArH), 5.56-5.55(2H, d, $^3J_{\text{HH}} = 6.8$, ArH), 3.92(3H, s, OMe); ^{13}C NMR (100 MHz, DMSO, d_6) δ_{C} : 189.6, 177.3, 161.0, 156.6, 141.5, 136.5, 136.1, 132.5, 132.3, 131.2, 130.8, 130.4, 130.2, 121.6, 121.5, 115.2, 115.0, 113.4, 111.0, 110.7, 55.8, 45.9.