Article

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Stereoselective Syntheses of Highly Functionalized Imidazolidines and Oxazolidines via Ring-Opening-Cyclization of Activated Aziridines and Epoxides with Amines and Aldehydes

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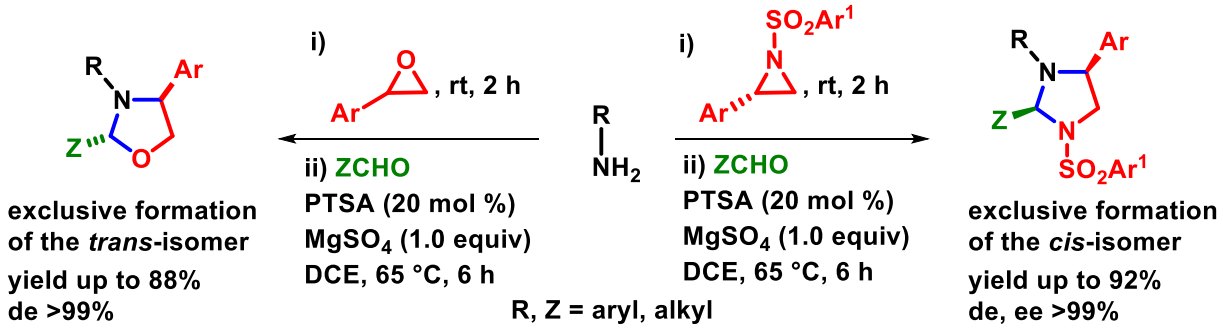
Abstract



A mild one-pot stereospecific synthetic route to highly functionalized imidazolidines and oxazolidines via S_N2-type ring-opening of the corresponding activated aziridines and epoxides with amines followed by PTSA catalyzed intramolecular cyclization with aldehydes has been developed. The methodology tolerates a variety of functional groups and furnishes the desired products in high yields (up to 92%) with excellent stereoselectivities (de, ee >99%). Interestingly, imidazolidines were formed as the *cis*-isomers whereas oxazolidines were produced as *trans*-isomers exclusively.

Introduction

Imidazolidine and Oxazolidine frameworks are widely found in a number of bioactive compounds, natural products and pharmaceuticals (Figure 1).[1,2] For example, chaetominine inhibits the growth of K562 human leukemia and SW1116 colon cancer cells (IC_{50}s = 20 and 28 nM, respectively).[1b] Alchorneine is known to work as a potential spasmolytic agent in dogs,[1c] whereas, cyanogramide effectively reverses the adriamycin induced resistance of K562/A02 and

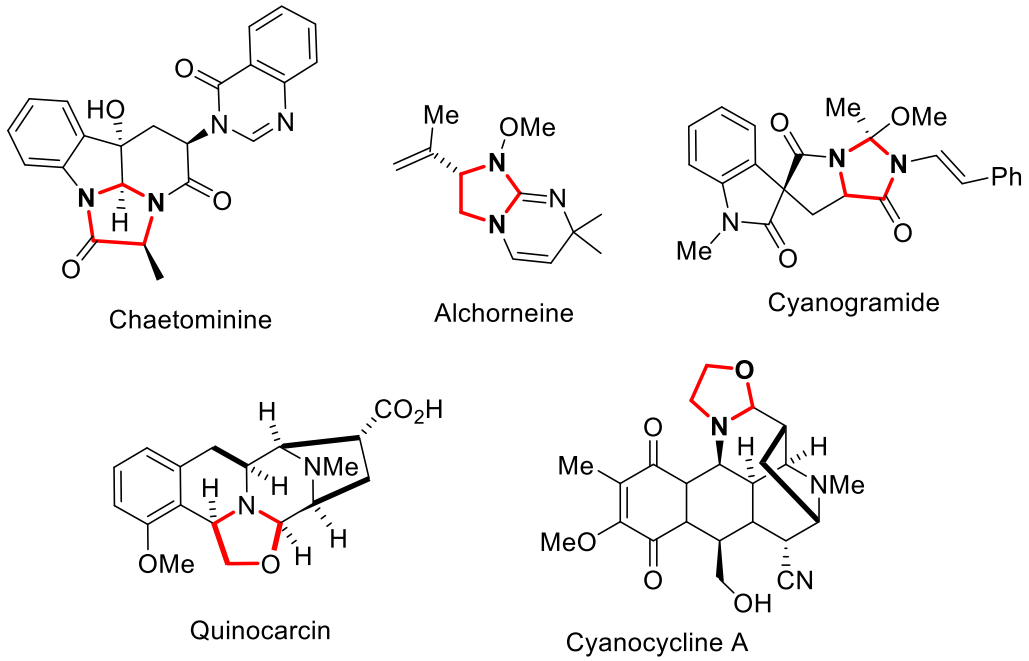


Figure 1. Biologically Active Imidazolidine and Oxazolidine scaffolds

MCF-7/Adr cells.[1e] Quinocarcin exhibits potent cytotoxic activity against P388 leukemia in vivo and good antimicrobial activity against both Gram-negative and Gram-positive bacteria,[2a] and cyanocycline A shows broad spectrum antimicrobial and antitumor activity.[2c] These structural motifs are used as versatile building blocks in bio-organic chemistry as well as, synthetic reagents, namely, auxiliaries, catalysts etc.[3,4] Moreover imidazolidines are easily transformed into imidazoles which are core structures in many significant biomolecules.[5]

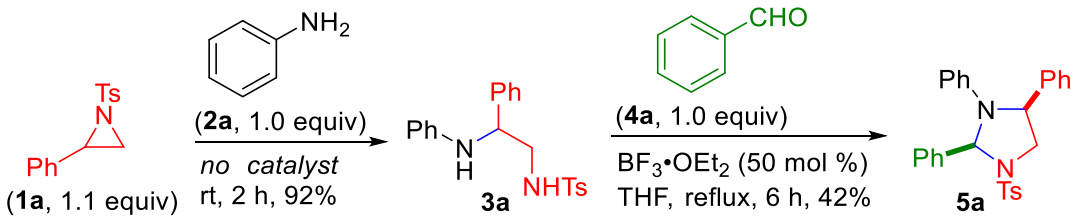
The general synthetic strategy for the preparation of imidazolidine and oxazolidine derivatives involves condensation of aldehydes, ketones or oxo-compounds with 1,2-diamines and 1,2-amino alcohols, respectively.[6,4b] Other synthetic methodologies for these two structural scaffolds include (3+2) formal cycloaddition,[7] 1,3-dipolar azomethine ylide-imine (AYI) cycloaddition,[8] tandem nucleophilic addition-cycloaddition,[9] C(sp^3)-H functionalization,[10] aza-Wacker reaction etc.[11] Interestingly, in recent years, the cycloaddition reaction of activated aziridines with different reacting partners, namely, cyclic N-sulfonyl imines,[7a] oxime ethers,[7b] glycine esters,[7c] aldehydes[7g,h] and N-alkylanilines[10a] etc. has been studied for the production of imidazolidines and oxazolidines. However, many of them apply environmentally hazardous metal salts to catalyze the process along with costly ligands. Considering the unique structural features and

biological activities of these two moieties, despite the advancement in the above mentioned areas,[7-11] a metal-free cost-effective synthetic strategy leading to the formation of highly functionalized diastereo- and enantiopure imidazolidines and oxazolidines from easily accessible starting materials is still highly desirable. Aziridines[12] and epoxides[13] are valuable building blocks in organic synthesis and nucleophilic ring-opening products obtained from these two small rings are often employed as important intermediates for the synthesis of bioactive nitrogen- and oxygen-containing heterocycles. Earlier, we reported the synthesis of imidazolines via $Cu(OTf)_2$-mediated [3+2] cycloaddition reaction of activated aziridines with nitriles.[14] However, the non-racemic imidazolines were obtained with reduced enantioselectivity. In continuation of our investigation on S_N2-type ring-opening transformations of aziridines and epoxides with amine nucleophiles,[15] we have developed a simple strategy for the syntheses of diastereo- and enantiopure highly substituted imidazolidines and oxazolidines via stereoselective S_N2-type ring-opening of aziridines and epoxides, respectively, with various amine nucleophiles followed by condensation with aldehydes under one-pot conditions. Herein, we wish to report our results in detail.

Results and Discussion

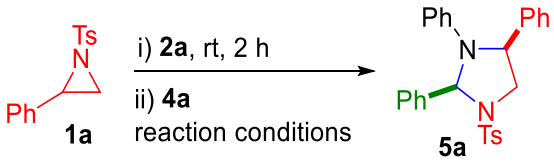
Our study began with the reaction of activated aziridine (**1a**, 1.1 equiv) with aniline (**2a**, 1.0 equiv) under neat and catalyst free condition. The reaction went efficiently via S_N2-type regioselective ring opening of **1a** by amine producing the ring-opening product **3a** in 92% yield in 2 h.[15b] **3a** was then reacted with benzaldehyde (**4a**, 1.0 equiv) in the presence of 50 mol % of $BF_3.OEt_2$ catalyst in refluxing THF for 6 h to provide the desired imidazolidine derivative (**5a**) as a single diastereomer in 42% yield (Scheme 1). Spectroscopic data confirmed the structure of **3a** and **5a** which was further supported by single crystal X-ray analysis.[16] The diastereoselective formation of **5a** raised our interest to increase the efficiency of our two-step protocol in terms of yield and pot-economy. We screened different Lewis acids, additives, and solvents to increase the yield of the cyclization step in a one-pot protocol. When the ring-opening product was reacted with **4a** in the presence of $BF_3{\cdot}OEt_2$ (100 mol %) in refluxing THF in a one-pot fashion, the imidazolidine derivative **5a** was obtained in 48% yield (entry 2, Table 1). Addition of 1.0 equiv of $MgSO_4$ keeping the conditions intact did not increase the yield much (entry 3).

Scheme 1. Ring-Opening-Cyclization of 2-Phenyl-N-tosylaziridine (1a) with Aniline (2a) and benzaldehyde (4a)



When $Cu(OTf)_2$ was used as the Lewis acid in the cyclization step, the yield of **5a** eroded further (entry 4). However, use of Lewis acids namely, $FeCl_3$ and $Sc(OTf)_3$, in refluxing THF, improved the yield to some extent (entry 5,6). Since the yield of **5a** was found to increase slightly using Lewis acid catalysts, couple of Brønsted acids namely, benzoic acid and PTSA, were examined in THF and DCE, respectively (entry 7–9). Improved yield was observed when PTSA (50 mol %) was used as the acid catalyst in DCE solvent (entry 9). Using PTSA (50 mol %) and $MgSO_4$ as the additive, **5a** was obtained with the maximum yield (entry 10).[12h] The best result was obtained using 20 mol % of PTSA and 100 mol % of $MgSO_4$ in DCE at 65 °C to afford **5a** in overall 84% yield (entry 11). All the results are described in Table 1.

Table 1. Optimization Studies for One-Pot Synthesis of Imidazolidine (5a)[a]



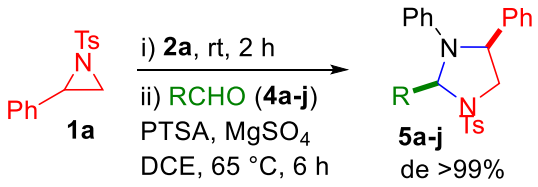
entry	reaction conditions[b]	**5a** (%)[c]
1	$BF_3{\cdot}OEt_2$ (50 mol %), THF, reflux, 10 h	45
2	$BF_3{\cdot}OEt_2$ (100 mol %), THF, reflux, 10 h	48
3	$BF_3{\cdot}OEt_2$ (100 mol %), $MgSO_4$ (100 mol %), THF, reflux, 8 h	54
4	$Cu(OTf)_2$ (50 mol %), THF, reflux, 10 h	35
5	$FeCl_3$ (50 mol %), THF, reflux, 8 h	42
6	$Sc(OTf)_3$ (50 mol %), THF, reflux, 8 h	55
7	$PhCO_2H$ (100 mol %), THF, reflux, 6 h	62

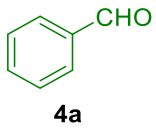
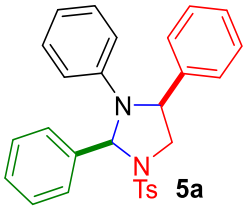
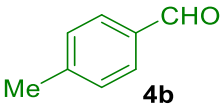
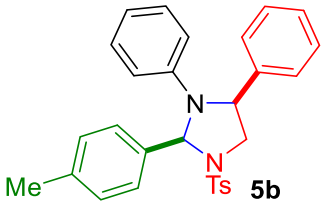
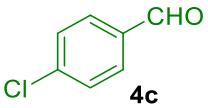
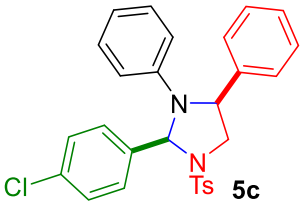
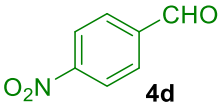
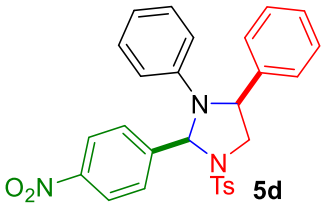
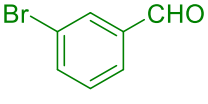
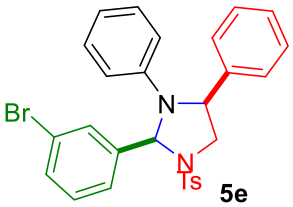
8	PTSA (50 mol %), THF, reflux, 6 h	69
9	PTSA (50 mol %), DCE, 65 °C, 6 h	75
10	PTSA (50 mol %), $MgSO_4$ (100 mol %), DCE, 65 °C, 6 h	86
11	PTSA (20 mol %), $MgSO_4$ (100 mol %), DCE, 65 °C, 6 h	84
12	PTSA (20 mol %), $MgSO_4$ (100 mol %), toluene, 65 °C, 8 h	72

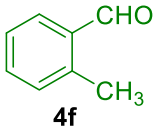
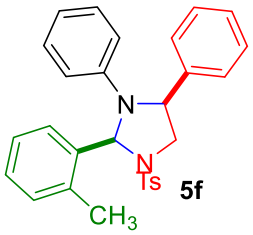
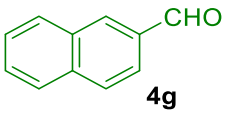
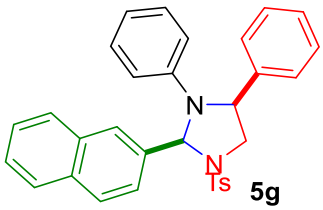
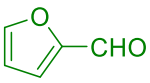
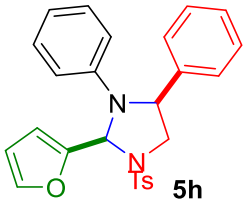
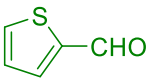
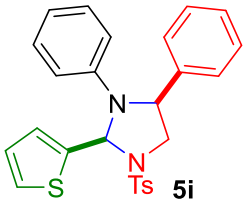
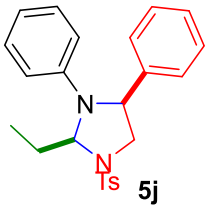
[a]Unless otherwise mentioned, 0.55 mmol of **1a**, 0.50 mmol of **2a**, 0.50 mmol of **4a** were reacted. [b]Reaction conditions were screened for the cyclization step only. [c]Yield of the isolated product.

The generalization of the strategy was made by the reaction of a variety of aldehydes **4a–h** with the ring-opening product **3a** under optimized conditions (Table 2). Aldehydes with electron donating group (−CH_3) and withdrawing groups (−Cl and –NO_2) did not affect the reaction producing imidazolidines **5b**−**d** in 78−88% yields as single diastereomers (entries 2−4). To evaluate the steric effect on the course of cyclization of the ring-opening product with aldehydes, we carried out the one-pot cyclization with *m*-bromobenzaldehyde (**4e**) and *o*-tolualdehyde (**4f**). The corresponding imidazolidine derivatives **5e**,**f** were isolated from the reaction mixture in high yields as single diastereomers (entries 5,6). When **3a** was reacted with 2-naphthaldehyde (**4g**) in one pot fashion, the corresponding product **5g** was obtained in 85% yield with excellent de (entry 7). Next, we explored hetaryl aldehydes under the optimized conditions. When **1a** was treated with **2a** in neat condition followed by addition of hetaryl aldehydes (**4h**,**i**) in presence of catalytic amount of PTSA and equimolar amount of $MgSO_4$ in DCE at 65 °C, the corresponding imidazolidine derivatives (**5h,i**) were obtained in high yields with excellent diastereoselectivities (entries 8,9). To evaluate the prospect of an alkyl aldehyde under similar reaction conditions, next, the ring-opening cyclization reaction was performed with propanal (**4j**), and to our great pleasure, the desired product **5j** was obtained in 80% yield as a single diastereomer (entry 10). All the results are summarized in Table 2.

Table 2. One-Pot Stepwise Synthesis of Imidazolidines (5a–j)[a]



entry	aldehyde (**4**)	imidazolidine (**5**)	yield (%)[b]	dr[c]
1	 **4a**	 **5a**	84	>99:1
2	 **4b**	 **5b**	86	>99:1
3	 **4c**	 **5c**	78	>99:1
4	 **4d**	 **5d**	88	>99:1
5	 **4e**	 **5e**	76	>99:1

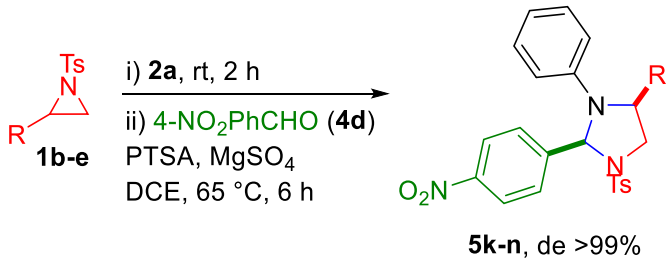
6	 4f	 5f	70	>99:1
7	 4g	 5g	85	>99:1
8	 4h	 5h	75	>99:1
9	 4i	 5i	72	>99:1
10	 4j	 5j	80	>99:1

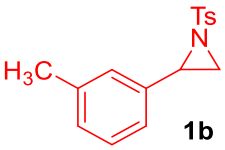
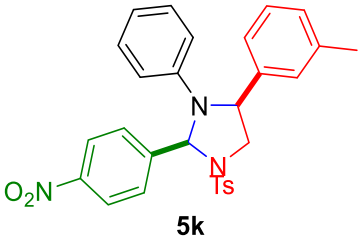
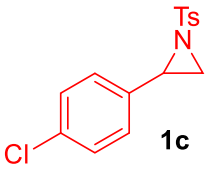
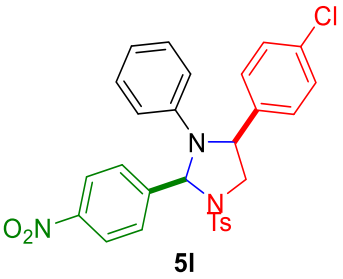
[a]Unless otherwise noted, 0.55 mmol of **1a**, 0.50 mmol of **2a**, 0.50 mmol of **4a–j**, 0.10 mmol of PTSA and 0.50 mmol of $MgSO_4$ were reacted. [b]Yields of isolated products. [c]Diastereomeric ratios have been determined by ^1H NMR analysis of the crude reaction mixture.

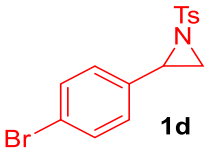
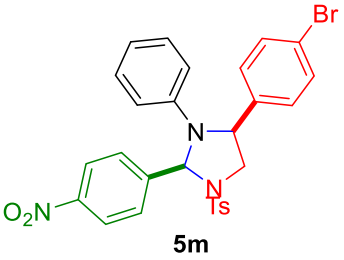
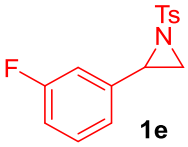
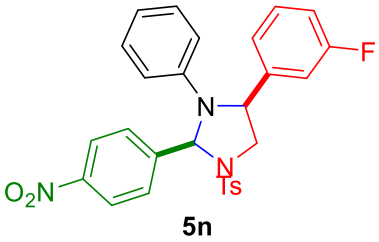
The strategy was further explored with several racemic 2-aryl-N-tosylaziridines **1b**–**e** under optimized reaction conditions (Table 3). The ring-opening reaction of aziridine (**1b**) possessing

electron-donating aryl group with aniline (**2a**) followed by cyclization with 4-nitrobenzaldehyde (**4d**) yielded imidazolidine derivative **5k** in 85% yield as a single diastereomer (entry 1). Similarly, 2-aryl-N-tosylaziridines with electron withdrawing halide groups in the phenyl ring (**1c**–**e**) underwent smooth transformation with **2a** and **4d** to yield imidazolidines **5l**–**n** in high yields with excellent diastereoselectivities (entries 2–4). All the results are described in Table 3.

Table 3. One-Pot Synthesis of Imidazolidines (5k–n) from Activated Aziridines[a]



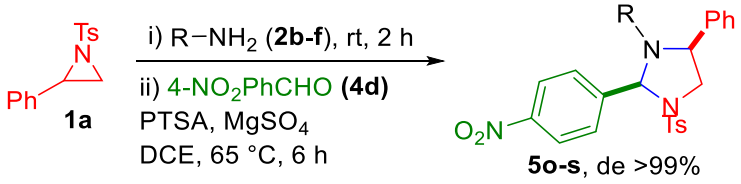
entry	aziridine (**1**)	imidazolidine (**5**)	yield (%)[b]	dr[c]
1	 **1b**	 **5k**	85	>99:1
2	 **1c**	 **5l**	82	>99:1

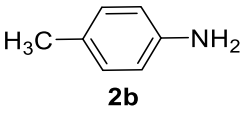
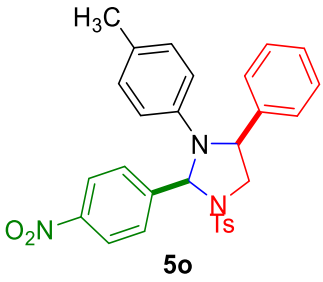
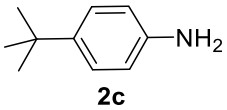
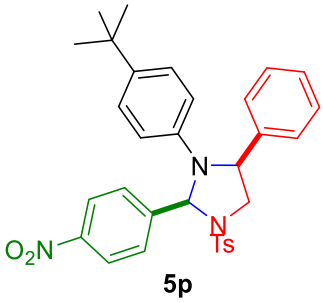
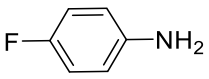
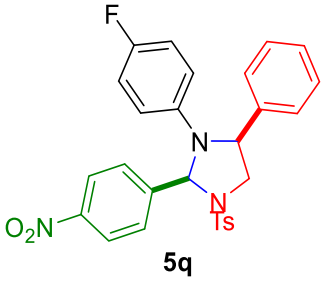
3	 **1d**	 **5m**	79	>99:1
4	 **1e**	 **5n**	76	>99:1

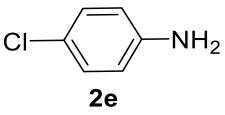
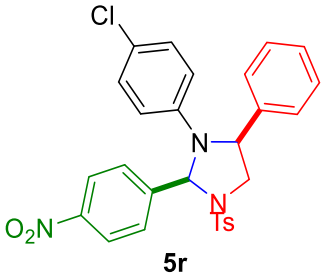
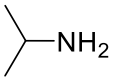
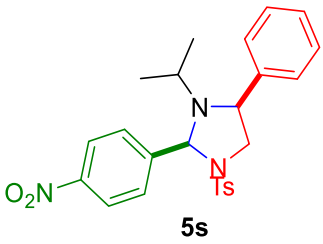
[a]Unless otherwise noted, 0.55 mmol of **1b–e**, 0.50 mmol of **2a**, 0.50 mmol of **4d**, 0.10 mmol of PTSA and 0.50 mmol of $MgSO_4$ were reacted. [b]Yields of isolated products. [c]Diastereomeric ratios have been determined by ^1H NMR analysis of the crude reaction mixture.

To generalize the methodology further, the ring-opening of aziridine **1a** was carried out with different aryl amines (**2b**–**e**) possessing both electron rich and deficient aryl groups (Table 4). The ring-opening of **1a** went efficiently with aryl amines, **2b**,**c**, followed by condensation with aldehyde **4d** to yield imidazolidines, **5o** and **5p**, respectively, in high yields with excellent diastereoselectivities (entries 1,2). Even with electron withdrawing aryl amines (**2d**,**e**), the ring-opening of **1a** followed by cyclization with **4d** underwent successfully to yield imidazolidines, **5q** and **5r**, respectively, in good yields as single diastereomers (entries 3,4). Unfortunately, the ring-opening products of aziridine **1a** with *ortho*- and *meta*-substituted anilines did not yield imidazolidine derivatives when cyclization was carried out in the presence of aldehydes. Next, the formation of imidazolidine was explored with alkyl amine, namely, isopropyl amine (**2f**), and as expected, **5s** was isolated from the reaction mixture in high yield with excellent diastereoselectivity (entry 5). All the results are described in Table 4.

Table 4. One-Pot Synthesis of Imidazolidines (5o–s) from Amines (2b–f)[a]



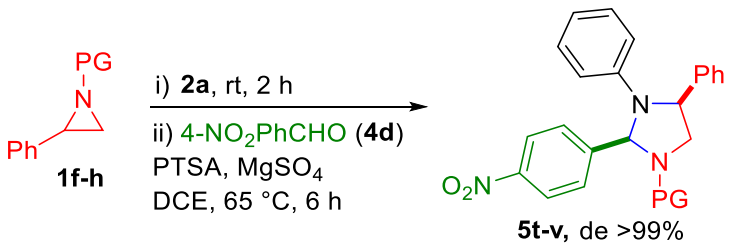
entry	amine (**2**)	imidazolidine (**5**)	yield (%)[b]	dr[c]
1	 **2b**	 **5o**	85	>99:1
2	 **2c**	 **5p**	82	>99:1
3	 **2d**	 **5q**	79	>99:1

4	 **2e**	 **5r**	76	>99:1
5	 **2f**	 **5s**	75	>99:1

[a]Unless otherwise noted, 0.55 mmol of **1a**, 0.50 mmol of **2b–f**, 0.50 mmol of **4d**, 0.10 mmol of PTSA and 0.50 mmol of $MgSO_4$ were reacted. [b]Yields of isolated products. [c]Diastereomeric ratios have been determined by ^1H NMR analysis of the crude reaction mixture.

Next, we studied the electronic effect of different arylsulfonyl groups (Table 5). Initially **1f** was treated with **2a** for 2 h followed by **4d** under optimized conditions. The reaction went smoothly and the imidazolidine derivative **5t** was formed in 87% yield as a single diastereomer (entry 1). Then, electron-donating (**1g**) and electron withdrawing (**1h**) groups were also examined as N-arylsulfonyl groups and in all the cases the formation of imidazolidine derivatives (**5u**,**v**) were observed in high yields with excellent diastereoselectivities (de >99%) (entries 2,3). All results are shown in Table 5.

Table 5. One-Pot Synthesis of Imidazolidines (5t–v) from 2-phenyl-N-sulfonylaziridines (1f–h)[a]

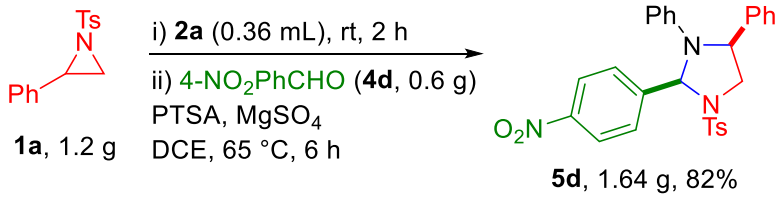


entry	2-phenyl-N-PG-aziridine (**1**)	imidazolidine (**5**)	yield (%)[b]	dr[c]
1	**1f**: PG = phenylsulfonyl	**5t**	87	>99:1
2	**1g**: PG = (4-(*tert*-butyl)phenyl)sulfonyl	**5u**	92	>99:1
3	**1h**: PG = (4-fluorophenyl)sulfonyl	**5v**	90	>99:1

[a]Unless otherwise noted, 0.55 mmol of **1f–h**, 0.50 mmol of **2a**, 0.50 mmol of **4d**, 0.10 mmol of PTSA and 0.50 mmol of $MgSO_4$ were reacted. [b]Yields of isolated products. [c]Diastereomeric ratios have been determined by ^1H NMR analysis of the crude reaction mixture.

To assess the efficiency of our developed protocol for one-pot ring-opening of aziridines with amines followed by cyclization with aldehydes, a gram-scale reaction was performed with aziridine **1a**, aniline (**2a**) and aldehyde **4d** under optimized reaction conditions. The effectiveness of the small-scale reaction was found to be similar upon scale-up producing **5d** in 82% yield (Scheme 2).

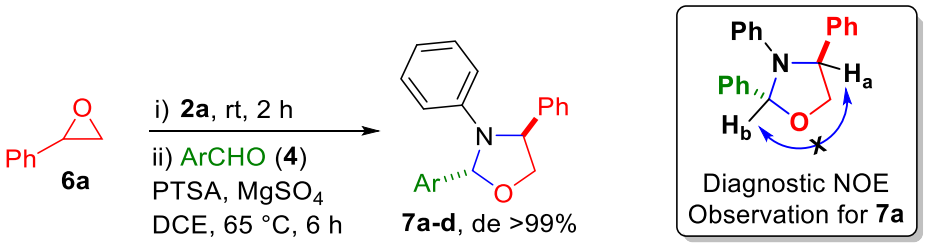
Scheme 2. Gram-scale Synthesis of Imidazolidine (5d)

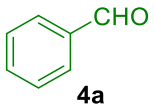
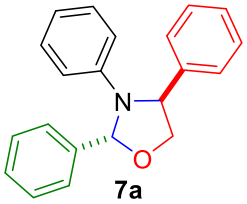
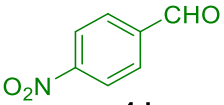
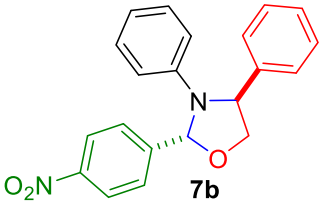
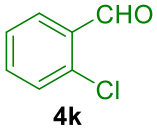
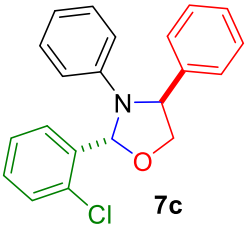


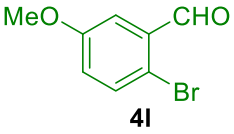
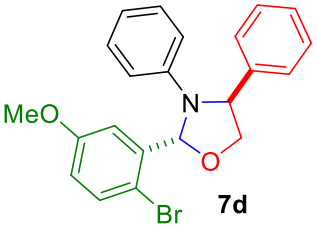
To expand the scope of the methodology, next, we explored 2-phenyloxirane (**6a**) for the ring-opening-cyclization reaction under optimized conditions (Table 6). When the ring-opening product obtained from the reaction between **6a** and **2a** was condensed with **4a** in one-pot conditions, the oxazolidine derivative **7a** was produced efficiently in 88% yield as a single diastereomer (entry 1). The successful formation of oxazolidine derivatives **7b,c** were also observed from electron withdrawing aromatic aldehydes, namely, 4-nitrobenzaldehyde (**4d**) and 2-chlorobenzadehyde (**4k**), respectively, in high yields with excellent stereoselectivities (entries 2,3). When, the ring-opening product was treated with disubstituted aldehyde, 2-bromo-5-methoxybenzaldehyde (**4l**), to our pleasure, the corresponding oxazolidine derivative **7d** was obtained with excellent yield and diastereoselectivity (entry 4). The relative 2,4-*trans*

stereochemistry of **7** was determined by NOESY experiment of **7a**.[16] All the results are detailed in Table 6.

Table 6. One-Pot Synthesis of Oxazolidines (7a–d) from 2-phenyl oxirane (6a), Aniline (2a) and Aldehydes (4)[a]



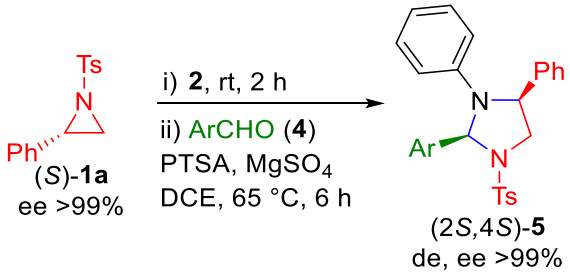
entry	aldehyde (**4**)	oxazolidine (**7**)	yield (%)[b]	dr[c]
1	 **4a**	 **7a**	88	>99:1
2	 **4d**	 **7b**	86	>99:1
3	 **4k**	 **7c**	76	>99:1

4	 **4l**	 **7d**	85	>99:1

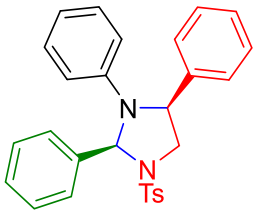
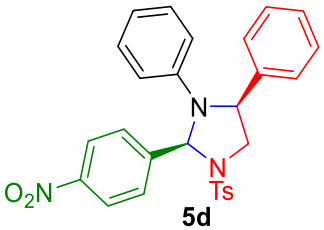
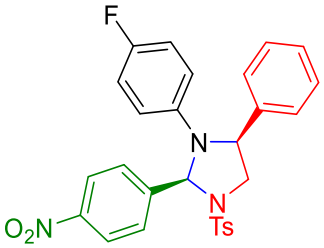
[a]Unless otherwise noted, 0.55 mmol of **6a**, 0.50 mmol of **2a**, 0.50 mmol of **4**, 0.10 mmol of PTSA and 0.50 mmol of $MgSO_4$ were reacted. [b]Yields of isolated products. [c]Diastereomeric ratios have been determined by ^1H NMR analysis of the crude reaction mixture.

The synthetic potential of the methodology was further demonstrated by the formation of non-racemic imidazolidine derivatives starting from enantiopure activated N-tosylaziridine (*S*)-**1a**, aryl amines **2** and aryl aldehydes **4** (Table 7). When (*S*)-**1a** was reacted with **2a**,**d** the ring-opening products upon treatment with benzaldehyde (**4a**) and *p*-nitrobenzaldehyde (**4d**) produced imidazolidine derivatives (*S*)-**5a,d** and (*S*)-**5q**, respectively, in high yields with excellent diastereo- and enantioselectivities (entries 1–3). The absolute configuration of **5** was determined as (2*S*,4*S*) based on the crystal structure of **5a**.[16] All results are shown in Table 7.

Table 7. One-Pot Asymmetric Synthesis of Imidazolidines (2*S*,4*S*)-5 from 2-phenyl-N-tosylaziridines (*S*)-1a, Aryl Amines (2) and Aryl Aldehydes (4)[a]



entry	aziridine (*S*)-**1a**	aryl amine (**2**)	aldehyde (**4**)	imidazolidine (**5**)	yield (%)[b]	de/ee[c] (%)

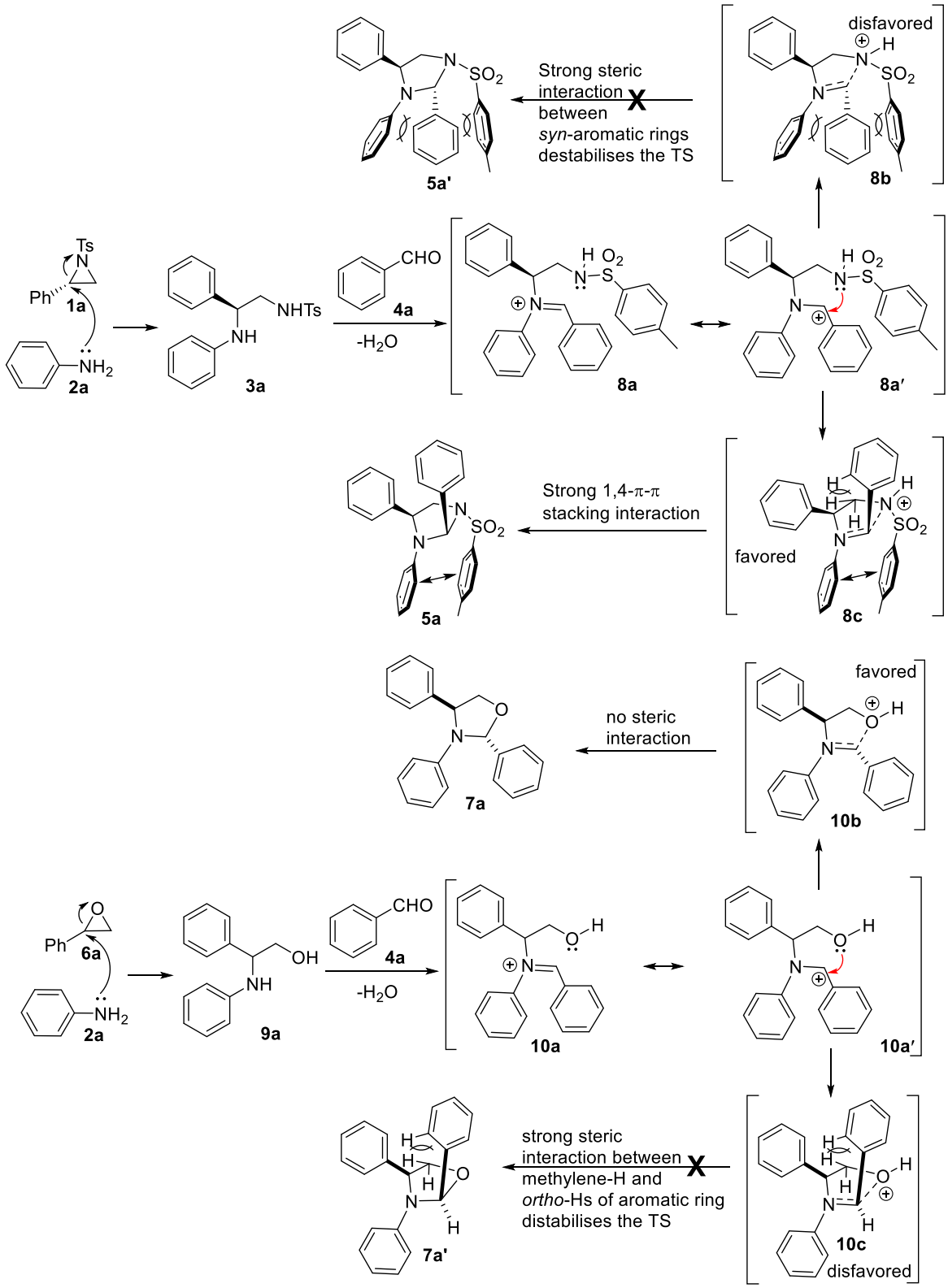
1	(*S*)-**1a**	**2a**	**4a**	 **5a**	84	>99/99
2	(*S*)-**1a**	**2a**	**4d**	 **5d**	88	>99/99
3	(*S*)-**1a**	**2d**	**4d**	 **5q**	79	>99/99

[a]Unless otherwise noted, 0.55 mmol of (***S***)-**1a**, 0.50 mmol of **2**, 0.50 mmol of **4**, 0.10 mmol of PTSA and 0.50 mmol of $MgSO_4$ were reacted. [b]Yields of isolated products. [c]Diastereomeric ratios have been determined by ^1H NMR analysis of the crude reaction mixture.

Mechanism

A plausible mechanism for the formation of imidazolidines and oxazolidines is depicted in Scheme 3. Based on our observations, we believe that the ring opening reactions of activated aziridines and epoxides proceed via a regioselective S_N2-type pathway as described by us earlier.[15b] Amine nucleophile **2a** attacks the aziridine **1a** at the benzylic position to produce the corresponding ring opening product **3a**, which in the presence of acid-catalyst PTSA and additive $MgSO_4$, forms the corresponding iminium ion **8a** when reacted with **4a**. Subsequently, intramolecular nucleophilic attack by the tosyl amide on iminium ion probably through the cationic intermediate **8a'** occurs in such a way that it leads to the more favorable TS **8c** where the electronic 1,4-π-π stacking interaction outweighs the steric repulsion arising out of the

Scheme 3. Plausible Mechanism



interaction between the *ortho*-hydrogens of aromatic ring at C-2 and methylene hydrogen at C-5 of the ring to produce the 2,4-*cis* diastereomer **5a** of imidazolidine derivatives as the only product. The formation of the other isomer **5a'** was not observed from the less stable TS **8b** probably due to strong steric hinderance between three *syn*-aromatic rings. On the contrary, in the case of epoxide **6a,** the intramolecular attack of the hydroxyl group on the cationic intermediate **10a'** leads to the stable species **10b** where aromatic rings at the 2,4-position of oxazolidine rings are anti to each other producing the major 2,4-*trans* diastereomer **7a**.[16] The formation of 2,4-*cis* diastereomer **7a'** through the TS **10c** was not observed probably due to a destabilizing steric repulsion between *ortho*-hydrogens of C-2 aromatic ring and one of the C-5 methylene hydrogens in oxazolidine rings.

Conclusion

In summary, we have described an efficient and straightforward protocol for the synthesis of imidazolidines and oxazolidines starting from cheap and readily available starting materials via regioselective ring-opening of activated aziridines and epoxides with different amine nucleophiles and a subsequent condensation with aldehydes under one-pot reaction condition. The prominent features of this environmentally benign methodology are mild reaction conditions, devoid of any metal-based Lewis acid, operational simplicity, wide substrate scope, high yields of the products, and excellent stereoselectivities (de, ee >99%). We believe that the described strategy would be very useful in organic synthesis.

Experimental Section

General Procedures. The analytical thin layer chromatography (TLC) was carried out for monitoring the progress of the reactions using silica gel 60 F254 precoated plates. Visualizations of the spots were accomplished with a UV lamp or I_2 stain. Active Aluminium oxide was used for flash column chromatographic purification using a combination of distilled ethyl acetate and petroleum ether as the eluent. Unless otherwise mentioned, all the reactions were carried out in oven-dried glassware under an atmosphere of nitrogen or argon using anhydrous solvents. Where appropriate, the solvents and all of the reagents were purified prior to use following the guidelines of Armarego and Chai.[17] The monosubstituted *N*-tosylaziridines (**1a**–**e**)[18] and *N*-arylsulfonylaziridines (**1f**–**h**)[19] were prepared by following earlier reports. All the commercial

reagents were used as received without further purification unless otherwise mentioned. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 400 MHz and 500 MHz. The chemical shifts were recorded in parts per million (ppm, δ) using tetramethylsilane (δ 0.00) as the internal standard. Splitting patterns of the ^{1}H NMR are mentioned as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m) etc. Proton-decoupled carbon nuclear magnetic resonance (^{13}C{^{1}H} NMR) spectra were recorded at 100 MHz and 125 MHz. HRMS were obtained using (ESI) mass spectrometer (TOF). KBr pellets were used for IR spectra of solid compounds. The melting point measurements were made using a hot stage apparatus and are reported as uncorrected. The enantiomeric excess (ee) was determined by chiral HPLC with Chiralpak AD-H and Lux 5u Cellulose-2 (detection at 254 nm) using hexane and isopropanol as the mobile phase and a UV/VIS detector. Optical rotations were measured using a 6.0 mL cell with a 1.0 dm path length and are reported as $[\alpha]^{25}_{D}$ (*c* in g per 100 mL solvent) at 25 °C.

General procedure for ring-opening of aziridines/oxiranes with amines followed by cyclization with aldehydes. A clean and dried double neck round-bottom flask under argon charged with aziridine/oxirane (0.55 mmol, 1.1 equiv) and (aromatic/alkyl) amine (0.50 mmol, 1.0 equiv) was allowed to stir at rt for 2 h. The formation of ring opening product was monitored by TLC. After complete consumption of amine, aldehyde (0.50 mmol, 1.0 equiv) dissolved in (2.0 mL) of DCE, PTSA (0.10 mmol, 0.2 equiv), $MgSO_4$ (0.50 mmol, 1.0 equiv) were added to this reaction mixture containing ring opening product and then again stirred at 65 °C in the oil bath for appropriate time. The formation of cyclized product and the progress of reaction was monitored by TLC. After completion, the aqueous layer was extracted with diethyl ether (3 × 10.0 mL), dried over anhydrous Na_2SO_4 followed by concentration under reduced pressure. The crude concentrate was purified by flash column chromatography on silica gel (230−400 mesh) using diethyl ether in petroleum ether as the eluent to afford the corresponding pure imidazolidine/oxazolidine product.

(2S,4S)-2,3,4-triphenyl-1-tosylimidazolidine (5a). The general method described above was followed when aziridine (S)-**1a** (150.3 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of benzaldehyde **4a** (51 µL, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford (2S,4S)-**5a** (190.9 mg, 0.42 mmol) as a white solid in 84% yield. R*f* 0.55 (20% diethyl ether in petroleum ether); MP 177–179 °C; $[\alpha]^{25}_{D}$ +56.0 (c 0.2 in CH_2Cl_2) for a >99% ee

sample. Optical purity was determined by chiral HPLC analysis (Lux 5u Cellulose-2 column), hexane–isopropanol, 95:5; flow rate = 1.0 mL/min; t_R 1: 27.4 min (minor), t_R 2: 13.9 min (major); IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 3060, 3028, 2943, 2873, 1597, 1500, 1449, 1349, 1334, 1306, 1232, 1212, 1165, 1119, 1088, 1060, 1029, 992, 960, 929, 860, 816, 749, 696, 671; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.29 (s, 3H), 3.23 (dd, 1H, J = 13.4, 10.5 Hz), 3.90 (dd, 1H, J = 10.4, 7.2 Hz), 4.29 (dd, 1H, J = 13.4, 7.1 Hz), 6.25 (d, 2H, J = 8.0 Hz), 6.38 (s, 1H), 6.75 (t, 1H, J = 7.3 Hz), 6.98 (d, 2H, J = 8.0 Hz), 7.05 (dd, 2H, J = 8.8, 7.3 Hz), 7.20–7.27 (m, 5H), 7.36–7.39 (m, 1H), 7.41–7.44 (m, 2H), 7.60 (d, 2H, J = 8.3 Hz), 7.74 (d, 2H, J = 7.7 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 21.4, 54.1, 63.1, 80.3, 113.2, 118.7, 126.2, 127.2, 127.5, 127.8, 128.5, 128.6, 128.7, 128.9, 129.8, 134.8, 139.3, 139.7, 144.4, 147.2; HRMS (ESI-TOF) calcd for $C_{28}H_{27}N_2O_2S$ $(M+H)^+$ 455.1793, found 455.1798.

3,4-diphenyl-2-(p-tolyl)-1-tosylimidazolidine (5b). The general method described above was followed when aziridine **1a** (150.3 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-methylbenzaldehyde **4b** (59 µL, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5b** (201.5 mg, 0.43 mmol) as a white solid in 86% yield. R*f* 0.66 (20% diethyl ether in petroleum ether); MP 189–191 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 3028, 2938, 2886, 1598, 1500, 1450, 1403, 1348, 1306, 1234, 1165, 1120, 1088, 1063, 1013, 960, 891, 869, 817, 750, 671; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.28 (s, 3H), 2.38 (s, 3H), 3.23 (dd, 1H, J = 13.4, 10.6 Hz), 3.88 (dd, 1H, J = 10.4, 7.1 Hz), 4.26 (dd, 1H, J = 13.4, 7.0 Hz), 6.23 (d, 2H, J = 8.0 Hz), 6.34 (s, 1H), 6.74 (t, 1H, J = 7.3 Hz), 6.97 (d, 2H, J = 8.0 Hz), 7.03 (t, 2H, J = 7.3 Hz), 7.18–7.26 (m, 7H), 7.60 (t, 4H, J = 8.3 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 21.1, 21.4, 54.1, 63.0, 80.3, 113.2, 118.6, 126.3, 127.1, 127.4, 127.7, 128.7, 128.8, 129.3, 129.7, 134.9, 136.7, 138.3, 139.3, 144.3, 147.2; HRMS (ESI-TOF) calcd for $C_{29}H_{29}N_2O_2S$ $(M+H)^+$ 469.1950, found 469.1958.

(4-chlorophenyl)-3,4-diphenyl-1-tosylimidazolidine (5c). The general method described above was followed when aziridine **1a** (150.3 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-chlorobenzaldehyde **4c** (70.2 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5c** (190.7 mg, 0.39 mmol) as a white solid in 78% yield. R*f* 0.65 (20% diethyl ether in petroleum ether); MP 134–136 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 2924, 1597, 1500, 1451,

1350, 1165, 1089, 1009, 960, 806, 750, 720, 694, 669; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.29 (s, 3H), 3.20 (dd, 1H, J = 13.5, 10.5 Hz), 3.88 (dd, 1H, J = 10.4, 7.1 Hz), 4.28 (dd, 1H, J = 13.3, 7.4 Hz), 6.23 (d, 2H, J = 8.1 Hz), 6.32 (s, 1H), 6.76 (t, 1H, J = 7.3 Hz), 6.99 (d, 2H, J = 8.0 Hz), 7.05 (dd, 2H, J = 8.8, 7.5 Hz), 7.16–7.18 (m, 2H), 7.20–7.25 (m, 2H), 7.26–7.28 (m, 1H), 7.40 (d, 2H, J = 8.6 Hz), 7.59 (d, 2H, J = 8.3 Hz), 7.67 (d, 2H, J = 8.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 21.5, 54.1, 63.2, 79.9, 113.2, 119.0, 126.2, 127.5, 127.9, 128.7, 128.8, 129.0, 129.8, 134.5, 134.6, 138.3, 139.1, 144.5, 147.0; HRMS (ESI-TOF) calcd for $C_{28}H_{26}ClN_2O_2S$ $(M+H)^+$ 489.1404, found 489.1409.

(2S,4S)-2-(4-nitrophenyl)-3,4-diphenyl-1-tosylimidazolidine (5d). The general method described above was followed when aziridine (S)-**1a** (150.3 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford (2S,4S)-**5d** (219.8 mg, 0.44 mmol) as a white solid in 88% yield. Gram-scale synthesis of **5d** was achieved when aziridine **1a** (1.2 g, 4.4 mmol) was reacted with aniline **2a** (0.36 mL, 4.0 mmol) at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (0.6 g, 4.0 mmol) along with PTSA (0.138 g, 0.80 mmol) and $MgSO_4$ (0.48 g, 4.0 mmol) in DCE at 65 °C for 6 h to afford **5d** (1.64 g, 3.28 mmol) as a white solid in 82% yield. R*f* 0.60 (20% diethyl ether in petroleum ether); MP 174–176 °C; $[\alpha]^{25}_D$ +48.0 (c 0.35 in CH_2Cl_2) for a >99% ee sample. Optical purity was determined by chiral HPLC analysis (Lux 5u Cellulose-2 column), hexane–isopropanol, 95:5; flow rate = 1.0 mL/min; t_R 1: 78.5 min (minor), t_R 2: 88.0 min (major); IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 3462, 3030, 2923, 2853, 1738, 1642, 1598, 1521, 1502, 1455, 1408, 1348, 1263, 1236, 1165, 1108, 1089, 1046, 1010, 898, 861, 816, 750, 676; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H), 3.17 (dd, 1H, J = 13.4, 10.4 Hz), 3.90 (dd, 1H, J = 10.4, 7.3 Hz), 4.30–4.35 (m, 1H), 6.23 (d, 2H, J = 8.0 Hz), 6.40 (s, 1H), 6.81 (t, 1H, J = 7.3 Hz), 7.01 (d, 2H, J = 8.0 Hz), 7.08 (dd, 2H, J = 8.6, 7.3 Hz), 7.15–7.17 (m, 2H), 7.22–7.30 (m, 3H), 7.62 (d, 2H, J = 8.6 Hz), 7.94 (d, 2H, J = 8.5 Hz), 8.29 (d, 2H, J = 8.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 21.5, 54.2, 63.3, 79.8, 113.2, 119.4, 123.9, 126.0, 127.4, 128.1, 128.3, 128.9, 129.1, 129.9, 134.3, 138.7, 144.8, 146.8, 147.0, 148.2; HRMS (ESI-TOF) calcd for $C_{28}H_{26}N_3O_4S$ $(M+H)^+$ 500.1644, found 500.1641.

2-(3-bromophenyl)-3,4-diphenyl-1-tosylimidazolidine (5e). The general method described above was followed when aziridine **1a** (150.3 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 3-bromobenzaldehyde **4e** (58 µL, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5e** (202.2 mg, 0.38 mmol) as a white solid in 76% yield. R*f* 0.64 (20% diethyl ether in petroleum ether); MP 160–162 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 3030, 2923, 2853, 1599, 1504, 1455, 1351, 1305, 1263, 1161, 1093, 1071, 1029, 894, 848, 813, 749, 666; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.37 (s, 3H), 3.84 (dd, 1H, *J* = 11.0, 2.4 Hz), 4.12 (dd, 1H, *J* = 11.0, 7.9 Hz), 5.21 (dd, 1H, *J* = 7.9, 2.4 Hz), 6.35 (d, 2H, *J* = 7.9 Hz), 6.48 (s, 1H), 6.61 (t, 1H, *J* = 7.3 Hz), 6.93-7.00 (m, 4H), 7.06-7.17 (m, 6H), 7.25–7.28 (m, 1H), 7.36 (d, 1H, *J* = 7.9 Hz), 7.39-7.41 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 21.6, 53.7, 61.5, 115.3, 118.3, 122.9, 126.0, 126.2, 127.1, 127.3, 128.8, 129.0, 129.7, 130.2, 130.4, 131.7, 135.9, 140.3, 141.2, 142.4, 143.6; HRMS (ESI-TOF) calcd for $C_{28}H_{26}BrN_2O_2S$ $(M+H)^+$ 533.0898, found 533.0891.

3,4-diphenyl-2-(o-tolyl)-1-tosylimidazolidine (5f). The general method described above was followed when aziridine **1a** (150.3 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 2-methylbenzaldehyde **4f** (58 µL, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5f** (163.9 mg, 0.35 mmol) as a white solid in 70% yield. R*f* 0.72 (10% diethyl ether in petroleum ether); MP 138–140 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 2925, 2854, 1598, 1501, 1463, 1351, 1213, 1164, 1089, 1034, 956, 936, 887, 814, 749, 672; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.31 (s, 3H), 2.77 (s, 3H), 3.49 (dd, 1H, *J* = 12.6, 10.3 Hz), 4.18 (dd, 1H, *J* = 10.3, 6.9 Hz), 4.35 (dd, 1H, *J* = 12.6, 6.9 Hz), 6.21 (d, 2H, *J* = 8.0 Hz), 6.48 (s, 1H), 6.75 (t, 1H, *J* = 7.4 Hz), 7.01–7.08 (m, 5H), 7.21–7.26 (m, 6H), 7.29–7.33 (m, 2H), 7.52 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 21.4, 22.7, 53.4, 61.6, 78.7, 114.4, 119.2, 126.1, 126.3, 127.5, 127.6, 127.9, 128.6, 128.7, 128.9, 129.7, 131.2, 131.5, 131.7, 137.2, 138.0, 139.3, 147.9; HRMS (ESI-TOF) calcd for $C_{29}H_{29}N_2O_2S$ $(M+H)^+$ 469.1950, found 469.1945.

2-(naphthalen-2-yl)-3,4-diphenyl-1-tosylimidazolidine (5g). The general method described above was followed when aziridine **1a** (150.3 mg, 0.55 mmol) **5e** was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 2-naphthaldehyde **4g** (78.1 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5g** (214.4 mg, 0.42 mmol) as a white solid in 85% yield. R*f* 0.44 (20% diethyl ether in petroleum ether); MP 179–181 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 2923, 2853, 1598, 1500, 1454, 1349, 1213, 1163, 1089, 1019, 959, 813, 749, 694, 672; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.29 (s, 3H), 3.28 (dd, 1H, *J* = 13.5, 10.5 Hz), 3.95 (dd, 1H, *J* = 10.4, 7.2 Hz), 4.32 (dd, 1H, *J* = 13.4, 7.1 Hz), 6.31 (d, 2H, *J* = 8.0 Hz), 6.53 (s, 1H), 6.77 (t, 1H, *J* = 7.3 Hz), 6.98 (d, 2H, *J* = 8.0 Hz), 7.06 (dd, 2H, *J* = 8.6, 7.3 Hz), 7.20–7.26 (m, 5H), 7.50–7.52 (m, 2H), 7.62 (d, 2H, *J* = 8.0 Hz), 7.84–7.93 (m, 4H), 8.16 (s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 21.8, 54.5, 63.5, 81.0, 113.7, 119.2, 125.4, 126.2, 126.67, 126.69, 126.8, 127.87, 127.91, 128.0, 128.2, 128.7, 129.0, 129.1, 129.3, 130.1, 133.5, 133.8, 139.6; HRMS (ESI-TOF) calcd for $C_{32}H_{29}N_2O_2S$ $(M+H)^+$ 505.1950, found 505.1958.

2-(furan-2-yl)-3,4-diphenyl-1-tosylimidazolidine (5h). The general method described above was followed when aziridine **1a** (150.3 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 2-furaldehyde **4h** (41 µL, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5h** (166.7 mg, 0.37 mmol) as a white solid in 75% yield. R*f* 0.76 (20% diethyl ether in petroleum ether); MP 133–135 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 2922, 2852, 1598, 1501, 1454, 1350, 1236, 1163, 1090, 1013, 956, 813, 747, 669; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.31 (s, 3H), 3.48 (dd, 1H, *J* = 12.8, 10.0 Hz), 4.06 (dd, 1H, *J* = 9.7, 7.1 Hz), 4.31 (dd, 1H, *J* = 12.6, 7.2 Hz), 6.35-6.38 (m, 4H), 6.58 (d, 1H, *J* = 6.3 Hz), 6.75 (t, 1H, *J* = 7.3 Hz), 7.03–7.08 (m, 4H), 7.22–7.24 (m, 4H), 7.28–7.29 (m, 1H), 7.42 (d, 1H, *J* = 1.0 Hz), 7.57 (d, 2H, *J* = 8.3 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 21.8, 54.7, 62.8, 75.0, 109.1, 110.8, 113.6, 119.2, 126.4, 127.8, 128.2, 129.1, 129.3, 130.1, 135.1, 139.7, 143.6, 144.6, 146.3, 152.7; HRMS (ESI-TOF) calcd for $C_{26}H_{25}N_2O_3S$ $(M+H)^+$ 445.1586, found 445.1581.

3,4-diphenyl-2-(thiophen-2-yl)-1-tosylimidazolidine (5i). The general method described above was followed when aziridine **1a** (150.3 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 2-thiophenecarboxaldehyde **4i** (46

µL, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5i** (165.8 mg, 0.36 mmol) as a white solid in 72% yield. R*f* 0.72 (20% diethyl ether in petroleum ether); MP 162–164 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 2918, 2850, 1598, 1500, 1453, 1351, 1163, 1089, 957, 813, 751, 700, 670; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 3.36 (dd, 1H, *J* = 12.8, 10.4 Hz), 3.99 (dd, 1H, *J* = 10.3, 7.3 Hz), 4.26–4.31 (m, 1H), 6.34 (d, 2H, *J* = 7.9 Hz), 6.54 (s, 1H), 6.75 (t, 1H, *J* = 7.3 Hz), 7.00–7.07 (m, 5H), 7.21–7.32 (m, 7H), 7.57 (d, 2H, *J* = 7.9 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 21.5, 53.9, 63.2, 77.6, 113.6, 119.1, 121.6, 126.1, 126.2, 127.38, 127.43, 127.8, 128.75, 128.84, 128.9, 129.8, 134.8, 137.6, 138.9, 145.2; HRMS (ESI-TOF) calcd for $C_{26}H_{25}N_2O_2S_2$ $(M+H)^+$ 461.1357, found 461.1351.

2-ethyl-3,4-diphenyl-1-tosylimidazolidine (5j). The general method described above was followed when aziridine **1a** (150.3 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of propanal **4j** (36 µL, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5j** (162.6 mg, 0.40 mmol) as a white solid in 80% yield. R*f* 0.62 (20% diethyl ether in petroleum ether); MP 139–141 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 3028, 2966, 2928, 1597, 1502, 1453, 1350, 1305, 1234, 1212, 1163, 1122, 1090, 1040, 1028, 990, 937, 851, 814, 748, 673; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.21 (t, 3H, J = 7.4 Hz), 1.82–1.90 (m, 1H), 1.97–2.04 (m, 1H), 2.24 (s, 3H), 3.36 (dd, 1H, *J* = 13.6, 9.9 Hz), 3.65–3.68 (m, 1H), 4.30 (dd, 1H, *J* = 13.7, 7.7 Hz), 5.33 (dd, 1H, *J* = 9.8, 3.9 Hz), 6.14 (d, 2H, *J* = 8.0 Hz), 6.68 (t, 1H, *J* = 7.3 Hz), 6.92 (d, 2H, *J* = 8.2 Hz), 7.02–7.05 (m, 2H), 7.12 (d, 2H, *J* = 7.0 Hz), 7.20–7.28 (m, 3H), 7.56 (d, 2H, *J* = 8.3 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 10.4. 21.7, 29.6, 54.3, 62.0, 80.1, 112.4, 118.1, 125.9, 127.7, 128.0, 129.1, 129.3, 130.0, 134.8, 140.5, 144.5, 146.1; HRMS (ESI-TOF) calcd for $C_{24}H_{27}N_2O_2S$ $(M+H)^+$ 407.1793, found 407.1790.

2-(4-nitrophenyl)-3-phenyl-4-(m-tolyl)-1-tosylimidazolidine (5k). The general method described above was followed when aziridine **1b** (158.0 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5k** (218.3 mg, 0.42 mmol) as a white solid in 85% yield. R*f* 0.67 (20% diethyl ether in petroleum ether); MP 164–166 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 3042, 2924, 2855, 1598, 1524, 1502, 1455, 1408, 1349, 1232, 1201, 1164, 1108, 1090, 1012, 992, 963, 893,

868, 824, 751, 696, 676; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.27 (s, 3H), 2.29 (s, 3H), 3.15 (dd, 1H, *J* = 13.6, 10.6 Hz), 3.85 (dd, 1H, *J* = 10.4, 7.1 Hz), 4.27–4.31 (m, 1H), 6.22 (d, 2H, *J* = 8.0 Hz), 6.38 (s, 1H), 6.80 (t, 1H, *J* = 7.3 Hz), 6.92–6.95 (m, 2H), 6.99–7.08 (m, 5H), 7.13–7.16 (m, 1H), 7.60 (d, 2H, *J* = 8.3 Hz), 7.92 (d, 2H, *J* = 8.6 Hz), 8.27 (d, 2H, *J* = 8.7 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 21.8, 54.7, 63.7, 80.1, 113.5, 119.7, 123.3, 124.2, 127.0, 127.8, 128.7, 129.2, 129.29, 129.34, 130.3, 134.7, 139.1, 139.2, 145.2, 147.2, 147.4, 148.6; HRMS (ESI-TOF) calcd for $C_{29}H_{28}N_3O_4S$ $(M+H)^+$ 514.1801, found 514.1806.

4-(4-chlorophenyl)-2-(4-nitrophenyl)-3-phenyl-1-tosylimidazolidine (5l). The general method described above was followed when aziridine **1c** (169.2 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5l** (218.9 mg, 0.41 mmol) as a white solid in 82% yield. R*f* 0.52 (20% diethyl ether in petroleum ether), MP 190–192 °C, IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 3064, 2925, 2855, 1598, 1522, 1502, 1493, 1455, 1349, 1264, 1233, 1200, 1165, 1090, 1013, 993, 961, 899, 847, 741, 667; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H), 3.13 (dd, 1H, *J* = 13.4, 10.4 Hz), 3.89 (dd, 1H, *J* = 10.4, 6.7 Hz), 4.31 (dd, 1H, *J* = 13.4, 6.7 Hz), 6.21 (d, 2H, *J* = 7.9 Hz), 6.39 (s, 1H), 6.83 (t, 1H, *J* = 7.3 Hz), 7.01 (d, 2H, *J* = 7.9 Hz), 7.07–7.11 (m, 4H), 7.24–7.25 (m, 2H), 7.61 (d, 2H, *J* = 8.6 Hz), 7.91 (d, 2H, *J* = 8.6 Hz), 8.29 (d, 2H, *J* = 8.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) 21.5, 54.1, 62.8, 79.8, 113.3, 119.7, 123.9, 127.4, 127.5, 128.2, 129.1, 129.3, 130.0, 133.9, 134.3, 137.3, 144.9, 146.6, 146.8, 148.3; HRMS (ESI-TOF) calcd for $C_{28}H_{25}ClN_3O_4S$ $(M+H)^+$ 534.1254, found 534.1258.

(4-bromophenyl)-2-(4-nitrophenyl)-3-phenyl-1-tosylimidazolidine (5m). The general method described above was followed when aziridine **1d** (193.7 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5m** (228.5 mg, 0.39 mmol) as a white solid in 79% yield. R*f* 0.54 (20% diethyl ether in petroleum ether); MP 203–205 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 2923, 1598, 1522, 1501, 1409, 1349, 1232, 1199, 1165, 1089, 1010, 961, 899, 862, 820, 751, 693, 678; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H), 3.13 (dd, 1H, *J* = 13.4, 10.4 Hz), 3.87 (dd, 1H, *J* = 10.4, 6.7 Hz), 4.29–4.34 (m, 1H), 6.20 (d, 2H, J = 8.0 Hz), 6.39 (s, 1H),

6.83 (t, 1H, *J* = 7.3 Hz), 7.00–7.11 (m, 6H), 7.41 (d, 2H, *J* = 8.6 Hz), 7.60 (d, 2H, *J* = 7.9 Hz), 7.90 (d, 2H, *J* = 9.2 Hz), 8.29 (d, 2H, *J* = 9.2 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 21.6, 54.1, 62.9, 79.9, 113.3, 119.8, 122.0, 124.0, 127.5, 127.8, 128.3, 129.2, 130.1, 132.4, 134.3, 137.9, 145.1, 146.6, 146.9, 148.3; HRMS (ESI-TOF) calcd for $C_{28}H_{25}BrN_3O_4S$ $(M+H)^+$ 578.0749, found 578.0748.

4-(3-fluorophenyl)-2-(4-nitrophenyl)-3-phenyl-1-tosylimidazolidine (5n). The general method described above was followed when aziridine **1e** (160.2 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5n** (196.6 mg, 0.38 mmol) as a white solid in 76% yield. R*f* 0.78 (20% diethyl ether in petroleum ether); MP 169–171 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 2923, 2852, 1598, 1523, 1501, 1453, 1348, 1201, 1164, 1089, 1010, 957, 895, 809, 750, 693, 675; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.30 (s, 3H), 3.15 (dd, 1H, *J* = 13.6, 10.4 Hz), 3.88 (dd, 1H, *J* = 10.3, 7.1 Hz), 4.29–4.33 (m, 1H), 6.21 (d, 2H, *J* = 8.0 Hz), 6.39 (s, 1H), 6.81–6.87 (m, 2H), 6.90–6.95 (m, 2H), 7.01 (d, 2H, *J* = 8.0 Hz), 7.07–7.10 (m, 2H), 7.23–7.27 (m, 1H), 7.60 (d, 2H, *J* = 8.1 Hz), 7.91 (d, 2H, *J* = 8.4 Hz), 8.29 (d, 2H, *J* = 8.7 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) δ 21.5, 54.0, 63.0, 79.8, 113.1 (d, $^{2}J_{C-F}$ = 22.7 Hz), 113.2, 115.1 (d, $^{2}J_{C-F}$ = 20.3 Hz), 119.7, 121.6, 124.0, 127.4, 128.2, 129.1, 130.0, 130.8 (d, $^{3}J_{C-F}$ = 8.3 Hz), 134.2, 141.5 (d, $^{4}J_{C-F}$ = 7.2 Hz), 145.0, 146.6, 146.8, 148.3, 163.1 (d, $^{1}J_{C-F}$ = 245.6 Hz); HRMS (ESI-TOF) calcd for $C_{28}H_{25}FN_3O_4S$ $(M+H)^+$ 518.1550, found 518.1551.

2-(4-nitrophenyl)-4-phenyl-3-(p-tolyl)-1-tosylimidazolidine (5o). The general method described above was followed when aziridine **1a** (150.3 mg, 0.55 mmol) and *p*-toluidine **2b** (53.5 mg, 0.50 mmol) dissolved in 1.0 mL of DCE was stirred at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5o** (218.3 mg, 0.42 mmol) as a white solid in 85% yield. R*f* 0.58 (20% diethyl ether in petroleum ether); MP 172–174 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 2922, 1598, 1518, 1453, 1348, 1200, 1164, 1089, 1010, 962, 898, 861, 804, 741, 699, 676; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.23 (s, 3H), 2.31 (s, 3H), 3.16 (dd, 1H, *J* = 13.4, 10.4 Hz), 3.91 (dd, 1H, *J* = 10.4, 6.7 Hz), 4.29 (dd, 1H, *J* = 13.4, 6.7 Hz), 6.14 (d, 2H, *J* = 8.6 Hz), 6.34 (s, 1H), 6.88 (d, 2H, *J* = 8.6 Hz), 7.03 (d, 2H, *J* = 8.6 Hz), 7.15–7.17 (m, 2H), 7.21–

7.30 (m, 3H), 7.62 (d, 2H, *J* = 7.9 Hz), 7.93 (d, 2H, *J* = 8.6 Hz), 8.28 (d, 2H, *J* = 9.2 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) δ 20.4, 21.6, 54.3, 63.5, 80.1, 113.4, 124.0, 126.1, 127.6, 128.1, 128.5, 128.8, 129.1, 129.5, 130.0, 134.5, 138.9, 144.7, 144.9, 147.4, 148.2; HRMS (ESI-TOF) calcd for $C_{29}H_{28}N_3O_4S$ $(M+H)^+$ 514.1801, found 514.1803.

3-(4-(tert-butyl)phenyl)-2-(4-nitrophenyl)-4-phenyl-1-tosylimidazolidine (5p). The general method described above was followed when aziridine **1a** (150.3 mg, 0.55 mmol) was reacted with 4-*tert*-butylaniline **2c** (79 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5p** (227.8 mg, 0.41 mmol) as a white solid in 82% yield. R*f* 0.70 (20% diethyl ether in petroleum ether); MP 185–187 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 3036, 2960, 2866, 1709, 1606, 1519, 1493, 1455, 1393, 1348, 1320, 1268, 1232, 1198, 1164, 1107, 1089, 1059, 1011, 963, 898, 861, 814, 754, 700, 676; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.26 (s, 9H), 2.28 (s, 3H), 3.16 (dd, 1H, *J* = 13.6, 10.6 Hz), 3.89 (dd, 1H, *J* = 10.4, 7.1 Hz), 4.29–4.33 (m, 1H), 6.16 (d, 2H, *J* = 8.9 Hz), 6.36 (s, 1H), 6.94 (d, 2H, *J* = 8.0 Hz), 7.08 (m, 2H), 7.14-7.16 (m, 2H), 7.22–7.28 (m, 3H), 7.59 (d, 2H, *J* = 8.3 Hz), 7.93 (d, 2H, *J* = 8.4 Hz), 8.27 (d, 2H, *J* = 8.7 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) δ 21.9, 31.8, 34.2, 54.7, 64.0, 80.2, 113.2, 124.2, 126.0, 126.4, 127.8, 128.4, 128.7, 129.4, 130.1, 134.7, 139.4, 142.5, 145.0, 145.1, 147.6; HRMS (ESI-TOF) calcd for $C_{32}H_{34}N_3O_4S$ $(M+H)^+$ 556.2270, found 556.2270.

(2S,4S)-3-(4-fluorophenyl)-2-(4-nitrophenyl)-4-phenyl-1-tosylimidazolidine (5q). The general method described above was followed when aziridine (S)-**1a** (150.3 mg, 0.55 mmol) was reacted with 4-fluoroaniline **2d** (47 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford (2S,4S)-**5q** (204.4 mg, 0.39 mmol) as a white solid in 79% yield. R*f* 0.75 (20% diethyl ether in petroleum ether); MP 163–165 °C; $[\alpha]^{25}_D$ +76.0 (c 0.5 in CH_2Cl_2) for a >99% ee sample. Optical purity was determined by chiral HPLC analysis (Chiralpak AD-H column), hexane–isopropanol, 98:2; flow rate = 1.0 mL/min; t_R 1: 71.9 min (minor), t_R 2: 58.6 min (major); IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 3057, 2925, 2854, 1598, 1522, 1508, 1453, 1407, 1348, 1266, 1233, 1210, 1199, 1164, 1108, 1089, 1059, 1009, 962, 897, 862, 817, 760, 699, 676; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 3.16 (dd, 1H, *J* = 13.4, 10.4 Hz), 3.87 (dd, 1H, *J* = 10.4, 7.3 Hz), 4.27–4.32 (m, 1H), 6.16 (dd, 2H, *J* = 9.1, 4.2

Hz), 6.29 (s, 1H), 6.77 (t, 2H, *J* = 8.5 Hz), 7.06–7.16 (m, 4H), 7.06 (d, 2H, *J* = 8.5 Hz), 7.16 (d, 2H, *J* = 7.9 Hz), 7.22–7.30 (m, 3H), 7.62 (d, 2H, *J* = 8.5 Hz), 7.91 (d, 2H, *J* = 8.5 Hz), 8.28 (d, 2H, *J* = 8.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 21.6, 54.4, 63.9, 80.3, 114.4 (d, $^3J_{C-F}$ = 8.3 Hz), 115.6 (d, $^2J_{C-F}$ = 28.6 Hz), 124.0, 126.1, 127.7, 128.4 (d, $^4J_{C-F}$ = 4.8 Hz), 129.3, 130.1, 134.5, 138.4, 143.3, 145.1, 147.0, 148.3, 156.9 (d, $^1J_{C-F}$ = 255.8 Hz); HRMS (ESI-TOF) calcd for $C_{28}H_{25}FN_3O_4S$ $(M+H)^+$ 518.1550, found 518.1557.

3-(4-chlorophenyl)-2-(4-nitrophenyl)-4-phenyl-1-tosylimidazolidine (5r). The general method described above was followed when aziridine **1a** (150.3 mg, 0.55 mmol) and 4-chloroaniline **2e** (63.7 mg, 0.50 mmol) dissolved in 1.0 mL of DCE was stirred at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5r** (202.9 mg, 0.38 mmol) as a white solid in 76% yield. R*f* 0.62 (20% diethyl ether in petroleum ether); MP 194–196 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 3064, 2925, 1597, 1523, 1495, 1453, 1408, 1348, 1265, 1233, 1200, 1165, 1089, 1058, 1008, 961, 897, 861, 845, 812, 754, 699, 676; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 3.16 (dd, 1H, *J* = 13.4, 10.4 Hz), 3.87 (dd, 1H, *J* = 10.4, 7.3 Hz), 4.30–4.35 (m, 1H), 6.15 (d, 2H, *J* = 8.5 Hz), 6.30 (s, 1H), 7.00–7.07 (m, 4H), 7.12 (d, 2H, *J* = 7.9 Hz), 7.22–7.30 (m, 3H), 7.62 (d, 2H, *J* = 7.9 Hz), 7.89 (d, 2H, *J* = 8.5 Hz), 8.27 (d, 2H, *J* = 8.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 21.6, 54.3, 63.7, 79.9, 114.4, 124.0, 124.6, 126.0, 127.6, 128.3, 128.4, 128.9, 129.3, 130.1, 134.3, 138.3, 145.2, 145.5, 146.5, 148.3; HRMS (ESI-TOF) calcd for $C_{28}H_{25}ClN_3O_4S$ $(M+H)^+$ 534.1254, found 534.1256.

3-isopropyl-2-(4-nitrophenyl)-4-phenyl-1-tosylimidazolidine (5s). The general method described above was followed when aziridine **1a** (150.3 mg, 0.55 mmol) was reacted with isopropylamine **2f** (40 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5s** (174.5 mg, 0.37 mmol) as a white solid in 75% yield. R*f* 0.44 (20% diethyl ether in petroleum ether); MP 110–112 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 2923, 2851, 1599, 1521, 1494, 1456, 1346, 1162, 1092, 1013, 854, 823, 756, 740, 700, 672; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.96 (d, 3H, *J* = 6.4), 1.02 (d, 3H, *J* = 6.4), 2.36 (s, 3H), 2.54–2.60 (m, 1H), 3.05–3.08 (m, 1H), 3.15–3.18 (m, 1H), 4.88–4.91 (m, 1H), 5.55 (s, 1H), 7.12 (d, 2H, *J* = 8.0 Hz), 7.21–7.29 (m, 5H), 7.45 (d, 2H, *J* = 8.3 Hz), 7.68 (d, 2H, *J* = 7.9 Hz), 8.11 (d, 2H, *J* = 8.7 Hz);

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) δ 17.9, 21.8, 22.7, 48.6, 54.0, 62.0, 80.3, 123.6, 127.5, 127.9, 128.0, 128.1, 128.8, 129.7, 129.8, 135.9, 140.5, 144.3, 148.1, 148.3; HRMS (ESI-TOF) calcd for $C_{25}H_{28}N_3O_4S$ $(M+H)^+$ 466.1801, found 466.1801.

2-(4-nitrophenyl)-3,4-diphenyl-1-(phenylsulfonyl)imidazolidine (5t). The general method described above was followed when aziridine **1f** (142.6 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5t** (211.2 mg, 0.43 mmol) as a white solid in 87% yield. R*f* 0.57 (20% diethyl ether in petroleum ether); MP 144–146 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 3064, 2926, 2855, 1600, 1524, 1447, 1408, 1349, 1233, 1200, 1168, 1090, 1011, 963, 898, 861, 823, 749, 699; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.18 (dd, 1H, *J* = 13.6, 10.6 Hz), 3.83 (dd, 1H, *J* = 10.3, 7.0 Hz), 4.26–4.30 (m, 1H), 6.23 (d, 2H, *J* = 8.0 Hz), 6.44 (s, 1H), 6.80 (t, 1H, *J* = 7.3), 7.05–7.15 (m, 4H), 7.21–7.29 (m, 5H), 7.47 (t, 1H, *J* = 7.6), 7.73 (d, 2H, *J* = 7.3 Hz), 7.93 (d, 2H, *J* = 8.3 Hz), 8.28 (d, 2H, *J* = 8.9 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) δ 54.6, 63.8, 80.2, 113.7, 119.9, 124.3, 126.4, 127.9, 128.5, 128.7, 129.5, 129.8, 134.1, 137.9, 139.0, 147.1, 147.3, 148.6; HRMS (ESI-TOF) calcd for $C_{27}H_{24}N_3O_4S$ $(M+H)^+$ 486.1488, found 486.1485

1-((4-(tert-butyl)phenyl)sulfonyl)-2-(4-nitrophenyl)-3,4-diphenylimidazolidine (5u). The general method described above was followed when aziridine **1g** (173.5 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5u** (249.1 mg, 0.46 mmol) as a white solid in 92% yield. R*f* 0.50 (20% diethyl ether in petroleum ether); MP 184–186 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 2963, 2927, 1597, 1524, 1502, 1455, 1401, 1348, 1233, 1199, 1168, 1112, 1086, 1010, 964, 898, 861, 757, 699; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.25 (s, 9H), 3.15–3.19 (m, 1H), 3.71–3.74 (m, 1H), 4.27–4.31 (m, 1H), 6.19 (d, 2H, *J* = 7.8 Hz), 6.43 (s, 1H), 6.78-6.81 (m, 1H), 7.05-7.13 (m, 4H), 7.22-7.28 (m, 5H), 7.64 (d, 2H, *J* = 8.0 Hz), 7.93 (d, 2H, *J* = 8.3 Hz), 8.28 (d, 2H, *J* = 8.3 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) δ 31.3, 35.5, 54.7, 63.8, 80.0, 113.6, 119.7, 124.2, 126.3, 126.7, 127.7, 128.4, 128.7, 129.5, 134.6, 139.2, 147.2, 147.3, 148.6, 158.2; HRMS (ESI-TOF) calcd for $C_{31}H_{32}N_3O_4S$ $(M+H)^+$ 542.2114, found 542.2119.

1-((4-fluorophenyl)sulfonyl)-2-(4-nitrophenyl)-3,4-diphenylimidazolidine (5v). The general method described above was followed when aziridine **1h** (152.5 mg, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **5v** (226.6 mg, 0.45 mmol) as a white solid in 90% yield. R*f* 0.54 (20% diethyl ether in petroleum ether); MP 90–92 °C; IR $\tilde{\nu}_{max}$ (KBr, cm^{-1}) 3064, 2927, 1593, 1523, 1501, 1493, 1454, 1405, 1349, 1294, 1237, 1212, 1200, 1170, 1155, 1088, 1076, 1010, 961, 898, 862, 822, 751, 697; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.20 (dd, 1H, J = 13.6, 10.6 Hz), 3.91 (dd, 1H, J = 10.3, 7.1 Hz), 4.28–4.32 (m, 1H), 6.27 (d, 2H, J = 8.0 Hz), 6.42 (s, 1H), 6.81–6.84 (m, 1H), 6.88–6.92 (m, 2H), 7.09–7.16 (m, 4H), 7.22–7.30 (m, 3H), 7.73–7.76 (m, 2H), 7.93 (d, 2H, J = 8.4 Hz), 8.29 (d, 2H, J = 8.7 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 54.5, 63.8, 80.2, 113.5, 117.0 (d, $^2J_{C–F}$ = 22.7 Hz), 120.1, 124.3, 126.4, 128.58, 128.63, 129.5 (d, $^3J_{C–F}$ = 8.3 Hz), 130.6, 130.7, 133.9 (d, $^4J_{C–F}$ = 2.7 Hz), 138.8, 147.0, 147.1, 148.6, 166.1 (d, $^1J_{C–F}$ = 255.8 Hz); HRMS (ESI-TOF) calcd for $C_{27}H_{23}FN_3O_4S$ $(M+H)^+$ 504.1393, found 504.1390.

2,3,4-triphenyloxazolidine (7a). The general method described above was followed when 2-phenyloxirane **6a** (0.06 mL, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of benzaldehyde **4a** (51 µL, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **7a** (117.5 mg, 0.39 mmol) as a thick liquid in 78% yield. R*f* 0.80 (20% diethyl ether in petroleum ether); IR $\tilde{\nu}_{max}$ (neat, cm^{-1}) 3062, 3029, 2924, 2868, 1599, 1503, 1453, 1363, 1342, 1287, 1211, 1157, 1098, 1076, 1028, 964, 918, 880, 841, 807, 751, 698; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.91 (dd, 1H, J = 8.6, 6.9 Hz), 4.43 (dd, 1H, J = 13.5, 6.9 Hz), 4.86 (t, 1H, J = 6.8 Hz), 6.05 (s, 1H), 6.56 (d, 2H, J = 7.9 Hz), 6.77 (t, 1H, J = 7.3 Hz), 7.12 (dd, 2H, J = 8.6, 7.3 Hz), 7.27–7.44 (m, 6H), 7.51 (d, 2H, J = 7.3 Hz), 7.68 (d, 2H, J = 7.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 65.2, 73.6, 94.8, 114.6, 119.0, 126.9, 127.6, 128.0, 129.0, 129.15, 129.22, 129.3, 140.4, 141.1, 147.2; HRMS (ESI-TOF) calcd for $C_{21}H_{20}NO$ $(M+H)^+$ 302.1545, found 302.1547.

2-(4-nitrophenyl)-3,4-diphenyloxazolidine (7b). The general method described above was followed when 2-phenyloxirane **6a** (0.06 mL, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 4-nitrobenzaldehyde **4d** (75.5

mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **7b** (148.9 mg, 0.43 mmol) as a thick liquid in 86% yield. R*f* 0.78 (20% diethyl ether in petroleum ether); IR $\tilde{\nu}_{max}$ (neat, cm^{-1}) 2924, 2854, 1599, 1521, 1504, 1455, 1344, 1278, 1210, 1161, 1077, 1014, 971, 938, 854, 817, 748, 701; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.99 (dd, 1H, J = 8.5, 1.7 Hz), 4.36 (dd, 1H, *J* = 8.5, 1.0 Hz), 5.18 (dd, 1H, *J* = 6.0, 1.5 Hz), 6.31 (d, 2H, *J* = 7.8 Hz), 6.49 (s, 1H), 6.64 (t, 1H, *J* = 7.4 Hz), 7.03 (dd, 2H, *J* = 7.3, 1.4 Hz), 7.26–7.29 (m, 3H), 7.32–7.35 (m, 2H), 7.60 (d, 2H, *J* = 8.6 Hz), 8.23 (d, 2H, *J* = 8.7 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 65.0, 73.5, 93.3, 114.1, 119.3, 123.9, 126.3, 127.9, 128.3, 129.0, 129.2, 139.9, 146.5, 147.3, 148.3; HRMS (ESI-TOF) calcd for $C_{21}H_{19}N_2O_3$ $(M+H)^+$ 347.1396, found 347.1396.

2-(2-chlorophenyl)-3,4-diphenyloxazolidine (7c). The general method described above was followed when 2-phenyloxirane **6a** (0.06 mL, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 2-chlorobenzaldehyde **4k** (70.3 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **7c** (127.3 mg, 0.38 mmol) as a thick liquid in 76% yield. R*f* 0.52 (10% diethyl ether in petroleum ether); IR $\tilde{\nu}_{max}$ (neat, cm^{-1}) 2921, 2854, 1599, 1572, 1503, 1456, 1369, 1284, 1203, 1190, 1068, 1001, 964, 924, 865, 802, 745, 703; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.97 (dd, 1H, *J* = 8.5, 1.1 Hz), 4.38 (dd, 1H, *J* = 8.6, 6.3 Hz), 5.15 (d, 1H, *J* = 5.1 Hz), 6.29 (d, 2H, *J* = 8.0 Hz), 6.60 (t, 1H, *J* = 7.4 Hz), 6.84 (s, 1H), 7.02 (dd, 2H, *J* = 8.6, 7.4 Hz), 7.00-7.04 (m, 1H), 7.15–7.34 (m, 7H), 7.48 (d, 1H, *J* = 8.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 62.0, 72.6, 88.6, 113.8, 117.1, 126.4, 126.6, 127.5, 128.2, 128.8, 129.0, 130.1, 130.5, 134.4, 135.1, 141.5, 142.3; HRMS (ESI-TOF) calcd for $C_{21}H_{19}ClNO$ $(M+H)^+$ 336.1155, found 336.1145.

2-(2-bromo-5-methoxyphenyl)-3,4-diphenyloxazolidine (7d). The general method described above was followed when 2-phenyloxirane **6a** (0.06 mL, 0.55 mmol) was reacted with aniline **2a** (45 µL, 0.50 mmol) at room temperature for 2 h followed by addition of 2-bromo-5-methoxybenzaldehyde **4l** (107.5 mg, 0.50 mmol) along with PTSA (17.2 mg, 0.10 mmol) and $MgSO_4$ (60.2 mg, 0.50 mmol) in DCE at 65 °C for 6 h to afford **7d** (173.8 mg, 0.42 mmol) as a thick liquid in 85% yield. R*f* 0.45 (10% diethyl ether in petroleum ether); IR $\tilde{\nu}_{max}$ (neat, cm^{-1}) 3024, 2923, 2853, 1599, 1573, 1504, 1455, 1366, 1289, 1206, 1189, 1072, 1001, 966, 925, 864, 803, 746, 701; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.68 (s, 3H), 3.98 (dd, 1H, *J* = 8.5, 1.2 Hz), 4.41

(dd, 1H, *J* = 8.5, 6.1 Hz), 5.17 (d, 1H, *J* = 4.8 Hz), 6.28 (d, 2H, *J* = 7.7 Hz), 6.61 (t, 1H, *J* = 7.3 Hz), 6.72 (s, 1H), 6.72-6.78 (m, 2H), 7.01–7.03 (m, 2H), 7.22–7.34 (m, 5H), 7.56 (dd, 1H, *J* = 12.2, 3.6 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) δ 55.5, 62.1, 72.6, 90.7, 114.0, 114.2, 115.0, 115.1, 117.3, 126.5, 127.6, 128.9, 129.1, 134.4, 137.6, 141.5, 142.3, 158.9; HRMS (ESI-TOF) calcd for $C_{22}H_{21}BrNO_2$ $(M+H)^+$ 410.0756, found 410.0739.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compounds, HPLC chromatograms for ee determination, and crystal structures (PDF)

X-ray crystallographic analysis of (2*S*,4*S*)-**5a** (CIF)

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Notes

The authors declare no competing financial interest.

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