



## Note

Practical synthesis of chiral  $\beta$ -telluro amines by ring-opening reaction of aziridines

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## ABSTRACT

A set of chiral  $\beta$ -tellurium amines and their selenium and sulfur-containing derivatives have been efficiently synthesized in good to excellent yields via the ring-opening reaction of chiral aziridines by chalcogen nucleophilic species.

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## 1. Introduction

Organotellurium chemistry is a very broad and exciting field with many opportunities for research and development of applications in organic synthesis [1,2]. Many different classes of organotellurium compounds have been prepared to date, and vinylic tellurides are certainly the most extensively studied ones, in view of their usefulness in a wide range of applications in organic synthesis [3] and in the total synthesis of natural products [4–6]. In addition to their utility in this field, the toxicological and pharmacological aspects of organotellurium compounds have also been recently reviewed [7].

Among the several classes of organotellurium compounds the functionalized alkyl tellurides are still scarcely studied. Recently, our research group has been working in the preparation and application of hydroxy tellurides in the tellurium/lithium exchange reaction. These compounds have been efficiently used as alternative organometallic sources of 1,4-dianion intermediates in the synthesis of diols [8], spiroketals [9], bioactive butenolides [10], and in the synthesis of natural products, such as ( $\pm$ )-frontalin [11] and (+)-endo-brevicommin [12]. The interesting results obtained with oxygen-containing organotellurium compounds served as inspiration for the design and application of many other functionalized organotellurium compounds.

On the other hand, aziridines, biologically relevant heterocycles widely found in natural products [13,14], represent a versatile and useful class of nitrogen-containing compounds in organic transformations [15], exemplified by the ring-opening reaction with nucle-

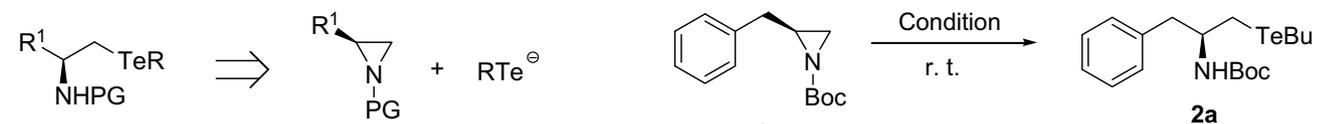
ophiles, resulting in interesting  $\beta$ -substituted nitrogenated compounds [16–20].

In this way, following our current interest in the development and application of functionalized organotellurium compounds in organic synthesis [8–12], we report herein the preparation of a modular series of nitrogen-containing organotellurium compounds and their selenium and sulfur analogues via the ring-opening reaction of easily available aziridines, as depicted in Fig. 1.

## 2. Results and discussion

Aiming to evaluate the performance of tellurium nucleophiles in the ring-opening reaction, aziridine **1a** was chosen as a model substrate, in order to determine the optimum conditions for the present study. Initially, the process was carried out in the presence of [BuTeH], easily generated in situ by reaction of elemental tellurium and *n*-BuLi in THF and EtOH as a proton source. Under these conditions, the tellurium atom was efficiently introduced by regioselective nucleophilic ring-opening at the less hindered carbon of aziridine **1a**, furnishing the  $\beta$ -telluro amine **2a** in 89% yield (Scheme 1, conditions A). The reaction was also performed in the presence of butyltelluroate anion, generated by reduction of BuTeTeBu with NaBH<sub>4</sub> in EtOH. However, no improvement could be observed, since the corresponding product **2a** was obtained in lower yield and after a longer reaction time (Scheme 1, conditions B). The reaction was also studied in the presence of BuTeMgBr as a nucleophilic source of tellurium. However, only traces of the corresponding product, starting aziridine **1a** and dibutyl ditelluride as by-product were observed in the present reaction (Scheme 1, conditions C).

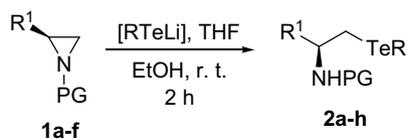
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 $\beta$ -telluro amineFig. 1. Retrosynthetic analysis of the chiral  $\beta$ -telluro amines.

Conditions A: *n*-BuLi/Te<sup>0</sup>, THF/EtOH, 2 h 89%  
 Conditions B: BuTeTeBu/NaBH<sub>4</sub>, EtOH, 3h 81%  
 Conditions C: BuTeMgBr, THF, 24 h traces

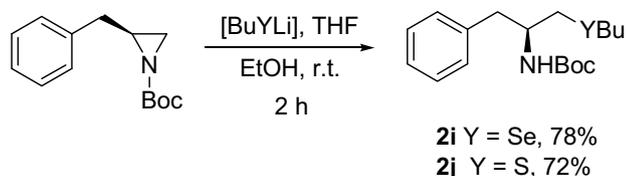
Scheme 1. Ring-opening reaction of aziridine **1a**.

**Table 1**  
 Preparation of chiral  $\beta$ -telluro amines by ring-opening reaction of aziridines



Entry	Aziridine	R <sup>-</sup> TeLi	Product	Yield <sup>a</sup> (%)
1		BuTeLi		89
2	<b>1a</b>	2-ThTeLi		74
3	<b>1a</b>	PhTeLi		80
4		BuTeLi		79
5		BuTeLi		81
6		BuTeLi		78
7		BuTeLi		84
8		BuTeLi		83

<sup>a</sup> Isolated yield of the corresponding product.



**Scheme 2.** Ring-opening reaction of aziridine **1a** with selenium and sulfur nucleophiles.

After determining the best procedure for generating the nucleophilic source of tellurium and the appropriated solvent, the ring-opening process was further expanded to a broader range of aziridines and tellurium anions in order to evaluate its scope and limitations (Table 1).

As can be seen, all the  $\beta$ -telluro amines were obtained in good to excellent yields from different aziridines. The ring-opening process of *N*-Boc aziridine **1a** was also evaluated in the presence of organotellurium species attached to heteroaryl and aryl groups (Table 1, entries 2 and 3), furnishing the corresponding products **2b** and **2c** in 74% and 80% yields, respectively. The ring-opening reaction was also performed in the presence of aziridines bearing a tosyl group (PG = Ts) instead of a *t*-butoxycarbonyl group (PG = Boc) as well as different lipophilic substituents ( $R^1$  = Bn, *i*-Pr, *i*-Bu, Me). In these cases, the corresponding products **2d–g** were obtained in up to 84% yield (Table 1, entries 4–7). A very simple  $\beta$ -tellurium amine **2h** was also prepared in 83% yield via the ring-opening reaction of *N*-Ts aziridine (Table 1, entry 8).

The successful ring-opening procedure with *n*-BuLi and elemental tellurium was also evaluated in the presence of aziridines with  $R^1$  = Bn and containing *N*-benzoyl (PG = Bz) and *N*-benzyloxycarbonyl (PG = Cbz) protecting groups. However, in both cases, only traces of the corresponding products were observed, the starting material was recovered and dibutyl ditelluride was detected as by-product.

At this point, it is important to emphasize that all organotellurium compounds described herein are very stable to the ambient light and can be stored and manipulated in the air. Most of them are almost odorless or present a smell not more unpleasant than most chemicals normally used in an organic synthesis laboratory.

Chiral organoselenium and organosulfur compounds containing nitrogen also represent important classes of compounds in organic synthesis. Among several applications, these compounds are useful chiral ligands in asymmetric catalysis [21,22]. In this way, the ring-opening reaction of aziridine **1a** was also evaluated in the presence of organochalcogen species containing selenium and sulfur. This process is already described in the literature [23–25]. However, in most cases, the nucleophilic species are obtained from the corresponding dichalcogenides which are transformed in situ into organochalcogenolates or organochalcogenols, or by using the bad smelling commercially available thiols. Thus, using a similar procedure described for the preparation of the organotellurium compounds **2a–h**, the desired organoselenium **2i** and organosulfur **2j** compounds were obtained in 78% and 72% yields, via the in situ generation of [BuSeLi] and [BuSLi], respectively (Scheme 2). In this way, we avoided the preparation of the corresponding dichalcogenides as well as the use of the corresponding thiol.

### 3. Conclusion

In summary, we have described a practical and concise synthesis of structurally diverse  $\beta$ -tellurium amines and their selenium and sulfur analogues in good to excellent yields via the ring-opening reaction of aziridines by a straightforward and flexible synthetic route. Further studies are in progress in our laboratory

concerning the tellurium/lithium exchange reaction of the nitrogen-containing tellurium compounds prepared herein and the results will be reported in due course.

## 4. Experimental

### 4.1. General

Elemental tellurium, selenium and sulfur (200 mesh) were purchased from Sigma Aldrich. All reagents and solvents were purified and dried using procedures described in the literature [26]. THF was distilled under nitrogen from sodium/benzophenone just before use. *n*-Butyllithium was titrated using 1,10-phenanthroline as indicator prior to use. All operations were carried out in flame-dried glassware. Column chromatographic separations were performed over Acros Organics silica gel (0.035–0.075 mm; pore diameter ca. 6 nm). The melting points were determined using a Büchi, model B-545. Optical rotations were determined on a Perkin Elmer 343 polarimeter and IR spectra were recorded on a Bomem MB-100 spectrophotometer. NMR spectra were recorded on Varian-Inova (300 MHz,  $^1\text{H}$ ; 75 MHz,  $^{13}\text{C}$ ) or Bruker model DRX-500 (500 MHz,  $^1\text{H}$ ; 125 MHz,  $^{13}\text{C}$ ) spectrometers using  $\text{CDCl}_3$  as solvent. The internal references were TMS ( $^1\text{H}$  NMR), the central peak of the  $\text{CDCl}_3$  signal ( $^{13}\text{C}$  NMR), a capillary of diphenyl ditelluride  $1 \text{ mol}^{-1}$  ( $^{125}\text{Te}$  NMR) and a capillary of diphenyl diselenide  $1 \text{ mol}^{-1}$  ( $^{77}\text{Se}$  NMR). High resolution mass spectroscopy was performed using a LC-MS – Bruker Daltonics instrument at the Microanalytical Laboratory of the Institute of Chemistry, University of São Paulo. Aziridines **1a** [27], **1b–e** [28] and **1f** [29] were prepared according to the procedures described in the literature.

### 4.2. (*S*)-*tert*-Butyl 1-(butyltellanyl)-3-phenylpropan-2-ylcarbamate (**2a**)

*n*-Butyllithium (1 mmol, 1.5 M in hexane) was slowly added at room temperature to a suspension of elemental tellurium (1.2 mmol) in dry THF (5 mL). Deoxygenated ethanol (2 mL) was added to the light yellow solution of lithium butyl telluroate so formed, and the resulting red-brown mixture was stirred at room temperature for 10 min and subsequently cooled to 0 °C. The aziridine **1a** (1 mmol) was added in a single portion, and the resulting mixture was stirred for 2 h at room temperature. The mixture was quenched with a saturated  $\text{NH}_4\text{Cl}$  solution and extracted with  $\text{CH}_2\text{Cl}_2$ , and the combined organic fractions were collected, dried over  $\text{MgSO}_4$ , and filtered. The solvent was removed in vacuo, yielding the crude product **2a**, which was purified by flash chromatography. Yield: 89%; white solid; m.p.: 69.4–71.4 °C;  $[\alpha]_D^{24} = +13.2$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ ); IR (KBr) 3364, 2959, 2926, 1688, 1516, 1166  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.30–7.27 (m, 2H), 7.23–7.17 (m, 3H), 4.70 (br s, 1H), 3.91 (br s, 1H), 2.86–2.74 (m, 4H), 2.63 (t,  $J = 7.5$  Hz, 2H), 1.68 (qui,  $J = 7.5$  Hz, 2H), 1.41 (s, 9H), 1.35 (sex,  $J = 7.5$  Hz, 2H), 0.90 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  155.0, 137.7, 129.3, 128.4, 126.5, 79.3, 51.8, 41.9, 34.2, 28.3, 25.0, 13.4, 10.2, 3.7;  $^{125}\text{Te}$  NMR ( $\text{CDCl}_3$ , 157 MHz)  $\delta$  121.4; HRMS-ESI  $m/z$  calculated for  $\text{C}_{18}\text{H}_{29}\text{NO}_2\text{Te} + \text{Na}^+$  441.1158, found 441.1155.

### 4.3. (*S*)-*tert*-Butyl 1-phenyl-3-(thiophen-2-yltellanyl)propan-2-ylcarbamate (**2b**)

*n*-Butyllithium (2 mmol, 1.5 M in hexane) was slowly added to a solution of thiophene (2 mmol) in dry THF (6 mL) at –78 °C. The reaction mixture was then stirred for 30 min at this temperature and allowed to warm to –40 °C and elemental tellurium (2 mmol) was added in one portion and the reaction mixture was stirred for

an additional 1 h at this temperature. Deoxygenated ethanol (3 mL) was added to the light yellow solution of lithium thiophen telluroate so formed, and the resulting red-brown mixture was stirred at room temperature for 10 min and subsequently cooled to 0 °C. The aziridine **1a** (1 mmol) was added in a single portion, and the resulting mixture was stirred for 2 h at room temperature. The mixture was quenched with a saturated NH<sub>4</sub>Cl solution and extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the combined organic fractions were collected, dried over MgSO<sub>4</sub>, and filtered. The solvent was removed in vacuo, yielding the crude product **2b**, which was purified by flash chromatography. Yield: 74%; yellow solid; m.p.: 85.4–87.4 °C;  $[\alpha]_D^{24} = +20.4$  ( $c = 1.0$ , CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 3371, 2973, 1690, 1523, 1169, 701 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.42 (dd,  $J = 5.5$  Hz,  $J = 1.5$  Hz, 1H), 7.40 (dd,  $J = 3.5$  Hz,  $J = 1.5$  Hz, 1H), 7.31–7.19 (m, 3H), 7.11–7.09 (m, 2H), 6.93 (dd,  $J = 5.5$  Hz,  $J = 3.5$  Hz, 1H), 4.62 (br s, 1H), 4.00 (br s, 1H), 3.00–2.88 (m, 3H), 2.82–2.78 (m, 1H), 1.39 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  154.9, 141.6, 137.5, 134.4, 129.3, 128.7, 128.5, 126.5, 97.4, 79.4, 52.0, 41.0, 28.3, 18.5; <sup>125</sup>Te NMR (CDCl<sub>3</sub>, 157 MHz)  $\delta$  248.3; HRMS-ESI  $m/z$  calculated for C<sub>18</sub>H<sub>23</sub>NO<sub>2</sub>STe + Na<sup>+</sup> 470.0409, found 470.0406.

#### 4.4. (S)-tert-Butyl 1-phenyl-3-(phenyltellanyl)propan-2-ylcarbamate (**2c**)

The  $\beta$ -telluroamine **2c** was prepared according to the procedure described to  $\beta$ -telluroamine **2a**, however PhLi was used instead of *n*-BuLi. Yield: 80%; white solid; m.p.: 81.7–83.7 °C;  $[\alpha]_D^{24} = +16.1$  ( $c = 1.0$ , CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 3364, 2976, 1687, 1516, 1248, 1165, 728 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.73–7.70 (m, 2H), 7.27–7.09 (m, 8H), 4.67–4.65 (m, 1H), 4.05–4.03 (m, 1H), 3.09–3.02 (m, 2H), 2.87–2.78 (m, 2H), 1.37 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  154.9, 138.5, 137.5, 129.3, 129.2, 128.4, 127.7, 126.5, 111.4, 79.3, 52.0, 42.0, 28.3, 16.0; <sup>125</sup>Te NMR (CDCl<sub>3</sub>, 157 MHz)  $\delta$  372.8; HRMS-ESI  $m/z$  calculated for C<sub>20</sub>H<sub>25</sub>NO<sub>2</sub>Te + Na<sup>+</sup> 464.0845, found 464.0844.

#### 4.5. (S)-N-(1-(Butyltellanyl)-3-phenylpropan-2-yl)-4-methylbenzenesulfonamide (**2d**)

The  $\beta$ -telluroamine **2d** was prepared according to the procedure described to  $\beta$ -telluroamine **2a**, however aziridine **1b** was used instead of aziridine **1a**. Yield: 79%; yellow oil;  $[\alpha]_D^{24} = -24.1$  ( $c = 1.0$ , EtOH); IR (film) 3268, 2958, 2926, 1598, 1453, 1328, 1156 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.58–7.56 (m, 2H), 7.21–7.16 (m, 5H), 7.01–6.98 (m, 2H), 4.80 (br s, 1H), 3.49–3.47 (m, 1H), 2.81 (dd,  $J = 12.5$  Hz,  $J = 4.0$  Hz, 1H), 2.74 (t,  $J = 7.0$  Hz, 2H), 2.69 (dd,  $J = 12.5$  Hz,  $J = 6.0$  Hz, 1H), 2.55 (t,  $J = 7.5$  Hz, 2H), 2.40 (s, 3H), 1.67–1.61 (m, 2H), 1.33 (sex,  $J = 7.5$  Hz, 2H), 0.89 (t,  $J = 7.0$  Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  143.1, 137.3, 136.8, 129.5, 128.5, 127.0, 126.6, 55.4, 42.1, 34.0, 24.9, 21.4, 13.3, 11.0, 4.3; <sup>125</sup>Te NMR (CDCl<sub>3</sub>, 157 MHz)  $\delta$  129.1; HRMS-ESI  $m/z$  calculated for C<sub>20</sub>H<sub>27</sub>NO<sub>2</sub>STe + Na<sup>+</sup> 498.0722, found 498.0714.

#### 4.6. (S)-N-(1-(Butyltellanyl)-3-methylbutan-2-yl)-4-methylbenzenesulfonamide (**2e**)

The  $\beta$ -telluroamine **2e** was prepared according to the procedure described to  $\beta$ -telluroamine **2a**, however aziridine **1c** was used instead of aziridine **1a**. Yield: 81%; yellow oil;  $[\alpha]_D^{24} = +12.7$  ( $c = 1.0$ , CH<sub>2</sub>Cl<sub>2</sub>); IR (film) 3275, 2959, 2928, 2872, 1325, 1157, 1092 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.79–7.77 (m, 2H), 7.30–7.28 (m, 2H), 5.03–5.01 (d,  $J = 8.0$  Hz, 1H), 3.08–3.06 (m, 1H), 2.81 (dd,  $J = 12.5$ ,  $J = 4.5$  Hz, 1H), 2.55 (dd,  $J = 12.5$ ,  $J = 7.0$  Hz, 1H), 2.47 (t,  $J = 7.0$  Hz, 2H), 2.41 (s, 3H), 1.80–1.74 (m, 1H), 1.63–1.56 (m, 2H), 1.31 (sex,  $J = 7.5$  Hz, 2H), 0.89 (t,  $J = 7.5$  Hz, 3H), 0.79 (d,  $J = 7.0$  Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  143.2, 138.1, 129.6, 127.1, 59.5, 34.1,

32.3, 24.9, 21.5, 19.3, 17.5, 13.3, 8.9, 4.0; <sup>125</sup>Te NMR (CDCl<sub>3</sub>, 157 MHz)  $\delta$  132.0; HRMS-ESI  $m/z$  calculated for C<sub>16</sub>H<sub>27</sub>NO<sub>2</sub>STe + Na<sup>+</sup> 450.0722, found 450.0718.

#### 4.7. (S)-N-(1-(Butyltellanyl)-4-methylpentan-2-yl)-4-methylbenzenesulfonamide (**2f**)

The  $\beta$ -telluroamine **2f** was prepared according to the procedure described to  $\beta$ -telluroamine **2a**, however aziridine **1d** was used instead of aziridine **1a**. Yield: 78%; yellow oil;  $[\alpha]_D^{24} = -8.8$  ( $c = 1.0$ , CH<sub>2</sub>Cl<sub>2</sub>); IR (film) 3275, 2957, 2927, 2870, 1329, 1158, 1092 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.78–7.75 (m, 2H), 7.30–7.28 (m, 2H), 5.06–5.04 (d,  $J = 8.5$  Hz, 1H), 3.36–3.30 (m, 1H), 2.79 (dd,  $J = 12.5$  Hz,  $J = 3.5$  Hz, 1H), 2.58 (dd,  $J = 12.5$  Hz,  $J = 6.5$  Hz, 1H), 2.50 (t,  $J = 7.0$  Hz, 2H), 2.41 (s, 3H), 1.62 (qui,  $J = 7.0$  Hz, 2H), 1.57–1.49 (m, 1H), 1.32 (sex,  $J = 7.0$  Hz, 2H), 1.26–1.22 (m, 2H), 0.89 (t,  $J = 7.0$  Hz, 3H), 0.80 (d,  $J = 7.0$  Hz, 3H), 0.69 (d,  $J = 7.0$  Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  143.2, 138.2, 129.6, 127.0, 52.0, 45.6, 34.1, 24.9, 24.4, 22.8, 21.7, 21.4, 13.3, 12.7, 4.1; <sup>125</sup>Te NMR (CDCl<sub>3</sub>, 157 MHz)  $\delta$  113.5; HRMS-ESI  $m/z$  calculated for C<sub>17</sub>H<sub>29</sub>NO<sub>2</sub>STe + Na<sup>+</sup> 464.0879, found 464.0875.

#### 4.8. (S)-N-(1-(Butyltellanyl)propan-2-yl)-4-methylbenzenesulfonamide (**2g**)

The  $\beta$ -telluroamine **2g** was prepared according to the procedure described to  $\beta$ -telluroamine **2a**, however aziridine **1e** was used instead of aziridine **1a**. Yield: 84%; yellow oil;  $[\alpha]_D^{24} = +3.3$  ( $c = 1.0$ , CH<sub>2</sub>Cl<sub>2</sub>); IR (film) 3271, 2958, 2870, 1326, 1158, 1093 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.78–7.75 (m, 2H), 7.31–7.27 (m, 2H), 4.93–4.91 (br s, 1H), 3.43–3.41 (br s, 1H), 2.75 (dd,  $J = 12.5$  Hz,  $J = 4.5$  Hz, 1H), 2.65 (dd,  $J = 12.5$  Hz,  $J = 6.5$  Hz, 1H), 2.52 (t,  $J = 7.0$  Hz, 2H), 2.42 (s, 3H), 1.63 (qui,  $J = 7.0$  Hz, 2H), 1.33 (sex,  $J = 7.0$  Hz, 2H), 1.12 (d,  $J = 6.5$  Hz, 3H), 0.89 (t,  $J = 7.0$  Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  143.3, 137.9, 129.6, 127.0, 50.3, 34.0, 24.9, 22.5, 21.5, 13.3, 12.8, 4.0; <sup>125</sup>Te NMR (CDCl<sub>3</sub>, 157 MHz)  $\delta$  145.2; HRMS-ESI  $m/z$  calculated for C<sub>14</sub>H<sub>23</sub>NO<sub>2</sub>STe + Na<sup>+</sup> 422.0409, found 422.0392.

#### 4.9. N-(2-(Butyltellanyl)ethyl)-4-methylbenzenesulfonamide (**2h**)

The  $\beta$ -telluroamine **2h** was prepared according to the procedure described to  $\beta$ -telluroamine **2a**, however aziridine **1f** was used instead of aziridine **1a**. Yield: 83%; yellow oil; IR (film) 3277, 2957, 2926, 2867, 1597, 1455, 1325, 1156 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.80–7.73 (m, 2H), 7.31–7.24 (m, 2H), 3.20 (t,  $J = 7.2$  Hz, 2H), 2.63 (t,  $J = 7.2$  Hz, 2H), 2.54 (t,  $J = 7.2$  Hz, 2H), 2.42 (s, 3H), 1.83 (qui,  $J = 7.2$  Hz, 2H), 1.32 (sex,  $J = 7.2$  Hz, 2H), 0.88 (t,  $J = 7.2$  Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  143.5, 137.1, 129.8, 127.1, 44.8, 34.2, 25.0, 21.5, 13.4, 3.3, 2.3; <sup>125</sup>Te NMR (CDCl<sub>3</sub>, 157 MHz)  $\delta$  192.2; HRMS-ESI  $m/z$  calculated for C<sub>13</sub>H<sub>21</sub>NO<sub>2</sub>STe + Na<sup>+</sup> 408.0253, found 408.0250.

#### 4.10. (S)-tert-Butyl 1-(butylselenanyl)-3-phenylpropan-2-ylcarbamate (**2i**)

The  $\beta$ -selenoamine **2i** was prepared according to the procedure described to  $\beta$ -telluroamine **2a**, however elemental selenium was used instead of elemental tellurium. Yield: 78%; white solid; m.p.: 63.6–65.6 °C;  $[\alpha]_D^{24} = +9.4$  ( $c = 1.0$ , CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 3362, 2963, 2927, 1686, 1526, 1513, 1166, 703 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.30–7.25 (m, 2H), 7.23–7.19 (m, 3H), 4.73 (br s, 1H), 4.04 (br s, 1H), 2.88–2.80 (m, 2H), 2.70–2.65 (m, 2H), 2.59 (t,  $J = 7.0$  Hz, 2H), 1.61 (qui,  $J = 7.0$  Hz, 2H), 1.41 (s, 9H), 1.38 (sex,  $J = 7.0$  Hz, 2H), 0.90 (t,  $J = 7.0$  Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  155.1, 137.7, 129.4, 128.4, 126.5, 79.3, 51.4, 40.3, 32.6, 28.8, 28.3,

24.9, 22.9, 13.5;  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ , 95 MHz)  $\delta$  104.1; HRMS-ESI  $m/z$  calculated for  $\text{C}_{18}\text{H}_{29}\text{NO}_2\text{Se} + \text{Na}^+$  394.1261, found 394.1256.

#### 4.11. (*S*)-*tert*-Butyl 1-(butylthio)-3-phenylpropan-2-ylcarbamate (**2j**)

The  $\beta$ -thioamine **2j** was prepared according to the procedure described to  $\beta$ -selenoamine **2i**, however elemental sulfur was used instead of elemental tellurium. Yield: 72%; white solid; m.p.: 57.3–59.3 °C;  $[\alpha]_{\text{D}}^{24} = +7.1$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ ); IR (KBr) 3360, 2959, 2930, 1686, 1528, 1515, 1167, 703  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.30–7.27 (m, 2H), 7.23–7.20 (m, 3H), 4.69 (br s, 1H), 3.99 (br s, 1H), 2.87–2.83 (m, 2H), 2.61–2.58 (m, 2H), 2.52 (t,  $J = 7.0$  Hz, 2H), 1.53 (qui,  $J = 7.0$  Hz, 2H), 1.45–1.35 (m, 11H), 0.90 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  155.2, 137.7, 129.4, 128.4, 126.4, 79.3, 51.1, 39.5, 36.0, 32.6, 31.8, 28.3, 21.9, 13.6; HRMS-ESI  $m/z$  calculated for  $\text{C}_{18}\text{H}_{29}\text{NO}_2\text{S} + \text{Na}^+$  346.1817, found 346.1813.

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