The Free Internet Journal for Organic Chemistry

Paper

Archive for Organic Chemistry

Arkivoc **2017**, part v, 314-326

Synthesis of substituted imid(thi)azolidines by [3+2] cycloaddition of aziridines with nitriles(isothiocyanates) via visible light photocatalysis

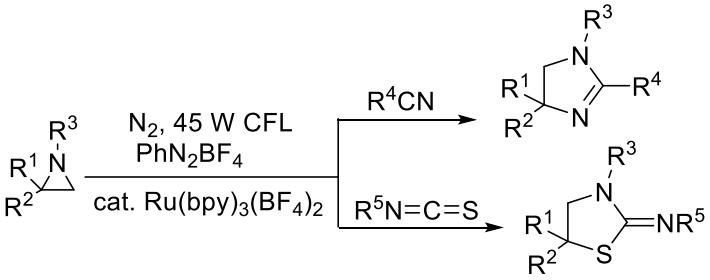
Qianwen Ye,[a] Xiaoliang Xu,*[a] Dongping Cheng,*[b] Baochuan Guan,[a] Hongfeng Ye,[a] and Xiaonian Li*[a]

[a]College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China
[b]College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou 310014, P. R. China
Email: xuxiaoliang@zjut.edu.cn, chengdp@zjut.edu.cn, xnli@zjut.edu.cn

Received 07-02-2017 **Accepted** 10-22-2017 **Published on line** 11-19-2017

Abstract

The [3+2] cycloaddition reaction of aziridines with nitriles (isothiocyanates) has been developed using visible light photocatalysis. Two types of five-membered heterocyclic compounds, imidazolidines and thiazolidines, were synthesized in mild conditions. An oxidative quenching cycle mechanism is probably involved.



Keywords: Aziridines, nitriles, isothiocyanates, [3+2] cycloaddition, photocatalysis

Introduction

Photoredox catalysis by means of visible light is considered an ideal route for green, economic and abundant chemical synthesis. Different from many conventional reagents, visible light can be used as a type of renewable source.[1-5] Since it was proposed by Ciamician in 1912, this concept has been almost silent for half a century or more.[6] It was not until 2008 that MacMillan firstly reported α-alkylation of aldehydes and ketones by photocatalysis, which attracted considerable attention from chemists.[7] Subsequently, many research groups have made extensive and outstanding contributions in this field[1] and photocatalysis has evolved into an important means in organic synthesis.

Imidazolines and thiazolines are important heterocyclic systems which have a wide range of applications in bio-activities[8-9] and pharmaceuticals.[10-11] Some derivatives are used for the synthesis of anti-inflammatory, antioxidant, anti-nociceptive and anticarcinogenic drugs. Additionally, imidazolines have been used as metal complex ligands[12] and auxiliary groups[13] in asymmetric synthesis.

Many methods have been developed for the synthesis of imidazolines and thiazolines. The traditional process for imidazolines is the cyclization of 1,2-diamines with carboxylic acids under rigorous conditions. Unfortunately, 1,2-diamines are not easy to synthesize and the substrate scopes are quite narrow.[14] Booker-Milburn and Zhou reported the preparation of imidazolines from olefins, *N*-chlorosaccharin (NCSacc) or NBS (cationic Br as initiator) and a nitrile in two steps under harsh conditions.[15-16] In 2016, Xu developed the synthesis of imidazoline via visible light catalysis from alkenes, an *N*-Ts-1-aminopyridinium salt and a nitrile but the transformation was unsuccessful for non-conjugated alkenes.[17] Catalyzed by Lewis acid or transition metals, the [3+2] cycloaddition of aziridines with nitriles can be performed to acquire imidazolines.[18-24] For the synthesis of 2-iminothiazolidines, the [3+2] cycloaddition reaction of aziridines with isothiocayanates could also be accomplished using several catalysts or stoichiometric reagents.[25-26]

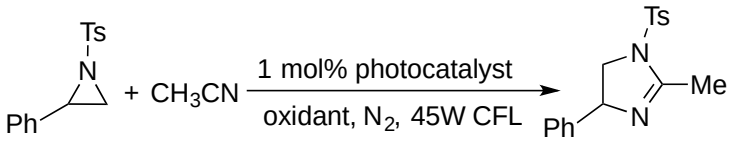
Results and Discussion

Although many methods have been reported for the synthesis of substituted imidazolidines and thiazolidines, it is important to find new synthetic methods from the viewpoint of synthetic diversity. In 2014, Xia group reported the ring opening reaction of aziridines by visible light photocatalysis with $Na_2S_2O_8$ as an oxidant.[27] According to the oxidative quenching cycle mechanism of visible light photocatalysis of this reaction, we speculated it might be possible to carry out a [3+2] cycloaddition reaction of aziridines and nitriles under these conditions.

In order to find optimal conditions, the reaction of aziridine **1a** and acetonitrile **2a** was performed with 1.2 eq of PhN_2BF_4 in the presence of 1 mol% $Ru(bpy)_3Cl_2{\cdot}6H_2O$ under air (Table 1). The reaction mixture was illuminated with a 45W white household lamp at room temperature for four hours monitored by TLC. We were delighted to find that the desired product **3a** could be isolated in 73% yield (entry 1). Extending the reaction time to five, six, and seven hours respectively, did not increase the yield. The reaction proceeded very slowly and the yields were very low in the absence of light or photocatalyst (entries 2-3). The yield was improved slightly when the reaction was carried out under a N_2 atmosphere (entry 4). The desired product could not be obtained without PhN_2BF_4, which indicated that an oxidant was essential for the reaction (entry 5). All of the tested catalysts promoted the reaction (entries 6-11), but the best yield was obtained using $Ru(bpy)_3(BF_4)_2$ as a photocatalyst (entry 8). Using I_2, DDQ, NBS, $Na_2S_2O_8$, $K_2S_2O_8$, or $PhI(OAc)_2$ as the substituted oxidant, the reaction failed (entry 12). A 64% yield of the product could be detected by GC analysis

when $(NH_4)_2S_2O_8$ was used as the oxidant (entry 13). The desired product could not be obtained when $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ ($E_{1/2}III^*/II$=+1.21 V vs SCE in CH_3CN) or $Ru(bpz)_3(PF_6)_2$ ($E_{1/2}III/II$=+1.86V vs SCE in CH_3CN) were tried in the absence of PhN_2BF_4 (entries 14-15). The yields were 7%, 15%, 30% and 70% respectively when PhN_2BF_4 was used at 5%, 10%, 20% and 50%. A small amount of biphenyl was detected by GC analysis.

Table 1. Optimization of the reaction conditions[a]



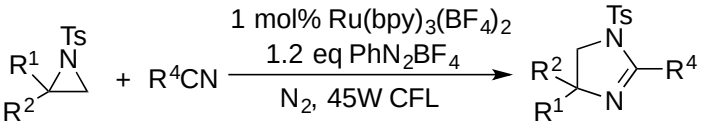
1a **2a** **3a**

Entry	Catalyst	Oxidant	Yield(%)[b]
1[c]	$Ru(bpy)_3Cl_2·6H_2O$	PhN_2BF_4	79(73)
2[d]	-	PhN_2BF_4	11
3[e]	$Ru(bpy)_3Cl_2·6H_2O$	PhN_2BF_4	2
4[f]	$Ru(bpy)_3Cl_2·6H_2O$	PhN_2BF_4	85(75)
5	$Ru(bpy)_3Cl_2·6H_2O$	-	0
6	EosinY	PhN_2BF_4	37
7	$Ir(ppy)_3$	PhN_2BF_4	87
8	$Ru(bpy)_3(BF_4)_2$	PhN_2BF_4	90(83)
9	$Ir(ppy)_2(dtbbpy)PF_6$	PhN_2BF_4	83
10	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	PhN_2BF_4	60
11	$Ru(bpz)_3(PF_6)_2$	PhN_2BF_4	20
12[g]	$Ru(bpy)_3(BF_4)_2$	see footnote	0
13	$Ru(bpy)_3(BF_4)_2$	$(NH_4)_2S_2O_8$	64
14	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	-	0
15	$Ru(bpz)_3(PF_6)_2$	-	0
16[h]	$Ru(bpy)_3(BF_4)_2$	PhN_2BF_4	see footnote

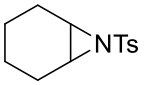
[a]**1a** (0.5 mmol), **2a** (40 mmol, 2 mL), oxidant (0.6 mmol, 1.2 eq), photocatalyst (0.005 mmol, 1 mol%), 45 W CFL (compact fluorescent lamp) irradiation under N_2 atmosphere at r.t. for 4 h unless otherwise noted. [b]Determined by GC (yield of isolated product based on **1a** in parentheses). [c]Under air. [d]No photocatalyst. [e]No light. [f]Under N_2. [g]Oxidants were I_2, DDQ, NBS, $PhI(OAc)_2$, $Na_2S_2O_8$, $K_2S_2O_8$. [h]CH_3CN (2.5 mmol, 5 eq), various solvents (2 mL), CH_2Cl_2, DCE, THF, DMSO, gave yields of 60%, 74%, 0%, 0% respectively.

With the optimal reaction conditions in hand, the substrate scope of the 2-alkyl(aryl)-*N*-tosylaziridine was investigated (Table 2). The substituent of the aryl ring of the 2-aryl-*N*-tosylaziridine, such as F, Cl, Me generated the cycloaddition products in good yields (**3b-e**). However, the bromo substituted starting material gave slightly lower yield (**3f**). 2-Methyl-2-phenyl-*N*-tosylaziridine, 2-octyl-*N*-tosylaziridine, *N*-tosylcyclohexanoaziridine, were also suitable for the reaction (**3g-i**). Next, several alkyl nitriles were examined and the corresponding products were obtained in moderate yields (**3j-n**). Only one nitrile group participated in the reaction when 1,4-dicyanobenzene was used as the substrate (**3m**).

Table 2. Cycloaddition reactions of aziridines and nitriles[a]



1 **2** **3**

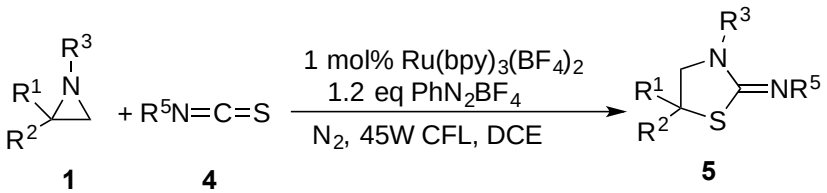
Entry	R^1; R^2	R^4	Yield(%)[b]
1	Ph; H (**1a**)	CH_3 (**2a**)	83 (**3a**[29])
2	4-FC_6H_4; H (**1b**)	**2a**	85 (**3b**)
3	4-ClC_6H_4; H (**1c**)	**2a**	84 (**3c**[30])
4	2-ClC_6H_4; H (**1d**)	**2a**	88 (**3d**[29])
5	4-MeC_6H_4; H (**1e**)	**2a**	76 (**3e**[29])
6	4-BrC_6H_4; H (**1f**)	**2a**	54 (**3f**[30])
7	Ph; Me (**1g**)	**2a**	55 (**3g**)
8	C_8H_{17}; H (**1h**)	**2a**	40 (**3h**)
9	 (**1i**)	**2a**	57 (**3i**[31])
10	**1a**	Ph (**2b**)	69 (**3j**[29])
11	**1a**	$PhCH_2$ (**2c**)	73 (**3k**[29])
12	**1a**	1-naphthyl (**2d**)	43 (**3l**)
13[c]	**1a**	4-NCC_6H_4 (**2e**)	40 (**3m**)
14	**1a**	4-MeC_6H_4 (**2f**)	53 (**3n**)

[a]**1** (0.5 mmol), **2** (**a**:40 mmol, **b**:20 mmol, **c**:17 mmol, **d**:14 mmol, **f**:17 mmol, 2 mL), PhN_2BF_4 (0.6 mmol, 1.2 eq), $Ru(bpy)_3(BF_4)_2$ (0.005 mmol, 1 mol%), 45W CFL, N_2, r.t., 4 h. [b]Yield of isolated product. [c]Nitrile (2.5 mmol, 5 eq), DCE (2 mL).

To further demonstrate the generality of the [3+2] cycloaddition reaction, we employed isothiocyanates **4** as dipolarophiles to synthesize 2-iminothiazolidines. Based on the reaction of **1a** and **2a**, the reaction conditions of **1a** and **4a** were screened briefly. The reaction did not proceed without light or photocatalyst. A lower yield was obtained under blue LED illumination perhaps because the six-membered ring dimer was formed as the by-product.[28] Diphenyl was also detected by GC analysis in the reaction mixture. Screening the solvent, oxidant, etc. showed the optimal conditions were similar to that for the synthesis of **3a** (see above).

A series of aryl or alkyl isothiocyanates were surveyed under the optimal conditions (Table 3). The expected products **5** were obtained in moderate yields. No obvious electronic effect was observed. The yield was slightly lower when 2-(2-chlorophenyl)-*N*-tosylaziridine **5d** was used as the substrate and the steric effect may be responsible for this result. 2-Phenyl-1-(phenylsulfonyl)aziridine **5q** was also a good candidate and afforded the corresponding product in 62% yield.

Table 3. Cycloaddition reactions of aziridines and isothiocyanates[a,b]

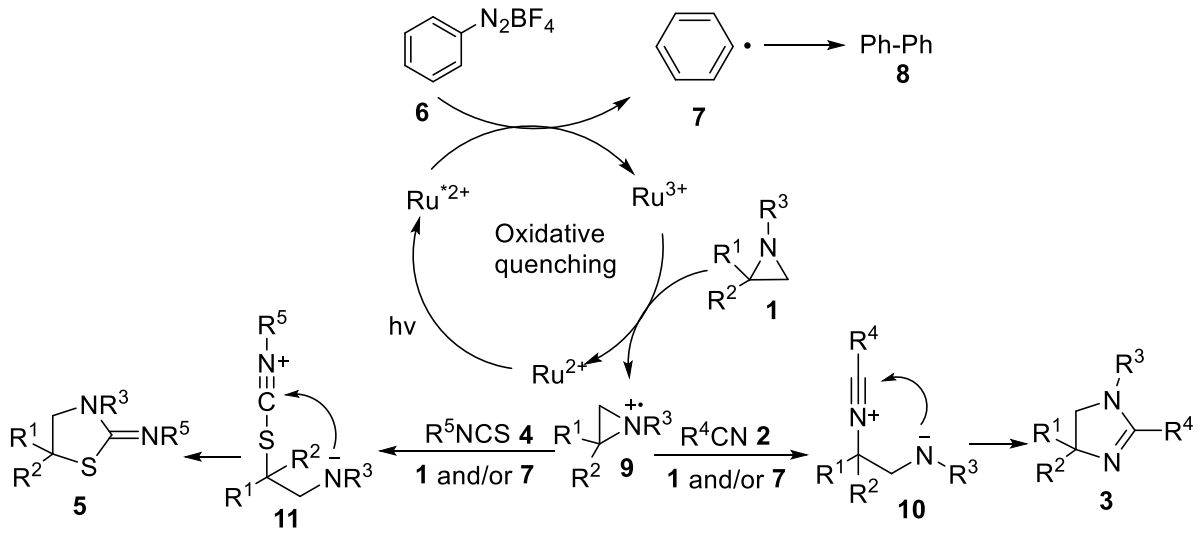


1 **4** **5**

Entry	R^1; R^2; R^3	R^5	Yield(%)
1	**1a**	Ph (**4a**)	59 (**5a**[32])
2	**1b**	**4a**	49 (**5b**[33])
3	**1e**	**4a**	55 (**5c**[34])
4	**1d**	**4a**	34 (**5d**[34])
5	**1f**	**4a**	55 (**5e**[34])
6	**1a**	4-$MeOC_6H_4$ (**4b**)	58 (**5f**[34])
7	**1a**	4-FC_6H_4 (**4c**)	53 (**5g**[34])
8	**1a**	2-MeC_6H_4 (**4d**)	48 (**5h**)
9	**1a**	4-BrC_6H_4 (**4e**)	47 (**5i**)
10	**1a**	4-ClC_6H_4 (**4f**)	51 (**5j**)
11	**1a**	^{i}Pr (**4g**)	52 (**5k**[35])
12	**1a**	cyclohexyl (**4h**)	54 (**5l**[34])
13	**1a**	C_4H_9 (**4i**)	52 (**5m**[34])
14	**1a**	$PhCH_2$ (**4j**)	48 (**5n**)
15	**1a**	1-methylbenzyl (**4k**)	49 (**5o**)
16	**1a**	1-naphthyl (**4l**)	48 (**5p**[33])
17	H; Ph; SO_2Ph (**1j**)	**4a**	62 (**5q**[34])

[a]**1** (0.5 mmol), **4** (1.5 mmol, 3 eq), PhN_2BF_4 (0.6 mmol, 1.2 eq), DCE (3 mL), $Ru(bpy)_3(BF_4)_2$ (0.005 mmol, 1 mol%), 45 W CFL, N_2, r.t., 10 h. [b]Yield of isolated product.

According to the literature[16] and the above experimental results, a plausible reaction mechanism is proposed in Scheme 1. Firstly, under the visible light, the ground state of Ru^{2+} is excited to provide Ru^{*2+} which is oxidized by PhN_2BF_4 **6** to produce Ru^{3+}. Thus, the diazonium salt is reduced to generate the phenyl radical **7** which produces **8** by homo-coupling. The aziridine **1** is oxidized to generate a nitrogen radical cation **9** by Ru^{3+} which itself is reduced to the original oxidation level, Ru^{2+}. Intermediate **9** is attacked by the dipolarophile, nitrile **2** or isothiocyanate **4**, to give the ion intermediates **10** or **11** via electron exchange with **1** or intermediate **7**, intramolecular cyclization then leading to the imidazoline **3** or thiazolidine **5**.



Scheme 1. A plausible reaction mechanism.

Conclusions

In summary, we have developed a [3+2] cycloaddition of aziridines with nitriles or isothiocyanates by visible light photocatalysis under simple and mild reaction conditions. The reaction is applicable to aryl and alkyl nitriles or isothiocyanates and various substituted imidazolines and iminothiazolidines can be prepared with moderate yields. Visible light as a clean energy source makes this route a good substitute for the existing synthetic protocols.

Experimental Section

General. All of the commercial reagents were used without further purification unless otherwise specified and were purchased from Aladdin, Macklin, Energy or Bide Pharmatech. All of the chemical reactions and manipulations were implemented in oven-dried glassware under an atmosphere of N_2 using standard Schlenk technique. The solvents were made absolutely anhydrous and freshly distilled prior to use. Reactions were monitored by thin-layer chromatography (TLC) on GF254 Silica plates, visualizing with UV-light (254 nm) or I_2 stain. ^{1}H NMR and ^{13}C NMR spectra were recorded in ppm at 500 MHz and 125 MHz using $CDCl_3$ as solvent and TMS as internal standard using a Bruker AVANCE III 500MHz Nuclear Magnetic Resonance Spectrometer. Low-resolution MS (Varian 1200 Mass Spectrum Analyzer) and HRMS (Bruker ApexIII Fourier Transform Ion Cyclotron Resonator) were obtained using ESI ionization. Elemental analyses were performed on a vario Micro cube. GC spectra were measured using an Agilent 7890B. Melting points were measured using a SGW® X-4.

General experimental procedure for synthesis of 3a-n

An 25 mL oven-dried Schlenk tube was equipped with a stirring bar, an aziridine **1** (0.5 mmol), PhN_2BF_4 (0.6 mmol, 1.2 eq), and $Ru(bpy)_3(BF_4)_2$ (0.005 mmol, 1 mol%). The mixture was degassed by using standard Schlenk techniques with an oil pump. Then a nitrile **2a-d, 2f** (**a**: 40mmol, **b**: 20mmol, **c**: 17mmol, **d**: 14mmol, **f**: 17mmol, 2 mL) or nitrile **2e** (2.5 mmol, 5 eq) and DCE (2 mL) were injected into the reaction tube. The reaction mixture was allowed to stir for 4 h under irradiation of 45 W CFL (compact fluorescent lamp) (FSL, YPZ220/45-S,

Luminous Flux (2580Lm) at rt, the distance fof the reaction vessel from the light bulb being about 5 cm. After the reaction was completed (TLC), to the mixture was added distilled water (10 mL) and product extracted with CH_2Cl_2 (3 × 30 mL) in a separatory funnel. The combined organic layers were dried (anhydrous Na_2SO_4). Afterwards, the organic solution was concentrated under reduced pressure using a rotary evaporator and purified by column chromatography on silica gel (200-300 mesh) (PE:EtOAc = 5-10:1) to give the pure product **3**.

2-Methyl-4-phenyl-1-tosyl-4,5-dihydro-1*H*-imidazole (3a). White solid, mp 97-98 °C (lit. 100-102 °C)[29]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77-7.76 (m, 2H, Ph in Ts), 7.37 (d, *J* 8.0 Hz, 2H, Ph in Ts), 7.30-7.25 (m, 3H, Ph), 7.07-7.05 (m, 2H, Ph), 5.03-4.99 (m, 1H, CH_2), 4.21-4.17 (m, 1H, CH_2), 3.65 (dd, *J* 9.8, 7.9 Hz, 1H, CHN=), 2.48 (s, 3H, Me in Ts), 2.42, 2.41 (ss, 3H, 2-Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 144.8, 141.5, 135.2, 130.1, 128.7, 127.7, 127.3, 126.4, 66.6, 55.5, 21.6, 16.8. MS (ESI): ($[M+H]^+$) 315.1.

2-Methyl-4-(4-fluorophenyl)-1-tosyl-4,5-dihydro-1*H*-imidazole (3b). Colorless gum; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* 8.3 Hz, 2H, Ph in Ts), 7.37 (d, *J* 8.2 Hz, 2H, Ph in Ts), 7.05-7.01 (m, 2H, Ph), 6.98-6.95 (m, 2H, Ph), 5.01-4.98 (m, 1H, CH_2), 4.20-4.16 (m, 1H, CH_2), 3.61 (dd, *J* 9.9, 7.8 Hz, 1H, CHN=), 2.48 (s, 3H, Me in Ts), 2.421, 2.418 (ss, 3H, 2-Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 161.3, 157.1, 145.0, 137.3, 135.1, 130.2, 129.8, 128.0, 128.1, 127.3, 127.1, 115.7, 115.5, 65.7, 55.6, 21.6, 16.8. MS (ESI): ($[M+H]^+$) 333.1. HRMS (ESI) calculated for $C_{17}H_{19}FN_2O_2S$ ($[M+H]^+$) 333.0995, found 333.1068. El. Anal. calculated for $C_{17}H_{18}FN_2O_2S$: C, 61.43; H, 5.16; N, 8.43; found C, 61.29; H, 5.45; N, 8.52.

2-Methyl-4-(4-chlorophenyl)-1-tosyl-4,5-dihydro-1*H*-imidazole (3c). White solid, mp 173-174 °C (lit. 170-172 °C)[30]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* 8.3 Hz, 2H, Ph in Ts), 7.36 (d, *J* 8.1 Hz, 2H, Ph in Ts), 7.26-7.23 (m, 2H, Ph), 7.01-6.99 (m, 2H, Ph), 5.01-4.96 (m, 1H, CH_2), 4.20-4.16 (m, 1H, CH_2), 3.59 (dd, *J* 9.9, 7.8 Hz, 1H, CHN=), 2.48 (s, 3H, Me in Ts), 2.413, 2.412 (ss, 3H, 2-Me,). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 144.9, 140.1, 135.1, 133.5, 130.2, 128.8, 127.8, 127.2, 65.8, 55.4, 21.6, 16.8. MS (ESI): ($[M+H]^+$) 349.1.

2-Methyl-4-(2-chlorophenyl)-1-tosyl-4,5-dihydro-1*H*-imidazole (3d). White solid, mp 133-135 °C (EtOAc-PE)[29]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* 8.3 Hz, 2H, Ph in Ts), 7.36-7.33 (m, 3H, Ph and Ph in Ts), 7.23-7.16 (m, 2H, Ph), 7.12-7.10 (m, 1H, Ph), 5.35-5.32 (m, 1H, CH_2), 4.34-4.30 (m, 1H, CH_2), 3.55 (dd, *J* 10.0, 7.7 Hz, 1H, CHN=), 2.452, 2.448 (ss, 6H, 2-Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7, 144.8, 139.5, 135.3, 132.3, 130.1, 129.4, 128.7, 127.5, 127.2, 127.1, 63.7, 54.8, 21.6, 16.9. MS (ESI): ($[M+H]^+$) 349.1.

2-Methyl-4-(*p*-tolyl)-1-tosyl-4,5-dihydro-1*H*-imidazole (3e). Colorless liquid[29]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* 8.3 Hz, 2H, Ph in Ts), 7.36 (d, *J* 8.1 Hz, 2H, Ph in Ts), 7.08 (d, *J* 7.9 Hz, 2H, Ph), 6.95 (d, *J* 8.0 Hz, 2H, Ph), 4.98-4.95 (m, 1H, CH_2), 4.19-4.15 (m, 1H, CH_2), 3.62 (dd, *J* 9.7, 8.0 Hz, 1H, CHN=), 2.48 (s, 3H, Me in Ts), 2.401, 2.398 (ss, 3H, 2-Me), 2.32 (s, 3H, CH_3 in tolyl). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2, 144.7, 138.6, 137.3, 135.2, 130.1, 129.3, 127.2, 126.3, 66.4, 55.5, 21.6, 21.1, 16.8. MS (ESI): ($[M+H]^+$) 329.1.

2-Methyl-4-(4-bromophenyl)-1-tosyl-4,5-dihydro-1*H*-imidazole (3f). Colorless liquid[30]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* 8.3 Hz, 2H, Ph), 7.41-7.38 (m, 2H, Ph in Ts), 7.36 (d, *J* 8.2 Hz, 2H, Ph in Ts), 6.96-6.93 (m, 2H, Ph), 4.99-4.95 (m, 1H, CH_2), 4.21-4.16 (m, 1H, CH_2), 3.58 (dd, *J* 9.9, 7.8 Hz, 1H, CHN=), 2.48 (s, 3H, Me in Ts), 2.412, 2.409 (ss, 3H, 2-Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 145.0, 140.6, 135.1, 131.8, 130.2, 128.1, 127.2, 121.6, 65.9, 55.4, 21.6, 16.8. MS (ESI): ($[M+H]^+$) 395.0.

2,4-Dimethyl-4-phenyl-1-tosyl-4,5-dihydro-1*H*-imidazole (3g). White solid, mp 82-83°C (EtOAc-PE); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* 8.3 Hz, 2H, Ph in Ts), 7.32-7.22 (m, 7H, Ph and Ph in Ts), 3.93 (d, *J* 9.6 Hz, 1H, CH_2), 3.81 (d, *J* 9.6 Hz, 1H, CH_2), 2.44 (s, 3H, Me in Ts), 2.39 (s, 3H, 2-Me), 1.47 (s, 3H, 4-Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 146.3, 144.6, 135.4, 130.0, 128.5, 127.1, 126.9, 125.0, 69.6, 61.1, 29.6, 21.6, 16.9. MS (ESI): ($[M+H]^+$) 329.1. HRMS (ESI) calculated for $C_{18}H_{21}N_2O_2S$ ($[M+H]^+$): 329.1318, found: 329.1245. El. Anal. calculated for $C_{18}H_{20}N_2O_2S$: C, 65.83; H, 6.14; N, 8.53; found C, 65.72; H, 6.37; N, 8.69.

2-Methyl-4-*n*-octyl-1-tosyl-4,5-dihydro-1*H*-imidazole (3h). Viscous oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* 8.3 Hz, 2H, Ph), 7.36 (d, *J* 8.1 Hz, 2H, Ph), 3.86-3.81 (m, 2H, CH_2N), 3.34 (dd, *J* 8.2, 6.3 Hz, 1H, CHN=), 2.46 (s, 3H, Me in Ts), 2.29 (s, 3H, 2-Me), 1.29-1.23 (m, 14H, 7-CH_2), 0.88 (t, *J* 7.0 Hz, 3H, CH_3 in n-octyl). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.0, 144.6, 135.4, 130.0, 127.2, 63.6, 53.2, 35.8, 31.8, 29.5, 29.4, 29.2, 25.6, 22.6, 21.6, 16.8, 14.1; MS (ESI): ($[M+H]^+$) 351.2. HRMS (ESI) calculated for $C_{19}H_{31}N_2O_2S$ ($[M+H]^+$) 351.2101, found 351.2028. El. Anal. calculated for $C_{19}H_{30}N_2O_2S$: C, 65.11; H, 8.63; N, 7.99; found C, 65.32; H, 8.59; N, 8.21.

2-Methyl-1-tosyl-3a,4,5,6,7,7a-hexahydro-1*H*-benzimidazole (3i). White solid, mp 112-113 °C (lit. 115-117 °C)[31]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* 8.3 Hz, 2H, Ph), 7.36 (d, *J* 8.2 Hz, 2H, Ph), , 3.13-3.07 (m, 1H, CHNTs), 2.88-2.82 (m, 1H, CH_2), 2.57-2.54 (m, 1H, CH_2), 2.46 (s, 3H, Me in Ts), 2.32, 2.31 (ss, 3H, 2-Me), 2.26-2.23 (m, 1H, CH_2), 1.88-1.78 (m, 2H, CH_2), 1.68-1.60 (m, 1H, CHN=), 1.37-1.22 (m, 3H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 144.6, 135.0, 130.0, 127.4, 70.2, 69.3, 30.56, 30.55, 25.0, 24.6, 21.6, 17.9. MS (ESI): ($[M+H]^+$) 293.1.

2,4-Diphenyl-1-tosyl-4,5-dihydro-1*H*-imidazole (3j). White solid, mp 164-165 °C (EtOAc-PE)[29]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.78 (m, 2H, 2-Ph), 7.56-7.53 (m, 1H, Ph in Ts), 7.47-7.41 (m, 4H, Ph in Ts and 2-Ph), 7.25-7.21 (m, 5H, Ph in Ts and 4-Ph), 6.70-6.98 (m, 2H, 4-Ph), 5.03-4.99 (m, 1H, CHN=), 4.48-4.43 (m, 1H, CH_2), 3.90-3.86 (m, 1H, CH_2), 2.44 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 144.7, 141.5, 134.5, 131.2, 130.1, 129.9, 129.8, 128.6, 127.7, 127.6, 127.4, 126.4, 67.8, 56.9, 21.6. MS (ESI): ($[M+H]^+$) 377.1.

2-Benzyl-4-phenyl-1-tosyl-4,5-dihydro-1*H*-imidazole (3k). Colorless liquid[29]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.40 (m, 4H, Ph in Ts), 7.38-7.25 (m, 6H, 4-Ph and 2-Ph), 7.21-7.18 (m, 2H, 2-Ph), 7.04-7.7.03 (m, 2H, 2-Ph), 5.08-5.05 (m, 1H, CHN=), 4.20-4.14 (m, 3H, CH_2 and CH_2 in benzyl), 3.62-3.59 (m, 1H, CH_2 in benzyl), 2.42 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.3, 144.5, 141.7, 135.4, 134.9, 129.9, 129.4, 128.7, 128.5, 127.6, 127.3, 127.0, 126.4, 66.9, 55.5, 35.7, 21.5. MS (ESI): ($[M+H]^+$) 391.1.

2-(1-Naphthalenyl)-4-phenyl-1-tosyl-4,5-dihydro-1*H*-imidazole (3l). White solid, mp 152-153 °C (EtOAc-PE); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* 8.2 Hz, 1H), 7.91 (d, *J* 8.4 Hz, 1H), 7.86 (d, *J* 8.1 Hz, 1H), 7.73 (d, *J* 6.8 Hz, 1H), 7.56-7.52 (m, 1H), 7.51-7.47 (m, 1H), 7.43-7.40 (m, 1H), 7.37-7.23 (m, 7H), 7.02 (d, *J* 8.1 Hz, 2H, Ph), 5.36 (dd, *J* 9.9, 8.8 Hz, 1H, CH_2), 4.62-4.58 (m, 1H, CH_2), 4.05 (dd, *J* 10.5, 8.4 Hz,1H, CHN=), 2.34 (s, 3H, Me in Ts). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7, 144.5, 141.6, 134.6, 133.2, 131.4, 130.8, 129.4, 128.8, 128.3, 127.7, 127.6, 127.3, 126.7, 126.5, 125.9, 125.2, 124.4, 68.2, 55.8, 21.5. MS (ESI): ($[M+H]^+$) 427.2; HRMS (ESI) calculated for $C_{26}H_{23}N_2O_2S$ ($[M+H]^+$) 427.1494, found 427.1475. El. Anal. calculated for $C_{26}H_{22}N_2O_2S$: C, 73.21; H, 5.20; N, 6.57; found C, 73.11; H, 5.36; N, 6.79.

2-(*p*-Benzonitrile)-4-phenyl-1-tosyl-4,5-dihydro-1*H*-imidazole (3m). White solid, mp 151-153 °C (EtOAc-PE); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* 8.3 Hz, 2H, 2-Ph), 7.75 (d, *J* 8.3 Hz,, 2H, Ph in Ts), 7.42 (d, *J* 8.2 Hz, 2H, Ph in Ts), 7.27-7.23 (m, 5H, 4-Ph), 6.97-6.95 (m, 2H, 2-Ph), 5.07-5.03 (m, 1H, CH_2), 4.47-4.43 (m, 1H, CH_2), 3.88 (dd, *J* 11.4, 8.1 Hz, 1H, CHN=), 2.46 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4 145.2, 140.9, 134.7, 134.1, 132.8, 131.6, 130.5, 130.0, 128.7, 127.7, 127.6, 126.3, 118.2, 114.7, 68.4, 56.8, 21.6. MS (ESI): ($[M+H]^+$) 402.1; HRMS (ESI) calculated for $C_{23}H_{20}N_3O_2S$ ($[M+H]^+$) 402.1259, found 402.1271. El. Anal. calculated for $C_{23}H_{19}N_3O_2S$: C, 68.81; H, 4.77; N, 10.47; found C, 68.92; H, 4.78; N, 10.32.

4-Phenyl-2-(*p*-tolyl)-1-tosyl-4,5-dihydro-1*H*-imidazole (3n). Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* 8.1 Hz, 2H, Ph in Ts), 7.43 (d, *J* 8.3 Hz, 2H, Ph in Ts), 7.28-7.26 (m, 2H, 2-Ph), 7.24-7.20 (m, 5H, 4-Ph), 6.98-6.96 (m, 2H, 2-Ph), 4.96 (dd, *J* 9.5, 8.4 Hz, 1H, CHN=), 4.43 (dd, *J* 11.4, 10.0 Hz, 1H, CH_2), 3.85 (dd, *J* 11.5, 8.1 Hz, 1H, CH_2), 2.45(s, 3H, Me in Ts), 2.44 (s, 3H, Me in tolyl). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 144.6, 141.7, 141.6, 134.5, 129.9, 129.8, 128.9, 128.54, 128.45, 127.6, 127.4, 127.3, 127.2, 127.0, 126.3, 67.8, 56.9, 21.63, 21.59. MS (ESI): ($[M+H]^+$) 391.2; HRMS (ESI) calculated for $C_{23}H_{23}N_2O_2S$ ($[M+H]^+$) 391.1492, found 391.1475. El. Anal. calculated for $C_{23}H_{22}N_2O_2S$: C, 70.74; H, 5.68; N, 7.17; found C, 70.58; H, 5.77; N, 7.33.

General experimental procedure for synthesis of 5a-q

An 25 mL oven-dried Schlenk tube was equipped with a stirring bar, an aziridine **1** (0.5 mmol), PhN_2BF_4 (0.6 mmol, 1.2 eq), and $Ru(bpy)_3(BF_4)_2$ (0.005 mmol, 1 mol%). The mixture was degassed by using standard Schlenk techniques with the oil pump. Then isothiocyanate **4** (1.5 mmol, 3 eq), and DCE (3 mL) were injected into the reaction tube. The reaction mixture was allowed to stir for 10 h under irradiation of 45 W CFL (FSL, YPZ220/45-S, Luminous Flux (2580Lm) at rt, the distance from the light bulb to the reaction vessel being about 5 cm. After the reaction was complete (TLC), the tot he mixture was added distilled water (10 mL) and product extracted with CH_2Cl_2 (3 × 30 ml) in separatory funnel. The combined the organic layers were dried (Na_2SO_4), the organic solution was concentrated under reduced pressure using a rotary evaporator and the residue purified by column chromatography on silica gel (200-300 mesh) (PE:EtOAc = 5-10:1) to give the pure product **5**.

***N*,5-Diphenyl-3-tosylthiazolidin-2-imine (5a).** White solid, mp 129-131 °C (lit. 132-133 °C)[32]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* 8.4 Hz, 2H, Ph in Ts), 7.38-7.33 (m, 7H, Ph in Ts and 5-Ph), 7.28-7.26 (m, 2H, PhN=), 7.08 (t, *J* 7.4 Hz,1H, PhN=), 6.81-6.79 (m, 2H, PhN=), 4.82 (dd, *J* 8.6, 6.5 Hz, 1H, CH_2), 4.62 (dd, *J* 10.4, 6.5 Hz, 1H, CH_2), 4.07 (dd, *J* 10.4, 8.6 Hz, 1H, CHS), 2.50 (s, 3H, -Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 150.1, 144.9, 136.5, 134.7, 129.24, 129.20, 129.05, 128.97, 128.8, 127.5, 124.3, 120.8, 56.8, 47.0, 21.7. MS (ESI): ($[M+H]^+$) 409.1.

***N*-Phenyl-5-(4-fluorophenyl)-3-tosylthiazolidin-2-imine (5b).** Viscous liquid[33]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* 8.3 Hz, 2H, Ph in Ts), 7.38-7.33 (m,4H, Ph in Ts and 5-Ph), 7.29-7.26 (m, 2H, PhN=), 7.10-7.07 (m, 1H, PhN=), 7.05-7.02 (m, 2H, 5-Ph), 6.80-6.79 (m, 2H, PhN=), 4.79 (dd, *J* 8.1, 6.5 Hz, 1H, CH_2), 4.58 (dd, *J* 10.5, 6.4 Hz, 1H, CH_2), 4.04 (dd, *J* 10.3, 8.3 Hz, 1H, CHS), 2.50 (s, 3H, -Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.7, 161.7, 151.8, 150.0, 145.0, 134.6, 132.5, 129.3, 129.24, 129.21, 129.15, 129.0, 124.4, 120.7, 116.1, 115.9, 56.8, 46.2, 21.7. MS (ESI): ($[M+H]^+$) 427.1; HRMS (ESI) calculated for $C_{22}H_{20}FN_2O_2S_2$ ($[M+H]^+$) 427.0945, found 427.0953.

***N*-Phenyl-5-(4-methylphenyl)-3-tosylthiazolidin-2-imine (5c).** White solid, mp 115-117 °C (EtOAc-PE)[34]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01-7.99 (m, 2H, Ph in Ts), 7.37 (d, *J* 8.0 Hz, 2H, Ph in Ts), 7.28-7.24 (m, 4H, PhN= and 5-Ph), 7.15 (d, *J* 8.0 Hz, 2H, 5-Ph), 7.10-7.06 (m, 1H, PhN=), 6.81-6.79 (m, 2H, PhN=), 4.79 (dd, *J* 8.8, 6.5 Hz, 1H, CH_2), 4.60 (dd, *J* 10.4, 6.4 Hz, 1H, CH_2), 4.03 (dd, *J* 10.4, 8.8 Hz, 1H, CHS), 2.50 (s, 3H, Me in Ts), 2.35 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 150.1, 144.9, 138.7, 134.7, 133.4, 129.7, 129.2, 129.1, 128.9, 127.4, 124.3, 120.8, 56.8, 46.9, 21.7, 21.1. MS (ESI): ($[M+H]^+$) 423.1; HRMS (ESI) calculated for $C_{23}H_{23}N_2O_2S_2$ ($[M+H]^+$) 423.1195, found 423.1195.

***N*-Phenyl-5-(2-chlorophenyl)-3-tosylthiazolidin-2-imine (5d).** Viscous yellow liquid[34]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* 8.3 Hz, 2H, Ph in Ts), 7.59-7.57 (m, 1H, 5-Ph), 7.42-7.36 (m, 3H, Ph in Ts and PhN=), 7.30-7.27 (m, 4H, PhN= and 5-Ph), 7.09 (t, *J* 7.4 Hz, 1H, PhN=), 6.81-6.79 (m, 2H, PhN=), 5.21-5.19 (m, 1H, CH_2), 4.52 (dd, *J* 10.6, 6.5 Hz, 1H, CH_2), 4.29 (dd, *J* 10.6, 5.4 Hz, 1H, CHS), 2.50 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 150.0, 145.0, 135.4, 134.6, 133.5, 129.9, 129.7, 129.24, 129.19, 129.0, 128.0, 127.6, 124.4, 120.7, 55.2, 43.5, 42.7, 21.7. MS (ESI): ($[M+H]^+$) 443.1; HRMS (ESI) calculated for $C_{22}H_{20}ClN_2O_2S_2$ ($[M+H]^+$) 443.0649, found 443.0652.

***N*-Phenyl-5-(4-bromophenyl)-3-tosylthiazolidin-2-imine (5e).** Colorless liquid[34]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* 8.3 Hz, 2H, 5-Ph), 7.49-7.46 (m, 2H, Ph in Ts), 7.37 (d, *J* 8.2 Hz, 2H, Ph in Ts), 7.30-7.22 (m, 4H, 5-Ph and PhN=), 7.09 (t, *J* 7.4 Hz, 1H, PhN=), 6.79 (d, *J* 7.4 Hz, 2H, PhN=), 4.76-4.73 (m, 1H, CH_2), 4.58 (dd, *J* 10.4, 6.4 Hz, 1H, CH_2), 4.05 (dd, *J* 10.4, 7.9 Hz, 1H, CHS), 2.50 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 149.9, 145.0, 135.9, 134.6, 132.2, 129.3, 129.2, 129.0, 124.5, 122.7, 120.7, 56.6, 46.3, 21.7. MS (ESI): ($[M+H]^+$) 489.0; HRMS (ESI) calculated for $C_{22}H_{20}BrN_2O_2S_2$ ($[M+H]^+$) 487.0144, found 487.0162.

***N*-(4-Methoxyphenyl)-5-phenyl-3-tosylthiazolidin-2-imine (5f).** Yellow liquid[34]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* 8.2 Hz, 2H, Ph in Ts), 7.37-7.34 (m, 7H, Ph in Ts, PhN= and 5-Ph), 6.82-6.77 (dd, *J* 8.8, 8.9 Hz, 4H, PhN=

and 5-Ph), 4.81 (dd, *J* 8.3, 6.6 Hz, 1H, CH_2), 4.60 (dd, *J* 10.3, 6.4 Hz, 1H, CH_2), 4.06 (dd, *J* 10.2, 8.7 Hz, 1H, CHS), 3.78 (s, 3H, OMe), 2.49 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6, 151.7, 144.8, 143.4, 136.7, 134.9, 129.2, 129.0, 128.7, 127.5 121.9, 114.2, 56.7, 55.4, 47.0, 21.7. MS (ESI): ($[M+H]^+$) 439.4; HRMS (ESI) calculated for $C_{23}H_{23}N_2O_3S_2$ ($[M+H]^+$) 439.1145, found 439.1162.

***N*-(4-Fluorophenyl)-5-phenyl-3-tosylthiazolidin-2-imine (5g).** Colorless liquid[34]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* 8.3 Hz, 2H, Ph in Ts), 7.38-7.34 (m, 7H, Ph in Ts and 5-Ph), 6.98-6.94 (m, 2H, PhN=), 6.778-6.75 (m, 2H, PhN=), 4.82 (dd, *J* 8.5, 6.5 Hz, 1H, CH_2), 4.61 (dd, *J* 10.4, 6.5 Hz, 1H, CH_2), 4.08 (dd, *J* 10.4, 8.5 Hz, 1H, CHS), 2.50 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 158.8, 152.4, 146.1, 145.0, 144.5, 136.4, 134.7, 129.3, 129.2, 129.1, 128.8, 127.5, 122.2, 122.1, 115.7, 115.6, 56.8, 47.1, 21.7. MS (ESI): ($[M+H]^+$) 427.2; HRMS (ESI) calculated for $C_{22}H_{20}FN_2O_2S_2$ ($[M+H]^+$) 427.0945, found 427.0964.

***N*-(2-Methylphenyl)-5-phenyl-3-tosylthiazolidin-2-imine (5h).** Viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* 8.3 Hz, 2H, Ph in Ts), 7.39-7.34 (m, 7H, Ph in Ts and 5-Ph), 7.14-7.08 (m, 2H, 2-Ph), 7.01-6.98 (m, 1H, 2-Ph), 6.69 (d, *J* 7.7 Hz, 1H, 2-Ph), 4.82 (dd, *J* 8.2, 6.5 Hz, 1H, CH_2), 4.65 (dd, *J* 10.4, 6.4 Hz, 1H, CH_2), 4.14 (dd, *J* 10.3, 8.3 Hz, 1H, CHS), 2.48 (s, 3H, Me in Ts), 1.95 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 149.2, 144.7, 136.8, 135.2, 130.3, 129.4, 129.3, 129.0, 128.9, 128.7, 127.4, 126.3, 124.3, 119.6, 57.0, 46.8, 21.6, 17.4. MS (ESI): ($[M+H]^+$) 423.1; HRMS (ESI) calculated for $C_{23}H_{23}N_2O_2S_2$ ($[M+H]^+$) 423.1195, found 423.1184. El. Anal. calculated for $C_{23}H_{22}N_2O_2S_2$: C, 65.38; H, 5.25; N, 6.63; found C, 65.29; H, 5.37; N, 6.89.

***N*-(4-Bromophenyl)-5-phenyl-3-tosylthiazolidin-2-imine (5i).** Viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* 8.2 Hz, 2H, Ph in Ts), 7.43-7.34 (m, 9H, Ph in Ts, 5-Ph and 2-Ph), 6.68 (d, *J* 8.6 Hz, 2H, 2-Ph), 4.83 (dd, *J* 8.5, 6.5 Hz, 1H, CH_2), 4.62 (dd, *J* 10.4, 6.5 Hz, 1H, CH_2), 4.08 (dd, *J* 10.3, 8.6 Hz, 1H, CHS), 2.50 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 148.9, 145.1, 136.3, 134.6, 132.0, 129.3, 129.14, 129.11, 128.9, 127.5, 122.6, 117.4, 56.8, 47.1, 21.7. MS (ESI): ($[M+H]^+$) 487.0; HRMS (ESI) calculated for $C_{22}H_{20}BrN_2O_2S_2$ ($[M+H]^+$) 487.0144, found 487.0124. El. Anal. calculated for $C_{22}H_{19}BrN_2O_2S_2$: C, 54.21; H, 3.93; N, 5.75; found C, 54.25; H, 3.68; N, 5.68.

***N*-(4-Chlorophenyl)-5-phenyl-3-tosylthiazolidin-2-imine (5j).** Viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* 8.3 Hz, 2H, Ph in Ts), 7.38-7.33 (m, 7H, Ph in Ts, 5-Ph and 2-Ph), 7.24-7.22 (m, 2H, 5-Ph), 6.75-6.72 (m, 2H, 2-Ph), 4.83 (dd, *J* 8.5, 6.5 Hz, 1H, CH_2), 4.62 (dd, *J* 10.3, 6.5 Hz, 1H, CH_2), 4.08 (dd, *J* 10.4, 8.5 Hz, 1H, CHS), 2.50 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 148.5, 145.1, 136.3, 134.6, 129.6, 129.3, 129.14, 129.10, 129.05, 128.9, 127.5, 122.2, 56.8, 47.1, 21.7. MS (ESI): ($[M+H]^+$) 443.1; HRMS (ESI) calculated for $C_{22}H_{20}ClN_2O_2S_2$ ($[M+H]^+$) 443.0649, found 443.0635. El. Anal. calculated for $C_{22}H_{19}ClN_2O_2S_2$: C, 59.65; H, 4.32; N, 6.32; found C, 59.38; H, 4.60; N, 6.34.

***N*-(Isopropyl)-5-phenyl-3-tosylthiazolidin-2-imine (5k).** White solid, mp 134-136 °C (EtOAc-PE)[35]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* 8.3 Hz, 2H, Ph in Ts), 7.39-7.34 (m, 5H, Ph in Ts and 5-Ph), 7.31-7.28 (m, 2H, 5-Ph), 4.78 (dd, *J* 8.5, 6.4 Hz, 1H, CH_2), 4.47 (dd, *J* 10.3, 6.3 Hz, 1H, CH_2), 3.87 (dd, *J* 10.2, 8.7 Hz, 1H, CHS), 3.11-3.07 (m, 1H, CH in isopropyl), 2.47 (s, 3H, Me in Ts), 1.14 (d, *J* 6.2 Hz, 3H, Me), 1.08 (d, *J* 6.2 Hz, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 144.4, 137.0, 134.9, 129.3, 129.0, 128.9, 128.6, 127.6, 57.7, 56.0, 46.9, 23.6, 23.4, 21.7. MS (ESI): ($[M+H]^+$) 375.1;

***N*-Cyclohexyl-5-phenyl-3-tosylthiazolidin-2-imine (5l).** White solid, mp 152-154 °C (EtOAc-PE)[34]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* 8.3 Hz, 2H, Ph in Ts), 7.39-7.28 (m, 7H, Ph in Ts and 5-Ph), 4.78 (dd, *J* 8.5, 6.3 Hz, 1H, CH_2), 4.47 (dd, *J* 10.3, 6.3 Hz, 1H, CH_2), 3.89 (dd, *J* 10.2, 8.5 Hz, 1H, CHS), 2.79-2.77 (m, 1H, CH in cyclohexyl), 2.46 (s, 3H, Me), 1.74-1.56 (m, 6H, cyclohexyl), 1.30-1.24 (m, 4H, cyclohexyl). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 144.3, 137.1, 135.0, 129.2, 129.0, 128.9, 128.6, 127.6, 56.0, 46.9, 33.5, 33.3, 25.7, 24.4, 21.7. MS (ESI): ($[M+H]^+$) 415.3; HRMS (ESI) calculated for $C_{22}H_{27}N_2O_2S_2$($[M+H]^+$) 415.1508, found 415.1510.

***N*-(*n*-Butyl)-5-phenyl-3-tosylthiazolidin-2-imine (5m).** Viscous liquid[34]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92-7.90 (m, 2H, Ph in Ts), 7.40-7.34 (m, 5H, Ph in Ts and 5-Ph), 7.31 (d, *J* 8.3 Hz, 2H, 5-Ph), 4.79 (dd, *J* 8.4, 6.3 Hz, 1H,

CH_2), 4.50 (dd, *J* 10.3, 6.3 Hz, 1H, CH_2), 3.93 (dd, *J* 10.2, 8.4 Hz, 1H, CHS), 3.24-3.19 (m, 1H, CH_2 in butyl), 3.11-3.07 (m, 1H, CH_2 in butyl), 2.46 (s, 3H, Me in Ts), 1.53-1.49 (m, 2H, CH_2 in butyl), 1.22-1.17 (m, 2H, CH_2 in butyl), 0.88 (t, *J* 7.4 Hz, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 144.4, 137.0, 135.1, 129.1, 129.0, 128.6, 127.6, 56.3, 55.9, 46.9, 32.8, 21.6, 20.4, 13.9. MS (ESI): ($[M+H]^+$) 389.3; HRMS (ESI) calculated for $C_{20}H_{25}N_2O_2S_2$ ($[M+H]^+$) 389.1352, found 389.1346.

***N*-Benzyl-5-phenyl-3-tosylthiazolidin-2-imine (5n).** White solid, mp 120-122 °C (EtOAc-PE); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* 8.2 Hz, 2H, Ph in Ts), 7.42-7.35 (m, 5H, Ph in benzyl), 7.29-7.24 (m, 3H, Ph in Ts and 5-Ph), 7.19 (d, *J* 8.1 Hz, 2H, 5-Ph), 7.16-7.14 (m, 2H, 5-Ph), 4.86 (dd, *J* 8.2, 6.5 Hz, 1H, CH_2), 4.56 (dd, *J* 10.3, 6.3 Hz, 1H, CH_2), 4.44 (d, *J* 15.2 Hz, 1H, CHS), 4.36 (d, *J* 15.2 Hz, 1H, CH_2-Ph), 4.01 (dd, *J* 10.2, 8.4 Hz, 1H, CH_2-Ph), 2.43 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 144.4, 139.4, 136.8, 135.1, 129.2, 129.1, 129.0, 128.8, 128.1, 127.6, 127.5, 126.6, 59.4, 56.5, 47.2, 21.6. MS (ESI): ($[M+H]^+$) 423.3; HRMS (ESI) calculated for $C_{23}H_{23}N_2O_2S_2$ ($[M+H]^+$) 423.1195, found 423.1195. El. Anal. calculated for $C_{23}H_{22}N_2O_2S_2$: C, 65.38; H, 5.25; N, 6.63 found C, 65.41; H, 5.32; N, 6.49.

***N*-(α-Methylbenzyl)-5-phenyl-3-tosylthiazolidin-2-imine (5o).** Viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* 8.3 Hz, 1/4×2H), 7.90 (d, *J* 8.2 Hz, 3/4×2H), 7.40-7.32 (m, 5H), 7.30-7.20 (m, 5+1/4×2H), 7.18-7.17 (m, 3/4×2H), 4.85-4.75 (m, 1H), 4.55-4.49 (m, 1H), 4.14-4.10 (m, 1H), 3.98-3.92 (m, 1H), 2.46 (s, 1/4×3H), 2.44 (s, 3/4×3H), 1.43 (d, *J* 6.5 Hz, 3/4×3H), 1.38 (d, *J* 6.5 Hz, 1/4×3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 145.1, 145.0, 144.4, 144.3, 136.9, 136.7, 135.3, 129.2, 129.05, 129.00, 128.9, 128.7, 128.6, 128.2, 128.1, 127.6, 127.5, 126.6, 126.57, 126.5, 126.4, 65.5, 65.4, 56.2, 56.0, 47.3, 47.1, 25.1, 24.6, 21.6. MS (ESI): ($[M+H]^+$) 437.1; HRMS (ESI) calculated for $C_{24}H_{25}N_2O_2S_2$ ($[M+H]^+$) 437.1352, found 437.1350. El. Anal. calculated for $C_{24}H_{24}N_2O_2S_2$: C, 66.03; H, 5.54; N, 6.42 found C, 65.88; H, 5.31; N, 6.25.

***N*-(α-Naphthyl)-5-phenyl-3-tosylthiazolidin-2-imine (5p).** Yellow solid, mp 133-135 °C (EtOAc-PE)[33]; δ 8.03 (d, *J* 8.3 Hz, 2H, naphthyl), 7.80 (d, *J* 8.2 Hz, 1H, Ph in Ts), 7.58 (d, *J* 8.3 Hz, 1H, Ph in Ts), 7.49-7.45 (m, 2H), 7.39-7.30 (m, 9H, 5-Ph, Ph in Ts and naphthyl), 6.87 (d, *J* 7.1 Hz, 1H, 5-Ph), 4.84 (dd, *J* 8.3, 6.5 Hz, 1H, CH_2), 4.72 (dd, *J* 10.4, 6.4 Hz, 1H, CH_2), 4.21 (dd, *J* 10.3, 8.4 Hz, 1H, CHS), 2.52 (s, 3H, Me). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 146.9, 144.8, 136.6, 135.4, 134.1, 129.5, 129.13, 129.05, 128.8, 127.7, 127.5, 126.2, 125.7, 125.3, 124.5, 123.9, 114.7, 56.9, 46.9, 21.7. MS (ESI): ($[M+H]^+$) 459.1; HRMS (ESI) calculated for $C_{26}H_{23}N_2O_2S_2$($[M+H]^+$) 459.1195, found 459.1203.

***N*,5-Diphenyl-3-(phenylsulfonyl)thiazolidin-2-imine (5q).** Viscous liquid[34]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* 7.5 Hz, 2H, Ph in Ts), 7.71 (t, *J* 7.5 Hz, 1H, Ph in Ts), 7.59 (t, *J* 7.8 Hz, 2H, Ph in Ts), 7.37-7.34 (m, 5H, 5-Ph), 7.29-7.25 (m, 2H, PhN=), 7.08 (t, *J* 7.4 Hz, 1H, PhN=), 6.78 (d, *J* 7.6 Hz, 2H, PhN=), 4.83 (dd, *J* 8.4, 6.5 Hz, 1H, CH_2), 4.64 (dd, *J* 10.4, 6.4 Hz, 1H, CH_2), 4.11 (dd, *J* 10.4, 8.5 Hz, 1H, CHS). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 149.9, 137.7, 136.5, 133.9, 129.14, 129.07, 128.98, 128.8, 128.6, 127.5, 124.4, 120.7, 56.8, 47.1. MS (ESI): ($[M+H]^+$) 395.1.

Acknowledgements

This work was supported by the Natural Science Foundation of Zhejiang Provincial (LY15B020004), the Natural Science Foundation of China (21602197) and the Open Research Fund Program of Collaborative Innovation Center of Membrane Separation and Water Treatment (2016YB07).

Supplementary Material

Copies of ^{1}H and ^{13}C NMR spectra for all isolated compounds.

References

1. Narayanam, J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2011**, *40*, 102. https://doi.org/10.1039/B913880N
2. Lu, Z.; Yoon, T. P. *Angew. Chem. Int. Ed.* **2012**, *51*, 10329. https://doi.org/10.1002/anie.201204835
3. Shi, L.; Xia, W. *Chem. Soc. Rev.* **2012**, *41*, 7687. https://doi.org/10.1039/c2cs35203f
4. Xuan, J.; Xia, X.; Zeng, T.; Lu, L.; Xiao, W. *Angew. Chem. Int. Ed*. **2014**, *53*, 5653. https://doi.org/10.1002/anie.201400602
5. Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. *J. Org. Chem.* **2016**, *81*, 6898. https://doi.org/10.1021/acs.joc.6b01449
6. Ciamician, G. *Science* **1912**, *36*, 385. https://doi.org/10.1126/science.36.926.385
7. Nicewicz, D. A.; MacMillan, D. W. C. *Science* **2008**, *322*, 77. https://doi.org/10.1126/science.1161976
8. Janvier, P.; Sun, X. W.; Bienayme, H.; Zhu, J. P. *J. Am. Chem. Soc*. **2002**, *124*, 2560. https://doi.org/10.1021/ja017563a
9. Krasavin, K. *Eur. J. Med. Chem.* **2015**, 97, 525. https://doi.org/10.1016/j.ejmech.2014.11.028
10. Evans, D. A.; Downey, C. W.; Hubbs, J. L. *J. Am. Chem. Soc.* **2003,** *125*, 8706. https://doi.org/10.1021/ja035509j
11. Murugana, R.; Anbazhaganb, S.; Narayanan, S. S. *Eur. J. Med. Chem.* **2009**, *44*, 3272. https://doi.org/10.1016/j.ejmech.2009.03.035
12. Kondo, M.; Nishi, T.; Hatanaka, T.; Funahashi, Y.; Nakamura, S. *Angew. Chem. Int. Ed.* **2015**, *54*, 8198. https://doi.org/10.1002/anie.201503098
13. Wang, C.; Qin, J.; Shen, X.; Riedel, R.; Harms, K.; Meggers, E. *Angew. Chem. Int. Ed.* **2016**, *55*, 685. https://doi.org/10.1002/anie.201509524
14. Busacca, C. A.; Bartholomeyzik, T.; Cheekoori, S.; Grinberg, N.; Lee, H.; Ma, S.; Saha, A.; Shen, S.; Senanayake, C. H. *J. Org. Chem*. **2008**, *73*, 9756. https://doi.org/10.1021/jo8024384
15. Booker-Milburn, K. I.; Guly, D. J.; Cox, B.; Procopiou, P. A. *Org. Lett*. **2003**, *5*, 3313. https://doi.org/10.1021/ol035374m
16. Zhou, L.; Zhou, J.; Tan, C. K.; Chen, J.; Yeung, Y. Y. *Org. Lett.* **2011**, *13*, 2448. https://doi.org/10.1021/ol2006902
17. Chen, J.; Yu, W.; Wei, Y.; Li, T.; Xu, P. *J. Org. Chem.* **2017**, *82*, 243. https://doi.org/10.1021/acs.joc.6b02377
18. Prasad, B. A. B.; Pandey, G.; Singh,V. K. *Tetrahedron Lett.* **2004**, *45*, 1137. https://doi.org/10.1016/j.tetlet.2003.12.015
19. Yadav, V. K.; Sriramurthy, V. *J. Am. Chem. Soc.* **2005**, *127*, 16366. https://doi.org/10.1021/ja055664t
20. Ghorai, M. K.; Das, K.; Kumar, A.; Ghosh, K. *Tetrahedron Lett.* **2005**, *46*, 4103. https://doi.org/10.1016/j.tetlet.2005.04.006
21. Ghorai, M. K.; Ghosh, K.; Das, K. *Tetrahedron Lett.* **2006**, *47*, 5399.

https://doi.org/10.1016/j.tetlet.2005.04.006
22. Wu, J.; Sun, X.; Xia, H. G. *Tetrahedron Lett.* **2006**, *47*, 1509. https://doi.org/10.1016/j.tetlet.2006.01.021
23. Li, R.; Jiang, H.; Liu, W. Y.; Gu, P. M.; Li, X. Q. *Chin. Chem. Lett.* **2014**, *25*, 583. https://doi.org/10.1016/j.cclet.2014.01.020
24. Hsueh, N.; Clarkson, G. J.; Shipman, M. *Org. Lett.* **2015**, *17*, 3632. https://doi.org/10.1021/acs.orglett.5b01777
25. Huang, C.Y.; Doyle, A. G. *Chem. Rev*. **2014**, *114*, 8153. https://doi.org/10.1021/cr500036t
26. Kuznetsov, M. A.; Kuznetsova, L. M.; Pankova, A. S. *Tetrahedron Lett.* **2016**, *57*, 3575. https://doi.org/10.1016/j.tetlet.2016.06.116
27. Sun, H.; Yang, C.; Lin, R.; Xia, W. *Adv. Synth. Catal.* **2014**, *356*, 2775. https://doi.org/10.1002/adsc.201400476
28. Chamchaang, W.; Pinhas, A. R. *J. Org. Chem.* **1990**, *55*, 2943. https://doi.org/10.1021/jo00296a070
29. Li, X.; Yang, X.; Chang, H.; Li, Y.; Ni, B.; Wei, W. *Eur. J. Org. Chem.* **2011**, 3122. https://doi.org/10.1002/ejoc.201100270
30. Gandhi, S.; Bisai, A.; Prasad, B. A. B.; Singh, V. K. *J. Org. Chem.* **2007**, *72*, 2133. https://doi.org/10.1021/jo062564c
31. Abe, T.; Takeda, H.; Miwa, Y.; Yamada, K.; Yanada, R.; Ishikura, M. *Helv. Chim. Acta* **2010**, *93*, 233. https://doi.org/10.1002/hlca.200900214
32. Nadir, U. K.; Joshi, S. *Indian J. Chem. B* **2003**, *42B*, 1760.
33. Gao, L.; Fu, K.; Zheng, G. *RSC Adv*. **2016**, *6*, 47192. https://doi.org/10.1039/C6RA04923K
34. Bhattacharyya, A.; Kavitha, C. V.; Ghorai, M. K. *J. Org. Chem*. **2016**, *81*, 6433. https://doi.org/10.1021/acs.joc.6b01551
35. Khalaj, A.; Khalaj, M. *J. Chem. Res.* **2016**, *40*, 445. https://doi.org/10.3184/174751916X14656621014049

