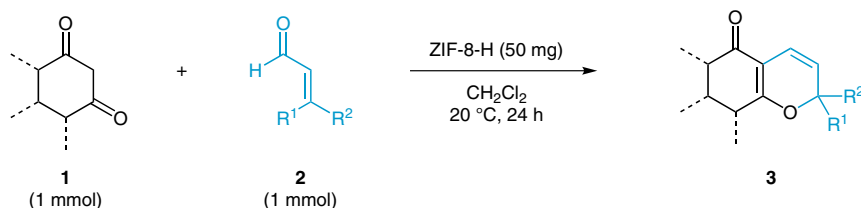
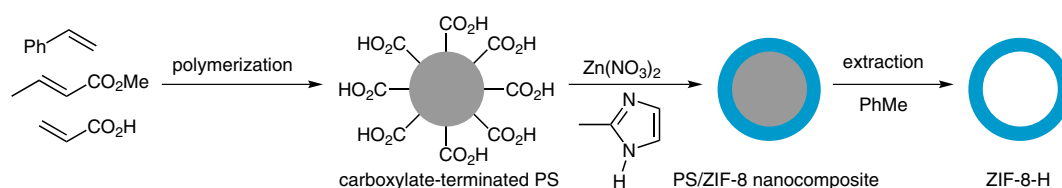
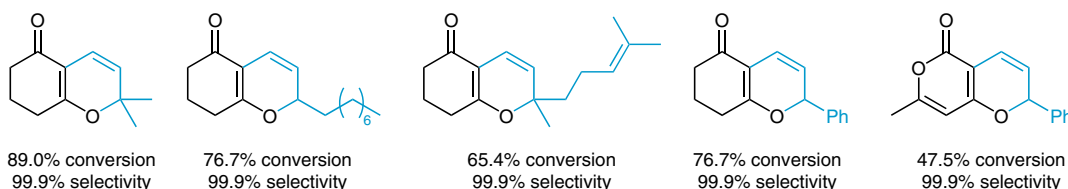


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Hollow Zeolitic Imidazolate Framework Nanospheres as Highly Efficient Cooperative Catalysts for [3+3] Cycloaddition Reactions
J. Am. Chem. Soc. **2014**, *136*, 13963–13966.

A Zeolitic Imidazolate Framework Catalyst for [3+3] Cycloadditions



Selected examples:



Significance: The authors developed a hollow-structured zeolitic imidazolate framework (ZIF-8-H) nanosphere as a catalyst for [3+3] cycloadditions. ZIF-8-H was prepared via complexation of carboxylic groups on the surface of nano-PS ($\phi = 400$ nm) with zinc ions and 2-methylimidazole, followed by subsequent removal of the PS nanosphere by extraction with toluene. The reaction of 1,3-dicarbonyl compounds **1** with α,β -unsaturated aldehydes **2** proceeded in the presence of ZIF-8-H to give the pyranal heterocycles **3** with up to 89.0% conversion and 99.9% selectivity.

Comment: The reaction of 1,3-hexanedione and 3-methyl-2-butenal proceeded in the presence of ZIF-8-H with 89.0% conversion, whereas the use of bulk ZIF-8 showed lower catalytic efficiency (73.2% conversion). Toluene vapor adsorption isotherm showed that ZIF-8-H absorbed toluene to a cage-filling level with a high adsorption amount (6.34 mmol/g). Based on this observation, the authors discussed that the limiting aperture size of ZIF-8-H exceeded the kinetic diameter of toluene (0.61 nm), which is much larger than the reported window size of ZIF-8 (0.34 nm).

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