Electronic Supplementary Information

Sulfonic acid-functionalized MIL-101(Cr) as a highly efficient heterogeneous catalyst for one-pot synthesis of 2-amino-4H-chromenes in aqueous medium

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1.1 Materials and instrumentation  

Cr(\textsubscript{NO\textsubscript{3}}\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O, terephthalic acid and all types of aldehydes were purchased from Sigma-Aldrich, USA. C\textsubscript{2}H\textsubscript{5}OH, HF, DCM, DMF were purchased from Merck, Germany. Chlorosulfonic acid, malononitrile, and resorcinol were purchased from Spectrochem Pvt. Ltd. All chemicals are analytical grade and used as purchased without further purification.

Powder x-ray diffraction (PXRD) of the materials was performed on Rigaku, Ultima IV X-ray diffractometer from using Cu-K\textsubscript{α} source (\(\lambda = 1.54 \text{ Å}\)). Field-emission scanning electron microscopy (FESEM, Sigma (Carl Zeiss)) was applied to investigate the size and morphology of the sample and EDS mapping was done in Oxford XMax 20 equipment. Specific surface area, pore volume, average pore diameter of the materials was measured with the Autosorb-1 (Quantachrome, USA) instrument at 77K. X-ray photoelectron spectroscopy was carried out on VG Microtech Multilab ESCA 3000 equipment with a non-monochromatized Mg K\textsubscript{α} radiation (hv = 1253.6 eV). FT-IR spectra (4000–400 cm\textsuperscript{-1}) are recorded on KBr discs in a Perkin–Elmer system 2000 FT-IR spectrophotometer. The S contents of the synthesized...
materials were calculated in a Leco S-144DR Dual Range Sulfur Analyzer (accuracy ±0.02) (ASTM D5016 - 08e1). Thermogravimetric analysis was carried out with TA SDT Q600 machine under N₂ atmosphere. ¹H and ¹³C NMR spectra are recorded in an AV-500 Avance-III 500 MHz FT-NMR spectrometer using DMSO-d₆ as a solvent.

Fig. S1 FT-IR spectra of (a) MIL-101(Cr), (b) MIL-101(Cr)-SO₃H and (c) recovered MIL-101(Cr)-SO₃H

Fig. S2 FESEM images of a) MIL-101(Cr), b) Fresh MIL-101(Cr)-SO₃H catalyst and c) recovered MIL-101(Cr)-SO₃H catalyst
Fig. S3 Thermogravimetric analysis of (a) MIL-101(Cr)-SO\(_3\)H and (b) MIL-101(Cr)

Table S1 Effect of solvent\(^a\)

<table>
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<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield(%)(^b)</th>
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<tr>
<td>1</td>
<td>Ethanol</td>
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</tr>
<tr>
<td>2</td>
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<td>Acetonitrile</td>
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<td>5</td>
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<td>DCM</td>
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<tr>
<td>7</td>
<td>Solvent free</td>
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</tr>
</tbody>
</table>

\(^a\)Reaction condition: benzaldehyde (1 mmol), resorcinol (1 mmol) and malononitrile (1 mmol), time =3h, reflux condition

\(^b\) Isolated yields are based on benzaldehyde

Table S2 Synthesis of 2-Amino-3-cyano-7-hydroxy-4-(4-chlorophenyl)-4H-chromene by different catalyst in the literature\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>TON</th>
</tr>
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</table>
| 1     | Na\(_2\)WO\(_4\)
\(\cdot2\)H\(_2\)O | 45        | 5      |
| 2     | FeCl\(_3\)          | 18        | <1    |
| 3     | AlCl\(_3\)
\(\cdot6\)H\(_2\)O | 12        | <1    |
| 4     | H\(_2\)WO\(_4\)      | 40        | 3.3   |
| 5\(^b\) | TAFMC-1            | 80        | 72.0  |
| 6\(^c\) | MIL-101(Cr)-SO\(_3\)H | 76        | 205.4 |

\(^a\)Reaction condition: 4-chlorobenzaldehyde (1 mmol), resorcinol (1 mmol), malononitrile (1 mmol), water=5 ml, catalyst =30 mg, \(^b\) TAFMC-1=Tungstic acid functionalized SBA-15

\(^c\) MIL-101(Cr)-SO\(_3\)H=0.37mol\%
1. NMR data recorded for compounds

2-Amino-3-cyano-7-hydroxy-4-(4-phenyl)-4H-chromene (Product 2a, Table 3)

![Structure of Product 2a](image)

Yellow solid: $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 9.72 (s, 1H), 7.32–7.29 (m, 2H), 7.22–7.16 (m, 3H), 6.87 (s, 2H), 6.54–6.38 (m, 2H), 6.19–6.18 (m, 1H), 4.62 (s, 1H); $^{13}$C NMR (500 MHz, DMSO-$d_6$) $\delta$ 160.6, 157.4, 146.7, 130.8, 129.8, 128.3, 127.7, 126.9, 121.0, 114.1, 112.7, 110.5, 102.5, 56.6, 29.9.

2-Amino-3-cyano-7-hydroxy-4-(4-chlorophenyl)-4H-chromene (Product 2b, Table 3)

![Structure of Product 2b](image)

Yellow solid: $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 9.24 (s, 1H), 7.37–7.32 (m, 2H), 7.27–7.20 (m, 2H), 6.95 (s, 2H), 6.91–6.89 (m, 1H), 6.36–6.33 (m, 1H), 6.22–6.21 (m, 1H) 4.41 (s, 1H); $^{13}$C NMR (500 MHz, DMSO-$d_6$) $\delta$ 160.6, 157.4, 146.7, 130.8, 129.0, 114.1, 112.3, 108.6, 102.6, 55.9, 29.8.

2-Amino-3-cyano-7-hydroxy-4-(4-bromophenyl)-4H-chromene (Product 2c, Table 3)

![Structure of Product 2c](image)

Yellow solid: $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 9.79 (s, 1H), 7.50–7.48 (d, 2H, $J = 10$ Hz), 7.15–7.13 (d, 2H, $J = 10$ Hz), 6.94 (s, 2H), 6.80–6.77 (d, 1H, $J = 10$ Hz), 6.54–6.52 (d, 1H, $J = 10$ Hz), 6.21–6.20 (d, 1H, $J = 5$ Hz), 4.66 (s, 1H); $^{13}$C NMR (500 MHz, DMSO-$d_6$) $\delta$ 160.6, 157.6, 149.1, 146.0, 132.5, 130.2, 130.1, 130.0, 120.1, 113.4, 112.9, 106.6, 102.9, 56.2, 29.9.
2-Amino-3-cyano-7-hydroxy-4-(4-methylphenyl)-4H-chromene (Product 2d, Table 3)

![Chemical Structure Image]

Yellow solid: $^1$H NMR (500 MHz, DMSO-d$_6$) δ 9.1 (s, 1H), 7.86–7.84 (d, 2H, $J = 10$ Hz), 7.41–7.39 (d, 2H, $J = 10$ Hz), 6.93 (s, 2H), 6.78–6.76 (d, 1H, $J = 10$ Hz), 6.59–6.55 (m, 1H), 6.19–6.17 (m, 1H), 4.66 (s, 1H), 2.39 (s, 3H); $^{13}$C NMR (500 MHz, DMSO-d$_6$) δ 161.5, 158.7, 146.0, 131.0, 130.4, 130.0, 129.0, 114.7, 113.7, 106.6, 102.8, 56.0, 29.8, 21.7.

2-Amino-3-cyano-7-hydroxy-4-(4-methoxyphenyl)-4H-chromene (Product 2e, Table 3)

![Chemical Structure Image]

Yellow solid: $^1$H NMR (500 MHz, DMSO-d$_6$) δ 9.2 (s, 1H), 7.92–7.90 (d, 2H, $J = 10$ Hz), 7.09–7.07 (d, 2H, $J = 10$ Hz), 6.94 (s, 2H), 6.90–6.88 (d, 1H, $J = 10$ Hz), 6.28–6.23 (m, 1H), 6.21–6.20 (m, 1H), 4.40 (s, 1H), 3.84 (s, 3H); $^{13}$C NMR (500 MHz, DMSO-d$_6$) δ 160.5, 158.9, 133.8, 130.2, 124.5, 115.4, 114.2, 106.7, 103.3, 77.2, 56.2, 29.9.

2-Amino-3-cyano-7-hydroxy-4-(4-hydroxyphenyl)-4H-chromene (Product 2f, Table 3)

![Chemical Structure Image]

Yellow solid: $^1$H NMR (500 MHz, DMSO-d$_6$) δ 9.73 (s, 1H), 6.99–6.97 (d, 2H, $J = 10$ Hz), 6.92 (s, 2H), 6.90 (s, 1H), 6.89–6.84 (m, 2H), 6.34 (s, 1H), 6.22–6.20 (d, 1H, $J = 10$ Hz) 4.3 (s, 1H); $^{13}$C NMR (500 MHz, DMSO-d$_6$) δ 160.2, 158.7, 134.1, 130.1, 123.0, 116.8, 115.3, 114.3, 106.7, 102.9, 55.7, 29.7.
2-Amino-3-cyano-7-hydroxy-4-(3-hydroxyphenyl)-4H-chromene (Product 2g, Table 3)

Yellow solid: $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 9.49 (b, 1H), 7.11–7.07 (m, 1H), 6.99-6.91 (m, 1H), 6.81 (s, 2H), 6.67–6.62 (m, 1H), 6.61–6.58 (m, 1H), 6.53–6.49 (m, 1H) 6.43-6.39 (m, 1H), 6.21-6.15 (m, 1H), 4.49 (s, 1H); $^{13}$C NMR (500 MHz, DMSO-$d_6$) $\delta$ 160.6, 158.7, 157.9, 149.2, 148.2, 130.2, 129.8, 121.1, 118.4, 114.4, 112.7, 106.6, 102.9, 56.8.

2-Amino-3-cyano-7-hydroxy-4-(4-nitrophenyl)-4H-chromene (Product 2h, Table 3)

Chocolate colour solid: $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 9.85 (b, 1H), 8.21–8.19 (d, 2H, $J = 10$ Hz), 7.47–7.45 (d, 2H, $J = 10$ Hz), 7.05 (s, 2H), 6.82–6.80 (d, 1H, $J = 10$ Hz), 6.52–6.50 (d, 1H, $J = 10$ Hz), 6.21-6.18 (m, 1H, $J = 10$ Hz), 4.87 (s, 1H); $^{13}$C NMR (500 MHz, DMSO-$d_6$) $\delta$ 160.8, 157.9, 154.1, 149.2, 146.6, 130.2, 129.0, 124.3, 120.7, 113.0, 112.6, 106.6, 102.8, 55.5, 29.9.

2-Amino-3-cyano-7-hydroxy-4-(2-nitrophenyl)-4H-chromene (Product 2i, Table 3)

Chocolate colour solid: $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 9.67 (s, 1H), 7.95-7.93 (m, 1H), 7.73-7.71 (m, 1H), 7.50-7.42 (m, 2H), 6.98-6.96 (m, 1H), 6.93 (s, 2H), 6.65-6.63 (d, 1H, $J = 10$ Hz), 6.15-6.12 (m, 1H), 4.03 (s, 1H); $^{13}$C NMR (500 MHz, DMSO-$d_6$) $\delta$ 160.1, 158.8, 152.4, 151.8, 135.3, 134.7, 130.0, 128.5, 127.3, 113.1, 112.8, 106.5, 102.8, 56.1, 29.9.
2-Amino-3-cyano-7-hydroxy-4-\((3\text{-nitrophenyl})\)-4H-chromene (Product 2j, Table 3)

Chocolate colour solid: \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 9.9 (s, 1H), 8.11-8.08 (m, 1H), 8.01-8.00 (m, 1H), 7.67-7.59 (m, 2H), 7.03 (s, 2H), 6.86-6.84 (d, 1H, \(J = 10\) Hz), 6.52-6.50 (m, 1H), 6.47-6.45 (d, 1H, \(J = 10\)Hz), 4.90 (s, 1H); \(^{13}\)C NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 160.8, 157.7, 149.2, 148.2, 134.6, 130.7, 130.3, 122.2, 122.0, 120.7, 113.0, 112.8, 106.5, 102.7, 55.6.

2-Amino-3-cyano-7-hydroxy-4-pyridyl-4H-chromene (Product 2k, Table 3)

Chocolate colour solid: \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 9.29 (s, 1H), 8.73–8.65 (m, 1H), 8.08–8.04 (m, 1H), 7.96-7.89 (m, 1H), 7.77 (s, 1H), 6.91-6.90 (m, 1H), 6.93 (s, 2H), 6.26-6.25 (m, 1H), 6.17-6.15 (m, 1H), 4.0 (s, 1H); \(^{13}\)C NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 165.7, 158.7, 149.5, 146.6, 137.7, 133.4, 130.0, 126.9, 124.8, 118.8, 106.5, 102.8, 57.3, 29.9.

2-Amino-3-cyano-7-hydroxy-4-furyl-4H-chromene (Product 2l, Table 3)

Chocolate colour solid: \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 9.17 (s, 1H), 7.52-7.45 (m, 1H), 6.92 (s, 2H), 6.90-6.88 (m, 1H), 6.42-6.41 (m, 1H), 6.37-6.31 (m, 1H), 6.16-6.14 (m, 1H), 6.11-6.09 (m, 1H), 5.45 (s, 1H); \(^{13}\)C NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 162.2, 158.8, 157.0, 142.7, 141.4, 130.0, 128.6, 120.3, 112.6, 110.4, 106.5, 102.8, 57.0, 28.3.