Journal of Molecular Catalysis A: Chemical 394 (2014) 74–82

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

$PdCl_2$ on modified poly(styrene-co-maleic anhydride): A highly active and recyclable catalyst for the Suzuki–Miyaura and Sonogashira reactions

Majid M. Heravi[a,*], Elaheh Hashemi[a], Yahya Shirazi Beheshtiha[a], Shervin Ahmadi[b], Tayebeh Hosseinnejad[a]

[a] *Department of Chemistry, School of Science, Alzahra University, Vanak, Tehran, Iran*
[b] *Iran Polymer and Petrochemical Institute, Tehran, Iran*

ARTICLE INFO

Article history:
Received 16 May 2014
Received in revised form 30 June 2014
Accepted 1 July 2014
Available online 9 July 2014

Keywords:
Polymer-supported catalyst
Poly(styrene-co-maleic anhydride)
Palladium catalyst
Cross-coupling reaction

ABSTRACT

The Suzuki–Miyaura and Sonogashira coupling were performed using a new, efficient, reusable and recyclable polymer-supported palladium catalyst. Poly(styrene-co-maleic anhydride) as polymer-support is modified with 2-aminothiazole. $PdCl_2$ was immobilized on this prepared support and its appearance was confirmed by scanning electron microscopy (SEM), energy dispersive spectroscopy analysis of X-rays (EDAX), inductively coupled plasma (ICP) analysis, and FT-IR techniques. In addition, a quantitative description for metal–ligand interactions in the aforementioned polymer-supported palladium complex is investigated by performing theoretical calculations using density functional theory techniques.

1. Introduction

The syntheses of many important and useful products (drugs, natural products, optical devices, etc.) require carbon–carbon bonds formation as central consequence in organic chemistry, via assembling the palladium (Pd) catalyzed cross-coupling reactions [1]. Among Pd-catalyzed reactions, Suzuki–Miyaura [2] and Sonogashira coupling [3] are effective for transformations of highly functionalized molecules in the syntheses of large and complex molecules from simpler precursors. They are practical in laboratory and operative in industry [1,4]. Since Pd-catalysts are expensive and sometimes remain slight contamination in the products, the application of these catalysts supported on insoluble polymers or in different common inorganic supports are much in demands and desirable. The known excellent coordination properties of Pd with a variety of organic ligands, containing P, N, O, and S, make it a very good candidate being easily converted to a typically heterogeneous and recyclable catalysts [5–7].

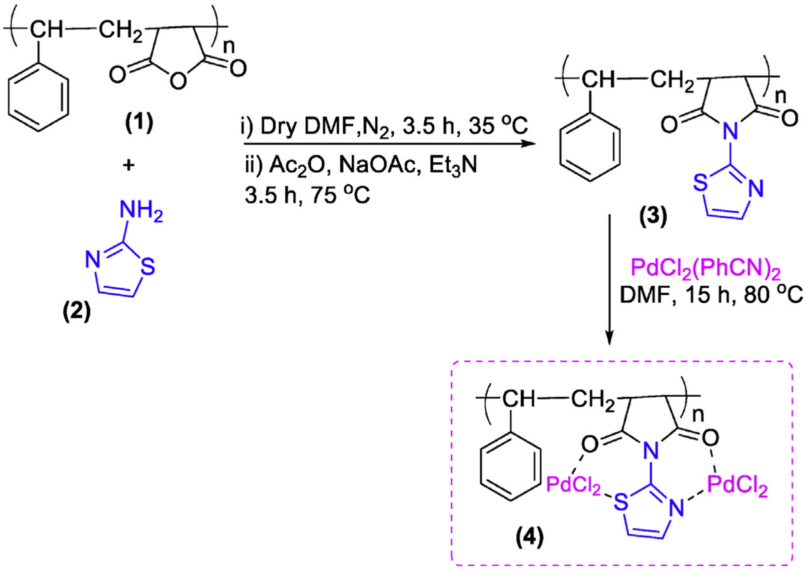
Poly(styrene-*co*-maleic anhydride) (SMA) as a commercially available co-polymer carrying reactive anhydride groups are susceptible being modified using different nucleophilic substances. These modified polymers can be used as polymer-support in the syntheses of different reagents [8–13] and preparation of various catalysts [14]. Reaction of SMA with *di*(2-pyridyl)methylamine for the syntheses of an effective and recoverable palladium catalyst being efficiently used in Heck, Suzuki and Sonogashira cross-coupling reactions, in neat water, was reported by Nàjera and co-workers in 2005 [14]. However, further investigation on this polymer as a support for the syntheses of new structures, via its reaction with other susceptible coordinating agents, has been largely overlooked.

In continuation of our studies on Pd-catalyzed reactions [15–24], our interest in the discovery of new heterogeneous catalysts [25–32] and encouraged with our very recent fascinating results from using modified SMA in click [33] and some multi-component reactions [34], herein, we wish to reveal our results on the syntheses of modified SMA using a simple coordinating agent such as 2-aminothiazole and examine the activity of this new synthesized support for the syntheses of an effective Pd-supported catalyst. Remarkably, in addition, the efficiency of this new Pd catalyst is examined in Suzuki and Sonogashira cross-coupling reactions, purposely under 'green' conditions. The reusability and recyclability of this heterogeneous catalyst is also examined and found being positive.

---

* Corresponding author. Tel.: +98 91 21329147; fax: +98 21 88041344.
E-mail address: mmh1331@yahoo.com (M.M. Heravi).

http://dx.doi.org/10.1016/j.molcata.2014.07.001
1381-1169/



Scheme 1. Syntheses of SMI–$PdCl_2$ catalyst.

2. Experimental

2.1. Materials

N,*N*-Dimethylformamide (DMF) and triethylamine (TEA) were distilled and kept over 4 Å molecular sieve before use. The other reagents were purchased from Aldrich and Merck with high-grade quality (except SMA) and used as they were received. The general formula of SMA (KARABOND SAM), used in this study, is $[(C_8H_8)_{0.6}(C_4H_2O_3)_{0.4}]_n$ with M_n (g/mol) = 86,666, M_w = 182,000, and M_w/M_n = 2.1.

2.2. Equipments

The ^1H NMR and ^{13}C NMR spectra were recorded, using a Bruker Ultrashield 400 and 100 MHz respectively Advance instrument, with DMSO-d_6 or $CDCl_3$ used as solvent. Proton resonances are designated as singlet (s), and multiplet (m). FTIR spectra were recorded using KBr disks on FT-IR Bruker Tensor 27 instrument in the 500–4000 cm^{-1} region. The vibrational transition frequencies are reported in wave numbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), and strong (s). Palladium content was measured by inductively coupled plasma (ICP) on a Varian Vistapro analyzer. The scanning electron micrographs of the catalyst surface were recorded using a Lecia Cambridge S 360 SEM instrument. All yields refer to isolated products.

2.3. The syntheses of catalyst

2.3.1. Preparation of SMI

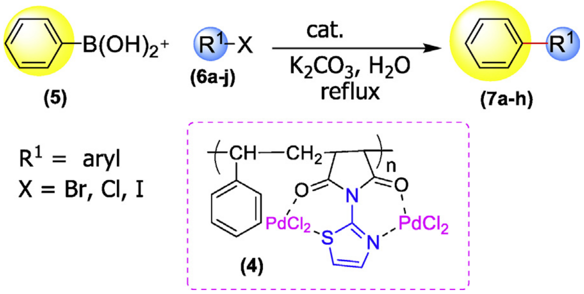
The chemical modification of SMA (1) was performed in two steps according to Lee et al. optimal reactive conditions [35]. SMA (1.00 g), 2-aminothiazole **2** (1.64 g, 16 mmol) and 15 ml dry DMF were added into a 100-ml glass reactor and then N_2 gas was charged into the reactor and then it was sealed. The reactor was placed into a thermostatic oil-bath on the oscillator and the reactive mixture was oscillated until the reagents were dissolved in DMF and kept oscillating at 35 °C for 3.5 h. Subsequently, 0.6 ml acetic anhydride, 0.33 g sodium acetate and 0.3 ml triethylamine were added into the reactor by syringe (Scheme 1). The temperature was continuously raised to 75 °C and oscillation continued for another 3.5 h. The reaction mixture was cooled to room temperature, and was poured slowly into 300 ml of vigorously stirring methanol. A fiber-like precipitated polymer was repeatedly washed with methanol, collected by filtration and dried under reduced pressure at 70 °C to constant weight. For further purification, the SMI polymer (3) was re-precipitated twice. The amine content of SMI was estimated by back titration using NaOH (0.2 N) [36,37]. For that, 10 ml of HCl (0.2 N) was added to 0.05 g of the SMI and the resulted mixture was stirred for 30 min. The SMI was removed and washed successively with deionized water. After that, the excess amount of HCl was titrated with NaOH (0.2 N) in the presence of phenolphthalein as an indicator. Amine sites content of the synthesized SMI found to be 3.82 mmol g^{-1}.

2.3.2. Preparation of Pd-supported catalyst

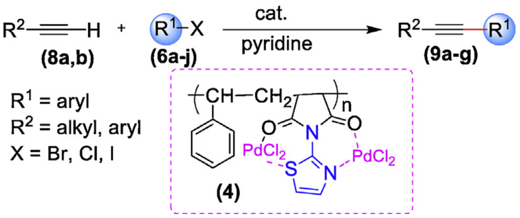
The SMI polymer 3 (1.0 g, 3.82 mmol amine site) was treated with $PdCl_2(PhCN)_2$ (1.0 g, 3 mmol) in DMF (10 ml), and the resulting mixture was heated at 80 °C for 15 h. The resulted brown polymer which impregnated with the metal complex was filtered and washed with acetonitrile to give the catalyst **4** (Scheme 1). After the filtration of the mixture, the SMI–$PdCl_2$ (**4**) washed with acetonitrile (2 × 20 ml) and dried under vacuum at 60 °C overnight (Scheme 1). For evaluation of the palladium content, the catalyst (30 mg) was treated with a mixture (5 ml) of hydrochloric acid and nitric acid (3:1, v/v) at 100 °C for 4 h. The resulting solution was then filtered, and the recovered resin beads were washed with distilled water (2.5 ml × 6). The filtrate was diluted to 50 ml with distilled water and analyzed by ICP-atomic emission spectrometry (AES). The palladium content was determined being 0.934 mmol g^{-1} (catalyst Pd loading was 9.94% w/w).

2.4. General procedure for the Suzuki coupling reaction

A mixture of an appropriate aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol, 0.18 g), K_2CO_3 (5.0 mmol, 0.69 g), H_2O (5 ml), and 0.02 g of catalyst was stirred under reflux (Scheme 2). After the completion of the reaction which was monitored by Thin Layer Chromatography (TLC) using *n*-hexane as eluent, the solution was filtered through a Büchner funnel to remove the resin, which was washed with acetone three times, dried under reduced pressured at 70 °C for 3 h. and stored for other consecutive reaction runs. Then the reaction product was extracted with CH_2Cl_2 (3 × 5 ml) and the solvent was removed on a rotary evaporator under reduced



Scheme 2. Suzuki coupling reaction in the presence of SMI–PdCl$_2$ catalyst.



Scheme 3. Sonogashira coupling reaction in the presence of SMI–PdCl$_2$ catalyst.

pressure. The crude was purified by flash column chromatography (hexane or hexane/ethyl acetate) to afford the desired corresponding coupling product. The symmetrical and unsymmetrical biaryls (**7a–h**) synthesized in this work have been reported previously and were identified by comparing of their melting points, IR and ^{1}H NMR, of selected product spectra with those of authentic samples, already reported in the literature and found to be identical [38,39]. The spectral (IR and ^{1}H NMR) data for the selected compound are as follows:

4-Methylbiphenyl (7c): ^{1}H NMR (400 MHz, CDCl3): δ = 7.60 (2H, ArH), 7.51 (2H, ArH), 7.46 (1H, ArH), 7.33 (2H, ArH), 7.25 (2H, ArH), 2.33 (3H, s) ppm; FT-IR (KBr, cm^{-1}): υ = 3050–2860 (C—H, str.), 1610–1440 (C=C, str.).

2.5. General procedure for the Sonogashira coupling reaction

A round-bottomed flask was charged with an aryl halide (1.0 mmol), an appropriate terminal alkyne (1.0 mmol), pyridine (1.0 mmol, 0.079 g), *n*-dodecane (15–20 mg) as an internal GC standard and the catalyst (0.02 g) under air atmosphere. The mixture was stirred at room temperature for 3 h. under aerobic conditions. After completion of the reaction, CHCl$_3$ was added and the mixture was filtered in order to recover the catalyst. The catalyst was washed with acetone, dried under reduced pressured at 70 °C for 3 h and stored for other consecutive reaction runs. After the completion of the reaction (monitored by GC analysis), the solvent was removed under vacuum, and the crude product was subjected to silica gel column chromatography using CHCl$_3$–CH$_3$OH (97:3) as eluent to afford the pure corresponding product (Scheme 3). IR and ^{1}H NMR data of a selected product were found to be identical with those of authentic samples [40]. The spectral (IR, Mass and ^{1}H NMR) data are as follows:

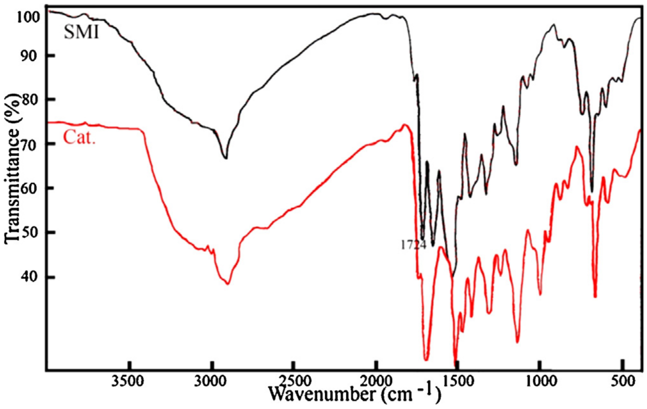


Fig. 2. FTIR spectrum of SMI and SMI–PdCl$_2$.

Diphenylacetylene (9a): ^{1}H NMR (CDCl$_3$, 400 MHz), δ = 7.53–7.49 (m, 4H), 7.30–7.21 (m, 6H) MS (EI): m/z (rel%) 178 (bp, M$^+$), 152 (24). FT-IR (KBr, cm^{-1}): υ = 3045–2930 (C—H, str.), 2050 (C ≡ C, str.). 1634–1477 (C=C, str.).

3. Results and discussion

3.1. Preparation and characterization of the Pd-supported catalyst

Modification of SMA (**1**) with 2-aminothiazole (**2**) was successfully performed in two steps under Lee et al. conditions (Scheme 1) [35]. The ^{1}H NMR spectrum of SMI was recorded in DMSO for the absolute determination value of conversion which showed a pattern similar to SMA [35] in addition of the expected aromatic protons for thiazole of residual 2-aminothiazole as illustrated in Fig. 1.

Moreover, the conversion of maleic anhydride moiety in SMA to maleimide was monitored by FT-IR spectrometer. Fig. 2 shows that after the reaction of SMA with 2-aminothiazole, a new imide band appears at 1724 cm^{-1} and no band is observed at 3300–3500 cm^{-1} expected for amino groups. Therefore it seems that the imidization of SMA was completed and no residual 2-aminothiazole was observed in the resulting SMI. The range of 1600–1500 cm^{-1} is

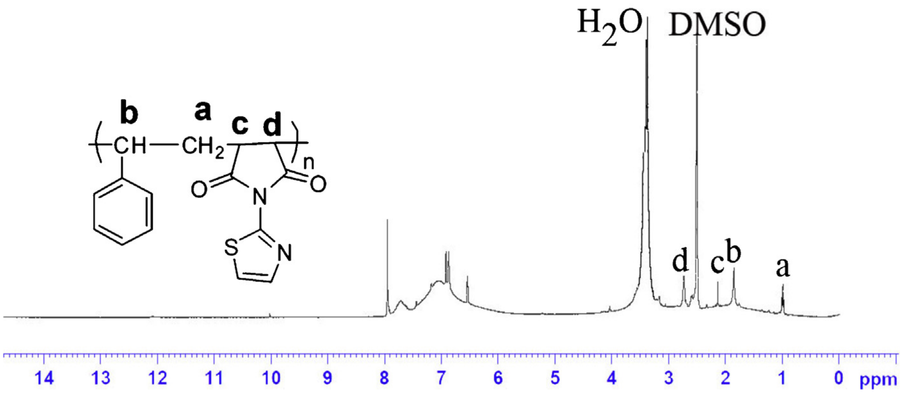
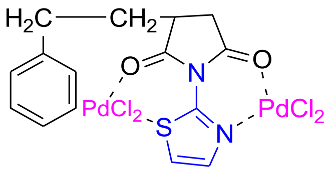


Fig. 1. ^{1}H NMR spectrum of SMI.



Scheme 4. A simple model for polymer-supported palladium catalyst.

attributed to the υ(C=C), υ(C=N), and υ(C=S) stretch of aromatic rings. In the polymer-supported palladium complexes, υ(C=C), υ(C=N), and υ(C=S) show a slight positive shift, indicating the palladium is chelated with both nitrogen and sulfur atoms of heterocyclic ring. Therefore, the polymer support can act as a multidentate chelate resulting in the increase of the amount of palladium in the structure of catalyst. High calculated palladium content from ICP-AES analysis, 9.94% w/w, can justify this prediction and viewpoint.

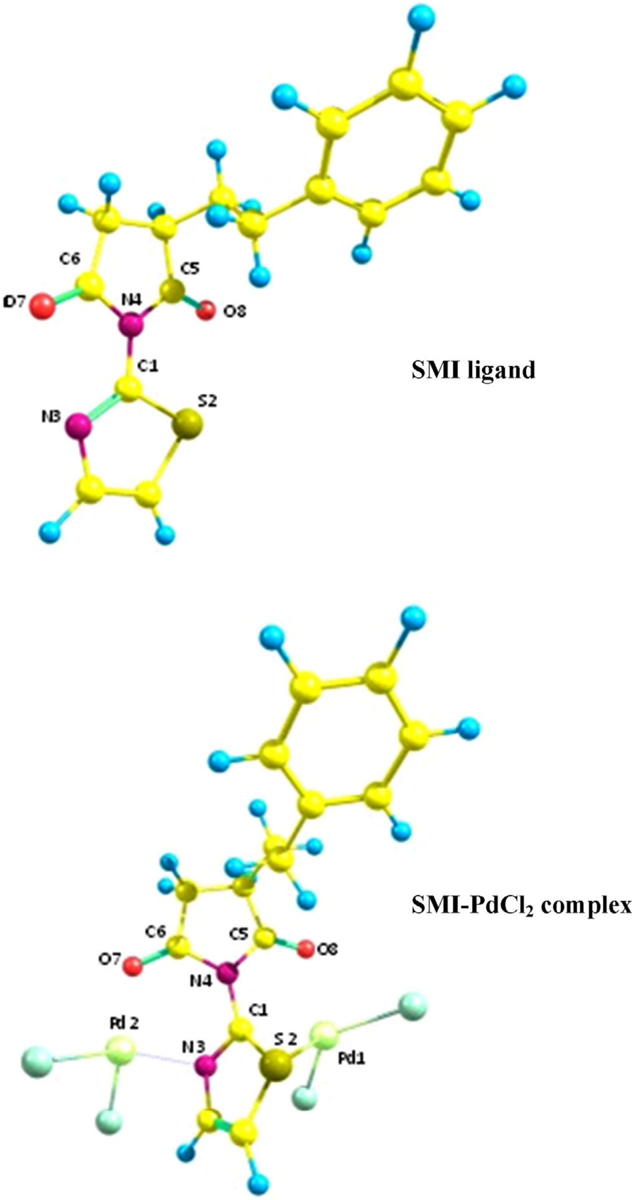


Fig. 3. Atomic numbering and energy-minimized structures obtained at M06/6-31G* level of theory for SMI ligand **3** and SMI–PdCl$_2$ complex **4**.

Table 1
The calculated values of some selected bond orders in SMI ligand **3** and SMI–PdCl$_2$ complex **4** obtained at M06/631G* level of theory. Note that the numbering of atoms for ligand and complex is in accordance with Fig. 1.

Bonded atoms	SMI ligand	SMI–PdCl$_2$ complex
C6—O7	1.792	1.683
C5—O8	1.924	1.657
N4—C6	0.980	0.997
N4—C5	0.912	0.985
C1—N3	1.567	1.513
C1—S2	1.120	0.987
C1—N4	0.902	0.932
Pd1—S2	–	0.553
Pd1—O7	–	0.136
Pd2—N3	–	0.251
Pd2—O8	–	0.240

Recently, we used computational study to confirm successfully the regio-selectivity of Sonogashira reaction [41]. Armed with this experience, we focused on obtaining a quantitative description for metal–ligand interactions in the aforementioned polymer-supported palladium complex by performing theoretical calculations using density functional theory techniques [42,43]. In this respect, we have employed an effective model for SMI ligand **3** and palladium–SMI complex **4** (as was illustrated in Scheme 4) considering that this model has a reliable comprise between accuracy and time saving efficiency of computational procedure. Thus, we have first determined the optimized structure of compounds **3** and **4** via DFT calculations at M06/6-31G* level of theory [44]. It should be mentioned that M06 functional has been introduced recently as a hybrid meta-GGA (generalized gradient approximation) exchange-correlation functional that was parametrized including both transition metals and nonmetals and was recommended for being applied in organometallic and inorganometallic thermochemistry, kinetic studies and noncovalent interactions. In the case of palladium, the effective core potential (ECP), LANL2TZ(f), was used together with the accompanying basis set to describe the valence electron density [45]. The stationary points were characterized as minima after verifying the presence of all real frequencies. All DFT computations have been performed using GAMESS suite of programs [46]. In Fig. 3 the theoretical optimized structures of compounds **3** and **4** obtained at M06/6-31G* level in the gas phase together with the atomic numbering, were presented.

We have also evaluated comparatively the bond order of some selected key bonds in SMI ligand **3** with its correspondent palladium complex **4** to characterize the variation of bond orders via complexation. In Table 1, the calculated bond orders of some selected chemical bonds in the coordination sphere have been listed. As we expected, and the results in Table 1 show that the bond order of carbonyl groups and also C=N and C=S bonds of aminothiazole ring shifted toward lower values due to the donation of shared electrons from these chemical bond to palladium through the complexation which is in agreement with our FT-IR spectroscopic observations.

In the next step, we concentrated on topological study of electron density via Quantum Theory of Atoms in Molecule (QTAIM) [47] to interpret the nature of metal–ligand interactions in SMI–PdCl$_2$ complex **4**. In this respect, we focused on the QTAIM analysis of M06/6-31G* calculated wave function of electron density using AIM2000 program package [48]. In Table 2, we have listed QTAIM calculated values of electron density, ρ_b, its Laplacian, $\nabla^2\rho_b$, electronic kinetic energy density, G_b, electronic potential energy density, V_b, total electronic energy density, H_b and $|V_b|/G_b$ ratio at some selected bond critical points (BCPs) for SMI ligand **3** and SMI–PdCl$_2$ complex **4**. It is important to state that the electron density at BCPs usually correlates with the strength of the bond between two atoms. Values of $\rho_b < 0.1$ au are indicative of a

Table 2
Mathematical properties of some selected BCPs in SMI ligand **3** and SMI–PdCl$_2$ complex **4**. The properties have been obtained via QTAIM analysis on the M06/6-31G* calculated wave function of electron density. All values in the parenthesis are corresponded to the BCPs of SMI ligand. Note that numbering of atoms is in accordance with Fig. 1.

Bonded atoms of BCPs	ρ_b	$\nabla^2\rho_b$	G_b	V_b	H_b	$\lvert V_b\rvert/G_b$
C1—S2	0.193 (0.197)	−0.337 (−0.342)	0.060 (0.067)	−0.205 (−0.219)	−0.145 (−0.152)	3.416 (3.268)
C1—N3	0.357 (0.372)	−0.622 (−1.031)	0.444 (0.364)	−1.044 (−0.986)	−0.600 (−0.622)	2.357 (2.708)
C1—N4	0.293 (0.290)	−0.787 (−0.871)	0.231 (0.188)	−0.659 (−0.595)	−0.428 (−0.407)	2.852 (3.164)
N4—C5	0.296 (0.278)	−0.906 (−0.799)	0.170 (0.156)	−0.567 (−0.513)	−0.397 (−0.357)	3.335 (3.288)
N4—C6	0.274 (0.298)	−0.777 (−0.913)	0.146 (0.192)	−0.487 (−0.612)	−0.341 (−0.420)	3.335 (3.187)
C5—O8	0.400 (0.422)	0.239 (0.269)	0.730 (0.789)	−1.400 (−1.510)	−0.670 (−0.721)	1.917 (1.913)
C6—O7	0.417 (0.431)	0.262 (0.160)	0.777 (0.740)	−1.489 (−1.441)	−0.712 (−0.701)	1.916 (1.947)
Pd1—S2	0.090	0.204	0.070	−0.090	−0.020	1.285
Pd1—O7	0.026	0.106	0.023	−0.019	0.004	0.826
Pd2—N3	0.096	0.364	0.119	−0.147	−0.028	1.235
Pd2—O8	0.036	0.355	0.090	−0.092	−0.002	1.022

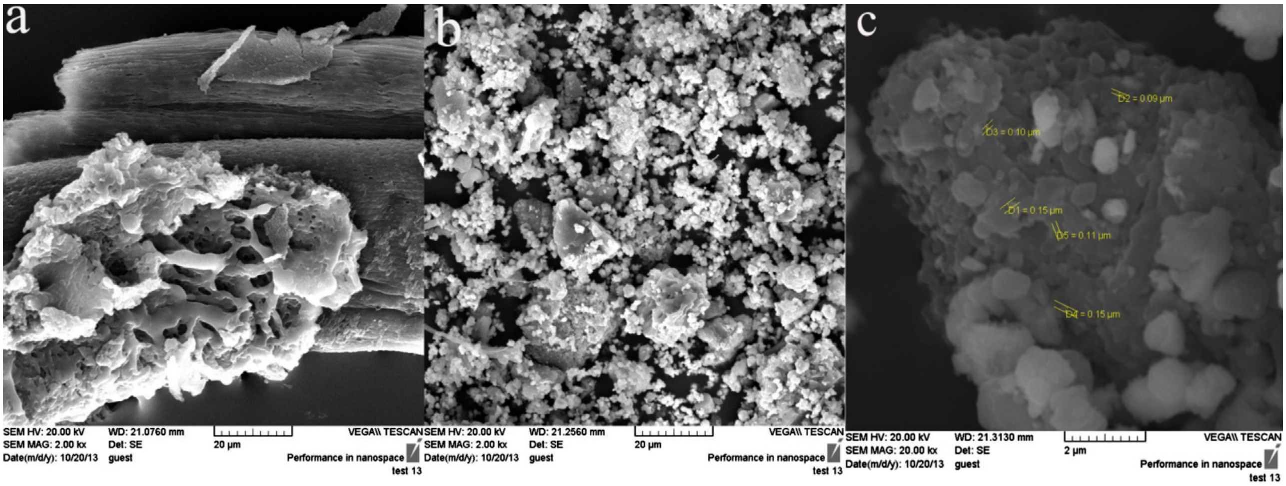


Fig. 4. SEM image of SMI support (a) and SMI–PdCl$_2$ (b and c).

closed-shell (i.e. predominantly electrostatic) interaction [49]; it is usually accompanied by a relatively small and positive value of $\nabla^2\rho_b$ [50]. By contrast, for a shared (i.e. predominantly covalent) interaction, ρ_b is usually >0.1 au [38] and $\nabla^2\rho_b$ is usually negative [51] and typically of the same order as ρ_b. Furthermore, a good reliable indicator for classifying interatomic interactions is the total electronic energy density, that is defined as $H_b = G_b + V_b$ at BCPs. In the closed-shell interactions, H_b has the positive value (viz., G_b is dominating) and for shared interactions, it is negative (viz., V_b is dominating).

According to the reported results of Table 2, the following facts can be discussed: (i) decrease in the calculated values of ρ_b at C═O, C═N and C—S BCPs via complexation, confirms the donation of shared electrons to the metal center and is in agreement with diminution in the stretching frequency of IR spectrum; (ii) the large values of electron density together with the negative values of $\nabla^2\rho_b$ and H_b approve the covalent character of C═O, C═N and C—S chemical bonds in SMI ligand **3** and Pd complex **4** and (iii) the small values of electron density with the positive values of $\nabla^2\rho_b$ and H_b at Pd1—S2, Pd1—O7, Pd2—N3 and Pd2—O8 BCPs disclose that the metal–ligand interactions comprise no covalent character. Moreover, the corresponding $1 < |V_b|/G_b < 2$ values confirms the presence of partially covalent-electrostatic interactions at these Pd1—S2, Pd1—O7, Pd2—N3 and Pd2—O8 BCPs.

The scanning electron micrographs (Fig. 4) of the polymer supported ligand and supported Pd-catalyst clearly showed the morphological change which occurred on the surface of SMI after being loaded with palladium. As vividly observed in Fig. 4, the polymer supported ligand have different size and roughness and the presence of Pd has caused obvious changes, in the polymer particle size and roughness of the surface. Energy dispersive spectroscopy analysis of X-rays (EDAX) data for the Pd-catalyst is given in Fig. 5. The EDAX data also proved the attachment of Pd on the surface of the polymer matrix.

3.2. Optimization of the reaction conditions

3.2.1. Suzuki coupling reaction

To examine the potency of the Pd-supported catalyst, it was used in the Suzuki coupling reaction between various aryl halides (**6a–j**) and phenylboronic acid **5**. The effects of base, solvent and reaction temperature were screened to optimize reaction conditions for coupling of iodobenzene (1 mmol) and phenylboronic acid (1.5 mmol) as the model reaction (Table 3). In the Suzuki–Miyaura coupling reaction, choice of solvent has a crucial role in the rate

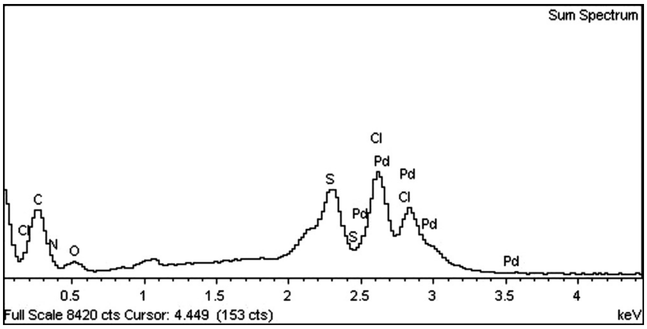


Fig. 5. EDAX data of SMI–PdCl$_2$.

Table 3
Screening reaction conditions of iodobenzene with phenylboronic acid under Suzuki protocol.[a]

Entry	Solvent	Temperature (°C)	Base	Cat. (g)	Time (h)	Yield[b] (%)
1	$MeOH/H_2O$ (3:1 v/v)	RT	K_2CO_3	0.02	3	98
2	H_2O	RT	K_2CO_3	0.02	4	90
3	CH_3OH	RT	K_2CO_3	0.02	4	89
6	CH_3CN	RT	K_2CO_3	0.02	5	89
7	1,4-Dioxane	RT	K_2CO_3	0.02	5	50
8	H_2O	50	K_2CO_3	0.02	3	96
9	H_2O	Reflux	K_2CO_3	0.02	2	97
10	H_2O	Reflux	K_2CO_3	0.01	4	93
11	H_2O	Reflux	–	0.02	2	5
12	H_2O	Reflux	Na_3PO_4	0.02	5	65
13	H_2O	Reflux	NaOAc	0.02	5	55
14	H_2O	Reflux	NaOH	0.02	5	50
15	H_2O	Reflux	pyridine	0.02	5	41
16	H_2O	Reflux	NEt_3	0.02	5	39
17	H_2O	Reflux	K_2CO_3	0.02 g of $PdCl_2$	5	4

[a] Iodobenzene (1 mmol) with phenylboronic acid (1.5 mmol), and base (5 mmol).
[b] Refers to the isolated yield.

and the product distribution. It has already been found that water profoundly increases the activity of the Suzuki–Miyaura catalyst [52,53]. Thus, we used, H_2O or $MeOH/H_2O$ (3:1, v/v), as green and relatively green solvents respectively. Although, the experimental results showed that in the cases that $MeOH/H_2O$ (3:1 v/v) system used as a solvent the time of the reaction for completion is shorter (Table 3, Entry 1), we chose neat H_2O as solvent (Table 3, Entries 8–16). Water as an inexpensive, eco-friendly, green, readily available, non-inflammable, and non-toxic solvent provides remarkable advantages over common organic solvents both from economic and environmental aspects and point of views [36,54,55] and is currently considered as one of the most suitable targets of sustainable chemistry [54]. In addition, using water as solvent not only minimized the homo-coupled product of phenylboronic acid, but also providing the facile separation of the desired product from homo-coupled product due to their different solubility, in water [52,53]. In addition, using of 0.02 g of catalyst at reflux conditions were found to be the optimal conditions (Table 3, Entries 8–10). As we expected, in the absence of any base, the reaction has a negligible progress (Table 3, Entry 11). For selection of the appropriate base, the effect of bases such as K_2CO_3, Na_3PO_4, NaOAc, NaOH, pyridine and NEt_3 was examined on the aforementioned coupling reaction. As a result, we found that the inorganic bases used were more effective than organic bases tested. K_2CO_3 as an easily available and inexpensive chemical was selected as a base of choice (Table 3, Entries 12–16). In order to discriminate the effect of the polymer supported catalyst (SMI–$PdCl_2$), the reaction was performed over palladium chloride in the same reaction conditions and in this case, a significant lower activity was observed (Table 3, Entry 17). Therefore, coupling reactions of aryl halides (1 mmol) with phenylboronic acid (1.5 mmol) in the presence of K_2CO_3 (5 mmol), and 0.02 g of the catalyst in water under reflux conditions were carried out to obtain comparatively better results.

These optimized reaction conditions were applied (Table 4) in the Suzuki cross-coupling reaction of various aryl halides and phenylboronic acid with 0.02 g of SMI–$PdCl_2$ (Pd/aryl halide molar ratio: 0.018). We examined the electronic and steric effects of various aryl halides bearing electron-donating and electron-withdrawing groups, focusing on the yields and the time required for conversion. According to the results presented in Table 4, aryl iodides and bromides with electron-donating and electron-withdrawing groups (Entries 1–9) both afforded excellent yields of coupling products in reasonable times. However, the coupling of 2-iodotoluene and 2-iodo-5-nitrotoluene with phenylboronic acid resulted in moderate yields (72 and 65% yield respectively) which may be attributed to the steric effect of 2-iodotoluene and 2-iodo-5-nitrotoluene.

It is absolutely clear that the reactivity of aryl chlorides was lower than aryl iodides and bromides in the Suzuki coupling reactions [36,56]. Aryl chlorides required longer reaction times and affording lower yields (Table 4, Entry 10).

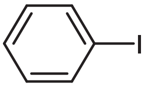
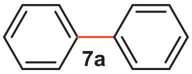
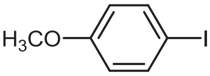
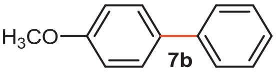
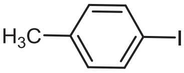
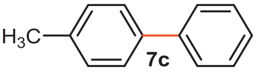
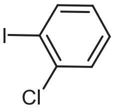
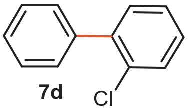
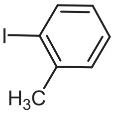
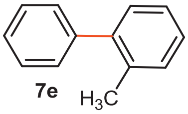
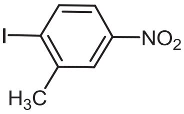
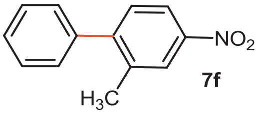
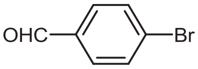
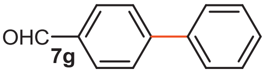
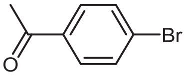
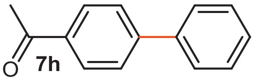
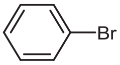
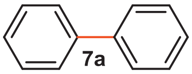
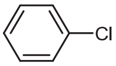
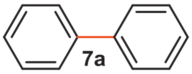
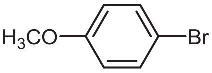
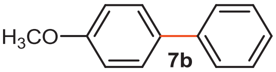
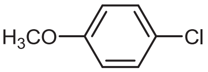
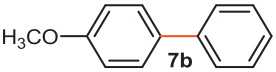
The turn-over frequency (TOF) value defined as the mol product/(mol catalyst. hour); was calculated from the isolated yield of product, the amount of palladium used and the reaction time. In all reactions, TOF parameter was determined and suggested that SMI–$PdCl_2$ as a good catalyst for this kind of reaction (Table 4).

3.2.2. *Sonogashira coupling reaction*

The solvent and copper-free Sonogashira coupling reaction was also examined in order to evaluate the catalyst efficiency. The optimized conditions for the coupling between iodobenzene and phenylacetylene as the model reaction are shown in Table 5. From of the bases examined, pyridine gave the best results: 98% GC yield of the corresponding coupled product **9a** (Table 5, Entry 4). It was observed that using inorganic bases such as Na_3PO_4, NaOAc, KOH, and K_2CO_3, and also low palladium concentration, decreases the yield of the product **9a** (Entries 6–10). As it was mentioned from the experimental section, the products were purified trough the column chromatography using $CHCl_3$–CH_3OH (97:3) as eluent. The application of hexane or hexane/ethyl acetate as eluent which is usually used in the purification of the Suzuki coupling products is not worthy since these eluent are not able to separate the by-products of this reaction, 1,3-diyne derivatives usually obtained from the hemo-coupling of terminal alkynes.

This optimized condition were applied for the copper- and solvent-free Sonogashira coupling of different alkynes (**8a** and **8b**) with various aryl halides (**6a–j**) containing electron-withdrawing or donating substituents in the presence of SMI–$PdCl_2$ as a catalyst. As illustrated in Table 6, the electron-neutral, electron-rich or electron-poor aryl iodides reacted with phenylacetylene under the optimized reaction conditions and generate the corresponding cross-coupling products in high yields (Table 6, Entries 1–7). The Sonogashira coupling of the less reactive terminal acetylene such as propargyl alcohol with different aryl iodides provided the corresponding products in high yields (Entries 8 and 9). As expected, the coupling of various aryl bromides with terminal alkynes produced the desired coupling product but in lower yield in comparison with their corresponding aryl iodides (Entries 10 and 11). The yields of coupling product **9a** of the aryl chloride under similar copper-free conditions were also much lower than their iodo and bromo counterparts (Entry 12).

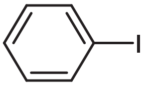
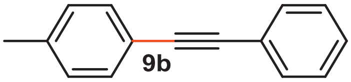
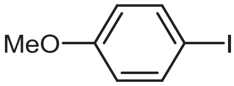
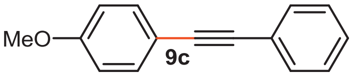
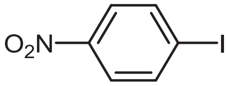
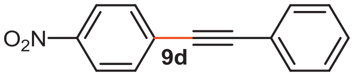
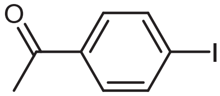
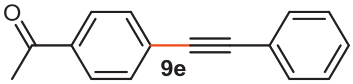
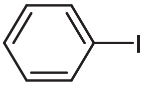
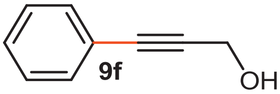
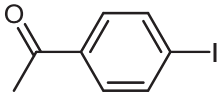
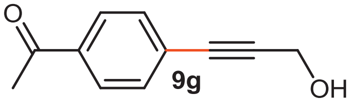
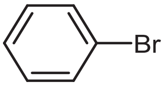
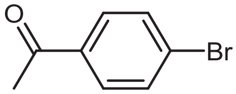
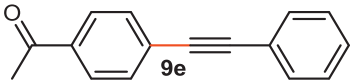
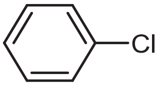
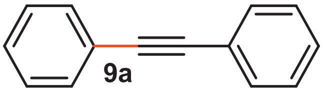
Table 4
Suzuki reaction of various aryl halides with phenylboronic acid.[a]

Entry	Substrate	Product	Yield[b] (%)	Time (h)	TOF (h^{-1})[c]	Mp (°C)/Lit. Mp [ref]
1		 **7a**	97	2	26.94	69–71/70–72 [38]
2		 **7b**	92	3	17.04	90–92/91–92 [38]
3		 **7c**	90	3	16.67	49–53/45–50 [38]
4		 **7d**	90	3	16.67	30–34/32.5–33.5 [38]
5		 **7e**	72	7	5.71	Colorless oil/colorless oil [38]
6		 **7f**	65	8	4.72	52–55/55–56 [39]
7		 **7g**	93	2	25.83	54–56/57–59 [38]
8		 **7h**	92	2	25.55	117–120/120–122 [38]
9		 **7a**	95	3	17.59	71–74/70–72 [38]
10		 **7a**	90	4	12.49	73–75/70–72 [38]
11		 **7b**	67	5	7.44	91–93/91–92 [38]
12		 **7b**	29	8	2.01	90–93/91–92 [38]

[a] Aryl halides (1 mmol) with phenylboronic acid (1.5 mmol), K_2CO_3 (5 mmol), and 0.02 g of catalyst in water under reflux.
[b] Refers to the isolated yield.
[c] Turn-over frequency.

It is also remarkable to note that resin did not suffer from extensive mechanical degradation after few times of running. For an ideal heterogeneous catalyst, supported catalyst should not leach to the reaction mixture and the recyclability of the supported catalyst is highly important. For investigation of these properties in our new synthesized catalyst, as illustrated in Fig. 6, the reusability of the catalyst in reactions of iodobenzene with phenylboronic acid (Suzuki reaction), and iodobenzene with phenylacetylene (Sonogashira reaction) as representative reactions in the presence of 0.02 g of SMI–$PdCl_2$ was examined. After the first run, the catalyst was separated by filtration, washed with acetone three times, and dried under reduced pressured at 70 °C for 3 h and stored for another consecutive reaction run. This dried catalyst was reused for another fresh reaction mixture without any further activation. The obtained results emphasized that the catalyst could be recovered and was reused up to at least 5 runs without any significant loss of activity. It is worthwhile to mention that, no noticeable loss of the weight of the catalyst after its usage in subsequent runs is observed. Afterwards, leaching of Pd from the SMI support into the reaction mixture of the Suzuki reaction was tested, using ICP-AES. The results show that the difference between the palladium content of the fresh catalyst and the reused catalyst, in 5th run, was

Table 6
Sonogashira reaction of various aryl halides and terminal acetylene.[a]

Entry	Substrate	Product	Yield[b] (%)
1		 **9a**	98 (93)
2		 **9b**	97
3		 **9c**	96
6		 **9d**	95
7		 **9e**	92
8		 **9f**	95
9		 **9g**	93 (87)
10		 **9a**	80
11		 **9e**	84
12		 **9a**	54

[a] Aryl halides (1 mmol) with phenylacetylene or propargyl alcohol (1 mmol), pyridine (1 mmol), and 0.02 g of catalyst. at r.t. in 3 h.
[b] Refers to GC yield, isolated yields are given in parentheses.

Table 5
Screening reaction conditions for the Sonogashira reaction of iodobenzene and phenylacetylene.[a]

Entry	Base	Cat. (g)	Yield[b] (%)
1	Et_3N	0.02	80
2	Et_2NH	0.02	65
3	Butylamine	0.02	45
4	Pyridine	0.02	98
5	Piperidine	0.02	74
6	Na_3PO_4	0.02	50
7	NaOAc	0.02	52
8	K_2CO_3	0.02	54
9	KOH	0.02	47
10	Pyridine	0.01	65

[a] Iodobenzene (1 mmol) with phenylacetylene (1 mmol), pyridine (1 mmol), and 0.02 g of cat. at r.t. in 3 h.
[b] Refers to GC yield.

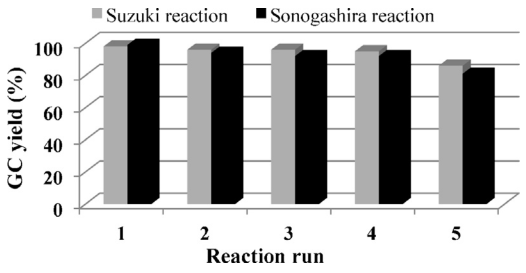


Fig. 6. The recyclability of the SMI–$PdCl_2$ in the preparation of **7a** and **9a**.

only 4.8% which indicated the low leaching amount of Pd catalyst into the reaction mixture.

4. Conclusions

In conclusion, we have synthesized a novel polymer-supported palladium complex being efficiently applicable to the Suzuki and Sonogashira reaction, as a clean and green catalyst. The catalyst exhibited not only high activity, but also afforded a diverse range of coupling products in good to excellent yields. In addition, the catalyst which is stable in the reaction conditions can be used with no pre-activation and can also be recycled for at least five consecutive cycles without an appreciable loss of activity. These benefits make this supported palladium catalyst as an interesting and useful alternative to other Pd heterogeneous catalytic systems and recommended, being tried in other Pd-catalyzed reactions.

Acknowledgements

M.M.H. is thankful to Alzahra University Research Council for partial receiving of his grant upon this publication.

References

[1] K.C. Nicolaou, P.G. Bulger, D. Sarlah, Angew. Chem. Int. Ed. 44 (2005) 4442–4489.
[2] N. Miyaura, K. Yamada, A. Suzuki, Tetrahedron Lett. 20 (1979) 3437–3440.
[3] K. Sonogashira, Y. Tohda, N. Hagihara, Tetrahedron Lett. 16 (1975) 4467–4470.
[4] R. Jana, T.P. Pathak, M.S. Sigman, Chem. Rev. 111 (2011) 1417–1492.
[5] A.F. Littke, G.C. Fu, Angew. Chem. Int. Ed. 37 (1998) 3387–3388.
[6] S.A. Patel, K.N. Patel, S. Sinha, B.V. Kamath, A.V. Bedekar, J. Mol. Catal. A: Chem. 332 (2010) 70–75.
[7] S.M. Islam, N. Salam, P. Mondal, A.S. Roy, J. Mol. Catal. A: Chem. 366 (2013) 321–332.
[8] R. Chinchilla, D.J. Dodsworth, C. Nàjera, J.M. Soriano, Tetrahedron Lett. 42 (2001) 4487–4489.
[9] R. Chinchilla, D.J. Dodsworth, C. Nàjera, J.M. Soriano, Tetrahedron Lett. 42 (2001) 7579–7581.
[10] R. Chinchilla, D.J. Dodsworth, C. Nàjera, J.M. Soriano, Bioorg. Med. Chem. Lett. 12 (2002) 1817–1820.
[11] R. Chinchilla, D.J. Dodsworth, C. Nàjera, J.M. Soriano, Synlett (2003) 809.
[12] R. Chinchilla, D.J. Dodsworth, C. Nàjera, J.M. Soriano, Tetrahedron Lett. 44 (2002) 463–466.
[13] R. Chinchilla, D.J. Dodsworth, C. Nàjera, J.M. Soriano, M. Yus, ARKIVOC (2003) 41–47.
[14] J. Gil-Molto, S. Karlstrom, C. Nàjera, Tetrahedron 61 (2005) 12168–12176.
[15] M.M. Heravi, A. Keivanloo, M. Rahimizadeh, M. Bakavoli, M. Ghassemzadeh, Tetrahedron Lett. 45 (2004) 5747–5749.
[16] M.M. Heravi, E. Hashemi, Tetrahedron 68 (2012) 9145–9178.
[17] M.M. Heravi, E. Hashemi, Monatsh. Chem. 143 (2012) 861–880.
[18] M.M. Heravi, E. Hashemi, F. Azimian, Tetrahedron 70 (2014) 7–21.
[19] M.M. Heravi, E. Hashemi, N. Ghobadi, Curr. Org. Chem. 17 (2013) 2192–2224.
[20] M.M. Heravi, E. Hashemi, N. Nazari, Mol. Divers. 18 (2014) 441–472.
[21] M.M. Heravi, S. Sadjadi, Tetrahedron 65 (2009) 7761–7775.
[22] M.M. Heravi, A. Fazeli, Heterocycles 81 (2010) 1979–2026.
[23] M.M. Heravi, A. Kivanloo, M. Rahimzadeh, M. Bakavoli, M. Ghassemzadeh, B. Neumuller, Tetrahedron Lett. 46 (2005) 1607–1610.
[24] J.M. Nuss, B.H. Levine, R.A. Rennels, M.M. Heravi, Tetrahedron Lett. 32 (1991) 5243–5246.
[25] M.M. Heravi, K. Bakhtiari, Z. Daroogheha, F.F. Bamoharram, J. Mol. Catal. A: Chem. 273 (2007) 99–101.
[26] M.M. Heravi, M. Tajbakhsh, A.N. Ahmadi, B. Mohajerani, Monatsh. Chem. 137 (2006) 175–179.
[27] M.M. Heravi, K. Bakhtiari, Z. Daroogheha, F.F. Bamoharram, Catal. Commun. 8 (2007) 1991–1994.
[28] M.M. Heravi, G. Rajabzadeh, F.F. Bamoharram, N. Seifi, J. Mol. Catal. A: Chem. 256 (2006) 238–241.
[29] M.M. Heravi, M. Khorasani, F. Derikvand, H.A. Oskoole, F.F. Bamoharrarm, Catal. Commun. 8 (2007) 1886–1890.
[30] M.M. Heravi, V. Zadsirjan, K. Bakhtiari, H.A. Oskooie, F.F. Bamoharrarm, Catal. Commun. 8 (2007) 315–318.
[31] M.M. Heravi, K. Bakhtiari, V. Zadsirjan, F.F. Bamoharrarm, O. Heravi, Bioorg. Med. Chem. Lett. 17 (2007) 4262–4265.
[32] H.A. Oskooie, M.M. Heravi, K. Bakhtiari, V. Zadsirjan, F.F. Bamoharram, Synlett (2006) 1768–1770.
[33] E. Hashemi, Y.S. Beheshtiha, S. Ahmadi, M.M. Heravi, Transit. Metal. Chem. 39 (2014) 593–601.
[34] M.M. Heravi, E. Hashemi, Y.S. Beheshtiha, K. Kamjou, M. Toolabi, N. Hosseintash, J. Mol. Catal. A: Chem. 392 (2014) 173–180.
[35] S.-S. Lee, T.O. Ahn, J Appl. Polym. Sci. 71 (1999) 1187–1191.
[36] R.J. Kalbasi, M. Kolahdoozan, S. Mozafari-Vanani, J. Solid State Chem. 184 (2011) 2009–2016.
[37] R.J. Kalbasi, M. Kolahdoozan, M. Rezaei, J. Ind. Eng. Chem. 18 (2012) 909–918.
[38] Q. Xu, W.-L. Duan, Z.-Y. Lei, Z.-B. Zhu, M. Shi, Tetrahedron 61 (2005) 11225–11229.
[39] Y. Yu, T. Hu, X. Chen, K. Xu, J. Zhang, J. Huang, Chem. Commun. 47 (2011) 3592–3594.
[40] T. Suzuka, Y. Okada, K. Ooshiro, Y. Uozumi, Tetrahedron 66 (2010) 1064–1069.
[41] T. Hosseinnejad, M.M. Heravi, R. Firouzi, J. Mol. Model. 19 (2013) 951–961.
[42] A.D. Becke, J. Chem. Phys. 98 (1993) 1372–1377.
[43] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785–789.
[44] D.G. Truhlar, Y. Zhao, Theor. Chem. Acc. 120 (2008) 215–241.
[45] L.E. Roy, P.J. Hay, R.L. Martin, J. Chem. Theor. Comput. 4 (2008) 1029–1031.
[46] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347–1363.
[47] R.F.W. Bader, Atoms in Molecules: A Quantum Theory, Oxford University Press, Oxford, UK, 1990.
[48] R.F.W. Bader, AIM2000 Program, ver 2.0, Hamilton, McMaster University, 2000.
[49] R.F.W. Bader, H. Essén, J. Chem. Phys. 80 (1983) 1943–1960.
[50] R.G.A. Bone, R.F.W. Bader, J. Phys. Chem. 100 (1996) 10892–10911.
[51] G.V. Bobrov, G.V. Popova, V.G. Tsirelson, Russ. J. Phys. Chem. 80 (2006) 584–659.
[52] R.B. Bedford, C.S.J. Cazin, S.J. Coles, T. Gelbrich, P.N. Horton, M.E. Hursthouse, M.E. Light, Organometallics 22 (2003) 987–999.
[53] M. Lamblin, L. Nassar-Hardy, J.-C. Hierso, E. Fouquet, F.-X. Felpin, Adv. Synth. Catal. 352 (2010) 33–79.
[54] P. Anastas, L.G. Heine, T.C. Williamson, Green Chemical Syntheses and Processes, American Chemical Society, Washington, DC, 2000.
[55] B. Cornils, W.A. Herrmann, Aqueous-Phase Organometallic Catalysis: Concept and Applications, 2nd and revised edn., Wiley–VCH, Weinheim, Germany, 2004.
[56] A.F. Littke, G.C. Fu, Angew. Chem. 114 (2002) 4350–4386.