# Pd-MCM-48: a novel recyclable heterogeneous catalyst for chemo- and regioselective hydrogenation of olefins and coupling reactions†

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A novel, heterogeneous Pd-MCM-48 catalyst has been developed by encapsulating palladium nanoparticles into the cubic phase of mesoporous MCM-48 matrix at room temperature. The catalyst demonstrated excellent chemo- and regioselectivity for the hydrogenation of olefins at room temperature within 30–80 min. The turnover frequency for the hydrogenation is very high (4400 $h^{-1}$). Interestingly, selectivity of the catalyst was significantly influenced by the mode of addition of palladium precursor. Moreover, the catalyst was also very effective for the coupling reactions with the formation of carbon–carbon and carbon–nitrogen bonds under ligand-free and aerobic conditions.

## Introduction

Silica supported heterogeneous palladium catalysts have been referred as "smart catalysts" in organic synthesis.[1] Recent synthetic improvements of mesoporous siliceous materials, promoted development of engineered silica based Pd-catalysts[2] where active Pd-species are encapsulated inside channels and/or pores.[2g] Among the various classes of mesoporous materials, MCM-48 is highly attractive due to the large surface area, pore volume and presence of the interpenetrating network of three-dimensional pores that is expected to facilitate molecular transport of reactants and products more efficiently than the uni-dimensional network in MCM-41.[3] Literature studies revealed that a number of Pd-MCM-41 catalysts have been reported for the efficient hydrogenation[2b] and coupling[2b,4] reactions. However, studies employing Pd-MCM-48 are scarce due to the tedious hydrothermal preparative method, requiring long reaction time (1–7 days) and a few Pd-MCM-48 catalysts have been reported in the literature.[2e–g] Thus, rapid and room temperature synthesis of Pd-MCM-48 has been long awaited. In this study, we are motivated to explore facile synthesis of Pd-MCM-48 and their possible applications. Chaudhari *et al.*[2e] developed anchored Pd-complex in MCM-48 for the hydrocarboxylation of olefins. Recently, Cheon *et al.*[2f] reported a ball shaped Pd-MCM-48 catalyst, prepared by chemical vapor infiltration of bis-1,1,1,5,5,5-hexafluoro-acetylacetonate Pd(II) salt into the MCM-48 template for the hydrogenation and removal of benzyl ether group. As a part of our research of catalysis[5] and MCM-48 material,[6] we have developed a facile protocol for the synthesis of MCM-48 at room temperature.[6a] Herein, we report synthesis of a novel heterogeneous Pd-MCM-48 catalyst for rapid and highly chemo- and regioselective hydrogenation of olefins and coupling reactions under ligand-free and aerobic conditions.

## Result and Discussion

At first, the Pd-MCM-48 catalyst (**1**) was prepared by encapsulating of Pd nanoparticles (Pd-NPs) into the cubic phase MCM-48 matrix followed by calcination and mild reduction by $H_2$ gas.

Powder X-ray diffraction study revealed the formation of cubic mesoporous MCM-48 (Fig. 1) while the transmission electron microscopy (TEM) image confirmed the presence of Pd NPs within the sample (Fig. 2).

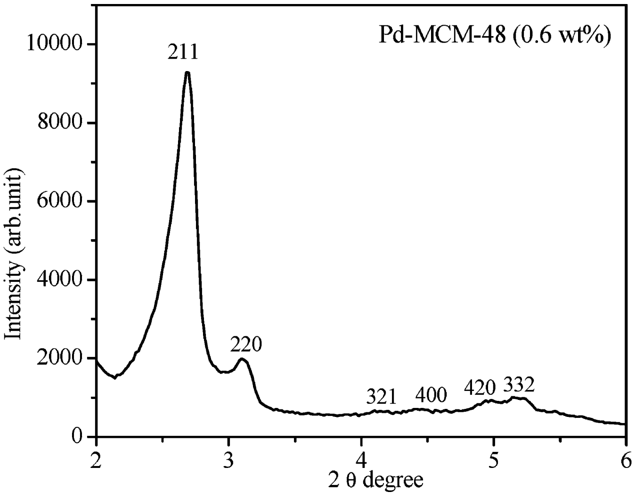

**Fig. 1** Powder X-ray diffraction pattern of Pd-MCM-48 (**1**, 0.6 wt%) showed the formation of mesoporous siliceous material.

The surface area of the Pd-MCM-48 was found to be much higher (~1800 $m^2g^{-1}$) with a higher metal dispersion of ~ 22% (CO pulse studies, see ESI) than earlier reported Pd-MCM-48 (3.3%).[2f] The Pd content (0.6 wt%) of the catalyst was determined by atomic absorption spectroscopy study. Because of the employed preparative conditions, most of the fine Pd particles (< 2 nm) are located inside the MCM-48 pores (~2.5 nm) while some particles (4–7 nm) are positioned outside the mesochannels yet highly dispersed. This well-characterized catalyst have been tested for the hydrogenation and coupling reactions.

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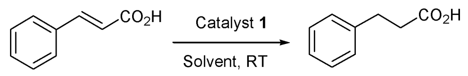
† Electronic supplementary information (ESI) available: Preparation of Pd Nanoparticles, details characterization of catalyst **1** by $N_2$ adsorption-desorption isotherm, preparation of catalyst **2**, reuse of the catalyst **1**, copies of $^1$H NMR spectra of all products listed in Tables 2–5 and Scheme 2. See DOI: 10.1039/c0ob00183j

**Table 1** Optimization of reaction conditions for the hydrogenation of cinnamic acid using catalyst **1**



| Entry | Catalyst | Amount of catalyst (mg) | Amount of Pd (mmol) | Solvent | Time (h) | Yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | Pd-MCM-48 (0.6 wt%) | 20 | $1.1 \times 10^{-3}$ | EtOH | 0.5 | 100 |
| 2 | Pd-MCM-48 (0.6 wt%) | 20 | $1.1 \times 10^{-3}$ | $H_2O$ | 0.5 | 100 |
| 3 | Pd-MCM-48 (0.6 wt%) | 10 | $0.5 \times 10^{-3}$ | EtOH | 0.5 | 75 |
| 4 | Pd-MCM-48 (0.6 wt%) | 20 | $1.1 \times 10^{-3}$ | Toluene | 0.5 | 82 |
| 5 | Si-MCM-48 | 20 | — | EtOH | 24 | 0 |

2.0 mmol of cinnamic acid was used in all cases.[a] Yields were determined by $^1H$ NMR spectra.

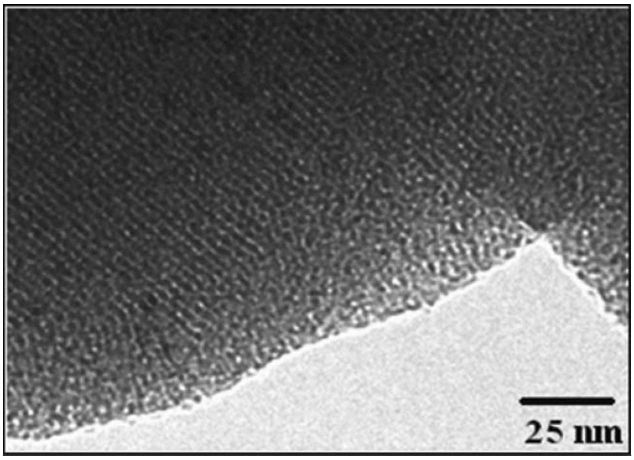
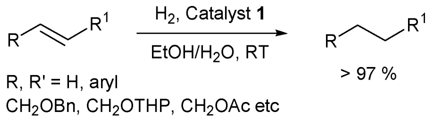


**Fig. 2** TEM image of Pd-MCM-48 catalyst (0.6%).

First, the catalyst **1** was tested for the hydrogenation of olefins using $H_2$ gas. It demonstrated excellent activity at room temperature in ethanol or water (Scheme 1).

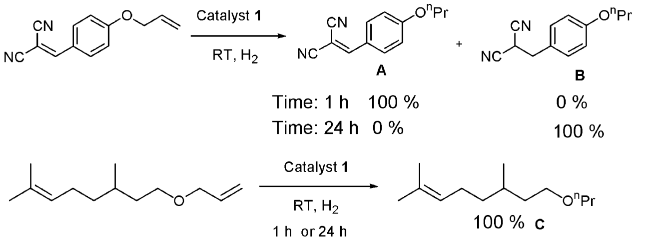


**Scheme 1** Selective hydrogenation of olefins using catalyst **1**.

The reaction conditions were optimized using hydrogenation of cinnamic acid as a model reaction and the results were presented in Table 1. Cinnamic acid (2 mmol) was hydrogenated completely in presence of 20 mg of catalyst **1** in ethanol or water at room temperature within 30 min.

We observed high chemoselective reduction of double bonds in the the presence of a reducible carbonyl group (entry 4, Table 2) using Pd-MCM-48 catalyst and $H_2$ gas at room temperature. The results were summarized in Table 2. The Pd-MCM-48 catalyzed hydrogenation of olefins was very fast (0.5–1 h) and high yielding (97–100%). The excellent reactivity of the catalyst is possibly due to the higher metal surface area (~95 $m^2g^{-1}$, see ESI) and dispersion of Pd metal in MCM-48 matrix. The double bonds were selectively hydrogenated in the presence of ketone, OAc, $CO_2Bu$ *etc.* Interestingly, this selectivity was opposite to the earlier reported Pd-MCM-48 (Pd was deposited on the surface of synthesized MCM-48),[2f] which led to removal of the benzyl group in the presence of double bonds. We attribute this drastic difference in the catalytic performance to the mode of Pd deposition; the activity is highly dependent on the preparative conditions employed. To explore further this structure–activity relationship, we synthesized another catalyst (**2**) by depositing Pd on synthesized MCM-48 (see ESI). The BET study reveals that the surface area of the catalyst **2** (Pd wt ~0.8%) is 637 $m^2g^{-1}$, which is much less than of the catalyst **1** with 12% metal dispersion and average crystallite size of 12 nm.

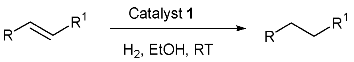
The catalyst **1** exhibited superior selectivity in hydrogenation of olefins (100%) over hydrogenolysis in contrast to the non-selective catalyst **2**, commercial Pd/C, ball shaped Pd-MCM-48[2f] and Pd-$SiO_2$.[2f] A comparative results of hydrogenation were presented in Table 3. Further, we established that the selectivity significantly was influenced the mode and time of addition of palladium precursors to the MCM-48 during its synthesis. Besides excellent chemoselectivity, catalyst **1** also exhibited significant regioselectivity. Therefore, terminal alkenes were hydrogenated selectively in the presence of tri-substituted alkenes (Scheme 2).

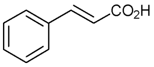
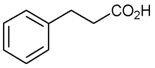
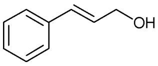
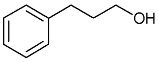
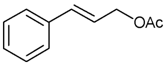
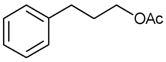
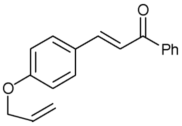
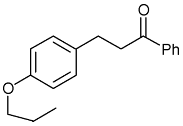
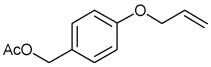
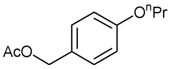
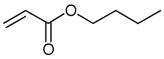
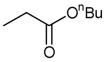
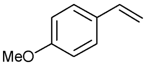
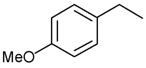


**Scheme 2** Regioselective hydrogenations olefins using catalyst **1**.

The excellent reactivity and selectivity of the catalyst **1** for hydrogenation has encouraged us to explore its catalytic performance towards coupling reactions with the formation of carbon-carbon bonds, which are of great synthetic importance in organic chemistry.[7] Over the past decades, countless studies report a number of practical properties of heterogeneous Pd-catalysts,[1c,2,4,7] including Pd-NPs,[7f–h] such as moisture stability, reusability, and capability of performing the reaction under ligands-free conditions. However, it is not uncommon for Heck and Suzuki coupling to take long reaction times when performed without phosphine and other ligands at the Pd-center.[7c,i] Here, for the first time, we report application of mesoporous Pd-MCM-48 catalyst for Heck and Suzuki coupling reactions under ligand-free and aerobic conditions. The catalyst **1** demonstrated excellent activity towards Heck coupling reactions. The results are summarized in Table 4.

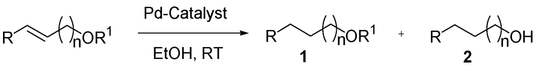
**Table 2** Pd-MCM-48 catalyzed hydrogenation of alkenes

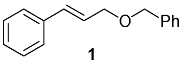
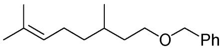
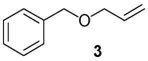
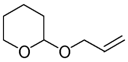


| Entry | Olefin | Time (min) | Product | Yield (%)[a] |
|---|---|---|---|---|
| 1 |  | 30 |  | 100 |
| 2 |  | 45 |  | 99 |
| 3 |  | 60 |  | 98 |
| 4 |  | 80 |  | 97 |
| 5 |  | 45 |  | 98 |
| 6 |  | 50 |  | 100 |
| 7 |  | 45 |  | 100 |

[a] Yields refers to isolated products charecterized by $^{1}H$ and $^{13}C$ NMR. 20 mg (0.6 wt%) of catalyst was used for 2 mmol of alkene.

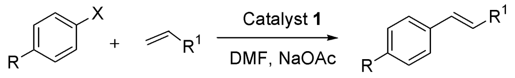
**Table 3** Comparative results for the selectivity for hydrogenation using different Pd-catalysts



| Alkene | Entry | Pd-Catalyst | Time (h) | Yield (%)[a] | |
|---|---|---|---|---|---|
| | | | | 1 | 2 |
|  1 | 1a | Catalyst **1**[b] | 1 | 100 | 0 |
| | 1b | Catalyst **2**[c] | 1 | 0 | 99 |
| | 1c | Pd/C[d] | 1 | 0 | 100 |
|  2 | 2a | Catalyst **1**[b] | 24 | 0 | 0 |
| | 2b | Catalyst **2**[c] | 4 | 0 | 100 |
| | 2c | Pd/C[d] | 2 | 0 | 100 |
|  3 | 3a | Catalyst **1**[b] | 1 | 99 | 0 |
| | 3b | Catalyst **2**[c] | 1 | 0 | 100 |
| | 3c | Pd/C[d] | 1 | 0 | 100 |
|  4 | 4a | Catalyst **1**[b] | 1 | 100 | 0 |
| | 4b | Catalyst **2**[c] | 4 | 0 | 100 |
| | 4c | Pd/C[d] | 2 | 0 | 100 |

[a] Yields and ratios were determined by $^{1}H$ NMR spectroscopic data. [b] Pd precursor was added during the preparation of MCM-48. [c] Pd precursor was diposited on synthesized MCM-48. [d] 10% Pd/C, purchased from Sigma-Aldrich.

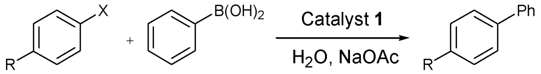
**Table 4** Pd-MCM-48 catalyzed Heck coupling reactions



| Entry | R | X | R$^1$ | Time (h) | Yield (%)$^a$ |
|---|---|---|---|---|---|
| 1 | H | Br | $CO_2Bu$ | 7 | 90 |
| 2 | H | I | $CO_2Bu$ | 5 | 98 |
| 3 | H | Br | CN | 6 | 92 |
| 4 | H | I | CN | 5 | 96 |
| 5 | H | I | Ph | 6 | 90 |
| 6 | $NO_2$ | Br | $CO_2Bu$ | 4 | 97 |
| 7 | $NO_2$ | Br | CN | 4 | 92 |
| 8 | $NO_2$ | Br | Ph | 4 | 90 |
| 9 | $NO_2$ | Br | 4-OMe$C_4H_9$ | 5 | 95 |
| 10 | OMe | I | Ph | 7 | 85 |
| 11 | $NO_2$ | Cl | $CO_2Bu$ | 12 | 0 |

[a] Yields refer to those of pure isolated products. 1 mmol of aryl halide, 2 mmol of alkene, 2 mmol of NaOAc and 40 mg (0.6 wt %) of catalyst **1** was added to 2 ml of DMF and heated at 100 °C.

**Table 5** Suzuki coupling using Pd-MCM-48 catalyst in water



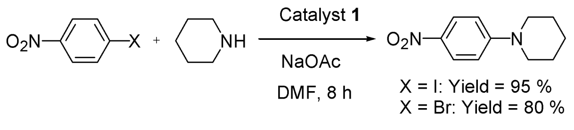
| Entry | R | X | Time (h) | Yield (%)$^a$ |
|---|---|---|---|---|
| 1 | H | Br | 4 | 92 |
| 2 | H | I | 3 | 99 |
| 3 | $NO_2$ | Cl | 8 | 85 |
| 4 | $NO_2$ | Br | 4 | 95 |
| 5 | Me | Br | 5 | 93 |
| 6 | Me | I | 3 | 98 |

[a] Yields refer to those of pure isolated products. 1 mmol of ArX, 1.5 mmol of phenylboronic acid, 2 mmol of NaOAc and 40 (0.6 wt %) mg of catalyst **1** was added to 2 ml of $H_2O$ and heated at 80 °C.

A number of aryl halides with electron donating and electron withdrawing groups were coupled with a variety of alkenes (*e.g.* butyl acrylate, acrylonitrile, styrene, 1-methoxy-4-vinylbenzene *etc.*) in the presence of 40 mg of catalyst **1** (0.6 wt%) and a mild base (NaOAc) in DMF. The reactions were efficient at 100 °C.

After successful application of catalyst **1** in Heck coupling, we investigate its efficiency for the Suzuki coupling. We observed that Pd-MCM-48 efficiently catalyzed the reaction of bromobenzene with phenylboronic acid in water at 80 °C in the presence of NaOAc. A variety of aryl halides including relatively inactive bromides and chlorides underwent coupling with phenylboronic acid under the optimized reaction conditions in shorter reaction times (3–8 h) yielding biaryl compounds in excellent yields (85–99%). The results are presented in Table 5.

Moreover, the catalyst **1** was also very efficient for a coupling reaction with formation of a carbon–nitrogen bond (Scheme 3).



**Scheme 3** Pd-MCM-48 catalyzed C–N bond formation.

We believe that the excellent activity of catalyst **1** is mostly due to its large surface area (~1800 m$^2$g$^{-1}$), higher metal dispersion (22%) and interpenetrating network of three dimensional pores of MCM-48. Finally, the recyclability of the catalyst has been investigated for both hydrogenation and coupling reactions. The catalyst can be reused at least ten times for hydrogenation with minimal loss of activity. However, for Heck reaction the yield has dropped to 70% in the fourth run. The results were summarized in Table 6 in the ESI.†

## Conclusion

In conclusion, we have developed a novel heterogeneous Pd-MCM-48 catalyst by encapsulating palladium nanoparticles in mesoporous siliceous MCM-48. The catalyst established remarkable activity towards regio- and chemoselective hydrogenation of olefins with very high turnover frequency (4400 h$^{-1}$) at room temperature. Thus, double bonds were selectively hydrogenated in the presence of O-benzyl and O-THP protecting groups. In addition, the catalyst was also very effective for the coupling reactions with formation of C–C and C–N bonds under ligand-free and aerobic conditions, including a usually inactive aryl chloride for Suzuki coupling. Interestingly, the mode of addition of palladium precursors to the MCM-48 greatly influences the selectivity for hydrogenation reactions. Exploration of further applications for the new catalyst in organic synthesis is under way.

## Experimental

### Chemicals used

Hexadecyltrimethylammoniumbromide (CTAB, 99+%, Acros), ethanol (absolute 200 Proof, AAPER), aqueous ammonia (Fisher), tetraethoxysilane (99%, Alfa Aesar), palladium(II) 2,4-pentanedionate (Alfa Aesar) and sodium terachloropalladate(II) ($Na_2[PdCl_4]$) (Pressure Chemicals) were used for the synthesis of Pd-MCM-48 materials. Dimethylaminopyridine (DMAP, 99%, Acros), toluene (Acros), tetra-*n*-octylammoniumbromide (TOAB, 98+% Alfa Aesar), sodium borohydride (98% Acros) and sodium sulfate anhydrous powder (Fisher) were used for the synthesis of Pd(0) nanoparticles. All the chemicals used for hydrogenation and coupling reactions were purchased form Sigma-Aldrich or Alfa-Aesar and used as received.

### Experimental procedure for the synthesis of Pd-MCM-48 (catalyst 1)

Initially, Pd(0) nanoparticles were synthesized according to the published procedure[8] by the reduction of $Na_2PdCl_4$ with $NaBH_4$ in the presence of *tetra*-*n*-octylammonium bromide (TOAB) as a capping and stabilizing agent. Pd-MCM-48 material was synthesized by the modified Stöber method[6a]. In a typical procedure, 50 mL of the Pd(0) nanoparticles solution (the concentration was adjusted to the required loading), 25 mL ethanol, 1.2 g (3.3 mmol) of CTAB, 6 mL of aq. $NH_3$ (0.09 mol) and 1.8 mL (8 mmol) of TEOS were sequentially added to a 125 mL polypropylene bottle, and stirred for 4 h at 300 rpm. The molar composition of the formed siliceous gel is 0.41 CTAB: 11 aq. $NH_3$: 1.0 TEOS: 53 EtOH: 344 $H_2O$. After 4 h, the mesoporous material was washed extensively with deionized water and dried overnight at 100 °C. The dried material was finely ground with a mortar and pestle and calcined at 550 °C (ramp rate of 3 °C per min.) for 6 h in an alumina crucible to remove the surfactant molecules. The calcined Pd-MCM-48 may contain Pd in the +2 oxidation state. In order to increase consistency in the catalyst's composition, this material was reduced in hydrogen-gas flow (20 mL/min) at 300 °C for 2 h in a tubular furnace. The content of palladium in the synthesized catalyst was determined by atomic absorption spectroscopy and found to be 0.6 wt%.

### Representative experimental procedure for the Pd-MCM-48 catalyzed hydrogenation of olefins

A mixture of *trans*-cinnamic acid (296 mg, 2 mmol) and catalyst **1** (20 mg) in ethanol (10 mL) was stirred under constant flow of $H_2$ (flow rate 20 mL/min) for 30 min untill completion of reaction (TLC). The catalyst was filtered out on filter paper and washed with ethanol (2 × 5 mL). The combined filtrates were evaporated to yield the pure hydrogenated product, 3-phenylpropanoic acid (300 mg, 99%) as white crystals (m.p. 48 °C). The FT-IR, $^1$H NMR and $^{13}$C NMR data were consistent with those reported in literature. The hydrogenation was also successful under a steady $H_2$ atmosphere (a balloon filled with $H_2$).

For hydrogenation in water, the reaction product was extracted with ethyl acetate, dried over $Na_2SO_4$. Evaporation in vacuum gave the pure hydrogenated product, 3-phenylpropanoic acid. For all the reactions listed in Table 1, 2 and 3, ethanol was used as solvent to avoid extraction from water. After the catalyst was filtered, washed with ethanol, and dried in air, it was reused for subsequent runs.

All the products listed in Table 1, 2 and 3 are known and their $^1$H NMR and $^{13}$C NMR data were consistent with the reported values. The products on Scheme 2 are not known and were additionally characterized by elemental analysis. The characterization data for the compounds A–C in Scheme 2 are given below:

### (4-Propoxybenzylidene)propanedinitrile (product A, Scheme 2)

Light yellowish liquid; IR (ν[cm$^{-1}$]) 3320, 2250, 2223, 1112, 910; NMR: $\delta_H$ (200 MHz, $CDCl_3$) 1.06 (t, *J* = 7.4 Hz, 3H), 1.86 (q, *J* = 7.4 Hz, 2H), 4.03 (t, *J* = 7.4 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.65 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 2H); NMR: $\delta_C$ ($CDCl_3$) 10.7, 22.6, 70.4, 112.0, 114.1 (2C), 115.8 (2C), 124, 133.8 (2C), 159.2, 164.8. Anal. calcd. for $C_{14}H_{14}N_2O$: C 74.31, H 6.24; N 12.38. Found: C 74.25, H 6.29; N 12.31.

### (4-Propoxybenzyl)propanedinitrile (product B, Scheme 2)

Colorless liquid; IR (ν[cm$^{-1}$]) 3320, 2225, 2200, 1650, 1100, 910 cm$^{-1}$; $\delta_H$ (200 MHz, $CDCl_3$) 1.03 (t, *J* = 8.0 Hz, 3H), 1.20 (q, *J* = 8.0 Hz, 2H), 1.80 (t, *J* = 8.0 Hz, 2H), 3.21 (d, *J* = 6.6 Hz, 1H), 3.70 (m, 2H), 3.88 (t, *J* = 8.0 Hz, 2H), 6.91(d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H); NMR: $\delta_C$ ($CDCl_3$) 10.6, 22.6, 25.5, 36.2, 69.8, 112.6 (2C), 115.4 (2C), 129.6, 130.6 (2C), 160.1. Anal. calcd. for $C_{14}H_{16}N_2O$: C 73.66, H 7.06; N 12.27. Found: C 73.71, H 6.98; N 12.34.

### 2,6-Dimethyl-8-propoxyoct-2-ene(product C, Scheme 2)

Colorless liquid; IR (ν[cm$^{-1}$]) 1655, 1090, 720 cm$^{-1}$; NMR: $\delta_H$ (200 MHz, $CDCl_3$) δ = 0.82–0.99 (m, 6H), 1.09–1.52 (m, 5H), 1.54–1.78 (m, 8H), 1.94–2.17 (m, 2H), 3.28–3.51 (m, 4H), 5.02–5.20 (m, 1H); NMR: $\delta_C$ ($CDCl_3$) 10.8, 17.8, 19,8, 23.2, 25.7, 25.9, 36.9, 37.5, 69.3, 72.8,125.1, 131.3. Anal. calcd. for $C_{13}H_{26}O$: C 78.72, H 13.21. Found: C 78.66, H 13.174.

### Representative experimental procedure for the Pd-MCM-48 catalyzed Heck coupling of butyl acrylate with iodobenzene

A mixture of iodobenzene (204 mg, 1 mmol), butyl acrylate (256 mg, 2 mmol), NaOAc (272 mg, 2 mmol) and catalyst **1** (40 mg, 0.6 wt%) was heated in DMF (2 mL) for 5 h till completion of reaction (TLC) at 100 °C. After the reaction mixture was cooled to room temperature and extracted with ethyl acetate, washed thoroughly with water (6 × 1 mL) to remove DMF, dried over $Na_2SO_4$, solvent was evaporated under vacuum to provide crude product, which was passed short silica gel column leading to pure 3-phenylacrylic acid butyl ester (187 mg, 98%) as colorless liquid. The product was characterized by FT-IR, $^1$H NMR and $^{13}$C NMR spectroscopic data and these data were in good agreements with literatures reported values.

### Representative experimental procedure for the Pd-MCM-48 catalyzed Suzuki coupling phenylboronic acid with iodobenzene

A mixture of iodobenzene (204 mg, 1 mmol), phenylboronic acid (183 mg, 1.5 mmol), NaOAc (272 mg, 2 mmol) and catalyst **1** (40 mg, 0.6 wt%) was heated in water (2 mL) for 3 h till completion of reaction (TLC) at 80 °C. After the reaction mixture was cooled to room temperature and extracted with ethyl acetate. The organic layer was washed thoroughly with water (3 × 2 mL), dried over $Na_2SO_4$, solvent was evaporated under vacuum to provide crude product, which was passed short silica gel column leading to pure biphenyl (152 mg, 99%) as white crystal. The product was characterized by IR, $^1$H NMR and $^{13}$C NMR spectroscopic data and these data were in good agreements with those literatures reported values.

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