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[2,3]-Sigmatropic Rearrangement of Allylic Selenimides: Strategy for the Synthesis of Peptides, Peptidomimetics, and *N*-Aryl Vinyl Glycines

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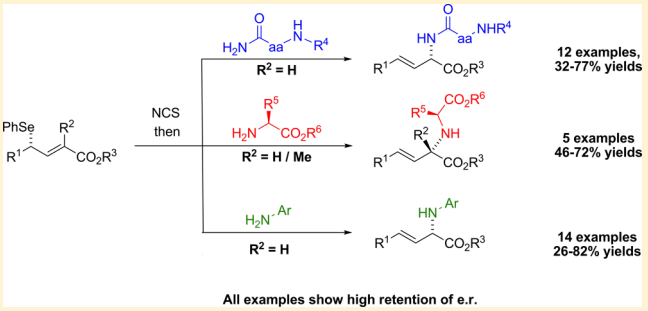
Supporting Information

ABSTRACT: The scope of the NCS-mediated amination/[2,3]-sigmatropic rearrangement of enantioenriched allylic selenides has been expanded to provide access to three new product classes. The use of *N*-protected amino acid amides provides a novel strategy for accessing peptide chains containing unnatural vinyl glycine amino acid residues. Also reported is the use of amino acid esters, allowing the diastereoselective synthesis of *N*,*N*-dicarboxymethylamines, a motif found in a number of pharmaceuticals. Furthermore, use of a range of *N*-aromatic and *N*-heteroaromatic amines allows the formation of enantioenriched *N*-arylamino acids, a motif found in a number of synthetically and biologically interesting compounds.



INTRODUCTION

The use of peptidomimetics has emerged as a powerful tool in the development of new drug compounds.[1] This approach relies on the synthesis of small molecules designed to resemble natural peptide substrates, while exhibiting improved druglike characteristics. Often, the design of peptidomimetics seeks to replace the peptide bond with a less readily hydrolyzable motif or incorporate unnatural amino acid side chains with the aim of improving metabolic and conformational stability, as well as biological activity.[2]

As part of our ongoing research program[3−6] into the [2,3]-sigmatropic rearrangement of allylic sulfimides and selenimides, we recently reported[7] an enantioselective synthesis of α-vinyl α-alkyl amino acid derivatives from allylic selenides and simple amides or carbamates (Scheme 1). Allylic selenides of high enantiomeric purity were accessed using organocatalytic enantioselective α-selenenylation of aldehydes,[8,9] followed by Wadsworth−Emmons olefination. The amination to give an allylic selenimide intermediate, followed by spontaneous rearrangement, was carried out using *N*-chlorosuccinimide and a carbamate under conditions reported by Hopkins and co-workers.[10] The use of selenium in place of sulfur (as we had used in earlier studies on related reactions[4,5]) offered several practical advantages; for instance, Se−N bond cleavage occurs during reaction workup, affording the protected amino acid derivative directly (in the sulfur studies further reactions were required to cleave the S−N bond), and commercial reagents could be used to carry out both the organocatalytic selenenylation and the amination/rearrangement.

While there are numerous examples in the literature of [2,3]-sigmatropic rearrangements of both racemic and enantioenriched allylic selenimides made in situ from simple protected primary amides and amines,[7,10−12] there is, to the best of our knowledge, only one example reporting the use of more complex amine sources in the rearrangement. In that example, Hopkins reported the formation of a racemic allylic secondary amine from the NCS-mediated reaction of *O*-benzyl-L-tyrosine ethyl ester hydrochloride with a racemic terminal allylic selenide.[10] We envisaged that further development of the methodology to allow tolerance of a wider range of more complex nitrogen sources may be challenging, since the additional functionality could potentially prove problematic under the electrophilic amination conditions. However, successful realization of this goal and incorporation into our enantioselective sequence (Scheme 1) would provide some highly valuable peptidomimetic motifs (Scheme 2). The use of *N*-protected amino acid amides would provide access to peptides containing an unnatural vinyl glycine (path a), in which the alkene functionality allows extensive possibilities for possible further modification. Aminating agents derived from *N*-unprotected amino acid esters would afford *N*,*N*-dicarboxymethylamines (path b), a class of peptidomimetics found in a number of pharmaceutical products.[13] Finally, the use of aromatic amines would provide access to a wide range of *N*-aryl vinyl glycine derivatives (path c). *N*-Arylated amino acids are

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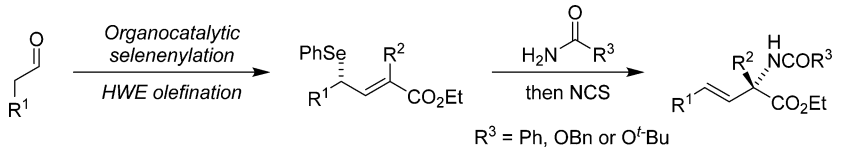
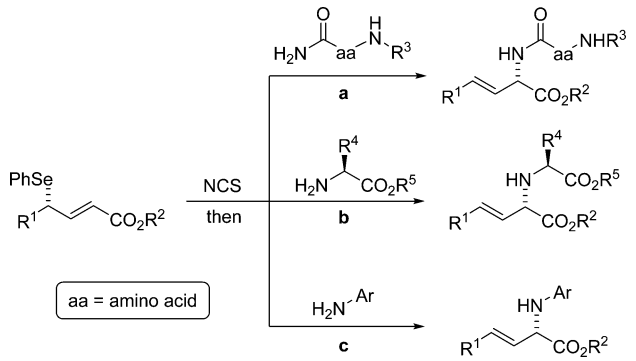
Scheme 1. Enantioselective Synthesis of α-Alkyl α-Vinyl Amino Acids[7]



Scheme 2. General Method for Amination/Rearrangement of Allylic Selenides with Amino Acid Amides (a), Amino Acid Esters (b), or Aromatic Amines (c)

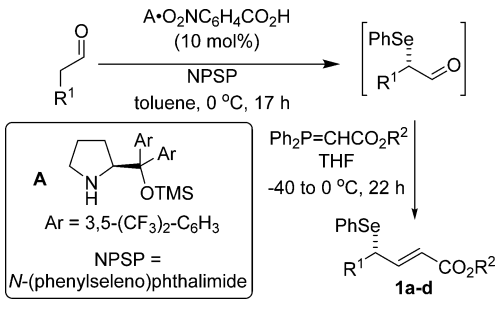


synthetically useful targets found in a broad range of biologically active compounds.[14−18]

RESULTS AND DISCUSSION

One-Pot Enantioselective Synthesis of Allylic Selenides. To provide the enantiomerically enriched allylic selenides required for this strategy, we employed a one-pot organocatalytic selenenylation/olefination protocol. The in situ Wittig reaction reported by Posner and co-workers[19,20] was used in preference to the Wadsworth−Emmons reactions required to access the trisubstituted olefins utilized in our previous work;[7] this circumvented the need for a filtration step prior to the olefination, making for a genuine one-pot protocol.[21] This method afforded (*E*)-allylic selenides **1a−d** in good yield, high enantiomeric purity, and high *E*:*Z* ratio (Table 1).

Table 1. One-Pot Synthesis of Allylic Selenides



entry	product	R^1	R^2	*E*:*Z*[a]	yield (*E*)[b]/%	er (*E*)[c]
1	**1a**	Bn	Et	98:2	45	97:3
2	**1b**	^{i}Pr	^{t}Bu	>99:1	84	98:2
3	**1c**	Et	^{t}Bu	>99:1	62	98:2
4	**1d**	Me	Et	>99:1	53	97:3

[a]Determined by ^{1}H NMR analysis of crude mixture. [b]Yield of *E* isomer after column chromatography. [c]Determined by chiral HPLC.

Synthesis of Vinyl Glycine Derivatives. Initial investigations into the use of amino acid derivatives in the amination/rearrangement focused on the reaction between allylic selenide **1a** and Cbz-protected proline amide (Cbz-L-Pro-NH_2). Pleasingly, the protected dipeptide ester **2a** was isolated in 60% yield (Table 2, entry 1) upon sequential addition of DIPEA and NCS to a solution of allylic selenide (1.5 equiv),[22] amino acid amide, and $HC(OMe)_3$/*p*-TSA.

Following this success, several further amino acid amides were prepared to test the scope of the reaction. Compatibility was shown for the Boc protecting group (Table 2, entry 2), as well as the use of noncyclic amino acid amides with alkyl, benzylm and phenyl side chains (entries 3−6). Functional group tolerance was further tested with substrates containing additional oxygen functionality; the use of serine- and tyrosine-derived amino acid amides gave yields that while moderate, 42% and 32%, respectively (entries 6 and 7), are nevertheless pleasing given the competing nucleophilicity of the unprotected hydroxyl functionality. The presence of an additional nitrogen functionality in the amino acid amides was also tolerated, as demonstrated in the use of tryptophan and azido-lysine derived amino acid amides: 48% and 77%, respectively (entries 8 and 9). The use of the more sterically hindered amide[23] $BocNHC(Me)_2CONH_2$ gave the desired product in a 39% yield (entry 10). Of particular note was the use of the dipeptide amide Boc-L-Leu-L-Ala-NH_2 (entry 11), which afforded the target tripeptide in 64% yield; however, when the reaction was performed using a tripeptide amide, the yield was reduced to 39% (entry 12).

While good levels of *E* selectivity were observed, in most cases the *Z* isomer of the product was also observed as a minor, inseparable side product. This is in contrast to previous studies with simple carbamates which showed complete selectivity for the *E* isomer.[7] In addition to the major *E* product, in all cases a small amount of a minor *E* diastereomer was also observable by ^{1}H NMR.[24] The formation of this minor diastereomer could conceivably be due to (a) the presence of 2−3% of the minor enantiomer in the starting allylic selenide (which was of 94−96% ee), (b) incomplete chirality transfer in the [2,3]-rearrangement, and (c) epimerization in the amine coupling partner. In previous work with achiral carbamate coupling partners we have observed essentially complete chirality transfer in the rearrangement,[7,12,19,20] suggesting that this is perhaps the least likely source of the minor diastereomer. In the majority of the examples, the diastereotopic peaks in the ^{1}H NMR spectra were not sufficiently resolved to allow accurate quantification of the product dr; however, in all such cases the dr can be estimated to be >95:5 through partial integration of overlapping multiplet peaks. In two examples, **2d**,**l**, accurate determination of the dr was possible. In the case of **2d**, the dr of the major *E* product was 97.5:2.5, indicating no significant loss of stereochemistry during the reaction (the starting selenide **1c** was 96% ee). In the case of the more readily racemized phenyl glycine amide, the product **2e** was formed in an 88.5:11.5 mixture of diastereomers, indicating that a higher degree of

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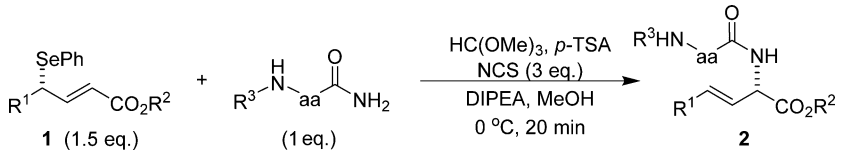
Table 2. Amination/Rearrangement with *N*-Protected Amino Acid Amides



entry	allylic selenide	amino acid amide	product	yield/%[a]	*E*:*Z*[b]	dr[c]
1	**1a**	CBz-L-Pro-NH_2	**2a**	60[d]	n/d	>95:5[e]
2	**1b**	Boc- L-Pro-NH_2	**2b**	60[f]	n/d	>95:5[e]
3	**1c**	Boc- L-Val-NH_2	**2c**	55	6:1	>95:5[e]
4	**1c**	Boc- L-Phe-NH_2	**2d**	59	7:1	97.2:2.5
5	**1c**	Boc-L-Phg-NH_2	**2e**	69	7.5:1	88.5:11.5
6	**1c**	Boc-L-Ser-NH_2	**2f**	42	8.5:1	>95:5[e]
7	**1c**	Boc-L-Tyr-NH_2	**2g**	32	7:1	>95:5[e]
8	**1c**	Cbz-L-Trp-NH_2	**2h**	48	7.5:1	>95:5[e]
9	**1c**	Fmoc-L-Lys(N_3)-NH_2	**2i**	77	4:1	>95:5[e]
10	**1c**	BocNHC$(Me)_2$CONH_2	**2j**	39	>20:1	>95:5[e]
11	**1c**	Boc-L-Leu-L-Ala-NH_2	**2k**	64	7.5:1	>95:5[e]
12	**1c**	Boc-L-Leu-L-Ala-L-Val-NH_2	**2l**	39	4:1	>95:5[e]

[a]Yield of *E*/*Z* mixture after column chromatography. [b]Determined from integration of ^{1}H NMR spectra purified material. [c]dr of the *E* isomer. [d]Using a 3:1 ratio of amide to allylic selenide, a 76% yield was obtained. [e]Estimated through integration of peaks in partially overlapping multiplet. [f]A 1.1:1 ratio of amide to allylic selenide was used.

epimerization occurred during this reaction, likely to be at the phenyl glycine chiral center.

Rearrangement using Amino Acid Esters. The use of *N*-unprotected amino acid esters as the nitrogen source in this reaction would give compounds with the unusual *N*,*N*-dicarboxymethylamine structural motif found in several angiotensin converting enzyme (ACE) inhibitors[13] (Figure 1)

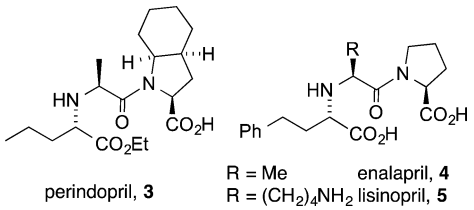
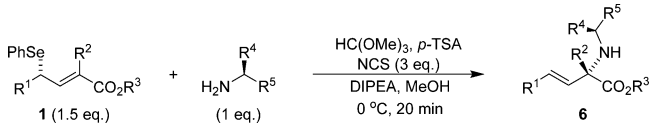


Figure 1. Examples of ACE inhibitors.

used to treat congestive heart failure and hypertension. Current methods of diastereoselective synthesis of this class of compounds include the S_N2 displacement by α-amino esters of enantiomerically pure α-sulfonyloxy esters[25−27] or α-halo esters,[28,29] which may be prepared from the corresponding amino acid derivatives. A diastereoselective conjugate addition has also been used as the key step in the synthesis of a *N*,*N*-dicarboxymethylamine.[30] A highly diastereoselective synthesis of enalapril **4** starting from an enantiomerically pure 1,2-amino alcohol has also been reported.[31,32]

L-Alanine benzyl ester was chosen as an initial test substrate, but the product could only be isolated in low yield using the protocol employed for the examples in Table 2. Optimisation studies revealed that methanol remained the solvent of choice, with the key observation being that an altered order of addition was crucial for a high-yielding reaction. Hence, NCS was initially added to the allylic selenide, DIPEA, and HC$(OMe)_3$/*p*-TSA prior to final addition of the amino acid ester. Product **6a** was then isolated in 72% yield (Table 3, entry 1). The functional group tolerance of the amino acid esters was tested with phenyl glycine and serine derived amino acid esters, giving the desired products in 60% and 54% yields, respectively (entries 2 and 3). However, with the serine example a significant decrease in dr was observed when the standard reaction conditions were employed. Further investigation found

Table 3. Amination/Rearrangement with Amino Acid Esters



entry	R^1	R^2	R^3	R^4	R^5	product	yield/%[a]	*E*:*Z*[a,b]	dr[c]
1	Et	H	^{t}Bu	Me	CO_2Bn	**6a**	72	8:1	>95:5[d]
2	Et	H	^{t}Bu	Ph	CO_2Me	**6b**	60	>25:1	96:4
3	Et	H	^{t}Bu	CH_2OH	CO_2Bn	**6c**	54[e]	>25:1	>95:5[d]
4	Me	H	Et	Me	CO_2Bn	**6d**	62	8:1	>95:5[d]
5	Et	Me	^{t}Bu	Me	CO_2Bn	**6e**	46	>25:1	>95:5[d]

[a]Yield of *E*/*Z* mixture after column chromatography. [b]Determined from integration of ^{1}H NMR spectra of purified material. [c]dr measured for the *E* isomer. [d]Estimated through integration of peaks in partially overlapping multiplets. [e]Required cooling to −45 °C and stirring for 12 h after NCS addition.

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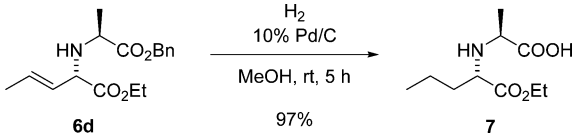
that a high level of diastereoselectivity could be achieved by lowering the reaction temperature to −45 °C, with a corresponding increase in reaction time. The reactions of an allylic selenide containing a shorter alkyl chain (62%, entry 4) and a trisubstituted allylic selenide[33] (46%, entry 5) were also successful, the latter providing access to *N*,*N*-dicarboxymethylamines containing a chiral quaternary carbon center.

Unlike the amino acid amide examples discussed above (see Table 2) in some cases careful column chromatography allowed separation of the *E* isomers from the *Z* isomers. In all cases, the product contained a small amount of a minor *E* diastereomer, observable by ^{1}H NMR.[24] Possible explanations for the presence of this minor *E* diastereomer in the [2,3]-rearrangement product are as discussed above. Again, overlapping resonances prevented accurate determination of the dr from the ^{1}H NMR spectra of most products, although as with the results above, the dr can be estimated to be >95:5 in all cases. In the example using the more readily racemized phenyl glycine (entry 2, Table 3), the ^{1}H spectrum of the product **6b** was sufficiently resolved to determine the dr of the *E* product as 96:4, indicating that only a small amount of epimerization occurred during the reaction (starting selenide **1c** was 96% ee).

The subsequent hydrogenation/hydrogenolysis of **6d** (Scheme 3) proceeded in 97% yield to provide access to *N*-

Scheme 3. Hydrogenation/Hydrogenolysis of 6d



[(*S*)-1-carbethoxybutyl]-(*S*)-alanine, a key intermediate in the synthesis of perindopril,[25,34] providing a new formal synthetic route to perindopril and its analogues from readily available aldehyde starting materials.

Synthesis of *N*-Aryl Vinyl Glycine Derivatives. With the aim of further extending the scope of *N*-substituted vinyl glycine products that may be accessed using the [2,3]-sigmatropic rearrangement of allylic selenides, we reasoned that aromatic amines may also be suitable reaction partners. Use of aromatic amines would provide access to *N*-arylated α-amino acids, common motifs found in a number of medicinally important and synthetically interesting biological agents; examples are found in hepatitis C virus replicator inhibitors,[14] ACE inhibitors,[15] anticoagulant factor Xa inhibitors,[16] the GPIIb/IIIa fibrinogen receptor antagonist Lotrafiban,[17] and compounds with antiulcer agent activity.[18] The majority of reported preparations of *N*-aryl amino acids rely upon metal-catalyzed Ullman-like reactions.[35−38] While these provide an efficient synthetic route, the formation of enantioenriched *N*-aryl amino acids requires enantioenriched amino acid starting materials; in addition, while chiral pool amino acids are easily obtained, unnatural amino acids require enantioselective synthesis which can be nontrivial. A number of alternative methods for the synthesis of optically active *N*-aryl amino acids starting from prochiral starting materials have also been developed. The majority involve the enantioselective addition of nucleophiles into *N*-aryl imino esters or amides. Selected examples of these are asymmetric Mannich reactions using chiral amino sulfonamide organocatalysis,[39] asymmetric Petasis reactions,[40,41] and enantioselective aza-Friedel−Crafts reactions.[42]

Previously the [2,3]-sigmatropic rearrangement of racemic allylic selenides with a limited range of simple anilines has been reported.[10] Expansion of this substrate scope to include a wide range of functionalized aromatic and heteroaromatic amines would provide a facile route to a diverse range of highly enantioenriched *N*-arylated vinyl glycine derivatives. Initial investigations into the rearrangement of allylic selenide **1c** (er 97:3[43]) with aniline, using the same order of addition as for amino acid ester substrates (Table 3), revealed that with a slight decrease in reaction temperature (to −20 °C), the desired product could be isolated in 75% yield. It was also found that having the commercially available amine in 1.5 equiv excess, with the allylic selenide as the limiting reagent, had no effect on the reaction yield; previously the nitrogen source had been used as the limiting reagent. Reactions using a closer to 1:1 ratio of amine to allylic selenide afforded decreased yields, with a 1.1 equiv excess of amine affording a yield of 54%. The er, determined by HPLC analysis following $LiAlH_4$ reduction of the ester to the primary alcohol (**9a**), was found to be 97:3, indicating complete retention of the enantioenrichment of the allylic selenide starting material (Table 4 entry 1).

With optimized conditions the scope was further expanded to a wide range of aromatic and heteroaromatic amines. Changing the substituents present on the aniline ring was found to have a profound effect on the yields of the reactions. It was found that electron-rich ring systems gave reduced yields, with *p*- and *o*-toluidine affording the desired rearrangement products in 61% and 49% yields, respectively (entries 2 and 3), and *p*-anisidine affording a much decreased yield of 31% (entry 4). It was found that the reduced yields with electron-rich anilines arose due to rapid, unproductive side reactions between the aniline and NCS. Further optimization with *p*-anisidine, the lowest yielding example, found that decreasing the number of equivalents of NCS resulted in an increase in yield, though with decreasing conversion of the allylic selenide. Improved conditions used 1.1 equiv of NCS and gave a yield of 54% with 22% of the remaining allylic selenide (entry 4). Attempts at increasing the conversion of the allylic selenide by increasing the time between the NCS and anisidine additions gave the desired increased conversion of allylic selenide but failed to increase the yield of the desired product.

In contrast, an example with a strongly electron withdrawing substituent, *p*-nitroaniline, gave an increased yield of 85% (entry 5). The use of 3-aminobenzyl alcohol also gave a good yield (62%, entry 6), despite the competing hydroxy nucleophilicity that had previously proved problematic (see examples above with amino acids and amino acid amides). The scope was then increased to include a number of heteroaromatic amines. Both 2-aminothiazole and 2-aminobenzothiazole provided the desired products in good yields (entries 7 and 8); however, the 2-aminothiazole example suffered from slight epimerization, giving the desired reaction product in an er of 94.5:5.5. Use of the more electron rich 2-amino-5-methoxybenzothiazole gave an increased yield of 82% (entry 9). A range of aminopyridines were then tested (entries 10−13), all proceeding with moderate to good yields (63−78%), demonstrating the reaction's tolerance for both halogen (entries 11 and 12) and nitrile functionalities (entry 13). Examples with additional heterocycles containing nitrogen atoms with exchangeable protons led to significantly reduced yields, with reactions using 3-aminopyrazole and 2-amino-

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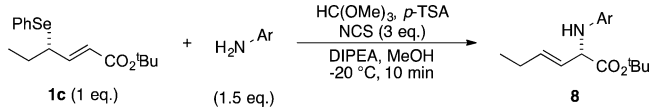
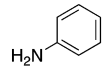
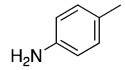
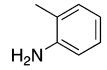
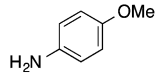
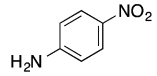
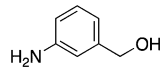
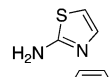
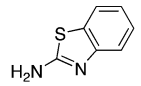
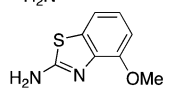
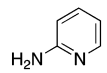
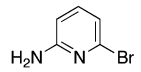
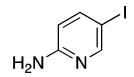
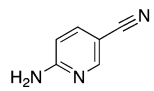
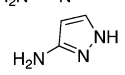
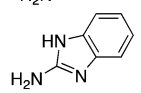
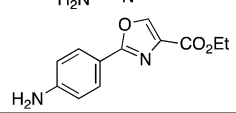
Table 4. Amination/Rearrangement with Aromatic Amines



Entry	Amine	Product	Yield / %[a]	E/Z[b]	e.r.[c]
1		**8a**	75	> 25:1	97:3[d]
2		**8b**	61	> 25:1	96.5:3.5
3		**8c**	49	> 25:1	96.5:3.5[d]
4		**8d**	31 (54)[e]	> 25:1	96.5:3.5
5		**8e**	85	> 25:1	96.5:3.5
6		**8f**	62	> 25:1	96.5:3.5
7		**8g**	73	> 25:1	94.5:5.5
8		**8h**	74	> 25:1	97:3
9		**8i**	82	> 25:1	96.5:3.5
10		**8j**	71	> 25:1	94.5:5.5
11		**8k**	70	> 25:1	96.5:3.5
12		**8l**	78	> 25:1	96.5:3.5
13		**8m**	63	> 25:1	96.5:3.5
14		**8n**	26	> 25:1	97:3
15		**8o**	43	> 25:1	97:3
16		**8p**	70	> 25:1	96.5:3.5

[a]Yield after column chromatography. [b]Determined from integration of ^{1}H NMR spectra. [c]Determined by chiral HPLC. [d]er determined following $LiAlH_4$ reduction to alcohol, **9a**, and **9c** respectively. [e]The use of 1.1 equiv of NCS afforded a 54% yield.

imidazole giving the desired rearrangement products in 26% and 43% yields, respectively (entries 14 and 15). Finally, an example with ethyl 2-(4-aminophenyl)oxazole-4-carboxylate gave a yield of 70%, (entry 16) demonstrating the compatibility of the reaction conditions with the oxazole functionality.

■ CONCLUSION

In conclusion, we have demonstrated that the amination/rearrangement of allylic selenides with amino acid amides provides a novel strategy for accessing a range of peptides containing an unnatural vinyl glycine amino acid. Furthermore, the strategy may be adapted for *N*-unprotected amino acid esters as a diastereoselective route to *N*,*N*-dicarboxymethyl-amines, a motif found in several pharmaceuticals, and the use of aromatic amines proceeded with good yields, providing access to a diverse range of highly enantioenriched *N*-aryl amino acids. Access to these three product classes highlights the versatility of the amination/[2,3]-rearrangement of allylic selenides as a method for the synthesis of enantioenriched allylic amine derivatives and has expanded the scope to a diverse range of previously unreported carbamates and alkyl and aromatic amines.

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EXPERIMENTAL SECTION

General Experimental Methods. Solvents were dried by passing through activated alumina, with the exception of methanol, which was dried by reflux over magnesium and iodine and then distillation and storage for at least 3 days over 3 Å molecular sieves. Aldehydes and DIPEA were distilled before use. *N*-Chlorosuccinimide was recrystallized from toluene. NPSP was prepared according to a literature procedure[44] and then further purified by trituration in ethanol. Catalyst **A** (2-[bis(3,5-bis(trifluoromethyl)phenyl)-trimethylsilanyloxymethyl]pyrrolidine) was prepared according to literature procedures.[45] Other reagents were used as received from commercial suppliers. Reaction temperatures were recorded as bath temperatures. Flash column chromatography was carried out using silica gel 40−60 μm or neutral alumina 32−200 μm. Analytical thin-layer chromatography (TLC) was performed using glass-backed plates precoated with silica gel 60 F_{254}. Melting points were obtained using a hot plate microscope and are uncorrected. Optical rotations were recorded with a path length of 0.5 dm at the stated temperature (°C) and concentration (*c*, in g/100 mL) and are quoted in units of (deg mL)/(g dm). Infrared analyses were recorded using an ATR FT-IR spectrometer. NMR analyses were recorded on an AV 400 or AV 500 spectrometer in $CDCl_3$ unless stated otherwise. Chemical shifts are quoted in ppm relative to TMS (as referenced to residual solvent: e.g., $CHCl_3$ δ_H 7.26, $CDCl_3$ δ_C 77.0), with coupling constants quoted in Hz and reported to the nearest 0.1 Hz. Mass spectrometry analyses were carried out using CI+ (NH_3), ES+, or EI+.

Synthesis of Amino Amides. Cbz-L-Pro-NH_2, Boc-L-Pro-NH_2, Boc-L-Phe-NH_2, Boc-L-Phg-NH_2, Boc-L-Tyr-NH_2, and Cbz-L-Trp-NH_2 were prepared by treatment of the corresponding *N*-protected amino acid with EDCI or DCC, HOBT, and aqueous ammonia.[46,47] Boc-L-Val-NH_2 was prepared by treatment of Boc-L-Val-OH with ethyl chloroformate and triethylamine, followed by aqueous ammonia.[48] BocNHC$(Me)_2$CONH_2 was prepared from aminobutyric acid by *N*-Boc protection followed by coupling with ammonia using DCC and HOBT.[49] Boc-L-Ser-NH_2 was prepared by treatment of serine-L-lactone[50] with liquid ammonia.[51] These compounds have been reported in the literature previously and characterization data corresponded with literature values.

Fmoc-L-Lys(N_3)-NH_2. The title compound was prepared from the treatment of Fmoc-L-Lys(N_3)-OH[52] (0.6 mmol) with EDCI, HOBt, and aqueous ammonia, following on the procedure of Ley.[46] This afforded the title compound as a white solid (144 mg, 63%): mp 111−114 °C; $[\alpha]_D^{28}$ −3.8° (*c* = 1.06, $CHCl_3$); IR 3395, 3317, 3201, 2947, 2096, 1674, 1532, 1450, 1253 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.76 (dt, *J* 7.6, 1.0, 2 H), 7.57 (d, *J* 7.4, 2 H), 7.40 (t, *J* 7.4, 2 H), 7.31 (td, *J* 7.5, 1.22 H), 6.11 (s, 1 H), 5.71 (s, 1 H), 5.47 (d, *J* 7.9, 1 H), 4.44 (d, *J* 6.8, 2 H), 4.20 (t, *J* 6.7, 2 H), 3.26 (t, *J* 6.7, 2 H), 2.02−1.80 (m, 2 H), 1.70−1.52 (m, 2 H), 1.49−1.36 (m, 2 H); δ_C (100 MHz, $CDCl_3$) 174.1, 156.4, 143.8, 141.46, 127.9, 127.2, 125.1, 120.2, 77.2, 67.1, 54.3, 51.2, 47.3, 32.0, 28.6, 22.7; *m*/*z* (ES+) 416 (100% $[MNa]^+$), 394 (83%, $[MH]^+$), 338 (26%, $[MH - CH_2N_3]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{21}H_{23}N_5O_3Na^+$ $[MNa]^+$ 416.1699, found 416.1695.

Boc-L-Leu-L-Ala-NH_2. The title compound was prepared by *N*-Boc-protection and *O*-methylation (methyl iodide, K_2CO_3, DMF) of commercially available H-Leu-Ala-OH, followed by treatment with 7 M methanolic ammonia for 20 h at room temperature[53] to give the desired compound in 28% overall yield: IR 3404, 3305, 2960, 2933, 2872, 1671, 1629, 1521, 1456, 1418 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.16 (d, *J* 6.0, 1 H), 6.78 (br s, 1 H), 6.02 (br s, 1 H), 5.23 (d, *J* 5.1, 1 H), 5.54−5.47 (m, 1 H), 4.11 (br s, 1 H), 1.17−1.63 (m, 1 H), 1.62−1.56 (m, 1 H), 1.52−1.44 (m, 1 H), 1.41 (s, 9 H), 1.36 (d, *J* 7.1, 3 H), 0.91 (t, *J* 6.1, 6 H); δ_C (100 MHz, $CDCl_3$) 174.9, 172.8, 155.9, 80.3, 53.4, 48.4, 41.1, 28.3, 24.7, 23.0, 21.8, 17.9; *m*/*z* (ES+) 365 (10%, $[M + MeCNNa]^+$), 340 (20%, $[MK]^+$), 324 (100%, $[MNa]^+$), 301 (5%, MH^+); HRMS (ES+/TOF) *m*/*z* calculated for $C_{14}H_{27}N_3O_4Na^+$ $[MNa]^+$ 324.1899, found 324.1884.

Boc-L-Leu-L-Ala-L-Val-NH_2. The title compound was prepared by coupling Boc-Leu-Ala-OH and HCl·H-Val-NH_2 (prepared from Boc-Val-NH_2 by treatment with concentrated HCl in ethyl acetate) with EDC and HOBT in DMF, affording the title compound in 32% overall yield: IR 3287, 3213, 2963, 2936, 2874, 1643, 1550, 1470, 1453 cm^{-1}; δ_H (400 MHz, MeOH-d_4) 4.40 (q, *J* 7.1, 1 H), 4.20 (d, *J* 6.4, 1 H), 4.05 (t, *J* 7.5, 1 H), 2.18 (app oct, *J* 6.8, 1 H), 1.74−1.61 (m, 1 H), 1.52 (t, *J* 7.2, 2 H), 1.45 (s, 9 H) 1.36 (d, *J* 7.1, 3 H), 0.97 (d, *J* 6.8, 3 H), 0.95 (d, *J* 6.5, 3 H), 0.94 (d, *J* 6.7, 3 H), 0.93 (d, *J* 6.6, 3 H); δ_C (100 MHz, MeOH-d_4) 176.1, 175.8, 1745.0, 157.9, 80.7, 59.9, 54.8, 50.5, 42.1, 31.5, 28.7, 25.9, 23.4, 22.0, 19.7, 18.3, 18.1; *m*/*z* (ES+) 439 (10%, $[MK]^+$), 423 (100%, $[MNa]^+$), 401 (10%, $[MH]^+$); HRMS (ES+/TOF) calculated for $C_{19}H_{37}N_4O_5^+$ $[MH]^+$ 401.2764, found 401.2752.

General Procedure for Organocatalytic α-Selenenylation/Olefination (Table 1).[54] To a solution of aldehyde (0.8 mmol) in toluene (0.6 mL) at 0 °C was added catalyst **A** (96 mg, 0.16 mmol) and *p*-nitrobenzoic acid (26 mg, 0.16 mmol). After the mixture was stirred for 10 min, *N*-phenylselenylphthalimide (75%, 388 mg, 0.96 mmol) was added and stirring was continued at the same temperature for 17 h. The reaction mixture was diluted with dry THF (4 mL) and cooled to −40 °C. To this mixture was added a solution of triphenylphosphorane (1.2 mmol) in THF (4 mL) at −40 °C, via cannula. The reaction mixture was stirred at the same temperature for 2 h before it was slowly warmed to 0 °C and stirred for a further 20 h. NH_4Cl (saturated aqueous, 1 mL) was added, and the reaction mixture was extracted three times with diethyl ether. The combined organic extracts were combined, washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. The product was purified by column chromatography on silica gel. Enantiomeric ratios were determined using chiral HPLC by comparison to a racemic sample prepared from the appropriate isolated α-selenenylated aldehyde[55] followed by Wittig reaction using the appropriate triphenylphosphorane.

(*S*)-Ethyl 5-Phenyl-4-phenylselenylpent-2-(*E*)-enoate (1a). The title compound was prepared according to the general procedure using hydrocinnamaldehyde and (carbethoxymethylene)-triphenylphosphorane; crude NMR indicated 47:1 *E*:*Z* ratio. Column chromatography (2.5:1 → 1:1 petroleum ether/CH_2Cl_2) afforded **1a** (65 mg, 45%) (previously reported literature yield 79%[20]), a colorless oil, as a pure *E* isomer: $[\alpha]_D^{21}$ −94.7° (*c* 1.14, $CHCl_3$); IR 3061w, 3028w, 2980w, 1710s, 1641, 1602w, 1578w, 1496, 1475, 1454, 1438 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.51−7.48 (m, 2 H), 7.30−7.21 (m, 6 H), 7.18−7.16 (m, 2 H), 6.94 (dd, *J* 15.5, 9.8, 1 H), 5.24 (dd, *J* 15.5, 0.8, 1 H), 4.12 (q, *J* 7.1, 2H), 3.99 (, dddd, *J* 9.8, 8.5, 6.4, 0.8, 1 H) 3.12 (dd, *J* 14.1, 6.4, 1 H), 3.05 (dd, *J* 14.1, 8.5, 1 H), 1.24 (t, *J* 7.1, 3 H); δ_C (100 MHz, $CDCl_3$) 166.0, 146.8, 138.4, 136.3, 129.0, 128.9, 128.5, 128.5, 128.0, 126.7, 120.2, 60.2, 46.6, 40.1, 14.2; *m*/*z* (CI+) 378 (90%, $[M + NH_4]^+$), 361 (25%, $[MH]^+$); HRMS (CI+-TOF) *m*/*z* calculated for $C_{19}H_{24}NO_2{}^{80}Se^+$ 378.0972, found 378.0970; enantiomeric ratio was determined as 97:3 by HPLC, Chiralcel OD-H column, 99.5:0.5 hexane/IPA, flow 1.0 mL min^{-1}, UV detection at 236 nm 21.8 min (minor), 23.3 min (major).

(*S*)-*tert*-Butyl 5-Methyl-4-phenylselenylhex-2-(*E*)-enoate (1b). The title compound was prepared according to the general procedure using isovaleraldehyde and (*tert*-butoxycarbonylmethylene)-triphenylphosphorane; crude NMR indicated >99:1 *E*:*Z* ratio. Column chromatography (20:1 → 10:1 petroleum ether/Et_2O) afforded **1b** (228 mg, 84%), a colorless oil, as a pure *E* isomer: $[\alpha]_D^{21}$ −163° (*c* 1.55, $CHCl_3$); IR 3059, 2963, 2930, 2873, 1708, 1642, 1579, 1476, 1463, 1438 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.50−7.47 (m, 2 H), 7.32−7.23 (m, 3 H), 6.79 (dd, *J* 15.3, 8.9, 1 H), 5.12 (dd, *J* 15.3, 0.5, 1 H), 3.53 (ddd, *J* 10.8, 6.7, 0.5, 1 H), 2.00 (app oct, *J* 6.7, 1 H), 1.43 (s, 9 H), 1.09 (d, *J* 6.7, 3 H), 1.04 (d, *J* 6.7, 3 H); δ_C (100 MHz, $CDCl_3$) 165.5, 144.8, 136.3, 128.9, 128.7, 128.1, 121.9, 80.1, 55.3, 32.0, 28.1, 21.5, 20.6; *m*/*z* (CI+) 358 (90%, $[M + NH_4]^+$), 341 (20%, $[MH]^+$), 302 (100%, $[M - (^tBu) + NH_4]^+$); HRMS (CI+-TOF) *m*/*z* calculated for $C_{17}H_{28}NO_2{}^{80}Se^+$ 358.1285, found 358.1291; enantiomeric ratio was determined as 98:2 by HPLC, Chiralcel OD-H column, 100% hexane, flow 1.0 mL min^{-1}, UV detection at 236 nm 18.2 min (minor), 20.1 min (major).

(*S*)-*tert*-Butyl 4-Phenylselenylhex-2-(*E*)-enoate (1c). The title compound was prepared according to the general procedure using

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butyraldehyde and (*tert*-butoxycarbonylmethylene)-triphenylphosphorane; crude NMR indicated >99:1 *E*:*Z* ratio. Column chromatography (40:1 → 10:1 petroleum ether/Et_2O) afforded **1c** (162 mg, 62%), a colorless oil, as a pure *E* isomer: $[\alpha]_D^{21}$ −124° (*c* 2.39, $CHCl_3$); IR 3059, 2875, 2973, 2933, 1707, 1642, 1579, 1476, 1456, 1438 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.55−7.52 (2 H, m), 7.34−7.27 (m, 3 H), 6.80 (dd, *J* 15.4, 9.6, 1 H), 5.28 (dd, *J* 15.4, 0.8, 1 H), 3.66 (dddd, *J* 9.6, 8.0, 6.4, 0.8, 1 H), 1.89−1.73 (m, 2 H), 1.05 (t, *J* 7.4, 3 H); δ_C (100 MHz, $CDCl_3$) 165.6, 146.4, 137.3, 136.4, 128.9, 128.2, 121.7, 80.1, 47.6, 28.1, 26.9, 12.9; *m*/*z* (CI+) 344 (80%, $[M + NH_4]^+$), 327 (20%, $[MH]^+$), 288 (100%, $[M - (^tBu) + NH_4]^+$), 270 (5%, $[M - (^tBu)]^+$); HRMS (CI+-TOF) *m*/*z* calculated for $C_{16}H_{26}NO_2{}^{80}Se^+$ 344.1129, found 344.1134; enantiomeric ratio was determined as 98:2 by HPLC, Chiralcel OD-H column, 100% hexane, flow 1.0 mL min^{-1}, UV detection at 236 nm 21.2 min (minor), 23.8 min (major).

Preparation of (*S*)-Ethyl 4-Phenylselenylbut-2-(*E*)-enoate (1d). The title compound was prepared according to the general procedure using propionaldehyde and (carbethoxymethylene)-triphenylphosphorane; crude NMR indicated >99:1 *E*:*Z* ratio. Column chromatography (40:1 → 20:1 petroleum ether/Et_2O) afforded **1d** (120 mg, 53%), a pale yellow oil, as a pure *E* isomer: $[\alpha]_D^{21}$ −93.1° (*c* = 1.313, CH_2Cl_2); IR 3072, 3056, 2978, 2924, 2866, 1712, 1643, 1438, 1259 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.52−7.50 (m, 2 H), 7.34−7.25 (m, 3 H), 6.98 (dd, *J* 15.5 and 8.6, 1 H), 5.38 (dd, *J* 15.5 and 1.1, 1 H), 4.15 (q, *J* 7.13, 2 H), 3.92−3.84(m, 1 H), 1.51 (d, *J* 6.88, 3 H), 1.26 (t, *J* 7.13, 3 H); δ_C (100 MHz, $CDCl_3$) 167.9, 148.9, 136.3, 129.1, 128.6, 128.1, 119.1, 60.4, 39.4, 19.7, 14.4; *m*/*z* (EI) 284 (99%, $[M]^+$), 239 (20%, $[M - CO_2Et]^+$), 185 (21%, $[M - CH{=}CHCO_2Et]^+$), 157 (57%, $[M - CH_3CHCH{=}CHCO_2Et]^+$), 127 (79%, $[M - Ph^{80}Se]^+$), 99 (100%, $[M - Ph^{80}SeCHCH_3]^+$); HRMS (CI+-TOF) *m*/*z* calculated for $C_{13}H_{16}O_2{}^{80}Se^+$ 284.0310, found 284.0314; enantiomeric ratio was determined as 97:3 by HPLC, Chiralcel OD-H column, 100% hexane, flow 0.5 mL min^{-1}, UV detection at 236 nm 65.6 min (minor), 76.6 min (major).

General Procedure for Amination/Rearrangement using Amides (Table 2). To a stirred solution of allylic selenide **1** (0.30 mmol) in dry methanol (1 mL), was added *N*-protected amino acid amide (0.20 mmol), trimethyl orthoformate (129 μL, 1.18 mmol), and *p*-toluenesulfonic acid (1 mg). After 0.5 h, the reaction mixture was cooled to 0 °C and diisopropylethylamine (209 μL, 1.20 mmol) and *N*-chlorosuccinimide (80 mg, 0.60 mmol) were added. The reaction mixture was stirred at 0 °C for 20 min, and then HCl (1 mL, aqueous, 1 M) was added, followed by saturated sodium bicarbonate solution (1 mL). The reaction mixture was then extracted three times into ethyl acetate, and the combined organic layers were washed twice with brine, dried (Na_2SO_4), concentrated under reduced pressure, and purified by column chromatography.

(*S*)-Benzyl 2-((*S*)-1-Ethoxycarbonyl-4-phenylbut-2-enylcarbamoyl)pyrrolidine-1-carboxylate (2a). The title compound was prepared according to the general procedure using (*S*)-ethyl 5-phenyl-4-phenylselenylpent-2-(*E*)-enoate (**1a**; 0.13 mmol) and Cbz-L-Pro-NH_2 (0.38 mmol) (neutral alumina, (2:1 → 1:2 petroleum ether/EtOAc): colorless oil (35 mg, 60%); $[\alpha]_D^{23}$ −22.8° (*c* 1.75, $CHCl_3$); IR 3154 br, 3077 br, 2958, 2793, 1771, 1685 s, cm^{-1}; δ_H (400 MHz, $CDCl_3$, 333 K) 7.31−7.12 (m, 10 H), 5.92−5.87 (br m, 1 H), 5.56−5.51 (br m, 1 H), 5.18−5.13 (br m, 2 H), 5.08−5.02 (m, 1 H), 4.40−4.36 (m, 1 H), 4.24−4.13 (m, 2 H), 3.57−3.51 (m, 2 H), 3.37−3.35 (m, 2 H), 2.72 (br s, 1 H), 2.06−1.93 (m, 2 H,, 1.91−1.86 (m, 1 H), 1.28−1.23 (m, 3 H,); δ_C (125 MHz, $CDCl_3$, 323 K, DEPT 135 and 90) 171.3 (C), 170.4 (broad, C), 155.8 (C), 139.5 (C), 136.6 (C), 133.0 (CH), 128.49 (CH), 128.46 (CH), 128.43 (CH), 128.0 (CH), 127.8 (CH), 126.2 (CH), 125.6 (CH), 67.3 (CH_2), 61.6 (CH_2), 60.6 (CH), 54.1 (CH), 47.2 (broad, CH_2), 38.4 (CH_2), 28.4 (broad, CH_2), 24.3 (broad, CH_2), 14.1 (CH_3); *m*/*z* (EI+) 450 (50%, $[M]^+$), 377 (25%, $[M-CO_2Et]^+$); HRMS (EI+-TOF) *m*/*z* calculated for $C_{26}H_{30}N_2O_5{}^+$ 450.2155, found 450.2154,. The diastereomeric mixture was prepared by the same method from racemic **1a**. Spectroscopic data agreed with the material prepared above. The following additional ^{13}C NMR signals were observed for the other diastereomer: 170.5 (C), 139.4 (C), 136.5 (C), 133.1 (CH), 128.5 (CH), 128.0 (CH), 125.4, (CH), 67.3 (CH_2), 60.8 (CH), 53.9 (CH), 47.2 (CH_2).

(*S*)-*tert*-Butyl 2-((*S*)-1-*tert*-Butoxycarbonyl-4-methylpent-2-enylcarbamoyl)pyrrolidine-1-carboxylate (2b). The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 5-methyl-4-phenylselenylhex-2-(*E*)-enoate (**1b**; 73 mg, 0.22 mmol), Boc-L-Pro-NH_2 (51 mg, 0.24 mmol) (silica gel, 4:1 → 3:2 petroleum ether/EtOAc): colorless oil (51 mg, 60%); $[\alpha]_D^{21}$ −10° (*c* 0.1, $CHCl_3$); IR 3320, 2975, 2933, 2873, 1736, 1675s, 1513, 1479, 1456, 1392s, 1367s cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.35 (br s, 0.5 H), 6.64 (br s, 0.5 H), 5.68−5.62 (m, 1 H), 5.40−5.37 (m, 1 H), 4.86 (br s, 1 H), 4.32−4.20 (m, 1 H), 3.47−3.32 (m, 2 H), 2.27 (app octet, *J* 6.7, 1 H), 2.13 (br s, 1 H), 1.91−1.87 (m, 3 H), 1.44 (s, 9 H) 1.43 (s, 9 H), 0.94 (d, *J* 6.7, 6 H); δ_C (100 MHz, $CDCl_3$; signals assigned to the rotameric form are denoted "rot") 171.8, 171.4 (rot), 169.9, 155.6, 154.6 (rot), 140.9, 140.4 (rot), 121.7, 82.0, 81.8 (rot), 80.7, 80.2 (rot), 61.0, 59.8 (rot), 54.4, 54.0 (rot), 47.0, 30.8, 30.7, 28.3, 27.9, 24.5, 23.7 (rot), 22.0, 22.0; *m*/*z* (ES+) 419 (100%, $[MNa]^+$), 397 (25%, $[MH]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{21}H_{37}N_2O_5$ $[MH]^+$ 397.2702, found 397.2689. The diastereomeric mixture was prepared by the same method from racemic **1b**. Spectroscopic data agreed with the material prepared above. The following additional signals were observed for the other diastereomer: δ_H (400 MHz, $CDCl_3$) 7.13 (br s, 0.5 H), 6.52 (br s, 0.5 H), 5.71 (ddd, *J* 15.5, 6.6, 1.5, 1 H), 0.95 (d, *J* 6.7, 6 H); δ_C (100 MHz, $CDCl_3$) 169.9, 154.6, 141.2, 121.6, 80.5, 61.3, 60.1 (rot), 54.2, 47.0, 31.1, 30.8, 28.3, 27.9, 22.0.

(2*S*)-*tert*-Butyl 2-((*S*)-2-*tert*-Butoxycarbonylamino-3-methylbutyrylamino)hex-3-enoate (2c). The title compound was prepared according to the general procedure using *tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate (**1c**) and Boc-L-Val-NH_2 (silica gel, 6:1 → 1:1 petroleum ether/EtOAc): light yellow foam (42 mg, 55%); $[\alpha]_D^{21}$ −2.5° (*c* 2.36, $CHCl_3$); IR 3315br, 2968, 2933, 2876, 1718, 1701, 1692, 1651s, 1517, 1501, 1457, cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.60−6.53 (br m, 1 H), 5.76 (dtd, *J* 15.4, 6.3, 1.3, 1 H), 5.42 (ddt, *J* 15.4, 6.1, 1.4, 1 H), 5.14 (d, *J* 7.5, 1 H), 4.89 (m, 1 H), 3.96 (app t, *J* 7.0, 1 H), 2.16−2.08 (m, 1 H), 2.06−2.00 (m, 2 H), 1.43 (s, 9 H), 1.42 (s, 9 H), 0.95 (d, *J* 6.7, 3 H), 0.95 (t, *J* 7.4, 3 H), 0.91 (d, *J* 6.8, 3 H); the following distinct signals for the *Z* isomer were observed, 5.64 (dt, *J* 9.1, 7.4, 1 H), 2.27−2.20 (m, 2 H), 1.00 (t, *J* 7.3, 3 H) and *E*:*Z* ratio was determined to be 6:1 by integration of the signals at 5.76 and 5.64, respectively; δ_C (100 MHz, $CDCl_3$) 170.8, 169.8, 155.8, 136.0, 123.1, 82.2, 79.7, 59.8, 54.5, 31.0, 27.9, 28.3, 19.2, 17.7, 13.1; *m*/*z* (ES+) 407 ($[MNa]^+$, 100%), 385 ($[MH]^+$, 20%),; HRMS (ES+/TOF) *m*/*z* calculated for $C_{20}H_{37}N_2O_5$ $[MH]^+$ 385.2702, found 385.2691. The diastereomeric mixture was prepared by the same method from racemic **1c**. Spectroscopic data agreed with the material prepared above. The following additional ^{13}C NMR signals were observed for the other diastereomer: δ_C (100 MHz, $CDCl_3$) 170.7, 170.0, 135.9, 123.3, 82.2, 59.6, 54.6, 30.8, 19.3, 17.4, 13.2.

(2*S*)-*tert*-Butyl 2-((*S*)-2-*tert*-Butoxycarbonylamino-3-phenylpropionylamino)hex-3-enoate (2d). The title compound was prepared according to the general procedure using *tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate (**1c**) and Boc-L-Phe-NH_2 (silica gel, 6:1 → 1:1 petroleum ether/EtOAc): colorless foam (51 mg, 59%); $[\alpha]_D^{21}$ −5.3° (*c* 2.25, $CHCl_3$); IR 3289br, 2978, 2933, 1733, 1716, 1688s, 1423, 1497, 1455 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.29−7.25 (m, 2 H), 7.23−7.18 (m, 3 H), 6.56 (d, *J* 7.4, 1 H), 5.69 (dtd, *J* 15.4, 6.3, 1.4, 1 H), 5.36 (ddt, *J* 15.4, 6.0, 1.5, 1 H), 5.08 (br s, 1 H), 4.84 (app t, *J* 6.4, 1 H), 4.40 (br s, 1 H), 3.07 (d, *J* 6.4, 2 H), 2.06−1.96 (m, 2 H), 1.43 (s, 9 H), 1.39 (s, 9 H), 0.95 (t, *J* 7.5, 3 H); the following distinct signals for the *Z* isomer were observed, 6.42 (d, *J* 7.2, 1 H), 5.62 (dt, *J* 10.1, 7.5, 1 H), 2.26−2.18 (m, 2 H), 1.03 (t, *J* 7.3, 3 H) and the *E*:*Z* ratio was determined to be 7:1 by integration of the signals at 5.69 and 5.62, respectively; δ_C (100 MHz, $CDCl_3$) 170.4, 169.6, 155.3, 136.5, 135.7, 129.4, 128.5, 126.9, 123.1, 82.2, 80.0, 55.6, 54.5, 38.3, 28.2, 27.9, 25.1, 13.1; *m*/*z* (ES+) 455 (100%, $[MNa]^+$), 433 (20%, $[MH]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{24}H_{37}N_2O_5$ $[MH]^+$ 433.2702, found 433.2704. The diastereomeric mixture was prepared by the same method from racemic **1c**. Spectroscopic data agreed with the material prepared above. The following additional NMR signals were observed

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for the other diastereomer: δ_H (400 MHz, $CDCl_3$) 6.43 (d, *J* 7.7, 1 H), 5.63−5.53 (br m, 1 H), 5.27 (dd, *J* 15.5, 6.0, 1 H), 4.86 (app t, *J* 6.4, 1 H), 1.43 (s, 9 H), 1.40 (s, 9 H), 0.94 (t, *J* 7.5, 3 H); δ_C (100 MHz, $CDCl_3$) 170.3, 169.8, 136.6, 135.8, 129.3, 128.6, 122.9, 82.2, 54.3, 38.6, 25.1, 13.1. The diastereomeric ratio of the material derived from the enantiomerically enriched allylic selenide was determined to be 97.5:2.5 by integration of the ^{1}H NMR signals at 5.36 (major) and 5.27 (minor) ppm.

(*S*)-*tert*-Butyl 2-((*S*)-2-*tert*-Butoxycarbonylamino-2-phenylethylamino)hex-3-enoate (2e). The title compound was prepared according to the general procedure using *tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate (**1c**) and Boc-L-Phg-NH_2 (silica gel, 10:1 → 3:1 petroleum ether/EtOAc): yellow oil (57.4 mg, 69%); $[\alpha]_D^{21}$ +53° (*c* 1.69, $CHCl_3$); IR 3308, 2975, 2934, 1717, 1656, 1512, 1496, 1456, 1392, 1366 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.41−4.27 (m, 5 H), 6.42 (d, *J* 7.6, 1 H), 5.95−5.55 (br s, 1 H), 5.77 (dtd, *J* 15.3, 6.1, 1.3, 1 H), 5.40 (ddt, *J* 15.3, 6.1, 1.6, 1 H), 5.20 (br s, 1 H), 4.88−4.84 (m, 1 H), 2.08−2.01 (m, 2 H), 1.41 (br s, 9 H), 1.37 (s, 9 H), 0.97 (t, *J*, 7.4, 3 H); the following distinct signals for the *Z* isomer were observed, 5.59 (dtd, *J* 10.5, 7.5, 1.0, 1 H), 5.03−4.97 (m, 1 H), 2.19−2.12 (m, 2 H) and the *E*:*Z* ratio was determined to be 7.5:1 by integration of the signals at 5.40 and 5.59 or 5.94−5.90, respectively; δ_C (100 MHz, $CDCl_3$) 169.3, 169.2, 155.1, 138.0, 136.2, 128.9, 128.3, 127.2, 123.0, 82.3, 80.0, 58.5, 54.9, 28.2, 27.8, 25.2, 13.1; *m*/*z* (ES+) 441 ($[MNa]^+$, 100%), 419 ($[MH]^+$, 25%); HRMS (ES+/TOF) *m*/*z* calculated for $C_{23}H_{35}N_2O_5$ $[MH]^+$ 419.2546, found 419.2533. The diastereomeric mixture was prepared by the same method from racemic **1c**. Spectroscopic data agreed with the material prepared above. The following additional NMR signals were observed for the other diastereomer: δ_H (400 MHz, $CDCl_3$) 6.32 (d, *J* 7.9, 1 H), 5.35−5.33 (m, 1 H), 4.94−4.91 (m, 1 H), 1.96−1.89 (m, 2 H), 1.45 (s, 9 H), 0.86 (t, *J* 7.5, 3 H); δ_C (100 MHz, $CDCl_3$) 169.7, 169.1, 135.2, 130.0, 127.3, 122.7, 82.5, 54.2, 27.9, 25.1. The diastereomeric ratio of the material derived from the enantiomerically enriched allylic selenide was determined to be 88.5:11.5 by integration of the ^{1}H NMR signals at 4.92 (minor) and 4.85 (major) ppm.

(*S*)-*tert*-Butyl 2-((*S*)-2-*tert*-Butoxycarbonylamino-2-hydroxypropionylamino)hex-3-enoate (2f). The title compound was prepared according to the general procedure using *tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate (**1c**) and Boc-L-Ser-NH_2 (silica gel, 3:1 → 1:2 petroleum ether/EtOAc): light yellow foam (31 mg, 42%); $[\alpha]_D^{21}$ −13.5° (*c* 0.74 $CHCl_3$); IR 3311, 2977, 2936, 1720, 1659, 1507, 1457 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.08 (br d, *J* 6.3, 1 H), 5.78 (dtd, *J* 15.5, 6.4, 1.5, 1 H), 5.57 (d, *J* 6.7, 1 H), 5.45 (ddt, *J* 15.5, 6.0, 1.6, 1 H), 4.92−4.87 (m, 1 H), 4.22 (br s, 1 H), 4.04 (d, *J* 10.7, 1 H), 3.68−3.62 (m, 1 H), 3.36 (br s, 1 H), 2.09−2.01 (m, 2 H), 1.45 (s, 9 H), 1.44 (s, 9 H), 0.97 (t, *J* 7.4, 3 H), the following distinct signals for the *Z* isomer were observed, 5.68 (dt, *J* 10.1, 7.5, 1 H), 5.21 (ddt, *J* 10.1, 9.1, 1.6, 1 H), 5.15−5.10 (m, 1 H), 2.26−2.19 (m, 2H), 1.02 (d, *J* 7.5, 3 H) and the *E*:*Z* ratio was determined to be 8.5:1 by integration of the signals at 2.09−2.01 and 2.26−2.19, respectively; δ_C (100 MHz, $CDCl_3$) 170.9, 170.0, 156.0, 136.1, 122.7, 82.5, 80.3, 63.0, 54.8, 54.7, 28.3, 27.8, 25.2, 13.1; *m*/*z* (ES+) 395 (100%, $[MNa]^+$), 373 (10%, $[MH]^+$); HRMS (ES+/TOF) *m*/z calculated for $C_{18}H_{33}N_2O_6$ $[MH]^+$ 373.2339, found 373.2346. The diastereomeric mixture was prepared by the same method from racemic **1c**. Spectroscopic data agreed with the material prepared above. The following additional NMR signals were observed for the other diastereomer: δ_H (400 MHz, $CDCl_3$) 4.09 (d, *J* 11.0, 1 H) 3.20 (br s, 1 H), 1.45 (s, 9 H), 1.45 (s, 9 H), 0.97 (t, *J* 7.4, 3 H); δ_C (100 MHz, $CDCl_3$) 136.2, 63.0, 25.2, 13.1.

(*S*)-*tert*-Butyl 2-((*S*)-2-*tert*-Butoxycarbonylamino-3-(4-hydroxyphenyl)propionylamido)hex-3-enoate (2g). The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate (**1c**) and Boc-L-Tyr-NH_2 (silica gel, 4:1 → 2:3 petroleum ether/EtOAc): pale orange oil (28.6 mg, 32%); $[\alpha]_D^{20}$ +29.04° (*c* = 0.619, $CHCl_3$); IR 3312, 2979, 1656, 1517, 1368, 1251 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.01 (t, *J* 7.5, 2 H), 6.76−6.66 (m, 2H), 6.60 (d, *J* 7.6, 1H), 6.53−6.37 (br s, 1H), 5.71 (dtd, *J* 15.5, 6.1, 1.3, 1H), 5.36 (ddt, *J* 15.5, 6.1, 1.6, 1H), 5.16−4.99 (m, 1H) 4.90−4.79 (m, 1H), 4.48−4.20 (m, 1H), 2.98 (m, 2H), 2.06−1.98 (m, 2 H), 1.43 (s, 9 H), 1.41 (s, 9 H), 0.95 (t, *J* 7.4, 3 H), the following distinct signals for the *Z* isomer were observed, 6.89 (d, *J* 7.6, 2H), 6.68 (d, *J* 7.6, 2H), 5.66−5.61 (m, 2H), 2.25−2.18 (m, 2H), 1.01 (t, *J* 7.4, 3H) and the *E*:*Z* ratio was determined to be 7:1 by integration of the signals at 0.95 and 1.01, respectively; δ_C (100 MHz, $CDCl_3$) 170.7, 169.7, 155.4, 155.1, 136.0, 130.5, 127.8, 123.0, 115.5, 82.4, 60.4, 54.6, 37.5, 28.2, 27.9, 25.2, 14.7, 13.1; *m*/*z* (ES+) 512 (23%, $[MNaMeCN]^+$) 471(100%, $[MNa]^+$), 449 (21%, $[MH]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{24}H_{36}N_2O_6Na$ $[MNa]^+$ 471.2471, found 471.2457. The diastereomeric mixture was prepared by the same method using racemic **1c**. Spectroscopic data agreed with the material above. The following additional signals were observed for the other diastereomer: δ_H (400 MHz, $CDCl_3$) 1.45 (s, 9 H), 1.42 (s, 9 H); δ_C (100 MHz, $CDCl_3$) 170.8, 115.6, 82.7, 54.7, 13.3.

(*S*)-*tert*-Butyl 2-((*S*)-2-(Benzyloxy)carbonylamino-3-(1*H*-indol-3-yl)propionylamino)hex-3-enoate (2h). The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate (**1c**) and Cbz-L-Trp-NH_2 (silica gel, 4:1 → 1:1.5 petroleum ether/EtOAc): pale yellow oil (48.4 mg, 48%); $[\alpha]_D^{20}$ + 11.9° (*c* = 1.844, $CHCl_3$); IR 3408, 3319, 2976, 1710, 1659, 1510, 1249, 1230 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.19 (br s, 1 H), 7.68 (d, *J* 7.7, 1 H), 7.38−7.28 (m, 6 H), 7.19 (t, *J* 7.7, 1 H), 7.10 (t, *J* 7.7, 1 H) and 7.06 (m, 1 H), 6.40 (d, *J* 6.9, 1 H), 5.65−5.49 (m, 2 H), 5.29 (apparent dd, *J* 15.6 and 6.0, 1 H), 5.11 (s, 2 H), 4.80 (t, *J* 6.7, 1 H), 4.62−4.50 (m, 1 H), 3.42−3.21 (dd, *J* 14.6 and 7.2, 1 H), 1.97 (p, *J* 7.2, 2 H), 1.42 (s, 9 H), 0.92 (t, *J* 7.4, 3 H), the following distinct signals for the *Z* isomer were observed, 4.89 (t, *J* 6.9, 1 H), 2.20 (p, *J* 7.3, 2 H), 1.01 (t, *J* 7.4, 3 H) and the *E*:*Z* ratio was determined to be 7.5:1 by integration of the signals at 0.92 and 1.01, respectively; δ_C (100 MHz, $CDCl_3$) 170.5, 169.5, 155.9, 136.2, 135.9, 128.5, 128.1, 128.0, 127.4, 123.4, 122.9, 122.2, 119.7, 118.8, 111.2, 82.1, 69.9, 60.3, 55.4, 54.7, 27.9, 25.1, 13.3, 14.2, 13.0; *m*/*z* (ES+) 512 (23%, $[MNaMeCN]^+$) 528 (100%, $[MNa]^+$), 506 (56%, $[MH]^+$), 450 (35%, $[M - CH_3CH_2CH{=}CH_2]^+$), 406 (12%, $[M - CO_2{}^tBu]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{29}H_{35}N_3O_5Na$ $[MNa]^+$ 528.2474, found 528.2480. The diastereomeric mixture was prepared by the same method using racemic **1c**. Spectroscopic data agreed with the material above. The following additional signals were observed for the other diastereomer: δ_H (400 MHz, $CDCl_3$) 5.19 (ddt, *J* 15.4, 6.1 and 1.5, 1 H) 1.40 (s, 9 H); δ_C (100 MHz, $CDCl_3$) 170.5, 169.8, 136.4, 122.9, 122.5, 54.7.

(*S*)-*tert*-Butyl 2-((*S*)-6-Azido-2-(9*H*-fluoren-9-ylmethoxy)-carbonylaminohexanylamino)hex-3-enoate (2i). The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate (**1c**) and Fmoc-L-Lys(N_3)-NH_2 (silica gel, 4:1 → 2:1 petroleum ether/EtOAc): pale yellow oil (37.1 mg, 66%); $[\alpha]_D^{20}$ +2.67° (*c* = 2.24, $CHCl_3$); IR 3304, 2968, 2095, 1729, 1655, 1530, 1247, 1151 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.76 (d, *J* 7.5, 2 H), 7.59 (d, *J* 7.4, 2 H), 7.44−7.35 (m, 2 H), 7.35−7.26 (m, 2 H), 6.58 (d, *J* 7.7, 1 H), 5.83−5.71 (m, 1 H), 5.55−5.36 (m, 2 H), 4.90 (t, *J* 7.1, 1 H), 4.48−4.31 (m, 2 H), 4.28−4.18 (m, 2 H), 3.27 (t, *J* 6.7, 2 H), 2.11−1.97 (m, 2 H), 1.96−1.82 (m, 1 H), 1.75−1.53 (m, 3 H), 1.44 (m, 11 H), 0.95 (t, *J* 7.4, 3 H), the following distinct signals for the *Z* isomer were observed, 6.70 (m, 2H), 5.71−5.64 (m, 2 H), 2.26 (m, 2 H), 1.03 (t, *J* 7.4, 3 H) and the *E*:*Z* ratio was determined to be 4:1 by integration of the signals at 5.83−5.71 and 5.71−5.64, respectively; δ_C (100 MHz, $CDCl_3$) 170.7, 169.8, 156.1, 143.8, 143.7, 141.2, 136.3, 127.7, 127.0, 125.0, 122.8, 119.9, 82.4, 67.1, 54.6, 51.1, 47.1, 32.5, 28.4, 27.9, 25.2, 22.5, 13.1; *m*/*z* (ES+) 584 (100%, $[MNa]^+$), 562 (90%, $[MH]^+$), 506 (53%, $[M - CH_3CH_2CH{=}CH_2]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{31}H_{39}N_5O_5Na$ $[MNa]^+$ 584.2849, found 584.2858. The diastereomeric mixture was prepared by the same method using racemic **1c**. Spectroscopic data agreed with the material above. The following additional signals were observed for the other diastereomer; δ_C (100 MHz, $CDCl_3$) 170.0, 136.4, 82.7, 54.6, 32.5, 13.3.

(*S*)-*tert*-Butyl 2-(2-*tert*-Butoxycarbonylamino-2-methylpropionylamino)hex-3-enoate (2j). The title compound was prepared according to the general procedure using *tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate (**1c**; 0.21 mmol) and BocNCH-

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$(Me)_2CONH_2$ (0.14 mmol) (silica gel, 3:1 → 1:2 petroleum ether/EtOAc): colorless needles (29 mg, 39%); mp 99−101.5 °C (Et_2O/*n*-hexane); $[\alpha]_D^{21}$ +17° (*c* 0.60 $CHCl_3$); IR 3333, 3302, 2981, 2968, 2932, 1742, 1719, 1688, 1654, 1519 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.92 (s br, 1 H), 5.79 (dtd, *J* 15.4, 6.3, 1.6, 1 H), 5.44 (ddt, *J* 15.4, 5.7, 1.6, 1 H), 4.96 (s br, 1 H), 4.91−4.87 (m, 1 H), 2.08−2.00 (m, 2 H), 1.51 (s, 3 H), 1.49 (s, 3 H), 1.45 (s, 9 H), 1.43 (s, 9 H), 0.96 (t, *J* 7.4, 3 H), the following distinct signals for the *Z* isomer were observed, 5.65 (dt, *J* 9.1, 7.4, 1 H), 2.30−2.23 (m, 2 H), 1.02 (t, *J* 7.5, 3 H) and the *E*:*Z* ratio was determined to be >20:1 by integration of the signals at 5.79 and 5.65, respectively; δ_C (100 MHz, $CDCl_3$) 173.9, 170.2, 154.5, 135.3, 123.5, 82.0, 80.0, 56.7, 54.4, 28.2, 27.9, 25.9, 25.3, 25.2, 13.2; *m*/*z* (ES+) 371 (15%, $[MH]^+$), 393 (100%, $[MNa]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{19}H_{35}N_2O_5$ $[MH]^+$ 371.2546, found 371.2546.

(*S*)-*tert*-Butyl 2-[(*S*)-2-((*S*)-2-*tert*-Butoxycarbonylaminopropionylamino)-4-methylpentanoylamino]hex-3-enoate (2k). The title compound was prepared according to the general procedure using *tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate (**1c**) and Boc-L-Leu-L-Ala-NH_2 (silica gel, 10:1 → 2:1 petroleum ether/EtOAc): white amorphous solid (60 mg, 64%); $[\alpha]_D^{21}$ −26° (*c* 1.78, $CHCl_3$); IR 3380, 3274, 1964, 2934, 1732, 1709, 1638s, 1516, 1454 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.08 (d, *J* 6.9, 1 H), 6.87 (d, *J* 6.9, 1 H), 5.73 (dtd, *J* 15.3, 6.3, 1.3, 1 H), 5.41 (ddt, *J* 15.5, 6.1, 1.5, 1 H), 5.17 (d, *J* 8.5, 1 H), 4.90−4.83 (m, 1 H), 4.64−4.55 (m, 1 H), 4.13 (br s, 1 H), 2.07−1.98 (m, 2 H), 1.70−1.52 (m, 3 H), 1.43 (s, 9 H), 1.41 (s, 9 H), 1.36 (d, *J* 7.0, 3 H), 0.95 (t, *J* 7.5, 3 H), 0.89 (d, *J* 6.6, 6 H,), the following distinct signals for the *Z* isomer were observed, 5.64 (dt, *J* 10.0, 7.4, 1 H), 2.26−2.18 (m, 2 H), 1.00 (t, *J* 7.5, 3 H) and the *E*:*Z* ratio was determined to be 7.5:1 by integration of the signals at 5.73 and 5.64, respectively; δ_C (100 MHz, $CDCl_3$) 172.5, 171.4, 169.8, 155.7, 135.8, 123.1, 82.1, 79.9, 54.6, 52.9, 48.7, 41.5, 28.3, 27.9, 25.2, 24.6, 23.0, 21.8, 18.3, 13.1; *m*/*z* (ES+) 492 (100%, $[MNa]^+$), 470 (15%, $[MH]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{24}H_{44}N_3O_6$ $[MH]^+$ 470.3230, found 470.3225. The diastereomeric mixture was prepared by the same method from racemic **1c**. Spectroscopic data agreed with the material prepared above. The following additional ^{13}C NMR signals were observed for the other diastereomer: δ_C (100 MHz, $CDCl_3$) 172.6, 171.3, 169.8, 135.7, 123.1, 82.1, 79.8, 54.5, 53.0, 25.2, 24.7, 13.2.

(*S*)-*tert*-Butyl 2-{(*S*)-2-[(*S*)-2-((*S*)-2-*tert*-Butoxycarbonylamino-4-methylpentanoylamino)propionylamino]-3-methylbutyrylamino}hex-3-enoate (2l). The title compound was prepared according to the general procedure using *tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate (**1c**; 0.1 mmol) and Boc-L-Leu-L-Ala-L-Val-NH_2 (0.067 mmol) (silica gel, 5:1 → 2:3 petroleum ether/EtOAc): white amorphous solid (15 mg, 39%); $[\alpha]_D^{21}$ +5.3° (*c* 0.75, $CHCl_3$); IR 3289, 2963, 2933, 2874, 1719, 1636, 1509, 1452 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.95 (d, *J* 8.8, 1 H), 6.90 (d, *J* 7.9, 1 H), 6.80 (d, *J* 6.8, 1 H), 5.76 (dtd, *J* 15.5, 6.3, 1.6, 1 H), 5.41 (ddt, *J* 15.5, 5.9, 1.7, 1 H), 5.42−5.34 (br s, 1 H), 4.93 (t, *J* 6.4, 1 H), 4.63−4.55 (m, 1 H), 4.32−4.27 (m, 1 H), 4.21−4.17 (m, 1 H), 2.92 (m, 1 H), 2.07 (m, 2 H), 1.78−1.70 (m, 1 H), 1.66−1.60 (m, 1 H), 1.46 (s, 9 H), 1.44 (s, 9 H), 1.38 (d, *J* 6.9, 3 H), 0.99−0.88 (m, 15 H); the following distinct signals for the *Z* isomer were observed, 6.80−6.75 (m, 2 H), 5.65 (dt, *J* 10.0, 7.5, 1 H), 5.25 (d, *J* 7.9, 1 H), 5.20−5.11 (m, 2 H), 4.53−4.49 (m, 1 H), 1.39 (d, *J* 6.9, 3 H), 1.02 (t, *J* 7.6, 3H) and the *E*:*Z* ratio was determined to be 4:1 by integration of the signals at 5.76 and 5.65, respectively; δ_C (100 MHz, $CDCl_3$) 173.3, 172.1, 170.7, 170.4, 156.0, 135.9, 123.0, 82.7, 80.2, 58.9, 54.2, 53.0, 48.5, 40.8, 30.3, 28.3, 28.0, 25.2, 24.7, 23.0, 21.6, 19.3, 17.7, 16.9, 13.1, the following distinct signals for the *Z* isomer were observed, 137.8, 123.1, 82.3, 58.1, 51.2, 48.9, 30.0, 27.9, 21.3, 17.5, 13.9; *m*/*z* (ES+) 591 (100%, $[MNa]^+$), 569 (15%, $[MH]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{29}H_{53}N_4O_7$ $[MH]^+$ 569.3914, found 569.3924. The diastereomeric mixture was prepared by the same method from racemic **1c**. Spectroscopic data agreed with the material prepared above. The following additional ^{13}C NMR signals were observed for the other diastereomer: δ_C (100 MHz, $CDCl_3$) 173.1, 172.4, 170.3, 170.0, 155.9, 136.3, 123.1, 82.5, 58.2, 54.6, 48.8, 40.9, 30.0, 25.2, 23.1, 19.4, 17.5, 13.2.

General Procedure for Amination/Rearrangement using Amino Acid Esters (Table 3). To a stirred solution of allylic selenide **1** (0.3 mmol) in dry methanol (1 mL) was added trimethyl orthoformate (129 μL, 1.18 mmol) and *p*-toluenesulfonic acid (1 mg). After 0.5 h, the reaction mixture was cooled to 0 °C, diisopropylethylamine (209 μL, 1.20 mmol) was added, and the mixture was stirred for 10 min. *N*-Chlorosuccinimide (80 mg, 0.60 mmol) was then added, and after a further 2 min the amino acid ester (0.20 mmol) was added. The reaction mixturte was held at 0 °C for 1 h, and then 1 M HCl(aq) (1 mL) was added, followed by saturated sodium bicarbonate solution (1 mL). The reaction mixture was then extracted three times into ethyl acetate, and the combined organic layers were washed twice with brine, dried (Na_2SO_4), concentrated under reduced pressure, and purified by column chromatography.

(*S*)-*tert*-Butyl 2-((*S*)-1-Benzyloxycarbonylethylamino)hex-3-enoate (6a). The title compound was prepared according to the general procedure using *tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate (**1c**) and *N*-Ala-CO_2Bn (silica gel, 7:1 → 5:1 petroleum ether/EtOAc): light yellow oil (50 mg, 72%); $[\alpha]_D^{21}$ +3.1° (*c* 2.58, $CHCl_3$); IR 2975, 2934, 1730, 1498, 1456, cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.38−7.3 (5 H, m), 5.74 (dtd, *J* 15.4, 6.3, 1.0, 1 H), 5.35 (ddt, *J* 15.4, 7.7, 1.6, 1 H) 5.18 (d, *J* 12.4, 1 H), 5.11 (d, *J* 12.4, 1 H), 3.72−3.70 (m, 1 H), 3.40 (q, *J* 7.0, 1 H), 2.06−1.98 (m, 2 H), 1.44 (s, 9 H), 1.32 (d, *J* 7.0, 3 H), 0.96 (t, *J* 7.4, 3 H); the following distinct signals for the *Z* isomer were observed, 5.63 (dtd, *J* 10.8, 7.4, 0.9, 1 H), 0.92 (d, *J* 7.5, 3 H) and the *E*:*Z* ratio was determined to be 8:1 by integration of the signals at 5.74 and 5.63 ppm, respectively; δ_C (100 MHz, $CDCl_3$) 175.0, 171.1, 136.7, 135.8, 128.5, 128.2, 128.1, 125.6, 81.3, 66.5, 62.8, 64.4, 28.0, 25.3, 19.1, 13.2; *m*/*z* (ES+) 370 (20%, $[MNa]^+$), 348 (100%, $[MH]^+$), 292 (40%, $[MH - CH_3CH_2CH{=}CH_2]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{20}H_{30}NO_4$ $[MH]^+$ 348.2175, found 348.2167. The diastereomeric mixture was prepared by the same method from racemic **1c**. The mixture was separable by careful column chromatography. Data for diastereomer: light yellow oil; IR 2977, 2934, 1729, 1499, 1456, 1393, 1369 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.39−7.30 (m, 5 H), 5.67 (dtd, *J* 15.4, 6.4, 1.0, 1 H), 5.32 (ddt, *J* 15.3, 7.7, 1.5, 1 H), 5.18−5.12 (m, 2 H), 3.70−3.68 (m, 1 H), 3.43 (q, *J* 7.0, 1 H), 2.04 (m, 2 H), 1.43 (s, 9 H), 1.33 (d, *J* 7.0, 3 H), 0.97 (t, *J* 7.4, 3 H); δ_C (100 MHz, $CDCl_3$) 174.9, 171.7, 137.1, 135.8, 128.5, 128.2, 128.1, 125.3, 81.4, 62.4, 62.0, 53.6, 28.0, 25.3, 19.0, 13.4; *m*/*z* (ES+) 370 (20%, $[MNa]^+$), 348 (100%, $[MH]^+$), 292 (40%, $[MH - CH_2{=}CMe_2]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{20}H_{30}NO_4$ $[MH]^+$ 348.2175, found 348.2176.

(*S*)-*tert*-Butyl 2-((*S*)-1-Benzyloxycarbonylethylamino)hex-3-enoate (6b). The title compound was prepared according to the general procedure using *tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate (**1c**) and *N*-Phg-CO_2Me (silica gel, 15:1 → 5:1 petroleum ether/EtOAc): light yellow oil (40 mg, 60%); $[\alpha]_D^{21}$ +107° (*c* 2.13, $CHCl_3$); IR 2970, 1730s, 1456, 1435, 1393, 1368 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.37−7.28 (m, 5 H), 5.66 (dtd, *J* 15.4, 6.3, 0.9, 1 H), 5.34 (ddt, *J* 15.4, 8.0, 1.6, 1 H), 4.40 (s, 1 H), 3.66 (s, 3 H), 3.56 (d, *J* 8.0, 1 H), 2.66 (br s, 1 H), 2.21−1.94 (m, 2 H), 1.41 (s, 9 H), 0.99 (t, *J* 7.5, 3 H); δ_C (100 MHz, $CDCl_3$) 172.9, 171.7, 137.7, 137.4, 128.7, 128.1, 127.8, 125.3, 81.3, 62.6, 61.7, 52.2, 27.9, 25.3, 13.3; *m*/*z* (ES+) 334 (100%, $[MH]^+$), 278 (40%, $[CH_3CH_2CH{=}CH_2]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{19}H_{28}NO_4$ $[MH]^+$ 334.2018, found 334.2013. The diastereomeric mixture was prepared by the same method from racemic **1c**. The mixture was separable by column chromatography. Data for diastereomer: light yellow oil; δ_H (400 MHz, $CDCl_3$) 7.39−7.30 (m, 5 H), 5.67 (dtd, *J* 15.5, 6.4, 1.2, 1 H), 5.39 (ddt, *J* 15.4, 7.1, 1.6, 1 H), 4.43 (s, 1 H), 3.68 (s, 3 H), 3.58 (d, *J* 7.1, 1 H), 2.72 (br s, 1 H), 2.09−2.01 (m, 2 H), 1.5 (s, 9 H), 0.98 (t, *J* 7.4, 3 H); δ_C (100 MHz, $CDCl_3$) 172.9, 172.0, 137.8, 136.3, 128.6, 128.1, 127.9, 125.4, 81.4, 62.8, 61.2, 52.3, 28.0, 25.4, 13.3. The diastereomeric ratio of the material derived from the enantiomerically enriched allylic selenide was determined to be 96:4 by integration of the ^1H NMR signals at 5.75 (minor) and 5.67 (major) ppm.

(*S*)-*tert*-Butyl ((2*S*)-1-(Benzyloxy)-3-hydroxy-1-oxopropan-2-ylamino)hex-3-enoate (6c). The title compound was prepared according to the general procedure from *tert*-butyl 4-phenylselenylhex-

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2-(*E*)-enoate (**1c**) and *N*-Ser-CO_2Bn, with cooling to −40 °C prior to the diisopropylethylamine addition. The reaction mixture was then held at −40 °C and stirred for 12 h after NCS addition (silica gel, 9:1 → 1:1 petroleum ether/EtOAc): pale yellow oil (39.5 mg, 54%); $[\alpha]_D^{18}$ +25.3° (*c* = 0.71, CH_2Cl_2); IR 3034, 2968, 2934, 2873, 1729, 1456, 1368, 1259, 1152, 1060 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.37−7.32 (m, 5 H), 5.78 (dtd, *J* 15.6, 6.3, 0.8, 1 H), 5.36 (ddt, *J* 15.5, 8.1, 1.7, 1 H), 5.18 (d, *J* 1.9, 2 H), 3.79−3.70 (m, 2 H), 3.64 (dd, *J* 10.9, 6.2, 1 H), 3.43 (dd, *J* 6.2, 4.1, 1 H), 2.21 (app br s, OH and NH, 2 H), 2.02 (ddd, *J* 7.6, 6.3, 1.6, 2 H), 1.45 (s, 9 H), 0.96 (t, *J* 7.4, 3 H); δ_C (100 MHz, $CDCl_3$) 172.5, 171.9, 137.7, 135.3, 128.6, 128.4, 128.1, 125.1, 81.7, 67.0, 63.1, 62.5, 60.5, 27.9, 25.3, 13.2; *m*/*z* (ES+) 386 (51%, $[MNa]^+$), 364 (100%, $[MH]^+$), 308 (33%, [MH − CH═$CHCH_2CH_3$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{20}H_{30}NO_5$ $[MH]^+$ 364.2124, found 364.2136. The diastereomeric mixture was prepared by the same method from racemic **1c**. Spectroscopic data agreed with the material above. The following additional signals were observed for the other diastereomer: δ_C (100 MHz, $CDCl_3$) 128.7, 128.6, 128.5, 128.4, 81.8, 67.1, 62.8, 60.2, 28.2, 25.5, 13.5.

(*S*)-Ethyl 2-((2*S*)-1-(Benzyloxy)-1-oxopropan-2-ylamino)-pent-3-enoate (6d). The title compound was prepared according to the general procedure using (*S*)-ethyl 4-phenylselenylbut-2-(*E*)-enoate (**1d**) and *N*-Ala-CO_2Bn (silica gel, 20:1 → 4:1 petroleum ether/EtOAc): pale yellow oil (37.7 mg, 62%); $[\alpha]_D^{21}$ +12.4° (*c* = 1.13, $CHCl_3$); IR 3036, 2981, 2939, 1733, 1456, 1370, 1240, 1154, 1028 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.39−7.31 (m, 5 H), 5.73 (dqd, *J* 15.5, 6.3, 0.89, 1 H). 5.39 (ddq, *J* 15.5, 8.0, 1.6, 1 H), 5.14 (q, *J* 12.3, 2 H), 4.17 (qd, *J* 7.1, 1.8, 2 H), 3.81 (d, *J* 8.0, 1 H), 3.39 (q, *J* 7.0, 1 H), 1.94 (br s, 1 H), 1.66 (dd, *J* 7.0, 3 H), 1.32 (d, *J* 6.9, 3 H), 1.25 (t, *J* 7.1, 3 H), the following distinct signals for the *Z* isomer were observed, 5.26 (ddd, *J* 11.0, 9.3, 1.8, 1 H), 1.59 (3H, dd, *J* 7.0, 1.8, 3 H) and the *E*:*Z* ratio was determined to be 8:1 by integration of the signals at 5.29 and 5.26, respectively; δ_C (100 MHz, $CDCl_3$) 175.0, 172.7, 135.7, 130.7, 128.6, 128.3, 128.1, 127.3, 66.6, 62.4, 61.1, 54.4, 19.1, 17.8, 14.1; *m*/*z* (ES+) 328 (100%, $[MNa]^+$), 306 (95%, $[MH]^+$), 232 (38%, [MH − $CO_2Et]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{17}H_{24}NO_4$ $[MH]^+$ 306.17080, found 306.17052. The diastereomeric mixture was prepared by the same method from racemic **1d**. Spectroscopic data agreed with the material above. The following additional signals were observed for the other diastereomer: δ_C (100 MHz, $CDCl_3$) 174.9, 172.3, 135.9, 131.0, 127.3, 66.8, 61.8, 61.4, 53.7, 19.1.

(*S*)-Ethyl (2*S*,3*E*)-2-{[(2*S*)-1-(Benzyloxy)-1-oxopropan-2-yl]-amino}-2-methylhex-3-enoate (6e). The title compound was prepared according to the general procedure from (*S*)-ethyl-2-methyl-4-(phenylselenyl)hex-2-(*E*)-enoate (0.15 mmol) and *N*-Ala-CO_2Bn (0.1 mmol) (silica gel, 19:1 → 1:1 petroleum ether/EtOAc): colorless oil (15.4 mg, 46%); $[\alpha]_D^{21}$ −8.99° (*c* = 0.89, CH_2Cl_2); IR 3068, 3036, 2979, 2964, 2935, 1731, 1455, 1375, 1292, 1146, 974 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.42−7.31 (m, 5 H), 5.71 (dt, *J* 15.8, 6.3, 1 H), 5.49 (dt, *J* 15.9, 1.6, 1 H), 5.23−5.19 (d, *J* 12.1, 1 H), 5.13 (d, *J* 12.1, 1 H), 4.16 (q, *J* 7.1, 2 H), 3.41 (q, *J* 7.1, 1 H), 2.52 (br s, 1 H), 1.38 (s, 3 H), 1.34 (d, *J* 7.1, 3 H), 1.28 (t, *J* 7.2, 3 H), 0.98 (t, *J* 7.4, 3 H); δ_C (100 MHz, $CDCl_3$) 176.4, 174.8, 135.7, 133.3, 130.8, 128.5, 128.3, 128.2, 66.4, 63.0, 61.1, 52.2, 25.4, 22.8, 21.3, 14.1, 13.3; *m*/*z* (ES+) 334 (100%, $[MH]^+$), 208 (87%); HRMS (ES+/TOF) *m*/*z* calculated for $C_{19}H_{28}NO_4$ $[MH]^+$ 334.2018, found 334.2030. The diastereomeric mixture was prepared by the same method from racemic (*S*)-ethyl-2-methyl-4-(phenylselenyl)hex-2-(*E*)-enoate. Spectroscopic data agreed with the material above. The following additional signals were observed for the other diastereomer: δ_C (100 MHz, $CDCl_3$) 133.6, 130.7, 63.0, 61.2, 52.2, 23.8, 14.2.

(2*S*)-2-(((2*S*)-1-Ethoxy-1-oxopentan-2-yl)amino)propanoic Acid (7). A suspension of (*S*)-ethyl 2-(1-(benzyloxy)-1-oxopropan-2-ylamino)pent-3-enoate (**6d**; 65 mg, 0.21 mmol) and 10% Pd/C (6.5 mg) in dry methanol (0.4 mL) was stirred for 5.5 h under hydrogen. Filtration through Celite and removal of solvent in vacuo afforded the title compound as a white solid (44.1 mg, 97%): mp 158−160 °C; $[\alpha]_D^{18}$ +7.98° (*c* = 1.00, EtOH); IR 2694, 2937, 2735, 1750, 1568, 1397, 1351 cm-1; δ_H (400 MHz, DMSO) 4.08 (q, *J* 7.0, 2 H), 3.26 (t, *J* 6.7, 1 H), 3.15 (q, *J* 6.9, 1 H), 1.57−1.46 (m, 2 H), 1.34−1.24 (m, 2 H), 1.19−1.14 (m, 6 H), 0.85 (t, *J* 7.8, 3 H); δ_C (100 MHz, DMSO) 175.6, 174.2, 60.1, 58.8, 54.5, 34.9, 18.8, 18.5, 14.2, 13.7); *m*/*z* (ES+) 218 (100%, [MH]+), 172 (53%, [MH − $COOH]^+$), 116 (28%, [MH − $CO_2Et]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{10}H_{20}NO_4$ $[MH]^+$ 218.1392, found 218.1398.

General Procedure for the Amination/Rearrangement of Allylic Selenides using Aromatic Amines. To a solution of allylic selenide (0.20 mmol) in dry methanol (1 mL) was added trimethyl orthoformate (129 μL, 1.18 mmol) and *p*-toluenesulfonic acid (1 mg). The solution was stirred for 30 min at room temperature before cooling to −20 °C; diisopropylethylamine (209 μL, 1.20 mmol) and then *N*-chlorosuccinimide (80 mg, 0.60 mmol) were added. The solution was stirred for 2 min, and then the aromatic amine (0.30 mmol) was added. The reaction mixture was stirred at −20 °C for 20 min, and then HCl (1 mL, aqueous, 1 M) was added, followed by saturated $NaHCO_3$ (1 mL). The reaction mixture was extracted three times into ethyl acetate, and the combined organic layers were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash column chromatography.

***tert*-Butyl (2*S*,3*E*)-2-(Phenylamino)hex-3-enoate (8a).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and aniline (silica gel, 80:1 *n*-hexane:Et_2O): clear oil (38.8 mg, 75%); $[\alpha]_D^{21}$ +50.2° (*c* = 1.39, $CHCl_3$); IR 3405, 2970, 2933, 2872, 1730, 1604, 1505, 1369, 1316, 1256, 1152 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.22−7.11 (m, 2H), 6.72 (tt, *J* 7.4 and 1.1, 1H), 6.65−6.57 (m, 2H), 5.91 (dtd, *J* 15.5, 6.4 and 1.3, 1H), 5.51 (ddt, *J* 15.5, 5.7 and 1.6, 1H), 4.46 (br d, *J* 6.4, 1H), 4.41 (br t, *J* 5.9, 1H), 2.14−2.02 (m, 2H), 1.46 (s, 9H), 0.99 (t, *J* 7.4, 3H); δ_C (100 MHz, $CDCl_3$) 171.4, 146.6, 135.9, 129.1, 124.7, 117.9, 113.5, 81.9, 59.1, 28.0, 25.3, 13.4; *m*/*z* (ES+) 262 (100% MH^+), 206 (37%, [MH − $CH_3CH_2CH═CH_2]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{16}H_{24}NO_2^+$ 262.1807, found 262.1801; the enantiomeric ratio could not be determined via HPLC analysis of the title compound; reduction to the primary alcohol allowed the enantiomeric ratio to be determined as 97:3 (see **9a** below).

***tert*-Butyl (2*S*,3*E*)-2-[(4-Methylphenyl)amino]hex-3-enoate (8b).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and *p*-toluidine (silica gel, 50:1 *n*-hexane:Et_2O): off-white solid (33.3 mg, 61%); mp 44−46 °C; $[\alpha]_D^{23}$ +63.2° (*c* = 1.24, $CHCl_3$); IR 3399, 2976, 2969, 2932, 2873, 1728, 1619, 1520, 1368, 1253, 1147 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.98 (d, *J* 8.1, 2H), 6.54 (d, *J* 8.2, 2H), 5.90 (dtd, *J* 15.4, 6.4 and 1.2, 1H), 5.50 (ddt, *J* 15.4, 5.8 and 1.6, 1H), 4.39 (br d, *J* 5.0, 1H), 4.32 (br s, NH, 1H), 2.24 (s, 3H), 2.14−2.01 (m, 2H), 1.46 (s, 9H), 0.99 (t, *J* 7.4, 3H); δ_C (100 MHz, $CDCl_3$) 171.6, 144.3, 135.8, 129.6, 127.0, 124.9, 81.8, 59.4, 28.0, 25.3, 20.4, 13.4; *m*/*z* (ES+) 276 (100%, MH^+), 220 (19%, [MH − $CH_3CH_2CH═CH_2]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{17}H_{26}NO_2^+$ 276.1964, found 276.1969; enantiomeric ratio was determined as 96.5:3.5 by HPLC, Chiralpak IA-3 column, 95:5 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 254 nm 4.9 min (major), 5.7 min (minor).

***tert*-Butyl (2*S*,3*E*)-2-[(2-Methylphenyl)amino]hex-3-enoate (8c).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and *o*-toluidine (silica gel, 50:1 *n*-hexane:Et_2O): pale yellow oil (26.9 mg, 49%); $[\alpha]_D^{23}$ +48.1° (*c* = 1.08, $CHCl_3$); IR 3420, 2967, 2932, 2874, 1728, 1606, 1510, 1368, 1256, 1149 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.12−7.03 (m, 2H), 6.67 (td, *J* 7.4 and 1.0, 1H), 6.49 (dd, *J* 8.5 and 1.0, 1H), 5.91 (dtd, *J* 15.4, 6.3 and 0.9, 1H), 5.54 (ddt, *J* 15.3, 5.4 and 1.5, 1H), 4.48−4.38 (m, 2H), 2.24 (s, 3H), 2.15−206 (m, 2H), 1.47 (s, 9H), 1.00 (t, *J* 7.4, 3H); δ_C (100 MHz, $CDCl_3$) 171.6, 144.7, 135.7, 130.1, 126.9, 124.8, 122.4, 117.3, 110.6, 81.9, 59.0, 28.0, 25.3, 17.5, 13.4; *m*/*z* (ES+) 276 (100%, MH^+), 220 (15%, [MH − $CH_3CH_2CH═CH_2]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{17}H_{26}NO_2^+$ 276.1964, found 276.1964; the enantiomeric ratio could not be determined via HPLC analysis of the title compound; reduction to the primary alcohol allowed the enantiomeric ratio to be determined as 96.5:3.5 (see **9c** below).

***tert*-Butyl (2*S*,3*E*)-2-[(4-Methoxy)amino]hex-3-enoate (8d).** The title compound was prepared according to the general procedure

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using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and *p*-anisidine with 1.1 equiv of NCS (silica gel, 20:1 *n*-hexane:EtOAc): orange oil (31.8 mg, 54%); $[\alpha]_D^{18}$ +41.3° (*c* = 0.93, $CHCl_3$); IR 3384, 2966, 2932, 1728, 1513, 1459, 1369, 1239, 1150 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.76 (d, *J* 8.9, 2H), 6.58 (d, *J* 8.9, 2H), 5.89 (dtd, *J* 15.5, 6.5 and 1.4, 1H), 5.49 (ddt, *J* 15.4, 6.0 and 1.6, 1H), 4.34 (br t, *J* 5.9, 1H), 4.15 (br d, *J* 6.3, 1H), 2.13−2.01 (m, 2H), 1.44 (s, 9H), 0.98 (t, *J* 7.4, 3H); δ_C (100 MHz, $CDCl_3$) 171.9, 152.6, 141.0, 136.1, 125.2, 115.1, 114.9, 81.9, 60.3, 55.9, 28.1, 25.2, 13.5; *m*/*z* (ES+) 292 (100% $[MH]^+$); HRMS (ES+/TOF) calculated for $C_{17}H_{26}NO_3^+$ 292.1913, found 292.1925; enantiomeric ratio was determined as 96.5:3.5 using HPLC, Chiralpak IA-3 column, 90:10 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 254 nm 5.9 min (minor), 7.6 min (major).

***tert*-Butyl (2*S*,3*E*)-2-[(4-Nitrophenyl)amino]hex-3-enoate (8e).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and 4-nitroaniline (silica gel, 19:1 *n*-hexane:EtOAc): yellow oil (52.2 mg, 85%); $[\alpha]_D^{15}$ +119.7° (*c* = 1.38, $CHCl_3$); IR 3377, 2972, 2933, 1726, 1597, 1504, 1475, 1313, 1148, 1110 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.07 (d, *J* 9.2, 2H), 6.53 (d, *J* 9.2, 2H), 5.86 (dtd, *J* 15.6, 6.5 and 1.4, 1H), 5.48 (ddt, *J* 15.5, 5.9 and 1.6, 1H), 5.36 (br s, 1H), 4.47 (dd, *J* 5.9 and 1.4, 1H), 2.15−2.04 (m, 2H), 1.48 (s, 9H), 0.98 (t, *J* 7.4, 3H); δ_C (100 MHz, $CDCl_3$) 170.0, 151.5, 138.5, 137.0, 126.2, 111.9, 83.0, 58.0, 27.9, 25.2, 13.3; *m*/*z* (ES+) 307 (100%, $[MH]^+$), 251 (49%, $[M - CH_3CH_2CH{=}CH]^+$); HRMS (ES+/TOF) calculated for $C_{16}H_{23}N_2O_4^+$ 307.1658, found 307.1665; enantiomeric ratio was determined as 96.5:3.5 using HPLC, Chiralpak IA-3 column, 95:5 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 224 nm 6.3 min (minor), 6.8 min (major).

***tert*-Butyl (2*S*,3*E*)-2-{[3-(Hydroxymethyl)phenyl]amino}-hexenoate (8f).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and 3-aminobenzyl alcohol (silica gel, 4:1 *n*-hexane:EtOAc): pale yellow oil (27.3 mg, 62%); $[\alpha]_D^{23}$ +20.7° (*c* = 0.86, CH_3OH); IR 3391, 2968, 2932, 2874, 1726, 1608, 1488, 1369, 1323, 1256, 1148 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7,14 (t, *J* 7.9, 1H), 6.70 (ddd, *J* 7.6, 1.6 and 0.8, 1H), 6.61 (t, *J* 2.0, 1H), 6.53 (ddd, *J* 8.1, 2.4 and 0.9, 1H), 5.89 (dtd, *J* 15.4, 6.4 and 1.4, 1H), 5.49 (ddt, *J* 15.4, 5.7 and 1.6, 1H), 4.58 (s, 2H), 4.51 (br s, 1H), 4.42 (br s, 1H), 2.14−2.01 (m, 2H), 1.73 (br s, 1H), 1.46 (s, 9H), 0.98 (t, *J* 7.4, 3H); δ_C (100 MHz, $CDCl_3$) 171.4, 146.9, 142.0, 136.0, 129.4, 124.5, 116.3, 112.7, 111.9, 82.0, 65.5, 58.9, 28.0, 25.3, 13.4; *m*/*z* (ES+) 292 (100%, $[MH]^+$), 236 (16%, $[MH - CH_3CH_2CH{=}CH]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{17}H_{26}NO_3^+$ 292.1913, found 292.1920; enantiomeric ratio was determined as 96.5:3.5 using HPLC, Chiralpak IA-3 column, 90:10 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 212 nm 10.6 min (minor), 13.4 min (major).

***tert*-Butyl (2*S*,3*E*)-2-[(1,3-Thiazol-2-yl)amino]hex-3-enoate (8g).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and 2-aminothiazole (silica gel, 8:1 to 4:1 *n*-hexane:EtOAc): colorless oil (39.4 mg, 73%); $[\alpha]_D^{24}$ +93.2° (*c* = 1.11, $CHCl_3$); IR 3326, 3198, 2969, 2933, 1726, 1619, 1523, 1368, 1255, 1148 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.12 (d, *J* 3.6, 1 H), 6.50 (d, *J* 3.6, 1H), 5.91 (dtd, *J* 15.6, 6.4 and 1.4, 1 H), 5.72 (br s, 1 H), 5.48 (ddt, *J* 15.4, 6.1 and 1.6, 1 H), 4.67 (ddd, *J* 7.3, 5.9 and 1.2, 1 H), 2.10 (ddt, *J* 7.6, 6.3 and 1.4, 2 H), 1.47 (s, $C(CH_3)_3$, 9 H), 0.99 (t, *J* 7.4, 3 H); δ_C (100 MHz, $CDCl_3$) 170.1, 168.2, 138.9, 136.7, 123.2, 107.3, 82.4, 60.1, 27.9, 25.3, 13.2; *m*/*z* (ES+) 269 (100%, $[MH]^+$), 214 (61%, $[MH-C(CH_3)_3]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{13}H_{20}N_2O_2S^+$ $[MH]^+$ 269.1324, found 269.1334; enantiomeric ratio was determined as 94.5:5.5 by HPLC, Chiralpak IA-3 column, 98:2 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 254 nm 30.3 min (minor), 70.8 min (major).

***tert*-Butyl (2*S*,3*E*)-2-[(1,3-Benzothiazol-2-yl)amino]hex-3-enoate (8h).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and 2-aminobenzothiazole (silica gel, 14:1 *n*-hexane:EtOAc): orange oil (46.8 mg, 74%); $[\alpha]_D^{23}$ +54.8° (*c* = 0.99, $CHCl_3$); IR 3314, 2973, 2932, 2875, 1725, 1599, 1540, 1456, 1445, 1368, 1153 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.59−7.54 (m, 2 H), 7.31 (ddd, *J* 7.7, 7.4 and 1.3, 1 H), 7.12 (td, *J* 7.6 and 1.2, 1 H), 6.14−5.93 (m includes (br s, 1 H) and (dtd, *J* 15.5, 6.4 and 1.5, 1 H)) 5.56 (ddt, *J* 15.5, 5.9 and 1.6, 1 H), 4.91 (d, *J* 5.9, 1 H), 2.18−2.05 (m, 2 H), 1.51 (s, 9 H), 1.01 (t, *J* 7.4, 3 H); δ_C (100 MHz, $CDCl_3$) 169.9, 165.4, 152.1, 136.7, 130.8, 125.8, 123.1, 121.8, 120.8, 119.2, 82.6, 59.5, 28.0, 25.3, 13.2; *m*/*z* (ES+) 319 (100%, $[MH]^+$), 263 (54%, $[MH - CH_3CH_2CH{=}CH_2]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{17}H_{23}N_2O_2S^+$ $[MH]^+$ 319.1480, found 319.1495; enantiomeric ratio was determined as 97:3 by HPLC, Chiralpak IA-3 column, 99:1 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 254 nm 21.1 min (minor), 34.7 min (major).

***tert*-Butyl (2*S*,3*E*)-2-[(4-Methoxy-1,3-benzothiazol-2-yl)-amino]hex-3-enoate (8i).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and 2-aminobenzothiazole (silica gel, 9:1 *n*-hexane:EtOAc): pale yellow oil/foam (57.1 mg, 82%); $[\alpha]_D^{17}$ +37.7° (*c* = 1.06, $CHCl_3$); IR 3396, 2971, 2937, 2906, 1729, 1589, 1546, 1479, 1369, 1327, 1254, 1154, 1048 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.19 (dd, *J* 7.9 and 1.0, 1 H), 7.03 (t, *J* 8.0, 1 H), 6.79 (dd, *J* 8.0 and 1.0, 1 H), 6.13 (br s, 1 H), 5.94 (dtd, *J* 15.4, 6.4 and 1.5, 1 H), 5.49 (ddt, *J* 15.5, 6.0 and 1.6, 1 H), 4.75 (br s, 1 H), 3.20 (s, 3 H), 2.10−2.03 (m, 2 H), 1.47 (s, 9 H), 0.97 (t, *J* 7.4, 3 H); δ_C (100 MHz, $CDCl_3$) 169.5, 164.9, 150.7, 141.5, 136.8, 131.8, 123.1, 122.2, 113.1, 107.2, 82.6, 59.9, 55.8, 27.9, 25.2, 13.1; *m*/*z* (ES+) 349 (100%, $[MH]^+$), 293 (47%, $[MH - CH_3CH_2CH{=}CH_2]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{18}H_{25}N_2O_3S^+$ 349.1586, found 349.1592; enantiomeric ratio was determined as 96.5:3.5 by HPLC, Chiralpak IA-3 column, 90:10 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 236 nm 7.8 min (minor), 10.3 min (major).

***tert*-Butyl (2*S*,3*E*)-2-[(pyridin-2-yl)amino]hex-3-enoate (8j).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and 2-aminopyridine (silica gel, 19:1 *n*-hexane:EtOAc): pale yellow oil (38.4 mg, 73%); $[\alpha]_D^{21}$ +23.6° (*c* = 1.27, $CHCl_3$); IR 3363, 2967, 2933, 2874, 1724, 1600, 1482, 1368, 1328, 1254, 1146, 967 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.07 (ddd, *J* 5.2, 2.0 and 0.9, 1 H), 7.38 (ddd, *J* 8.2, 7.2 and 1.9, 1 H), 6.57 (ddd, *J* 7.2, 5.1 and 1.0, 1 H), 6.40 (dt, *J* 8.4 and 1.0, 1 H), 5.87 (dtd, *J* 15.6, 6.4 and 1.5, 1 H), 5.55 (1 H, ddt, *J* 15.5, 6.4 and 1.5, 1 H), 5.07 (br d, *J* 7.5, 1 H), 4.85 (ddd, *J* 7.5, 5.8 and 1.4, 1 H), 2.12−2.00 (m, 2 H), 1.45 (s, 9 H), 0.97 (t, *J* 7.4, 3 H); δ_C (100 MHz, $CDCl_3$) 171.3, 157.4, 147.9, 137.2, 135.5, 124.3, 113.4, 108.1, 81.7, 56.9, 28.0, 25.3, 13.3; *m*/*z* (ES+) 263 (19%, $[MH]^+$), 207 (100%, $[MH - CH_3CH_2CH{=}CH_2]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{15}H_{23}N_2O_2^+$ 263.1760, found 263.1765; enantiomeric ratio was determined 94.5:5.5 by HPLC, Chiralpak IA-3 column, 96:4 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 268 nm 10.9 min (minor), 22.1 min (major).

***tert*-Butyl (2*S*,3*E*)-2-[(6-Bromopyridin-2-yl)amino]hex-3-enoate (8k).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and 2-amino-6-bromopyridine (silica gel, 20:1 *n*-hexane:EtOAc): pale yellow oil (52.0 mg, 76%); $[\alpha]_D^{19}$ +23.6° (*c* = 1.19, $CHCl_3$); IR 3353, 2971, 2934, 2876, 1722, 1594, 1557, 1491, 1150 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.20 (t, *J* 7.8, 1 H), 6.73 (d, *J* 7.5, 1 H), 6.28 (d, *J* 8.1, 1 H), 5.86 (dtd, *J* 15.4, 6.4 and 1.5, 1 H), 5.48 (ddt, *J* 15.4, 6.1 and 1.61, 1 H), 5.26 (br d, *J* 7.4, 1 H), 4.74 (ddd, *J* 7.3, 6.1 and 1.2, 1 H), 2.12−2.09 (m, 2 H), 1.46 (s, 9 H), 0.97 (t, *J* 7.5, 3 H); δ_C (100 MHz, $CDCl_3$) 170.7, 157.3, 140.1, 139.2, 136.2, 123.7, 116.4, 105.9, 82.0, 57.0, 27.9, 25.3, 13.3; *m*/*z* (ES+) 343 (88%, $[MH + 2]^+$). 341 (82% $[MH]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{15}H_{22}N_2O_2{}^{79}Br^+$ 341.0865, found 341.0850; enantiomeric ratio was determined as 96.5:3.5 by HPLC, Chiralpak IA-3 column, 95:5 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 236 nm 8.6 min (minor), 12.3 min (major).

***tert*-Butyl (2*S*,3*E*)-2-[(5-Iodopyridin-2-yl)amino]hex-3-enoate (8l).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and 2-amino-5-iodopyridine (silica gel, 9:1 *n*-hexane:EtOAc): clear oil (60.2 mg, 78%); $[\alpha]_D^{27}$ +34.9° (*c* = 0.97, $CHCl_3$); IR 3359, 2967, 2933, 2873, 1722, 1586, 1476, 1368, 1256, 1149, 966 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.22 (dd, *J* 2.3 and 0.7, 1H), 7.58 (dd, *J* 8.7 and 2.3, 1H), 6.27

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(dd, *J* 8.7 and 0.8, 1H), 5.84 (dtd, *J* 15.5, 6.4 and 1.5, 1H), 5.51 (ddt, *J* 15.5, 5.8 and 1.5, 1H), 5.16 (br d, *J* 7.4, NH, 1H), 4.78 (ddd, *J* 7.4, 6.0 and 1.3, 1H), 2.12−2.30 (m, 2H), 1.45 (s, 9H), 0.97 (t, *J* 7.4, 3H); δ_C (100 MHz, $CDCl_3$) 171.0, 156.1, 153.6, 144.7, 135.9, 123.9, 110.4, 81.9, 77.4, 56.8., 28.0, 25.3, 13.3; *m*/*z* (ES+) 389 (100%, $[MH]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{15}H_{22}N_2O_2{}^{127}I^+$ 389.0726, found 389.0717; enantiomeric ratio was determined as 96.5:3.5 by HPLC, Chiralpak IA-3 column, 90:10 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 236 nm 8.6 min (minor), 12.3 min (major).

***tert*-Butyl (2*S*,3*E*)-2-[(5-Cyanopyridin-2-yl)amino]hex-3-enoate (8m).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and 2-amino-5-cyanopyridine (silica gel, 9:1 *n*-hexane:EtOAc): off-white crystalline solid (36.6 mg, 63%); mp 94−97 °C; $[\alpha]_D{}^{22}$ +74.0° (*c* = 1.01, $CHCl_3$); IR 3356, 2979, 2935, 2216, 1721, 1603, 1575, 1512, 1392, 1365, 1230, 1150 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.38 (dd, *J* 2.1 and 0.8, 1H), 7.55 (dd, *J* 8.8 and 2.2, 1H), 6.42 (dd, *J* 8.8 and 0.8, 1H), 5.84 (dtd, *J* 15.4, 6.4 and 1.5, 1H), 5.67 (br d *J* 6.3, 1H), 5.51 (ddt, *J* 15.5, 6.0 and 1.6, 1H), 4.90 (br t, *J* 6.1, 1H), 2.07 (ddt, *J* 7.6, 6.4 and 1.4, 1H), 1.47 (s, 9H), 0.98 (t, *J* 7.4, 3H); δ_C (100 MHz, $CDCl_3$) 170.3, 158.4, 153.0, 139.4, 136.4, 123.2, 118.4, 107.9, 97.7, 82.5, 56.5, 27.9, 25.3, 13.2); *m*/*z* (ES+) 288 (36%, $[MH]^+$), 232 (100%, $[M - CH_3CH_2CH{=}CH_2]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{16}H_{22}N_3O_2{}^+$ 288.1712, found 288.1726; enantiomeric ratio was determined as 96.5:3.5 by HPLC, Chiralpak IA-3 column, 90:10 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 236 nm 7.6 min (minor), 33.4 min (major).

***tert*-Butyl (2*S*,3*E*)-2-[(1*H*-Pyrazol-3-yl)amino]hex-3-enoate (8n).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and 3-aminopyrazole (silica gel, 4:1 *n*-hexane:EtOAc): pale orange oil (13.0 mg, 26%); $[\alpha]_D{}^{23}$ +16.2° (*c* = 0.617, $CHCl_3$); IR 3298, 2965, 2934, 1729, 1555, 1368, 1255, 1154 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.31 (d, *J* 2.4, 1H), 5.89 (dtd, *J* 15.6, 6.4 and 1.3, 1H), 5.63 (d, *J* 2.4, 1H), 5.53 (ddt, *J* 15.4, 6.0 and 1.5, 1H), 4.51 (d, *J* 6.0, 1H), 4.40 (br s, 1H), 2.13−2.01 (m, 2H), 1.44 (s, 9H), 0.98 (t, *J* 7.4, 3H); δ_C (100 MHz, $CDCl_3$) 171.9, 155.3, 135.6, 130.2, 125.0, 91.9, 81.5, 59.9, 28.0, 25.3, 13.3; *m*/*z* (ES+) 252 (92%, $[MH]^+$), 196 (100%, $[MH - CH_3CH_2CH{=}CH]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{13}H_{22}N_3O_2{}^+$ 252.1707, found 252.1716; enantiomeric ratio was determined as 97:3 using HPLC, Chiralpak IA-3 column, 90:10 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 252 nm 15.5 min (minor), 19.7 min (major).

***tert*-Butyl (2*S*,3*E*)-2-[(1*H*-1,3-Benzodiazol-2-yl)amino]hex-3-enoate (8o).** The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and 2-aminobenzimidazole (silica gel, 3:1 *n*-hexane:EtOAc): off-white solid (52.0 mg, 43%); mp gradual decomposition at >155 °C; $[\alpha]_D{}^{17}$ +32.9° (*c* = 1.03, $CHCl_3$); IR 3303, 3060, 2970, 2934, 2877, 1707, 1602, 1463, 1369, 1259, 1041 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.24−7.15 (m, 2H), 7.02−6.96 (m, 2H), 5.96 (br s, 1H), 5.88 (dtd, *J* 15.5, 6.4 and 1.5, 1H), 5.55 (ddt, *J* 15.5, 5.9 and 1.5, 1H), 5.06 (dd, *J* 5.9 and 1.5, 1H), 2.05−1.96 (m, 2H), 1.44 (s, 9H), 0.92 (t, *J* 7.4, 3H); δ_C (100 MHz, $CDCl_3$) 171.7, 154.0, 137.8, 136.0, 123.8, 120.5, 112.4, 82.6, 58.1, 27.9, 25.2, 13.1; *m*/*z* 302 (100%, MH^+), 246 (69%, $[MH - CH_3CH_2CH{=}CH]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{17}H_{24}N_3O_2{}^+$ 302.1863, found 302.1876; enantiomeric ratio was determined as 97:3 using HPLC, Chiralpak IA-3 column, 90:10 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 254 nm 11.2 min (minor), 26.0 min (major).

Ethyl 2-(4-{[(3*E*)-1-(*tert*-Butoxy)-1-oxohex-3-en-2-yl]amino}-phenyl)-1,3-oxazole-4-carboxylate (8p). The title compound was prepared according to the general procedure using (*S*)-*tert*-butyl 4-phenylselenylhex-2-(*E*)-enoate and ethyl 2-(4-aminophenyl)oxazole-4-carboxylate (silica gel, 4:1 *n*-hexane:EtOAc: white solid (56.2 mg, 70%); mp 98−102 °C; $[\alpha]_D{}^{26}$ +57.7° (*c* = 0.84, $CHCl_3$); IR 3373, 3155, 3138, 2976, 2935, 2874, 1727, 1612, 1507, 1370m, 1320, 1251, 1144, 1113 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.17 (s, 1H), 7.89 (d, *J* 8.7, 2H), 6.60 (d, *J* 8.7, 2H), 5.88 (dtd, *J* 15.1, 6.4 and 1.3, 1H), 4.89 (ddt, *J* 15.2, 5.8 and 1.4, 1H), 4.89 (br d, *J* 6.6, 1H), 4.45 (br t, *J* 5.9, 1H), 4.20 (q, *J* 7.1, 2H), 2.13−1.99 (m, 2H), 1.46 (s, 9H), 1.38 (t, *J* 7.2, 3H), 0.97 (t, *J* 7.4, 3H); δ_C (100 MHz, $CDCl_3$) 170.7, 163.2, 161.7, 148.8, 142.6, 136.4, 134.2, 128.4, 123.8, 115.7, 112.9, 82.4, 61.1, 58.3, 27.9, 25.42 14.3, 13.3; *m*/*z* 401 (100% $[MH]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{22}H_{29}N_2O_5{}^+$ 401.2076, found 401.2079; enantiomeric ratio was determined as 96.5:3.5 using HPLC, Chiralpak IA-3 column, 90:10 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 236 nm 15.5 min (minor), 30.8 min (major).

(2*S*,3*E*)-2-(Phenylamino)hex-3-en-1-ol (9a). To a stirred solution of *tert*-butyl (2*S*,3*E*)-2-(phenylamino)hex-3-enoate (0.11 mmol) in THF (0.8 mL) at 0 °C under argon was added dropwise a solution of $LiAlH_4$ in THF (1.0 M, 0.33 mmol). The solution was stirred at 0 °C for a further 1.5 h and then quenched with distilled H_2O (6 mL). The reaction mixture was extracted three times into CH_2Cl_2, and the extract was dried with Na_2SO_4 and concentrated under reduced pressure. Further purification by flash column chromatography provided the product as a clear oil (17.8 mg, 79%): $[\alpha]_D{}^{22}$ +39.0° (*c* = 0.81, CH_3OH); IR 3369, 3052, 3024, 2962, 2929, 2873, 1601, 1501, 1317, 1261, 1027, 967 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.17 (tt, *J* 7.5 and 2.1, 2H), 6.76−6.71 (m, 1H), 6.70−6.66 (m, 1H), 5.79 (dtd, *J* 15.5, 6.3 and 1.3, 1H), 5.37 (ddt, *J* 15.5, 6.1 and 1.5, 1H), 4.01−3.95 (m, 1H), 3.74 (dd, *J* 10.8 and 4.6, 1H), 3.61 (dd, *J* 10.9 and 6.5, 1H), 2.05 (ddt, *J* 7.6, 6.3 and 1.3, 2H), 0.97 (t, *J* 7.4, 3H); δ_C (100 MHz, $CDCl_3$) 147.2, 135.7, 129.2, 126.9, 118.1, 114.1, 65.3, 57.4, 25.4, 13.5; *m*/*z* (ES+) 192 (100%, MH^+), 136 (21%, $[MH - CH_3CH_2CH{=}CH_2]^+$); HRMS (ES+/TOF) *m*/*z* calculated for $C_{12}H_{18}NO^+$ 192.1388, found 192.1391; enantiomeric ratio was determined as 97:3 by HPLC, Chiralpak IA-3 column, 95:5 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 254 nm 13.1 min (major), 14.0 min (minor).

(2*S*,3*E*)-2-[(2-Methylphenyl)amino]hex-3-en-1-ol (9c). To a stirred solution of *tert*-butyl (2*S*,3*E*)-2-[(2-methylphenyl)amino]hex-3-enoate (34 mg, 0.12 mmol) in dry THF (0.8 mL) under argon at 0 °C was added dropwise a solution of $LiAlH_4$ in THF (1.0 M, 036 mmol). The solution was stirred at 0 °C for a further 1.5 h and then quenched with distilled H_2O (6 mL). The reaction mixture was extracted three times into CH_2Cl_2, and the extract was dried with Na_2SO_4 and concentrated under reduced pressure. Further purification by flash column chromatography provided the product as a clear oil (21.0 mg, 85%): $[\alpha]_D{}^{23}$ +65.3° (*c* = 0.76, $CHCl_3$); IR 3346, 2968, 2934, 2874, 1712, 1501, 1456, 1326, 1222, 1153, 1045 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.15−7.04 (m, 2H), 6.71−6.66 (m, 2H), 5.78 (dtd, *J* 15.4, 6.2 and 1.2, 1H), 5.40 (ddt, *J* 15.5, 6.1 and 1.6, 1H), 4.03 (tdd, *J* 6.1, 4.8 and 1.2, 1H), 3.77 (dd, *J* 10.9 and 4.5, 1H), 3.65 (dd, *J* 10.9 and 6.4, 1H), 2.19 (s, 3H), 2.06 (ddt, *J* 6.3 and 1.3, 2H), 0.98 (t, *J* 7.4, 3H); δ_C (100 MHz, $CDCl_3$) 145.1, 135.6, 130.2, 127.0, 126.8, 122.7, 117.6, 111.6, 65.3, 57.2, 25.4, 17.6, 13.4; *m*/*z* (EI+) 205 (325, $[M]^+$), 174 (100% $[M - CH_2OH]^+$); HRMS (EI+/TOF) calculated for $C_{13}H_{19}NO^+$ 205.1467, found 205.1463; enantiomeric ratio was determined as 96.5:3.5 by HPLC, Chiralpak IA-3 column, 90:10 *n*-hexane:IPA, flow 1 mL min^{-1}, UV detection at 254 nm 7.6 min (minor), 10.1 min (major).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving ^1H and ^{13}C NMR spectra and, where appropriate, HPLC traces and measurement of diastereotopic ratios for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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