Two in One: A Brønsted Acid Grafted Photoactive Covalent Organic Framework as Metal-free Dual Photocatalyst for Aerobic Oxidative C-C Cleavage

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**Abstract:** Covalent organic frameworks (COFs) are highly promising photocatalysts with tunable photophysical properties. So far, they have been mainly used as components with a singular functionality, serving either as a photosensitizer or as solid support. The application of COFs multicomponent photocatalysis is challenging. Introducing a second catalytic site in the photoactive COF scaffold to form a dual photocatalyst is the next step toward green chemistry by expanding the boundaries of visible-light-driven photoredox catalysis. Herein, we present a dual photocatalyst in which Brønsted acid sites are incorporated in a photoactive COF to form a metal-free dual photocatalyst for aerobic oxidative C-C bond cleavage of cycloalkanones. The abundant Brønsted acid catalytic sites activate the substrates, while the large π-conjugated, crystalline and highly porous COF photocatalytically accelerates the catalytic cycle and provides an ideal microenvironment in its uniform and ordered channels. This is the first report on a dual Brønsted acid / photoactive COF scaffold.

**Keywords:** Covalent Organic Frameworks; Brønsted Acid; Heterogeneous Photocatalysis; Dual Photocatalyst; C-C Bond Cleavage.
Introduction

The selective cleavage of C-C bonds to form new chemical bonds is scientifically and technologically very important and forms a valuable tool for synthetic fine chemistry, pharmaceutical synthesis, and petrochemical conversions [1-3]. Especially, the C-C bond cleavage of cycloalkanones, prevalent in natural products and pharmaceuticals, could provide strategic bond disconnections in the synthesis of complex bioactive molecules [4-7]. However, due to the large C-C bond dissociation energy (~332 kJ/mol) and the absence of intrinsic ring strain tension, the C-C bond cleavage of cycloalkanones remains a huge challenge. Considerable efforts have been carried out to develop catalysts that facilitate the C-C bond cleavage of cycloalkanones. Various thermal catalysts, containing transition metals, heteropolyacids, or nitroso reagents have been developed for this purpose (Scheme 1a and 1b) [8-10]. In 2019, Dong et al. reported a general C-C bond cleavage procedure driven by aromatization of a pre-aromatic intermediate that is formed in situ. This reaction, suitable for various ketone substrates, is catalyzed by an iridium complex combined with an organophosphorus ligand at high temperature [11]. In 2021, Huang et al. reported a selective C-C bond cleavage of cycloalkanones using NaN\textsubscript{2}O and HCl to produce keto acids or oximes via a nitroso cycloalkanone intermediate [12]. These excellent studies provide inspiration for subsequent research. On the downside, these homogeneous catalytic systems require noble transition metal-based catalysts combined with strong acids [13]. Visible-light-driven organic transformations would give a green and sustainable alternative to these transformations. Guo et al. presented a homogeneous photocatalytic system composed of rosolic acid in concentrated H\textsubscript{2}SO\textsubscript{4} or alternatively Copper(II) trifluoromethanesulfonate to perform the aerobic oxidative cleavage of cycloalkanones driven by visible light [14-15]. Both systems showed a high selectivity
and were the first examples of a successful photocatalyst for this reaction. Still, they rely on homogeneous catalysts, which are costly and not easily recyclable, producing toxic residuals. In this context, the crystalline and highly porous covalent organic frameworks (COFs) are very appealing candidates as heterogeneous photocatalysts.

COFs are built up from organic building blocks linked by covalent bonds and are crystalline porous organic polymers with a well-defined topology and pore structure [16-20]. Their flexible structural design produces materials that are highly ordered and crystalline, exhibit a large surface area and an extended π-conjugated framework with controllable porosity and functionalities [21-22]. The large surface area is not only beneficial for the introduction of catalytic sites but also provides an ideal microenvironment to ensure a fast mass transport during the catalytic reaction and good accessibility of the active sites [23-25]. Furthermore, the highly ordered, crystalline, and extended π-conjugated framework ensures efficient separation of the electron-hole pairs and provide a transfer path for photogenerated electrons, which facilitate the transport and transformation of photogenerated electrons [26-28].

Up to now, the photocatalytic application of COFs has been mainly limited to CO$_2$ reduction or one of the half-reactions for water splitting reactions [27, 29-30]. Only a few COFs have been investigated for visible-light-driven organic transformations, and they are all based on single components that served either as a photosensitizer or as solid support [31-32]. The application of COFs in two-component or multi-component photocatalysis remains to be further explored. Recently, a few transition metal-decorated photoactive COFs has been applied to the carbon-heteroatom cross-coupling reactions [33-34]. For instance, we reported a novel triazine-based COF dual, two-component catalyst, bearing single atom Ni-sites for efficient S-C cross-coupling [35]. Herein, we hypothesized that COFs could form an ideal metal-free platform, utilizing
a two-in-one strategy to combine photoredox and Brønsted acid sites as a dual catalyst to drive organic transformations. As a proof of concept, we present our results that merge Brønsted acid sites in a porphyrin-based COF, creating an ultrastable heterogeneous dual photocatalyst for C-C bond cleavage of cycloalkanones (Scheme 1c).

**Results and Discussion**

Dong’s group reported a novel multicomponent one-pot polymerization strategy to fabricate COFs with quinoline linkage [36-37]. This strategy provides an extraordinary platform to simultaneously integrate various functional groups into one COF framework. Inspired by this strategy, we chose the well-known porphyrin-based COF-367 [38] and 4-vinylbenzenesulfonic acid as the photoactive COF scaffold and the Brønsted acid site, respectively. Under solvothermal conditions, 6M acetic acid, boron trifluoride etherate (BF₃·OEt₂), and 2,3-dicyano-5,6-dichloro-9,10-phenanthraquinone (DDQ) were added (as catalysts) to a solution that contains the building blocks 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (TPA), biphenyl-4,4′-dicarboxaldehyde (BPDA) and sodium 4-vinylbenzenesulfonate (VBS) to synthesize a quinoline-linked two-component COF. (Figure 1a). For simplicity, we abbreviate this COF-based dual photocatalyst as COF-367-SO₃H. Because of the imine to quinoline linkage transformation, COF-367-SO₃H not only introduces a second catalytically active site but also increases the stability of the framework. Also, this combination enhances the conjugation of the framework, which improves the visible light absorption and is reported to stimulate the migration of photogenerated electron-hole pairs [39-41].

The morphology of COF-367-SO₃H was examined by scanning electron microscopy (SEM), showing the uneven rough flaky structure (see Supporting
Information Figure S1). The crystalline structure of COF-367-SO$_3$H was determined by means of powder X-ray diffraction (PXRD) analysis. As shown in Figure 1b, COF-367-SO$_3$H exhibited intense reflections in the low-angle region, the relatively sharp diffraction peaks indicate a good crystallinity of the material. The peaks at $2\theta = 2.98^\circ$, $5.93^\circ$, and $8.48^\circ$ correspond to the (100), (200), and (300) facets, respectively, whereas the index of the PXRD patterns in primitive tetragonal lattice and the presence of a broader diffraction peak at higher $2\theta$ (~25.2$^\circ$) corresponding to the (001) facet suggests the formation of a 2D layered material stacking in the c direction through $\pi$-$\pi$ interactions. An eclipsed AA stacking mode is favored over a staggered AB stacking mode in the structural modeling of COF-367-SO$_3$H. Pawley refinement of the full experimental PXRD profile was carried out, yielding the final unit cell parameters are $a = b = 30.1256$ Å, $c = 3.58553$ Å, and $\alpha = \beta = \gamma = 90^\circ$, which has the low residual values and acceptable profile differences ($R_{wp} = 4.53\%$ and $R_p = 3.28\%$).

The chemical structure of the COF-367-SO$_3$H was confirmed by means of Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and elemental analysis (EA). As shown in Figure 1c, the typical C=N vibration peak at 1637 cm$^{-1}$ in COF-367 has disappeared, and new vibration peaks in COF-367-SO$_3$H at 1588 cm$^{-1}$ and 1538 cm$^{-1}$ have appeared, which originates from the quinolyl moiety [42-43]. Meanwhile, the peaks at 1238 cm$^{-1}$ and 1182 cm$^{-1}$ are assignable to the asymmetric and symmetric stretching vibrations of O=S=O, respectively. Also, the peak at 1032 cm$^{-1}$ can be attributed to the S-O stretching vibrational [44-46]. These vibrations indicate the formation of quinoline linkage and the successful introduction of the -SO$_3$H group. Additionally, the XPS spectra further supported the formation of quinoline-linked COF-367-SO$_3$H. The peaks of N 1s at 397.8 and 398.8 eV were clearly observed in both COF-367 and COF-367-SO$_3$H, and attributed to the C=N and C-N bonds [47-48],
derived from imine-linkage and porphyrin building blocks (Figure 1d, Figure S3). Unsurprisingly, the peak at 399.8 eV in the COF-367-SO$_3$H sample was clearly observed, which originated from the quinolyl N atom [15, 48-49]. This observation further confirmed the formation of a quinoline linkage. All these findings demonstrate a successful synthesis of the quinoline-linked COF-367-SO$_3$H.

The surface area of the COF-367-SO$_3$H was evaluated by Ar adsorption-desorption experiments at 87 K. As shown in Figure 1e, a sharp increase in the gas uptake is observed at low relative pressures (P/P$_0$ < 0.1), indicating the presence of micropores. The Brunauer-Emmett-Teller (BET) surface area and total pore volume (at P/P$_0$=0.97) are 638 m$^2$/g and 0.63 cm$^3$/g, respectively. The pore-size distribution (PSD) was calculated to be 1.78 nm in diameter using Ar at 87 K quenched solid density functional theory (QSDFT) carbon model (Figure S4). This PSD is well-matched with the theoretical PSD (1.83 nm), which is derived from the theoretical model. Compared with COF-367 (BET surface area, total pore volume, and pore sizes are 1632 m$^2$/g, 0.99 cm$^3$/g, and 2.2 nm, respectively), the BET surface area, total pore volume, and pore sizes of COF-367-SO$_3$H are distinctly decreased. This is caused by the internal cavities of the COF-367-SO$_3$H being partially filled by the benzenesulfonic acid group and in second order also by the higher weight of the material per unit cell. Nonetheless, the structure of COF-367-SO$_3$H still presents a persistent open structure, permitting good diffusion of the substrates to the catalytically active sites [50-51].

In addition to persistent porosity, thermal and chemical stability is also critical for the practical implementation of a heterogeneous catalyst. As indicated in Figure S5, the thermogravimetric analysis (TGA) shows that the COF-367-SO$_3$H possesses excellent thermal stability up to 415 °C in air. Generally, imine-based COFs are stable in common organic solvents and boiling water [52-53]. However, under more extreme conditions,
such as strong reducing or oxidizing solutions, most of them degrade quickly. Interestingly, with the imine linkage converted to a quinoline linkage, COF-367-SO$_3$H exhibits remarkable chemical stability. It can withstand strong oxidative and reductive conditions (3 M KMnO$_4$ or 3 M NaBH$_4$ aqueous) as well as the highly concentrated strong acids or bases (12 M HCl or 14 M NaOH aqueous) for more than one week. After such treatment, no alteration in the PXRD pattern, FT-IR spectrum, and Ar adsorption/desorption isotherms were observed (Figure S6, Figure S7, and Figure S8), implying the excellent chemical stability of COF-367-SO$_3$H. The outstanding thermal and chemical stability have significant benefits for COF-367-SO$_3$H as a heterogeneous photocatalyst, which allows it to expand the application range and operate under a variety of harsh circumstances.

The optical behavior of COF-367-SO$_3$H was investigated to verify if the COF-367-SO$_3$H could work under visible light solely. At room temperature, a solid-state UV-Vis absorption experiment was performed, and the result indicates that the COF-367-SO$_3$H can be activated in the UV, visible, and even near-infrared regions (Figure S9). The optical band gap of COF-367-SO$_3$H was analyzed to be 1.57 eV, which is smaller than that of COF-367 (1.73 eV). This can be explained by the introduction of the conjugated quinoline linkage, which brings about the extended conjugation in the x and y directions of the COF structure, resulting in a higher conductivity for the transmission of electrons [29, 54-55]. In comparison to other COF-based photocatalysts, such as LZU-190 [56], COF-JLU-25 [57], Ru-COF [58], and BBO-COF [59] (optical bandgaps are 2.02, 2.4, 1.94, and 2.24 eV, respectively), COF-367-SO$_3$H shows enhanced absorption in the visible light range. As a result, the COF-367-SO$_3$H provides a suitable platform for organic transformations triggered by visible light.
### Table 1. COF-367-SO₃H dual-catalyzed aerobic oxidative C–C bond cleavage of cycloalkanones: influence of reaction parameters.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Variation from the standard conditions</th>
<th>Yield (%)[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Standard conditions[a]</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>No light (dark)</td>
<td>N.R.</td>
</tr>
<tr>
<td>3</td>
<td>No O₂</td>
<td>N.R.</td>
</tr>
<tr>
<td>4</td>
<td>No COF-367-SO₃H</td>
<td>N.R.</td>
</tr>
<tr>
<td>5</td>
<td>COF-367 instead of COF-367-SO₃H</td>
<td>N.R.</td>
</tr>
<tr>
<td>6</td>
<td>Benzenesulfonic acid instead of COF-367-SO₃H</td>
<td>N.R.</td>
</tr>
<tr>
<td>7</td>
<td>COF-367 physical mixed VSB instead of COF-367-SO₃H</td>
<td>46</td>
</tr>
<tr>
<td>8</td>
<td>0.5 mol % COF-367-SO₃H</td>
<td>35</td>
</tr>
<tr>
<td>9</td>
<td>1 mol % COF-367-SO₃H</td>
<td>63</td>
</tr>
</tbody>
</table>

[a] Standard conditions: Under an O₂ atmosphere in the balloon, the mixture of 1a (0.20 mmol), 2 mol% COF-367-SO₃H, and absolute ethanol (2 mL, 2a) add to a 10 ml vial, then a 150W Xenon lamp (λ > 400 nm) irradiation for 24 h with a fan cooling at room temperature. [b] yield was determined by ¹H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard.

So far, we have shown that the COF-367-SO₃H possesses a high crystallinity, permanent porosity, outstanding stability, and promising photoredox properties. In order to validate its photocatalytic properties, visible-light-driven aerobic oxidative C–C bond cleavage of cycloalkanones was carried out. α-Phenylcyclohexanone (1a) and ethanol (2a) were used as model substrates for the optimization of the reaction conditions (Table 1). Under an O₂ atmosphere in the balloon, a reaction mixture of 1a (0.5 mmol), and 2 mol % COF-367-SO₃H in absolute ethanol (2 ml) was irradiated with a 150W UV-filtered Xenon lamp (λ > 400 nm). After 24 hours, an excellent yield (83%) of the desired ε-keto ester 3a was obtained at room temperature, even comparable to homogeneous systems (Table 1, entry 1). The reaction does not proceed in the absence of light, the absence of O₂, or the absence of the photocatalyst COF-367-SO₃H (Table 1, entries 2-4). When the one-component COF-367 without the Brønsted acid
functionalization, was used instead of the two-component COF-367-SO$_3$H also no conversion was observed, implying that the Brønsted acid is essential (Table 1, entry 5). Additionally, when COF-367-SO$_3$H was replaced by benzenesulfonic acid, there was also no product, indicating that the photoactive center also plays a crucial role in this aerobic oxidative C-C bond cleavage reaction (Table 1, entry 6). Interestingly, when the benzenesulfonic acid as a cocatalyst was physically mixed with COF-367 (Table 1, entry 7), a moderate yield of the product 3a was observed (46%), significantly lower than the use of the dual-COF-367-SO$_3$H. Based on these results, it is clear that both photosensitive COF scaffold and the Brønsted acid catalytic species are required to perform the aerobic oxidative C-C bond cleavage reaction. As expected, when the amount of catalyst was increased, the yield also increased significantly from 35% to 63% when the quantity of catalyst was increased from 0.5 mol% to 1 mol%, respectively (Table 1, entries 8–9).

With the optimal conditions in hand, the scope of substrates was extended to investigate the wider applicability of the COF-367-SO$_3$H as a dual photocatalyst in aerobic oxidative C-C bond cleavage of cycloalkanones and their derivatives reactions. Various alcohols and three 2-aryl cycloalkanones (cyclohexanones, cyclopentanone, and cyclobutanone) were chosen as substrates. The reactions were run using the standard conditions (Table 1, entry 1). All corresponding ε-keto esters were produced in acceptable to excellent yields (38-92%). When comparing 3a - 3e, it is clear that the length of the carbon chain has no significant influence on the yield. Both acyclic and cyclic alcohols were also amenable, yielding the desired products 3f and 3g in 69% and 78%, respectively. Not only alkyl alcohols but also aryl alcohols were inserted in good yields.
When phenethyl alcohol was added to the reaction, the corresponding ε-keto ester 3h was produced in a good yield (79%). Furthermore, also phenols are converted; phenol or 4-tert-butylphenol was added to the reaction, offering the phenolic esters 3i and 3j with moderate yields. The decrease in yield may be caused by the lower activity of phenols compared to aliphatic alcohols [60]. Additionally, by comparing 3c, 3k, and 3l, we can conclude that the primary, secondary, and tertiary alcohols behave similarly.

It is worth mentioning that various types of functional groups such as unsaturated C=C or C≡C bonds and halogens are nicely maintained in the esters, demonstrating the high functional group tolerance. Also, in addition to various alcohols, 2-aryl cyclopentanone and cyclobutanone yielded the ε-keto esters 3r and 3s in moderate yields. All these experiments evidence that the COF-367-SO₃H catalyst can transform a wide range of substrates with a high functional group tolerance.

Next, we investigated the recyclability of the photocatalyst, which is another important aspect of the practical implementation. We ran the model reaction (Table 1, entry 1) five times. As can be seen from Figure 2a, after five cycles, the catalyst still can be recovered and reused without loss of catalytic activity. After five cycles of catalysis, no apparent change in the PXRD patterns of the COF-367-SO₃H catalyst (Figure S10), indicating that the crystalline structure of the COF is retained upon the regeneration. Also, negligible in the FT-IR spectrum and Ar adsorption isotherms prove that the chemical structure survived either (Figure S11 and Figure S12).

In order to elucidate the reaction mechanism, photophysical experiments were performed. To determine whether there is an electron transfer between the excited state of COF-367-SO₃H (marked as COF-367-SO₃H*) and the α-phenylcyclohexanone (1a), steady-state emission quenching of COF-367-SO₃H with varying 1a concentration was performed (Figure S13). The result showed a negligible quenching effect of substrate
1a to the fluorescence intensity of COF-367-SO₃H. This indicates that there is no electron transfer between COF-367-SO₃H* and the substrate 1a [61-63]. Subsequently, time-resolved emission spectroscopy was employed (Figure 2b). The fluorescence decay was monitored at 650 nm and was best fitted by two-exponential decays (R² > 0.99). Interestingly, the excited-state lifetime for COF-367-SO₃H* is dramatically reduced from 13.93 μs for Ar-saturated to 8.54 μs for O₂-saturated 1a ethanol solution. These experimental results clearly demonstrate that an energy transfer between COF-367-SO₃H* and molecular oxygen is preferred over an electron transfer between COF-367-SO₃H* and the reaction substrate [64-65]. So, we used a well-known ¹O₂ scavenger, 1,3-diphenylisobenzofuran (DPBF) to monitor the ¹O₂ generation. DPBF is highly reactive toward ¹O₂, which can form endoperoxide and then rapidly decomposes to 1,2-dibenzoylbenzene. Upon visible-light irradiation (λ > 400 nm) and in the presence of COF-367-SO₃H, UV-Vis absorption spectroscopy shows that the absorption peak at 412 nm, which is the DPBF-specific absorption peak, is decreased sharply, indicating the fast formation of ¹O₂ (Figure 2c) [66-68]. These results imply that ¹O₂ is the reactive oxygen species in this oxidative C-C bond cleavage reaction.

We also performed a set of experiments to identify the reaction intermediates (For details, please see the Supporting Information). First of all, a well-known radical scavenger, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was employed to determine whether a radical process is involved in this reaction. When the TEMPO (2 equiv.) was added to the model reaction (Table 1, entry 1), the ε-keto esters 3a were not produced, meaning that the reaction has been fully prevented. We were able to isolate the TEMPO-adduct product and analyze it by ¹H NMR (Figure S1), implying a process of carbon radical formation was involved in this oxidative C-C bond cleavage reaction [69]. Finally, according to previous homogeneous catalyst case reports, enol ester and
peroxy alcohol are possible intermediates [12, 14-15, 70-71]. In order to examine the possible reaction intermediates, an enol ester 4a and a peroxy alcohol 5a were synthesized (For details, please see the Supporting Information). Both of them gave the desired products, confirming that they are the possible intermediates in this reaction.

Based on the above-mentioned results, we propose the following mechanism for the aerobic oxidative C-C bond cleavage of cycloalkanones reaction (Figure 2d). In this dual-catalytic process, the photocatalytic process and the Brønsted acid catalytic process are connected to each other through a synergistic effect. Under Brønsted acid conditions, the cycloalkanone undergoes a classical hemiacetal reaction to afford intermediate II via protonation of the carbonyl and nucleophilic attack by the alcohol. Subsequently, the intermediate II dehydrates to deliver vinyl ether III. Meanwhile, the photosensitive COF-367-SO$_3$H generates an excited state COF-367-SO$_3$H* species under the visible-light irradiation, which can efficiently activate molecular oxygen (O$_2$) to produce the more active singlet oxygen (O$_2$). The highly active O$_2$ rapidly combines with the C=C bond of vinyl ether III to form a dioxetane intermediate IV [72]. Finally, through a facile homolytic cleavage process of the O-O bond and C-C bond of the dioxetane intermediate IV [73], the targeted aerobic oxidative C-C bond cleavage product ε-keto esters V is formed.

**Conclusion**

In summary, we have developed a novel quinoline-linked COF-based dual catalyst via a multicomponent one-pot polymerization strategy. The photoactive COF acts as the photocatalyst while the grafted Brønsted acid acts as the acid catalytic site for the visible-light-driven aerobic oxidative C-C bond cleavage of cycloalkanones. The resulting COF-367-SO$_3$H exhibits high catalytic activity, broad substrate adaptability,
as well as outstanding recyclability and stability due to the large surface area, permanent porosity, long-range conjugation as well as an orderly arrangement of catalytic sites. This work not only provides an environmentally benign and sustainable way to achieve the C-C bond cleavage of cycloketones for distal keto ester production but also demonstrates the ability to graft Brønsted acid catalytic sites in a photoactive COF scaffold and to form a dual catalyst to synergistically perform organic transformations.

**Supporting Information**

Materials and instrumentation, experimental details, synthesis process, supplementary table and figures can be available in the *Supporting Information*.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**References**


Scheme 1. C-C bond Cleavage of Cycloalkanones.

Previous work:

Figure 1. (a) A synthetic scheme of COF-367-SO3H; (b) Top and (c) side views of COF-367-SO3H; (d) PXRD pattern of COF-367-SO3H; (e) FT-IR spectrum of COF-367-SO3H and COF-367; (f) N 1s XPS spectra of COF-367-SO3H.
**Scheme 2.** The scope of substrates. Reaction conditions: Under an O2 atmosphere, the mixture of 1 (0.20 mmol), 2 mol% COF-367-SO3H, and various alcohols (2 mL, 2) add to a 10 ml vial, then a 150W Xenon lamp (λ > 400 nm) irradiation for 24 h with a fan cooling at R.T. Yield (%) was determined by 1H NMR spectroscopy with CH3NO2 as an internal standard.
Figure 2. (a) Assessment of the reusability of COF-367-SO3H. The reusability tests were carried out under identical conditions (Table 1, entry 1). (b) Time-resolved emission spectroscopy for COF-367-SO3H in O2 or Ar-saturated ethanol suspension. (c) UV–vis absorption spectra of DPBF upon visible-light irradiation with COF-367-SO3H. (d) Proposed mechanism of a COF-367-SO3H catalyzed aerobic oxidative C-C bond cleavage of cycloalkanones reaction.