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Organophotoredox Catalyzed Cascade Radical Annulation of 2-(Allyloxy)arylaldehydes with *N*-(acyloxy)phthalimides: Towards Alkylated Chroman-4-one Derivatives

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Dedication ((optional))

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Abstract: An organophotoredox catalyzed efficient and robust approach for the synthesis of highly important 3-alkyl substituted chroman-4-one scaffold is developed using visible light induced radical cascade cyclization strategy. The reaction is initiated through the generation of alkyl radicals from *N*-(acyloxy)phthalimides under photoredox conditions, which subsequently undergo intermolecular cascade radical cyclization on 2-(allyloxy)arylaldehydes to afford chroman-4-one scaffolds. The presented strategy is attractive with regard to mild reaction conditions, operational simplicity, high functional group tolerance and broad substrate scope.

The chroman-4-one framework belongs to the privileged class of heterocycles and constitutes an integral part of numerous natural products, pharmaceuticals and biologically active compounds.[1] They exhibit a variety of physiological and biological activities, such as antibacterial, anti-HIV, anti-tobacco mosaic virus and SIRT2 inhibitors, to name a few (Figure 1). Consequently, significant efforts have been made towards the development of efficient, atom-economic and robust approaches to access a range of functionally orchestrated chorman-4-ones.[2] For example, a base promoted and microwave-assisted condensation of 2-hydroxyacetophenones with aliphatic aldehydes, and *N*-heterocyclic carbene (NHC) catalyzed intramolecular Stetter reactions are among the representative methods.[2a, 2c, 2d] Recently, cascade radical cyclization of 2-(allyloxy)arylaldehydes triggered by diverse radicals, such as phosphoryl, acyl, and alkyl have evolved as an alternate and efficient approach allowing access to chroman-4-one derivatives.[3] Among these methodologies, the cascades those are initiated by alkyl radicals captivated our attention. In 2018, Chen, Yu and coworkers documented a silver-catalyzed decarboxylative radical cyclization of 2-(allyloxy)arylaldehydes using *tert*-carboxylic acids as the reaction partner at 80 °C (Scheme 1a).[3a] Subsequently, authors reported another alkyl radical initiated cyclization employing active methylene containing 1,3-dicarbonyls as radical precursors.[3f] More recently, Liu group developed a cross-coupling of 2-(allyloxy)arylaldehydes with cyclopropanols to afford carbonyl containing alkyl substituted chroman-4-ones (Scheme 1b).[3b] Despite these important contributions the existing methods require multistep synthesis of organocatalysts, usage of higher loading of metal catalysts, higher reaction temperature and superstoichiometric amount of strong oxidant. Considering significant applications of chroman-4-ones, it is needless to mention that the development of more straightforward, milder and environmentally benign approaches for the synthesis of this scaffold is highly desired.

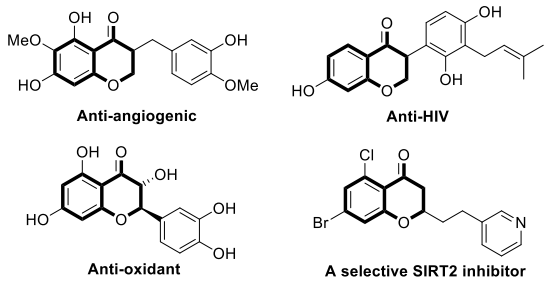
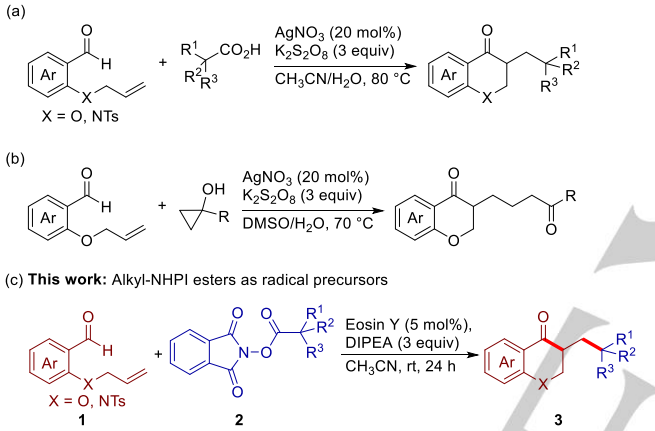


Figure 1. Selective examples of biologically active chroman-4-one scaffolds.

In this regard, visible light-mediated photoredox catalysis represents a powerful alternative and environment-friendly tool in fostering of modern synthetic chemistry.[4] Additionally, it has recently been revealed that redox-active *N*-(acyloxy)phthalimides (NHPI esters) participate in an exciting range of single electron transfer (SET)-based cross-coupling reactions under photolytic conditions.[5] NHPI esters are bench stable and readily available feedstock that can easily be prepared from the corresponding carboxylic acids and *N*-

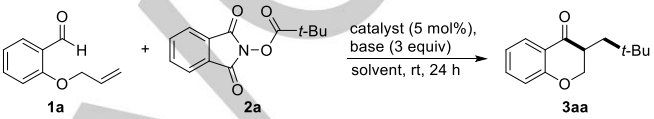
hydroxyphthalimide under standard coupling conditions.[6] Following Okada's initial discovery[7] of redox properties of NHPI esters and their ability to serve as a precursor of alkyl radicals under photoredox catalysis; the recent years have witnessed an upsurge in the applications of NHPI esters in a multitude of transformations, including decarboxylative alkylations[8] and chemoselective tandem radical cyclizations.[9] We were intrigued by the possibility of reacting alkyl radical generated from NHPI esters under visible light irradiation with 2-(allyloxy)arylaldehydes to construct the alkyl-substituted chroman-4-one scaffold. Such a visible photoredox catalysis driven tandem radical strategy would be highly efficient and fascinating from the perspective of green chemistry. As part of our ongoing program on photoredox catalysis[10] and driven by our interest in *N*-(acyloxy)phthalimides as redox-active esters,[5] we herein disclose a hitherto unknown Eosin Y catalyzed cascade radical annulation of NHPI esters and 2-(allyloxy)arylaldehydes to yield 3-alkyl substituted chroman-4-ones under visible light irradiation (Scheme 1c).



Scheme 1. Synthesis of alkyl substituted chroman-4-one derivatives.

Recently, Eosin Y has gained popularity as a photocatalyst enabling an array of photochemical reactions.[4g, 4h] König and coworkers documented an elegant Eosin Y catalyzed decarboxylative alkylation of acrylates using NHPI esters as the alkyl radical precursors under visible light irradiation.[8p] Accordingly, we began our studies through reacting 1 equiv of 2-(allyloxy)arylaldehyde **1a** with 3 equiv of NHPI ester **2a** in the presence of 5 mol% of photoredox catalyst Eosin Y using 3 equiv of *N,N*-diisopropylethylamine (DIPEA) as the base and CH_3CN as solvent under blue LED irradiation (440 nm) at room temperature under argon atmosphere (Table 1, see the SI for detailed optimization table). Gratifyingly, the desired product **3aa** was obtained in 71% yield (entry 1). Subsequent screening of various photocatalysts established Eosin Y as the most effective catalyst with all other catalysts leading to decrement of chemical yield. The organo-photocatalysts, such as Rose Bengal, Fluorescein and commonly employed metallic photocatalyst $[Ru(bpy)_3]Cl_2$ failed to improve the yield (entries 2-4). Switching of base from DIPEA to DABCO (1,4-diazabicyclo[2.2.2]octane) completely ceased the photochemical reaction (entry 5), whereas yield deteriorated upon replacement of DIPEA with bases such as Et_3N and 2,6-Lutidine (entries 6-7). Interestingly, the reaction did work in the presence of inorganic base K_3PO_4, albeit lower yield was obtained (entry 8). Among the various solvents tested, CH_3CN remained to be the optimal one (entries 9-11). Lowering of Eosin Y loading from 5 mol% to 2.5 mol% (entry 12) or DIPEA loading from 3 equiv to 1.5 equiv (entry 13) led to inferior results. Notably, the yield plummeted to 42% upon reducing **2a** loading from 3 equiv to 1.5 equiv (entry 14). Subsequent control experiments showed that Eosin Y, DIPEA and visible light irradiation are indispensable to the success of this cascade process (entries 15-17). Importantly, the argon atmosphere was crucial to the positive outcome of the reaction as the yield substantially reduced to 37% upon carrying out the reaction under the air atmosphere (entry 18).

Table 1. Optimization of the reaction conditions[a]

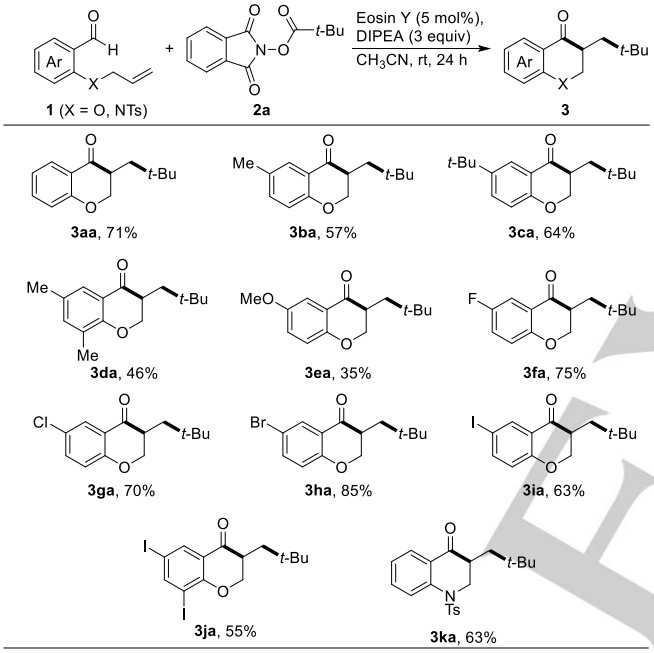


Entry	Catalyst	Base	Solvent	Yield (%)[b]
1	Eosin Y	DIPEA	CH_3CN	71
2	Rose bengal	DIPEA	CH_3CN	44
3	Fluorescein	DIPEA	CH_3CN	33
4	$[Ru(bpy)_3]Cl_2$	DIPEA	CH_3CN	59
5	Eosin Y	DABCO	CH_3CN	ND
6	Eosin Y	Et_3N	CH_3CN	29
7	Eosin Y	2,6-Lutidine	CH_3CN	67
8	Eosin Y	K_3PO_4	CH_3CN	32
9	Eosin Y	DIPEA	1,4-Dioxane	55
10	Eosin Y	DIPEA	DCM	70
11	Eosin Y	DIPEA	DMF	67
12[c]	Eosin Y	DIPEA	CH_3CN	65
13[d]	Eosin Y	DIPEA	CH_3CN	45
14[e]	Eosin Y	DIPEA	CH_3CN	42
15	-……	DIPEA	CH_3CN	Trace
16	Eosin Y	-…..	CH_3CN	ND
17[f]	Eosin Y	DIPEA	CH_3CN	ND
18[g]	Eosin Y	DIPEA	CH_3CN	37

[a] Reaction Conditions: 0.30 mmol scale using **1a** (1 equiv), **2a** (3 equiv), catalyst (5 mol%), base (3 equiv) and solvent (3 mL) under argon atmosphere. [b] Isolated yields. [c] Using 2.5 mol% Eosin Y. [d] Using 1.5 equiv DIPEA. [e] Using 1.5 equiv of **2a**. [f] In the absence of light. [g] Air atmosphere. ND = not detected.

With optimized conditions in hand, we embarked on the exploration of scope of the alkyl radical triggered cascade manifold through reacting a range of electronically and structurally diverse 2-(allyloxy)arylaldehydes **1** with an array of NHPI esters **2** derived from the corresponding carboxylic acids.

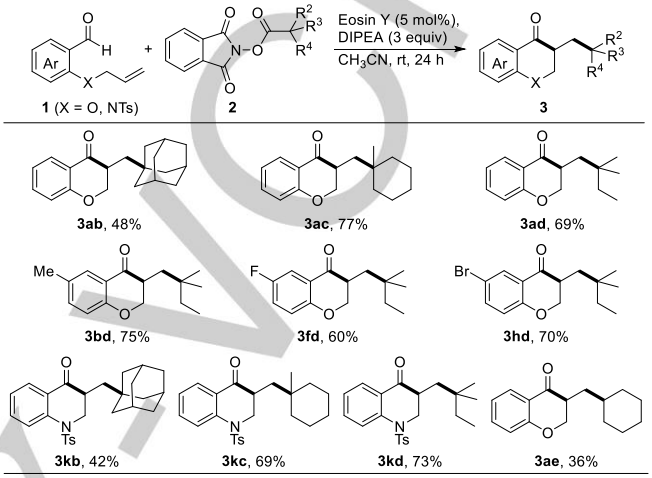
First we studied the effect of electronically distinct substitution patterns on the phenyl ring of 2-(allyloxy)arylaldehydes **1** (Scheme 2). Pleasingly, diverse electron-rich substrates bearing alkyl groups (**1a**-**c**), dialkyl group (**1d**) and methoxy group (**1e**) underwent smooth transformation to yield the corresponding cross-coupled products **3aa**-**3ea** in moderate to good yields (35%-71%). Delightfully, the cascade tolerates the presence of several electron-withdrawing groups on the phenyl ring (-F, -Cl, -Br, -I) and similar or better reactivities than those with electron-donating counterpart were observed to afford the respective products **3fa**-**3ia** in good yields. Importantly, di-iodo substituted substrate **1j** participated in the process to furnish product **3ja** in 55% yield. We were pleased to find that *N*-allyl-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide **1k** demonstrated good reactivity and the corresponding heteroaryl moiety **3ka** was obtained in 63% yield.



[a] Reaction Conditions: 0.30 mmol scale using **1a** (1 equiv), **2a** (3 equiv), catalyst (5 mol%), base (3 equiv) and solvent (3 mL) under argon atmosphere.

Scheme 2. Scope of 2-(allyloxy)arylaldehydes[a]

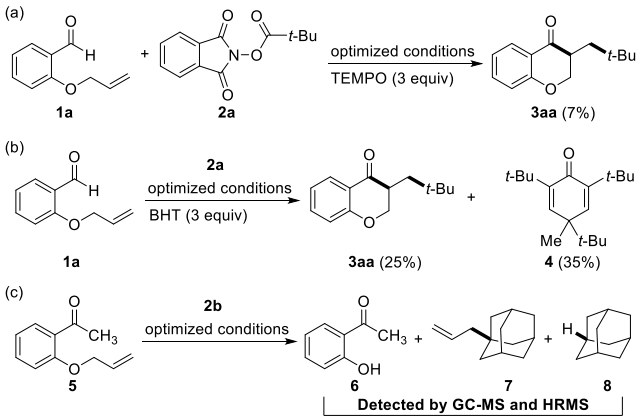
We next explored the generality of the reaction by varying NHPI esters **2** (Scheme 3). We resumed by evaluating the reactivity of tertiary carbon-centered radicals and were glad to note that sterically bulky adamantyl radical underwent planned radical cyclization to provide the desired product **3ab** in 48% yield. Tertiary radical derived from NHPI ester of 1-methyl-1-cyclohexane carboxylic acid furnished **3ac** in 77% yield. Moreover, acyclic tertiary alkyl radical generated from NHPI ester of 2,2-dimethylbutanoic acid reacted with a range of electronically diverse 2-(allyloxy)arylaldehydes (**1a**-**b, 1f, 1h**) to afford the corresponding 4-alkylated chroman-4-one derivatives (**3ad**, **3bd**, **3fd**, **3hd**) in good yields (60%-75%). Pleasingly, the *N*-tosyl substituted analogue **1k** participated in the alkyl radical cascade annulation through reaction with various cyclic and acyclic tertiary radicals to provide the desired 2,3-dihydroquinolin-4-one scaffolds (**3kb**, **3kc**, **3kd**) in moderate to good yields. Notably, NHPI ester derived from secondary cyclohexane carboxylic acid was well accommodated in the cascade process giving **3ae** in an acceptable chemical yield. In general, NHPI esters derived from secondary carboxylic acids were less reactive and primary NHPI esters were not suitable substrates for this radical cascade process. This could presumably be due to the inherent less stability of the corresponding primary and secondary alkyl radicals.



[a] Reaction Conditions: 0.30 mmol scale using **1a** (1 equiv), **2a** (3 equiv), catalyst (5 mol%), base (3 equiv) and solvent (3 mL) under argon atmosphere.

Scheme 3. Scope of *N*-(acyloxy)phthalimides[a]

To gain further insight into this photocatalytic cascade process, a few control experiments were carried out (Scheme 4). The yield of **3aa** drastically reduced to 7% when **1a** and **2a** were allowed to react under optimized conditions in the presence of 3 equiv of TEMPO (2,2,6,6-tetramethyl-1-piperidine-1-oxyl) as the radical scavenger (Scheme 4a). On the other hand, carrying out the same reaction in the presence of another radical scavenger BHT (2,6-di-*tert*-butyl-4-methylphenol) led to the formation of **3aa** (25%) and an adduct **4** (35%) resulting from the trapping of initially generated *tert*-butyl radical by BHT (Scheme 4b). These experiments explicitly established the intermediacy of radicals in the presented cascade process. Interestingly, the reaction of ketone **5** with **2b** under optimized conditions led to the formation of 2-hydroxy acetophenone **6**, allylated adamantane **7** and adamantane **8**, which were detected by GC-MS and HRMS (Scheme 4c) (see the SI for details). Presumably, the radical intermediate generated through the addition of adamantyl radical on the C=C double bond could not undergo intramolecular cyclization owing to the less reactivity of pendant ketone functionality, which ultimately led to the fragmentation and formation of **6** and **7**. This interesting control experiment does not only reaffirm the intermediacy of alkyl radicals in this process but also unequivocally established the requirement of high reactivity of carbonyl functionality towards the success of the annulation process.



Scheme 4. Control experiments.

To shed light on the mechanism of the cascade process, fluorescence quenching studies were carried out. In Stern-Volmer studies (see SI for details) significant quenching of fluorescence emission of Eosin Y was observed by NHPI ester **2a**, rather than with 2-(allyloxy)arylaldehyde **1a** or DIPEA, indicating that the reaction proceeded through an oxidative quenching of Eosin Y (Figure 2).[9g]

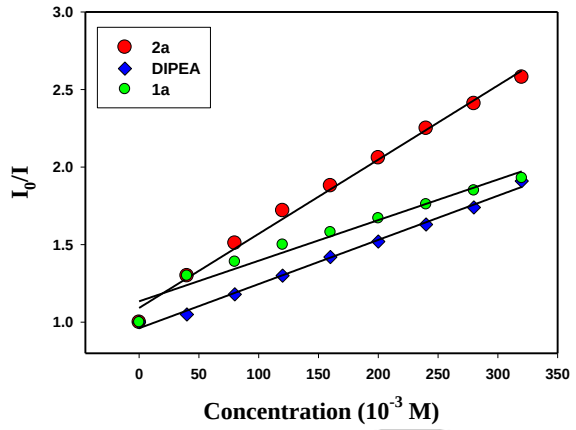
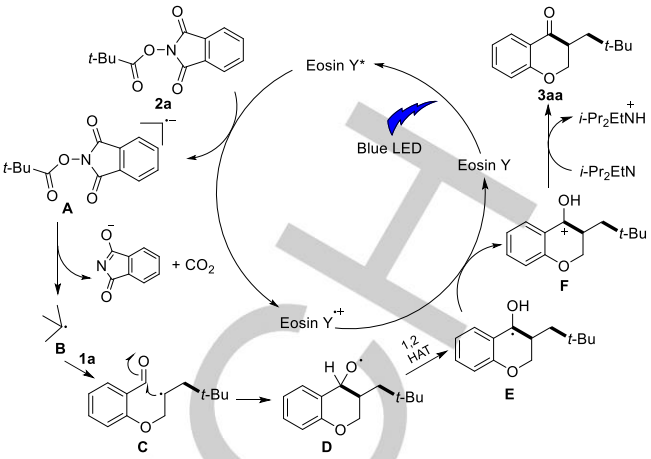


Figure 2. Fluorescence quenching of Eosin Y by **1a**, NHPI ester **2a** and DIPEA.

Based on our studies and previous reports,[4h, 4i, 9g] a plausible mechanism is depicted in Scheme 5. The reaction begins by photoexcitation of Eosin Y by visible light to give the corresponding excited Eosin Y*, which then undergoes oxidative quenching by single electron transfer (SET) to NHPI ester **2a** to generate the radical anion **A** along with Eosin $Y^{\bullet+}$. Subsequent fragmentation of **A** leads to tertiary radical **B** along with the formation of phthalimide anion and CO_2. Thus generated radical **B** then undergoes intermolecular addition on the C=C bond of **1a** affording another radical **C**, which immediately undergoes intramolecular cyclization on the pendant aldehyde moiety to furnish radical intermediate **D**. The carbon-centered radical **E** formed following a 1,2-hydrogen atom transfer (HAT) on **D** then undergoes oxidation by Eosin $Y^{\bullet+}$ and subsequent deprotonation delivers the desired product **3aa**.



Scheme 5. Proposed mechanism of the radical cascade cyclization.

In summary, we have developed a straightforward and convenient organophotoredox catalyzed decarboxylative radical cascade annulation of 2-(allyloxy)arylaldehydes and *N*-(acyloxy)phthalimides towards the construction of biologically important 3-alkylated chroman-4-one scaffolds in moderate to good yields. Importantly, the presented methodology also allowed an efficient access to alkylated 2,3-dihydroquinolin-4-ones in good yields. The protocol is significant as it does not require any metal catalyst and the reactions were carried under mild conditions. Further applications of NHPI esters in combination with photocatalysis towards creating densely functionalized molecular frameworks are currently ongoing in our laboratory.

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Keywords: Photocatalysis • Redox-active ester • *N*-(acyloxy)phthalimide • Radicals • Chroman-4-one

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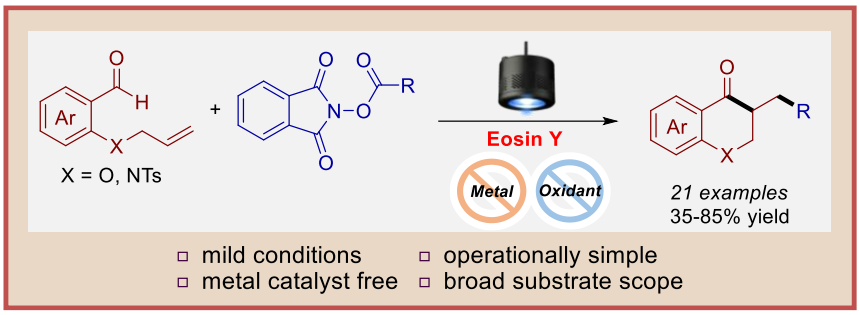

We have developed a mild, metal-free, operationally simple and convenient approach towards the construction of biologically important chroman-4-one scaffolds through an organophotoredox catalyzed decarboxylative radical cascade annulation of 2-(allyloxy)arylaldehydes and *N*-(acyloxy)phthalimides. The reaction proceeds through the intermediacy of radicals and the products were obtained in moderate to good yields.

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