

# Supporting information

## **Halloysite Nanotubes (HNTs)@ZIF-67 Composites – a New Type of Heterogeneous Catalyst for Knoevenagel Condensation Reaction**

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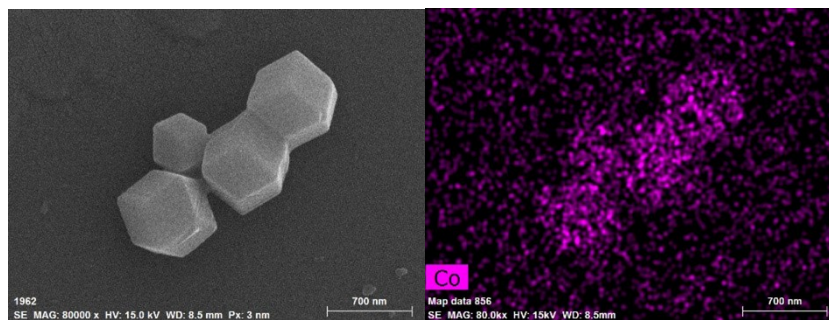


Figure S1. SEM micrograph of the as-synthesized ZIF-67.

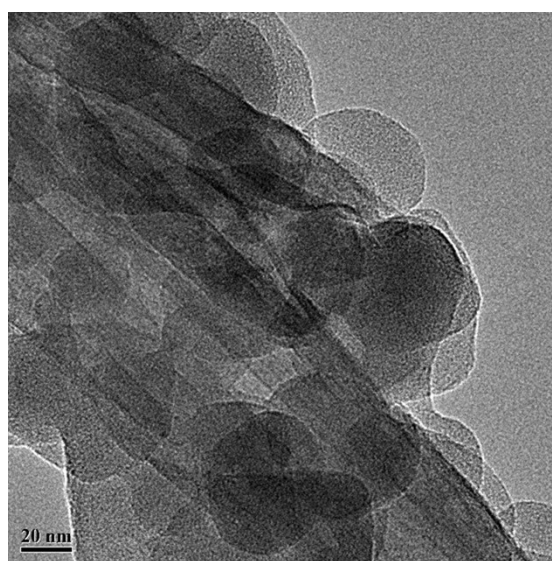


Figure S2. TEM micrograph of the as-synthesized HNTs/ZIF-67.

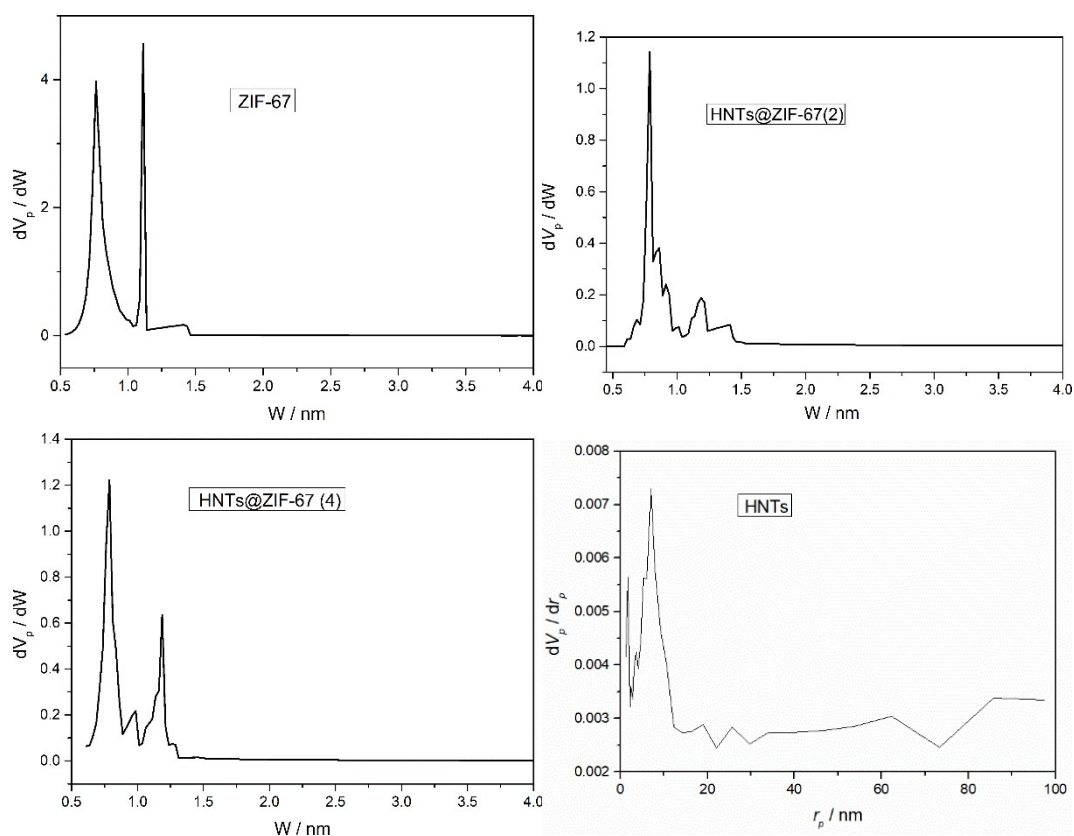


Figure S3. Pore size distribution according to the Horvath-Kawazoe or DH method for the as-synthesized ZIF-67, HNTs@ZIF-67(2), HNTs@ZIF-67(4) and HNTs.

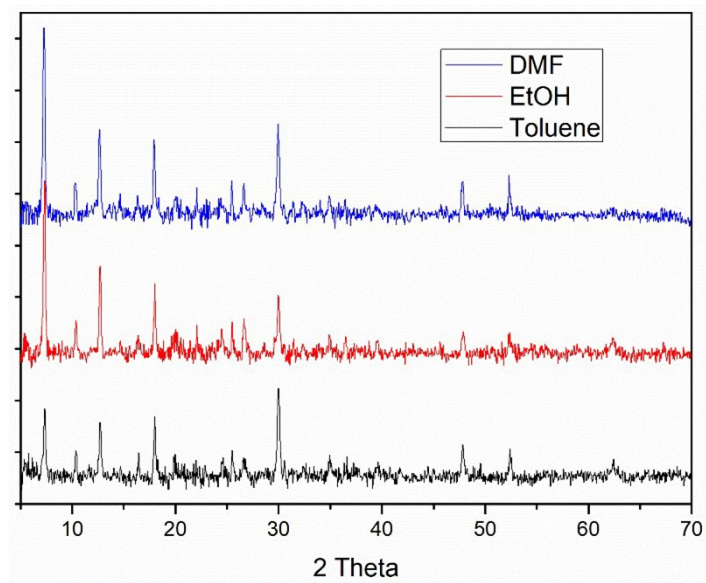


Figure S4. The PXRD patterns of the as-synthesized HNTs@ZIF-67 in the organic solvents.

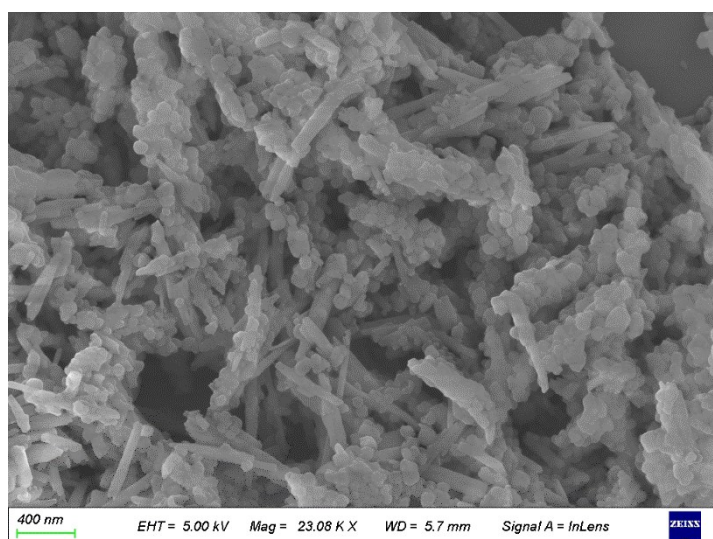
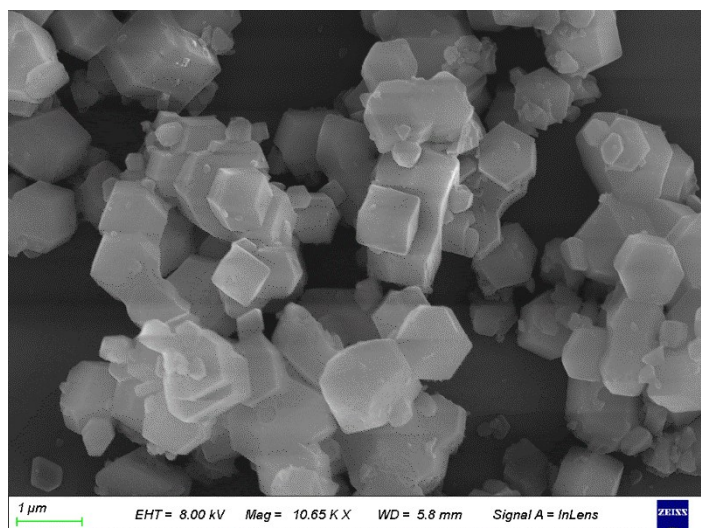


Figure S5. SEM of the used ZIF-67 (upper) and HNTs@ZIF-67 (below).

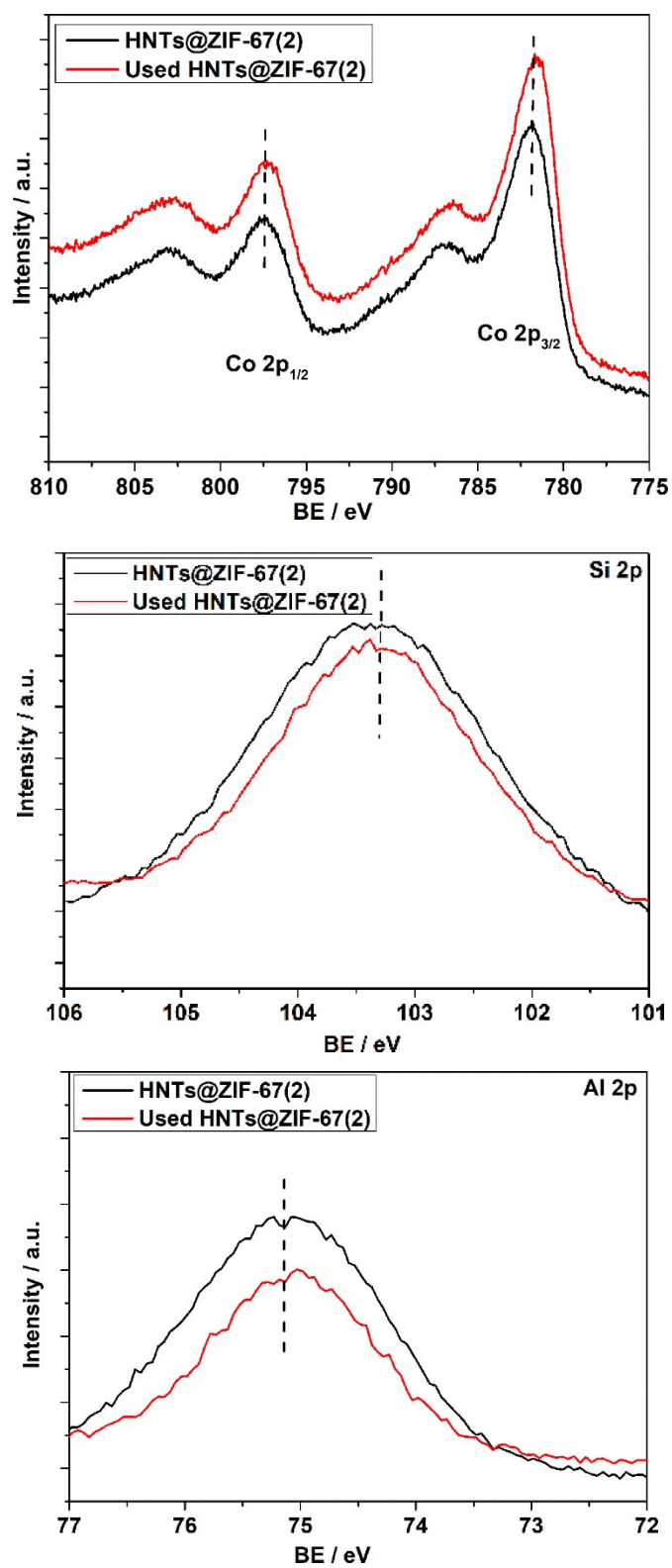


Figure S6. The XPS patterns of as-synthesized HNTs@ZIF-67 and used HNTs@ZIF-67.

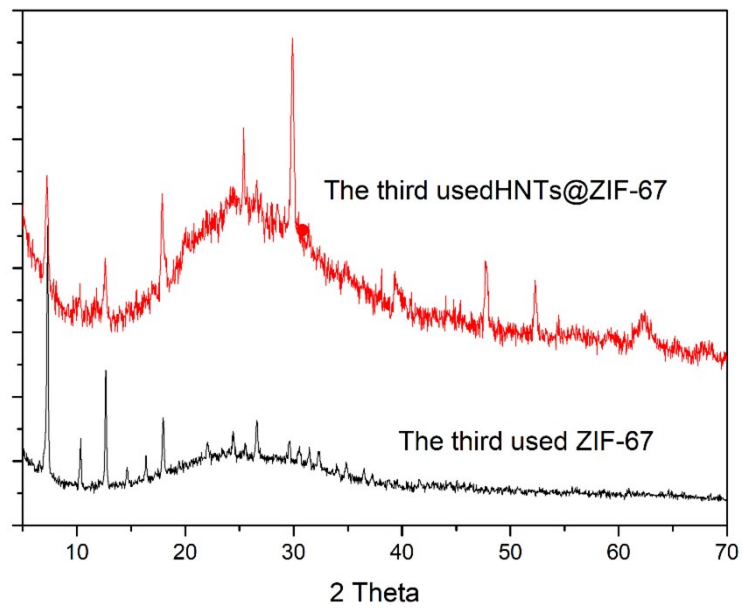


Figure S7. The PXRD patterns of the third used ZIF-67 and HNTs@ZIF-67.

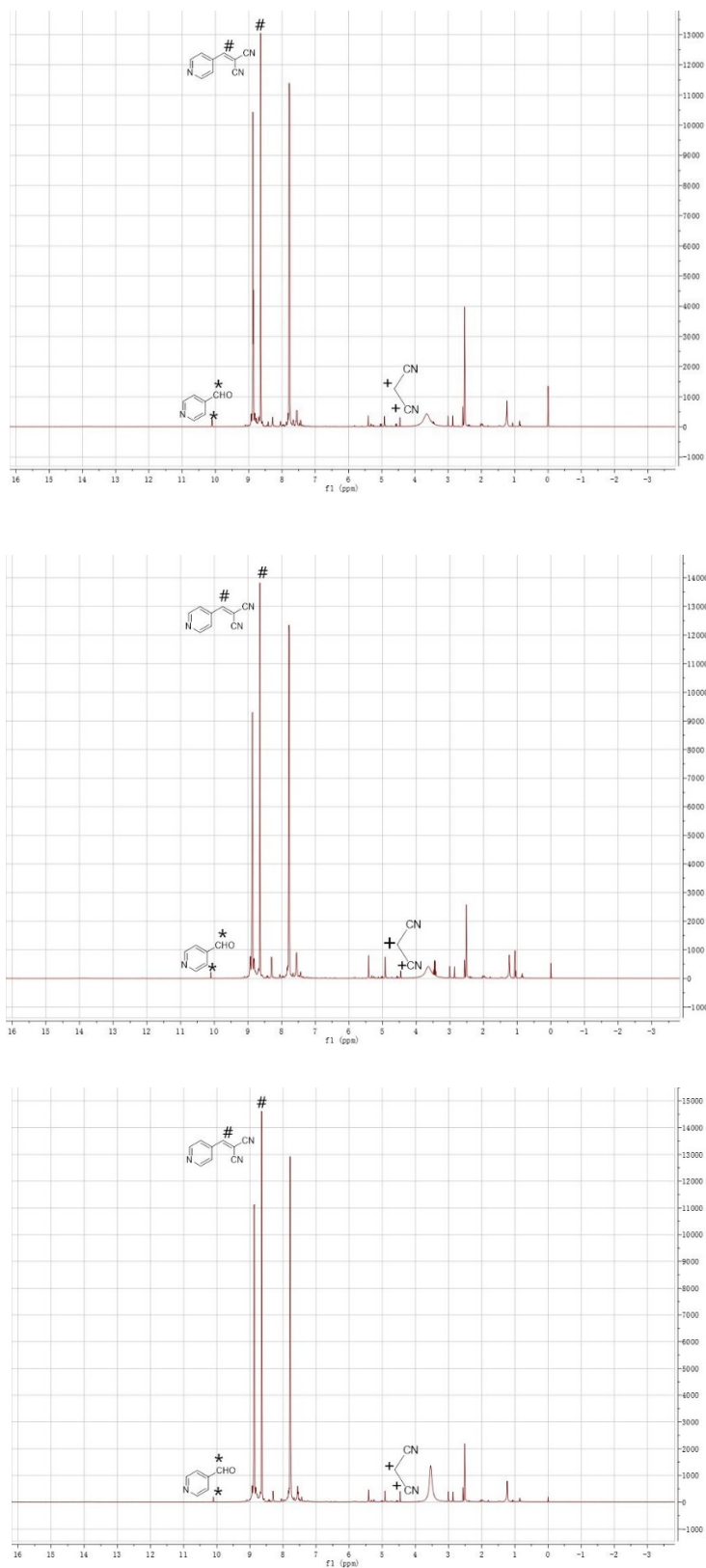


Figure S8. <sup>1</sup>H NMR spectra of the products from the Knoevenagel condensation reactions of 4-pyridinecarboxaldehyde with malononitrile in EtOH using the as-synthesized ZIF-67 as a catalyst: first run (upper), second run (middle) and third run (below).



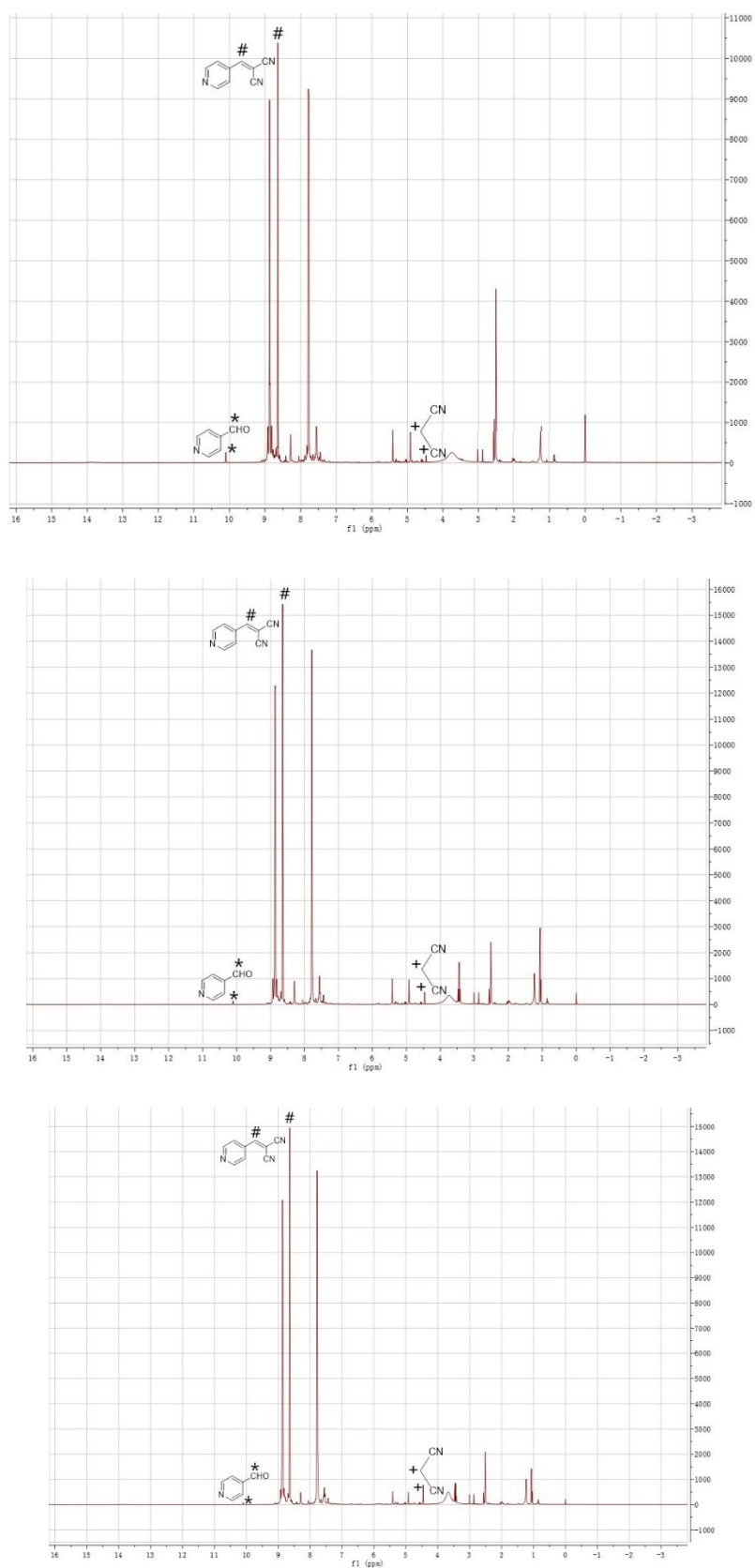


Figure S9. <sup>1</sup>H NMR spectra of the products from the Knoevenagel condensation reactions of 4-pyridinecarboxaldehyde with malononitrile in EtOH using the as-synthesized HNTs@ZIF-67 as a catalyst: first run (upper), second run (middle) and third run (below).

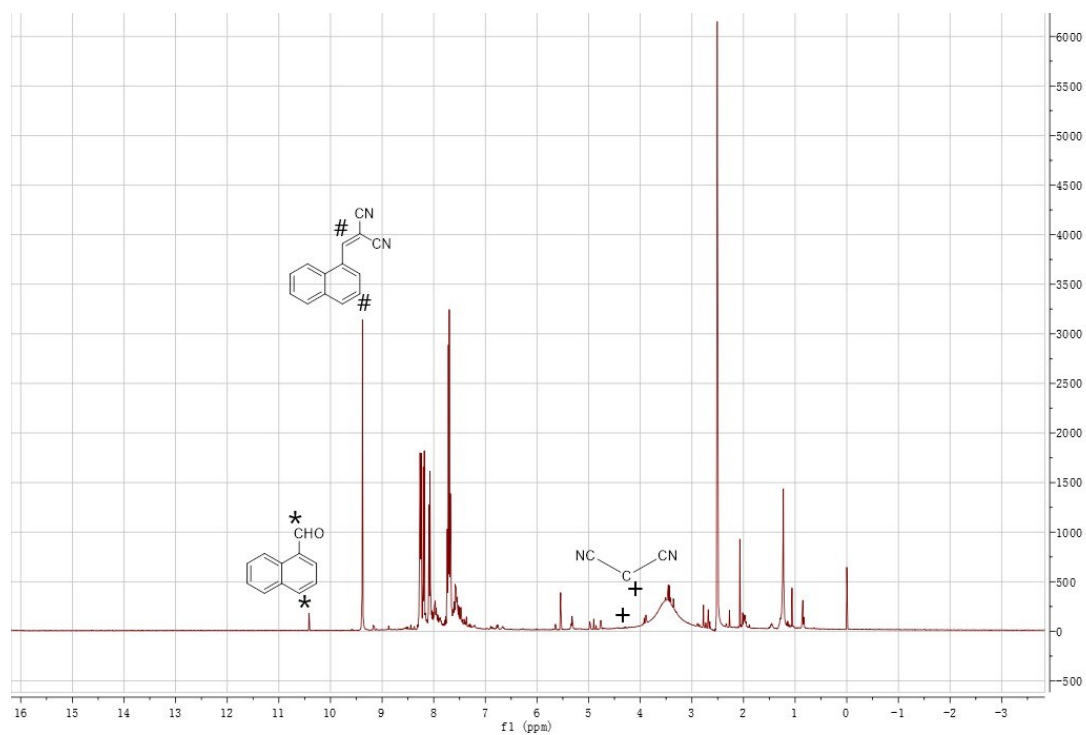


Figure S10.  $^1\text{H}$  NMR spectra of the product from the Knoevenagel condensation reaction of 1-naphthaldehyde with malononitrile in EtOH using the as-synthesized HNTs@ZIF-67 as a catalyst.

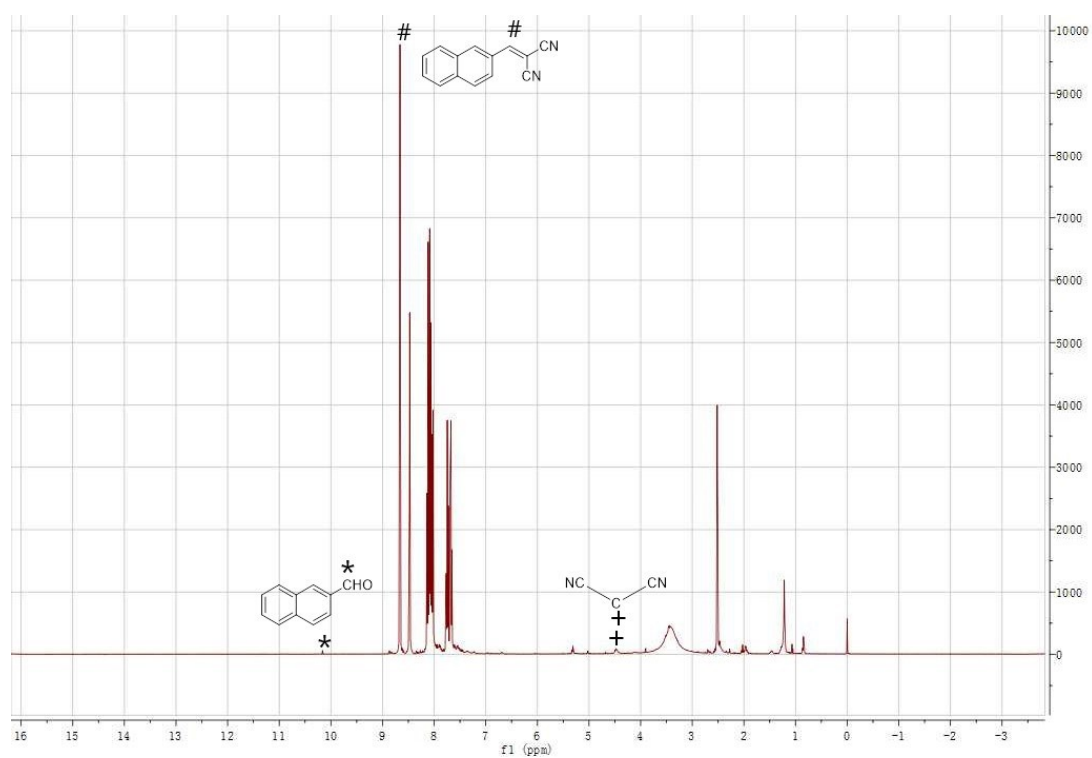


Figure S11. <sup>1</sup>H NMR spectra of the product from the Knoevenagel condensation reaction of 2-naphthaldehyde with malononitrile in EtOH using the as-synthesized HNTs@ZIF-67 as a catalyst.

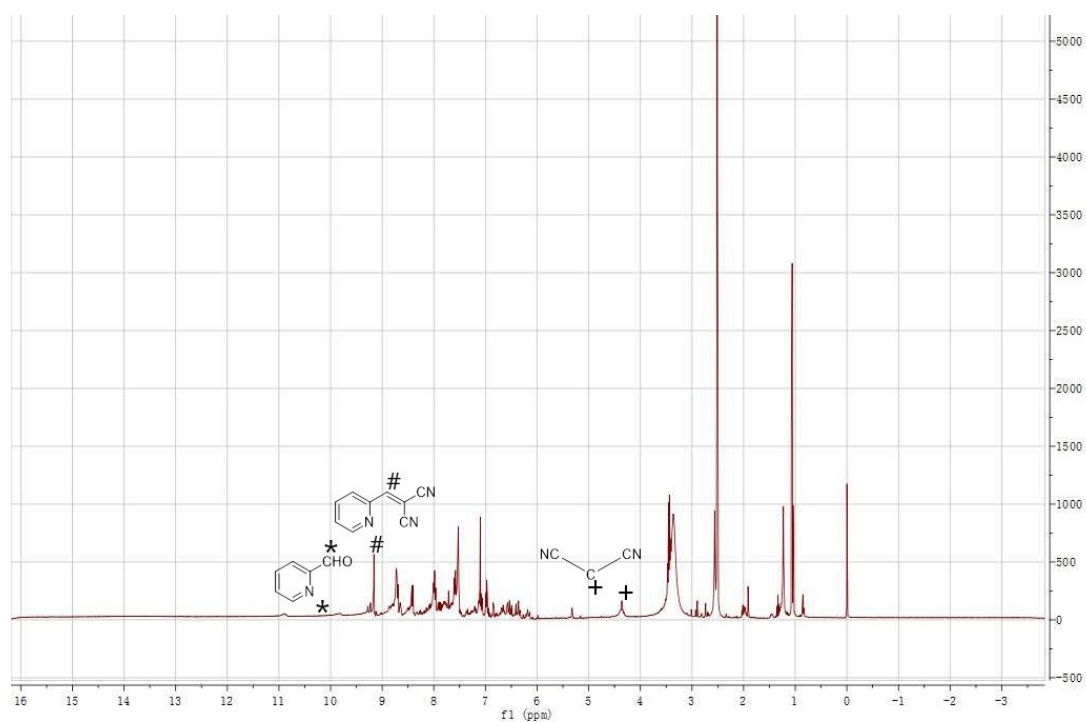




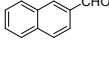
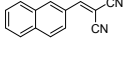
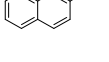
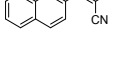

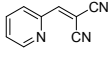

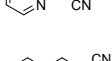

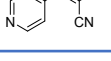

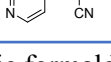


Figure S12. <sup>1</sup>H NMR spectra of the product from the Knoevenagel condensation reaction of 2-pyridinecarboxaldehyde with malononitrile in EtOH using the as-synthesized HNTs@ZIF-67 as a catalyst.

Table S1. The as-synthesized ZIF-67 catalyzed Knoevenagel condensation reaction of larger conjugated/heterocycle aromatic formaldehyde with malononitrile.

Entry	Formaldehyde	Product	Solvent	Yield(%)
1			EtOH	93
2			Toluene	80
3			EtOH	97
4			Toluene	99
5			EtOH	99
6			Toluene	99
7			EtOH	98
8			Toluene	99

Reaction conditions: 0.5 mmol aromatic formaldehyde, 0.5 mmol malononitrile, 10 mg ZIF-67, 5 mL EtOH or Toluene, 5h and air atmosphere at room temperature.