PAPER

DDQ-catalyzed oxidative α-allylation of isochromans under aerobic conditions†

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The allylation of isochromans at the α-position *via* aerobic DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) catalysis is described. This process involves the DDQ oxidation of various isochromans under mild conditions to generate oxocarbenium intermediates, which are effectively stabilized in equilibration in the presence of acid before undergoing allylation. Molecular oxygen and *tert*-butyl nitrite are employed as an environmentally benign oxidant and mediator, respectively, in the catalytic cycle. The transformation of an allylated product to biologically active molecules has also been successfully demonstrated.

Introduction

Isochromans, also known as 3,4-dihydro-1*H*-2-benzopyrans, are commonly found in biologically active compounds. In particular, α-substituted isochromans serve as key scaffolds in agents targeting neurotransmitter regulation (Fig. 1). For instance, sonepiprazole is an antipsychotic isochroman analogue that acts as a selective dopamine receptor D4 antagonist.[1] U-54537 is another D4 antagonist,[2] while Penidicitrinin B is a natural product known for its potent antioxidant activity.[3] Additionally, compound **4** functions as a calcium channel receptor antagonist,[4] and PNU-109291 is a highly selective 5-HT$_{1D}$ agonist.[5] These structural motifs are thus pharmaceutically important, and various synthetic methods to α-substituted isochromans have been developed.

Due to the significance of α-substituted isochromans, extensive efforts have been made toward their synthesis. One of the general approaches involves the formation of carbon–oxygen bond through intramolecular electrophilic aromatic substitution reactions of oxonium intermediate (Scheme 1a).[6] While this strategy provides easy access to α-substituted isochromans, the installation of functionalities typically requires multiple, labor-intensive steps. Alternatively, the coupling reaction of isochromans with nucleophiles at the α-position *via* an oxocarbenium intermediate, generated either by acid-

catalyzed elimination from α-activating substrates or direct oxidative C–H activation, offers a direct synthetic route to α-substituted isochromans (Scheme 1b).[7]

Since Li's group first reported oxidative α-functionalization of isochromans as an atom- and step-economical strategy,[8] various oxidative C–C bond forming reactions using carbon nucleophiles such as ketones, allyl species, acetylenes, and aryl rings have been developed.[9] Both metal and organic oxidants have been employed for α-functionalization, with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) being particularly effective in promoting C–H activation of isochromans.[10] Initially, α-substituted isochromans were synthesized using stoichiometric amounts of DDQ, but this method posed challenges in purification for large-scale synthesis and raised toxicity concerns. Only a few examples of DDQ catalyzed α-functionalization of isochromans have been reported. For example, Floreancig reported DDQ-catalyzed synthesis of α-substituted isochromans using MnO$_2$ as a co-oxidant,[11] while Muramatsu and Li demonstrated organocatalytic arylation, alkylation, and amidation with a DDQ/PIFA co-oxidant system.[12] Although DDQ-catalyzed systems are well-established for alcohol and benzylic oxidations,[13] their application to direct C–H activation of isochromans remains underexplored (Scheme 2).

Recently, we reported aerobic DDQ-catalyzed α-allylation of tetrahydroisoquinolines using NaNO$_2$ and molecular oxygen.[14] In line with our ongoing interest in DDQ catalyzed C–H activation,[15] we sought to extend this strategy to synthesize α-substituted isochromans. In this approach, we envisioned that DDQ-catalyzed oxidation of isochroman under aerobic conditions would generate an oxocarbenium intermediate, which could then react with neutral allyl nucleophile to afford α-substituted isochromans. Herein, we report the aerobic oxidative C–H allylation of isochromans using DDQ catalysis.

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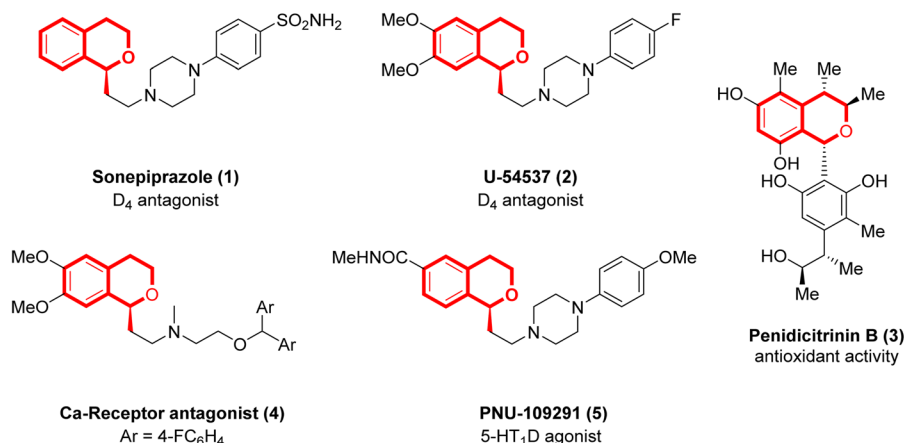
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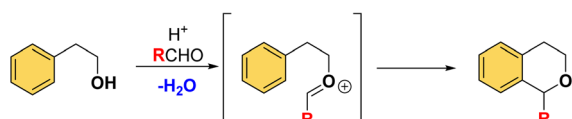
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Fig. 1 Representative biologically active α-substituted isochromans.
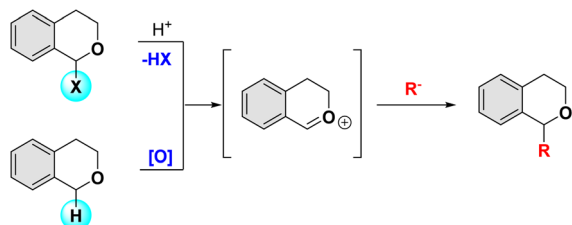
Scheme 1 General methods for the synthesis of α-substituted isochromans.

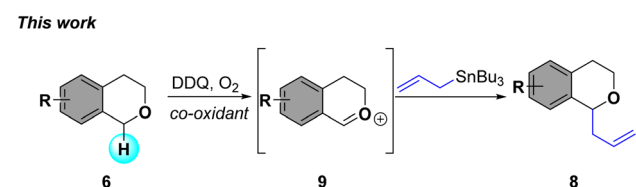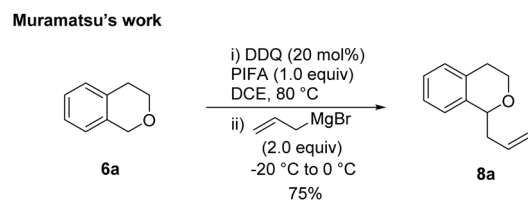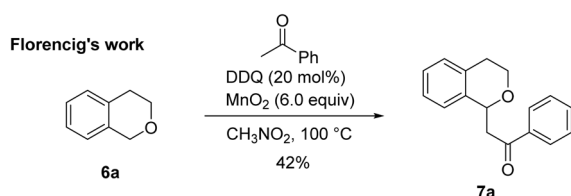Scheme 2 DDQ catalyzed α-substitution of isochromans.

Results and discussion

Initially, we begin with the oxidative allylation of isochromans using a stoichiometric amount of DDQ while screening reaction conditions. As demonstrated in Table 1, the oxidative allylations

Table 1 Initial screening of reactions conditions in the presence of a stoichiometric amount of DDQ[a]

Method A: i) DDQ, **MS 4Å,** DCE, rt, 0.5 h; ii) allylSnBu₃, 24 h

Method B: i) DDQ, **H₂O**, DCE, rt, 24 h; ii) allylSnBu₃, LiClO₄, **acid**, 24 h

Entry	Method	Acid	Solvent	Temp (°C)	Yield[b] (%)
1	A		CH₃CN	25	NR[e]
2	A		DCE	25	7
3[c]	A		DCE	25	11
4	A		DCE	80	18
5	B	TFA	DCE	25	10
6	B	TFA	DCE	80	28
7	B	MSA	DCE	80	59
8[d]	B	CBSA	DCE	80	58

[a] Reaction conditions: (Method A) (i) **6a** (0.15 mmol), DDQ (0.22 mmol), MS 4 Å (20 mg), solvent (0.1 M), rt, 0.5 h; (ii) allyltributyl stannane (0.22 mmol), 24 h. (Method B) (i) **6a** (0.37 mmol), DDQ (0.37 mmol), H₂O (0.41 mmol), DCE (0.1 M), rt, 24 h; (ii) allyltributyl stannane (0.75 mmol), LiClO₄ (0.37 mmol), acid (0.075 mmol), 24 h. [b] Isolated yield. [c] LiClO₄ (0.5 equiv.) was added. [d] The reaction mixture was stirred for 6 h before allylstannane was added. [e] No reaction.

were investigated under both anhydrous and hydrous conditions. DDQ-promoted allylations of isochroman **6a** with allyl stannane at room temperature after treatment with molecular sieves, yielded little or no product **8a** (entries 1–3). Increasing the reaction temperature slightly improved the yield, reaching only 18%. We speculated that such low yields could be attributed to the instability of the oxocarbenium intermediate. The Liu group discovered that DDQ oxidation of isochroman in the presence of H_2O afforded a mixture of hemiacetal **10** and dimerized acetals **11** and **12**, which reversibly formed oxocarbenium ion upon treatment with acid.[16] Based on this study, we further explored the allylation reactions using an acid as a catalyst under hydrous condition. When H_2O (1.1 equiv.) was added to the mixture of isochroman and DDQ, followed by addition of allyl stannane in the presence of TFA, the desired α-allyl isochroman was obtained in 28% yield. Notably, $LiClO_4$ was used to activate oxocarbenium ion.[17] Finally, the reaction was performed at 80 °C in the presence of methanesulfonic acid (MSA) or *p*-chlorobenzenesulfonic acid (CBSA) to afford **8a** in approximately 60% yield. Thus, Brønsted acid played an important role in the formation and activation of the oxocarbenium ion in this DDQ-stoichiometric allylation process.
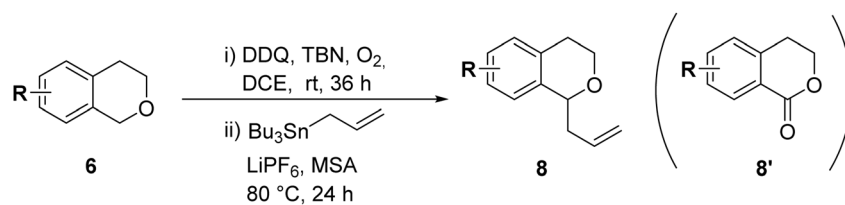
Encouraged by these preliminary results, we turned our attention to optimize the reaction conditions for catalytic DDQ allylation of isochroman. Considering eco-friendly process for catalytic allylation, we have selected molecular oxygen as an oxidant. However, TBN (*tert*-butyl nitrite) was also required as a mediator to regenerate DDQ from 2,3-dichloro-5,6-

dicyanohydroquinone ($DDQH_2$) due to high oxidation potential of $DDQH_2$.[18] Thus, DDQ and TBN co-catalytic system was explored under both photochemical and thermal conditions as shown in Table 2. First, the allylation of isochroman with allylstannane was performed in the presence of DDQ and TBN under molecular oxygen along upon blue led irradiation to give **8a** in low yield. The yield of the reactions did not increase when the amount of reagents was changed or $LiClO_4$ was used as an activating additive, whereas the use of $LiPF_6$ improved the reaction yield up to 30% (entry 5). Interestingly, the yield of allylated product further increased when the reactions proceeded without water (entries 6 and 7). In most cases, however, we observed unidentified side products under photochemical reaction conditions, which is presumably due to strong oxidizing capability of DDQ, resulted from increased reduction potential of $^3DDQ^*$ ($E^*_{red} = 3.18$ V *vs.* SCE).[19] On the contrary, the reactions without light irradiation generally proceeded smoothly to afford the desired allylated isochroman in higher yields compared to the results from the photochemical reactions (entries 8–11). In particular, we observed the highest yield of **8a** when the allylation was performed without water (entry 10). It is noted that a small amount of lactone **8a′** was also formed in some cases by simple oxidation of the corresponding lactol **10**, generated from addition of water to oxocarbenium intermediate (entry 11). We observed the yield decreased when the reaction was performed in the presence of molecular sieves, which indicated that water, generated during oxidation of $DDQH_2$ to DDQ in the catalytic cycle (*vide infra*), is crucial to

Table 2 Optimization of DDQ/TBN-catalyzed allylation[a]

i) DDQ, TBN, O_2, H_2O
DCE, hν or no light

ii) Bu_3Sn ⌒
MSA, $LiClO_4$ or $LiPF_6$

6a → **8a** (**8a′**)

Entry	DDQ (mol%)	TBN (equiv.)	H_2O (equiv.)	Additive (equiv.)	Blue LED	Yield[b] (%)
1	10	0.5	2.0	$LiClO_4$ (1.0)	On	8
2	10	1.0	2.0	$LiClO_4$ (1.0)	On	12
3	10	2.0	2.0	$LiClO_4$ (1.0)	On	12
4	10	1.0	2.0	$LiClO_4$ (0.5)	On	25
5	10	0.2	2.0	$LiPF_6$ (0.5)	On	30
6	10	1.0	—	$LiPF_6$ (0.5)	On	37
7	20	0.2	—	$LiPF_6$ (0.5)	On	36
8	20	1.0	2.0	$LiPF_6$ (0.5)	Off	39
9	20	0.2	2.0	$LiPF_6$ (0.5)	Off	63
10	20	0.2	—	$LiPF_6$ (0.5)	Off	76
11	30	0.2	2.0	$LiPF_6$ (0.5)	Off	51[cd]
12	20	0.2	—	$LiPF_6$ (0.5)	Off	50[e]
13	20	0.2	—	—[f]	Off	16
14	20	0.2	—	—[g]	Off	NR[h]
15	20	0.2	—	$LiPF_6$ (0.5)	Off	41[i]

[a] Reaction conditions: (i) **1a** (0.37 mmol), DDQ, TBN, H_2O, O_2 bubbling (1 h), blue LED (18W) irradiation or no light, DCE (3.7 mL), rt, 24 or 36 h; (ii) allyltributyl stannane (0.75 mmol), additives, MSA (0.075 mmol), 80 °C, 24 h. [b] Isolated yield. [c] 65% conversion. [d] **8a′** was produced in 3% yield. [e] The reaction was performed in the presence of molecular sieves 4 Å. [f] The reaction was performed without $LiPF_6$ only. [g] The reaction was performed without both $LiPF_6$ and MSA. [h] No reaction. [i] The reaction was performed without oxygen bubbling.

Table 3 Scope of DDQ/TBN-catalyzed aerobic allylation of isochromans 6[a]

Entry	Product		Yield (%)	
			8[b]	8′
1	8b	H$_3$C	76	8
2	8c	CH$_3$	80 (2.2 : 1)[c]	7
3	8d	CH$_3$	72 (2.9 : 1)[c]	10
4	8e	MeO	50 (75)	14
5	8f	MeO	66 (90)	—
6	8g	MeO, MeO	48	42
7	8h	F	18 (30)	—
8	8i	Cl	33 (54)	—
9	8j	Br	34 (49)	—
10	8k	F	41 (59)	—
11	8l	Cl	37 (52)	—

Table 3 *(Contd.)*

Entry	Product	Yield (%) 8[b]	8′
12	**8m**	12 (22)	—
13	**8n**	NR[d]	—
14	**8o**	NR[d]	—

[a] Reaction conditions: (i) **6** (0.37 mmol), DDQ (0.074 mmol), TBN (0.074 mmol), O₂, DCE (3.7 mL), 0 °C or rt, 36 h; (ii) allyltributyl stannane (0.75 mmol), LiPF₆ (0.19 mmol), MSA (0.075 mmol), 80 °C, 24 h. [b] Isolated yield. Yields in the parentheses are based upon recovered starting material. [c] Only the diastereomeric ratio was obtained by the analysis of ¹H NMR spectrum. [d] No reaction.

promote reversible formation of oxocarbenium under the optimized reaction condition (entry 12). The yield was dropped without LiPF₆ additive (entry 13), and no reaction occurred without both MSA and LiPF₆ (entry 14). The allylated product **8a** was produced in low yield without oxygen bubbling (entry 15).
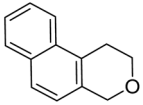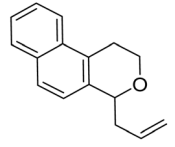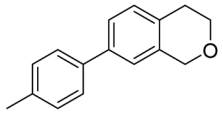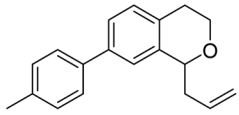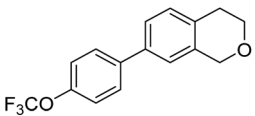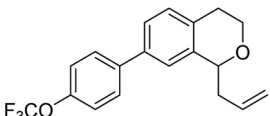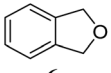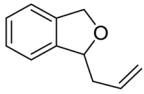
With the optimized reaction conditions established, we investigated the substrate scope of DDQ-catalyzed aerobic allylation of various isochromans, as shown in Table 3. In general, electron-rich isochromans turned out to be the best substrates for this oxidative α-allylation process. Allylation of isochromans **6b–6d**, which contain methyl substituents either on the phenyl ring or the tetrahydropyran ring, afforded the corresponding products **8b–8d** in good yields (entries 1–3). When substrates with high electron donating groups, such as 6- or 7-methoxy isochromans **6e/6f** and 6,7-dimethoxy isochroman **6g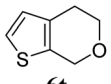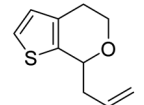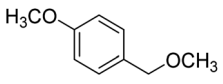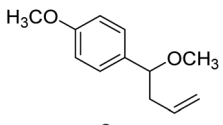**, were subjected to the standard reaction conditions, the desired products **8e–8g** were obtained in moderate yields (entries 4–6). It should be noticed that most of electron-rich substrates also formed lactones **8′** as side products *via* oxidation of lactol intermediates (*e.g.*, **10**). In particular, the highly activated substrate **6g** produced lactone **8g′** in significant yield, reflecting its enhanced susceptibility to oxidation. In the case of halogen-substituted isochromans **6h–6l**, the reactions proceeded slowly, yielding α-allylisochromans **8h–8l** in relatively low yields due to incomplete consumption of the starting materials (entries 7–11). Moreover, the reactions of isochromans **6m**, **6n** and **6o**,

containing acetoxy, cyano and aldehyde groups, yielded little or no desired products, indicating that electron-deficient substrates are not well-suited to this DDQ-catalyzed allylation process (entries 12–14). Importantly, no lactones **8′** were observed in the reactions of electron-deficient substrates, which could confirm that oxocarbenium intermediates were not well generated likely to their low reactivity toward oxidation. These results demonstrate that the presence of electron-donating groups is critical for achieving efficient oxidative allylation in this DDQ/TBN/O₂ catalytic system.

Under the same reaction conditions, the oxidative allylation of other cyclic and acyclic ethers was investigated as summarized in Table 4. Benzoisochroman **6p** and 7-aryl isochromans **6q/6r** underwent allylation efficiently, affording the corresponding products **8p–8r**. However, **8r**, having trifluoromethoxyphenyl at the 7-position, was obtained in low yield, with a large amount of starting material remaining. In contrast, isochroman analogues such as 1,3-dihydroisobenzofuran **6s** and thienopyran **6t** were not well-tolerated, giving **8s** and **8t** in only 29% and 30% yield, respectively. Additionally, no desired product was observed when simple benzyl ether **6u** was subjected to the reaction.

A plausible mechanism for the allylation of isochroman in the DDQ/TBN/O₂ catalytic system is outlined in Scheme 3. According to Floreancig and colleagues,[20] the reaction begins with hydride abstraction from isochroman **6a** by either DDQ
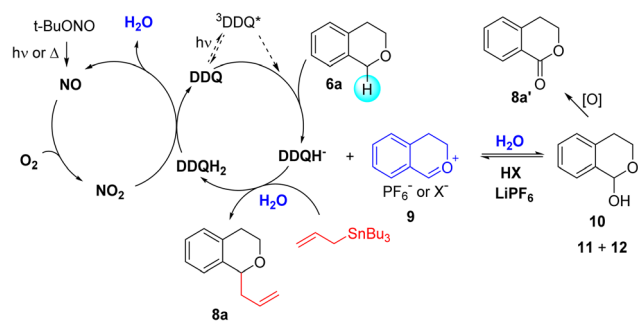
Table 4 DDQ/TBN-catalyzed aerobic allylation of other cyclic or acyclic ethers 6^a

cyclic or benzyl ethers → allylated cyclic or benzyl ethers

i) DDQ, TBN, O₂, DCE, rt, 36 h
ii) Bu₃Sn⌒ LiPF₆, MSA, 80 °C, 24 h

6 → **8**

| Entry	Substrate	Product	Yield (%) 8^b	$8'$ (lactone)
1	6p	8p	86	8
2	6q	8q	49 (62)	21
3	6r	8r	31 (77)	17
4	6s	8s	29	—
5	6t	8t	30 (33)	
6	6u	8u	NR^c	

^{a} Reaction conditions: (i) **6** (0.37 mmol), DDQ (0.074 mmol), TBN (0.074 mmol), O₂, DCE (3.7 mL), 0 °C or rt, 36 h; (ii) allyltributyl stannane (0.75 mmol), LiPF₆ (0.19 mmol), MSA (0.075 mmol), 80 °C, 24 h. ^{b} Isolated yield. ^{c} No reaction.

(thermal) or excited ^{3}DDQ* (photochemical), generating an oxocarbenium ion **9**, which then forms intermediate **10**, **11**, or **12** in the presence of H₂O. Methanesulfonic acid (MSA) promotes the degradation of these intermediates, regenerating the oxocarbenium ion.[16a] LiPF₆ may further assist in their decomposition, forming an oxocarbenium⁺-PF₆⁻ ion pair that enhances nucleophilic addition of allylstannane.[16b] In the catalytic cycle, nitrogen monoxide (NO), derived from the thermal or photochemical decomposition of TBN, is converted to NO₂ in the presence of O₂. NO₂, in turn, oxidizes DDQH₂ back to DDQ, producing H₂O to facilitate the formation of intermediates **10–12**. As the water is generated within the catalytic cycle, the reaction proceeds without addition of water. Notably, in electron-rich substrates, lactones **8′** are frequently formed through the oxidation of intermediate **10**. In contrast, electron-poor isochromans do not undergo this oxidation, owing to their limited conversion to oxocarbenium intermediate **9**. These findings indicate that activated isochromans bearing electron-donating substituents are suited for the current oxidative allylation process.

Scheme 3 Proposed mechanism of DDQ-catalyzed aerobic allylation.
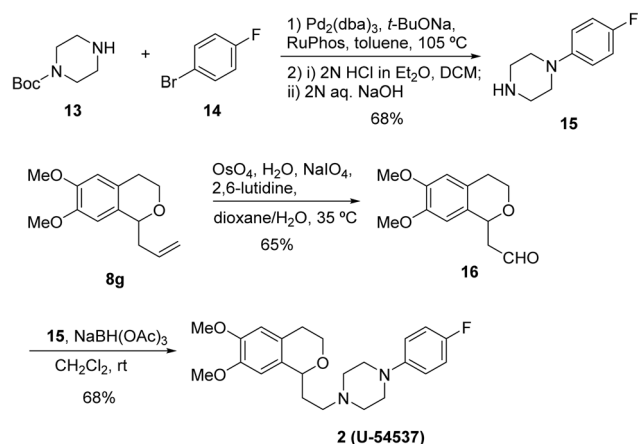
Scheme 4 Synthesis of U-54537 (**2**) starting from α-allyl isochroman **8g**.

Next, we investigated the further transformation of allylated product to biologically useful isochroman derivatives as depicted in Scheme 4. Thus, U-54537 (**2**), known as D$_4$ antagonist, was selected as a target molecule. Pd-catalyzed amination of *N*-Boc-piperazine **13**, followed by removal of Boc protective group, afforded 1-(4-fluorophenyl)piperazine **15** in 68% yield. Oxidative cleavage of **8g** using modified Lemieux–Johnson oxidation (OsO$_4$, NaIO$_4$ and 2,6-lutidine)[21] proceeded to give the corresponding aldehyde **16**, which was subjected to reductive amination with piperazine **15** in the presence of NaBH(OAc)$_3$ to produce the target molecule **2** successfully.

Conclusions

In this study, we have developed the oxidative allylation of iso-chromans using DDQ/TBN/O$_2$ catalytic system. This process showed a direct oxidative functionalization of various isochro-man derivatives at the benzylic α-position. Several key features of this method highlighted: (1) DDQ is employed as a thermo or photochemical organocatalyst to activate C–H bond at the α-position of isochromans; (2) the formation of reactive oxo-carbenium species is controlled by DDQ-oxidation capacity, along with the reversible generation of stable intermediates promoted by water, acid and additive; (3) molecular oxygen serves as an environmentally benign oxidant in the catalytic

cycle. Additionally, the synthetic utility of the allylated product was demonstrated by its transformation into biologically active molecule.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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