Novel iron doped calcium oxalates as promising heterogeneous catalysts for one-pot multi-component synthesis of pyranopyrazoles

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Fig. S1. EDX spectra of (a) 0.5 Fe-CaOx/glu (b) 1.0 Fe-CaOx/glu (c) 2.0 Fe-CaOx/glu (d) 3.0 Fe-CaOx/glu

Table S1: Optimization of the amount of 2.0 Fe-CaOx/glu as catalyst in the model reaction

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<tr>
<th>Entry</th>
<th>Catalyst (mg)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>15</td>
<td>91</td>
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<td>2</td>
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</tr>
<tr>
<td>5</td>
<td>50</td>
<td>15</td>
<td>92</td>
</tr>
</tbody>
</table>

aReaction conditions: 3-fluoro benzaldehyde (1.0 mmol), malononitrile (1.0 mmol), hydrazine hydrate (1.0 mmol), dimethyl acetylenedicarboxylic acid (1.0 mmol), catalyst (20 mg) and ethanol (5.0 mL) were refluxed at 50 °C.
Fig. S2. $^1$H-NMR spectrum of methyl 6-amino-5-cyano-4-(3-fluorophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate

Fig. S3. $^{15}$N-NMR spectrum of methyl 6-amino-5-cyano-4-(3-fluorophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate
Fig. S4. $^{13}$C-NMR spectrum of methyl 6-amino-5-cyano-4-(3-fluorophenyl)-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate

Spectral data of products:

Entry 1:

6-amino-4-(4-Methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile; $^{1}$H NMR (400 MHz, DMSO-d$_6$) 3.65 (s, 3H, OCH$_3$), 3.70 (s, 3H, OCH$_3$), 4.68 (s, 1H, CH), 6.83 (d, $J = 8.52$ Hz, 2H, ArH), 6.99 (s, 1H, NH$_2$), 7.03 (t, $J = 8.88$ Hz, 2H, ArH), 13.69 (s, 1H, NH). $^{13}$C NMR (100 MHz, DMSO-d$_6$): 36.19, 51.71, 54.92, 58.03, 113.53, 114.56, 128.34, 129.93, 137.03, 157.85, 160.02, 160.44; $^{15}$N NMR (40.55 MHz, DMSO-d$_6$) δ 7.08 (s, 2H, NH$_2$).

Entry 2:

6-amino-4-(4-Bromophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile; $^{1}$H NMR (400 MHz, DMSO-d$_6$) 3.64 (s, 3H, OCH$_3$), 4.75 (s, 1H, CH), 7.08 (s, 1H, NH$_2$), 7.47 (d, $J = 8.28$ Hz, 2H, ArH), 7.72 (d, $J = 8.36$ Hz, 1H, ArH), 7.82 (d, $J = 8.48$ Hz, 1H, ArH), 13.77 (s, 1H, NH). $^{13}$C NMR (100 MHz, DMSO-d$_6$): 32.23, 51.62, 56.28, 103.92, 109.77, 115.35, 119.45, 122.00, 133.56, 151.04, 153.11, 156.47, 160.74; $^{15}$N NMR (40.55 MHz, DMSO-d$_6$) δ 7.08 (s, 2H, NH$_2$).

Entry 3:

6-amino-4-(4-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile; $^{1}$H NMR (400 MHz, DMSO-d$_6$) 3.66 (s, 3H, OCH$_3$), 4.78 (s, 1H, CH), 7.06 (s, 1H, NH$_2$), 7.16 (d, $J = 5.68$ Hz, 2H, ArH), 7.35 (d, $J = 5.52$ Hz, 2H, ArH), 13.78 (s, 1H, NH). $^{13}$C NMR (100 MHz, DMSO-d$_6$): 32.23, 51.62, 56.28, 103.92, 109.77, 115.35, 119.45, 122.00, 133.56, 151.04, 153.11, 156.47, 160.74; $^{15}$N NMR (40.55 MHz, DMSO-d$_6$) δ 7.08 (s, 2H, NH$_2$).
MHz, DMSO-d$_6$): 36.98, 52.23, 57.88, 104.11, 120.57, 128.69, 129.77, 144.32, 155.78, 158.78, 160.72; $^{15}$N NMR (40.55 MHz, DMSO-d$_6$) $\delta$ 7.06 (s, 2H, NH$_2$).

Entry 4:

6-amino-4-(3-Hydroxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile;-$^1$H NMR (400 MHz, DMSO-d$_6$) 3.66 (s, 3H, OCH$_3$), 4.63 (s, 1H, CH), 6.53 (s, 1H, ArH), 6.59 – 6.62 (m, 2H, ArH), 6.83 (s, 1H, NH$_2$) 7.09 (t, $J = 7.8$ Hz, 1H, ArH), 9.29 (s, 1H, OH), 13.24 (s, 1H, NH). $^{13}$C NMR (100 MHz, DMSO-d$_6$): 36.14, 57.26, 97.66, 113.80, 114.10, 118.15, 120.77, 129.23, 135.53, 145.93, 154.79, 154.80, 157.13, 158.00, 160.80; $^{15}$N NMR (40.55 MHz, DMSO-d$_6$) $\delta$ 7.06 (s, 2H, NH$_2$).

Entry 5:

6-amino-4-(2-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile;-$^1$H NMR (400 MHz, DMSO-d$_6$) 3.57 (s, 3H, OCH$_3$), 5.26 (s, 1H, CH), 7.05 (s, 1H, NH$_2$), 7.21 – 7.25 (m, 2H, ArH), 7.38 (dd, $J = 7.68$ Hz, 0.96 Hz, 1H, ArH), 7.56 – 7.59 (m, 1H, ArH), 13.76 (s, 1H, NH). $^{13}$C NMR (100 MHz, DMSO-d$_6$): 32.71, 51.62, 56.86, 104.21, 111.45, 120.53, 121.24, 123.23, 128.45, 137.25, 146.39, 152.25, 155.82, 158.46, 160.42; $^{15}$N NMR (40.55 MHz, DMSO-d$_6$) $\delta$ 7.05 (s, 2H, NH$_2$).

Entry 6:

6-amino-5-cyano-4-(thiophen-2-yl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate;-$^1$H NMR (400 MHz, DMSO-d$_6$) 3.75 (s, 3H, OCH$_3$), 5.14 (s, 1H, CH), 6.92 (t, $J = 0.96$ Hz, 1H, ArH$_3$), 6.96 (d, $J = 1.88$ Hz, 1H, ArH), 7.12 (s, 2H, NH$_2$), 7.34 (d, $J = 3.56$ Hz, 1H, ArH), 13.81 (s, 1H, NH). $^{13}$C NMR (100 MHz, DMSO-d$_6$): 31.13, 32.59, 52.39, 58.22, 104.70, 120.60, 124.71, 125.08, 127.09, 128.75, 129.36, 131.44, 134.22, 138.88, 149.91, 155.36, 156.23, 158.93, 160.92; $^{15}$N NMR (40.55 MHz, DMSO-d$_6$) $\delta$ 7.12 (s, 2H, NH$_2$).

Entry 7:

6-amino-5-cyano-4-(furan-2-yl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate;-$^1$H NMR (400 MHz, DMSO-d$_6$) 3.75 (s, 3H, OCH$_3$), 4.93 (s, 1H, CH), 6.16 (d, $J = 2.08$ Hz, 1H, ArH$_3$), 6.35 (d, $J = 0.96$ Hz, 1H, ArH), 7.10 (s, 2H, NH$_2$), 7.48 (d, $J = 1.52$ Hz, 1H, ArH), 13.78 (s, 1H, NH). $^{13}$C NMR (100 MHz, DMSO-d$_6$): 31.18, 52.38, 55.20, 101.96, 105.96, 110.79, 120.50, 129.43, 142.46, 155.72, 158.97, 161.42; $^{15}$N NMR (40.55 MHz, DMSO-d$_6$) $\delta$ 7.10 (s, 2H, NH$_2$).
Entry 1:

$^1$H NMR spectrum of 6-amino-4-(4-Methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

$^{15}$N NMR spectrum of 6-amino-4-(4-Methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile
$^{13}$C NMR spectrum of 6-amino-4-(4-Methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

Entry 2:

$^1$H NMR spectrum of 6-amino-4-(4-Bromophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile
$^{15}$N NMR spectrum of 6-amino-4-(4-Bromophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

$^{13}$C NMR spectrum of 6-amino-4-(4-Bromophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile
Entry 3:

$^1$H NMR spectrum of 6-amino-4-(4-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

$^{13}$C NMR spectrum of 6-amino-4-(4-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile
Entry 4:

$^1$H NMR spectrum of 6-amino-4-(3-Hydroxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

$^{15}$N NMR spectrum of 6-amino-4-(3-Hydroxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile
$^{13}$C NMR spectrum of 6-amino-4-(3-Hydroxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

Entry 5:

$^1$H NMR spectrum of 6-amino-4-(2-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile
$^{15}$N NMR spectrum of 6-amino-4-(2-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile

$^{13}$C NMR spectrum of 6-amino-4-(2-Chlorophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile
Entry 6:

$^1$H NMR spectrum of 6-amino-5-cyano-4-(thiophen-2-yl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate

$^{13}$C NMR spectrum of 6-amino-5-cyano-4-(thiophen-2-yl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate
Entry 7:

\(^1\)H NMR spectrum of 6-amino-5-cyano-4-(furan-2-yl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate

\(^{13}\)C NMR spectrum of 6-amino-5-cyano-4-(furan-2-yl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-3-carboxylate