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Organoselenium-Catalyzed Enantioselective Synthesis of 2-Oxazolidinones from Alkenes

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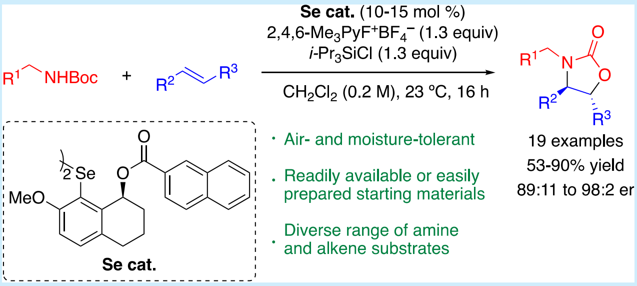
ABSTRACT: An operationally simple method for generating enantioenriched 2-oxazolidinones from *N*-Boc amines and mono- or *trans*-disubstituted alkenes via chiral organoselenium catalysis is described. Critical to the success of the transformation was the inclusion of triisopropylsilyl chloride (TIPSCl), likely because it sequestered fluoride generated by the oxidant (*N*-fluorocollidinium tetrafluoroborate) throughout the reaction and suppressed side reactivity. The scope of both the amine and alkene substrates was explored, generating a variety of 2-oxazolidinones in modest to high yields with high enantioselectivities.

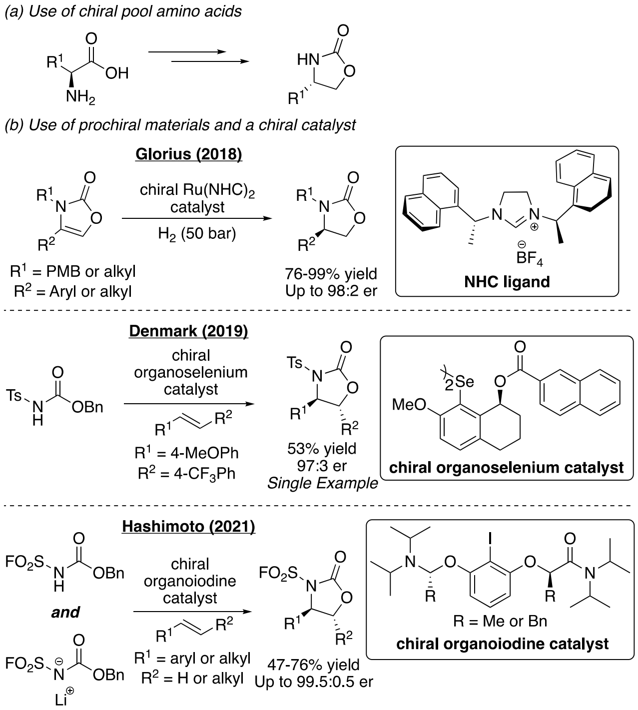


Enantiomerically enriched 2-oxazolidinones are a highly versatile class of heterocycles that have seen extensive use as both pharmaceutically active compounds[1] and as chiral auxiliaries for asymmetric synthesis.[2] Established methods of generating enantioenriched 2-oxazolidinones employ chiral pool amino acids as the *N*,*O*-nucleophiles upon reduction to their corresponding β-amino alcohols and cyclization with $C{=}O^{2+}$ electrophiles such as phosgene or carbonyl diimidazole (Scheme 1a).[3] Although this method is straightforward and robust, the functionality incorporated into the 2-oxazolidinone backbone is limited to that of commercially available or readily synthesizable amino acids.

An alternative route for creating enantiomerically enriched 2-oxazolidinones would be through the enantioselective functionalization of prochiral starting materials using a chiral catalyst. For example, Glorius and co-workers have reported a method for the Ru-catalyzed enantioselective hydrogenation of 2-oxazolones to their corresponding 2-oxazolidinones using a chiral NHC ligand (Scheme 1b).[4] The transformation provides high yields and enantioselectivities for an extensive array of substrates; however, this reaction requires the preinstallation of the C−N and C−O bonds of the 2-oxazolone starting material via a multistep sequence.

A more direct route to synthesizing enantiomerically enriched 2-oxazolidinones arises from the enantioselective oxyamination of feedstock alkenes using an NC(O)O nucleophile to directly deliver the 2-oxazolidinone in a single step. The viability of this transformation was demonstrated for the first time by our group in 2019 using *N*-tosylbenzylcarbamate as the nucleophile to capture the intermediate seleniranium ion generated by oxidative activation of a chiral diselenide (Scheme 1b).[5] It should be noted that this concept was not explored further at the time owing to the assumption that the tosyl group was required to enhance the acidity of the

Scheme 1. Chiral 2-Oxazolidinone Synthesis



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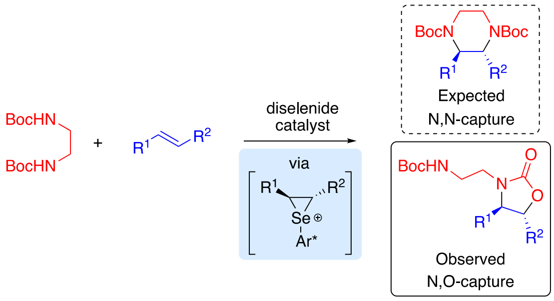
nitrogen atom to enable deprotonation. Since this initial discovery, Hashimoto and co-workers reported the use of a chiral organoiodine catalyst and a unique *N*-sulfonylated carbamate (as an *N,O*-nucleophile) to enantioselectively difunctionalize alkenes and generate 2-oxazolidinones in modest yields and high enantioselectivities (Scheme 1b).[6] One of the main highlights of this method is the ability to difunctionalize unactivated terminal alkenes (with modest enantioselectivities compared to the activated styrenyl substrates), but the transformation does require superstoichiometric quantities of the carbamate nucleophile and substitution at nitrogen is limited by the required sulfonyl group.

In the course of our search for other bifunctional nucleophiles, doubly *N*-Boc protected ethylene-1,2-diamine was subjected to the selenium-redox reaction conditions in anticipation of forming a 2,3-disubstituted piperazine. However, to our surprise, the 2-oxazolidinone product was formed instead (Scheme 2).

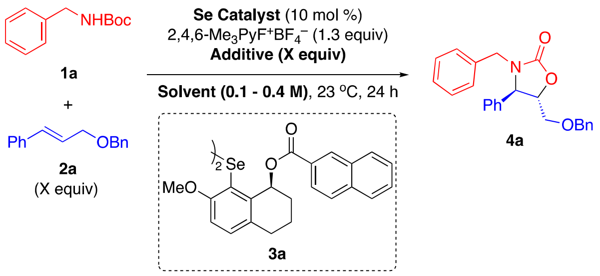
Scheme 2. Expected Diamination Product vs Observed Oxyamination Product



The importance of this discovery was not necessarily that *N*-Boc protected amines can serve as NC(O)O nucleophiles (as shown previously using *N*-Cbz protected amines (Scheme 1b)), but rather that the nitrogen of the carbamate does not require a tosyl group for the reaction to be productive. This logic may seem counterintuitive as both the Boc and tosyl groups decrease the nucleophilicity of the nitrogen atom; but it has been empirically observed that deactivation of the nucleophile is necessary to prevent catalyst death stemming from the heteroatomic nucleophile (in this case nitrogen) outcompeting the olefin for capture of the electrophilic selenium species. Examples of nitrogen capture of diphenyl diselenides in the presence of an oxidant are reported to generate seleneneamide species;[7] and while these species are able to undergo *β*-aminoselenation of olefins, the transformation is not viable under catalytic conditions.

With this initial discovery that simple *N*-Boc protected amines could serve as competent bifunctional nucleophiles using selenium-redox catalysis, an optimization campaign was performed by surveying the conditions outlined in Table 1. Although the reaction was discovered using doubly *N*-Boc protected ethylene-1,2-diamine, it was quickly realized that this substrate would be a poor nucleophile with which to evaluate conditions since the substrate contains two *separate* nucleophilic sites and would lead to side reactivity by oligomerization/polymerization. Therefore, the simpler *N*-Boc benzylamine was selected as the nucleophile for further evaluation.

Table 1. Optimization of Oxyamination Reaction Conditions[a]



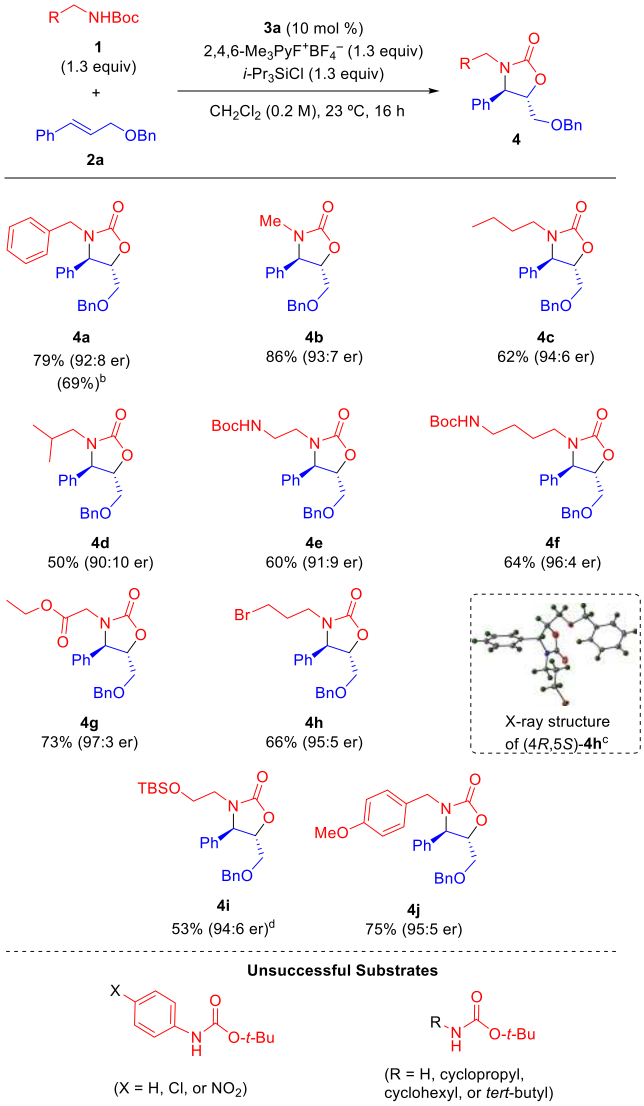
entry	1a/2a ratio	Se cat.	solvent	conc. (M)	additive[b,c]	yield (%)[d,e]
1	1:1.2	$(PhSe)_2$	MeCN	0.2	NaF	trace
2	1:1.2	$(PhSe)_2$	MeCN	0.2	**N/A**	trace
3	1:1.2	$(PhSe)_2$	$\mathbf{(CH_2Cl)_2}$	0.2	N/A	<5
4	1:1.2	$(PhSe)_2$	$\mathbf{CH_2Cl_2}$	0.2	N/A	<5
5	1:1.2	$(PhSe)_2$	CH_2Cl_2	0.2	**TIPSCl**	76
6	1:1.2	$(PhSe)_2$	CH_2Cl_2	**0.1**	TIPSCl	72
7	1:1.2	$(PhSe)_2$	CH_2Cl_2	**0.4**	TIPSCl	62
8	**1:1**	$(PhSe)_2$	CH_2Cl_2	0.2	TIPSCl	61
9	**1.3:1**	$(PhSe)_2$	CH_2Cl_2	0.2	TIPSCl	80
10	1.3:1	**3a**	CH_2Cl_2	0.2	TIPSCl	82 (62)[f]

[a] All reactions were performed on a 0.1 mmol scale. [b] 2.5 equiv of NaF. [c] 1.3 equiv of TIPSCl. [d] Yields were obtained by quantitative ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. [e] Yield in parentheses is an isolated yield. [f] Enantiomeric ratio of 92:8 determined by CSP-HPLC. See the Supporting Information for details.

By analogy to the previously reported oxyamination,[8] it was found that NaF had no effect on the reaction as had been noted in the diamination process[5] (entry 1 vs 2); although it should be noted that some form of base (e.g., 2,4,6-collidine formed after F$^+$ transfer) must be included in the reaction to facilitate the removal of the N−H proton of the carbamate and the proton of the *tert*-butyl group to liberate isobutylene. Examining the reaction dependency on solvent showed negligible reactivity in acetonitrile and only slightly greater consumption of starting material in 1,2-dichloroethane and dichloromethane, but still with poor yields of the 2-oxazolidinone product (entries 2−4). The greatest impact to successful reactivity was found to be the addition of triisopropylsilyl chloride (TIPSCl) (entry 4 vs 5). It was postulated that the silane reagent could serve in a number of roles, including generating an imidate from the Boc group, or as a fluoride scavenger[9] to suppress a number of deleterious fluoride-induced processes including elimination, nucleophilic displacement of the selenium-/seleniranium-ion or capturing arylselenenyl fluorides (*vide infra*). (For a survey of other silyl chlorides see the Supporting Information for details). Increasing or decreasing the reaction concentration resulted in only poorer yields (entries 5−7) relative to the previous 0.2 M concentration. Evaluation of the nucleophile **1a** and alkene **2a** stoichiometry showed that a slight excess of *N*-Boc amine relative to the alkene gave greater yields and allowed for full consumption of the alkene (entry 8 vs 9). Lastly, chiral catalyst **3a** afforded a 62% yield of **4a** with an enantiomeric ratio of 92:8.

With optimized reaction conditions obtained, the nucleophile scope was explored using a variety of different *N*-Boc protected amines (Table 2). Simple *N*-Boc protected alkyl

Table 2. Nucleophile Scope for Different *N*-Substitution of 2-Oxazolidinones[a]



[a] All reactions were performed on a 1.0 mmol scale. Yields are of isolated, analytically pure material. Enantiomeric ratios were determined after chromatographic purification by CSP-HPLC. [b] Reaction was run on 0.5 g scale. Yield is of isolated, analytically pure material. [c] 50% probability ellipsoid displayed. [d] 15 mol % **3a** used. See the Supporting Information for details.

amines provided products **4a**, **4b**, and **4c** in good yields with high levels of enantioselectivity. The reactivity of the nucleophile was influenced by steric factors as substrates containing *β*-branching of the *N*-Boc protected amine gave only modest yields of the respective 2-oxazolidinone (**4d**). Hindered substrates containing *α*-branching (e.g., *N*-Boc-cyclohexylamine, *N*-Boc-cyclopropylamine, or *N*-Boc-*tert*-butylamine) resulted in poor reactivity, giving crude yields (by ^{1}H qNMR) ranging from 0−45%. The reaction also performs well for *N*-Boc amines containing both mildly nucleophilic (**4e** and **4f**) and electrophilic moieties (**4g** and **4h**). As mentioned previously, stronger nucleophiles are not competent in this reaction owing to their competitive consumption of either oxidant or catalyst; therefore, alcohol containing substrates should be protected if used in the reaction (**4i**).

Lastly, the absolute configuration of the 2-oxazolidinone products was assigned by an X-ray crystal structure analysis of **4h**, in which the resulting configuration of the product indicates formation of the seleniranium ion on the *Re*-face of **2a** in agreement with previous results with catalyst (*S*,*S*)-**3a**.[5,8,10]

N-Boc protected aniline nucleophiles gave disappointing results compared to aliphatic amine nucleophiles. ^{1}H NMR analysis of reaction mixtures showed nearly quantitative recovery of nucleophile and ∼30% recovery of alkene when phenyl-*tert*-butyl carbamate and **2a** were used. This observation suggests that the *N*-Boc aniline may not be nucleophilic enough to capture the seleniranium ion compared to the rate of capture by extraneous nucleophiles such as other olefins or chloride produced from TIPSCl. Compared to previously employed nitrogen nucleophiles (bis-*N*-tosyl urea and *N*-tosylbenzamides) that were competent in capturing the generated seleniranium ion, the less deactivated *N*-Boc aniline should be *more* nucleophilic; thus, it was hypothesized that the nucleophile may require deprotonation prior to its attack at the seleniranium ion, as was observed previously in diamination and oxyamination reports.[5,8] Subsequent experiments employing different bases to deprotonate the *N*-Boc aniline and increase its nucleophilicity were unsuccessful and only gave more complex reaction mixtures; therefore, the current lack of productive reactivity is not entirely understood at the time. Lastly, it was surprising to find that simple *tert*-butyl carbamate did not perform well for this transformation. Although free N−H containing 2-oxazolidinones cannot be directly synthesized by this method, *tert*-butyl (4-methoxybenzyl)carbamate generated the corresponding 2-oxazolidinone **4j** in high yield and can be converted into the N−H containing 2-oxazolidinone by oxidative debenzylation of the *para*-methoxybenzyl (PMB) group in the presence of the *O*-benzyl group.[11]

Investigation of the alkene scope (Table 3) began by testing *trans*-substituted alkenes that were previously successful in the diamination and oxyamination procedures.[5,8] Alkenes such as (*E*)-stilbene, (*E*)-2-methylstyrene, and (*E*)-cinnamyl chloride gave their respective 2-oxazolidinones (**4k**, **4l**, and **4m**) in modest yields with high enantioselectivity. The bulkier alkene (*E*)-2-(3-(benzyloxy)prop-1-en-1-yl)naphthalene gave product **4n** in slightly diminished yield and enantioselectivity. It may be postulated that steric crowding of the 2-naphthyl group obstructs the trajectory of the incoming nucleophile toward the formed seleniranium ion and slows the rate of capture, resulting in poorer yield owing to deleterious consumption of the seleniranium ion and poorer enantioselectivity owing to reversible formation of the seleniranium via olefin-to-olefin migration.[12,13] In contrast to our previous reports on diamination and oxyamination,[5,8] monosubstituted alkenes with an aryl substituent are ideal substrates for this transformation, giving products **4o**, **4p**, **4q**, **4r**, and **4s** in modest to high yields with excellent enantioselectivities. These substrates highlight that the chiral organoselenium catalyst **3a** is able to provide high enantiofacial discrimination of terminal alkenes containing an aryl substituent and is not limited to solely *trans*-disubstituted olefins. This newly engendered reactivity *and* enantioselectivity is likely a consequence of the increased nucleophilicity of the *N*-Boc amines relative to previously employed nucleophiles.

With respect to the electronic nature of the alkene, it has been observed that both significantly electron-rich and

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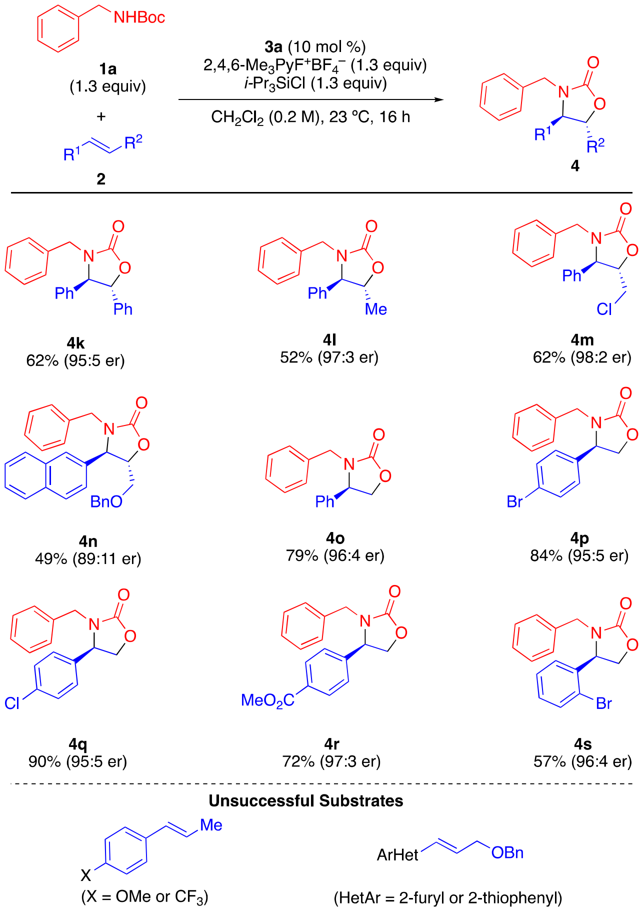
Table 3. Alkene Scope for Different 4- and 4,5-Substitution of 2-Oxazolidinones[a]



4k 62% (95:5 er)
4l 52% (97:3 er)
4m 62% (98:2 er)
4n 49% (89:11 er)
4o 79% (96:4 er)
4p 84% (95:5 er)
4q 90% (95:5 er)
4r 72% (97:3 er)
4s 57% (96:4 er)

[a] All reactions were performed on a 1.0 mmol scale. Yields are of isolated, analytically pure material. Enantiomeric ratios were determined after chromatographic purification by CSP-HPLC. See the Supporting Information for details.

electron-deficient olefins perform poorly for this reaction, with substrates such as (*E*)-1-methoxy-4-(prop-1-en-1-yl)benzene and (*E*)-1-(prop-1-en-1-yl)-4-(trifluoromethyl)benzene giving 35% and 20% crude yields by ^{1}H NMR analysis, respectively. Substrates containing heteroaromatic substituents attached to the alkene such as furans and thiophenes were observed to be unproductive, generally leading to full consumption of alkene with a significant amount of unreacted *N*-Boc amine. Thiophenes have been previously shown to be compatible with the oxidant used in this transformation;[5,8] therefore, it appears to be an issue of nucleophilicity that may not be ameliorated simply by modification of the reaction conditions.

On the basis of previous studies from these laboratories on related organoselenium-catalyzed alkene difunctionalizations, a putative catalytic cycle is outlined in Figure 1. Initial oxidation of the dimeric catalyst **3a** generates an activated selenium(II) electrophile that can be intercepted by an alkene to form the reactive seleniranium ion and one equivalent of arylselenium(II) fluoride (Figure 1a). It is well-known that arylselenium(II) fluorides are highly unstable and can rapidly hydrolyze or disproportionate to their corresponding arylselenium(IV) trifluorides;[14] thus, it is surmised that TIPSCl may help to remediate the formation of off-cycle catalytic species such as aryl selenium fluoride or trifluoride (Figure 1b). Although the identity of the active catalytic species after the first turnover is not known, *some* arylselenium(II) electrophile **I** must react with the alkene to generate the seleniranium ion **II**. Opening of the seleniranium ion occurs by nucleophilic attack of the *N*-Boc amine, giving identical site selectivity of attack as our previous oxyamination report (i.e., nitrogen attacking the more electrophilic site), and yielding the *β*-selenenyl intermediate **III** after deprotonation of the nitrogen by 2,4,6-collidine. A subsequent oxidation by *N*-fluorocollidinium tetrafluoroborate generates the selenium(IV) nucleofuge in intermediate **IV** that can be displaced to generate the 2-oxazolidinone product along with isobutylene after deprotonation by 2,4,6-collidine. Each turnover of the reaction generates one equivalent of an arylselenium(II) fluoride that can be converted to an arylselenenyl chloride by the stoichiometric amount of TIPSCl present. One thing to note is that arylselenium(II) chlorides can undergo chloroselenylation of alkenes,[15] which is not observed. This process is, however, reversible at room temperature[16] and the regenerated seleniranium ion may be irreversibly captured by the more competent nucleophile. Regardless, the fate of the selenium catalyst throughout the reaction is still unknown and is under investigation.[17]

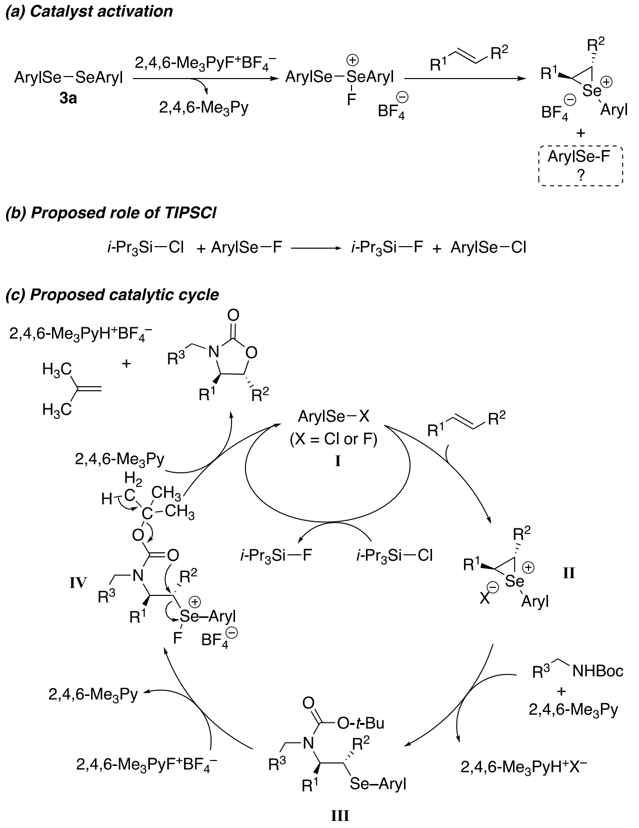


Figure 1. Catalyst activation, proposed role of TIPSCl, and proposed catalytic cycle.

In conclusion, enantioenriched 2-oxazolidinones have been generated from simple feedstock alkenes and *N*-Boc protected amines using chiral organoselenium catalysis. The transformation includes a variety of both *N*-substituents of the carbamate nucleophile and aryl-/alkyl-substituents of the alkene to afford products in modest yields with high enantioselectivities. Future efforts will be aimed toward creating a more active catalyst that allows for: (1) enantiodiscrimination of alkenes other than monosubstituted

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or *trans*-disubstituted and (2) the functionalization of unactivated alkenes that lack an aromatic substituent.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.4c02377.

> Experimental procedures, characterization data for all new compounds, copies of spectra and chromatograms, and X-ray crystallographic data for **4h** (PDF)

Accession Codes

CCDC 2366031 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.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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