Schiff base supported MCM-41 catalyzed the Knoevenagel Condensation in water

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Supporting Information

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**General Information.** All the commercial available reagents and the anhydrous solvents were purchased from Aladdin and used without further purification. The samples were analyzed using FT-IR spectroscopy (using a Bruker equinix 55 in KBr matrix in the range of 4000–400 cm$^{-1}$). The X-ray powder diffraction (XRD) of the catalysts was carried out on a instrument (Rigaku R-axis Spider, Japan) using nickel filtered Cu Kα radiation. Scanning electron microscope (SEM) studies were performed on LEO1430VP, Germany. Transmission electron microscope (TEM) images were obtained from a (Hitachi H-600, Japan) instrument. $^1$HNMR spectra were recorded on an INOVA 400 MHz FT-NMR spectrometer, using CDCl$_3$ as solvent and TMS as internal reference (chemical shifts, in ppm). $^{13}$CNMR spectra were collected at INOVA 400 MHz FT-NMR spectrometer, using CDCl$_3$ as solvent and TMS as internal reference (chemical shifts, in ppm). Mass spectroscopy data of the product was collected at a Hewlett-Packard HP1100 LC/MSD instrument. Purification of reaction products were carried out by column chromatography using Qingdao silica gel (300-400 mesh). Analytical thin-layer chromatography (TLC) was performed on silica gel GF254 (Qingdao, China) with ethyl acetate and petroleum ether (60-90 °C). Melting points were determined on an Elemental digital melting points apparatus and were uncorrected.

**Experimental Section**

General procedure for the synthesis of Schiff base supported MCM-41

The preparation of $L_1$ and $L_2$ were performed according to the previous literature$^1$. $L_3$ was prepared by the reaction of $L_2$ (1 g) and 2-phenyl-2H-1,2,3-triazole-4-carbaldehyde (2 mmol) in ethanol (40 mL) in the presence of glacial acetic acid. Afterwards, this mixture was refluxed for 24 h, with continuous stirring, under dry nitrogen atmosphere. The solution was cooled to room temperature and the powder was filtered, washed with diethyl ether and dichloromethane.
General procedure for the synthesis of α,β-unsaturated dicyanides (2a as an example)

The reaction mixture of benzaldehyde (75 µL, 0.75 mmol), malononitrile (0.033 g, 0.5 mmol), L₃ (0.005 g) was stirred at room temperature in water (1.5 mL) for 3 h. The mixture was extracted with dichloromethane (5×5 mL). Notably, the catalyst was still kept in the water phase and then the water phase was directly used for the next cycle. The combined organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated by evaporation. The crude product was purified by Column chromatography on silica gel (petroleumether/ethyl acetate 30:1) to give product 2a (76.3 mg, 99%) as a white solid.

Physical data of compounds isolated

2a: White solid: M.p. = 87-89 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.92 (m, 2H), 7.78 (s, 1H), 7.64 (m, 1H), 7.55 (m, 2H).

2b: White solid: M.p. = 133-134 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.81 (m, 2H), 7.72 (s, 1H), 7.34 (m, 2H), 2.46 (s, 3H).

2c: Yellow solid: M.p. = 88-89 °C; ¹H NMR (400 MHz, CDCl₃): δ = 8.31 (s, 1H), 8.19 (m, 1H), 7.58 (m, 1H), 7.08 (m, 1H), 6.09 (m, 1H), 3.92 (s, 3H).

2d: White solid: M.p. = 106-107 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.74 (s, 1H), 7.45 (m, 3H), 7.18 (m, 1H), 3.86 (s, 3H).

2e: Yellow solid: M.p. = 117-119 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.91 (m, 2H), 7.65 (s, 1H), 7.01 (m, 2H), 3.91 (s, 3H).

2f: White solid: M.p. = 159-160 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.85 (m, 2H), 7.73 (s, 1H), 7.52 (m, 2H).

2g: White solid: M.p. = 165-167 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.77 (m, 2H), 7.70 (m, 3H).

2h: White solid: M.p. = 129-130 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.96 (m, 2H), 7.75 (s, 1H), 7.24 (m, 2H).

2i: Yellow solid: M.p. = 73-75 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.80 (m, 1H), 7.51 (s, 1H), 7.37 (m, 1H), 6.72 (m, 1H).
2j: Yellow solid: M.p. = 160-161 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.52 (s, 1H), 8.13 (m, 2H), 8.0 (s, 1H), 7.51 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 147.91, 141.25, 138.71, 137.54, 129.68, 129.55, 128.49, 119.57, 112.77, 112.14; MS: m/z = 222.1 [M+1], 246.2 [M+Na].

2k: Yellow solid: M.p. = 172-173 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.65 (s, 1H), 8.27 (m, 1H), 8.11 (m, 1H), 7.96 (m, 2H), 7.51 (m, 3H).
Compound 2a

Compound 2b
Compound 2c

[Chemical structure and NMR spectrum]

Compound 2d

[Chemical structure and NMR spectrum]
Compound 2e

Compound 2f
Compound 2g

Compound 2h
Compound 2i

![Compound 2i spectrum and structure](image)

Compound 2j

![Compound 2j spectrum and structure](image)
Compound 2k

Reference