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Iridium-Catalyzed and Ligand Controlled Carbonylative Synthesis of Flavones from Simple Phenols and Internal Alkynes

Fengxiang Zhu,[a] Zechao Wang,[a] Yahui Li,[a] and Xiao-Feng Wu*[a]

Abstract: Flavones are important natural products with diverse biological activities. In this communication, a novel procedure on carbonylative synthesis of flavones has been developed by using simple phenols and internal alkynes as the substrates and various flavones were isolated in moderate to good yields with excellent regioselectivity and functional group tolerance by using iridium as the catalyst system. Notably, this is the first example on directly carbonylative annulation of non pre-activated phenols and alkynes to produce flavones, and the chosen of ligand proven to be critical for the success of this transformation.

Flavones as an important class of naturally occurring heterocycles are exhibit diverse biological activities, such as anti-cancer, anti-inflammatory and antioxidant activities and also have been widely used in pharmaceutical industries.[1] Due to their importance, many name reactions have been developed for their preparation,[2] such as Claisen condensation, Kostanecki–Robinson reaction, Baker-Venkatamaran rearrangement. However, challenges of these procedures include poor functional group tolerance and relative harsh reaction conditions are still need to be solved. Remarkably, procedures started from salicylaldehydes and alkynes have been established as well.[2s-2u] Under the catalysis of transition metal catalysts, flavones can be produced in good yields.

Transition metal-catalyzed carbonylative reactions as a powerful tool in modern organic synthesis have been broadly used in both academic and industrial.[3] Numerous interesting compounds can be prepared easily and atom economically by carbonylation procedures. Among all the reported methodologies, carbonylative procedures for the synthesis of flavones have also been developed (Figure 1). Most of the procedures are based on using 2-halophenols and terminal alkynes as the substrates (Figure 1, eq. a).[4,5] The reactions proceeded via palladium-catalyzed carbonylative Sonogashira coupling and followed by intramolecular cyclization to give 2-substituted flavones. Synthetic procedure with 2-bromofluoroarenes and ketones has been established as well for the production of 2,3-disubstituted flavones (Figure 1, eq. b).[6] The reaction sequence consisted by alkoxycarbonylation / Claisen-Hasse rearrangement / intramolecular nucleophilic aromatic substitution. Additionally, a methodology started from aryl bromides and 2-hydroxyacetophenones to provide 2-aryl flavones has been achieved as well (Figure 1, eq. c).[7] Although these processes hold their own advantages, their limitations are obviously as well. For one example, in general, pre-activated or highly functionalized compounds are required as the substrates, these pre-activation and functionalization steps will definitely generate waste and increase total cost. From retrosynthetic analysis point of view, and considered the disadvantages and limitations of the strategies shown in Figure 1, the most ideal manner for flavones preparation will be staring from simple phenols, CO and alkynes (Scheme 1). With abundant and readily available simple phenols as the starting materials and proceeds via [3+2+1] type annulation, the requests of atom-efficiency and sustainable chemistry can be perfectly matched, and such type a new methodology will certainly be attractive.

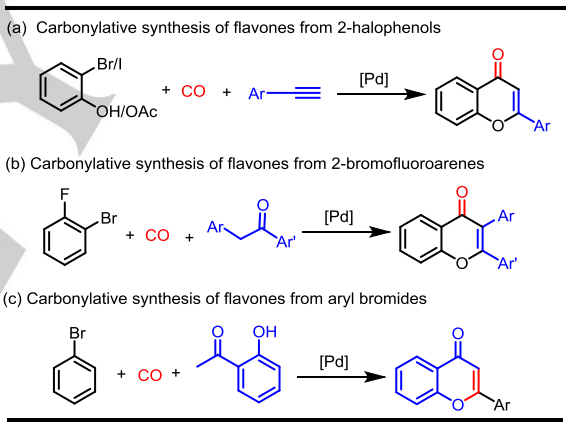
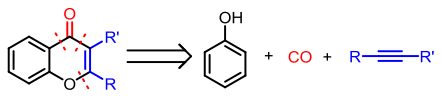
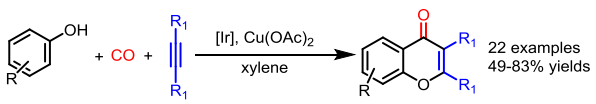


Figure 1. Transition metal-catalyzed carbonylative synthesis of flavones.



Scheme 1. Retrosynthetic analysis for flavones synthesis: an ideal procedure.



Scheme 2. A novel Ir-catalyzed carbonylative synthesis of flavones from phenols.

With this idea in mind (Scheme 1) and based on our continual interests in carbonylation reactions and experience,[8] this idea has finally been realized after a careful optimization study (Scheme 2). By the using iridium salt as the catalyst and

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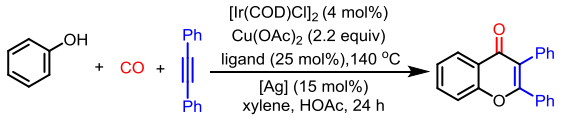
$Cu(OAc)_2$ as the oxidant, carbonylative cyclization of simple phenols with internal alkynes proceeded smoothly to the corresponding flavones. Good yields of the desired flavones can be isolated with excellent selectivity without the presence of any directing group. Remarkably, this represents the first example on carbonylative annulation of simple phenols and alkynes to produce flavones.

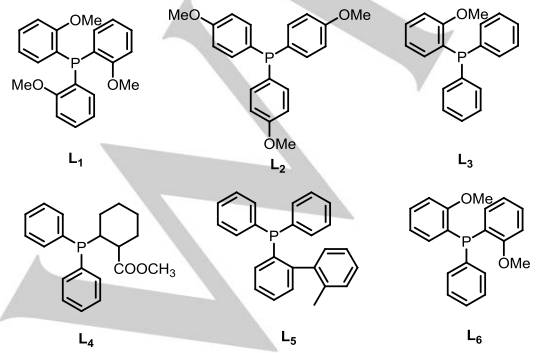
Table 1. Optimization of the reaction conditions.[a]



1a 2a 3aa

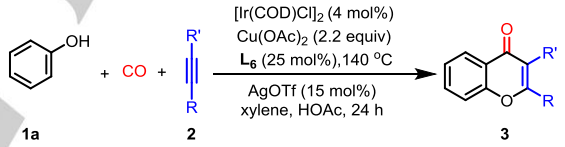
Entry	Catal.	Ligand	Additive	Yield(%)[b]
1	$[Ir(COD)Cl]_2$	PPh_3	AgOAc	7
2	$[Ir(COD)Cl]_2$	PPh_3	$AgOOCCF_3$	11
3	$[Ir(COD)Cl]_2$	PPh_3	AgOTf	15
4	$[Ir(COD)Cl]_2$	PPh_3	$AgBF_4$	9
5	$[Ir(COD)Cl]_2$	PPh_3	$AgSbF_6$	4
6	Ir(acac)(COD)	PPh_3	AgOTf	14
7	$Ir(acac)(CO)_2$	PPh_3	AgOTf	12
8	$[Cp^*IrCl_2]_2$	PPh_3	AgOTf	9
9	$IrCl_3$	PPh_3	AgOTf	-
10	$Ir(acac)_3$	PPh_3	AgOTf	-
11	$[Ir(COD)Cl]_2$	L_1	AgOTf	45
12	$[Ir(COD)Cl]_2$	L_2	AgOTf	9
13	$[Ir(COD)Cl]_2$	L_3	AgOTf	17
14	$[Ir(COD)Cl]_2$	L_4	AgOTf	13
15	$[Ir(COD)Cl]_2$	L_6	AgOTf	76
16	$[Ir(COD)Cl]_2$	P(*o*-tolyl)$_3$	AgOTf	-
17	$[Ir(COD)Cl]_2$	DPEphos	AgOTf	-
18	$[Ir(COD)Cl]_2$	Xantphos	AgOTf	-
19	$[Ir(COD)Cl]_2$	1,10-Phen.	AgOTf	-
20[c]	$[Ir(COD)Cl]_2$	L_6	AgOTf	-
21[d]	$[Ir(COD)Cl]_2$	L_6	AgOTf	-
22[e]	$[Ir(COD)Cl]_2$	L_6	AgOTf	33

[a] phenol (0.4 mmol),1,2-diphenylethyne (0.2 mmol), [Ir] (8 mol%), ligand (25 mol%), $Cu(OAc)_2$ (0.44 mmol) 140 ^{0}C, *p*-xylene (2 mL), HOAc (0.1 mL), 24 h, CO (20 bar). [b] GC yields using hexadecane as internal standard. [c] CF_3COOH instead of HOAc. [d] HOTf instead of HOAc. [e] PivOH instead of HOAc. DPEphos: (Oxydi-2,1-phenylene)bis(diphenylphosphine). Xantphos: 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene. 1,10-Phen: 1,10-Phenanthrolin.

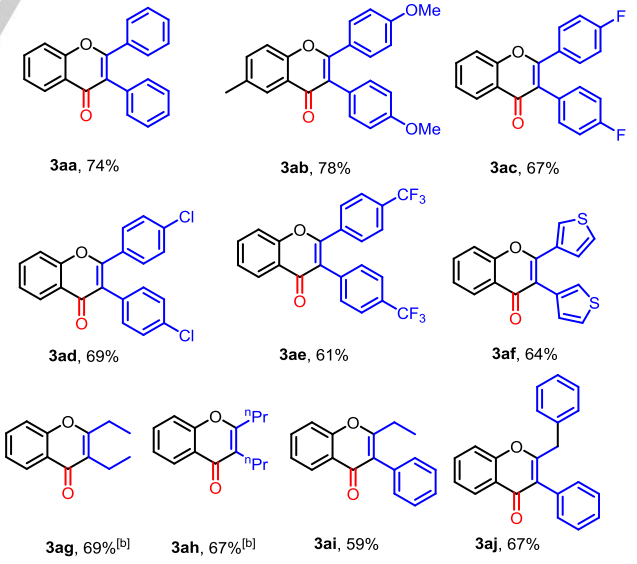


Initially, we chose phenol (**1a**) and 1, 2-diphenylethyne (**2a**) as the model substrates with $[Ir(COD)Cl]_2$ as the catalyst, $Cu(OAc)_2$ as the oxidant in *p*-xylene to establish this carbonylation procedure (Table 1). To our delight, 4-15% yields of the desired 3,4-diphenyl-2*H*-chromen-4-one (**3aa**) can be detected in the testing of different silver salt additives (Table 1, entries 1-5). Among them, silver triflate gave the best results (Table 1, entry 3). Encouraged by this primary result, we subsequently tested the effects of iridium catalysts (Table 1, entries 6-10). No transformation of substrates were observed in the absence of iridium catalyst and comparable yields can be obtained with Ir(I) pre-catalysts [Ir(acac)(COD) and $Ir(acac)(CO)_2$] as the catalysts as well (Table 1, entries 6-7). Ir(III) complexes were checked without exception, 8% yield can be obtained with $[Cp^*IrCl_2]_2$ as the catalyst but no product could be detected with $IrCl_3$ or $Ir(acac)_3$ (Table 1, entries 9-10). The variations of ligands have been tested as well (Table 1, entries 11-18). From the obtained results, the effects of ligands seem to be important for this transformation. 76% of the desired flavone can be successfully formed when using bis(2-methoxyphenyl)(phenyl)phosphane (**L_6**) as the ligand (Table 1, entry 15). To our surprise, no product can be detected when using P(*o*-tolyl)$_3$, DPEphos, Xantphos or Phen. as the ligand (Table 1, entries 16-19). Additionally, no better results can be obtained as well with the other acids such as CF_3COOH, TfOH and PivOH (Table 1, entries 20-22).

Table 2. Ir-catalyzed flavones synthesis: Substrate scope of alkynes.[a]



1a 2 3



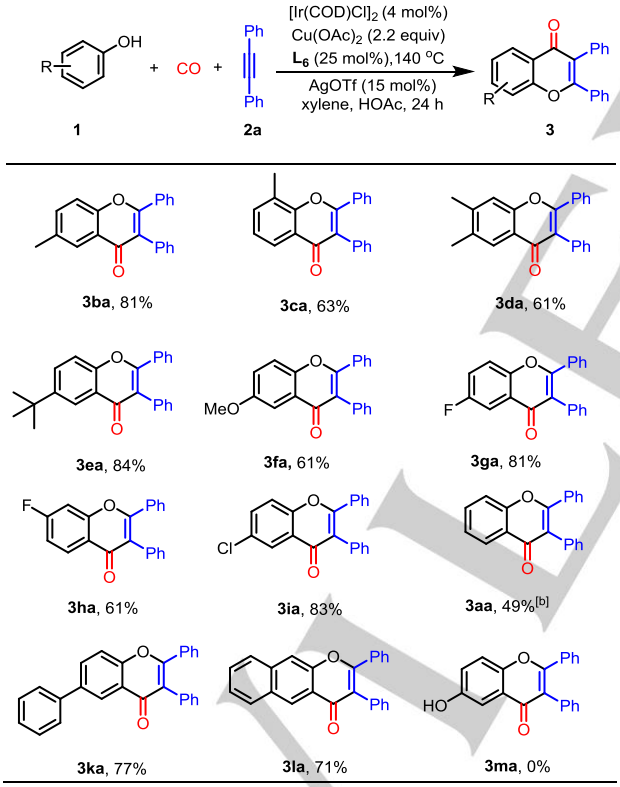
[a] Phenol (0.4 mmol),alkynes (0.2 mmol), $[Ir(COD)Cl]_2$ (4 mol%), **L_6** (25 mol%), $Cu(OAc)_2$ (0.44 mmol), AgOTF (15 mol%), CO (20 bar), 140 ^{o}C, *p*-xylene (2 mL), HOAc (0.1 mL), 1d, isolated yield. [b] Phenol (0.2 mmol), alkynes (0.4 mmol), $[Ir(COD)Cl]_2$ (4 mol%), **L_1** (25 mol%), $Cu(OAc)_2$ (0.44

mmol), AgOTF (15 mo%l), CO (20 bar), 140 °C, *p*-xylene(2 mL), HOAc (0.1 mL), 24 h, isolated yield.

With the optimum conditions in hand, we carried out the generality and limitation testing of this new procedure. Firstly, a variety of alkynes **2** were tested with phenol **1a** under our standard conditions (Table 2). Both aromatic and aliphatic internal alkynes can be effectively transformed with phenol, and afford the corresponding products in good to excellent yields and chemoselectivity. Bis(thiophen-2-yl)ethyne can be applied as well and gave the corresponding flavone derivative in good yield and chemoselectivity (Table 2, **3af**). But-1-yn-1-ylbenzene and prop-1-yne-1,3-diyldibenzene as examples of unsymmetrical alkyne can be reacted successfully as well with good results under standard conditions (Table 2, **3ai, 3aj**).

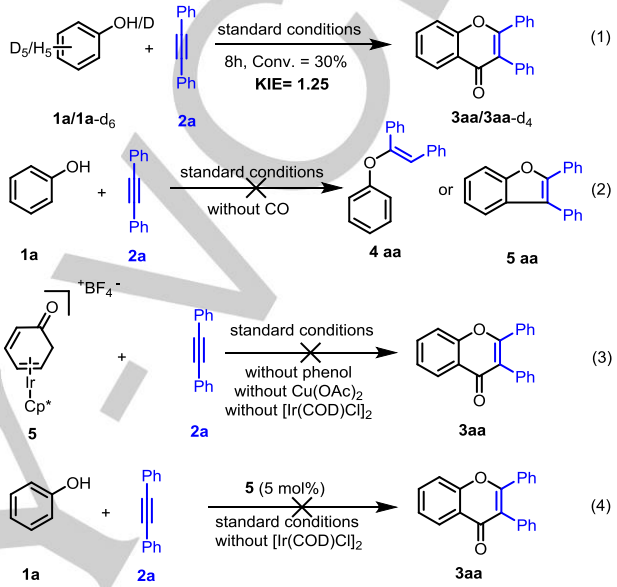
Subsequently, different phenols were tested (Table 3). Phenols with electron-donating or electron-withdrawing functional groups are all suitable substrates for this methodology. Good yields and selectivity can be achieved in all the tested cases. However, no reaction occurred when using hydroquinone as starting material.

Table 3. Ir-catalyzed flavones synthesis: Substrate of scope of phenols.[a]

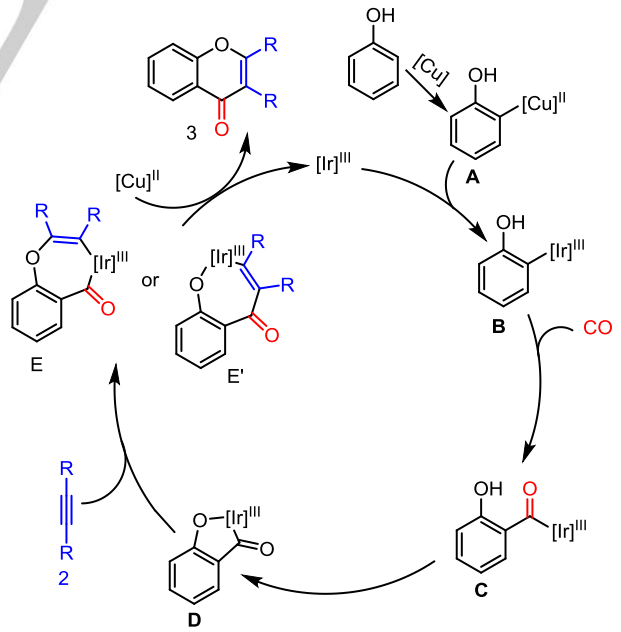


[a] Phenol (0.4 mmol), alkynes (0.2 mmol), $[Ir(COD)Cl]_2$ (4 mol%), $\mathbf{L_6}$ (25 mol%), $Cu(OAc)_2$ (0.44 mmol), AgOTF (15 mol%), CO (20 bar), 140 °C, *p*-xylene (2 mL), HOAc (0.1 mL), 24 h, isolated yield. [b] 3j is 4-iodophenol.

In order to get some insight to the reaction pathway, some control experiments were performed (Scheme 3). The KIE (kinetic isotope effect) result from deuterated phenol proven that C-H activation is not the rate determination step in this methodology (Scheme 1, eq. 1).[9] Under identical conditions but in the absence of carbon monoxide, (1-phenoxyethene-1, 2-diyl)dibenzene (**4aa**) or 2, 3-diphenylbenzofuran (**5aa**) could not been detected (Scheme 1, eq. 2). This excludes the possibility with **4aa** could be an intermediate. Then $PhOIrCp^*(BF_4)$ was prepared and applied in our reaction (Scheme 1, eq. 3 and 4).[10] No reaction occurred with either equivalent or catalytic amount of $PhOIrCp^*(BF_4)$ which excludes its possible involvement as a reaction intermediate.



Scheme 3. Control experiments.



Scheme 4. Proposed reaction mechanism.

Based on our results and literature[11], a possible reaction mechanism is proposed (Scheme 4). Initially, phenol reacted with copper acetate to give the corresponding *ortho*-activated

copper-phenol complex **A** which will go transmetalation with Ir(III) which was produced from Ir(I) oxidation. After the coordination and insertion of CO, the corresponding iridium intermediate **C** will be formed which then provide the corresponding five-membered iridium cycle **D** through X ligand exchangement. Afterwards, internal alkyne comes and produces seven-membered iridium cycle **E** or **E'** after coordination and insertion steps. The final flavone will be eliminated after reductive elimination and the together with Ir(I) complex which will be reoxidized into Ir(III) by $Cu(OAc)_2$.

In conclusion, a novel carbonylative annulation reaction for the direct synthesis of flavones from simple phenols and alkynes has been developed. With iridium as the catalyst, various flavones were prepared in good to excellent yields and with good selectivity. Remarkably, this represents the first example on directly carbonylative annulation of non pre-activation phenols and alkynes to produce flavones.

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General procedure: A 4 mL screw-cap vial was charged with $[Ir(COD)Cl]_2$ (4 mol%), L_6 (25 mol%), alkyne (0.2 mmol), phenol (0.4 mmol), $Cu(OAc)_2$ (0.44 mmol), AgOTf (15 mol%), *p*-xylene (2 mL), HOAc (0.1 mL) and an oven-dried stirring bar. The vial was closed by Teflon septum and phenolic cap and connected with atmosphere with a needle. Then the vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL). At room temperature, the autoclave is flushed with carbon monoxide for three times and 20 bar of carbon monoxide was charged. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction is allowed to be heated under 140 ^{o}C for 24 hours. Afterwards, the autoclave is cooled to room temperature and the pressure was carefully released. After removal of solvent under reduced pressure, pure product was obtained by column chromatography on silica gel (eluent: pentane/ethyl acetate = 20:1).

Keywords: Iridium catalyst • carbonylation • domino reaction • flavones synthesis • annulation

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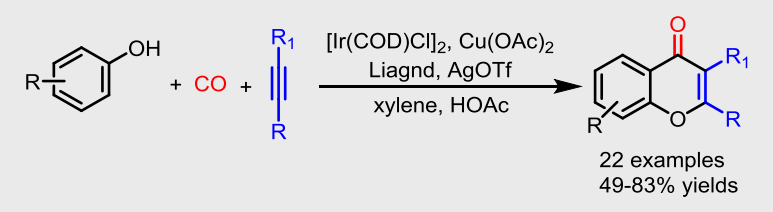

A novel carbonylative annulation reaction for the direct synthesis of flavones from phenols and alkynes has been developed. With iridium as the catalyst, various flavones were prepared in good to excellent yields and with good selectivity. Remarkably, this is the first example on directly carbonylative annulation of simple phenols and alkynes to produce flavones.

*Fengxiang Zhu, Zechao Wang, Yahui Li, and Xiao-Feng Wu**

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Iridium-Catalyzed and Ligand Controlled Carbonylative Synthesis of Flavones from Simple Phenols and Internal Alkynes