Supplementary data

**Synthesis of methyl 6-amino-5-cyano-4-aryl-2,4-dihydropyran[2,3-c]pyrazole-3-carboxylates using nano-ZnZr4(PO4)6 as an efficient catalyst**

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**SPECTRAL DATA FOR ALL COMPOUNDS**

**Spectral data for compounds 5a-5j:**

*Methyl 6-amino-5-cyano-2,4-dihydro-4-(4-nitrophenyl) pyrano [2,3-c]pyrazole-3-carboxylate (5a)* White crystals; mp 242–243 °C (lit.²⁵ 244-245 °C); IR (KBr) (v_max/cm⁻¹): 3385, 3324, 3265, 2955, 2201, 1488, 1390, 1027; ¹H NMR (400 MHz, DMSO-d₆):  δ (ppm) 3.63 (3H, s, OMe), 4.69 (1H, s, CH), 7.18 -7.25 (4H, m, H-Ar), 7.49 (2H, NH₂), 13.69 (1H, s, NH); ¹³C NMR (100MHz, DMSO-d₆): δ (ppm) 37.88 (CH), 52.22 (OMe), 58.46 (C), 104.87 (C), 120.84 (CN), 127.69 (2CH), 127.91 (C) 129.27 (2CH), 136.16 (C), 145.47 (C), 155.82 (C), 158.88 (C), 160.65 (C=O); Anal. Calcd. For C₁₅H₁₁N₅O₅: C, 52.79; H, 3.25; N, 20.52; Found C, 52.83; H, 3.21; N,

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Methyl 6- amino- 5- cyano- 4- (2-fluorophenyl)-2,4-dihydropyranoo [2,3-c]pyrazole-3-carboxylate (5b) White crystals; mp 248–250 °C, IR (KBr) (v max/cm⁻¹): 3427, 3299, 3187, 2956, 2193, 1723, 1637, 1601, 1489, 1400, 1044. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 3.59 (3H, s, OMe), 5.00 (1H, s, CH), 7.08 – 7.24 (4H, m, CH), 7.23 (2H, NH₂), 13.76 (1H, s, NH); ¹³C NMR (100 MHz, DMSO-d₆): δ (ppm) 31.66 (CH), 52.19 (OMe), 56.61 (C), 103.45 (C), 115.65 (CH), 115.87 (CN), 120.57 (CH), 124.82 (CH), 129.19 (CH), 129.27 (C), 130.50 (C), 131.72 (C), 158.79 (C), 159.14 (C), 160.97 (C=O); Anal. Calcd. for C₁₅H₁₁FN₄O₃: C, 57.33; H, 3.53; N, 17.83; Found C, 57.27; H, 3.46; N, 17.76.

Methyl 6-amino-5-cyano-4- (4-methoxylphenyl) -2,4-dihydro pyrano[2,3-c]pyrazole-3-carboxylate (5c) White crystals; mp 238-240 °C, IR (KBr) (v max/cm⁻¹): 3428, 3323, 3214, 2924, 2194, 1728, 1639, 1602, 1475, 1392, 1110; ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 3.64 (3H, s, OMe), 3.69 (3H, s, OMe), 4.67 (1H, s, CH), 6.81 (2H, NH₂), 7.00-7.20 (4H, m, CH), 13.70 (1H, s, NH) ¹³C NMR (100 MHz, DMSO-d₆): δ (ppm) 36.70 (CH), 52.21 (OCH₃ ester), 55.41 (OMe), 58.59 (C), 105.05 (C), 114.02 (CN), 120.84 (2CH), 128.87 (2CH), 129.14 (C), 137.53 (C), 155.78 (C), 158.36 (C), 158.90 (C), 160.53 (C=O) Anal. Calcd for C₁₆H₁₄N₄O₃: C, 58.89; H, 4.32; N, 17.17; Found C, 58.80; H 4.28; N, 17.26.

Methyl 6-amino-5-cyano-2,4-dihydropyran-4- p-tolyl pyrano[2,3-c]pyrazole-3-carboxylate (5d) White crystals, mp 242–244°C, IR (KBr) (v max/cm⁻¹): 3390, 3325, 3215, 2952, 2194, 1724, 1645, 1605, 1480, 1393, 1393, 1049; ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 2.22 (3H, s, Me), 3.63 (3H, s, OMe), 4.67 (1H, s, CH), 6.99-7.15
Methyl 6-amino-5-cyano-2,4-dihydro-[3-nitrophenyl]pyrano[2,3-c]pyrazole-3-carboxylate (5e) white Crystals, m. p. 234-235 °C (lit.25 236-237 °C)IR (KBr) ($\nu_{\text{max}}$/cm$^{-1}$): 3399, 3326, 3265, 2955, 2201, 1488; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 3.68 (3H, s, OMe), 4.71 (1H, s, CH), 7.20 -7.27 (4H, m, H-Ar), 7.51 (2H, NH$_2$), 13.70 (1H, s, NH); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm)37.91 (CH), 52.30 (OMe), 58.47 (C), 104.89 (C), 120.88 (CN), 127.69 (CH), 127.91 (C)128.8 (CH), 129.31 (CH),131. 12 (CH), 136.26 (C), 145.52 (C), 155.90 (C), 158.91 (C), 160.79 (C=O);Anal. Calcd For C$_{15}$H$_{11}$N$_5$O$_5$: C, 52.79; H, 3.25; N, 20.52; Found C, 52.70; H, 3.18; N, 20.61.

Methyl 6-amino-5-cyano-4-phenyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate (5f) white crystals;m. p. 231-232 °C (lit.25 231-232 °C)IR (KBr) ($\nu_{\text{max}}$/cm$^{-1}$): 3389, 3329, 3268, 2960, 2209, 1729, 1654, 1613; $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 3.59 (3H, s, OMe), 4.690 (1H, s, CH), 7.05–7.28 (5H, m, CH), 7.24 (2H, NH$_2$), 13.74 (1H, s, NH); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 37.45 (CH), 52.16 (OCH$_3$), 58.17 (C), 104.65 (C), 120.73 (CN), 127.10 (CH), 127.79 (CH), 128.68 (CH), 129.18 (C), 145.36 (C), 155.87 (C), 158.84 (C), 160.61 (C=O); Anal. Calcd. for C$_{15}$H$_{12}$N$_4$O$_3$: C, 60.81; H, 4.08; N, 18.91; Found C, 60.73; H, 4.16; N, 18.96.
Methyl 6-amino-5-cyano-2,4-dihydro-4-(2,3-dimethoxyphenyl) pyrano[2,3-c]pyrazole-3-carboxylate (5g) white crystals; m. p. 239-241 °C, IR (KBr) (ν_max/cm⁻¹): 3428, 3290, 3160, 2938, 2188, 1733, 1640, 1605, 1485, 1395, 1050; ¹H NMR (400 MHz, DMSO-d₆) δ (ppm) 3.53 (3H, s, OMe), 3.59 (3H, s, OMe), 3.75 (3H, s, OMe), 4.90 (1H, s, CH), 6.58-6.93 (5H, m, H-Ar and NH₂), 13.58 (1H, s, NH); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm) 33.27 (CH), 52.10 (CH₃ ester), 55.95 (OMe), 60.20 (C), 104.73 (C), 111.92 (CN), 121.05 (C), 123.74 (CH), 128.94 (CH), 137.74 (C), 146.88 (C), 152.75 (C), 156.37 (C), 158.95 (C), 161.03 (C=O); Anal. Calcd for C₁₇H₁₆N₄O₅: C, 57.30; H, 4.53; N, 15.72; Found: C, 57.42; H, 4.42; N, 15.79.

Methyl 6-amino-5-cyano-2,4-dihydro-4-(2-methoxyphenyl) pyrano[2,3-c]pyrazole-3-carboxylate (5h) white crystals; m. p. 210–212 °C (lit. 25212-214 °C) IR (KBr) (ν_max/cm⁻¹): 3412, 3232, 3269, 2939, 2196, 1719, 1651, 1610, 1488, 1390, 1027; ¹H NMR (400 MHz, DMSO-d₆) δ 3.57 (3H, s, OMe), 3.67 (3H, s, OMe), 4.99 (1H, s, CH), 6.89–7.17 (4H, m, H-Ar), 7.02 (2H, NH₂), 13.76 (1H, s, NH); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm) 37.31 (CH), 52.25 (CH₃ ester), 55.37 (OMe), 57.94 (C), 104.51 (C), 111.99 (CN), 113.90 (CH), 119.93 (CH), 120.75 (CH), 125.70 (C), 129.00 (CH), 129.84 (C), 146.96 (C), 152.75 (C), 156.37 (C), 158.95 (C), 160.70 (C=O); Anal. Calcd for C₁₆H₁₄N₄O₄: C, 58.89; H, 4.32; N, 17.17; Found: C, 58.95; H, 4.27; N, 17.26.

Methyl 6-amino-5-cyano-2,4-dihydropyrano-4-otoly pyrano[2,3-c]pyrazole-3-carboxylate (5i) White crystals, m. p. 237–239°C (lit. 25239-240), IR (KBr) (ν_max/cm⁻¹).
Methyl 6-amino-5-cyano-2,4-dihydro-4-(3-methoxyphenyl) pyrano [2,3-c]pyrazole-3-carboxylate (5j) white crystals; m. p. 205–207 °C (lit. 25208-210 °C)

IR (KBr) (ν_max/cm⁻¹): 3412, 3320, 3260, 2934, 2194, 1714, 1655, 1613, 1485, 1394, 1025; ¹H NMR (400 MHz, DMSO-d₆) δ 3.57 (3H, s, OMe), 3.66 (3H, s, OMe), 4.98 (1H, s, CH), 6.82-7.10 (4H, m, H-Ar), 7.02 (2H, NH₂), 13.70 (1H, s, NH); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm) 37.30 (CH), 52.21 (CH₃ ester), 55.35 (OMe), 57.94 (C), 104.55 (C), 111.83 (CN), 113.82 (CH), 119.92 (CH), 120.70 (CH), 125.82(C), 129.06 (CH), 129.80 (C), 146.93(C), 158.82 (C), 159.42 (C), 160.73 (C=O); Anal. Calcd for C₁₆H₁₄N₄O₆: C, 58.89; H, 4.32; N, 17.17; Found: C, 58.90; H, 4.22; N, 17.21.
IR of 5a

\[ \text{NO}_2 \]
\[ \text{MeO}_2\text{C} \]
\[ \text{CN} \]
\[ \text{NH}_2 \]

\[ \text{H} \text{NMR of } 5a \]

\[ \text{BRAUER} \]

\[ \text{1H NMR of } 5a \]
IR of 5b
$^{13}$C NMR of 5b

IR of 5c
$^1$H NMR of 5c

$^{13}$C NMR of 5c
IR of 5d

^1^H NMR of 5d
$^1$H NMR of 5d

IR of 5e
$^1$H NMR of 5e

IR of 5f
$^1$H NMR of 5f

IR of 5g
IR of 5h

$^1$H NMR of 5h