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Synthesis of 3-acyl-1-hydroxy-1*H*-indole-5,6-dicarbonitriles

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4-(1-Chloro-3-oxo-1-phenylprop-1-en-2-yl)-5-nitrobenzene-1,2-dicarbonitrile 4a: Yield 64 %, mp 129-130 °C (ethanol). IR (ν/cm^{-1}): 2240 (C≡N), 1678 (C=O), 1615 (C=C), 1532 (NO_2), 1350 (NO_2). MS, *m*/*z* (%): 339 [M^+] (1), 337 [M^+] (8), 292 (17), 274 (32), 228 (21), 215 (28), 201 (23), 200 (21), 176 (20), 169 (22), 153 (54), 126 (62), 125 (92), 105 (100), 89 (29), 77 (69), 63 (36), 43 (42). ^{1}H NMR (DMSO-d_6) δ: ***E*** –isomer 87 %, 7.64 (t, 2H, H-3', H-5', *J* 7.3 Hz), 7.67 (t, 1H, H-4', *J* 7.3 Hz), 7.72 (d, 2H, H-2', H-6', *J* 7.3 Hz), 8.63 (s, 1H, H-3), 9.06 (s, 1H, H-6), 9.43 (s, 1H, COH). ***Z*** –isomer 13%, 7.39 (m, 4H, H-2', H-3',H-5',H-6'), 7.46 (t, 1H, H-4', *J* 7.3 Hz), 8.04 (s, 1H, H-3), 8.93 (s, 1H, H-6), 10.30 (s, 1H, COH). Found (%):C, 60.20; H, 2.28; N, 12.41. $C_{17}H_8ClN_3O_3$. Calculated (%): C, 60.46; H, 2.39; N, 12.44.

4-[1-Chloro-1-(4-methylphenyl)-3-oxoprop-1-en-2-yl]-5-nitrobenzene-1,2-dicarbonitrile 4b: Yield 72 %, mp 167-168 °C (ethanol). IR (ν/cm^{-1}): 2239 (C≡N), 1665 (C=O), 1614 (C=C), 1586 (Ar), 1534 (NO_2), 1351 (NO_2). MS, *m*/*z* (%): 353 [M^+] (1), 351 [M^+] (3), 322 [M-COH] (10), 288 (16), 215 (8), 167 (15), 139 (21), 119 (100), 91 (24). ^{1}H NMR (DMSO-d_6) δ: ***E*** –isomer 90 %, 2.45 (s, 3H, Me), 7.42 (d, 2H, H-3', H-5', *J* 8.0 Hz), 7.60 (d, 2H, H-2', H-6', *J* 8.0 Hz), 8.57(s, 1H, H-3), 9.02 (s, 1H, H-6), 9.42 (s, 1H, COH). ***Z*** –isomer 10% 2.30 (s, 3H, Me), 7.18 (d, 2H, H-3', H-5', *J* 8.0 Hz), 7.28 (d, 2H, H-2', H-6' *J* 8.0 Hz), 8.04(s, 1H, H-3), 8.91 (s, 1H, H-6), 10.27 (s, 1H, COH). Found (%):C, 61.20; H, 2.68; N, 11.89. $C_{18}H_{10}ClN_3O_3$. Calculated (%): C, 61.46; H, 2.87; N, 11.95.

4-[1-Chloro-3-oxo-1-(thiophen-2-yl)prop-1-en-2-yl]-5-nitrobenzene-1,2-dicarbonitrile 4d: Yield 59 %, mp 158-160 °C (ethanol). IR (ν/cm^{-1}): 2241 (C≡N), 1666 (C=O), 1599 (Ar), 1536 (NO_2), 1354 (NO_2). MS, *m*/*z* (%): 345 (2), 343 [M^+] (5), 314 [M-COH] (10), 308 (14), 298 (40), 280 (38), 270 (20), 249 (16), 235 (62), 221 (92), 209 (35), 194 (21), 189 (47), 180 (18), 169 (28), 161 (85), 159 (100), 133 (28), 132 (27), 126 (24), 113 (58), 111 (43), 95 (72), 69 (13). ^{1}H NMR (DMSO-d_6) δ: ***E*** –isomer 81 %, 7.32 (d.d., 1H, H-4', ^3J 3.2 Hz, ^3J 5.2 Hz), 7.78(d, 1H, H-3', *J* 3.2 Hz), 8.17 (d, 1H, H-5', *J* 5.2 Hz), 8.58 (s, 1H, H-3), 9.02 (s, 1H, H-6), 9.71 (s, 1H, COH). ***Z*** – isomer 19%, 7.14 (d.d., 1H, H-4', ^3J 3.2 Hz, ^3J 5.2 Hz), 7.48 (d, 1H, H-3', *J* 3.2 Hz), 7.98 (d,

1H, H-5', *J* 5.2 Hz,), 8.43(s, 1H, H-3), 9.06 (s, 1H, H-6), 10.25(s, 1H, COH). Found (%):C, 51.22; H, 1.68; N, 12.08. $C_{15}H_6ClN_3O_3S$. Calculated (%): C, 52.41; H, 1.76; N, 12.22.

3-Benzoyl-1-hydroxy-1*H*-indole-5,6-dicarbonitrile 5a: Yield 53 %, mp 205-206 °C (ethanol). IR (ν/cm^{-1}): 3563 (OH), 2227 (C≡N), 1667 (C=O), 1590 (Ar). MS, *m*/*z* (%): 287 [M$^+$] (17), 271 [M$^+$-O] (5), 210 (18), 115 (25), 77(100). ^{1}H NMR (DMSO-d_6) δ: 7.58 (t, 2H, H-3', H-5', *J* 7.8 Hz), 7.68 (t, 1H, H-4', *J* 7.8 Hz), 7.85 (d, 2H, H-2', H-6', *J* 7.8 Hz), 8.46 (s, 1H, H-4), 8.61 (s, 1H, H-2), 8.81 (s, 1H, H-7), 12.89 (s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 188.59, 138.65, 137.77, 133.71, 132.08, 128.62 (2C), 128.59 (2C), 128.39, 124.59, 116.96, 116.85, 116.66, 110.54, 107.47, 106.85. Found (%):C, 70.83; H, 3.11; N, 14.58. $C_{17}H_9N_3O_2$. Calculated (%): C, 71.08; H, 3.16; N, 14.63.

1-Hydroxy-3-(4-methoxybenzoyl)-1*H*-indole-5,6-dicarbonitrile 5c: Yield 71 %, mp 291-293 °C (ethanol). IR (ν/cm^{-1}): 3582 (OH), 2230 (C≡N), 1631 (C=O), 1587 (Ar). MS, *m*/*z* (%): 317 [M$^+$] (3), 301 [M$^+$-O] (100), 270 (24), 194 (84), 135 (86), 92 (39). ^{1}H NMR (DMSO-d_6) δ:3,87 (s, 3H, OMe), 7.10 (d, 2H, H-3', H-5', *J* 8.7 Hz), 7.87 (d, 2H, H-2', H-6', *J* 8.7 Hz), 8.44 (s, 1H, H-4), 8.62 (s, 1H, H-2), 8.77 (s, 1H, H-7), 12.86 (s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ: 187.20, 162.59, 137.22, 133.64, 131.09 (2C), 129.07, 128.59, 124.80, 117.16, 116.86, 116.58, 114.01 (2C), 110.80, 107.34, 106.63, 55.56. Found (%):C, 67.92; H, 3.32; N, 13.14. $C_{18}H_{11}N_3O_3$. Calculated (%): C, 68.14; H, 3.49; N, 13.24.

1-Hydroxy-3-(2-thienylcarbonyl)-1*H*-indole-5,6-dicarbonitrile 5d: Yield 48 %, mp 234-235 °C (ethanol). IR (ν/cm^{-1}): 3568 (O-H), 2238 (C≡N), 1654 (C=O), 1586 (Ar). MS, *m*/*z* (%): 293 [M$^+$] (31), 276 [M$^+$-OH] (27), 111 (100). ^{1}H NMR (DMSO-d_6) δ: 7.31 (d.d, 1H, H-4', ^3J 3.9 Hz, ^3J 4.9 Hz), 8.06 (d.d, 1H, H-5', ^3J 4.9 Hz, ^4J 0.8 Hz), 8.07 (d.d, 1H, H-3', ^3J 3.9 Hz, ^4J 0.8 Hz), 8.45 (s, 1H, H-4), 8.79 (s, 1H, H-2), 8.99 (s, 1H, H-7), 12.93 (s, 1H, OH). Found (%):C, 61.32; H, 2.28; N, 17.24. $C_{15}H_7N_3O_2S$. Calculated (%): C, 61.43; H, 2.41; N, 14.33.

1-Methoxy-3-(4-methylbenzoyl)-1*H*-indole-5,6-dicarbonitrile 6b: Yield 83 %, mp 274-275 °C (ethanol). IR (ν/cm^{-1}): 2235 (C≡N), 1642 (C=O), 1607 (Ar). MS, *m*/*z* (%): 315 [M$^+$] (33), 284 [M$^+$-MeO] (3), 224 (27), 119 (22), 91 (100), 65 (93). ^{1}H NMR (DMSO-d_6) δ: 2.43 (s, 3H, Me), 4.26 (s, 3H, OMe), 7.40 (d, 2H, H-3', H-5', *J* 8.0 Hz), 7.81 (d, 2H, H-2', H-6', *J* 8.0 Hz), 8.64 (s, 1H, H-4), 8.83 (s, 1H, H-2), 8.90 (s, 1H, H-7). Found (%):C, 72.12; H, 4.08; N, 13.29. $C_{19}H_{13}N_3O_2$. Calculated (%): C, 72.37; H, 4.16; N, 13.33.

1-Methoxy-3-(4-methoxybenzoyl)-1*H*-indole-5,6-dicarbonitrile 6c: Yield 79 %, mp 250-251 °C (ethanol). IR (ν/cm^{-1}): 2237 (C≡N), 1659 (C=O), 1615, 1585 (Ar). MS, *m*/*z* (%): 331 [M$^+$] (100), 300 [M$^+$-MeO] (41), 272 (27), 135 (17). ^{1}H NMR (DMSO-d_6) δ: 3.88 (s, 3H, OMe), 4.26

(s, 3H, OMe), 7.11 (d, 2H, H-3', H-5', *J* 8.4 Hz), 7.91 (d, 2H, H-2', H-6', *J* 8.4 Hz), 8.59 (s, 1H, H-4), 8.79 (s, 1H, H-2), 8.86 (s, 1H, H-7). Found (%):C, 68.67; H, 3.78; N, 12.54. $C_{19}H_{13}N_3O_3$. Calculated (%): C, 68.88; H, 3.95; N, 12.68.

1-Methoxy-3-(2-thienylcarbonyl)-1*H*-indole-5,6-dicarbonitrile 6d: Yeld 66 %, mp 253-254 °C (ethanol). IR (ν/cm^{-1}): 2234 (C≡N), 1621 (C=O), 1514 (Ar). MS, *m*/*z* (%): 307 [M$^+$] (100), 276 [M$^+$-MeO] (56), 248 (36), 111 (44). ^{1}H NMR (DMSO-d_6) δ: 4.29 (s, 3H, OMe), 7.33 (d.d, 1H, H-4',^3J 3.8 Hz, ^3J 4.9 Hz), 8.09 (d.d, 1H, H-5', ^3J 4.9 Hz, ^4J 1.0 Hz), 8.15 (d.d, 1H, H-3', ^3J 3.8 Hz, ^4J 1.0 Hz), 8.64 (s, 1H, H-4), 8.80 (s, 1H, H-2), 9.23 (s, 1H, H-7). Found (%):C, 62.24; H, 2.88; N, 13.61. $C_{16}H_9N_3O_2S$. Calculated (%): C, 62.53; H, 2.95; N, 13.67.

3-Formyl-1-methoxy-2-(4-methylphenyl)-1*H*-indole-5,6-dicarbonitrile 7b: Yield 77 %, mp 240-241 °C (decomp.). IR (ν/cm^{-1}): 2228 (C≡N), 1658 (C=O), 1609 (Ar). MS, *m*/*z* (%): 315 [M$^+$] (43), 300 (41), 284 [M$^+$- OMe] (100), 254 (16). ^{1}H NMR (DMSO-d_6) δ: 2.46 (s, 3H, Me), 3.92 (s, 3H, OMe), 7.50 (d, 2H, H-3', H-5', *J* 8.2 Hz), 7.76 (d, 2H, H-2', H-6', *J* 8.2 Hz), 8.69 (s, 1H, H-4), 8.78 (s, 1H, H-7), 9.80 (s, 1H, COH). ^{13}C NMR (DMSO-d_6) δ: 185.22, 149.19, 141.34, 132.03, 130.66 (2C), 129.60 (2C), 127.26, 122.89, 121.48, 116.70, 116.60, 116.47, 110.49, 108.45, 108.07, 66.97, 21.01. Found (%):C, 72.09; H, 4.08; N, 13.30. $C_{19}H_{13}N_3O_2$. Calculated (%): C, 72.37; H, 4.16; N, 13.33.

3-Formyl-1-methoxy-2-(4-methoxyphenyl)-1*H*-indole-5,6-dicarbonitrile 7c: Yield 44 %, mp 246-248°C (decomp.). IR (ν/cm^{-1}): 2228 (C≡N), 1664 (C=O), 1611 (Ar). MS, *m*/*z* (%): 331 [M$^+$] (51), 300 [M$^+$-MeO] (100), 257 (51), 228 (18). ^{1}H NMR (DMSO-d_6) δ: 3.89 (s, 3H, OMe), 3.91 (s, 3H, OMe), 7.23 (d, 2H, H-3', H-5', *J* 8.8 Hz), 7.82 (d, 2H, H-2', H-6', *J* 8.8 Hz), 8.66 (s, 1H, H-4), 8.81 (s, 1H, H-7), 9.82 (s, 1H, COH). Found (%):C, 68.56; H, 3.78; N, 12.59. $C_{19}H_{13}N_3O_3$. Calculated (%): C, 68.88; H, 3.95; N, 12.68.

3-Formyl-1-methoxy-2-(2-thienyl)-1*H*-indole-5,6-dicarbonitrile 7d: Yield 70 %, mp 242-244°C (decomp.). IR (ν/cm^{-1}): 2226 (C≡N), 1660 (C=O), 1605 (Ar). MS, *m*/*z* (%): 307 [M$^+$] (10), 276 [M$^+$-MeO] (100), 221 (24), 204 (39), 139 (18), 109 (14). ^{1}H NMR (DMSO-d_6) δ: 4.08 (s, 3H, OMe), 7.42 (d.d., 1H, H-4', ^3J 5.0 Hz, ^3J 3.8 Hz), 8.06 (d.d., 1H, H-3', ^3J 3.8 Hz, ^4J 1.0 Hz), 8.12 (d.d., 1H, H-5', ^3J 5.0 Hz, ^4J 1.0 Hz), 8.69 (s, 1H, H-4), 8.81 (s, 1H, H-7), 10.12 (s, 1H, COH). Found (%):C, 62.37; H, 2.81; N, 13.61. $C_{16}H_9N_3O_2S$. Calculated (%): C, 62.53; H, 2.95; N, 13.67.