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# Aza-Payne rearrangement of α,α-disubstituted-aziridinemethanols

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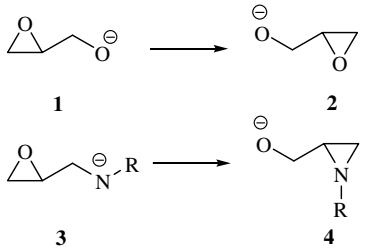
**Abstract**—The aza-Payne rearrangement of activated *N*-Ts-α,α-disubstituted-aziridinemethanols, induced by NaOH in the mixed solvent $^{t}$BuOH/$H_2O$/THF (4:5:1) or NaH in a mixed solvent of THF/HMPA (10:1), as well as some *N*-Boc-α,α-disubstituted-aziridinemethanols with the latter reagent/solvent combination, provides the corresponding epoxides in up to 99% yield.

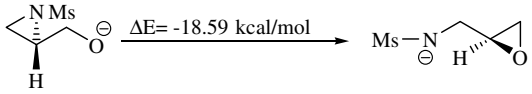

## 1. Introduction

Owing to the utility of aziridines as chiral building blocks[1] and their biological activity,[2] the aza-Payne rearrangement of aziridinemethanols has been of much interest especially as a synthetic route to bioactive compounds.[3]

The Payne rearrangement, as exemplified by the conversion of **1** to **2** in Scheme 1, has been the object of much study[4] as has been the 'aza-Payne'[5] variant (conversion of **3** to **4** as shown in Scheme 1). Clean intramolecular $S_N2$ substitution is observed.[6] The aza-Payne reaction is reversible[5a] and the epoxide can be favored over the aziridine if the nitrogen anion is well stabilized. For example, from ab initio calculations, the energy minimum of aza anion **6** was predicted to be 18.6 kcal/mol lower than that of oxa anion **5**[5a] (Scheme 2).



**Scheme 1.**



**Scheme 2.**

To induce the aza-Payne rearrangement of **3**, where R is either H or alkyl, $^{n}$BuLi can be used for anion formation in THF, but reasonable yields are obtained only when a Lewis acid ($AlMe_3$) is added.[7] As predicted from the calculated relative stabilities of **5** and **6**, the reaction becomes easier and requires less drastic reagents when proceeding in the other direction (in general terms from **4** to **3** in Scheme 2), providing the aziridine nitrogen is activated with a strongly electron withdrawing group. For example, tosylation of the nitrogen atom as illustrated for **7a**, leads to excellent yields (65–99%) of **7b** on rearrangement (Scheme 3). The use of mesyl as an activating group is also effective: rearrangement of **8a** under standard Payne conditions (potassium hydride in THF–HMPA as solvent) affords **8b** in good (80%) yield.[5a] However, the protecting groups Boc and trityl, **9a** and **9b**, on the nitrogen atom are reported to be not effective in promoting rearrangement under analogous conditions (Scheme 3).[8]

The role of the substituents in aza-Payne rearrangements is quite important. *N*-Tosyl-oxiranemethyl amines α,α-disubstituted adjacent to the nitrogen-bearing carbon are

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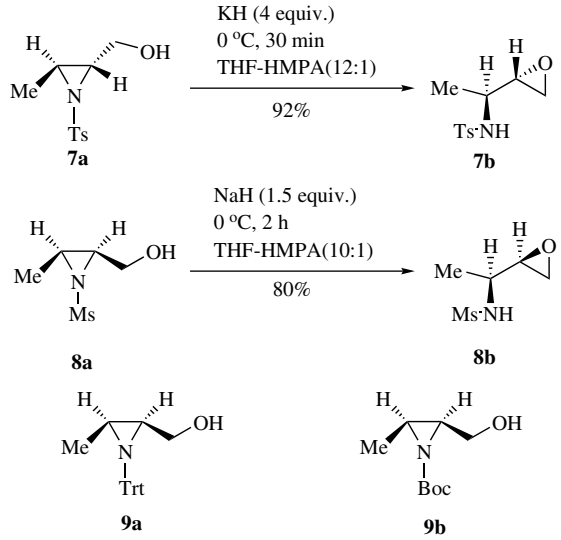
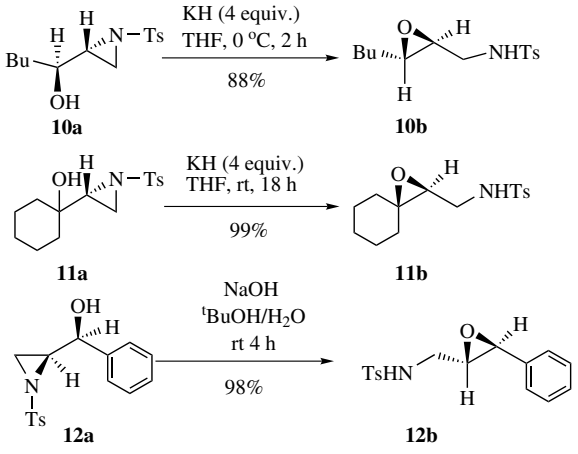



**Scheme 3.**

reported to rearrange (5% aqueous NaOH at 100 °C) to *N*-tosyl-aziridines (**3** to **4** in Scheme 1). On the other hand, aziridinemethanols having a primary (**7a** and **8a**) or secondary hydroxymethyl group (**10a**) all afford high yields of epoxides as rearrangement products (**4** to **3** in Scheme 1) as illustrated with the examples shown in Scheme 4. The potential reversibility of aza-Payne rearrangements has been pointed out.[5a] Aziridinemethanol **11a**, possessing a tertiary hydroxyl group, also rearranged slowly in THF in the presence of KH to give solely epoxy sulfonamide **11b**.[5a] We have also reported that **12a**, which bears a phenyl adjacent to the hydroxyl group, rearranges smoothly to **12b**.[9]




**Scheme 4.**

Herein we examine the scope and potential of the aza-Payne rearrangement more closely for the specific case of enantiomerically pure α,α-disubstituted-aziridinemethanols, that is, examples where the oxygen-bearing carbon is α,α-disubstituted in anticipation that this fully substituted carbon would end up in the three-membered ring, an epoxide in contrast to the literature.[8]

## 2. Results and discussion

### 2.1. The aza-Payne rearrangement of *N*-tosyl α,α-disubstituted-aziridinemethanols

The reaction of methyl *N*-tritylaziridine-2-carboxylates **13** and **14**, readily obtained from L-serine and L-threonine,[10] with a Grignard reagent in THF at room temperature, followed by removal of the trityl group in situ with $H_2SO_4$ in MeOH/$H_2O$ solvent,[11] provided aziridinemethanols **15a–d** and **16a–d** in 69–90% yield. Tosylation of aziridinemethanols **15a–d** and **16a–d** led to **17a–d** and **18a–c** in 87–96% yield. Tosylation of **16d** failed to provide an isolable product. The subsequent aza-Payne rearrangement reactions of these tosylates to epoxy sulfonamides **19a–d** and **20a–c** are shown in Scheme 5 and the results are summarized in Table 1.

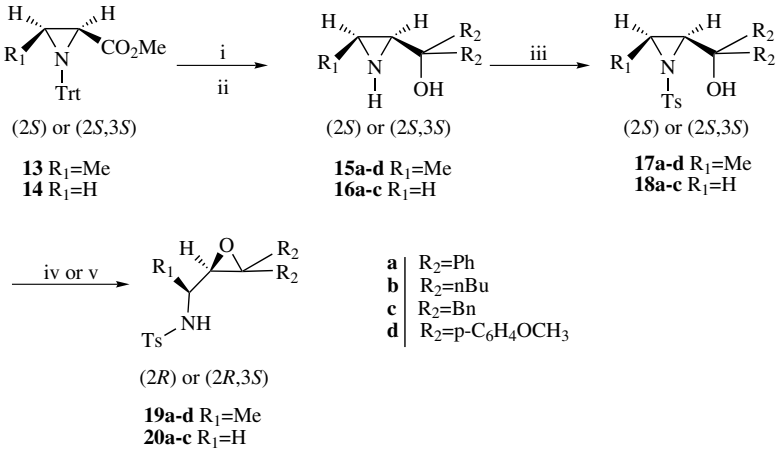
The rearranged products were obtained in high isolated yields. HPLC analysis revealed single peaks in all cases indicative of diastereomeric purity **18a–c**. On the basis of extensive literature precedents,[5a] all products are assumed to be the result of $S_N2$ substitution and are enantiomerically pure. There are significant differences in conversion times for the various alcohols with the use of NaOH as base and phenyl substituted **17a** and **18a** seem to be most reactive. However, when using a stronger base, NaH, the differences in conversion times are far less. It does appear that *n*-butyl substituted compounds **17b** and **18b** do react in general somewhat more slowly.

Disubstitution on the hydroxy-bearing carbon of the *N*-tosyl aziridines studied here clearly promotes rearrangement to the corresponding epoxide (**4** to **3** in Scheme 1). The α,α-disubstitution will, of course, lead to an increase in basicity of the alkoxide as anticipated from inductive effects and ion pairing, as has previously been discussed.[6]

### 2.2. The aza-Payne rearrangement of *N*-Boc α,α-disubstituted-aziridinemethanols

To determine whether *N*-Boc protected aziridinemethanols (Boc should stabilize the nitrogen anion by resonance) would give analogous results, *N*-Boc aziridinemethanols **21** and **22** were synthesized in high yield (Scheme 6). *N*-Boc aziridinemethanol **21a** rearranged to epoxy sulfonamide **23a** in 70% yield after stirring for 24 h with NaOH in mixed $^t$BuOH/$H_2O$/THF (4:5:1). The yield increased to 96% on reaction with NaH in THF/HMPA (10:1) for a period of 4 h. In a similar manner, *N*-Boc aziridine **21d** afforded a low yield (30%) of aza-Payne rearrangement product **23d** with the NaOH reaction system and a higher yield (80%) with NaH reaction system. The other *N*-Boc aziridines **21b**, **21c**, **22a**, **22b**, **22c** provided no rearrangement products with either NaOH or NaH and the starting materials were recovered (Table 2).

A methyl group on the C-3 position of aziridine **21a** appears to favor the rearrangement of *N*-Boc aziridinemethanols (compare entries 1 and 5 in Table 2). This is also in line with our failure to prepare **18d** and **22d** (Scheme 7).




**Scheme 5.** Reagents and conditions: (i) $R_2Br$, Mg, THF; (ii) $MeOH/H_2O/H_2SO_4$ (60:8:3); (iii) TsCl (1 equiv), Py; (iv) 0.28 N NaOH in $^tBuOH/H_2O$/THF (4:5:1) rt; (v) NaH in THF/HMPA (10:1) rt.

**Table 1.** Aza-Payne rearrangement of *N*-tosyl-aziridinemethanols **17** and **18** to epoxy sulfonamides **19** and **20**

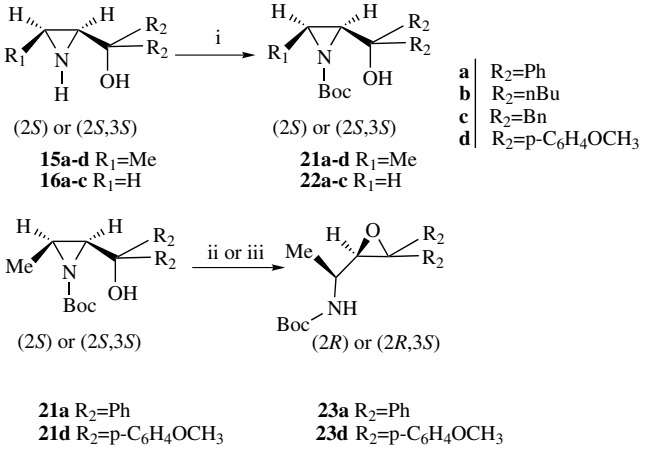
| Entry | Starting material | NaOH[a] | | NaH[b] | | Product |
|---|---|---|---|---|---|---|
| | | Time (h) | Yield[c] (%) | Time | Yield[d] (%) | |
| 1 | **17a** | 1 | 96 | 5 min | 99 | **19a** |
| 2 | **17b** | 8 | 86 | 1 h | 90 | **19b** |
| 3 | **17c** | 2 | 90 | 30 min | 96 | **19c** |
| 4 | **17d** | 24 | 97 | 2 h | 96 | **19d** |
| 5 | **18a** | 1 | 95 | 10 min | 98 | **20a** |
| 6 | **18b** | 8 | 83 | 1 h | 95 | **20b** |
| 7 | **18c** | 10 | 89 | 1 h | 96 | **20c** |

[a] Solvent: $^tBuOH/H_2O$/THF (4:5:1).
[b] Solvent: THF/HMPA (10:1).
[c] Isolated yield.
[d] Determined by HPLC.

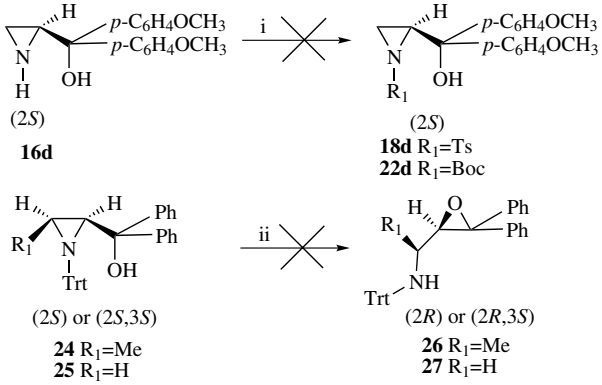
**Table 2.** Aza-Payne rearrangement of *N*-Boc-aziridinemethanol **21** to epoxy sulfonamide **23**

| Entry | Starting material | NaOH[a] | | NaH[b] | | Product |
|---|---|---|---|---|---|---|
| | | Time (h) | Yield (%) | Time (h) | Yield (%) | |
| 1 | **21a** | 24 | 70[d] | 4 | 96[c] | **23a** |
| 2 | **21b** | 24 | —[e] | 4 | —[e] | |
| 3 | **21c** | 24 | —[e] | 4 | —[e] | |
| 4 | **21d** | 24 | 30[d] | 4 | 80[c] | **23d** |
| 5 | **22a** | 24 | —[e] | 4 | —[e] | |
| 6 | **22b** | 24 | —[e] | 4 | —[e] | |
| 7 | **22c** | 24 | —[e] | 4 | —[e] | |

[a] Solvent: $^tBuOH/H_2O$/THF (4:5:1).
[b] Solvent: THF/HMPA (10:1).
[c] Isolated yield.
[d] Detected by HPLC.
[e] No reaction.




**Scheme 6.** Reagents and conditions: (i) $(Boc)_2O$, $NEt_3$, THF; (ii) 0.28 M NaOH in $^tBuOH/H_2O$/THF (4:5:1); (iii) NaH in THF/HMPA (10:1).




**Scheme 7.** Reagents and conditions: (i) $(Boc)_2O$, $NEt_3$, THF or TsCl (1 equiv), Py; (ii) 0.28 M NaOH in $^tBuOH/H_2O$/THF (4:5:1) or NaH in THF/HMPA (10:1).

Not unexpectedly, aziridinemethanols **24** and **25** do not undergo the rearrangement.

## 3. Conclusion

In conclusion, the effective aza-Payne rearrangement of *N*-Ts aziridinemethanols and *N*-Boc aziridinemethanols

provides a potential synthesis of functional amino alcohol. The substituted groups (on C-3 position and hydroxy-bearing carbon) of aziridinemethanols clearly effected the rearrangement.

## 4. Experimental

### 4.1. General

$^1$H NMR and $^{13}$C NMR spectra were obtained at a Varian Mercy 300 MHz spectrometer. IR spectra were recorded on a Perkin Elmer 983 spectrometer. MS spectra were recorded on a Finnigan-LC Qadvantage spectrometer (ESI), and the Optical rotations were measured at 20 °C using the D-line by means of a Perkin–Elmer 343 plus polarimeter. Melting points were determined on a XT-4 apparatus (uncorrected). Elemental analyses were carried out on a VarioEL III(German) instrument. Silica gel was used for analytical and flash chromatography. Organic extracts were dried over $MgSO_4$ and filtered before removal of the solvent. All reactions employing dry solvents were run under nitrogen. THF was dried (sodium/benzophenone) and distilled.

### 4.2. General procedure for the synthesis of 15 and 16

To a stirred suspension of magnesium turnings (2.40 g, 100 mmol, 4.0 equiv) in THF (100 mL) was gradually added bromide (100 mmol, 4.0 equiv). After heating the Grignard reagent for 2 h, aziridinecarboxylate **13** or **14** (25.0 mmol) in THF (20 mL) was added dropwise over a period of 20 min. The reaction was monitored with TLC (hexane–ethyl acetate, 3:1). After 3 h the reaction was quenched with saturated aqueous $NH_4Cl$ (60 mL). The crude reaction mixture was extracted with ethyl acetate ($3 \times 100$ mL) and the combined organic layers dried over $MgSO_4$ and concentrated. The crude product was dissolved in a mixture of MeOH, water and concentrated $H_2SO_4$ (60:8:3) (150 mL) by sonication for 5 min. After stirring for 24 h and subsequent addition of water (100 mL) under ice conditions, the solution was basified with 30% NaOH to pH = 10. After the mixture was extracted with ethyl acetate ($3 \times 100$ mL), the organic phase was washed with satd $NaHCO_3$ ($3 \times 50$ mL), satd NaCl ($3 \times 50$ mL) dried over $MgSO_4$, and concentrated in vacuo. The crude was purified by flash column chromatography to yield **15** or **16**.

**4.2.1. (2*S*,3*S*)-3-Methylaziridin-2-yl(diphenyl)methanol 15a.** Prepared as described in the general procedure from aziridinecarboxylate **13** (8.93 g, 25.0 mmol) and bromobenzene (10.5 mL, 100 mmol, 4.0 equiv) to afford **15a** (4.84 g, 81%). Purified by flash column chromatography (hexane–ethyl acetate, 5:1). White solid. Mp 91 °C; $[\alpha]_D^{20} = +80.0$ (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta$ 1.08 (d, $CH_3$, 3H, $J = 5.7$), 2.40 (m, C(3)H, 1H), 2.95 (d, C(2)H, 1H, $J = 6.0$), 7.17–7.54 (m, Ar, 10H); IR ($\nu_{max}$/cm$^{-1}$): 3444, 3256, 3087, 3055, 3021, 2986, 2958, 2928, 1599, 1492, 1447, 1425, 1360, 1172, 1061.

**4.2.2. (2*S*,3*S*)-3-Methylaziridin-2-yl(dibutyl)methanol 15b.** Prepared as described in the general procedure from aziridinecarboxylate **13** (8.93 g, 25.0 mmol) and 1-bromobutane (10.77 mL, 100 mmol, 4.0 equiv) to afford **15b** (3.88 g, 78%). Purified by flash column chromatography (hexane–ethyl acetate, 2:1). Colorless oil. $[\alpha]_D^{20} = -10.5$ (*c* 0.5, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta$ 0.91–0.92 (m, $CH_3$, 6H), 1.31–1.54 (m, ($CH_2$,$CH_3$), 15H), 1.98 (m, C(3)H, 1H), 2.10 (m, C(2)H, 1H); IR ($\nu_{max}$/cm$^{-1}$): 3303, 2957, 2862, 1467, 1416, 1379, 1259, 1144, 998, 846.

**4.2.3. (2*S*,3*S*)-3-Methylaziridin-2-yl(dibenzyl)methanol 15c.** Prepared as described in the general procedure from aziridinecarboxylate **13** (8.93 g, 25.0 mmol) and benzyl bromide (11.96 mL, 100 mmol, 4.0 equiv) to afford **15c** (5.00 g, 75%). Purified by flash column chromatography (hexane–ethyl acetate, 3:1). White solid. Mp 50–51 °C; $[\alpha]_D^{20} = -23.2$ (*c* 0.5, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta$ 1.24 (d, $CH_3$, 3H, $J = 5.1$), 2.06–2.10 (m, (C(3)H, C(2)H), 2H), 2.93 (m, $CH_2$(Bn), 2H), 3.08 (m, $CH_2$(Bn), 2H), 7.31–7.45 (m, Ar, 10H); IR ($\nu_{max}$/cm$^{-1}$): 3314, 3083, 3060, 3027, 2924, 1602, 1495, 1454, 1417, 1353, 1301, 1087, 1047, 844.

**4.2.4. (2*S*,3*S*)-3-Methylaziridin-2-yl(bis(4-methoxyphenyl))-methanol 15d.** Prepared as described in the general procedure from aziridinecarboxylate **13** (8.93 g, 25.0 mmol) and 1-bromo-4-methoxybenzene (12.52 mL, 100 mmol, 4.0 equiv) to afford **15d** (5.23 g, 70%). Purified by flash column chromatography (hexane–ethyl acetate, 3:1). White solid. Mp 138 °C; $[\alpha]_D^{20} = +58.7$ (*c* 0.5, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta$ 1.08 (d, $CH_3$, 3H, $J = 6.0$), 2.33 (m, C(3)H, 1H), 2.83 (d, C(2)H, 1H, $J = 6.3$), 3.76 (s, $OCH_3$, 3H), 3.80 (s, $OCH_3$, 3H), 6.79–7.42 (m, Ar, 8H); IR ($\nu_{max}$/cm$^{-1}$): 3324, 3000, 2956, 2930, 2837, 1607, 1582, 1509, 1461, 1420, 1295, 1245, 1172, 1109, 1033, 1003, 984.

**4.2.5. (2*S*)-Aziridin-2-yl(diphenyl)methanol 16a.** Prepared as described in the general procedure from aziridinecarboxylate **14** (8.59 g, 25.0 mmol) and bromobenzene (10.5 mL, 100 mmol, 4.0 equiv) to afford **16a** (5.06 g, 90%). Purified by flash column chromatography (hexane–ethyl acetate, 5:1). White solid. Mp 155–157 °C; $[\alpha]_D^{20} = -22.6$ (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta$ 1.73 (d, C(3)H, 1H, $J = 3.3$), 1.82 (d, C(3)H, 1H, $J = 3.6$), 2.87 (m, C(2)H, 1H), 7.22–7.45 (m, Ar, 10H); IR ($\nu_{max}$/cm$^{-1}$): 3309, 3000, 1599, 1488, 1425, 1363, 1312, 1271, 1242, 1217, 1199, 1179, 1106, 1082.

**4.2.6. (2*S*)-Aziridin-2-yl(dibutyl)methanol 16b.** Prepared as described in the general procedure from aziridinecarboxylate **14** (8.59 g, 25.0 mmol) and 1-bromobutane (10.77 mL, 100 mmol, 4.0 equiv) to afford **16b** (3.19 g, 69%). Purified by flash column chromatography (hexane–ethyl acetate, 2:1). Colorless oil. $[\alpha]_D^{20} = -21.4$ (*c* 10.0, THF); $^1$H NMR ($CDCl_3$): $\delta$ 0.84 (m, $CH_3$, 6H), 1.26–1.44 (m, $CH_2$, 12H), 1.53 (m, C(3)$H_2$, 2H), 1.92 (m, C(2)H, 1H); IR ($\nu_{max}$/cm$^{-1}$): 3472, 3061, 3025, 1597, 1490, 1445, 1331, 1180, 1158, 1031, 1011, 932, 913, 891.

**4.2.7. (2*S*)-Aziridin-2-yl(dibenzyl)methanol 16c.** Prepared as described in the general procedure from aziridinecarboxylate **14** (8.59 g, 25.0 mmol) and benzyl bromide (11.96 mL, 100 mmol, 4.0 equiv) to afford **16c** (4.81 g, 76%). Purified by flash column chromatography

(hexane–ethyl acetate, 2:1). White solid. Mp 75–76 °C; $[\alpha]_D^{20} = -28.4$ (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 1.16 (s, C(3), 1H), 1.48 (s, C(3), 1H), 2.06 (s, C(2), 1H), 2.87 (d, $CH_2$(Bn), 4H), 7.23–7.45 (s, Ar, 10H); IR ($\nu_{max}$/$cm^{-1}$): 3261, 3057, 3030, 3004, 2946, 2912, 1602, 1496, 1452, 1311, 1266, 1192, 1099, 1082, 1060, 1050.

**4.2.8. (2*S*)-Aziridin-2-yl(bis(4-methoxyphenyl))methanol 16d.** Prepared as described in the general procedure from aziridinecarboxylate **14** (8.59 g, 25.0 mmol) and 1-bromo-4-methoxybenzene (12.52 mL, 100 mmol, 4.0 equiv) to afford **16d** (5.77 g, 81%). Purified by flash column chromatography (hexane–ethyl acetate, 2:1). Colorless oil. $[\alpha]_D^{20} = +67.0$ (*c* 9.0, THF); $^1H$ NMR ($CDCl_3$): $\delta$ 2.79 (m, C(3)$H_2$, 1H), 3.09 (m, C(3)$H_2$, 1H), 3.77 (s, $OCH_3$, 3H), 3.80 (s, $OCH_3$, 3H), 4.78 (m, C(2)H, 1H), 6.86–7.61 (m, Ar, 8H); IR ($\nu_{max}$/$cm^{-1}$): 3338, 2939, 2839, 1668, 1599, 1574, 1510, 1489, 1449, 1420, 1303, 1253, 1168, 1111, 1032, 832.

### 4.3. General procedure for the synthesis of 17 and 18

To a stirred solution of aziridinemethanol **15** or **16** (10.0 mmol) in pyridine (20 mL) was gradually added 4-methylbenzene-1-sulfonyl chloride (1.91 g, 10.0 mmol) in THF (5 mL) at 0 °C, and then the mixture allowed to warm to rt and the stirring continued for 24 h. The reaction was quenched with 50 mL of 5% HCl at 0 °C with stirring. The mixture was extracted with ethyl acetate and the extract washed successively with 5% HCl, satd $CuSO_4$ ($3 \times 50$ mL), satd $NaHCO_3$ ($3 \times 50$ mL), and brine ($3 \times 50$ mL), and dried over $MgSO_4$. The usual workup was followed by flash chromatography over silica gel with petroleum ether–ethyl acetate (5:1) to yield **17** or **18**.

**4.3.1. (2*S*,3*S*)-(3-Methyl-1-tosylaziridin-2-yl)diphenylmethanol 17a.** Prepared as described in the general procedure from aziridinemethanol **15a** (2.39 g, 10.0 mmol) to afford **17a** (3.74 g, 95%) as a crystalline mass. Mp 175 °C; $[\alpha]_D^{20} = +22.1$ (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 1.28 (d, $CH_3$, 3H, $J = 5.7$), 2.40 (s, $CH_3$, 3H), 3.15 (m, C(3)H, 1H), 3.69 (d, C(2)H, 1H, $J = 6.9$), 7.12–7.57 (m, Ar, 14H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 12.5 ($CH_3$), 21.9 ($CH_3$), 40.5 (C-3), 52.4 (C-2), 74.7 (CHOH), 125.8 (2×, =CH), 126.1 (2×, =CH), 127.1 (1×, =CH), 127.7 (1×, =CH), 128.0 (2×, =CH), 128.4 (2×, =CH), 128.5 (2×, =CH), 129.9 (2×, =CH), 134.6 (×, =Cquat), 143.7 (1×, =Cquat), 144.7 (1×, =Cquat), 147.2 (1×, =Cquat); IR ($\nu_{max}$/$cm^{-1}$): 3473, 3088, 3059, 3027, 1597, 1495, 1448, 1315, 1152, 1053; MS-ESI 392 *m*/*z* (M−1). Anal. Calcd for $C_{23}H_{23}NO_3S$: C, 70.20; H, 5.89; N, 3.56; S, 8.15. Found: C, 70.25; H, 5.88; N, 3.55; S, 8.10.

**4.3.2. (2*S*,3*S*)-(3-Methyl-1-tosylaziridin-2-yl)dibutylmethanol 17b.** Prepared as described in the general procedure from aziridinemethanol **15b** (1.99 g, 10.0 mmol) to afford **17b** (3.39 g, 96%) as a solid. Mp 95–96 °C; $[\alpha]_D^{20} = -5.2$ (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 0.83–0.91 (m, $CH_3$, 6H), 1.15–1.63 (m, ($CH_2$,$CH_3$), 15H), 2.44 (s, $CH_3$, 3H), 2.70 (d, C(3)H, 1H, $J = 7.5$), 2.88 (m, C(2)H, 1H), 7.33 (d, Ar, 2H, $J = 7.5$), 7.81 (d, Ar, 2H, $J = 8.1$); $^{13}C$ NMR ($CDCl_3$): $\delta$ 13.0 ($CH_3$), 14.1 ($CH_3$), 14.2 ($CH_3$), 21.8 ($CH_3$), 23.2 ($CH_2$), 23.5 ($CH_2$), 25.3 ($CH_2$), 25.9 ($CH_2$), 35.6 (C-3), 40.8 ($CH_2$), 41.3 ($CH_2$), 50.4 (C-2), 72.3 (CHOH), 128.2 (2×, =CH), 126.1 (2×, =CH), 135.3 (1×, =Cquat), 144.9 (1×, =Cquat): IR ($\nu_{max}$/$cm^{-1}$): 3503, 2939, 2867, 1597, 1083, 997; MS-ESI 352 *m*/*z* (M−1). Anal. Calcd for $C_{19}H_{31}NO_3S$: C, 64.55; H, 8.84 N, 3.96 S, 9.07. Found: C, 64.52; H, 8.87; N, 3.95; S, 9.04.

**4.3.3. (2*S*,3*S*)-(3-Methyl-1-tosylaziridin-2-yl)dibenzylmethanol 17c.** Prepared as described in the general procedure from aziridinemethanol **15c** (2.67 g, 10.0 mmol) to afford **17c** (3.84 g, 91%) as a solid. Mp 102–103 °C; $[\alpha]_D^{20} = -58.5$ (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 0.50 (d, $CH_3$, 3H, $J = 5.7$), 1.82 (s, OH, 1H), 2.42 (s, $CH_3$, 3H), 2.61 (m, C(3)H, 1H), 2.78 (m, $CH_2$(Bn), 2H), 2.91 (m, $CH_2$(Bn), 2H), 2.96 (d, C(2)H, 1H, $J = 7.2$), 7.12–7.84 (m, Ar, 14H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 11.7 ($CH_3$), 21.9 ($CH_3$), 42.7 ($CH_2$), 43.3 ($CH_2$), 49.1 (C-3), 50.1 (C-2), 73.5 (CHOH), 126.8 (1×, =CH), 127.0 (1×, =CH), 128.1 (2×, =CH), 128.2 (2×, =CH), 128.5 (2×, =CH), 130.0 (2×, =CH), 131.1 (2×, =CH), 131.2 (2×, =CH), 135.4 (×, =Cquat), 136.3 (1×, =Cquat), 136.7 (1×, =Cquat), 144.9 (1×, =Cquat); IR ($\nu_{max}$/$cm^{-1}$): 3485, 3063, 3030, 2934, 1596, 1496, 1454, 1401, 1304, 1290, 1242, 1157, 1111, 1091, 1048, 1017, 976; MS-ESI 420 *m*/*z* (M−1). Anal. Calcd for $C_{25}H_{27}NO_3S$: C, 71.23; H, 6.46; N, 3.32; S, 7.61. Found: C, 71.18; H, 6.56; N, 3.41; S, 7.82.

**4.3.4. (2*S*,3*S*)-(3-Methyl-1-tosylaziridin-2-yl)bis(4-methoxyphenyl)methanol 17d.** Prepared as described in the general procedure from aziridinemethanol **15d** (2.99 g, 10.0 mmol) to afford **17d** (3.99 g, 88%) as a solid. Mp 153–154 °C; $[\alpha]_D^{20} = +32.3$ (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 1.30 (d, $CH_3$, 3H, $J = 6.3$), 2.41 (s, $CH_3$, 3H), 3.11 (m, C(3)H, 1H), 3.61 (d, C(2)H, 1H, $J = 7.2$), 3.77 (s, $OCH_3$, 3H), 3.78 (s, $OCH_3$, 3H), 6.65–7.60 (m, Ar, 12H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 12.3 ($CH_3$), 21.6 ($CH_3$), 40.4 (C-3), 52.2 (C-2), 55.18 ($CH_3O$), 55.22 ($CH_3O$), 74.2 (CHOH), 113.4 (2×, =CH), 113.6 (2×, =CH), 126.9 (2×, =CH), 127.2 (2×, =CH), 127.8 (2×, =CH), 129.6 (2×, =CH), 134.6 (1×, =Cquat), 135.9 (1×, =Cquat), 139.5 (×, =Cquat), 144.4 (1×, =Cquat), 158.5 (1×, =Cquat), 158.7 (1×, =Cquat); IR ($\nu_{max}$/$cm^{-1}$): 3479, 3030, 2952, 2930, 2835, 1610, 1510, 1463, 1451, 1416, 1317, 1304, 1251, 1154, 968; MS-ESI 452 *m*/*z* (M−1). Anal. Calcd for $C_{25}H_{27}NO_5S$: C, 66.20; H, 6.00; N, 3.09; S, 7.07. Found: C, 66.31; H, 5.86; N, 2.98; S, 7.05.

**4.3.5. (2*S*)-(1-Tosylaziridin-2-yl)diphenylmethanol 18a.** Prepared as described in the general procedure from aziridinemethanol **16a** (2.25 g, 10.0 mmol) to afford **18a** (3.68 g, 97%) as a solid. Mp 163–164 °C; $[\alpha]_D^{20} = -35.3$ (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 2.41 (s, $CH_3$, 3H), 2.54 (d, C(3)$H_2$, 1H, $J = 4.5$), 2.61 (s, OH, 1H), 2.71 (d, C(3)$H_2$, 1H, $J = 6.9$), 3.74 (m, C(2)H, 1H), 7.17–7.66 (m, Ar, 14H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 21.9 ($CH_3$), 30.0 (C-3), 47.0 (C-2), 74.8 (CHOH), 126.3 (2×, =CH), 126.5 (2×, =CH), 127.6 (1×, =CH), 127.9 (1×, =CH), 128.1 (2×, =CH), 128.5 (2×, =CH), 128.6 (2×, =CH), 129.9 (2×, =CH), 134.6 (×, =Cquat), 143.4 (1×, =Cquat), 144.8 (1×, =Cquat), 145.1 (1×, =Cquat); IR ($\nu_{max}$/$cm^{-1}$): 3463, 3025, 1596, 1494, 1447, 1336, 1319, 1186, 1161, 1094,

1002, 983, 922, 901; MS-ESI 378 *m/z* (M−1). Anal. Calcd for $C_{22}H_{21}NO_3S$: C, 69.63; H, 5.58; N, 3.69; S, 8.45. Found: C, 69.72; H, 5.54; N, 3.65; S, 8.36.

**4.3.6. (2*S*)-(1-Tosylaziridin-2-yl)dibutylmethanol 18b.** Prepared as described in the general procedure from aziridinemethanol **16b** (1.85 g, 10.0 mmol) to afford **18b** (2.95 g, 87%) as a solid. Mp 100–101 °C; $[\alpha]_D^{20} = -24.1$ (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 0.82 (m, $CH_3$, 3H), 0.90 (m, $CH_3$, 3H), 1.13–1.63 (m, $CH_2$, 12H), 2.42 (m, C(3)$H_2$, 1H), 2.45 (s, $CH_3$, 3H), 2.60 (d, C(3)$H_2$, 1H, $J = 6.0$), 2.82 (m, C(2)H, 1H), 7.35 (d, Ar, 2H, $J = 8.1$), 7.83 (d, Ar, 2H, $J = 8.4$); $^{13}C$ NMR ($CDCl_3$): $\delta$ 14.3 ($CH_3$), 14.4 ($CH_3$), 22.0 ($CH_3$), 23.4 ($CH_2$), 23.6 ($CH_2$), 25.6 (2×, $CH_2$), 30.6 (C-3), 36.1 ($CH_2$), 40.0 ($CH_2$), 46.3 (C-2), 70.9 (CHOH), 128.4 (2×, =CH), 130.0 (2×, =CH), 134.9 (1×, =Cquat), 145.0 (1×, =Cquat); IR ($\nu_{max}/cm^{-1}$): 3486, 2949, 2866, 1597, 1465, 1360, 1332, 1304, 1288, 1242, 1157, 1136, 1085, 1035, 966; MS-ESI 338 *m/z* (M−1). Anal. Calcd for $C_{18}H_{29}NO_3S$: C, 63.68; H, 8.61; N, 4.13; S, 9.44. Found: C, 63.52; H, 8.78; N, 4.18; S, 9.39.

**4.3.7. (2*S*)-(1-Tosylaziridin-2-yl)dibenzylmethanol 18c.** Prepared as described in the general procedure from aziridinemethanol **16c** (2.53 g, 10.0 mmol) to afford **18c** (3.71 g, 91%) as a solid. Mp 106–107 °C; $[\alpha]_D^{20} = -47.4$ (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 2.42 (s, $CH_3$, 3H), 2.81 (dd, $CH_2$(Bn), 2H), 2.94 (dd, $CH_2$(Bn), 2H), 2.90 (m, C(3)$H_2$, 1H), 3.45 (m, C(3)$H_2$, 2H), 3.63 (m, C(2)H, 1H), 4.94 (s, NH, 1H), 7.11–7.81 (m, Ar, 14H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 21.6 ($CH_3$), 43.8 ($CH_2$), 44.9 ($CH_2$), 47.7 (C-3), 59.2 (C-2), 75.2 (CHOH), 126.s (1×, =CH), 127.1 (1×, =CH), 128.0 (2×, =CH), 128.3 (2×, =CH), 128.6 (2×, =CH), 129.6 (2×, =CH), 130.6 (2×, =CH), 130.8 (2×, =CH), 134.8 (×, =Cquat), 135.7 (1×, =Cquat), 136.1 (1×, =Cquat), 144.8 (1×, =Cquat); IR ($\nu_{max}/cm^{-1}$): 3486, 3257, 3086, 3062, 3028, 2944, 2921, 1736, 1597, 1496, 1454, 1368, 1318, 1229, 1157, 1117, 1093, 968, 938; MS-ESI 406 *m/z* (M−1). Anal. Calcd for $C_{24}H_{25}NO_3S$: C, 70.73; H, 6.18; N, 3.44; S, 7.87. Found: C, 70.72; H, 6.38; N, 3.43; S, 7.83.

### 4.4. General procedure for aza-Payne rearrangement with NaOH in a mixture of $^t$BuOH–$H_2O$–THF

To a stirred solution a 10 mL of 0.28 M NaOH in a mixture of $^t$BuOH–$H_2O$–THF (4:5:1) was added **17** or **18** (2.5 mmol) at room temperature, and then stirring was continued for several hours. The reaction was quenched with 20 mL of water at 0 °C with stirring. The mixture was extracted with diethyl ether and the extract washed successively with saturated citric acid, brine, 5% $NaHCO_3$, and brine, and dried over $MgSO_4$. The usual workup followed by flash chromatography over silica gel with petroleum ether–ethyl acetate (5:1) to yield **19** or **20**.

**4.4.1. (2*R*,3*S*)-*N*-(1-(3,3-Diphenyloxiran-2-yl)ethyl)-4-methylbenzenesulfonamide 19a.** Prepared as described in the general procedure from **17a** (0.98 g, 2.5 mmol) for 1 h to afford **19a** (0.94 g, 96%) as a crystalline mass. Mp 179–180 °C; $[\alpha]_D^{20} = +130.7$ (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 1.20 (d, $CH_3$, 3H, $J = 6.6$), 2.46 (s, $CH_3$, 3H), 2.67 (m, CH, 1H), 3.32 (d, C(3)H, 1H, $J = 8.7$), 4.81 (d, NH, 1H, $J = 5.1$), 7.04–7.70 (m, Ar, 14H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 18.4 ($CH_3$), 21.8 ($CH_3$), 50.0 (C(NH)), 67.6 (C-3), 67.7 (C-2), 127.5 (4×, =CH), 127.7 (1×, =CH), 128.1 (1×, =CH), 128.4 (2×, =CH), 128.5 (2×, =CH), 128.6 (2×, =CH), 129.8 (2×, =CH), 136.4 (×, =Cquat), 137.2 (1×, =Cquat), 139.7 (1×, =Cquat), 143.5 (1×, =Cquat); IR ($\nu_{max}/cm^{-1}$): 3471, 3293, 3059, 3029, 1599, 1493, 1446, 1332, 1151, 1090; MS-ESI 392 *m/z* (M−1). Anal. Calcd for $C_{23}H_{23}NO_3S$: C, 70.20; H, 5.89; N, 3.56; S, 8.15. Found: C, 70.10; H, 5.76; N, 3.60; S, 8.11.

**4.4.2. (2*R*,3*S*)-*N*-(1-(3,3-Dibutyloxiran-2-yl)ethyl)-4-methylbenzenesulfonamide 19b.** Prepared as described in the general procedure from **17b** (0.88 g, 2.5 mmol) for 8 h to afford **19b** (0.76 g, 86%) as a solid. Mp 50 °C; $[\alpha]_D^{20} = +36.2$ (*c* 0.5, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 0.83–0.88 (m, $CH_3$, 6H), 1.16–1.65 (m, ($CH_2$,$CH_3$) 15H), 2.41 (s, $CH_3$, 3H), 2.54 (d, CH, 1H, $J = 4.2$), 3.05 (m, C(3)H, 1H), 7.29 (d, Ar, 2H, $J = 4.2$), 7.77 (d, Ar, 2H, $J = 3.9$); $^{13}C$ NMR ($CDCl_3$): $\delta$ 14.1 ($CH_3$), 14.2 ($CH_3$), 19.6 ($CH_3$), 21.7 ($CH_3$), 22.9 ($CH_2$), 23.0 ($CH_2$), 27.2 ($CH_2$), 27.3 ($CH_2$), 29.9 ($CH_2$), 30.5 ($CH_3$), 35.0 (CH(NH)), 49.5 (C-3), 65.6 (C-2), 127.6 (2×, =CH), 129.7 (2×, =CH), 137.4 (1×, =Cquat), 143.5 (1×, =Cquat); IR ($\nu_{max}/cm^{-1}$): 3298, 3029, 2957, 2860, 1600, 1496, 1467, 1417, 1376, 1351, 1325, 1309, 1167, 1090, 1044, 982, 947; MS-ESI 352 *m/z* (M−1). Anal. Calcd for $C_{19}H_{31}NO_3S$: C, 64.55; H, 8.84; N, 3.96; S, 9.07. Found: C, 64.56; H, 8.79; N, 3.98; S, 9.01.

**4.4.3. (2*R*,3*S*)-*N*-(1-(3,3-Dibenzyloxiran-2-yl)ethyl)-4-methylbenzenesulfonamide 19c.** Prepared as described in the general procedure from **17c** (1.05 g, 2.5 mmol) for 2 h to afford **19c** (0.95 g, 90%) as a solid. Mp 130–131 °C; $[\alpha]_D^{20} = -28.9$ (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 1.29 (d, $CH_3$, 3H, $J = 6.6$), 2.37 (s, $CH_3$, 3H), 2.43 (s, CH, 1H), 2.53 (dd, $CH_2$(Bn), 2H), 2.79 (dd, $CH_2$(Bn), 2H), 3.27 (m, C(3)H, 1H), 4.87 (s, NH, 1H), 7.02–7.81 (m, Ar, 14H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 19.6 ($CH_3$), 21.7 ($CH_3$), 36.1 ($CH_2$), 40.9 ($CH_2$), 49.7 (C(NH)), 64.7 (C-3), 65.6 (C-2), 127.0 (1×, =CH), 127.1 (1×, =CH), 127.6 (2×, =CH), 128.6 (2×, =CH), 128.7 (2×, =CH), 129.7 (2×, =CH), 129.8 (4×, =CH), 136.4 (×, =Cquat), 136.6 (1×, =Cquat), 137.4 (1×, =Cquat), 143.7 (1×, =Cquat); IR ($\nu_{max}/cm^{-1}$): 3301, 3063, 3028, 2925, 1604, 1495, 1456, 1438, 1318, 1302, 1155, 1093, 1062, 1002, 802; MS-ESI 420 *m/z* (M−1). Anal. Calcd for $C_{25}H_{27}NO_3S$: C, 71.23; H, 6.46; N, 3.32; S, 7.61. Found: C, 71.25; H, 6.58; N, 3.28; S, 7.65.

**4.4.4. (2*R*,3*S*)-*N*-(1-(3,3-Bis(4-methoxyphenyl)oxiran-2-yl)-ethyl)-4-methylbenzenesulfonamide 19d.** Prepared as described in the general procedure from **17d** (1.13 g, 2.5 mmol) for 24 h to afford **19d** (1.10 g, 97%) as a solid. Mp 65–66 °C; $[\alpha]_D^{20} = -26.2$ (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 1.43 (d, $CH_3$, 3H, $J = 6.3$), 2.44 (s, $CH_3$, 3H), 3.77 (s, $OCH_3$, 3H), 3.80 (s, $OCH_3$, 3H), 3.89 (m, C(3)H, 1H), 4.80 (m, CH(NH), 1H), 6.70–7.42 (m, Ar, 12H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 14.3 ($CH_3$), 21.5 ($CH_3$), 48.9 (C-3), 54.3 (C-2), 55.2 ($CH_3O$), 55.5 ($CH_3O$), 76.2 (CHOH), 113.2 (2×, =CH), 113.5 (2×, =CH), 126.3 (2×, =CH), 127.2 (2×, =CH), 127.8 (2×, =CH), 129.6 (2×, =CH), 143.1 (1×, =Cquat), 143.4 (1×, =Cquat), 146.0 (×,

=Cquat), 158.4 (1×, =Cquat), 159.7 (1×, =Cquat), 162.9 (1×, =Cquat); IR ($\nu_{max}$/cm$^{-1}$): 3478, 3304, 3025, 2964, 2836, 1611, 1581, 1513, 1461, 1330, 1301, 1250, 1183, 1150, 1089, 1027; MS-ESI 452 *m*/*z* (M−1). Anal. Calcd for $C_{25}H_{27}NO_5S$: C, 66.20; H, 6.00; N, 3.09; S, 7.07. Found: C, 66.25; H, 5.94; N, 3.01; S, 6.98.

**4.4.5. (2*R*)-*N*-((3,3-Diphenyloxiran-2-yl)methyl)-4-methylbenzenesulfonamide 20a.** Prepared as described in the general procedure from **18a** (0.95 g, 2.5 mmol) for 1 h to afford **20a** (0.90 g, 95%) as a solid. Mp 114–115 °C; $[\alpha]_D^{20} = +84.3$ (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta$ 2.39 (s, $CH_3$, 3H), 2.82 (m, $CH_2$, 1H), 3.02 (m, $CH_2$, 1H), 3.58 (m, C(2)H, 1H), 7.12–7.64 (m, Ar, 14H); $^{13}$C NMR ($CDCl_3$): $\delta$ 21.8 ($CH_3$), 44.6 (C(NH)), 47.0 (C-3), 73.7 (C-2), 125.4 (2×, =CH), 125.6 (2×, =CH), 126.3 (1×, =CH), 1265 (1×, =CH), 128.4 (2×, =CH), 128.5 (2×, =CH), 128.8 (2×, =CH), 129.9 (2×, =CH), 136.3 (×, =Cquat), 137.5 (1×, =Cquat), 139.9 (1×, =Cquat), 143.8 (1×, =Cquat); IR ($\nu_{max}$/cm$^{-1}$): 3463, 3265, 3062, 1597, 1496, 1461, 1422, 1343, 1328, 1164, 1091, 1049; MS-ESI 378 *m*/*z* (M−1). Anal. Calcd for $C_{22}H_{21}NO_3S$: C, 69.63; H, 5.58; N, 3.69; S, 8.45. Found: C, 69.68; H, 5.60; N, 3.71; S, 8.42.

**4.4.6. (2*R*)-*N*-((3,3-Dibutyloxiran-2-yl)methyl)-4-methylbenzenesulfonamide 20b.** Prepared as described in the general procedure from **18b** (0.85 g, 2.5 mmol) for 8 h to afford **20b** (0.70 g, 83%) as a solid. Mp 57–58 °C; $[\alpha]_D^{20} = +37.4$ (*c* 0.5, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta$ 0.87–0.89 (m, $CH_3$, 6H), 1.26–1.59 (m, $CH_2$, 12H), 2.43 (s, $CH_3$, 3H), 2.81 (d, $CH_2$(NHTs), 1H, $J = 2.1$), 2.96 (m, $CH_2$(NHTs), 1H), 3.31 (m, C(3)H, 1H), 4.63 (d, NH, 1H), 7.33 (s, Ar, 2H), 7.77 (s, Ar, 2H); $^{13}$C NMR ($CDCl_3$): $\delta$ 14.1 ($CH_3$), 14.2 ($CH_3$), 21.7 ($CH_3$), 22.9 ($CH_2$), 23.1 ($CH_2$), 26.9 ($CH_2$), 27.5 (C-3), 30.2 ($CH_2$), 34.7 ($CH_2$), 42.7 (CH(NH)), 60.9 (C-3), 64.6 (C-2), 127.3 (2×, =CH), 130.0 (2×, =CH), 137.0 (1×, =Cquat), 143.9 (1×, =Cquat); IR ($\nu_{max}$/cm$^{-1}$): 3295, 3028, 2958, 2933, 2867, 1597, 1465, 1436, 1330, 1304, 1288, 1158, 1091, 1073, 1051, 884; MS-ESI 338 *m*/*z* (M−1). Anal. Calcd for $C_{18}H_{29}NO_3S$: C, 63.68; H, 8.61; N, 4.13; S, 9.44. Found: C, 63.62; H, 8.70; N, 4.08; S, 9.43.

**4.4.7. (2*R*)-*N*-((3,3-Dibenzyloxiran-2-yl)methyl)-4-methylbenzenesulfonamide 20c.** Prepared as described in the general procedure from **18c** (1.02 g, 2.5 mmol) for 10 h to afford **20c** (0.91 g, 89%) as a solid. Mp 105–106 °C; $[\alpha]_D^{20} = +40.5$ (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta$ 2.42 (s, $CH_3$, 3H), 2.43 (s, CH, 1H), 2.68 (dd, $CH_2$(Bn), 2H), 2.78 (dd, $CH_2$(Bn), 2H), 2.95 (m, C(3)$H_2$, 1H), 3.11 (m, C(3)$H_2$, 1H), 3.42 (m, C(2)H, 1H), 4.87 (s, NH, 1H), 7.04–7.75 (m, Ar, 14H); $^{13}$C NMR ($CDCl_3$): $\delta$ 21.8 ($CH_3$), 36.7 ($CH_2$), 40.7 ($CH_2$), 42.9 (C(NH)), 60.0 (C-3), 64.5 (C-2), 127.0 (1×, =CH), 127.1 (1×, =CH), 127.3 (2×, =CH), 128.6 (2×, =CH), 128.9 (2×, =CH), 129.5 (2×, =CH), 130.0 (2×, =CH), 130.1 (2×, =CH), 136.1 (×, =Cquat), 136.7 (1×, =Cquat), 136.9 (1×, =Cquat), 143.9 (1×, =Cquat); IR ($\nu_{max}$/cm$^{-1}$): 3290, 3085, 3061, 3028, 2924, 1601, 1496, 1453, 1437, 1332, 1320, 1306, 1149, 1094, 1065, 1041, 945; MS-ESI 406 *m*/*z* (M−1). Anal. Calcd for $C_{24}H_{25}NO_3S$: C, 70.73; H, 6.18; N, 3.44; S, 7.87. Found: C, 70.69; H, 6.25; N, 3.41; S, 7.73.

### 4.5. General procedure for the synthesis of 21 and 22

To a stirred solution of aziridinemethanol **15** or **16** (10.0 mmol) and $NEt_3$ (2.78 mL 20.0 mmol) in THF (20 mL) was gradually added $(Boc)_2O$ (2.62 g, 12.0 mmol) in THF (5 mL) at 0 °C, and then the mixture was allowed to warm to rt and the stirring was continued for 24 h. To the mixture was added ethyl acetate and washed successively with saturated citric acid, brine, 5% $NaHCO_3$, and brine, and dried over $MgSO_4$. The usual workup followed by flash chromatography over silica gel with petroleum ether–ethyl acetate (5:1) to yield **21** (or **22**).

**4.5.1. (2*S*,3*S*)-*tert*-Butyl 2-(hydroxydiphenylmethyl)-3-methylaziridine-1-carboxylate 21a.** Prepared as described in the general procedure from **15a** (2.39 g, 10.0 mmol) to afford **21a** (3.22 g, 95%) as a solid. Mp 141–142 °C; $[\alpha]_D^{20} = -1.5$ (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta$ 1.21 (d, $CH_3$, 3H, $J = 6.0$), 1.40 (s, $(CH_3)_3C$, 9H), 2.65 (m, C(3)H, 1H), 3.34 (d, C(2)H, 1H, $J = 6.6$), 3.36 (s, OH, 1H), 7.19–7.52 (m, Ar, 10H); $^{13}$C NMR ($CDCl_3$): $\delta$ 13.4 ($CH_3$), 28.2 (3×, $(CH_3)_3C$)) 38.8 (C-3), 49.4 (C-2), 74.9 (CHOH), 82.0 (C), 126.4 (2×, =CH), 126.7 (2×, =CH), 127.3 (2×, =CH), 128.2 (4×, =CH), 144.2 (1×, =Cquat), 148.1 (1×, =Cquat), 162.5 (C=O); IR ($\nu_{max}$/cm$^{-1}$): 3486, 3026, 3003, 1720, 1494, 1449, 1391, 1296, 1247, 1152, 1006; MS-ESI 338 *m*/*z* (M−1). Anal. Calcd for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.30; H, 7.38; N, 4.07.

**4.5.2. (2*S*,3*S*)-*tert*-Butyl 2-(hydroxybis(4-methoxyphenyl))-3-methylaziridine-1-carboxylate 21d.** Prepared as described in the general procedure from **15d** (2.99 g, 10.0 mmol) to afford **21d** (3.76 g, 94%) as a solid. Mp 146–148 °C; $[\alpha]_D^{20} = -9.8$ (*c* 0.5, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta$ 1.22 (d, $CH_3$, 3H, $J = 5.4$), 1.42 (s, $(CH_3)_3C$, 9H), 2.60 (m, C(3)H, 1H), 3.25 (d, C(2)H, 1H, $J = 6.3$), 3.76 (s, $OCH_3$, 3H), 3.79 (s, $OCH_3$, 3H), 6.78–7.41 (m, Ar, 8H); IR ($\nu_{max}$/cm$^{-1}$): 3509, 3009, 2980, 2956, 2834, 1708, 1609, 1585, 1509, 1466, 1439, 1421, 1369, 1303, 1254, 1170, 1151, 1040, 1012; MS-ESI 398 *m*/*z* (M−1). Anal. Calcd for $C_{23}H_{29}NO_5$: C, 69.15; H, 7.32; N, 3.51. Found: C, 69.23; H, 7.28; N, 3.69.

### 4.6. General procedure for aza-Payne rearrangement with NaH in a mixture of HMPA–THF

To a stirred suspension of NaH (24 mg, 1 mmol) in a mixture of THF (2 mL) and HMPA (0.33 mL) at −30 °C under nitrogen was added **21** (0.25 mmol) in THF (2 mL), and then the mixture allowed to warm to rt and the stirring continued for 4 h. The reaction was quenched with 2 mL of 5% citric acid at −30 °C with stirring. The mixture was extracted with diethyl ether and the extract was washed successively with saturated citric acid (3 × 50 mL), brine (3 × 50 mL), 5% $NaHCO_3$ (3 × 50 mL), and brine (3 × 50 mL), and dried over $MgSO_4$. The usual workup followed by flash chromatography over silica gel with petroleum ether–ethyl acetate (5:1) to yield **23** as a crystalline mass.

**4.6.1. (2*R*,3*S*)-*tert*-Butyl 1-(3,3-diphenyloxiran)-2-yl)ethylcarbamate 23a.** Prepared as described in the general procedure from **21a** (84.9 mg, 0.25 mmol) to afford **23a** (81.5 mg, 96%) as a solid. Mp 103–104 °C; $[\alpha]_D^{20} = +78.0$ (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 1.18 (d, $CH_3$, 3H, $J = 6.0$), 1.39 (s, $(CH_3)_3C$, 9H), 3.28 (m, C(3)H, 1H), 3.38 (d, C(2)H, 1H), 7.26–7.43 (m, Ar, 10H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 18.4 ($CH_3$), 28.6 (3×, $(CH_3)_3C$)) 46.5 (CH(NH)), 66.6 (C-3), 68.4 (C-2), 82.0 (C), 127.4 (1×, =CH), 127.7 (1×, =CH), 128.1 (2×, =CH), 128.2 (2×, =CH), 128.5 (2×, =CH), 128.6 (2×, =CH), 136.9 (1×, =Cquat), 140.6 (1×, =Cquat), 155.2 (C=O); IR ($\nu_{max}/cm^{-1}$): 3434, 2976, 1716, 1497, 1448, 1394, 1370, 1291, 1230, 1163, 1050, 1027, 942; MS-ESI 338 *m*/*z* (M−1). Anal. Calcd for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.28; H, 7.45; N, 4.05.

**4.6.2. (2*R*,3*S*)-*tert*-Butyl 1-(3,3-bis(4-methoxyphenyl)oxiran)-2-yl)ethylcarbamate 23d.** Prepared as described in the general procedure from **21d** (100 mg, 0.25 mmol) to afford **23d** (80 mg, 80%) as a liquid. Mp 40 °C; $[\alpha]_D^{20} = +20.0$ (*c* 0.6, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 1.12 (d, $CH_3$, 3H, $J = 5.7$), 1.38 (s, $(CH_3)_3C$, 9H), 2.61 (m, CH, 1H), 3.32 (d, C(2)H, 1H, $J = 6.3$), 3.71 (s, $OCH_3$, 3H), 3.74 (s, $OCH_3$, 3H), 6.76–7.28 (m, Ar, 8H); IR ($\nu_{max}/cm^{-1}$): 3369, 2958, 2956, 2854, 1711, 1611, 1583, 1514, 1461, 1366, 1298, 1247, 1172, 1032, 833; MS-ESI 398 *m*/*z* (M−1). Anal. Calcd for $C_{23}H_{29}NO_5$: C, 69.15; H, 7.32; N, 3.51. Found: C, 69.13; H, 7.26; N, 3.50.

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