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ARTICLE

Peroxy Mediated Csp2-Csp3 Dehydrogenative Coupling: Regioselective Functionalization of Coumarins and Coumarin-3-carboxylic acids

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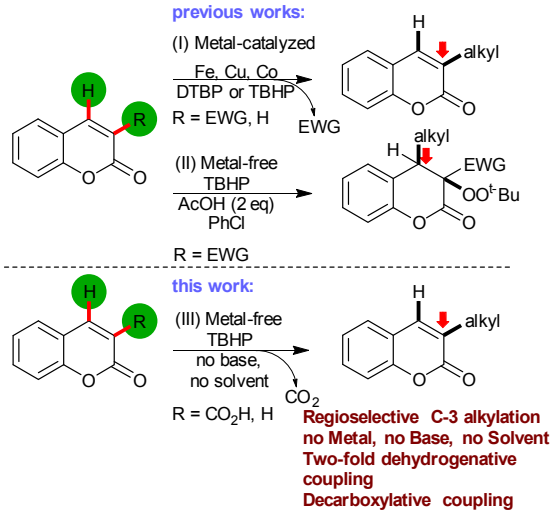
A regioselective direct alkylation of coumarins at C-3 via cross-dehydrogenative coupling of unactivated Csp2-Csp3 bonds is developed. The protocol employs *tert*-butyl hydroperoxide as the sole reagent of the reaction to combine coumarins and ethers in reasonable yields under metal- and solvent-free reaction conditions. The protocol also worked well with coumarin-3-carboxylic acids to unveil a rare instance of catalyst-free tandem alkylation/decarboxylation reaction with conservation of the double bond.

Introduction

The formation of C–C bonds is fundamentally important due to the ubiquitous nature of these bonds in naturally occurring products and biologically and pharmaceutically active compounds. Direct coupling of two different C–H centers, known as cross-dehydrogenative coupling (CDC) has become the central focus in C–C bond forming reactions in terms of efficiency and atom economy.[1] Pioneered by Li et. al., extensive progress has been made in transition metal catalyzed CDC reactions in the past decade.[2] The current trend in organic synthesis and especially in the pharmaceutical industry however, is to avoid any poisonous and costly transition-metal catalysts or metal oxidants in CDC reactions as a highly desirable and challenging synthetic procedure for the next generation's C–C bond formations. This protocol may find great applications especially in highly appreciable pasting of functionalities containing oxygen on heteroarenes, via radical activation of inactive Csp^3-H bonds of ethers and alcohols, converting these compounds to high-value pharmacophore adducts.[3] Although the metal-catalyzed strategy for the direct alkylation of electron-deficient heteroarenes, pioneered by Minisci,[4] is well documented, the more challenging metal-free approach has been scarcely investigated.

Coumarins, well-known as key scaffolds in many naturally-occurring and synthetic compounds, represent notable activities such as antimicrobial, antibacterial, anti-inflammatory, antioxidant and anti-HIV activities.[5] In addition they are prevalent in numerous compounds that are of material interest because of their optical activities.[6] Due to their importance, regioselective functionalization of coumarins has become an attractive research topic and is being actively pursued by several research groups.[7] Direct installation of olefins and arenes at C-3 position of these privileged motifs has already been achieved employing precious Pd-metal catalysts[8] resulting in π-extended biologically active adducts. Since 2014 however, a great deal of attention has been devoted to C-3 alkylation of coumarins with alkanes and ethers by cost effective metals including Cu[9], Fe[10] and Co[11] (Scheme 1, **I**).



Scheme 1. Direct alkylation of coumarins

Recently, the groups of Zhou and Ge reported an iron catalyzed cross-coupling of ethers and coumarins to construct ether substituted coumarins at α–position.[10b] Later, Du et. al. developed a cobalt-catalyzed regioselective C-3 alkylation of coumarins with a series of (cyclo)alkyl ethers.[11] Despite the

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importance of these contributions, the high amount of toxic benzene co-solvent together with the need of an amidine base limits severely the application of these methodologies in organic synthesis. Besides, the more desirable metal-free strategy as an alternative synthetic approach for direct instalment of functionalities on this scaffold is rarely covered. The only contribution to the field of metal-free alkylation of coumarins was recently made by Patel and involved C4-cycloalkylation C3-peroxidation of 3-substitued coumarins (scheme 1, **II**).[10a] Very recently, we have unveiled successive metal-free regioselective C-H functionalizations of coumarins towards expedient synthesis of 3-aroyl[12a] and 3-arylcoumarins.[12b] Inspired by radical reactions as a more natural strategy with good scope and practicality for synthesis of complicated pharmaceuticals herein, we uncover a versatile metal-free assembly of the Csp2-Csp3 bonds from coumarins and (cyclo)alkyl ethers via a two-fold C-H activation reaction. This protocol features good yields and high regioselectivities, without the need for excessive pre-activation reactions and toxic metals and could serve as an alternative approach for regioselective functionalization of coumarins under mild reaction conditions.

Results & discussion

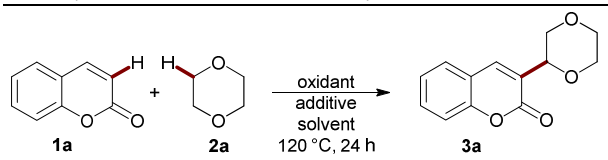
We conducted our initial investigation on the reaction of coumarin (**1a**) and 1,4-dioxane (**2a**) in presence of *tert*-butyl hydroperoxide (TBHP) (4.0 eq.) and various solvents (Table 1, entries 1-5). Satisfyingly, TBHP in acetonitrile gave the desired product **3a** in 35% yield (entry 3). While consumption of iodide salt additives exhibited inferior results, addition of some organic tertiary amine bases like DBU and DABCO, promoted the radical-based CDC reaction (entries 6-11). To our delight, a 70% yield of the product was obtained even in absence of any bases and solvents (entry 12). Unfortunately, a decrease in loading of TBHP to 2.0 eq., led to a severe drop in the yield (entry 13). Although a comparable yield was obtained with di-*tert*-butyl peroxide (DTBP), utilization of other oxidants even in presence of different acids suppressed the reaction drastically (entries 14-20). The control experiment in the absence of the oxidant resulted in recovery of starting materials. Gratifyingly, employing TBHP (4.0 eq.) at 120 °C under metal-free conditions, led to alkylated coumarin exclusively at C-3 position in 70% isolated yield. This approach offers a practical and facile functionalization of coumarins with ethers without any requisite of toxic metals, additives and solvents and could find numerous applications in pharmaceutics and industry.

With the optimized reaction conditions in hand, we assessed the scope and generality of the approach utilizing a variety of coumarin derivatives (Table 2). Methyl substituted coumarins resulted the desired products **3b** and **3c** even more practically in 78% and 82% yields, respectively. 7- And 8-alkoxy substituted substrates also went through the reaction smoothly and afforded the corresponding products **3d**, **3e** and **3f** in moderate to good yields. Unfortunately, no satisfactory result was observed when 4-substituted coumarin was employed. The inefficiency of the reaction may be rationalized to an increase in steric encumbrance (**3g**).

Interestingly, bromo- and chloro- substituted coumarins which facilitate further functionalization of the scaffold via cross-coupling techniques, were also tolerant to reaction conditions, affording alkylated coumarins **3h** and **3i** in good yields. Gratifyingly, benzochromenone likewise participated well in this transformation and resulted the desired product **3j** in 78% yield.

Afterward, the tolerance of this reaction to a range of cyclic as well as linear ethers was examined (Table 2). Ethereal entities such as tetrahydrofuran, tetrahydropyran and 1,3-dioxolane were utilized and the CDC reactions proceeded smoothly to functionalize Csp3-H bonds in moderate to good yields (**3k**-**3q**). Notably, when coumarin was reacted with 1,3-dioxolane, a 1:1 regioisomeric mixture of both 2- and 4-substituted dioxolane adducts were composed (**3n** and **3n'**, respectively). Unfortunately, electron deficient coumarin bearing a nitro group was not tolerated under the reaction condition (**3r**). Further investigation revealed that the two-fold regioselective alkylation protocol was also compatible to acyclic ethers such as diethyl ether, di-n-butyl ether and dimethoxy ethane, and generated alkyl coumarins **3s**-**3v** in satisfactory yields. Furthermore, under the transition-metal-free reaction coumarin reacted well with a simple alkane such as

Table 1 Optimization of reaction conditions for alkylation of coumarin **1a**[a]



1a 2a 3a

Entry	Oxidant	Additive	Solvent	Yield (%)[b]
1	TBHP	—	DMSO	25
2	TBHP	—	DMF	23
3	TBHP	—	ACN	35
4	TBHP	—	Toluene	0
5	TBHP	—	H_2O	33
6	TBHP	TBAI	—	0
7	TBHP	KI	—	0
8	TBHP	K_2CO_3	—	42
9	TBHP	Cs_2CO_3	—	22
10	TBHP	DBU	—	56
11	TBHP	DABCO	—	60
12	**TBHP**	—	—	**70**
13[c]	TBHP	—	—	40
14	AIBN	—	—	<5
15	$K_2S_2O_8$	—	—	0
16	DTBP	—	—	68
17	BPO	—	—	<5
18[d]	BPO	TFA	—	<5
19[d]	BPO	TsOH	—	<5
20[d]	$K_2S_2O_8$	TFA	H_2O	15

[a]Reaction conditions: Coumarin **1a** (0.2 mmol), 1,4-dioxane (0.4 mL), oxidant (4 eq.), additive (20 mol%), solvent (0.4 mL), 120 °C, 24 h; [b]Isolated yield; [c]TBHP (2 eq.) was used; [d]Oxidant (1.3 eq.) and additive (1.3 eq.) were used. AIBN = Azobisisobutyronitrile, BPO = benzoyl peroxide, DTBP = di-tert-butyl peroxide, TBHP = tert-Butyl hydroperoxide, TFA = trifluoroacetic acid.

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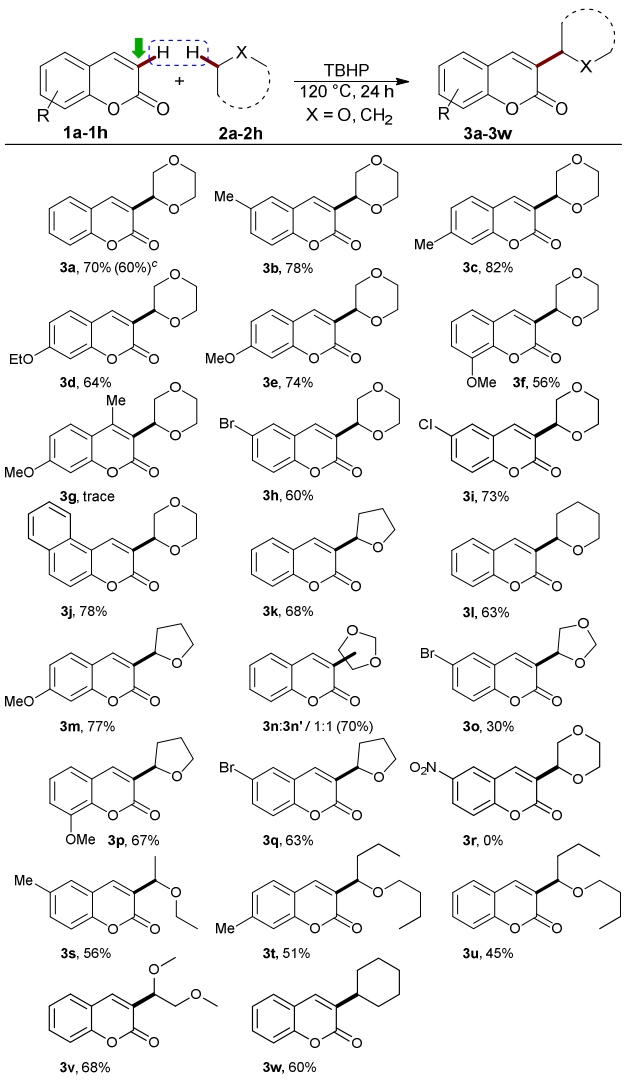
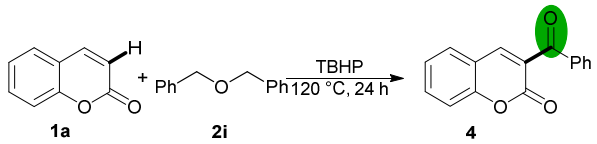
cyclohexane and furnished **3w** in 60% isolated yield. Finally, the reaction could be scaled up to 2.0 mmol without significant loss of efficiency (**3a**, Table 2).

Table 2 Scope of the two-fold C-H functionalization of coumarins with ethers[a,b]

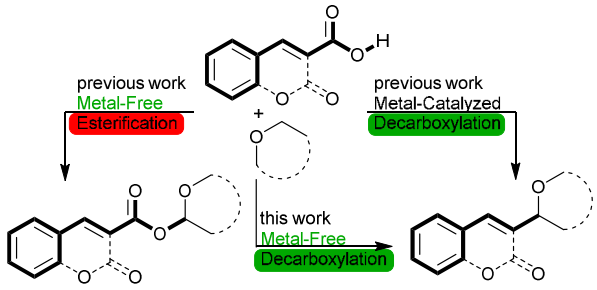


[a]All reactions were run under the optimized reaction conditions. [b]Isolated yield. [c]2.0 mmol scale.

Interestingly, when dibenzyl ether was used as coupling partner in this transformation, 3-alkyl coumarin was not observed and instead, 3-aroyl coumarin **4** was achieved (Scheme 2). Although benzyl ether is claimed to serve as aroyl (ArCO−) surrogate both under palladium(II) and copper(I/II)-catalysed aroylation reactions,[13] but to the best of our knowledge, this process is the first example of converting benzyl ether to its aroyl equivalent in the absence of any metal catalyst.



Scheme 2. Metal-free CDC benzoylation of coumarin with benzyl ether.



Scheme 3. Decarboxylation versus Esterification in the presence and absence of metals.

On the other hand, typical procedures for construction of coumarins, leave behind a surplus carboxyl group at C-3 position of coumarins which should be removed prior to functionalizations.[14] Although metal-catalyzed decarboxylative functionalization of coumarin-3-carboxylic acids is well documented[15] however, there is no precedence for metal-free decarboxylation of this scaffold. Recently, Wan et. al.[16] as well as Mao and Xu et. al.[17] reported on metal-free reactions of ethers and some similar carboxylic acids which both accompanied with conservation of carboxyl group generating esterification products (Scheme 3).

Furthermore, Xiao et. al.[18] has recently communicated catalyst-free functionalizations of coumarin-3-carboxylic acids which led to regioselective alkylation/heteroarylation of coumarins at C-4 with subsequent reduction of the double bond to build up 3,4-dihydrocoumarins. Consequently, we hypothesized that a metal-free one-pot cascade reaction combining direct alkylation and decarboxylation process would find great application in synthetic organic chemistry. To our delight, the optimum conditions used for coupling of coumarins and ethers also worked well for functionalization of coumarin-3- carboxylic acids so that when coumarin-3-carboxylic acid and dioxane

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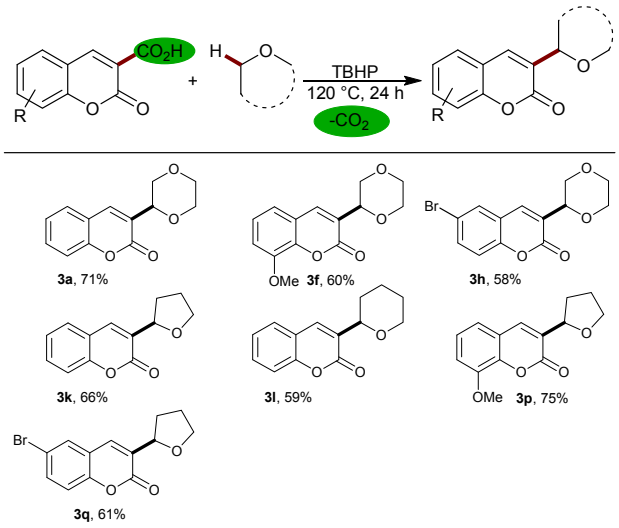
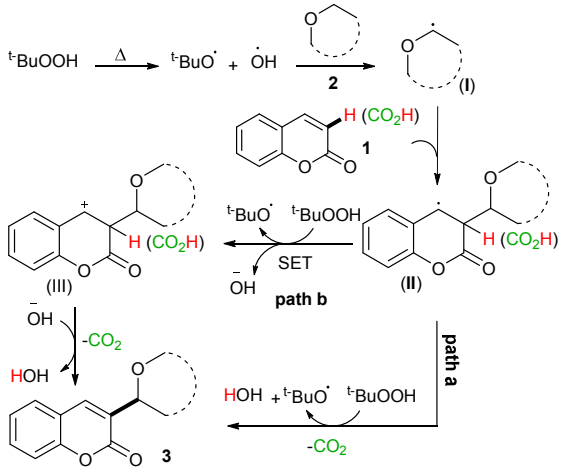
Table 3 Scope of cascade decarboxylative functionalization of coumarins[a,b]



[a]All reactions were run under the optimized reaction conditions. [b]Isolated yield.



Scheme 4. Proposed mechanism of TM-free alkylation of coumarins/coumarin carboxylic acids.

were reacted in presence of TBHP, a comparable yield of the desired product **3a** was obtained (Table 3). Similar achievements were raised in functionalization of coumarin-3-carboxylic acid derivatives with cyclic ethers. 8-Methoxy coumarin-3-carboxylic acid afforded even superior results (**3f** and **3p**). This protocol admits interesting synthetic attributes, such as regioselective tandem alkylation/decarboxylation process with a fruitful conservation of double bond functionality under mild and environmentally compassionate reaction conditions without the requisite for addition of any salts and bases.

To get insight to the mechanism of this reaction, 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO) as a radical scavenger was added (2.0 equiv.) into the reaction mixture of coumarin and THF under the optimized reaction conditions. The reaction was fully suppressed in presence of TEMPO and the desired product **3k** could not be obtained (see SI). The result indicates that the reaction may involve a radical process. A putative mechanism is outlined in Scheme 4. Initially, TBHP decomposes to tert-butoxy and hydroxyl radicals under heating. Next, each of the radicals may abstract Csp3–H of ether to generate radical intermediate **I**. Subsequently, selective addition of **I** to C-3 position of coumarin(-3-carboxylic acid) affords the more stable benzyl radical intermediate (**II**). Hydrogen abstraction by hydroxyl radical (path **a**) or a competitive single electron-transfer pathway (path **b**) are the proposed tips which result in construction of the coumarin backbone. More probably, the reaction proceeds via path **b** where radical intermediate (**II**) loses an electron to TBHP to reduce it to tert-butoxy radical and a hydroxide anion.[19] Finally deprotonation/darcarboxylation of intermediate **III** under the basic conditions regenerates double bond leading to the desired product **3**.

Conclusions

In summary, an efficient cross-dehydrogenative coupling of coumarins and inactive ethers under ultimate metal-free circumstances is presented. The protocol provides an environmentally benign approach to alkylated coumarins regioselectively at C-3 employing *tert*-butyl hydroperoxide exclusively. Moreover, based on this protocol an unprecedented facile tandem alkylation/decarboxylation of coumarin-3-carboxylic acids with ethers for construction of privileged 3-alkyl coumarins is conceived. This practical innovative approach with a broad substrate scope, may render this method as a valuable alternative to hitherto transition-metal-catalyzed cross-coupling methods for broadening the library of coumarins, which are especially prevalent in pharmaceutical industry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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