

A New Seleno-Aza-Payne-Type Rearrangement of Aziridinylmethyl Tosylates Mediated by Tetraselenotungstate

Devarajulu Sureshkumar,^[a] Srinivasamurthy Koutha,^[a] and Srinivasan Chandrasekaran*^[a,b]

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Tetraselenotungstate **1** reacts with simple (*N*-tosylaziridinyl)-methyl tosylate derivatives to give allylamine derivatives as the only products by an unprecedented seleno-aza-Payne-type rearrangement. When the methodology is extended to disubstituted (*N*-tosylaziridinyl)methyl tosylates, regio- and stereospecific ring-opening of the aziridines occurs to afford

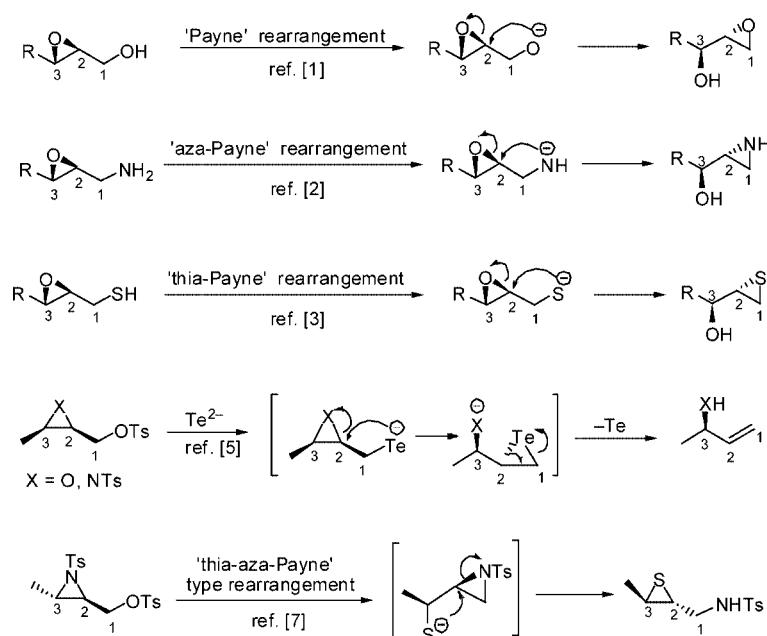
allylamine derivatives as the major products and cyclic five-membered diselenides as the minor products in good yields under mild reaction conditions without using any Lewis acid or base.

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Introduction

Intramolecular nucleophilic displacement of aziridines/epoxides with oxygen (Payne rearrangement),^[1] nitrogen (aza-Payne),^[2] sulfur (thia-Payne),^[1c,3] selenium^[4] and tellurium

nucleophiles^[5] are well demonstrated in the literature (Scheme 1). Ring-opening of aziridines with nucleophiles and subsequent reaction manipulation have found widespread application in the synthesis of biologically important acyclic and cyclic compounds.^[6] We recently reported a



Scheme 1. Different types of Payne rearrangement.

[a] Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India
Fax: +91-80-2360-2423
E-mail: scn@orgchem.iisc.ernet.in

[b] Jawaharlal Nehru Center for Advanced Scientific Research, Jakkur, Bangalore, India

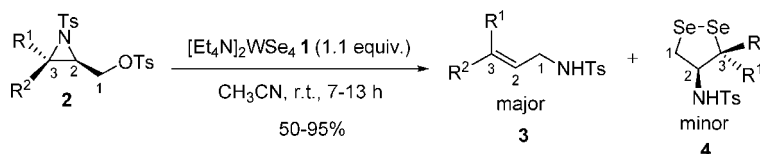
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thia-aza-Payne-type rearrangement of aziridinylmethyl tosylate derivatives using benzytriethylammonium tetrathiomolybdate.^[7]

In continuation of our work on the use of tetraethylammonium tetraselenotungstate^[8] ([Et₄N]₂WSe₄, **1**) as an efficient selenium transfer reagent, it was of interest to study



Scheme 2. New seleno-aza-Payne-type rearrangement.



Scheme 3. Seleno-aza-Payne-type rearrangement of aziridinylmethyl tosylates.

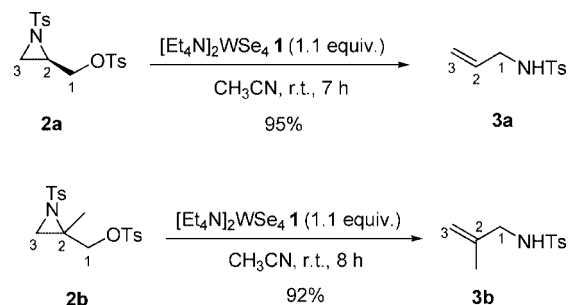
the ring-opening of (*N*-tosylaziridinyl)methyl tosylate derivatives using tetraselenotungstate **1**.^[9] We found that (*N*-tosylaziridinyl)methyl tosylates undergo an unusual rearrangement with **1** to give allylamine derivatives with excellent regio- and stereocontrol (Scheme 2).

In this article we report the results of regio- and stereo-specific nucleophilic ring-openings of aziridinylmethyl tosylate derivatives **2** with **1** to afford a number of allylamine derivatives **3** (by a seleno-aza-Payne-type rearrangement) in good yields as the major products, together with cyclic diselenides **4** as the minor products (Scheme 3). The overall result of this rearrangement is that nitrogen migration occurs from C2/C3 to the C1 carbon atom to form the allylamine derivative through the formation of a selenirane intermediate. This rearrangement is totally different from the well-known Payne,^[1] aza-Payne,^[2] thia-Payne^[3] and telluride-mediated^[5] rearrangements reported in the literature so far. In all the previously reported cases,^[1-5] leaving groups such as tosylate or mesylate undergo reaction first, followed by aziridine ring-opening to give 2-substituted allylamine or allyl alcohol derivatives, whereas in the present case the ring-opening of the aziridine takes place first, followed by the reaction of the tosylate to give 2,3-disubstituted allylamine derivatives **3** as the major products and cyclic five-membered diselenides **4** as the minor products (Scheme 3).

Results and Discussion

Ring-Opening of Mono- and 2,2-Disubstituted (*N*-Tosylaziridinyl)methyl Tosylates with **1**

Treatment of simple ($\pm$)-aziridinylmethyl tosylate **2a**^[10] with tetraselenotungstate **1** (1.1 equiv., CH₃CN, 28 °C, 7 h) led to the formation of allylamine derivative^[11] **3a** as the only product in almost quantitative yield. In the reaction of the 2,2-disubstituted aziridinylmethyl tosylate **2b**, allylamine derivative **3b** was also the only product (Scheme 4).

Scheme 4. Ring-opening of mono- and 2,2-disubstituted aziridinylmethyl tosylates with **1**.

Ring-Opening of 2,3-Disubstituted (*N*-Tosylaziridinyl)methyl Tosylates with **1**

In order to address the issue of whether the reaction of **1** takes place at the tosylate first or the aziridine ring opens first, and also to assess the regio- and stereospecificity of aziridine ring-opening, this methodology was then extended to the reaction of the *trans*-2,3-disubstituted aziridinylmethyl tosylate^[5b,12] **2c** with **1** (1.1 equiv., CH₃CN, 28 °C, 11 h). This led to the formation of the *trans*-allylamine derivative **3c** as the major product and the cyclic diselenide **4c** as the minor product (4:1) with excellent regio- and stereocontrol (Scheme 5).

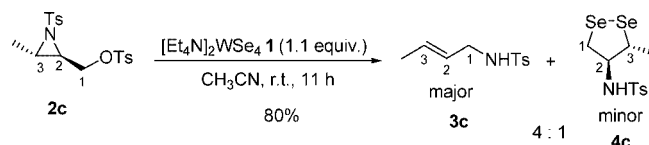
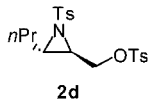
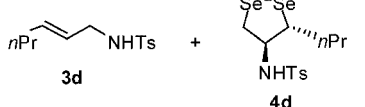
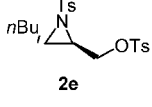
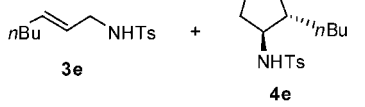
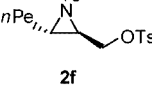
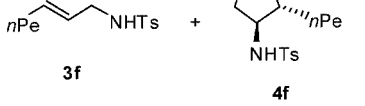
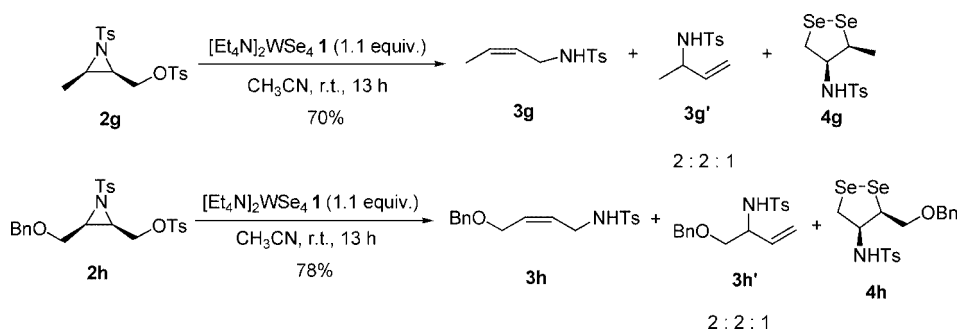
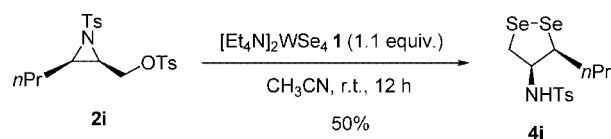
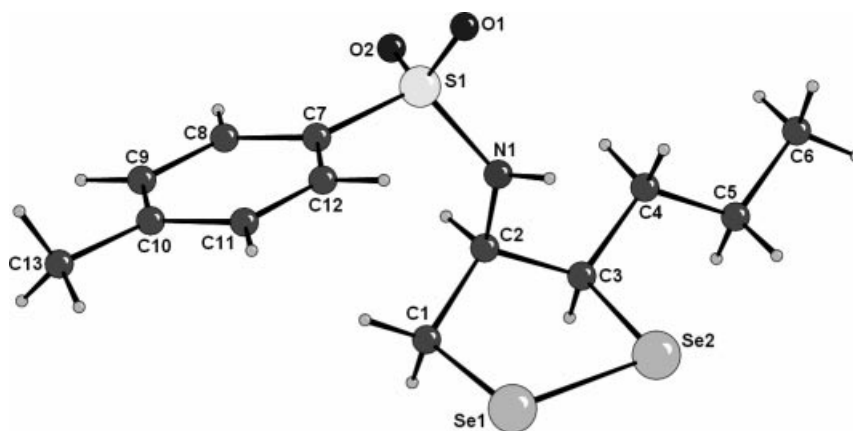
Scheme 5. Regio- and stereospecific ring-opening of aziridinylmethyl tosylate **2c** with **1**.

Table 1. Synthesis of *trans*-allylamine and cyclic diselenide derivatives.

Entry	<i>trans</i> -Aziridine tosylate	Product	Ratio	Time [h]	Yield [%]
1	 2d	 3d + 4d	4 : 1	10	81
2	 2e	 3e + 4e	4 : 1	11	86
3	 2f	 3f + 4f	4 : 1	12	80

Scheme 6. Ring-opening of *cis*-aziridinylmethyl tosylates **2g** and **2h** with **1**.

Subsequently, the reactions between **1** and a number of *trans*-2,3-disubstituted aziridinylmethyl tosylates (**2d–2f**) were studied, and in all the cases the reactions proceeded smoothly to give the *trans*-allylamine derivatives (**3d–3f**) as the major products and the cyclic diselenides (**4d–4f**) as the minor products, with excellent regio- and stereocontrol (Table 1).

Scheme 7. Ring-opening of *cis*-aziridinylmethyl tosylate **2i** with **1**.Figure 1. X-ray CAMERON diagram of compound **4i**.

The reaction between the *cis*-2,3-disubstituted aziridinylmethyl tosylate **2g** and **1** (1.1 equiv., CH₃CN, 28 °C, 13 h) led to the formation of a mixture of allylamine derivatives **3g** and **3g'** as major products and the cyclic diselenide **4g** as the minor product (2:2:1). Similarly, **2h** gave **3h**, **3h'** and **4h** in 2:2:1 ratio on treatment with **1** (Scheme 6).

The *cis*-2,3-disubstituted aziridinylmethyl tosylate **2i** failed to undergo the rearrangement, but gave the cyclic diselenide **4i** as the only product in 50% yield (Scheme 7). The regio- and stereochemical outcome of the reaction was confirmed by single-crystal X-ray analysis of compound **4i**^[13] (Figure 1).

Ring-Opening of 2,3,3-Trisubstituted (*N*-Tosylaziridinyl)-methyl Tosylate **2j** with **1**

The reaction between the 2,3,3-trisubstituted aziridinylmethyl tosylate **2j** and **1** (1.1 equiv., CH₃CN, 28 °C, 8 h) furnished the tertiary allylamine derivative **3j** as the major product in good yield, together with the cyclic diselenide **4j**

(4:1) as the minor product (Scheme 8). The structure of cyclic diselenide **4j**^[14] was confirmed by single-crystal X-ray analysis (Figure 2).

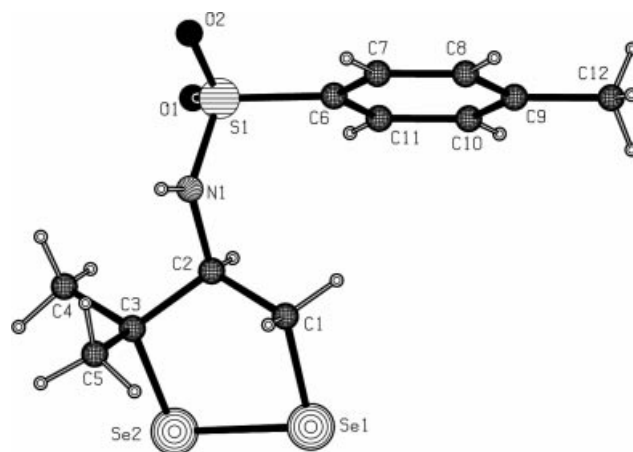
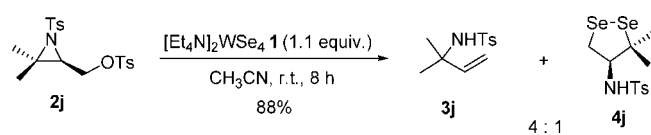


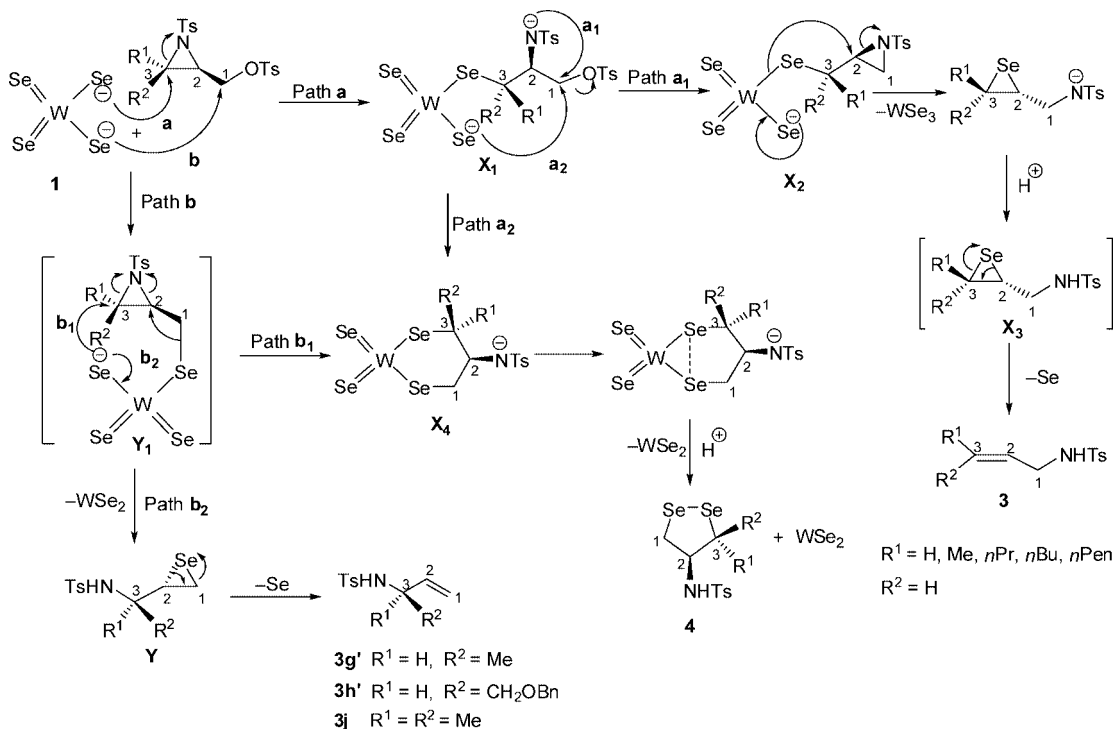
Figure 2. X-ray PLATON diagram of compound **4j**.



Scheme 8. Ring-opening of the trisubstituted aziridinylmethyl tosylate **2j** with **1**.

Tentative Mechanism of the Seleno-Aza-Payne Type Rearrangement

A tentative mechanism for the formation of products **3** and **4**, based on the results of this investigation, is presented in Scheme 9. In the course of this seleno-aza-Payne-type re-



Scheme 9. Tentative mechanism for the formation of **3** and **4**.

arrangement to form **3**, nitrogen migration occurs from C2/ C3 to the C1 position, with the elimination of elemental selenium from selenirane intermediate **X₃** under the given reaction conditions.^[4] During the formation of **3**, the reaction follows Path **a** in all the substrates, except in the case of **2j**. In Path **a**, tetraselenotungstate **1** attacks the aziridine at C3 in an S_N2 fashion to give intermediate **X₁**, which can further undergo two types of reactions, along Path **a₁** or Path **a₂**. In Path **a₁**, intramolecular displacement of a tosyl (OTs) group by a nitrogen nucleophile would give a new aziridine intermediate **X₂**, which would be followed by ring-opening of the newly formed aziridine by the selenium nucleophile to give selenirane intermediate **X₃** with the elimination of WSe₃ as the byproduct, with **X₃** finally undergoing elimination of selenium to give allylamine derivatives **3** (observed experimentally) under the given reaction conditions (Path **a₁**). In Path **a₂**, intramolecular displacement of the tosyl group by the selenium nucleophile would give the six-membered intermediate **X₄**, which could undergo Se–Se bond formation by an internal redox process^[15] with the elimination of WSe₂ as byproduct to give the cyclic diselenide derivatives **4** (observed experimentally).

The reaction between compound **2j** and **1** appears to follow Path **b** exclusively. In Path **b**, tetraselenotungstate **1** at-

tacks the aziridine at the C1 position in an S_N2 fashion to give intermediate **Y₁**, which can further undergo two types of reactions: either along Path **b₁** or Path **b₂**. Along Path **b₁**, nucleophilic ring-opening of the aziridine at the more substituted carbon atom^[16] C3 with the selenium nucleophile would give a six-membered intermediate **X₄**, which would further undergo a redox transformation to give the cyclic diselenide derivatives **4** as described in the case of Path **a₂**. Along Path **b₂**, the selenium nucleophile attacks the aziridine at C2 to give the selenirane intermediate **Y** with the elimination of WSe₂ as the byproduct. The intermediate **Y** can be expected to undergo selenium elimination to give allylamine derivatives **3** (observed experimentally only in the cases of **2g**, **2h** and **2j**). In the cases of **2g** and **2h**, the reactions appear to follow both Path **a** and Path **b** to give mixtures of allylamine derivatives and cyclic diselenide derivatives (Scheme 6).

X-ray Crystallographic Studies of Compounds **4i** and **4j**

Single crystals of cyclic diselenides **4i** and **4j** were grown at room temperature and under ambient pressure by slow concentration of their dilute solutions in chloroform and

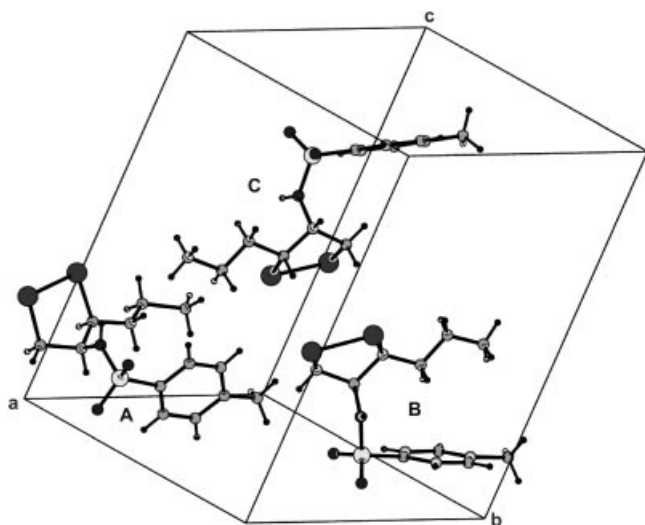


Figure 3. The three molecules in the asymmetric unit of compound **4i**.

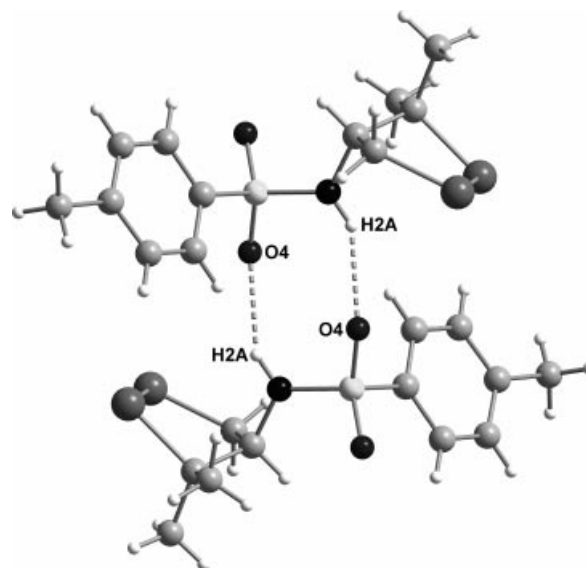


Figure 5. The pseudoaxial conformer of **4j** forms a centrosymmetric dimer through N–H···O hydrogen bonding.

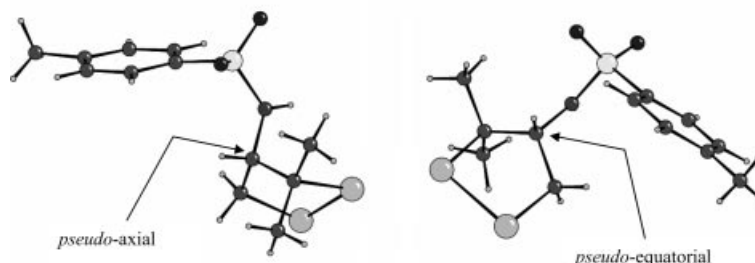


Figure 4. CAMERON diagram of compound **4j** showing two conformers in the asymmetric unit.

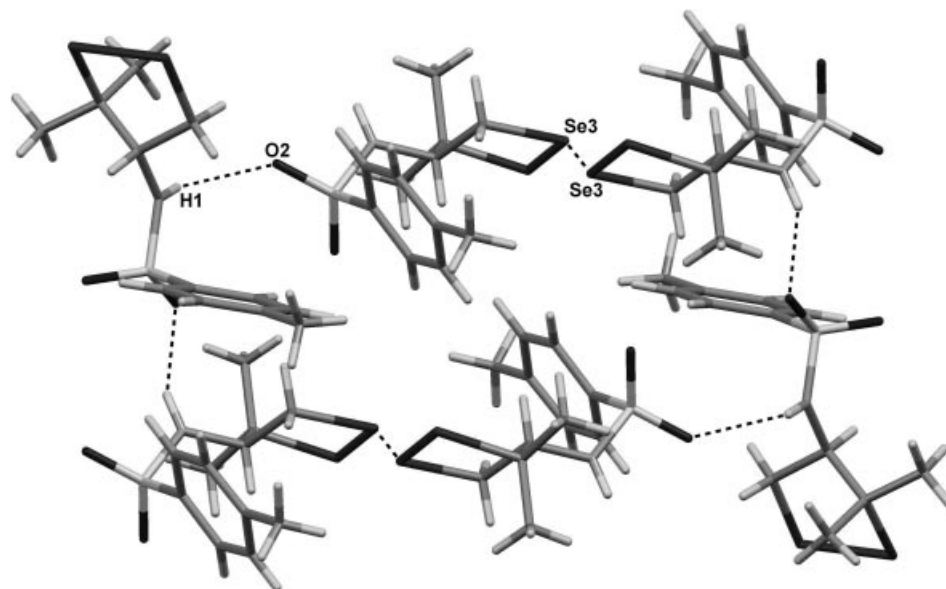


Figure 6. The pseudoequatorial conformer of **4j** forms a hexamer through N–H $\cdots$ O hydrogen bonding and Se $\cdots$ Se interaction.

methanol mixtures. In each case a crystal of suitable size and well-defined morphology was selected from the batch obtained and was then mounted inside a Lindemann capillary. Common features of the crystal analyses are that all compounds crystallize in the anhydrous state and that N–H $\cdots$ O hydrogen bonds are responsible for the supramolecular assembly of the molecules.

In compound **4i**, there are three molecules in the asymmetric unit, in which molecules A and B exist in similar conformations (i.e., tosyl group and propyl groups are *cis* to each other), whereas in the case of molecule C, tosyl and propyl groups are *trans* to each other as shown in Figure 3.

Interestingly, in compound **4j** we observed that there are two conformers present in the asymmetric unit. In one conformer the *N*-substituent exists in a pseudoaxial position, while in the other it exists in a pseudoequatorial position, as shown in Figure 4.

In the X-ray structure of **4j**, the pseudoaxial conformer forms a dimer through intermolecular N–H $\cdots$ O (N2–H2A $\cdots$ O4: 2.271 Å; 142.44°) hydrogen bonding with another pseudoaxial conformer (Figure 5), whereas the pseudoequatorial conformer forms a hexamer through both intermolecular N–H $\cdots$ O (N1–H1 $\cdots$ O2: 2.291 Å; 130.17°) hydrogen bonding and Se $\cdots$ Se (Se3 $\cdots$ Se3: 3.423 Å; 149.99°) interaction with other pseudoequatorial conformers as shown in Figure 6.

Conclusions

We have shown that (*N*-tosylaziridinyl)methyl tosylates undergo a new type of seleno-aza-Payne rearrangement with **1** to give allylamine derivatives as the major products and cyclic diselenides as the minor products with good regio- and stereocontrol. Reasonable mechanisms for the formation of the products have been postulated. The ready

availability of aziridines both in racemic and in optically pure form and the ease and effectiveness of this methodology should make this a useful addition for the synthesis of allylamine derivatives with excellent regio- and stereocontrol.

Experimental Section

General Experimental Procedures: All reactions were performed in oven-dried apparatus, and reaction mixtures were stirred magnetically. Melting points reported are uncorrected. Infrared spectra were recorded using an FT-IR instrument and the frequencies are reported in wave number (cm^{−1}). ¹H and ¹³C NMR spectra were recorded with a 300 MHz/400 MHz and 75 MHz/100 MHz spectrometer, respectively. Chemical shifts are reported in parts per million downfield from the internal reference (tetramethylsilane). Multiplicity is indicated using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad). Coupling constants are reported wherever necessary in Hertz (Hz). Mass spectra were recorded with a Q-TOF electrospray instrument.

General Procedure for the Synthesis of (*N*-Tosylaziridinyl)methyl Tosylates:^[5,10] Pyridine (0.17 mL, 2.1 mmol), DMAP (10 mg, 0.08 mmol) and *p*-toluenesulfonyl chloride (0.270 g, 1.4 mmol) were added at −15 °C to a solution of the appropriate aziridinyl-methanol^[7,12] (0.68 mmol) in CH₂Cl₂ (2 mL). After stirring at −15 °C for 24 h, the solution was diluted with diethyl ether (50 mL) and washed with water, HCl (1 M), saturated NaHCO₃ and water. The organic phase was dried with MgSO₄ and concentrated in vacuo. Chromatography on silica gel (EtOAc/hexanes 20%) gave the corresponding tosylates **2** in high purity.

Compound 2b: *R*_f = 0.60 (EtOAc/hexanes, 3:7). Yield: 0.281 g, 91%; m.p. 90 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.77 (d, *J* = 8.1 Hz, 4 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 7.28 (d, *J* = 8.1 Hz, 2 H), 4.03 (d, *J* = 10.5 Hz, 1 H), 3.93 (d, *J* = 10.5 Hz, 1 H), 2.61 (s, 1 H), 2.46 (s, 3 H), 2.44 (s, 3 H), 2.37 (s, 1 H), 1.67 (s, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 145.2, 144.4, 136.9, 132.5, 129.9, 129.6,

127.9, 127.5, 72.9, 46.6, 39.0, 21.7, 21.6, 15.9 ppm. IR (neat): $\tilde{\nu}_{\max}$ = 1596, 1367, 1321, 1161, 972, 832, 670 cm^{-1} . HR-MS: calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_5\text{S}_2$ $[\text{M} + \text{Na}]^+$ 418.0759; found 418.0766.

Compound 2c: R_f = 0.65 (EtOAc/hexanes, 3:7). Yield: 0.210 g, 78%. ^1H NMR (300 MHz, CDCl_3): δ = 7.79 (d, J = 8.4 Hz, 2 H), 7.64 (d, J = 8.4 Hz, 2 H), 7.30 (d, J = 8.4 Hz, 4 H), 4.17 (dd, J = 11.0, 5.7 Hz, 1 H), 3.96 (dd, J = 11.0, 6.3 Hz, 1 H), 3.04–2.99 (m, 1 H), 2.79–2.71 (m, 1 H), 2.44 (s, 6 H), 1.56 (d, J = 6.3 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 145.1, 144.3, 137.0, 132.4, 129.8, 129.5, 127.8, 127.4, 68.4, 45.0, 43.6, 21.7, 21.6, 14.1 ppm. IR (neat): $\tilde{\nu}_{\max}$ = 1597, 1495, 1453, 1361, 1324, 1177, 1092, 970, 815, 709, 685, 664 cm^{-1} . HR-MS: calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_5\text{S}_2$ $[\text{M} + \text{Na}]^+$ 418.0759; found 418.0768.

Compound 2d: R_f = 0.70 (EtOAc/hexanes, 3:7). Yield: 0.218 g, 76%. ^1H NMR (300 MHz, CDCl_3): δ = 7.79 (d, J = 8.1 Hz, 2 H), 7.68 (d, J = 8.1 Hz, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.31 (d, J = 8.1 Hz, 2 H), 4.26 (dd, J = 11.4, 6.3 Hz, 1 H), 4.14 (dd, J = 11.4, 6.0 Hz, 1 H), 2.98–2.93 (m, 1 H), 2.73–2.67 (m, 1 H), 2.44 (s, 3 H), 2.43 (s, 3 H), 1.85–1.63 (m, 2 H), 1.46–1.23 (m, 2 H), 0.89 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 145.1, 144.3, 136.7, 132.4, 129.9, 129.5, 127.9, 127.5, 68.0, 47.5, 44.9, 30.9, 21.6, 21.5, 20.6, 13.5 ppm. IR (neat): $\tilde{\nu}_{\max}$ = 1597, 1365, 1323, 1160, 966, 814, 693 cm^{-1} . HR-MS: calcd. for $\text{C}_{20}\text{H}_{25}\text{NO}_5\text{S}_2$ $[\text{M} + \text{Na}]^+$ 446.1072; found 446.1086.

Compound 2e: R_f = 0.70 (EtOAc/hexanes, 3:7). Yield: 0.213 g, 72%. ^1H NMR (300 MHz, CDCl_3): δ = 7.79 (d, J = 8.4 Hz, 2 H), 7.68 (d, J = 8.4 Hz, 2 H), 7.32 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 8.4 Hz, 2 H), 4.27 (dd, J = 10.8, 5.7 Hz, 1 H), 4.14 (dd, J = 10.8, 6.3 Hz, 1 H), 2.98–2.93 (m, 1 H), 2.71–2.66 (m, 1 H), 2.45 (s, 3 H), 2.44 (s, 3 H), 1.77–1.70 (m, 2 H), 1.29–1.27 (m, 4 H), 0.85 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 145.1, 144.3, 136.7, 132.4, 129.9, 129.5, 127.9, 127.5, 127.4, 68.0, 47.7, 44.9, 29.4, 28.8, 22.0, 21.6, 21.5, 13.8 ppm. IR (neat): $\tilde{\nu}_{\max}$ = 1597, 1364, 1324, 1160, 1094, 965, 814, 693, 667 cm^{-1} . HR-MS: calcd. for $\text{C}_{21}\text{H}_{27}\text{NO}_5\text{S}_2$ $[\text{M} + \text{Na}]^+$ 460.1228; found 460.1239.

Compound 2f: R_f = 0.70 (EtOAc/hexanes, 3:7). Yield: 0.184 g, 60%. ^1H NMR (300 MHz, CDCl_3): δ = 7.79 (d, J = 8.4 Hz, 2 H), 7.68 (d, J = 8.4 Hz, 2 H), 7.32 (d, J = 8.4 Hz, 2 H), 7.30 (d, J = 8.4 Hz, 2 H), 4.27 (dd, J = 10.8, 5.7 Hz, 1 H), 4.15 (dd, J = 10.8, 6.3 Hz, 1 H), 2.96 (dd, J = 10.2, 5.7 Hz, 1 H), 2.69 (dd, J = 10.2, 6.6 Hz, 1 H), 2.44 (s, 3 H), 2.43 (s, 3 H), 1.74–1.69 (m, 1 H), 1.28–1.24 (m, 7 H), 0.85 (t, J = 6.3 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 145.1, 144.3, 136.7, 132.4, 129.9, 129.5, 127.8, 127.5, 67.9, 47.7, 44.9, 31.0, 29.0, 26.9, 22.3, 21.6, 21.5, 13.8 ppm. IR (neat): $\tilde{\nu}_{\max}$ = 1597, 1365, 1325, 1160, 1095, 969, 814, 693, 666 cm^{-1} . HR-MS: calcd. for $\text{C}_{22}\text{H}_{29}\text{NO}_5\text{S}_2$ $[\text{M} + \text{Na}]^+$ 474.1385; found 474.1385.

Compound 2g: R_f = 0.70 (EtOAc/hexanes, 3:7). Yield: 0.188 g, 70%. ^1H NMR (300 MHz, CDCl_3): δ = 7.76 (d, J = 8.1 Hz, 2 H), 7.68 (d, J = 8.1 Hz, 2 H), 7.33 (d, J = 8.1 Hz, 4 H), 3.99 (d, J = 6.3 Hz, 2 H), 3.03–2.92 (m, 2 H), 2.45 (s, 6 H), 1.17 (d, J = 5.4 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 145.2, 144.8, 134.5, 132.3, 129.9, 129.7, 127.8, 65.9, 40.7, 38.9, 21.6, 11.9 ppm. IR (neat): $\tilde{\nu}_{\max}$ = 1592, 1371, 1331, 1168, 966, 835, 671 cm^{-1} . HR-MS: calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_5\text{S}_2$ $[\text{M} + \text{Na}]^+$ 418.0759; found 418.0759.

Compound 2h: R_f = 0.65 (EtOAc/hexanes, 3:7). Yield: 0.232 g, 68%. ^1H NMR (300 MHz, CDCl_3): δ = 7.77 (d, J = 8.1 Hz, 2 H), 7.62 (d, J = 8.1 Hz, 2 H), 7.28–7.21 (m, 9 H), 4.38 (brs, 2 H), 4.09 (dd, J = 11.4, 5.1 Hz, 1 H), 3.99 (dd, J = 11.4, 6.9 Hz, 1 H), 3.49 (d, J = 4.8 Hz, 1 H), 3.15–3.04 (m, 2 H), 2.41 (s, 6 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 145.1, 144.9, 137.2, 133.9, 132.1, 129.8, 129.6, 128.3, 127.9, 127.7, 127.5, 72.9, 66.3, 65.9, 41.6, 39.9,

21.5 ppm. IR (neat): $\tilde{\nu}_{\max}$ = 1597, 1366, 1330, 1189, 1093, 972, 815, 727, 666 cm^{-1} . HR-MS: calcd. for $\text{C}_{25}\text{H}_{27}\text{NO}_6\text{S}_2$ $[\text{M} + \text{Na}]^+$ 524.1177; found 524.1191.

Compound 2i: R_f = 0.70 (EtOAc/hexanes, 3:7). Yield: 0.186 g, 65%. ^1H NMR (300 MHz, CDCl_3): δ = 7.77 (d, J = 8.1 Hz, 2 H), 7.69 (d, J = 8.1 Hz, 2 H), 7.33 (d, J = 8.1 Hz, 4 H), 3.99 (d, J = 6.6 Hz, 2 H), 3.04 (dd, J = 13.8, 6.6 Hz, 1 H), 2.86 (dd, J = 13.8, 7.5 Hz, 1 H), 2.45 (s, 6 H), 1.44–1.17 (m, 4 H), 0.84 (t, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 145.2, 144.8, 134.3, 132.2, 129.9, 129.6, 127.9, 127.8, 66.1, 43.6, 40.8, 28.6, 21.6, 20.4, 13.5 ppm. IR (neat): $\tilde{\nu}_{\max}$ = 1597, 1366, 1328, 1161, 1092, 975, 815, 720, 667 cm^{-1} . HR-MS: calcd. for $\text{C}_{20}\text{H}_{25}\text{NO}_5\text{S}_2$ $[\text{M} + \text{Na}]^+$ 446.1072; found 446.1081.

Compound 2j: R_f = 0.60 (EtOAc/hexanes, 3:7). Yield: 0.183 g, 66%. ^1H NMR (300 MHz, CDCl_3): δ = 7.77 (d, J = 8.1 Hz, 2 H), 7.64 (d, J = 8.1 Hz, 2 H), 7.31 (d, J = 8.1 Hz, 2 H), 7.29 (d, J = 8.1 Hz, 2 H), 4.02 (dd, J = 10.8, 5.7 Hz, 1 H), 3.86 (dd, J = 10.8, 6.6 Hz, 1 H), 3.13 (t, J = 6.6 Hz, 1 H), 2.45 (s, 3 H), 2.43 (s, 3 H), 1.22 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 145.1, 144.0, 137.5, 132.3, 129.9, 129.5, 127.8, 127.3, 67.3, 51.2, 48.1, 21.6, 21.5, 21.2, 20.8 ppm. IR (neat): $\tilde{\nu}_{\max}$ = 1595, 1366, 1326, 965, 816, 682, 665 cm^{-1} . HR-MS: calcd. for $\text{C}_{19}\text{H}_{23}\text{NO}_5\text{S}_2$ $[\text{M} + \text{Na}]^+$ 432.0915; found 432.0927.

General Procedure for the Seleno-Aza-Payne-Type Rearrangement:

Tetraselenotungstate **1** (0.417 g, 0.55 mmol) was added in one portion to a well-stirred solution of the appropriate aziridinylmethyl tosylate **2** (0.50 mmol) in CH_3CN (7 mL), and the mixture was stirred at room temperature (28 °C) for the given time (7–13 h). The solvent was evaporated under reduced pressure and the black residue was extracted with $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (1:5, 3×10 mL) and filtered through a Celite pad. The filtrate was concentrated, and the residue was purified by flash column chromatography on silica gel using ethyl acetate and toluene (2%) as eluent to give the corresponding allylamine derivatives **3** and cyclic diselenides **4** in good yields.

Compound 3a: R_f = 0.70 (EtOAc/toluene, 3:7). Yield: 0.100 g, 95%. ^1H NMR (300 MHz, CDCl_3): δ = 7.77 (d, J = 8.1 Hz, 2 H), 7.31 (d, J = 8.1 Hz, 2 H), 5.76–5.65 (m, 1 H), 5.17 (d, J = 17.0 Hz, 1 H), 5.09 (d, J = 10.2 Hz, 1 H), 4.84 (t, J = 6.0 Hz, 1 H), 3.58 (t, J = 6.0 Hz, 1 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.4, 136.8, 132.9, 129.7, 127.1, 117.6, 45.7, 21.5 ppm. IR (neat): $\tilde{\nu}_{\max}$ = 3283, 1429, 1323, 1159, 1093, 814, 666 cm^{-1} . HR-MS: calcd. for $\text{C}_{10}\text{H}_{13}\text{NO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 234.0565; found 234.0568.

Compound 3b: R_f = 0.70 (EtOAc/toluene, 3:7). Yield: 0.104 g, 92%. ^1H NMR (300 MHz, CDCl_3): δ = 7.76 (d, J = 8.1 Hz, 2 H), 7.31 (d, J = 8.1 Hz, 2 H), 4.93 (t, J = 6.3 Hz, 1 H), 4.83 (d, J = 14.7 Hz, 2 H), 3.47 (d, J = 6.3 Hz, 2 H), 2.43 (s, 3 H), 1.68 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.3, 140.4, 136.8, 129.6, 127.0, 112.6, 48.9, 21.4, 20.0 ppm. IR (neat): $\tilde{\nu}_{\max}$ = 3284, 1446, 1324, 1159, 1093, 813, 662 cm^{-1} . HR-MS: calcd. for $\text{C}_{11}\text{H}_{15}\text{NO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 248.0721; found 248.0718.

Compound 3c: R_f = 0.60 (EtOAc/toluene, 3:7). Yield: 0.072 g, 64%. ^1H NMR (300 MHz, CDCl_3): δ = 7.75 (d, J = 8.1 Hz, 2 H), 7.31 (d, J = 8.1 Hz, 2 H), 5.61–5.51 (m, 1 H), 2.63 (s, 1 H), 5.37–5.30 (m, 1 H), 4.45 (brs, 3 H), 3.50 (t, J = 6.3 Hz, 1 H), 2.43 (s, 3 H), 1.60 (d, J = 6.3 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.4, 136.9, 129.8, 129.6, 127.1, 125.6, 45.3, 21.5, 17.6 ppm. IR (neat): $\tilde{\nu}_{\max}$ = 3283, 1434, 1324, 1159, 1093, 814, 660 cm^{-1} . HR-MS: calcd. for $\text{C}_{11}\text{H}_{15}\text{NO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 248.0721; found 248.0718.

Compound 4c: R_f = 0.65 (EtOAc/toluene, 3:7). Yield: 0.031 g, 16%. ^1H NMR (300 MHz, CDCl_3): δ = 7.78 (d, J = 8.1 Hz, 2 H), 7.33

(d, J = 8.1 Hz, 2 H), 5.33 (d, J = 15.3 Hz, 1 H), 4.64 (d, J = 8.7 Hz, 1 H), 3.69 (m, 1 H), 3.25 (dd, J = 10.8, 3.3 Hz, 1 H), 3.06 (d, J = 10.8 Hz, 1 H), 2.45 (s, 3 H), 1.37 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.8, 138.1, 129.9, 126.9, 66.2, 51.9, 34.6, 22.8, 21.6 ppm. ^{77}Se NMR (76 MHz, CDCl_3): δ = 360.4, 205.4 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3275, 1333, 1159, 1092, 1040, 814, 658 cm^{-1} . HR-MS: calcd. for $\text{C}_{11}\text{H}_{15}\text{NO}_2\text{SSe}_2$ [$\text{M} + \text{Na}$] $^{+}$ 407.9052; found 407.9058.

Compound 3d: R_f = 0.65 (EtOAc/toluene, 3:7). Yield: 0.082 g, 65%. ^1H NMR (300 MHz, CDCl_3): δ = 7.75 (d, J = 8.1 Hz, 2 H), 7.31 (d, J = 8.1 Hz, 2 H), 5.59–5.48 (m, 1 H), 5.36–5.26 (m, 1 H), 4.39 (t, J = 5.4 Hz, 1 H), 3.52 (t, J = 6.0 Hz, 2 H), 2.43 (s, 3 H), 1.93 (q, J = 13.8, 6.9 Hz, 2 H), 1.37–1.22 (m, 2 H), 0.84 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.4, 137.0, 134.9, 129.7, 127.1, 124.5, 45.4, 34.1, 22.0, 21.5, 13.6 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3283, 1325, 1159, 1094, 813, 667 cm^{-1} . HR-MS: calcd. for $\text{C}_{13}\text{H}_{19}\text{NO}_2\text{S}$ [$\text{M} + \text{Na}$] $^{+}$ 276.1034; found 276.1040.

Compound 4d: R_f = 0.70 (EtOAc/toluene, 3:7). Yield: 0.031 g, 15%. ^1H NMR (300 MHz, CDCl_3): δ = 7.78 (d, J = 8.1 Hz, 2 H), 7.33 (d, J = 8.1 Hz, 2 H), 5.20 (d, J = 10.2 Hz, 1 H), 4.73 (brd, J = 9.9 Hz, 1 H), 3.52–3.48 (m, 1 H), 3.19 (dd, J = 10.5, 3.6 Hz, 3 H), 3.07 (d, J = 10.5 Hz, 1 H), 2.44 (s, 3 H), 1.53–1.21 (m, 4 H), 0.83 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.8, 138.2, 129.9, 64.9, 58.9, 38.1, 35.3, 21.5, 21.4, 13.4 ppm. ^{77}Se NMR (76 MHz, CDCl_3): δ = 330.2, 203.9 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3278, 1334, 1160, 1095, 816, 672 cm^{-1} . HR-MS: calcd. for $\text{C}_{13}\text{H}_{19}\text{NO}_2\text{SSe}_2$ [$\text{M} + \text{Na}$] $^{+}$ 435.9365; found 435.9386.

Compound 3e: R_f = 0.65 (EtOAc/toluene, 3:7). Yield: 0.092 g, 69%. ^1H NMR (300 MHz, CDCl_3): δ = 7.76 (d, J = 8.4 Hz, 2 H), 7.30 (d, J = 8.4 Hz, 2 H), 5.59–5.49 (m, 1 H), 5.34–5.22 (m, 1 H), 4.67 (t, J = 6.1 Hz, 1 H), 3.52 (dt, J = 6.9, 1.0 Hz, 2 H), 2.43 (s, 3 H), 1.93–1.91 (m, 2 H), 1.27–1.21 (m, 4 H), 0.65 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.3, 137.0, 134.9, 129.6, 127.1, 124.2, 45.3, 34.7, 30.9, 22.0, 21.4, 13.8 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3282, 1326, 1168, 1094, 813, 664 cm^{-1} . HR-MS: calcd. for $\text{C}_{14}\text{H}_{21}\text{NO}_2\text{S}$ [$\text{M} + \text{Na}$] $^{+}$ 290.1191; found 290.1190.

Compound 4e: R_f = 0.70 (EtOAc/toluene, 3:7). Yield: 0.036 g, 17%. ^1H NMR (300 MHz, CDCl_3): δ = 7.78 (d, J = 8.1 Hz, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 5.23 (d, J = 9.9 Hz, 1 H), 3.50–3.45 (m, 1 H), 3.20 (dd, J = 11.1, 3.6 Hz, 1 H), 3.08 (dd, J = 11.1, 2.1 Hz, 1 H), 2.44 (s, 3 H), 1.57–1.35 (m, 3 H), 1.28–1.19 (m, 3 H), 0.85 (t, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.8, 138.1, 129.9, 126.9, 64.9, 59.1, 35.7, 35.3, 30.4, 21.9, 21.5, 13.8 ppm. ^{77}Se NMR (76 MHz, CDCl_3): δ = 331.9, 205.1 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3281, 1336, 1165, 1094, 817, 673 cm^{-1} . HR-MS: calcd. for $\text{C}_{14}\text{H}_{21}\text{NO}_2\text{SSe}_2$ [$\text{M} + \text{Na}$] $^{+}$ 449.9521; found 449.9549.

Compound 3f: R_f = 0.65 (EtOAc/toluene, 3:7). Yield: 0.089 g, 64%. ^1H NMR (300 MHz, CDCl_3): δ = 7.75 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 8.4 Hz, 2 H), 5.59–5.49 (m, 1 H), 5.34–5.25 (m, 1 H), 4.48 (t, J = 6.0 Hz, 1 H), 3.54 (t, J = 6.0 Hz, 2 H), 2.43 (s, 3 H), 1.95–1.89 (m, 2 H), 1.31–1.16 (m, 6 H), 0.66 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.3, 137.1, 135.2, 129.6, 127.1, 124.2, 45.4, 32.0, 31.2, 28.5, 22.4, 21.5, 13.9 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3279, 1326, 1159, 1094, 813, 665 cm^{-1} . HR-MS: calcd. for $\text{C}_{15}\text{H}_{23}\text{NO}_2\text{S}$ [$\text{M} + \text{Na}$] $^{+}$ 304.1347; found 304.1343.

Compound 4f: R_f = 0.70 (EtOAc/toluene, 3:7). Yield: 0.035 g, 16%. ^1H NMR (300 MHz, CDCl_3): δ = 7.78 (d, J = 8.4 Hz, 2 H), 7.32 (d, J = 8.4 Hz, 2 H), 5.21 (d, J = 9.9 Hz, 1 H), 4.75–4.69 (m, 1 H), 3.51–3.45 (m, 1 H), 3.20 (dd, J = 10.8, 3.9 Hz, 1 H), 3.08 (dd, J = 10.8, 1.5 Hz, 1 H), 2.44 (s, 3 H), 1.54–1.35 (m, 2 H), 1.32–1.13 (m, 6 H), 0.86 (t, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3):

δ = 143.8, 138.2, 129.9, 126.9, 64.9, 59.2, 35.9, 35.3, 31.0, 21.5, 13.9 ppm. ^{77}Se NMR (76 MHz, CDCl_3): δ = 332.2, 205.5 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3275, 1337, 1159, 1092, 814, 659 cm^{-1} . HR-MS: calcd. for $\text{C}_{15}\text{H}_{23}\text{NO}_2\text{SSe}_2$ [$\text{M} + \text{Na}$] $^{+}$ 463.9678; found 463.9680.

Compounds 3g and 3g': R_f = 0.65 (EtOAc/toluene, 3:7). Yield: 0.063 g, 56%. ^1H NMR (400 MHz, CDCl_3): δ = 7.77–7.74 (m, 4 H), 7.32–7.27 (m, 4 H), 5.63–5.25 (m, 2 H), 5.05 (d, J = 17.2 Hz, 1 H), 4.96 (d, J = 10.4 Hz, 1 H), 4.72 (d, J = 7.2 Hz, 1 H), 4.52 (t, J = 6.6 Hz, 1 H), 3.93–3.86 (m, 1 H), 3.61 (t, J = 8.4 Hz, 1 H), 2.43 (s, 3 H), 2.42 (s, 3 H), 1.54 (d, J = 6.8 Hz, 3 H), 1.16 (d, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 143.4, 143.2, 138.9, 137.9, 136.9, 129.6, 128.8, 127.2, 127.1, 115.1, 51.6, 39.8, 21.5, 21.4, 12.8 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3283, 1456, 1166, 1092, 817, 651 cm^{-1} . HR-MS: calcd. for $\text{C}_{11}\text{H}_{15}\text{NO}_2\text{S}$ [$\text{M} + \text{Na}$] $^{+}$ 248.0721; found 248.0725.

Compound 4g: R_f = 0.65 (EtOAc/toluene, 3:7). Yield: 0.027 g, 14%. ^1H NMR (300 MHz, CDCl_3): δ = 7.79 (d, J = 8.1 Hz, 2 H), 7.32 (d, J = 8.4 Hz, 2 H), 5.21 (d, J = 9.9 Hz, 1 H), 4.97–4.73 (m, 1 H), 3.99–3.91 (m, 1 H), 3.21 (dd, J = 10.5, 3.3 Hz, 1 H), 2.84 (dd, J = 10.6, 2.4 Hz, 1 H), 2.44 (s, 3 H), 1.39 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.5, 138.3, 129.5, 126.1, 62.7, 53.7, 35.4, 23.3, 21.5 ppm. ^{77}Se NMR (76 MHz, CDCl_3): δ = 245.3, 297.6 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3280, 1335, 1163, 1096, 1039, 816, 654 cm^{-1} . HR-MS: calcd. for $\text{C}_{11}\text{H}_{15}\text{NO}_2\text{SSe}_2$ [$\text{M} + \text{Na}$] $^{+}$ 407.9052; found 407.9056.

Compound 3h: R_f = 0.65 (EtOAc/toluene, 3:7). Yield: 0.051 g, 31%. ^1H NMR (300 MHz, CDCl_3): δ = 7.70 (d, J = 8.1 Hz, 2 H), 7.37–7.26 (m, 7 H), 5.72–5.65 (m, 1 H), 5.54–5.46 (m, 1 H), 4.43 (s, 2 H), 3.95 (d, J = 6.3 Hz, 2 H), 3.59 (d, J = 6.9 Hz, 2 H), 2.41 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.4, 137.7, 136.8, 130.0, 129.6, 128.4, 127.8, 127.7, 127.1, 72.5, 65.4, 40.3, 21.5 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3279, 1597, 1330, 1160, 1093, 814, 699, 665 cm^{-1} . HR-MS: calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_2\text{S}$ [$\text{M} + \text{Na}$] $^{+}$ 354.1140; found 354.1125.

Compound 3h': R_f = 0.60 (EtOAc/toluene, 3:7). Yield: 0.052 g, 32%. ^1H NMR (300 MHz, CDCl_3): δ = 7.71 (d, J = 8.4 Hz, 2 H), 7.37–7.21 (m, 7 H), 5.75–5.63 (m, 1 H), 5.19–5.07 (m, 2 H), 5.01 (d, J = 6.6 Hz, 1 H), 4.40 (s, 3 H), 3.96–3.88 (m, 1 H), 3.44–3.35 (m, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.2, 137.6, 137.4, 135.1, 129.5, 128.4, 127.8, 127.6, 127.2, 117.4, 73.1, 71.7, 55.7, 21.5 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3284, 1328, 1160, 1091, 815, 666 cm^{-1} . HR-MS: calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_2\text{S}$ [$\text{M} + \text{Na}$] $^{+}$ 354.1140; found 354.1146.

Compound 4h: R_f = 0.70 (EtOAc/toluene, 3:7). Yield: 0.036 g, 15%. ^1H NMR (300 MHz, CDCl_3): δ = 7.76 (d, J = 8.4 Hz, 2 H), 7.39–7.28 (m, 7 H), 5.43 (d, J = 9.9 Hz, 1 H), 4.92–4.86 (m, 1 H), 4.45 (d, J = 3.0 Hz, 2 H), 4.04 (dt, J = 9.9, 3.3 Hz, 1 H), 3.89 (dd, J = 9.9, 6.9 Hz, 1 H), 3.61 (dd, J = 9.9, 7.8 Hz, 1 H), 3.23 (dd, J = 10.8, 3.3 Hz, 1 H), 2.89 (dd, J = 10.8, 3.2 Hz, 1 H), 2.42 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.8, 137.9, 137.4, 129.9, 128.5, 127.9, 127.7, 126.9, 73.5, 69.3, 60.9, 53.4, 35.9, 21.6 ppm. ^{77}Se NMR (76 MHz, CDCl_3): δ = 287.0, 212.3 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3281, 1335, 1157, 1093, 812, 663 cm^{-1} . HR-MS: calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_2\text{SSe}_2$ [$\text{M} + \text{Na}$] $^{+}$ 513.9470; found 513.9486.

Compound 4i: R_f = 0.70 (EtOAc/toluene, 3:7). Yield: 0.103 g, 50%; m.p. 128 °C. ^1H NMR (300 MHz, CDCl_3): δ = 7.79 (d, J = 8.1 Hz, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 5.23 (d, J = 10.2 Hz, 1 H), 4.82 (dd, J = 10.0, 2.4 Hz, 1 H), 3.87–3.81 (m, 1 H), 3.17 (dd, J = 10.0, 2.7 Hz, 1 H), 2.85 (dd, J = 11.1, 1.8 Hz, 1 H), 2.44 (s, 3 H), 1.83–1.62 (m, 2 H), 1.33–1.21 (m, 2 H), 0.85 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.7, 138.3, 129.8, 126.9, 62.1,

56.9, 36.0, 32.0, 23.8, 21.5, 13.9 ppm. ^{77}Se NMR (76 MHz, CDCl_3): δ = 281.1, 217.8 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3274, 1332, 1155, 1091, 812, 669 cm^{-1} . HR-MS: calcd. for $\text{C}_{13}\text{H}_{19}\text{NO}_2\text{SSe}_2$ [$\text{M} + \text{Na}$] $^+$ 435.9365; found 435.9370.

Compound 3j: R_f = 0.70 (EtOAc/toluene, 3:7). Yield: 0.084 g, 70%. ^1H NMR (300 MHz, CDCl_3): δ = 7.77 (d, J = 8.1 Hz, 2 H), 7.28 (d, J = 8.1 Hz, 2 H), 5.78 (dd, J = 17.3, 10.8 Hz, 1 H), 5.09 (d, J = 17.3 Hz, 1 H), 5.06 (s, 1 H), 4.94 (d, J = 10.8 Hz, 1 H), 2.43 (s, 3 H), 1.29 (s, 6 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.5, 142.8, 140.1, 129.3, 127.1, 112.7, 57.1, 27.7, 21.4 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3274, 1323, 1147, 1093, 664 cm^{-1} . HR-MS: calcd. for $\text{C}_{12}\text{H}_{17}\text{NO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$ 262.0878; found 262.0876.

Compound 4j: R_f = 0.75 (EtOAc/toluene, 3:7). Yield: 0.036 g, 18%; m.p. 139 °C. ^1H NMR (300 MHz, CDCl_3): δ = 7.78 (d, J = 8.1 Hz, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 5.08 (d, J = 10.2 Hz, 1 H), 4.27–4.21 (m, 1 H), 3.26 (dd, J = 10.5, 3.6 Hz, 1 H), 2.83 (dd, J = 10.6, 2.4 Hz, 1 H), 2.44 (s, 3 H), 1.59 (s, 3 H), 1.47 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 143.7, 138.2, 129.9, 126.9, 69.3, 62.3, 33.7, 30.7, 23.4, 21.6 ppm. ^{77}Se NMR (76 MHz, CDCl_3): δ = 419.8, 219.6 ppm. IR (neat): $\tilde{\nu}_{\text{max}}$ = 3275, 1333, 1158, 1091, 813, 670 cm^{-1} . HR-MS: calcd. for $\text{C}_{12}\text{H}_{17}\text{NO}_2\text{SSe}_2$ [$\text{M} + \text{Na}$] $^+$ 421.9208; found 421.9248.

CCDC-292063 (**4i**) and -292057 (**4j**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Copies of ^1H , ^{13}C and ^{77}Se NMR spectra of all the new compounds.

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- [13] Crystal structure data for compound **4i**: The structure was solved by direct methods (SIR92). Refinement was by full-matrix, least-squares procedures on F^2 by using SHELXL-97. Crystal system: monoclinic, space group: $P2_1$, cell parameters: a = 10.118(9), b = 17.381(15), c = 14.942(13) Å, β = 109.705(14)°, V = 2474(4) Å³, Z = 6, $\rho_{\text{calcd.}}$ = 1.66 g cm^{-3} , $F(000)$ = 1224, μ = 4.61 mm^{-1} , λ = 0.71073 Å. Total number of least-squares parameters = 514. R_1 = 0.063 for 8917 $F_o > 4\sigma(F_o)$ and 0.102 for all 17787 data. wR_2 = 0.158, GOF = 1.005, restrained GOF = 1.005 for all data.
- [14] Crystal structure data for compound **4j**: Crystal system: monoclinic, space group: $P\bar{1}$, cell parameters: a = 23.244(14), b = 17.470(11), c = 7.518(5) Å, β = 90.471(12)°, V = 3053(3) Å³, Z = 8, $\rho_{\text{calcd.}}$ = 1.73 g cm^{-3} , $F(000)$ = 1568, μ = 4.975 mm^{-1} , λ = 0.71073 Å. Total number of least-squares parameters = 331. R_1 = 0.043 for 6355 $F_o > 4\sigma(F_o)$ and 0.078 for all 23643 data. wR_2 = 0.104, GOF = 1.013, restrained GOF = 1.013 for all data.
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