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Asymmetric Photocatalytic C(sp^3)−H Bond Addition to α-Substituted Acrylates

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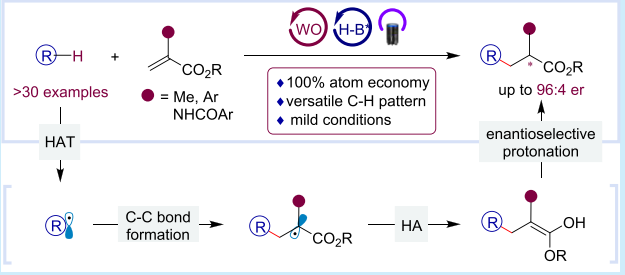
ABSTRACT: Asymmetric functionalization of inert C(sp^3)−H bonds is a straightforward approach to realize versatile bond-forming events, allowing the precise assembly of molecular complexity with minimal functional manipulations. Here, we describe an asymmetric photocatalytic C(sp^3)−H bond addition to α-substituted acrylates by using tetrabutylammonium decatungstate (TBADT) as a hydrogen atom transfer (HAT) photocatalyst and chiral phosphoric acid as a chiral proton-transfer shuttle. This protocol is supposed to occur via a radical/ionic relay process, including a TBADT-mediated HAT to cleave the inert C(sp^3)−H bond, a 1,4-radical addition, a back hydrogen abstraction, and an enantioselective protonation. A variety of inert C−H bond patterns and α-substituted acrylates are well tolerated to enable the rapid synthesis of enantioenriched α-stereogenic esters from simple raw materials.

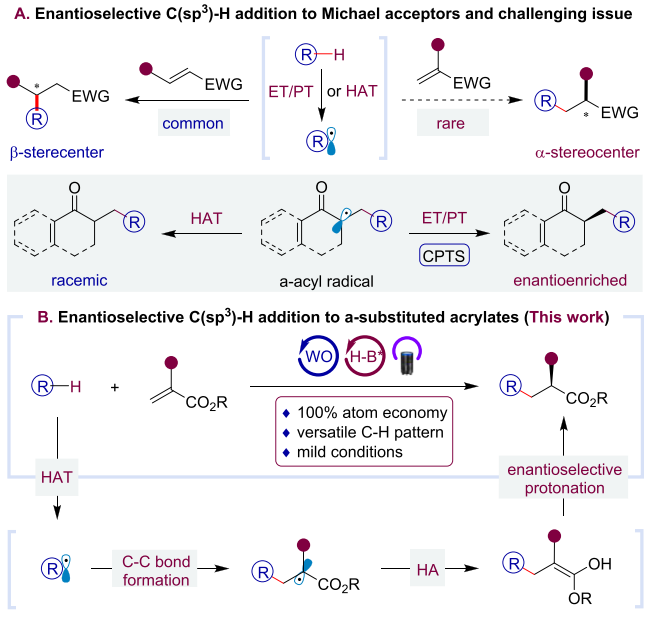


The direct asymmetric functionalization of inert C(sp^3)−H bonds represents an entirely new perspective in comparison with the conventional logic of organic synthesis,[1] allowing for the rapid assembly of densely functionalized molecules from simple molecules and with minimal functional manipulations. Among the advent of modern methods of C(sp^3)−H bond activation, hydrogen atom transfer (HAT) stands out as an attractive process because it can mediate inert C(sp^3)−H bond activation with mild conditions and thereby generate highly reactive alkyl radicals that can be leveraged to forge versatile chemical bonds.[2] However, due to the high reactivity of radical intermediates,[3] successful catalytic strategies for controlling the stereochemical outcome of HAT-mediated C(sp^3)−H functionalization are still underdeveloped.[4]

The reaction of C(sp^3)−H bond addition to Michael acceptors is one of the most widely utilized transformations in the light-mediated HAT literatures (Scheme 1A).[5] In recent years, the combination of HAT photocatalyst and small-molecule chiral catalysts[6] has proven to be efficient catalytic systems for enantioselective C(sp^3)−H bond addition to electrophilic alkenes,[7] enabling the direct asymmetric alkylation of versatile inert C(sp^3)−H bonds with 100% atom economy and mild conditions. While the use of chiral amine[7a] and Lewis acid[7b] as cocatalysts has provided encouraging results in generating the β-stereocenter via a stereocontrolled radical addition to prochiral alkene, the generation of the α-stereocenter still lies in the lack of effective strategy for stereoinduction.[8,7c]

To address this issue, our group has recently described preliminary results concerning an asymmetric photocatalytic

Scheme 1. Enantioselective C(sp^3)−H Addition to Michael Acceptors



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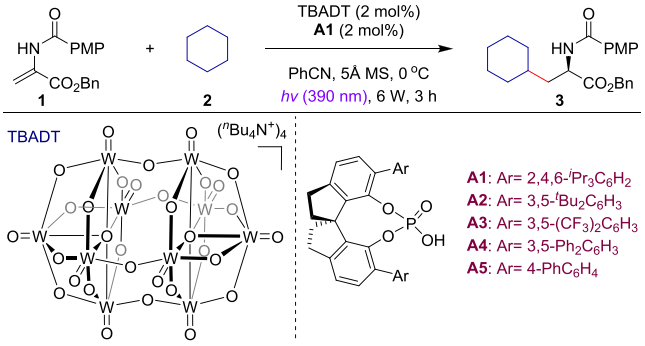
C(sp^3)−H bond addition to versatile exocyclic enone[7c] with the use of tetrabutylammonium decatungstate (TBADT)[9] as a HAT photocatalyst and chiral phosphoric acid as a chiral proton-transfer shuttle (CPTS).[10] This protocol is supposed to occur via a radical/ionic relay process, and the key enantiodetermining step is the enantioselective protonation of in situ generated cyclic ketoenol with CPTS (Scheme 1A). In the same way, a C(sp^3)−H bond addition to α,β-unsaturated ester may also be viable to generate a transient ester enolate. However, enantioselective protonation of this less stable intermediate may be more difficult than cyclic ketoenol.[11] In addition, for the hydrocarbon substrates bearing relatively low dissociation energy of C(sp^3)−H bonds, the existence of a nonstereoselective HAT pathway[12] to afford racemic products makes it more challenging to achieve high levels of enantioinduction (Scheme 1A).[13] Given these challenges, we imagine that acyclic α-substituted acrylates might be superior alkylating agents for asymmetric functionalization of a wider range of inert C(sp^3)−H bonds (Scheme 1B) because of their structural diversity and the potential to regulate steric hindrance,[14] albeit with the risk of a side reaction of radical polymerization.[15] Therefore, we propose that a TBADT-mediated HAT process is capable of cleaving the inert C(sp^3)−H bond to generate a carbon-centered radical, which then undergoes a Giese radical addition to α-substituted acrylate to give an α-acyl radical. Back hydrogen abstraction (HA) from the reducing photocatalyst to an α-acyl radical furnishes an enol species, and enantioenriched α-stereogenic ester is yielded via enantioselective protonation with CPTS.[16]

Dehydroalanine esters, a useful kind of α-substituted acrylates, are widely used as fundamental building blocks for the synthesis of enantioenriched α-amino acid derivatives.[17,18] Therefore, we initially targeted the development of an enantioselective C(sp^3)−H bond addition to N-acyl dehydroalanine benzyl ester **1** with the use of TBADT as a HAT photocatalyst and chiral spiro phosphoric acid (*S*)-**A1** as a CPTS (Table 1), enabling a facile and highly atom-economic approach to prepare chiral α-amino esters.[19] To our delight, the desired C(sp^3)−H addition product **3** was smoothly furnished in 89% NMR yield and with 95:5 er by exposing **1** and cyclohexane **2** to near-ultraviolet light in benzonitrile (entry 1). The examination of a range of chiral spiro phosphoric acids revealed that the substituents at the 6,6′-positions of the SPINOL had obvious influence on enantioinduction, and (*S*)-**A1** still turned out to be a superior CPTS (entries 2−5). The evaluation of other reaction parameters was shown in the Supporting Information. Interestingly, this reaction also proceeded well in the absence of chiral phosphoric acid (*S*)-**A1** (entry 6), implying the existence of an alternative nonstereoselective pathway. Considering the high levels of enantioselectivity in the presence of chiral phosphoric acid (*S*)-**A1**, the reaction rate of the enantioselective pathway was certain to be much faster than that of the nonstereoselective pathway (entry 1 vs entry 6). In the absence of 5 Å MS, **3** was afforded in a slightly eroded NMR yield but with maintained enantioselectivity (entry 7), suggesting that 5 Å MS might not only serve as a desiccant to lighten H_2O-mediated nonstereoselective protonation but also act as a solid acid[20] to promote the Giese radical addition. Finally, control experiments verified that both HAT photocatalyst TBADT and near-ultraviolet light were essential to the success of the reaction (entries 8 and 9). A

Table 1. Optimization of Reaction Conditions[a]



entry	variation	yield (%)[b]	er[c]
1	none	89	95:5
2	**A2** instead of **A1**	46	80:20
3	**A3** instead of **A1**	52	82:18
4	**A4** instead of **A1**	76	86:14
5	**A5** instead of **A1**	55	64:36
6	no **A1**	54	N.D.
7	no 5 Å MS	78	95:5
8	no TBADT	<1	N.D.
9	no light	<1	N.D.
10[d]	gram-scale reaction	95	94:6

[a]Reaction conditions: **1** (0.1 mmol), **2** (4 mmol), TBADT (0.002 mmol), **A1** (0.002 mmol), PhCN (0.5 mL), 5 Å MS (30 mg), 0 °C, under nitrogen, 6 W 390 nm LEDs, 3 h. [b]Determined by ^{1}H NMR analysis of the crude reaction mixture based on 1,3,5-triacetylbenzene as an internal standard. [c]Determined by chiral-phase HPLC analysis. [d]**1** (3 mmol), **2** (120 mmol), TBADT (0.06 mmol), **A1** (0.06 mmol), PhCN (15 mL), 5 Å MS (900 mg), 10 °C, under nitrogen, 40 W 390 nm LEDs, 6 h. PMP = *p*-methoxyphenyl.

gram-scale reaction of *N*-acyl dehydroalanine benzyl ester **1** and cyclohexane **2** conducted under slightly altered reaction conditions furnished the desired product **3** in a slightly enhanced yield and with maintained enantioselectivity (entry 10).

With the optimal reaction conditions in hand, the scope of this asymmetric C(sp^3)−H bond addition protocol was examined (Scheme 2). The variations at either *N*-acyl groups or the ester substituents of *N*-acyl dehydroalanines were nicely tolerated to afford the corresponding C(sp^3)−H addition products (**4**−**7**) in moderate to good yields and with high levels of enantioselectivity. With respect to the hydrocarbon substrates, the reaction tolerated a wide range of cyclic hydrocarbons and methylarenes. For example, 5-, 7-, and 8-membered cycloalkanes were smoothly converted to the corresponding alkylated products (**8**−**10**) in good to excellent yields and with good enantioselectivities. Methylarenes bearing either electron-donating or electron-withdrawing substituents in the *ortho*-, *meta*-, and *para*-position of the aromatic moiety were capable of delivering C(sp^3)−H adducts (**11**−**22**) with good levels of enantioselectivity. Notably, 3-methylthiophene could also be directly alkylated at the benzylic site (**23**) in 43% yield and with 93:7 er. Isopentyl benzoate was capable of undergoing site-selective tertiary C(sp^3)−H alkylation to provide the corresponding C(sp^3)−H adduct (**24**) in moderate yield, albeit with a slightly decreased enantioselectivity. In addition, 1,3-benzodioxole, phenyl ethers, and methyl *tert*-butyl ether were amenable to afford the desired coupling products (**25**−**29**) through enantioselective C(sp^3)−H alkylation occurring exclusively at the carbon atom adjacent

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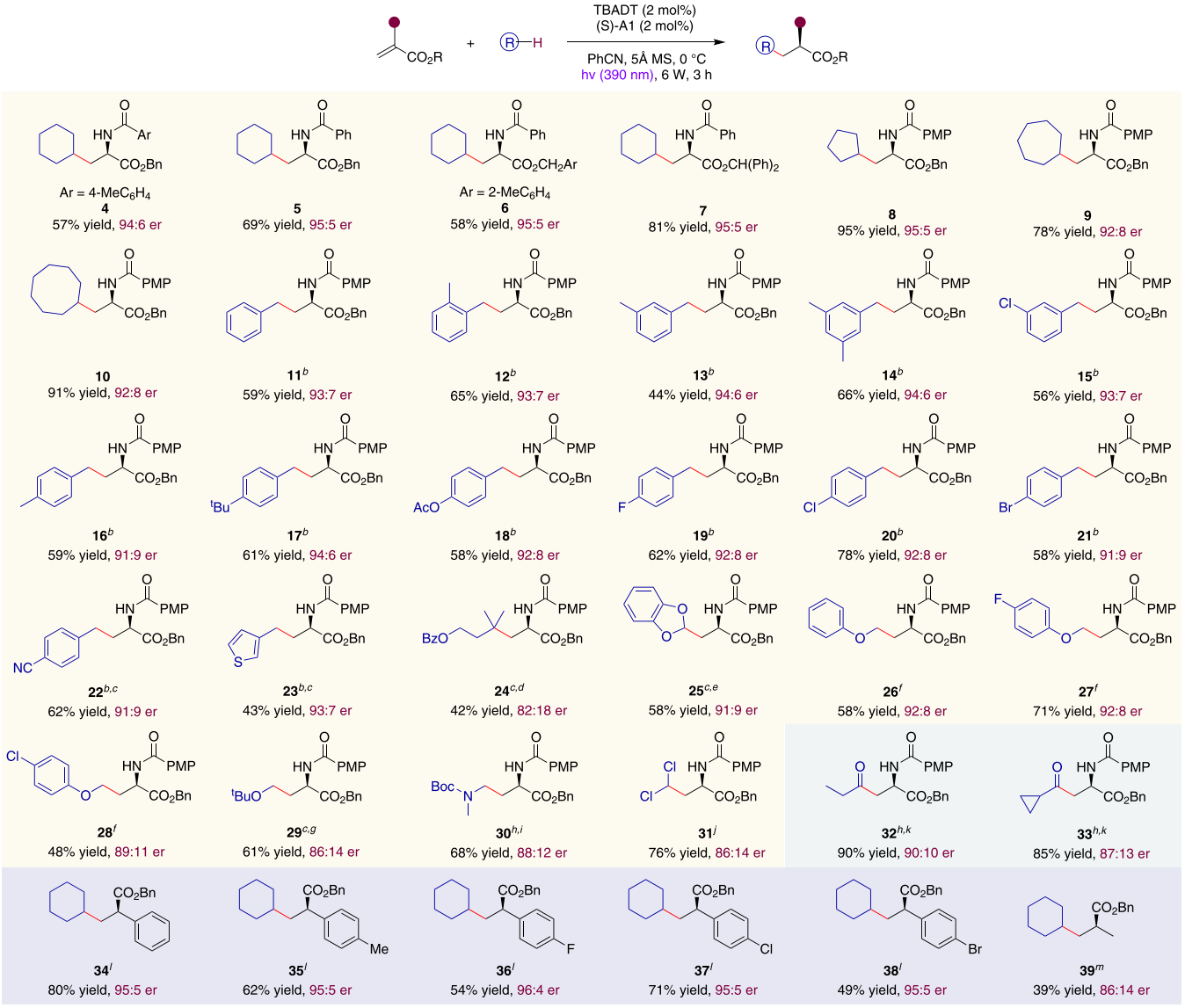
Scheme 2. Substrate Scope[a]



[a]Unless indicated otherwise, reactions run with N-acyl dehydroalanine ester (0.1 mmol), cyclic alkane (4 mmol), TBADT (0.002 mmol), (*S*)-**A1** (0.002 mmol), PhCN (0.5 mL), 5 Å MS (30 mg), 0 °C, under nitrogen, 6 W 390 nm LEDs, 3 h. The absolute configurations of **26** and **37** were assigned based on X-ray crystallography, and the absolute configurations of all other compounds were assigned by analogy. [b]With 20 equiv of methylarene. [c]With 5 mol % (*S*)-**A1**. [d]With 20 equiv of isopentyl benzoate. [e]With 10 equiv of benzodioxole, 0.5 mL MeCN. [f]With 60 equiv of ether, 2 mL of PhCN/CH_2Cl_2 (1:1). [g]With 20 equiv of ether, 1 mL of MeCN. [h]With 10 mol % (*S*)-**A1**. [i]With 2 equiv of dimethylcarbamate, 0.25 mL of MeCN. [j]With 3 mL of CH_2Cl_2. [k]With 2 equiv of aldehyde, 0.5 mL CH_2Cl_2. [l]With 0.5 mL of PhCN/CD_2Cl_2 (1:9), rt, 8 h. [m]With 0.5 mL of PhCN/CH_2Cl_2 (1:1), rt, 4 h.

to the oxygen. Aliphatic amide and dichloromethane were also viable to afford the corresponding C(sp^3)−H adducts (**30**−**31**) with acceptable results. In particular, aliphatic aldehydes, capable of serving as acyl radical precursors, were employed successfully to provide chiral hydroacylation-type products (**32**−**33**) in high yields and synthetically useful enantioselectivities.

Notably, α-aryl acrylates were capable of serving as effective substrates in asymmetric C(sp^3)−H addition under slightly altered conditions. Either electron-donating or electron-withdrawing functional groups at the *para*-position were suitable to deliver the corresponding adducts (**34**−**38**) in 49−80% yields and with 94:6 to 96:4 er. It should be noted that this protocol was also applicable by using readily available methacrylate, furnishing the C(sp^3)−H adduct (**39**) with synthetically acceptable results.

To gain some insight into the mechanism of this photocatalytic C(sp^3)−H bond addition protocol, a series of deuterium labeling experiments were performed (Scheme 3). In the presence and absence of chiral spiro phosphoric acid (*S*)-**A1**, the incorporation of an excess amount of D_2O into the reaction of *N*-acyl dehydroalanine benzyl ester **1** and toluene **40** afforded the corresponding deuterated product **11**-$\mathbf{d_1}$ with 82% and 93% deuteration, respectively (Scheme 3a). The observed high levels of deuterium incorporation suggested that the nonstereoselective pathway was significantly less likely to be a direct hydrogen atom transfer from toluene to an α-acyl radical intermediate but most likely to be a H_2O-mediated

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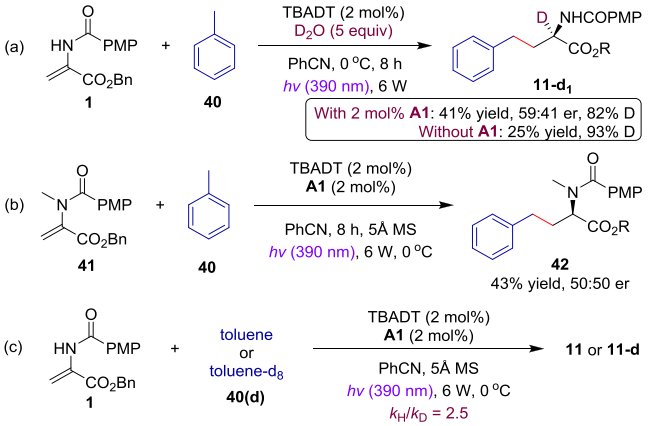
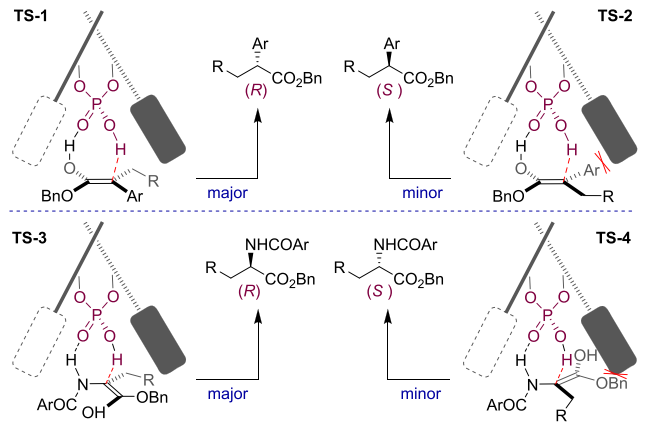
Scheme 3. Control Experiments and Kinetic Studies



protonation of the carbanion intermediate.[21] In addition, a significant decrease of enantioselectivity (Scheme 3a), observed in the presence of an excess amount of D_2O, strongly indicated that enantioselective protonation of the carbanion intermediate should constitute the main enantio-differentiating step in this protocol, and chiral spiro phosphoric acid was capable of showing a significant acceleration effect on the proton shift step in comparison with H_2O. Interestingly, the block of the amide N−H moiety in *N*-acyl dehydroalanine **41** also resulted in the generation of the corresponding C(sp^3)−H adduct **42** but the enantioinduction completely disappeared (Scheme 3b), implying that the amide N−H bond might play a key role in the enantio-differentiating step probably through a hydrogen-bonding interaction with chiral spiro phosphoric acid (*S*)-**A1**.[22] Furthermore, kinetic studies toward clarifying the rate-determining step were also carried out (Scheme 3c). A significant deuterium kinetic isotope effect (KIE, k_H/k_D = 2.5) was observed for the reaction of **1** and **40(*d*)**, suggesting that the TBADT-mediated C(sp^3)−H bond cleavage was involved in the rate-determining step.

The absolute configuration of these C(sp^3)−H adducts is unambiguously established by X-ray crystallographic analysis of product **26** and **37**. Based on these mechanistic studies, two plausible stereochemical pathways for protonation are speculated to rationalize the absolute configuration (Scheme 4). With regard to the α-aryl ester enolate, a CPTS-assisted [1,3]-proton shift[23] is a plausible pathway to generate the final product from transition state **TS-1** with an *R*-configuration,[24] and transition state **TS-2** is disfavored by the steric repulsion between the aryl group of the enol and the 2,4,6-triisopropyphenyl group of chiral spiro phosphoric acid (*S*)-**A1**. For the α-amidoester enolate, as suggested by Zhu and Zhou,[22] the presence of the N−H bond is also capable of serving as a hydrogen-bond donor to facilitate seven-membered-ring transition states **TS-3** and **TS-4**. The sterically demanding benzyl ester moiety is oriented to minimize interaction with the bulky substituent of (*S*)-**A1**; thus, the formation of *R*-configuration is favored (**TS-3** vs **TS-4**).

Scheme 4. Proposed Stereochemical Pathways for Protonation



In summary, we have developed an asymmetric photocatalytic C(sp^3)−H bond addition to α-substituted acrylates by using TBADT as a HAT catalyst and chiral spiro phosphoric acid as a chiral proton-transfer shuttle. This protocol is supposed to occur via a radical/ionic relay process, including a TBADT-mediated HAT to cleave the inert C(sp^3)−H bond, a 1,4-radical addition, a back hydrogen abstraction, and an enantioselective protonation. A wide variety of inert C(sp^3)−H bond patterns and α-substituted acrylates are nicely tolerated to enable rapid synthesis of enantioenriched α-stereogenic esters from simple raw materials. We anticipate that this report will facilitate the future development of asymmetric functionalization of inert C(sp^3)−H bonds through the combination of photocatalysis and organocatalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00801.

Complete experimental procedures and characterization data for the prepared compounds (PDF)

Accession Codes

CCDC 2024891 and 2046103 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.

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Notes

The authors declare no competing financial interest.

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