Intramolecular Nucleophilic Deselenenylation Reactions Promoted by Benzeneselenenyl Triflate. Stereospecific Synthesis of Vicinal Amino Alcohol Precursors

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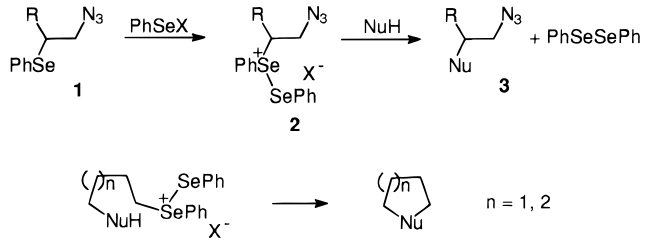
After activation with electrophilic selenenylating agents, the phenylseleno group of vicinal azido selenides, containing internal oxygen or nitrogen nucleophilic substituents, readily undergoes intramolecular nucleophilic displacement to afford azido-substituted heterocyclic compounds. This intramolecular substitution occurs with inversion of configuration at the carbon atom bearing the selenium atom. Starting from acetamido selenides and carbamato selenides, a stereocontrolled synthesis of the vicinal amino alcohol precursor oxazolines and oxazolidin-2-ones has been developed.

Introduction

Organoselenium reagents are now largely used in organic synthesis since they allow several important chemo-, regio-, and stereoselective reactions to be effected under mild experimental conditions.[1−4] Very few selenium-containing compounds find practical application, and in most cases the selenium functionality, which in general is a phenylselenenyl group, must therefore be removed at the end of the conversion. Owing to the versatility of this function, one can use this final step to further elaborate the organic molecule. Deselenenylation reactions can be effected directly on the selenides or after transformation into selenoxides, selenones, or selenonium salts. Simple replacement of the PhSe group by hydrogen can be effected with Raney nickel, nickel boride,[5] or with tri-*n*-butyltin hydride[6] in the presence of AIBN. This represents a convenient way to produce carbon radicals. The PhSe group can be replaced by an allyl group using allyltributyltin.[7] Interesting conversions can be performed by electron transfer reactions. The dissociative reduction of an aryl alkyl selenide produces an arylselenium anion and a carbanion.[8] Similarly, the dissociative oxidation produces an arylselenium cation and a carbocation.[4] The best known and most widely used deselenenylation reaction is the *syn*-elimination of selenoxides which represents the mildest general olefin-forming reaction.[9−11] When the selenoxide is allylic, the equilibrium lies largely toward the selenenic ester which is readily hydrolyzed to the allylic alcohol.[12] Selenoxides which cannot give rise to one of these two processes readily undergo nucleophilic substitution reactions.[13] The selenonyl group of selenones is an even better leaving group.[14] Finally, substitution reactions can be effected on the selenonium salts which form as intermediates when an alkyl phenyl selenide is treated with halogens or with an electrophilic selenenylating agent.[15,16] In a recent communication we reported that selenonium salt intermediates can be used to effect a mild and very simple synthesis of substituted azides by deselenenylation of vicinal azido selenides.[17]

Scheme 1



As indicated in Scheme 1, after treatment with electrophilic selenenylating agents, the vicinal azido selenides **1** can easily give rise to nucleophilic substitution reactions to afford a variety of substituted azides **3**. The attack of the electrophilic selenenylating agents on the selenium atom of the selenides **1** generates the selenonium ion **2** in which the diphenyl diselenide acts as a very good leaving group.[17]

We now report that this procedure can be applied to phenyl alkyl selenides containing an internal nucleophile so that an intramolecular displacement of the phenylse-

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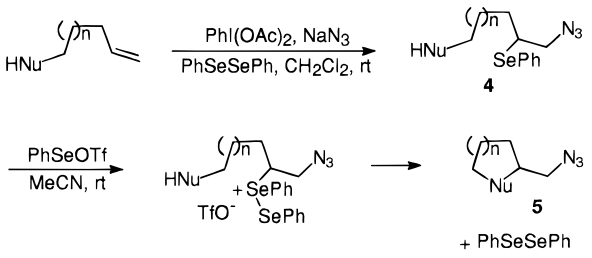
Scheme 2



lenenyl group can occur (Scheme 1). This represents a new kind of ring-closure reaction which leads to the formation of interesting heterocyclic compounds. We describe in this paper the conversion of vicinal azido selenides, containing a suitably positioned oxygen or nitrogen nucleophile, into azido-substituted heterocyclic compounds and those of vicinal acetamido and carbamato selenides into oxazolines and oxazolidin-2-ones, respectively.

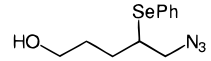
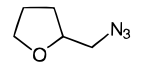
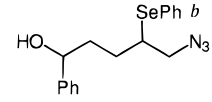
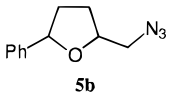
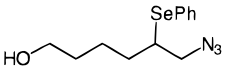
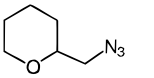
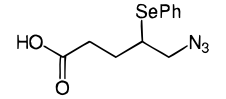
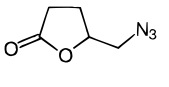
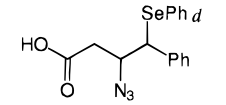
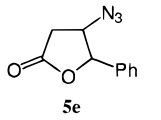
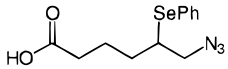
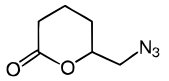
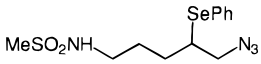
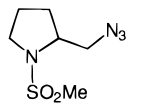
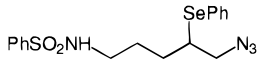
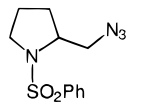
Results and Discussion

The selenium-induced deselenenylation reactions were simply carried out by stirring for a few hours at room temperature a solution of the selenides (1.0 mmol) and benzeneselenenyl triflate[18] (1.1 mmol) in acetonitrile or in methylene chloride. After the usual workup, the reaction mixtures were chromatographed through a silica gel column to afford pure diphenyl diselenide and the cyclization products.

The first experiments which were carried out concerned the intramolecular nucleophilic deselenenylation of the hydroxy, carboxy, and sulfonamido azido selenides **4** which were easily obtained, starting from alkenols, alkenoic acids, and alkenyl sulfonamides, using our recently reported procedure[19] for the radical azido phenylselenenylation of alkenes (Scheme 2). The reactions of compounds **4** with PhSeOTf afforded the azido-substituted heterocyclic compounds **5** (Scheme 2). The results of these experiments are collected in Table 1. The hydroxy azido selenides **4a** and **4b** (entries 1 and 2) gave the 2-(azidomethyl)tetrahydrofurans **5a** and **5b** very rapidly and in satisfactory yield. Compound **5b** was obtained as a mixture of two diastereoisomers which could not be separated. Compound **4c** (entry 3) required longer reaction times to afford the pyran derivative **5c**. The carboxy derivatives **4d** and **4f** presented a similar behavior. The formation of the δ-lactone **5f** required longer reaction time than that of the γ-lactone **4d**. The radical azido selenenylation of *trans*-styrylacetic acid should afford the two diastereoisomeric azido selenides **4e**. As a matter of fact this reaction gave rise to a mixture of the *trans* azido lactone **5e** and of one of the two isomeric azido selenides of **4e**. This latter isomer, when treated with benzeneselenenyl triflate, gave the *cis* azido lactone **5e** (Table 1, entry 5). The structures of the two isomers were demonstrated by differential NOE experiments. The formation of the *trans* azido lactone from the azido selenenylation of the *trans*-styrylacetic acid cannot be easily explained. Nevertheless, the results described above seem to indicate that the ring-closure reaction is a stereospecific process. This seems to be confirmed by the results obtained with the methyl ester of styrylacetic acid. In this case the azido selenenylation reaction gave the expected mixture of the two isomeric methyl esters of **4e** in a 1:1 ratio. This mixture was directly deselenenylated with PhSeOTf and afforded a 1:1 mixture of the *cis* and *trans* azido lactones **5e** which were easily separated by column chromatography.

The last two examples reported in Table 1 (entries 7 and 8) concern the cyclization reactions which are effected by nitrogen nucleophiles. The starting products employed for these experiments, **4g** and **4h**, were the azido selenides of the alkenyl sulfonamides. The deselenenylation of these two products afforded the 2-(azidomethyl) *N*-methyl and *N*-phenylsulfonamido pyrrolidines **5g** and **5h**. On the contrary, when the same reaction was effected starting from the seleno azide of 5-alkenyl amine,

Table 1. Conversion of Vicinal Azido Selenides 4 into Heterocyclic Compounds 5 Promoted by PhSeOTf in MeCN at Room Temperature

Entry	Azido Selenide	time (h)	Reaction Product	Yield (%)[a]
1	 **4a**	2	 **5a**	47
2	 **4b**	1	 **5b**	60[b]
3	 **4c**	10	 **5c**	58
4	 **4d**	6	 **5d**	65[c]
5	 **4e**	1	 **5e**	79[e]
6	 **4f**	28	 **5f**	45
7	 **4g**	8[f]	 **5g**	59
8	 **4h**	7[f]	 **5h**	50

a) Yields of isolated products after column chromatography. *b*) 1:1 Mixture of two diastereoisomers. *c*) This product was obtained in 73% yield starting from the amide. *d*) Single isomer. *e*) Starting from a 1:1 mixture of the methyl esters a 1:1 mixture of *cis* and *trans* isomers was obtained (85%). *f*) These reactions were run in methylene chloride.

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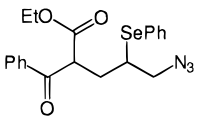
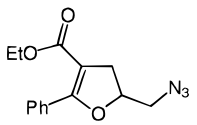
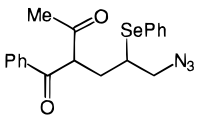
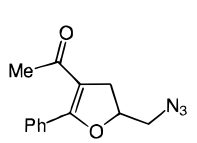
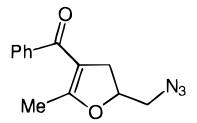
Table 2. Conversion of Vicinal Azido Selenides 6 into Heterocyclic Compounds 7 Promoted by PhSeOTf in Methylene Chloride at Room Temperature

Entry	Azido Selenide	time (h)	Reaction Product	Yield (%)[a]
1	 **6a**	5	 **7a**	62
2	 **6b**	2	 **7b**	37
		10	 **7c**	37

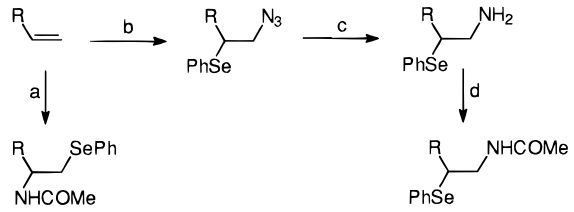
a) Yields of isolated products after column chromatography.

no cyclization products could be obtained. These results were not completely unexpected since a similar behavior is presented by the alkenyl amines in respect to the related cyclization reactions induced by electrophilic reagents. It is in fact well documented that in the presence of electrophilic reagents primary alkenyl amines do not give cyclization products[20] whereas good results are obtained starting from alkenyl amines N-substituted with electron-withdrawing substituents.[21−25]

Further examples of the versatility of the presently described deselenenylation reaction are reported in Table 2. In these cases the nucleophile which effects the displacement reaction is the oxygen atom of an enolizable carbonyl compound. Good results were obtained from the reactions of the azido selenides of the allyl β-keto ester **6a** and of the allyl β-diketone **6b** which afforded dihydrofuran derivatives. In the first case (entry 1) a single product, **7a**, was obtained. The reaction of the β-diketone **6b** (entry 2) gave instead a 1:1 mixture of the two possible cyclization products **7b** and **7c**. These two products could be easily separated by column chromatography.

The examples reported above indicate that the present deselenenylation procedure, together with the regioselective radical azido selenenylation of alkenes, can be very useful to synthesize several azido-substituted heterocyclic compounds. These compounds are interesting intermediates since the azido group can be used to effect several conversions leading to the formation of more complex molecules.[26]

Scheme 3



a) $(NH_4)_2S_2O_8$, PhSeSePh, CF_3SO_3H, MeCN/H_2O (10:1), rt
b) $PhI(OAc)_2$, NaN_3, PhSeSePh, CH_2Cl_2, rt
c) 1) PPh_3, THF, 2) H_2O; d) MeCOCl, Et_3N, THF

We have then used the intramolecular deselenenylation of selenides promoted by benzeneselenenyl triflate to develop a simple approach to the stereocontrolled synthesis of oxazolines and oxazolidin-2-ones. These compounds have considerable synthetic relevance since they can be easily converted into vicinal amino alcohols.[27,28] The experiments described below not only demonstrated that these syntheses can be easily effected but they also gave useful information about the stereochemical course of the deselenenylation process. Owing to the structure of the substrates employed, this important aspect of the process could not be investigated in the case of the reactions of the azido selenides described above, although some indications arose from the reactions leading to the formation of the two isomers of **5e**.

The synthesis of oxazolines was realized starting from vicinal acetamido selenides. In this case the nucleophile which effects the displacement reaction is the oxygen atom of the acetamido group. Acetamido selenides were prepared in two different and complementary ways. As indicated in Scheme 3, in the case of terminal alkenes the two methods afford the two regioisomeric acetamido selenides.

The first method is the electrophilic amido selenenylation of alkenes which is effected with PhSeCl, acetonitrile, and water in the presence of trifluoromethanesulfonic acid.[29] We have sligthly modified this procedure by replacing PhSeCl with benzeneselenenyl sulfate (easily obtained from PhSeSePh by oxidation with ammonium persulfate) which is a much stronger electrophilic reagent.[4,30] These reactions are both regiospecific (Markovnikov orientation) and stereospecific (*anti* addition). This method was employed for the synthesis of compounds **8c**, **8d**, *erythro*-**8f**, and *trans*-**8h** (Table 3). The synthesis of the other acetamido selenides reported in Table 3 was instead effected starting from the corresponding azido selenides. The azido group was first reduced to the amino group, using triphenylphosphine and water,[31] and this was then converted into the acetamido group by treatment with acetyl chloride. The radical azido selenenylation of alkenes occurs with an anti-Markovnikov orientation, and therefore compounds **8a**, **8b**, and **8e** were obtained starting from styrene, 1-octene, and allyl benzamide, respectively. In the case of acenaphthylene the azido selenenylation afforded a

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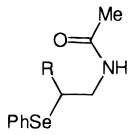
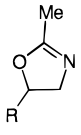
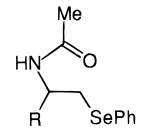
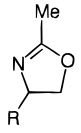
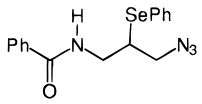
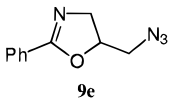
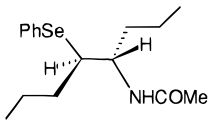
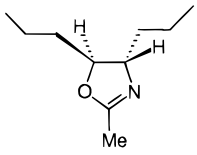
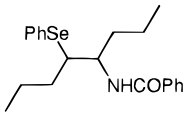
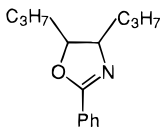
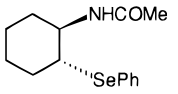
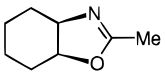
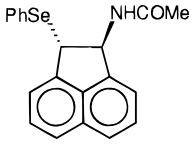
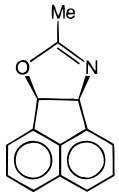
(30) Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Bartoli, D. *Tetrahedron Lett.* **1989**, *30*, 1417.
(31) Gololobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1353.

Table 3. Conversion of Vicinal Acetamido Selenides 8 into Oxazolines 9 Promoted by PhSeOTf in Methylene Chloride at Room Temperature

Entry	Acetamido Selenide	time (h)	Reaction Product	Yield (%)[a]
1	 **8a** : R = Ph	5	 **9a**	62[b]
2	**8b:** R = C_6H_{13}	10	**9b**	50
3	 **8c** : R = Ph	2	 **9c**	77[b]
4	**8d:** R = C_6H_{13}	7	**9d**	71
5	 **8e**	6	 **9e**	72
6	 **8f**	5	 **9f**	65
7	 **8g**[c]	5	 **9g**[c]	74
8	 **8h**	24	 **9h**	50
9	 **8i**	2	 **9i**	86

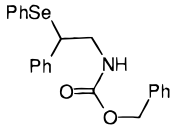
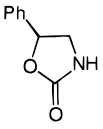
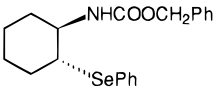
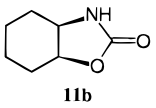
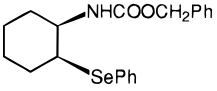
a) Yields of isolated products after column chromatography. *b*) Similar results were obtained from the reactions promoted by phenylselenenyl sulfate in acetonitrile. *c*) 1:1 mixture of the two stereoisomers.

single stereoisomer which was transformed into the acetamido selenide. The small value of the vicinal coupling constant[32] indicates that this is the *trans* isomer **8i**. As expected, the radical azido selenenylation of *trans*-4-octene gave instead a 1:1 mixture of two stereoisomers. These were transformed into a 1:1 mixture of the benzamido selenides **8g** which could not be separated.

The results of the reactions of the amido selenides **8a**−**i** with PhSeOTf are collected in Table 3. The cyclization reactions proceeded smoothly in every case and afforded the expected oxazolines **9a**−**i** in good yield. Also included in Table 3 is the reaction of the azido selenide **8e** which gave rise to the interesting 5-(azidomethyl)oxazoline **9e**. Of particular importance were the results obtained from

(32) Dewar, M. J. S.; Fahey, R. C. *J. Am. Chem. Soc.* **1963**, *85*, 2245.

Table 4. Conversion of Vicinal Carbamato Selenides 10 into Oxazolidin-2-ones 11 Promoted by PhSeOTf in Methylene Chloride at Room Temperature

Entry	Carbamato Selenide	time (h)	Reaction Product	Yield (%)[a]
1	 **10a**	1.5	 **11a**	71
2	 **10b**	1.5	 **11b**	80
3	 **10c**	24	No reaction	

a) Yields of isolated products after column chromatography.

the acetamido selenides having a defined stereochemistry (Table 3, entries 6, 8, and 9). A single oxazoline was obtained in every case. *erythro*-**8f** gave the *trans* oxazoline **9f** and the *trans* compounds **8h** and **8i** gave the *cis* oxazolines **9h** and **9i**, respectively. In agreement with these results, the 1:1 mixture of the *erythro*- and *threo*-**8g** gave a 1:1 mixture of the *trans* and *cis* oxazolines **9g**. Similar results were obtained from the above described cyclization reaction of the 1:1 mixture of the methyl esters of **4e**. Thus, the whole of these experimental data clearly indicates that the presently reported intramolecular substitution on the selenonium ion intermediates is a stereospecific process which occurs with inversion of configuration at the carbon atom bearing the phenylseleno group.

Further evidence came from the reactions carried out on carbamato selenides **10** which afforded the oxazolidin-2-ones **11** (Table 4). The starting products were prepared from the corresponding azido selenides which were reduced to the amines and then treated with benzyl chloroformate. The radical azido selenenylation of cyclohexene gave a 3:1 mixture of the two stereoisomers which were directly transformed into the two isomeric carbamato selenides **10b** and **10c**. These were easily separated by column chromatography. The structures of the two isomers were assigned on the basis of their NMR spectra and were also confirmed by an independent synthesis of **10b** starting from the known[33] *trans*-1-azido-2-(phenylseleno)cyclohexane. Under the usual conditions, **10a** gave **11a** in good yield. The *trans* isomer **10b** was easily converted into the *cis* oxazolidin-2-one **11b**, whereas the *cis* isomer **10c**, in which the intramolecular displacement with inversion of configuration cannot occur, was recovered unchanged even after prolonged reaction times. The results obtained from the reactions of the acetamido and carbamato selenides demonstrate that the presently described deselenenylation reaction represents a convenient procedure to effect the stereospecific synthesis of oxazoline and oxazolidin-2-one deriva-

(33) (a) Denis, J. N.; Vicens, J.; Krief, A. *Tetrahedron Lett.* **1979**, 2697. (b) Hassner, A.; Amarasekara, A. S. *Tetrahedron Lett.* **1987**, *28*, 5185.

tives. These reactions therefore can be usefully employed for the synthesis of stereodefined vicinal amino alcohols.

All the cyclization reactions described above were effected with PhSeOTf in methylene chloride at room temperature. However, other selenenylating agents with a non-nucleophilic counterion can be employed. Indeed, compounds **9a** and **9c** were obtained in good yield from **8a** and **8c** (Table 3, entries 1 and 3) when the PhSeOTf was replaced by the less expensive benzeneselenenyl sulfate which can be easily prepared from diphenyl diselenide.[4,30]

In conclusion, from the results described in this paper it can be anticipated that the stereospecific deselenenylation of selenides promoted by electrophilic selenenylating agents can find a more general application and that it can also be applied to the synthesis of complex molecules.

Experimental Section

Product identification was effected by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analyses.[21]

Physical and spectral data of compounds **5d**,[34] **6a**,[26] **8c**,[29] **8d**,[35] **8h**,[29] **9a**,[36] **9c**,[37] **9f**,[38] **9h**,[37,38] and **11b**[39] have already been reported in the literature.

Preparation of Azido Selenides. These compounds were prepared according to the recently reported procedure.[19]

5-Azido-4-(phenylseleno)-1-pentanol (4a) (56% yield): oil; ^{1}H NMR δ 7.7−7.4 (m, 2 H), 7.4−7.2 (m, 3 H), 3.7−3.1 (m, 5 H), 2.0−1.5 (m, 5 H); ^{13}C NMR δ 135.3, 133.2, 129.2, 128.1, 62.3, 56.0, 44.4, 30.7, 28.9; MS *m*/*z* (relative intensity) 285 (6), 157 (42), 91 (15), 78 (52), 77 (42), 71 (100). Anal. Calcd for $C_{11}H_{15}N_3OSe$: C, 46.49; H, 5.32; N, 14.78. Found: C, 46.40; H, 5.32; N, 14.78.

5-Azido-4-(phenylseleno)-1-phenyl-1-pentanol (4b) (47% yield): oil; ^{1}H NMR δ 7.6−7.43 (m, 2 H), 7.4−7.16 (m, 8 H), 4.78−4.6 (m, 1 H), 3.54 (dd, 1 H, J = 12.5, 5.5 Hz), 3.45−3.28 (m, 1 H), 3.25−3.18 (m, 1 H), 2.2−1.72 (m, 5 H); ^{13}C NMR δ 135.4, 129.1, 128.5, 128.1, 127.7, 125.8, 125.7, 74.3, 73.8, 55.9, 44.5, 44.3, 36.9, 36.7, 28.8, 28.5; MS *m*/*z* (relative intensity) 315 (14), 184 (20), 158 (100), 157 (20), 104 (93), 91 (45), 77 (38), 55 (77). Anal. Calcd for $C_{17}H_{19}N_3OSe$: C, 56.67; H, 5.31; N, 11.66. Found: C, 56.80; H, 5.42; N, 11.48.

6-Azido-5-(phenylseleno)-1-hexanol (4c) (56% yield): oil; ^{1}H NMR δ 7.66−7.5 (m, 2 H), 7.47−7.22 (m, 3 H), 3.8−3.34 (m, 5 H), 3.31−3.12 (m, 1 H), 1.95−1.21 (m, 6 H); ^{13}C NMR δ 135.0, 128.9, 127.8, 127.2, 62.1, 55.6, 44.4, 32.1, 23.7; MS *m*/*z* (relative intensity) 299 (13), 157 (89), 85 (100), 78 (85), 77 (72), 56 (55), 41 (98). Anal. Calcd for $C_{12}H_{17}N_3OSe$: C, 48.33; H, 5.75; N, 14.09. Found: C, 48.24; H, 5.69; N, 14.17.

5-Azido-4-(phenylseleno)pentanoic acid (4d) (71% yield): oil; ^{1}H NMR δ 9.5 (br s, 1 H), 7.65−7.5 (m, 2 H), 7.48−7.21 (m, 3 H), 3.62 (dd, 1 H, J = 12.5, 5.4 Hz), 3.42 (dd, 1 H, J = 12.5, 7.6 Hz), 3.31−3.14 (m, 1 H), 2.8−2.6 (m, 2 H), 2.28−2.04 (m, 1 H), 1.95-1.7 (m, 1 H); ^{13}C NMR δ 179.1, 135.5, 129.3, 128.3, 126.9, 55.9, 43.6, 32.1, 27.3. Anal. Calcd for $C_{11}H_{13}N_3O_2Se$: C, 44.31; H, 4.39; N, 14.09. Found: C, 44.22; H, 4.49; N, 14.01.

3-Azido-4-phenyl-4-(phenylseleno)butanoic acid (4e) (26% yield): oil; ^{1}H NMR δ 9.4 (br s, 1 H), 7.52−7.35 (m, 2 H), 7.35−7.08 (m, 8 H), 4.44−4.18 (m, 2 H), 2.95 (dd, 1 H, J = 16.9, 3.5 Hz), 2.46 (dd, 1H, J = 16.9, 8.9 Hz); ^{13}C NMR δ 176.5, 138.4, 135.3, 129.2, 128.6, 128.5, 128.3, 127.8, 62.3, 52.3, 38.6. Anal. Calcd for $C_{16}H_{15}N_3O_2Se$: C, 53.34; H, 4.20; N, 11.66. Found: C, 53.40; H, 4.28; N, 11.54. **Methyl ester**: (1:1 mixture of two isomers) (72% yield): oil; ^{1}H NMR δ 7.49−7.35 (m, 4 H), 7.34−7.1 (m, 16 H), 4.45−4.22 (m, 4 H), 3.7 (s, 3 H), 3.66 (s, 3H), 2.85 (dd, 1 H, J = 16.5, 3.8 Hz), 2.53−2.38 (m, 2 H), 2.43 (dd, 1 H, J = 16.5, 8.9 Hz); ^{13}C NMR δ 170.8, 170.7, 139.1, 138.5, 135.4, 135.3, 129.1, 128.9, 128.8, 128.6, 128.4, 128.2, 128.1, 127.7, 127.2, 63.7, 62.6, 53.3, 52.2, 51.9, 38.5, 38.2. Anal. Calcd for $C_{17}H_{17}N_3O_2Se$: C, 54.55; H, 4.58; N, 11.23. Found: C, 54.49; H, 4.65; N, 11.33.

6-Azido-5-(phenylseleno)hexanoic acid (4f) (60% yield): oil; ^{1}H NMR δ 10.5 (br s, 1 H), 7.7−7.5 (m, 2 H), 7.5−7.18 (m, 3 H), 3.7−3.32 (m, 2 H), 3.3−3.1 (m, 1 H), 2.58−2.24 (m, 2 H), 2.14−1.46 (m, 4 H); ^{13}C NMR δ 179.3, 135.3, 129.1, 128.0, 127.4, 55.7, 44.0, 33.4, 31.7, 22.6. Anal. Calcd for $C_{12}H_{15}N_3O_2Se$: C, 46.16; H, 4.84; N, 13.46. Found: C, 46.08; H, 4.85; N, 13.41.

***N*-[5-Azido-4-(phenylseleno)pentyl]methanesulfonamide (4g)** (56% yield): oil; ^{1}H NMR δ 7.64−7.5 (m, 2 H), 7.4−7.32 (m, 3 H), 4.61 (t, 1 H, J = 6.0 Hz), 3.58 (dd, 1 H, J = 12.5, 5.2 Hz), 3.42 (dd, 1 H, J = 12.5, 7.5 Hz), 3.26−3.16 (m, 3 H), 2.9 (s, 3 H), 2.0−1.48 (m, 4 H); ^{13}C NMR δ 135.0, 129.0, 127.9, 127.1, 55.5, 43.8, 42.5, 39.7, 29.2, 27.8. Anal. Calcd for $C_{12}H_{18}N_4O_2SSe$: C, 39.89; H, 5.02; N, 15.51. Found: C, 39.86; H, 5.08; N, 15.39.

***N*-[5-Azido-4-(phenylseleno)pentyl]benzenesulfonamide (4h)** (49% yield): oil; ^{1}H NMR δ 7.94−7.78 (m, 2 H), 7.68−7.4 (m, 5 H), 7.36−7.16 (m, 3 H), 4.72 (t, 1 H, J = 6.3 Hz), 3.54 (dd, 1 H, J = 12.5, 5.2 Hz), 3.35 (dd, 1 H, J = 12.5, 7.5 Hz), 3.16−2.84 (m, 3 H), 1.88−1.36 (m, 4 H); ^{13}C NMR δ 139.6, 135.1, 132.4, 129.0, 128.9, 127.9, 126.8, 55.5, 43.8, 42.5, 29.2, 27.4. Anal. Calcd for $C_{17}H_{20}N_4O_2SSe$: C, 48.23; H, 4.76; N, 13.23. Found: C, 48.15; H, 4.84; N. 13.31.

6-Azido-5-(phenylseleno)-3-benzoylhexan-2-one (6b) (70% yield): oil; ^{1}H NMR δ 8.15−7.91 (m, 4 H), 7.7−7.14 (m, 16 H), 5.1−4.9 (m, 2 H), 3.75−3.4 (m, 4 H), 3.37−3.18 (m, 1 H), 3.18−2.98 (m, 1 H), 2.72−2.42 (m, 2 H), 2.3−1.94 (m, 2 H), 2.14 (s, 3 H), 2.04 (s, 3 H); ^{13}C NMR δ 202.6, 202.5, 195.8, 195.6, 136.3, 135.0, 134.7, 133.7, 129.2, 129.1, 128.8, 128.7, 128.6, 128.5, 128.1, 127.5, 60.9, 60.5, 56.2, 56.1, 43.4, 42.6, 31.9, 31.5, 28.5, 28.2. Anal. Calcd for $C_{19}H_{19}N_3O_2Se$: C, 57.00; H, 4.78; N, 10.50. Found: C, 57.02; H, 4.70; N, 10.61.

***N*-[3-Azido-2-(phenylseleno)propyl]benzamide (8e)** (52% yield): oil; ^{1}H NMR δ 7.8−7.66 (m, 2 H), 7.66−7.19 (m, 8 H), 6.93−6.72 (m, 1 H), 3.97−3.38 (m, 5 H); ^{13}C NMR δ 167.6, 134.9, 131.4, 129.2, 128.3, 128.1, 127.3, 126.8, 53.8, 43.6, 42.2. Anal. Calcd for $C_{16}H_{16}N_4OSe$: C, 53.49; H, 4.49; N, 15.59. Found: C, 53.55; H, 4.41; N, 15.62.

Preparation of Acetamido Selenides. Method A. A solution of trifluoromethanesulfonic acid (1 mmol) in water (1 mL) and acetonitrile (5 mL) was added to a mixture of the olefin (1 mmol), diphenyl diselenide (0.55 mmol), and ammonium persulfate (0.6 mmol) in acetonitrile (20 mL). The mixture was refluxed for 2 h and then poured on 10% aqueous Na_2CO_3 and extracted with Et_2O. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated. The reaction products were obtained in pure form after chromatography on silica gel using Et_2O as eluant. Reaction yields and physical and spectral data of the reaction products are reported below.

***N*-[[1-Propyl-2-(phenylseleno)]pentyl]acetamide (8f)** (80% yield): oil; ^{1}H NMR δ 7.6−7.45 (m, 2 H), 7.3−7.15 (m, 3 H), 5.6 (d, 1 H, J = 8.3 Hz), 4.25−4.0 (m, 1 H), 3.45−3.3 (m, 1 H), 2.0−1.3 (m, 11 H), 0.9 (t, 6 H, J = 7.0 Hz); ^{13}C NMR δ 169.3, 133.3, 130.6, 128.9, 126.9, 54.2, 52.2, 36.1, 32.4, 22.8, 21.2, 19.1, 13.7, 13.5; MS *m*/*z* (relative intensity) 327 (6), 268 (44), 170 (53), 157 (13), 128 (43), 114 (41), 72 (100). Anal. Calcd for $C_{16}H_{25}NOSe$: C, 58.89; H, 7.72; N, 4.29. Found: C, 58.96; H, 7.69; N, 4.18.

Method B. A solution of triphenylphosphine (1.1 mmol) in THF (3 mL) was slowly added at rt to a solution of seleno azide (1 mmol) in THF (5 mL). The progress of the reaction was monitored by TLC. When the starting product was consumed, water (1 mL) was added and the mixture was warmed at 40 °C for 20 h. The solvent was evaporated, and the residue was dried over P_2O_5. The crude product was

(34) Olsen, R. K.; Bhat, K. L.; Wardle, R. B.; Hennen, W. J.; Kini, G. D. *J. Org. Chem.* **1985**, *50*, 896.
(35) Yoshida, M.; Satoh, N.; Kamigata, N. *Chem. Lett.* **1989**, 1433.
(36) Padwa, A.; Gasdaska, J. R.; Tomas, M.; Turro, N. J.; Cha, Y.; Gould, I. R. *J. Am. Chem. Soc.* **1986**, *108*, 6739.
(37) Bellucci, G.; Bianchini, R.; Chiappe, C. *J. Org. Chem.* **1991**, *56*, 3067.
(38) Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. *Tetrahedron Lett.* **1988**, *29*, 1049.
(39) Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. *J. Chem. Soc., Chem. Commun.* **1987**, 1447.

dissolved in THF (10 mL) and cooled at 0° C. Triethylamine (2 mmol) and acetyl chloride (1.1 mmol) were added, and the mixture was stirred for 4 h. The mixture was then treated with hydrochloric acid (3% solution in water) and extracted with Et_2O. The organic layer was washed with brine and dried (Na_2SO_4). The reaction products were obtained in pure form after chromatography on silica gel using Et_2O as eluant. Reaction yields and physical and spectral data of the reaction products are reported below.

***N*-[2-Phenyl-2-(phenylseleno)ethyl]acetamide (8a)** (84% yield): oil; ^{1}H NMR δ 7.5−7.38 (m, 2 H), 7.36−7.04 (m, 8 H), 6.2 (t, 1 H, J = 5.7 Hz), 4.44 (dd, 1 H, J = 8.2, 7.9 Hz), 3.82 (dd, 1 H, J = 13.8, 7.9 Hz), 3.7 (dd, 1 H, J = 13.8, 8.2 Hz), 1.75 (s, 3 H); ^{13}C NMR δ 169.9, 139.4, 134.7, 128.8, 128.3, 127.7, 127.5, 127.2, 46.4, 44.0, 22.7; MS *m*/*z* (relative intensity) 260 (1), 162 (48), 120 (100), 103 (12), 77 (10), 43 (14). Anal. Calcd for $C_{16}H_{17}NOSe$: C, 60.38; H, 5.38; N, 4.40. Found: C, 60.43; H, 5.35; N, 4.29.

***N*-[2-(Phenylseleno)octyl]acetamide (8b)** (64% yield): oil; ^{1}H NMR δ 7.62−7.48 (m, 2 H), 7.36−7.2 (m, 3 H), 5.95 (br s, 1 H), 3.59 (ddt, 1 H, J = 9.4, 7.7, 6.4 Hz), 3.35−3.17 (m, 2 H), 1.9 (s, 3 H), 1.68−1.4 (m, 4 H), 1.36−1.16 (m, 6 H), 0.88 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ 169.9, 134.7, 128.9, 128.0, 127.5, 46.0, 43.7, 32.8, 31.4, 28.8, 27.5, 22.9, 22.3, 13.8; MS *m*/*z* (relative intensity) 327 (7), 198 (31), 170 (100), 157 (21), 128 (51), 43 (76). Anal. Calcd for $C_{16}H_{25}NOSe$: C, 58.89; H, 7.72; N, 4.29. Found: C, 58.80; H, 7.75; N, 4.36.

***N*-[[1-Propyl-2-(phenylseleno)]pentyl]benzamide (8g)** (1:1 mixture of two isomers) (77% yield): oil; ^{1}H NMR δ 8.22−8.08 (m, 2 H), 7.76−7.22 (m, 16 H), 7.2−7.08 (m, 2 H), 6.38 (d, 1H, J = 9.2 Hz), 6.3 (d, 1 H, J = 9.5 Hz), 4.54−4.32 (m, 2 H), 3.52 (dt, 1 H, J = 7.6, 3.3 Hz), 3.39 (ddd, 1 H, J = 7.9, 5.8, 2.6 Hz), 1.82−1.12 (m, 16 H), 1.04−0.74 (m, 12 H); ^{13}C NMR δ 167.0, 166.9, 134.4, 133.3, 132.9, 131.2, 131.1, 130.3, 129.8, 129.0, 128.6, 128.3, 128.1, 127.4, 126.9, 126.7, 126.6, 54.5, 53.1, 52.6, 52.5, 36.3, 35.3, 32.8, 21.2, 21.1, 19.2, 13.8, 13.6; MS *m*/*z* (relative intensity) 389 (1), 268 (14), 176 (12), 105 (100), 77 (28). Anal. Calcd for $C_{21}H_{27}NOSe$: C, 64.94; H, 7.01; N, 3.61. Found: C, 65.02; H, 7.12; N, 3.58.

trans-**1-Acetamido-2-(phenylseleno)acenaphthene (8i)** (76% yield): oil; ^{1}H NMR 7.8−7.05 (m, 11 H), 6.03 (dd, 1 H, J = 8.8, 1.1 Hz), 5.76 (d, 1 H, J = 8.8 Hz), 4.88 (d, 1 H, J = 1.1 Hz), 1.94 (s, 3 H); ^{13}C NMR δ 169.2, 142.3, 142.0, 135.4, 130.8, 128.6, 128.1, 128.0, 124.5, 123.8, 120.9, 120.5, 62.0, 50.4, 23.0. Anal. Calcd for $C_{20}H_{17}NOSe$: C, 65.58; H, 4.68; N, 3.82. Found: C, 65.54; H, 4.79; N, 3.88.

Preparation of Carbamato Selenides. The carbamato selenides were prepared according to the procedure described above (method B) for the synthesis of the acetamido selenides using benzyl chloroformate (1.1 mmol) instead of acetyl chloride. Reaction yields and physical and spectral data of the reaction products are reported below.

***O*-Benzyl *N*-[2-(Phenylseleno)-2-phenylethyl]carbamate (10a)** (83% yield): oil; ^{1}H NMR δ 7.52−7.06 (m, 15 H), 5.02 (s, 2 H), 5.0 (br s, 1 H), 4.4 (t, 1 H, J = 7.9 Hz), 3.9−3.58 (m, 2 H); ^{13}C NMR δ 155.9, 139.4, 136.3, 135.0, 128.9, 128.5, 128.3, 127.9, 127.7, 127.4, 66.5, 47.0, 45.6; MS *m*/*z* (relative intensity) 304 (1), 157 (13), 146 (68), 128 (100), 91 (17), 77 (27). Anal. Calcd for $C_{22}H_{21}NO_2Se$: C, 64.39; H, 5.16; N, 3.41. Found: C, 64.32; H, 5.28; N, 3.51.

***O*-Benzyl *trans*-*N*-[2-(Phenylseleno)cyclohexyl]carbamate (10b)** (66% yield): mp 88−90 °C; ^{1}H NMR δ 7.6−7.5 (m, 2 H), 7.4−7.1 (m, 8 H), 5.16 (s, 2 H), 5.06 (d, 1 H, J = 8.7 Hz), 3.52 (ddt, 1 H, J = 10.1, 8.7, 4.2 Hz), 2.99 (dt, 1 H, J = 10.1, 3.9 Hz), 2.2−2.0 (m, 2 H), 1.7−1.1 (m, 6 H); ^{13}C NMR δ 155.6, 136.6, 135.6, 128.8, 128.3, 127.9, 127.7, 66.5, 54.4, 48.2, 33.8, 33.7, 26.3, 24.4; MS *m*/*z* (relative intensity) 281 (19), 158 (37), 157 (11), 81 (100), 77 (14). Anal. Calcd for $C_{20}H_{23}NO_2Se$: C, 61.85; H, 5.97; N, 3.61. Found: C, 61.93; H, 5.88; N, 3.74.

***O*-Benzyl *cis*-*N*-[2-(Phenylseleno)cyclohexyl]carbamate (10c)** (22% yield): mp 90−92 °C; ^{1}H NMR δ 7.6−7.4 (m, 2 H), 7.4−7.1 (m, 8 H), 5.24 (d, 1 H, J = 8.7 Hz), 5.02 (AB system, 2 H), 3.85−3.65 (m, 2 H), 2.2−2.0 (m, 1 H), 2.0−1.8 (m, 1 H), 1.8−1.2 (m, 6 H); ^{13}C NMR δ 155.3, 136.5, 133.7, 130.0, 128.9, 128.3, 127.8, 127.1, 66.4, 52.3, 52.1, 32.2, 30.3, 24.0, 22.3; MS *m*/*z* (relative intensity) 281 (26), 158 (25), 157 (11), 81 (100), 77 (11). Anal. Calcd for $C_{20}H_{23}NO_2Se$: C, 61.85; H, 5.97; N, 3.61. Found: C, 61.81; H, 6.04; N, 3.70.

Deselenenylation Reactions. General Procedure. The selenide (1 mmol) was added to a solution of PhSeOTf[18] (1.1 mmol) in acetonitrile or in methylene chloride (10 mL) stirred under nitrogen at 0° C. The progress of the reaction was monitored by TLC and GLC. The crude mixture was filtered over Al_2O_3(Grade III)/Na_2CO_3. The filtrate was dried (Na_2SO_4) and evaporated. The reaction products were obtained in pure form after column chromatography on silica gel using petroleum ether/Et_2O (70/30) as eluant. Reaction yields of isolated products are indicated in Tables 1−4. Physical and spectral data of the reaction products are reported below.

2-(Azidomethyl)tetrahydrofuran (5a): oil; ^{1}H NMR δ 4.16−4.0 (m, 1 H), 3.99−3.73 (m, 2 H), 3.37 (dd, 1 H, J = 12.7, 4.0 Hz), 3.22 (dd, 1 H, J = 15.8, 12.7 Hz), 2.1−1.85 (m, 3 H), 1.77−1.6 (m, 1 H); ^{13}C NMR δ 77.7, 68.4, 54.5, 28.7, 25.8; MS *m*/*z* (relative intensity) 99 (1), 71 (100), 43 (77), 41 (53). Anal. Calcd for $C_5H_9N_3O$: C, 47.23; H, 7.13; N, 33.05. Found: C, 47.16; H, 7.03; N, 33.12.

2-(Azidomethyl)-5-phenyltetrahydrofuran (5b). Isomer A: oil; ^{1}H NMR δ 7.4−7.15 (m, 5 H), 5.07 (dd, 1 H, J = 7.2, 6.2 Hz), 4.51−4.36 (m, 1 H), 3.48 (dd, 1 H, J = 12.7, 4.1 Hz), 3.31 (dd, 1 H, J = 12.7, 5.3 Hz), 2.5−2.3 (m, 1 H), 2.22−2.05 (m, 1 H), 2.02−1.8 (m, 2 H); ^{13}C NMR δ 128.3, 127.3, 125.5, 81.0, 78.3, 54.7, 35.0, 29.4. Isomer B: oil; ^{1}H NMR δ 7.42−7.2 (m, 5 H), 4.91 (dd, 1 H, J = 7.8, 6.4 Hz), 4.34−4.18 (m, 1 H), 3.55−3.33 (m, 2 H), 2.43−2.04 (m, 2 H), 1.99−1.78 (m, 2 H); ^{13}C NMR δ 128.3, 127.3, 125.7, 81.6, 78.0, 54.9, 34.1, 28.8. MS *m*/*z* (relative intensity) (Isomers A and B) 147 (94), 129 (43), 105 (27), 91 (100), 77 (20), 41 (29). Anal. Calcd for $C_{11}H_{13}N_3O$: C, 65.01; H, 6.45; N, 20.67. Found: C, 64.90; H, 6.36; N, 20.81.

2-(Azidomethyl)tetrahydropyran (5c): oil; ^{1}H NMR δ 4.16−3.92 (m, 1 H), 3.62−3.1 (m, 4 H), 2.0−1.32 (m, 6 H); ^{13}C NMR δ 77.9, 69.6, 56.9, 30.2, 27.0, 24.2; MS *m*/*z* (relative intensity) 85 (100), 67 (26), 57 (29), 43 (40), 41 (63). Anal. Calcd for $C_6H_{11}N_3O$: C, 51.05; H, 7.85; N, 29.77. Found: C, 51.15; H, 7.99; N, 29.80.

4-Azido-5-phenyl-4,5-dihydro-3*H*-furan-2-one (5e). *cis*-Isomer: oil; ^{1}H NMR δ 7.48−7.28 (m, 5 H), 5.62 (d, 1 H, J = 4.3 Hz), 4.5 (ddd, 1 H, J = 6.2, 4.3, 1.3 Hz), 2.97 (dd, 1 H, J = 17.6, 6.2 Hz), 2.66 (dd, 1 H, J = 17.6, 1.3 Hz); ^{13}C NMR δ 173.6, 128.9, 128.6, 126.1, 125.1, 83.3, 61.5, 36.2. Anal. Calcd for $C_{10}H_9N_3O_2$: C, 59.11; H, 4.46; N, 20.68. Found: C, 59.19; H, 4.33; N, 20.78. *trans*-Isomer: oil; ^{1}H NMR δ 7.55−7.25 (m, 5 H), 5.33 (d, 1 H, J = 5.0 Hz), 4.23 (ddd, 1 H, J = 7.5, 6.0, 5.0 Hz), 2.97 (dd, 1 H, J = 17.7, 7.5 Hz), 2.66 (dd, 1 H, J = 17.7, 6.0 Hz); ^{13}C NMR δ 171.7, 129.2, 125.1, 84.7, 64.0, 34.4; MS *m*/*z* (relative intensity) 203 (1), 148 (18), 105 (100), 77 (41), 42 (50). Anal. Calcd for $C_{10}H_9N_3O_2$: C, 59.11; H, 4.46; N, 20.68. Found: C, 59.07; H, 4.52; N, 20.55.

6-(Azidomethyl)tetrahydropyran-2-one (5f): oil; ^{1}H NMR δ 4.57−4.32 (m, 1 H), 3.64−3.32 (m, 2 H), 2.75−2.28 (m, 2 H), 2.12−1.54 (m, 4 H); ^{13}C NMR δ 170.1, 78.3, 54.2, 29.1, 24.7, 18.0; MS *m*/*z* (relative intensity) 155 (1), 99 (100), 71 (43), 55 (50), 43 (46), 42 (25), 41 (29). Anal. Calcd for $C_6H_9N_3O_2$: C, 46.45; H, 5.85; N, 27.08. Found: C, 46.54; H, 5.93; N, 27.02.

1-(Methylsulfonyl)-2-(azidomethyl)pyrrolidine (5g): oil; ^{1}H NMR δ 3.97−3.79 (m, 1 H), 3.6−3.28 (m, 4 H), 2.88 (s, 3 H), 2.16−1.84 (m, 4 H); ^{13}C NMR δ 58.7, 54.7, 49.1, 35.0, 29.3, 24.3; MS *m*/*z* (relative intensity) 148 (87), 70 (100), 41 (20). Anal. Calcd for $C_6H_{12}N_4O_2S$: C, 35.28; H, 5.92; N, 27.43. Found: C, 35.21; H, 6.03; N, 27.40.

1-(Benzenesulfonyl)-2-(azidomethyl)pyrrolidine (5h): oil; ^{1}H NMR δ 7.9−7.78 (m, 2 H), 7.68−7.46 (m, 3 H), 3.8−3.63 (m, 1 H), 3.6−3.38 (m, 3 H), 3.28−3.08 (m, 1 H), 1.96−1.43 (m, 4 H); ^{13}C NMR δ 134.3, 132.8, 129.0, 127.3, 58.8, 55.0, 49.3, 29.1, 23.8; MS *m*/*z* (relative intensity) 210 (79), 141 (49), 77 (100), 51 (17), 41 (14). Anal. Calcd for $C_{11}H_{14}N_4O_2S$: C, 49.61; H, 5.30; N, 21.04. Found: C, 49.72; H, 5.25; N, 21.01.

2-Phenyl-3-(ethoxycarbonyl)-5-(azidomethyl)-4,5-dihydrofuran (7a): oil; ^{1}H NMR δ 7.88−7.72 (m, 2 H), 7.46−7.31 (m, 3 H), 4.97−4.79 (m, 1 H), 4.14 (q, 2 H, J = 7.0 Hz), 3.56−3.36 (m, 2 H), 3.22 (dd, 1 H, J = 15.3, 10.5 Hz), 2.89 (dd, 1 H,

J = 15.3, 7.6 Hz), 1.22 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ 164.7, 164.1, 130.3, 129.4, 129.1, 127.5, 102.2, 79.5, 59.7, 54.2, 34.4, 14.0; MS m/z (relative intensity) 273 (1), 216 (14), 171 (22), 122 (17), 115 (18), 105 (100), 77 (37). Anal. Calcd for $C_{14}H_{15}N_3O_3$: C, 61.53; H, 5.53; N, 15.38. Found: C, 61.39; H, 5.62; N, 15.26.

2-Phenyl-3-acetyl-5-(azidomethyl)-4,5-dihydrofuran (7b): oil; ^{1}H NMR δ 7.67−7.48 (m, 5 H), 5.02−4.84 (m, 1 H), 3.54 (dd, 1 H, J = 13.3, 4.1 Hz), 3.48 (dd, 1 H, J = 13.3, 5.6 Hz), 3.25 (dd, 1 H, J = 15.1, 10.6 Hz), 2.93 (dd, 1 H, J = 15.1, 7.5 Hz), 1.98 (s, 3 H); ^{13}C NMR δ 193.8, 164.9, 130.4, 130.3, 128.9, 128.1, 114.3, 80.0, 54.1, 34.2, 28.6; MS m/z (relative intensity) 243 (1), 171 (22), 105 (94), 77 (34), 43 (100). Anal. Calcd for $C_{13}H_{13}N_3O_2$: C, 64.19; H, 5.39; N, 17.27. Found: C, 64.16; H, 5.45; N, 17.37.

2-Methyl-3-benzoyl-5-(azidomethyl)-4,5-dihydrofuran (7c): oil; ^{1}H NMR δ 7.65−7.3 (m, 5 H), 4.92−4.76 (m, 1 H), 3.52 (dd, 1 H, J = 13.1, 3.7 Hz), 3.41 (dd, 1 H, J = 13.1, 6.0 Hz), 3.19 (dd, 1 H, J = 14.8, 10.4 Hz), 2.89 (dd, 1 H, J = 14.8, 7.4 Hz), 1.83 (s, 3H); ^{13}C NMR δ 192.5, 167.5, 140.5, 130.9, 128.1, 127.5, 112.2, 80.2, 54.1, 34.0, 15.0; MS m/z (relative intensity) 243 (6), 185 (27), 105 (100), 77 (64), 43 (52). Anal. Calcd for $C_{13}H_{13}N_3O_2$: C, 64.19; H, 5.39; N, 17.27. Found: C, 64.16; H, 5.45; N, 17.37.

2-Methyl-5-hexyl-4,5-dihydrooxazole (9b): oil; ^{1}H NMR δ 4.58−4.41 (m, 1 H), 3.86 (ddq, 1 H, J = 13.8, 9.5, 1.4 Hz), 3.4 (ddq, 1 H, J = 13.8, 7.5, 1.4 Hz), 1.94 (t, 3 H, J = 1.4 Hz), 1.72−1.19 (m, 10 H), 0.9 (t, 3 H, J = 6.6 Hz); ^{13}C NMR δ 164.6, 79.6, 59.4, 35.2, 31.4, 28.8, 24.8, 22.2, 13.7; MS m/z (relative intensity) 169 (2), 84 (34), 55 (100), 43 (30). Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31; N, 8.27. Found: C, 71.04; H, 11.20; N, 8.38.

2-Methyl-4-hexyl-4,5-dihydrooxazole (9d): mp 77−78 °C; ^{1}H NMR δ 4.3 (dd, 1 H, J = 9.2, 7.8 Hz), 4.12−3.9 (m, 1 H), 3.81 (t, 1 H, J = 7.8 Hz), 1.98 (s, 3 H), 1.72−1.12 (m, 10 H), 0.88 (t, 3 H, J = 7.0 Hz); ^{13}C NMR δ 164.0, 72.2, 66.0, 35.7, 31.4, 28.9, 25.6, 22.2, 13.6, 13.4; MS m/z (relative intensity) 169 (1), 140 (15), 99 (33), 84 (100), 56 (72), 43 (57). Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31; N, 8.27. Found: C, 71.04; H, 11.20; N, 8.38.

2-Phenyl-5-(azidomethyl)-4,5-dihydrooxazole (9e): oil; ^{1}H NMR δ 8.06−7.9 (m, 2 H), 7.58−7.35 (m, 3 H), 4.96−4.82 (m, 1 H), 4.15 (dd, 1 H, J = 15.0, 9.8 Hz), 3.82 (dd, 1 H, J = 15.0, 7.0 Hz), 3.46 (d, 2 H, J = 5.2 Hz); ^{13}C NMR δ 163.5, 131.3, 128.2, 128.1, 127.2, 78.0, 57.6, 53.8. Anal. Calcd for $C_{10}H_{10}N_4O$: C, 59.40; H, 4.98; N, 27.71. Found: C, 59.49; H, 4.87; N, 27.63.

2-Phenyl-4,5-dipropyl-4,5-dihydrooxazole (9g): oil; ^{1}H NMR δ 8.2−7.85 (m, 4 H), 7.52−7.39 (m, 6 H), 4.74−4.55 (m, 1 H), 4.36−4.08 (m, 2 H), 3.9−3.74 (m, 1 H), 1.82−1.41 (m, 16 H), 1.05−0.85 (m, 12 H); ^{13}C NMR δ 162.3, 130.7, 128.3, 128.2, 127.9, 84.6, 82.5, 71.6, 67.9, 38.0, 32.5, 31.3, 20.3, 19.8, 18.7, 18.3, 14.0, 13.9, 13.7; MS m/z (relative intensity) (isomer A): 231 (5), 188 (100), 130 (43), 104 (48), 77 (28); (isomer B): 231 (8), 188 (100), 130 (91), 104 (74), 77 (45). Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.83; H, 9.09; N, 6.12.

***cis*-(±)-8-Methyl-6b,9a-dihydroacenaphth[1,2-*d*]oxazole (9i):** mp 125−126 °C; ^{1}H NMR δ 7.85−7.69 (m, 2 H), 7.64−7.49 (m, 4 H), 6.18 (d, 1 H, J = 7.5 Hz), 5.91 (dq, 1 H, J = 7.5, 1.1 Hz), 1.94, (d, 3 H, J = 1.1 Hz); ^{13}C NMR δ 165.3, 142.9, 140.5, 131.7, 128.5, 128.0, 125.9, 124.3, 122.0, 120.8, 84.4, 75.3, 14.1; MS m/z (relative intensity) 209 (77), 168 (100), 140 (67), 84 (31), 43 (27). Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.27; H, 5.38; N, 6.76.

5-Phenyl-4,5-dihydrooxazol-2-one (11a): oil; ^{1}H NMR δ 7.46−7.3 (m, 5 H), 6.64 (br s, 1 H), 5.6 (dd, 1 H, J = 8.8, 8.2 Hz), 3.98 (dd, 1 H, J = 8.8, 8.2 Hz), 3.54 (t, 1 H, J = 8.2 Hz); ^{13}C NMR δ 160.0, 138.5, 128.8, 125.6, 77.8, 48.2; MS m/z (relative intensity) 163 (19), 107 (100), 79 (30), 77 (11). Anal. Calcd for $C_9H_9NO_2$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.29; H, 5.61; N, 8.49.

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