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Visible Light Driven and Copper-Catalyzed C(sp^3)−H Functionalization of *O*-Pentafluorobenzoyl Ketone Oximes

Danhua Wu, Shuang-Shuang Cui, Fengling Bian,* and Wei Yu*

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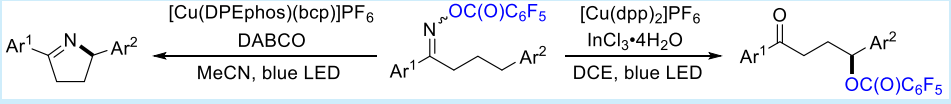
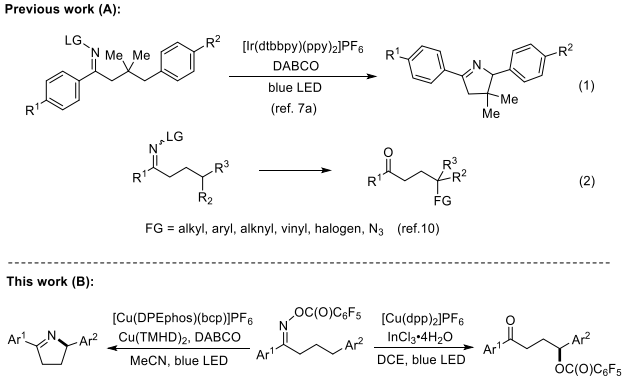


ABSTRACT: The C(sp^3)−H functionalization of *O*-pentafluorobenzoyl ketone oximes was implemented under visible light irradiation with copper complexes as catalysts. The reactions involve iminyl-radical-mediated intramolecular hydrogen atom transfer as the key step, with the iminyl radicals being generated via copper-effected N−O cleavage. The reaction afforded 3,4-dihydro-2*H*-pyrroles under the conditions of $[Cu(DPEphos)(bcp)]PF_6$ and DABCO, while γ-pentafluorobenzoyloxy ketones were produced predominantly when $[Cu(dpp)_2]PF_6$ and $InCl_3{\cdot}4H_2O$ were used as catalysts.

Iminyl-radical-mediated reactions are of current research interest because of their potential usefulness in the synthesis of nitrogen-containing compounds.[1] Apart from the intramolecular addition that has long been recognized as a valuable tool for the preparation of dihydropyrrole derivatives,[2] iminyl-radical-mediated intramolecular hydrogen atom transfer (HAT)[3] and fragmentation[4] are highly useful for the preparation of functionalized ketones and nitriles as well as nitrogen heterocycles. The employment of visible light photoredox catalysis enables convenient generation of iminyl radicals from readily accessible precursors and thus largely promotes the applications of iminyl radicals in organic synthesis.[5]

Intramolecular HAT mediated by nitrogen-centered radicals constitutes a valuable tool for the site-selective C(sp^3)−H functionalization of organic compounds.[3,6] In this context, much attention has been focused recently toward applying the iminyl-radical-mediated intramolecular 1,5-HAT to the preparation of benzene-fused cyclohexanones,[7] nitrogen heterocycles,[8] β-amino alcohols,[9] and γ-functionalized ketones.[10] Encouraged by these achievements, we set out to develop new C(sp^3)−H functionalization methods on the basis of this chemistry. Previous study by Nevado showed that 3,4-dihydro-2*H*-pyrroles can be prepared from *O*-acyl ketone oximes by employing visible light photoredox catalysis with $[Ir(dtbbpy)(ppy)_2]PF_6$ as catalyst, but this protocol has only been applied to *gem*-dimethyl-substituted oxime precursors (Scheme 1A, reaction 1).[7a] It was expected that *O*-acyl oximes without a *gem*-dimethyl group can be converted in the same way. Moreover, we envisioned that *O*-acyl oximes would undergo acyloxy transfer to give γ-acyloxy ketones, a transformation that has not been reported in spite of its apparent feasibility (Scheme 1, reaction 2).[11] Indeed, we found that by using $[Cu(DPEphos)(bcp)]PF_6$ as the photocatalyst, *O*-pentafluorobenzoyl ketone oximes can be converted to 3,4-dihydro-2*H*-pyrroles in good yield. When $[Cu(dpp)_2]PF_6$ and $InCl_3{\cdot}4H_2O$ were used as catalysts, on the other hand, the same substrates reacted to afford γ-acyloxy ketones (Scheme 1B). Herein, we report these results.

Scheme 1. C(sp^3)−H Functionalization via Intermediary of Oxime-Derived Iminyl Radicals



Copper(I) complexes have recently risen into prominence as an economical and environmentally benign alternative for the precious ruthenium or iridium complexes in photocatalysis.[12] The capacity of copper complexes to enable transformations via inner-sphere ligand exchange provides an effective means for carbon-heteroatom coupling that may not be fulfilled easily with other commonly used photocatalysts. We believed that

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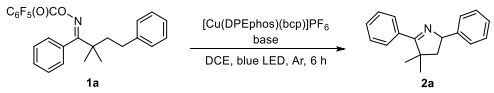
these merits of copper complexes could benefit the iminyl-radical-mediated C−H functionalization. With this consideration in mind, we applied several reported Cu(I) complexes to the cyclization of *O*-pentafluorobenzoyl ketone oxime **1a**. Among these complexes, [Cu(DPEphos)(bcp)]PF_6[13] exhibited the best catalytic capacity. As shown in Table 1, **1a** can be converted to 3,4-dihydro-2*H*-pyrrole **2a** in high yield in dichloroethane (DCE) by blue light irradiation with [Cu(DPEphos)(bcp)]PF_6 as the photocatalyst. The presence of an organic base such as 1,4-diazabicyclo[2.2.2]octane (DABCO), Et_3N, or *i*-Pr_2NEt is necessary for the reaction to proceed, but 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was much less effective and no reaction took place when 4-dimethylaminopyridine (DMAP) was used (details on optimization of reaction conditions are presented in the Supporting Information (SI); see Tables S1−S3).

Table 1. Screening Conditions for the Cyclization of 1a[a]



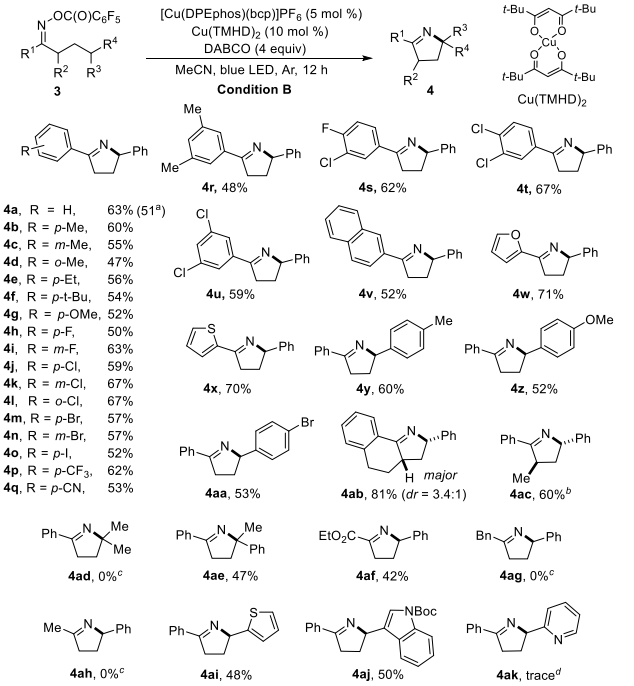
entry	mol % of [Cu^I]	base (equiv)	yield of **2a** (%)[b]
1	–	DABCO (4.0)	N.R.
2	5.0	DABCO (4.0)	92
3	5.0	DABCO (3.0)	80
4	2.5	DABCO (4.0)	76
5	5.0	–	N.R.
6	5.0	DABCO (4.0)	N.R.[c]
7	5.0	Et_3N (4.0)	80
8	5.0	*i*-Pr_2NEt (4.0)	80
9	5.0	DBU (4.0)	28
10	5.0	DMAP (4.0)	0[d]

[a]The reaction was conducted on 0.1 mmol scale under an argon atmosphere in 2 mL of dichloroethane (DCE) at ambient temperature (<28 °C). An 18 W blue LED apparatus was used as the light source. [b]Isolated yield. [c]Control experiment in the dark. [d]**1a** decomposed. [Cu^I] = [Cu(DPEphos)(bcp)]PF_6.

The optimal conditions (Table 1, entry 2) were then applied to a variety of *gem*-dimethyl-substituted *O*-pentafluorobenzoyl oximes **1**, and the result is depicted in Scheme 2. The desired transformations took place uneventfully, and the corresponding cyclization products were obtained in good to excellent yield. The substituent at the phenyl ring neighboring to the imino group has some influence on the reaction, but this effect does not correlate with their electron-donating or electron-withdrawing capacity.

When *gem*-dimethyl-lacking **3a** was subjected to these conditions, cyclization product **4a** was generated in a moderate yield of 32%. To improve this result, we explored more conditions (Tables S4 and S5 in SI) and found that by adding 10 mol % of $Cu(TMHD)_2$ into the system (in CH_3CN), the yield of cyclization product **4a** can be raised to 63% (Scheme 3). Scaling up the reaction to 10 mmol scale resulted in a slight loss in yield (Scheme 3, footnote a).

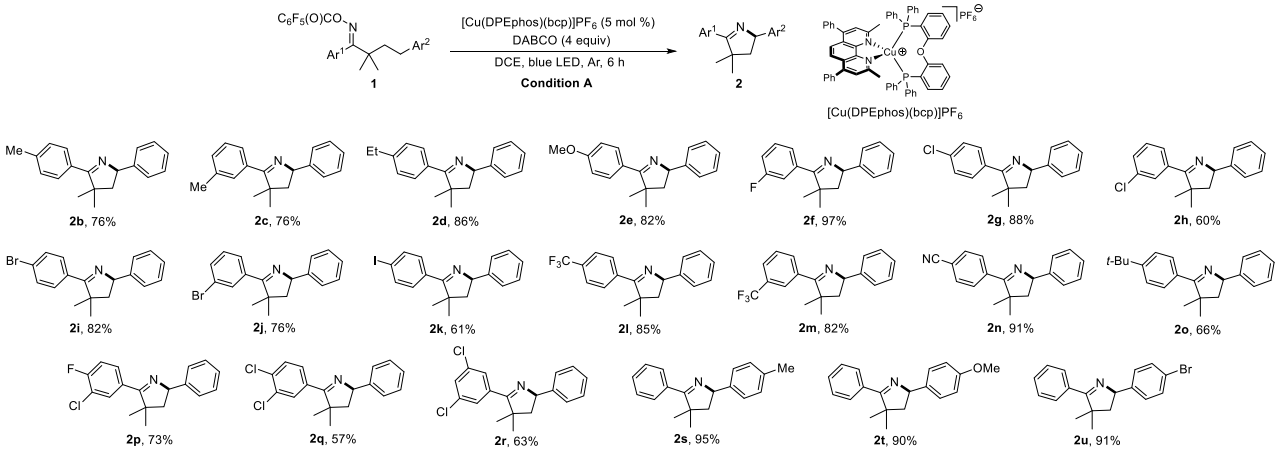
Scheme 3. Scope of the Modified Protocol



The reaction was conducted on 0.1 mmol scale at a concentration of 0.05 M.
[a]The reaction was conducted on 10 mmol scale. [b]A trace amount of the other isomer was detected.
[c]S. M. decomposed. [d]13% of S. M. and 22% of the ketone precursor were recovered.

The scope of the modified protocol was examined next by applying it to more substrates. As shown in Scheme 3, variously substituted 3,4-dihydro-2*H*-pyrroles **4** were generated

Scheme 2. Reaction of *gem*-Dimethyl *O*-Pentafluorobenzoyl Oximes



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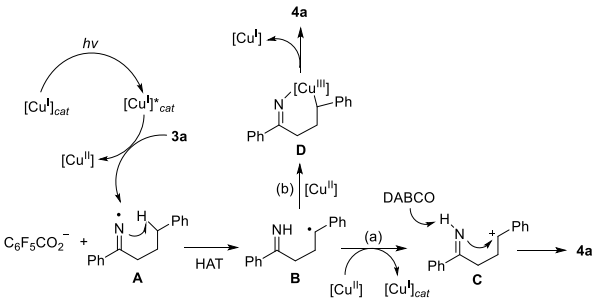
from the corresponding *O*-pentafluorobenzoyl ketone oxime precursors (**3**) in moderate to good yield under the indicated conditions. Compound **4af**, which incorporates an ethoxycarbonyl rather than an aryl group at the 2-position, was prepared as well. However, this protocol does not work for substrates having an alkyl attached to the iminyl carbon (**4ag** and **4ah**) or lacking an aryl ring at the γ-position (**4ad**), and it is invalid for the preparation of pyridyl-bearing **4ak**.

These cyclization reactions are believed to proceed via iminyl radical-mediated 1,5-HAT, which was confirmed by radical trapping and inhibition experiment with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (Scheme S1, reactions 1 and 2 in SI). A luminescence quenching experiment indicates that $[Cu(DPEphos)(bcp)]PF_6$* can be quenched by **3a**, while DABCO has no such effect (Figures S3 and S4 in SI).

Apparently the iminyl radical was generated by the interaction of *O*-pentafluorobenzoyl oximes with $[Cu(DPEphos)(bcp)]PF_6$*, which probably involves a single-electron transfer (SET) process. The reduction potential of **3a** was measured to be −1.3 V vs SCE in MeCN (Figure S6 in SI), lower than the oxidation potential of $[Cu(DPEphos)(bcp)]PF_6$* (−1.02 V vs SCE[13c]). However, it has been proven that SET reaction with an endothermicity of 1.0 V can still take place rapidly as long as the subsequent steps are thermodynamically favorable,[14] and thus SET oxidation of $[Cu(DPEphos)(bcp)]PF_6$* by *O*-pentafluorobenzoyl ketone oximes would be a viable pathway under the current circumstances.

On the basis of above analyses, the cyclization reaction is rationalized with a mechanism shown in Scheme 4. With **3a** as an example, the initial SET between photoexcited $[Cu(DPEphos)(bcp)]PF_6$ and **3a** generates iminyl radical **A**, which undergoes 1,5-HAT to form carbon radical **B**. **B** is converted to **4a** via intermediacy of carbocation **C** (path (a)), or through copper-mediated C−N coupling (path (b)). Both path (a) and path (b) require the participation of $[Cu^{II}]$ species, and it explains why the yield of **3a** was improved by the addition of $Cu(TMHD)_2$. That **4ad** and **4ak** were not obtained is more consistent with the mechanism of path (a), as in these two cases a carbocation-stabilizing aryl group is lacking at the γ-position.

Scheme 4. Proposed Mechanism for the Formation 3,4-Dihydro-2*H*-pyrroles



From Table 1 it can be seen that DABCO plays a critical role in the reaction. Apart from its function as a base to remove the proton from intermediate **B**, we assume that DABCO might also serve as a ligand to prevent the binding of $C_6F_5CO_2^-$ with the $[Cu^{II}]$ species. The copper catalyst is liable to dissociate after being oxidized to $[Cu^{II}]$,[13c,15] and the oxidizing capacity of $[Cu^{II}]$ would be compromised if the $C_6F_5CO_2^-$ anion is bonded to it.

Having acquired the above results, we went on to explore conditions to engender the acyloxy transfer from the oxime nitrogen in **3** to the γ-carbon. After extensive screening of the reaction conditions, we found that the anticipated transformation can be enabled with the assistance of $InCl_3{\cdot}4H_2O$. Under the optimal conditions which employed 5 mol % of $[Cu(dpp)_2]PF_6$[16] and 1.0 equiv of $InCl_3{\cdot}4H_2O$ as the catalyst, **3a** reacted in DCE under blue light irradiation to give **5a** in a yield of 70% (Scheme 5). The structure of **5a** was confirmed by X-ray crystallographic analysis (CCDC No. 2055827). The optimal reaction temperature was found to be 38 °C. Notably, the reaction can also take place in the dark, albeit in a lower yield (43%) (details on optimization of reaction conditions are listed in Tables S6−S8 in SI).

This new protocol (Condition C) provides an atom-economical means for the preparation of γ-acyloxy ketones (Scheme 5). This protocol not only allows aryl ketones to be functionalized at the γ-position but also is suitable for the acyloxylation of aliphatic ketones (**5ag** and **5ah**). However, substrates bearing a methoxy group at the *para* position of the phenyl ring did not react well. In the case of **3g**, dihydronaphthalen-1(2*H*)-one **6g** was generated in 17% yield along with **5g**. The reaction of **3z**, on the other hand, resulted in the formation of a complex mixture.[17] This protocol is also unsuitable for preparing compounds **5ai**, **5aj**, and **5ak**. When **1a** was treated with this protocol, **7al** was generated besides the acyloxy transfer product **5al**.

The radical trapping experiment with TEMPO indicates that this acyloxy transfer also involves intermediacy of the iminyl radical (Scheme S1, reactions 3 and 4 in SI). Under the condition of blue light irradiation, the iminyl radical should derive from SET reduction of **3** (E_{red} for **3a** = −1.5 V vs SCE in DCE, Figure S7 in SI) by photoexcited $[Cu(dpp)_2]PF_6$ (E_{ox}° = −1.11 V vs SCE[18]), as indicated by the quenching of luminescence of $[Cu(dpp)_2]PF_6$* by **3a** (Figures S5 in SI). However, this mechanism cannot explain why the reaction also took place in the dark. $[Cu(dpp)_2]PF_6$ at the ground state is a poor reductant (E_{ox}° = +0.69 V vs SCE[18]); it cannot reduce **3** via SET. We assume that, under the latter circumstance, the only way to engender the iminyl radical from **3** is through oxidative N−O insertion by $[Cu^I]$ followed by homolytic N−$[Cu^{III}]O_2CC_6F_5$ cleavage (Scheme 6). The radical trapping experiment lent support to this mechanism (Scheme S1, reaction 4 in SI). When the reaction of **3a** was conducted in the dark, **5a** was formed in 21% yield along with the TEMPO-trapped product (37% yield), whereas only the TEMPO-trapped product was obtained under the condition of blue light irradiation. The fact that **5a** can still be formed in the presence of TEMPO indicates the proximity of the $C_6F_5CO_2$-$[Cu^{II}]$ species and iminyl radical **B**, which might be incorporated in the same solvent cage. As a result, a certain amount of **B** was coupled to $C_6F_5CO_2$-$[Cu^{II}]$ before they diffused away from each other.

$InCl_3{\cdot}4H_2O$ was found to be necessary for the acyloxy transfer reaction to take place. As illustrated in Scheme 6, we believe that $InCl_3{\cdot}4H_2O$ facilitates the reaction by enhancing the hydrogen abstraction capacity of the iminyl radical[7a,10f] as well as by promoting hydrolysis of the HAT-derived imine. Formation of **5ag** and **5ah** under these conditions confirms the beneficial effect of $InCl_3{\cdot}4H_2O$ on the HAT step. In addition, $InCl_3{\cdot}4H_2O$ might also play an important role for $[Cu(dpp)_2]$-

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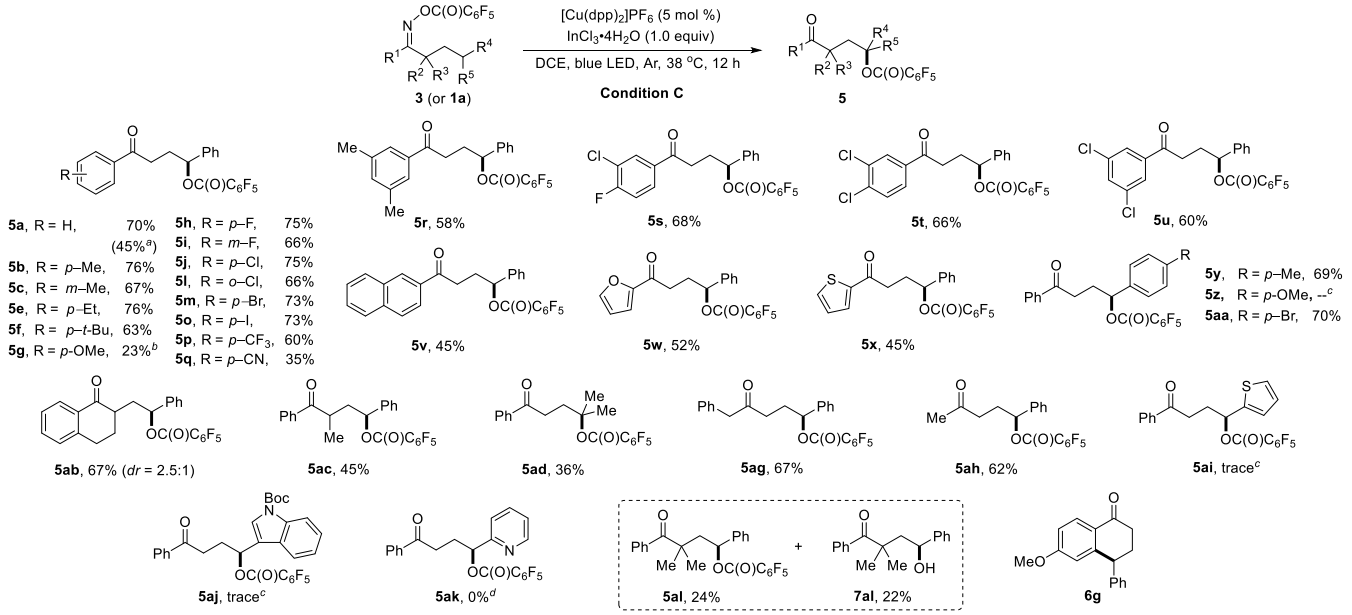
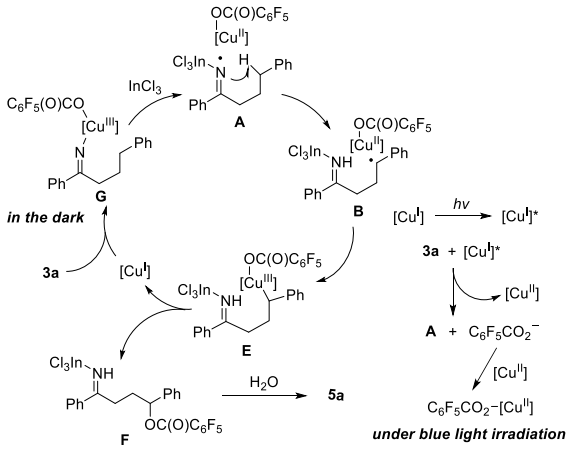
Scheme 5. Scope of the Pentafluorobenzoyloxy Transfer Reaction



The reaction was conducted on 0.1 mmol scale unless otherwise indicated. A 10 W blue LED ribbon was used as the light source.
[a]The reaction was conducted on 4 mmol scale. [b]Besides **5g**, **6g** was obtained in 17% yield. [c]A complex mixture was generated. [d]S.M. decomposed to the oxime.

Scheme 6. Proposed Mechanism for the Formation of γ-Pentafluorobenzoyloxy Ketones



PF_6 regeneration by preventing the carbonyl in **5** from binding with the copper.

In summary, we have developed two new photocatalytic protocols for the site-selective C(sp^3)−H functionalization of ketone *O*-acyl oximes. These methods employ copper complexes to convert *O*-pentafluorobenzoyl oximes to iminyl radicals under visible light irradiation. By using different copper catalysts and adopting different conditions, the same precursors can be guided to follow two different pathways to deliver 3,4-dihydro-2*H*-pyrroles and γ-pentafluorobenzoyloxy ketones, respectively. Besides their synthetic implications, the present results demonstrate the versatility of copper complexes as photocatalysts, which is worthy of further exploitation for iminyl radical-mediated coupling reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c02133.

Experimental procedures; optimization of reaction conditions; luminescence quenching experiment; cyclic voltammetry measurement; characterization data; crystallographic data for compound **5a** (CCDC 2055827); copies of NMR spectra (PDF)

Accession Codes

CCDC 2055827 contains 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.

■ AUTHOR INFORMATION

Corresponding Authors

Fengling Bian − *College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, China*; Email: bianfl@lzu.edu.cn

Wei Yu − *State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou, Gansu 73000, China*; orcid.org/0000-0002-3131-3080; Email: yuwei@lzu.edu.cn

Authors

Danhua Wu − *College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, China*

Shuang-Shuang Cui − *College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.1c02133

Notes

The authors declare no competing financial interest.

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(17) The *para*-OMe in **3z** probably rendered the HAT-derived carbon radical being oxidized to the corresponding carbocation, from which other products were formed. **3ai** and **3aj** failed to be converted probably because of the same reason.

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