## Organic & Biomolecular Chemistry



View Article Online

## COMMUNICATION

Check for updates

**Cite this:** Org. Biomol. Chem., 2021, **19**, 7353

Received 19th July 2021, Accepted 6th August 2021 DOI: 10.1039/d1ob01400e

rsc.li/obc

# Palladium-catalyzed carbonylative synthesis of aryl esters from *p*-benzoquinones and aryl triflates<sup>†</sup>

Siqi Wang,<sup>a</sup> Jian-Shu Wang,<sup>a</sup> Zhengjie Le,<sup>a</sup> Jun Ying<sup>b</sup>\*<sup>a</sup> and Xiao-Feng Wu<sup>b</sup>\*<sup>b,c</sup>

A palladium-catalyzed dicarbonylation of *p*-benzoquinones with aryl triflates has been developed. Using  $Cr(CO)_6$  as the CO source, the reaction proceeds smoothly and efficiently to give a series of aryl esters in moderate to good yields (up to 90%).

*p*-Benzoquinones as a class of key structural motifs are prevalent in numerous pharmaceuticals, natural products, and biologically active molecules, which are found to exhibit diverse pharmacological properties such as anti-inflammatory, anti-tumor, anti-viral, and so on.<sup>1,2</sup> In addition, *p*-benzoquinone derivatives are also versatile building blocks in the synthesis of

various useful organic molecules.<sup>3</sup> However, examples of the direct synthesis of aryl esters from *p*-benzoquinone are still limited.<sup>4–7</sup> For instance, Ison and co-workers reported an iridium-catalyzed C–H functionalization of benzoic acids and *p*-benzoquinone for the rapid construction of a series of benzo [*c*]chromen-6-ones in 2011 (Scheme 1a).<sup>4</sup> In 2015, Mal and Bose developed a direct cross redox coupling of aldehydes or alcohols and *p*-benzoquinone in the presence of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O and TBHP to afford a variety of aryl esters (Scheme 1b).<sup>5</sup>

Table 1 Screening of the reaction conditions<sup>a</sup>



**Scheme 1** Aryl ester synthesis from *p*-benzoquinones.

<sup>a</sup>Department of Chemistry, Key Laboratory of Surface & Interface Science of Polymer Materials of Zhejiang Province, Zhejiang Sci-Tech University, Hangzhou 310018, China. E-mail: yingjun@zstu.edu.cn

<sup>c</sup>Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany. E-mail: xiao-feng.wu@catalysis.de

$ \begin{array}{c} 0\\ +\\ 0\\ 1a\\ \end{array} \begin{array}{c} 0\\ 1a\\ \end{array} \begin{array}{c} 0\\ 0\\ 1a\\ \end{array} \begin{array}{c} 0\\ 0\\ 1a\\ \end{array} \begin{array}{c} 0\\ 0\\ 0\\ 0\\ \end{array} \begin{array}{c} 0\\ 0\\ 0\\ 0\\ 3ab\\ \end{array} \begin{array}{c} 0\\ 0\\ 0\\ 3ab\\ \end{array} $					
Entry	[Pd]	Ligand	Base	Solvent	Yield (%)
1	$Pd(OAc)_2$	$PPh_3$	$K_2CO_3$	Toluene	n.r.
2	$Pd(OAc)_2$	PCy <sub>3</sub>	$K_2CO_3$	Toluene	Trace
3	$Pd(OAc)_2$	DPPF	$K_2CO_3$	Toluene	56
4	$Pd(OAc)_2$	DPPP	$K_2CO_3$	Toluene	45
5	$Pd(OAc)_2$	DPPF	$Cs_2CO_3$	Toluene	35
6	$Pd(OAc)_2$	DPPF	$K_3PO_4$	Toluene	16
7	$Pd(OAc)_2$	DPPF	$Et_3N$	Toluene	43
8	$Pd(OAc)_2$	DPPF	$K_2CO_3$	MeCN	49
9	$Pd(OAc)_2$	DPPF	$K_2CO_3$	Dioxane	34
10	$Pd(OAc)_2$	DPPF	$K_2CO_3$	DMF	28
11 <sup>b</sup>	$Pd(OAc)_2$	DPPF	K <sub>2</sub> CO <sub>3</sub>	Toluene	81
12 <sup>b</sup>	PdCl <sub>2</sub>	DPPF	$K_2CO_3$	Toluene	5
13 <sup>b</sup>	$Pd(TFA)_2$	DPPF	$K_2CO_3$	Toluene	61
$14^{b}$	$Pd(PPh_3)_2Cl_2$	DPPF	$K_2CO_3$	Toluene	75
15 <sup>b,c</sup>	$Pd(OAc)_2$	DPPF	$K_2CO_3$	Toluene	75
$16^{b,d}$	$Pd(OAc)_2$	DPPF	$K_2CO_3$	Toluene	0
$17^{b,e}$	$Pd(OAc)_2$	DPPF	$K_2CO_3$	Toluene	0
$18^{b,f}$	$Pd(OAc)_2$	DPPF	$K_2CO_3$	Toluene	56

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol), **2b** (3.5 equiv.),  $Cr(CO)_6$  (1.5 equiv.), catalyst (10 mol%), ligand (20 mol%), base (2.0 equiv.),  $H_2O$  (4.0 equiv.), solvent (1.5 mL), 90 °C, 24 h, isolated yield. <sup>*b*</sup> **1a** (0.2 mmol) and **2b** (1.0 equiv.); the yield was calculated based on 0.1 mmol of **2b**. <sup>*c*</sup>  $H_2O$  (2.0 equiv.). <sup>*d*</sup>  $MO(CO)_6$  instead of  $Cr(CO)_6$ . <sup>*e*</sup>  $Fe_2(CO)_9$  instead of  $Cr(CO)_6$ . <sup>*f*</sup> TFBen instead of  $Cr(CO)_6$ . DPPF: bis (diphenylphosphino)ferrocene.

<sup>&</sup>lt;sup>b</sup>Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 116023 Dalian, Liaoning, China

 $<sup>\</sup>dagger\,Electronic$  supplementary information (ESI) available: General comments, a general procedure, analytical data, and NMR spectra. See DOI: 10.1039/ d1ob01400e

Transition-metal-catalyzed carbonylative reactions have emerged as one of the most powerful and straightforward approaches to establish valuable carbonyl-containing compounds.<sup>8,9</sup> To the best of our knowledge, there has been no report on the direct carbonylative synthesis of aryl esters from *p*-benzoquinone. Recently, our group developed a palladium-catalyzed double carbonylative cyclization of propargyl alcohols and aryl triflates to construct 4-aroyl-furan-2(5H)-ones with Cr(CO)<sub>6</sub> as the CO surrogate.<sup>10</sup> *p*-Toluquinone was needed to assist the CO release from  $Cr(CO)_6$  and stabilize the palladium intermediates. During the study process of this reaction, a trace amount of ester from *p*-toluquinone and aryl triflates was detected. As a part of our longstanding interest in carbonylation chemistry,11 we now disclose a palladium-catalyzed dicarbonylation of *p*-benzoquinones and aryl triflates using  $Cr(CO)_6$  as the CO source, and various aryl esters were produced in moderate to good yields (Scheme 1c).

Initially, *p*-toluquinone **1a** was treated with *p*-tolyl triflate **2b** in the presence of  $Pd(OAc)_2$  as the catalyst and various phosphine ligands in toluene at 90 °C for 24 h (Table 1, entries 1–4). It was found that the reaction with DPPF gave the highest yield (56%) of the desired product **3ab** (Table 1, entry 3). Then, several bases were examined, and lower yields were achieved (Table 1, entries 5–7). The reaction with other solvents such as

MeCN, dioxane, and DMF afforded reduced yields of **3ab** (Table 1, entries 8–10). To our delight, the yield was significantly improved to 81% when the amount of **2b** employed (Table 1, entry 11) was changed. Subsequently, a series of palladium catalysts were investigated, and the reactions all gave decreased yields (Table 1, entries 12–14). Using a reduced amount of H<sub>2</sub>O slightly decreased the reaction yield (Table 1, entry 15). Additionally, no product was observed when Mo  $(CO)_6$  or Fe<sub>2</sub>(CO)<sub>9</sub> was used as the carbonyl source (Table 1, entries 16 and 17). It was found that the reaction utilizing benzene-1,3,5-triyl triformate (TFBen) as the CO source led to **3ab** in 56% yield (Table 1, entry 18). Notably, a monoester product could be obtained as the by-product in this process.

Then, the scope of aryl triflates 2 in the reaction with *p*-toluquinone **1a** was investigated under the optimal reaction conditions (Table 1, entry 11) as shown in Scheme 2. For substrates bearing *para*-electron-donating or -withdrawing groups, the reaction gave the corresponding products **3aa–ah** in moderate to high yields (55–83%). It was found that the reaction with *meta*-substituted phenyl triflates afforded the desired products **3ai–al** in 63–90% yields. Also, *ortho*-Me and -OMe substituted phenyl triflates were successfully transformed to products **3am** and **3an** in 83% and 71% yield, respectively. Furthermore, good yields of products **3ao–aq** were obtained



Scheme 2 Scope of aryl triflates. Reaction conditions: 1a (0.2 mmol), 2 (0.2 mmol), Cr(CO)<sub>6</sub> (1.5 equiv.), Pd(OAc)<sub>2</sub> (10 mol%), DPPF (20 mol%), K<sub>2</sub>CO<sub>3</sub> (2.0 equiv.), H<sub>2</sub>O (4.0 equiv.), toluene (1.5 mL), 90 °C, 24 h, isolated yield and calculated based on 0.1 mmol of 2. <sup>a</sup> PhI (0.2 mmol) was used. <sup>b</sup> PhBr (0.2 mmol) was used. <sup>c</sup> 2t (0.8 equiv.).

#### **Organic & Biomolecular Chemistry**

when disubstituted compounds were tested. Additionally, the reaction with 2-naphthyl triflate and 1-naphthyl triflate led to the expected product **3ar** and **3as** in high yields. It is note-worthy that the vinyl triflate **2t** can be smoothly converted to product **3at** in 57% yield as well. Decreased yields were obtained when iodobenzene or bromobenzene was applied.

Subsequently, we turn to test a couple of *p*-benzoquinone derivatives **1** in the reaction with *p*-tolyl triflate **2b** (Scheme 3). The reaction with benzoquinone **1b** in the presence of TFBen as the CO surrogate furnished product **3bb** in 59% yield. It was shown that a good yield (80%) of product **3cb** was achieved when 2,5-dimethyl-benzoquinone **1c** was subjected to the reaction system. Also, the reaction with 2,6-dimethyl-benzoquinone **1d** worked well to give product **3db** in 70% yield. Moreover, 53% yield of product **3eb** was obtained in the reaction with naphthoquinone **1e**. Interestingly, with Cr(CO)<sub>6</sub> and TFBen as the co-carbonyl sources, *t*Bu-benzoquinone **1f** was transformed to the mono-carbonylated product **3fb** in 40% yield, which was attributed to the steric hindrance of the *t*Bu group on **1f**.

In order to show the scalability of this method, a scale-up reaction was performed. When 1 mmol *p*-toluquinone **1a** was tested in the reaction with *p*-tolyl triflate **2b**, 72% yield of the desired product **3ab** was achieved (Scheme 4a). Moreover, the reaction with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) under the standard conditions proceeded smoothly to give **3ab** in 61% yield, which indicated that the reaction pathway did not involve a radical intermediate (Scheme 4b). Additionally, when 2-methylhydroquinone **4** was treated with *p*-tolyl triflate **2b** under the standard conditions, the target product **3ab** was obtained in 59% yield (Scheme 4c). This suggested that 2-methylhydroquinone **4** was probably the key intermediate in this reaction.

On the basis of previous reports,  $^{7-10}$  a plausible mechanism for palladium-catalyzed dicarbonylation of *p*-benzoquinones





Scheme 4 Scale-up reaction and control experiments.



Scheme 5 Plausible mechanism.

and aryl triflates is proposed (Scheme 5). Initially, the active Pd(0) catalyst, formed from the reaction of Pd(II) with DPPF, undergoes oxidative addition with *p*-tolyl triflate **2b** to generate the Pd(II) species **A**. Meanwhile, CO is released from Cr(CO)<sub>6</sub> and inserted to **A**, leading to the acyl Pd(II) complex **B**. Subsequently, reduction of *p*-toluquinone **1a** in the presence of Cr(CO)<sub>6</sub> and H<sub>2</sub>O might generate 2-methylhydroquinone **4**. Nucleophilic substitution of **4** with two molecules of **B** gives the Pd(II) intermediate **C**. Finally, reductive elimination of **C** furnishes the final product **3ab** and regenerates the active Pd (0) species for the next catalytic cycle.

In conclusion, we have developed a facile method for the synthesis of aryl esters *via* palladium-catalyzed dicarbonylation of *p*-benzoquinones and aryl triflates with  $Cr(CO)_6$  as the CO source. A variety of aryl esters were prepared in moderate to good yields in this protocol.

### Conflicts of interest

There are no conflicts to declare.

## Notes and references

- 1 P. R. Dandawate, A. C. Vyas, S. B. Padhye, M. W. Singh and J. B. Baruah, *Mini-Rev. Med. Chem.*, 2010, **10**, 436– 454.
- 2 P. Silakari, Priyanka and P. Piplani, *Mini-Rev. Med. Chem.*, 2020, **20**, 1586–1609.
- 3 I. Abraham, R. Joshi, P. Pardasani and R. T. Pardasani, *J. Braz. Chem. Soc.*, 2011, **22**, 385–421.
- 4 K. L. Engelman, Y. Feng and E. A. Ison, *Organometallics*, 2011, **30**, 4572–4577.
- 5 A. Bose and P. Mal, J. Org. Chem., 2015, 80, 11219-11225.
- 6 (a) W. Yang, J. Wang, Z. Wei, Q. Zhang and X. Xu, J. Org. Chem., 2016, 81, 1675–1680; (b) M. T. Molina, C. Navarro, A. Moreno and A. G. Csáky, J. Org. Chem., 2009, 74, 9573– 9575.

- 7 (a) W. Wang, S. Wang, Q. Zhang, Q. Liu and X. Xu, Chem. Commun., 2015, 51, 661–664; (b) Y. Dong, J.-T. Yu, S. Sun and J. Cheng, Chem. Commun., 2020, 56, 6688–6691.
- 8 (a) Q. Liu, H. Zhang and A. Lei, Angew. Chem., Int. Ed., 2011, 50, 10788–10799; (b) S. Zhao and N. P. Mankad, Catal. Sci. Technol., 2019, 9, 3603–3613.
- 9 (a) S. Sumino, A. Fusano, T. Fukuyama and I. Ryu, Acc. Chem. Res., 2014, 47, 1563–1574; (b) J.-B. Peng, F.-P. Wu and X.-F. Wu, Chem. Rev., 2019, 119, 2090–2127.
- 10 J. Ying, Z. Le and X.-F. Wu, Org. Chem. Front., 2020, 7, 2757–2760.
- 11 (a) J. Ying, H. Wang, X. Qi, J.-B. Peng and X.-F. Wu, *Eur. J. Org. Chem.*, 2018, 688–692; (b) Q. Gao, J.-M. Lu, L. Yao, S. Wang, J. Ying and X.-F. Wu, *Org. Lett.*, 2021, 23, 178–182; (c) J. Ying, Z. Le and X.-F. Wu, *Org. Lett.*, 2020, 22, 194–198; (d) J. Ying, L.-Y. Fu, G. Zhong and X.-F. Wu, *Org. Lett.*, 2019, 21, 5694–5698.