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Heterogeneous gold-catalyzed oxidative cross-coupling of propargylic acetates with arylboronic acids leading to (*E*)-α-arylenones

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ABSTRACT

An efficient heterogeneous gold-catalyzed oxidative cross-coupling of propargylic acetates with arylboronic acids has been developed that proceeds smoothly in the presence of Selectfluor and provides a general and powerful tool for the preparation of various valuable α-arylenones with moderate to good yields, excellent *E*-selectivity, and recyclability of the gold catalyst. The reaction is the first example of hetero- geneous gold-catalyzed arylative rearrangement of propargylic acetates for construc- tion of complex enones.

Keywords: Gold; Oxidative cross-coupling; Propargylic acetate; α-Arylenone; Heterogeneous catalysis

Introduction

The development of efficient synthetic routes to α,β-enone structural motif is of great importance as this bifunctional unit is one of the main structural components in a large number of biologically active natural products [1]. α,β-Enones are versatile intermediates in the synthesis of natural products, pharmaceuticals, agrochemicals, and other useful materials. Traditionally, α,β-enones are prepared via aldol conden- sation or via a Wittig, Horner-Wadsworth-Emmons or Peterson olefination reaction

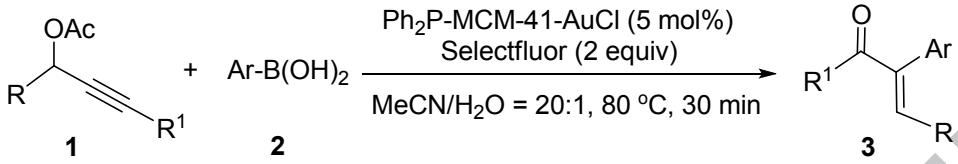
[2]. The Meyer-Schuster rearrangement of readily available propargylic alcohols is a potentially useful alternative strategy for the construction of α,β-enones due to its high atom economy [3]. The classical Meyer-Schuster rearrangement reaction involves heating the propargylic alcohol in the presence of a strong acid which is not tolerant of many functional groups, thereby having rather limited usage due to narrow substrate scope [3a].

Recently, extensive efforts have been devoted to the development of highly effective transition metal-catalyzed Meyer-Schuster rearrangement reactions and a wide variety of transition metals including V [4], Mo [5], Cu [6], Ag [7], Re [8], Ru [9], Rh [10], In [11], and Hg [12] have been reported to be used as efficient catalysts for this transformation. During the past two decades, homogeneous gold-catalyzed organic reactions have been developed into a highly efficient and powerful tool for the synthesis of valuable building blocks [13]. Recently, gold-catalyzed Meyer-Schuster reaction of propargylic alcohols [14] or rearrangement of propargylic esters [15] have attracted much attention owing to their high efficiency and mild conditions, and greatly enriched the synthetic methodologies of α,β-unsaturated carbonyl compounds. Besides, gold(I)-catalyzed arylative rearrangement of propargylic acetates and arylative Meyer-Schuster rearrangement of propargylic alcohols under dual gold/ photoredox catalytic conditions have also been reported for the preparation of α-arylenones [16], which are highly useful intermediates in the synthesis of organic materials since they possess an extended conjugation. Although these gold-catalyzed rearrangement reactions of propargylic alcohols or esters are highly efficient for

construction of α,β-unsaturated carbonyl compounds, the non-recyclability of expensive homogeneous gold catalysts and the decay of cationic gold greatly restrict their application in large-scale synthesis or multistep syntheses. Recycle of homogeneous metal catalysts is a task of great economic and environmental importance, especially when expensive and/or toxic heavy metal catalysts are used in chemical and pharmaceutical industries [17]. Immobilization of the existing homogeneous gold complexes on various solid supports appears to be an attractive solution to this problem [18].

Recently, mesoporous MCM-41 material has proven to be an ideal heterogeneous support for immobilization of homogeneous metal catalysts because of its outstanding advantages including ultrahigh surface area, large and defined pore size, big pore volume, high thermal stability and the existence of a large number of Si–OH groups on the inner surface, in comparison with other solid supports [19]. In recent years, functionalized MCM-41-supported Au(I) or Au(III) complexes have been successfully used in a variety of organic reactions as highly efficient and recyclable catalysts [20]. Very recently, we reported the synthesis of diphenylphosphine-functionalized MCM- 41-supported gold(I) complex [Ph_2P-MCM-41-AuCl] and its successful application to the regiospecific hydroamination of electron-rich or electron-poor internal alkynes with anilines [21]. In order to further expand our Au(I)-MCM-41 chemistry toolbox [20g, h, 21], herein we report the heterogeneous gold-catalyzed oxidative cross- coupling of propargylic acetates and arylboronic acids with Ph_2P-MCM-41-AuCl as a recyclable gold(I) catalyst leading to (*E*)-α-arylenones

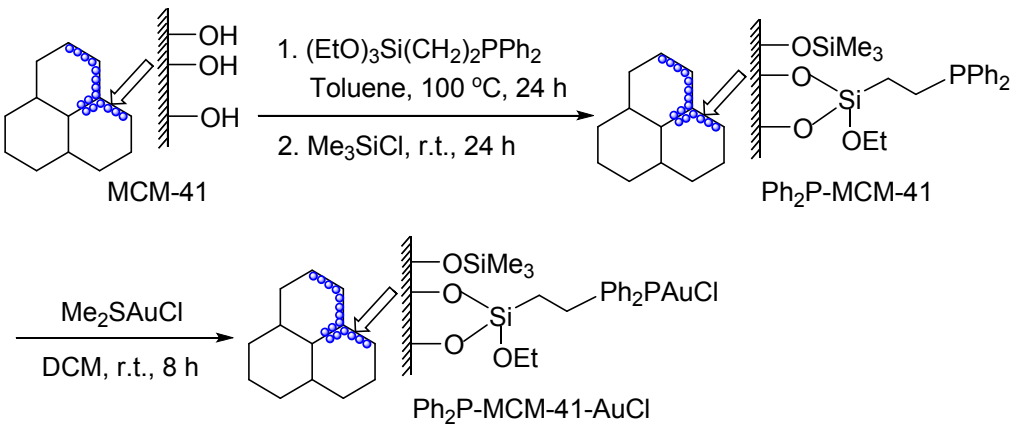
(Scheme 1).



Scheme 1. Heterogeneous gold-catalyzed synthesis of (*E*)-α-arylenones.

Results and discussions

The Ph_2P-MCM-41-AuCl complex could be easily prepared *via* a simple two-step procedure as illustrated in Scheme 2 [21]. First, diphenylphosphine-functionalized MCM-41 material (Ph_2P-MCM-41) was obtained by the condensation reaction of the mesoporous MCM-41 with commercially available 2-(diphenylphosphino)ethyltri-ethoxysilane in toluene at 100 °C for 24 h, followed by the treatment with Me_3SiCl in toluene at room temperature for 24 h. Then Ph_2P-MCM-41 reacted with Me_2SAuCl in dichloromethane (DCM) at room temperature for 8 h to provide the Ph_2P-MCM-41 - AuCl complex as a gray powder. The gold content of the heterogeneous gold(I) complex was determined to be 0.35 mmol g^{-1} according to the ICP-AES analysis.

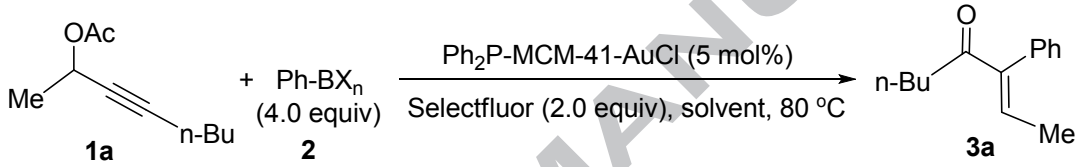


Scheme 2. Preparation of Ph_2P-MCM-41-AuCl.

The Ph_2P-MCM-41-AuCl complex was then used as the catalyst for the oxidative cross-coupling of propargylic acetates and organometallic reagents with Selectfluor as the oxidant. In our initial screening experiments, arylboronates/arylboronic acids were chosen as the external arylmetallic reagents due to their stability and easy availability. Oct-3-yn-2-yl acetate **1a** was selected as a model substrate to optimize the reaction conditions and the results are listed in Table 1. When $PhBF_3K$ was used as the arylmetal reagent in anhydrous MeCN as solvent at 80 ºC for 2 h, the formation of the desired **3a** was not observed (entry 1). The use of various phenylboronates such as $PhB(OCH_2)_2$, PhB(pin) and $PhB[O(CH_2)_3O]$ as coupling partners afforded cross-coupling product **3a** in moderate yields (entries 2-4). To our delight, a commercially readily available and inexpensive $PhB(OH)_2$ also gave the desired product **3a** in 48% yield (entry 5). In order to further improve the yield, we next examined the effect of H_2O on the reaction with $PhB(OH)_2$ as coupling partner. Gratifyingly, the yield of **3a** could be improved to 59% by using a MeCN/H_2O (100:1) mixed solvent (entry 6). When a MeCN/H_2O (20:1) solvent mixture was used, the reaction afforded the desired **3a** in 71% yield (entry 7), but further increasing water concentration in MeCN resulted in a decreased yield (entry 8). When 1.5 equiv of Selectfluor and 3.0 equiv of $PhB(OH)_2$ were used, the yield of **3a** was decreased to 49% (entry 9). Finally, the amount of the gold(I) catalyst was also screened. Reducing the amount of the catalyst to 2.5 mol% also resulted in a decreased yield and required a longer reaction time (entry 10), Increasing the amount of the catalyst could shorten the reaction time, but

did not improve the yield significantly (entry 11). When a homogeneous Ph_3PAuCl (5 mol%) was used as the catalyst, the desired **3a** was also isolated in 71% yield (entry 12), which indicating that the catalytic activity of Ph_2P-MCM-41-AuCl was comparable to that of Ph_3PAuCl. Thus, the optimized conditions for this transformation are the use of Ph_2P-MCM-41-AuCl (5 mol%), $PhB(OH)_2$ (4.0 equiv), Selectfluor (2.0 equiv) in MeCN/H_2O (20:1) as solvent at 80 ºC under Ar for 30 min (entry 7).

Table 1 Optimization of reaction conditions.[a]



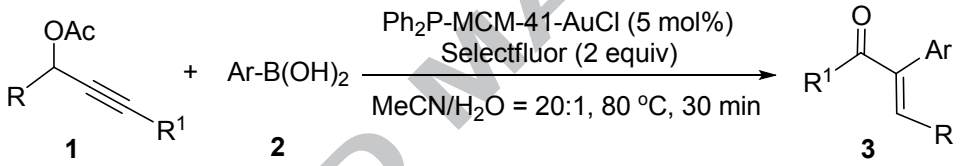
Entry	Ph-BX_n	Solvent	Time (min)	Yield (%)[b]
1	$PhBF_3K$	MeCN	120	0
2	$PhB(OCH_2)_2$	MeCN	60	45
3	PhB(pin)	MeCN	60	37
4	$PhB[O(CH_2)_3O]$	MeCN	60	46
5	$PhB(OH)_2$	MeCN	60	48
6	$PhB(OH)_2$	MeCN/H_2O (100:1)	30	59
7	$PhB(OH)_2$	MeCN/H_2O (20:1)	30	71
8	$PhB(OH)_2$	MeCN/H_2O (5:1)	30	55
9[c]	$PhB(OH)_2$	MeCN/H_2O (20:1)	60	49
10[d]	$PhB(OH)_2$	MeCN/H_2O (20:1)	60	51
11[e]	$PhB(OH)_2$	MeCN/H_2O (20:1)	15	72
12[f]	$PhB(OH)_2$	MeCN/H_2O (20:1)	15	71

[a] Reaction conditions: **1a** (0.6 mmol), **2** (2.4 mmol), Selectfluor (1.2 mmol), Ph_2P-MCM-41-AuCl (5 mol%) in solvent (6.0 mL) at 80 ºC under Ar. [b] Isolated yield. [c] 1.5 equiv of Selectfluor and 3.0 equiv of $PhB(OH)_2$ were used. [d] 2.5 mol% of Ph_2P-MCM-41-AuCl was used. [e] 10 mol% of Ph_2P-MCM-41-AuCl was used. [f] 5 mol% of Ph_3PAuCl was used as the catalyst.

With the optimized reaction conditions in hand, we started to study the scope of this heterogeneous gold-catalyzed oxidative cross-coupling reactions by using a wide range of propargylic acetates and various arylboronic acids as substrates and the results are summarized in Table 2. A variety of propargylic acetates **1a-1e** bearing various alkyl or cycloalkyl groups on both ends of the propargyl moiety underwent the oxidative cross-coupling with $PhB(OH)_2$ **2a** smoothly to give the corresponding (*E*)-α-phenylenones **3a-3e** in good yields (entries 1-5). Similarly, a wide variety of propargylic acetates **1f-1t** having various aryl groups at either end of the propargyl moiety reacted well in this transformation, thus providing a variety of (*E*)-α-phenyl-enones **3f-3t** in 54-67% yields (entries 6-20). In addition, acetate **1u** having two phenyl groups on both ends of the propargyl moiety also proved to be a suitable substrate and produced the expected **3u** in moderate yield (entry 21). Notably, the reaction also worked well with a substrate without substitution at the propargylic position, yielding a β-unsubstituted (*E*)-α-phenylenone **3v** in 61% yield (entry 22). We next examined the scope of arylboronic acids. Electron-rich arylboronic acids such as *p*-tolylboronic acid **2b** or *m*-tolylboronic acid **2c** displayed a similar reactivity with $PhB(OH)_2$ **2a** and the reactions with propargylic acetate **1d** afforded the target products **3w** and **3x** in 71-72% yields (entries 23 and 24). However, 4-methoxy-phenylboronic acid with a strong electron-donating group did not furnish the desired product, which may be due to the incompatibility of the anisole ring with strongly oxidative Selectfluor. Electron-deficient arylboronic acids such as 4-chlorophenyl-boronic acid **2d** and 4-(methoxycarbonyl)phenylboronic acid **2e** showed a relatively

lower reactivity than $PhB(OH)_2$ **2a** and the reactions with propargylic acetate **1d** gave the desired products **3y** and **3z** in acceptable yields (entries 25 and 26). In addition, the oxidative cross-coupling reactions of various propargylic acetates with substituted phenylboronic acids also proceeded effectively to provide the corresponding (*E*)-α-arylenones **3a'-3d'** in respectful yields (entries 27-30). It is noteworthy that all the oxidative cross-coupling reactions proceeded with 100% *E*-selectivity and the formation of *Z*-isomers was not observed.

Table 2 Synthesis of (*E*)-α-arylenones by heterogeneous gold-catalyzed oxidative cross-coupling reaction.[a]



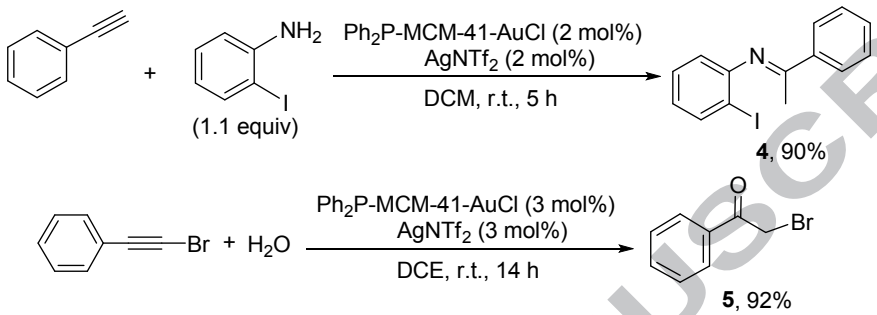
Entry	R	R^1	Ar	Product	Yield (%)[b]
1	Me	*n*-Bu	Ph	**3a**	71
2	Me	cyclohexyl	Ph	**3b**	69
3	cyclohexyl	cyclohexyl	Ph	**3c**	70
4	cyclohexyl	*n*-Bu	Ph	**3d**	68
5	$PhCH_2$	*n*-Bu	Ph	**3e**	68
6	Ph	*n*-Bu	Ph	**3f**	62
7	4-BrC_6H_4	*n*-Bu	Ph	**3g**	58
8	Me	Ph	Ph	**3h**	59
9	Me	4-$MeOC_6H_4$	Ph	**3i**	61
10	Ph	cyclohexyl	Ph	**3j**	61
11	cyclohexyl	Ph	Ph	**3k**	65
12	3-BrC_6H_4	*n*-Bu	Ph	**3l**	60
13	Ph	*t*-Bu	Ph	**3m**	62

14	*n*-Pr	Ph	Ph	**3n**	54
15	4-$AcOC_6H_4$	*n*-Bu	Ph	**3o**	64
16	4-BrC_6H_4	cyclohexyl	Ph	**3p**	67
17	4-MeC_6H_4	*n*-Bu	Ph	**3q**	63
18	Me	4-MeC_6H_4	Ph	**3r**	62
19	Ph	$ClCH_2CH_2CH_2$	Ph	**3s**	63
20	Me	4-ClC_6H_4	Ph	**3t**	65
21	Ph	Ph	Ph	**3u**	53
22	H	Ph	Ph	**3v**	61
23	cyclohexyl	*n*-Bu	4-MeC_6H_4	**3w**	72
24	cyclohexyl	*n*-Bu	3-MeC_6H_4	**3x**	71
25	cyclohexyl	*n*-Bu	4-ClC_6H_4	**3y**	58
26[c]	cyclohexyl	*n*-Bu	4-$MeOCOC_6H_4$	**3z**	55
27	4-BrC_6H_4	*n*-Bu	4-MeC_6H_4	**3a'**	67
28	Me	4-$MeOC_6H_4$	4-MeC_6H_4	**3b'**	60
29	$PhCH_2$	*n*-Bu	3-MeC_6H_4	**3c'**	68
30	$PhCH_2$	*n*-Bu	4-ClC_6H_4	**3d'**	59

[a] Reaction conditions: **1** (0.6 mmol), **2** (2.4 mmol), Selectfluor (1.2 mmol), Ph_2P-MCM-41-AuCl (5 mol%) in MeCN/H_2O = 20:1 (6.0 mL) at 80 ºC under Ar for 30 min. [b] Isolated yield. [c] MeCN/H_2O = 100:1

In order to further expand the application field of Ph_2P-MCM-41-AuCl, we also conducted heterogeneous gold(I)-catalyzed hydroamination reaction of phenylacetylene with 2-iodoaniline and hydration reaction of (bromoethynyl)benzene with Ph_2P-MCM-41-AuCl as catalyst (Scheme 3). In the presence of Ph_2P-MCM-41-AuCl (2 mol%) and $AgNTf_2$ (2 mol%), the hydroamination of phenylacetylene with 2-iodoaniline (1.1 equiv) in DCM proceeded effectively at room temperature to give the Markovnikov addition product (*E*)-2-iodo-*N*-(1-phenylethylidene)aniline (**4**) in 90%

yield after 5 h. The hydration reaction of (bromoethynyl)benzene also worked well in DCE at room temperature with the same catalysts, thereby affording the desired 2-bromo-1-phenylethanone (**5**) in 92% yield.

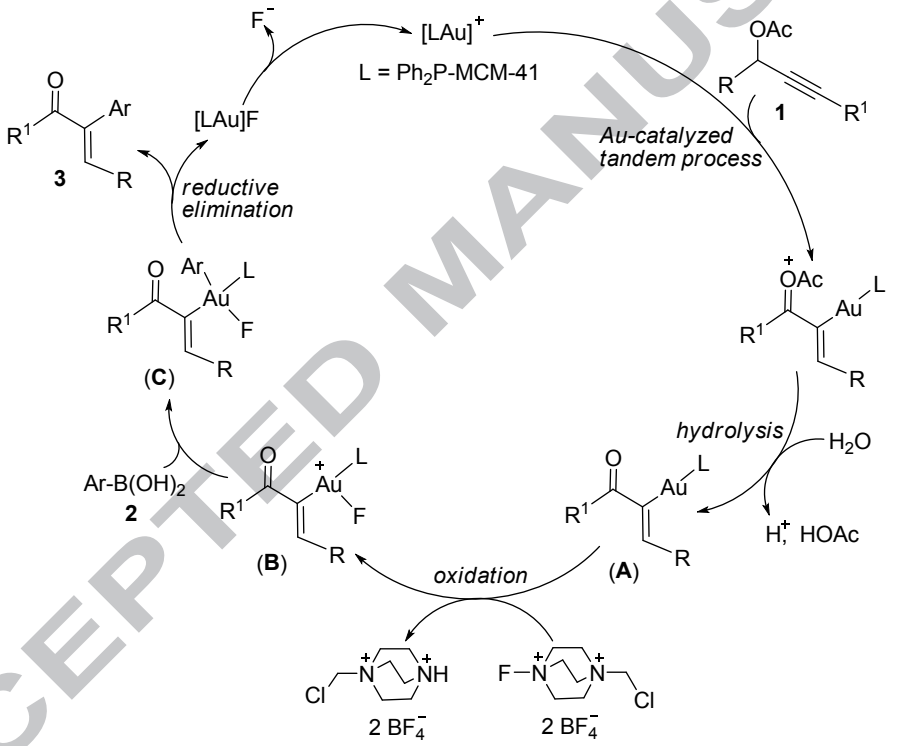


Scheme 3. Heterogeneous gold(I)-catalyzed hydroamination of phenylacetylene and hydration of (bromoethynyl)benzene.

To verify whether Ph_2P-MCM-41-AuCl is actually functioning in a heterogeneous manner, or whether it is merely a reservoir for more active soluble forms of Au, the hot-filtration test was performed [22]. For this, the oxidative cross-coupling reaction of oct-3-yn-2-yl acetate **1a** with $PhB(OH)_2$ **2a** was conducted until a conversion of approximately 30%. Then the gold(I) catalyst was removed from the reaction mixture by filtration at the reaction temperature (80 ºC), and the filtrate was again stirred at 80 ºC for 30 min. It was found that the filtered solution did not exhibit any further reactivity, and no gold species could be detected in the solution by ICP-AES analysis. These results exclude the possibility of a contribution to the observed conversion from the leached gold species, indicating that the gold(I) catalyst was stable during the oxidative cross-coupling reaction and actually functioning in a heterogeneous manner.

A plausible reaction mechanism for this heterogeneous gold-catalyzed oxidative cross-coupling reaction is shown in Scheme 4 [16a]. Firstly, the tandem reactions of

propargylic acetate **1** catalyzed by Ph_2P-MCM-41-AuCl provide an MCM-41-bound vinyl-Au(I) intermediate **A** upon hydrolysis, which is then oxidized by Selectfluor to form an MCM-41-bound vinyl-Au^+(III)F intermediate **B**. Subsequent transmetalation between intermediate **B** and $ArB(OH)_2$ **2** leads to the formation of an MCM-41-bound vinyl-Au(III)F-Ar intermediate **C**. Finally, intermediate **C** could undergo reductive elimination to afford the desired α-arylenone **3** and regenerate the gold(I) catalyst.

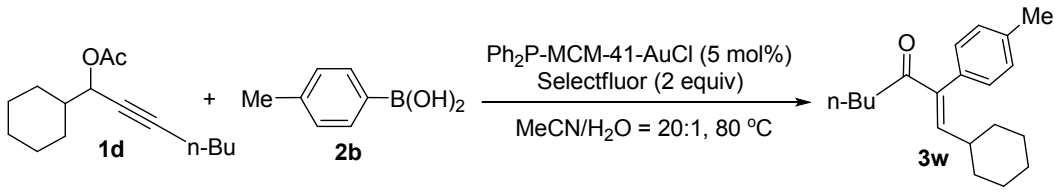


Scheme 4. Proposed catalytic cycle.

A long catalyst lifetime and the easy recyclability of the catalyst are highly desirable for the practical application of a supported precious metal catalyst. The recycle efficiency of Ph_2P-MCM-41-AuCl was investigated in the oxidative cross-coupling reaction of 1-cyclohexylhept-2-ynyl acetate **1d** with *p*-tolylboronic acid **2b**. After completion of the reaction, the gold catalyst was recovered by a simple filtration of the reaction mixture, and washed with distilled water and acetone. After being

dried at 80 ºC under vacuum for 1 h, it can be reused directly without further purification. The recovered gold catalyst was used in the next run, and almost the same yield of **3w** was observed for seven consecutive cycles (Table 3). However, a slower reaction kinetic was observed after three cycles, which may be due to loss of the catalyst during the recovery process by filtration. To determine if the phosphine ligand was oxidized to the phosphine oxide during the reaction under the strongly oxidative conditions, the recovered gold catalyst after seven consecutive cycles was subjected to hydrolysis under basic conditions. ^{31}P NMR spectrum of the silyl attachment obtained showed a strong signal at δ 39.1 ppm, which indicating that gold is strongly coordinated with the phosphine [23], and the oxidation of the phosphine ligand to the phosphine oxide did not occur. The structure of the recovered gold(I) catalyst after the first catalytic cycle was also investigated by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 1, the XPS spectrum demonstrated that all the gold species in the recovered gold(I) catalyst were present in Au(I) oxidation state [24], corresponding to the bonding energies around at 84.9 eV (Au $4f^{7/2}$) and 88.6 eV (Au $4f^{5/2}$), which indicating that the catalyst recycle is attributed by the Au(I) complex, not the gold nanoparticles formed by the decomposition of the Au(I) complex. In addition, ICP-AES analysis was performed on the recovered catalyst after seven consecutive runs, the gold content was found to be 0.34 mmol g^{-1}, which revealing almost the same gold content as the fresh one.

Table 3 Recycle of the Ph_2P-MCM-41-AuCl catalyst.[a]



Entry	Catalyst cycle	Time (min)	Yield [b] (%)	Entry	Catalyst cycle	Time (min)	Yield [b] (%)
1	1st (fresh)	30	72	5	5th	60	71
2	2nd	30	71	6	6th	90	70
3	3rd	30	72	7	7th	120	69
4	4th	40	70				

[a] Reaction conditions: **1d** (0.6 mmol), **2b** (2.4 mmol), Selectfluor (1.2 mmol), Ph_2P-MCM-41-AuCl (5 mol%) in MeCN/H_2O = 20:1 (6.0 mL) at 80 ºC under Ar. [b] Isolated yield.

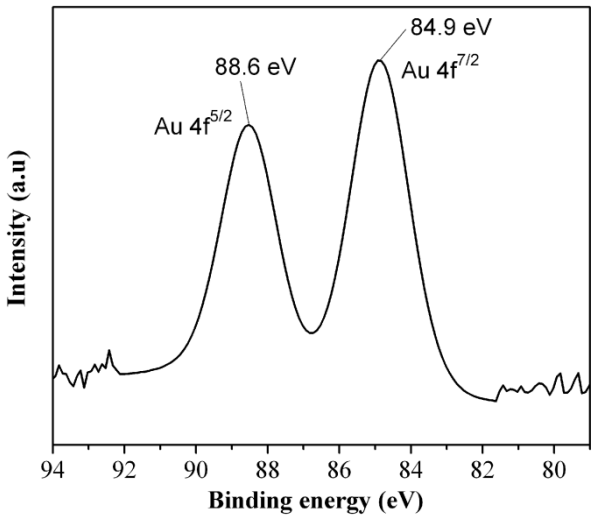


Fig. 1. XPS spectrum of the recovered gold(I) catalyst.

Conclusions

In conclusion, we have developed a highly efficient heterogeneous gold-catalyzed oxidative cross-coupling of propargylic acetates with arylboronic acids, leading to a one-step synthesis of (*E*)-α-arylenones. The reactions generated a wide variety of (*E*)-α-arylenones in moderate to good yields with excellent *E*-selectivity and were

applicable to a wide range of propargylic acetates and various arylboronic acids. Importantly, this heterogeneous gold(I) catalyst can easily be prepared *via* a simple procedure from commercially available reagents, and recovered by filtration of the reaction solution and recycled up to seven times with almost consistent activity. The present method provides a novel, efficient and practical route for the synthesis of a wide variety of (*E*)-α-arylenones.

Acknowledgements

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Research Highlights

► The Ph_2P-MCM-41-AuCl complex can be easily prepared by a simple procedure.

► Heterogeneous gold-catalyzed oxidative cross-coupling reaction is first reported.

► The reaction generates a variety of (*E*)-α-arylenones in moderate to good yields.

► The Au(I) catalyst can be recycled up to 7 times with almost consistent activity.

► Our catalytic system provides a novel and practical route to (*E*)-α-arylenones.

Graphical Abstract

Heterogeneous gold-catalyzed oxidative cross-coupling of propargylic acetates with arylboronic acids leading to (*E*)-α-arylenones

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