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ORIGINAL PAPER

Palladium nanoparticles on amino-modified silica-catalyzed C–C bond formation with carbonyl insertion

Elham Etemadi-Davan[1] · Dariush Khalili[1] · Ali Reza Banazadeh[2] · Ghazal Sadri[1] · Pourya Arshad[1]

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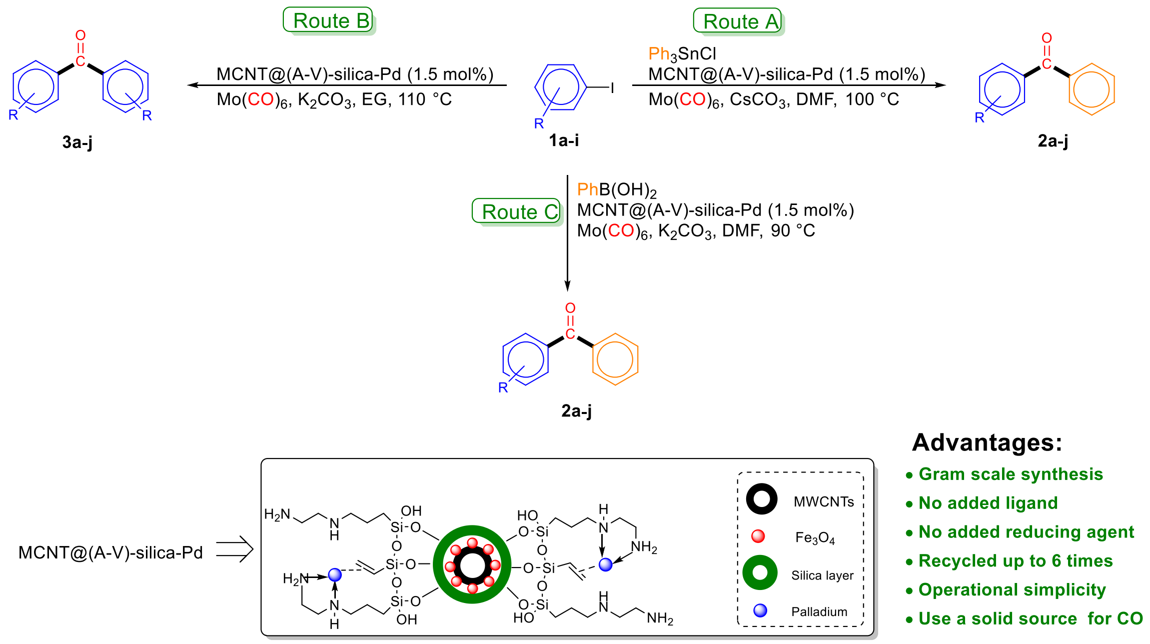
Abstract

A practical and heterogeneously catalyzed Stille, homo-coupling, and Suzuki carbonylation reaction has been reported using Pd nanoparticles supported on amino-vinyl silica-functionalized magnetic carbon nanotube ($CNT@Fe_3O_4@SiO_2$-Pd) for the efficient synthesis of symmetrical and unsymmetrical diaryl ketones from aryl iodides. A wide variety of symmetrical and unsymmetrical diaryl ketones were obtained in high yields under CO gas-free conditions using $Mo(CO)_6$ as an efficient carbonyl source. Considering the atom economy of Ph_3SnCl, less than an equimolar amount can be applied in Stille transformation, which is of great importance due to the toxicity of organotin derivatives. Moreover, no phosphine ligand and external reducing agent were necessary in these coupling carbonylation reactions. This heterogeneous Pd catalyst offers high activity with very low palladium leaching. Finally, the catalyst can be reused and recycled for six steps without loss in activity, exhibiting good example of sustainable methodology.

Graphic abstract



Advantages:

- Gram scale synthesis
- No added ligand
- No added reducing agent
- Recycled up to 6 times
- Operational simplicity
- Use a solid source for CO

Supplementary information The online version of this article (https://doi.org/10.1007/s13738-021-02171-6) contains supplementary material, which is available to authorized users.

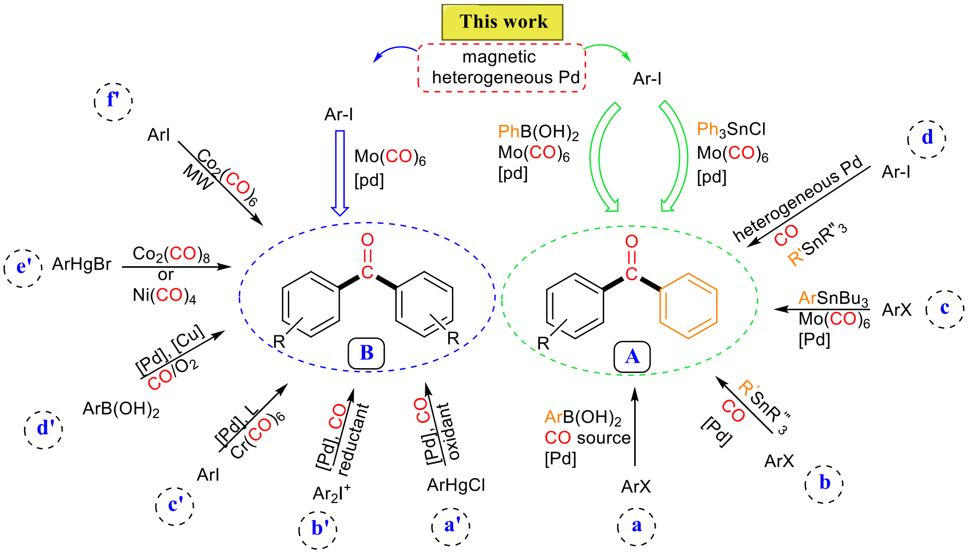
Extended author information available on the last page of the article

Keywords Stille reaction · Homo-coupling carbonylation · Suzuki carbonylation · Diaryl Ketones · Phosphine-free · Heterogeneous catalysis

Introduction

Pd-catalyzed carbonylative cross-coupling reactions are one of the attractive and straightforward routes for the formation of multiple bonds in single step, which excludes the need for multi-step reactions and isolation of the intermediates. Unsymmetrical (A) and symmetrical (B) diaryl ketones as value-added carbonylation products [1–4] are important privileged intermediates present in many biologically active natural products and can be obtained via Suzuki [1, 3, 5, 6] or Stille carbonylation [5, 6] reactions (Scheme 1: a, b). A variety of synthetic methods including Pd-catalyzed reactions have been reported for the synthesis of symmetrical ketones but not much have been reported for the unsymmetrical ones. In this regard, homogeneous [7–10] and heterogeneous [11–14] Pd catalysts were used for carbonylation cross-coupling reactions. The obvious difficult separation of homogeneous catalysts made chemists to develop heterogeneous catalyst, although the former one has high selectivity and give better yields. Magnetic heterogeneous Pd catalysts have attracted much attention owing to the ease of separation by an external magnet [15, 16]. Organotin compounds such as Me_4Sn, Et_4Sn, $^nPr_3RSn$, Bu_4Sn, Bu_3RSn (R: vinyl, allyl, 1-naphthyl, 4-fluorophenyl, 3-pyridyl, phenyl) were applied for the Stille transformation (Scheme 1, c, d) [17, 18]. The drawbacks encountered with the mentioned route were the application of more than stoichiometric amounts of organotin derivatives and gaseous CO (in most of the reactions) albeit only very few protocols were reported in the presence of $Mo(CO)_6$ [19, 20]. Due to the toxicity and difficulties in handling and running experiments in laboratory with gaseous CO, applying other alternatives such as metal carbonyls is desirable.

Besides, the chemistry of symmetrical diaryl ketones via carbonylation is still underdeveloped. Performing this reaction has been described with R-M [21, 22] (ArHgCl, Ar_4Sn) and R-X [23, 24] (Ar_2I^+: diaryliodonium) in the presence of Pd catalyst and gaseous CO in which oxidative and reductive conditions were required, respectively (Scheme 1: a′, b′). Utilizing reducing and oxidative reagents under harsh conditions for the preparation of the starting materials is the obstacle that renders these reactions more practical. Recently, the Pd/heterogeneous P(III) catalytic system and $Cr(CO)_6$ as a solid metal carbonyl source were employed to construct symmetrical diaryl ketone from aryl iodides (Scheme 1: c′) [25–28]. Another methodology for the preparation of diaryl ketones is palladium-catalyzed oxidative carbonylation of nontoxic boronic acid derivatives (Scheme 1: d′) [29]. Moreover, non-catalytic systems in the presence of unstable $Co_2(CO)_8$ and highly toxic $Ni(CO)_4$ were also used, which suffers from the production of toxic side products (Scheme 1, e′) [30, 31]. Additionally, ultrafast carbonylation of aryl iodides using $Co_2(CO)_8$ under microwave irradiation was also reported (Scheme 1, f′) [32]. From the perspective of isolation challenges, the ideal solution to overcome this issue is to immobilize the homogeneous Pd catalyst onto various solid supports [11–14]. In this regard, carbon nanotubes (CNTs) due to their large specific surface area, porous structure, strong adsorption capacity, and high chemical and mechanical stability have been of great research interest as a promising Pd support [33, 34]. However, the tendency of the nanocatalysts to aggregate reduces the available surface area, which might limit using of CNTs in the organic



Scheme 1 Different approaches for the synthesis of unsymmetrical and symmetrical ketones

synthesis [35]. To conquer this issue, magnetic nanoparticles coated with silica have been used to improve the chemical stability of the magnetite nanoparticles by shielding the magnetic dipole interaction

with the silica shell [36, 37]. In continuation of our previous work [38], we herein use our previously synthesized heterogeneous Pd catalyst (CNT@Fe_3O_4@SiO_2-Pd) for phosphine and ligand-free Stille, homo-coupling, and Suzuki carbonylation of aryl iodides in the presence of magnetic Pd catalyst with $Mo(CO)_6$ as a solid source of carbon monoxide. Sol–gel monomers containing amine functional groups are known to coordinate more strongly with Pd ions to stabilize the metal NPs in the silica matrix [39, 40]. Nevertheless, external chemical reducing agents or reduction condition is required to have more efficient metal ions reduction. Recent reports in the literature affirm the potential application of vinyl groups in the silica matrix to facilitate the reduction of Pd ions and stabilize Pd in its zero oxidation state [41–44]. Hence, using a vinyl group in the structure of the catalyst offers the best option to decrease the need for an external reducing agent. The present catalytic system exhibited remarkable activity in carbonylation reactions and can be easily recycled. The reactions proceeded smoothly without any external reducing agent and phosphine ligands, yielding a variety of symmetrical and unsymmetrical ketones in good-to-high yields.

Experimental

General procedure for carbonylative Stille coupling of aryl iodides with $Mo(CO)_6$ using MCNTs@(A-V)-silica-Pd catalyst

MCNTs@(A-V)-silica-Pd (1.5% mol%) was added to a mixture of aryl iodide (1 mmol), $Mo(CO)_6$ (1 mmol), Cs_2CO_3 (1.5 mmol), Ph_3SnCl (0.4 mmol) in DMF (3 mL) in a flask, and the reaction was stirred at 100 °C for an appropriate time under atmospheric pressure. Then, the reaction was cooled down to room temperature followed by separation of the catalyst by an external magnet. The mixture was washed with 10 mL water, and the crude product was isolated using EtOAc (3 × 10 mL). The organic phases were combined and dried over Na_2SO_4, evaporated, and purified by column chromatography on silica gel (n-hexane/EtOAc) to deliver the desired ketone in high yields.

General procedure for carbonylative homo-coupling of aryl iodides with $Mo(CO)_6$ using MCNTs@(A-V)-silica-Pd catalyst

Aryl iodide (2 mmol) was added to a flask containing a stirring mixture of MCNTs@(A-V)-silica-Pd catalyst (1.5 mol %), K_2CO_3 (2.5 mmol), $Mo(CO)_6$ (1 mmol), and EG (3 mL) at 110 °C. After the completion of the reaction, an external magnet was used to separate the catalyst from the cooled reaction mixture. Then, 10 mL of H_2O was added followed by extraction using EtOAc (3 × 10 mL). The combined organic phases were dried over Na_2SO_4. Filtration of the crude mixture followed by evaporation of the solvent and column chromatography on silica gel (*n*-hexane/EtOAc) afforded the desired symmetrical diaryl ketones in high yields.

Results and discussion

Several research groups have demonstrated the efficient routes for the synthesis of deposited Pd NPs on organically modified silica [43, 44]; however, the main disadvantage was the low surface area of the catalysts. Taking into account other groups research, our recent paper on Fe_3O_4@(A-V)-silica-Pd MNPs synthesis, and also the properties of carbon nanotubes (CNTs) as a suitable Pd support due to its large surface area and high chemical and mechanical stability, we decided to focus our efforts on studying the potential application of CNT@Fe_3O_4@(A-V)-silica-Pd MNPs in carbonylative coupling reactions. Initially, CNTs were functionalized with carboxyl groups under microwave irradiation, which differs from traditional purification methods in taking less time, the possibility of high sample throughput, and finally having control over amenable pressure and temperature [45, 46]. The functionalized CNTs were magnetized by the addition of an alkaline solution of Fe^{2+} and Fe^{3+}, which subsequently coated with uniform silica shell over applying tetraethyl orthosilicate (TEOS).

Then, the silica layer was functionalized by adding a mixture of vinyltriethoxysilane (VTEOS) and [3-(2-aminoethylamino)propyl] trimethoxysilane (AEAPS) [47, 48]. At this point, Pd precursor (10 ml of 5 mM $PdCl_2$ in 1 mM H_2SO_4) was added to deliver Pd NPs on functionalized silica shell over MCNTs without the need for any external reducing agent for reduction of Pd(II) to Pd(0) due to the capability of the amino-vinyl-functionalized silica for the reduction step [41, 42] (Scheme 2). The catalyst was completely characterized by TEM, XRD, VSM, FTIR, and TGA analysis (Supporting section).

Performance of MCNTs@(A-V)-silica-Pd in the Stille carbonylation of aryl iodides

Having synthesized and fully characterized the catalyst, we wish to explore the Stille carbonylation of aryl iodides. We initiated our research using 4-iodotoluene, Ph_3SnCl, [Pd], $Cr(CO)_6$, and K_2CO_3 in DMF at 100 °C. Fortunately, the reaction provides 4-methylbenzophenone (**2a**) in 42% yield (Table 1, entry 1). A variety of bases

Scheme 2 Synthesis of CNT@Fe_3O_4@(A-V)-silica-Pd MNPs

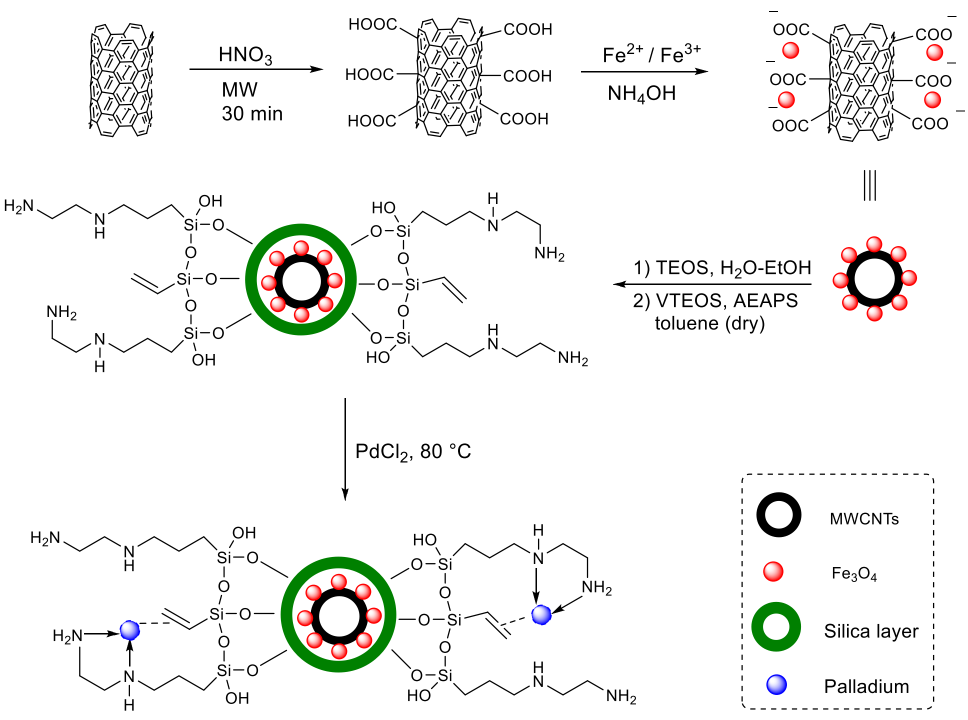
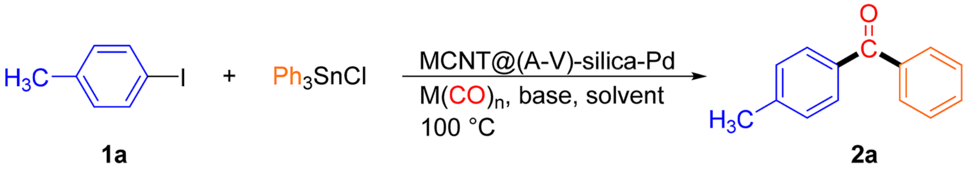


Table 1 Optimization parameters for the reaction of 4-iodotoluene with Ph_3SnCl



Entry	Solvent	Base	Metal carbonyl	Time (h)	**2a** %[a]
1	DMF	K_2CO_3	$Cr(CO)_6$	24	42
2	DMF	Et_3N	$Cr(CO)_6$	24	11
3	DMF	KOAc	$Cr(CO)_6$	24	19
4	DMF	Cs_2CO_3	$Cr(CO)_6$	24	68
5	DMF	NaOH	$Cr(CO)_6$	24	15
6[b]	DMF	Cs_2CO_3	$Cr(CO)_6$	24	68
7[c]	**DMF**	**Cs_2CO_3**	**$Mo(CO)_6$**	**4.5**	**92**
8	DMF	Cs_2CO_3	$W(CO)_6$	4.5	26
9	DMF	Cs_2CO_3	$Co_2(CO)_8$	4.5	37
10[d]	DMF	Cs_2CO_3	$Mo(CO)_6$	4.5	80
11[e]	DMF	Cs_2CO_3	$Mo(CO)_6$	4.5	76
12	Toluene	Cs_2CO_3	$Mo(CO)_6$	4.5	0
13	PEG 400	Cs_2CO_3	$Mo(CO)_6$	4.5	13
14	EG	Cs_2CO_3	$Mo(CO)_6$	4.5	0

Reaction conditions: 4-iodotoluene (1 mmol), Ph_3SnCl (0.4 mmol), metal carbonyl (1 mmol), base (1.2 mmol), [Pd] (1.5 mol %), and solvent (3 mL) was used unless otherwise noted

[a] Isolated yields

[b] 2 mol% of [Pd] were used

[c] Bold value signifies the best reaction conditions

[d] 1 mol% of [Pd] was used

[e] Temperature was 80 °C

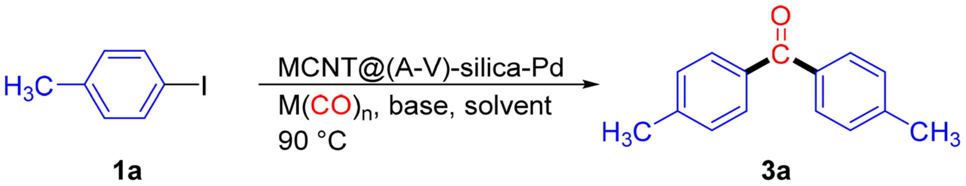
were tested substantially, and among them, Cs_2CO_3 gave a relatively higher yield (entries 2–5). It is important to note that increasing the amount of catalyst is not effective (entry 6). Then, the choice of other metal carbonyls was tested and higher yields were obtained upon treating with $Mo(CO)_6$ (entries 7–9). It was also found that decreasing the amount of the [Pd] catalyst and temperature reduced the yield of **2a** to 80% and 76%, respectively. Other solvents such as toluene, PEG-400, and ethylene glycol (EG) were also checked in the presence of $Mo(CO)_6$, but they did not yield any significant amount of **2a** (entries 10–14).

The substrate scope of aryl iodides was then investigated under the aforementioned optimal reaction condition (Table 3).

Performance of MCNTs@(A-V)-silica-Pd nanocatalyst in homo-coupling carbonylation of aryl iodides

To extend the applicability of the catalyst, we decided to scrutinize homo-coupling carbonylation of aryl iodides (Table 2). To start with, we carried out the reaction of 4-iodotoluene (**1a**) with $W(CO)_6$, $Mo(CO)_6$, $Cr(CO)_6$, and $Co(CO)_8$ with KOAc as the base in PEG 400 with 1.5 mol % of our newly synthesized [Pd] catalyst. The outcome of the reactions revealed the inefficiency of $W(CO)_6$ albeit $Mo(CO)_6$, $Cr(CO)_6$, and $Co(CO)_8$ delivered 4-methylbenzophenone (**3a**) in 52%, 17%, and 25% yields, respectively. As a result, $Mo(CO)_6$ was selected as the carbonyl source for the optimization reactions (entries 1–4). In the course of these studies, several organic and inorganic bases were studied in

Table 2 Carbonylative homo-coupling reaction of 4-iodotoluene with Pd catalyst under different conditions



Entry	Solvent	Metal carbonyl	Base	Time (h)	**3a** (%)
1	PEG 400	$W(CO)_6$	KOAc	12	0
2	PEG 400	$Mo(CO)_6$	KOAc	12	52
3	PEG 400	$Cr(CO)_6$	KOAc	12	17
4	PEG 400	$Co(CO)_8$	KOAc	12	25
5	PEG 400	$Mo(CO)_6$	NaOH	12	12
6	PEG 400	$Mo(CO)_6$	K_2CO_3	12	61
7	PEG 400	$Mo(CO)_6$	DABCO	12	18
8	PEG 400	$Mo(CO)_6$	$^nPr_3N$	12	8
9	PEG 400	$Mo(CO)_6$	Cs_2CO_3	12	55
10	PEG 400	$Mo(CO)_6$	Pyridine	12	10
11	EG	$Mo(CO)_6$	K_2CO_3	8	80
12	DMF	$Mo(CO)_6$	K_2CO_3	8	66
13	Toluene	$Mo(CO)_6$	K_2CO_3	8	49
14	Dioxane	$Mo(CO)_6$	K_2CO_3	8	58
15	PEG 200	$Mo(CO)_6$	K_2CO_3	8	42
16	Diglyme	$Mo(CO)_6$	K_2CO_3	8	26
17[a]	EG	$Mo(CO)_6$	K_2CO_3	7	80
18[b,c]	**EG**	$\mathbf{Mo(CO)_6}$	$\mathbf{K_2CO_3}$	**7**	**86**
19	EG	$Cr(CO)_6$	K_2CO_3	7	78
20[d]	EG	$Mo(CO)_6$	K_2CO_3	12	0

All the reactions were performed using 1-iodo-4-methylbenzene (2 mmol), $M(CO)_6$ (1 mmol), base (1.2 mmol), [Pd] (1.5 mol %), and solvent (3 mL) at 90 °C unless otherwise noted

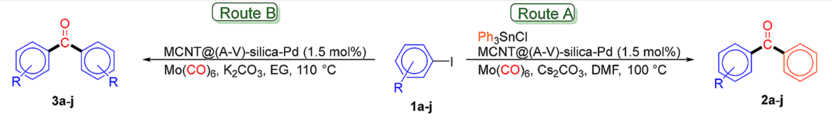
[a] The reaction was performed using 2 mol% Pd

[b] The temperature was 110 °C

[c] Bold value signifies the best reaction conditions

[d] Bromobenzene was used instead of iodotoluene

Table 3 Unsymmetrical and symmetrical diaryl ketone synthesis starting from aryl iodides



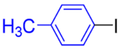
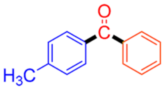
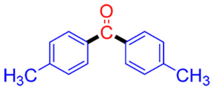
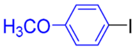
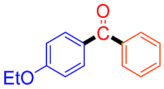
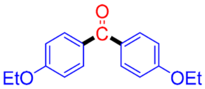
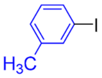
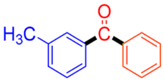
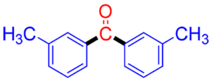
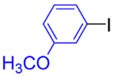
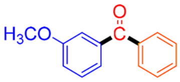
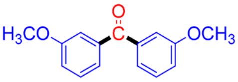
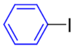
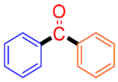
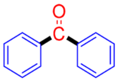
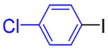
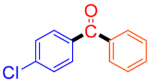
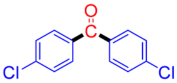
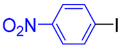
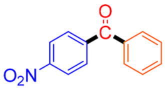
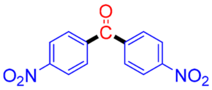
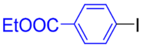
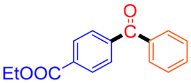
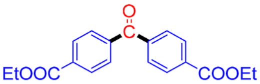
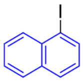
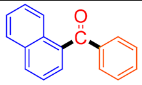
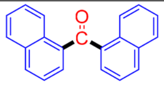
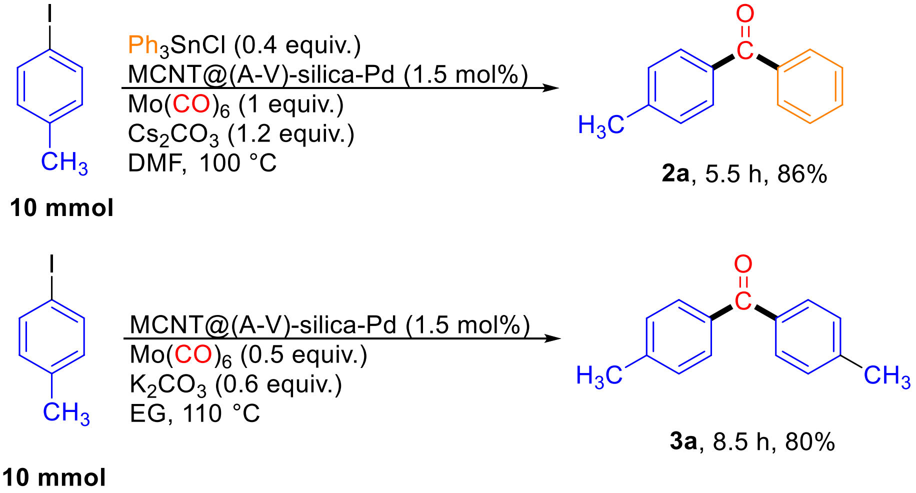
Entry	Aryl iodide	Route A	Route B
1		 **2a**, 4.5 h, 92%^{a}	 **3a**, 7 h, 86%
2		 **2b**, 5 h, 87%	 **3b**, 7.7 h, 85%
3		 **2c**, 5.2 h, 89%	 **3c**, 7.7 h, 85%
4		 **2d**, 6 h, 82%	 **3d**, 6 h, 78%
5		 **2e**, 3.8 h, 91%	 **2e**, 5.6 h, 90%
6		 **2f**, 5 h, 88%	 **3f**, 6.8 h, 90%
7		 **2g**, 12 h, 27%	 **3g**, 14 h, 22%
8		 **2h**, 12 h, 94%	 **3h**, 14 h, 90%
9		 **2i**, 6.6 h, 77%	 **3i**, 8.2 h, 74%

Table 3 (continued)

^{1}H NMR and ^{13}C NMR of all the products were taken and compared to the authentic samples [47, 48]

^{a}Isolated yield

Scheme 3 Gram-scale synthesis of symmetrical and unsymmetrical diaryl ketones



PEG 400, which did not improve the yield of **3a** greatly, and it was found that K_2CO_3 is slightly better than KOAc (entries 5–10). Therefore, our effort was made to replace PEG 400 with other solvents using K_2CO_3 as the base. Exploration of the impact of solvents modified the yield of **3a** to 80% yield in ethylene glycol (EG) (entries 11–16). The yield of **3a** was not enhanced by further increasing the amount of catalyst (entry 17). Thereafter, the reaction temperature was further investigated; the obtained results indicated that the yield of **3a** was enhanced by raising the temperature to 110 °C (entry 18). Later, $Cr(CO)_6$ was checked under this optimized reaction conditions, and **3a** was obtained in 78% yield along with the formation of 4-methylbiphenyl as the side product in 17% yield, which demonstrates the efficiency of $Mo(CO)_6$ among the carbonyl sources giving less amount of the competing uncarbonylated 4-methylbiphenyl as the side product. Having established the reaction conditions for 4-iodotoluene (**1a**), we were delighted to perform the reaction for other aryl electrophiles like bromobenzene under the identical reaction condition; however, the reaction was failed to react successfully.

With these novel findings in hand, we study the scope of Stille and homo-coupling carbonylation for variety of aryl iodides in the presence of [Pd] catalyst (Table 3). As can be seen from Table 3, MCNTs@(A-V)-silica-Pd catalyst is an effective catalyst for the construction of both symmetrical and unsymmetrical ketones in the presence of electron-donating, electron-withdrawing, and steric-hindered aryl iodides. High yields were obtained for iodobenzene substituted with electron-donating groups such as methyl and methoxy at the *para* and *meta* position. However, *para*-substituted substrates gave slightly higher yield than their meta-substituted analogs (Table 3, entries 1–4). Notably, aryl iodide bearing a chloro group was also tolerated in this method and delivered the corresponding products **2f** and **3f** in good-to-excellent yields (entry 6).

Electron-deficient iodoarenes are known to be prone to endure noncarbonylative coupling to biaryl by-products [49, 50]. It was found that lower yields were obtained when electron-withdrawing groups such as $-NO_2$ and -COOEt groups were present on aryl iodides (entries 7 and 8). Moreover, reactions of bulky 1-iodonaphthalene also proceeded effectively to furnish the desired products **2i** and **3i** in 77 and 74% yields, respectively. As turnover numbers (TONs) and turnover frequencies (TOFs) make heterogeneous catalysis very cost efficient and usually represents the catalytic activity of the catalyst, these two important factors were calculated for Stille carbonylative reactions of triphenyltin chloride with 4-iodotoluene in the presence of nanomagnetic Pd catalyst. This reaction produces relatively high TON (3.63×10^2; mol product per mol [Pd]) and TOF (80.6 h^{-1}).

Encouraged by the obtained results (Table 3), the gram-scale application of our catalytic system was also tested in Stille and homo-coupling carbonylation by starting from 10 mmol of 1-iodo-4-methylbenzene to furnish the desired products **2a** and **3a** in 86 and 80% yield (Scheme 3).

In order to find out whether the palladium leaches out from the solid catalyst to the solution during the reaction, a hot filtration test was done for the Stille carbonylation of 4-iodotoluene with Ph_3SnCl to achieve **2a** as the product. After 2 h, the catalyst was separated from the reaction mixture using an external magnet under hot conditions, which delivered **2a** in 54% yield. Then, the filtrate was allowed to react further, which revealed no further conversion of

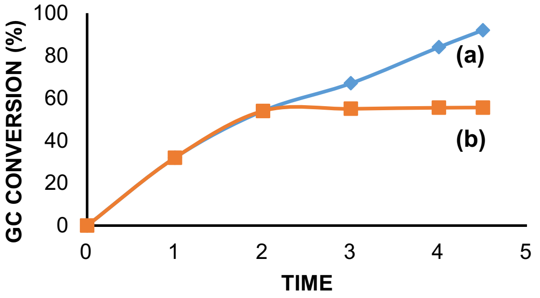


Fig. 1 **a** Time interval plot for Stille carbonylation of 4-iodotoluene with Ph_3SnCl over Pd magnetic nanocatalyst and **b** after removing of the catalyst at 54% product formation. Yields were determined by GC, with dodecane as an internal standard

4-iodotoluene to **2a** thereafter (Fig. 1). This observation confirms that no appreciable leaching of palladium occurs from the nanocatalyst under hot conditions.

In addition, ICP analysis showed a negligible amount of Pd (less than 0.1%) metal in the solution. Since the cost of transition metal-supported catalysts is often high, the recycling and recovery of them are a great concern from the practical, economic, and environmental points of view. Therefore, the recyclability of the catalyst was examined for the preparation of **2a** starting with 4-iodotoluene in the presence of 1.5 mol % of the catalyst in DMF at 100 °C. For the recycling experiment, the MCNTs@(A-V)-silica-Pd catalyst was easily recovered from the reaction mixture with an external magnet (Fig. 2a), and then, the separated catalyst was in identical reaction conditions. Finally, recycling experiments showed that the catalytic activity remained almost unchanged after being reused for six consecutive runs (Fig. 2b).

To investigate the structure of the catalyst and the presence of pd nanoparticles on silica cores after Stille carbonylation reaction, the TEM analysis of the catalyst after the third run was taken, which is indicative of the preservation of the shape of the catalyst (Fig. 3).

After successful implementation of the Stille and homo-coupling carbonylation of aryl iodides, we shifted our attention to use our Pd catalyst in carbonylative Suzuki reactions of aryl iodides with arylboronic acids.

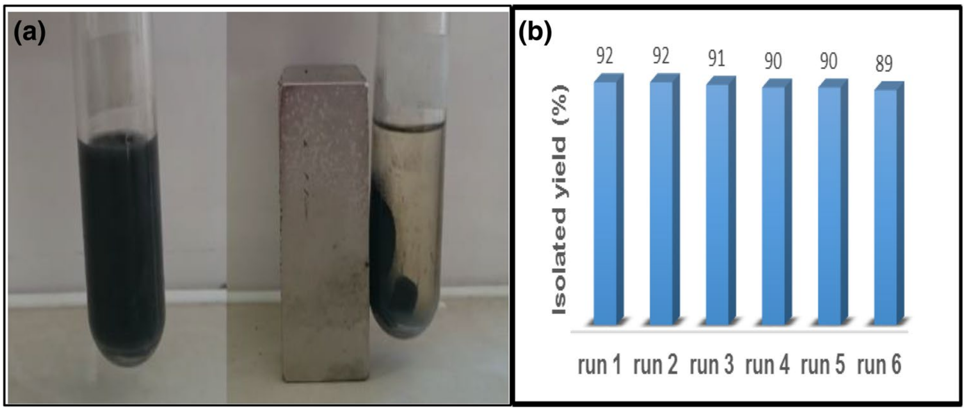


Fig. 2 **a** Photograph showing the magnetic separation of the catalyst. **b** The recyclability results of MCNTs@(A-V)-silica-Pd catalyst in the Stille carbonylation of 4-iodotoluene with Ph_3SnCl

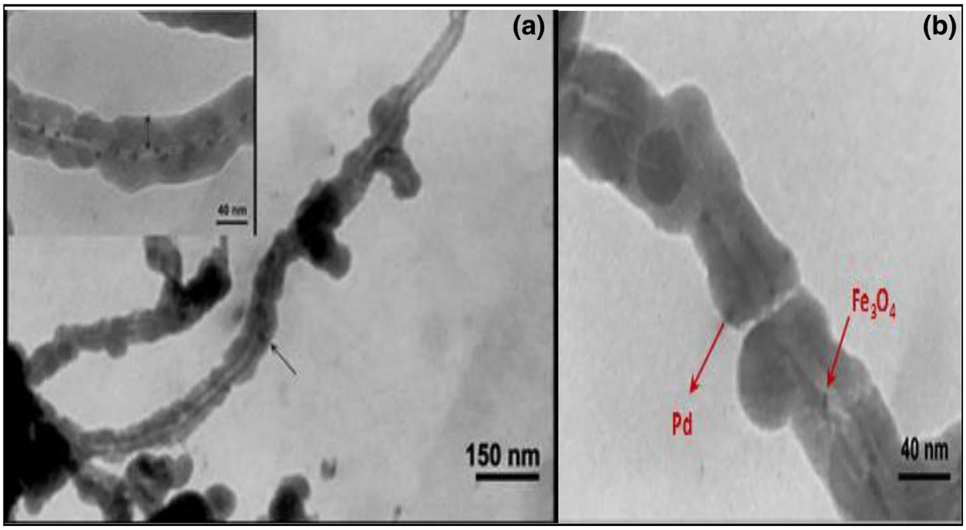


Fig. 3 **a** TEM image of MCNTs@(A-V)-silica-Pd and MCNTs@(A-V)-silica (inset) nanocomposites. **b** TEM image of the recycled catalyst after the third run

This reaction has received a great deal of attention as a promising and powerful method for synthesizing diverse biaryl ketones owing to the commercial availability of stating materials and high atom economy [49, 51–54]. Having smoothly achieved the synthesis of biaryl ketones through Stille and homo-coupling carbonylation of aryl iodides, the Suzuki carbonylation reaction was explored with iodotoluene and phenylboronic acid in the presence of $Mo(CO)_6$ under the same conditions as Stille coupling except that K_2CO_3 and 90 °C were chosen as the more proper condition. Because of the heterogeneous nature of the magnetic catalyst, the reaction was performed for 8 h to reach a maximum 94% conversion of iodotoluene. A higher reaction temperature (> 90 °C) and longer reaction time only resulted in the increase in the amount of biphenyl as the by-product. This observation is mainly due to the instability of ArCO-Pd-I at high temperature, which is accompanied with the removal of the CO moiety [55, 56]. Unfortunately, our protocol does not provide satisfactory yields in the case of aryl bromides or chlorides, which is not unusual observation in Suzuki carbonylation reaction [11, 57]. With this standard conditions in hand, carbonylative Suzuki reactions were conducted on a variety of commercially available aryl iodides (Table 4).

The iodoarenes featuring with the electron-donating group such as -Me and -OMe at the *para*-position were prone to deliver the carbonylation products **2a**–**b** in excellent yields (Table 4, entries 1 and 2). *Meta*-substituted iodobenzenes were similarly found to be suitable substrates for this transformation and gave the corresponding biaryl ketones in good yields (entries 3 and 4). The reaction of aryl iodides bearing electron-withdrawing groups such as –Cl, $-NO_2$ and –COOEt also proceeded well, giving the desired products **2f**–**h** in moderate-to-good yields under optimized reaction conditions (entries 6–8). It is noteworthy that bulky 1-iodonaphthalene could undergo the carbonylative cross-coupling reactions with phenylboronic acid effectively, affording the desired product **2i** in good yield (entry 9). The present protocol was also successfully applied for the double carbonylation of 1,4-diiodobenzene, providing diketone **2j** in 83% yield (entry 10).

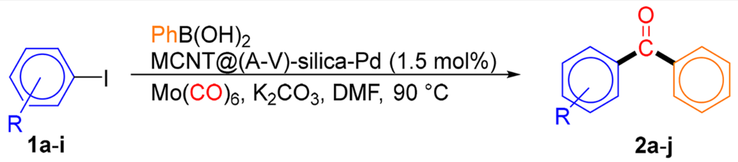
To check the merit of the present method, the results of our catalytic system were compared with some reported methods in the literature used in the synthesis of benzophenone **2e** (Table 5). It is evident that the catalytic activity, recyclability, and reaction conditions of the MCNTs@(A-V)-silica-Pd is better or comparable than other catalytic systems.

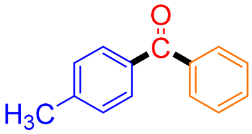
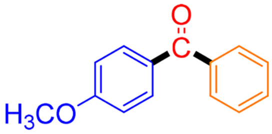
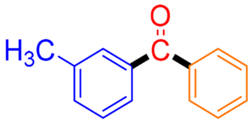
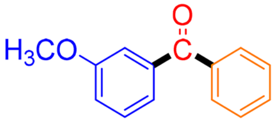
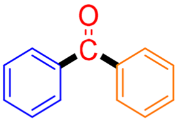
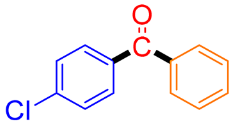
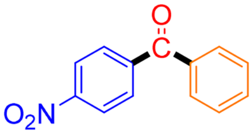
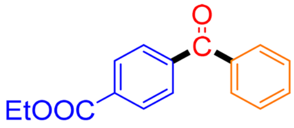
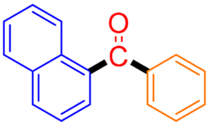
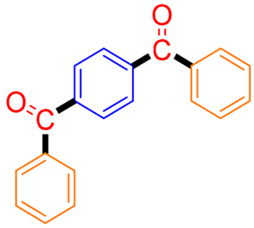
Based on the previous reports regarding the capability of vinyl groups in the silica matrix to reduce Pd ions [41, 42] and also XRD analysis (SI) which confirms the presence of Pd (0) [38, 58], the following mechanism for carbonylative Suzuki reactions was proposed (Scheme 4) [59, 60].

Conclusions

In conclusion, the efficient carbonylative Stille, Suzuki, and homo-coupling of aryl iodides were reported using $Mo(CO)_6$ as the solid metal carbonyl source and MCNTs@(A-V)-silica-Pd as a heterogeneous and magnetic catalyst, which was prepared under phosphine-free conditions due to the coordination of VTEOS and AEAPS groups on silica to palladium. The catalyst was fully characterized and used for the preparation of unsymmetrical and symmetrical diaryl ketones in high yields with high functional group tolerance. Moreover, in the Stille carbonylation, 0.4 mmol of Ph_3SnCl was used (less than equimolar) with respect to aryl iodides (1 mmol), which is an important issue due to the toxicity of organostannanes. Besides, in the homo-coupling carbonylation, this is the first report in which a heterogeneous magnetic catalyst was applied. Hot filtration test and ICP analysis were done which confirmed the heterogeneous nature of the catalyst. Finally, the ease in separation of the catalyst using an external magnet and its recyclability after six executive runs without the loss in catalytic activity, not required handling of gaseous CO and high-pressure reactors are the advantages of the catalyst.

Table 4 Carbonylative Suzuki reactions of phenylboronic acid with aryl iodides **1a–i** in the presence of nanomagnetic Pd catalyst



		
Entry 1: **2a**, 8 h, 90%[a] (trace)[b]	Entry 2: **2b**, 7 h, 92%	Entry 3: **2c**, 9 h, 82%
		
Entry 4: **2d**, 8 h, 84%	Entry 5: **2e**, 10 h, 81%	Entry 6: **2f**, 12 h, 70%
		
Entry 7: **2g**, 12 h, 59%	Entry 8: **2h**, 12 h, 63%	Entry 9: **2i**, 10 h, 78%
		
Entry 10: **2j**, 12 h, 83%		

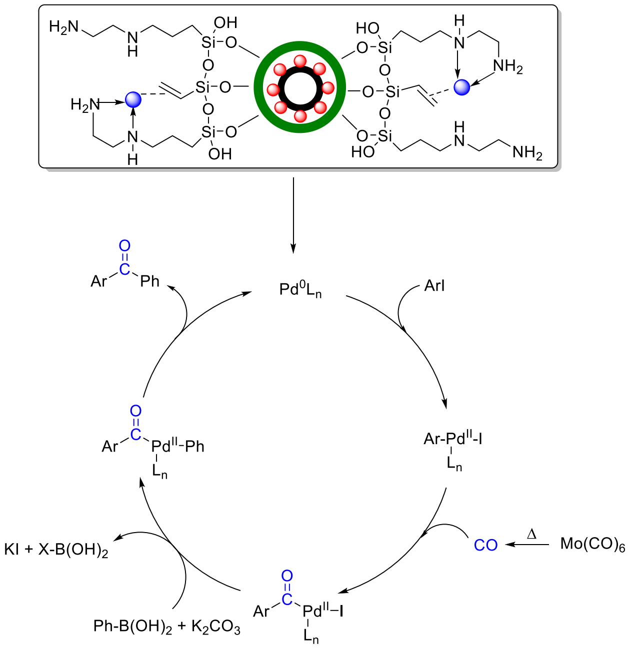
Reaction conditions: iodoarene (1.0 mmol), phenylboronic acid (1.1 mmol), $M(CO)_6$ (1 mmol), base (1.1 mmol), [Pd] (1.5 mol %), solvent (3.0 mL) at 90 °C

[a] Isolated yields

[b] Using the corresponding aryl bromide and chloride

Table 5 Comparison of the efficiency of the present method with other systems for the synthesis of benzophenone **2e** via homo-coupling carbonylation and carbonylative Suzuki reactions in the presence of MCNTs@(A-V)-silica-Pd

Entry	System, conditions	Time	Yield (%)	Recyclability	References
1	CO, $LiPdCl_3$-$CuCl_2$, CH_3CN, r.t.	1 h	29	–	[21]
2	CO, $Ar_2I^+Br^-$, $Pd(OAc)_2$, Zn, Acetone, r.t.	1 h	61	–	[23]
3	$Cr(CO)_6$, $PdCl_2$, P-ligand, KOAc, PEG, 90 °C	2 h	78	–	[28]
4	CO/O_2, $Pd(PPh_3)_2Cl_2$, CuCl, DMF, 80 °C	24 h	76	–	[29]
5	CO_2CO_8, PhHgBr, under N_2, dry THF, r.t.	2 h	83	–	[30, 31]
6	CO_2CO_8, Microwave, CH_3CN, sealed tube	2 min	78	–	[32]
7	CO, $Pd(OAc)_2$, K_3PO_4, ^{t}BuCOOH, PEG-400, r.t.	4 h	96	9	[1]
8	CO, PS-Pd-NHC, K_2CO_3, toluene, 100 °C,	10 h	94	4	[6]
9	$Mo(CO)_6$, MCNTs@(A-V)-silica-Pd, K_2CO_3, DMF, 90 °C	10 h	81	6	This work



Scheme 4 Proposed mechanism for carbonylative Suzuki reactions of aryl iodides

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this article.

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Authors and Affiliations

Elham Etemadi-Davan[1] · Dariush Khalili[1] · Ali Reza Banazadeh[2] · Ghazal Sadri[1] · Pourya Arshad[1]

✉ Elham Etemadi-Davan
etemadidavan@shirazu.ac.ir

✉ Dariush Khalili
khalili@shirazu.ac.ir

[1] Department of Chemistry, Shiraz University, Shiraz 71454, Iran

[2] Department of Chemistry and Biochemistry, Texas Tech. University, Lubbock 79409, TX, USA