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Tandem aziridine ring opening-disulfide formation-reduction-Michael addition in one-pot mediated by tetrathiomolybdate

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ABSTRACT

A detailed study of tetrathiomolybdate mediated tandem regio- and stereoselective ring opening of aziridine, disulfide formation, reduction of disulfide bond and Michael reaction in a one-pot operation is reported. This constitutes four reactions that take place in one-pot operation. In the reaction of $[BnEt_3N]_4MoS_4$ with an aziridine derived from cyclohexene and in the absence of Michael acceptor intermediates sulfonamidodisulfide and sulfonamidothiol were isolated and fully characterized. It has also been shown that it is possible to carry out selective opening of the aziridine ring in the presence of an epoxide. By incorporating a suitable Michael acceptor as part of the substrate, intramolecular 1,4-addition could be performed, to achieve the synthesis of sulfur containing acyclic, cyclic amino acid ester derivatives and thia-bicyclo[3.3.1]nonane derivatives in good yields.

1. Introduction

After the discovery of the Ugi four-component four-center reaction, multicomponent reactions (MCR) involving tandem processes with at least three different simple substrates have emerged as an extremely powerful synthetic tool in organic synthesis especially in the field of combinatorial chemistry and drug discovery.[1] This methodology allows facile formation of several new covalent C–C and C–X (X=O, N, S, Se) bonds in a one-pot operation with high levels of molecular complexity and diversity. This would be quite close to the concept of an ideal synthesis and is particularly well adapted for parallel synthesis. To synthesize sulfur containing organic compounds by MCR approach, very few reports are available in the literature due to the lack of efficient sulfur transfer reagents.[2] In earlier reports, we presented results on the nucleophilic ring opening of various aziridines with benzyltriethylammonium tetrathiomolybdate[3] $[BnEt_3N]_2MoS_4$, **1** and demonstrated the utility of this methodology for the synthesis of ß-sulfonamidodisulfides,[4] ß-sulfonamidosulfides[5] and a number of interesting sulfur heterocycles with high regio- and stereocontrol.

In continuing our studies to explore the redox chemistry associated with Mo–S systems,[6] we found that tetrathiomolybdate **1** can mediate not only the aziridine ring opening to form a disulfide bond but can also cleave the disulfide bond under appropriate reaction conditions.[7] Herein, we report a systematic study of tetrathiomolybdate mediated tandem regio- and stereoselective ring opening of aziridine, disulfide formation, *in situ* reduction of disulfide bond followed by Michael reaction to give a variety of ß-sulfonamidosulfide derivatives in good yields. The main advantage of this methodology is that four reactions involving three components take place in a tandem fashion in one-pot.

2. Results and discussion

Our investigation began with the study of nucleophilic ring opening of optically pure *N*-tosyl-2-benzyl aziridine[8] **2** with **1** [2.2 equiv, CH_3CN, 28 °C, 3–8 h] in the presence of different Michael acceptors **3**, which underwent smooth aziridine ring opening followed by disulfide formation, *in situ* reduction of disulfide bond and Michael reaction in a tandem fashion to afford ß-sulfonamidosulfides **4** in good yields with full regiocontrol (Scheme 1). This reaction was tested with different Michael acceptors such as methyl acrylate **3a**, phenyl vinyl sulfone **3b**, methyl methacrylate **3c**, methyl 2-acetamidoacrylate **3d**, acrylonitrile **3e**, ethyl vinyl ketone **3f** and benzyl acrylate **3g** (Table 1). In all cases the reaction worked very well resulting in good yields of the products. Reaction of **3c** and **3d** led to the formation of 1:1 diastereomeric mixture of thia-amino acid derivatives **4c** and **4d**, respectively in good yields.

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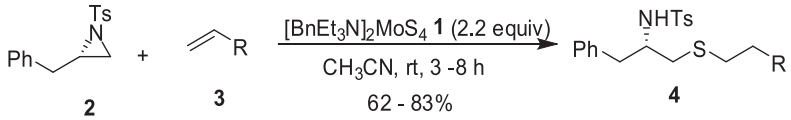
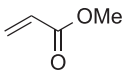
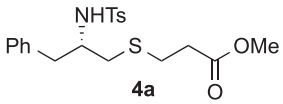
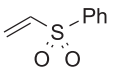
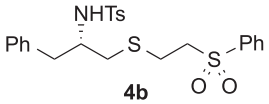
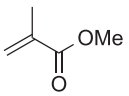
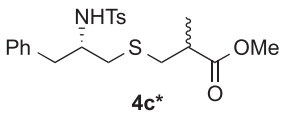
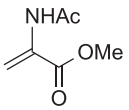
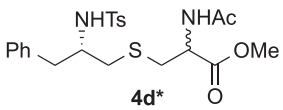
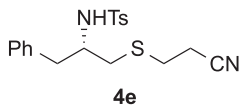
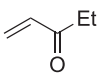
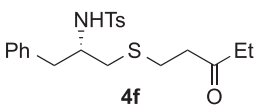
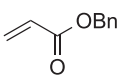
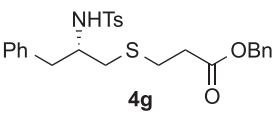
0040-4020/



Scheme 1. Tandem aziridine opening, disulfide formation, reduction and Michael reaction.

Results of this investigation with different Michael acceptors are summarized in Table 1.

Table 1
Synthesis of thio-amino acids by tandem multi-step reactions

Entry	Michael acceptor	Product	Time (h)	Yield (%)
1	 **3a**	 **4a**	3	85
2	 **3b**	 **4b**	4	74
3	 **3c**	 **4c***	7	66
4	 **3d**	 **4d***	8	60
5	 **3e**	 **4e**	5	50
6	 **3f**	 **4f**	4	78
7	 **3g**	 **4g**	6	55

*compounds **4c** and **4d** were isolates as 1:1 mixture of diastereomers.

2.1. Ring opening of mono-substituted aziridines 5 followed by Michael reaction with 3a in the presence of 1

To study the scope of this methodology further, reactions were carried out with different aziridines and methyl acrylate **3a** was chosen as the Michael acceptor. First we treated enantiomerically pure mono-substituted aziridines[8] **5** with **1** [2.2 equiv, CH_3CN, 28 °C, 2–8 h] in the presence of **3a** to afford sulfur-containing amino-acid (*ß*-sulfonamidosulfides) derivatives **6** in good yields (Scheme 2). Changing the substituents on the aziridine ring from a methyl to tertiary butyl group did not affect the reactivity profile of the aziridine. In fact, in all cases the reaction worked very well with very good regioselectivity. In the case of methionine derived aziridine **5g** and tryptophan derived aziridine **5i**, the reaction proceeded very well without affecting the additional functional groups (CH_3S– and –NH) present in the molecules (Table 2, entry 7 and 9). The results are summarized in Table 2.

2.2. Ring opening of carbohydrate derived aziridines followed by Michael reaction with 3a in the presence of 1

In order to expand the scope of this methodology and to study the reactivity of other aziridines having different functionality and complexity, D-glucose and D-mannitol derived aziridines **7a**[9] and **7b**[10] were treated with **1** [2.2 equiv, CH_3CN, 28 °C, 4–5 h] in the presence of **3a** to afford the corresponding sulfur-containing sugar amino acid conjugates **8a** and **8b**, respectively in good yields. This tandem multi-step reaction worked equally well in the case of complex aziridine derived from carbohydrates to give the desired products in good yields (Scheme 3).

2.3. Ring opening of 2,2-disubstituted aziridines with 1 followed by Michael reaction

Having successfully demonstrated the efficiency of ring opening reactions with **1** the stage was set for carrying out the reaction of 2,2-disubstituted aziridines. Treatment of **9** with **1** [2.2 equiv, CH_3CN, 28 °C, 3–6 h] in the presence of **3a** furnished the substituted sulfur-containing amino-acid derivatives **10** in good yields (Scheme 4). Although it has been reported in the literature that **9a** can undergo ring opening from the less hindered as well as the more hindered side with sulfur nucleophiles,[11] in our case aziridine ring opening with **1** took place exclusively from the sterically less substituted carbon centre with full regiocontrol. This methodology has been extended to the synthesis of *ß*-methyl cystinol derived.

ß-sulfonamidosulfides **10c** and *ß*-methyl homo cystinol derived *ß*-sulfonamidosulfide **10d** in a single step from the corresponding aziridines **9c** and **9d**, respectively in good yields (Table 3, entry 3 and 4).

2.4. Regio- and stereoselective ring opening of 2,3-disubstituted aziridines 11 followed by Michael reaction with 3a in the presence of 1

To demonstrate the stereoselectivity in the ring opening of 2,3-disubstituted aziridines with **1**, *meso*-*N*-tosyl-2,3-diethylaziridine **11a**[12] was treated with **1** (2.2 equiv; CH_3CN, 28 °C, 10 h) in the presence of **3a** to afford exclusively the sulfur-containing amino-acid derivative **12a** (*anti*-isomer; 68% yield). In the case of (±)-*trans*-*N*-tosyl-2,3-diethylaziridine **11b**,[12] sulfur-containing amino-acid derivative **12b** (*syn*-isomer) was obtained in 70% yield under the same reaction conditions (Scheme 5, Table 4).

In order to assess the regio- and stereoselectivity together in the same substrate, (±)-*cis*-*N*-tosyl-2-isopropyl-3-methylaziridine **11c**[4] was treated with **1** (2.2 equiv; CH_3CN, 28 °C, 12 h) in presence of **3a** to afford exclusively the *anti*-amino-acid derivative **12c** in 65% yield. In the case of (±)-*trans*-*N*-tosyl-2-isopropyl-3-methylaziridine **11d**,[4] the *syn*-amino-acid derivative **12d** was obtained in 68% yield under the same reaction conditions. Here, tetrathiomolybdate **1** attacks the aziridines **11c** and **11d** at the less hindered C2 carbon site in a S_N2 fashion with regio- and stereocontrol and with complete inversion (Table 4, entry 3 and 4) followed by 1,4-addition to form **12c** and **12d**, respectively.

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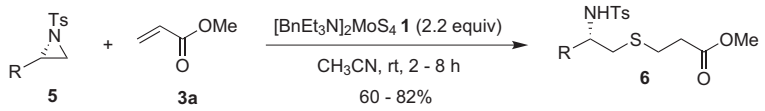
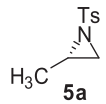
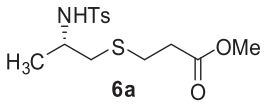
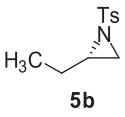
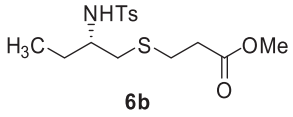
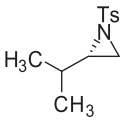
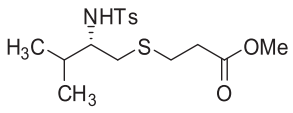
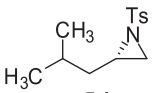
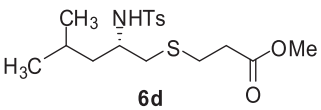
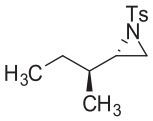
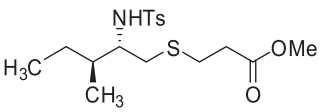
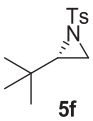
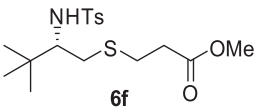
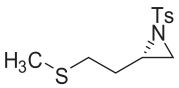
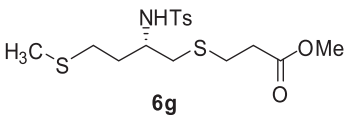
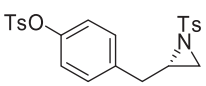
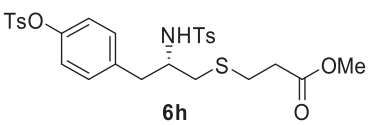
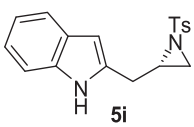
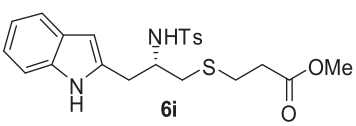


Scheme 2. Tandem multi-step reaction of mono-substituted aziridines with methyl acrylate **3a**.

Table 2
Synthesis of β-aminosulfides by tandem multi-step reaction

Entry	Optically pure aziridines	Product	Time (h)	Yield (%)
1	 **5a**	 **6a**	2	82
2	 **5b**	 **6b**	3	80
3	 **5c**	 **6c**	5	78
4	 **5d**	 **6d**	5	76
5	 **5e**	 **6e**	6	70
6	 **5f**	 **6f**	8	75
7	 **5g**	 **6g**	4	63
8	 **5h**	 **6h**	3	72
9	 **5i**	 **6i**	8	60

2.5. Ring opening of aziridines derived from cyclic system followed by Michael addition with 3a in the presence of 1

Next, this methodology was extended to study the reaction of aziridines derived from cyclic systems. The aziridines **13** were synthesized starting from the corresponding cyclic olefins using sharpless aziridination protocol.[13] Reaction of aziridines **13** with **1** [2.2 equiv, CH_3CN, 28 °C, 4–24 h] in the presence of **3a** led to facile ring opening in a stereoselective manner to afford amino-acid derivatives **14** (*trans*-isomer) in very good yields (Scheme 6 and Table 5). It is interesting to note that the reaction can be performed efficiently with substrate **13c** containing two free hydroxy groups. The reaction in the case of aziridine **13e** was considerably slower and it gave the ring-opened product **14e** in only 40% yield. When

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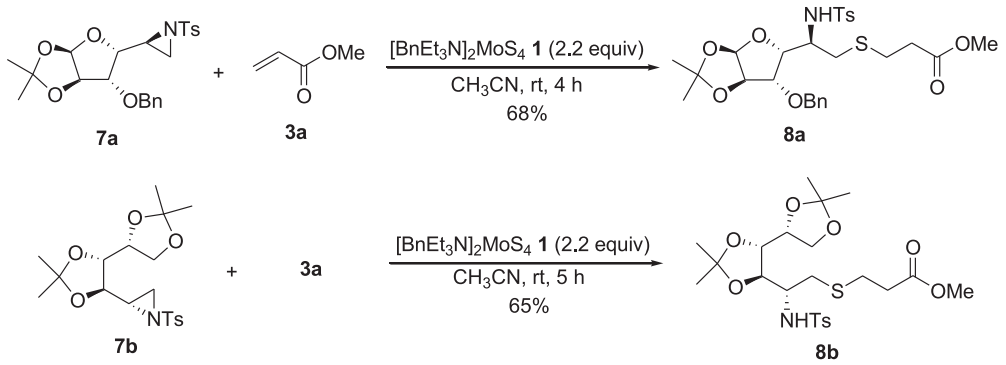
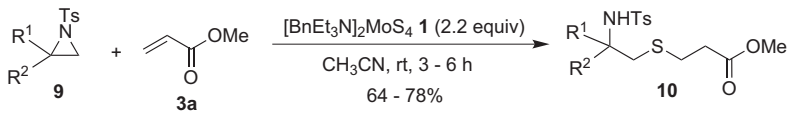
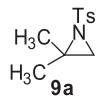
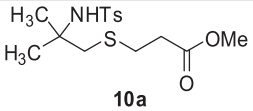
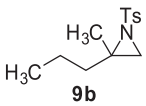
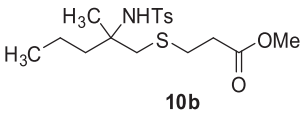
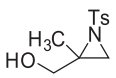
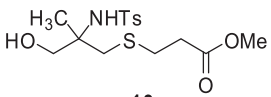
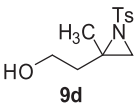
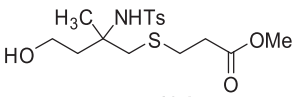


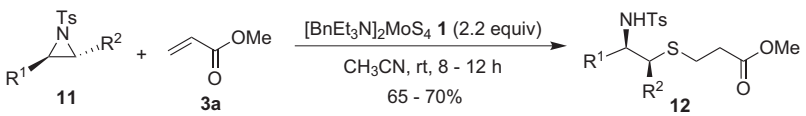
Scheme 3. Tandem multi-step reaction of carbohydrate derived aziridines **7a** and **7b** with **1**.



Scheme 4. Tandem multi-step reaction of 2,2-disubstituted aziridines **9** with methyl acrylate **3a**.

Table 3
Ring opening of 2,2-disubstituted aziridines **9** with **1** followed by Michael reaction with **3a**

Entry	2,2-Disubstituted aziridines	β-Substituted β-aminodisulfide	Time (h)	Yield (%)
1	 **9a**	 **10a**	3	78
2	 **9b**	 **10b**	4	75
3	 **9c**	 **10c**	5	68
4	 **9d**	 **10d**	6	64



Scheme 5. Tetrathiomolybdate **1** mediated regio- and stereoselective ring opening of 2,3-disubstituted aziridines **11** and Michael reaction with **3a** in tandem multi-step reaction.

the reaction was extended to aziridine **13f** with **1** it failed to undergo the reaction even after 24 h and the aziridine **13f** was recovered unchanged. The failure of the reaction may be attributed to the puckered nature of the cyclooctane conformation.

2.6. Tentative mechanism of tandem multi-step reactions with aziridines mediated by tetrathiomolybdate 1

It is reasonable to visualize the nucleophilic attack of tetrathiomolybdate **1** on the aziridine **13b** in a S_N2 fashion with regio- and stereocontrol and with complete inversion. The ring opening of aziridine **13b** with **1** occurs first followed by disulfide formation[14] to furnish **13g**, which undergoes reduction of the disulfide bond in the presence of second equivalent of **1** to form the thiolate **13h** in situ,[7] which finally undergoes 1,4-addition to Michael acceptor **3a** to form *ß*-sulfonamidosulfide derivative **14b** as shown in Scheme 7. To gain further insight into the reaction pathway and mechanism that has been postulated, the aziridine **13b** was treated with excess tetrathiomolybdate **1** [2.2 equiv, CH_3CN, 28 °C] in the absence of Michael acceptor and was allowed to react for a longer time (24 h). Under these conditions the intermediates *trans-ß*-sulfonamidodisulfide[4] **13g** and thiol **13h′** were isolated in approximately 1:1 ratio

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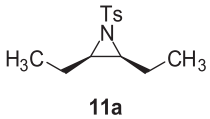
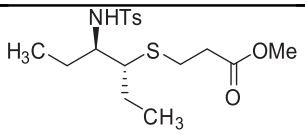
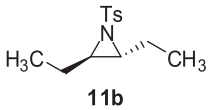
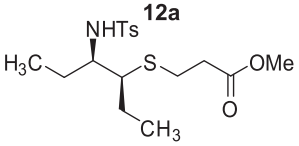
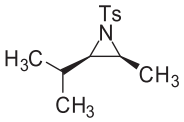
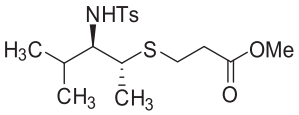
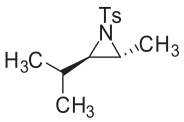
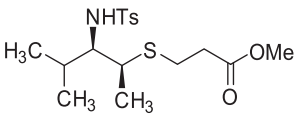
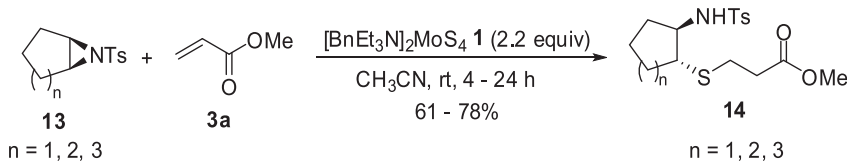
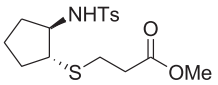
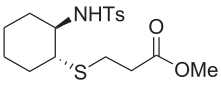
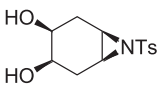
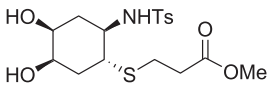
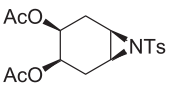
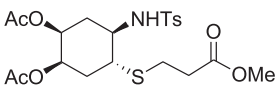
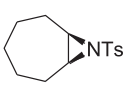
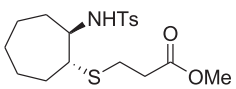
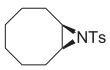
Table 4
Regio- and stereoselective ring opening of 2,3-disubstituted aziridines with **1** followed by Michael reaction with **3a**

Entry	2,3-Disubstituted aziridines	β-Aminodisulfides	Time (h)	Yield (%)
1	 **11a**	 **12a**	10	68
2	 **11b**	 **12b**	9	70
3	 **11c**	 **12c**	12	65
4	 **11d**	 **12d**	8	68



Scheme 6. Multi-step reaction of 2,3-disubstituted cyclic-aziridines **13** with **3a** in the presence of **1**.

Table 5
Synthesis of cyclic *trans*- thia-amino acid esters **14**

Entry	Aziridines	Product	Time (h)	Yield (%)
1	 **13a**	 **14a**	4	78
2	 **13b**	 **14b**	6	72
3	 **13c**	 **14c**	6	62
4	 **13d**	 **14d**	6	70
5	 **13e**	 **14e**	24	40
6	 **13f**	No reaction	24	—

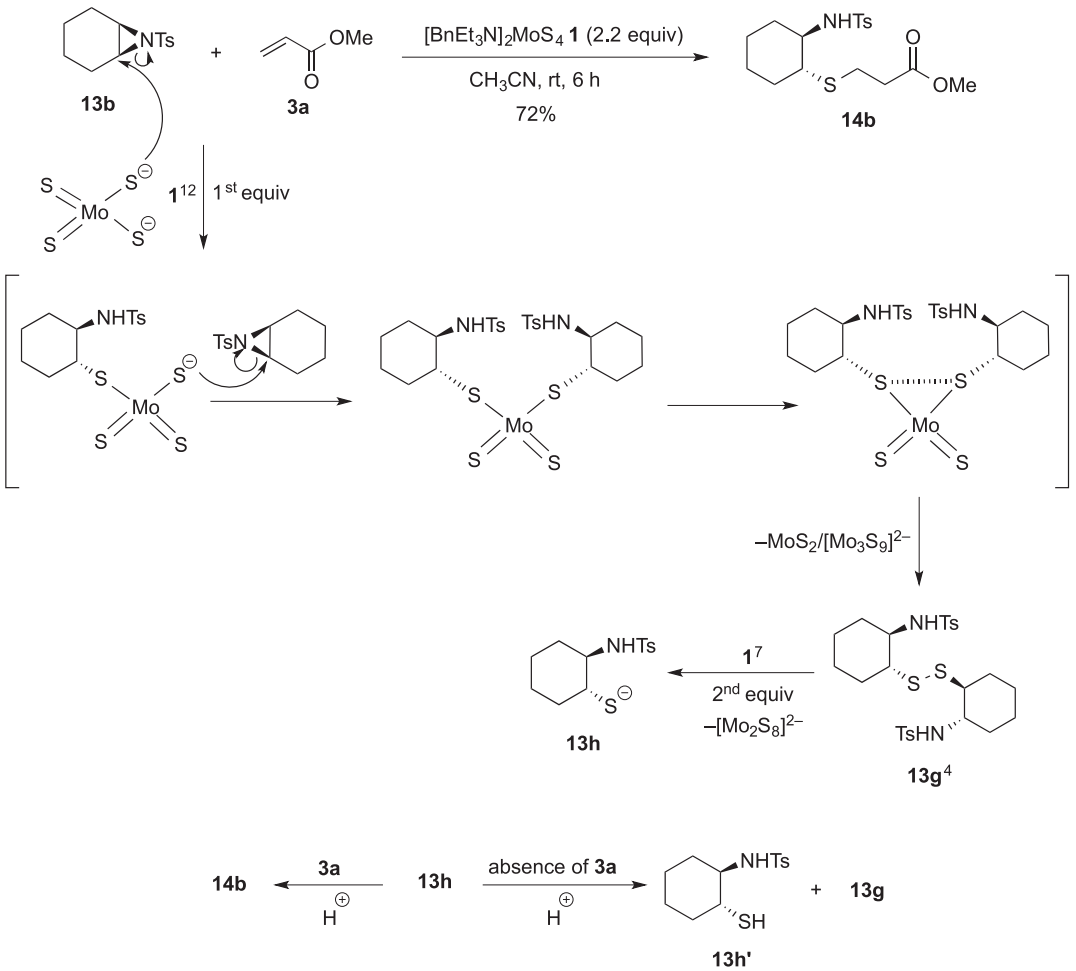
after work up. The structure of intermediate **13h′** was further confirmed by X-ray crystallography[15] (Fig. 1).

2.7. Selective ring opening of aziridines with 1 in the presence of epoxides followed by Michael reaction with 3a

To demonstrate the selective ring opening of aziridines in the presence of epoxides, aziridino-epoxides[16] **15b**–**15e** were synthesized from the corresponding 1,4-cyclic dienes using Sharpless aziridination protocol [1,4-diene, 3 mmol; CAT (Chloramine-T), 3.3 mmol; PTAB ($PhMe_3N^+Br_3^-$), 0.3 mmol; 15 mL CH_3CN, 28 °C, 12 h] followed by epoxidation using *m*-CPBA as the reagent.[17] Treatment of aziridino-epoxides **15a**–**15e** with **1** (2.2 equiv, CH_3CN, 28 °C) in the presence of **3a** resulted in the exclusive formation of products **16a**–**16e**, respectively in good yields (Scheme 8 and Table 6). In all the cases epoxide ring remained unaffected under the reaction conditions.

2.8. Ring opening of aziridines followed by intramolecular Michael reaction mediated by 1

By incorporating a suitable Michael acceptor in the same aziridine, intramolecular 1,4 addition could be performed in a single pot operation. Selective aziridination at the electron rich olefin of (*R*)-carvone using Sharpless aziridination protocol afforded the carvone derived aziridine **17** as a diastereomeric mixture (dr=1:1) in good yield. Treatment of the diastereomeric mixture of aziridine **17** with tetrathiomolybdate **1** (2.2 equiv; CH_3CN, 28 °C, 10 h) yielded two diastereomers of thia-bicyclo[3.3.1]nonane derivatives **18a**



Scheme 7. Tentative mechanism for tetrathiomolybdate **1** mediated tandem multi-step ring opening of aziridine, disulfide formation, disulfide bond cleavage followed by Michael reaction.

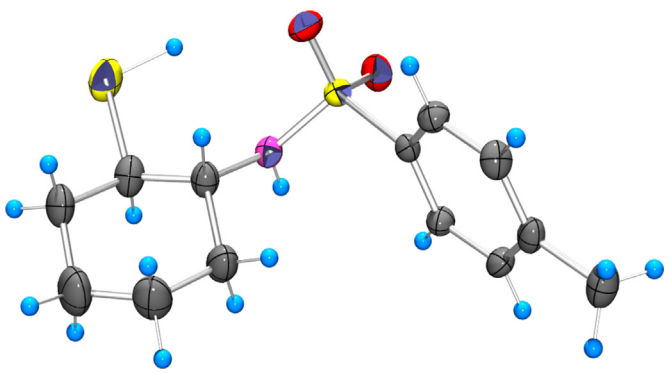
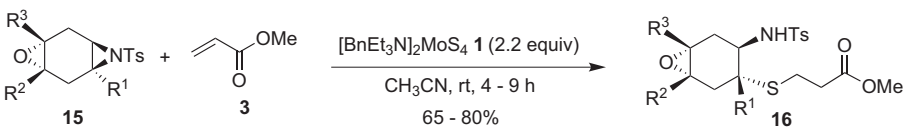


Fig. 1. Molecular structure of **13h′**.

and **18b** (1:1), respectively in 88% yield (Scheme 9). These diastereomers were easily separated using column chromatography [using ethyl acetate and hexanes (2:8) as an eluant]. Compound **18a** was isolated as very good quality crystals with a melting point of 174 °C, whereas compound **18b** was isolated as fluffy, colorless solid with the melting point of 223 °C. The solid-state structure of **18a** was confirmed by single crystal X-ray analysis[18] (Fig. 2). The same methodology was extended to (*S*)-carvone derived aziridine to synthesize the opposite enantiomer.

Next, this methodology was extended to study the reaction of aziridine derived from (−)-perillaldehyde. Reaction of aziridines **19** with **1** [2.2 equiv, CH_3CN, 28 °C 10 h] led to facile aziridine ring opening in a regioselective manner and subsequent intramolecular Michael reaction to afford an inseparable diastereomeric mixture of thia-bicyclo[3.3.1]nonane derivatives **20a** and **20b** (1:1) in 81% yield (Scheme 10).



Scheme 8. Tandem multi-step reaction of aziridino-epoxides **15** with **1** in the presence of **3a**.

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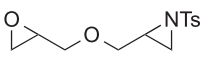
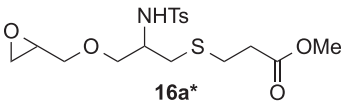
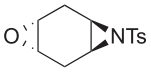
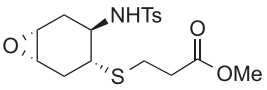
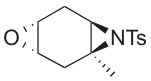
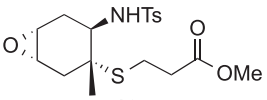
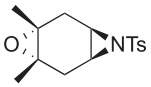
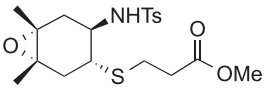
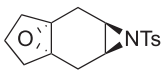
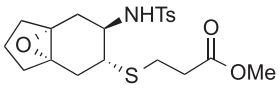
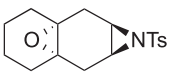
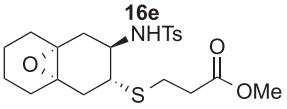
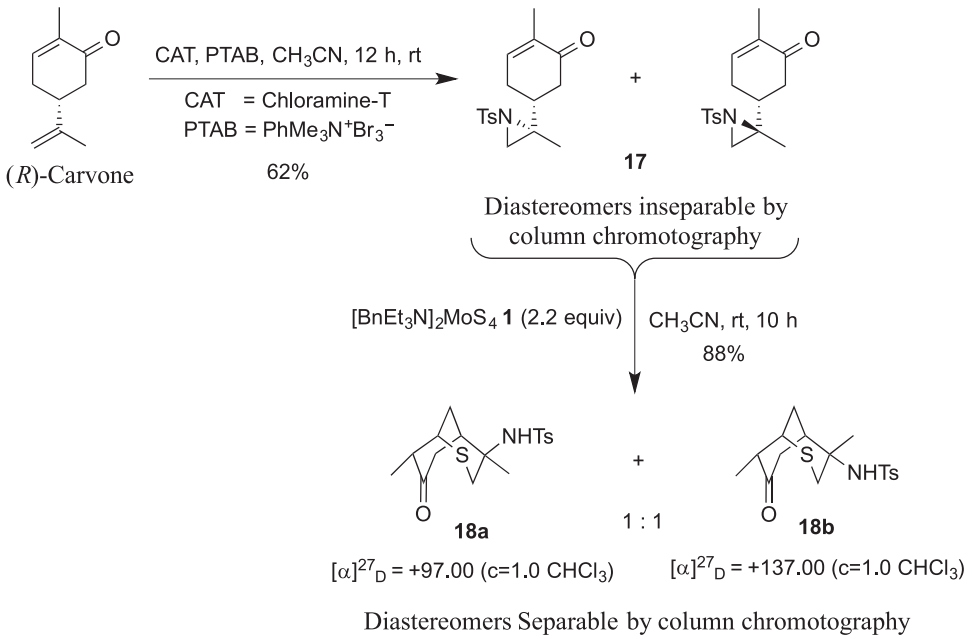
Table 6
Selective aziridine ring opening in presence of epoxides followed by Michael reaction

Entry	*trans*-Aziridino-epoxides	Product	Time (h)	Yield (%)
1	 **15a***	 **16a***	4	65
2	 **15b**	 **16b**	6	80
3	 **15c**	 **16c**	8	70
4	 **15d**	 **16d**	9	77
5	 **15e**	 **16e**	5	70
6	 **15f**	 **16f**	6	72

* compounds **15*** and **16*** are 1:1 mixture of diastereomers.



Scheme 9. Tandem intramolecular multi-step reaction in the synthesis of thiabicyclo[3.3.1]nonane derivative **18**.

2.9. Application of this methodology for the synthesis of tetrahydrothiophane derived amino ester derivatives

By incorporating an α,β-unsaturated ester in the aziridine backbone in an appropriate fashion, it is possible to synthesize sulfur containing unnatural amino acids. Aziridination of homo allylic alcohol **21** using Sharpless aziridination protocol gave aziridino-alcohol **22** in 56% yield. Swern oxidation of **22** followed by Wittig reaction at −78 °C in one-pot gave *trans*-α,β-unsaturated aziridino ester **23** in 62% yield.[19] The formation of *Z*-isomer of **23** was detected as a minor product during the course of reaction, but it could not be isolated in pure form by column chromatography due to its instability.[20]

Treatment of aziridine **23** with **1** [2.2 equiv, CH_3CN, 28 °C, 5 h] led to facile aziridine ring opening in a regioselective manner to afford a single diastereomer of tetrahydrothiophane derived *cis*-ω-

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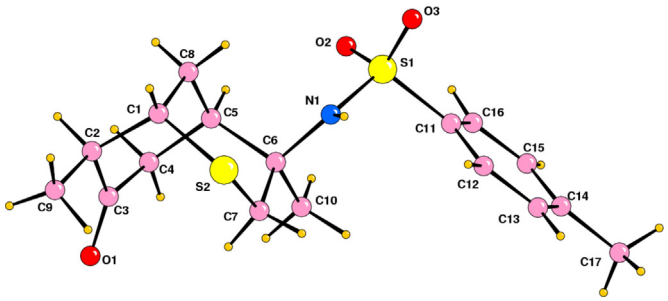
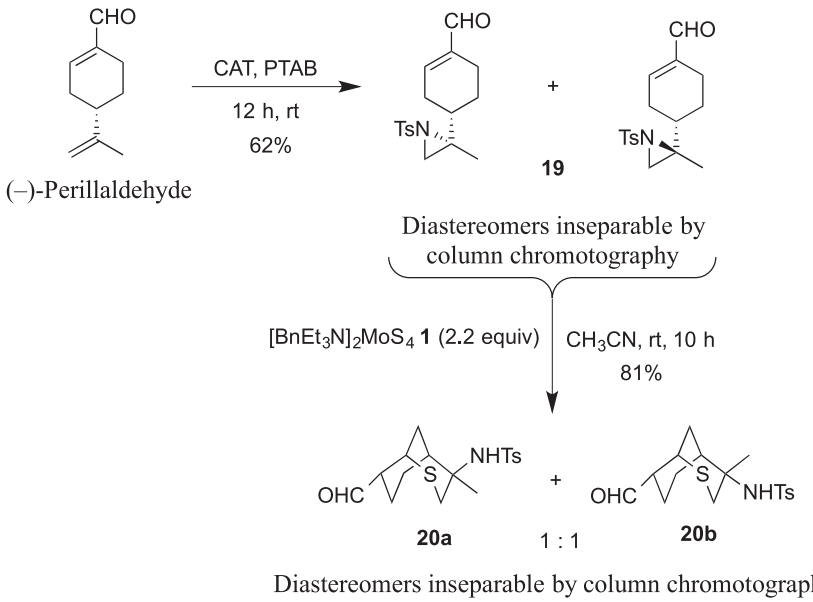
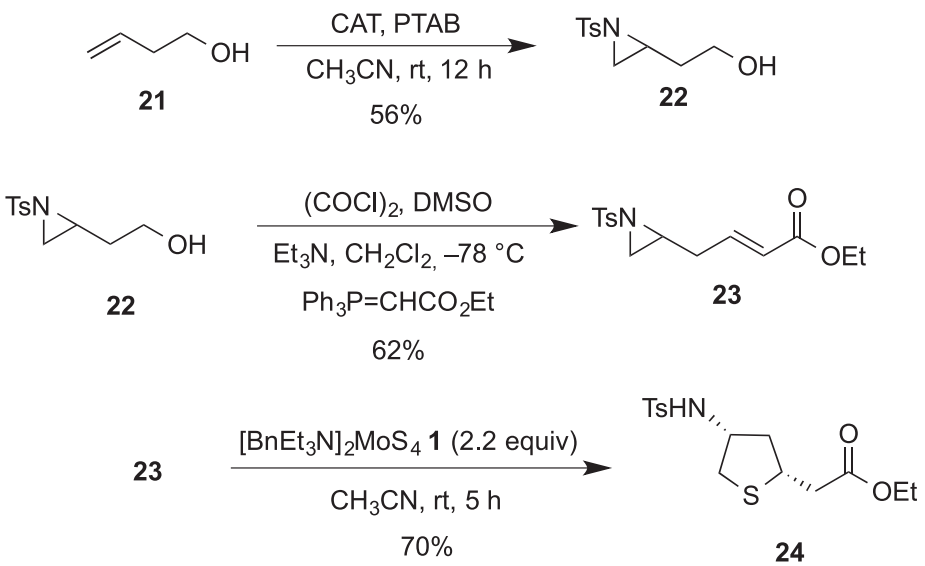


Fig. 2. X-ray CAMERON structure of compound **18a**.

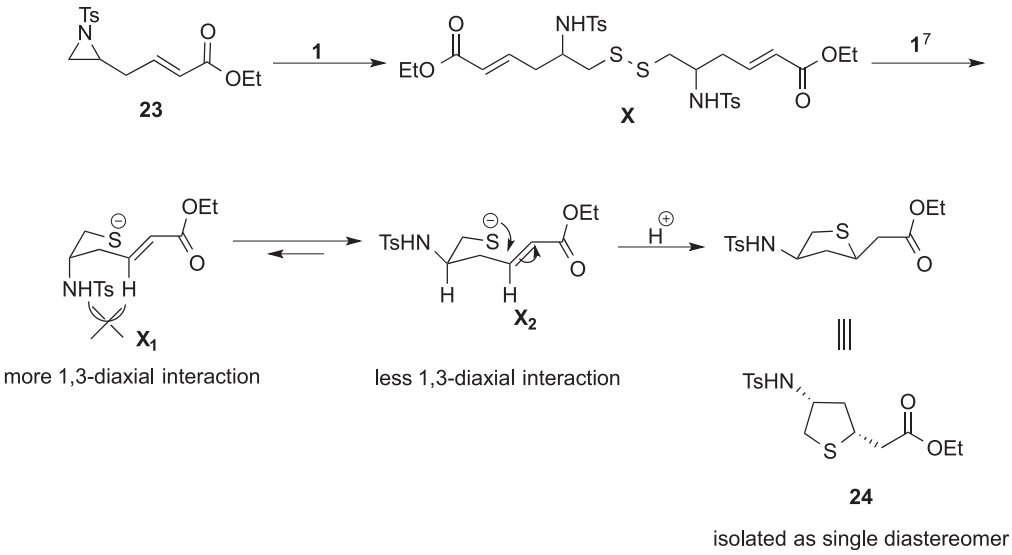
amido ester **24** in 70% yield (Scheme 11). In order to confirm the formation of a single diastereomer during the reaction, ^{1}H NMR of **24** was recorded on the crude product, which clearly indicates the formation of a single diastereomer. The formation of only one diastereomer during the reaction can be explained as shown in Scheme 12. Reaction of **23** with **1** furnishes intermediate disulfide **X**, which further undergoes reductive cleavage of disulfide bond[7] in the presence of excess reagent **1** to give thiolate intermediates $\mathbf{X_1}$ and $\mathbf{X_2}$. In the chair-like intermediate[21] $\mathbf{X_1}$ the −NHTs group exists in an axial position whereas in the case of chair-like intermediate $\mathbf{X_2}$ the −NHTs group exists in the equatorial position. We hypothesize that the faster rate of 5-*exo*-*trig* thia-cyclization of the *pseudo*-equatorial intermediate $\mathbf{X_2}$ could lead to the formation of single diastereomer **24** as shown in Scheme 12. The structure of compound **24** was confirmed by ^{1}H, ^{13}C, DEPT, ^{1}H–^{1}H, ^{1}H–^{13}C and NOESY studies. Recrystallization of **24** in ethyl acetate and hexane mixture provided good quality crystals, which were subjected to X-ray crystallographic investigation in order to determine the stereo chemical outcome of the reaction. The X-ray structure of **26**[22] shown in Fig. 3 clearly confirms that amido and ester groups are *cis* to each other.



Scheme 10. Tandem intramolecular multi-step reaction in the synthesis of amido-thiabicyclo[3.3.1]nonanal derivative **20**.



Scheme 11. Synthesis of sulfur containing unnatural amino acid derivative **24**.



Scheme 12. Proposed mechanism for the formation of single diastereomer **24**.

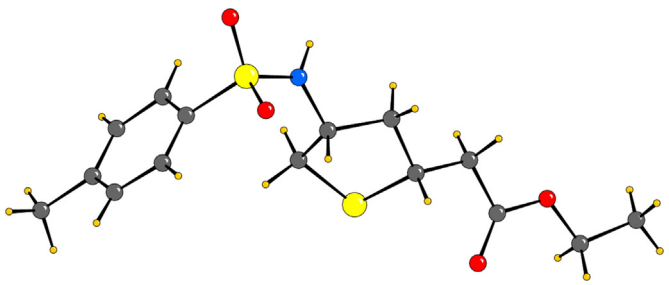
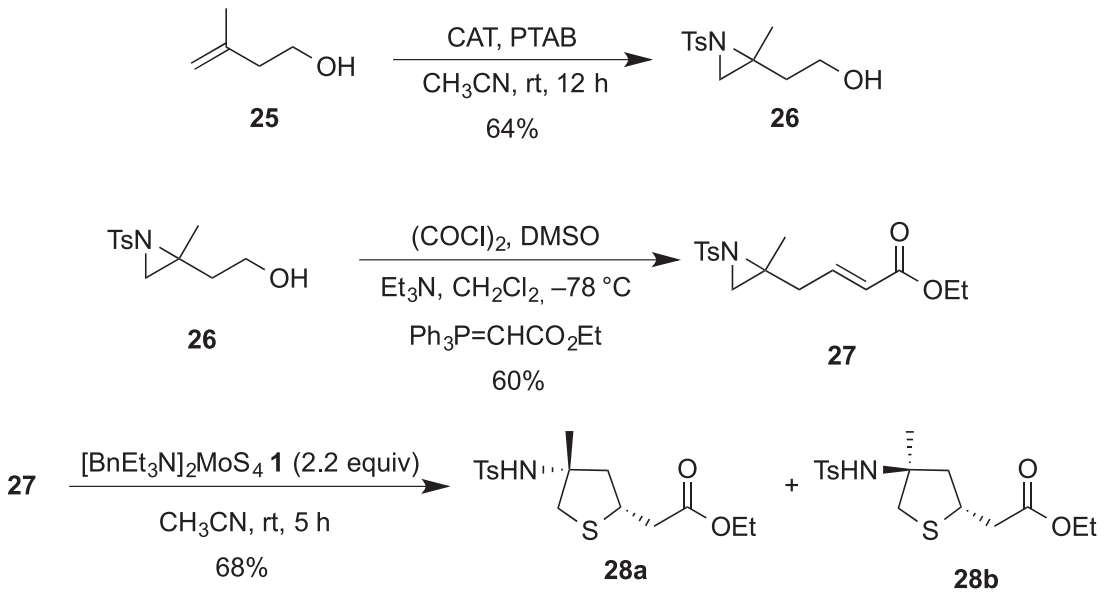


Fig. 3. X-ray CAMERON structure of compound **24**.

In the next stage, 3-methy-3-buten-1-ol **25** was converted to 2,2-disubstituted aziridine having *trans*-α,β-unsaturated ester **27** as shown in Scheme 13. As expected, treatment of aziridine **27** with tetrathiomolybdate **1** furnished the mixture of diastereomers **28a** and **28b** (dr=1:1) in good yields. Diastereomers **28a** and **28b** were formed in equal ratio due to the similar sizes of Me/NHTs.

3. Conclusion

In summary, we have demonstrated the efficiency of tandem multi-step aziridine/epoxide ring opening, disulfide formation, reductive cleavage of disulfide bond and Michael addition in a one-pot operation using tetrathiomolybdate **1** resulting in interesting and unusual molecular structures. The intermediacy of thiolate in the multi-step reaction was established by isolation of the thiol intermediate **13h**′ in the absence of Michael acceptor and the compound was fully characterized by X-ray structure analysis. Using this methodology, a number of *ß*-sulfonamidosulfides were synthesized in good yields. It has been shown that selective aziridine ring opening followed by Michael reaction can be performed in the case of aziridino-epoxides. Tetrahydrothiophene based



Scheme 13. Synthesis of sulfur containing unnatural amino acid derivatives **30a** and **30b**.

amino acid derivatives **24** and **28** have also been synthesized in good yields. Further, this methodology has been used for the construction of thiabicyclo[3.3.1]nonane system in high yield with good regio- and diastereoselectivity.

4. Experimental section

4.1. General procedure for sharpless aziridination

To a mixture of an appropriate olefin (3 mmol) and TsNClNa.3H_2O (CAT) (0.930 g, 3.3 mmol) in CH_3CN (15 mL), was added phenyltrimethylammonium tribromide, (PTAB) (0.113 g, 0.3 mmol) at 28 °C. After 12 h of vigorous stirring, the reaction mixture was concentrated and filtered through a short column of silica gel and eluted with 10% EtOAc in hexanes. After evaporation of solvent, the resultant solid was purified by flash column chromatography to yield the corresponding aziridines in good yield.

4.1.1. (R)-2-Methyl-5-(2-methyl-1-tosylaziridin-2-yl)cyclohex-2-en-1-one ***17***. Colorless liquid; R_f=0.40 (EtOAc/hexanes, 3:7); Yield: 0.689 g, 72%; IR (neat) ν_{max}: 1671, 1451, 1320, 1159, 959, 847, 713, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 7.81 (d, J=8.4 Hz, 2H), 7.32 (d, J=8.4 Hz, 2H), 6.72 (br s, 1H), 2.63 (s, 1H), 2.44 (s, 3H), 2.28 (m, 3H), 2.17 (s, 2H), 1.76 (s, 3H), 1.74 (s, 3H), 1.69 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 198.5, 198.4, 144.1, 144.0, 143.9, 143.6, 137.6, 137.5, 135.5, 135.3, 129.4, 127.2, 51.4, 51.1, 42.8, 41.9, 40.2, 40.1, 39.6, 39.5, 28.2, 27.9, 21.5, 15.8, 15.5, 15.0; HRMS *m/z*: calcd for $C_{17}H_{21}NO_3SNa^+$[M+Na^+]: 342.1140; found: 342.1145.

4.1.2. 2-(2-Methyl-1-tosylaziridin-2-yl)ethan-1-ol ***28***. Colorless liquid; R_f=0.65 (silica gel, EtOAc/hexanes, 1:1); Yield: 0.489 g, 64%; IR (neat) ν_{max}: 3525, 1597, 1318, 1158, 943, 818, 709 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, J=8.3 Hz, 2H), 7.32 (d, J=8.3 Hz, 2H), 3.78 (m, 2H), 2.61 (s, 1H), 2.43 (s, 3H), 2.38 (s, 1H), 2.03 (m, 1H), 1.76 (m, 1H), 1.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.0, 137.4, 129.5, 127.2, 59.2, 48.8, 40.9, 39.5, 21.5, 18.9; HRMS. *m/z*: calcd for $C_{12}H_{17}NO_3SNa^+$ [M+Na^+]: 278.0827; found: 278.0836.

4.2. General procedure for ring opening of monosubstituted aziridines followed by Michael reaction in the presence of 1

Tetrathiomolybdate **1** (0.670, 1.00 mmol) was added to a well-stirred solution of appropriate monosubstituted aziridine (0.50 mmol) and methyl acrylate **3a** (0.054 mL, 0.6 mmol) in CH_3CN (3 mL). The reaction mixture was stirred at room temperature (28 °C) for 2–8 h. The solvent was evaporated under reduced pressure, the black residue was extracted with CH_2Cl_2:Et_2O (1:5, 3× 10 mL) and filtered through a Celite pad. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel to give corresponding β-sulfonamidosulfide derivatives in good yields.

4.2.1. Methyl-(S)-3-((2-((4-methylphenyl)sulfonamido)-3-phenylpropyl)thio)propanoate ***4a***. Colorless liquid; R_f=0.40 (EtOAc/hexane, 3:7); Yield: 0.173 g, 85%; $[\alpha]_D^{27}$ +32.00 (c=1.0, $CHCl_3$); IR (neat) ν_{max}: 3284, 1735, 1330, 1157, 813, 745, 701, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, J=8.1 Hz, 2H), 7.23–7.20 (m, 5H), 7.01 (m, 2H), 4.88 (d, J=6.9 Hz, 1H), 3.71 (s, 3H), 3.55–3.53 (m, 1H), 2.86 (dd, J=13.5, 6.6 Hz, 1H), 2.74 (dd, J=14.4, 7.2 Hz, 1H), 2.69–2.65 (m, 2H), 2.61–2.52 (m, 4H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 143.3, 136.9, 136.5, 129.6, 129.3, 128.6, 126.9, 126.7, 54.3, 51.9, 39.6, 36.7, 34.3, 27.7, 21.5; HRMS *m/z*: calcd for $C_{20}H_{25}NO_4S_2Na^+$[M+Na^+]: 430.1123; found: 430.1134.

4.2.2. (S)-4-Methyl-N-(1-phenyl-3-((2-(phenylsulfonyl)ethyl)thio) propan-2-yl)benzenesulfonamide ***4b***. Colorless liquid; R_f=0.40 (EtOAc/hexane, 3:7); Yield: 0.180 g, 74%; $[\alpha]_D^{27}$ +54.00 (c=1.0, $CHCl_3$); IR (neat) ν_{max}: 3282, 1321, 1150, 1085, 813, 738, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.94 (d, J=8.1 Hz, 2H), 7.72–7.51 (m, 5H), 7.21–7.17 (m, 5H), 6.95–6.93 (m, 2H), 4.70 (d, J=6.6 Hz, 1H), 3.49–3.41 (m, 1H), 3.38–3.22 (m, 2H), 2.87–2.51 (m, 6H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.5, 138.8, 136.5, 136.1, 134.0, 129.7, 129.1, 128.7, 128.1, 126.9, 126.8, 55.9, 54.1, 39.5, 36.6, 24.6, 21.5; HRMS *m/z*: calcd for $C_{24}H_{27}NO_4S_3Na^+$[M+Na^+]: 512.1000; found: 512.1011.

4.2.3. Methyl-2-methyl-3-(((S)-2-((4-methylphenyl)sulfonamido)-3-phenylpropyl)thio)propanoate ***4c***. Colorless liquid; R_f=0.40 (EtOAc/hexane, 3:7); Yield: 0.139 g, 66%; IR (neat) ν_{max}: 3282, 1734, 1455, 1329, 1158, 814, 746, 701, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 7.61 (d, J=8.1 Hz, 2H), 7.23–7.19 (m, 5H), 7.02–7.01 (m, 2H), 4.92 (d, J=7.5 Hz, 1H), 3.71 (s, 3H), 3.57–3.48 (m, 1H), 2.85 (dd, J=13.8, 6.6 Hz, 1H), 2.77–2.45 (m, 6H), 2.41 (s, 3H), 1.19 (d, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 175.4, 175.3, 143.3, 137.1, 136.6, 136.5, 129.6, 129.3, 129.2, 128.6, 127.0, 126.7, 54.4, 54.2, 51.9, 40.1, 40.0, 39.7, 39.6, 37.2, 37.1, 36.1, 21.5, 16.9, 16.8; HRMS *m/z*: calcd for $C_{21}H_{27}NO_4S_2Na^+$[M+Na^+]: 444.1279; found: 444.1287.

4.2.4. Methyl N-acetyl-S-((S)-2-((4-methylphenyl)sulfonamido)-3-phenylpropyl)cysteinate ***4d***. Colorless liquid; R_f=0.40 (EtOAc/hexane, 3:7); Yield: 0.139 g, 60%; IR (neat) ν_{max}: 3287, 1744, 1656, 1534, 1436, 1322, 1156, 1091, 813, 743, 702, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 7.59 (d, J=8.1 Hz, 2H), 7.23–7.19 (m, 10H), 6.98 (br s, 4H), 6.47 (d, J=7.2 Hz, 1H), 6.39 (d, J=8.1 Hz, 1H), 5.37 (d, J=7.8 Hz, 1H), 4.92–4.89 (m, 2H), 4.80–4.78 (m, 1H), 3.78 (m, 3H), 3.75 (s, 3H), 3.58–3.52 (m, 2H), 3.00–2.84 (m, 4H), 2.80–2.57 (m, 7H), 2.41 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 171.2, 170.3, 143.4, 143.2, 136.9, 136.6, 136.4, 129.6, 129.2, 128.7, 128.6, 126.9, 126.8, 126.7, 54.4, 54.3, 52.8, 52.7, 52.4, 52.1, 39.8, 39.6, 38.3, 37.4, 35.7, 34.9, 23.2, 23.0, 21.5; HRMS *m/z*: calcd for $C_{22}H_{28}N_2O_5S_2Na^+$[M+$Na^+$]: 487.1337; found: 487.1331.

4.2.5. (S)-N-(1-((2-Cyanoethyl)thio)-3-phenylpropan-2-yl)-4-methylbenzenesulfonamide ***4e***. Colorless liquid; R_f=0.50 (EtOAc/hexane, 3:7); Yield: 0.94 g, 50%; $[\alpha]_D^{27}$ +42.00 (c=1.0, $CHCl_3$); IR (neat) ν_{max}: 3288, 2261, 1741, 1334, 1160, 810, 741, 703, 668 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, J=8.1 Hz, 2H), 7.28–7.22 (m, 5H), 7.21 (m, 2H), 4.91 (d, J=6.9 Hz, 1H), 3.50–3.48 (m, 1H), 2.87 (dd, J=13.5, 6.5 Hz, 1H), 2.78 (dd, J=14.2, 7.1 Hz, 1H), 2.70–2.68 (m, 2H), 2.64–2.50 (m, 4H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.3, 137.0, 136.6, 130.0, 129.6, 128.3, 126.5, 126.7, 121.2, 48.4, 40.2, 36.6, 34.7, 28.3, 22.3; HRMS *m/z*: calcd for $C_{19}H_{22}N_2O_2S_2Na^+$[M+$Na^+$]: 397.1020; found: 397.1026.

4.2.6. (S)-4-Methyl-N-(1-((3-oxopentyl)thio)-3-phenylpropan-2-yl) benzenesulfonamide ***4f***. Colorless liquid; R_f=0.45 (EtOAc/hexane, 3:7); Yield: 0.173 g, 78%; $[\alpha]_D^{27}$ +56.00 (c=1.0, $CHCl_3$); IR (neat) ν_{max}: 3285, 1706, 1334, 1154, 816, 742, 702, 667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, J=8.2 Hz, 2H), 7.25–7.20 (m, 5H), 7.02 (m, 2H), 4.81 (d, J=6.8 Hz, 1H), 3.58–3.54 (m, 1H), 2.84 (dd, J=13.4, 6.5 Hz, 1H), 2.72 (dd, J=13.4, 7.3 Hz, 1H), 2.71–2.67 (m, 2H), 2.60–2.51 (m, 4H), 2.42 (s, 3H) 2.2 (q, J=7.2 Hz, 2H), 1.42 (t, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 210.2, 143.1, 136.6, 136.5, 129.5, 129.4, 128.2, 126.6, 126.6, 52.0, 46.4, 39.4, 36.9, 34.5,

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27.8, 21.5, 19.2; HRMS *m/z*: calcd for $C_{21}H_{27}NO_3S_2Na^+$[M+Na^+]: 428.1330; found: 428.1336.

4.2.7. Benzyl-(S)-3-((2-((4-methylphenyl)sulfonamido)-3-phenylpropyl)thio)propanoate ***4g***. Colorless liquid; R_f=0.5 0 (EtOAc/hexane, 3:7); Yield: 0.133 g, 55%; $[\alpha]_D^{27}$ +32.00 (*c*=1.0, $CHCl_3$); IR (neat) ν_{max}: 3292, 1732, 1330, 1154, 812, 743, 698, 661 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, *J*=8.1 Hz, 2H), 7.36–7.34 (m, 5H), 7.18–7.16 (m, 5H), 7.01–6.98 (m, 2H), 5.15 (s, 2H), 4.88 (d, *J*=7.2 Hz, 1H), 3.56–3.49 (m, 1H), 2.84 (dd, *J*=13.8, 6.9 Hz, 1H), 2.75–2.68 (m, 3H), 2.65–2.52 (m, 4H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 143.3, 137.0, 136.5, 135.7, 129.6, 129.3, 128.6, 128.3, 127.0, 126.7, 66.6, 54.3, 39.7, 36.8, 34.6, 27.6, 21.5; HRMS *m/z*: calcd for $C_{26}H_{29}NO_4S_2Na^+$[M+Na^+]: 506.1436; found: 506.1432.

4.2.8. Methyl-(S)-3-(2-(4-methylphenylsulfonamido)propylthio) propanoate ***6a***. Colorless liquid; R_f=0.40 (EtOAc/hexanes, 3:7); Yield: 0.138 g, 80%; $[\alpha]_D^{27}$ +16.00 (*c*=1.0, $CHCl_3$); IR (neat) ν_{max}: 3276, 1736, 1436, 1331, 1160, 1093, 664 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J*=8.1 Hz, 2H), 7.31 (d, *J*=8.1 Hz, 2H), 4.97 (d, *J*=6.6 Hz, 1H), 3.71 (s, 3H), 3.48–3.40 (m, 1H), 2.65–2.48 (m, 6H), 2.43 (s, 3H), 1.14 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1, 143.4, 137.5, 129.7, 127.1, 51.9, 48.9, 39.3, 34.3, 27.4, 21.5, 20.6; HRMS *m/z*: calcd for $C_{14}H_{21}NO_4S_2$[M+Na^+]: 354.0810; found: 354.0815.

4.2.9. Methyl-(S)-3-(2-(4-methylphenylsulfonamido)butylthio)propanoate ***6b***. Colorless liquid; R_f=0.40 (EtOAc/hexanes, 3:7); Yield: 0.138 g, 80%; $[\alpha]_D^{27}$ +29.20 (*c*=1.0, CH_2Cl_2); IR (neat) ν_{max}: 3283, 1737, 1436, 1326, 1157, 1093, 816, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J*=8.4 Hz, 2H), 7.31 (d, *J*=8.4 Hz, 2H), 5.21 (d, *J*=7.5 Hz, 1H), 3.70 (s, 3H), 3.32–3.22 (m, 2H), 2.69–2.62 (m, 2H), 2.54–2.49 (m, 3H), 2.43 (s, 3H), 1.67–1.53 (m, 1H), 1.49–1.36 (m, 1H), 0.77 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1, 143.3, 137.7, 129.5, 126.9, 54.5, 51.7, 37.0, 34.3, 27.6, 26.6, 21.4, 9.8; HRMS *m/z*: calcd for $C_{15}H_{23}NO_4S_2$[M+Na^+]: 368.0966; found: 368.0976.

4.2.10. Methyl-(S)-3-(3-methyl-2-(4-methylphenylsulfonamido)butylthio)propanoate ***6c***. Colorless liquid; R_f=0.40 (EtOAc/hexanes, 3:7); Yield: 0.140 g, 78%; $[\alpha]_D^{27}$ −25.00 (*c*=1.0, $CHCl_3$); IR (neat) ν_{max}: 3285, 1737, 1437, 1327, 1159, 1093, 815, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J*=8.1 Hz, 2H), 7.31 (d, *J*=8.1 Hz, 2H), 5.01 (d, *J*=8.4 Hz, 1H), 3.70 (s, 3H), 3.19–3.12 (m, 1H), 2.69–2.45 (m, 6H), 2.43 (s, 3H), 1.98–1.84 (m, 1H), 0.80 (d, *J*=7.2 Hz, 3H), 0.66 (dd, *J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1, 143.3, 137.7, 129.6, 127.1, 58.3, 51.8, 34.8, 29.9, 27.6, 21.5, 18.9, 17.5; HRMS *m/z*: calcd for $C_{16}H_{25}NO_4S_2$[M+Na^+]: 382.1123; found: 382.1125.

4.2.11. Methyl-(S)-3-(4-methyl-2-(4-methylphenylsulfonamido)pentylthio)propanoate ***6d***. Colorless liquid; R_f=0.40 (EtOAc/hexanes, 3:7); Yield: 0.142 g, 76%; $[\alpha]_D^{27}$ −76.05 (*c*=1.0, CH_2Cl_2); IR (neat) ν_{max}: 3282, 1738, 1436, 1332, 1159, 1093, 815, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J*=8.1 Hz, 2H), 7.31 (d, *J*=8.1 Hz, 2H), 4.94 (d, *J*=8.4 Hz, 1H), 3.71 (s, 3H), 3.49–3.37 (m, 1H), 2.71–2.64 (m, 3H), 2.55–2.47 (m, 3H), 2.43 (s, 3H), 1.57–1.30 (m, 3H), 0.81 (d, *J*=6.6 Hz, 3H), 0.67 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 143.4, 137.8, 129.6, 127.1, 51.8, 51.3, 43.2, 38.2, 34.4, 27.9, 24.3, 22.8, 21.6, 21.5; HRMS *m/z*: calcd for $C_{17}H_{27}NO_4S_2$[M+Na^+]: 396.1279; found: 396.1299.

4.2.12. Methyl-3-((2S,3S)-3-methyl-2-(4-methylphenylsulfonamido) pentylthio)propanoate ***6e***. Colorless liquid; R_f=0.50 (EtOAc/hexanes, 3:7); Yield: 0.131 g, 70%; $[\alpha]_D^{27}$ +22.36 (*c*=1.0, CH_2Cl_2); IR (neat) ν_{max}: 3286, 1738, 1437, 1332, 1158, 816, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J*=8.1 Hz, 2H), 7.30 (d, *J*=8.1 Hz, 2H), 5.09 (d, *J*=8.1 Hz, 1H), 3.69 (s, 3H), 3.26–3.18 (m, 1H), 2.84–2.45 (m, 6H), 2.43 (s, 3H), 1.72–1.61 (m, 1H), 1.48–1.35 (m, 1H), 1.07–0.92 (m, 1H), 0.82 (t, *J*=7.2 Hz, 3H), 0.80 (t, *J*=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1, 143.3, 137.6, 129.5, 127.1, 57.0, 51.8, 36.9, 34.2, 34.1, 27.3, 24.5, 21.4, 14.8, 11.4; HRMS *m/z*: calcd for $C_{17}H_{27}NO_4S_2$[M+Na^+]: 396.1279; found: 396.1269.

4.2.13. (S)-Methyl-3-(3,3-dimethyl-2-(4-methylphenylsulfonamido) butylthio)propanoate ***6f***. Colorless liquid; R_f=0.50 (EtOAc/hexanes, 3:7); Yield: 0.140 g, 75%; $[\alpha]_D^{27}$ −71.00 (*c*=1.0, $CHCl_3$); IR (neat) ν_{max}: 3295, 1736, 1331, 1155, 1019, 814, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J*=8.1 Hz, 2H), 7.29 (d, *J*=8.1 Hz, 2H), 5.04 (d, *J*=9.6 Hz, 1H), 3.69 (s, 3H), 3.32–3.25 (m, 1H), 2.72 (dd, *J*=13.5, 5.7 Hz, 1H), 2.58–2.45 (m, 5H), 2.43 (s, 3H), 0.86 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 143.2, 138.4, 129.4, 127.1, 61.5, 51.8, 35.4, 34.6, 34.2, 28.6, 26.9, 21.5; HRMS *m/z*: calcd for $C_{17}H_{27}NO_4S_2$[M+Na^+]: 396.1279; found: 396.1288.

4.2.14. (S)-Methyl-3-((2-((4-methylphenyl)sulfonamido)-4-(methylthio)butyl)thio ***6g***. Colorless liquid; R_f=0.55 (EtOAc/hexane, 3:7); Yield: 0.123 g, 63%; $[\alpha]_D^{27}$ −132.08 (*c*=1.0, $CHCl_3$); IR (neat) ν_{max}: 3242, 1746, 1346, 1162, 825, 745, 668 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J*=8.1 Hz, 2H), 7.32 (d, *J*=8.1 Hz, 2H), 5.31 (d, *J*=8.1 Hz, 1H), 3.68 (s, 3H), 3.77–3.63 (m, 1H), 3.02 (dd, *J*=14.2, 4.3 Hz, 1H), 2.76 (dd, *J*=14.2, 6.7 Hz, 1H), 2.45 (s, 3H), 2.38–2.17 (m, 4H), 1.95 (s, 3H), 1.90–1.82 (m, 3H), 1.71–1.69 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.8, 143.5, 137.6, 129.9, 127.3, 62.1, 52.5, 44.4, 35.6, 34.2, 32.2, 30.3, 21.7, 15.3; HRMS *m/z*: calcd for $C_{16}H_{25}NO_4S_3Na^+$[M+Na^+]: 414.0843; found: 414.0846.

4.2.15. (S)-Methyl-3-(2-(4-methylphenylsulfonamido)-3-(4-(tosyloxy)phenyl)propylthio)propanoate ***6h***. Colorless liquid; R_f=0.60 (EtOAc/hexanes, 3:7); Yield: 0.208 g, 72%; $[\alpha]_D^{27}$ −54.00 (*c*=1.0, $CHCl_3$); IR (neat) ν_{max}: 3277, 1742, 1434, 1335, 1169, 821, 667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, *J*=7.8 Hz, 2H), 7.57 (d, *J*=7.8 Hz, 2H), 7.32 (d, *J*=8.1 Hz, 2H), 7.22 (d, *J*=8.1 Hz, 2H), 6.93 (d, *J*=8.4 Hz, 2H), 6.79 (d, *J*=8.4 Hz, 2H), 4.94 (d, *J*=7.2 Hz, 1H), 3.71 (s, 3H), 3.56–3.45 (m, 1H), 2.84 (dd, *J*=14.0, 6.4 Hz, 1H), 2.71–2.60 (m, 2H), 2.84 (dd, *J*=14.7, 6.9 Hz, 1H), 2.71–2.60 (m, 4H), 2.54 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 148.4, 145.4, 143.6, 136.9, 135.7, 132.3, 130.4, 130.0, 129.8, 129.7, 128.4, 126.9, 122.4, 54.2, 51.9, 39.1, 36.8, 34.3, 27.7, 21.7, 21.5; HRMS *m/z*: calcd for $C_{27}H_{31}NO_7S_3$[M+Na^+]: 600.1160; found: 600.1165.

4.2.16. (S)-Methyl-3-(3-(1H-indol-2-yl)-2-(4-methylphenylsulfonamido)propylthio)propanoate ***6i***. Colorless liquid; R_f=0.40 (EtOAc/hexane, 1:1); Yield: 0.134 g, 60%; $[\alpha]_D^{27}$ −25.41 (*c*=1.0, $CHCl_3$); IR (neat) ν_{max}: 3274, 1741, 1431, 1336, 1163, 811, 661 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.09 (br s, 1H), 7.81 (d, *J*=8.4 Hz, 2H), 7.51 (d, *J*=8.4 Hz, 2H), 7.29 (s, 1H), 7.19–7.14 (m, 1H), 7.07–6.95 (m, 4H), 4.92 (d, *J*=6.6 Hz, 1H), 3.71 (s, 3H), 3.60–3.52 (m, 1H), 3.06 (dd, *J*=14.7, 6.3 Hz, 1H), 2.89 (dd, *J*=14.7, 6.9 Hz, 1H), 2.78–2.71 (m, 3H), 2.66–2.51 (m, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 143.2, 136.5, 136.2, 129.4, 127.1, 126.8, 123.1, 122.1, 119.6, 118.6, 111.1, 110.5, 53.2, 51.9, 36.9, 34.4, 29.4, 27.7, 21.5; HRMS *m/z*: calcd for $C_{22}H_{26}N_2O_4S_2Na^+$[M+$Na^+$]: 469.1232; found: 469.1244.

4.2.17. Methyl-3-(((R)-2-((3aR,5R,6S,6aR)-6-(benzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3] dioxol-5-yl)-2-((4-methylphenyl) sulfonamido)ethyl)thio)propanoate ***8a***. Colorless liquid; R_f=0.50 (EtOAc/hexane, 1:1); Yield: 0.192 g, 68%; IR (neat) ν_{max}: 3279, 1737, 1331, 1215, 1162, 1075, 1026, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, *J*=8.1 Hz, 2H), 7.37 (d, *J*=8.1 Hz, 2H), 7.26–7.22 (m, 5H), 5.72 (d, *J*=3.9 Hz, 1H), 5.15 (d, *J*=5.1 Hz, 1H), 4.52 (dd, *J*=56.4, 11.7 Hz, 2H), 4.53 (d, *J*=3.6 Hz, 1H), 4.28 (dd, *J*=7.5, 3.0 Hz, 1H), 3.89 (d, *J*=3.0 Hz, 1H), 3.80–3.73 (m, 1H), 3.69 (s, 3H), 2.84 (dd, *J*=14.4, 6.3 Hz, 1H), 2.72 (m, 3H), 2.52 (t, *J*=6.9 Hz, 2H), 2.39 (s, 3H), 1.45 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 137.2, 136.8,

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129.4, 128.6, 128.2, 127.8, 127.4, 111.9, 104.5, 81.9, 81.4, 79.1, 71.4, 52.3, 51.8, 34.4, 34.1, 27.8, 26.7, 26.2, 21.5; HRMS *m/z*: calcd for $C_{27}H_{35}NO_8S_2Na^+$[M+Na^+]: 588.1702; found: 588.1704.

4.2.18. Methyl-3-(((R)-2-((4-methylphenyl)sulfonamido)-2-((4S,4′R,5R)-2,2,2′,2′-tetramethyl-[4,4′-bi(1,3-dioxolan)]-5-yl)ethyl) thio)propanoate ***8b****.* Colorless liquid; R_f=0.50 (EtOAc/hexane, 1:1); Yield: 0.168 g, 65%; IR (neat) ν_{max}: 3291, 2986, 1739, 1159, 1070, 669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J*=8.1 Hz, 2H), 7.31 (d, *J*=8.1 Hz, 2H), 5.13 (d, *J*=9.9 Hz, 1H), 4.21 (dd, *J*=7.8, 1.2 Hz, 1H), 4.11 (dd, *J*=8.4, 6.3 Hz, 1H), 4.01–3.94 (m, 1H), 3.74–3.55 (m, 3H), 3.71 (s, 3H), 2.73–2.59 (m, 3H), 2.56–2.43 (m, 3H), 2.43 (s, 3H), 1.40 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1, 143.7, 138.1, 129.8, 127.0, 109.8, 100.5, 78.3, 77.5, 76.9, 67.9, 52.3, 51.8, 34.9, 34.3, 26.9, 26.8, 26.7, 26.2, 25.1, 21.5; HRMS *m/z*: calcd for $C_{23}H_{35}NO_8S_2Na^+$[M+Na^+]: 540.1702; found: 540.1718.

4.3. General procedure for regio- and stereoselective ring opening of 2,2-disubstituted and 2,3-disubstituted aziridines followed by Michael reaction in the presence of 1

Tetrathiomolybdate **1** (0.670, 1.00 mmol) was added to a well-stirred solution of appropriate 2,2-disubstituted or 2,3- di-substituted aziridine (0.50 mmol) and methyl acrylate **3a** (0.054 mL, 0.6 mmol) in CH_3CN (3 mL). The reaction mixture was stirred at room temperature (28 °C) for 3–12 h. The solvent was evaporated under reduced pressure, the black residue was extracted with CH_2Cl_2:Et_2O (1:5, 3× 10 mL) and filtered through a Celite pad. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel to give corresponding amino acid derivatives in good yields.

4.3.1. Methyl-3-((2-methyl-2-((4-methylphenyl)sulfonamido)propyl) thio)propanoate ***10a****.* Colorless liquid; R_f=0.40 (EtOAc/hexane, 3:7); Yield: 0.135 g, 78%; IR (neat) ν_{max}: 3282, 1737, 1436, 1323, 1151, 1093, 998, 815, 663 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J*=8.1 Hz, 2H), 7.29 (d, *J*=8.1 Hz, 2H), 5.25 (s, 1H), 3.71 (s, 3H), 2.84 (t, *J*=7.2 Hz, 2H), 2.73 (m, 2H), 2.61 (t, *J*=7.2 Hz, 2H), 2.42 (s, 3H), 1.22 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 142.9, 140.1, 129.4, 126.9, 56.8, 51.8, 45.9, 34.6, 28.9, 26.9, 21.4; HRMS *m/z*: calcd for $C_{15}H_{23}NO_4S_2Na^+$[M+Na^+]: 368.0966; found: 368.0976.

4.3.2. Methyl-3-(2-methyl-2-(4-methylphenylsulfonamido)pentylthio)propanoate ***10b****.* Colorless liquid; R_f=0.6 (EtOAc/hexanes, 3:7); Yield: 0.140 g, 75%; IR (neat) ν_{max}: 3286, 1736, 1437, 1326, 1152, 1093, 663 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J*=8.1 Hz, 2H), 7.28 (d, *J*=8.1 Hz, 2H), 5.06 (s, 1H), 3.71 (s, 3H), 2.82 (t, *J*=6.9 Hz, 2H), 2.75 (s, 2H), 2.61 (t, *J*=6.9 Hz, 2H), 2.42 (s, 3H), 1.56–1.37 (m, 2H), 1.28–1.16 (m, 2H), 1.16 (s, 3H), 0.81 (t, *J*=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 143.0, 140.1, 129.4, 126.9, 59.5, 51.8, 44.0, 42.1, 34.7, 28.8, 23.4, 21.4, 16.8, 14.1; HRMS *m/z*: calcd for $C_{17}H_{27}NO_4S_2$[M+Na^+]: 396.1279; found: 396.1279.

4.3.3. Methyl-3-(3-hydroxy-2-methyl-2-(4-methylphenylsulfonamido)propylthio)propanoate ***10c****.* Colorless liquid; R_f=0.40 (EtOAc/hexanes, 1:1); Yield: 0.123 g, 68%; IR (neat) ν_{max}: 3515, 3274, 1735, 1437, 1321, 1154, 1092, 815, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J*=8.4 Hz, 2H), 7.30 (d, *J*=8.4 Hz, 2H), 5.34 (s, 1H), 3.71 (s, 3H), 3.58 (d, *J*=6.6 Hz, 2H), 2.87–2.68 (m, 4H), 2.60 (t, *J*=7.2 Hz, 2H), 2.43 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 143.5, 139.5, 129.7, 126.9, 67.3, 60.3, 51.9, 41.1, 34.5, 28.7, 21.5, 20.9; HRMS *m/z*: calcd for $C_{15}H_{23}NO_4S_2$[M+Na^+]: 384.0915; found: 384.0928.

4.3.4. Methyl-3-(4-hydroxy-2-methyl-2-(4-methylphenylsulfonamido)butylthio)propanoate ***10d****.* Colorless liquid; R_f=0.45 (EtOAc/hexanes, 1:1); Yield: 0.120 g, 64%; IR (neat) ν_{max}: 3505, 3284, 1736, 1439, 1325, 1154, 1092, 815, 664 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J*=8.1 Hz, 2H), 7.28 (d, *J*=8.1 Hz, 2H), 5.93 (s, 1H), 3.77 (br s, 1H), 3.72 (s, 3H), 2.89 (s, 2H), 2.82 (t, *J*=7.2 Hz, 2H), 2.60 (t, *J*=7.2 Hz, 2H), 2.42 (s, 3H), 1.98–1.71 (m, 4H), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 143.0, 140.4, 129.7, 129.5, 127.0, 126.8, 59.4, 59.1, 51.9, 43.8, 41.0, 34.6, 28.9, 23.7, 21.5; HRMS *m/z*: calcd for $C_{16}H_{25}NO_5S_2$[M+Na^+]: 398.1072; found: 398.1086.

4.3.5. Methyl-3-(((3R,4R*)-4-((4-methylphenyl)sulfonamido)hexan-3-yl)thio)propanoate* ***12a****.* Colorless liquid; R_f=0.40 (EtOAc/hexane, 3:7); Yield: 0.127 g, 68%; IR (neat) ν_{max}: 3286, 1738, 1332, 1160, 816, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J*=8.1 Hz, 2H), 7.29 (d, *J*=8.1 Hz, 2H), 4.95 (d, *J*=8.1 Hz, 1H), 3.71 (s, 3H), 3.33–3.27 (m, 1H), 2.81–2.75 (m, 3H), 2.59 (t, *J*=7.5 Hz, 2H), 2.43 (s, 3H), 1.72–1.55 (m, 2H), 1.32–1.22 (m, 2H), 0.95 (t, *J*=7.5 Hz, 3H), 0.68 (t, *J*=7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 143.2, 138.1, 129.6, 126.9, 59.3, 52.4, 51.8, 34.7, 26.9, 24.6, 23.9, 21.5, 12.3, 10.7; HRMS *m/z*: calcd for $C_{17}H_{27}NO_4S_2Na^+$[M+Na^+]: 396.1279; found: 396.1279.

4.3.6. Methyl-3-(((3S,4R*)-4-((4-methylphenyl)sulfonamido)hexan-3-yl)thio)propanoate* ***12b****.* Colorless liquid; R_f=0.50 (EtOAc/hexane, 3:7); Yield: 0.131 g, 70%; IR (neat) ν_{max}: 3293, 1737, 1437, 1337, 1161, 1092, 816, 666 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J*=8.1 Hz, 2H), 7.30 (d, *J*=8.1 Hz, 2H), 5.21 (d, *J*=9.3 Hz, 1H), 3.73 (s, 3H), 3.30–3.25 (m, 1H), 2.83–2.58 (m, 3H), 2.51 (t, *J*=7.2 Hz, 2H), 2.43 (s, 3H), 1.53–1.37 (m, 2H), 1.29–1.17 (m, 2H), 0.95 (t, *J*=7.2 Hz, 3H), 0.75 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 143.2, 138.3, 129.5, 127.0, 57.9, 55.6, 51.9, 34.5, 33.8, 28.2, 27.3, 22.5, 21.5, 12.3, 10.6; HRMS *m/z*: calcd for $C_{17}H_{27}NO_4S_2Na^+$[M+Na^+]: 396.1279; found: 396.1264.

4.3.7. Methyl-3-((2R,3R*)-4-methyl-3-(4-methylphenylsulfonamido)pentan-2-ylthio)propanoate* ***12c****.* Colorless liquid; R_f=0.60 (EtOAc/hexanes, 3:7); Yield: 0.121 g, 65%; IR (neat) ν_{max}: 3291, 1737, 1437, 1329, 1159, 1093, 666 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, *J*=8.1 Hz, 2H), 7.28 (d, *J*=8.1 Hz, 2H), 4.90 (d, *J*=9.3 Hz, 1H), 3.70 (s, 3H), 3.17–3.01 (m, 2H), 2.99–2.64 (m, 2H), 2.56 (d, *J*=7.2 Hz, 2H), 2.41 (s, 3H), 1.92–1.77 (m, 1H), 1.18 (d, *J*=6.9 Hz, 3H), 0.86 (t, *J*=7.2 Hz, 3H), 0.78 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 143.0, 139.0, 129.4, 126.9, 64.7, 51.8, 43.2, 34.5, 30.9, 25.6, 21.4, 20.6, 19.6; HRMS *m/z*: calcd for $C_{17}H_{27}NO_4S_2$[M+Na^+]: 396.1279; found: 396.1279.

4.3.8. Methyl-3-((2S,3R*)-4-methyl-3-(4-methylphenylsulfonamido)pentan-2-ylthio)propanoate* ***12d****.* Colorless liquid; R_f=0.60 (EtOAc/hexanes, 3:7); Yield: 0.127 g, 68%; IR (neat) ν_{max}: 3296, 1738, 1439, 1326, 1159, 1093, 667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J*=8.1 Hz, 2H), 7.28 (d, *J*=8.1 Hz, 2H), 4.93 (d, *J*=9.9 Hz, 1H), 3.70 (s, 3H), 3.38–3.35 (m, 1H), 3.32–3.25 (m, 1H), 2.75–2.54 (m, 2H), 2.48 (t, *J*=6.9 Hz, 2H), 2.42 (s, 3H), 1.99–1.91 (m, 1H), 1.23 (d, *J*=6.9 Hz, 3H), 0.82 (t, *J*=6.9 Hz, 3H), 0.78 (t, *J*=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 143.1, 138.6, 129.5, 127.0, 62.2, 51.8, 45.6, 34.4, 28.9, 27.1, 21.5, 21.1, 19.4, 17.5; HRMS *m/z*: calcd for $C_{17}H_{27}NO_4S_2$[M+Na^+]: 396.1279; found: 396.1286.

4.3.9. Methyl-3-(((1R,2R*)-2-((4-methylphenyl)sulfonamido)cyclopentyl)thio)propanoate* ***14a****.* Colorless liquid; R_f=0.60 (EtOAc/hexane, 3:7); Yield: 0.139 g, 78%; IR (neat) ν_{max}: 3272, 1737, 1437, 1330, 1159, 1093, 815, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J*=8.1 Hz, 2H), 7.32 (d, *J*=8.1 Hz, 2H), 5.08 (d, *J*=8.4 Hz, 1H), 3.71 (s, 3H), 3.34–3.28 (m, 1H), 2.98–2.91 (m, 1H), 2.70 (t, *J*=6.9 Hz, 2H), 2.55 (t, *J*=6.9 Hz, 2H), 2.44 (s, 3H), 2.13–1.96 (m, 2H), 1.71–1.61 (m, 2H), 1.54–1.38 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 143.5, 137.1, 129.7, 127.2, 60.4, 51.8, 50.0, 34.5, 31.9, 31.0, 26.1, 21.9, 21.5;

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HRMS *m/z*: calcd for $C_{16}H_{23}NO_4S_2Na^+$[M+Na^+]: 380.0966; found: 380.0970.

4.3.10. Methyl-3-(((1R,2R*)-2-((4-methylphenyl)sulfonamido)cyclohexyl)thio)propanoate* ***14b***. Colorless liquid; R_f=0.65 (EtOAc/hexane, 3:7); Yield: 0.134 g, 72%; IR (neat) ν_{max}: 3278, 1745, 1438, 1334, 1161, 1096, 816, 667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, *J*=8.2 Hz, 2H), 7.36 (d, *J*=8.2 Hz, 2H), 5.34 (d, *J*=8.4 Hz, 1H), 3.73 (s, 3H), 3.34–3.28 (m, 1H), 2.93–2.90 (m, 1H), 2.71 (t, *J*=6.9 Hz, 2H), 2.56 (t, *J*=6.9 Hz, 2H), 2.47 (s, 3H), 2.14–1.97 (m, 2H), 1.70–1.62 (m, 4H), 1.56–1.35 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.6, 143.4, 137.2, 129.8, 127.1, 61.5, 52.0, 50.5, 35.1, 32.1, 31.2, 26.3, 21.8, 21.6, 21.5; HRMS *m/z*: calcd for $C_{17}H_{25}NO_4S_2Na^+$[M+Na^+]: 394.1123; found: 394.1120.

4.3.11. Methyl-3-((1R,2R*,4S*,5R*)-4,5-dihydroxy-2-(4-methylphenylsulfonamido)cyclohexylthio) pro-panoate* ***14c***. Colorless liquid; R_f=0.30 (EtOAc/hexanes, 1:1); Yield: 0.125 g, 62%; IR (neat) ν_{max}: 3480, 3304, 1732, 1436, 1157, 1092, 815, 664 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, *J*=8.4 Hz, 2H), 7.31 (d, *J*=8.4 Hz, 2H), 6.34 (br s, 1H), 3.88–3.82 (m, 2H), 3.71 (s, 3H), 3.29 (br s, 1H), 3.09–3.08 (m, 2H), 2.98 (br s, 1H), 2.81–2.71 (m, 2H), 2.67–2.55 (m, 2H), 2.43 (s, 3H), 2.35–2.25 (m, 1H), 2.08–2.00 (m, 1H), 1.75–1.60 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 143.4, 137.6, 129.7, 126.9, 69.6, 67.3, 51.9, 51.8, 45.7, 34.4, 30.3, 30.2, 26.7, 21.5; HRMS *m/z*: calcd for $C_{17}H_{25}NO_6S_2$[M+Na^+]: 426.1021; found: 426.1040.

4.3.12. (1S,2R*,4R*,5R*)-4-(3-Methoxy-3-oxopropylthio)-5-(4-methylphenylsulfonamido)cyclo hexane-1,2-diyl diacetate* ***14d***. Colorless liquid; R_f=0.80 (EtOAc/hexanes, 1:1); Yield: 0.170 g, 70%; IR (neat) ν_{max}: 3281, 1739, 1437, 1247, 1158, 1038, 1019, 815, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J*=8.1 Hz, 2H), 7.33 (d, *J*=8.1 Hz, 2H), 5.42 (d, *J*=4.8 Hz, 1H), 5.18 (bt, *J*=3.0 Hz, 1H), 4.94–4.91 (m, 1H), 3.72 (s, 3H), 3.11–2.98 (m, 1H), 2.98–2.80 (m, 1H), 2.65–2.56 (m, 1H), 2.51–2.46 (m, 4H), 2.43 (s, 3H), 2.37–2.22 (m, 1H), 2.07 (s, 3H), 2.05 (s, 3H), 1.87–1.68 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9, 169.9, 169.7, 143.8, 136.5, 129.8, 127.2, 68.9, 67.8, 43.9, 34.2, 31.7, 24.9, 21.5, 20.9; HRMS *m/z*: calcd for $C_{21}H_{29}NO_8S_2$[M+Na^+]: 510.1232; found: 510.1220.

4.3.13. Methyl-3-(((1R,2R*)-2-((4-methylphenyl)sulfonamido)cycloheptyl)thio)propanoate* ***14e***. Colorless liquid; R_f=0.70 (EtOAc/hexane, 3:7); Yield: 0.77 g, 40%; IR (neat) ν_{max}: 3282, 1750, 1435, 1332, 1165, 1101, 814, 669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J*=8.1 Hz, 2H), 7.34 (d, *J*=8.1 Hz, 2H), 5.34 (d, *J*=8.4 Hz, 1H), 3.72 (s, 3H), 3.35–3.26 (m, 1H), 2.93–2.90 (m, 1H), 2.72 (t, *J*=6.9 Hz, 2H), 2.58 (t, *J*=6.9 Hz, 2H), 2.46 (s, 3H), 2.13–1.96 (m, 2H), 1.72–1.61 (m, 6H), 1.56–1.35 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.4, 143.4, 137.2, 129.5, 127.3, 60.3, 51.7, 50.1, 34.6, 31.9, 31.1, 26.2, 21.9, 21.6, 1.4, 21.5; HRMS *m/z*: calcd for $C_{18}H_{27}NO_4S_2Na^+$[M+Na^+]: 408.1279; found: 408.1281.

4.3.14. N,N′-((1R,1′R*,2R*,2′R*)-Disulfanediylbis(cyclohexane-2,1-diyl))bis(4-methylbenzene sulfonamide)* ***13g***. Colorless solid; R_f=0.60 (EtOAc/hexane, 3:7); Yield: 0.097 g, 68%; mp: 160 °C; IR (neat) ν_{max}: 3289, 1323, 1157, 811, 664 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 1: 1 mixture of diastereomers): δ 7.78 (d, *J*=8.1 Hz, 2H), 7.31 (d, *J*=8.1 Hz, 2H), 5.36 (d, *J*=6.9 Hz, 1H), 3.49–3.47 (m, 1H), 2.73–2.68 (m, 1H), 2.43 (s, 3H), 2.13–2.09 (m, 1H), 1.69–1.68 (m, 1H), 1.66–1.56 (m, 2H), 1.40–1.19 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 143.3, 138.3, 129.7, 127.0, 56.8, 55.7, 33.3, 32.3, 25.0, 23.9, 21.6; HRMS *m/z*: calcd for $C_{26}H_{36}N_2O_4S_4Na^+$[M+$Na^+$]: 591.1456; found: 591.1462.

4.3.15. N-((1R,2R*)-2-Mercaptocyclohexyl)-4-methylbenzenesulfonamide* ***13h′***. Colorless slid; R_f=0.75 (EtOAc/hexane, 3:7); Yield: 0.097 g, 68%; mp: 112 °C; IR (neat) ν_{max}: 3275, 1321, 1157, 811, 664 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J*=8.1 Hz, 2H), 7.30 (d, *J*=8.1 Hz, 2H), 4.93 (d, *J*=6.4 Hz, 1H), 2.84–2.79 (m, 1H), 2.64–2.55 (m, 1H), 2.43 (s, 3H), 2.22–2.09 (m, 2H), 1.67–1.63 (m, 3H), 1.42–1.35 (m, 2H), 1.28–1.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4, 137.4, 129.6, 127.3, 60.3, 43.8, 36.7, 34.0, 25.7, 24.5, 21.6; HRMS *m/z*: calcd for $C_{13}H_{19}NO_2S_2Na^+$[M+Na^+]: 308.0755; found: 308.0757.

4.4. General procedure for selective ring opening of aziridine followed by Michael reaction of aziridino-epoxides in the presence of 1

Tetrathiomolybdate **1** (0.670, 1.00 mmol) was added to a well-stirred solution of appropriate aziridino-epoxide (0.50 mmol) and methyl acrylate **3a** (0.054 mL, 0.6 mmol) in CH_3CN (3 mL). The reaction mixture was stirred at room temperature (28 °C) for 4–9 h. The solvent was evaporated under reduced pressure, the black residue was extracted with CH_2Cl_2:Et_2O (1:5, 3× 10 mL) and filtered through a Celite pad. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel to give corresponding epoxy amino acid derivatives in good yields.

4.4.1. Methyl-3-(2-(4-methylphenylsulfonamido)-3-(oxiran-2-yl-methoxy)propylthio)propanoate ***16a***. Colorless liquid; R_f=0.40 (EtOAc/hexane, 3:7); Yield: 0.196 g, 65%; IR (neat) ν_{max}: 3277, 1735, 1437, 1334, 1159, 1092, 816, 666 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 7.78 (d, *J*=8.4 Hz, 4H), 7.31 (d, *J*=8.4 Hz, 4H), 5.32 (d, *J*=7.2 Hz, 1H), 5.27 (d, *J*=7.5 Hz, 1H), 3.69 (s, 6H), 3.68–3.59 (m, 4H), 3.50–3.22 (m, 6H), 3.08–3.03 (m, 2H), 2.78 (m, 2H), 2.69–2.63 (m, 8H), 2.56–2.51 (m, 6H), 2.39 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 172.1, 143.5, 137.5, 129.7, 127.1, 71.8, 71.7, 70.7, 52.8, 51.8, 50.5, 44.0, 34.3, 33.7, 27.4, 21.5; HRMS *m/z*: calcd for $C_{17}H_{25}NO_6S_2Na^+$[M+Na^+]: 426.1021; found: 426.1036.

4.4.2. Methyl-3-((1S,3R*,4R*,6R*)-4-(4-methylphenylsulfonamido)-7-oxabicyclo[4.1.0]heptan-3-ylthio)propanoate* ***16b***. Colorless liquid; R_f=0.45 (EtOAc/hexanes, 1:1); Yield: 0.540 g, 80%; IR (neat) ν_{max}: 3273, 1735, 1435, 1328, 1159, 1091, 815, 669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J*=8.4 Hz, 2H), 7.31 (d, *J*=8.4 Hz, 2H), 5.27 (d, *J*=3.6 Hz, 1H), 3.71 (s, 3H), 3.17 (br s, 1H), 3.11 (t, *J*=4.2 Hz, 1H), 3.03 (m, 1H), 2.87–2.81 (m, 1H), 2.58–2.26 (m, 6H), 2.42 (s, 3H), 2.12–2.02 (m, 1H), 1.77 (dq, *J*=9.6, 5.4, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.8, 143.7, 136.5, 129.7, 127.2, 52.4, 51.9, 50.9, 49.5, 44.2, 34.1, 32.6, 31.1, 24.2, 21.5; HRMS *m/z*: calcd for $C_{17}H_{23}NO_5S_2Na^+$[M+Na^+]: 408.0915; found: 408.0921.

4.4.3. Methyl-3-(((1S,3R*,4R*,6R*)-1,6-dimethyl-4-((4-methylphenyl)sulfonamido)-7-oxabicyclo [4.1.0]heptan-3-yl)thio) propanoate* ***16c***. Colorless liquid; R_f=0.40 (EtOAc/hexane, 3:7); Yield: 0.159 g, 77%; IR (neat) ν_{max}: 3264, 1735, 1438, 1330, 1160, 1091, 906, 815, 663 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J*=8.1 Hz, 2H), 7.31 (d, *J*=8.1 Hz, 2H), 5.35 (d, *J*=3.6 Hz, 1H), 3.70 (s, 3H), 3.05–2.96 (m, 1H), 2.73 (dd, *J*=15.0, 4.8 Hz, 1H), 2.56–2.47 (m, 2H), 2.42 (s, 3H), 2.41–2.38 (m, 2H), 2.99–2.25 (m, 1H), 2.26 (dd, *J*=15.3, 6.9 Hz, 1H), 2.08 (dd, *J*=15.3, 10.5 Hz, 1H), 1.73 (dd, *J*=15.0, 9.9 Hz, 1H), 1.26 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9, 143.6, 136.5, 129.7, 127.2, 62.6, 61.4, 51.9, 50.4, 44.9, 39.0, 37.4, 34.2, 24.0, 21.5, 20.4, 19.2; HRMS *m/z*: calcd for $C_{19}H_{27}NO_5S_2Na^+$[M+Na^+]: 436.1228; found: 436.1230.

4.4.4. Methyl-3-(((3aS,5R*,6R*,7aR*)-6-((4-methylphenyl)sulfonamido)hexahydro-1H-3a,7a-epoxyinden-5-yl)thio)propanoate* ***16d***. Colorless liquid; R_f=0.50 (EtOAc/hexane, 3:7); Yield: 0.149 g, 70%; IR (neat) ν_{max}: 3265, 1737, 1436, 1333, 1160, 1091, 664 cm^{-1}; ^1H

NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J*=8.1 Hz, 2H), 7.32 (d, *J*=8.1 Hz, 2H), 5.52 (d, *J*=3.9 Hz, 1H), 3.70 (s, 3H), 3.15–3.08 (m, 1H), 2.79 (dd, *J*=14.7, 4.8 Hz, 1H), 2.61–2.51 (m, 2H), 2.43 (s, 3H), 2.37–2.29 (m, 4H), 2.15 (dd, *J*=15.0, 9.3 Hz, 1H), 1.97–1.86 (m, 2H), 1.75 (dd, *J*=15.0, 8.7 Hz, 1H), 1.56–1.32 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9, 143.6, 136.5, 129.7, 127.2, 67.1, 66.2, 51.8, 50.6, 44.7, 34.1, 33.8, 32.6, 31.3, 30.9, 24.7, 21.5, 19.7; HRMS *m/z*: calcd for $C_{20}H_{27}NO_5S_2Na^+[M+Na^+]$: 448.1228; found: 448.1248.

4.4.5. Methyl-3-(((2R,3R*,4aR*,8aS*)-3-((4-methylphenyl)sulfonamido)octahydro-4a,8a-epoxy naphthalen-2-yl)thio)propanoate* ***16e***. Colorless liquid; R_f=0.50 (EtOAc/hexanes, 3:7); Yield: 0.158 g, 72%; IR (neat) ν_{max}: 3269, 2934, 1737, 1437, 1328, 1159, 1092, 664 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J*=8.4 Hz, 2H), 7.31 (d, *J*=8.4 Hz, 2H), 5.22 (d, *J*=3.0 Hz, 1H), 3.71 (s, 3H), 3.10–2.96 (m, 1H), 2.79 (dd, *J*=14.7, 4.5 Hz, 1H), 2.57 (dd, *J*=11.1, 6.9 Hz, 1H), 2.51–2.44 (m, 2H), 2.42 (s, 3H), 2.40–2.37 (m, 2H), 2.26–2.03 (m, 3H), 1.93–1.63 (m, 4H), 1.57 -1.19 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.8, 143.7, 136.3, 129.7, 127.3, 62.7, 61.4, 51.9, 50.0, 45.0, 38.8, 37.4, 34.2, 30.8, 28.9, 23.7, 21.5, 20.3, 19.6; HRMS *m/z*: calcd for $C_{21}H_{29}NO_5S_2Na+[M+Na^+]$: 462.1385; found: 462.1382.

4.5. Synthesis of thia-bicyclononane derivatives 18a and 18b

Tetrathiomolybdate **1** (0.670, 1.00 mmol) was added to a well-stirred solution of aziridine **17** (0.160 g, 0.50 mmol) in CH_3CN (3 mL) and it was stirred at room temperature (28 °C) for 3 h. The solvent was evaporated under reduced pressure, the black residue was extracted with CH_2Cl_2:Et_2O (1:5, 3× 10 mL) and filtered through a Celite pad. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel to give thia-bicyclononane derivatives **18a** and **18b** as white solids.

4.5.1. N-((1R,4S,5S,8S)-4,8-Dimethyl-7-oxo-2-thiabicyclo[3.3.1]nonan-4-yl)-4-methylbenzenesulfon-amide ***18a***. Colorless solid; R_f=0.40 (EtOAc/hexanes, 3:7); Yield: 0.077 g, 44%; mp: 174 °C; $[\alpha]_D^{27}$ +97.00 (*c*=1.0, $CHCl_3$); IR (neat) ν_{max}: 3284, 1706, 1420, 1316, 1152, 1018, 667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, *J*=8.4 Hz, 2H), 7.28 (d, *J*=8.4 Hz, 2H), 5.82 (s, 1H), 2.97 (br s, 1H), 2.86 (br s, 2H), 2.71 (m, 1H), 2.58 (s, 1H), 2.54 (d, *J*=5.0 Hz, 2H), 2.41 (s, 3H), 2.23 (td, *J*=7.2, 3.3 Hz, 1H), 1.96 (d, *J*=15.0 Hz, 1H), 1.24 (s, 3H), 1.23 (d, *J*=6.0Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.1, 143.2, 140.2, 129.3, 126.9, 56.1, 49.6, 43.5, 41.8, 40.6, 33.6, 31.6, 23.8, 21.4, 12.8; HRMS *m/z*: calcd for $C_{17}H_{23}$ $NO_3S_2Na^+[M+Na^+]$: 376.1017, found: 376.1033.

4.5.2. N-((1R,4R,5S,8S)-4,8-Dimethyl-7-oxo-2-thiabicyclo[3.3.1]nonan-4-yl)-4-methylbenzenesulfon-amide ***18b***. Colorless solid; R_f=0.30 (EtOAc/hexanes, 3:7); Yield: 0.078 g, 44%; mp: 223 °C; $[\alpha]_D^{27}$ +137.00 (*c*=1.0, $CHCl_3$); IR (neat) ν_{max}: 3274, 1704, 1332, 1159, 1091, 909, 815, 732, 663 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, *J*=8.4 Hz, 2H), 7.29 (d, *J*=8.4 Hz, 2H), 4.74 (s, 1H), 2.92 (m, 2H), 2.71–2.45 (m, 5H), 2.42 (s, 3H), 2.31 (td, *J*=13.8, 3.6 Hz, 1H), 2.05 (d, *J*=13.8 Hz, 1H), 1.64 (s, 3H), 1.19 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.1, 143.3, 140.1, 129.6, 126.8, 58.9, 50.0, 42.6, 41.9, 41.4, 32.9, 31.5, 22.9, 21.5, 12.6; HRMS *m/z*: calcd for $C_{17}H_{23}NO_3S_2Na^+[M+Na^+]$: 376.1017; found: 376.1030.

4.5.3. N-((1S,4R,5R,8R)-4,8-Dimethyl-7-oxo-2-thiabicyclo[3.3.1]nonan-4-yl)-4-methylbenzenesulfon-amide ***enant-18a***. Colorless solid; R_f=0.50 (EtOAc/hexanes, 3:7); Yield: 0.078 g, 44%; mp: 176 °C; $[\alpha]_D^{27}$ −96.00 (*c*=1.0, $CHCl_3$); IR (neat) ν_{max}: 3289, 1705, 1316, 1154, 1092, 818, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J*=8.1 Hz, 2H), 7.28 (d, *J*=8.1 Hz, 2H), 5.83 (s, 1H), 2.99–2.97 (m, 1H), 2.92–2.86 (m, 2H), 2.76–2.67 (m, 1H), 2.58–2.53 (m, 3H), 2.42 (s, 3H), 2.27–2.19 (m, 1H), 1.97 (d, *J*=15.0 Hz, 1H), 1.24 (s, 3H), 1.23 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.1, 143.1, 140.4, 129.6, 126.7, 56.0, 49.7, 43.5, 41.7, 40.5, 33.5, 31.7, 23.9, 21.5, 12.8; HRMS *m/z*: calcd for $C_{17}H_{23}NO_3S_2[M+Na^+]$: 376.1017; found: 376.1030.

4.5.4. N-((1S,4S,5R,8R)-4,8-Dimethyl-7-oxo-2-thiabicyclo[3.3.1]nonan-4-yl)-4-methylbenzenesulfon-amide ***enant-18b***. Colorless solid; R_f=0.40 (EtOAc/hexanes, 3:7); Yield: 0.077 g, 44%; mp: 225 °C; $[\alpha]_D^{27}$ −138.00 (*c*=1.0, $CHCl_3$); IR (neat) ν_{max}: 3255, 1690, 1437, 1329, 1156, 1092, 816, 666 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, *J*=8.1 Hz, 2H), 7.29 (d, *J*=8.1 Hz, 2H), 4.83 (s, 1H), 2.99–2.84 (m, 2H), 2.72–2.38 (m, 5H), 2.42 (s, 3H), 2.31 (td, *J*=14.4, 3.6 Hz, 1H), 2.06 (d, *J*=14.4 Hz, 1H), 1.60 (s, 3H), 1.19 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.3, 143.3, 129.7, 126.8, 58.9, 50.0, 42.6, 41.9, 41.4, 32.9, 31.5, 23.0, 21.5, 12.6; HRMS *m/z*: calcd for $C_{17}H_{23}NO_3S_2[M+Na^+]$: 376.1017; found: 376.1025.

4.5.5. N-((1S,4R,5R,8R)-8-Formyl-4-methyl-7-oxo-2-thiabicyclo[3.3.1]nonan-4-yl)-4-methyl-benzene sulfonamide ***20a*** *and N-((1S,4S,5R,8R)-8-formyl-4-methyl-7-oxo-2-thiabicyclo[3.3.1] nonan-4-yl)-4-methylbenzenesulfonamide* ***20b***. Colorless liquid; R_f=0.50 (EtOAc/hexanes, 3:7); Yield: 0.138 g, 81%; IR (neat) ν_{max}: 3277, 1723, 1321, 1155, 1092, 980, 815, 735, 663 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 9.64 (s, 1H), 9.61 (s, 1H), 7.77 (d, *J*=8.1 Hz, 4H), 7.29 (d, *J*=8.1 Hz, 4H), 5.63 (s, 1H), 5.01 (s, 1H), 3.21–3.02 (m, 4H), 2.77–2.61 (m, 4H), 2.43 (s, 3H), 2.42 (s, 3H), 2.33–2.24 (m, 2H), 2.09–1.51 (m, 14H), 1.31 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 203.3, 202.9, 143.2, 142.9, 140.5, 140.4, 129.6, 129.5, 126.8, 126.7, 58.6, 56.4, 54.6, 54.5, 38.6, 36.9,36.4, 35.6, 32.4, 32.3, 32.2, 31.0, 24.9, 24.5, 24.4, 24.2, 21.5, 21.4, 20.3; HRMS *m/z*: calcd for $C_{17}H_{23}NO_3S_2Na^+[M+Na^+]$: 376.1017; found: 376.1028.

4.6. Synthesis of ethyl-(*E*)-4-(1-tosylaziridin-2-yl)but-2-enoate 23

To a stirred solution of oxalyl chloride (0.26 mL, 3.0 mmol) in dry CH_2Cl_2 (20 mL) at −78 °C under argon was added drop wise a solution of DMSO (0.71 mL, 10.0 mmol) in dry CH_2Cl_2 (2 mL). After 20 min, a solution of the aziridino-alcohol **22** (0.482 g, 2.0 mmol) in CH_2Cl_2 (2 mL) was added to the above reagent at −78 °C, and the mixture was stirred for 30 min when diisopropylethylamine (0.7 mL, 40 mmol) was added drop wise to the above solution at −78 °C, and the mixture was stirred for 0.5 h at that temperature. (Ethoxycarbonymethylene)triphenylphosphate (1.34 g, 4 mmol) was added to the mixture at −78 °C, and the mixture was stirred for 2 h during, which time it was allowed to warm to 0. °C. The mixture was extracted with Et_2O and the extract was washed successively with water, 10% aqueous citric acid, water, saturated aqueous $NaHCO_3$ and water, and dried over $MgSO_4$. After concentration under reduced pressure an oily residue was isolated, which was flash chromatographed on silica gel, eluting with hexanes-EtOAc (3:1) to give the *trans*-ester **23** (383 mg, 62%) as colorless oil. The *cis*-isomer of **23** could not be isolated in a pure state due to its instability. Colorless liquid; R_f=0.60 (EtOAc/hexanes, 3:7); IR (neat) ν_{max}: 1730, 1724, 1661, 1582, 1326, 1162, 1042, 951, 832, 712, 670, 651 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, *J*=8.4 Hz, 2H), 7.34 (d, *J*=8.4 Hz, 2H), 6.67 (td, *J*=15.6, 6.2 Hz, 1H), 5.82 (td, *J*=15.6, 1.5 Hz, 1H), 4.16 (q, *J*=7.2 Hz, 2H), 2.86–2.79 (m, 1H), 2.69 (d, *J*=6.6 Hz, 1H), 2.45 (s, 3H), 2.35–2.17 (m, 2H), 2.12 (d, *J*=4.5 Hz, 1H), 1.28 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.7, 144.7, 142.3, 129.7, 127.9, 127.4, 123.9, 60.3, 38.0, 33.5, 32.9, 21.6, 14.2; HRMS *m/z*: calcd for $C_{15}H_{19}NO_4SNa^+[M+Na^+]$: 332.0932; found: 332.0939.

4.6.1. Ethyl-(E)-4-(2-methyl-1-tosylaziridin-2-yl)but-2-enoate ***27***. Colorless liquid; R_f=0.60 (EtOAc/hexanes, 3:7); Yield: 0.388 g,

60%; IR (neat) ν_{max}: 1722, 1715, 1656, 1597, 1324, 1159, 1038, 946, 830, 709, 669, 647 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, J=8.4 Hz, 2H), 7.32 (d, J=8.4 Hz, 2H), 6.90–6.80 (m, 1H), 5.91 (d, J=15.3 Hz, 1H), 4.19 (q, J=7.2 Hz, 2H), 2.61 (s, 1H), 2.59 (dd, J=13.5, 7.5 Hz, 2H), 2.43 (s, 3H), 2.36 (s, 1H), 1.63 (s, 3H), 1.29 (t, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.8, 143.9, 142.7, 137.3, 129.4, 127.2, 124.6, 60.2, 48.6, 40.1, 40.0, 21.4, 18.8, 14.1; HRMS m/z: calcd for $C_{16}H_{21}NO_4SNa^+$[M+Na^+]: 346.1089; found: 346.1096.

4.7. General procedure for synthesis of tetrahydrothiophane derivatives

Tetrathiomolybdate 1 (0.670, 1.00 mmol) was added to a well-stirred solution of aziridine **23**/**27** (0.50 mmol) in CH_3CN (3 mL) and it was stirred at room temperature (28 °C) for 5–6 h. The solvent was evaporated under reduced pressure, the black residue was extracted with CH_2Cl_2:Et_2O (1:5, 3× 10 mL) and filtered through a Celite pad. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel to give tetrahydrothiophane derivatives in good yields.

4.7.1. Ethyl-2-((2S,4S*)-4-((4-methylphenyl)sulfonamido)tetrahydrothiophen-2-yl)acetate* ***24***. Colorless liquid; R_f=0.40 (EtOAc/hexane, 3:7); Yield: 0.113 g, 66%; IR (neat) ν_{max}: 3266, 1731, 1330, 1159, 1093, 815, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, J=8.4 Hz, 2H), 7.32 (d, J=8.4 Hz, 2H), 5.02 (d, J=8.1 Hz, 1H), 4.12 (q, J=7.2 Hz, 2H), 3.94 (m, 1H), 3.71–3.58 (m, 1H), 2.88 (dd, J=11.1, 6.3 Hz, 1H), 2.68–2.52 (m, 3H), 2.44 (s, 3H), 2.42–2.31 (m, 1H), 1.59–1.49 (m, 1H), 2.42 (t, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2, 143.8, 137.2, 129.9, 127.0, 60.7, 57.0, 41.9, 41.8, 39.5, 36.8, 21.5, 14.1; HRMS m/z: calcd for $C_{15}H_{21}NO_4S_2Na^+$[M+Na^+]: 366.0810; found: 366.0825.

4.7.2. Ethyl-2-((2R,4S*)-4-methyl-4-((4-methylphenyl)sulfonamido) tetrahydrothiophen-2-yl)acetate* ***28a*** *and ethyl-2-((2S*,4S*)-4-methyl-4-((4-methylphenyl)sulfonamido)tetrahydrothiophen-2-yl) acetate* ***28b***. Colorless liquid; R_f=0.40 (EtOAc/hexane, 3:7); Yield: 0.121 g, 68%; IR (neat) ν_{max}: 3273, 1731, 1328, 1157, 1093, 1022, 815, 667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 7.79 (d, J=8.4 Hz, 2H), 7.29 (d, J=8.4 Hz, 2H), 5.53 (s, 1H), 5.38 (s, 1H), 4.17–4.09 (m, 2H), 3.78–3.54 (m, 1H), 3.01 (d, J=10.5 Hz, 1H), 2.86–2.50 (m, 3H), 2.43 (s, 3H), 2.17 (dd, J=12.9, 6.9 Hz, 1H), 1.90–1.83 (m, 1H), 1.28–1.22 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 171.4, 171.2, 143.3, 143.2, 139.8, 139.7, 129.6, 129.5, 126.9, 126.8, 67.1, 65.3, 60.7, 48.4, 47.7, 44.5, 42′.7, 41.7, 41.6, 41.5, 39.8, 23.8, 23.7, 21.5, 14.1; HRMS m/z: calcd for $C_{16}H_{23}NO_4S_2Na^+$[M+Na^+]: 380.0966; found: 380.0977.

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18. The structure was solved by direct methods (SIR92). Refinement was by full-matrix least-squares procedures on F^2 by using SHELXL-97. CCDC No. 631953. Crystal system: Orthorhombic, space group: $P2_1$, cell parameters: a=10.879(8), b=6.214(4), c=13.814(9) Å, α=90.00°, β=106.64(1)°, γ=90.00°, V=894.7(3) $Å^3$, Z=2, ρ_{calcd}=1.31 g cm^{-3}, F(000)=376, μ=0.31 mm^{-1}, λ=0.71073 Å. Total number l.s. parameters=208. $R1$=0.031 for 3145 $F_o>4\alpha(F_o)$ and 0.032 for all 6441 data. $wR2$=0.085, GOF=1.132, restrained GOF=1.132 for all data.
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22. The structure was solved by direct methods (SIR92). Refinement was by full-matrix least-squares procedures on F^2 by using SHELXL-97. CCDC No. 631953. Crystal system: Orthorhombic, space group: $P2_12_12_1$, cell parameters: a=7.061(5), b=8.740(6), c=27.116(1) Å, α=90.00°, β=90.00°, γ=90.00°, V=1673.5(2) $Å^3$, Z=4, ρ_{calcd}=1.36 g cm^{-3}, F(000)=728, μ=0.33 mm^{-1}, λ=0.71073 Å. Total number l.s. parameters=201. $R1$=0.124 for 2962 $F_o>4\alpha(F_o)$ and 0.0.148 for all 11803 data. $wR2$=0.27, GOF=1.256, restrained GOF=1.256 for all data.