Pergamon

Tetrahedron 55 (1999) 3191–3208

TETRAHEDRON

Asymmetric Electrophilic Methoxyselenenylations and Cyclizations with 3-Camphorseleno Derivatives

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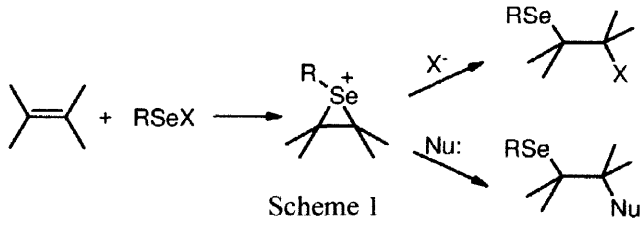
Received 3 September 1998; revised 6 October 1998; accepted 7 October 1998

Abstract: A series of novel 3-camphor-based diselenides, differing in substitution at C-2, was prepared. The corresponding allyl selenides were used as protecting groups for the diselenide moieties in several subsequent transformations. The diastereoselective methoxyselenenylation of alkenes was achieved with methanolic selenenyl triflates derived from the camphor diselenides, of which the 2-keto analogue proved the most effective. Diastereoselective electrophilic cyclizations of unsaturated alcohols, carboxylic acids and amides were most effectively performed with the corresponding selenenyl chloride, containing a *spiro*-oxazolidinone moiety at C-2 of the camphor residue. The absolute configurations of several products were determined by reductive deselenization.

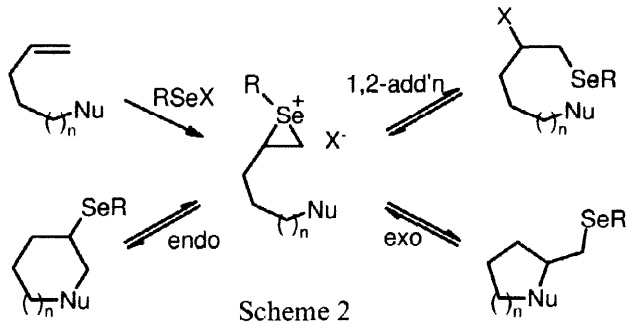
Dedicated to the memory of Professor Sir Derek H.R. Barton

Selenenyl chlorides and certain other electrophiles of general structure RSeX undergo 1,2-additions to olefins and related unsaturated substrates.[1,2] Typically, these reactions proceed *via* bridged seleniranium ion intermediates, resulting in the stereospecific *anti* incorporation of the moieties RSe and X. When the addition is performed in the presence of an external nucleophile, the latter can react with the seleniranium ion, resulting in its incorporation into the product instead of the original leaving group X (Scheme 1).[2] The regiochemistry of such processes with unsymmetrical olefins generally favours formation of the corresponding Markovnikov adduct (where X or the external nucleophile attack the more substituted olefinic



Scheme 1

carbon atom).[2,3] Furthermore, when a nucleophile is tethered to the alkene substrate, intramolecular attack upon the seleniranium ion takes place, leading to a cyclized product[2c,4] (Scheme 2). The term cyclofunctionalization has been employed to denote such processes.[5] Removal of the selenium residue in the



Scheme 2

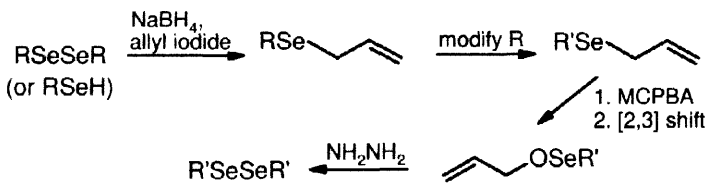
PII: S0040-4020(98)01133-8

final step can be accomplished reductively, or oxidatively by selenoxide *syn*-elimination, affording saturated or unsaturated products. The synthetic usefulness of these processes is well-established.[2,4,5]

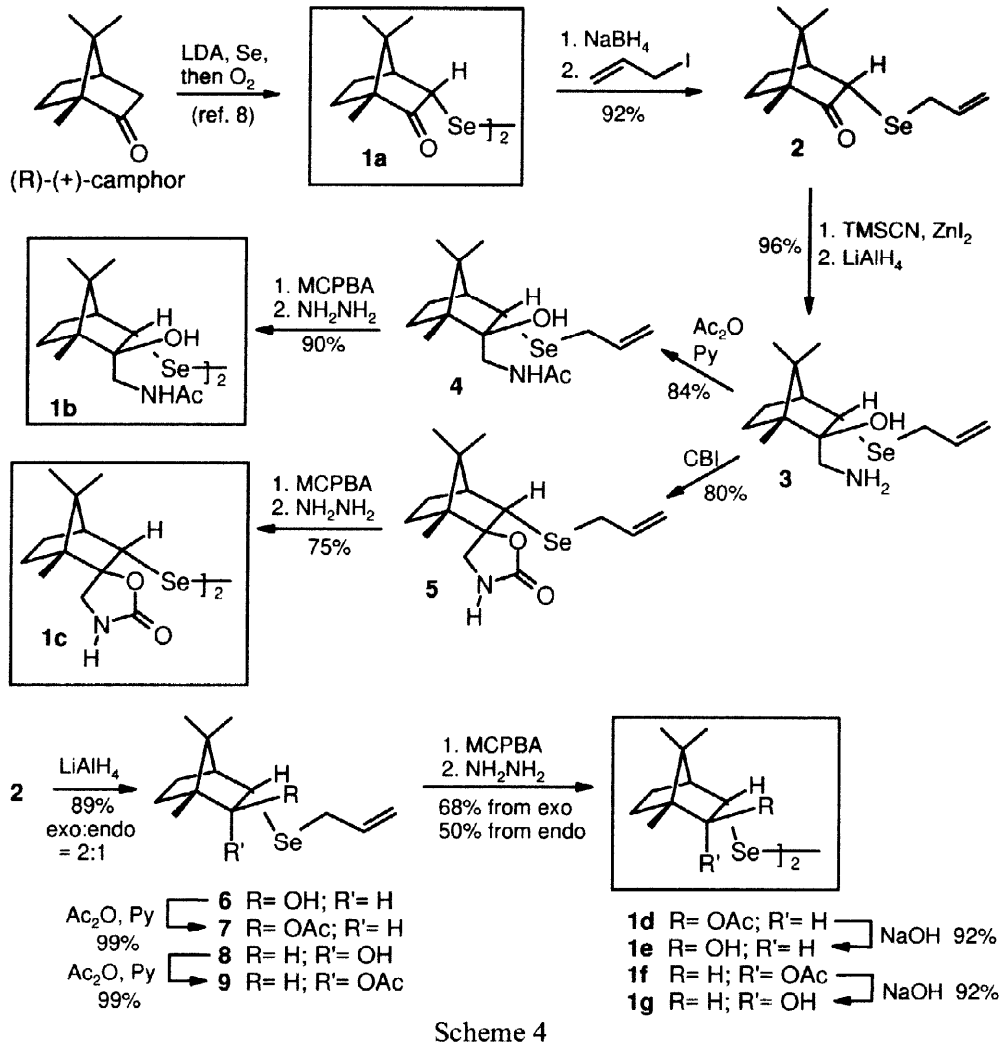
A recent variation of this chemistry consists of using a chiral moiety R* instead of R in the original selenium electrophile to control the stereochemistry of new chiral centers developed during the process. This results in diastereoselective additions or cyclizations, ultimately leading to the enantioselective formation of deselenized products. Thus, asymmetric methoxyselenenylations,[6] where the external nucleophile is methanol, and asymmetric cyclofunctionalizations[6a,6g,6o,7] have attracted considerable recent interest, using a variety of chiral selenium electrophiles. We considered that the camphorseleno moiety might be particularly suitable for these types of reactions for several reasons. Both antipodes of camphor are commercially available and we recently reported the efficient preparation of diselenide **1a** in one step from (*R*)-(+)-camphor and elemental selenium.[8] The 2-keto group of **1a** also provides the opportunity to modify the structure by, for example, introducing bulky substituents, groups capable of coordinating with the selenium atom at the adjacent site, or groups that can preorganize the reactants by hydrogen-bonding with the nucleophile. Moreover, the diselenide functionality can be used for conveniently generating a series of more powerful electrophiles. We now report the preparation of several modified camphorseleno diselenides, their conversion into selenenic electrophiles and an evaluation of their efficacy in methoxyselenenylations,[9a,10] and cyclofunctionalizations.[9b]

Preparation of Camphor Diselenides

Diselenide **1a** was prepared on a scale of 50-100 g and was used as the starting material for diselenides **1b**-**1g**. The vigorous conditions required for the reduction of ketone and nitrile functions at the C-2 position in subsequent transformations (*vide infra*) resulted in simultaneous cleavage of the C-Se bond when the diselenide moiety was present. To prevent this, an effective method for protecting the diselenide moiety[11] as the corresponding allyl selenide was devised and is shown in Scheme 3. Deprotection was achieved by oxidation, spontaneous [2,3]sigmatropic rearrangement of the resulting selenoxide[12] and reductive workup. Thus, diselenide **1a** was protected as the allyl selenide **2**, followed by cyanohydrin formation and reduction with lithium aluminum hydride (Scheme 4). The resulting amino alcohol **3** was then N-acetylated to **4** or cyclized to the corresponding *spiro*-oxazolidinone **5** with N,N'-carbonylbis(imidazole) (CBI). Deprotection was achieved by oxidation with *m*-chloroperbenzoic acid (MCPBA), followed by a [2,3]shift and workup with hydrazine to afford the desired modified diselenides **1b** and **1c**. The modified diselenide **1b** contains an *endo* nucleophilic amido group in close proximity to the *endo* selenium atom. Coordination between electrophilic selenium centers and nucleophilic heteroatoms such as N or O have been shown to play a key role in the stereoselectivity manifested by other chiral auxiliary groups used in selenium chemistry.[6a,6k,6n] On the other hand, the rigid *spiro*-oxazolidinone moiety at C-2 of **1c** blocks access to one side of the selenium substituent at C-3. Thus, selenenic electrophiles derived from diselenides **1b** and **1c** might be expected to provide improved stereoselectivity compared to **1a**. Similarly, reduction of **2** with lithium aluminum hydride furnished a mixture of *exo* and *endo* alcohols (**6** and **8**, respectively), which afforded acetates **7** and **9**, respectively. Deprotection of the allyl selenide group in the usual manner provided diselenides **1d** and **1f**, which afforded **1e** and **1g** after saponification (Scheme 4). Comparison of the stereoselectivities afforded by *exo* and *endo* alcohol isomers (or their acetates) was expected to reveal the effects of O-Se coordination, since the *endo* isomers are more suitably oriented for such interactions.



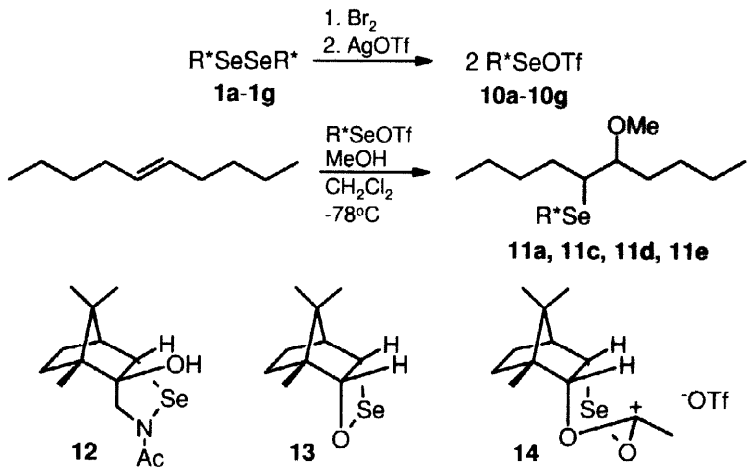
Scheme 3



Scheme 4

Methoxyselenenylations

A comparison of the different camphorseleno groups shown in Scheme 4 in asymmetric methoxyselenenylations was performed under a standard set of conditions in order to determine the best candidate for further optimization. Diselenides **1a-1g** were converted *in situ* into the corresponding selenenyl triflates **10a-10g** in dichloromethane-methanol at -78°C, followed by the addition of *trans*-5-decene (Scheme 5). The results are shown in Table 1. Under these conditions, the triflate **10b** failed to react with the alkene to afford the adduct **11**, but underwent cyclization to the corresponding selenenamide **12**, which is a stable, isolable compound that has been reported previously.[13] The *endo*-acetoxy and -hydroxy triflates **10f** and **10g**, respectively, also failed to afford **11**, with substantial amounts of the parent diselenides being recovered after hydrolytic workup. A possible explanation for the failure of the latter to effect the methoxyselenenylation of the alkene is that cyclic species **13** and **14** were formed analogously to **12**, but in this case underwent subsequent hydrolysis and disproportionation[14] to produce the recovered diselenides **1f** and **1g**. Thus, strongly nucleophilic groups suitably positioned for forming intramolecular covalent bonds with the selenium atom of the camphorseleno triflates are incompatible with methoxyselenenylation. In contrast, the remaining selenenyl triflates **10a**, **10c**, **10d** and **10e** afforded the corresponding adducts **11a**, **11c**, **11d** and **11e**, respectively. Moreover, Table 1 indicates that triflate **10a** provided both the highest yield of the correspon-



Scheme 5

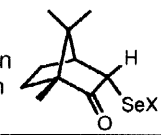
ding adduct, as well as the highest diastereomeric ratio (d.r.). Since the parent diselenide **1a** was produced in just one step from camphor and selenium, its superior effectiveness in this process is especially fortunate.

Attempts at optimization of the diastereoselectivity of the reaction with electrophiles derived from **1a** with *cis*- and *trans*-5-decene are shown in Table 2. An increase in the temperature to -42°C lowered the d.r. significantly compared to -78°C, while lowering it further to -95°C had little effect. Ether and toluene as cosolvents gave comparable d.r.'s to those obtained in dichloromethane. The selenenyl chloride and bromide derived from **1a** produced more complex product mixtures and the reaction with the relatively sluggish chloride had to be carried out at room temperature. The corresponding selenenyl tetrafluoroborate and hexafluorophosphate (generated *in situ* by use of $AgBF_4$ and $AgPF_6$ instead of AgOTf in Scheme 5) were comparable to the triflate **10a**. Based on these results, we chose the conditions of entry 1 in Table 2 for further experiments with other alkenes.

Table 1.[a] Methoxyselenenylation of *trans*-5-decene with different selenenyl triflates

entry	R*SeOTf	isolated yield of **11** (%)	d.r.[b,c]
1	**10a**	88	94:6
2	**10b**	d	
3	**10c**	65	66:34
4	**10d**	63	82:18
5	**10e**	51	85:15
6	**10f**	e	
7	**10g**	e	

(a) All reactions were performed in dichloromethane at -78°C. (b) d.r.=diastereomeric ratio. (c) Measured by NMR integration. (d) Triflate **10b** cyclized to **12**. (e) No methoxyselenenylation occurred under these conditions.

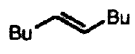
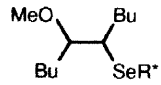
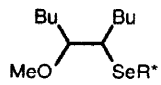
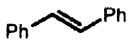
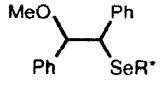
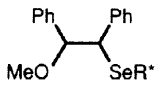
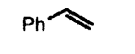
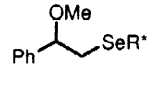
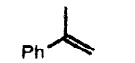
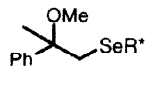
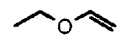
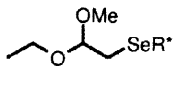
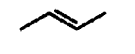
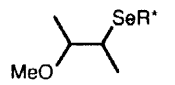
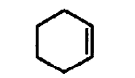
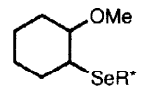
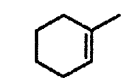
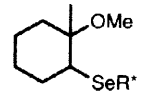
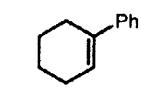
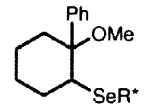
Table 2. Methoxyselenenylation of *cis*- and *trans*-5-decene with 

entry	X	geometry	solvent	temp. °C	d.r.[a,b]
1	OTf	trans	CH_2Cl_2	-78	94:6
2	OTf	trans	CH_2Cl_2	-95	95:5
3	OTf	trans	CH_2Cl_2	-42	83:17
4	OTf	trans	Et_2O	-78	92:8
5	OTf	trans	PhMe	-78	93:7
6	BF_4	trans	CH_2Cl_2	-78	92:8
7	OTf	cis	CH_2Cl_2	-78	75:25
8	BF_4	cis	CH_2Cl_2	-78	77:23
9	PF_6	cis	CH_2Cl_2	-78	78:22
10	Br	trans	CH_2Cl_2	-78	c
11	Cl	trans	CH_2Cl_2	23	c

(a) d.r.=diastereomeric ratio. (b) Measured by NMR integration. (c) A complex mixture was obtained.

Table 3 shows that the procedure provides moderate to high d.r.'s with a series of alkyl-, aryl-, mono-, di- and trisubstituted alkenes. As observed previously with other chiral selenenic electrophiles,[6a,6b,6h,6i] *trans*-olefins gave superior d.r.'s compared to *cis* olefins (see entry 1 vs. 2 and entry 3 vs. 4). It has been pointed out that it is the facial selectivity during the initial formation of the seleniranium ion intermediate that determines the diastereoselectivity of addition in the case of a *trans*-olefin. On the other hand, identical seleniranium ions are formed from attack of the electrophile upon the two faces of a

Table 3.[a] Methoxyselenenylations of olefins with **10a**

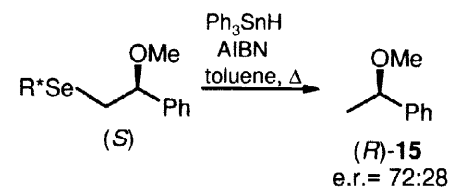
entry	substrate	product	isolated yield (%)	d.r.[b,c]
1			88	94:6
2			88	75:25
3			65[d]	84:16
4			66	69:31
5			77	74:26
6			88	83:17
7			71	81:19
8			69	87:13
9			71	75:25
10			90	84:16
11			73	86:14

(a) All reactions were performed in dichloromethane at -78°C. (b) d.r. = diastereomeric ratio. (c) Measured by ^{1}H- or ^{77}Se-NMR integration. (d) The product contained a small amount of diselenide **1a** after chromatography. The yield is based on NMR integration of the isolated product mixture.

symmetrical *cis*-olefin, and the diastereoselectivity is thus determined by the site of attack by the nucleophile upon the seleniranium ion in the product-forming step.[6f]

In each example in Table 3, the mixture of diastereomers was isolated by chromatography and the d.r. was determined by ^{1}H or ^{77}Se NMR integration. In the case of *cis*-stilbene (entry 4), the product could not be separated from a small amount of diselenide **1a** that was formed as a byproduct and the reported yield is based on NMR integration of the isolated mixture.

The absolute configuration of the new stereocenter in the adduct derived from styrene (entry 5) was determined by reductive deselenization to **15** with triphenyltin hydride[15] (Scheme 6). Comparison of the product by GC analysis on a chiral Cyclodex B column with authentic (*R*)-methyl ether **15**, derived from the *O*-methylation of (*R*)-1-phenylethanol, indicated that the major enantiomer from the deselenization also had the *R*-configuration. Therefore, the corresponding stereocenter in the major diastereomer of the adduct had the *S* configuration. There was an excellent correlation between the d.r of the adduct (74:26) and the enantiomeric ratio (e.r.) of the deselenized product (72:28). The absolute configurations of new stereocenters in the other products in Table 3 are not known with certainty at this time.

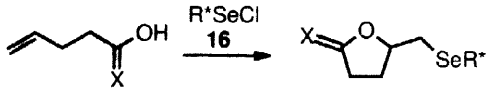


Scheme 6

Cyclofunctionalizations

The cyclofunctionalization of unsaturated alcohols and carboxylic acids was also investigated. These reactions can be performed with selenenyl chlorides **16**, derived from the corresponding diselenides **1** with sulfuryl chloride, and generation of the more reactive triflates proved unnecessary. In order to evaluate the efficacy of various camphorseleno moieties, we performed cyclizations of two test substrates under identical conditions, in dichloromethane at -78°C. The results with 4-penten-1-ol and 4-pentenoic acid are shown in Table 4. It is interesting to note that the camphor auxiliary containing the 2-keto group that had provided the best results in methoxyselenenylations afforded very poor diastereoselectivity in cyclofunctionalizations (entry 1 and 2), whereas the *spiro*-oxazolidinone analogue proved highly effective in the latter processes (entry 5 and 6), but not in the former. Additional experiments revealed that again higher temperatures

Table 4.[a] **Cyclization of 4-penten-1-ol and 4-pentenoic acid with selenenyl chlorides 16**



entry	R*SeCl	X	isolated yield (%)	d.r.[b,c]
1	**16a**	H,H	57	58:42
2		O	87	53:47
3	**16b**	H,H	66	71:29
4		O	73	73:27
5	**16c**	H,H	89	90:10
6		O	85	93:7
7	**16e**	H,H	99	52:48
8		O	81	51:49
9	**16g**	H,H	82	65:35
10		O	100	64:36

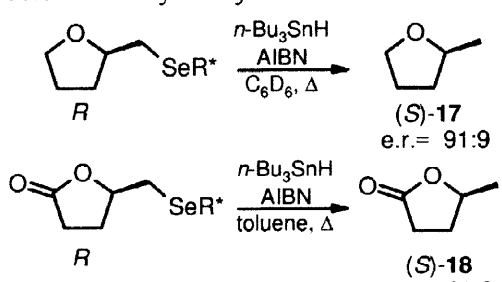
(a) All reactions were performed in dichloromethane at -78°C. (b) d.r. = diastereomeric ratio. (c) Measured by NMR integration.

resulted in lower d.r.'s while further cooling to -95°C gave comparable, or in some cases improved, diastereoselectivity. The use of ether, toluene or methanol as the solvent gave inferior results and the inclusion of triethylamine resulted in more complex product mixtures. With this information in hand, we proceeded to investigate the cyclization of other unsaturated alcohols and carboxylic acids in dichloromethane at -95 °C, using the selenenyl chloride **16c**. The results are shown in Table 5.

Table 5 shows that d.r.'s ranging from modest to excellent are available with a wide variety of substrates. In general, mono- and 1,2-disubstituted alkenes gave the best results. In contrast to the methoxyselenenylations effected with **10a**, and to cyclofunctionalizations reported with other chiral selenium electrophiles,[6a,7b] *cis*-alkenes gave comparable or better d.r.'s than *trans*-alkenes.

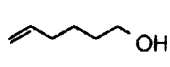
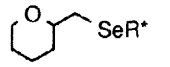
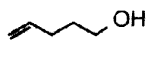
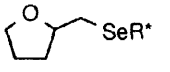
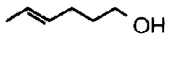
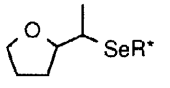
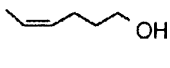
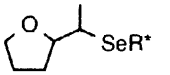
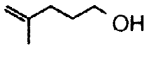
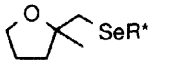
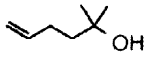
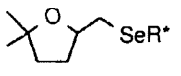
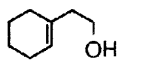
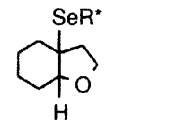
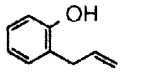
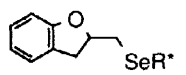
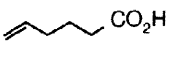
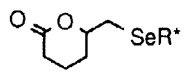
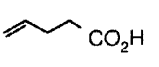
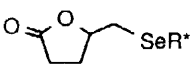
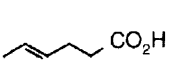
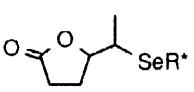
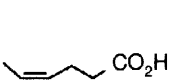
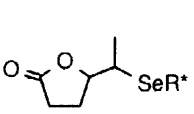
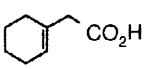
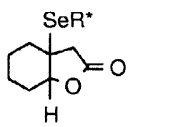
In general, the reactions were performed at -95°C for 45 min, after which time the colour of the selenenyl chloride had disappeared. The mixtures were then warmed to room temperature and subjected to chromatography over silica-gel. Longer reaction times were required for the consumption of the selenenyl chloride in entry 7 (4 h at -95°C) and 13 (8 h at -95°C and 12 h at room temperature). In several examples, NMR analysis of the crude mixture prior to chromatography indicated the presence of different products from the ones listed in Table 5. Thus, in entry 10, the corresponding 1,2-addition product (see Scheme 2) was tentatively identified, but it reacted further during chromatography to form the expected lactone shown in the Table. In entries 3 and 11, NMR spectra of the initial crude materials indicated mixtures of *exo* and *endo* cyclization products (see Scheme 2). In entry 11, equilibration to the *exo*-lactone shown in the Table again occurred during chromatography, while in entry 3, treatment with a catalytic amount of *p*-toluenesulfonic acid was required in order to complete the transformation to the corresponding *exo* cyclic ether.[16] These observations are consistent with the following scenario. The overall stereochemical outcome of the process is determined by the facial selectivity in the initial step, leading to the formation of diastereomeric seleniranium ions, regardless of which of the three products in Scheme 2 is/are ultimately formed. This step requires low temperatures for optimum diastereoselectivity. Subsequent product formation via either the 1,2-addition pathway or via *endo* or *exo* cyclization is stereospecific (*anti* attack upon the seleniranium ion) and reversible. Thus, equilibration between the three products proceeds via the same seleniranium ion diastereomers, whose ratio remains unchanged. The diastereoselectivity is therefore established in the first step at -95°C, while the nature of the final product (1,2-, *exo* or *endo*) is determined subsequently and under thermodynamic control in the above protocol. Only the major products were isolated, characterized and shown in the Table.

The absolute configurations of two representative products in Table 5 from entries 2 and 10 were determined by tin hydride deselenization to afford products **17** and **18**, which have known specific rotations. Thus, it was established by polarimetry that the major enantiomer of **17** and **18** in each case had the *S*- configuration, and therefore the corresponding stereocenters in both selenides were *R*. (Scheme 7). There was again excellent agreement between the e.r.'s of the products and the d.r.'s of their selenide precursors. As with methoxyselenenylations, the extrapolation of these results to obtain the absolute configurations of new stereocenters in other products in Table 5 cannot be made with certainty.



Scheme 7

Table 5.[a] Cyclizations of alkenols and alkenoic acids with **16c**

entry	substrate	product	isolated yield (%)	d.r.[b,c]
1			96	87:13
2			87	84:16
3			92	85:15
4			80	95:5
5			93	71:29
6			61	84:16
7			73	57:43
8			93	92:8
9			87	91:9
10			81	>95:5
11			80	89:11
12			78	91:9
13			66	67:33

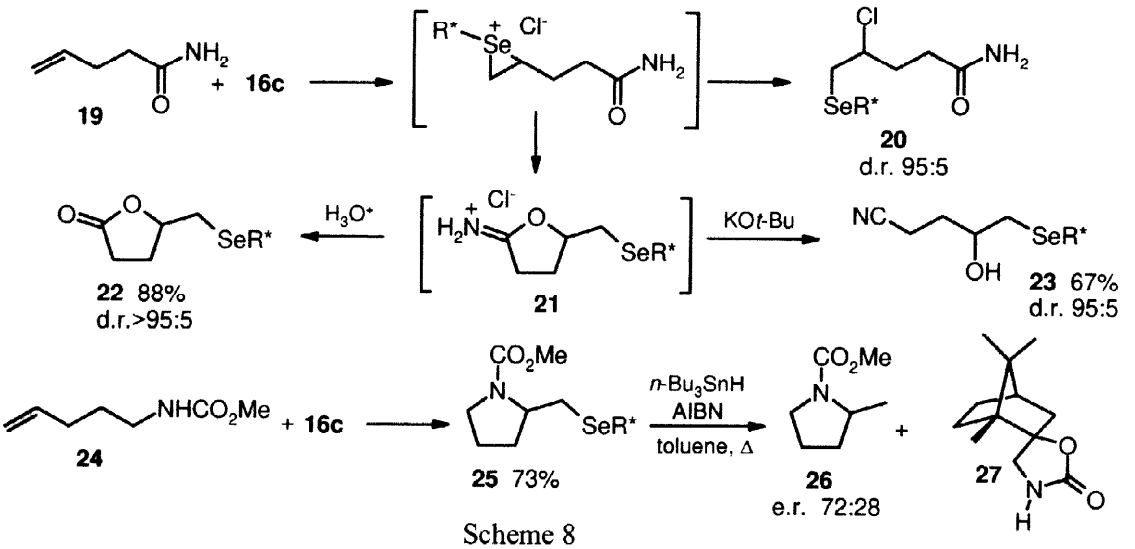
(a) All reactions were performed in dichloromethane at -95°C. (b) d.r. = diastereomeric ratio. (c) Measured by NMR integration, except in entry 7 where diastereomers were separated.

We also investigated the cyclofunctionalization of amide **19** and urethane **24** with selenenyl chloride **16c**. Surprisingly, amide **19** did not furnish the corresponding lactam, but instead afforded other products dependent upon the conditions. Thus, under neutral conditions, the unstable 1,2-addition product **20** was obtained. When the reaction was performed in the presence of *p*-toluenesulfonic acid, or when **20** was exposed to silica-gel, the product was the lactone **22**, identical to the product in entry 10 in Table 5. Finally, when the reaction was repeated in the presence of potassium t-butoxide, the hydroxy nitrile **23** was isolated. Evidently, the ambident amide nucleophile cyclizes through the carbonyl oxygen atom and generates the iminium ion **21**, which undergoes hydrolysis or elimination to afford **22** and **23**, respectively. It is noteworthy that all three products were obtained with very high d.r.'s (Scheme 8). Urethane **24**, on the other hand, cyclized to the corresponding lactam **25** as expected. Unforunately, the d.r. could not be determined accurately by NMR integration because of overlapping signals. Consequently, the product was subjected to deselenization and the e.r. of the lactam **26** was determined by GC with a Cyclodex B column (Scheme 8).

Conclusions

In conclusion, these experiments show that camphor-based selenium electrophiles are useful reagents for asymmetric transformations. They afford modest to excellent diastereoselectivity in both methoxyselenenylations and cyclofunctionalizations, depending on the nature of the substrate. While methoxyselenenylations require selenium reagents with non-nucleophilic counterions (e.g. triflate), cyclofunctionalizations proceed efficiently with the corresponding selenenyl chlorides, although equilibration of the initial product mixture is sometimes required to obtain optimum results. Both types of reaction give considerably higher diastereoselectivity at low temperatures. Furthermore, these mechanistically related processes place surprisingly different demands upon the C-2 substituent of the camphor moiety. Thus, while the 2-keto moiety of **10a** gave the best results in methoxyselenenylations and the *spiro*-oxazolidinone group of **16c** proved ineffective, the converse was

true for cyclofunctionalizations. Further work is in progress to ascertain more precisely the role played by the C-2 substituent, which may include steric, coordination and/or hydrogen-bonding effects, in determining the stereoselectivity, and to extend this work to other types of asymmetric selenium chemistry.



Scheme 8

Experimental Section

NMR spectra were recorded on a Bruker ACE 200 or AM 400 spectrometer in $CDCl_3$ solution unless otherwise indicated. Chemical shifts of ^{77}Se NMR spectra are reported relative to dimethyl selenide as the standard. Chromatography was performed on flash grade silica-gel. GC was performed on a 30 m Cyclodex B column (J & W Scientific Co.). Diselenide **1a** was prepared as described previously.[8] Ether (*R*)-**15** was prepared by treating (*R*)-1-phenylethanol (Aldrich Chemical Co.) with NaH and methyl iodide in THF. It had an e.r. >98:2 when analyzed by GC on a chiral column. Other reagents were purchased and purified as required. Organic solutions were dried over anhydrous Na_2SO_4 or $MgSO_4$.

Allyl *endo*-3-camphoryl selenide (2). Sodium borohydride (4.14 g, 110 mmol) was added in portions to an ice-cooled solution of diselenide **1a** (10.0 g, 21.7 mmol) in 200 mL of ethanol. The reaction mixture was stirred for an additional 1 h at room temperature. Allyl iodide (8.0 mL, 88 mmol) was added and stirring was continued for 45 min. The mixture was poured into 500 mL of ether, washed with 5% HCl solution, three times with water and brine, and was dried and concentrated *in vacuo*. The residue was chromatographed (elution with 10% ethyl acetate-hexanes) to afford 10.9 g (92%) of **2** as a pale yellow oil: IR (film) 1735, 1630 cm^{-1}; ^1H NMR δ 6.04-5.83 (m, 1 H), 5.13-5.01 (m, 2 H), 3.64-3.61 (m, 1 H), 3.57 (dd, *J*= 12.0, 8.6 Hz, 1 H), 3.30 (ddd, J= 11.4, 7.5, 0.7 Hz, 1 H), 2.17-2.13 (m, 1 H), 1.94-1.40 (m, 4 H), 1.02 (s, 3 H), 0.93 (s, 3 H), 0.90 (s, 3 H); mass spectrum, *m/z* (relative intensity) 272 (42, M^+), 231 (3), 152 (82), 41 (100). Anal. calc'd. for $C_{13}H_{20}OSe$: C, 57.56; H, 7.43. Found: C, 57.59; H, 7.39.

Amino alcohol 3. A mixture of selenide **2** (18.9 g, 69.8 mmol), trimethylsilyl cyanide (10.2 mL, 76.5 mmol) and ZnI_2 (2.23 g, 6.99 mmol) was stirred for 2 days. The mixture was diluted with 300 mL of ether, washed twice with water and brine, dried, filtered through Celite and concentrated *in vacuo* to afford 24.8 g (96%) of the corresponding cyanohydrin trimethylsilyl ether, which solidified on standing: mp 49-53°C; IR (film) 2228, 1630 cm^{-1}; ^1H NMR δ 5.94-5.85 (m, 1 H), 5.08-5.04 (m, 1 H), 5.00-4.98 (m, 1 H), 3.45 (dd, *J*= 3.7, 1.9 Hz, 1 H), 3.22 (d, *J*= 7.5 Hz, 1 H), 3.20 (d, *J*= 8.1 Hz, 1 H), 1.84-1.81 (m, 1 H), 1.77-1.53 (m, 4 H), 1.07 (s, 3 H), 0.96 (s, 3 H), 0.95 (s, 3 H), 0.27 (s, 9 H); mass spectrum, *m/z* (relative intensity) 371 (8, M^+),

330 (2), 250 (62), 151 (13), 95 (84), 83 (100). Anal. calc'd. for $C_{17}H_{29}NOSeSi$: C, 55.12; H, 7.89; N, 3.78. Found: C, 55.39; H, 7.54; N, 3.90.

The above cyanohydrin (24.0 g, 64.8 mmol) in 100 mL of anhydrous ether was added over 1 h to an ice-cooled suspension of 12.3 g (325 mmol) of $LiAlH_4$ in 100 mL of ether. The mixture was refluxed for 9 h and cooled to room temperature. Water (13 mL), 4 N NaOH solution (13 mL) and water (39 mL) were added cautiously with vigorous stirring. The mixture was filtered, the aqueous layer was removed, and the ether layer was dried and concentrated *in vacuo* to afford 20.1 g (100%) of **3** as a colourless oil: IR (film) 3395, 3305, 1630 cm^{-1}; ^1H NMR δ 5.97-5.84 (m, 1 H), 5.11-4.99 (m, 2 H), 3.39-3.36 (m, 1 H), 3.23-3.17 (m, 2 H), 2.96 (d, *J*= 12.4 Hz, 1 H), 2.53 (d, *J*= 12.4 Hz, 1 H), 1.80-1.75 (m, 1 H), 1.69-1.27 (m, 4 H); 1.21 (s, 3 H), 0.90 (s, 3 H), 0.83 (s, 3 H). The crude product was employed without further purification in subsequent procedures.

Acetamide 4. Amino alcohol **3** (5.20 g, 17.1 mmol) was stirred in 30 mL of a 2:1 mixture of of pyridine and acetic anhydride at room temperature for 16 h. The mixture was poured into 100 mL of ether, washed twice with 5% HCl solution and K_2CO_3 solution, dried and concentrated *in vacuo*. The residue was chromatographed (elution with 60% ethyl acetate-hexanes) to afford 4.98 g (84%) of **4** as a yellow oil: IR (film) 3309, 1649 cm^{-1}; ^1H NMR δ 6.22 (br s, 1 H), 6.05-5.84 (m, 1 H), 5.15-5.01 (m, 2 H), 3.81 (dd, *J*= 14.3, 7.8 Hz, 1 H), 3.43-3.39 (m, 1 H), 3.28-3.10 (m, 4 H), 2.04 (s, 3 H), 1.84-1.80 (m, 1 H), 1.66-1.22 (m, 4 H), 1.14 (s, 3 H), 0.95 (s, 3 H), 0.89 (s, 3 H); mass spectrum, *m/z* (relative intensity) 345 (3, M^+), 304 (7), 224 (41), 109 (63), 72 (68), 43 (100). Anal. calc'd. for $C_{16}H_{27}NO_2Se$: C, 55.81; H, 7.90; N, 4.07. Found: C, 56.15; H, 7.98; N, 4.02.

Diselenide 1b. A suspension of 2.17 g (7.2 mmol) of 57% MCPBA in 10 mL of dichloromethane was added to a stirred solution of acetamide **4** (1.42 g, 4.13 mmol) in 50 mL of dichloromethane at -78°C. The mixture was warmed to -40°C over 25 min, and diethylamine was added until the mixture became homogeneous (ca. 4 mL). Ethyl vinyl ether (3 mL) was added and the mixture was maintained at -28°C for 4 h with occasional swirling. Hydrazine (0.65 mL, 20.7 mmol) was added and the mixture was stirred at room temperature for 30 min. The solution was diluted with 50 mL of dichloromethane, washed twice with 1.5 N NaOH solution, water and brine, dried and concentrated *in vacuo*. The product was chromatographed (elution with 10% methanol-ethyl acetate) to afford 1.13 g (90%) of **1b** as a yellow foam: IR (Nujol) 3291, 1635 cm^{-1}; ^1H NMR δ 6.18-6.07 (m, 2 H), 4.03-4.00 (m, 2 H), 3.70 (dd, *J*= 14.4, 7.2 Hz, 2 H), 3.55 (s, 2 H), 3.34 (dd, J= 14.4, 4.7 Hz, 2 H), 2.04 (s, 6 H), 2.08-2.03 (m, 2 H), 1.67-1.26 (m, 8 H), 1.17 (s, 6 H), 0.94 (s, 6 H), 0.90 (s, 6 H); mass spectrum, *m/z* (relative intensity) 608 (1, M^+), 305 (10), 287 (16), 206 (64), 109 (65), 43 (100). Anal. calc'd. for $C_{26}H_{44}N_2O_4Se_2$: C, 51.48; H, 7.31; N, 4.62. Found: C, 51.22; H, 7.23; N, 4.55.

Oxazolidinone 5. Amino alcohol **3** (980 mg, 3.24 mmol) and N,N'-carbonylbis(imidazole) (579 mg, 3.57 mmol) were stirred in 5 mL of dry THF for 7 h at room temperature. The solution was poured into 50 mL of ether, washed with 5% HCl solution and brine, dried and concentrated *in vacuo*. The residue was chromatographed (elution with 60% ethyl acetate-hexanes) to afford 849 mg (80%) of **5** as a white powder: mp 112-113°C (from ethyl acetate-hexanes); IR (film) 3381, 1714, 1631 cm^{-1}; ^1H NMR δ 5.91 (br s, 1 H), 5.95-5.73 (m, 1 H), 5.09-5.00 (m, 2 H), 4.07 (d, *J*= 9.2 Hz, 1 H), 3.67 (dd, *J*= 3.8, 2.5 Hz, 1 H), 3.55 (d, *J*= 9.2 Hz, 1 H), 3.26-3.16 (m, 2 H), 1.96-1.92 (m, 1 H), 1.82-1.18 (m, 4 H), 1.14 (s, 3 H), 0.93 (s, 3 H), 0.91 (s, 3 H); mass spectrum, *m/z* (relative intensity) 329 (100, M^+), 288 (16), 228 (21), 164 (23), 126 (27), 41 (36). Anal. calc'd. for $C_{15}H_{23}NO_2Se$: C, 54.88; H, 7.06; N, 4.27. Found: C, 54.58; H, 6.96; N, 4.25.

Diselenide 1c. The product**1c** was prepared in 75% yield from **5** by the same procedure as employed in the preparation of **1b**: mp 278-282 °C (from ethanol); IR (Nujol) 3262, 1748 cm^{-1}; ^1H NMR δ 5.59 (br s, 2 H), 4.15 (dd, *J*= 3.9, 2.2 Hz, 2 H), 3.85 (d, *J*= 9.5 Hz, 2 H), 3.57 (d, *J*= 9.5 Hz, 2 H), 2.12-2.08 (m, 2 H), 1.64-1.25 (m, 6 H), 1.17 (s, 6 H), 1.11-1.04 (m, 2 H), 0.94 (s, 12 H); mass spectrum, *m/z* (relative intensity) 576 (11, M^+), 369 (3), 208 (100), 164 (48), 147 (42), 41 (56). Anal. calc'd. for $C_{24}H_{36}N_2O_4Se_2$: C, 50.18; H, 6.32; N, 4.88. Found: C, 50.34; H, 6.25; N, 4.90.

***exo*-Alcohol 6 and *endo*-alcohol 8.** Selenide **2** (5.01 g, 18.5 mmol) in 40 mL of dry ether was added over 5 min to an ice-cooled suspension of $LiAlH_4$ (2.11 g, 55.7 mmol) in 20 mL of dry ether. The mixture

was stirred for 4 h at room temperature. Water (2 mL), 4 N NaOH solution (2 mL) and water (6 mL) were cautiously added with vigorous stirring. The mixture was filtered, dried and concentrated *in vacuo*. The residue was chromatographed (elution with 20% ethyl acetate-hexanes) to afford 1.54 g (30%) of the *endo*-alcohol **8**, followed by 3.00 g (59%) of the *exo*-alcohol **6**, each obtained as a colourless oil.

exo-Alcohol **6**: IR (film) 3457, 1632 cm^{-1}; ^1H NMR δ 6.10-5.89 (m, 1 H), 5.15-4.98 (m, 2 H), 3.54 (d, *J*= 3.9 Hz, 1 H), 3.39-3.37 (m, 1 H), 3.26 (br d, *J*= 6.7 Hz, 2 H), 1.82-1.80 (m, 1 H), 1.80 (br s, 1 H), 1.69-1.51 (m, 4 H), 1.08 (s, 3 H), 0.89 (s, 6 H); mass spectrum, *m/z* (relative intensity) 274 (14, M^+), 233 (5), 153 (9), 95 (34), 83 (90), 41 (100). Anal. calc'd for $C_{13}H_{22}OSe$: C, 57.14; H, 8.11. Found: C, 56.79; H, 7.63.

endo-Alcohol **8**: IR (film) 3448, 1631 cm^{-1}; ^1H NMR δ 6.00-5.79 (m, 1 H), 5.10-4.99 (m, 2 H), 3.73-3.71 (m, 2 H), 3.13 (d, *J*=7.7 Hz, 2 H), 1.93-1.89 (m, 1 H), 1.83-1.55 (m, 2 H), 1.36-1.13 (m, 2 H), 0.95 (s, 3 H), 0.91 (s, 3 H), 0.89 (s, 3 H); mass spectrum, *m/z* (relative intensity) 274 (21, M^+), 233 (8), 153 (15), 95 (41), 83 (100), 41 (71). Anal. calc'd. for $C_{13}H_{22}OSe$: C, 57.14; H, 8.11. Found: C, 57.34; H, 7.91.

***exo*-Acetate 7**. Alcohol **6** (3.70 g, 13.6 mmol) was heated at 105°C in 50 mL of a 2:1 solution of pyridine and acetic anhydride for 14 h. The solution was cooled, poured into 100 mL of ether, washed three times with 5% HCl solution, water and brine, dried and concentrated *in vacuo* to afford 4.24 g (99%) of **7** as a yellow oil: IR (film) 1732, 1670 cm^{-1}; ^1H NMR δ 6.01-5.80 (m, 1 H), 5.04-4.96 (m, 1 H), 4.96-4.93 (m, 1 H), 4.82 (d, *J*= 4.0 Hz, 1 H), 3.44-3.42 (m, 1 H), 3.17 (d, *J*= 7.7 Hz, 2 H), 2.06 (s, 3 H), 1.86-1.84 (m, 1 H), 1.72-1.53 (m, 3 H), 1.38-1.21 (m, 1 H), 1.04 (s, 3 H), 0.90 (s, 3 H), 0.79 (s, 3 H). The crude product was employed without further purification in subsequent procedures.

***endo*-Acetate 9**. Product **9** was obtained in 99% yield as a colourless oil from alcohol **8** via the same procedure used in the preparation of **7**. IR (film) 1740, 1631 cm^{-1}; ^1H NMR δ 5.91-5.74 (m, 1 H), 5.06-4.94 (m, 3 H), 3.66 (ddd, *J*= 9.6, 4.2, 2.3 Hz, 1 H), 3.08 (d, *J*=7.8 Hz, 1 H), 3.06 (d, *J*= 7.5 Hz, 1 H), 2.14 (s, 3 H), 1.89-1.62 (m, 3 H), 1.35-1.22 (m, 1 H), 0.99 (s, 3 H), 0.95 (s, 3 H), 0.82 (s, 3 H). The crude product was employed without further purification in subsequent procedures.

Diselenide 1d. Product**1d** was prepared in 68% yield from **7** by the same procedure as employed in the preparation of **1b**: yellow solid, mp 114-116°C (from ethanol); IR (Nujol) 1730 cm^{-1}; ^1H NMR δ 4.70 (d, *J*= 4.2 Hz, 2 H), 3.87 (ddd, *J*= 4.1, 4.1, 1.4 Hz, 2 H), 2.07 (s, 6 H), 1.99-1.95 (m, 2 H), 1.78-1.53 (m, 6 H), 1.28-1.19 (m, 2 H), 1.06 (s, 6 H), 0.91 (s, 6 H), 0.79 (s, 6 H); mass spectrum, *m/z* (relative intensity) 550 (12, M^+), 135 (94), 43 (100). Anal. calc'd. for $C_{24}H_{38}O_4Se_2$: C, 52.56; H, 6.98. Found: C, 52.39; H, 6.76.

Diselenide 1e. Compound **1d** (1.68 g, 3.06 mmol) was heated at 70°C for 6 h in 35 mL of dioxane and 20 mL of 1 N aqueous NaOH solution. The mixture was concentrated *in vacuo*, the residue was taken up in 100 mL of ether, washed with water and brine, dried and evaporated to afford 1.31 g (92%) of **1e** as a yellow solid: mp 125-129°C (from ethanol); IR (Nujol) 3341 cm^{-1}; ^1H NMR δ 3.83 (ddd, *J*= 3.9, 3.9, 2.3 Hz, 2 H), 3.73-3.71 (m, 2 H), 3.03 (s, 2 H), 2.03-1.99 (m, 2 H), 1.67-1.47 (m, 6 H), 1.10 (s, 6 H), 1.40-1.00 (m, 2 H), 0.89 (s, 6 H), 0.88 (s, 6 H); mass spectrum, *m/z* (relative intensity) 466 (10, M^+), 296 (8), 135 (90), 83 (100). Anal. calc'd. for $C_{20}H_{34}O_2Se_2$: C, 51.73; H, 7.38. Found: C, 51.66; H, 7.11.

Diselenide 1f. Product**1f** was prepared in 50% yield from **7** by the same procedure as employed in the preparation of **1b**: yellow solid, mp 124-125°C (from ethanol); IR (Nujol) 1731 cm^{-1}; ^1H NMR δ 5.16 (dd, *J*= 9.8, 2.0 Hz, 2 H), 4.10 (ddd, *J*= 9.7, 4.1, 2.6 Hz, 2 H), 2.10 (s, 6 H), 1.97-1.93 (m, 2 H), 1.87-1.74 (m, 4 H), 1.70-1.64 (m, 2 H), 1.35-1.20 (m, 2 H), 1.01 (s, 6 H), 0.97 (s, 6 H), 0.81 (s, 6 H); mass spectrum, *m/z* (relative intensity) 550 (1, M^+), 135 (67), 43 (100). Anal. calc'd. for $C_{24}H_{38}O_4Se_2$: C, 52.56; H, 6.98. Found: C, 52.27; H, 6.71.

Diselenide 1g. Product **1g** was prepared in 92% yield from **1f** by the same procedure as employed in the preparation of **1e**: yellow solid, mp 126-130°C (from ethanol); IR (Nujol) 3487 cm^{-1}; ^1H NMR δ 4.25 (ddd, *J*= 9.2, 4.2, 2.5 Hz, 2 H), 3.96 (d, *J*= 8.9 Hz, 2 H), 2.71 (br s, 2 H), 2.03-1.99 (m, 2 H), 1.87-1.74 (m, 2 H), 1.66-1.40 (m, 4 H), 1.29-1.14 (m, 2 H), 0.95 (s, 6 H), 0.92 (s, 6 H), 0.88 (s, 6 H); mass spectrum, *m/z* (relative intensity) 466 (17, M^+), 296 (3), 135 (69), 95 (100). Anal. calc'd. for $C_{20}H_{34}O_2Se_2$: C, 51.73; H, 7.38. Found: C, 51.55; H, 7.07.

Methoxyselenenylations in Tables 1-3. The same general procedure as given for entry 1 of Table 3 below was employed in Tables 1 and 2, using *cis*- or *trans*-5-decene, with the variations indicated in the Tables. D.r.'s were measured by integration of ^{1}H NMR signals from protons at C-3 or C-4 of the camphor moiety, which were generally well-separated for the two diastereomers, or by integration of the methoxy or camphor methyl signals. In entry 7 of Table 3, the respective ^{77}Se NMR signals were integrated. Spectroscopic properties for the other adducts in Table 3 are given below. Assignments of ^{13}C NMR signals are tentative because of frequent coincidence between signals from the two stereoisomers and the low intensity of peaks from the minor products.

Methoxyselenenylation of *trans*-5-decene (Typical procedure, Table 3, entry 1). Diselenide **1a** (50 mg, 0.11 mmol) and 100 mg of 4 Å molecular sieves were stirred in 3 mL of dry dichloromethane. A 1 M solution of bromine (0.11 mL, 0.11 mmol) in tetrachloromethane was added dropwise at -78°C under nitrogen, with stirring. After 15 min, a 0.70 M methanol solution of silver triflate (0.45 mL, 0.30 mmol) was added, followed after another 15 min by *trans*-5-decene (0.10 mL, 0.53 mmol). Stirring was continued for 1 h at -78°C. The reaction was quenched with aqueous $NaHCO_3$ solution, diluted with 10 mL of dichloromethane, washed with water and brine, dried, filtered, and concentrated *in vacuo*. The residue was chromatographed (elution with 5% ethyl acetate-hexanes) to afford 78 mg (88%) of the addition product as a pale yellow oil: IR (film), 1738 (C=O) cm^{-1}; ^{1}H NMR major diastereomer: δ 3.78 (d, *J*= 4.7 Hz, 1 H), 3.42 (s, 3 H), 3.49-3.32 (m, 2 H), 2.21-2.19 (m, 1 H), 1.86-1.25 (m, 16 H), 1.02 (s, 3 H), 0.93 (s, 3 H), 0.92 (s, 3 H), 0.92-0.89 (m, 6 H); minor diastereomer: δ 3.99 (d, *J*= 4.8 Hz, 1 H), 3.39 (s, 3 H); ^{13}C NMR major diastereomer: δ 218.5, 85.4, 58.4, 58.2, 48.9, 47.0, 46.6, 46.0, 31.7, 31.4, 30.9, 30.6, 28.5, 23.7, 23.1, 22.8, 19.8, 14.3 (two signals), 14.2, 10.0; minor diastereomer: δ 85.8, 57.9, 30.7 (two signals), 23.5, 19.8; mass spectrum, *m/z* (relative intensity) 402 (21, M$^+$), 370 (19), 230 (50), 151 (65), 101 (100), 69 (99). Exact mass calc'd for $C_{21}H_{38}O_2Se$: 402.2040. Found: 402.2059.

Methoxyselenenylation of *cis*-5-decene (Table 3, entry 2). IR (film) 1738 cm^{-1}; ^{1}H NMR, major diastereomer: δ 3.65 (d, *J*= 4.6 Hz, 1 H), 3.40 (s, 3 H), 3.48-3.25 (m, 2 H), 2.25-2.21 (m, 1 H), 1.91-1.01 (m, 16 H), 1.02 (s, 3 H), 0.93 (s, 3 H), 0.91 (s, 3 H), 0.99-0.61 (m, 6 H); minor diastereomer: δ 3.75 (d, *J*= 3.4 Hz, 1 H), 3.38 (s, 3 H), 2.18-2.17 (m, 1 H); ^{13}C NMR, major diastereomer: δ 218.6, 84.9, 58.4, 57.9, 49.0, 48.9, 46.7, 45.6, 32.0, 31.1, 30.9, 30.6, 28.9, 28.8, 23.7, 22.8, 19.8 (two signals), 14.3 (two signals), 10.0; minor diastereomer: δ 84.8, 58.3, 58.0, 47.0, 45.5, 31.7, 31.1, 30.6, 29.9, 23.6, 23.0, 19.9, 14.2; mass spectrum, *m/z* (relative intensity) 402 (10, M$^+$), 370 (5), 230 (14), 171 (29), 151 (17), 101 (100). Exact mass calc'd for $C_{21}H_{38}O_2Se$: 402.2040. Found: 402.2055.

Methoxyselenenylation of *trans*-stilbene (Table 3, entry 3). The adduct could not be separated from a small amount of diselenide **1a**, and the yield as well as the d.r. given in Table 3 is based on ^{1}H NMR integration: ^{1}H NMR, major diastereomer: δ 7.55-7.13 (m, 10 H), 4.71 (d, *J*= 9.3 Hz, 1 H), 4.55 (d, *J*= 9.2 Hz, 1 H), 3.12 (s, 3 H), 2.72-2.69 (m, 1 H), 2.04-1.26 (m, 5 H,), 0.88 (s, 3 H), 0.83 (s, 3 H), 0.51 (s, 3 H); minor diastereomer: δ 3.11-2.99 (m, 3 H), 0.60 (s, 3 H).

Methoxyselenenylation of *cis*-stilbene (Table 3, entry 4). IR (film) 1735 cm^{-1}; ^{1}H-NMR, major diastereomer: δ 7.23-7.09 (m, 10 H), 4.87 (d, *J*= 9.4 Hz, 1 H), 4.55 (d, *J*= 9.4 Hz, 1 H), 3.27 (s, 3 H), 3.05-3.00 (m, 1 H), 2.00-0.93 (m, 5 H), 0.88 (s, 3 H), 0.84 (s, 3 H), 0.54 (s, 3 H); minor diastereomer: δ 3.29 (s, 3 H), 0.92 (s, 3 H); ^{13}C NMR, major diastereomer: δ 139.5, 129.6, 128.3 (two signals), 128.0, 127.6, 127.5, 127.3, 88.2, 57.3, 56.7, 49.0, 48.4, 46.3, 30.8, 24.1, 23.3, 20.0, 19.4, 9.9; minor diastereomer: δ 129.2, 128.6, 51.5, 47.0, 46.9, 19.8, 19.6, 10.0; mass spectrum, *m/z* (relative intensity) 442 (5, M$^+$), 410 (10), 321 (100), 211 (41), 121 (60). Exact mass calc'd for $C_{25}H_{30}O_2Se$ 442.1415. Found: 442.1423.

Methoxyselenenylation and deselenization of styrene (Table 3, entry 5). IR (film) 1735 cm^{-1}; ^{1}H NMR, major diastereomer: δ 7.37-7.26 (m, 5 H), 4.48 (dd, *J*= 8.6, 4.5 Hz, 1 H), 3.56-3.54 (m, 1 H), 3.27 (s, 3 H), 3.26-2.96 (m, 2 H), 2.14-2.10 (m, 1 H), 1.82-1.38 (m, 4 H), 0.99 (s, 3 H), 0.91 (s, 3 H), 0.81 (s, 3 H); minor diastereomer: δ 4.39-4.42 (t, *J*= 7.1 Hz, 1 H), 3.25 (s, 3 H), 2.06-2.04 (m, 1 H), 0.98 (s, 3 H), 0.89 (s, 3 H), 0.79 (s, 3 H); ^{13}C NMR, major diastereomer: δ 218.7, 141.4, 128.7, 128.2, 126.8, 84.4, 57.2, 48.6, 48.5, 47.3, 46.9, 32.0, 30.7, 29.9, 23.5, 19.8 (two signals), 9.9; minor diastereomer: δ 128.3, 127.2, 84.6, 31.2,

30.7, 23.5, 19.7; mass spectrum, *m/z* (relative intensity) 366 (9, M^+), 334 (16), 230 (11), 121 (100). Exact mass calc'd for $C_{19}H_{26}O_2Se$: 366.1100. Found: 366.1063.

A mixture of AIBN (10 mg) and triphenyltin hydride (192 mg, 0.55 mmol) was added dropwise to a refluxing solution of the above product (100 mg, 0.27 mmol) in 2 mL of toluene under nitrogen. After 2 h, additional triphenyltin hydride (96 mg, 0.27 mmol) and AIBN (5 mg) were added, and heating was continued for 1 h. The reaction mixture was separated by chromatography (elution with hexanes followed by 10% ether-hexanes). The solvent was removed by distillation, followed by Kugelrohr distillation of the residue (bp 70-90 °C, 130 mmHg) to afford the methyl ether **15** as a colourless oil, the e.r. of which was determined to be 74:26 by GC on a Cyclodex B column. The absolute configuration of the major enantiomer was assigned by comparison with an authentic sample of the (*R*)-enantiomer. The NMR spectrum of the product was identical to that of the authentic sample.

Methoxyselenenylation of α-methylstyrene (Table 3, entry 6). IR (film) 1740 cm^{-1}; ^1H NMR, major diastereomer: δ 7.39-7.14 (m, 5 H), 3.31-3.05 (m, 3 H), 3.06 (s, 3 H), 1.95-1.93 (m, 1 H), 1.65 (s, 3 H), 1.72-1.26 (m, 4 H), 0.89 (s, 3 H), 0.79 (s, 3 H), 0.66 (s, 3 H); minor diastereomer: δ 3.04 (s, 3 H), 1.89-1.85 (m, 1 H), 1.63 (s, 3 H), 0.87 (s, 3 H); ^{13}C NMR, major diastereomer: δ 218.6, 144.0, 128.4, 127.5, 126.5, 79.6, 79.2, 58.3, 51.1, 48.3, 46.8, 46.6, 38.2, 30.7, 23.4, 23.2, 19.8, 9.8; minor diastereomer: δ 127.6, 126.7, 58.2, 51.1, 48.4, 46.8, 38.0, 30.6, 23.5, 19.7; mass spectrum, *m/z* (relative intensity) 380 (6, M^+), 348 (5), 135 (100), 43 (47). Exact mass calc'd for $C_{20}H_{28}O_2Se$: 380.1257. Found: 380.1271.

Methoxyselenenylation of ethyl vinyl ether (Table 3, entry 7). IR (film) 1746 cm^{-1}; ^1H NMR, major diastereomer: δ 4.70 (t, *J*= 5.5 Hz, 1 H), 3.89 (dd, *J*= 4.4, 1.9 Hz, 1 H), 3.76-3.71 (m, 1 H), 3.59-3.54 (m, 1 H), 3.37 (s, 3 H), 3.01 (dd, *J*= 12.8, 5.8 Hz, 1 H), 2.91 (dd, *J*= 12.8, 5.2 Hz, 1H), 2.21-2.20 (m, 1 H), 1.80-1.40 (m, 4 H), 1.21 (t, *J*= 7.1 Hz, 3 H), 1.01 (s, 3 H), 0.92 (s, 3 H), 0.90 (s, 3 H); minor diastereomer: δ 3.36 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR, major diastereomer: δ 218.5, 104.6, 62.5, 58.4, 53.8, 48.5, 47.2, 47.0, 30.7, 26.8, 23.5, 19.8 (two signals), 15.5, 9.9; minor diastereomer: δ 62.7, 53.5, 29.9. ^{77}Se NMR, major diastereomer: δ 191.6; minor diastereomer: δ 193.7; mass spectrum: *m/z* (relative intensity) 334 (1, M^+), 302 (4), 89 (100), 61 (53). Exact mass calculated for $C_{15}H_{26}O_3Se$: 334.1049. Found: 334. 1053.

Methoxyselenenylation of *trans*-2-butene (Table 3 , entry 8). IR (film): 1729 cm^{-1}; ^1H NMR, major diastereomer: δ 3.77 (d, *J*= 4.8 Hz, 1 H), 3.38-3.72 (m, 2 H), 3.37 (s, 3 H), 2.21-2.20 (m, 1 H), 2.05-1.50 (m, 4 H), 1.46 (d, *J*=7.0 Hz, 3 H), 1.21 (d, *J*= 6.2 Hz, 3 H), 1.03 (s, 3 H), 0.93 (s, 3 H), 0.92 (s, 3 H); minor diastereomer: δ 3.95 (d, *J*= 4.6 Hz, 1 H), 3.36 (s, 3 H), 1.02 (s, 3 H), 0.91 (s, 3 H); ^{13}C NMR, 218.7, 80.9, 58.3, 57.0, 49.0, 47.1, 45.7, 41.0, 30.7, 23.8, 19.9, 19.8, 17.4, 16.8, 9.9; minor diastereomer: δ 81.5, 56.9, 49.0, 46.2, 41.1, 41.0, 23.6, 19.8, 18.4, 16.8, 16.4; mass spectrum, *m/z* (relative intensity) 318 (5, M^+), 230 (8), 152 (33), 87 (46), 41 (100). Exact mass calc'd for $C_{15}H_{26}O_2Se$: 318.1100. Found: 318.1078.

Methoxyselenenylation of cyclohexene (Table 3 , entry 9). IR (film) 1739 cm^{-1}; ^1H NMR, major diastereomer: δ 4.09-4.07 (m, 1 H), 3.38 (s, 3 H), 3.36-3.18 (m, 2 H), 2.21-1.25 (m, 13 H), 1.02 (s, 3 H), 0.92 (s, 6 H); minor diastereomer: δ 3.99-3.40 (m, 1 H), 1.01 (s, 3 H), 0.90 (s, 6 H); ^{13}C NMR, major diastereomer: δ 218.2, 83.6, 58.3, 56.5, 48.8, 47.1 (two signals), 43.0, 31.4, 30.8, 30.1, 25.5, 23.6, 23.3, 20.0, 19.9, 9.9; minor diastereomer: δ 85.0, 56.8, 49.2, 47.3, 44.5, 32.6, 31.0, 26.3, 24.0, 23.7, 20.0, 19.8; mass spectrum, *m/z* (relative intensity) 344 (8, M^+), 312 (11), 230 (12), 151 (11), 113 (78), 81 (100), 45 (53). Exact Mass calc'd for $C_{17}H_{28}O_2Se$: 344.1257. Found: 344.1242.

Methoxyselenenylation of 1-methylcyclohexene (Table 3 , entry 10). IR (film) 1734 cm^{-1}; ^1H NMR, major diastereomer: δ 3.91 (d, *J*= 4.7 Hz, 1 H), 3.57 (dd, *J*= 9.1, 3.9 Hz, 1 H), 3.26 (s, 3 H), 2.23-2.17 (m, 1 H), 1.89-1.40 (m, 12 H), 1.31 (s, 3 H), 1.02 (s, 3 H), 0.92 (s, 6 H); minor diastereomer: δ 3.42 (dd, *J*= 10.1, 3.8 Hz, 1 H) 3.22 (s, 3 H), 1.27 (s, 3 H) 0.90 (s, 6 H); ^{13}C NMR, major diastereomer: δ 218.5, 68.0, 58.3, 48.7, 48.6, 47.1, 47.0, 46.5, 34.9, 30.7, 29.9, 25.1, 23.7, 22.6, 21.6, 19.9, 10.0, 9.9; minor diastereomer: δ 48.9, 23.6, 22.8, 19.8; mass spectrum, *m/z* (relative intensity) 358 (14, M^+), 326 (12), 207 (45), 95 (100), 41 (61). Exact mass calc'd for $C_{18}H_{30}O_2Se$: 358.1413. Found: 358.1403.

Methoxyselenenylation of 1-phenylcyclohexene (Table 3 , entry 11). IR (film) 1737 cm^{-1}; ^1H NMR, major diastereomer: δ 7.50-7.21 (m, 5 H), 3.14-3.01 (m, 1 H), 2.99 (s, 3 H), 2.69-2.36 (m, 2 H), 2.32 (dd, *J*= 4.5, 1.4 Hz, 1 H), 2.10-1.00 (m, 11 H), 0.93 (s, 3 H), 0.77 (s, 3 H), 0.48 (s, 3 H); minor diastereomer:

δ 3.76-3.57 (m, 1 H), 2.96 (s, 3 H), 2.29-2.19 (m, 1 H); ^{13}C NMR, major diastereomer: δ 216.9, 143.8, 128.2, 128.0, 127.5, 80.8, 58.2, 50.6, 49.1, 48.7, 47.4, 46.5, 30.8, 30.2, 25.4, 23.0, 22.2, 21.1, 20.4, 19.8, 9.7; minor diastereomer: δ 144.1, 128.1, 127.4, 80.6, 58.1, 51.0, 50.5, 48.5, 46.8, 46.7, 30.6, 30.0, 25.4, 25.3, 23.4, 22.2, 19.5, 9.8; mass spectrum, *m/z* (relative intensity) 420 (28, M^+), 388 (30), 269 (100), 189 (56), 91 (97). Exact mass calc'd for $C_{23}H_{32}O_2Se$: 420.1570. Found: 420.1552.

Cyclizations in Tables 4-5. The same general procedure as given for entry 1 of Table 5 (*vide infra*) was employed in Table 4, using 4-penten-1-ol and 4-pentenoic acid as substrates, with the variations indicated in the Table. The same procedure was also used for the other examples in Table 5, with variations as indicated below. D.r.'s were measured by integration of ^{1}H NMR signals from protons at C-3 of the camphor moiety, which were generally well-separated for the two diastereomers, or of signals from protons attached to oxygen-substituted carbon atoms. Assignments of ^{13}C NMR signals are tentative because of frequent coincidence between signals from the two stereoisomers and the low intensity of peaks from the minor products.

Cyclization of 5-hexen-1-ol (Table 5, entry 1). Sulfuryl chloride (14 μL, 0.17 mmol) was added to a mixture of diselenide **1c** (99.5 mg, 0.17 mmol) and ca. 20 mg of 4 Å molecular sieves in 5 mL of dichloromethane, and stirring was continued for 15 min. The resulting orange mixture was cooled to -95°C, 46 μL (0.38 mmol) of 5-hexen-1-ol was added and the orange colour was immediately discharged. The mixture was stirred for an additional 45 min at -95°C and was then filtered through Celite and concentrated *in vacuo*. The residue was chromatographed (elution with ethyl acetate) to afford 129 mg (96%) of the corresponding cyclic ether diastereomers as a colourless oil: IR (film) 3285, 1756 cm^{-1}; ^{1}H NMR, major diastereomer: δ 5.41 (s, 1 H), 4.08 (d, *J*= 9.2 Hz, 1 H), 3.99 (dt, *J*= 11.2, 1.9 Hz, 1 H), 3.77-3.76 (m, 1 H), 3.54 (d, *J*= 9.2 Hz, 1 H), 3.47-3.40 (m, 2 H), 2.79 (dd, *J*= 12.0, 7.7 Hz, 1 H), 2.64 (dd, *J*= 12.0, 4.6 Hz, 1 H), 2.03-2.01 (m, 1 H), 1.87-1.79 (m, 1 H), 1.71-1.68 (m, 1 H), 1.67-1.26 (m, 7 H), 1.15 (s, 3 H), 1.06 (ddd, *J*= 13.3, 9.1, 4.1 Hz, 1 H), 0.93 (s, 3 H), 0.92 (s, 3 H); minor diastereomer: δ 5.46 (s, 1 H), 2.74-2.70 (m, 1 H); ^{13}C NMR, major diastereomer: δ 159.1, 93.1, 68.7, 68.6, 55.5, 52.9, 52.1, 48.1, 46.6, 32.0 (two signals) 28.8, 25.8, 23.3, 22.5, 20.4, 20.1, 10.9; minor diastereomer: δ 48.1, 31.0; mass spectrum, *m/z* (relative intensity) 387 (13, M^+), 343 (12), 288 (61), 208 (62), 85 (100). Exact mass calc'd for $C_{18}H_{29}NO_3Se$: 387.1313. Found: 387.1305.

Cyclization and deselenization of 4-penten-1-ol (Table 5, entry 2). IR (film) 3273, 1768 cm^{-1}; ^{1}H NMR (C_6D_6), major diastereomer: δ 6.78 (br s, 1 H), 4.05-3.99 (m, 1 H), 3.93-3.92 (m, 1 H), 3.86-3.76 (m, 2 H), 3.63-3.57 (m, 1 H), 3.10 (d, *J*= 9.4 Hz, 1 H), 2.80 (dd, *J*= 12.1, 5.8 Hz, 1 H), 2.69 (dd, *J*= 12.2, 5.8 Hz, 1 H), 1.85-1.83 (m, 1 H), 1.81-1.24 (m, 7 H), 1.15 (s, 3 H), 1.10-1.00 (m, 1 H), 0.74 (s, 3 H), 0.65 (s, 3 H); minor diastereomer: δ 4.08-4.07 (m, 1 H), 1.89-1.87 (m, 1 H), 1.17 (s, 3 H). ^{13}C NMR (C_6D_6), major diastereomer: δ 160.2, 92.8, 79.4, 68.6, 56.4, 53.3, 52.8, 48.5, 47.1, 32.2, 30.9, 29.2, 26.6, 23.0, 20.8, 20.6, 11.1; minor diastereomer: δ 92.8, 80.1, 68.5, 56.2, 52.7, 48.5, 32.4, 30.6, 30.5, 27.3, 24.1; mass spectrum, *m/z* (relative intensity) 373 (16, M^+), 288 (63), 208 (89), 71 (100). Exact mass calc'd for $C_{17}H_{27}NO_3Se$: 373.1156. Found: 373.1175.

A mixture of AIBN (10 mg) and tri-*n*-butyltin hydride (0.39 mL, 1.45 mmol) was added to a refluxing solution of the above product (240 mg, 0.643 mmol) in 1.5 mL of C_6D_6 under nitrogen. After 2 h, additional AIBN (5 mg) and tri-*n*-butyltin hydride (0.19 mL) were added and heating was continued for 1 h. The mixture was distilled and only the fraction with bp 75-79°C was collected. A second distillation afforded a C_6D_6 solution of **17** with no contaminating camphor or tin residues (NMR). Trichloroethylene was added to serve as an internal standard and the concentration of **17** was determined by NMR integration. $[\alpha]_D$ +22.1° (c 1.7); lit.[17] $[\alpha]_D$ +27.01 for the *S*-enantiomer. This corresponds to an e.r. of 91:9 (cf. d.r.= 84:16 in entry 2 of Table 5 and 90:10 in entry 5 of Table 4.

Cyclization of (*E*)-4-hexen-1-ol (Table 5, entry 3). The procedure of entry 1 was followed, except that the crude product was dissolved in 5 mL of dichloromethane and stirred with 14 mg of *p*-toluenesulfonic acid for 14 h prior to chromatography to afford the product as a colourless oil: IR (film) 3283, 1747 cm^{-1}; ^{1}H NMR, major diastereomer: δ 5.85 (br s, 1 H), 3.95 (d, *J*= 9.1 Hz, 1 H), 3.96-3.89 (m, 1 H), 3.74 (dd, *J*= 3.8,

2.7 Hz, 1 H), 3.57 (d, *J*= 9.2 Hz, 1 H), 3.46-3.31 (m, 2 H), 2.67-2.60 (m, 1 H), 2.24-2.19 (m, 1 H), 1.97-1.95 (m, 1 H), 1.74-1.57 (m, 3 H), 1.36 (d, *J*= 6.1 Hz, 3 H), 1.49-1.24 (m, 3 H), 1.16 (s, 3 H), 1.07 (ddd, *J*= 13.5, 9.2, 4.2 Hz, 1 H), 0.93 (s, 6 H); minor diastereomer: δ 5.80 (br s, 1 H), 3.82 (dd, *J*= 3.9, 2.5 Hz, 1 H), 3.57 (d, *J*= 9.3 Hz, 1 H), 2.75-2.67 (m, 1 H), 1.37 (d, *J*= 6.0 Hz, 3 H), 1.18 (s, 3 H); ^{13}C NMR, major diastereomer: δ 159.5, 92.7, 78.6, 68.0, 54.5, 52.9, 52.4, 47.9, 46.7, 44.8, 33.1, 28.6, 27.9, 22.4, 20.9, 20.3, 19.9, 10.8; minor diastereomer: δ 159.4, 92.6, 77.8, 52.6, 52.1, 48.1, 46.4, 43.6, 33.0, 22.5, 21.0, 20.4, 10.8; mass spectrum, *m/z* (relative intensity) 387 (20, M^+), 288 (30), 208 (46), 99 (96), 41 (100). Exact mass calc'd for $C_{18}H_{29}NO_3Se$: 387.1313. Found: 387.1329.

Cyclization of (*Z*)-4-hexen-1-ol (Table 5, entry 4). IR (film) 3282, 1754 cm^{-1}; ^{1}H NMR (C_6D_6), major diastereomer: δ 6.37 (br s, 1 H), 3.98-3.97 (m, 1 H), 3.85-3.74 (m, 2 H), 3.77 (d, *J*= 9.2 Hz, 1 H), 3.65 (m, 1 H), 3.13-3.07 (m, 1 H), 3.03 (d, *J*= 9.3 Hz, 1 H), 1.85-1.83 (m, 1 H), 1.80-1.51 (m, 4 H), 1.49 (d, *J*= 7.1 Hz, 3 H), 1.37-1.31 (m, 2 H), 1.17 (s, 3 H), 1.13-1.00 (m, 1 H), 0.74 (s, 3 H), 0.74-0.68 (m, 1 H), 0.66 (s, 3 H); minor diastereomer: δ 6.28 (br s, 1 H), 4.20-4.19 (m, 1 H), 3.69 (d, *J*= 9.3 Hz, 1 H), 1.92-1.90 (m, 1 H), 1.43 (d, *J*= 7.1 Hz, 3 H); ^{13}C NMR, major diastereomer: δ 158.9, 93.1, 83.2, 68.6, 53.0, 52.9, 52.7, 46.6, 40.6, 30.2, 29.7, 28.8, 26.1, 22.7, 20.4, 20.1, 19.5, 10.9; mass spectrum, *m/z* (relative intensity) 387 (13, M^+), 288 (39), 208 (65), 148 (74), 41 (100). Exact mass calc'd for $C_{18}H_{29}NO_3Se$: 387.1313. Found: 387.1318.

Cyclization of 4-methyl-4-penten-1-ol (Table 5, entry 5). IR (film) 3297, 1755 cm^{-1}; ^{1}H NMR (C_6D_6), major diastereomer: δ 6.46 (br s, 1 H), 4.14-4.12 (m, 1 H), 3.79 (d, *J*= 9.3 Hz, 1 H), 3.88-3.69 (m, 2 H), 3.05 (d, *J*= 9.3 Hz, 1 H), 2.82 (d, *J*= 11.8 Hz, 1 H), 2.74 (d, *J*= 12.3 Hz, 1 H), 1.92-1.90 (m, 1 H), 1.85-1.60 (m, 4 H), 1.52-1.47 (m, 1 H), 1.38-1.37 (m, 1 H), 1.32 (s, 3 H), 1.18 (s, 3 H), 1.08-1.00 (m, 1 H), 0.73 (s, 3 H), 0.71-0.69 (m, 1 H), 0.65 (s, 3 H); minor diastereomer: δ 6.53 (br s, 1 H), 3.92-3.90 (m, 1 H), 2.85 (d, *J*= 11.3 Hz, 1 H), 1.29 (s, 3 H), 1.16 (s, 3 H); ^{13}C NMR, major diastereomer: δ 159.2, 93.1, 82.4, 67.8, 55.9, 55.6, 52.9, 52.0, 48.0, 46.6, 37.2, 36.9, 28.8, 26.3, 22.4, 20.4, 20.0, 10.8; minor diastereomer: δ 28.8; mass spectrum, *m/z* (relative intensity) 387 (5, M^+), 288 (6), 208 (8), 149 (25), 129 (33), 85 (100). Exact mass calc'd for $C_{18}H_{29}NO_3Se$: 387.1313. Found: 387.1315.

Cyclization of 2,2-dimethyl-4-penten-1-ol (Table 5, entry 6). IR (film) 3281, 1758 cm^{-1}; ^{1}H NMR, major diastereomer: δ 5.32 (br s, 1 H), 4.18-4.12 (m, 1 H), 4.03 (d, *J*= 9.1 Hz, 1 H), 3.83-3.81 (m, 1 H), 3.54 (d, *J*= 9.1 Hz, 1 H), 2.82-2.71 (m, 2 H), 2.14-2.03 (m, 1 H), 2.02-1.99 (m, 1 H), 1.78-1.70 (m, 3 H), 1.68-1.54 (m, 1 H), 1.48-1.30 (m, 2 H), 1.26 (s, 3 H), 1.22 (s, 3 H), 1.15 (s, 3 H), 1.09-1.04 (m, 1 H), 0.93 (s, 3 H), 0.92 (s, 3 H); minor diastereomer: δ 5.29 (br s, 1 H), 3.90-3.88 (m, 1 H), 1.27 (s, 3 H); ^{13}C NMR, major diastereomer: δ 159.3, 92.9, 81.4, 78.4, 77.9, 55.1, 52.8, 51.8, 46.5, 38.5, 32.0, 30.7, 29.1, 28.7, 27.9, 22.3, 20.4, 20.0, 10.8; minor diastereomer: δ 81.4, 55.5, 52.8, 51.9, 48.0, 38.4, 32.1, 31.0, 29.1, 27.9; mass spectrum, *m/z* (relative intensity) 401 (17, M^+), 288 (43), 208 (70), 99 (79), 43 (100). Exact mass calc'd for $C_{19}H_{31}NO_3Se$: 401.1473. Found: 401.1450.

Cyclization of 2-(1-cyclohexenyl)ethanol (Table 5, entry 7). The procedure of entry 1 was followed, except that 4 h at -95°C was required to discharge the colour of the selenenyl chloride. Chromatography (elution with 60% ethyl acetate-hexanes) afforded the separated diastereomers.

Minor diastereomer (less polar): IR (film) 3284, 1756 cm^{-1}; ^{1}H NMR: δ 5.08 (br s, 1 H), 3.98-3.87 (m, 3 H), 3.76-3.74 (m, 1 H), 3.66 (dd, *J*= 3.8, 2.8 Hz, 1 H), 3.60 (d, *J*= 9.2 Hz, 1 H), 2.34-2.21 (m, 1 H), 2.15 (ddd, *J*= 12.2, 7.8, 4.2 Hz, 1 H), 1.92-1.90 (m, 1 H), 1.90-1.81 (m, 1 H), 1.75-1.33 (m, 10 H), 1.18 (s, 3 H), 1.10-1.06 (m, 1 H), 0.94 (s, 6 H); ^{13}C NMR: δ 159.0, 92.6, 80.7, 65.0, 53.8, 53.1, 49.9, 48.1, 46.8, 41.5, 33.9, 28.7, 26.2, 22.9, 22.3, 20.4, 20.1 (two signals), 10.9; mass spectrum, *m/z* (relative intensity) 413 (5, M^+), 228 (10), 208 (8), 125 (100). Exact mass calc'd for $C_{20}H_{31}NO_3Se$: 413.1473. Found: 413.1479.

Major diastereomer (more polar): IR (film) 3232, 1761 cm^{-1}; ^{1}H NMR: δ 5.07 (br s, 1 H), 3.97-3.86 (m, 3 H), 3.76-3.74 (m, 1 H), 3.66 (dd, *J*= 3.8, 2.9 Hz, 1 H), 3.61 (d, *J*= 9.0 Hz, 1 H), 2.31-2.24 (m, 1 H), 2.16 (ddd, *J*= 12.4, 7.8, 4.4 Hz, 1 H), 1.91-1.89 (m, 1 H), 1.85-1.81 (m, 1 H), 1.75-1.33 (m, 10 H), 1.18 (s, 3 H), 1.07 (ddd, *J*= 13.5, 9.3, 4.0 Hz, 1 H), 0.94 (s, 6 H); ^{13}C NMR: δ 159.0, 92.6, 80.9, 65.1, 53.8, 53.1, 52.9, 50.1, 46.8, 41.4, 33.3, 29.7, 28.7, 26.3, 22.8, 22.2, 20.4, 20.3, 20.1, 10.9; mass spectrum, *m/z* (relative

intensity) 413 (6, M^+), 228 (16), 208 (10), 125 (100). Exact mass calc'd for $C_{20}H_{31}NO_3Se$: 413.1473. Found: 413.1477.

Cyclization of 2-(3-propenyl)phenol (Table 5, entry 8). IR (film) 3298, 1747 cm^{-1}; ^1H NMR, major diastereomer: δ 7.14-7.05 (m, 2 H), 6.88-6.76 (m, 2 H), 5.84 (br s, 1 H), 4.46 (quintet, *J*= 6.6 Hz, 1 H), 4.02 (d, *J*= 9.5 Hz, 1 H), 3.75-3.73 (m, 1 H), 3.53 (d, *J*= 9.6 Hz, 1 H), 3.36 (dd, *J*= 13.8, 6.1 Hz, 1 H), 3.07-2.98 (m, 2 H), 2.93 (dd, *J*= 13.9, 7.3 Hz, 1 H), 2.00-1.98 (m, 1 H), 1.61-1.55 (m, 1 H), 1.43 (ddd, *J*= 12.7, 12.7, 4.3 Hz, 1 H), 1.32 (ddd, *J*= 13.0, 8.9, 4.2 Hz, 1 H), 1.10 (s, 3 H), 1.03 (ddd, *J*= 13.4, 9.2, 4.0 Hz, 1 H), 0.91 (s, 3 H), 0.90 (s, 3 H); minor diastereomer: δ 5.80 (br s, 1 H), 4.40-4.38 (m, 1 H), 4.11 (d, *J*= 9.4 Hz, 1 H), 1.95-1.93 (m, 1 H), 1.11 (s, 3 H), 0.92 (s, 3 H), 0.88 (s, 3 H); ^{13}C NMR, major diastereomer: δ 154.4, 131.8, 128.3, 123.9, 120.1, 115.7, 109.4, 93.6, 61.8, 56.2, 52.8, 51.7, 48.1, 46.7, 39.3, 32.8, 28.7, 22.4, 20.3, 19.9, 10.7; minor diastereomer: δ 131.6, 126.3, 120.2, 116.0, 35.5, 20.2, 20.0, 10.8; mass spectrum, *m/z* (relative intensity) 421 (32, M^+), 377 (19), 288 (27), 244 (77), 208 (27), 131 (94), 91 (94), 44 (100). Exact mass calc'd for $C_{21}H_{27}NO_3Se$: 421.1127. Found: 421.1159.

Cyclization of 5-hexenoic acid (Table 5, entry 9). IR (film) 3277, 1756 cm^{-1}; ^1H NMR, major diastereomer: δ 6.28 (br s, 1 H), 4.04 (d, *J*= 9.1 Hz, 1 H), 4.05-4.02 (m, 1 H), 3.69-3.68 (m, 1 H), 3.60 (d, *J*= 9.4 Hz, 1 H), 3.07 (dd, *J*= 12.7, 5.6 Hz, 1 H), 2.95 (dd, *J*= 12.8, 7.8 Hz, 1 H), 2.47-2.33 (m, 2 H), 2.15-2.10 (m, 1 H), 2.05-2.03 (m, 1 H), 1.94-1.77 (m, 1 H), 1.75-1.60 (m, 3 H), 1.47 (ddd, *J*= 12.9, 12.9, 4.3 Hz, 1 H), 1.29 (ddd, *J*= 13.3, 8.9, 4.4 Hz, 1 H), 1.15 (s, 3 H), 1.07 (ddd, *J*= 13.5, 9.3, 4.1 Hz, 1 H), 0.94 (s, 3 H), 0.93 (s, 3 H); minor diastereomer: δ 4.12 (d, *J*= 9.8 Hz, 1 H), 3.77-3.76 (m, 1 H); ^{13}C NMR, major diastereomer: δ 171.0, 159.1, 92.8, 79.7, 56.5, 52.9, 52.0, 48.1, 46.6, 29.5, 29.3, 28.7, 27.6, 22.4, 20.3, 19.9, 18.2, 10.7; minor diastereomer: δ 79.6, 56.8, 52.8, 52.2, 46.6, 29.8, 29.4, 27.8, 18.3 (two signals), 18.2, 10.7; mass spectrum, *m/z* (relative intensity) 401 (8, M^+), 287 (19), 208 (44), 113 (45), 55 (69), 41 (100). Exact mass calc'd for $C_{18}H_{27}NO_4Se$: 401.1124. Found: 401.1108.

Cyclization and deselenization of 4-pentenoic acid (Table 5, entry 10). IR (film) 3321, 1732 cm^{-1}; ^1H NMR ($CDCl_3$-C_6D_6 1:1), major diastereomer: δ 4.72 (br s, 1 H), 4.27-4.21 (m, 1 H), 3.68 (dd, *J*= 3.6, 2.7 Hz, 1 H), 3.62 (d, *J*= 9.3 Hz, 1 H), 3.07 (d, *J*= 9.3 Hz, 1 H), 2.61-2.53 (m, 2 H), 2.21 (ddd, *J*= 17.8, 9.8, 4.7 Hz, 1 H), 2.11-2.02 (m, 1 H), 1.89-1.87 (m, 1 H), 1.84-1.76 (m, 1 H), 1.51-1.38 (m, 2 H), 1.29-1.14 (m, 3 H), 1.12 (s, 3 H), 0.78 (s, 3 H), 0.76 (s, 3 H); ^{13}C NMR, major diastereomer: δ 176.5, 159.2, 92.9, 79.3, 56.6, 52.9, 52.0, 48.2, 46.7, 42.9, 29.3, 28.8, 27.7, 22.4, 20.3, 19.9, 10.8; mass spectrum, *m/z* (relative intensity) 387 (19, M^+), 288 (15), 208 (100), 83 (98). Exact mass calc'd for $C_{17}H_{25}NO_4Se$: 387.0951. Found: 387.0951. No signals that could be attributed to the minor diastereomer were observed in either the ^1H or ^{13}C NMR spectra.

A mixture of AIBN (10 mg) and tri-*n*-butyltin hydride (0.40 mL, 1.49 mmol) was added to a refluxing solution of the above product (257 mg, 0.66 mmol) in 2 mL of toluene under nitrogen. After 2 h, additional AIBN (5 mg) and tri-*n*-butyltin hydride (0.20 mL) were added and heating was continued for 1 h. The mixture was concentrated and chromatographed (elution with 10%-50% ether-hexanes, followed by pure ether). The solvent was removed by distillation from the fraction eluting with 50% ether-hexanes and the residue was subjected to Kugelrohr distillation to afford 27 mg (40%) of **18**, bp 105-115°C, 39 mmHg; $[\alpha]_D$ -27.9° (c 2.0); lit.[18] $[\alpha]_D$ -29.6 (c 1.29 CH_2Cl_2) for the *S*-enantiomer. This represents an e.r. of 97:3. The product had IR and NMR spectra in close agreement with the literature. The fraction eluting with ether afforded 122 mg (88%) of *spiro*-oxazolidinone **27** (*vide infra*).

Cyclization of (*E*)-4-hexenoic acid (Table 5, entry 11). IR (film) 3263, 1767 cm^{-1}; ^1H NMR, major diastereomer: δ 5.69 (br s, 1 H), 4.53 (m, 1 H), 3.98 (d, *J*= 9.2 Hz, 1 H), 3.87-3.86 (m, 1 H), 3.59 (d, *J*= 9.3 Hz, 1 H), 3.28-3.11 (m, 1 H), 2.67-2.50 (m, 2 H), 2.39-2.30 (m, 1 H), 2.12-2.01 (m, 1 H), 2.00-1.98 (m, 1 H), 1.64-1.55 (m, 1 H), 1.55-1.49 (m, 1 H), 1.45 (d, *J*= 7.3 Hz, 3 H), 1.25 (ddd, *J*= 13.2, 9.1, 4.5 Hz, 1 H), 1.17 (s, 3 H), 1.06 (ddd, *J*= 13.6, 9.3, 3.8 Hz, 1 H), 0.93 (s, 3 H), 0.92 (s, 3 H); irradiation of the m at δ 3.28-3.11 collapsed the d at δ 1.45 into a s; minor diastereomer: δ 3.81-3.80 (m, 1 H), 3.58 (d, *J*= 9.1 Hz, 1 H); ^{13}C NMR, major diastereomer: δ 176.6, 159.6, 92.8, 83.2, 55.5, 52.7, 52.4, 48.0, 46.8, 40.5, 28.8, 28.6, 25.3, 22.4, 20.1, 19.8, 18.5, 10.7; minor diastereomer: δ 176.7, 159.4, 92.6, 83.4, 54.2, 52.8, 52.5, 46.6, 46.5, 39.8,

28.5, 24.8, 22.5, 20.2, 19.8, 18.1, 10.7; mass spectrum, *m/z* (relative intensity) 401 (11, M^+), 288 (11), 208 (48), 55 (100). Exact mass calc'd for $C_{18}H_{27}NO_4Se$: 401.1108. Found: 401.1115.

Cyclization of (*Z*)-4-hexenoic acid (Table 5, entry 12). IR (film) 3300, 1768, 1755 cm^{-1}; ^1H NMR (C_6D_6), major diastereomer: δ 6.47 (br s, 1 H), 4.19 (ddd, *J*= 7.4, 4.0, 4.0 Hz, 1 H), 3.89-3.88 (m, 1 H), 3.63 (d, *J*= 9.4 Hz, 1 H), 3.06 (d, *J*= 9.4 Hz, 1 H), 2.94 (dq, *J*= 7.0, 4.6 Hz, 1 H), 2.29-2.07 (m, 2 H), 1.84-1.82 (m, 1 H), 1.78-1.61 (m, 2 H), 1.34 (d, *J*= 7.1 Hz, 3 H), 1.32-1.21 (m, 2 H), 1.20 (s, 3 H), 1.03 (ddd, J= 12.9, 12.9, 4.8 Hz, 1 H), 0.73 (s, 3 H), 0.70-0.68 (m, 1 H), 0.65 (s, 3 H); irradiation of the dq at δ 2.94 collapsed the d at δ 1.34 to a s; minor diastereomer: δ 6.34 (br s, 1 H), 4.09-4.04 (m, 1 H), 3.67 (d, *J*= 9.4 Hz, 1 H), 2.88-2.85 (m, 1 H), 1.88-1.86 (m, 1 H); ^{13}C NMR, major diastereomer: δ 176.7, 159.2, 92.8, 83.2, 54.4, 53.0, 52.5, 48.2, 46.7, 39.2, 28.9, 28.7, 25.1, 22.6, 20.3, 20.0, 18.4, 10.8; minor diastereomer: δ 83.7, 29.0, 22.5; mass spectrum, *m/z* (relative intensity) 401 (9, M^+), 288 (5), 208 (39), 83 (53), 41 (100). Exact mass calc'd for $C_{18}H_{27}NO_4Se$: 401.1108. Found: 401.1120.

Cyclization of (1-cyclohexenyl)acetic acid (Table 5, entry 13). The procedure of entry 1 was followed, except that 8 h at -95°C, followed by 12 h at room temperature, was required to discharge the colour of the selenenyl chloride. IR (film) 3318, 1772, 1760 cm^{-1}; ^1H NMR, major diastereomer: δ 5.75 (br, s, 1 H), 4.45-4.41 (m, 1 H), 3.83 (d, *J*= 9.3 Hz, 1 H), 3.63 (d, *J*= 9.3 Hz, 1 H), 3.60-3.58 (m, 1 H), 2.81-2.67 (m, 2 H), 2.04-1.45 (m, 11 H), 1.35-1.21 (m, 1 H), 1.18 (s, 3 H), 1.07 (ddd, *J*= 13.7, 9.4, 4.1 Hz, 1 H), 0.94 (s, 6 H); minor diastereomer: δ 5.68 (br s, 1 H), 3.78 (d, *J*= 9.4 Hz, 1 H), 3.56-3.55 (m, 1 H), 0.95 (s, 3 H); ^{13}C NMR, major diastereomer: δ 174.8, 165.7, 92.3, 82.7, 53.5, 53.4, 53.0, 48.2, 46.9, 46.8, 45.3, 33.8, 28.6, 25.7, 22.8, 21.4, 20.3, 20.0, 19.7, 10.8; minor diastereomer: δ 174.7, 82.6, 53.7, 53.5, 47.1, 46.1, 45.7, 45.5, 34.3, 26.2, 22.8, 21.3, 20.4, 19.8, 10.7; mass spectrum, *m/z* (relative intensity) 427 (8, M^+), 228 (32), 208 (20), 148 (72), 41 (100). Exact mass calc'd for $C_{20}H_{29}NO_4Se$: 427.1266. Found: 427.1299.

Reactions of 4-pentenamide (19) with selenenyl chloride 16c. Diselenide **1c** (50 mg, 0.087 mmol) was dissolved in 3 mL of dichloromethane at 0°C. Sulfuryl chloride (6.9 μL, 0.087 mmol) was added and stirring was continued for 10 min. The resulting solution of **16c** was cooled to -78°C, amide **19** (21 mg, 0.21 mmol) was added, and the orange colour was discharged immediately. The mixture was stirred for an additional 1 h, and was then concentrated *in vacuo* and rapidly chromatographed (elution with ethyl acetate) to afford 37 mg (ca. 50%) of the crude chloride **20** as a colourless oil with d.r. 95:5 (NMR integration), which was converted into lactone **22** upon prolonged standing or slow chromatography; IR (film) 3228, 1752, 1668, 751 cm^{-1}; ^1H NMR, major diastereomer: δ 6.25 (br s, 1 H), 6.01 (br s, 2 H), 4.14-4.05 (m, 1 H), 4.02 (d, *J*= 8.9 Hz, 1 H), 3.58 (m, 2 H), 3.13 (dd, *J*= 13.1, 5.1 Hz, 1 H), 2.93 (m, 1 H), 2.50-2.43 (m, 2 H), 2.18-1.23 (m, 7 H), 1.15 (s, 3 H), 0.94 (s, 3 H), 0.93 (s, 3 H); minor diastereomer: δ 6.18 (br s, 1 H).

Diselenide **1c** (100 mg, 0.17 mmol) was converted into the selenenyl chloride **16c** as in the preceding procedure. The resulting solution was cooled to -95°C, amide **19** (41 mg, 0.41 mmol) was added, and the orange colour was discharged immediately. After 1 h, the mixture was warmed to room temperature and *p*-toluenesulfonic acid (10 mg) was added. After 10 h, the solution was concentrated *in vacuo*, and the residue was chromatographed (elution with ethyl acetate) to afford 118 mg (88%) of lactone **22**, obtained as a colourless oil, which had ^1H and ^{13}C NMR spectra identical to those of the sample from entry 10 in Table 5. Only one diastereomer was detected.

The reaction of amide **19** and selenenyl chloride **16c** (generated from 0.17 mmol of **1c**) was performed as in the above procedure. After 1 h, the mixture was warmed to room temperature and potassium *t*-butoxide (117 mg, 1.05 mmol) was added. After 4 h, the solution was concentrated *in vacuo*, and was chromatographed (elution with ethyl acetate) to afford 90 mg (67%) of **23** as a colourless oil: IR (film) 3360, 2247, 1749 cm^{-1}; ^1H NMR δ 5.71 (br s, 1 H), 4.06 (d, *J*= 9.3 Hz, 1 H), 3.85 (br s, 1 H), 3.77 (dd, *J*= 3.9, 2.4 Hz, 1 H), 3.59 (d, *J*= 9.4 Hz, 1 H), 3.09-3.07 (m, 1 H), 2.84 (dd, *J*= 12.6, 5.1 Hz, 1 H), 2.70 (dd, *J*= 12.6, 7.4 Hz, 1 H), 2.54 (dd, *J*= 7.7, 6.7 Hz, 2 H), 2.07-2.00 (m, 1 H), 1.97-1.21 (m, 6 H), 1.16 (s, 3 H), 0.94 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (C_6D_6) δ 160.2, 120.5, 93.2, 70.0, 57.2, 53.2, 53.0, 48.6, 47.2, 33.2, 32.6, 29.2, 23.0, 20.6, 20.5, 14.1, 11.1; mass spectrum, *m/z* (relative intensity) 386 (16, M^+), 288 (34), 208 (77), 83 (100). Exact mass calc'd for $C_{17}H_{26}N_2O_3Se$: 386.1102. Found: 386.1102. Only one diastereomer was detected.

Cyclization and deselenization of methyl N-(5-pentenyl)carbamate (24). Diselenide **1c** (100 mg, 0.17 mmol) was converted into the selenenyl chloride **16c** as in the preceding procedure. The resulting solution was cooled to -78°C, carbamate **24** (60 mg, 0.42 mmol) was added, and the orange colour was discharged immediately. After 1 h, the mixture was warmed to room temperature and silica-gel (100 mg) was added to the mixture. Stirring was continued overnight, the mixture was filtered, washed with brine, dried and chromatographed (elution with 80% ethyl acetate-hexanes) to afford 110 mg (73%) of lactam **25** as a colourless oil: IR (film) 3377, 1774, 1701 cm^{-1}; ^1H NMR, major diastereomer: δ 5.50 (br s, 1 H); 4.09-3.95 (m, 3 H), 3.71-3.65 (m, 3 H), 3.55 (d, *J*= 5.1 Hz, 1 H,), 2.00-1.20 (m, 13 H), 1.15 (s, 3 H), 0.92 (s, 6 H); minor diastereomer: 5.72 (br s, 1 H); ^{13}C NMR (C_6D_6), major diastereomer: δ 170.0, 155.5, 88.0, 59.1, 51.6, 51.3, 50.8, 48.5, 47.9, 47.2, 34.2, 30.7, 30.6, 27.8, 24.0, 23.9, 21.3, 20.1, 11.8; minor diastereomer: δ 58.8, 58.3, 52.1, 51.1, 49.3, 48.2, 47.4, 31.5, 29.3, 24.1, 23.8, 23.2, 20.9, 20.1; mass spectrum, *m/z* (relative intensity) 430 (5, M^+), 288 (15), 208 (10), 128 (100). Exact mass calc'd for $C_{19}H_{30}N_2O_4Se$: 430.1374. Found: 430.1366.

A mixture of AIBN (10 mg) and tri-*n*-butyltin hydride (138 μL, 0.52 mmol) was added to a refluxing solution of **25** (110 mg, 0.26 mmol) in 2 mL of toluene under nitrogen. After 2 h, additional tri-*n*-butyltin hydride (69 μL, 0.26 mmol) and AIBN (5 mg) were added, and heating was continued for 1 h. The reaction mixture was separated by chromatography (elution with hexanes followed by 10-50% diethyl ether-hexanes) to afford 8 mg (20%) of carbamate **26**[19] as a yellow oil, followed by 49 mg (91%) of *spiro*-oxazolidinone **27**. The e.r. of **26** was determined to be 72:28 by GC on a chiral Cyclodex B column. Compound **27**: mp 148°C (from benzene-hexanes); IR (Nujol) 3246, 1744 cm^{-1}; ^1H NMR 5.75 (br s, 1 H), 3.70 (d, *J*= 8.2 Hz, 1 H), 3.25 (d, *J*= 8.6 Hz, 1 H), 2.40 (ddd, *J*= 13.9, 4.4, 3.2 Hz, 1 H), 1.85-1.81 (m, 1 H), 1.77-1.37 (m, 3 H), 1.07 (s, 3 H), 1.23-0.99 (m, 2 H), 0.90 (s, 3 H), 0.89 (s, 3 H); mass spectrum, *m/z* (relative intensity) 209 (8, M^+), 194 (10), 148 (29), 95 (100). Anal. calc'd. for $C_{12}H_{19}NO_2$: C, 68.87; H, 9.15; N, 6.69. Found: C, 69.12; H, 9.26; N, 6.65.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support and for a Postgraduate Scholarship to B.P.D. We thank Dr. R. Yamdagni, Ms. Q. Wu and Ms. D. Fox for mass spectra and elemental analyses.

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