

## Research Article

# Synthesis, Characterization, and Catalytic Activity of Pd(II) Salen-Functionalized Mesoporous Silica

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Salen ligand synthesized from 2-hydroxybenzaldehyde and 2-hydroxy-1-naphthaldehyde was used as a palladium chelating ligand for the immobilization of the catalytic site. Mesoporous silica supported palladium catalysts were prepared by immobilizing Pd(OAc)<sub>2</sub> onto a mesoporous silica gel through the coordination of the imine-functionalized mesoporous silica gel. The prepared catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), inductivity couple plasma (ICP), nitrogen adsorption-desorption, and Fourier transform infrared (FT-IR) spectroscopy. The solid catalysts showed higher activity for the hydroamination of C-(tetra-O-acetyl-β-D-galactopyranosyl)allene with aromatic amines compared with the corresponding homogenous catalyst. The heterogeneous catalytic system can be easily recovered by simple filtration and reused for up to five cycles with no significant loss of catalytic activity.

## 1. Introduction

The synthesis of nitrogen containing compounds is of great importance in basic research and industrial processes due to these important structures playing vital roles in drug research and development [1, 2]. Among the several methods to form C–N bond from N–H bond, hydroamination of unsaturated C=C bonds has the benefit of being cost effective and feasible, and it is widely used by many researchers worldwide [3–7]. Allenes are a unique class of organic compounds with two cumulated double bonds [8]. There has been much interest in using them as starting material for the synthesis of allylamines. Only a small number of transition-metal catalyzed intermolecular hydroamination reactions of allenenes have been described [9–14]. Previously, we reported the addition of amines to allene using Pd(OAc)<sub>2</sub>, from which a mixture of the desired allylic amine and a minor amount of dienic amine was obtained [15]. Following this, the gold catalytic hydroamination of allene was investigated to give the desired allylic

amine with a moderate to good yield [16]. However, this reported method suffers from disadvantages, such as long reaction time, expensive catalyst, and unstable operating state. The practical application of the catalyst in liquid phase reactions is hindered by both high cost and difficulties in catalyst separation and recycling. The common catalysts for these reactions are generally homogeneous systems, which cause difficulties in recycling the catalyst and aggregation of metal nanoparticles [17]. Thus, a heterogeneous system for the metal catalyst is a reasonable step to avoid these problems, and it is feasible to overcome such limitations by employing Pd on a solid support [18]. When considering this, silica fulfils many of the required aspects as an appropriate solid support for the deposition of palladium catalysts [19, 20]. There have been several methods established towards the preparation of supported Pd-catalysts [21]. Silica, due to its inexpensive, comfortable, accessibility, high thermal resistant, high pore volume, and narrow pore size distribution characteristics, has been the focus of significant consideration

compared to other operative supports like polymeric ionic liquid, alumina, MCM-41, SBA-15, and so on [22, 23]. Among the various N-based ligands, Schiff bases are well known as ligands for the complexation of metal ions and as catalysis because of their easy preparation and being simple and cost effective starting materials with high resistance under a variety of conditions. Therefore, many researchers have developed several approaches to immobilize palladium Schiff-base complexes on solid supports [24]. To date, only a few palladium(II) complexes attached to functionalized mesoporous silica supports have been synthesized and successfully applied in organic reactions. However, no catalytic study has focused on the hydroamination of allene using palladium supported on mesoporous materials as catalysts. In our ongoing efforts to develop greener organic reactions, we now report a simple strategy for the preparation and characterization of a novel Salen-functionalized mesoporous silica supported Pd Schiff-base complex as a reusable catalyst and its application for the hydroamination of C-(tetra-O-acetyl- $\beta$ -D-galactopyranosyl)allene (**1**) with aromatic amines.

## 2. Experimental

**2.1. General.** All the starting materials, reagents, solvents, and eluents were commercial and used as purchased without purification. Flash column chromatography was performed using a silica gel 60 (230–400 mesh). Allene (**1**) was prepared according to a previously described method [25, 26].

**2.2. Material Characterization.** The prepared catalyst was characterized by various techniques, such as SEM, SEM-EDX, XRD, FT-IR, and BET. XRD measurements were performed with a D8 Advance Bruker diffractometer with the Cu-K $\alpha_1$  and Cu-K $\alpha_2$  radiations over a wide  $2\theta$  range of 0°–80°. Scanning electron micrographs (SEM) and energy dispersive X-ray (EDX) analyses were operated on a JEOL JSM-6460LV microscope. The IR spectrum was obtained using a FT-IR spectrophotometer (Bruker, Tensor 27). The surface area and porosity were measured with a Quantachrome Autosorb 1-MP. The palladium content was analyzed by an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 3000 DV, Perkin Elmer, EUA).

**2.3. Catalyst Preparation.** The catalyst was easily prepared from commercially available starting materials as shown in Scheme 1.

**2.3.1. General Procedure for Preparation of Imine-Functionalized Silica Gel (Salen-Silica): SiO<sub>2</sub>@ Imine.** A commercially available silica gel (230–400 mesh) was dried by heating at 120°C for 12 h prior to use.

**Method A.** Salicylaldehyde or 3-hydroxy-2-naphthaldehyde (42.86 mol) and then 3-aminopropyltriethoxysilane (APTES) (10 mL, 42.86 mol) were added to toluene (60 mL). A yellowish color showed immediately due to the formation of the imine. The resulting solution was stirred at a refluxing temperature under a nitrogen atmosphere for 7 h. After cooling, the solid silica gel (20 g) was added to the mixture and stirred

at a refluxing temperature under a nitrogen atmosphere for 7 h, and then the solids were filtered and washed thoroughly with toluene until the washings were colorless. The solid product was dried in air at 120°C overnight before being used in the next step, and the resulting materials were denoted as SiO<sub>2</sub>@ imineSA and SiO<sub>2</sub>@ imineNA for salicylaldehyde and 2-hydroxy-1-naphthaldehyde, respectively.

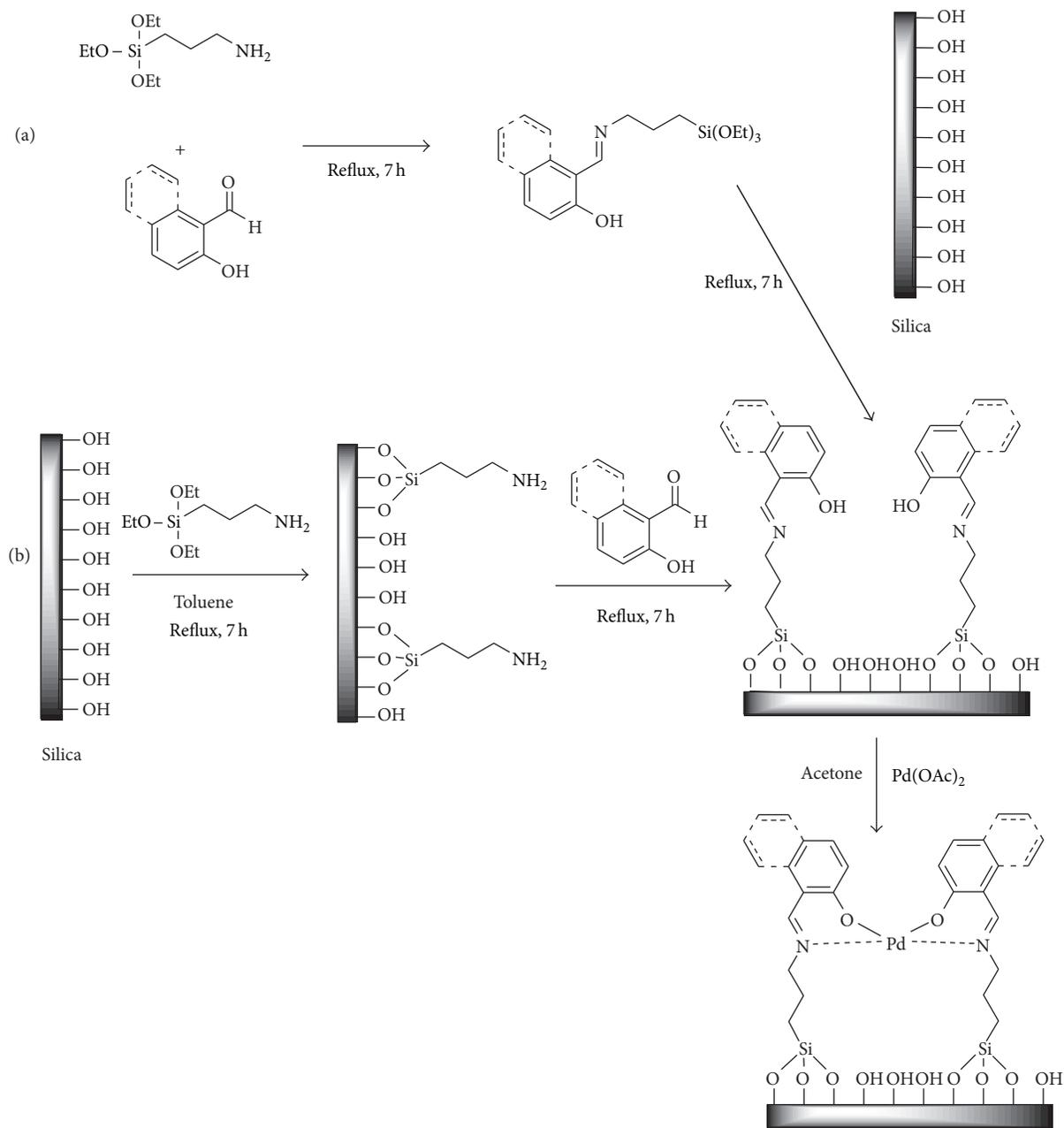
**Method B.** Silica gel (20 g) was added to 60 mL of toluene. To this slurry, 42.86 mole of APTES was added and the resultant slurry was heated at 110°C under a nitrogen atmosphere for 7 h, and then salicylaldehyde or 2-hydroxy-1-naphthaldehyde (42.86 mol) was added to the slurry and stirred at a refluxing temperature under a nitrogen atmosphere for 7 h. Following this, the solids were filtered and washed thoroughly with toluene until the washings were colorless. The solid product was dried in air at 120°C overnight and denoted as SiO<sub>2</sub>@ imineSB and SiO<sub>2</sub>@ imineNB for salicylaldehyde and 2-hydroxy-1-naphthaldehyde, respectively.

### 2.3.2. General Procedure for Immobilization of Pd(OAc)<sub>2</sub> onto Salen-Silica

**Method I.** To a round-bottomed flask, palladium acetate (415.68 mg, 1.73 mmol) and acetone (100 mL) were added. The solution was stirred at room temperature for 30 min under a nitrogen atmosphere and then 5 g of SiO<sub>2</sub>@ imineSA was added. The mixture was stirred at room temperature for 24 h. The deposited solids were filtered from the solvent and washed repeatedly through the Soxhlet extraction with ethanol and acetone until the washings were colorless, and they were dried overnight at 120°C and denoted as SiO<sub>2</sub>@ imineSA-Pd-I.

**Method II.** To a round-bottomed flask, palladium acetate (415.68 mg, 1.73 mmol) and acetone (100 mL) were added. The solution was stirred at room temperature for 30 min under a nitrogen atmosphere and then 5 g of Salen-silica was added. The mixture was refluxed while being stirred for 4 h. The deposited solids were separated from the solvent by filtration and washed repeatedly for Soxhlet extraction with ethanol and acetone, until the washings were colorless, and they were dried overnight at 120°C and denoted as SiO<sub>2</sub>@ imineSA-Pd-II, SiO<sub>2</sub>@ imineSB-Pd-II, SiO<sub>2</sub>@ imineNA-Pd-II, and SiO<sub>2</sub>@ imineNB-Pd-II.

**2.4. Procedure for Hydroamination of Allene (**1**).** All reactions were run under an air atmosphere. A reaction tube was charged with allene (**1**) (0.27 mmol), amine (0.81 mmol), Pd catalyst (90 mg, 5 mol%), trifluoroacetic acid (20 mol%), and THF (0.5 mL). The reaction mixture was allowed to proceed while being stirred at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered off and the solvent was evaporated under reduced pressure, after which the residue was purified by flash column chromatography on silica gel to yield the product. The solid compounds were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.



SCHEME 1: Synthetic strategy for the preparation of the silica gel supported Pd catalyst. (a) Homogeneous route for mesoporous silica functionalization (method A) and (b) heterogeneous route for mesoporous silica functionalization (method B).

**3a:**  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.17 (2H, apt,  $J$  8.4 and 7.2), 6.71 (1H, apt,  $J$  8.4 and 7.2), 6.60 (2H, d,  $J$  7.6), 5.98 (1H, dt,  $J$  15.6 and 5.2), 5.82 (1H, q,  $J$  15.6 and 5.2), 5.37 (1H, m), 5.28 (1H, dd,  $J$  10.4 and 6.0), 5.10 (1H, dd,  $J$  10.4 and 3.6), 4.81 (1H, apt,  $J$  6.0 and 5.2), 4.00–4.16 (3H, m), 3.75–3.95 (3H, m), 1.97–2.15 (12H, 4  $\times$  s);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.52, 170.19, 170.06, 169.87, 147.64, 134.47, 129.27, 123.49, 117.87, 113.14, 72.53, 68.31, 68.29, 68.01, 61.83, 45.62, 20.73, 20.69, 20.66.

**3b:**  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.79 (2H, d,  $J$  8.8), 6.60 (2H, d,  $J$  8.8), 5.97 (1H, dt,  $J$  15.6 and 5.2), 5.85 (1H, q,

$J$  15.6 and 5.2), 5.37 (1H, m), 5.31 (1H, dd,  $J$  10.4 and 6.0), 5.13 (1H, dd,  $J$  10.4 and 3.2), 4.81 (1H, apt,  $J$  6.0 and 5.2), 4.00–4.15 (3H, m), 3.75–3.87 (3H, m), 3.74 (3H, s), 1.99–2.15 (12H, 4  $\times$  s);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.53, 170.23, 170.13, 170.08, 152.44, 141.82, 134.79, 123.41, 114.92, 114.57, 72.50, 68.40, 68.33, 68.04, 68.01, 61.87, 45.94, 20.72, 20.70, 20.66.

**3c:**  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.09 (1H, apt,  $J$  8.4 and 8.0), 6.15–6.30 (3H, m), 5.99 (1H, dt,  $J$  15.6 and 5.2), 5.87 (1H, q,  $J$  15.6 and 5.6), 5.38–5.40 (1H, m), 5.29 (1H, dd,  $J$  10.4 and 6.0), 5.11 (1H, dd,  $J$  10.4 and 3.2), 4.80 (1H, apt,  $J$  6.0 and 5.2),

4.00–4.15 (4H, m), 3.82 (2H, d 5.2), 3.75 (3H, s), 1.96–2.16 (12H, 4 × s);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.53, 170.20, 170.04, 169.89, 160.84, 149.10, 134.52, 130.04, 123.49, 106.18, 102.82, 99.28, 72.52, 68.29, 68.07, 68.00, 61.86, 55.01, 45.61, 20.73, 20.68, 20.63.

**3d:**  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.87 (1H, dt,  $J$  7.6 and 1.6), 6.78 (1H, dd,  $J$  8.0 and 1.2), 6.69 (1H, dt,  $J$  7.6 and 1.2), 6.58 (1H, dd,  $J$  8.0 and 1.2), 6.02 (1H, dt,  $J$  15.6 and 5.2), 5.87 (1H, q,  $J$  15.6 and 5.6), 5.37 (1H, d,  $J$  3.2), 5.29 (1H, dd,  $J$  10.4 and 6.0), 5.12 (1H, dd,  $J$  10.4 and 3.2), 4.82 (1H, apt,  $J$  6.0 and 5.2), 4.00–4.16 (3H, m), 3.75–3.86 (3H, m), 3.85 (3H, s), 1.98–2.13 (12H, 4 × s);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.47, 170.20, 170.04, 169.88, 146.95, 137.59, 134.84, 123.30, 121.23, 117.01, 109.57, 72.62, 68.29, 68.09, 68.05, 61.88, 55.41, 45.47, 20.75, 20.72, 20.68, 20.65.

**3e:**  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.99 (2H, d,  $J$  8.4), 6.55 (2H, d,  $J$  8.4), 6.00 (1H, dt,  $J$  15.6 and 5.2), 5.86 (1H, q,  $J$  15.6 and 5.6), 5.37 (1H, d,  $J$  3.2), 5.31 (1H, dd,  $J$  10.4 and 6.0), 5.11 (1H, dd,  $J$  10.4 and 3.6), 4.79 (1H, apt,  $J$  6.0 and 5.6), 4.00–4.16 (4H, m), 3.82 (2H, d  $J$  5.2), 2.22 (3H, s), 1.99–2.13 (12H, 4 × s);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.50, 170.19, 170.04, 169.86, 145.37, 134.73, 129.76, 127.09, 123.34, 113.35, 72.59, 68.24, 68.05, 68.00, 61.83, 46.03, 20.70, 20.67, 20.34.

**3f:**  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.06 (1H, t,  $J$  7.6), 6.55 (1H, d,  $J$  7.6), 6.38–6.48 (2H, d, m), 6.01 (1H, dt,  $J$  15.6 and 5.2), 5.87 (1H, q,  $J$  15.6 and 5.2), 5.39 (1H, dd,  $J$  3.6 and 1.6), 5.31 (1H, dd,  $J$  10.4 and 6.0), 5.12 (1H, dd,  $J$  10.4 and 3.6), 4.81 (1H, apt,  $J$  6.0 and 5.2), 4.00–4.15 (4H, m), 3.84 (2H, d,  $J$  5.2), 2.27 (3H, s), 1.97–2.14 (12H, 4 × s);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.48, 170.16, 170.01, 169.83, 147.67, 138.98, 134.61, 129.13, 123.31, 118.75, 113.88, 110.19, 72.57, 68.26, 68.02, 67.96, 61.80, 45.65, 21.54, 20.70, 20.65.

**3g:**  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.09 (2H, d,  $J$  8.8), 6.58 (2H, d,  $J$  8.8), 6.01 (1H, dt,  $J$  15.6 and 5.2), 5.88 (1H, q,  $J$  16.0 and 5.2), 5.38–5.40 (1H, m), 5.30 (1H, dd,  $J$  10.4 and 5.6), 5.11 (1H, dd,  $J$  10.4 and 2.8), 4.82 (1H, apt,  $J$  6.0 and 5.2), 3.75–4.18 (6H, m), 1.93–2.14 (12H, 4 × s);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.64, 170.17, 170.08, 169.77, 152.98, 138.32, 132.15, 126.36, 124.85, 111.39, 72.24, 68.45, 68.23, 67.95, 67.82, 61.73, 44.89, 20.73, 20.69, 20.64.

**3h:**  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.55 (1H, d,  $J$  8.0), 7.40 (1H, s), 7.32 (1H, apt,  $J$  8.8 and 8.0), 6.90 (1H, d,  $J$  8.0), 5.99 (1H, dt,  $J$  15.6 and 5.2), 5.92 (1H, q,  $J$  15.6 and 5.2), 5.37–5.40 (1H, m), 5.31 (1H, dd,  $J$  10.4 and 5.6), 5.10 (1H, dd,  $J$  10.4 and 2.8), 4.82 (1H, apt,  $J$  6.0 and 5.2), 4.00–4.19 (4H, m), 3.93 (2H, d,  $J$  5.2), 1.96–2.17 (12H, 4 × s);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.61, 170.18, 170.07, 169.85, 149.44, 148.44, 132.92, 129.81, 124.40, 119.04, 112.38, 106.52, 72.39, 68.35, 68.25, 67.92, 61.73, 45.31, 20.72, 20.69, 20.66.

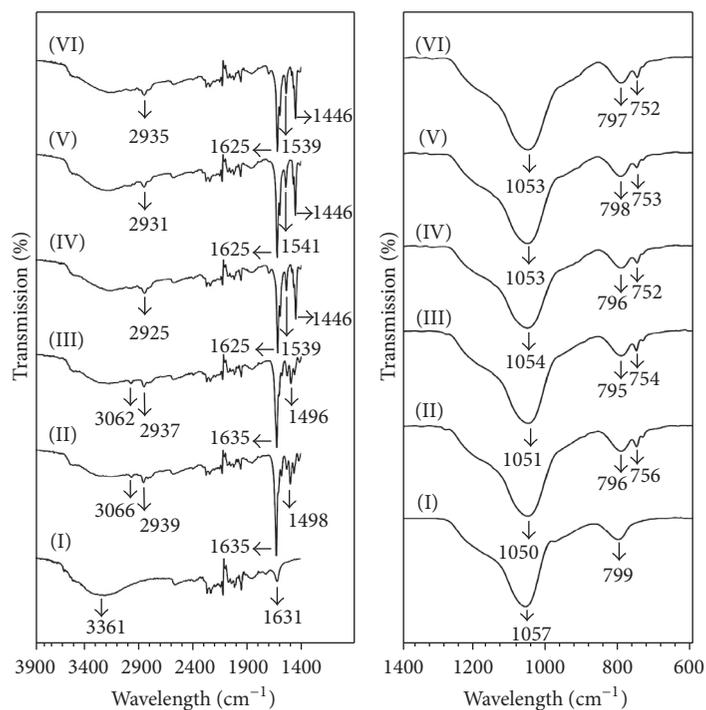
**3i:**  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.84 (2H, d,  $J$  8.8), 6.59 (2H, d,  $J$  8.8), 5.97 (1H, dt,  $J$  15.6 and 5.2), 5.85 (1H, q,  $J$  15.6 and 5.2), 5.35–5.40 (1H, m), 5.29 (1H, dd,  $J$  10.4 and 5.6), 5.10 (1H, dd,  $J$  10.4 and 3.2), 4.81 (1H, apt,  $J$  6.0 and 5.2), 4.0–4.17 (4H, m), 3.93 (2H, d,  $J$  4.8), 2.50 (3H, s), 1.96–2.16 (12H, 4 × s);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.43, 170.53, 170.15, 170.03, 169.78, 151.74, 133.05, 130.78, 130.73, 127.01, 124.12, 111.73, 111.66, 72.32, 68.35, 67.92, 67.85, 61.74, 44.83, 25.98, 20.70, 20.65, 20.60.

**2.5. Recycling Studies.** Recycling studies were carried out using the procedure for the hydroamination of allene (1) (0.27 mmol) with aniline (0.81 mmol), Pd catalyst ( $\text{SiO}_2@$  imineNB-Pd-II, 90 mg, 5 mol%), trifluoroacetic acid (20 mol%), and THF (0.5 mL). After the reaction, the catalyst was separated from the reaction mixture by filtration through a sintered glass funnel. The separated catalyst was washed with dichloromethane (3 × 1 mL), dried in a vacuum, and reused again to check its recycling efficiency.

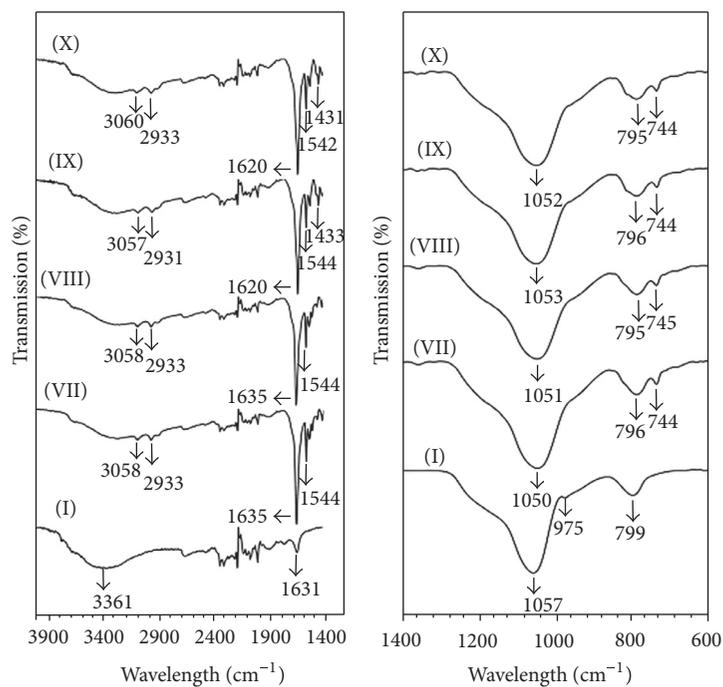
### 3. Results and Discussion

**3.1. Synthesis and Characterization of Catalyst.** The preparation of the palladium immobilized on the Salen-silica is shown in Scheme 1. Salen was covalently bonded to the commercially available silica gel (230–400 mesh) giving the Salen-silica. It was readily prepared by two different approaches. The first route for the functionalized mesoporous silica used the homogenous system (method A) for the preparation of the silylating agent by the reaction of 3-aminopropyltriethoxysilane (APTES) with salicylaldehyde or 3-hydroxy-2-naphthaldehyde. The product was condensed with the silanol group of the solid silica gel to give the imine-functionalized silica gel (Scheme 1(a)). The solid powders from salicylaldehyde and 3-hydroxy-2-naphthaldehyde were designated as  $\text{SiO}_2@$  imineSA and  $\text{SiO}_2@$  imineNA, respectively. In the second route, the heterogeneous system (method B) involved the reaction of the silica gel with the APTES to give aminosilica followed by a condensation with salicylaldehyde or 3-hydroxy-2-naphthaldehyde to provide the Salen-silica (Scheme 1(b)). The solid powders from the reaction of salicylaldehyde and 3-hydroxy-2-naphthaldehyde were designated as  $\text{SiO}_2@$  imineSB and  $\text{SiO}_2@$  imineNB, respectively. Finally, the precursor  $\text{SiO}_2@$  imineSA was applied for the synthesis of the Pd complex by reacting with  $\text{Pd}(\text{OAc})_2$  in acetone at room temperature for 24 h (method I) to give the product, designated as  $\text{SiO}_2@$  imineSA-Pd-I. The Pd complexes of  $\text{SiO}_2@$  imineSA,  $\text{SiO}_2@$  imineSB,  $\text{SiO}_2@$  imineNA, and  $\text{SiO}_2@$  imineNB were also obtained by reacting with  $\text{Pd}(\text{OAc})_2$  in acetone under reflux conditions for 4 h (method II) to provide the resulting products, and they were designated as  $\text{SiO}_2@$  imineSA-Pd-II,  $\text{SiO}_2@$  imineSB-Pd-II,  $\text{SiO}_2@$  imineNA-Pd-II, and  $\text{SiO}_2@$  imineNB-Pd-II, respectively. The characterization of the  $\text{SiO}_2@$  imine and Salen-silica supported Pd complex were done on the basis of their properties, such as via FT-IR, XRD, SEM, SEM-EDX, ICP-OES, and  $\text{N}_2$  adsorption-desorption spectra data.

The silanol ( $\equiv\text{Si-OH}$ ) groups on the surface of the silica showed a significant qualification through silylation. Figure 1 shows the FT-IR spectra of (I)  $\text{SiO}_2$ , (II)  $\text{SiO}_2@$  imineSA, (III)  $\text{SiO}_2@$  imineSB, (IV)  $\text{SiO}_2@$  imineSA-Pd-II, (V)  $\text{SiO}_2@$  imineSB-Pd-II, and (VI)  $\text{SiO}_2@$  imineSA-Pd-II. According to Figure 1, the characteristic silica bands combined with a silica backbone can be clearly detected in all spectra. The characteristic Si–O–Si bands at 1057 and 799  $\text{cm}^{-1}$ , present in all samples, are assigned to the silica network. The spectrum of the free silica displays a typical broad band at 3361  $\text{cm}^{-1}$  due to the vibration of the H bond of the silanol



(a)



(b)

FIGURE 1: (a) FT-IR of (I)  $\text{SiO}_2$ , (II)  $\text{SiO}_2@$  imineSA, (III)  $\text{SiO}_2@$  imineSB, (IV)  $\text{SiO}_2@$  imineSA-Pd-II, (V)  $\text{SiO}_2@$  imineSB-Pd-II, and (VI)  $\text{SiO}_2@$  imineSA-Pd-II. (b) FT-IR of (I)  $\text{SiO}_2$ , (VII)  $\text{SiO}_2@$  imineNA, (VIII)  $\text{SiO}_2@$  imineNB, (IX)  $\text{SiO}_2@$  imineNA-Pd-II, and (X)  $\text{SiO}_2@$  imineNB-Pd-II.

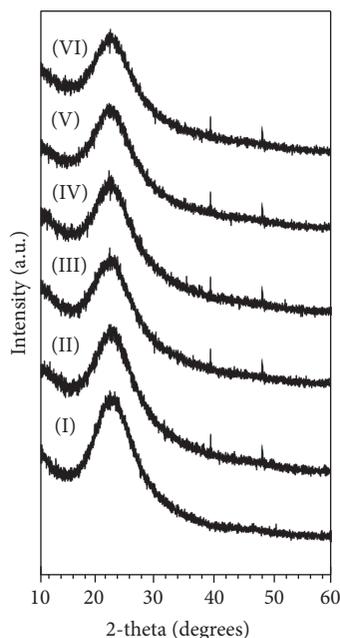


FIGURE 2: XRD patterns of (I)  $\text{SiO}_2$ , (II)  $\text{SiO}_2@$  imineSA, (III)  $\text{SiO}_2@$  imineSB, (IV)  $\text{SiO}_2@$  imineSA-Pd-II, (V)  $\text{SiO}_2@$  imineSB-Pd-II, and (VI)  $\text{SiO}_2@$  imineSA-Pd-II.

group and water of the siloxane backbone. The spectra of all the samples (Figures 1(a) and 1(b)) of the modified silica were identified by the presence of two weak bands at  $3058\text{--}3066$  and  $2931\text{--}2939\text{ cm}^{-1}$  due to the vibration of the aromatic and aliphatic C-H groups, respectively. Meanwhile, the bending vibration of the Si-OH on the free silica at  $975\text{ cm}^{-1}$  significantly decreased after grafting with APTES. The Schiff bases display strong bands at  $1635$  and  $1498\text{ cm}^{-1}$  due to the azomethine (C=N) and phenolic (C-O) stretching modes, respectively. The band at  $1635\text{ cm}^{-1}$ , upon the reaction of the Salen complex with Pd, shifted to a lower frequency ( $1625\text{ cm}^{-1}$  for  $\text{SiO}_2@$  imineSA-Pd and  $\text{SiO}_2@$  imineSB-Pd;  $1625\text{ cm}^{-1}$  for  $\text{SiO}_2@$  imineNA-Pd and  $\text{SiO}_2@$  imineNB-Pd), which indicated the formation of a Pd complex. The powder X-ray diffraction patterns of the parent silica gel ( $\text{SiO}_2$ ) and palladium immobilized Salen-silica are shown in Figure 2.

The patterns have a broad peak of  $2\theta = 22.4^\circ$ , which indicated that the material had low crystallinity or the amorphous nature of the silica. A few decreases in the intensity were identified for the Pd(II)-Salen-silica that confirmed the immobilization of the Salen-silica. This decrease in intensity could be due to the covering of the pores in the silica surface during the metalation.

In good agreement with the XRD, the SEM images of the free silica and supported Pd(II)-Schiff-base@ $\text{SiO}_2$  samples (Figure 3) showed the ordered channel structure of the mesoporous materials, which is stored during the complex grafting. The silica gel did not change significantly in size or gathered state under the supported processes in method II, but the presence of palladium caused a significant decrease

in the silica particle size from the preparation with method I. Although the palladium particles and their dispersions are not clearly visible from the SEM spectra, considering the results of the SEM-EDX (Figure 4) and the ICP-OES, it was possible to define the palladium attachment on the surface of the silica supports. The presence of palladium in the Pd(II)-Schiff-base@ $\text{SiO}_2$  samples could be clearly seen from Figure 4. The amount of adhered palladium was evaluated by ICP-OES, as shown in Table 1.

The results from the  $\text{N}_2$  adsorption-desorption isotherms of the silica-based samples and the respective textural parameters containing the specific surface area (SBET), the pore diameter, and the total pore volume ( $V_{\text{total}}$ ) are summarized in Table 1. The isotherms of all samples showed typical type IV patterns corresponding to the IUPAC definitions of porosity (Figure 5). The specific surface area provided by the BET method for the free  $\text{SiO}_2$  was  $411.16\text{ m}^2\text{g}^{-1}$ , which upon functionalization by methods A and B with salicylaldehyde and 3-hydroxy-2-naphthaldehyde gave  $\text{SiO}_2@$  imineSA,  $\text{SiO}_2@$  imineSB,  $\text{SiO}_2@$  imineNA, and  $\text{SiO}_2@$  imineNB, which were reduced to  $340.58$ ,  $366.92$ ,  $273.49$ , and  $268.89\text{ m}^2\text{g}^{-1}$ , respectively. In addition, the nitrogen adsorption-desorption studies indicated that a significant decrease in pore size by the imine-functionalization of the silica channels was monitored. There was not much difference in the surface areas of the various catalysts (entries 6–10, Table 1), with values between ca.  $302$  and  $358\text{ m}^2\text{g}^{-1}$ . Different surface areas and pore volumes can support different activities of the porous solid catalysts, but there was no support due to different pore volumes and BET surface areas in this study.

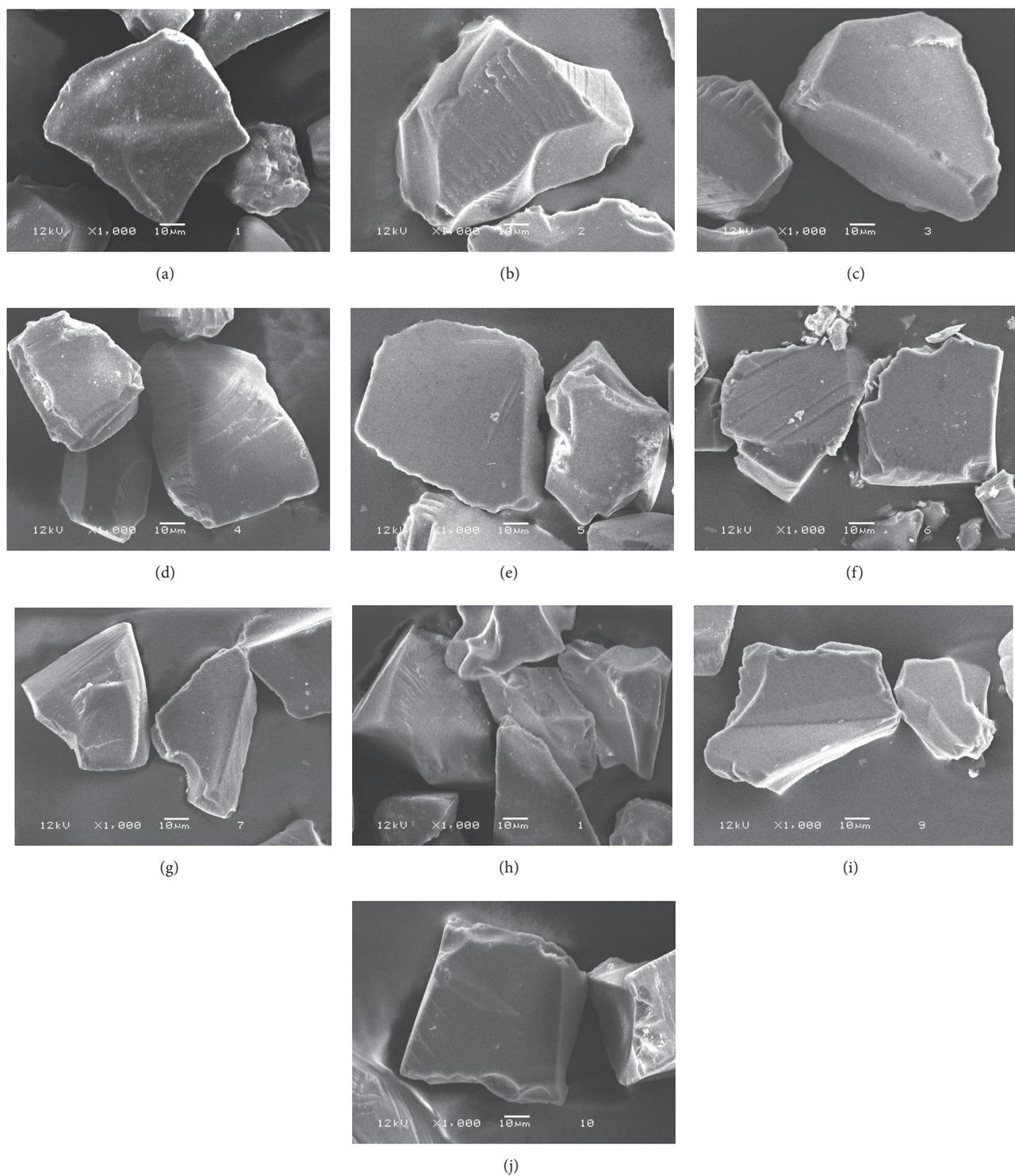


FIGURE 3: SEM image of (a)  $\text{SiO}_2$ , (b)  $\text{SiO}_2@ \text{imineSA}$ , (c)  $\text{SiO}_2@ \text{imineSA-Pd-II}$ , (d)  $\text{SiO}_2@ \text{imineSB}$ , (e)  $\text{SiO}_2@ \text{imineSB-Pd-II}$ , and (f)  $\text{SiO}_2@ \text{imineSA-Pd-I}$ , (g)  $\text{SiO}_2@ \text{imineNA}$ , (h)  $\text{SiO}_2@ \text{imineNA-Pd-II}$ , (i)  $\text{SiO}_2@ \text{imineNB}$ , and (j)  $\text{SiO}_2@ \text{imineNB-Pd-II}$ .

3.2. *Catalytic Hydroamination.* After structural characterization of the prepared Pd(II) immobilized on Salen-functionalized silica,  $\text{SiO}_2@ \text{imineSA-Pd-II}$ ,  $\text{SiO}_2@ \text{imineSA-Pd-I}$ ,  $\text{SiO}_2@ \text{imineSB-Pd-II}$ ,  $\text{SiO}_2@ \text{imineNA-Pd-II}$ , and

$\text{SiO}_2@ \text{imineNB-Pd-II}$ , its catalytic activity was investigated via the hydroamination of allene (**1**). The starting material was prepared as previously described. The reaction between the allene (**1**) and the aniline (**2a**) was selected as the model

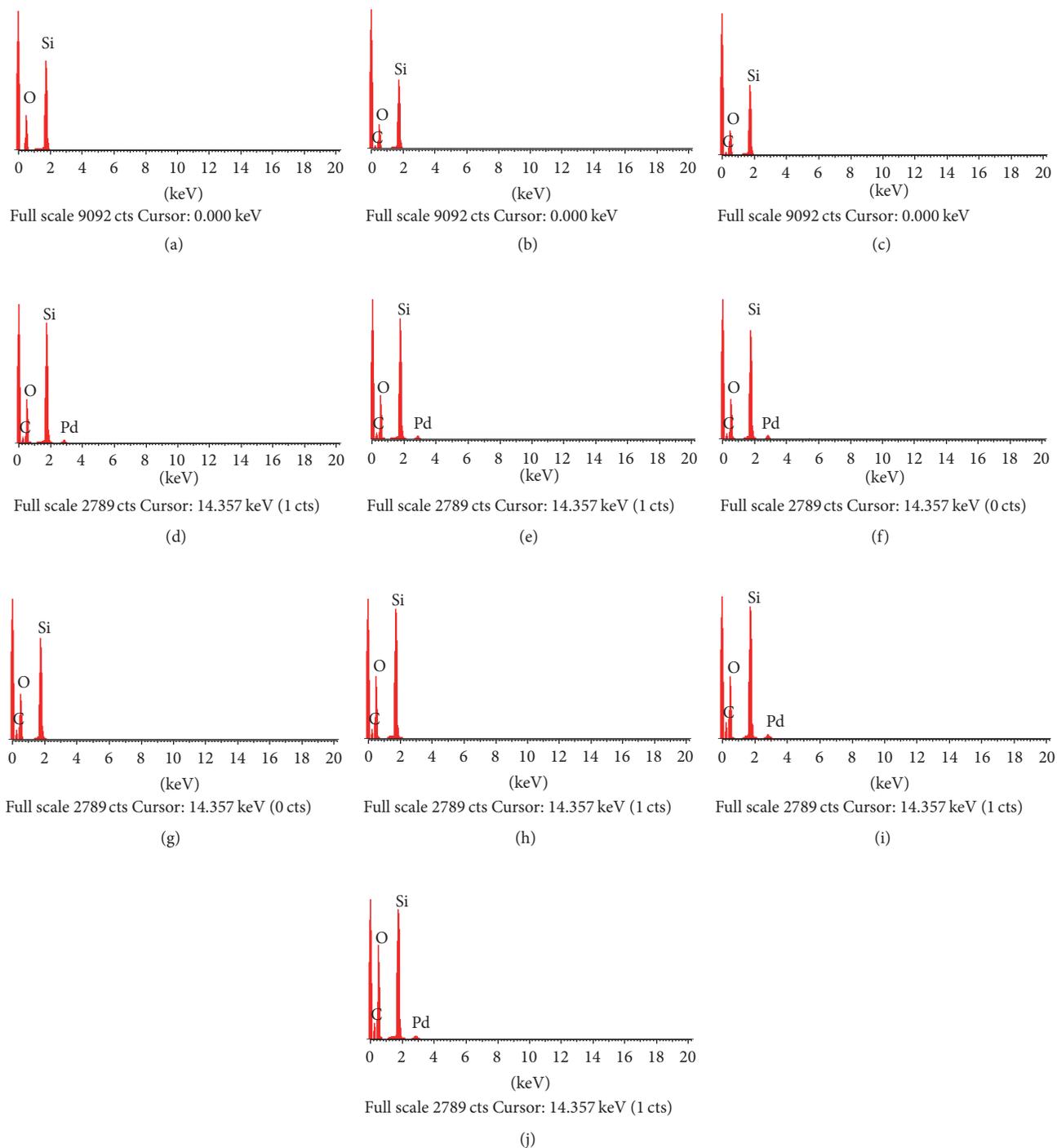


FIGURE 4: EDS spectrum of (a)  $\text{SiO}_2$ , (b)  $\text{SiO}_2@$  imineSA, (c)  $\text{SiO}_2@$  imineSB, (d)  $\text{SiO}_2@$  imineSA-Pd-II, (e)  $\text{SiO}_2@$  imineSB-Pd-II, (f)  $\text{SiO}_2@$  imineSA-Pd-I, (g)  $\text{SiO}_2@$  imineNA, (h)  $\text{SiO}_2@$  imineNB, (i)  $\text{SiO}_2@$  imineNA-Pd-II, and (j)  $\text{SiO}_2@$  imineNB-Pd-II.

reaction using THF as the solvent and TFA as the additive with 5 mol% palladium catalyst, as shown in Table 2.

The reaction was successfully operated at room temperature under air without any special precautions. To verify the effect of the imine-functionalization on the catalysis,  $\text{SiO}_2@$  imineSA-Pd-II,  $\text{SiO}_2@$  imineSA-Pd-I,  $\text{SiO}_2@$  imineSB-Pd-II,

$\text{SiO}_2@$  imineNA-Pd-II,  $\text{SiO}_2@$  imineNB-Pd-II, and homogeneous  $[\text{Pd}(\text{OAc})_2]$  were compared as catalysts (with the same palladium content) under identical conditions. It is necessary to note that  $\text{SiO}_2@$  imineSA-Pd-I exhibited the same yield as indicated by the homogeneous  $[\text{Pd}(\text{OAc})_2]$  (entries 1 and 3, Table 2). Then, when comparing with

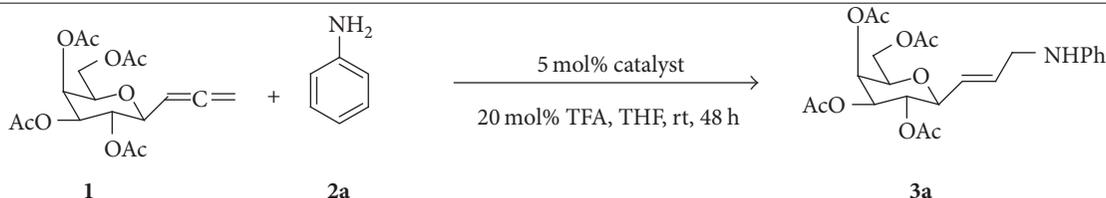
TABLE 1: Surface area, total pore volume, pore size distribution, and amount of Pd loaded on the surface of the silica-based materials.

Entry	Materials	$S_{\text{BET}}^{\text{a}}$ ( $\text{m}^2 \text{g}^{-1}$ )	Total pore volume <sup>b</sup> ( $\text{cm}^3 \text{g}^{-1}$ )	Mean pore diameter <sup>c</sup> (nm)	Pd content <sup>d</sup> $\pm$ SD <sup>e</sup> ( $\text{mg g}^{-1}$ )
1	SiO <sub>2</sub>	411.16	0.860	4.18	NA <sup>f</sup>
2	SiO <sub>2</sub> @ imineSA	340.58	0.503	2.95	NA <sup>f</sup>
3	SiO <sub>2</sub> @ imineSB	366.92	0.589	3.21	NA <sup>f</sup>
4	SiO <sub>2</sub> @ imineNA	273.49	0.430	3.14	NA <sup>f</sup>
5	SiO <sub>2</sub> @ imineNB	268.89	0.416	3.10	NA <sup>f</sup>
6	SiO <sub>2</sub> @ imineSA-Pd-II	358.63	0.505	2.82	30.74 $\pm$ 0.42
7	SiO <sub>2</sub> @ imineSA-Pd-I	302.64	0.429	2.83	33.6 $\pm$ 1.52
8	SiO <sub>2</sub> @ imineSB-Pd-II	365.38	0.539	2.95	29.58 $\pm$ 1.63
9	SiO <sub>2</sub> @ imineNA-Pd-II	322.64	0.416	2.58	25.85 $\pm$ 0.72
10	SiO <sub>2</sub> @ imineNB-Pd-II	305.41	0.407	2.65	25.12 $\pm$ 0.77

<sup>a</sup>BET method used in N<sub>2</sub> sorption. <sup>b</sup>Single-point pore volume at  $P/P_0 = 0.975$ . <sup>c</sup>Adsorption average pore diameter by BET method. <sup>d</sup>Determined by ICP-OES analysis. <sup>e</sup>Average of triplicates  $\pm$  SD. <sup>f</sup>Not applicable.

TABLE 2: Optimization of reaction conditions of C-(tetra-O-acetyl- $\beta$ -D-galactopyranosyl)allene (**1**) with aniline (**2a**).<sup>a</sup>

Entry	Catalyst	Yield <sup>b</sup> (%)
1	Pd(OAc) <sub>2</sub>	<b>3a</b> 30
2	SiO <sub>2</sub> @ imineSA-Pd-II	17
3	SiO <sub>2</sub> @ imineSA-Pd-I	34
4	SiO <sub>2</sub> @ imineSB-Pd-II	16
5	SiO <sub>2</sub> @ imineNA-Pd-II	50
6	SiO <sub>2</sub> @ imineNB-Pd-II	60



<sup>a</sup>All reactions were carried out with conditions: C-(tetra-O-acetyl- $\beta$ -D-galactopyranosyl)allene (**1**) (0.27 mmol) and aniline (0.81 mmol) in 0.5 mL of solvent for 48 h. <sup>b</sup>Isolated yields.

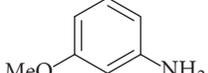
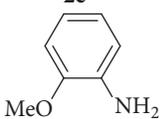
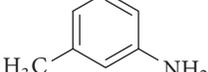
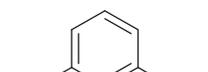
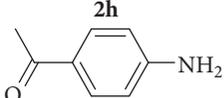
the imine-functionalization of silica from salicylaldehyde, the activity was significantly decreased with imineSA-Pd-II and SiO<sub>2</sub>@ imineSB-Pd-II (entries 2 and 4, Table 2). However, in the presence of the imine-functionalization of silica from 3-hydroxy-2-naphthaldehyde, SiO<sub>2</sub>@ imineNA-Pd-II, and SiO<sub>2</sub>@ imineNB-Pd-II, the reaction proceeded with an improved yield of the desired product (**3a**) (entries 5 and 6, Table 2). In addition, the formation of diallylated acetate and diallylated amine was not observed as minor products. The recycling ability of SiO<sub>2</sub>@ imineNB-Pd-II for the hydroamination of **1** with aniline was evaluated. After the recovery of the catalyst, it was reused directly without further purification. The catalyst could be successfully recycled for five consecutive cycles for the hydroamination of **1** with aniline and no significant loss of catalytic activity was

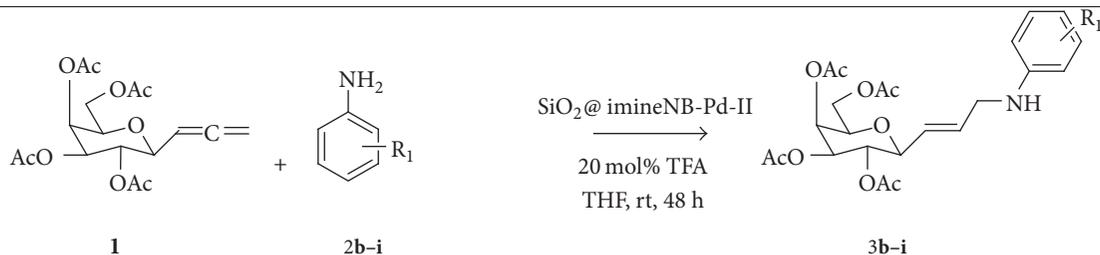
observed after the fifth cycle. Additionally, palladium leaching in SiO<sub>2</sub>@ imineNB-Pd-II was determined. The palladium content of the clear filtrates obtained upon filtration after the reaction was < 0.2 ppm, from ICP-OES analyses.

To test the extent and restrictions of our catalyst, SiO<sub>2</sub>@ imineNB-Pd-II, we also studied the hydroamination of **1** with substituted anilines (**2b-i**) bearing an electron-poor or an electron-rich group on the benzene ring provided to the corresponding allylamines (**3b-i**) (Table 3).

According to previous reports, the results also showed that the onset potential for the heterogeneous catalyst was more positive than under the homogenous condition. This could be due to the reduced formation of diallylated amine and diallylated acetate as byproducts.

TABLE 3: Hydroamination of *C*-(tetra-*O*-acetyl- $\beta$ -*D*-galactopyranosyl)allene (**1**) with aromatic amines<sup>a</sup>.

Entry	Amine	Product (%) <sup>b</sup>
1	 <b>2b</b>	<b>3b</b> (26)
2	 <b>2c</b>	<b>3c</b> (32)
3	 <b>2d</b>	<b>3d</b> (41)
4	 <b>2e</b>	<b>3e</b> (76)
5	 <b>2f</b>	<b>3f</b> (78)
6	 <b>2g</b>	<b>3g</b> (18)
7	 <b>2h</b>	<b>3h</b> (18)
8	 <b>2i</b>	<b>3i</b> (23)



<sup>a</sup>Reaction condition: *C*-(tetra-*O*-acetyl- $\beta$ -*D*-galactopyranosyl)allene (**1**) (0.27 mmole) and aniline (0.81 mmole) in 0.5 mL of solvent for 48 h;  $\text{SiO}_2@ \text{imineNB-Pd-II}$  (5 mol%); TFA (20 mol%). <sup>b</sup>Isolated yields.

#### 4. Conclusion

A novel mesoporous silica supported palladium(II)-based heterogeneous catalyst has been successfully synthesized by immobilizing  $\text{Pd}(\text{OAc})_2$  onto a Salen-functionalized silica gel via coordination. The supported catalyst exhibited good activity for the hydroamination of allene (**1**) with a variety

of aromatic amines. It could be easily recovered by simple separation even after the catalyst was reused for a fifth cycle with no significant loss of catalytic activity.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

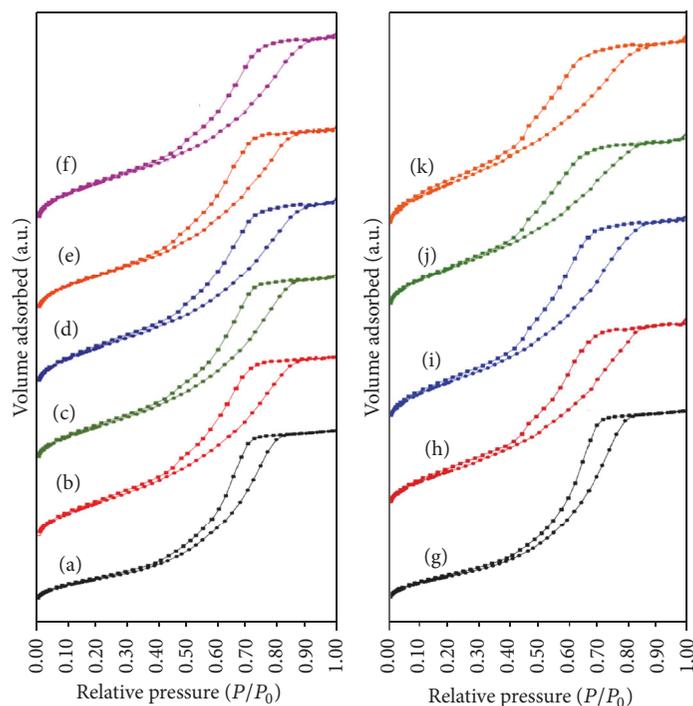


FIGURE 5:  $N_2$  adsorption-desorption isotherms of the silica-based materials: (a)  $SiO_2$ , (b)  $SiO_2@$  imineSA, (c)  $SiO_2@$  imineSB, (d)  $SiO_2@$  imineSA-Pd-II, (e)  $SiO_2@$  imineSB-Pd-II, (f)  $SiO_2@$  imineSA-Pd-I, (g)  $SiO_2$ , (h)  $SiO_2@$  imineNA, (i)  $SiO_2@$  imineNB, (j)  $SiO_2@$  imineNA-Pd-II, and (k)  $SiO_2@$  imineNB-Pd-II.

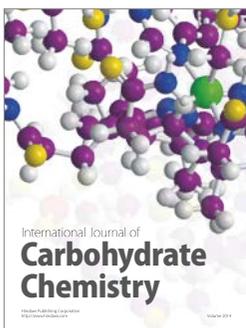
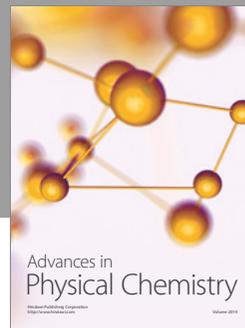
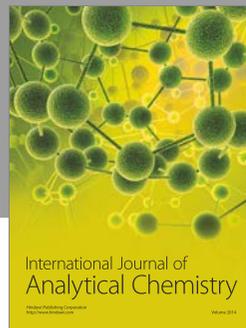
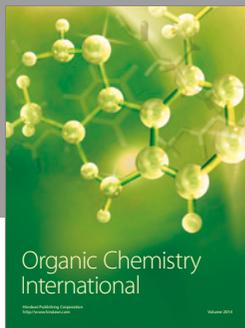
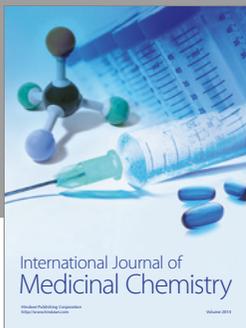
## Acknowledgments

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