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Cooperation of *Cis* Vicinal Acceptors for Donor–Acceptor Cyclopropane Activation: TfOH-Promoted Ring-Opening/Aryl Shift Rearrangement to 3- and 5-Ylidenebutenolides

Jiru Shao, Qinyuan Luo, Hongyan Bi, and Sunewang R. Wang*

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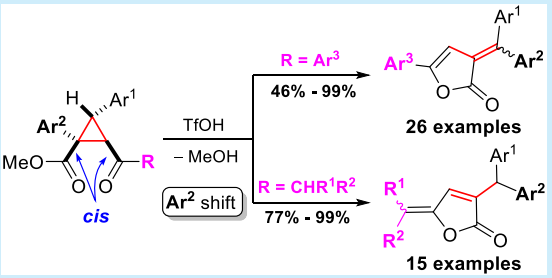
ABSTRACT: A convenient route to 3- and 5-ylidenebutenolides from readily available *cis*-2-acylcyclopropane-1-carboxylates is described. Upon exposure to TfOH, synergistic activation of the vicinal acceptors in *cis*-2-acylcyclopropane-1-carboxylates generates highly strained bicyclic oxocarbenium ion intermediates, which undergo the ring-opening/aryl shift/deprotonation cascade process to form the 3- or 5-ylidenebutenolides depending on the acyl group. On the other hand, the corresponding *trans* isomers, from which it is difficult to form such oxocarbenium ions, are inactive under the same conditions.

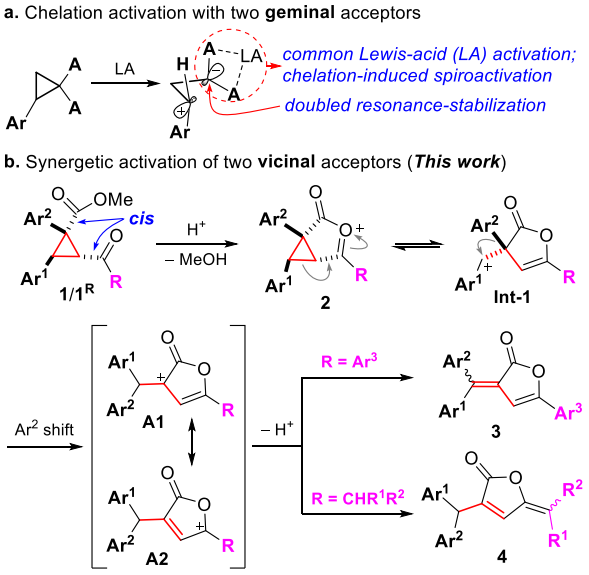


As an important class of activated small-ring molecules, vicinal donor–acceptor-substituted cyclopropanes (DACs) have served as versatile building blocks for the synthesis of diverse acyclic and (poly)cyclic compounds.[1] A certain combination of the donor and acceptor groups is very important for their synthetic use.[2] Generally, a single acceptor is sufficient for DACs with very strong electron donors such as alkoxy groups to realize the selective transformations under mild conditions. If the donors are electronically neutral or deficient, for example, the phenyl and alkyl substituents, one more geminal acceptor is typically required to enhance the reactivity.[3] More than the strengthened resonance stabilization for the negative charge in the zwitterionic intermediates by a second acceptor, the chelation of Lewis acid to both geminal acceptors in DACs forming an unusually more reactive spiro structure, akin to a "spiroactivation" effect, also facilitates the ring-opening (Scheme 1, a).[4] Thus, malonate diester group is popularly used as the acceptors. However, the malonate diester groups renders further functionalization of the cyclopropanes cumbersome.[5]

As frequently used acceptors in DACs, though the acyl group is slightly more electron-withdrawing than the ester group,[2] quite a few aryl cyclopropyl ketones, usually activated by the highly electron-rich aromatic rings like indolyl or poly(methoxy)aryl groups, have been reported for mild and selective ring-opening transformations.[6−8] With activation by the additional ring strain, bicyclic cyclopropyl ketones and bicyclo[1.1.0]butane esters represent another small class of the known reactive DACs with one single acceptor.[9]

Recently, Maulide's group has disclosed a temporary generation of a cyclopropyl oxocarbenium ion from α-cyclopropylacetals under mild conditions, providing a new strategy for activating 2-arylcyclopropane-1-carboxaldehydes.[10]

Scheme 1. Strategies for Activating DACs with Aryl Donors



In our recent study on $P(NMe_2)_3$-mediated reductive (3 + 2) annulation reaction of benzils with pyrylium salts,[11] the high reactivity of the annelated cyclopropyl oxocarbenium ions gave

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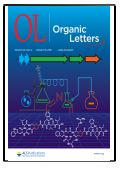

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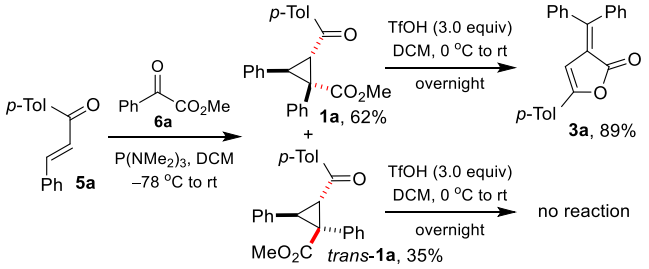
us a new idea for the activation of the arylated DACs with two vicinal acceptors, i.e., the ketone and ester groups. Proton-promoted closure of such two carbonyl-based acceptors in **1**/**1**^{R} gives the cyclopropane-fused oxocarbenium ion **2** that is more susceptible to the ring-opening, thus providing a general approach for the activation of the arylated DAC ketones rather than only aldehydes.[8,10] Herein, we report an efficient synthesis of 3- and 5-ylidenebutenolides (**3** and **4**), the core structural moieties widely found in natural products, bioactive molecules, and important synthetic intermediates,[12] from readily available *cis*-2-acylcyclopropane-1-carboxylates[13] as the implementation of the aforementioned idea for DAC activation followed by an unexpected aryl shift arrangement (Scheme 1, b).

As a point of departure, the DAC isomers **1a**/*trans*-**1a** were prepared by the Kukhtin−Ramirez cyclopropanation of chalcone **5a** with methyl benzoylformate **6a** and P(NMe$_2$)$_3$ (Scheme 2).[13b] To our delight, upon treatment with 3.0 equiv

Scheme 2. Preparation and TfOH-Promoted Ring-Opening Reactions of DAC Isomers 1a and *trans*-1a



of TfOH, DAC **1a** with the ketone group residing *cis* to the ester group afforded 3-arylidenebutenolide **3a** in 89% isolated yield, whereas *trans*-**1a** with both carbonyls disposed *trans* to each other remained intact. Moreover, upon heating at 43 °C, the reaction of *trans*-**1a** led to its decomposition to give a complicated mixture. On the other hand, the screening of the solvents and the amount of TfOH used indicated that the reaction of **1a** promoted by 3.5 equiv of TfOH in DCM gave **3a** in 99% yield as the optimum result.[14] Additionally, the structures of *trans*-**1a** and **3a** were confirmed by single-crystal X-ray crystallography[14] to further support the observed stereodependent ring-opening process.

Once the optimum conditions for the conversion of DAC **1a** to 3-arylidene butenolide **3a** were found, other DACs in this process were investigated. As shown in Figure 1, a wide range of arylated DACs with various aroyl acceptors reacted smoothly to produce 3-arylidenebutenolides **3** in good to excellent yields. Specifically, with respect to the *para* substituents on the Ar^1/Ar^2 aromatic rings, the bromo (**1d**) and chloro (**1e**) groups showed better performance than the nonsubstituted (**1b**) and methyl (**1c**) ones. Though the fluorinated DAC **1f** seems to be less reactive, a quantitative yield of **3f** was obtained under heating conditions. Nevertheless, the halo groups at the *meta*- (**1h**) or *ortho*- (**1i**) positions of the Ar^1/Ar^2 aromatic rings showed a small drop on the yields of the desired products under heating. Remarkably, for DAC **1g** bearing the more electron-deficient Ar^1/Ar^2 groups, 58% of the substrate was converted and **3g** was isolated in 48% yield under heating. Two geometric isomers were produced in a nearly 1:1 ratio from DACs with different Ar^1/Ar^2 groups without steric hindrance. However, high selectivity up to 20:1 ratio is achievable by the installment of

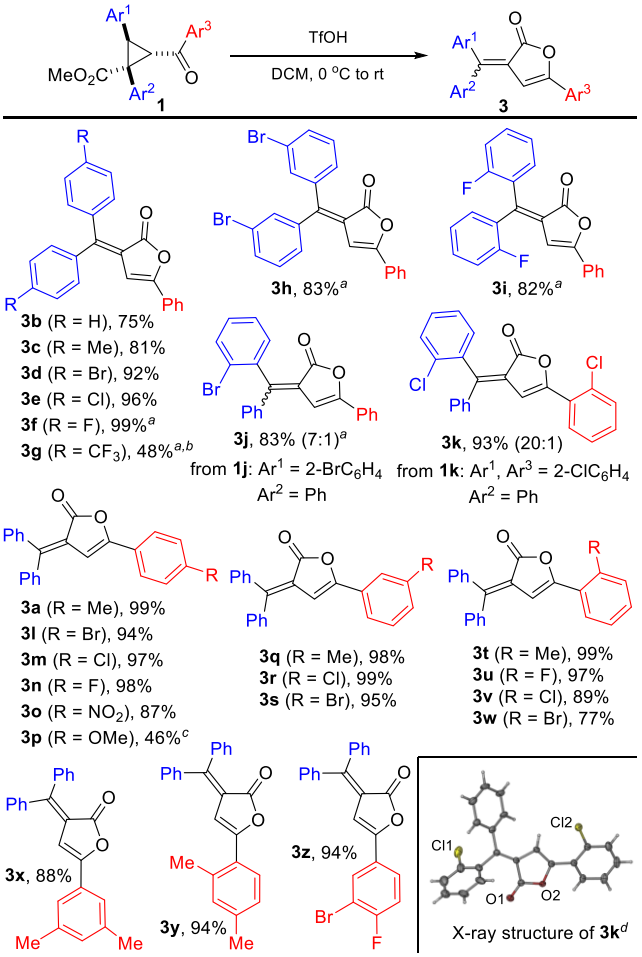


Figure 1. Scope for 3-arylidenebutenolides **3**: **1** (0.15 mmol, 1.0 equiv) and TfOH (0.53 mmol, 3.5 equiv) in DCM (2.0 mL), in sealed tube, 0 °C to rt, overnight. Isolated yield. (a) Heated at 43 °C overnight after warming to rt. (b) TfOH (5.0 equiv); 42% of **1g** was recovered. (c) TfOH (6.0 equiv); 51% of **1p** was recovered. (d) Thermal ellipsoid is set at 50% probability.

an *o*-bromo (**1j**) or *o*-chloro (**1k**) group on Ar^1 or/and Ar^3 rings. The geometric assignment of the favored 3-arylidenebutenolide was unambiguously determined based on the X-ray structure of **3j**. With respect to the aroyl groups, the methyl, halo, and nitro groups at the *para*- (**1a**,**1l**−**o**), *meta*- (**1q**−**s**), and *ortho*- (**1t**−**w**) positions and the disubstituted ones (**1x**−**z**) on the Ar^3 ring are well tolerated and afforded the desired products in good to excellent yields. Unfortunately, DACs with aroyl groups derived from heteroaromatic rings like 2-thienoyl, 2-furoyl, and nicotinoyl failed for this reaction, but that with the aroyl groups derived from highly electron-rich aromatic rings such as *p*-anisoyl (**1p**) gave the desired product in 46% yield with moderate conversion.

To expand the utility of this ring-opening reaction, reactions with alkanoylated DACs **1**^{R} were then studied. To our surprise, reaction of isobutyryl DAC **1**^{R}**a** gave 5-alkylidenebutenolide **4a** in 97% yield under the same conditions. The reason for the sole formation of **4a** without the 3-arylidenebutenolide isomer is not clear, possibly attributed to the higher stability of the resonance allylic cation **A**$_2$ stabilized by the acyloxy group (Scheme 1, b), which is more easily attacked by the nucleophiles as seen in the formation of **7** and **9** (vide infra). Encouraged by this, a variety of 5-alkylidenebutenolides

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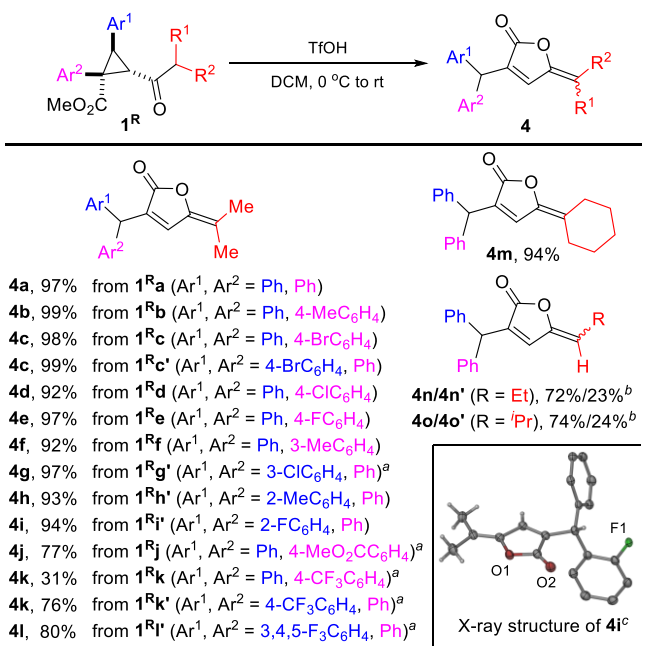
4 were then synthesized from DACs $\mathbf{1}^{R}$ in good to excellent yields (Figure 2). Generally, isobutyryl DACs with the methyl

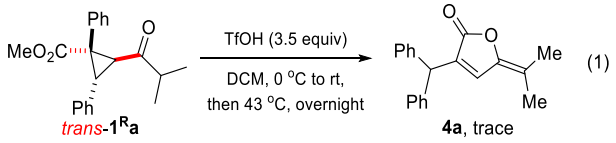


4a, 97% from $\mathbf{1}^{R}\mathbf{a}$ (Ar^1, Ar^2 = Ph, Ph)
4b, 99% from $\mathbf{1}^{R}\mathbf{b}$ (Ar^1, Ar^2 = Ph, 4-MeC_6H_4)
4c, 98% from $\mathbf{1}^{R}\mathbf{c}$ (Ar^1, Ar^2 = Ph, 4-BrC_6H_4)
4c, 99% from $\mathbf{1}^{R}\mathbf{c}'$ (Ar^1, Ar^2 = 4-BrC_6H_4, Ph)
4d, 92% from $\mathbf{1}^{R}\mathbf{d}$ (Ar^1, Ar^2 = Ph, 4-ClC_6H_4)
4e, 97% from $\mathbf{1}^{R}\mathbf{e}$ (Ar^1, Ar^2 = Ph, 4-FC_6H_4)
4f, 92% from $\mathbf{1}^{R}\mathbf{f}$ (Ar^1, Ar^2 = Ph, 3-MeC_6H_4)
4g, 97% from $\mathbf{1}^{R}\mathbf{g}'$ (Ar^1, Ar^2 = 3-ClC_6H_4, Ph)[a]
4h, 93% from $\mathbf{1}^{R}\mathbf{h}'$ (Ar^1, Ar^2 = 2-MeC_6H_4, Ph)
4i, 94% from $\mathbf{1}^{R}\mathbf{i}'$ (Ar^1, Ar^2 = 2-FC_6H_4, Ph)
4j, 77% from $\mathbf{1}^{R}\mathbf{j}$ (Ar^1, Ar^2 = Ph, 4-$MeO_2CC_6H_4$)[a]
4k, 31% from $\mathbf{1}^{R}\mathbf{k}$ (Ar^1, Ar^2 = Ph, 4-$CF_3C_6H_4$)[a]
4k, 76% from $\mathbf{1}^{R}\mathbf{k}'$ (Ar^1, Ar^2 = 4-$CF_3C_6H_4$, Ph)[a]
4l, 80% from $\mathbf{1}^{R}\mathbf{l}'$ (Ar^1, Ar^2 = 3,4,5-$F_3C_6H_4$, Ph)[a]

Figure 2. Scope for 5-alkylidenebutenolides **4**: $\mathbf{1}^{R}$ (0.15 mmol, 1.0 equiv) and TfOH (0.53 mmol, 3.5 equiv) in DCM (2.0 mL), in sealed tube, 0 °C to rt, overnight. Isolated yield. (a) Heated at 43 °C overnight after warming to rt. (b) TfOH (2.0 equiv). (c) Thermal ellipsoid is set at 50% probability.

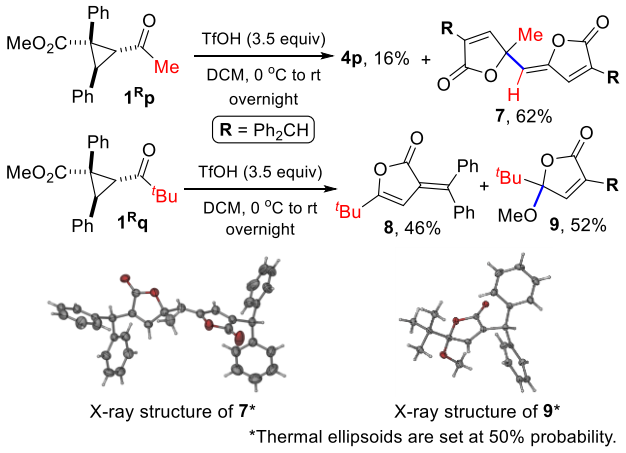
and halo groups at the *para*-($\mathbf{1}^{R}\mathbf{b}$–$\mathbf{e}$), *meta*- ($\mathbf{1}^{R}\mathbf{f}$ and $\mathbf{1}^{R}\mathbf{g}'$), or *ortho*- ($\mathbf{1}^{R}\mathbf{h}'$ and $\mathbf{1}^{R}\mathbf{i}'$) positions of the Ar^1/Ar^2 aromatic rings proceed well. More importantly, for these reactive DAC substrates, the interchange of the Ar^1 and Ar^2 groups led to no significant change in the product yields ($\mathbf{1}^{R}\mathbf{c}$ and $\mathbf{1}^{R}\mathbf{c}'$), thus providing two alternatives for the synthesis of 3-diarylmethyl-5-alkylidenebutenolides.[15] DACs with highly electron-deficient aromatic rings are less reactive; thus, heating is needed to promote the reaction. Specifically, **4j** was obtained from the ester-substituted phenyl DAC $\mathbf{1}^{R}\mathbf{j}$ in 77% yield under heating. Though the reaction with CF_3-substituted DAC $\mathbf{1}^{R}\mathbf{k}$ only gave **4k** in 31% yield even under heating, the reaction of its isomer $\mathbf{1}^{R}\mathbf{k}'$ with the aryl groups interchanged afforded **4k** in a well-improved yield. According to the proposed reaction sequence depicted in Scheme 1, the electron deficiency of the migrating aryl group (Ar^2 in $\mathbf{1}^{R}$) suppressed the reaction more than that of the donor aryl group (Ar^1 in $\mathbf{1}^{R}$).[16] Thus, **4l** was smoothly isolated in 80% yield from $\mathbf{1}^{R}\mathbf{l}'$ with the 3,4,5-trifluorophenyl group as the donor aryl group under heating. Similar to $\mathbf{1}^{R}\mathbf{a}$, DAC $\mathbf{1}^{R}\mathbf{m}$ with the cyclohexyl group reacted to give the desired 5-alkylidenebutenolide **4m** in 94% yield as well. For DACs $\mathbf{1}^{R}\mathbf{n}$ and $\mathbf{1}^{R}\mathbf{o}$ with one of the R^1/R^2 groups as the hydrogen atom, **4n**/**4n**′ and **4o**/**4o**′ were isolated in excellent combined yields but with moderate selectivities of the exocyclic double bond. The skeletal structure of **4** was clearly confirmed by the X-ray structure of **4i**, and the configuration of the exocyclic double bond in **4n** was assigned by the NOESY spectroscopic studies.[14]

Although the alkanoyl DACs are generally more reactive than the aroyl ones, *trans*-$\mathbf{1}^{R}\mathbf{a}$ showed similar reactivity to *trans*-**1a**. Upon treatment with TfOH, *trans*-$\mathbf{1}^{R}\mathbf{a}$ was unreactive at rt and afforded a messy mixture including a trace amount of **4a** under heating (eq 1), indicating the prerequisite of the two *cis* vicinal carbonyl motifs for this selective ring-opening process.



Notably, the reactions of the acetyl and pivaloyl DACs differ from the aforementioned DACs with the alkanoyl group bearing one or two α-hydrogens, whereas that of the cinnamoyl DAC results in a messy mixture. For example, the reaction with the acetyl DAC $\mathbf{1}^{R}\mathbf{p}$ afforded **7** in 62% yield, a dimer of the related 5-methylidenebutenolide **4p** as shown by single-crystal X-ray crystallography, along with a low yield of **4p** (Scheme 3).[17] On the other hand, besides the expected 3-

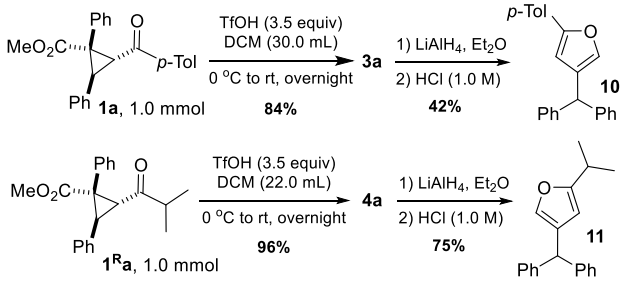
Scheme 3. TfOH-Promoted Reactions of Acetyl and Pivaloyl DACs



arylidenebutenolide **8**, butenolide **9** possibly via an addition of the in situ formed methanol to **8** was also isolated in 52% yield from the reaction of the pivaloyl DAC $\mathbf{1}^{R}\mathbf{q}$ (Scheme 3).

As exemplified by **1a** and $\mathbf{1}^{R}\mathbf{a}$ in Scheme 4, both 3- and 5-ylidenebutenolides were readily synthesized on a 1 mmol scale

Scheme 4. Scaled-up Reaction and Transformations



reaction, and both products were then successfully converted to diarylfurylmethanes[18] by reduction with $LiAlH_4$.[19]

In conclusion, a novel DAC activation strategy based on the cooperative cyclization of two vicinal acceptors is successfully practicalized, providing a simple and convenient route to highly substituted 3- and 5-ylidenebutenolides from readily available *cis*-2-acylcyclopropane-1-carboxylates under mild

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conditions. After the common ring-opening and aryl-shift steps, the reaction diverges to different types of butenolide derivatives depending on the structure of the acyl acceptor. By contrast, DACs with the *trans* vicinal acceptors show the attenuated and unselective reactivity under the same conditions. Furthermore, this DAC activation mode enables the selective ring-opening reaction of DACs bearing the aryl donors deactivated by strongly electron-deficient groups like the ester and CF_3 groups. Interestingly, the reaction seems to be more sensitive to the electronic nature of the migrating aryl group (Ar^2 in $\mathbf{1}^R$) than that of the donor aryl group (Ar^1 in $\mathbf{1}^R$), demonstrating the validity of the synergistic interaction between the *cis* vicinal acceptors for overcoming the electronic deficiency of the donor in DAC activation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03976.

Experimental procedures, characterization data, and spectra (PDF)

Accession Codes

CCDC 2047388−2047393 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Sunewang R. Wang − *Chang-Kung Chuang Institute, School of Chemistry and Molecular Engineering and Shanghai Engineering Research Center of Molecular Therapeutics and New Drug Development, East China Normal University, Shanghai 200241, China;* orcid.org/0000-0002-7099-2928; Email: rxwang@chem.ecnu.edu.cn

Authors

Jiru Shao − *Chang-Kung Chuang Institute, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200241, China*

Qinyuan Luo − *Chang-Kung Chuang Institute, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200241, China*

Hongyan Bi − *Chang-Kung Chuang Institute, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200241, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c03976

Notes

The authors declare no competing financial interest.

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