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Rhodium-Catalyzed Enamine Homologation of Sulfides with Triazoles as Carbene Precursor

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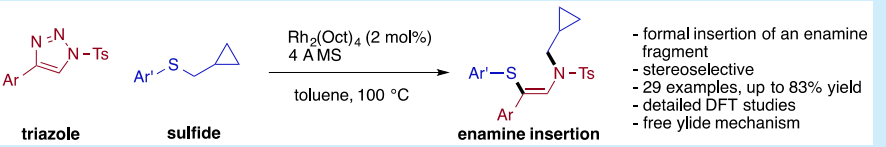

ABSTRACT: We report on Rh(II)-catalyzed enamine homologation reactions of triazoles with cyclopropylmethyl sulfides. This reaction proceeds via Dimroth rearrangement of triazoles followed by rhodium-catalyzed ylide formation. This ylide, however, does not undergo classic rearrangement reactions. Instead, it undergoes a selective, intramolecular alkylation reaction to yield cyclopropylmethyl-substituted enamides. The application of this reaction was evaluated with different triazoles and sulfides, which underline the special reactivity of cyclopropylmethyl sulfides (29 examples, up to 83% yield).

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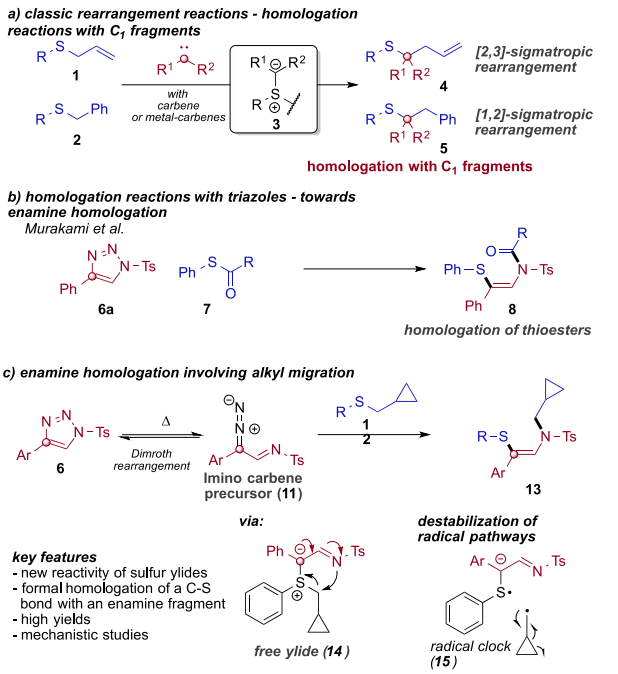
Rearrangement reactions based on ylide intermediates have witnessed significant advances over the past decade.[1,2] Sulfur ylides can be readily accessed under neutral reaction conditions from electrophilic carbene intermediates that undergo ylide formation with a nucleophilic sulfide reaction partner.[2−4] Today, a variety of different rearrangement reactions are known in organic synthesis, among which the [2,3]-sigmatropic rearrangement of allyl sulfides **1** and the [1,2]-sigmatropic rearrangement reaction of benzylic **2** or cyclic sulfides are probably the best studied systems, which provide the reaction product of a formal C_1-homologation reaction (Scheme 1a).[3,4]

Diazoalkanes are the most commonly employed class of reagent to access the carbene reaction partner under metal-catalyzed, photochemical or thermal reaction conditions.[5,6] However, the high reactivity of diazoalkanes also represents one of the major drawbacks of these reagents. To overcome these limitations, approaches using continuous flow to access the diazoalkane in flow or the *in situ* synthesis of diazoalkanes have emerged in the past decade as important technology-based approaches.[7,8] From a carbene precursor perspective,[9] a variety of reagents, such as tosyl hydrazones,[10] hydrazones,[11] cycloheptatrienes,[12] cyclopropenes,[13] and triazoles,[14] have been studied as safe alternatives to avoid the handling of diazoalkanes and to access the carbene reactivity in a safe manner. A particularly intriguing reactivity lies within triazole heterocycles **6** that, upon heating, undergo a Dimroth rearrangement to expose a transient diazoalkane, which can form an imino-substituted carbene precursor **11** (Scheme 1c).[15] An intriguing feature of triazoles lies within the potential for a formal insertion reaction of an enamine fragment into X−H or C−H bonds, as previously demonstrated by Murakami,[16] Fokin,[17] and others.[18]

Scheme 1. Classic Sigmatropic Rearrangement versus Homologation with Imino Carbenes



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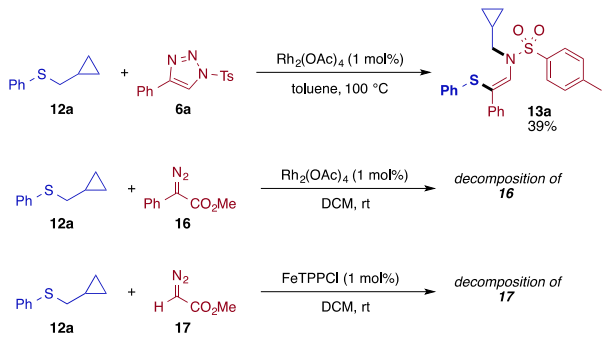
In the context of the formal insertion reaction into C−X bonds, Murakami and coworkers reported on the reaction of thioesters **7**, which underwent a similar formal insertion reaction of an enamine fragment, yet with limitations on the transfer of acyl groups (Scheme 1b).[19] Anbarasan and Yadagiri observed a similar reaction pattern in the reaction of triazoles with benzyl sulfides, yet only an inseparable mixture of enamine insertion and [1,2]-sigmatropic rearrangement could be observed.[20] To the best of our knowledge, a high-yielding, selective process toward the formal homologation of sulfides with an enamine fragment involving the migration of an alkyl group has not yet been reported (Scheme 1c).

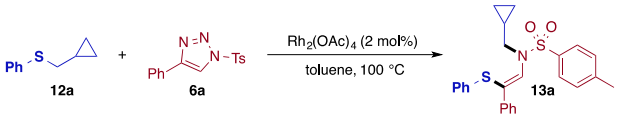
We hypothesized that destabilization or hindering of the radical pathway of [1,2]-sigmatropic rearrangement[21,22] via an irreversible reaction should result in a favored ionic reaction mechanism and as a consequence improve the chemoselectivity in favor of this enamine homologation. We assumed that the introduction of a cyclopropane ring might serve as a useful structural feature to disfavor radical intermediates and to prevent a competing [1,2]-sigmatropic rearrangement reaction via decomposition of potential radical intermediates via radical clock **15** (Scheme 1c). Gratifyingly, when studying the cyclopropylmethyl thioether **12a**, we could observe the exclusive formation of the enamine homologation product **13a** in moderate isolated yield without accompanying byproducts arising from the [1,2]-sigmatropic rearrangement reaction. Further studies on the reactivity of commonly used donor/acceptor diazoalkanes (methyl phenyldiazoacetate, **16**) and acceptor diazoalkanes (ethyl diazoacetate, **17**) revealed that no product of [1,2]-sigmatropic rearrangement reaction could be observed with sulfide **12a**, thus underlining the distinct reactivity of imino-substituted carbenes in this reaction (Scheme 2).

Scheme 2. Evaluation of Suitable Carbene Precursors



We next embarked on studies to further improve the reaction yield of this homologation reaction and first studied the influence of reaction stoichiometry, temperature, concentration, and solvent (Table 1, entries 1−10). The best yields were obtained when using 2 equiv of triazole **6a** using toluene as a solvent (Table 1, entry 2). Importantly, this reaction is compatible with a range of different solvents, and comparable yields were obtained when using *m*-xylene, 1,2-DCE, or chloroform solvent (Table 1, entries 5−8). The use of molecular sieves further improved the reaction yield (Table 1 entry 13) probably via diminishing the potential hydrolysis of intermediate imines or the enamine reaction product. Subsequent studies on the influence of the Rh(II) catalyst revealed $Rh_2(Oct)_4$ to give the best yield (Table 1, entry 15).

Table 1. Optimization of Reaction Conditions

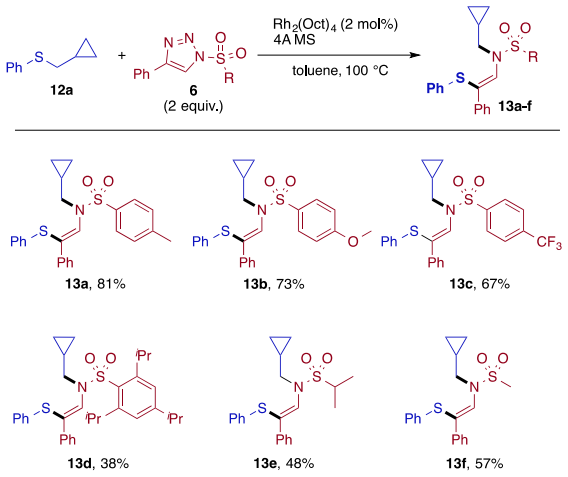


no.[a]	catalyst	solvent	12a/6a	% yield[b]
1	$Rh_2(OAc)_4$	toluene	1:1	39
2	$Rh_2(OAc)_4$	toluene	1:2	65
3	$Rh_2(OAc)_4$	toluene	1:3	59
4	$Rh_2(OAc)_4$	toluene	2:1	40
5	$Rh_2(OAc)_4$	*m*-xylene	1:2	55
6	$Rh_2(OAc)_4$	$CHCl_3$	1:2	50
7	$Rh_2(OAc)_4$	1,2-DCE	1:2	56
8	$Rh_2(OAc)_4$	dioxane	1:2	54
9[b]	$Rh_2(OAc)_4$	toluene	1:2	51
10[c]	$Rh_2(OAc)_4$	toluene	1:2	60
11[d]	$Rh_2(OAc)_4$	toluene	1:2	62
12[e]	$Rh_2(OAc)_4$	toluene	1:2	43
13[f]	$Rh_2(OAc)_4$	toluene	1:2	76
14[f]	$Rh_2(esp)_2$	toluene	1:2	75
15[f]	$Rh_2(Oct)_4$	toluene	1:2	81
16[f]	$Rh_2(Piv)_4$	toluene	1:2	56

[a]Reaction conditions: **6a** and **12a** (0.2 mmol scale, equivalents as indicated) and catalyst (2 mol %) were dissolved in the solvent indicated (2.0 mL) and stirred at 100 °C for 12 h. Yields refer to isolated products. [b]80 °C reaction temperature. [c]110 °C reaction temperature. [d]4 mL of solvent. [e]1 mL if solvent. [f]With 4 Å molecular sieves (60 mg).

With the optimized conditions in hand, we next investigated the influence of the *N*-protecting group of the triazole heterocycle (Scheme 3). Whereas para substitution of

Scheme 3. Evaluation of Different *N*-Protecting Groups



arylsulfonyl protecting groups was tolerated (**13a−c**), the sterically demanding triisopropyl phenyl group was less tolerated, and a significantly reduced yield was observed (**13d**). It is interesting to note that alkylsulfonyl protecting groups were also tolerated, and the enamine homologation product was exclusively obtained in moderate yield (**13e,f**).

We then focused on the influence of the substitution pattern of the aromatic ring of the sulfide and triazole reaction partner (Scheme 4). Substitution of the aryl-sulfide with halogens or electron-withdrawing or electron-donating groups in the ortho

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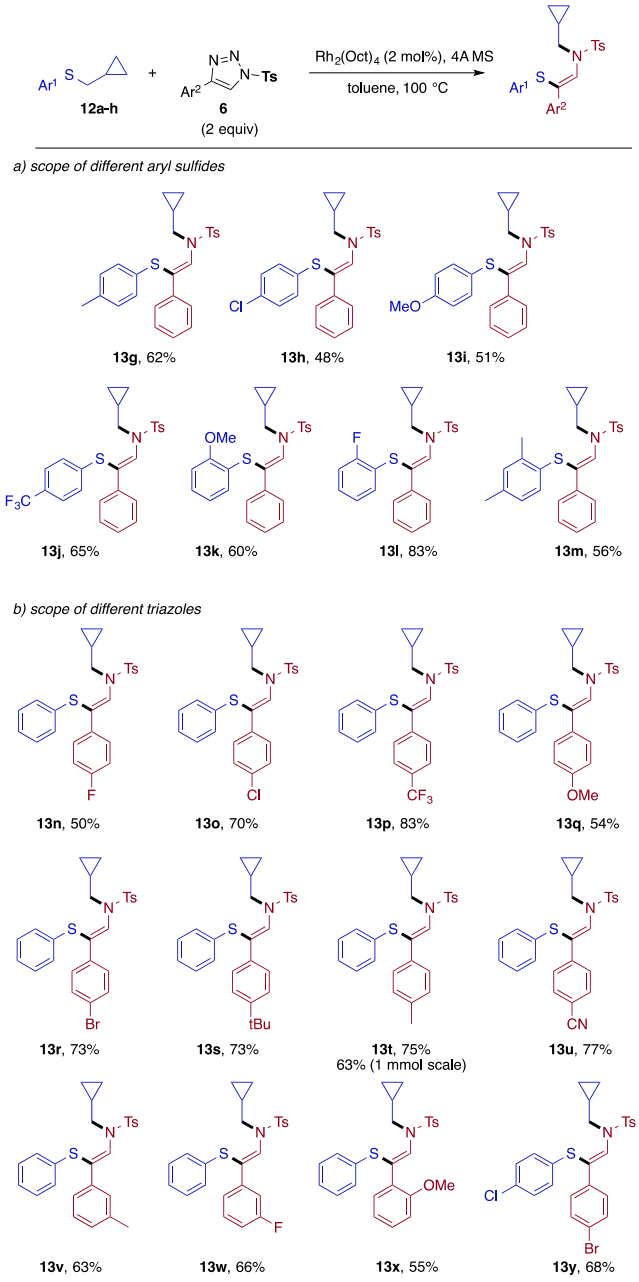
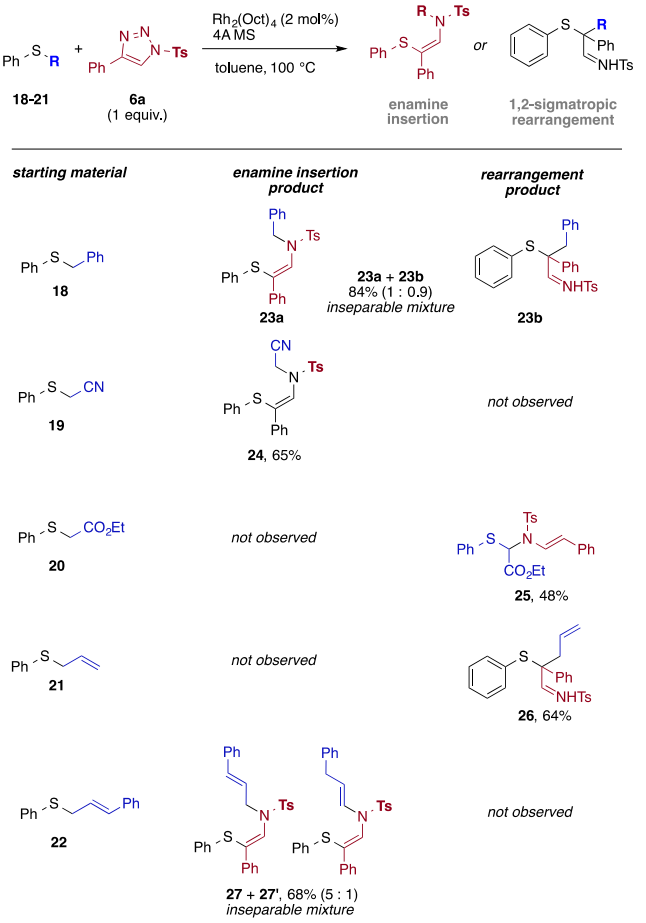
Scheme 4. Substrate Scope of the Homologation Reaction



Scheme 5. Substrate Scope of *S*-Alkyl Groups



or para position proved compatible, yet a reduced yield of the desired homologation product was obtained (**13h−m**), thus showing that the aromatic ring of the sulfide has a significant influence on the efficiency of this homologation reaction. Notably, electron-donating substituents had a detrimental effect on the reaction yield in both the para and ortho positions, and a substantial decrease in the reaction yield was observed (Scheme 4, **13h,i,k**). Studies on the applicability of different triazoles revealed a similar trend in reactivity (Scheme 4b). High product yields were obtained in the case of para substitution with halogens, alkyl groups, or electron-withdrawing groups. Strongly electron-donating groups had a detrimental effect on the product yield. Investigations on the 1 mmol scale revealed a slightly reduced yield (**13t**).

Finally, we evaluated the migratory aptitude of different *S*-alkyl groups (Scheme 5). For this purpose, we studied different substitution patterns of the aliphatic group that can facilitate this homologation reaction. Thioanisole gave a complex, inseparable mixture of different reaction products and represents a clear limitation of the present methodology. Under the present reaction conditions, benzyl phenyl sulfide **18** reacted unselectively to the products of [1,2]-sigmatropic rearrangement **23b** and enamine insertion **23a**, which might be explained by the high stability of a putative intermediate benzyl radical in the case of [1,2]-sigmatropic rearrangement. When introducing an electron-withdrawing nitrile group (**19**) to facilitate the nucleophilic substitution step, we could observe an enamine insertion reaction, and product **24** was obtained in good yield with no byproduct from the rearrangement, as observed by the ^{1}H NMR spectroscopy of the crude reaction mixture. On the contrary, in the case of an ester electron-withdrawing group (**20**), [2,3]-sigmatropic rearrangement occurred to yield **25**.[23] Allyl sulfide **21** underwent a selective [2,3]-sigmatropic rearrangement reaction in high yield, as it was also previously observed by Anbarasan and coworkers.[20] A surprising observation was made using a cinnamyl-substituted sulfide **22**. In this case, we did not observe the product of a classic rearrangement; instead, selective homologation occurred to give **27**, which is a mixture of double-bond isomers. The high reaction temperature might be the reason for the isomerization of the double bond. This unexpected outcome in the case of different substitution patterns of allyl sulfides might be explained by the differences in steric hindrance for nucleophilic substitution versus rearrangement, leading to a favored homologation reaction.

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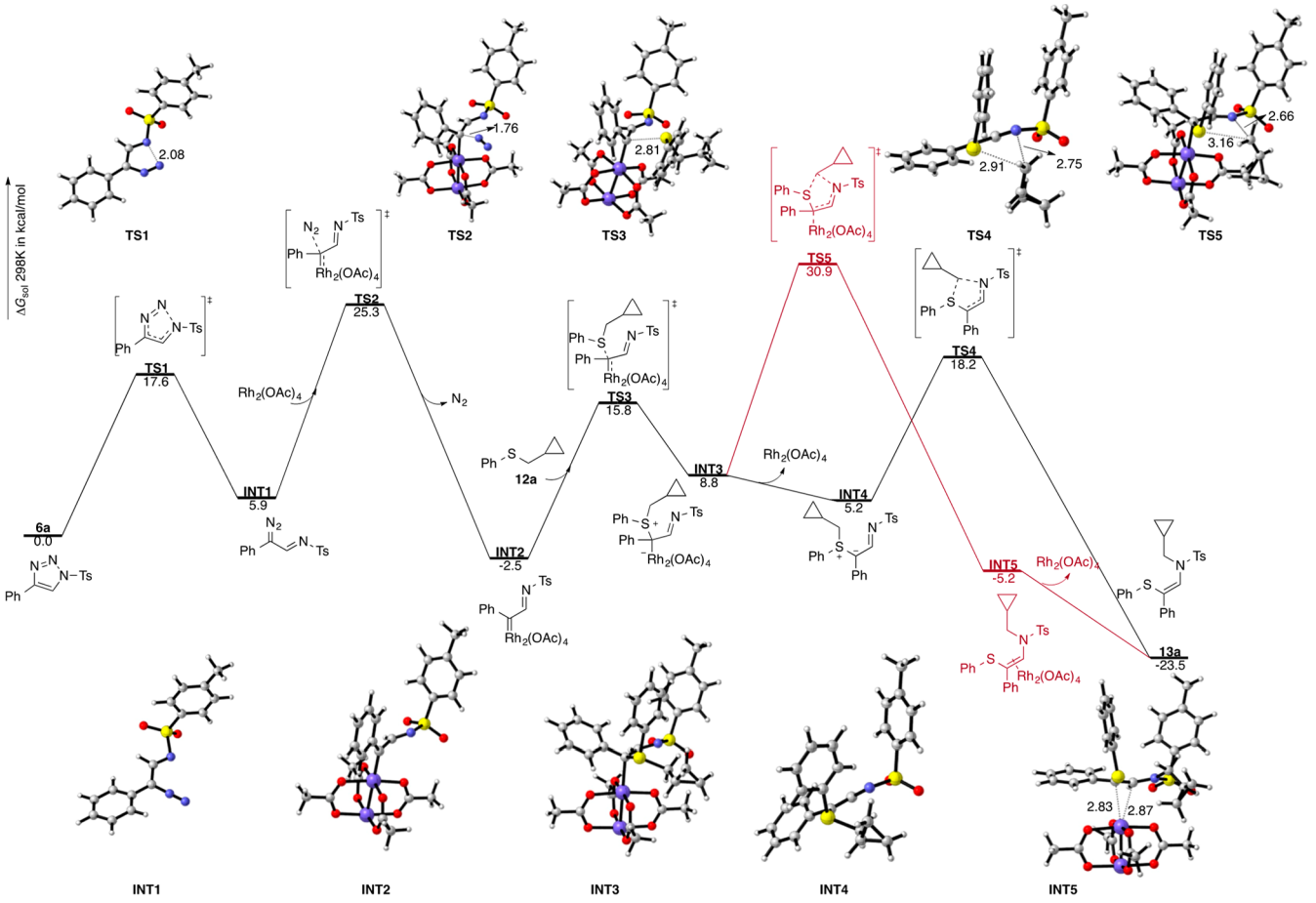
Scheme 6. DFT Studies at the B3LYP/6-311+G(d,p)/LANL2DZ//B3LYP/6-31G(d)/LANL2DZ Level on the Reaction Mechanism of the Enamine Homologation with Triazoles



To investigate the reaction mechanism of this enamine homologation reaction, we studied the reaction of triazole **6a** with cyclopropylmethyl sulfide **12a** by density functional theory (DFT) calculations at the B3LYP/6-311+G(d,p)/LANL2DZ//B3LYP/6-31G(d)/LANL2DZ level (Scheme 6). The calculations reveal that the formation of rhodium carbene complex **INT2** is preceded by Dimroth rearrangement with a relatively high-energy-barrier rhodium carbene complex-forming event, which rationalizes the high reaction temperatures required in this transformation. In line with our previous experience on the formation of ylide intermediates, the **INT2** undergoes a facile addition reaction with cyclopropylmethyl sulfide **12a** to give a metal-bound ylide intermediate **INT3**. This intermediate can now undergo a direct alkyl migration reaction via the high-lying transition state **TS5** with an activation free energy of 22.1 kcal/mol to give a side-on coordinated enamine product. Subsequent release of the rhodium catalyst provides the final reaction product **13a**. Alternatively, the metal-bound ylide **INT3** undergoes demetalation to give the free ylide intermediate **INT4**, which is 3.6 kcal/mol downhill in energy. This free ylide intermediate then undergoes alkyl migration via a relatively low-lying transition state **TS4** and an activation free energy of 13.0 kcal/mol to directly give the observed reaction product **13a**. These calculations demonstrate that this enamine homologation presumably proceeds via a free ylide intermediate and rationalize the high selectivity that we have observed in this reaction.

In summary, we herein report on a rhodium-catalyzed homologation reaction of alkyl aryl sulfides with triazole heterocycles via an imino carbene intermediate (29 examples, up to 83% yield). In this unusual reaction, we showcase that imino carbenes can form ylides that do not undergo classic rearrangement pathways but preferentially react in an intramolecular alkylation reaction to give the product of an enamine homologation. This observation now expands the reactivity pattern of ylide intermediates toward the formal insertion of an enamine fragment into a C−S bond.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02330.

Experimental procedures, characterizations, and analytical data (PDF)

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Notes

The authors declare no competing financial interest.

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