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To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201901866

Link to VoR: http://dx.doi.org/10.1002/ejoc.201901866

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FULL PAPER

Cascade Synthesis of 4-Arylcoumarins: Pd-Catalyzed Arylations and Cyclizations with (*E*)-Ethyl 3-(2-hydroxyaryl)acrylates and Triarylantimony Difluorides

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Abstract: Herein we describe a simple general method for the synthesis of 4-arylcoumarins using pentavalent organoantimony compounds. The reactions of 3-(2-hydroxyaryl)acrylates with triarylantimony difluorides in the presence of $Pd(OAc)_2$ (10 mol%) and 2,2'-bipyridyl (10 mol%) at 80 ºC under aerobic conditions afforded 4-arylcoumarins in good-to-excellent yields. This protocol involves a cascade oxidative Heck-type arylation followed by cyclization, with all of the aryl groups in the triarylantimony difluoride transferred to the coupling products. Triarylantimony difluorides resulted in better outcomes than those obtained with other pentavalent organoantimony or bismuth compounds.

Introduction

Coumarin is an important building block for natural products and biologically active compounds.[1] Among these, 4-arylcoumarins have attracted significant interest because of their potential as biological and pharmaceutical therapeutic agents.[1e] As examples, compound **I**[2] exhibits potent cytotoxic activity on a CEM leukemia cell line, MK-0633 **II**[3] is a potent inhibitor of 5-lipoxygenase, dihalide **III**[4] is potently cytotoxic to a CA-4-resistant colon adenocarcinoma cell line, and compound **IV**[5] show modest activity against Mycobacterium tuberculosis strain H37Rv (Figure 1).

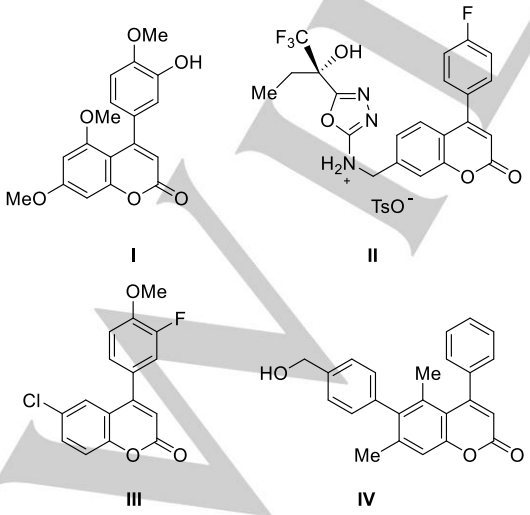

Figure 1. Biologically active 4-arylcoumarins

In addition, many methods for the synthesis of 4-arylcoumarins have been developed.[6] Pd-catalyzed coupling reactions, such as the Suzuki and Stille reactions[7] of 4-halogeno-, tosyl-, and triflate-substituted coumarins with arylboronic acids and stannanes, and the oxidative Heck reactions[8] of 4-*H* coumarins with arylboronic acids are among powerful tools for the synthesis of 4-arylcoumarins. Moreover, Pd-catalyzed domino reactions using oxidative Heck-type reactions of 3-(2-hydroxyaryl)acrylates followed by cyclization have recently been reported as effective methods for their synthesis. In 2005, Cacchi et al. reported the pioneering domino reactions of 3-(2-hydroxyaryl)acrylates with aryl halides in the presence of $Pd(OAc)_2$ (5 mol%) in a molten mixture of *n*-Bu_4NOAc and *n*-Bu_4NBr at 100 ºC.[9] Correia et al. reported the reactions of 3-(2-hydroxyaryl)acrylates with arenediazonium salts using $Pd(OAc)_2$ (10 mol%) in the presence $CaCO_3$ (1 equiv.) as a base.[10] Wang and Ramón independently developed similar reactions using diaryliodonium tetrafluoroborates and triflates as aryl sources in the presence of $Pd(OAc)_2$ (10 mol%) and PdO-Fe_3O_4 (2.5 mol%).[11,12] In 2018, Chen et al. reported an improved method using aryl iodides in the presence of 10 mol% $PdCl_2(CH_3CN)_2$ and 2 equiv. of NaOAc in water.[13] While, these methods are complementary, each reaction has several drawbacks in terms of substrate scope and efficiency; hence, the development of new arylation methods is a continuing requirement. In particular, there are few universal highly efficient methods for installing of electron-deficient aryl groups at the 4-position of coumarin using this type reaction.

Pd-catalyzed coupling reactions using organoantimony compounds have recently received attention.[14] Among these, pentavalent organoantimony compounds such as triarylantimony dicarboxylates $\{Ar_3Sb[OC(O)R]_2\}$ and tetraphenyantimony carboxylates $\{Ph_4Sb[OC(O)R]\}$ act as effective arylating agents in Pd-catalyzed Heck-type reactions.[15] Moreover, triarylantimony diacetates $[Ar_3Sb(OAc)_2]$ and dichlorides $[Ph_3SbCl_2]$ have been reported as aryl donors for Stille-type reactions.[16] We have also developed $Ar_3Sb(OAc)_2$ as efficient aryl donors in base-free Suzuki-type reactions and Cu- and base-free Sonogashira-type reactions.[17] Moreover, we recently showed that triarylantimony difluorides (Ar_3SbF_2) serve as arylating reagents for the Pd-catalyzed *β*-selective C–H arylation of thiophenes.[18] However, many of these reactions require to be improved due to the low atomic efficiency of substituents on antimony. Moreover, to the best of our knowledge, there are no reports of domino reaction for the synthesis of heterocycles using organoantimony compounds. Herein, we report a Pd-catalyzed

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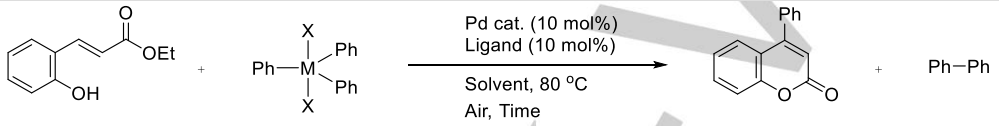
reaction for the synthesis of 4-arylcoumarins using (*E*)-ethyl 3-(2-hydroxyaryl)acrylates with Ar_3SbF_2 under aerobic condition in the absence of a base. The overall process is a cascade reaction involving oxidative Heck-type arylation followed by cyclization; Ar_3SbF_2 was found to be an atom economical and superior agent for introducing an aryl group at the 4-position of coumarin.

Results and Discussion

We initially focused our attention on determining the optimal conditions for the synthesis of 4-phenylcoumarin **10** using (*E*)-ethyl 3-(2-hydroxyphenyl)acrylate **1a** and various organoantimony and bismuth reagents **2a–9**. The results of experiments designed to identify suitable substrates, catalysts, ligands, and solvents for the cascade reaction are summarized in Table 1. We first reacted **1a** (0.75 mmol) with Ph_3SbF_2 **2a** (0.25 mmol) and $Pd(OAc)_2$ (10 mol%) in DMF at 80 ºC under aerobic conditions using the catalytic system developed by Han and Wang[11] (entry 1); however, biphenyl **11** was obtained as the main product and the expected coumarin derivative **10** was produced in low yield (16%). The effect of the ligand was next examined under the same conditions (entries 2–8); the addition of a ligand was found to be effective, with 2,2'-bipyridyl giving the best result (entry 4). Several commercially available Pd catalysts were also screened (entries 4 and 9–13) but $Pd(OAc)_2$ provided the best outcomes in terms of the yield of **10** (entry 4). Solvent screening revealed that the reaction proceeded efficiently in DMF (92%), NMP (86%), DMSO (83%), DMA (71%), and 1,2-DCE (69%), whereas 1,4-dioxane, and toluene were inefficient reaction solvents (entries 4 and 14–20). The product was obtained in low yield when the reaction was carried out under argon or oxygen (entries 21 and 22).

Table 1. Pd-catalyzed reaction of (*E*)-ethyl 3-(2-hydroxyphenyl)acrylate **1a** with organoantimony and bismuth reagents.[a]



1a **2a-9** **10** **11**

Entry	Compd.	M	X	Pd cat.	Ligand [b]	Solvent	Time (h)	Yield (%)[c] **10**	**11**
1	**2a**	Sb	F	$Pd(OAc)_2$	---	DMF	24	16	79
2	**2a**	Sb	F	$Pd(OAc)_2$	1,10-phen	DMF	4	83	1
3	**2a**	Sb	F	$Pd(OAc)_2$	4,7-diMe-1,10-phen	DMF	24	80	18
4	**2a**	Sb	F	$Pd(OAc)_2$	2,2'-bipyridyl	DMF	3	92 (89)[d]	2
5	**2a**	Sb	F	$Pd(OAc)_2$	TMEDA	DMF	24	71	17
6	**2a**	Sb	F	$Pd(OAc)_2$	DMEDA	DMF	24	65	13
7	**2a**	Sb	F	$Pd(OAc)_2$	BINAP	DMF	24	13	59
8	**2a**	Sb	F	$Pd(OAc)_2$	triethylamine	DMF	24	23	66
9	**2a**	Sb	F	$PdCl_2$	2,2'-bipyridyl	DMF	24	---	---
10	**2a**	Sb	F	$PdCl_2(PPh_3)_2$	2,2'-bipyridyl	DMF	24	---	---
11	**2a**	Sb	F	$PdCl_2(CH_3CN)_2$	2,2'-bipyridyl	DMF	24	---	---
12	**2a**	Sb	F	$Pd(dba)_2$	2,2'-bipyridyl	DMF	3	70	---
13	**2a**	Sb	F	$Pd(PPh_3)_4$	2,2'-bipyridyl	DMF	24	77	7
14	**2a**	Sb	F	$Pd(OAc)_2$	2,2'-bipyridyl	NMP	4	86	2
15	**2a**	Sb	F	$Pd(OAc)_2$	2,2'-bipyridyl	DMSO	24	83	9
16	**2a**	Sb	F	$Pd(OAc)_2$	2,2'-bipyridyl	DMA	3	71	1
17	**2a**	Sb	F	$Pd(OAc)_2$	2,2'-bipyridyl	1,2-DCE	24	69	2
18	**2a**	Sb	F	$Pd(OAc)_2$	2,2'-bipyridyl	1,4-Dioxane	24	47	---
19	**2a**	Sb	F	$Pd(OAc)_2$	2,2'-bipyridyl	Toluene	24	45	---
20	**2a**	Sb	F	$Pd(OAc)_2$	2,2'-bipyridyl	CH_3CN	24	27	1
21[e]	**2a**	Sb	F	$Pd(OAc)_2$	2,2'-bipyridyl	DMF	24	22	7
22[f]	**2a**	Sb	F	$Pd(OAc)_2$	2,2'-bipyridyl	DMF	3	66	---
23[g]	**2a**	Sb	F	$Pd(OAc)_2$	2,2'-bipyridyl	DMF	6	37	25
24[h]	**2a**	Sb	F	$Pd(OAc)_2$	2,2'-bipyridyl	DMF	24	28	37
25	**3**	Sb	Cl	$Pd(OAc)_2$	2,2'-bipyridyl	DMF	24	---	---
26	**4**	Sb	OAc	$Pd(OAc)_2$	2,2'-bipyridyl	DMF	24	64	6
27	**5**	Sb	---	$Pd(OAc)_2$	2,2'-bipyridyl	DMF	24	4	---
28	**6**	Bi	F	$Pd(OAc)_2$	2,2'-bipyridyl	DMF	24	35	55
29	**7**	Bi	Cl	$Pd(OAc)_2$	2,2'-bipyridyl	DMF	24	11	19
30	**8**	Bi	OAc	$Pd(OAc)_2$	2,2'-bipyridyl	DMF	24	9	78
31	**9**	Bi	---	$Pd(OAc)_2$	2,2'-bipyridyl	DMF	24	19	30

[a] Reaction conditions: **1a** (0.75 mmol), **2a–9** (0.25 mmol).

[b] 1,10-phen = 1,10-phenanthroline; 4,7-diMe-1,10-phen = 4,7-dimethyl-1,10-phenanthroline; TMEDA = *N,N,N',N'*-tetramethylethylenediamine; DMEDA = *N,N'*-dimethylethylenediamine; BINAP = (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl.

[c] GC yield using dibenzyl as internal standard. The yield 100% corresponds to the formation of 0.75 mmol of **10** and 0.375 mmol of **11**.

[d] Isolated yield.

[e] Under Ar.

[f] Under O_2.

[g] $Pd(OAc)_2$ (5 mol%), 2,2'-bipyridyl (5 mol%).

[h] Added base (NaOAc: 0.75 mmol).

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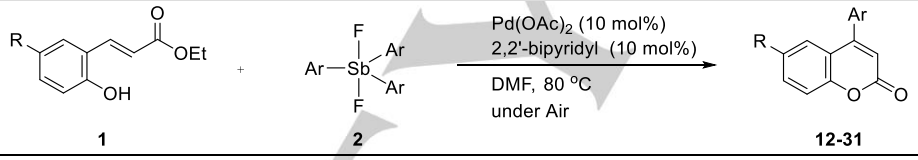
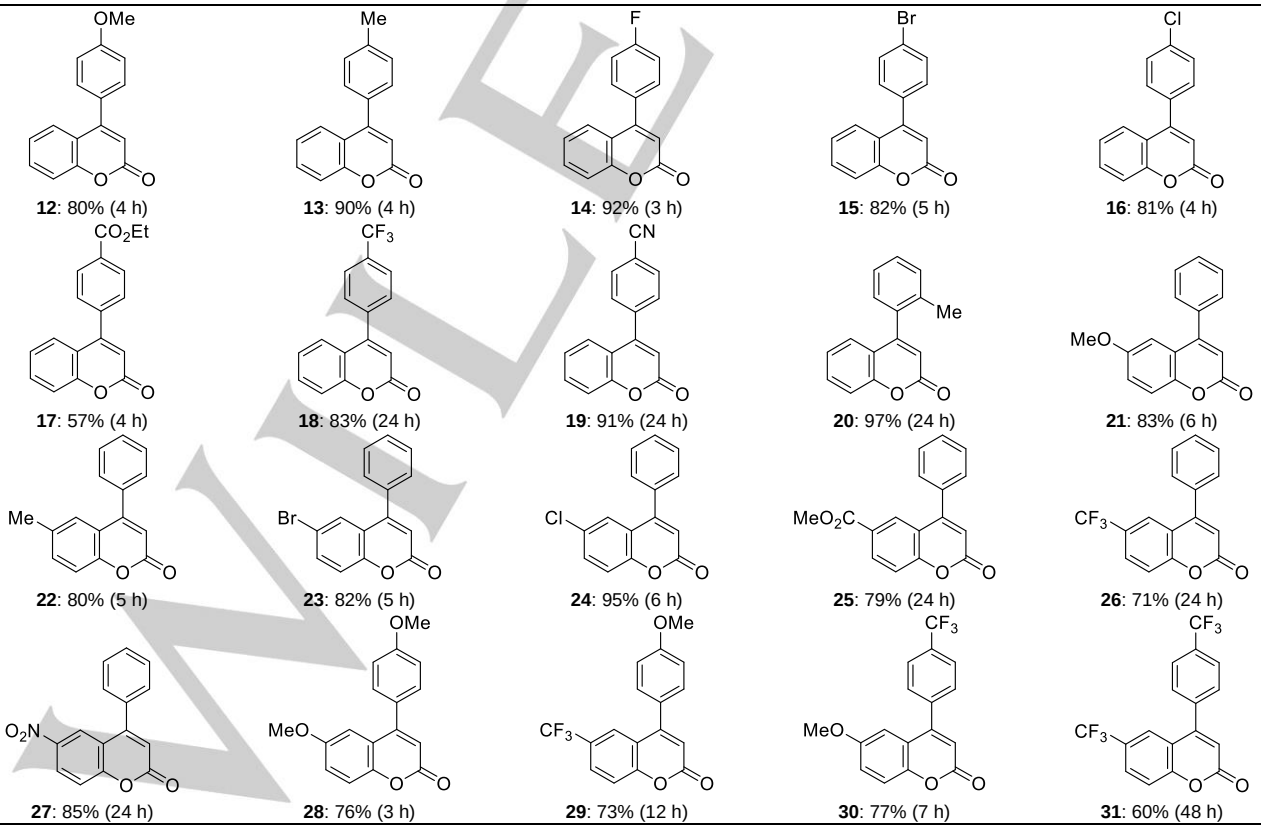
The reaction is easy to operate under aerobic conditions, and are therefore considered to be optimal for this reaction. Decreasing the $Pd(OAc)_2$ and 2,2'-bipyridyl loadings from 10 to 5 mol% resulted in a significantly lower yield of **10** (entry 23), and the yield of **10** was also significantly lower when a base, such as sodium acetate, was included in the reaction (entry 24). To evaluate the efficiencies of aryl donors, we examined the reactions of acrylate **1a** with organoantimony and bismuth reagents **2a–9** (entries 4 and 25–31). The reaction proceeded efficiently using Ph_3SbF_2 **2a** (92%) and triphenylantimony diacetate **4** (64%). On the other hand, the reaction did not proceed with antimony reagents **3** and **5**, and similar bismuth reagents **6**–**9** gave biphenyl **11** as the main product. The best result was obtained when acrylate **1a** (0.75 mmol) was treated with Ph_3SbF_2 (0.25 mmol) using $Pd(OAc)_2$ (10 mol%) and 2,2'-bipyridyl (10 mol%) as the catalytic system in DMF at 80 ºC under aerobic conditions. This reaction is characterized by all three phenyl groups on the antimony in **2a** participating in the reaction. Moreover, the known reaction of an aryl halides and an arenediazonium salts requires the addition of a base or an ammonium salt,[9,10,13] but current reaction does not need them.

To demonstrate the efficiency and generality of the above-mentioned protocol, the reactions of various hydroxyarylacrylates **1** (0.75 mmol) and Ar_3SbF_2 **2** (0.25 mmol) were investigated under the optimized conditions, the results of which are summarized in Table 2. The key arylating reagents, Ar_3SbF_2 **2a–j** were easily prepared by the oxidative fluorination of triarylstibanes (Ar_3Sb) with nitrosyl tetrafluoroborate according to our reported.[19] The yields of the products are based on all three aryl groups on the antimony in **2** participating in the reaction. The reaction of acrylate **1a** with Ar_3SbF_2 **2b–i** bearing electron-donating or electron-withdrawing groups on the phenyl ring afforded the corresponding products **12–16**, **18**, and **19** in good-to-excellent yields; the ester derivative **17** was the exception. In the reactions using aryl halides, diazonium salts, and iodonium salts as the aryl donors, the yields tend to be lower for substrates bearing an electron-withdrawing groups.[9-11] This protocol, which uses Ar_3SbF_2, gives 4-arylcoumarin derivatives substituted with electron-withdrawing groups, such as trifluoromethyl and nitro, on the phenyl ring in high yields, even though prolonged reactions are required. Moreover, a sterically hindered *ortho*-substituted Sb compound also gave the corresponding product **20** without any difficulty. Various hydroxyarylacrylates **1b–h** bearing different electron-donating and electron-withdrawing groups at the 5-position of the benzene ring were reacted with Ph_3SbF_2 **2a** to afford the corresponding products **21–27** in good-to-excellent yields. Among these results, the synthesis of 4-phenylcoumarin derivatives bearing electron-withdrawing groups, such as methoxycarbonyl, trifluoromethyl, and nitro, on the benzene ring of the coumarin is the first example of this type of cascade reaction. Moreover, the scrambling reactions of hydroxyarylacrylates **1b** and **g**, and Ar_3SbF_2

Table 2. Synthesis of 4-arylcoumarins by the reaction of (2-hydroxyaryl)acrylates **1** with Ar_3SbF_2 **2**. [a,b]



1 **2** **12-31**



[a] Reagents and conditions: **1** (0.75 mmol), Ar_3SbF_2 (0.25 mmol), $Pd(OAc)_2$ (0.025 mmol), and 2,2'-bipyridyl (0.025 mmol) in DMF at 80 °C under air.
[b] Isolated yield.

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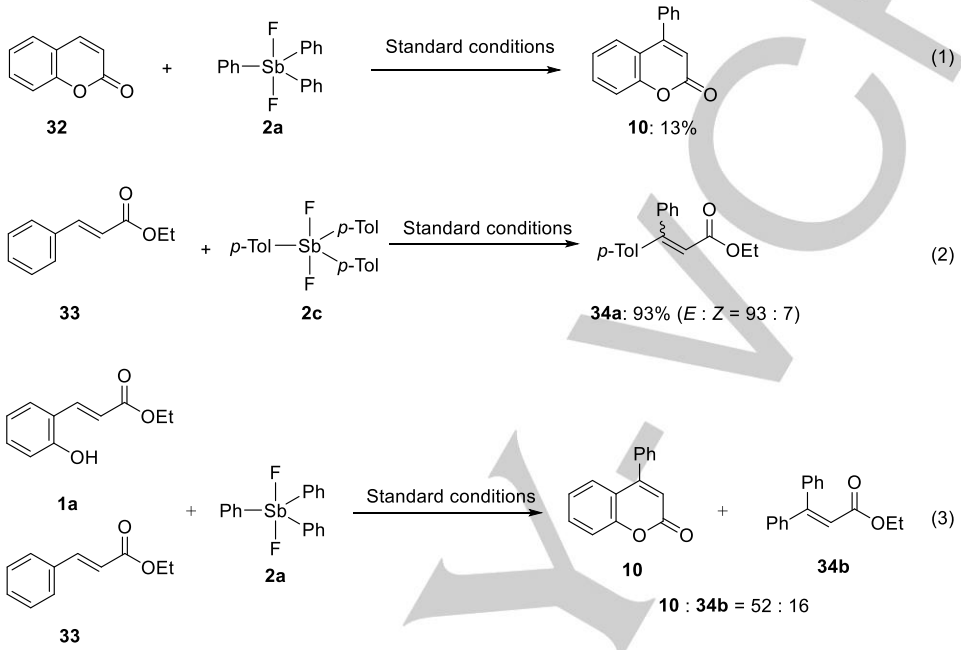
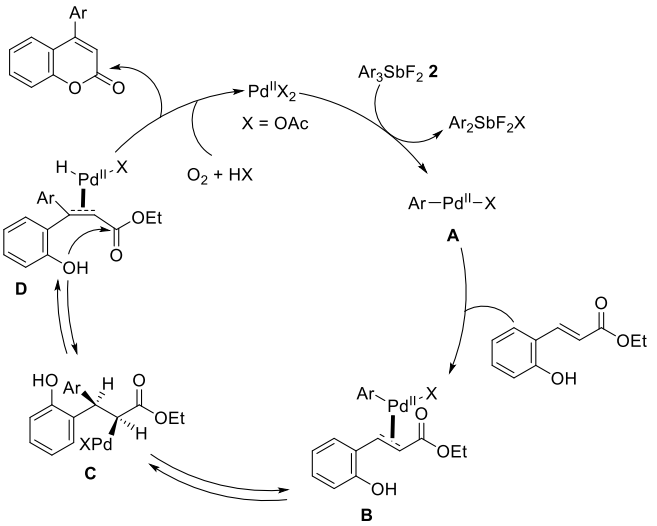
2b and **h** bearing methoxy and trifluoromethyl groups gave the corresponding products **28–31** in satisfactory yields, even though long reaction times are required when both contain electron-withdrawing groups.

A control experiment was carried out to investigate the reaction pathway and mechanisms. The reaction of coumarin **32** with Ph_3SbF_2 **2a** under the standard conditions gave **10** in only 13% yield [Scheme 1-(1)]. On the other hand, the reaction of ethyl cinnamate **33** with *p*-Tol_3SbF_2 **2c** afforded the Heck-type products **34a** in the yield of 93% [Scheme 1-(2)]. The stereochemistry of the main Heck-type product **34a** was determined by ^{1}H NMR spectroscopy to be *E* (*E* : *Z* = 93 : 7). These results suggest that a Heck-type arylation takes place in the first step of this reaction, followed by cyclization. Moreover, the competitive reaction of a 1:1:0.3 mixture of **1a**:**33**:**2a** gave 4-phenylcoumarine **10** and ethyl 3,3-diphenylacrylate **34b** in yields of 52% and 16% yield, respectively [Scheme 1-(3)].



Scheme 1. Control experiment

At the present, reaction mechanism operating in this cascade reaction process remains unclear. We consider that the mechanism would be similar to that of the cascade reaction for the synthesis of 4-arylcoumarins from 3-(2-hydroxyaryl)acrylates and diaryliodonium salts by Ramón et al.,[12] the Heck-type reaction of cinnamate derivatives with aryldiazonium salts by Correia et al.,[20] and the reaction of alkenes with arylsulfonyl hydrazines by Kwong et al. [21] The initial step in the reaction presumably involves the transmetalation between Pd^{II} catalyst and Ar_3SbF_2 to form $ArPd^{II}X$ **A** with the liberation of Ar_2SbF_2X. The coordination of **A** to the alkene produces π-complex **B**, followed by insertion to form the σ-complex **C**; subsequent *β*-hydride elimination forms complex **D**, which undergoes reductive elimination and cyclization to produce 4-arylcoumarin, Pd^0, and HX. At the end of the first cycle, Pd^0 is converted into $Pd^{II}X_2$ by aerobic oxidation. The formation of a Heck-adduct bearing a hydroxyl group at the 2-position of the benzene ring, namely ethyl (*E*)-3-(2-hydroxyphenyl)-3-phenylacrylate, in this reaction could not be confirmed on the NMR timescale. At present, we known that all the aryl groups of Ar_3SbF_2 participate in this reaction, but the second and third catalytic cycles remain unknown.



Scheme 2. Possible mechanisms

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Conclusion

In conclusion, we demonstrated a simple method for the synthesis of 4-arylcoumarins from hydroxycinnamates by oxidative Heck-arylation with triarylantimony difluorides, followed by cyclization. Triarylantimony difluoride was found to be an excellent arylating agent, with all three of its aryl groups involved under mild reaction condition in the absence of any additive such as a base. Furthermore, triarylantimony difluorides with various electron-donating and electron-withdrawing groups afforded the corresponding coumarin derivatives in satisfactory yields. Triarylantimony difluoride is a stable compound with low toxicity and is expected to be used as an organic synthesis reagent.[19,22] Detailed mechanistic studies into this cascade reaction, and the reactions of triarylantimony difluorides with other coupling partners, are in progress.

Experimental Section

General Information

All chromatographic separations were accomplished with Silica Gel 60N (Kanto Chemical Co., Inc.). Thin-layer chromatography (TLC) was performed with Macherey-Nagel Sil G25 UV_{254} pre-coated TLC plates. Reagents were used without further purification unless otherwise specified. Melting points were recorded on a Yanagimoto micro melting point hot-stage apparatus (MP-S3) and are not corrected. IR spectra were recorded on a SHIMADZU FTIR-8400S spectrophotometer and are reported in frequency of absorption (cm^{-1}). Only selected IR peaks are reported. ^{1}H NMR (TMS: δ = 0.00 as an internal standard), ^{13}C NMR ($CDCl_3$: δ = 77.00 as an internal standard) and ^{19}F NMR (trifluoromethylbenzene: δ = -64.0 as an external standard) spectra were recorded on a JEOL ECZ-400S (400 MHz, 100 MHz and 376 MHz) spectrometer in $CDCl_3$ unless otherwise stated. Mass spectra (MS) were obtained on a JEOL JMS-SX-102A instrument. HRMS (ESI) spectra were recorded on Agilent 6230 Accurate-Mass TOF LC/MS system using electrospray ionization. Triphenylantomony difluoride **2a–j** were prepared according to the reported procedures;[19] spectroscopic data are in accordance with the literature.

Synthesis of 4-arylchromenes

Triarylantiomony difluoride (0.25 mmol), 3-(2-hydroxyaryl) acrylates (0.75 mmol, 3 equiv.), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 10 mol%) and 2,2'-bipyridyl (3.9 mg, 0.025 mmol, 10 mol%) in DMF (1.5 mL) were heated at 80 ºC under an air atmosphere. After the reaction was complete, the mixture was allowed to cool to room temperature and diluted with CH_2Cl_2 (10 mL) and H_2O (15 mL). The reaction mixture was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layer was washed with brine (30 mL), dried over $MgSO_4$ and the solvent was removed in vacuo. The crude residue was purified by column chromatography on silica gel to afford **10, 12–31**. 4-arylchromenes **10**, **12–24**, **27** and **28** were prepared according to the reported procedures;[7d,8b,11,13] spectroscopic data are in accordance with the literature.

Methyl 4-phenyl-(2-oxo-*2H*-chromen)-6-carboxylate (25)

Colorless needles (166.1 mg, 79%); R_f = 0.6 (Hexane/EtOAc 3:1); m.p.: 163–165 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23–8.20 (m, 2H; Ar–H), 7.58–7.56 (m, 3H; Ar–H), 7.48–7.45 (m, 3H; Ar–H), 6.44 (s, 1H; Ar–H), 3.89 ppm (s, 3H; OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7 (C), 159.9 (C), 157.0 (C), 155.4 (C), 134.6 (C), 132.8 (CH), 130.0 (CH), 129.1 (CH), 128.4 (CH), 126.3 (C), 118.8 (C), 117.6 (CH), 115.8 (CH), 52.4 ppm (CH_3); IR (KBr): ν^- = 1717 (s) (C=O), 1734 (vs) cm^{-1} (C=O); HRMS (ESI): *m/z* calced for $C_{17}H_{12}O_4$ $[M]^+$: 280.0733; found: 280.0738.

6-Trifluoromethyl-4-phenyl-*2H*-chromen-2-one (26)

Colorless needles (154.6 mg, 71%); R_f = 0.4 (Hexane/EtOAc 5:1); m.p.: 127–129 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.77 (m, 2H; Ar–H), 7.60–7.57 (m, 3H; Ar–H), 7.52 (d, $J_{H,H}$ = 8.7 Hz, 1H; Ar–H), 7.47–7.43 (m, 2H; Ar–H), 6.47 ppm (s, 1H; Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6 (C), 156.0 (C), 154.9 (C), 134.2 (C), 130.2 (CH), 129.2 (CH), 128.5 (q, $^3J_{C,F}$ = 2.9 Hz, CH), 128.3 (CH), 126.7 (q, $^2J_{C,F}$ = 34 Hz, C), 124.5 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 123.5 (q, $^1J_{C,F}$ = 272 Hz, CF_3), 119.1 (C), 118.2 (CH), 116.4 ppm (CH); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.0 ppm; IR (KBr): ν^- = 1728 (vs) cm^{-1} (C=O); HRMS (ESI): *m/z* calced for $C_{16}H_9F_3O_2$ $[M]^+$: 290.0554; found: 290.0557.

6-Trifluoromethyl-4-(4-methoxyphenyl)-*2H*-chromen-2-one (29)

Colorless needles (175.3 mg, 73%); R_f = 0.5 (Hexane/CH_2Cl_2 1:5); m.p.: 123–125 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, $J_{H,H}$ = 1.4 Hz, 1H; Ar–H), 7.79 (dd, $J_{H,H}$ = 8.7, 2.3 Hz, 1H; Ar–H), 7.51 (d, $J_{H,H}$ = 8.7 Hz, 1H; Ar–H), 7.41 (dt, $J_{H,H}$ = 8.7, 3.2 Hz, 2H; Ar–H), 7.09 (dt, $J_{H,H}$ = 8.7, 2.7 Hz, 2H; Ar–H), 6.44 (s, 1H; Ar–H), 3.92 ppm (s, 3H; OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2 (C), 159.9 (C), 156.1 (C), 154.6 (C), 129.9 (CH), 128.4 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 126.6 (q, $^2J_{C,F}$ = 34 Hz, C), 126.5 (C), 124.6 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 123.6 (q, $^1J_{C,F}$ = 272 Hz, CF_3), 119.3 (C), 118.2 (CH), 115.7 (CH), 114.7 (CH), 55.5 ppm (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -61.9 ppm; IR (KBr): ν^- = 1773 (vs) cm^{-1} (C=O); HRMS (ESI): *m/z* calced for $C_{17}H_{11}F_3O_3$ $[M]^+$: 320.0656; found: 320.0660.

6-Methoxy-4-(4-trifluoromethylphenyl)-*2H*-chromen-2-one (30)

Colorless flakes (185.0 mg, 77%); R_f = 0.6 (Hexane/ EtOAc 5:2); m.p.: 184–185 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, $J_{H,H}$ = 8.2 Hz, 2H; Ar–H), 7.60 (d, $J_{H,H}$ = 7.8 Hz, 2H; Ar–H), 7.38 (d, $J_{H,H}$ = 9.1 Hz, 1H; Ar–H), 7.16 (dd, $J_{H,H}$ = 9.1, 3.2 Hz, 1H; Ar–H), 6.80 (d, $J_{H,H}$ = 3.2 Hz, 1H; Ar–H), 6.39 (s, 1H; Ar–H), 3.75 ppm (s, 3H; OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4 (C), 156.0 (C), 153.8 (C), 148.5 (C), 138.8 (C), 131.8 (q, $^2J_{C,F}$ = 33 Hz, C), 128.8 (CH), 126.0 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 123.7 (q, $^1J_{C,F}$ = 273 Hz, CF_3), 119.2 (CH), 118.8 (C), 118.4 (CH), 116.2 (CH), 109.6 (CH), 55.8 ppm (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.7 ppm; IR (KBr): ν^- = 1717 (vs) cm^{-1} (C=O); HRMS (ESI): *m/z* calced for $C_{17}H_{11}F_3O_3$ $[M]^+$: 320.0659; found: 320.0664.

6-Trifluoromethyl-4-(4-trifluoromethylphenyl)-*2H*-chromen-2-one (31)

Colorless prisms (161.2 mg, 60%); R_f = 0.3 (Hexane/EtOAc 10:1); m.p.: 113–115 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.82 (m, 3H; Ar–H), 7.65 (d, $J_{H,H}$ = 1.4 Hz, 1H; Ar–H), 7.61–7.54 (m, 3H; Ar–H), 6.49 ppm (s, 1H; Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1 (C), 156.0 (C), 153.4 (C), 137.8 (C), 132.4 (q, $^2J_{C,F}$ = 34 Hz, C), 129.0 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 128.8 (CH), 127.1 (q, $^2J_{C,F}$ = 34 Hz, C), 126.4 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 124.0 (q, $^3J_{C,F}$ = 3.9 Hz, CH), 123.7 (q, $^1J_{C,F}$ = 273 Hz, CF_3), 123.4 (q, $^1J_{C,F}$ = 273 Hz, CF_3), 118.6 (C), 118.4 (CH), 117.1 ppm (CH); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -63.3, -64.1 ppm; IR (KBr): ν^- = 1728 (vs) cm^{-1} (C=O); HRMS (ESI): *m/z* calced for $C_{17}H_8F_6O_2$ $[M]^+$: 358.0424; found: 358.0427.

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Acknowledgements

This research was supported by a Nagai Memorial Research Scholarship from the Pharmaceutical Society of Japan (Y. K.), and JSPS KAKENHI (Grant Number JP19K07005) (S. Y.). The authors also thank Aichi Gakuin University for generous financial support.

Keywords: antimony • acrylate • coumarin • palladium catalyst • cascade reaction

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10.1002/ejoc.201901866

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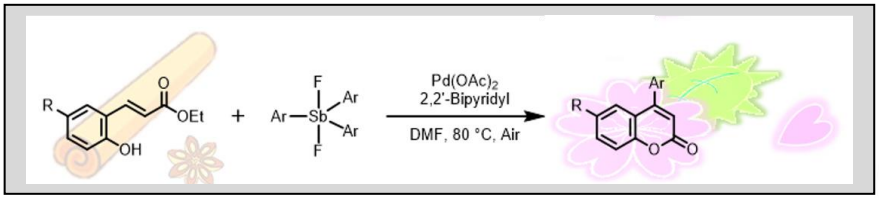

The reactions of 3-(2-hydroxyaryl)acrylates with triarylantimony difluorides in the presence of $Pd(OAc)_2$ and 2,2'-bipyridyl under aerobic conditions afforded 4-arylcoumarins in good-to-excellent yields with all of the aryl groups in the triarylantimony difluoride transferred to the coupling products. This protocol increases the synthetic scope of 4-arylcoumarins, especially those bearing electron-withdrawing groups that are more difficult to prepare using previous methods.

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