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Synthesis of Optically Active α-Phenylselenyl Carbonyl Derivatives

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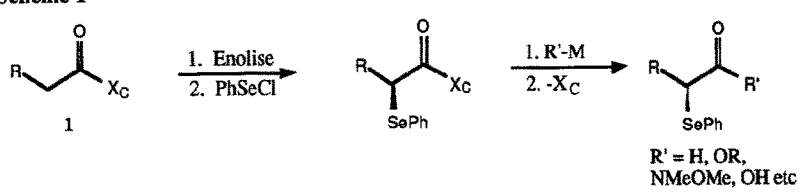
Abstract: Homochiral silyl enol ethers derived from *N*-acyl oxazolidinones can be phenyselenylated in high diastereoselectivity and good yield with phenylselenyl chloride. Removal of the chiral auxiliary is accompanied by some epimerisation, leading to isolation of the corresponding α-phenylselenyl methyl esters in moderate enantiomeric excess. A slightly improved enantiomeric excess is achieved if 4(*S*)-benzyl-2-oxazolidinethione **17** is used as a chiral auxiliary.

Introduction

Considering the wide applications of α-phenylselenyl carbonyl compounds in organic synthesis,[1] we sought to devise a general route to a wide variety of enantiomerically pure α-phenylselenyl carbonyl derivatives. One such approach would be the diastereoselective phenylselenylation of the enolate derived from a homochiral "Evans" *N*-acyl oxazolidinone[2] of general type **1** followed by removal of the chiral auxiliary (X_C)[3] (Scheme 1).

Scheme 1

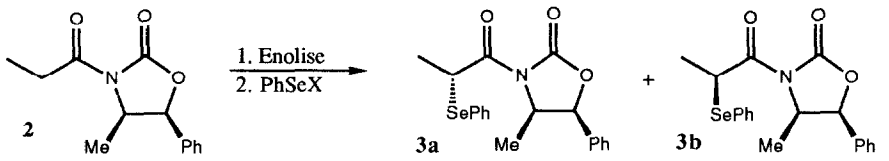


Results and Discussion

A) Diastereoselective Phenylselenylation

Early attempts to phenylselenylate various enolates (Li, B, Na or K) derived from **2** with either *N*-phenylselenophthalimide[4] or phenylselenyl chloride led to disappointing levels of stereocontrol (Table 1). Yields were generally poor. The only general observations which could be made regarding stereoselectivity were that the boron enolates gave the lowest levels of stereoselectivity, sodium enolates the greatest.

Table 1 Phenylselenylation of Chiral Imide Enolates Formed from **2**

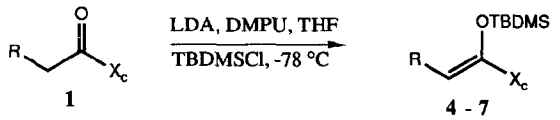


Entry	X	T/°C	Enolate	Yield[a]/%	Ratio[b] **3a**:**3b**
1	Cl	-78	Li[d]	41	55:45
2	Cl	-78	Li[e]	42	20:80
3	Cl	-78	B(*n*-Bu)$_2$[f]		45:55
4	NPSP[c]	-78	B(*n*-Bu)$_2$[f]		69:31
5	Cl	-95	Na[g]	70	20:80
6	Cl	-95	K[h]		24:76
7	NPSP	-95	K[h]		28:72

Notes: (a) combined yield of both diastereoisomers **3**; (b) ratio determined by either NMR or GC; **3a** was assumed to be the major diastereoisomer on the basis of earlier work;[2,5] (c) NPSP = *N*-phenylselenophthalimide; (d) generated using Li bis(trimethylsilyl)amide (LiHMDS) (1.1 equiv) in THF; (e) generated using lithium diisopropylamide (LDA); (f) generated using *n*-Bu$_2$BOTf (1.1 equiv) and NEt$_3$ (1.2 equiv.); (g) generated using NaHMDS; (h) generated using KHMDS.

However, formation and isolation of the corresponding *tert*-butyldimethylsilyl enol ether **4** - **7** (Table 2) following a modified literature procedure which had been shown to be successful in analogous sulfenylation reactions,[5] and subsequent phenylselenylation was more successful (Table 3). A mixed solvent system of dichloromethane/THF appeared to be the most effective for phenylselenylation; in either ether or pentane solution much lower diastereoselectivity was obtained (Entries 6 & 7, Table 3). Typically, a solution of the silyl enol ether in dichloromethane/THF was treated with a solution of phenylselenyl chloride in dichloromethane at -100 °C, until an orange colour persisted. Isolation of the product by chromatography on silica gel or crystallisation gave the α-phenylselenyl imide. In many cases, a single recrystallisation gave material having greater than 99% d.e. (GC). Isolated yields were moderate to good. Use of *N*-phenylselenophthalimide resulted in a much slower reaction, yielding a complex mixture of products. The reaction appears to tolerate a variety of chiral auxiliaries and acyl groups (Table 3).

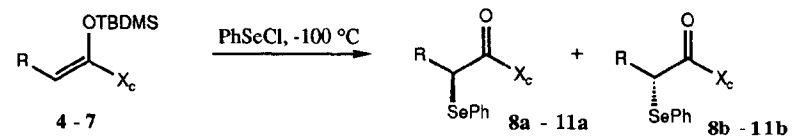
Table 2 Generation of Silyl Enol Ethers **4 - 7**



1 **4 - 7**

Entry	R	X_C[3]	Product (yield/%)
1	Me	X_V	**4** 99
2	Me_2CH	X_V	**5** 97
3	$Me(CH_2)_4$	X_V	**6** 93
4	Me_2CH	X_P	**7** 97

Table 3 Phenylselenylation of Imide Silyl Enol Ethers **4 - 7**



4 - 7 **8a - 11a** **8b - 11b**

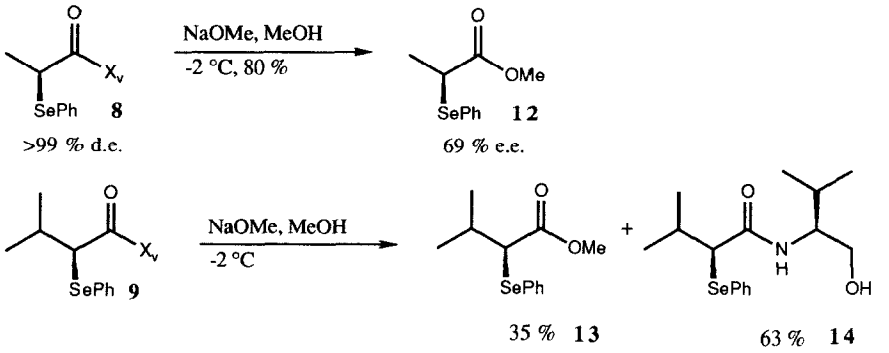
Entry	Silyl Enol Ether	Solvent	Ratio[a] (a:b)		Product (yield[b]/%)
1	**4**	THF/CH_2Cl_2	86:14	**8**	61
2	**4**	pentane	65:35	**8**	
3	**4**	ether	74:26	**8**	
4	**5**	THF/CH_2Cl_2	97:3	**9**	62
5	**6**	THF/CH_2Cl_2	80:20	**10**	86
6	**7**	THF/CH_2Cl_2	7:93[c)]	**11**	74

(a) determined by GC of the crude reaction mixture, with stereochemical assignments based on earlier work;[2,5] (b) combined yield of both diastereoisomers; (c) ratio determined by ^1H NMR.

B) Auxiliary Cleavage

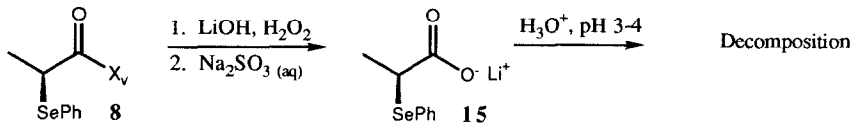
Because of the powerful ability of a phenylselenyl group to stabilise an α-carbanion,[6] and the high reactivity of a C-Se bond, auxiliary cleavage proved troublesome, as anticipated. Reductive methods ($LiAlH_4$,[7] $LiBH_4$,[8] sodium bis(methoxyethoxy)aluminium hydride,[9] and DIBAL-H) or attempted transamidation ($AlMe_3$, HNMeOMe)[10] led to C-Se bond cleavage. Methanolysis of **8** with sodium methoxide in methanol gave partially racemised ester **12** in 69 % e.e. [measured using $Eu(tfc)_3$]. On the more hindered substrate **9**, identical conditions gave predominantly attack at the "endocyclic" carbonyl, to yield on work-up the hydroxy amide **14** (Scheme 2).

Scheme 2



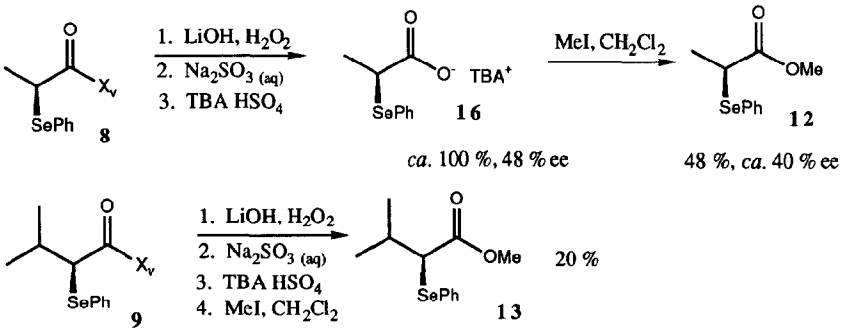
Surprisingly application of the lithium hydrogen peroxide mediated cleavage procedure reported by Evans[11] resulted in clean conversion of **8a** into the lithium carboxylate **15** with no apparent oxidation of selenium (Scheme 3). Quantitative recovery of the chiral auxiliary was achieved even for the hindered substrate **9**, confirming the extraordinary selectivity of this reagent. However, subsequent acidification of **15** in the work-up repeatedly led to total decomposition of starting material, and it was concluded that α-phenylseleno acids were not stable under these conditions.[12]

Scheme 3



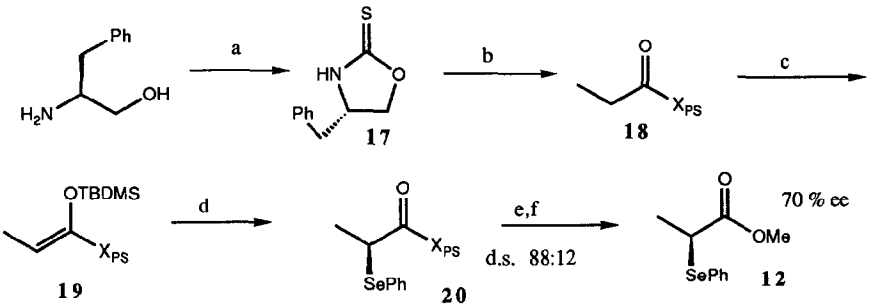
In order to avoid the acidification step, the tetra-*n*-butylammonium (TBA) salt **16** was prepared (Scheme 4). Alkylation[13] of this with methyl iodide led to formation of the methyl ester **12** in moderate yield. This was accompanied by formation of iodine and diphenyldiselenide, suggesting transient formation of PhSeI by attack of the liberated iodide on the methyl ester **12**. The enantiomeric excess of methyl ester **12** derived by this procedure was measured as approximately 40 % [using Eu(tfc)3]. The enantiomeric excess of the parent TBA salt **16** was 48 % [as measured by ^{1}H NMR analysis in the presence of (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol[14]], demonstrating that epimerisation prior to auxiliary cleavage rather than racemisation afterwards was occurring.

Scheme 4



Fujita and co-workers[15] have shown that *N*-acyl-2-oxazolidinethiones are readily and cleanly cleaved with nucleophiles to afford the corresponding carboxylic acid derivative. In order to establish whether a more labile chiral auxiliary would enable cleavage to proceed with lower loss of enantiomeric purity, benzyl-2-oxazolidinethione **17** was prepared (Scheme 5). Subjecting the derived phenylselenide **20** (recrystallised to >99 % d.e.) to the same cleavage conditions which were applied to **11** gave an almost identical yield of methyl ester **12**, but in increased enantiomeric excess (70 % e.e.).

Scheme 5



Reagents and conditions: (a) CS_2, KOH, EtOH, H_2O, 75 °C, 4 h, 35 %; (b) CH_3CH_2COCl, pyridine, benzene, 2h, 25 °C, 87 %; (c) LDA, DMPU, TBDMSCl, 96 %; (d) PhSeCl, THF, CH_2Cl_2, 37 %; (e) i, LiOH, H_2O_2, H_2O, THF, ii, Na_2SO_3 (aq), iii, TBA HSO_4, LiOH, CH_2Cl_2; (f) MeI, CH_2Cl_2, 47 % (3 steps).

Conclusion

Diastereomerically pure α-phenylselenyl carboximides can be formed in good yield with good stereoselectivity by treatment of a homochiral silyl enol ether with PhSeCl at low temperature. Many methods for the removal of the chiral auxiliary were tried. The only method which did not either cause C-Se bond cleavage or endocyclic carbonyl attack was the use of lithium hydrogen peroxide in H_2O/THF. Although this causes some epimerisation, partially racemised TBA salts of α-phenylselenyl carboxylic acids could be

formed in quantitative yield and subsequent alkylation with methyl iodide gave the corresponding methyl esters in moderate yield with no further loss of enantiomeric purity. The new chiral auxiliary 4(*S*)-benzyl-2-oxazolidinethione was synthesised in an attempt to facilitate auxiliary cleavage, and an analogous series of operations gave α-phenylselenyl methyl ester **12** in improved enantiomeric excess.

Acknowledgements

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Experimental

^{1}H NMR spectra were recorded on Bruker AC-250 (250 MHz), Bruker WM-250 (250 MHz) and Bruker WM-400 (400 MHz) instruments. ^{13}C NMR spectra were recorded on a Bruker WM-400 (100 MHz) or Bruker AM-250 (62.5 MHz) machine using proton decoupling. In most cases an attached proton test experiment (APT) was run to aid assignment of signals. Infra-red spectra were recorded on a Perkin-Elmer 1310 spectrophotometer or a Perkin Elmer 1600 FT spectrophotometer. Electron impact (EI) mass spectra were determined using an A.E.I. MS 902 (low resolution spectra) or an A.E.I. MS 30 (high resolution spectra) instrument. Chemical ionisation (CI) were performed on a VG ZAB-E instrument at the SERC Mass Spectrometry Service Centre, University College of Swansea. CI spectra were recorded using NH_3 as the carrier gas. Optical rotations were measured using a Perkin-Elmer 241 polarimeter, in a cell of 1 dm path length. The concentration (c) is expressed in g/100 ml. Specific rotations, denoted as $[\alpha]_D^T$, imply units of $^\circ dm^2g^{-1}$ (T = temp °C). Microanalyses were carried out by the staff of the University Chemical Laboratory Microanalytical Department, Cambridge. Melting points (m.p.) were determined using a Büchi 510 melting point apparatus (open capilliaries used) and are uncorrected. Analytical thin layer chromatography (TLC) was carried out on Merck pre-coated 0.25mm thick plates of Kieselgel 60 F_{254}. Flash chromatography was carried out using Merck Kieselgel 60 (230-400 mesh). Gas chromatography (GC) was carried out using a Carlo Erba 4130 instrument with a S.G.E. BP5 (5% phenylmethylsiloxane stationary phase) 25m column (diameter 0.33mm), carrier gas (helium) flow rate 2 cm^3min^{-1} and flame ionisation detection. The oven temperature was initially at 150 °C and heated at a rate of 10.0 °C/min for 13 min and held at 280 °C for 10 min unless otherwise stated. Non-aqueous reactions were carried out under an atmosphere of nitrogen or argon where appropriate. Dry THF was distilled from potassium in a recycling still, using benzophenone ketyl as indicator. Other dry solvents were purified by standard techniques.[16] Ether refers to diethyl ether. Brine refers to a saturated solution of sodium chloride in water.

3[4S, (Z)]-[1-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-1-propenyl]-4-(1-methylethyl)-2-oxazolidinone [5] **4**

A solution of *n*-butyllithium (13.9 cm^3 of a 1.6 $moldm^{-3}$ solution in hexane, 22.2 mmol) was added to a rapidly stirring solution of dry diisopropylamine (3.64 cm^3, 26.0 mmol) in dry THF (70 cm^3) precooled to -50 °C under nitrogen. The mixture was warmed to room temperature and stirred for 15 minutes, and then cooled to -78 °C. A solution of (*S*)-(+)-4-methylethyl-3-propionyl-2-oxazolidinone[2] (3.43 g, 18.6 mmol) in THF (15 cm^3 + 5 cm^3 rinse) was added slowly, keeping the temperature below -68 °C. The mixture was stirred at -78 °C for 45 minutes, and then treated with 1,2-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (20 cm^3). Five minutes later, a solution of *tert*-butyldimethylsilyl chloride (TBDMSCl) (3.36 g, 22.3 mmol) in THF (15 cm^3) was added slowly, keeping the temperature below -75 °C. The mixture was allowed to warm to room temperature and poured into water (150 cm^3) and extracted with 1:1 ether/hexane (3 x 150 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated *in vacuo* to yield a pale straw-coloured oil. Purification by column chromatography (silica, 2:1 hexane/ether as eluant) yielded the *silyl enol ether* **4** (5.50 g, 99%) as a colourless oil. $[\alpha]_D^{21}$ -62 (*c* 3.26 in $CHCl_3$); (Found: C, 60.2; H, 9.8; N, 4.5. $C_{15}H_{29}NO_3Si$ requires C, 60.16; H, 9.76; N, 4.67%); R_f 0.29 (2:1 hexane/ether); ν_{max} (CCl_4)/cm^{-1} 1770 (C=O) and 1685 (C=C); δ_H (250 MHz; $CDCl_3$) 4.82 (1H, q, *J* 6.5, C*H*=C), 4.28-4.11 (1H, m, NC*H*), 4.10-3.98 (1H, m, C*H*O), 3.96-3.84 (1H, m, C*H'*O), 2.01 (1H, ddq, *J* 6.7, 3.2 and 3.0, Me_2CH), 1.59 (3H, d, *J* 6.5, *Me*CH=C),

0.93 (9H, s, *tBu*), 0.88 (3H, d, *J* 3.2, *Me*), 0.85 (3H, d, *J* 3.0, *Me*), 0.17 (3H, s, Si*Me*) and 0.12 (3H, s, Si*Me*); δ_C (100 MHz; $CDCl_3$) 156.0 (s), 138.2 (s), 103.4, (d) 63.1 (t), 58.8 (d), 28.6 (d), 25.6 (q), 18.0 (s), 17.5 (q), 14.9 (q), 10.9 (q), -4.59 (q), and -4.79 (q); *m/z* (CI) 373 (1%), 300 [(M+H)$^+$, 100], 242 (19), 203 (2), 186 (3), 156 (2), 132 (2), 90 (2) and 74 (1) (Found (CI): MH$^+$, 300.1995. $C_{15}H_{30}NO_3Si$ requires *M*, 300.1995).

3[4S, (Z)]-[1-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-3-methyl-1-butenyl]-4-(1-methylethyl)-2-oxazolidinone **5**

The same procedure as described for compound **4** was followed. The *silyl enol ether* **5** was isolated as a colourless oil (97%). $[\alpha]_D^{25}$ -63 (*c* 0.77 in $CHCl_3$); (Found: C, 62.2; H, 10.4; N, 4.4. $C_{17}H_{33}NO_3Si$ requires C, 62.34; H, 10.16; N, 4.28%); R_f 0.42 (3:1 hexane/ether); ν_{max} (cm^{-1})/CCl_4 1780 (C=O) and 1685 (C=C); δ_H (250 MHz; $CDCl_3$) 4.61 (1H, d, *J* 9.6, C*H*=C), 4.20 (1H, q, *J* 8.9, C*H*O), 4.03 (1H, dd, *J* 8.9 and 5.7, C*H'*O), 3.95-3.87 (1H, m, NC*H*), 2.83-2.50 (1H, m, Me_2CHCH=C), 2.15-1.98 (1H, m, Me_2CH), 1.02-0.88 (21H, m, *Me* x 4 and *tBu*), 0.18 (3H, s, Si*Me*) and 0.13 (3H, s, Si*Me*); δ_C (100 MHz; $CDCl_3$) 158.8 (s), 135.9 (s), 116.7 (d), 63.3 (t), 59.1 (d), 28.9 (d), 25.6 (q), 25.2 (d), 22.8 (q), 22.7 (q), 18.0 (s), 17.5 (q), 15.2 (q), -4.56 (q) and -5.07 (q); *m/z* (CI) 442 (7%), 328 [(M+H)$^+$, 100], 270 (9), 244 (5), 231 (3), 214 (4), 147 (2), 132 (2) and 90 (2) (Found (CI): MH$^+$, 328.2308. $C_{17}H_{34}NO_3Si$ requires *M*, 328.2308).

3[4S, (Z)]-[1-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-1-heptenyl]-4-(1-methylethyl)-2-oxazolidinone **6**

The same procedure as described for compound **4** was followed. The *silyl enol ether* **6** was isolated as a colourless oil (93%). $[\alpha]_D^{25}$ -64 (*c* 1.93 in $CHCl_3$); R_f 0.42 (1:1 hexane/ether); ν_{max} (CCl_4)/cm^{-1} 1770 (C=O) and 1670 (C=C); δ_H (250 MHz; $CDCl_3$) 4.75 (1H, dd, *J* 5.0 and 3.8, C*H*=C), 4.20 (1H, q, *J* 5.6, C*H*N), 4.10-4.00 (1H, m, C*H*O), 3.98-3.86 (1H, m, C*H'*O), 2.20-1.90 (3H, m, Me_2CH and CH_2C=C), 1.42-1.18 (6H, m, $CH_2CH_2CH_2$), 0.93 (9H, s, *tBu*), 0.92-0.80 (9H, m, *Me*CH_2 and Me_2CH), 0.16 (3H, s, Si*Me*) and 0.12 (3H, s, Si*Me*); δ_C (100 MHz; $CDCl_3$) 155.9 (s), 137.4 (s), 109.3 (d), 63.1 (t), 58.9 (d), 31.5 (t), 28.9 (t), 28.7 (d), 25.6 (q), 25.3 (t), 22.4 (t), 18.0 (s), 17.5 (q), 15.0 (q), 14.0 (q), -4.58 (q) and -4.88 (q); *m/z* (CI) 430 (6%), 356 [(M+H)$^+$, 100], 298 (22), 242 (22), 147 (28) and 130 (24) (Found (CI): MH$^+$, 356.2621. $C_{19}H_{38}NO_3Si$ requires *M*, 356.2621).

3[4R, (Z)]-[1-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-3-methyl-1-butenyl]-4-(1-methylphenyl)-2-oxazolidinone **7**

The same procedure as described for compound **4** was followed. The *silyl enol ether* **7** was obtained as a colourless oil (97%), which solidified to a white waxy solid mp 59.5-60.5 °C after refrigeration for several weeks. $[\alpha]_D^{25}$ +42 (*c* 1.27 in $CHCl_3$); (Found: C, 67.1; H, 8.7; N, 3.9. $C_{21}H_{33}NO_3Si$ requires C, 67.16; H, 8.86; N, 3.73%); R_f 0.30 (1:1 hexane/ether); ν_{max} (CCl_4)/cm^{-1} 1785 (C=O) and 1680 (C=C); δ_H (250 MHz; $CDCl_3$) 7.34-7.13 (5H, m, phenyl), 4.69 (1H, d, *J* 9.6, C*H*=C), 4.17-4.00 (3H, m, C*H*N and CH_2O), 3.18 (2H, dd, *J* 13.6 and 3.4, PhCH_2), 2.66-2.54 (1H, m, Me_2CH), 1.07-1.00 (15H, m, Me_2CH and *tBu*), 0.22 (3H, s, Si*Me*) and 0.16 (3H, s, Si*Me*); δ_C (100 MHz; $CDCl_3$) 155.3 (s), 135.7 (d), 135.5 (s), 129.1 (s), 128.9 (d), 127.1 (d), 117.3 (d), 66.6 (t), 56.3 (d), 38.1 (t), 28.9 (d), 25.6(q), 23.1 (q), 22.8 (q), 16.8 (s), -4.46 (q) and -4.95 (q); *m/z* (CI) 376 [(M+H)$^+$, 100%], 318 (11), 292 (70), 279 (14), 262 (27), 251 (5), 234 (4), 217 (9), 195 (17) and 184 (16) (Found (CI): MH$^+$, 376.2308. $C_{21}H_{34}NO_3Si$ requires *M*, 376.2308).

[3(2R),4S]-3-(2-Phenylseleno-1-oxopropyl)-4-(1-methylethyl)-2-oxazolidinone **8a**

Silyl enol ether **4** (5.18 g, 0.0173 mol) was dissolved in dichloromethane (40 cm^3) and THF (10 cm^3) and cooled to -100 °C under dry nitrogen with stirring. A solution of phenylselenyl chloride (3.65 g, 0.019 mol) in THF (4 cm^3) and dichloromethane (12 cm^3) was added dropwise over 25 minutes. The mixture was warmed slowly to room temperature. A small sample taken for GC analysis indicated the ratio of diastereoisomers to be 14:86. The mixture was diluted with ethyl acetate (400 cm^3) and poured into brine (250 cm^3). The phases were separated and the aqueous phase was extracted with ethyl acetate (3 x 200 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated *in vacuo* to yield a bright orange oil. Purification by column chromatography (silica, 3:2 hexane/ether as eluant) yielded a cloudy oil which crystallised on standing. Recrystallisation gave the *selenide* **8a** as almost transparent crystals (3.362 g, 57%) mp 82-83 °C (ethyl acetate/hexane), and a second crop (0.227 g, 4%). GC indicated the diastereomeric purity of the first crop to be >99:1. $[\alpha]_D^{21}$ +145 (*c* 3.733, $CHCl_3$); (Found C, 52.9; H, 5.55; N, 4.1. $C_{15}H_{19}NO_3Se$ requires C, 52.95; H, 5.63; N, 4.12%); R_f 0.33 (1:1 hexane/ether); ν_{max} (CCl_4)/cm^{-1} 1785 (C=O) and 1695 (C=O); δ_H (250 MHz; $CDCl_3$) 7.47-7.22 (5H, m, phenyl), 5.02 (1H, q, *J* 7.0, C*H*SePh), 4.58-4.43 (1H, m, C*H*N), 4.32-4.22 (2H, m, CH_2O), 2.43 (1H, ddq, *J* 7.4, 7.0 and 6.9, Me_2CH), 1.39 (3H, d, *J* 7.0, *Me*CHSePh), 1.02 (3H, d, *J* 6.9, *Me*) and 0.95 (3H, s, *J* 7.0, *Me*); δ_C (100 MHz; $CDCl_3$) 172.5 (s), 153.8 (s), 137.0 (s), 128.94 (d), 128.88 (d), 125.8 (d), 63.0 (t), 58.3 (d), 34.1 (d), 28.2 (d), 18.1 (q), 16.3 (q) and 14.7 (q); *m/z* (EI) 341 (M^+, 45%), 212 (33), 184 (100), 157 (18), 142 (7), 130 (24), 116 (12) and 105 (66) (Found: M^+, 341.0530, $C_{15}H_{19}NO_3{}^{80}Se$ requires *M*, 341.0530).

[3(2R),4S]-3-(2-Phenylseleno-3-methyl-1-oxobutyl)-4-(1-methylethyl)-2-oxazolidinone **9a**

The same procedure as described for compound **8a** was followed. The *selenide* **9a** was isolated as a single diastereoisomer after recrystallisation (75 %) mp 84-85 °C (ethyl acetate/hexane); $[\alpha]_D^{21}$ +47 (*c* 0.86 in $CHCl_3$); (Found: C, 55.3; H, 6.4; N, 3.9. $C_{17}H_{23}NO_3Se$ requires C, 55.43; H, 6.29; N, 3.80%); R_f 0.36 (1:1 hexane/ether); ν_{max} (CCl_4)/cm^{-1} 1790 (C=O) and 1695 (C=O); δ_H (250 MHz; $CDCl_3$) 7.57-7.53 (2H, m, phenyl), 7.34-7.23 (3H, m, phenyl), 4.86 (1H, d, *J* 10.3, C*H*SePh), 4.53-4.47 (1H, m, C*H*N), 4.31-4.19 (2H, m, CH_2O), 2.48-2.36 (1H, m, Me_2CHCHN), 2.11-1.96 (1H, m, Me_2CH), 1.17 (3H, d, *J* 6.7, *Me*CHCHSePh), 0.960 (3H, d, *J* 7.2, *Me*CHCHSePh), 0.957 (3H, d, *J* 5.9, *Me*) and 0.93 (3H, d, *J* 7.2, Me); δ_C (100 MHz; $CDCl_3$) 171.5 (s), 154 (s), 135.7 (d), 128.9 (d), 128.5 (d), 110.0 (s), 62.8 (t), 58.3 (d), 49.0 (d), 28.8 (d), 28.1 (d), 21.0 (q), 20.8 (q), 18.0 (q) and 14.6 (q); *m/z* (EI) 369 (M^+, 57%), 240 (22), 212 (55), 198 (3), 186 (5), 170 (5), 185 (39) and 83 (100) (Found: M^+, 369.0843. $C_{17}H_{23}NO_3{}^{80}Se$ requires *M*, 369.0843).

[3(2R),4S]-3-(2-Phenylseleno-1-oxoheptyl)-4-(1-methylethyl)-2-oxazolidinone **10a**

The same procedure as described for compound **8a** was followed. The initial mixture of diastereoisomers was purified by flash column chromatography to afford the major diastereoisomer, *selenide* **10a**, as a colourless oil (69 %). $[\alpha]_D^{25}$+58 (*c* 1.52 in $CHCl_3$); (Found: C, 57.8; H, 6.7; N, 3.7. $C_{19}H_{27}NO_3Se$ requires C, 57.57; H, 6.87; N, 3.53%); R_f 0.38 (1:1 ether/hexane); ν_{max} (CCl_4)/cm^{-1} 1775 (C=O) and 1691 (C=O); δ_H (250 MHz; $CDCl_3$) 7.54-7.51 (2H, m, phenyl), 7.39-7.26 (3H, m, phenyl), 4.95 (1H, t, *J* 7.4, C*H*SePh), 4.59-4.47 (1H, m, C*H*N), 4.33-4.22 (2H, m, CH_2O), 2.52-2.39 (1H, m, Me_2CH), 1.81-1.50 (2H, m, $CH_2CHSePh$), and 1.43-0.81 (15H, m, $CH_3CH_2CH_2CH_2C$ andMe_2CH); δ_C(100 MHz; $CDCl_3$) 171.8 (s), 153.6 (s), 136.4 (d), 128.7 (d), 128.6 (d), 126.1 (s), 62.8 (t), 58.2 (d), 39.9 (d), 31.2 (t), 30.2 (t), 28.1 (d), 27.3 (t), 22.3 (t), 17.9 (q), 14.5

(q) and 13.8 (q); *m/z* (EI) 397 (M^+, 93%), 268 (46), 240 (100), 130 (63), 111 (58) and 55 (94) (Found: M^+, 397.1156. $C_{19}H_{27}NO_3{}^{80}Se$ requires *M*, 397.1156).

[3(2S),4R]-3-(2-Phenylseleno-3-methyl-1-oxobutyl)-4-(1-methylphenyl)-2-oxazolidinone **11b**

The same procedure as described for compound **8a** was followed. The major diastereoisomer, *selenide* **11b**, was obtained as a colourless glass (69 %) after flash column chromatography. $[\alpha]_D^{25}$ -11 (*c* 1.16 in $CHCl_3$); (Found C, 60.6; H, 5.4; N, 3.5. $C_{21}H_{23}NO_3Se$ requires C, 60.58; H, 5.57; N, 3.36%); R_f 0.16 (2:1 hexane/ether); ν_{max} (CCl_4)/cm^{-1} 1785 (C=O) and 1695 (C=O); δ_H (250 MHz; $CDCl_3$) 7.64-7.60 (2H, m, phenyl), 7.37-7.14 (8H, m, phenyl), 4.91 (1H, d, *J* 10.1, C*H*SePh), 4.76-4.66 (1H, m, C*H*N), 4.23-4.04 (2H, m, CH_2O), 3.30 (1H, dd, *J* 13.4 and 3.4, PhCH'*H*), 2.63 (1H, dd, *J* 13.4 and 9.9, PhCH*H*'), 2.18-2.05 (1H, m, C*H*Me_2), 1.21 (3H, d, *J* 6.6, Me'*Me*CH) and 1.01 (3H, d, *J* 6.5, *Me*'MeCH); δ_C (100 MHz; $CDCl_3$) 171.8 (s), 153.2 (s), 136.0 (d), 135.5 (s), 129.5 (d), 129.2 (s), 129.0 (d), 128.6 (d), 127.4 (d), 65.9 (t), 55.3 (d), 49.2 (d), 37.5 (t), 29.4 (d), 21.09 (q) and 21.00 (q); *m/z* (EI) 417 (M^+, 46%), 260 (25), 240 (25), 213 (12), 178 (18), 157 (10), 117 (2), 105 (32), 91 (34) and 83 (100) (Found: M^+, 417.0843. $C_{21}H_{23}NO_3{}^{80}Se$ requires *M*, 417.0843).

(2R)-2-Phenylselenopropanoic acid, methyl ester **12**

Method i) Sodium methoxide (1.83 cm^3 of a 0.13 $moldm^{-3}$ solution in methanol, 0.238 mmol) was added slowly to a stirred solution of imide **8a** (77.01 mg, 0.226 mmol) in dry methanol (3 cm^3) precooled to -2°C under nitrogen. After 30 minutes the reaction was warmed to room temperature and carefully neutralised from pH 9 by addition of 2 $moldm^{-3}$ $HCl_{(aq)}$ (5 drops). The mixture was poured into brine (20 cm^3) and extracted with ethyl acetate (4 x 50 cm^3). The combined organic phases were dried ($MgSO_4$) and evaporated *in vacuo*. Purification by column chromatography (silica, 4:1 hexane/ether as eluant) gave the *methyl ester* **12** as a pale yellow oil (49.95 mg, 91%). $[\alpha]_D^{21}$(*c* 2.588 in $CHCl_3$) -128, approximately 69 % e.e.; R_f 0.53 (1:1 hexane/ether); ν_{max} (CCl_4)/cm^{-1} 1735 (C=O); δ_H (250 MHz; $CDCl_3$) 7.60-7.57 (2H, m, phenyl), 7.34-7.23 (3H, m, phenyl), 3.77 (1H, q, *J* 7.1, C*H*SePh), 3.63 (3H, s, *Me*O), 1.52 (3H, d, *J* 7.1, *Me*SePh); δ_C (100 MHz; $CDCl_3$) 173.8 (s), 135.8 (d), 129.0 (d), 128.8 (d), 127.6 (s), 52.1 (q), 37.1 (d) and 17.7 (q); *m/z* (EI) 272 (M^+, 100%), 115 (25) and 73 (66) (Found: M^+, 272.0316. $C_{12}H_{16}O_2{}^{80}Se$ requires *M*, 272.0316).

Method ii) The imide **8a** (78.0 mg, 0.23 mmol) was dissolved in THF (6 cm^3) and water (2 cm^3), and cooled to 0°C under nitrogen. 30% aqueous hydrogen peroxide solution (0.15 cm^3, 1.4 mmol) was added dropwise, followed immediately by lithium hydroxide.H_2O (19.2 mg, 0.458 mmol). The mixture was stirred in the ice bath for ten minutes, then removed and allowed to warm to room temperature. The mixture was stirred for 60 minutes and then quenched at 0 °C by adding 2.0 $moldm^{-3}$ $Na_2SO_{3(aq)}$ until starch/iodide paper failed to colour. The THF was evaporated *in vacuo*, and the oxazolidinone auxiliary was extracted from the aqueous phase with dichloromethane (2 x 10 cm^3). Tetra-*n*-butylammonium hydrogen sulfate (78 mg, 0.23 mmol) and lithium hydroxide.H_2O (10 mg, 0.23 mmol) were added, the aqueous phase was extracted with dichloromethane (4 x 30 cm^3). The combined dichloromethane extracts were dried ($MgSO_4$) and concentrated *in vacuo* to a volume of approximately 10 cm^3. To this was added methyl iodide (0.050 cm^3, 0.78 mmol). After five minutes an orange/brown colour formed, which could be immediately discharged with a solution of sodium thiosulfate. The mixture was stirred for 90 minutes and then washed with brine (20 cm^3). The organic phase was dried ($MgSO_4$) and concentrated to a yellow gum. Purification by column

chromatography yielded *methyl ester* **12**, as a colourless oil, identical to previous samples in all respects except for optical rotation: $[\alpha]_D^{21}$ -107 (*c* 2.10 in $CHCl_3$). Chiral shift studies on 20 mg of this material ($CDCl_3$, 30 mg $Eu(tfc)_3$) indicated the enantiomeric excess of the material to be 58 %.

A sample of the *tetra-n-butylammonium salt* **16** was prepared by the procedure described above and evaporated to dryness. Data for **16**: δ_H (400 MHz; $CDCl_3$) 7.56-7.55 (2H, m, Ph), 7.25-7.14 (3H, m, Ph), 3.97 (1H, q, *J* 8.5, C*H*SePh), 3.32-3.27 (2H, m, CH_2N), 1.66-1.58 (11H, m, CH_2CH_2N, *Me*CHSePh), 1.46-1.37 (8H, m, CH_2CH_2CH_2N), and 0.97 (12H, d, *J* 7.4, *Me*CH_2); δ_C (100 MHz; $CDCl_3$) 176.7, 133.2, 132.2, 128.6, 126.1, 58.8, 45.4, 24.1, 20.7, 19.7 and 13.7.

Method iii) The imide **20a** (63.9 mg, 0.158 mmol) was dissolved in dry THF (6 cm^3) and water (2 cm^3), and cooled to 0° C under nitrogen. 30 % aqueous hydrogen peroxide solution (0.11 cm^3, 0.95 mmol) was added dropwise, followed immediately by lithium hydroxide.H_2O (13.3 mg, 0.317 mmol). The mixture was stirred in the ice bath for ten minutes, then removed and allowed to warm to room temperature. The mixture was stirred for 60 minutes and then quenched at 0 °C by adding 2.0 $moldm^{-3}$ $Na_2SO_{3\,(aq)}$ until starch/iodide paper failed to colour. The mixture was warmed to room temperature and the mixture evaporated *in vacuo* to remove THF. The chiral auxiliary was extracted from the aqueous phase with dichloromethane (1 x 10 cm^3). Tetra-n-butylammonium hydrogen sulfate (53.6 mg, 0.158 mmol) and lithium hydroxide (6.63 mg, 0.158 mmol) were added and extracted with dichloromethane (5 x 15 cm^3). The combined dichloromethane extracts were dried ($MgSO_4$) and evaporated *in vacuo* . To this was added methyl iodide (0.020ml, 0.316 mmol). The mixture was stirred for 90 minutes and then washed with brine (20 cm^3). The organic phase was dried ($MgSO_4$) and concentrated to a yellow gum. Purification by column chromatography yielded *methyl ester* **12** as a colourless oil (18.4 mg, 47 %), identical to previous samples in all respects except for optical rotation: $[\alpha]_D^{21}$ -133 (*c* 1.84 in $CHCl_3$).

(4S)-4-Methylphenyl-2-oxazolidinethione **17**

(4*S*)-(-)-2-Amino-3-phenyl-1-propanol (10.0 g, 0.066 mol) was dissolved in 95% ethanol (25 cm^3) and water (5 cm^3). The solution was stirred and cooled to 0 °C under nitrogen and treated with carbon disulfide (4.40 cm^3, 0.073 mol) followed by a solution of potassium hydroxide (11.1 g in ethanol (25 cm^3) and water (15 cm^3)) at such a rate as to keep the temperature at 0 °C. The mixture was warmed to room temperature and heated at 75 °C for 4 hours. The mixture was cooled to room temperature, carefully acidified with ice-cold 1.0 $moldm^{-3}$ $HCl_{(aq)}$, and extracted with dichloromethane (3 x 100 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated *in vacuo*. Purification by column chromatography (silica, dichloromethane as eluant) afforded *oxazolidinethione* **17** (4.35 g, 34%) as a pale viscous oil, which solidified after extended refrigeration to a white solid, mp 56-57 °C. It was not possible to recrystallise the solid, despite several attempts. $[\alpha]_D^{21}$ -107 (*c* 2.89 in $CHCl_3$); (Found: C, 62.2; H, 5.7; N, 7.3. $C_{10}H_{11}NOS$ requires C, 62.31; H, 5.86; N, 7.31%); R_f 0.23 (dichloromethane); ν_{max} (CCl_4)/cm^{-1} 3470 (NH) and 1480 (C=S); δ_H (250 MHz; $CDCl_3$) 8.25 (1H, br s, N*H*), 7.37-7.15 (5H, m, Ph), 4.65 (1H, t, *J* 8.3, OC*H*H'), 4.42-4.23 (2H, m, OCH*H'* and C*H*N) and 2.95-2.88 (2H, m, PhCH_2); δ_C (100 MHz; $CDCl_3$) 189.6 (s), 135.2 (s), 129.2, (d) 129.0 (d), 127.5 (d), 74.8 (t), 57.8 (d) and 40.5 (t); *m/z* (EI) 193 (M^+, 24%), 139 (11), 102 (53), 91 (100), 84 (47) and 42 (72) (Found M^+, 193.0561. $C_{10}H_{11}NOS$ requires *M*, 193.0561).

(4S)-4-Methylphenyl-3-(oxopropyl)-2-oxazolidinethione **18**

The oxazolidinethione **17** (4.35 g, 0.023 mol) was dissolved in dry benzene (30 cm^3) and stirred under nitrogen. Pyridine (dried over NaOH) (2.00 cm^3, 0.025 mol) was added, followed two minutes later by a solution of freshly distilled propionyl chloride (2.15 cm^3, 0.025 mol) in benzene (20 cm^3). A yellow precipitate rapidly formed, leaving a clear pale yellow supernatant. The mixture was stirred at room temperature for 105 minutes. The mixture was diluted with dichloromethane (130 cm^3) and washed with 1 $moldm^{-3}$ $HCl_{(aq)}$ (70 cm^3) and brine (50 cm^3). The aqueous extracts were back-extracted with dichloromethane (50 cm^3). The combined organic phases were dried ($MgSO_4$), and evaporated *in vacuo* to yield a yellow oil which solidified on standing. Recrystallisation gave *propyl thione* **18** (4.20 g, 75 %) as fine white needles , m.p. 82-83.5 °C (ethyl acetate/hexane); $[\alpha]_D^{21}$ +130 (*c* 1.69, $CHCl_3$); (Found: C, 62.5; H, 6.1; N, 5.5. $C_{13}H_{15}NO_2S$ requires C, 62.63; H, 6.06; N, 5.62%); R_f 0.42 (1:1 hexane/ether); $\nu_{max}(CCl_4)/cm^{-1}$ 1710 (C=O) and 1410 (C=S); δ_H(250 MHz; $CDCl_3$) 7.34 (5H, m, phenyl), 4.95-4.86 (1H, m, C*H*N), 4.32-4.21 (2H, m, CH_2O), 3.46-3.13 (3H, m, CH_2CO, C*H*H'Ph), 2.75 (1H, dd, *J* 13.2 and 10.0, CH*H*'Ph) and 1.19 (3H, t, *J* 7.2, $MeCH_2$); δ_C(100 MHz; $CDCl_3$) 185.4 (s), 174.8 (s), 135.3 (s), 129.4 (d), 129.0 (d), 127.4 (d), 74.3 (t), 60.0 (d), 37.6 (t), 31.4 (t) and 8.55 (q); *m/z* (CI) 250 ($[M+H]^+$, 100%), 194 (48), 162 (3), 117 (3), 108 (3), 100 (3) and 91 (3) (Found (CI): M^+, 249.0824. $C_{13}H_{15}NO_2S$ requires *M*, 249.0824). A second crop of **18** (0.69 g, 12 %) was also collected.

(3[4S,(Z)]-[1-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-1-propenyl]-4-(1-methylphenyl)-2-oxazolidinethione **19**

A solution of *n*-butyllithium (3.30 cm^3 of a 1.6 $moldm^{-3}$ solution in hexane, 5.28 mmol) was added to a rapidly stirring solution of dry diisopropylamine (0.90 cm^3, 6.42 mmol) in dry THF (40 cm^3) precooled to -50 °C under nitrogen. The mixture was warmed to 0 °C and stirred for 15 minutes. The mixture was cooled to -72 °C. Imide (**18**) (1.00 g, 4.02 mmol) as a solution in THF (10 cm^3 + 5 cm^3 rinse) was cannulated slowly into the reaction mixture keeping the temperature below -70 °C. The mixture was stirred at -75 °C for 45 minutes, and then treated with DMPU (8 cm^3). Five minutes later a solution of *tert*-butyldimethylsilyl chloride (TBDMSCl) (0.791 g, 5.25 mmol) in THF (5 cm^3) was added slowly, keeping the temperature below -72 °C. The mixture was allowed to warm to room temperature and poured into water (100 cm^3), and extracted with hexane (5 x 60 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated *in vacuo* to yield a yellow oil. Purification by column chromatography (silica, 6:1 hexane/ethyl acetate as eluant) yielded *silyl enol ether* **19** (1.40 g, 96 %) as a colourless oil, which slowly crystallised on standing mp 49-51 °C (pentane). $[\alpha]_D^{21}$ -30 (*c* 2.23 in $CHCl_3$); R_f 0.45 (1:1 hexane/ether); $\nu_{max}(CCl_4)/cm^{-1}$ 1710 (C=O) and 1450 (C=S); δ_H(250 MHz; $CDCl_3$) 7.35-7.11 (5H, m, phenyl), 5.07 (1H, q, *J* 6.9, MeC*H*), 4.41-4.16 (3H, m, CH_2O and C*H*N), 3.23 (1H, dd, *J* 13.4 and 3.1, C*H*H'Ph), 2.61 (1H, dd, *J* 13.4 and 9.7, CH*H*'Ph), 1.71 (3H, d, *J* 6.9, *Me*CH), 0.98 (9H, s, *t*Bu), 0.28 (3H, s, Si*Me*) and 0.18 (3H, s, Si*Me*); δ_C(100 MHz; $CDCl_3$) 186.5 (s), 138.4, (s) 135.3 (s), 129.01 (d), 128.97 (d), 127.3 (d), 107.6 (d), 71.3 (t), 60.0 (d), 37.9 (t), 37.9 (t), 25.6 (q), 18.0 (s), 11.0 (q), -4.20 (q) and -4.53 (q); *m/z* (CI) 478 (1%), 364 ($[M+H]^+$, 100), 308 (7), 250 (6), 214 (3), 194 (10), 132 (3), 117 (2), 91 (5) and 74 (2) (Found (CI): M^+, 363.1688. $C_{19}H_{29}NO_2SSi$ requires *M*, 363.1688).

[3(2R),4S]-3-(2-Phenylseleno-1-oxopropyl)-4-(1-methylphenyl)-2-oxazolidinethione **20a**

Silyl enol ether **19** (0.512 g, 1.408 mmol was dissolved in dry dichloromethane (6 cm^3) and dry THF (1 cm^3) and cooled to -100 °C under dry nitrogen with stirring. A solution of phenylselenyl chloride (270 mg, 1.41 mol) in THF (1 cm^3) and dichloromethane (4 cm^3) was added dropwise. The mixture was warmed slowly to room temperature. The mixture was poured into brine and diluted with ethyl acetate. The layers were separated and the aqueous phase was extracted with ethyl acetate. The combined organic extracts were dried ($MgSO_4$) and evaporated *in vacuo* to yield a bright red/orange oil. Purification by column chromatography (silica, 7:1 hexane / ethyl acetate as eluant) yielded two fractions (28 mg, 5 %) and (180 mg, 32 %) as very sticky gums, identified as diastereomeric products **20b** and **20a** by ^1H NMR. The major diastereoisomer solidified after trituration with ice-cold hexane. Recrystallisation gave *selenide* **20a** as a white powder (110 mg, 19 %), m.p. 104-106 °C (ethyl acetate/hexane) (Found: C, 56.2; H, 4.6; N, 3.6. $C_{19}H_{19}NO_2SSe$ requires C, 56.43; H, 4.74; N, 3.46 %);$[\alpha]_D^{21}$ +129 (*c* 0.99 in $CHCl_3$); R_f 0.39 (1:1 hexane/ether); $\nu_{max}(CCl_4)/cm^{-1}$ 1685 (CO) and 1480 (CS); δ_H(250 MHz; $CDCl_3$) 7.58-7.54 (2H, m, phenyl), 7.42-7.28 (8H, m, phenyl); 5.88 (1H, q, *J* 6.9, C*H*SePh); 5.07-4.97 (1H, m, C*H*N), 4.33-4.13 (2H, m, CH_2O); 3.34 (1H, dd, *J* 13.3 and 3.5, C*H*H'Ph), 2.84 (1H, dd, *J* 13.3 and 10.1, CH*H*'Ph) and 1.42 (3H, d, *J* 6.9, *Me*CHSePh); δ_C(62.5 MHz; $CDCl_3$) 184.9 (s), 173.0 (s), 137.4 (d), 135.2 (s), 129.5 (d), 129.2 (d), 129.1 (d), 129.0 (d), 127.5 (d), 126.1(s), 70.1 (t), 59.9 (d), 37.3 (t), 34.4 (d) and 16.4 (q); *m/z* (CI) 406 ([M+H]$^+$, 100%), 346 (1), 284 (2), 248 (44), 209 (4), 194 (73), 162 (2), 134 (3), 108 (5) and 91 (5) (Found (CI): MH$^+$ 406.0380. $C_{19}H_{20}NO_2S^{80}Se$ requires *M*, 406.0380).

Notes and References

1. See for example: (a) Krief, A.; Dumont, W.; van Ende, D.; Halazy, S.; Labar, D.; Labourer, J.-L.; Lê, T. Q. *Heterocycles* **1989**, *28*, 1203-1228. (b) Sarkar, T. K.; Ghosh, S. K.; Satapathi, T. K. *Tetrahedron* **1990**, *46*, 1885-1898. (c) Paulmier, C.; Outurquin, F.; Plaquevent, J.-C. *Tetrahedron Lett.* **1988**, *29*, 5893-5896. (d) Danishefsky, S. J.; Pearson, W. H.; Segmuller, B. E. *J. Am Chem. Soc.* **1985**, *107*, 1280.

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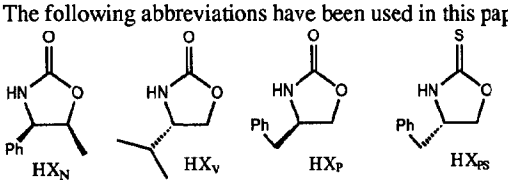
3. The following abbreviations have been used in this paper:



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