

Electronic Supplementary information

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

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1.1 Materials and instrumentation

Cr (NO₃)₃.9H₂O, terephthalic acid and all types of aldehydes were purchased from Sigma-Aldrich, USA. C₂H₅OH, 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 α source ($\lambda = 1.54 \text{ \AA}$). 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 α radiation ($h\nu = 1253.6 \text{ eV}$). FT-IR spectra (4000–400 cm⁻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 N_2 atmosphere. 1H and ^{13}C NMR spectra are recorded in an AV-500 Avance-III 500 MHz FT-NMR spectrometer using $DMSO-d_6$ as a solvent.

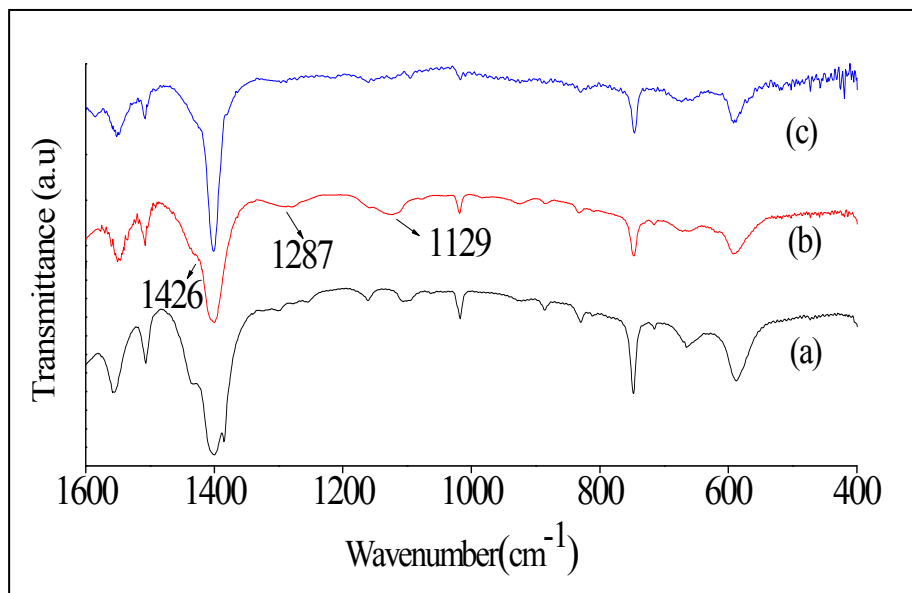


Fig. S1 FT-IR spectra of (a) MIL-101(Cr), (b) MIL-101(Cr)- SO_3H and (c) recovered MIL-101(Cr)- SO_3H

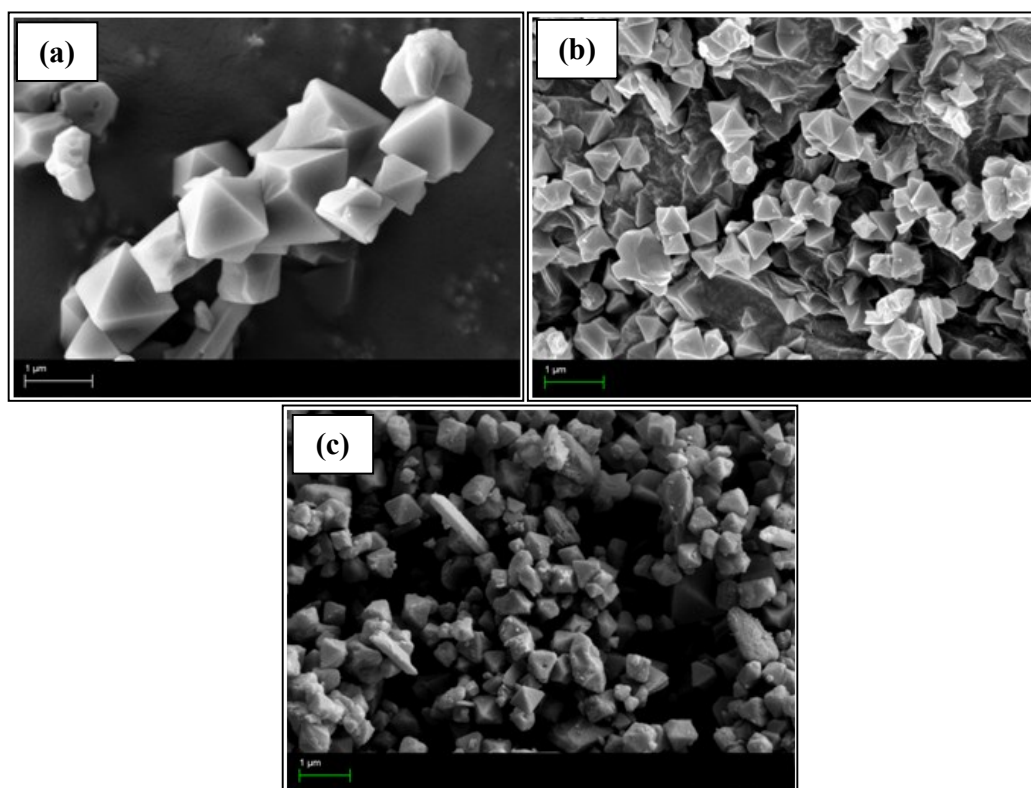


Fig. S2 FESEM images of a) MIL-101(Cr), b) Fresh MIL-101(Cr)- SO_3H catalyst and c) recovered MIL-101(Cr)- SO_3H catalyst

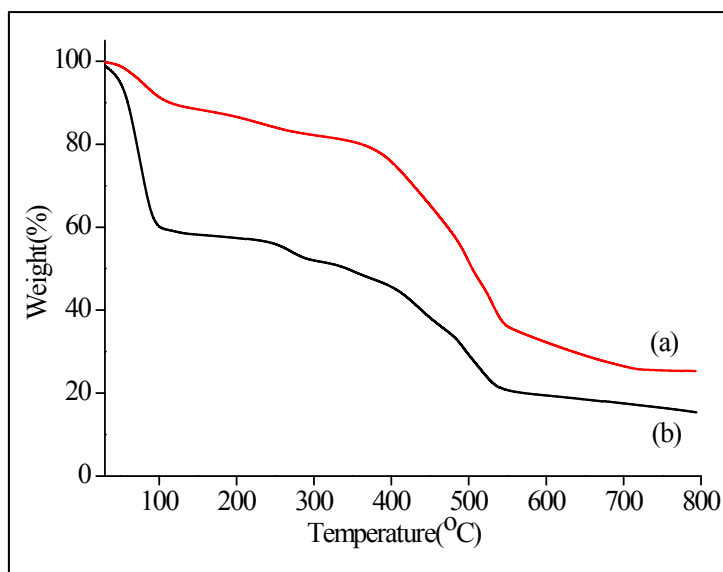


Fig. S3 Thermogravimetric analysis of (a) MIL-101(Cr)-SO₃H and (b) MIL-101(Cr)

Table S1 Effect of solvent^a

Entry	Solvent	Yield(%) ^b
1	Ethanol	75
2	Methanol	70
3	Acetonitrile	30
4	Water	82
5	THF	17
6	DCM	15
7	Solvent free	25

^aReaction 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

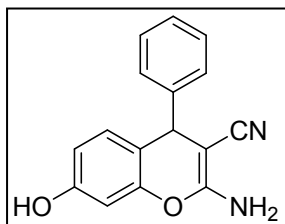
Entry	Catalyst	Yield (%)	TON
1	Na ₂ WO ₄ ·2H ₂ O	45	5
2	FeCl ₃	18	<1
3	AlCl ₃ ·6H ₂ O	12	<1
4	H ₂ WO ₄	40	3.3
5 ^b	TAFMC-1	80	72.0
6 ^c	MIL-101(Cr)-SO ₃ H	76	205.4

^aReaction condition: 4-chlorobenzaldehyde (1 mmol), resorcinol (1 mmol), malononitrile (1mmol),water=5 ml, catalyst =30 mg, ^bTAFMC-1=Tungstic acid functionalized SBA-15

^cMIL-101(Cr)-SO₃H=0.37mol%

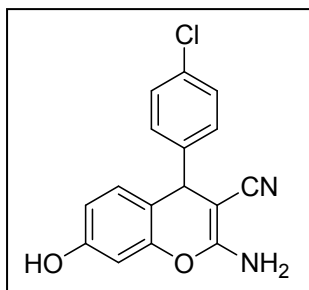
1. NMR data recorded for compounds

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



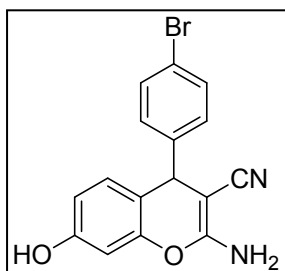
Yellow solid: ^1H NMR (500 MHz, DMSO- d_6) δ 9.72 (s, 1H), 7.32–7.29 (m, 2H), 7.22–7.16 (m, 3H), 6.87 (s, 2H), 6.54–6.38 (m, 2H), 6.19–6.18 (m, 1H), 4.62 (s, 1H); ^{13}C NMR (500 MHz, DMSO- d_6) δ 160.6, 157.4, 146.7, 130.8, 129.8, 128.9, 127.7, 126.9, 121.0, 114.1, 112.7, 106.5, 102.5, 56.6, 29.9.

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



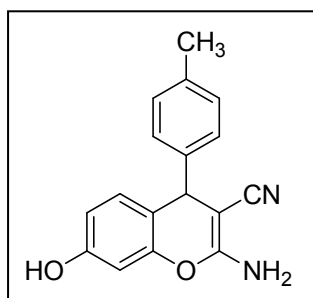
Yellow solid: ^1H NMR (500 MHz, DMSO- d_6) δ 9.24 (s, 1H), 7.37–7.32 (m, 2H), 7.27–7.20 (m, 2H), 6.95 (s, 2H), 6.91–6.89 (m, 1H), 6.36–6.33 (m, 1H), 6.22–6.21 (m, 1H), 4.41 (s, 1H); ^{13}C NMR (500 MHz, DMSO- d_6) δ 160.6, 158.7, 157.5, 146.4, 135.9, 134.3, 131.5, 130.1, , 129.0, 114.1, 112.3, 106.6, 102.9, 55.9, 29.8.

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



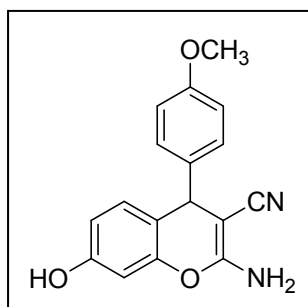
Yellow solid: ^1H NMR (500 MHz, DMSO- d_6) δ 9.79 (s, 1H), 7.50–7.48 (d, 2H, J = 10 Hz), 7.15–7.13 (d, 2H, J = 10 Hz), 6.94 (s, 2H), 6.80–6.77 (d, 1H, J = 10 Hz), 6.54–6.52 (d, 1H, J = 10 Hz), 6.21–6.20 (d, 1H, J = 5 Hz), 4.66 (s, 1H); ^{13}C NMR (500 MHz, DMSO- d_6) δ 160.6, 157.6, 149.1, 146.0, 132.5, 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)



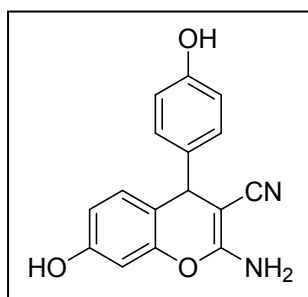
Yellow solid: ^1H NMR (500 MHz, DMSO- d_6) δ 9.1 (s, 1H), 7.86–7.84 (d, 2H, J = 10 Hz), 7.41–7.39 (d, 2H, J = 10 Hz), 6.93 (s, 2H), 6.78–6.76 (d, 1H, J = 10 Hz), 6.59–6.55 (m, 1H), 6.19–6.17 (m, 1H), 4.66 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (500 MHz, DMSO- d_6) δ 161.5, 158.7, 146.0, 131.0, 130.4, 130.0, 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)



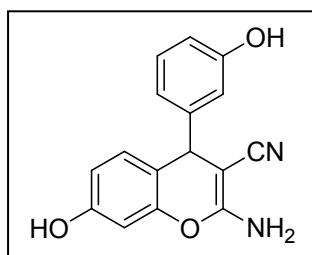
Yellow solid: ^1H NMR (500 MHz, DMSO- d_6) δ 9.2 (s, 1H), 7.92–7.90 (d, 2H, J = 10 Hz), 7.09–7.07 (d, 2H, J = 10 Hz), 6.94 (s, 2H), 6.90–6.88 (d, 1H, J = 10 Hz), 6.28–6.23 (m, 1H), 6.21–6.20 (m, 1H), 4.40 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (500 MHz, DMSO- d_6) δ 160.5, 158.9, 133.8, 130.2, 124.5, 115.4, 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)



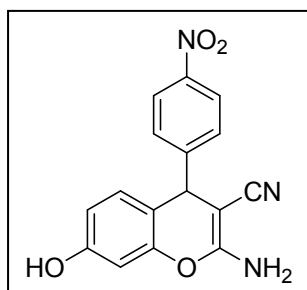
Yellow solid: ^1H NMR (500 MHz, DMSO- d_6) δ 9.73 (s, 1H), 6.99–6.97 (d, 2H, J = 10 Hz), 6.92 (s, 2H), 6.90 (s, 1H), 6.89–6.84 (m, 2H), 6.34 (s, 1H), 6.22–6.20 (d, 1H, J = 10 Hz), 4.3 (s, 1H); ^{13}C NMR (500 MHz, DMSO- d_6) δ 160.2, 158.7, 134.1, 130.1, 123.0, 116.8, 115.3, 114.3, 106.7, 102.9, 55.7, 29.7.

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



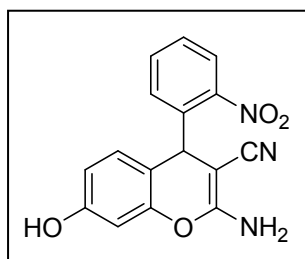
Yellow solid: ^1H NMR (500 MHz, DMSO- d_6) δ 9.49 (b, 1H), 7.11–7.07 (m, 1H), 6.99–6.91(m, 1H), 6.81 (s, 2H), 6.67–6.62 (m, 1H), 6.61–6.58 (m, 1H), 6.53–6.49 (m, 1H) 6.43–6.39 (m, 1H), 6.21–6.15 (m, 1H), 4.49 (s, 1H); ^{13}C NMR (500 MHz, DMSO- d_6) δ 160.6, 158.7, 157.9, 149.2, 148.2, 130.2, 129.8,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



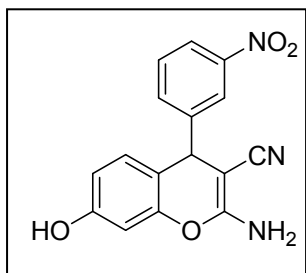
Chocolate colour solid: ^1H NMR (500 MHz, DMSO- d_6) δ 9.85 (b, 1H), 8.21–8.19 (d, 2H, J = 10 Hz), 7.47–7.45 (d, 2H, J = 10 Hz), 7.05 (s, 2H), 6.82–6.80 (d, 1H, J = 10 Hz), 6.52–6.50 (d, 1H, J = 10 Hz), 6.21–6.18 (m, 1H, J = 10 Hz), 4.87 (s, 1H); ^{13}C NMR (500 MHz, DMSO- d_6) δ 160.8, 157.9, 154.1, 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)



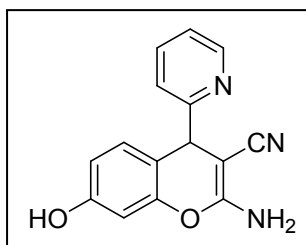
Chocolate colour solid: ^1H NMR (500 MHz, DMSO- d_6) δ 9.67 (s, 1H), 7.95–7.93 (m, 1H), 7.73–7.71(m, 1H), 7.50–7.42 (m, 2H), 6.98–6.96 (m, 1H), 6.93 (s, 2H), 6.65–6.63 (d, 1H, J = 10 Hz), 6.15–6.12 (m, 1H), 4.03(s, 1H); ^{13}C NMR (500 MHz, DMSO- d_6) δ 160.1, 158.8, 152.4, 151.8, 135.3, 134.7, 130.0, 128.5, 127.3, 113.1, 112.8, 106.5, 102.8, 56.1, 29.9.

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



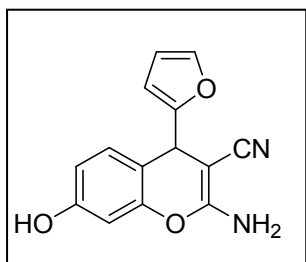
Chocolate colour solid: ^1H NMR (500 MHz, DMSO- d_6) δ 9.9 (s, 1H), 8.11-8.08 (m, 1H), 8.01-8.00 (m, 1H), 7.67-7.59 (m, 2H), 7.03 (s, 2H), 6.86-6.84 (d, 1H, $J = 10$ Hz), 6.52-6.50 (m, 1H), 6.47-6.45 (d, 1H, $J = 10$ Hz), 4.90 (s, 1H); ^{13}C NMR (500 MHz, DMSO- d_6) δ 160.8, 157.7, 149.2, 148.2, 134.6, 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: ^1H NMR (500 MHz, DMSO- d_6) δ 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) δ 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: ^1H NMR (500 MHz, DMSO- d_6) δ 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) δ 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.