Supplementary Information

Pd-IL@H-UiO-66-NH$_2$: A hollow multi-functional hierarchical composite for tandem catalysis

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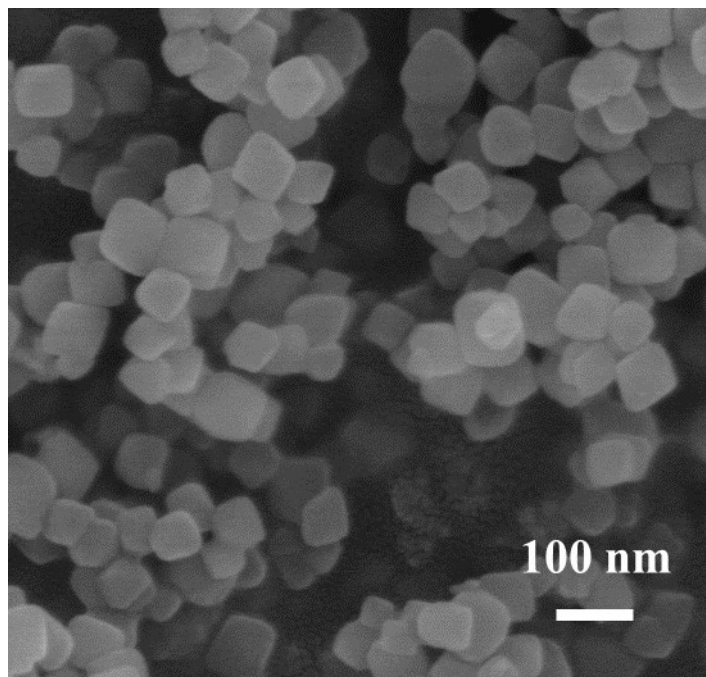*E-mail:,xyyang@whut.edu.cn, changgang2016@whut.edu.cn (G. G. Chang)*

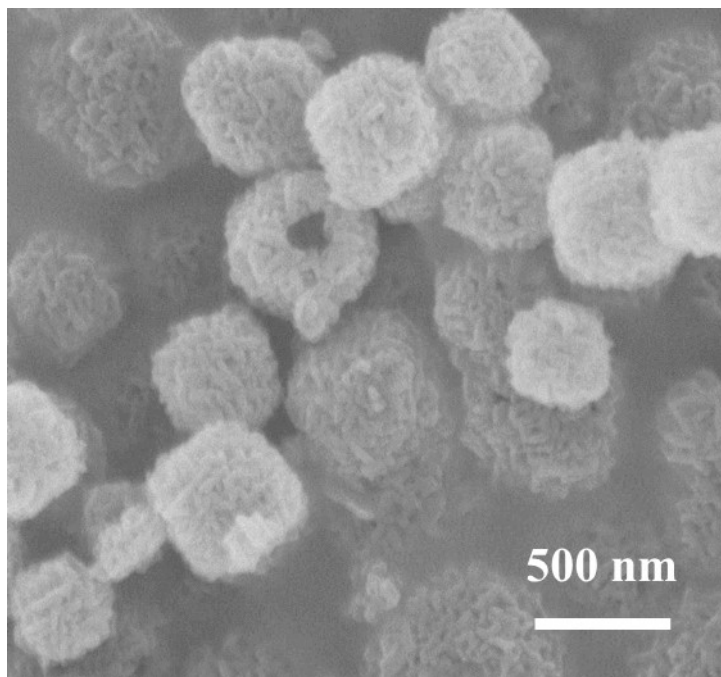**Figure S1** SEM image of traditional UiO-66-NH$_2$ (UiO-66-NH$_2$-T).

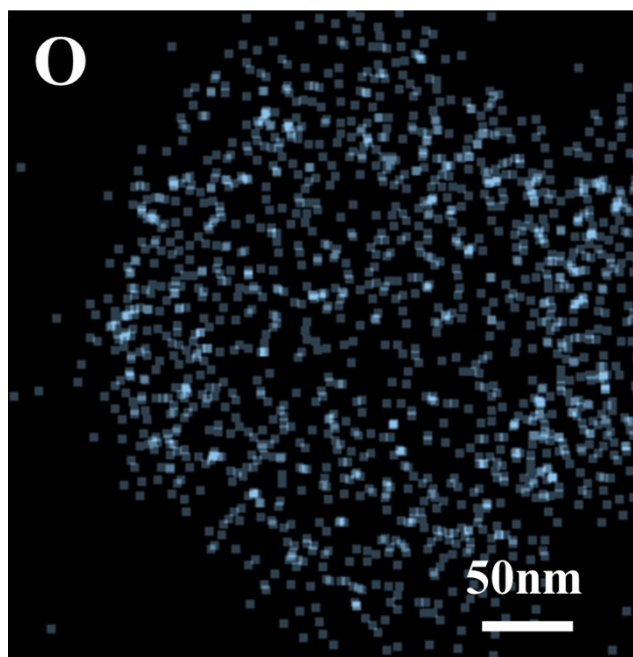**Figure S2** SEM image of IL@H-UiO-66-NH$_2$.

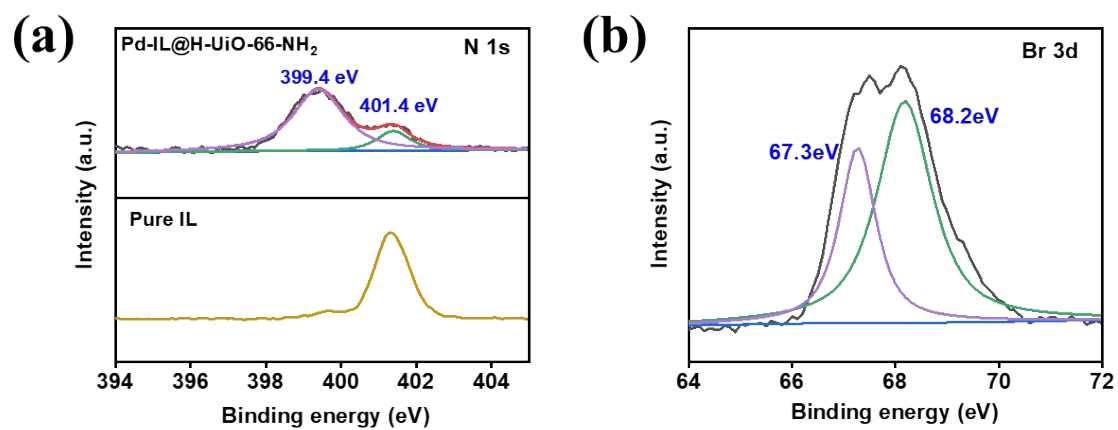**Figure S3.** EDS elemental mappings of O.

Figure S4. (a) High-resolution N 1s XPS spectra of Pd-IL@H-UiO-66-NH$_2$ and pure IL, (b) Br 3d XPS spectra of Pd-IL@H-UiO-66-NH$_2$.
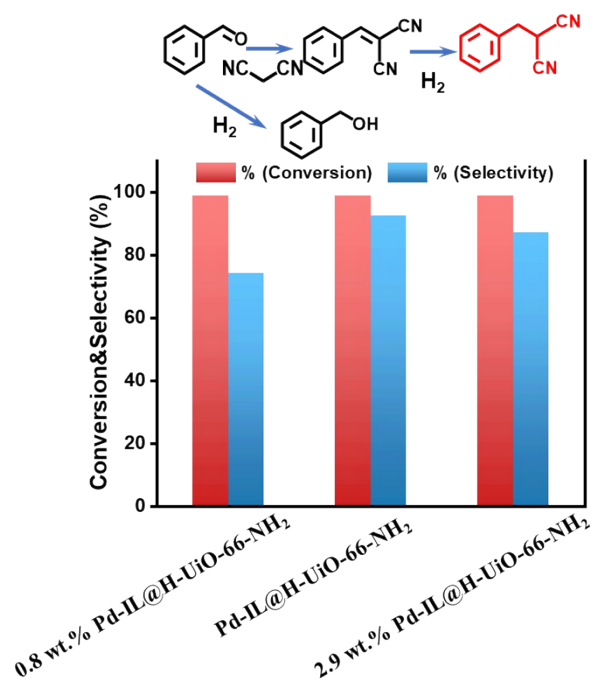
Figure S5. The catalysts with different loading of Pd for one-pot Knoevenagel condensation-hydrogenation reaction.
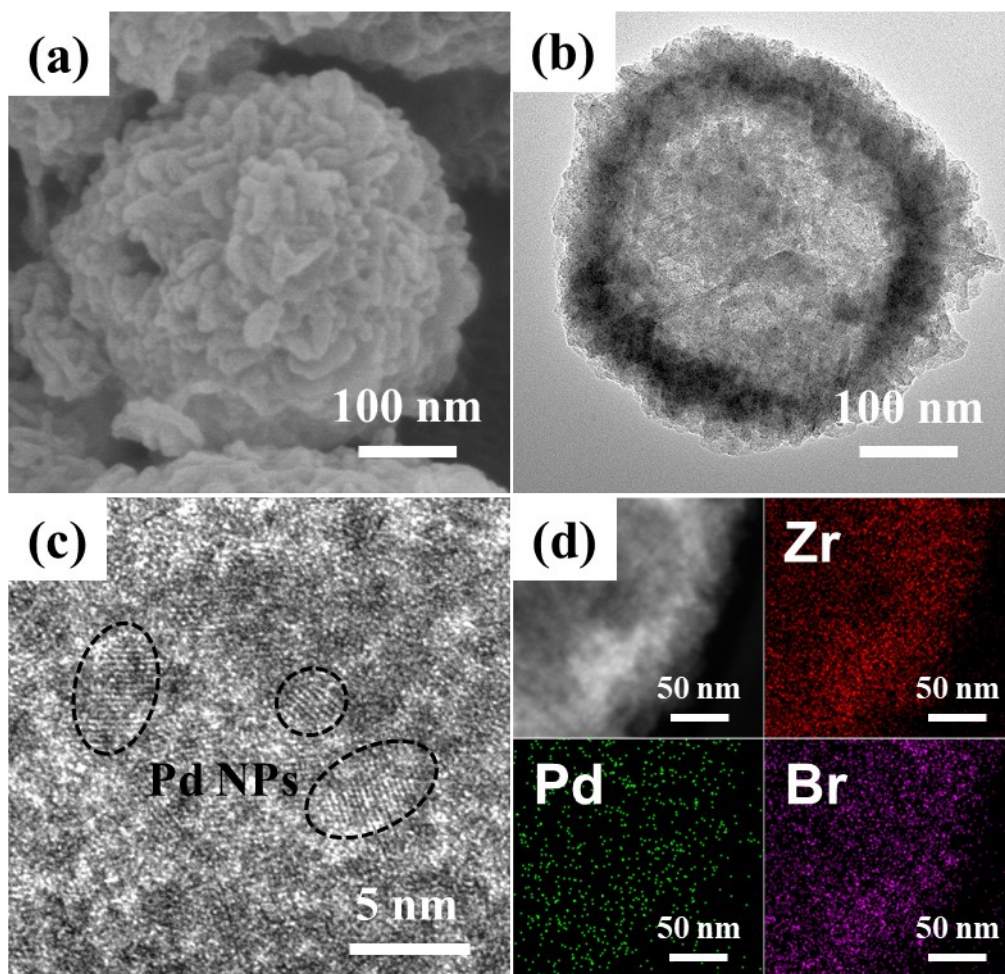
Figure S6 (a) SEM image of Pd-IL@H-UiO-66-NH$_2$ after five successive recycles; (b) TEM images of used Pd-IL@H-UiO-66-NH$_2$; (c) High resolution TEM images of used Pd-IL@H-UiO-66-NH$_2$; (d) HAADF-STEM image of Pd-IL@H-UiO-66-NH$_2$ after five successive recycles and the corresponding EDS elemental mappings of Pd, Zr and Br.
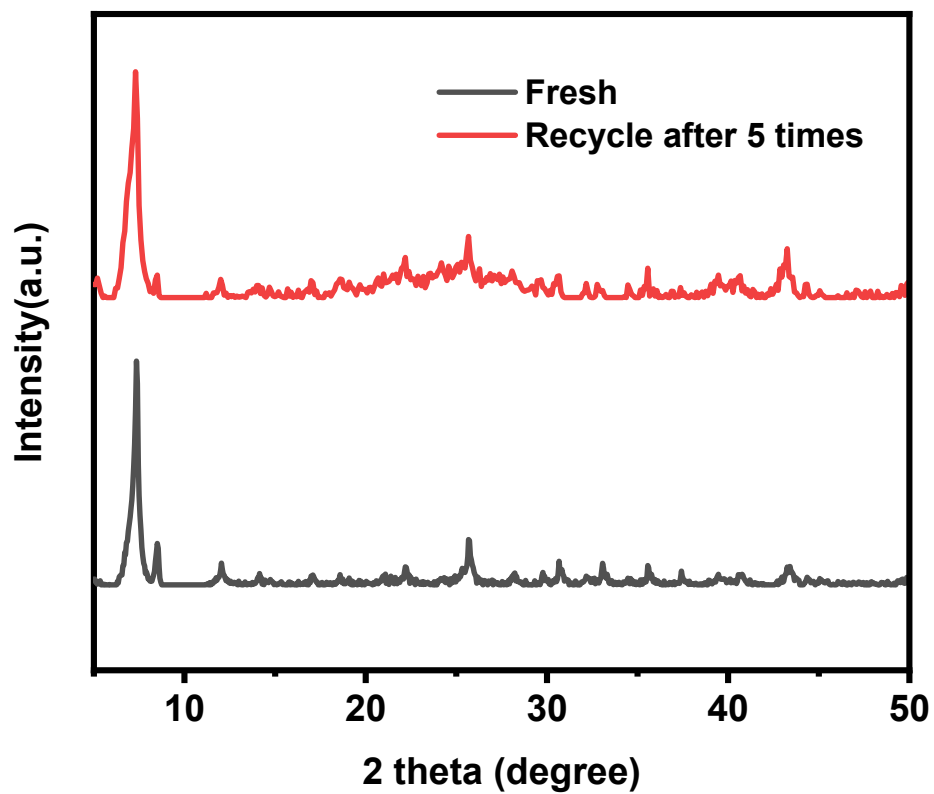
Figure S7 XRD patterns of Pd-IL@H-UiO-66-NH$_2$ after reusage for 5 times.

In our reaction system, all substances can be gasified within the programmed temperature range of gas chromatography. Therefore, we chose the relatively convenient GC-MS for calibration and analysis. Wherein, the substrate and by-product was calibrated by standard substances, and the reaction product benzylmalononitrile was analyzed by GC-MS. It has been able to track the substrates, products and by-products in the reaction process in detail. In view of the complexity of tandem catalysis and the small-scale reaction, it is very difficult and beyond our ability to separate pure samples from small amounts of complex mixtures. We have supplemented the detailed GC-MS data and demonstrated the calculation method of the selectivity and conversion in the reaction. The relative data was also added in the revised supporting information and highlighted in yellow.
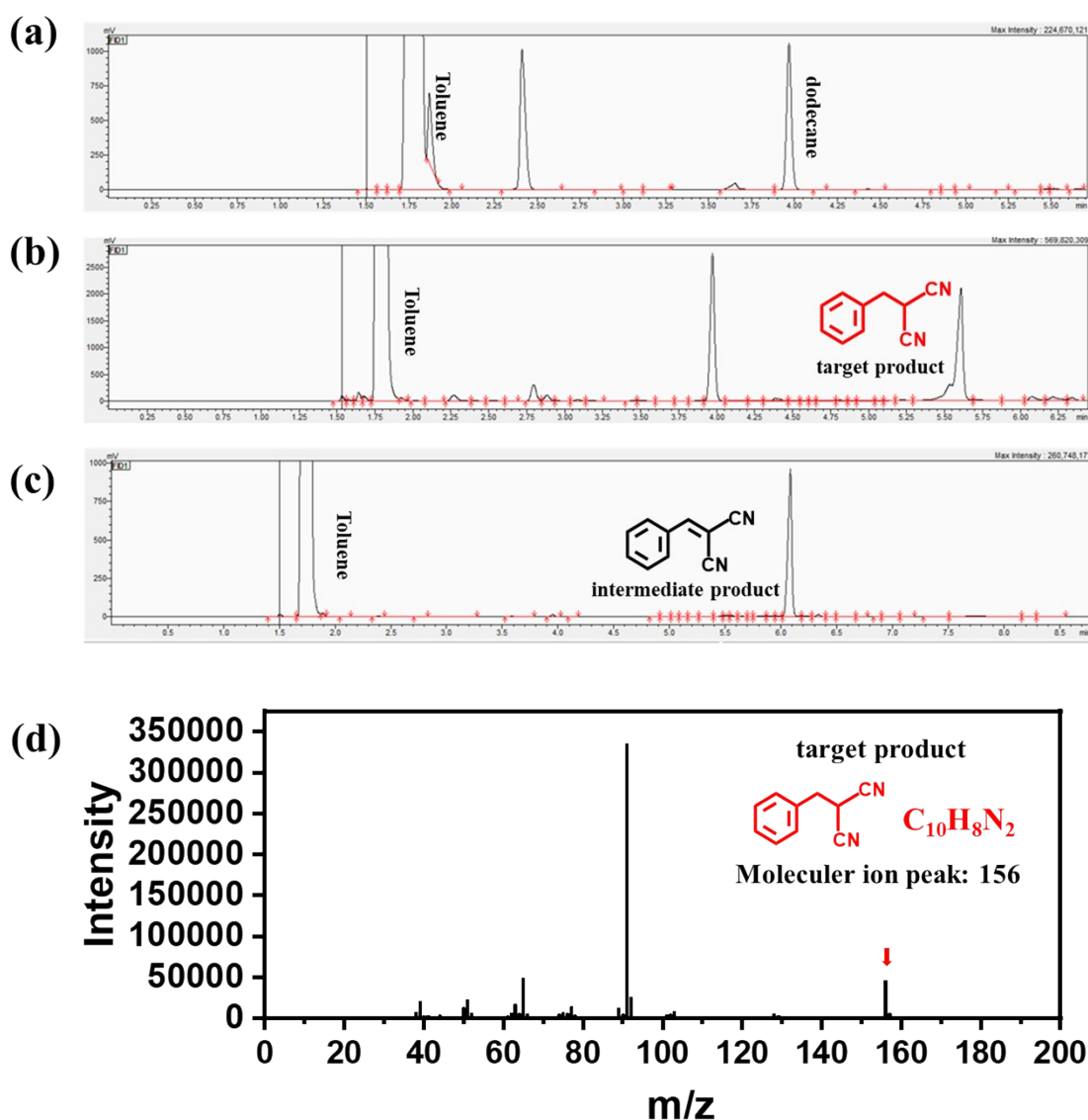
Figure S8. Gas chromatogram of mixed substrates: (a) before reaction; (b) after tandem reaction, (c) GC of intermediate product, (d) GC-MS of target product.

The detailed estimation method of conversion and selectivity:

$Con.(\%) = \dfrac{a-b}{a} \times 100\%$ (a = S $_{benzaldehyde}$ /S$_{dodecane}$ (Before reaction); b = S $_{benzaldehyde}$ /S$_{dodecane}$ (After reaction))

$Sel.(\%) = \dfrac{S_{benzylmalononitrile}}{S_{benzylmalononitrile} + S_{Byproducts}} \times 100\%$

Table S1. The specific surface area of the samples.

Sample	Surface Area(m²/g)
UiO-66-NH$_2$	625
IL@UiO-66-NH$_2$	585
IL@H-UiO-66-NH$_2$	329
Pd-IL@H-UiO-66-NH$_2$	435

Table S2: ICP catalyst Pd-IL@H-UiO-66-NH$_2$ before and after the one-pot Knoevenagel condensation-hydrogenation reaction.

Ru content (wt.%)	Pd-IL@H-UiO-66-NH$_2$
Before the reaction	1.9
After the 5 cycles	1.7