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# Switchable Reactivity of Cyclopropane Diesters toward (3 + 3) and (3 + 2) Cycloadditions with Benzoquinone Esters

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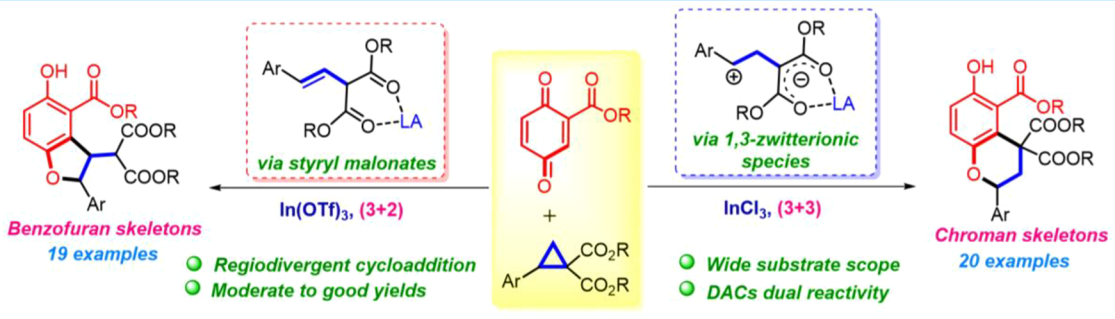


**ABSTRACT:** Herein, we describe an unprecedented (3 + 3) cycloaddition reaction of the donor−acceptor cyclopropanes with quinone esters toward the construction of chroman scaffolds in moderate to good yields. Interestingly, the strategy is also adjustable toward a (3 + 2) cycloaddition by just switching the Lewis acid to furnish benzofuran scaffolds. Based on the choice of Lewis acid used, the same set of precursors has been used to deliver the benzopyran and benzofuran derivatives.

Heterocyclic compounds are privileged structural motifs that have been found as an important core in many natural products.[1] In particular, oxygen-containing heterocyclic frameworks are widely known for their biological and pharmaceutical activities.[2] However, benzopyran derivatives often possess antitumor, antibiotic, and antioxidant properties.[3] Due to their inherent biological properties, chromans have acquired immense attraction in medicinal and organic chemistry. Furthermore, the benzopyran moiety is also a part of PPAR$\gamma$ and PPAR$\alpha/\gamma$ agonists. These PPARs play a very crucial role in the control of different pathological disorders, like hyperlipidaemia, obesity, type 2 diabetes, and neurodegenerative and cardiovascular diseases.[4] (Figure 1)

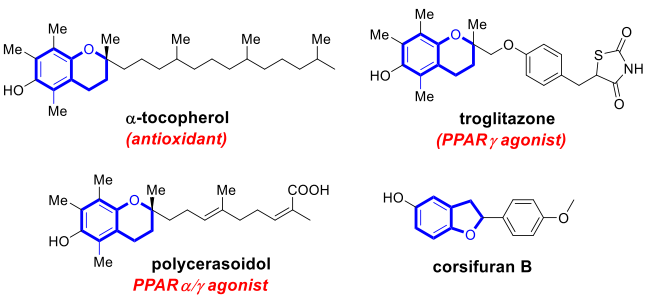


**Figure 1.** Representative natural products and pharmaceuticals containing chroman and benzofuran skeletons.

In addition, bioactive benzopyran scaffolds are used as neuroprotectors in various neurological disorders such as Alzheimer's disease.[5] On the other hand, benzofuran derivatives also represent a wide variety of heterocycles and are found as a core structure in many bioactive molecules.[6] They show a wide range of pharmacological properties and are featured in most clinically used drugs. Indeed, these functionalized derivatives are widely known for their physiological and chemotherapeutic properties, which has made the development of new and time-efficient approaches for the synthesis of these pivotal skeletons more desirable and attractive in the synthetic community.[7]

Over time, donor−acceptor cyclopropanes (DACs) have appeared as one of the most versatile building blocks for the synthesis of various carbo- and heterocycles.[8] Due to the presence of vicinal donor and acceptor groups and high ring strain in the cyclopropane, the cleavage of the carbon−carbon bond occurs effortlessly. These 1,3 zwitterionic species exhibit several transformations like ring opening, rearrangements, ring expansion, and cycloaddition reactions.[9] Out of these, cycloaddition reactions with reaction partners such as imines,

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carbonyls, dienes, alkynes, and nitrones are most investigated.[10] Also, the cycloaddition reactions for the construction of numerous nitrogen heterocycles are extensively studied using DACs as 1,3 dipolar species.[11] On the contrary, the formation of oxygen heterocycles (chromans) using DACs as 1,3 dipolar species for the cycloaddition reactions is less explored. Also, these activated cyclopropanes undergo many rearrangement reactions, most commonly the *in situ* generation of styryl malonates.[12] Interestingly, these styryl malonates can further be a part of cycloaddition reactions by using a suitable reaction partner.[13] Our group has significantly utilized the strain-driven reactivity of DACs for a variety of annulation and cycloaddition reactions to synthesize valuable heterocycles.[14]

On the other hand, quinone esters (QE) have attained substantial attention due to their electrophilic nature.[15] In the past years, there have been very few reports on the reactivity of quinone derivatives with strained ring systems. In 2016, Zhao's group demonstrated the formal (3 + 2) cycloaddition of *p*-quinone methides with vinyl epoxides/cyclopropanes using a palladium precursor and a chiral *bis*-phosphine.[16] Recently, Wang and Luo's group reported the $Sc(OTf)_3$-catalyzed formal (3 + 3) cycloaddition reaction of diaziridines and quinones toward the construction of tricyclic 1,3,4-oxadiazinanes.[17] Very recently, our group also presented the synthesis of tetrahydrofurobenzopyran and tetrahydrofurobenzofuran systems via an *in situ* ring-expansion (Cloke–Wilson rearrangement) of the cyclopropane carbaldehydes followed by a [2 + *n*] cycloaddition with the quinone derivatives.[18] Despite these elegant approaches, we believe quinone esters and DACs would provide a simple and efficient route for the (3 + 3) and (3 + 2) regiodivergent cycloaddition reaction of DACs with quinone esters toward the construction of functionalized oxacycles (chroman and benzofuran derivatives). In this context, we delineate a catalyst-controlled cycloaddition reaction of DACs, a source of 1,3-zwitterionic species as well as 2-styryl malonate by fine-tuning of Lewis acid with the same reaction partner (quinone esters) to furnish densely functionalized five- and six-membered oxacycles (Scheme 1).

We started our investigation using dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (DAC) **1a** and quinone ester **2a** as model substrates. Initially, the reaction was performed using $BF_3{\cdot}OEt_2$ (20 mol %) in dichloromethane at room temperature that lead to the formation of a complex mixture (Table 1, entry 1). Then the reaction was carried out using $Sc(OTf)_3$, and it was found that a new product **4aa** was encountered along with the desired product **3aa** (Table 1, entry 2). After analyzing the data, it was confirmed that a (3 + 2) cycloaddition had taken place. Compound **4aa** was characterized by means of its spectral data. Different Lewis acids like $Cu(OTf)_2$, $Yb(OTf)_3$, $Mg(OTf)_2$, and $In(OTf)_3$ in dichloromethane were examined for the transformation (Table 1, entries 3–6). In all cases, **4aa** was the main product, and **3aa** was attained in very low yields. Further screening of Lewis acids such as $MgI_2$, $MgBr_2$, and $FeCl_3$ proved useful for the transformation, and the improved yield of the desired product **3aa** was obtained with $FeCl_3$ (Table 1, entries 7–9). Therefore, we next examined $InCl_3$ (20 mol %) in DCM, and we were pleased to obtain the targeted cycloadduct **3aa** in 60% yield (Table 1, entry 10). The spectroscopic data and single-crystal X-ray analysis data confirmed the formation of the desired chroman. Delightfully, decreasing the catalyst loading to 10 mol % resulted in 70% yield (Table 1, entry 11). Next, the optimization regarding the five-membered oxacycles were carried out. Initially, the DACs remained unconsumed, resulting in a lower yield of **4aa**.

**Scheme 1. : Previous Reports on the Reactivity of Quinone Derivatives with Strained Ring Systems**

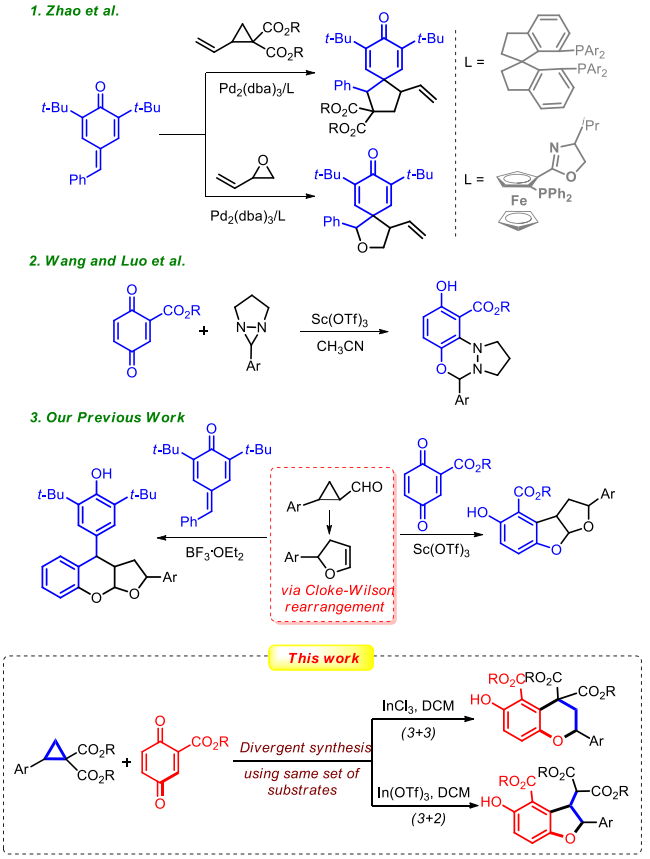
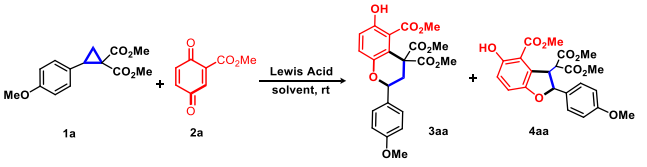



**Table 1. Optimization of the Reaction Conditions**[a]




| Entry | Catalyst | Loading (mol %) | Solvent[c] | Time (h) | Yield (%)[d] 3aa | Yield (%)[d] 4aa |
|---|---|---|---|---|---|---|
| 1 | $BF_3{\cdot}OEt_2$ | 0.2 | DCM | 1 | - | - |
| 2 | $Sc(OTf)_3$ | 0.2 | DCM | 1 | 15 | 50 |
| 3 | $Cu(OTf)_2$ | 0.2 | DCM | 1.5 | 10 | 40 |
| 4 | $Yb(OTf)_3$ | 0.2 | DCM | 2 | trace | 42 |
| 5 | $Mg(OTf)_2$ | 0.2 | DCM | 0.5 | 10 | 25 |
| 6 | $In(OTf)_3$ | 0.2 | DCM | 5 | trace | 56 |
| 7 | $MgI_2$ | 0.2 | DCM | 12 | 30 | - |
| 8 | $MgBr_2$ | 0.2 | DCM | 8 | 25 | - |
| 9 | $FeCl_3$ | 0.2 | DCM | 0.5 | 45 | - |
| 10 | $InCl_3$ | 0.2 | DCM | 0.5 | 60 | trace |
| 11 | $InCl_3$ | 0.1 | DCM | 0.8 | 70 | trace |
| 12[b] | $In(OTf)_3$ | 0.2 | DCM | 1 | trace | 75 |
| 13 | $InCl_3$ | 0.1 | DCE | 0.8 | 55 | - |

[a]Reactions were carried out with 1 equiv of **1a** and 1 equiv of **2a** in solvent (0.1 M). [b]Reactions were carried out with 1 equiv of **1a** and 1.2 equiv of **2a** in solvent (0.2 M). [c]DCM = dichloromethane, DCE = dichloroethane, $CH_3CN$ = acetonitrile. [d]Isolated yield.



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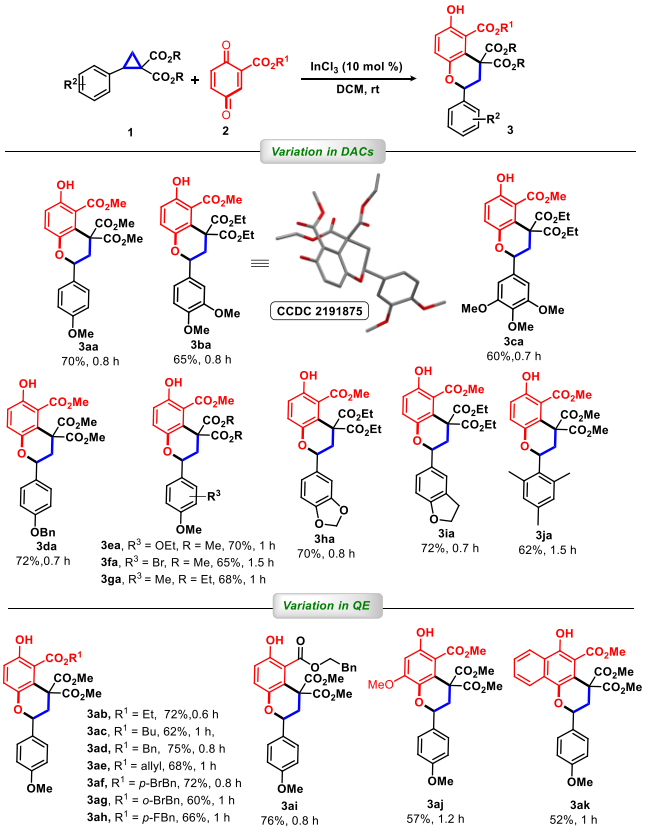
Further, attempting the reaction with 1.2 equiv of **2a** and 20 mol % of catalyst afforded the product **4aa** in 75% yield (Table 1, entry 12). Further, both reactions were performed in various solvents like DCE, $CHCl_3$, $CH_3CN$, and toluene, resulting in a decreased yield of the final product (Table 1, entry 13) (for more information, see the Supporting Information). However, DCM was the solvent of choice in both cases. $AlCl_3$ and $TiCl_4$ proved ineffective for both transformations (see the Supporting Information). After many trials, we finally got the optimal reaction conditions for both transformations, where $InCl_3$ (10 mol %) was the most effective Lewis acid for the (3 + 3) cycloaddition. On the contrary, (3 + 2) cycloaddition was successfully carried out using $In(OTf)_3$ (20 mol %) in dichloromethane in good yields.

With the optimized reaction conditions in hand, we first explored the substrate scope of the (3 + 3) cycloaddition reaction employing a wide range of DA cyclopropanes possessing different substituents on the aryl ring. Cyclopropanes bearing electron-rich substituents at the *para*-position of the aryl ring, such as 4-methoxy, 3,4-dimethoxy, 3,4,5-trimethoxy, and 4-benzyloxy, delivered the desired products **3aa**, **3ba**, **3ca**, and **3da** in moderate to good yields. Next, cyclopropanes having other substituents on the aryl ring along with the methoxy group at the *para*-position were also evaluated. Gratifyingly, groups such as ethoxy, bromo, and methyl at the *meta*-position furnished the targeted (3 + 3) cycloadducts **3ea**, **3fa**, and **3ga** in 65−70% yields. Substituents like methylenedioxy and benzofuran on the aryl ring gave the corresponding products **3ha** and **3ia** in good yields. Cyclopropane having a mesityl substituent on the aryl ring rendered the corresponding product **3ja** in 62% yield. Less electron-rich and halogen-substituted DACs proved inappropriate for the transformation. Later, we evaluated the substrate scope using quinone esters with a range of alkoxy groups. To our pleasure, all of the variations in the esters group, such as ethyl, butyl, benzyl, allyl, *para*-substituted benzyl, *ortho*-substituted benzyl, and phenethyl esters afforded the desired product **3ab**−**3ai** in moderate to good yields. On the other hand, quinone ketones and unsubstituted quinones were also tested; unfortunately, no product formation was observed. Also, methoxy-substituted QE and naphthoquinone esters gave the products **3aj** and **3ak** in appreciable yields (Scheme 2)

Further, the generality and viability of the (3 + 2) cycloaddition reaction were investigated with respect to various DA cyclopropanes. The treatment of dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (DAC) **1a** with quinone ester **2a** provided the corresponding product **4aa** in 75% yield. Cyclopropanes possessing 3,4-dimethoxy, 4-benzyloxy, and methylenedioxy groups on the vicinal phenyl ring of the DACs furnished the anticipated product **4ba**, **4ca**, and **4da** in moderate to good yields. Electron-rich DACs having an *N*,*N*-dimethyl group at the *para*-position were also well-tolerated and provided the cycloadduct **4ea** in 70% yield. Cyclopropanes with multiple substitutions at the aryl ring proved suitable for the desired transformation. The presence of substituents like ethoxy, bromo, and methyl accompanying the methoxy group at the *para* position gave the corresponding products **4fa**, **4ga**, and **4ha** in 68%, 62%, and 74% yields, respectively. Other aryl substituents like benzofuran derivatives afforded the desired product **4ia** in 72% yields. The reaction was also attempted with less electron-rich DACs such as those substituted with 4-tolyl, 4-isopropylphenyl, and 2,4,6-trimethylphenyl groups, but unfortunately, we did not get the

**Scheme 2. Substrate Scope of DACs and Quinones for (3 + 3) Cycloaddition**[a,b]




[a]Standard reaction conditions: **1a** (0.37 mmol), **2a** (0.37 mmol), indium chloride (10 mol %) at room temperature in DCM (4 mL). [b]Isolated yield.

desired product. Next, QEs with different ester groups were also screened, where those with ethyl, butyl, benzyl, and allyl esters offered the targeted products **4ab**, **4ac**, **4ad**, and **4ae** in moderate to good yields. QEs with substituted benzyl and phenethyl esters also procured the corresponding products **4af**−**4ai** in good yields. Other derivatives like methoxy-substituted QE and naphthoquinone esters gave the products **4aj** and **4ak** in 54% and 58% yields, respectively (Scheme 3).

To gain mechanistic insights, control experiments were carried out. First, 2-styryl malonate was synthesized according to the reported literature, and it was treated with QE **2a** under the optimized conditions, which furnished **4aa** in 70% yield (Scheme 4a), confirming that pathway II proceeds *via* 2-styryl malonate intermediate. Also, the cycloaddition reaction of enantiopure cyclopropane (*S*)-**1a** and QE **2a** was performed in the presence of $InCl_3$, which led to the expected product, which was found to be essentially racemic (Scheme 4b). This racemization of the final product indicated that pathway I followed an $S_N1$ mechanism that would involve the formation of a carbocationic or zwitterionic intermediate.

Based on the above experiments and literature reports,[13] a mechanism has been proposed for the designed formal (3 + 3) and (3 + 2) cycloaddition reactions (Scheme 5). In pathway I, $InCl_3$ activates the C−C bond of the DAC and generates a zwitterionic intermediate **A**. At the same time, the quinone ester **2** is activated by the Lewis acid and attacks intermediate **A** on the cationic part to form a new C−O bond *via* $S_N1$ fashion to give intermediate **B**, which further undergoes ring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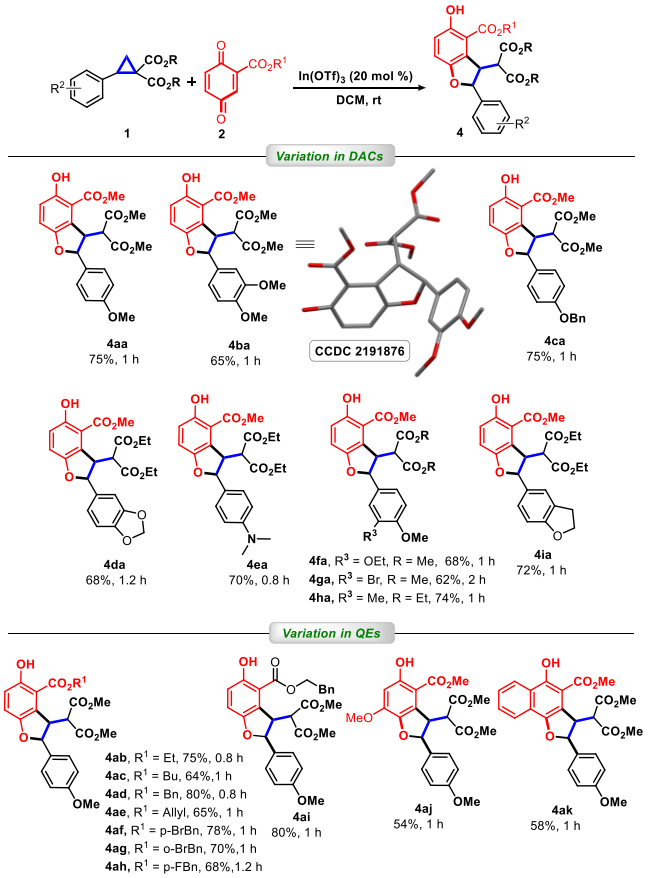
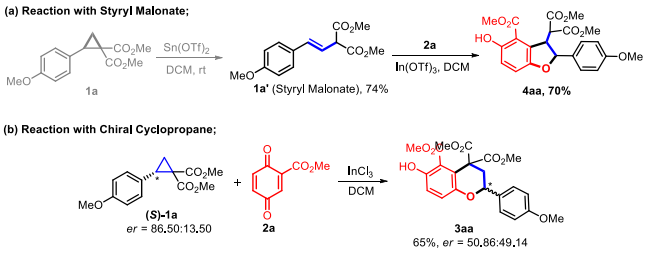
**Scheme 3. : Substrate Scope of DACs and Quinones for (3 + 2) Cycloaddition**[a,b]




[a]Standard reaction conditions: **1a** (0.37 mmol), **2a** (0.44 mmol), indium triflate (20 mol %) at room temperature in DCM (2 mL). [b]Isolated yield.

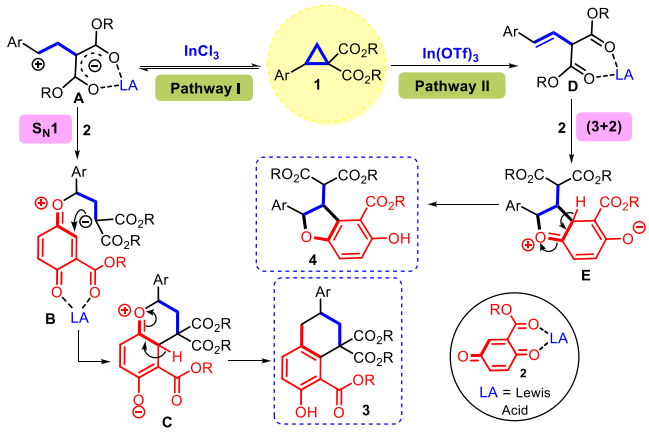
**Scheme 4. Control Experiments**



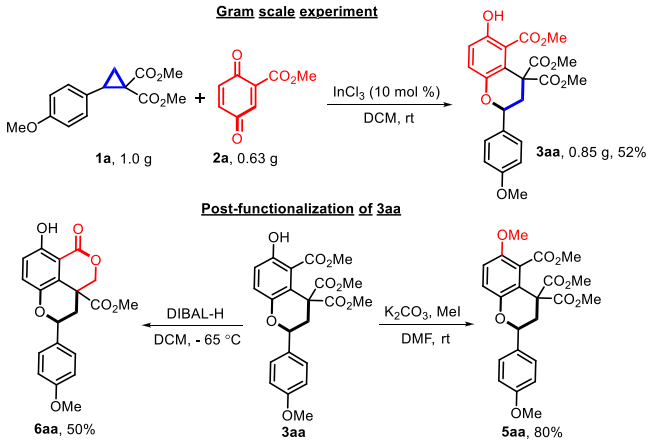

closure followed by the aromatization of **C** to deliver the anticipated chroman derivative **3**. In pathway II, to synthesize benzofuran derivatives, the DAC rearranges itself into the styryl malonate **D**, which subsequently participates in a formal (3 + 2) cycloaddition to produce **4**.

To further showcase the synthetic utility of the designed protocol, a gram-scale experiment was performed where cyclopropane diester and QE were subjected to the optimized reaction conditions. In this scaled-up reaction, **3aa** was obtained in 52% yields. Furthermore, the final product **3aa** was subjected to the methylation of the phenolic hydroxyl group using methyl iodide and base, which resulted in the synthesis of **5aa** in 80% yields. The treatment of **3aa** with DIBAL-*H* resulted in the formation of tetrahydro-2*H*-pyrano-[3,4,5-*de*]chromene scaffolds **6aa** in 50% yield (Scheme 6).

**Scheme 5. Plausible Mechanism for the Desired Transformations**




**Scheme 6. Follow-Up Chemistry**




In summary, we have developed a straightforward and efficient method for the construction of diverse chroman and benzofuran skeletons *via* Lewis acid-catalyzed cycloaddition reaction of DACs and quinones. By careful tuning of Lewis acids, we could achieve either (3 + 3) or (3 + 2) cycloaddition reaction with the same reaction partners, and consequently, the designed protocol represents the regiodivergent synthesis of functionalized benzo-fused six- and five-membered oxacycles. The practicality of this methodology was also confirmed by the gram-scale experiment. The final chroman skeleton could be further derivatized to the 6-methoxy-2-(4-methoxyphenyl)-chroman and tetrahydro-2*H*-pyrano[3,4,5-*de*]chromene scaffolds, indicating the synthetic utility of the designed protocol. The novel methodology exhibits a new synthetic route to access functionalized benzofuzed six- and five-membered oxacycles that make up part of numerous bioactive molecules.

## ■ ASSOCIATED CONTENT

### Data Availability Statement

The data underlying this study are available in the published article and its online Supporting Information.

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.2c03446.

Experimental procedures, characterization data, and copies of NMR spectra (PDF)



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FAIR data, including the primary NMR FID files, for compounds **3aa**−**3ja**, **3ab**−**3ak**, **4aa**−**4ia**, **4ab**−**4ak**, **5aa**, and **6aa** (ZIP)

### Accession Codes

CCDC 2191875−2191876 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Author Contributions

All authors have given approval to the final version of the manuscript

### Notes

The authors declare no competing financial interest.

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