JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
Cite This: J. Am. Chem. Soc. 2019, 141, 19161−19170
pubs.acs.org/JACS

Catalytic, Enantioselective *syn*-Diamination of Alkenes

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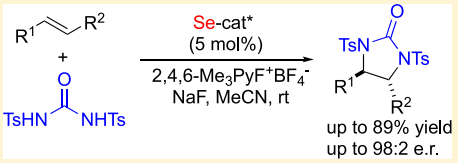
Supporting Information

ABSTRACT: The enantioselective, vicinal diamination of alkenes represents one of the stereocontrolled additions that remains an outstanding challenge in organic synthesis. A general solution to this problem would enable the efficient and selective preparation of widely useful, enantioenriched diamines for applications in medicinal chemistry and catalysis. In this article, we describe the first enantioselective, *syn*-diamination of simple alkenes mediated by a chiral, enantioenriched organoselenium catalyst together with a *N,N′*-bistosyl urea as the bifunctional nucleophile and *N*-fluorocollidinium tetrafluoroborate as the stoichiometric oxidant. Diaryl, aryl-alkyl, and alkyl-alkyl olefins bearing a variety of substituents are all diaminated in consistently high enantioselectivities but variable yields. The reaction likely proceeds through a Se(II)/Se(IV) redox catalytic cycle reminiscent of the *syn*-dichlorination reported previously. Furthermore, the *syn*-stereospecificity of the transformation shows promise for highly enantioselective diaminations of alkenes with no strong steric or electronic bias.



INTRODUCTION

Enantioenriched, vicinal diamines are frequently encountered across the many disciplines of chemistry. They are prevalent in a wide variety of natural products, drugs, and other biologically active molecules and are frequently employed as ligands or in the preparation of ligands for asymmetric synthesis and catalysis (Figure 1).[1] Vicinal diamines are found in the most ubiquitous natural products, for example, vitamins such as biotin, and 2,3-diamino acids[2] present in peptide antibiotics,[3] antitumor agents,[4] and other biologically active molecules.[5] The presence of a vicinal diamine moiety is also required for the activity of certain neurokinin 1 (NK_1) antagonists,[6] for example, rolapitant,[7] an antiemetic agent for chemotherapy patients,[9] and antiproliferative agents such as nutlin-3.[8] Furthermore, many different chiral, enantioenriched auxiliaries, ligands, and catalysts for organic synthesis are derived from vicinal diamines,[9] including Noyori enantioselective hydrogenation catalysts,[10] N-heterocyclic carbenes,[11] and various ligands for asymmetric additions of organometallic reagents.[9b,12] Many of these chiral diamines are still most frequently obtained in enantioenriched form by classical resolution,[13] stereocontrolled transformations of enantioenriched starting materials,[5,14] or functional group interconversion of amino acids and other chiral pool materials.[1,2b,15]

BACKGROUND

Only recently have methods for the enantioselective preparation of chiral, enantioenriched vicinal diamines from achiral starting materials come to the fore. Early attempts to extend the Sharpless asymmetric dihydroxylation[16] to catalytic diamination were largely unsuccessful. Catalytic turnover cannot be achieved, owing to slow decomplexation of osmium from the bidentate diamine product. Thus, osmium-mediated diaminations instead require prior preparation of the diimidoosmium reagent, which must be employed in stoichiometric amounts for addition to the alkene substrate.[17]

The catalytic, enantioselective, oxidative diamination of olefins is perhaps the most conceptually straightforward approach to the preparation of enantioenriched vicinal diamines, however alternative methods involving (reductive) carbon−carbon bond formation have also been described.[18] Alkene diamination has more recently been achieved in large part with palladium and copper catalysts,[19] by N−N bond activation of hydrazine derivatives to oxidize the catalytic metal species and to generate the nucleophile (Scheme 1). These methods, limited by the need for high-energy reagents, have been expanded to engage more common N−H nucleophiles. This approach requires an oxidant (e.g., N-fluorinated amine, hypervalent iodine reagent, or inorganic oxidant) to return the palladium or copper species into the catalytic cycle.[20] However, methods employing an exogenous oxidizing agent are largely limited to substrates with at least one of the nitrogen nucleophiles tethered to the alkene, except in the case of aryldienes.[20g]

In 2011, Muñiz and co-workers disclosed the current, most general method for intermolecular diamination of alkenes, mediated by stoichiometric quantity of a chiral, enantioenriched, hypervalent iodine complex (Scheme 2).[21] 1,2-Bis(dimethanesulfonyl)amines are obtained in good to excellent yields and enantioselectivities from a variety of unsubstituted styrenes. Structural refinement of the iodoarene reagent and introduction of *m*-CPBA as the stoichiometric oxidant allowed for the development of a catalytic, enantioselective method that provides excellent yields and improved enantioselectivities.[22] Furthermore, *trans*-1,2-disubstituted alkenylbenzenes undergo diamination to afford *anti*-

Received: October 19, 2019
Published: November 19, 2019

DOI: 10.1021/jacs.9b11261
J. Am. Chem. Soc. 2019, 141, 19161−19170

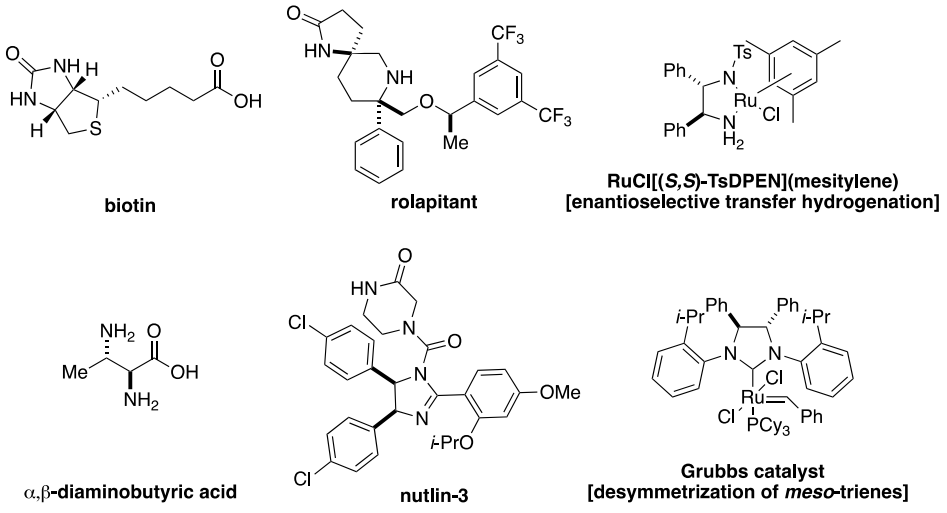
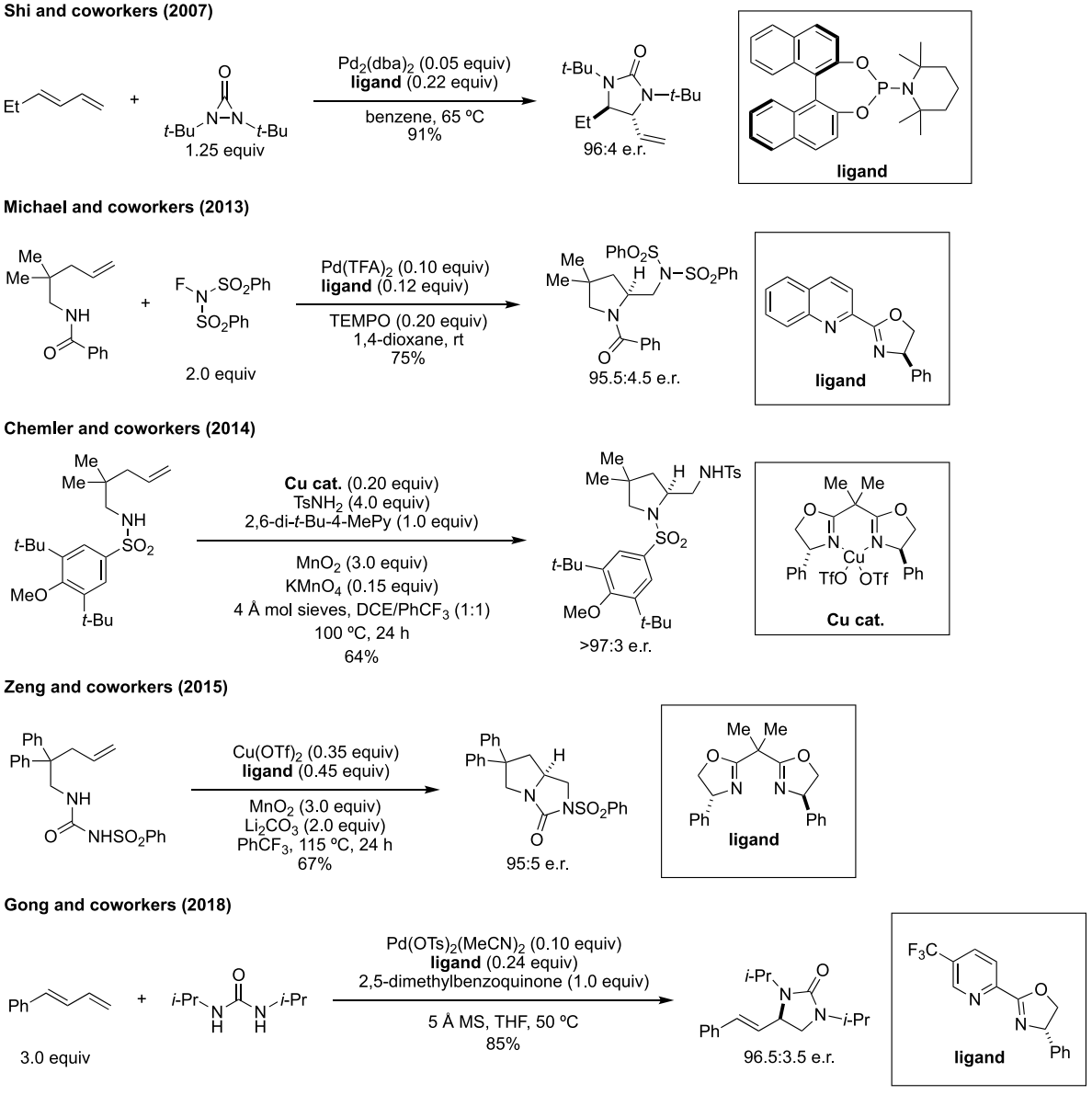


Figure 1. Diamines in natural products, drugs, and catalysts for enantioselective transformations.

Scheme 1. Metal-Catalyzed, Catalytic, Enantioselective Diamination of Alkenes



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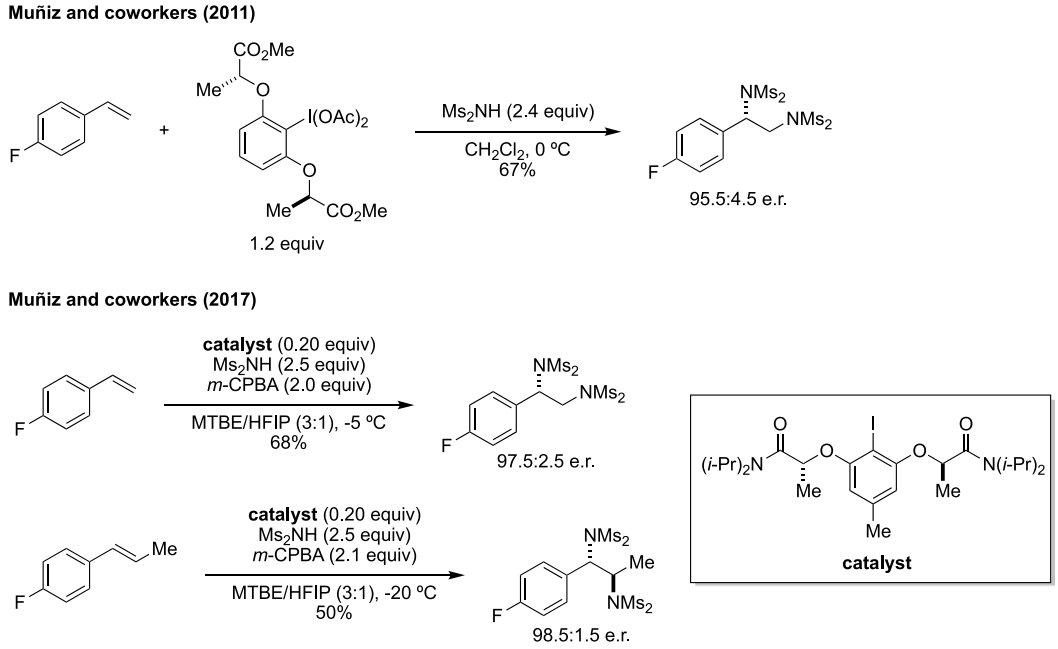
Scheme 2. Iodoarene-Mediated and -Catalyzed Diamination of Alkenes



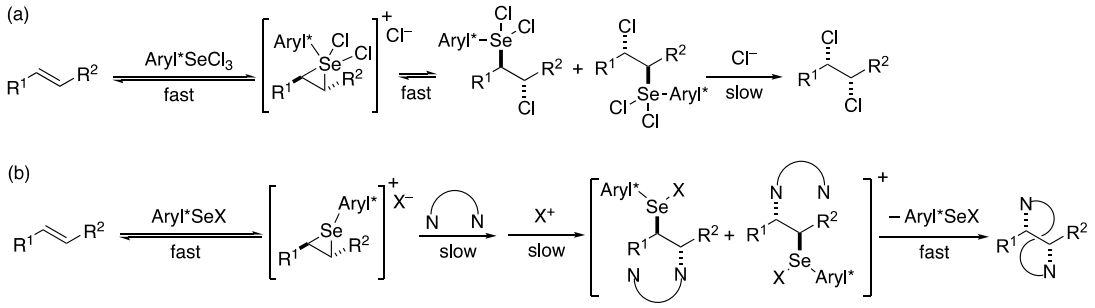


Figure 2. (a) Redox catalyzed *syn*-dichlorination. (b) Hypothetical redox-catalyzed *syn*-diamination.

1,2-diaminated products, however with catalytic turnover numbers (TONs) limited to ca. 2 for all substrates evaluated.

Although the diastereoselectivities for the vicinally diaminated products are excellent, the observed preference for a net *anti* addition to form product is unexpected for an iodoamination−displacement sequence. To explain this outcome, Muñiz and co-workers propose that the initially formed iodoamination product undergoes an anchimerically assisted displacement of the iodine to form a bis(methanesulfonyl)-aziridinium ion, followed by opening of the aziridinium ion with a second molecule of bismethanesulfonimide to afford the product. It is possible that the intramolecular process is outcompeting intermolecular displacement of the iodoarene−a detour that could potentially be remedied by the use of a bifunctional nucleophile to afford *syn*-diaminated products.

A recent report from these laboratories disclosed the design and synthesis of chiral, enantioenriched diselenides for the development of a catalytic, enantioselective *syn*-dichlorination of alkenes, by employing a Se(II)/Se(IV) redox cycle.[23,24] Unfortunately, enantioselectivities are modest using a wide variety of structurally distinct diselenides. The modest selectivities likely result from the reversibility of seleniranium ion formation (the enantiodetermining step) and slow intermolecular displacement of the arylselenium(IV) intermediate by chloride to form the product (Figure 2a). To address both issues, we hypothesized that the use of a stronger nucleophile (e.g., N) delivered as a bifunctional reagent could accelerate the displacement of the arylselenium(IV) leaving group by virtue of intramolecularity thereby capturing the kinetically controlled formation of the initial seleniranium ion, with attendant improvement of enantioselectivity (Figure 2b). The hypothetical sequence in Figure 2b also illustrates a critically important component of *syn* vs *anti* vicinal functionalizations, namely that regioselectivity is irrelevant in the *syn* manifold because the two constitutional isomers converge to a single enantiomer.

■ RESEARCH PLAN

Accordingly, our mechanistic insights on the failure to achieve high selectivity in *syn*-dichlorination led to the formulation of an unprecedented, enantioselective *syn*-diamination using our Se(II)/Se(IV) redox-catalysis platform in combination with bifunctional nucleophiles. Reactivity was to be evaluated prior to any investigation of enantioselectivity−a library of chiral, enantioenriched diselenides was already on hand, but the specific composition of the bifunctional nucleophiles needed to be established. Preliminary experiments focused on the identification of an effective combination of nitrogen nucleophile, oxidant, base, and solvent, with diphenyl diselenide as the precatalyst. Several parameters had to be

DOI: 10.1021/jacs.9b11261
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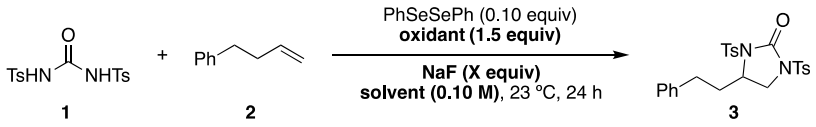
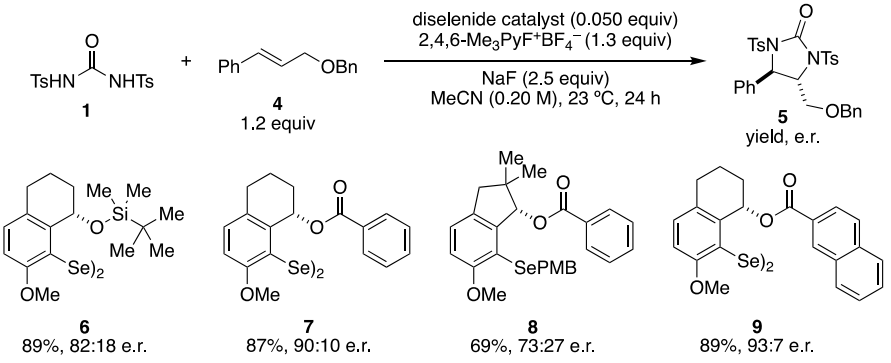
Table 1. Optimization of Diamination Reaction Conditions[a]



entry	ratio 1:2	oxidant	NaF equiv	solvent	yield (%)[b]
1	2:1	$PyF^+BF_4^-$	2.5	MeCN	20
2	2:1	$2,6\text{-}Cl_2PyF^+BF_4^-$	2.5	MeCN	18
3	2:1	$2,4,6\text{-}Me_3PyF^+BF_4^-$	2.5	MeCN	62
4	2:1	$2,4,6\text{-}Me_3PyF^+BF_4^-$	0	MeCN	43
5	2:1	$2,4,6\text{-}Me_3PyF^+BF_4^-$	5	MeCN	58
6	1.2:1	$2,4,6\text{-}Me_3PyF^+BF_4^-$	2.5	MeCN	60
7	1:2	$2,4,6\text{-}Me_3PyF^+BF_4^-$	2.5	MeCN	58
8	1:1.2	$2,4,6\text{-}Me_3PyF^+BF_4^-$	2.5	MeCN	59
9	1:1.2	$2,4,6\text{-}Me_3PyF^+BF_4^-$	2.5	CH_2Cl_2	21
10	1:1.2	$2,4,6\text{-}Me_3PyF^+BF_4^-$	2.5	PhMe	16
11	1:1.2	$2,4,6\text{-}Me_3PyF^+BF_4^-$	2.5	$ClCH_2CH_2Cl$	20
12	1:1.2	$2,4,6\text{-}Me_3PyF^+BF_4^-$	2.5	THF	5
13	**1:1.2**	**$2,4,6\text{-}Me_3PyF^+BF_4^-$**[c]	**2.5**	**MeCN**	**59**

[a]All reactions were performed on 0.10 mmol scale. Refer to Supporting Information for more details. [b]Yield determined by ^1H NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard. [c]1.3 equiv of $2,4,6\text{-}Me_3PyF^+BF_4^-$.

Scheme 3. Evaluation of Chiral, Enantioenriched Diselenide Catalysts



carefully controlled: (1) the pK_a of the nitrogen nucleophile, (2) the pK_a and solubility of the base, and (3) the redox potential of the stoichiometric oxidant. Relatively non-acidic N−H nucleophiles would not likely have a large enough equilibrium concentration of the conjugate base to engage the seleniranium ion, and stronger or more soluble bases could potentially lead to the elimination of selenium-containing intermediates to afford olefinic byproducts. More strongly oxidizing stoichiometric oxidants also had the potential to react directly with the nucleophile, resulting in unproductive consumption of both. Furthermore, the selection of the oxidant would also be informed by the compatibility of its reduced byproduct with the components of the reaction mixture. For example, oxidants that produce nucleophilic byproducts (e.g., NFSI and $PyF^+BF_4^-$) could favor competitive capture of the seleniranium ion to form disulfonimido or pyridinium products,[20a,25] whereas oxidants that produce particularly basic byproducts (e.g., Selectfluor) could favor eliminative deselenenylation.[24a−c]

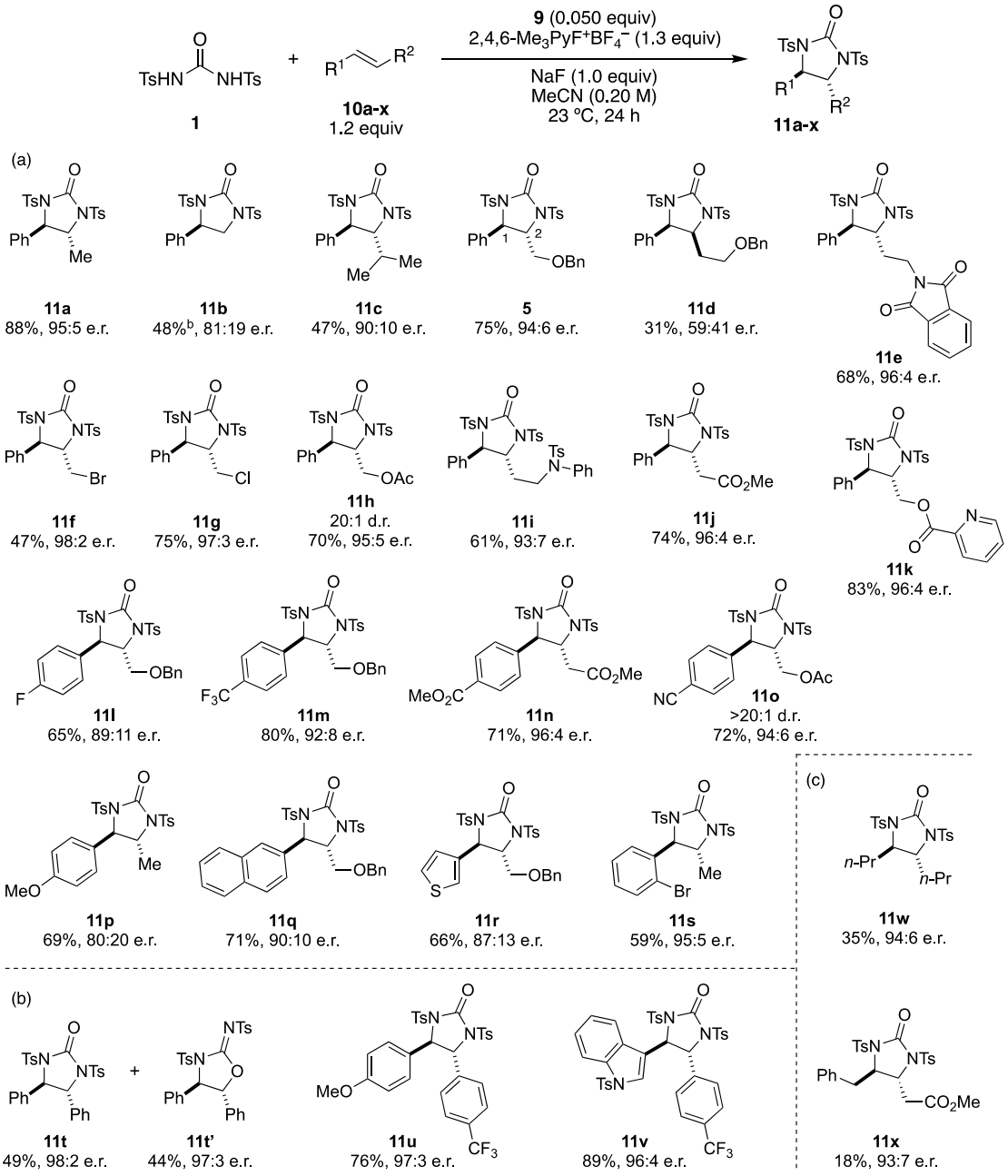
RESULTS

Reaction Development. Initial evaluation of reactivity began with 4-phenyl-1-butene as a test substrate. *N,N′*-Bis(toluenesulfonyl)urea was identified early on as a uniquely reactive dinucleophile, which had the distinct advantage of forming 1,2-ditosylimidazolidin-2-ones that could be selectively manipulated to other products. A variety of alternative bifunctional nucleophiles, including *N*-carbamoyl and acyl ureas, *N*-aryl sulfamides, *N*-sulfonyl oxamides, *N*-sulfonyl amidines, and *N*-sulfonyl guanidines were also evaluated throughout the course of reaction development, but none afforded the desired difunctionalized product (see Supporting Information). Organic and inorganic bases such as pyridine, DABCO, potassium carbonate, and cesium carbonate afforded trace or no yield, whereas sodium fluoride appeared to be uniquely suited to the transformation (Table 1).

1-Fluoro-2,4,6-trimethylpyridinium tetrafluoroborate ($2,4,6\text{-}Me_3PyF^+BF_4^-$) was optimal for the diamination reaction, whereas the unsubstituted 1-fluoropyridinium tetrafluoroborate ($PyF^+BF_4^-$) and 1-fluoro-2,6-dichloropyridinium tetrafluoroborate ($2,6\text{-}Cl_2PyF^+BF_4^-$) gave very low yields (entries 1 and 2). Sodium fluoride was important to obtain yields in excess of 50% but did not appear to be required for the reaction to proceed (entry 4). Increasing equivalents of sodium fluoride did not, however, improve the yield (entry 5). The stoichiometry of alkene and urea appeared to have relatively little effect on the yield (entries 6−8). Alkene **2** was employed in excess to allow for full consumption of the urea reagent **1** and thereby simplify purification of the product mixture. Acetonitrile uniquely afforded good yields compared to the

DOI: 10.1021/jacs.9b11261
J. Am. Chem. Soc. 2019, 141, 19161−19170

Table 2. Scope of *syn*-Diamination Reaction[a]



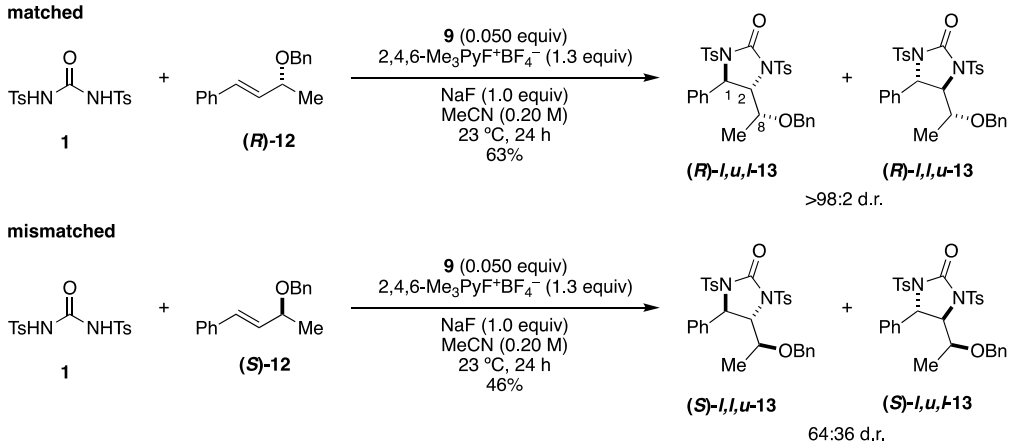
[a]All reactions were performed on 1.00 mmol scale. Enantiomeric ratios were determined after chromatographic purification by chiral stationary phase HPLC. Yields are of isolated, analytically pure material. Refer to Supporting Information for more details. [b]With 2.5 equiv of NaF.

other solvents surveyed (entries 9−12). Reactions in the other solvents were more heterogeneous, and the reduced yields may be a consequence of the insolubility of certain reaction components. Finally, the amount of oxidant could be reduced to 1.3 equiv without any impact on the rate or yield (entry 13).

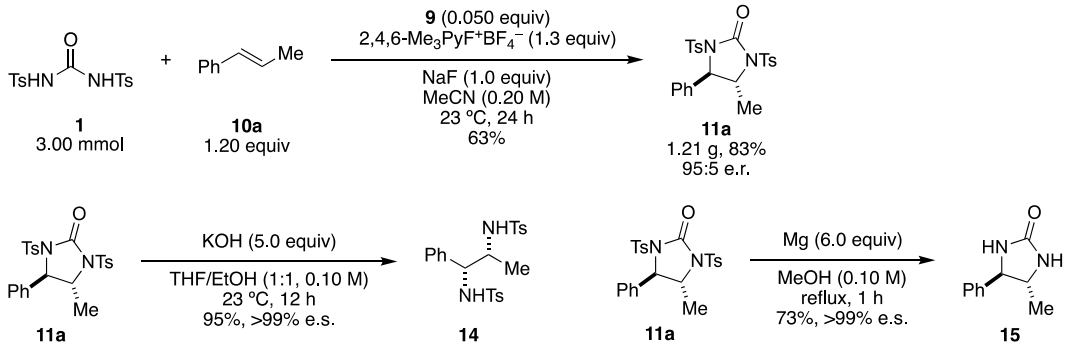
Chiral, enantioenriched diselenide catalysts were then surveyed using these conditions (Scheme 3). Catalysts were selected for evaluation on the basis of their performance (rate of reaction and selectivity) in the enantioselective *syn*-dichlorination of alkenes.[23a] Cinnamyl benzyl ether **4** was selected for optimization of enantiomeric ratio because it afforded better enantioselectivity compared to terminal olefin **2**. Catalyst **6** afforded very good yield and modest enantioselectivity. A priori assessment of the reaction conditions suggests the silyl ether may be (partially) cleaved by sodium fluoride to afford a different catalytic species that exhibits reduced enantioselectivity. Accordingly, the silyl ether was exchanged for a benzoate ester in diselenide **7**, which afforded a similar yield and greatly improved enantioselectivity. Based on the success of benzoate **7**, a benzoate derivative of the indane *tert*-butyldimethylsilyl ether organoselenium catalyst previously employed by Maruoka and co-workers (**8**)[24d] was also surveyed and showed poor selectivity and yield. On the other hand, extending the benzoate ester **6** to the 2-naphthoate ester **9** resulted in further improvement to the enantiomeric ratio with no change in the yield. Analogous diselenides bearing pivaloyl, 1-adamantanecarbonyl, 1-naphthalenecarbonyl, and 9-anthracenecarbonyl esters were also

DOI: 10.1021/jacs.9b11261
J. Am. Chem. Soc. 2019, 141, 19161−19170

Scheme 4. Diastereoselective Reactions To Evaluate Substrate vs Catalyst Control



Scheme 5. Synthetic Transformations of the Imidazolidin-2-one Product



surveyed, each affording poorer yield and enantioselectivity than the 2-naphthoate **9**.

Reaction Generality. The scope of substrates for the diamination reaction was next surveyed (Table 2). It was found early on that use of 1 equiv of sodium fluoride was sufficient and led to improved reaction homogeneity. The diamination reaction is general across a wide variety of *trans*-1,2-disubstituted alkenes bearing many kinds of substituents, to afford *syn*-difunctionalized products (Table 2a). *β*-Methylstyrene reacted smoothly to afford the imidazolidin-2-one product **11a** 88% yield with an e.r. of 95:5. Removing substitution or increasing steric bulk at the *β*-position to the alkene resulted in a decrease in yield and e.r. (**11b** and **11c**). However, introduction of 2-substitution on the aromatic ring did not result in any change to the enantiomeric ratio (**11s**). Introduction of an electron-withdrawing group at the *β*-position did not have a significant effect on enantiomeric ratio, but in some cases led to a decrease in yield (**5**, **11f**–**11h**, and **11j**). The stereochemical course of the reaction was established by single-crystal X-ray diffraction of product **5**.[26a] The absolute configuration (1*R*,2*S*)-**5**, is consistent with the absolute configuration found for a *syn*-dichlorination product formed by structurally related catalysts.[23a] Reaction with a *cis*-1,2-disubstituted alkene afforded product in low yield and enantiomeric ratio, however *syn*-diastereoselectivity was maintained (**11d**). Protected amines (**11e** and **11i**), methyl esters (**11j** and **11n**), electron-deficient pyridines (**11k**), and cinnamyl halides (**11f** and **11g**), and cinnamyl acetates (**11h** and **11o**) were all compatible with these reaction conditions. The presence of an acetate group on the alkene *β*-substituent resulted in the formation of a small amount of the *anti*-diastereomer, perhaps as a result of anchimeric assistance by the carbonyl oxygen (**11h** and **11o**). Notably, this effect was not observed for the nicotinate **11k** or the methyl esters **11j** or **11n**. Electron-poor styrenes generally afforded products in good yields and selectivities (**11l**–**11o**), whereas electron-rich sryrenes afforded products with lower enantiomeric ratios (**11p** and **11r**).

Diaryl alkenes were also competent reaction partners, affording mixtures of imidazolidin-2-one and 2-imino-1,3-oxazolidine products (Table 2b). Reaction with stilbene afforded a ∼1:1 mixture of products **11t** and **11t′**, each with excellent enantiomeric ratios. However, unsymmetrical diaryl olefins afforded products with significantly higher selectivities for the imidazolidinone products (**11u**, **11v**) in good yields and enantioselectivities. Product **11t** was likewise found by single crystal X-ray diffraction analysis to have the (*R*,*R*) absolute configuration resulting from the same enantiofacial selectivity as in **5**.[26b] Dialkyl alkenes underwent diamination in the standard reaction conditions with very good enantioselectivities, however in significantly reduced yield (**11w**, **11x**) (Table 2c). These reactions were particularly slow, and the urea reagent **1** was observed to decompose to 4-toluenesulfonamide over the course of the reaction. Attempts to modify reaction conditions to improve the yield by increasing catalyst loading or concentration, or modifying the solvent, base, or oxidant were unsuccessful. This class of alkenes represents an important focus of further investigation with other catalysts and bifunctional nucleophiles. For example, diphenyl diselenide catalyzed the formation of racemic **11x** in 43% yield. The enantioselective formation of product **11x** from unsymmetrical alkene **10x** represents a crucial advantage of this

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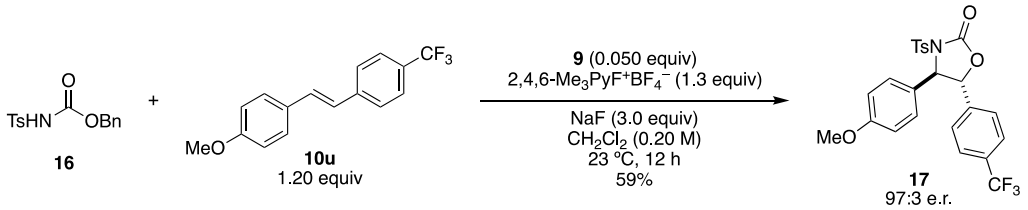
J. Am. Chem. Soc. 2019, 141, 19161−19170

Scheme 6. *syn*-Oxyamination



method. Because the process is *syn* stereospecific, the site selectivity of the addition is irrelevant. Were this an *anti* stereospecific process, the enantioselectivity would most certainly be much poorer.

Although enantioselective reactions are important for synthesis, reagent controlled diastereoselective reactions are perhaps more important for late-stage transformations in target oriented synthesis. To evaluate the relative effects of substrate vs catalyst control, both enantiomers of chiral alkene **12** were subjected to the standard reaction conditions (Scheme 4). Substrate (*R*)-**12** underwent matched substrate- and catalyst-controlled diamination with (*S*)-**9** to form diastereomer (*R*)-*l,u,l*-**13**,[27] with absolute configuration assigned by analogy to **5**, and a d.r. of >98:2. Contrariwise, (*S*)-**12** underwent mismatched diamination with (*S*)-**9** to a mixture of (*S*)-*l,l,u*-**13** and (*S*)-*l,u,l*-**13** in a 64:36 ratio. Substrate controlled selectivity apparently favored the *l,u,l*-diastereomer, but this selectivity was partially overturned by catalyst controlled selectivity for the (*Re,Si*) face of the alkene to prefer the *l,l,u*-diastereomer in the mismatched case.

The enantioenriched imidazolidin-2-one products generated by this reaction can be prepared on gram scale and readily transformed into useful synthetic intermediates by operationally simple techniques (Scheme 5). Reaction of β-methylstyrene proceeded smoothly at 3.00 mmol scale to afford 1.21 g (83% yield) of **11a** with an e.r. of 95:5. Treatment of **11a** with potassium hydroxide in THF/EtOH at room temperature afforded the *syn*-ditosylamide **14** in 95% yield. Alternatively, treatment with magnesium in refluxing methanol afforded the desulfonylated imidazolidinone **15** in 73% yield.

Oxyamination of stilbenes with carbamate reagent **16** was also possible with varying degrees of success (Scheme 6). Replacement of MeCN for CH_2Cl_2 was required for the reaction to proceed, and more equivalents of NaF were needed to improve the yield. Alkene **10u** was transformed to oxazolidin-2-one **17** in 59% yield with an e.r. of 97:3, as a single constitutional isomer. However, the reaction was observed to stall at 8 h with incomplete consumption of **16** on the basis of ^{1}H NMR analysis of the crude reaction mixture. A variety of substituted stilbenes were evaluated and found to reach greater conversion at smaller scales and stall at significantly reduced conversion upon scale-up. Investigations to determine the cause of reaction stalling and to develop a more general oxyamination protocol are underway.

DISCUSSION

A proposed catalytic cycle is illustrated in Figure 3. Initial oxidation of the diselenide precatalyst **9** likely affords the arylselenium(II) intermediate **I** and *sym*-collidine as the byproduct. Unsubstituted *N*-fluoropyridinium tetrafluoroborate ($PyF^+BF_4^-$) generates an equivalent of pyridine as its byproduct that could potentially mediate eliminative deselenenylation of selenium-containing reaction intermediates.

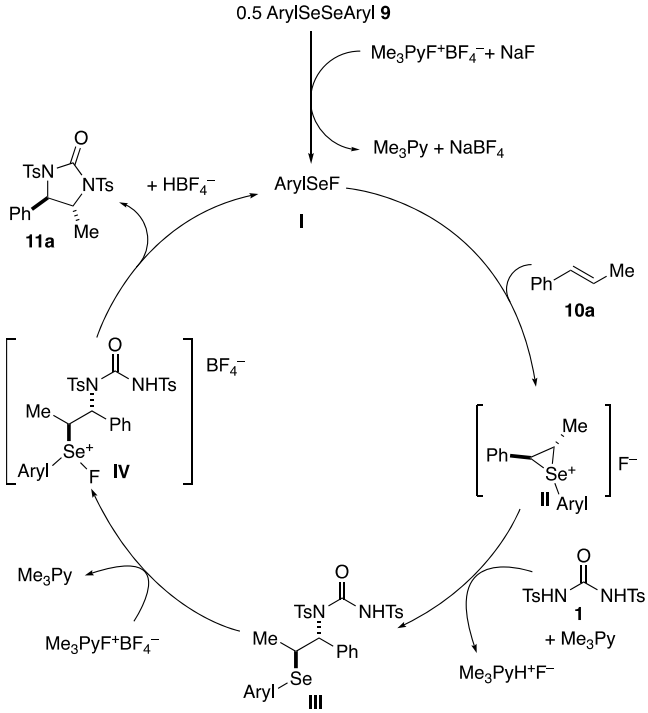


Figure 3. Proposed catalytic cycle.

Oxidants that produce unhindered, strongly basic byproducts, like Selectfluor, are likely similarly ill-suited for this transformation. On the other hand, the basic nitrogen of the collidine byproduct produced by 2,4,6-$Me_3PyF^+BF_4^-$ is more sterically encumbered and less likely to engage in these unproductive elimination reactions. N−F reagents with higher oxidation potentials, for example, 2,6-$Cl_2PyF^+BF_4^-$ and Selectfluor,[28] could lead to unproductive, direct oxidation of the nucleophile or olefin and consequently reduce the yield of the desired product.

The electrophilic arylselenium(II) species **I** could then react with alkene **10a** to form seleniranium ion intermediate **II** in a concerted fashion. This step is likely enantiodetermining, with the enantioselectivity resulting from kinetic enantiofacial selectivity. The rate of this reaction step and the associated enantiofacial selectivity are significantly lower for *cis*-alkenes (e.g., **10d**) for different but related reasons. *cis*-Alkenes, unlike *trans*-alkenes, allow orientation of both groups on the alkene away from any significant steric interactions with the substituent (i.e., chiral moiety) on the selenium atom in the key seleniranium ion. Thus, approaches to the *Re* or *Si* face of a *cis*-olefin have comparatively little energetic difference.[29] On the other hand, formation of a seleniranium ion from a *cis*-alkene comes at a greater energetic cost, as the groups on the alkene experience stronger eclipsing interactions with one

DOI: 10.1021/jacs.9b11261
J. Am. Chem. Soc. 2019, 141, 19161−19170

another as the alkene carbons rehybridize in a concerted fashion ($sp^2 \rightarrow sp^3$), leading to lower reaction rates.[30]

It is possible that seleniranium ion formation is reversible and that enantioselectivity results from thermodynamic equilibration of diastereomeric seleniranium ions, however this mechanistic regime was previously found to afford poor selectivities.[23a] Seleniranium ion formation may instead be occurring at the Se(IV) oxidation state, however PhSeF does not appear to undergo oxidation to $PhSeF_3$ with 2,4,6-$Me_3PyF^+BF_4^-$ alone, instead requiring donor ligands such as chloride or an alkyl group on Se[31] (N.B. $PhSeF_3$ is typically prepared by reaction of Ph_2Se_2 with XeF_2).[32] The deprotonated nitrogen nucleophile could potentially serve such as a ligand to enable this oxidation prior to seleniranium ion formation.

Regardless of the oxidation state of selenium, opening of the seleniranium ion by **1**, likely after deprotonation by collidine, could then afford intermediate **III**. The pK_a of **1** is calculated to be 1.38 ± 2.00,[33] well within the necessary range to protonate collidine (the pK_b-H of 2,4-dimethylpyridinium is ca. 4.5).[34] This intermolecular, nucleophilic ring opening is likely to be the turnover-limiting step and becomes especially slow with alkene substrates that are not accelerated by aromatic stabilization of a benzylic carbocation (e.g., dialkyl olefins **10w** and **10x**).

Oxidation to the arylselenium(IV) intermediate **IV** then allows for intramolecular displacement of selenium by the second urea nitrogen to afford **11a** and regenerate the electrophilic selenium species **I**. Because only 1 equiv of collidine is formed for each catalytic turnover, a catalytic equivalent of base is required to neutralize the acid that is formed in the second displacement. Sodium fluoride could be serving as the base and to sequester the HF formed as sodium bifluoride. In circumstances in which the second displacement is accelerated, for example, with diaryl alkenes such as stilbene, the rate of displacement by the carbonyl oxygen could become competitive with the rate of deprotonation and displacement by the second nitrogen, resulting in a mixture of products **11t** and **11t′**.

CONCLUSIONS

In summary, we have developed the first intermolecular, enantioselective, *syn*-stereospecific diamination of alkenes. The method employs a chiral, enantioenriched arylselenium reagent as a redox catalyst for alkene oxidation and C−N bond formation. A wide variety of *trans*-1,2-disubstituted alkenes are diaminated in good yields and enantioselectivities. Aryl-alkyl olefins afford the best yields and selectivities, and preliminary examination of diaryl- and dialkyl-olefins shows promise for further method development. The product of *syn*-addition to the alkene is obtained exclusively in almost all cases, affording the potential to circumvent the issue of site-selectivity inherent in *anti*-stereospecific diaminations of electronically unbiased alkenes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b11261.

Experimental procedures, characterization data for all new compounds along with copies of spectra and chromatograms, and data for (1*R*,2*S*)-**5** and (*R*,*R*)-**11t** (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the National Science Foundation (NSF CHE1664376) the National Institutes of Health (GM R35 127010) for generous financial support. We are also grateful for the support services of the NMR, mass spectrometry X-ray crystallographic, and microanalytical laboratories of the University of Illinois at Urbana−Champaign.

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DOI: 10.1021/jacs.9b11261
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