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Fully Substituted Conjugate Benzofuran Core: Multiyne Cascade Coupling and Oxidation of Cyclopropenone

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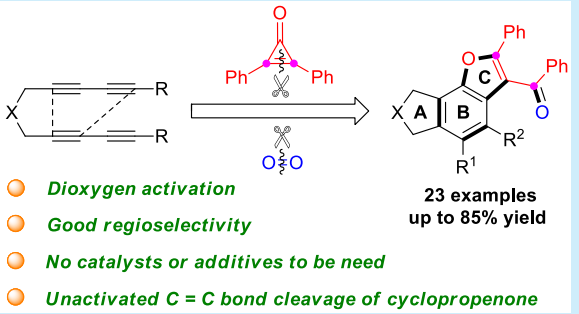
ABSTRACT: An unprecedented C═C double bond cleavage of cyclopropenone and dioxygen activation by multiyne cascade coupling has been developed. This chemistry provides a novel, simple, and efficient approach to synthesize fully substituted conjugate benzofuran derivatives from simple substrates under mild conditions. The density functional theory (DFT) calculations reveal that the unique homolytic cleavages of cyclopropenone and molecular oxygen are crucial to the success of this reaction.



Benzofuran-based motifs are widely found in natural products and biologically active compounds.[1] In particular, fully substituted conjugate benzofuran cores are ubiquitous structures in many leading drug candidates and serve as precursors for the construction of related molecules.[2] For example, rifampicin has a significant antitubercular activity.[3] Usnic acid, which is isolated from *Usnea longissima*, has selective antioxidant action in reducing oxidative damage (Figure 1).[4] Given their widespread applications, several efficient methodologies have been developed for the construction of functionalized benzofurans.[5]

To data, there are two general strategies to assemble a fully substituted conjugate benzofuran core in the literature. The first strategy is based on transition metal-catalyzed C−H functionalization, which can directly introduce the desired functional groups to the substituted patterns (Scheme 1a).[6] The second strategy proceeds via annulation, which capitalizes on individual construction of the benzene or five-membered heteroarenes (Scheme 1b).[7] Although these transformations are efficient and general, harsh reaction conditions, expensive catalyst systems, and prefunctionalized substrates are the unavoidable issues associated with them. Therefore, the development of mild and metal-free strategies toward fully substituted conjugate benzofuran is highly desirable.

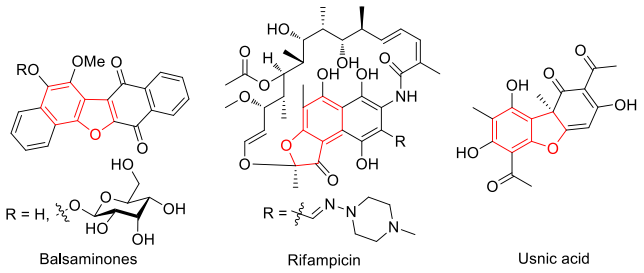
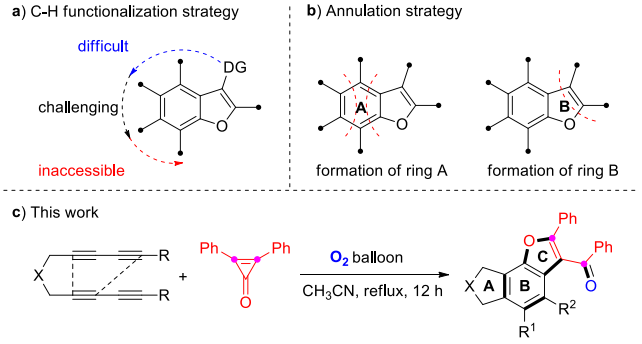


Figure 1. Fully substituted conjugate benzofuran-containing natural products and drug candidates.

Scheme 1. Different Strategies in Attaining Benzofuran with Pattern-Tunable Substituents and Our Work



Arynes are the most reactive organic species and have been broadly employed in numerous organic syntheses.[8] In particular, the thermal cycloisomerization of tethered multiynes to give benzyne intermediates has led to aryne chemistry becoming a blossoming area in recent years.[9] This so-called hexadehydro-Diels−Alder (HDDA) reaction, demonstrated by

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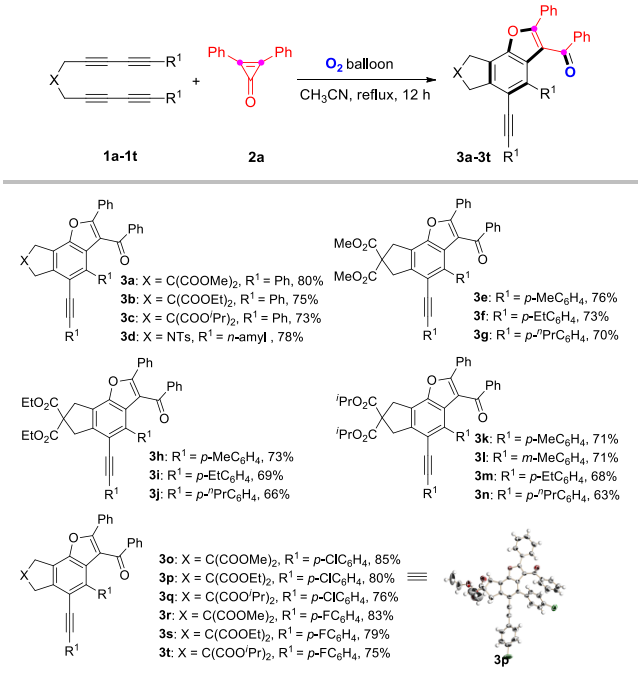
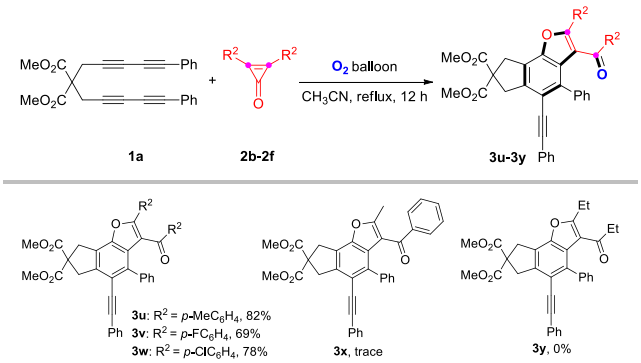
Scheme 2. Substrate Scope of Tetraynes[a,b]



[a]Reaction conditions: tetraynes **1** (1.0 mmol), 2,3-diphenylcycloprop-2-enone **2a** (1.2 equiv), H_2O (1.0 equiv), acetonitrile (2 mL), stirred at 95 °C under O_2 for 12 h. [b]Isolated yield.

Scheme 3. Substrate Scope of Cyclopropenones[a,b]

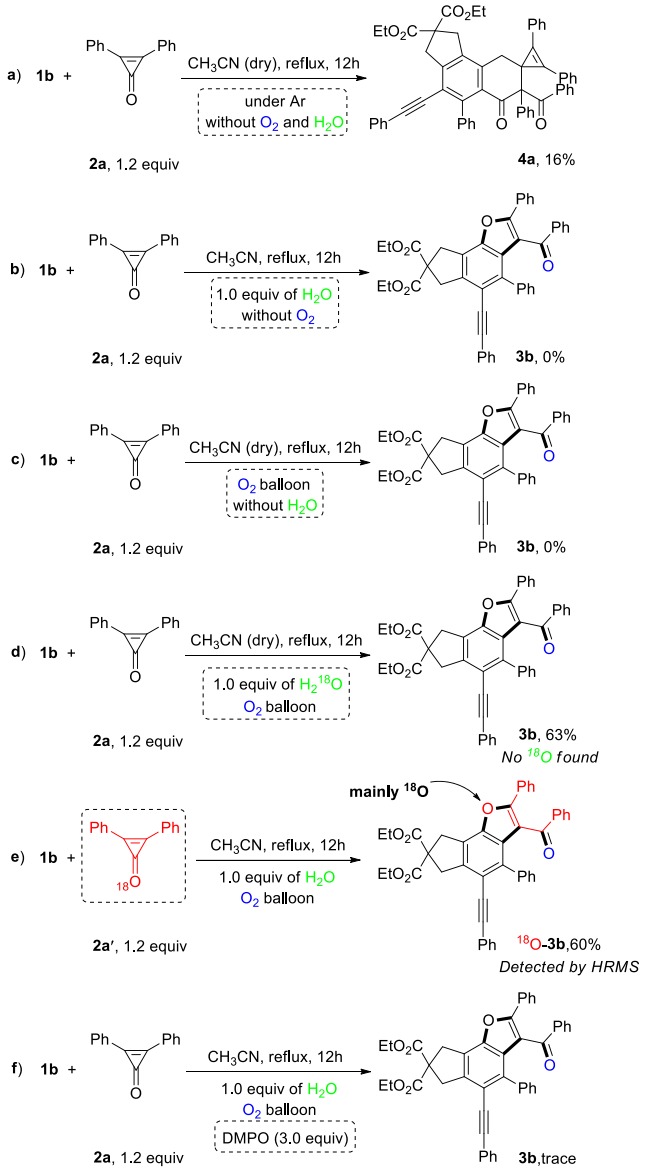


[a]Reaction conditions: dimethyl 2,2-bis(5-phenylpenta-2,4-diyn-1-yl)-malonate **1a** (1.0 mmol), cyclopropenones **2** (1.2 equiv), H_2O (1.0 equiv), acetonitrile (2 mL), stirred at 95 °C under O_2 for 12 h. [b]Isolated yield.

Hoye's group in 2012,[10] can prepared polysubstituted arenes in "one-pot" process.[11] As a part of our research on the efficient construction of polysubstituted arenes via HDDA-derived benzyne chemistry,[12] herein we report an unexpected metal-free C=C double bond cleavage of cyclopropenone, dioxygen activation by multiyne cascade coupling, and reassembled into fully substituted conjugate benzofuran derivatives (Scheme 1c).

When tetrayne **1p** and 2,3-diphenylcycloprop-2-enone **2a** were initially investigated in our multicomponent coupling of tetrayne for the corresponding C−O/C−S difunctionalized benzene derivative synthesis,[13] to our delight, an unexpected fully substituted conjugate benzofuran **3p** was obtained in 12% yield in DMSO under air. In contrast, when the reaction was performed under an Ar atmosphere, no product **3p** was

Scheme 4. Control Experiments



obtained. It seems that molecular oxygen is essential for this transformation. After a brief screening of different reaction parameters, including solvent, temperature, and molar ratio of reactants, the optimal reaction conditions were identified as follows: 1.0 equiv of tetraynes under O_2 atmosphere reacted with 1.2 equiv of cyclopropenes and 1.0 equiv of H_2O in acetonitrile (2 mL) at 95 °C for 12 h. Further investigation of the catalysts indicated that the copper catalyst was an effective system in oxygenation with molecular oxygen,[14] but the reaction proceeded well without metal catalysts or other additives.

The scope of tetrayne substrates was investigated under the optimized conditions. As depicted in Scheme 2, various tetraynes containing different functional groups worked well leading to the desired benzofurans (**3a**−**3t**) in moderate to good yields (ranging from 63% to 85%). When tolerated, tetrayne substrates bearing different esters (OMe, OEt, and O^{i}Pr) gradually decreased in yields (**3a** (80%), **3b** (75%), and **3c** (73%)). By contrast, the substituted groups in the aryl ring of tetraynes bearing electron-withdrawing groups, including

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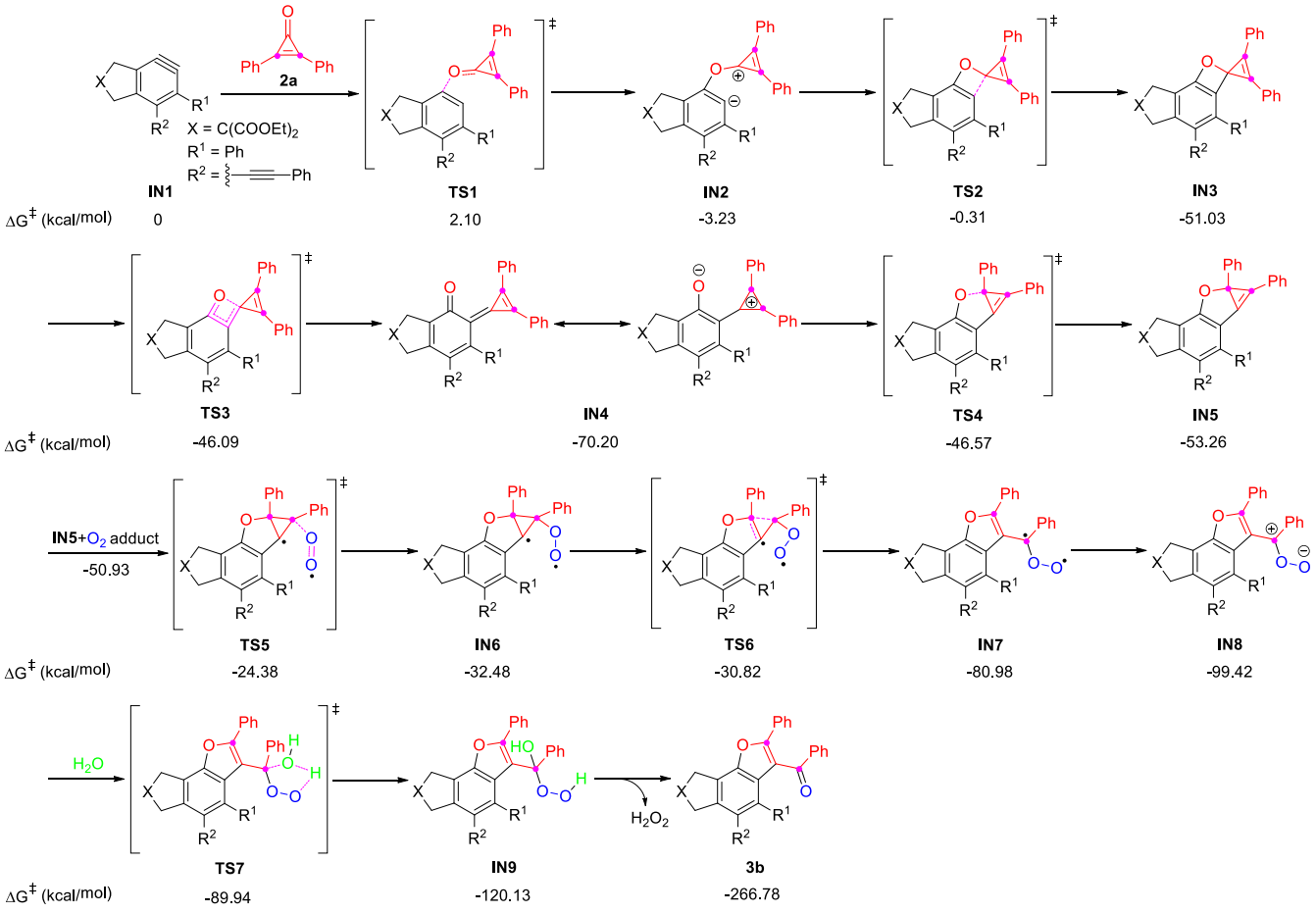
Scheme 5. Relative Free-Energy Profiles for the Reaction of 1b and 2a in CH_3CN



para-Cl and *para*-F (**3o** and **3r**), exhibited higher yields than the electron-donating groups, such as *para*-Me, *meta*-Me, *para*-Et, and *para*-^{n}Pr (**3k**−**3n**), likely because the electron-withdrawing groups increased the reactivity. Compound **3o** was isolated with the highest yield (85%) among the examined substrates. Notably, the *N*-tetrayne substrate that contained alkyl groups instead of phenyl or substituted phenyl groups also generated products with good regioselectivity (**3d** (78%)). Moreover, the structures of **3o**, **3p**, and **3q** were confirmed by X-ray diffraction (CCDC 2044192 (**3o**), 2044191 (**3p**), and 2044195 (**3q**)).

Encouraged by the above results, the scope of cyclopropenones was then examined, and the results are shown in Scheme 3. Electron-donating *para*-Me substituted 2,3-diarylcycloprop-2-enone **2b** showed a slightly higher reactivity and furnished **3u** in 82% yields. Furthermore, 2,3-diphenylcycloprop-2-enones with halogens (F, Cl) at the *para*-position of the phenyl ring reacted smoothly with **1a**, providing the desired products (**3v** and **3w**) in 69% and 78% yields, respectively. Unfortunately, the more challenging substrates 2-methyl-3-phenylcycloprop-2-enone **2e** and 2,3-diethylcycloprop-2-enone **2f** failed to undergo this process, and no desired products were detected. It is noteworthy that these reactions showed high regioselectivity with only one isomer detected. These results indicated the potential of the HDDA-derived benzynes of current multiyne cascade coupling with cyclopropenones for the synthesis of fully substituted conjugate benzofuran derivatives.

Several control experiments were performed to elaborate the reaction mechanism clearly (Scheme 4). When tetrayne substrate **1b** was employed to react with **2a** under Ar in the absence of O_2 and H_2O (see the SI), a spiro-cyclic compound **4a** was obtained in 16% yield instead of **3b** (Scheme 4a), and the configuration of **4a** was further confirmed by X-ray diffraction (CCDC 2044193). Similarly, the model reactions also cannot occur when only 1.0 equiv of H_2O or O_2 was involved in these reactions (Scheme 4b and c), which highlighted the essential roles of molecular oxygen and H_2O in this transformation. Meanwhile, ^{18}O-labeling experiments were carried out to elucidate the origin of the oxygen atom of the ketonic carbonyl group. When the reaction was carried out in the presence of 1.0 equiv of $H_2{}^{18}O$, no ^{18}O-labeled product was detected (Scheme 4d). In contrast, ^{18}O-product was detected by HRMS in the final product (see the SI) when ^{18}O-labeled cyclopropenone **2a′** was used in the reaction system (Scheme 4e). These results demonstrated that the oxygen atom of the ketonic carbonyl group in the product was originated from molecular oxygen. In addition, **3b** was not observed in the presence of 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) under the optimized conditions, which revealed that the reaction might occur through a radical process (Scheme 4f).

On the basis of the above control experiments, a plausible mechanism was proposed and further elucidated by density functional theory (DFT) calculations at the B3LYP+D3(BJ)/6-311+G(2d,p) level of theory (see also the SI) to gain further insight into the reaction mechanism (Scheme 5). Initially, we

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expect an attack by the strongly nucleophilic oxygen of the cyclopropenone **2a** at the HDDA-derived benzyne intermediate **IN1**, formed zwitterionic intermediate **IN2** via **TS1**. This species can underwent a ring closure to the spirocyclic benzoxete intermediate **IN3** via **TS2**.[15] Because of the ring strain, the intermediate **IN3** exhibited ring opening to afford an *o*-quinone intermediate **IN4** via **TS3**. On the basis of previous reports,[13] the zwitterion intermediate **IN4** could be formed by a resonance structure of *o*-quinone intermediate **IN4**. In the next step, the formation of a five-membered furan ring intermediate **IN5** (unstable) was anticipated because of the participation of **IN4** in the nucleophilic attack process via **TS4**. Followed by homolytic cleavage of the C═C bond, the tertiary carbon radical to be trapped by O_2 to generate the key intermediate **IN6** via **TS5**.[16] Then, the peroxide radical intermediate **IN6** underwent an intramolecular radical coupling to provide a more stable intermediate **IN7** via **TS6**. Zwitterionic intermediate **IN8**, a polarization form of **IN7**, also experienced nucleophilic attack in the presence of residual water to form hydroxy hydroperoxide intermediate **IN9** via **TS7**.[17] Finally, hydroxy hydroperoxide intermediate **IN9** underwent homolytic O−O bond scission, followed by C−O bond fragmentation, and then removal of a molecule of hydrogen peroxide to afford the desired product **3b**.[18] Compared with previous work,[19] this transformation provided an example where the C═C double bond cleavage of the cyclopropenone, probably because the highly substituted arene species **IN4** were not allowed to react with another aryne. The computed free-energy variations validated the rationality of the proposed reaction mechanism. All of these processes were feasible at 95 °C.

In summary, we have demonstrated a novel approach to synthesize fully substituted conjugate benzofuran derivatives through a chemical bond cleavage and reassembly strategy. In this reaction, both the benzene and furan rings were simultaneously constructed, whereas the multiyne cascade coupling was performed to produce HDDA-derived benzyne intermediate and trapped by the cyclopropenone. Following this strategy, there might be more possibilities for the incorporation of functional groups in the ring-forming process, which could obviate aforementioned challenges of C−H functionalization and the dependence of arenes. DFT calculations showed that the unexpected homolytic cleavage of cyclopropenone and dioxygen activation were crucial to the success of this reaction. Because of its metal-free nature, this reaction satisfied the particular purity requirements of biological and medicinal chemistry. Further work on the applications and scope extension of this protocol is ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01304.

Experimental procedures for all reactions, spectroscopic characterization data for all new compounds, details of computational methods, and copies of ^{1}H and ^{13}C NMR spectra (PDF)

Accession Codes

CCDC 2044191−2044193 and 2044195 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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Notes

The authors declare no competing financial interest.

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