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**Carbonylation Reactions in Water** 

# CROYAL SOCIETY OF CHEMISTRY

## Journal Name

## COMMUNICATION

Received 00th January 20xx, Accepted 00th January 20xx Pei-Sen Gao<sup>a,b</sup>, Kan Zhang<sup>a</sup>, Ming-Ming Yang<sup>a</sup>, Shan Xu<sup>a</sup>, Hua-Ming Sun<sup>a</sup>, Jin-Lei Zhang<sup>a</sup>, Zi-Wei Gao<sup>a</sup>\*, Wei-Qiang Zhang<sup>a</sup>\*, Li-Wen Xu<sup>a,b</sup>\*

A Robust Multifunctional Ligand-controlled Palladium-Catalyzed

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#### Abstract

A novel, hydrophilic and recyclable methoxypolyethylene glycol (PEG)-modulated *s*-triazine-based multifunctional Schiff base/*N*,*P*-ligand L9 was prepared and used in Pd-catalyzed Heck-type carbonylative coupling reactions, affording diverse chalcone derivatives and 1,4-dicarbonyl esters in good yields.

 $\alpha,\beta$ -Unsaturated ketones are key intermediates in the preparation of novel bioactive compounds. Particularly, chalcone derivatives are an important class of flavonoids. They are traditionally prepared from simple aldehydes and ketones via Claisen–Schmidt condensation under strong basic conditions. Undoubtfully, this is a robust method for the preparation of 1,3-diarylpropen-1-ones with a broad substrate scope. However, it is still essential to develop general and efficient synthetic methods for  $\alpha$ , $\beta$ -unsaturated ketones, especially unsaturated 1,4-dicarbonyl esters that have been rarely studied. Since the pioneering work of Heck and coworkers, Pd-catalyzed carbonylative Heck reaction has become one of the powerful methods for the preparation of complex carbonyl compounds in the past few decades.<sup>1</sup> Notably, most carbonylative Heck reactions were achieved for intramolecular versions<sup>2</sup> till 2010. Beller's group in 2010 achieved a challenging intermolecular Heck-type carbonylative coupling between aryl triflates and diverse vinyl-group containing compounds, producing an array of chalcone derivatives via Pd/Dppp catalytic system for the first time.<sup>1g</sup> Next, Beller's group developed a general method to access the similar compounds using a novel [(cinnamyl)PdCl]<sub>2</sub> /bulky imidazolyl phosphine ligand catalytic system starting from commercially available aromatic halides. However, this intermolecular

reaction suffers from unsatisfactory yields of chalcone derivatives.<sup>1f</sup> Considering the general catalytic mechanism for Pd-catalyzed carbonylative Heck reaction<sup>1i</sup>, it is not an easy task to achieve the transformation efficiently due to the occurrence of several competing reactions, such as Heck reaction and the formation of N, N'-diethylbenzamide via the nucleophilic substitution of acyl-Pd intermediate with NEt<sub>3</sub>. Therefore, it is essential to develop an efficient synthetic approach for this type of carbonylative Heck coupling reaction. From the standpoint of green chemistry, there is still room for the development of a more environmentally benign catalytic system for Heck-type carbonylative coupling reaction in water under a relatively low CO pressure. In other words, the development of novel, recyclable, water-soluble and efficient catalytic system for carbonylative Heck reaction in aqueous phase is of significant interest. It is known that phosphine ligands often play a crucial role in Pd-catalyzed cross-coupling reactions. Since Casalnuovo's pioneering report on the use of Pd(TPPMS)<sub>3</sub> (TPPMS ¼ sodium diphenyl (3-sulfonato) phenylphosphine) for Suzuki, Heck, and Sonogashira couplings of aryl halides in water/organic solvent mixtures, numerous examples of hydrophilic phosphine ligands have been reported as effective cross-coupling catalysts.<sup>3</sup> These phosphine ligands generally include: a) phosphines with anionic substituents,<sup>4</sup> b) phosphines with cationic substituents,  $^{5}$  c) phosphines with neutral hydrophilic substituents, <sup>6</sup> d) phosphines supported on water-soluble polymers.<sup>7</sup>

In recent years, we have reported several useful methods for the construction of *s*-triazine-derived donor-acceptor/donor- $\pi$ acceptor molecules starting from commercially available 1,3,5triazine chloride to develop a recyclable *s*-triazine-modified *N*,*P*-ligands/Pd catalytic system for controllable allylation in PEG-400.<sup>8</sup> We believed that the exploration of novel watersoluble and efficient ligands based on *s*-triazine could solve the following problems: inefficiency of catalyst towards carbonylative Heck reaction in aqueous media, nonrecyclability of catalytic system, difficulty of separating products from reaction mixtures. Herein, we report our recent findings on the design and synthesis of a novel, hydrophilic and

<sup>&</sup>lt;sup>a.</sup> Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education (MOE) and School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, P. R. China

<sup>&</sup>lt;sup>b.</sup> Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, P. R. China

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efficient methoxypolyethylene glycol modified *s*-triazine-based multifunctional *N*,*P*-ligand for Pd-catalyzed carbonylative Heck coupling reaction in water to afford novel  $\alpha$ , $\beta$ -unsaturated 1,4-dicarbonyl esters.

Table 1. Discovery of a Pd-catalyzed ligand-controlled Heck carbonylation reaction in water  $^{\rm a}$ 



 $Pd(OAc)_2$  (2 mol%) and L1 (10 mol%) as catalyst,  $Cs_2CO_3$  (0.6 mmol) as base and water (0.5 mL) as solvent. The reaction was performed at 95°C.

Initially, we evaluated a model reaction of phenyl triflate 1a, with styrene 2a (3 equiv) in the presence of CO using different Pd(OAc)<sub>2</sub>/ligand catalytic systems. Under the standard conditions, the desired product 1,3-di-phenylpropen-1-one was obtained in 44% yield (Table 1, Entry 1). However, N,N'dimethylbenzamide (25% yield) and Heck coupling products (trace amounts) were detected. When ligand L1 or Pd catalyst was not used, no carbonylative product was obtained (Table 1, Entry 2). Because N,N'-dimethylbenzamide was formed due to the decomposition of NEt<sub>3</sub> (Table 1, Entry 4), other bases were used in place of NEt<sub>3</sub> (Table S1) To our delight, Cs<sub>2</sub>CO<sub>3</sub> was superior to other bases, affording 1,3-diphenylpropen-1-one in 90% yield. When phenyl halides (-Cl, -Br, -I) were used as substrates, no desired product was obtained (Table 1, Entry 3). Interestingly, when 1,4-dioxane was used as the solvent instead of water, the yield of desired 1,3-diphenylpropen-1one dramatically increased to 90% probably because of the stability of Pd/L1 catalyst in organic solvents. Other ligands were also screened in the titled reaction (Table S4). Notably, When Dppp was used as a ligand in this reaction, the product was obtained in only 7% yield (Table 1, Entry 6).

To better understand the relationship between catalytic performance and ligand structure, we modified the substitution pattern of *s*-triazine and evaluated the catalytic performance of the titled reaction in 1,4-dioxane (Scheme 1). Both **L1** and **L4** afforded the desired product in good yields, 90% and 88% respectively. However, **L2** bearing a –Cl group could not afford the desired product. When **L5** was used in the reaction, the targeted product was obtained in only 33% yield. Without a phosphine unit in the ligand, for example **L7**, no desired product was obtained. Biphosphine ligand **L5** could afforded **3a** in 81% yield. Without the help of the *s*-triazine core, for example, **L6**, a slight amount of **3a** was obtained.





Scheme 1. Relationship between the catalytic performance and ligand structure under general conditions (Table 1, entry 5).

Based on the investigation of the relationship between the catalytic performance and structure of imine-phosphine ligands, we hypothesized that the yield of carbonylative Heck coupling reaction in water would be improved by introducing hydrophilic groups into the s-triazine core. One simple strategy is the replacement of -Cl group in L2 by a water-soluble methoxypolyethylene glycol unit. Therefore, the nucleophilic substitution of L2 with ethylene glycol was performed under strong basic conditions. The desired product L9 (methoxypolyethylene glycol 2000 grafted s-triazinal N,Pligand) was obtained in 77% yield . The procedure for the preparation of L9 is shown in scheme 2. In the first step, 1,3,5triazine chloride reacted with MeOH, furnishing S2 in 80% yield. Then, the second Cl atom was substituted with ophenylenediamine via Pd-catalyzed Buchwald–Hartwig reaction, affording S3 in 55% yield. L2 was obtained via condensation of **S3** and DPPBde (2-(diphenylwater-soluble phosphino)benzaldehyde). Finally. methoxypolyethylene was attached to L2 via nucleophilic substitution under strong basic conditions, producing L9 in a moderate yield. FT-IR, <sup>31</sup>P-NMR, and elemental analyses clearly showed that L2 unit was successfully grafted with methoxypolyethylene glycol 2000 (Figs. S2 and S3).

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Scheme 2. Synthetic routes of L9 starting from 1,3,5-triazine chloride.



 Table 2. Substrate scope of Pd-catalyzed carbonylative Heck reaction with styrenes.

Entry	Ar <sub>1</sub>	Ar <sub>2</sub>	Product	Yield of <b>3</b> (%)	
1	Ph	Ph	3a	85	
2	(p-OMe)Ph	Ph	3b	82	
3	( <i>o</i> -OMe)Ph	Ph	3c	81	
4	( <i>p</i> -Br)Ph	Ph	3d	88	
5	( <i>p-</i> Br)Ph	(p-OMe)Ph	3e	86	
6	( <i>p</i> -NO₂)Ph	Ph	3f	44	
7	( <i>p</i> -F)Ph	Ph	3g	35	
8	Ph	(p-Ph)1,3-dienyl	3h	77	
9	2-naphthol	Ph	3i	80	
10	(p-OMe)Ph	(p-OMe)Ph	Зј	82	
11	<i>m</i> -thiophenyl	Ph	3k	85	
12	( <i>p</i> -OMe)Ph	( <i>m</i> -NO₂)Ph	31	86	
13	<i>m</i> -thiophenyl	( <i>p-</i> Me)Ph	3m	81	
14	( <i>m-</i> Cl)Ph	( <i>p</i> -F)Ph	3n	77	
15	( <i>p</i> -Cl)Ph	( <i>m</i> -NO₂)Ph	30	38	
16	( <i>m</i> -Me)Ph	Ph	Зр	78	
17	( <i>m</i> -Br)Ph	Ph	3q	73	
18	( <i>m</i> -Br)Ph	( <i>m</i> -Me)Ph	3r	75	

With **L9** in hand, its catalytic performance was evaluated in the carbonylative Heck reaction between PhOTf, CO, and styrene under the standard conditions (Scheme 3). To our delight, **3a** was obtained in 90% yield in this case. Encouraged by this result, the scope of the reaction was investigated. Phenyl triflates bearing both electron-donating and halides groups afforded the corresponding chalcones in moderate yields (73–88% yields). However, phenyl triflates bearing strong electron withdrawing groups, such as  $-NO_2$  and -F, produced poor **3f** 

3g, and 3o in poor yields, 44 %, 35 % and 38%, respectively. Using the catalyst Pd(OAc)\_2/L9, chalcones bearing thiophenyl groups, such as 3k and 3m, were obtained in 85% and 81% yields, respectively.

To check the recyclability of catalyst Pd(OAc)<sub>2</sub>/L9 in water, the carbonylative Heck coupling of phenyl triflate 1a, CO and styrene was examined in the presence of 2 mol% Pd(OAc)<sub>2</sub> and 10 mol% of L9. The catalytic system could be reused for five times and the yields of 3a in each run were 90%, 82%, 82%, 75% and 63%. Because of the loss of activated Pd species, the yield of 3a obviously decreased to 63% after five runs. Nevertheless, we believe that it is the first example of a recyclable Pd catalyst for carbonylative Heck reaction in water. Next, we evaluated the reaction performance of phenyl triflates and methyl acrylate using Pd(OAc)<sub>2</sub>/L9 catalyst system under 5 atm of CO. Product 5a was obtained in 90% yield and a slight amount of benzoic anhydride was monitored by <sup>1</sup>H-NMR analysis. Then the substrate scope of this reaction was evaluated using various acrylates and substituted phenyl triflates (Table 2). Phenyl triflates with  $-{}^{\rho}$ Cl (1i),  $-{}^{\rho}$ Me (1h and **1j**),  $-{}^{\rho}CF_{3}$  (**1l**),  $-{}^{\rho}OMe$  (**1f** and **1g**) groups afforded the desired products in good yields. Acrylate bearing -Me (5a), -Et (5b, 5i, **5j**), -<sup>n</sup>Bu (**5c**), -<sup>'</sup>Bu (**5d**), -Ph (**5f**, **5h**) and -Bn (**5e**, **5g**) are well tolerated in the reaction. Furthermore, Pd(OAc)<sub>2</sub>/L9 catalytic system could also be applied in the carbonylative Heck coupling with  $\alpha$ -methyl substituted acrylates. Under the optimized conditions, 5m and 5n could be obtained in moderate yields, 71% and 70%, respectively.

Table 5. Substrate Scope of Pu-catalyzed carbonylative-neck reaction with activates									
	+ \\CO R <sub>3</sub> 4	Pd(OAc) <sub>2</sub> DR <sub>2</sub>	CO (5 bar) (2 mol%), L9 CS <sub>2</sub> CO <sub>3</sub> (3 ec ter, 95 °C, 20	$\begin{array}{c} (10 \text{ mol}\%) \\ 0 \\ 0 \\ h \\ h \end{array} > R_1 \prod_{i=1}^{n} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $	5				
Entry	$R_1$	R <sub>2</sub>	R <sub>3</sub>	Product	Yield of <b>5</b> (%)				
1	Н	Me	Н	5a	90				
2	Н	Et	Н	5b	88				
3	н	"Bu	н	5c	85				
4	Н	<sup>′</sup> Bu	Н	5d	88				
5	Н	Bn	Н	5e	82				
6	<i>p</i> -OMe	Ph	Н	5f	80				
7	<i>p</i> -OMe	Bn	Н	5g	80				
8	<i>p</i> -Me	Ph	Н	5h	88				
9	<i>p</i> -Cl	Et	Н	5i	90				
10	<i>p</i> -Me	Et	Н	5j	91				
11	Н	p -ClPh	Н	5k	88				
12	<i>p</i> -CF <sub>3</sub>	Ph	Н	51	91				
13	Н	Me	Me	5m	71				
14	н	Et	Me	5n	70				

Table 2. Culturate Coope of Dal astal and south an detice Hash assation

Then we focused on the chemical derivation of Heck-type carbonylative products **3**. Na<sub>2</sub>CO<sub>3</sub>-prompted [3+2] cycloaddition of substituted chalcones **3** (**3c**, **3d**, **3f**) with *N*-benzyl-2-bromo-2-methyl propanamide **6** smoothly progressed

in HFIP at room temperature, affording novel and polysubstituted  $\gamma$ -lactams **7** (**7a**, **7b**, **7c**). (Scheme 3)



In summary, an efficient, hydrophilic and recyclable methoxypolyethylene glycol grafted *s*-triazine-based *N*,*P*-ligand for Pd-catalyzed carbonylative Heck coupling reaction was developed in this study, providing a straightforward, effective and mild route for the preparation of diverse  $\alpha$ , $\beta$ -unsaturated ketones. In the presence of Pd(OAc)<sub>2</sub> and hydrophilic ligand **L9**, diverse 1,4-dicarbonyl esters could also be obtained in satisfactory yields. Although this catalytic system could be recycled several runs with slightly decreased yields, the methoxypolyethylene glycol grafted *s*-triazine-based *N*,*P*-ligand **L9** still proved to be a multifunctional and useful ligand in homogeneous catalysis and green chemistry.

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## Graphic Abstract

## A Robust Multifunctional Ligand-controlled Palladium-Catalyzed

### **Carbonylation Reactions in Water**

Pei-Sen Gao, Kan Zhang, Ming-Ming Yang, Shan Xu, Hua-Ming Sun, Jin-Lei Zhang, Zi-Wei Gao\*, Wei-Qiang Zhang \*, Li-Wen Xu\*



A novel and robust methoxypolyethylene glycol (PEG)-modulated s-triazine-based multifunctional and hydrophilic Schiff base/N,P-ligand L9 was successfully employed in the Pd-catalyzed Heck-type carbonylative coupling reactions, yielding a variety of chalcone derivatives and 1,4-dicarbonyl esters in good yields.