One-Pot Tandem Reactions with a Bifunctional Solid Catalyst

Significance: A mesoporous silica catalyst 3 bearing both Brønsted base and acid groups was prepared by immobilization of 3-aminopropyltriethoxysilane [(EtO)3Si(CH2)3NH2] and phosphotungstic acid (H₃PW₁₂O₄₀) to a mesoporous silica. Catalyst 3 drove the tandem deacetalization–Henry reaction and deacetalization–Knoevenagel reaction of 4 with nitromethane and malononitrile to give trans-1-nitro-2-phenylethylene 5 and benzylidene malononitrile 6 in 92% and 91% yield, respectively.

Comment: The acid/base properties were controlled by the ratio and surface concentration of an amino group and phosphotungstate. Catalyst 3 was characterized by XANES (X-ray absorption near-edge structure spectrum), BET, BJH, ³¹P NMR, ²⁵Si and ¹³C CP-MAS NMR spectroscopy and GC-MS. Catalyst 3 was recovered by filtration and reused several times without significant loss of catalytic activity (4th use: 5 in 90% isolated yield, 6 in 91% isolated yield).