

## Supplementary data

### Synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles using disulfonic acid imidazolium chloroaluminate as a dual and heterogeneous catalyst

Ahmad Reza Moosavi-Zare,<sup>a\*</sup> Mohammad Ali Zolfigol,<sup>b\*</sup> Ehsan Noroozizadeh,<sup>b</sup> Mahsa Tavasoli,<sup>b</sup> Vahid Khakyzadeh,<sup>b</sup> Abdolkarim Zare<sup>c</sup>

<sup>a</sup>*Faculty of Chemistry, Bu-Ali Sina University, Hamedan, 6517838683, Iran.*

<sup>b</sup>*Department of Chemistry, University of Syyed Jamaledin Asadabadi, Asadabad, 6541835583, Iran.*

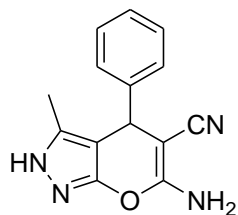
<sup>c</sup>*Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Iran*

\*Corresponding author. Fax: +988118257407, *E-mail addresses:* moosavizare@yahoo.com, [mzolfigol@yahoo.com](mailto:mzolfigol@yahoo.com).

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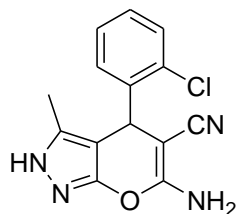
Data of compounds.....	2
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### Data of Compounds:



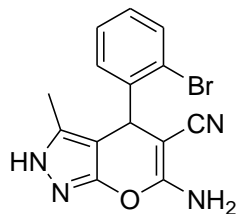
#### 6-amino-3-methyl-4-phenyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (1).

FT-IR (KBr)  $\nu_{\max}(\text{cm}^{-1})$ : 1045, 2193, 3172, 3311, 3374.  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 1.77 (s, 3H), 4.58 (s, 1H), 6.85 (s, 2H), 7.15-7.23 (m, 3H), 7.29-7.33 (m, 2H), 12.08 (s, 1H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.69, 36.19, 57.15, 97.60, 120.74, 126.69, 127.42, 128.39, 135.53, 144.40, 154.73, 160.83.



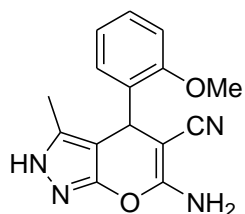
#### 6-amino-4-(2-chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (3).

FT-IR (KBr)  $\nu_{\max}(\text{cm}^{-1})$ : 764, 1053, 2190, 3169, 3314, 3392.  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 1.76 (s, 3H), 5.06 (s, 1H), 6.93 (s, 2H), 7.17 (d,  $J = 4.0$  Hz, 1H), 7.25-7.30 (m, 2H), 7.40 (d,  $J = 8.0$  Hz, 1H), 12.11 (s, 1H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.49, 33.40, 55.69, 96.81, 120.37, 127.72, 128.55, 129.44, 130.67, 131.92, 135.33, 140.88, 154.91, 161.26.



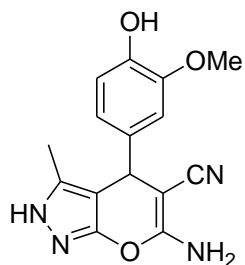
**6-amino-4-(2-bromophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4).**

FT-IR (KBr)  $\nu_{\max}(\text{cm}^{-1})$ : 550, 1052, 2190, 3155, 3310, 3392.  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 1.75 (s, 3H), 5.06 (s, 1H), 6.94 (s, 2H), 7.15-7.19 (m, 2H), 7.31 (d,  $J = 8.0$  Hz, 1H), 7.57 (d,  $J = 8.0$  Hz, 1H), 12.12 (s, 1H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.62, 35.84, 55.93, 96.99, 120.26, 122.37, 128.24, 128.87, 130.90, 132.58, 133.39, 135.36, 154.85, 161.17; CHN Analysis: Anal. Calcd for  $\text{C}_{14}\text{H}_{11}\text{BrN}_4\text{O}$ : C, 50.77; H, 3.35; N, 16.92. Found: C, 50.68; H, 3.27; N, 16.97.



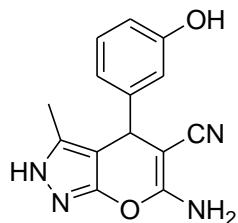
**6-amino-4-(2-methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5 carbonitrile (5).**

FT-IR (KBr)  $\nu_{\max}(\text{cm}^{-1})$ : 1047, 2195, 2837, 3160, 3313, 3376.  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 1.78 (s, 3H), 3.77 (s, 3H), 4.96 (s, 1H), 6.77 (s, 2H), 6.87-6.91 (m, 1H), 6.96-7.00 (m, 2H), 7.17-7.21 (m, 1H), 11.99 (s, 1H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.45, 29.09, 55.53, 56.33, 97.78, 111.26, 120.77, 120.84, 127.86, 128.57, 132.07, 134.99, 155.04, 156.31, 161.43.



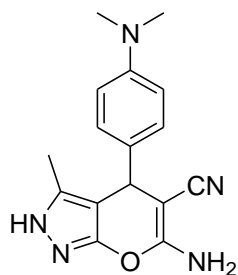
**6-amino-4-(4-hydroxy-3-methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (6).**

FT-IR (KBr)  $\nu_{\max}(\text{cm}^{-1})$ : 1029, 2195, 2981, 3220, 3274, 3328, 3412, 3490.  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 1.81 (s, 3H), 3.70 (s, 3H), 4.49 (s, 1H), 6.52-6.55 (m, 1H), 6.69-6.71 (m, 2H), 6.77 (s, 2H), 8.83 (s, 1H), 12.04 (s, 1H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.79, 35.79, 55.57, 57.59, 97.85, 111.57, 115.37, 119.72, 120.87, 135.34, 135.55, 145.19, 147.29, 154.68, 160.64.



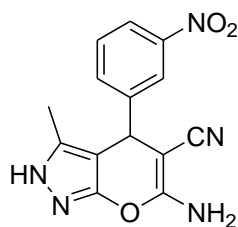
**6-amino-4-(3-hydroxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (7).**

FT-IR (KBr)  $\nu_{\max}(\text{cm}^{-1})$ : 1048, 2177, 3167, 3307, 3362.  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 1.74 (s, 3H), 4.41 (s, 1H), 6.46-6.55 (m, 3H), 6.76 (s, 2H), 7-7.04 (m, 1H), 9.23 (s, 1H), 12.00 (s, 1H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.72, 36.13, 57.21, 97.65, 113.78, 114.09, 118.14, 120.77, 129.22, 135.51, 145.93, 154.72, 157.38, 160.80.



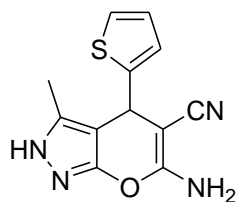
**6-amino-4-(4-(dimethylamino)phenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (8).**

FT-IR (KBr)  $\nu_{\max}(\text{cm}^{-1})$ : 1053, 2189, 3172, 3305, 3385.  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 1.78 (s, 3H), 3.34 (s, 6H), 4.44 (s, 1H), 6.65 (d,  $J = 8.0$  Hz, 2H), 6.73 (s, 2H), 6.95 (d,  $J = 8.0$  Hz, 2H), 12.02 (s, 1H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.74, 35.32, 57.95, 98.14, 112.28, 120.92, 127.93, 132.01, 135.43, 149.18, 154.75, 160.51.



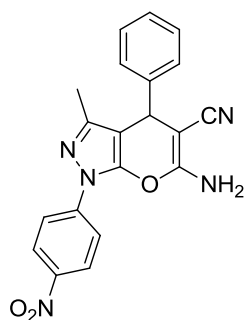
**6-amino-3-methyl-4-(3-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (9).**

FT-IR (KBr)  $\nu_{\max}(\text{cm}^{-1})$ : 1041, 2195, 3117, 3225, 3474.  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 1.80 (s, 3H), 4.87 (s, 1H), 7.03 (s, 2H), 7.64-7.66 (m, 2H), 8.01 (s, 1H), 8.10-8.12 (m, 1H), 12.19 (s, 1H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.71, 35.61, 56.114, 96.63, 120.47, 121.80, 121.94, 130.21, 134.34, 135.86, 146.79, 147.85, 154.66, 161.11.



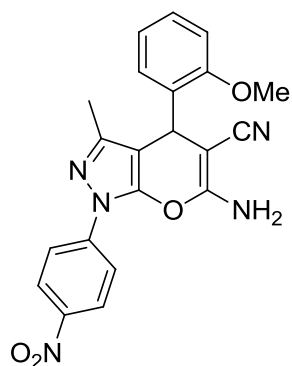
**6-amino-3-methyl-4-(thiophen-2-yl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (10).**

FT-IR (KBr)  $\nu_{\max}(\text{cm}^{-1})$ : 1044, 2192, 3176, 3315, 3362.  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 1.84 (s, 3H), 4.92 (s, 1H), 6.86-6.94 (m, 4H), 7.29-7.30 (m, 1H), 12.09 (s, 1H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 9.69, 31.36, 57.56, 97.52, 120.57, 124.32, 124.93, 126.47, 136, 149.72, 154.26, 160.61.



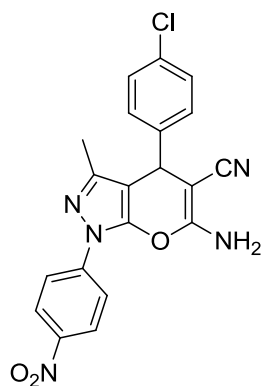
**6-amino-3-methyl-1-(4-nitrophenyl)-4-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (11).**

$^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 1.79 (s, 3H), 4.69 (s, 1H), 7.26-7.32 (m, 5H), 7.35 (s, 2H), 8.10 (d,  $J = 9.2$  Hz, 2H), 8.30 (d,  $J = 9.2$  Hz, 2H),  $^{13}\text{C-NMR}$  (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 12.6, 18.5, 55.9, 99.9, 119.3, 125.5, 127.1, 127.8, 128.5, 142.3, 143.1, 144.2, 144.6, 147.5, 159.1.  $m/z = 373$  ( $\text{M}^+$ ); CHN Analysis: Anal. Calcd for  $\text{C}_{20}\text{H}_{15}\text{N}_5\text{O}_3$ : C, 64.34; H, 4.05; N, 18.78. Found: C, 64.39; H, 3.97; N, 18.69.



**6-amino-4-(2-methoxyphenyl)-3-methyl-2-(4-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (12).**

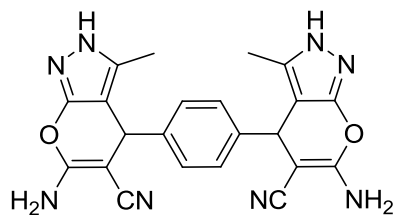
FT-IR (KBr)  $\nu_{\max}(\text{cm}^{-1})$ : 1059, 2186, 2837, 3206, 3327, 3384.  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 1.80 (s, 3H), 3.79 (s, 3H), 5.02 (s, 1H), 6.92-6.94 (m, 1H), 7.02-7.04 (m, 1H), 7.10-7.12 (m, 1H), 7.22-7.24 (m, 3H), 8.09 (d,  $J = 9.1$  Hz, 2H), 8.00 (d,  $J = 8.0$  Hz, 2H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 12.33, 29.86, 55.66, 57.28, 99.95, 111.47, 119.17, 119.80, 120.84, 125.03, 128.43, 129.12, 130.66, 142.42, 144.20, 144.99, 147.27, 156.64, 159.76.  $m/z = 403$  ( $\text{M}^+$ ); CHN Analysis: Anal. Calcd for  $\text{C}_{21}\text{H}_{17}\text{N}_5\text{O}_4$ : C, 62.53; H, 4.25; N, 17.36. Found: C, 62.43; H, 4.31; N, 17.27.



**6-amino-4-(4-chlorophenyl)-3-methyl-1-(4-nitrophenyl)-1,4-dihydropyranopyrazole-5-carbonitrile (13).**

FT-IR (KBr)  $\nu_{\max}(\text{cm}^{-1})$ : 1062, 2194, 3206, 3329, 3418;  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 1.84 (s, 3H), 4.75 (s, 1H), 7.21 (s, 2H), 7.32 (d,  $J = 6.0$  Hz, 2H), 7.41 (d,  $J = 6.0$  Hz, 2H), 8.12 (d,  $J = 8.0$  Hz, 2H), 8.31 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C-NMR}$  (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 13.06, 36.58, 58.71, 100.01, 119.86, 120.01, 125.42, 129.03, 130.18, 132.30, 142.69, 142.89, 145.03, 145.33, 147.95, 159.75;  $m/z = 407$  ( $\text{M}^+$ ); CHN Analysis: Anal. Calcd for  $\text{C}_{20}\text{H}_{14}\text{ClN}_5\text{O}_3$ : C, 58.90; H, 3.46; N, 17.17. Found: C, 58.81; H, 3.54; N, 17.11.





**4,4'-(1,4-phenylene)bis(6-amino-3-methyl-2,4-dihydropyranopyrazole-5-carbonitrile)**

**(14):**

FT-IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 744, 1394, 1491, 1598, 2191, 3225, 3329; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 2.43 (s, 6H), 4.64 (s, 2H), 6.76-6.89 (m, 4H), 7.04-7.23 (m, 4H), 12.00 (s, 2H), <sup>13</sup>C-NMR (150 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 10.41, 35.95, 57.15, 97.76, 120.83, 126.81, 127.67, 135.63, 142.78, 154.71, 160.88; MS: *m/z* = 426 (M<sup>+</sup>); CHN Analysis: Anal. Calcd for C<sub>22</sub> H<sub>18</sub> N<sub>8</sub> O<sub>2</sub>: C, 61.96; H, 4.25; N, 26.28. Found: C, 62.09; H, 4.17; N, 26.19.