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Synthesis of *S*-functionalized thioesters using thioaroylate ions derived from carboxylic acids and tetrathiomolybdate via acyloxyphosphonium intermediates

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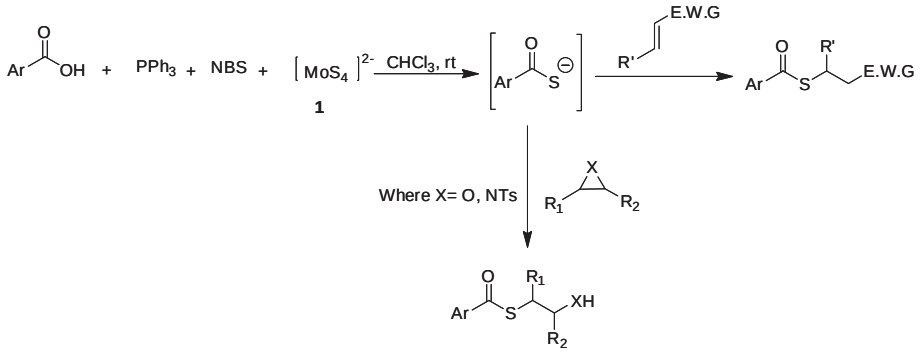
ABSTRACT

Thioaroylate ions generated in situ from acyloxyphosphonium salts and tetrathiomolybdate upon Michael addition or ring opening of three membered systems led to a facile synthesis of *S*-functionalized thioesters. While the ring opening of aziridines gave very good yield of the products, Michael addition and epoxide ring opening gave moderate yields.

1. Introduction

Over the past few decades, extensive efforts have been made to develop methodologies that form carbon–sulfur bonds in the synthesis of molecules with various biological applications. Although a great deal of effort has been directed toward the use of nucleophilic thiols[1] for the formation of C–S bond, thioacids[2] have not been explored in organic synthesis as they are less nucleophilic and hence less reactive. But, the thioesters obtained from thioacids as nucleophiles are synthetically more valuable because of their widespread application in pharmaceutical chemistry[3] and also they serve as key intermediates in the synthesis of various bioactive molecules.[4] Moreover, thioesters are used as coupling partners in organometallic reactions,[5] building blocks for the synthesis of heterocyclic compounds,[6] and acyl transfer[7] reactions. Additionally the thioester functionality could be readily transformed to a more versatile SH group under mild reaction conditions.[8]



Scheme 1. General reaction scheme for the synthesis of thioesters.

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Generally, the synthetic methods adopted for thioester formation are direct coupling of a thiol with the parent carboxylic acid and an activating agent,[9] or the coupling of thiol with acid anhydride[9] or acid chloride.[9] Other methods include the reaction of thioacids with suitable electrophilic reagents, such as alkyl halides,[2a] and Michael acceptors.[2b,2c,2f] These methodologies, however, suffer from limitations, such as the limited availability of starting thioacids and thiols and also the practical difficulty associated in handling them.

In our earlier work we had shown the use of benzyltriethylammonium tetrathiomolybdate,[10] $(PhCH_2N)_2MoS_4$ **1** for the in situ generation of thioaroylate ion from acyloxyphosphonium intermediates.[11] This methodology was used in the synthesis of thioesters from alkyl halides[12] and alcohols.[13] In this paper, we present our results on the application of our methodology to the synthesis of *S*-functionalized thioesters (Scheme 1).

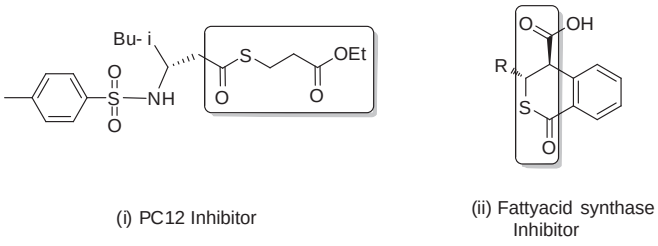


Figure 1. Structure of some pharmacologically important Michael adducts.

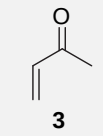
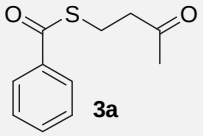
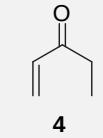
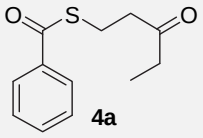
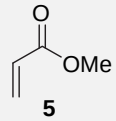
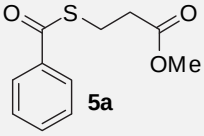
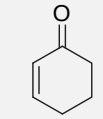
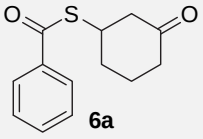
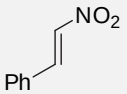
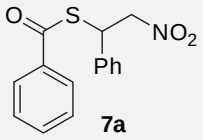
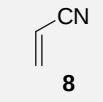
2. Results and discussion

2.1. Michael addition

The Michael adducts derived from conjugate addition with thioacids as nucleophiles are present in a number of pharmacologically important compounds (Fig. 1). These compounds are generally synthesized[3d,14] via multistep processes involving the coupling of carboxylic acid with the corresponding thiol as the final step due to the inaccessibility of the starting thioacids for Michael addition reaction. In general, conjugate addition reaction with thioacid as nucleophiles also requires longer reaction time in the absence of a catalyst owing to their lower nucleophilicity. Thus, we decided to explore our protocol for the formation of functionalized thioesters through Michael addition in the same pot thereby reducing the number of steps involved in the process.

Accordingly, benzoic acid **2a** (1.0 equiv) was first treated with PPh_3 and NBS to form the corresponding activated intermediate followed by the addition of reagent **1** to generate thioaroylate ion,[12,13] which on treatment with a Michael acceptor gave the corresponding thioester **3a**–**7a** in 50–65% yield (Scheme 2).

Table 1
Reaction of various Michael acceptors with thiobenzoate ion

Entry	Michael acceptors	Product	Time (h)	Yield %
1	 **3**	 **3a**	2	60
2	 **4**	 **4a**	2	65
3	 **5**	 **5a**	5	50
4	 **6**	 **6a**	0.5	52
5	 **7**	 **7a**	3	62
6	 **8**	–	12	No reaction

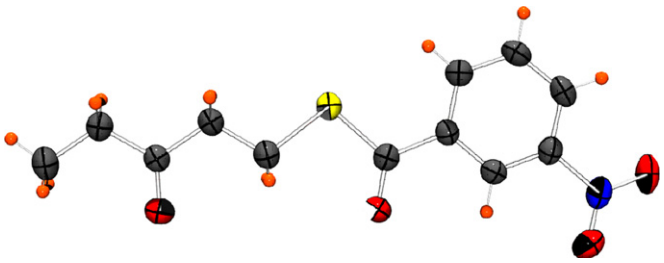
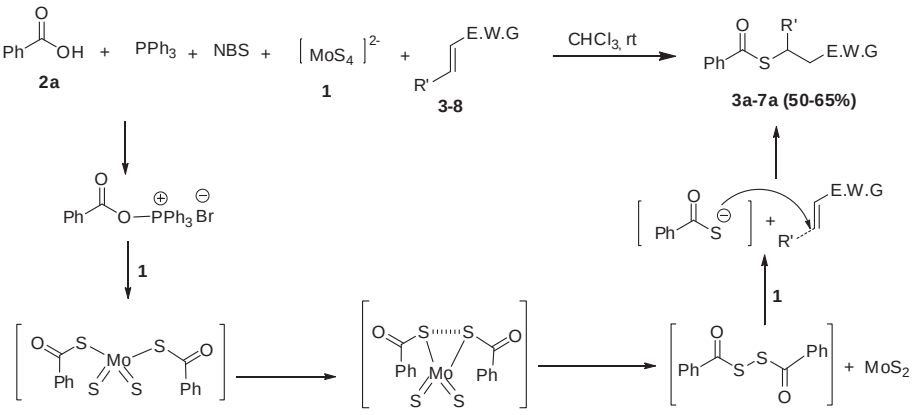
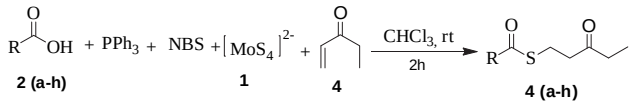


Figure 2. ORTEP diagram of compound **4h**.

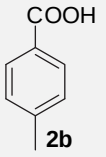
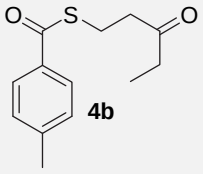
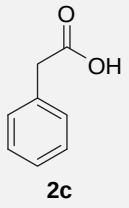
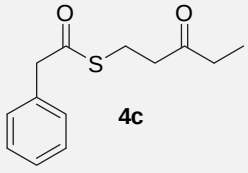
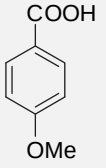
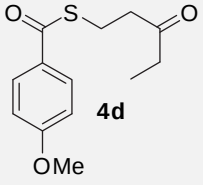
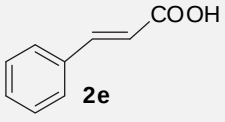
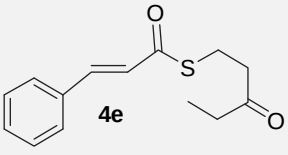
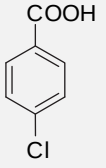
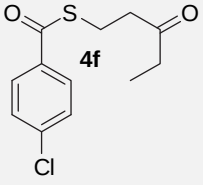
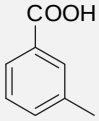
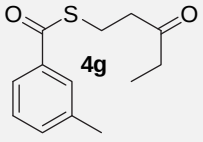
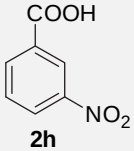
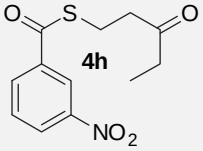


Scheme 2. Reaction of various Michael acceptors with thiobenzoate ion.

Table 2
Reaction of ethyl vinyl ketone **4** with various carboxylic acids



2 (a-h) 1 4 4 (a-h)

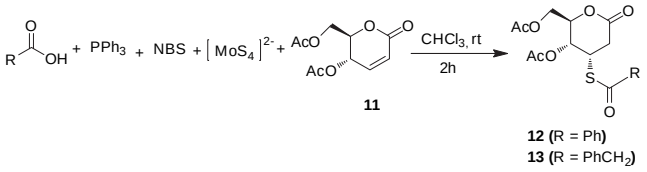
Entry	Carboxylic acid	Product	Yield (%)
1	 2b	 4b	63
2	 2c	 4c	68
3	 2d	 4d	61
4	 2e	 4e	61
5	 2f	 4f	62
6	 2g	 4g	65
7	 2h	 4h	60

Using benzoic acid as the standard we then studied the reactivity of other Michael acceptors to show the generality of the methodology. It was observed that ethyl vinyl ketone gave maximum yield of the corresponding Michael adduct. Nitrostyrene and methyl vinyl ketone also gave good yields of the corresponding thioesters whereas methyl acrylate and cyclohexenone gave moderate yields of the products. Acrylonitrile was inert to the reaction conditions even after 12 h and gave no thioester product. The results of this study are summarized in Table 1.

The methodology was then extended to other carboxylic acids as well to show the synthetic versatility of the reaction, using ethyl vinyl ketone as the standard Michael acceptor. The structure of compound **4h** was confirmed by single crystal X-ray analysis (Fig. 2). The results of this study are summarized in Table 2.

The methodology was then extended to the synthesis of carbohydrate based thioesters to show the synthetic utility of our reaction. At first, 1,2,3,4-tetra-*O*-acetyl-glucuronic[15] acid **9** was treated with ethyl vinyl ketone under the same reaction conditions (Scheme 3) to obtain the corresponding thioester **10** in 52% yield.

Subsequently a carbohydrate derived Michael acceptor[16] **11** (from glucose via glucol intermediate) was treated with benzoic acid to give C-3 thioester **12** with high diastereoselectivity (dr 98:2) in 60% yield. Similar reaction of phenyl acetic acid gave the thioester **13** (dr 90:10) in 55% yield (Scheme 4). The stereochemistry at the newly formed C–S bond was assigned based on COSY and coupling constant values for **12** and by analogy for **13**.



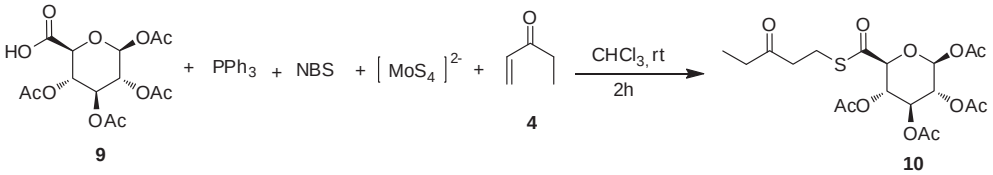
11

Scheme 4. Synthesis of C-3 thioesters **12** and **13** from glucol derived Michael acceptor, **11**.

Finally, we attempted an intramolecular reaction to synthesize γ-thiolactone **18** starting from L-arabinose **14**. Acetonide protection of C_2 and C_3 hydroxyl groups of L-arabinose (Scheme 5) gave 2,3-*O*-isopropylidene-L-erythrose **15**, which on further reaction with Wittig reagent, ethyl triphenylphosphoranylidineacetate, gave the corresponding conjugated ester[17] **16** in 54% yield with *Z* isomer as the major product. PDC oxidation of **16** gave the corresponding carboxylic acid **17** in 62% yield. Compound **17** was then treated with PPh_3, NBS, and tetrathiomolybdate **1** to form the corresponding thiolactone **18** (2:1 mixture of diastereomers) in 50% yield.

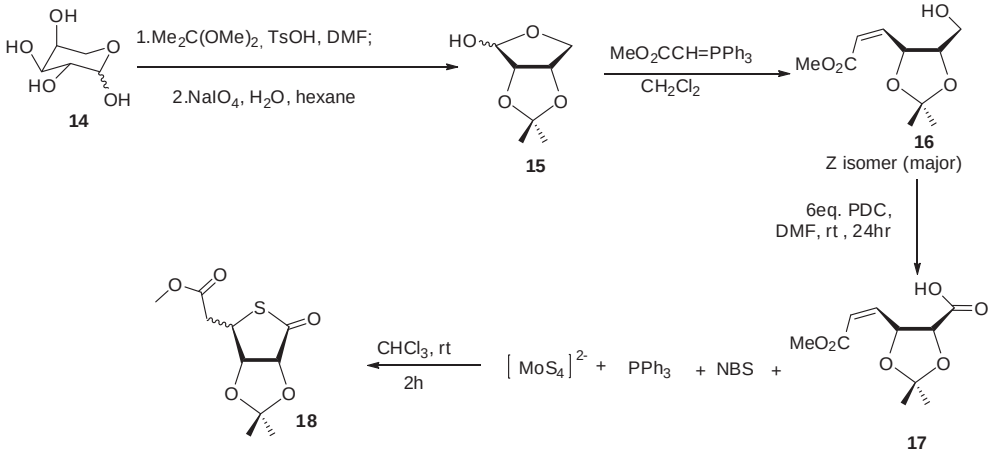
2.2. Aziridine and epoxide ring opening

As further exploration of this methodology, we attempted the ring opening of three membered heterocycles, such as aziridines and epoxides to synthesize various *S*-2-functionalized thioesters, which are present in a number of bioactive molecules (Fig. 3). Unlike Michael addition presented earlier, nucleophilic ring opening of epoxides and aziridines with thioacids as nucleophiles is less common.



9 4 10

Scheme 3. Synthesis of glucuronic based Michael thioester **10**.



Scheme 5. Synthesis of thiolactone, **18** through intramolecular Michael addition.

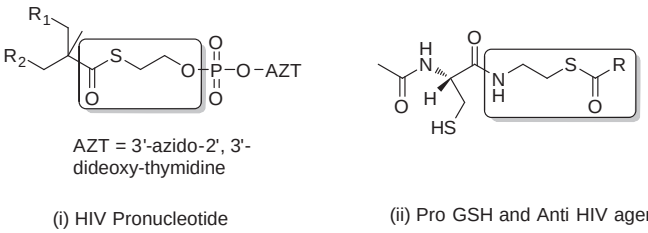


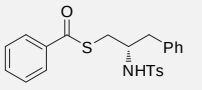
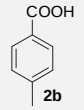
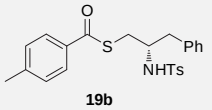
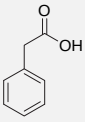
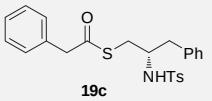
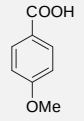
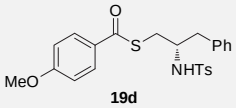
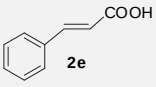
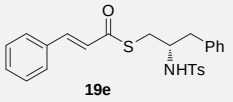
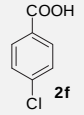
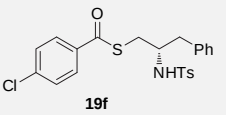
Figure 3. Structures of some bioactive molecules containing *S*-2-functionalized thioesters.

Initially, we took commercially available chiral aziridine, ((*S*)-(+)-2-benzyl-1-(*p*-toluenesulfonyl)-aziridine) **19** for the ring opening reaction. Thus reaction of benzoic acid, PPh_3, NBS, and tetrathiomolybdate, **1** in the presence of **19** gave the corresponding functionalized thioester **19a** in a highly regioselective fashion (Scheme 6). The reaction was then carried out with other carboxylic acids to show generality of the methodology. A variety of thioesters were obtained in good yield and the results of this study are summarized in Table 3.

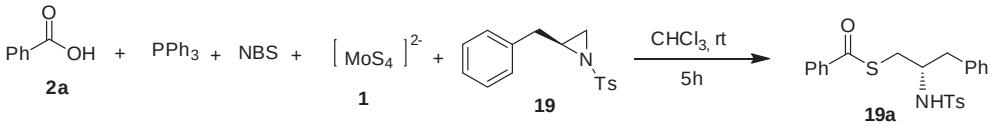
The reaction was then carried out with other activated aziridines (**20**–**25**) prepared via Sharpless aziridination protocol.[18] The ring opening reactions were facile and the resultant thioesters were obtained in good yield. The results of this study are summarized in Table 4.

We were then interested in studying the reactivity profile of thioaroylate ions toward bifunctionalised systems. For this study, we initially synthesized a molecule containing both an aziridine and a tosyl group. Thus, compound **27** synthesized from aziridino alcohol **26**[19] on treatment with benzoic acid (1.05 equiv), PPh_3 (1.1 equiv), NBS (1.1 equiv), and tetrathiomolybdate **1** (1.05 equiv) gave thioester **28** in 74% yield. This results from initial ring opening of aziridine (at the benzylic position) with the thioaroylate to give **27a** followed by intramolecular displacement of the tosylate with the amide nitrogen. However, in the presence of excess thioaroylate ion, compound **27** gave the corresponding bisthioester **29** in 75% yield. This can be rationalized by attack of thioaroylate at the aziridine ring as well as displacement of the tosylate (Scheme 7).

Table 3
Reaction of various carboxylic acids with aziridine **19**

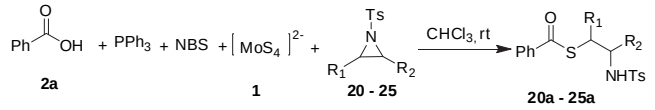
Entry	Carboxylic acid	Product	Time (h)	Yield (%)
1	 **2a**	 **19a**	5	88
2	 **2b**	 **19b**	5	83
3	 **2c**	 **19c**	5.5	91
4	 **2d**	 **19d**	4	92
5	 **2e**	 **19e**	4.5	90
6	 **2f**	 **19f**	5.5	87

We then attempted the ring opening of epoxides with thioaroylates to give the corresponding *S*-2-hydroxy thioesters. Accordingly, benzoic acid **2a** (1.0 equiv) PPh_3, NBS, and tetrathiomolybdate **1** were stirred together to generate thiobenzoate ion which was



Scheme 6. Ring opening of aziridine, **19** with thiobenzoate ion.

Table 4
Reaction of various aziridines with thiobenzoate ion



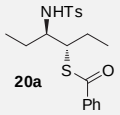
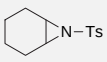
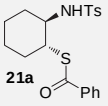
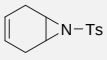
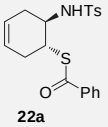
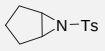
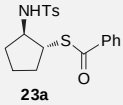
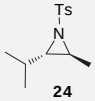
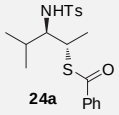
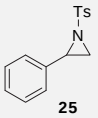
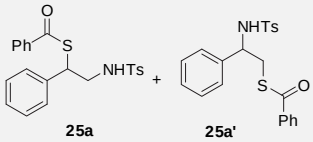
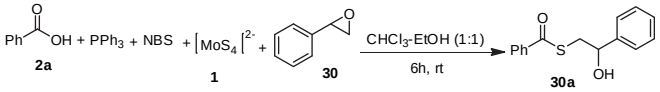
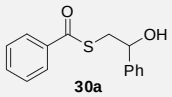
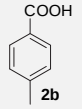
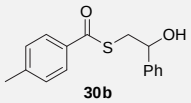
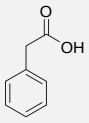
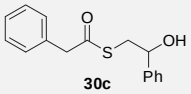
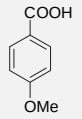
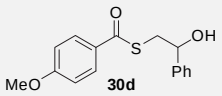
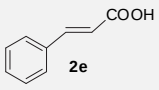
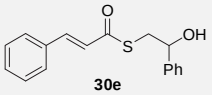
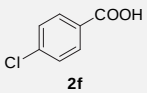
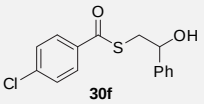
Entry	Aziridine	Product	Time (h)	Yield (%)
1	 **20**	 **20a**	14	83
2	 **21**	 **21a**	2	85
3	 **22**	 **22a**	4	88
4	 **23**	 **23a**	2	82
5	 **24**	 **24a**	12	81
6	 **25**	 **25a** **25a'**	6	80

Table 5
Reaction of various carboxylic acids with styrene epoxide

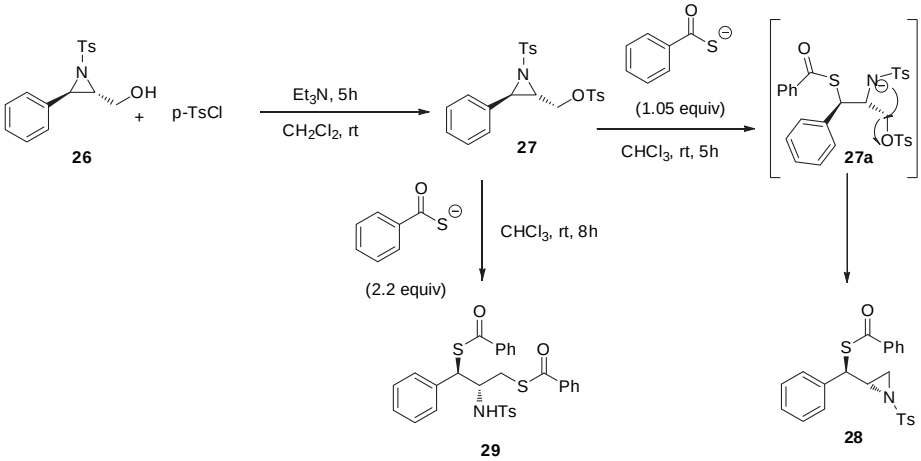


Entry	Carboxylic acid	Product	Yield (%)
1	 **2a**	 **30a**	62
2	 **2b**	 **30b**	65
3	 **2c**	 **30c**	62
4	 **2d**	 **30d**	64
5	 **2e**	 **30e**	63
6	 **2f**	 **30f**	59

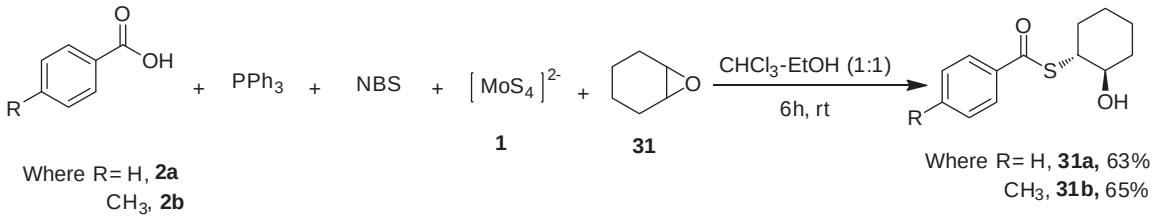
then treated with styrene oxide to give the corresponding functionalized thioester **30a** in 62% yield in a highly regioselective fashion by ring opening at the less substituted carbon. The reaction was then carried out with other carboxylic acids as well and the results of this study are summarized in Table 5.

Reaction of cyclohexene oxide **31** under the reaction conditions with benzoic acid gave the corresponding *trans S*-2-hydroxycyclohexyl thioester **31a** in 63% yield and similar reaction with *p*-toluic acid provided the thioester **31b** in 65% yield (Scheme 8).

In order to demonstrate the chemoselectivity of the reaction of thioaroylate ion, we attempted ring opening of cyclohexadiene

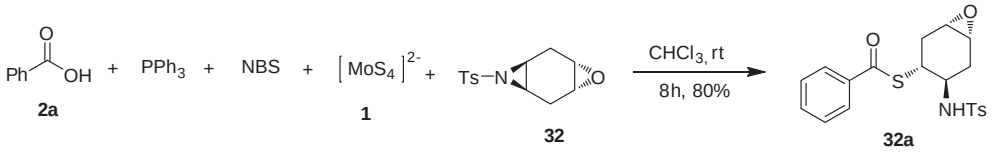


Scheme 7. Reaction of aziridine tosylate, **27** with thiobenzoate ion.



Scheme 8. Ring opening of cyclohexene oxide with carboxylic acids.

derived *trans*-aziridino epoxide **32**.[20] When compound **32** was treated with benzoic acid, PPh_3, NBS, and tetrathiomolybdate **1**, it gave the corresponding aziridine ring opened product **32a** in 80% yield without affecting the epoxide unit (Scheme 9) as aziridines are more reactive than epoxides.



Scheme 9. Chemoselective ring opening of aziridine in the presence of epoxide.

3. Conclusions

In conclusion, a variety of *S*-functionalized thioesters have been synthesized from carboxylic acids and benzyltriethylammonium tetrathiomolybdate **1** via acyloxyphosphonium intermediates by in situ generation of thioaroylate ions. These thioaroylate ions on further treatment with Michael acceptors and three membered heterocycles gave the corresponding *S*-functionalized thioesters. Michael addition, when carried out in an intramolecular fashion gave the thiolactone **18** thereby demonstrating the synthetic utility of the methodology. We have also described the synthesis of C-3 sugar thioesters **12** and **13** via conjugate addition of benzoic/phenyl acetic acid derived thioaroylates to Michael acceptor **11**. Aziridine and epoxide ring opening on the other hand gave the corresponding *S*-2-sulfanamido and *S*-2-hydroxy thioesters.

4. Experimental section

4.1. General

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 ('Purification of laboratory chemicals', 3rd ed.; Perrin, D.D., Armarego, W.L.F; Pergamon Press: Oxford, 1988). 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. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. NMR spectra were recorded on 300 or 400 MHz instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations explain the multiplicity s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad. IR spectra were recorded on a FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Micromass Q-TOF mass spectrometer.

4.2. General procedure for Michael addition (3a–7a, 4b–h) in one pot

To a well stirred solution of the corresponding carboxylic acid (1.0 mmol), PPh_3 (1.1 mmol), and NBS (1.1 mmol) in $CHCl_3$ (5 mL) (stirred for 10 min) was added benzyltriethylammonium tetrathiomolybdate **1** (2.0 mmol). The corresponding Michael acceptor (2.0 mmol) was then added after 20 min and stirring was continued for 2 h at room temperature (28 °C). Diethyl ether (20 mL) was then added to the reaction mixture followed by filtration through a Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with diethyl ether (20 mL) and filtered again through a Celite pad. The combined extract was evaporated and the residue was purified by column chromatography on silica gel to give the corresponding Michael adducts.

*4.2.1. S-(3-Oxobutyl) benzothioate (**3a**).* Colorless liquid. Yield: 0.125 g, 60%; IR (Neat): 1717, 1661, 1208, 915 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97–7.93 (m, 2H), 7.60–7.54 (m, 1H), 7.48–7.21 (m, 2H), 3.26 (t, *J*=6.6 Hz, 2H), 2.88 (t, *J*=6.6 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 206.3, 191.9, 136.9, 133.4, 128.6, 127.2, 43.4, 29.9, 22.8; HRMS *m*/*z*: calcd for $C_{11}H_{12}O_2SNa^+$ [M+Na^+]: 231.0456; found: 231.0455.

*4.2.2. S-(3-Oxopentyl) benzothioate (**4a**).* Colorless liquid. Yield: 0.144 g, 65%; IR (Neat): 1714, 1663, 1209 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.96–7.94 (m, 2H), 7.59–7.55 (m, 1H), 7.46–7.42 (m, 2H), 3.27 (t, *J*=6.8 Hz, 2H), 2.85 (t, *J*=6.8 Hz, 2H), 2.45 (q, *J*=7.2 Hz, 2H), 1.08 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 209.2, 191.9, 136.9, 133.4, 128.6, 127.1, 42.0, 36.6, 22.9, 7.7; HRMS *m*/*z*: calcd for $C_{12}H_{14}O_2SNa^+$ [M+Na^+]: 245.0612; found: 245.0606.

*4.2.3. S-(3-Oxocyclohexyl) benzothioate (**6a**).* Colorless liquid. Yield: 0.122 g, 52%; IR (Neat): 1712, 1683, 1210, 913 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.95–7.91 (m, 2H), 7.60–7.55 (m, 1H), 7.47–7.42 (m, 2H), 4.11–4.07 (m, 1H), 2.87–2.84 (m, 1H), 2.82–2.36 (m, 4H), 2.30–2.23 (m, 1H), 2.14–1.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 207.8, 190.5, 136.8, 133.5, 128.6, 127.2, 47.3, 41.6, 40.9, 31.2, 24.3; HRMS *m*/*z*: calcd for $C_{13}H_{14}O_2SNa^+$ [M+Na^+]: 257.0612; found: 257.0601.

*4.2.4. S-(3-Oxopentyl) 4-methylbenzothioate (**4b**).* Colorless liquid. Yield: 0.149 g, 63%; IR (Neat): 1715, 1659, 1410, 1212 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.84 (d, *J*=8.2 Hz, 2H), 7.23 (d, *J*=8.2 Hz, 2H), 3.26 (t, *J*=6.8 Hz, 2H), 2.84 (t, *J*=6.8 Hz, 2H), 2.44 (q, *J*=7.3 Hz, 2H), 2.40

(s, 3H), 1.07 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 209.3, 191.5, 144.3, 134.3, 129.2, 127.2, 42.1, 36.0, 22.7, 21.6, 7.6; HRMS m/z: calcd for $C_{13}H_{16}O_2SNa^+$ [M+Na$^+$]: 259.0769; found: 259.0764.

*4.2.5. S-(3-Oxopentyl) 2-phenylethanethioate (**4c**).* Colorless liquid. Yield: 0.161 g, 68%; IR (Neat): 1712, 1689, 1410, 1018 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.35–7.25 (m, 5H), 3.80 (s, 2H), 3.05 (t, J=6.8 Hz, 2H), 2.70 (t, J=6.8 Hz, 2H), 2.37 (q, J=7.3 Hz, 2H), 1.03 (t, J=7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 209.0, 197.3, 133.4, 129.4, 128.6, 127.4, 50.4, 41.7, 35.9, 23.1, 7.6; HRMS m/z: calcd for $C_{13}H_{16}O_2SNa^+$ [M+Na$^+$]: 259.0761; found: 259.0769.

*4.2.6. S-(3-Oxopentyl) 4-methoxybenzothioate (**4d**).* Colorless liquid. Yield: 0.143 g, 61%; IR (Neat): 1715, 1654, 1602, 1168 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.93 (d, J=9.3 Hz, 2H), 6.92 (d, J=9.3 Hz, 2H), 3.86 (s, 3H), 3.25 (t, J=6.9 Hz, 2H), 2.84 (t, J=6.9 Hz, 2H), 2.43 (q, J=7.2 Hz, 2H), 1.07 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 209.3, 190.4, 163.9, 129.9, 129.4, 113.8, 55.5, 42.3, 36.1, 22.9, 7.7; HRMS m/z: calcd for $C_{13}H_{16}O_3SNa^+$ [M+Na$^+$]: 275.0718; found: 275.0708.

*4.2.7. (E)-S-(3-Oxopentyl) 3-phenylprop-2-enethioate (**4e**).* Colorless liquid. Yield: 0.151 g, 61%; IR (Neat): 1714, 1656, 1615, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.60 (d, J=15.8 Hz, 1H), 7.55–7.51 (m, 2H), 7.41–7.39 (m, 2H), 6.69 (d, J=15.8 Hz, 1H), 3.21 (t, J=6.8 Hz, 2H), 2.82 (t, J=6.8 Hz, 2H), 2.44 (q, J=7.3 Hz, 2H), 1.08 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 209.2, 189.8, 140.6, 134.0, 130.5, 128.9, 128.3, 124.8, 42.0, 36.0, 22.9, 7.7; HRMS m/z: calcd for $C_{14}H_{16}O_2SNa^+$ [M+Na$^+$]: 271.0769; found: 271.0768.

*4.2.8. S-(3-Oxopentyl) 4-chlorobenzothioate (**4f**).* Colorless liquid. Yield: 0.167 g, 65%; IR (Neat): 1716, 1664, 1588, 1206, 915 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.90–7.87 (m, 2H), 7.46–7.40 (m, 2H), 3.27 (t, J=6.8 Hz, 2H), 2.85 (t, J=6.8 Hz, 2H), 2.45 (q, J=7.2 Hz, 2H), 1.08 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 209.1, 190.8, 139.8, 135.2, 128.9, 128.5, 41.9, 36.0, 23.0, 7.7; HRMS m/z: calcd for $C_{12}H_{13}ClO_2SNa^+$ [M+Na$^+$]: 279.0222; found: 279.0223.

*4.2.9. S-(3-Oxopentyl) 3-methylbenzothioate (**4g**).* Colorless liquid. Yield: 0.146 g, 62%; IR (Neat): 1715, 1658, 1247, 1151 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.74 (d, J=6.8 Hz, 2H), 7.39–7.26 (m, 2H), 3.26 (t, J=6.8 Hz, 2H), 2.84 (t, J=6.8 Hz, 2H), 2.45 (q, J=7.2 Hz, 2H), 2.40 (s, 3H), 1.08 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 209.3, 192.1, 138.5, 136.9, 134.2, 128.5, 127.6, 124.4, 42.1, 36.0, 22.9, 22.1, 7.7; HRMS m/z: calcd for $C_{13}H_{16}O_2SNa^+$ [M+Na$^+$]: 259.0769; found: 259.0772.

*4.2.10. S-(3-Oxopentyl) 3-nitrobenzothioate (**4h**).* Light yellow solid. Yield: 0.160 g, 60%; mp 72 °C; IR (Neat): 1713, 1651, 1531, 1348 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 8.77 (t, J=2.1 Hz, 1H), 8.45–8.41 (m, 1H), 8.28–8.25 (m, 1H), 7.67 (t, J=8.0 Hz, 1H), 3.34 (t, J=6.3 Hz, 2H), 2.89 (t, J=6.3 Hz, 2H), 2.47 (q, J=7.2 Hz, 2H), 1.09 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 208.7, 189.9, 148.4, 138.2, 129.9, 127.5, 122.1, 41.6, 36.0, 23.3, 7.6; HRMS m/z: calcd for $C_{12}H_{13}NO_4SNa^+$ [M+Na$^+$]: 290.0463; found: 290.0449.

4.3. Synthesis of *S*-3-oxopentanyl 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranosiduronthioate 10

To a well stirred mixture of 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranuronic acid **9** (0.362 g, 1.0 mmol), PPh_3 (0.288 g, 1.1 mmol), and NBS (0.196 g, 1.1 mmol) in $CHCl_3$ (5 mL) (stirred for 10 min) was added benzyltriethylammonium tetrathiomolybdate **1** (1.22 g, 2.0 mmol). Ethyl vinyl ketone (0.2 mL, 2.0 mmol) was then added after 20 min and stirring was continued for 2 h at room temperature (28 °C). Diethyl ether (20 mL) was then added to the reaction mixture followed by filtration through a Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with diethyl ether (20 mL) and filtered again through a Celite pad. The combined extract was evaporated and the residue was purified by column chromatography on silica gel to give compound **10** as a colorless liquid (0.240 g, 52%).

$[\alpha]_D^{25}$ +23.3 (c 1.7, $CHCl_3$); IR (Neat): 1759, 1714, 1685, 1370, 1216, 1041 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.77 (d, J=7.8 Hz, 1H), 5.32–5.09 (m, 3H), 4.15 (d, J=9.3 Hz, 1H), 3.08–3.02 (m, 2H), 2.71 (t, J=6.6 Hz, 2H), 2.43 (q, J=7.2 Hz, 2H), 2.14 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H) 1.06 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.0, 195.2, 169.8, 169.3, 169.1, 168.7, 91.2, 77.9, 71.9, 70.1, 68.9, 41.1, 35.9, 22.2, 20.7, 20.6, 20.5, 7.6; HRMS m/z: calcd for $C_{19}H_{26}O_{11}SNa^+$ [M+Na$^+$]: 485.1094; found: 485.1100.

4.4. Synthesis of 4,5-di-*O*-acetyl-3-benzoyl-2-deoxy-3-thio-D-ribo-hexopyanoso-1,5-lactone 12

To a well stirred solution of benzoic acid **2a** (0.122 g, 1.0 mmol), PPh_3 (0.288 mg, 1.1 mmol), and NBS (0.196 g, 1.1 mmol) in $CHCl_3$ (5 mL) (stirred for 10 min) was added benzyltriethylammonium tetrathiomolybdate **1** (1.22 g, 2.0 mmol). Michael acceptor, 11 (0.482 g, 2.0 mmol) was then added after 20 min and stirring was continued for 2 h at room temperature (28 °C). Diethyl ether (20 mL) was then added to the reaction mixture followed by filtration through a Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with diethyl ether (20 mL) and filtered again through a Celite pad. The combined extract was evaporated and the residue was purified by column chromatography on silica gel to give the corresponding adduct **12** as a colorless liquid (0.220 g, 60%).

$[\alpha]_D^{26}$ +24.5 (c 0.8, $CHCl_3$); IR (Neat): 1749, 1669, 1213, 906 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.92 (m, 2H), 7.64–7.60 (m, 1H), 7.50–7.46 (m, 2H), 5.32 (t, J=3.2 Hz, 1H), 4.77 (dd, J_1=4.0 Hz, J_2=7.6 Hz, 1H), 4.57 (ddd, J_1=3.2 Hz, J_2=6.0 Hz, J_3=10.4 Hz, 1H), 4.40 (d, J=4.0 Hz, 2H), 3.06 (dd, J_1=6.0 Hz, J_2=18.0 Hz, 1H), 2.95 (dd, J_1=10.4 Hz, J_2=18.0 Hz, 1H), 2.19 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 189.1, 170.2, 169.7, 166.7, 135.9, 134.2, 128.9, 127.4, 78.3, 67.8, 63.2, 36.9, 32.7, 29.7, 20.7; HRMS m/z: calcd for $C_{17}H_{18}O_7SNa^+$ [M+Na$^+$]: 389.0671; found: 389.0659.

4.5. Synthesis of 4,5-di-*O*-acetyl-2-deoxy-3-phenylacetyl-3-thio-D-ribo- hexopyanoso-1,5-lactone 13

The same procedure as that for compound **12** was followed.

Yield: 0.231 g, 55%; $[\alpha]_D^{27}$ +13.9 (c 1.6, $CHCl_3$); IR (Neat): 1748, 1697, 1372, 1222, 1033 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.25 (m, 5H), 5.20 (t, J=3.4 Hz, 1H), 4.67 (q, J=3.9 Hz, 1H), 4.32 (d, J=3.9, 2H), 4.30–4.27 (m, 1H), 3.84 (s, 2H), 2.91 (dd, J_1=6.0 Hz, J_2=18.0 Hz, 1H), 2.78 (dd, J_1=10.4 Hz, J_2=18.0 Hz, 1H), 2.13 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 170.1, 169.6, 166.5, 132.4, 129.6, 128.8, 127.8, 78.1, 67.4, 63.1, 50.4, 37.1, 32.4, 20.6; HRMS m/z: calcd for $C_{18}H_{20}O_7SNa^+$ [M+Na$^+$]: 403.0827; found: 403.0828.

4.6. Synthesis of (4*R*,5*R*)-5-((*Z*)-2-(methoxycarbonyl)vinyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylic acid 17

To a solution of compound **16** (188 mg, 1 mmol) in DMF (10 ml) was added PDC (2.25 g, 6.0 mmol). The solution was stirred for 24 h at room temperature. Solvent was removed under vacuum; ethyl acetate (20 mL) was added to the residue and filtered through a Celite pad. The solvent was evaporated to give compound **17** as a colorless liquid (0.219 g, 95%).

$[\alpha]_D^{23}$ +15.8 (c 1.9, $CHCl_3$); IR (Neat): 3235, 1724, 1221, 1204 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.7 (broad s, 1H), 6.16 (dd, J_1=6.9 Hz, J_2=11.4 Hz, 1H) 5.92 (dd, J_1=1.5 Hz, J_2=11.4 Hz, 1H) 5.80 (dt, J_1=1.5 Hz, J_2=6.9 Hz, 1H) 4.86 (d, J=7.5 Hz, 1H), 3.67 (s, 3H), 1.55 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.3, 165.8, 143.0,

122.8, 117.7, 76.6, 75.0, 51.7, 26.7, 25.3; HRMS *m*/*z*: calcd for $C_{10}H_{14}O_6Na^+$ [M+Na$^+$]: 253.0688; found: 253.0682.

4.7. Methyl 2-((3a*S*, 6a*R*)-tetrahydro-2,2-dimethyl-4-oxothieno[3,4-d]dioxol-6-yl)acetate 18

To a well stirred solution of **17** (0.23 g, 1 mmol), PPh_3 (0.288 mg, 1.1 mmol), and NBS (0.196 g, 1.1 mmol) in $CHCl_3$ (5 mL) (stirred for 10 min) was added benzyltriethylammonium tetrathiomolybdate **1** (0.913 g, 1.5 mmol). The reaction mixture was stirred for 2 h at room temperature (28 °C). Diethyl ether (20 mL) was then added to the reaction mixture followed by filtration through a Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with diethyl ether (20 mL) and filtered again through a Celite pad. The combined extract was evaporated and the residue was purified by column chromatography on silica gel to give the Michael adduct **18** (0.123 g, 50%) as a mixture of diastereomers (2:1).

$[\alpha]_D^{24}$ −32.0 (*c* 0.6, $CHCl_3$); IR (Neat): 2924, 1788, 1734, 1713, 1375, 1233 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.83–4.79 (m, 1.5H), 4.69 (d, *J*=4.5 Hz, 0.5H), 4.64 (dd, J_1=4.8 Hz, J_2=0.6 Hz, 1H), 4.37–4.31 (m, 0.5H), 4.18 (t, *J*=6.9 Hz, 1H), 3.75 (s, 1.5H), 3.73 (s, 3H), 3.09 (dd, J_1=6.9 Hz, J_2=17.4 Hz, 0.5H), 2.96–2.86 (m, 2.5H), 1.48 (s, 3H), 1.46 (s, 1.5H), 1.39 (s, 4.5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.2, 170.4, 112.8, 112.7, 85.1, 83.6, 80.4, 52.2, 52.1, 44.8, 41.3, 39.6, 35.5, 27.4, 26.0, 25.8; HRMS *m*/*z*: calcd for $C_{10}H_{14}O_5SNa^+$ [M+Na$^+$]: 269.0460; found: 269.0468.

4.8. General procedure for aziridine ring opening (19a–f and 20a–25a)

To a well stirred solution of the corresponding carboxylic acid (1.2 mmol), PPh_3 (1.3 mmol), and NBS (1.3 mmol) in $CHCl_3$ (5 mL) (stirred for 10 min) was added benzyltriethylammonium tetrathiomolybdate **1** (1.2 mmol). The aziridine (1.0 mmol) was then added after 20 min and stirred at room temperature (28 °C) until the disappearance of the starting aziridine. Diethyl ether (20 mL) was then added to the reaction mixture followed by filtration through a Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with diethyl ether (20 mL) and filtered again through a Celite pad. The combined extract was evaporated and the residue was purified by column chromatography on silica gel to give the corresponding product.

*4.8.1. (S)-S-(2-(4-Methylphenylsulfonamido)-3-phenylpropyl) benzothioate (**19a**).* White solid. Yield: 0.374 g, 88%; mp=72 °C; $[\alpha]_D^{26}$ −17.5 (*c* 1.27, $CHCl_3$); IR (Neat): 3287, 1664, 1159, 912 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.84 (d, *J*=8.4 Hz, 2H), 7.60–7.57 (m, 3H), 7.47–7.41 (m, 2H), 7.26–7.22 (m, 3H), 7.14–7.11 (m, 2H), 7.03 (d, *J*=8.4 Hz, 2H), 5.01 (d, *J*=6.9 Hz, 1H), 3.72–3.62 (m, 1H), 3.16–2.87 (m, 4H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 191.8, 143.0, 136.4, 133.7, 129.5, 129.4, 128.7, 128.6, 127.8, 127.4, 127.0, 126.8, 55.6, 41.6, 32.5, 21.4; HRMS *m*/*z*: calcd for $C_{23}H_{23}NO_3S_2Na^+$ [M+Na$^+$]: 448.1017; found: 448.1021.

*4.8.2. (S)-S-(2-(4-Methylphenylsulfonamido)-3-phenylpropyl) 4-methylbenzothioate (**19b**).* White solid. Yield: 0.364 g, 83%; mp=80 °C; $[\alpha]_D^{26}$ −22.7 (*c* 4.8, $CHCl_3$); IR (Neat): 3293, 2924, 1660, 1160 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.03 (d, *J*=8.1 Hz, 2H), 7.59 (d, *J*=8.1 Hz, 2H), 7.29–7.23 (m, 5H), 7.17–7.1 (m, 2H), 7.03 (d, *J*=8.4 Hz, 2H), 5.04 (d, *J*=6.9 Hz, 1H), 3.70–3.59 (m, 1H), 3.14–2.87 (m, 4H), 2.43 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 182.2, 144.7, 142.9, 137.2, 136.5, 129.5, 129.4, 128.7, 127.5, 127.0, 126.8, 55.7, 41.6, 32.3, 21.7, 21.4; HRMS *m*/*z*: calcd for $C_{24}H_{25}NO_3S_2Na^+$ [M+Na$^+$]: 462.1174; found: 462.1160.

*4.8.3. (S)-S-(2-(4-Methylphenylsulfonamido)-3-phenylpropyl) 2-phenylethanethioate (**19c**).* Colorless liquid. Yield: 0.399 g, 91%; $[\alpha]_D^{26}$ −15.1 (*c* 4.05, $CHCl_3$); IR (Neat): 3294, 2921, 1645, 1159 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.58 (d, *J*=7.8 Hz, 2H), 7.36–7.18 (m, 10H), 6.99–6.97 (m, 2H), 4.80 (d, *J*=6.9 Hz, 1H), 3.76 (s, 2H), 3.63–3.52 (m, 1H), 3.00–2.86 (m, 2H), 2.76 (d, *J*=6.6 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 197.4, 143.2, 137.3, 136.3, 133.2, 129.5, 129.3, 128.7, 128.6, 127.6, 127.0, 126.8, 55.0, 50.4, 40.7, 33.2, 21.5; HRMS *m*/*z*: calcd for $C_{24}H_{25}NO_3S_2Na^+$ [M+Na$^+$]: 462.1174; found: 462.1171.

*4.8.4. (S)-S-(2-(4-Methylphenylsulfonamido)-3-phenylpropyl) 4-methoxybenzothioate (**19d**).* White solid. Yield: 0.419 g, 92%; mp=124 °C; $[\alpha]_D^{26}$ −17.9 (*c* 3.30, $CHCl_3$); IR (Neat): 3290, 2923, 1651, 1018 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.82 (d, *J*=8.4 Hz, 2H), 7.59 (d, *J*=8.1 Hz, 2H), 7.28–7.22 (m, 3H), 7.15–7.12 (m, 2H), 7.04 (d, *J*=8.1 Hz, 2H), 5.11 (d, *J*=6.9 Hz, 1H), 3.88 (s, 3H), 3.69–3.59 (m, 1H), 3.14–2.86 (m, 4H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 190.4, 164.1, 142.9, 137.4, 136.6, 129.5, 129.2, 128.7, 127.0, 113.8, 55.9, 55.6, 41.7, 32.3, 21.5; HRMS *m*/*z*: calcd for $C_{24}H_{25}NO_4S_2Na^+$ [M+Na$^+$]: 478.1123; found: 478.1127.

*4.8.5. (S,E)-S-(2-(4-Methylphenylsulfonamido)-3-phenylpropyl) 3-phenylprop-2-enethioate (**19e**).* White solid. Yield: 0.406 g, 90%; mp=125 °C; $[\alpha]_D^{26}$ −42.08 (*c* 2.46, $CHCl_3$); IR (Neat): 3289, 2922, 1614, 1158, 1038 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.63 (d, *J*=8.1 Hz, 2H), 7.58–7.43 (m, 3H), 7.42–7.41 (m, 3H), 7.27–7.09 (m, 6H), 6.59 (d, *J*=15.6, 1H), 5.03 (d, *J*=6.6 Hz, 1H), 3.67–3.59 (m, 1H), 3.12–2.83 (m, 4H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 190.0, 143.1, 141.4, 137.3, 136.5, 133.8, 130.9, 129.5, 129.4, 129.0, 128.7, 128.5, 127.1, 126.8, 124.2, 55.7, 41.4, 32.5, 21.4; HRMS *m*/*z*: calcd for $C_{26}H_{27}NO_3S_2Na^+$ [M+Na$^+$]: 474.1174; found: 474.1156.

*4.8.6. (S)-S-(2-(4-Methylphenylsulfonamido)-3-phenylpropyl) 4-chlorobenzothioate (**19f**).* White solid. Yield: 0.414 g, 90%; mp=53 °C; $[\alpha]_D^{26}$ −18.63 (*c* 2.95, $CHCl_3$); IR (Neat): 3291, 2923, 1647, 1160 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.78 (d, *J*=8.7 Hz, 2H), 7.58 (d, *J*=8.1 Hz, 2H), 7.42 (d, *J*=8.7 Hz, 2H), 7.26–7.22 (m, 3H), 7.12–7.05 (m, 4H), 4.98 (d, *J*=7.5 Hz, 1H), 3.74–3.59 (m, 1H), 3.13–3.10 (m, 2H), 2.99–2.85 (m, 2H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 190.6, 143.1, 140.2, 136.3, 129.5, 128.9, 128.7, 127.0, 126.9, 55.4, 41.5, 32.9, 21.4; HRMS *m*/*z*: calcd for $C_{23}H_{22}ClNO_3S_2Na^+$ [M+Na$^+$]: 482.0627; found: 482.0624.

*4.8.7. S-(4-(4-Methylphenylsulfonamido)hexan-3-yl) benzothioate (**20a**).* White solid. Yield: 0.324 g, 83%; mp=104 °C; IR (Neat): 3281, 1661, 1160, 909 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.90–7.87 (m, 2H), 7.82 (d, *J*=7.8 Hz, 2H), 7.61–7.57 (m, 1H), 7.48–7.42 (m, 2H), 7.25 (d, *J*=7.8 Hz, 2H), 4.84 (d, *J*=9.3 Hz, 1H), 3.59–3.52 (m, 1H), 3.50–3.41 (m, 1H), 2.38 (s, 3H), 1.73–1.37 (m, 4H), 0.97–0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 191.0, 143.3, 137.8, 136.6, 133.5, 129.5, 128.6, 127.4, 127.3, 58.2, 50.8, 25.4, 25.0, 21.5, 11.9, 10.7; HRMS *m*/*z*: calcd for $C_{20}H_{25}NO_3S_2Na^+$ [M+Na$^+$]: 414.1174; found: 414.1173.

*4.8.8. S-(2-(4-Methylphenylsulfonamido)cyclohexyl) benzothioate (**21a**).* White solid. Yield: 0.330 g, 85%; mp=140 °C; IR (Neat): 3285, 2939, 1642, 1328, 1159 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.79–7.73 (m, 2H), 7.63–7.54 (m, 3H), 7.46–7.41 (m, 2H), 6.92 (d, *J*=7.8 Hz, 2H), 5.26 (d, *J*=6.9 Hz, 1H), 3.50–3.41 (m, 1H), 3.21–3.01 (m, 1H), 2.25 (s, 3H), 1.77–1.25 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): 193.4, 142.5, 136.4, 133.7, 129.6, 129.3, 128.4, 127.4, 126.8, 59.0, 46.4, 36.4, 32.5, 25.9, 24.5, 21.4; HRMS *m*/*z*: calcd for $C_{20}H_{23}NO_3S_2Na^+$ [M+Na$^+$]: 412.1017; found: 412.1037.

*4.8.9. S-(6-(4-Methylphenylsulfonamido)cyclohex-3-en-1-yl) benzothioate (**22a**).* White solid. Yield: 0.341 g, 88%; mp=100 °C; IR (Neat): 3281, 1661, 1158, 1092 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$):

7.81 (d, J=8.4 Hz, 2H), 7.67–7.57 (m, 3H), 7.53–7.41 (m, 2H), 7.07 (d, J=8.4 Hz, 2H), 5.62 (s, 2H), 5.25 (br s, 1H), 3.88–3.81 (m, 1H), 3.61–3.51 (m, 1H), 2.65–2.53 (m, 2H), 2.43–2.12 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 192.6, 142.9, 136. 4, 133.6, 129.4, 128.5, 127.7, 127.4, 126.8, 125.0, 124.8, 53.8, 42.1, 33.7, 30.5, 21.4; HRMS m/z: calcd for $C_{20}H_{21}NO_3S_2Na^+$ [M+Na$^+$]: 410.0861; found: 410.0869.

*4.8.10. S-(2-(4-Methylphenylsulfonamido)cyclopentyl) benzothioate (**23a**).* White solid. Yield: 0.307 g, 82%; mp=137 °C; IR (Neat): 3274, 1660, 1159 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.79 (d, J=7.2 Hz, 2H), 7.66–7.58 (m, 3H), 7.48–7.43 (m, 2H), 7.00 (d, J=7.2 Hz, 2H), 5.53 (d, J=5.1 Hz, 1H), 3.76–3.67 (m, 1H), 3.48–3.38 (m, 1H), 2.22 (s, 3H), 2.19–2.09 (m, 2H), 1.86–1.54 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 193.2, 142.9, 137.3, 136.3, 133.7, 129.4, 128.5, 127.4, 127.1, 62.6, 46.4, 33.6, 29.4, 22.0, 21.4; HRMS m/z: calcd for $C_{19}H_{21}NO_3S_2Na^+$ [M+Na$^+$]: 398.0861; found: 398.0865.

*4.8.11. S-(4-Methyl-3-(4-methylphenylsulfonamido)pentan-2-yl) benzothioate (**24a**).* White solid. Yield: 0.317 g, 81%; mp=134 °C; IR (Neat): 3286, 1658, 1158 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.80–7.73 (m, 4H), 7.59–7.40 (m, 3H), 7.20 (d, J=7.5 Hz, 2H), 4.99 (d, J=9.9 Hz, 1H), 3.91–3.85 (m, 1H), 3.48–3.36 (m, 1H), 2.37 (s, 3H), 1.93–1.87 (m, 1H), 1.26 (d, J=7.2 Hz, 3H), 0.97 (d, J=6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 191.0, 143.0, 138.8, 136.7, 133.4, 129.4, 128.5, 127.2, 127.1, 63.2, 41.8, 31.0, 21.5, 20.5, 18.8, 16.9; HRMS m/z: calcd for $C_{20}H_{25}NO_3S_2Na^+$ [M+Na$^+$]: 414.1174; found: 414.1170.

*4.8.12. S-(2-(4-Methylphenylsulfonamido)-1-phenylethyl) benzothioate (**25a**) and S-(2-(4-methylphenylsulfonamido)-2-phenylethyl) benzothioate (**25a′**).* White solid. Yield: 0.311 g, 80%; mp=119 °C (for mixture); (R_1:R_2=4:3) IR (Neat): 3282, 1662, 1330, 1157 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.90–7.84 (m, 2H^{R1}+2H^{R2}), 7.74 (d, J=8.4 Hz, 2H^{R1}), 7.63–7.55 (1H^{R1}+3H^{R2}), 7.48–7.40 (m, 2H^{R1}+2H^{R2}), 7.32–7.21 (m, 7H^{R1}+5H^{R2}), 7.00 (d, J=7.8 Hz, 2H^{R2}), 5.51 (d, J=6.3 Hz, 1H^{R2}), 4.81–4.74 (m, 2H^{R2}), 4.59–4.52 (m, 1H^{R1}), 3.68–3.59 (m, 1H^{R1}), 3.54–3.48 (m, 1H^{R1}), 3.56–3.52 (m, 1H^{R2}), 3.24 (dd, J_1=4.2 Hz, J_2=14.1 Hz, 1H^{R2}), 2.40 (s, 3H^{R1}), 2.24 (s, 3H^{R2}); ^{13}C NMR (75 MHz, $CDCl_3$): 190.3, 143.5, 143.0, 140.1, 136.3, 133.8, 129.7, 129.3,; HRMS m/z: calcd for $C_{20}H_{23}NO_3S_2Na^+$ [M+Na$^+$]: 412.1017; found: 412.1037.

4.9. Synthesis of *S*-(phenyl(1-tosylaziridin-2-yl)methyl) benzothioate 28

To a well stirred solution of benzoic acid **2a** (0.128 g, 1.05 mmol), PPh_3 (0.275 g, 1.05 mmol), and NBS (0.187 g, 1.05 mmol) in $CHCl_3$ (5 mL) (stirred for 10 min) was added benzyltriethylammonium tetrathiomolybdate **1** (0.639 g, 1.05 mmol). To this was added the corresponding aziridine tosylate **27** (0.457 g, 1 mmol) and the reaction mixture was stirred for 5 h at room temperature (28 °C). Diethyl ether (20 mL) was then added to the reaction mixture followed by filtration through a Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with diethyl ether (20 mL) and filtered again through a Celite pad. The combined extract was evaporated and the residue was purified by column chromatography on silica gel to give the corresponding aziridine thioester **28** (0.313 g, 74%) as a white solid.

Mp=104 °C; IR (Neat): 1665, 1597, 1327, 1162 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.86–7.85 (m, 2H), 7.62 (d, J=8.0 Hz, 2H), 7.59–7.56 (m, 1H), 7.46–7.42 (m, 2H), 7.21–7.18 (m, 5H), 7.10 (d, J=8.0 Hz, 2H), 4.66 (d, J=7.6 Hz, 1H), 3.26–3.22 (m, 1H), 2.81 (d, J=6.8 Hz, 1H), 2.38–2.33 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 189.7, 144.3, 136.8, 136.2, 134.5, 133.8, 129.5, 128.7, 128.6, 128.3, 128.0, 127.8, 127.4, 47.8, 43.9, 32.5, 21.6; HRMS m/z: calcd for $C_{23}H_{21}NO_3S_2Na^+$ [M+Na$^+$]: 446.0861; found: 446.0859.

4.10. Synthesis of *S,S′*-(2-(4-methylphenylsulfonamido)-1-phenylpropane-1,3-diyl) dibenzothioate, 29

To a well stirred solution of benzoic acid **2a** (0.268 g, 2.2 mmol), PPh_3 (0.576 g, 2.2 mmol), and NBS (0.392 g, 2.2 mmol) in $CHCl_3$ (8 mL) (stirred for 10 min) was added benzyltriethylammonium tetrathiomolybdate **1** (1.34 g, 2.2 mmol). To this was added aziridine tosylate **27** (0.457 g, 1 mmol) and the reaction mixture was stirred for 8 h at room temperature (28 °C). Diethyl ether (30 mL) was then added to the reaction mixture followed by filtration through a Celite pad. The residue was again extracted with CH_2Cl_2 (10 mL) followed by extraction with diethyl ether (30 mL) and filtered again through a Celite pad. The combined extract was evaporated and the residue was purified by column chromatography on silica gel to give the corresponding bisthioester **29** as a white solid (0.421 g, 75%).

Mp=153 °C; IR (Neat): 3282, 1666, 1597, 1208, 1158 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.93–7.90 (m, 2H), 7.82–7.79 (m, 2H), 7.66–7.55 (m, 4H), 7.48–7.21 (m, 9H), 7.01 (d, J=8.4 Hz, 2H), 5.16 (d, J=3.6 Hz, 1H), 5.06 (d, J=9.0 Hz, 1H), 4.16–4.07 (m, 1H), 3.24 (dd, J_1=9.0 Hz, J_2=14.1 Hz, 1H), 3.04 (dd, J_1=5.1 Hz, J_2=14.1 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 191.6, 189.6, 143.1, 137.8, 136.8, 136.4, 133.7, 133.6, 129.4, 128.9, 128.6, 128.5, 128.4, 128.2, 127.5, 127.4, 127.2, 58.3, 52.4, 31.3; HRMS m/z: calcd for $C_{30}H_{27}NO_4S_3Na^+$ [M+Na$^+$]: 584.1000; found: 584.0987.

4.11. General procedure for epoxide ring opening (30a–f, 31a, and 31b)

To a well stirred solution of the corresponding carboxylic acid (1.0 mmol), PPh_3 (1.1 mmol), and NBS (1.1 mmol) in $CHCl_3$–EtOH (1:1) mixture (6 mL) (stirred for 10 min) was added benzyltriethylammonium tetrathiomolybdate **1** (1.2 mmol). The corresponding epoxide (1.2 mmol) was then added after 20 min and stirring was continued for 6 h at room temperature (28 °C). Diethyl ether (20 mL) was then added to the reaction mixture followed by filtration through a Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with diethyl ether (20 mL) and filtered again through a Celite pad. The combined extract was evaporated and the residue was purified by column chromatography on silica gel to give the corresponding product.

*4.11.1. S-(2-Hydroxy-2-phenylethyl) benzothioate (**30a**).* Colorless liquid. Yield: 0.160 g, 62%; IR (Neat): 3448, 1660, 1207 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 8.01–7.98 (m, 2H), 7.62–7.57 (m, 1H), 7.49–7.29 (m, 7H), 4.94 (dd, J_1=3.6 Hz, J_2=8.4 Hz, 1H), 3.54 (dd, J_1=8.4 Hz, J_2=13.8, 1H), 3.30 (dd, J_1=8.4 Hz, J_2=13.8 Hz, 1H), 2.72 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 192.4, 142.5, 133.6, 128.7, 128.6, 128.0, 127.4, 125.8, 73.4, 38.0; HRMS m/z: calcd for $C_{15}H_{14}O_2SNa^+$ [M+Na$^+$]: 281.0612; found: 281.0606.

*4.11.2. S-(2-Hydroxy-2-phenylethyl) 4-methylbenzothioate (**30b**).* White solid. Yield: 0.150 g, 65%; mp=63 °C; IR (Neat): 3402, 1657, 1606, 914 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 7.88 (d, J=8.1 Hz, 2H), 7.47–7.40 (m, 2H), 7.37–7.23 (m, 5H), 4.94–4.89 (m, 1H), 3.51 (dd, J_1=3.6 Hz, J_2=14.1 Hz, 1H), 3.28 (dd, J_1=8.4 Hz, J_2=14.1 Hz, 1H), 2.86 (d, J=3.6 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 192.6, 145.1, 143.1, 134.7, 129.8, 129.1, 128.5, 128.0, 126.3, 73.9, 38.4, 22.2; HRMS m/z: calcd for $C_{16}H_{16}O_2SNa^+$ [M+Na$^+$]: 295.0769; found: 295.0767.

*4.11.3. S-(2-Hydroxy-2-phenylethyl) 2-phenylethanethioate (**30c**).* Colorless liquid. Yield: 0.169 g, 62%; IR (Neat): 3371, 1677,

1018 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 7.36–7.25 (m, 10H), 4.80 (d, J=9.0 Hz, 1H), 3.86 (s, 2H), 3.31 (dd, J_1=4.2 Hz, J_2=14.1 Hz, 1H), 3.09 (dd, J_1=9.0 Hz, J_2=14.1 Hz, 1H), 2.51 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 198.4, 142.8, 133.8, 130.1, 129.2, 129.0, 128.5, 128.0, 126.3, 73.7, 50.9, 36.7; HRMS m/z: calcd for $C_{16}H_{16}O_2SNa^+$ [M+Na^+]: 295.0769; found: 295.0768.

*4.11.4. S-(2-Hydroxy-2-phenylethyl) 4-methoxybenzothioate (**30d**).* White solid. Yield: 0.184 g, 64%; mp=45 °C; IR (Neat): 3436, 1601, 1168 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 7.98 (d, J=9.0 Hz, 2H), 7.48–7.29 (m, 5H), 6.94 (d, J=9.0 Hz, 2H), 4.94–4.92 (m, 1H), 3.87 (s, 3H), 3.52 (dd, J_1=3.6 Hz, J_2=14.1 Hz, 1H), 3.28 (dd, J_1=3.6 Hz, J_2=14.1 Hz, 1H), 2.87 (d, J=2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 191.1, 164.1, 142.7, 129.7, 128.6, 128.0, 125.9, 113.9, 73.6, 55.6, 38.0; HRMS m/z: calcd for $C_{16}H_{16}O_2SNa^+$ [M+Na^+]: 311.0718; found: 311.0706.

*4.11.5. (E)-S-(2-Hydroxy-2-phenylethyl) 3-phenylprop-2-enethioate (**30e**).* White solid. Yield: 0.179 g, 63%; mp=59 °C; IR (Neat): 3448, 1652, 1615, 1042 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 7.66 (d, J=15.9 Hz, 1H), 7.57–7.31 (m, 10H), 6.76 (d, J=15.9 Hz, 1H), 4.94–4.91 (m, 1H), 3.48 (dd, J_1=3.9 Hz, J_2=14.1 Hz, 1H), 3.26 (dd, J_1=8.4 Hz, 1H, J_2=14.1 Hz, 1H), 2.78 (d, J=3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 190.5, 142.6, 141.4, 134.0, 130.9, 129.1, 128.6, 125.9, 124.6, 73.5, 38.1; HRMS m/z: calcd for $C_{17}H_{16}O_2SNa^+$ [M+Na^+]: 307.0769; found: 307.0763.

*4.11.6. S-(2-Hydroxy-2-phenylethyl) 4-chlorobenzothioate (**30f**).* White solid. Yield: 0.173 g, 59%; mp=59 °C; IR (Neat): 3457, 1666, 1588, 1206 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 7.93 (d, J=8.4 Hz, 2H), 7.47–7.30 (m, 7H), 4.95–4.92 (m, 1H), 3.54 (dd, J_1=3.6 Hz, J_2=13.8 Hz, 1H), 3.31 (dd, J_1=8.4 Hz, J_2=13.8 Hz, 1H), 2.66 (d, J=3.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 191.5, 142.7, 140.4, 135.3, 129.3, 129.0, 128.9, 128.4, 126.1, 73.6, 38.3; HRMS m/z: calcd for $C_{16}H_{17}ClO_2SNa^+$ [M+Na^+]: 315.0222; found: 315.0210.

*4.11.7. S-(2-Hydroxycyclohexyl) benzothioate (**31a**).* Colorless liquid. Yield: 0.149 g, 63%; IR (Neat): 3421, 1659, 912 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 7.99–7.96 (m, 2H), 7.61–7.56 (m, 1H), 7.48–7.43 (m, 2H), 3.67–3.53 (m, 2H), 2.48 (d, J=3.9 Hz, 1H), 2.19–2.11 (m, 2H), 1.83–1.73 (m, 2H), 1.61–1.26 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 192.7, 136.9, 133.6, 128.6, 127.5, 73.3, 0.3, 35.2, 32.2, 25.9, 24.1; HRMS m/z: calcd for $C_{13}H_{16}O_2SNa^+$ [M+Na^+]: 259.0769; found: 259.0771.

*4.11.8. S-(2-Hydroxycyclohexyl) 4-methylbenzothioate (**31b**).* White solid. Yield: 0.163 g, 65%; mp=69 °C; IR (Neat): 3420, 1653, 913 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 7.87 (d, J=8.1 Hz, 2H), 7.24 (d, J=8.1 Hz, 2H), 3.65–3.49 (m, 2H), 2.61 (br s, 1H), 2.41 (s, 3H), 2.19–2.10 (m, 2H), 1.82–1.72 (m, 2H), 1.60–1.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 192.8, 144.9, 134.9, 129.7, 128.0, 73.8. 50.6, 35.6, 32.7, 26.4, 24.6, 22.2; HRMS m/z: calcd for $C_{14}H_{18}O_2SNa^+$ [M+Na^+]: 273.0925; found: 273.0933.

4.12. Synthesis of *S*-(4-(4-methylphenylsulfonamido)-7-oxabicyclo[4.1.0]heptan-3-yl) benzothioate, 32a

To a well stirred solution of benzoic acid **2a** (0.128 g, 1.05 mmol), PPh_3 (0.275 g, 1.05 mmol), and NBS (0.187 g, 1.05 mmol) in $CHCl_3$ (5 mL) (stirred for 10 min) was added benzyltriethylammonium tetrathiomolybdate **1** (0.639 g, 1.05 mmol). To this was added the corresponding aziridine epoxide, **32** (0.265 g, 1 mmol) and the reaction mixture was stirred for 8 h at room temperature (28 °C). Diethyl ether (20 mL) was then added to the reaction mixture followed by filtration through a Celite pad. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with diethyl ether (20 mL) and filtered again through a Celite pad. The combined extract was evaporated and the residue was purified by column chromatography on silica gel to give the corresponding aziridine thioester **32a** (0.322 g, 80%) as a white solid.

Mp=104 °C; IR (Neat): 3288, 1660, 1159, 911 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.83–7.80 (m, 2H), 7.67 (d, J=8.0 Hz, 2H), 7.61–7.58 (m, 1H), 7.47–7.42 (m, 2H), 7.11 (d, J=8.0 Hz, 2H), 5.47 (d, J=8.8 Hz, 1H), 3.78–3.73 (m, 1H), 3.51–3.43 (m, 1H), 2.55 (dd, J_1=5.4 Hz, J_2=16.0 Hz, 1H), 2.48–2.42 (m, 1H), 2.34 (m, 1H), 2.34 (s, 3H), 2.10–1.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 191.2, 143.0, 138.3, 136.3, 133.8, 129.6, 128.6, 127.4, 126.6, 52.1, 51.3, 51.2, 39.4, 30.8, 28.6, 21.5; HRMS m/z: calcd for $C_{20}H_{21}NO_4S_2Na^+$ [M+Na^+]: 426.0810; found: 426.0804.

Compounds **5a**[21] and **7a**[21] are reported.

Crystallographic data (excluding structure factors) for the structures (**4h**) in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-731527. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.Uk).

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Supplementary data

Copies of the ^1H, and ^{13}C NMR spectra for all new compounds are attached. Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.06.028. These data include MOL files and InChIKeys of the most important compounds described in this article.

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