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Eco-friendly heteropoly acid supported on natural clay for the synthesis of calix[4]resorcinarene derivatives

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The catalytic activity of green catalyst heteropoly-11-tungsto-1-vanadophosphoric acid, $H_4[PVW_{11}O_{40}]$ (HPV) supported on activated natural clay (HPVAC) has been tested towards the synthesis of calix[4]resorcinarene under solvent-free condition. It is a one-pot multi-component condensation reaction of four moles of aromatic aldehydes with four moles of resorcinol. The advantages of the protocol, solvent-free heterogeneous reaction condition, simple workup procedure, short reaction time, high yield of products and reusability of the catalyst make this method to declare as green approach for synthesis of calix[4]resorcinarene.

Keywords: Heteropoly acid, Activated Natural Clay, Calix[4]-resorcinarene, Green synthesis, Heterogeneous reaction

The calix[4]resorcinarene, a subclass of calixarenes, has macrocyclic structure of cyclic tetramers. calix[4]resorcinarene and its derivatives as macrocyclic receptors possess a variety of applications as dendrimers in biological systems[1], nanoparticles[2], nano-capsule[3], supramolecular tectons[4], optical chemosensors[5], host molecules[6], components in liquid crystals[7], selective membranes[8,9], HPLC stationary phases[10], surface reforming agents[11], ion channel mimics[12] and metal ion extraction agents[13]. Besides, some calix[4]arenes show metal ion recognition properties[14, 15].

A number of synthetic routes have been reported for the preparation of calix[4]resorcinarene derivatives by employing some Lewis acid catalyst such as $[Yb(H_2O)_9](OTf)_3$[16], $H_3[PW_{12}O_{40}]$ / Conc. HCl[17], Conc. HCl under microwave irradiations[18, 19] and Fe_3O_4 nanoparticle[20]. However, the methods using these catalysts suffer from the drawbacks such as low product yield, cumbersome product isolation and long reaction time. Here is an attempt to synthesize and characterize calix[4]resorcinarene derivatives using a green eco-friendly catalyst ,heteropoly acid supported on activated natural clay minerals (HPVAC) .

Experimental Section

Materials

All commercially available chemicals were obtained from Sigma Aldrich and used without further purification. A series of HPV supported activated natural clay catalysts (HPVAC) were prepared by varying the loading amount of HPV *viz.* 10, 20, and 30% (w/w) on to the activated natural clay and characterized by the reported literature procedure from our laboratory[21]. FT-IR spectra were recorded using Shimadzu IR Affinity-1 FT-IR Spectrophotometer as KBr discs. ^{1}H and ^{13}C-NMR spectra were recorded by Bruker 300 and 100 MHz NMR instrument with DMSO-d_6 as solvent and TMS as internal reference. Elemental analysis was performed on Elementar Vario EL III equipment.

General procedure for the preparation of calix[4]resorcinarene

A mixture of aldehyde (4 mmol), resorcinol (4 mmol) and HPVAC-20 (catalyst) were heated in oil bath at 120°C for 30 min. The completion of reaction was ascertained by TLC (ethyl acetate / n-hexane: 7:3) and after completion, 15 mL of ethanol was added to dissolve the crude product. The catalyst was recovered by simple filtration. And the ethanol solution was poured into cold water to get precipitate. The product was filtered and washed with 30 mL of water. The product was dried in an air oven (Scheme 1). The product was analyzed and identified by melting point, FT-IR, ^{1}H-NMR and ^{13}C-NMR analysis.

Results and Discussion

Optimization of catalytic condition

Condensation of four moles of 4-chloro-benzaldehyde with four moles of resorcinol in the presence of catalyst was taken as a standard reaction for the optimization study in the synthesis of 2,4,6, 8-tetrakis(4-chlorophenyl)-1,3,5,7(1,3)-tetrabenzena-cyclooctaphan-14,16,34,36,54,56, 74,76-octaol. This