

# Ring-Closure Reactions through Intramolecular Displacement of the Phenylselenonyl Group by Nitrogen Nucleophiles: A New Stereospecific Synthesis of *N*-Tosyl and *N*-Benzoyl-1,3-oxazolidin-2-ones from $\beta$ -Hydroxyalkyl Phenyl Selenides

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**Abstract:** A new and convenient method for the stereospecific synthesis of variously substituted 1,3-oxazolidin-2-ones from the easily available  $\beta$ -hydroxyalkyl phenyl selenides is presented. After transformation into the *N*-tosyl or *N*-benzoyl carbamates, the selenides were oxidized to the corresponding selenones. The key step of the process is the ring-closure reaction, which occurs by stereospecific intramolecular nucleophilic substitution of the selenone group by the nitrogen atom of the carbamate. Enantiomerically pure 1,3-oxazolidin-2-one derivatives can be easily prepared by using enantiomerically pure  $\beta$ -hydroxyalkyl phenyl selenides as starting materials.

**Keywords:** carbamates • cyclization • heterocycles • stereoselectivity • substitution reactions

## Introduction

1,3-Oxazolidin-2-ones are important heterocyclic compounds<sup>[1]</sup> that display good antibacterial properties<sup>[2]</sup> and are used prolifically in pharmaceutical chemistry.<sup>[3]</sup> The synthesis of these cyclic carbamates is generally performed by condensation of 1,2-amino alcohols<sup>[4]</sup> with carbonyl derivatives such as phosgene,<sup>[5]</sup> triphosgene,<sup>[6]</sup> isocyanates,<sup>[4]</sup> chloroformates,<sup>[7]</sup> ureas,<sup>[8]</sup> or diethyl carbonate.<sup>[9]</sup> The catalyzed addition of CO<sub>2</sub>,<sup>[10]</sup> and the palladium-catalyzed oxidative carbonylation<sup>[11]</sup> of  $\beta$ -amino alcohols have also been employed. Other methods include the reaction of epoxides with isocyanates,<sup>[12]</sup> and the reaction of alkenes with *N*-bromosuccinimide and isocyanates.<sup>[13]</sup> An alternative strategy for the preparation of 1,3-oxazolidin-2-ones involves the cyclization of aryl and benzoylcarbamate derivatives of epoxy alcohols or bromohydrins.<sup>[14]</sup> Chiral, non-racemic 1,3-oxazolidin-2-ones, known as Evans' chiral auxiliaries,<sup>[15]</sup> have been successfully employed in a wide range of asymmetric reactions such as aldol condensations, alkylations, and Diels–Alder re-

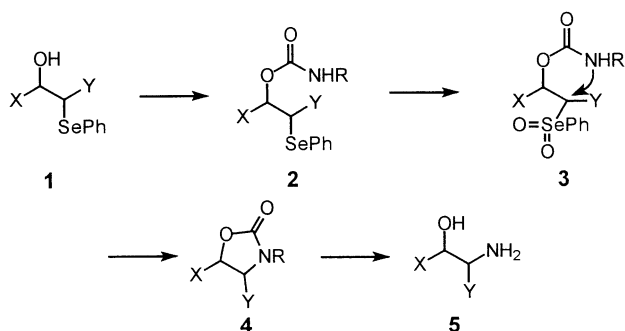
actions. In turn, these have been used to effect the stereoselective synthesis of several natural and pharmaceutical products.<sup>[16]</sup>

Herein we report a new and convenient stereospecific synthesis (Scheme 1) of substituted *N*-tosyl or *N*-benzoyl-1,3-oxazolidin-2-ones **4** starting from  $\beta$ -hydroxyalkyl phenyl selenides **1**. We also describe the further transformation of **4** into the *N*-substituted 1,2-amino alcohols **5**.

## Results and Discussion

The reaction sequence employed in the present work is schematically illustrated in Scheme 1. The  $\beta$ -hydroxyalkyl phenyl selenides **1** used as starting materials are easily available intermediates that have been used for several interesting synthetic applications.<sup>[17]</sup> By reaction with tosyl or benzoyl isocyanate in CH<sub>2</sub>Cl<sub>2</sub> or CCl<sub>4</sub> at room temperature, these compounds are rapidly converted into their *N*-tosyl or *N*-benzoyl carbamate derivatives **2**, respectively. Treatment of these  $\beta$ -carbamoyloxyalkyl phenyl selenides with an excess of *m*-chloroperoxybenzoic acid (*m*-CPBA) in THF or CH<sub>2</sub>Cl<sub>2</sub>, in the presence of potassium hydrogenphosphate,<sup>[18]</sup> afforded the corresponding selenones **3**. The *N*-tosyl or *N*-benzoyl-1,3-oxazolidin-2-ones **4** were then obtained as a result of the displacement of the selenonyl group by the nitrogen atom of the carbamic group. This cyclization reaction, which represents the crucial step of the entire process,

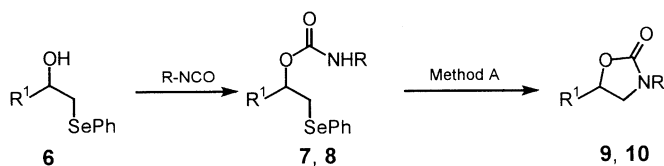
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Scheme 1. Synthesis of 1,3-oxazolidin-2-ones **4** from  $\beta$ -hydroxyalkyl phenyl selenides **1**. R = Ts or Bz.

is a stereospecific intramolecular nucleophilic substitution, and occurs easily because of the great leaving ability of the selenonyl group. The leaving ability of the selenonyl group has already been observed in intermolecular<sup>[19]</sup> and intramolecular<sup>[20]</sup> substitution reactions that involve carbon or oxygen nucleophiles. However, little is known about cyclization reactions promoted by nitrogen atoms<sup>[21]</sup> in which heterocycles that contain nitrogen are formed.

Preliminary experiments were carried out using hydroxyalkyl phenyl selenides **6**, in which the selenium atom is attached to a primary carbon atom (Scheme 2). As a result,



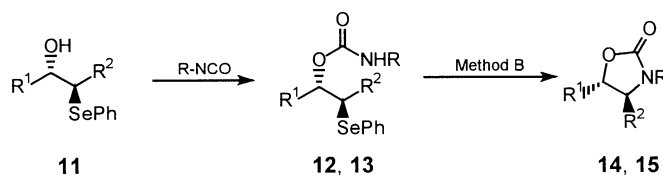
Scheme 2. Synthesis of *N*-tosyl and *N*-benzoyl 5-substituted 1,3-oxazolidin-2-ones. R = Ts: **7** and **9**; R = Bz: **8** and **10**.

slightly different conditions were required to effect the cyclization reactions of the *N*-tosyl or the *N*-benzoyl carbamates.

Oxidation of the *N*-tosyl carbamates **7** to the corresponding selenones was effected with *m*-CPBA in THF at 0°C in the presence of potassium hydrogenphosphate (Scheme 2, Method A). These selenones then spontaneously underwent cyclization. The *N*-benzoyl carbamates **8** were oxidized under the same conditions employed for **7**, but to undergo clean cyclization it was necessary to use acetone rather than THF as the solvent. Moreover, the reaction was conducted at room temperature and in the presence of powdered potassium carbonate. The selenones obtained from the *N*-tosyl carbamates **7** could not be isolated, but their formation could be inferred by thin-layer chromatography (TLC). On the other hand, formation of the corresponding selenones from the *N*-benzoyl carbamates **8** was clearly demonstrated both by TLC and <sup>13</sup>C NMR spectroscopy of the crude reaction mixtures. In particular, a signal characteristic of a methylene linked to a selenonyl group<sup>[20c]</sup> was observed at  $\delta \approx 66$  ppm.

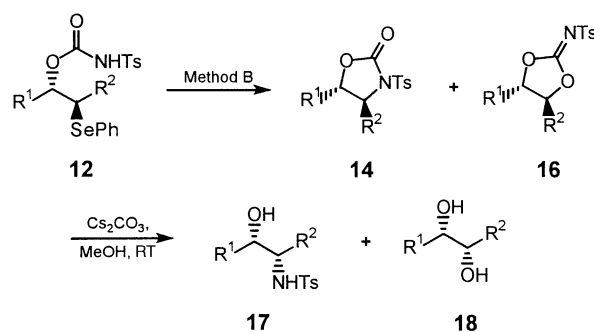
The yields obtained for the *N*-tosyl-1,3-oxazolidin-2-ones **9** and *N*-benzoyl-1,3-oxazolidin-2-ones **10** are reported in Table 1. For the sake of simplicity, only the structures of the starting hydroxyalkyl phenyl selenides **6** are indicated in the Table. From the data reported in Table 1, it can be seen that compounds **9** and **10** were obtained in good to excellent yields. This indicates that the procedure has general application and that a number of functional groups in the carbamate molecule are tolerated under the mild reaction conditions employed.

Different procedures were required for cyclization of the *N*-tosyl **12** or *N*-benzoyl carbamates **13**, which were prepared from the hydroxyalkyl phenyl selenides **11**, as the phenylseleno group is linked to a secondary carbon atom (Scheme 3).



Scheme 3. Synthesis of *N*-tosyl and *N*-benzoyl 4,5-disubstituted 1,3-oxazolidin-2-ones. R = Ts: **12** and **14**; R = Bz: **13** and **15**.

The  $\beta$ -(*N*-tosylcarbamoyloxy)alkyl phenyl selenides **12a** and **12b** were oxidized to the corresponding selenones in CH<sub>2</sub>Cl<sub>2</sub> at 18°C in the presence of K<sub>2</sub>HPO<sub>4</sub> (Method B). Unfortunately, subsequent cyclization of the selenones gave rise to inseparable mixtures of 1,3-oxazolidin-2-ones **14a** or **14b**, and tosyl iminocarbonates **16a** or **16b**, respectively, the latter being derived from competitive O-cyclization (Scheme 4).



Scheme 4. Cyclization and subsequent hydrolysis of compound **12**.

Hydrolysis of the reaction mixtures with cesium carbonate in methanol afforded the *N*-tosyl-1,2-amino alcohols **17a** and **17b**, and these could easily be separated from the corresponding 1,2-diols **18a** and **18b**. Attempts to exclusively obtain the oxazolidin-2-ones by changing solvents and/or the base used, were unsuccessful. However, it should be noted

Table 1. Synthesis of 5-substituted-*N*-tosyl **9** and *N*-benzoyl-1,3-oxazolidin-2-ones **10** from hydroxyalkyl phenyl selenides **6**.<sup>[a]</sup>

	Hydroxyselenides <b>6</b>	Oxazolidinones <b>9</b>	Yield [%] <sup>[b,c]</sup>	Oxazolidinones <b>10</b>	Yield [%] <sup>[b]</sup>
<b>a</b>			96		89
<b>b</b>			81		
<b>c</b>			75		93
<b>d</b>			69		
<b>e</b>			92		69
<b>f</b>			75		
<b>g</b>			79		
<b>h</b>					62
<b>i</b>			86		
<b>l</b>					77
<b>m</b>					80

[a] Method A was employed. [b] Yields are based on the amount of the carbamate employed. [c] The *N*-tosyl-1,3-oxazolidin-2-ones were not purified by chromatography.

that the selenone from carbamate **12c** was easily transformed into the corresponding *N*-tosyl-1,3-oxazolidin-2-one **14c** under the conditions employed for compounds **8**. The results of these experiments are reported in Table 2.

Oxidation of the *N*-benzoyl carbamates **13** occurred smoothly in CH<sub>2</sub>Cl<sub>2</sub> at 18 °C in the presence of K<sub>2</sub>HPO<sub>4</sub> (Method B). However, cyclization of the resultant selenones to give the 4,5-disubstituted *N*-benzoyl oxazolidin-2-ones **15** occurred only after powdered potassium hydroxide (carba-

mates **13a**, **13d**, and **13f**) or potassium carbonate (carbamates **13b** and **13e**) were added to the reaction mixtures. These bases are probably necessary to partially deprotonate the carbamate nitrogen, and thus, afford a stronger nucleophilic reagent. To prevent β-elimination of the selenoxide intermediate, cyclization of carbamate **13g** was effected with K<sub>2</sub>HPO<sub>4</sub> in 2-propanol. The results of these experiments are collected in Table 3. The data indicates that formation of the 4,5-disubstituted oxazolidin-2-ones by cyclization of the selenones derived from the *N*-benzoyl carbamates proceeds more cleanly than cyclization of the selenones derived from the *N*-tosyl carbamates. Moreover, removal of the tosyl group is generally more difficult than removal of the benzoyl group.<sup>[22]</sup>

The structures of the 1,3-oxazolidin-2-ones obtained from the experiments reported in Table 3 clearly indicate that intramolecular substitution of the phenylselenonyl group by the nitrogen atom is a stereospecific reaction that occurs with in-

Table 2. Oxidation of *N*-tosyl carbamates **12** with *m*-CPBA in the presence of K<sub>2</sub>HPO<sub>4</sub>.<sup>[a]</sup>

<i>N</i> -Tosyl carbamates <b>12</b>	Reaction products	Yield [%]
		40
		48
		73 <sup>[c]</sup>

[a] The oxidation–cyclization reaction was effected with Method B. [b] After hydrolysis of the reaction mixtures with cesium carbonate in methanol. [c] Under the reaction conditions employed for compounds **8**.

Table 3. Synthesis of 4,5-disubstituted-*N*-benzoyl-1,3-oxazolidin-2-ones **15**.<sup>[a]</sup>

<i>N</i> -Benzoyl carbamates <b>13</b>	Oxazolidinones <b>15</b>	Yield [%]
		73 <sup>[b]</sup>
		74 <sup>[c]</sup>
		69 <sup>[b]</sup>
		80 <sup>[c]</sup>
		44 <sup>[b]</sup>
		81 <sup>[d]</sup>

[a] The reaction was effected with Method B. [b] Powdered potassium hydroxide was added. [c] Powdered potassium carbonate was added. [d] The reaction was carried out with potassium hydrogenphosphate in 2-propanol.

version of configuration at the carbon atom  $\alpha$  to the selenonyl group (Scheme 3).<sup>[21b]</sup>

Interestingly, enantiomerically pure 1,3-oxazolidin-2-ones, as well as the corresponding 1,2-amino alcohols, are formed when enantiomerically pure  $\beta$ -hydroxyalkyl phenyl selenides, are used. More importantly, the  $\beta$ -hydroxyalkyl phenyl selenides required can themselves be easily obtained in several ways. They can be prepared by the ring opening of commercially available epoxides with sodium phenyl selenolate.<sup>[23]</sup> Alternatively, halohydrins or lactones can be employed as starting materials. Several examples of these syntheses are described in the experimental section.

Thus, the enantiomerically pure  $\beta$ -hydroxyalkyl phenyl selenides **19**, in which the selenium atom is attached to a primary carbon atom, and therefore, have structures similar to **6**, were converted into the corresponding benzoyl carbamates

**20** by treatment with benzoyl isocyanate (Table 4). The oxidation–cyclization procedure was then effected as described above for compounds **8** to afford the optically active (*ee*  $\geq$  98%) 5-substituted *N*-benzoyl-1,3-oxazolidin-2-ones **21**. The results of these experiments, which are collected in Table 4, confirm the great versatility of the procedure described in this paper. In particular, the mild conditions employed are compatible with various kinds of substituents. For example, the  $\beta$ -hydroxyalkyl phenyl selenide **19a** reacted with tosyl isocyanate to afford the corresponding *N*-tosyl carbamate **22a**, which after oxidation and cyclization according to Method A formed the enantiomerically pure *N*-tosyl-1,3-oxazolidin-2-one **23a** in good yield.

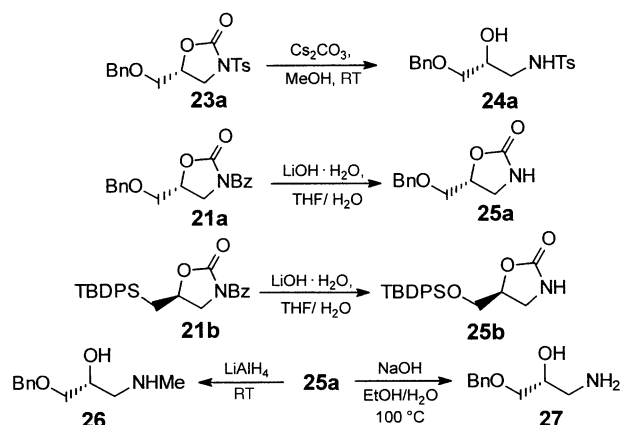
The substituted 1,3-oxazolidin-2-ones prepared in this paper can easily be converted

Table 4. Preparation of enantiomerically pure *N*-benzoyl-5-substituted-1,3-oxazolidin-2-ones **21** from enantiomerically pure  $\beta$ -hydroxyalkyl phenyl selenides **19**.<sup>[a]</sup>

$\beta$ -Hydroxyalkyl phenyl selenides <b>19</b>	<i>N</i> -Benzoyl carbamates <b>20</b>	Yield [%]	Oxazolidinones <b>21</b>	Yield [%]
		97		88
		92		77
		67		67
				75 <sup>[b]</sup>
		98		82
		89		74
		58 <sup>[c]</sup>		79
				56 <sup>[b][d]</sup>

[a] The reaction was effected under the conditions employed for compounds **8**. [b] The yield was calculated from the starting hydroxyselenide. The corresponding carbamate was not isolated. [c] The yield was calculated from the starting epoxide. [d] Major diastereoisomer.

into other useful compounds in both a regio- and stereospecific manner. Among these, is an important class of derivatives, namely the 1,2-amino alcohols.<sup>[24]</sup> As indicated in Scheme 5, upon treatment with catalytic amounts of cesium



Scheme 5. Examples of the hydrolysis of optically active 5-substituted 1,3-oxazolidin-2-ones

carbonate at room temperature, *N*-tosyl-1,3-oxazolidin-2-one **23a** was smoothly cleaved to give the *N*-tosyl-1,2-amino alcohol **24a**. Treatment of **21a** and **21b** with lithium hydroxide monohydrate resulted in selective removal of the benzoyl group to give the simple 1,3-oxazolidinones **25a** and **25b**, respectively. Reductive cleavage of **25a** was then affected with lithium aluminum hydride to afford the optically active *N*-methyl-1,2-amino alcohol **26**. Alternatively, hydrolysis of **25a** with sodium hydroxide in a mixture of ethanol and water at 100 °C afforded the enantiomerically pure 1,2-amino alcohol **27**.

In conclusion, we have described a new and convenient method for the stereospecific synthesis of variously substituted 1,3-oxazolidin-2-ones starting from the easily available  $\beta$ -hydroxyalkyl phenyl selenides. The key step of this process is the ring-closure reaction in which stereospecific intramolecular nucleophilic substitution of the selenonyl group is effected by the nitrogen atom of the carbamate. The results obtained also confirm that the selenonyl group is an extremely good leaving group. We have also demonstrated that enantiomerically pure 5-substituted *N*-benzoyl-1,3-oxazolidin-2-ones can be easily prepared from enantiomerically pure  $\beta$ -hydroxyalkyl phenyl selenides. This newly developed methodology has general application, and may represent a valid alternative to the procedures previously reported in the literature.<sup>[4–14]</sup>

## Experimental Section

**General:** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance DR 200 spectrometer at 200 and 50.3 MHz, respectively (*J* values are given in Hz). FT-IR spectra were recorded with a Jasco model 410 spectrometer. GC-MS analyses were effected with an HP-6890 gas chromatograph (dimethyl silicone column; 12.5 m) equipped with an HP-5973 mass-selective detector at an ionizing voltage of 70 eV. Melting points are uncorrected. Optical rotations were measured in a 50 mm cell with a

Jasco DIP-1000 digital polarimeter. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer. Commercial grade Et<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, CCl<sub>4</sub>, and THF were used without purification. Column chromatography was performed with Merck silica gel 60 (70–230 mesh).

The starting  $\beta$ -hydroxyalkyl phenyl selenides **6a**,<sup>[25]</sup> **6c**,<sup>[26]</sup> **6d**,<sup>[27]</sup> **6f**,<sup>[27]</sup> **6m**,<sup>[28]</sup> **11a**,<sup>[29]</sup> **11c**,<sup>[27]</sup> **11d**,<sup>[27]</sup> **11g**,<sup>[27]</sup> and **19a**<sup>[26]</sup> were prepared as described in the literature. Compounds **11b** and **11f** were obtained by regio- and stereospecific hydroxyselenation of the corresponding allylic ethers<sup>[30]</sup> using phenylselenenyl chloride.<sup>[31]</sup> Compound **6l** was prepared by acidic hydrolysis of the corresponding oxazoline,<sup>[32]</sup> while **6g** was obtained by alkaline hydrolysis and subsequent esterification of the corresponding  $\gamma$ -lactone with diazomethane.<sup>[32]</sup> The  $\beta$ -hydroxyalkyl phenyl selenides **6b**, **6e**, **6h**, **6i**, **11e**, **19g**, and **19h** were prepared as reported in the literature by regiospecific ring opening of the corresponding racemic or chiral, non-racemic epoxides using sodium phenyl selenolate in ethanol.<sup>[33]</sup> Compound **19e** was obtained by cleavage of the corresponding hydroxy  $\gamma$ -lactone with sodium phenyl selenolate in DMF<sup>[34]</sup> upon heating at reflux. Compounds **19d** and **19f** were obtained by S<sub>N</sub>2 displacement of the corresponding chlorohydrins with sodium phenyl selenolate in HMPA.<sup>[35]</sup> Yields, as well as physical and spectral data are reported below.

Most of the optically active epoxides, chlorohydrins, and the hydroxy  $\gamma$ -lactone were commercially available and had an enantiomeric excess (*ee*) equal or greater than 98%.

The epoxides required for the preparation of compounds **19g**<sup>[36a]</sup> and **19h**<sup>[36b]</sup> were obtained according to the procedures reported in the literature. Compound **19g**, which was not isolated, was directly transformed into the corresponding carbamate.

**1-(Phenylseleno)but-3-en-2-ol (6b):**<sup>[37]</sup> Yield: 38%, oil; <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 138.8, 133.1 (2C), 129.3, 129.2 (2C), 127.3, 116.0, 70.9, 36.2 ppm.

**1-Butoxy-3-(phenylseleno)propan-2-ol (6e):** Yield: 55%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 7.60–7.47 (m, 2H; CH), 7.30–7.20 (m, 3H; CH), 3.90–3.70 (m, 1H; CH), 3.57–3.35 (m, 4H; CH<sub>2</sub>), 3.10 (dd, <sup>2</sup>*J*(H,H) = 12.7 and <sup>3</sup>*J*(H,H) = 6.0 Hz, 1H; CH<sub>2</sub>), 3.01 (dd, <sup>2</sup>*J*(H,H) = 12.7 and <sup>3</sup>*J*(H,H) = 6.8 Hz, 1H; CH<sub>2</sub>), 2.69 (d, <sup>3</sup>*J*(H,H) = 4.5 Hz, 1H; OH), 1.63–1.15 (m, 4H; CH<sub>2</sub>), 0.91 ppm (t, <sup>3</sup>*J*(H,H) = 7.2 Hz, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 132.5 (2C), 128.9 (2C), 127.9, 126.9, 73.1, 71.1, 69.2, 31.6, 31.4, 19.0, 13.7 ppm; GC-MS: *m/z* (%): 288 (47) [*M*]<sup>+</sup>, 183 (38), 157 (38), 113 (23), 77 (18), 57 (100), 41 (30); elemental analysis calcd (%) for C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>Se (287.3): C 54.36, H 7.02; found: C 54.53, H 7.15.

**Methyl 4-hydroxy-5-(phenylseleno)pentanoate (6g):** Yield: 78%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 7.50–7.40 (m, 2H; CH), 7.25–7.15 (m, 3H; CH), 3.70–3.55 (m, 1H; CH), 3.58 (s, 3H; OCH<sub>3</sub>), 3.05 (dd, <sup>2</sup>*J*(H,H) = 12.7 and <sup>3</sup>*J*(H,H) = 4.0 Hz, 1H; CH<sub>2</sub>), 2.83 (dd, <sup>2</sup>*J*(H,H) = 12.7 and <sup>3</sup>*J*(H,H) = 8.3 Hz, 1H; CH<sub>2</sub>), 2.50 (brs, 1H; OH), 2.43 (dt, <sup>2</sup>*J*(H,H) = 9.1 and <sup>3</sup>*J*(H,H) = 3.1 Hz, 1H; CH<sub>2</sub>), 2.36 (dt, <sup>2</sup>*J*(H,H) = 9.1 and <sup>3</sup>*J*(H,H) = 2.6 Hz, 1H; CH<sub>2</sub>), 1.96–1.60 ppm (m, 2H; CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 174.1, 132.9 (2C), 129.2 (2C), 128.7, 127.3, 69.1, 51.6, 36.7, 31.3, 30.4 ppm; GC-MS: *m/z* (%): 256 (16) [*M*–32]<sup>+</sup>, 171 (32), 157 (36), 91 (64), 85 (100), 77 (33); elemental analysis calcd (%) for C<sub>12</sub>H<sub>16</sub>O<sub>3</sub>Se (287.2): C 50.18, H 5.61; found: C 50.16, H 5.60.

**10-(1,3-Dioxolan-2-yl)-1-(phenylseleno)decan-2-ol (6h):** Yield: 80%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 7.58–7.46 (m, 2H; CH), 7.30–7.20 (m, 3H; CH), 4.84 (t, <sup>3</sup>*J*(H,H) = 4.7 Hz, 1H; CH), 4.02–3.75 (m, 4H; CH<sub>2</sub>), 3.74–3.56 (m, 1H; CH), 3.12 (dd, <sup>2</sup>*J*(H,H) = 12.6 and <sup>3</sup>*J*(H,H) = 3.7 Hz, 1H; CH<sub>2</sub>), 2.88 (dd, <sup>2</sup>*J*(H,H) = 12.6 and <sup>3</sup>*J*(H,H) = 8.4 Hz, 1H; CH<sub>2</sub>), 2.50 (brs, 1H; OH), 1.72–1.19 ppm (m, 16H; CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 132.9 (2C), 129.5, 129.1 (2C), 127.1, 104.6, 69.8, 64.7 (2C), 37.1, 36.6, 33.8, 29.4 (4C), 25.7, 24.0 ppm; GC-MS: *m/z* (%): 386 (7), 172 (15), 157 (8), 73 (100); elemental analysis calcd (%) for C<sub>19</sub>H<sub>30</sub>O<sub>3</sub>Se (385.4): C 59.21, H 7.85; found: C 59.13, H 7.67.

**2-[2-Hydroxy-3-(phenylseleno)propyl]-1*H*-isoindol-1,3-(2*H*)-dione (6i):** Yield: 98%; m.p. 84 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 7.90–7.79 (m, 2H; CH), 7.78–7.70 (m, 2H; CH), 7.60–7.50 (m, 2H; CH), 7.30–7.15 (m, 3H; CH), 4.15–3.95 (m, 1H; CH), 3.88 (m, 2H; CH<sub>2</sub>), 3.77 (brs, 1H; OH), 3.12 (dd, <sup>2</sup>*J*(H,H) = 13.0 and <sup>3</sup>*J*(H,H) = 5.3 Hz, 1H; CH<sub>2</sub>),

3.00 ppm (dd,  $^2J(\text{H,H})=13.0$  and  $^3J(\text{H,H})=7.0$  Hz, 1H; CH<sub>2</sub>);  $^{13}\text{C}$  NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=168.6$  (2C), 134.1 (2C), 133.2 (2C), 131.8 (2C), 129.9 (2C), 129.2, 127.4, 123.4 (2C), 69.0, 43.2, 33.6 ppm; elemental analysis calcd (%) for C<sub>17</sub>H<sub>15</sub>NO<sub>3</sub>Se (360.3): C 56.68, H 4.20, N 3.89; found: C 56.69, H 4.23, N 3.87.

**N-[2-Hydroxy-3-(phenylseleno)propyl]benzamide (6l)**: Yield: 67%; m.p. 137–141 °C;  $^1\text{H}$  NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=7.78$ –7.68 (m, 2H; CH), 7.61–7.37 (m, 4H; CH), 4.50 (s, 2H; CH<sub>2</sub>), 3.90 (dd,  $^2J(\text{H,H})=10.2$  and  $^3J(\text{H,H})=4.8$  Hz, 1H; CH<sub>2</sub>), 3.85 (brs, 1H; OH), 3.78 (dd,  $^2J(\text{H,H})=10.2$  and  $^3J(\text{H,H})=7.0$  Hz, 1H; CH<sub>2</sub>), 3.42 (dt,  $^3J(\text{H,H})=7.0$  and 4.8 Hz, 1H; CH), 2.95–2.88 (m, 1H; CH), 1.70–1.25 (m, 4H; CH<sub>2</sub>), 0.90 ppm (t,  $^3J(\text{H,H})=6.9$  Hz, 3H; CH<sub>3</sub>);  $^{13}\text{C}$  NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=137.5$ , 134.6 (2C), 129.1 (2C), 128.4 (2C), 127.7 (5C), 73.3, 72.8, 71.4, 51.2, 37.2, 19.0, 14.0 ppm; elemental analysis calcd (%) for C<sub>19</sub>H<sub>24</sub>O<sub>2</sub>Se (363.4): C 62.80, H 6.66; found: C 62.82, H 6.64.

**(2SR,3RS)-1-(Benzoyloxy)-2-(phenylseleno)hexan-3-ol (11b)**: Yield: 91%, oil;  $^1\text{H}$  NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=7.60$ –7.50 (m, 2H; CH), 7.40–7.15 (m, 8H; CH), 4.50 (s, 2H; CH<sub>2</sub>), 3.90 (dd,  $^2J(\text{H,H})=10.2$  and  $^3J(\text{H,H})=4.8$  Hz, 1H; CH<sub>2</sub>), 3.85 (brs, 1H; OH), 3.78 (dd,  $^2J(\text{H,H})=10.2$  and  $^3J(\text{H,H})=7.0$  Hz, 1H; CH<sub>2</sub>), 3.42 (dt,  $^3J(\text{H,H})=7.0$  and 4.8 Hz, 1H; CH), 2.95–2.88 (m, 1H; CH), 1.70–1.25 (m, 4H; CH<sub>2</sub>), 0.90 ppm (t,  $^3J(\text{H,H})=6.9$  Hz, 3H; CH<sub>3</sub>);  $^{13}\text{C}$  NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=137.5$ , 134.6 (2C), 129.1 (2C), 128.4 (2C), 127.7 (5C), 73.3, 72.8, 71.4, 51.2, 37.2, 19.0, 14.0 ppm; elemental analysis calcd (%) for C<sub>19</sub>H<sub>24</sub>O<sub>2</sub>Se (363.4): C 62.80, H 6.66; found: C 62.82, H 6.64.

**(2SR,3SR)-1,4-Bis(benzoyloxy)-3-(phenylseleno)butan-2-ol (11e)**: Yield: 79%, oil;  $^1\text{H}$  NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=7.60$ –7.50 (m, 2H; CH), 7.38–7.14 (m, 13H; CH), 4.49 (m, 2H; CH<sub>2</sub>), 4.48 (m, 2H; CH<sub>2</sub>), 4.30–4.17 (m, 1H; CH), 3.89 (dd,  $^2J(\text{H,H})=9.9$  and  $^3J(\text{H,H})=7.4$  Hz, 1H; CH<sub>2</sub>), 3.80 (dd,  $^2J(\text{H,H})=9.9$  and  $^3J(\text{H,H})=4.4$  Hz, 1H; CH<sub>2</sub>), 3.71 (dd,  $^2J(\text{H,H})=9.4$  and  $^3J(\text{H,H})=6.4$  Hz, 1H; CH<sub>2</sub>), 3.65 (dd,  $^2J(\text{H,H})=9.4$  and  $^3J(\text{H,H})=5.8$  Hz, 1H; CH<sub>2</sub>), 3.55–3.44 (m, 1H; CH), 2.95 ppm (d,  $^3J(\text{H,H})=3.6$  Hz, 1H; OH);  $^{13}\text{C}$  NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=137.9$ , 137.7, 134.0 (2C), 129.4, 129.0 (2C), 128.4 (3C), 127.7 (4C), 127.3 (2C), 126.9 (2C), 73.3, 73.2, 72.6, 72.0, 70.8, 48.7 ppm; elemental analysis calcd (%) for C<sub>24</sub>H<sub>26</sub>O<sub>3</sub>Se (441.4): C 65.30, H 5.94; found: C 65.22, H 5.96.

**4-(Benzoyloxy)-2-methyl-3-(phenylseleno)butan-2-ol (11f)**: Yield: 94%, oil;  $^1\text{H}$  NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=7.65$ –7.50 (m, 2H; CH), 7.38–7.12 (m, 8H; CH), 4.51 (m, 2H; CH<sub>2</sub>), 3.90 (m, 2H; CH<sub>2</sub>), 3.73 (s, 1H; OH), 3.34 (dd,  $^3J(\text{H,H})=6.7$  and 5.2 Hz, 1H; CH), 1.38 (s, 3H; CH<sub>3</sub>), 1.35 ppm (s, 3H; CH<sub>3</sub>);  $^{13}\text{C}$  NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=137.3$ , 134.2 (2C), 129.9, 129.2 (2C), 128.5 (2C), 127.9, 127.8 (2C), 127.6, 73.4, 73.3, 72.1, 59.7, 29.2, 27.0 ppm; elemental analysis calcd (%) for C<sub>18</sub>H<sub>22</sub>O<sub>3</sub>Se (349.3): C 61.89, H 6.35; found: C 61.90, H 6.33.

**(1S)-1-Phenyl-2-(phenylseleno)ethanol (19d)**<sup>[23,27]</sup>: Yield: 72%, oil;  $[\alpha]_{\text{D}}^{25} = +14.4$  ( $c=1.54$  in CHCl<sub>3</sub>).

**Methyl (3S)-3-hydroxy-4-(phenylseleno)butanoate (19e)**: Yield: 55%, oil;  $^1\text{H}$  NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=7.58$ –7.46 (m, 2H; CH), 7.30–7.20 (m, 3H; CH), 4.22–4.08 (m, 1H; CH), 3.67 (s, 3H; OCH<sub>3</sub>), 3.22–2.92 (m, 2H; CH<sub>2</sub>), 3.10 (brs, 1H; OH), 2.67 (dd,  $^2J(\text{H,H})=16.0$  and  $^3J(\text{H,H})=4.3$  Hz, 1H; CH<sub>2</sub>), 2.55 ppm (dd,  $^2J(\text{H,H})=16.0$  and  $^3J(\text{H,H})=7.7$  Hz, 1H; CH<sub>2</sub>);  $^{13}\text{C}$  NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=172.3$ , 132.7 (2C), 129.3, 129.1 (2C), 127.1, 67.1, 51.7, 40.2, 34.6 ppm; GC-MS:  $m/z$  (%): 274 (50) [ $M$ ]<sup>+</sup>, 172 (32), 157 (54), 117 (100), 91 (55), 77 (30); elemental analysis calcd (%) for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>Se (273.2): C 48.36, H 5.17; found: C 48.53, H 5.14.

**(3S)-3-Hydroxy-4-(phenylseleno)butanenitrile (19f)**: Yield: 77%, oil;  $[\alpha]_{\text{D}}^{25} = -22.71$  ( $c=4.82$  in CHCl<sub>3</sub>);  $^1\text{H}$  NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=7.60$ –7.50 (m, 2H; CH), 7.35–7.25 (m, 3H; CH), 3.96 (ddtd,  $^3J(\text{H,H})=7.5$ , 6.0, 5.2, and 4.2 Hz, 1H; CH), 3.12 (dd,  $^2J(\text{H,H})=13.0$  and  $^3J(\text{H,H})=5.2$  Hz, 1H; CH<sub>2</sub>), 3.02 (d,  $^3J(\text{H,H})=4.2$  Hz, 1H; OH), 3.00 (dd,  $^2J(\text{H,H})=13.0$  and  $^3J(\text{H,H})=7.5$  Hz, 1H; CH<sub>2</sub>), 2.69 (dd,  $^2J(\text{H,H})=16.7$  and  $^3J(\text{H,H})=5.2$  Hz, 1H; CH<sub>2</sub>), 2.59 ppm (dd,  $^2J(\text{H,H})=16.7$  and  $^3J(\text{H,H})=6.0$  Hz, 1H; CH<sub>2</sub>);  $^{13}\text{C}$  NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=133.3$  (2C), 129.4 (2C), 128.0, 127.8, 117.1, 66.2, 34.5, 24.9 ppm; GC-MS:  $m/z$  (%): 241 (100) [ $M$ ]<sup>+</sup>, 171 (61), 157 (61), 91 (64), 77 (32), 51 (15); elemental analysis calcd (%) for C<sub>10</sub>H<sub>11</sub>NOSe (240.2): C 50.01, H 5.13, N 4.19; found: C 50.03, H 5.15, N 4.20.

**tert-Butyl (1S,2R)- and (1S,2S)-1-(cyclohexylmethyl)-2-hydroxy-3-(phenylseleno)propylcarbamate (19h)**: Yield: 67%, oil; mixture of diastereoisomers (82:18);  $^1\text{H}$  NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=7.57$ –7.45 (m, 4H; CH), 7.30–7.20 (m, 6H; CH), 4.71 (d,  $^3J(\text{H,H})=9.6$  Hz, 1H; NH), 4.62 (d,  $^3J(\text{H,H})=6.9$  Hz, 1H; NH), 3.85–3.65 (m, 2H; CH), 3.61–3.49 (m, 2H; CH), 3.22–2.85 (m, 4H; CH<sub>2</sub>), 3.00 (brs, 2H; OH), 1.88–0.66 (m, 26H; CH and CH<sub>2</sub>), 1.45 ppm (s, 18H; CH<sub>3</sub>);  $^{13}\text{C}$  NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=156.1$  (2C), 138.1 (2C), 133.0 (2C), 129.2 (4C), 128.9 (2C), 127.3 (2C), 79.2 (2C), 73.3, 71.3, 52.3, 51.0, 40.6, 37.4, 34.3 (2C), 34.2 (2C), 33.6 (2C), 32.8, 32.3, 28.3 (6C), 26.5 (2C), 26.3 (2C), 26.1 ppm (2C); elemental analysis calcd (%) for C<sub>21</sub>H<sub>33</sub>NO<sub>3</sub>Se (426.5): C 59.14, H 7.80, N 3.28; found: C 59.22, H 7.78, N 3.17.

**Preparation of 19b and 19c**: Sodium hydride (0.106 g, 4.4 mmol) was added to a solution of diphenyl diselenide (0.628 g, 2 mmol) in dry THF (30 mL). The suspension was refluxed for 2 h, allowed to cool to room temperature, and then HMPA (1 mL) was added. (*S*)-(+)-Glycidyl butyrate (0.691 g, 4.8 mmol) was added to the resultant orange solution and after 1 h the reaction was quenched with HCl (5 mL, 10%). The reaction mixture was extracted with diethyl ether and the combined organic layers were dried over sodium sulfate and evaporated. The reaction product was purified by chromatography on a silica-gel column using a mixture of diethyl ether and light petroleum (2:8) as eluent. Compound **19c** was obtained in 25% yield. The corresponding diol derivative (30% yield) was also isolated and was selectively silylated at the primary hydroxy group under standard conditions<sup>[38]</sup> to afford **19b**. The crude hydroxy selenide was then immediately transformed into the corresponding benzoyl carbamate. Yields, as well as physical and spectral data are reported below.

**(2R)-2-Hydroxy-3-(phenylseleno)propylbutyrate (19c)**: Yield: 25%, oil;  $[\alpha]_{\text{D}}^{25} = -42.57$  ( $c=2.81$  in CHCl<sub>3</sub>);  $^1\text{H}$  NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=7.63$ –7.50 (m, 2H; CH), 7.40–7.20 (m, 3H; CH), 4.21 (dd,  $^2J(\text{H,H})=11.4$  and  $^3J(\text{H,H})=4.3$  Hz, 1H; CH<sub>2</sub>), 4.12 (dd,  $^2J(\text{H,H})=11.4$  and  $^3J(\text{H,H})=5.6$  Hz, 1H; CH<sub>2</sub>), 3.95 (dddt,  $^3J(\text{H,H})=7.5$ , 5.6, 5.2, and 4.3 Hz, 1H; CH), 3.09 (dd,  $^2J(\text{H,H})=12.9$  and  $^3J(\text{H,H})=5.2$  Hz, 1H; CH<sub>2</sub>), 2.98 (dd,  $^2J(\text{H,H})=12.9$  and  $^3J(\text{H,H})=7.5$  Hz, 1H; CH<sub>2</sub>), 2.74 (d,  $^3J(\text{H,H})=4.3$  Hz, 1H; OH), 2.30 (t,  $^3J(\text{H,H})=7.3$  Hz, 2H; CH<sub>2</sub>), 1.63 (sext,  $^3J(\text{H,H})=7.3$  Hz, 2H; CH<sub>2</sub>), 0.95 ppm (t,  $^3J(\text{H,H})=7.3$  Hz, 3H; CH<sub>3</sub>);  $^{13}\text{C}$  NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=173.6$ , 133.1 (2C), 129.3, 129.2 (2C), 127.5, 68.5, 66.7, 35.9, 32.2, 18.3, 13.6 ppm; GC-MS  $m/z$  (%): 302 (75) [ $M$ ]<sup>+</sup>, 214 (26), 183 (32), 157 (57), 145 (90), 77 (25), 71 (100); elemental analysis calcd (%) for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>Se (301.2): C 51.83, H 6.02, N 15.93; found: C 51.82, H 6.00, N 15.95.

#### Synthesis of the *N*-tosyl- and *N*-benzoyl carbamates

**General procedure**: Under an inert atmosphere, tosyl or benzoyl isocyanate (1.1 mmol) was added to a solution of the  $\beta$ -hydroxyalkyl phenyl selenide (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) (CCl<sub>4</sub> for compounds **11d**, **11f**, **19d**, **19g**, and **19h**). The reaction was stirred at room temperature until TLC analysis did not show any more starting alcohol to be present (1–24 h), and the solvent was then evaporated. The crude tosyl carbamate derivatives were sufficiently pure to be employed directly without further purification. On the other hand, the crude benzoyl carbamates were purified by column chromatography on silica gel using a mixture of diethyl ether and light petroleum (4:6) as eluent. Yields, as well as physical and spectral data are reported below. Compounds **20d** and **20h** were used without purification.

**1-(Phenylseleno)methylundecyl-(4-methylphenyl)sulfonylcarbamate (7a)**: Yield: 98%, oil;  $^1\text{H}$  NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=7.95$ –7.82 (m, 2H; CH), 7.50 (brs, 1H; NH), 7.45–7.36 (m, 2H; CH), 7.35–7.18 (m, 5H; CH), 4.87 (dq,  $^3J(\text{H,H})=6.9$  and 6.0 Hz, 1H; CH), 2.95 (m, 2H; CH<sub>2</sub>), 2.42 (s, 3H; CH<sub>3</sub>), 1.68–1.45 (m, 2H; CH<sub>2</sub>), 1.38–1.04 (m, 16H; CH<sub>2</sub>), 0.90 ppm (t,  $^3J(\text{H,H})=6.3$  Hz, 3H; CH<sub>3</sub>);  $^{13}\text{C}$  NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=150.0$ , 144.9, 135.6, 133.1 (2C), 129.9 (2C), 129.5 (2C), 129.1, 128.3 (2C), 127.3, 76.9, 33.5, 31.9, 31.3, 29.5 (2C), 29.3 (3C), 24.9, 22.6, 21.6, 14.1 ppm; IR:  $\tilde{\nu}=3239$ , 2925, 2854, 1749, 1438, 1348, 1163, 1090 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>26</sub>H<sub>37</sub>NO<sub>4</sub>Se (538.6): C 57.98, H 6.92, N 2.60; found: C 57.89, H 8.95, N 2.52.

**1-(Phenylseleno)methylprop-2-enyl-(4-methylphenyl)sulfonylcarbamate (7b)**: Yield: 98%, oil;  $^1\text{H}$  NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta=7.80$  (d,  $^3J(\text{H,H})=8.3$  Hz, 2H; CH), 7.40–7.05 (m, 7H; CH), 5.63 (ddd,  $^3J(\text{H,H})=17.4$ , 10.4, and 6.3 Hz, 1H; CH), 5.28–4.94 (m, 3H; CH), 5.00

(brs, 1H; NH), 2.95 (dd,  $^2J(\text{H,H})=12.8$  and  $^3J(\text{H,H})=6.6$  Hz, 1H; CH<sub>2</sub>), 2.87 (dd,  $^2J(\text{H,H})=12.8$  and  $^3J(\text{H,H})=6.5$  Hz, 1H; CH<sub>2</sub>), 2.34 ppm (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=149.5, 145.1, 135.5, 134.7, 133.9 (2C), 129.6 (2C), 129.2 (2C), 128.4 (2C), 127.5 (2C), 119.1, 76.8, 31.1, 21.7 ppm; elemental analysis calcd (%) for C<sub>18</sub>H<sub>19</sub>NO<sub>4</sub>Se (424.4): C 50.94, H 4.51, N 3.30; found: C 50.92, H 4.52, N 3.33.

**1-[(Phenylseleno)methyl]pent-4-ethyl-(4-methylphenyl)sulfonylcarbamate (7c):** Yield: 98%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=7.88–7.68 (m, 2H; CH), 7.65 (brs, 1H; NH), 7.40–7.10 (m, 7H; CH), 5.75–5.45 (m, 1H; CH), 5.05–4.65 (m, 3H; CH), 2.88 (m, 2H; CH<sub>2</sub>), 2.32 (s, 3H; CH<sub>3</sub>), 1.90–1.50 ppm (m, 4H; CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=150.0, 145.0, 136.9, 135.6, 133.1 (2C), 129.6 (2C), 129.2 (2C), 128.3, 127.4 (2C), 126.4, 115.0, 76.3, 32.6, 31.2, 29.1, 21.7 ppm; elemental analysis calcd (%) for C<sub>20</sub>H<sub>23</sub>NO<sub>4</sub>SSe (452.4): C 53.09, H 5.12, N 3.10; found: C 53.10, H 5.13, N 3.11.

**1-Phenyl-2-(phenylseleno)ethyl-(4-methylphenyl)sulfonylcarbamate (7d):** Yield: 80%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=8.00–7.90 (m, 2H; CH), 7.75 (brs, 1H; NH), 7.46–7.14 (m, 12H; CH), 5.79 (dd,  $^3J(\text{H,H})=7.7$  and 6.2 Hz, 1H; CH), 3.30 (dd,  $^2J(\text{H,H})=12.9$  and  $^3J(\text{H,H})=7.7$  Hz, 1H; CH<sub>2</sub>), 3.20 (dd,  $^2J(\text{H,H})=12.9$  and  $^3J(\text{H,H})=6.2$  Hz, 1H; CH<sub>2</sub>), 2.46 ppm (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=149.5, 145.0, 137.9, 133.3 (2C), 129.6 (2C), 129.1 (2C), 128.7 (3C), 128.5 (2C), 128.3 (2C), 127.4 (2C), 126.5 (2C), 78.2, 33.0, 21.6 ppm; elemental analysis calcd (%) for C<sub>22</sub>H<sub>21</sub>NO<sub>4</sub>SSe (474.4): C 55.75, H 4.46, N 2.95; found: C 55.64, H 4.48, N 2.82.

**2-Butoxy-1-[(phenylseleno)methyl]ethyl-(4-methylphenyl)sulfonylcarbamate (7e):** Yield: 86%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=8.00–7.90 (m, 2H; CH), 7.50–7.40 (m, 2H; CH), 7.38–7.16 (m, 5H; CH), 5.45 (brs, 1H; NH), 4.96 (ddt,  $^3J(\text{H,H})=6.8$ , 6.4, and 4.4 Hz, 1H; CH), 3.54 (m, 2H; CH<sub>2</sub>), 3.32 (m, 2H; CH<sub>2</sub>), 3.11 (dd,  $^2J(\text{H,H})=13.0$  and  $^3J(\text{H,H})=6.8$  Hz, 1H; CH<sub>2</sub>), 3.01 (dd,  $^2J(\text{H,H})=13.0$  and  $^3J(\text{H,H})=6.4$  Hz, 1H; CH<sub>2</sub>), 2.44 (s, 3H; CH<sub>3</sub>), 1.51–1.18 (m, 4H; CH<sub>2</sub>), 0.88 ppm (t,  $^3J(\text{H,H})=7.0$  Hz, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=149.7, 145.0, 135.5, 132.7 (2C), 129.5 (2C), 129.2 (2C), 129.1, 128.4 (2C), 127.3, 75.3, 71.3, 70.0, 31.5, 27.3, 31.6, 19.1, 13.8 ppm; elemental analysis calcd (%) for C<sub>21</sub>H<sub>27</sub>NO<sub>5</sub>SSe (484.5): C 52.06, H 5.62, N 2.89; found: C 52.08, H 5.64, N 2.88.

**4-Oxo-1-[(phenylseleno)methyl]pentyl-(4-methylphenyl)sulfonylcarbamate (7f):** Yield: 98%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=7.91–7.80 (m, 2H; CH), 7.40–7.10 (m, 7H; CH), 5.30 (s, 1H; NH), 4.90–4.70 (m, 1H; CH), 2.90 (m, 2H; CH<sub>2</sub>), 2.46–2.22 (m, 2H; CH<sub>2</sub>), 2.38 (s, 3H; CH<sub>3</sub>), 2.10–1.70 (m, 2H; CH<sub>2</sub>), 2.00 ppm (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=207.8, 150.2, 144.9, 135.5, 133.1, 132.9 (2C), 129.6 (2C), 129.5, 129.1, 128.2, 127.3, 126.2, 75.8, 38.7, 31.1, 29.8, 27.3, 21.4 ppm; elemental analysis calcd (%) for C<sub>20</sub>H<sub>23</sub>NO<sub>5</sub>SSe (468.4): C 51.28, H 4.95, N 2.98; found: C 51.26, H 4.97, N 2.95.

**Methyl 4-(((4-methylphenyl)sulfonyl)aminocarbonyloxy)-5-(phenylseleno)pentenoate (7g):** Yield: 78%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=7.93–7.83 (m, 2H; CH), 7.45–7.35 (m, 2H; CH), 7.34–7.14 (m, 5H; CH), 5.10 (brs, 1H; NH), 4.86 (ddt,  $^3J(\text{H,H})=8.3$ , 6.2, and 4.0 Hz, 1H; CH), 3.61 (s, 3H; OCH<sub>3</sub>), 2.96 (dd,  $^2J(\text{H,H})=13.0$  and  $^3J(\text{H,H})=6.2$  Hz, 1H; CH<sub>2</sub>), 2.88 (dd,  $^2J(\text{H,H})=13.0$  and  $^3J(\text{H,H})=6.2$  Hz, 1H; CH<sub>2</sub>), 2.39 (s, 3H; CH<sub>3</sub>), 2.20 (m, 2H; CH<sub>2</sub>), 2.05–1.80 ppm (m, 2H; CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=173.8, 150.0, 145.0, 135.4, 133.0 (2C), 129.8, 129.6 (2C), 129.2, 128.2 (2C), 127.9, 127.4, 75.8, 51.8, 30.9, 29.5, 28.6, 21.6 ppm; elemental analysis calcd (%) for C<sub>20</sub>H<sub>23</sub>NO<sub>6</sub>SSe (484.4): C 49.59, H 4.79, N 2.89; found: C 49.67, H 4.78, N 2.78.

**2-(1,3-Dioxo-1,3-dihydro-2H-isoindol-2-yl)-1-[(phenylseleno)methyl]ethyl-(4-methylphenyl)sulfonylcarbamate (7i):** Yield: 98%, wax; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=8.20 (brs, 1H; NH), 7.94–7.65 (m, 6H; CH), 7.55–7.42 (m, 2H; CH), 7.32–7.14 (m, 5H; CH), 5.20–5.04 (m, 1H; CH), 3.94 (m, 2H; CH<sub>2</sub>), 3.00 (m, 2H; CH<sub>2</sub>), 2.38 ppm (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=168.0 (2C), 149.7, 144.6, 135.3, 134.0 (2C), 133.5 (2C), 131.6, 129.6, 129.4 (2C), 129.2, 129.1, 128.8, 127.8, 127.6, 126.3, 123.4, 123.2, 74.2, 40.1, 28.7, 21.4 ppm; elemental analysis calcd (%) for C<sub>25</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>Se (557.5): C 53.86, H 3.98, N 5.03; found: C 53.89, H 3.96, N 5.05.

**1-[(Phenylseleno)methyl]undecylbenzoylcarbamate (8a):** Yield: 99%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=7.88 (brs, 1H; NH),

7.82–7.72 (m, 2H; CH), 7.64–7.40 (m, 5H; CH), 7.30–7.11 (m, 3H; CH), 5.09 (quintet,  $^3J(\text{H,H})=6.2$  Hz, 1H; CH), 3.15 (d,  $^3J(\text{H,H})=6.2$  Hz, 2H; CH<sub>2</sub>), 1.88–1.68 (m, 2H; CH<sub>2</sub>), 1.41–1.11 (m, 16H; CH<sub>2</sub>), 0.90 ppm (t,  $^3J(\text{H,H})=6.8$  Hz, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=164.9, 150.4, 133.2, 132.9, 132.8 (2C), 129.7, 129.0, 128.6 (2C), 128.0, 127.6, 127.4, 127.1, 75.8, 33.5, 31.8, 31.2, 29.4 (2C), 29.3 (2C), 29.2, 25.0, 22.6, 14.0 ppm; elemental analysis calcd (%) for C<sub>26</sub>H<sub>35</sub>NO<sub>3</sub>Se (488.5): C 63.92, H 7.22, N 2.87; found: C 63.94, H 7.40, N 2.75.

**1-[(Phenylseleno)methyl]pent-4-enylbenzoylcarbamate (8c):** Yield: 88%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=8.10 (s, 1H; NH), 7.82–7.72 (m, 2H; CH), 7.60–7.40 (m, 6H; CH), 7.30–7.10 (m, 2H; CH), 5.74 (ddt,  $^3J(\text{H,H})=17.1$ , 10.2, and 6.5 Hz, 1H; CH), 5.10 (quintet,  $^3J(\text{H,H})=6.6$  Hz, 1H; CH), 5.08–4.91 (m, 2H; CH<sub>2</sub>), 3.12 (m, 2H; CH<sub>2</sub>), 2.20–2.01 (m, 2H; CH<sub>2</sub>), 1.91–1.72 ppm (m, 2H; CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=164.7, 150.2, 136.9, 132.8 (3C), 129.6, 129.0 (2C), 128.6 (2C), 127.5 (2C), 127.1 (2C), 115.3, 75.3, 32.6, 31.1, 29.2 ppm; elemental analysis calcd (%) for C<sub>20</sub>H<sub>21</sub>NO<sub>3</sub>Se (402.3): C 59.70, H 5.26, N 3.48; found: C 59.71, H 5.28, N 3.50.

**2-Butoxy-1-[(phenylseleno)methyl]ethylbenzoylcarbamate (8e):** Yield: 99%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=8.30 (s, 1H; NH), 7.82–7.77 (m, 2H; CH), 7.60–7.40 (m, 5H; CH), 7.30–7.12 (m, 3H; CH), 5.20–5.12 (m, 1H; CH), 3.71 (dd,  $^2J(\text{H,H})=10.8$  and  $^3J(\text{H,H})=4.6$  Hz, 1H; CH<sub>2</sub>), 3.66 (dd,  $^2J(\text{H,H})=10.8$  and  $^3J(\text{H,H})=4.0$  Hz, 1H; CH<sub>2</sub>), 3.48–3.31 (m, 2H; CH<sub>2</sub>), 3.20 (d,  $^3J(\text{H,H})=6.6$  Hz, 2H; CH<sub>2</sub>), 1.60–1.47 (m, 2H; CH<sub>2</sub>), 1.40–1.28 (m, 2H; CH<sub>2</sub>), 0.90 ppm (t,  $^3J(\text{H,H})=7.0$  Hz, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=164.8, 149.9, 132.9, 132.8, 132.6, 129.4, 129.2, 129.1 (2C), 127.8 (2C), 127.6, 127.0 (2C), 74.3, 71.2, 70.1, 31.4, 27.1, 19.1, 13.8 ppm; elemental analysis calcd (%) for C<sub>21</sub>H<sub>25</sub>NO<sub>5</sub>Se (434.4): C 58.06, H 5.80, N 3.22; found: C 58.40, H 5.78, N 3.24.

**9-(1,3-Dioxolan-2-yl)-1-[(phenylseleno)methyl]nonylbenzoylcarbamate (8h):** Yield: 98%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=8.10 (s, 1H; NH), 7.84–7.74 (m, 2H; CH), 7.63–7.40 (m, 5H; CH), 7.30–7.22 (m, 3H; CH), 5.08 (quintet,  $^3J(\text{H,H})=6.1$  Hz, 1H; CH); 4.82 (t,  $^3J(\text{H,H})=4.8$  Hz, 1H; CH), 4.00–3.76 (m, 4H; CH<sub>2</sub>), 3.13 (m, 2H; CH<sub>2</sub>), 1.81–1.56 (m, 6H; CH<sub>2</sub>), 1.47–1.09 ppm (m, 10H; CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=164.8, 150.3, 132.9, 132.8 (3C), 129.7, 129.0 (2C), 128.6 (2C), 127.6 (2C), 127.1, 104.5, 75.8, 64.7 (2C), 37.7, 33.5, 31.1, 29.3, 29.2 (2C), 29.1, 25.0, 23.9 ppm; elemental analysis calcd (%) for C<sub>27</sub>H<sub>35</sub>NO<sub>5</sub>Se (532.5): C 60.90, H 6.62, N 2.63; found: C 60.81, H 6.63, N 2.38.

**2-(Benzoylamino)-1-[(phenylseleno)methyl]ethylbenzoylcarbamate (8l):** Yield: 96%; m.p. 60–62 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=8.75 (s, 1H; NH), 7.87–7.72 (m, 2H; CH), 7.70–7.12 (m, 13H; CH), 6.25 (brs, 1H; NH), 5.18 (ddt,  $^3J(\text{H,H})=6.9$ , 6.3, and 5.6 Hz, 1H; CH), 3.84 (t,  $^3J(\text{H,H})=5.6$  Hz, 2H; CH<sub>2</sub>), 3.20 (dd,  $^2J(\text{H,H})=13.3$  and  $^3J(\text{H,H})=6.9$  Hz, 1H; CH<sub>2</sub>), 3.09 ppm (dd,  $^2J(\text{H,H})=13.3$  and  $^3J(\text{H,H})=6.9$  Hz, 1H; CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=167.8, 165.3, 151.2, 133.8, 133.1, 132.9 (2C), 132.5, 131.5, 129.2 (2C), 128.7 (2C), 128.5, 128.4 (2C), 127.8 (2C), 127.3, 127.1 (2C), 75.2, 39.1, 28.4 ppm; elemental analysis calcd (%) for C<sub>24</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub>Se (481.4): C 59.88, H 4.61, N 5.82; found: C 59.86, H 4.63, N 5.84.

**4-tert-Butyl-1-(phenylseleno)cyclohexylbenzoylcarbamate (8m):** Yield: 99%; m.p. 147–150 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=7.90–7.73 (m, 1H; CH), 7.80 (brs, 1H; NH), 7.65–7.39 (m, 6H; CH), 7.30–7.11 (m, 3H; CH), 5.10 (s, 2H; CH<sub>2</sub>), 2.65–2.48 (m, 2H; CH<sub>2</sub>), 1.73–1.56 (m, 2H; CH<sub>2</sub>), 1.54–1.12 (m, 4H; CH<sub>2</sub>), 1.12–0.90 (m, 1H; CH), 0.87 ppm (s, 9H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=166.2, 149.9, 133.0, 132.6 (2C), 132.5, 129.8, 128.8 (2C), 128.3 (2C), 127.6 (2C), 126.8, 94.3, 46.8, 36.7, 34.7 (2C), 32.0, 27.1 (3C), 22.1 ppm (2C); elemental analysis calcd (%) for C<sub>25</sub>H<sub>31</sub>NO<sub>3</sub>Se (472.5): C 63.55, H 6.61, N 2.96; found: C 63.57, H 6.63, N 2.98.

**(1S,2R)-2-(Phenylseleno)-1-propylpentyl-(4-methylphenyl)sulfonylcarbamate (12a):** Yield: 98%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=7.91 (d,  $^3J(\text{H,H})=8.3$  Hz, 2H; CH), 7.53–7.45 (m, 2H; CH), 7.40–7.20 (m, 5H; CH), 5.00 (s, 1H; NH), 4.90 (dt,  $^3J(\text{H,H})=8.8$  and 4.1 Hz, 1H; CH), 3.20 (dt,  $^3J(\text{H,H})=8.8$  and 4.5 Hz, 1H; CH), 2.42 (s, 3H; CH<sub>3</sub>), 1.80–1.30 (m, 6H; CH<sub>2</sub>), 1.30–1.05 (m, 2H; CH<sub>2</sub>), 0.90 (t,  $^3J(\text{H,H})=6.6$  Hz, 3H; CH<sub>3</sub>), 0.82 ppm (t,  $^3J(\text{H,H})=7.4$  Hz, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=150.1, 144.9, 135.6, 134.9 (2C), 129.5

(3C), 129.0 (2C), 128.3 (2C), 127.7, 79.8, 50.2, 33.3, 33.2, 21.6, 21.2, 18.6, 13.6 ppm (2C); elemental analysis calcd (%) for  $C_{22}H_{29}NO_4Se$  (482.5): C 54.76, H 6.06, N 2.90; found: C 54.69, H 6.98, N 2.93.

**(1RS)-1-[(1SR)-2-(Benzyloxy)-1-(phenylseleno)ethyl]butyl-(4-methylphenyl)sulfonylcarbamate (12b)**: Yield: 98%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 7.90 (d,  $^3J(H,H)$  = 8.3 Hz, 2H; CH), 7.55–7.42 (m, 2H; CH), 7.40–7.20 (m, 10H; CH), 7.25 (s, 1H; NH), 5.14 (dt,  $^3J(H,H)$  = 6.2 and 5.0 Hz, 1H; CH), 4.42 (m, 2H;  $CH_2$ ), 3.75–3.60 (m, 2H;  $CH_2$ ), 3.59–3.44 (m, 1H; CH), 2.43 (s, 3H;  $CH_3$ ), 1.70–1.54 (m, 2H;  $CH_2$ ), 1.22–1.04 (m, 2H;  $CH_2$ ), 0.80 ppm (t,  $^3J(H,H)$  = 7.3 Hz, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 150.0, 144.8, 137.7, 135.6, 134.6 (2C), 129.6 (3C), 129.5 (3C), 129.1, 128.2 (2C), 127.8 (3C), 126.3, 77.7, 72.8, 69.9, 48.1, 33.6, 21.5, 18.4, 13.6 ppm; elemental analysis calcd (%) for  $C_{27}H_{31}NO_5Se$  (560.6): C 57.85, H 5.57, N 2.50; found: C 57.88, H 5.58, N 2.50.

**(1RS,2RS)-2-(Phenylseleno)cyclohexyl-(4-methylphenyl)sulfonylcarbamate (12c)**: Yield: 98%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 7.93 (d,  $^3J(H,H)$  = 8.3 Hz, 2H; CH), 7.70 (brs, 1H; NH), 7.50–7.40 (m, 2H; CH), 7.38–7.15 (m, 5H; CH), 4.66 (ddd,  $^3J(H,H)$  = 9.1 and 3.8 Hz, 1H; CH), 3.08 (ddd,  $^3J(H,H)$  = 9.8, 9.1, and 3.9 Hz, 1H; CH), 2.40 (s, 3H;  $CH_3$ ), 2.15–1.97 (m, 2H;  $CH_2$ ), 1.74–1.50 (m, 2H;  $CH_2$ ), 1.48–1.15 ppm (m, 4H;  $CH_2$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 149.9, 144.6, 135.4, 135.1 (2C), 129.0 (2C), 128.6 (2C), 128.0 (2C), 127.4 (2C), 77.8, 45.1, 31.5, 30.7, 24.9, 22.9, 21.3 ppm; elemental analysis calcd (%) for  $C_{20}H_{23}NO_4Se$  (452.4): C 53.09, H 5.12, N 3.10; found: C 53.07, H 5.15, N 3.80.

**(1SR,2RS)-2-(Phenylseleno)-1-propylpentylbenzoylcarbamate (13a)**: Yield: 91%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 7.85–7.35 (m, 8H; CH), 7.28–7.00 (m, 2H; CH), 6.04 (brs, 1H; NH), 5.07 (dt,  $^3J(H,H)$  = 9.4 and 3.7 Hz, 1H; CH), 3.48 (ddd,  $^3J(H,H)$  = 8.3, 4.5, and 3.7 Hz, 1H; CH), 2.00–1.20 (m, 8H;  $CH_2$ ), 0.95 (t,  $^3J(H,H)$  = 6.9 Hz, 3H;  $CH_3$ ), 0.90 ppm (t,  $^3J(H,H)$  = 6.9 Hz, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 164.8, 150.5, 134.6, 134.5, 132.6, 131.7, 130.1, 129.2 (2C), 128.8, 128.5, 127.9, 127.5, 127.3, 78.4, 50.2, 32.8, 32.2, 21.2, 18.6, 13.6, 13.2 ppm; elemental analysis calcd (%) for  $C_{22}H_{27}NO_3Se$  (432.4): C 61.11, H 6.29, N 3.24; found: C 61.23, H 6.20, N 3.22.

**(1RS)-1-[(1SR)-2-(Benzyloxy)-1-(phenylseleno)ethyl]butylbenzoylcarbamate (13b)**: Yield: 93.4%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 8.05 (s, 1H; NH), 7.80–7.70 (m, 2H; CH), 7.65–7.50 (m, 2H; CH), 7.48–7.38 (m, 3H; CH), 7.35–7.12 (m, 8H; CH), 5.35–5.23 (m, 1H; CH), 4.50 (m, 2H;  $CH_2$ ), 3.81–3.66 (m, 3H; CH and  $CH_2$ ), 1.84–1.64 (m, 2H;  $CH_2$ ), 1.48–1.25 (m, 2H;  $CH_2$ ), 0.87 ppm (t,  $^3J(H,H)$  = 7.2 Hz, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 164.7, 150.4, 137.7, 134.5 (2C), 132.9, 132.7, 129.0 (2C), 128.6 (3C), 128.2 (2C), 127.6 (3C), 127.5 (3C), 76.7, 72.7, 70.2, 48.0, 33.4, 18.6, 13.6 ppm; elemental analysis calcd (%) for  $C_{27}H_{29}NO_4Se$  (510.5): C 63.53, H 5.73, N 2.74; found: C 63.55, H 5.74, N 2.75.

**(1R,2S)-1-Methyl-2-(phenylseleno)cyclohexylbenzoylcarbamate (13d)**: Yield: 98%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 7.80–7.65 (m, 2H; CH), 7.70 (s, 1H; NH), 7.64–7.41 (m, 5H; CH), 7.31–7.12 (m, 3H; CH), 4.05 (dd,  $^3J(H,H)$  = 9.0 and 4.0 Hz, 1H; CH), 2.38–1.92 (m, 4H;  $CH_2$ ), 1.88–1.33 (m, 4H;  $CH_2$ ), 1.72 ppm (s, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 165.1, 149.0, 134.2 (2C), 133.2, 132.7, 130.3, 129.0 (2C), 128.6 (2C), 127.6 (2C), 127.3, 87.6, 51.3, 35.7, 30.5, 24.6, 22.3, 22.1 ppm; elemental analysis calcd (%) for  $C_{21}H_{23}NO_3Se$  (416.4): C 60.58, H 5.57, N 3.36; found: C 60.60, H 5.59, N 3.37.

**(1RS,2RS)-3-(Benzyloxy)-1-[(benzyloxy)methyl]-2-(phenylseleno)propylbenzoylcarbamate (13e)**: Yield: 90%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 7.85 (s, 1H; NH), 7.77–7.68 (m, 2H; CH), 7.60–7.50 (m, 3H; CH), 7.50–7.42 (m, 2H; CH), 7.32–7.16 (m, 13H; CH), 5.56 (td,  $^3J(H,H)$  = 5.8 and 3.6 Hz, 1H; CH), 4.50 (m, 2H;  $CH_2$ ), 4.48 (m, 2H;  $CH_2$ ), 3.88 (dd,  $^2J(H,H)$  = 10.3 and  $^3J(H,H)$  = 5.6 Hz, 1H;  $CH_2$ ), 3.82 (dd,  $^2J(H,H)$  = 10.3 and  $^3J(H,H)$  = 5.6 Hz, 1H;  $CH_2$ ), 3.80 (dd,  $^2J(H,H)$  = 9.2 and  $^3J(H,H)$  = 5.8 Hz, 1H;  $CH_2$ ), 3.76 (dd,  $^2J(H,H)$  = 9.2 and  $^3J(H,H)$  = 5.8 Hz, 1H;  $CH_2$ ), 3.68 ppm (td,  $^3J(H,H)$  = 5.6 and 3.6 Hz, 1H; CH);  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 163.3, 149.8, 137.8, 134.0 (2C), 133.0, 132.9, 129.1 (2C), 128.8 (3C), 128.4 (6C), 127.8 (5C), 127.6 (3C), 74.4, 73.2, 73.1, 70.4, 69.4, 45.5 ppm; elemental analysis calcd (%) for  $C_{32}H_{31}NO_5Se$  (588.6): C 65.30, H 5.31, N 2.38; found: C 65.32, H 5.32, N 2.40.

### 3-(Benzyloxy)-1,1-dimethyl-2-(phenylseleno)propylbenzoylcarbamate

**(13f)**: Yield: 85%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 8.09 (s, 1H; NH), 7.74–7.43 (m, 5H; CH), 7.42–7.11 (m, 10H; CH), 4.43 (m, 2H;  $CH_2$ ), 4.19 (dd,  $^3J(H,H)$  = 6.2 and 4.6 Hz, 1H; CH), 3.93 (dd,  $^2J(H,H)$  = 10.8 and  $^3J(H,H)$  = 6.2 Hz, 1H;  $CH_2$ ), 3.82 (dd,  $^2J(H,H)$  = 10.8 and  $^3J(H,H)$  = 4.6 Hz, 1H;  $CH_2$ ), 1.72 (s, 3H;  $CH_3$ ), 1.68 ppm (s, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 164.9, 149.3, 137.7, 133.9 (2C), 133.0, 132.5, 129.8, 128.9 (2C), 128.4 (2C), 128.1 (2C), 127.4 (4C), 127.3 (2C), 86.3, 72.7, 70.7, 52.9, 25.6, 25.1 ppm; elemental analysis calcd (%) for  $C_{26}H_{27}NO_4Se$  (496.5): C 62.90, H 5.48, N 2.82; found: C 62.72, H 5.50, N 2.70.

### (1SR,2RS)-3-Cyano-1-methyl-2-(phenylseleno)propylbenzoylcarbamate

**(13g)**: Yield: 79%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 8.60 (s, 1H; NH), 7.90–7.73 (m, 2H; CH), 7.70–7.20 (m, 8H; CH), 5.10 (quintet,  $^3J(H,H)$  = 6.5 Hz, 1H; CH), 3.34 (q,  $^3J(H,H)$  = 6.5 Hz, 1H; CH), 2.85 (m, 2H;  $CH_2$ ), 1.52 ppm (d,  $^3J(H,H)$  = 6.5 Hz, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 165.0, 150.3, 136.1 (2C), 133.0, 132.6, 129.5 (2C), 129.1, 128.8 (2C), 127.7 (2C), 126.1, 118.2, 74.5, 43.3, 21.1, 18.8 ppm; elemental analysis calcd (%) for  $C_{19}H_{18}N_2O_3Se$  (401.3): C 56.86, H 4.52, N 6.98; found: C 58.88, H 4.54, N 7.00.

### (1S)-2-(Benzyloxy)-1-[(phenylseleno)methyl]ethylbenzoylcarbamate

**(20a)**: Yield: 97%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 8.02 (s, 1H; NH); 7.80–7.70 (m, 2H; CH), 7.60–7.40 (m, 5H; CH), 7.38–7.14 (m, 8H; CH), 5.24–5.11 (m, 1H; CH), 4.45 (m, 2H;  $CH_2$ ), 3.76 (dd,  $^2J(H,H)$  = 10.7 and  $^3J(H,H)$  = 4.6 Hz, 1H;  $CH_2$ ), 3.69 (dd,  $^2J(H,H)$  = 10.7 and  $^3J(H,H)$  = 4.0 Hz, 1H;  $CH_2$ ), 3.18 ppm (m, 2H;  $CH_2$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 164.8, 150.0, 137.4, 132.8, 132.7, 132.6 (2C), 132.5, 129.3, 129.1 (2C), 128.6 (2C), 128.3 (2C), 127.7 (2C), 127.6 (2C), 127.1, 74.2, 73.2, 69.5, 27.0 ppm; elemental analysis calcd (%) for  $C_{24}H_{23}NO_4Se$  (468.4): C 61.54, H 4.95, N 2.99; found: C 61.52, H 4.97, N 3.00.

### (1R)-2-[(tert-Butyl(diphenyl)silyloxy)-1-[(phenylseleno)methyl]ethylbenzoylcarbamate (20b)

**(20b)**: Yield: 92%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 7.75–7.21 (m, 18H; CH), 7.50 (s, 1H; NH), 7.20–7.14 (m, 2H; CH), 5.14 (dddd,  $^3J(H,H)$  = 6.4, 6.1, 5.2, and 4.8 Hz, 1H; CH), 3.96 (dd,  $^2J(H,H)$  = 11.1 and  $^3J(H,H)$  = 4.8 Hz, 1H;  $CH_2$ ), 3.88 (dd,  $^2J(H,H)$  = 11.1 and  $^3J(H,H)$  = 5.2 Hz, 1H;  $CH_2$ ), 3.29 (dd,  $^2J(H,H)$  = 13.2 and  $^3J(H,H)$  = 6.1 Hz, 1H;  $CH_2$ ), 3.20 (dd,  $^2J(H,H)$  = 13.2 and  $^3J(H,H)$  = 6.4 Hz, 1H;  $CH_2$ ), 1.07 ppm (s, 9H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 164.6, 149.7, 145.5, 135.6 (2C), 135.5, 133.1, 132.9, 132.8, 129.8 (2C), 129.6, 129.1 (2C), 128.8 (2C), 128.7 (2C), 127.7 (4C), 127.5 (3C), 127.2, 75.7, 63.9, 27.3, 26.8 (3C), 19.2 ppm; elemental analysis calcd (%) for  $C_{33}H_{35}NO_4SeSi$  (616.7): C 64.27, H 5.72, N 2.27; found: C 64.36, H 5.81, N 2.26.

### (2R)-2-[(Benzoylamino)carbonyloxy]-3-(phenylseleno)propylbutyrate

**(20c)**: Yield: 67%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 8.55 (s, 1H; NH), 7.90–7.77 (m, 2H; CH), 7.62–7.38 (m, 5H; CH), 7.31–7.11 (m, 3H; CH), 5.29–5.16 (m, 1H; CH), 4.37 (dd,  $^2J(H,H)$  = 12.0 and  $^3J(H,H)$  = 3.7 Hz, 1H;  $CH_2$ ), 4.27 (dd,  $^2J(H,H)$  = 12.0 and  $^3J(H,H)$  = 5.8 Hz, 1H;  $CH_2$ ), 3.17 (dd,  $^2J(H,H)$  = 13.1 and  $^3J(H,H)$  = 6.3 Hz, 1H;  $CH_2$ ), 3.08 (dd,  $^2J(H,H)$  = 13.1 and  $^3J(H,H)$  = 6.5 Hz, 1H;  $CH_2$ ), 2.23 (t,  $^3J(H,H)$  = 7.3 Hz, 2H;  $CH_2$ ), 1.58 (sextet,  $^3J(H,H)$  = 7.3 Hz, 2H;  $CH_2$ ), 0.90 ppm (t,  $^3J(H,H)$  = 7.3 Hz, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 172.8, 164.7, 149.8, 132.7 (3C), 132.5, 129.0 (2C), 128.7, 128.4 (2C), 127.5 (2C), 127.2, 72.8, 63.4, 35.5, 26.9, 17.9, 13.3 ppm; elemental analysis calcd (%) for  $C_{21}H_{23}NO_5Se$  (448.4): C 56.25, H 5.17, N 3.12; found: C 56.23, H 5.19, N 3.11.

### Methyl (3S)-3-[(benzoylamino)carbonyloxy]-4-(phenylseleno)butanoate

**(20e)**: Yield: 98%; m.p. 44–46°C;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 8.40 (s, 1H; NH), 7.85–7.74 (m, 2H; CH), 7.61–7.35 (m, 5H; CH), 7.30–7.10 (m, 3H; CH), 5.39 (dddd,  $^3J(H,H)$  = 7.2, 6.3, 5.6, and 5.4 Hz, 1H; CH), 3.55 (s, 3H;  $OCH_3$ ), 3.27 (dd,  $^2J(H,H)$  = 13.3 and  $^3J(H,H)$  = 5.6 Hz, 1H;  $CH_2$ ), 3.18 (dd,  $^2J(H,H)$  = 13.3 and  $^3J(H,H)$  = 6.3 Hz, 1H;  $CH_2$ ), 2.88 (dd,  $^2J(H,H)$  = 16.2 and  $^3J(H,H)$  = 5.4 Hz, 1H;  $CH_2$ ), 2.75 ppm (dd,  $^2J(H,H)$  = 16.2 and  $^3J(H,H)$  = 7.2 Hz, 1H;  $CH_2$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta$  = 170.0, 164.7, 149.8, 132.8, 132.6, 132.5 (2C), 129.1 (2C), 128.8 (2C), 128.5 (2C), 127.6, 127.1, 71.8, 51.7, 37.7, 30.0 ppm; elemental analysis calcd (%) for  $C_{19}H_{19}NO_5Se$  (420.4): C 54.29, H 4.56, N 3.33; found: C 54.27, H 4.54, N 3.35.



**(1S)-2-Cyano-1-[(phenylseleno)methyl]ethylbenzoylcarbamate (20 f):** Yield: 89%, oil;  $[\alpha]_D^{25} = +58.74$  ( $c = 3.01$  in  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 8.75$  (s, 1H; NH), 7.90–7.75 (m, 2H; CH), 7.62–7.35 (m, 5H; CH), 7.31–7.15 (m, 3H; CH), 5.10 (ddt,  $^3J(\text{H,H}) = 7.6, 5.6$ , and 5.0 Hz, 1H; CH), 3.28 (dd,  $^2J(\text{H,H}) = 13.4$  and  $^3J(\text{H,H}) = 5.6$  Hz, 1H;  $\text{CH}_2$ ), 3.05 (dd,  $^2J(\text{H,H}) = 13.4$  and  $^3J(\text{H,H}) = 7.6$  Hz, 1H;  $\text{CH}_2$ ), 2.89 ppm (d,  $^3J(\text{H,H}) = 5.0$  Hz, 2H;  $\text{CH}_2$ );  $^{13}\text{C NMR}$  (50 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 164.9, 149.4, 133.0, 132.8$  (2C), 132.3, 129.2 (2C), 128.5 (2C), 127.9, 127.7 (2C), 127.6, 115.8, 70.0, 28.6, 22.1 ppm; elemental analysis calcd (%) for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_5\text{Se}$  (387.3): C 55.82, H 4.16, N 7.23; found: C 55.80, H 4.14, N 7.25.

**(1S,2S)-2-(Dibenzylamino)-3-phenyl-1-[(phenylseleno)methyl]propylbenzoylcarbamate (20 g):** Yield: 58%; m.p. 46–48 °C;  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 7.64$ –7.50 (m, 2H; CH), 7.50–7.00 (m, 24H; CH), 5.43 (ddd,  $^3J(\text{H,H}) = 7.2, 6.8$ , and 4.6 Hz, 1H; CH), 3.65 (m, 4H;  $\text{CH}_2$ ), 3.43 (ddd,  $^3J(\text{H,H}) = 7.8, 7.2$ , and 5.8 Hz, 1H; CH), 3.30 (dd,  $^2J(\text{H,H}) = 13.5$  and  $^3J(\text{H,H}) = 6.8$  Hz, 1H;  $\text{CH}_2$ ), 3.20 (dd,  $^2J(\text{H,H}) = 14.5$  and  $^3J(\text{H,H}) = 5.8$  Hz, 1H;  $\text{CH}_2$ ), 3.03 (dd,  $^2J(\text{H,H}) = 13.5$  and  $^3J(\text{H,H}) = 6.8$  Hz, 1H;  $\text{CH}_2$ ), 2.76 ppm (dd,  $^2J(\text{H,H}) = 14.5$  and  $^3J(\text{H,H}) = 7.8$  Hz, 1H;  $\text{CH}_2$ );  $^{13}\text{C NMR}$  (50 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 164.3, 150.1, 140.4, 139.2$  (2C), 133.5 (2C), 132.9, 132.8, 129.9, 129.0 (2C), 128.9 (4C), 128.7 (4C), 128.4 (3C), 128.3 (2C), 127.6 (2C), 127.2 (2C), 125.8 (2C), 123.6, 75.8, 60.6, 54.2 (2C), 32.1, 30.9 ppm; elemental analysis calcd (%) for  $\text{C}_{38}\text{H}_{36}\text{N}_2\text{O}_5\text{Se}$  (647.7): C 70.47, H 5.60, N 4.33; found: C 70.55, H 5.58, N 4.15.

**(1S)-2-(Benzoyloxy)-1-[(phenylseleno)methyl]ethyl-(4-methylphenyl)sulfonylcarbamate (22 a):** Yield: 98%, oil;  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 8.38$  (s, 1H; NH), 7.90 (d,  $^3J(\text{H,H}) = 8.3$  Hz, 2H; CH), 7.50–7.10 (m, 12H; CH), 5.10 (dddd,  $^3J(\text{H,H}) = 6.9, 6.3, 4.0$ , and 2.0 Hz, 1H; CH), 4.39 (m, 2H;  $\text{CH}_2$ ), 3.66 (dd,  $^2J(\text{H,H}) = 10.4$  and  $^3J(\text{H,H}) = 2.0$  Hz, 1H;  $\text{CH}_2$ ), 3.60 (dd,  $^2J(\text{H,H}) = 10.4$  and  $^3J(\text{H,H}) = 4.0$  Hz, 1H;  $\text{CH}_2$ ), 3.10 (dd,  $^2J(\text{H,H}) = 13.0$  and  $^3J(\text{H,H}) = 6.9$  Hz, 1H;  $\text{CH}_2$ ), 3.01 (dd,  $^2J(\text{H,H}) = 13.0$  and  $^3J(\text{H,H}) = 6.3$  Hz, 1H;  $\text{CH}_2$ ), 2.40 ppm (s, 3H;  $\text{CH}_3$ );  $^{13}\text{C NMR}$  (50 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 149.9, 144.8, 137.3, 135.4, 132.7$  (2C), 129.5, 129.4, 129.0 (2C), 128.2 (3C), 127.6 (2C), 127.5 (2C), 127.2, 126.2, 75.1, 73.0, 69.3, 27.0, 21.5 ppm; elemental analysis calcd (%) for  $\text{C}_{24}\text{H}_{25}\text{NO}_5\text{SSe}$  (518.5): C 55.60, H 4.86, N 2.70; found: C 55.57, H 4.99, N 2.62.

#### Conversion of $\beta$ -carbamoyloxy selenides into 5-substituted *N*-tosyl or *N*-benzoyl-1,3-oxazolidin-2-ones

**Method A:** Powdered potassium hydrogenphosphate (0.870 g, 5 mmol) and *meta*-chloroperoxybenzoic acid (0.688 g, 4 mmol) were added to a solution of the crude *N*-tosyl carbamate **7** (1 mmol) in THF (15 mL) at 0 °C. The progress of the reaction (1–9 h) was monitored by TLC and the mixture was allowed to slowly reach room temperature. When the selenone was completely consumed the reaction was quenched with saturated aqueous  $\text{Na}_2\text{CO}_3$  (10 mL) and extracted with diethyl ether. The combined organic layers were washed with a solution of NaOH (10%) to eliminate the tosylamide impurity, dried over sodium sulfate, and evaporated to give the 1,3-oxazolidin-2-one **9** in pure form. For compounds **8** the reaction mixture was stirred until the starting selenide had been completely transformed (2 h) into the corresponding selenone, as indicated by TLC and  $^{13}\text{C NMR}$  analysis, and the reaction mixture was then concentrated in vacuo. The residue was suspended in reagent-grade acetone (20 mL) and powdered potassium carbonate was added at room temperature. The disappearance of the selenone was monitored by TLC (2–24 h), and the mixture was then concentrated in vacuo, poured into water, and extracted with diethyl ether. The organic layer was dried over sodium sulfate and evaporated. The reaction product was purified by column chromatography on silica gel using a mixture of diethyl ether and light petroleum (2:8) as eluent. Yields, as well as physical and spectral data are reported below.

**5-Decyl-3-[(4-methylphenyl)sulfonyl]-1,3-oxazolidin-2-one (9 a):** Yield: 96%, oil;  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 7.90$ –7.80 (m, 2H; CH), 7.40–7.30 (m, 2H; CH), 4.60–4.40 (m, 1H; CH), 4.09 (dd,  $^2J(\text{H,H}) = 9.0$  and  $^3J(\text{H,H}) = 7.9$  Hz, 1H;  $\text{CH}_2$ ), 3.57 (dd,  $^2J(\text{H,H}) = 9.0$  and  $^3J(\text{H,H}) = 7.2$  Hz, 1H;  $\text{CH}_2$ ), 2.40 (s, 3H;  $\text{CH}_3$ ), 1.80–1.10 (m, 18H;  $\text{CH}_2$ ), 0.95 ppm (t,  $^3J(\text{H,H}) = 6.6$  Hz, 3H;  $\text{CH}_3$ );  $^{13}\text{C NMR}$  (50 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 151.6, 145.5, 133.8, 129.7$  (2C), 128.0 (2C), 74.6, 49.5, 34.0, 31.7, 29.3, 29.2, 29.1 (2C), 28.9, 24.2, 22.5, 21.5, 13.9 ppm; IR:

$\tilde{\nu} = 2920, 2851, 1759, 1369, 1177 \text{ cm}^{-1}$ ; GC-MS:  $m/z$  (%): 381 (2)  $[\text{M}-64]^+$ , 155 (15), 108 (100), 91 (38); elemental analysis calcd (%) for  $\text{C}_{20}\text{H}_{31}\text{NO}_4\text{S}$  (381.5): C 62.96, H 8.19, N 3.67; found: C 62.99, H 8.31, N 3.68.

**3-[(4-Methylphenyl)sulfonyl]-5-vinyl-1,3-oxazolidin-2-one (9 b):** Yield: 81%, oil;  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 7.92$  (d,  $^3J(\text{H,H}) = 8.2$  Hz, 2H; CH), 7.38 (d,  $^3J(\text{H,H}) = 8.2$  Hz, 2H; CH), 5.81 (ddd,  $^3J(\text{H,H}) = 17.1, 10.3$ , and 6.5 Hz, 1H; CH), 5.50–5.30 (m, 2H;  $\text{CH}_2$ ), 4.98 (ddd,  $^3J(\text{H,H}) = 8.1, 7.3$ , and 6.5 Hz, 1H; CH), 4.18 (dd,  $^2J(\text{H,H}) = 9.2$  and  $^3J(\text{H,H}) = 8.1$  Hz, 1H;  $\text{CH}_2$ ), 3.70 (dd,  $^2J(\text{H,H}) = 9.2$  and  $^3J(\text{H,H}) = 7.3$  Hz, 1H;  $\text{CH}_2$ ), 2.45 ppm (s, 3H;  $\text{CH}_3$ );  $^{13}\text{C NMR}$  (50 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 151.4, 145.8, 133.7, 132.3, 129.9$  (2C), 128.1 (2C), 120.6, 74.6, 49.5, 21.6 ppm; GC-MS:  $m/z$  (%): 203 (28)  $[\text{M}-64]^+$ , 155 (21), 118 (34), 91 (100), 56 (25); elemental analysis calcd (%) for  $\text{C}_{12}\text{H}_{13}\text{NO}_4\text{S}$  (267.3): C 53.92, H 4.90, N 5.24; found: C 53.95, H 4.93, N 5.27.

**5-But-3-enyl-3-[(4-methylphenyl)sulfonyl]-1,3-oxazolidin-2-one (9 c):** Yield: 75%, oil;  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 7.92$  (d,  $^3J(\text{H,H}) = 8.3$  Hz, 2H; CH), 7.38 (d,  $^3J(\text{H,H}) = 8.3$  Hz, 2H; CH), 5.75 (ddd,  $^3J(\text{H,H}) = 16.9, 10.2$ , and 6.6 Hz, 1H; CH), 5.12–4.98 (m, 2H;  $\text{CH}_2$ ), 4.55 (ddd,  $^3J(\text{H,H}) = 8.2, 7.2$ , and 5.5 Hz, 1H;  $\text{CH}_2$ ), 4.12 (dd,  $^2J(\text{H,H}) = 9.0$  and  $^3J(\text{H,H}) = 8.2$  Hz, 1H;  $\text{CH}_2$ ), 3.63 (dd,  $^2J(\text{H,H}) = 9.0$  and  $^3J(\text{H,H}) = 7.2$  Hz, 1H;  $\text{CH}_2$ ), 2.45 (s, 3H;  $\text{CH}_3$ ), 2.27–2.08 (m, 2H;  $\text{CH}_2$ ), 1.98–1.58 ppm (m, 2H;  $\text{CH}_2$ );  $^{13}\text{C NMR}$  (50 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 151.5, 145.7, 136.0, 133.9, 129.8$  (2C), 128.1 (2C), 116.3, 73.8, 49.5, 32.2, 28.4, 21.6 ppm; elemental analysis calcd (%) for  $\text{C}_{14}\text{H}_{17}\text{NO}_4\text{S}$  (295.4): C 56.90, H 5.80, N 4.74; found: C 56.68, H 5.82, N 4.56.

**3-[(4-Methylphenyl)sulfonyl]-5-phenyl-1,3-oxazolidin-2-one (9 d):** Yield: 69%; m.p. 100–103 °C;  $^1\text{H NMR}$  (200 MHz,  $[\text{D}_6]\text{DMSO}$ , 25 °C, TMS):  $\delta = 8.02$ –7.90 (m, 2H; CH), 7.60–7.30 (m, 7H; CH), 5.83 (t,  $^3J(\text{H,H}) = 7.8$  Hz, 1H; CH), 4.61 (m, 1H;  $\text{CH}_2$ ), 4.00 (m, 1H;  $\text{CH}_2$ ), 2.50 ppm (s, 3H;  $\text{CH}_3$ );  $^{13}\text{C NMR}$  (50 MHz,  $[\text{D}_6]\text{DMSO}$ , 25 °C, TMS):  $\delta = 151.3, 145.7, 136.7, 133.7, 130.0$  (2C), 129.2, 128.9 (2C), 127.9 (2C), 126.1 (2C), 75.3, 51.1, 21.1 ppm; GC-MS:  $m/z$  (%): 253 (17)  $[\text{M}-64]^+$ , 149 (83), 105 (28), 91 (100), 65 (23), 56 (37); elemental analysis calcd (%) for  $\text{C}_{16}\text{H}_{15}\text{NO}_4\text{S}$  (317.4): C 60.55, H 4.76, N 4.41; found: C 60.53, H 4.78, N 4.44.

**5-(Butoxy)methyl-3-[(4-methylphenyl)sulfonyl]-1,3-oxazolidin-2-one (9 e):** Yield: 79%, oil;  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 7.99$ –7.89 (m, 2H; CH), 7.43–7.30 (m, 2H; CH), 4.61 (ddd,  $^3J(\text{H,H}) = 8.95, 6.1$ , and 3.9 Hz, 1H; CH), 4.08 (dd,  $^2J(\text{H,H}) = 9.0$  and  $^3J(\text{H,H}) = 8.95$  Hz, 1H;  $\text{CH}_2$ ), 3.95 (dd,  $^2J(\text{H,H}) = 9.0$  and  $^3J(\text{H,H}) = 6.1$  Hz, 1H;  $\text{CH}_2$ ), 3.55 (m, 2H;  $\text{CH}_2$ ), 3.40 (m, 2H;  $\text{CH}_2$ ), 2.45 (s, 3H;  $\text{CH}_3$ ), 1.50–1.12 (m, 4H;  $\text{CH}_2$ ), 0.88 ppm (t,  $^3J(\text{H,H}) = 6.6$  Hz, 3H;  $\text{CH}_3$ );  $^{13}\text{C NMR}$  (50 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 151.6, 145.5, 134.2, 129.8$  (2C), 128.1 (2C), 72.7, 71.7, 69.8, 46.1, 31.4, 21.6, 19.0, 13.0 ppm; IR:  $\tilde{\nu} = 2960, 1788, 1372, 1173 \text{ cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_{15}\text{H}_{21}\text{NO}_5\text{S}$  (327.4): C 55.03, H 6.49, N 4.28; found: C 55.01, H 6.50, N 4.30.

**3-[(4-methylphenyl)sulfonyl]-5-(3-oxobutyl)-1,3-oxazolidin-2-one (9 f):** Yield: 75%, oil;  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 7.85$ –7.75 (m, 2H; CH), 7.32–7.22 (m, 2H; CH), 4.56–4.40 (m, 1H; CH), 4.03 (dd,  $^2J(\text{H,H}) = 9.2$  and  $^3J(\text{H,H}) = 8.1$  Hz, 1H;  $\text{CH}_2$ ), 3.52 (dd,  $^2J(\text{H,H}) = 9.2$  and  $^3J(\text{H,H}) = 6.9$  Hz, 1H;  $\text{CH}_2$ ), 2.50 (t,  $^3J(\text{H,H}) = 7.0$  Hz, 2H;  $\text{CH}_2$ ), 2.34 (s, 3H;  $\text{CH}_3$ ), 2.04 (s, 3H;  $\text{CH}_3$ ), 2.00–1.60 ppm (m, 2H;  $\text{CH}_2$ );  $^{13}\text{C NMR}$  (50 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 206.9, 151.5, 145.8, 133.7, 129.9$  (2C), 128.1 (2C), 73.6, 49.6, 37.8, 29.9, 28.0, 21.6 ppm; IR:  $\tilde{\nu} = 3259, 1763, 1714, 1363, 1177 \text{ cm}^{-1}$ ; GC-MS:  $m/z$  (%): 254 (4)  $[\text{M}-77]^+$ , 156 (65), 112 (48), 91 (100), 65 (26), 43 (40); elemental analysis calcd (%) for  $\text{C}_{14}\text{H}_{17}\text{NO}_5\text{S}$  (311.4): C 54.01, H 5.50, N 4.50; found: C 54.12, H 5.53, N 4.33.

**Methyl 3-3-[(4-methylphenyl)sulfonyl]-2-oxo-1,3-oxazolidin-5-yl)propanoate (9 g):** Yield: 92%, oil;  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 7.87$  (d,  $^3J(\text{H,H}) = 8.3$  Hz, 2H; CH), 7.31 (d,  $^3J(\text{H,H}) = 8.3$  Hz, 2H; CH), 4.66–4.45 (m, 1H; CH), 4.10 (dd,  $^2J(\text{H,H}) = 9.1$  and  $^3J(\text{H,H}) = 8.1$  Hz, 1H;  $\text{CH}_2$ ), 3.62 (s, 3H;  $\text{OCH}_3$ ), 3.59 (dd,  $^2J(\text{H,H}) = 9.1$  and  $^3J(\text{H,H}) = 6.9$  Hz, 1H;  $\text{CH}_2$ ), 2.40 (m, 2H;  $\text{CH}_2$ ), 2.39 (s, 3H;  $\text{CH}_3$ ), 2.02–1.85 ppm (m, 2H;  $\text{CH}_2$ );  $^{13}\text{C NMR}$  (50 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 172.4, 151.3, 145.8, 133.7, 129.9$  (2C), 128.1 (2C), 73.4, 51.8, 49.4, 29.3, 28.8, 21.6 ppm; IR:  $\tilde{\nu} = 2954, 1784, 1736, 1369, 1172 \text{ cm}^{-1}$ ; GC-MS:  $m/z$  (%): 297 (1)  $[\text{M}-32]^+$ , 172 (57), 140 (100), 108 (39), 91 (93), 65 (23); ele-

mental analysis calcd (%) for  $C_{14}H_{17}NO_6S$  (327.4): C 51.30, H 4.23, N 4.28; found: C 51.50, H 4.25, N 4.29.

**2-(3-[(4-Methylphenyl)sulfonyl]-2-oxo-1,3-oxazolidin-5-yl)methyl-1*H*-isoindol-1,3-(2*H*)-dione (9i):** Yield: 86%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 7.90 (d,  $^3J(H,H)$  = 8.3 Hz, 2H; CH), 7.86–7.68 (m, 4H; CH), 7.30 (d,  $^3J(H,H)$  = 8.3 Hz, 2H; CH), 4.88 (dddd,  $^3J(H,H)$  = 8.2, 6.6, 6.2, and 5.6 Hz, 1H; CH), 4.16 (dd,  $^2J(H,H)$  = 9.6 and  $^3J(H,H)$  = 8.2 Hz, 1H;  $CH_2$ ), 4.02 (dd,  $^2J(H,H)$  = 14.3 and  $^3J(H,H)$  = 6.6 Hz, 1H;  $CH_2$ ), 3.91 (dd,  $^2J(H,H)$  = 9.6 and  $^3J(H,H)$  = 6.2 Hz, 1H;  $CH_2$ ), 3.85 (dd,  $^2J(H,H)$  = 14.3 and  $^3J(H,H)$  = 5.6 Hz, 1H;  $CH_2$ ), 2.40 ppm (s, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 167.6 (2C), 150.8, 145.7, 134.3 (2C), 133.6, 131.4 (2C), 129.8 (2C), 128.1 (2C), 123.5 (2C), 71.0, 47.4, 39.9, 21.5 ppm; elemental analysis calcd (%) for  $C_{19}H_{16}N_2O_6S$  (400.4): C 56.99, H 4.03, N 7.00; found: C 56.97, H 4.00, N 7.03.

**(3*aRS*,7*aSR*)-3-[(4-Methylphenyl)sulfonyl]hexahydro-1,2-benzoxazol-2(3*H*)-one (14c):** Yield: 73%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 7.87 (d,  $^3J(H,H)$  = 8.2 Hz, 2H; CH), 7.25 (d,  $^3J(H,H)$  = 8.2 Hz, 2H; CH), 4.53–4.43 (m, 1H; CH), 4.27 (dt,  $^3J(H,H)$  = 9.4 and 6.0 Hz, 1H; CH), 2.35 (s, 3H;  $CH_3$ ), 2.25–1.98 (m, 2H;  $CH_2$ ), 1.84–1.70 (m, 1H; CH), 1.69–1.10 ppm (m, 5H; CH and  $CH_2$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 152.1, 145.3, 135.4, 129.6 (2C), 128.4 (2C), 75.0, 57.4, 28.0, 26.3, 21.6, 20.5, 18.7 ppm; elemental analysis calcd (%) for  $C_{14}H_{17}NO_4S$  (295.4): C 56.93, H 5.80, N 4.74; found: C 56.75, H 5.92, N 4.76.

**(5*R*)-5-[(Benzyloxy)methyl]-3-(4-methylphenyl)sulfonyl-1,3-oxazolidin-2-one (23a):** Yield: 88%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 7.86 (d,  $^3J(H,H)$  = 8.2 Hz, 2H; CH), 7.35–7.12 (m, 7H; CH), 4.61 (dddd,  $^3J(H,H)$  = 9.0, 6.1, 3.8, and 3.7 Hz, 1H; CH), 4.44 (s, 2H;  $CH_2$ ), 4.06 (dd,  $^2J(H,H)$  = 9.1 and  $^3J(H,H)$  = 9.0 Hz, 1H;  $CH_2$ ), 3.93 (dd,  $^2J(H,H)$  = 9.0 and  $^3J(H,H)$  = 6.1 Hz, 1H;  $CH_2$ ), 3.59 (dd,  $^2J(H,H)$  = 11.0 and  $^3J(H,H)$  = 3.7 Hz, 1H;  $CH_2$ ), 3.52 (dd,  $^2J(H,H)$  = 11.0 and  $^3J(H,H)$  = 3.8 Hz, 1H;  $CH_2$ ), 2.38 ppm (s, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 151.1, 145.5, 137.0, 134.0, 130.2 (2C), 128.4 (2C), 128.0, 127.9 (2C), 127.5 (2C), 73.4, 72.5, 69.1, 46.1, 21.5 ppm; GC-MS:  $m/z$  (%): 361 (1) [ $M$ ]<sup>+</sup>, 255 (15), 155 (23), 91 (100), 65 (12), 107 (13); elemental analysis calcd (%) for  $C_{18}H_{19}NO_3S$  (361.4): C 59.82, H 5.30, N 3.88; found: C 59.85, H 5.32, N 3.86.

**3-Benzoyl-5-decyl-1,3-oxazolidin-2-one (10a):** Yield: 89%; m.p. 83–85 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 7.70–7.60 (m, 2H; CH), 7.60–7.34 (m, 3H; CH), 4.65 (dtd,  $^3J(H,H)$  = 7.9, 7.6, and 5.7 Hz, 1H; CH), 4.19 (dd,  $^2J(H,H)$  = 10.9 and  $^3J(H,H)$  = 7.9 Hz, 1H;  $CH_2$ ), 3.78 (dd,  $^2J(H,H)$  = 10.9 and  $^3J(H,H)$  = 7.6 Hz, 1H;  $CH_2$ ), 1.95–1.15 (m, 18H;  $CH_2$ ), 0.89 ppm (t,  $^3J(H,H)$  = 6.7 Hz, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 169.7, 152.8, 132.7, 132.2, 128.9 (2C), 127.7 (2C), 74.4, 48.7, 34.4, 31.8, 29.4 (2C), 29.3, 29.2, 29.1, 24.4, 22.6, 14.0 ppm; IR:  $\tilde{\nu}$  = 2921, 1790, 1772, 1681, 1354, 1195  $cm^{-1}$ ; GC-MS:  $m/z$  (%): 331 (2) [ $M$ ]<sup>+</sup>, 105 (100), 77 (16); elemental analysis calcd (%) for  $C_{20}H_{29}NO_3$  (332.4): C 72.47, H 8.82, N 4.23; found: C 72.48, H 8.83, N 4.25.

**3-Benzoyl-5-but-3-enyl-1,3-oxazolidin-2-one (10c):** Yield: 93%; m.p. 72–74 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 7.70–7.60 (m, 2H; CH), 7.60–7.30 (m, 3H; CH), 5.80 (ddd,  $^3J(H,H)$  = 17.0, 10.3, and 6.6 Hz, 1H; CH), 5.16–5.00 (m, 2H;  $CH_2$ ), 4.64 (dtd,  $^3J(H,H)$  = 7.8, 7.6, and 5.5 Hz, 1H; CH), 4.16 (dd,  $^2J(H,H)$  = 10.9 and  $^3J(H,H)$  = 7.8 Hz, 1H;  $CH_2$ ), 3.96 (dd,  $^2J(H,H)$  = 10.9 and  $^3J(H,H)$  = 7.6 Hz, 1H;  $CH_2$ ), 2.35–2.08 (m, 2H;  $CH_2$ ), 2.05–1.70 ppm (m, 2H;  $CH_2$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 169.9, 152.7, 136.2, 132.7, 132.2, 128.9 (2C), 127.7 (2C), 116.2, 73.6, 48.6, 32.5, 28.6 ppm; GC-MS:  $m/z$  (%): 245 (3) [ $M$ ]<sup>+</sup>, 105 (100), 77 (24); elemental analysis calcd (%) for  $C_{14}H_{15}NO_3$  (245.3): C 68.56, H 6.16, N 5.71; found: C 68.68, H 6.18, N 5.60.

**3-Benzoyl-5-(butoxymethyl)-1,3-oxazolidin-2-one (10e):** Yield: 69%; m.p. 61–62 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 7.70–7.60 (m, 2H; CH), 7.58–7.34 (m, 3H; CH), 4.73 (ddt,  $^3J(H,H)$  = 8.5, 5.8, and 3.6 Hz, 1H; CH), 4.16 (dd,  $^2J(H,H)$  = 10.8 and  $^3J(H,H)$  = 8.5 Hz, 1H;  $CH_2$ ), 4.04 (dd,  $^2J(H,H)$  = 10.8 and  $^3J(H,H)$  = 5.8 Hz, 1H;  $CH_2$ ), 3.71 (dd,  $^2J(H,H)$  = 10.9 and  $^3J(H,H)$  = 3.6 Hz, 1H;  $CH_2$ ), 3.60 (dd,  $^2J(H,H)$  = 10.9 and  $^3J(H,H)$  = 3.6 Hz, 1H;  $CH_2$ ), 3.52 (t,  $^3J(H,H)$  = 6.5 Hz, 2H;  $CH_2$ ), 1.68–1.48 (m, 2H;  $CH_2$ ), 1.48–1.18 (m, 2H;  $CH_2$ ), 0.91 ppm (t,  $^3J(H,H)$  = 7.2 Hz, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 169.6, 152.8, 132.8, 132.1, 128.8, 128.7, 127.7, 127.6, 72.6, 71.7, 70.5, 45.5, 31.5, 19.1, 13.8 ppm; GC-MS:  $m/z$  (%): 205 (10) [ $M$ –72]<sup>+</sup>, 105 (100), 77 (25);

elemental analysis calcd (%) for  $C_{15}H_{19}NO_4$  (277.3): C 64.97, H 6.91, N 5.05; found: C 64.99, H 6.90, N 5.04.

**3-Benzoyl-5-(8-(1,3-dioxolan-2-yl)octyl)-1,3-oxazolidin-2-one (10h):** Yield: 62%; m.p. 89–91 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 7.71–7.36 (m, 5H; CH), 4.84 (t,  $^3J(H,H)$  = 4.7 Hz, 1H; CH), 4.64 (ddd,  $^3J(H,H)$  = 7.9, 7.6, and 5.7 Hz, 1H; CH), 4.18 (dd,  $^2J(H,H)$  = 10.9 and  $^3J(H,H)$  = 7.9 Hz, 1H;  $CH_2$ ), 4.01–3.78 (m, 4H;  $CH_2$ ), 3.77 (dd,  $^2J(H,H)$  = 10.9 and  $^3J(H,H)$  = 7.6 Hz, 1H;  $CH_2$ ), 1.95–1.18 ppm (m, 16H;  $CH_2$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 169.7, 152.8, 132.7, 122.1, 128.9 (2C), 127.7 (2C), 104.5, 74.3, 64.7 (2C), 48.7, 34.3, 33.7, 29.3, 29.2, 29.1, 29.0, 24.3, 23.9 ppm; elemental analysis calcd (%) for  $C_{21}H_{29}NO_5$  (375.5): C 67.18, H 7.79, N 3.73; found: C 67.20, H 7.80, N 3.71.

***N*-[(3-Benzoyl-2-oxo-1,3-oxazolidin-5-yl)methyl]benzamide (10l):** Yield: 77%; m.p. 110–113 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 7.85–7.75 (m, 2H; CH), 7.63–7.22 (m, 8H; CH), 6.79 (t,  $^3J(H,H)$  = 6.4 Hz, 1H; NH), 4.90 (dddd,  $^3J(H,H)$  = 8.3, 7.2, 6.4, and 3.5 Hz, 1H; CH), 4.24 (dd,  $^2J(H,H)$  = 11.3 and  $^3J(H,H)$  = 8.3 Hz, 1H;  $CH_2$ ), 3.98 (dd,  $^2J(H,H)$  = 11.3 and  $^3J(H,H)$  = 7.2 Hz, 1H;  $CH_2$ ), 3.96 (ddd,  $^2J(H,H)$  = 14.7 and  $^3J(H,H)$  = 6.4 and 3.5 Hz, 1H;  $CH_2$ ), 3.75 ppm (dt,  $^2J(H,H)$  = 14.7 and  $^3J(H,H)$  = 6.4 Hz, 1H;  $CH_2$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 169.4, 168.3, 152.8, 133.5, 132.5, 132.3, 131.8, 128.8 (2C), 128.4 (2C), 127.9, 127.7, 127.3, 127.1, 73.1, 66.2, 42.1 ppm; IR:  $\tilde{\nu}$  = 3364, 3067, 1805, 1777, 1678, 1528, 1360, 1197  $cm^{-1}$ ; elemental analysis calcd (%) for  $C_{18}H_{16}N_2O_4$  (324.3): C 66.66, H 4.97, N 8.64; found: C 66.54, H 4.99, N 8.52.

**3-Benzoyl-8-(*tert*-butyl)-1-oxa-3-azaspiro[4.5]decan-2-one (10m):** Yield 80%; m.p. 142–145 °C;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 7.70–7.60 (m, 2H; CH), 7.60–7.35 (m, 3H; CH), 3.80 (s, 2H;  $CH_2$ ), 2.20–2.00 (m, 2H;  $CH_2$ ), 1.82–1.42 (m, 6H;  $CH_2$ ), 1.20–1.00 (m, 1H; CH), 0.90 ppm (s, 9H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 170.1, 152.4, 133.0, 132.2, 129.0 (2C), 127.8 (2C), 79.6, 54.7, 46.8, 36.7 (2C), 32.4, 27.5 (3C), 22.6 ppm (2C); elemental analysis calcd (%) for  $C_{19}H_{23}NO_3$  (315.4): C 72.35, H 7.99, N 4.44; found: C 72.37, H 7.97, N 4.43.

**(5*R*)-3-Benzoyl-5-[(benzyloxy)methyl]-1,3-oxazolidin-2-one (21a):** Yield: 90%; m.p. 93–94 °C;  $[\alpha]_D^{25}$  = –17.76 ( $c$  = 3.63 in  $CHCl_3$ );  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 7.60–7.43 (m, 3H; CH), 7.42–7.28 (m, 7H; CH), 4.75 (ddt,  $^3J(H,H)$  = 8.5, 5.8, and 3.5 Hz, 1H; CH), 4.59 (m, 2H;  $CH_2$ ), 4.16 (dd,  $^2J(H,H)$  = 10.8 and  $^3J(H,H)$  = 8.5 Hz, 1H;  $CH_2$ ), 4.04 (dd,  $^2J(H,H)$  = 10.8 and  $^3J(H,H)$  = 5.8 Hz, 1H;  $CH_2$ ), 3.77 (dd,  $^2J(H,H)$  = 10.8 and  $^3J(H,H)$  = 3.5 Hz, 1H;  $CH_2$ ), 3.65 ppm (dd,  $^2J(H,H)$  = 10.8 and  $^3J(H,H)$  = 3.5 Hz, 1H;  $CH_2$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 169.4, 152.6, 137.1, 132.7, 131.9 (2C), 128.6 (3C), 128.5 (2C), 127.8, 127.6 (2C), 73.5, 72.4, 69.7, 45.3 ppm; IR:  $\tilde{\nu}$  = 2894, 1764, 1682, 1367  $cm^{-1}$ ; elemental analysis calcd (%) for  $C_{18}H_{17}NO_4$  (311.3): C 69.44, H 5.50, N 4.50; found: C 69.53, H 5.39, N 4.51.

**(5*S*)-3-Benzoyl-5-[(*tert*-butyl(diphenyl)silyloxy)methyl]-1,3-oxazolidin-2-one (21b):** Yield: 77%; m.p. 100–102 °C;  $[\alpha]_D^{25}$  = +32.75 ( $c$  = 4.60 in  $CHCl_3$ );  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 7.72–7.56 (m, 6H; CH), 7.54–7.33 (m, 9H; CH), 4.77–4.65 (m, 1H; CH), 4.19 (m, 2H;  $CH_2$ ), 3.98 (dd,  $^2J(H,H)$  = 11.6 and  $^3J(H,H)$  = 3.4 Hz, 1H;  $CH_2$ ), 3.77 (dd,  $^2J(H,H)$  = 11.6 and  $^3J(H,H)$  = 3.1 Hz, 1H;  $CH_2$ ), 1.08 ppm (s, 9H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 169.5, 152.7, 135.5 (4C), 132.8, 132.4, 132.2, 132.0, 130.0 (2C), 128.9 (2C), 127.9 (4C), 127.6 (2C), 73.3, 63.9, 44.8, 26.7 (3C), 19.2 ppm; IR:  $\tilde{\nu}$  = 2930, 1790, 1682, 1113  $cm^{-1}$ ; elemental analysis calcd (%) for  $C_{27}H_{29}NO_4Si$  (459.6): C 70.56, H 6.36, N 3.05; found: C 70.54, H 6.35, N 3.03.

**[(5*S*)-3-Benzoyl-2-oxo-1,3-oxazolidin-5-yl]methylbutyrate (21c):** Yield: 67%; m.p. 77–79 °C;  $[\alpha]_D^{25}$  = +4.15 ( $c$  = 3.44 in  $CHCl_3$ );  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 7.70–7.50 (m, 3H; CH), 7.50–7.38 (m, 2H; CH), 4.86 (dddd,  $^3J(H,H)$  = 8.6, 6.3, 4.7, and 3.5 Hz, 1H; CH), 4.38 (dd,  $^2J(H,H)$  = 12.4 and  $^3J(H,H)$  = 3.5 Hz, 1H;  $CH_2$ ), 4.27 (dd,  $^2J(H,H)$  = 12.4 and  $^3J(H,H)$  = 4.7 Hz, 1H;  $CH_2$ ), 4.24 (dd,  $^2J(H,H)$  = 11.1 and  $^3J(H,H)$  = 8.6 Hz, 1H;  $CH_2$ ), 3.95 (dd,  $^2J(H,H)$  = 11.1 and  $^3J(H,H)$  = 6.3 Hz, 1H;  $CH_2$ ), 2.36 (t,  $^3J(H,H)$  = 7.3 Hz, 2H;  $CH_2$ ), 1.68 (sextet,  $^3J(H,H)$  = 7.3 Hz, 2H;  $CH_2$ ), 0.95 ppm (t,  $^3J(H,H)$  = 7.3 Hz, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25 °C, TMS):  $\delta$  = 172.9, 169.4, 152.2, 144.5, 132.4, 128.9 (2C), 127.8 (2C), 71.0, 63.4, 45.2, 35.7, 18.2, 13.5 ppm; GC-MS:  $m/z$  (%): 291 (1) [ $M$ ]<sup>+</sup>, 247 (6), 177 (20), 105 (100), 77 (32); IR:  $\tilde{\nu}$  = 2965, 1793, 1776, 1736, 1674, 1343, 1162  $cm^{-1}$ ; elemental analysis calcd

(%) for  $C_{15}H_{17}NO_5$  (201.3): C 61.85, H 5.88, N 4.81; found: C 61.83, H 5.86, N 4.80.

**(5S)-3-Benzoyl-5-phenyl-1,3-oxazolidin-2-one (21d)**: Yield: 75%; m.p. 134–137°C;  $[\alpha]_D^{20} = +78.35$  ( $c = 1.52$  in  $CHCl_3$ );  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 7.74$ – $7.64$  (m, 2H; CH),  $7.62$ – $7.32$  (m, 8H; CH),  $5.64$  (dd,  $^3J(H,H) = 8.1$  and  $8.0$  Hz, 1H; CH),  $4.47$  (dd,  $^2J(H,H) = 11.1$  and  $^3J(H,H) = 8.1$  Hz, 1H;  $CH_2$ ),  $4.08$  ppm (dd,  $^2J(H,H) = 11.1$  and  $^3J(H,H) = 8.0$  Hz, 1H;  $CH_2$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 169.6$ ,  $152.7$ ,  $136.6$ ,  $132.5$ ,  $132.4$ ,  $129.4$ ,  $129.1$  (2C),  $129.0$ ,  $127.8$  (3C),  $125.7$  (2C),  $75.1$ ,  $50.8$  ppm; elemental analysis calcd (%) for  $C_{16}H_{13}NO_3$  (267.3): C 71.9, H 4.90, N 5.24; found: C 72.04, H 4.99, N 5.14.

**Methyl [(5S)-3-benzoyl-2-oxo-1,3-oxazolidin-5-yl]acetate (21e)**: Yield: 82%; m.p. 79–82°C;  $[\alpha]_D^{25} = +44.42$  ( $c = 5.15$  in  $CHCl_3$ );  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 7.70$ – $7.60$  (m, 2H; CH),  $7.60$ – $7.50$  (m, 1H; CH),  $7.48$ – $7.35$  (m, 2H; CH),  $5.00$  (dddd,  $^3J(H,H) = 8.2$ ,  $7.2$ ,  $6.7$ , and  $6.1$  Hz, 1H; CH),  $4.29$  (dd,  $^2J(H,H) = 11.2$  and  $^3J(H,H) = 8.2$  Hz, 1H;  $CH_2$ ),  $3.89$  (dd,  $^2J(H,H) = 11.2$  and  $^3J(H,H) = 7.2$  Hz, 1H;  $CH_2$ ),  $3.72$  (s, 3H;  $OCH_3$ ),  $2.92$  (dd,  $^2J(H,H) = 16.8$  and  $^3J(H,H) = 6.1$  Hz, 1H;  $CH_2$ ),  $2.78$  ppm (dd,  $^2J(H,H) = 16.8$  and  $^3J(H,H) = 6.7$  Hz, 1H;  $CH_2$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 169.4$ ,  $169.1$ ,  $152.2$ ,  $132.5$ ,  $132.2$ ,  $128.9$  (2C),  $127.7$  (2C),  $69.8$ ,  $52.1$ ,  $48.3$ ,  $38.3$  ppm; IR:  $\tilde{\nu} = 2955$ ,  $1786$ ,  $1740$ ,  $1680$ ,  $1329$ ,  $1209$   $cm^{-1}$ ; elemental analysis calcd (%) for  $C_{13}H_{13}NO_5$  (263.3): C 59.31, H 4.98, N 5.32; found: C 59.30, H 4.96, N 5.30.

**[(5R)-3-Benzoyl-2-oxo-1,3-oxazolidin-5-yl]acetonitrile (21f)**: Yield: 74%; m.p. 119–122°C;  $[\alpha]_D^{25} = -24.68$  ( $c = 2.79$  in MeOH);  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 7.72$ – $7.61$  (m, 2H; CH),  $7.60$ – $7.50$  (m, 1H; CH),  $7.50$ – $7.37$  (m, 2H; CH),  $5.05$ – $4.88$  (m, 1H; CH),  $4.32$  (dd,  $^2J(H,H) = 11.3$  and  $^3J(H,H) = 8.4$  Hz, 1H;  $CH_2$ ),  $3.96$  (dd,  $^2J(H,H) = 11.3$  and  $^3J(H,H) = 5.8$  Hz, 1H;  $CH_2$ ),  $3.05$  ppm (m, 2H;  $CH_2$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 168.1$ ,  $150.9$ ,  $131.9$ ,  $131.3$ ,  $128.0$  (2C),  $126.9$  (2C),  $114.8$ ,  $68.0$ ,  $46.6$ ,  $22.3$  ppm; IR:  $\tilde{\nu} = 2979$ ,  $2260$ ,  $1784$ ,  $1685$ ,  $1375$ ,  $1207$ ,  $1054$   $cm^{-1}$ ; elemental analysis calcd (%) for  $C_{12}H_{10}N_2O_3$  (230.2): C 62.60, H 4.38, N 12.17; found: C 62.71, H 4.40, N 12.25.

**(5R)-3-Benzoyl-5-[(1S)-1-(dibenzylamino)-2-phenylethyl]-1,3-oxazolidin-2-one (21g)**: Yield: 79%; m.p. 45–48°C;  $[\alpha]_D^{25} = +10.27$  ( $c = 1.90$  in  $CHCl_3$ );  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 7.54$ – $7.00$  (m, 20H; CH),  $4.67$ – $4.52$  (m, 1H; CH),  $4.02$  (dd,  $^2J(H,H) = 11.2$  and  $^3J(H,H) = 8.2$  Hz, 1H;  $CH_2$ ),  $3.68$  (dd,  $^2J(H,H) = 11.2$  and  $^3J(H,H) = 7.4$  Hz, 1H;  $CH_2$ ),  $3.60$  (m, 4H;  $CH_2$ ),  $3.17$ – $2.93$  ppm (m, 3H; CH and  $CH_2$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 169.3$ ,  $152.5$ ,  $139.4$ ,  $138.6$  (2C),  $132.7$ ,  $132.1$ ,  $129.5$  (2C),  $128.8$  (3C),  $128.7$  (3C),  $128.5$  (3C),  $128.4$  (3C),  $127.7$  (2C),  $127.3$  (2C),  $126.4$ ,  $74.6$ ,  $61.8$ ,  $54.7$  (2C),  $47.5$ ,  $32.5$  ppm; elemental analysis calcd (%) for  $C_{32}H_{30}N_2O_3$  (490.6): C 78.34, H 6.16, N 5.71; found: C 78.36, H 6.14, N 5.70.

**tert-Butyl (1S)-1-[(5S)-3-benzoyl-2-oxo-1,3-oxazolidin-5-yl]-2-cyclohexylethylcarbamate (21h)**: Major diastereoisomer; yield: 49%; m.p. 170–173°C;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 7.70$ – $7.32$  (m, 5H; CH),  $4.70$ – $4.50$  (m, 2H; CH and  $CH_2$ ),  $4.22$ – $4.00$  (m, 2H; CH),  $3.95$  (brs, 1H; NH),  $1.90$ – $0.70$  (m, 13H; CH and  $CH_2$ ),  $1.40$  ppm (s, 9H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 169.3$ ,  $155.9$ ,  $152.0$ ,  $132.8$ ,  $132.3$ ,  $128.9$  (2C),  $127.8$  (2C),  $80.2$ ,  $76.0$ ,  $49.6$ ,  $46.0$ ,  $39.6$ ,  $34.1$ ,  $33.6$ ,  $32.5$ ,  $28.2$  (3C),  $26.3$ ,  $26.2$ ,  $26.0$  ppm.

**tert-Butyl (1S)-1-[(5R)-3-benzoyl-2-oxo-1,3-oxazolidin-5-yl]-2-cyclohexylethylcarbamate (21i)**: Minor diastereoisomer; Yield: 7%; m.p. 152–155°C;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 7.70$ – $7.30$  (m, 5H; CH),  $4.72$ – $4.52$  (m, 1H; CH),  $4.50$  (brs, 1H; NH),  $4.27$ – $3.81$  (m, 3H; CH and  $CH_2$ ),  $1.92$ – $0.70$  (m, 13H; CH and  $CH_2$ ),  $1.43$  ppm (s, 9H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 169.6$ ,  $155.5$ ,  $152.6$ ,  $133.2$ ,  $132.4$ ,  $129.0$  (2C),  $127.9$  (2C),  $80.3$ ,  $76.0$ ,  $50.5$ ,  $45.7$ ,  $39.6$ ,  $34.1$ ,  $33.6$ ,  $32.1$ ,  $29.7$ ,  $28.3$  (3C),  $26.3$ ,  $26.2$  ppm; elemental analysis of the mixture calcd (%) for  $C_{25}H_{32}N_2O_5$  (416.5): C 66.32, H 7.74, N 6.73; found: C 66.20, H 7.78, N 6.65.

**Conversion of *N*-tosyl carbamate 12a and 12b into *N*-tosylamido alcohols 17a and 17b**

**Method B**: Solid *m*-chloroperoxybenzoic acid (0.688 g, 4 mmol) was added to a mixture of *N*-tosyl carbamate 12a or 12b (1 mmol) and powdered potassium hydrogenphosphate (0.870 g, 5 mmol) in  $CH_2Cl_2$  (15 mL) at 18°C. The resultant mixture was stirred for 3–4 h and was then concentrated in vacuo. Aqueous sodium carbonate (10%) was added and the mixture was extracted with diethyl ether. The combined

organic layers were dried over sodium sulfate and concentrated in vacuo. The residue was dissolved in methanol (10 mL) and a catalytic amount of cesium carbonate (0.04 g) was added. The mixture was stirred overnight and the solvent was removed under reduced pressure. The residue was purified by column chromatography using a mixture of diethyl ether and ethyl acetate (8:2) as eluent to afford 17a or 17b, respectively. Reaction yields are reported in Table 2, while physical and spectral data are reported below.

***N*-[(1*SR*,2*SR*)-2-Hydroxy-1-propylpentyl]-[(4-methylphenyl)sulfonamide (17a)**: Yield: 40%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 7.72$  (d,  $^3J(H,H) = 8.3$  Hz, 2H; CH),  $7.25$  (d,  $^3J(H,H) = 8.3$  Hz, 2H; CH),  $5.19$  (d,  $^3J(H,H) = 8.8$  Hz, 1H; NH),  $3.60$ – $3.40$  (m, 1H; CH),  $3.13$  (dtd,  $^3J(H,H) = 8.8$ ,  $6.6$ , and  $2.9$  Hz, 1H; CH),  $2.37$  (s, 3H;  $CH_3$ ),  $2.25$  (brs, 1H; OH),  $1.60$ – $1.00$  (m, 8H;  $CH_2$ ),  $0.77$  (t,  $^3J(H,H) = 6.9$  Hz, 3H;  $CH_3$ ),  $0.71$  ppm (t,  $^3J(H,H) = 7.3$  Hz, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 143.0$ ,  $138.3$ ,  $129.4$  (2C),  $126.8$  (2C),  $72.0$ ,  $57.3$ ,  $36.0$ ,  $34.5$ ,  $21.3$ ,  $18.7$  (2C),  $13.8$ ,  $13.7$  ppm; GC-MS:  $m/z$  (%):  $256$  (2) [ $M-43$ ] $^+$ ,  $226$  (100),  $155$  (55),  $91$  (61),  $72$  (24); elemental analysis calcd (%) for  $C_{15}H_{25}NO_3S$  (299.4): C 60.17, H 8.42, N 4.68; found: C 60.25, H 8.53, N 4.56.

***N*-[(1*RS*,2*RS*)-1-(Benzoyloxy)methyl]-2-hydroxypentyl]-[(4-methylphenyl)sulfonamide (17b)**: Yield: 48%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 7.75$  (d,  $^3J(H,H) = 8.3$  Hz, 2H; CH),  $7.40$ – $7.18$  (m, 7H; CH),  $5.55$  (d,  $^3J(H,H) = 7.4$  Hz, 1H; NH),  $4.40$  (m, 2H;  $CH_2$ ),  $3.87$ – $3.77$  (m, 1H; CH),  $3.51$  (m, 2H;  $CH_2$ ),  $3.37$ – $3.24$  (m, 1H; CH),  $2.96$  (brs, 1H; OH),  $2.42$  (s, 3H;  $CH_3$ ),  $1.40$ – $1.05$  (m, 4H;  $CH_2$ ),  $0.76$  ppm (t,  $^3J(H,H) = 6.7$  Hz, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 143.1$ ,  $138.1$ ,  $137.3$ ,  $129.5$  (2C),  $128.4$  (2C),  $127.8$ ,  $127.6$  (2C),  $126.9$  (2C),  $73.2$ ,  $71.8$ ,  $71.7$ ,  $55.7$ ,  $35.5$ ,  $21.4$ ,  $18.6$ ,  $13.8$  ppm; elemental analysis calcd (%) for  $C_{20}H_{27}NO_4S$  (377.5): C 63.63, H 7.21, N 3.71; found: C 63.69, H 7.24, N 3.73.

**Synthesis of the 4,5-disubstituted *N*-benzoyl-1,3-oxazolidin-2-ones 15**: The *N*-benzoyl carbamates 13 were treated with *m*-chloroperoxybenzoic acid as described above in Method B. The nature of the substrates (see Table 3) determined whether powdered potassium hydroxide (0.392 g, 7 mmol) or potassium carbonate (0.692 g, 5 mmol) was then added to the reaction mixture and stirring was continued until the selenone was consumed (3–24 h). The reaction mixture was then concentrated, poured into water, and extracted with diethyl ether. The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and evaporated. The reaction products were separated by column chromatography on silica gel using a mixture of diethyl ether and light petroleum (8:2) as eluent. The physical and spectral data for compound 15d have already been reported in the literature.<sup>[14c]</sup> The physical and spectral data for the new compounds are reported below.

**(4*RS*,5*RS*)-3-Benzoyl-4,5-dipropyl-1,3-oxazolidin-2-one (15a)**: Yield: 73%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 7.72$ – $7.39$  (m, 5H; CH),  $4.32$  (dt,  $^3J(H,H) = 7.3$  and  $4.8$  Hz, 1H; CH),  $4.29$  (ddd,  $^3J(H,H) = 8.6$ ,  $4.8$ , and  $3.5$  Hz, 1H; CH),  $1.95$ – $1.35$  (m, 8H;  $CH_2$ ),  $1.00$  (t,  $^3J(H,H) = 7.2$  Hz, 3H;  $CH_3$ ),  $0.99$  ppm (t,  $^3J(H,H) = 7.1$  Hz, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 169.9$ ,  $153.0$ ,  $133.4$ ,  $132.2$ ,  $128.9$  (2C),  $127.8$  (2C),  $79.1$ ,  $59.4$ ,  $37.0$ ,  $34.1$ ,  $18.0$ ,  $17.5$ ,  $13.8$ ,  $13.6$  ppm; GC-MS:  $m/z$  (%):  $275$  (16) [ $M$ ] $^+$ ,  $105$  (100),  $77$  (31); elemental analysis calcd (%) for  $C_{16}H_{21}NO_3$  (275.3): C 69.79, H 7.69, N 5.09; found: C 69.81, H 7.70, N 5.07.

**(4*RS*,5*RS*)-3-Benzoyl-4-[(benzyloxy)methyl]-5-propyl-1,3-oxazolidin-2-one (15b)**: Yield: 74%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 7.70$ – $7.60$  (m, 2H; CH),  $7.60$ – $7.48$  (m, 1H; CH),  $7.45$ – $7.20$  (m, 7H; CH),  $4.64$  (dt,  $^3J(H,H) = 7.7$  and  $4.9$  Hz, 1H; CH),  $4.58$  (m, 2H;  $CH_2$ ),  $4.40$  (td,  $^3J(H,H) = 4.9$  and  $2.6$  Hz, 1H; CH),  $3.91$  (dd,  $^2J(H,H) = 9.9$  and  $^3J(H,H) = 4.9$  Hz, 1H;  $CH_2$ ),  $3.69$  (dd,  $^2J(H,H) = 9.9$  and  $^3J(H,H) = 2.6$  Hz, 1H;  $CH_2$ ),  $1.80$ – $1.38$  (m, 4H;  $CH_2$ ),  $0.97$  ppm (t,  $^3J(H,H) = 7.1$  Hz, 3H;  $CH_3$ );  $^{13}C$  NMR (50 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 170.0$ ,  $152.9$ ,  $137.3$ ,  $133.2$ ,  $132.2$ ,  $128.9$  (2C),  $128.4$  (2C),  $127.9$  (2C),  $127.7$  (2C),  $127.6$ ,  $76.9$ ,  $73.4$ ,  $67.1$ ,  $59.3$ ,  $36.6$ ,  $17.7$ ,  $13.6$  ppm; GC-MS:  $m/z$  (%):  $353$  (1) [ $M$ ] $^+$ ,  $246$  (29),  $105$  (100),  $77$  (25); elemental analysis calcd (%) for  $C_{21}H_{23}NO_4$  (353.4): C 71.37, H 6.56, N 3.96; found: C 71.49, H 6.64, N 3.88.

**(4*SR*,5*SR*)-3-Benzoyl-4,5-bis[(benzyloxy)methyl]-1,3-oxazolidin-2-one (15c)**: Yield: 80%, oil;  $^1H$  NMR (200 MHz,  $CDCl_3$ , 25°C, TMS):  $\delta = 7.60$ – $7.16$  (m, 15H; CH),  $4.84$ – $4.65$  (m, 2H; CH),  $4.55$ – $4.31$  (m, 4H;

CH<sub>2</sub>), 3.98–3.74 ppm (m, 4H; CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 169.6, 152.9, 137.2, 137.1, 133.1, 132.1 (2C), 128.9 (2C), 128.6 (3C), 128.4 (3C), 127.9 (2C), 127.8, 127.7, 127.6, 75.3, 73.6, 73.4, 67.4, 65.1, 56.3 ppm; elemental analysis calcd (%) for C<sub>26</sub>H<sub>25</sub>NO<sub>3</sub> (431.5): C 72.37, H 5.84, N 3.25; found: C 72.39, H 5.82, N 3.27.

### 3-Benzoyl-4-[(benzyloxy)methyl]-5,5-dimethyl-1,3-oxazolidin-2-one

**(15f)**: Yield: 44%, oil; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 7.67–7.46 (m, 2H; CH), 7.45–7.21 (m, 8H; CH), 4.52 (s, 2H; CH<sub>2</sub>), 4.33 (dd, <sup>3</sup>J(H,H) = 5.6 and 2.7 Hz, 1H; CH), 3.89 (dd, <sup>2</sup>J(H,H) = 10.1 and <sup>3</sup>J(H,H) = 5.6 Hz, 1H; CH<sub>2</sub>), 3.80 (dd, <sup>2</sup>J(H,H) = 10.1 and <sup>3</sup>J(H,H) = 2.7 Hz, 1H; CH<sub>2</sub>), 1.56 (s, 3H; CH<sub>3</sub>), 1.54 ppm (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 170.1, 152.5, 137.3, 133.3, 132.3 (2C), 128.8 (2C), 128.4, 127.8 (2C), 127.6 (2C), 126.8, 81.4, 73.4, 65.7, 62.5, 28.5, 21.3 ppm; elemental analysis calcd (%) for C<sub>20</sub>H<sub>21</sub>NO<sub>4</sub> (339.4): C 70.78, H 6.24, N 4.13; found: C 70.80, H 6.22, N 4.12.

**Synthesis of the 1,3-oxazolidinone 15g**: Potassium hydrogenphosphate (0.870 g, 5 mmol) and *m*-chloroperoxybenzoic acid (0.688 g, 4 mmol) were added to a solution of *N*-benzoyl carbamate **13g** (1 mmol) in isopropyl alcohol (20 mL) at room temperature. After about 2 h the mixture was concentrated in vacuo, diluted with water, and extracted with diethyl ether. The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and evaporated. Product **15g** was obtained in pure form after column chromatography on silica gel using a mixture of diethyl ether and light petroleum (2:8) as eluent.

### [(4*R*,5*R*)-3-Benzoyl-5-methyl-2-oxo-1,3-oxazolidin-4-yl]acetonitrile

**(15g)**: Yield: 81%; m.p. 128–131 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 7.75–7.35 (m, 5H; CH), 4.60 (dq, <sup>3</sup>J(H,H) = 6.5 and 6.3 Hz, 1H; CH), 6.32 (td, <sup>3</sup>J(H,H) = 6.5 and 3.0 Hz, 1H; CH), 3.08 (dd, <sup>2</sup>J(H,H) = 17.3 and <sup>3</sup>J(H,H) = 6.5 Hz, 1H; CH<sub>2</sub>), 2.87 (dd, <sup>2</sup>J(H,H) = 17.3 and <sup>3</sup>J(H,H) = 3.0 Hz, 1H; CH<sub>2</sub>), 1.51 ppm (d, <sup>3</sup>J(H,H) = 6.3 Hz, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 170.0, 151.7, 133.0, 132.3, 129.2 (2C), 127.9 (2C), 115.1, 74.7, 57.3, 19.9, 19.4 ppm; GC-MS: *m/z* (%): 244 (13) [*M*–1]<sup>+</sup>, 105 (100), 77 (26); elemental analysis calcd (%) for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub> (244.2): C 63.93, H 5.30, N 11.47; found: C 63.85, H 5.42, N 11.49.

**Ring cleavage of the *N*-tosyl-1,3-oxazolidin-2-one 23a**: A catalytic amount of cesium carbonate (0.03 g) was added to a solution of *N*-tosyl-1,3-oxazolidin-2-one **23a** (1 mmol) in methanol (10 mL). The reaction was stirred at room temperature for 12 h and was then concentrated in vacuo. The residue was purified by chromatography on a silica-gel column using a mixture of light petroleum and ethyl acetate (6:4) as eluent. The physical and spectral data for compound **24a** are reported below.

### *N*-[(2*R*)-3-(Benzyloxy)-2-hydroxypropyl]-4-(methylphenyl)sulfonamide

**(24a)**: Yield: 72%; m.p. 68–70 °C; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +8.35 (*c* = 2.00 in CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 7.70 (d, <sup>3</sup>J(H,H) = 8.3 Hz, 2H; CH), 7.40–7.14 (m, 5H; CH), 7.25 (d, <sup>3</sup>J(H,H) = 8.3 Hz, 2H; CH), 5.42 (dd, <sup>3</sup>J(H,H) = 7.1 and 5.6 Hz, 1H; NH), 4.46 (s, 2H; CH<sub>2</sub>), 3.86 (dddd, <sup>3</sup>J(H,H) = 6.8, 5.9, 4.7, and 3.9 Hz, 1H; CH), 3.45 (dd, <sup>2</sup>J(H,H) = 9.9 and <sup>3</sup>J(H,H) = 4.7 Hz, 1H; CH<sub>2</sub>), 3.39 (dd, <sup>2</sup>J(H,H) = 9.9 and <sup>3</sup>J(H,H) = 5.9 Hz, 1H; CH<sub>2</sub>), 3.10 (brs, 1H; OH), 3.08 (dd, <sup>2</sup>J(H,H) = 13.0 and <sup>3</sup>J(H,H) = 3.9 Hz, 1H; CH<sub>2</sub>), 2.91 (dd, <sup>2</sup>J(H,H) = 13.0 and <sup>3</sup>J(H,H) = 6.8 Hz, 1H; CH<sub>2</sub>), 2.40 ppm (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 143.4, 137.5, 136.6, 129.7 (2C), 128.4 (2C), 127.8 (2C), 127.7, 127.0 (2C), 73.4, 71.6, 68.9, 45.7, 21.4 ppm; GC-MS: *m/z* (%): 274 (1) [*M*–61]<sup>+</sup>, 184 (23), 155 (42), 91 (100), 74 (16); elemental analysis calcd (%) for C<sub>17</sub>H<sub>21</sub>NO<sub>4</sub>S (335.4): C 60.87, H 6.31, N 4.18; found: C 60.85, H 6.33, N 4.15.

**Removal of the benzoyl group from *N*-benzoyl-1,3-oxazolidin-2-ones 21a and 21b**: *N*-benzoyl-1,3-oxazolidin-2-one **21a** or **21b** (1 mmol) and lithium hydroxide monohydrate (0.084 g, 2 mmol) were stirred at room temperature in a mixture of THF and water (10 mL, 3:1) for 4 h. The reaction mixture was then concentrated and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added. The solution was dried over sodium sulfate and evaporated, and the residue was purified by chromatography using diethyl ether as eluent. The physical and spectral data for compound **25b** have already been reported in the literature.<sup>[39]</sup>

**(5*R*)-5-[(benzyloxy)methyl]-1,3-oxazolidin-2-one (25a)**:<sup>[40]</sup> Yield: 84%, oil; [ $\alpha$ ]<sub>D</sub><sup>26</sup> = –7.99 (*c* = 2.60 in CHCl<sub>3</sub>).

**Reductive hydrolysis of 25a**: LiAlH<sub>4</sub> (1 M solution, 2 mL) was added dropwise to a solution of **25a** (0.207 g, 1 mmol) in dry THF (10 mL) at 0 °C. The mixture was stirred at room temperature for about 1 h and was then refluxed for 1 h. Methanol was added to the cooled reaction mixture, and this was then dried over sodium sulfate and concentrated at reduced pressure. The residue was purified by chromatography on silica gel using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and methanol (6:4) as eluent to afford pure **26**.

**(2*R*)-1-(Benzyloxy)-3-(methylamino)propan-2-ol (26)**: Yield: 84%, oil; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +0.45 (*c* = 8.00 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 7.37–7.24 (m, 5H; CH), 4.53 (s, 2H; CH<sub>2</sub>), 3.92 (ddt, <sup>3</sup>J(H,H) = 7.2, 5.8, and 4.7 Hz, 1H; CH), 3.47 (m, 2H; CH<sub>2</sub>), 3.33 (s, 1H; OH), 3.30 (s, 1H; NH), 2.64 (m, 2H; CH<sub>2</sub>), 2.40 ppm (s, 3H; CH<sub>3</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 137.9, 128.3 (2C), 127.6 (3C), 73.3, 72.9, 68.3, 54.1, 36.0 ppm; elemental analysis calcd (%) for C<sub>11</sub>H<sub>17</sub>NO<sub>2</sub> (195.3): C 67.66, H 8.78, N 7.17; found: C 67.78, H 8.90, N 7.19.

**Hydrolysis of 25a**: Oxazolidin-2-one **25a** (0.207 g, 1 mmol) was refluxed with a 10% sodium hydroxide solution (10 mL), and was then allowed to cool to room temperature. The solution was extracted with diethyl ether, the organic phase was washed with brine, and pure compound **27**<sup>[41]</sup> was obtained after evaporation of the solvent.

**(2*R*)-1-Amino-3-(benzyloxy)propan-2-ol (27)**: Yield: 94%, oil; [ $\alpha$ ]<sub>D</sub><sup>27</sup> = +6.25 (*c* = 2.76 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 7.35–7.20 (m, 5H; CH), 4.50 (m, 2H; CH<sub>2</sub>), 3.79–3.65 (m, 1H; CH), 3.44 (m, 2H; CH<sub>2</sub>), 2.80 (brs, 3H; NH<sub>2</sub> and OH), 2.80–2.60 ppm (m, 2H; CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ = 137.9, 128.3 (2C), 127.6 (3C), 73.2, 72.5, 70.8, 44.3 ppm; elemental analysis calcd (%) for C<sub>10</sub>H<sub>15</sub>NO<sub>2</sub> (181.2): C 66.27, H 8.34, N 7.73; found: C 66.29, H 8.35, N 7.75.

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- [1] M. E. Dyen, D. Swern, *Chem. Rev.* **1967**, *67*, 197–246.
- [2] a) W. A. Gregory, D. R. Brittelli, C. L. Wang, M. A. Wuonola, R. J. McRipley, D. C. Eustice, V. S. Eberly, P. T. Bartholomew, A. M. Slee, M. Forbes, *J. Med. Chem.* **1989**, *32*, 1673–1681; b) M. R. Barbachyn, C. W. Ford, *Angew. Chem.* **2003**, *115*, 2056–2070; *Angew. Chem. Int. Ed.* **2003**, *42*, 2010–2023.
- [3] a) S. Grabley, H. Kluge, H. U. Hoppe, *Angew. Chem.* **1987**, *99*, 692–694; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 690–693; b) K. Mori, M. Seki, *Eur. J. Org. Chem.* **1999**, 2965–2967; c) A. Mai, M. Artico, M. Esposito, R. Ragno, G. Sardella, S. Massa, *Farmaco* **2003**, *58*, 231–241.
- [4] J. Ager, I. Prakash, D. R. Schaad, *Chem. Rev.* **1996**, *96*, 835–875, and references therein.
- [5] O. Tamura, M. Hashimoto, Y. Kobayashi, T. Katoh, K. Nakatani, M. Kamada, I. Hayakawa, T. Akiba, S. Terashima, *Tetrahedron Lett.* **1992**, *33*, 3487–3490.
- [6] C. Gibson, K. Gillon, S. Cook, *Tetrahedron Lett.* **1998**, *39*, 6733–6736.
- [7] a) K. Ruck-Braun, A. Stamm, S. Engel, H. Kunz, *J. Org. Chem.* **1997**, *62*, 967–975; b) R. J. Maleski, C. E. Osborne, S. M. Cline, *J. Heterocycl. Chem.* **1991**, *28*, 1937–1939; c) H. J. Knolker, T. Braxmeier, *Tetrahedron Lett.* **1998**, *39*, 9407–9410.
- [8] M. Suzuki, T. Yamazaki, H. Ohta, K. Shima, K. Ohi, S. Nishiyama, T. Sugai, *Synlett* **2000**, 189–192.
- [9] J. R. Gage, D. A. Evans, *Org. Synth.* **1990**, *68*, 77–82.
- [10] B. Gabriele, G. Salerno, D. Brindisi, M. Costa, G. Chiusoli, *Org. Lett.* **2000**, *2*, 625–627.

- [11] M. A. Casadei, M. Feroci, A. Inesi, L. Rossi, G. Sotgiu, *J. Org. Chem.* **2000**, *65*, 4759–4761.
- [12] S. Knapp, P. J. Kukkola, S. Sharma, T. G. Murali Dhar, A. B. J. Naughton, *J. Org. Chem.* **1990**, *55*, 5700–5730.
- [13] C. Heathcock, A. Hassner, *Angew. Chem.* **1963**, *75*, 344–345; *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 213–214.
- [14] a) W. J. Jr., Farrissey, A. Munim-Nashu, *J. Heterocycl. Chem.* **1970**, *7*, 331–333; b) W. R. Roush, M. A. Adam, *J. Org. Chem.* **1985**, *50*, 3752–3757; c) S. Knapp, P. J. Kukkola, S. Sharma, S. Pietranico, *Tetrahedron Lett.* **1987**, *28*, 5399–5402d) S. W. McCombie, T. L. Nagabhushan, *Tetrahedron Lett.* **1987**, *28*, 5395–5398.
- [15] D. A. Evans, J. Bartroli, T. Shih, *J. Am. Chem. Soc.* **1981**, *103*, 2127–2129.
- [16] D. J. Ager, I. Prakash, D. R. Schaad, *Aldrichimica Acta* **1997**, *30*, 3–12, and references therein.
- [17] a) C. Paulmier, *Selenium Reagents and Intermediates in Organic Synthesis*, Pergamon, Oxford, **1986**, p. 319; b) S. Tomoda, M. Iwaoka in *Top. Curr. Chem.* (Ed.: T. Wirth), Springer, Berlin, **2000**, pp. 55–80; c) L. Engman, V. Gupta in *Organoselenium Chemistry- A Practical Approach*. (Ed.: T. G. Back), Oxford, New York, **2000**, pp. 67–90; d) M. Tiecco in *Top. Curr. Chem.* (Ed.: T. Wirth), Springer, Berlin, **2000**, pp. 7–54.
- [18] M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, D. Bartoli, *Gazz. Chim. Ital.* **1987**, *117*, 423–427.
- [19] A. Krief, W. Dumont, J. J. Denis, *J. Chem. Soc. Chem. Commun.* **1985**, 571–572.
- [20] a) M. Shimizu, T. Kuwajima, *J. Org. Chem.* **1980**, *45*, 4063–4065; b) M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, D. Bartoli, *Tetrahedron* **1986**, *42*, 4889–4886; c) M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, *Tetrahedron* **1986**, *42*, 4897–4906; d) A. Krief, W. Dumont, A. F. De Mahieu, *Tetrahedron Lett.* **1988**, *29*, 3265–3268; e) A. Krief, W. Dumont, A. F. De Mahieu, *Tetrahedron Lett.* **1988**, *29*, 3269–3272.
- [21] a) A. Toshimitsu, C. Hirose, S. Tanimoto, S. Uemura, *Tetrahedron Lett.* **1992**, *33*, 4017–4020; b) A. Toshimitsu, H. Fuji, *Chem. Lett.* **1992**, 2017–2018.
- [22] a) G. Sabitha, S. Abraham, B. V. S. Reddy, J. S. Yadav, *Synlett* **1999**, 1745–1746; b) Olofsson, P. Somfai, *J. Org. Chem.* **2002**, *67*, 8574–8583.
- [23] T. Kataoka, T. Iwama, S. Tsujiyama, K. Kanematsu, T. Iwamura, S. Watanabe, *Chem. Lett.* **1999**, 257–258.
- [24] S. C. Bergmeier, *Tetrahedron* **2000**, *56*, 2561–2576.
- [25] A. Krief, J. Remion, *Tetrahedron Lett.* **1976**, 3743–3746.
- [26] L. Engman, V. Gupta, *J. Org. Chem.* **1997**, *62*, 157–173.
- [27] M. Tiecco, L. Testaferri, A. Temperini, L. Bagnoli, F. Marini, C. Santi, *Synlett* **2001**, 1767–1771.
- [28] S. Uemura, K. Ohe, N. Sugita, *J. Chem. Soc. Perkin Trans. 1* **1990**, 1697–1703.
- [29] M. Tingoli, M. Tiecco, L. Testaferri, A. Temperini, *Synth. Commun.* **1998**, *28*, 1769–1778.
- [30] M. Chini, P. Crotti, L. A. Filippin, C. Gardelli, E. Giovani, F. Macchia, M. Pineschi, *J. Org. Chem.* **1993**, *58*, 1221–1227.
- [31] S. Uemura, A. Toshimitsu, T. Aoai, H. Owada, M. Okano, *J. Chem. Soc. Chem. Commun.* **1980**, 412–413.
- [32] M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, D. Bartoli, R. Balducci, *J. Org. Chem.* **1990**, *55*, 429–433.
- [33] a) K. B. Sharpless, R. F. Lauer, *J. Am. Chem. Soc.* **1973**, *95*, 2697–2699; b) D. Liotta, *Organoselenium Chemistry*, Wiley Interscience, New York, **1987**.
- [34] R. M. Scarborough, A. B. Smith, *Tetrahedron Lett.* **1977**, 4361–4364.
- [35] D. Liotta, H. Santiesteban, *Tetrahedron Lett.* **1977**, 4369–4372.
- [36] a) J. Barluenga, B. Baragana, J. M. Concellon, *J. Org. Chem.* **1995**, *60*, 6696–6699; b) W. T. Ashton, C. L. Cantone, L. C. Meurer, R. L. Tolman, W. J. Greenlee, A. A. Patchett, R. J. Lynch, T. W. Schorn, J. F. Strouse, P. K. Sieg, *J. Med. Chem.* **1992**, *35*, 2103–2112.
- [37] A. Cravador, A. Krief, *Tetrahedron Lett.* **1981**, *22*, 2491–2494.
- [38] S. Hanessian, P. Lavalley, *Can. J. Chem.* **1975**, *53*, 2975–2979.
- [39] D. J. Madar, H. Kopecka, D. Pireh, J. Pease, M. Pluschchev, R. J. Sciotti, P. E. Wiedeman, S. W. Djuric, *Tetrahedron Lett.* **2001**, *42*, 3681–3684.
- [40] G. Viti, R. Nannicini, R. Ricci, V. Pestellini, L. Abelli, M. Furio, *Eur. J. Med. Chem.* **1994**, *29*, 401–406.
- [41] W. L. Nelson, J. E. Wennerstrom, S. Raman Sankar, *J. Org. Chem.* **1990**, *55*, 1006–1012.

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