SUPPORTING INFORMATION

InCl₃-assisted synthesis of pyrano[2,3-*a*]carbazoles via multi-component reaction

Ezhumalai Yamuna,^a Karnam Jayarampillai Rajendra Prasad^{b*}

^aDepartment of Chemistry, Tamkang University, Tamsui- 25137, Taiwan.

^bDepartment of Chemistry, Bharathiar University, Coimbatore-641046, India.

*General procedure for the preparation of pyrano[2,3-*a*]carbazoles (2/3 a-d)*

To a mixture of 1-hydroxycarbazole (1 mmol), Malononitrile (1 mmol) and benzaldehyde/Isatin (1 mmol), InCl₃ (25 mol %) was dissolved in CH₃CN and subjected to microwave irradiation (Biotage microwave oven, 70°C, 2 bar pressure) for 10 min. The progress of the reaction was monitored by thin-layer chromatography. Upon cooling, the product precipitated from the reaction mixture, which was filtered, dried, and recrystallized from ethanol.

*2-Amino-9-methyl-4-phenyl-4,11-dihydropyrano[2,3-*a*]carbazole-3-carbonitrile (2b);*

Light yellow solid (0.322 g, 92 %); mp: 264 °C; IR (KBr) 3469, 3419, 3329, 2196, 1632 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 2.51 (s, 3H, 9-CH₃), 4.88 (s, 1H, benzylic hydrogen), 6.66 (s, 2H, 2-NH₂), 7.02 (d, 1H, 5-H, *J* = 8.50 Hz), 7.18--7.11 (m, 3H, 2'-H, 4'-H & 6'-H), 7.20 (t, 2H, 3'-H & 5'-H, *J* = 8.0 Hz), 7.24 (d, 1H, 8-H, *J* = 8.50 Hz), 7.36 (s, 1H, 10-H), 7.54 (d, 1H, 6-H, *J* = 8.50 Hz), 8.01 (d, 1H, 7-H, *J* = 8.50 Hz), 11.40 (bs, 1H, 11-H); ¹³C NMR (CDCl₃, 125 MHz) δ: 21.20, 41.32, 58.03, 112.12, 116.42, 119.21, 119.53, 120.12, 120.44, 120.49, 120.62, 120.83, 123.84, 127.42, 128.71, 130.12, 135.03, 138.42, 146.32, 160.41. MS: *m/z* (%) 351 (M⁺, 100), 349 (19), 336 (6), 259 (21), 234 (14), 153 (11), 108 (9),

* Corresponding author e-mail: prasad_125@yahoo.com

77 (12); Anal. Calcd for $C_{23}H_{17}N_3O$: C, 78.61; H, 4.88; N, 11.96%. Found : C, 78.65; H, 4.92; N, 11.99%.

2'-Amino-2-oxo-11'H-spiro[indoline-3,4'-pyrano[2,3-a]carbazole]-3'-carbonitrile (3a);

Light yellow solid (0.351 g, 93%); mp: 168 °C; IR (KBr) 3432, 3329, 3290, 2217, 1717, 1637 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.21 (s, 2H, 2-NH₂), 6.29 (d, 1H, 5-H, $J = 8.0$ Hz), 7.02 (d, 1H, 4'-H, $J = 7.5$ Hz), 7.11 (t, 1H, 5'-H, $J = 7.5$ Hz), 7.18 (t, 1H, 6'-H, $J = 7.5$ Hz), 7.30 (d, 1H, 7'-H, $J = 7.5$ Hz), 7.36 (dt, 1H, 9-H, $J = 8.0$ Hz, $J = 1.0$ Hz), 7.45 (dt, 1H, 8-H, $J = 8.0$ Hz, $J = 1.0$ Hz), 7.50 (dd, 1H, 10-H, $J = 8.0$ Hz, $J = 1.0$ Hz), 7.78 (d, 1H, 6-H, $J = 8.0$ Hz), 8.08 (d, 1H, 7-H, $J = 8.0$ Hz), 10.73 (bs, 1H, 1'-H), 11.23 (bs, 1H, 11-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 52.33, 58.42, 112.21, 116.76, 118.71, 119.14, 119.42, 119.76, 120.61, 122.23, 122.83, 123.83, 124.21, 124.89, 125.32, 126.12, 126.92, 131.41, 134.32, 140.41, 147.43, 160.20, 163.54. MS: m/z (%) 378 (M^+ , 100), 247 (24), 131 (17), 213 (15), 165 (23), 119 (8), 115 (6). Anal. Calcd for $C_{23}H_{14}N_4O_2$: C, 73.01; H, 3.73; N, 14.81%. Found: C, 73.05; H, 3.69; N, 14.86%.

2'-Amino-9'-methyl-2-oxo-11'H-spiro[indoline-3,4'-pyrano[2,3-a]carbazole]-3'-carbonitrile (3b);

Brown solid (0.352 g, 90 %); mp: 142 °C; IR (KBr) 3415, 3353, 3286, 2181, 1716, 1613 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.20 (s, 2H, 2-NH₂), 6.89 (d, 1H, 5-H, $J = 8.0$ Hz), 7.00 (d, 1H, 4'-H, $J = 8.0$ Hz), 7.12 (t, 1H, 5'-H, $J = 8.0$ Hz), 7.21 (t, 1H, 6'-H, $J = 8.0$ Hz), 7.25 (d, 1H, 7'-H, $J = 8.0$ Hz), 7.46 (s, 1H, 10-H), 7.51 (d, 1H, 8-H, $J = 8.0$ Hz), 7.66 (d, 1H, 6-H, $J = 8.0$ Hz), 8.01 (d, 1H, 7-H, $J = 8.0$ Hz), 10.69 (bs, 1H, N'-H), 11.74 (bs, 1H, 11-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 21.52, 52.23, 58.47, 111.62, 116.47, 118.77, 119.32, 119.72, 120.43, 120.57, 120.67, 120.73, 121.21, 122.88, 124.39, 124.52, 124.98, 130.48, 131.15, 134.38, 139.79, 146.76, 160.18, 163.63. MS: m/z (%) 392 (M^+ , 100), 273 (21), 192 (17), 179

14), 144 (9), 129 (15), 119 (10), 118 (9). Anal. Calcd for $C_{24}H_{16}N_4O_2$: C, 73.46; H, 4.11; N, 14.28%. Found : C, 73.39; H, 4.15; N, 14.24%.

2-Amino-10-methyl-4-phenyl-4,11-dihydropyrano[2,3-a]carbazole-3-carbonitrile (2c);

Light yellow solid (0.315 g, 90 %); mp: 282 °C; IR (KBr) 3475, 3417, 3318, 2189, 1648 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.53 (s, 3H, 10-CH₃), 4.78 (s, 1H, benzylic hydrogen), 6.68 (s, 2H, 2-NH₂), 7.08 (d, 1H, 5-H, $J = 8.00$ Hz), 7.22-7.10 (m, 3H, 2'-H, 4'-H & 6'-H), 7.26 (t, 2H, 3'-H & 5'-H, $J = 8.0$ Hz), 7.28 (t, 1H, 8-H, $J = 8.00$ Hz), 7.40 (d, 1H, 9-H, $J = 8.00$ Hz), 7.63 (d, 1H, 6-H, $J = 8.00$ Hz), 7.94 (d, 1H, 7-H, $J = 8.00$ Hz), 11.22 (bs, 1H, 11-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 16.80, 41.41, 58.05, 116.17, 118.19, 119.12, 119.49, 120.32, 120.71, 120.83, 121.43, 121.72, 122.92, 126.34, 127.34, 128.11, 135.14, 139.19, 145.88, 160.83. MS: m/z (%) 351 (M^+ , 100), 349 (21), 336 (11), 259 (10), 234 (9), 153 (7), 108 (11), 77 (10); Anal. Calcd for $C_{23}H_{17}N_3O$: C, 78.61; H, 4.88; N, 11.96%. Found : C, 78.56; H, 4.83; N, 11.91%.

2'-Amino-10'-methyl-2-oxo-11'H-spiro[indoline-3,4'-pyrano[2,3-a]carbazole]-3'-carbonitrile (3c);

Brown solid (0.352 g, 90 %); mp: 172 °C; IR (KBr) 3416, 3351, 3285, 2176, 1715, 1613 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.27 (s, 2H, 2-NH₂), 6.89 (d, 1H, 4'-H, $J = 8.0$ Hz), 7.10 (t, 1H, 5'-H, $J = 8.0$ Hz), 7.18 (t, 1H, 6'-H, $J = 8.0$ Hz), 7.26 (t, 1H, 7'-H, $J = 8.0$ Hz), 7.28 (t, 1H, 8-H, $J = 8.0$ Hz), 7.33 (d, 1H, 5-H, $J = 8.0$ Hz), 7.42 (d, 1H, 9-H, $J = 8.0$ Hz), 7.55 (d, 1H, 6-H, $J = 8.0$ Hz), 7.83 (d, 1H, 7-H, $J = 8.0$ Hz), 10.77 (bs, 1H, N'-H), 11.83 (bs, 1H, 11-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 16.74, 52.12, 58.44, 117.10, 118.18, 119.10, 119.19, 119.43, 120.17, 120.37, 120.74, 121.33, 121.66, 124.19, 124.38, 125.12, 126.63, 131.12, 134.41, 139.39, 160.24, 163.32. MS: m/z (%) 392 (M^+ , 100), 273 (18), 192 (23), 179 (17), 144 (8), 129 (13), 119 (11), 118 (8). Anal. Calcd for $C_{24}H_{16}N_4O_2$: C, 73.46; H, 4.11; N, 14.28%. Found : C, 73.40; H, 4.16; N, 14.26%.

2-Amino-8-methyl-4-phenyl-4,11-dihydropyrano[2,3-a]carbazole-3-carbonitrile (2d);

Light yellow solid (0.315 g, 90 %); mp: 215 °C; IR (KBr) 3442, 3306, 3212, 2216, 1647 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 2.45 (s, 3H, 8-CH₃), 4.89 (s, 1H, benzylic hydrogen), 6.64 (s, 2H, 2-NH₂), 6.89 (d, 1H, 5-H, $J = 8.0$ Hz), 7.21-7.16 (m, 3H, 2'-H, 4'-H & 6'-H), 7.30 (t, 2H, 3'-H & 5'-H, $J = 8.0$ Hz), 7.39 (dt, 1H, 9-H, $J_o = 8.0$ Hz, $J_m = 2.0$ Hz), 7.52 (d, 1H, 10-H, $J = 8.0$ Hz), 7.68 (d, 1H, 6-H, $J = 8.0$ Hz), 7.89 (s, 1H, 7-H), 11.12 (bs, 1H, 11-H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 21.60, 41.20, 58.14, 111.73, 116.68, 119.36, 119.43, 120.42, 120.83, 121.43, 121.93, 124.17, 126.32, 127.69, 128.75, 128.94, 135.01, 139.12, 146.59, 160.32; MS: m/z (%) 351 (M^+ , 100), 349 (12), 336 (8), 259 (16), 234 (6), 153 (8), 108 (14), 77 (18); Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{N}_3\text{O}$: C, 78.61; H, 4.88; N, 11.96%. Found : C, 78.58; H, 4.84; N, 11.92%.

2'-Amino-8'-methyl-2-oxo-11'H-spiro[indoline-3,4'-pyrano[2,3-a]carbazole]-3'-carbonitrile (3d);

Brown solid (0.368 g, 94 %); mp: 168 °C; IR (KBr) 3432, 3358, 3293, 2187, 1713, 1619 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 6.19 (s, 2H, 2-NH₂), 6.25 (d, 1H, 5-H, $J = 8.0$ Hz), 7.02 (d, 1H, 4'-H, $J = 8.0$ Hz), 7.11 (t, 1H, 5'-H, $J = 8.0$ Hz), 7.25 (t, 1H, 6'-H, $J = 8.0$ Hz), 7.29 (d, 1H, 7'-H, $J = 8.0$ Hz), 7.38 (t, 1H, 9-H, $J = 8.0$ Hz), 7.48 (d, 1H, 10-H, $J = 8.0$ Hz), 7.73 (d, 1H, 6-H, $J = 8.0$ Hz), 7.87 (s, 1H, 7-H), 10.71 (bs, 1H, N'-H), 11.65 (bs, 1H, 11-H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 21.31, 52.14, 58.38, 111.54, 116.17, 118.19, 119.23, 119.43, 120.63, 120.82, 120.94, 120.99, 124.37, 124.45, 124.63, 125.46, 125.89, 128.42, 131.15, 134.43, 139.15, 146.96, 160.38, 163.34. MS: m/z (%) 392 (M^+ , 100), 273 (19), 192 (21), 179 (20), 144 (12), 129 (10), 119 (8), 118 (6). Anal. Calcd for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_2$: C, 73.46; H, 4.11; N, 14.28%. Found : C, 73.41; H, 4.16; N, 14.34%.

IR Spectrum of compound **2a**

^1H -NMR Spectrum of compound **2a**

^{13}C -NMR Spectrum of compound **2a**

^1H -NMR Spectrum of compound **2c**

^1H -NMR Spectrum of compound **2d**

IR Spectrum of compound **3a**

¹H-NMR Spectrum of compound **3a**

¹³C-NMR Spectrum of compound **3a**

¹H-NMR Spectrum of compound **3d**