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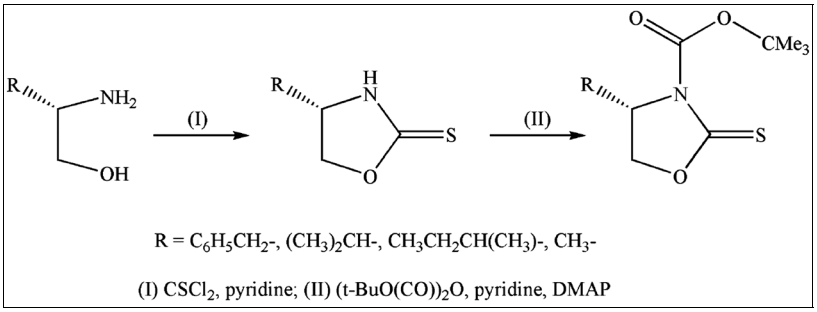

Oxazolidinethione compounds were synthesized starting from racemic and enantiopure β-amino alcohols. The molecular structure of oxazolidinethione **6a** was elucidated by single-crystal x-ray crystallography. Oxazolidinethione compounds screened for antimicrobial activity showed mild minimum inhibitory concentration values.

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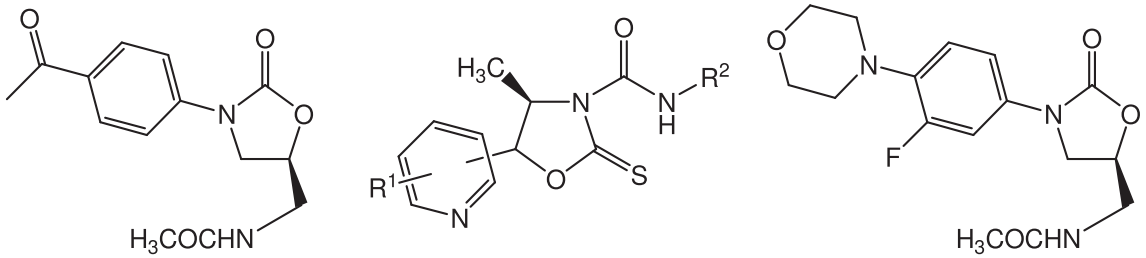
INTRODUCTION

Oxazolidinethiones have been the subject of extensive studies because of their important biological activity [1]. The chemistry of oxazolidine-2-thiones has received considerable attention because of the wide variety of biological activities exhibited by their derivatives, namely D-fructose transporter inhibitors [2], antithyroid [3,4], antifertility [5,6], inhibition of dopamine β-hydroxylase [7], antibacterial (**1**) [8,9], insecticidal, and herbicidal activities (**2**) [10].

oxazolidinthiones are the sulfur analogs of oxazolidinones, and the syntheses of their new derivatives are very important in biological activity studies.

The increasing availability of enantiopure *vic*-aminoalcohols has stimulated interest in developing chemistry, which makes use of oxazolidinone/oxazolidinthiones [13,14]. Oxazolidinethiones have been used synthetically in other ways, primarily as chiral auxiliaries [15–17], but also as intermediates in the synthesis of enantiopure protected aryl-β-hydroxyl-α-amino acids [18] and 1-(*Boc*)-amino-1-alkenyl-



In addition, oxazolidinones are a new class of totally synthetic antibacterial compounds. These compounds have been known to inhibit translation at the initiation phase of protein synthesis [11]. Linezolid (**3**) is a member of oxazolidinones and is totally synthetic compound. Unlike oxazolidinones, the thio-analogs of linezolid did not inhibit the growth of Gram positive bacteria [12]. In general, phosphonate esters [19], as a derivative for kinetic resolutions [20], as pseudo-C-nucleosides [21], in radical reactions [22], and as precursors for other oxazolidines [23]. Carbon disulfide [24], thiophosgene [21,25], or bis (imidazolyl)thione [22,23] have been used to prepare them from the corresponding amino alcohols, as well as hydroxide addition to isothiocyanates [21] and cycloaddition

of aldehydes to anions of substituted methyl isothiocyanates [18,19].

Cyclic thionocarbonates and cyclic sulfate esters are five membered similar heterocycles with oxazolidinethiones and their synthesis and reactions have been investigated in the literature [25,26].

RESULTS AND DISCUSSION

β-Amino alcohols **4(a–e)** were converted to their corresponding oxazolidinethiones **5(a–e)** by treatment with thiophosgene and triethylamine in dichloromethane at 0°C. Their ^{13}C NMR spectra showed a C═S resonance at δ: 189.0, 5-C resonance at δ: 73.5–76.9, and 4-C resonance at δ: 52.5–62.4 for the other two ring carbons. N-*t-boc* derivatives **6(a–e)** were obtained via the reactions of oxazolidinethiones **5(a–e)** with triethylamine, di-*tert*-butyl dicarbonate and DMAP in dichloromethane. Here, the electron withdrawing N-*t-boc* protection was carried out to investigate the ring opening capacity of this heterocyclic ring system with nucleophiles (Figure 1).

In order to understand more about these heterocyclic systems, the molecular structures of **6a** was measured by single crystal x-ray diffraction.

X-ray diffraction structure analysis. To determine the crystal structure of the **6a** compound, x-ray diffraction data were collected at MoK_α radiation at room temperature on an CAD4 diffractometer (Enraf-Nonius, Delft, The Netherlands) operating in ω/2θ scan mode. The lattice parameters and their estimated standard deviations were determined from a least-squares refinement of 20 centered reflections in the range of $8.39 \leq \theta \leq 18.34°$ by using CAD4 Express [27]. Data reduction was carried out using XCAD4 [28]. The structure was solved by direct method and refined by full matrix least-square technique using the programs SHELXS97 and SHELXL97 [29], respectively.

For all non-hydrogen atoms, anisotropic displacement parameters were refined and H atoms on the C2 and C4 atoms were located in a difference Fourier map and refined isotropically. Other hydrogen atoms were placed geometrically, and a riding model was used with Uiso(H) = 1.2 Ueq (C) and Uiso(H) = 1.5 Ueq(CH3). The ORTEP [30] drawing of the molecule is shown in Figure 2. The data collection details, crystal data, and refinement parameters are summarized in Table 1. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. Selected bond lengths and angles are given in Table 3. Hydrogen bond and molecular packing geometry of the title molecule were calculated with PLATON [31], and hydrogen bonding geometry is summarized in Table 4.

From the structure of **6a** compound, the heterocyclic ring is in a twist-boat conformation, it twisted on C2–C3 bond (Fig. 3); S1 and C5 atoms of the substituents are equatorial, whereas C4 atom is axial. The bonding at the nitrogen atom is planar. The ring bond from nitrogen to the thiocarbonyl group (N1–C1: 1.355(6) Å) is *longer* than the ring bond from oxygen to the thiocarbonyl group (O1–C1: 1.342(6) Å). Because of the electron withdrawing *tert*-boc group, there is a less electron delocalization from the ring nitrogen atom into the thione bond (C═S), an increase in the electron delocalization from oxygen into the thiocarbonyl group, and there is a marginal lengthening of the sp^3C–O bond (O1–C3: 1.450 (6) Å).

From the structure of **6a**, it appears that acylation of the nitrogen atom has had the desired effect of increasing the interaction of the thiocarbonyl group with the ring oxygen atom, and thus improving the leaving group characteristic of this oxygen at 5-C of the ring system. Some preliminary investigations have been made with sulfur nucleophiles on the reactions of cyclic thionocarbamate **6d**, and some successful ring opening reactions were observed by breaking of C–O bond of the heterocycle, and this work was published before [32].

Antimicrobial activity studies [33,34]. Antifungal and antibacterial activities of five new oxazolidinethione compounds were tested by microdilution broth method recommended by National Committee for Clinical Laboratory Standards [33,34]. According to these procedure, antibacterial

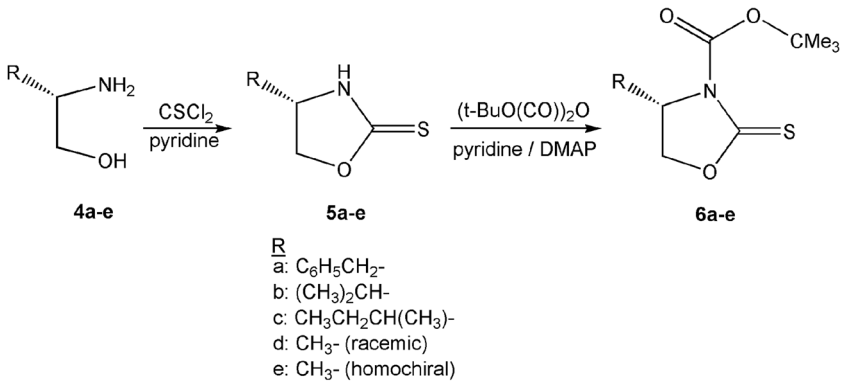


Figure 1. The synthesis of oxazolidine-2-thiones and their *N-t*-boc derivatives.

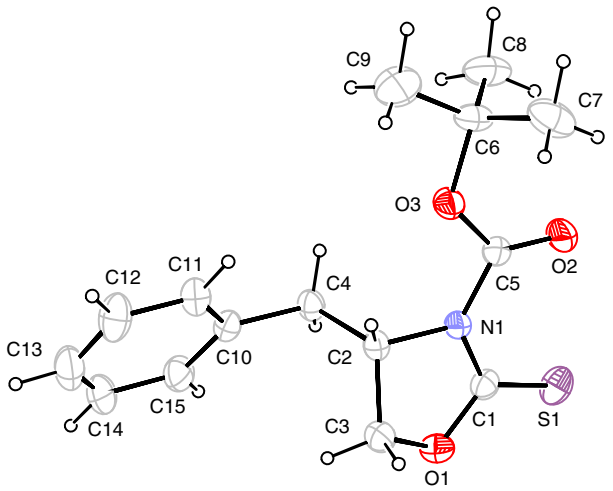


Figure 2. The molecular structure of the compound **6a** with the atomic numbering scheme. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 1

Crystal data and results of structure refinement for **6a**.

Formula	C15 H19 N O3 S
Formula weight [g/mol]	293.37
Temperature [K]	295(2)
Wavelength [Å]	0.71073
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions: [Å, °]	$a = 8.5151(16)$, $b = 11.594(2)$, $c = 16.175(2)$
Cell volume [Å^3]	1596.9(5)
Z	4
Calculated density [g/cm^3]	1.22
Crystal color/shape/size [mm]	Colorless/prism/ $0.400 \times 0.175 \times 0.15$
$F(000)$	624
Absorption coefficient [mm^{-1}]	0.209
Absorption correction type	psi-scan
T_{max}/T_{min}	0.966/0.762
θ-range for data collection [°]	2.16–23.53
Limiting indices	$-9 \le h \le 0$, $0 \le k \le 13$, $-18 \le l \le 0$
Reflections collected/ unique	1377/848
Refinement method	Full-matrix least-squares on F^2
Parameters	194
Goodness-of-fit on F^2	1.099
Final R indices [I > 2σ(I)]	$R_1 = 0.0473$, $wR_2 = 0.1046$
Largest diff. peak and hole [e/Å^3]	0.236, −0.211

Additional material available from Cambridge Crystallographic Data Center as deposition No: CCDC 892838 comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

activity was determined against the following micro-organisms: *Staphylococcus aureus* (ATCC 29213), *Enterococcus faecalis* (ATCC 29212), *Escherichia coli* (ATCC 25922), and

Table 2

Atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms.

$$U_{eq} = \left(1/3\right)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$$

Atom	x	y	Z	U_{eq} (Å^2)
S1	0.1914(2)	0.62993(16)	0.61162(11)	0.0839(6)
O3	0.2704(5)	0.7536(3)	0.3498(2)	0.0690(13)
O2	0.2581(7)	0.5953(3)	0.4284(2)	0.0931(16)
O1	0.2658(5)	0.8458(4)	0.6114(2)	0.0747(12)
N1	0.2604(5)	0.7755(3)	0.4850(3)	0.0523(12)
C1	0.2417(7)	0.7503(5)	0.5662(3)	0.0605(16)
C2	0.2737(7)	0.9025(4)	0.4728(4)	0.0556(16)
C3	0.3253(8)	0.9366(5)	0.5582(4)	0.0708(18)
C4	0.1121(8)	0.9516(5)	0.4472(5)	0.0584(17)
C5	0.2632(7)	0.6979(5)	0.4198(3)	0.0594(16)
C6	0.2758(8)	0.6957(6)	0.2687(4)	0.0741(19)
C7	0.4166(9)	0.6200(7)	0.2635(5)	0.111(3)
C8	0.1258(9)	0.6250(7)	0.2583(4)	0.110(3)
C9	0.2817(13)	0.7941(7)	0.2097(4)	0.147(4)
C10	0.1237(7)	1.0810(5)	0.4347(4)	0.0577(16)
C11	0.2073(7)	1.1271(5)	0.3716(4)	0.0696(16)
C12	0.2196(9)	1.2461(6)	0.3616(5)	0.098(3)
C13	0.1450(10)	1.3168(6)	0.4161(6)	0.098(3)
C14	0.0582(11)	1.2726(7)	0.4785(5)	0.104(3)
C15	0.0465(9)	1.1543(6)	0.4881(4)	0.082(2)

Table 3

Selected bond lengths (Å) and bond angles (°).

S1–C1	1.634(6)	C1–O1–C3	109.3(4)
O1–C1	1.342(6)	C1–N1–C2	110.5(4)
O1–C3	1.450(6)	C1–N1–C5	126.9(5)
O2–C5	1.199(6)	C2–N1–C5	122.6(5)
N1–C1	1.355(6)	N1–C1–S1	130.6(4)
N1–C2	1.490(7)	O1–C1–N1	109.3(4)
N1–C5	1.387(7)	S1–C1–O1	120.0(4)
C2–C3	1.503(7)	N1–C2–C3	99.2(4)
C2–C4	1.545(8)	N1–C2–C4	109.4(5)
		C5–O3–C6	123.2(4)
		C3–C2–C4	114.2(6)
		O1–C3–C2	104.6(5)

Table 4

Details of the hydrogen bonding geometry of compound **6a**.

D–H···A	D–H (Å)	A···H (Å)	D···A (Å)	D–H···A (°)
C4–H4B···O3	0.94(5)	2.58(5)	3.093(8)	115(4)
C7–H7A···O2	0.96	2.45	3.003(9)	116
C8–H8A···O2	0.96	2.45	2.993(8)	116
C13–H13···O2i	0.93	2.49	3.375(8)	159

Symmetry codes [i: $x,1+y,z$].
D, donor; A, acceptor; H, hydroge.

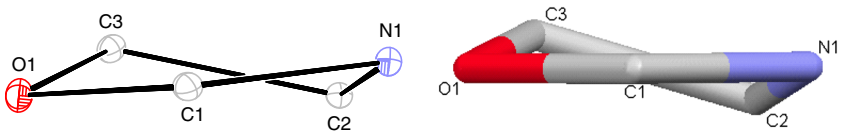


Figure 3. Twist-boat conformation of heterocyclic ring for the **6a** compound. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 5

Antifungal and antibacterial activities of the oxazolidinethione compounds (MIC in μg/mL).

Compound	*Staphylococcus aureus* ATCC 29213	*Pseudomonas aeruginosa* ATCC 27853	*Escherichiacoli* ATCC 25922	*Enterococcusfaecalis* ATCC 29212	*Candidaalbicans* ATCC 90028	*Candida parapsilosis* ATCC 90018
5a	512	256	512	256	128	128
5c	256	256	512	256	256	256
6a	1024	512	512	256	128	128
6b	512	256	512	256	256	128
Ciprofloxacin	0.25–	0.25–	<0.0625–	0.25–	–0.25	–1
Fluconazole						

MIC, minimum inhibitory concentration.

Pseudomonas aeruginosa (ATCC 27853). The following yeast-like fungi were used for antifungal activity studies: *Candida albicans* (ATCC 90028) and *Candida parapsilosis* (ATCC 90018).

The reference compounds were dissolved in DMSO. The stock solutions of the synthesized compounds were prepared in sterile distilled water. Test was performed in Mueller Hinton Broth (BBL, MD, USA) for bacteria. Fungi were cultivated in Sabouraud Dextrose Agar (Merck, KGaA, Darmstadt, Germany). RPMI-1640 medium (ICN-Flow, Aurora, OH, USA) with L-glutamin buffered with 3-(N-morpholino)propanesulphonic acid (Buffer-ICN-Flow) at pH = 7.4 was used as the test medium. The final inoculum densities were 5×10^5 cfu/mL for bacteria and $0.5–2.5 \times 10^3$ cfu/mL for fungi. The dilutions in the test medium were prepared in the wells of the microtiter plates at the required concentration of 1024–1.0 μg/mL, and for reference compounds at 64–0.0625 μg/mL. Fluconazole and ciprofloxacin were used as the reference compounds for fungi and bacteria, respectively. The microtiter plates were incubated for 18–24 h at 35°C.

The results were expressed as minimum inhibitory concentration (MIC) values. MIC was defined as the lowest concentration of the compound that inhibited visible growth of the micro-organisms. It was established that dilution of DMSO lacked antimicrobial activity against any of the test micro-organisms. The MIC values of the compounds are presented in the Table 5.

EXPERIMENTAL

All reagents were of commercial quality, and reagent quality solvents were used without further purification. Optical rotations were measured on a Rudolph Research Analytical Autopol IV automatic polarimeter; $[\alpha]_D$-values are given in units of 10^{-1} deg $cm^2\,g^{-1}$. IR spectra (KBr) were recorded on a Shimadzu FTIR DR-8001 FT infrared spectrophotometer. NMR spectra were recorded on a Bruker DPX-400 MHz FT-NMR for ^1H and 100 MHz for ^{13}C, with the chemical shifts (δ) reported in parts per million (ppm) relative to TMS, and the coupling constants (J) quoted in Hertz. $CDCl_3$ was used as a solvent and an internal standard. Mass spectra were obtained on an Agilent 5973 Network Mass Selective Detector via HPP7-M Direct Insertion Probe. The purity of the compounds was assessed by TLC on silica gel 60 F_{254}. Column chromatography was conducted on silica gel 60 (mesh size 0.063–0.200 mm). Melting points were measured on a Thomas Hoover Capillary Melting Point Apparatus.

General synthetic method for oxazolidine-2-thiones [35]. Thiophosgene (1.0 mmol) in dichloromethane (2 mL) was added to the stirring solution of β-amino alcohol (**4**) (1.0 mmol) and triethylamine (2.5 mmol) in CH_2Cl_2 (100 mL) at 0°C. After the mixture was stirred for 30 min at 0°C, the reaction was quenched with 10% $NaHSO_4$. The organic phase was separated, washed with 1 M NH_4OH, dried over Na_2SO_4, filtered, and concentrated in vacuo. Crude material was purified with column chromatography to afford oxazolidin-2-tiyon (**5**).

General synthetic method for *N-t*-boc derivatives [36]. Triethylamine (1.0 mmol), di-*tert*-butyl dicarbonate (2.0 mmol), and 4-(dimethylamino)pyridine (1.0 mmol) was added to the stirring solution of oxazolidine-2-thione (**5**) (1.0 mmol) in methylene chloride. The solution was stirred under argon atmosphere at 25°C for 7 h. Volatilities were removed, and the residue was purified on silica gel via routine column chromatography. Elution with ethyl acetate/hexane (1:3) gave N-*tert*-butoxycarbonyl-oxazolidine-2-thiones (**6**).

(4S)-4-benzyl-1,3-oxazolidine-2-thione (5a): 4a. (0.5 g, 3.38 mmol) was used according to the general method to afford the product as yellow oil (1.1 g, 62%); R_f 0.65 (1:1 EtOAc-hexane), $[\alpha]_{589}^{23} = +52.94°$ (c 0.136, CH_3CN); ^1H-NMR ($CDCl_3$, 400 MHz) δ_H 8.28 (1H, br-s, NH), 7.19 (2H, d, J = 7.2 Hz, C_6H_5), 7.31 (3H, 2 × t, J = 7.3 Hz, C_6H_5), 4.65 (1H, t, J = 8.5 Hz, 5-H_α), 4.34

(2H, m, 5-H_β and 4-H), 2.93 (2H, m, CH_2Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 189.5 (C═S), 135.3, 129.1, 129.1, 127.4, 74.7 (5-C), 57.8 (4-C), 40.4 (CH_2Ph); IR (KBr) ν_{max} (neat/cm^{-1}) 3028, 1812, 1642, 1515, 1328; MS (EI) *m/z* 193 (M^+, 83%), 117 ($M+H^+$ – Ph, 11%), 102 (boc + H^+, 98%), 91 ($PhCH_2$, 100%). *Anal*. Calcd for $C_{10}H_{11}NOS$: C, 62.15; H, 5.74; N, 7.25. Found: C, 62.36; H, 5.97; N, 7.11%.

(4S)-4-isopropyl-1,3-oxazolidine-2-thione (5b): 4b. (1.9 g, 18.0 mmol) was used according to the general method to afford the product as yellow oil (2.2 g, 77%); R_f 0.56 (1:2 EtOAc-hexane); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ_H 9.04 (1H, br-s, NH), 4.71 (1H, t, J = 9.1 Hz, 5-H_α), 4.40 (1H, dd, J = 6.7 and 9.1 Hz, 5-H_β), 3.93 (1H, m, 4-H), 1.85 (1H, m, CH), 1.00 (3H, d, J = 6.8 Hz, CH_3), 0.95 (3H, d, J = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 189.4 (C═S), 73.5 (5-C), 62.4 (4-C), 31.8 (CH), 17.9 (2 × CH_3); IR (KBr) ν_{max} (neat/cm^{-1}) 2963, 1743, 1526, 1272, 1171; MS (EI) *m/z* 145 (M^+, 100%), 102 (M^+ – $CH(CH_3)_2$, 54%), 42 ($CH(CH_3)_2$ – H, 50%). *Anal*. Calcd for $C_6H_{11}NOS$: C, 49.62; H, 7.63; N, 9.64. Found: C, 49.41; H, 7.34; N, 9.28%.

***(4S)-4-sec*-Butyl-1,3-oxazolidine-2-thione (5c): 4c.** (1.00 g, 8.53 mmol) was used according to the general method to afford the product as white solid (0.96 g, 71%); mp 145–153°C, R_f 0.57 (1:2 EtOAc-hexane); $[\alpha]_{589}^{30} = -44.18°$ (c 0.91, MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.99 (1H, br-s, NH), 4.73 (1H, t, J = 8.4 Hz, 5-H_α), 4.18 (2H, m, 5-H_β and 4-H), 1.64 (1H, m, CH), 1.38 (2H, m, CH_2), 0.88 (3H, d, J = 4.2 Hz, CH_3), 0.86 (3H, d, J = 4.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) 189.0 (C═S), 75.8 (5-C), 55.1 (4-C), 43.5 (CH), 25.1 (CH_2), 22.8 (CH_3), 21.8 (CH_3); IR (KBr) ν_{max} (neat/cm^{-1}) 3500, 1792, 1560; MS (EI) *m/z* 159.0 (M^+, 100%), 117, 102, 57. *Anal*. Calcd for $C_7H_{13}NOS$: C, 52.79; H, 8.23; N, 8.80. Found: C, 52.44; H, 8.01; N, 8.53%.

4-Methyl-1,3-oxazolidine-2-thione (5d): 4d. (0.75 g, 10.0 mmol) was used according to the general method to afford the product as yellow solid (0.32 g, 27%); mp 77°C, R_f 0.34 (1:2 EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.63 (1H, br-s, NH), 4.79 (2H, m, 5-H_2), 4.25 (1H, m, 4-H), 1.37 (3H, d, J = 5.9 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 189.3 (C═S), 76.9 (5-C), 52.5 (4-C), 20.0 (CH_3); IR (KBr) ν_{max} (neat/cm^{-1}) 3167, 1532, 1285, 1181; MS (EI) *m/z* 117 (M^+, 100%), 102, 86, 42. *Anal*. Calcd for C_4H_7NOS: C, 41.00; H, 6.02; N, 11.95. Found: C, 41.28; H, 5.81; N, 11.74%.

(4S)-4-Methyl-1,3-oxazolidine-2-thione (5e): 4e. (1.93 g, 25.6 mmol) was used according to the general method to afford the product as yellow solid (1.09 g, 36%); mp 77°C, R_f 0.34 (1:2 EtOAc-hexane); $[\alpha]_{589}^{23} = +35.28°$ (c 0.36, MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.63 (1H, br-s, NH), 4.79 (2H, m, 5-H_2), 4.25 (1H, m, 4-H), 1.37 (3H, d, J = 5.9 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 189.3 (C═S), 76.9 (5-C), 52.5 (4-C), 20.0 (CH_3); IR (KBr) ν_{max} (neat/cm^{-1}) 3167, 1532, 1285, 1181; MS (EI) *m/z* 117 (M^+, 100%), 102, 86, 42. *Anal*. Calcd for C_4H_7NOS: C, 41.00; H, 6.02; N, 11.95. Found: C, 41.17; H, 5.76; N, 11.81%.

***(4S)-4-Benzyl-2-thioxo-oxazolidine-3-carboxylic acid tert*-butyl ester (6a): 5a.** (0.50 g, 2.59 mmol) was used according to the general method to afford the product as white solid (0.76 g, 100%) and recrystallized from hexane–dichloromethane (1:1); R_f 0.69 (1:2 EtOAc-hexane); $[\alpha]_{589}^{23} = +25.34°$ (c 0.146, MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.19 (2H, d, J = 7.2 Hz, C_6H_5), 7.31 (3H, 2 × t, J = 7.3 Hz, C_6H_5), 4.69 (1H, m, 4-H), 4.28 (2H, m, 5-H_2), 3.29 (1H, dd, J = 3.5 and 13.3 Hz, $CH_\alpha Ph$), 2.83 (1H, dd, J = 10.0 and 13.3 Hz, $CH_\beta Ph$), 1.61 (9H, s, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 184.3 (C═O), 149.2 (C═S), 135.1, 129.5, 129.3, 129.1, 128.6, 127.4 (Ph), 84.9 (CMe_3), 70.2 (5-C), 60.2 (4-C), 38.4 (CH_2Ph), 28.0 (3 × CH_3); IR (KBr) ν_{max} (neat/cm^{-1}) 2980, 1759, 1722, 1370; MS (EI) *m/z* 193 ($M+H^+$ – boc, 75%), 117 ($M+H^+$ – Ph, 8%), 102 (boc + H^+, 96%), 91 ($PhCH_2$, 100%). *Anal*. Calcd for $C_{15}H_{19}NO_3S$: C, 61.41; H, 6.53; N, 4.77. Found: C, 61.28; H, 6.35; N, 4.45%.

***(4S)-4-Isopropyl-2-thioxo-oxazolidine-3-carboxylic acid tert*-butyl ester (6b): 5b.** (0.50 g, 3.44 mmol) was used according to the general method to afford the product as yellow solid (0.457 g, 54%); R_f 0.67 (1:2 EtOAc-hexane); $[\alpha]_{589}^{23} = +34.24°$ (c 0.184, MeOH); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ_H 4.33 (3H, m, 4-H and 5-H_2), 2.23 (1H, m, CH), 1.50 (9H, s, 3 × CH_3), 0.88 (3H, d, J = 7.3 Hz, CH_3), 0.86 (3H, d, J = 7.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 183.9 (C═O), 148.5 (C═S), 83.7 (CMe_3), 66.6 (5-C), 62.6 (4-C), 29.6 ($CHMe_2$), 26.9 (3 × CH_3), 17.2 (CH_3), 14.1 (CH_3); IR (KBr) ν_{max} (neat/cm^{-1}) 3109, 1812, 1722, 1368; MS (EI) *m/z* 245 (M^+, 5%), 189 ($M+H^+$ – CMe_3, 100%), 145 ($M+H^+$ – boc, 33%), 102 ($M+H^+$ – boc – $CHMe_2$, 91%), (CMe_3, 96%). *Anal*. Calcd for $C_{11}H_{19}NO_3S$: C, 53.85; H, 7.81; N, 5.71. Found: C, 53.66; H, 7.53; N, 5.41%.

***(4S)-4-sec*-Butyl-2-thioxo-oxazolidine-3-carboxylic acid *tert*-butyl ester (6c): 5c.** (0.50 g, 3.14 mmol) was used according to the general method to afford the product as yellow oil (0.63 g, 39%); R_f 0.52 (1:2 EtOAc-hexane); $[\alpha]_{589}^{27} = +80.88°$ (c 1.36, MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 4.37 (2H, m, 5-H_2), 4.09 (1H, m, 4-H), 1.46 (1H, m, CH), 1.40 (9H, s, 3 × CH_3), 1.29 (2H, m, CH_2), 0.8 (6H, m, 2 × CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 184.5 (C═O), 149.0 (C═S), 84.3 (CMe_3), 71.5 (5-C), 58.0 (4-C), 41.4 (CH), 27.7 (3 × CH_3), 24.6 (CH_2), 23.5 ($CHCH_3$), 21.4 (CH_2CH_3); IR (KBr) ν_{max} (neat/cm^{-1}) 3337, 2979, 1770, 1689, 1524. *Anal.* Calcd for $C_{12}H_{21}NO_3S$: C, 55.57; H, 8.16; N, 5.40. Found: C, 55.23; H, 7.84; N, 5.12%.

***4-Methyl-2-thioxo-oxazolidine-3-carboxylic acid tert*-butyl ester (6d): 5d.** (1.11 g, 9.47 mmol) was used according to the general method to afford the product as yellow solid (1.98 g, 96%) and recrystallized from EtOAc; mp 98°C, R_f 0.58 (1:2 EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 4.60 (1H, m, 4-H), 4.53 (1H, t, J = 8.5 Hz, 5-H_α), 4.15 (1H, dd, J = 3.0 and 8.5 Hz, 5-H_β), 1.58 (9H, s, $C(CH_3)_3$), 1.46 (3H, d, J = 6.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 184.4 (C═O), 149.3 (C═S), 84.7 (CMe_3), 72.9 (5-C), 55.4 (4-C), 28.0 (3 × CH_3), 19.3 (CH_3); IR (KBr) ν_{max} (neat/cm^{-1}) 2986, 1759, 1356, 1252, 1157; MS (EI) *m/z* 217 (M^+), 162, 144, 118, 102, 84, 57, 41. *Anal*. calcd for $C_9H_{15}NO_3S$: C, 49.75; H, 6.96; N, 6.45. Found: C, 49.49; H, 6.66; N, 6.29%.

***(4S)-4-Methyl-2-thioxo-oxazolidine-3-carboxylic acid tert*-butyl ester (6e): 5e.** (0.50 g, 4.30 mmol) was used according to the general method to afford the product as yellow solid (0.40 g, 44%); mp 98°C, R_f 0.60 (1:2 EtOAc-hexane); $[\alpha]_{589}^{23} = +73.42°$ (c 1.2, MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 4.54 (1H, m, 4-H), 3.51 (1H, dd, J = 7.4 and 11.0, 5-H_α), 2.73 (1H, d J = 11.0 Hz, 5-H_β), 1.46 (9H, s, $C(CH_3)_3$), 1.40 (3H, d, J = 6.3 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 170.2 (C═O), 149.1 (C═S), 83.8 (CMe_3), 55.3 (5-C), 32.2 (4-C), 28.3 (3 × CH_3), 19.4 (CH_3); IR (KBr) ν_{max} (neat/cm^{-1}) 2986, 1759, 1356, 1252, 1157; MS (EI) *m/z* 217 (M^+), 162, 144, 118, 102, 84, 57, 41; *Anal.* calcd for $C_9H_{15}NO_3S$: C, 49.75; H, 6.96; N, 6.45; S, 14.76. Found: C, 50.01; H, 6.71; N, 6.36; S, 14.35%.

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