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Graphical Abstract

An efficient method for the palladium-catalyzed arylation/cyclization of *ortho*-hydroxylcinnamate ester derivatives with diaryliodonium salts is described. A range of 4-arylcoumarins are obtained in good to excellent yield. Furthermore, the route can be applied to the synthesis of versatile building block of 5-lipoxygenase inhibitor.

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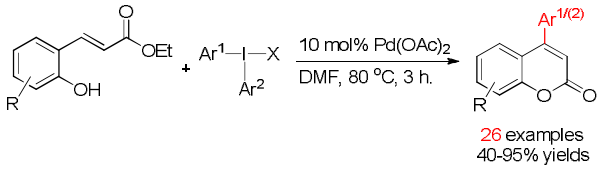

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Synthesis of 4-Arylcoumarins *via* Palladium-catalyzed Arylation/Cyclization of *ortho*-Hydroxylcinnamates with Diaryliodonium Salts

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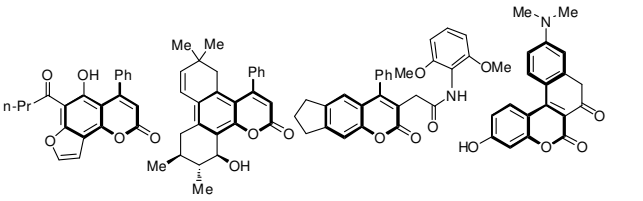
ABSTRACT

The palladium-catalyzed arylation/cyclization of *ortho*-hydroxylcinnamate ester derivatives by using diaryliodonium(III) salts has been developed. With this method, 4-arylcoumarins were easily prepared in good to excellent yields under base-free conditions. Additionally, this protocol provided an efficient alternative for the preparation of related 4-arylated coumarin compounds which are useful on the access to 5-lipoxygenase inhibitors.

Introduction

Arylcoumarins, also known as neoflavones, are a family of widely distributed natural substances in various plants (**A**, **B**, Figure 1),[1] which exhibit a broad range of biological activities (**C**, Figure 1).[2] Moreover, many of their derivatives have been extensively investigated for the outstanding optical properties with potential application in photonic materials (**D**, Figure 1).[3] In general, the synthesis of this class of arylcoumarins relied on three strategies: one is the construction of coumarin scaffolds by condensation/cyclization reactions, for examples, classical Wittig, Pechmann, Perkin and Knoevenagel reactions are frequently employed to prepare 3- or 4-arylcoumarins.[4] The other is that transition metal catalyzed cyclization through intramolecular or intermolecular C-H functionalization of aromatic rings with alkynes.[5] Another strategy is based on cross coupling reactions catalyzed by transition metals to directly functionalize the coumarin nucleus.[6] Palladium-catalyzed Suzuki and Stille coupling, rhodium or nickel catalyzed Suzuki- and Negishi-type coupling reactions to synthesize 4-coumarins, were well documented.[7, 8]

Cacchi reported in 2005 a palladium-catalyzed tandem Heck arylation/cyclization of *ortho*-hydroxylcinnamate ester derivatives with aryl halides in a molten *n*-Bu_4NOAc/*n*-Bu_4NBr mixture at 100 °C, in which 4-arylcoumarins were synthesized in



A: Furanoracemosone, typical neoflavone in natural sources. B: (+)-inophyllum B, natural products with anti-HIV properties. C: ACAT inhibitors, bio-active agents in pharmacology. D: Fluorogenic chromophore, molecular sturctures in photonic materials.

Figure 1. Selective samples of 4-arylcoumarin derivatives.

good yields.[9] Later, Ulgheri synthesized 4-phenylcoumarin intermediate by employing a similar procedure with a purpose to prepare (*S*)-tolterodine in pharmaceutical research.[10] In 2012, Correia described a mild and operationally simple protocol by employing arenediazonium salts at 60 °C in replace of phenyl halides under palladium catalysis in the presence of one equivalent $CaCO_3$ as base, this procedure afforded 4-arylcoumarin derivatives in high yields. It is noteworthy that the basicity of the reaction medium was crucial for the efficiency as described in the paper.[11] Considering the importance of 4-arylcoumarins, the search for alternatives of arylating reagents in this protocol in order to improve the synthetic efficiency while under mild conditions is still desirable.

Diaryliodonium salts ($Ar_2I^+X^-$) as electrophilic arylating agents, which allowed direct arylation of alkenes, are actively

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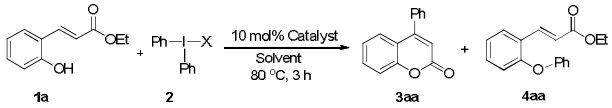
studied due to their environmentally benign nature and unique reactivity.[12] In this context, several groups had made major contributions in the alkene arylation for Heck-type coupling reactions by using hypervalent iodine(III) reagent in a straightforward way.[13] Additionally, Gaunt pioneered an electrophilic carbofunctionalization of allylic amides with diaryliodonium salts for the preparation of oxazines *via* copper catalysis.[14] Very recently, we described a diarylation of activated alkenes by using diaryliodonium(III) salts.[15] The aromatic electrophilic species were generated by using of metal catalysts in combination with diaryliodonium salts, then a sequent C-H functionalization cascade reaction formed arylated oxindoles. With a continuation to our project of arylations of alkenes, herein, we reported the synthesis of 4-arylcoumarins *via* palladium-catalyzed arylation/cyclization reactions by using diaryliodonium salts.

Results and Discussion

Initially, an investigation of Pd-catalyzed arylation/cyclization of cinnamate ester **1a** with diphenyliodonium triflate **2a** was carried out. It is pleased to find that the desired product of **3aa** was obtained in 70% yield under the presence of 10 mol% $Pd(OAc)_2$ as catalyst (Table 1, entry 1). After examining the solvent effect with experiments performed in toluene, dioxane and *N*, *N*-dimethyl formamide (DMF), the best yield of 84% (**3aa)** was achieved when the reaction was performed in DMF as solvent (Table 1, entries 2-4). To evaluate the catalytic activity of copper catalysts in the reaction, interestingly, no desired product **3aa** was observed but resulting in the formation of oxygen-arylated product of **4aa** after screening CuI, $Cu(OTf)_2$ and $Cu(OAc)_2$ as catalysts (Table 1, entries 5-7). Changing the catalyst to palladium(0) variant of $Pd(PPh_3)_4$ also furnished the product **3aa** in the good yield of 80% (Table 1, entry 8). The influence of counter-anions of diaryliodonium salts was studied; the results showed that counter-anions (OTf, BF_4 and PF_6) did not have significant effect on reactivity (Table 1, entries 4, 9-10). For a comparison of iodonium salts with arenediazonium salts as arylating agents,[11] inorganic bases were employed in the reaction as additives. In sharp contrast, weak base such as $NaHCO_3$ has a negative effect on the efficiency with small amount of oxygen-phenylated product **4aa** (Table 1, entry 11). Additives of K_2CO_3 decreased the yield of **3aa** dramatically (10%) but giving **4aa** in a good yield of 70% (Table 1, entry 11). A transition metal-free condition using strong bases of KO^{t}Bu as promoters were exmined,[16] only oxygen-phenylated product **4aa** was isolated in an excellent yield of 90% (Table 1, entry 13). Notably, when iodobenzene was used for replacement of diphenyliodonium salts under standard conditons, the 4-aryl-coumarin **3aa** was obtained in only 15% yield (Table 1, entry 14).

With the optimized reaction conditions in hand, we turned our attention to explore the reaction scope of substrates **1** with diphenyliodonium triflate **2a**. As shown in Table 2, cinnamate ester **1** reacts well with either mono- or di-substituted substituents, the desired products **3ab-3ak** were obtained in good to excellent yields of 70-95%. Of note, the cinnamate ester **1j** bearing a base senstive hydroxyl group reacted well in this protocol, **3aj** was obtained in 85% yield. Very interestingly, both 4-phenylcoumarin products of **3ag** with an electron-donating diethylamno group and **3ai** with methoxyl group at 7-position of coumarin nucleus were obtained in 85% and 95% yields, respectively, which can emit strong fluorescence under the irradiation of ultraviolet light due to the enhancement of intramolecular charge transfer by substituent effects.[17]

Table 1. Screening of Reaction Conditions for Arylation/Cyclization of Cinnamate Ester **1a**.[a]



1a **2** **3aa** **4aa**

Entry	X	Catalyst	Solvent	Yield (%) of **3aa**[b]
1	OTf	$Pd(OAc)_2$	DCE	70
2	OTf	$Pd(OAc)_2$	Toluene	74
3	OTf	$Pd(OAc)_2$	Dioxane	80
4	OTf	$Pd(OAc)_2$	DMF	84
5	OTf	CuI	DMF	0 (30)[c]
6	OTf	$Cu(OTf)_2$	DMF	0 (25)[c]
7	OTf	$Cu(OAc)_2$	DMF	0 (30)[c]
8	OTf	$Pd(PPh_3)_4$	DMF	80
9	BF_4	$Pd(OAc)_2$	DMF	81
10	PF_6	$Pd(OAc)_2$	DMF	79
11[d]	OTf	$Pd(OAc)_2$	DMF	71 (5)[c]
12[e]	OTf	$Pd(OAc)_2$	DMF	10 (70)[c]
13[f]	OTf	--	DMF	0 (90)[c]
14	PhI	$Pd(OAc)_2$	DMF	15

[a]Reaction conditions: **1a** (0.5 mmol), **2** (1 mmol), catalyst (0.05 mmol), and solvents (2 mL) at 80 °C for 3 h.

[b]Isolated yield.

[c]The numbers in brackets are isolated yield of **4aa**, 16 h.

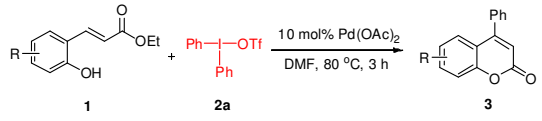
[d]$NaHCO_3$ (0.5 mmol) as additives was used.

[e]K_2CO_3 (0.5 mmol) as additives was used.

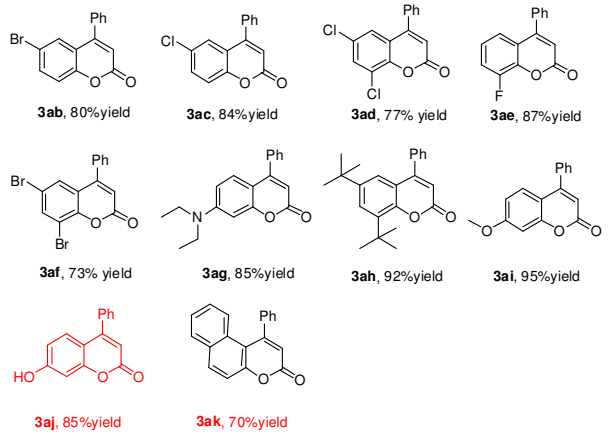
[f]only KO^{t}Bu (0.6 mmol) was used.

A π-expanded 4-phenylcoumarin[17] of **3ak** was readily synthesized in 70% yield from corresponding naphthol substrate with this procedure (Table 2).

Table 2. Palladium-catalyzed Arylation/Cyclization of Cinnamate Ester **1** for the Preparation of 4-Arylcoumarins.[a,b]



1 **2a** **3**



3ab, 80%yield **3ac**, 84%yield **3ad**, 77% yield **3ae**, 87%yield

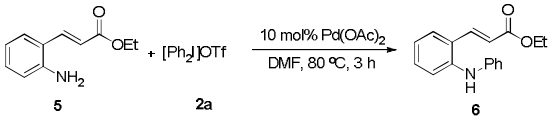
3af, 73% yield **3ag**, 85%yield **3ah**, 92%yield **3ai**, 95%yield

3aj, 85%yield **3ak**, 70%yield

[a] **1** (0.5 mmol), **2a** (1 mmol), $Pd(OAc)_2$ (0.05 mmol), and DMF (2 mL) at 80 °C for 3 h.

[b]Isolated yield.

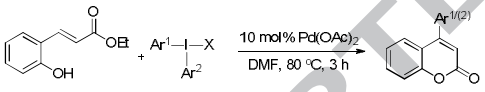
Additionally, substrate (**5**) of (*E*)-ethyl 3-(2-aminophenyl)-acrylate with amino group was prepared by Wittig reaction using corresponding benzaldehyde. Treatment of **5** with diphenyliodonium triflate **2a** under standard conditions in the presence of $Pd(OAc)_2$ as catalyst, only afforded nitrogen-arylated product of **6** in 25% yield after 3 hours at 80 °C (Scheme 1).



Scheme 1. The reaction of **5** with **2a** under the standard conditions.

Subsequently, we examined the structural diversity of various diaryliodonium salts **2** as arylating partners (Table 3). As shown in Table 3, a wide variety of functionalities regardless of the electronic nature of the substituents were well tolerated in the arylation/cyclization of (*E*)-ethyl 3-(2-hydroxyphenyl)acrylate (**1a**). As a result, various 4-arylcoumarin products were obtained in good yields (Table 3, entries 2-10). Aryl groups with substituents ranging from electron-donating to electron withdrawing groups could be transferred efficiently with the symmetric iodonium salts **2a-j**. Steric factor severely affected the reactivity, bis-(2,4,6-trimethylphenyl)-iodonium triflate **2f** gave a decreased yield of 40% (Table 3, entry 11). Unsymmetrical aryl-mesityl iodonium reagents were also employed in the reaction of **1a**, we were delighted to find that aryl-mesityl iodonium salts with the aryl groups displaying electron-rich or electro-deficient worked well. Moreover, aryl-mesityl iodonium salts bearing a range of methyl-substituted phenyl rings on the *ortho*-, *meta*- and *para*-positions can readily transferred Ar to the desired products together with 4-mesitylcoumarin derivated products. As can be seen, the ratio of product mixture could be depended on the steric effect of aryl rings (2/1-5.5/1; Table 3, entries 12-14). It was worth to mention that the unsymmetrical salt [(4-$MeOC_6H_4$)(4-ClC_6H_4)I]OTf transferred the Ar group to the desired products **3fa/3ca** in yield of 80% with ratio of 1.4:1 (Table 3, entry 16). When [(2-thienyl)(Ph)I]OTf was employed under the standard conditions, 3na was formed exclusively. Interestingly, the heteroatomic ring was transferred to the product which is in contrast to our previous report (Table 3, entry 17).[15a]

Table 3. Scope of diverse iodonium salts for Arylation/Cyclization of Cinnamate Ester **1a**.[a]



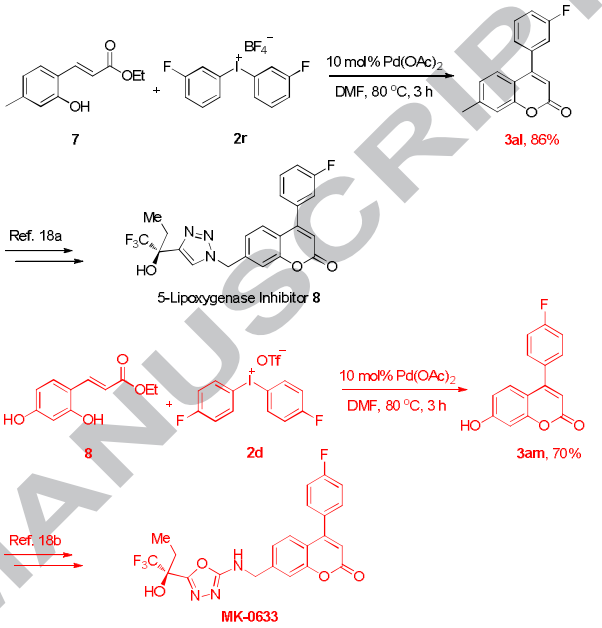
Entry	$Ar^1(Ar^2)$	2	X	Product	Yield (%)[b]
1	$(C_6H_5)_2$	**2a**	OTf	**3aa**	84
2	$(4\text{-}BrC_6H_4)_2$	**2b**	OTf	**3ba**	75
3	$(4\text{-}ClC_6H_4)_2$	**2c**	OTf	**3ca**	79
4	$(4\text{-}FC_6H_4)_2$	**2d**	OTf	**3da**	70
5	$(4\text{-}^tBuC_6H_4)_2$	**2e**	OTf	**3ea**	85
6	$(4\text{-}MeOC_6H_4)_2$	**2f**	OTf	**3fa**	86
7	$(2\text{-}MeC_6H_4)_2$	**2g**	BF_4	**3ga**	73
8	$(4\text{-}MeC_6H_4)_2$	**2h**	OTf	**3ha**	76
9	$(3\text{-}NO_2C_6H_4)_2$	**2i**	PF_6	**3ia**	51
10	$(4\text{-}CF_3C_6H_4)_2$	**2j**	BF_4	**3ja**	70
11	$(Mesityl)_2$	**2k**	OTf	**3ka**	40
12	2-MeC_6H_4(Mesityl)	**2l**	OTf	**3ga/3ka**	68(2:1)[c]
13	3-MeC_6H_4(Mesityl)	**2m**	OTf	**3la/3ka**	62 (4:1)[c]
14	4-MeC_6H_4(Mesityl)	**2n**	OTf	**3ha/3ka**	65(5.5:1)[c]
15	4-$CO_2EtC_6H_4$(Mesityl)	**2o**	OTf	**3ma/3ka**	71(6:1)[c]
16	4-$MeOC_6H_4$(4-ClC_6H_4)	**2p**	OTf	**3fa/3ca**	80 (1.4:1)[c]
17	C_6H_4(2-Thienyl)	**2q**	OTf	**3na**	46

[a]**1a** (0.5 mmol), **2** (1 mmol), $Pd(OAc)_2$ (0.05 mmol), and DMF (2 mL) at 80 °C for 3 h.

[b]Isolated yield.

[c] The radio of different arylated coumarins.

To illustrate the reaction scope for potential utility, we chose the substrate **7** bearing a methyl substituent on the 7-position, to produce useful molecules. The 4-arylcoumarin product **3al** was obtained by arylation with iodonium salt **2r** in 86% yield, **3ak** is a versatile building block which can be readily converted to the known molecule 5-lipoxygenase inhibitor **8** in several steps according to the literature (Scheme 2).[18a] Furthermore, another novel MK-0633 of 5-lipoxygenase inhibitor could also be easily accessed with 4-arylcoumarin of **3am**.[18b] Overall, apart from traditional von Pechmann condensation, this method could afford an alternative to the preparation of 4-arylcoumarin core related pharmaceutical leading compounds.



Scheme 2. The preparation of 5-lipoxygenase inhibitors.

Conclusion

In summary, by using diaryliodonium(III) salts, the palladium-catalyzed arylation/cyclization of *ortho*-hydroxylcinnamate ester derivatives of activated alkenes has been developed. 4-arylated coumarin derivatives were synthesized in the yields of 40-95%. The applicability of this method with the aim to construction of relevant pharmaceutical agents of 5-lipoxygenase inhibitor was preliminary studied. More importantly, the method is very efficient and tolerant of a variety of substituents. In consideration with the importance of coumarin fragments, application of this method in preparation of the relevant compounds for further transformations is being actively explored in our laboratory, therefore, it is anticipated that some valuable chemicals could be produced by using this method in the future.

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Supplementary Material

Representative synthetic procedure, analytical data of products and NMR spectra.