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One-pot preparation of 4-aryl-3-bromocoumarins from 4-aryl-2-propynoic acids with diaryliodonium salts, TBAB, and $Na_2S_2O_8$

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Full Research Paper

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Abstract

Various 4-aryl-3-bromocoumarins were smoothly obtained in moderate yields in one pot by treating 3-aryl-2-propynoic acids with diaryliodonium triflates and K_2CO_3 in the presence of CuCl, followed by the reaction with tetrabutylammonium bromide (TBAB) and $Na_2S_2O_8$. The obtained 3-bromo-4-phenylcoumarin was transformed into 4-phenylcoumarin derivatives bearing C–H, C–S, C–N, and C–C bonds at 3-position.

Introduction

Coumarin is a benzo-α-pyrone and one of the typical heterocyclic compounds. The importance of coumarins arises from the fact that the coumarin skeleton is present in many natural products extracted from plants [1-3] and some of them show potent pharmacological activities, such as antidepressant [4], antimicrobial [5,6], antioxidants [7,8], anti-inflammatory [9,10], antinociceptive [11], antitumor [1], antiasthmatic [12], and antiviral including anti-HIV [13,14].

Comprehensive synthetic studies of coumarins and their derivatives have been carried out [15,16]. Typically, coumarins are prepared by the acid-catalyzed condensation of 2-alkynoic acids and phenols or the condensation of β-ketoesters and phenols (the Pechmann condensation) [17]. Recent studies for the metal-catalyzed reactions for the synthesis of the coumarin skeleton are as follows: the $Yb(OTf)_3$-catalyzed microwave irradiation of phenols and propynoic acids [18], the $Pd(OAc)_2$-catalyzed

oxidative cyclocarbonylation of 2-vinylphenols at 110 °C [19], the $FeCl_3$-catalyzed areneselenyl-cyclization of aryl 2-alkynoates with ArSeSeAr at rt [20], and the Rh-catalyzed annulation of arylthiocarbamates with alkynes/AgOTf/$Cu(OAc)_2$ at 120 °C [21]. As examples of the transition-metal-free construction of the coumarin skeleton, the Brønsted acid-catalyzed reaction of phenols and propynoic acids [22] and the (−)-riboflavin-catalyzed photochemical reaction of cinnamic acids [23] were reported recently. Moreover, the use of radical cyclization for the construction of the coumarin skeleton has become widespread. Examples include the radical addition–cyclization reactions of aryl 2-alkynoates with $RC(=O)CO_2H/AgNO_3$(cat.)/$K_2S_2O_8$ at 60 °C [24], with $Cu(OAc)_2$/1-trifluoromethyl-3,3-dimethyl-1,2-benziodoxole (Togni reagent) at 60 °C [25], with $R_2P(=O)H/Ag_2CO_3$(cat.)/$Mg(NO_3)_2$ at 100 °C [26], with $BrCF_2CO_2Et$/*fac*-Ir(ppy)$_3$(cat.) under irradiation at rt [27], with R-CH=O/(*n*-Bu)$_4$NBr (TBAB, cat.)/$K_2S_2O_8$ at 90 °C [28], with $ArSO_2H$/Eosin Y(cat.)/*tert*-butyl hydrogen peroxide (TBHP) at rt [29], and with $ArSO_2NHNH_2$/*n*-Bu_4NI(cat.)/TBHP at 80 °C [30].

In addition, the formation of coumarins via the bromine-radical-mediated reaction of aryl 2-alkynoates with TBAB/$K_2S_2O_8$ at 90 °C [31], the cyanomethyl-radical-mediated reaction of aryl 2-alkynoates with *tert*-butyl peroxybenzoate (TBPB)/acetonitrile at 130 °C [32], the sunlight-promoted reaction of aryl 2-alkynoates with *N*-iodosuccinimide (NIS) at rt [33], and the visible-light-mediated reaction of aryl 2-alkynoates with *N*-bromosuccinimide (NBS) at rt [34], where those reactions proceed via radical spiro-cyclization and then radical 1,2-carboxyl group migration, were reported.

On the other hand, diaryliodonium salts are very useful for the C-arylation of active CH groups, the O-arylation of OH groups, and the N-arylation of NH groups under metal-free conditions [35-39]. For example, treatment of arenecarboxylic acids and alkanecarboxylic acids with diaryliodonium salts and *t*-BuOK under toluene refluxing conditions provides the corresponding aryl carboxylates in good yields [40,41]. However, the O-arylation of 2-alkynoic acids, which are much more acidic than arenecarboxylic acids and alkanecarboxylic acids, and therefore, the conjugate bases of 2-alkynoic acids are much less nucleophilic than those of arenecarboxylic acids and alkanecarboxylic acids, was not studied. On the other hand, it is known that 4-arylcoumarins have antitumor activity [42]. Therefore, the one-pot preparation of 4-arylcoumarins from 3-aryl-2-alkynoic acids via aryl esters and cyclization is attractive and important.

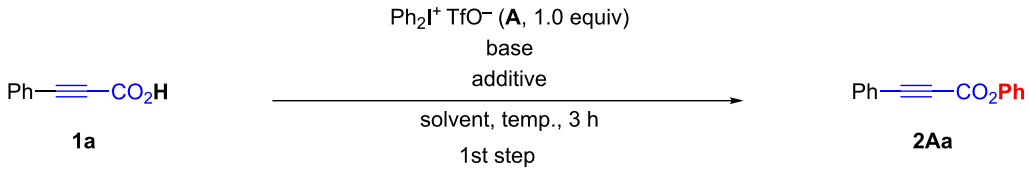
Here, as part of our ongoing investigation of the synthetic use of diaryliodonium salts for the preparation of heterocyclic compounds [43-46], we would like to report an efficient one-pot preparation of 4-aryl-3-bromocoumarins by treatment of 3-aryl-2-propynoic acids with diaryliodonium triflate in the presence of a base, followed by the reaction with tetrabutylammonium bromide (TBAB) and $Na_2S_2O_8$ in a mixture of 1,2-dichloroethane and water [31].

Results and Discussion

First, treatment of 3-phenyl-2-propynoic acid (**1a**, 0.5 mmol) with diphenyliodonium triflate (**A**, 1.0 equiv) in the presence of CuCl (5 mol %) and K_2CO_3 (1.0 equiv) in dichloromethane (3.0 mL) at 40 °C based on a previous report [46] gave phenyl 3-phenyl-2-propynoate (**2Aa**) in 46% yield, as shown in Table 1, entry 1. When the amount of the solvent was increased to 7.5 mL under the same conditions, the yield of phenyl ester **2Aa** was increased to 74% (Table 1, entry 2). Under the same conditions, the base was changed to NaH, Cs_2CO_3, *t*-BuOK, $NaNH_2$, and K_3PO_4 instead of K_2CO_3. However, the yield of phenyl ester **2Aa** was moderate to low (Table 1, entries 3–7). When the amount of K_2CO_3 was reduced to 0.5 equiv under the same conditions as those in entry 2, the yield of phenyl ester **2Aa** was increased to 80% (Table 1, entry 8). When CuCl was changed to CuI and CuBr, the difference of the yield of phenyl ester **2Aa** was small, but CuCl gave the highest yield (Table 1, entries 8–10). Then, the reaction temperature was changed to 0 °C, rt, 50 °C, and 60 °C under the same conditions as those in entry 8, and phenyl ester **2Aa** was obtained in 83% yield at 50 °C (Table 1, entries 11–14). On the other hand, when the present reaction was carried out without CuCl under the same conditions, phenyl ester **2Aa** was not obtained at all (Table 1, entry 15).

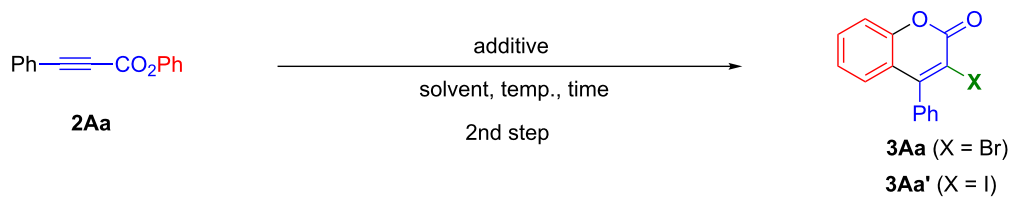
Then, the iodocyclization of phenyl ester **2Aa** to 3-iodo-4-phenylcoumarin (**3Aa'**) with *N*-iodosuccinimide (NIS, 2.0 equiv)/$BF_3{\cdot}Et_2O$ (2.0 or 1.1 equiv) was studied based on the previous reports [45,46], as shown in Table 2. However, 3-iodo-4-phenylcoumarin (**3Aa'**) was obtained in low to moderate yields (Table 2, entries 1 and 2). To improve the yield of 3-halo-4-phenylcoumarins **3Aa** or **3Aa'**, the halocyclization of **2Aa** with *N*-bromosuccinimide (NBS, 2.0 equiv)/$BF_3{\cdot}Et_2O$ (1.1 equiv), with 1,3-diiodo-5,5-dimethylhydantoin (DIH, 2.0 equiv)/$BF_3{\cdot}Et_2O$ (1.1 equiv), and with 1,3-dibromo-5,5-dimethylhydantoin (DBH, 2.0 equiv)/$BF_3{\cdot}Et_2O$ (1.1 equiv) was carried out to form 3-bromo-4-phenylcoumarin (**3Aa**), 3-iodo-4-phenylcoumarin (**3Aa'**), and 3-bromo-4-phenylcoumarin (**3Aa**) in 28, 49 and 46% yields, respectively (Table 2, entries 3–5). The treatment of phenyl ester **2Aa** with molecular iodine (2.0 equiv)/K_2CO_3 (2.0 equiv) did not generate 3-iodo-4-phenylcoumarin (**3Aa'**) at all (Table 2, entry 6). Thus, the iodonium-based or bromonium-based electrophilic cyclization of phenyl 3-phenyl-2-propynoate (**2Aa**) does not proceed effi-

Table 1: O-Phenylation of 3-phenyl-2-propynoic acid (**1a**) with diphenyliodonium triflate (**A**).



entry	base	solvent (mL)	additive (mol %)	temp. (°C)	yield (%)
1	K_2CO_3 (1.0)	CH_2Cl_2 (3.0)	CuCl (5)	40	46
2	K_2CO_3 (1.0)	CH_2Cl_2 (7.5)	CuCl (5)	40	74
3	NaH (1.0)	CH_2Cl_2 (7.5)	CuCl (5)	40	24
4	Cs_2CO_3 (0.5)	CH_2Cl_2 (7.5)	CuCl (5)	40	17
5	*t*-BuOK (1.0)	CH_2Cl_2 (7.5)	CuCl (5)	40	48
6	$NaNH_2$ (1.0)	CH_2Cl_2 (7.5)	CuCl (5)	40	9
7	K_3PO_4 (1.0)	CH_2Cl_2 (7.5)	CuCl (5)	40	30
8	K_2CO_3 (0.5)	CH_2Cl_2 (7.5)	CuCl (5)	40	80
9	K_2CO_3 (0.5)	CH_2Cl_2 (7.5)	CuI (5)	40	78
10	K_2CO_3 (0.5)	CH_2Cl_2 (7.5)	CuBr (5)	40	77
11	K_2CO_3 (0.5)	CH_2Cl_2 (7.5)	CuCl (5)	0	11
12	K_2CO_3 (0.5)	CH_2Cl_2 (7.5)	CuCl (5)	rt	71
13	**K_2CO_3 (0.5)**	**DCE (7.5)**	**CuCl (5)**	**50**	**83**
14	K_2CO_3 (0.5)	DCE (7.5)	CuCl (5)	60	75
15	K_2CO_3 (0.5)	DCE (7.5)	–	50	0

Table 2: Halocyclization of phenyl 3-phenyl-2-propynoate (**2Aa**) to 3-halo-4-phenylcoumarins **3Aa** and **3Aa'**.



entry	additive (equiv)	solvent (mL)	temp. (°C)	time (h)	yield (%)
1	NIS (2.0), $BF_3{\cdot}Et_2O$ (2.0)	CH_2Cl_2 (3.0)	40	1	36 (**3Aa'**)
2	NIS (2.0), $BF_3{\cdot}Et_2O$ (1.1)	CH_2Cl_2 (3.0)	40	1	45 (**3Aa'**)
3	NBS (2.0), $BF_3{\cdot}Et_2O$ (1.1)	CH_2Cl_2 (3.0)	40	1	28 (**3Aa**)
4	DIH (2.0), $BF_3{\cdot}Et_2O$ (1.1)	CH_2Cl_2 (3.0)	40	1	49 (**3Aa'**)
5	DBH (2.0), $BF_3{\cdot}Et_2O$ (1.1)	CH_2Cl_2 (3.0)	40	1	46 (**3Aa**)
6	I_2 (2.0), K_2CO_3 (2.0)	CH_3CN (3.0)	40	1	0
7	TBAB (2.0), $Na_2S_2O_8$ (1.5)	DCE:H_2O (1:1, 5.0)	90	19	68 (**3Aa**)
8	TBAI (2.0), $Na_2S_2O_8$ (1.5)	DCE:H_2O (1:1, 5.0)	90	19	45 (**3Aa'**)
9	**TBAB (2.0), $Na_2S_2O_8$ (1.0)**	**DCE:H_2O (1:1, 5.0)**	**90**	**19**	**79** (**3Aa**)
10	TBAB (2.0), $Na_2S_2O_8$ (2.0)	DCE:H_2O (1:1, 5.0)	90	19	51 (**3Aa**)
11	TBAB (2.5), $Na_2S_2O_8$ (1.0)	DCE:H_2O (1:1, 5.0)	90	19	69 (**3Aa**)
12	TBAB (2.0), $K_2S_2O_8$ (1.0)	DCE:H_2O (1:1, 5.0)	90	19	71 (**3Aa**)
13	TBAB (2.0), $(NH_4)_2S_2O_8$ (1.0)	DCE:H_2O (1:1, 5.0)	90	19	69 (**3Aa**)
14	TBAB (2.0), Oxone® (1.0)	DCE:H_2O (1:1, 5.0)	90	19	37 (**3Aa**)

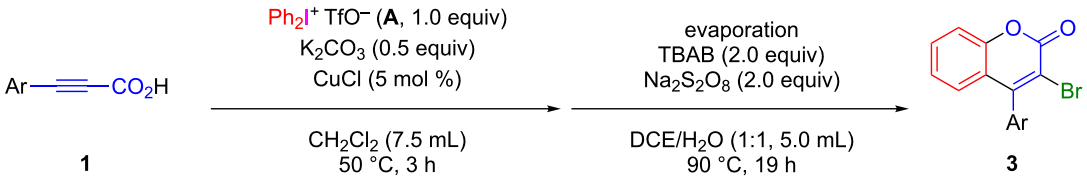
ciently. Then, the bromo-radical-based cyclization of phenyl 3-phenyl-2-propynoate (**2Aa**) with tetrabutylammonium bromide (TBAB, 2.0 equiv)/$Na_2S_2O_8$ (1.5 equiv) [31] in a mixture of 1,2-dichloroethane (DCE) and water at 90 °C was carried out to give 3-bromo-4-phenylcoumarin (**3Aa**) in 68% yield (Table 2, entry 7). When the iodocyclization of phenyl ester **2Aa** with tetrabutylammonium iodide (TBAI, 2.0 equiv)/$Na_2S_2O_8$ (1.5 equiv) was carried out, the yield of iodocyclization product **3Aa'** was decreased to 45% (Table 2, entry 8). When the bromocyclization of phenyl ester **2Aa** with TBAB (2.0 equiv)/$Na_2S_2O_8$ (1.0 equiv) in a mixture of DCE and water at 90 °C was carried out, 3-bromo-4-phenylcoumarin (**3Aa**) was obtained in 79% yield (Table 2, entry 9). When $Na_2S_2O_8$ was increased to 2.0 equivalents or TBAB was increased to 2.5 equivalents under the same conditions, the yields of 3-bromo-4-phenylcoumarin (**3Aa**) were decreased to 51 and 69%, respectively (Table 2, entries 10 and 11). Moreover, when $Na_2S_2O_8$ was changed to $K_2S_2O_8$, $(NH_4)_2S_2O_8$, and Oxone® ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$), the yields of 3-bromo-4-phenylcoumarin (**3Aa**) were decreased to 71, 69 and 37%, respectively (Table 2, entries 12–14). Thus, it was confirmed that the treatment of phenyl ester **2Aa** with TBAB (2.0 equiv)/$Na_2S_2O_8$ (1.0 equiv) in a mixture of DCE and water at 90 °C for 19 h was the most efficient, giving 3-bromo-4-phenylcoumarin (**3Aa**) in good yield (Table 2, entry 9).

Finally, based on the results in Table 1 and Table 2, the one-pot preparation of 4-aryl-3-bromocoumarins **3** from 3-aryl-2-propynoic acids **1** was carried out. 3-Aryl-2-propynoic acids **1**, such as 3-phenyl-2-propynoic acid (**1a**), 3-(*o*-methylphenyl)-2-propynoic acid (**1b**), 3-(*m*-methylphenyl)-2-propynoic acid (**1c**), 3-(*p*-methylphenyl)-2-propynoic acid (**1d**), 3-(*p*-methoxyphenyl)-2-propynoic acid (**1e**), 3-(*p*-fluorophenyl)-2-propynoic acid (**1f**), 3-(*p*-chlorophenyl)-2-propynoic acid (**1g**), 3-(*o*-chlorophenyl)-2-propynoic acid (**1h**), 3-(*m*-chlorophenyl)-2-propynoic acid (**1i**), 3-(*p*-bromophenyl)-2-propynoic acid (**1j**), 3-(*p*-biphenyl)-2-propynoic acid (**1k**), 3-(naphthalen-2'-yl)-2-propynoic acid (**1l**), and 3-(naphthalen-1'-yl)-2-propynoic acid (**1m**), were treated with diphenyliodonium triflate (**A**, 1.0 equiv) in the presence of CuCl and K_2CO_3 in CH_2Cl_2 for 3 h under refluxing conditions. After removal of the solvent, the second-step treatment of the reaction mixture with TBAB (2.0 equiv) and $Na_2S_2O_8$ (2.0 equiv) in a mixture of DCE and water at 90 °C for 19 h gave 4-aryl-3-bromocoumarins **3Aa**–**3Am** in moderate yields, respectively, as shown in Scheme 1. As a gram-scale experiment, treatment of 3-phenyl-2-propynoic acid (**1a**, 8 mmol) with diphenyliodonium triflate **A** in the presence of CuCl and K_2CO_3 in CH_2Cl_2 for 3 h, followed by removal of the solvent and the reaction with TBAB and $Na_2S_2O_8$ in a mixture of DCE and water at 90 °C for 19 h gave 3-bromo-4-phenylcoumarin (**3Aa**) in 52% yield. For 3-aryl-2-propynoic acids bearing heteroaromatic groups, treatment of 3-(benzothiophen-2'-yl)-2-propynoic acid (**1n**) and 3-(benzofuran-2'-yl)-2-propynoic acid (**1o**) under the same procedure and conditions gave the corresponding coumarins **3An** and **3Ao** in moderate yields, respectively. Under the present procedure and conditions, use of 2-hexynoic acid (**1p**), a 3-alkyl-2-propynoic acid, provided 3-bromo-4-propylcoumarin (**3Ap**) in 42% yield, as shown in Scheme 1.

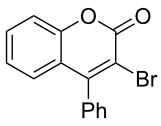
Then, other diaryliodonium triflates were used instead of diphenyliodonium triflate (**A**). Treatment of 3-phenyl-2-propynoic acid (**1a**) with diaryliodonium triflates (1.0 equiv), such as di(*p*-methylphenyl)iodonium triflate (**B**), di(*tert*-butylphenyl)iodonium triflate (**C**), di(*p*-chlorophenyl)iodonium triflate (**D**), and di(*p*-bromophenyl)iodonium triflate (**E**), in the presence of CuCl and K_2CO_3 in CH_2Cl_2 for 3 h under refluxing conditions, followed by removal of the solvent and the reaction with TBAB (2.0 equiv) and $Na_2S_2O_8$ (2.0 equiv) in a mixture of DCE and water at 90 °C for 19 h gave 3-bromo-4-phenylcoumarin derivatives **3Ba**–**3Ea** bearing methyl, *tert*-butyl, chloro, and bromo groups at 7-position in good to moderate yields, respectively, as shown in Scheme 2.

As regards the synthetic utilization of the products in the present one-pot reaction, treatment of 3-bromo-4-phenylcoumarin (**3Aa**) with Zn in ethanol under refluxing conditions gave 4-phenylcoumarin (**4Aa**) in 81% yield. Treatment of 3-bromo-4-phenylcoumarin (**3Aa**) with *p*-toluenethiol/*N,N'*-dimethylethylenediamine (DMEDA)/K_2CO_3 in the presence of CuI in toluene at refluxing temperature and with *p*-methoxybenzamide/DMEDA/K_2CO_3 in the presence of CuI in toluene at refluxing temperature generated 3-(4-methylbenzenesulfenyl)-4-phenylcoumarin (**5Aa**) and 3-(4-methoxylbenzoylamino)-4-phenylcoumarin (**6Aa**) in 62 and 51% yields, respectively. The Pd-catalyzed coupling reactions of 3-bromo-4-phenylcoumarin (**3Aa**) with 4-methylstyrene/K_2CO_3/$PdCl_2(Ph_3P)_2$, with phenylacetylene/$PdCl_2(Ph_3P)_2$/Et_3N and with $PhB(OH)_2$/K_2CO_3/$PdCl_2(Ph_3P)_2$ provided the corresponding C–C bonded coumarin derivatives **7Aa**, **8Aa**, and **9Aa** in 79, 60 and 76% yields, respectively (Scheme 3).

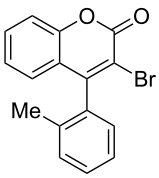
To support the present bromocyclization reaction to form 4-aryl-3-bromocoumarins with TBAB and $Na_2S_2O_8$ at the second step, the present one-pot preparation of 3-bromo-4-phenylcoumarin (**3Aa**) from 3-phenyl-2-propynoic acid (**1a**) was carried out in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl radical (TEMPO, 2.0 equiv) or 2,6-di(*tert*-butyl-*p*-cresol (BHT, 3.0 equiv) at the second step under the same procedure and conditions, but 3-bromo-4-phenylcoumarin (**3Aa**) was not obtained at all in both reactions. Thus, the present bromocyclization of the formed phenyl 3-phenyl-2-propynoate (**2Aa**)



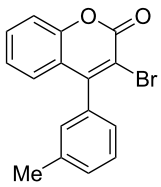
product, yield



3Aa (54%)
(52%)[a]



3Ab (57%)



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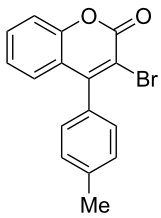

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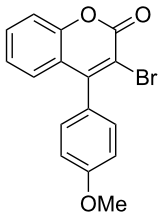

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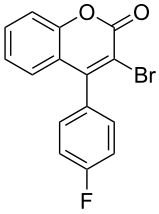

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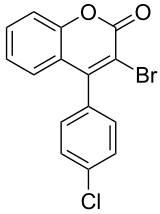

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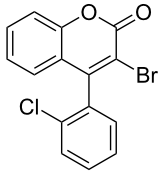

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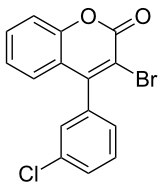

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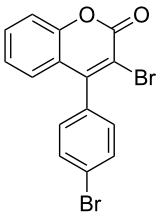
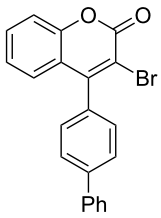
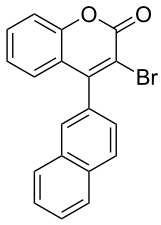


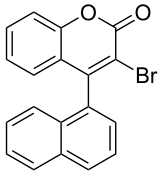
3Aj (51%)



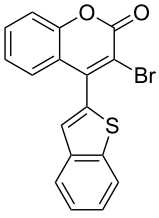
3Ak (57%)



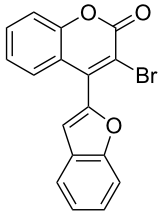
3Al (50%)



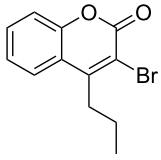
3Am (56%)



3An (46%)

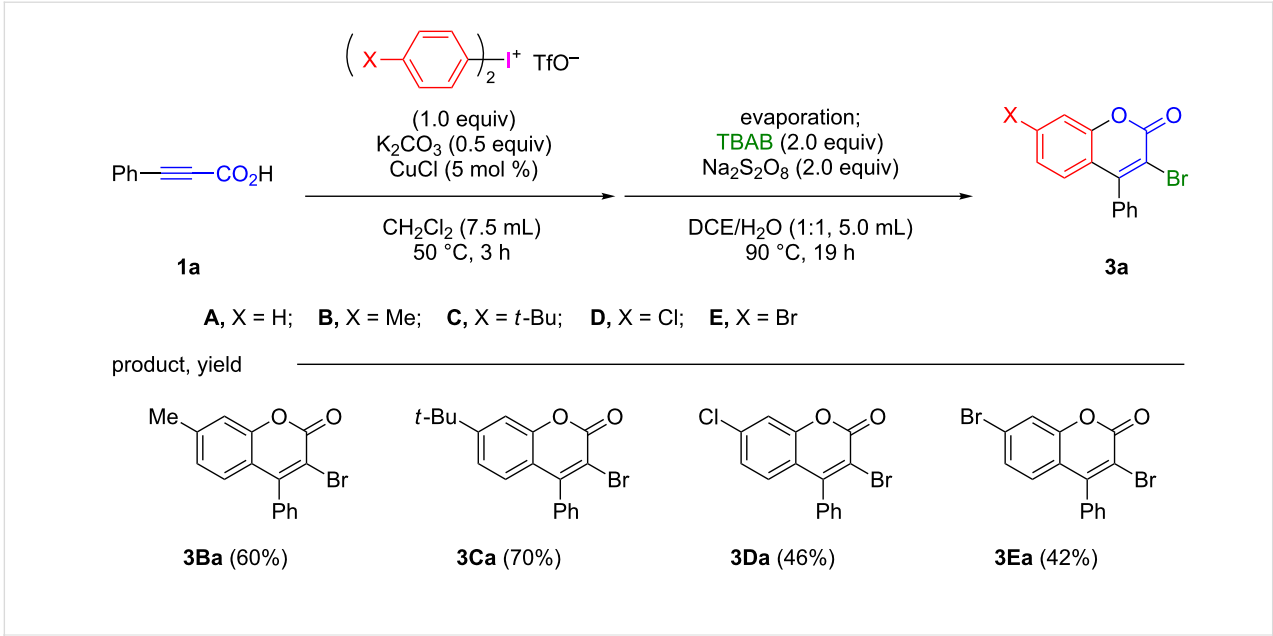


3Ao (43%)

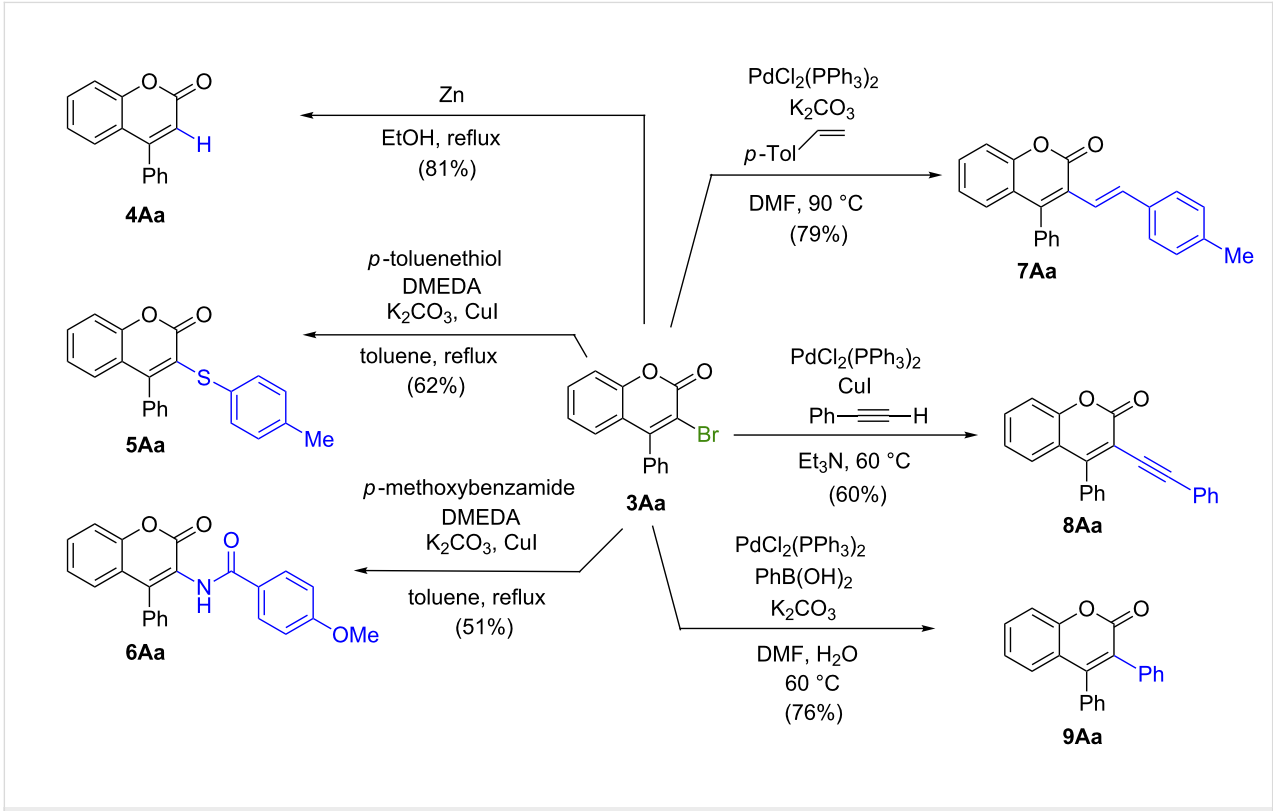


3Ap (42%)[b]

Scheme 1: One-pot preparation of 4-aryl-3-bromocoumarins **3** from 3-aryl-2-propynoic acids **1** with diphenyliodonium triflate (**A**).
[a]3-Phenyl-2-propynoic acid (**1a**, 8.0 mmol) was used. [b]The first reaction step was conducted with K_2CO_3 (1.0 equiv) under refluxing conditions.



Scheme 2: One-pot preparation of 3-bromo-4-phenylcoumarins **3a** from 3-phenyl-2-propynoic acid (**1a**) with daryliodonium triflates **B**–**E**.



Scheme 3: Derivatization of 3-bromo-4-phenylcoumarin.

with TBAB and $Na_2S_2O_8$ in a mixture of DCE and water is a radical-mediated bromocyclization reaction. X-ray crystallographic analysis of 3-bromo-7-chloro-4-phenylcoumarin (**3Da**), which was formed by the subsequent treatment of 3-phenyl-2-propynoic acid (**1a**) with di(*p*-chlorophenyl)iodonium triflate (**D**) and then with TBAB and $Na_2S_2O_8$, was carried out, as shown in Figure 1. Based on those results, the possible reaction pathway is shown in Scheme 4.

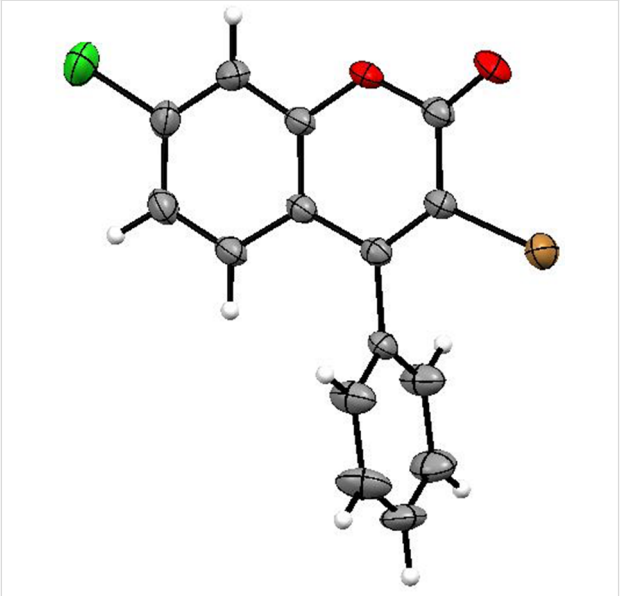
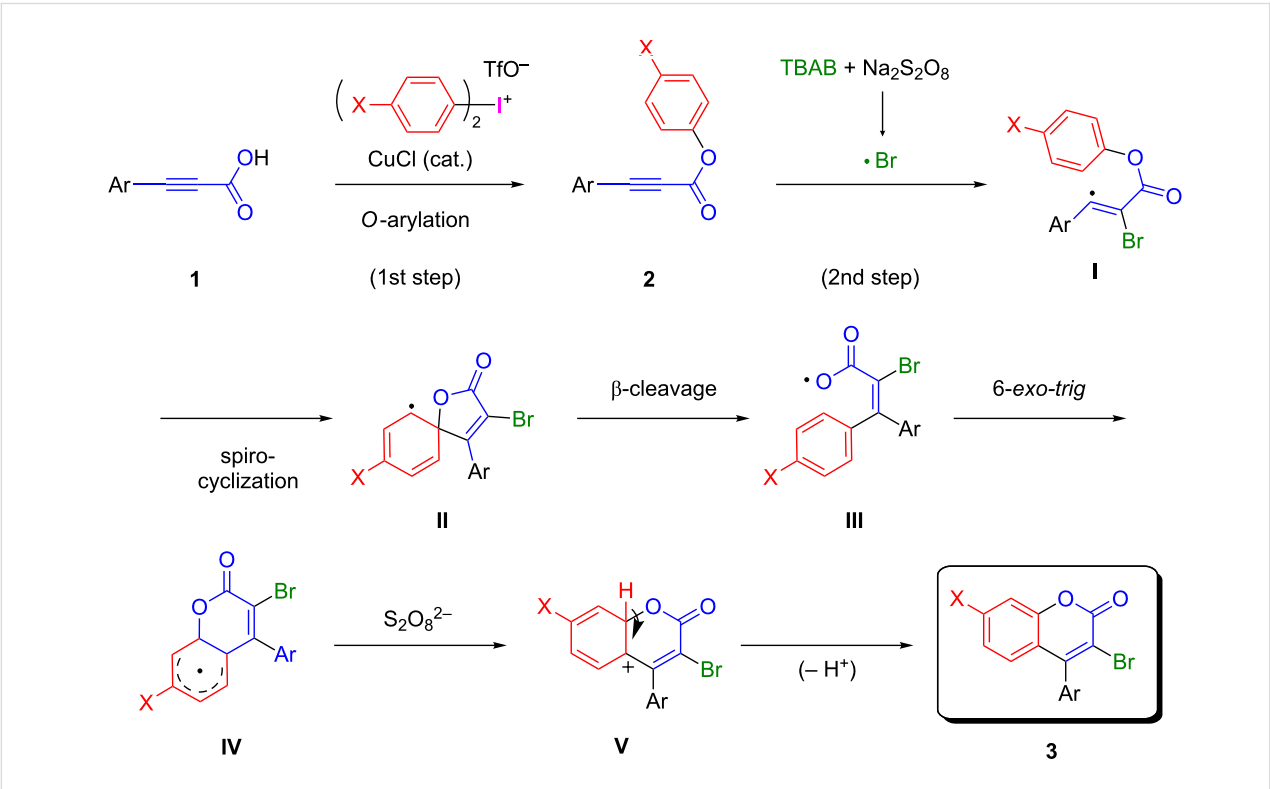


Figure 1: ORTEP of 3-bromo-7-chloro-4-phenylcoumarin (**3Da**).

The O-arylation of 3-aryl-2-propynoic acid **1** with diaryliodonium triflate in the presence of K_2CO_3 and CuCl occurs to form aryl 3-aryl-2-propynoate **2** (1st step). The bromocyclization of aryl 3-aryl-2-propynoate **2** with TBAB and $Na_2S_2O_8$ proceeds via a bromoradical addition to the triple bond to form very reactive vinyl radical **I** [47]. *Ipso*-cyclization of the vinyl radical **I** occurs to form spiro radical intermediate **II**. Then, β-cleavage of the spiro radical intermediate **II** proceeds to form carboxyl radical **III**. *6-Exo-trig* cyclization of the carboxyl radical **III** onto the aromatic ring takes place to form adduct radical **IV**, which would be rapidly oxidized by $Na_2S_2O_8$ to form cation intermediate **V**. Smooth deprotonation of cation intermediate **V** occurs to generate 4-aryl-3-bromocoumarin **3** (2nd step). The radical *ipso*-cyclization of the formed vinyl radical and its 1,2-carboxyl group migration agree with previously reported results [31-34].

Conclusion

The successive treatment of 3-aryl-2-propynoic acids with diaryliodonium triflates in the presence of K_2CO_3 and CuCl, and then with tetrabutylammonium bromide (TBAB) and $Na_2S_2O_8$ gave 4-aryl-3-bromocoumarins bearing hydrogen, methyl, *tert*-butyl, chloro, and bromo groups at 7-position in moderate yields, respectively. In one of the obtained 4-aryl-3-bromocoumarins, the C–Br bond of 3-bromo-4-phenylcoumarin was smoothly converted into 4-phenylcoumarins bearing C–H, C–S, C–N, and C–C bonds at 3-position. We believe the present method will be useful for the preparation of various 4-arylcoumarin derivatives due to its simple one-pot synthesis.



Scheme 4: Possible reaction pathway.

Supporting Information

Supporting Information File 1

NMR charts of all coumarin derivatives **3Aa**–**3Ap**, **3Ba**–**3Ea**, and **4Aa**–**9Aa**, and X-ray analytical data of **3Da**.
[https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-14-22-S1.pdf]

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References

1. Lacy, A. *Curr. Pharm. Des.* **2004,** *10,* 3797–3811. doi:10.2174/1381612043382693
2. Musa, M. A.; Badisa, V. L. D.; Latinwo, L. M.; Waryoba, C.; Ugochukwu, N. *Anticancer Res.* **2010,** *30,* 4613–4617.
3. Medina, F. G.; Marrero, J. G.; Macías-Alonso, M.; González, M. C.; Córdova-Guerrero, I.; García, A. G. T.; Osegueda-Robles, S. *Nat. Prod. Rep.* **2015,** *32,* 1472–1507. doi:10.1039/C4NP00162A
4. Sashidhara, K. V.; Kumar, A.; Chatterjee, M.; Rao, K. B.; Singh, S.; Verma, A. K.; Palit, G. *Bioorg. Med. Chem. Lett.* **2011,** *21,* 1937–1941. doi:10.1016/j.bmcl.2011.02.040
5. Ostrov, D. A.; Hernández-Prada, J. A.; Corsino, P. E.; Finton, K. A.; Le, N.; Rowe, T. C. *Antimicrob. Agents Chemother.* **2007,** *51,* 3688–3698. doi:10.1128/AAC.00392-07
6. Chimenti, F.; Bizzarri, B.; Bolasco, A.; Secci, D.; Chimenti, P.; Granese, A.; Carradori, S.; Rivanera, D.; Zicari, A.; Scaltrito, M. M.; Sisto, F. *Bioorg. Med. Chem. Lett.* **2010,** *20,* 4922–4926. doi:10.1016/j.bmcl.2010.06.048
7. Kostova, I.; Bhatia, S.; Grigorov, P.; Balkansky, S.; Parmar, V. S.; Prasad, A. K.; Saso, L. *Curr. Med. Chem.* **2011,** *18,* 3929–3951. doi:10.2174/092986711803414395
8. Xi, G.-L.; Liu, Z.-Q. *J. Agric. Food Chem.* **2015,** *63,* 3516–3523. doi:10.1021/acs.jafc.5b00399
9. Bansal, Y.; Sethi, P.; Bansal, G. *Med. Chem. Res.* **2013,** *22,* 3049–3060. doi:10.1007/s00044-012-0321-6
10. Fylaktakidou, K. C.; Hadjipavlou-Litina, D. J.; Litinas, K. E.; Nicolaides, D. N. *Curr. Pharm. Des.* **2004,** *10,* 3813–3833. doi:10.2174/1381612043382710
11. De Almeida Barros, T. A.; De Freitas, L. A. R.; Filho, J. M. B.; Nunes, X. P.; Giulietti, A. M.; De Souza, G. E.; Dos Santos, R. R.; Soares, M. B. P.; Villarreal, C. F. *J. Pharm. Pharmacol.* **2010,** *62,* 205–213. doi:10.1211/jpp.62.02.0008
12. Sánchez-Recillas, A.; Navarrete-Vázquez, G.; Hidalgo-Figueroa, S.; Rios, M. Y.; Ibarra-Barajas, M.; Estrada-Soto, S. *Eur. J. Med. Chem.* **2014,** *77,* 400–408. doi:10.1016/j.ejmech.2014.03.029
13. Hwu, J. R.; Lin, S.-Y.; Tsay, S.-C.; De Clercq, E.; Leyssen, P.; Neyts, J. *J. Med. Chem.* **2011,** *54,* 2114–2126. doi:10.1021/jm101337v
14. Ong, E. B. B.; Watanabe, N.; Saito, A.; Futamura, Y.; El Galil, K. H. A.; Koito, A.; Najimudin, N.; Osada, H. *J. Biol. Chem.* **2011,** *286,* 14049–14056. doi:10.1074/jbc.M110.185397
15. Vekariya, R. H.; Patel, H. D. *Synth. Commun.* **2014,** *44,* 2756–2788. doi:10.1080/00397911.2014.926374
16. Žalubovskis, R. *Chem. Heterocycl. Compd. (Engl. Transl.)* **2015,** *51,* 607–612. doi:10.1007/s10593-015-1748-8
17. Sethna, S.; Phadke, R. *Org. React.* **2011,** *7,* 1–58. doi:10.1002/0471264180.or007.01
18. Fiorito, S.; Epifano, F.; Taddeo, V. A.; Genovese, S. *Tetrahedron Lett.* **2016,** *57,* 2939–2942. doi:10.1016/j.tetlet.2016.05.087
19. Ferguson, J.; Zeng, F.; Alper, H. *Org. Lett.* **2012,** *14,* 5602–5605. doi:10.1021/ol302725x
20. Mantovani, A. C.; Goulart, T. A. C.; Back, D. F.; Menezes, P. H.; Zeni, G. *J. Org. Chem.* **2014,** *79,* 10526–10536. doi:10.1021/jo502199q
21. Zhao, Y.; Han, F.; Yang, L.; Xia, C. *Org. Lett.* **2015,** *17,* 1477–1480. doi:10.1021/acs.orglett.5b00364
22. Choi, H.; Kim, J.; Lee, K. *Tetrahedron Lett.* **2016,** *57,* 3600–3603. doi:10.1016/j.tetlet.2016.06.039
23. Metternich, J. B.; Gilmour, R. *J. Am. Chem. Soc.* **2016,** *138,* 1040–1045. doi:10.1021/jacs.5b12081
24. Yan, K.; Yang, D.; Wei, W.; Wang, F.; Shuai, Y.; Li, Q.; Wang, H. *J. Org. Chem.* **2015,** *80,* 1550–1556. doi:10.1021/jo502474z
25. Li, Y.; Lu, Y.; Qiu, G.; Ding, Q. *Org. Lett.* **2014,** *16,* 4240–4243. doi:10.1021/ol501939m
26. Mi, X.; Wang, C.; Huang, M.; Zhang, J.; Wu, Y.; Wu, Y. *Org. Lett.* **2014,** *16,* 3356–3359. doi:10.1021/ol5013839
27. Fu, W.; Zhu, M.; Zou, G.; Xu, C.; Wang, Z.; Ji, B. *J. Org. Chem.* **2015,** *80,* 4766–4770. doi:10.1021/acs.joc.5b00305
28. Mi, X.; Wang, C.; Huang, M.; Wu, Y.; Wu, Y. *J. Org. Chem.* **2015,** *80,* 148–155. doi:10.1021/jo502220b
29. Yang, W.; Yang, S.; Li, P.; Wang, L. *Chem. Commun.* **2015,** *51,* 7520–7523. doi:10.1039/C5CC00878F
30. Wei, W.; Wen, J.; Yang, D.; Guo, M.; Wang, Y.; You, J.; Wang, H. *Chem. Commun.* **2015,** *51,* 768–771. doi:10.1039/C4CC08117J
31. Qiu, G.; Liu, T.; Ding, Q. *Org. Chem. Front.* **2016,** *3,* 510–515. doi:10.1039/C6QO00041J
32. Yu, Y.; Zhuang, S.; Liu, P.; Sun, P. *J. Org. Chem.* **2016,** *81,* 11489–11495. doi:10.1021/acs.joc.6b02155
33. Ni, S.; Cao, J.; Mei, H.; Han, J.; Li, S.; Pan, Y. *Green Chem.* **2016,** *18,* 3935–3939. doi:10.1039/C6GC01027J
34. Feng, S.; Li, J.; Li, Z.; Sun, H.; Shi, H.; Wang, X.; Xie, X.; She, X. *Org. Biomol. Chem.* **2017,** *15,* 8820–8826. doi:10.1039/C7OB02199B
35. Aradi, K.; Tóth, B. L.; Tolnai, G. L.; Novák, Z. *Synlett* **2016,** *27,* 1456–1485. doi:10.1055/s-0035-1561369
36. Olofsson, B. *Top. Curr. Chem.* **2015,** *373,* 135–166. doi:10.1007/128_2015_661
37. Fañanás-Mastral, M. *Synthesis* **2017,** *49,* 1905–1930. doi:10.1055/s-0036-1589483
38. Stuart, D. R. *Chem. – Eur. J.* **2017,** *23,* 15852–15863. doi:10.1002/chem.201702732
39. Cao, C. K.; Sheng, J.; Chen, C. *Synthesis* **2017,** *49,* 5081–5092. doi:10.1055/s-0036-1589515
40. Petersen, T. B.; Khan, R.; Olofsson, B. *Org. Lett.* **2011,** *13,* 3462–3465. doi:10.1021/ol2012082
41. Jalalian, N.; Petersen, T. B.; Olofsson, B. *Chem. – Eur. J.* **2012,** *18,* 14140–14149. doi:10.1002/chem.201201645

42. Mutai, P.; Breuzard, G.; Pagano, A.; Allegro, D.; Peyrot, V.; Chibale, K. *Bioorg. Med. Chem.* **2017,** *25,* 1652–1665. doi:10.1016/j.bmc.2017.01.035
43. Kakinuma, Y.; Moriyama, K.; Togo, H. *Synthesis* **2013,** *45,* 183–188. doi:10.1055/s-0032-1316824
44. Miyagi, K.; Moriyama, K.; Togo, H. *Heterocycles* **2014,** *89,* 2122–2136. doi:10.3987/COM-14-13071
45. Sasaki, T.; Miyagi, K.; Moriyama, K.; Togo, H. *Org. Lett.* **2016,** *18,* 944–947. doi:10.1021/acs.orglett.5b03651
46. Sasaki, T.; Moriyama, K.; Togo, H. *J. Org. Chem.* **2017,** *82,* 11727–11734. doi:10.1021/acs.joc.7b01433
47. Togo, H. *Advanced Free Radicals for Organic Synthesis;* Chapter 3; Elsevier: Oxford, 2004; pp 75–94.

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