REACTIVITY RANGE OF A CHIRAL 1,3-OXAZOLIDINE-2-THIONE OBTAINED FROM VEGETABLE SOURCE THROUGH CHEMO-ENZYMATIC PROCESSING

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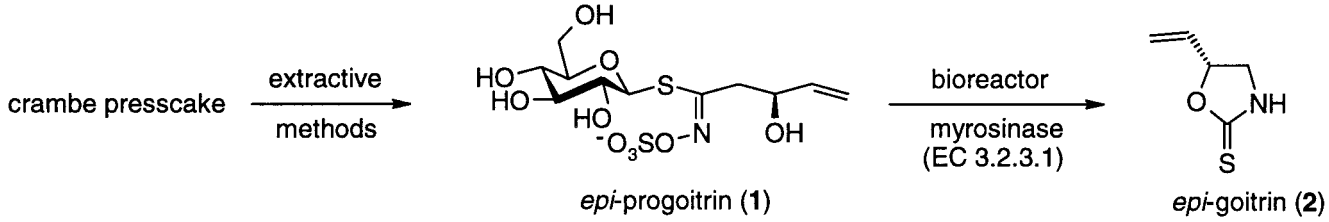
Abstract - Original chemo-enzymatic processing of *epi*-progoitrin (**1**), a glucosinolate extracted from crambe presscake, produces (5*R*)-5-vinyl-1,3-oxazolidine-2-thione (**2**) in enantiomerically pure form. The reactivity range of this chiron is investigated.

Dedicated to Prof. Teruaki Mukaiyama on the occasion of his 73rd birthday.

Crambe abyssinica is an emergent industrial crop for the production of high-erucic oil with good mechanic and thermic properties. Erucic acid derivatives have also been developed as plasticizers, lubricants and phytochemical adjuvants. Moreover, crambe oil offers the benefit of being a renewable natural product with a low environmental impact.[1]

On the other hand, the defatted meal obtained from *Crambe abyssinica* after crushing of the seeds and hexane extraction of the cake is a very good source for *epi*-progoitrin (**1**). Enantiomerically pure *epi*-goitrin ((5*R*)-5-vinyl-1,3-oxazolidine-2-thione) (**2**) can be readily produced from the preceding glucosinolate through a biotechnological process based upon myrosinase immobilization.[2,3]



epi-progoitrin (**1**) *epi*-goitrin (**2**)

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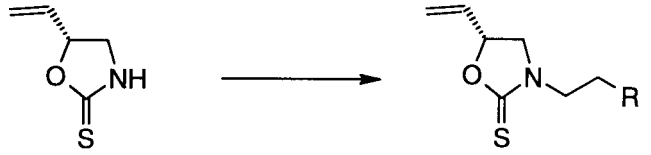
As compared with their oxo-analogues which have been largely studied as chiral auxiliaries, the use of 1,3-oxazolidine-2-thiones shows some advantages : these heterocycles have a strong UV absorption and they were shown to be more efficient in aldol-type reactions.[4,5]

With the aim to produce enantiomerically pure multipurpose fine chemicals, we have investigated the reactivity range of the heteroatomic sites of this 1,3-oxazolidine-2-thione. This heterocyclic functional family is closely connected to the thionocarbamate ambident function, which displays two electron-rich centers, differentiated according to the HSAB theory [6] : the sulfur atom shows a soft base character while the nitrogen atom possesses a hard base character.[7]

• *N*-alkylation

Epi-goitrin (**2**) can be alkylated by Michael acceptors of type CH_2=CH-EWG in order to introduce functionalized external chains. The reaction takes place in triethylamine to afford compounds (**3a-e**) with good to excellent yields.



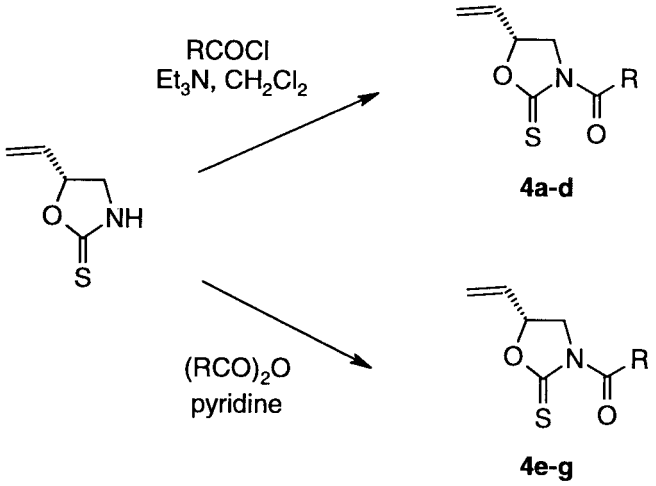
2 **3a-e**

3a	R = COMe	93 %
3b	COOMe	93 %
3c	CN	88 %
3d	SOPh	56 %
3e	SO_2Ph	85 %

Regiospecific *N*-alkylation shows to be efficient with a range of electron-withdrawing groups (COR, COOR, CN, SOR, SO_2R).

• *N*-acylation

Acyl chlorides or carboxylic anhydrides usually behave like hard electrophilic species and therefore, regiospecific *N*-acylation occurs. [8,9]



4a-d

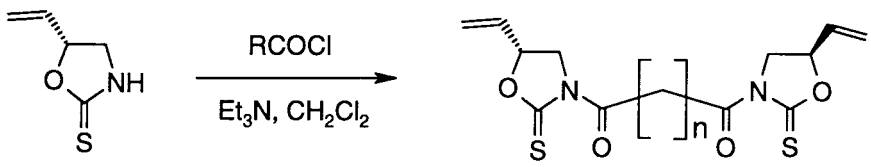
4a	R = Ph	97 %
4b	$C_{11}H_{23}$	88 %
4c	CH_3CH=CH	68 %
4d	PhCH=CH	85 %

4e-g

4e	R = Me	95 %
4f	Et	99 %
4g	OtBu	81 %

N-Acylated derivatives of **2** can be further used in asymmetric aldol additions (compounds (**4e**) and (**4f**)) or conjugate additions (compounds (**4c**) and (**4d**)).

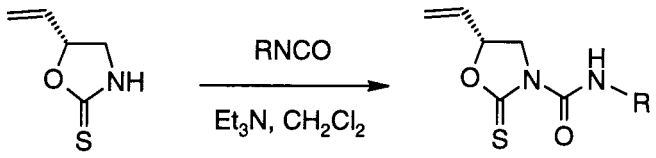
As an extension, we also describe a simple synthesis of enantiomerically pure C_2-symmetric bis-*N*-acyloxazolidinethiones which can show for instance a bolaphilic behaviour.



5a	n =	4	57 %
5b		8	91 %
5c		10	75 %

5a-c

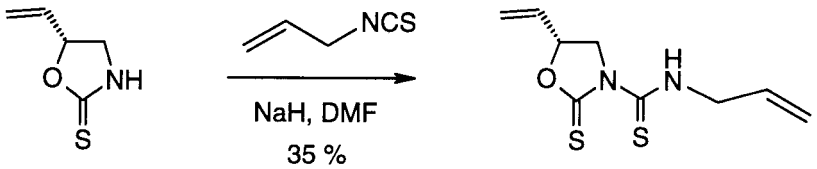
Enlarging the scope of the reaction to other acylating agents such as isocyanates has been envisaged in order to furnish complex multiheteroatom structures which constitute a new class of enantiomerically pure ureas, related to the « uron » herbicide class.



6a	R = iPr	99%
6b	Ph	66%
6c	4-Cl C_6H_4	73%
6d	3,4-diCl C_6H_3	72%
6e	4-Br C_6H_4	60%

6a-e

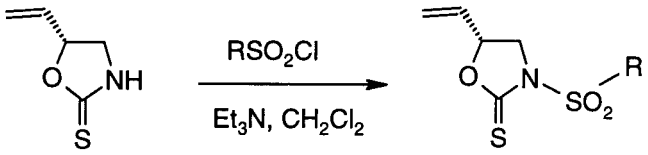
In using isothiocyanates - which are known to be less reactive than isocyanates - the reaction gives poor yields of thiourea. Moreover, sodium hydride activation of **2** is required :



7

- *N*-Sulfonylation

N-Functionalization affords complex enantiopure sulfonamido derivatives.

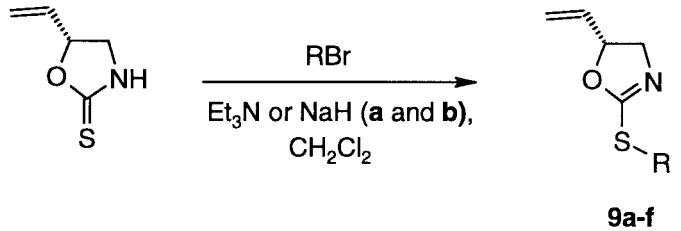


8a	R =	Ph	85 %
8b		4-Me C_6H_4	78 %
8c		4-Br C_6H_4	92 %

8a-c

- *S*-Alkylation

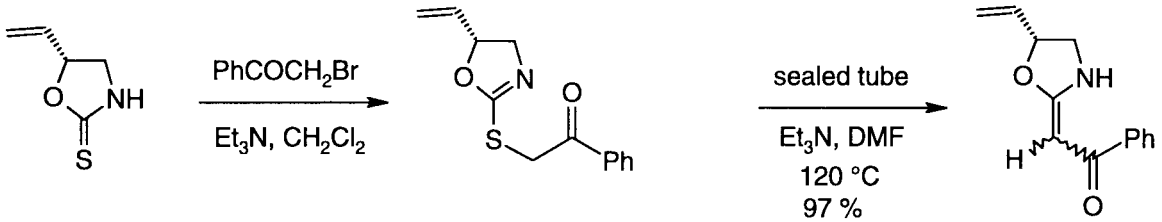
Reagents of RX type being mostly soft electrophilic species, *S*-alkylation to produce enantiomerically pure complex oxazolines is generally observed.[10]



9a-f

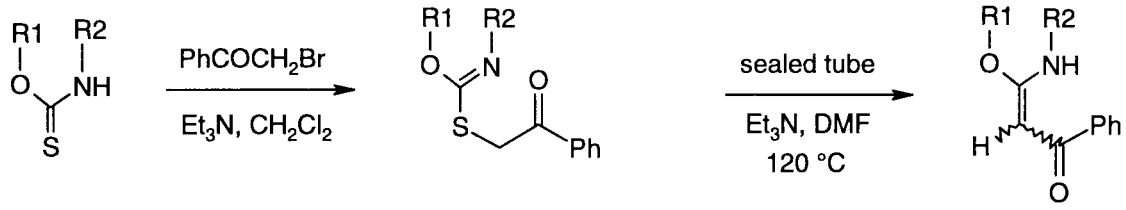
9a	$R = CH_2CH{=}CH_2$	81 %
9b	CH_2Ph	80 %
9c	CH_2COPh	74 %
9d	CH_2CN	85 %
9e	CH_2COOEt	82 %
9f	CH_2COOMe	88 %

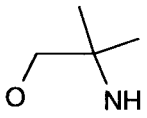
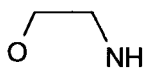
S-Alkylation has also been investigated as a prelude to an original extension of the Eschenmoser reaction.[11] This coupling reaction represents a versatile procedure to prepare vinylogous amides and urethanes by alkylation of a thiolactam with a suitable electrophilic partner, followed by sulfur extrusion.



9 c **11 d**

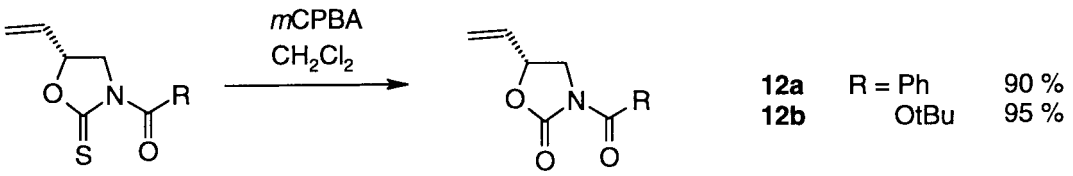
Extension of the reaction to other oxazolidine-2-thiones or even acyclic thionocarbamates was also shown to be feasible.



		10a-c	**11a-c**
a	R1 =  R2 = O NH	93 %	34 %
b	R1 =  R2 = O NH	81 %	65%
c	R1 = Et R2 = Ph	92 %	53%

- Oxidative desulfurization

A large variety of methods for the transformation of the thiocarbonyl group into the carbonyl group involving inorganic and organic reagents has been developed.[12] In our hands, protection of the nitrogen atom was required prior to oxidative desulfurization of *epi*-goitrin. This transformation was investigated so as to give access to novel enantiopure 1,3-oxazolidin-2-ones - a family of important molecules both in therapeutics[13] and in stereocontrolled synthesis.[14]



4a & 4g 12a & 12b

12a	R = Ph	90 %
12b	OtBu	95 %

As a conclusion, while exploring miscellaneous chemical modification approaches of biotechnologically produced *epi*-goitrin (**2**), we have exemplified the ambident character of the thionocarbamate function, which displays a hard basic center (NH) and a soft basic center (S). A wide range of enantiomerically pure precursors with diverse potential applications in fine chemistry (therapeutics, phytoprotection) can be prepared from readily available (*R*)-*epi*-goitrin (**2**).

EXPERIMENTAL

Melting points were determined on a Köfler hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Bruker Avance DPX250 at 250 MHz and 62.89 MHz respectively. The coupling constants (J) are reported in Hz and the chemical shifts (δ) in ppm downfield from tetramethylsilane as the internal standard. Specific rotations were measured at 20 °C using a Perkin-Elmer polarimeter 141. IR spectra were measured using a Perkin-Elmer FT Paragon 1000 PC spectrophotometer. HRMS spectra were recorded on a VG analytical 70 SV. Evaporation, *in vacuo*, was conducted with a Büchi rotary evaporator. Analytical TLC was carried out on precoated silica gel 60F-254 plates (E. Merck) and spots were detected by UV light (254 nm). Flash column chromatography was performed on Kieselgel 60 (230-400 mesh) silica gel (E. Merck).

Typical procedure for *N*-alkylation reactions :

Epi-goitrin (**2**) (0.1 g, 0.774 mmol) was dissolved in triethylamine (3 mL), methyl vinyl ketone (97 µL, 1.161 mmol) was added and the mixture was stirred under reflux for 16 h. After cooling, the reaction mixture was washed with water and extracted with dichloromethane. The organic layer was dried over magnesium sulfate and evaporated *in vacuo*. The residue was purified by flash chromatography (eluent : petroleum ether / ethyl acetate = 1/1) to provide compound (**3a**) (0.143 g, 93%) as a syrup : $[\alpha]_D^{20}$ +7° (*c* 1, $CHCl_3$) ; IR (NaCl) ν : 1614 (C=C), 1678 (CO) ; ^{1}H NMR δ : 2.10 (s, 3H, $COCH_3$), 2.86 (t, J_{vic} = 6.5 Hz, 2H, CH_2CO), 3.52 (dd, $J_{4b\text{-}5}$ = 8.0 Hz, J_{gem} = 10.0 Hz, 1H, H_{4b}), 3.70 (t, J_{vic} = 6.5 Hz, 2H, NCH_2), 3.95 (t, $J_{4a\text{-}5}$ = 10.3 Hz, 1H, H_{4a}), 5.01 (m, 1H, H_5), 5.26 (d, $J_{7cis\text{-}6}$ = 10.3 Hz, 1H, H_{7cis}), 5.35 (d, $J_{7trans\text{-}6}$ = 17.3 Hz, 1H, H_{7trans}), 5.80 (m, $J_{6\text{-}5}$ = 6.8 Hz, H_6) ; ^{13}C NMR δ : 30.5 (CH_3), 40.9 (CH_2CO), 42.9 (CH_2N), 54.8 (C_4), 79.4 (C_5), 120.6 (C_7), 133.6 (C_6), 187.3 (CS), 207.2 (CO) ; HRMS : calcd for $C_9H_{13}NO_2S$ (199.0667), found (199.0674).

Table 1. ^{1}H NMR spectral data for *N*-alkylated *epi*-goitrins (**3b-e**).

Compound	H_{4b}	H_{4a}	H_5	H_6	H_{7cis}	H_{7trans}	R
3b	dd, 3.58	t, 4.07	m, 5.15	m, 5.92	d, 5.37	d, 5.45	CH_2, t, 2H, 2.77
	J = 8.1	J = 10.0		J = 7.0	J = 10.5	J = 16.7	J = 6.4
	J = 9.8						NCH_2, m, 2H, 3.89
							OCH_3, s, 3H, 3.71
3c	dd, 3.75	t, 4.15	m, 5.23	m, 5.96	d, 5.40	d, 5.51	CH_2, t, 2H, 2.88
	J = 8.0	J = 10.0		J = 6.9	J = 10.3	J = 17.1	J = 6.7
	J = 9.9						NCH_2, m, 2H, 3.91
3d[a]	dd, 3.51	t, 4.11	m, 4.99	m, 5.75-5.96	d, 5.32	d, 5.41	CH_2, m, 2H, 2.94-3.13
	J = 8.5	J = 9.6	m, 5.13		J = 10.4	J = 16.2	NCH_2, m, 2H, 3.28-3.42
	J = 9.8						H_{4a} and NCH_2, m, 5H, 3.78-4.06
	dd, 3.68						H_{ar}, m, 2H, 7.53-7.61
	J = 7.7						
	J = 9.8						
3e	dd, 3.67	t, 4.00	m, 5.09	m, 5.88	d, 5.34	d, 5.43	CH_2, m, 2H, 3.54
	J = 8.0	J = 8.8		J = 7.0	J = 10.5	J = 17.3	NCH_2, m, 2H, 4.10
	J = 9.8						H_{ar}, m, 2H, 7.53-7.61
							H_{ar}, m, 1H, 7.63-7.70
							H_{ar}, m, 2H, 7.86-7.93

[a]: (1:1) mixture of epimeric sulfoxides

Table 2. ^{13}C NMR spectral data for *N*-alkylated *epi*-goitrins (**3b-e**).

Compound	C_2	C_4	C_5	C_6	C_7	NCH_2	CH_2	R
3b	187.6	54.4	79.3	133.6	120.7	44.1	31.7	52.4, 172.3
3c	187.6	54.0	79.4	132.7	121.0	43.9	15.6	117.9
3d[a]	188.0	54.7	79.6	133.5	121.1	42.1	53.5	124.2, 129.9, 131.7, 143.1
	187.8	55.3	79.7	133.3	120.9	41.8	53.9	
3e	187.9	54.7	79.9	133.3	121.2	41.9	53.3	128.2, 130.0, 134.7, 143.1

[a]: (1:1) mixture of epimeric sulfoxides

Typical procedures for *N*-acylation reactions :

Procedure A - *Epi*-goitrin (**2**) (0.50 g, 3.88 mmol) was dissolved in dichloromethane (10 mL), triethylamine (0.35 mL, 2.52 mmol) and benzoyl chloride (0.90 mL, 7.76 mmol) were added to the mixture which was then stirred at rt for 24 h. The reaction mixture was washed with 5 % aqueous $NaHCO_3$ and extracted with dichloromethane. The organic layer was dried over magnesium sulfate and evaporated *in vacuo*. The residue was purified by flash chromatography (eluent : petroleum ether/ethyl acetate = 8/2) to afford (**4a**) as a syrup (0.857 g, 95%) ; $[\alpha]_D^{20}$ -31° (*c* 1, $CHCl_3$) ; IR (KBr) ν : 1705 (CO) ; ^{1}H-NMR δ : 4.02 (dd, $J_{4b\text{-}5}$ = 8.1 Hz, J_{gem} = 11.1 Hz, 1H, $\mathbf{H_{4b}}$), 4.34 (t, $J_{4a\text{-}5}$ = 8.8 Hz, 1H, $\mathbf{H_{4a}}$), 5.24 (m, 1H, $\mathbf{H_5}$), 5.45 (d, $J_{7cis\text{-}6}$ = 10.2 Hz, 1H, $\mathbf{H_{7cis}}$), 5.54 (d, $J_{7trans\text{-}6}$ = 17.9 Hz, 1H, $\mathbf{H_{7trans}}$), 5.98 (m, $J_{6\text{-}5}$ = 6.6 Hz, $\mathbf{H_6}$), 7.39 (m, 1H, $\mathbf{H_{ar}}$), 7.53 (m, 2H, $\mathbf{H_{ar}}$), 7.66 (m, 2H, $\mathbf{H_{ar}}$) ; ^{13}C NMR δ : 52.0 (C_4), 80.3 (C_5), 121.8 (C_7), 128.5, 129.8, 133.0, 133.6 (C_{ar}), 133.1 (C_6), 171.3 (CO), 185.5 (CS) ; HRMS : calcd for $C_{12}H_{11}NO_2S$ (233.0510), found (233.0504).

Procedure B - *Epi*-goitrin (**2**) (0.20 g, 1.55 mmol) was dissolved in pyridine (5 mL), a large excess of acetic anhydride (2 mL) was added to the mixture which was then stirred at rt for 18 h. Pyridine was coevaporated with the help of toluene. The residue was purified by flash chromatography (eluent : petroleum ether / ethyl acetate = 7/3) to provide **4e** (0.251 g, 95%) as a syrup : $[\alpha]_D^{20}$ +24° (*c* 1, $CHCl_3$) ; IR (NaCl) ν : 1704 (CO) ; ^{1}H NMR δ : 2.78 (s, 3H, $\mathbf{CH_3}$), 3.77 (dd, $J_{4b\text{-}5}$ = 8.1 Hz, J_{gem} = 11.4 Hz, 1H, $\mathbf{H_{4b}}$), 4.25 (t, $J_{4a\text{-}5}$ = 8.5 Hz, 1H, $\mathbf{H_{4a}}$), 5.08 (m, 1H, $\mathbf{H_5}$), 5.31 (d, $J_{7cis\text{-}6}$ = 10.4 Hz, 1H, $\mathbf{H_{7cis}}$), 5.39 (d, $J_{7trans\text{-}6}$ = 17.3 Hz, 1H, $\mathbf{H_{7trans}}$), 5.82 (m, $J_{6\text{-}5}$ = 6.5 Hz, $\mathbf{H_6}$) ; ^{13}C NMR δ : 26.5 (CH_3), 52.0 (C_4), 79.6 (C_5), 121.7 (C_7), 132.7 (C_6), 171.7 (CO), 185.8 (CS) ; HRMS : calcd for $C_7H_9NO_2S$ (171.0354), found (171.0346).

Table 3. ^{1}H NMR spectral data for *N*-acylated *epi*-goitrins (**4b-g**).

Compound	H_{4b}	H_{4a}	H_5	H_6	H_{7cis}	H_{7trans}	R
4b	dd, 3.83 J = 8.1 J = 11.5	t, 4.29 J = 8.7	m, 5.08	m, 5.86 J 6.8	d, 5.34 J = 10.3	d, 5.43 J = 17.1	CH_3, t, 3H, 0.80 J = 6.8 CH_2, m, 16H, 1.12-1.19 CH_2, m, 2H, 1.60 CH_2, t, 2H, 3.19 J = 7.1
4c	dd, 3.88 J = 8.0 J = 11.5	t, 4.30 J = 8.8	m, 5.12	m, 5.89 J = 6.8	d, 5.38 J = 10.5	d, 5.45 J = 17.3	CH_3, dd, 3H, 1.92 J = 7.0, J = 1.5 CH-CH_3, m, 1H, 7.02 CH-CO, bd, 1H, 7.65 J = 15.0

4d	dd, 4.03 J = 8.1 J = 11.5	t, 4.44 J = 8.6	m, 5.20	m, 5.98 J = 8.1	d, 5.47 J = 10.3	d, 5.55 J = 17.1	H_{ar}, m, 3H, 7.42 H_{ar}, m, 2H, 7.63 CH-CO, d, 1H, 7.78 CH-Ph, d, 1H, 8.44 J = 15.7
4f	dd, 3.82 J = 8.0 J = 11.5	t, 4.28 J = 8.8	m, 5.08	m, 5.84 J = 6.8	d, 5.33 J = 11.0	d, 5.40 J = 17.0	CH_3, t, 3H, 1.07 CH_2, qd, 2H, 3.17 J = 3.0, J = 7.3
4g	dd, 3.85 J = 8.2 J = 10.7	dd, 4.27 J = 8.5	m, 5.10	m, 5.93 J = 6.7	d, 5.43 J = 10.2	d, 5.50 J = 17.0	CH_3, s, 9H, 1.57

Table 4. ^{13}C NMR spectral data for *N*-acylated *epi*-goitrins (**4b-g**).

Compound	C_2	C_4	C_5	C_6	C_7	CO	R
4b	185.5	52.0	80.3	133.1	121.8	171.3	7.4, 21.4, 32.3, 36.8, 44.6
4c	185.5	51.9	79.4	132.4	122.1	171.4	19.8, 124.4, 147.8
4d	185.7	52.3	79.9	132.7	121.8	167.1	118.7, 129.1, 129.3, 131.2, 135.0, 146.0
4f	185.3	52.1	79.4	132.9	121.4	175.3	8.8, 31.5
4g	185.0	53.2	80.0	133.6	122.3	150.5	29.1, 86.1

General procedure for the synthesis of bis-*N*-acyloxazolidine-2-thiones :

Epi-goitrin (**2**) (0.25 g, 1.94 mmol) was dissolved in dichloromethane (5 mL), triethylamine (0.30 mL, 2.13 mmol) and adipoyl chloride (0.15 mL, 1.06 mmol) were added to the mixture which was then stirred at rt for 5 h. The reaction mixture was hydrolysed by 0.5N HCl, washed with 5% aqueous $NaHCO_3$, extracted with dichloromethane then dried over magnesium sulfate. Compound (**5a**) was crystallised from MeOH (0.203 g, 57 %) as a colorless solid : mp 136-138 °C ; $[\alpha]_D^{20}$ +46° (*c* 1, $CHCl_3$) ; IR (KBr) ν : 1685 (CO), 2947 (CH_2) ; ^{1}H-NMR δ : 1.80 (m, 2H, $\mathbf{CH_2}$), 3.36 (m, 2H, $\mathbf{COCH_2}$), 3.93 (dd, $J_{4b\text{-}5}$ = 8.1 Hz, J_{gem} = 11.6 Hz, 1H, $\mathbf{H_{4b}}$), 4.25 (t, $J_{4a\text{-}5}$ = 8.7 Hz, 1H, $\mathbf{H_{4a}}$), 5.14 (m, 1H, $\mathbf{H_5}$), 5.45 (d, $J_{7cis\text{-}6}$ = 10.4 Hz, 1H, $\mathbf{H_{7cis}}$), 5.51 (d, $J_{7trans\text{-}6}$ = 17.2 Hz, 1H, $\mathbf{H_{7trans}}$), 5.93 (m, $J_{6\text{-}5}$ = 6.3 Hz, $\mathbf{H_6}$) ; ^{13}C NMR δ : 24.1 (CH_2), 37.3

($COCH_2$), 52.1(C_4), 79.4 (C_5), 121.6 (C_7), 132.8 (C_6), 174.4 (CO), 185.3 (CS) ; HRMS : calcd for $C_{16}H_{20}N_2O_4S_2$ (368.0864), found (368.0849).

Table 5. ^{1}H NMR spectral data for bis-*N*-acyloxazolidine-2-thiones (**5b-c**).

Compound	H_{4b}	H_{4a}	H_5	H_6	H_{7cis}	H_{7trans}	R
5b	dd, 3.93	t, 4.35	m, 5.15	m, 5.93	d, 5.41	d, 5.49	CH_2, m, 4H, 1.27-1.45
	J = 8.0	J = 9.0		J = 7.1	J = 10.3	J = 17.1	CH_2, m, 2H, 1.51-1.79
	J = 10.2						CH_2, t, 2H, 3.27
							J = 7.0
5c	dd, 3.94	t, 4.36	m, 5.15	m, 5.93	d, 5.42	d, 5.51	CH_2, m, 6H, 1.24-1.40
	J = 8.1	J = 8.7		J = 6.9	J = 10.3	J = 17.1	CH_2, m, 2H, 1.63-1.72
	J = 11.6						CH_2, t, 2H, 3.28
							J = 7.2

Table 6. ^{13}C NMR spectral data for bis-*N*-acyloxazolidine-2-thiones (**5b-c**).

Compound	C_2	C_4	C_5	C_6	C_7	CO	R
5b	184.7	52.1	79.4	132.8	121.6	174.9	24.8, 29.3, 29.5, 37.6
5c	185.1	52.1	79.3	132.8	121.5	174.9	24.8, 29.4, 29.7, 37.6

Typical procedure for the synthesis of *N*-substituted ureas :

Epi-goitrin (**2**) (0.25 g, 1.94 mmol) was dissolved in dichloromethane (5 mL), triethylamine (0.35 mL, 2.52 mmol) and isopropyl isocyanate (0.57 mL, 5.82 mmol) were added at 0 °C to the reaction mixture which was then stirred at rt for 24 h. Methanol was added and the mixture was hydrolysed, extracted with dichloromethane and dried over magnesium sulfate. The residue was purified by flash chromatography (eluent : petroleum ether / ethyl acetate 7/3) to afford **6a** (0.412 g, 99%) as a syrup : $[\alpha]_D^{20}$ +39° (*c* 1, $CHCl_3$) ; IR (NaCl) ν : 1543 (NH), 1702 (CO), 1972 (CH_2) ; ^{1}H NMR δ : 1.14 (d, J = 7.0 Hz, 3H, CH_3), 3.86 (m, 1H, CH), 3.87 (dd, J_{4b-5} = 8.0 Hz, J_{gem} = 11.2 Hz, 1H, H_{4b}), 4.32 (t, J_{4a-5} = 9.1 Hz, 1H, H_{4a}), 5.07 (m, 1H, H_5), 5.33 (d, J_{7cis-6} = 11.0 Hz, 1H, H_{7cis}), 5.40 (d, $J_{7trans-6}$ = 17.0 Hz, 1H, H_{7trans}), 5.84 (m, J_{6-5} = 6.8 Hz, H_6), 9.35 (s, 1H, NH) ; ^{13}C NMR δ : 22.9 (CH_3), 43.5 (CH), 51.9(C_4), 79.2 (C_5), 121.4 (C_7), 132.9 (C_6), 150.6 (CO), 185.4 (CS) ; HRMS : calcd for $C_9H_{14}N_2O_2S$ (214.0776), found (214.0785).

Table 7. ^{1}H NMR spectral data for *N*-substituted ureas (**6b-e**).

Compound	H_{4b}	H_{4a}	H_5	H_6	H_{7cis}	H_{7trans}	NH	R
6b	dd, 4.09 J = 8.1 J = 11.3	t, 4.53 J = 9.0	m, 5.22	m, 5.97 J = 6.8	d, 5.49 J = 10.3	d, 5.54 J = 17.6	11.75	H_{ar}, m, 1H, 7.16 J = 2.9, J = 6.9 H_{ar}, m, 2H, 7.36 H_{ar}, m, 2H, 7.54
6c	dd, 4.08 J = 8.0 J = 11.2	t, 4.51 J = 9.0	m, 5.23	m, 5.97 J = 6.8	d, 5.50 J = 10.3	d, 5.57 J = 18.1	11.80	H_{ar}, d, 2H, 7.31 J = 8.8 Hz H_{ar}, d, 2H, 7.49
6d	dd, 4.08 J = 7.5 J = 12.5	t, 4.52 J = 10.0	m, 5.23	m, 5.92 J 7.3	d, 5.50 J = 10.0	d, 5.56 J = 17.5	11.82	H_{ar}, m, 4H, 7.45-7.49
6e	dd, 4.07 J = 8.0 J = 11.5	t, 4.51 J = 9.0	m, 5.23	m, 5.97 J = 7.0	d, 5.50 J = 10.5	d, 5.55 J = 17.5	11.90	H_{ar}, m, 2H, 7.33-7.43 H_{ar}, d, 1H, 7.78 J = 2.3

Table 8. ^{13}C NMR spectral data for *N*-substituted ureas (**6b-e**).

Compound	C_2	C_4	C_5	C_6	C_7	CO	R
6b	184.0	50.5	77.9	131.1	120.6	147.5	119.0, 123.7, 128.1, 135.7
6c	185.4	51.9	79.2	132.9	121.4	150.6	121.6, 129.6, 130.1, 135.8
6d	185.5	51.9	79.4	136.3	122.1	148.2	117.8, 121.9, 132.5
6e	185.5	51.8	79.5	132.4	122.3	148.8	119.6, 122.0, 126.3, 131.0

(5*R*) 3-(*N*-Allyl)thiocarboxamido-5-vinyloxazolidine-2-thione (7):

Epi-goitrin (**2**) (0.25 g, 1.94 mmol) was dissolved in dichloromethane (5 mL), 60% sodium hydride (0.126 mg, 2.52 mmol) and allyl isothiocyanate (0.57 mL, 5.82 mmol) were added to the mixture and stirring at rt was maintained for 24 h. The mixture was hydrolysed, extracted with dichloromethane then dried over magnesium sulfate. Compound (**7**) was crystallised from EtOH (0.070 g, 35 %) as a colorless solid : mp 72-74 °C ; $[\alpha]_D^{20}$ +10° (*c* = *1*, $CHCl_3$) ; IR (KBr) ν : 3442 (NH), 3109 (CH_2) ; ^{1}H NMR δ : 4.29 (tt, J = 1.8 Hz, J = 5.3 Hz, 2H, $\mathbf{CH_2}$), 4.40 (dd, $J_{4b\text{-}5}$ = 8.0 Hz, J_{gem} = 11.5 Hz, 1H, $\mathbf{H_{4b}}$), 4.89 (t, $J_{4a\text{-}5}$ = 9.0 Hz, 1H, $\mathbf{H_{4a}}$), 5.14 (m, 1H, $\mathbf{H_5}$), 5.27 (dq, $J_{Z\text{-}CH}$ = 10.5 Hz, 1H, $\mathbf{H_Z}$), 5.36 (dq, $J_{E\text{-}CH}$ = 17.3 Hz, 1H, $\mathbf{H_E}$) 5.42

(d, J_{7cis-6} = 10.8 Hz, 1H, $\mathbf{H_{7cis}}$), 5.53 (d, $J_{7trans-6}$ = 18.0 Hz, 1H, $\mathbf{H_{7trans}}$), 5.87-6.01 (m, 2H, **CH** and $\mathbf{H_6}$), 11.93 (s, 1H, **NH**) ; ^{13}C NMR δ : 49.3 (CH_2), 56.9 (C_4), 79.0 (C_5), 118.4 and 122.1 ($\mathbf{C}H_2$=CH and C_7), 122.1 (C_7), 131.8 and 132.5 (**C**H=CH_2 and C_6), 178.1 and 183.3 (2 CS) ; HRMS : calcd for $C_9H_{12}N_2OS_2$ (228.0391), found (228.0400).

Typical procedure for *N*-sulfonylation reactions :

Epi-goitrin (**2**) (0.2 g, 1.548 mmol) was dissolved in dichloromethane (5 mL), triethylamine (0.28 mL, 2.02 mmol) and phenylsulfonyl chloride (0.30 mL, 2.32 mmol) were added to the mixture which was stirred at rt for 18 h. The reaction mixture was extracted with dichloromethane then dried over magnesium sulfate. The residue was purified by flash chromatography (eluent : petroleum ether / ethyl acetate = 7/3) to furnish compound (**8a**) (0.354 g, 85%) as a syrup : $[\alpha]_D^{20}$ +35° (*c* 1, $CHCl_3$) ; IR (KBr) ν : 1370 (SO_2) ; ^{1}H NMR δ : 4.00 (dd, J = 7.8 Hz, J = 9.9 Hz, 1H, $\mathbf{H_{4b}}$), 4.48 (dd, J = 8.4 Hz, 1H, $\mathbf{H_{4a}}$), 5.17 (m, 1H, $\mathbf{H_5}$), 5.43 (d, J = 10.4 Hz, 1H, $\mathbf{H_{7cis}}$), 5.43 (d, J = 17.1 Hz, 1H, $\mathbf{H_{7trans}}$), 5.85 (m, 1H, $\mathbf{H_6}$), 7.34 (m, 2H, $\mathbf{H_{ar}}$), 7.68 (tt, J = 1.4 Hz, J = 7.3 Hz, 1H, $\mathbf{H_{ar}}$), 8.06 (m, 2H, $\mathbf{H_{ar}}$) ; ^{13}C NMR δ : 53.8 (C_4), 80.2 (C_5), 122.2 (C_7), 129.5, 129.7, 135.3 and 136.3 (C_{ar}), 132.1 (C_6), 183.8 (CS) ; HRMS : calcd for $C_{11}H_{11}NO_3S_2$ (269.0180), found (269.0172).

Table 9. ^{1}H NMR spectral data for *N*-sulfonylated *epi*-goitrins (**8b-c**).

Compound	H_{4b}	H_{4a}	H_5	H_6	H_{7cis}	H_{7trans}	R
8b	dd, 4.01	t, 4.48	m, 5.16	m, 5.89	d, 5.44	d, 5.49	CH_3, s, 3H, 2.47
	J = 8.1	J = 8.3		J = 6.8	J = 10.0	J = 16.1	H_{ar}, d, 2H, 7.38
	J = 10.0						H_{ar}, d, 2H, 7.98
							J = 8.3
8c	dd, 3.99	t, 4.48	m, 5.19	m, 5.86	d, 5.41	d, 5.46	H_{ar}, d, 2H, 7.69
	J = 8.0	J = 8.2		J = 6.7	J = 10.2	J = 16.0	H_{ar}, d, 1H, 7.94
	J = 10.0						J = 8.8

Table 10. ^{13}C NMR spectral data for *N*-sulfonylated *epi*-goitrins (**8b-c**).

Compound	C_2	C_4	C_5	C_6	C_7	R
8b	183.8	53.8	80.2	132.1	122.2	129.5, 129.7, 135.3, 136.3
8c	183.6	53.7	80.3	131.9	122.4	130.8, 131.1, 132.7, 135.5

Typical procedure for *S*-alkylation reactions:

Epi-goitrin (**2**) (0.1 g, 0.774 mmol) was dissolved in acetonitrile (5 mL), 60 % sodium hydride (0.034 g, 0.851 mmol) and allyl bromide (0.08 mL, 0.929 mmol) were added to the mixture which was stirred at rt

for 3h. The reaction mixture was hydrolysed, extracted with dichloromethane and dried over magnesium sulfate. The residue was purified by flash chromatography (eluent : petroleum ether / ethyl acetate = 7/3) to furnish compound (**9a**) (0.106 g, 81%) as a syrup : $[\alpha]_D^{20}$ +34° (*c* 1, $CHCl_3$) ; IR (NaCl) ν : 1609 (C=N) ; ^{1}H NMR δ : 3.59 (dd, $J_{4b\text{-}5}$ = 7.8 Hz, J_{gem} = 13.5 Hz, 1H, $\mathbf{H_{4b}}$), 3.65 (s, 2H, $\mathbf{CH_2}$), 4.02 (t, $J_{4a\text{-}5}$ = 9.5 Hz, 1H, $\mathbf{H_{4a}}$), 5.07 (m, 1H, $\mathbf{H_5}$), 5.14 (m, $J_{E\text{-}CH2}$ = 10.0 Hz, 1H, $\mathbf{H_E}$), 5.23 (d, $J_{7cis\text{-}6}$ = 10.5 Hz, 1H, $\mathbf{H_{7cis}}$), 5.26 (d, $J_{Z\text{-}CH2}$ = 17.0 Hz, 1H, $\mathbf{H_Z}$), 5.31 (d, $J_{7trans\text{-}6}$ = 17.0 Hz, 1H, $\mathbf{H_{7trans}}$), 5.91 (m, $J_{6\text{-}5}$ = 7.0 Hz, 2H, CH and $\mathbf{H_6}$); ^{13}C NMR δ : 34.9 (CH_2), 60.6 (C_4), 82.7 (C_5), 118.4 (CH_2), 118.7 (C_7), 133.1 (CH), 136.0 (C_6), 165.2 (CS) ; HRMS : calcd for $C_8H_{11}NOS$ (169.0561), found (169.0566).

Table 11. ^{1}H NMR spectral data for *S*-alkylated *epi*-goitrins (**9b-f**).

Compound	H_{4b}	H_{4a}	H_5	H_6	H_{7cis}	H_{7trans}	R
9b	dd, 3.55 J = 7.2 J = 13.6	t, 3.98 J = 9.5	m, 5.06	m, 5.90 J = 6.9	d, 5.26 J = 10.4	d, 5.33 J = 17.9	CH_2, s, 2H, 4.26 H_{ar}, m, 5H, 7.24-7.42
9c	dd, 3.59 J = 8.1 J = 13.7	t, 4.02 J = 9.5	m, 5.07	m, 5.82 J = 7.0	5.24 J = 10.3	5.31 J = 17.4	CH_2, m, 2H, 4.62 H_{ar}, t, 2H, 7.48 J = 7.4 H_{ar}, t, 1H, 7.60 H_{ar}, d, 2H, 8.01 J = 7.6
9d	dd, 3.61 J = 7.8 J = 13.7	t, 4.04 J = 9.5	m, 5.11	m, 5.87 J = 7.1	d, 5.25 J = 10.3	d, 5.31 J = 17.1	CH_2, s, 2H, 3.76
9e	dd, 3.51 J = 7.7 J = 13.7	t, 3.94 J = 9.5	m, 5.00	m, 5.81 J = 7.0	d, 5.17 J = 10.2	d, 5.25 J = 17.2	CH_3, t, 3H, 1.21 J = 7.0 CH_2, 2d, 2H, 3.69 and 3.76 J = 16.2 CH_2, q, 2H, 4.13
9f	dd, 3.64 J = 8.6 J = 13.9	t, 4.06 J = 9.6	m, 5.04	m, 5.85 J 7.0	d, 5.21 J = 10.4	d, 5.29 J = 17.1	CH_3, s, 3H, 3.72 CH_2, 2d, 2H, 3.75 and 3.81 J = 16.6

Table 12. ^{13}C NMR spectral data for *S*-alkylated *epi*-goitrins (**9b-f**).

Compound	C_2	C_4	C_5	C_6	C_7	R
9b	165.4	60.7	82.8	136.0	118.4	36.6, 128.0, 129.4, 137.0
9c	164.9	60.6	83.3	135.8	118.6	40.8, 128.9, 129.2, 134.2, 193.4
9d	162.2	60.5	84.2	135.4	119.1	17.8, 116.4
9e	162.6	60.6	81.6	134.1	116.8	12.8, 32.7, 58.9, 167.1
9f	164.2	60.5	83.4	135.7	118.5	34.1, 59.2, 169.3

4,4-Dimethyl-2-phenacylthio-1,3-oxazoline (10a)

This compound was prepared according to the method previously described for **9a.** The residue was purified by flash chromatography (eluent : petroleum ether / ethyl acetate = 7/3) to furnish compound (**10a**) (0.887 g, 93%) as a syrup : IR (NaCl) ν : 1609 (C=N), 1693 (CO) ; ^1H NMR δ : 1.28 (s, 6H, CH_3), 4.04 (s, 2H, CH_2), 4.59 (s, 2H, H_5), 7.47 (m, 2H, H_{ar}), 7.60 (m, 1H, H_{ar}), 8.03 (m, 2H, H_{ar}) ; ^{13}C NMR δ : 26.5, (CH_3), 38.5 (CH_2), 66.4 (C_4), 79.2 (C_5), 126.8, 132.0, 133.8 (C_{ar}), 161.0 (C_2), 191.7 (CO) ; HRMS : calcd for $C_{13}H_{15}NO_2S$ (249.0823), found (249.0834).

2-Phenacylthio-1,3-oxazoline (10b)

This compound was prepared according to the method previously described for **9a.** The residue was purified by flash chromatography (eluent : petroleum ether / ethyl acetate = 6/4) to furnish compound (**10b**) (1.720 g, 80%) as a syrup : IR (NaCl) ν : 1614 (C=N), 1678 (CO) ; ^1H NMR δ : 3.88 (t, J = 9.1 Hz, 2H, H_4), 4.40 (t, 2H, H_5), 4.63 (s, 2H, CH_2), 7.49 (m, 2H, H_{ar}), 7.61 (m, 1H, H_{ar}), 8.02 (m, 2H, H_{ar}) ; ^{13}C NMR δ : 39.0 (CH_2), 53.3 (C_4), 68.3 (C_5), 127.1, 132.4, 134.0 (C_{ar}), 163.8 (C_2), 191.7 (CO) ; HRMS : calcd for $C_{11}H_{11}NO_2S$ (221.0510), found (221.0522).

Phenyl *O*-ethyl-*S*-phenacyl thiocarbimidate (10c)

This compound was prepared according to the method previously described for **9a.** The residue was purified by flash chromatography (eluent : petroleum ether / ethyl acetate = 8/2) to furnish compound (**10c**) (0.456 g, 92%) as a syrup : IR (NaCl) ν : 1597 (C=N), 1682 (CO) ; ^1H NMR δ : 1.55 (t, J = 7.0 Hz, 3H, CH_3), 4.28 (s, 2H, CH_2), 4.29 (q, 2H, CH_2), 6.90 (m, 2H, H_{ar}), 7.04 (m, 1H, H_{ar}), 7.26 (m, 2H, H_{ar}), 7.43 (m, 2H, H_{ar}), 7.55 (m, 1H, H_{ar}), 7.93 (m, 2H, H_{ar}); ^{13}C NMR δ : 15.0 (CH_3), 38.7 (CH_2CO), 66.3 (CH_2), 122.7, 124.9, 129.7, 134.6, 136.9, 148.3 (C_{ar}), 157.2 (C-O), 194.4 (CO) ; HRMS : calcd for $C_{17}H_{17}NO_2S$ (299.0980), found (299.0964).

Typical procedure for Eschenmoser reactions:

A mixture of compound (**9c**) (0.12 g, 0.485 mmol) and triethylamine (0.081 mL, 0.582 mmol) was dissolved in dimethylformamide (2 mL) in a sealed tube,. The mixture was stirred at 120 °C for 2 h. The reaction mixture was evaporated *in vacuo* and the residue was purified by flash chromatography (eluent : petroleum ether / ethyl acetate = 1/1) to furnish compound (**11d**) (0.104 g, 97%) which was crystallised as a brownish solid : mp 102-104 °C ; $[\alpha]_D^{20}$ + 66° (*c* 1, $CHCl_3$) ; IR (KBr) ν : 1631 (CO), 3259 (NH) ; ^{1}H NMR δ : 3.56 (dd, $J_{4b\text{-}5}$ = 7.6 Hz, J_{gem} = 9.6 Hz, 1H, $\mathbf{H_{4b}}$), 3.97 (dd, $J_{4a\text{-}5}$ = 8.8 Hz, 1H, $\mathbf{H_{4a}}$), 5.15 (m, 1H, $\mathbf{H_5}$), 5.40 (d, $J_{7cis\text{-}6}$ = 10.5 Hz, 1H, $\mathbf{H_{7cis}}$), 5.49 (d, $J_{7trans\text{-}6}$ = 17.1 Hz, 1H, $\mathbf{H_{7trans}}$), 5.65 (s, 1H, C**H**), 5.97 (m, $J_{6\text{-}5}$ = 7.1 Hz, 1H, $\mathbf{H_6}$), 7.38-7.45 (m, 3H, $\mathbf{H_{ar}}$), 7.84-7.88 (m, 2H, $\mathbf{H_{ar}}$) ; ^{13}C NMR δ : 48.7 (C_4), 74.6 (CH), 80.7 (C_5), 120.5 (C_7), 127.2 and 128.6 (C_{ar}), 131,0 (C_{ar}), 134.0 (C_6), 188.0 (CO) ; HRMS : calcd for $C_{13}H_{13}NO_2$ (215.0946), found (215.0953).

2-Benzoylmethylene-4,4-dimethyl-1,3-oxazolidine (11a)

This compound was prepared according to the method previously described for **11d.** The residue was purified by flash chromatography (eluent : ethyl acetate) to furnish compound (**11a**) (0.028 g, 65 %) as a syrup : IR (NaCl) ν : 1626 (CO) ; ^{1}H NMR δ : 1.35 (s, 6H, $\mathbf{CH_3}$), 4.29 (s, 2H, $\mathbf{H_5}$), 5.54 (s, 1H, C**H**), 7.38 (m, 3H, $\mathbf{H_{ar}}$), 7.82 (m, 2H, $\mathbf{H_{ar}}$), 10.00 (**NH**) ; ^{13}C NMR δ : 27.1, (CH_3), 59.9 (C_4), 74.1 (CH), 81.7 (C_5), 126.8, 128.4, 131.0, 140.2 (C_{ar}), 74.1 (C_2), 169.6 (C-O), 188.7 (CO) ; HRMS : calcd for $C_{13}H_{15}NO_2$ (217.1103), found (217.1092).

2-Benzoylmethylene-1,3-oxazolidine(11b)

This compound was prepared according to the method previously described for **11d.** The residue was purified by flash chromatography (eluent : petroleum ether / ethyl acetate = 7/3) to furnish compound (**11b**) (0.060 g, 34%) as a syrup : IR (NaCl) ν : 1623 (CO) ; ^{1}H NMR δ : 3.83 (t, J = 8.0 Hz, 2H, $\mathbf{H_4}$), 4.51 (t, 2H, $\mathbf{H_5}$), 5.64 (s, 1H, **CH**), 7.39 (m, 3H, $\mathbf{H_{ar}}$), 7.85 (m, 2H, $\mathbf{H_{ar}}$) ; ^{13}C NMR δ : 43.5 (C_4), 67.8 (C_5), 74.6 (CH), 127.3, 128.6, 131.0 (C_{ar}), 163.0 (C-O), 171.2 (CO) ; HRMS : calcd for $C_{11}H_{11}NO_2$ (189.0790), found (189.0778).

3-Ethoxy-1-phenyl-3-phenylamino prop-2-enone (11c)

This compound was prepared according to the method previously described for **11d.** The residue was purified by flash chromatography (eluent petroleum ether / ethyl acetate = 9/1) to furnish compound (**11c**) (0.047 g, 53%) as a syrup : IR (NaCl) ν : 1630 (CO) ; ^{1}H NMR δ : 1.50 (t, J = 7.0 Hz, 3H, $\mathbf{CH_3}$), 4.28 (q, 2H, $\mathbf{CH_2}$), 5.57 (s, 1H, C**H**), 7.10-7.92 (m, 10H, $\mathbf{H_{ar}}$), 13.18 (NH); ^{13}C NMR δ : 14.7 (CH_3), 65.4 (CH_2), 75.9 (CH), 122.0, 124.4, 127.2, 128.7, 129.4, 131.2, 138.0, 140.9 (C_{ar}), 166.6 (C-O), 187.8 (CO) ; HRMS : calcd for $C_{17}H_{17}NO_2$ (267.1259), found (267.1273).

Typical procedure for oxidative desulfurizations:

Compound (**4a**) (0.29 g, 1.24 mmol) was dissolved in methylene chloride (10 mL) and *m*-chloroperoxybenzoic acid (0.644 g, 3.73 mmol) was added to the mixture which was then stirred at rt for 0.5 h. The reaction mixture was hydrolysed by 5 % aqueous $NaHCO_3$, extracted with dichloromethane and dried over magnesium sulfate. After evaporation *in vacuo*, the residue was purified by flash chromatography (eluent : methylene chloride / methanol = 95/5) to furnish compound (**12a**) (0.255 g, 95%) which was recrystallised from ethanol as a white solid : mp 108-110 °C ; $[\alpha]_D^{20}$ -37° (*c* 1, $CHCl_3$) ; IR (KBr) ν : 1675 (CO), 1790 (CO), 3054 (CH_{ar}) ; ^{1}H NMR δ : 3.92 (dd, $J_{4b\text{-}5}$ = 7.4 Hz, J_{gem} = 11.0 Hz, 1H, $\mathbf{H_{4b}}$), 4.29 (t, J = 8.1 Hz, 1H, $\mathbf{H_{4a}}$), 5.13 (m, 1H, $\mathbf{H_5}$), 5.47 (d, $J_{7cis\text{-}6}$ = 9.8 Hz, 1H, $\mathbf{H_{7cis}}$), 5.56 (d, $J_{7trans\text{-}6}$ = 17.1 Hz, 1H, $\mathbf{H_{7trans}}$), 5.99 (m, $J_{6\text{-}5}$ = 6.4 Hz, 1H, $\mathbf{H_6}$), 7.41-7.48 (m, 3H, $\mathbf{H_{ar}}$), 7.53-7.60 (m, 1H, $\mathbf{H_{ar}}$), 7.65-7.69 (m, 1H, $\mathbf{H_{ar}}$) ; ^{13}C NMR δ : 49.2 (C_4), 74.9 (C_5), 120.8 (C_7), 128.3 and 129.0 (C_{ar}), 132,9 (C_{ar}), 133.5 (C_6), 153.0 and 170.2 (2 CO) ; HRMS : calcd for $C_{12}H_{11}NO_3$ (217.0739), found (217.0742).

(*5R*)-*N*-*tert*-Butoxycarbonyl-5-vinyl-1,3-oxazolidin-2-one (12b)

This compound was prepared from **4g** according to the method described for **12a**. The residue was purified by flash chromatography (eluent : petroleum ether/ethyl acetate = 6/4) to furnish compound (**12b**) (0.20 g, 85%) which was recrystallised from ethanol as a white solid : mp 102-104 °C ; $[\alpha]_D^{20}$ +16° (*c* 1, $CHCl_3$) ; IR (KBr) ν : 1706 (CO), 1823 (CO) ; ^{1}H NMR δ : 1.42 (s, 9H, CH_3), 3.54 (dd, $J_{4b\text{-}5}$ = 7.2 Hz, J_{gem} = 10.2 Hz, 1H, $\mathbf{H_{4b}}$), 4.00 (t, $J_{4a\text{-}5}$ = 8.5 Hz, 1H, $\mathbf{H_{4a}}$), 4.83 (m, 1H, $\mathbf{H_5}$), 5.26 (d, $J_{7cis\text{-}6}$ = 10.5 Hz, 1H, $\mathbf{H_{7cis}}$), 5.35 (d, $J_{7trans\text{-}6}$ = 17.0 Hz, 1H, $\mathbf{H_{7trans}}$), 5.79 (m, $J_{6\text{-}5}$ = 6.5 Hz, 1H, $\mathbf{H_6}$) ; ^{13}C NMR δ : 27.9 (CH_3), 48.6 (C_4), 73.5 (C_5), 83.9 (C_{tBu}), 119.8 (C_7), 133.5 (C_6), 155.8 and 160.2 (2 CO) ; HRMS : calcd for $C_{10}H_{15}NO_4$ (213.1001), found (213.1012).

Table 13. General data.

Compound	$[\alpha]_D^{20}$ (*c* 1, $CHCl_3$)	mp (°C)	Formula	HRMS calcd	HRMS found	IR ν (cm^{-1})
3b	+40		$C_9H_{13}NO_3S$	215.0616	215.0626	1736 (CO), 2951 (CH_2)
3c	+60		$C_8H_{10}N_2OS$	182.0514	182.0417	2251 (CN), 2928 (CH_2)
3d	+28		$C_{13}H_{15}NO_2S_2$	281.0544	281.0536	1040 (SO), 2922 (CH_2)
3e	-		$C_{13}H_{15}NO_3S_2$	297.0493	297.0501	1297 (SO_2)
4b	+27	< 48	$C_{17}H_{29}NO_2S$	311.1919	311.1927	1693 (CO), 2923 and 2953 (CH_2)
4c	+15		$C_9H_{11}NO_2S$	197.0510	197.0531	1643 (C=C), 1683 (CO)
4d	-30	< 48	$C_{14}H_{13}NO_2S$	259.0667	259.0646	1641 (C=C), 1683 (CO)
4f	+48		$C_8H_{11}NO_2S$	185.0510	185.0523	1699 (CO), 2983 (CH_2)
4g	-78	120-122	$C_{10}H_{15}NO_3S$	229.0773	229.0780	1759 (CO), 2977 (CH_3)
5b	+33	120-122	$C_{20}H_{28}N_2O_4S_2$	424.1490	424.1504	1686 (CO), 2925 (CH_2)

5c	+37	80-82	$C_{22}H_{32}N_2O_4S_2$	452.1803	452.1792	1693 (CO), 2921 (CH_2)
6b	+48	118-120	$C_{12}H_{12}N_2O_2S$	248.0619	248.0643	1563 (NH), 1703 (CO), 3028 (CH)
6c	+70	150-152	$C_{12}H_{11}N_2O_2ClS$	282.0230	282.0231	1600 (NH), 1715(CO)
				284.0200	284.0200	
6d	+43	146-148	$C_{12}H_{10}N_2O_2Cl_2S$	315.9840	315.9845	1594 (NH), 1717 (CO), 3033 (CH)
				317.9810	317.9814	
				319.9781	319.9783	
6e	+45	150-152	$C_{12}H_{11}N_2O_2BrS$	325.9725	325.9729	1598 (NH), 1715 (CO)
				327.9704	327.9707	
8b	+35	100-102	$C_{12}H_{13}NO_3S_2$	283.0337	283.0341	1369 (SO_2)
8c	+23	80-82	$C_{11}H_{10}NO_3BrS_2$	346.9285	346.9279	1373 (SO_2)
				348.9265	348.9260	
9b	+9		$C_{12}H_{13}NOS$	219.0718	219.0695	1605 (C=N)
9c	+35		$C_{13}H_{13}NO_2S$	247.0667	247.0652	1596 (C=N), 1651 (CO)
9d	+48		$C_7H_8N_2OS$	168.0357	168.0353	1601 (C=N), 2245 (CN)
9e	+21		$C_9H_{13}NO_3S$	215.0616	215.0617	1614 (C=N), 1739 (CO)
9f	+23		$C_8H_{11}NO_3S$	201.0460	201.0456	1615 (C=N), 1744 (CO)

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