One-Pot Synthesis of β-Amino/β-Hydroxy Selenides and Sulfides from Aziridines and Epoxides

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Abstract: Diaryl disulfides and diselenides undergo facile cleavage on treatment with rongalite (sodium hydroxymethanesulfinate) to generate the corresponding thiolate and selenolate species in situ, which effect the ring opening of aziridines and epoxides in a regioselective manner. A simple, mild, cost-effective protocol has been developed to prepare β-amino and β-hydroxy sulfides and selenides in a one-pot operation.

Key words: β-amino selenide, β-amino sulfide, β-hydroxy selenide, β-hydroxy sulfide, rongalite, aziridine, epoxide

In recent years the synthesis of peptidomimetic molecules has become an increasingly popular area in the field of drug design.[1] Specifically, synthetic routes to sulfanyl- and selanyl-substituted unnatural amino acids and its derivatives, which are the building blocks for the synthesis of modified thio- and seleno-proteins,[2] have attracted attention due to their interesting structural and biological properties. The seleno-proteins play an important role in metabolic processes, glutathione peroxidase (GPx) for example, acts as a peroxide scavenger.[3a] In addition to the interesting properties of thio- and seleno- proteins, simple organosulfur and organoselenium compounds exhibit many useful biological and medicinal properties.[4] They are generally targeted as compounds with antioxidant, antitumor, and antimicrobial activity and many of these compounds are competitive inhibitors for target proteins.[3] Apart from the biological applications, enantiomerically pure β-amino or β-hydroxy sulfides and selenides are excellent ligands for transition-metal-based asymmetric catalysis.[5] Keeping in mind the wide range of applications of these analogues, general synthetic methodologies to prepare sulfur- and selenium-containing derivatives of amino acids in a simple, efficient, stereoregulated manner is greatly appreciated and remains a challenge. A myriad of work has been devoted towards the synthesis of these analogues.[6]

Unsymmetrical sulfides are generally prepared from alkyl halides by nucleophilic substitution of thiols in the presence of a base and a suitable solvent.[7] A number of transition-metal-catalyzed coupling reactions have been developed to synthesize these sulfides, which are shown to be mild and selective.[8] Introduction of the selenium moiety is generally carried out by reductive cleavage of diselenides or from selenocyanates followed by coupling with an alkyl halide in one pot, since most of the selenols are unstable and are oxidized spontaneously to the corresponding diselenides in air. Reducing agents, such as $NaBH_4$, Na/NH_3, Bu_3SnH, and $LiAlH_4$, have been used for the synthesis of selenides.[9] Ranu et al. developed an indium(I) iodide mediated cleavage of diaryl diselenides and diaryl disulfides.[10]

Generally, β-amino or β-hydroxy sulfides and selenides are prepared using the same methodology starting from an amino alcohol, followed by conversion of the hydroxy group into a good leaving group and subsequent nucleophilic substitution with thiolate or in situ generated selenolate.[11] Later, aziridines and epoxides were found to be the best starting materials to prepare these analogues in a stereo- and regiocontrolled manner.[12] Wakselman et al. demonstrated the synthesis of perfluoroalkyl sulfides by the treatment of perfluoroalkyl halides with an organic disulfide mediated by rongalite.[13] Tang et al. reported the synthesis of alkyl aryl sulfides mediated by sodium dithionite, sodium thiosulfate, or rongalite (sodium hydroxymethanesulfinate, **1**) and compared the rates and percentage of conversion and it was found that rongalite is the most efficient reducing agent for disulfides and for the synthesis of sulfides.[14]

Following these literature reports, we attempted the synthesis of β-amino and β-hydroxy chalcogenides in a one-pot process mediated by rongalite. Herein, we report our comprehensive study on the aziridine/epoxide ring opening with sulfur and selenium nucleophiles derived from disulfides/diselenides in the presence of rongalite (sodium hydroxymethanesulfinate, **1**), which led to an efficient synthesis of β-amino- and β-hydroxy selenides and sulfides from the corresponding diselenides and disulfides under mild conditions (Scheme 1).

Reaction of enantiopure *N*-tosylaziridine **2** with diphenyl diselenide (**3a**) mediated by rongalite (**1**) was carried out by the addition of **3a** (0.5 equiv) to a well-stirred solution of aziridine **2** in *N*,*N*-dimethylformamide, followed by the addition of potassium carbonate (2 equiv) and rongalite (**1**, 3 equiv) at room temperature (20 min) resulting in the regioselective ring opening of the aziridine **2** to form the expected β-amino selenide **4a** in 98% yield[15] (Scheme 2).

A mechanism has been proposed for the reduction of diselenide **3a** followed by the ring opening of aziridine **2** (Scheme 3).[14b] Rongalite when treated with a base decomposes to formaldehyde and HSO_2^-, which transfers a sin-

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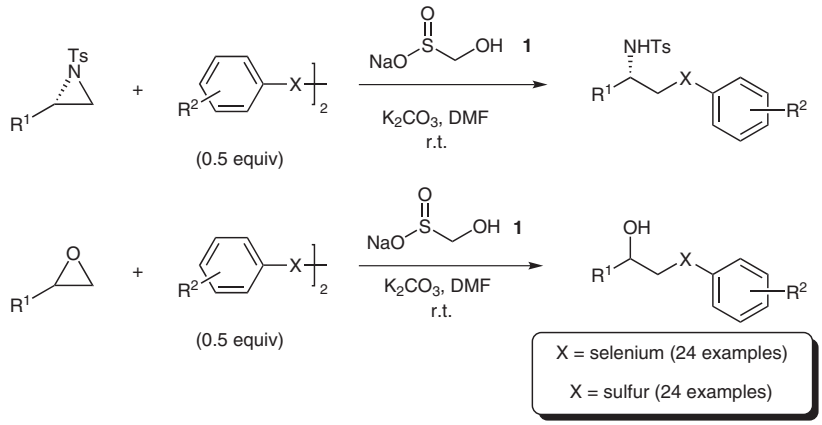
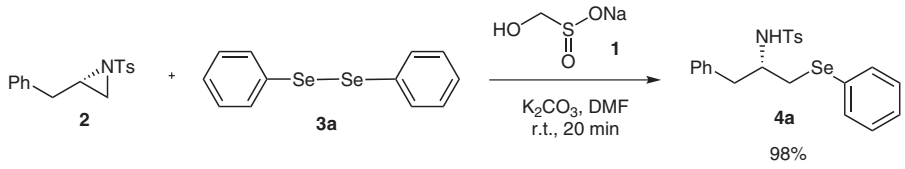
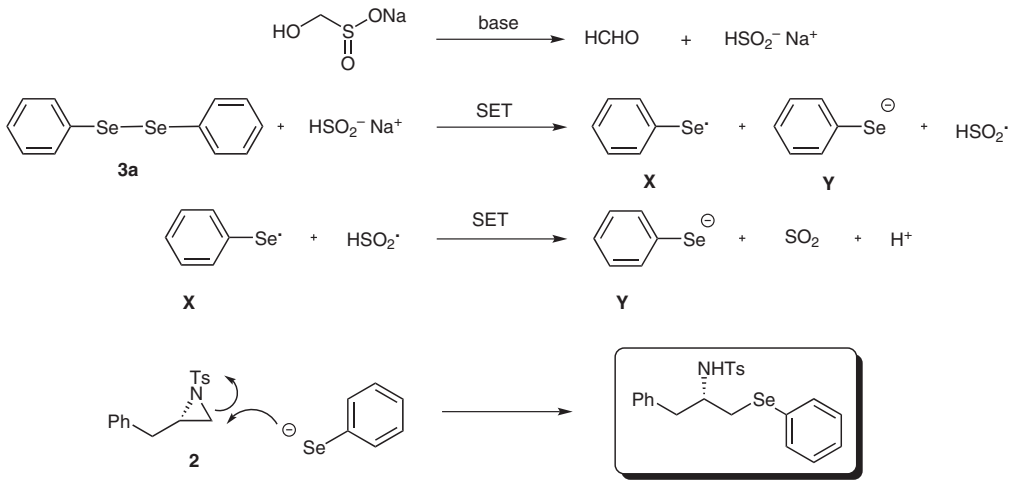


Scheme 1 General scheme for the synthesis of β-amino and β-hydroxy selenides and sulfides



Scheme 2 Nucleophilic ring opening of **2** with diphenyl diselenide (**3a**) mediated by **1**



Scheme 3 Mechanism for the formation of β-amino selenides

gle electron to the diselenide resulting in the formation of a radical anion intermediate. The intermediate may spontaneously disproportionate into a radical **X** and anionic species **Y**. The selenium radical **X** further gets reduced to anionic species **Y**, by another single electron transfer (SET). The attack of **Y** on aziridine in a regioselective manner at the less hindered carbon gives the desired β-amino selenide.

The mildness of the reaction conditions and the excellent yield obtained encouraged us to explore the scope and generality of the methodology. A wide range of diselenides **3b–g** were selected to study the ring-opening reaction with phenylalanine-derived aziridine **2**. All diaryl diselenides were synthesized from the corresponding anilines by a diazotization, selenocyanation, and reduction sequence.[16] The results of our study are summarized in Table 1. Diselenides **3b–f** reacted with aziridine **2** leading to the corresponding β-amino selenides **4b–f**, respectively, in excellent yield. In the case of 2-(4,5-dihydrooxazol-2-yl)-substituted diselenide **3d** the cleavage was slower relative to the other diselenides due to steric crowding at the *ortho*-position. The 4,5-dihydrooxazol-2-yl group is a masked carboxylic acid and it can be deprotected after the reaction.[17] An aliphatic diselenide like dibenzyl diselenide (**3g**) failed to react with rongalite to give the selenolate even after stirring for 24 hours at room temperature.

To expand the scope of this methodology, we decided to study the reactivity of other aziridines bearing different functionalities and complexity in the structure, with diphenyl diselenide (**3a**). The reaction of aziridines **5a–j**[18] with diphenyl diselenide (**3a**) mediated by rongalite (r.t., 20 min), resulted in the formation of the corresponding β-amino selenides **6a–j** in excellent yield (Table 2).

Table 1 Synthesis of Phenylalanine-Derived β-Amino Selenides **4**

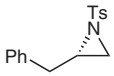
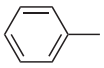
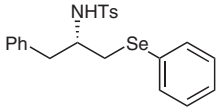
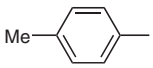
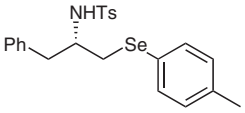
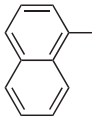
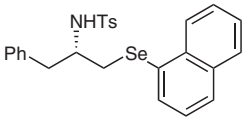
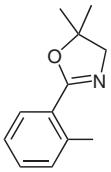
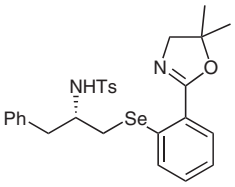
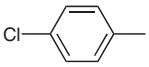
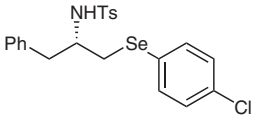
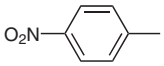
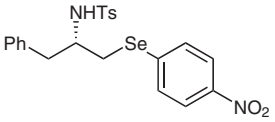
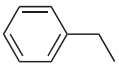
Entry	Reactant	R-Se-Se-R	Product	Time	Yield (%)
1	 **2**	 **3a**	 **4a**	20 min	98
2	**2**	 **3b**	 **4b**	30 min	97
3	**2**	 **3c**	 **4c**	30 min	93
4	**2**	 **3d**	 **4d**	60 min	89
5	**2**	 **3e**	 **4e**	20 min	95
6	**2**	 **3f**	 **4f**	20 min	94
7	**2**	 **3g**	no reaction	24 h	–

Table 2 Synthesis of β-Amino Selenides **6** from Diphenyl Diselenide (**3a**) and Various Aziridines

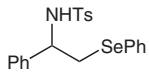
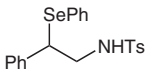
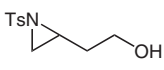
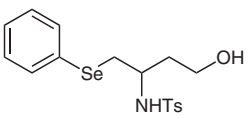
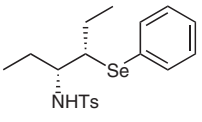
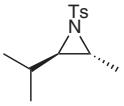
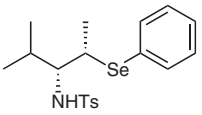
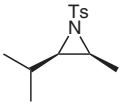
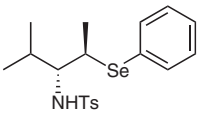
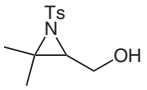
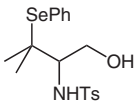
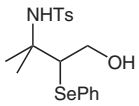
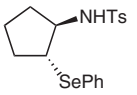
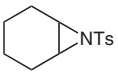
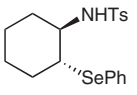
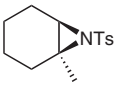
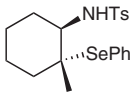
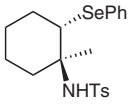
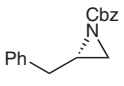
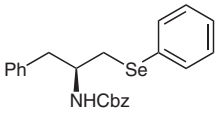
Entry	Reactant[a]	Product		Time (min)	Yield (%)
1	 **5a**	 **6a**	 **6a′**	20	96 (1.1:1)[b]
2	 **5b**	 **6b**		30	94
3	 **5c**	 **6c**		40	95

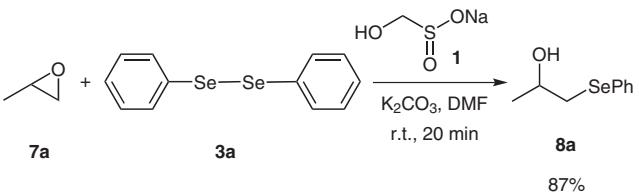
Table 2 Synthesis of β-Amino Selenides **6** from Diphenyl Diselenide (**3a**) and Various Aziridines (continued)

Entry	Reactant[a]	Product		Time (min)	Yield (%)
4	 **5d**	 **6d**		40	92
5	 **5e**	 **6e**		40	90
6	 **5f**	 **6f**	 **6f′**	30	83 (1:1.7)[b]
7	 **5g**	 **6g**		30	92
8	 **5h**	 **6h**		30	94
9	 **5i**	 **6i**	 **6i′**	30	86 (1:1.8)[b]
10	 **5j**	 **6j**		45	95

[a] Compounds **5a–i** are racemic and the relative stereochemistry is represented, **5j** was derived enantiomerically pure from L-phenylalanine.
[b] Based on ^{1}H NMR integration values.

Styrene-derived aziridine **5a** reacted with diphenyl diselenide (**3a**) to give an inseparable mixture of regioisomers **6a** and **6a′** in the ratio 1.1:1.[19] The regioisomers arise due to similar reactivity profile of the less hindered carbon and the benzylic center. The aziridines **5b–h** underwent facile ring opening in the usual manner at the less hindered carbon center to give the desired products **6b–h**. In the case of the trisubstituted aziridine **5f**, the reaction gave a 1.7:1 regioisomeric mixture of products **6f/6f′**. This can be explained on the basis of the competition of nucleophilic attack in a S_N1 like pathway at the tertiary center and S_N2 fashion at the secondary center. The same kind of regioisomeric mixture **6i/6i′** is obtained in the methylcyclohexene-derived aziridine **5i**. Since deprotection of the tosyl group involves harsh conditions, the same methodology has been demonstrated using benzyloxycarbonyl (Cbz) protected aziridine **5j**. The Cbz-protected aziridine **5j** underwent ring opening smoothly in 45 minutes to give the β-amino selenide **6j** in 95% yield.

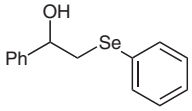
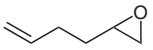
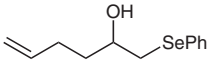
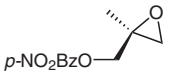
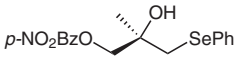
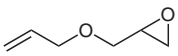
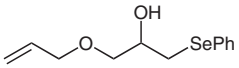
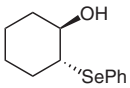
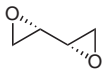
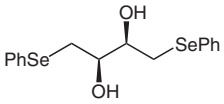
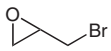
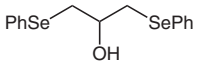
The versatility of the reaction was explored further by extending the methodology to the ring opening of epoxides. When propylene oxide was treated with diphenyl diselenide (**3a**) and rongalite, the reaction proceeded cleanly (DMF, r.t., 20 min) to give the β-hydroxy selenide **8a** in 87% yield (Scheme 4).



Scheme 4 Nucleophilic ring opening of epoxides with diphenyl diselenide (**3a**) mediated by **1**

The scope of the methodology was further investigated by using various epoxides to study the reactivity. The epoxides **7b–h** were treated with diphenyl diselenide (**3a**) and rongalite under the same conditions leading to the formation of β-hydroxy selenides **8b–h** in excellent yields (Table 3). Ring opening in the case of styrene oxide (**7b**),

Table 3 Synthesis of β-Hydroxy Selenides **8** from Diphenyl Diselenide (**3a**) and Various Epoxides

Entry	Reactant[a]	Product	Time (min)	Yield (%)
1	 **7b**	 **8b**	20	97
2	 **7c**	 **8c**	20	95
3	 **7d**	 **8d**	20	91
4	 **7e**	 **8e**	20	95
5	 **7f**	 **8f**	30	94
6	 **7g**	 **8g**	30	93
7	 **7h**	 **8h**	30	92

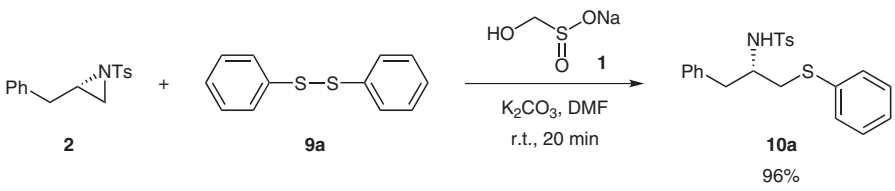
[a] All compounds except **7d** were racemic, *p*-NO_2Bz = *p*-nitrobenzoyl.

(unlike the styrene-derived aziridine **5a)** resulted in a single regioisomer **8b** in 95% yield following the S_N2 pathway exclusively. The reaction was further extended to bis-epoxides, to give bis-selenides. The reaction of bis-epoxide **7g** yielded the corresponding bis-selenide **8g** (93%). The bis-selenide **8g** is an important precursor for making the *trans*-furofuran moiety in the total synthesis of (–)-kumausallene.[20] Similarly, in the reaction of epibromohydrin **7h**, the corresponding bis-selenide **8h** was obtained in 92% yield.

Having demonstrated the ability of rongalite to cleave the diselenide bond and its application to the synthesis of β-amino selenides and β-hydroxy selenides, the chemistry was extended to the synthesis of β-amino sulfides and β-hydroxy sulfides by reductive cleavage of diaryl disulfides.

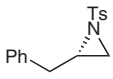
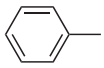
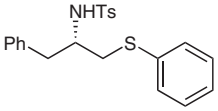
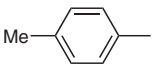
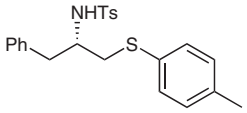
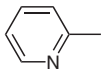
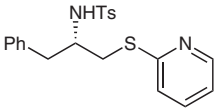
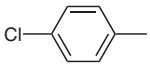
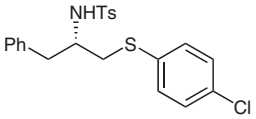
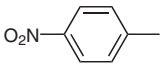
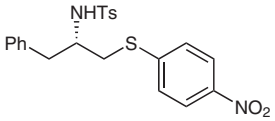
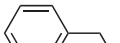
As in the case of diselenides, disulfides can also undergo reductive cleavage in the presence of rongalite. The reaction was carried out by the addition of diphenyl disulfide (**9a**, 0.5 equiv) to a solution of phenylalanine-derived aziridine **2** in *N*,*N*-dimethylformamide, followed by the addition of potassium carbonate (2 equiv). The mixture was stirred vigorously followed by the addition of rongalite (3 equiv).[15] The reaction proceeded smoothly (20 min) to give the corresponding β-amino sulfide **10a** as the sole product in 96% yield (Scheme 5). The facile reactivity and the excellent yield obtained encouraged us to explore the reaction with various disulfides to check the generality of this methodology.

Phenylalanine-derived aziridine **2** was taken as a standard and reacted with various organic disulfides. The reaction of disulfides **9b–f** with aziridine **2** mediated by rongalite



Scheme 5 Nucleophilic ring opening of **2** with diphenyl disulfide (**9a**) mediated by **1**

Table 4 Synthesis of Phenylalanine-Derived β-Amino Sulfides **10**

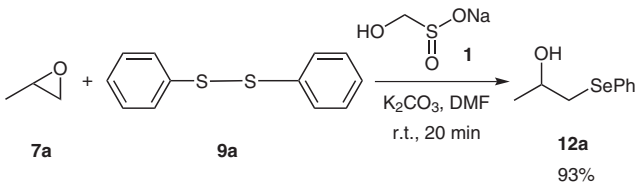
Entry	Reactant	R-S-S-R	Product	Time	Yield (%)
1	 **2**	 **9a**	 **10a**	20 min	96
2	**2**	 **9b**	 **10b**	30 min	96
3	**2**	 **9c**	 **10c**	30 min	92
4	**2**	 **9d**	 **10d**	20 min	94
5	**2**	 **9e**	 **10e**	20 min	95
6	**2**	 **9f**	no reaction	24 h	–

gave the corresponding β-amino sulfides **10b–e** in excellent yield (Table 4). As in the case of dibenzyl diselenide (**3g**), dibenzyl disulfide (**9f**) also failed to react with aziridine **2** even after 24 hours.

The methodology was further extended to various aziridines. The aziridines **5a–k** were treated with diphenyl disulfide (**9a**, 0.5 equiv) followed by the addition of potassium carbonate and rongalite and the reaction (r.t., 20 min) resulted in the formation of β-amino sulfides **11a–k** in excellent yields (Table 5). In the case of styrene-derived aziridine **5a**, the reaction led to a regioisomeric mixture of β-amino sulfides **11a/11a′** in 1:1 ratio with a total yield of 96%.

The aziridines **5d**,**e** underwent ring opening smoothly from the less hindered side. Since the isopropyl group blocks the approach of the incoming nucleophile, the nucleophile attacks at the less hindered side of the aziridine to give **10d**,**e** as the sole products in excellent yield. With trisubstituted aziridine **5f**, a regioisomeric mixture of β-amino sulfides **11f** and **11f′** were formed in 90% yield in the ratio 3:1. Cbz-protected aziridine **5j** was successfully converted into Cbz-β-amino sulfide **11j** in 96% yield, which can be converted into the free amine by simple deprotection.

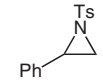
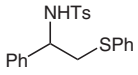
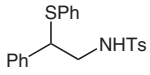
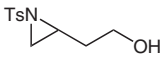
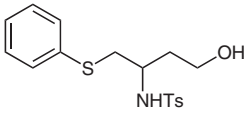
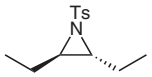
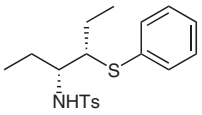
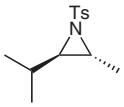
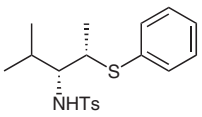
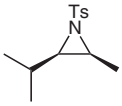
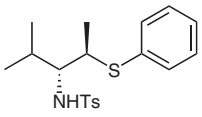
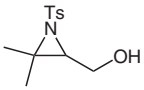
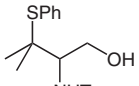
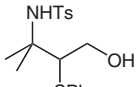
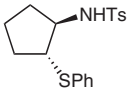
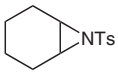
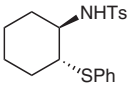
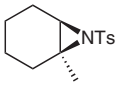
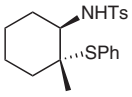
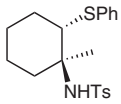
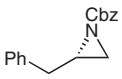
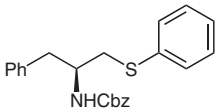
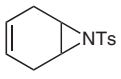
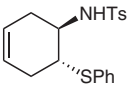
Following the efficient ring opening of aziridines, the reaction was extended to study the ring opening of epoxides. To compare the reactivity differences between the selenium and sulfur nucleophiles, the same set of epoxides were taken for the study. Initially, propylene oxide **7a** was treated with diphenyl disulfide (**9a**) and rongalite in *N*,*N*-dimethylformamide to give **12a** as the sole product in 93% yield (Scheme 6). The reaction of various epoxides **7b–h** with diphenyl disulfide (**9a**) and rongalite gave the corresponding β-hydroxy sulfides **12b–h** in excellent yields (Table 6).



Scheme 6 Nucleophilic ring opening of epoxides with diphenyl disulfide (**9a**) mediated by **1**

In summary, reductive cleavage of diaryl disulfides and diselenides mediated by rongalite followed by the ring opening of aziridines provides an easy access to β-amino sulfides and β-amino selenides in a stereospecific and re-

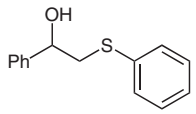
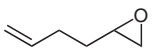
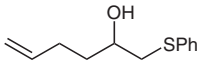
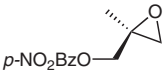
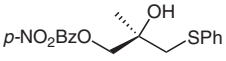
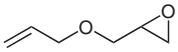
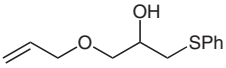
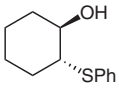
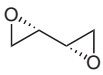
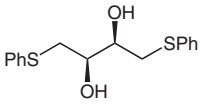
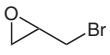
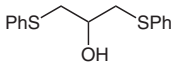
Table 5 Synthesis of β-Amino Sulfides **11** from Diphenyl Disulfide (**9a**) and Various Aziridines

Entry	Reactant[a]	Product		Time (min)	Yield (%)
1	 **5a**	 **11a**	 **11a′**	20	96 (1:1)[b]
2	 **5b**	 **11b**		30	94
3	 **5c**	 **11c**		40	95
4	 **5d**	 **11d**		40	94
5	 **5e**	 **11e**		40	92
6	 **5f**	 **11f**	 **11f′**	30	90 (3:1)[b]
7	 **5g**	 **11g**		30	92
8	 **5h**	 **11h**		30	93
9	 **5i**	 **11i**	 **11i′**	30	89 (4:1)[b]
10	 **5j**	 **11j**		45	96
11	 **5k**	 **11k**		30	94

[a] Compounds **5a–i**, **5k** are racemic and the relative stereochemistry is represented, **5j** was derived enantiomerically pure from L-phenylalanine.
[b] Based on the ^{1}H NMR integration values.

gioselective manner under mild conditions in a one-pot operation. The methodology would be of interest due to the cost-effective and metal-free reaction conditions and high yield. The reaction has been extended further to the ring opening of epoxides in a stereospecific and regiose-

Table 6 Synthesis of β-Hydroxy Sulfides **12** from Diphenyl Disulfide (**9a**) and Various Epoxides

Entry	Reactant[a]	Product	Time (min)	Yield (%)
1	 **7b**	 **12b**	20	97
2	 **7c**	 **12c**	20	94
3	 **7d**	 **12d**	20	91
4	 **7e**	 **12e**	20	93
5	 **7f**	 **12f**	30	93
6	 **7g**	 **12g**	30	94
7	 **7h**	 **12h**	30	94

[a] All compounds except **7d** were racemic; *p*-NO_2Bz = *p*-nitrobenzoyl.

lective manner for the synthesis of β-hydroxy sulfides and selenides in excellent yields.

All reactions were carried out in oven-dried apparatus using dry solvents under anhydrous conditions, unless otherwise noted. Reaction mixtures were stirred magnetically unless otherwise stated. Commercial grade solvents were distilled and dried according to literature procedures.[21] Analytical TLC was performed on commercial plates coated with silica gel GF_{254} (0.25 mm). Silica gel (230–400 mesh) was used for column chromatography. Melting points determined are uncorrected. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. IR spectra were recorded on a FT-IR spectrometer. NMR spectra were recorded on 300 or 400 MHz instruments and chemical shifts are cited with respect to $SiMe_4$ as internal (^{1}H and ^{13}C) and Me_2Se (^{77}Se) as external standard. High resolution mass spectra (HR-MS) were recorded on an electro-spray mass spectrometer. All novel compounds were fully characterized. All known compounds had spectroscopic data consistent with the literature: **4a**,[22a] **6a**,[21b] **6b**,[22b] **6h**,[22b] **8a**,[12d] **8b**,[22d] **8h**,[22e] **10a**,[12a] **10d**,[12c] **11a**,[12a] **11c**,[12c] **11g**,[12a] **11h**,[12a] **11j**,[22f] **11k**,[22g] **12a**,[22h] **12b**,[22i] **12f**,[22j] **12h**.[22k] r.t. = 28 °C.

β-Amino Selenides or β-Hydroxy Selenides; General Procedure

To a well-stirred soln of aziridine or epoxide (0.2 mmol, 1 equiv) in DMF (2 mL) was added the diselenide (0.1 mmol, 0.5 equiv) followed by K_2CO_3 (0.4 mmol, 2 equiv) and rongalite (**1**, 0.6 mmol, 3 equiv). The mixture was stirred at r.t. for 30–60 min (TLC monitoring). After complete consumption of the starting material, H_2O was added to quench the reaction and it was extracted with CH_2Cl_2 (2 × 10 mL). The organic layer was separated and dried (anhyd Na_2SO_4). The crude product was purified by column chromatography (silica gel).

(*S*)-1-Phenyl-3-(4-tolylselanyl)-*N*-tosylpropan-2-amine (4b)

Colorless oil; yield: 97%; R_f = 0.3 (EtOAc–hexanes, 2:8).

$[\alpha]_D^{25}$ –52.9 (*c* 2, $CHCl_3$).

IR (neat): 3280, 3027, 2922, 1598, 1492, 1330, 1158, 1093, 806, 615 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 6.3 Hz, 2 H), 7.30 (d, *J* = 6.0 Hz, 2 H), 7.16–7.15 (m, 3 H), 7.1–7.05 (m, 4 H), 6.93–6.91 (m, 2 H), 4.83 (d, *J* = 5.1 Hz, 1 H), 3.52–3.45 (m, 1 H), 3.07 (dd, *J* = 3.3, 9.6 Hz, 1 H), 2.94 (dd, *J* = 4.8, 10.2 Hz, 1 H), 2.80–2.71 (m, 1 H), 2.37 (s, 3 H), 2.34 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0, 137.3, 136.8, 136.5, 133.3, 130.0, 129.4, 129.2, 128.5, 126.9, 126.6, 125.3, 54.5, 40.2, 33.1, 21.5, 21.1.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 236.096.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{25}N_2NaO_2SSe$: 482.0669; found: 482.0669.

(*S*)-1-(1-Naphthylselanyl)-3-phenyl-*N*-tosylpropan-2-amine (4c)

Colorless oil; yield: 93%; R_f = 0.4 (EtOAc–hexanes, 2:8).

$[\alpha]_D^{25}$ –67.3 (*c* 1, $CHCl_3$).

IR (neat): 3276, 3054, 2923, 1498, 1328, 1158, 767, 748, 665 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27–8.24 (m, 1 H), 7.88–7.81 (m, 2 H), 7.69 (d, *J* = 6.0 Hz, 1 H), 7.57–7.52 (m, 2 H), 7.37 (t, *J* = 39.0 Hz, 1 H), 7.34 (m, 2 H), 7.16–7.11 (m, 3 H), 6.88 (d, *J* = 8.4 Hz, 4 H), 4.76 (d, *J* = 7.2 Hz, 1 H), 3.53–3.42 (m, 1 H), 3.10 (dd, *J* = 4.5, 12.9 Hz, 1 H), 2.99 (dd, *J* = 6.6, 13.8 Hz, 1 H), 2.83–2.76 (m, 2 H), 2.26 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.9, 136.6, 136.5, 134.1, 132.8, 129.5, 129.3, 129.2, 128.7, 128.6, 128.4, 127.4, 126.8, 126.7, 126.6, 126.3, 125.8, 54.5, 40.3, 32.7, 31.4.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 181.220.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{25}NNaO_2SSe$: 518.0669; found: 518.0668.

(*S*)-1-[2-(5,5-Dimethyl-4,5-dihydrooxazol-2-yl)phenylselanyl]-3-phenyl-*N*-tosylpropan-2-amine (4d)

Colorless oil; yield: 89%; R_f = 0.3 (EtOAc–hexanes, 3:7).

$[\alpha]_D^{25}$ –34.1 (*c* 1, $CHCl_3$).

IR (neat): 3281, 2968, 2960, 1646, 1455, 1314, 1157, 1030, 963, 813, 733, 655 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (m, 1 H), 7.45 (d, *J* = 6.0 Hz, 2 H), 7.26–7.19 (m, 6 H), 7.05–7.0 (m, 4 H), 5.74 (d, *J* = 5.4 Hz, 1 H), 4.10 (s, 2 H), 3.62–3.57 (m, 1 H), 3.02–2.92 (m, 3 H), 2.76 (dd, *J* = 4.8, 9.9 Hz, 1 H), 2.32 (s, 3 H), 1.45 (s, 3 H), 1.44 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.1, 143.4, 137.5, 133.1, 131.4, 131.3, 130.4, 129.9, 129.4, 129.1, 127.3, 127.2, 126.2, 79.4, 69.1, 59.6, 41.5, 32.3, 29.1, 29.0, 22.0.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 255.64.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{27}H_{30}N_2NaO_3SSe$: 565.104; found: 565.1035.

(*S*)-1-(4-Chlorophenylselanyl)-3-phenyl-*N*-tosylpropan-2-amine (4e)
Yield: 95%; mp 62 °C; R_f = 0.4 (EtOAc–hexanes, 2:8).

$[\alpha]_D^{25}$ –54.4 (*c* 2, $CHCl_3$).

IR (neat): 3282, 2924, 1598, 1475, 1325, 1159, 1090, 813, 743, 700, 665 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.8 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.22–7.03 (m, 7 H), 6.93–6.90 (m, 2 H), 4.88 (d, *J* = 6.9 Hz, 1 H), 3.51–3.36 (m, 1 H), 3.12 (dd, *J* = 4.8, 12.9 Hz, 1 H), 2.94 (dd, *J* = 6.3, 13.8 Hz, 1 H), 2.87–2.69 (m, 2 H), 2.38 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.2, 136.3, 134.1, 129.5, 129.3, 129.1, 128.6, 128.4, 126.9, 126.7, 126.4, 54.4, 40.2, 33.11, 21.5.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 245.881.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{22}ClNNaO_2SSe$: 502.0123; found: 502.0121.

(*S*)-1-(4-Nitrophenylselanyl)-3-phenyl-*N*-tosylpropan-2-amine (4f)
Yield: 94%; mp 117 °C; R_f = 0.5 (EtOAc–hexanes, 4:6).

$[\alpha]_D^{25}$ –66.0 (*c* 1, $CHCl_3$).

IR (neat): 3447, 3295, 1596, 1574, 1513, 1343, 1158, 1066, 851 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.06–8.04 (m, 2 H), 7.47–7.26 (m, 2 H), 7.21–7.11 (m, 5 H), 6.95–6.93 (m, 2 H), 4.88 (d, *J* = 5.4 Hz, 1 H), 3.57–3.53 (m, 1 H), 3.29 (dd, *J* = 3.6, 9.9 Hz, 1 H), 3.07 (dd, *J* = 5.1, 9.9 Hz, 1 H), 2.93 (dd, *J* = 5.1, 7.5 Hz, 1 H), 2.78–2.73 (m, 2 H), 2.38 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.3, 143.5, 140.4, 136.5, 136.0, 129.6, 129.2, 128.8, 127.9, 127.0, 12.9, 123.9, 54.4, 40.4, 32.1, 21.5.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 271.059.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{22}N_2NaO_4SSe$: 513.0364; found: 513.0364.

4-(Phenylselanyl)-3-(tosylamino)butan-1-ol (6b)
Colorless oil; yield: 94%; R_f = 0.3 (EtOAc–hexanes, 3:7).

IR (neat): 3475, 2961, 2939, 2789, 1616, 1600, 1493, 1325, 1204, 1093, 1023, 745, 667 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.4, Hz, 2 H), 7.41–7.38 (m, 2 H), 7.30–7.19 (m, 5 H), 5.29 (d, *J* = 8.4 Hz, 1 H), 3.83–3.76 (m, 1 H), 3.69–3.55 (m, 2 H), 3.09 (dd, *J* = 3.6, 12.9 Hz, 1 H), 2.69 (dd, *J* = 6.9, 12.9 Hz, 1 H), 2.41 (s, 3 H), 2.18 (s, 1 H), 1.88–1.78 (m, 1 H), 1.66–1.55 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.5, 138.5, 133.1, 129.7, 129.3, 127.4, 127.0, 58.9, 51.1, 36.5, 34.1, 21.5.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 243.28.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{21}NNaO_3SSe$: 422.0305; found: 422.0304.

(3*R,4*S**)-4-(Phenylselanyl)-*N*-tosylhexan-3-amine (6c)**
Yield: 95%; mp 62 °C; R_f = 0.5 (EtOAc–hexanes, 3:7).

IR (neat): 3475, 2961, 2939, 2789, 1616, 1600, 1493, 1325, 1204, 1093, 1023, 745, 667 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.4 Hz, 2 H), 7.38–7.18 (m, 7 H), 5.2 (d, *J* = 9.6 Hz, 1 H), 3.40–3.31 (m, 1 H), 2.83 (td, *J* = 3.3, 6.5 Hz, 1 H), 2.40 (s, 3 H), 1.77–1.64 (m, 2 H), 1.61–1.50 (m, 1 H), 1.36–1.21 (m, 1 H), 0.96–0.84 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.1, 133.9, 129.7, 129.5, 129.4, 129.2, 127.5, 126.9, 58.3, 57.4, 28.2, 24.2, 21.5, 13.0, 10.6.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 294.45.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{25}NNaO_2Se$: 434.0669; found: 434.0676.

(3*R,4*S**)-2-Methyl-4-(phenylselanyl)-*N*-tosylpentan-3-amine (6d)**
Colorless oil; yield: 92%; R_f = 0.3 (EtOAc–hexanes, 1:9).

IR (neat): 3480, 2962, 2939, 2784, 1626, 1600, 1443, 1325, 1164, 1090, 1033, 747, 667 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.1 Hz, 2 H), 7.40–7.37 (m, 2 H), 7.31–7.17 (m, 5 H), 4.94 (d, *J* = 9.9 Hz, 1 H), 3.36 (ddd, *J* = 0.1, 0.9, 4.5 Hz, 1 H), 3.15–3.06 (m, 1 H), 2.38 (s, 3 H), 2.09–1.99 (m, 1 H), 1.38 (d, *J* = 7.5 Hz, 3 H), 0.84 (d, *J* = 5.1 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0, 138.6, 134.4, 129.6, 129.4, 129.0, 127.7, 126.9, 63.0, 45.4, 29.9, 21.5, 21.0, 20.4, 17.3, 16.9.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 363.35.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{25}NNaO_2SSe$: 434.0669; found: 434.0646.

(3*R,4*R**)-2-Methyl-4-(phenylselanyl)-*N*-tosylpentan-3-amine (6e)**
Yield: 90%; mp 65 °C; R_f = 0.3 (EtOAc–hexanes, 1:9).

IR (neat): 3288, 2963, 2873, 1598, 1437, 1327, 1157, 1093, 1031, 814, 741, 667 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.1 Hz, 2 H), 7.54–7.51 (m, 2 H), 7.30–7.22 (m, 5 H), 4.84 (d, *J* = 6.3 Hz, 1 H), 3.53 (dd, *J* = 3.0, 4.2 Hz, 1 H), 3.18–3.11 (m, 1 H), 2.39 (s, 3 H), 1.96–1.80 (m, 1 H), 1.25 (d, *J* = 6.9 Hz, 3 H), 0.80 (d, *J* = 7.2 Hz, 3 H), 0.75 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.9, 138.7, 135.3, 129.4, 129.0, 128.4, 127.8, 126.9, 64.8, 44.0, 31.6, 21.4, 20.6, 20.3, 19.5.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 342.3.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{25}NNaO_2SSe$: 434.0669; found: 434.0682.

(1*R,2*R**)-2-(Phenylselanyl)-*N*-tosylcyclopentan-3-amine (6g)**
Colorless oil; yield: 92%; R_f = 0.4 (EtOAc–hexanes, 2:8).

IR (neat): 3273, 2978, 2853, 1590, 14, 1356, 1150, 1190, 1030, 823, 746, 663 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.8 Hz, 2 H), 7.38 (d, *J* = 7.8 Hz, 2 H), 7.36–7.18 (m, 5 H), 5.13 (d, *J* = 4.2 Hz, 1 H), 3.38–3.28 (m, 2 H), 2.43 (s, 3 H), 2.16–2.01 (m, 2 H), 1.70–1.42 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.3, 136.9, 135.0, 129.6, 128.9, 128.0, 127.8, 127.2, 60.0, 47.3, 31.6, 30.7, 21.9, 21.5.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 352.8.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{21}NNaO_2SSe$: 418.0356; found: 418.0349.

(*S*)-*N*-(Benzyloxycarbonyl)-1-phenyl-3-(phenylselanyl)propan-3-amine (6j)
Yield: 95%; mp 74 °C; R_f = 0.6 (EtOAc–hexanes, 2:8).

$[\alpha]_D^{25}$ +15.1 (*c* 1, $CHCl_3$).

IR (neat): 3287, 3030, 2928, 1700, 1511, 1253, 1024, 738, 696 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.1 (m, 15 H), 5.02 (s, 2 H), 4.94 (d, *J* = 6.9 Hz, 1 H), 4.15–4.12 (m, 1 H), 3.05 (d, *J* = 3.3 Hz, 2 H), 2.90 (d, *J* = 7.2 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.5, 137.2, 132.8, 129.3, 129.2, 128.5, 128.4, 128.0, 127.9, 127.1, 126.6, 66.6, 52.2, 40.2, 32.5.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 240.56.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{23}NNaO_2Se$: 448.0792; found: 448.08.

1-(Phenylselanyl)hex-5-en-1-ol (8c)
Colorless oil; yield: 95%; R_f = 0.5 (EtOAc–hexanes, 2:8).

IR (neat): 3417, 3073, 2927, 1640, 1578, 1477, 1427, 1072, 1022, 912, 736, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (m, 2 H), 7.27–7.24 (m, 3 H), 5.83–5.72 (m, 1 H), 4.98–4.92 (m, 2 H), 3.72–3.66 (m, 1 H), 3.12 (dd, *J* = 3.6, 12.9 Hz, 1 H), 2.89 (dd, *J* = 8.7, 12.9 Hz, 1 H), 2.22–2.07 (m, 2 H), 1.66–1.59 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.0, 133.0, 129.3, 129.2, 127.2, 114.9, 69.4, 37.0, 35.6, 30.0.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 233.71.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{16}NaOSe$: 279.0264; found: 279.0264.

(*R*)-2-Methyl-1-(4-nitrobenzoyl)-3-(phenylselanyl)propan-2-ol (8d)
Colorless oil; yield: 91%; R_f = 0.4 (EtOAc–hexanes, 3:7).

$[\alpha]_D^{25}$ +11.5 (*c* 2, $CHCl_3$).

IR (neat): 3472, 3056, 2978, 1725, 1526, 1274, 1104, 718 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 8.7 Hz, 2 H), 8.11 (d, *J* = 8.7 Hz, 2 H), 7.58–7.54 (m, 2 H), 7.21–7.19 (m, 3 H), 4.36 (d, *J* = 11.1 Hz, 1 H), 4.31 (d, *J* = 11.1 Hz, 1 H), 3.32 (d, *J* = 12.6 Hz, 1 H), 3.18 (d, *J* = 12.6 Hz, 1 H), 2.48 (s, 1 H), 1.42 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.2, 150.6, 135.0, 133.0, 130.7, 130.1, 129.2, 127.4, 123.5, 71.5, 70.8, 39.4, 24.7.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 228.01.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{17}NNaO_5Se$: 418.017; found: 418.0184.

1-(Allyloxy)-3-(phenylselanyl)propan-2-ol (8e)
Colorless oil; yield: 95%; R_f = 0.6 (EtOAc–hexanes, 2:8).

IR (neat): 3436, 3073, 2860, 1578, 1478, 1421, 1108, 929, 736, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.50 (m, 2 H), 7.26–7.21 (m, 2 H), 5.92–5.79 (m, 1 H), 5.28–5.14 (m, 2 H), 3.96–3.88 (m, 3 H), 3.54–3.43 (m, 2 H), 3.12–2.86 (m, 2 H), 2.85 (d, *J* = 4.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.3, 132.6, 129.6, 129.1, 127.0, 117.2, 72.7, 69.4, 31.8.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 242.423.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{16}NaO_2Se$: 295.0213; found: 295.0211.

(2*R,3*R**)-1,4-Bis(phenylselanyl)butane-2,3-diol (8g)**
Yield: 93%; mp 76°C; R_f = 0.5 (EtOAc–hexanes, 4:6).

IR (neat): 3417, 3173, 2927, 1428, 1032, 1022, 920, 746, 687 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.44 (m, 2 H), 7.25–7.21 (m, 3 H), 3.74 (dd, *J* = 5.4, 8.1 Hz, 1 H), 3.06–3.04 (m, 2 H), 2.93 (d, *J* = 5.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.9, 129.1, 129.0, 127.2, 71.3, 33.1, 32.6.

^{77}Se NMR (75 MHz, $CDCl_3$): δ = 244.61.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{18}NaO_2Se_2$: 424.9535; found: 424.9544.

β-Amino Sulfides/β-Hydroxy Sulfides; General Procedure
To a well-stirred soln of aziridine or epoxide (0.2 mmol, 1 equiv) in DMF (2 mL) was added the disulfide (0.1 mmol, 0.5 equiv) followed by K_2CO_3 (0.4 mmol, 2 equiv) and rongalite (**1**, 0.6 mmol, 3 equiv). The mixture was stirred at r.t. for 30–60 min (TLC monitoring). After complete consumption of the starting material, H_2O was added to quench the reaction and it was extracted with CH_2Cl_2 (2 × 10 mL). The organic layer was separated and dried (anhyd Na_2SO_4). The crude product was further purified by column chromatography (silica gel).

(*S*)-1-Phenyl-3-(2-pyridylsulfanyl)-*N*-tosylpropan-2-amine (10c)
Yield: 92%; mp 63°C; R_f = 0.5 (EtOAc–hexanes, 3:7).

$[\alpha]_D^{25}$ –63.4 (*c* 1, $CHCl_3$).

IR (neat): 3278, 3062, 2924, 1666, 1581, 1454, 1332, 1159, 1092, 739, 665 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.44–8.42 (m, 1 H), 7.93 (d, *J* = 4.2 Hz, 1 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 7.49 (dt, *J* = 2.1, 7.2 Hz, 1 H), 7.31–7.05 (m, 9 H), 3.61–3.52 (m, 1 H), 4.23 (dd, *J* = 4.2, 13.5 Hz, 1 H), 3.03 (dd, *J* = 7.5, 14.7 Hz, 1 H), 2.97–2.88 (m, 2 H), 2.36 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.5, 148.9, 142.7, 137.5, 136.4, 129.5, 128.5, 127.0, 126.6, 122.7, 120.2, 56.7, 41.9, 33.8, 21.4.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{22}N_2NaO_2S_2$: 421.1020; found: 412.1016.

(*S*)-1-(4-Nitrophenylsulfanyl)-1-phenyl-*N*-tosylpropan-2-amine (10e)
Yield: 95%; mp 121 °C; R_f = 0.4 (EtOAc–hexanes, 3:7).

$[\alpha]_D^{25}$ –62.1 (*c* 1, $CHCl_3$).

IR (neat): 3263, 2923, 1578, 1511, 1336, 1154, 1089, 741, 662 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 9 Hz, 2 H), 7.48 (d, *J* = 8.1 Hz, 2 H), 7.27–7.18 (m, 5 H), 6.99 (d, *J* = 6.3 Hz, 2 H), 6.98–6.95 (m, 2 H), 4.90 (d, *J* = 6.9 Hz, 1 H), 3.59–3.48 (m, 1 H), 3.30 (dd, *J* = 4.5, 13.8 Hz, 1 H), 3.08–2.93 (m, 2 H), 2.77 (dd, *J* = 6.9, 13.8 Hz, 1 H), 2.37 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.6, 145.3, 143.5, 136.4, 135.9, 129.6, 128.8, 127.0, 126.9, 126.7, 123.9, 53.8, 39.7, 36.4, 21.5.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{22}N_2NaO_4S_2$: 465.0919; found: 465.0914.

4-(Phenylsulfanyl)-(tosylamino)butan-1-ol (11b)
Colorless oil; yield: 94%; R_f = 0.3 (EtOAc–hexanes, 3:7).

IR (neat): 3483, 3293, 2966, 3931, 2874, 1635, 1598, 1440, 1325, 1159, 1093, 1033, 747, 667 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.1 Hz, 2 H), 7.19–7.13 (m, 7 H), 5.40 (d, *J* = 8.1 Hz, 1 H), 3.73 (ddd, *J* = 3.3, 9.0, 11.7 Hz, 1 H), 3.56–3.45 (m, 2 H), 3.06 (dd, *J* = 4.2, 14.1 Hz, 1 H), 2.68 (dd, *J* = 7.2, 14.1 Hz, 1 H), 2.33 (s, 3 H), 1.86–1.71 (m, 2 H), 1.60–1.49 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.5, 137.2, 135.2, 129.8, 129.7, 129.1, 127.0, 126.6, 59.0, 39.1, 35.5, 21.5.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{19}NNaO_3S_2$: 360.0704; found: 360.0712.

(3*R,4*S**)-2-Methyl-4-(phenylsulfanyl)-*N*-tosylpentan-3-amine (11d)**
Colorless oil; yield: 94%; R_f = 0.3 (EtOAc–hexanes, 1:9).

IR (neat): 3483, 3293, 2966, 3931, 2874, 1635, 1598, 1440, 1325, 1159, 1093, 1033, 747, 667 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.4 Hz, 2 H), 7.26–7.19 (m, 7 H), 4.97 (d, *J* = 9.9 Hz, 1 H), 3.41–3.34 (m, 1 H), 3.14–3.06 (m, 1 H), 2.39 (s, 3 H), 2.11–1.99 (m, 1 H), 1.23 (d, *J* = 6.9 Hz, 3 H), 0.88–0.84 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0, 138.7, 135.0, 131.8, 129.4, 128.9, 127.0, 62.5, 48.7, 29.3, 21.5, 21.0, 19.2, 17.6.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{25}NNaO_2S_2$: 386.1224; found: 386.1223.

(3*R,4*R**)-2-Methyl-4-(phenylsulfanyl)-*N*-tosylpentan-3-amine (11e)**

Yield: 92%; mp 67°C; R_f = 0.3 (EtOAc–hexanes, 1:9).

IR (neat): 3289, 2965, 2929, 1598, 1439, 1327, 1160, 1093, 1025, 909, 748, 665 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.4 Hz, 2 H), 7.39–7.31 (m, 2 H), 7.31–7.22(m, 5 H), 4.87 (d, *J* = 9.0 Hz, 1 H), 3.47 (ddd, *J* = 3.0, 4.2, 22.2 Hz, 1 H), 3.22–3.15 (m, 1 H), 2.39 (s, 3 H), 2.02–1.88 (m, 1 H), 1.16 (d, *J* = 7.2 Hz, 3 H), 0.8 (d, *J* = 6.9 Hz, 3 H), 0.77 (d, *J* = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0, 138.6, 134.3, 132.5, 129.4, 128.4, 127.3, 126.9, 63.9, 47.4, 30.4, 21.4, 20.7, 19.4, 19.2.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{25}NNaO_2S_2$: 386.1224; found: 386.1235.

1-(Phenylsulfanyl)hex-5-en-2-ol (12c)

Colorless oil; yield: 94%; R_f = 0.4 (EtOAc–hexanes, 2:8).

IR (neat): 3409, 2912, 1640, 1584, 1480, 1439, 1069, 1025, 912, 738, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.19 (m, 5 H), 5.86–5.73 (m, 1 H), 5.05–4.94 (m, 2 H), 3.73–3.65 (m, 1 H), 3.15 (dd, *J* = 3.6, 14.1 Hz, 1 H), 2.85 (dd, *J* = 9.0, 14.1 Hz, 1 H), 2.5 (d, *J* = 3 Hz, 1 H), 2.29–2.07 (m, 2 H), 1.66–1.59 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.0, 135.3, 130.0, 129.0, 126.6, 115.0, 68.9, 42.1, 35.1, 29.9.

HRMS: *m*/*z* [M + K]$^+$ calcd for $C_{12}H_{16}NaOS$: 247.0559; found: 247.0564.

(*R*)-2-Methyl-1-(4-nitrobenzoyl)-3-(phenylsulfanyl)propan-2-ol (12d)

Yield: 91%; mp 52°C; R_f = 0.4 (EtOAc–hexanes, 3:7).

$[\alpha]_D^{25}$ +6.0 (*c* 2, $CHCl_3$).

IR (neat): 3483, 3293, 2966, 3931, 2874, 1635, 1598, 1440, 1325, 1159, 1093, 1033, 747, 667 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 7.2 Hz, 2 H), 8.14 (d, *J* = 7.2 Hz, 2 H), 7.44–7.41 (m, 2 H), 7.27–7.13 (m, 3 H), 4.36 (d, *J* = 11.4, 1 H), 4.30 (d, *J* = 11.4 Hz, 1 H), 3.32 (d, *J* = 12 Hz, 1 H), 3.20 (d, *J* = 12 Hz, 1 H), 2.73 (s, 1 H), 1.40 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3, 150.6, 136.1, 135.0, 130.7, 130.2, 129.1, 126.8, 123.5, 71.9, 70.4, 44.4, 24.3.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{17}NNaO_5S$: 370.0725; found: 370.0724.

1-(Allyloxy)-3-(phenylsulfanyl)propan-2-ol (12e)

Colorless oil; yield: 93%; R_f = 0.6 (EtOAc–hexanes, 2:8).

IR (neat): 3435, 3914, 3860, 1584, 1481, 1439, 1108, 930, 739, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.35 (m, 2 H), 7.29–7.24 (m, 2 H), 7.20–7.15 (m, 1 H), 5.91–5.80 (m, 1 H), 5.28–5.15 (m, 2 H), 3.98–3.87 (m, 3 H), 3.53 (dd, *J* = 4.2, 9.9 Hz, 1 H), 3.47 (dd, *J* = 6.0, 9.9 Hz, 1 H), 3.11 (dd, *J* = 6.0, 13.8 Hz, 1 H), 3.03 (dd, *J* = 4.2, 13.8 Hz, 1 H), 2.91 (d, *J* = 4.5 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.5, 134.2, 129.5, 128.9, 126.2, 117.2, 72.3, 72.2, 68.9, 37.3.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{16}NaO_2S$: 247.0769; found: 247.0784.

(2*R,3*R**)-1,4-Bis(phenylsulfanyl)butane-2,3-diol (12g)**

Colorless oil; yield: 94%; R_f = 0.5 (EtOAc–hexanes, 4:6).

IR (neat): 3483, 3293, 2966, 3931, 2874, 1635, 1598, 1440, 1325, 1159, 1093, 1033, 747, 667 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.16 (m, 5 H), 3.73 (dd, *J* = 5.4, 8.7 Hz, 1 H), 3.12–3.07 (m, 2 H), 3.91 (d, *J* = 5.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.8, 129.9, 129.0, 126.6, 70.2, 38.1.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{18}NaO_2S_2$: 424.9535; found: 424.9544.

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