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Phenylation Reaction

N-Heterocyclic Carbene/Potassium Ion Cooperatively Catalyzed Phenylation Reactions of α,β-Unsaturated Acylazoliums

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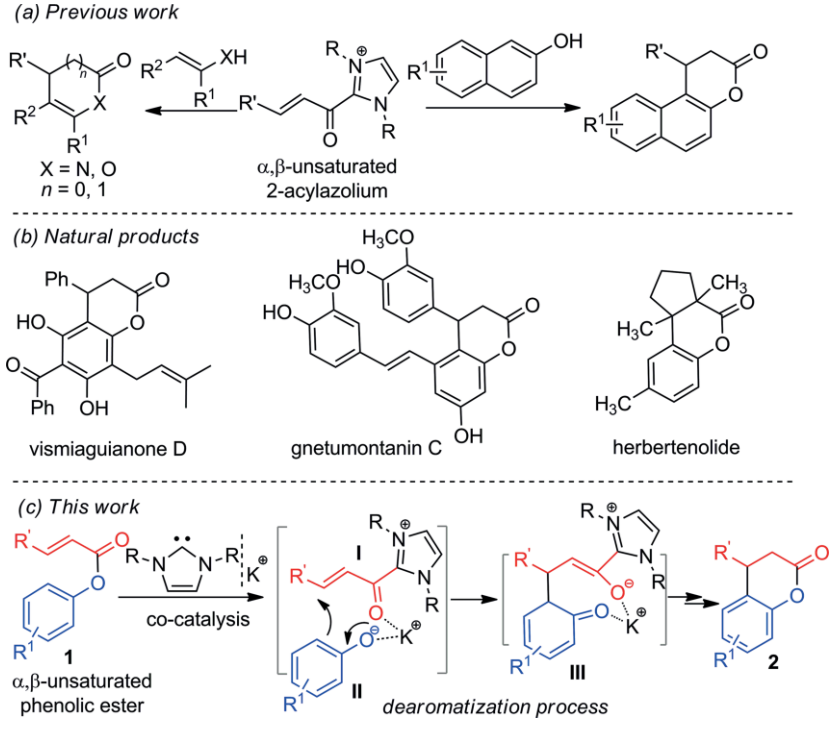
Abstract: A catalytic phenylation reaction of α,β-unsaturated acylazoliums with in-situ-generated phenolates was developed. A combination of N-heterocyclic carbene and potassium ion cooperatively catalyzed the generation of α,β-unsaturated acylazoliums and phenolates from α,β-unsaturated phenolic esters for the efficient [3+3] annulation, which involves a dearomatization–rearomatization process. The approach gives good yields and excellent regioselectivities, and the products could be easily converted into high-value polycyclic derivatives. Mechanistic studies demonstrated that the potassium ion plays a vital role in this reaction.

Introduction

N-Heterocyclic-carbene (NHC) catalysis of α,β-unsaturated carbonyl compounds has emerged as a powerful strategy for a variety of carbon–carbon and carbon–heteroatom bond-forming reactions.[1,2] The NHC-catalyzed generation of α,β-unsaturated acylazoliums from various α,β-unsaturated carbonyl compounds is now well established.[1a] As an important 1,3-biselectrophilic intermediate, α,β-unsaturated acylazoliums enable bond formation with nucleophiles both at the β-carbon atom and at the acyl position (Scheme 1, a).[3] The nucleophiles that have been most well investigated are reactive enol or enamine substrates, such as enolizable ketones and aldehydes,[4] silyl enol ethers,[5] sulfur ylides,[6] imines, and vinylogous amides.[7]



Scheme 1. Carbene/Lewis-acid-cocatalyzed phenylation reaction.

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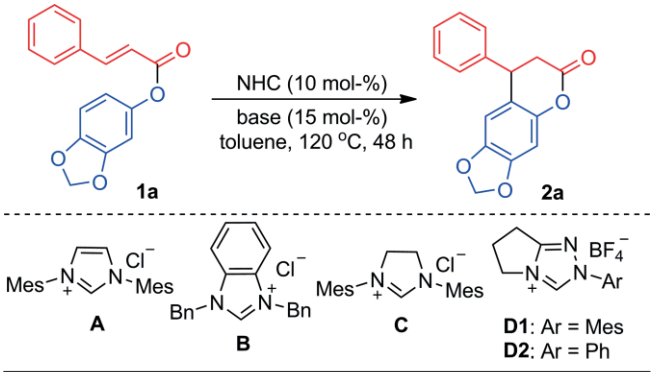
On the other hand, relatively unreactive nucleophiles, such as aromatic compounds, have been much less extensively investigated. In 2009, Bode and coworkers published an elegant paper on the NHC-catalyzed Claisen rearrangement of α,β-unsaturated acylazoliums with 2-naphthols as the nucleophile.[8a,8b] Later, Biju and coworkers reported a similar NHC-catalyzed annulation reaction with 2-bromoenals and β-naphthols as substrates.[8c] Recently, You and coworkers found that the asymmetric annulation of enals and 2-naphthols could be effectively achieved under oxidative conditions using new triazolium salts derived from L-phenylalanine.[8d] Phenols have proved to be more challenging motifs than naphthols due to the fact that the energy barrier for breaking the aromaticity of phenols is significantly higher than that of naphthol compounds.[9] Thus, the direct NHC-catalyzed reaction of α,β-unsaturated acylazoliums with simple phenols is of great value, but remains underdeveloped.

The 3,4-dihydrocoumarin core is widely found in a variety of biologically active molecules and natural products that show anti-inflammatory, antioxidant, anticoagulant, antibiotic, and antiviral properties (Scheme 1, b).[10] In this paper, we report a new carbene/potassium-ion-cocatalyzed annulation reaction of an α,β-unsaturated acylazolium with a phenolate as a nucleophile (Scheme 1, c). The key step involves the dearomatization[11] and 1,4-addition of phenolate **II** to α,β-unsaturated acylazolium intermediate **I**, which is generated by the addition of the NHC catalyst to α,β-unsaturated phenolic ester **1**.[12] The issue of dearomatization of the phenyl ring was addressed by invoking the synergy of the NHC organocatalysis and the potassium ion. The potassium ion may behave as a Lewis acid to both activate the phenolate and increase the electrophilicity of the α,β-unsaturated acylazolium.[13,14,4b,4f] Notably, although potassium salts have been widely used in NHC catalysis, to the best of our knowledge, the cocatalysis effect of the potassium ion has not been reported before. In addition to demonstrating a new nucleophilic phenylation reaction of the α,β-unsaturated acylazolium intermediate, this study opens a concise route to clinically significant 3,4-dihydrocoumarin derivatives.

Results and Discussion

We started by using α,β-unsaturated phenolic ester **1a**, derived from sesamol, as the model substrate (Table 1). *t*BuONa and toluene were chosen as the base and reaction solvent, respectively. When exposed to imidazolium catalyst IMes (**A**), the expected annulation product (i.e., **2a**) was formed in a low but encouraging 6 % yield (Table 1, entry 1). This proof-of-principle result clearly revealed that activation and dearomatization of the phenyl group using the NHC organocatalyst was feasible. Cs_2CO_3, MeONa, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), and NEt_3 were also tested as bases, but none of these led to any formation of **2a** (Table 1, entries 2–5). Inspired by the work of Scheidt[13,14a–14e] on Lewis acid cooperative catalysis, several Lewis acids were investigated to improve the reactivity. $Sc(OTf)_3$ showed only a small effect on the reaction yield (Table 1, entry 6), but LiCl was found to have a dramatic influence on the reaction outcome (Table 1, entry 7). The reaction yield increased to 65 % when KCl was used as the cocatalyst (Table 1, entry 8). We then found that using *t*BuOK instead of the combination of *t*BuONa and KCl gave a similar result (Table 1, entry 9). To evaluate the effect of the potassium ion on the reaction, the macrocyclic polyether 18-crown-6 was added to form a stable complex with K^+. The dramatic drop in yield shows that the potassium ion plays a vital role in this annulation reaction (Table 1, entry 10). The use of other potassium salts, such as K_3PO_4 and K_2CO_3, also gave moderate yields of the product (Table 1, entries 11 and 12). This observation further confirms our hypothesis on the NHC/K^+ cooperative catalysis. We then tested other NHC catalysts, but these gave results no better than that obtained with the IMes catalyst (Table 1, entries 13–16). No product was observed in the absence of an NHC catalyst (Table 1, entry 17). Elevating the reaction temperature did not improve the result (Table 1, entry 18), but increasing the catalyst loading to 20 mol-% gave a 71 % yield of **2a** after 48 h at 120 °C (Table 1, entry 19). Finally, we found that by using NHC catalyst **A** (20 mol-%) and *t*BuOK (30 mol-%) at 130 °C for only 24 h, a quantitative conversion of α,β-unsaturated phenolic ester **1a**

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



Entry	NHC	Base	Additive	Yield [%][b]
1	**A**	*t*BuONa	–	6
2	**A**	MeONa	–	n.d.
3	**A**	Cs_2CO_3	–	n.d.
4	**A**	DBU	–	n.d.
5	**A**	NEt_3	–	n.d.
6[c]	**A**	*t*BuONa	$Sc(OTf)_3$	<5
7[c]	**A**	*t*BuONa	LiCl	61
8[d]	**A**	*t*BuONa	KCl	65
9	**A**	*t*BuOK	–	68
10[c]	**A**	*t*BuOK	18-crown-6	<5
11	**A**	K_2CO_3	–	54
12	**A**	K_3PO_4	–	21
13	**B**	*t*BuOK		17
14	**C**	*t*BuOK	–	n.d.
15	**D1**	*t*BuOK	–	n.d.
16	**D2**	*t*BuOK	–	n.d.
17	–	*t*BuOK	–	n.d.
18[e]	**A**	*t*BuOK	–	66
19[f]	**A**	*t*BuOK	–	71
20[g]	**A**	*t*BuOK	–	72

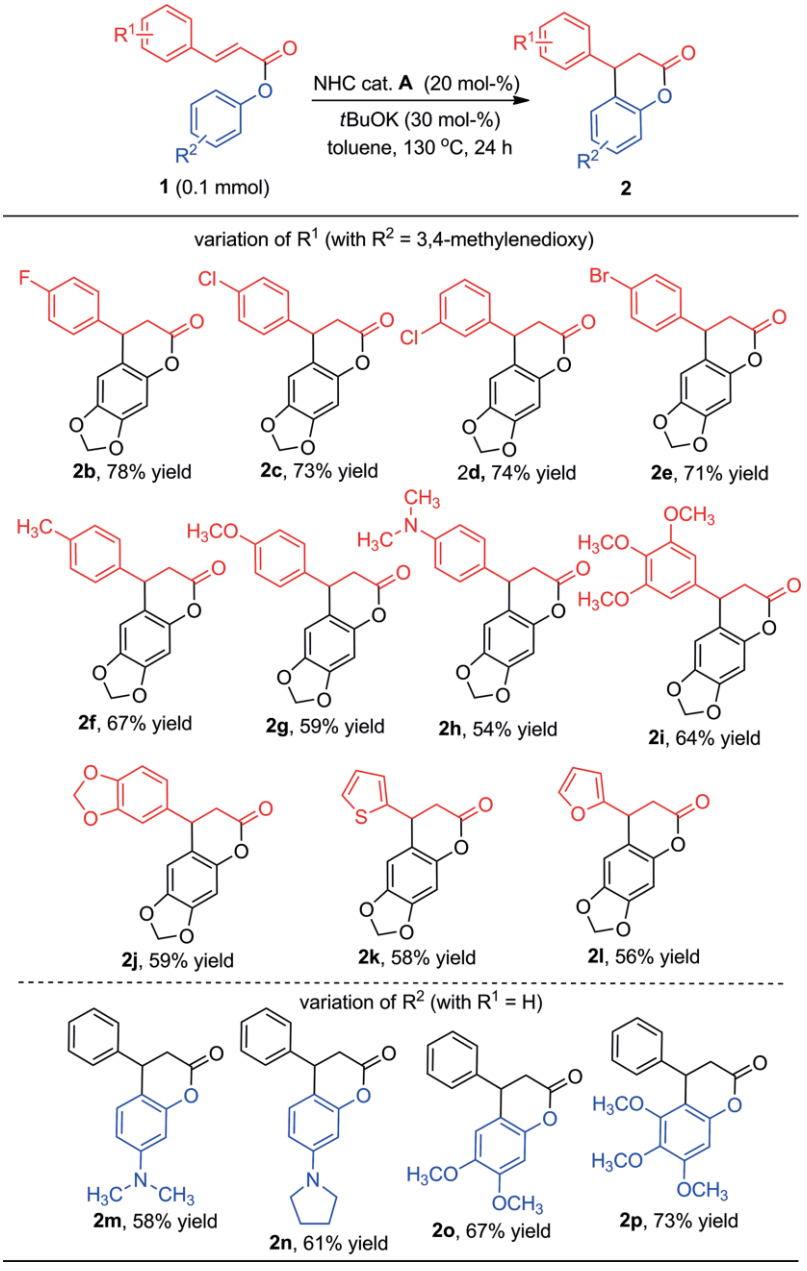
[a] Reaction conditions: **1a** (0.1 mmol), NHC catalyst (10 mol-%), base (15 mol-%), solvent (1 mL) at 120 °C for 48 h. [b] Isolated yield. [c] 30 mol-% of additive was added. [d] 15 mol-% of KCl was added. [e] The reaction was stirred at 130 °C. [f] NHC **A** (20 mol-%), *t*BuOK (30 mol-%) at 120 °C. [g] NHC **A** (20 mol-%), *t*BuOK (30 mol-%) at 130 °C for 24 h; n.d.: not determined.

could be achieved, with the formation of **2a** in 72 % yield as a single regioisomer (Table 1, entry 20).

Having established acceptable reaction conditions, the substrate scope of the α,β-unsaturated phenolic ester component was evaluated (Table 2). First, we explored a series of α,β-unsaturated esters in which R^2 was a 3,4-methylenedioxy group. A substrate beating an electron-withdrawing group (**2b**) on the β-phenyl moiety worked well in this reaction. The fact that the reaction tolerates the presence of functional groups [e.g., halogen (**2c**–**2e**) and alkyl (**2f**) groups] could be useful for structure–activity relationship (SAR) studies.[15] The presence of an electron-rich substituent on the aryl ring (**2g**–**2j**), although decreasing the electrophilicity of the alkene moiety, was well tolerated, and gave the desired annulation products in good yields. Replacement of the β-phenyl substituent with a heteroaryl (**2k**, **2l**) unit had little effect on the reaction outcome. However, methyl-substituted α,β-unsaturated phenolic esters did not give the annulation products under the optimal reaction conditions. Most of the starting materials remained intact when the reaction was carried out at 130 °C for 24 h.

Next, we investigated the scope of the reaction in terms of varying the R^2 group (with R^1 = H, Table 2). When the α,β-unsaturated phenolic ester was replaced by another electron-donating group, such as *m*-$N(CH_3)_2$ or *m*-$N(CH_2)_4$, a high yield

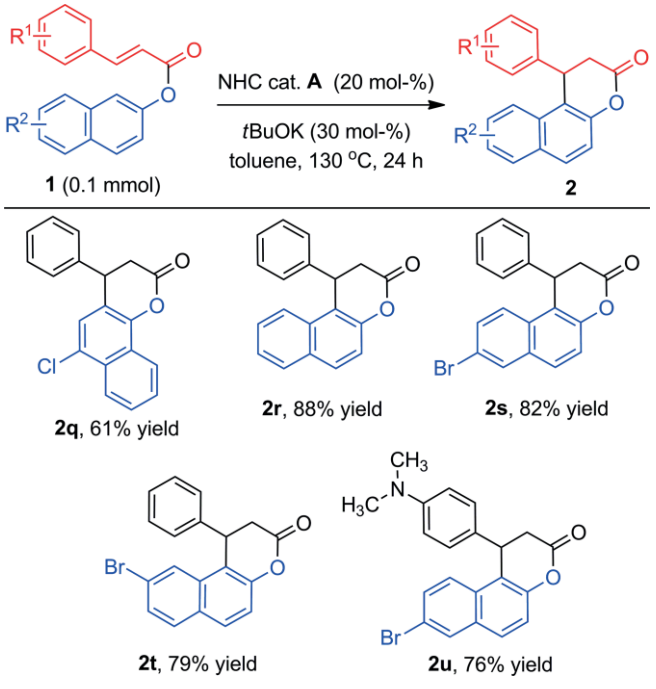
Table 2. Scope of the reaction in terms of α,β-unsaturated phenolic esters.[a]



[a] Reaction conditions: **1** (0.1 mmol), NHC catalyst **A** (20 mol-%), *t*BuOK (30 mol-%), toluene (1 mL) at 130 °C for 24 h; yields refer to products isolated by column chromatography.

and excellent regiocontrol were still observed (**2m**, **2n**). Additionally, the reaction could also be applied to other multi-substituted phenolic esters (**2o**, **2p**).

α,β-Unsaturated naphtholic esters **1** were then examined to further expand the scope of this arylation reaction. Under the standard conditions, substrates containing substituted fused aromatic groups led to the corresponding products (i.e., **2q**–**2u**) in high yields and with excellent regioselectivities (Scheme 2). Notably, in contrast to the study by Bode, Biju, and You,[8] 1-naphthol worked well to give the desired annulation product (i.e., **2q**).

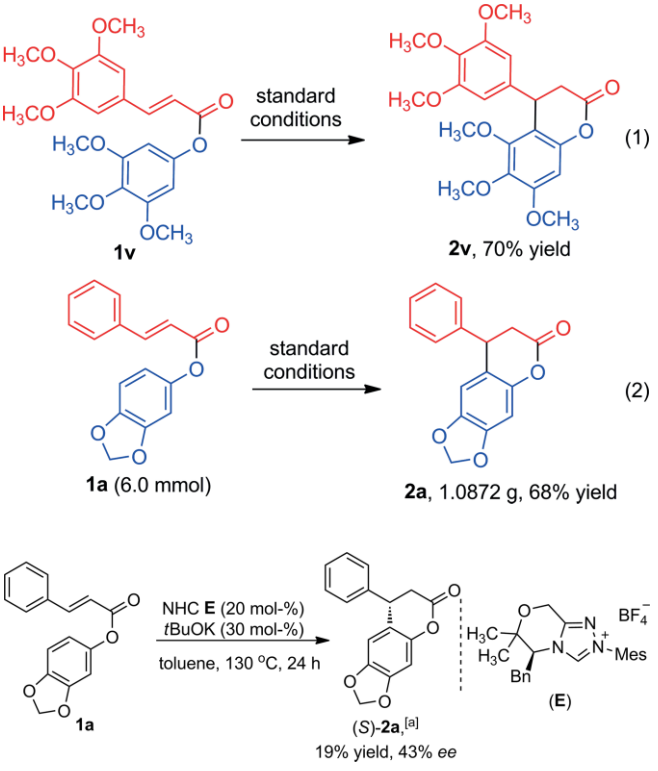


Scheme 2. Scope of the reaction in terms of α,β-unsaturated naphtholic esters. Reaction conditions: **1** (0.1 mmol), NHC catalyst **A** (20 mol-%), *t*BuOK (30 mol-%), toluene (1 mL) at 130 °C for 24 h; isolated yields by column chromatography.

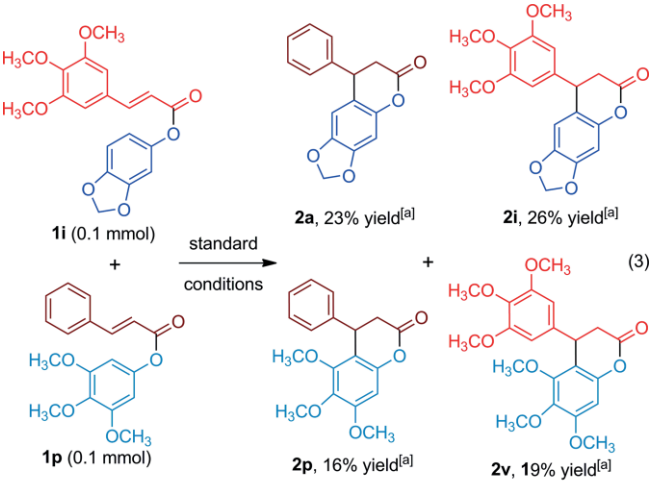
Substrate **1v** reacted smoothly under the standard conditions [Equation (1)] to give polymethoxy substituted product **2v**. In addition, a larger-scale reaction was carried out. This gave the desired product without any loss of efficiency, as shown by the gram-scale preparation of **2a** [Equation (2)].

A preliminary enantioselective study of this method was carried out using several triazolium salts (see the Supporting Information for details). We were delighted to find that when **E** was used as the chiral carbene precursor, annulation product (*S*)-**2a** was obtained in 19 % yield with a promising 43 % *ee* (Scheme 3).

A crossover study was carried out to gain a deeper insight into the reaction mechanism [Equation (3)].[17] A mixture of substrates **1i** and **1p** was subjected to the standard conditions. Besides the expected products **2i** and **2p**, crossover products **2a** and **2v** were observed in 23 and 19 % yields. These results suggest that an α,β-unsaturated acylazolium intermediate is directly generated from the ester with the NHC catalyst; the reaction probably takes place through the 1,4-addition of the α,β-unsaturated acylazoliums with the in-situ-generated phenolates.

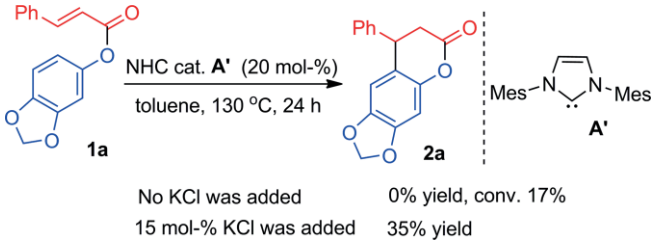


Scheme 3. Preliminary enantioselective studies of the reaction. [a] The absolute configuration of the major enantiomer was assigned based on a comparison of optical rotation data with literature values.[16]



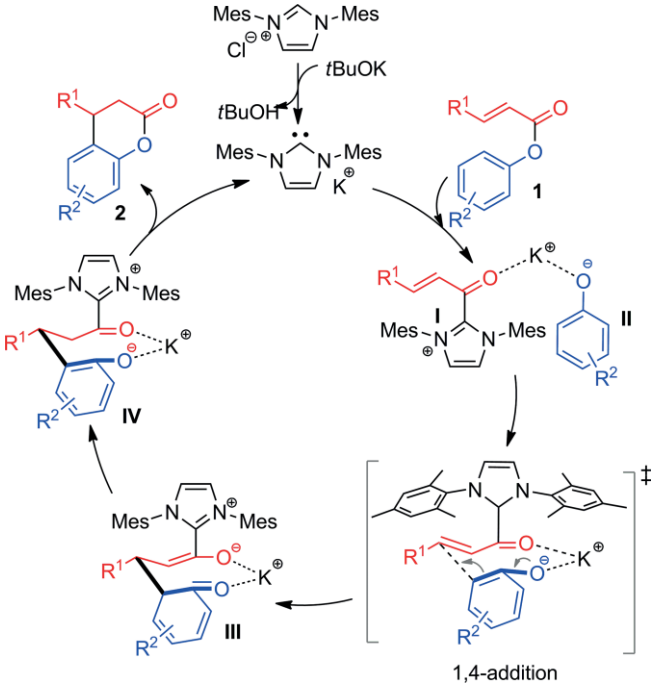
[a] The yield was determined by ^{1}H NMR analysis of the crude product.

To investigate the effect of potassium ion on the reaction, the following control experiments were designed (Scheme 4). Free carbene **A′** was prepared[18] and was subjected to the reaction conditions, but no product was observed when the reaction was carried out at 130 °C for 24 h. However, when the reaction was run in the presence of KCl (15 mol-%) under otherwise identical conditions, the desired product was obtained in 35 % yield.



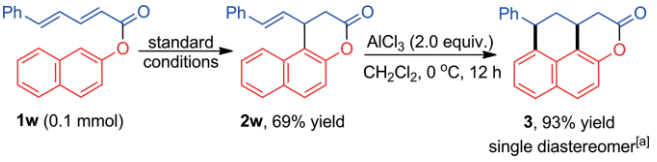
Scheme 4. Control experiments.

Based on the results described above, a reaction mechanism is proposed in Scheme 5. Deprotonation of the imidazolium precatalyst salt with *t*BuOK gives the carbene catalyst and the potassium ion. Addition of the NHC catalyst to ester **1** then leads to the formation of α,β-unsaturated acylazolium **I** and phenolate **II**. The potassium ion and the NHC cooperatively activate the α,β-unsaturated acylazolium to allow the addition of the relatively unreactive nucleophile. Dearomatization and 1,4-addition of phenolate **II** with **I** gives intermediate **III**, which undergoes tautomerization, rearomatization, and lactone formation to give product **2** and regenerate the NHC catalyst. In the overall hypothesized process, only a catalytic amount of base is needed, and the stability of the product may be the driving force for the reaction.



Scheme 5. Postulated reaction pathway.

Naphthalene-fused polycyclic structure **3** is the core skeleton of a variety of natural products and biologically active molecules.[19] Using our method, **2w** could easily be prepared from readily available substrates (Scheme 6), which further gave fused tetracyclic compound **3** in excellent yield and with excellent stereoselectivity.



Scheme 6. Synthetic transformation of the product. [a] The relative configuration of **3** was assigned on the basis of its NOESY spectrum (see the Supporting Information).

Conclusions

In conclusion, we have developed an effective phenylation reaction of α,β-unsaturated acylazoliums with in-situ-generated phenolates as the nucleophiles. The challenge associated with the dearomatization of the phenolates was overcome by using an NHC/potassium ion cooperative catalytic strategy. Additionally, α,β-unsaturated naphtholic esters were well tolerated, and derivatization of the resulting cyclic products provided high-value polycyclic structures. Mechanistic studies were also carried out to demonstrate that the presence of the potassium ion was essential for this reaction. The exploration of other related NHC-catalyzed arylation reactions is currently underway in our lab.

Experimental Section

General Information: Commercially available materials purchased from Alfa Aesar or Aldrich was used as received. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplet), etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a 100 MHz spectrometer. Mass spectral analysis (ESI-MS) was carried out with a mass spectrometer. The determination of *ee* was carried out by chiral phase HPLC analysis. Optical rotations were measured with a polarimeter using a 1 mL cell with a 1 cm path length, and are reported as follows: $[\alpha]_D^{20}$. Analytical thin-layer chromatography (TLC) was carried out on precoated silica gel plates (0.2 mm thickness), which were visualized using a UV lamp.

Typical Procedure for the Catalytic Reactions: NHC **A** (0.02 mmol), *t*BuOK (0.03 mmol), α,β-unsaturated phenolic ester **1a** (0.1 mmol) and toluene (1 mL) were put into a dry sealed tube equipped with a magnetic stirrer bar. The mixture was stirred in the sealed tube at 130 °C for about 24 h under a nitrogen atmosphere until **1a** was completely consumed (monitored by TLC). The mixture was then concentrated under reduced pressure. The resulting crude residue was purified by column chromatography on silica gel (hexanes/EtOAc, 5:1) to give the desired product (i.e., **2a**).

8-Phenyl-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]chromen-6-one (2a): White solid (19.4 mg, 72 %), m.p. 133.0–134.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.22 (m, 3 H), 7.15 (d, J = 8.1 Hz, 2 H), 6.65 (s, 1 H), 6.39 (s, 1 H), 5.94 (s, 2 H), 4.22 (t, J = 6.8 Hz, 1 H), 3.06–2.93 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 147.5, 146.2, 144.4, 140.4, 129.1, 127.7, 127.4, 117.9, 107.3, 101.7, 99.1, 40.6,

37.0 ppm. MS (ESI): m/z =$C_{16}H_{13}O_4$ [M + H] 269.1; found 269.1. HRMS (ESI): calcd. for $C_{16}H_{13}O_4$ [M + H] 269.0808; found 269.0794.

8-(4-Fluorophenyl)-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]chromen-6-one (2b): White solid (22.3 mg, 78 %), m.p. 144.0–145.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.09 (m, 2 H), 7.08–6.96 (m, 2 H), 6.65 (s, 1 H), 6.38 (s, 1 H), 5.95 (s, 2 H), 4.21 (t, J = 6.7 Hz, 1 H), 3.10–2.83 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 162.1 (d, J = 245.0 Hz), 147.6, 146.1, 144.5, 136.2 (d, J = 4.0 Hz), 129.0 (d, J = 8.0 Hz), 117.6, 116.0 (d, J = 21.0 Hz), 107.1, 101.7, 99.2, 39.9, 37.1 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –114.6 ppm. MS (ESI): m/z = 287.1 [M + H]. HRMS (ESI): calcd. for $C_{16}H_{12}FO_4$ [M + H] 287.0714; found 287.0698.

8-(4-Chlorophenyl)-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]chromen-6-one (2c): White solid (22.0 mg, 73 %), m.p. 134.0–135.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.4 Hz, 2 H), 7.08 (d, J = 8.3 Hz, 2 H), 6.65 (s, 1 H), 6.38 (s, 1 H), 5.96 (s, 2 H), 4.20 (t, J = 6.4 Hz, 1 H), 3.12–2.82 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 147.7, 146.2, 144.5, 139.0, 133.6, 129.3, 128.8, 117.2, 107.1, 101.8, 99.2, 40.1, 36.9 ppm. MS (ESI): m/z = 303.1 [M + H]. HRMS (ESI): calcd. for $C_{16}H_{12}ClO_4$ [M + H] 303.0419; found 303.0412.

8-(3-Chlorophenyl)-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]chromen-6-one (2d): White solid (22.3 mg, 74 %), m.p. 101.0–102.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.18 (m, 2 H), 7.12 (s, 1 H), 7.07–6.98 (m, 1 H), 6.65 (s, 1 H), 6.39 (s, 1 H), 5.96 (s, 2 H), 4.20 (t, J = 6.6 Hz, 1 H), 3.18–2.76 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 147.7, 146.1, 144.5, 142.5, 134.9, 130.4, 127.9, 127.6, 125.6, 116.8, 107.1, 101.8, 99.2, 40.3, 36.8 ppm. MS (ESI): m/z = 302.9 [M + H]. HRMS (ESI): calcd. for $C_{16}H_{12}ClO_4$ [M + H] 303.0419; found 303.0386.

8-(4-Bromophenyl)-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]chromen-6-one (2e): White solid (24.6 mg, 71 %), m.p. 167.0–168.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, J = 8.4 Hz, 2 H), 7.02 (d, J = 8.3 Hz, 2 H), 6.65 (s, 1 H), 6.38 (s, 1 H), 5.95 (s, 2 H), 4.18 (t, J = 6.7 Hz, 1 H), 3.11–2.79 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 147.7, 146.2, 144.5, 139.5, 132.2, 129.1, 121.6, 117.1, 107.1, 101.8, 99.2, 40.1, 36.8 ppm. MS (ESI): m/z = 347.0 [M + H]. HRMS (ESI): calcd. for $C_{16}H_{12}BrO_4$ [M + H] 346.9913; found 346.9906.

8-(*p*-Tolyl)-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]chromen-6-one (2f): White solid (19.0 mg, 67 %), m.p. 131.0–132.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (d, J = 7.9 Hz, 2 H), 7.03 (d, J = 8.0 Hz, 2 H), 6.65 (s, 1 H), 6.39 (s, 1 H), 5.94 (d, J = 1.7 Hz, 2 H), 4.18 (t, J = 8.0 Hz, 1 H), 3.13–2.78 (m, 2 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7, 147.4, 146.2, 144.4, 137.4, 129.8, 127.3, 118.2, 107.3, 101.7, 99.1, 40.3, 37.0, 21.0 ppm. MS (ESI): m/z = 283.2 [M + H]. HRMS (ESI): calcd. for $C_{17}H_{15}O_4$ [M + H] 283.0965; found 283.0978.

8-(4-Methoxyphenyl)-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]-chromen-6-one (2g): White solid (18.5 mg, 59 %), m.p. 134.0–135.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, J = 8.6 Hz, 2 H), 6.87 (d, J = 8.7 Hz, 2 H), 6.64 (s, 1 H), 6.39 (s, 1 H), 5.94 (s, 2 H), 4.17 (t, J = 8.0 Hz, 1 H), 3.79 (s, 3 H), 3.13–2.76 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7, 159.0, 147.4, 146.1, 144.4, 132.3, 128.5, 118.4, 114.5, 107.2, 101.6, 99.1, 55.3, 39.8, 37.1 ppm. MS (ESI): m/z = 299.0 [M + H]. HRMS (ESI): calcd. for $C_{17}H_{15}O_5$ [M + H] 299.0914; found 299.0906.

8-[4-(Dimethylamino)phenyl]-7,8-dihydro-6*H*-[1,3]dioxolo-[4,5-*g*]chromen-6-one (2h): Yellow solid (16.8 mg, 54 %), m.p. 122.0–123.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.00 (d, J = 8.7 Hz, 2 H), 6.69 (d, J = 8.8 Hz, 2 H), 6.63 (s, 1 H), 6.39 (s, 1 H), 5.93 (dd, J = 2.9, 1.3 Hz, 1 H), 4.10 (t, J = 8.0 Hz, 1 H), 3.04–2.84 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 150.0, 147.2, 146.1, 144.3, 128.2, 127.7, 119.1, 112.9, 107.3, 101.6, 99.0, 40.5, 39.7, 37.2 ppm. MS (ESI): m/z = 312.2 [M + H]. HRMS (ESI): calcd. for $C_{18}H_{18}NO_4$ [M + H] 312.1230; found 312.1218.

8-(3,4,5-Trimethoxyphenyl)-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]-chromen-6-one (2i): White solid (22.9 mg, 64 %), m.p. 192.0–193.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.65 (s, 1 H), 6.44 (s, 1 H), 6.35 (s, 2 H), 5.96 (s, 2 H), 4.15 (t, J = 8.0 Hz, 1 H), 3.83 (s, 3 H), 3.81 (s, 6 H), 3.10–2.87 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 153.6, 147.5, 146.1, 144.4, 137.4, 136.1, 117.8, 107.2, 104.4, 101.7, 99.0, 60.8, 56.1, 40.9, 37.0 ppm. MS (ESI): m/z = 358.9 [M + H]. HRMS (ESI): calcd. for $C_{19}H_{19}O_7$ [M + H] 359.1125; found 359.1114.

8-(Benzo[*d*][1,3]dioxol-5-yl)-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]-chromen-6-one (2j): Pale yellow solid (18.4 mg, 59 %), m.p. 140.0–141.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.76 (d, J = 8.5 Hz, 1 H), 6.64 (s, 1 H), 6.62–6.57 (m, 2 H), 6.41 (s, 1 H), 5.95 (s, 4 H), 4.14 (t, J = 8.0 Hz, 1 H), 3.15–2.70 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 148.3, 147.5, 147.0, 146.1, 144.4, 134.2, 120.8, 118.0, 108.6, 107.6, 107.2, 101.7, 101.2, 99.1, 40.3, 37.2 ppm. MS (ESI): m/z = 313.0 [M + H]. HRMS (ESI): calcd. for $C_{17}H_{13}O_6$ [M + H] 313.0707; found 313.0692.

8-(Thiophen-2-yl)-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]chromen-6-one (2k): White solid (15.8 mg, 58 %), m.p. 115.0–116.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (dd, J = 5.1, 1.2 Hz, 1 H), 6.94 (dd, J = 5.1, 3.5 Hz, 1 H), 6.88–6.79 (m, 1 H), 6.66–6.62 (m, 1 H), 6.57 (s, 1 H), 5.96 (dd, J = 3.3, 1.3 Hz, 2 H), 4.47 (t, J = 6.1 Hz, 1 H), 3.07 (d, J = 6.1 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 147.7, 145.7, 144.4, 143.7, 127.1, 125.1, 125.0, 117.6, 106.9, 101.7, 99.2, 37.3, 36.0 ppm. MS (ESI): m/z = 274.5 [M + H]. HRMS (ESI): calcd. for $C_{14}H_{11}O_4S$ [M + H] 275.0373; found 275.0364.

8-(Furan-2-yl)-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]chromen-6-one (2l): Colorless solid, m.p. 121.0–122.0 °C (15.3 mg, 56 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, J = 1.2 Hz, 1 H), 6.61 (s, 1 H), 6.57 (s, 1 H), 6.30 (dd, J = 3.2, 1.9 Hz, 1 H), 6.06 (d, J = 3.2 Hz, 1 H), 5.96 (dd, J = 6.1, 1.3 Hz, 2 H), 4.27 (t, J = 5.9 Hz, 1 H), 3.19–2.90 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 152.9, 147.8, 146.0, 144.4, 142.6, 115.4, 110.4, 107.0, 106.8, 101.7, 99.3, 34.6, 33.8 ppm. MS (ESI): m/z = 259.0 [M + H]. HRMS (ESI): calcd. for $C_{14}H_{11}O_5$ [M + H] 259.0601; found 259.0583.

6-(Dimethylamino)-4-phenylchroman-2-one (2m): White solid (15.5 mg, 58 %), m.p. 115.0–116.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.30 (m, 2 H), 7.29–7.23 (m, 1 H), 7.20–7.12 (m, 2 H), 6.80 (d, J = 8.6 Hz, 1 H), 6.52–6.33 (m, 2 H), 4.25 (t, J = 6.2 Hz, 1 H), 3.14–2.86 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 152.6, 151.1, 141.4, 129.0, 128.6, 127.5, 127.3, 112.8, 108.6, 100.5, 40.4, 40.0, 37.7 ppm. MS (ESI): m/z = 268.3 [M + H]. HRMS (ESI): calcd. for $C_{17}H_{18}NO_2$ [M + H] 268.1332; found 268.1319.

4-Phenyl-6-(pyrrolidin-1-yl)chroman-2-one (2n): White solid (17.9 mg, 61 %), m.p. 173.0–174.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.29 (m, 2 H), 7.28–7.22 (m, 1 H), 7.15 (d, J = 7.1 Hz, 2 H), 6.78 (d, J = 8.4 Hz, 1 H), 6.35–6.22 (m, 2 H), 4.24 (t, J = 6.7 Hz, 1 H), 3.26 (t, J = 6.5 Hz, 4 H), 3.09–2.92 (m, 2 H), 2.00 (t, J = 6.6 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 152.6, 148.4, 141.6, 128.9, 128.7, 127.5, 127.3, 111.7, 108.0, 99.6, 47.7, 40.0, 37.8, 25.4 ppm. MS (ESI): m/z = 294.3 [M + H]. HRMS (ESI): calcd. for $C_{19}H_{20}NO_2$ [M + H] 294.1489; found 294.1495.

6,7-dimethoxy-4-phenylchroman-2-one (2o): White solid (19.1 mg, 67 %), m.p. 154.0–155.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.31 (m, 2 H), 7.31–7.25 (m, 1 H), 7.22–7.08 (m, 2 H), 6.69 (s, 1 H), 6.46 (s, 1 H), 4.27 (t, J = 6.6 Hz, 1 H), 3.88 (s, 3 H), 3.73 (s, 3 H), 3.11–2.93 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 149.2, 145.8, 145.5, 140.8, 129.1, 127.6, 127.4, 116.1, 110.6, 101.2, 56.2, 56.1,

40.5, 37.4 ppm. MS (ESI): *m/z* = 285.2 [M + H]. HRMS (ESI): calcd. for $C_{17}H_{17}O_4$ [M + H] 285.1121; found 285.1109.

5,6,7-Trimethoxy-4-phenylchroman-2-one (2p): White solid (22.9 mg, 73 %), m.p. 146.0–147.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.24 (m, 2 H), 7.24–7.17 (m, 1 H), 7.14–7.07 (m, 2 H), 6.51 (s, 1 H), 4.57 (dd, *J* = 5.3, 3.7 Hz, 1 H), 3.87 (s, 3 H), 3.82 (s, 3 H), 3.65 (s, 3 H), 3.05–2.95 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 153.7, 150.5, 147.7, 141.7, 139.0, 128.9, 127.2, 126.7, 110.9, 96.8, 61.0, 60.9, 56.1, 37.1, 35.4 ppm. MS (ESI): *m/z* = 315.1 [M + H]. HRMS (ESI): calcd. for $C_{18}H_{19}O_5$ [M + H] 315.1227; found 315.1216.

6-Chloro-4-phenyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-one (2q): Pale green solid, m.p.(18.8 mg, 61 %), m.p. 127.0–128.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36–8.28 (m, 1 H), 8.24–8.17 (m, 1 H), 7.75–7.50 (m, 2 H), 7.40–7.26 (m, 3 H), 7.21–7.13 (m, 3 H), 4.43 (t, *J* = 6.6 Hz, 1 H), 3.28–3.01 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 145.7, 140.0, 130.7, 129.3, 127.9, 127.51, 127.48, 127.4, 125.1, 124.7, 124.4, 121.7, 120.2, 40.9, 37.0 ppm. MS (ESI): *m/z* = 309.1 [M + H]. HRMS (ESI): calcd. for $C_{19}H_{14}ClO_2$ [M + H] 309.0677; found 309.0658.

1-Phenyl-1*H*-benzo[*f*]chromen-3(2*H*)-one (2r): White solid (24.2 mg, 88 %), m.p. 164–165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.6 Hz, 2 H), 7.79 (d, *J* = 8.1 Hz, 1 H), 7.52–7.40 (m, 2 H), 7.35 (d, *J* = 8.9 Hz, 1 H), 7.28–7.16 (m, 3 H), 7.12 (d, *J* = 7.7 Hz, 2 H), 4.95 (d, *J* = 6.4 Hz, 1 H), 3.31–3.07 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 149.8, 140.6, 131.1, 131.0, 129.9, 129.2, 128.8, 127.6, 127.5, 126.9, 125.3, 123.1, 117.61, 117.56, 37.7, 37.5 ppm. MS (ESI): *m/z* = 275.2 [M + H]. HRMS (ESI): calcd. for $C_{19}H_{15}O_2$ [M + H] 275.1067; found 275.1054.

8-Bromo-1-phenyl-1*H*-benzo[*f*]chromen-3(2*H*)-one (2s): White solid (28.9 mg, 82 %), m.p. 120.0–121.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (s, 1 H), 7.71 (d, *J* = 8.9 Hz, 1 H), 7.61 (d, *J* = 9.0 Hz, 1 H), 7.46 (d, *J* = 8.9 Hz, 1 H), 7.32 (d, *J* = 8.9 Hz, 1 H), 7.26–7.12 (m, 3 H), 7.07 (d, *J* = 7.2 Hz, 2 H), 4.87 (d, *J* = 4.0 Hz, 1 H), 3.50–2.70 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 150.0, 140.2, 132.2, 130.8, 130.7, 129.6, 129.3, 129.0, 127.7, 126.8, 124.8, 119.2, 118.8, 117.9, 37.7, 37.3 ppm. MS (ESI): *m/z* = 352.9 [M + H]. HRMS (ESI): calcd. for $C_{19}H_{14}BrO_2$ [M + H] 353.0172; found 353.0161.

9-Bromo-1-phenyl-1*H*-benzo[*f*]chromen-3(2*H*)-one (2t): White solid (27.9 mg, 79 %), m.p. 173.0–174.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (s, 1 H), 7.82 (d, *J* = 8.9 Hz, 1 H), 7.71 (d, *J* = 8.7 Hz, 1 H), 7.50 (dd, *J* = 8.7, 1.7 Hz, 1 H), 7.35 (d, *J* = 8.9 Hz, 1 H), 7.31–7.17 (m, 3 H), 7.14–7.07 (m, 2 H), 4.90–4.83 (m, 1 H), 3.30–2.98 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 150.4, 140.0, 132.3, 130.3, 129.8, 129.4, 129.3, 128.7, 127.7, 126.8, 125.4, 122.1, 118.0, 117.0, 37.5, 37.3 ppm. MS (ESI): *m/z* = 353.1 [M + H]. HRMS (ESI): calcd. for $C_{19}H_{14}BrO_2$ [M + H] 353.0172; found 353.0156.

8-Bromo-1-[4-(dimethylamino)phenyl]-1*H*-benzo[*f*]chromen-3(2*H*)-one (2u): Yellow solid (30.1 mg, 76 %), m.p. 145.0–146.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 1.9 Hz, 1 H), 7.75–7.63 (m, 2 H), 7.48 (dd, *J* = 9.0, 1.9 Hz, 1 H), 7.32 (d, *J* = 8.9 Hz, 1 H), 6.92 (d, *J* = 8.7 Hz, 2 H), 6.57 (d, *J* = 8.7 Hz, 2 H), 4.79 (t, *J* = 4.3 Hz, 1 H), 3.30–2.99 (m, 2 H), 2.84 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 149.8, 149.7, 132.1, 130.5, 129.6, 128.5, 127.6, 127.4, 125.0, 119.0, 118.8, 118.7, 112.9, 40.4, 37.5, 36.7 ppm. MS (ESI): *m/z* = 396.3 [M + H]. HRMS (ESI): calcd. for $C_{21}H_{19}BrNO_2$ [M + H] 396.0594; found 396.0583.

5,6,7-Trimethoxy-4-(3,4,5-trimethoxyphenyl)chroman-2-one (2v): White solid (28.3 mg, 70 %), m.p. 168.0–169.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.51 (s, 1 H), 6.33 (s, 2 H), 4.51 (dd, *J* = 5.3, 3.5 Hz, 1 H), 3.88 (s, 3 H), 3.84 (s, 3 H), 3.79 (s, 3 H), 3.78 (s, 6 H), 3.74 (s, 3 H), 3.05–2.92 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 153.6, 153.4, 150.4, 147.5, 138.9, 137.4, 137.0, 110.7, 103.7, 96.6, 61.1, 60.9, 60.7, 56.01, 59.97, 37.0, 35.5 ppm. MS (ESI): *m/z* = 405.0 [M + H]. HRMS (ESI): calcd. for $C_{21}H_{25}O_8$ [M + H] 405.1544; found 405.1532.

Procedure for the Enantioselectivity Study of the Catalytic Reaction: NHC **E** (0.02 mmol), *t*BuOK (0.03 mmol), α,β-unsaturated phenolic ester **1a** (0.1 mmol), and toluene (1 mL) were put into a dry sealed tube equipped with a magnetic stirrer bar. The mixture was stirred in the sealed tube at 130 °C for about 24 h under a nitrogen atmosphere until **1a** was completely consumed (monitored by TLC). The resulting crude residue was purified by column chromatography on silica gel (hexanes/EtOAc, 5:1) to give the desired product (*S*)-**2a** (5.2 mg, 19 %) as a white solid. $[\alpha]_D^{20}$ = +1.3 (*c* = 0.8, $CHCl_3$); 43 % *ee* as determined by HPLC (IA, 75:25 hexanes/*i*PrOH, 0.5 mL/min, λ = 220 nm), t_{major} = 20.8 min, t_{minor} = 21.4 min.

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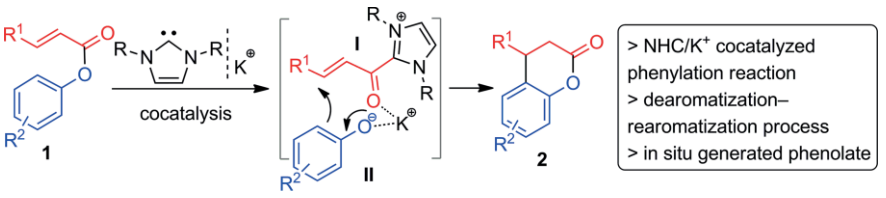
Phenylation Reaction



A catalytic phenylation reaction of α,β-unsaturated acylazoliums was developed. A combination of N-heterocyclic carbene and potassium ion cooperatively catalyzed the cyclization of α,β-unsaturated acylazoliums with phenol 581 ates, which are directly generated from α,β-unsaturated phenolic esters. Mechanistic studies demonstrated that the potassium ion plays a vital role in this reaction.

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