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Allylic C−H Activations Using Cu(II) 2-Quinoxalinol Salen and *tert*-Butyl Hydroperoxide

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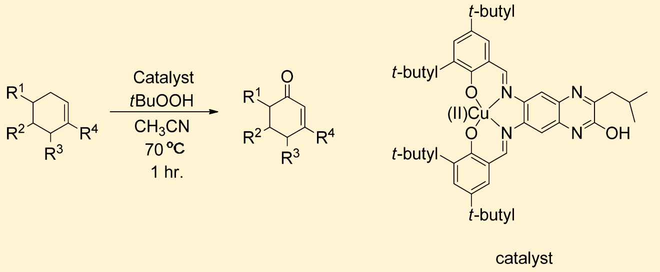
Supporting Information

ABSTRACT: Using a Cu(II) 2-quinoxalinol salen complex as the catalyst and *tert*-butyl hydroperoxide (TBHP) as the oxidant, allylic activations of olefin substrates can be converted to the corresponding enones or 1,4-enediones. Excellent yields can be achieved (up to 99%) within a very short reaction time and with great tolerance for additional functional groups. Possible mechanistic pathways have been characterized using Raman spectroscopy, cyclic voltammetry, and theoretical calculations.



■ INTRODUCTION

The regioselective activation of allylic C−H bonds is of wide interest, and the subsequent oxidation of the to the enone or enedione products of such reactions are common building blocks in multistep organic syntheses.[1,2] The direct transformations of alkenes to the corresponding α,β-unsaturated enones or 1,4-enediones are particularly important in the synthesis of natural products and synthetic drug precursors.[3−9] Although alternative organocatalytic allylic oxidations have been reported,[10−12] the high efficiency of metal-catalyzed allylic oxidations is remarkable.[13−28] An oxidant such as *tert*-butyl hydroperoxide (TBHP) has been used in combination with various metal catalysts including chromium compounds,[13,14] sodium chlorite,[28] copper iodide,[29] dirhodium caprolactamate,[19−23] ruthenium trichloride,[30] bismuth salt,[26] cobalt acetate,[24,25] palladium(II) salts,[16−18] manganese(III) acetate,[15] and ferric chloride.[27] While these previous investigations have reported promising results, numerous limitations remain, e.g., harsh reaction conditions, difficult workup and/or purification procedures, production of harmful waste, low functional group tolerance, and high costs. The two major drawbacks of current methods using TBHP as an oxidant are long reaction time and low regioselectivity of the *tert*-butyl peroxy radical, which results in the formation of numerous isomeric byproducts (e.g., **1**).[22]

The first disadvantage of long reaction times has been addressed by Doyle and co-workers to some extent using a dirhodium caprolactamate catalytic system in which the reaction is found to be completed in much less time.[19] In this system, t-BuOO$^\bullet$ still formed and acts as an oxidant, and hence, regioselectivity remains a problem.[22] Although the most effective metallic catalysts to date are those that are capable of carrying out one-electron redox processes, such as Fe(II)/Fe(III), Cu(I)/Cu(II), Co(II)/Co(III),[19,31] less research has been done using Cu as a catalyst in allylic oxidation, even though copper is widely used in naturally occurring metalloenzymes to facilitate synthesis.[32] For example, galactose oxidase (GOase), a copper-containing metalloenzyme secreted by the fungus *Fusarium* spp., is critical in the oxidation of primary alcohols to aldehydes.[33,34]

Previously, we have reported a new catalytic system that consists of Cu(II) 2-quinoxalinol salen (salqu) complex **1** as catalyst and TBHP as the oxidant for the oxidation of benzylic methylenes into carbonyl groups.[35] Quantitative yields are obtained while different functional groups remain intact. In allylic oxidation using this system, multiple isomeric products are possible. Here, we describe the application of Cu(II) salqu complex **2** in allylic oxidation of olefins to address commonly encountered problems as found in other similar catalytic systems, specifically, long reaction time, low selectivity, harsh conditions, low functional group tolerance, and high cost.[14−28] In addition, we wanted to better characterize the reactivity of the copper complex and the nature of the catalytic mechanistic pathway, in the hopes of subsequently gaining insight as to how we might further exploit these catalyst systems.

■ RESULTS AND DISCUSSION

We began our investigations by examining the allylic oxidation of 1-acetyl-1-cyclohexene **3** using Cu(II) salqu complex **2** as the catalyst (eq 2). For ease of comparison with other catalytic systems, we carried out the oxidation on a millimole scale using 0.5 mol % catalyst loading. For the optimization of TBHP required, the first solvent used was acetonitrile. The reaction was monitored by gas chromatography (GC). Within 1 h of the initiation of the reaction, the yield of the corresponding 1,4-enedione product (**4**) increased from 65% to 99% when the TBHP ratio changed from 1 equiv to 3 equiv. The addition of

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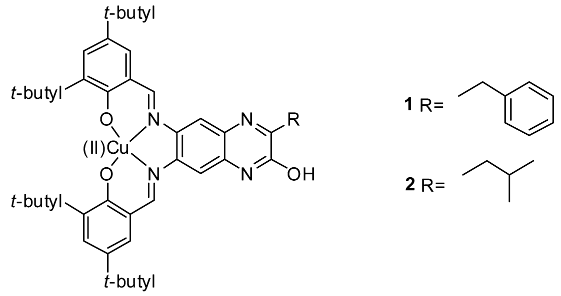
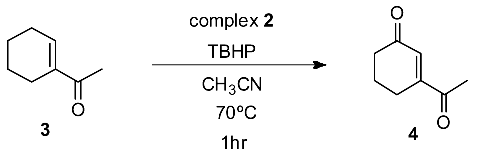


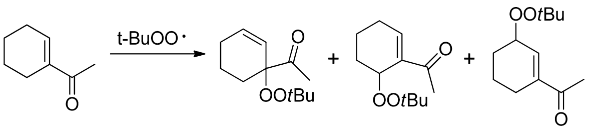


(2)

more TBHP did not result in a further improvement in the yield (Figure 1). The Cu(II) salqu system only requires 3 equiv of TBHP, much less than other reported catalytic methods that required 5−10 equiv.[19,22] Theoretically, only 1 equiv of TBHP is consumed in the allylic oxidation of olefins to enones; however, excess TBHP is required because of the decomposition of TBHP during reaction process. The reduced requirement for TBHP in the Cu(II) salqu system is indicative of the better activation of TBHP leading to a different improved efficiency mechanism.

Using 3 equiv of TBHP and 0.5 mol % of complex **2**, the effect of different solvents on the oxidation of 1-acetyl-1-cyclohexene **3** for 1 h (Figure 1) was also tested. The reaction rates were evaluated on the basis of the yields found after 1 h. Reactions proceeded much more slowly in dichloromethane and chloroform than in acetonitrile. This is consistent with our previous observations.[36] The reaction in DMF had a moderate yield, while the yield of the reaction in DMSO was extremely low. One noticeable feature that distinguishes acetonitrile from other solvents is the oxygen solubility. Oxygen has a greater solubility in acetonitrile (8.1 mM) than most other commonly used organic solvents, such as DMF (4.5 mM) and DMSO (2.1 mM).[37] The surprisingly low yields in DMSO could be also be ascribed to the ligation of the solvent molecule by the catalyst complex, which would prevent the catalyst from functioning normally.[38] To determine whether the oxygen concentration has an influence on the reaction rate, a control experiment was performed in CH_3CN degassed with argon. In this case, only 18% yield was observed after 1 h of reaction time as compared to 99% yield in regular distilled acetonitrile. This result indicated that dioxygen played a crucial role in this conversion.

In most metal-catalyzed allylic oxidations using TBHP as the oxidant, the addition of base would accelerate the reaction because of the facile decomposition of the *tert*-butyl peroxy ether intermediates under basic conditions (Scheme 1).[17,19,39] However, in this case, the addition of 50 mol % of K_2CO_3 did not bring any change to the reaction rate in our system. This result suggests two possibilities: (1) the decomposition of *tert*-butyl peroxy ether intermediate is not the rate-determining step or (2) the *tert*-butyl peroxy ether intermediate was not formed. Since the decomposition of *tert*-butyl peroxy ether is known to be slow and can be greatly accelerated by the addition of base,[17,19,39] the reaction time should decrease with the addition of a base if *tert*-butyl peroxy ether is formed in our system. Thus, it is reasonable to rule out the first scenario. A reaction mechanism bypassing the formation of *tert*-butyl peroxy ether represents a new and alternative pathway to those reported previously.[15−19] This mechanism might subsequently lead to improved selectivity because it would limit the formation of additional isomers as side products along with the formation of desired peroxy ether (eq 1).[17,18,22]



(1)

Allylic oxidations of a variety of representative olefins were examined using 0.5 mol % of complex **2** and 3 equiv of TBHP in CH_3CN at 70 °C (Table 1). Most of the substrates can be converted to the corresponding products with excellent yields with a very short reaction time. The yields typically ranged between 74 and 99%. The nature of the substrates meant that the products were often quite volatile and were, thus, best measured by gas chromatography. In the case of the synthesis of 5,6-dihydro-[1,1′-biphenyl]-3(4*H*)-one (Table 1, entry 3), the product was isolated and purified using flash column chromatography using hexane/ethyl acetate (4:1) as eluent, resulting in a still quite impressive isolated yield of 88%. In the one outlier, the low yield resulting from the 1-nitro-1-cyclohexene precursor (Table 1, entry 11, only 11%) could be due to the strong binding between the nitro group and the Cu(II) of complex **2** that would poison the catalyst. It could

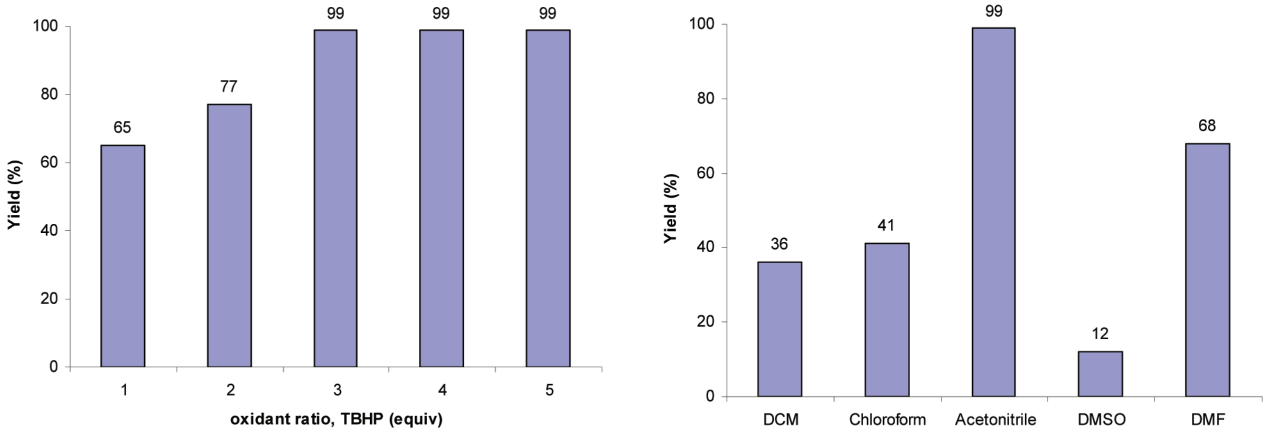


Figure 1. Effects of oxidant ratio and solvents on reaction yields.

Scheme 1. Decomposition of *tert*-Buytl Peroxy Ether under Basic Conditions

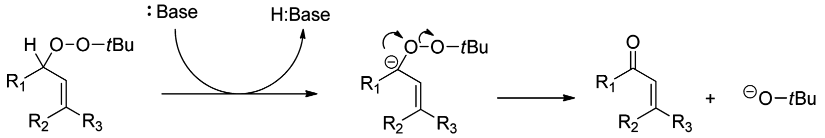
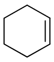
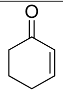
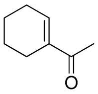
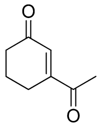
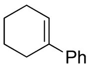
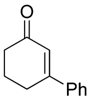
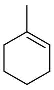
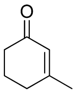
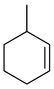
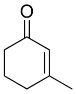
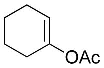
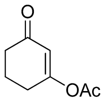
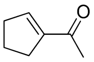
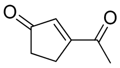
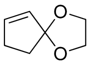
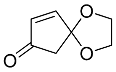
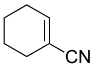
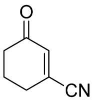
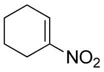
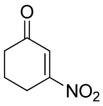


Table 1. Cu(II) Salqu Catalyzed Allylic Oxidation of Olefins

Entry	Substrate	Product	Time (h)	Yield[a] (%)
1			1	74
2			1	99
3			1	91 88[b] 80[c]
4			1	86
5			1	78
6			2	88
7			2	89
8			1	94
9			1	94
10			24	11

[a] GC yields with 1,2-dichlorobenzene added as internal standard. [b] Isolated yield obtained from flash column chromatography using hexane/ethyl acetate (4:1) as eluent. [c] Isolated yield of reaction in gram-scale.

also be the result of the strong electron-withdrawing capability of the nitro group that could destabilize the radical intermediate. Also worth noting is that 3-methylcyclohexene and 1-methylcyclohexene yielded the same oxidation product (entries 4 and 5). This is further evidence supporting a radical mechanism.

To further explore the nature of this catalytic cycle, experiments were performed to characterize the role of the copper species in the reaction. It has been documented that TBHP can easily bind to tridentate mononuclear Cu(II) species to form a Cu(II) *tert*-butyl peroxo complex whose crystal structure showed a distorted tetrahedral binding geometry of the Cu(II) center.[40] By comparing the resonance Raman spectra of LCu(II)OO-*t*-Bu and LCu(II)^{18}O^{18}O-*t*-Bu obtained at 77 K with an excitation at 568.2 nm, five peaks at 471, 640, 754, 834, and 884 cm^{-1} were assigned to the O–O moiety, while the one at 754 cm^{-1} was very small.[41] Meanwhile, little has been done to demonstrate the binding of TBHP to a tetradentate mononuclear Cu(II) complex. In our study, resonance Raman was also employed to provide evidence about the binding between TBHP and Cu(II) salqu (Figure 2).

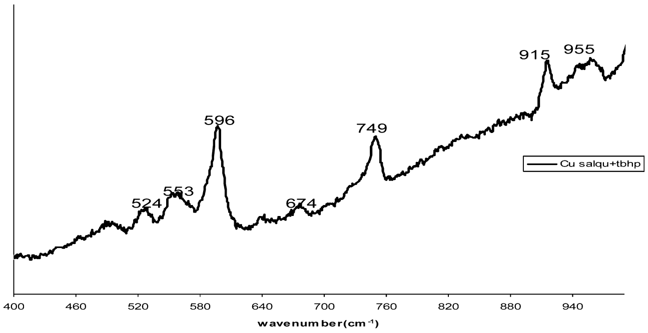
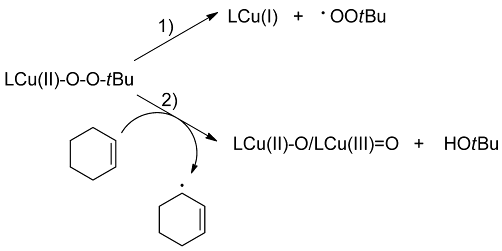


Figure 2. Resonance Raman spectroscopy of Cu(II) salqu with TBHP.

The peaks at 596, 749, 915, and 955 cm^{-1} are in a similar pattern with reported resonance Raman data associated with the O–O moiety from TBHP upon binding.[41] All these bands shifted from 70 to 120 cm^{-1} to greater wavenumbers compared to the previously reported data, indicating a higher vibration frequency of the O–O moiety, i.e., a higher energy for the O–O bond.

For the Cu(II) *tert*-butyl peroxo intermediate, the two possible energetically favorable reaction pathways are (1) reductive cleavage of the Cu–O bond forming Cu(I) and *tert*-butyl peroxyl radical or (2) the homolytic cleavage of the O–O bond caused by direct H abstraction from the substrate resulting in a Cu(III)–oxo and *tert*-butyl alcohol (Scheme 2).[41] Given the fact that the addition of 50 mol % of K_2CO_3 to the oxidation of 1-acetyl-1-cyclohexene did not bring about a change to the reaction rate, indicating that the intermediacy of

Scheme 2. Possible Reaction Pathways of LCu(II)OO-*t*-Bu



tert-butyl peroxy ether did not form, the reductive cleavage of the Cu−O bond was not likely to occur in our catalytic system. Although it is challenging to prove the formation of Cu(III)−oxo, it is notable that Cu(III) can be stabilized by a noninnocent ligand such as salen.[42,43]

An experiment using cyclic voltammetry with Cu(II) salqu demonstrated two quasi-reversible oxidtions ($E^{\circ\prime}$ = +547, +802 mV vs Fc^+/Fc) (Figure 3) that could be ascribed to the sequential single electron oxidations of the phenolic moieties.[42] The pattern of quasi-reversible CV peaks of Cu(II) salqu complex suggested the capability of stabilizing Cu(III) by enabling the equilibrium between $[Cu(III)L]^+$ and $[Cu(II)L^{\bullet}]^+$ as seen in previous reports with salen complexes.[42,43] Calculation at the B3LYP/6-311+G(d,p) level also showed that salqu ligand could stabilize Cu(III) better than salen by enhancing the spin density dispersion on the heterocyclic quinoxalinol backbone; i.e., the spin density of triplet $[Cu(III)L]^+$ is nore delocalized with salqu ligand than salen ligand (Figure 4).

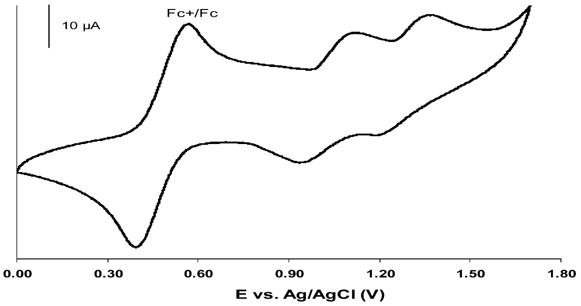


Figure 3. Cyclic voltamagram of Cu(II) salqu with supporting electrolyte 0.1 M tetrabutyl ammonium tetrafluoroborate in 5 mL of CH_2Cl_2 and 1 mM ferrocene internal standard, reference Ag/AgCl, counter electrode Pt gauze (A = 0.77 cm^2), and the working electrode was a glassy carbon disk (d = 0.3 cm, A = 0.071 cm^2).

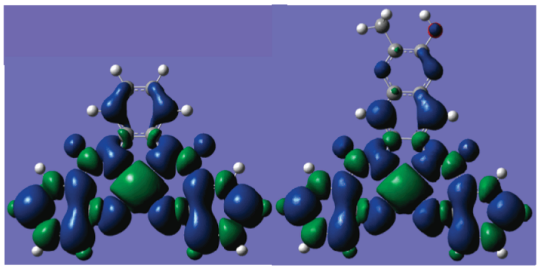
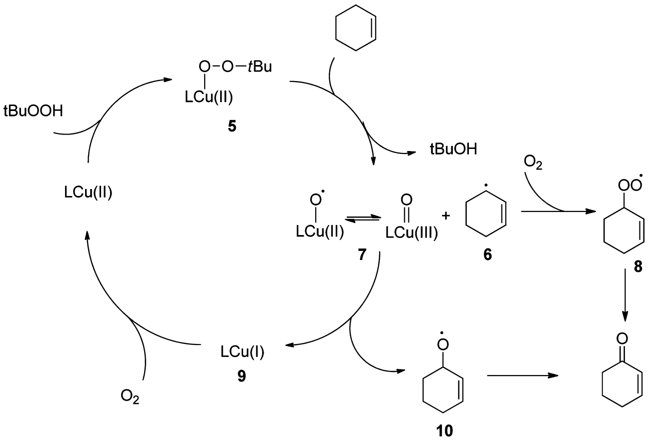


Figure 4. Spin density of [LCu(III)]+ with 0.0004 au isosurface density (L = salen and salqu).

In addition, a EPR signal loss during reaction was observed,[44] suggesting the transformation of a EPR-active species (LCu(II), d^9) to a EPR-silent species. This could be rationalized in terms of the formation of a LCu(I) d^{10} species or a low-spin, diamagnetic Cu(III) d^8 species that equilibrates with a ferromagnetically coupled Cu(II)−ligand−radical species as reported previously with Cu(II) salen complex.[43]

From this, it is reasonable to believe that TBHP will bind to Cu(II) salqu complex (LCu(II)) at the beginning of the reaction (Scheme 3). As mentioned before, the resulting Cu(II) *tert*-butyl peroxo complex **5** is likely to undergo a homolytic cleavage of the O−O bond upon reacting with substrate, yielding *tert*-butyl alcohol, allylic radical **6**, and LCu(II)-O$^{\bullet}$/LCu(III)=O **7**. As proven earlier, dioxygen played a crucial role in our system. One possible way for dioxygen to participate is to react with the allylic radical to form allylic peroxyl radical **8** that can be converted to enone product. The active copper complex **7** can also react with the allylic radical **6** resulting in LCu(I) **9** and allylic oxyl radical **10**, and the latter can be converted to enone as well. Both LCu(I) and LCu(II)-O$^{\bullet}$/LCu(III)=O are EPR-silent species. The postulated formation of LCu(I) and LCu(II)-O$^{\bullet}$/LCu(III)=O is in agreement with our observation in EPR experiment. Copper at an oxidation state of +1 favors a tetrahedral geometry, while the rigid salqu ligand only provides a square planar environment. Hence, the oxidation of LCu(I) **9** to LCu(II) will easily occur. This could be another place where dioxygen was involved. In addition, the mismatch of Cu(I) and binding geometry gives an explanation of our earlier observation about Cu(II) salqu catalyst consumption in steroids oxidation.[36]

Scheme 3. Proposed Catalytic Cycle for Allylic Oxidation Catalyzed by Cu(II) Salqu



Using this proposed catalytic cycle, the regioselectivity and other observed experimental results can be better explained. The allylic radical **6** was formed by hydrogen abstraction when olefin reacted with LCu(II)OO-*t*-Bu **5** instead of the hydrogen abstraction by *t*-BuOO$^{\bullet}$. Because of the bulkiness of the reactive Cu(II) peroxo core induced by the two *tert*-butyl groups from the ligand, the hydrogen abstraction is preferred at the sterically less hindered position. The regioselectivity is thus enhanced. For 3-methyl-1-cyclohexene (Table 1, entry 5), the radical formed at the 3-position is thermodynamically more favored, while the radical formed at the 6-position is sterically more favored. Since the methyl group provides little bulkiness, the formation of the energetically favored intermediate overrides the other. Once the radical is formed at the 3-position, the enone product is energetically more favored than the allylic alcohol that can be formed by the oxidation at that position. In addition, the reaction at the 1-position of the radical intermediate was sterically favored. Affected by these factors, the oxidation of 3-methyl-1-cyclohexene does not have as good a yield as other substrates. In the cyclic voltammetry experiment, the oxidation potentials of the Cu(II) salqu complex were 100 and 150 mV higher than those of the Cu(II) salen (+450, +650 mV vs Fc^+/Fc in CH_2Cl_2 at the same scan rate),[42] indicating a more difficult formation of the $[Cu(II)L^{\bullet}]^+$. No direct electron transfer from the salqu ligand was required in our system on the basis of the proposed catalytic cycle.

■ CONCLUSIONS

In summary, we have reported the first Cu(II) complex catalyzed, regioselective allylic oxidation of olefins to enones and 1,4-enediones. Excellent yields (up to 99%) can be achieved in a very short reaction time (1 h). Tolerance of a variety of functional groups is exhibited. The behavior of the Cu(II) salqu complex as catalyst can be characterized to explain the improved regioselectivity, and a different mechanism of using TBHP from current methods involving the binding of TBHP to Cu(II), homolytic cleavage of O−O bond, and the formation of Cu(III)−oxo is proposed. Further experiments in our ongoing investigations will be used to elucidate the role of dioxygen in this reaction and whether it is possible to use dioxygen as oxident or to use this for additional catalytic reactions.

■ EXPERIMENTAL SECTION

General Methods. All reagents were obtained commercially without further purification. The *tert*-butyl hydroperoxide used is 5.0−6.0 M solution in decane purchased from a commercial supplier. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 and 100 MHz, respectively, as solutions in $CDCl_3$; chemical shift (δ) are reported in ppm relative to Me_4Si. Chromatographic purifications were performed using (60 Å, 70−230 mesh) silica gel. HRMS data were collected with electronspray ionization. All products have been previously described, and ^{1}H, ^{13}C NMR data are in accordance with literature data. Raman spectrscopic data was collected using the 785 nm line (6 mW) from an air-cooled argon ion laser as the excitation source. Raman spectra were collected and analyzed using a Renishaw via Raman microscope system. In the cyclic voltammetry experiments, the electrochemical circuit was controlled using an Epsilon electrochemistry workstation.

The CW EPR spectrum was measured at X-band (9 GHz) frequency on a spectrometer fitted with an ER-4119-HS high sensitivity perpendicular-mode cavity. General EPR conditions were as follows: microwave frequency, 9.385 GHz; field modulation frequency, 100 kHz; field modulation amplitude, 0.6 mT. The Oxford Instrument ESR 900 flow cryostat in combination with the ITC4 temperature controller was used for measurements in the 4−300 K range using a helium flow. Measurements at 77 K were performed by fitting the cavity with a liquid nitrogen finger Dewar.

Procedure for Cyclic Voltammetry Experiment. Electrochemical measurements were carried out at room temperature using a three-electrode setup in a home-built glass cell (20 mL total volume). The supporting electrolyte was 0.1 M tetrabutyl ammonium tetrafluoroborate in 5 mL of CH_2Cl_2 with 1 mM ferrocene as internal standard, the reference electrode was homemade Ag/AgCl wire, and the counter electrode was Pt gauze (A = 0.77 cm^{2}). The working electrode was a glassy carbon disk (d = 0.3 cm, A = 0.071 cm^{2}). Before electrochemical measurement, the solution was purged with N_2 for 15 min. Cyclic voltammogram of 1 mM Cu(II) salqu was recorded in 5 mL of CH_2Cl_2 described above between 0.0 and 1.7 V using a scan rate of 100 mV/s.

Procedure for Raman Spectroscopy. In a 20 mL vial equipped with a stirring bar, Cu(II) salqu complex (5 μmol) was dissolved in CH_2Cl_2 (10 mL) followed by the addition of TBHP (20 μmol). After 15 min of strring, several drops of the Cu(II) salqu solution was taken and allowed to evaporate on a gold foil. The residue was excited at the 785 nm line (6 mW), and the Raman spectrum was collected.

Synthesis of Cu(II) Salqu Complex 2. The Cu(II) salqu complex **2** was synthesized following a published procedure.[36,37]

Cu(II) Salqu Complex 2. IR (KBr): 3429 (br), 2955, 2909, 2868, 1661, 1556, 1524, 1495, 1462, 1423, 1385, 1202 cm^{-1}. UV−vis ($CHCl_3$): 250 (ε = 35 600 M^{-1} cm^{-1}), 285 (ε = 27 140 M^{-1} cm^{-1}), 330 (ε = 31 340 M^{-1} cm^{-1}), 460 nm (ε = 39 280 M^{-1} cm^{-1}). HRMS-ESI: (m + H)/z calcd for $C_{42}H_{55}N_4O_3Cu$ 726.3570, found 726.3575. This is consistent with previous reports.[36,37]

Representative Procedure for Allylic Oxidation. To a 50 mL round-bottomed flask charged with a stirring bar were sequentially added complex **2** (2.5 μmol), CH_3CN (10 mL), 1-phenyl-1-cyclohexene (0.5 mmol), and t-BuOOH (1.5 mmol). After the reaction was stirred at 70 °C for 1 h, solvent was removed under reduced pressure. The residue was purified by flash column chromatography with hexane/ethyl acetate (3:1, v/v) as eluent to yield 76.1 mg yellowish oil as product (88%).

Representative Procedure for Allylic Oxidation (Gram Scale). To a 400 mL round-bottomed flask charged with a stirring bar were sequentially added complex **2** (50 μmol), CH_3CN (200 mL), 1-phenyl-1-cyclohexene (10 mmol), and t-BuOOH (30 mmol). After the reaction was stirred at 70 °C for 1 h, solvent was removed under reduced pressure. The residue was purified by flash column chromatography with hexane/ethyl acetate (3:1, v/v) as eluent to yield 1.38 g yellowish oil as product (80%).

Procedure for Yield Determination by GC. To the reaction flask was added 1,2-dichlorobenzene (0.5 mmol) after 1 h. A 150 μL aliquot of reaction solution was then taken to collect GC data. The yield was determined by the equation yield = (area of the peak for product)/(area of the peak for internal standard).

2-Cyclohexenone (Entry 1, Table 1). ^{1}H NMR: δ 7.03 (m, 1 H), 6.01 (m, 1 H), 2.43, (m, 2 H), 2.37 (m, 2 H), 2.03 (m, 2 H). ^{13}C NMR: δ 199.6, 150.9, 129.8, 38.1, 25.7, 22.8. HRMS-EI: m/z calcd for C_6H_8O 96.0575, found 96.0582.

3-Acetyl-2-cyclohexenone (Entry 2, Table 1). ^{1}H NMR: δ 6.58 (bs, 1 H), 2.50 (m, 2 H), 2.48 (m, 2 H), 2.41 (s, 3 H), 2.00 (m, 2 H). ^{13}C NMR: δ 201.5, 200.1, 154.6, 132.5, 37.9, 26.2, 23.4, 21.9. HRMS-EI: m/z calcd for $C_8H_{10}O_2$ 138.0681, found 138.0687.

3-Phenyl-2-cyclohenenone (Entry 3, Table 1). ^{1}H NMR: δ 7.55−7.53 (m, 2 H), 7.42−7.41 (m, 3H), 6.43 (t, J = 1.2 Hz, 1 H), 2.78 (m, 2 H), 2.49 (t, J = 6.0 Hz, 2 H), 2.18−2.13 (m, 2 H). ^{13}C NMR: δ 200.0, 159.9, 139.0, 130.0, 128.8, 126.1, 125.5, 37.3, 28.1, 22.8. HRMS-EI: m/z calcd for $C_{12}H_{12}O$ 172.0888, found 172.0881,

3-Methyl-2-cyclohexenone (Entries 4 and 5, Table 1). ^{1}H NMR: δ 5.88 (d, J = 1.5 Hz, 1 H), 2.32 (t, J = 6.3 Hz, 2 H), 2.31−2.26 (m, 2 H), 2.02−1.98 (m, 2 H), 1.96 (s, 3 H). ^{13}C NMR: δ 199.9, 162.9, 127.0, 37.4, 31.4, 24.9, 23.1. HRMS-EI: m/z calcd for $C_7H_{10}O$ 110.0732, found 110.0728.

3-Acetoxy-2-cyclohexenone (Entry 6, Table 1). ^{1}H NMR: δ 5.92 (s, 1 H), 2.54 (t, J = 6.8 Hz, 2 H), 2.42 (t, J = 6.4 Hz, 2 H), 2.23 (s, 3 H), 2.09 (m, 2 H). ^{13}C NMR: δ 200.0, 170.0, 167.4, 117.5, 36.6, 28.3, 21.2, 21.2. HRMS-EI: m/z calcd for $C_8H_{10}O_3$ 154.0630, found 154.0626.

3-Acetyl-2-cyclopentenone (Entry 7, Table 1). ^{1}H NMR: δ 6.67 (t, J = 2.0 Hz, 1 H), 2.83−2.80 (m, 2 H), 2.56−2.51 (m, 2 H), 2.50 (s, 3 H). ^{13}C NMR: δ 210.6, 197.3, 169.3, 137.0, 35.4, 27.8, 26.3. HRMS-EI: m/z calcd for $C_7H_8O_2$ 124.0524, found 124.0520.

4-Cyclopentene-1,3-dione Monoethylene Ketal (Entry 8, Table 1). ^{1}H NMR: δ 7.20 (d, J = 6.0 Hz, 1 H), 6.19 (d, J = 6.0 Hz, 1 H), 4.03 (m, 4 H), 2.60 (s, 2 H). ^{13}C NMR: δ 204.0, 156.3, 135.4, 111.6, 65.2, 45.2. HRMS-EI: m/z calcd for $C_7H_8O_3$ 140.0473, found 140.0465.

3-Cyano-2-cyclohexenone (Entry 9, Table 1). ^{1}H NMR: δ 6.52 (s, 1 H), 2.57 (dt, J = 6.0 Hz, 2.0 Hz, 2 H), 2.54 (t, J = 6.2 Hz, 2 H). 2.13 (m, 2 H). ^{13}C NMR: δ 196.6, 138.6, 131.1, 117.0, 37.2, 27.6, 22.0. HRMS-EI: m/z calcd for C_7H_7NO 121.0528, found 121.0525.

3-Nitro-2-cyclohexenone (Entry 10, Table 1). ^{1}H NMR: δ 6.91 (m, 1 H), 2.10 (m, 2 H), 2.51 (t, J = 6.4 Hz, 2 H), 2.19−2.15 (m, 2 H). ^{13}C NMR: δ 198.0, 164.0, 125.8, 37.1, 24.4, 21.0. HRMS-EI: m/z calcd for $C_6H_7NO_3$ 141.0426, found 141.0431.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra and theoretical calculation data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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