Supporting Information

Sulfamic Acid: A Mild, Efficient and Cost-Effective Catalyst for Synthesis of Indoloquinoxalines at ambient temperature

Pravin G. Hegade, Mansing M. Mane, Jayavant. D. Patil, Dattaprasad M. Pore*

Department of Chemistry, Shivaji University, Kolhapur 416 004, India

E-mail: p_dattaprasad@rediffmail.com

Table of content:

Page No.

A	General information	1
B	Typical procedure	1
C	Spectral data of representative synthesized Quinoxalines	2-21

A. General:

IR spectra were recorded on a Perkin–Elmer FT-IR 783 spectrophotometer. NMR spectra were recorded on a BrukerAC-300 MHz spectrometer in DMSO- d_6 using tetramethylsilane as an internal standard. Mass spectra were recorded on a Shimadzu QP2010 GCMS.

B. Typical procedure:

To a 25 ml round bottom flask, a mixture of isatin / acenaphthoquinone / 2-hydroxynaphthoquinone/ ninhydrin (1 mmol), *o*-phenylene diamine (1 mmol) in ethanol (95 %, 10 mL) and sulfamic acid (20 mol %) was added. The reaction mixture was stirred at ambient temperature for time mentioned in Table II, monitored by TLC. After completion of reaction, the mixture was filtered washed with ethanol and dried to furnish the desired pure products in high yields.

Table 2, Entry 1 : Yellow solid; M.P. 287 °C (lit. 290-292 °C)^{13a}; IR (KBr): 3401, 3115, 3065, 2824, 1617, 1596, 1407, 1338, 1244, 1210, 1135, 765, 746 cm⁻¹, ¹H-NMR (300 MHz, DMSO-d₆) : δ 7.26-7.31 (t, 1H, *J* = 15Hz), 7.49-7.76 (m, 4H), 7.99-8.01 (d, 1H, *J* = 6Hz), 8.16-8.19 (d, 1H, *J* = 9Hz), 8.29-8.32 (d, 1H, *J* = 9Hz), 11.78 (s, 1H) ; ¹³C NMR (75 MHz, DMSO-d₆): 112.16, 119.54, 120.65, 122.44 125.78, 127.73, 128.52, 129.29, 131.08, 139.07, 140.27, 140.63, 144.38, 146.32, MS(EI) (m/z): 219 (M⁺), 207, 192, 164, 129, 102, 90, 75, 63, 50.

Table 2, Entry 2 : Yellow solid; M.P. >300 °C (lit. 309 °C)¹⁴; IR (KBr): 3100, 1618, 1595, 1490, 1369, 1336, 1248, 1206, 1123, 917 cm⁻¹, ¹H-NMR (300 MHz, DMSO-d₆) : δ 3.91 (s, 3H), 7.31-7.35 (m, 1H), 7.50-7.53 (d, 1H, *J* = 9Hz), 7.68-7.85 (m, 3H), 8.04-8.07 (d, 1H, *J* = 9Hz), 8.22-8.24 (d, 1H, *J* = 6Hz), 11.82 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆): 56.22, 104.98, 113.42, 119.77, 120.85, 126.25, 127.89, 129.12, 129.44, 138.84, 139.02, 140.16, 140.64, 146.70, 154.68, MS(ESI) (m/z): 249 (M⁺), 234, 206, 179, 152, 129, 102, 90, 76, 63, 51.

Table 2, Entry 3 : Yellow solid; M.P. >300 °C; IR (KBr): 3100, 2850, 1617, 1393, 1210, 1467, 1280, 1120, 889 cm⁻¹, ¹H-NMR (300 MHz, DMSO-d₆) : δ 7.54-7.57 (d, 1H, *J* = 9Hz), 7.72-7.77 (m, 1H), 7.80-7.85 (m, 2H), 8.07-8.10 (dd, 1H, *J* = 3Hz, *J* = 9Hz), 8.23-8.26 (d, 1H, *J* = 9Hz), 8.46-8.47 (d, 1H, *J* = 3Hz), 12.21 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆): 112.96, 114.34, 121.31, 124.80, 126.53, 127.96, 129.42, 129.53, 133.79, 138.98, 139.20, 140.91, 143.09, 146.36, MS(ESI) (m/z): 297 (M⁺), 218, 191, 164, 148, 140, 116, 102, 90, 75, 63, 50.

Table 2, Entry 4 : Yellow solid; M.P. >300 °C ; IR (KBr): 3200, 1618, 1588, 1492, 1331, 1273, 1201, 1138, 867 cm⁻¹, ¹H-NMR (300 MHz, DMSO-d₆) : δ 2.46 (s, 3H), 2.53 (s, 3H), 7.25 (s, 1H), 7.60-7.72 (m, 2H), 7.93 (s, 1H), 7.99-8.02 (d, 1H, *J* = 9Hz), 8.10-8.18 (t, 1H, *J* = 12Hz), 11.75 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆): 16.98, 21.30, 119.22, 119.62, 121.38, 125.81, 127.79, 128.49, 129.92, 133.37, 139.09, 140.59, 141.75, 146.81, MS(ESI) (m/z): 246 (M⁺), 232, 219, 205, 179, 123, 90, 77, 65, 51.

Table 2, Entry 5 : Yellow solid; M.P. >293 °C (lit. 295-296 °C)¹⁴ ; IR (KBr): 3166, 1729, 1703, 1615, 1555, 1450, 1334, 1202, 1246, 823, 790, 758. cm⁻¹, ¹H-NMR (300 MHz, DMSO-d₆) : δ 2.39 (s, 3H), 7.23 – 7.42 (m, 4H), 7.74-7.77 (d, 1H, *J* = 9Hz), 8.11 (s, 1H), 8.35 - 8.37 (d, 1H, *J* = 6Hz),

11.62 (s, 1H, -NH); ^{13}C NMR (75 MHz, DMSO- d_6): 20.88, 111.89, 115.17, 116.12, 119.13, 123.11, 124.38, 125.10, 131.01, 133.05, 133.30, 135.16, 143.88, 146.85, 148.08.

Table 2, Entry 6: Pale yellow solid; M.P. 221 °C (lit. 221-225 °C)^{13f}; ^1H -NMR (300 MHz, DMSO- d_6) : δ 7.68-7.73 (m, 1H), 7.81-7.84 (m, 1H), 7.86-7.94 (m, 3H), 8.06-8.08 (dd, 1H, $J = 1\text{Hz}$, $J = 7\text{Hz}$), 8.11-8.14 (dd, 1H, $J = 8.1\text{Hz}$), 8.15-8.17 (dd, 1H, $J = 1.8\text{Hz}$, $J = 8.1$) ^{13}C NMR (75 MHz, DMSO- d_6): 122.74, 124.68, 129.79, 130.83, 131.40, 132.91, 133.24, 137.42, 142.27, 142.56, 156.68, 189.90, MS(ESI) (m/z): 232 (M^+), 204, 177, 130, 102, 76, 63.

Table 2, Entry 7: Pale yellow solid; M.P. 222-224 °C ; ^1H -NMR (300 MHz, DMSO- d_6) : δ 7.38-7.41 (d, 1H, $J = 9\text{Hz}$), 7.45-7.52 (m, 2H), 7.66-7.69 (dd, 1H, $J = 3$, $J = 3\text{ Hz}$), 7.84-7.87 (t, 1H, $J = 6\text{Hz}$), 8.22-8.23 (d, 1H, $J = 3\text{Hz}$), 8.33-8.35 (t, 1H, $J = 3\text{Hz}$), 12.04 (s, 1H, -NH); ^{13}C NMR (75 MHz, DMSO- d_6): 113.65, 115.22, 118.39, 119.72, 123.76, 124.53, 125.67, 127.78, 131.04, 132.49, 136.39, 143.75, 146.55, 146.96.

Table 2, Entry 8: White Solid; M.P 243 °C (lit. 242-245 °C)^{13f}; IR (KBr): 3052, 1616, 1483, 1435, 1299, 1209, 1097, 1032, 831, 783 cm^{-1} , ^1H -NMR (300 MHz, DMSO- d_6) : δ 7.84-7.87 (dd, 2H, $J = 3.6\text{Hz}$, $J = 6\text{Hz}$), 7.92-7.97 (dd, 2H, $J = 9\text{Hz}$, $J = 8.1\text{Hz}$), 8.20-8.23 (dd, 2H, $J = 3\text{Hz}$, $J = 6\text{Hz}$), 8.29-8.32 (d, 2H, $J = 6\text{Hz}$), 8.41-8.44 (d, 2H, $J = 7.2\text{Hz}$), ^{13}C NMR (75 MHz, DMSO- d_6): 122.58, 129.59, 129.88, 130.12, 130.19, 130.46, 131.53, 141.15, 153.87, MS(ESI) (m/z): 254 (M^+), 201, 178, 151, 113, 87, 63.

Table 2, Entry 9: Yellow solid; M.P 263 °C; ^1H -NMR (300 MHz, DMSO- d_6) : δ 7.20 (s, 1H), 7.85-7.93 (m, 4H), 8.15-8.17 (d, 1H, $J = 6\text{Hz}$), 8.28-8.34 (m, 2H), 9.25-9.28 (t, 1H, $J = 6\text{Hz}$), 11.59 (s, 1H), ^{13}C NMR (75 MHz, DMSO- d_6): 103.73, 123.25, 125.17, 128.10, 128.63, 129.61, 129.93, 130.06, 131.52, MS(ESI) (m/z): 246 (M^+), 218, 190, 164, 130, 102, 77, 63.

Table 2, Entry 1:

Table 2, Entry 2:

Table 2, Entry 3:

Table 2, Entry 4:

Table 2, Entry 5:

Table 2, Entry -6:

Table 2, Entry -7:

Table 2, Entry -8:

Table 2, Entry 9:

Table 2, Entry 10:

Table 2, Entry 11:

Table 2, Entry 12: