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A new convenient approach to chiral β-aryl(heteroaryl)alkylamines

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Abstract—Chiral β-aryl(heteroaryl)alkylamines have been prepared from *N*-tosyl alkylaziridines via regiospecific nucleophilic ring opening and subsequent desulfonylation in good to excellent yields. The corresponding aziridines are easily obtained from commercially available (*S*)-α-amino acids, so this method is the first effective route to asymmetric β-aryl(heteroaryl)alkylamines.

1. Introduction

β-Aryl(heteroaryl)alkylamines are of considerable interest in organic and medicinal chemistry. These compounds exert their pharmacological effects by multiple actions at serotonin (5-HT) receptor subtypes.[1] Recent work has suggested the potential use of some β-aryl-(heteroaryl)alkylamines in a number of therapeutic areas such as those related to the desynchronization of biological rhythms, disturbed sleep–wake cycles and depression.[2] To date, however, no satisfactory model correlates the stereochemical configuration of β-aryl-(heteroaryl)alkylamines and their affinity for receptors. But it should be noted that the activity of enantiomers would be expected to exhibit twice the potency of the racemic material.[3] There are many methods allowing the synthesis of β-aryl(heteroaryl)alkylamines but to date, the production of optically active compounds has been described only via the optical resolution of racemates. It is important to note that such resolution often leads to the desired products only with moderate yields and enantiomeric purity.[4] The purpose of the work reported herein is development of asymmetric synthesis of β-aryl(heteroaryl)alkylamines.

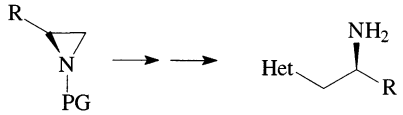
2. Results and discussion

2.1. Synthesis of starting chiral *N*-tosyl aziridines

We reasoned that chiral aziridines are convenient synthetic precursors to chiral β-aryl(heteroaryl)alkylamines as it is well known that monosubstituted aziridines are attacked by nucleophiles exclusively at the less hindered site.[5] Thus, cleavage of chiral aziridines with aryl and heteroaryl organometallic reagents could offer a straightforward route to chiral β-aryl(heteroaryl)-alkylamines (Scheme 1). However, this transformation has not been employed previously.

The presence of a suitable electron-withdrawing protecting group is necessary for effective ring opening. There are several protecting groups that could serve as activators of aziridine cleavage such as diphenylphosphinyl (Dpp),[6] diethoxyphosphoryl[7] and sulfonyl.[8] In our synthesis, we chose the tosyl group as the activator. It is known that *N*-tosyl aziridines could be easily synthesized from commercially available natural α-amino acids using a one-pot modification of Craig's protocol[9] and following this procedure, we prepared *N*-tosyl aziridines from phenylalanine, leucine and valine (Scheme 2).

In the case of the alanine derivative, ring closure was unacceptably slow. To overcome this problem the last step of the procedure was modified and ring closure was carried out using potassium hydroxide in methanol[10] (Scheme 3).



Scheme 1.

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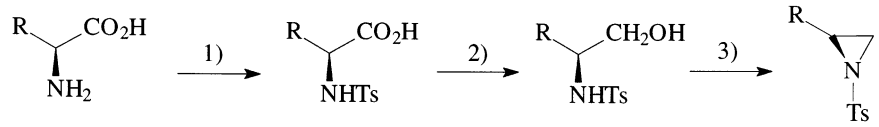
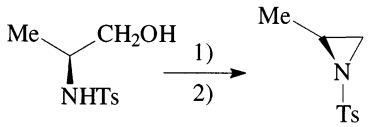
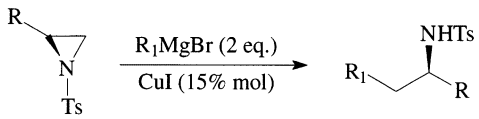


Scheme 2. (1) TsCl, EtN^iPr_2; (2) $LiAlH_4$; (3) TsCl, Et_3N, DMAP; R = Bn, *i*-Bu, *i*-Pr.



Scheme 3. (1) TsCl, Py.; (2) KOH, MeOH.



Scheme 4.

The yields of starting aziridines are given in Table 1.

2.2. Nucleophilic ring opening of *N*-tosyl aziridines

Readily available (2*S*)-benzyl-*N*-tosylaziridine was chosen as a model substrate in the screening experiments searching for the best cleaving organometallic reagent. Various lithium, zinc and magnesium derivatives of thiophene were used as the organometallic reagents. It was found that the desired β-aryl(heteroaryl)alkylamine was obtained only by cleavage of the aziridine ring with the Grignard reagent in the presence of catalytic amounts (15 mol%) of copper(I) iodide (Scheme 4). The use of alternative organometallic reagents did not furnish the required product. A number of articles concerning the reactions of activated aziridines including chiral ones[11] with Grignard reagents[12] and other organometallic reagents[13] have been published in the literature.

The nucleophilic ring opening of a range of *N*-tosyl aziridines with various aromatic and heteroaromatic Grignard reagents (Table 2) was then investigated.

The reaction occurred smoothly to give *N*-tosylamides arising from attack of nucleophile at the less substituted ring carbon of the aziridine in good yields (63–89%). A mixture of regioisomers was detected only in the case of reaction with 3-indolyl magnesium bromide, which could be explained by the fact that ether was used as the solvent in this reaction due to the poor solubility of 3-indolyl magnesium bromide in THF. In all of the other experiments THF was used as the solvent. The ratio of isomers was determined by ^1H NMR spectral analysis and it was found to be 1:1 in the case of cleavage of (2*S*)-methyl-*N*-tosylaziridine and 3:1 in the case of cleavage of (2*R*)-*iso*-propyl-*N*-tosylaziridine with preference to the C(3) ring-opened regioisomer.

Table 1. Preparation of the starting *N*-tosyl aziridines

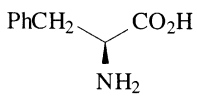
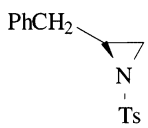
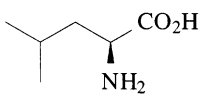
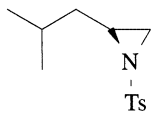
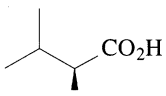
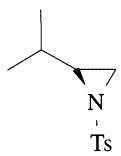
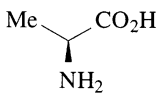
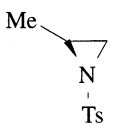
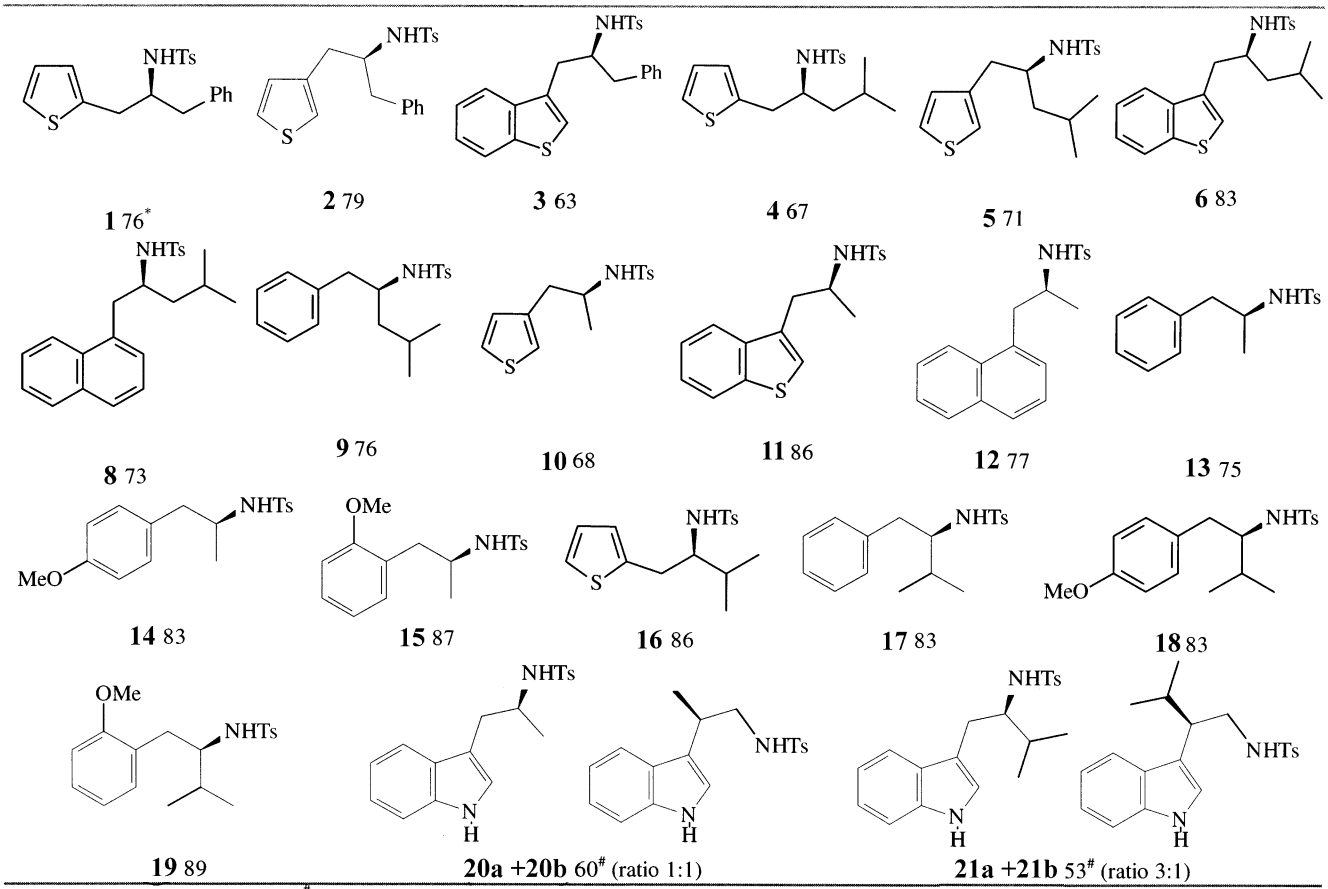
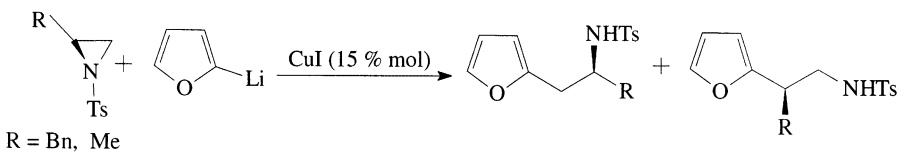
Starting (*S*)-amino acid	Product	Overall yield,%
		66
		54
		62
		45

Table 2. Tosylamides prepared by nucleophilic ring opening of *N*-tosyl aziridines



* Isolated yield of tosylamide,%. #Overall yield of two regioisomers,%.



Scheme 5.

Even the bulky *iso*-propyl substituent did not afford complete regiocontrol. This regioselectivity problem is currently under investigation in our laboratory.

Reaction with 2-furyl magnesium bromide did not yield the ring-opened product even when the reaction was carried out in refluxing THF. The use of the lithium reagent in the presence of catalytic amounts of copper(I) iodide alleviated the problem but caused a lack of selectivity. It should be noted that in this case the bulk of the alkyl substituent had no influence on the ratio of regioisomers. In the case of (2*S*)-benzyl-*N*-tosylaziridine the ratio of regioisomers was almost the same as for (2*S*)-methyl-*N*-tosylaziridine (Scheme 5 and Table 3).

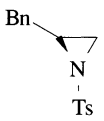
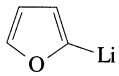
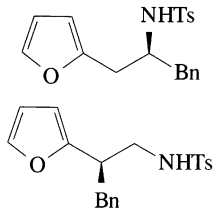
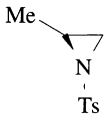
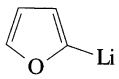
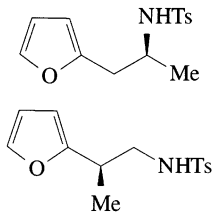
2.3. The desulfonylation of tosylamides

Having demonstrated that *N*-tosyl aziridines could be cleaved effectively, we turned our attention to *N*-deprotection. Even though a wide variety of synthetic methods for the cleavage of the N–S bond are available,[14–16] most of them require drastic conditions and yields of desulfonylated products are moderate.[8] However, recent work showed that desulfonylation could be carried out with magnesium in methanol under ultrasonic conditions[17] (Scheme 6). The latter proved to be a very mild method and afforded the desulfonylated products in good yields. It is also important to note that in all the cases studied, no racemization of the stereogenic center was observed. Therefore, we applied this method in our investigations.

The yields of β-aryl(heteroaryl)alkylamine hydrochlorides were reasonable (Table 4).

In the case of deprotection of β-furylalkylamines, the desired products were not isolated. This fact could be explained by the instability of the furan ring to acidic conditions which had applied on the step of purifying

Table 3. Tosylamides prepared by cleavage with 2-furyllithium

Compound	Aziridine	Reagent	Product	Yield,%
22			 Ratio 1.1:1	96*
23			 Ratio 1:1	98

* Overall yield of two regioisomers

these substances. To determine the optical purity of β-aryl(heteroaryl)alkylamines we have analyzed the ^{19}F NMR spectrum of the (*S*)-MPTA[18] derivative of these products. We observed only one signal for the CF_3 groups of the (*S*)-MPTA amide in the spectrum. The chemical shift of the signal was in the range −71.2 to −73.2 ppm. Therefore, we assume that β-aryl-(heteroaryl)alkylamines were prepared as single enantiomers.

Tosylamides offered the possibility for providing of selective *N*-alkylation (Scheme 7). We have synthesized the *N*-methyl substituted derivative of **11**. The procedure is very simple and straightforward. The target product **35** was prepared in 75% overall yield.

It should be noted that *N*-alkylation of racemic β-aryl-(heteroaryl)alkylamines could essentially abolish the affinity at receptors.[19]

3. Conclusion

We have described the first effective route to asymmetric β-aryl(heteroaryl)alkylamines from commercially available (*S*)-α-amino acids. Grignard reagents in the presence of catalytic amounts of copper(I) iodide are the nucleophiles of choice for the ring opening of *N*-tosyl aziridines. The tosyl group could be easily removed using magnesium in methanol under ultrasonic conditions.

4. Experimental

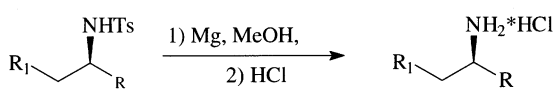
4.1. General

^1H, ^{13}C and ^{19}F NMR spectra were recorded on Varian VXR-400 spectrometers with TMS or $CFCl_3$ as an internal standard. The IR spectra were obtained on UR-20 spectrometer in films. The enantiomeric excesses of the prepared compounds were determined by ^{19}F NMR spectroscopy using (*S*)-MPTA derivatives. Acylation of β-aryl(heteroaryl)alkylamines was performed with the (*S*)-MPTA-chloride in dichloromethane solution in the presence of pyridine.

THF, toluene and diethyl ether were dried and distilled according to standard procedures.[20] All operations with air-sensitive compounds were conducted under argon by means of usual Schlenk-type techniques. Starting aziridines were prepared from commercially available α-amino acids with e.e. = 98%.[9]

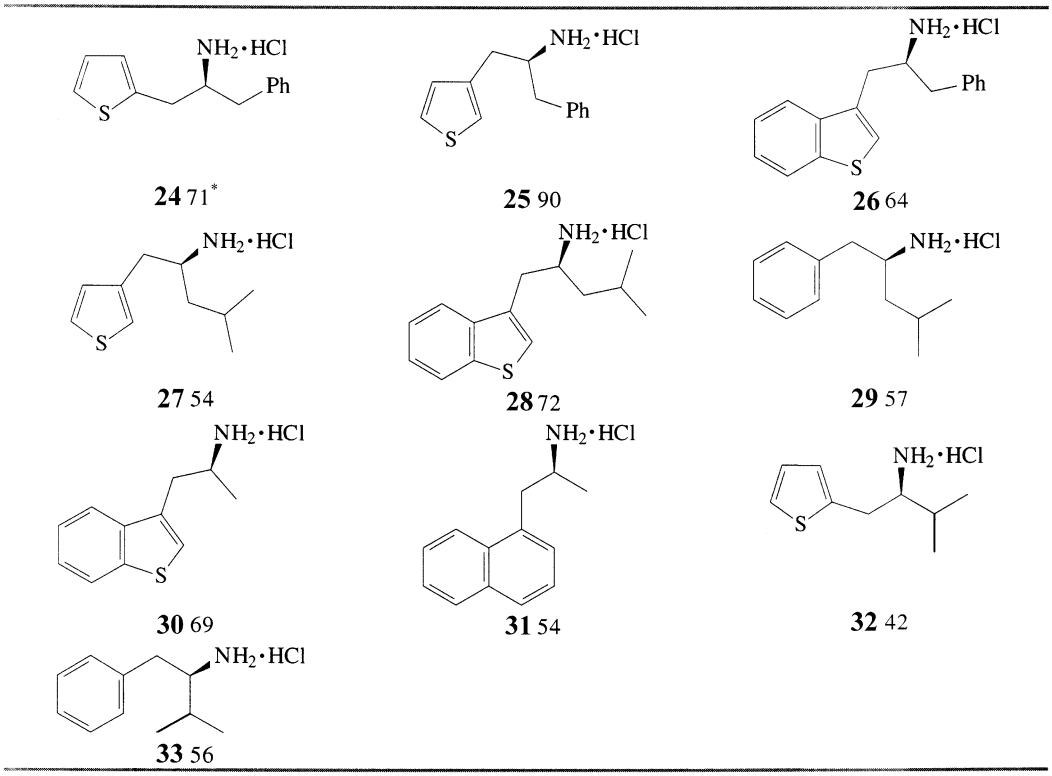
4.2. General procedure for ring opening of *N*-tosyl aziridines with Grignard reagents

To Mg (0.17 g, 7 mmol) in a flame-dried flask under Ar THF (10 mL) was added. The solution of corresponding aryl(heteroaryl)bromide (7.1 mmol) in THF (5 mL) was added dropwise. The mixture was stirred for 30 min at rt, then cooled to −30°C and dry CuI (0.2 g, 1.05 mmol) was added. The suspension was stirred for 30 min at −30°C, then cooled to −78°C. A solution of the corresponding 2-alkyl-1-[(4-methylphenyl)sulfonyl]-aziridine (3.5 mmol) in THF (10 mL) was added dropwise. The suspension was stirred at −78°C for 15 min, then at 0°C for 1 h, after which time it was partitioned between NH_4Cl and ether, the aqueous layer extracted

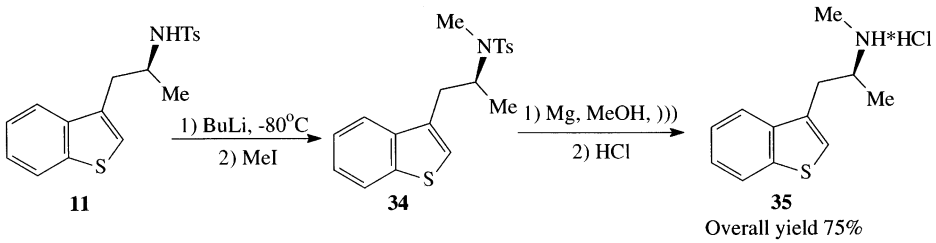


Scheme 6.

Table 4. Desulfonylation of tosylamides



* Isolated yield of β-aryl(heteroaryl)alkylamine hydrochloride,%.



Scheme 7.

with ether (3×15 mL), the organic layers dried (Na_2SO_4), filtered and the solvent removed in vacuo to leave a brown oil which was purified by chromatography on silica gel with hexane–dichloromethane (1:1) as eluent.

4.2.1. *N*-[(1*S*)-1-Benzyl-2-(2-thienyl)ethyl]-4-methylbenzenesulfonamide 1. White solid, yield 0.99 g (76%); mp 96–97°C; [Found: C, 64.56; H, 5.68. $C_{20}H_{21}NO_2S_2$ requires: C, 64.66, H, 5.70%]; ν_{max}/cm^{-1} 3320 (NH); δ_H (400 MHz, $CDCl_3$): 2.49 (3H, s, C$\underline{H}_3$ of Ts), 2.77–2.96 (2H, m, C$\underline{H}_2$ of α-Ph), 3.06–3.18 (2H, m, C$\underline{H}_2$ of α-Th), 3.72–3.81 (1H, m, C$\underline{H}$NH), 5.12 (1H, d, $J=7.4$ Hz, N$\underline{H}$), 6.88–6.90 (1H, m, C$\underline{H}$-3Th), 6.98–7.02 (1H, m, C$\underline{H}$-4Th), 7.12–7.17 (2H, m, C$\underline{H}$-5Th, C$\underline{H}$-Ph), 7.23 (2H, d, $J=8.2$ Hz, C$\underline{H}$-2,6-Ts), 7.28–7.32 (4H, m, 4C$\underline{H}$-Ph), 7.63 (2H, d, $J=8.2$ Hz, C$\underline{H}$-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 21.5 (C$\underline{H}_3$, Ts), 34.8 (C$\underline{H}_2$, α-Th), 40.8 (C$\underline{H}_2$, α-Ph), 55.5 (C$\underline{H}$NH), 124.2 (C$\underline{H}$5-Th), 126.5 (C$\underline{H}$4-Th), 126.8 (C$\underline{H}$3-Th), 127.0 (C$\underline{H}$2, C$\underline{H}$6-Ts), 129.6 (C$\underline{H}$3, C$\underline{H}$5-Ts), 138.0 (C$\underline{H}$1-Ts), 138.7 (C$\underline{H}$2-Th), 143.2 (C$\underline{H}$4-Ts).

4.2.2. *N*-[(1*S*)-1-Benzyl-2-(3-thienyl)ethyl]-4-methylbenzenesulfonamide 2. White solid, yield 1.03 g (79%); mp 100–101°C; [Found: C, 64.41; H, 5.72. $C_{20}H_{21}NO_2S_2$ requires: C, 64.66; H, 5.70%]; ν_{max}/cm^{-1} 3310 (NH); δ_H (400 MHz, $CDCl_3$): 2.38 (3H, s, C$\underline{H}_3$, of Ts), 2.66–2.87 (4H, m, 2C$\underline{H}_2$), 3.61 (1H, m, C$\underline{H}$NH), 4.42 (1H, d, $J=6.9$ Hz, N$\underline{H}$), 6.77 (1H, dd, $J=4.9$ Hz, $J=1.1$ Hz, C$\underline{H}$-4Th), 6.90 (1H, dd, $J=2.0$ Hz, $J=1.1$ Hz, C$\underline{H}$-2Th), 7.02 (1H, dd, $J=4.9$ Hz, $J=2.0$ Hz, C$\underline{H}$-5Th), 7.14 (1H, d, $J=8.2$ Hz, C$\underline{H}$-2,6-Ts), 7.16–7.24 (5C$\underline{H}$, m, Ph), 7.46 (1H, d, $J=8.2$ Hz, C$\underline{H}$-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 21.5 (C$\underline{H}_3$, Ts), 35.0 (C$\underline{H}_2$, α-Th), 40.7 (C$\underline{H}_2$, α-Ph), 55.4 (C$\underline{H}$NH), 121.7 (C$\underline{H}$5-Th), 122.6 (C$\underline{H}$2-Th), 125.8 (C$\underline{H}$4-Ph), 126.6 (C$\underline{H}$4-Th), 126.8 (C$\underline{H}$3, C$\underline{H}$5-Ph), 128.5 (C$\underline{H}$2, C$\underline{H}$6-Ts), 129.4 (C$\underline{H}$3, C$\underline{H}$5-Ts), 129.5 (C$\underline{H}$2, C$\underline{H}$6-Ph),

136.9, 137.0, 137.1 (C1-Ph, C1-Ts, C3-Th), 143.0 (C4-Ts).

4.2.3. *N*-[(1*S*)-2-(1-Benzothien-3-yl)-1-benzylethyl]-4-methylbenzenesulfonamide 3. White solid, yield 0.93 g (62%); mp 129–130°C; [Found: C, 68.41; H, 5.61. $C_{24}H_{23}NO_2S_2$ requires: C, 68.38; H, 5.50%]; ν_{max}/cm^{-1} 3250 (NH); δ_H (400 MHz, $CDCl_3$): 2.20 (3H, s, CH_3 of Ts), 2.81–3.00 (4H, m, $2CH_2$), 3.54–3.64 (1H, m, CHNH), 4.33 (1H, d, $J=6.1$ Hz, NH), 6.83 (1H, d, $J=8.2$ Hz, CH-2,6-Ts), 6.98–7.04 (3H, m, CH-3,5-Ts, 1CH-Bth), 7.15–7.24 (7H, m, 5CH-Ph, 2CH-Bth), 7.33 (1H, d, $J=7.9$ Hz, CH-7Bth), 7.71 (1H, d, $J=8.3$ Hz, CH-4Bth); δ_C (100 MHz, $CDCl_3$): 21.4 (CH_3, Ts), 33.7 (CH_2, α-Bth), 41.8 (CH_2, α-Ph), 54.6 (CHNH), 121.4 (C4-Bth), 122.6 (C2-Bth), 123.9 (C7-Bth), 124.0 (C6-Bth), 126.3 (C3, C5-Ph), 126.6 (C5-Bth), 128.5 (C2, C6-Ts), 129.1 (C3, C5-Ts), 129.4 (C2, C6-Ph), 131.8 (C4-Ph), 136.1 (C3-Bth), 137.2 (C1-Ph), 138.3 (C1-Ts), 140.4 (C8-Bth), 142.5 (C9-Bth, C4-Ts).

4.2.4. 4-Methyl-*N*-[(1*S*)-3-methyl-1-(2-thienylmethyl)-butyl]benzenesulfonamide 4. Yellow oil, yield 0.79 g (67%); [Found: C, 60.56; H, 6.90. $C_{17}H_{23}NO_2S_2$ requires: C, 60.50; H, 6.87%]; ν_{max}/cm^{-1} 3330 (NH); δ_H (400 MHz, $CDCl_3$): 0.61 (3H, d, $J=6.6$ Hz, $CH_2CH(CH_3)_2$), 0.72 (3H, d, $J=6.6$ Hz, $CH_2CH(CH_3)_2$), 1.15 (2H, t, $J=7.2$ Hz, $CH_2CH(CH_3)_2$), 1.45–1.58 (1H, m, $CH_2CH(CH_3)_2$), 2.35 (3H, s, CH_3 of Ts), 2.81 (2H, t, $J=7.2$ Hz, CH_2-α-Th), 3.38–3.50 (1H, m, CHNH), 4.52 (1H, d, $J=8.4$ Hz, NH), 6.62 (1H, d, $J=0.9$ Hz, CH-3Th), 6.82 (1H, dd, $J=0.9$ Hz, $J=1.2$ Hz, CH-4Th), 7.04 (1H, d, $J=1.2$ Hz, CH-5Th), 7.22 (2H, d, $J=7.8$ Hz, CH-2,6-Ts), 7.63 (2H, d, $J=7.8$ Hz, CH-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 21.4 (CH_3, Ts), 21.7, 22.7 (2C, $CH_2CH(CH_3)_2$), 24.3 ($CH_2CH(CH_3)_2$), 35.3 (CH_2, α-Th), 43.4 ($CH_2CH(CH_3)_2$), 52.4 (CHNH), 124.3 (C5-Th), 126.7 (C4-Th), 126.8 (C3-Th), 127.0 (C2, C6-Ts), 129.6 (C3, C5-Ts), 138.0 (C1-Ts), 138.5 (C2-Th), 143.2 (C4-Ts).

4.2.5. 4-Methyl-*N*-[(1*S*)-3-methyl-1-(3-thienylmethyl)-butyl]benzenesulfonamide 5. White solid, yield 0.84 g (71%); mp 74–75°C; [Found: C, 60.71; H, 6.98. $C_{17}H_{23}NO_2S_2$ requires: C, 60.50; H, 6.87%]; ν_{max}/cm^{-1} 3240 (NH); δ_H (400 MHz, $CDCl_3$): 0.62 (3H, d, $J=6.9$ Hz, $CH_2CH(CH_3)_2$), 0.74 (3H, d, $J=6.9$ Hz, $CH_2CH(CH_3)_2$), 1.13 (2H, t, $J=6.5$ Hz, $CH_2CH(CH_3)_2$), 1.45–1.55 (1H, m, $CH_2CH(CH_3)_2$), 2.36 (3H, s, CH_3 of Ts), 2.60 (1H, dd, $J=14.7$ Hz, $J=6.0$ Hz, CH_2-α-Th), 2.69 (1H, dd, $J=14.7$ Hz, $J=6.2$ Hz, CH_2-α-Th), 3.39–3.49 (1H, m, CHNH), 4.24 (1H, d, $J=8.2$ Hz, NH), 6.72 (1H, dd, $J=5.0$ Hz, $J=1.0$ Hz, CH-4Th), 6.79 (1H, dd, $J=1.0$ Hz, $J=2.6$ Hz, CH-2Th), 7.14 (1H, dd, $J=5.0$ Hz, $J=2.6$ Hz, CH-5Th), 7.22 (2H, d, $J=8.3$ Hz, CH-2,6-Ts), 7.66 (2H, d, $J=8.3$ Hz, CH-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 21.5 (CH_3, Ts), 21.8, 22.8 (2C, $CH_2CH(CH_3)_2$), 24.4 ($CH_2CH(CH_3)_2$), 35.7 (CH_2, α-Th), 43.8 ($CH_2CH(CH_3)_2$), 52.1 (CHNH), 122.6 (C2-Th), 125.6 (C5-Th), 127.0 (C2, C6-Ts), 128.8 (C4-Th), 129.6 (C3, C5-Ts), 136.9 (C3-Th), 138.0 (C1-Ts), 143.2 (C4-Ts).

4.2.6. *N*-[(1*S*)-1-(1-Benzothien-3-ylmethyl)-3-methylbutyl]-4-methylbenzenesulfonamide 6. White solid, yield 1.13 g (83%); mp 75–76°C; [Found: C, 65.14; H, 6.53. $C_{21}H_{25}NO_2S_2$ requires: C, 65.08; H, 6.50%]; ν_{max}/cm^{-1} 3280 (NH); δ_H (400 MHz, $CDCl_3$): 0.58 (3H, d, $J=6.4$ Hz, $CH_2CH(CH_3)_2$), 0.77 (3H, d, $J=6.4$ Hz, $CH_2CH(CH_3)_2$), 1.21–1.38 (2H, m, $CH_2CH(CH_3)_2$), 1.48–1.59 (1H, m, $CH_2CH(CH_3)_2$), 2.26 (3H, s, CH_3 of Ts), 2.87–2.91 (2H, m, CH_2, α-Bth), 3.46–3.54 (1H, m, CHNH), 4.56 (1H, d, $J=7.7$ Hz, NH), 6.98 (1H, s, CH-2Bth), 7.02 (2H, d, $J=8.4$ Hz, CH-2,6-Ts), 7.23–7.27 (2H, m, 2CH-Bth), 7.51 (2H, d, $J=8.4$ Hz, CH-3,5-Ts), 7.52–7.55 (1H, d, CH-Bth), 7.71–7.74 (1H, m, 1CH-Bth); δ_C (100 MHz, $CDCl_3$): 21.5 (CH_3, Ts), 22.0, 22.8 (2C, $CH_2CH(CH_3)_2$), 24.5 ($CH_2CH(CH_3)_2$), 34.9 (CH_2, α-Bth), 44.8 ($CH_2CH(CH_3)_2$), 51.7 (CHNH), 121.6 (C4-Bth), 122.7 (C2-Bth), 123.8 (C7-Bth), 124.0 (C6-Bth), 124.1 (C5-Bth), 126.7 (C2, C6-Ts), 129.4 (C3, C5-Ts), 132.0 (C3-Bth), 137.3 (C1-Ts), 138.7 (C8-Bth), 140.4 (C9-Bth), 143.0 (C4-Ts).

4.2.7. 4-Methyl-*N*-[(1*S*)-3-methyl-1-(1-naphtylmethyl)-butyl]benzenesulfonamide 7. White oil, yield 0.97 g (73%); [Found: C, 72.51; H, 7.17. $C_{23}H_{27}NO_2S$ requires: C, 72.40; H, 7.13%]; ν_{max}/cm^{-1} 3260 (NH); δ_H (400 MHz, $CDCl_3$): 0.47 (3H, d, $J=6.6$ Hz, $CH_2CH(CH_3)_2$), 0.74 (2H, d, $J=6.6$ Hz, $CH_2CH(CH_3)_2$), 1.15–1.24 (1H, m, $CH_2CH(CH_3)_2$), 1.35–1.44 (1H, m, $CH_2CH(CH_3)_2$), 1.51–1.61 (1H, m, $CH_2CH(CH_3)_2$), 2.17 (3H, s, CH_3 of Ts), 2.95–3.02 (1H, m, CH_2, α-Npht), 3.05–3.14 (1H, m, CH_2, α-Npht), 3.49–3.57 (1H, m, CHNH), 5.18 (1H, d, $J=5.7$ Hz, NH), 6.89 (2H, d, $J=8.5$ Hz, CH-2,6-Ts), 7.08 (1H, d, $J=6.0$ Hz, CH-Npht), 7.18 (1H, dd, $J=7.1$ Hz, $J=8.2$ Hz, CH-Npht), 7.31–7.37 (2H, m, CH-Npht), 7.44 (2H, d, $J=8.5$ Hz, CH-3,5-Ts), 7.08 (1H, d, $J=8.2$ Hz, CH-Npht), 7.64–7.68 (1H, m, CH-Npht), 7.77–7.81 (1H, m, 1CH-Npht); δ_C (100 MHz, $CDCl_3$): 21.2 (CH_3, Ts), 21.7, 22.8 ($CH_2CH(CH_3)_2$), 24.2 ($CH_2CH(CH_3)_2$), 39.6 (CH_2, α-Npht), 44.8 ($CH_2CH(CH_3)_2$), 52.4 (CHNH), 123.4 (C9-Npht), 125.1 (C8-Npht), 125.3 (C3-Npht), 125.8 (C6-Npht), 126.5 (C2, C6-Ts), 127.1 (C7-Npht), 127.8 (C2-Npht), 128.5 (C4-Npht), 129.0 (C3, C5-Ts), 131.7 (C1-Npht), 133.7 (C5-Npht), 133.8 (C10-Npht), 137.2 (C1-Ts), 142.5 (C4-Ts).

4.2.8. *N*-[(1*S*)-1-Benzyl-3-methylbutyl]-4-methylbenzenesulfonamide 8. White solid, yield 0.88 g (76%); mp 73–74°C; [Found: C, 68.74; H, 7.58. $C_{19}H_{25}NO_2S$ requires: C, 68.85; H, 7.60%]; ν_{max}/cm^{-1} 3230 (NH); δ_H (400 MHz, $CDCl_3$): 0.59 (3H, d, $J=6.7$ Hz, $CH_2CH(CH_3)_2$), 0.73 (3H, d, $J=6.7$ Hz, $CH_2CH(CH_3)_2$), 1.11–1.17 (2H, m, $CH_2CH(CH_3)_2$), 1.47–1.55 (1H, m, $CH_2CH(CH_3)_2$), 2.34 (3H, s, CH_3 of Ts), 2.59–2.62 (2H, m, CH_2, α-Ph), 3.38–3.48 (1H, m, CHNH), 4.27 (1H, d, $J=8.4$ Hz, NH), 6.95 (2H, d, $J=8.4$ Hz, CH-2,6-Ts), 7.11–7.21 (5CH, m, Ph), 7.63 (2H, d, $J=8.4$ Hz, CH-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 21.5 (CH_3, Ts), 21.7, 22.8 (2C, $CH_2CH(CH_3)_2$), 24.3 ($CH_2CH(CH_3)_2$), 41.6 (CH_2, α-Ph), 43.8 ($CH_2CH(CH_3)_2$), 52.9 (CHNH), 126.5 (C4-Ph), 127.0 (C2, C6-Ts), 128.4 (C2, C6-Ph), 129.6 (C3, C5-Ts), 129.7 (C3, C5-Ph), 137.0 (C1-Ph), 138.0 (C1-Ts), 143.1 (C4-Ts).

4.2.9. 4-Methyl-*N*-[(1*S*)-1-methyl-2-(3-thienyl)ethyl]-benzenesulfonamide 9. White oil, yield 0.70 g (68%); [Found: C, 56.93; H, 5.80. $C_{14}H_{17}NO_2S_2$ requires: C, 56.92; H, 5.80]; ν_{max}/cm^{-1} 3230 (NH); δ_H (400 MHz, $CDCl_3$): 1.08 (3H, d, $J=6.5$ Hz, CHC$\underline{H}_3$), 2.41 (3H, s, C$\underline{H}_3$ of Ts), 2.70 (2H, d, $J=6.5$ Hz, C$\underline{H}_2$-α-Th), 3.47–3.55 (1H, m, C$\underline{H}$NH), 4.51 (1H, d, $J=7.2$ Hz, N$\underline{H}$), 6.75 (1H, dd, $J=4.8$ Hz, $J=1.1$ Hz, C$\underline{H}$-4Th), 6.88 (1H, dd, $J=2.9$ Hz, $J=1.1$ Hz, C$\underline{H}$-2Th), 7.02 (1H, dd, $J=4.8$ Hz, $J=2.9$ Hz, C$\underline{H}$-5Th), 7.25 (1H, d, $J=8.2$ Hz, C$\underline{H}$-2,6-Ts), 7.66 (1H, d, $J=8.2$ Hz, C$\underline{H}$-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 21.3 (C$\underline{H}_3$), 21.5 (C$\underline{H}_3$, Ts), 37.6 (C$\underline{H}_2$), 50.2 (C$\underline{H}$NH), 122.5 (C2-Th), 125.8 (C5-Th), 127.0 (C2, C6-Ts), 128.5 (C4-Th), 129.6 (C3, C5-Ts), 137.2 (C3-Th), 137.7 (C1-Ts), 143.2 (C4-Ts).

4.2.10. *N*-[(1*S*)-2-(1-Benzothien-3-yl)-1-methylethyl]-4-methylbenzenesulfonamide 10. White solid, yield 1.00 g (86%); mp 102–103°C; [Found: C, 62.57; H, 5.61. $C_{18}H_{19}NO_2S_2$ requires: C, 62.58; H, 5.54%]; ν_{max}/cm^{-1} 3250 (NH); δ_H (400 MHz, $CDCl_3$): 1.18 (3H, d, $J=6.5$ Hz, CHC$\underline{H}_3$), 2.32 (3H, s, C$\underline{H}_3$ of Ts), 2.89 (1H, dd, $J=14.5$ Hz, $J=6.7$ Hz, C$\underline{H}_2$-α-Bth), 2.98 (1H, dd, $J=14.5$ Hz, $J=7.1$ Hz, C$\underline{H}_2$-α-Bth), 3.55–3.63 (1H, m, C$\underline{H}$NH), 4.62 (1H, d, $J=6.7$ Hz, N$\underline{H}$), 7.03–7.07 (3H, m, 2C$\underline{H}$-Ts, C$\underline{H}$-Bth), 7.25–7.33 (3H, m, 3C$\underline{H}$-Bth), 7.50–7.54 (3H, m, 2C$\underline{H}$-Ts, C$\underline{H}$-Bth), 7.77–7.81 (1H, m, C$\underline{H}$-4Bth); δ_C (100 MHz, $CDCl_3$): 21.5 (C$\underline{H}_3$, Ts), 22.0 (C$\underline{H}_3$), 36.6 (C$\underline{H}_2$), 49.3 (C$\underline{H}$NH), 121.6 (C4-Bth), 122.8 (C7-Bth), 123.8 (C2-Bth), 124.0 (C6-Bth), 124.2 (C5-Bth), 126.7 (C2, C6-Ts), 129.4 (C3, C5-Ts), 132.0 (C3-Bth), 137.0 (C1-Ts), 138.5 (C9-Bth), 140.5 (C8-Bth), 143.0 (C4-Ts).

4.2.11. 4-Methyl-*N*-[(1*S*)-1-methyl-2-(1-naphtyl)ethyl]-benzenesulfonamide 11. White solid, yield 0.91 g (77%); mp 79–80°C; [Found: C, 70.64; H, 6.31. $C_{20}H_{21}NO_2S$ requires: C, 70.77; H, 6.24%]; ν_{max}/cm^{-1} 3250 3240 (NH); δ_H (400 MHz, $CDCl_3$): 1.19 (3H, d, $J=6.6$ Hz, CHC$\underline{H}_3$), 2.30 (3H, s, C$\underline{H}_3$-Ts), 3.06 (1H, dd, $J=4.0$ Hz, $J=7.3$ Hz, C$\underline{H}_2$-α-Npht), 3.19 (1H, dd, $J=14.0$ Hz, $J=7.1$ Hz, C$\underline{H}_2$-α-Npht), 3.56–3.65 (1H, m, C$\underline{H}$NH), 4.65 (1H, d, $J=6.4$ Hz, N$\underline{H}$), 6.96 (2H, d, $J=8.1$ Hz, C$\underline{H}$-2,6-Ts), 7.17 (1H, d, $J=7.1$ Hz, C$\underline{H}$-2Npht), 7.31 (1H, t, $J=7.1$ Hz, C$\underline{H}$-3Npht), 7.37–7.48 (4H, m, 2C$\underline{H}$-Npht, C$\underline{H}$-3,5-Ts), 7.68 (1H, d, $J=8.4$ Hz, C$\underline{H}$-2Npht), 7.75–7.80 (1H, m, 1C$\underline{H}$-Npht); δ_C (100 MHz, $CDCl_3$): 21.5 (C$\underline{H}_3$, Ts), 22.0 (C$\underline{H}_3$), 36.6 (C$\underline{H}_2$), 49.3 (C$\underline{H}$NH), 123.4 (C9-Npht), 125.1 (C8-Npht), 125.3 (C3-Npht), 125.8 (C6-Npht), 126.5 (C2, C6-Ts), 127.1 (C7-Npht), 127.8 (C2-Npht), 128.5 (C4-Npht), 129.0 (C3, C5-Ts), 131.7 (C1-Npht), 133.7 (C5-Npht), 133.8 (C10-Npht), 137.2 (C1-Ts), 142.5 (C4-Ts).

4.2.12. 4-Methyl-*N*-[(1*S*)-1-methyl-2-phenylethyl]benzenesulfonamide 12. White oil, yield 0.76 g (75%); [Found C, 66.48; H, 6.65. $C_{16}H_{19}NO_2S$ requires: C, 66.40; H, 6.62%]; ν_{max}/cm^{-1} 3220 (NH); δ_H (400 MHz, $CDCl_3$): 1.08 (3H, d, $J=6.5$ Hz, CHC$\underline{H}_3$), 2.41 (3H, s, C$\underline{H}_3$ of Ts), 2.65–2.68 (2H, m, C$\underline{H}_2$Ph), 3.47–3.55 (1H, m, C$\underline{H}$NH), 4.30 (1H, d, $J=7.4$ Hz, N$\underline{H}$), 7.00 (2H, d, $J=8.4$ Hz, C$\underline{H}$-2,6-Ts), 7.18–7.24 (5C$\underline{H}$, m, Ph), 7.61 (2H, d, $J=8.4$ Hz, C$\underline{H}$-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 21.3 (C$\underline{H}_3$), 21.5 (C$\underline{H}_3$, Ts), 43.4 (C$\underline{H}_2$), 50.8 (C$\underline{H}$NH), 126.7 (C4-Ph), 127.0 (C2, C6-Ts), 128.5 (C2, C6-Ph), 129.4 (C3, C5-Ts), 129.6 (C3, C5-Ph), 137.0 (C1-Ph), 137.6 (C1-Ts), 143.1 (C4-Ts).

4.2.13. *N*-[(1*S*)-2-(4-Methoxyphenyl)-1-methylethyl]-4-methylbenzenesulfonamide 13. White solid, yield 0.93 g (83%); mp 101–102°C; [Found: C, 64.06; H, 6.76. $C_{17}H_{21}NO_3S$ requires: C, 63.92; H, 6.63%]; ν_{max}/cm^{-1} 3250 (NH); δ_H (400 MHz, $CDCl_3$): 1.01 (3H, d, $J=6.6$ Hz, CHC$\underline{H}_3$), 2.34 (3H, s, C$\underline{H}_3$-Ts), 2.54 (2H, d, $J=6.6$ Hz, C$\underline{H}_2$Ar), 3.35–3.43 (1H, m, C$\underline{H}$NH), 3.70 (3H, s, OC$\underline{H}_3$), 4.53 (1H, d, $J=7.2$ Hz, N$\underline{H}$), 6.66 (2H, d, $J=8.7$ Hz, C$\underline{H}$-3,5-Ar), 6.85 (2H, d, $J=8.8$ Hz, C$\underline{H}$-2,6-Ar), 7.14 (2H, d, $J=8.4$ Hz, C$\underline{H}$-2,6-Ts), 7.55 (2H, d, $J=8.4$ Hz, C$\underline{H}$-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 21.2 (C$\underline{H}_3$), 21.4 (C$\underline{H}_3$, Ts), 42.4 (C$\underline{H}_2$), 51.0 (C$\underline{H}$NH), 55.1 (C$\underline{H}_3$, OMe), 113.8 (C3, C5-Ar), 126.9 (C2, C6-Ts), 129.1 (C1-Ar), 129.5 (C3, C5-Ts), 130.2 (C2, C6-Ar), 137.7 (C1-Ts), 143.0 (C4-Ts), 158.3 (C4-Ar).

4.2.14. *N*-[(1*S*)-2-(2-Methoxyphenyl)-1-methylethyl]-4-methylbenzenesulfonamide 14. White oil, yield 0.97 g (87%); [Found: C, 63.76; H, 6.54. $C_{17}H_{21}NO_3S$ requires: C, 63.92; H, 6.63%]; ν_{max}/cm^{-1} 3260 (NH); δ_H (400 MHz, $CDCl_3$): 1.21 (3H, d, $J=6.4$ Hz, CHC$\underline{H}_3$), 2.35 (3H, s, C$\underline{H}_3$-Ts), 2.56 (1H, dd, $J=13.8$ Hz, $J=5.2$ Hz, C$\underline{H}_2$Ar), 2.70 (1H, dd, $J=13.8$ Hz, $J=8.5$ Hz, C$\underline{H}_2$Ar), 3.39–3.50 (1H, m, C$\underline{H}$NH), 3.72 (3H, s, OC$\underline{H}_3$), 4.95 (1H, d, $J=6.1$ Hz, N$\underline{H}$), 6.71 (1H, d, $J=8.4$ Hz, C$\underline{H}$-3-Ar), 6.76 (1H, t, $J=7.4$ Hz, C$\underline{H}$-4-Ar), 6.89 (1H, d, $J=7.4$ Hz, C$\underline{H}$-6-Ar), 7.07 (2H, d, $J=8.5$ Hz, C$\underline{H}$-2,6-Ts), 7.14 (1H, t, $J=7.8$ Hz, C$\underline{H}$-5-Ar), 7.44 (2H, d, $J=8.5$ Hz, C$\underline{H}$-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 21.4 (C$\underline{H}_3$, Ts), 22.6 (CHC$\underline{H}_3$), 37.6 (C$\underline{H}_2$), 50.8 (C$\underline{H}$NH), 55.2 (C$\underline{H}_3$, OMe), 110.4 (C3-Ar), 120.7 (C5-Ar), 125.9 (C1-Ar), 126.7 (C2, C6-Ts), 128.0 (C4-Ar), 129.2 (C3, C5-Ts), 131.1 (C6-Ar), 137.2 (C1-Ts), 142.5 (C4-Ts), 157.0 (C2-Ar).

4.2.15. 4-Methyl-*N*-[(1*R*)-3-methyl-1-(2-thienylmethyl)-propyl]benzenesulfonamide 15. White solid, yield 0.97 g (86%); mp 64–65°C; [Found: C, 60.31; H, 6.68. $C_{16}H_{21}NO_2S_2$ requires: C, 60.50; H, 6.87%]; ν_{max}/cm^{-1} 3350 (NH); δ_H (400 MHz, $CDCl_3$): 0.83 (3H, d, $J=6.9$ Hz, CH(C$\underline{H}_3$)$_2$), 0.87 (3H, d, $J=6.9$ Hz, CH(C$\underline{H}_3$)$_2$), 1.73–1.82 (1H, m, C$\underline{H}$(CH$_3$)$_2$), 2.40 (3H, s, C$\underline{H}_3$-Ts), 2.82–2.86 (2H, m, C$\underline{H}_2$-α-Th), 3.22–3.30 (1H, m, C$\underline{H}$NH), 4.64 (1H, d, $J=8.7$ Hz, N$\underline{H}$), 6.67 (1H, d, $J=3.4$ Hz, C$\underline{H}$-3Th), 6.85 (1H, dd, $J=5.1$ Hz, $J=3.4$ Hz, C$\underline{H}$-4Th), 7.08 (1H, d, $J=5.1$ Hz, C$\underline{H}$-5Th), 7.25 (2H, d, $J=8.2$ Hz, C$\underline{H}$-2,6-Ts), 7.70 (2H, d, $J=8.2$ Hz, C$\underline{H}$-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 17.4, 19.0 (2C, CH(C$\underline{H}_3$)$_2$), 21.5 (C$\underline{H}_3$, Ts), 29.8 (C$\underline{H}$(CH$_3$)$_2$), 32.0 (C$\underline{H}_2$, α-Th), 60.2 (C$\underline{H}$NH), 124.2 (C5-Th), 126.3 (C4-Th), 126.9 (C3-Th), 127.0 (C2, C6-Ts), 129.6 (C3, C5-Ts), 137.9 (C1-Ts), 139.2 (C2-Th), 143.1 (C4-Ts).

4.2.16. *N*-[(1*R*)-3-Benzyl-2-methylpropyl]-4-methylbenzenesulfonamide 16. White oil, yield 0.92 g (83%); [Found: C, 68.19, H, 7.35; $C_{18}H_{23}NO_2S$ requires: C, 68.10; H, 7.30%]; ν_{max}/cm^{-1} 3310 (NH); δ_H (400 MHz,

$CDCl_3$): 0.85 (3H, d, $J=6.8$ Hz, $CH(CH_3)_2$), 0.87 (3H, d, $J=6.8$ Hz, $CH(CH_3)_2$), 1.75–1.84 (1H, m, $CH(CH_3)_2$), 2.37 (3H, s, CH_3-Ts), 2.53 (1H, dd, $J=13.9$ Hz, $J=6.9$ Hz, CH_2Ph), 2.65 (1H, dd, $J=13.9$ Hz, $J=7.2$ Hz, CH_2Ph), 3.27–3.34 (1H, m, CHNH), 4.86 (1H, d, $J=8.3$ Hz, NH), 6.96 (2H, d, $J=8.4$ Hz, CH-2,6-Ts), 7.12–7.18 (5H, m, 5CH-Ph), 7.60 (2H, d, $J=8.4$ Hz, CH-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 16.8, 18.6 (2C, $CH(CH_3)_2$), 21.4 (CH_3, Ts), 29.9 ($CH(CH_3)_2$), 37.7 (CH_2Ph), 60.5 (CHNH), 126.2 (C4-Ph), 126.8 (C2, C6-Ts), 128.3 (C2, C6-Ph), 129.0 (C3, C5-Ts), 129.4 (C3, C5-Ph), 137.7 (C1-Ph), 137.8 (C1-Ts), 142.7 (C4-Ts).

4.2.17. *N*-[(1*R*)-2-(4-Methoxybenzyl)-2-methylpropyl]-4-methylbenzenesulfonamide 17. White solid, yield 1.02 g (84%); mp 73–74°C; [Found: C, 65.44; H, 7.37. $C_{19}H_{25}NO_3S$ requires: C, 65.68; H, 7.25%]; ν_{max}/cm^{-1} 3230 (NH); δ_H (400 MHz, $CDCl_3$): 0.86 (3H, d, $J=4.6$ Hz, $CH(CH_3)_2$), 0.88 (3H, d, $J=4.6$ Hz, $CH(CH_3)_2$), 1.77–1.85 (1H, m, $CH(CH_3)_2$), 2.38 (3H, s, CH_3-Ts), 2.45 (1H, dd, $J=14.0$ Hz, $J=7.1$ Hz, CH_2Ar), 2.60 (1H, dd, $J=14.0$ Hz, $J=7.0$ Hz), 3.22–3.29 (1H, m, CHNH), 3.74 (3H, s, OCH_3), 4.84 (1H, d, $J=8.3$ Hz, NH), 6.66 (2H, d, $J=8.5$ Hz, CH-3,5-Ar), 6.86 (2H, d, $J=8.5$ Hz, CH-2,6-Ar), 7.15 (2H, d, $J=8.4$ Hz, CH-2,6-Ts), 7.58 (2H, d, $J=8.4$ Hz, CH-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 17.1, 18.5 (2C, $CH(CH_3)_2$), 21.3 (CH_3, Ts), 30.1 ($CH(CH_3)_2$), 36.7 (CH_2Ar), 55.0 (OCH_3), 60.7 (CHNH), 113.8 (C3, C5-Ar), 126.8 (C2, C6-Ts), 129.3 (C3, C5-Ts), 129.7 (C1-Ar), 130.0 (C2, C6-Ar), 137.9 (C1-Ts), 142.7 (C4-Ts), 158.1 (C4-Ar).

4.2.18. *N*-[(1*R*)-2-(2-Methoxybenzyl)-2-methylpropyl]-4-methylbenzenesulfonamide 18. White solid, yield 1.08 g (89%); mp 75–76°C; [Found: C, 65.75; H, 7.32. $C_{19}H_{25}NO_3S$ requires: C, 65.68; H, 7.25%]; ν_{max}/cm^{-1} 3240 (NH); δ_H (400 MHz, $CDCl_3$): 0.93 (3H, d, $J=2.5$ Hz, $CH(CH_3)_2$), 0.95 (3H, d, $J=2.5$ Hz, $CH(CH_3)_2$), 1.94–2.02 (1H, m, $CH(CH_3)_2$), 2.33 (3H, s, CH_3-Ts), 2.49–2.61 (2H, m, CH_2Ar), 3.25–3.32 (1H, m, CHNH), 3.73 (3H, s, OCH_3), 4.94 (1H, d, $J=6.7$ Hz, NH), 6.64 (1H, d, $J=8.1$ Hz, CH-3-Ar), 6.71 (1H, t, $J=7.4$ Hz, CH-4-Ar), 6.83 (1H, d, $J=7.5$ Hz, CH-6-Ar), 7.01 (2H, d, $J=8.4$ Hz, CH-2,6-Ts), 7.08 (1H, t, $J=7.7$ Hz, CH-5-Ar), 7.38 (2H, d, $J=8.4$ Hz, CH-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 17.2, 18.0 (2C, $CH(CH_3)_2$), 21.4 (CH_3, Ts), 30.7 ($CH(CH_3)_2$), 31.7 (CH_2Ar), 55.1 (OCH_3), 60.3 (CHNH), 110.3 (C3-Ar), 120.7 (C5-Ar), 126.3 (C1-Ar), 126.6 (C2, C6-Ts), 127.6 (C4-Ar), 129.1 (C3, C5-Ts), 130.9 (C6-Ar), 137.3 (C1-Ts), 142.2 (C4-Ts), 157.0 (C2-Ar).

4.3. General procedure for ring opening of *N*-tosyl aziridines with 3-indolylmagnesiumbromide

Indole (0.84 g, 7.2 mmol) was placed in an oven-dried flask under Ar. A solution of ethylmagnesium bromide (3 M, 6.3 mmol) in Et_2O was added dropwise and the mixture was stirred at rt for 45 min. The resulting Grignard reagent was cooled to −30°C and dry CuI (0.22 g, 1.2 mmol) was added. The suspension was stirred for 30 min at −30°C, then was cooled to −78°C and solution of corresponding 2-alkyl-1-[(4-methylphenyl)sulfonyl]aziridine (4 mmol) in Et_2O (10 mL) was added dropwise. The suspension was stirred at −78°C for 1 h, then at 0°C for 1 h, after which time it was partitioned between NH_4Cl and ether, the aqueous layer extracted with ether (3×5 mL), the organic layers dried (Na_2SO_4), filtered and the solvent removed in vacuo to leave brown oil which was purified by chromatography on silica gel with dichloromethane as eluent.

4.3.1. The mixture of *N*-[(1*S*)-2-(1*H*-indol-3-yl)-1-methylethyl]-4-methylbenzenesulfonamide 19a and *N*-[(2*R*)-2-(1*H*-indol-3-yl)propyl]-4-methylbenzenesulfonamide 19b (ratio 1:1). White oil, yield 0.79 g (60%); **19a** δ_H (400 MHz, $CDCl_3$): 1.15 (3H, d, $J=6.5$ Hz, $CHCH_3$), 2.32 (3H, s, CH_3-Ts), 2.75–2.87 (2H, m, CH_2-α-Ind), 3.49–3.57 (1H, m, CHNH), 4.52 (1H, d, $J=6.2$ Hz, NH), 8.06 (1H, s, NH-Ind), 6.90–7.65 (9H, m, CH-Ind); **19b** δ_H (400 MHz, $CDCl_3$): 1.33 (3H, d, $J=6.7$ Hz, $CHCH_3$), 1.59–1.65 (1H, m, CH-α-Ind), 2.37 (3H, s, CH_3-Ts), 3.17–3.22 (2H, m, CH_2NH), 4.37–4.42 (1H, m, NH), 6.90–7.65 (9H, m, CH-Ind), 8.10 (1H, s, NH-Ind).

4.3.2. The mixture of *N*-[(1*R*)-1-(1*H*-indol-3-ylmethyl)-2-methylpropyl]-4-methylbenzenesulfonamide 20a and *N*-[(2*S*)-1-(1*H*-indol-3-yl)-3-methylbutyl]-4-methylbenzenesulfonamide 20b (ratio 3:1). White oil, yield 63% (0.90 g); **20a** δ_H (400 MHz, $CDCl_3$): 0.87 (3H, d, $J=6.9$ Hz, $CH(CH_3)_2$), 0.93 (3H, d, $J=6.9$ Hz, $CH(CH_3)_2$), 1.92–2.02 (1H, m, $CH(CH_3)_2$), 2.29 (3H, s, CH_3-Ts), 2.67 (1H, dd, $J=14.7$ Hz, $J=7.6$ Hz, CH_2-α-Ind), 2.84 (1H, dd, $J=14.7$ Hz, $J=6.3$ Hz, CH_2-α-Ind), 3.30–3.38 (1H, m, CHNH), 4.50 (1H, d, $J=6.2$ Hz, NH), 6.90–7.65 (9H, m, CH-Ind, Ts), 7.95 (1H, s, NH-Ind); **20b** δ_H (400 MHz, $CDCl_3$): 0.72 (6H, d, $J=6.5$ Hz, $CH(CH_3)_2$ (**21b**)), 2.40 (3H, s, CH_3-Ts (**21b**)), 3.10–3.18 (1H, m, CH_2NH (**21b**)), 4.19–4.23 (1H, m, CH_2NH (**21b**)), 6.90–7.65 (9H, m, CH-Ind, Ts), 8.12 (1H, s, NH-Ind).

4.4. General procedure for ring opening of *N*-tosyl aziridines with 2-furyllithium

A solution of furan (0.51 mL, 7 mmol) in THF (10 mL) in a flame-dried flask under Ar was cooled to 0°C. A solution of BuLi (*c* 1.6 M in hexane, 4.7 mL, 7.1 mmol) was added dropwise. The resulting solution was stirred for 30 min at rt, then cooled to −30°C and dry CuI (0.2 g, 1.05 mmol) was added. The suspension was stirred for 30 min at −30°C, then was cooled to −78°C and solution of corresponding 2-alkyl-1-[(4-methylphenyl)-sulfonyl]aziridine (3.5 mmol) in THF (10 mL) was added dropwise. The suspension was stirred at −78°C for 15 min, then at 0°C for 1 h, after which time it was partitioned between NH_4Cl and ether, the aqueous layer extracted with ether (3×5 mL), the organic layers dried (Na_2SO_4), filtered and the solvent removed in vacuo to leave brown oil which was purified by chromatography on silica gel with hexane–dichloromethane (1:1) as eluent.

4.4.1. *N*-[(1*S*)-1-Benzyl-2-(2-furyl)ethyl]-4-methylbenzenesulfonamide 21. White solid, yield 0.67 g (54%); mp 71°C; [Found: C, 67.65, H, 6.07. $C_{20}H_{21}NO_3S$ requires: C, 67.58, H, 5.95%]; ν_{max}/cm^{-1} 3270 (NH); δ_H (400 MHz, $CDCl_3$): 2.29 (3H, s, CH$_3$-Ts), 2.62–2.68 (4H, m, 2CH$_2$), 3.57–3.66 (1H, m, CHNH), 4.86 (1H, d, $J=7.4$ Hz, NH), 5.94 (1H, dd, $J=3.3$ Hz, $J=1.0$ Hz, CH-3Fu), 6.16 (1H, dd, $J=3.3$ Hz, $J=2.7$ Hz, CH-4Fu), 6.98 (2H, d, $J=8.2$ Hz, CH-2,6-Ts), 7.06–7.13 (5H, m, 5CH-Ph), 7.17 (1H, dd, $J=2.7$ Hz, $J=1.0$ Hz, CH-5Fu), 7.48 (2H, d, $J=8.2$ Hz, CH-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 21.3 (CH$_3$, Ts), 32.4 (CH$_2$, α-Fu), 40.6 (CH$_2$, α-Ph), 54.1 (CHNH), 108.0 (C4-Fu), 110.1 (C3-Fu), 126.4 (C4-Ph), 126.8 (C2, C6-Ts), 128.3 (C3, C5-Ph), 129.3 (C3, C5-Ts), 129.4 (C2, C6-Ph), 137.0 (C1-Ts), 137.2 (C1-Ph), 141.6 (C5-Fu), 142.8 (C4-Ts), 151.1 (C2-Fu).

4.4.2. *N*-[(1*S*)-2-(2-Furyl)-1-methylethyl]-4-methylbenzenesulfonamide 22. White solid, yield 0.50 g (51%); mp 76°C; [Found: C, 59.71; H, 6.35. $C_{14}H_{17}NO_3S$ requires: C, 60.19; H, 6.13%]; ν_{max}/cm^{-1} 3260 (NH); δ_H (400 MHz, $CDCl_3$): 1.02 (3H, d, $J=6.6$ Hz, CHCH$_3$), 2.35 (3H, s, CH$_3$-Ts), 2.62 (2H, d, $J=6.0$ Hz, CH$_2$-α-Fu), 3.47–3.58 (1H, m, CHNH), 4.62 (1H, d, $J=7.6$ Hz, NH), 5.93 (1H, d, $J=3.3$ Hz, CH-3Fu), 6.18 (1H, dd, $J=3.3$ Hz, $J=1.7$ Hz, CH-4Fu), 7.18 (1H, d, $J=1.7$ Hz, CH-5Fu), 7.22 (2H, d, $J=8.3$ Hz, CH-2,6-Ts), 7.69 (2H, d, $J=8.3$ Hz, 2CH-3,5-Ts); δ_C (100 MHz, $CDCl_3$): 21.2 (CH$_3$, Ts), 21.5 (CH$_3$), 35.3 (CH$_2$), 48.9 (CHNH), 107.8 (C4-Fu), 110.2 (C3-Fu), 127.0 (C2, C6-Ts), 129.6 (C3, C5-Ts), 137.8 (C1-Ts), 141.8 (C5-Fu), 143.2 (C4-Ts), 151.3 (C2-Fu).

4.5. General procedure for desulfonylation

To a suspension of Mg (0.45 g, 20 mmol) in MeOH (5 mL) was added a solution of the corresponding *N*-tosylalkyl-2-aryl(heteroaryl)amine (2 mmol) in MeOH (10 mL). The resulting suspension was sonicated for 1 h until consumption of the starting material was complete. The reaction mixture was then diluted with aqueous NH_4Cl and extracted with ether (3×5 mL). The organic layer was dried over $MgSO_4$ and evaporated. To resulting oil ethanolic solution HCl (0.5 mL, *c* 2 M) was added. Hydrochloride was precipitated, filtered and washed with ether.

4.5.1. (2*S*)-1-Phenyl-3-(2-thienyl)-2-propanamine hydrochloride 23. White solid, yield 0.36 g (71%); mp 171–172°C; [Found: C, 61.29; H, 6.24. $C_{13}H_{16}ClNS$ requires: C, 61.52; H, 6.35%]; δ_H (400 MHz, $CDCl_3$): 2.75–2.87 (2H, m, CH$_2$Ph), 2.93–3.01 (2H, m, CH$_2$-αTh), 3.61–3.68 (1H, m, CHNH$_3$Cl), 7.02 (1H, dd, $J=3.7$ Hz, $J=1.1$ Hz, CH-3Th), 7.21–7.36 (6H, m, CH-4Th, 5CH-Ph), 7.50 (1H, dd, $J=2.9$ Hz, $J=1.1$ Hz, CH-5Th), 8.22–8.31 (3H, br s, NH$_3$Cl); δ_C (100 MHz, $CDCl_3$): 29.5 (CH$_2$, α-Th), 38.3 (CH$_2$, α-Ph), 51.4 (CHNH$_3$Cl), 124.4 (C4-Ph), 125.1 (C5-Th), 127.0 (C3-Th), 127.2 (C4-Th), 128.5 (C3, C5-Ph), 129.4 (C2, C6-Ph), 136.4 (C1-Ph), 138.4 (C2-Th).

4.5.2. (2*S*)-1-Phenyl-3-(3-thienyl)-2-propanamine hydrochloride 24. White solid, yield 0.46 g (90%); mp 189–190°C; [Found: C, 61.54; H, 6.53. $C_{13}H_{16}ClNS$ requires: C, 61.52; H, 6.35%]; δ_H (400 MHz, $CDCl_3$): 2.80–2.87 (1H, m, CH$_2$Ph), 2.98–3.09 (2H, m, CH$_2$Ph, CH$_2$-αTh), 3.13–3.21 (1H, m, CH$_2$Ph), 3.54–3.63 (1H, m, CHNH$_3$Cl), 6.96–7.04 (2H, m, CH-3Th, CH-4Th), 7.21–7.35 (5H, m, CH-Ph), 7.41 (1H, d, $J=4.9$ Hz, CH-5Th), 8.02–8.38 (3H, br s, NH$_3$Cl); δ_C (100 MHz, $CDCl_3$): 33.5 (CH$_2$, α-Th), 38.2 (CH$_2$, α-Ph), 51.5 (CHNH$_3$Cl), 122.6 (C2-Th), 124.4 (C4-Ph), 126.3 (C5-Th), 128.3 (C4-Th), 128.5 (C3, C5-Ph), 129.4 (C2, C6-Ph), 136.4 (C1-Ph), 136.6 (C3-Th).

4.5.3. (2*S*)-(1-Benzothien-3-yl)-3-phenyl-2-propanamine hydrochloride 25. White solid, yield 0.38 g (63%); mp 232–233°C; [Found: C, 67.36; H, 6.08. $C_{17}H_{18}ClNS$ requires: C, 67.20; H, 5.97%]; δ_H (400 MHz, $CDCl_3$): 2.89 (1H, dd, $J=13.9$ Hz, $J=7.0$ Hz, CH$_2$Ph), 3.01–3.14 (2H, m, CH$_2$Ph, CH$_2$-αTh), 3.24 (1H, dd, $J=14.8$ Hz, $J=7.1$ Hz, CH$_2$-α-Th), 3.67–3.75 (1H, m, CHNH$_3$Cl), 7.22–7.39 (7H, m, 5CH-Ph, CH-5,6-Bth), 7.63–7.69 (1H, m, CH-2,7-Bth), 7.94–7.99 (1H, m, CH-4-Bth), 8.25–8.40 (3H, br s, NH$_3$Cl); δ_C (100 MHz, $CDCl_3$): 30.7 (CH$_2$, α-Bth), 38.2 (CH$_2$, α-Ph), 51.5 (CHNH$_3$Cl), 121.5 (C7-Bth), 123.0 (C4-Bth), 124.1 (C5-Bth), 124.4 (C4-Ph), 125.3 (C2-Bth), 126.8 (C6-Bth), 128.6 (C3, C5-Ph), 129.4 (C2, C6-Ph), 130.6 (C3-Bth), 136.4 (C1-Ph), 138.4 (C9-Bth), 139.8 (C8-Bth).

4.5.4. (2*S*)-4-Methyl-1-(3-thienyl)-2-pentanamine hydrochloride 26. White solid, yield 0.24 g (54%); mp 223–224°C; [Found: C, 54.73; H, 8.32. $C_{10}H_{18}ClNS$ requires: C, 54.65; H, 8.26%]; δ_H (400 MHz, $CDCl_3$): 0.77 (3H, d, $J=6.5$ Hz, CH$_2$CH(CH$_3$)$_2$), 0.81 (3H, d, $J=6.5$ Hz, CH$_2$CH(CH$_3$)$_2$), 1.19–1.27 (1H, m, CH$_2$CH(CH$_3$)$_2$), 1.38–1.47 (1H, m, CH$_2$CH(CH$_3$)$_2$), 1.66–1.75 (1H, m, CH$_2$CH(CH$_3$)$_2$), 2.83 (1H, dd, $J=14.3$ Hz, $J=8.0$ Hz, CH$_2$-α-Th), 2.98 (1H, dd, $J=14.3$ Hz, $J=5.2$ Hz, CH$_2$-α-Th), 3.32–3.37 (1H, m, CHNH$_3$Cl), 7.04 (1H, d, $J=5.1$ Hz, CH-4Th), 7.32 (1H, s, CH-2Th), 7.41 (1H, d, $J=5.1$ Hz, CH-5Th), 8.08–8.25 (3H, br s, NH$_3$Cl); δ_C (100 MHz, $CDCl_3$): 21.8, 22.6 (2C, CH$_2$CH(CH$_3$)$_2$), 23.4 (CH$_2$CH(CH$_3$)$_2$), 33.2 (CH$_2$, α-Th), 41.0 (CH$_2$CH(CH$_3$)$_2$), 49.3 (CHNH$_3$Cl), 122.6 (C2-Th), 126.3 (C5-Th), 128.6 (C4-Th), 136.6 (C3-Th).

4.5.5. (2*S*)-1-(1-Benzothien-3-yl)-4-methyl-2-pentanamine hydrochloride 27. White solid, yield 0.39 g (72%); mp 258–259°C; [Found: C, 62.45; H, 7.57. $C_{14}H_{20}ClNS$ requires: C, 62.32; H, 7.47%]; δ_H (400 MHz, $CDCl_3$): 0.76 (3H, d, $J=6.5$ Hz, CH$_2$CH(CH$_3$)$_2$), 0.80 (3H, d, $J=6.5$ Hz, CH$_2$CH(CH$_3$)$_2$), 1.17–1.26 (1H, m, CH$_2$CH(CH$_3$)$_2$), 1.38–1.47 (1H, m, CH$_2$CH(CH$_3$)$_2$), 1.65–1.75 (1H, m, CH$_2$CH(CH$_3$)$_2$), 2.83 (1H, dd, $J=14.1$ Hz, $J=8.0$ Hz, CH$_2$-α-Bth), 2.98 (1H, dd, $J=14.1$ Hz, $J=5.2$ Hz, CH$_2$-α-Bth), 3.31–3.37 (1H, m, CHNH$_3$Cl), 7.37–7.44 (2H, m, CH-5,6-Bth), 7.62 (1H, s, CH-2-Bth), 7.93–8.01 (2H, m, CH-4,7-Bth), 8.07–8.21 (3H, br s, NH$_3$Cl); δ_C (100 MHz, $CDCl_3$): 21.8, 22.6 (2C, CH$_2$CH(CH$_3$)$_2$), 23.4 (CH$_2$CH(CH$_3$)$_2$), 31.7 (CH$_2$, α-Bth), 41.0 (CH$_2$CH(CH$_3$)$_2$), 49.8 (CHNH$_3$Cl), 121.5 (C7-Bth), 123.0 (C4-Bth), 124.1 (C5-Bth), 124.3 (C2-

Bth), 125.9 (C6-Bth), 130.8 (C3-Bth), 138.4 (C9-Bth), 139.8 (C8-Bth).

4.5.6. (2*S*)-4-Methyl-1-phenyl-2-pentanamine hydrochloride 28. White solid, yield 0.24 g (57%); mp 260–261°C; [Found: C, 67.54; H, 9.49. $C_{12}H_{20}ClN$ requires: C, 67.43; H, 9.43%]; δ_H (400 MHz, $CDCl_3$): 0.73 (3H, d, $J=6.5$ Hz, $CH_2CH(CH_3)_2$), 0.79 (3H, d, $J=6.5$ Hz, $CH_2CH(CH_3)_2$), 1.16–1.25 (1H, m, $CH_2CH(CH_3)_2$), 1.38–1.47 (1H, m, $CH_2CH(CH_3)_2$), 1.65–1.75 (1H, m, $CH_2CH(CH_3)_2$), 2.73 (1H, dd, $J=13.7$ Hz, $J=8.1$ Hz, CH_2Ph), 3.01 (1H, dd, $J=13.7$ Hz, $J=5.3$ Hz, CH_2Ph), 3.30–3.37 (1H, m, $CHNH_3Cl$), 7.22–7.37 (5H, m, CH-Ph), 8.06–8.14 (3H, br s, NH_3Cl); δ_C (100 MHz, $CDCl_3$): 21.8, 22.7 (2C, $CH_2CH(CH_3)_2$), 23.4 ($CH_2CH(CH_3)_2$), 38.4 (CH_2Ph), 40.9 ($CH_2CH(CH_3)_2$), 50.2 ($CHNH_3Cl$), 126.8 (C4-Ph), 128.6 (C2, C6-Ph), 129.3 (C3, C5-Ph), 136.6 (C1-Ph).

4.5.7. (2*S*)-1-(1-Benzothien-3-yl)-2-propanamine hydrochloride 29. White solid, yield 0.31 g (69%); mp 197–198°C; [Found: C, 58.14; H, 6.21. $C_{11}H_{14}ClNS$ requires: C, 58.01; H, 6.20%]; δ_H (400 MHz, $CDCl_3$): 1.18 (3H, d, $J=6.4$ Hz, $CHCH_3$), 2.89 (1H, dd, $J=14.0$ Hz, $J=9.3$ Hz, CH_2-α-Bth), 3.33 (1H, dd, $J=14.0$ Hz, $J=5.2$ Hz, CH_2-α-Bth), 3.43–3.51 (1H, m, $CHNH_3Cl$), 7.35–7.44 (2H, m, CH-5,6-Bth), 7.60 (1H, s, CH-2-Bth), 7.95–7.99 (2H, m, CH-4,7-Bth), 8.33–8.41 (3H, br s, NH_3Cl); δ_C (100 MHz, $CDCl_3$): 17.8 (CH_3), 32.8 (CH_2), 46.5 ($CHNH_3Cl$), 121.8 (C7-Bth), 122.9 (C4-Bth), 124.1 (C5-Bth), 124.3 (C2-Bth), 124.8 (C6-Bth), 131.2 (C3-Bth), 138.5 (C9-Bth), 139.7 (C8-Bth).

4.5.8. (2*S*)-1-(1-Naphtyl)-2-propanamine hydrochloride 30. White solid, yield 0.24 g (54%); mp 230–231°C; [Found: C, 70.59; H, 7.34. $C_{13}H_{16}ClN$ requires: C, 70.42; H, 7.27%]; δ_H (400 MHz, $CDCl_3$): 1.13 (3H, d, $J=6.7$ Hz, $CHCH_3$), 3.09 (1H, dd, $J=13.3$ Hz, $J=9.8$ Hz, CH_2-α-Npht), 3.40–3.51 (1H, m, $CHNH_3Cl$), 3.65 (1H, dd, $J=13.3$ Hz, $J=4.7$ Hz, CH_2-α-Npht), 7.36–7.47 (2H, m, CH-2,3-Npht), 7.50–7.59 (2H, m, CH-6,7-Npht), 7.83 (1H, d, $J=8.1$ Hz, CH-8-Npht), 7.93 (1H, d, $J=7.8$ Hz, CH-5-Npht), 8.24 (1H, d, $J=8.3$ Hz, CH-4-Npht), 8.32–8.51 (3H, br s, NH_3Cl); δ_C (100 MHz, $CDCl_3$): 17.7 (CH_3), 37.2 (CH_2), 47.3 ($CHNH_3Cl$), 123.8 (C6-Npht), 125.6 (C5-Npht), 125.8 (C7-Npht), 126.3 (C4-Npht), 127.6 (C3-Npht), 127.9 (C2-Npht), 128.7 (C8-Npht), 131.5 (C9-Npht), 133.0 (C1-Npht), 123.6 (C10-Npht).

4.5.9. (2*R*)-3-Methyl-1-(2-thienyl)-2-butanamine hydrochloride 31. White solid, yield 0.17 g (42%); mp 124–125°C; [Found: C, 52.63; H, 7.91. $C_9H_{16}ClNS$ requires: C, 52.54; H, 7.84%]; δ_H (400 MHz, $CDCl_3$): 0.91 (3H, d, $J=7.0$ Hz, $CH(CH_3)_2$), 0.97 (3H, d, $J=7.0$ Hz, $CH(CH_3)_2$), 1.82–1.90 (1H, m, $CH(CH_3)_2$), 3.05–3.12 (2H, m, CH_2-α-Th), 3.15–3.21 (1H, m, $CHNH_3Cl$), 6.99 (1H, dd, $J=5.0$ Hz, $J=3.5$ Hz, CH-4Th), 7.03 (1H, dd, $J=3.5$ Hz, $J=1.1$ Hz, CH-3Th), 7.41 (1H, dd, $J=5.0$ Hz, $J=1.1$ Hz, CH-5Th), 8.09–8.22 (3H, br s, NH_3Cl); δ_C (100 MHz, $CDCl_3$): 16.9, 18.3 (2C, $CH(CH_3)_2$), 28.6 ($CH(CH_3)_2$), 29.6 (CH_2-α-Th), 57.1 ($CHNH_3Cl$), 125.0 (C5-Th), 126.9 (C3-Th), 127.2 (C4-Th), 138.4 (C2-Th).

4.5.10. (2*R*)-3-Methyl-1-phenyl-2-butanamine hydrochloride 32. White solid, yield 0.22 g (56%); mp 169–170°C; [Found: C, 66.22; H, 9.14. $C_{11}H_{18}ClN$ requires: C, 66.15; H, 9.08%]; δ_H (400 MHz, $CDCl_3$): 0.90 (3H, d, $J=6.9$ Hz, $CH(CH_3)_2$), 0.95 (3H, d, $J=6.9$ Hz, $CH(CH_3)_2$), 1.77–1.86 (1H, m, $CH(CH_3)_2$), 2.80 (1H, dd, $J=13.9$ Hz, $J=7.7$ Hz, CH_2Ph), 2.94 (1H, dd, $J=13.9$ Hz, $J=6.5$ Hz, CH_2Ph), 3.18–3.25 (1H, m, $CHNH_3Cl$), 7.20–7.35 (5H, m, CH-Ph), 8.15–8.27 (3H, br s, NH_3Cl); δ_C (100 MHz, $CDCl_3$): 16.9, 18.3 (2C, $CH(CH_3)_2$), 28.6 ($CH(CH_3)_2$), 35.2 (CH_2Ph), 57.2 ($CHNH_3Cl$), 126.6 (C4-Ph), 128.5 (C2, C6-Ph), 129.2 (C3, C5-Ph), 137.2 (C1-Ph).

4.6. *N*-Alkylation of β-aryl(heteroaryl)alkylamines

4.6.1. *N*-[(2*S*)-(1-Benzothien-3-yl)-1-methylethyl]-*N*,4-dimethylbenzenesulfonamide 33. A solution of *N*-[(1*S*)-2-(1-benzothien-3-yl)-1-methylethyl]-4-methylbenzenesulfamide **10** (1 g, 2.9 mmol) in THF (10 mL) in a flame-dried flask under Ar was cooled to −78°C. A solution of BuLi (*c* 1.6 M in hexane, 1.9 mL, 3.1 mmol) was added dropwise. The suspension was stirred for 15 min at −78°C and MeI (0.2 mL, 3.1 mmol) was added and then stirred at rt for 1 h, after which time it was partitioned between NH_4Cl and ether, the aqueous layer extracted with ether (3×15 mL), the organic layers dried (Na_2SO_4), filtered and the solvent removed in vacuo to leave brown oil which was purified by chromatography on silica gel with hexane–dichloromethane (1:1) as eluent. White solid, yield 0.88 g (85%); mp 100–101°C; [Found: C, 63.23; H, 5.71. $C_{19}H_{21}NO_2S_2$ requires: C, 63.48; H, 5.89%]; δ_H (400 MHz, $CDCl_3$): 0.96 (3H, d, $J=6.7$ Hz, $CHCH_3$), 2.35 (3H, s, CH_3-Ts), 2.80 (3H, s, CH_3NTs), 2.87 (1H, dd, $J=14.1$ Hz, $J=8.5$ Hz, CH_2-α-Bth), 3.03 (1H, dd, $J=14.1$ Hz, $J=6.1$ Hz, CH_2-α-Bth), 4.38–4.47 (1H, m, CHNTs), 7.12 (1H, s, CH-2-Bth), 7.15 (2H, d, $J=8.2$ Hz, CH-2,6-Ts), 7.30–7.39 (2H, m, CH-5,6-Bth), 7.55 (2H, d, $J=8.2$ Hz, CH-3,5-Ts), 7.72 (1H, d, $J=7.8$ Hz, CH-7-Bth), 7.72 (1H, d, $J=7.6$ Hz, CH-4-Bth); δ_C (100 MHz, $CDCl_3$): 16.9 ($CHCH_3$), 21.4 (CH_3, Ts), 27.7 (CH_3NTs), 34.2 (CH_2), 52.1 (CHNTs), 121.6 (C4-Bth), 122.8 (C7-Bth), 123.3 (C2-Bth), 124.0 (C6-Bth), 124.2 (C5-Bth), 126.7 (C2, C6-Ts), 129.5 (C3, C5-Ts), 132.5 (C3-Bth), 136.8 (C1-Ts), 138.6 (C9-Bth), 140.4 (C8-Bth), 142.9 (C4-Ts).

4.6.2. (2*S*)-1-(1-Benzothien-3-yl)-*N*-methyl-2-propanamine hydrochloride 34. Compound **34** was prepared by following the general procedure for desulfonylation described above. White solid, yield 0.42 g (87%); mp 167–168°C; [Found: C, 59.65; H, 6.73. $C_{12}H_{16}ClNS$ requires: C, 59.61; H, 6.67%]; δ_H (400 MHz, $CDCl_3$): 1.15 (3H, d, $J=6.3$ Hz, $CHCH_3$), 2.51–2.62 (4H, m, $NH_2(CH_3)Cl$, CH_2-α-Bth), 3.02 (1H, dd, $J=14.7$ Hz, $J=11.1$ Hz, CH_2-α-Bth), 3.45–3.49 (1H, m, $CHNH_2(CH_3)Cl$), 7.34–7.43 (2H, m, CH-5,6-Bth), 7.61 (1H, s, CH-2-Bth), 7.95–8.01 (2H, m, CH-4,7-Bth), 9.30–9.55 (3H, br s, $NH_2(CH_3)Cl$); δ_C (100 MHz, $CDCl_3$): 15.1 ($CHCH_3$), 29.4 ($NH_2(CH_3)Cl$), 31.3 (CH_2), 53.5 ($CHNH_2(CH_3)Cl$), 122.0 (C4-Bth), 123.0

(C7-Bth), 123.9 (C2-Bth), 124.2 (C6-Bth), 124.4 (C5-Bth), 125.0 (C3-Bth), 138.4 (C9-Bth), 139.7 (C8-Bth).

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