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Diastereoselective One-Pot Synthesis of Oxazolines Using Sulfur Ylides and Acyl Imines

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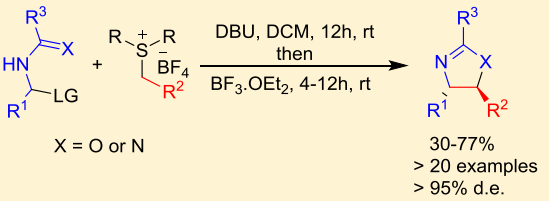
Supporting Information

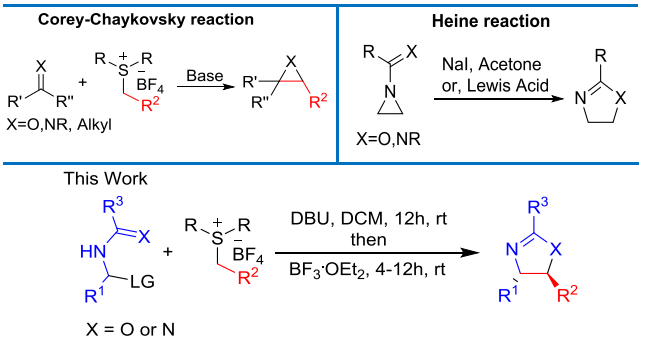
ABSTRACT: This work describes an extended version of the Corey−Chaykovsky reaction to access oxazolines using sulfur ylides and stable precursors of acyl imines. The reaction proceeds through a mixture of aziridines and oxazolines, which provides the *trans*-oxazolines following in situ Heine-type aziridine ring expansion upon treatment with BF_3·OEt_2. Following the same one-pot procedure, amidine imides react with the sulfur ylides to provide imidazolines.



INTRODUCTION

The oxazoline scaffold is an important constituent in bioactive natural products and therapeutics.[1] In addition, many asymmetric catalytic reactions have been reported where oxazolines are key components in ligand structures.[2] Considering the significance of this versatile scaffold, multiple synthetic methods have been reported, but most are focused on cyclodehydration,[3] aldol condensations,[4] or condensation reactions with amino alcohols.[5] Construction of the C4−C5 bond is a less common alternative approach but represents a facile and divergent strategy to incorporate functionalities in the C-2, C-4 and C-5 positions of the oxazoline. We report herein a modified Corey−Chaykovsky-type reaction, followed by an in situ aziridine ring expansion reaction, analogous to the Heine reaction, to access highly substituted oxazolines is a one-pot sequence (Scheme 1).

Scheme 1



In Corey−Chaykovsky reactions,[6] different aldehydes, imines, or alkenes are treated with various sulfur ylides to form epoxides, aziridines, and cycloalkanes, respectively (Scheme 1).[7] In the Heine reaction, 2-substituted oxazolines or imidazolines are prepared via the ring expansion of benzoylated aziridines or imidoyl aziridines, respectively.[8] Herein, we treated stable acyl imines with sulfur ylides to render oxazolines in a one-pot sequence primarily as the *trans*-oxazoline diastereomer (Scheme 1).

Aggarwal and co-worker previously reported an example of an *N*-benzoylimine which reacted with a 3-furyl sulfonium salt to form the anticipated aziridine but with an oxazoline as the side product in low yield.[9] This isolation of the oxazoline was unfortunately limited because of (1) the extended synthesis and instability of the acylimine starting material, (2) the resulting low yielding product mixture, and consequently, (3) a very limited scope. However, this inspiring result lets us to further explore their observations as a new method for oxazoline synthesis, by evaluating stable acylimine precursors and a Heine-type ring expansion of the aziridine intermediates, to access *trans*-oxazolines.

RESULTS AND DISCUSSION

First, 1-benzotriazolyl-*N*-benzoyl-1-phenyl methyl amine (**1**) was evaluated as a stable precursor to form *N*-benzoylbenzaldimine in situ.[10] The acylimine precursor **1**, was treated with benzyldimethylsulfonium tetrafluoroborate salt (**2a**) in dichloromethane (DCM), acetonitrile (CH_3CN), and tetrahydrofuran (THF) and screened for product formation in the presence of several bases (Table 1). Bases included, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,1,3,3-tetramethylguanidine (TMG), 1,3,4,6,7,8-hexahydro-1-methyl-2*H*-pyrimido[1,2-*a*]pyrimidine (MTBD), imidazoline, potassium carbonate (K_2CO_3), potassium hydride (KH), and lithium bis(trimethylsilyl) amide (LiHMDS). Among the bases tested, DBU, MTBD, K_2CO_3, and KH provided the known aziridines and oxazoline (**3a**) as a 1:2 mixture of products by NMR.[11] Confident that we could readily convert the aziridine to the oxazoline product at a later stage with a Lewis acid (Scheme 1),[8d] our initial goal was to maximize conversion of the starting material to the aziridine/oxazoline products, with the least number of variables. Therefore, we optimized the reaction

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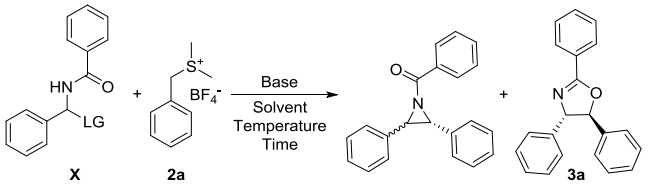
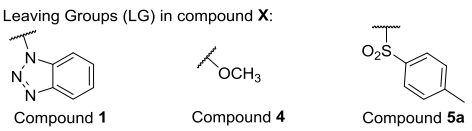
Table 1. Optimization of Oxazoline Synthesis with Different Leaving Groups in Compound X





entry	2a equiv	base	base equiv.	solvent	temp.	time (h)	% yield[a]
Reactions with Compound 1							
1	1.5	MTBD	2.5	DCM	RT	2.5	48
2	2.5	MTBD	4	DCM	RT	2.5	73
3	2.5	MTBD	4	CH_3CN	RT	2.5	57
4	2.5	MTBD	4	THF	RT	4	48
5	2.5	MTBD	5	THF	RT	4	52
6	2.5	DBU	4	THF	RT	4	60
7	2.5	DBU	5	THF	RT	4	63
8	3.5	DBU	5	THF	RT	4	69
9	3.5	DBU	5	THF	reflux	7	48
10	3.5	DBU	5	THF	0 °C	7	52
11	5	DBU	10	THF	RT	7	76
12	2.5	K_2CO_3	4	THF	RT	4	5
13	2.5	KH	4	THF	RT	4	21
14	2.5	KH	15	THF	RT	4	31
15	3.5	KH	15	THF	reflux	7	0
16	3.5	KH	15	THF	0 °C	7	0
17	7	KH	15	THF	RT	7	41
Reactions with Compound 4							
19	3.5	DBU	5	THF	RT	8	20
20	3.5	DBU	5	THF	reflux	8	32
21	3.5	DBU	10	THF	reflux	8	29
22	5	DBU	5	THF	reflux	8	28
23	3.5	DBU	10	THF	reflux	8	29
24	3.5	KH	5	THF	RT	8	0
Reactions with Compound 5a							
25	5	Cs_2CO_3	10	DCM	RT	12	69
26	5	DBU	10	DCM	RT	12	84
27	3.5	DBU	5	DCM	RT	12	85
28	5	DBU	10	THF	RT	12	60
29	3.5	DBU	5	THF	RT	12	48
30	1	DBU	1	DCM	RT	12	11
31	1	DBU	2	DCM	RT	12	72
32	1.2	DBU	2	DCM	RT	12	65
33	1.2	DBU	2.5	DCM	RT	12	77
34	1.5	DBU	2	DCM	RT	12	79
35	**1.5**	**DBU**	**3**	**DCM**	**RT**	**12**	**84**
36	1.5	DBU	4	DCM	RT	12	82
37	2	DBU	2.5	DCM	RT	12	79
38	2	DBU	4	DCM	RT	12	86
39	2	DBU	5	DCM	RT	12	85

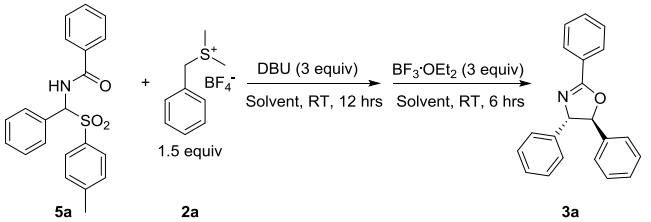
[a]Mixture of trans/cis aziridine and *trans*-oxazoline. RT = room temperature.

conditions next with the most promising bases of our initial screen. It was found that 5 equivalents of sulfonium salt (**2a**) and 10 equiv of DBU gave 76% conversion (Table 1, entry 11) to a 1:2 mixture of the aziridine/oxazoline products.

Next, we examined the stable acylimine precursor, 1-methoxy-*N*-benzoyl-1-phenyl-methylamine (**4**), with the methoxide as its leaving group.[12] Unfortunately, all attempts provided lower conversions to the desired products compared to precursor **1**. We subsequently, evaluated *N*-(phenyl(tosyl)-methyl)benzamide (**5a**), where *p*-toluene sulfinate serves as the in situ leaving group.[13] We presumed that the toluene sulfinate would provide a better leaving group ($pK_a \approx 1.99$)[14] than the previously mentioned precursors, thus resulting in faster acylimine formation. Several conditions were screened with this precursor (Table 1), including Cs_2CO_3 as a base according to the previous reports.[15] Gratifyingly, 3.5 equiv of sulfonium salt (**2a**) and 5 equivalents of DBU in DCM, provided 85% conversion (Table 1, entry 27) to the aziridine/oxazoline product mixture (1:2). The optimal loading amount of the starting material was determined next by altering the equivalents of base and sulfonium salt. Reduction of the amounts of base and sulfur ylide to 1.5 equiv of sulfonium salt (**2a**) and 3 equiv of base did not significantly reduce product formation (84% conversion, Table 1, entry 35) and were therefore selected as the conditions for our future studies.

In the second stage of our studies, we examined the aziridine to oxazoline conversion, which is typically conducted under mild acidic conditions.[8d] To convert the aziridine to oxazoline as part of a one-pot sequence, the reaction was exposed to number of Lewis acids, including $CuCl_2$, $ZnCl_2$, TMSCl, $BF_3{\cdot}OEt_2$, $AlCl_3$, and $TiCl_4$ (see Table S1), following the optimized reaction conditions detailed in Table 1 (entry 35). Among these, $BF_3{\cdot}OEt_2$ gave complete conversion of *cis*- and *trans*-aziridine to only *trans*-oxazoline in 6 h. $BF_3{\cdot}OEt_2$ was then used to confirm the yield of oxazoline in six different solvents (DCM, DME, DMSO, CH_3CN, THF, and toluene). Among these solvents, DME and DCM produced an overall yield of 61 and 60%, respectively, of only the *trans*-oxazoline. None of the other solvents gave higher yields (Table 2). We hypothesize

Table 2. Solvent Screening of Oxazoline Synthesis from Compound 5a



entry	solvent	% yield
1	DCM	**60**
2	DME	61
3	THF	55
4	CH_3CN	53
5	DMSO	55
6	Toluene	23

that the thermodynamically more stable *trans*-oxazoline is formed upon isomerization of the cationic intermediate during the ring expansion (Scheme 2). Considering the similarity in overall yields, DCM was determined as our optimum solvent to avoid a solvent exchange procedural step.

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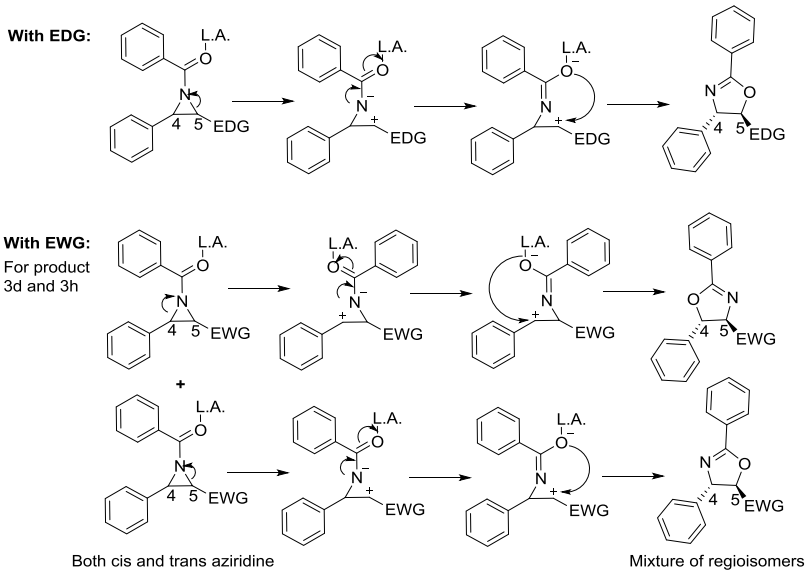
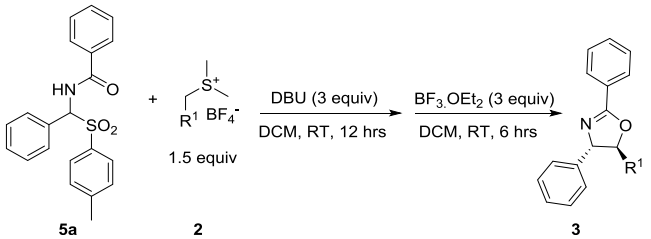
Scheme 2. Ring Opening Mechanism of Aziridine to Oxazoline Providing Two Regioisomers[a]



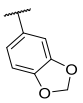
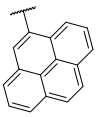
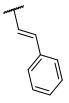
[a]EWG = EW group. EDG = ED group.

After establishing the optimal reaction conditions, we explored the substrate scope by reacting various sulfonium salts with compound **5a**. As shown in Table 3, various sulfonium salts bearing either electron-withdrawing or electron-donating groups readily underwent the reaction in 37−70% overall yield over the two consecutive steps.

Table 3. Scope of Oxazoline Synthesis with Different Sulfonium Salts (2)



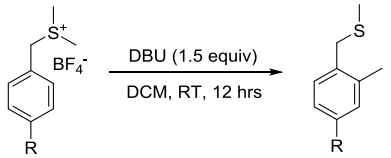
5a 2 3

Entry	2 with R^1	R^2	Product	% Yield
1a		H	**3a**	60
1b		OCH_3	**3b**	51[a]
1c		NO_2	**3c**	37[b]
2			**3e**	**70**
3			**3f**	52
4			**3g**	64

[a]Ran for 12 h after addition of $BF_3{\cdot}OEt_2$. [b]Ran for 4 h after addition of $BF_3{\cdot}OEt_2$.

Interestingly, the nitro-substituted product **3c** was formed in a relative low yield, even though a sulfonium salt containing an electron-withdrawing (EW) group is more reactive than one containing an electron-donating (ED) group. To investigate this further, we studied four sulfonium salts (Table 4, entry 1−4) and upon exposure to DBU, we observed up to 82% of the Stevens rearranged products.[16] From this result, we speculate that using a tetrahydrothiophene instead of dimethyl sulfide with the EW group containing sulfonium salt might reduce this undesired rearrangement.

Table 4. Stevens Rearrangement of Sulfur Ylides



2 6

entry	R	product	% yield
1	H	**6c**	28
2	OCH_3		N/A
3	NO_2	**6a**	82
4	CF_3	**6b**	73

Subsequently, compound **5a** was treated with 1-(4-nitrobenzyl)tetrahydrothiophenium tetrafluoroborate (**7c**) and subsequently optimized to produce 75% of the aziridine/oxazoline product mixture, when using 4 equiv of DBU (Table 5, entry 6).

Under these newly optimized conditions, the same reaction was performed with the addition of $BF_3{\cdot}OEt_2$, which improved the yields of the nitro-substituted *trans*-oxazoline from 37 to 57% (Table 6, entry 1b). A few other tetrahydrothiophene-containing sulfonium salts (**7**) were evaluated with compound **5a** (Table 6). In general, by preventing the Stevens rearrangement, the yields were improved for sulfonium salts containing EW R_1 moieties. When compared to the dimethylsulfonium salts (**2**), the tetrahydrothiophene-contain-

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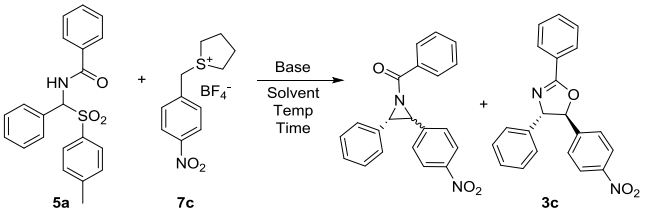
Table 5. Optimization of Oxazoline Synthesis with Tetrahydrothiophene Containing Sulfonium Salt (7c)



entry	7c equiv	base	base equiv	solvent	temp.	time (h)	% yield[a]
1	1.5	MTBD	3	DCM	RT	12	39
2	1.2	DBU	3	DCM	RT	12	28
3	1.2	DBU	4	DCM	RT	12	56
4	1.5	DBU	3	DCM	RT	12	66
5	1.5	DBU	3	DCM	0 °C	12	55
6	1.5	DBU	4	DCM	RT	12	**75**
7	2	DBU	4	DCM	RT	12	74
8	2	DBU	5	DCM	RT	12	72
9[b]	1.5	DBU	3	DCM	RT	12	49

[a]Mixture with *trans*, *cis* aziridines and *trans* oxazoline. [b]With dimethyl sulfonium salt (**2c**).

Table 6. Scope of Oxazoline Synthesis with Different Sulfonium Salts (7)

entry	R^1	product	% yield
1a	H (**7a**)	**3a**	51
1b	NO_2 (**7c**)	**3c**	57[b]
1c	F (**7d**)	**3d**	66[a]
1d	CF_3 (**7h**)	**3h**	55[a]

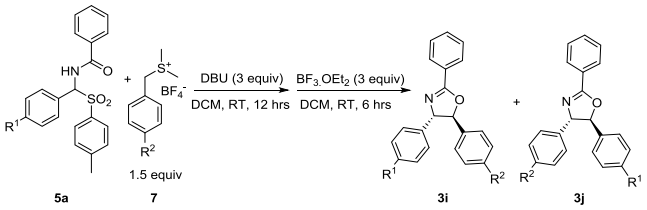
[a]Mixture of regioisomer of *trans*-oxazoline. [b]Ran for 4 h after addition of $BF_3{\cdot}OEt_2$.

ing sulfonium salts (**7**) yielded the corresponding oxazolines in slightly lower yields when neutral or ED sulfur ylides were used.

In addition to a competing Stevens rearrangement, our results also revealed that when EW groups (F, $-CF_3$) are used in the starting material (Table 6, entry 1c and 1d, sulfonium salt **7d** or **7h**), regioisomers of the oxazoline products (**3**) can be formed, via aziridine-ring opening at the C-4 position or C-5 position (Scheme 2). When an ED group ($-OCH_3$) is used, only one regioisomer is formed, as the aziridines primarily open at the C-5 position, as anticipated. The regioisomer of the nitro-containing oxazoline (Table 8, entry 13, **3v**), compound **3c**, was not detected; however, a significant amount of the corresponding oxazole product was observed. The ease of in situ oxidation of this nitro-substituted regioisomer could account for its absence.[17]

To gain insight into the mechanism, the EWG-containing acylimine precursor (Table 7, **5d**) was treated with EDG-containing sulfonium salt (Table 7, **7b**). In addition, the EDG-containing acylimine precursor (Table 7, **5b**) was treated with EWG-containing sulfonium salts (Table 7, **7h**). As anticipated, 40% of only *trans*-oxazoline (**3i**) was isolated from the reaction between **5d** and **7b**, whereas 69% of a 1:1 mixture of the two regioisomers of the *trans*-oxazoline **3i/j** was isolated from the reaction between **5b** and **7h**. These results support the proposed ring opening mechanism depicted in Scheme 2, where the most stabilized carbocation is attacked by the amide oxygen.

Table 7. Regioselective Formation of Oxazolines

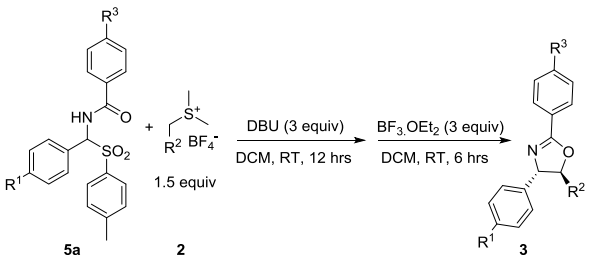


R^1	R^2	product	% yield
$-CF_3$ (**5d**)	$-OCH_3$ (**7b**)	**3i**	40
$-OCH_3$ (**5b**)	$-CF_3$ (**7h**)	**3i/j**	69[a]

[a]1:1 mixture of *trans*-oxazoline regioisomer (**3i** and **3j**).

Next, we examined the scope of this reaction to produce trans oxazolines containing ED and withdrawing groups, using the imine precursor **5a** and sulfur ylide **2** (Table 8). The addition of EW groups on both fragments rendered the *trans* oxazoline **3k** in 72% yield and **3w** in 58% yield, whereas starting materials containing an ED group provided only 34% of the trans oxazoline (**3m**). To further explore the synthetic utility of this methodology, we chose two sulfonium salts, (Table 8, R^2 = **2e** and **2a**), and varied the acylimine precursor **5a**. The electron rich sulfur ylide **2e** provided good yields with substrate **5a** containing both ED and withdrawing groups in the R^1 or R^3 position of **5a**. However, the aryl sulfur ylide **2a** provided modest product formation (41–69%) using a range of electron poor imine precursors (**5c**–**5f**, entry 10–13). Consistent with our previous results (Table 6, entry 1b), the

Table 8. Scope of Oxazoline Synthesis with Different Substitutions in the R^1, R^2, and R^3 Position



Entry	R^1	R^2	R^3	Product	% Yield
1	CF_3 (**5d**)	Ar- CF_3 (**7h**)	H	**3k**	72[a]
2	F (**5e**)	Ar-F (**2d**)	H	**3l**	57
3	OCH_3 (**5b**)	Ar-OCH_3 (**2b**)	H	**3m**	34[b]
4	CN (**5f**)	Ar-CN (**7i**)	H	**3w**	58[a]
5	F (**5e**)		H	**3n**	57
6	CF_3 (**5d**)		H	**3o**	62
7	CN (**5f**)		H	**3p**	77
8	H (**5g**)	**2e**	$-OCH_3$	**3q**	74
9	H (**5h**)		$-NO_2$	**3r**	51
10	-F (**5e**)		H	**3s**	41[c]
11	$-CF_3$ (**5d**)		H	**3t**	61
12	-CN (**5f**)		H	**3u**	69
13	$-NO_2$ (**5c**)	**2a**	H	**3v**	30

[a]Reaction was ran for 9 h after 4 equiv of DBU. [b]Additional 1 equiv of $BF_3{\cdot}OEt_2$ was added and ran for another 6 h. [c]3:1 mixture of *trans*-oxazoline regioisomers (**3s**:**3d**).

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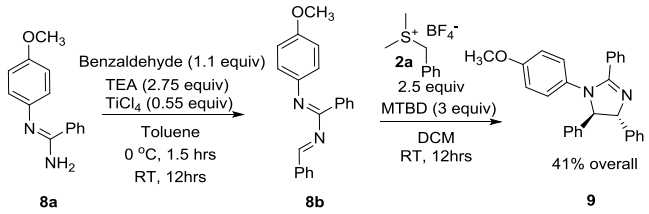
product **3v** was isolated in low yields (30%) with a significant amount of its corresponding oxazole as the side product. A slightly lower yield was obtained in a gram scale (6 mmol of **5f**) synthesis of **3w**, which provided 49% of the trans oxazoline product.

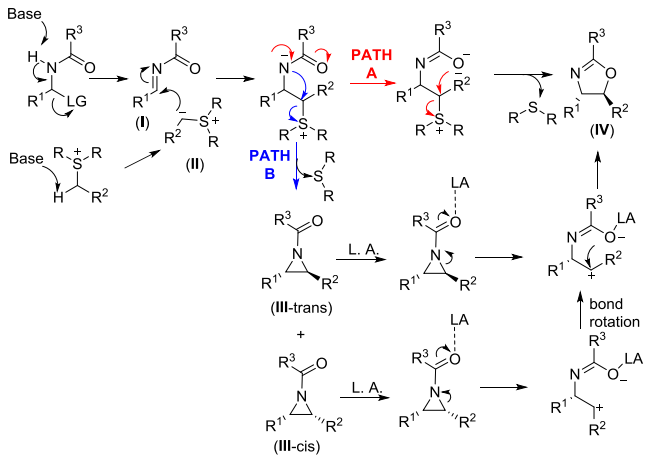
Further expansion of this methodology can readily be envisioned to generate imidazoline scaffolds. While a stable precursor of 1,3-diaza-1,3-butadiene was difficult to form, we used a previously reported method utilizing the amidine **8a**,[18] to generate the reactive intermediate **8b**, which was used without further purification.[19] As anticipated, the diazadiene reacted with **2a** in the presence of MTBD to produce the imidazoline **9** in an overall yield of 41% from the amidine **8a** (Scheme 3).

Scheme 3. Synthesis of Imidazoline



A possible mechanism consistent with our findings described above is depicted in Scheme 4. The reaction first involves

Scheme 4. Proposed Mechanism



deprotonation of the acyl imine precursor to form the acylimine (**I**) and the sulfonium salt to form a sulfur ylide (**II**). Next, the sulfur ylide makes a nucleophilic addition to the imine, and subsequent nucleophilic substitution by nitrogen or oxygen releases the sulfide to form a mixture of the *cis/trans*-aziridines (**III**) (path B) and/or *trans*-oxazoline (**IV**) (path A), respectively. Next, $BF_3{\cdot}OEt_2$ interacts with the oxygen and facilitates ring opening of the aziridine. The intermediate cationic form of the cis/trans aziridines can isomerize and ring closure affords the more thermodynamically stable *trans*-oxazoline (**IV**) as the sole diastereomer detected.

CONCLUSIONS

In summary, we herein report a one-pot, Corey–Chaykovsky–Heine reaction to access oxazolines in good to moderate yield, using sulfur ylides and stable precursors of acyl imines. In the oxazoline synthesis, the reaction sequence involves the formation of both aziridines and oxazolines, where the aziridines are subsequently converted in situ to the *trans*-oxazolines by using a Lewis acid. The reaction suffers from a competing Steven rearrangement when electron poor dimethyl sulfur ylides are used. This can be largely avoided using tetrahydrothiophene-based sulfur ylides. Only the *trans*-oxazoline products were detected and the reaction can be extended to imidazolines upon selection of suitable starting imines.

EXPERIMENTAL SECTION

General Information. Commercially available reagents were used without additional purification. All reactions were performed under an argon or nitrogen atmosphere with commercial-grade reagents. THF was distilled from sodium and benzophenone under nitrogen. DCM (CH_2Cl_2) was purified through a column packed with dry alumina and was dispensed by a nitrogen pressure delivery system. All flasks were oven-dried overnight and cooled under nitrogen. All NMR spectra were recorded on a 500 MHz spectrometer. A mass spectrometer ionization method was ESI with a Quadrupole detector. Infrared spectra were recorded on a Jasco Series 6600 FTIR spectrometer and melting points (mp) were taken on a MEL-TEMP capillary apparatus.

General Method to Synthesize Oxazolines (3). To a solution of dry DCM (20 mL) in a 50 mL dry round bottom flask, sulfonium salt (1.5 equiv, 0.38 mmol) was added followed by DBU (3 or 4 equiv) and the appropriate amide (1 equiv, 0.25 mmol) at room temperature. The reaction was stirred for a total of 12 h under argon. After this, $BF_3{\cdot}OEt_2$ (3 equiv, unless otherwise indicated) was added by the syringe through the rubber septum dropwise for 5 min and stirred for an additional 6 h. After this, 20 mL of 1 M NaOH solution was added and the mixture was extracted with 2 × 15 mL of DCM, using a separatory funnel. The organic layers were combined, dried over Na_2SO_4, and concentrated using a rotary evaporator. The desired compound was purified and isolated using automated CombiFlash chromatography (silica gel, 20–40 microns, gradient 2–20% ethyl acetate in hexane).

*2,4,5-Triphenyl-4,5-dihydrooxazole (**3a**).*[20] Isolated as a solid (45 mg, 60%). mp 98–100 °C. IR: 3031, 2918, 1648, 1493, 1448, 1324, 1062 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-*d*): δ 8.26–8.10 (m, 2H), 7.60–7.55 (m, 1H), 7.52–7.48 (m, 2H), 7.48–7.29 (m, 10H), 5.45 (d, J = 7.6 Hz, 1H), 5.26 (d, J = 7.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-*d*): δ 164.1, 142.0, 140.5, 131.8, 129.0, 128.9, 128.7, 128.5, 128.5, 127.8, 127.5, 126.8, 125.7, 89.0, 79.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{21}H_{18}NO^+$), 300.1383; found, 300.1387.

*5-(4-Methoxyphenyl)-2,4-diphenyl-4,5-dihydrooxazole (**3b**).* Isolated as a colorless solid (42 mg, 51%). mp 118–121 °C. IR: 3030, 2956, 1645, 1513, 1449, 1246, 1063, 1024 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-*d*): δ 8.16 (d, J = 7.3 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.3 Hz, 2H), 7.34–7.27 (m, 5H), 7.00–6.91 (m, 2H), 5.39 (d, J = 7.8 Hz, 1H), 5.26 (d, J = 7.8 Hz, 1H), 3.83 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-*d*): δ 164.1, 159.8, 142.0, 132.3, 131.8, 128.8, 128.7, 128.5, 127.8, 127.5, 127.4, 126.7, 114.3, 89.1, 78.6, 55.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{22}H_{20}NO_2^+$), 330.1489; found, 330.1495.

*5-(4-Nitrophenyl)-2,4-diphenyl-4,5-dihydrooxazole (**3c**).* Isolated as a yellowish solid (32 mg, 37%). mp 101–104 °C. IR: 3028, 2921, 1649, 1522, 1340, 1060 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-*d*): δ 8.27 (d, J = 8.8 Hz, 2H), 8.19–8.09 (m, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 4H), 7.41 (t, J = 7.3 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.32–7.28 (m, 2H), 5.52 (d, J = 7.7 Hz, 1H), 5.16 (d, J = 7.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-*d*): δ 163.9, 147.9, 147.6, 141.1, 132.1, 129.1, 128.7, 128.6, 128.3, 126.9, 126.8, 126.2, 124.3, 87.7, 79.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{21}H_{17}N_2O_3^+$), 345.1234; found, 345.1241.

*5-(4-Fluorophenyl)-2,4-diphenyl-4,5-dihydrooxazole (**3d**).* Isolated as a white solid (53 mg, 66% with regioisomer). mp 53–56 °C. IR: 3032, 2923, 1648, 1508, 1322 1223, 1062 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-*d*): δ 8.13 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.4 Hz,

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1H), 7.50−7.46 (m, 2H), 7.42−7.28 (m, 7H), 7.10 (t, J = 8.6 Hz, 2H), 5.40 (d, J = 7.7 Hz, 1H), 5.20 (d, J = 7.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-d): δ 164.0, 163.7 (d, J = 246 Hz), 141.7, 136.2, 131.8, 128.9, 128.5, 127.9, 127.5 (d, J = 8 Hz), 127.3, 126.7, 125.7, 116.0 (d, J = 21.5 Hz), 88.4, 79.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{21}H_{17}FNO^+$), 318.1289; found, 318.1293.

*5-(Benzo[d][1,3]dioxol-5-yl)-2,4-diphenyl-4,5-dihydro Oxazole (**3e**).* Isolated as a white solid (60 mg, 70%). mp 121−122 °C. IR: 3033, 2980, 1636, 1491, 1444, 1248, 1063, 1020 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-d): δ 8.18−8.10 (m, 2H), 7.58−7.53 (m, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.2 Hz, 2H), 7.35−7.28 (m, 3H), 6.89 (s, 1H), 6.82 (s, 2H), 5.98 (s, 2H), 5.33 (d, J = 7.7 Hz, 1H), 5.23 (d, J = 7.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-d): δ 164.0, 148.3, 147.8, 142.0, 134.2, 131.7, 128.9, 128.6, 128.5, 127.8, 127.5, 126.7, 119.7, 108.5, 106.2, 101.3, 89.1, 78.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{22}H_{18}NO_3^+$), 344.1281; found, 344.1284.

*2,4-Diphenyl-5-(pyren-4-yl)-4,5-dihydrooxazole (**3f**).* Isolated as a white solid (55 mg, 52%). mp 131−135 °C. IR: 3028, 2980, 1648, 1600, 1577, 1448, 1317, 1240, 1061 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-d): δ 8.39−8.29 (m, 2H), 8.23−7.98 (m, 8H), 7.89 (d, J = 9.3 Hz, 1H), 7.61 (m, 3H), 7.53−7.35 (m, 5H), 6.53 (d, J = 7.2 Hz, 1H), 5.46 (d, J = 7.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-d): δ 164.3, 142.0, 133.7, 131.9, 131.4, 131.3, 130.6, 129.0, 128.9, 128.7, 128.1, 128.1, 127.7, 127.6, 127.5, 127.5, 127.3, 126.2, 125.6, 125.4, 125.2, 125.1, 124.8, 122.9, 122.5, 86.9, 79.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{22}H_{20}NO_2^+$), 424.1696; found, 424.1699.

*2,4-Diphenyl-5-((E)-styryl)-4,5-dihydrooxazole (**3g**).* Isolated as a white solid (52 mg, 64%). mp 105−108 °C. IR: 3025, 2924,1646, 1601, 1578, 1449, 1324, 1059 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-d): δ 8.12 (dd, J = 8.3, 1.2 Hz, 2H), 7.57−7.53 (m, 1H), 7.50−7.43 (m, 4H), 7.43−7.27 (m, 8H), 6.68 (d, J = 15.8 Hz, 1H), 6.44 (dd, J = 15.8, 7.9 Hz, 1H), 5.17 (d, J = 7.9 Hz, 1H), 5.05 (td, J = 7.9, 0.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-d): δ 164.0, 141.6, 135.9, 133.6, 131.7, 128.8, 128.7, 128.6, 128.5, 128.4, 127.8, 127.6, 126.8, 126.8, 126.6, 88.8, 76.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{23}H_{20}NO^+$), 326.1539; found, 326.1544.

*2,4-Diphenyl-5-(4-(trifluoromethyl)phenyl)-4,5-dihydro Oxazole (**3h**).* Isolated as a mixture (51 mg, 55% yield) with its regioisomer (**3t**). IR: 3032, 2988, 1675, 1650, 1320, 1281, 1063 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-d): δ 8.18−8.13 (m, 2H), 7.67 (m, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.52−7.31 (m, 9H), 5.49 (d, J = 7.7 Hz, 1H), 5.20 (d, J = 7.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-d): δ 164.0, 144.4, 141.4, 132.0, 130.5 (q, J = 32.4 Hz), 129.0, 128.7, 128.6, 128.1, 127.1, 126.8, 125.9 (q, J = 3.7 Hz), 125.9, 122.9, 88.1, 79.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{22}H_{17}F_3NO^+$), 368.1257; found, 368.1258.

*5-(4-Methoxyphenyl)-2-phenyl-4-(4-(trifluoromethyl) phenyl)-4,5-dihydrooxazole (**3i**).* Isolated as a white solid (40 mg, 40%). mp 99−101 °C. IR: 3062, 2925, 1647, 1513, 1322, 1247, 1064 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-d): δ 8.18−8.09 (m, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.59−7.55 (m, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.33−7.30 (m, 2H), 6.98−6.95 (m, 2H), 5.32 (s, 2H), 3.85 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-d): δ 164.7, 160.0, 146.0, 131.9, 131.7, 129.9 (q, J = 32.4 Hz), 128.7, 128.5, 127.5, 127.3, 127.1, 125.8 (q, J = 3.7 Hz), 123.1, 114.4, 88.9, 78.3, 55.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{23}H_{19}F_3NO_2^+$), 398.1362; found, 398.1367.

*4-(4-Methoxyphenyl)-2-phenyl-5-(4-(trifluoromethyl) phenyl)-4,5-dihydrooxazole (**3j**).* Isolated as a white solid (combined yield **3i**/**3j** (1:1) as poorly separable mixture is 69 mg, 69%). A small amount of pure **3j** was used for complete characterization. mp 95−97 °C. IR: 3063, 2926, 1646, 1514, 1322, 1248, 1065 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-d): δ 8.12 (d, J = 7.6 Hz, 2H), 7.66 (d, J = 8.1 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.53−7.41 (m, 4H), 7.22 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 5.44 (d, J = 7.7 Hz, 1H), 5.12 (d, J = 7.7 Hz, 1H), 3.82 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-d): δ 163.7, 159.4, 144.5, 133.5, 131.9, 130.7 (q, J = 32.4 Hz), 128.6, 128.6, 128.0, 127.2, 125.9 (q, J = 3.7 Hz), 125.8, 125.1, 114.4, 88.2, 78.8, 55.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{23}H_{19}F_3NO_2^+$), 398.1362; found, 398.1365.

*4,5-Bis(4-(trifluoromethyl)phenyl)-2-phenyl-4,5-dihydrooxazole (**3k**).* Isolated as a white solid (79 mg, 72%). mp 98−101 °C. IR: 3058, 2924, 1694, 1322, 1109, 1062 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-d): δ 8.14 (dd, J = 8.2, 1.0 Hz, 2H), 7.69 (dd, J = 14.7, 8.2 Hz, 4H), 7.62−7.58 (m, 1H), 7.53−7.47 (m, 4H), 7.43 (d, J = 8.2 Hz, 2H), 5.44 (d, J = 7.8 Hz, 1H), 5.26 (d, J = 7.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-d): δ 164.7, 145.3, 143.8, 132.2, 130.8 (q, J = 32.7 Hz), 130.5 (q, J = 32.5 Hz), 128.7, 128.7, 127.2, 126.8, 126.1 (q, J = 3.4 Hz), 126.0 (q, J = 3.4 Hz), 126.0, 125.1, 122.8, 88.0, 78.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{23}H_{16}F_6NO^+$), 436.1131; found, 436.1134.

*4,5-Bis(4-fluorophenyl)-2-phenyl-4,5-dihydrooxazole (**3l**).* Isolated as a white solid (48 mg, 57%). mp 85−88 °C. IR: 3053, 2923, 1650, 1604, 1507, 1319, 1219, 1063 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-d): δ 8.17−8.06 (m, 2H), 7.59−7.53 (m, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.32 (m, 2H), 7.27−7.24 (m, 2H), 7.16−6.99 (m, 4H), 5.34 (d, J = 7.8 Hz, 1H), 5.17 (d, J = 7.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-d): δ 164.1, 163.8 (d, J = 246 Hz), 163.4 (d, J = 245 Hz), 137.5 (d, J = 3 Hz), 135.9 (d, J = 3 Hz), 131.9, 128.6, 128.6, 128.4 (d, J = 8 Hz), 127.5 (d, J = 8 Hz), 127.2, 116.0 (d, J = 21.5 Hz), 115.7 (d, J = 21.5 Hz), 88.5, 78.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{21}H_{16}F_2NO^+$), 336.1194; found, 336.1200.

*4,5-Bis(4-methoxyphenyl)-2-phenyl-4,5-dihydrooxazole (**3m**).* Isolated as a white solid (31 mg, 34%). mp 93−95 °C. IR: 3063, 2927, 1645, 1609, 1509, 1241, 1146, 1029 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-d): δ 8.17−8.08 (m, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H), 6.92 (dd, J = 14.1, 8.7 Hz, 4H), 5.34 (d, J = 7.8 Hz, 1H), 5.18 (d, J = 7.8 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H). $^{13}C\{^1H\}$NMR (126 MHz, $CHCl_3$-d): δ 163.8, 159.8, 159.2, 134.2, 132.4, 131.6, 128.6, 128.4, 127.9, 127.7, 127.3, 114.3, 114.2, 89.1, 78.3, 55.3, 55.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{23}H_{22}NO_3^+$), 360.1594; found, 360.1599.

*5-(Benzo[d][1,3]dioxol-5-yl)-4-(4-fluorophenyl)-2-phenyl-4,5-dihydrooxazole (**3n**).* Isolated as a yellowish solid (52 mg, 57%). mp 80−83 °C. IR: 3038, 2922, 1638, 1504, 1492, 1444, 1336, 1248, 1227, 1062, 1032 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-d): δ 8.14−8.08 (m, 2H), 7.55 (d, J = 7.5 Hz, 1H), 7.49 (d, J = 7.8 Hz, 2H), 7.27−7.23 (m, 2H), 7.07 (t, J = 8.7 Hz, 2H), 6.86 (d, J = 1.6 Hz, 1H), 6.84−6.78 (m, 2H), 6.00 (s, 2H), 5.26 (d, J = 7.8 Hz, 1H), 5.18 (d, J = 7.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-d): δ 164.1, 163.4 (d, J = 246 Hz), 148.3, 147.9, 137.7, 133.9, 131.8, 128.6, 128.5, 128.3 (d, J = 8 Hz), 127.3, 119.7, 115.8 (d, J = 21.5 Hz), 108.5, 106.1, 101.3, 89.2, 78.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{22}H_{17}FNO_3^+$), 362.1187; found, 362.1187.

*5-(Benzo[d][1,3]dioxol-5-yl)-2-phenyl-4-(4-(trifluoro methyl)-phenyl)-4,5-dihydrooxazole (**3o**).* Isolated as a pink solid (64 mg, 62%). mp 87−90 °C. IR: 3067, 2904, 1638, 1487, 1447, 1319, 1247, 1127, 1065, 1038 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-d): δ 8.14−8.08 (m, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 1.4 Hz, 1H), 6.84−6.77 (m, 2H), 6.00 (s, 2H), 5.27 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-d): δ 164.6, 148.4, 148.1, 145.8, 133.6, 132.0, 129.9 (q, J = 32.4 Hz), 128.6, 128.6, 127.2, 127.0, 125.8 (q, J = 3.7 Hz), 123.0, 119.9, 108.5, 106.2, 101.4, 89.0, 78.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{23}H_{17}F_3NO_3^+$), 412.1155; found, 412.1157.

*4-(5-(Benzo[d][1,3]dioxol-5-yl)-2-phenyl-4,5-dihydro Oxazol-4-yl)benzonitrile (**3p**).* Isolated as a colorless solid (71 mg, 77%). mp 112−114 °C. IR: 3062, 2978, 2227, 1643, 1489, 1445, 1210, 1037 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-d): δ 8.10 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 6.88−6.82 (m, 2H), 6.80 (dd, J = 8.0, 1.7 Hz, 1H), 6.01 (s, 2H), 5.27 (d, J = 8.0 Hz, 1H), 5.23 (d, J = 8.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-d): δ 164.9, 148.5, 148.2, 147.1, 133.2, 132.7, 132.1, 128.7, 128.6, 127.4, 126.9, 120.0, 118.7, 111.7, 108.6, 106.2, 101.4, 88.9, 78.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for ($C_{23}H_{17}N_2O_3^+$), 369.1234; found, 369.1234.

*5-(Benzo[d][1,3]dioxol-5-yl)-2-(4-methoxyphenyl)-4-phenyl-4,5-dihydrooxazole (**3q**).*[21] Isolated as a white solid (69 mg, 74%). mp 93−95 °C. IR: 3029, 2979, 1643, 1608, 1501, 1488, 1446, 1339, 1243,

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1146, 1038 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-*d*): δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.39−7.27 (m, 5H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.87 (s, 1H), 6.83−6.78 (m, 2H), 5.99 (s, 2H), 5.29 (d, *J* = 7.6 Hz, 1H), 5.17 (d, *J* = 7.6 Hz, 1H), 3.89 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-*d*): δ 163.8, 162.4, 148.2, 147.8, 142.1, 134.3, 130.4, 128.8, 127.7, 126.7, 119.9, 119.7, 113.8, 108.4, 106.2, 101.3, 89.0, 78.8, 55.5. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for ($C_{23}H_{20}NO_4^+$), 374.1387; found, 374.1387.

*5-(Benzo[d][1,3]dioxol-5-yl)-2-(4-nitrophenyl)-4-phenyl-4,5-dihydrooxazole (**3r**).*[22] Isolated as a yellowish solid (50 mg, 51%). mp 118−120 °C. IR: 3068, 2919, 1641, 1594, 1511, 1491, 1335, 1253, 1072, 1040 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-*d*): δ 8.37−8.25 (m, 4H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.29−7.26 (m, 2H), 6.88−6.77 (m, 3H), 6.00 (s, 2H), 5.38 (d, *J* = 8.1 Hz, 1H), 5.26 (d, *J* = 8.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-*d*): δ 162.1, 149.7, 148.4, 148.1, 141.1, 133.3, 133.3, 129.6, 129.0, 128.1, 126.6, 123.7, 120.0, 108.5, 106.2, 101.4, 89.8, 78.9. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for ($C_{22}H_{17}N_2O_5^+$), 389.1132; found, 389.1133.

*4-(4-Fluorophenyl)-2,5-diphenyl-4,5-dihydrooxazole (**3s**).* Isolated as a white solid (33 mg, 41% with its regioisomer). mp 89−93 °C. IR: 3032, 2980, 1651, 1507, 1319, 1222, 1063 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-*d*): δ 8.19−8.07 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.43−7.34 (m, 5H), 7.28 (dd, *J* = 6.0, 2.7 Hz, 2H), 7.11−7.02 (m, 2H), 5.36 (d, *J* = 7.8 Hz, 1H), 5.21 (d, *J* = 7.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-*d*): δ 164.2, 163.4 (d, *J* = 246 Hz), 140.2, 137.7, 131.8, 129.0, 128.6, 128.6, 128.5, 128.5 (d, *J* = 8 Hz), 127.3, 125.7, 115.8 (d, *J* = 21.5 Hz), 89.1, 78.4. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for ($C_{21}H_{17}FNO^+$), 318.1289; found, 318.1292.

*2,5-Diphenyl-4-(4-(trifluoromethyl)phenyl)-4,5-dihydro Oxazole (**3t**).* Isolated as a white solid (56 mg, 61%). mp 92−95 °C. IR: 3031, 2923, 1645, 1619, 1321, 1120, 1065, 1019 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-*d*): δ 8.22−8.11 (m, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.47−7.35 (m, 7H), 5.39 (d, *J* = 7.9 Hz, 1H), 5.32 (d, *J* = 7.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-*d*): δ 164.7, 145.9, 139.9, 132.0, 130.2 (q, *J* = 32.4 Hz), 129.1, 128.8, 128.7, 128.6, 127.2, 127.1, 125.9 (q, *J* = 3.7 Hz), 125.8, 123.0, 88.9, 78.5. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for ($C_{22}H_{17}F_3NO^+$), 368.1257; found, 368.1261.

*4-(2,5-Diphenyl-4,5-dihydrooxazol-4-yl)benzonitrile (**3u**).* Isolated as a colorless solid (56 mg, 69%). mp 116−118 °C. IR: 3065, 2923, 2225, 1643, 1323, 1278, 1088, 1065 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-*d*): δ 8.13 (d, *J* = 7.4 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.47−7.39 (m, 5H), 7.36 (d, *J* = 6.8 Hz, 2H), 5.34 (d, *J* = 7.9 Hz, 1H), 5.30 (d, *J* = 7.9 Hz, 1H). $^{13}C\{^1H\}$NMR (126 MHz, $CHCl_3$-*d*): δ 165.0, 147.1, 139.6, 132.7, 132.1, 129.2, 128.9, 128.7, 128.6, 127.5, 127.0, 125.8, 118.7, 111.7, 88.8, 78.5. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for ($C_{22}H_{17}N_2O^+$), 325.1335; found, 325.1338.

*4-(4-Nitrophenyl)-2,5-diphenyl-4,5-dihydrooxazole (**3v**).* Isolated as a yellowish solid (26 mg, 30%). mp 82−85 °C. IR: 3031, 2923, 1678, 1601, 1518, 1343, 1316, 1064 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$-*d*): δ 8.24 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52−7.41 (m, 7H), 7.38−7.34 (m, 2H), 5.37−5.32 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-*d*): δ 165.1, 149.1, 147.6, 139.5, 132.2, 129.2, 129.0, 128.7, 128.6, 127.6, 127.0, 125.9, 124.1, 88.8, 78.3. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for ($C_{21}H_{17}N_2O_3^+$), 345.1234; found, 345.1239.

*4,4′-(2-Phenyl-4,5-dihydrooxazole-4,5-diyl) Dibenzonitrile (**3w**).* Isolated as a white solid (50 mg, 58%). mp 146−148 °C. ^1H NMR (500 MHz, $CHCl_3$-*d*), 8.12 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.73 (dd, *J* = 14.2, 8.3 Hz, 4H), 7.63−7.59 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 5.40 (d, *J* = 7.7 Hz, 1H), 5.23 (d, *J* = 7.7 Hz, 1H). $^{13}C\{^1H\}$NMR (126 MHz, $CHCl_3$-*d*): δ 164.9, 146.3, 144.8, 133.0, 132.9, 132.4, 128.7, 128.7, 127.5, 126.4, 126.2, 118.5, 118.3, 112.8, 112.2, 87.6, 78.7. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for ($C_{23}H_{16}N_3O^+$), 350.1288; found, 350.1291.

*1-(4-Methoxyphenyl)-2,4,5-triphenyl-4,5-dihydro-1H-imidazole (**9**).* To a solution of dry DCM (20 mL) in a 50 mL dry round bottom flask was added benzyldimethyl sulfonium tetrafluoroborate (2.5 equiv) followed by MTBD (3 equiv) and subsequently, crude *N*-(benzylidene)-*N*′-(4-methoxyphenyl) benzimidamide (**8b**) (1 equiv). The reaction was stirred for 12 h at room temperature. After this, the solvent was evaporated and the crude product was purified using automated CombiFlash chromatography (silica gel 20−40 microns, using 25% ethyl acetate in hexane) to yield imidazoline **9** (trans only) as an oil in 41% (42 mg) yield overall from **8a**. IR: 3053, 3027, 2922, 2837, 1611, 1570, 1504, 1149, 1424, 1374, 1330, 1285, 1245, 1173, 1125, 1074. ^1H NMR (500 MHz, $CHCl_3$-*d*): δ 7.73 (d, *J* = 7.4 Hz, 2H), 7.45−7.26 (m, 13H), 6.70 (d, *J* = 8.9 Hz, 2H), 6.60 (d, *J* = 8.9 Hz, 2H), 5.12 (d, *J* = 7.2 Hz, 1H), 4.65 (d, *J* = 7.2 Hz, 1H), 3.67 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CHCl_3$-*d*): δ 163.6, 156.9, 143.7, 143.4, 136.6, 131.0, 130.1, 129.2, 129.0, 128.7, 128.1, 127.8, 127.3, 126.9, 126.6, 126.1, 114.1, 79.3, 78.4, 55.3. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for ($C_{28}H_{25}N_2O^+$), 405.1961; found, 405.1967.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b00883.

Detailed experimental procedures and spectroscopy data for all compounds synthesized, including the starting materials (**1**), (**4**), (**5a−5h**), and dimethylsulfonium salts (**2a−2h**), rearranged products (**6a−6c**), tetrahydrothiophene salts (**7a−d**, **7h**), and amidine precursors (**8a−8b**) (PDF)

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Notes

The authors declare no competing financial interest.

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