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Chitosan/ionic liquid form a renewable and reusable catalyst system used for the synthesis of highly functionalized spiro derivatives

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Supplementary data

General experimental details and spectral data of all compounds associated with this article can be found as supplementary information.

(5a) **6'-Amino-3'-methyl-2-oxo-1'-phenyl-1'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-5'-carbonitrile**

Yellow powder; m.p. 228-230°C; IR (KBr, *v*, cm^{-1}): 3462, 3310, 3141, 3070, 2196, 1704, 1655, 1597, 1520, 1466, 1391, 1324, 1214, 1123, 1070, 934, 753; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)= 1.57 (s, 3H), 6.97 (d, J = 7.6 Hz, 1H), 7.06 (t, J = 7.2 Hz, 1H), 7.38 (d, J = 7.2 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.2 Hz, 1H), 7.52-7.55 (m, 4H), 7.78 (d, J = 8.0 Hz, 2H), 10.72 (s, 1H).

(5b) 6'-Amino-5-fluoro-2-oxo-3'-phenyl-1'H-spiro[indoline 3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile

White powder; m.p. 256-257 °C; IR (KBr, ν, cm^{-1}): 3386, 3315, 3256, 3158, 3060, 2998, 2190, 1716, 1645, 1587, 1485, 1408, 1182, 1057, 874, 696; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)= 6.72 (q, J = 4.4 Hz, 1H,), 6.87 (d, J = 7.6 Hz, 2H,), 6.66-6.89 (m, 2H,), 7.18 (t, J = 7.6 Hz, 2H,), 7.24 (t, J = 7.70 Hz, 1H,), 7.33 (s, 2H), 10.56 (s, 1H), 12.91 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm)= 57.02, 62.70, 102.79, 118.47, 117.55, 119.97, 120.03, 123.17,123.54, 126.41, 136.17, 136.21, 136.80, 144.20, 144.27, 145.80, 145.95, 163.76, 164.16, 167.53, 169.83, 186.20;.

(5c) 6'-Amino-5-methyl-2-oxo-3'-phenyl-1'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-5' carbonitrile

Brown powder; m.p. 246-247 °C; IR (KBr, *v*, cm^{-1}): 3382, 3314, 3240, 3135, 2191, 1708, 1658, 1596, 1497, 1411, 1311, 1206, 1060, 815, 699; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)= 2.19 (s, 3H,), 6.66 (d, J = 7.6 Hz, 1H,), 6.82 (d, J = 8.0 Hz, 2H,), 6.87 (s, 1H,), 6.87 (d, J = 8.0 Hz, 1H,), 7.18 (t, J = 7.6 Hz, 2H,), 7.23-7.29 (m, 3H,), 10.39 (s, 1H,), 12.87 (s, 1H,); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm)= 28.48, 55.56, 64.46, 105.31, 117.49, 125.85, 132.89, 135.23, 135.28, 135.91, 136.79, 137.23, 139.38, 142.37, 148.85, 147.33, 163.89, 169.58, 185.89;

(5d) 6'-Amino-4-chloro-2-oxo-3'-phenyl-1'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-5'-carbonitrile

White powder; m.p. >300 °C; IR (KBr, *v*, cm^{-1}): 3392, 3316, 3255, 3132, 2187, 1716, 1657, 1587, 1493, 1411, 1312, 1131, 1068, 921, 715; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)= 6.74 (t, J = 5.2 Hz, 1H,), 6.85 (s, 2H,), 6.91(t, J = 6.8 Hz, 1H,), 7.19-7.25 (m, 3H,), 7.29-7.33 (m, 3H), 10.77 (s, 1H), 12.92 (s, 1H,); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm)= 55.92, 61.55, 101.29, 116.85, 126.27, 128.65, 135.18, 136.29, 136.85, 137.96, 137.84, 138.69, 138.68, 146.88, 152.44, 164.21, 168.57, 185.27;

(5e)Ethyl 6'amino-2-oxo-3'-phenyl-1'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-5'-carboxylate

White powder; m.p. 243-244 °C; IR (KBr, *v*, cm^{-1}): 3484, 3364, 3265, 3174, 3056, 2980, 1716, 1664, 1617, 1479, 1412, 1299, 1149, 1099, 1045, 932, 753; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)= 0.68 (t, J = 7.2 Hz, 3H,), 3.66(q, J = 6.8 Hz, 2H,), 6.48 (d, J = 7.6 Hz, 1H,), 6.62 (d, J = 7.6 Hz, 2H), 6.86 (t, J = 7.2 Hz, 1H), 6.95 (d, J = 7.2 Hz, 1H), 7.08 (t, J = 7.2 Hz, 1H), 7.16 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 1H), 8.07 (s, 2H), 9.96 (s, 1H,), 12.62 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm)= 14.18, 48.41, 59.90, 75.72, 98.92, 108.13, 123.50, 123.89, 127.55, 127.94, 128.69, 128.88, 137.33, 138.29, 140.73, 155.62, 163.58, 168.29, 177.90;

(5f) **6'-Amino-2-oxo-3'-phenyl-1'*H*-spiro[indoline-3,4'pyrano[2,3-*c*]pyrazole]-5'-carbonitrile**

White powder; m.p. 281-283 °C; IR (KBr, *v*, cm^{-1}): 3388, 3314, 3242,3144, 2908, 2182, 1709, 1645, 1599, 1498, 1408, 1325, 1218, 1065, 928, 745; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)= 6.76 (d, J = 8.0Hz, 1H,), 6.82 (d, J = 7.6 Hz, 2H,), 6.92 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 7.15-7.17 (m, 3H), 7.26 (d, J = 8.4 Hz, 1H), 7.28 (s, 2H), 10.52 (s, 1H), 12.91 (s, 1H);

(5g) 6'-Amino-1-methyl-2-oxo-3'-phenyl-1'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-5'-carbonitrile

White powder; m.p. 283-285 °C; IR (KBr, *v*, cm^{-1}): 3452, 3295, 3176, 3034, 2928, 2194, 1692, 1632, 1606, 1505, 1398, 1035, 919, 696; ^{1}HNMR (400 MHz, DMSO-d_6): δ (ppm)= 2.98 (s, 3H,), 6.74 (d, J =7.2 Hz, 2H), 6.90 (d, J = 7.6 Hz, 1H,), 6.98 (t, J = 7.6 Hz,1H,), 7.08 (d, J = 7.2 Hz, 1H,), 7.19 (t, J = 8.0 Hz, 2H,), 7.25 (q, J = 7.6 Hz, 2H), 7.33 (s, 2H), 12.90 (s, 1H);

(5h) 6'-Amino-3'-methyl-2-oxo-1'-(*m*-tolyl)-1'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-5'-carbonitrile

White powder; m.p. 200-201 °C; IR (KBr, *v*, cm^{-1}): 3368, 3316, 3188, 3039, 2972, 2208, 1711, 1661, 1615, 1526, 1471, 1398, 1227, 1126, 1038, 748; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)= 1.55 (s 3H), 2.42 (s, 3H), 6.96 (d, J = 7.6 Hz, 1H), 7.04 (t, J = 7.2 Hz, 1H), 7.16-7.19 (m, 2H), 7.29 (t, J = 8.0 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.56-7.62 (m, 4H,), 10.876(s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm)= 12.75, 19.62, 22.17, 48.91, 57.23, 97.41, 110.99, 118.27, 119.16, 121.65, 126.71, 128.99, 128.27, 131.27, 133.17, 136.24, 140.19, 142.65, 144.85, 145.92, 162.18, 178.67;

(5i)**6'-Amino-5-chloro-3'-methyl-2-oxo-1'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-5'-carbonitrile**

White powder; m.p. 298-299°C; IR (KBr, *v*, cm^{-1}): 3394, 3345, 3138, 2970, 2185, 1709, 1646, 1585, 1496, 1411, 1305, 1160, 1055, 826, 695; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)= 1.17 (s, 3H), 6.84 (d, J = 8.4 Hz, 1H), 7.23 (s, 1H), 7.38 (s, 2H), 7.39-7.41 (m, 1H), 10.83 (s, 1H), 12.42 (s, 1H).

(5j) **6'-amino-5-bromo-3'-methyl-2-oxo-1'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile**

White powder; m.p. 281-282 °C; IR (KBr, *v*, cm^{-1}): 3416, 3397, 3349, 3128, 2185, 1716, 1642, 1584, 1498, 1413, 1305, 1209, 1159, 1056, 950, 828, 693; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)= 1.58 (s, 3H,), 6.88 (d, J = 8.0 Hz, 1H,), 7.25 (s, 1H,), 7.28 (s, 2H,), 7.45 (d, J = 7.6 Hz, 1H,), 10.73 (s, 1H,), 12.34 (s, 1H,);

(5k) **6'-Amino-6-bromo-3'-methyl-2-oxo-1'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-5' carbonitrile**

White powder; m.p. >300 °C; IR (KBr, *v*, cm^{-1}): 3475, 3305, 3250, 3180, 3120, 3036, 2815, 2200, 1709, 1642, 1608, 1491, 1411, 1317, 1048,

989, 761; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)= 1.58 (s, 3H), 7.01-7.05 (m, 2H), 7.18 (d, J = 7.6 Hz, 1H), 7.24 (s, 2H), 10.85 (s, 1H), 12.31 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 16.13, 52.18, 62.84, 105.78, 121.55, 126.49, 131.34, 133.18, 134.40, 139.92, 142.77, 152.19, 164.28, 169.45, 185.79.

(5l)**6'-Amino-5-fluoro-3'-methyl-2-oxo-1'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-5'-carbonitrile**

Light yellow powder; m.p. 275-276 °C; IR (KBr, v, cm-^{1}): 3470, 3350, 3160, 2978, 2197, 1713, 1645, 1590, 1492, 1410, 1318, 1180, 1060, 822, 797; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)= 1.68 (s, 3H), 6.90-7.15 (m, 3H), 7.37 (s, 2H), 10.72 (s, 1H), 12.42 (s, 1H).

(5m)**6'-Amino-3',5-dimethyl-2-oxo-1'*H*-spiro[indoline-3,4'-pyrano[2,3- *c*]pyrazole]-5'-carbonitrile**

red powder; m.p. 280-281 °C; IR (KBr, v, cm^{-1}): 3395, 3349, 3149, 2921, 2180, 1710, 1649, 1585, 1500, 1412, 1318, 1212, 1060, 825, 690; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm)= 1.56 (s, 3H), 2.23 (s, 3H), 6.78 (d, J = 8.0 Hz, 1H), 6.85 (s, 1H), 7.05 (d, J = 7.2 Hz, 1H), 7.16 (s, 2H), 10.46 (s, 1H), 12.21 (s, 1H).

(5n) 6′-Amino-3′-methyl-2-oxo-1′H-spiro[indoline-3,4′-pyrano[2,3-c]pyrazole]-5′-carbonitrile

red powder mp: 284−285 °C. IR (KBr ν cm^{-1}): 3424, 3385, 3341, 3135, 2189, 1715, 1648, 1589, 1527, 1419, 1325, 1211, 1160, 1059, 936, 700 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ:= 1.55 (s, 3H,), 2.24 (s, 3H), 6.92 (s, 1H,), 7.03 (s, 2H,), 7.18(S, 1H), 7.24 (s, 1H,), 10.57 (s, 1H,), 12.26 (s, 1H,).

(5o) **6'-Amino-4-bromo-3'-methyl-2-oxo-1'-phenyl-1'*H*-spiro[indoline -3,4'-pyrano[2,3-*c*]pyrazole]-5'-carbonitrile**

White powder; m.p. 289-291 °C; IR (KBr, v, cm^{-1}): 3354, 3323, 3198, 2201, 1728, 1661, 1584, 1529, 1447, 1398, 1128, 1078, 769; ^{1}HNMR (400 MHz, DMSO-d_6): δ (ppm)= 1.62 (s, 3H), 6.98 (d, J = 7.2 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.26 (t, J = 8.0 Hz, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.70 (s, 2H), 7.78 (d,J = 8.0 Hz, 2H), 11.06 (s, 1H).