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$BF_3 \cdot OEt_2$-Mediated Highly Regioselective S_N2-Type Ring-Opening of *N*-Activated Aziridines and *N*-Activated Azetidines by Tetraalkylammonium Halides

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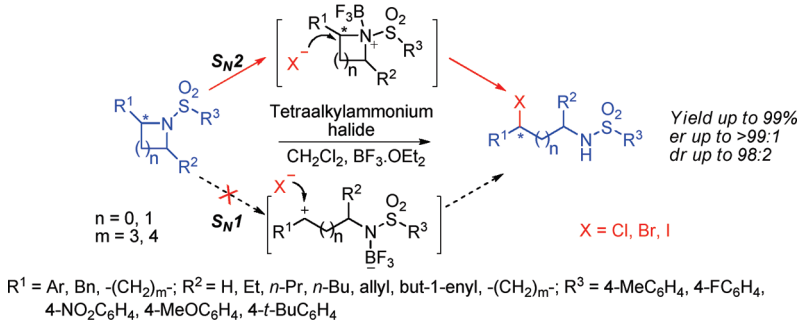

A highly regioselective Lewis acid-mediated S_N2-type ring-opening of *N*-sulfonylaziridines and azetidines with tetraalkylammonium halides in CH_2Cl_2 solution to afford 1,2- and 1,3-haloamines in excellent yields is described. An easy diastereoselective route toward substituted chiral *N*-tosylaziridines has been developed. The mechanism of ring-opening via S_N2 pathway has been confirmed by the formation of chiral haloamines with excellent er and dr. Chloroamines obtained from 2,3-disubstituted aziridines were converted to the chiral *N*-tosylamines via radical dehalogenation.

Introduction

Aziridines and azetidines are important aza-heterocycles in organic synthesis due to their biological significance and enormous synthetic potential as building blocks.[1] The reactivity profile of these heterocycles is attributed to their inherent ring-strain, diversity of substituents, and activation by suitable Lewis acids (LA).[1f] Recently, *N*-tosylaziridines and azetidines have been utilized extensively for the chemical transformations involving rearrangement in association with ring expansion,[2] cycloaddition,[3] and ring-opening by a variety of carbon and heteroatom nucleophiles.[4] However,

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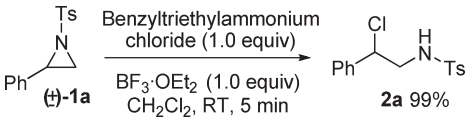
regio- and stereoselectivity during the ring-opening still remain as major challenges. Recently, LA-mediated regioselective ring-openings of enantiopure 2-aryl-*N*-tosylaziridines by several nucleophiles such as nitriles, carbonyls, and alcohols to provide nonracemic products in moderate to high ee have been reported by us.[5] A similar chemistry was also observed for azetidines.[5e,6] We proposed S_N2-type mechanisms for these transformations in contrast to the earlier reports involving 1,3- and 1,4-dipolar intermediates.[3a,g,h]

During further mechanistic investigation of such reactions we found that tetraalkylammonium halides in combination with $BF_3 \cdot OEt_2$ act as an efficient reagent-system for the regioselective S_N2-type ring-opening of *N*-sulfonylaziridines and azetidines by halides. However, tetraalkylammonium halides have earlier been known to open the aziridines in the presence of β-cyclodextrin[7a] and ammonium-12-molybdophosphate,[7b] and opening by fluoride ion with TBAF has also been reported.[7c,d] The long reaction time, pH dependence, and inefficiency to access chloroamines make these methods less attractive. We have earlier reported the opening of *N*-tosylaziridines with ZnX_2 (X = halogen) leading to β-haloamines.[5a] Other methods for the synthesis of β-haloamines from regioselective ring-opening of aziridines include using HCl,[7e,1h] $MgBr_2$,[7f] Amberlyst-15/LiCl,[7g] $CeCl_3$,[7h] InX_3,[7i] $BF_3 \cdot OEt_2$ as a fluorine source,[7j] zirconyl chloride,[7k] and PPh_3/X_2.[7l] Regioselective as well as stereoselective ring-opening of trisustituted chiral aziridines with oxygen, nitrogen, sulfur, and halogen nucleophiles has been repoted recently.[7m] Most of these methodologies suffer from disadvantages such as long reaction time, formation of other inseparable regioisomers, requirement of high temperature, etc. Recently, synthesis of β-chloroamines from imines[8a] and acyclic and cyclic β-haloamines via in situ generated aziridinium ions has been reported.[8b,c] Haloamination[9] and aminohalogenation[10] methods are also found to be useful for this purpose. Needless to say such haloamines are of immense synthetic[11a] and biological[11b] utility. Surprisingly, the opening of azetidines by halides to give γ-haloamines has not been studied, except for our earlier report on the ring-opening of 2-aryl-*N*-sulfonylazetidines by ZnI_2.[6a]

SCHEME 1. Opening of (±)-2-Phenyl-*N*-tosylaziridine



Hence, it is desirable to develop a mild and efficient method for the regio- and stereoselective ring-opening of substituted aziridines and azetidines to afford β- and γ-haloamines. In this article, we describe a highly efficient approach toward β- and γ-haloamines via regioselective S_N2-type ring-opening of *N*-sulfonylaziridines and azetidines by tetraalkyl ammonium halides in the presence of $BF_3 \cdot OEt_2$ as the LA in excellent yields with high ee and de.

Results and Discussion

Our study began with the ring-opening of (±)-2-phenyl-*N*-tosylaziridine **1a** using 1.0 equiv of benzyltriethylammonium chloride (BTEAC) in the presence of 1.0 equiv of $BF_3 \cdot OEt_2$ in CH_2Cl_2 medium at rt. To our delight, reaction was completed within 5 min to afford chloroamine **2a** as the only product in 99% yield (Scheme 1). The high regioslectivity is in accordance with the experimental[3a,5] as well as extensive computational studies.[12]

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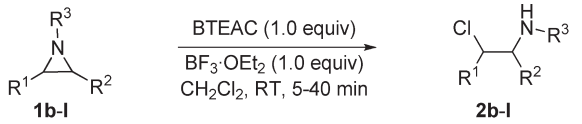
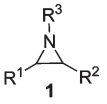
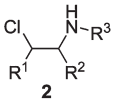
SCHEME 2. Opening of *N*-Activated Aziridines by BTEAC



R^1 = H, Ph, 4-ClC_6H_4, 3-ClC_6H_4, 4-BrC_6H_4 R^2 = H, Bn R^1, R^2 = -$(CH_2)_4$-, -$(CH_2)_3$-
R^3 = Ts, 4-$FC_6H_4SO_2$, 4-$NO_2C_6H_4SO_2$, 4-$MeOC_6H_4SO_2$, 4-*t*-$BuC_6H_4SO_2$, 4-$NO_2C_6H_4CO$

TABLE 1. Opening of Activated Aziridines by BTEAC

entry	aziridine	haloamine	Time (min)	yield (%)[a]
	 **1**	 **2**		
1	**1b:** R^1 = 4-ClC_6H_4, R^2 = H, R^3 = Ts	**2b**	5	96
2	**1c:** R^1 = 3-ClC_6H_4, R^2 = H, R^3 = Ts	**2c**	5	97
3	**1d:** R^1 = 4-BrC_6H_4, R^2 = H, R^3 = Ts	**2d**	5	95
4[b]	**1e:** R^1 = H, R^2 = CH_2Ph, R^3 = Ts	**2e**	5	82[c]
5	**1f:** R^1 = Ph, R^2 = H, R^3 = 4-$FC_6H_4SO_2$	**2f**	15	97
6	**1g:** R^1 = Ph, R^2 = H, R^3 = 4-$NO_2C_6H_4SO_2$	**2g**	30	90
7	**1h:** R^1 = Ph, R^2 = H, R^3 = 4-$MeOC_6H_4SO_2$	**2h**	5	95
8	**1i:** R^1 = Ph, R^2 = H, R^3 = 4-*t*-$BuC_6H_4SO_2$	**2i**	5	95
9	**1j:** R^1 = Ph, R^2 = H, R^3 = 4-$NO_2C_6H_4CO$	**2j**	40	91
10	**1k:** R^1, R^2 = -$(CH_2)_4$-, R^3 = Ts	**2k**	5	92
11	**1l:** R^1, R^2 = -$(CH_2)_3$-, R^3 = Ts	**2l**	5	93

[a]Yields of isolated products after column chromatographic purification. [b]2 equiv of BTEAC was used. [c]Another separable regioisomer was also obtained in 13% yield.[15]

Reaction was found to be sluggish with lesser amounts of $BF_3 \cdot OEt_2$. Other metal-containing LAs such as $Zn(OTf)_2$ and $Cu(OTf)_2$ were found to be less efficient. However, $Sc(OTf)_3$ reacted similar to $BF_3 \cdot OEt_2$. Upon screening various solvents such as diethyl ether, benzene, DMF, THF, and 1, 4-dioxane, only CH_2Cl_2 was found to be the solvent of choice in terms of efficiency of the reaction and yield of the product. Further, the methodology was generalized for a number of activated aziridines (Scheme 2) and the results are summarized in Table 1.

Substitution of the 2-aryl group did not affect the reactivity of the aziridine significantly (entries 1−3, Table 1) and the haloamines **2b**−**d**[13,14] were obtained as the only products. In the case of benzyl aziridine **1e**, probably because of reduced electrophilicity at the homobenzylic position, attack of the chloride ion took place at the less substituted carbon center producing **2e** as the major regioisomer (entry 4).[15] Aziridines **1f**−**g** with electron withdrawing groups at the *N*-arylsulfonyl part were found to react at slower rates compared to **1a** (entries 5 and 6).

However, aziridines **1h**−**i** showed reactivity similar to that of **1a** affording chloroamines **2h**−**i** in excellent yields (entries 7 and 8, Table 1). Interestingly, aziridines with other *N*-protecting (activating) functionalities that are generally more easily removable[16] such as 2-phenyl-*N*-(*p*-nitrosulfonyl)aziridine **1g** and 2-phenyl-*N*-(*p*-nitrobenzoyl)aziridine **1j** were also found to undergo ring-opening reaction leading to the formation of corresponding chloroamine **2g** and **2j**,[17] respectively, in excellent yield within 40 min (entries 6 and 9, Table 1). Bicyclic aziridines **1k**,**l** reacted smoothly to afford

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(15) 2-Benzyl *N*-tosyl aziridine **1e** gives two separable regioisomers **2e** and **2e′** as follows (see the Supporting Information for spectra of the crude mixture.)

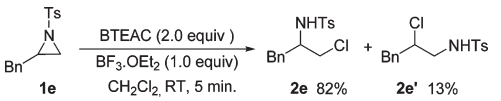

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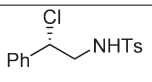
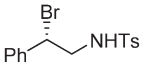
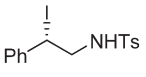
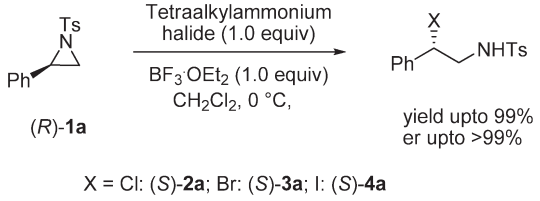
TABLE 2. Ring-Opening of (*R*)-2-Phenyl-*N*-tosylaziridine (*R*)-1a by Tetraalkylammonium Halides

entry	tetralkylammonium halide	haloamine[a]	time (min)	yield (%)[b]	er[c]
1	$BnEt_3N^{\oplus}\ Cl^{\ominus}$ (BTEAC)	 (*S*)-**2a**	5	98	95:5
2	$n\text{-}Bu_4N^{\oplus}\ Br^{\ominus}$ (TBAB)	 (*S*)-**3a**	2	99	>99:1
3	$n\text{-}Bu_4N^{\oplus}\ I^{\ominus}$ (TBAI)	 (*S*)-**4a**	<1	96	93:7

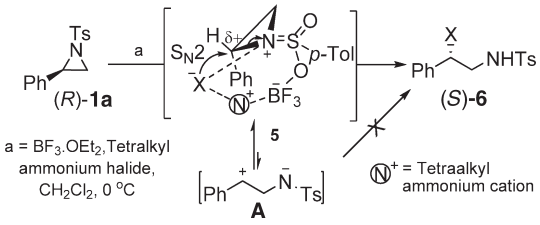
[a]Major enantiomer. [b]Yields of isolated products after column chromatographic purification. [c]Determined by chiral HPLC (see the Supporting Information).

SCHEME 3. Ring-Opening of (*R*)-2-Phenyl-*N*-tosylaziridine by Tetraalkylammonium Halides



X = Cl: (*S*)-**2a**; Br: (*S*)-**3a**; I: (*S*)-**4a**

SCHEME 4. Mechanism for Ring-Opening of (*R*)-2-Phenyl-*N*-tosylaziridine



trans-haloamines **2k**,**l** in excellent yields (entries 10 and 11, Table 1).

To study the mechanism of the reaction, enantiopure (*R*)-**1a** was subjected to ring-opening by 1.0 equiv of tetraalkylammonium halides, using 1.0 equiv of $BF_3 \cdot OEt_2$ in CH_2Cl_2 medium at 0 °C, and interestingly, the corresponding haloamines (*S*)-**2a**−**4a** were obtained in excellent yields with very high er (Scheme 3, Table 2). The reaction rate was found to increase with increasing nucleophilicity of the halide ions ($Cl^- < Br^- < I^-$), and in the case of iodide, reaction was instantaneous.

On the basis of the experimental results, a plausible mechanism for the ring-opening of (*R*)-**1a** is depicted in Scheme 4. During the reaction, $BF_3 \cdot OEt_2$ becomes coordinated with the sulfonamide oxygen of aziridine generating a highly reactive intermediate **5** that is stabilized by tetraalkylammonium salt and the racemization of (*R*)-**1a** via the 1,3 dipolar intermediate **A** is avoided. The halide ion associated with the tetraalkylammonium cation attacks at the benzylic position of **5** in an S_N2 fashion affording the haloamine (*S*)-**6**. The er of haloamine **4a** was found to decrease with increasing reaction time and temperature, probably due to the labile C−I bond at the benzylic position.

The present work is an important advancement in this field and further supports our earlier proposed mechanism. In the presence of tetraalkylammonium salt the racemization of (*R*)-**1a** is controlled and the products (Table 2) were obtained with excellent ee even in CH_2Cl_2 solvent where very poor ee was observed in all our earlier studies.[5,6]

After successful demonstration of the S_N2-type ring-opening of (*R*)-**1a**, we intended to extend this methodolgy to a wide variety of substituted chiral aziridines. For this purpose, we needed an efficient method for the diastereoselective synthesis of substituted *N*-tosylaziridines. Synthesis of substituted chiral aziridines has always been an intriguing area of research.[1c,d] Herein, we report a highly diastereoselective approach toward substituted *N*-tosylaziridines starting from *N*-Boc-(L)-phenylglycine **7** (Scheme 5, Table 3).

Reaction of *N*-Boc-(L)-phenylglycine **7** with *N*,*O*-dimethylhydroxylamine hydrochloride, Et_3N, and DCC produced the Weinreb amide **8**, which on treatment with an excess of Grignard reagents resulted in the formation aminoketones **9a**−**e**. The diastereoselective reduction of **9a**−**e** with $NaBH_4$ in methanol at −20 °C provided the *N*-Boc-amino alcohols **10a**−**e** with excellent dr (from ^1H NMR).[18] One-pot removal of the Boc group by TFA followed by tosylation in the presence of Et_3N afforded the *N*-Ts amino alcohols **11a**−**e** in excellent yields (over two steps).[19] The *anti*-stereochemistry of amino alcohol **11a**[20a] (major diastereomer) was confirmed by single crystal X-ray data (see the Supporting Information). Aziridines **12a**−**e** were obtained by stereoselective *N*-heterocyclization of amino alcohols **11a**−**e**, using Mitsunobu protocol (PPh_3-DEAD),

(18) For similar preparation of *N*-Boc-amino alcohol see: Zhou, Z. H.; Tang, Y. L.; Li, K. Y.; Liu, B.; Tang, C. C. *Heteroatom Chem.* **2003**, *14*, 603.

(19) Corresponding *N*-Ts-amino ketones led to the *N*-Ts-amino alcohols in poor dr with use of several methods for reduction including $NaBH_4$.

(20) (a) Ibuka, T.; Nakai, K.; Akaji, M.; Tamamura, H.; Fujii, N.; Yamamoto, Y. *Tetrahedron* **1996**, *52*, 11739. (b) Toumi, M.; Couty, F.; Evano, G. *Tetrahedron Lett.* **2008**, *49*, 1175.

SCHEME 5. Synthesis of Disubstituted Aziridines 12a−e

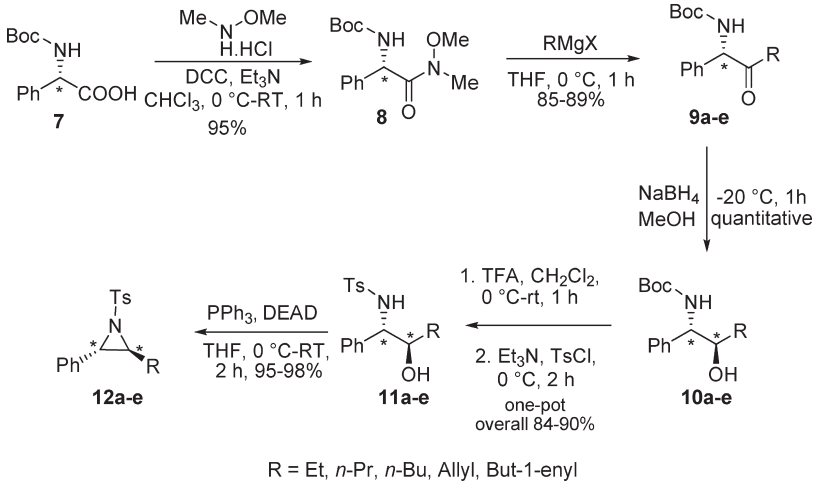
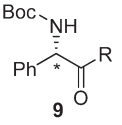
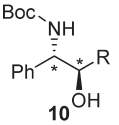
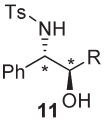
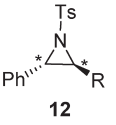


TABLE 3. Synthesis of Disubstituted Aziridines

entry	aminoketone	*N*-Boc amino alcohol	*N*-Ts amino alcohol	aziridine
	% yield[a]	% yield[a] (dr)[b]	% yield[a] (dr)[b]	% yield[a] (dr)[b]
				
	9	10	11	12
1	**9a**: R = Et,	**10a**	**11a**	**12a**
	87	quant. (94:6)	86 (94:6)	95 (94:6)
2	**9b**: R = *n*-Pr,	**10b**	**11b**	**12b**
	89	quant. (>99:1)	88 (>99:1)	98 (>99:1)
3	**9c**: R = *n*-Bu,	**10c**	**11c**	**12c**
	89	quant. (>99:1)	90 (>99:1)	95 (>99:1)
4	**9d**: R = Allyl,	**10d**	**11d**	**12d**
	85	quant. (>99:1)	84 (>99:1)	96 (>99:1)
5	**9e**: R = But-1-enyl,	**10e**	**11e**	**12e**
	86	quant. (>99:1)	87 (>99:1)	97 (>99:1)

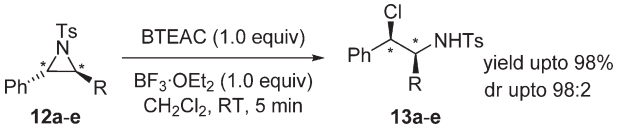
[a]Yields of isolated products after column chromatographic purification. [b]dr values given in parentheses are based on ^{1}H NMR of the crude rection mixture.

in excellent yields and in diastereopure forms except for **11a** (Table 3). All the newly synthesized compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR, and HRMS data.

Next the ring-opening protocol of monosubstituted aziridines by tetrabutyl ammonium salts was extended to disubstituted aziridines.

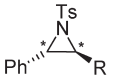
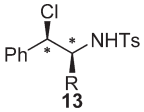
Aziridines **12a−e** were treated with 1.0 equiv of BTEAC and 1.0 equiv of $BF_3 \cdot OEt_2$ in CH_2Cl_2 medium at rt for 5 min to provide the chloroamines **13a−e** in excellent yields and high dr (Scheme 6, Table 4). Excellent diastereoselectivity obtained during the ring-opening of **12a−e** again supports the S_N2-type mechanism.

SCHEME 6. Opening of Substituted Chiral *N*-Sulfonylaziridines by BTEAC



Next, the synthetic significance of these chiral β-haloamines has been demonstrated by their convertion into the

TABLE 4. Opening of Substituted Chiral *N*-Sulfonylaziridines by BTEAC

entry	aziridine (dr)	chloroamine[a]	yield[b] (%)	dr[c]
	 **12**	 **13**		
1	**12a**: R= Et (96:4)	**13a**	96	93:7
2	**12b**: R= *n*-Pr (>99:1)	**13b**	95	97:3
3	**12c**: R= *n*-Bu (>99:1)	**13c**	98	98:2
4	**12d**: R= Allyl (>99:1)	**13d**	92	96:4
5	**12e**: R= But-1-enyl (>99:1)	**13e**	92	98:2

[a]Stereochemistry based on precursor aziridines. [b]Yields of isolated products after column chromatographic purification. [c]dr values determined by ^{1}H NMR of crude reaction mixture.

SCHEME 7. Dechlorination of Chloroamines

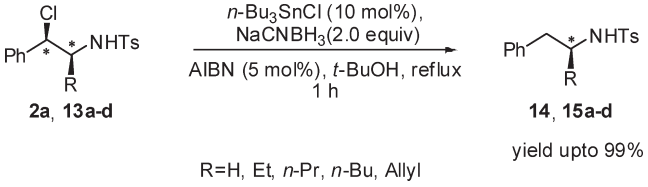
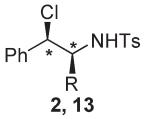
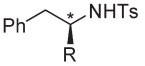


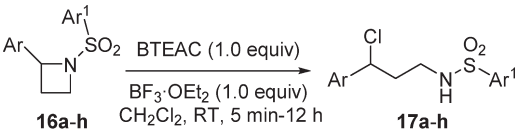
TABLE 5. Dechlorination of Chloroamines

entry	Haloamines (dr)	amines	yield[a] (%)
	 **2, 13**	 **14, 15**	
1[b]	**2a:** R = H	**14**	99
2	**13a:** R = Et (93:7)	**15a**	95
3	**13b:** R = *n*-Pr (97:3)	**15b**	98
4	**13c:** R = *n*-Bu (98:2)	**15c**	95
5	**13d:** R = Allyl (96:4)	**15d**	97

[a]Yields of isolated products after column chromatographic purification. [b]**2a** is a racemic compound, synthesized from racemic **1a**.

corresponding chiral amines. Synthesis of chiral amines is an area of great interest due to their utility as new ligands and chiral synthons and their occurrence as subunits in chiral drugs.[21] When chloroamines **2a** and **13a**−**d** were treated with 2.0 equiv of $NaCNBH_3$ in the presence of catalytic *n*-Bu_3SnCl and AIBN in *t*-BuOH medium[22] under reflux condition, the corresponding *N*-tosylamines **14** and **15a**−**d** were produced in excellent yields (Scheme 7; Table 5).

SCHEME 8. Ring-Opening of *N*-Sulfonylazetidines by BTEAC

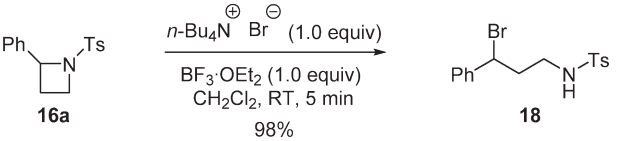


After successful demonstration of the ring-opening of *N*-sulfonylaziridines, we further extended this methodology for the ring-opening of *N*-sulfonylazetidines to obtain 1,3-haloamines. To our delight, when azetidines **16a**−**h** were subjected to the ring-opening condition with use of 1.0 equiv of BTEAC and 1.0 equiv of $BF_3\cdot OEt_2$ in CH_2Cl_2 medium, the corresponding chloroamines **17a**−**h** were obtained in excellent yields except for entry 5 (Scheme 8; Table 6) and the observed regioselectivity is consistent with the literature reports.[3g,6] On the basis of our earlier experience[5,6] and the results with 2-aryl-*N*-tosylaziridines,[5] we believe 2-aryl-*N*-tosylazetidines will follow a similar S_N2-type mechanism during ring-opening by halides.[23]

2-Phenyl-*N*-tosylazetidine **16a** upon treatment with TBAB in the presence of $BF_3\cdot OEt_2$ afforded the corresponding bromoamine **18** in 98% yield within 5 min (Scheme 9).

In an interesting observation when **16a** was reacted with TBAB in the presence of $BF_3\cdot OEt_2$ for longer times even after completion (time > 5 min), some part of the **18** was found to be

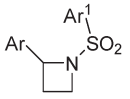
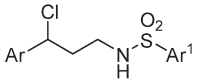
SCHEME 9. Opening of 2-Phenyl *N*-Sulfonylazetidine by TBAB



(21) (a) Enders, D.; Reinhold, U. *Tetrahedron: Asymmetry* **1997**, *8*, 1895. (b) Bloch, R. *Chem. Rev.* **1998**, *98*, 1407. (c) Kobayashi, S.; Ishitani, H. *Chem. Rev.* **1999**, *99*, 1069.

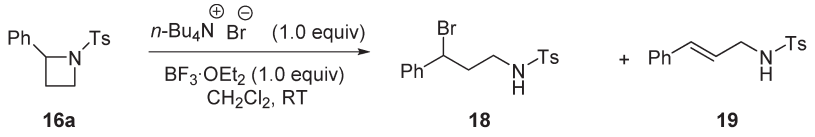
(22) Corey, E. J.; Suggs, J. W. *J. Org. Chem.* **1975**, *40*, 2554.

TABLE 6. Opening of *N*-Sulfonylazetidines by BTEAC

entry	Azetidine	Chloroamine	time	yield (%)[a]
	 **16**	 **17**		
1	**16a**: Ar = Ph, Ar^1 = 4-MeC_6H_4	**17a**	10 min	95
2	**16b**: Ar = 4-ClC_6H_4, Ar^1 = 4-MeC_6H_4	**17b**	2 h	85
3	**16c**: Ar = 3-BrC_6H_4, Ar^1 = 4-MeC_6H_4	**17c**	5 min	95
4	**16d**: Ar = 2-ClC_6H_4, Ar^1 = 4-MeC_6H_4	**17d**	30 min	90
5	**16e**: Ar = 4-$NO_2C_6H_4$, Ar^1 = 4-MeC_6H_4	**17e**	12 h	35
6	**16f**: Ar = Ph, Ar^1 = 4-FC_6H_4	**17f**	15 min	73
7	**16g**: Ar = Ph, Ar^1 = 4-$MeOC_6H_4$	**17g**	5 min	94
8	**16h**: Ar = Ph, Ar^1 = 4-*t*-BuC_6H_4	**17h**	5 min	84

[a]Yields of isolated products after column chromatographic purification.

SCHEME 10. In Situ Conversion of Bromoamine 18 to Allylamine 19



	Time	**18** : **19**
Reaction Prolongation	5 min	100 : 0
	23 h	80 : 20
	45 h	74 : 26

converted into allylamine **19** (Scheme 10). The formation of product **19** was confirmed by studying the ^{1}H NMR spectra of the reaction mixture at different time intervals: 5 min, 23 h, and 45 h. This result is consisent with our earlier work where we reported ring-opening rearrangement of 2-aryl-*N*-sulfonylazetidines to the corresponding allylamines.[6c]

Conclusion

In conclusion, we have developed an efficient route toward 1,2- and 1,3-haloamines via regio- and stereoselective ring-opening of *N*-sulfonylaziridines and azetidines by halides using tetraalkylammonium halides in the presence of $BF_3 \cdot OEt_2$. Haloamines obtained from chiral 2, 3-disubstituted-*N*-tosylaziridines were transformed to the corresponding chiral *N*-tosylamines. Formation of haloamines in high er and dr from enantiopure 2-phenyl-*N*-tosylaziridines provided convincing evidence in support of our earlier proposed S_N2-type ring-opening mechanism.

Experimental Section

General Procedure 1: Ring-Opening of Activated Aziridine with BTEAC in the Presence of $BF_3 \cdot OEt_2$ (Scheme 1; Table 1). To a stirred solution of aziridine (1.0 equiv) and BTEAC (1.0 equiv) in dry CH_2Cl_2 (0.2 mL for 0.1 mmol of aziridine) was added $BF_3 \cdot OEt_2$ (1.0 equiv) dropwise at rt and the reaction was continued for the appropriate time (Scheme 1, Table 1). After completion of the reaction (monitored by TLC), it was quenched with water. The product was extracted by CH_2Cl_2 (3×2.0 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified by flash column chromatography on silica gel (230−400 mesh) with ethyl acetate in petroleum ether as the eluent.

(23) The er of 1,3-haloamine resulting from the ring-opening of enantiopure (*S*)-2-phenyl-*N*-tosylazetidine could not be determined by chiral hplc analysis as the enantiomers were inseparable in the available chiral hplc columns. In an attempt to determine the er of the 1,3-haloamine indirectly, when *N*-(3-chloro-3-phenylpropyl)-4-methylbenzenesulfonamide was treated with NaH in DMF at 60 °C, the starting 2-phenyl-*N*-tosylazetidine was regenerated in nonracemic form (based on chiral hplc analysis) indicating the *N*-(3-chloro-3-phenylpropyl)-4-methylbenzenesulfonamide must be in nonracemic form. This result clearly suggests that LA mediated opening of 2-phenyl-*N*-tosylazetidine by BTEAC to follow an S_N2-type mechanism similar to 2-phenyl-*N*-tosylaziridine.

General Procedure 2: Ring-Opening of (*R*)-1a with Tetraalkylammonium Halides in the Presence of $BF_3 \cdot OEt_2$ (Scheme 3, Table 2). To a stirred solution of (*R*)-**1a** (1.0 equiv) and tetraalkylammonium halide (1.0 equiv) in dry CH_2Cl_2 (0.2 mL for 0.1 mmol of aziridine) was added $BF_3 \cdot OEt_2$ (1.0 equiv) dropwise at 0 °C and the reaction was continued for the appropriate time (Table 2). After completion of the reaction (monitored by TLC), it was quenched with water. The product was extracted by CH_2Cl_2 (3 × 2.0 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent the crude product was purified by flash column chromatography on silica gel (230−400 mesh) with ethyl acetate in petroleum ether as the eluent.

General Procedure 3: Synthesis of Amino Ketones (Scheme 5, Table 3). Alkyl halide (ethyl bromide or *n*-propyl bromide or *n*-butyl bromide or allyl chloride or 4-bromo-1-butene) (4.0 equiv) was dissolved in dry THF (2.0 mL for 0.5 mmol of Weinreb amide) and one fourth of this solution was added dropwise to Mg turning (4.0 equiv) (suspended in 1.0 mL of dry THF in the presence of a pinch of molecular iodine) under ice-cold condition. After the disappearance of the yellow color, the rest of the alkyl halide solution was added dropwise. The stirring was continued until all Mg was consumed. Further, Weinreb amide **8** (1.0 equiv), dissolved in dry THF (2.0 mL), was added dropwise at 0 °C and the reaction was continued for another hour at the same temperature. The reaction was quenched by dropwise addition of saturated aq NH_4Cl at 0 °C. The crude reaction mixture was extracted with ethyl acetate (3 × 2.0 mL), washed with brine, and dried over anhydrous Na_2SO_4 then the solvent was removed under reduced pressure. After column chromatographic purification on silica gel (230−400 mesh) with ethyl acetate in petroleum ether as the eluent, amino ketones **9a**−**e** were obtained as white solids.

General Procedure 4: Synthesis of *N*-Boc-Amino Alcohols (Scheme 5, Table 3). To a stirred solution of amino ketones (**9a**−**e**) (1.0 equiv) in dry methanol (10 mL for 1.0 mmol of **9a**−**e**) at −20 °C was added sodium borohydride (2.0 equiv) in one lot and stirring was continued at the same temperature for 1 h. The reaction was then quenched with water. The resulting mixture was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (25 mL) and washed successively with water and brine. After drying over anhydrous Na_2SO_4 and removing the solvent, **10a**−**e** were obtained in quantitative yields pure enough to proceed for the next step.

General Procedure 5: Synthesis of *N*-Ts-Amino Alcohols (Scheme 5, Table 3). To a stirred solution of *N*-Boc-amino alcohols (**10a**−**e**) (1.0 equiv) in dry CH_2Cl_2 (5.0 mL for 1.0 mmol of **10a**−**e**) at 0 °C was added TFA (1.0 mL) dropwise and the stirring was continued at rt for 1 h.The reaction temperature was brought to 0 °C again and Et_3N (2.2 mL) was added dropwise with care. After 5 min, TsCl (1.2 equiv) was added in portions at the same temperature and the reaction was continued for an additional 2 h at 0 °C. After completion of the reaction (monitored by TLC), the reaction mixture was washed with 5% aq HCl (5.0 mL), water (5.0 mL), and brine (3.0 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent, the crude reaction mixture was subjected to flash column chromatography on silica gel (230−400 mesh) with ethyl acetate in petroleum ether as the eluent affording **11a**−**e** as white solids.

General Procedure 6: Synthesis of 2,3-Disubstituted-*N*-tosylaziridines (Scheme 5, Table 3). To a stirred solution of PPh_3 (1.5 equiv) and *N*-Ts-amino alcohols (**11a**−**e**) (1.0 equiv) in dry THF (2.0 mL for 0.5 mmol of **11a**−**e**) was added DEAD (1.5 equiv) dropwise at 0 °C then the reaction was continued for 2 h at rt. After completion of the reaction (monitored by TLC), the solvent was removed and the crude product was purified by column chromatography on silica gel (230−400 mesh) with ethyl acetate in petroleum ether as the eluent affording aziridines **12a**−**e**.

General Procedure 7: Ring-Opening of Disubstituted Aziridines with BTEAC in the Presence of $BF_3 \cdot OEt_2$ (Scheme 6, Table 4). To a stirred solution of aziridine (**12a**−**e**) (1.0 equiv) and BTEAC (1.0 equiv) in dry CH_2Cl_2 (0.2 mL for 0.1 mmol of aziridine) was added $BF_3 \cdot OEt_2$ (1.0 equiv) dropwise at rt then the reaction was continued for 5 min. After completion of the reaction (monitored by TLC), it was quenched with water. The product was extracted by CH_2Cl_2 (3 × 2.0 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent the crude product was purified by flash column chromatography on silica gel (230−400 mesh) with ethyl acetate in petroleum ether as the eluent.

General Procedure 8: Dechlorination of Chloroamines (Table 5). To a stirred suspension of $NaCNBH_3$ (2.0 equiv), chloroamine (**2a**, **13a**,**b**) (1.0 equiv), and AIBN (5 mol %) in *t*-BuOH (1.0 mL for 0.1 mmol of chloroamine) was added *n*-Bu_3SnCl (10 mol %) then the mixture was refluxed for 1 h at 85 °C. After completion (monitored by TLC) the reaction was quenched with water and the product was extracted by ethyl acetate (3 × 2.0 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified by flash column chromatography on silica gel (230−400 mesh) with ethyl acetate in petroleum ether as the eluent.

General Procedure 9: Ring-Opening of *N*-Sulfonylazetidines with BTEAC in the Presence of $BF_3 \cdot OEt_2$ (Table 6). To a stirred solution of azetidine (1.0 equiv) and BTEAC (1.0 equiv) in dry CH_2Cl_2 (1.0 mL for 0.25 mmol of azetidine) was added $BF_3 \cdot OEt_2$ (1.0 equiv) at rt and the reaction was continued for the appropriate time (Table 6). After completion of the reaction (monitored by TLC) it was quenched with water, then the product was extracted with CH_2Cl_2 (3 × 2.0 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent the crude product was purified by flash column chromatography on silica gel (230−400 mesh) with ethyl acetate in petroleum ether as the eluent.

***N*-(2-Chloro-2-phenylethyl)-4-methylbenzenesulfonamide (2a).** The general procedure 1 described above was followed when **1a** (100 mg, 0.37 mmol) was treated with BTEAC (84 mg, 0.37 mmol) and $BF_3 \cdot OEt_2$ (46 μL, 0.37 mmoL) in dry CH_2Cl_2 (0.7 mL) at rt for 5 min to afford **2a** as a white solid (113 mg, 99% yield). R_f 0.25 (ethyl acetate−petroleum ether, 1:5); $[\alpha]^{25}_D$ +102.7 (*c* 0.31, $CHCl_3$); IR ν_{max} (KBr, cm^{-1}) 3262, 2924, 2854, 1330, 1158, 708, 551; ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.31−3.44 (m, 2H), 4.74 (t, J = 6.6 Hz, 1H), 4.79 (dd, J = 7.2, 2.2 Hz, 1H), 7.11−7.29 (m, 7H), 7.66 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 50.3, 61.6, 127.0, 127.1, 128.9, 129.1, 129.8, 136.9, 137.7, 143.5. Anal. Calcd for $C_{15}H_{16}ClNO_2S$: C 58.15, H 5.21, N 4.52. Found: C 58.12, H 5.23, N 4.50. For (*S*)-**2a** er 95:5; enantiomeric purity was determined by chiral hplc analysis (Chiralpak AD-H column), hexane−isopropanol 95:5, flow rate = 1.0 mL/min; $t_R(1)$ = 28.93 min (minor), $t_R(2)$ = 36.77 min (major).

***N*-(2-Chloro-2-(4-chlorophenyl)ethyl)-4-methylbenzenesulfonamide (2b).**[13] The general procedure 1 described above was followed when **1b** (100 mg, 0.32 mmol) was treated with BTEAC (73 mg, 0.32 mmol) and $BF_3 \cdot OEt_2$ (40 μL, 0.32 mmol) in dry CH_2Cl_2 (0.7 mL) at rt for 5 min to afford **2b** as a white solid (107 mg, 96% yield). Mp 101−102 °C; R_f 0.44 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (KBr, cm^{-1}) 3286, 2924, 2854, 1597, 1493, 1411, 1329, 1213, 1160, 1091, 1015, 830, 814, 753, 705, 662, 626, 552, 535; ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.31−3.38 (m, 2H), 4.78−4.85 (m, 2H), 7.14−7.25 (m, 6H), 7.64 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 50.2, 60.8, 126.9, 128.6, 129.1, 129.9, 134.9, 136.3, 136.8, 143.9; HRMS (ESI) for $C_{15}H_{15}Cl_2NO_2S$, $(M + H)^+$ found 344.0276, calcd 344.0279.

***N*-(2-Chloro-2-(3-chlorophenyl)ethyl)-4-methylbenzenesulfonamide (2c).** The general procedure 1 described above was

followed when **1c** (100 mg, 0.32 mmol) was treated with BTEAC (73 mg, 0.32 mmol) and $BF_3 \cdot OEt_2$ (40 μL, 0.32 mmol) in dry CH_2Cl_2 (0.7 mL) at rt for 5 min to afford **2c** as a white solid (107 mg, 97% yield). Mp 86−88 °C; R_f 0.42 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (KBr, cm^{-1}) 3283, 3064, 2924, 2854, 1598, 1576, 1477, 1432, 1329, 1186, 1160, 1093, 1019, 839, 814, 789, 750, 692, 663, 551; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.33−3.42 (m, 2H), 4.75−4.81 (m, 2H), 7.10−7.27 (m, 6H), 7.65 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 50.2, 60.7, 125.5, 126.9, 127.4, 129.2, 129.9, 130.1, 134.7, 136.8, 139.7, 143.9; HRMS (ESI) for $C_{15}H_{15}Cl_2NO_2S$ (M + H)$^+$ found 344.0278, calcd 344.0279.

***N*-(2-(4-Bromophenyl)-2-chloroethyl)-4-methylbenzenesulfonamide (2d).**[14] The general procedure 1 described above was followed when **1d** (100 mg, 0.28 mmol) was treated with BTEAC (64 mg, 0.28 mmol) and $BF_3 \cdot OEt_2$ (35 μL, 0.28 mmol) in dry CH_2Cl_2 (0.6 mL) at rt for 5 min to afford **2d** as a white solid (103 mg, 95% yield). Mp 115−117 °C; R_f 0.42 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (KBr, cm^{-1}) 3283, 3064, 2924, 2854, 1595, 1490, 1407, 1329, 1212, 1185, 1160, 1093, 1074, 1011, 814, 748, 667, 624, 552, 530; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.37−3.43 (m, 2H), 4.79−4.85 (m, 2H), 7.14 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 50.2, 60.9, 123.1, 126.9, 128.9, 129.9, 132.1, 136.8, 143.9; HRMS (ESI) for $C_{15}H_{15}BrClNO_2S$ (M + H)$^+$ found 387.9772, calcd 387.9774.

***N*-(1-Chloro-3-phenylpropan-2-yl)-4-methylbenzenesulfonamide (2e).** The general procedure 1 described above was followed when **1e** (100 mg, 0.35 mmol) was treated with BTEAC (80 mg, 0.35 mmol) and $BF_3 \cdot OEt_2$ (44 μL, 0.35 mmol) in dry CH_2Cl_2 (0.7 mL) at rt for 5 min to afford **2e** as a white solid (93 mg, 82% yield). Mp 95−97 °C; R_f 0.43 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (KBr, cm^{-1}) 3264, 2925, 2854, 1599, 1495, 1459, 1433, 1347, 1315, 1298, 1156, 1091, 1072, 981, 953, 918, 887, 852, 810, 751, 697, 663, 628, 586, 554, 509; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.76 (dd, J = 13.7, 6.4 Hz, 1H), 2.87 (dd, J = 13.6, 7.8 Hz, 1H), 3.41−3.50 (m, 2H), 3.65−3.73 (m, 1H), 4.89 (d, J = 8.0 Hz, 1H), 7.03−7.07 (m, 2H), 7.15−7.26 (m, 5H), 7.64 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 38.2, 46.8, 55.0, 126.8, 126.9, 128.7, 129.1, 129.7, 136.0, 137.1, 143.5; HRMS (ESI) for $C_{16}H_{18}ClNO_2S$ (M + H)$^+$ found 324.0829, calcd 324.0825.

***N*-(2-Chloro-3-phenylpropyl)-4-methylbenzenesulfonamide (2e′).** The general procedure 1 described above was followed when **1e** (100 mg, 0.35 mmol) was treated with BTEAC (80 mg, 0.35 mmol) and $BF_3 \cdot OEt_2$ (44 μL, 0.35 mmol) in dry CH_2Cl_2 (0.7 mL) at rt for 5 min to afford **2e′** as a white solid (15 mg, 13% yield). IR ν_{max} (KBr, cm^{-1}) 3264, 2925, 2854, 1599, 1495, 1459, 1433, 1347, 1315, 1298, 1156, 1091, 1072, 981, 953, 918, 887, 852, 810, 751, 697, 663, 628, 586, 554, 509; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.88−3.07 (m, 3H), 3.20−3.26 (m, 1H), 3.98−4.05 (m, 1H), 4.87 (t, J = 6.8 Hz, 1H), 7.05−7.07 (m, 2H), 7.16−7.24 (m, 5H), 7.62 (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 41.7, 48.3, 61.7, 127.0, 127.2, 128.6, 129.2, 129.8, 136.3, 136.6, 143.7.

***N*-(2-Chloro-2-phenylethyl)-4-fluorobenzenesulfonamide (2f).** The general procedure 1 described above was followed when **1f** (100 mg, 0.36 mmol) was treated with BTEAC (82 mg, 0.36 mmol) and $BF_3 \cdot OEt_2$ (45 μL, 0.36 mmol) in dry CH_2Cl_2 (0.7 mL) at rt for 15 min to afford **2f** as a white solid (110 mg, 97% yield). Mp 65−68 °C; R_f 0.33 (ethyl acetate−petroleum ether, 1:4); IR ν_{max} (KBr, cm^{-1}) 3274, 3056, 2966, 2868, 1597, 1497, 1460, 1426, 1401, 1330, 1267, 1202, 1163, 1112, 1089, 1080, 1039, 1027, 999, 872, 836, 771, 754, 700, 665, 634, 604, 573, 551, 538, 521; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36−3.42 (m, 2H), 4.83 (dd, J = 8.1, 5.6 Hz, 1H), 4.90 (t, J = 6.6 Hz, 1H), 7.10−7.30 (m, 7H), 7.77−7.80 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 50.4, 61.7, 116.5, 116.7, 125.6, 127.3, 128.9, 129.1, 129.3, 129.8, 129.9, 136.1, 137.7, 164.3, 166.3; HRMS (ESI) for $C_{14}H_{13}ClFNO_2S$ (M + H)$^+$ found 314.0417, calcd 314.0418. Anal. Calcd for $C_{14}H_{13}ClFNO_2S$: C 53.59, H 4.18, N 4.46. Found: C 53.13, H 4.04, N 4.01.

***N*-(2-Chloro-2-phenylethyl)-4-nitrobenzenesulfonamide (2g).** The general procedure 1 described above was followed when **1g** (100 mg, 0.33 mmol) was treated with BTEAC (75 mg, 0.33 mmol) and $BF_3 \cdot OEt_2$ (41 μL, 0.33 mmol) in dry CH_2Cl_2 (0.7 mL) at rt for 30 min to afford **2g** as a white solid (101 mg, 90% yield). Mp 122−125 °C; R_f 0.26 (ethyl acetate−petroleum ether, 1:4); IR ν_{max} (KBr, cm^{-1}) 3265, 3107, 2929, 2855, 1609, 1532, 1495, 1454, 1421, 1348, 1313, 1279, 1243, 1214, 1165, 1108, 1090, 1078, 1040, 1012, 1001, 882, 854, 828, 769, 740, 700, 683, 660, 623, 595, 557, 524; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38−3.54 (m, 2H), 4.86 (dd, J = 8.1, 5.6 Hz, 1H), 4.97 (t, J = 6.3 Hz, 1H), 7.23−7.30 (m, 5H), 7.95 (dd, J = 6.8, 1.7 Hz, 2H), 8.28 (dd, J = 6.8, 1.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 50.6, 61.7, 124.6, 127.2, 128.3, 128.4, 129.1, 129.4, 137.4, 145.9, 150.2; HRMS (ESI) for $C_{14}H_{13}ClN_2O_4S$ (M − HCl)$^+$ found 305.0599, calcd 305.0596.

***N*-(2-Chloro-2-phenylethyl)-4-methoxybenzenesulfonamide (2h).** The general procedure 1 described above was followed when **1h** (100 mg, 0.35 mmol) was treated with BTEAC (80 mg, 0.35 mmol) and $BF_3 \cdot OEt_2$ (44 μL, 0.35 mmol) in dry CH_2Cl_2 (0.7 mL) at rt for 5 min to afford **2h** as a white solid (108 mg, 95% yield). R_f 0.18 (ethyl acetate−petroleum ether, 1:4); IR ν_{max} (KBr, cm^{-1}) 3261, 3070, 2931, 2839, 1598, 1580, 1499, 1454, 1426, 1332, 1307, 1257, 1211, 1158, 1118, 1091, 1077, 1032, 1000, 964, 878, 836, 816, 801, 769, 729, 700, 654, 630, 608, 564, 527; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.34−3.40 (m, 2H), 3.81 (s, 3H), 4.74 (t, J = 6.1 Hz, 1H), 4.81 (dd, J = 8.3, 5.9 Hz, 1H), 6.91−6.94 (m, 2H), 7.21−7.29 (m, 5H), 7.70−7.72 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 50.4, 55.8, 61.8, 114.5, 127.3, 129.0, 129.2, 129.3, 131.5, 137.9, 163.2; HRMS (ESI) for $C_{15}H_{16}ClNO_3S$ (M + H)$^+$ found 326.0619, calcd 326.0618.

4-*tert*-Butyl-*N*-(2-chloro-2-phenylethyl)benzenesulfonamide (2i). The general procedure 1 described above was followed when **1i** (100 mg, 0.32 mmol) was treated with BTEAC (73 mg, 0.32 mmol) and $BF_3 \cdot OEt_2$ (40 μL, 0.32 mmol) in dry CH_2Cl_2 (0.7 mL) at rt for 5 min to afford **2i** as a white solid (106 mg, 95% yield). Mp 79−81 °C; R_f 0.40 (ethyl acetate−petroleum ether, 1:4); IR ν_{max} (KBr, cm^{-1}) 3288, 3074, 2925, 2852, 1593, 1496, 1455, 1428, 1329, 1297, 1239, 1168, 1154, 1091, 1073, 1027, 906, 842, 771, 718, 693, 550, 519; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 9H), 3.39−3.44 (m, 2H), 4.77−4.86 (m, 2H), 7.20−7.29 (m, 5H), 7.47 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.2, 35.3, 50.4, 61.8, 126.4, 126.9, 127.3, 129.0, 129.2, 136.9, 137.9, 156.9; HRMS (ESI) for $C_{18}H_{22}ClNO_2S$ (M + H)$^+$ found 352.1139, calcd 352.1138.

***N*-(2-Chloro-2-phenylethyl)-4-nitrobenzamide (2j).**[17] The general procedure 1 described above was followed when **1j** (100 mg, 0.37 mmol) was treated with BTEAC (84 mg, 0.37 mmol) and $BF_3 \cdot OEt_2$ (46 μL, 0.37 mmol) in dry CH_2Cl_2 (0.7 mL) at rt for 40 min to afford **2j** as a white solid (102 mg, 91% yield). Mp 102−103 °C; R_f 0.28 (ethyl acetate−petroleum ether, 1:4); IR ν_{max} (KBr, cm^{-1}) 3320, 3081, 3031, 2924, 2855, 1642, 1601, 1536, 1493, 1434, 1354, 1322, 1301, 1252, 1212, 1176, 1154, 1109, 1050, 858, 830, 771, 725, 701, 628, 554, 528; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90−3.93 (m, 2H), 5.44−5.49 (m, 1H), 6.85 (d, J = 7.6 Hz, 1H), 7.28−7.35 (m, 5H), 7.89 (dd, J = 6.8, 1.7 Hz, 2H), 8.20 (dd, J = 7.1, 1.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 47.4, 54.3, 123.9, 126.6, 128.3, 128.5, 128.9, 137.8, 139.4, 149.7, 165.1; HRMS (ESI) for $C_{15}H_{13}ClN_2O_3$, (M + H)$^+$ found 305.0691, calcd 305.0693.

***trans*-*N*-(2-Chlorocyclohexyl)-4-methylbenzenesulfonamide (2k).** The general procedure 1 described above was followed when **1k** (100 mg, 0.40 mmol) was treated with BTEAC (91 mg, 0.40 mmol) and $BF_3 \cdot OEt_2$ (50.0 μL, 0.40 mmol) in dry CH_2Cl_2 (0.8 mL) at rt for 5 min to afford **2k** as a white solid (106 mg, 92% yield). Mp

101−103 °C; R_f 0.42 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (KBr, cm^{-1}) 3255, 3049, 2947, 2903, 2868, 1595, 1494, 1465, 1447, 1422, 1334, 1319, 1302, 1290, 1257, 1184, 1156, 1118, 1095, 1037, 1023, 932, 882, 867, 811, 705, 670, 584, 550, 523, 505; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15−1.29 (m, 3H), 1.49−1.65 (m, 3H), 2.08−2.21 (m, 2H), 2.36 (s, 3H), 2.98−3.04 (m, 1H), 3.60−3.66 (m, 1H), 4.86 (d, J = 5.4 Hz, 1H), 7.24 (d, J = 8.5 Hz, 2H), 7.68−7.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 23.4, 24.5, 32.6, 35.0, 58.8, 62.2, 127.3, 129.6, 136.9, 143.5; HRMS (ESI) for $C_{13}H_{18}ClNO_2S$ $(M + H)^+$ found 288.0823, calcd 288.0825.

trans*-*N*-(2-Chlorocyclopentyl)-4-methylbenzenesulfonamide (2*l*).** The general procedure 1 described above was followed when **1*l (100 mg, 0.42 mmol) was treated with BTEAC (96 mg, 0.42 mmol) and $BF_3\cdot OEt_2$ (53.0 μL, 0.42 mmol) in dry CH_2Cl_2 (0.8 mL) at rt for 5 min to afford **2*l*** as a white solid (107 mg, 93% yield). R_f 0.42 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (KBr, cm^{-1}) 3269, 2975, 2923, 1598, 1494, 1443, 1414, 1379, 1324, 1292, 1237, 1184, 1162, 1120, 1096, 1081, 1038, 1020, 917, 901, 815, 706, 668, 572, 551, 517; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31−1.38 (m, 1H), 1.59−1.79 (m, 3H), 2.02−2.13 (m, 2H), 2.37 (s, 3H), 3.48−3.53 (m, 1H), 3.99−4.02 (m, 1H), 5.23 (d, J = 5.5 Hz, 1H), 7.26 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 21.7, 30.6, 33.4, 62.7, 63.7, 127.3, 129.9, 136.9, 143.9; HRMS (ESI) for $C_{12}H_{16}ClNO_2S$ $(M + H)^+$ found 274.0668, calcd 274.0669.

(*S*)-*N*-(2-Bromo-2-phenylethyl)-4-methylbenzenesulfonamide [(*S*)-3a]. The general procedure 2 described above was followed when (*R*)-**1a** (100 mg, 0.37 mmol) was treated with TBAB (119 mg, 0.37 mmol) and $BF_3\cdot OEt_2$ (46 μL, 0.37 mmol) in dry CH_2Cl_2 (0.8 mL) at 0 °C for 2 min to afford (*S*)-**3a** as a white solid (130 mg, 99% yield). Mp 111−113 °C; R_f 0.25 (ethyl acetate−petroleum ether, 1:5); $[\alpha]^{25}_D$ +67.6 (*c* 0.34, $CHCl_3$); IR ν_{max} (KBr, cm^{-1}) 3263, 2923, 2853, 1331, 1157, 696, 550; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.47−3.52 (m, 2H), 4.75 (t, J = 6.4 Hz, 1H), 4.83 (t, J = 6.4 Hz, 1H), 7.17−7.26 (m, 7H), 7.65 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 50.0, 52.6, 127.0, 127.6, 129.0, 129.1, 129.8, 136.9, 138.1, 143.8. Anal. Calcd for $C_{15}H_{16}BrNO_2S$: C 50.86, H 4.55, N 3.95. Found: C 50.83, H 4.56, N 3.92. er > 99:1. Enantiomeric purity was determined by chiral hplc analysis (Chiralpak AD-H column), hexane−isopropanol 95:5, flow rate = 1.0 mL/min; $t_R(1)$ = 27.96 min (minor), $t_R(2)$ = 34.83 min (major).

(*S*)-*N*-(2-Iodo-2-phenylethyl)-4-methylbenzenesulfonamide [(*S*)-4a]. The general procedure 2 described above was followed when (*R*)-**1a** (100 mg, 0.37 mmol) was treated with TBAI (137 mg, 0.37 mmol) and $BF_3\cdot OEt_2$ (46 μL, 0.37 mmol) in dry CH_2Cl_2 (0.8 mL) at 0 °C and stirred for < 1 min to afford (*S*)-**4a** as a white solid (143 mg, 96% yield). R_f 0.25 (ethyl acetate−petroleum ether, 1:5); $[\alpha]^{25}_D$ +54.5 (*c* 0.33, $CHCl_3$); IR ν_{max} (KBr, cm^{-1}) 3286, 2923, 2852, 1323, 1153, 847, 697, 667, 551; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.40−3.48 (m, 1H), 3.59−3.66 (m, 1H), 4.65 (t, J = 6.3 Hz, 1H), 4.94 (t, J = 7.8 Hz, 1H), 7.18−7.26 (m, 7H), 7.64 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 29.8, 51.2, 127.0, 127.5, 128.7, 129.1, 129.8, 136.9, 139.8, 143.8; HRMS (ESI) for $C_{15}H_{16}INO_2S$ $(M + H)^+$ calcd 402.0025, found 402.0025; er = 93:7. Enantiomeric purity was determined by chiral hplc analysis (Chiralpak AD-H column), hexane:isopropanol 95: 5, flow rate = 1.0 mL/min), $t_R(1)$ = 26.69 min (minor), $t_R(2)$ = 32.89 min (major).

***tert*-Butyl 2-(Methoxy(methyl)amino)-2-oxo-1-phenylethylcarbamate (8).** To an ice-cold mixture of *N*-*tert*-butoxycarbonyl-L-phenylglycine **7** (2.51 g, 10 mmol), *N*,*O*-dimethylhydroxylamine hydrochloride (975 mg, 10 mmol), and triethylamine (2.1 mL, 15 mmol) in dry chloroform (20 mL) was added DCC (2.1 g,10 mmol) at intervals. The resulting mixture was stirred at the same temperature for 1 h. The reaction mixture was filtered, and the residual solid (*N*,*N*-dicyclohexylurea) was washed with cold chloroform. The combined filtrate was concentrated and the crude product was purified through flash column chromatography with ethyl acetate in petroleum ether as the eluent to afford the pure Weinreb amide **8** as a thick liquid (2.80 g, 95% yield). R_f 0.30 (ethyl acetate−petroleum ether, 3:7); $[\alpha]^{25}_D$ +120.0 (*c* 1.15, CH_2Cl_2); IR ν_{max} (neat, cm^{-1}) 3334, 2976, 2930, 1713, 1663, 1491, 1389, 1367, 1309, 1248, 1167, 1048, 1019, 993, 953, 880, 836, 757, 700, 627; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39 (s, 9H), 3.16 (s, 3H), 3.44 (s, 3H), 5.70 (d, J = 7.0 Hz, 1H), 5.77 (d, J = 7.25 Hz, 1H), 7.25−7.37 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.4, 32.4, 55.1, 61.2, 79.8, 127.8, 128.2, 128.9, 138.1, 155.1, 171.4; HRMS (ESI) for $C_{15}H_{22}N_2O_4$ $(M + H)^+$ found 295.1659, calcd 295.1658.

(*S*)-*tert*-Butyl 2-Oxo-1-phenylbutylcarbamate (9a). The general procedure 3 described above was followed when **8** (147 mg, 0.5 mmol) was treated with ethyl magnesium bromide (ethyl bromide, 0.15 mL, 2.0 mmol, Mg 49 mg, 2.0 mmol) in dry THF (2 mL) at 0 °C with stirring at rt for 1 h to afford **9a** as a white solid (115 mg, 87% yield). Mp 80−83 °C; R_f 0.49 (ethyl acetate−petroleum ether, 1:4); $[\alpha]^{25}_D$ +302.0 (*c* 0.85, CH_2Cl_2); IR ν_{max} (KBr, cm^{-1}) 3398, 3061, 2975, 2938, 1698, 1495, 1412, 1388, 1364, 1315, 1294, 1242, 1211, 1171, 1115, 1067, 1009, 925, 889, 855, 783, 757, 704, 651, 589, 545, 468; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.97 (t, J = 7.25 Hz, 3H), 1.39 (s, 9H), 2.34−2.41 (m, 2H), 5.27 (d, J = 6.0 Hz, 1H), 5.92 (br s, 1H), 7.25−7.36 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.7, 28.3, 32.9, 63.9, 79.8, 127.8, 128.4, 129.1, 137.2, 154.9, 206.6; HRMS (ESI) for $C_{15}H_{21}NO_3$, $(M + H)^+$ found 264.1606, calcd 264.1600.

(*S*)-*tert*-Butyl 2-Oxo-1-phenylpentylcarbamate (9b). The general procedure 3 described above was followed when **8** (147 mg, 0.5 mmol) was treated with *n*-propylmagnesium bromide (*n*-propyl bromide, 0.18 mL, 2.0 mmol, Mg, 49 mg, 2.0 mmol) in dry THF (2 mL) at 0 °C with stirring at rt for 1 h to afford **9b** as a white solid (123 mg, 89% yield). Mp 54−56 °C; R_f 0.51 (ethyl acetate−petroleum ether, 1:4); $[\alpha]^{25}_D$ +273.0 (*c* 2.6, CH_2Cl_2); IR ν_{max} (KBr, cm^{-1}) 3392, 3061, 2967, 2934, 2877, 1697, 1495, 1408, 1390, 1366, 1317, 1290, 1248, 1232, 1169, 1128, 1078, 1067, 1013, 935, 893, 865, 782, 758, 737, 702, 674, 632, 591, 553, 471, 439; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.71 (t, J = 7.5 Hz, 3H), 1.33 (s, 9H), 1.36−1.52 (m, 2H), 2.22−2.32 (m, 2H), 5.19 (d, J = 6.0 Hz, 1H), 5.85 (br s, 1H), 7.19−7.32 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5, 17.1, 28.3, 41.5, 64.1, 79.8, 127.9, 128.4, 129.1, 137.0, 154.9, 205.9; HRMS (ESI) for $C_{16}H_{23}NO_3$ $(M + Na)^+$ found 300.1579, calcd 300.1576.

(*S*)-*tert*-Butyl 2-Oxo-1-phenylhexylcarbamate (9c). The general procedure 3 described above was followed when **8** (147 mg, 0.5 mmol) was treated with *n*-butyl magnesium bromide (*n*-butyl bromide, 0.21 mL, 2.0 mmol; Mg, 49 mg, 2.0 mmol) in dry THF (2 mL) at 0 °C with stirring at rt for 1 h to afford **9c** as a white solid (130 mg, 89% yield). Mp 61−63 °C; R_f 0.53 (ethyl acetate−petroleum ether, 1:4); $[\alpha]^{25}_D$ +273.0 (*c* 0.8, CH_2Cl_2); IR ν_{max} (KBr, cm^{-1}) 3391, 3060, 2972, 2935, 2875, 1697, 1496, 1455, 1408, 1389, 1365, 1314, 1294, 1246, 1224, 1170, 1126, 1081, 1070, 1042, 1023, 998, 938, 896, 863, 783, 702, 671, 620, 551; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.78 (t, J = 7.0 Hz, 3H), 1.09−1.51 (m, 4H), 1.39 (s, 9H), 2.29−2.37 (m, 2H), 5.25 (d, J = 6.5 Hz, 1H), 5.92 (br s, 1H), 7.25−7.36 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 22.1, 25.8, 28.4, 39.4, 64.2, 79.9, 127.9, 128.5, 129.2, 137.2, 154.9, 206.2.

(*S*)-*tert*-Butyl 2-Oxo-1-phenylpent-4-enylcarbamate (9d).[20b] The general procedure 3 described above was followed when **8** (147 mg, 0.5 mmol) was treated with allyl magnesium chloride (allyl chloride, 0.16 mL, 2.0 mmol; Mg, 49 mg, 2.0 mmol) in dry THF (2 mL) at 0 °C with stirring at rt for 1 h to afford **9d** as a white solid (117 mg, 85% yield). Mp 64−66 °C; R_f 0.49 (ethyl acetate−petroleum ether, 1:4); IR ν_{max} (KBr, cm^{-1}) 3379, 3069, 2979, 2935, 1727, 1687, 1521, 1456, 1424, 1391, 1368, 1314, 1295, 1272, 1243, 1172, 1076, 1042, 1018, 993, 924, 869, 784, 751, 710, 622, 593, 496; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.39 (s, 9H),

3.07−3.16 (m, 2H), 5.00 (dd, J = 17.2, 1.5, Hz, 1H), 5.12 (dd, J = 10.1, 1.2 Hz, 1H), 5.33 (d, J = 6.3 Hz, 1H), 5.73−5.82 (m, 1H), 5.85 (br s, 1H), 7.22−7.38 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.4, 44.4, 63.9, 80.0, 119.6, 128.1, 128.7, 129.2, 129.3, 129.6, 136.7, 154.9, 203.9.

(*S*)-*tert*-Butyl 2-Oxo-1-phenylhex-5-enylcarbamate (9e). The general procedure 3 described above was followed when **8** (147 mg, 0.5 mmol) was treated with but-1-enylmagnesium bromide (4-bromo-1-butene, 0.20 mL, 2.0 mmol; Mg, 49 mg, 2.0 mmol) in dry THF (2 mL) at 0 °C with stirring at rt for 1 h to afford **9e** as a white solid (124 mg, 86% yield). Mp 59−61 °C; R_f 0.53 (ethyl acetate−petroleum ether, 1:4); $[\alpha]^{25}_D$ +250.0 (c 0.6, CH_2Cl_2); IR ν_{max} (KBr, cm^{-1}) 3299, 3064, 2980, 2935, 1721, 1699, 1680, 1542, 1495, 1455, 1409, 1392, 1367, 1323, 1279, 1253, 1171, 1091, 1075, 1054, 1030, 1009, 997, 969, 915, 887, 779, 749, 705, 619, 582; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.39 (s, 9H), 2.11−2.29 (m, 2H), 2.39−2.50 (m, 2H), 4.87−4.91 (m, 2H), 5.26 (d, J = 6.0 Hz, 1H), 5.59−5.67 (m, 1H), 5.89 (br s, 1H), 7.25−7.37 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.5, 28.1, 28.3, 38.7, 64.2, 79.9, 115.5, 127.9, 128.5, 129.2, 136.4, 136.9, 154.9, 205.2.

***tert*-Butyl (1*S*,2*R*)-2-Hydroxy-1-phenylbutylcarbamate (10a).** The general procedure 4 described above was followed when **9a** (263 mg, 1.0 mmol) was treated with $NaBH_4$ (76 mg, 2.0 mmol) in dry MeOH (10 mL) at −20 °C for 1 h to afford **10a** as a white solid (265 mg, quantitative yield). Mp 128−130 °C; R_f 0.36 (ethyl acetate−petroleum ether, 1:3); $[\alpha]^{25}_D$ +24.0 (c 0.55, CH_2Cl_2); IR ν_{max} (KBr, cm^{-1}) 3377, 3009, 2971, 2931, 1681, 1528, 1460, 1389, 1368, 1321, 1297, 1255, 1228, 1173, 1110, 1082, 1043, 1019, 967, 883, 856, 840, 754, 706, 647, 615, 596, 518; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89 (t, J = 7.6 Hz, 3H), 0.95−1.42 (m, 2H), 1.35 (s, 9H), 3.71−3.73 (m, 1H), 4.59 (br s, 1H), 5.38 (br s, 1H), 7.19−7.29 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.3, 27.0, 28.3, 58.7, 75.8, 79.6, 126.5, 127.7, 128.4, 138.4, 155.4.

***tert*-Butyl (1*S*,2*R*)-2-Hydroxy-1-phenylpentylcarbamate (10b).** The general procedure 4 described above was followed when **9b** (277 mg, 1.0 mmol) was treated with $NaBH_4$ (76 mg, 2.0 mmol) in dry MeOH (10 mL) at −20 °C for 1 h to afford **10b** as a white solid (279 mg, quantitative yield). Mp 143−145 °C; R_f 0.43 (ethyl acetate−petroleum ether, 1:3); $[\alpha]^{25}_D$ +35.0 (c 1.7, CH_2Cl_2); IR ν_{max} (KBr, cm^{-1}) 3370, 3047, 3006, 2968, 2917, 2872, 1680, 1531, 1459, 1391, 1369, 1296, 1254, 1172, 1136, 1109, 1045, 1015, 955, 914, 881, 842, 780, 755, 705, 665, 631, 596, 518, 461; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.86 (t, J = 7.25 Hz, 3H), 1.08−1.17 (m, 1H), 1.23−1.53 (m, 3H), 1.38 (s, 9H), 3.86−3.88 (m, 1H), 4.63 (br s, 1H), 5.45 (br s, 1H), 7.22−7.36 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 19.0, 28.3, 36.1, 58.9, 74.0, 79.7, 126.5, 127.6, 128.4, 138.4, 155.4.

***tert*-Butyl (1*S*,2*R*)-2-Hydroxy-1-phenylhexylcarbamate (10c).** The general procedure 4 described above was followed when **9c** (291 mg, 1.0 mmol) was treated with $NaBH_4$ (76 mg, 2.0 mmol) in dry MeOH (10 mL) at −20 °C for 1 h to afford **10c** as a white solid (293 mg, quantitative yield). Mp 106−108 °C; R_f 0.47 (ethyl acetate−petroleum ether, 1:3); $[\alpha]^{25}_D$ +15.0 (c 1.1, CH_2Cl_2); IR ν_{max} (KBr, cm^{-1}) 3372, 3040, 3005, 2967, 2936, 2873, 1681, 1529, 1460, 1391, 1368, 1344, 1296, 1252, 1172, 1078, 1044, 1017, 1002, 884, 843, 779, 756, 703, 664, 631, 597, 518; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.85 (t, J = 7.2 Hz, 3H), 1.09−1.53 (m, 6H), 1.40 (s, 9H), 3.84−3.86 (m, 1H), 4.64 (br s, 1H), 5.46 (br s, 1H), 7.25−7.35 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 22.5, 27.9, 28.3, 33.7, 58.9, 74.3, 79.7, 126.5, 127.6, 128.4, 138.4, 155.4.

***tert*-Butyl (1*S*,2*R*)-2-Hydroxy-1-phenylpent-4-enylcarbamate (10d).**[20b] The general procedure 4 described above was followed when **9d** (275 mg, 1.0 mmol) was treated with $NaBH_4$ (76 mg, 2.0 mmol) in dry MeOH (10 mL) at −20 °C for 1 h to afford **10d** as a white solid (277 mg, quantitative yield). R_f 0.39 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (KBr, cm^{-1}) 3381, 3070, 3006, 2975, 2926, 2855, 1688, 1526, 1457, 1390, 1367, 1294, 1252, 1172, 1104, 1077, 1041, 1015, 968, 913, 876, 778, 757, 737, 704, 621, 595, 510; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34 (s, 9H), 1.82−1.90 (m, 1H), 2.14−2.20 (m, 1H), 3.89−3.91 (br m, 1H), 4.60 (br s, 1H), 4.99−5.11 (m, 2H), 5.36 (br s, 1H), 5.68−5.78 (m, 1H), 7.21−7.31 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.4, 38.7, 58.7, 73.3, 79.8, 118.5, 126.7, 127.8, 128.0, 128.6, 134.3, 155.5.

***tert*-Butyl (1*S*,2*R*)-2-Hydroxy-1-phenylhex-5-enylcarbamate (10e).** The general procedure 4 described above was followed when **9e** (289 mg, 1.0 mmol) was treated with $NaBH_4$ (76 mg, 2.0 mmol) in dry MeOH (10 mL) at −20 °C for 1 h to afford **10e** as a white solid (291 mg, quantitative yield). Mp 100−102 °C; R_f 0.46 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (KBr, cm^{-1}) 3370, 3065, 3042, 3005, 2971, 2942, 1680, 1643, 1531, 1457, 1415, 1392, 1368, 1346, 1299, 1252, 1171, 1108, 1080, 1037, 1011, 964, 933, 905, 888, 873, 843, 780, 755, 737, 704, 668, 633, 594, 517, 461; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.19−1.26 (m, 1H), 1.39 (s, 9H), 1.48−1.54 (m, 1H), 2.07−2.12 (m, 1H), 2.18−2.23 (m, 1H), 3.87 (br s, 1H), 4.60 (br s, 1H), 4.92−5.00 (m, 2H), 5.40 (br s, 1H), 5.72−5.77 (m, 1H), 7.24−7.34 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.4, 30.2, 33.2, 59.2, 73.9, 79.8, 115.3, 126.6, 127.8, 128.6, 138.1, 155.5.

***N*-((1*S*,2*R*)-2-Hydroxy-1-phenylbutyl)-4-methylbenzenesulfonamide (11a).**[20a] The general procedure 5 described above was followed when **10a** (265 mg, 1.0 mmol) was treated with TFA (1.0 mL) in dry CH_2Cl_2 (5 mL) at 0 °C and stirred for 1 h at rt. To the reaction mixture was added Et_3N (2.2 mL) and TsCl (229 mg, 1.2 mmol) at 0 °C with stirring for 2 h at the same temperature to afford **11a** as a white solid (275 mg, 86% yield). Mp 126−128 °C; R_f 0.18 (ethyl acetate−petroleum ether, 1:3); $[\alpha]^{25}_D$ +45.0 (c 2.05, CH_2Cl_2); IR ν_{max} (KBr, cm^{-1}) 3490, 3293, 3067, 2965, 2936, 2904, 2877, 1598, 1497, 1454, 1418, 1396, 1378, 1363, 1319, 1306, 1264, 1158, 1134, 1088, 1066, 1039, 1020, 997, 965, 913, 808, 762, 704, 664, 623, 596, 566, 544; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.89 (t, J = 7.6 Hz, 3H), 1.04−1.13 (m, 1H), 1.30−1.41 (m, 1H), 2.32 (s, 3H), 3.76−3.79 (m, 1H), 4.32 (dd, J = 8.3, 3.8 Hz, 1H), 5.52 (d, J = 8.3 Hz, 1H), 7.01−7.18 (m, 7H), 7.49 (d, J = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.3, 21.5, 26.7, 61.6, 76.0, 127.1, 127.7, 127.9, 128.3, 129.3, 136.4, 137.4, 143.1.

***N*-((1*S*,2*R*)-2-Hydroxy-1-phenylpentyl)-4-methylbenzenesulfonamide (11b).** The general procedure 5 described above was followed when **10b** (279 mg, 1.0 mmol) was treated with TFA (1.0 mL) in dry CH_2Cl_2 (5 mL) at 0 °C and stirred for 1 h at rt. To the reaction mixture was added Et_3N (2.2 mL) and TsCl (229 mg, 1.2 mmol) at 0 °C with stirring for 2 h to afford **11a** as a white solid (293 mg, 88% yield). Mp 113−115 °C; R_f 0.23 (ethyl acetate−petroleum ether, 1:3); $[\alpha]^{25}_D$ +47.0 (c 2.3, CH_2Cl_2); IR ν_{max} (KBr, cm^{-1}) 3505, 3328, 3033, 2954, 2869, 1599, 1496, 1457, 1413, 1378, 1342, 1319, 1289, 1259, 1195, 1158, 1120, 1090, 1053, 1033, 1020, 935, 917, 893, 809, 761, 704, 691, 663, 600, 572, 546, 523; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.81 (t, J = 7.1 Hz, 3H), 1.02−1.03 (m, 1H), 1.22−1.29 (m, 2H), 1.37−1.40 (m, 1H), 2.31 (s, 3H), 3.83−3.88 (m, 1H), 4.28 (dd, J = 8.1, 3.7 Hz, 1H), 5.48 (d, J = 8.1 Hz, 1H), 7.00−7.16 (m, 7H), 7.48 (d, J = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 18.9, 21.4, 35.7, 61.8, 74.1, 126.9, 127.6, 127.9, 128.2, 129.2, 136.3, 137.4, 143.0.

***N*-((1*S*,2*R*)-2-Hydroxy-1-phenylhexyl)-4-methylbenzenesulfonamide (11c).** The general procedure 5 described above was followed when **10c** (293 mg, 1.0 mmol) was treated with TFA (1.0 mL) in dry CH_2Cl_2 (5 mL) at 0 °C and stirred for 1 h at rt. To the reaction mixture was added Et_3N (2.2 mL) and TsCl (229 mg, 1.2 mmol) at 0 °C with stirring for 2 h to afford **11c** as a white solid (313 mg, 90% yield). Mp 133−135 °C; R_f 0.27 (ethyl acetate−petroleum ether, 1:3); $[\alpha]^{25}_D$ +43.0 (c 2.15, CH_2Cl_2); IR ν_{max} (KBr, cm^{-1}) 3499, 3324, 3090, 3065, 3035, 2939, 2922, 2858, 1599, 1495, 1458, 1411, 1379, 1352, 1318, 1288, 1266, 1253, 1195, 1156, 1087, 1055, 1020, 912, 842, 809, 760,

705, 691, 664, 601, 573, 530; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82 (t, J = 7.2 Hz, 3H), 1.00−1.05 (m, 1H), 1.17−1.37 (m, 5H), 2.32 (s, 3H), 3.83−3.85 (m, 1H), 4.29 (dd, J = 8.3, 3.8 Hz, 1H), 5.42 (d, J = 8.3 Hz, 1H), 7.01−7.18 (m, 7H), 7.49 (d, J = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 21.4, 22.4, 27.8, 33.3, 61.7, 74.4, 126.9, 127.6, 127.9, 128.2, 129.2, 136.3, 137.3, 142.9.

***N*-((1*S*,2*R*)-2-Hydroxy-1-phenylpent-4-enyl)-4-methylbenzenesulfonamide (11d).** The general procedure 5 described above was followed when **10d** (277 mg, 1.0 mmol) was treated with TFA (1.0 mL) in dry CH_2Cl_2 (5 mL) at 0 °C and stirred for 1 h at rt. To the reaction mixture was added Et_3N (2.2 mL) and TsCl (229 mg, 1.2 mmol) at 0 °C for 2 h to afford **11d** as a white solid (278 mg, 84% yield). Mp 82−84 °C; R_f 0.23 (ethyl acetate−petroleum ether, 1:3); $[\alpha]^{25}_D$ +43.0 (c 1.6, CH_2Cl_2); IR ν_{max} (KBr, cm^{-1}) 3487, 3323, 3062, 3034, 3005, 2923, 2854, 1641, 1599, 1495, 1456, 1413, 1353, 1319, 1287, 1262, 1211, 1186, 1158, 1090, 1058, 1020, 994, 971, 935, 911, 843, 809, 764, 751, 703, 685, 662, 567, 544, 511; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.81−1.87 (m, 1H), 2.10−2.15 (m, 1H), 2.32 (s, 3H), 3.94−3.95 (m, 1H), 4.32 (dd, J = 8.5, 4.0 Hz, 1H), 5.00−5.13 (m, 2H), 5.45−5.48 (br m, 1H), 5.66−5.74 (m, 1H), 6.98−7.19 (m, 7H), 7.48 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 38.2, 61.4, 73.3, 118.8, 127.1, 127.8, 128.1, 128.3, 129.4, 133.9, 136.3, 137.4, 143.1.

***N*-((1*S*,2*R*)-2-Hydroxy-1-phenylhex-5-enyl)-4-methylbenzenesulfonamide (11e).** The general procedure 5 described above was followed when **10e** (291 mg, 1.0 mmol) was treated with TFA (1.0 mL) in dry CH_2Cl_2 (5 mL) at 0 °C and stirred for 1 h at rt. To the reaction mixture was added Et_3N (2.2 mL) and TsCl (229 mg, 1.2 mmol) at 0 °C with stirring for 2 h to afford **11e** as a white solid (301 mg, 87% yield). Mp 157−159 °C; R_f 0.23 (ethyl acetate−petroleum ether, 1:3); $[\alpha]^{25}_D$ +42.0 (c 0.55, CH_2Cl_2); IR ν_{max} (KBr, cm^{-1}) 3499, 3329, 3064, 3035, 2950, 2922, 2854, 1641, 1599, 1496, 1454, 1413, 1371, 1351, 1332, 1316, 1287, 1252, 1155, 1088, 1061, 1020, 997, 945, 912, 810, 760, 706, 691, 665, 599, 570, 521; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.12−1.18 (m, 1H), 1.38−1.42 (m, 1H), 2.00−2.04 (m, 1H), 2.11−2.16 (m, 1H), 2.31 (s, 3H), 3.87−3.89 (m, 1H), 4.27 (dd, J = 8.6, 4.0 Hz, 1H), 4.89−4.96 (m, 2H), 5.65−5.68 (m, 1H), 7.01−7.15 (m, 7H), 7.49 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 30.0, 32.7, 61.9, 73.8, 115.4, 127.1, 127.7, 127.9, 128.4, 129.4, 136.4, 137.4, 137.8, 143.2.

(2*S*,3*S*)-2-Ethyl-3-phenyl-1-tosylaziridine (12a). The general procedure 6 described above was followed when **11a** (160 mg, 0.5 mmol) was treated with PPh_3 (197 mg, 0.75 mmol) and DEAD (0.12 mL, 0.75 mmol) in dry THF (2 mL) at 0 °C with stirring for 2 h at rt to afford **12a** as a colorless liquid (143 mg, 95% yield). R_f 0.39 (ethyl acetate−petroleum ether, 15:85); $[\alpha]^{25}_D$ +68.0 (c 6.3, CH_2Cl_2); IR ν_{max} (neat, cm^{-1}) 3063, 2964, 2923, 2853, 1598, 1552, 1496, 1457, 1420, 1323, 1234, 1185, 1159, 1090, 1019, 905, 852, 814, 773, 749, 696, 678, 611, 589, 538; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.16 (t, J = 7.5 Hz, 3H), 2.07−2.12 (m, 1H), 2.24−2.29 (m, 1H), 2.38 (s, 3H), 2.79−2.83 (m, 1H), 3.77 (d, J = 4.5 Hz, 1H), 7.13−7.15 (m, 2H), 7.21−7.31 (m, 5H), 7.88 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5, 21.7, 22.3, 48.8, 54.8, 126.5, 127.3, 128.1, 128.6, 129.6, 135.6, 137.8, 143.9; HRMS (ESI) for $C_{17}H_{19}NO_2S$ (M + H)$^+$ found 302.1215, calcd 302.1215.

(2*S*,3*S*)-2-Phenyl-3-propyl-1-tosylaziridine (12b). The general procedure 6 described above was followed when **11b** (167 mg, 0.5 mmol) was treated with PPh_3 (197 mg, 0.75 mmol) and DEAD (0.12 mL, 0.75 mmol) in dry THF (2 mL) at 0 °C with stirring for 2 h at rt to afford **12b** as a colorless liquid (155 mg, 98% yield). R_f 0.42 (ethyl acetate−petroleum ether, 15:85); $[\alpha]^{25}_D$ +51.0 (c 2.3, CH_2Cl_2); IR ν_{max} (neat, cm^{-1}) 3032, 2961, 2929, 2872, 1598, 1497, 1457, 1419, 1381, 1324, 1305, 1291, 1247, 1200, 1184, 1160, 1093, 1045, 1018, 925, 913, 814, 747, 711, 696, 682, 611, 591, 577, 542; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.98 (t, J = 7.6 Hz, 3H), 1.52−1.61 (m, 2H), 1.93−2.08 (m, 1H), 2.22−2.32 (m, 1H), 2.37 (s, 3H), 2.78−2.81 (m, 1H), 3.77 (d, J = 4.4 Hz, 1H), 7.11−7.13 (m, 2H), 7.22−7.24 (m, 5H), 7.79 (d, J = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 21.2, 21.6, 30.5, 48.9, 53.4, 126.3, 127.2, 128.0, 128.5, 129.5, 135.5, 137.7, 143.9; HRMS (ESI) for $C_{18}H_{21}NO_2S$ (M + H)$^+$ found 316.1373, calcd 316.1371.

(2*S*,3*S*)-2-Butyl-3-phenyl-1-tosylaziridine (12c). The general procedure 6 described above was followed when **11c** (174 mg, 0.5 mmol) was treated with PPh_3 (197 mg, 0.75 mmol) and DEAD (0.12 mL, 0.75 mmol) in dry THF (2 mL) at 0 °C with stirring for 2 h at rt to afford **12c** as a colorless liquid (156 mg, 95% yield). R_f 0.44 (ethyl acetate−petroleum ether, 15:85); $[\alpha]^{25}_D$ +49.0 (c 1.45, CH_2Cl_2); IR ν_{max} (neat, cm^{-1}) 3064, 3033, 2958, 2927, 2871, 1598, 1497, 1458, 1418, 1380, 1324, 1305, 1290, 1238, 1198, 1185, 1160, 1089, 1021, 947, 905, 844, 814, 782, 758, 711, 697, 612, 593, 542; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.92 (t, J = 7.5 Hz, 3H), 1.35−1.59 (m, 4H), 2.00−2.09 (m, 1H), 2.26−2.32 (m, 1H), 2.38 (s, 3H), 2.79−2.82 (m, 1H), 3.77 (d, J = 4.6 Hz, 1H), 7.12−7.14 (m, 2H), 7.22−7.26 (m, 5H), 7.80 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 21.6, 22.3, 28.3, 30.1, 48.9, 53.6, 126.4, 127.2, 128.0, 128.5, 129.5, 135.5, 137.8, 143.8; HRMS (ESI) for $C_{19}H_{23}NO_2S$ (M + H)$^+$ found 330.1528, calcd 330.1528.

(2*S*,3*S*)-2-Allyl-3-phenyl-1-tosylaziridine (12d). The general procedure 6 described above was followed when **11d** (166 mg, 0.5 mmol) was treated with PPh_3 (197 mg, 0.75 mmol) and DEAD (0.12 mL, 0.75 mmol) in dry THF (2 mL) at 0 °C with stirring for 2 h at rt to afford **12d** as a colorless liquid (150 mg, 96% yield). R_f 0.40 (ethyl acetate−petroleum ether, 15:85); $[\alpha]^{25}_D$ +57.0 (c 1.05, CH_2Cl_2); IR ν_{max} (neat, cm^{-1}) 3065, 3033, 2923, 2852, 1642, 1598, 1497, 1456, 1418, 1324, 1291, 1252, 1198, 1185, 1160, 1116, 1089, 1020, 996, 950, 928, 895, 815, 761, 712, 697, 608, 590, 552, 537; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.38 (s, 3H), 2.82−2.90 (m, 2H), 2.99−3.04 (m, 1H), 3.81 (d, J = 4.6 Hz, 1H), 5.11 (dd, J = 10.3, 1.2 Hz, 1H), 5.16 (dd, J = 17.2, 1.7 Hz, 1H), 5.90−5.96 (m, 1H), 7.13−7.15 (m, 2H), 7.23−7.26 (m, 5H), 7.80 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7, 32.8, 48.6, 51.9, 117.7, 126.5, 127.4, 128.2, 128.6, 129.6, 133.9, 135.3, 137.7, 144.1; HRMS (ESI) for $C_{18}H_{19}NO_2S$ (M + H)$^+$ found 314.1215, calcd 314.1215.

(2*S*,3*S*)-2-(But-3-enyl)-3-phenyl-1-tosylaziridine (12e). The general procedure 6 described above was followed when **11e** (173 mg, 0.5 mmol) was treated with PPh_3 (197 mg, 0.75 mmol) and DEAD (0.12 mL, 0.75 mmol) in dry THF (2 mL) at 0 °C with stirring for 2 h at rt to afford **12e** as a colorless liquid (159 mg, 97% yield). R_f 0.43 (ethyl acetate−petroleum ether, 15:85); $[\alpha]^{25}_D$ +54.0 (c 1.8, CH_2Cl_2); IR ν_{max} (neat, cm^{-1}) 3065, 3033, 2979, 2925, 2855, 1641, 1598, 1497, 1455, 1418, 1323, 1291, 1253, 1185, 1160, 1116, 1089, 1019, 997, 970, 904, 814, 753, 711, 697, 610, 589, 553, 540; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.12−2.20 (m, 1H), 2.24−2.43 (m, 3H), 2.38 (s, 3H), 2.82−2.85 (m, 1H), 3.78 (d, J = 4.6 Hz, 1H), 4.98−5.07 (m, 2H), 5.77−5.91 (m, 1H), 7.09−7.17 (m, 2H), 7.21−7.27 (m, 5H), 7.80 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7, 28.1, 32.1, 48.9, 52.9, 116.2, 126.5, 127.4, 128.2, 128.6, 129.6, 135.4, 136.9, 137.8, 144.1; HRMS (ESI) for $C_{19}H_{21}NO_2S$ (M + H)$^+$ found 328.1374, calcd 328.1371.

***N*-((1*R*,2*S*)-1-Chloro-1-phenylbutan-2-yl)-4-methylbenzenesulfonamide (13a).** The general procedure 7 described above was followed when **12a** (75 mg, 0.25 mmol) was treated with BTEAC (57 mg, 0.25 mmol) and $BF_3\cdot OEt_2$ (31 μL, 0.25 mmol) in dry CH_2Cl_2 (0.5 mL) at rt for 5 min to afford **13a** as a colorless liquid (81 mg, 96% yield). R_f 0.33 (ethyl acetate−petroleum ether, 15:85); $[\alpha]^{25}_D$ −18.0 (c 0.6, CH_2Cl_2); IR ν_{max} (neat, cm^{-1}) 3284, 3062, 3029, 2970, 2935, 2878, 1598, 1494, 1452, 1420, 1333, 1305, 1227, 1184, 1161, 1092, 1062, 1023, 909, 841, 814, 766, 701, 666,

627, 611, 576, 550; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.67 (t, J = 7.4 Hz, 3H), 1.39−1.46 (m, 2H), 2.40 (s, 3H), 3.47−3.50 (m, 1H), 4.71 (d, J = 9.2 Hz, 1H), 4.98 (d, J = 2.9 Hz, 1H), 7.21−7.32 (m, 7H), 7.78 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.9, 21.3, 21.5, 61.3, 67.2, 126.9, 127.2, 128.2, 128.4, 129.7, 137.4, 137.9, 143.5; HRMS (ESI) for $C_{17}H_{20}ClNO_2S$ $(M + H)^+$ found 338.0982, calcd 338.0982.

***N*-((1*R*,2*S*)-1-Chloro-1-phenylpentan-2-yl)-4-methylbenzenesulfonamide (13b).** The general procedure 7 described above was followed when **12b** (79 mg, 0.25 mmol) was treated with BTEAC (57 mg, 0.25 mmol) and $BF_3\cdot OEt_2$ (31 μL, 0.25 mmol) in dry CH_2Cl_2 (0.5 mL) at rt for 5 min to afford **13b** as a colorless liquid (83 mg, 95% yield). R_f 0.34 (ethyl acetate−petroleum ether, 15:85); $[\alpha]^{25}{}_D$ −23.0 (c 0.7, CH_2Cl_2); IR ν_{max} (neat, cm^{-1}) 3284, 3030, 2960, 2873, 1598, 1494, 1451, 1420, 1331, 1160, 1093, 1027, 926, 814, 766, 701, 666, 607, 577, 550; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.59 (t, J = 7.2 Hz, 3H), 0.84−0.92 (m, 1H), 1.18−1.23 (m, 2H), 1.34−1.39 (m, 1H), 2.35 (s, 3H), 3.51−3.54 (m, 1H), 4.81(br s, 1H), 4.95 (d, J = 3.5 Hz, 1H), 7.18−7.27 (m, 7H), 7.74 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.4, 18.5, 21.5, 30.2, 59.5, 67.5, 126.9, 127.2, 128.2, 128.4, 129.7, 137.3, 138.0, 143.6; HRMS (ESI) for $C_{18}H_{22}ClNO_2S$ $(M + H)^+$ found 352.1139, calcd 352.1138.

***N*-((1*R*,2*S*)-1-Chloro-1-phenylhexan-2-yl)-4-methylbenzenesulfonamide (13c).** The general procedure 7 described above was followed when **12c** (82 mg, 0.25 mmol) was treated with BTEAC (57 mg, 0.25 mmol) and $BF_3\cdot OEt_2$ (31 μL, 0.25 mmol) in dry CH_2Cl_2 (0.5 mL) at rt for 5 min to afford **13c** as a colorless liquid (90 mg, 98% yield). R_f 0.36 (ethyl acetate−petroleum ether, 15:85); $[\alpha]^{25}{}_D$ −28.0 (c 0.4, CH_2Cl_2); IR ν_{max} (neat, cm^{-1}) 3283, 3063, 3030, 2956, 2927, 2860, 1599, 1494, 1452, 1419, 1380, 1334, 1289, 1184, 1161, 1093, 1033, 940, 892, 841, 814, 766, 701, 665, 629, 611, 577, 550; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.65 (t, J = 7.2 Hz, 3H), 0.83−0.92 (m, 1H), 0.93−1.09 (m, 2H), 1.13−1.21 (m, 1H), 1.28−1.36 (m, 1H), 1.39−1.47 (m, 1H), 2.41 (s, 3H), 3.51−3.60 (m, 1H), 4.86 (d, J = 9.5 Hz, 1H), 5.02 (d, J = 3.2 Hz, 1H), 7.25−7.33 (m, 7H), 7.80 (d, J = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 21.6, 22.1, 27.5, 27.9, 59.8, 67.7, 127.2, 127.3, 128.3, 128.6, 129.9, 137.5, 138.1, 143.8; HRMS (ESI) for $C_{19}H_{24}ClNO_2S$ $(M + H)^+$ found 366.1297, calcd 366.1295.

***N*-((1*R*,2*S*)-1-Chloro-1-phenylpent-4-en-2-yl)-4-methylbenzenesulfonamide (13d).** The general procedure 7 described above was followed when **12d** (78 mg, 0.25 mmol) was treated with BTEAC (57 mg, 0.25 mmol) and $BF_3\cdot OEt_2$ (31 μL, 0.25 mmol) in dry CH_2Cl_2 (0.5 mL) at rt for 5 min to afford **13d** as a colorless liquid (80 mg, 92% yield). R_f 0.32 (ethyl acetate−petroleum ether, 15:85); $[\alpha]^{25}{}_D$ −30.0 (c 1, CH_2Cl_2); IR ν_{max} (neat, cm^{-1}) 3285, 3064, 3030, 2961, 2924, 1599, 1494, 1449, 1417, 1334, 1305, 1261, 1185, 1160, 1092, 1019, 922, 813, 766, 701, 665, 604, 570, 549; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.06−2.11 (m, 1H), 2.22−2.28 (m, 1H), 2.35 (s, 3H), 3.57−3.62 (m, 1H), 4.71 (br s, 1H), 4.87−4.94 (m, 2H), 5.01 (d, J = 4 Hz, 1H), 5.26−5.34 (m, 1H), 7.17−7.27 (m, 7H), 7.65 (d, J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 33.3, 59.1, 66.2, 119.2, 127.2, 127.3, 128.4, 128.5, 129.6, 132.8, 137.3, 137.5, 143.6; HRMS (ESI) for $C_{18}H_{20}ClNO_2S$ $(M + H)^+$ found 350.0985, calcd 350.0982.

***N*-((1*R*,2*S*)-1-Chloro-1-phenylhex-5-en-2-yl)-4-methylbenzenesulfonamide (13e).** The general procedure 7 described above was followed when **12e** (82 mg, 0.25 mmol) was treated with BTEAC (57 mg, 0.25 mmol) and $BF_3\cdot OEt_2$ (31 μL, 0.25 mmol) in dry CH_2Cl_2 (0.5 mL) at rt for 5 min to afford **12e** as a colorless liquid (84 mg, 92% yield). R_f 0.33 (ethyl acetate−petroleum ether, 15:85); $[\alpha]^{25}{}_D$ −8.0 (c 0.95, CH_2Cl_2); IR ν_{max} (neat, cm^{-1}) 3282, 3064, 2924, 2854, 1598, 1494, 1450, 1418, 1327, 1160, 1092, 1019, 911, 814, 700, 665, 577, 550; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36−1.41 (m, 1H), 1.43−1.51 (m, 1H), 1.64−1.70 (m, 1H), 1.92−1.95 (m, 1H), 2.36 (s, 3H), 3.52−3.57 (m, 1H), 4.64−4.86 (m, 2H), 4.94 (d, J = 3.5 Hz, 1H), 5.37−5.45 (m, 1H), 7.19−7.29 (m, 7H), 7.75 (d, J = 8.05 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 27.3, 29.2, 59.1, 67.5, 115.3, 127.0, 127.1, 128.3, 128.5, 129.8, 136.9, 137.1, 137.9, 143.7; HRMS (ESI) for $C_{19}H_{22}ClNO_2S$ $(M + H)^+$ found 364.1139, calcd 364.1138.

4-Methyl-*N*-phenethylbenzenesulfonamide (14). The general procedure 8 described above was followed when **2a** (31 mg, 0.1 mmol) was reacted with $NaCNBH_3$ (13 mg, 0.2 mmol), Bu_3SnCl (3 μL, 0.01 mmol), and AIBN (0.82 mg, 0.005 mmol) in dry t-BuOH (1.0 mL) and the reaction mixture was refluxed at 85 °C for 1 h to afford **14** as a white solid (27 mg, 99% yield). Mp 51−53 °C; R_f 0.23 (ethyl acetate−petroleum ether, 1:5); IR ν_{max} (KBr, cm^{-1}) 3449, 3266, 3088, 3063, 3030, 2910, 2862, 1599, 1486, 1454, 1437, 1419, 1364, 1320, 1291, 1156, 1094, 1064, 1038, 1020, 970, 945, 906, 844, 813, 729, 695, 582, 549; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.74 (t, J = 7.5 Hz, 2H), 3.18−3.20 (m, 2H), 4.45 (br s, 1H), 7.06 (d, J = 6.9 Hz, 2H), 7.20−7.28 (m, 5H), 7.67 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 35.7, 44.2, 126.8, 127.0, 128.7, 129.7, 136.8, 137.6, 143.4; HRMS (ESI) for $C_{15}H_{17}NO_2S$ $(M + H)^+$ found 276.1058, calcd 276.1058.

(*S*)-4-Methyl-*N*-(1-phenylbutan-2-yl)benzenesulfonamide (15a). The general procedure 8 described above was followed when **13a** (34 mg, 0.1 mmol) was reacted with $NaCNBH_3$ (13 mg, 0.2 mmol), Bu_3SnCl (3 μL, 0.01 mmol), and AIBN (0.82 mg, 0.005 mmol) in dry t-BuOH (1.0 mL) and the reaction mixture was refluxed at 85 °C for 1 h to afford **15a** as a colorless liquid (29 mg, 95% yield). R_f 0.31 (ethyl acetate−petroleum ether, 15:85); IR ν_{max} (neat, cm^{-1}) 3285, 3028, 2965, 2928, 1599, 1495, 1453, 1422, 1326, 1158, 1092, 1023, 914, 814, 745, 702, 665, 580, 550; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.74 (t, J = 7.5 Hz, 3H), 1.23−1.35 (m, 1H), 1.40−1.47 (m, 1H), 2.34 (s, 3H), 2.60 (d, J = 6.3 Hz, 2H), 3.27−3.31 (m, 1H), 4.30 (br s, 1H), 6.93−6.94 (m, 2H), 7.09−7.19 (m, 5H), 7.57 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.9, 21.6, 27.3, 40.9, 56.5, 126.6, 127.1, 128.6, 129.6, 129.7, 137.3, 137.8, 143.2; HRMS (ESI) for $C_{17}H_{21}NO_2S$, $(M + H)^+$ found 304.1375, calcd 304.1371, $(M + Na)^+$ found 326.1196, calcd 326.1191.

(*S*)-4-Methyl-*N*-(1-phenylpentan-2-yl)benzenesulfonamide (15b). The general procedure 8 described above was followed when **13b** (35 mg, 0.1 mmol) was reacted with $NaCNBH_3$ (13 mg, 0.2 mmol), Bu_3SnCl (3 μL, 0.01 mmol), and AIBN (0.82 mg, 0.005 mmol) in dry t-BuOH (1.0 mL) and the reaction mixture was refluxed at 85 °C for 1 h to afford **15b** as a colorless liquid (31 mg, 98% yield). R_f 0.32 (ethyl acetate−petroleum ether, 15:85); IR ν_{max} (neat, cm^{-1}) 3285, 3028, 2957, 2926, 2856, 1598, 1494, 1453, 1422, 1324, 1158, 1092, 1022, 814, 743, 702, 666, 581, 551; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.77 (t, J = 7.2, Hz, 3H), 1.15−1.42 (m, 4H), 2.41 (s, 3H), 2.66 (d, J = 6.9 Hz, 2H), 3.41−3.45 (m, 1H), 4.32 (br s, 1H), 6.99 (d, J = 6.3 Hz, 2H), 7.17−7.25 (m, 5H), 7.65 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 18.7, 21.6, 36.6, 41.3, 54.8, 126.6, 127.1, 128.6, 129.6, 129.7, 137.2, 137.9, 143.2; HRMS (ESI) for $C_{18}H_{23}NO_2S$, $(M + H)^+$ found 318.1527, calcd 318.1528.

(*S*)-4-Methyl-*N*-(1-phenylhexan-2-yl)benzenesulfonamide (15c). The general procedure 8 described above was followed when **13c** (37 mg, 0.1 mmol) was reacted with $NaCNBH_3$ (13 mg, 0.2 mmol), Bu_3SnCl (3 μL, 0.01 mmol), and AIBN (0.82 mg, 0.005 mmol) in dry t-BuOH (1.0 mL) and the reaction mixture was refluxed at 85 °C for 1 h to afford **15c** as a white solid (32 mg, 95% yield). Mp 72−75 °C; R_f 0.34 (ethyl acetate−petroleum ether, 15: 85); IR ν_{max} (KBr, cm^{-1}) 3282, 3028, 2955, 2930, 2861, 1599, 1495, 1453, 1423, 1324, 1158, 1091, 1034, 814, 747, 701, 665, 581, 551; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70 (t, J = 7.0 Hz, 3H), 1.06−1.39 (m, 6H), 2.34 (s, 3H), 2.61 (d, J = 6.1 Hz, 2H), 3.33−3.38 (m, 1H), 4.19 (br s, 1H), 6.93−6.95 (m, 2H), 7.12−7.19 (m, 5H), 7.58 (d, J = 8.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 21.5, 22.3, 27.5, 34.0, 41.2, 54.9, 126.5, 127.0, 128.4, 129.4, 129.5, 137.1, 137.8, 143.1;

HRMS (ESI) for $C_{19}H_{25}NO_2S$ $(M + H)^+$ found 332.1682, calcd 332.1684.

(*S*)-4-Methyl-*N*-(1-phenylpent-4-en-2-yl)benzenesulfonamide (15d). The general procedure 8 described above was followed when **13d** (35 mg, 0.1 mmol) was reacted with $NaCNBH_3$ (13 mg, 0.2 mmol), Bu_3SnCl (3 μL, 0.01 mmol), and AIBN (0.82 mg, 0.005 mmol) in dry *t*-BuOH (1.0 mL) and the reaction mixture was refluxed at 85 °C for 1 h to afford **15d** as a white solid (31 mg, 97% yield). Mp 99−101 °C; R_f 0.31 (ethyl acetate−petroleum ether, 15:85); IR ν_{max} (KBr, cm^{-1}) 3320, 3034, 2923, 1780, 1597, 1495, 1456, 1366, 1292, 1173, 1135, 1091, 1020, 811, 755, 702, 667, 589, 550; ^1H NMR (400 MHz, $CDCl_3$) δ 1.53−1.61 (m, 1H), 1.88−1.95 (m, 1H), 2.09−2.21 (m, 1H), 2.35−2.42 (m, 2H), 2.37 (s, 3H), 4.84−5.06 (m, 3H), 5.40 (d, J = 6.8 Hz, 1H), 5.52−5.63 (m, 1H), 7.07−7.35 (m, 7H), 7.41 (d, J = 8.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 34.1, 64.2, 78.9, 119.2, 128.5, 128.7, 129.1, 129.2, 131.0, 133.0, 134.7, 145.0, 151.8; HRMS (ESI) for $C_{18}H_{21}NO_2S$ $(M + H)^+$ found 316.1379, calcd 316.1371.

***N*-(3-Chloro-3-phenylpropyl)-4-methylbenzenesulfonamide (17a).** The general procedure 9 described above was followed when **16a** (72 mg, 0.25 mmol) was treated with BTEAC (57 mg, 0.25 mmol) and $BF_3 \cdot OEt_2$ (31 μL, 0.25 mmol) in dry CH_2Cl_2 (1.0 mL) at rt for 10 min to afford **17a** as a white solid (77 mg, 95% yield). Mp 76−78 °C; R_f 0.38 (ethyl acetate−petroleum ether, 1: 3); IR ν_{max} (KBr, cm^{-1}) 3282, 3063, 3032, 2924, 1598, 1494, 1453, 1326, 1257, 1159, 1093, 1019, 941, 879, 815, 759, 698, 664, 615, 571, 551; ^1H NMR (400 MHz, $CDCl_3$) δ 2.12−2.18 (m, 2H), 2.37 (s, 3H), 3.06 (br m, 2H), 4.54 (br s, 1H), 4.85 (dd, J = 6.3, 8.3 Hz, 1H), 7.19−7.33 (m, 7H), 7.66 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 39.6, 40.8, 60.4, 126.8, 127.1, 128.5, 128.7, 129.8, 136.8, 140.7, 143.6; HRMS (ESI) for $C_{16}H_{18}ClNO_2S$ $(M + H)^+$ found 324.0829, calcd 324.0825.

***N*-(3-Chloro-3-(4-chlorophenyl)propyl)-4-methylbenzenesulfonamide (17b).** The general procedure 9 described above was followed when **16b** (81 mg, 0.25 mmol) was treated with BTEAC (57 mg, 0.25 mmol) and $BF_3 \cdot OEt_2$ (31 μL, 0.25 mmol) in dry CH_2Cl_2 (1.0 mL) at rt for 2 h to afford **17b** as a white solid (76 mg, 85% yield). Mp 74−76 °C; R_f 0.41 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (KBr, cm^{-1}) 3281, 3065, 2925, 1597, 1493, 1412, 1325, 1259, 1185, 1159, 1093, 1037, 1015, 937, 814, 739, 719, 706, 664, 622, 576, 551, 525; ^1H NMR (400 MHz, $CDCl_3$) δ 2.09−2.15 (m, 2H), 2.37 (s, 3H), 3.02−3.08 (m, 2H), 4.64 (br s, 1H), 4.86 (t, J = 7.3 Hz, 1H), 7.16−7.26 (m, 6H), 7.66 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 39.6, 40.6, 59.4, 127.1, 128.2, 128.9, 129.8, 134.3, 136.7, 139.3, 143.7; HRMS (ESI) for $C_{16}H_{17}Cl_2NO_2S$ $(M + H)^+$ found 358.0438, calcd 358.0435.

***N*-(3-(3-Bromophenyl)-3-chloropropyl)-4-methylbenzenesulfonamide (17c).** The general procedure 9 described above was followed when **16c** (92 mg, 0.25 mmol) was treated with BTEAC (57 mg, 0.25 mmol) and $BF_3 \cdot OEt_2$ (31 μL, 0.25 mmol) in dry CH_2Cl_2 (1.0 mL) at rt for 5 min to afford **17c** as a colorless liquid (96 mg, 95% yield). R_f 0.37 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (neat, cm^{-1}) 3281, 2924, 2853, 1596, 1427, 1325, 1258, 1158, 1093, 1019, 880, 814, 781, 695, 665, 551; ^1H NMR (400 MHz, $CDCl_3$) δ 2.08−2.13 (m, 2H), 2.38 (s, 3H), 3.05−3.10 (m, 2H), 4.54−4.56 (m, 1H), 4.79−4.83 (m, 1H), 7.12−7.39 (m, 6H), 7.67 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 39.6, 40.6, 59.3, 122.7, 125.6, 127.1, 129.8, 129.9, 130.3, 131.6, 136.8, 143.0, 143.7; HRMS (ESI) for $C_{16}H_{17}BrClNO_2S$ $(M + H)^+$ found 401.9933, calcd 401.9930.

***N*-(3-Chloro-3-(2-chlorophenyl)propyl)-4-methylbenzenesulfonamide (17d).** The general procedure 9 described above was followed when **16d** (81 mg, 0.25 mmol) was treated with BTEAC (57 mg, 0.25 mmol) and $BF_3 \cdot OEt_2$ (31 μL, 0.25 mmol) in dry CH_2Cl_2 (1.0 mL) at rt for 30 min to afford **17d** as a colorless liquid (81 mg, 90% yield). R_f 0.39 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (neat, cm^{-1}) 3281, 3065, 2924, 2854, 1597, 1472, 1441, 1327, 1185, 1159, 1093, 1035, 877, 814, 757, 727, 697, 664, 573, 551; ^1H NMR (400 MHz, $CDCl_3$) δ 2.10−2.15 (m, 2H), 2.36 (s, 3H), 3.09−3.15 (m, 2H), 4.52−4.53 (m, 1H), 5.34 (t, J = 6.8 Hz, 1H), 7.17−7.46 (m, 6H), 7.68 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 38.7, 40.7, 56.4, 127.1, 127.5, 128.4, 129.6, 129.7, 129.8, 132.4, 136.8, 138.1, 143.6; HRMS (ESI) for $C_{16}H_{17}Cl_2NO_2S$ $(M + H)^+$ found 358.0436, calcd 358.0435.

***N*-(3-Chloro-3-(4-nitrophenyl)propyl)-4-methylbenzenesulfonamide (17e).** The general procedure 9 described above was followed when **16e** (83 mg, 0.25 mmol) was treated with BTEAC (57 mg, 0.25 mmol) and $BF_3 \cdot OEt_2$ (31 μL, 0.25 mmol) in dry CH_2Cl_2 (1.0 mL) at rt for 12 h to afford **17e** as a colorless liquid (32 mg, 35% yield). R_f 0.36 (ethyl acetate−petroleum ether, 3:7); IR ν_{max} (neat, cm^{-1}) 3287, 3079, 2924, 2854, 1599, 1523, 1495, 1453, 1419, 1349, 1261, 1159, 1094, 1017, 939, 854, 815, 753, 699, 665, 621, 576, 551; ^1H NMR (400 MHz, $CDCl_3$) δ 2.09−2.22 (m, 2H), 2.37 (s, 3H), 3.01−3.15 (m, 2H), 4.59 (t, J = 6.4 Hz, 1H), 5.01 (dd, J = 9.3, 5.1 Hz, 1H), 7.25 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H), 8.13 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 39.7, 40.4, 58.6, 124.0, 127.1, 127.9, 129.9, 136.7, 143.9, 147.7, 147.9; HRMS (ESI) for $C_{16}H_{17}ClN_2O_4S$ $(M + H)^+$ found 369.0678, calcd 369.0676.

***N*-(3-Chloro-3-phenylpropyl)-4-fluorobenzenesulfonamide (17f).** The general procedure 9 described above was followed when **16f** (73 mg, 0.25 mmol) was treated with BTEAC (57 mg, 0.25 mmol) and $BF_3 \cdot OEt_2$ (31 μL, 0.25 mmol) in dry CH_2Cl_2 (1.0 mL) at rt for 15 min to afford **17f** as a colorless liquid (60 mg, 73% yield). R_f 0.39 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (neat, cm^{-1}) 3287, 3105, 3067, 3033, 2925, 2854, 1593, 1494, 1454, 1418, 1329, 1293, 1259, 1239, 1166, 1154, 1093, 1029, 1015, 968, 944, 877, 839, 818, 759, 698, 615, 571, 549; ^1H NMR (400 MHz, $CDCl_3$) δ 2.14−2.19 (m, 2H), 3.04−3.11 (m, 2H), 4.69 (br s, 1H), 4.83−4.89 (m, 1H), 7.11−7.27 (m, 7H), 7.79−7.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.7, 40.9, 60.5, 116.3, 116.5, 126.8, 128.6, 128.8, 129.8, 129.9, 140.6, 163.9, 166.5; HRMS (ESI) for $C_{15}H_{15}ClFNO_2S$ $(M + H)^+$ found 328.0592, calcd 328.0574, $(M + Na)^+$ found 350.0390, calcd 350.0394.

***N*-(3-Chloro-3-phenylpropyl)-4-methoxybenzenesulfonamide (17g).** The general procedure 9 described above was followed when **16g** (76 mg, 0.25 mmol) was treated with BTEAC (57 mg, 0.25 mmol) and $BF_3 \cdot OEt_2$ (31 μL, 0.25 mmol) in dry CH_2Cl_2 (1.0 mL) at rt with stirring for 5 min to afford **17g** as a colorless liquid (80 mg, 94% yield). R_f 0.42 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (neat, cm^{-1}) 3281, 3064, 3031, 2928, 2842, 1597, 1579, 1498, 1455, 1441, 1416, 1325, 1303, 1261, 1180, 1153, 1095, 1025, 969, 941, 877, 834, 804, 760, 698, 670, 629, 615, 560; ^1H NMR (400 MHz, $CDCl_3$) δ 2.10−2.18 (m, 2H), 3.01−3.11 (m, 2H), 3.81 (s, 3H), 4.27 (t, J = 6.3 Hz, 1H), 4.86 (dd, J = 8.0, 6.4 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 7.16−7.29 (m, 5H), 7.72 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.6, 40.8, 55.6, 60.5, 114.4, 126.8, 128.5, 128.7, 129.2, 131.4, 140.8, 163.0; HRMS (ESI) for $C_{16}H_{18}ClNO_3S$ $(M + H)^+$ found 340.0773, calcd 340.0774.

4-*tert*-Butyl-*N*-(3-chloro-3-phenylpropyl)benzenesulfonamide (17h). The general procedure 9 described above was followed when **16h** (82 mg, 0.25 mmol) was treated with BTEAC (57 mg, 0.25 mmol) and $BF_3 \cdot OEt_2$ (31 μL, 0.25 mmol) in dry CH_2Cl_2 (1.0 mL) at rt with stirring for 5 min to afford **17h** as a colorless liquid (77 mg, 84% yield). R_f 0.45 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (neat, cm^{-1}) 3283, 3063, 3033, 2963, 2926, 2855, 1596, 1493, 1455, 1419, 1399, 1365, 1326, 1293, 1261, 1198, 1163, 1113, 1089, 1019, 940, 836, 801, 759, 698, 629, 581, 550, 506; ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 (s, 9H), 2.12−2.17 (m, 2H), 3.07−3.12 (m, 2H), 4.51−4.53 (m, 1H), 4.84−4.87 (m, 1H), 7.14−7.28 (m, 5H), 7.44−7.47 (m, 2H), 7.70 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.1, 35.1, 39.7, 40.8, 60.5,

126.2, 126.8, 126.9, 128.5, 128.7, 136.8, 140.8, 156.6; HRMS (ESI) for $C_{19}H_{24}ClNO_2S$ $(M + H)^+$ found 366.1295, calcd 366.1295.

***N*-(3-Bromo-3-phenylpropyl)-4-methylbenzenesulfonamide (18).** To a stirred solution of **16a** (72 mg, 0.25 mmol) and TBAB (81 mg, 0.25 mmol) in dry CH_2Cl_2 (1.0 ML) was added $BF_3 \cdot OEt_2$ (31 μL, 0.25 mmol) at rt and the reaction was continued for 5 min. After completion of the reaction (monitored by TLC) it was quenched with water (1 mL), then the product was extracted by CH_2Cl_2 (3 × 2.0 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent the crude product was purified through flash column chromatography on silica gel (230−400 mesh) with ethyl acetate in petroleum ether as the eluent to afford **18** as a white solid (90 mg, 98% yield). Mp 104−106 °C; R_f 0.38 (ethyl acetate−petroleum ether, 1:3); IR ν_{max} (KBr, cm^{-1}) 3263, 3033, 2922, 2856, 1597, 1493, 1457, 1437, 1326, 1156, 1093, 1067, 1020, 897, 828, 809, 776, 725, 701, 674, 571, 549; ^1H NMR (400 MHz, $CDCl_3$) δ 2.19−2.39 (m, 2H), 2.37(s, 3H), 3.03−3.08 (m, 2H), 4.51−4.55 (m, 1H), 4.91−4.95 (m, 1H), 7.18−7.27 (m, 7H), 7.66 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 39.6, 41.7, 51.9, 127.1, 127.2, 128.6, 128.8, 129.8, 136.8, 141.1, 143.6; HRMS (ESI) for $C_{16}H_{18}BrNO_2S$ $(M + H)^+$ found 368.0324, calcd 368.03199.

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Supporting Information Available: Copies of ^1H and ^{13}C spectra for all new compounds, HPLC chromatograms for ee determination, and X-ray crystallographic data of **11a**. This material is available free of charge via the Internet at http://pubs.acs.org.