Electronic Supplementary Information

Utilisation of gold nanoparticles on amine-functionalised UiO-66 (NH_2-UiO-66) nanocrystals for selective tandem catalytic reactions

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1. Detailed Synthetic Techniques and Reaction Conditions

All standard chemicals were bought from Sigma-Aldrich, Acros Organics or VWR International and used without further purification.

Synthesis of UiO-66: In a 250 mL glass reaction bottle was measured $ZrCl_4$ (0.640 g; 2.75 mmol), terephthalic acid (0.473 g; 2.85 mmol) and N,N'-dimethylformamide (40 mL), then sonicated for 5 mins to dissolve all compounds. Benzoic acid (3.36 g; 27.50 mmol) was added and the solution sonicated for a further 5 mins until complete dissolution occurred. The bottle was capped and placed in a preheated convection oven at 120 ^{o}C for 48 hours, then allowed to cool to RT naturally. Suspensions of the pale yellow product were collected by centrifugation at 10,000 rpm for 15 minutes. The supernatant was decanted off and the product washed twice with methanol (2 × 60 mL), collecting each time by centrifugation as before. Products were then dried ready for analysis or further experiments.

Synthesis of NH_2-UiO-66: In a 100 mL glass reaction bottle was measured $ZrCl_4$ (0.163 g; 0.70 mmol), 2-aminoterephthalic acid (0.13 g; 0.72 mmol) and N,N'-dimethylformamide (40 mL), then sonicated for 5 mins to dissolve all compounds. Benzoic acid (0.85 g; 7.00 mmol) was added and the solution sonicated for a further 5 mins until complete dissolution occurred. The bottle was capped and placed in a preheated convection oven at 120 ^{o}C for 48 hours, then allowed to cool to RT naturally. Suspensions of the pale yellow product were collected by centrifugation at 10,000 rpm for 15 minutes. The supernatant was decanted off and the product washed twice with methanol (2 × 60 mL), collecting each time by centrifugation as before. Products were then dried ready for analysis or further experiments.

Synthesis of Colloidal Au NPs: In a 150 mL glass vessel was measured methanol (80 mL), $HAuCl_4$ solution (0.38 mL; 10.61 mg/mL in H_2O) and PVP solution (0.20 mL; 6.50 mg/mL in H_2O) and stirred vigorously. To the stirred solution, a freshly prepared aqueous solution of $NaBH_4$ (0.51 mL; 0.1 M) was added dropwise over a period of 3 minutes, then left to stir for a further 2 hours.

For a 1 wt % loading of Au NPs, UiO-66 or NH_2-UiO-66 (200 mg) was added to the stirred Au NP sol and left to stir for 24 hours. The pink-purple powdered product was collected by centrifugation at 10,000 rpm for 15 minutes, the supernatant decanted and washed twice with methanol (2 × 40 mL), collected by centrifugation each time as before. Products were then dried ready for analysis or further experiments.

Cinnamylidene Malononitrile (Propanedinitrile-2-(3-phenyl-2-propen-1-ylidene)): The synthetic method was adapted from a literature reference.[1] To a glass vial (21 mL) was measured cinnamaldehyde (0.793 g; 6.0 mmol), malononitrile (0.396 g; 6.0 mmol), imidazole (0.041 g; 0.6 mmol) and dichloromethane (12 mL). The mixture was stirred at RT for 2 hours.

The mixture was transferred to a separating funnel, water (15 mL) was added and products extracted using 2 × 10 mL of dichloromethane and dried over $MgSO_4$. Evaporation of the solvent yielded large, yellow crystals. The product was confirmed by ^{1}H NMR and referenced against reported data[2] [^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.27 (d, 2H, J= 9.84 Hz), 7.45-7.47 (m, 3H), 7.59-7.61 (m, 3H)].

Catalytic Reactions: To a glass reactor was measured catalyst, reactants, chlorobenzene (as an internal standard) and *tert*-butanol as a solvent in pre-determined concentrations. The RBF was immersed in a preheated oil bath at 70 ^{o}C with stirring and left for the desired amount of time. Samples were extracted at varying time intervals, centrifuged and capped in a vial for GC analysis. (For specific conditions, see respective figures and tables)

Gas Chromatography (GC) Analysis: All reaction samples and kinetic samples were analysed by GC-FID (flame ionisation detector) using a Perkin Elmer Clarus 480 fitted with an autosampler. Components were identified against known commercial standards (with the exception of cinammylidene malononitrile) and quantified using an internal standard method with chlorobenzene.

Catalytic Calculations:

Conversion calculations

$$Conversion\ (\%) = \frac{reactant_{initial}\ (mol) - reactant_{final}\ (mol)}{reactant_{initial}\ (mol)} \times 100$$

Mass Balance (MB) calculations

$$MB\ (\%) = \frac{reactant\ (mol) + product\ (mol)}{reactant_{initial}\ (mol)} \times 100$$

Selectivity calculations

$$Selectivity\ (\%) = \frac{product\ (mol)}{reactant_{initial}\ (mol) - reactant_{final}\ (mol)} \times MB\ (\%) \times 100$$

2. Thermogravimetric Analysis (TGA)

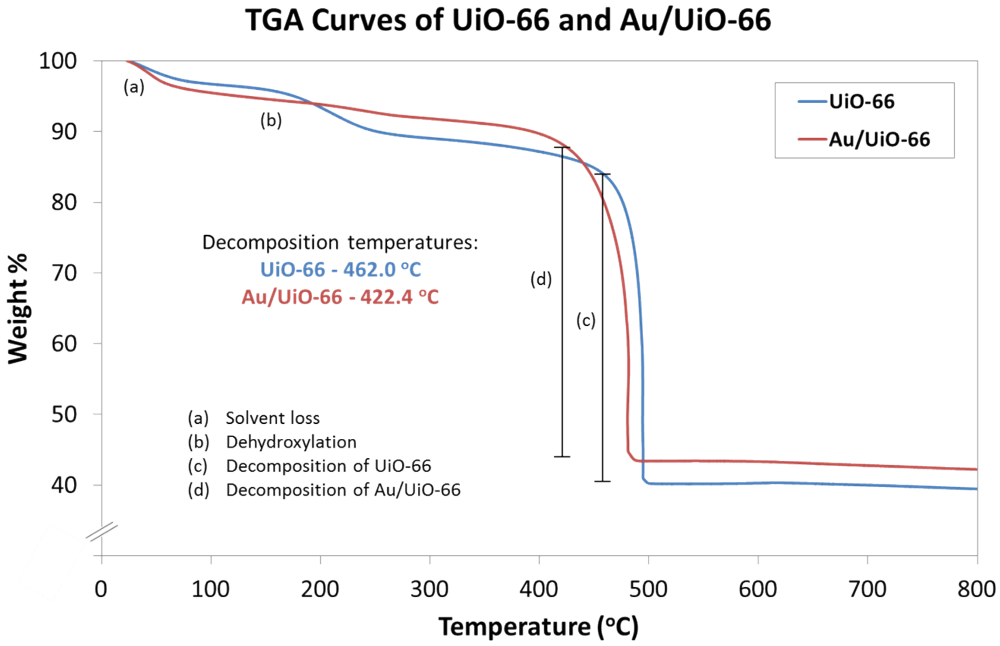

Fig. S1 TGA curves of UiO-66 and Au/UiO-66.
Conditions: Ramp 2 °C/min to 800 °C in 40 % air/N_2 mixture.

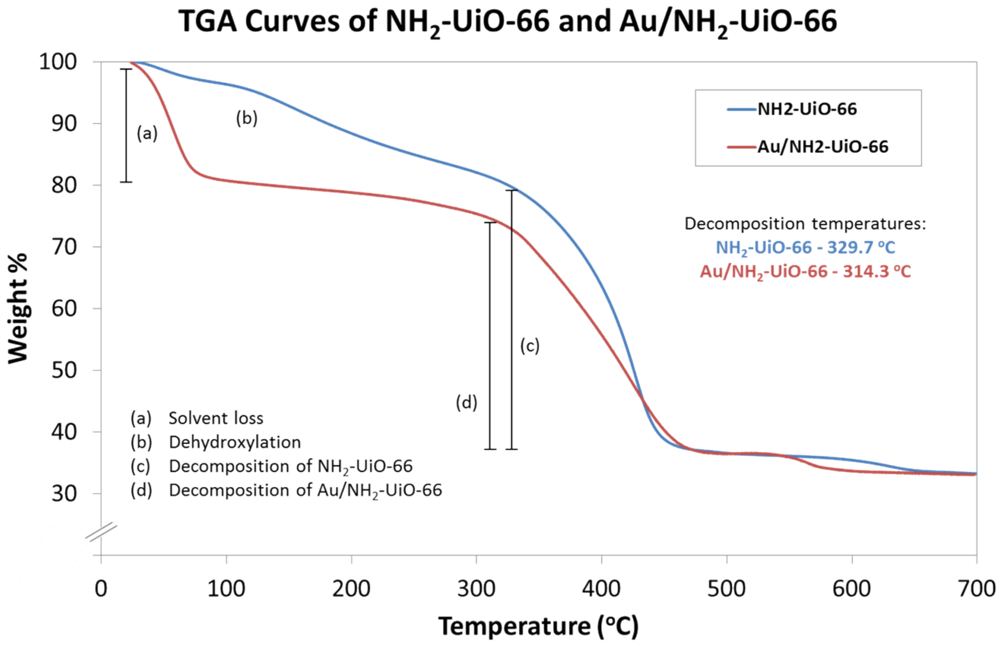

Fig. S2 TGA curves of NH_2-UiO-66 and Au/NH_2-UiO-66.
Conditions: Ramp 2 °C/min to 800 °C in 40 % air/N_2 mixture.

3. Brunauer-Emmett-Teller (BET) Gas Adsorption Surface Analysis

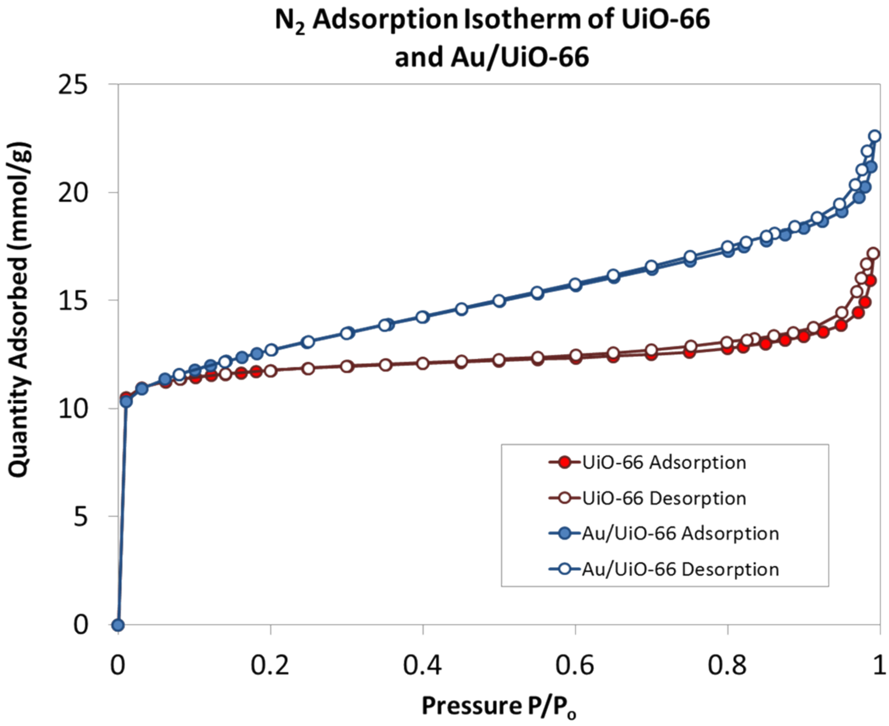

Fig. S3 N$_2$ adsorption/desorption isotherms of UiO-66 and Au/UiO-66 for surface area analysis.

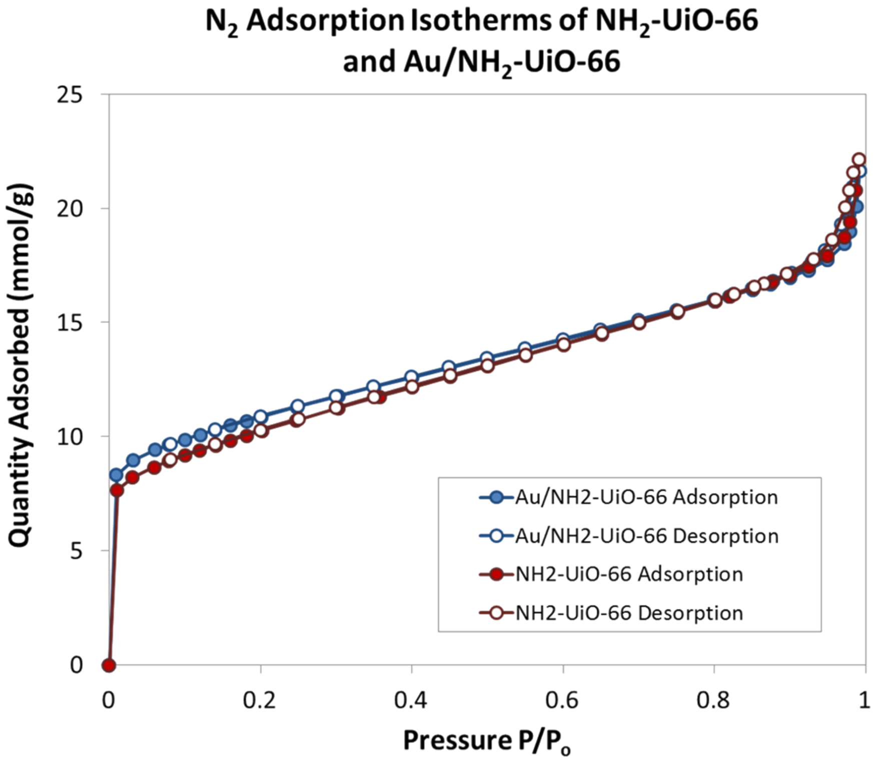

Fig. S4 N$_2$ adsorption/desorption isotherms of NH$_2$-UiO-66 and Au/NH$_2$-UiO-66 for surface area analysis.

4. Powder X-ray Diffraction (PXRD)

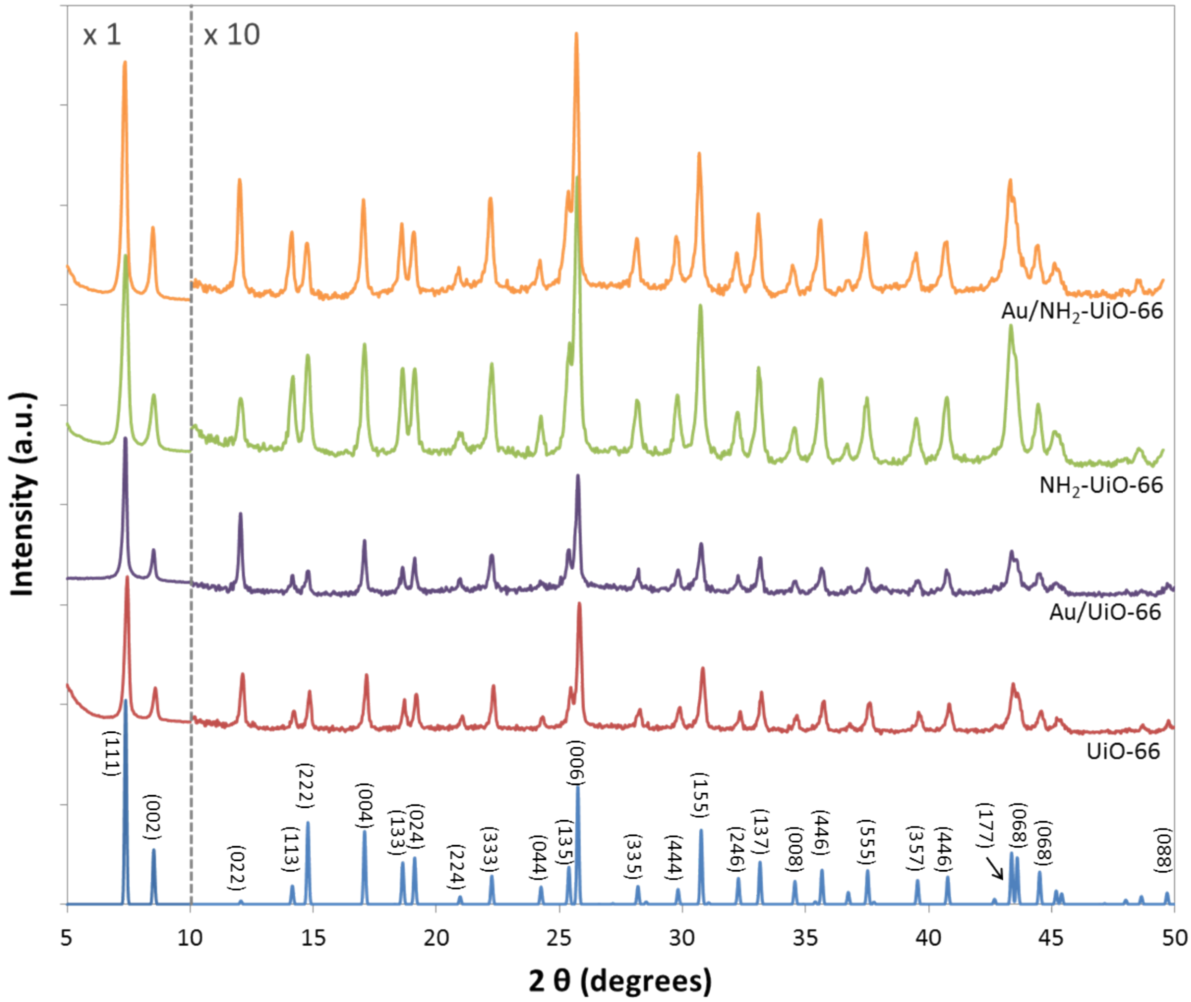

Fig. S5 Simulated PXRD pattern of UiO-66 (blue) and patterns of UiO-66 (red), Au/UiO-66 (purple), NH$_2$-UiO-66 (green) and Au/NH$_2$-UiO-66 (orange).

5. Fourier Transform Infrared Spectroscopy (FT-IR)

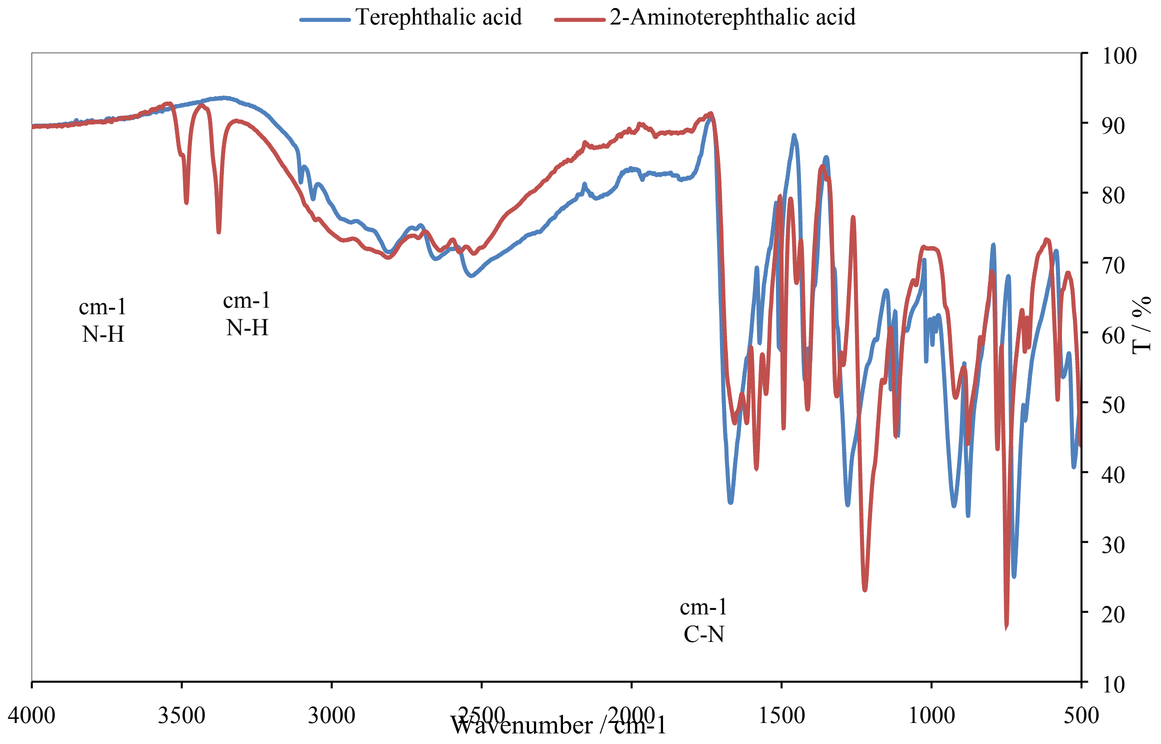

Fig. S6 FT-IR of terephthalic acid (blue) and 2-aminoterephthalic acid (red) with C-N and N-H stretches labelled

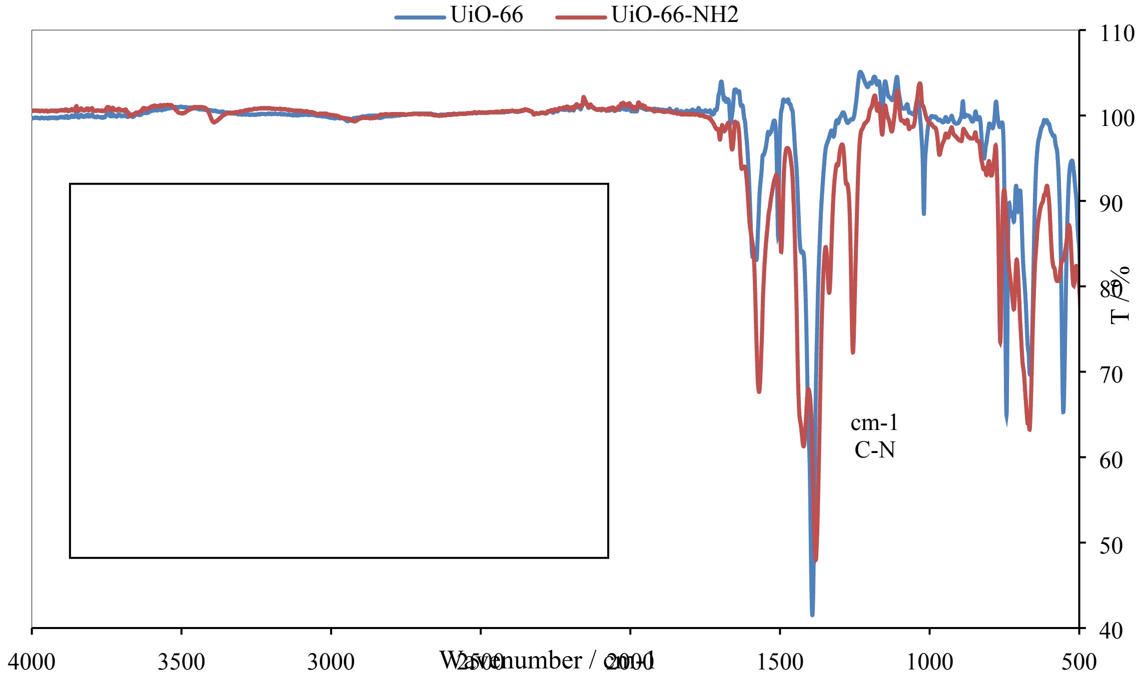

Fig. S7 FT-IR of UiO-66 (blue) and NH_2-UiO-66 (red), with C-N stretch labelled and insert of the 3100 to 3600 cm^{-1} region to highlight N-H stretches

6. Oxidation Catalysis

Table S1 Catalytic data for the oxidation of cinnamyl alcohol to cinnamaldehyde on Au/UiO-66 catalyst

Catalyst	Time (Hrs)	Yield (%)	Conv. (%)[a]	Sel. (%)[b]
Blank	10	7	8	88
Au/UiO-66	6	94	95	> 99

[a] Conversion of cinnamyl alcohol. [b] Selectivity to cinnamaldehyde. Reaction conditions: cinnamyl alcohol (0.1 g), chlorobenzene (0.2 g), catalyst (40 mg), *tert*-butanol (8 mL), TBHP (70 wt % in H_2O; 0.124 mL), reflux setup, T = 70 °C.

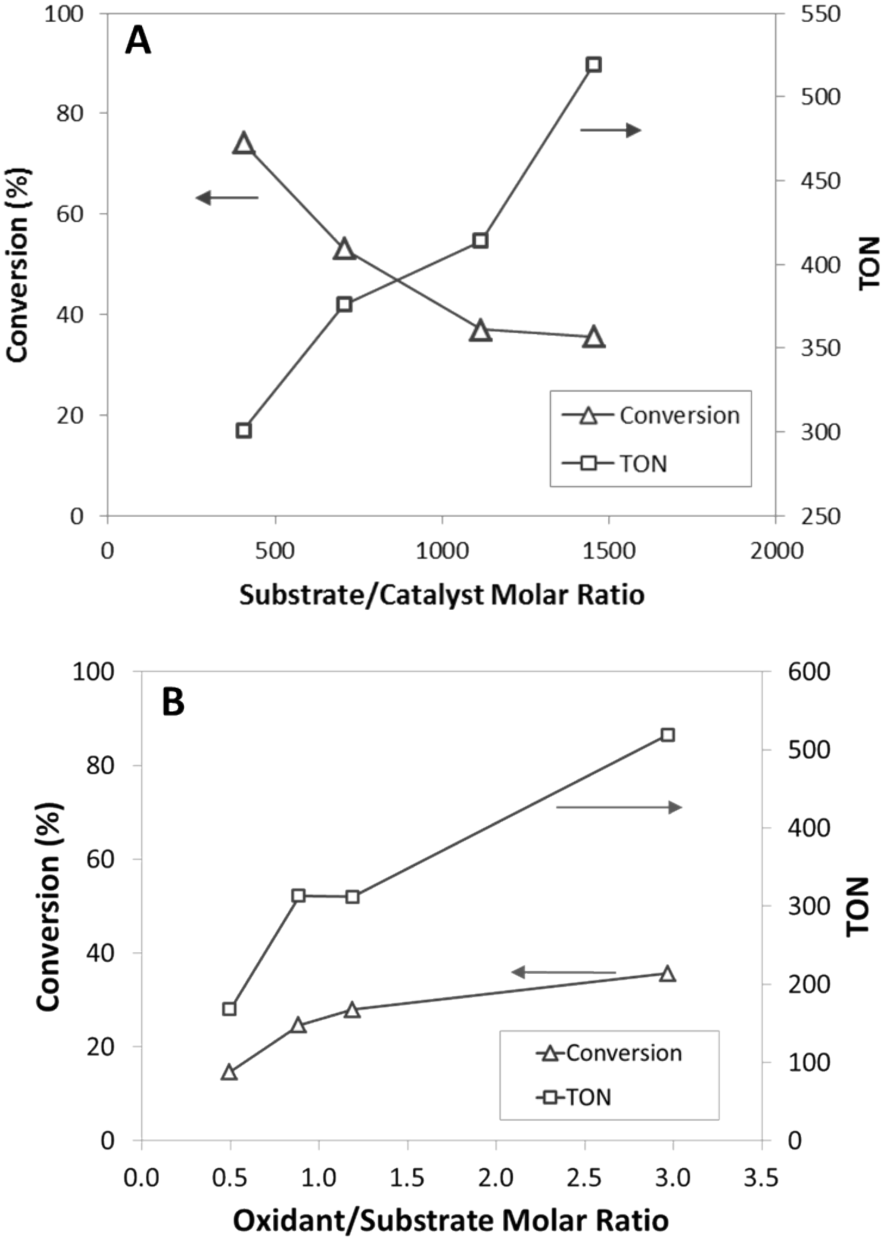

Fig. S8 Effect of substrate (A) and oxidant (B) concentrations on conversions and TONs for the oxidation of cinnamyl alcohol to cinnamaldehyde. Reaction conditions: Au/UiO-66 catalyst (10 mg; 1 wt % metal), chlorobenzene as internal standard (80 mg), TBHP (70 wt % in H_2O), *tert*-butanol (7 mL), stirred for 5 hours at 70 °C.

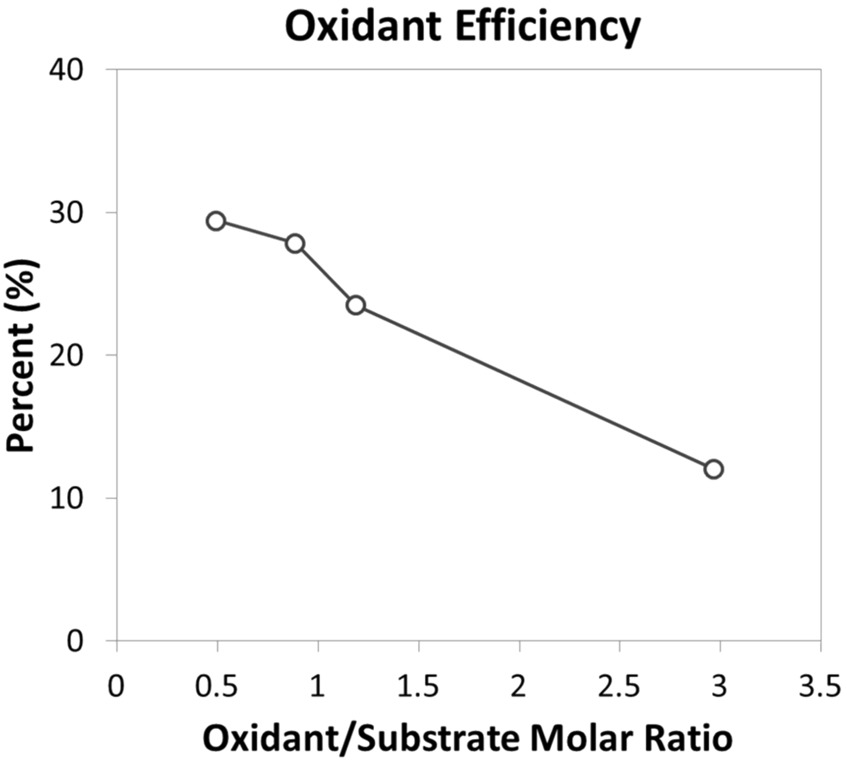

Fig. S9 Changes in oxidant efficiency with oxidant/substrate molar ratios. Au/UiO-66 catalyst (10 mg; 1 wt % metal), chlorobenzene as internal standard (80 mg), TBHP (70 wt% in H_2O; 0.245 mL), *tert*-butanol (7 mL), stirred for 5 hours at 70 °C.

7. Knoevenagel Condensation

Table S2 Catalytic data for the Knoevenagel condensation of cinnamaldehyde with malononitrile using NH_2-UiO-66 as a catalyst

Catalyst	Time (Hrs)	Yield (%)	Conv. (%)[a]	Sel. (%)[b]
Blank	24	37	40	93
NH_2-UiO-66	24	81	83	97

[a] Conversion of cinnamaldehyde. [b] Selectivity to cinnamylidene malononitrile. Reaction conditions: cinnamaldehyde (0.1 g), chlorobenzene (0.2 g), catalyst (40 mg), malononitrile (0.1 g), *tert*-butanol (8 mL), reflux, T = 90 °C.

8. Mechanism of Knoevenagel Condensation

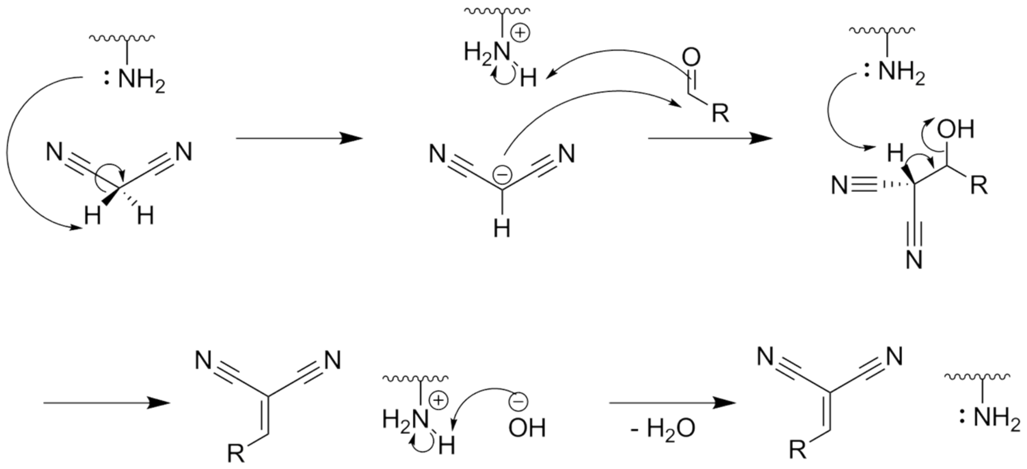

Fig. S10 Mechanism of amine/base catalysed Knoevenagel condensation of an aldehyde with malononitrile by abstraction of methylene hydrogen atoms

9. References

1. M. M. Heravi, M. H. Tehrani, K. Bakhtiari and H. A. Oskooie, *J. Chem. Res.*, 2006, **2006**, 561.

2. A. Karam, N. Villandier, M. Delample, C. K. Koerkamp, J.-P. Douliez, R. Granet, P. Krausz, J. Barrault and F Jérôme, *Chem. Eur. J.*, 2008, **14**, 10196.