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Base-promoted aminoethylation of thiols with 2-oxazolidinones: a simple synthesis of 2-aminoethyl sulfides

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Abstract—A simple synthesis of 2-aminoethyl sulfides using a base-promoted reaction of 2-oxazolidinones with thiols is described. An application of this method to the synthesis of chiral 2-aminoethyl sulfides and sulfur-containing heterocyclic compounds is also presented.

1. Introduction

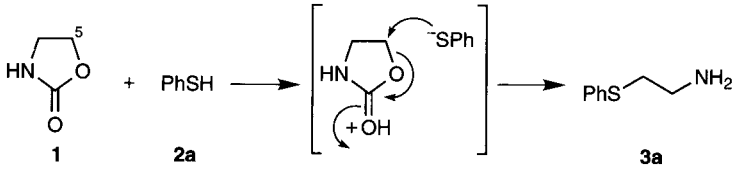
2-Aminoethyl sulfides are versatile intermediates in organic synthesis.[1] Some of them have been employed as key structural elements of biologically active compounds.[2] Of the several methods available for the synthesis of 2-aminoethyl sulfides,[1–3] probably the simplest one is the reaction of thiols with aziridines.[2c,3a,d,h] However, aziridine and its derivatives are not commercially available at the present time due to their toxic and carcinogenic properties.[4] Therefore, 2-aminoethyl sulfides have commonly been prepared from the corresponding 2-aminoethyl alcohols via several steps.[1c–e,i,2b,3e,g] On the other hand, Poindexter and his coworkers reported that heating a mixture of 2-oxazolidinone (**1**) and benzenethiol (**2a**) at 150°C without a solvent provided 2-(phenylthio)ethylamine (**3a**) in 60% yield (Scheme 1).[5] Formation of **3a** from **1** and **2a** has been suggested to proceed via protonation at the carbonyl oxygen atom of **1** with acidic benzenethiol followed by an attack of the resulting thiolate anion on the 5-position of the protonated **1** (Scheme 1). The method, therefore, was applicable for acidic aromatic thiols but not for non-acidic aliphatic thiols such as octanethiol.

We have recently found that 2-aminoethyl sulfide (**3a**) could be obtained in high yield simply by heating a mixture of 2-oxazolidinone (**1**) and benzenethiol in the presence of alkoxides.[6] This method could also be extended to the reaction with alkanethiols to give the corresponding 2-aminoethyl sulfides. The present paper describes a full account of the work in this area, including an application of the method to the synthesis of chiral 2-aminoethyl sulfides and sulfur-containing heterocyclic compounds.

2. Results and discussion

A mixture of **1** and a stoichiometric amount of sodium benzenethiolate (prepared from benzenethiol (**2a**) and sodium ethoxide) was heated in boiling EtOH for 24 h to give **3a** in 60% yield, along with *N*-ethoxycarbonyl-2-aminoethanol (**4**: R=Et)[†] (24% yield) and a small quantity of the starting material **1** (Scheme 2).

Formation of **3a** from **1** can be best explained in terms of a nucleophilic attack of benzenethiolate anion on the 5-position of **1**[7] followed by an elimination of carbon dioxide. A partial anion exchange between sodium benzenethiolate and EtOH used as a solvent might occur under the reaction conditions, and hence the resulting ethoxide anion would



Scheme 1.

Keywords: oxazolidines/oxazolidinones; sulfides; thiazines; thiols.
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† An oil; IR ($CHCl_3$) ν 3300, 1700 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.25 (t, J=7.3 Hz, 3H, CH_3), 2.48 (br s, 1H, OH), 3.34 (dt, J=5.4, 4.9 Hz, 2H, NCH_2), 3.71 (t, J=4.9 Hz, 2H, CH_2OH), 4.12 (q, J=7.3 Hz, 2H, CH_2CH_3), 5.13 (br s, 1H, NH).

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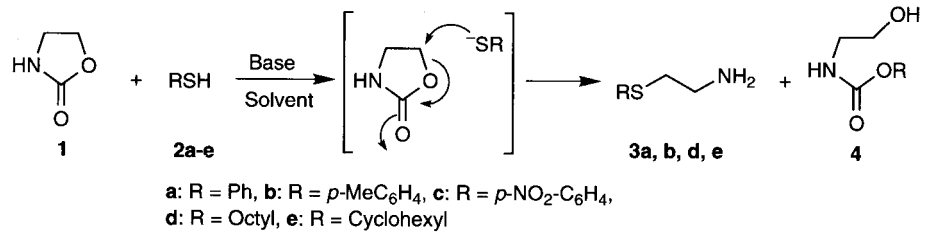
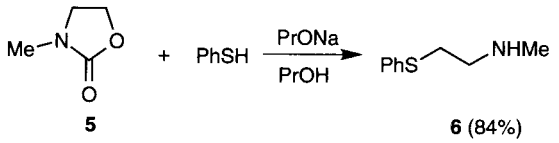


Scheme 2.

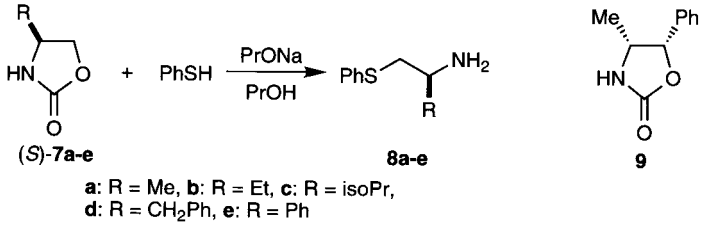
Table 1. Reaction of **1** and benzenethiol (**2a**)

Entry	Solvent	Base	**1**:**2a**:Base	Time (h)	Products, % Yield[a]	
					3a	**4**
1	EtOH	EtONa	1:1:1	24	60[b]	24 (R=Et)
2	EtOH	EtONa	1:2:1	24	73[b]	trace (R=Et)
3	EtOH	EtONa	1:3:2	24	81[b]	trace (R=Et)
4	PrOH	PrONa	1:1:1	24	74[b]	7 (R=Pr)
5	PrOH	PrONa	1:2:1	12	88	0
6	PrOH	PrONa	1:3:2	6	98	0
7	*t*-BuOH	*t*-BuOK	1:2:1	6	90	0
8	THF	NaH	1:1:1	24	56[b]	–
9	THF	NaH	1:2:1	15	74	–
10	THF	NaH	1:3:2	8	79	–
11	THF	DBU	1:3:2	24	63[b]	–

[a] Yields are based on **1**.
[b] A small quantity of **1** was detected in the crude reaction mixture but not isolated.



Scheme 3.



Scheme 4.

attack the carbonyl carbon atom of **1** to give **4** (R=Et).[‡] We therefore next examined a similar reaction with 2 equiv. of benzenethiol, whereupon the formation of **4** (R=Et) was greatly diminished and compound **3a** was obtained in 73% yield (based on **1**).

A more detailed study of the reaction of **1** with benzenethiol (**2a**) was carried out. The results are summarized in Table 1. Heating a mixture of **1**, **2a** and NaOEt in a ratio of 1:3:2 gave much higher yield (81% based on **1**) of **3a** as compared to entry 2 after 24 h of heating (entry 3). When a similar reaction was carried out in PrOH, the boiling point of which (97°C) is higher than that (78°C) of EtOH, not only was the reaction time significantly reduced (6 h) but the yield of **3a** was also improved to 98% (entry 6). Another good result was obtained by heating a 1:2:1 mixture of **1**, **2a** and *tert*-BuOK in boiling *tert*-BuOH (bp 83°C) for 6 h; these conditions gave **3a** in 90% yield (entry 7). This aminoethylation reaction could also be performed in an aprotic solvent such as tetrahydrofuran (THF) by using sodium hydride or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base, but the yields of **3a** were relatively lower (56–79%) (entries 8–11) than those obtained using alcohol as a solvent.

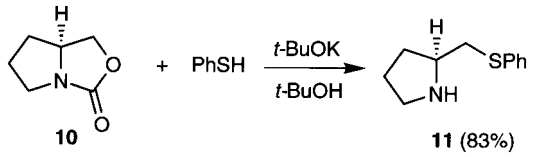
Unless otherwise stated, the following experiments were carried out by heating a 1:3:2 mixture of 2-oxazolidinones, thiols and PrONa in boiling PrOH as described above for entry 6 in Table 1.

The reaction of *p*-toluenethiol (**2b**) with **1** gave **3b** in 93% yield (Scheme 2). However, the reaction of *p*-nitrobenzenethiol (**2c**) with **1** was very sluggish, giving a complex mixture of products after prolonged heating. This is probably because the thiolate anion formed from **2c** is highly stabilized by the *p*-nitro group, thereby reducing the nucleophilicity of the anion. The aliphatic thiols such as octanethiol (**2d**) and cyclohexanethiol (**2e**) reacted smoothly with **1** to give the corresponding 2-aminoethyl sulfides **3d** and **3e** in 81 and 74% yields, respectively.

N-Methyl-2-oxazolidinone (**5**) reacted with benzenethiol much faster than did 2-oxazolidinone (**1**). The reaction was completed within 30 min (compare with that for entry 6 in Table 1) to give *N*-methyl-2-(phenylthio)ethylamine (**6**) in 84% yield (Scheme 3). It is assumed that in the case of 2-oxazolidinone (**1**), the NH proton is partially removed under basic conditions, thereby causing the electrophilicity to descend towards the benzenethiolate anion.

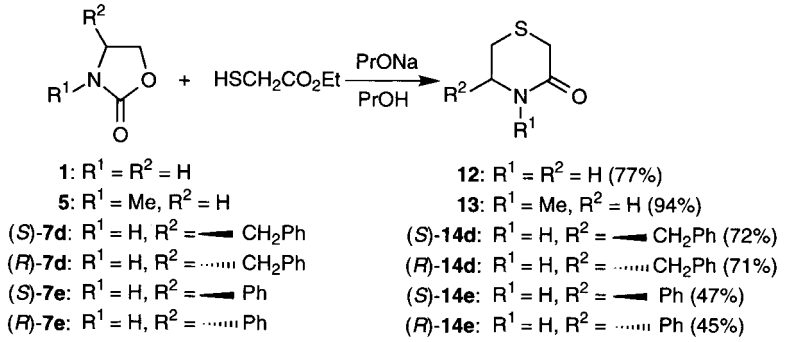
Chiral 2-aminoethyl sulfides and the corresponding thiols have frequently been used as catalysts for the enantioselective addition of organometallic reagents to carbonyl

[‡] Compound **4** (R=Et) seems to be in equilibrium with **1** under the reaction conditions. Indeed, treatment of **4** (R=Et) with EtONa (2 equiv.) in refluxing EtOH for 30 min gave a 1.3:1 mixture of **4** (R=Et) and **1**.



Scheme 5.

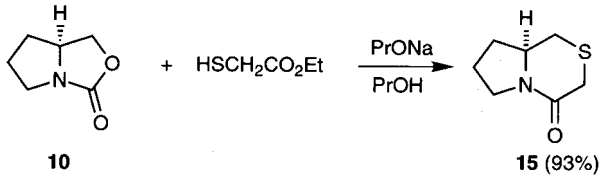
Encouraged by the success of the aminoethylation of aliphatic thiols such as **2d**,**e**, ethyl thioglycolate was treated with **1** to give 3-thiomorpholinone (**12**) in 77% yield (Scheme 6). When a similar reaction was carried out with *tert*-BuOK in boiling *tert*-BuOH, only an 18% yield of **12** was obtained. These results may be explained by assuming that the thiolate anion derived from ethyl thiogylcolate is



Scheme 6.

compounds.[1a–c,f,g] The reactions of (4*S*)-substituted 2-oxazolidinones (*S*)-**7a**–**e** with benzenethiol gave the corresponding chiral (1*S*)-substituted 2-(phenylthio)ethylamines **8a**–**e** in 78–90% yields, respectively (Scheme 4). The 4,5-disubstituted 2-oxazolidinone **9**, however, provided no desired 2-aminoethyl sulfide. This is probably because an S_N2 attack of the thiolate anion on the 5-position of **9** is prevented by the sterically more-demanding phenyl group.

The chiral bicyclic 2-oxazolidinone **10**, prepared from L-prolinol in one step,[8] was treated with benzenethiol in the presence of *tert*-BuOK in boiling *tert*-BuOH to give the expected chiral 2-aminoethyl sulfide **11** in 83% yield (Scheme 5).

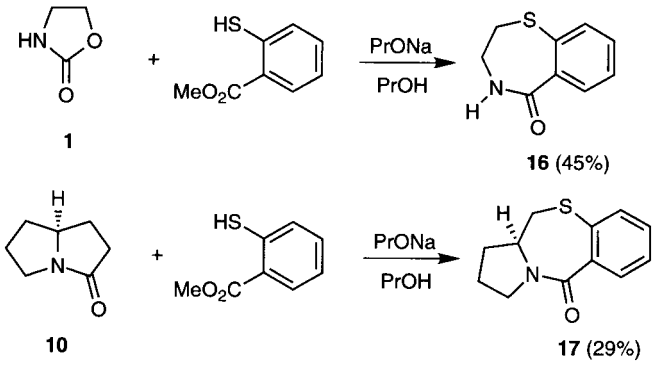


Scheme 7.

relatively stable due to the presence of an electron-attracting ethoxycarbonyl group, and hence the reaction with oxazolidinone (**1**) requires a much higher reaction temperature. The *N*-methyl congener **5** also provided *N*-methylthiomorpholinone (**13**) in 94% yield. (*S*)-4-Benzyl-2-oxazolidinone ((*S*)-**7d**) and its antipode (*R*)-**7d** afforded the optically active thiomorpholinone (*S*)-**14d** and (*R*)-**14d** in 72 and 71% yields, respectively. Similarly, (*S*)-4-phenyl-2-oxazoilidinone ((*S*)-**7e**) and (*R*)-**7e** afforded (*S*)-**14e** and (*R*)-**14e**, respectively, though their yields were relatively low (47 and 45% yields, respectively). On the other hand, the reaction of **10** with ethyl thioglycolate gave the chiral bicyclic compound **15** in 93% yield (Scheme 7).

The reaction of 2-oxazolidinone (**1**) with methyl thiosalicylate gave benzo-1,4-thiazepin-5(2*H*)-one (**16**) in 45% yield. Similarly, compound **10** reacted with methyl thiosalicylate to give chiral tricyclic compound **17** in 29% yield, along with several by-products (Scheme 8).

In summary, we have shown that 2-oxazolidinones work as latent aziridine equivalents in the reaction of thiolates to give 2-aminoethyl sulfides including chiral derivatives and sulfur-containing heterocyclic compounds. Clearly, the



Scheme 8.

present method is far superior in simplicity and yield to any thus far reported for the syntheis of 2-aminoethyl sulfides such as **3**, **6**, **8** and **11**.

3. Experimental

Melting points are uncorrected. IR spectra were recorded with a Shimadzu FTIR-8100 spectrophotometer. ^{1}H NMR spectra were measured on a JEOL JNM-EX-270 or a JEOL JNM-GSX 500 spectrometer for solutions in $CDCl_3$. δ values quoted are relative to tetramethylsilane. Optical rotations were measured with a Horiba SEPA-300 polarimeter. High-resolution mass spectra (HRMS) were obtained with a JEOL JMS-SX 102A instrument. Column chromatography was performed on silica gel 60 PF_{254} (Nacalai Tesque) under pressure.

3.1. Materials

2-Oxazolidinone (**1**), *N*-methyl-2-oxazolidinone (**5**), (*S*)-4-benzyl-2-oxazolidinone ((*S*)-**7d**), (*R*)-4-benzyl-2-oxazolidinone ((*R*)-**7d**), (*S*)-4-phenyl-2-oxazolidinone ((*S*)-**7e**), and (*R*)-4-phenyl-2-oxazolidinone ((*R*)-**7e**) were commercially available. (*S*)-4-methyl-2-oxazolidinone ((*S*)-**7a**),[9] (*S*)-4-ethyl-2-oxazolidinone ((*S*)-**7b**),[9] and (*S*)-4-isopropyl-2-oxazolidinone ((*S*)-**7c**)[9,10] were prepared according to the reported procedure. (7a*S*)-Perhydro-7*H*-pyrrolo[1,2-c]-oxazol-3-one (**10**) ($[\alpha]^{23}_D=-31.6$ (*c* 1.5, $CHCl_3$), lit.[11] $[\alpha]^{20}_D=-35.1$ (*c* 0.702, $CHCl_3$)) was prepared according to the procedure described for the preparation of the corresponding (7a*R*)-isomer.[8]

3.1.1. 2-(Phenylthio)ethylamine (3a). *General procedure.* After sodium (97 mg, 4.22 mmol) had been dissolved in PrOH (20 ml), benzenethiol (655 mg, 6.04 mmol) was added and the mixture was stirred at room temperature for 30 min. To this was added 2-oxazolidinone (**1**) (181 mg, 2.08 mmol) and the mixture was heated under reflux for 6 h. The solvent was evaporated off, water was added to the residue, and the whole mixture was extracted with Et_2O. The extract was dried ($MgSO_4$) and concentrated, and the residue was chromatographed on silica gel ($CHCl_3$–MeOH (10:1)) to give **3a**[3b] (312 mg, 98%) as an oil: IR ($CHCl_3$) ν 3360, 3290 cm^{-1}; ^{1}H NMR (270 MHz) δ 2.50 (brs, 2H), 2.93 (t, *J*=5.6 Hz, 2H), 3.04 (t, *J*=5.6 Hz, 2H), 7.15–7.40 (m, 5H). Using a procedure similar to that described for the preparation of **3a**, the following compounds were obtained.

3.1.2. 2-(4-Methylphenylthio)ethylamine (3b). Yield 93%; an oil; IR ($CHCl_3$) ν 3380 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.45 (s, 2H), 2.32 (s, 3H), 2.85–2.88 (m, 2H), 2.94–2.98 (m, 2H), 7.09 (d, *J*=7.8 Hz, 2H), 7.27–7.29 (m, 2H). HRMS Calcd for $C_9H_{13}NS$: 167.0769. Found: 167.0771.

3.1.3. 2-(Octylthio)ethylamine (3d).[2f] Yield 81%; an oil; IR ($CHCl_3$) ν 3400 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.88 (t, *J*=6.8 Hz, 3H), 1.27–1.33 (m, 8H), 1.37 (qn, *J*=6.8 Hz, 2H), 1.58 (qn, *J*=7.3 Hz, 2H), 2.51 (t, *J*=7.3 Hz, 2H), 2.65 (t, *J*=6.4 Hz, 2H), 2.71 (br s, 2H), 2.92 (t, *J*=6.4 Hz, 2H).

3.1.4. 2-(Cyclohexylthio)ethylamine (3e).[2d] Yield 74%; an oil; IR ($CHCl_3$) ν 3380 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.20–1.37 (m, 5H), 1.59–1.63 (m, 1H), 1.75–1.78 (m, 2H), 1.80–1.99 (m, 2H), 2.45 (brs, 2H), 2.61–2.68 (m, 1H), 2.67 (t, *J*=6.4 Hz, 2H), 2.90 (t, *J*=6.4 Hz, 2H).

3.1.5. *N*-Methyl-2-(phenylthio)ethylamine (6).[3b] Yield 84%; an oil; ^{1}H NMR (270 MHz) δ 2.39 (br s, 3H), 2.75–2.88 (m, 2H), 3.01–3.14 (m, 2H), 3.30 (s, 1H), 7.12–7.55 (m, 5H).

3.1.6. (*S*)-1-Methyl-2-(phenylthio)ethylamine (8a).[1m] Yield 89%; an oil; IR ($CHCl_3$) ν 3370 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.17 (d, *J*=6.3 Hz, 3H), 1.79 (brs, 2H), 2.70–2.81 (m, 1H), 3.00–3.14 (m, 2H), 7.15–7.39 (m, 5H); $[\alpha]^{24}_D=+52.6$ (*c* 2.0, $CHCl_3$) [lit.[1m] $[\alpha]^{26}_D=+42.7$ (*c* 1.01, $CHCl_3$)]; HRMS Calcd for $C_9H_{13}NS$: 167.0769. Found: 167.0770.

3.1.7. (*S*)-1-(Phenylthiomethyl)propylamine (8b). Yield 80%; colorless oil; IR ($CHCl_3$) ν 3370 cm^{-1}; ^{1}H NMR (270 MHz) δ 0.95 (t, *J*=7.3 Hz, 3H), 1.36–1.56 (m, 2H), 1.80 (brs, 2H), 2.74 (dd, *J*=12.5 and 8.6 Hz, 1H), 2.78–2.89 (m 1H), 3.13 (dd, *J*=12.5 and 3.3 Hz, 1H), 7.15–7.38 (m, 5H); $[\alpha]^{24}_D=+61.8$ (*c* 1.7, $CHCl_3$); HRMS Calcd for $C_{10}H_{15}NS$: 181.0925. Found: 181.0930.

3.1.8. (*S*)-2-Methyl-1-(phenylthiomethyl)propylamine (8c). Yield 78%; an oil; IR ($CHCl_3$) ν 3465 cm^{-1}; ^{1}H NMR (270 MHz) δ 0.92 (d, *J*=6.6 Hz, 3H), 0.94 (d, *J*=6.6 Hz, 3H), 1.61–1.70 (m, 1H), 1.65 (brs, 2H), 2.66–2.77 (m, 2H), 3.12–3.23 (m 1H), 7.19–7.37 (m, 5H); $[\alpha]^{27}_D=+93.6$ (*c* 0.4, $CHCl_3$); Anal. Calcd for $C_{11}H_{17}NS$: C, 67.63; H, 8.77; N, 7.17. Found: C, 67.34; H, 8.84; N, 6.87.

3.1.9. (*S*)-2-Phenyl-1-(phenylthiomethyl)ethylamine (8d).[3d] Yield 90%; an oil; IR ($CHCl_3$) ν 3360 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.52 (brs, 2H), 2.66 (dd, *J*=13.2 and 7.9 Hz, 1H), 2.80 (dd, *J*=13.2 and 7.5 Hz, 1H), 2.88 (dd, *J*=16.5 and 4.4 Hz, 1H), 3.09–3.24 (m 2H), 7.15–7.33 (m, 10H); $[\alpha]^{24}_D=+43.7$ (*c* 1.00, $CHCl_3$); HRMS Calcd for $C_{15}H_{17}NS$: 243.1081. Found: 243.1080.

3.1.10. (*S*)-1-Phenyl-2-(phenylthio)ethylamine (8e). Yield 89%; colorless crystals; mp: 69–70°C; IR ($CHCl_3$) ν 3370 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.76 (brs, 2H), 3.02 (dd, *J*=13.9 and 9.6 Hz, 1H), 3.30 (dd, *J*=13.9 and 4.0 Hz, 1H), 4.10 (dd, *J*=9.5 and 4.0 Hz, 1H), 7.18–7.41 (m, 10H); $[\alpha]^{24}_D=-24.2$ (*c* 1.00, $CHCl_3$); HRMS Calcd for $C_{14}H_{15}NS$: 229.0925. Found: 229.0924.

3.1.11. (*S*)-(+)-2-[(Phenylthio)methyl]pyrrolidine (11).[1c,3c] Yield 83%; an oil; IR ($CHCl_3$) ν 3345 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.42–2.02 (m, 4H), 2.84–3.09 (m, 4H), 3.03 (s, 1H), 3.25–3.35 (m, 1H), 7.11–7.39 (m, 5H); $[\alpha]^{26}_D=+16.8$ (*c* 1.12, $CHCl_3$) (lit.[1c] $[\alpha]^{20}_D=+16.8$ (*c* 0.56, $CHCl_3$), lit.[3e] $[\alpha]^{20}_D=+20$ (*c* 0.56, $CHCl_3$)).

3.1.12. 3-Thiomorpholinone (12).[3a] Yield 77%; mp: 90–91°C (lit.[3a] mp 90–91°C); IR ($CHCl_3$) ν 3405, 1665 cm^{-1}; ^{1}H NMR (500 MHz) δ 2.80–2.84 (m, 2H), 3.31 (s, 2H), 3.61–3.65 (m, 2H), 6.59 (brs, 1H).

3.1.13. 4-Methyl-3-thiomorpholinone (13).[3a] Yield 94%; an oil; IR ($CHCl_3$) ν 1650 cm^{-1}; ^1H NMR (500 MHz) δ 2.85–2.88 (m, 2H), 3.01 (s, 3H), 3.32 (s, 2H), 3.60–3.63 (m, 2H).

3.1.14. (5*S*)-5-Benzyl-3-thiomorpholinone [(*S*)-14d]. Yield 72%; mp: 126–127.5°C; IR ($CHCl_3$) ν 3400, 1655 cm^{-1}; ^1H NMR (270 MHz) δ 2.61 (dd, J=13.5 and 8.3 Hz, 1H), 2.73–2.88 (m, 2H), 2.96 (dd, J=13.5 and 5.9 Hz, 1H), 3.25 (dd, J=16.8 and 1.3 Hz, 1H), 3.35 (d, J=17.2 Hz, 1H), 3.91 (dddd, J=8.3, 5.9, 3.1 and 1.3 Hz, 1H), 5.94 (brs, 1H), 7.15–7.40 (m, 5H); $[\alpha]^{22}_D$=−43.1 (c 0.5, $CHCl_3$); Anal. Calcd for $C_{11}H_{13}NOS$: C, 63.73; H, 6.32; N, 6.76. Found: C, 63.79; H, 6.31; N, 6.73.

3.1.15. (5*R*)-Benzyl-3-thiomorpholinone [(*R*)-14d]. Yield 71%; mp: 126–128°C; $[\alpha]^{21}_D$=+44.6 (c 0.5, $CHCl_3$); Anal. Calcd for $C_{11}H_{13}NOS$: C, 63.73; H, 6.32; N, 6.76. Found: C, 63.56; H, 6.24; N, 6.60.

3.1.16. (5*S*)-Phenyl-3-thiomorpholinone [(*S*)-14e]. Yield 47%; mp: 137–138°C; IR ($CHCl_3$) ν 3385, 1655 cm^{-1}; ^1H NMR (270 MHz) δ 2.81 (dd, J=13.7 and 9.8 Hz, 1H), 2.92 (ddq, J=13.7, 3.9 and 1.0 Hz, 1H), 3.33 (dd, J=17.1 and 1.5 Hz, 1H), 3.49 (d, J=17.1 Hz, 1H), 4.84 (ddd, J=9.0, 3.2, and 1.5 Hz, 1H), 6.02 (brs, 1H), 7.30–7.40 (m, 5H); $[\alpha]^{23}_D$=+168.5 (c 0.5, $CHCl_3$); Anal. Calcd for $C_{10}H_{11}NOS$: C, 62.15; H, 5.74; N, 7.25. Found: C, 62.15; H, 5.67; N, 7.19.

3.1.17. (5*R*)-5-Phenyl-3-thiomorpholinone [(*R*)-14e]. Yield 45%; mp: 136.5–137°C; $[\alpha]^{23}_D$=−176.5 (c 0.5, $CHCl_3$); Anal. Calcd for $C_{10}H_{11}NOS$: C, 62.15; H, 5.74; N, 7.25. Found: C, 62.22; H, 5.69; N, 7.14.

3.1.18. (6*S*)-1-Aza-4-thiabicyclo[4.3.0]nonan-2-one (15). Yield 93%; an oil; IR ($CHCl_3$) ν 1620 cm^{-1}; ^1H NMR (270 MHz) δ 1.54–2.27 (m, 4H), 2.57 (dd, J=12.5 and 11.5 Hz, 1H), 2.89 (dd, J=12.5 and 3.0 Hz, 1H), 3.28 (d, J=16.1 Hz, 1H), 3.38 (d, J=16.5 Hz, 1H), 3.52–3.58 (m, 2H), 3.75–3.85 (m, 1H); $[\alpha]^{23}_D$=+38.7 (c 1.25, $CHCl_3$); HRMS Calcd for $C_7H_{11}NOS$: 157.0561. Found: 157.0564.

3.1.19. 1,4-Benzothiazepin-5(2*H*)-one (16).[12] Yield 45%; mp: 194–195°C (lit.[12] mp 191–191.5°C); IR ($CHCl_3$) ν 3420, 1655 cm^{-1}; ^1H NMR (270 MHz) δ 3.14–3.20 (m, 2H), 3.33–3.44 (m, 2H), 7.27 (brs, 1H), 7.35–7.75 (m, 4H).

3.1.20. (11a*S*)-2,3,11,11a-Tetrahydro-5-oxo-1*H*,5*H*-pyrrolo-[2,1-*c*][1,4]benzothiazepine (17).[13] Yield 29%; an oil; IR ($CHCl_3$) ν 1630 cm^{-1}; ^1H NMR (270 MHz) δ 1.80–2.16 (m, 4H), 2.88 (t, J=11.9 Hz, 1H), 3.31 (dd, J=11.9 and 4.6 Hz, 1H), 3.59–3.76 (m, 2H), 3.81–3.90 (m, 1H), 7.21–7.73 (m, 4H); $[\alpha]^{24}_D$=+508.8 (c 1.0, $CHCl_3$) (lit.[13] $[\alpha]^{23}_D$=+502 (c 1.0, $CHCl_3$)).

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