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Cyclic Sulfur Ylides Derived from Gleason-Type Chiral Auxiliaries for the Asymmetric Synthesis of Epoxy Amides

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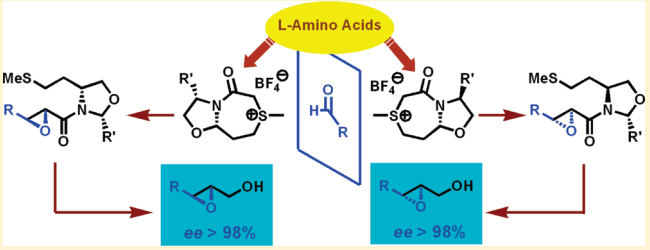
Supporting Information

ABSTRACT: Gleason-type chiral auxiliaries were used for the synthesis of a novel class of sulfonium salts, obtained via methylation of the sulfide with Meerwein's salt. The salts were reacted with aldehydes under basic conditions to provide epoxy amides, which were reduced to their corresponding epoxy alcohols in excellent enantiomeric excesses. Interestingly, it was feasible to synthesize both enantiomeric epoxy alcohols depending on which of the sulfonium salts, prepared from L-amino acids (**6** and **9** from L-valine or **15** and **16** from L-serine) was employed.



INTRODUCTION

Chiral sulfur ylides are proving to occupy a relevant position in the asymmetric syntheses of epoxides, aziridines, and cyclopropanes as evidenced by the flurry of research activity in the past few years.[1] The design of chiral entities in the form of sulfur ylides offers an interesting alternative to the laureated Sharpless asymmetric epoxidation[2] and, in some cases, may represent a shorter and even more efficient approach to the corresponding epoxides.[3] In this area, particularly interesting are the glycidic amides whose enantiomeric synthesis by use of sulfur ylides[4] or diazoamides[5] or via epoxidation of α,β-unsaturated amides[6] have received special attention by virtue of their potential applications in organic synthesis. In fact, we have devoted significant efforts toward this type of products, synthesized via stabilized sulfur ylides,[7] and demonstrated their utility in the synthesis of natural bioactive compounds.[8] As an extension of these studies, we have recently reported the design, synthesis and reactivity of novel chiral sulfur ylides derived from the corresponding sulfonium salts **1** and **2**, prepared from L- and D-methionines respectively, which provided excellent results in the epoxidation process with respect to chemical and stereochemical yields (Scheme 1, part a).[9] Prompted by these results,[10] we decided to explore new reagents of this type. Inspired by the commercially available chiral auxiliary **5**, prepared and exploited by Gleason in asymmetric alkylations[11,12] and in Mannich-type reactions,[13] we surmised that its corresponding sulfonium salt could represent a precursor for a bicyclic-type sulfur ylide, a chiral reagent with exciting prospects in the asymmetric epoxidations of carbonyl compounds. Toward this aim, we prepared sulfonium salt **6** by treatment of **5** with Meerwein's salt in 81% yield (Scheme 1, part b). The present article reports the reactivity of the sulfonium salt **6** with carbonyl compounds and its synthetic potential in asymmetric synthesis of epoxyamides. In addition, the scope of other Gleason-type chiral auxiliaries derived from other amino acids in the chemistry of sulfur ylides is explored.

RESULTS AND DISCUSSION

With sulfonium salt **6** in hand, we proceeded to investigate its reactivity toward carbonyl compounds and the resulting stereochemical induction. Initial results obtained by reaction of sulfonium salt **6** with simple aromatic and aliphatic aldehydes, under basic conditions, revealed that both the chemical yields, and the degrees of stereochemical induction of the resulting epoxyamides **7** were as high as obtained previously with sulfonium salts **1** and **2**.[9] In some cases, the yields could be improved over the initial conditions (procedure a) by the addition of DMSO during the *in situ* formation of the corresponding ylide (see Table 1, procedure b). Determination of the absolute stereochemistry was possible by transformation of the epoxy amides into the corresponding epoxy alcohols by treatment with Super-H.[14] Subsequent inspection of the physical and spectroscopic properties of these epoxy alcohols, as well as analysis by GC−MS of their corresponding Mosher esters,[15] confirmed the formation of epoxy alcohols **3** with very high ee (>98%) (Table 1).[16]

For the sulfonium salts **1** and **2**, the stereochemical outcome of the reaction with aldehydes is defined by the configuration of the starting α-amino acid; however, for the Gleason-type sulfonium salt the presence of two chiral centers in its structure made us wonder which of them could be determining the stereochemical outcome. To address this question, we decided to prepare the diastereoisomer of **5** at the aminal functional group. To this aim, a modification of the original Gleason protocol to prepare sulfide **5** was targeted, which consisted of extended treatment of the

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Scheme 1. Design and Synthesis of New Chiral Sulfonium Salts from Gleason-Type Chiral Auxiliaries

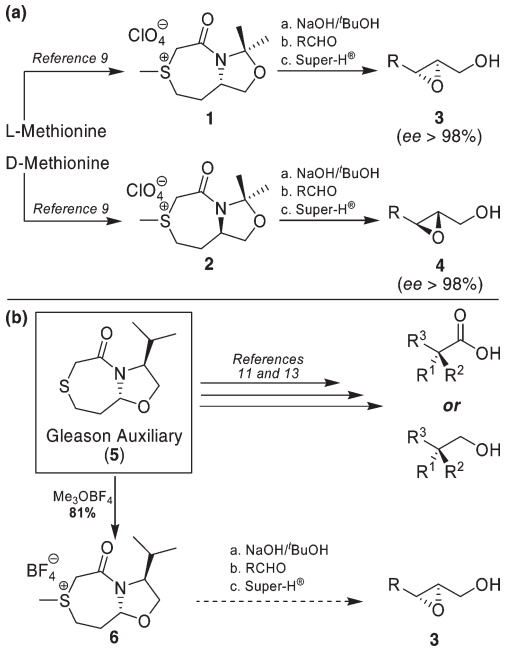
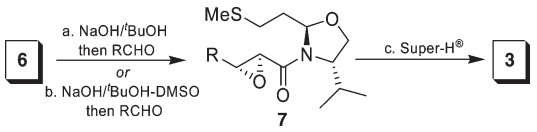


Table 1. Reaction of Sulfur Ylide Derived from Sulfonium Salt 6 with Aldehydes



entry	aldehyde	epoxyamide (yield %; de %)	epoxyalcohol (yield %)[c]
1	PhCHO	**7a** (80; >98)[a]	**3a** (72)
2	4-MeC_6H_4CHO	**7b** (89; >98)[b]	**3b** (76)
3	2-MeC_6H_4CHO	**7c** (73; >98)[b]	**3c** (51)
4	4-$MeOC_6H_4CHO$	**7d** (75; >98)[b]	**3d** (75)
5	4-ClC_6H_4CHO	**7e** (76; >98)[a]	**3e** (71)
6	CH_3CH_2CHO	**7f** (41; >98)[a]	**3f** (44)
7	$(CH_3)_2CHCHO$	**7g** (73; >98)[a]	**3g** (69)
8	Chx-CHO	**7h** (82; >98)[a]	**3h** (65)
9	$CH_3(CH_2)_5CHO$	**7i** (79; >98)[a]	**3i** (62)

[a] 1.0 equiv of **6**, 1.0 equiv of a 3.0 M aqueous NaOH or 1.0 equiv of Na^{t}BuO, ^{t}BuOH, 25 °C, 3 h; then 1.1 equiv of RCHO, overnight. [b] 1.0 equiv of **6**, 1.0 equiv of a 1.0 M aqueous NaOH, ^{t}BuOH/DMSO (10/1), 25 °C, 1 h; then 1.1 equiv of RCHO, overnight. [c] 2.5 equiv Super-H, THF, 0 °C, 0.5 h.

amino acetal precursor with $BF_3 \cdot OEt_2$, providing a separable 2:1 mixture of diastereoisomers corresponding to the bicyclic sulfides **5** and **8**, respectively. Subsequent isolation of sufficient amounts of the minor isomer **8** and subjection to the same synthetic sequence as for **5** provided sulfonium salt **9** (Scheme 2). This sulfonium salt was then reacted with aromatic aldehydes under basic conditions to afford epoxyamides **10** in generally good yields (Table 2). Reduction of these epoxyamides

Scheme 2. Synthesis of Epoxy Alcohols 4 from Minor Diastereoisomer 8

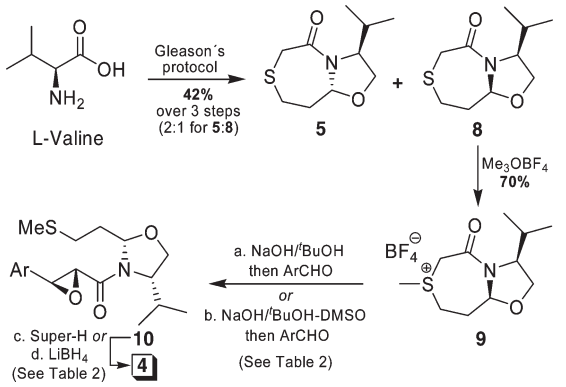


Table 2. Reaction of Sulfur Ylide Derived from Sulfonium Salt 9 with Aromatic Aldehydes

entry	aldehyde	epoxyamide (yield %; de %)	epoxyalcohol (yield %)
1	PhCHO	**10a** (95; >98)[a]	**4a** (34)[d]
2	4-MeC_6H_4CHO	**10b** (73; >98)[b]	**4b** (41)[c]
3	2-MeC_6H_4CHO	**10c** (63; >98)[b]	**4c** (45)[c]
4	4-$MeOC_6H_4CHO$	**10d** (86; >98)[b]	**4d** (38)[c]
5	4-ClC_6H_4CHO	**10e** (76; >98)[b]	**4e** (43)[d]

[a] 1.0 equiv of **9**, 1.0 equiv of a 3.0 M aqueous NaOH or 1.0 equiv of Na^{t}BuO, ^{t}BuOH, 25 °C, 3 h; then 1.1 equiv of RCHO, overnight. [b] 1.0 equiv of **9**, 1.0 equiv of a 1.0 M aqueous NaOH, ^{t}BuOH/DMSO (10/1), 25 °C, 1 h; then 1.1 equiv of RCHO, overnight. [c] 2.5 equiv Super-H, THF, 0 °C, 0.5 h. [d] 5.0 equiv $LiBH_4$, THF, 0 → 25 °C, 1.0 h.

to their corresponding epoxyalcohols by the action of Super-H revealed the opposite stereochemistry (epoxyalcohols **4**) to that obtained from sulfonium salt **6** (Scheme 2).

Interestingly, in contrast to the good results obtained with sulfonium salt **6**, aliphatic aldehydes showed a significant difference in reactivity when reacted with sulfonium salt **9**. Thus, whereas aromatic aldehydes provided good yields and diastereoselectivities in the formation of epoxyamides **10a**−**e**, as described above in Table 2, the aliphatic aldehydes delivered mixtures of *cis*/*trans* epoxyamides in moderate combined yields. The formation of the *cis*/*trans* mixture of epoxyamides, as well as their ratios were confirmed and determined by their transformation into the corresponding epoxy alcohols and subsequent NMR analyses.[17] This transformation was carried out by treatment of the inseparable mixtures **10f**−**i**:**7′f**−**i** with Super-H to obtain epoxy alcohols **4f**−**i**:**3′f**−**i**, which were separated by chromatographic methods. Inspection of the spectroscopic and physical properties of the pure epoxy alcohols, especially their specific rotations, allowed us to identify them as the *trans* epoxy alcohols **4f**−**i** and the *cis* isomers **3′f**−**i**[18] (Scheme 3).

In addition to the unexpected results found with the aliphatic aldehydes, another remarkable observation for the epoxy amides resulting from sulfonium salt **9** was their reductions to the above-mentioned epoxy alcohols by the action of Super-H, which proceeded in moderate to poor yields in all cases (Table 2 and Scheme 3). In order to improve the yield of this reduction, we investigated other reductive methods including the use of

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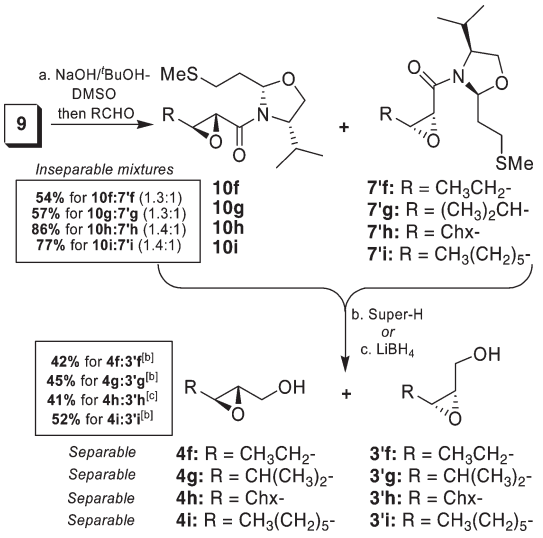
Scheme 3. Reaction of Sulfur Ylide Derived from Sulfonium Salt 9 with Aliphatic Aldehydes



$LiBH_4$,[19] RedAl,[20] $LiAlH_4$[21] $Cp_2Zr(H)Cl$,[22] and $LiNH_2BH_3$.[23] With exception of $LiBH_4$, which provided results similar to that using Super-H as the reducing agent, the other agents failed to provide improved results.

Despite these drawbacks, we concluded that the stereochemistry of the chiral center located at the aminal functional group of the bicyclic system in the sulfonium salt served to control the stereochemical course of the reaction. In this way, it was feasible to prepare both enantiomeric epoxy alcohols from a common L-amino acid.

A theoretical rationale for the observed stereochemical outcome can be proposed based on the conformational analyses of sulfur ylides derived from sulfonium salts **6** and **9** (Scheme 4), which show an unexpected preference for the methyl group on the sulfur atom to adopt a pseudoaxial disposition.[24] Taking into account the preferred conformations of the sulfur ylides together with the assumption of a *cisoid* approach of the aldehyde to the ylide, with the two polar groups in a near eclipsed orientation,[25] make plausible the transition state $\mathbf{I}^{\ddagger}$ (path B) as the most favorable in contrast to the transition state derived from path A. With the betaine intermediate **I** formed, the subsequent step should involve rotation around the C−C bond to give the betaine **II** with the alkoxy and sulfonium groups in an antiperiplanar arrangement, prior to the intramolecular nucleophilic attack of the alkoxy group to deliver epoxy amide **7**.

On the other hand, for the reaction of aldehydes with the sulfur ylide derived from **9**, the stereochemical course could follow a similar path compared to the previous case. However, in this occasion, an additional steric repulsion present in transition state $\mathbf{III}^{\ddagger}$ between the aliphatic chain of the starting aldehyde and the alkyl group of the sulfur ylide could explain the important preference for this reaction to follow the pathway toward *cis* epoxides through transition state $\mathbf{III}'^{\ddagger}$ in which this interaction is not present. Consequently, this scenario could explain the lack of diastereoselectivity observed in the formation of the corresponding epoxy amides, where essentially a 1:1 mixture of *E*:*Z* epoxy amides **10** and **7′** is observed. The experimental results obtained for these reactions lend support to the proposed rationale for the observed stereoselectivity of ylides **6** and **9**.

Given these encouraging results, the possibility of extending this type of sulfonium salts to other L-amino acids led us to consider L-serine as an interesting starting material to prepare chiral sulfonium salts that would possess a tail in the form of a hydroxymethyl group amenable to a linkage to a polyfluorinated tag[26] or attachment to a resin for fluorous or solid phase[27] synthesis, respectively. To this aim, we initially examined the validity of a L-serine derivative, choosing H-Ser(Bn)-OH[28] as a suitable substrate for the synthesis of this class of chiral sulfur ylides. Thus, O-benzyl L-serine was transformed into the hydroxy amide **12** by reduction with lithium aluminum hydride to its corresponding serinol derivative,[29] followed by reaction with ester **11** in the presence of BuLi. According to the modified Gleason procedure, applied before for L-valine, **12** was treated with $BF_3 \cdot OEt_2$ to obtain a separable 2:1 mixture assigned to the diastereoisomers **13** and **14**, respectively, in a 70% combined yield. Subsequent treatment of **13** and **14** with Meerwein's salt afforded the corresponding sulfonium salts **15** and **16** in 81% yields for both cases (Scheme 5).

As for sulfonium salts **6** and **9**, **15** and **16** were explored as potential new chiral reagents for the asymmetric synthesis of epoxy amides. Thus, in a similar procedure as described before for **6** and **9**, **15** and **16** were separately reacted with various aromatic and aliphatic aldehydes under typical basic conditions. Not surprisingly, we obtained almost identical results in the formation of the corresponding epoxy amides **17** and **18** and in their transformations into the epoxy alcohols **3** and **4**, compared to those obtained with salts **6** and **9**. In addition, the same problems found with aliphatic aldehydes were observed including the formation of mixtures of *cis*/*trans* epoxyamides **18g**−**h** from sulfonium salt **16** and poor yields in the reduction process (Table 3).

It is worthy to emphasize that the synthetic value of the described asymmetric epoxidation methodology lies with the utility of the resulting epoxyamides together with their corresponding epoxy alcohols, thus representing versatile building blocks for the stereoselective construction of 1,2-functionalized systems.[30] In fact, for the particular case of glycidic amides, we have demonstrated their synthetic potential in reactions with nucleophiles, which display excellent reactivities and regioselectivities at the C-2 position with nitrogen, oxygen, carbon, and sulfur nucleophiles.[8−10,31]

■ CONCLUSIONS

In conclusion, we have described the synthesis and reactivity of novel chiral sulfur ylides, based upon the bicyclic ylides described by us earlier,[9] but using Gleason-type chiral auxiliaries as the chirality source. The results obtained in the formation of the corresponding epoxy amides were satisfactory in terms of chemical yields and stereochemical induction, thus illustrating the synthetic potential that this kind of reagents may offer in asymmetric synthesis. Interestingly, the extension of this methodology to various L-amino acids in conjuction with the possibility of preparing both diastereoisomers from the same chiral source represent significant advantages compared with other asymmetric methodologies, which generally require a pair of enantiomers to have access to both diastereoisomers. In addition to these features, the very mild conditions for these reactions are particularly useful for aromatic aldehydes but not for aliphatic aldehydes. For these later cases, their reactions with sulfonium salts **9** and **16** require a more profound and detailed study in

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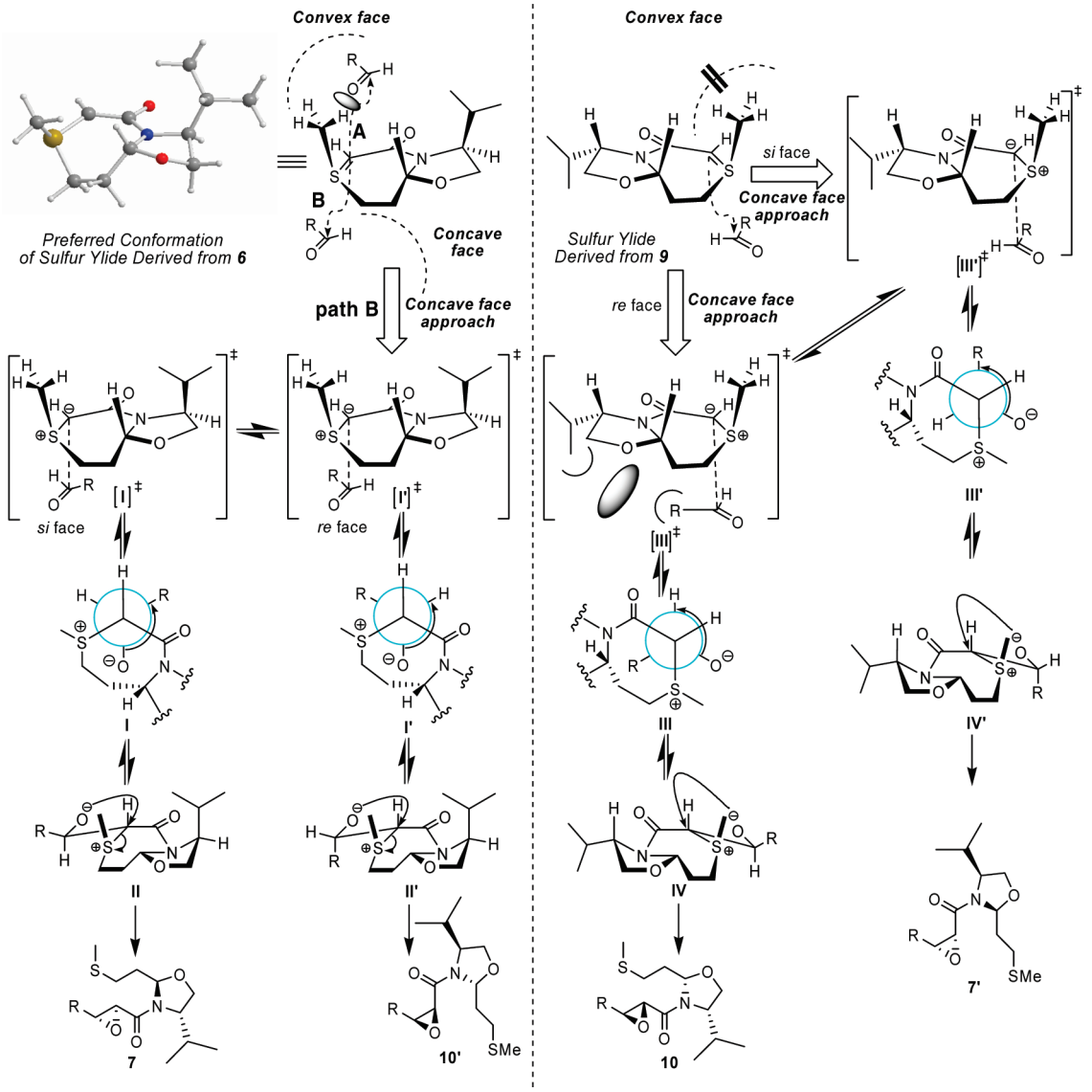
Scheme 4. Rationale of the Stereochemical Outcome of Reactions of 6 and 9 with Aliphatic Aldehydes



order to extend the methodology to a broader group of carbonyl compounds.

EXPERIMENTAL SECTION

General Techniques. All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium benzophenone, and methylene chloride (CH_2Cl_2) and benzene (PhH) from calcium hydride. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. All solutions used in workup procedures were saturated unless otherwise noted. All reagents were purchased at highest commercial quality and used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm silica gel plates (60F-254) using UV light as visualizing agent and 7% ethanolic phosphomolybdic acid or *p*-anisaldehyde solution and heat as developing agents. Silica gel (60, particle size 0.040−0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on 0.25, 0.50, or 1 mm silica gel plates (60F-254). NMR spectra were recorded on a 400 MHz instrument and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; band, several overlapping signals; b, broad. Optical rotations were recorded on a 241 polarimeter. High resolution mass spectra (HRMS) were recorded on a mass spectrometer under fast atom bombardment (FAB) conditions.

Synthesis of Sulfonium Salts. *Sulfonium Salt* ***6***. To a solution of commercially available Gleason auxiliary **5** (747 mg, 3.47 mmol, 1.0 equiv) in dry acetonitrile (12 mL) was added Meerwein salt at room temperature (636 mg, 4.17 mmol, 1.2 equiv). After 12 h, the reaction was quenched by the addtion of MeOH (0.2 mL), and the solvents were evaporated under reduced pressure. To the resulting white solid was added MeOH (5 mL,) and then the mixture was sonicated for the dispersion of the salt. The solid was filtered and washed with cooled MeOH (1 × 3 mL). After drying under high vacuum, sulfonium salt **6** (887 mg, 81%) was obtained as a white solid: mp 179−185 °C; $[\alpha]^{25}_D$ = +4.1° (*c* 0.12, H_2O); ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.77 (d, J = 6.9 Hz, 3 H), 0.85 (d, J = 7.0 Hz, 3 H), 2.26−2.48 (m, 2 H), 2.99 (s, 3 H),

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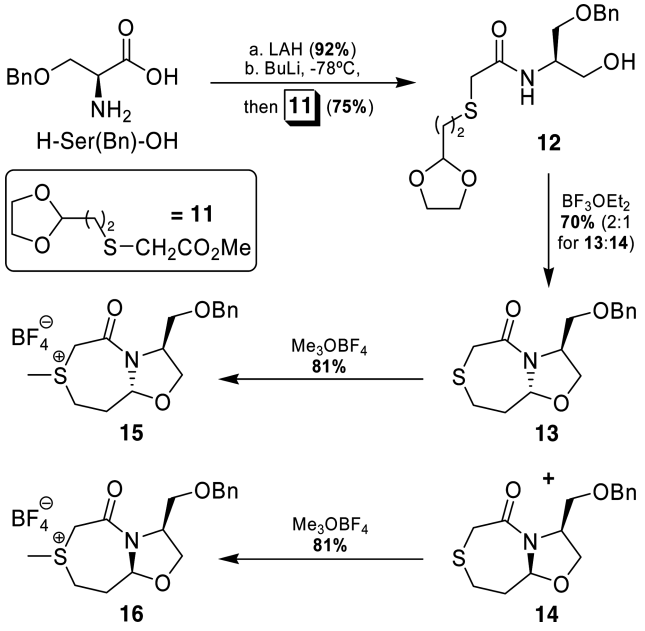
Scheme 5. Synthesis of Sulfonium Salts 15 and 16 from H-Ser(Bn)-OH

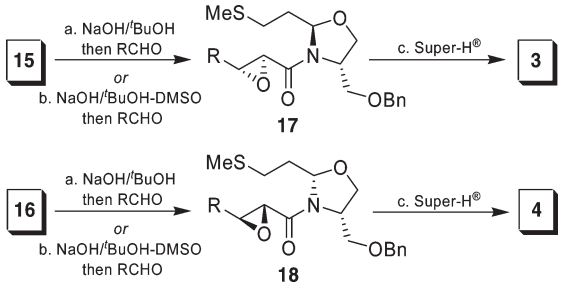


3.49 (bs, 1 H), 3.65 (dt, J = 12.5, 3.1 Hz, 1 H), 3.75−3.84 (m, 1 H), 3.93−4.10 (m, 4 H), 4.66 (d, J = 12.8 Hz, 1 H), 5.53 (d, J = 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 15.7, 19.0, 26.4, 27.0, 30.9, 43.9, 61.5, 64.8, 87.8, 158.3. Anal. Calcd for $C_{11}H_{20}BF_4NO_2S$: C, 41.66; H, 6.36; N, 4.42. Found : C, 41.30; H, 6.24; N, 4.59.

*Cyclic Sulfides **5** and **8***. To a dry flask was added $LiAlH_4$ (2.22 g, 55.51 mmol, 1.3 equiv), and the flask was purged under Ar. At 0 °C, dry THF (150 mL) was added, followed by L-valine (5.0 g, 46.7 mmol, 1.0 equiv) portionwise. The reaction mixture was then heated at reflux for 1 h and after this time cooled to 0 °C. An aqueous KOH solution (4.2 mL, 4.4 M) was carefully added, and then the crude mixture was stirred and heated under reflux for 30 min. The resulting crude mixture was allowed to warm to room temperature, filtered through Celite, and washed with THF. The solvents were then evaporated under reduced pressure to recover finally L-valinol (4.21 g, 87%) as a yellow oil that was used in the next reaction without further purification. To a solution of L-valinol (1.14 g, 11.05 mmol, 1.2 equiv) in dry THF (21 mL) was added *n*-BuLi (1.15 mL, 1.6 M in hexanes, 1.84 mmol, 0.2 equiv) at 0 °C. After 10 min at this temperature, a solution of ester **11**[11] (1.90 g, 9.21 mmol, 1.0 equiv) in dry THF (5 mL) was added. The mixture was then stirred for 18 h and quenched by the addition of a saturated aqueous NH_4Cl solution. The resulting mixture was extracted three times with EtOAc, and the combined organic extracts washed with brine, dried over anhydrous $MgSO_4$, and filtered. The solvents were evaporated under reduced pressure, and the resulting crude (2.51 g) was used in the next reaction without further purification. The previous crude product (2.51 g, 9.05 mmol, 1.0 equiv) was dissolved in dry CH_2Cl_2 (16 mL), and $BF_3 \cdot OEt_2$ (1.4 mL, 11.05 mmol, 1.2 equiv) was added at room temperature. After 96 h, the crude reaction was treated with a saturated aqueous $NaHCO_3$ solution, which was carefully added until no more CO_2 release was observed. The crude mixture was then extracted three times with CH_2Cl_2, and the organic extracts washed with brine, dried over anhydrous $MgSO_4$, and filtered. After evaporation of the solvent under reduced pressure, the crude was purified by flash column chromatography (silica gel, 30% EtOAc to 50% EtOAc in hexanes) to obtain compounds **5**[32] (747 mg, 38%) and its diastereoisomer **8**[11] (399 mg, 20%) as white solids. **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (d, J = 7.0 Hz, 3 H), 0.86 (d, J = 7.0 Hz, 3 H), 2.05 (dddd, J = 14.1, 12.4, 10.0, 3.5 Hz, 1 H), 2.24 (dddd, J = 14.1, 4.4, 2.9, 1.3 Hz, 1 H), 2.45 (dtd, J = 14.0, 7.0 3.9 Hz, 1 H), 2.78 (dddd, J = 6.0, 4.8, 3.6, 1.6 Hz, 1 H), 2.94 (ddd, J = 14.4, 12.3, 2.9 Hz, 1 H), 3.18 (dd, J = 14.6, 1.6 Hz, 1 H), 3.26 (d, J = 14.6 Hz, 1 H), 3.92 (dd, J = 9.1, 2.6 Hz, 1 H), 3.97 (dd, J = 9.1, 6.3 Hz, 1 H), 4.15 (ddd, J = 6.4, 3.7, 2.8 Hz, 1 H), 5.24 (dd, J = 10.0, 0.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8, 19.2, 27.5, 29.6, 36.2, 36.5, 61.7, 65.3, 90.2, 167.9. **8**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, J = 6.7 Hz, 3 H), 0.98 (d, J = 6.9 Hz, 3 H), 1.81−1.98 (m, 2 H), 2.40 (td, J = 13.9, 3.2 Hz, 1 H), 2.78 (td, J = 14.6, 7.0, 3.8 Hz, 1 H), 2.96 (ddd, J = 14.6, 12.8, 2.7 Hz, 1 H), 3.21 (s, 2 H), 3.66 (dd, J = 8.8, 5.6 Hz, 1 H), 3.94 (d, J = 8.8 Hz, 1 H), 4.00 (dd, J = 8.4, 5.6 Hz, 1 H), 5.03 (d, J = 9.7 Hz, 1 H); ^{13}C NMR (100 MHz, D_2O) δ 18.9, 30.6, 30.7, 36.5, 36.8, 61.7, 67.4, 89.8, 170.0; FAB HRMS (NBA) m/e 216.1062, M + H$^+$ calcd for $C_{10}H_{17}NO_2S$ 216.1058.

*Sulfonium Salt **9***. Sulfonium salt **9** (409 mg, 70%) was obtained from sulfide 8 (381 mg, 1.77 mmol) following the same procedure as described before for **6**. **9**: white solid; mp 185−187 °C; ^{1}H NMR (400 M + Hz, DMSO-d_6) δ 0.86 (d, J = 6.7 Hz, 3 H), 0.89 (d, J = 6.6 Hz, 3 H), 1.79 (sext, J = 6.8 Hz, 1 H), 1.90 (sext, J = 8.0 Hz, 1 H), 2.65 (d, J = 15.2 Hz, 1 H), 3.01 (s, 3 H), 3.70−3.80 (m, 3 H), 3.96−4.06 (m, 3 H), 4.62 (d, J = 14.0 Hz, 1 H), 5.29 (d, J = 9.6 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 18.8, 19.0, 26.1, 30.2, 31.7, 40.4, 44.2, 62.0, 67.2, 88.0, 161.8. Anal. Calcd for $C_{11}H_{20}BF_4NO_2S$: C, 41.66; H, 6.36; N, 4.42. Found : C, 41.54; H, 6.28; N, 4.53.

Table 3. Reactions of Sulfur Ylides Derived from Sulfonium Salts 15 and 16 with Aldehydes



entry	aldehyde	epoxyamide (yield %; de %)	epoxyalcohol (yield %)[c]
1	PhCHO	**17a** (76; >98)[a]	**3a** (96)
2	4-MeC$_6$H$_4$CHO	**17b** (60; >98)[a]	**3b** (87)
3	2-MeC$_6$H$_4$CHO	**17c** (76; >98)[a]	**3c** (54)
4	4-MeOC$_6$H$_4$CHO	**17d** (70; >98)[a]	**3d** (73)
5	4-ClC$_6$H$_4$CHO	**17e** (50; >98)[a]	**3e** (50)
6	(CH$_3$)$_2$CHCHO	**17g** (48; >98)[a]	**3g** (47)
7	Chx-CHO	**17h** (49; >98)[a]	**3h** (69)
8	CH$_3$(CH$_2$)$_5$CHO	**17i** (51; >98)[b]	**3i** (85)
9	PhCHO	**18a** (57; >98)[b]	**4a** (50)
10	4-MeC$_6$H$_4$CHO	**18b** (90; >98)[b]	**4b** (34)
11	2-MeC$_6$H$_4$CHO	**18c** (60; >98)[a]	**4c** (44)
12	4-MeOC$_6$H$_4$CHO	**18d** (72; >98)[a]	**4d** (52)
13	4-ClC$_6$H$_4$CHO	**18e** (78; >98)[a]	**4e** (37)
14	(CH$_3$)$_2$CHCHO	**18g** + its *cis* isomer (77; *E*:*Z* 1.3:1)[b]	**4g** + its *cis* isomer (41; *E*:*Z* 1.3:1)
15	Chx-CHO	**18h** + its *cis* isomer (83; *E*:*Z* 2.1:1)[b]	**4h** + its *cis* isomer (45; *E*:*Z* 2.1:1)

[a] 1.0 equiv of **15** or **16**, 1.1 equiv of a 3.0 M aqueous NaOH or 1.1 equiv of Na^{t}BuO, ^{t}BuOH, 25 °C, 3 h; then 1.0 equiv of RCHO, overnight. [b] 1.0 equiv of **15** or **16**, 1.0 equiv of a 1.0 M aqueous NaOH, ^{t}BuOH/DMSO (10/1), 25 °C, 1 h; then 1.0 equiv of RCHO, overnight. [c] 2.5 equiv of Super-H, THF, 0 °C, 0.5 h.

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Amide **12**. To a dry flask was added $LiAlH_4$ (1.33 g, 33.3. mmol, 1.0 equiv), and the flask was purged under argon. After addition at 0 °C of dry THF (100 mL), L-benzylserine (5.0 g, 25.6 mmol, 1.0 equiv) was added portionwise. After completion of the addition, the reaction mixture was refluxed for 1 h, then cooled to 0 °C and treated with an aqueous KOH solution (5.0 mL, 4.4 M) which was carefully added. The resulting suspension was then heated at reflux for 30 min. After this time, the crude mixture was allowed to recover room temperature, filtered through Celite, and the solids washed with THF. The solvents were then evaporated under reduced pressure, to obtain L-benzylserinol (4.28 g, 92%) as a yellow oil that was used in the next reaction without further purification. To a solution of the resulting aminoalcohol (2.0 g, 11.05 mmol, 1.2 equiv) in dry THF (21 mL) and at 0 °C was added *n*-BuLi (1.15 mL, 1.6 M in hexanes, 1.84 mmol, 0.2 equiv) dropwise. After 10 min, a solution of the ester **11** (1.9 g, 9.2 mmol, 1.0 equiv) in dry THF (5 mL) was added. The mixture was then stirred for 18 h, after which it was treated with a saturated aqueous NH_4Cl solution. The resulting mixture was extracted three times with EtOAc, and the organic extracts were washed with brine, dried over anhydrous $MgSO_4$, and filtered. After evaporation of the solvents under reduced pressure, the resulting crude was purified by flash column chromatography (silica gel, 100% EtOAc) to yield compound **12** (2.44 g, 75% over two steps) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.85−1.91 (m, 2 H), 2.57−2.62 (m, 2 H), 3.18 (s, 2 H), 3.38 (m, 2 H), 3.55 (dd, J = 9.6, 4.7 Hz, 1 H), 3.60−3.67 (m, 2 H), 3.71−3.78 (m, 3H), 3.85−3.89 (m, 1 H), 4.07 (tt, J = 9.2, 4.6 Hz, 1 H), 4.48 (s, 2 H), 4.86 (t, J = 4.5 Hz, 1 H), 7.21−7.33 (m, 5 H), 7.40 (d, J = 8.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.1, 33.2, 36.1. 50.8, 62.5, 64.7, 69.4, 73.1, 102.6, 127.4, 127.6, 128.2, 137.5, 169.0; FAB HRMS (NBA) m/e 356.1538, M + H^+ calcd for $C_{17}H_{25}NO_5S$ 356.1532.

Sulfides ***13*** *and* ***14***. A solution of amide **12** (1.95 g, 5.5 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was treated with $BF_3\cdot OEt_2$ (0.84 mL, 6.6 mmol, 1.2 equiv) in exactly the same manner as for the L-valinol derivative, described above, to obtain cyclic sulfides **13** (761 mg, 47%) and **14** (381 mg, 23%) as white solids. **13**: mp 92−96 °C; $[\alpha]^{25}_D$ = +73.5° (*c* 2.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99−2.01 (m, 1 H), 2.19−2.27 (m, 1 H), 2.73−2.81 (m, 1 H), 2.92 (ddd, J = 14.9, 12.3, 2.8 Hz, 1 H), 3.16 (s, 2 H), 3.43 (t, J = 8.7 Hz, 1 H), 3.76 (dd, J = 8.9, 3.4 Hz, 1 H), 4.04−4.13 (m, 2 H), 4.35 (ddt, J = 5.8, 3.4, 2.4 Hz, 1 H), 4.46 (d, J = 11.9 Hz, 1 H), 4.52 (d, J = 11.9 Hz, 1 H), 5.21 (dd, J = 10.0, 1.0 Hz, 1 H), 7.23−7.34 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.7, 35.9, 36.4, 56.1, 67.8, 73.2, 89.9, 127.6, 128.3, 137.9, 168.0; FAB HRMS (NBA) m/e 294.1157, M + H^+ calcd for $C_{15}H_{19}NO_3S$ 294.1164. **14**: mp 91−95 °C; $[\alpha]^{25}_D$ = −28.4° (*c* 2.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66−1.72 (m, 1 H), 2.32 (d, J = 14.2 Hz, 1 H), 2.66 (dt, J = 14.8, 3.7 Hz, 1 H), 2.86 (ddd, J = 14.9, 12.8, 2.5 Hz, 1 H), 3.10 (s, 2 H), 3.37 (t, J = 9.0 Hz, 1 H), 3.57 (dd, J = 9.0, 3.9 Hz, 1 H), 3.71 (dd, J = 8.8, 5.7 Hz, 1 H), 4.08 (d, J = 8.8 Hz, 1 H), 4.33 (dt, J = 9.1, 4.6 Hz, 1 H), 4.45 (d, J = 11.9 Hz, 1 H), 4.48 (d, J = 11.9 Hz, 1 H), 4.97 (d, J = 9.5 Hz, 1 H), 7.14−7.26 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.6, 36.6, 37.2, 56.0, 67.9, 68.4, 73.3, 90.0, 127.7, 128.4, 137.9, 169.3; FAB HRMS (NBA) m/e 294.1161, M + H^+ calcd for $C_{15}H_{19}NO_3S$ 294.1164.

Sulfonium Salt ***15***. Sulfonium salt **15** (687 mg, 81%) was obtained from sulfide **13** (634 mg, 2.16 mmol) following the same procedure as described before for **6**. **15**: white solid; mp 142−144 °C; $[\alpha]^{25}_D$ = +17.5° (*c* 0.4, H_2O); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.23−2.40 (m, 2 H), 2.91 (s, 3 H), 3.28 (t, J = 8.6 Hz, 2 H), 3.54−3.65 (m, 1 H), 3.66−3.77 (m, 1 H), 3.87−3.97 (m, 2 H), 3.99−4.05 (m, 1 H), 4.12−4.20 (bs, 1 H), 4.36−4.53 (m, 3 H), 5.41 (d, J = 7.1 Hz, 1 H), 7.18−7.33 (m, 5 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 26.2, 30.5, 43.6, 56.0, 66.7, 67.3, 72.2, 87.6, 127.5, 128.2, 138.0, 158.6. Anal. Calcd for $C_{16}H_{22}NO_3SBF_4$ C, 48.66; H, 5.61; N, 3.54; S, 8.11; O, 12.14. Found : C, 48.51; H, 5.38; N, 3.78; S, 7.97; O, 12.55.

Sulfonium Salt ***16***. Sulfonium salt **16** (397 mg, 81%) was obtained from sulfide **14** (320 mg, 1.49 mmol) following the same procedure as described before for **6**. **16**: white solid; mp 147−149 °C; $[\alpha]^{23}_D$ = +39.2° (*c* 0.51, H_2O); ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.90−2.00 (m, 1 H), 2.60 (td, J = 15.3, 3.1 Hz, 1 H), 3.01 (s, 3 H), 3.45 (d, J = 5.8 Hz, 2 H), 3.70−3.76 (m, 2 H), 3.89 (dd, J = 8.6, 6.1 Hz, 1 H), 4.01−4.05 (m, 2 H), 4.37 (c, J = 5.4 Hz, 1 H), 4.52 (s, 2 H), 4.59 (d, J = 13.7 Hz, 1 H), 5.33 (d, J = 9.4 Hz, 1 H), 7.28−7.39 (m, 5 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 26.2, 31.7, 43.9, 56.0, 67.5, 68.1, 72.3, 88.1, 127.6, 128.4, 138.1, 160.6. Anal. Calcd for $C_{16}H_{22}NO_3SBF_4$ C, 48.66; H, 5.61; N, 3.54; S, 8.11; O, 12.14. Found : C, 48.55; H, 5.48; N, 3.75; S, 7.88; O, 12.35.

Synthesis of Epoxyamides 7, 10, 17, and 18. *General Procedure A.* To a suspension of the sulfonium salt (**6**, **9**, **15**, or **16**) (1.0 equiv) in *t*BuOH (0.1 M) was added a 3.0 M aqueous NaOH solution (1.0 equiv) at room temperature. After 3 h at this temperature, a solution of aldehyde (1.1 equiv) in *t*BuOH (0.1 M) was added, and the resulting reaction mixture was stirred overnight. The crude mixture was then diluted with AcOEt, and the organic solution was sequentially washed with saturated aqueous NH_4Cl solution and brine. The organic layer was then separated, dried ($MgSO_4$), and filtered. Concentration under reduced pressure provided a crude product that was purified by flash column chromatography (silica gel, AcOEt in hexanes in a range of 20−50% of AcOEt) to afford the corresponding epoxy amide.

General Procedure B. To a suspension of the sulfonium salt (**6**, **9**, **15** or **16**) (1.0 equiv) in *t*BuOH (0.1 M) was added DMSO (*t*BuOH/DMSO: 10/1) followed by a 1.0 M aqueous NaOH solution (1.0 equiv) at room temperature. After 1 h at this temperature, a solution of aldehyde (1.1 equiv) in *t*BuOH (0.1 M) was added, and the resulting reaction mixture was stirred overnight. After this time the reaction mixture was worked up in the same way as described above in procedure A, and the resulting crude product was purified by flash column chromatography (silica gel, AcOEt in hexanes) to obtain the corresponding pure epoxy amide.

Epoxy Amide ***7a***. Preparation by procedure A and purification by flash column chromatography (silica gel, 30% EtOAc in hexanes) (80%): colorless oil; $[\alpha]^{30}_D$ = +116.8° (*c* 0.65, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 1.5:1 ratio) δ (major) 0.80 (d, J = 6.8 Hz, 3 H), 0.85 (d, J = 6.9 Hz, 3 H), 1.67 (s, 3 H), 1.69−1.77 (m, 1 H), 1.81−1.93 (m, 2 H), 2.35−2.49 (m, 1 H), 2.51−2.63 (m, 1 H), 3.47 (d, J = 1.8 Hz, 1 H), 3.95 (dd, J = 9.5, 1.4 Hz, 1 H), 3.99−4.04 (m, 2 H), 4.14−4.18 (m, 1 H), 5.59 (dd, J = 8.7, 1.8 Hz, 1 H), 7.24−7.38 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 15.7, 19.3, 27.5, 29.3, 30.7, 32.5, 34.3, 58.2, 58.4, 60.4, 65.8, 89.9, 125.5, 128.7, 128.9, 135.1, 164.3; FAB HRMS (NBA) m/e 336.1639, M + H^+ calcd for $C_{18}H_{25}NO_3S$ 336.1633.

Epoxy Amide ***7b***. Preparation by procedure B and purification by flash column chromatography (silica gel, 30% EtOAc in hexanes) (89%): colorless oil; $[\alpha]^{25}_D$ = +106.8° (*c* 1.0, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) (two rotamers in a 1.5:1 ratio) δ (major) 0.82 (d, J = 7.2 Hz, 3 H), 0.85 (d, J = 7.2 Hz, 3 H), 1.61−1.76 (m, 1 H), 1.73 (s, 3 H), 2.04−2.14 (m, 2 H), 2.33 (s, 3 H), 2.41−2.66 (m, 2 H), 3.46 (d, J = 2.0 Hz, 1 H), 3.81−4.09 (m, 3 H), 4.10−4.22 (m, 1 H), 5.57 (dd, J = 8.6, 1.7 Hz, 1 H), 7.11−7.17 (m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (major) 15.0, 15.2, 19.3, 21.2, 27.5, 29.3, 30.9, 32.5, 34.5, 58.3, 58.5, 60.4, 65.8, 87.7, 90.0, 125.7, 127.9, 129.4, 164.3; FAB HRMS (NBA) m/e 350.1785, M + H^+ calcd for $C_{19}H_{27}NO_3S$ 350.1790.

Epoxy Amide ***7c***. Preparation by procedure B and purification by flash column chromatography (silica gel, 30% EtOAc in hexanes) (73%): colorless oil; $[\alpha]^{25}_D$ = +62.5° (*c* 1.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 1.6:1 ratio) δ (major) 0.84 (d, J = 7.0 Hz, 3 H), 0.88 (d, J = 6.7 Hz, 3 H), 1.68−1.74 (m, 1 H), 1.74 (s, 3 H), 1.74−2.00 (m, 2 H), 2.36 (s, 3 H), 2.40−2.65 (m, 2 H), 3.37 (d, J = 1.9 Hz, 1 H), 3.94 (dd, J = 9.5, 1.1 Hz, 1 H), 4.00−4.06 (m, 1 H), 4.14−4.21 (m, 1 H), 4.21 (d, J = 1.8 Hz, 1 H), 5.61 (dd, J = 8.8, 1.8 Hz, 1 H),

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7.10−7.28 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.6, 18.7, 19.3, 29.3, 30.6, 32.6, 34.3, 56.4, 57.3, 60.3, 65.6, 89.9, 123.8, 126.3, 128.4, 130.1, 133.4, 136.2, 164.5; FAB HRMS (NBA) *m/e* 350.1779, M + H^+ calcd for $C_{19}H_{27}NO_3S$ 350.1790.

Epoxy Amide ***7d***. Preparation by procedure B and purification by flash column chromatography (silica gel, 30% EtOAc in hexanes) (75%): colorless oil; $[\alpha]^{25}_D$ = +127.3° (*c* 1.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 1.5:1 ratio) δ (major) 0.81 (d, *J* = 6.9 Hz, 3 H), 0.84 (d, *J* = 6.9 Hz, 3 H), 1.64−1.78 (m, 1 H), 1.73 (s, 3 H), 1.80−1.93 (m, 2 H), 2.35−2.64 (m, 2 H), 3.46 (d, *J* = 1.9 Hz, 1 H), 3.78 (s, 3 H), 3.97 (d, *J* = 1.8 Hz, 1 H), 3.99−4.04 (m, 2 H), 4.13−4.18 (m, 1 H), 5.57 (dd, *J* = 8.8, 1.8 Hz, 1 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 7.18 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.8, 19.3, 27.5, 29.2, 30.7, 32.5, 34.4, 55.3, 58.2, 60.4, 61.1, 65.8, 89.9, 114.2, 127.0, 160.1, 164.5; FAB HRMS (NBA) *m/e* 366.1745, M + H^+ calcd for $C_{19}H_{27}NO_4S$ 366.1739.

Epoxy Amide ***7e***. Preparation by procedure A and purification by flash column chromatography (silica gel, 50% EtOAc in hexanes) (76%): colorless oil; $[\alpha]^{25}_D$ = +127.5° (*c* 1.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 1.5:1 ratio) δ (major) 0.84 (d, *J* = 6.9 Hz, 3 H), 0.88 (d, *J* = 6.9 Hz, 3 H), 1.71−1.80 (m, 1 H), 1.79 (s, 3 H), 1.84−1.96 (m, 2 H), 2.37−2.67 (m, 2 H), 3.45 (d, *J* = 1.8 Hz, 1 H), 4.00 (d, *J* = 1.8 Hz, 1 H), 4.01−4.08 (m, 2 H), 4.16−4.20 (m, 1 H), 5.60 (dd, *J* = 8.8, 1.8 Hz, 1 H), 7.23 (d, *J* = 8.5 Hz, 2 H), 7.35 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) = 15.2, 19.3, 29.2, 30.6, 32.6, 34.5, 57.5, 58.0, 60.4, 61.2, 65.8, 89.9, 109.5, 126.9, 129.0, 133.7, 134.7, 163.9; FAB HRMS (NBA) *m/e* 370.1241 M + H^+ calcd for $C_{18}H_{24}ClNO_3S$ 370.1244.

Epoxy Amide ***7f***. Preparation by procedure A and purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) (41%): colorless oil; $[\alpha]^{25}_D$ = +49.8° (*c* 0.95, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a ~ 2:1 ratio) δ (major) 0.82−0.90 (m, 3 H), 0.88 (d, *J* = 6.9 Hz, 3 H), 0.95 (d, *J* = 6.9 Hz, 3 H), 0.97−1.05 (m, 2 H), 1.54−1.81 (m, 1 H), 1.86−2.13 (m, 2 H), 2.08 (s, 3 H), 2.29−2.40 (m, 1 H), 2.49−2.63 (m, 1 H), 3.09 (dt, *J* = 6.3, 2.0 Hz, 1 H), 3.25 (d, *J* = 2.0 Hz, 1 H), 4.00 (dd, *J* = 10.0, 4.9 Hz, 1 H), 4.05 (dd, *J* = 10.0, 3.5 Hz, 1 H), 4.10−4.15 (m, 1 H), 5.54 (dd, *J* = 8.8, 1.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) (major) δ 9.5, 15.7, 19.4, 24.5, 29.3, 30.9, 32.6, 43.3, 54.1, 59.7, 60.2, 65.7, 89.8, 165.6; FAB HRMS (NBA) *m/e* 288.1630, M + H^+ calcd for $C_{14}H_{25}NO_3S$ 288.1633.

Epoxy Amide ***7g***. Preparation by procedure A and purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) (73%): colorless oil; $[\alpha]^{25}_D$ = +39.8° (*c* 1.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 1.8:1 ratio) δ (major) 0.86 (d, *J* = 6.9 Hz, 3 H), 0.94 (d, *J* = 6.9 Hz, 3 H), 0.96 (d, *J* = 6.8 Hz, 3 H), 1.00 (d, *J* = 6.8 Hz, 3 H), 1.61−1.72 (m, 2 H), 1.99−2.11 (m, 1 H), 2.07 (s, 3 H), 2.27−2.37 (m, 1 H), 2.48−2.61 (m, 2 H), 2.93 (dd, *J* = 6.3, 1.8 Hz, 1 H), 3.27 (d, *J* = 1.8 Hz, 1 H), 3.94−4.01 (m, 1 H), 4.00 (d, *J* = 5.8 Hz, 1 H), 4.03−4.07 (m, 1 H), 5.53 (dd, *J* = 8.7, 1.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.5, 18.1, 18.6, 19.4, 29.2, 29.9, 30.7, 32.6, 34.9, 53.3, 60.2, 63.5, 65.6, 89.8, 165.6; FAB HRMS (NBA) *m/e* 302.1798 M + H^+ calcd for $C_{15}H_{27}NO_3S$ 302.1790.

Epoxy Amide ***7h***. Preparation by procedure A and purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) (82%): colorless oil; $[\alpha]^{25}_D$ = +29.2° (*c* 0.88, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 1.5:1 ratio) δ (major) 0.86 (d, *J* = 6.9 Hz, 3 H), 0.94 (d, *J* = 6.9 Hz, 3 H), 1.04−1.25 (m, 5 H), 1.60−1.82 (m, 5 H), 1.87−1.95 (m, 1 H), 2.07 (s, 3 H), 2.27−2.38 (m, 1 H), 2.49−2.61 (m, 2 H), 2.93 (dd, *J* = 6.3, 2.0 Hz, 1 H), 3.29 (d, *J* = 2.0 Hz, 1 H), 3.94−4.01 (m, 1 H), 4.00 (d, *J* = 6.2 Hz, 1 H), 4.03−4.07 (m, 1 H), 5.23 (dd, *J* = 8.7, 1.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.6, 19.4, 25.4, 25.5, 26.0, 28.7, 29.1, 29.5, 30.7, 32.6, 39.3, 53.1, 60.2, 62.7, 65.6, 89.8, 165.7; FAB HRMS (NBA) *m/e* 342.2096, M + H^+ calcd for $C_{18}H_{31}NO_3S$ 342.2103.

Epoxy Amide ***7i***. Preparation by procedure A and purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) (79%): colorless oil; $[\alpha]^{25}_D$ = +12.5° (*c* 0.15, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 1.6:1 ratio) δ (major) 0.86 (t, *J* = 6.6 Hz, 3 H), 0.88 (d, *J* = 6.9 Hz, 3 H), 0.95 (d, *J* = 6.9 Hz, 3 H), 1.23−1.39 (m, 7 H), 1.40−1.59 (m, 3 H), 1.64−1.73 (m, 1 H), 1.88−1.93 (m, 1 H), 2.09 (s, 3 H), 2.30−2.40 (m, 1 H), 2.51−2.61 (m, 2 H), 3.10 (ddd, *J* = 6.2, 4.6, 1.8 Hz, 1 H), 3.22 (d, *J* = 1.9 Hz, 1 H), 3.83 (d, *J* = 11.9 Hz, 1 H), 3.99−4.06 (m, 2 H), 5.54 (dd, *J* = 8.7, 1.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 14.0, 14.6, 18.6, 22.9, 24.5, 28.1, 29.3, 29.6, 31.5, 31.7, 34.4, 53.0, 56.3, 60.4, 69.4, 87.6, 165.0; FAB HRMS (NBA) *m/e* 344.2264, M + H^+ calcd for $C_{18}H_{32}NO_3S$ 344.2259.

Epoxy Amide ***10a***. Preparation by procedure A and purification by flash column chromatography (silica gel, 30% EtOAc in hexanes) (95%): colorless oil; $[\alpha]^{25}_D$ = −178.5 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 1.6:1 ratio) δ (major) 0.98 (d, *J* = 6.7 Hz, 3 H), 1.05 (d, *J* = 6.9 Hz, 3 H), 1.77−1.91 (m, 2 H), 1.93−2.03 (m, 1 H), 2.13 (s, 3 H), 2.44−2.51 (m, 1 H), 2.58−2.71 (m, 1 H), 3.53 (s, 1 H), 3.71 (dd, *J* = 7.7, 5.8 Hz, 1 H), 3.77 (t, *J* = 7.1 Hz, 1 H), 4.05 (d, *J* = 8.8 Hz, 1 H), 4.15 (s, 1 H), 5.36 (dd, *J* = 7.9, 1.6 Hz, 1 H), 7.30−7.38 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 18.7, 19.8, 29.3, 31.2, 33.7, 57.3, 57.7, 61.9, 68.5, 89.6, 125.7, 128.7, 128.9, 135.4, 165.8; FAB HRMS (NBA) *m/e* 336.1628, M + H^+ calcd for $C_{18}H_{25}NO_3S$ 336.1633.

Epoxy Amide ***10b***. Preparation by procedure B and purification by flash column chromatography (silica gel, 30% EtOAc in hexanes) (73%): colorless oil; $[\alpha]^{25}_D$ = −130.5 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 1.7:1 ratio) δ (major) 0.95 (d, *J* = 6.7 Hz, 3 H), 1.03 (d, *J* = 6.9 Hz, 3 H), 1.75−1.88 (m, 2 H), 1.92−2.01 (m, 1 H), 2.11 (s, 3 H), 2.34 (s, 3 H), 2.42−2.51 (m, 1 H), 2.56−2.69 (m, 1 H), 3.51 (d, *J* = 1.7 Hz, 1 H), 3.68 (dd, *J* = 7.9, 5.7 Hz, 1 H), 3.74 (dd, *J* = 8.8, 5.5 Hz, 1 H), 4.03 (d, *J* = 8.4 Hz, 1 H), 4.09 (d, *J* = 1.7 Hz, 1 H), 5.34 (dd, *J* = 8.1, 2.4 Hz, 1 H), 7.13−7.20 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 18.8, 19.8, 21.2, 29.2, 31.2, 33.7, 57.2, 57.7, 61.9, 68.5, 89.5, 125.7, 129.4, 132.3, 138.9, 166.0; FAB HRMS (NBA) *m/e* 350.1792, M + H^+ calcd for $C_{19}H_{27}NO_3S$ 350.1790.

Epoxy Amide ***10c***. Preparation by procedure B and purification by flash column chromatography (silica gel, 30% EtOAc in hexanes) (63%): colorless oil; $[\alpha]^{25}_D$ = −117.0 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 1.7:1 ratio) δ (major) 0.99 (d, *J* = 6.7 Hz, 3 H), 1.05 (d, *J* = 7.0 Hz, 3 H), 1.78−1.87 (m, 1 H), 1.89−2.06 (m, 2 H), 2.14 (s, 3 H), 2.40 (s, 3 H), 2.44−2.55 (m, 1 H), 2.59−2.72 (m, 1 H), 3.45 (d, *J* = 1.8 Hz, 1 H), 3.73−3.81 (m, 2 H), 4.08 (d, *J* = 8.8 Hz, 1 H), 4.31 (d, *J* = 1.8 Hz, 1 H), 5.40 (dd, *J* = 8.1, 2.6 Hz, 1 H), 7.17−7.28 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 14.9, 15.9, 18.6, 19.3, 29.4, 30.6, 34.3, 56.4, 60.3, 61.1, 65.6, 87.6, 123.9, 126.2, 128.3, 130.1, 133.4, 136.2, 164.5; FAB HRMS (NBA) *m/e* 350.1786, M + H^+ calcd for $C_{19}H_{27}NO_3S$ 350.1790.

Epoxy Amide ***10d***. Preparation by procedure B and purification by flash column chromatography (silica gel, 50% EtOAc in hexanes) (86%): colorless oil; $[\alpha]^{25}_D$ = −264.9 (*c* 0.7, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 1.7:1 ratio) δ (major) 0.97 (d, *J* = 6.7 Hz, 3 H), 1.05 (d, *J* = 6.9 Hz, 3 H), 1.73−1.92 (m, 2 H), 1.94−2.02 (m, 1 H), 2.12 (s, 3 H), 2.43−2.53 (m, 1 H), 2.57−2.70 (m, 1 H), 3.52 (d, *J* = 1.6 Hz, 1 H), 3.71 (dd, *J* = 7.8, 5.7 Hz, 1 H), 3.76 (dd, *J* = 8.8, 5.6 Hz, 1 H), 3.80 (s, 3 H), 4.03 (s, 1 H), 4.09 (d, *J* = 1.2 Hz, 1 H), 5.35 (dd, *J* = 8.0, 2.2 Hz, 1 H), 6.89 (d, *J* = 8.6 Hz, 2 H), 7.22 (d, *J* = 8.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 18.7, 19.8, 29.2, 31.2, 33.7, 55.3, 57.2, 57.6, 61.9, 68.5, 89.5, 114.2, 127.1, 160.2, 166.1; FAB HRMS (NBA) *m/e* 366.1742, M + H^+ calcd for $C_{19}H_{27}NO_4S$ 366.1739.

Epoxy Amide ***10e***. Preparation by procedure B and purification by flash column chromatography (silica gel, 50% EtOAc in hexanes) (76%): colorless oil; $[\alpha]^{25}_D$ = −152.5 (*c* 0.5, CH_2Cl_2); ^{1}H NMR

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(400 MHz, $CDCl_3$) (two rotamers in a 1.6:1 ratio) δ (major) 0.98 (d, J = 6.7 Hz, 3 H), 1.05 (d, J = 6.2 Hz, 3 H), 1.78−2.05 (m, 3 H), 2.13 (s, 3 H), 2.43−2.54 (m, 1 H), 2.58−2.71 (m, 1 H), 3.47 (d, J = 1.6 Hz, 1 H), 3.69 (dd, J = 7.9, 5.7 Hz, 1 H), 3.78 (dd, J = 8.9, 5.4 Hz, 1 H), 4.06 (d, J = 9.0 Hz, 1 H), 4.14 (d, J = 1.1 Hz, 1 H), 5.35 (dd, J = 7.5, 1.8 Hz, 1 H), 7.25 (d, J = 8.4 Hz, 2 H), 7.35 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 18.7, 19.8, 29.3, 31.3, 33.7, 57.4, 62.0, 68.5, 89.6, 127.0, 129.0, 134.8, 165.5; FAB HRMS (NBA) m/e 370.1239 M + H^+ calcd for $C_{18}H_{24}ClNO_3S$ 370.1244.

Epoxy Amide ***10f***. Preparation by procedure B and purification by flash column chromatography (silica gel, 50% EtOAc in hexanes) (54% combined yield of **10f** together with its *cis* isomer **7′f**): colorless oil; $[\alpha]^{25}_D$ = −48.9 (c 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of *E*:*Z* isomers in a 1.3:1 proportion and the *E* isomer as two rotamers in a 1.9:1 ratio) δ (*E* isomer, major rotamer) 0.90−1.03 (m, 9 H), 1.57−1.81 (m, 3 H), 1.92−2.00 (m, 2 H), 2.10 (s, 3 H), 2.57−2.64 (m, 2 H), 3.16 (s, 1 H), 3.27 (s, 1 H), 3.70−3.82 (m, 2 H), 4.05 (d, J = 8.8 Hz, 1 H), 5.29 (d, J = 7.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 9.7, 15.1, 18.7, 19.7, 24.5, 29.3, 31.1, 33.8, 53.2, 59.1, 62.0, 68.4, 89.5, 167.1; FAB HRMS (NBA) m/e 288.1628, M + H^+ calcd for $C_{14}H_{25}NO_3S$ 288.1633.

Epoxy Amide ***10g***. Preparation by procedure B and purification by flash column chromatography (silica gel, 50% EtOAc in hexanes) (57% combined yield of **10g** together with its *cis* isomer **7′g**): colorless oil; $[\alpha]^{25}_D$ = −43.4 (c 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of *E*:*Z* isomers in a 1.3:1 proportion and the *E* isomer as two rotamers in a 1.6:1 ratio) δ (*E* isomer, major rotamer) 0.86−1.12 (m, 12 H), 1.52−1.70 (m, 1 H), 1.74−1.85 (m, 1 H), 1.90−2.01 (m, 2 H), 2.10 (s, 3 H), 2.58−2.69 (m, 2 H), 2.99 (d, J = 6.5 Hz, 1 H), 3.30 (s, 1 H), 3.63−3.81 (m, 2 H), 4.05 (d, J = 8.4 Hz, 1 H), 5.31 (dd, J = 3.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 18.7, 18.9, 20.0, 26.5, 29.3, 30.0, 31.0, 34.1, 52.6, 54.1, 62.0, 68.5, 89.3, 166.7; FAB HRMS (NBA) m/e 302.1786 M + H^+ calcd for $C_{15}H_{27}NO_3S$ 302.1790.

Epoxy Amide ***10h***. Preparation by procedure B and purification by flash column chromatography (silica gel, 50% EtOAc in hexanes) (86% combined yield of **10h** together with its *cis* isomer **7′h**): colorless oil; $[\alpha]^{25}_D$ = −37.2 (c 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of *E*:*Z* isomers in a 1.4:1 proportion and the *E* isomer as two rotamers in a 1.7:1 ratio) δ (*E* isomer, major rotamer) 0.90−1.06 (m, 6 H), 1.11−1.40 (m, 7 H), 1.66−1.87 (m, 5 H), 1.93−2.02 (m, 2 H), 2.11 (s, 3 H), 2.57−2.68 (m, 2 H), 3.00 (dd, J = 6.6, 1.8 Hz, 1 H), 3.33 (d, J = 1.9 Hz, 1 H), 3.63−3.78 (m, 2 H), 4.06 (d, J = 8.4 Hz, 1 H), 5.30−5.33 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 18.7, 25.3, 25.5, 26.0, 28.8, 29.1, 29.2, 29.5, 31.0, 35.6, 39.4, 52.4, 53.7, 62.1, 68.5, 89.3, 166.8; FAB HRMS (NBA) m/e 342.2106, M + H^+ calcd for $C_{18}H_{31}NO_3S$ 342.2103.

Epoxy Amide ***10i***. Preparation by procedure B and purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) (77% combined yield of **10i** together with its *cis* isomer **7′i**): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of *E*:*Z* isomers in a 1.4:1 proportion and the *E* isomer as two rotamers in a 2:1 ratio) δ (*E* isomer, major rotamer) 0.85 (t, J = 6.9 Hz, 3 H), 0.99 (d, J = 6.6 Hz, 3 H), 1.04 (d, J = 6.9 Hz, 3 H), 1.21−1.36 (m, 7 H), 1.40−1.50 (m, 2 H), 1.54−1.65 (m, 1 H), 1.72−1.84 (m, 1 H), 1.91−2.00 (m, 2 H), 2.09 (s, 3 H), 2.55−2.67 (m, 2 H), 3.17 (td, J = 5.3, 1.1 Hz, 1 H), 3.25 (d, J = 1.2 Hz, 1 H), 3.69−3.82 (m, 2 H), 4.05 (d, J = 8.7 Hz, 1 H), 5.30 (dd, J = 7.9, 2.3 Hz, 1 H), 7.22−7.36 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 14.0, 15.2, 15.8, 19.3, 22.5, 25.7, 27.6, 28.9, 29.3, 29.5, 30.8, 31.6, 54.4, 55.1, 58.8, 65.7, 87.7, 89.9, 165.6; FAB HRMS (NBA) m/e 344.2261, M + H^+ calcd for $C_{18}H_{32}NO_3S$ 344.2259.

Epoxy Amide ***17a***. Preparation by procedure A and purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) (76%): colorless oil; $[\alpha]^{25}_D$ = +127.0 (c 1.9, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 2.3:1 ratio) δ (major) 1.66−1.79 (m, 2 H), 2.11 (s, 3 H), 2.38−2.49 (m, 1 H), 2.51−2.65 (m, 1 H), 3.33 (dd, J = 9.2, 6.5 Hz, 1 H) 3.37−3.43 (m, 2 H), 3.59 (d, J = 1.9 Hz, 1 H), 3.96−4.03 (m, 2 H), 4.05 (d, J = 1.9 Hz, 1 H), 4.28 (d, J = 12.1 Hz, 1 H), 4.33 (d, J = 12.1 Hz, 1 H), 5.56 (dd, J = 8.9, 1.9 Hz, 1 H), 7.21−7.28 (m, 6 H), 7.30−7.36 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 29.3, 30.7, 55.3, 58.2, 67.9, 70.5, 73.5, 89.6, 125.7, 127.7, 128.0, 128.5, 128.7, 127.8, 128.9, 135.4, 164.8; FAB HRMS (NBA) m/e 414.1745, M + H^+ calcd for $C_{23}H_{27}NO_4S$ 414.1739.

Epoxy Amide ***17b***. Preparation by procedure A and purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) (60%): colorless oil; $[\alpha]^{25}_D$ = +136.0 (c 1.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 2.3:1 ratio) δ (major) 1.65−1.75 (m, 2 H), 2.07 (s, 3 H), 2.30 (s, 3 H), 2.33−2.46 (m, 1 H), 2.48−2.60 (m, 1 H), 3.30 (dd, J = 9.2, 6.3 Hz, 1 H) 3.34−3.41 (m, 2 H), 3.53 (d, J = 1.9 Hz, 1 H), 3.90−3.95 (m, 2 H), 3.97 (d, J = 1.7 Hz, 1 H), 4.18−4.27 (m, 2 H), 5.52 (dd, J = 8.9, 1.9 Hz, 1 H), 6.99−7.03 (m, 1 H), 7.09−7.11 (m, 4 H), 7.18−7.23 (m, 3 H), 7.25−7.29 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 21.2, 29.3, 30.7, 55.2, 58.3, 67.9, 70.5, 73.5, 89.6, 125.7, 127.7, 128.0, 128.4, 129.3, 132.3, 137.1, 138.7, 164.9; FAB HRMS (NBA) m/e 428.1908, M + H^+ calcd for $C_{24}H_{29}NO_4S$ 428.1896.

Epoxy Amide ***17c***. Preparation by procedure A and purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) (76%): colorless oil; $[\alpha]^{25}_D$ = +71.8 (c 2.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 2.1:1 ratio) δ (major) 1.71−1.82 (m, 2 H), 2.12 (s, 3 H), 2.39 (s, 3 H), 2.41−2.66 (m, 2 H), 3.38−3.49 (m, 2 H), 3.53 (d, J = 1.9 Hz, 1 H), 4.07−4.12 (m, 3 H), 4.25 (d, J = 1.9 Hz, 1 H), 4.34 (s, 2 H), 5.59 (dd, J = 8.9, 1.9 Hz, 1 H), 7.07−7.12 (m, 1 H), 7.13−7.28 (m, 6 H), 7.31−7.37 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 18.9, 29.3, 30.5, 55.1, 56.2, 57.2, 67.8, 70.3, 73.5, 89.5, 124.1, 126.2, 127.7, 128.4, 130.1, 133.5, 136.4, 137.0, 165.0; FAB HRMS (NBA) m/e 428.1905, M + H^+ calcd for $C_{24}H_{29}NO_4S$ 428.1896.

Epoxy Amide ***17d***. Preparation by procedure A and purification by flash column chromatography (silica gel, 30% EtOAc in hexanes) (70%): colorless oil; $[\alpha]^{25}_D$ = +123.0 (c 1.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 2.3:1 ratio) δ (major) 1.67−1.76 (m, 2 H), 2.09 (s, 3 H), 2.36−2.50 (m, 1 H), 2.50−2.63 (m, 1 H), 3.30−3.44 (m, 2 H), 3.57 (d, J = 1.9 Hz, 1 H), 3.77 (s, 3 H), 3.91−4.04 (m, 2 H), 3.97 (d, J = 1.7 Hz, 1 H), 4.25 (s, 2 H), 4.44−4.56 (m, 1 H), 5.54 (dd, J = 8.9, 1.8 Hz, 1 H), 6.85 (d, J = 8.7 Hz, 2 H), 7.03−7.08 (m, 1 H), 7.15 (d, J = 8.7 Hz, 2 H), 7.21−7.34 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 29.2, 30.7, 55.2, 58.1, 67.9, 70.5, 73.5, 89.5, 114.2, 127.1, 127.7, 127.9, 128.4, 160.1, 165.0; FAB HRMS (NBA) m/e 444.1856, M + H^+ calcd for $C_{24}H_{29}NO_5S$ 444.1845.

Epoxy Amide ***17e***. Preparation by procedure A and purification by flash column chromatography (silica gel, 30% EtOAc in hexanes) (50%): colorless oil; $[\alpha]^{25}_D$ = +105.7 (c 1.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 2.8:1 ratio) δ (major) 1.60−1.75 (m, 2 H), 2.07 (s, 3 H), 2.33−2.48 (m, 1 H), 2.49−2.61 (m, 1 H), 3.30 (dd, J = 9.2, 6.9 Hz, 1 H), 3.35 (dd, J = 9.9, 3.1 Hz, 1 H), 3.51 (d, J = 1.8 Hz, 1 H), 3.92−3.97 (m, 1 H), 3.97 (d, J = 1.7 Hz, 1 H), 4.05 (dd, J = 9.2, 5.3 Hz, 1 H), 4.24 (s, 2 H), 4.40−4.54 (m, 1 H), 5.52 (dd, J = 8.9, 1.8 Hz, 1 H), 6.98−7.03 (m, 1 H), 7.09 (d, J = 8.5 Hz, 2 H), 7.14−7.31 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 29.2, 30.6, 55.3, 58.0, 67.8, 70.6, 73.5, 89.6, 127.0, 127.7, 128.0, 128.5, 129.0, 134.0, 136.9, 164.6; FAB HRMS (NBA) m/e 448.1356, M + H^+ calcd for $C_{23}H_{26}ClNO_4S$ 448.1349.

Epoxy Amide ***17g***. Preparation by procedure A and purification by flash column chromatography (silica gel, 30% EtOAc in hexanes) (48%): colorless oil; $[\alpha]^{25}_D$ = +47.2 (c 1.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 2.4:1 ratio) δ (major) 0.86 (d, J = 7.0 Hz, 3 H), 0.91 (d, J = 6.8 Hz, 3 H), 1.59−1.71 (m, 1 H), 2.04 (s, 3 H), 2.26−2.36 (m, 1 H), 2.44−2.60 (m, 3 H), 2.88 (dd, J = 6.2, 2.0 Hz, 1 H),

3.26 (d, J = 2.0 Hz, 1 H), 3.43 (bs, 1 H), 3.99−4.09 (m, 2 H), 4.25−4.33 (m, 1 H), 4.48 (s, 2 H), 5.46 (dd, J = 8.9, 1.9 Hz, 1 H), 7.21−7.32 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 18.2, 29.3, 55.0, 53.2, 55.3, 63.5, 67.9, 70.4, 73.6, 89.4, 127.8, 128.0, 128.4, 128.6, 166.0; FAB HRMS (NBA) m/e 380.1905, M + H$^+$ calcd for $C_{20}H_{29}NO_4S$ 380.1896.

Epoxy Amide ***17h***. Preparation by procedure A and purification by flash column chromatography (silica gel, 30% EtOAc in hexanes) (49%): colorless oil; $[\alpha]^{25}_D$ = +48.9 (c 0.7, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 2.8:1 ratio) δ (major) 0.93−1.33 (m, 6 H), 1.50−1.78 (m, 8 H), 2.06 (s, 3 H), 2.42−2.63 (m, 2 H), 3.30 (d, J = 2.0 Hz, 1 H), 3.41−3.47 (m, 2 H), 4.00−4.10 (m, 1 H), 4.26−4.35 (m, 2 H), 4.49 (s, 2 H), 5.47 (dd, J = 8.8, 1.7 Hz, 1 H), 7.22−7.35 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 25.4, 25.6, 26.0, 28.8, 29.0, 29.2, 29.7, 30.7, 30.9, 38.9, 53.0, 55.1, 62.4, 68.0, 70.4, 73.6, 89.4, 127.8, 128.6, 137.3, 166.1; FAB HRMS (NBA) m/e 420.2215, M + H$^+$ calcd for $C_{23}H_{33}NO_4S$ 420.2209.

Epoxy Amide ***17i***. Preparation by procedure B and purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) (51%): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 2.4:1 ratio) δ (major) 0.86 (t, J = 6.9 Hz, 3 H), 1.14−1.36 (m, 9 H), 1.62−1.74 (m, 1 H), 1.84−2.02 (m, 2 H), 2.08 (s, 3 H), 2.48−2.61 (m, 2 H), 3.03 (dt, J = 8.0, 2.0 Hz, 1 H), 3.23 (d, J = 2.0 Hz, 1 H), 3.41−3.49 (m, 2 H), 3.60−3.73 (m, 1 H), 4.07 (s, 2 H), 4.51 (s, 2 H), 5.51 (dd, J = 8.8, 1.7 Hz, 1 H), 7.23−7.35 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 16.5, 18.3, 18.5, 19.7, 23.2, 23.3, 29.1, 29.3, 29.8, 30.8, 53.2, 55.0, 63.5, 67.9, 70.4, 73.5, 73.6, 83.3, 89.4, 127.7, 127.8, 128.1, 128.5, 128.6, 137.4, 165.9; FAB HRMS (NBA) m/e 422.2371, M + H$^+$ calcd for $C_{23}H_{35}NO_4S$ 422.2365.

Epoxy Amide ***18a***. Preparation by procedure B and purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) (57%): colorless oil; $[\alpha]^{25}_D$ = −83.2 (c 1.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 4:1 ratio) δ (major) 1.76−1.87 (m, 1 H), 2.11 (s, 3 H), 2.37−2.48 (m, 1 H), 2.56−2.61 (m, 2 H), 3.52 (dd, J = 9.4, 6.6 Hz, 1 H), 3.58 (dd, J = 9.3, 7.6 Hz, 1 H), 3.86 (dd, J = 9.1, 5.7 Hz, 1 H), 3.91 (d, J = 1.9 Hz, 1 H), 4.01 (d, J = 9 0.1 Hz, 1 H), 4.04 (d, J = 1.8 Hz, 1 H), 4.20 (dd, J = 12.7, 6.5 Hz, 1 H), 4.55 (s, 2 H), 5.37 (dd, J = 7.5, 2.4 Hz, 1 H), 7.25−7.37 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 28.7, 33.6, 55.6, 57.3, 57.7, 68.6, 70.9, 73.5, 89.6, 125.8, 127.7, 128.0, 128.5, 128.6, 128.8, 130.1, 135.4, 137.3, 166.2; FAB HRMS (NBA) m/e 414.1735, M + H$^+$ calcd for $C_{23}H_{27}NO_4S$ 414.1739.

Epoxy Amide ***18b***. Preparation by procedure B and purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) (90%): colorless oil; $[\alpha]^{25}_D$ = −61.3° (c 1.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 4.3:1 ratio) δ (major) 1.73−1.82 (m, 1 H), 2.09 (s, 3 H), 2.34 (s, 3 H), 2.34−2.43 (m, 1 H), 2.53−2.58 (m, 2 H), 3.49 (dd, J = 9.3, 6.6 Hz, 1 H), 3.55 (dd, J = 9.2, 7.6 Hz, 1 H), 3.83 (dd, J = 9.1, 5.7 Hz, 1 H), 3.88 (d, J = 1.9 Hz, 1 H), 3.97−3.99 (m, 2 H), 4.17 (dd, J = 12.9, 6.7 Hz, 1 H), 4.52 (s, 2 H), 5.34 (dd, J = 7.5, 2.4 Hz, 1 H), 7.09−7.18 (m, 4 H), 7.26−7.36 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 21.2, 28.7, 33.5, 55.6, 57.2, 57.7, 68.6, 70.9, 73.5, 89.6, 125.8, 127.7, 128.0, 128.5, 129.3, 132.3, 138.8, 166.3; FAB HRMS (NBA) m/e 428.1905, M + H$^+$ calcd for $C_{24}H_{29}NO_4S$ 428.1896.

Epoxy Amide ***18c***. Preparation by procedure A and purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) (60%): colorless oil; $[\alpha]^{25}_D$ = −24.2° (c 1.9, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 4.4:1 ratio) δ (major) 1.76−1.84 (m, 1 H), 2.12 (s, 3 H), 2.37−2.45 (m, 1 H), 2.40 (s, 3 H), 2.55−2.61 (m, 2 H), 3.52 (td, J = 8.2, 1.7 Hz, 1 H), 3.58 (ddd, J = 9.1, 7.4, 1.6 Hz, 1 H), 3.76 (d, J = 1.9 Hz, 1 H), 3.86 (ddd, J = 8.9, 5.6, 1.6 Hz, 1 H), 4.06 (d, J = 9.0 Hz, 2 H), 4.19 (d, J = 1.7 Hz, 1 H), 4.24 (t, J = 6.5 Hz, 1 H), 4.51−4.58 (m, 2 H), 5.39 (dt, J = 7.5, 1.8 Hz, 1 H), 7.17−7.21 (m, 4 H), 7.23−7.35 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 18.9, 28.8, 33.6, 55.7, 55.9, 56.5, 68.7, 70.7, 73.5, 89.6, 124.4, 126.2, 127.7, 128.0, 128.3, 128.5, 130.1, 133.7, 136.3, 137.2, 166.3; FAB HRMS (NBA) m/e 428.1892, M + H$^+$ calcd for $C_{24}H_{29}NO_4S$ 428.1896.

Epoxy Amide ***18d***. Preparation by procedure A and purification by flash column chromatography (silica gel, 30% EtOAc in hexanes) (72%): colorless oil; $[\alpha]^{25}_D$ = −77.8° (c 1.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 4.1:1 ratio) δ (major) 1.77−1.84 (m, 1 H), 2.11 (s, 3 H), 2.36−2.44 (m, 1 H), 2.55−2.60 (m, 2 H), 3.52 (dd, J = 9.4, 6.6 Hz, 1 H), 3.58 (dd, J = 9.3, 7.5 Hz, 1 H), 3.81 (s, 3 H), 3.85 (dd, J = 9.1, 5.6 Hz, 1 H), 3.90 (d, J = 1.9 Hz, 1 H), 3.98 (d, J = 1.9 Hz, 1 H), 4.00 (d, J = 9.1 Hz, 1 H), 4.20 (dd, J = 12.7, 6.5 Hz, 1 H), 4.55 (s, 2 H), 5.36 (dd, J = 7.4, 2.4 Hz, 1 H), 6.88 (d, J = 8.8 Hz, 2 H), 7.18 (d, J = 8.7 Hz, 2 H), 7.29−7.37 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 28.7, 33.6, 55.3, 55.6, 57.2, 57.6, 68.6, 71.0, 73.5, 89.6, 114.1, 127.2, 127.7, 128.0, 128.5, 137.3, 160.2, 166.3; FAB HRMS (NBA) m/e 444.1849, M + H$^+$ calcd for $C_{24}H_{29}NO_5S$ 444.1845.

Epoxy Amide ***18e***. Preparation by procedure A and purification by flash column chromatography (silica gel, 30% EtOAc in hexanes) (78%): colorless oil; $[\alpha]^{25}_D$ = −79.7° (c 1.7, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (two rotamers in a 4.6:1 ratio) δ (major) 1.82−1.90 (m, 1 H), 2.17 (s, 3 H), 2.43−2.51 (m, 1 H), 2.62−2.67 (m, 2 H), 3.59 (dd, J = 9.3, 6.3 Hz, 1 H), 3.65 (dd, J = 9.1, 8.1 Hz, 1 H), 3.94 (dd, J = 9.2, 5.8 Hz, 1 H), 3.96 (d, J = 1.8 Hz, 1 H), 4.06 (d, J = 8.9 Hz, 1 H), 4.08 (d, J = 1.8 Hz, 1 H), 4.25 (dd, J = 12.8, 6.3 Hz, 1 H), 4.61 (s, 2 H), 5.43 (dd, J = 7.5, 2.3 Hz, 1 H), 7.23 (d, J = 8.5 Hz, 2 H), 7.30−7.44 (m, 7 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 28.6, 33.4, 55.7, 57.0, 57.3, 68.6, 71.0, 73.5, 89.6, 127.1, 127.7, 128.0, 128.5, 128.8, 133.9, 134.6, 137.1, 165.8; FAB HRMS (NBA) m/e 448.1343, M + H$^+$ calcd for $C_{23}H_{26}ClNO_4S$ 448.1349.

Epoxy Amide ***18g***. Preparation by procedure B and purification by flash column chromatography (silica gel, 50% EtOAc in hexanes) (77% combined yield of **18g** together with its *cis* isomer): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of *E*:*Z* isomers in a 1.3:1 proportion and the *E* isomer as two rotamers in a 4:1 ratio) δ (*E* isomer, major rotamer) 0.96 (d, J = 6.9 Hz, 3 H), 1.01 (d, J = 6.7 Hz, 3 H), 1.63 (td, J = 13.5, 6.8 Hz, 1 H), 1.68−1.79 (m, 1 H), 1.92−2.09 (m, 2 H), 2.06 (s, 3 H), 2.26−2.36 (m, 1 H), 2.51−2.55 (m, 2 H), 2.88 (dd, J = 6.5, 2.0 Hz, 1 H), 3.45−3.54 (m, 2 H), 3.54 (d, J = 1.9 Hz, 1 H), 4.06 (dd, J = 13.3, 9.0 Hz, 1 H), 4.18 (dt, J = 12.8, 6.5 Hz, 1 H), 4.52 (d, J = 11.8 Hz, 1 H), 4.57 (d, J = 11.9 Hz, 1 H), 5.28 (dd, J = 7.6, 2.5 Hz, 1 H), 7.26−7.35 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 16.6, 19.6, 23.16, 23.24, 29.1, 29.7, 39.3, 53.2, 55.1, 63.5, 68.0, 70.4, 73.5, 83.2, 89.4, 127.8, 128.1, 128.6, 137.3, 166.1; FAB HRMS (NBA) m/e 380.1889, M + H$^+$ calcd for $C_{20}H_{29}NO_4S$ 380.1896.

Epoxy Amide ***18h***. Preparation by procedure B and purification by flash column chromatography (silica gel, 50% EtOAc in hexanes) (83% combined yield of **18h** together with its *cis* isomer): colorless oil; $[\alpha]^{25}_D$ = −12.3° (c 2.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of *E*:*Z* isomers in a 2.1:1 proportion and the *E* isomer as two rotamers in a 4.6:1 ratio) δ (*E* isomer, major rotamer) 1.01−1.26 (m, 7 H), 1.59−1.81 (m, 6 H), 1.90−2.06 (m, 2 H), 2.06 (s, 3 H), 2.26−2.36 (m, 1 H), 2.49−2.55 (m, 2 H), 2.88 (dd, J = 8.6, 2.0 Hz, 1 H), 3.50 (dd, J = 11.4, 4.1 Hz, 1 H), 3.55 (d, J = 2.1 Hz, 1 H), 4.05 (dd, J = 13.7, 9.1 Hz, 1 H), 4.52 (d, J = 12.6 Hz, 1 H), 4.56 (d, J = 12.0 Hz, 1 H), 5.28 (dd, J = 7.3, 2.2 Hz, 1 H), 7.27−7.35 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (major) 15.2, 25.0, 25.3, 26.0, 28.6, 29.0, 29.4, 33.8, 39.4, 52.5, 54.0, 62.4, 68.7, 70.6, 73.5, 89.2, 127.7, 128.0, 128.5, 137.2, 166.8;); FAB HRMS (NBA) m/e 420.2212, M + H$^+$ calcd for $C_{23}H_{33}NO_4S$ 420.2209.

Synthesis of Epoxy Alcohols 3 and 4. *General Procedure A.* To a solution of epoxyamide **7**, **17**, **10**, or **18** (1.0 equiv) in dry THF (0.1 M) was added Super-H (1 M in THF, 2.5 equiv) at 0 °C. The mixture was stirred for 30 min at this temperature prior to be quenched by carefully addition of a saturated aqueous of NH_4Cl solution. Dilution with diethyl ether was followed by separation of both phases, and the aqueous phase was extracted twice with more diethyl ether. The organic

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layer was washed with brine, dried over anhydrous $MgSO_4$, and filtered. The solvents were then removed by evaporation under reduced pressure, and the crude product purified by flash column chromatography (silica gel, 20% → 50% AcOEt in hexanes) to obtain pure epoxy alcohol.

Epoxy Alcohol ***3a***. 72% from epoxy amide **7a**, 96% from epoxy amide **17a**. Identical physical and spectroscopic data as reported in the literature.[33]

Epoxy Alcohol ***3b***. 76% from epoxy amide **7b**, 87% from epoxy amide **17b**. Identical physical and spectroscopic data as reported in the literature.[34]

Epoxy Alcohol ***3c***. 51% from epoxy amide **7c**, 54% from epoxy amide **17c**. **3c**: colorless oil; R_f = 0.50 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_D$ = −0.63 (*c* 1.0, CH_2Cl_2); IR (neat) ν_{max}: 3395, 3023, 2919, 2868 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20−7.12 (m, 4 H), 4.05 (d, *J* = 2.3 Hz, 1 H), 3.85−3.78 (m, 1 H), 3.88 (d, *J* = 2.2 Hz, 1 H), 3.77 (ddd, *J* = 12.7, 7.6, 3.9 Hz, 1 H), 3.21 (dt, *J* = 4.0, 2.3 Hz, 1 H), 2.33 (s, 3 H), 1.92 (dd, *J* = 7.6, 5.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 53.5, 61.2, 61.4, 124.2, 126.0, 127.7, 129.7, 134.9, 135.8; FAB HRMS (NBA) *m*/*e* 187.0737, M + Na^+ calcd for $C_{10}H_{12}O_2$ 187.0735.

Epoxy Alcohol ***3d***. 75% from epoxy amide **7d**, 73% from epoxy amide **17d**. Identical physical and spectroscopic data as reported in the literature.[35]

Epoxy Alcohol ***3e***. 71% from epoxy amide **7e**, 50% from epoxy amide **17e**. Identical physical and spectroscopic data as reported in the literature.[36]

Epoxy Alcohol ***3f***. 44% from epoxy amide **7f**. Identical physical and spectroscopic data as reported in the literature.[37]

Epoxy Alcohol ***3g***. 69% from epoxy amide **7g**, 47% from epoxy amide **17g**. Identical physical and spectroscopic data as reported in the literature.[18c]

Epoxy Alcohol ***3h***. 65% from epoxy amide **7h**, 69% from epoxy amide **17h**. Identical physical and spectroscopic data as reported in the literature.[18c]

Epoxy Alcohol ***3i***. 62% from epoxy amide **7i**, 85% from epoxy amide **17i**. Identical physical and spectroscopic data as reported in the literature.[38]

Epoxy Alcohol ***4a***. 50% from epoxy amide **18a**. Identical physical and spectroscopic data as reported in the literature.[39]

Epoxy Alcohol ***4b***. 41% from epoxy amide **10b**, 34% from epoxy amide **18b**. Identical physical and spectroscopic data as reported in the literature.[34]

Epoxy Alcohol ***4c***. 45% from epoxy amide **10c**, 44% from epoxy amide **18c**. [**4c**]**:** colorless oil; R_f = 0.50 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_D$ = +0.59 (*c* 1.0, CH_2Cl_2); IR (neat) ν_{max} 3395, 3023, 2919, 2868 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20−7.12 (m, 4 H), 4.05 (d, *J* = 2.3 Hz, 1 H), 3.85−3.78 (m, 1 H), 3.88 (d, *J* = 2.2 Hz, 1 H), 3.77 (ddd, *J* = 12.7, 7.6, 3.9 Hz, 1 H), 3.21 (dt, *J* = 4.0, 2.3 Hz, 1 H), 2.33 (s, 3 H), 1.92 (dd, *J* = 7.6, 5.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 53.5, 61.2, 61.4, 124.2, 126.0, 127.7, 129.7, 134.9, 135.8; FAB HRMS (NBA) *m*/*e* 187.0742, M + Na^+ calcd for $C_{10}H_{12}O_2$ 187.0735.

Epoxy Alcohol ***4d***. 38% from epoxy amide **10d**, 52% from epoxy amide **18d**. Identical physical and spectroscopic data as reported in the literature.[35]

Epoxy Alcohol ***4e***. 37% from epoxy amide **18e**. Identical physical and spectroscopic data as reported in the literature.[40]

Epoxy Alcohols ***4f*****:*****3′f***. 42% combined yield from a 1.3:1 mixture of epoxy amides **10f:7′f**. Separation by flash column chromatography (silica gel, 20% AcOEt in hexanes) provided pure epoxy alcohols **4f** (24%) and **3′f** (18%). **4f**: Identical physical and spectroscopic data as reported in the literature.[41] **3′f**: Identical physical and spectroscopic data as reported in the literature:[18a] R_f = 0.42 (silica gel, 40% AcOEt in hexanes); $[\alpha]^{25}_D$ = +13.0 (*c* 0.6, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 1.07 (t, *J* = 7.5 Hz, 3 H), 1.49−1.71 (m, 2 H), 3.03 (dd, *J* = 6.9, 6.0, 4.4 Hz, 1 H), 3.19 (dt, *J* = 7.0, 4.2 Hz, 1 H), 3.70 (dd, *J* = 12.1, 6.9 Hz, 1 H), 3.88 (dd, *J* = 12.0, 3.7 Hz, 1 H).

Epoxy Alcohols ***4g*****:*****3′g***. 45% combined yield from a 1.3:1 mixture of epoxy amides **10g:7′g**, 41% combined yield from a 1.3:1 mixture of epoxy amides **18g:17′g**. Separation by flash column chromatography (silica gel, 20% AcOEt in hexanes) provided pure epoxy alcohols **4g** (25%) and **3′g** (20%). **4g**: Identical physical and spectroscopic data as reported in the literature.[42] **3′g**: Identical physical and spectroscopic data as reported in the literature:[18b] R_f = 0.47 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_D$ = −25.6 (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (d, *J* = 6.9 Hz, 3 H), 1.11 (d, *J* = 6.9 Hz, 3 H), 1.43−1.53 (m, 1 H), 2.72 (dd, *J* = 9.4, 4.4 Hz, 1 H), 3.18 (dt, *J* = 7.3, 4.3 Hz, 1 H), 3.68 (dd, *J* = 12.2, 7.1 Hz, 1 H), 4.04 (dd, *J* = 12.0, 4.5 Hz, 1 H).

Epoxy Alcohols ***4h*****:*****3′h***. 45% combined yield from a 2.1:1 mixture of epoxy amides **18h:17′ h**.

Epoxy Alcohols ***4i*****:*****3′i***. 52% combined yield from a 1.4:1 mixture of epoxy amides **10i:7′i**. Separation by flash column chromatography (silica gel, 20% AcOEt in hexanes) provided pure epoxy alcohols **4i** (30%) and **3′i** (22%). **4i**: Identical physical and spectroscopic data as reported in the literature:[38] white foam; R_f = 0.39 (silica gel, 30% AcOEt in hexanes); $[\alpha]^{25}_D$ = −22.5° (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3 H), 1.25−1.37 (m, 6 H), 1.41−1.46 (m, 2 H), 1.54−1.59 (m, 2 H), 1.89 (dd, *J* = 6.5, 6.1 Hz, 1 H), 2.92 (dt, *J* = 4.9, 2.5 Hz, 1 H), 2.95 (dt, *J* = 5.7, 2.5 Hz, 1 H), 3.61 (ddd, *J* = 11.5, 7.0, 4.4 Hz, 1 H), 3.90 (ddd, *J* = 12.6, 5.3, 2.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 22.4, 25.8, 28.9, 31.5, 31.6, 56.0, 58.7, 61.9. **3′i**: Identical physical and spectroscopic data as reported in the literature:[18d] white foam; R_f = 0.43 (silica gel, 30% AcOEt in hexanes); $[\alpha]^{25}_D$ = −2.9° (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 6.9 Hz, 3 H), 1.28−1.48 (m, 6 H), 1.48−1.76 (m, 5 H), 3.06 (ddd, *J* = 6.8, 5.5, 4.4 Hz, 1 H), 3.18 (dt, *J* = 6.9, 4.2 Hz, 1 H), 3.71 (ddd, *J* = 12.1, 6.8 Hz, 1 H), 3.84−3.92 (m, 1 H).

General Procedure B. A solution of epoxyamide **10** (1.0 equiv) in dry THF (0.1 M) was treated with $LiBH_4$ (2 M in THF, 5.0 equiv) at 0 °C to allowed to reach room temperature. The mixture was stirred for 1 h at this temperature and then quenched by carefully addition of a saturated aqueous of NH_4Cl solution. Dilution with diethyl ether was followed by separation of both phases and the aqueous phase was extracted twice with more diethyl ether. The organic layer was washed with brine, dried over anhydrous $MgSO_4$ and filtered. The solvents were then removed by evaporation under reduced pressure, and the crude product purified by flash column chromatography (silica gel, 20% → 50% AcOEt in hexanes) to obtain pure epoxy alcohol.

Epoxy Alcohol ***4a***. 34% from epoxy amide **10a**. Identical physical and spectroscopic data as reported in the literature.[39]

Epoxy Alcohol ***4e***. 43% from epoxy amide **10e**. Identical physical and spectroscopic data as reported in the literature.[40]

Epoxy Alcohols ***4h*****:*****3′h***. 41% combined yield from a 1.4:1 mixture of epoxy amides **10 h:7′h**). Separation by flash column chromatography of the crude obtained of the reduction of the mixture **10 h:7′h** (silica gel, 20% AcOEt in hexanes) provided pure epoxy alcohols **4h** (24%) and **3′h** (17%). **4h**: Identical physical and spectroscopic data as reported in the literature.[18c] **3′h**: Identical physical and spectroscopic data as reported in the literature:[18c] R_f = 0.55 (silica gel, 50% AcOEt in hexanes); $[\alpha]^{25}_D$ = +5.6 (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 1.09−1.27 (m, 6 H), 1.60−1.76 (m, 5 H), 1.96 (bd, 1 H), 2.79 (dd, *J* = 9.4, 4.3 Hz, 1 H), 3.18 (dt, *J* = 7.5, 4.3 Hz, 1 H), 3.68 (ddd, *J* = 15.5, 12.0, 7.4 Hz, 1 H), 3.85 (ddd, *J* = 15.5, 12.0, 4.5 Hz, 1 H).

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and spectroscopic data of all new compounds, as well as ^1H- and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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