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Supporting Information

Facile synthesis of pyranopyrazoles and 3,4-dihydropyrimidin-2(1*H*)-ones by Ti-grafted polyamidoamine dendritic silica hybrid catalyst *via* dual activation route.

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Spectral characterization data of compounds 1a-1k

5-Ethoxycarbonyl-6-methyl-4-phenyl-3,4 -dihydropyrimidin-2(1H)-one **(Table 3c, 1a)**: White solid, LCMS (M^+1) m/z 261; IR (KBr): 3240, 2945, 1610, 678 cm^{-1}; ^{1}HNMR (400MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.16 (s, 1H), 6.86 (s, 5H), 5.14 (s, 1H), 3.97 (q, *J* = 6.4 Hz, 2H), 2.23 (s, 3H), 1.10 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 154.2, 149.8, 146.2, 129.6, 127.9, 128.5, 99.3, 59.9, 56.0, 18.5, 15.1 ppm

5-Ethoxycarbonyl-6-methyl-4-(2-hydroxyphenyl)- 3,4-dihydropyrimidin-2(1H)-one **(Table 3c, 1b)**: White solid, LCMS (M^+1) m/z 276.1; IR (KBr): 1705,1748, 2926, 3084, 3224 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.3 (s, 1H), 8.14 (s, 1H), 7.87 (s, 1H), 7.46-6.95 (m, 4H), 5.24 (s, 1H,), 3.92 (q, *J* = 7.1 Hz , 2H), 2.23 (s, 3H), 1.08 (t, *J* = 7.1Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 168.3, 160.2, 143.1, 135.4, 130.2, 127.3, 126.7, 125.8, 105.6, 63.2, 58.2, 20.1, 19.8, 15.5 ppm

5-(Ethoxycarbonyl)-6-methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-one **(Table 3c, 1c)**: White solid, LCMS (M^+1) m/z 290.1; IR (KBr): 3242, 2956, 1704, 1681, 1504 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.1 (s, 1H), 7.7 (s, 1H), 7.1 (d, *J* = 8.2 Hz , 2H), 6.9 (d, *J* = 8.2 Hz, 2H), 5.1 (d, *J* = 2.6 Hz 1H), 3.9 (q, *J* = 7.0 Hz, 2H), 3.7 (s, 3H), 2.2 (s, 3H), 1.1 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}CNMR (100MHz, DMSO-d_6): δ 198.4, 160.5, 155.1, 149.8, 138.4, 130.7, 118.9, 113.6, 58.1, 56.3, 32.2, 22.8 ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-thione **(Table 3c, 1d)**: White solid, LCMS (M^+1) m/z 307; IR (KBr): 3256, 1659, 1595, 1569 cm^{-1}; ^{1}H NMR

(400 MHz, DMSO-*d6*): δ 9.89 (s, 1H), 9.3 (s, 1H), 7.2 (d, *J* = 8.1 Hz 2H), 6.7 (d, *J* = 8.1 Hz, 2H), 5.2 (s, 1H), 4.1 (q, *J* = 7.2 Hz, 2H), 2.3 (s, 3H), 1.2 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 173.9, 174.3, 165.9, 126.8, 158.5, 145.2, 135.9, 128.0, 114.0, 101.5, 59.8, 55.3, 53.6, 17.4, 14.3 ppm.

5-(Ethoxycarbonyl)-6-methyl-4-(2-naphthyl)-3,4-dihydropyrimidin-2(1H)-one **(Table 3c, 1e)**: Yellow Solid, LCMS (M^+) m/z 310.5; IR (KBr): 3245, 3118, 2977, 1698, 1647, 1431, 1231, 1088, 790 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.01 (s,1H), 8.28 (d, *J* = 8.2 Hz, 1 H), 7.80 (d, *J* =8.2Hz , 1 H), 7.75 (t, *J* =8.1Hz, 1 H), 7.40-7.55 (m, 5H), 6.10 (s, 1 H), 3.75 (q, *J* =7.1Hz, 2 H), 2.32 (s, 3 H), 0.90 (t, *J* =7.1Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): 165.1, 152.3, 147.3, 148.2,135.3, 134.5, 128.0, 126.6, 122.5, 98.5, 61.4, 53.5, 18.2, 15.5 ppm

5-(Ethoxycarbonyl)-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-one **(Table 3c, 1f)**: White solid, LCMS (M^+1) m/z 294; IR (KBr): 3233, 3093, 2976, 2933, 1701, 1643 670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.3 (s, 1H), 7.8 (s, 1H), 7.40–7.30 (m, 4H), 5.1 (s, 1H), 3.9 (q, *J* =7.2Hz, 2H), 2.3 (s, 3H), 1.0 (t, *J* =7.2Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.0, 151.4, 148.9, 141.2, 131.7, 129.2, 128.7, 98.2, 58.9, 51.9, 17.9 ppm

5-(Ethoxycarbonyl)-6-methyl-4-(4-chlorophenyl)-3,4-dihydropyrimidin-2(1H)-thione **(Table 3c, 1g)**: White solid, LCMS (M^+) m/z 310.1; IR (KBr): 3255, 1657, 1560 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.0 (s, 1H), 9.30 (s, 1H), 7.15 (m, 4 H), 5.25 (s, 1 H), 4.10 (q, *J* =7.1Hz, 2 H,), 2.41 (s, 3 H), 1.13 (t, *J* =7.1Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.3, 169.0, 150.3, 148.4,137.3, 133.6, 135.4, 105.4, 64.7, 55.5, 19.2, 17.0 ppm

5-(Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-thione **(Table 3c, 1h):** White solid, LCMS (M^+) m/z 276; IR (KBr): 3282, 1615, 1575, 1268 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1 H), 7.15 (m, 5 H), 5.8 (s, 1 H,), 4.57 (s, 1H), 3.85 (q, *J* =7.1Hz, 2H), 2.15 (s, 3 H), 0.95 (t, *J* =7.1Hz 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.4, 164.2, 159.8, 146.2, 129.6, 127.9, 128.5, 99.3, 62.3, 59.9, 18.5, 15.5 ppm

5-(Ethoxycarbonyl)-6-methyl-4-(4-bromophenyl)-3,4-dihydropyrimidin-2(1H)-one **(Table 3c, 1i)**: White solid; LCMS (M^+) m/z 339; IR (KBr): 3233, 3093, 2976, 2933, 1701, 1643 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.2 (s, 1H), 7.5 (s, 1H), 7.40–7.30 (m, 4H), 4.9 (s, 1H), 3.3 (q, *J*

=7.0Hz, 2H), 2.0 (s, 3H), 0.89 (t, *J* =7.0Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.0, 149.4, 146, 137.2, 128.7, 125.2, 123.7, 97.2, 56.9, 47.9, 15.9 ppm

5-(Ethoxycarbonyl)-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one **(Table 3c, 1j)**: White solid, LCMS(M^+) m/z 305; IR (KBr): 3233, 3000, 1710, 1675, 1630, 1613, 1560, 1524, 1309 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.30(s, 1H), 8.25 (d, *J* =8.4Hz 2H), 7.90 (s, 1H), 7.50 (d, *J* =8.4Hz 2H), 5.15 (d, 1H), 3.90 (q, *J* =7.1Hz , 2H), 2.34 (s, 3H), 1.10 (t, *J* =7.1Hz, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.7, 151.3, 149.3, 146.4, 126.8, 123.7, 59.3, 52.8,17.8, 13.7 ppm

Ethyl 6-Methyl-2-oxo-4-(4-styryl)-3,4-dihydropyrimidine-5-carboxylate **(Table 3c 1k)**: Colorless crystals, LCMS (M^+) 286 m/z IR (KBr): 3241, 1704, 1650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.5 (s, 1H), 7.80 (s, 1 H), 7.15 (m, 5 H), 6.35 (d, *J* =4.0Hz, 1 H), 6.08 (dd, 14.5, 4.0Hz, 1 H), 5.24 (d, *J* =4.0Hz, 1H), 3.9 (q, *J* =7.1Hz, 2 H, 2.19 (s, 3 H), 1.08 (t, *J* =7.1Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 159.6, 152.5, 140.2, 135.0 131.6, 132.1, 130.5, 128.2, 99.8, 61.2, 53.8, 18.7, 15.2 ppm

Spectral characterization data of compounds 2a-2n

6-Amino-2,4-dihydro-3-methyl-4-phenylpyrano-[2,3-c]pyrazole-5-carbonitrile **(Table 4b, 2a**): White solid, GC-MS 252(M^+); IR (KBr): 3410, 3356, 3167, 2990, 1646, 1596, 1399, 1276 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.77 (s, 3H), 4.80 (s, 1H), 6.89 (s, 2H), 7.05-7.35 (m, 5H), 12.05(s, 1H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ 146.5, 136.5, 128.7, 127.9, 126.9, 121.0, 58.1, 36.8, 10.1 ppm

6-Amino-2,4-dihydro-3-methyl-4-(4-methoxyphenyl)pyrano-[2,3-c]pyrazole-5-carbonitrile **(Table 4b, 2b)**: White solid, GC-MS 282(M^+); IR (KBr): 3485, 3258, 2185,1608, 1442 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.75 (s, 3H),3.80 (s, 3H), 4.58 (s, 1H), 6.88 (d, *J* =8.1Hz, 2H), 6.88 (d, *J* =8.1Hz, 2H), 7.09 (s, 2H), 12.10 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 160.5, 156.3, 155.8, 144.2, 136.8, 118.5, 114.2, 111.5, 107.4, 57.9, 55.1, 36.2, 9.89 ppm

6-Amino-2,4-dihydro-3-methyl-4-(3-nitrophenyl)pyrano-[2,3-c]pyrazole-5-carbonitrile **(Table 4b, 2c)**: Brown solid, GC-MS 297 (M^+); IR (KBr): 3385, 3278, 2189, 1622,1456 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80 (s, 3H), 4.92 (s, 1H), 6.90 (s, 2H), 7.81 (s, 1H), 7.78 (d, *J* =8.5Hz,

1H), 7.42-7.45 (m, 2H), 12.12 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 148.8, 146.2, 141.8, 135.3, 134.1 ,130.0, 127.6, 124.7, 121.4, 120.2, 59.6, 32.5,10.78 ppm

6-Amino-2,4-dihydro-3-methyl-4-(4-styryl)pyrano-[2,3-c]pyrazole-5-carbonitrile **(Table 4b, 2d)**: Colorless crystal, GC-MS 297 (M^+) 278; IR (KBr): 3485, 33241, 2856, 1704, 1650, 1325 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89 (s, 3H), 4.88 (s, 1H), 6.38 (d, 14.2Hz, 1H) 6.18 (dd, 14.2, 4.0Hz 1 H), 5.24 (d, 4.0Hz, 1H), 7.05-7.16 (m, 5H), 7.8 (s, 2H), 12.1 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 167.5, 159.3, 158.8, 149.2, 136.8, 134.5, 128.5, 127.1, 114.4, 58.9, 57.1, 38.2, 10.8 ppm

6-Amino-2,4-dihydro-3-methyl-4-(4-chlorophenyl)pyrano-[2,3-c]pyrazole-5-carbonitrile **(Table 4b, 2e)**: White solid, GC-MS 286(M^+); IR (KBr): 3485, 3258, 2185,1608, 1442,755 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.79 (s, 3H), 3.92 (s, 3H), 4.88 (s, 1H), 7.22 (d, *J* =8.2Hz, 2H), 7.22 (d, *J* =8.2Hz , 2H), 7.2 (s, 2H), 12.15 (s, 1H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ 165.5, 162.3, 160.8, 148.2, 142.8, 126.3, 122.2, 120.4, 115.4, 62.9, 38.2, 13.0 ppm

6-Amino-2,4-dihydro-3-methyl-4-(2-hydroxyphenyl)pyrano-[2,3-c]pyrazole-5-carbonitrile (**Table4b, 2f)**: White solid, GC-MS 268(M^+); IR (KBr): 3485, 3258, 2185, 1608, 1442 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.82 (s, 3H), 4.54 (s, 1H), 5.32 (s, 1H), 6.98-7.25 (m, 4H), 6.87 (s, 2H), 12.01 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): 167.5, 148.8, 136.7, 131.8, 126.2, 117.5, 114.4, 110.8, 105.1, 49.7, 19.3, 15.5 ppm

6-Amino-2,4-dihydro-3-methyl-4-(4-bromophenyl)pyrano-[2,3-c]pyrazole-5-carbonitrile **(Table 4b, 2g)**: White solid, GC-MS 330 (M^+); IR (KBr): 3485, 3258, 2185, 1608, 1442, 755 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.70 (s, 3H), 3.72 (s, 3H), 4.68 (s, 1H), 6.79 (d, *J* =8.1Hz, 2H), 6.79 (d, *J* =8.0Hz, 2H), 6.98 (s, 2H), 12.03 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 160.5, 156.3, 155.8, 144.2, 136.8, 118.5, 114.2, 113.4, 107.4, 57.9, 34.2, 12.0 ppm

6-Amino-2,4-dihydro-3-methyl-4-(4-nitrophenyl)pyrano-[2,3-c]pyrazole-5-carbonitrile **(Table 4b, 2h)**: White solid, GC-MS 296 (M^+); IR (KBr): 3385, 3278, 2189, 1622,1456 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.72 (s, 3H), 3.79 (s, 3H), 4.89 (s, 1H), 7.29 (d, *J* =8.5Hz, 2H), 7.27 (d, *J* =8.5Hz, 2H), 7.01 (s, 2H), 12.13 (s, 1H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): δ 172.5, 168.3, 165.8, 149.2, 140.8, 127.5, 124.2, 121.4, 115.4, 60.1, 20.2, 14.9 ppm

6-Amino-2,4-dihydro-3-methyl-4-(4-hydroxyphenyl)pyrano-[2,3-c]pyrazole-5-carbonitrile **(Table 4b, 2i)**: White solid, GC-MS 268(M^+); IR (KBr): 3485, 3258, 2185, 1608, 1442 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.75 (s, 3H), 4.14 (s, 1H) 5.38 (s, 1H), 7.01 (d, *J* =8.2Hz, 2H), 7.13 (d, *J* =8.2Hz , 2H), 6.87 (s, 2H), 11.8 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 165.1, 159.0, 157.8, 146.2, 138.8, 124.1, 117.2, 116.5, 113.4, 59.9, 37.2, 12.8 ppm

6-Amino-2,4-dihydro-3-methyl -4-(2-nitrophenyl) pyrano-[2,3-c]pyrazole-5-carbonitrile **(Table 4b, 2j)**: White solid; GC-MS 297 (M^+); IR (KBr): 3375, 3258, 2169, 1602, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.82 (s, 3H), 5.16 (s, 1H,), 7.12 (s, 2H), 7.35-7.59 (m, 4H), 12.4 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170, 152, 140, 138.4, 128.2, 120.1, 118.4, 115.2, 110.1, 56.7, 22.3, 19.5 ppm

6-Amino-2,4-dihydro-3-methyl -4-(**thiophen-2-yl*****)pyrano-[2,3-c]pyrazole-5-carbonitrile*** **(Table 4b, 2k)**: White solid; IR (KBr): 3368, 3148, 2890, 2569, 1602, 1454 cm^{-1}; ^1H NMR (DMSO-d6, 400 MHz) δ 1.95 (s, 3H), 5.03 (s, 1H), 6.96-6.99 (m, 3H), 7.04 (d, *J* =8.0Hz ,1H), 7.41 (d, *J* =8.4Hz, 1H), 12.2 (s, 1H) ppm

6-Amino-2,4-dihydro-3-methyl-4-(methyl)pyrano-[2,3-c]pyrazole-5-carbonitrile **(Table 4b, 2l)**: Whitesolid, GC-MS 190(M^+); IR (KBr): 3485, 3232, 2187,1641 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.42 (s, 3H), 1.9 (s, 3H), 3.86 (q, *J* =7.2Hz, 1H), 7.09 (s, 2H), 12.4 (s, 1H) ppm

6-Amino-1,4-dihydro-3,4-dimethyl-4-p-tolyl-pyrano[2,3-c]pyrazole-5-carbonitrile **(Table 4b, 2m)***:* White solid, GC-MS 266(M^+); IR (KBr): 3439, 2980, 2185, 1645, 1516, 1349, 1026, 763 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.62 (s, 3H), 1.8 (s, 3H), 2.66 (s, 3H), 6.92 (s, 2H) 7.09-7.18 (m, 5H), 2.09 (s,1H) ppm

6-amino-3-methyl-1H-spiro(cyclohexane)-1,4-pyrano[2,3-c]pyrazole-5-carbonitrile **(Table 4b 2n)**: White solid, GC-MS 244(M^+); IR (KBr): 3244, 2179, 1629, 1491, 1406, 1053, 717 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.62-185 (m, 4H), 1.9 (s, 3H), 7.12 (s, 2H), 12.09 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6,100 MHz) δ 162.1, 154.8, 134.6, 124.6, 103.8, 60.8, 33.2, 32.8, 31.7, 30.7, 12.0 ppm