Rh_2(II)-Catalyzed Intermolecular N-Aryl Aziridination of Olefins using Nonactivated N-Atom Precursors

Wrickban Mazumdar,[a†] Tianning Deng,[a†] Yuki Yoshinaga,[a] Pooja B. Patel,[a] Dana Malo,[a,b] Tala Malo,[b] Donald J. Wink[a] and Tom G. Driver[a,*]

[a] University of Illinois at Chicago, Department of Chemistry, 845 West Taylor Street, MC 111, Chicago, Illinois, USA 60607

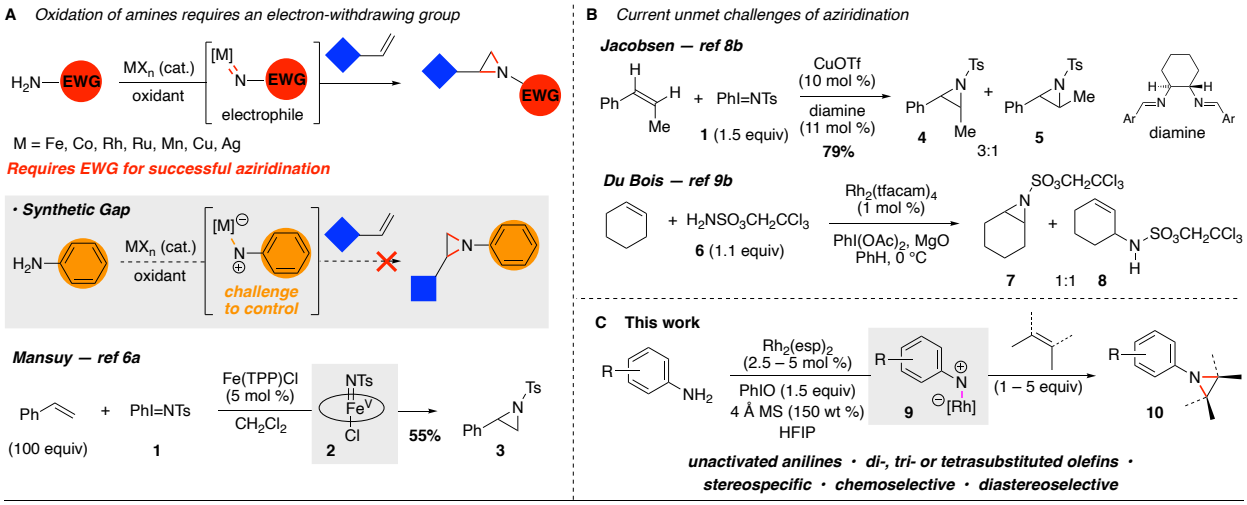
[b] Hinsdale South High School, 7401 Clarendon Hills Road, Darien, Illinois, USA 60561

[†] These authors contributed equally.

ABSTRACT. The development of the first intermolecular Rh_2(II)-catalyzed aziridination of olefins using anilines as nonactivated N-atom precursors and an iodine(III) reagent as the stoichiometric oxidant is reported. This reaction requires the transfer of an *N*-aryl nitrene fragment from the iminoiodinane intermediate to a Rh_2(II)-carboxylate catalyst; in the absence of a catalyst only diaryldiazene formation was observed. This N-aryl aziridination is general and can be successfully realized using as little as 1 equivalent of the olefin. Di-, tri- and tetrasubstituted cyclic- or acylic olefins can be employed as substrates, and a range of aniline- and heteroarylamine N-atom precursors are tolerated. The Rh_2(II)-catalyzed N-atom transfer to the olefin is stereospecific, chemo- and diastereoselective to produce the *N*-aryl aziridine as the only amination product. Because the chemistry of nonactivated *N*-aryl aziridines is underexplored, the reactivity of *N*-aryl aziridines was explored towards a range of nucleophiles to stereoselectively access privileged 1,2 stereodiads unavailable from epoxides, and removal of the *N*-2,4-dinitrophenyl group was demonstrated to show that functionalized primary amines can be constructed.

INTRODUCTION. Increasing molecular complexity through aziridination has the promise to minimize wasteful functional group manipulation inherent in traditional C–N bond forming transformations.[1] While catalysis of olefin cyclopropanation and epoxidation is well-established,[2,3] the development of catalytic methods for the aziridination of olefins has lagged behind,[4] despite the presence of aziridines in molecules that exhibit important biological activity.[5] Traditional approaches and recent advances in aziridination methods require an activated N-atom precursor, such as an iminoiodinane or an azide, with a strong *N*-electron-withdrawing group such as a sulfonyl-, carboxylate- or phosphoryl functionality (Scheme 1A).[6,7] While these activated N-atom precursors improved the efficiency of synthesis of these strained *N*-heterocycles, these aziridinations remain limited by their lack of stereospecificity (Scheme 1B).[8] Progress has been made towards the generation of iminoiodinanes in situ through the oxidation of amines, such as sulfamate ester **6**;[9,10] however, the chemoselectivity of N-atom transfer to cycloalkenes in these processes is poor and mixtures of aziridination- and allylic C–H bond amination products **7** and **8** are observed.[9b,c] The current limitations of catalytic N-atom transfer methods for intermolecular aziridination to preactivated reagents or amines with *N*-electron withdrawing groups obstructs the catalytic convergent synthesis of *N*-aryl aziridines.[11] Instead, *N*-aryl aziridines can be synthesized through substitution reaction sequences (e.g. intramolecular cyclization and *N*-arylation),[12,13] or through N-atom transfer to an olefin using an aryl azide.[14] These processes, however, are step-inefficient, require a large excess of olefin or use an energetic and unstable azide N-atom precursor. These limitations underscore the need to develop new synthetic methods to efficiently and selectively construct aziridines from olefins to fill this gap in contemporary synthetic repertoire and facilitate access to important synthetic intermediates that not only appear in the total syntheses of the mitomycins,[15] virantmycins,[16] and FR-66979,[17] but could be used in conjunction with a ring-opening event to construct essential 1,2-stereodiads

that appear in a diverse array of important biologically active compounds.[18] During our investigations into accessing nitrenoids from nonactivated anilines using an iodine(III) oxidant to construct 3*H*-indoles or benzazepinones,[19] we found that the reactivity of the in situ generated iminoiodinane was limited to intramolecular reactions. We were curious if we could overcome this limitation by transferring the *N*-aryl nitrene from iodine to a transition metal to enable intermolecular N-atom transfer reactions with nonactivated amines such as anilines. Herein, we disclose a general and robust method for *N*-aryl aziridination where Rh_2(II) complexes effectively catalyze the intermolecular N-atom transfer of nonactivated anilines to olefins in a stereospecific, chemoselective and diastereoselective process.

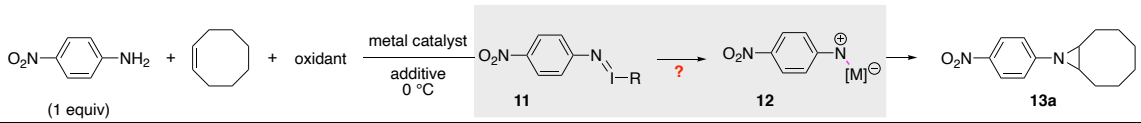


Scheme 1. A. Prior art in N-atom transfer to olefins to construct aziridines; B. Current aziridination processes lack stereospecificity and chemoselectivity in N-atom transfer to olefins; C. The development of stereospecific, chemoselective and diastereoselective Rh_2(II)-catalyzed aziridination using nonactivated anilines as the N-atom precursor.

RESULTS AND DISCUSSION. To determine if anilines could be used as the N-atom source in intermolecular metal-catalyzed reactions, the aziridination of cyclooctene using 4-nitroaniline was investigated (Table 1). Our optimization study started by investigating $PhI(O_2CCF_3)_2$ (PIFA) as the oxidant in trifluoroethanol (TFE) because of its success to promote the oxidative cyclization-migration reactions of *ortho*-alkenyl anilines. In the absence of a transition metal catalyst, no cyclooctene aziridine was observed; only diaryldiazene was obtained (entry 1). A screen of common N-atom transfer catalysts revealed that copper- and rhodium(II) complexes catalyzed the formation of *N*-aryl aziridine **13a** when MgO was added to consume the trifluoroacetic acid by-product (entries 2 – 8). While only modest yields of **13a** were observed using copper salts, irrespective of the oxidation state of copper or the counterion (entries 2 – 5), Rh_2(II) carboxylates were found to be efficient catalysts (entries 6 – 8). Despite our efforts, Rh_2(II) complexes, *N*-aryl aziridine **13a** could be obtained in only 78% using PIFA as the oxidant. We anticipated that the yield of aziridination might be limited by a trifluoroacetic acid-mediated process before it was consumed by MgO. We posited that this process might be circumvented using an iodine(III) oxidant that produced a neutral by-product. Towards this end, we investigated using iodosobenzene (PhIO) as the stoichiometric oxidant because the by-product is water, which could be removed from the reaction mixture using molecular sieves if it proved detrimental to the reaction outcome. Using 1.5 equiv of PhIO proved to be beneficial, providing aziridine **13a** with an improved yield using half the loading of $Rh_2(esp)_2$ (5 mol %) when 150 mol % of 4 Å molecular sieves were added (entry 9). Our next investigations focused on reducing the excess amount of the olefin (entries 10 – 12). To our delight, we found that a nearly quantitative yield of *N*-aryl aziridine **13a** could be obtained using only 1 equivalent of cyclooctene if the solvent was switched to hexafluoroisopropanol (HFIP) and the reaction time was decreased to 90 minutes. Because HFIP could

potentially limit the solubility of the olefin or aniline component, we investigated the use of co-solvents and found that aziridination smoothly occurred using a 1:1 mixture of CH_2Cl_2 and HFIP without adversely affecting the yield of **13a** (entry 13).

Table 1. Optimization of aziridination of cyclooctene using 4-nitroaniline as the N-atom source.



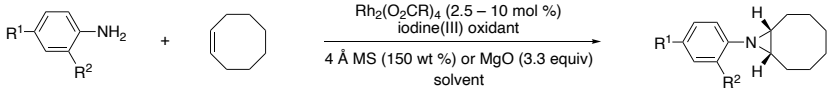
entry	catalyst (mol %)	cyclooctene (equiv)	oxidant (equiv)[a]	additive (equiv)	solvent (M)	time (h)	yield, %[b]
1	...	20	PIFA (2.0)	...	TFE (0.2)	3.5	0
2	CuI (10)	20	PIFA (2.0)	MgO (3.3)	TFE (0.2)	3.5	21
3	CuBr (10)	20	PIFA (2.0)	MgO (3.3)	TFE (0.2)	3.5	42
4	$(CuOTf)_2$•PhH (10)	20	PIFA (2.0)	MgO (3.3)	TFE (0.2)	3.5	40
5	$Cu(OTf)_2$ (10)	20	PIFA (2.0)	MgO (3.3)	TFE (0.2)	3.5	42
6	$Rh_2(OAc)_4$ (10)	20	PIFA (2.0)	MgO (3.3)	TFE (0.2)	3.5	75
7	$Rh_2(O_2CC_3F_7)_4$ (10)	20	PIFA (2.0)	MgO (3.3)	TFE (0.2)	3.5	78
8	$Rh_2(esp)_2$ (10)	20	PIFA (2.0)	MgO (3.3)	TFE (0.2)	3.5	40
9	$Rh_2(esp)_2$ (5)	6	PhIO (1.5)	4 Å MS (1.5)	TFE (0.1)	1.5	85
10	$Rh_2(esp)_2$ (5)	10	PhIO (1.5)	4 Å MS (1.5)	HFIP (0.1)	1.5	80
11	$Rh_2(esp)_2$ (5)	2	PhIO (1.5)	4 Å MS (1.5)	HFIP (0.1)	1.5	96
12	$Rh_2(esp)_2$ (5)	1	PhIO (1.5)	4 Å MS (1.5)	HFIP (0.1)	1.5	97[c]
13	$Rh_2(esp)_2$ (5)	1	PhIO (1.5)	4 Å MS (1.5)	HFIP/CH_2Cl_2 (0.1)	1.5	90

[a] Oxidant added by syringe pump over 1 h. [b] As determined using ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard. [c] Isolated yield after neutral alumina chromatography.

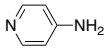
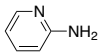
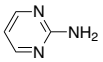
After identifying the optimal conditions for using 4-nitroaniline as the N-atom source, we examined the scope of the aziridination reaction with regards to the aniline (Table 2). We found that *N*-aryl aziridines could be constructed from a range of anilines although slight modification of the reaction conditions was required. For anilines bearing a nitro-, cyano- or acetyl-*para*-substituent, the combination $Rh_2(esp)_2$ and iodosobenzene proved to be the optimal combination to afford aziridines **13a** – **13c**, although CH_2Cl_2 was required as a co-solvent for dissolution of the latter two anilines (entries 1 – 3). Using these conditions with 4-iodo-, 4-bromoaniline produced only a diaryldiazene by-product (entries 4 and 5). For these two anilines, *N*-aryl aziridine formation could be achieved using PIFA as the oxidant and rhodium perflourobutyrate as the N-atom transfer catalyst and MgO as the additive (entries 4 and 5). These conditions proved ideal to enable the formation of biphenyl aziridine **13f** in 91% (entry 6). Unfortunately, the Rh_2(II)-catalyzed aziridination reaction does not tolerate electron-donating alkoxy substituents: submission of 4-methyoxyaniline to reaction conditions (irrespective of the Rh_2(II) carboxylate catalyst or iodine(III) oxidant) resulted in only decomposition (entry 7). The addition of an additional nitro-group, however, restored reactivity to enable the formation of 4-nitro-2-methyoxyphenyl aziridine **13h** using the combination of $Rh_2(esp)_2$, PhIO as oxidant, and a 1:1 mixture of HFIP and CH_2Cl_2 (entry 8). 2,4-Dinitroaniline was also investigated as the N-atom source because the 2,4-DNP could potentially be removed from the product (*vide infra*).[20] While this aniline did require additional optimization because of its poor solubility, we found that 2,4-dinitrophenyl aziridine **13i** could be obtained in 91% using 10 mol % of $Rh_2(OAc)_4$, PIFA as the oxidant, MgO as an additive if a 1:1 mixture of TFE and ethyl acetate were used as the reaction solvent (entry 9). The inclusion of ethyl acetate was critical to the success of this N-atom transfer reaction because it solubilized 2,4-dinitroaniline. Heterocyclic amines also proved to be competent

N-atom precursors: aminopyridyl aziridines **13j** and **13k** could be synthesized in nearly quantitative yield using only 2.5 mol % of $Rh_2(esp)_2$, PhIO as oxidant (entries 10 and 11); and even 2-aminopyrimidine was found to be a competent N-atom precursor requiring only 1 equivalent of cyclooctene to afford **13l** in 77% although a slightly higher reaction temperature was required (entry 12). For every aniline examined, selection of a co-solvent that dissolved the aniline to pair with the fluorinated solvent (TFE or HFIP) was critical for the success of the N-atom transfer reaction.

Table 2. Exploring the effect of changing the identity of the aniline on the aziridination.



(1 equiv) (1 – x equiv) **13**

entry	aniline R^1	aniline R^2	cyclooctene (equiv)	$Rh_2(O_2CR)_4$ (mol %)	oxidant (equiv)	additive (equiv)	solvent (M)	time (h)	yield, %[b]
1	O_2N	H	1	$Rh_2(esp)_2$ (5)	PhIO (1.5)	4 Å MS (150 wt %)	HFIP (0.1)	1.5	**13a**, 97
2	NC	H	1	$Rh_2(esp)_2$ (5)	PhIO (1.5)	4 Å MS (150 wt %)	HFIP/CH_2Cl_2 (0.1)	1.5	**13b**, 92
3	Ac	H	1	$Rh_2(esp)_2$ (5)	PhIO (1.5)	4 Å MS (150 wt %)	HFIP/CH_2Cl_2 (0.1)	1.5	**13c**, 53
4	I	H	12	$Rh_2(O_2CC_3F_7)_4$ (10)	PIFA (2.0)	MgO (3.3)	TFE (0.2)	3	**13d**, 72
5	Br	H	12	$Rh_2(O_2CC_3F_7)_4$ (10)	PIFA (2.0)	MgO (3.3)	TFE (0.2)	3	**13e**, 42
6	Ph	H	2	$Rh_2(O_2CC_3F_7)_4$ (2.5)	PIFA (2.0)	MgO (3.3)	TFE (0.2)	3	**13f**, 91
7	MeO	H	1	$Rh_2(esp)_2$ (5)	PhIO (1.5)	4 Å MS (150 wt %)	HFIP/CH_2Cl_2 (0.1)	1.5	**13g**, dec
8	O_2N	MeO	10	$Rh_2(esp)_2$ (10)	PhIO (1.5)	4 Å MS (150 wt %)	HFIP (0.1)	1.5	**13h**, 50
9	O_2N	O_2N	2	$Rh_2(OAc)_4$ (10)	PIFA (1.5)	MgO (3.3)	TFE/AcOEt (0.1)	1	**13i**, 91
10			5	$Rh_2(esp)_2$ (2.5)	PhIO (1.5)	4 Å MS (150 wt %)	HFIP/MeCN (0.1)	1	**13j**, 98
11			1	$Rh_2(esp)_2$ (2.5)	PhIO (1.5)	4 Å MS (150 wt %)	HFIP (0.1)	1	**13k**, 99
12			1	$Rh_2(esp)_2$ (2.5)	PhIO (1.5)	4 Å MS (150 wt %)	HFIP (0.1)	1	**13l**, 77[c]

[a] Oxidant added by syringe pump over 1 h. [b] Isolated yield after neutral alumina chromatography. [c] Reaction temperature was 40 °C.

Using 4-nitroaniline as the N-atom precursor, a series of cycloalkenes and acyclic olefins were investigated to interrogate the scope of the reaction (Scheme 2). Irrespective of the size of the cycloalkene, *N*-aryl aziridines **15a** – **15c** were synthesized as the only N-atom transfer products using 5 mol % of $Rh_2(esp)_2$ and PhIO as the stoichiometric oxidant although 1.5 equiv of cyclohexene or cyclopentene were required to achieve the best yield. To our delight, our aziridination was not limited to disubstituted olefins: 1-methylcyclohexene and 1-alkylcyclooctenes were successfully converted to aziridines **15d** – **15f** in high yields; even tetrasubstituted olefins, such as 1,2-dimethylcyclooctene, could be aziridinated to afford **15g** in nearly quantitative yield. Dienes proved to be competent substrates: aziridination of 1,3-cyclooctadiene occurred efficiently to afford only **15h**. Our $Rh_2(esp)_2$-catalyzed aziridination was also stereoselective. A single diastereomer of aziridine **15i** was formed from 3-methylcyclooctene. Diastereoselective N-atom transfer to 3-methylcyclohexenes was also observed to afford **15j** and **15k**, albeit the former in a modest yield. Despite the presence of the weakened allylic methine C–H bond in these 3-substituted cycloalkenes, no allylic C–H bond amination was observed. Aziridination of norbornene also smoothly occurred to afford aziridine **15k** as the only diastereomer.

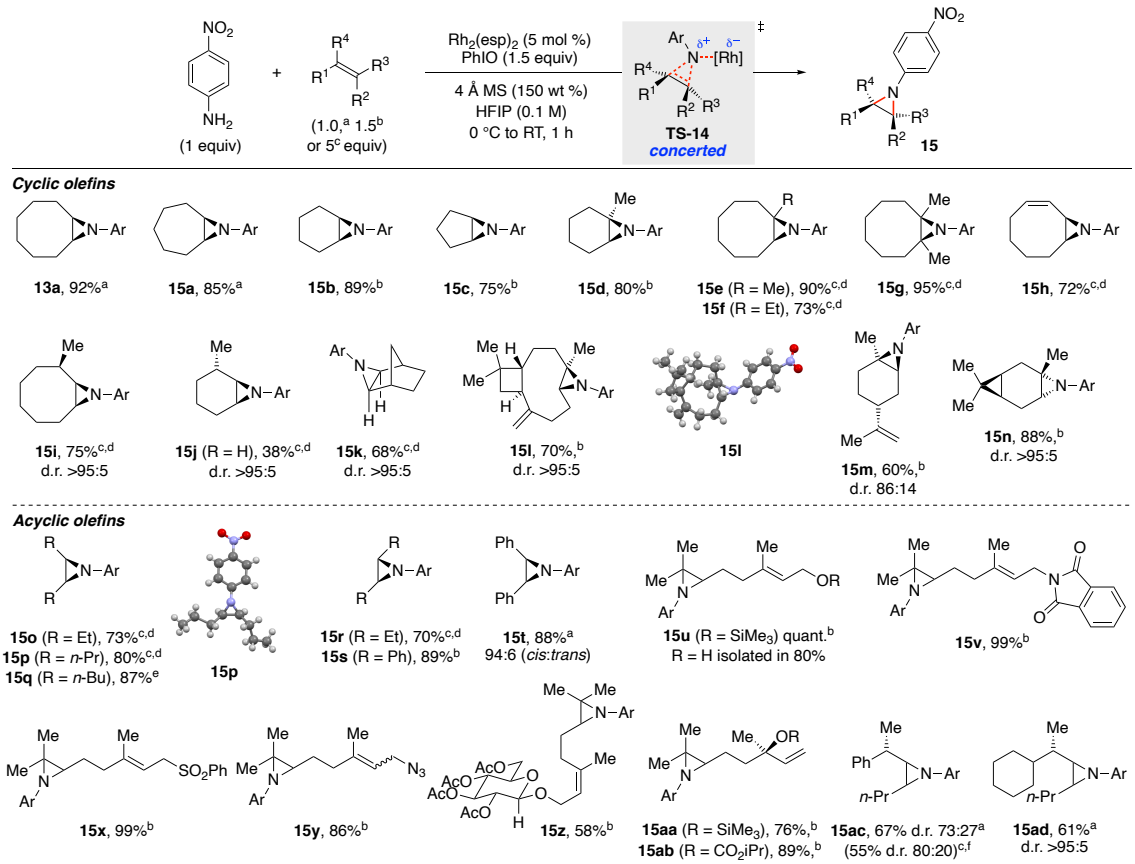
A series of terpene natural products were examined as substrates to determine if our Rh_2(II)-catalyzed aziridination could be used to functionalize selectively complex substrates with multiple potential sites of reaction. Submission of (–)-β-caryophyllene to reaction conditions resulted in chemoselective transfer of the *N*-aryl nitrene to the trisubstituted olefin moiety to produce aziridine **15l** as the only product as a single diastereomer. The structure of **15l** was confirmed by X-ray crystallography.[21] Chemoselective aziridination of (+)-limonene was also observed to produce only aziridine **15m** as an 86:14 mixture of diastereomers. Improved diastereoselectivity was observed when the terpene bore a sterically larger homoallylic substituent: Rh_2(II)-catalyzed aziridination of (+)-3-carene produced **15n** as a single diastereomer in high yield. Together these results illustrate that our aziridination enables the functionalization of complex, chiral natural products in a chemo- and diastereoselective fashion.

These successes spurred us to examine Rh_2(II)-catalyzed aziridination of acyclic olefins using 4-nitroanilines as the N-atom source and iodosobenzene as the stoichiometric oxidant. While monosubstituted olefins remain incompatible with our method, *N*-aryl nitrene transfer to acyclic *Z*-olefins was stereospecific providing only *cis*-substituted aziridines **15o** – **15q** in high yields. The stereochemistry of 1-aryl-2,3-dipropylaziridine **15p** was confirmed by X-ray crystallography.[22] Aziridination of *E*-3-hexene was also stereospecific to access only aziridine **15r**. We interpret the stereospecificity of the aziridination of *E*- and *Z*-olefins to indicate that cyclization occurs via transition state **TS-14** where both C–N bonds are formed in a concerted fashion from attack of the olefin onto the electrophilic rhodium *N*-aryl nitrene.[23] To test the robustness of the stereospecificity our process, *E*- and *Z*-stilbene were investigated as substrates. *E*-Stilbene reacted smoothly to afford aziridine **15s** in 89%, and submission of *Z*-stilbene (a 131:1 mixture of isomers) to reaction conditions produced aziridine **15t** in 88% yield as a 94:6 mixture of *cis*- and *trans*-isomers. The high stereospecificity observed indicates that even with substrates that could stabilize a charged- or radical intermediate formed in a stepwise mechanism, that a concerted mechanism is still preferred.

The functional group tolerance of our Rh_2(II)-catalyzed aziridination was tested using geraniol- and (–)-linalool derivatives. While geraniol was not tolerated, we found that geraniol trimethylsilyl ether was converted to aziridine **15u** in quantitative yield, and the silyl-group was cleaved during alumina chromatography purification of **15u** to enable facile access to the alcohol. Together with the chemoselectivity observed with (–)-β-caryophyllene, the isolation of aziridine **15u** as the only product from geraniol trimethylsilyl ether suggests that the chemoselectivity of our Rh_2(II)-catalyzed is electronically controlled with N-atom transfer occurring to the more electron-rich olefin. Changing the identity of allylic ether substituent in geraniol did not change the chemoselectivity of the process and illustrated the functional group tolerance our reaction. Our Rh_2(II)-catalyzed N-atom reaction occurred smoothly to geraniol-derivatives containing a phthalimide-, a sulfone-, or even an azide substituent to produce aziridines **15v** – **15y** in high yields. Geranyl β-pentacylglucoside was also tolerated as a substrate to afford aziridine **15z** as a mixture of diastereomers. In addition to geranyl derivatives, (–)-linalool was also used as a scaffold to examine the broadness of our reaction. We found that aziridines **15aa** and **15ab** bearing a tertiary silyl ether or ester could be synthesized efficiently as a 1:1 mixture of diastereomers.

While no diastereoselectivity was observed using linalool derivatives, acyclic olefins bearing allylic stereocenters were investigated in our N-atom transfer reaction to determine if allylic strain could influence the reaction outcome. In comparison to the high diastereoselectivity exhibited by chiral cycloalkenes, N-atom transfer to a chiral, racemic acyclic olefin bearing an allylic phenyl stereocenter proved to be less stereoselective providing aziridine **15ac** in 67% as a 73:27 mixture of diastereomers. The stereoselectivity could be improved to 81:19 if the reaction temperature was maintained at 0 °C. Changing the identity of the allylic substituent from phenyl to cyclohexane dramatically improved the diastereoselectivity to afford aziridine **15ad** as a >95:5 mixture of diastereomers. Similar to the site-selectivity observed with cyclic olefins, no allylic C–H bond amination was obtained even when a weak tertiary benzylic C–H bond was

present. Together these results illustrate that our Rh_2-catalyzed N-atom transfer to olefins is stereospecific and chemo- and diastereoselective.

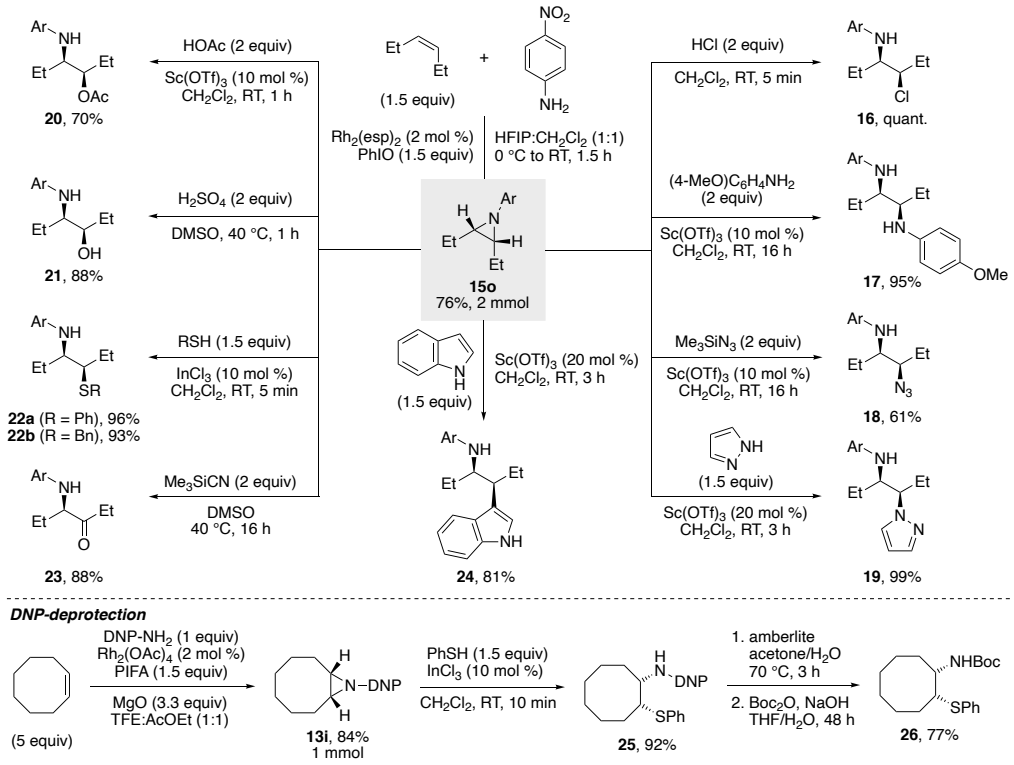


d 1:1 HFIP:CH_2Cl_2; e 2 equiv of olefin used; f Reaction temperature maintained at 0 °C

Scheme 2. Scope and limitations of aziridination of olefins using 4-nitroaniline as the N-atom source.

In contrast to ring-opening reactions of epoxides, the reactivity of aziridines, particularly *N*-aryl aziridines, is underexplored because of the challenges associated with constructing them.[4c,18a,b,24] To showcase the power of our aziridination method, we examined the reactivity of aziridine **15o** towards a variety of nucleophiles. For this study, it was synthesized in 76% on a 2 mmol scale using only 2 mol % of $Rh_2(esp)_2$ to highlight the scalable nature of our reaction. Initially, we focused our attention on examining nucleophiles that would afford products that cannot be accessed from epoxides. Towards that end, we exposed aziridine **15o** to HCl in CH_2Cl_2 produced 1,2-chloroamine **16** in quantitative yield. We also examined the Lewis acid-catalyzed addition of nitrogen nucleophiles to afford 1,2-diamines, a privileged structural motif.[18,25] While $B(C_6F_5)_3$ and titanium binolate Lewis acids proved to be impotent,[26] we found 10 mol % of $Sc(OTf)_3$ in CH_2Cl_2 to effectively catalyze the addition of 4-methoxyaniline, Me_3SiN_3 or 1,2-pyrazole to produce 1,2-diamine **17** in 95%, azide **18** in 61% or **19** in 70% as single diastereomers.[27] Oxygen nucleophiles were also well suited for ring-opening to produce 1,2-aminoacetate **20** in 70% or 1,2-aminoalcohol in 85%. Mercaptans required 10 mol % of $InCl_3$ to achieve ring-opening to construct vicinal 1,2-aminothiols **22a** and **22b** in 96% and 93% as single diastereomers.[28] In the absence of a nucleophile and Lewis acid, oxidative ring-opening of aziridine **15o** was observed to provide α-amino ethyl ketone **23** in 88%.[29] While this reaction is well established for activated aziridines,[9c,30] it has not been reported for nonactivated aziridines. Carbon–carbon bonds could also be constructed diastereoselectively using indole as a nucleophile to produce **24** in 81%. We also examined dearylation of *N*-DNP cyclooctene aziridine **13i**. For this investigation, aziridine **13i** was prepared in 84% yield on a 1 mmol scale. Ring-opening using

thiophenol and 10 mol % of $InCl_3$ produced *syn*-aminothioether **25** in 92%. Dearylation was achieved smoothly by exposing **25** to amberlite to produce the primary amine, which was converted to the Boc-carbamate to ease isolation to afford **26** in 77%. Together, these nucleophilic ring-opening- and dearylation reactions underscore the synthetic potential embedded in *N*-aryl aziridines to enable diastereoselective access to an extensive range of 1,2-functionalized amines.



Scheme 3. Functionalization reactions of aziridine **13i** and **15o**.

CONCLUSION.

A general method for the intermolecular aziridination of di-, tri- or tetrasubstituted cyclic or acylic olefins with anilines has been developed using a Rh_2(II)-catalyst and an iodine(III) reagent as the stoichiometric oxidant. This discovery addresses an unmet need to broaden two-component coupling aziridination technology beyond activated N-atom precursors or electron-poor amines while avoiding competitive C–H insertion pathways. The Rh_2(II)-catalyzed N-atom transfer described above is stereospecific, chemo- and diastereoselective, gives *N*-aryl aziridines as the only amination products and can be realized without using excess reagents. Electron-deficient or electron-neutral anilines and heteroarylamines can be employed as N-atom precursors and respond to oxidant, Rh_2(II)-carboxylate catalyst, and reaction medium tuning to account for electronic trends and solubility differences. The reactivity of the nonactivated N-aryl aziridine products of the Rh_2(II)-catalyzed N-atom transfer process has been assessed to provide an understanding of the reactivity patterns of these uncommon, strained rings. Treatment with a variety of nucleophiles results in the diastereoselective formation of a range of 1,2-functionalized secondary aryl amines (including 1,2 diamines, 1,2-thioamines, 1,2-aminoacetates, and α-aminoketones), many of which are inaccessible from the related ring-opening of epoxides. To further underscore the synthetic utility of the process, we demonstrated that the use of 2,4-dinitroaniline as an N-atom precursor enables synthesis of primary amines through dearylation of the ring-opened product. Together our results illustrate that the Rh_2(II)-catalyzed intermolecular aziridination of olefins using simple anilines as the N-atom source facilitates access to a

broad range of functionalized secondary amines that are challenging to construct using existing synthetic technology.

METHODS.

9-(4-Nitrophenyl)-9-azabicyclo[6.1.0]nonane 13a. To a 10 mL round bottom flask equipped with a magnetic stir bar was added 27.6 mg of 4-nitroaniline (0.2 mmol, 1.0 equiv), 7.6 mg of $Rh_2(esp)_2$ (0.01 mmol, 0.05 equiv), 41.4 mg of 4 Å MS (150 wt %) and 0.026 mL of *cis*-cyclooctene (0.2 mmol, 1.0 equiv). The resulting mixture was cooled to 0 °C under argon, and a solution of 66.0 mg of PhIO (0.3 mmol, 1.5 equiv) in 2 mL of HFIP was added dropwise over an hour. After an additional 30 min, analysis of the reaction progress using thin layer chromatography indicated that the reaction was complete. The reaction mixture was concentrated *in vacuo*, and the resulting residue was purified by MPLC using a neutral alumina column (20:1 hexanes:EtOAc) to produce the product as a light yellow solid (47.9 mg, 97%). The spectra data matched that reported by Cenini and co-workers:[14d] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 2.32 (m, 2H), 2.22 (m, 2H), 1.66 – 1.69 (m, 2H), 1.50 – 1.66 (m, 2H), 1.42 – 1.50 (m, 6H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 161.8 (C), 142.2 (C), 125.2 (CH), 120.2 (CH), 44.3 (CH), 27.0 (CH_2), 26.8 (CH_2), 26.4 (CH_2); ATR-FTIR (thin film): 2924, 2858, 1589, 1499, 1328, 1226, 1105, 872 cm^{-1}.

Data availability. The data supporting the results of this study are available within this pare and its Supplementary Information. Crystallographic data for aziridines **15l** and **15p** have been deposited at Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC 2083953 and 2083825. This data can be obtained free of charge from the CCDC (http://www.ccdc.cam.ac.uk/data_request/cif)

Acknowledgments

We are grateful to the National Science Foundation (CHE-1564959) and the National Institutes of Health, NIGMS (GM138388) for their generous financial support. We thank Mr. Furong Sun (UIUC) for high resolution mass spectrometry data.

Author contributions

W. Mazumdar, T. Deng, Y. Yoshinaga, and T. Driver conceived and designed the experiments. W. Mazumdar, T. Deng, Y. Yoshinaga, P. Patel, D. Malo, and T. Malo performed experiments. D. Wink performed the X-Ray crystallography. T. Driver wrote the manuscript.

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