Heterocycle Synthesis

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Iridium-Catalyzed Carbonylative Synthesis of Chromenones from Simple Phenols and Internal Alkynes at Atmospheric Pressure

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Abstract: *A novel procedure on the carbonylative synthesis of chromenones has been developed. With simple phenols and internal alkynes as the substrates, various chromenones were isolated in moderate to good yields with excellent regioselectivity and functional-group tolerance by using iridium as the catalyst and copper as the promotor at atmospheric pressure. Notably, this is the first example on carbonylative annulation of simple phenols and alkynes.*

Coumarin was first isolated by Vogel in 1820 as a natural product from the Tonka bean, and then was synthesized for the first time by William Henry Perkin.[1] This ring system represents an important class of natural products present in a wide variety of natural sources and has a wide range of pharmacological properties, such as anti-HIV, anti-TB, anticancer, anti-inflammatory, anticonvulsant and MAO inhibitory properties.[2] Hence it continues to attract attention from synthetic chemists and medicinal chemists, and many synthetic methods have been developed for their preparation.[3] Among the known methodologies, palladium-catalyzed carbonylative cyclization of 2-iodophenols with alkynes was established by Larock and Kadnikov in 2000.[3f,g] Through this type of transformation, CO, as a cheap and abundant C1 source, can be effectively introduced to coumarins. However, the main issue of this method is the use of 2-iodophenol as a substrate as it requires tedious preactivation and has limited availability and low stability. To meet the requests of atom efficiency and sustainable chemistry, a new methodology, which directly uses simple phenols as the reactant in carbonylative synthesis of coumarins is highly demanded.

Transition metal catalyzed carbonylative transformations and their applications in heterocycle synthesis are considered an important part of domino reactions.[4] However, the catalysts applied are mainly focused on palladium- or rhodium-related catalysts. Although iridium-based catalysts have been successfully explored in C−H activation reactions.[5] The application of an iridium catalyst in carbonylation is still limited to the Cativa process, which has been industrialized for the preparation of acetic acid from methanol,[6] and has recently been extended to hydroformylation of alkenes.[7] From both academic and practical points of view, it will be interesting to explore the applications of iridium catalysts in carbonylation chemistry. Additionally, a corporative catalyst system or catalyst relay is also attractive. Herein we report our new results on the carbonylative synthesis of coumarins from simple phenols and alkynes with CO gas at atmospheric pressure. Moderate to good yields of the desired products were isolated with excellent selectivity. Notably, this report is the first on carbonylative annulation of simple phenols and internal alkynes.

Initially, phenol (**1a**) and 1,2-diphenylethyne (**2a**) were chosen as the model substrates in the presence of [{Ir(COD)Cl}$_2$] as the catalyst and *p*-xylene as the solvent to establish this carbonylation procedure (Table 1). To our delight, 44 % yield of the desired 3,4-diphenyl-2*H*-chromen-2-one (**3a**) was formed with Cu(OAc)$_2$ (10 mol %) as the cocatalyst and silver trifluoroacetate (AgTFA; 2 equiv) as the oxidant with CO gas (1 bar; entry 1). Encouraged by this exciting primary result, we subsequently tested the effects of copper cocatalysts (entries 2–8). No reaction occurred in the absence of a copper cocatalyst (entry 2). Decreased yields were obtained with copper halogen salts as the cocatalysts (entries 3–5), and Cu(OTf)$_2$ and Cu(TFA)$_2$ were also not effective cocatalysts (entries 6 and 7). As expected, 34 % of the desired product can be formed with copper(II) pivalate [Cu(OPiv)$_2$] as the cocatalyst (entry 8). Then various oxidants were tested with iridium and copper as the catalyst system (entries 9–15). Not surprisingly, no reaction occurred in the absence of an oxidant (entry 9). The other tested silver salts and oxidants resulted in very low yields of the target product, and the starting materials were recovered (entries 10–14). Interestingly, 21 % of 3,4-diphenyl-2*H*-chromen-2-one can be produced with Cu(OAc)$_2$ both as the cocatalyst and oxidant (entry 15). However, AgTFA still proved to be the superior oxidant. Then the effects of iridium precatalysts were tested. No transformation of substrates were observed in the absence of the iridium catalyst and comparable yields can also be obtained with the iridium(I) precatalysts [Ir(acac)(COD)] and [Ir(acac)(CO)$_2$] (entries 16–18). Iridium(III) complexes were checked without exception, 24 % yield can be obtained with [{Cp*IrCl$_2$}$_2$] as the catalyst but no product could be detected with either IrCl$_3$ or [Ir(acac)$_3$] (entries 19–21). The variation of ligands, CO pressure, temperature, and additives have been tested as well, but no better yields can be obtained (see the Supporting Information). At this stage, the combination of [{Ir(COD)Cl}$_2$], Cu(OAc)$_2$, and AgOOCCF$_3$ has been proven to be the best catalyst system with 44 % product yield. We suspect that the failure in catalyst regeneration might be responsible for the non-improved results. Hence, 5 bar of air was introduced to our best reaction conditions, but

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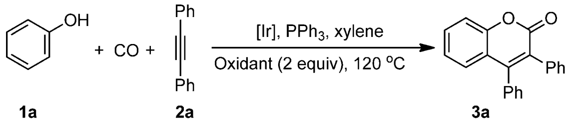
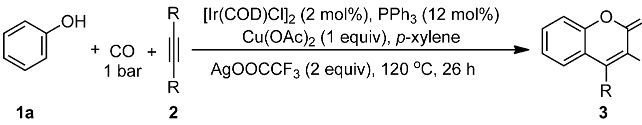
Table 1: Optimization of the reaction conditions.[a]

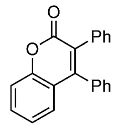


Entry	[Catal] (mol%)	[Cu]	Oxidant	Yield [%][b]
1	[{Ir(COD)Cl}$_2$]	Cu(OAc)$_2$	AgOOCCF$_3$	44
2	[{Ir(COD)Cl}$_2$]	–	AgOOCCF$_3$	–
3	[{Ir(COD)Cl}$_2$]	CuCl$_2$	AgOOCCF$_3$	5
4	[{Ir(COD)Cl}$_2$]	CuF$_2$	AgOOCCF$_3$	21
5	[{Ir(COD)Cl}$_2$]	CuCl	AgOOCCF$_3$	15
6	[{Ir(COD)Cl}$_2$]	Cu(OTf)$_2$	AgOOCCF$_3$	–
7	[{Ir(COD)Cl}$_2$]	Cu(OOCCF$_3$)$_2$	AgOOCCF$_3$	–
8	[{Ir(COD)Cl}$_2$]	Cu(OPiv)$_2$	AgOOCCF$_3$	34
9	[{Ir(COD)Cl}$_2$]	Cu(OAc)$_2$	–	–
10	[{Ir(COD)Cl}$_2$]	Cu(OAc)$_2$	AgOAc	<1
11	[{Ir(COD)Cl}$_2$]	Cu(OAc)$_2$	Ag$_2$CO$_3$	3
12	[{Ir(COD)Cl}$_2$]	Cu(OAc)$_2$	DDQ	<1
13	[{Ir(COD)Cl}$_2$]	Cu(OAc)$_2$	K$_2$S$_2$O$_8$	<1
14	[{Ir(COD)Cl}$_2$]	Cu(OAc)$_2$	BQ	<1
15	[{Ir(COD)Cl}$_2$]	Cu(OAc)$_2$	Cu(OAc)$_2$	21
16	–	Cu(OAc)$_2$	AgOOCCF$_3$	–
17	[Ir(acac)(COD)]	Cu(OAc)$_2$	AgOOCCF$_3$	38
18	[Ir(acac)(CO)$_2$]	Cu(OAc)$_2$	AgOOCCF$_3$	33
19	[{Cp*IrCl$_2$}$_2$]	Cu(OAc)$_2$	AgOOCCF$_3$	24
20	IrCl$_3$	Cu(OAc)$_2$	AgOOCCF$_3$	–
21	[Ir(acac)$_3$]	Cu(OAc)$_2$	AgOOCCF$_3$	–
22[c]	[{Ir(COD)Cl}$_2$]	Cu(OAc)$_2$	AgOOCCF$_3$	–
23[d]	[{Ir(COD)Cl}$_2$]	Cu(OAc)$_2$	AgOOCCF$_3$	58
24[e]	[{Ir(COD)Cl}$_2$]	Cu(OAc)$_2$)	AgOOCCF$_3$	65
25[f]	[{Ir(COD)Cl}$_2$]	Cu(OAc)$_2$	AgOOCCF$_3$	80
26[g]	[{Ir(COD)Cl}$_2$]	Cu(OAc)$_2$	AgOOCCF$_3$	61

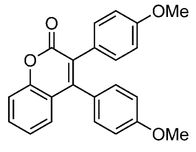
[a] Phenol (0.3 mmol), 1,2-diphenylethyne (0.15 mmol), [Ir] (4 mol%), Cu(OAc)$_2$ (10 mol%), PPh$_3$ (12 mol%), 120 °C, oxidant (2 equiv), *p*-xylene(1.5 mL), 26 h, CO (1 bar). [b] Determined by GC using hexadecane as the internal standard. Calculated based on the amount of alkyne used. [c] Air (5 bar). [d] Cu(OAc)$_2$ (30 mol%). [e] Cu(OAc)$_2$ (50 mol%). [f] Cu(OAc)$_2$ (1 equiv). [g] Cu(OAc)$_2$ (2 equiv). acac = acetylacetonate, BQ = 1,4-benzoquinone, COD = 1,5-cyclooctadiene, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, Piv = pivaloyl, Tf = trifluoromethanesulfonyl.

Table 2: Coumarin synthesis: Substrate scope of alkynes.[a]

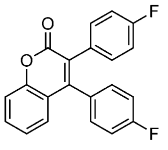




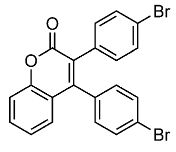
3aa, 78%



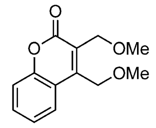
3ab, 83%



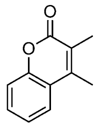
3ac, 81%



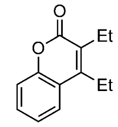
3ad, 68%



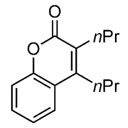
3ae, 81%



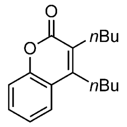
3af, 63%



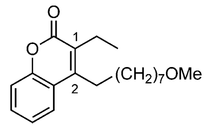
3ag, 79%



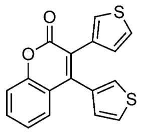
3ah, 89%



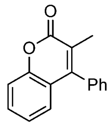
3ai, 89%



3aj, 87% (1.1:1)[b]



3ak, 82%



3al, 69%

[a] Phenol (0.3 mmol), alkynes (0.15 mmol), [Ir(COD)Cl]$_2$ (2 mol%), PPh$_3$ (12 mol%), Cu(OAc)$_2$ (0.15 mmol), AgOOCCF$_3$ (0.3 mmol), CO (1 bar), 120 °C, xylene(1.5 mL), 26 h. Yield of the isolated product is calculated based on the amount of alkyne used. [b] Regioselectivity ratio (the major isomer is substituted at the 2 position as drawn).

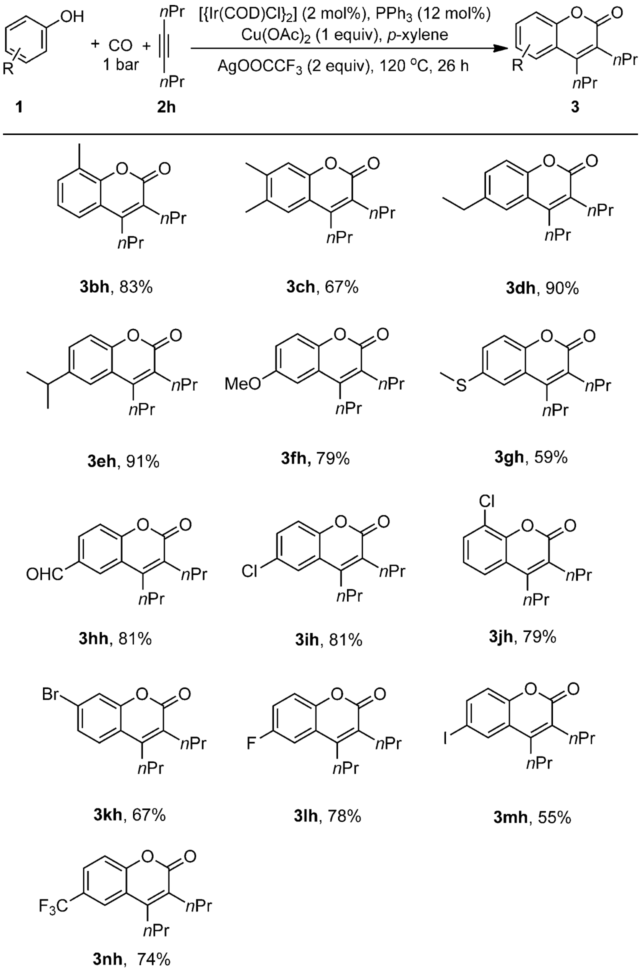
no product was detected (entry 22). This phenomenon can be explained by the decomposition of the substrates and catalysts under pressure of oxygen. Then the amount of cocatalyst, Cu(OAc)$_2$, was increased. Indeed, the yield can be improved to 58% in the presence of 30 mol% of Cu(OAc)$_2$ (entry 23). To our delight, 80% of the desired chromenone can be successfully formed with an equivalent amount of Cu(OAc)$_2$ (entry 25).

With the optimum reaction conditions in hand, we tested the the generality and limitations of this new procedure. Firstly, a variety of alkynes (**2**) were tested with **1a** under our standard reaction conditions (Table 2). Both aromatic and aliphatic internal alkynes can be effectively transformed with phenol, and affords the corresponding products in good to excellent yields and chemoselectivity. The bromide substituent, as an important functional group in cross-coupling transformations, can be tolerated and provides 68% of the desired annulated product, which is ready for further functionalization (**3ad**). Bis(thiophen-2-yl)ethyne can be applied as well and gives the corresponding chromenone in good yield and chemoselectivity (**3ak**). Prop-1-yn-1-ylbenzene as an example of an unsymmetrical alkyne can be reacted successfully as well. Good yield and excellent region- and chemoselectivity were obtained (**3al**).

Subsequently, with oct-4-yne (**2h**) as the model substrate, different phenols were tested (Table 3). Phenols with electron-donating and electron-withdrawing functional groups are all suitable substrates for this methodology. Good yields and selectivity can be achieved in all the tested cases. Methylthiol and formyl groups were well tolerated under our oxidative conditions (**3gh**, **3hh**). Halogen substituents can be tolerated as well, including relatively stable chlorides and bromides and highly activated iodides, and good yields of the corresponding products can be isolated (**3ih**, **3jh**, **3kh**, **3mh**). Given the importance of fluorinated molecules, fluorine- and trifluoromethyl-substituted chromenones can be produced in good yields as well (**3lh**, **3nh**). However, terminal alkynes failed in our procedure.

To gain insight into the reaction pathway, some control experiments were performed (see the Supporting Informa-

Table 3: Coumarin synthesis: Substrate of scope with respect to the phenols.[a]



3bh, 83% **3ch**, 67% **3dh**, 90%

3eh, 91% **3fh**, 79% **3gh**, 59%

3hh, 81% **3ih**, 81% **3jh**, 79%

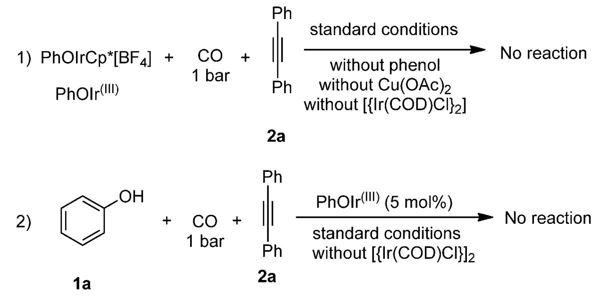
3kh, 67% **3lh**, 78% **3mh**, 55%

3nh, 74%

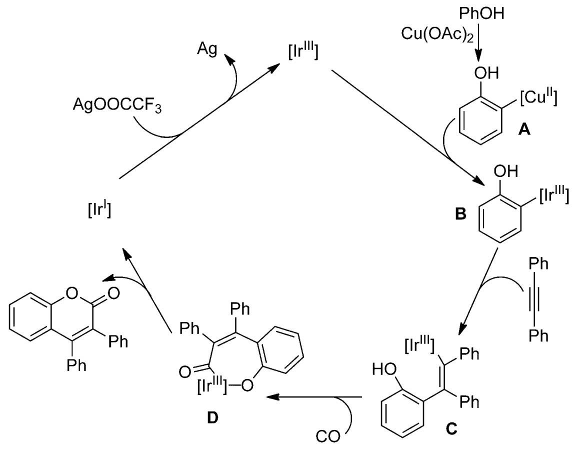
[a] Phenols (0.3 mmol), oct-4-yne (0.15 mmol), [{Ir(COD)Cl}$_2$] (2 mol%), PPh_3 (12 mol%), $Cu(OAc)_2$ (0.15 mmol), $AgOOCCF_3$ (0.3 mmol), CO (1 bar), 120 °C, p-xylene (1.5 mL), 26 h. Yield of the isolated product. Calculated based on the amount of alkyne used.

tion). The KIE (kinetic isotope effect) resulting from deuterated phenol proves that C–H activation is not the rate-determining step in this methodology.[8] Under identical reaction conditions, but in the absence of carbon monoxide, the transformation of either phenol or diphenylacetylene was not observed. Phenyl (*E*)-2,3-diphenylacrylate and 2-hydroxybenzaldehyde, as the possible intermediates, were prepared and used as starting materials under the same reaction conditions, and both of them were found intact. Then PhOIrCp*(BF_4) was prepared and applied in our reaction (Scheme 1).[9] No reaction occurred with either one equivalent or a catalytic amount of PhOIrCp*(BF_4), thus excluding it as possible reaction intermediate.

Based on our results and literature,[10] a possible reaction pathway is proposed (Scheme 2). At the beginning, phenol reacts with copper acetate to give the corresponding *ortho*-activated copper-phenol complex **A** which will transmetalate with Ir^{III} (produced from Ir^{I} oxidation). Then the produced Ir^{III}-phenoxy complex **B** will react with alkyne to produce the alkyne-inserted intermediate **C**. An acyliridium complex (**D**) will be formed after the coordination and insertion of carbon monoxide with **C**. Finally the chromenone product will be produced after reductive elimination. And the generated Ir^{I} speciec will be reoxidized by $AgOOCCF_3$ to Ir^{III} and silver metal is formed at the end of the reaction.



Scheme 1. Experiments with the iridium complex.



Scheme 2. Proposed reaction mechanism.

In conclusion, a novel carbonylative annulation reaction for the direct synthesis of coumarins from phenols and alkynes has been developed. With iridium as the catalyst and copper as the promotor, various coumarins were prepared in good to excellent yields and with good selectivity at atmospheric pressure. Remarkably, this represents the first example on carbonylative annulation of simple phenols and alkynes.

Experimental Section

General procedure: Under an open atmosphere, a 4 mL screw-cap vial was charged with [{Ir(COD)Cl}$_2$] (2 mol%), PPh_3 (12 mol%), alkyne (0.15 mmol), phenol (0.3 mmol), $Cu(OAc)_2$ (0.15 mmol), $AgOOCCF_3$ (0.3 mmol), *p*-xylene (1.5 mL) and an oven-dried stirring bar. The vial was closed by a Teflon septum and a phenolic cap and connected to the atmosphere through 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 1 bar of carbon monoxide was charged. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction was heated at 120 °C for 26 hours. Afterwards, the autoclave was cooled to room temperature and the pressure 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).

Acknowledgments

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Keywords: annulations · carbonylation · heterocycles · iridium · reaction mechanisms

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