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Electronic Supporting Information

Tandem catalysis with bifunctional site-isolated Lewis acid-Brønsted base metal-organic framework, NH_2-MIL-101(Al)

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General information

All the reagents and solvents employed were commercially available, and unless otherwise noted, used as supplied without further purification. Acetonitrile was dried by filtration through alumina according to the procedure of Grubbs.[1] ^{1}H NMR, ^{13}C NMR spectra were recorded at ambient temperature using a 500 MHz Bruker spectrometer. ESI-MS spectra were obtained from the Microanalytical Laboratory of the Pohang University of Science and Technology, Pohang, Korea. Powder XRD diffractograms were obtained on a Bruker D8 Advance system equipped with a Cu sealed tube (λ = 1.54178 Å). Following conditions were used: 40 kV, 40 mA, increment = 0.05º, scan speed = 0.3 s/step. All reactions were carried out under normal atmosphere using a 10 mL screw cap vial. 2-methyl-2-phenyloxirane (**2**), 2,2-diphenyloxirane (**3**), and NH_2-MIL-101 (Al) were synthesized according to literature procedure. The BET surface area (2114 m^2/g) and total pore volume 530 cm^3 (STP/g) of NH_2-MIL-101 (Al) is similar to that of reported value.[3] The catalyst was activated at 100 °C and evacuated and purged with N_2 with minimum 3 cycles prior to use.

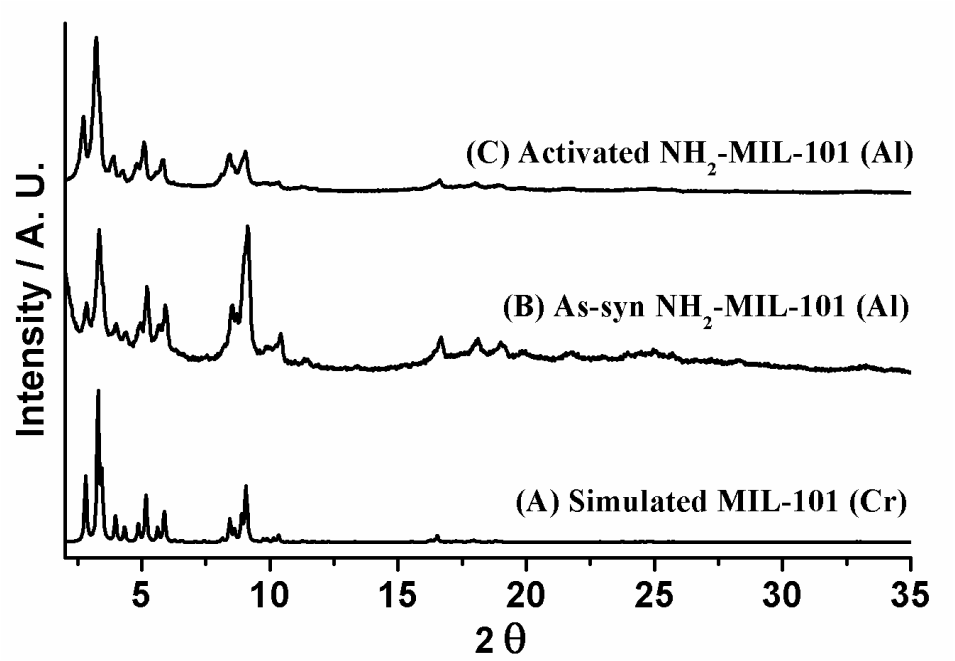

Fig. S1. PXRD patterns for (A) activated sample of NH_2-MIL-101(Al). (B) as-synthesized NH_2-MIL-101(Al). (C) Simulated MIL-101(Cr).

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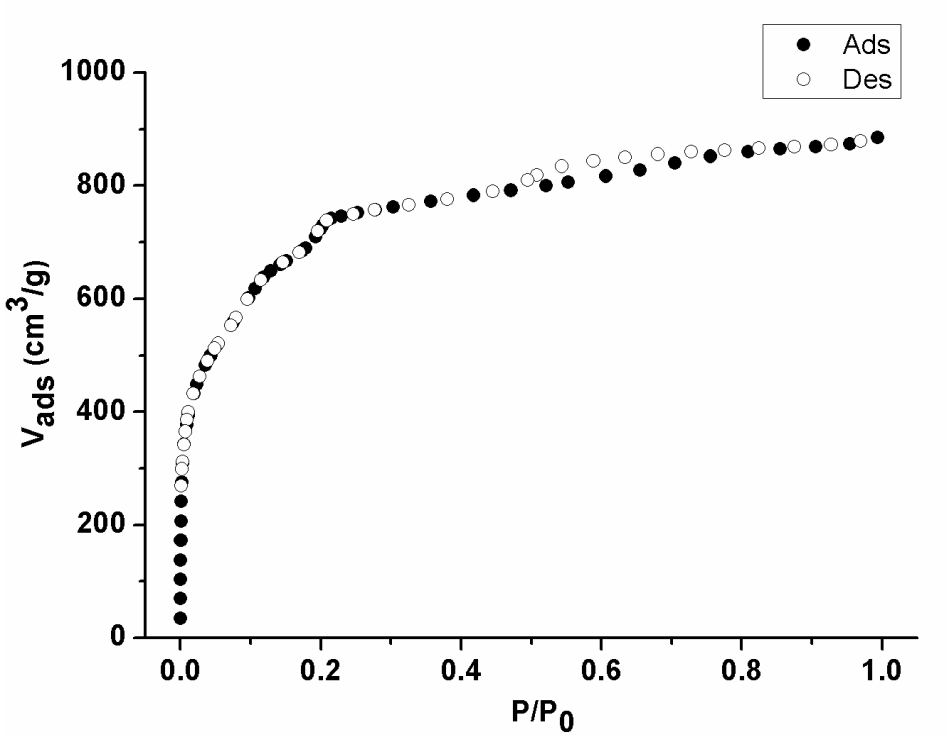
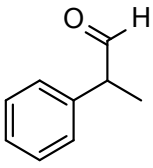


Fig. S2. (a) N_2 adsorption isotherm for NH_2-MIL-101(Al) at 77 K (black round circle symbol represent adsorption and white round circle symbol represents desorption).

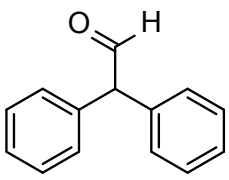
General procedure for the Meinwald rearrangement.

To a loaded catalyst, NH_2-MIL-101 (10 mol%) in acetonitrile, corresponding epoxide (0.13 mmol) in acetonitrile was added, and the reaction mixture was stirred at 60 °C for 1 to 2 days. Upon completion of the reaction as monitored by TLC or NMR, the mixture was cooled to rt and diluted with 5 mL of EtOAc. The catalyst was recovered by centrifugation at 3000 rpm for 15 min and the supernatant liquid was collected and evaporated to dryness. The crude product was purified by column chromatography using silica gel 60 (230–400 mesh). The catalyst was washed repeatedly with EtOAc, dried and reused when required.



2-(2-phenylpropylidene)-propanedinitrile (5a):

Yield: 13 mg (75%); eluent: Hexane-EtOAc: 9:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.46 (d, 3H), 3.64 (d, 1H), 7.21-7.40(m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) 14.8, 53.2, 127.7, 128.5, 129.2, 137.9, 201.3. ESI-MS (m/z): Found: 132.93 (M - 1), Calculated: (133.06).



2-diphenylprop-1-ene-1,1-dicarbonitrile (6a):

Yield: 18 mg (70%); eluent: Hexane-EtOAc: 9:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.91 (d, 1H), 7.23-7.39 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) 64.2, 127.7, 129.1, 129.3, 136.4, 198.7. ESI-MS (m/z): Found:

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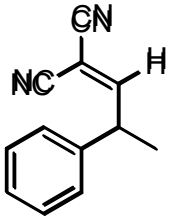
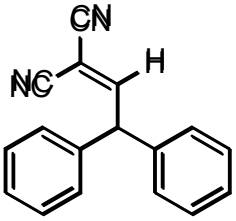
195.08 (M - 1), Calculated: 195.09.

General procedure for the Meinwald rearrangement - Knoevenagel condensation

To a loaded catalyst, NH_2-MIL-101 (10 mol%) in acetonitrile, corresponding epoxide (0.13 mmol) and malononitrile (0.13 mmol) were added and the reaction mixture was stirred at 60 °C for 2 to 4 days. Upon completion of the reaction as monitored by TLC or NMR, the mixture was cooled to rt and diluted with 5 mL of EtOAc. The catalyst was recovered by centrifugation at 3000 rpm for 15 min and the supernatant liquid was collected and evaporated to dryness. The crude product was purified by column chromatography. The catalyst was washed repeatedly with EtOAc, dried and reused when required.



2-(2-phenylpropylidene)-propanedinitrile (5b):
Yield: 17.5 mg (70%); eluent: Hexane-EtOAc: 9:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.57 (d, 3H), 4.15 (h, 1H), 7.24-7.41(m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 19.8, 43.1, 88.1, 110.7, 112.2, 127.2, 128.4, 129.7, 139.4, 171.7. ESI-MS (m/z): Found: 181.08 (M - 1), Calculated: 181.08.



2-(2,2-diphenylethylidene)-propanedinitrile (6b)[4] Yield: 21 mg (70%); eluent: Hexane-EtOAc: 9:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 5.46 (s, 1H), 7.14-7.18 (m, 4H), 7.24-7.41(m, 6H), 7.86 (d, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 53.4, 89.1, 110.7, 112.1, 128.2, 128.4, 129.5, 138.4, 168.1. ESI-MS (m/z): Found: 242.98 (M - 1), Calculated: (243.10).

General procedure for control experiments

To a loaded catalyst, $AlCl_3$ (10 mol%) or dimethyl 2-aminoterephthalate (10 mol%) or a mixture of $AlCl_3$ or dimethyl 2-aminoterephthalate (each 10 mol%) in acetonitirle, corresponding epoxide (0.13 mmol) and malononitrile (0.13 mmol) were added and the reaction mixture was stirred at 60 °C for 2 days. On completion of the reaction, the mixture was cooled to rt and diluted with 20 mL of water and extracted with EtOAc. The organic layer was stored over sodium sulfate and evaporated to dryness. The crude product was analyzed by ^{1}H NMR.

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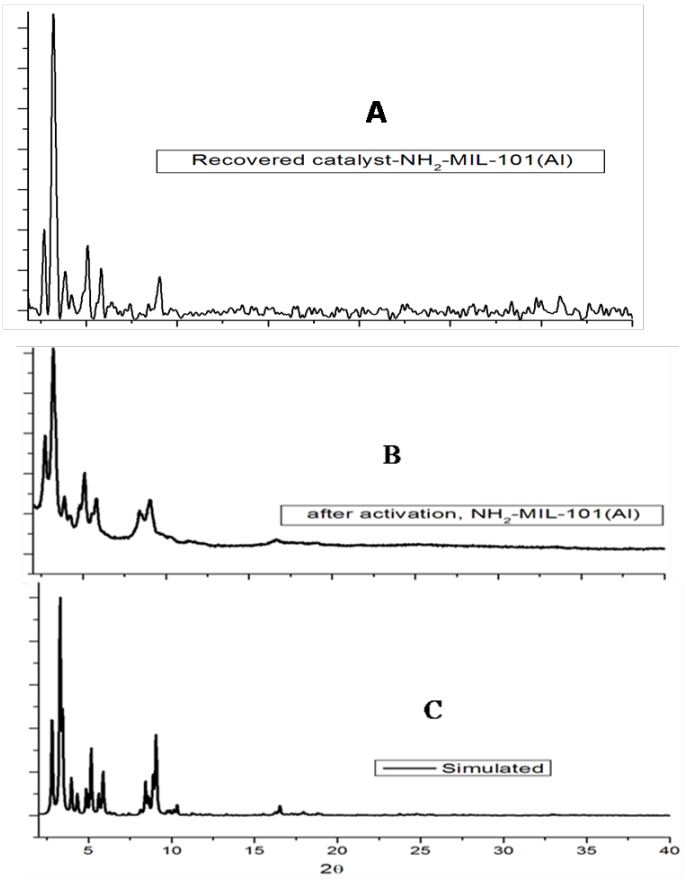

Fig. S3 (A) PXRD of recovered catalyst after 1st cycle. (B) Activated sample of NH_2-MIL-101(Al) (C) Simulated MIL-101(Cr)

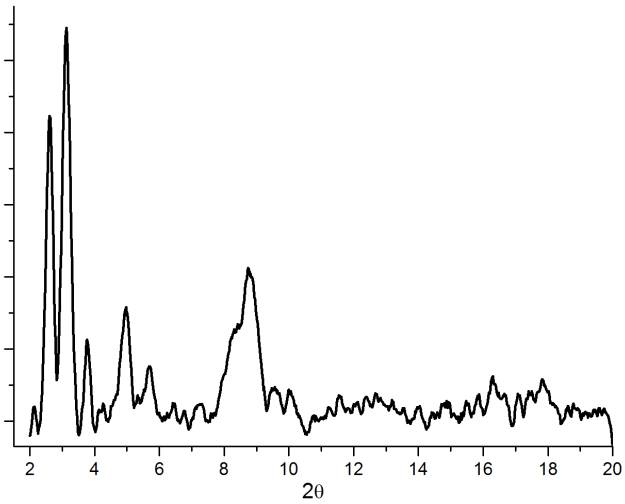

Fig. S4 PXRD of recovered catalyst after 2nd cycle

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1. A. B Pangborn, M. A Giardello, R. H. Grubbs, R. K. Rosen, and F. J. Timmers,. O*rganometallics* 1996**, 15**, 1518.
2. J. A. Ciaccio, A. L. Drahus, R. M. Meis, C. T. Tingle, M. Smrtka and R. Geneste, R. *Syn. Commun*. 2003, **33**, 2135.
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4. B. Kozik, J. Wilamowski, M. Gora and J. J. Sepoi *Tetrahedron* 2008, **64**, 6452.