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SUPPLEMENTARY MATERIAL TO

Green one-pot, four-component synthesis of spiro[indoline-3,4′--pyrano[2,3-*c*]pyrazole] derivatives using amino-functionalized nanoporous silica under solvent-free conditions

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SPECTRAL DATA FOR THE SPIRO[INDOLINE-3,4′-PYRANO[2,3-*c*]PYRAZOLE] DERIVATIVES **5a**–**f**

*6′-Amino-3′-methyl-2-oxo-1′*H*-spiro[indoline-3,4′-pyrano[2,3-*c*]pyrazole]--5′-carbonitrile (**5a**)*. M.p.: 278–280 °C; Anal. Calcd. for $C_{15}H_{11}N_5O_2$: C, 61.43; H, 3.78; N, 23.88 %. Found: C, 61.51; H, 3.66; N, 23.69 %; IR (KBr, cm^{-1}): 3337 (NH stretching of secondary amine), 3389 and 3131 (NH_2 stretching of primary amine), 2182 (CN stretching of nitrile), 1712 (CO stretching of amide), 1641 (C=N stretching of pyrazole ring), 1583, 1519, 1497, 1470, 1410, 1319, 1285, 1207, 1154, 1053, 930, 754, 697; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.52 (3H, *s*, CH_3), 6.90 (1H, *d*, *J* = 7.6 Hz, Ar-H), 6.97–7.04 (2H, *m*, Ar-H), 7.22–7.26 (3H, *m*, Ar-H & NH_2), 10.60 (1H, *s*, NH), 12.29 (1H, *s*, NH); ^{13}C--NMR (62.9 MHz, DMSO-d_6, δ / ppm): 9.4, 47.7, 55.3, 95.8, 110.1, 119.2, 123.0, 124.3, 129.3, 133.0, 135.2, 141.8, 155.7, 162.9, 178.5; EIMS (*m*/*z* (relative abundance)): 293 (4), 267 (30), 208 (12), 179 (12), 152 (14), 140 (15), 115 (17), 66 (28), 43 (63), 29 (100).

*6′-Amino-5-bromo-3′-methyl-2-oxo-1′*H*-spiro[indoline-3,4′-pyrano[2,3-*c*]-pyrazole]-5′-carbonitrile (**5b**)*. M.p.: 281–283 °C; Anal. Calcd. for $C_{15}H_{10}BrN_5O_2$: C, 48.41; H, 2.71; N, 18.82 %. Found: C, 48.51; H, 2.69; N, 18.90 %; IR (KBr, cm^{-1}): 3346 (NH stretching of secondary amine), 3133 (NH_2 stretching of primary amine), 2181 (CN stretching of nitrile), 1713 (CO stretching of amide), 1643 (C=N stretching of pyrazole ring), 1608, 1580, 1499, 1473, 1412, 1297, 1206, 1156, 1053, 922, 821, 692; ^{1}H-NMR (250 MHz, DMSO-d_6, δ / ppm): 1.55 (3H, *s*, CH_3), 6.86 (1H, *s*, Ar-H), 7.21–7.36 (4H, *m*, Ar-H and

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NH_2), 10.75 (1H, *s*, NH), 12.33 (1H, *s*, NH); ^{13}C-NMR (62.9 MHz, DMSO-d_6, δ / ppm): 9.4, 47.9, 54.9, 95.1, 112.2, 114.6, 119.1, 127.7, 132.2, 135.2, 135.5, 141.1, 155.6, 162.9, 178.0.

*6′-Amino-1-benzyl-3′-methyl-2-oxo-1′*H*-spiro[indoline-3,4′-pyrano[2,3-*c*]-pyrazole]-5′-carbonitrile (**5c**)*. M.p.: 268–270 °C; Anal. Calcd. for $C_{22}H_{17}N_5O_2$: C, 68.92; H, 4.47; N, 18.27 %. Found: C, 68.71; H, 4.39; N, 18.47 %; IR (KBr, cm^{-1}): 3390 (NH stretching of secondary amine), 3235 and 3149 (NH_2 stretching of primary amine), 2197 (CN stretching of Nitrile), 1708 (CO stretching of amide), 1638 (C=N stretching of pyrazole ring), 1596, 1487, 1403, 1337, 1191, 1157, 1075, 1025, 913, 752, 705; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.34 (3H, *s*, CH_3), 4.91 (1H, *d*, J = 15.6 Hz, CH_2), 5.00 (1H, *d*, J = 15.6 Hz, CH_2), 7.02–7.07 (2H, *m*, Ar-H), 7.12 (1H, *d*, J= 6.4 Hz, Ar-H), 7.25–7.34 (6H, *m*, Ar-H & NH_2), 7.40 (2H, *d*, J = 7.2 Hz, Ar-H), 12.32 (1H, *s*, NH); ^{13}C-NMR (62.9 MHz, DMSO-d_6, δ / ppm): 9.4, 43.6, 47.5, 55.3, 95.6, 109.7, 119.2, 123.7, 124.9, 127.9, 129.0, 129.4, 132.3, 135.3, 136.5, 142.4, 155.7, 163.1, 177.1; EIMS (*m*/*z* (relative abundance)): 383 (10), 354 (12), 292 (35), 282 (35), 267 (20), 220 (10), 125 (10), 91 (36), 73 (44), 58 (100).

*6′-Amino-5-chloro-3′-methyl-2-oxo-1′*H*-spiro[indoline-3,4′-pyrano[2,3-*c*]-pyrazole]-5′-carbonitrile (**5d**)*. M.p.: 296–298 °C; Anal. Calcd. for $C_{15}H_{10}ClN_5O_2$: C, 54.97; H, 3.08; N, 21.37 %. Found: C, 55.01; H, 3.10; N, 21.43 %; IR (KBr, cm^{-1}): 3346 (NH stretching of secondary amine), 3135 (NH_2 stretching of primary amine), 2181 (CN stretching of nitrile), 1713 (CO stretching of amide), 1644 (C=N stretching of pyrazole ring), 1611, 1580, 1498, 1476, 1413, 1299, 1207, 1157, 1051, 949, 921, 973, 823, 692; ^{1}H-NMR (250 MHz, DMSO-d_6, δ / ppm): 1.56 (3H, *s*, CH_3), 6.89–7.31 (5H, *m*, Ar-H & NH_2), 10.76 (1H, *s*, NH), 12.34 (1H, *s*, NH) ppm; ^{13}C-NMR (62.9 MHz, DMSO-d_6, δ / ppm): 9.4, 48.0, 54.9, 95.1, 11.7, 119.1, 125.0, 127.0, 129.3, 135.1, 135.2, 140.7, 155.6, 162.9, 178.2.

*6′-Amino-2-oxo-3′-phenyl-1′*H*-spiro[indoline-3,4′-pyrano[2,3-*c*]pyrazole]--5′-carbonitrile (**5e**)*. M.p.: 279–281 °C; Anal. Calcd. for $C_{20}H_{13}N_5O_2$: C, 67.60; H, 3.69; N, 19.71 %. Found: C, 67.71; H, 3.69; N, 19.75 %; IR (KBr, cm^{-1}): 3385 (NH stretching of secondary amine), 3307 and 3239 (NH_2 stretching of primary amine), 2186 (CN stretching of nitrile), 1705 (CO stretching of amide), 1651 (C=N stretching of pyrazole ring), 1599, 1582, 1497, 1472, 1408, 1320, 1209, 1058, 857, 747, 677; ^{1}H-NMR (250 MHz, DMSO-d_6, δ / ppm): 6.73–7.28 (11H, *m*, Ar-H & NH_2), 10.52 (1H, *s*, NH), 12.92 (1H, *s*, NH); ^{13}C-NMR (62.9 MHz, DMSO-d_6, δ / ppm): 48.0, 56.7, 95.7, 110.2, 118.9, 122.9, 124.8, 127.6, 128.6, 128.8, 129.2, 129.4, 134.4, 139.4, 142.0, 156.3, 162.2, 178.6.

*Ethyl 6′-amino-3′-methyl-2-oxo-1′*H*-spiro[indoline-3,4′-pyrano[2,3-*c*]pyrazole]-5′-carboxylate (**5f**)*. M.p.: 280–282 °C; Anal. Calcd. for $C_{17}H_{16}N_4O_4$: C, 59.99; H, 4.74; N, 16.46 %. Found: C, 60.08; H, 4.77; N, 16.54 %; IR (KBr, cm^{-1}):

3385 (NH stretching of secondary amine), 3281 and 3188 (NH_2 stretching of primary amine), 3083 & 3027 (CH stretching of aromatic ring), 2925 and 2854 (CH stretching of alkyl groups), 1715 (CO stretching of amide), 1665 (C=N stretching of pyrazole ring), 1613, 1539, 1472, 1400, 1290, 1222, 1155, 1098, 1036, 923, 767; ^{1}H-NMR (250 MHz, DMSO-d_6, δ / ppm): 0.67 (3H, *t*, J = 7.5 Hz, CH_3), 1.55 (3H, *s*, CH_3), 3.65 (2H, *q*, J = 7.5 Hz , OCH_2), 6.78–7.08 (4H, *m*, Ar-H), 8.02 (2H, *s*, NH_2), 10.37 (1H, *s*, NH), 12.16 (1H, *s*, NH); ^{13}C-NMR (62.9 MHz, DMSO-d_6, δ / ppm): 9.3, 13.5, 47.4, 59.1, 74.5, 97.5, 109.1, 122.0, 123.0, 127.7, 131.9, 135.1, 137.0, 142.3, 154.8, 163.2, 168.6, 180.1; EIMS (*m*/*z* (relative abundance)): 340 (2), 312 (7), 267 (100), 239 (22), 170 (8), 68 (15), 42 (25), 29 (100).