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MECHANISTIC INSIGHT INTO CATALYTIC AEROBIC CHEMOSELECTIVE α -OXIDATION OF ACYLPYRAZOLES

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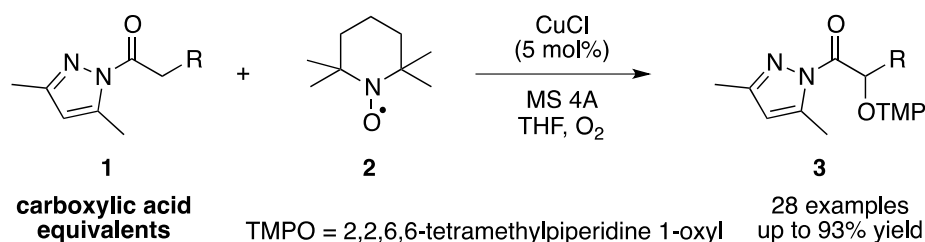
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Abstract – Mechanistic studies on catalytic aerobic chemoselective α -oxidation of acylpyrazoles, including control experiments, kinetic isotope effect experiments, and radical clock experiments, are described. The key to promoting the reaction was the in-situ generation of a copper(II) peroxo complex, which serves as a Lewis acid/Brønsted base cooperative catalyst for efficient enolization. The present catalysis was applicable to late-stage α -oxidation of functionalized acylpyrazoles. A preliminary diastereoselective reaction using readily available chiral acylpyrazoles demonstrated that the present catalysis provided access to optically active α -hydroxy acid derivatives.

INTRODUCTION

Late-stage α -oxidation of carboxylic acid derivatives offers expeditious access to a diverse set of bioactive natural and non-natural α -hydroxy acid derivatives.^{1,2} Rubottom oxidation and Davis oxidation, most commonly utilized, however, are limited to the simple substrates because more than a stoichiometric amount of strong base is required for enolization.^{3,4} Efficient aerobic α -oxidation reactions under mild conditions were recently reported.⁵ Although these methods are highly atom-economical and allow for direct installation of a protecting group-free hydroxy group, the substrate scopes are limited to readily enolizable α,α -disubstituted carbonyls for efficient enolization and suppression of undesired over-oxidation. To synthesize useful α -secondary- α -hydroxy carboxylic acid derivatives, we focused on acylpyrazoles as enolate precursors of carboxylic acid derivatives.⁶ Acylpyrazoles can be easily prepared by conventional methods using acid chloride or combined use of carboxylic acid and a condensation reagent, and exhibit relatively high acidity of the α -proton due to weak amide conjugation. In conjunction with the low pK_a value of the α -proton, the bidentate coordination mode enables chemoselective

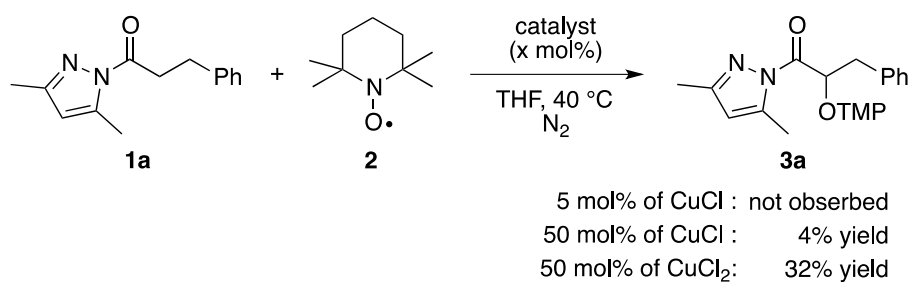
enolization over readily enolizable carbonyls. Based on the hypothesis that the use of a Lewis acid or Lewis acid/Brønsted base cooperative catalyst would allow for efficient enolization of acylpyrazoles without an external base, we recently developed a catalytic aerobic chemoselective α -oxidation of acylpyrazoles using TEMPO as an oxygenating reagent (Scheme 1).^{7,8} Herein we report detailed mechanistic studies on catalytic aerobic α -oxidation of acylpyrazoles through a series of control experiments, kinetic isotope effect (KIE) experiments, and radical clock experiments. Late-stage α -oxidation using functionalized acylpyrazoles was achieved, leading to hitherto-unexplored α -hydroxy acid derivatives. A preliminary diastereoselective reaction using an *l*-menthol-derived chiral auxiliary demonstrated the synthetic utility of the present α -oxidation method.



Scheme 1. Catalytic Aerobic Chemoselective α -Oxidation of Acylpyrazoles

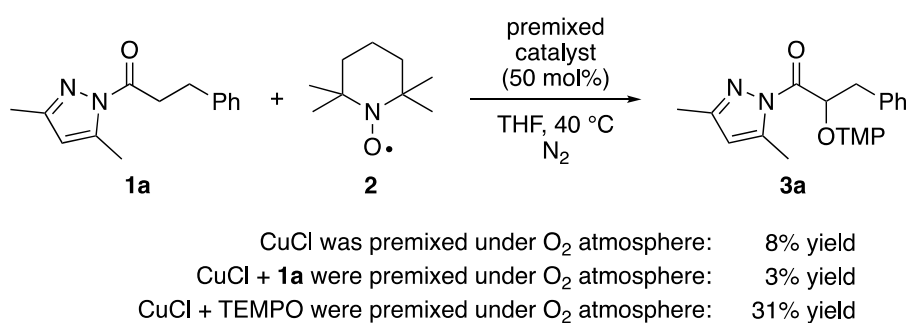
RESULTS AND DISCUSSION

We performed various control experiments to gain insight into in situ-generated copper species (Scheme 2). To investigate the role of oxygen, the reaction was performed under N_2 atmosphere using 5 mol% or 50 mol% of CuCl . In these cases, product **3a** was produced in less than 5% yield. These results differed completely from that of the previous chiral amine-catalyzed reaction,⁸ suggesting that oxygen was critical for promoting the reaction. In contrast, 50 mol% of CuCl_2 promoted the reaction more efficiently and product **3a** was observed in 32% yield. These results indicated that copper(II) salts derived from copper(I) and oxygen are the actual catalytic species.⁹

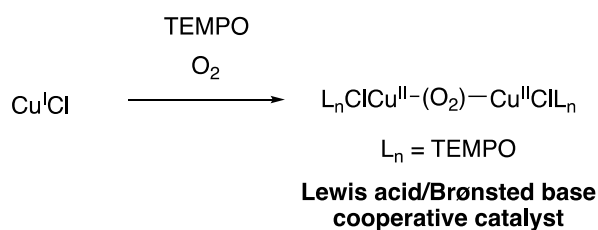


Scheme 2. Substoichiometric Copper-Mediated Reaction under Nitrogen Atmosphere

Several copper(II) catalysts were prepared by premixing CuCl under different conditions and their catalytic activity was evaluated under N₂ atmosphere (Scheme 3). The copper catalyst simply premixed under O₂ atmosphere afforded product **3a** in 8% yield. We speculated that an insoluble copper species would be generated without any ligand. Thus, we next premixed the CuCl in the presence of acylpyrazoles. Product **3a**, however, was observed in only 3% yield. On the other hand, premixing CuCl with TEMPO under O₂ atmosphere delivered product **3a** in 31% yield. These results suggested that TEMPO is essential for generating an actual copper(II) species with the assistance of O₂.¹⁰ Neither Cu(OH)₂, Cu₂O, nor CuO afforded the product, suggesting that copper hydroxide and μ -hydroxo complex were not the actual catalytic species, but instead, the copper(II) peroxo complex served as a Lewis acid/Bronsted base cooperative catalyst (Scheme 4).¹¹

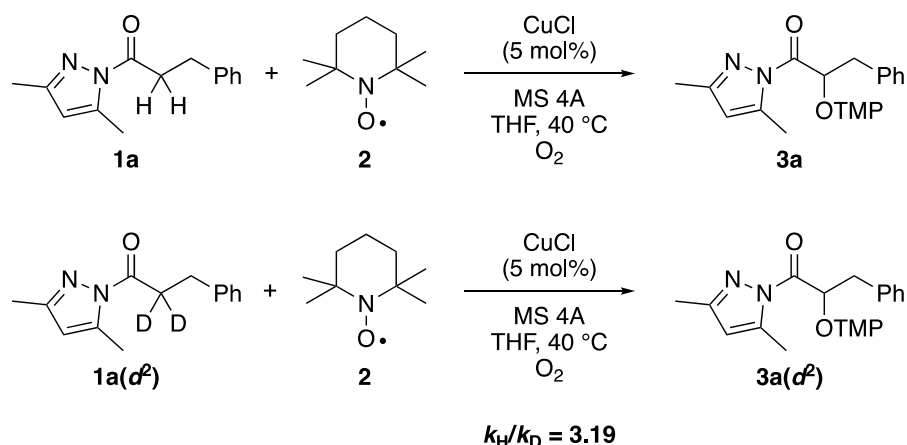


Scheme 3. Actual Catalyst Generation using CuCl under O₂ atmosphere



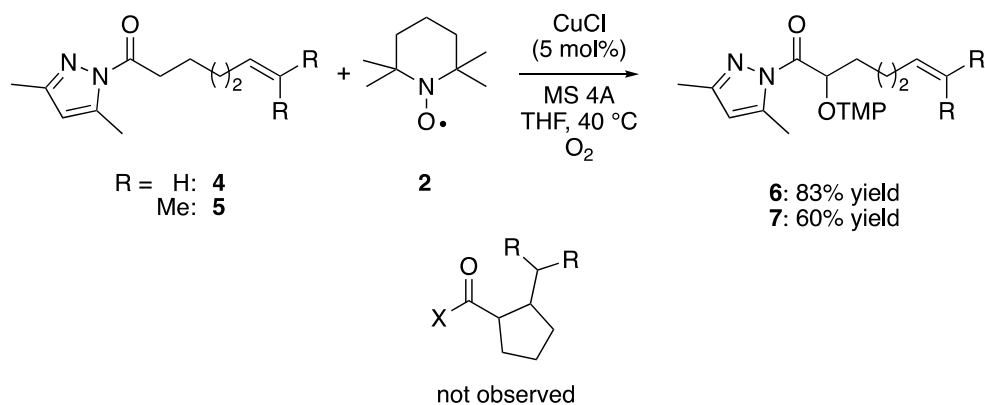
Scheme 4. Proposed Active Catalyst Generation

A KIE study was performed next using deuterated acylpyrazole **1a(d²)** (Scheme 5).¹² A large KIE ($k_{\text{H}}/k_{\text{D}} = 3.19$) was observed from two parallel reactions using **1a/1a(d²)**, indicating that enolization of acylpyrazole largely contributes to the turnover-limiting step. The KIE study prompted us to add an external base to facilitate the enolization step. No improvement was observed by adding various external bases, however, presumably because the copper(II) peroxo complex serves as an actual Bronsted base for enolization.



Scheme 5. Kinetic Isotope Effect Study by Two Parallel Reactions

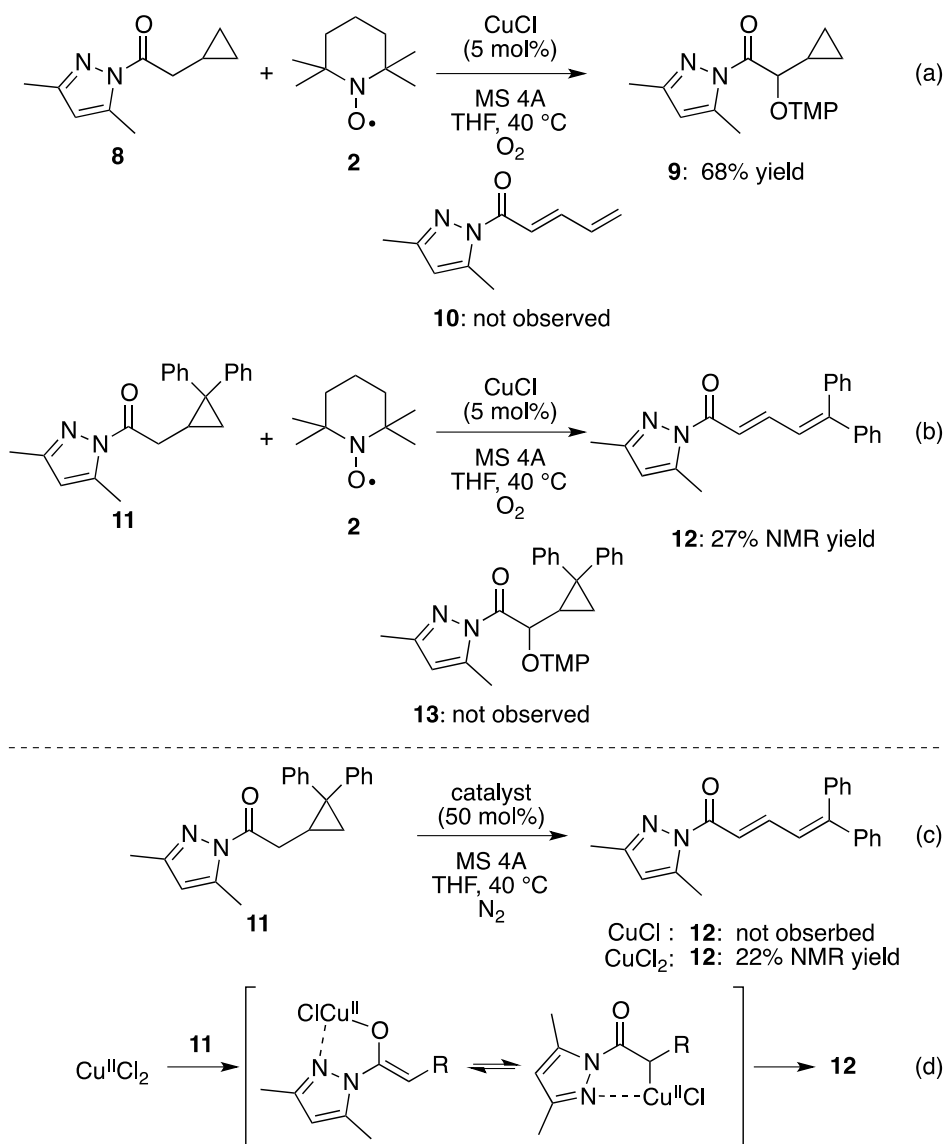
Next, we investigated the possibility of a single-electron transfer-based mechanism. α -Radical trapping experiments were performed under the optimized conditions using substrates with a C–C double bond at the 5-position (Scheme 6). The α -oxidation proceeded smoothly to afford products **6** and **7** without forming a cyclized product. These results suggest that α -radical species are not involved in the present α -oxidation.¹³



Scheme 6. Attempt to Capture α -Radical Species

We also performed cyclopropane radical clock experiments (Scheme 7).¹⁴ When α -cyclopropyl-substituted substrate **8** was subjected to the optimized conditions, α -oxidation product **9** was obtained in high yield (Scheme 7a). On the other hand, when α -diphenylcyclopropyl-substituted substrate **11** was used, the desired α -oxidation product was not observed, and instead, fragmentation of the cyclopropane ring was observed and diene **12** was detected in 27% yield (Scheme 7b). The omission of TEMPO and O_2 using 50 mol% CuCl did not afford ring-opened product **12** (Scheme 7c). In sharp contrast, 50 mol% CuCl_2 promoted fragmentation of the cyclopropane ring, even in the absence of

TEMPO under N₂ atmosphere. These results indicated that an α -C-bound copper(II) enolate was involved in the present reaction (Scheme 7d), and CuCl could not generate the enolate without TEMPO and O₂.



Scheme 7. Control Experiments using α -Cyclopropyl Substrates

Based on a series of mechanistic studies, a plausible catalytic cycle is depicted in Figure 1. First, active copper(II) peroxo dimer species **I** is generated with the assistance of both TEMPO and oxygen. TEMPO remains coordinated to the copper complex throughout the catalytic cycles.¹⁰ This active copper(II) species **I** serves as a Lewis acid/Brønsted base cooperative catalyst,¹⁵ allowing for chemoselective and facilitated enolization of acylpyrazole under mild conditions without adding of an external base. The corresponding copper enolate is in equilibrium between O-bound copper **II** and α -C-bound copper **III**,¹⁶ which is stabilized by pyrazole coordination. Subsequent coupling with TEMPO affords product **3** with

regeneration of the copper(I) catalyst. A catalytic cycle through the copper(III) intermediate via one electron oxidation by TEMPO, followed by reductive elimination, cannot be ruled out.

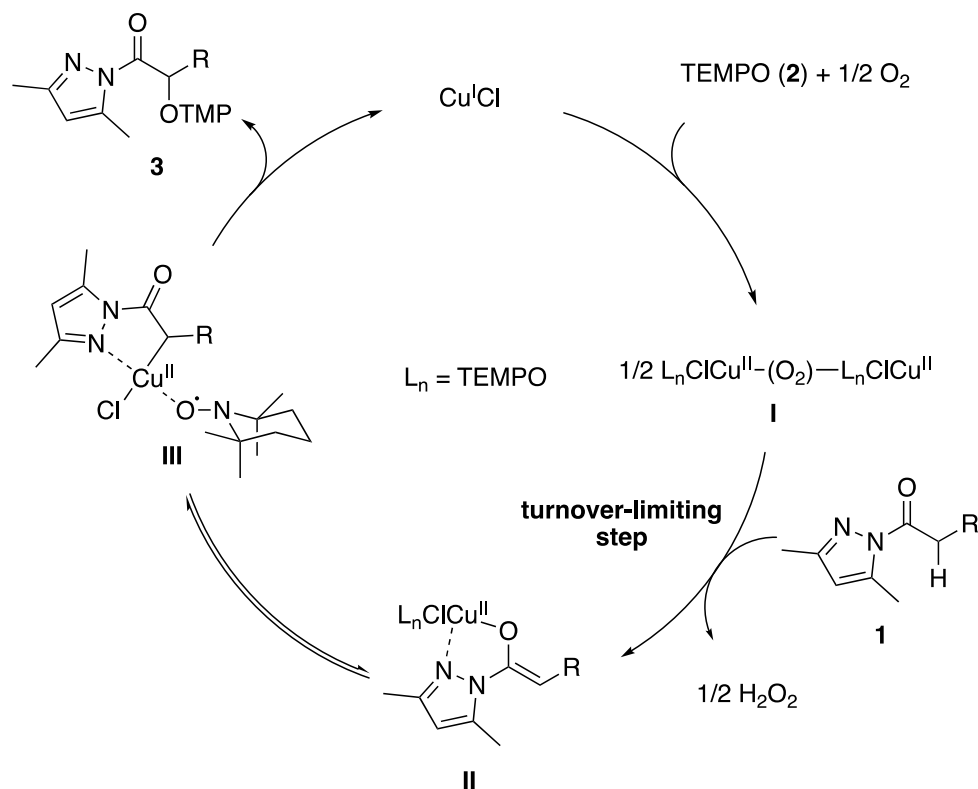
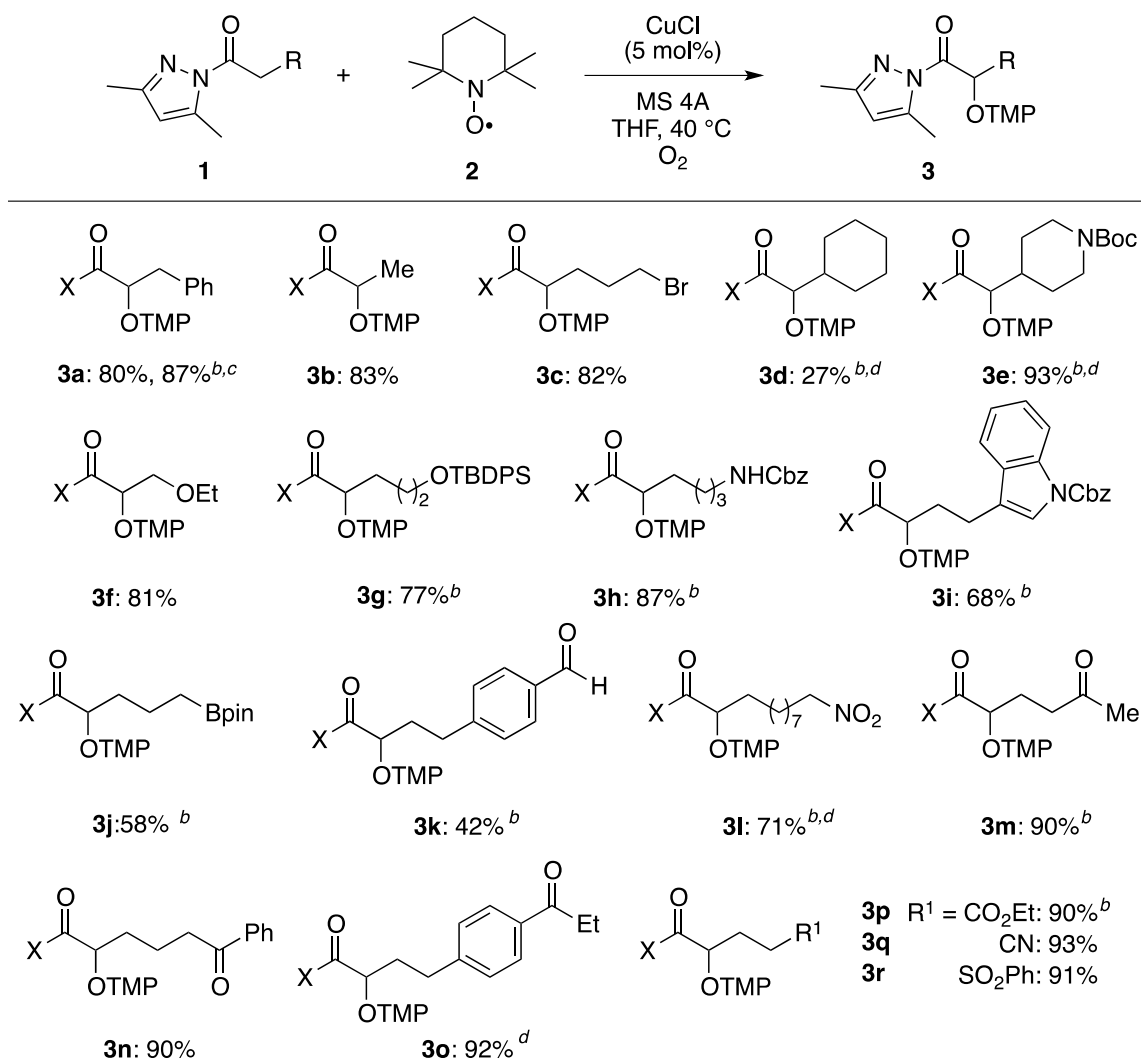


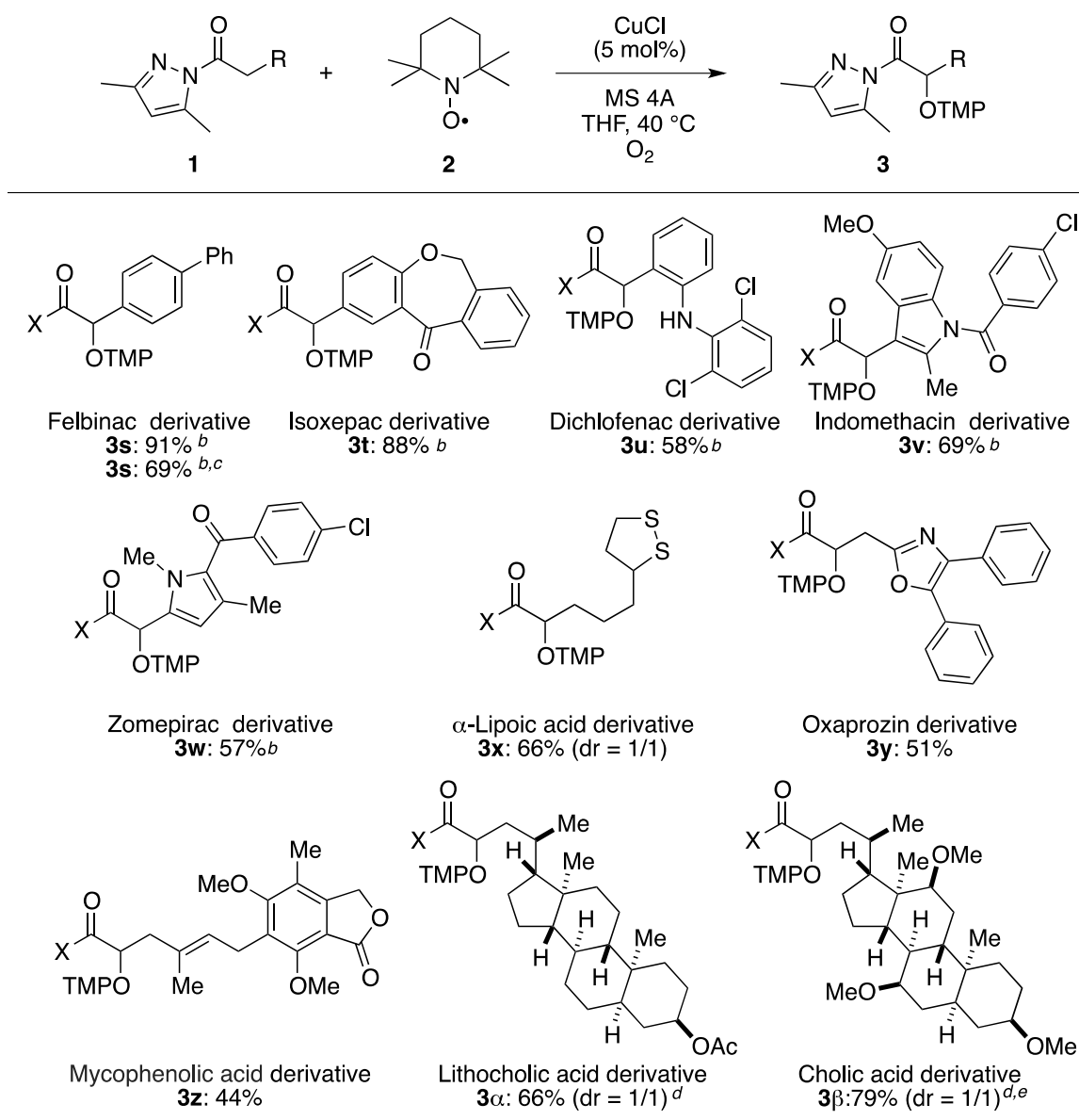
Figure 1. Plausible Catalytic Cycle

We next turned our attention to the substrate scope of acylpyrazoles to demonstrate the utility of the present catalysis (Table 1). The reaction could be run in gram scale without any detrimental effects (**3a**). Various functionalities, such as alkyl halide, protected nitrogen, oxygen, indole, and boronate ester, were applicable to the present catalysis, and α -oxidized products were isolated in synthetically useful yields (**3c-3j**). The competitive electrophilic aldehyde survived under the optimized conditions (**3k**). Highly chemoselective α -oxidation of acylpyrazoles was achieved even in the presence of nitroalkane, ketone, ester, nitrile, and sulfone (**3l-3r**).¹⁷

Table 1. Substrate Scope of Acylpyrazoles^a

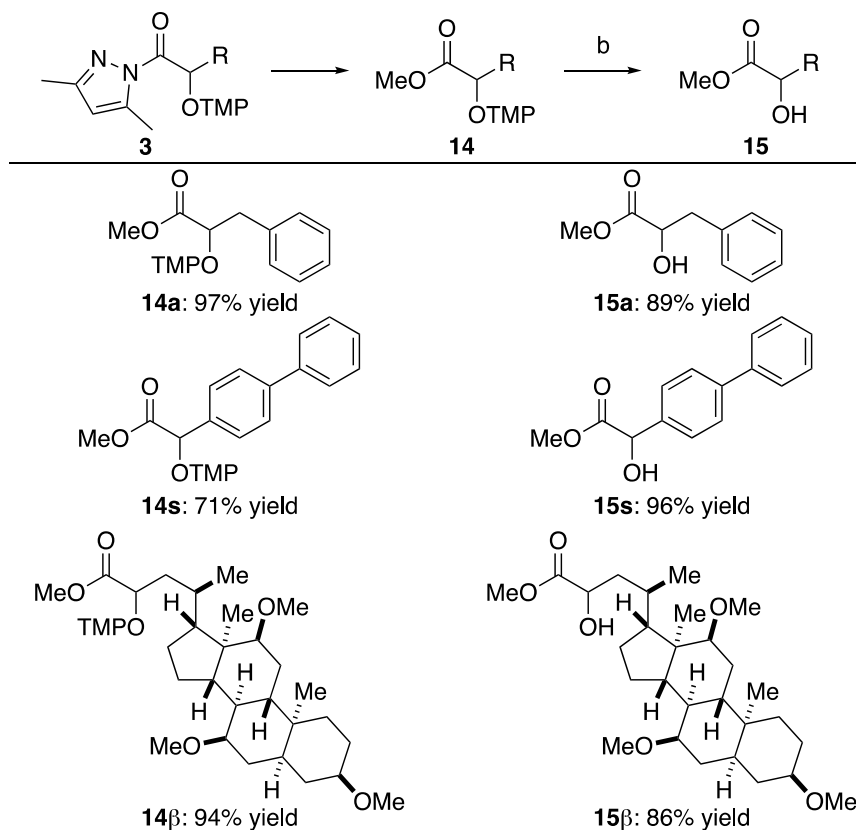
^a Conditions: **1a** (0.3 mmol), **2** (0.2 mmol), THF (0.2 mL), 24 h. Isolated yields were shown. ^b Reaction time was 48 h. ^c Gram scale (5.0 mmol) synthesis. 48 h. ^d 10 mol% CuCl was used. TMPO stands for 2,2,6,6-tetramethylpiperidine 1-oxyl. X stands for 3,5-dimethylpyrazolyl group.

Further utility of the present catalysis was demonstrated by late-stage α -oxidation using various pharmaceuticals and natural product-derived acylpyrazoles (Table 2). The present catalysis could be performed under air atmosphere, although the efficiency was slightly decreased. α -Aryl functionalized acylpyrazoles could be used under milder conditions and the products were isolated in good yields (**3s-3w**). Functionalized α -aliphatic acylpyrazoles also provided the product in good yields (**3x-3β**).

Table 2. Late-Stage α -Oxidation of Acylpyrazoles^a

^a Conditions: **1a** (0.3 mmol), **2** (0.2 mmol), THF (0.2 mL), 24 h. Isolated yields were shown. ^b Reaction was performed at room temperature. ^c Reaction was performed under air atmosphere instead of oxygen atmosphere. ^d Reaction time was 48 h. ^e 10 mol% CuCl was used. TMP stands for 2,2,6,6-tetramethylpiperidine 1-oxyl. X stands for 3,5-dimethylpyrazolyl group.

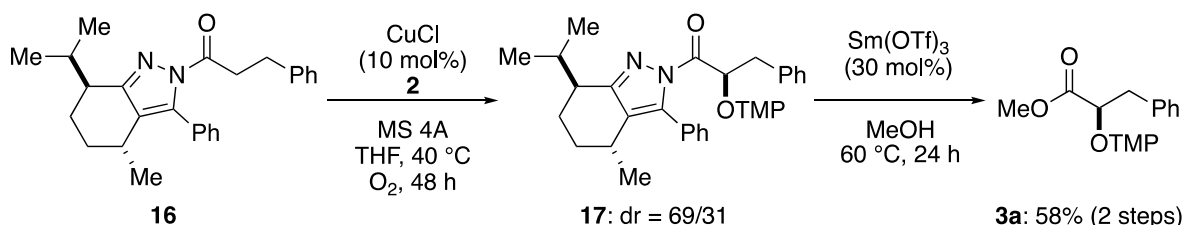
We next examined transformations of the products (Scheme 8). We previously demonstrated that acylpyrazoles could be transformed into various functionalities such as carboxylic acid, ester, amide, ketone, aldehyde, and alcohol.⁷ Transformation into ester was achieved with a catalytic amount of Sm(OTf)₃ in methanol (**14**).¹⁸ Reductive O-N bond cleavage proceeded with Zn dust in AcOH, affording α -hydroxy esters in high yield (**15**).



^a Reaction conditions: (a) Sm(OTf)₃ (20 mol%), MeOH, 60 °C. (b) Zn dust (40 equiv.), AcOH/THF/H₂O, 50 °C.

Scheme 8. Transformation of the Product

We also applied the present catalytic aerobic α -oxidation reaction to the synthesis of optically active α -hydroxy acid derivatives. Although preliminary investigation using chiral ligands provided unsatisfactory results, the present catalysis was extended to a diastereoselective reaction using readily available *l*-menthol as a chiral auxiliary (Scheme 9).¹⁹ While the diastereoselectivity was moderate, these results demonstrated the potential to efficiently access optically active α -hydroxy acid derivatives.



Scheme 9. Preliminary Diastereoselective Reaction

In conclusion, we developed a highly chemoselective α -oxidation of acylpyrazoles under aerobic conditions without the addition of an external base. Mild conditions enabled late-stage α -oxidation,

leading to functionalized α -hydroxy acid derivatives. Mechanistic studies revealed that the copper(II) peroxy species, generated in situ from CuCl with TEMPO under O₂ atmosphere, serves as a Lewis acid/Brønsted base cooperative catalyst, allowing for chemoselective activation of acylpyrazole over an acidic α -proton, such as a nitroalkyl functionality.

EXPERIMENTAL

All reactions were carried out using heat gun dried glassware under a positive pressure of dry argon unless otherwise noted. Catalytic reactions were run under oxygen atmosphere. Air- and moisture-sensitive liquids were transferred via a syringe and a stainless-steel needle. Reactions were magnetically stirred and monitored by thin layer chromatography using Merck Silica Gel 60 F254 plates. All work-up and purification procedures were carried out with reagent-grade solvents under ambient atmosphere. Flash chromatography was performed using silica gel 60N (spherical neutral, particle size 40–50 μ m) purchased from Kanto Chemical Co. Ltd. NMR was recorded on 500 MHz Bruker Advanced III. Chemical shifts for proton are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CDCl₃: δ 7.26 ppm). For ¹³C-NMR, chemical shifts were reported in the scale relative to NMR solvent (CDCl₃: 77.0 ppm) as an internal reference. NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, dd: doublet of doublets, dt: doublet of triplets, t: triplet, q: quartet, quin: quintet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. Infrared (IR) spectra were recorded on with Shimadzu FTIR-8400. High-resolution mass spectroscopy (HRMS) was obtained with Waters ACQUITY UPLCR–LCT-Premier™ XE system and Bruker MicrOTOF II. Copper complex was measured by Bruker MicrOTOF II.

Starting Material and Product. All acylpyrazoles and corresponding α -oxidation products were reported previously.⁷

General procedure for catalytic α -oxidation of acylpyrazoles. CuCl (1.0 mg, 0.010 mmol) and dried MS 4A (50 mg) were added to a 4 mL vial under inert atmosphere. To the vial was added the addition of TEMPO **2** (0.031 g, 0.20 mmol) followed by acylpyrazole **1** (0.30 mmol) and dry THF (0.20 mL) via syringe with stainless-steel needle. After filling the vial with oxygen, the resulting orange suspension was stirred at 40 °C for 24 h and diluted with EtOAc. The diluted solution was filtered through silica gel short pad column and washed with EtOAc (ca. 30 mL). After evaporation of the solvent under reduced pressure, the crude mixture was purified by silica gel column chromatography to give the desired product **3**.

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